Molecular Editing of Aza-arene C–H Bonds by Distance, Geometry and Chirality

Zhoulong Fan,[1] Xiangyang Chen,[2] Keita Tanaka,[1] Han Seul Park,[1] Nelson Y. S. Lam,[1] Jonathan J. Wong,[2] K. N. Houk,[2,*] Jin-Quan Yu[1,*]

[1]Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037, United States. [2]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States.

Table of Contents

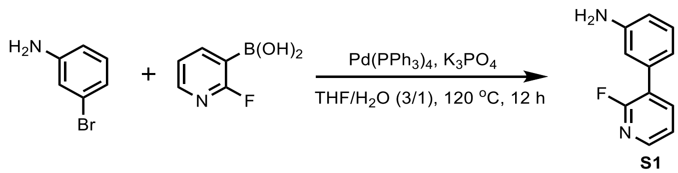
1. General Information

All reactions were performed in round-bottom flasks, sealed tubes or vials. Liquids and solutions were transferred with syringes and pipettes. Unless otherwise stated, all solvents and chemical reagents were obtained from commercial sources and used without further purifications. The analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254 and spots were visualized by UV light at 254 nM. Column chromatography was performed using E. Merck silica (60, particle size 0.043-0.063 mm), and preparative TLC (pTLC) was performed on Merck silica plates (60F254). ^{1}H and ^{13}C NMR were recorded on Bruker AVIII HD 600 NMR spectrometer equipped with a 5 mm CPDCH (C–H) CryoProbe. Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. The residual solvent peaks were used as internal standard ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; CD_3OD: 3.31 ppm ^{1}H NMR, 49.00 ppm ^{13}C NMR; Acetone-d_6: 2.05 ppm ^{1}H NMR, 29.84 ppm ^{13}C NMR). NMR data is denoted with apparent multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and combinations thereof. ^{19}F NMR spectra were recorded on Bruker AV NEO 399 NMR spectrometer equipped with a 5 mm BBFO Smart Probe, and were fully decoupled by broad band proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Chiral separation and detection were conducted on the Agilent Technologies supercritical fluid chromatography (SFC) system using commercially available chiral columns. IR spectra were recorded with a Nicolet 380 FTIR with an ATR attachment and selected peaks are reported in cm^{-1}. Melting points (mp) were measured on a Stuart SMP50 automatic melting point apparatus and are uncorrected. Optical rotations were recorded on a Rudolph Research Analytical Autopol III Automatic Polarimeter. The single crystal X-ray diffraction studies were carried out on a Bruker Smart APEX II CCD diffractometer equipped with Cu K_{α} radiation or Bruker D8-Venture 3-circle diffractometer equipped with a Photon 3 detector and Mo K_{α} radiation.

2. Experimental Section

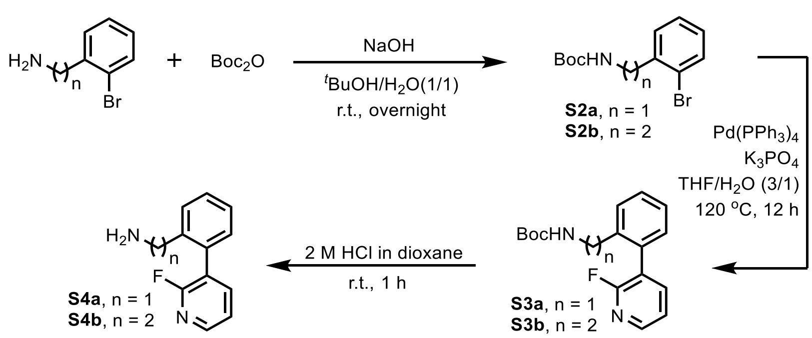
2.1 Preparation of Templates and Template Chaperones

Synthesis of **S1**



To a solution of K_3PO_4 (1.27 g, 6 mmol) in water (10 mL) was added 3-bromoaniline (516 mg, 3 mmol), 2-fluoro-3-pyridylboronic acid (634 mg, 4.5 mmol), $Pd(PPh_3)_4$ (347 mg, 0.3 mmol), and THF (30 mL). The Schlenk tube was evacuated and refilled with nitrogen three times, then sealed and put into a preheated oil bath at 120 ^{o}C for 12 h. After completion, the reaction mixture was cooled to room temperature. Water (100 mL) was added and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/ethyl acetate (EA) (70/30, v/v) to provide the product **S1** (441 mg, 78% yield) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.85 (ddd, *J* = 9.6, 7.4, 2.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.88 (s, 1H), 6.76 – 6.70 (m, 1H), 3.78 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.41 (d, *J* = 240.5 Hz), 146.64, 146.20, 146.10, 140.63 (d, *J* = 4.4 Hz), 134.93 (d, *J* = 4.9 Hz), 129.65, 124.08 (d, *J* = 28.2 Hz), 121.71 (d, *J* = 4.4 Hz), 119.10, 115.29 (d, *J* = 28.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.28. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{10}FN_2^+$ $[M+H]^+$ 189.0828, found 189.0828.

Synthesis of **S4a,b**



To a solution of NaOH (480 mg, 12 mmol) in water (6 mL) was added Boc_2O (1.57 g, 7.2 mmol), ^tBuOH (6 mL) and amine (6 mmol). The resulting mixture was stirred at room temperature for overnight. After completion, the reaction mixture was extracted with EA (50 mL x 3). The organic layers were collected, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (97/3, v/v) to provide the product **S2a** (or **S2b**).

For **S2a:** (1.1 g, colorless oil, 65% yield) ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 (td, *J* = 7.7, 1.8 Hz, 1H), 5.02 (s, 1H), 4.39 (d, *J* = 6.3 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.74, 137.97, 132.74, 129.78, 128.96, 127.66, 123.55, 79.66, 44.90, 28.40. HRMS (ESI-TOF) *m/z* Calcd for $C_8H_9BrNO_2^+$ $[M-^tBu+2H]^+$ 229.9817, found 229.9824.

For **S2b:** (1.6 g, pale white solid, 89% yield) ^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.09 (ddd, *J* = 7.9, 6.8, 2.2 Hz, 1H), 4.60 (s, 1H), 3.39 (t, *J* = 6.9 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.85, 138.41, 132.91, 131.03, 128.16, 127.54, 124.63, 79.23, 40.26, 36.38, 28.41. HRMS (ESI-TOF) *m/z* Calcd for $C_9H_{11}BrNO_2^+$ $[M-^tBu+2H]^+$ 243.9973, found 243.9980.

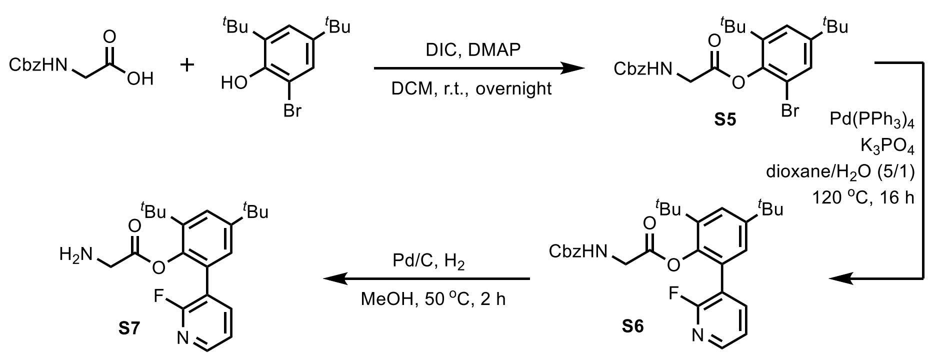
Following the procedure for synthesis of **S1** with 3 mmol of **S2a** (or **S2b**), the residue was purified by silica gel chromatography eluting with hexane/EA (85/15, v/v) to provide the product **S3a** (or **S3b**).

For **S3a:** (725 mg, colorless oil, 80% yield) ^1H NMR (600 MHz, $CDCl_3$) δ 8.27 – 8.23 (m, 1H), 7.72 (ddd, *J* = 9.4, 7.3, 1.9 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.37 – 7.34 (m, 1H), 7.28 (ddd, *J* = 7.1, 4.9, 1.9 Hz, 1H), 7.21 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.77 (s, 1H), 4.19 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.35 (d, *J* = 237.8 Hz), 155.67, 147.13 (d, *J* = 15.3 Hz), 141.94 (d, *J* = 4.9 Hz), 137.31, 132.97 (d, *J* = 4.5 Hz), 130.41, 129.12, 128.42, 127.53, 122.83 (d, *J* = 32.3 Hz), 121.59 (d, *J* = 4.7 Hz), 79.55, 42.24, 28.37. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.48. HRMS (ESI-TOF) *m/z* Calcd for. $C_{13}H_{12}FN_2O_2^+$ $[M-^tBu+2H]^+$ 247.0883, found 247.0888.

For **S3b:** (787 mg, pale yellow oil, 83% yield) ^1H NMR (600 MHz, $CDCl_3$) δ 8.25 (ddd, *J* = 4.9, 2.0, 1.1 Hz, 1H), 7.71 (ddd, *J* = 9.4, 7.3, 2.0 Hz, 1H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.31 (td, *J* = 7.4, 1.5 Hz, 1H), 7.28 (ddd, *J* = 7.1, 4.9, 1.8 Hz, 1H), 7.19 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.45 (s, 1H), 3.23 (q, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.40 (d, *J* = 238.1 Hz), 155.68, 146.95 (d, *J* = 14.6 Hz), 142.15 (d, *J* = 5.5 Hz), 137.36, 133.86 (d, *J* = 3.9 Hz), 130.46, 129.60, 128.94, 126.62, 123.54 (d, *J* = 32.0 Hz), 121.47 (d, *J* = 4.8 Hz), 79.22, 40.89, 33.44, 28.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.14. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{14}FN_2O_2^+$ $[M\text{-}^t\text{Bu}+2H]^+$ 261.1039, found 261.1044.

Adding **S3a** (or **S3b**) (2.5 mmol) into a 2N HCl solution (14 mL). The reaction mixture was stirred at room temperature for 1 h. The mixture was basified with 10% aqueous NaOH solution (100 mL) and extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated to give the crude product **S4a** (or **S4b**). This product was used in the next step without further purification.

Synthesis of **S7**

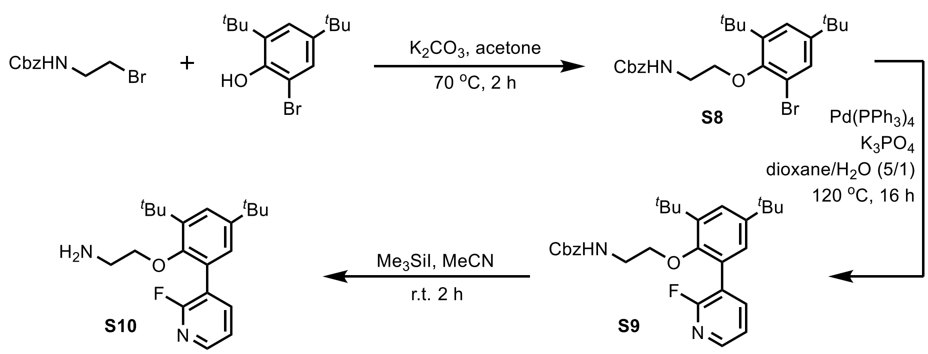


To a solution of Cbz-Gly-OH (2.51 g, 12 mmol), 4-bromo-2,6-di-tert-butyphenol (2.85 g, 10 mmol), and DMAP (183 mg, 1.5 mmol) in DCM (50 mL) at 0 °C was added DIC (2.32 mL, 15 mmol). The solution was warmed to room temperature and stirred for overnight. The insolubles were filtered and discarded. The filtrate was evaporated and purified by silica gel chromatography eluting with hexane/EA (92/8, v/v) to provide the product **S5** (3.5 g, 74% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.3 Hz, 1H), 7.39 – 7.30 (m, 6H), 5.37 (s, 1H), 5.16 (s, 2H), 4.34 (d, *J* = 5.7 Hz, 2H), 1.32 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.05, 156.15, 150.14, 143.91, 143.07, 136.13, 128.56, 128.44, 128.24, 128.15, 123.90, 117.57, 67.23, 43.56, 35.34, 34.85, 31.29, 30.43. HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{31}BrNO_4^+$ $[M+H]^+$ 476.1436, found 476.1435.

Following the procedure for synthesis of **S1** with dioxane instead of THF as a co-solvent with 5 mmol of **S5**, the residue was purified by silica gel chromatography eluting with hexane/EA (70/30, v/v) to provide the product **S6** (345 mg, 14% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.0 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.33 (h, *J* = 6.7, 6.1 Hz, 5H), 7.23 – 7.19 (m, 1H), 7.18 (s, 1H), 5.08 (s, 2H), 5.03 – 4.96 (m, 1H), 3.86 (s, 2H), 1.37 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.19, 163.33, 160.34 (d, *J* = 240.5 Hz), 155.84, 148.99, 147.14 (d, *J* = 14.4 Hz), 144.18, 142.31 (d, *J* = 5.5 Hz), 141.22, 136.09, 128.53, 128.23, 128.12, 126.10, 125.32, 121.32 (d, *J* = 4.9 Hz), 120.97 (d, *J* = 30.2 Hz), 67.14, 43.01, 35.00, 34.83, 31.42, 30.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{34}FN_2O_4^+$ $[M+H]^+$ 493.2503, found 493.2506.

To a stirred solution of **S6** (340 mg, 0.7 mmol) in MeOH (5 mL) was added Pd/C (70 mg). The resulting mixture was stirred at 50 ^{o}C for 2 h under hydrogen atmosphere. Upon completion, the reaction mixture was filtered. The filtrate was concentrated to afford the crude amine **S7**, which was used in the next step without further purification.

Synthesis of **S10**

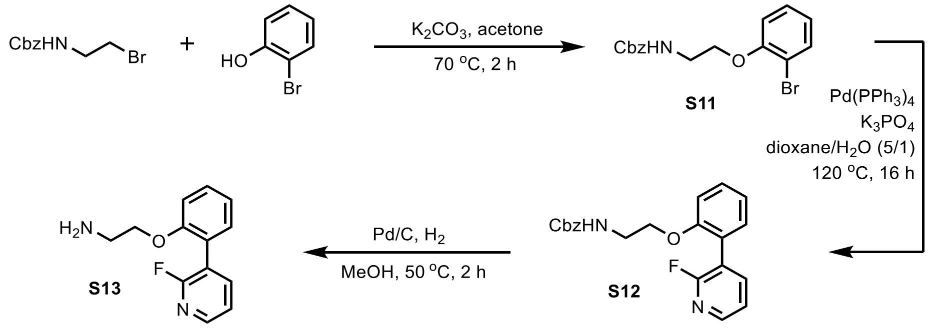


Benzyl 2-bromoethylcarbamate (2.06 g, 8 mmol), 4-bromo-2,6-di-tert-butyphenol (2.28 g, 8 mmol), and K_2CO_3 (2.76 g, 20 mmol) were charged in the flask and acetone (50 mL) was added to this mixture. The resulting mixture was refluxed for 2 h. The insolubles were filtered and discarded. The filtrate was evaporated and purified by silica gel chromatography eluting with hexane/EA (88/12, v/v) to provide the product **S8** (3.3 g, 89% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 7.34 – 7.30 (m, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 5.35 (s, 1H), 5.15 (s, 2H), 4.13 (t, *J* = 5.1 Hz, 2H), 3.66 (q, *J* = 5.4 Hz, 2H), 1.36 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.55, 151.78, 147.66, 144.13, 136.66, 128.95, 128.52, 128.12, 128.09, 123.95, 117.82, 71.09, 66.71, 41.34, 35.80, 34.59, 31.32, 31.08. HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{33}BrNO_3^+$ $[M+H]^+$ 462.1644, found 462.1642.

Following the procedure for synthesis of **S6** with 5 mmol of **S8**, the residue was purified by silica gel chromatography eluting with hexane/EA (70/30, v/v) to provide the product **S9** (287 mg, 12% yield) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 1H), 7.86 (ddd, *J* = 9.4, 7.4, 2.0 Hz, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 4.4 Hz, 4H), 7.35 – 7.33 (m, 1H), 7.18 – 7.15 (m, 1H), 7.14 (s, 1H), 5.08 (s, 2H), 4.88 (s, 1H), 3.49 – 3.46 (m, 2H), 3.22 (q, *J* = 5.3 Hz, 2H), 1.41 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.48 (d, *J* = 239.7 Hz), 156.12, 153.19, 146.73, 146.63, 146.11, 142.39, 142.07 (d, *J* = 6.1 Hz), 136.60, 128.54, 128.17, 128.14, 126.86 – 126.33 (m), 125.13, 122.21 (d, *J* = 32.0 Hz), 121.30 (d, *J* = 5.5 Hz), 71.61, 66.67, 40.87, 35.41, 34.60, 31.45, 30.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.59. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{36}FN_2O_3^+$ $[M+H]^+$ 479.2710, found 479.2711.

To a stirred solution of **S9** (250 mg, 0.52 mmol) in MeCN (5 mL) was added Me_3SiI (370 μL, 2.6 mmol). The resulting mixture was stirred at room temperature for 2 h. The reaction was quenched with MeOH. The resulting mixture was concentrated to give the crude amine **S10**, which was used in the next step without further purification.

Synthesis of **S13**

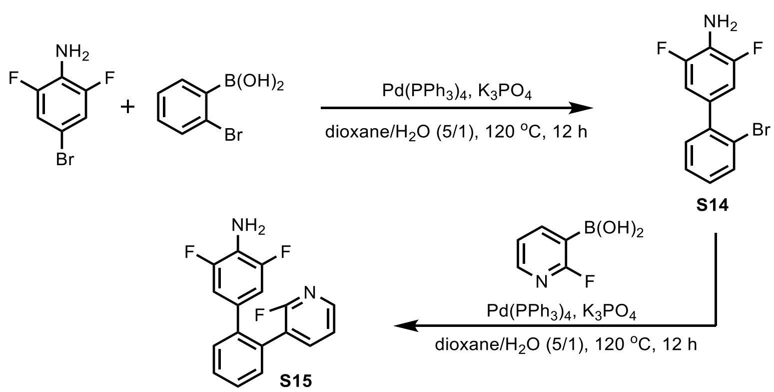


Following the procedure for synthesis of **S8** with 5 mmol of 2-bromophenol, the residue was purified by silica gel chromatography eluting with hexane/EA (85/15, v/v) to provide the product **S11** (1.3 g, 75% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.31 (ddd, *J* = 8.5, 5.2, 2.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.90 – 6.87 (m, 1H), 6.87 – 6.84 (m, 1H), 5.33 (s, 1H), 5.12 (s, 2H), 4.10 (t, *J* = 5.1 Hz, 2H), 3.66 (q, *J* = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.44, 154.82, 136.41, 133.40, 128.59, 128.55, 128.17, 128.14, 122.49, 113.65, 112.40, 68.43, 66.87, 40.53. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{16}BrNO_3Na^+$ $[M+Na]^+$ 372.0211, found 372.0211.

Following the procedure for synthesis of **S6** with 3.7 mmol of **S11**, the residue was purified by silica gel chromatography eluting with hexane/EA (70/30, v/v) to provide the product **S12** (596 mg, 44% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.4 Hz, 1H), 7.76 (ddd, *J* = 9.3, 7.3, 2.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.33 – 7.29 (m, 1H), 7.28 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.22 (t, *J* = 5.8 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 5.09 (s, 2H), 5.03 (s, 1H), 4.08 (t, *J* = 5.1 Hz, 2H), 3.52 (q, *J* = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.70 (d, *J* = 239.8 Hz), 156.39, 155.63, 146.48 (d, *J* = 14.7 Hz), 145.41, 142.06 (d, *J* = 5.4 Hz), 136.48, 131.20, 130.20, 128.51, 128.10, 128.06, 123.48 – 123.38 (m), 121.33 – 121.22 (m), 112.15, 67.52, 66.76, 40.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.80. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{20}FN_2O_3^+$ $[M+H]^+$ 367.1458, found 367.1458.

Following the procedure for synthesis of **S7** with Pd/C (40%, w/w) with 1 mmol of **S12**. The crude product **S13** was obtained and used in the next step without further purification.

Synthesis of **S15**

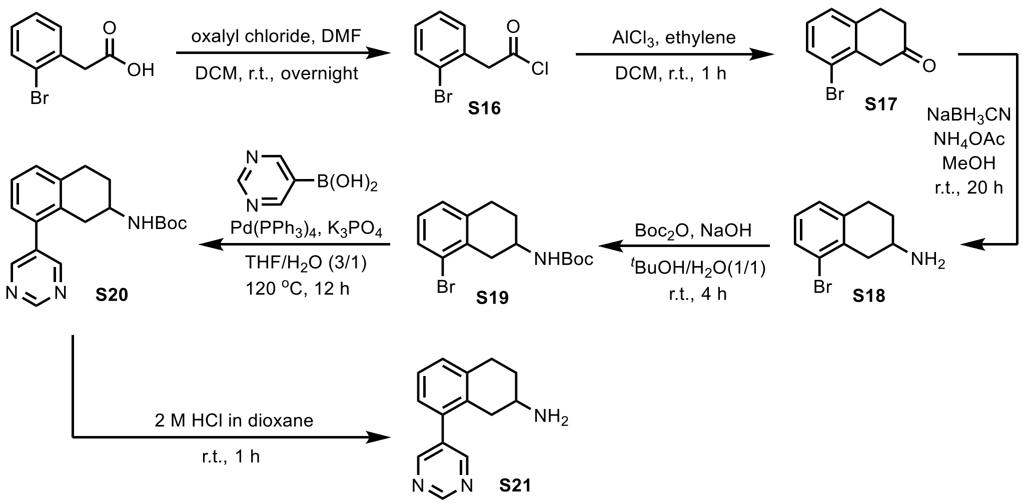


Following the procedure for synthesis of **S6** with 3 mmol of 4-bromo-2,6-difluoroanaline, the residue was purified by silica gel chromatography eluting with hexane/EA (95/5, v/v) to provide the product **S14** (699 mg, 82% yield) as a brown solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.20 – 7.16 (m, 1H), 6.92 (dd, *J* = 7.3, 2.0 Hz, 2H), 3.80 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.35 (dd, *J* = 240.2, 8.6 Hz), 140.67, 133.28, 131.21, 129.88 (t, *J* = 9.0 Hz), 128.87, 127.49, 123.41 (t, *J* = 16.5

Hz), 122.61, 112.27 (dd, J = 16.7, 6.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.51. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_9BrF_2N^+$ $[M+H]^+$ 283.9886, found 283.9894.

Following the procedure for synthesis of **S6** with 1 mmol of **S14**, the residue was purified by silica gel chromatography eluting with hexane/EA (85/15, v/v) to provide the product **S15** (177 mg, 59% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (ddd, J = 4.9, 2.0, 1.1 Hz, 1H), 7.57 (ddd, J = 9.5, 7.4, 2.0 Hz, 1H), 7.47 (td, J = 7.5, 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.6 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.14 (ddd, J = 7.3, 4.9, 1.8 Hz, 1H), 6.59 (dd, J = 7.4, 2.0 Hz, 2H), 3.68 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.99, 159.40, 151.55 (dd, J = 240.1, 8.5 Hz), 146.61 (d, J = 14.4 Hz), 142.19 (d, J = 4.5 Hz), 139.88 (d, J = 2.7 Hz), 132.43 (d, J = 4.5 Hz), 130.90 (d, J = 1.7 Hz), 130.20, 128.93, 127.58, 123.71 (d, J = 30.8 Hz), 122.89, 121.27 (d, J = 4.5 Hz), 111.89 (dd, J = 16.5, 6.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.42, -135.22. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{12}F_3N_2^+$ $[M+H]^+$ 301.0953, found 301.0952.

Synthesis of **S18**[1,2] and **S21**



To a stirred solution of 2-bromophenylacetic acid (25 g, 116.3 mmol) in DCM (200 mL) at 0 °C was added DMF (100 μL) and oxalyl chloride (10.83 mL, 127.9 mmol). The reaction solution was warmed to room temperature and stirred for overnight. The mixture was concentrated to obtain the crude product **S16**, which was used in the next step without further purification.

To a stirred suspension of high-quality $AlCl_3$ (31 g, 232.6 mmol) in DCM (150 mL) at -10 °C was added a solution of **S16** (116.3 mmol) in DCM (100 mL) over 30 min. Then, ethylene was bubbled into the reaction mixture at -10 °C for 1 h. After full conversion (GC-MS detection), the ethylene flow was stopped and the reaction mixture continued to be stirred at -10 °C for 15 min. Then the mixture was poured slowly into a beaker containing lots of ice. [Caution: addition of ice into the reaction mixture causes significant exotherms which can lead to explosions] The layers were separated, and the collected organic phase was sequentially washed with water (500 mL x 2), saturated $NaHCO_3$ solution (500 mL), and brine, dried with Na_2SO_4, and concentrated. The residue was dissolved in MeCN (200 mL), washed with pentane to remove polyethylene, and concentrated to give the product **S17** (24 g, 92% for two steps) as a pale black solid, which was used in the next step without further purification.

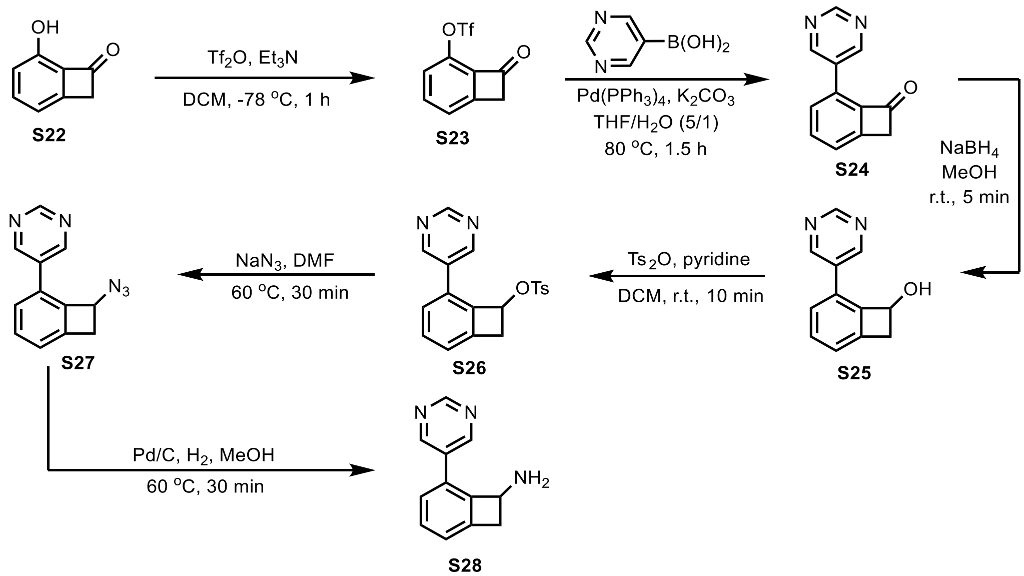
To a solution of **S17** (24 g, 106.7 mmol) and NH_4OAc (65.8 g, 853.6 mmol) in MeOH (250 mL) at room temperature was added $NaBH_3CN$ (8 g, 128 mmol). The resulting mixture was stirred for 20 h. The reaction mixture was basified with 10% aqueous NaOH solution (250 mL) and evaporated. Then water (500 mL) was added and the solution was extracted with EA (200 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated to afford the crude product **S18** as brown oil, which was used in the next step without further purification.

Following the procedure for synthesis of **S2a** with 30 mmol of crude **S18**, the residue was purified by silica gel chromatography eluting with hexane/EA (95/5, v/v) to provide the product **S19** (3.3 g, 34% yield for above two steps) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 4.60 (s, 1H), 3.98 (s, 1H), 3.16 (dd, *J* = 17.2, 5.6 Hz, 1H), 2.88 (q, *J* = 6.7, 5.4 Hz, 2H), 2.52 (dd, *J* = 17.1, 8.5 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.72 – 1.64 (m, 1H), 1.47 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.24, 134.04, 130.10, 127.94, 127.22, 125.75, 79.43, 46.60, 36.88, 28.78, 28.44, 28.10. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{13}BrNO_2^+$ $[M+H]^+$ 270.0130, found 270.0139.

Following the procedure for synthesis of **S1** with 4.3 mmol of **S19** and 8.6 mmol of 5-pyrimidinylboronic acid, the residue was purified by silica gel chromatography eluting with hexane/EA (85/15, v/v) to provide the product **S20** (1.22 g, 87% yield) as pale yellow glue. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.69 (s, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 4.56 (s, 1H), 3.91 (s, 1H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.87 (dd, *J* = 16.3, 5.1 Hz, 1H), 2.47 (dd, *J* = 16.3, 8.8 Hz, 1H), 2.12 (s, 1H), 1.73 (ddt, *J* = 9.8, 7.8, 2.0 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.38, 156.61, 155.11, 136.79, 135.00, 134.80, 132.37, 129.78, 127.78, 126.44, 79.51, 46.46, 34.98, 28.99, 28.39, 28.06. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}N_3O_2^+$ $[M+H]^+$ 326.1869, found 326.1865.

Following the procedure for synthesis of **S4a** with 2.2 mmol of **S20**. The crude product **S21** was obtained and used in the next step without further purification.

Synthesis of **S28**



S23 was synthesized according to modified literature procedures:[3] To a stirred solution of **S22** (1.6 g, 12 mmol) in DCM (100 mL) at -78 °C was sequentially added Et_3N (3.34 mL, 24 mmol) and Tf_2O (3.03 mL, 18 mmol). The reaction solution was stirred at -78 °C for 1 h. Saturated NH_4Cl solution (100 mL) was added to quench the reaction. Then water (150 mL) was added and the solution was extracted with DCM (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (85/15, v/v) to provide **S23** (3.1 g, 97% yield) as colorless oil.

For **S22**:[4] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.01 (d, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.27, 152.58, 150.56, 138.60, 132.10, 116.20, 114.97, 51.16.

For **S23**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.25 (m, 1H), 4.10 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.69, 152.48, 139.25, 137.71, 137.45, 123.92, 121.31, 118.69 (q, J = 320.9 Hz), 53.41. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.54. HRMS (ESI-TOF) *m/z* Calcd for $C_9H_6F_3O_4S^+$ $[M+H]^+$ 266.9939, found 266.9944.

To a solution of K_2CO_3 (1.7 g, 12.5 mmol) in water (4 mL) was added **S23** (565 mg, 2.5 mmol), 5-pyrimidinylboronic acid (620 mg, 5 mmol), $Pd(PPh_3)_4$ (289 mg, 0.25 mmol), and THF (20 mL). The Schlenk tube was evacuated and refilled with nitrogen for three times. Then sealed and put into a preheated oil bath at 80 ^oC for 1.5 h. After completion, the reaction mixture was cooled to room temperature. Water (100 mL) was added and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (60/40, v/v) to provide the product **S24** (299 mg, 61% yield) as a white flocculent solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.37 (s, 2H), 9.24 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.3 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.18, 158.60, 155.44, 152.15, 144.78, 136.00, 129.03, 129.02, 125.49, 124.08, 52.12. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_9N_2O^+$ $[M+H]^+$ 197.0715, found 197.0713.

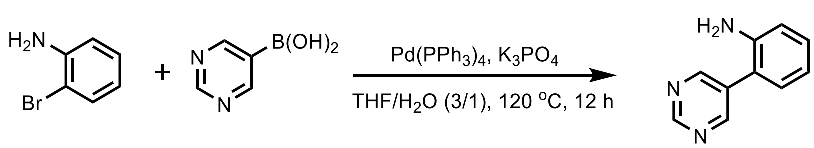
To a solution of **S24** (98 mg, 0.5 mmol) in MeOH (5 mL) at room temperature was slowly added $NaBH_4$ (38 mg, 1 mmol). The resulting mixture was stirred for 5 min. The reaction mixture was evaporated. Then water (50 mL) was added and the solution was extracted with EA (20 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated to afford the crude product **S25** (99 mg, quant.) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.21 (s, 2H), 9.14 (s, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 5.45 (ddd, J = 8.4, 4.5, 1.9 Hz, 1H), 3.71 (dd, J = 14.3, 4.5 Hz, 1H), 3.21 – 3.13 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.39, 155.38, 145.26, 143.47, 131.09, 130.71, 129.48, 124.62, 124.31, 70.85, 42.48. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{11}N_2O^+$ $[M+H]^+$ 199.0871, found 199.0874.

To a solution of **S25** (99 mg, 0.5 mmol) in DCM (5 mL) at room temperature was added pyridine (402 μL, 5 mmol) and Ts_2O (815 mg, 2.5 mmol). The resulting mixture was stirred for 5 min. Water (10 mL) was added and the mixture was extracted with DCM (5 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with DCM/EA (50/50, v/v) to provide the product **S26** (176 mg, quant.) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.90 (s, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.1 Hz, 1H), 5.83 (dd, J = 4.2, 1.8 Hz, 1H), 3.66 (dd, J = 14.8, 4.2 Hz, 1H), 3.44 (d, J = 14.8 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.88, 155.25, 145.33, 143.60, 139.12, 133.05, 132.13, 130.52, 130.36, 130.09, 128.04, 126.05, 123.98, 75.00, 40.22, 21.72. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{17}N_2O_3S^+$ $[M+H]^+$ 353.0960, found 353.0958.

To a solution of **S26** (176 mg, 0.5 mmol) in DMF (5 mL) was added NaN_3 (98 mg, 1.5 mmol). The reaction mixture was stirred at 60 °C for 30 min. Then water (10 mL) was added and the mixture was extracted with EA (10 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with DCM/EA (70/30, v/v) to provide the product **S27** (89 mg, 80% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.08 (s, 2H), 7.53 – 7.48 (m, 2H), 7.24 (d, J = 6.9 Hz, 1H), 5.06 (d, J = 2.8 Hz, 1H), 3.73 (dd, J = 14.5, 4.8 Hz, 1H), 3.43 – 3.36 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.83, 155.19, 143.63, 140.82, 131.22, 130.81, 129.73, 125.68, 124.11, 59.29, 38.21. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{10}N_5^+$ $[M+H]^+$ 224.0936, found 224.0942.

Following the procedure for synthesis of **S7** with 0.4 mmol of **S27** at 60 °C for 30 min. The crude product **S28** was obtained and used in the next step without further purification.

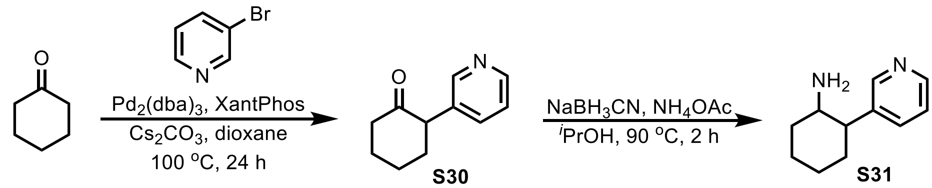
Synthesis of **S29**



S29

Following the procedure for synthesis of **S1**, purification by silica gel chromatography eluting with hexane/EA (50/50, v/v) afforded product **S29** (328 mg, 64% yield) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.88 (s, 2H), 7.25 (td, J = 7.7, 1.6 Hz, 1H), 7.10 (dd, J = 7.6, 1.6 Hz, 1H), 6.89 (td, J = 7.5, 1.2 Hz, 1H), 6.81 (dd, J = 8.1, 1.2 Hz, 1H), 3.72 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.44, 156.97, 143.86, 133.41, 130.56, 130.26, 119.97, 119.36, 116.28. HRMS (ESI-TOF) *m/z* Calcd for $C_{10}H_{10}N_3^+$ $[M+H]^+$ 172.0875, found 172.0875.

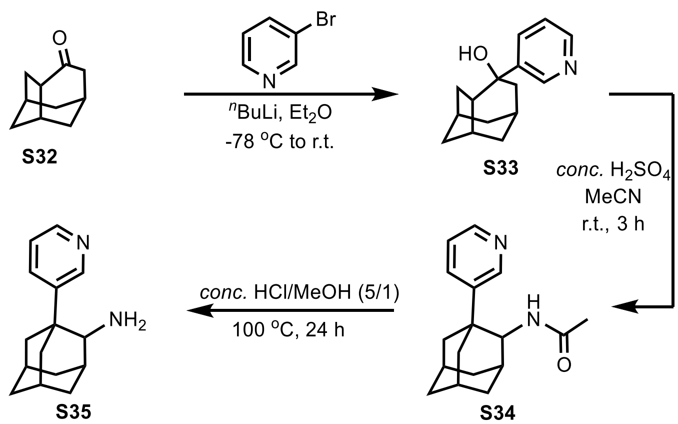
Synthesis of **S31**[5]



To a solution of $Pd_2(dba)_3$ (14 mg, 0.015 mmol), XantPhos (21 mg, 0.036 mmol), and Cs_2CO_3 (2.15g, 6.6 mmol) in dioxane (3 mL) was added cyclohexanone (622 μL, 6 mmol) and 3-bromopyridine (289 μL, 3 mmol). The Schlenk tube was evacuated and refilled with nitrogen for three times. Then sealed and put into a preheated oil bath at 100 °C for 24 h. After completion, the reaction mixture was cooled to room temperature. Water (100 mL) was added and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (50/50, v/v) to provide the product **S30** (140 mg, 27% yield) as a pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.38 (d, *J* = 2.2 Hz, 1H), 7.49 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 3.63 (dd, *J* = 12.7, 5.5 Hz, 1H), 2.56 (dddd, *J* = 13.9, 4.6, 3.1, 1.5 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.32 – 2.27 (m, 1H), 2.21 (ddq, *J* = 9.2, 6.0, 3.2 Hz, 1H), 2.03 (dddd, *J* = 8.4, 6.7, 4.1, 2.8 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.85 (dddd, *J* = 16.2, 8.9, 4.2, 1.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 209.18, 149.91, 148.29, 136.29, 134.29, 123.25, 54.93, 42.22, 35.43, 27.80, 25.45. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{14}NO^+$ $[M+H]^+$ 176.1075, found 176.1081.

To a solution of **S30** (100 mg, 0.57 mmol) and NH_4OAc (439 mg, 5.7 mmol) in ^{i}PrOH (5 mL) at room temperature was added $NaBH_3CN$ (71 mg, 1.14 mmol). The sealed tube was put into a preheated oil bath at 90 °C for 2 h. The reaction mixture was basified with 10% aqueous NaOH solution (50 mL) and evaporated. Then water (50 mL) was added and the solution was extracted with EA (20 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated to afford the crude product **S31** as brown oil, which was used in the next step without further purification.

Synthesis of **S35**[6]



To a solution of 3-bromopyridine (586 μL, 6 mmol) in Et_2O (20 mL) at -78 ^oC was slowly added ^nBuLi (6 mmol). **S32** (450 mg, 3 mmol) in Et_2O (10 mL) was added after the solution was stirred for 30 min. The reaction mixture was stirred for 2 h (-78 ^oC, 1 h; r.t., 1h). Cooling to 0 ^oC, saturated NH_4Cl solution (50 mL) was added to quench the reaction. Then saturated $NaHCO_3$ solution (100 mL) was added and the solution was extracted with EA (50 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (15/85, v/v) to provide the product **S33** (289 mg, 42% yield) as a white solid.

For **S32**: ^1H NMR (600 MHz, $CDCl_3$) δ 2.76 – 2.71 (m, 1H), 2.62 (q, *J* = 6.0 Hz, 1H), 2.55 (dd, *J* = 17.9, 2.7 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.32 – 2.27 (m, 1H), 2.25 (dt, *J* = 9.6, 4.7 Hz, 1H), 2.00 – 1.93 (m, 2H), 1.83 – 1.79 (m, 1H), 1.74 (dtt, *J* = 11.4, 4.1, 2.0 Hz, 1H), 1.71 – 1.66 (m, 2H), 1.64 (dd, *J* = 11.2, 2.7 Hz, 1H), 1.54 (ddd, *J* = 13.1, 5.2, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 216.79, 51.18, 45.09, 41.43, 38.18, 37.44, 37.31, 37.20, 34.88, 29.58.

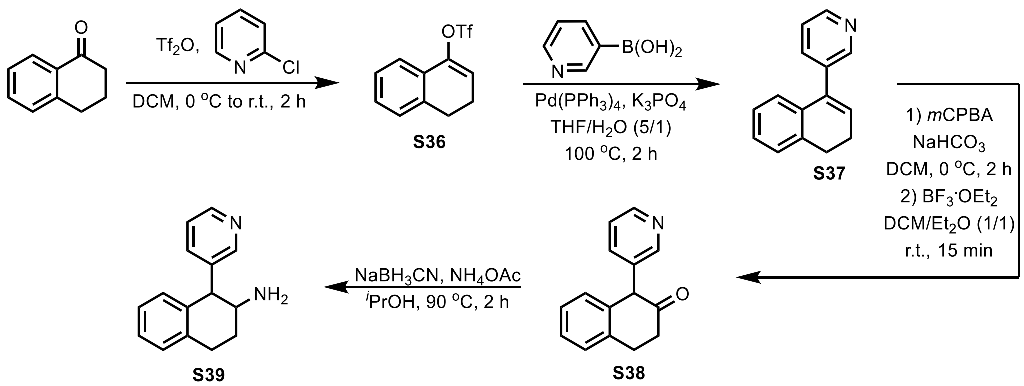
For **S33**: *Diastereomer 1:* ^1H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.4 Hz, 1H), 8.47 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.82 (ddd, *J* = 8.1, 2.4, 1.6 Hz, 1H), 7.28 – 7.26 (m, 1H), 2.79 – 2.74 (m, 1H), 2.48 (q, *J* = 6.3 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.33 – 2.23 (m, 2H), 2.23 – 2.16 (m, 2H), 1.97 (s, 1H), 1.84 (ddt, *J* = 13.6, 5.6, 2.8 Hz, 1H), 1.77 – 1.72 (m, 2H), 1.61 (dd, *J* = 11.0, 3.0 Hz, 1H), 1.47 (dd, *J* = 12.4, 3.1 Hz, 1H), 1.37 (dt, *J* = 13.2, 3.0 Hz, 1H), 1.27 (dt, *J* = 12.8, 2.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.10, 147.70, 144.22, 133.73, 123.22, 75.46, 44.96, 42.36, 41.75, 39.75, 36.30, 35.85, 33.79, 32.30, 28.79. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{20}NO^+$ $[M+H]^+$ 230.1545, found 230.1548. *Diastereomer 2:* ^1H NMR (600 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.5 Hz, 1H), 8.49 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.95 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.28 (dd, *J* = 8.1, 4.7

Hz, 1H), 2.92 – 2.85 (m, 1H), 2.80 (dd, *J* = 14.6, 8.9 Hz, 1H), 2.35 – 2.29 (m, 1H), 2.26 (t, *J* = 4.2 Hz, 1H), 2.22 (ddd, *J* = 13.1, 3.1, 1.5 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.88 (dddd, *J* = 13.0, 10.5, 5.2, 2.3 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.54 (dd, *J* = 10.8, 3.1 Hz, 2H), 1.20 – 1.16 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.31, 148.07, 144.12, 134.19, 123.20, 74.09, 45.02, 42.45, 41.79, 40.17, 35.64, 34.72, 34.14, 31.43, 29.13. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{20}NO^+$ $[M+H]^+$ 230.1545, found 230.1544.

To 10 ml of MeCN at 0 ^{o}C was slowly added *conc.* H_2SO_4 (3.75 mL) and **S33** (114 mg, 1.5 mmol). The reaction mixture was warm to room temperature and stirred for 3 h. Then the mixture was poured into ice and basified with 10% KOH solution (100 mL). The suspension was filtered and the solid residue was washed with water and hexane. Using rotovap to dry the residue gave product **S34** (284 mg, 70% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.5 Hz, 1H), 8.45 (d, *J* = 3.5 Hz, 1H), 7.70 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.25 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.43 (d, *J* = 9.1 Hz, 1H), 4.49 (d, *J* = 8.9 Hz, 1H), 2.20 – 2.12 (m, 3H), 2.07 – 1.99 (m, 4H), 1.91 (dq, *J* = 12.9, 2.8 Hz, 1H), 1.83 – 1.79 (m, 1H), 1.78 – 1.74 (m, 2H), 1.74 (s, 3H), 1.73 – 1.68 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.01, 147.73, 147.07, 141.88, 133.37, 123.31, 55.29, 45.77, 38.67, 36.70, 36.47, 34.97, 32.75, 30.90, 28.19, 27.60, 23.39. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{23}N_2O^+$ $[M+H]^+$ 271.1810, found 271.1813.

To a solution of **S34** (100 mg, 0.37 mmol) in MeOH (2 mL) was added 10 mL of *conc.* HCl. The solution was put into a preheated oil bath at 100 ^{o}C for 24 h. The reaction mixture was evaporated and basified with 10% aqueous NaOH solution (50 mL). Then water (50 mL) was added and the solution was extracted with EA (20 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated to afford the crude product **S35** as brown oil, which was used in the next step without further purification.

Synthesis of **S39**



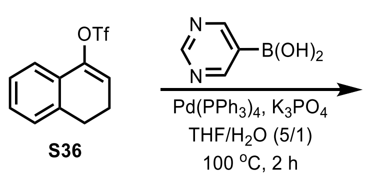
To a solution of α-tetralone (4.55 mL, 34.2 mmol) and 2-chloropyridine (3.5 mL, 37.6 mmol) in DCM (100 mL) at 0 °C was slowly added Tf_2O (6.4 mL, 37.6 mmol) under N_2 protection. The reaction mixture was warm to room temperature and stirred for 2 h. After completion, the mixture was evaporated, and redissolved in hexane. The solution was filtered and the filtrate was concentrated. The residue was purified by silica gel chromatography eluting with hexane to provide the product **S36** (4.9 g, 52% yield) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.27 – 7.24 (m, 2H), 7.17 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.01 (t, *J* = 4.8 Hz, 1H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.51 (td, *J* = 8.2, 4.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.37, 136.22, 129.18, 129.18, 128.67, 127.75, 126.94, 121.23, 117.74, 116.50 (d, *J* = 320.2 Hz), 26.85, 22.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{10}F_3O_3S^+$ $[M+H]^+$ 279.0303, found 279.0308.

To a solution of K_3PO_4 (8.48 g, 40 mmol) in water (15 mL) was added 3-pyridylboronic acid (4.92 g, 40 mmol), **S36** (5.56 g, 20 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol), and THF (60 mL). The Schlenk tube was evacuated and refilled with nitrogen for three times. Then sealed and put into a preheated oil bath at 100 °C for 2 h. After completion, the reaction mixture was cooled to room temperature. Water (250 mL) was added and the mixture was extracted with EA (150 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (70/30, v/v) to provide the product **S37** (3.9 g, 94% yield) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 2.3 Hz, 1H), 8.56 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.63 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.28 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.17 (td, *J* = 7.3, 1.4 Hz, 1H), 7.11 (td, *J* = 7.5, 1.6 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.12 (t, *J* = 4.7 Hz, 1H), 2.88 – 2.83 (m, 2H), 2.42 (td, *J* = 8.0, 4.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.67, 148.39, 136.67, 136.61, 136.29, 136.05, 134.29, 129.27, 127.77, 127.41, 126.39, 124.92, 123.02, 28.04, 23.47. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{14}N^+$ $[M+H]^+$ 208.1126, found 208.1126.

S38 was synthesized according to modified literature procedures:[7] To a solution of **S37** (1.51 g, 7.3 mmol) in DCM (50 mL) at 0 °C was sequentially added $NaHCO_3$ (1.84 g, 21.9 mmol) and *m*CPBA (21.9 mmol). The reaction mixture was stirred at 0 °C for 2 h. Then $Na_2S_2O_3$ solid and 10% aqueous NaOH solution (100 mL) were sequentially added and the solution was extracted with DCM (50 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was redissolved in 50 mL of DCM/Et_2O (50/50, v/v) and $BF_3{\cdot}Et_2O$ (18.3 mmol) was added. The solution was stirred at r.t. for 15 min and evaporated in the fume hood. Then 10% aqueous NaOH solution (100 mL) was added and the solution was extracted with EA (50 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (65/35, v/v) to provide the product **S38** (260 mg, 16% yield) as pale yellow oil. [Note: **S38** is easy to be oxidized in the air and quickly used for next step]

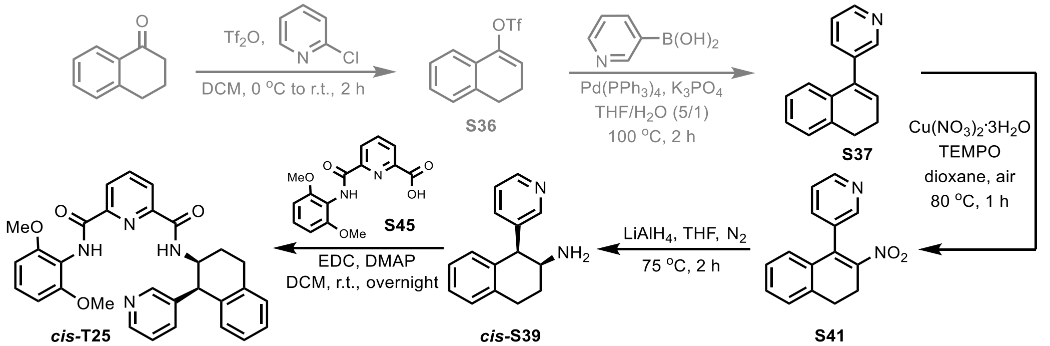
Following the procedure for synthesis of **S31** with 1.1 mmol of **S38**. The crude product **S39** was obtained and used in the next step without further purification.

Synthesis of **S40**



Following the procedure for synthesis of **S37** with 3 mmol of **S36**, purification by silica gel chromatography eluting with hexane/EA (70/30, v/v) afforded product **S40** (593 mg, 95% yield) as pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.73 (s, 2H), 7.24 – 7.20 (m, 2H), 7.15 (td, *J* = 7.6, 2.0 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.18 (t, *J* = 4.7 Hz, 1H), 2.89 (t, *J* = 8.0 Hz, 2H), 2.49 – 2.45 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.53, 156.46, 136.52, 134.20, 133.64, 133.45, 130.96, 128.05, 127.93, 126.64, 124.51, 27.86, 23.50. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}N_2^+$ $[M+H]^+$ 209.1079, found 209.1082.

Optimized route for synthesis of ***cis*-T25**[8]

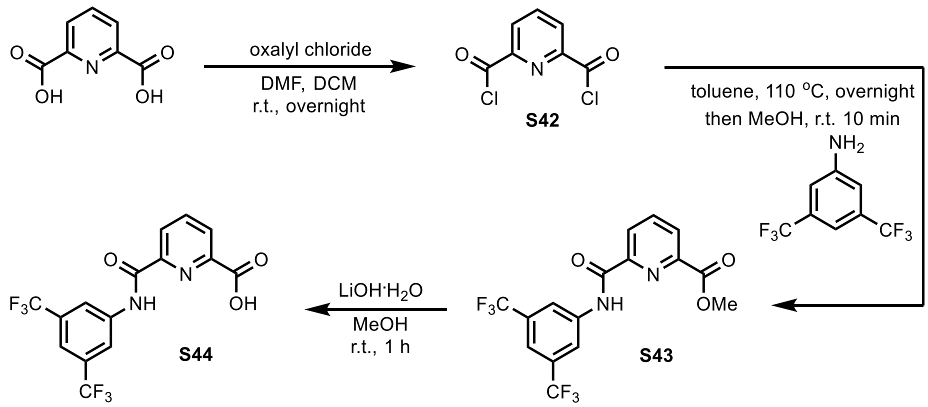


To a solution of **S37** (3.1 g, 15 mmol) in dioxane (150 mL) was sequentially added $Cu(NO_3)_2\cdot 3H_2O$ (7.26 g, 30 mmol) and TEMPO (937 mg, 6 mmol). The flask was keeping open and the reaction mixture was stirred at 80 ^oC for 1 h. After filtering off the precipitate, 10% aqueous NaOH solution (200 mL) was added into the filtrate and the solution was extracted with EA (100 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA (70/30, v/v) to provide the product **S41** (1.7 g, 45% yield) as a yellow solid. ^1H NMR (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.46 (s, 1H), 7.55 (dt, J = 7.8, 1.9 Hz, 1H), 7.40 (dd, J = 7.8, 4.8 Hz, 1H), 7.32 (td, J = 7.4, 1.3 Hz, 1H), 7.28 (d, J = 6.9 Hz, 1H), 7.15 (td, J = 7.7, 1.2 Hz, 1H), 6.73 – 6.70 (m, 1H), 3.14 – 3.07 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.50, 148.77, 146.87, 136.16, 136.04, 135.99, 132.99, 130.49, 128.98, 127.96, 127.20, 123.42, 28.15, 25.81. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{13}N_2O_2^+$ $[M+H]^+$ 253.0977, found 253.0983.

To a solution of LAH (24 mmol) in THF (60 mL) at 0 ^oC was slowly added a solution of **S41** (1.5 g, 6 mmol) in THF (40 mL) under N_2 protection. After warming to the room temperature, the flask was put into a preheated oil bath at 75 ^oC for 2 h. Upon completion, 1 mL of water, 1 mL of 15 % aqueous NaOH solution, 3 mL of water, and Na_2SO_4 solid were sequentially added. Then, the reaction mixture was filtered. Water (300 mL) was added and the solution was extracted with EA (100 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated to afford the crude product *cis*-**S39** as brown oil, which was used in the next step without further purification.

To a solution of **S45** (1.8 g, 6 mmol), *cis*-**S39** (1.12 g, 5 mmol), and DMAP (61 mg, 0.5 mmol) in DCM (50 mL) at 0 ^oC was added EDC (1.44 g, 7.5 mmol). The solution was warmed to room temperature and stirred for overnight. The reaction mixture was evaporated and purified by silica gel chromatography eluting with EA to provide the product *cis*-**T25** (509 mg, 17% yield) as a white solid. If necessary, MeOH can be used to further recrystallization.

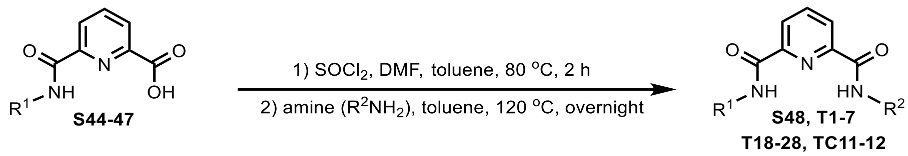
Synthesis of **S44**



To a stirred solution of 2,6-pyridinedicarboxylic acid (6.68 g, 40 mmol) in DCM (100 mL) at 0 °C was added DMF (40 μL) and oxalyl chloride (7.8 mL, 92 mmol). The reaction solution was warmed to room temperature and stirred for overnight. The mixture was concentrated to obtain the crude product **S42**, which was then dissolved in toluene (100 mL). 3,5-Bis(trifluoromethyl)aniline (4.4 mL, 28 mmol) was added to the solution at room temperature. The reaction mixture was put into a preheated oil bath at 110 °C for overnight. Upon completion, MeOH (10 mL) was added to quench the reaction. The solvent was removed. The recrystallization from MeOH afforded the product **S43** (14.6 g, 93% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.50 (d, *J* = 8.9 Hz, 1H), 8.35 (s, 2H), 8.32 (s, 1H), 8.12 (t, *J* = 7.8 Hz, 1H), 7.67 (s, 1H), 4.08 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.64, 161.75, 149.14, 146.65, 139.24, 138.97. 132.46 (q, *J* = 33.7 Hz), 128.10 (d, *J* = 6.5 Hz), 125.81, 123.15 (q, *J* = 273.0 Hz), 119.77 (q, *J* = 4.3 Hz), 118.59 – 116.89 (m), 53.18. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.63. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{11}F_6N_2O_3^+$ $[M+H]^+$ 393.0674, found 393.0672.

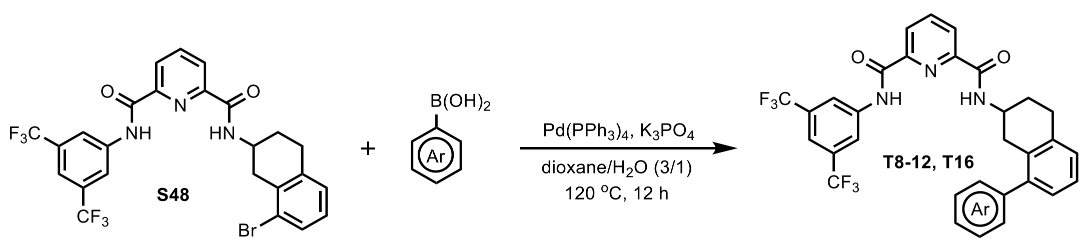
To a solution of **S43** (14.6 g, 37.3 mmol) in MeOH (100 mL) was added $LiOH·H_2O$ (6.3 g, 149.2 mmol). The resulting mixture was stirred at room temperature for 1 h. The mixture was acidified with 2N HCl solution (500 mL) and extracted with EA (300 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated to give the product **S44** (10 g, 71% yield) as a white solid. ^{1}H NMR (600 MHz, CD_3OD) δ 8.61 (s, 2H), 8.31 (dd, J = 7.7, 1.6 Hz, 2H), 8.10 (t, J = 7.7 Hz, 1H), 7.69 (s, 1H). ^{13}C NMR (151 MHz, CD_3OD) δ 169.56, 163.35, 152.59, 147.89, 140.27, 137.87, 131.40 (q, J = 33.2 Hz), 126.55, 122.95, 122.51 (q, J = 271.8 Hz), 118.94 (dd, J = 8.9, 3.4 Hz), 116.28 – 115.01 (m). ^{19}F NMR (376 MHz, CD_3OD) δ -63.26. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_9F_6N_2O_3^+$ $[M+H]^+$ 379.0517, found 379.0518.

Synthesis of **S48**, **T1-7, T18-28, TC11-12**



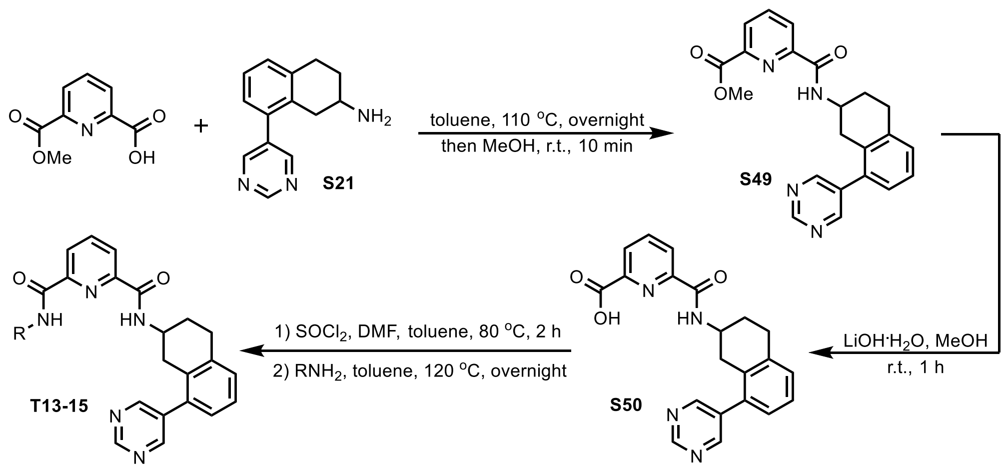
To a solution of **S44-47** (1 mmol) in dry toluene (20 mL) was added DMF (3 drops) and thionyl chloride (181 μL, 2.5 mmol) under nitrogen protection. The reaction mixture was stirred at 80 ^{o}C for 2 h. After completion, the mixture was concentrated and redissolved in dry toluene (20 mL). Amine (1 mmol) was added, and the reaction solution was stirred at 120 ^{o}C for overnight. The mixture was concentrated and purified by silica gel chromatography eluting with hexane/EA to provide the corresponding product **S48**, **T1-7, T18-28, TC11-12.**

Synthesis of **T8-12, T16**



To a solution of K_3PO_4 (127 mg, 0.6 mmol) in water (1 mL) was added **S48** (176 mg, 0.3 mmol), arylboronic acid (0.6 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), and dioxane (3 mL). The Schlenk tube was evacuated and refilled with nitrogen for three times. The reaction solution was stirred at 120 ^{o}C for 12 h. After completion, the reaction mixture was cooled to room temperature. Water (100 mL) was added and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA to provide the product **T8-12, T16.**

Synthesis of **T13-15**

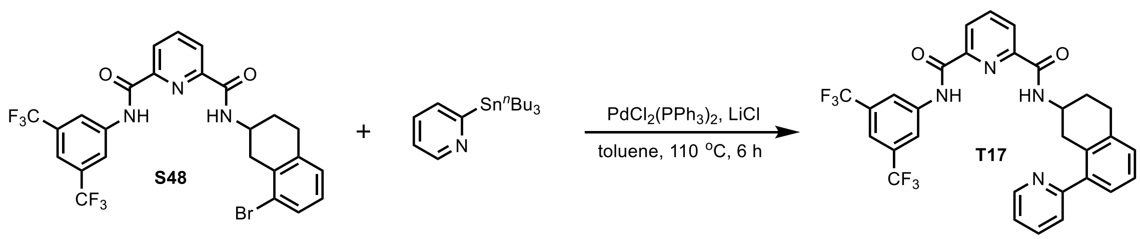


To a solution of 2,6-Pyridinedicarboxylic acid monomethyl ester (592 mg, 2.9 mmol) in toluene (40 mL) was added amine **S21** (484 mg, 2 mmol) under nitrogen protection. The reaction mixture was stirred at 110 ^{o}C for overnight. Upon completion, MeOH (2 mL) was added to quench the reaction. The solvent was removed. The recrystallization from MeOH afforded the product **S49** (621 mg, 80% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.72 (s, 2H), 8.36 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.21 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.00 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.06 (dd, *J* = 7.2, 1.7 Hz, 1H), 4.42 – 4.36 (m, 1H), 4.01 (s, 3H), 3.12 – 3.07 (m, 2H), 2.97 (dd, *J* = 16.2, 4.4 Hz, 1H), 2.73 (dd, *J* = 16.2, 10.0 Hz, 1H), 2.29 – 2.26 (m, 1H), 1.98 – 1.90 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.94, 162.87, 157.41, 156.63, 150.07, 146.52, 138.57, 136.76, 135.02, 134.79, 132.48, 129.79, 127.83, 127.32, 126.51, 125.46, 52.95, 46.08, 34.63, 28.96, 28.80. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{21}N_4O_3^+$ $[M+H]^+$ 389.1614, found 389.1615.

To a solution of **S49** (608 mg, 1.5 mmol) in MeOH (10 mL) was added $LiOH{\cdot}H_2O$ (252 mg, 6 mmol). The resulting mixture was stirred at room temperature for 1 h. The mixture was acidified with 2N HCl solution (50 mL) and extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated to give the product **S50** (477 mg, 85% yield) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.80 (s, 2H), 8.38 (d, *J* = 7.7 Hz, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.06 (d, *J* = 6.6 Hz, 1H), 4.41 (t, *J* = 10.1 Hz, 1H), 3.12 – 3.04 (m, 2H), 2.89 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.77 (dd, *J* = 16.2, 10.4 Hz, 1H), 2.23 (dd, *J* = 12.1, 3.4 Hz, 1H), 1.95 – 1.88 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.38, 162.74, 160.36, 156.61, 156.57, 149.78, 139.12, 136.74, 135.32, 134.25, 132.46, 129.99, 127.76, 127.20, 126.62, 126.07, 46.20, 34.77, 29.06, 29.02. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{18}N_4O_3^+$ $[M+H]^+$ 375.1457, found 375.1455.

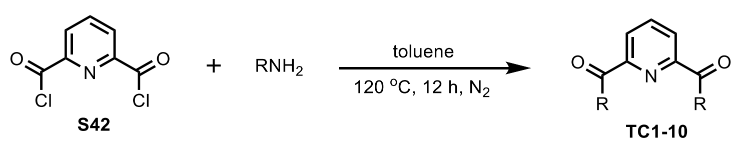
To a solution of **S50** (235 mg, 0.6 mmol) in dry toluene (10 mL) was added DMF (3 drops) and thionyl chloride (109 μL, 1.5 mmol) under nitrogen protection. The reaction mixture was stirred at 80 °C for 2 h. After completion, the mixture was concentrated and redissolved in dry toluene (10 mL). Amine (0.6 mmol) was added and the reaction solution was stirred at 120 °C for overnight. The mixture was concentrated and purified by silica gel chromatography eluting with hexane/EA to provide the corresponding product **T13-15.**

Synthesis of **T17**

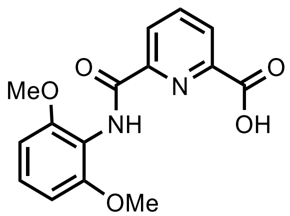


To a solution of **S48** (117 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (9.8 mg, 0.014 mmol), LiCl (48 mg, 1.14 mmol) in toluene (10 mL) was added 2-(tributylstannyl)pyridine (96 μL, 0.3 mmol). The Schlenk tube was evacuated and refilled with nitrogen for three times. The reaction solution was stirred at 110 °C for 6 h. Saturated KF solution (50 mL) was added and the mixture was stirred for 30 min. After filtration, saturated $NaHCO_3$ solution (100 mL) was added and the mixture was extracted with EA (50 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with hexane/EA to provide the product **T17.**

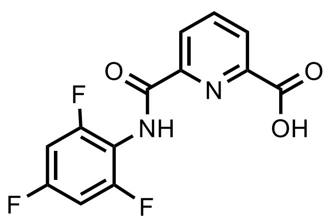
Synthesis of **TC1-10**



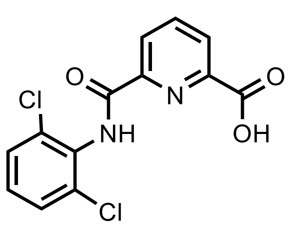
To a stirred solution of 2,6-pyridinedicarbonyl dichloride (255 mg, 1.25 mmol) in toluene (10 mL) was added amine (2.75 mmol). The reaction solution was stirred at 120 °C for 12 h. Upon completion, the reaction mixture was filtered. The residue was washed with toluene and MeOH or purified by silica gel chromatography eluting with hexane/EA to afford the corresponding product **TC1-10**.



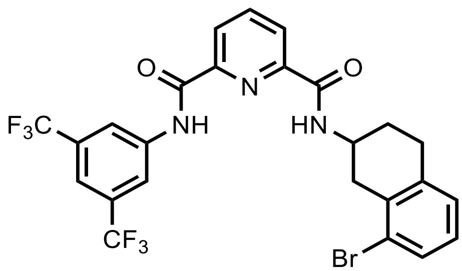
6-((2,6-Dimethoxyphenyl)carbamoyl)picolinic acid (S45) Following procedure for synthesis of **S44**, **S45** was obtained as a white solid in 52% yield. ^{1}H NMR (600 MHz, CD_3OD) δ 8.38 (ddd, *J* = 14.2, 7.7, 1.1 Hz, 2H), 8.21 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 8.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 165.67, 162.64, 155.80, 149.41, 146.18, 138.76, 127.87, 126.60, 125.01, 112.75, 103.52, 54.54. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{15}N_2O_5^+$ $[M+H]^+$ 303.0981, found 303.0986.



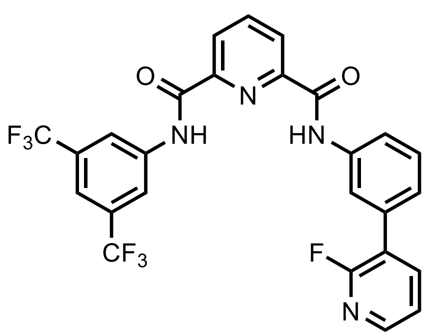
6-((2,4,6-Trifluorophenyl)carbamoyl)picolinic acid (S46) Following procedure for synthesis of **S44**, **S46** was obtained as a white solid in 90% yield. ^{1}H NMR (600 MHz, CD_3OD) δ 8.41 (ddd, *J* = 8.6, 7.7, 1.1 Hz, 2H), 8.24 (t, *J* = 7.8 Hz, 1H), 7.06 – 7.01 (m, 2H). ^{13}C NMR (151 MHz, CD_3OD) δ 165.53, 162.99, 160.09 (t, *J* = 14.9 Hz), 159.17 (dd, *J* = 15.6, 7.4 Hz), 157.50 (dd, *J* = 15.5, 7.3 Hz), 148.40, 146.35, 139.01, 127.21, 125.30, 99.82 (dd, *J* = 29.6, 26.9 Hz). ^{19}F NMR (376 MHz, CD_3OD) δ -109.39 (t, *J* = 6.1 Hz), -114.84 (d, *J* = 6.5 Hz). HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_8F_3N_2O_3^+$ $[M+H]^+$ 297.0487, found 297.0489.



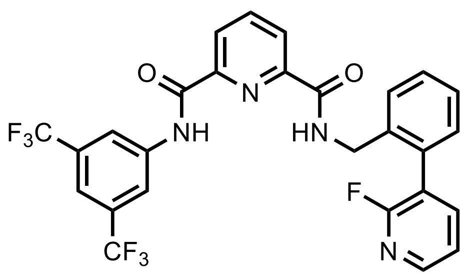
6-((2,6-Dichlorophenyl)carbamoyl)picolinic acid (S47) Following procedure for synthesis of **S44**, **S47** was obtained as a white solid in 85% yield. ^{1}H NMR (600 MHz, CD_3OD) δ 8.42 (t, *J* = 8.1 Hz, 2H), 8.25 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (151 MHz, CD_3OD) δ 165.49, 162.66, 148.54, 146.30, 139.04, 133.83, 131.78, 128.75, 127.87, 127.16, 125.31. HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_9Cl_2N_2O_3^+$ $[M+H]^+$ 310.9990, found 310.9997.



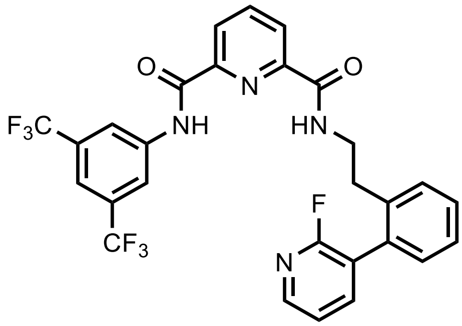
***N*^{2}-(3,5-Bis(trifluoromethyl)phenyl)-*N*^{6}-(8-bromo-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (S48)** Purification by silica gel chromatography eluting with hexane/EA (75/25, v/v), white solid, 40% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.18 (s, 2H), 8.12 (t, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.68 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 4.61 (qdd, *J* = 8.4, 5.5, 3.1 Hz, 1H), 3.26 (dd, *J* = 17.1, 5.6 Hz, 1H), 2.97 (q, *J* = 7.3, 6.1 Hz, 2H), 2.84 (dd, *J* = 17.1, 7.7 Hz, 1H), 2.20 – 2.15 (m, 1H), 2.00 – 1.90 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.73, 161.64, 149.19, 147.84, 139.68, 138.64, 137.93, 133.28, 132.56 (q, *J* = 33.7 Hz), 130.41, 128.01, 127.67, 126.23, 125.80, 125.68, 123.05 (q, *J* = 273.0 Hz), 120.02 – 119.53 (m), 118.24 – 117.85 (m), 45.63, 36.34, 28.07, 27.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.52. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{19}BrF_6N_3O_2^+$ $[M+H]^+$ 586.0565, found 586.0566.



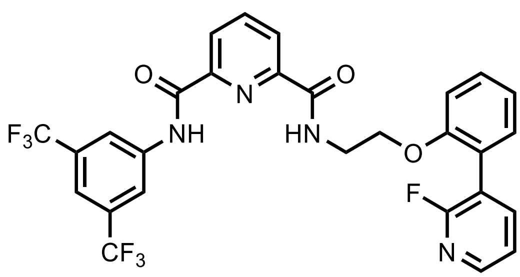
N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(3-(2-fluoropyridin-3-yl)phenyl)pyridine-2,6-dicarboxamide (T1) Purification by silica gel chromatography eluting with hexane/EA (60/40, v/v), white solid, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.82 (s, 1H), 9.52 (s, 1H), 8.51 (dd, J = 16.6, 7.7 Hz, 2H), 8.31 (s, 2H), 8.21 (d, J = 4.8 Hz, 1H), 8.17 (t, J = 7.7 Hz, 1H), 7.96 (s, 1H), 7.91 – 7.85 (m, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.38 (d, J = 7.5 Hz, 1H), 7.28 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.72, 161.38, 160.26 (d, J = 239.5 Hz), 149.14, 148.22, 146.77 (d, J = 15.2 Hz), 140.69, 139.96, 138.62, 137.18, 134.97, 132.62 (q, J = 33.9 Hz), 129.62, 126.39, 126.12, 125.70, 123.10 (d, J = 28.2 Hz), 123.03 (d, J = 273.0 Hz), 122.02 – 121.76 (m), 120.99, 120.65, 120.14 (d, J = 3.4 Hz), 118.29 (dt, J = 7.6, 3.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.61, -73.59. HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{16}F_7N_4O_2^+$ $[M+H]^+$ 549.1161, found 549.1167.



N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2-(2-fluoropyridin-3-yl)benzyl)pyridine-2,6-dicarboxamide (T2) Purification by silica gel chromatography eluting with hexane/EA (65/35, v/v), white solid, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.54 (s, 2H), 8.46 (dd, J = 7.8, 1.2 Hz, 1H), 8.42 (dd, J = 7.8, 1.2 Hz, 1H), 8.27 (ddd, J = 4.9, 2.0, 1.2 Hz, 1H), 8.24 (q, J = 5.0 Hz, 1H), 8.12 (t, J = 7.8 Hz, 1H), 7.82 (ddd, J = 10.1, 7.3, 2.0 Hz, 1H), 7.67 (s, 1H), 7.65 (dd, J = 7.7, 1.4 Hz, 1H), 7.48 (td, J = 7.5, 1.6 Hz, 1H), 7.45 (td, J = 7.5, 1.6 Hz, 1H), 7.38 (ddd, J = 7.2, 4.9, 2.1 Hz, 1H), 7.30 (dd, J = 7.5, 1.5 Hz, 1H), 4.94 (s, 1H), 4.14 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.60, 161.81, 160.44 (d, J = 230.2 Hz), 148.99, 148.07, 147.40 (d, J = 15.4 Hz), 142.23 (d, J = 4.8 Hz), 139.55, 138.98, 136.21, 133.44 (d, J = 3.7 Hz), 132.38 (q, J = 33.5 Hz), 130.62, 130.54, 129.72, 128.52, 125.92, 125.61, 123.20 (q, J = 273.2 Hz), 122.90 (d, J = 33.8 Hz), 122.43 (d, J = 4.1 Hz), 120.64 – 119.49 (m), 117.89 (d, J = 4.5 Hz), 41.75. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.52, -71.88. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{18}F_7N_4O_2^+$ $[M+H]^+$ 563.1318, found 563.1320.

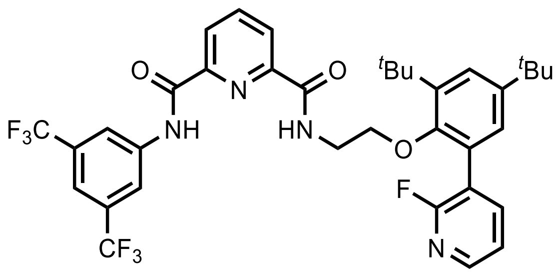


N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2-(2-fluoropyridin-3-yl)phenethyl)pyridine-2,6-dicarboxamide (T3) Purification by silica gel chromatography eluting with hexane/EA (65/35, v/v), colorless oil, 71% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.45 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.40 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.27 (s, 2H), 8.17 (ddd, *J* = 4.9, 2.0, 1.0 Hz, 1H), 8.10 (t, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 5.8 Hz, 1H), 7.71 (ddd, *J* = 9.6, 7.3, 2.0 Hz, 1H), 7.66 (s, 1H), 7.42 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.32 – 7.27 (m, 2H), 7.23 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.72 (q, *J* = 6.5 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.26, 161.99, 160.18 (d, *J* = 234.4 Hz), 149.04, 148.03, 147.05 (d, *J* = 14.7 Hz), 142.31 (d, *J* = 4.6 Hz), 139.45, 138.83, 137.02, 133.89 (d, *J* = 3.8 Hz), 132.33 (q, *J* = 33.6 Hz), 130.54, 129.35, 129.14, 127.05, 126.02, 125.66, 123.43 (d, *J* = 32.5 Hz), 123.13 (q, *J* = 273 Hz), 121.95 (d, *J* = 4.4 Hz), 120.50 – 119.97 (m), 117.95 (d, *J* = 4.0 Hz), 39.61, 32.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.51, -71.84. HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{20}F_7N_4O_2^+$ $[M+H]^+$ 577.1474, found 577.1477.

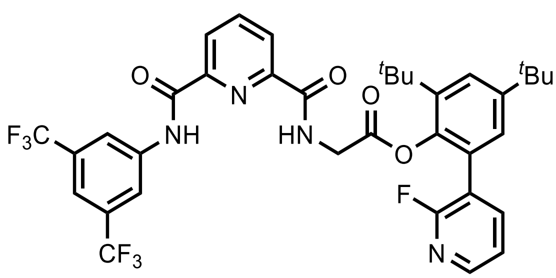


N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2-(2-(2-fluoropyridin-3-yl)phenoxy)ethyl)pyridine-2,6-dicarboxamide (T4) Purification by silica gel chromatography eluting with hexane/EA (70/30, v/v), colorless oil, 56% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.50 (ddd, *J* = 10.2, 7.8, 1.2 Hz, 2H), 8.30 (s, 3H), 8.12 (t, *J* = 7.8 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.77 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.60 (s, 1H), 7.42 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.25 (dd, *J* = 4.9, 2.3 Hz, 1H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 4.30

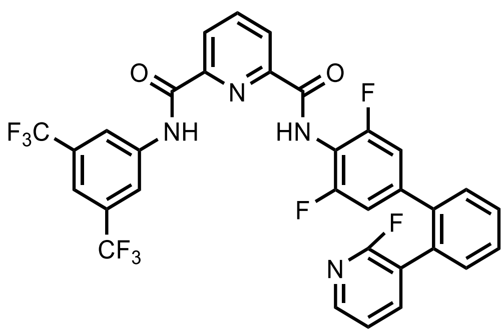
– 4.23 (m, 2H), 3.91 (q, *J* = 5.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.67, 162.51, 160.54 (d, *J* = 234.9 Hz), 155.25, 149.23, 148.70, 146.14 (d, *J* = 15.3 Hz), 142.17 (d, *J* = 5.6 Hz), 139.13, 138.99, 131.95 (q, *J* = 33.5 Hz), 130.85, 130.54, 126.29, 126.01, 123.30 (d, *J* = 4.5 Hz), 123.12 (q, *J* = 272.4 Hz), 122.17 (d, *J* = 4.1 Hz), 121.56, 121.51 – 121.29 (m), 121.17, 118.06 – 117.62 (m), 111.40, 67.25, 39.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.63, -69.15. HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{20}F_7N_4O_3^+$ $[M+H]^+$ 593.1424, found 593.1435.



***N*^2^-(3,5-Bis(trifluoromethyl)phenyl)-*N*^6^-(2-(2,4-di-*tert*-butyl-6-(2-fluoropyridin-3-yl)phenoxy)ethyl)pyridine-2,6-dicarboxamide (T5)** Purification by silica gel chromatography eluting with hexane/EA (70/30, v/v), white solid, 36% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.46 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.41 (s, 2H), 8.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.12 (t, *J* = 7.8 Hz, 1H), 8.04 (t, *J* = 6.0 Hz, 1H), 7.87 (ddd, *J* = 9.3, 7.3, 2.0 Hz, 1H), 7.67 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.60 (s, 1H), 7.49 (d, *J* = 2.5 Hz, 1H), 7.17 (ddd, *J* = 7.0, 4.9, 1.7 Hz, 1H), 7.11 – 7.08 (m, 1H), 3.62 (s, 4H), 1.46 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.22, 163.03, 160.52 (d, *J* = 239.3 Hz), 153.05, 149.11, 148.94, 146.94, 145.77 (d, *J* = 14.1 Hz), 142.36, 141.71 (d, *J* = 5.3 Hz), 139.46, 139.11, 132.86 – 130.97 (m), 127.60 (d, *J* = 4.8 Hz), 126.28, 125.84 – 125.68 (m), 123.13 (q, *J* = 272.9 Hz), 123.08 (d, *J* = 31.7 Hz), 122.07 (d, *J* = 4.7 Hz), 120.96 – 119.74 (m), 117.96 – 117.13 (m), 72.40, 39.42, 35.41, 34.68, 31.45, 31.03. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.69, -71.14. HRMS (ESI-TOF) *m/z* Calcd for $C_{36}H_{36}F_7N_4O_3^+$ $[M+H]^+$ 705.2676, found 705.2672.

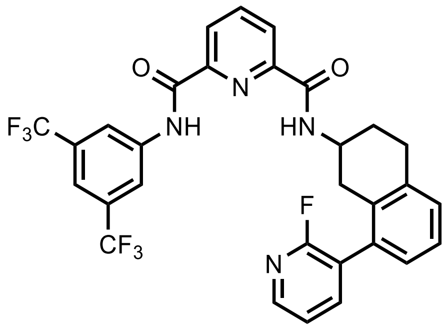


2,4-Di-*tert*-butyl-6-(2-fluoropyridin-3-yl)phenyl (6-((3,5-bis(trifluoromethyl)phenyl)carbamoyl)picolinoyl)glycinate (T6) Purification by silica gel chromatography eluting with hexane/EA (65/35, v/v), white solid, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.51 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.46 (d, *J* = 8.1 Hz, 3H), 8.21 (d, *J* = 3.7 Hz, 1H), 8.17 – 8.08 (m, 2H), 7.84 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.34 (t, *J* = 5.6 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 4.50 (s, 1H), 3.79 (s, 1H), 1.35 (d, *J* = 4.0 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.61, 163.17, 161.97, 149.47, 148.35 (d, *J* = 8.4 Hz), 146.93 (d, *J* = 14.1 Hz), 144.42, 141.36, 139.57, 139.04, 132.28 (q, *J* = 33.5 Hz), 127.54 (d, *J* = 4.5 Hz), 126.06 (d, *J* = 2.3 Hz), 125.73, 125.61, 123.14 (q, *J* = 273.2 Hz), 120.60 (dd, *J* = 6.0, 3.0 Hz), 118.17 – 117.45 (m), 41.59, 34.99, 34.88, 31.40, 30.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.57, -70.69. HRMS (ESI-TOF) *m/z* Calcd for $C_{36}H_{34}F_7N_4O_4^+$ $[M+H]^+$ 719.2468, found 719.2464.

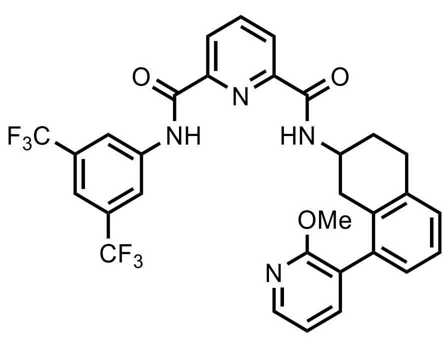


***N*^2^-(3,5-Bis(trifluoromethyl)phenyl)-*N*^6^-(3,5-difluoro-2'-(2-fluoropyridin-3-yl)-[1,1'-biphenyl]-4-yl)pyridine-2,6-dicarboxamide (T7)** Purification by silica gel chromatography eluting with hexane/EA (60/40, v/v), white solid, 52% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.22 (s, 1H), 9.43 (s, 1H), 8.54 (ddd, *J* = 15.3, 7.8, 1.1 Hz, 2H), 8.26 (s, 2H), 8.18 (t, *J* = 7.8 Hz, 1H), 8.13 (dt, *J* = 4.1, 1.2 Hz, 1H), 7.73 (ddd, *J* = 9.4, 7.4, 2.0 Hz, 1H), 7.61 (s, 1H), 7.52 – 7.48 (m, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.24 (ddd, *J* = 7.4, 4.9, 1.6 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.04, 162.02, 159.88 (d, *J* = 240.4 Hz), 158.11 (d, *J* = 6.1 Hz), 156.44 (d, *J* = 5.8 Hz), 148.21, 148.06, 146.85 (d, *J* = 14.0 Hz), 142.25 (d, *J* = 4.9 Hz), 141.90 – 141.52 (m), 139.68, 138.98 – 138.82 (m), 138.78, 132.32 (q, *J* = 33.5 Hz), 132.26 (d, *J* = 4.8 Hz), 131.11, 129.95, 129.27, 128.73, 126.52, 126.26, 123.45 (d, *J* = 30.8 Hz), 123.02 (q, *J* = 273.0 Hz), 121.82 (d, *J* = 5.0 Hz), 120.66 – 119.85 (m), 118.02 (dd, *J* = 8.6, 4.0

Hz), 112.79 – 112.49 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.65, -70.66, -119.25. HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{18}F_9N_4O_2^+$ $[M+H]^+$ 661.1286, found 661.1291.

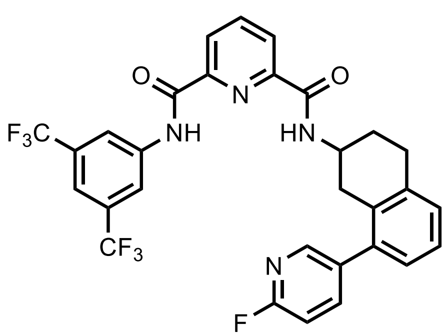


***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-(8-(2-fluoropyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T8)** Purification by silica gel chromatography eluting with hexane/EA (65/35, v/v), white solid, 57% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.43 (td, *J* = 7.7, 1.2 Hz, 2H), 8.20 (d, *J* = 4.2 Hz, 1H), 8.15 (s, 2H), 8.09 (t, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 59.2 Hz, 2H), 7.63 (s, 1H), 7.29 (d, *J* = 15.4 Hz, 1H), 7.25 (s, 1H), 7.22 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 4.56 (h, *J* = 5.9 Hz, 1H), 2.97 (m, 2H), 2.74 (m, 2H), 2.13 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.01, 162.02, 160.09 (d, *J* = 234.4 Hz), 148.93, 148.09, 146.87 (d, *J* = 14.5 Hz), 142.12, 139.43, 138.89, 136.07, 134.10, 132.29, 132.20 (q, *J* = 33.3 Hz), 129.50, 127.82, 126.47, 125.96, 125.61, 123.43 (d, *J* = 32.3 Hz), 123.08 (q, *J* = 272.9 Hz), 122.07, 120.35 – 120.21 (m), 117.96 – 117.77 (m), 45.34, 33.30, 28.19, 27.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.53, -72.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{22}F_7N_4O_2^+$ $[M+H]^+$ 603.1631, found 603.1638.

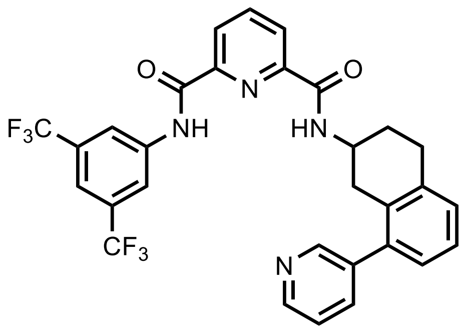


***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-(8-(2-methoxypyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T9)** Purification by silica gel chromatography eluting with hexane/EA (70/30, v/v), white solid, 56% yield. ^{1}H NMR (600

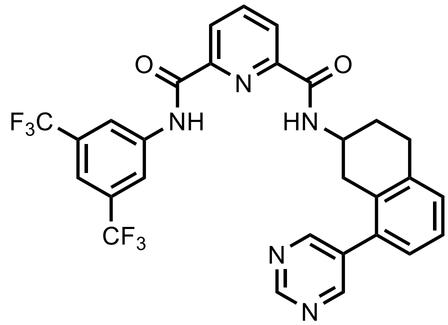
MHz, $CDCl_3$) rotameric mixture, resonances for the minor rotamer are enclosed in parenthesis [ ]: δ [9.51 (s, 0.31H)], 9.39 (s, 1H), 8.47 (dd, *J* = 12.9, 7.8 Hz, 2H), [8.43 (d, *J* = 7.9 Hz, 0.65H)], 8.20 (dd, *J* = 5.0, 2.0 Hz, 1H), [8.18 – 8.16 (m, 0.34H)], 8.13 (t, *J* = 7.8 Hz, 2H), 8.04 (s, 2H), 7.89 (d, *J* = 7.4 Hz, 1H), [7.69 (s, 0.34H)], 7.61 (s, 1H), [7.57 (d, *J* = 8.4 Hz, 0.31H)], 7.52 (dd, *J* = 7.2, 2.0 Hz, 1H), [7.36 (d, *J* = 6.0 Hz, 0.34H)], [7.25 – 7.14 (m, 2.62H)], [7.07 – 7.01 (m, 2.34H)], [6.90 (t, *J* = 6.1 Hz, 0.32H)], [4.57 (s, 1.35H)], [3.93 (s, 1H)], 3.76 (s, 3H), [3.13 (dt, *J* = 15.0, 6.9 Hz, 0.32H)], [3.06 (dd, *J* = 11.9, 4.7 Hz, 0.67H)], 2.98 (t, *J* = 7.6 Hz, 2H), 2.84 – 2.68 (m, 2H), [2.50 (dd, *J* = 16.6, 7.4 Hz, 0.33H)], 2.38 (dq, *J* = 11.7, 5.9 Hz, 1H), [2.25 (s, 0.32H)], [2.04 (dtd, *J* = 11.0, 8.2, 4.1 Hz, 1.34H)]. ^{13}C NMR (151 MHz, $CDCl_3$) rotameric mixture, resonances for the minor rotamer are enclosed in parenthesis [ ]: δ 162.40, [162.36], 161.69, [161.64], [161.01], 159.91, [149.39], 149.22, 147.76, [147.71], 146.38, [146.31], 139.79, 139.64, [138.99], 138.68, [138.61], 137.58, 136.02, [135.47], 132.33 (q, *J* = 33.5 Hz), 131.90, 129.06, [128.71], [128.06], 127.90, 126.62, [126.31], [126.26], 126.01, 125.72, [125.69], 124.21, [124.17], 122.97 (q, *J* = 272.8 Hz), 120.11 – 119.77 (m), [119.75], 118.05 (dq, *J* = 8.9, 4.6, 3.8 Hz), 117.68, 116.81 – 116.62 (m), [53.64], 53.34, [45.38], 44.89, [33.31], 32.56, [28.28], [27.31], 26.72, 25.57. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.58, [-65.50]. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{25}F_6N_4O_3^+$ $[M+H]^+$ 615.1831, found 615.1837.



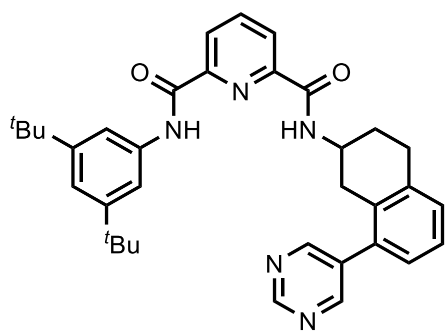
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-(8-(6-fluoropyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T10)** Purification by silica gel chromatography eluting with hexane/EA (65/35, v/v), white solid, 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.42 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.25 (s, 2H), 8.08 – 8.01 (m, 2H), 7.90 (d, *J* = 2.4 Hz, 1H), 7.70 (td, *J* = 8.1, 2.5 Hz, 1H), 7.65 (s, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.44 – 4.36 (m, 1H), 2.96 (dt, *J* = 17.4, 5.1 Hz, 1H), 2.87 (ddd, *J* = 17.1, 10.4, 6.3 Hz, 1H), 2.70 (dd, J = 16.2, 5.0 Hz, 1H), 2.52 (dd, J = 16.1, 9.6 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.86 (dtd, J = 12.4, 10.4, 6.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.78 (d, J = 240.1 Hz), 162.74, 161.85, 148.85, 148.11, 147.23 (d, J = 14.3 Hz), 141.91 (d, J = 8.3 Hz), 139.69, 138.85, 137.31, 135.84, 134.74 (d, J = 5.0 Hz), 132.41 (q, J = 33.6 Hz), 131.71, 129.12, 127.80, 126.41, 126.12, 125.79, 123.07 (q, J = 272.9 Hz), 120.06 (q, J = 4.1 Hz), 118.53 – 117.55 (m), 109.31 (d, J = 37.2 Hz), 45.92, 34.71, 28.77, 28.34. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.53, -72.68. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{22}F_7N_4O_2^+$ $[M+H]^+$ 603.1631, found 603.1649.



***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-(8-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T11)** Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), white solid, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.52 (dd, J = 4.9, 1.7 Hz, 1H), 8.42 (dd, J = 7.8, 1.2 Hz, 1H), 8.40 – 8.37 (m, 2H), 8.22 (s, 2H), 8.07 (t, J = 7.8 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.66 (s, 1H), 7.59 (dt, J = 7.8, 1.9 Hz, 1H), 7.31 (dd, J = 7.8, 4.9 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.01 (d, J = 6.7 Hz, 1H), 4.43 (ddt, J = 13.8, 9.0, 4.6 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.79 (dd, J = 16.3, 4.9 Hz, 1H), 2.59 (dd, J = 16.2, 9.2 Hz, 1H), 2.07 (d, J = 12.4 Hz, 1H), 1.93 – 1.84 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.70, 161.92, 149.69, 149.00, 148.22, 148.11, 139.60, 138.87, 138.59, 136.97, 136.58, 135.85, 132.38 (q, J = 33.6 Hz), 131.60, 128.94, 127.84, 126.39, 126.13, 125.74, 123.44, 123.09 (q, J = 273.0 Hz), 120.22 – 120.08 (m), 118.20 – 117.69 (m), 45.89, 34.63, 28.73, 28.23. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.48. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 585.1725, found 585.1729.

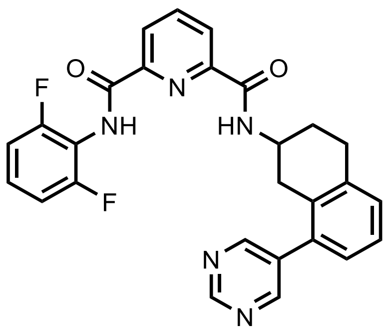


***N^2*-(3,5-Bis(trifluoromethyl)phenyl)-*N^6*-(8-(pyrimidin-5-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T12)** Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), white solid, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.85 (s, 1H), 9.16 (s, 1H), 8.65 (s, 2H), 8.42 (dd, *J* = 7.8, 1.7 Hz, 2H), 8.21 (s, 2H), 8.09 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.67 (s, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.52 – 4.43 (m, 1H), 3.08 – 2.98 (m, 2H), 2.87 (dd, *J* = 16.2, 5.0 Hz, 1H), 2.65 (dd, *J* = 16.2, 9.1 Hz, 1H), 2.18 – 2.11 (m, 1H), 1.99 – 1.92 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.64, 161.72, 157.39, 156.61, 148.99, 148.01, 139.71, 138.70, 136.24, 134.78, 134.76, 132.51 (q, *J* = 33.6 Hz), 131.75, 129.82, 127.96, 126.79, 126.25, 125.80, 123.06 (q, *J* = 273.2 Hz), 120.17 – 119.80 (m), 118.32 – 117.89 (m), 45.75, 34.67, 28.63, 28.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.51. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{22}F_6N_5O_2^+$ $[M+H]^+$ 586.1678, found 586.1677.



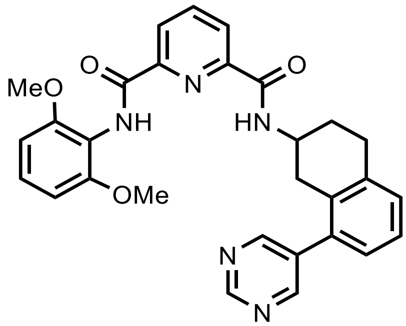
***N^2*-(3,5-Di-*tert*-butylphenyl)-*N^6*-(8-(pyrimidin-5-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T13)** Purification by silica gel chromatography eluting with hexane/EA (30/70, v/v), white solid, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 9.18 (s, 1H), 8.71 (s, 2H), 8.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.37 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.07 (dd, *J* =

6.3, 2.6 Hz, 1H), 4.49 (tdd, *J* = 10.0, 8.7, 3.3 Hz, 1H), 3.21 – 3.09 (m, 2H), 3.06 (dd, *J* = 16.6, 4.7 Hz, 1H), 2.72 (dd, *J* = 16.3, 9.0 Hz, 1H), 2.33 – 2.26 (m, 1H), 1.98 (dtd, *J* = 12.6, 9.7, 6.3 Hz, 1H), 1.37 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.82, 161.23, 157.47, 156.59, 151.97, 149.20, 148.78, 139.38, 136.35, 136.31, 134.96, 134.88, 132.15, 129.83, 128.07, 126.69, 125.43, 125.37, 119.41, 115.21, 45.80, 35.02, 34.62, 31.44, 28.72, 28.29. HRMS (ESI-TOF) *m/z* Calcd for $C_{35}H_{40}N_5O_2^+$ $[M+H]^+$ 562.3182, found 562.3181.

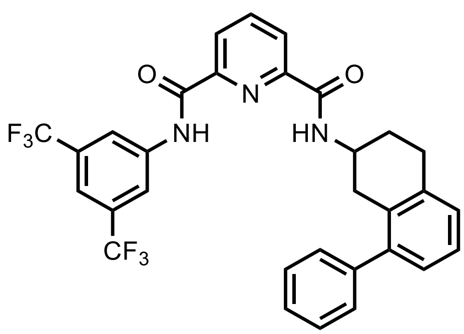


N

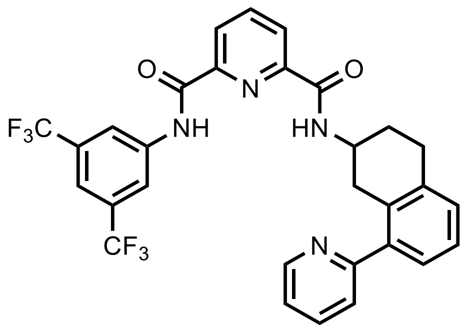
N^2-(2,6-Difluorophenyl)-N^6-(8-(pyrimidin-5-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T14) Purification by silica gel chromatography eluting with hexane/EA (20/80, v/v), white solid, 51% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.95 (s, 1H), 8.70 (s, 2H), 8.42 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.39 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.08 (t, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.28 (ddd, *J* = 8.5, 6.1, 2.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.05 – 7.02 (m, 3H), 4.47 (tq, *J* = 14.4, 5.4, 4.3 Hz, 1H), 3.13 – 3.06 (m, 2H), 3.00 (dd, *J* = 16.1, 5.0 Hz, 1H), 2.71 (dd, *J* = 16.2, 9.3 Hz, 1H), 2.28 – 2.24 (m, 1H), 1.96 (ddt, *J* = 12.5, 9.8, 4.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.64, 161.59, 158.70 (d, *J* = 5.2 Hz), 157.43, 157.04 (d, *J* = 5.2 Hz), 156.59, 148.99, 147.91, 139.35, 136.62, 134.89 (d, *J* = 2.8 Hz), 132.10, 129.81, 128.02 (t, *J* = 9.8 Hz), 127.89, 126.61, 125.82, 125.72, 113.47, 111.95 (dd, *J* = 19.8, 4.3 Hz), 45.88, 34.57, 28.76, 28.27. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.93. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{22}F_2N_5O_2^+$ $[M+H]^+$ 486.1742, found 486.1739.



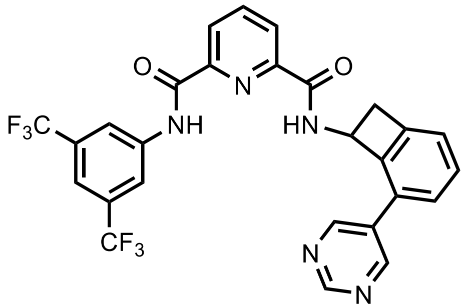
N^2-(2,6-Dimethoxyphenyl)-N^6-(8-(pyrimidin-5-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T15) Purification by silica gel chromatography eluting with EA, white solid, 50% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.76 (s, 1H), 8.69 (s, 2H), 8.41 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.34 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.02 (dd, *J* = 6.8, 2.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.48 – 4.42 (m, 1H), 3.84 (s, 6H), 3.09 (qq, *J* = 10.7, 6.0, 5.0 Hz, 2H), 3.01 (dd, *J* = 16.1, 4.9 Hz, 1H), 2.70 (dd, *J* = 16.2, 9.4 Hz, 1H), 2.27 (dd, *J* = 11.4, 4.4 Hz, 1H), 1.96 – 1.89 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.91, 161.61, 157.43, 156.59, 155.59, 148.96, 148.67, 138.99, 136.68, 134.93, 134.88, 132.27, 129.77, 128.20, 127.87, 126.58, 125.52, 125.12, 113.50, 104.48, 56.15, 45.86, 34.57, 28.86, 28.44. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{28}N_5O_4^+$ $[M+H]^+$ 510.2141, found 510.2455.



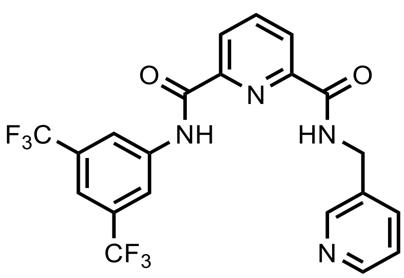
N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(8-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T16) Purification by silica gel chromatography eluting with hexane/EA (70/30, v/v), white solid, 89% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.42 (ddd, *J* = 7.7, 5.6, 1.1 Hz, 2H), 8.15 (s, 2H), 8.09 (t, *J* = 7.8 Hz, 1H), 7.69 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 – 7.30 (m, 1H), 7.27 (t, *J* = 1.8 Hz, 1H), 7.26 (s, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 4.52 (qdd, *J* = 8.4, 4.9, 3.3 Hz, 1H), 3.05 (dd, J = 14.9, 5.8 Hz, 3H), 2.73 (dd, J = 16.5, 8.1 Hz, 1H), 2.23 (ddtd, J = 9.5, 7.3, 4.2, 3.7, 1.6 Hz, 1H), 1.98 (dtd, J = 12.7, 8.7, 6.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.46, 161.68, 149.36, 147.78, 142.74, 141.26, 139.60, 138.61, 135.70, 132.56 (q, J = 33.6 Hz), 131.25, 129.03, 128.23, 128.12, 127.83, 127.09, 126.24, 125.59, 123.06 (q, J = 273.0 Hz), 119.91 (q, J = 4.1 Hz), 118.48 – 117.90 (m), 45.80, 34.23, 28.57, 27.72. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.49. HRMS (ESI-TOF) *m/z* Calcd for $C_{31}H_{24}F_6N_3O_2^+$ $[M+H]^+$ 584.1773, found 584.1780.



***N²*-(3,5-Bis(trifluoromethyl)phenyl)-*N⁶*-(8-(pyridin-2-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (T17)** Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), white solid, 35% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.01 (d, J = 6.7 Hz, 1H), 8.47 – 8.43 (m, 2H), 8.41 (d, J = 7.7 Hz, 1H), 8.07 (t, J = 7.8 Hz, 1H), 7.92 (s, 2H), 7.72 (td, J = 7.7, 1.8 Hz, 1H), 7.55 (s, 1H), 7.47 (dd, J = 7.8, 1.2 Hz, 1H), 7.28 (d, J = 4.8 Hz, 2H), 7.22 (t, J = 4.5 Hz, 1H), 7.11 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H), 4.58 (h, J = 6.2 Hz, 1H), 3.09 (dd, J = 15.7, 4.3 Hz, 1H), 2.87 (dt, J = 16.0, 5.2 Hz, 1H), 2.76 (ddd, J = 16.1, 10.3, 6.0 Hz, 1H), 2.68 (dd, J = 15.7, 5.4 Hz, 1H), 2.45 (dt, J = 13.8, 5.6 Hz, 1H), 1.83 – 1.74 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.14, 162.31, 159.91, 149.57, 148.64, 148.06, 140.20, 139.37, 139.17, 138.96, 137.34, 133.04, 131.94 (q, J = 33.7 Hz), 128.31, 126.98, 126.28, 125.92, 125.40, 124.43, 123.09 (q, J = 273.0 Hz), 122.25, 120.24 (q, J = 4.2 Hz), 118.01 – 116.98 (m), 45.77, 30.98, 29.18, 27.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 585.1725, found 585.1728.

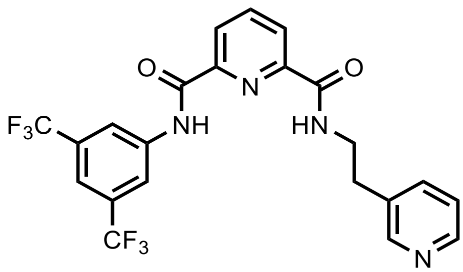


***N*^2-(3,5-Bis(trifluoromethyl)phenyl)- *N*^6-(5-(pyrimidin-5-yl)bicyclo[4.2.0]octa-1(6),2,4-trien-7-yl)pyridine-2,6-dicarboxamide (T18)** Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), pale yellow solid, 56% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 9.01 (s, 1H), 8.98 (s, 2H), 8.46 (d, J = 9.3 Hz, 1H), 8.41 (dd, J = 13.3, 7.5 Hz, 2H), 8.12 – 8.03 (m, 3H), 7.58 (s, 1H), 7.46 – 7.40 (m, 2H), 7.18 (d, J = 6.9 Hz, 1H), 6.03 (ddd, J = 9.5, 5.2, 2.5 Hz, 1H), 3.86 (dd, J = 14.6, 5.2 Hz, 1H), 3.33 (dd, J = 14.5, 2.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.32, 162.01, 157.54, 154.83, 148.93, 148.19, 144.37, 142.46, 139.62, 138.50, 132.29 (q, J = 33.6 Hz), 130.68, 130.62, 129.09, 126.56, 125.97, 125.37, 124.12, 122.93 (q, J = 273.0 Hz), 120.41 (dd, J = 8.7, 4.2 Hz), 118.35 – 117.96 (m), 50.42, 40.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.66. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{18}F_6N_5O_2^+$ $[M+H]^+$ 558.1365, found 558.1369.

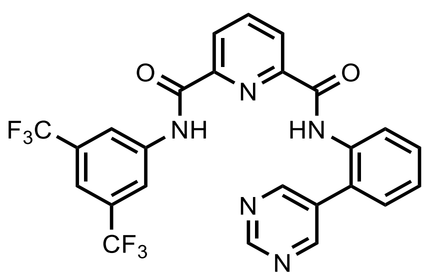


***N*^2-(3,5-Bis(trifluoromethyl)phenyl)-*N*^6-(pyridin-3-ylmethyl)pyridine-2,6-dicarboxamide (T19)** Purification by silica gel chromatography eluting with hexane/EA (20/80, v/v), white solid, 43% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.03 (t, J = 6.4 Hz, 1H), 8.51 (d, J = 7.8 Hz, 2H), 8.44 (dd, J = 4.9, 1.6 Hz, 1H), 8.22 (d, J = 2.2 Hz, 1H), 8.17 (t, J = 7.8 Hz, 1H), 8.06 (s, 2H), 7.68 (dt, J = 8.0, 2.0 Hz, 1H), 7.57 (s, 1H), 7.20 (dd, J = 7.9, 4.8 Hz, 1H), 4.56 (d, J = 6.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.88, 162.18, 148.88, 148.72, 148.71, 148.33, 139.64, 138.81, 136.40, 134.65, 132.18 (q, J = 33.6 Hz), 126.30, 125.96, 124.24, 123.00 (q, J = 272.9

Hz), 120.38 (dd, J = 7.8, 4.1 Hz), 118.03 – 117.65 (m), 40.77. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.65. HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{15}F_6N_4O_2^+$ $[M+H]^+$ 469.1099, found 469.1093.

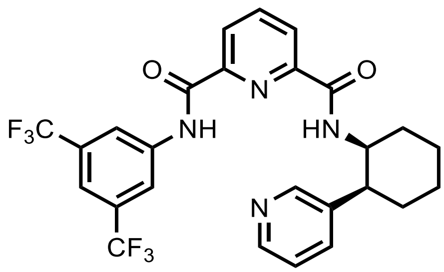


N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2-(pyridin-3-yl)ethyl)pyridine-2,6-dicarboxamide (T20) Purification by silica gel chromatography eluting with hexane/EA (20/80, v/v), pale yellow solid, 45% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.49 – 8.41 (m, 4H), 8.24 (s, 2H), 8.15 (t, J = 7.8 Hz, 1H), 8.11 (d, J = 6.5 Hz, 1H), 7.65 (s, 1H), 7.58 (dt, J = 7.8, 1.9 Hz, 1H), 7.25 (dd, J = 7.7, 4.8 Hz, 1H), 3.71 (q, J = 6.6 Hz, 2H), 2.96 (t, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.56, 161.98, 150.10, 149.22, 148.20, 148.11, 139.65, 138.79, 136.74, 134.65, 132.35 (q, J = 33.6 Hz), 126.13, 125.85, 123.91, 123.10 (q, J = 273.2 Hz), 120.74 – 119.75 (m), 118.23 – 117.79 (m), 40.56, 32.93. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.51. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{17}F_6N_4O_2^+$ $[M+H]^+$ 483.1256, found 483.1255.

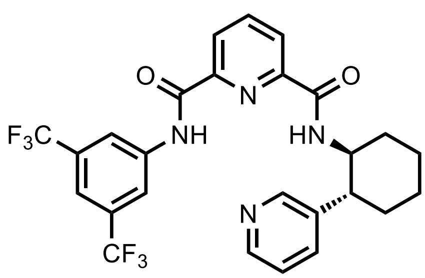


N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2-(pyrimidin-5-yl)phenyl)pyridine-2,6-dicarboxamide (T21) Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), colorless oil, 49% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.43 (s, 1H), 9.12 (s, 1H), 9.00 (s, 2H), 8.94 (s, 1H), 8.50 (ddd, J = 12.2, 7.8, 1.2 Hz, 2H), 8.45 (d, J = 8.3 Hz, 1H), 8.34 (s, 2H), 8.17 (t, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.58 (dt, J = 8.6, 4.3 Hz, 1H), 7.40 (d, J = 4.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.80, 161.27, 157.87, 156.95, 149.19, 148.60, 139.89, 138.29, 134.09, 132.39 (q, J = 33.6 Hz), 132.25, 130.54, 130.27, 126.65, 126.29, 126.23, 123.34, 123.12

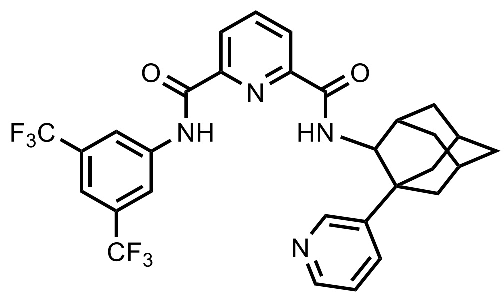
(q, J = 273.3 Hz), 121.44 (dd, J = 8.9, 5.0 Hz), 118.69 – 118.21 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.52. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{16}F_6N_5O_2^+$ $[M+H]^+$ 532.1208, found 532.1207.



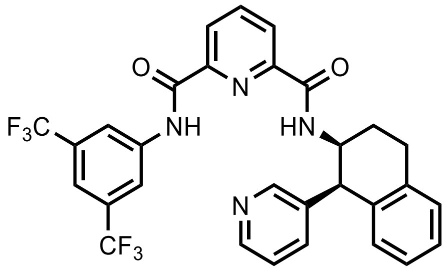
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-*cis*-(2-(pyridin-3-yl)cyclohexyl)pyridine-2,6-dicarboxamide (*cis*-T22)** Purification by silica gel chromatography eluting with DCM/EA (50/50, v/v), colorless oil, 12% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.35 – 8.31 (m, 2H), 8.30 (d, J = 2.3 Hz, 1H), 8.28 (d, J = 7.8 Hz, 3H), 8.02 (t, J = 7.8 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.64 (s, 1H), 7.61 (dt, J = 8.0, 2.0 Hz, 1H), 7.13 (dd, J = 8.0, 4.8 Hz, 1H), 4.12 (ddt, J = 15.3, 11.4, 4.0 Hz, 1H), 2.66 (td, J = 11.8, 3.2 Hz, 1H), 2.15 (dd, J = 12.6, 3.7 Hz, 1H), 1.86 – 1.75 (m, 3H), 1.52 – 1.43 (m, 2H), 1.40 (ddd, J = 16.2, 8.1, 3.3 Hz, 1H), 1.34 – 1.27 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.88, 162.37, 149.53, 149.51, 148.24, 147.86, 139.27, 139.24, 138.91, 134.35, 132.28 (q, J = 33.3 Hz), 126.03, 125.53, 123.97, 123.10 (q, J = 273.2 Hz), 120.56 (q, J = 4.8, 4.2 Hz), 118.20 – 117.58 (m), 52.94, 47.26, 34.38, 33.53, 25.81, 25.24. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.57. HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 537.1725, found 537.1725.



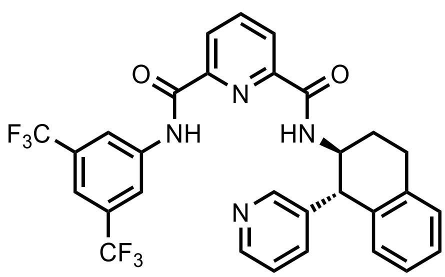
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-*trans*-(2-(pyridin-3-yl)cyclohexyl)pyridine-2,6-dicarboxamide (*trans*-T22)** Purification by silica gel chromatography eluting with DCM/EA (50/50, v/v), colorless oil, 10% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.65 (d, J = 2.3 Hz, 1H), 8.48 (s, 2H), 8.43 (dd, J = 4.8, 1.6 Hz, 1H), 8.40 (dd, J = 7.7, 1.2 Hz, 1H), 8.25 (dd, J = 7.8, 1.2 Hz, 1H), 8.07 (t, J = 7.8 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.65 (dt, J = 8.0, 2.0 Hz, 1H), 7.23 (dd, J = 7.9, 4.8 Hz, 1H), 4.56 (dq, J = 8.1, 3.9 Hz, 1H), 3.18 (dt, J = 11.2, 3.9 Hz, 1H), 2.19 – 2.13 (m, 1H), 2.08 (dt, J = 12.3, 4.1 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.84 (dddd, J = 26.2, 12.7, 7.3, 3.6 Hz, 2H), 1.66 – 1.62 (m, 1H), 1.59 – 1.54 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.61, 162.02, 149.50, 148.46, 148.21, 148.16, 139.66, 139.00, 137.96, 135.78, 132.60 (q, J = 33.6 Hz), 125.95, 125.62, 123.68, 123.16 (q, J = 273.2 Hz), 120.10 (dd, J = 8.6, 4.2 Hz), 118.05 (d, J = 4.1 Hz), 49.86, 43.29, 30.62, 26.13, 25.10, 21.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.62. HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 537.1725, found 537.1728.



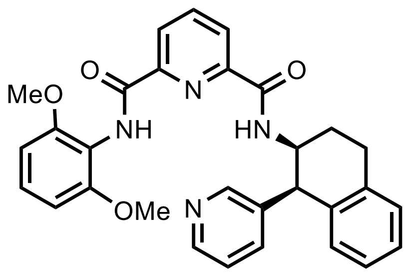
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-((1*R*,3*S*,5*R*,7*S*)-1-(pyridin-3-yl)adamantan-2-yl)pyridine-2,6-dicarboxamide (T23)** Purification by silica gel chromatography eluting with hexane/EA (15/85, v/v), white solid, 20% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.70 (d, J = 1.7 Hz, 1H), 8.41 (dd, J = 4.7, 1.6 Hz, 1H), 8.38 (s, 2H), 8.35 (dd, J = 7.7, 1.1 Hz, 1H), 8.23 (dd, J = 7.8, 1.1 Hz, 1H), 8.04 (t, J = 7.8 Hz, 1H), 7.81 (ddd, J = 8.2, 2.5, 1.6 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.24 (dd, J = 8.1, 4.7 Hz, 1H), 4.58 (dd, J = 8.5, 3.1 Hz, 1H), 2.40 (q, J = 3.2 Hz, 1H), 2.38 – 2.32 (m, 1H), 2.30 – 2.23 (m, 3H), 2.16 (p, J = 3.2 Hz, 1H), 2.12 (dt, J = 12.9, 2.7 Hz, 1H), 2.02 (dq, J = 12.9, 3.0 Hz, 1H), 1.95 – 1.88 (m, 3H), 1.85 – 1.81 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.27, 161.75, 149.26, 147.97, 147.87, 146.90, 141.74, 139.67, 138.94, 133.13, 132.67 (q, J = 33.6 Hz), 125.85, 125.42, 123.62, 123.14 (q, J = 273 Hz), 120.02 – 119.38 (m), 118.16 – 117.76 (m), 56.61, 44.81, 38.85, 36.56, 36.34, 35.44, 32.68, 31.20, 28.08, 27.70. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.64. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{27}F_6N_4O_2^+$ $[M+H]^+$ 589.2038, found 589.2037.



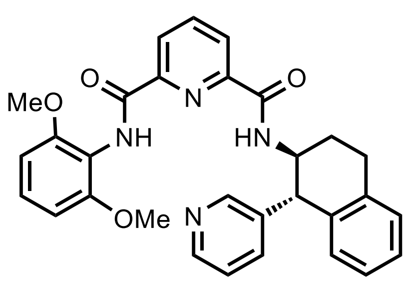
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-*cis*-(1-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*cis*-T24)** Purification by silica gel chromatography eluting with DCM/EA (80/20, v/v), colorless oil, 25% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.67 (d, *J* = 2.3 Hz, 1H), 8.46 (ddd, *J* = 13.7, 7.8, 1.2 Hz, 2H), 8.40 (s, 2H), 8.32 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.13 (t, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 7.26 (s, 1H), 7.26 – 7.25 (m, 1H), 7.24 – 7.18 (m, 2H), 7.18 – 7.13 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 4.93 – 4.87 (m, 1H), 4.56 (d, *J* = 5.6 Hz, 1H), 3.18 (ddd, *J* = 17.8, 11.4, 6.5 Hz, 1H), 3.11 (ddd, *J* = 17.4, 6.1, 2.4 Hz, 1H), 1.92 (ddt, *J* = 9.4, 6.1, 3.1 Hz, 1H), 1.81 (ddt, *J* = 18.8, 12.7, 6.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.71, 162.25, 151.18, 149.56, 148.69, 148.18, 139.49, 138.82, 138.40, 136.99, 135.86, 135.58, 132.22 (q, *J* = 33.6 Hz), 130.55, 128.99, 127.39, 126.71, 126.32, 126.22, 123.64, 123.23 (q, *J* = 273 Hz), 121.50 (q, *J* = 4.3 Hz), 118.35 – 118.03 (m), 47.94, 45.73, 28.45, 24.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.41. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 585.1725, found 585.1729.



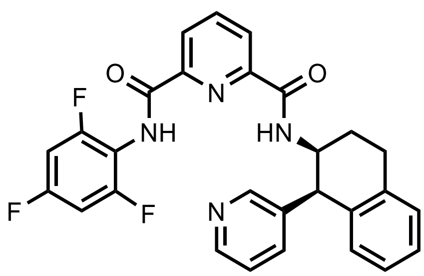
***N*²-(3,5-Bis(trifluoromethyl)phenyl)-*N*⁶-*trans*-(1-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*trans*-T24)** Purification by silica gel chromatography eluting with DCM/EA (50/50, v/v), colorless oil, 15% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.53 – 8.48 (m, 2H), 8.42 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.39 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.24 (s, 2H), 8.11 (t, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.70 (s, 1H), 7.44 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.60 – 4.54 (m, 1H), 4.37 (d, *J* = 6.1 Hz, 1H), 3.17 (dt, *J* = 17.6, 6.3 Hz, 1H), 3.06 (dt, J = 17.6, 7.1 Hz, 1H), 2.23 (dddd, J = 14.0, 7.9, 6.3, 2.8 Hz, 1H), 2.04 (dq, J = 13.4, 6.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.76, 161.71, 150.49, 149.18, 148.47, 147.98, 139.69, 139.04, 138.72, 136.28, 135.81, 134.70, 132.54 (q, J = 33.5 Hz), 130.80, 129.13, 127.50, 126.88, 126.06, 125.74, 123.82, 123.12 (q, J = 273 Hz), 119.93 (dd, J = 8.1, 3.8 Hz), 118.40 – 117.95 (m), 51.81, 48.55, 26.00, 24.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.46. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{23}F_6N_4O_2^+$ $[M+H]^+$ 585.1725, found 585.1730.



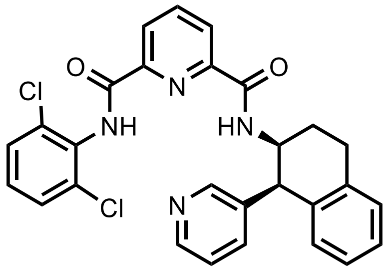
N^2-(2,6-Dimethoxyphenyl)-N^6-*cis*-(1-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*cis*-T25) Purification by silica gel chromatography eluting with EA, white solid, 17% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.40 (m, 2H), 8.37 (d, J = 7.8 Hz, 1H), 8.30 (s, 1H), 8.06 (t, J = 7.8 Hz, 1H), 8.02 (d, J = 4.4 Hz, 1H), 7.40 (d, J = 9.3 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.28 (t, J = 8.4 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.02 (dd, J = 7.9, 4.9 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.68 (d, J = 8.5 Hz, 2H), 4.82 (dddd, J = 12.3, 9.2, 5.6, 3.4 Hz, 1H), 4.55 (d, J = 5.8 Hz, 1H), 3.83 (s, 6H), 3.22 – 3.07 (m, 2H), 2.03 – 1.96 (m, 1H), 1.90 (qd, J = 12.1, 6.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.80, 161.66, 155.72, 151.72, 149.19, 148.61, 148.21, 139.05, 137.69, 136.77, 135.90, 135.79, 130.63, 128.92, 128.22, 127.14, 126.51, 125.68, 125.01, 122.67, 113.51, 104.41, 56.07, 48.06, 46.02, 28.40, 24.55. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{29}N_4O_4^+$ $[M+H]^+$ 509.2189, found 509.2187.



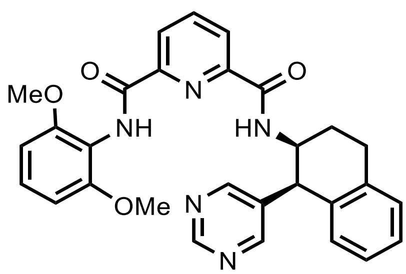
N^2-(2,6-Dimethoxyphenyl)-N^6-*trans*-(1-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*trans*-T25) Purification by silica gel chromatography eluting with EA, white solid, 20% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.45 (d, *J* = 6.2 Hz, 2H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 8.00 (dt, *J* = 14.6, 8.2 Hz, 2H), 7.48 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.21 – 7.17 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 4.56 (ddt, *J* = 11.1, 8.2, 3.9 Hz, 1H), 4.29 (d, *J* = 6.9 Hz, 1H), 3.86 (s, 6H), 3.14 (dt, *J* = 17.4, 6.8 Hz, 1H), 3.03 (dt, *J* = 17.3, 6.4 Hz, 1H), 2.22 (dtd, *J* = 13.3, 6.6, 2.5 Hz, 1H), 1.98 (dt, *J* = 14.0, 7.1 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.07, 161.36, 155.47, 150.58, 148.89, 148.49, 148.33, 139.21, 139.01, 136.39, 135.87, 135.62, 130.61, 128.93, 128.03, 126.93, 126.49, 125.48, 124.90, 123.59, 113.58, 104.44, 56.17, 51.93, 48.90, 26.71, 25.86. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{29}N_4O_4^+$ $[M+H]^+$ 509.2189, found 509.2180.



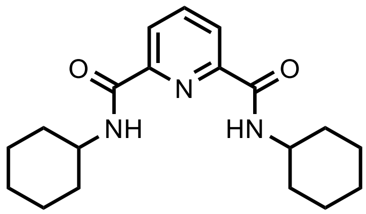
N^2-*cis*-(1-(Pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)-N^6-(2,4,6-trifluorophenyl)pyridine-2,6-dicarboxamide (*cis*-T26) Purification by silica gel chromatography eluting with DCM/EA (80/20, v/v), white solid, 19% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.59 (d, *J* = 2.3 Hz, 1H), 8.41 (ddd, *J* = 11.8, 7.8, 1.2 Hz, 2H), 8.11 – 8.06 (m, 2H), 7.31 (d, *J* = 9.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.87 – 6.82 (m, 2H), 4.83 (tdt, *J* = 9.2, 5.8, 3.2 Hz, 1H), 4.52 (d, *J* = 5.8 Hz, 1H), 3.17 (ddd, *J* = 17.8, 11.8, 6.3 Hz, 1H), 3.08 (ddd, *J* = 17.4, 6.0, 2.3 Hz, 1H), 1.96 (ddd, *J* = 11.9, 5.8, 2.7 Hz, 1H), 1.80 (qd, *J* = 12.5, 6.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.57, 162.43, 160.41 (t, *J* = 14.9 Hz), 159.62 (dd, *J* = 15.4, 7.2 Hz), 157.95 (dd, *J* = 15.3, 7.4 Hz), 151.45, 149.28, 148.29, 148.21, 139.27, 138.18, 136.91, 135.93, 135.63, 130.60, 128.96, 127.25, 126.59, 126.05, 125.79, 123.40, 101.12 – 100.23 (m), 47.83, 45.78, 28.48, 24.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.98 (t, *J* = 5.2 Hz), -116.18 (d, *J* = 6.6 Hz). HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{22}F_3N_4O_{2+}$ $[M+H]^+$ 503.1695, found 503.1697.



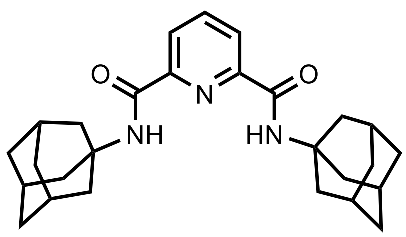
N^2-(2,6-Dichlorophenyl)-N^6-*cis*-(1-(pyridin-3-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*cis*-T27) Purification by silica gel chromatography eluting with DCM/EA (80/20, v/v), white solid, 13% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.50 (d, *J* = 2.3 Hz, 1H), 8.43 (ddd, *J* = 11.9, 7.8, 1.2 Hz, 2H), 8.10 (t, *J* = 7.8 Hz, 1H), 8.00 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 9.5 Hz, 1H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 1H), 4.81 (dddd, *J* = 12.6, 9.2, 5.8, 3.2 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 1H), 3.18 (ddd, *J* = 17.8, 11.6, 6.3 Hz, 1H), 3.10 (ddd, *J* = 17.4, 6.1, 2.4 Hz, 1H), 1.99 (ddd, *J* = 12.4, 6.1, 3.0 Hz, 1H), 1.89 – 1.81 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.49, 161.55, 151.50, 148.97, 148.33, 148.24, 139.35, 137.90, 136.83, 135.82, 135.76, 134.07, 132.08, 130.63, 128.93, 128.84, 128.49, 127.19, 126.56, 125.88, 125.61, 123.18, 47.96, 45.79, 28.39, 24.49. HRMS (ESI-TOF) *m/z* Calcd for $C_{28}H_{23}Cl_2N_4O_2^+$ $[M+H]^+$ 517.1198, found 517.1183.



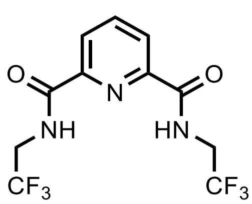
N^2-(2,6-Dimethoxyphenyl)-N^6-*cis*-(1-(pyrimidin-5-yl)-1,2,3,4-tetrahydronaphthalen-2-yl)pyridine-2,6-dicarboxamide (*cis*-T28) Purification by silica gel chromatography eluting with DCM/EA (35/65, v/v), colorless oil, 23% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.54 (s, 1H), 8.43 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.38 (s, 2H), 8.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 2H), 4.79 (dddd, *J* = 12.0, 8.7, 5.7, 3.1 Hz, 1H), 4.67 (d, *J* = 5.6 Hz, 1H), 3.82 (s, 6H), 3.20 – 3.12 (m, 2H), 2.03 – 1.99 (m, 1H), 1.89 – 1.81 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.29, 161.56, 158.15, 157.27, 155.60, 149.50, 148.40, 139.14, 135.67, 134.73, 134.45, 130.44, 129.11, 128.10, 127.59, 126.87, 125.95, 125.05, 113.54, 104.42, 56.09, 48.33, 43.83, 28.15, 24.46. HRMS (ESI-TOF) *m/z* Calcd for $C_{29}H_{28}N_5O_4^+$ $[M+H]^+$ 510.2141, found 510.2138.



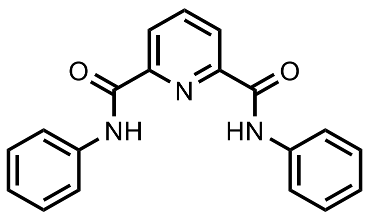
***N*²,*N*⁶-Dicyclohexylpyridine-2,6-dicarboxamide (TC1)** Recrystallization from MeOH, white solid, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.8 Hz, 2H), 8.01 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 4.01 (tdd, *J* = 12.3, 7.2, 4.0 Hz, 2H), 2.05 (dt, *J* = 8.6, 2.4 Hz, 4H), 1.77 (dq, *J* = 12.4, 4.1 Hz, 4H), 1.67 (ddd, *J* = 13.0, 6.3, 2.5 Hz, 2H), 1.47 (ddt, *J* = 11.4, 10.0, 3.5 Hz, 4H), 1.36 (ddd, *J* = 13.6, 10.6, 3.5 Hz, 4H), 1.31 – 1.25 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.47, 149.05, 138.95, 124.88, 48.23, 32.99, 25.56, 24.72. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{28}N_3O_2^+$ $[M+H]^+$ 330.2182, found 330.2183.



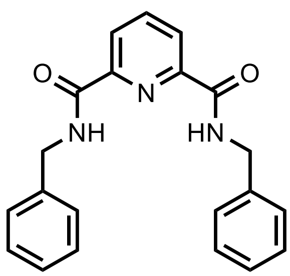
***N*²,*N*⁶-Di((1s,3s)-adamantan-1-yl)pyridine-2,6-dicarboxamide (TC2)** Purification by silica gel chromatography eluting with hexane/EA (70/30, v/v), white solid, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.7 Hz, 2H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.49 (s, 2H), 2.17 (d, *J* = 1.8 Hz, 18H), 1.79 – 1.73 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.06, 149.27, 138.99, 124.14, 51.68, 41.48, 36.35, 29.46. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{36}N_3O_2^+$ $[M+H]^+$ 434.2808, found 434.2807.



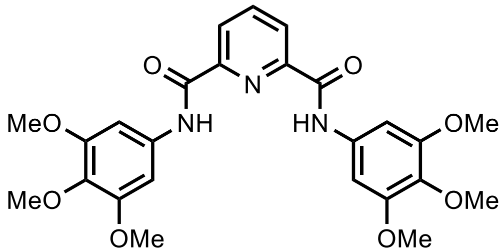
N^{2},*N*^{6}**-Bis(2,2,2-trifluoroethyl)pyridine-2,6-dicarboxamide (TC3)** Recrystallization from DCM/hexane, white solid, 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.8 Hz, 2H), 8.12 (t, *J* = 7.8 Hz, 1H), 7.87 (s, 2H), 4.20 (qd, *J* = 9.0, 6.7 Hz, 4H). ^{13}C NMR (151 MHz, CD_3OD) δ 164.38, 147.62, 138.95, 124.06 (q, *J* = 278.3 Hz), 124.85, 39.85 (q, *J* = 35.1 Hz), 39.76 (q, *J* = 35.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.79. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_{10}F_6N_3O_2^+$ $[M+H]^+$ 330.0677, found 330.0682.



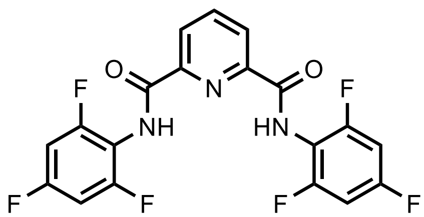
N^{2},*N*^{6}**-Diphenylpyridine-2,6-dicarboxamide (TC4)** Recrystallization from MeOH, white solid, 56% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 10.51 (s, 2H), 8.49 (d, *J* = 7.7 Hz, 2H), 8.34 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.98 (dd, *J* = 8.7, 1.1 Hz, 4H), 7.42 (dd, *J* = 8.6, 7.4 Hz, 4H), 7.18 (tt, *J* = 7.4, 1.1 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 160.91, 148.99, 139.29, 137.95, 128.25, 124.77, 123.72, 120.01. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{16}N_3O_2^+$ $[M+H]^+$ 318.1243, found 318.1245.



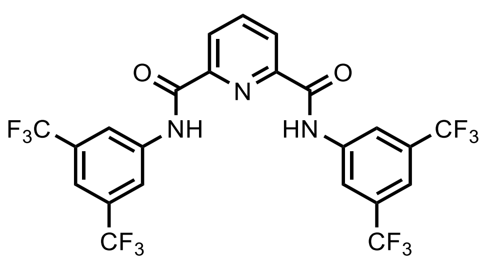
N^{2},*N*^{6}**-Dibenzylpyridine-2,6-dicarboxamide (TC5)** Purification by silica gel chromatography eluting with hexane/EA (50/50, v/v), white solid, 52% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.19 (s, 2H), 8.37 (d, *J* = 7.7 Hz, 2H), 8.24 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.30 (d, *J* = 4.7 Hz, 8H), 7.25 – 7.20 (m, 2H), 4.59 (d, *J* = 6.5 Hz, 4H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 162.84, 148.83, 138.95, 138.79, 127.91, 126.79, 126.45, 124.16, 41.99. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{20}N_3O_2^+$ $[M+H]^+$ 346.1556, found 346.1555.



***N*²,*N*⁶-Bis(3,4,5-trimethoxyphenyl)pyridine-2,6-dicarboxamide (TC6)** Recrystallization from MeOH, white solid, 80% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 10.42 (s, 2H), 8.47 (d, J = 7.7 Hz, 2H), 8.34 (dd, J = 8.1, 7.3 Hz, 1H), 7.44 (s, 4H), 3.87 (s, 12H), 3.73 (s, 6H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 160.60, 152.94, 148.91, 139.42, 134.52, 133.87, 124.60, 97.72, 59.29, 54.96. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{28}N_3O_8^+$ $[M+H]^+$ 498.1876, found 498.1867.

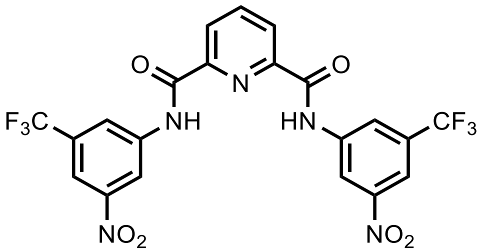


***N*²,*N*⁶-Bis(2,4,6-trifluorophenyl)pyridine-2,6-dicarboxamide (TC7)** Recrystallization from toluene, white solid, 85% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 10.20 (s, 2H), 8.51 (d, J = 7.8 Hz, 2H), 8.39 (dd, J = 8.2, 7.3 Hz, 1H), 7.12 (dd, J = 9.0, 7.6 Hz, 4H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 161.69, 159.94, 159.36 (dd, J = 15.7, 7.4 Hz), 157.70 (dd, J = 15.8, 7.6 Hz), 147.79, 139.65, 125.40, 100.90 – 99.71 (m). ^{19}F NMR (376 MHz, Acetone-d_6) δ -112.75 (t, J = 5.7 Hz), -112.79 (t, J = 6.2 Hz), -118.00 (d, J = 5.5 Hz), -118.04 (d, J = 6.4 Hz). HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{10}F_6N_3O_2^+$ $[M+H]^+$ 426.0677, found 426.0669.

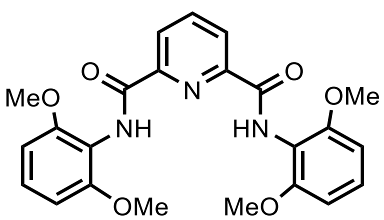


***N*²,*N*⁶-Bis(3,5-bis(trifluoromethyl)phenyl)pyridine-2,6-dicarboxamide (TC8)** Recrystallization from MeOH, white solid, 95% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 11.13 (s, 2H), 8.73 (s, 4H), 8.57 (d, J = 7.7 Hz, 2H), 8.44 (dd, J = 8.1, 7.3 Hz, 1H), 7.83 (dt, J = 1.6, 0.9 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 161.56, 147.94, 139.87 (d, J = 33.6 Hz), 131.24

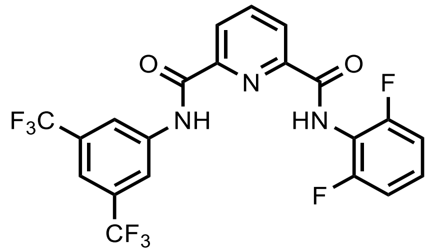
(q, J = 33.5 Hz), 125.57, 123.07 (q, J = 271.8 Hz), 119.83 – 119.52 (m), 117.16 – 115.69 (m). ^{19}F NMR (376 MHz, Acetone-d_6) δ -61.04. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{12}F_{12}N_3O_2^+$ $[M+H]^+$ 590.0738, found 590.0742.



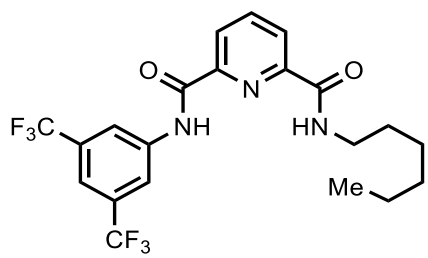
***N*²,*N*⁶-Bis(3-trifluoromethyl-5-nitrophenyl)pyridine-2,6-dicarboxamide (TC9)** Recrystallization from MeOH, pale white solid, 96% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 11.24 (s, 2H), 9.28 (s, 2H), 8.82 (s, 2H), 8.58 (d, J = 7.7 Hz, 2H), 8.45 (t, J = 7.7 Hz, 1H), 8.30 (s, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 161.74, 148.56, 147.864, 147.856, 140.08 (d, J = 24.2 Hz), 131.20 (q, J = 33.6 Hz), 125.75, 122.76 (q, J = 272.1 Hz), 121.73 (q, J = 3.6 Hz), 117.52, 114.73 (q, J = 4.1 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -61.01. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{12}F_6N_5O_6^+$ $[M+H]^+$ 544.0692, found 544.0691.



***N*²,*N*⁶-Bis(2,6-dimethoxyphenyl)pyridine-2,6-dicarboxamide (TC10)** Purification by silica gel chromatography eluting with hexane/EA (30/70, v/v), pale white solid, 90% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 9.81 (s, 2H), 8.42 (d, J = 7.7 Hz, 2H), 8.27 (dd, J = 8.1, 7.4 Hz, 1H), 7.25 (t, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 4H), 3.78 (s, 12H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 161.19, 156.24, 149.20, 138.68, 127.52, 124.20, 114.23, 103.81, 54.89. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{24}N_3O_6^+$ $[M+H]^+$ 438.1665, found 438.1660.

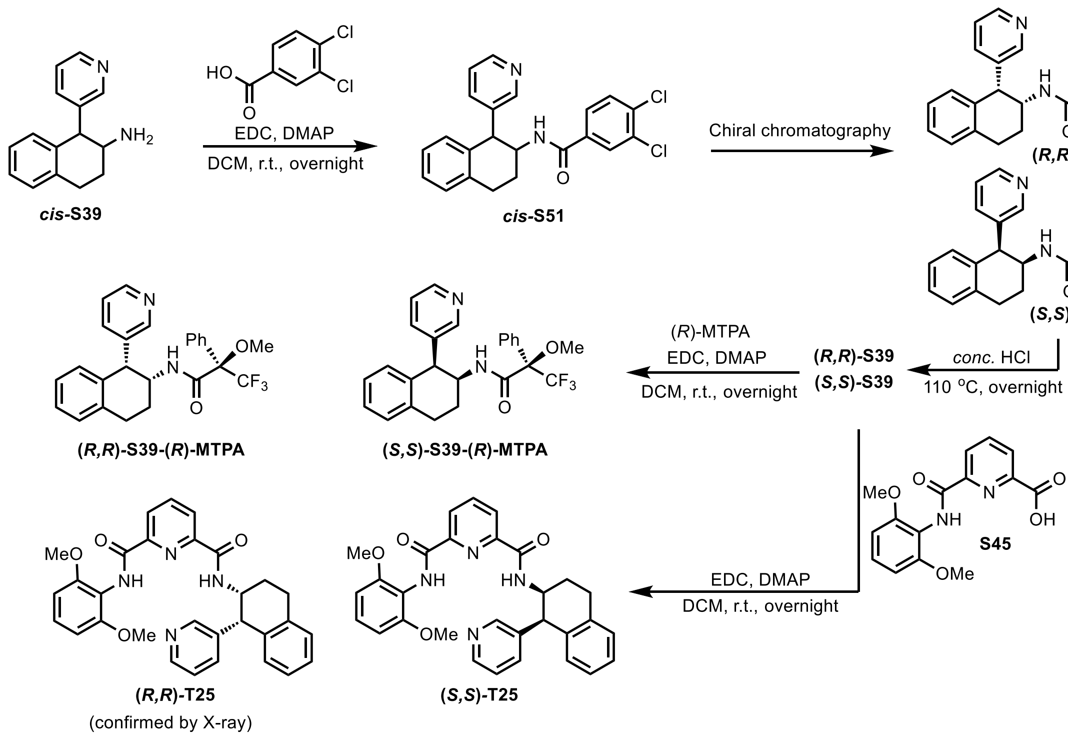


N^2-(3,5-Bis(trifluoromethyl)phenyl)-N^6-(2,6-difluorophenyl)pyridine-2,6-dicarboxamide (TC11) Recrystallization from MeOH, pale white solid, 82% yield. ^{1}H NMR (600 MHz, Acetone-d_6) δ 10.93 (s, 1H), 10.07 (s, 1H), 8.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.53 – 8.47 (m, 3H), 8.41 (t, *J* = 7.8 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.46 (tt, *J* = 8.5, 6.2 Hz, 1H), 7.16 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 161.75, 161.49, 159.09 (d, *J* = 4.9 Hz), 157.43 (d, *J* = 5.0 Hz), 148.06, 147.97, 139.73, 139.68, 131.98 – 130.00 (m), 128.42 (t, *J* = 10.0 Hz), 125.50 (d, *J* = 17.5 Hz), 123.01 (q, *J* = 272.0 Hz), 119.88 (q, *J* = 4.3 Hz), 116.62 (dt, *J* = 8.5, 4.2 Hz), 113.67 (t, *J* = 16.8 Hz), 111.36 (dd, *J* = 19.8, 4.4 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -60.97, -116.09. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{12}F_8N_3O_2^+$ $[M+H]^+$ 490.0802, found 490.0801.



N^2-(3,5-bis(trifluoromethyl)phenyl)-N^6-hexylpyridine-2,6-dicarboxamide (TC12) Purification by silica gel chromatography eluting with hexane/EA (60/40, v/v), pale white solid, 92% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.50 (d, *J* = 7.7 Hz, 2H), 8.31 (s, 2H), 8.16 (t, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 6.2 Hz, 1H), 7.70 (s, 1H), 3.53 (q, *J* = 6.8 Hz, 2H), 1.66 (td, *J* = 14.3, 13.8, 6.7 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 2H), 1.31 (td, *J* = 3.9, 1.8 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.24, 161.80, 149.41, 147.89, 139.67, 138.76, 132.57 (d, *J* = 33.7 Hz), 126.17, 125.56, 123.06 (q, *J* = 272.9 Hz), 120.21 – 119.61 (m), 118.15 – 117.99 (m), 39.89, 31.47, 29.74, 26.77, 22.56, 13.97. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.62. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{22}F_6N_3O_2^+$ $[M+H]^+$ 462.1616, found 462.1620.

2.2 Preparation and Determination Absolute Configuration of (*S*,*S*)-T25



Following the procedure for synthesis of ***cis*-T25** with ***cis*-S39** and 3,4-dichlorobenzoic acid. Compound ***cis*-S51** was obtained as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.26 (d, *J* = 2.3 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.22 (tt, *J* = 4.3, 1.7 Hz, 3H), 7.17 (ddd, *J* = 7.8, 4.7, 0.9 Hz, 1H), 7.12 (ddd, *J* = 7.7, 6.1, 2.6 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 5.72 (d, *J* = 8.1 Hz, 1H), 4.72 – 4.67 (m, 1H), 4.66 (d, *J* = 5.7 Hz, 1H), 3.18 – 3.08 (m, 2H), 1.92 – 1.84 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.78, 151.17, 148.21, 137.87, 137.17, 136.15, 135.87, 135.47, 134.10, 133.25, 130.81, 130.75, 129.23, 128.89, 127.18, 126.63, 125.82, 123.12, 49.17, 45.31, 28.36, 24.09. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{19}Cl_2N_2O^+$ $[M+H]^+$ 397.0874, found 397.0880.

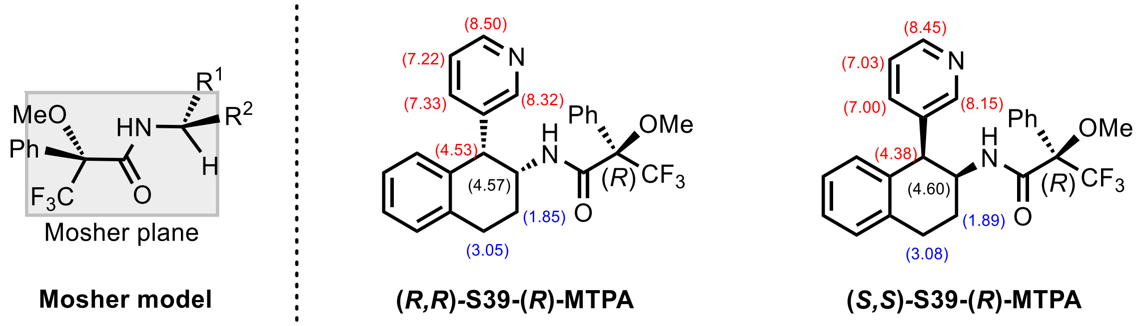
(*R*,*R*)-S51 and **(*S*,*S*)-S51** were separated by chiral chromatography on a chiralpak OD column (30% IPA/hexane, 6.0 mL/min). Retention time: 15 min [**(*R*,*R*)-S51**], 19 min [**(*S*,*S*)-S51**]. For **(*R*,*R*)-S51**, $[\alpha]_D^{21}$ = + 202.1 (*c* 0.1, $CHCl_3$). For **(*S*,*S*)-S51**, $[\alpha]_D^{21}$ = – 168.1 (*c* 0.1, $CHCl_3$).

***(R,R)*-S39** and ***(S,S)*-S39** were prepared through treating ***(R,R)*-S51** and ***(S,S)*-S51** with *conc.* HCl at 110 ^{o}C for overnight. The reaction mixture was basified with 10% aqueous NaOH solution and extracted with EA. The crude products were used in the next step without further purification.

Following the procedure for synthesis of ***cis*-T25** with ***(R,R)*-S39** [or ***(S,S)*-S39]** and **S45**. Compounds ***(R,R)*-T25** and ***(S,S)*-T25** were obtained. If necessary, ***(S,S)*-T25** can be further purified through recrystallization from ^{i}PrOH to increase the ee value to > 99%. For ***(R,R)*-T25,** $[\alpha]_D^{21}$ = + 104.0 (*c* 0.1, $CHCl_3$). For ***(S,S)*-T25,** $[\alpha]_D^{21}$ = – 81.1 (*c* 0.1, $CHCl_3$).

Following the procedure for synthesis of ***cis*-T25** with ***(R,R)*-S39** [or ***(S,S)*-S39]** and Mosher reagent ***(R)*-MTPA**. Compounds ***(R,R)*-S39-*(R)*-MTPA** and ***(S,S)*-S39-*(R)*-MTPA** were obtained as colorless oil. For ***(R,R)*-S39-*(R)*-MTPA,** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.32 (d, *J* = 2.0 Hz, 1H), 7.46 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.33 (dt, *J* = 7.9, 2.1 Hz, 1H), 7.22 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.11 – 7.08 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 4.60 – 4.55 (m, 1H), 4.53 (d, *J* = 5.7 Hz, 1H), 3.24 (q, *J* = 1.5 Hz, 3H), 3.10 – 3.01 (m, 2H), 1.92 – 1.86 (m, 1H), 1.84 – 1.79 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.72, 151.43, 148.32, 137.98, 136.75, 136.04, 135.38, 132.26, 130.65, 129.52, 128.86, 128.67, 127.58 (q, *J* = 1.3 Hz), 127.08, 126.56, 123.85 (q, *J* = 221.4 Hz), 123.06, 83.91 (q, *J* = 26.0 Hz), 54.92 (q, *J* = 2.1 Hz), 48.69, 45.76, 28.08, 24.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.73. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{24}F_3N_2O_2^+$ $[M+H]^+$ 441.1790, found 441.1792. $[\alpha]_D^{21}$ = + 173.5 (*c* 0.1, $CHCl_3$). For ***(S,S)*-S39-*(R)*-MTPA,** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.15 (d, *J* = 2.1 Hz, 1H), 7.50 (td, *J* = 6.3, 5.1, 3.0 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.22 – 7.18 (m, 2H), 7.10 – 7.07 (m, 1H), 7.03 (ddd, *J* = 7.9, 4.7, 0.9 Hz, 1H), 7.00 (dt, *J* = 7.9, 2.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 8.7 Hz, 1H), 4.63 – 4.58 (m, 1H), 4.38 (d, *J* = 5.6 Hz, 1H), 3.31 (t, *J* = 1.6 Hz, 3H), 3.11 – 3.05 (m, 2H), 1.91 – 1.87 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.51, 151.25, 148.16, 137.89, 136.79, 135.73, 135.56, 132.27, 130.50, 129.56, 128.97, 128.71, 127.52 (q, *J* = 1.3 Hz), 127.14, 126.53, 123.63 (q, *J* = 221.0 Hz), 123.05, 83.73, 54.89 (q, *J* = 1.5 Hz), 48.30, 45.80, 27.90, 24.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.39. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{24}F_3N_2O_2^+$ $[M+H]^+$ 441.1790, found 441.1792. $[\alpha]_D^{21}$ = – 129.2 (*c* 0.1, $CHCl_3$).

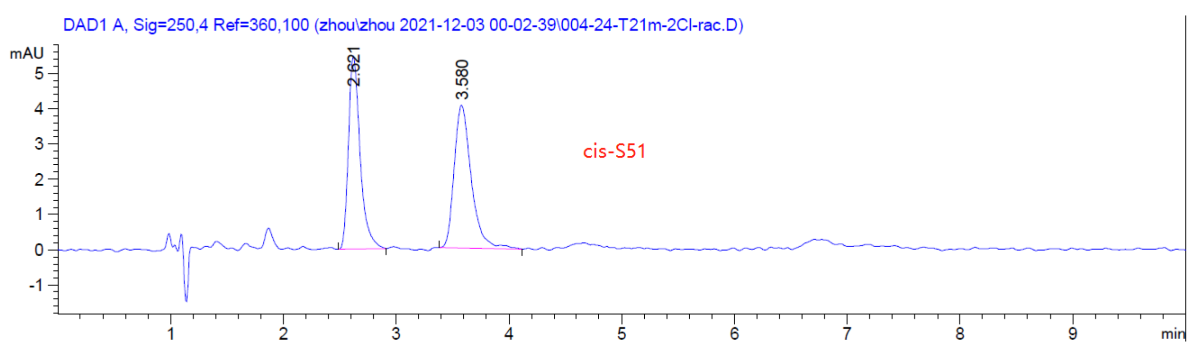
Mosher's method analysis:



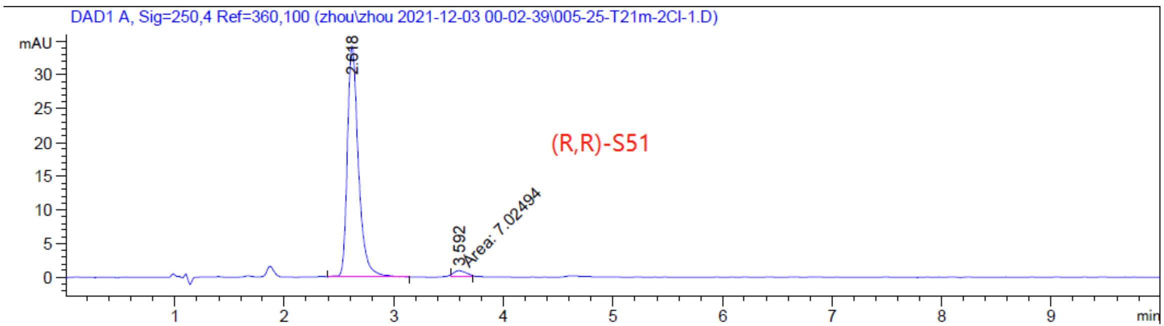
Considering mosher model, the protons in the R^2 of the molecule are shifted upfield relative to the protons in the R^1, which is the result of anisotropic shielding of phenyl group. In **(*R*,*R*)-S39-(*R*)-MTPA**, the pyridine portion is *trans* to the phenyl group. In **(*S*,*S*)-S39-(*R*)-MTPA**, the pyridine portion is *cis* to the phenyl group. Therefore, the absolute configurations of all derivatives are confirmed. These configurations are also confirmed by the X-ray of **(*R*,*R*)-T25**.

Chiral SFC spectra:

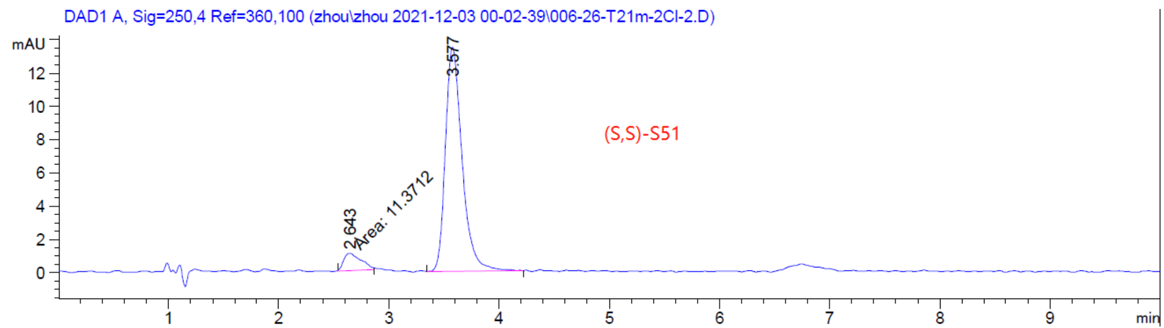
The enantiomeric purities of ***cis*-S51, (*R*,*R*)-S51** and **(*S*,*S*)-S51** were determined by SFC analysis on a chiralpak OD column (30% IPA/CO_2, 3.0 mL/min). The enantiomeric purities of ***cis*-T25, (*R*,*R*)-T25** and **(*S*,*S*)-T25** were analyzed on a Waters UPC2 SFC with a Phenomenex CEL1 column (3 um, 4.6 x 250 mm) under isocratic conditions (3.3 mL/min, 40% IPA/CO_2, 1600 psi backpressure) at 30 °C.



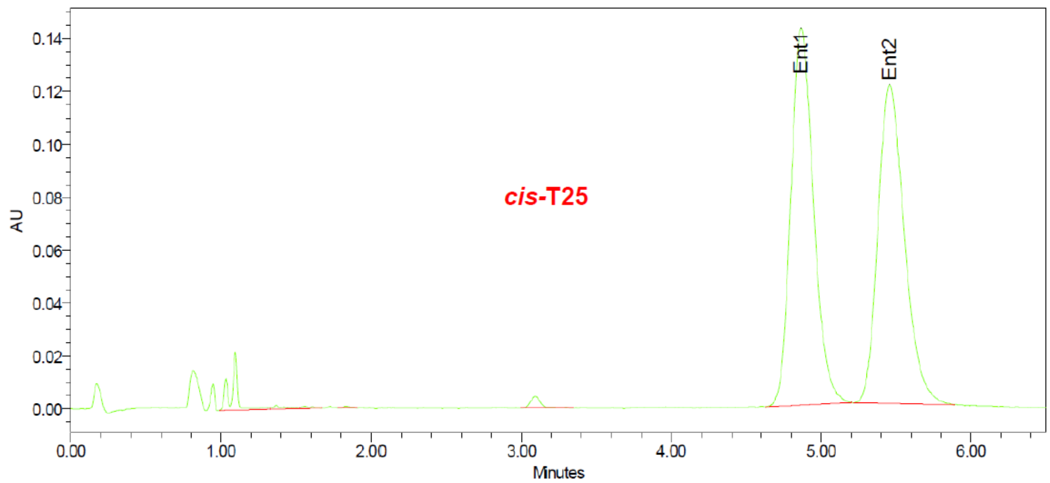
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.621	BB	0.1101	39.30210	5.45293	47.8904
2	3.580	BB	0.1594	42.76466	4.04414	52.1096



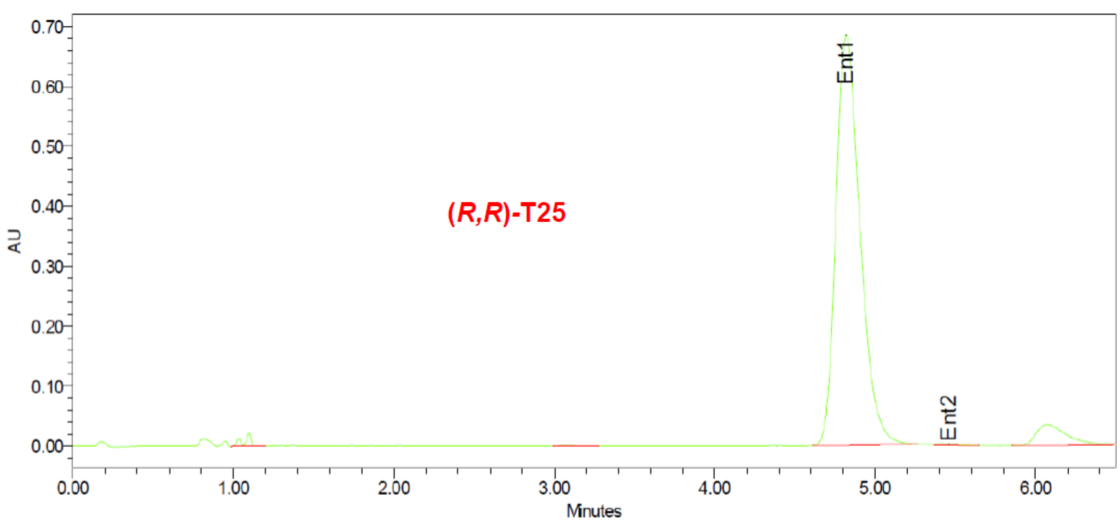
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.618	BB	0.1081	240.23790	34.13319	97.1589
2	3.592	MM	0.1316	7.02494	8.89742e-1	2.8411



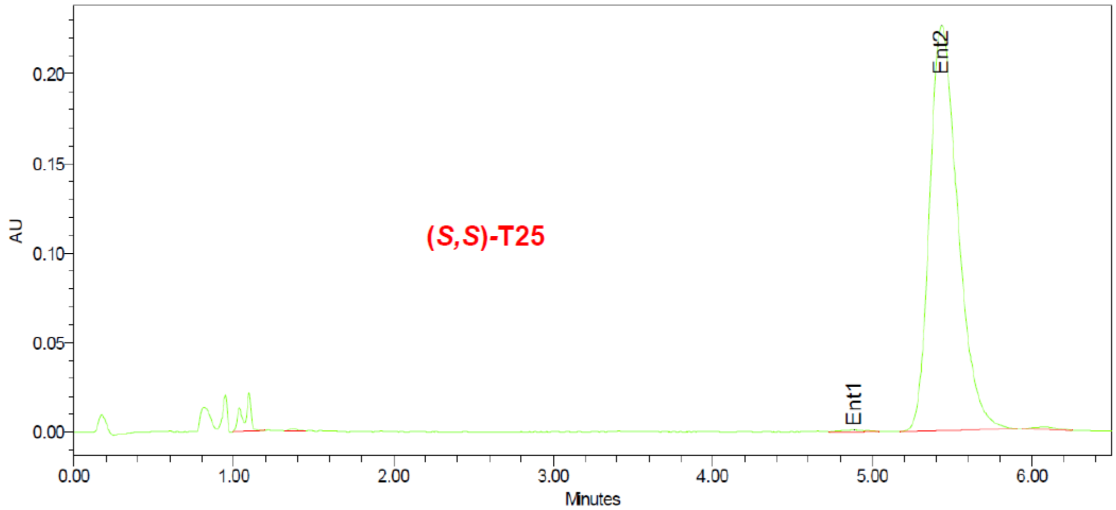
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.643	MM	0.1825	11.37122	1.03864	7.4439
2	3.577	BB	0.1606	141.38776	13.45976	92.5561



	Channel Name	Name	RT	Area	Height (μV)	ent1	ent2	ee
1	UV213		1.10	65920	22023	50.38	49.62	0.76
2	UV213		1.37	7952	1569	50.38	49.62	0.76
3	UV213		1.56	3918	814	50.38	49.62	0.76
4	UV213		1.83	2572	692	50.38	49.62	0.76
5	UV213		3.09	22161	4417	50.38	49.62	0.76
6	UV213	Ent1	4.87	1504957	142569	50.38	49.62	0.76
7	UV213	Ent2	5.46	1482311	120630	50.38	49.62	0.76



	Channel Name	Name	RT	Area	Height (μV)	ent1	ent2	ee
1	UV213		1.10	62292	21833	99.88	0.12	99.76
2	UV213		3.08	7424	1270	99.88	0.12	99.76
3	UV213	Ent1	4.82	7176859	684004	99.88	0.12	99.76
4	UV213	Ent2	5.46	8669	892	99.88	0.12	99.76
5	UV213		6.07	463495	35044	99.88	0.12	99.76



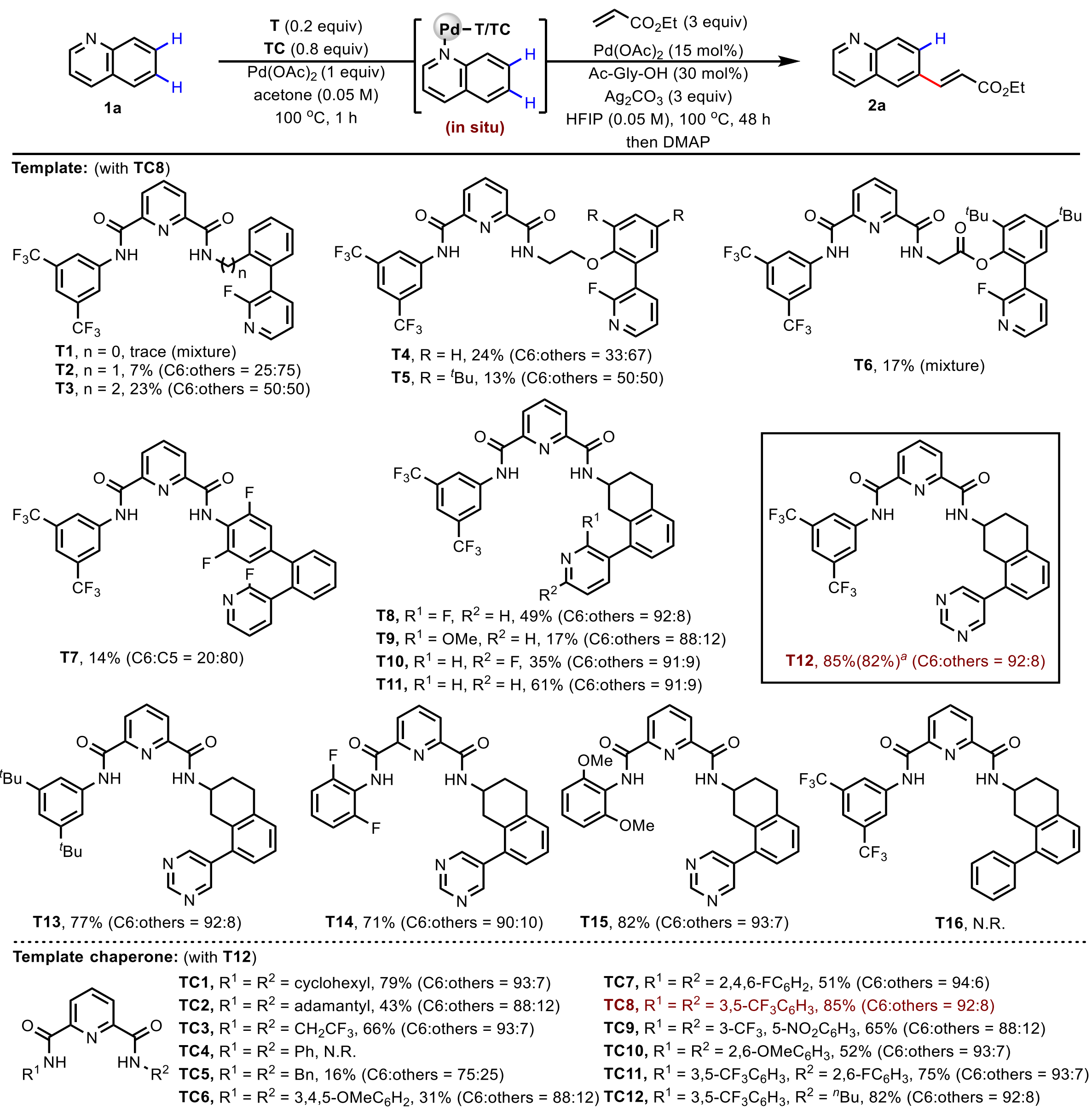
	Channel Name	Name	RT	Area	Height (µV)	ent1	ent2	ee
1	UV213		1.10	66545	21282	0.36	99.64	-99.29
2	UV213		1.37	4264	1485	0.36	99.64	-99.29
3	UV213	Ent1	4.89	9985	1015	0.36	99.64	-99.29
4	UV213	Ent2	5.43	2788992	226026	0.36	99.64	-99.29
5	UV213		6.07	15320	1579	0.36	99.64	-99.29

2.3 Condition Optimization and Template Chaperone Role

(a) Condition Optimization

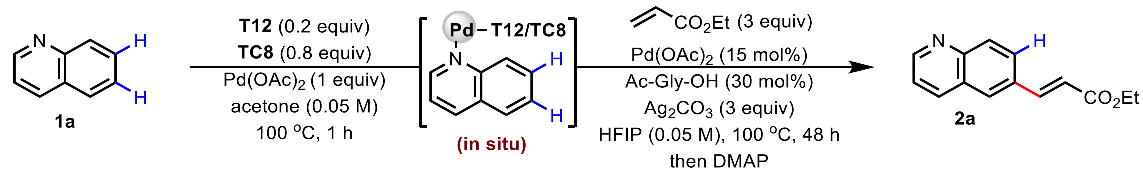
Screening reactions were carried out on 0.02 mmol scale. Yield was based on ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. Selectivity was based on ^1H NMR, GC-MS and LC-MS analysis. The yield of single target product is shown in tables.

Table S1. Template optimization for C6-selective C–H olefination of quinoline



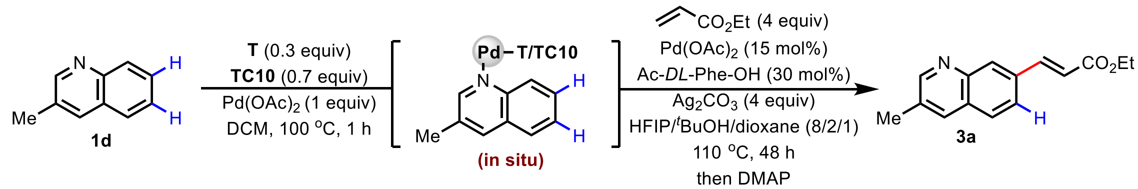
[a]Isolated yield on 0.1 mmol scale.

Table S2. Condition optimization for C6-selective C–H olefination of quinoline

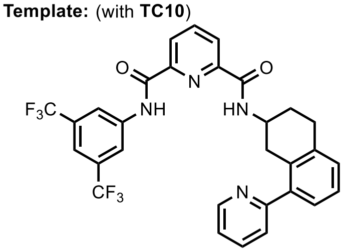


Entry	Deviation from standard conditions	Yield (%), Selectivity (C6:others)
1	none	85, (92:8)
2	**T12** (1 equiv), *w/o* **TC8**	84, (92:8)
3	**TC8** (1 equiv), *w/o* **T12**	N.R., (-)
4	$Pd(OAc)_2$ (0.2 equiv) in 1st step, *w/o* **TC8**	27, (83:17)
5	DCM instead of acetone	75, (92:8)
6	MeCN instead of acetone	80, (92:8)
7	*w/o* $Pd(OAc)_2$ in 2nd step	N.R., (-)
8	*w/o* Ac-Gly-OH	9, (67:33)
9	*w/o* Ag_2CO_3	48, (90:10)
10	$Pd(MeCN)_2Cl_2$ instead of $Pd(OAc)_2$ in 2nd step	60, (89:11)
11	Ac-*L*-Phe-OH instead of Ac-Gly-OH	41, (90:10)
12	TFA-Gly-OH instead of Ac-Gly-OH	25, (87:13)
13	Formyl-Gly-OH instead of Ac-Gly-OH	62, (93:7)
14	AgOAc instead of Ag_2CO_3	70, (91:9)
15	$Cu(OAc)_2$ instead of Ag_2CO_3	27, (80:20)

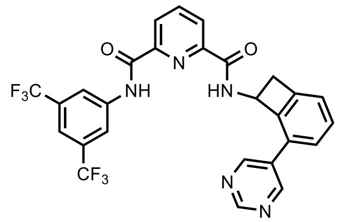
Table S3. Template optimization for C7-selective C–H olefination of 3-methylquinoline



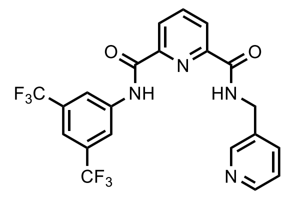
Template: (with **TC10**)



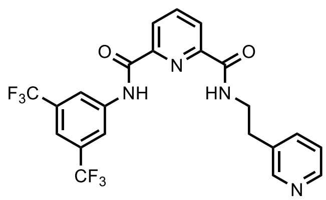
T17, trace (mixture)



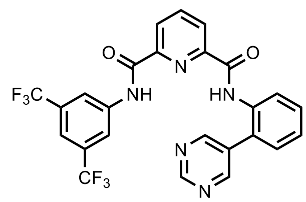
T18, trace (mixture)



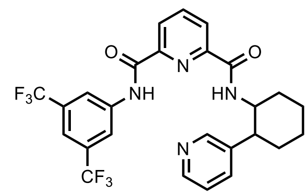
T19, 5% (C7:others = 38:62)



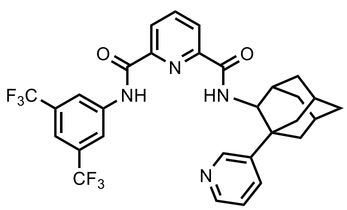
T20, 11% (C7:others = 57:43)



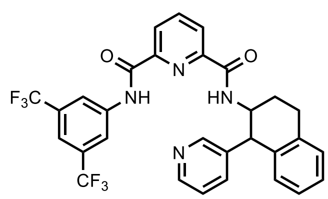
T21, 7% (C7:others = 50:50)



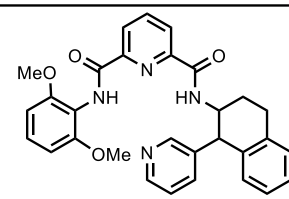
***cis*-T22**, 17% (C7:others = 85:15)
***trans*-T22**, 15% (C7:others = 80:20)



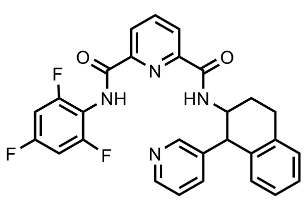
T23, 21% (C7:others = 83:17)



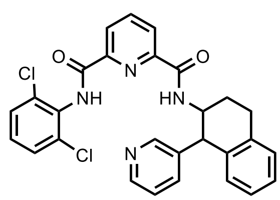
***cis*-T24**, 24% (C7:others = 91:9)
***trans*-T24**, 35% (C7:others = 90:10)



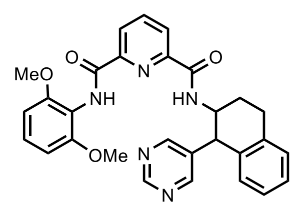
***cis*-T25**, 67%(64%)[a] (C7:others = 96:4)
***trans*-T25**, 35% (C7:others = 89:11)



***cis*-T26**, 27% (C7:others = 90:10)



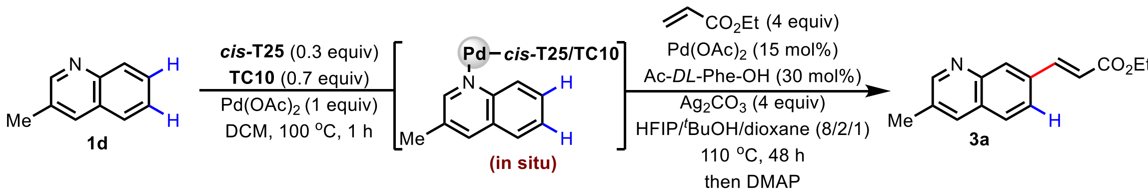
***cis*-T27**, 23% (C7:others = 86:14)



***cis*-T28**, 19% (C7:others = 86:14)

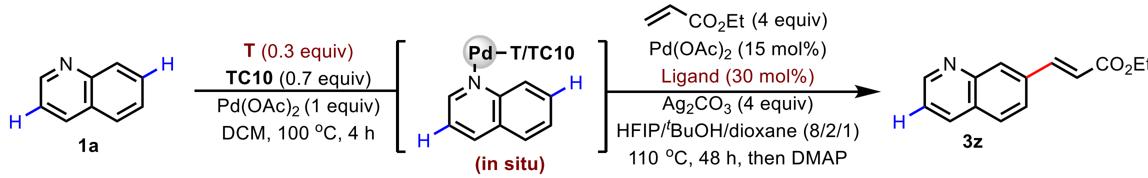
[a]Isolated yield on 0.05 mmol scale.

Table S4. Condition optimization for C7-selective C–H olefination of 3-methylquinoline

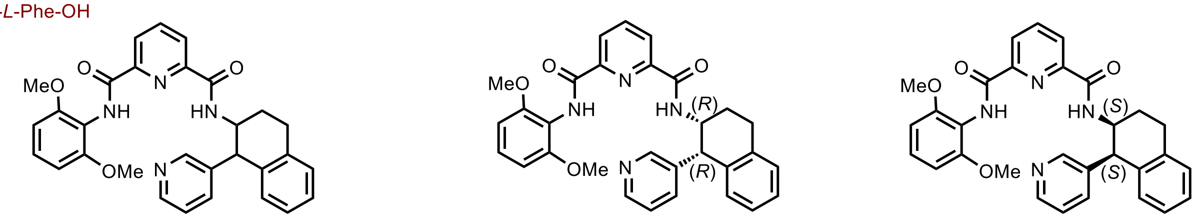


Entry	Deviation from standard conditions	Yield (%), Selectivity (C7:others)
1	none	67, (96:4)
2	***cis*-T25** (1 equiv), *w/o* **TC10**	60, (96:4)
3	**TC10** (1 equiv), *w/o* ***cis*-T25**	N.R., (-)
4	$Pd(OAc)_2$ (0.3 equiv) in 1st step, *w/o* **TC10**	33, (84:16)
5	acetone instead of DCM	53, (96:4)
6	MeCN instead of DCM	56, (94:6)
7	*w/o* $Pd(OAc)_2$ in 2nd step	N.R., (-)
8	*w/o* Ac-*DL*-Phe-OH	N.R., (-)
9	*w/o* Ag_2CO_3	6, (96:4)
10	$Pd(MeCN)_2Cl_2$ instead of $Pd(OAc)_2$ in 2nd step	39, (94:6)
11	Ac-Gly-OH instead of Ac-*DL*-Phe-OH	30, (89:11)
12	Ac-*L*-Phe-OH instead of Ac-*DL*-Phe-OH	53, (96:4)
13	Ac-*D*-Phe-OH instead of Ac-*DL*-Phe-OH	56, (96:4)
14	AgOAc instead of Ag_2CO_3	40, (94:6)
15	$Cu(OAc)_2$ instead of Ag_2CO_3	5, (-)
16	HFIP instead of solvent mixture	39, (96:4)
17	^{t}BuOH instead of solvent mixture	48, (96:4)
18	dioxane instead of solvent mixture	10, (96:4)
19	HFIP/^{t}BuOH (4/1) instead of solvent mixture	32, (96:4)

Table S5. Condition optimization for C7-selective C–H olefination of quinoline

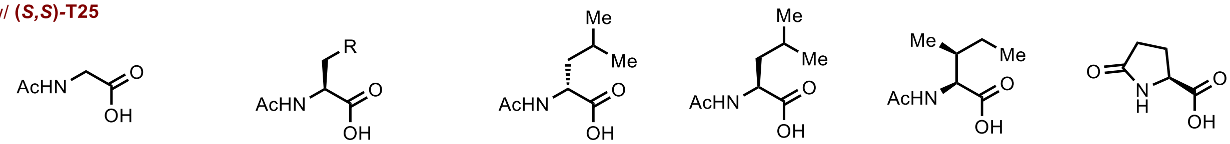


w/ Ac-*L*-Phe-OH



***cis*-T25**, 28% (C7:C3 = 50:50, mono:di = 67:33)[a] **(*R,R*)-T25**, 31% (C7:C3 = 50:50, mono:di = 50:50) **(*S,S*)-T25**, 42% (C7:C3 = 88:12)

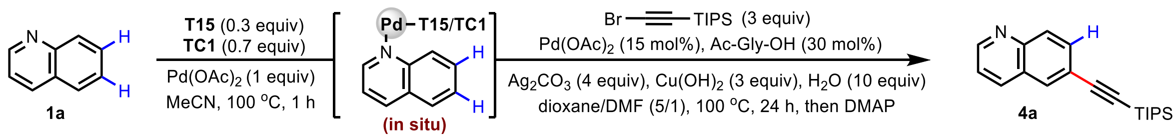
w/ **(*S,S*)-T25**



(Ac-Gly-OH)	R = Cy, 46% (C7:C3 = 86:14)	(Ac-*D*-Leu-OH)	(Ac-*L*-Leu-OH)	(Ac-*L*-Ile-OH)	(*L*-pGlu-OH)
20% (C7:C3 = 50:50)	R = ^{t}Bu, 10% (C7:C3 = 67:33)	29% (C7:C3 = 50:50) (mono:di = 50:50)	55% (C7:C3 = 88:12) 54% (C7:C3 = 90:10)[b]	43% (C7:C3 = 86:14)	8% (C7:C3 = 25:75)

[a]Di-product represents both C3 and C7-olefinated quinoline. [b]Using $Pd(MeCN)_2Cl_2$.

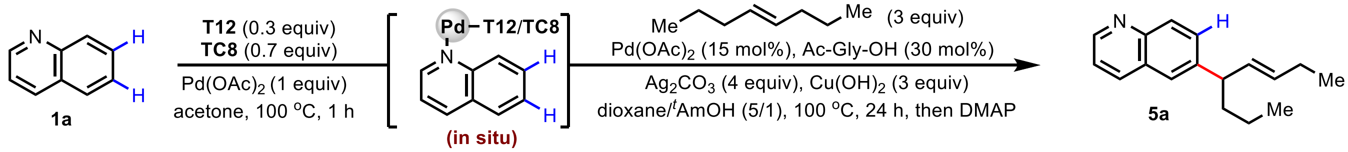
Table S6. Condition optimization for C6-selective C–H alkynylation of quinoline



Entry	Deviation from standard conditions	Yield (%), Selectivity (C6:others)
1	none	72(66)[a], (96:4)
2	*w/o* $Pd(OAc)_2$ in 2nd step	N.R., (-)
3	*w/o* Ac-Gly-OH	7, (-)
4	*w/o* Ag_2CO_3	9, (92:8)
5	*w/o* $Cu(OH)_2$	23, (90:10)
6	*w/o* H_2O	64, (96:4)
7	*w/o* DMF	67, (96:4)
8	$Pd(MeCN)_2Cl_2$ instead of $Pd(OAc)_2$ in 2nd step	33, (96:4)
9	$Cu(OAc)_2$ instead of $Cu(OH)_2$	30, (89:11)
10	Cu_2O instead of $Cu(OH)_2$	28, (88:12)
11	HFIP instead of standard solvent	N.R., (-)

[a]Isolated yield on 0.1 mmol scale.

Table S7. Condition optimization for C6-selective C–H allylation of quinoline



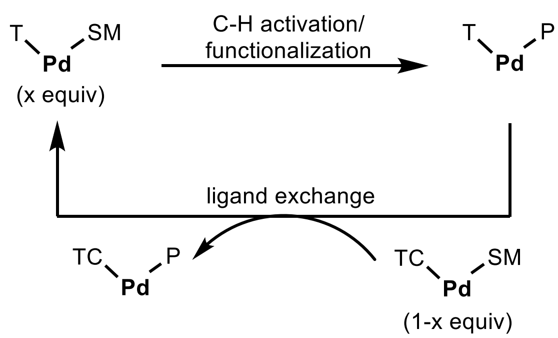
Entry	Deviation from standard conditions	Yield (%), Selectivity (C6:others)
1	none	76(75)[a], (91:9)
2	*w/o* $Pd(OAc)_2$ in 2nd step	N.R., (-)
3	*w/o* Ac-Gly-OH	N.R., (-)
4	*w/o* Ag_2CO_3	41, (91:9)
5	*w/o* $Cu(OH)_2$	33, (90:10)
6	*w/o* ^{t}AmOH	52, (91:9)
7	**T15**/**TC10** instead of **T12**/**TC8**	66, (91:9)
8	Cu_2O instead of $Cu(OH)_2$	41, (90:10)
9	dioxane/HFIP (5/1) instead of solvent mixture	39, (85:15)

[a]Isolated yield on 0.1 mmol scale.

(b) Template Chaperone Role

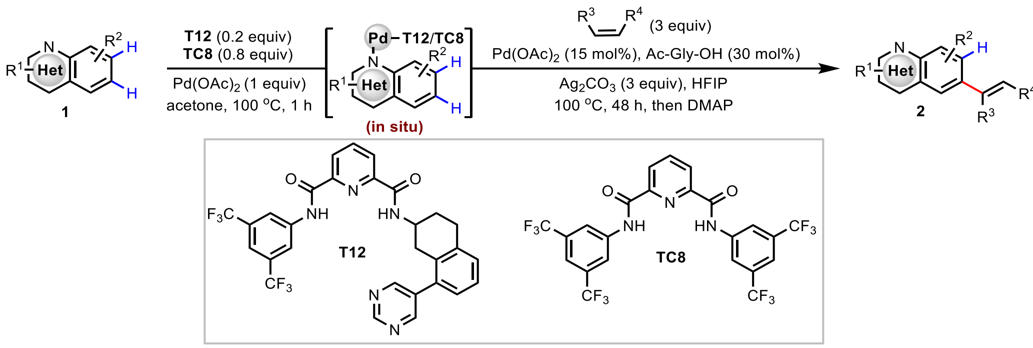
A key challenge in executing the remote functionalization of azine-containing heterocycles is the deleterious binding effect of the azine nitrogen to the active Pd catalyst. Our initial report on the non-covalent template (**T**)-mediated C5–H olefination required a stoichiometric loading of the Pd-containing **T** complex to mask the azine nitrogen, as well as to enable **T** to direct the Pd catalyst to the appropriate site. In this manuscript, we found that the loading of **T** could be reduced by using a much simpler template chaperone (**TC**).

We propose the following role and catalytic cycle of template (**T**) in the presence of **TC**. Substrate-**T** complex is the only competent species capable of recruiting the Pd catalyst and directing it to the required site (C6 or C7). Upon reaction, product-**T** complex is proposed to form, which undergoes template exchange with another substrate-**TC** complex to regenerate the competent substrate-**T** species for the next C–H activation catalytic cycle. In addition to statistical effects, we hypothesize that product-**T**/substrate-**TC** turnover is also promoted by increased steric hindrance from the functionalized product, disfavoring product binding to **T** relative to the substrate-**T**. In addition, the sum of **T** and **TC** loading enables all substrate azine nitrogens to be suitably masked to mitigate catalyst poisoning, enabling the active Pd catalyst to carry out the required activation and functionalization steps.



SM, starting material; T, template; TC, template chaperone; P, product

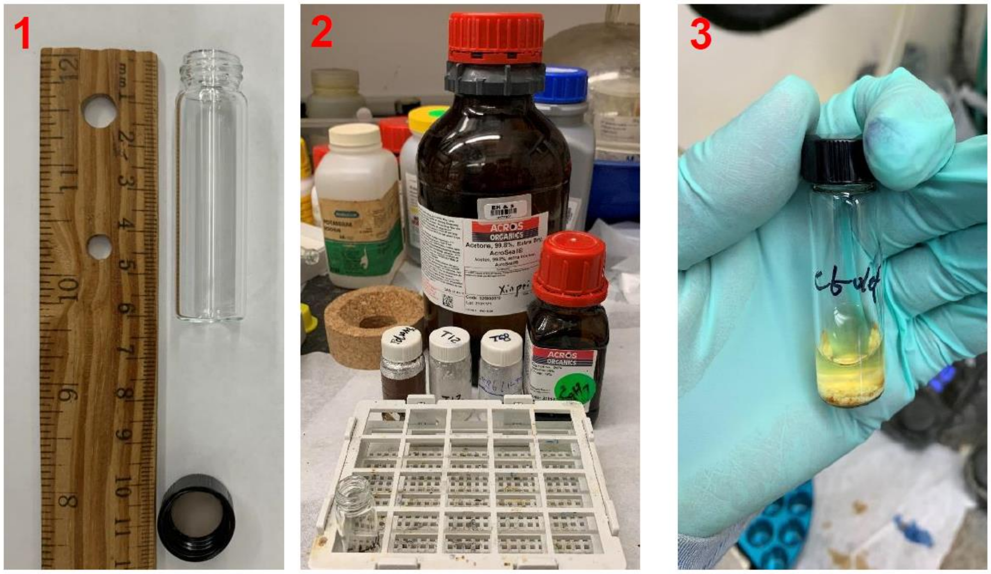
2.4 General Procedure for C6-Selective C–H Olefination



A pressure resistant reaction vial was charged with bicyclic aza-arene (0.1 mmol), **T12** (11.7 mg, 0.02 mmol), **TC8** (47.1 mg, 0.08 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and acetone (2 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Ac-Gly-OH (3.5 mg, 0.03 mmol), Ag_2CO_3 (82.7 mg, 0.3 mmol), HFIP (2 ml), and olefin (0.3 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 48 h (600 – 1200 rpm). After cooling to room temperature, a solution of DMAP (36.7 mg, 0.3 mmol) in toluene (1 mL) and **TC8** (23.5 mg, 0.04 mmol) was added [Note: If the product release is incomplete, more DMAP should be added]. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using EA as the eluent to give the product mixture for determing the site-selectivity by ^1H NMR analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the product **2** and **TC-Pd-DMAP** complex.

Graphical Procedure for C6-Selective C–H Olefination

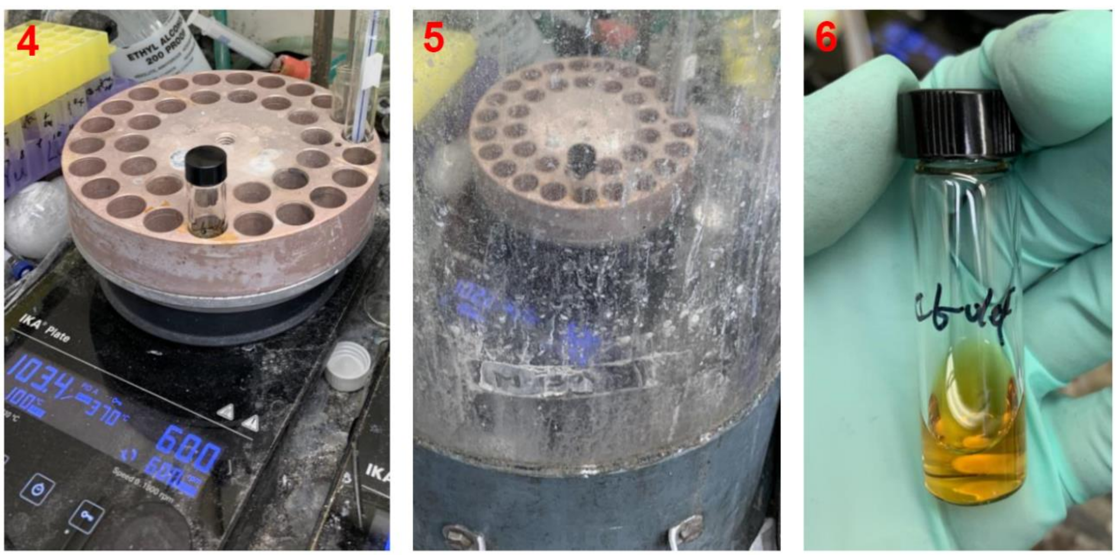
Representative example of preparation of **2a** (0.1 mmol scale)



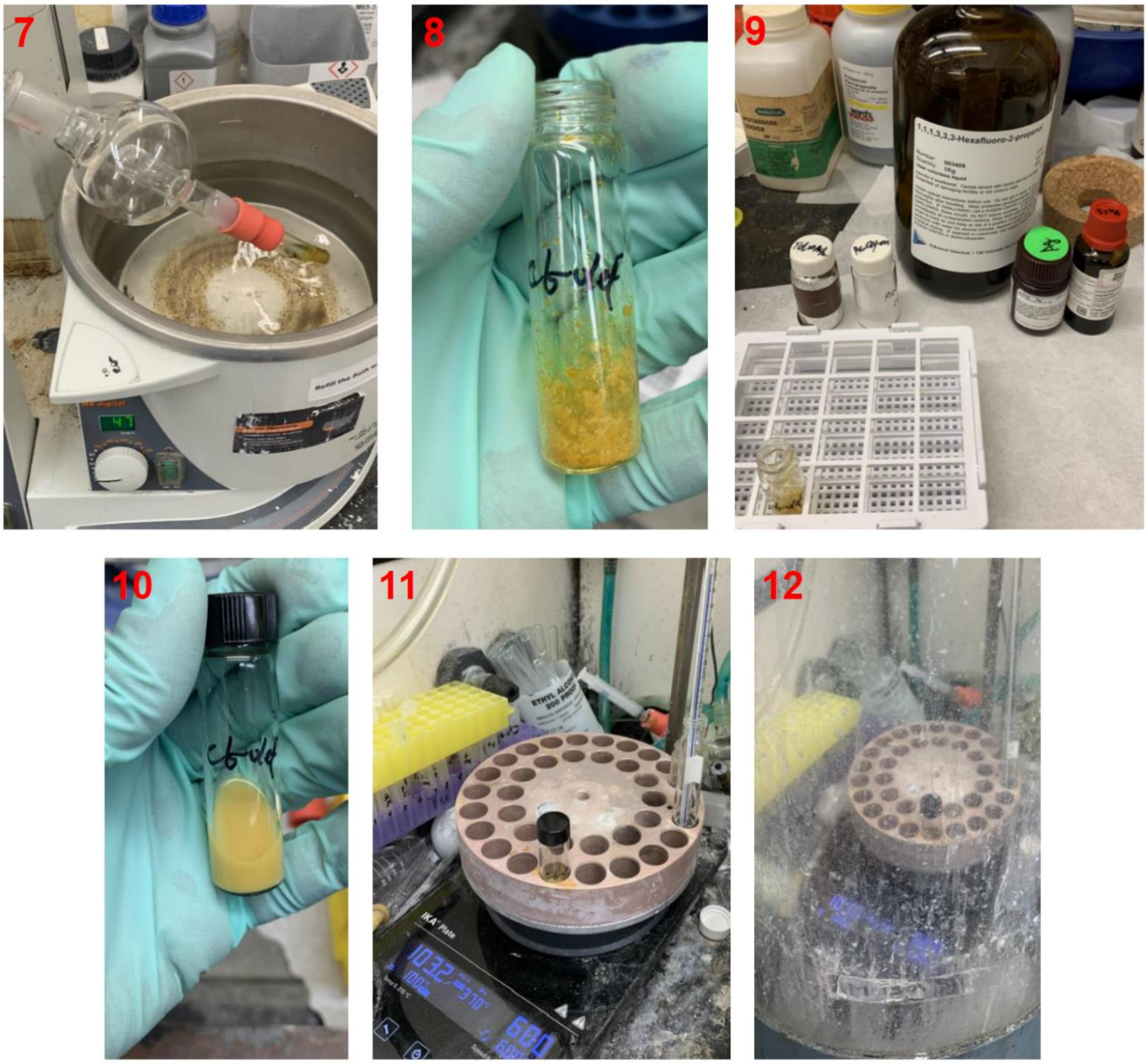
Fisherbrand™ class B clear glass threaded vial.
Volume: 7.4 mL; length: 60 mm.
Fisher Catalog No. 03-338C.

DWK life sciences Wheaton™ black phenolic screw cap.
Mfr: W240822
Fisher Catalog No. 02-927-102

Step 1 to 3: Reaction set up for template complexation.



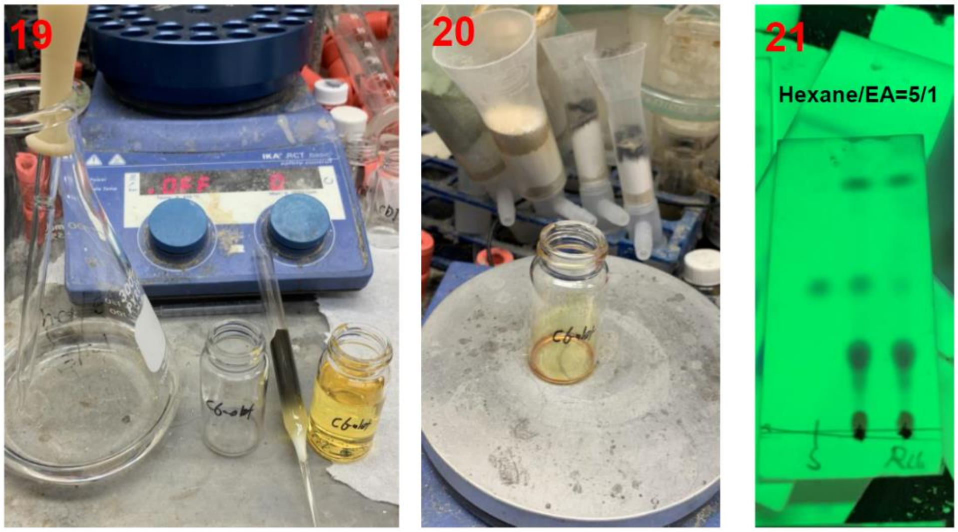
Step 4 to 6: Preparation of template complexation at 100 °C. A blast shield was used for safety. The resulting solution is shown in 6.



Step 7 to 8: Solvent switch prior to C6-selective olefination.

Step 9 to 12: Reaction set up for C6-selective olefination. A blast shield was used for safety.

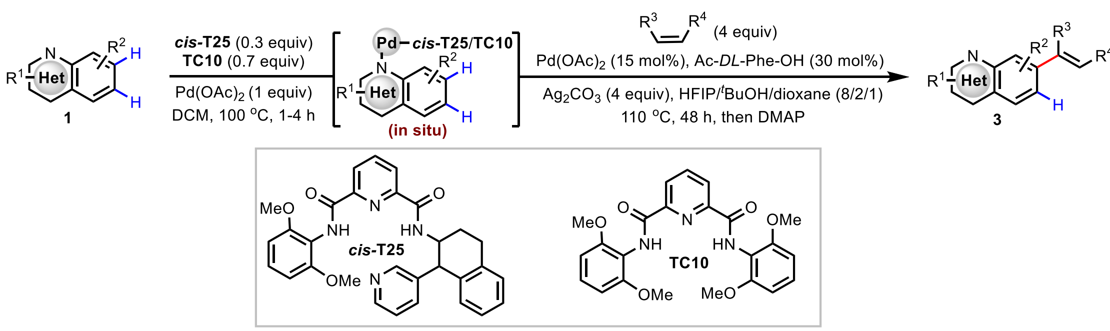
Step 13 to 15: First workup (product release) for C6-selective olefination.



Step 16 to 20: Further workup (reaction workup) for C6-selective olefination.

Step 21: Representative TLC of reaction after first workup (product release).

2.5 General Procedure for C7-Selective C–H Olefination

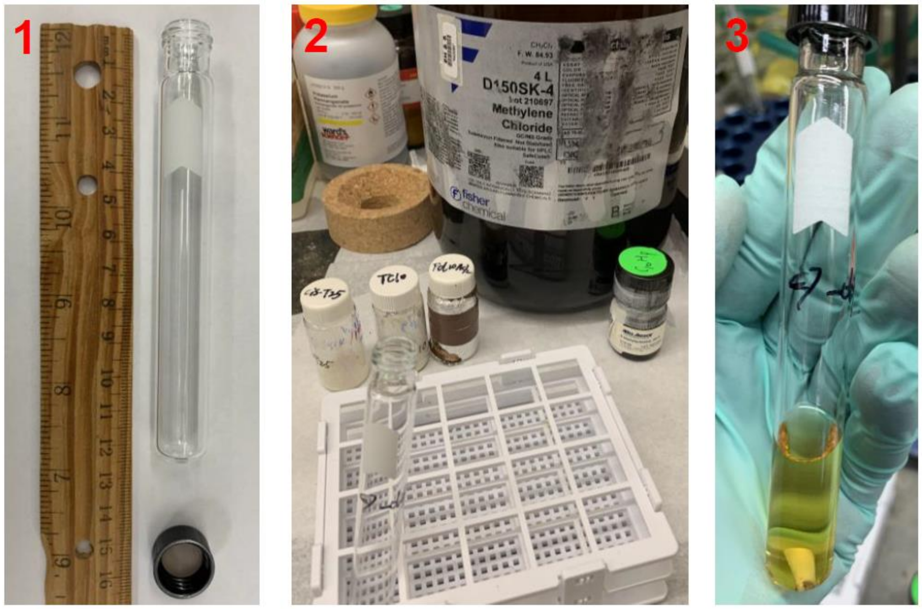


A pressure resistant reaction vial was charged with bicyclic aza-arene (0.05 mmol), ***cis*-T25** (7.6 mg, 0.015 mmol), **TC10** (15.3 mg, 0.035 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and DCM (5 mL). The reaction mixture was stirred at 100 °C for 1 – 4 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), Ac-*DL*-Phe-OH (3.1 mg, 0.015 mmol), Ag_2CO_3 (55.2 mg, 0.2 mmol), HFIP/^{t}BuOH/dioxane (4 ml/1 mL/0.5 mL), and olefin (0.2 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 48 h (600 – 1200 rpm). After cooling to room temperature, DMAP (91.6 mg, 0.75 mmol) was added [Note: If the product release is incomplete, more DMAP should be added]. The mixture was stirred at 110 °C for 1 h. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using hexane/EA (50:50, v/v) as the eluent to give the product mixture for determing the site-selectivity by ^{1}H NMR analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the products **3a-3y**.

For synthesis of **3z**, **3aa** to **3ad**, a pressure resistant reaction vial was charged with bicyclic aza-arene (0.05 mmol), **(*S,S*)-T25** (7.6 mg, 0.015 mmol) [Note: High optical purity (> 95% ee) is required for obtaining high selectivity], **TC10** (15.3 mg, 0.035 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and DCM (5 mL). The reaction mixture was stirred at 100 ^oC for 4 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(MeCN)_2Cl_2$ (3.9 mg, 0.015 mmol) [Note: 30 mol% catalyst was used when increasing the scale], Ac-*L*-Leu-OH (5.2 mg, 0.03 mmol), Ag_2CO_3 (55.2 mg, 0.2 mmol), HFIP/^{t}BuOH/dioxane (4 ml/1 mL/0.5 mL), and ethyl acrylate (21.7 µL, 0.2 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 48 h (1200 rpm). After cooling to room temperature, DMAP (91.6 mg, 0.75 mmol) was added. The mixture was stirred at 110 °C for 1 h. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using hexane/EA (50:50, v/v) as the eluent to give the product mixture for determing the site-selectivity by ^{1}H NMR analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the products **3z**, **3aa** to **3ad**.

Graphical Procedure for C7-Selective C–H Olefination

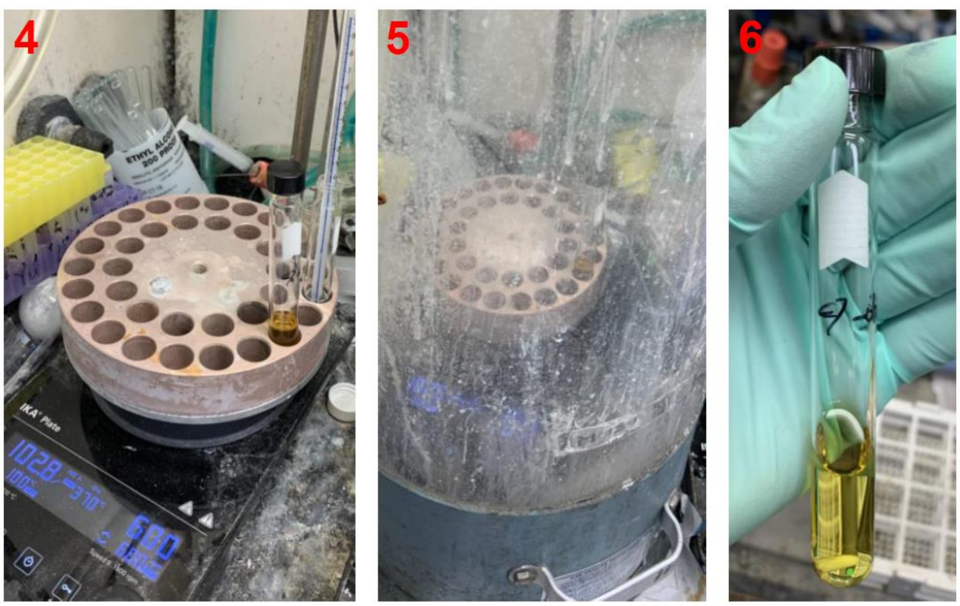
Representative example of preparation of **3a** (0.05 mmol scale)



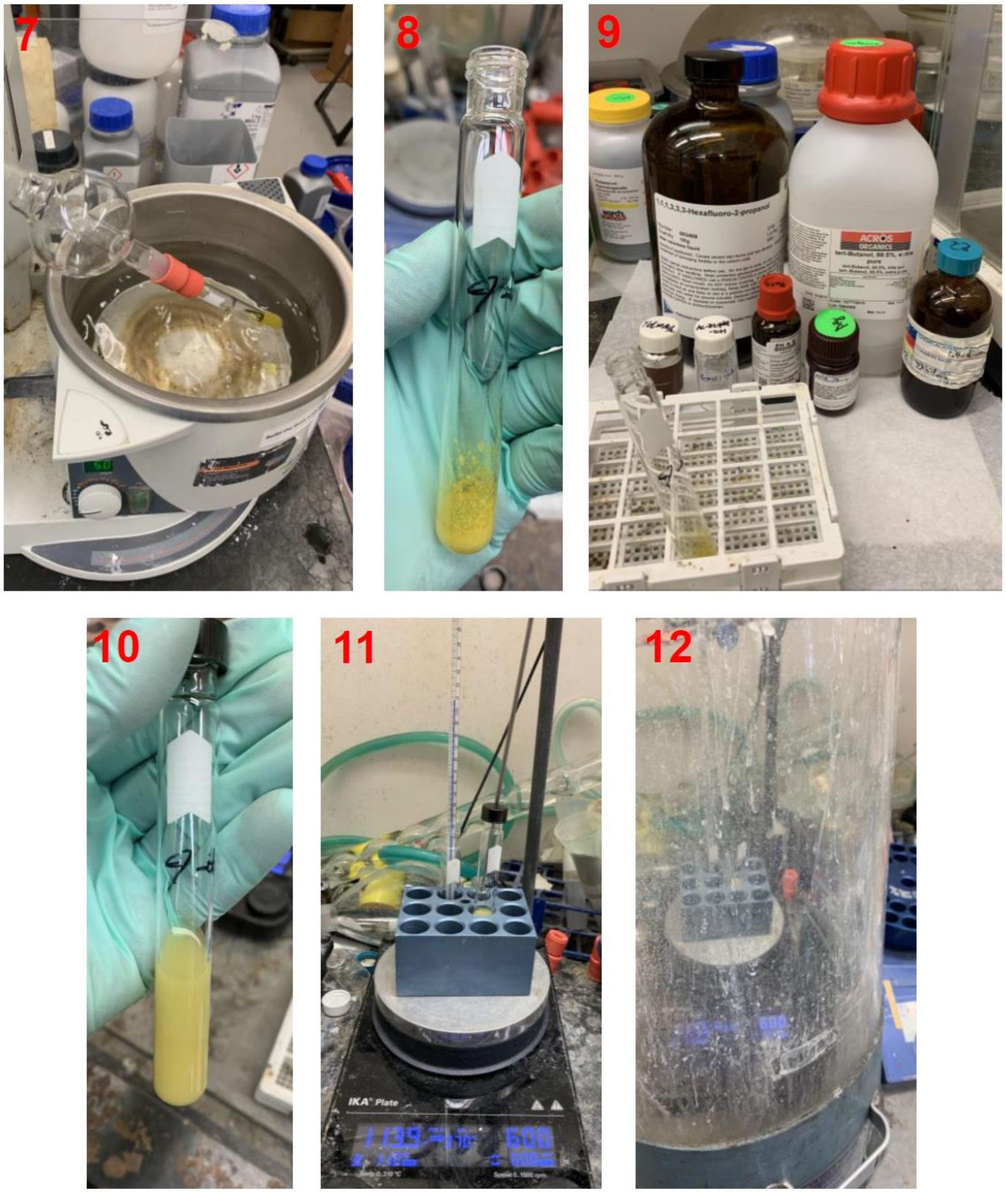
Fisherbrand™ reusable glass tube.
Capacity: 16 mL; length: 125 mm.
Fisher Catalog No.14-959-25C.

DWK life sciences Wheaton™ black phenolic screw cap.
Mfr: W240822
Fisher Catalog No. 02-927-102

Step 1 to 3: Reaction set up for template complexation.



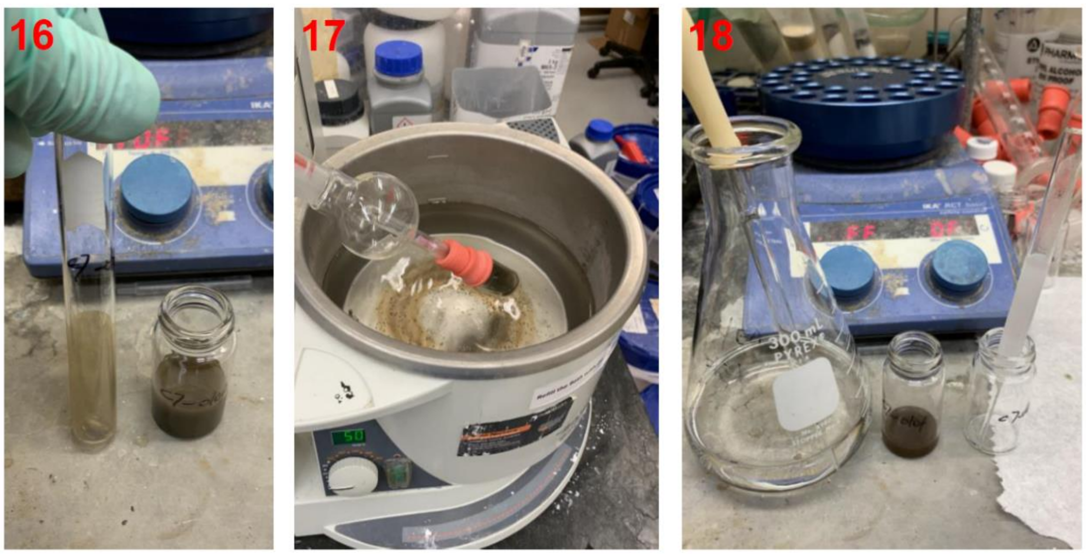
Step 4 to 6: Preparation of template complexation at 100 ºC. A blast shield was used for safety. The resulting solution is shown in 6.



Step 7 to 8: Solvent switch prior to C7-selective olefination.

Step 9 to 12: Reaction set up for C7-selective olefination. A blast shield was used for safety.

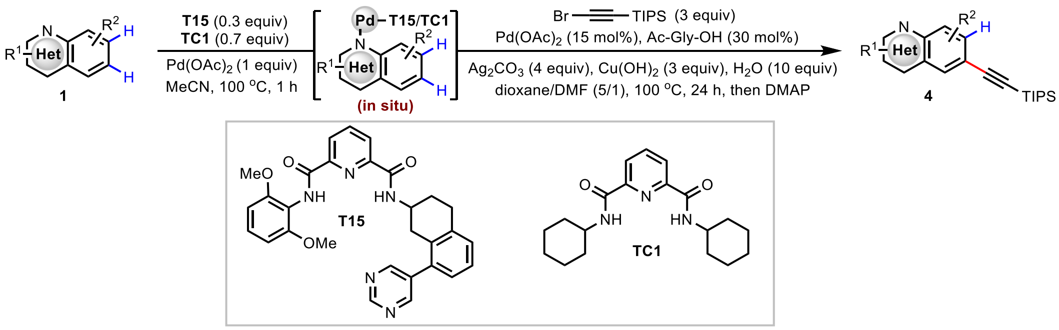
Step 13 to 15: First workup (product release) for C7-selective olefination.



Step 16 to 20: Further workup (reaction workup) for C7-selective olefination.

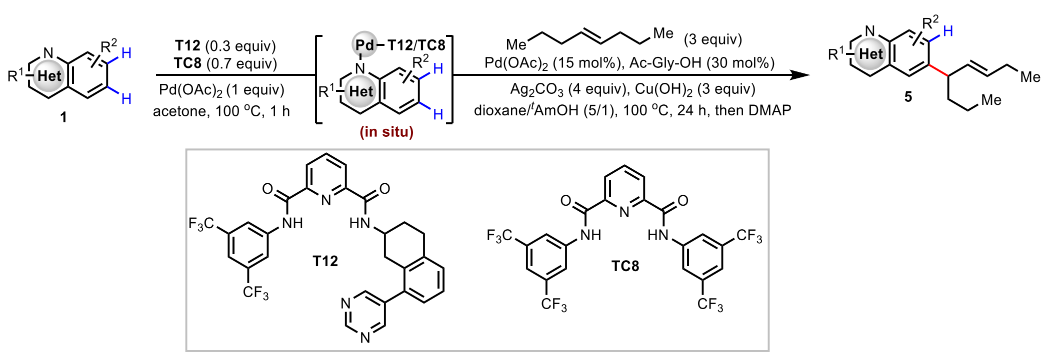
Step 21: Representative TLC of reaction after first workup (product release).

2.6 General Procedure for C6-Selective C–H Alkynylation



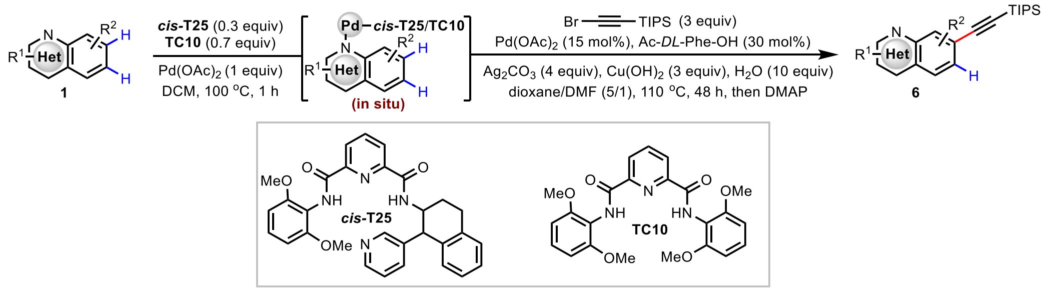
A pressure resistant reaction vial (set up analogous to 2.4) was charged with bicyclic aza-arene (0.1 mmol), **T15** (15.2 mg, 0.03 mmol), **TC1** (23 mg, 0.07 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and MeCN (2 mL). The reaction mixture was stirred at 100 °C for 1 h then concentrated *in vacuo*. $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Ac-Gly-OH (3.5 mg, 0.03 mmol), Ag_2CO_3 (110 mg, 0.4 mmol), $Cu(OH)_2$ (29.2 mg, 0.3 mmol), H_2O (18 µL, 1 mmol), dioxane/DMF (2.5 mL/0.5 mL), and triisopropylsilyl acetylene bromide (78.4 mg, 0.3 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 24 h (600 – 1200 rpm). After cooling to room temperature, DMAP (73.4 mg, 0.6 mmol) and TFE (1 mL) were added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using hexane/EA (50:50, v/v) as the eluent to give the product mixture for determing the site-selectivity by GC-MS and LC-MS analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the product **4**.

2.7 General Procedure for C6-Selective C–H Allylation



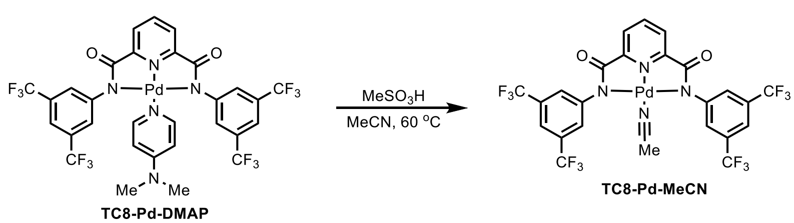
A pressure resistant reaction vial (set up analogous to 2.4) was charged with bicyclic aza-arene (0.1 mmol), **T12** (17.6 mg, 0.03 mmol), **TC8** (41.2 mg, 0.07 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and acetone (2 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Ac-Gly-OH (3.5 mg, 0.03 mmol), Ag_2CO_3 (110 mg, 0.4 mmol), $Cu(OH)_2$ (29.2 mg, 0.3 mmol), dioxane/^{t}AmOH (2.5 mL/0.5 mL), and (*E*)-4-octene (47 µL, 0.3 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 24 h (600 – 1200 rpm). After cooling to room temperature, DMAP (183.2 mg, 1.5 mmol) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using hexane/EA (50:50, v/v) as the eluent to give the product mixture for determing the site-selectivity by GC-MS and LC-MS analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the product **5**.

2.8 General Procedure for C7-Selective C–H Alkynylation



A pressure resistant reaction vial (set up analogous to 2.5) was charged with bicyclic aza-arene (0.05 mmol), *cis*-**T25** (7.6 mg, 0.015 mmol), **TC10** (15.3 mg, 0.035 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and DCM (5 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), Ac-*DL*-Phe-OH (3.1 mg, 0.015 mmol), Ag_2CO_3 (55.2 mg, 0.2 mmol), $Cu(OH)_2$ (14.6 mg, 0.15 mmol), H_2O (9 μL, 0.5 mmol), dioxane/DMF (2.5 mL/0.5 mL), and triisopropylsilyl acetylene bromide (39.2 mg, 0.15 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 48 h (600 – 1200 rpm). After cooling to room temperature, DMAP (36.7 mg, 0.3 mmol) and TFE (500 μL) were added. The mixture was stirred at 110 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM, and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using hexane/EA (50:50, v/v) as the eluent to give the product mixture for determing the site-selectivity by GC-MS and LC-MS analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC to afford the product **6**.

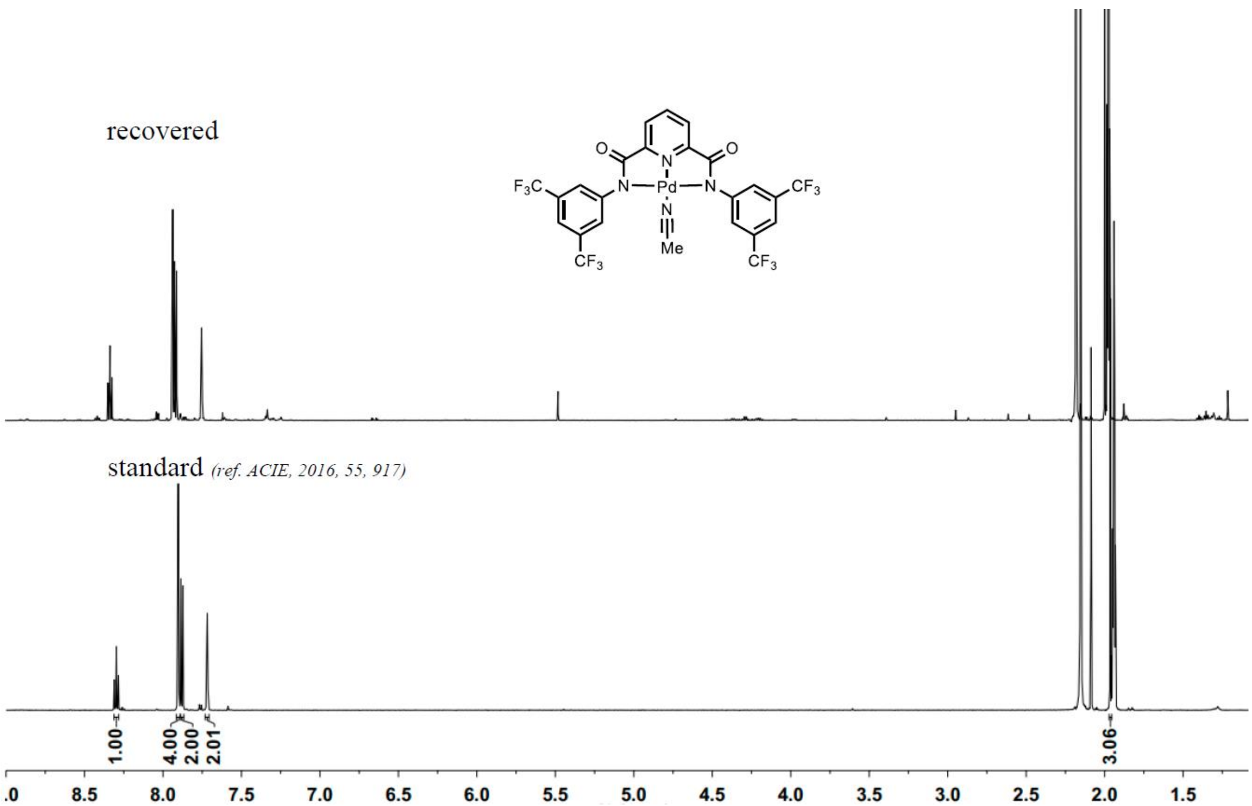
2.9 Recycling of Pd and Analysis of Remaining Pd in Product[9,10]

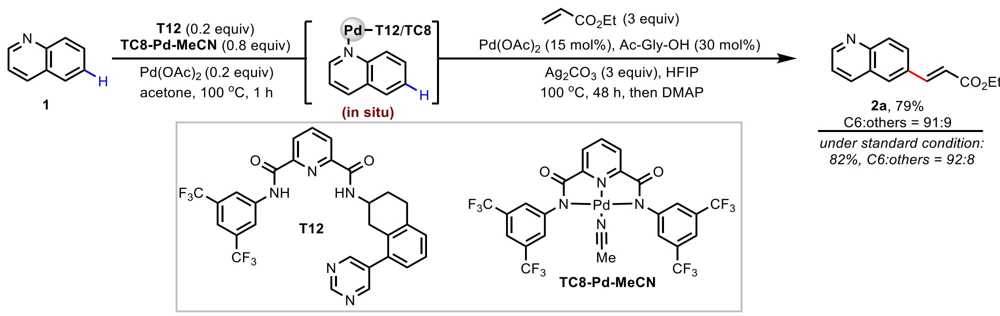


(a) Recycling of Pd

TC8-Pd-DMAP complex was dissolved in MeCN and $MeSO_3H$ (1 equiv) was added. The resulting mixture was heated at 60 °C for 2 h. After removing the solvent, water was added and extracted with DCM. The organic layer was dried with Na_2SO_4 and concentrated. This crude mixture was redissolved in MeCN and additional $MeSO_3H$ (0.5 equiv) was added. The resulting mixture was heated at 60 °C for 30 min. After removing the solvent, water was added and extracted with DCM. The organic layer was dried with Na_2SO_4 and concentrated to give **TC8-Pd-MeCN** complex in 93 % yield.

According to the procedure 2.4, 80% Pd species (**TC8-Pd-DMAP**) was recovered based on total 1.15 equiv of Pd loadings. Converting **TC8-Pd-DMAP** to active **TC8-Pd-MeCN** gave 93% yield. Therefore, the total Pd recovering yield is 74%.





(b) Analysis of Remaining Pd in Product

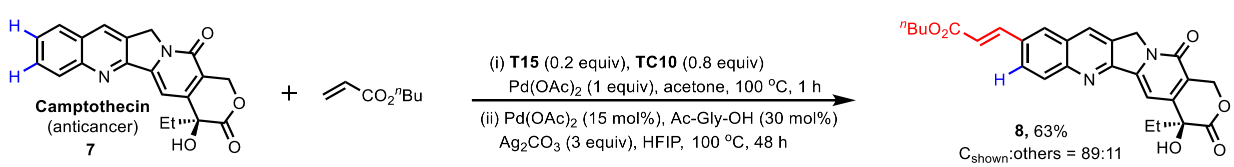
i) Further purification of olefinated quinoline 1a with palladium scavenger

A reaction vial was charged with **1a** (50 mg), sodium diethyldithiocarbamate trihydrate (991 mg, 20 equiv), MeCN (5 mL) and water (2 mL). The reaction mixture was stirred at 60 °C for 12 h then concentrated *in vacuo*. Then water (10 mL) was added and the solution was extracted with EA (5 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by a preparative TLC using hexane/EA (3/1) as eluent. ICP-MS Pd-content: 9.5 ppm.

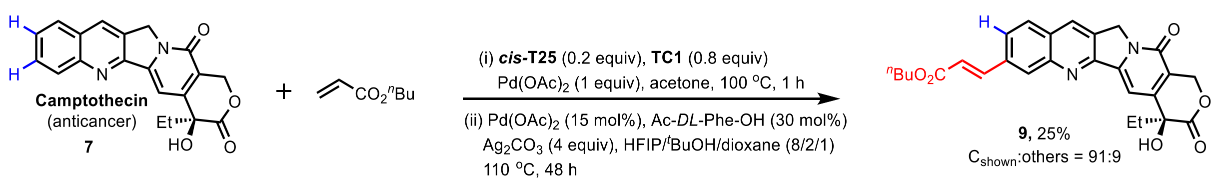
ii) ICP-MS analysis (UCSD *ECAL*)

The determination of Pd was performed by ICP-MS (Thermo Scientific iCAP RQ ICP-MS) on a mass to charge ration of 105. The sample was digested in 1% HNO_3 (Fisher Optima, MilliQ H_2O) as follows: 5 mL of 1% HNO_3 was added to vial containing 15.3 mg of compound **1a**. After sonication, the sample dissolved completely, and was further diluted 10 x before analysis. Sample was measured via external calibration (Inorganic Ventures CMS-2) monitoring 115In as an internal standard. Pd concentration was measured as follows: 2.909 ng/mL.

2.10 Procedure for Remote Site-Selective C–H Activation of Camptothecin



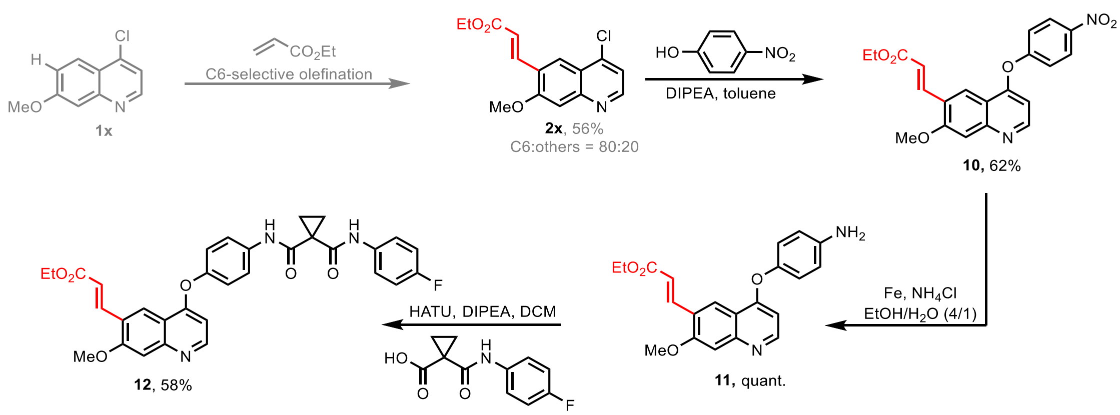
A pressure resistant reaction vial was charged with Camptothecin **7** (35 mg, 0.1 mmol), **T15** (10.2 mg, 0.02 mmol), **TC10** (35 mg, 0.08 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and acetone (2 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Ac-Gly-OH (3.5 mg, 0.03 mmol), Ag_2CO_3 (82.7 mg, 0.3 mmol), HFIP (2 ml), and n-butyl acrylate (42.7 μL, 0.3 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 48 h. After cooling to room temperature, a solution of DMAP (36.7 mg, 0.3 mmol) in toluene (1 mL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM/MeOH (5/1), and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using DCM/MeOH (10/1) as the eluent to give the product mixture for test the site-selectivity by ^{1}H NMR analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC using EA/acetone (5/1) as eluent to afford the product **8** (30 mg, 63% yield, C_{shown}:others = 89:11) as a pale yellow solid. TLC: R_f = 0.3 (EA/acetone = 5/1). mp: 100-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.01 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.99 (d, *J* = 1.8 Hz, 1H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.68 (s, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 5.75 (d, *J* = 16.3 Hz, 1H), 5.33 – 5.29 (m, 3H), 4.26 (t, *J* = 6.7 Hz, 2H), 1.93 (dd, *J* = 14.3, 7.3 Hz, 1H), 1.88 (dd, *J* = 14.3, 7.3 Hz, 1H), 1.74 – 1.71 (m, 2H), 1.49 – 1.45 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.88, 166.68, 157.60, 153.29, 150.12, 149.71, 146.14, 142.92, 134.12, 131.31, 130.53, 129.37, 129.21, 128.39, 128.17, 120.66, 119.07, 98.40, 72.72, 66.36, 64.77, 50.05, 31.64, 30.77, 19.22, 13.77, 7.83. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{27}N_2O_6^+$ $[M+H]^+$ 475.1869, found 475.1874. $[\alpha]_D^{21}$ = + 11.6 (*c* 0.1, $CHCl_3$/MeOH, 4/1, v/v). IR (film) ν_{max} 2923, 2853, 1737, 1657, 1594, 1459, 1377, 1233, 1161, 1108, 1050, 833 cm^{-1}.



A pressure resistant reaction tube was charged with Camptothecin **7** (35 mg, 0.1 mmol), ***cis*-T25** (15 mg, 0.03 mmol), **TC1** (23 mg, 0.07 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and acetone (5 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Ac-*DL*-Phe-OH (6.2 mg, 0.03 mmol),

Ag_2CO_3 (110 mg, 0.4 mmol), HFIP/^{t}BuOH/dioxane (8 ml/2 mL/1 mL), and n-butyl acrylate (57, 0.4 mmol) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 48 h. After cooling to room temperature, a solution of DMAP (36.7 mg, 0.3 mmol) in toluene (1 mL) was added. The mixture was stirred at 110 °C for 30 min. Upon completion, the mixture was passed through a short pad of Celite, washed with DCM/MeOH (5/1), and concentrated. A portion of the sample was passed through a short pad of silica (in the glass dropper) using DCM/MeOH (10/1) as the eluent to give the product mixture for test the site-selectivity by ^{1}H NMR analysis. The remaining material and the sample for analysis were combined and purified by a preparative TLC using DCM/^{i}PrOH (40/1) as eluent to afford the product **9** (11.8 mg, 25% yield, C_{shown}:others = 91:9) as a pale yellow solid. TLC: R_f = 0.2 (DCM/^{i}PrOH = 40/1). mp: 238-240 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.30 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.82 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.68 (s, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 5.75 (d, *J* = 16.2 Hz, 1H), 5.33 – 5.30 (m, 3H), 4.27 (t, *J* = 6.7 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.75 – 1.71 (m, 2H), 1.49 – 1.45 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.86, 166.63, 157.60, 153.32, 150.14, 149.07, 146.11, 143.16, 136.73, 130.78, 130.53, 129.40, 128.88, 128.70, 125.98, 121.05, 119.02, 98.29, 72.72, 66.35, 64.79, 50.09, 31.64, 30.77, 19.23, 13.77, 7.83. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{27}N_2O_6^+$ $[M+H]^+$ 475.1869, found 475.1869. $[\alpha]_D^{21}$ = – 5.5 (*c* 0.1, $CHCl_3$/MeOH, 4/1, v/v). IR (film) ν_{max} 2960, 2929, 1747, 1710, 1656, 1597, 1461, 1378, 1276, 1261, 1176, 1156, 1106, 1046, 751 cm^{-1}.

2.11 Procedure for Synthesis of Cabozantinib Analogue 12

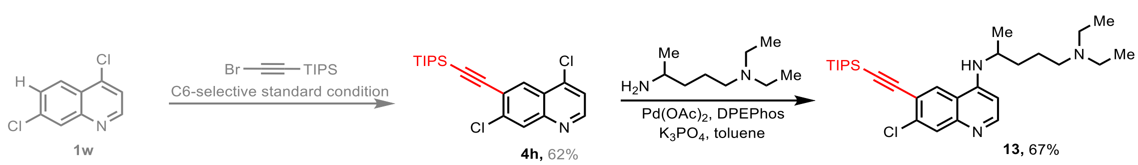


To a solution of **2x** (36.7 mg, 0.19 mmol) in dry toluene (3 mL) was added DIPEA (79 μL, 0.48 mmol) and 4-nitrophenol (52.9 mg, 0.38 mmol). The reaction mixture was stirred at 120 °C for overnight. After completion, the mixture was concentrated and purified by a preparative TLC using DCM/EA (20/1) as eluent to afford the product **10** (46.4 mg, 62% yield) as a white solid. TLC: R_f = 0.4 (DCM/EA = 20/1). mp: 138-140 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.1 Hz, 1H), 8.38 – 8.33 (m, 3H), 8.07 (d, *J* = 16.2 Hz, 1H), 7.48 (s, 1H), 7.30 (d, *J* = 9.1 Hz, 2H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.63 (d, *J* = 5.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.97, 160.02, 160.00, 159.82, 152.37, 152.32, 144.71, 139.19, 126.27, 126.25, 122.42, 121.48, 120.34, 116.12, 107.67, 105.24, 60.64, 55.96, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{19}N_2O_6^+$ [M+H]$^+$ 395.1243, found 395.1238. IR (film) ν_{max} 2978, 1708, 1618, 1565, 1522, 1490, 1454, 1344, 1308, 1231, 1172, 1008, 863 cm^{-1}.

To a solution of **10** (19.7 mg, 0.05 mmol) in EtOH/H_2O (1 mL/0.25 mL) was added Fe dust (14 mg, 0.25 mmol) and NH_4Cl (26.7 mg, 0.5 mmol). The reaction mixture was stirred at 65 °C for 1 h. After completion, water (5 mL) was added and the mixture was extracted with EA (3 mL x 3). The combined organic layers were dried with Na_2SO_4 and concentrated. The residue was purified by a preparative TLC using EA/DCM (5/1) as eluent to afford the product **11** (18.2 mg, quant. yield) as a pale yellow solid. TLC: R_f = 0.4 (EA/DCM = 5/1). mp: 142-144 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.3 Hz, 1H), 8.53 (s, 1H), 8.11 (d, *J* = 16.2 Hz, 1H), 7.41 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.77 – 6.74 (m, 3H), 6.40 (d, *J* = 5.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.21, 163.05, 159.43, 152.53, 151.87, 145.80, 144.34, 139.65, 125.08, 123.12, 122.17, 120.71, 116.31, 115.85, 107.28, 102.50, 60.49, 55.80, 14.37. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{21}N_2O_4^+$ [M+H]$^+$ 365.1501, found 365.1502. IR (film) ν_{max} 3361, 2977, 1703, 1619, 1571, 1508, 1454, 1351, 1307, 1270, 1230, 1206, 1178, 1036, 1010, 848 cm^{-1}.

To a solution of **11** (18.2 mg, 0.05 mmol), aliphatic acid (16.7 mg, 0.075 mmol), and DIPEA (16.5 μL, 0.1 mmol) in DCM (3 mL) at 0 °C was added HATU (28.5 mg, 0.075 mmol). The solution was warmed to room temperature and stirred for overnight. The reaction mixture was evaporated and purified by a preparative TLC using EA/DCM (5/1) as eluent to provide the product **12** (16.5 mg, 58% yield) as pale yellow oil. TLC: R_f = 0.3 (EA/DCM = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.90 (s, 1H), 8.57 (d, *J* = 5.3 Hz, 1H), 8.49 (s, 1H), 8.09 (d, *J* = 16.1 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.48 (dd, *J* = 9.1, 4.8 Hz, 2H), 7.41 (s, 1H), 7.17 (d, *J* = 8.9 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 16.1 Hz, 1H), 6.42 (d, *J* = 5.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 1.75 – 1.71 (m, 2H), 1.68 – 1.65 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.27, 168.82, 167.23, 162.18, 160.60, 159.53, 158.98, 152.44, 151.98, 150.50, 139.57, 135.10, 133.10 (d, *J* = 3.0 Hz), 125.35, 122.95, 122.79, 122.74, 122.49, 121.72, 120.87, 115.87, 115.84, 115.72, 107.34, 102.99, 60.58, 55.83, 29.21, 17.61, 14.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.55. HRMS (ESI-TOF) *m/z* Calcd for $C_{32}H_{29}FN_3O_6^+$ $[M+H]^+$ 570.2040, found 570.2049. IR (film) ν_{max} 3062, 2360, 1683, 1617, 1504, 1453, 1408, 1350, 1307, 1228, 1207, 1176, 1036, 1012, 982, 834, 735 cm^{-1}.

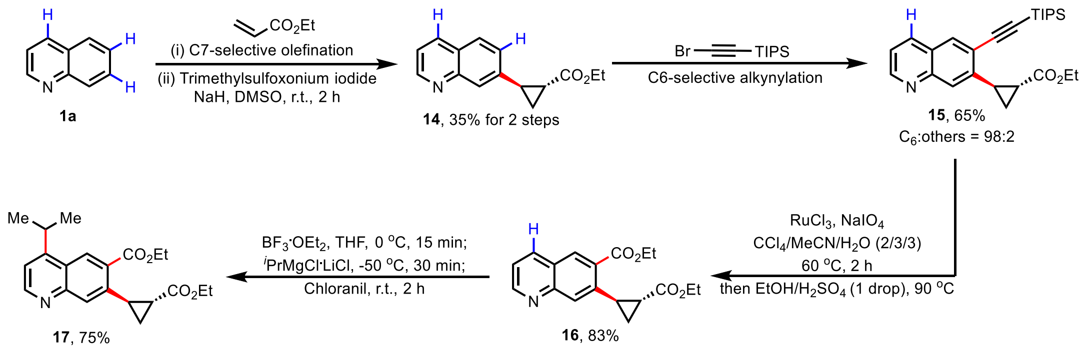
2.12 Procedure for Synthesis of Chloroquine Analogue 13



To a solution of **4h** (11.3 mg, 0.03 mmol), $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), DPEPhos (3.2 mg, 0.006 mmol), and K_3PO_4 (12.7 g, 0.06 mmol) in dry toluene (2 mL) was added amine (8.7 μL, 0.045 mmol). The vial was filled with N_2, then sealed and put into a preheated oil bath at 120 °C for 3 h. After completion, the reaction mixture was basified with 10% aqueous NaOH solution (10 mL) and the solution was extracted with EA (3 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by a preparative TLC using THF/hexane/Et_3N (10/1/0.005) as eluent to provide the product **13** (10 mg, 67% yield) as colorless oil. TLC: R_f = 0.5 (THF/hexane/Et_3N = 10/1/0.005). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 1H), 8.11 (s, 1H), 7.98 (s, 1H), 6.38 (d, *J* = 5.6 Hz, 1H), 6.09 (s, 1H), 3.73 (d, *J* = 6.8 Hz, 1H), 2.82 (q, *J* = 7.3 Hz, 4H), 2.70 (d, *J* = 7.7 Hz, 2H), 1.91 (dt, *J* = 13.9, 6.5 Hz, 1H), 1.83 – 1.74 (m, 3H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.17 (m, 27H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.16, 136.50, 128.93, 126.02, 124.96, 123.06, 119.57, 117.34, 103.06, 99.39, 96.88, 62.78, 52.05, 48.37, 46.90, 33.89, 29.96, 20.05, 18.72, 11.38. HRMS (ESI-TOF) *m/z* Calcd for

$C_{29}H_{47}ClN_3Si^+$ $[M+H]^+$ 500.3228, found 500.3230. IR (film) ν_{max} 2940, 2864, 2158, 1611, 1568, 1452, 1356, 1254, 1193, 1154, 1071, 995, 883, 800, 753, 676 cm^{-1}.

2.13 Procedure for Iterative C–H Activation of Quinoline



3z was synthesized according to the general procedure 2.5.

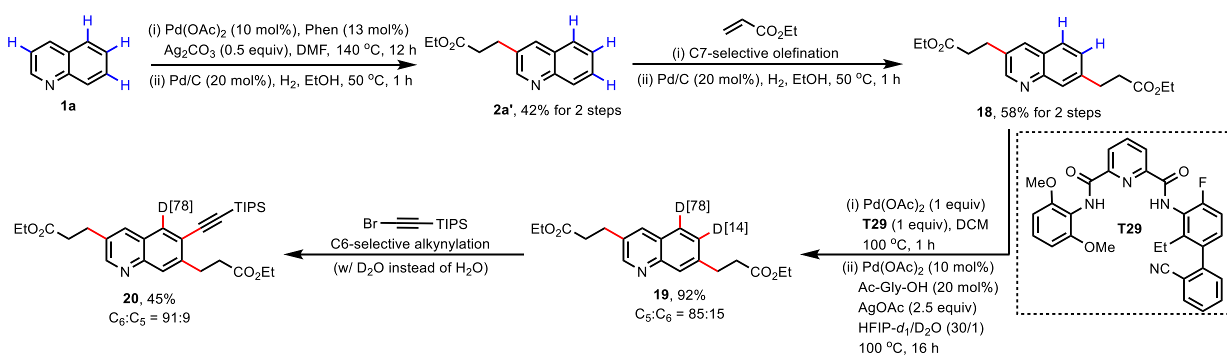
To a solution of NaH (6 mg, 0.15 mmol) in dry DMSO was added trimethylsulfoxonium iodide (33 mg, 0.15 mmol). The mixture was stirred at room temperature for 0.5 h. **3z** (22.7 mg, 0.1 mmol) in dry DMSO was added and the mixture was stirred at room temperature for 2 h. Water (10 mL) was added and the solution was extracted with EA (3 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by a preparative TLC using DCM/EA (8/1, v/v) as eluent to afford the product **14 (**16 mg, 66% yield) as a white solid. TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 65-67 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (ddd, *J* = 8.2, 2.0, 0.9 Hz, 1H), 7.79 (dt, *J* = 1.5, 0.7 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.32 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.72 (ddd, *J* = 9.1, 6.4, 4.1 Hz, 1H), 2.06 (ddd, *J* = 8.3, 5.3, 4.1 Hz, 1H), 1.72 (ddd, *J* = 9.2, 5.4, 4.7 Hz, 1H), 1.48 (ddd, *J* = 8.5, 6.4, 4.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.13, 150.78, 148.33, 141.95, 135.73, 127.90, 127.01, 125.76, 125.69, 120.69, 60.86, 26.25, 24.70, 17.37, 14.27. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1181, found 242.1191. IR (film) ν_{max} 2982, 1719, 1625, 1504, 1460, 1408, 1369, 1325, 1181, 1045, 966, 939, 890, 831 cm^{-1}.

15 was synthesized according to the general procedure 2.6. Colorless oil. TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.07 (ddd, *J* =

8.5, 1.9, 0.7 Hz, 1H), 7.98 (s, 1H), 7.59 (s, 1H), 7.35 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.16 (dddd, *J* = 9.2, 6.5, 4.3, 0.7 Hz, 1H), 2.09 (ddd, *J* = 8.5, 5.4, 4.3 Hz, 1H), 1.75 – 1.72 (m, 1H), 1.50 – 1.46 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 3.0 Hz, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.78, 151.24, 147.78, 142.92, 135.24, 132.48, 126.53, 124.19, 123.10, 121.30, 104.44, 96.69, 60.70, 24.54, 24.50, 18.71, 17.29, 14.22, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{26}H_{36}NO_2Si^+$ $[M+H]^+$ 422.2515, found 422.2514. IR (film) ν_{max} 2941, 2864, 2151, 1726, 1622, 1591, 1562, 1462, 1406, 1321, 1179, 1047, 1018, 995, 918, 884, 825, 677 cm^{-1}.

A reaction vial was charged with **15** (21 mg, 0.05 mmol), $RuCl_3$ (1 mg, 0.005 mmol), $NaIO_4$ (43.2 mg, 0.2 mmol) and CCl_4/MeCN/H_2O (500 μL/750 μL/750 μL). The mixture was stirred at 60 ^{o}C for 2 h then concentrated *in vacuo*. Water (10 mL) was added and the solution was extracted with EA (5 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was re-dissolved in EtOH (2 mL) and *conc.* H_2SO_4 (1 drop) was added. The mixture was stirred at 90 ^{o}C for overnight then concentrated *in vacuo*. 10% aqueous NaOH solution (10 mL) was added and the solution was extracted with EA (5 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by a preparative TLC using hexane/EA (1/1, v/v) as eluent to afford the product **16** (13 mg, 83% yield) as colorless oil. TLC: R_f = 0.5 (hexane/EA = 1/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.41 (s, 1H), 8.21 (d, *J* = 7.5 Hz, 1H), 7.85 (s, 1H), 7.43 (dd, *J* = 8.2, 4.1 Hz, 1H), 4.48 – 4.44 (m, 1H), 4.42 – 4.38 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.28 – 3.24 (m, 1H), 1.89 (dt, *J* = 7.9, 4.9 Hz, 1H), 1.70 (dd, *J* = 9.3, 4.7 Hz, 1H), 1.53 (ddd, *J* = 8.0, 5.1, 3.5 Hz, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.41, 167.04, 152.58, 149.24, 140.78, 136.61, 131.51, 130.60, 127.75, 126.20, 121.66, 61.54, 60.68, 25.55, 23.80, 15.91, 14.32, 14.27. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{20}NO_4^+$ $[M+H]^+$ 314.1392, found 314.1407. IR (film) ν_{max} 2931, 1722, 1625, 1569, 1458, 1406, 1321, 1265, 1208, 1182, 1069, 1046 cm^{-1}.

17 was synthesized according to modified literature procedure:[11] A reaction via was charged with **16** (9.4 mg, 0.03 mmol) in dry THF and cooled to 0 °C. $BF_3{\cdot}OEt_2$ (4 μL, 0.033 mmol) was added and stirred at 0 ^{o}C for 0.5 h. Then, ^{i}PrMgCl·LiCl (0.036 mmol) was added at -30 ^{o}C and stirring at room temperature for 0.5 h. Chloranil (14.8 mg, 0.06 mmol) was added and the mixture continuously stirred at room temperature for 1.5 h. The mixture was quenched with 10% aqueous NaOH solution (10 mL) and extracted with EA (5 mL x 3). The organic phase was washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by a preparative TLC using hexane/EA (1/1, v/v) as eluent to afford the product **17** (8 mg, 75% yield) as colorless oil. TLC: R_f = 0.5 (hexane/EA = 1/1). ^1H NMR (600 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.6 Hz, 1H), 8.67 (s, 1H), 7.84 (s, 1H), 7.32 (d, *J* = 4.6 Hz, 1H), 4.49 – 4.46 (m, 1H), 4.42 – 4.39 (m, 1H), 4.22 (d, *J* = 7.2 Hz, 2H), 3.79 – 3.76 (m, 1H), 3.24 (dtd, *J* = 6.9, 2.4, 1.0 Hz, 1H), 1.90 – 1.88 (m, 1H), 1.70 – 1.67 (m, 1H), 1.54 – 1.52 (m, 1H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.41 (dd, *J* = 6.8, 1.8 Hz, 6H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.48, 167.57, 155.58, 152.60, 149.52, 139.89, 130.16, 128.64, 127.09, 124.95, 117.55, 61.58, 60.67, 28.40, 25.50, 23.72, 23.05, 15.86, 14.32, 14.28. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{26}NO_4^+$ $[M+H]^+$ 356.1862, found 356.1871. IR (film) ν_{max} 2967, 1723, 1620, 1588, 1447, 1406, 1320, 1265, 1215, 1180, 1070, 1048, 859 cm^{-1}.

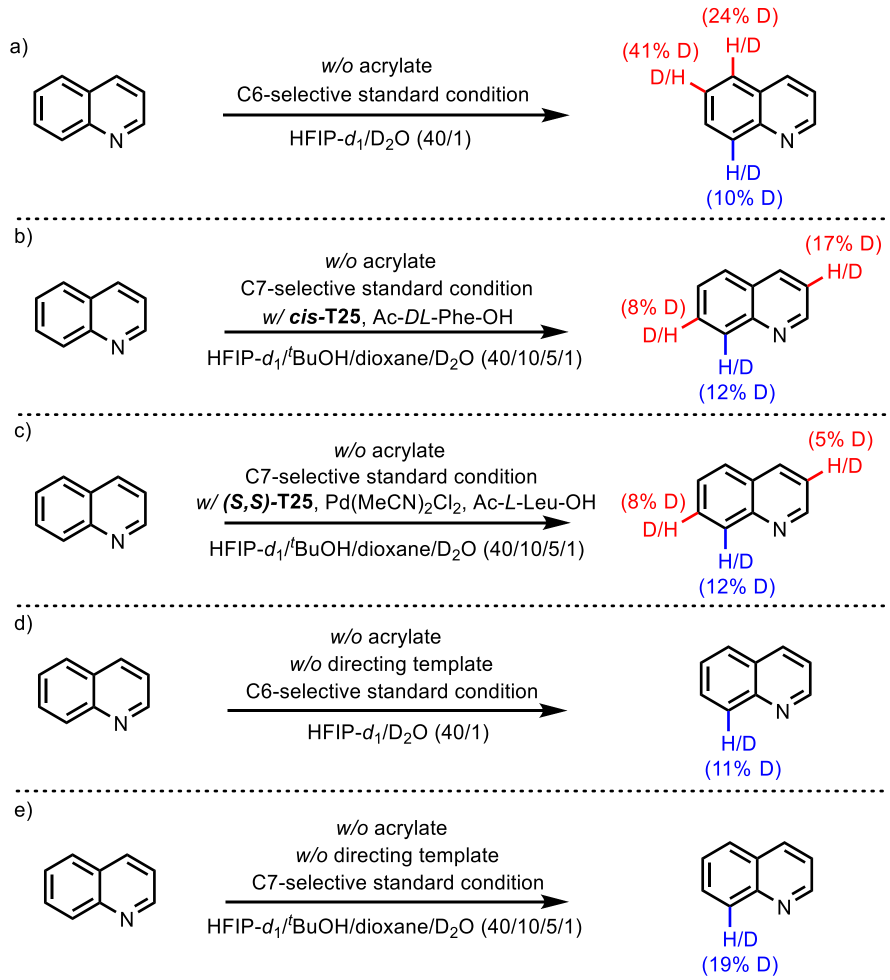


18 was synthesized according to the literature procedure[12] and general procedure 2.5. White solid. TLC: R_f = 0.3 (hexane/EA = 3/1). mp: 75-77 °C. ^1H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.3 Hz, 1H), 7.93 (d, *J* = 1.2 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.16 – 4.11 (m, 4H), 3.14 (dt, *J* = 17.9, 7.7 Hz, 4H), 2.73 (q, *J* = 7.6 Hz, 4H), 1.27 – 1.22 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.70, 172.36, 151.79, 147.21, 141.68, 134.21, 132.77, 128.00, 127.66, 127.46, 126.59, 60.66, 60.55, 35.52, 35.47, 31.05, 28.22, 14.23, 14.20. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}NO_4^+$ $[M+H]^+$ 330.1705, found 330.1711. IR (film) ν_{max} 2921, 1724, 1423, 1376, 1334, 1296, 1179, 1056, 1022, 906, 816 cm^{-1}.

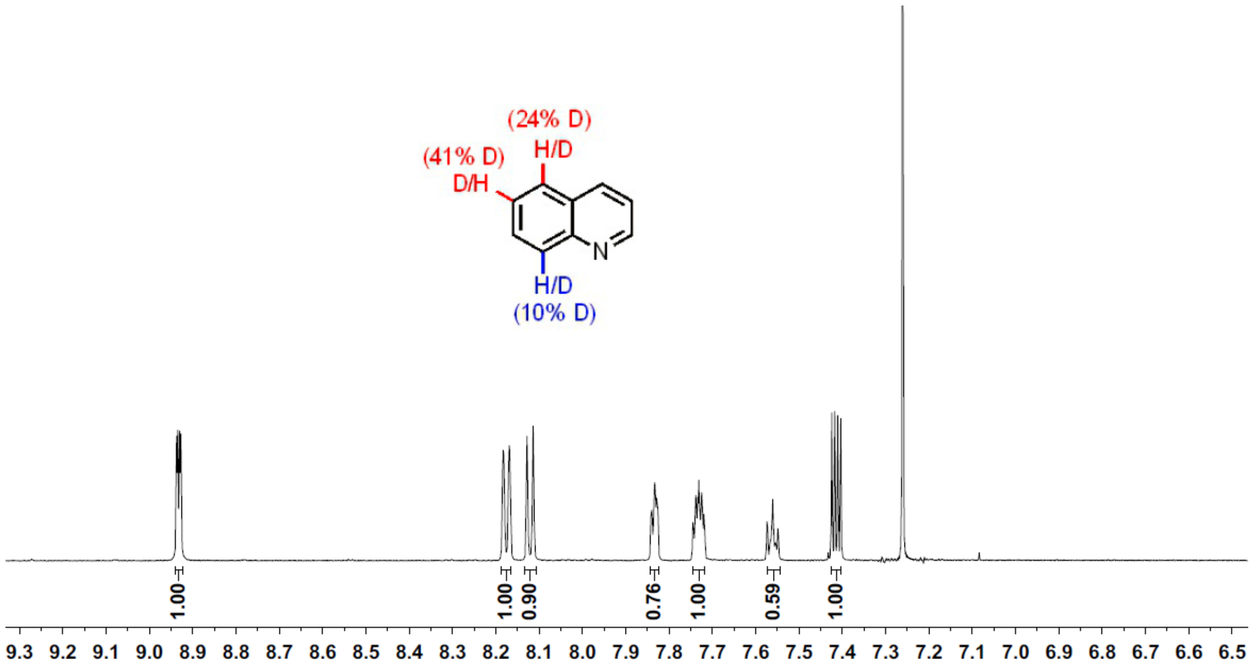
19 was synthesized according to modified literature procedure:[13] A pressure resistant reaction vial was charged with **18** (33 mg, 0.1 mmol), **T29** (52.4 mg, 0.1 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol) and DCM (2 mL). The reaction mixture was stirred at 100 °C for 1 h then concentrated *in vacuo*. $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Ac-Gly-OH (2.3 mg, 0.02 mmol), AgOAc (41.8 mg, 0.25 mmol), HFIP-d_1 (1.2 mL), and D_2O (40 µL) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 16 h. After cooling to room temperature, a solution of DMAP (36.7 mg, 0.3 mmol) in toluene (1 mL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (2/1, v/v) as eluent to afford the partially deuterated product **19** (30.4 mg, 92% yield, C_5:C_6 = 85:15). White solid. TLC: R_f = 0.3 (hexane/EA = 3/1). mp: 75-77 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.9 Hz, 1H), 7.93 (s, 1H), 7.87 (s, 1H), 7.70 (d, *J* = 9.0 Hz, 0.22H), 7.40 (s, 0.86H), 4.16 – 4.11 (m, 4H), 3.14 (dt, *J* = 17.9, 7.6 Hz, 4H), 2.72 (t, *J* = 7.5 Hz, 4H), 1.23 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.71, 172.37, 151.78, 147.20, 141.69, 134.18, 132.77, 127.89, 127.64, 126.52, 60.66, 60.56, 35.52, 35.47, 31.06, 28.22, 14.22, 14.20. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{23}DNO_4^+$ [M+H]$^+$ 331.1768, found 331.1769. IR (film) ν_{max} 2982, 1729, 1451, 1374, 1276, 1180, 1042, 906, 763, 749 cm^{-1}.

20 was synthesized according to the general procedure 2.6 except using D_2O instead of H_2O. Colorless oil. TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.4 Hz, 1H), 7.92 (s, 0.22H), 7.87 (d, *J* = 0.9 Hz, 2H), 4.13 (dd, *J* = 8.2, 7.2 Hz, 4H), 3.32 – 3.29 (m, 2H), 3.11 (d, *J* = 7.6 Hz, 2H), 2.79 – 2.77 (m, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.25 – 1.21 (m, 6H), 1.16 (d, *J* = 3.6 Hz, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.58, 172.27, 152.44, 146.61, 142.52, 133.61, 133.42, 132.35, 128.27, 126.27, 122.26, 104.51, 96.12, 60.69, 60.44, 35.31, 34.70, 30.23, 28.19, 18.70, 14.24, 14.20, 11.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{43}DNO_4Si^+$ [M+H]$^+$ 511.3102, found 511.3110. IR (film) ν_{max} 2942, 2865, 1734, 1466, 1373, 1293, 1178, 1045, 1018, 883, 791, 675 cm^{-1}.

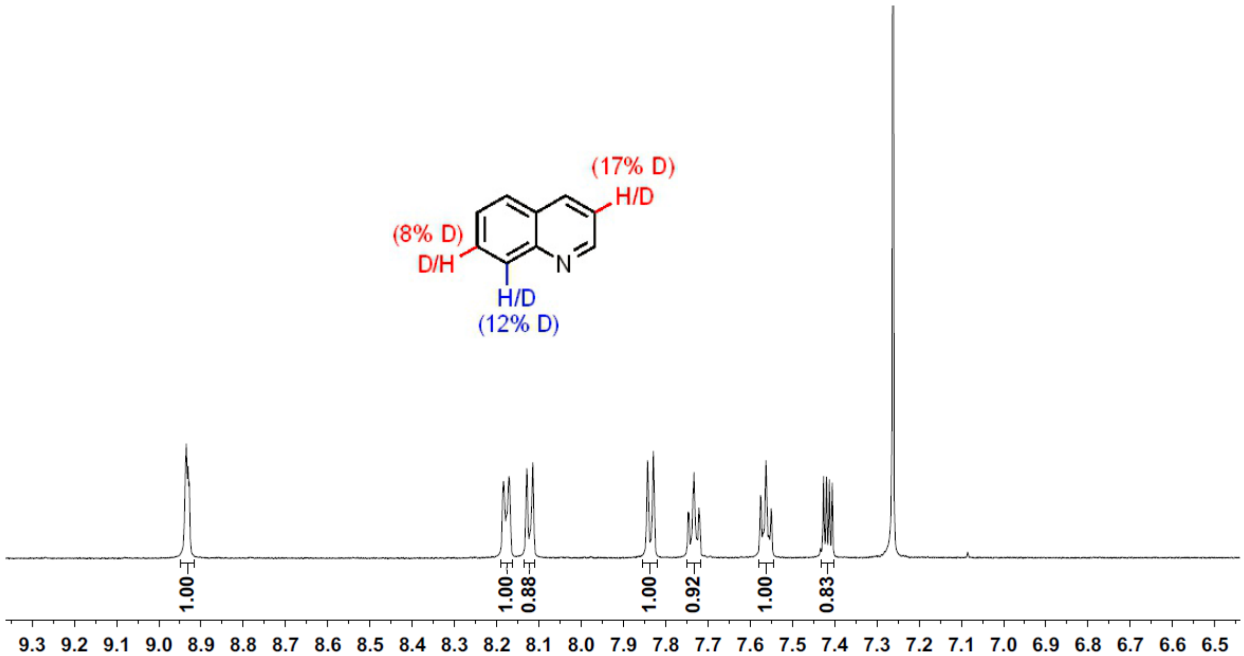
2.14 Isotopic Labelling Studies



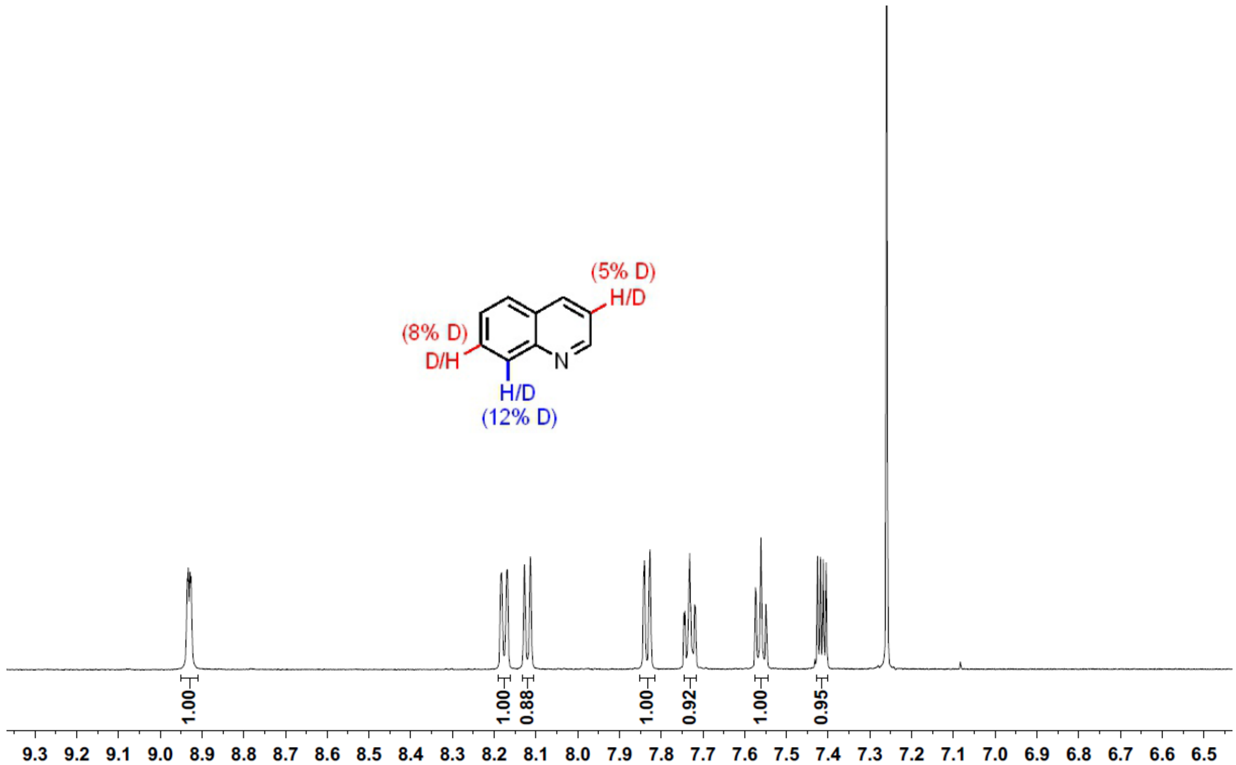
a) A pressure resistant reaction vial was charged with quinoline (2.6 mg, 0.02 mmol), **T12** (2.3 mg, 0.004 mmol), **TC8** (9.4 mg, 0.016 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and acetone (1 mL). The reaction mixture was stirred at 100 ^{o}C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-Gly-OH (0.7 mg, 0.006 mmol), Ag_2CO_3 (16 mg, 0.06 mmol), HFIP-d_1 (400 μL), and D_2O (10 μL) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 24 h. After cooling to room temperature, a solution of DMAP (7.3 mg, 0.06 mmol) in toluene (200 μL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (5/1, v/v) as eluent to afford the partially deuterated quinoline. ^{1}H NMR spectrum was shown below:



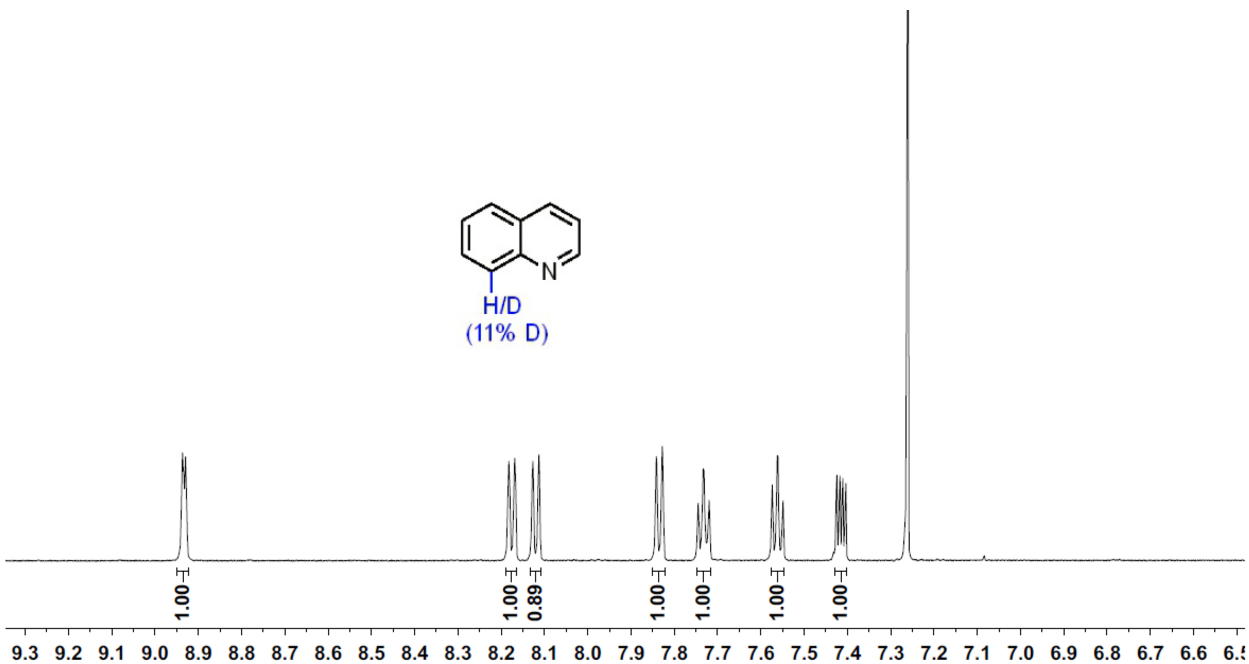
b) A pressure resistant reaction vial was charged with quinoline (2.6 mg, 0.02 mmol), ***cis*-T25** (3 mg, 0.006 mmol), **TC10** (6.1 mg, 0.014 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and DCM (2 mL). The reaction mixture was stirred at 100 ^oC for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-*DL*-Phe-OH (1.2 mg, 0.006 mmol), Ag_2CO_3 (22 mg, 0.08 mmol), and HFIP-d_1/^{t}BuOH/dioxane/D_2O (400 μL/100 μL/50 μL/10 μL) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 24 h. After cooling to room temperature, a solution of DMAP (7.3 mg, 0.06 mmol) in toluene (200 μL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (5/1, v/v) as eluent to afford the partially deuterated quinoline. ^1H NMR spectrum was shown below:



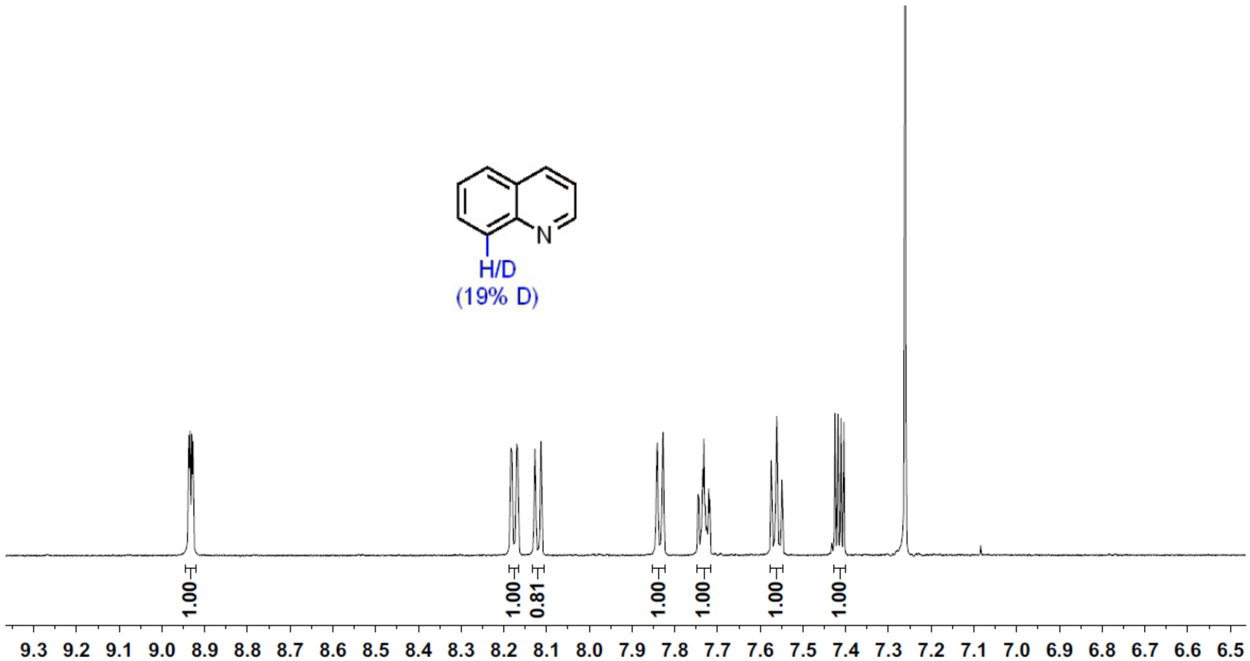
c) A pressure resistant reaction vial was charged with quinoline (2.6 mg, 0.02 mmol), **(*S*,*S*)-T25** (3 mg, 0.006 mmol), **TC10** (6.1 mg, 0.014 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and DCM (2 mL). The reaction mixture was stirred at 100 ºC for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(MeCN)_2Cl_2$ (0.8 mg, 0.003 mmol), Ac-*L*-Leu-OH (1.0 mg, 0.006 mmol), Ag_2CO_3 (22 mg, 0.08 mmol), and HFIP-d_1/^{t}BuOH/dioxane/D_2O (400 µL/100 µL/50 µL/10 µL) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 24 h. After cooling to room temperature, a solution of DMAP (7.3 mg, 0.06 mmol) in toluene (200 µL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (5/1, v/v) as eluent to afford the partially deuterated quinoline. ^{1}H NMR spectrum was shown below:



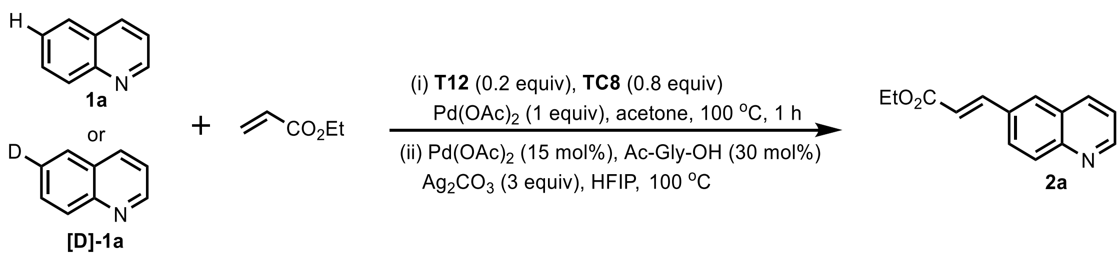
d) A pressure resistant reaction vial was charged with quinoline (2.6 mg, 0.02 mmol), **TC8** (11.8 mg, 0.02 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and acetone (1 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-Gly-OH (0.7 mg, 0.006 mmol), Ag_2CO_3 (16 mg, 0.06 mmol), HFIP-d_1 (400 μL), and D_2O (10 μL) were added in the reaction vial. The vial was capped and allowed to stir at 100 °C for 24 h. After cooling to room temperature, a solution of DMAP (7.3 mg, 0.06 mmol) in toluene (200 μL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (5/1, v/v) as eluent to afford the partially deuterated quinoline. ^{1}H NMR spectrum was shown below:



e) A pressure resistant reaction vial was charged with quinoline (2.6 mg, 0.02 mmol), **TC10** (8.7 mg, 0.02 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and DCM (2 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-*DL*-Phe-OH (1.2 mg, 0.006 mmol), Ag_2CO_3 (22 mg, 0.08 mmol), and HFIP-d_1/^{t}BuOH/dioxane/D_2O (400 μL/100 μL/50 μL/10 μL) were added in the reaction vial. The vial was capped and allowed to stir at 110 °C for 24 h. After cooling to room temperature, a solution of DMAP (7.3 mg, 0.06 mmol) in toluene (200 μL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was concentrated. The residue was purified by a preparative TLC using hexane/EA (5/1, v/v) as eluent to afford the partially deuterated quinoline. ^{1}H NMR spectrum was shown below:

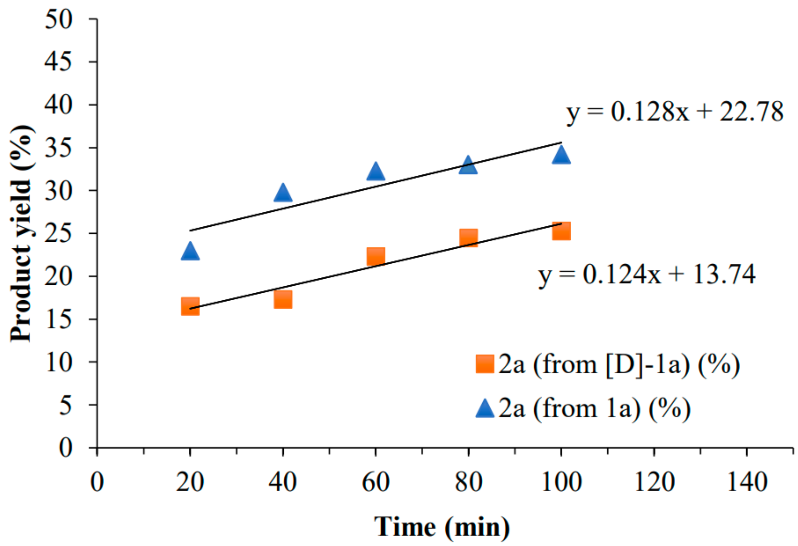


2.15 Kinetic Isotope Effect (KIE) Studies

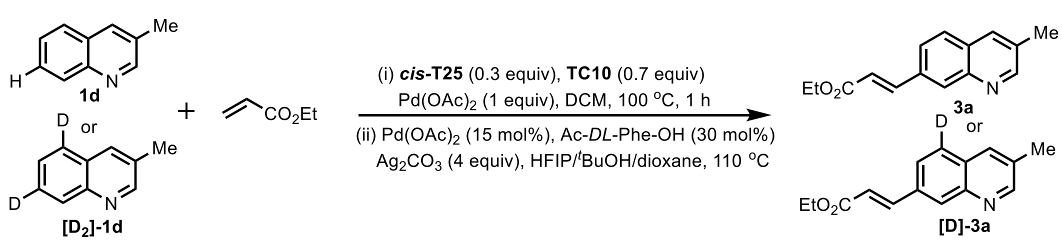


To 5 sets of pressure resistant vials were charged with **1a** (2.6 mg, 0.02 mmol) or **[D]-1a**[14] (2.6 mg, 0.02 mmol), **T12** (2.3 mg, 0.004 mmol), **TC8** (9.4 mg, 0.016 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and acetone (0.5 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-Gly-OH (0.7 mg, 0.006 mmol), Ag_2CO_3 (16 mg, 0.06 mmol), HFIP (400 μL), and ethyl acrylate (6.5 μL, 0.06 mmol) were added in the reaction vials. The vials were capped and allowed to stir at 100 °C. The reactions were monitored and removed 1 set of reactions after 20 min. The vials were quickly cooled to room temperature using dry ice. A solution of DMAP (7.3 mg, 0.06 mmol) in toluene (0.2 mL) was added. The mixture was stirred at 100 °C for 30 min. Upon completion, the mixture was passed through a short pad of silica (in the glass dropper) using hexane/EA (1/1, v/v) as the eluent to give the product mixture for ^{1}H NMR analysis. The processes have been monitored up to 100 min and provided the following yields:

Time (min)	20	40	60	80	100
2a (from **[D]-1a**)/%	16.5	17.3	22.3	24.5	25.3
2a (from **1a**)/%	23.0	29.8	32.3	33.0	34.2

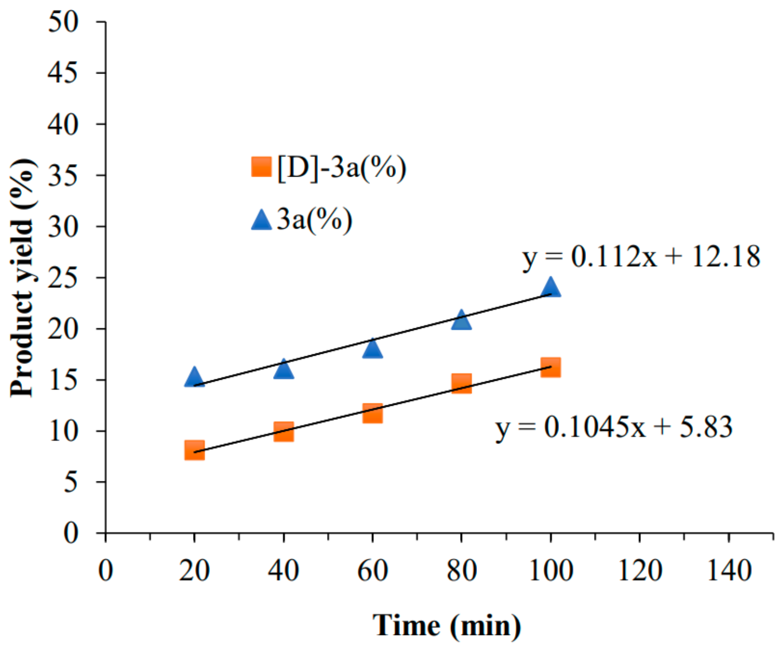


For C6-H activation, $k_H/k_D = 0.128/0.124 = 1.03$.



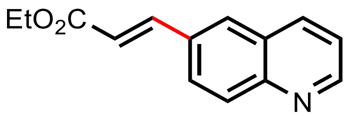
To 5 sets of pressure resistant vials were charged with **1d** (2.8 mg, 0.02 mmol) or **[D$_2$]-1d**[15] (2.9 mg, 0.02 mmol), ***cis*-T25** (3 mg, 0.006 mmol), **TC10** (6 mg, 0.014 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and DCM (1 mL). The reaction mixture was stirred at 100 °C for 1 h [Caution: A blast shield was used to mitigate the potential risk of an explosion; we note that in our hands this never occurred] then concentrated *in vacuo*. $Pd(OAc)_2$ (0.7 mg, 0.003 mmol), Ac-*DL*-Phe-OH (1.2 mg, 0.006 mmol), Ag_2CO_3 (11 mg, 0.08 mmol), HFIP/^{t}BuOH/dioxane (1.6 mL/400 μL/200 μL), and ethyl acrylate (8.6 μL, 0.08 mmol) were added in the reaction vials. The vials were capped and allowed to stir at 110 °C. The reactions were monitored and removed 1 set of reactions after 20 min. The vials were quickly cooled to room temperature using dry ice. A solution of DMAP (7.3 mg, 0.06 mmol) in toluene (0.2 mL) was added. The mixture was stirred at 110 °C for 30 min. Upon completion, the mixture was passed through a short pad of silica (in the glass dropper) using hexane/EA (1/1, v/v) as the eluent to give the product mixture for ^{1}H NMR analysis. The processes have been monitored up to 100 min and provided the following yields:

Time (min)	20	40	60	80	100
[D]-3a (from **[D$_2$]-1d**)/%	8.1	9.9	11.7	14.6	16.2
3a (from **1d**)/%	15.3	16.1	18.1	20.9	24.1

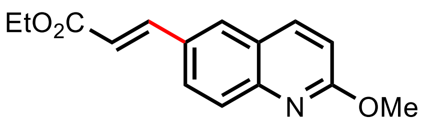


For C7-H activation, k_H/k_D = 0.112/0.1045 = 1.07.

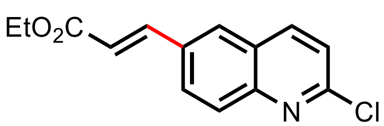
2.16 Spectroscopic Data of Compounds



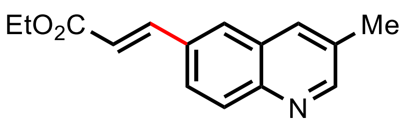
Ethyl (*E*)-3-(quinolin-6-yl)acrylate (2a) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2a** as colorless oil (18.6 mg, 82%, C6:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.6 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 9.3 Hz, 1H), 7.91 (dd, J = 4.6, 2.6 Hz, 2H), 7.85 (d, J = 16.0 Hz, 1H), 7.44 (dd, J = 8.3, 4.3 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.80, 151.34, 149.04, 143.61, 136.48, 132.73, 130.27, 129.23, 128.27, 127.28, 121.87, 119.65, 60.69, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$ 228.1025, found 228.1028. IR (film) ν_{max} 2982, 1708, 1636, 1501, 1369, 1280, 1265, 1176, 1036, 981, 835 cm^{-1}.



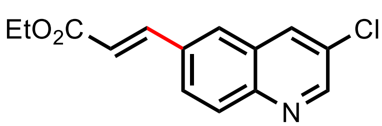
Ethyl (*E*)-3-(2-methoxyquinolin-6-yl)acrylate (2b) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2b** as a white solid (12.6 mg, 49%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 67-69 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 1H), 7.84 – 7.79 (m, 4H), 6.92 (d, J = 8.8 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.08 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.05, 163.26, 147.82, 144.10, 138.90, 130.25, 128.79, 127.98, 127.61, 124.97, 118.04, 113.90, 60.53, 53.60, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ $[M+H]^+$ 258.1130, found 258.1132. IR (film) ν_{max} 2983, 1707, 1617, 1600, 1478, 1389, 1368, 1278, 1230, 1162, 1024, 980, 827 cm^{-1}.



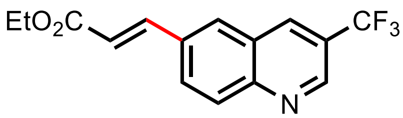
Ethyl (*E*)-3-(2-chloroquinolin-6-yl)acrylate (2c) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2c** as a white solid (11.5 mg, 44%, C6:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 107-109 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.92 (dd, J = 8.8, 1.9 Hz, 1H), 7.90 (s, 1H), 7.82 (d, J = 16.0 Hz, 1H), 7.43 (d, J = 8.6 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.3 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.65, 151.76, 148.58, 143.13, 139.11, 133.19, 129.35, 128.65, 128.51, 126.86, 123.21, 120.11, 60.78, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0634. IR (film) ν_{max} 2981, 1711, 1642, 1579, 1453, 1341, 1284, 1244, 1163, 1096, 983, 830, 733 cm^{-1}.



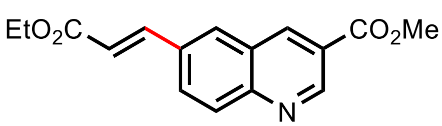
Ethyl (*E*)-3-(3-methylquinolin-6-yl)acrylate (2d) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2d** as a white solid (18 mg, 75%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 67-69 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, J = 2.1 Hz, 1H), 8.05 (d, J = 9.4 Hz, 1H), 7.92 (s, 1H), 7.85 – 7.82 (m, 3H), 6.56 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 153.36, 147.33, 143.85, 135.06, 132.69, 131.41, 129.97, 128.71, 128.12, 126.26, 119.34, 60.66, 18.78, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1181, found 242.1182. IR (film) ν_{max} 2981, 1707, 1636, 1502, 1440, 1367, 1340, 1304, 1284, 1162, 1038, 980, 831 cm^{-1}.



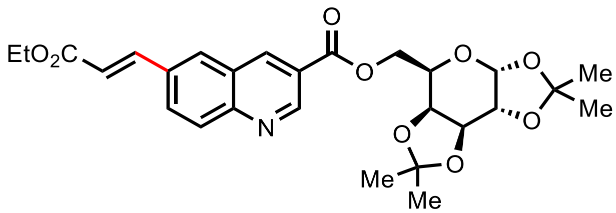
Ethyl (*E*)-3-(3-chloroquinolin-6-yl)acrylate (2e) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2e** as a white solid (17.5 mg, 67%, C6:others = 98:2). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 96-98 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (d, J = 2.4 Hz, 1H), 8.14 (d, J = 2.7 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.89 (dd, J = 8.8, 2.0 Hz, 1H), 7.84 – 7.80 (m, 2H), 6.58 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.58, 150.51, 146.90, 143.08, 134.22, 133.86, 130.23, 129.31, 128.49, 128.10, 127.45, 120.39, 60.79, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0632. IR (film) ν_{max} 2990, 1706, 1636, 1331, 1282, 1179, 1091, 1034, 974, 825, 737 cm^{-1}.



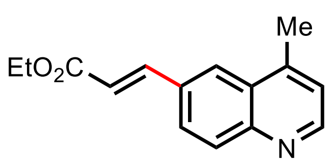
Ethyl (*E*)-3-(3-(trifluoromethyl)quinolin-6-yl)acrylate (2f) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2f** as a white solid (19.2 mg, 65%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 139-141 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.0 Hz, 1H), 8.46 (s, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.01 (s, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.49, 150.01, 146.88 (q, *J* = 3.5 Hz), 142.71, 134.33 – 134.02 (m), 130.42, 129.55, 129.51, 126.40, 124.42 (q, *J* = 32.9 Hz), 122.58, 120.86, 60.87, 14.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.62. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{13}F_3NO_2^+$ $[M+H]^+$ 296.0898, found 296.0898. IR (film) ν_{max} 2998, 1704, 1637, 1354, 1321, 1245, 1222, 1157, 1122, 979, 928, 841 cm^{-1}.



Methyl (*E*)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)quinoline-3-carboxylate (2g) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2g** as a white solid (23.9 mg, 84%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 156-158 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.45 (d, *J* = 2.1 Hz, 1H), 8.85 (d, *J* = 1.3 Hz, 1H), 8.16 (d, *J* = 9.5 Hz, 1H), 8.02 – 8.00 (m, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.57, 165.56, 150.89, 150.52, 142.94, 138.98, 133.67, 130.29, 130.09, 129.59, 126.95, 123.77, 120.44, 60.81, 52.63, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{16}NO_4^+$ $[M+H]^+$ 286.1079, found 286.1078. IR (film) ν_{max} 1722, 1703, 1636, 1447, 1347, 1313, 1291, 1238, 1187, 1102, 991, 937, 841 cm^{-1}.

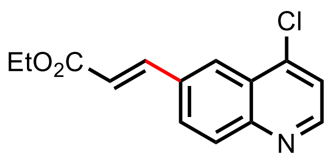


((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 6-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)quinoline-3-carboxylate (2h) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2h** as a white solid (44.6 mg, 87%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 135-137 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46 (d, *J* = 2.1 Hz, 1H), 8.85 (d, *J* = 1.9 Hz, 1H), 8.16 (d, *J* = 9.4 Hz, 1H), 8.02 – 8.00 (m, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 5.59 (d, *J* = 5.0 Hz, 1H), 4.68 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.63 – 4.54 (m, 2H), 4.38 – 4.35 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.25 (ddd, *J* = 7.8, 4.5, 1.9 Hz, 1H), 1.52 (d, *J* = 21.7 Hz, 6H), 1.39 – 1.34 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.58, 164.96, 150.97, 150.56, 142.96, 139.09, 133.64, 130.28, 130.15, 129.60, 126.92, 123.70, 120.42, 109.84, 108.89, 96.35, 71.16, 70.79, 70.51, 66.13, 64.64, 60.80, 26.07, 26.00, 24.97, 24.51, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{32}NO_9^+$ [M+H]$^+$ 514.2077, found 514.2077. $[\alpha]_D^{21}$ = – 46.9 (*c* 0.1, $CHCl_3$). IR (film) ν_{max} 2985, 2935, 1716, 1639, 1380, 1289, 1253, 1212, 1168, 1103, 1069, 1004, 896, 838 cm^{-1}.

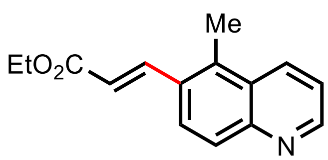


Ethyl (*E*)-3-(4-methylquinolin-6-yl)acrylate (2i) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2i** as a white solid (12.3 mg, 51%, C6:others = 89:11). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 105-107 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.3 Hz, 1H), 8.10 – 8.06 (m, 2H), 7.91 – 7.86 (m, 2H), 7.26 (d, *J* = 4.5 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.83, 151.08, 148.83, 144.85, 144.02, 132.37, 130.81, 128.30, 126.82, 125.62, 122.63, 119.39, 60.67, 18.63, 14.36. HRMS (ESI-TOF) *m/z* Calcd for

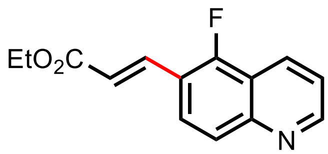
$C_{15}H_{16}NO_2^+$ [M+H]$^+$ 242.1181, found 242.1181. IR (film) ν_{max} 2981, 1707, 1635, 1590, 1443, 1369, 1314, 1281, 1265, 1174, 1036, 980, 844 cm^{-1}.



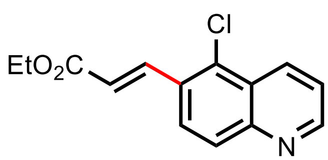
Ethyl (*E*)-3-(4-chloroquinolin-6-yl)acrylate (2j) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2j** as a white solid (15.4 mg, 59%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 109-111 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 4.7 Hz, 1H), 8.32 (d, *J* = 1.9 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.95 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.89 (d, *J* = 16.0 Hz, 1H), 7.52 (d, *J* = 4.7 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.58, 150.71, 149.82, 143.26, 143.03, 133.78, 130.68, 128.25, 126.64, 125.35, 121.98, 120.49, 60.79, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ [M+H]$^+$ 262.0635, found 262.0637. IR (film) ν_{max} 2983, 1711, 1638, 1501, 1445, 1366, 1309, 1262, 1177, 1161, 1037, 982, 844, 763 cm^{-1}.



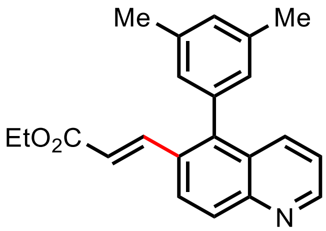
Ethyl (*E*)-3-(5-methylquinolin-6-yl)acrylate (2k) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2k** as a pale yellow solid (8.7 mg, 36%, C6:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 64-66 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.26 (d, *J* = 15.8 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.46 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 2.77 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.94, 150.60, 149.00, 141.91, 134.66, 133.09, 130.83, 128.13, 127.95, 127.43, 121.38, 120.94, 60.69, 14.35, 14.20. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ [M+H]$^+$ 242.1181, found 242.1183. IR (film) ν_{max} 2981, 1711, 1630, 1377, 1289, 1251, 1177, 1035, 979, 836, 809 cm^{-1}.



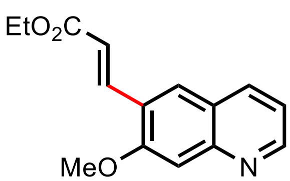
Ethyl (*E*)-3-(5-fluoroquinolin-6-yl)acrylate (2l) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2l** as a white solid (11.5 mg, 47%, C6:others = 97:3). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 48-50 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.48 (ddd, *J* = 8.5, 1.8, 0.8 Hz, 1H), 8.06 (d, *J* = 16.2 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 8.9, 7.6 Hz, 1H), 7.50 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.64 (d, *J* = 16.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.59, 156.26 (d, *J* = 263.7 Hz), 151.94, 149.59 (d, *J* = 3.4 Hz), 135.82 (d, *J* = 3.9 Hz), 129.92 (d, *J* = 5.9 Hz), 127.00 (d, *J* = 3.9 Hz), 125.80 (d, *J* = 4.3 Hz), 121.86 (d, *J* = 3.2 Hz), 121.33 (d, *J* = 5.8 Hz), 119.18 (d, *J* = 16.6 Hz), 117.54 (d, *J* = 10.4 Hz), 60.80, 14.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.88. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}FNO_2^+$ $[M+H]^+$ 246.0930, found 246.0932. IR (film) ν_{max} 2981, 1711, 1638, 1383, 1295, 1256, 1177, 1065, 1038, 983, 831, 811 cm^{-1}.



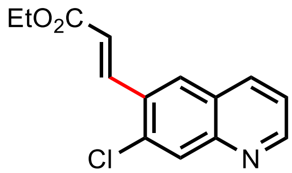
Ethyl (*E*)-3-(5-chloroquinolin-6-yl)acrylate (2m) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2m** as a white solid (9.6 mg, 37%, C6:others = 97:3). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 88-90 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.68 (ddd, *J* = 8.6, 1.7, 0.9 Hz, 1H), 8.35 (d, *J* = 15.9 Hz, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.55 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.34 – 4.31 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.39, 151.61, 149.32, 139.97, 133.69, 132.48, 130.44, 128.90, 127.01, 126.89, 122.50, 122.29, 60.88, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0638. IR (film) ν_{max} 2982, 1712, 1633, 1556, 1369, 1280, 1252, 1179, 1037, 984, 833, 808 cm^{-1}.



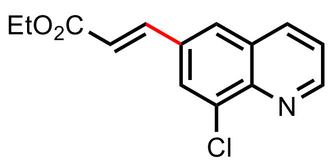
Ethyl (*E*)-3-(5-(3,5-dimethylphenyl)quinolin-6-yl)acrylate (2n) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2n** as a white solid (20.2 mg, 61%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 125-127 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.81 (ddd, *J* = 8.5, 1.7, 0.8 Hz, 1H), 7.58 (d, *J* = 15.9 Hz, 1H), 7.24 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.04 (tt, *J* = 1.6, 0.7 Hz, 1H), 6.80 (dp, *J* = 1.2, 0.6 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.83, 150.81, 148.81, 142.79, 142.02, 137.99, 136.04, 135.80, 130.34, 129.86, 129.23, 128.44, 128.18, 126.50, 121.46, 119.65, 60.44, 21.37, 14.26. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{22}NO_2^+$ $[M+H]^+$ 332.1651, found 332.1656. IR (film) ν_{max} 2978, 1708, 1618, 1488, 1461, 1306, 1257, 1169, 1034, 985, 853 cm^{-1}.



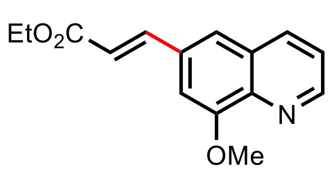
Ethyl (*E*)-3-(7-methoxyquinolin-6-yl)acrylate (2o) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 1/1) furnished compound **2o** as a white solid (11.3 mg, 44%, C6:others = 80:20). TLC: R_f = 0.3 (hexane/EA = 2/1). mp: 95-97 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 (d, *J* = 2.9 Hz, 1H), 8.10 – 8.04 (m, 2H), 7.94 (s, 1H), 7.45 (s, 1H), 7.29 (dd, *J* = 8.2, 4.3 Hz, 1H), 6.71 (d, *J* = 16.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.11, 158.98, 151.50, 150.28, 139.49, 136.14, 128.76, 126.12, 123.14, 121.12, 119.66, 107.58, 60.59, 55.83, 14.37. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ $[M+H]^+$ 258.1130, found 258.1135. IR (film) ν_{max} 2978, 1707, 1618, 1488, 1461, 1306, 1277, 1257, 1168, 1033, 985, 853 cm^{-1}.



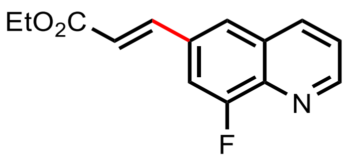
Ethyl (*E*)-3-(7-chloroquinolin-6-yl)acrylate (2p) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2p** as a white solid (12.3 mg, 47%, C6:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 86-88 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.22 – 8.14 (m, 3H), 8.08 (s, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.19, 152.21, 148.73, 140.10, 136.19, 135.30, 131.96, 129.96, 127.13, 126.81, 122.25, 121.94, 60.86, 14.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0635. IR (film) ν_{max} 2981, 1710, 1636, 1612, 1473, 1305, 1266, 1176, 1035, 978, 868, 766 cm^{-1}.



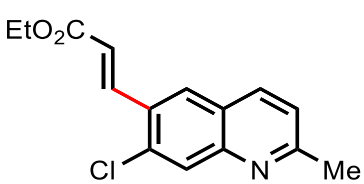
Ethyl (*E*)-3-(8-chloroquinolin-6-yl)acrylate (2q) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2q** as a white solid (10.7 mg, 41%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 64-66 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.06 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.05 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.43, 151.80, 145.10, 142.27, 136.95, 134.53, 133.01, 129.42, 128.08, 127.24, 122.68, 120.61, 60.82, 14.30. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0639. IR (film) ν_{max} 2982, 1708, 1639, 1482, 1370, 1277, 1177, 1036, 980, 858, 786, 750 cm^{-1}.



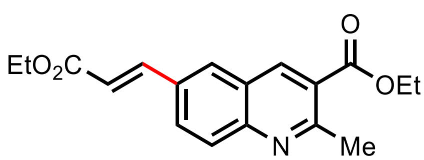
Ethyl (*E*)-3-(8-methoxyquinolin-6-yl)acrylate (2r) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 1/1) furnished compound **2r** as a white solid (21 mg, 82%, C6:others = 90:10). TLC: R_f = 0.3 (hexane/EA = 2/1). mp: 79-81 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.81 (d, *J* = 15.9 Hz, 1H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.20 (d, *J* = 1.7 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.76, 155.79, 150.24, 144.13, 141.32, 136.40, 132.95, 129.19, 122.46, 121.92, 119.33, 104.61, 60.70, 56.09, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ [M+H]$^+$ 258.1130, found 258.1130. IR (film) ν_{max} 2980, 1707, 1637, 1500, 1381, 1282, 1261, 1177, 1038, 980, 852 cm^{-1}.



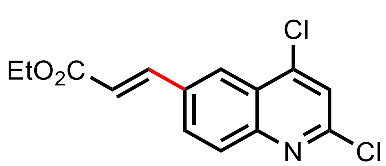
Ethyl (*E*)-3-(8-fluoroquinolin-6-yl)acrylate (2s) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2s** as a white solid (13.5 mg, 55%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 76-78 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dt, *J* = 8.4, 1.6 Hz, 1H), 7.80 (d, *J* = 15.9 Hz, 1H), 7.71 (s, 1H), 7.61 (dd, *J* = 11.3, 1.8 Hz, 1H), 7.52 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.48, 158.31 (d, *J* = 258.4 Hz), 151.39 (d, *J* = 2.1 Hz), 142.74 (d, *J* = 2.8 Hz), 139.39 (d, *J* = 12.6 Hz), 136.22 (d, *J* = 3.4 Hz), 133.11 (d, *J* = 7.8 Hz), 129.78 (d, *J* = 3.0 Hz), 125.01 (d, *J* = 4.0 Hz), 122.86, 120.50, 110.93 (d, *J* = 19.9 Hz), 60.83, 14.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.92. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}FNO_2^+$ [M+H]$^+$ 246.0930, found 246.0937. IR (film) ν_{max} 2981, 1707, 1639, 1501, 1375, 1280, 1256, 1177, 1088, 1035, 980, 856, 788 cm^{-1}.



Ethyl (*E*)-3-(7-chloro-2-methylquinolin-6-yl)acrylate (2t) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2t** as a white solid (21.2 mg, 77%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 64-66 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 16.0 Hz, 1H), 8.08 (s, 1H), 8.04 – 8.02 (m, 2H), 7.31 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 15.9 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.74 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.32, 161.35, 148.45, 140.27, 136.18, 135.26, 130.93, 129.22, 126.84, 125.04, 122.94, 121.64, 60.79, 25.53, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{15}ClNO_2^+$ $[M+H]^+$ 276.0791, found 276.0793. IR (film) ν_{max} 2983, 1711, 1612, 1476, 1370, 1308, 1267, 1201, 1175, 1033, 978, 867 cm^{-1}.

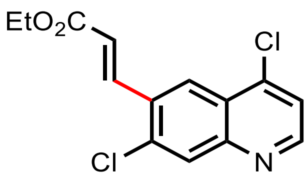


Ethyl (*E*)-3-(7-chloroquinolin-6-yl)acrylate (2u) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2u** as a white solid (18.2 mg, 58%, C6:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 86-88 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.83 (d, J = 16.0 Hz, 1H), 6.57 (d, J = 16.0 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.00 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.72, 166.26, 159.69, 149.32, 143.25, 140.03, 132.71, 129.65, 129.39, 129.36, 125.80, 124.76, 119.74, 61.57, 60.73, 25.76, 14.34, 14.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{20}NO_4^+$ $[M+H]^+$ 314.1392, found 314.1393. IR (film) ν_{max} 2980, 1713, 1636, 1591, 1446, 1367, 1286, 1240, 1212, 1172, 1066, 836 cm^{-1}.

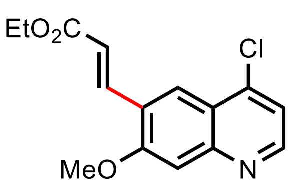


Ethyl (*E*)-3-(2,4-dichloroquinolin-6-yl)acrylate (2v) The general procedure 2.4 was followed except using **T8** (0.2 equiv) and purification by preparative TLC (hexane/EA = 20/1) furnished compound **2v** as a white solid (14.4 mg, 49%, C6:others = 95:5). TLC: R_f = 0.3 (hexane/EA =

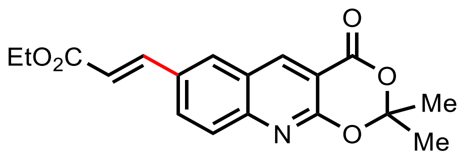
30/1). mp: 94-96 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, J = 1.9 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.96 (dd, J = 8.8, 1.9 Hz, 1H), 7.86 (d, J = 16.0 Hz, 1H), 7.55 (s, 1H), 6.61 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.44, 150.87, 148.81, 144.62, 142.81, 134.10, 129.77, 129.51, 125.37, 125.07, 122.76, 120.89, 60.86, 14.33. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{12}Cl_2NO_2^+$ $[M+H]^+$ 296.0245, found 296.0250. IR (film) ν_{max} 2982, 1712, 1639, 1565, 1436, 1396, 1311, 1173, 1097, 1036, 980, 844 cm^{-1}.



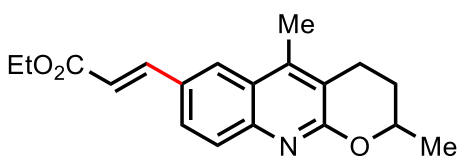
Ethyl (*E*)-3-(4,7-dichloroquinolin-6-yl)acrylate (2w) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2w** as a white solid (24.5 mg, 83%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 105-107 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, J = 4.7 Hz, 1H), 8.46 (s, 1H), 8.19 (t, J = 8.0 Hz, 2H), 7.50 (d, J = 4.7 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.05, 151.72, 149.43, 142.83, 139.69, 136.45, 132.97, 130.27, 125.24, 123.57, 123.09, 121.98, 60.96, 14.32. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{12}Cl_2NO_2^+$ $[M+H]^+$ 296.0245, found 296.0248. IR (film) ν_{max} 2981, 1713, 1638, 1607, 1545, 1470, 1304, 1262, 1198, 1175, 1027, 977, 882, 864, 797, 681 cm^{-1}.



Ethyl (*E*)-3-(4-chloro-7-methoxyquinolin-6-yl)acrylate (2x) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 1/1) furnished compound **2x** as a pale yellow solid (16.3 mg, 56%, C6:others = 80:20). TLC: R_f = 0.3 (hexane/EA = 2/1). mp: 115-117 °C. ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, J = 4.7 Hz, 1H), 8.33 (s, 1H), 8.08 (d, J = 16.1 Hz, 1H), 7.45 (s, 1H), 7.36 (d, J = 4.7 Hz, 1H), 6.76 (d, J = 16.1 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.04 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.93, 159.55, 151.18, 151.04, 142.69, 139.07, 127.03, 125.00, 121.88, 121.34, 119.82, 107.91, 60.68, 56.00, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{15}ClNO_3^+$ $[M+H]^+$ 292.0740, found 292.0742. IR (film) ν_{max} 2980, 1709, 1616, 1554, 1487, 1446, 1337, 1303, 1266, 1166, 1031, 983, 856, 749, 690 cm^{-1}.

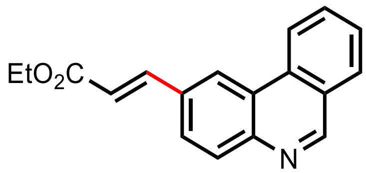


Ethyl (*E*)-3-(2,2-dimethyl-4-oxo-4H-[1,3]dioxino[4,5-b]quinolin-7-yl)acrylate (2y) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2y** as a white solid (13.0 mg, 40%, C_{shown}:others = 86:14). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 192-194 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.02 – 7.98 (m, 2H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 16.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.86 (s, 6H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.53, 160.27, 158.75, 150.85, 142.66, 142.62, 132.59, 131.41, 130.17, 128.81, 125.58, 120.15, 109.51, 107.07, 60.82, 26.65, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{18}NO_5^+$ $[M+H]^+$ 328.1185, found 328.1191. IR (film) ν_{max} 2986, 1747, 1702, 1623, 1454, 1370, 1292, 1180, 1036, 981, 918, 835 cm^{-1}.

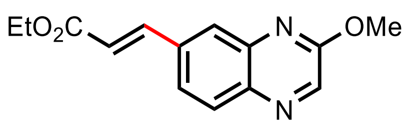


Ethyl (*E*)-3-(2,5-dimethyl-3,4-dihydro-2H-pyrano[2,3-b]quinolin-7-yl)acrylate (2z) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2z** as a white solid (10.3 mg, 33%, C_{shown}:others = 89:11). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 184-186 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 15.9 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.77 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 4.41 (ddt, *J* = 12.6, 6.3, 4.2 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.03 – 2.98 (m, 1H), 2.91 – 2.85 (m, 1H), 2.57 (d, *J* = 0.9 Hz, 3H), 2.18 – 2.14 (m, 1H), 1.85 – 1.79 (m, 1H), 1.53 (d, *J* = 6.3 Hz, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.15, 160.89, 147.03, 144.72, 144.69, 129.94, 128.77, 126.67, 125.42, 125.04, 117.66, 117.05, 73.48, 60.51, 28.81,

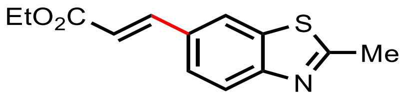
23.53, 21.36, 14.38, 13.93. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_3^+$ $[M+H]^+$ 312.1600, found 312.1599. IR (film) ν_{max} 2976, 2932, 1707, 1633, 1589, 1442, 1396, 1370, 1311, 1272, 1203, 1175, 1134, 1079, 1040, 960, 832, 750 cm^{-1}.



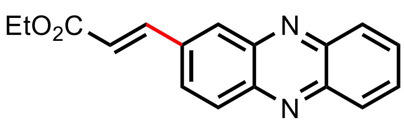
Ethyl (*E*)-3-(phenanthridin-2-yl)acrylate (2aa) The general procedure 2.4 was followed except using **T15** (0.2 equiv) and **TC10** (0.8 equiv) and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2aa** as a pale yellow solid (13.6 mg, 49%, C_{shown}:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 95-97 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.67 (s, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.97 – 7.89 (m, 3H), 7.75 (t, *J* = 7.5 Hz, 1H), 6.64 (dd, *J* = 15.9, 1.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 154.53, 145.50, 144.14, 133.10, 132.36, 131.43, 130.84, 128.99, 128.00, 126.86, 126.63, 124.30, 123.47, 121.81, 119.40, 60.68, 14.37. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{16}NO_2^+$ $[M+H]^+$ 278.1181, found 278.1185. IR (film) ν_{max} 2980, 1708, 1635, 1366, 1296, 1242, 1174, 1037, 981, 832 cm^{-1}.



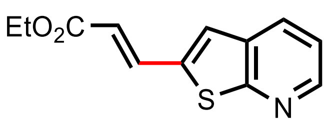
Ethyl (*E*)-3-(3-methoxyquinoxalin-6-yl)acrylate (2ab) The general procedure 2.4 was followed except using **T15** (0.2 equiv) and **TC10** (0.8 equiv) and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2ab** as a white solid (19.6 mg, 76%, C7:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 15/1). mp: 94-96 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.73 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.11 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.67, 158.19, 143.48, 140.58, 140.36, 139.72, 136.19, 129.55, 127.72, 124.98, 120.43, 60.74, 53.87, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{15}N_2O_3^+$ $[M+H]^+$ 259.1083, found 259.1089. IR (film) ν_{max} 2981, 1710, 1637, 1577, 1462, 1386, 1347, 1308, 1289, 1222, 1174, 1158, 1022, 983, 831 cm^{-1}.



Ethyl (*E*)-3-(2-methylbenzo[d]thiazol-6-yl)acrylate (2ac) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **2ac** as a white solid (11.6 mg, 47%, C6:others = 86:14). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 59-61 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 15.9 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 4.28 (t, *J* = 7.1 Hz, 2H), 2.85 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.96, 166.89, 154.62, 143.98, 136.43, 131.32, 125.54, 122.69, 121.62, 118.50, 60.59, 20.32, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0745, found 248.0747. IR (film) ν_{max} 2980, 1707, 1634, 1520, 1455, 1411, 1367, 1325, 1253, 1170, 1037, 981, 858, 823 cm^{-1}.

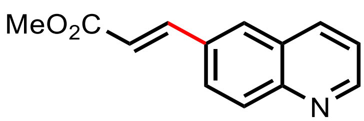


Ethyl (*E*)-3-(phenazin-2-yl)acrylate (2ad) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ad** as a white solid (15.6 mg, 56%, C_{shown}:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 107-109 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.5 Hz, 1H), 8.20 – 8.15 (m, 3H), 7.96 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.87 (dd, *J* = 16.0, 0.6 Hz, 1H), 7.80 (dt, *J* = 6.6, 3.3 Hz, 2H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.26 (t, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.83, 150.81, 148.81, 142.79, 142.02, 137.99, 136.04, 135.80, 130.34, 129.86, 129.23, 128.44, 128.18, 126.50, 121.46, 119.65, 60.44, 21.37, 14.26. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{15}N_2O_2^+$ $[M+H]^+$ 279.1134, found 279.1135. IR (film) ν_{max} 2980, 1712, 1636, 1511, 1442, 1366, 1308, 1284, 1170, 1038, 980, 830, 757 cm^{-1}.

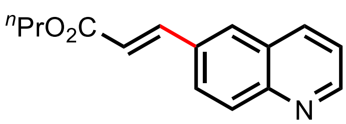


Ethyl (*E*)-3-(thieno[2,3-b]pyridin-2-yl)acrylate (2ae) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ae** as a white solid

(19.6 mg, 84%, C6:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 59-61 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (dd, J = 4.6, 1.6 Hz, 1H), 8.04 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 (dd, J = 15.7, 0.7 Hz, 1H), 7.41 (s, 1H), 7.32 (dd, J = 8.0, 4.6 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.27, 161.89, 148.12, 139.81, 137.40, 133.19, 131.56, 125.68, 120.99, 120.13, 60.84, 14.30. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{12}NO_2S^+$ $[M+H]^+$ 234.0589, found 234.0593. IR (film) ν_{max} 2981, 1709, 1629, 1573, 1508, 1382, 1301, 1265, 1172, 1150, 1038, 967, 838 cm^{-1}.

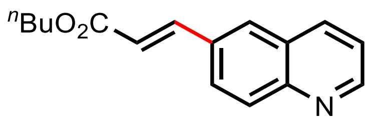


Methyl (*E*)-3-(quinolin-6-yl)acrylate (2af) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2af** as a white solid (12.4 mg, 58%, C6:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 76-78 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.7 Hz, 1H), 8.19 – 8.17 (m, 1H), 8.11 (d, J = 9.3 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.86 (d, J = 16.0 Hz, 1H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.23, 151.39, 149.08, 143.91, 136.47, 132.63, 130.32, 129.31, 128.25, 127.25, 121.88, 119.14, 51.86. HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{12}NO_2^+$ $[M+H]^+$ 214.0868, found 214.0871. IR (film) ν_{max} 2950, 1711, 1638, 1589, 1501, 1434, 1330, 1308, 1281, 1193, 1170, 1038, 981, 835 cm^{-1}.

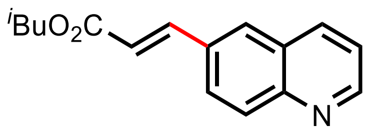


Propyl (*E*)-3-(quinolin-6-yl)acrylate (2ag) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ag** as a pale yellow solid (16.6 mg, 69%, C6:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 47-49 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.7 Hz, 1H), 8.17 (dd, J = 8.4, 1.2 Hz, 1H), 8.10 (d, J = 9.3 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.85 (d, J = 16.2 Hz, 1H), 7.44 (dd, J = 8.2, 4.2 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 1.76 (q, J = 6.9 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.88, 151.34, 149.06, 143.59, 136.45, 132.73, 130.28, 129.22, 128.27, 127.28, 121.86, 119.65, 66.33, 22.11, 10.48. HRMS (ESI-TOF) *m/z* Calcd for

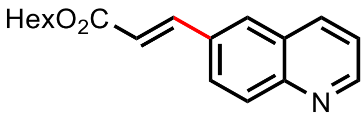
$C_{15}H_{16}NO_2^+$ [M+H]$^+$ 242.1181, found 242.1185. IR (film) ν_{max} 2967, 1708, 1636, 1589, 1501, 1461, 1389, 1309, 1280, 1173, 982, 835 cm^{-1}.



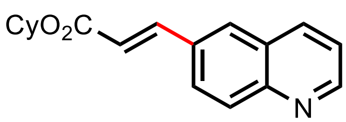
Butyl (*E*)-3-(quinolin-6-yl)acrylate (2ah) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ah** as colorless oil (20.4 mg, 80%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.91 (dq, *J* = 4.5, 2.0 Hz, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 1.74 – 1.70 (m, 2H), 1.46 (dt, *J* = 14.8, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.89, 151.34, 149.06, 143.57, 136.45, 132.74, 130.28, 129.22, 128.27, 127.28, 121.86, 119.67, 64.62, 30.79, 19.22, 13.77. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{18}NO_2^+$ [M+H]$^+$ 256.1338, found 256.1343. IR (film) ν_{max} 2958, 2872, 1709, 1637, 1501, 1461, 1386, 1328, 1305, 1280, 1172, 981, 835 cm^{-1}.



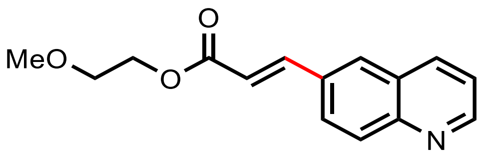
Isobutyl (*E*)-3-(quinolin-6-yl)acrylate (2ai) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ai** as a white solid (21.2 mg, 83%, C6:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 67-69 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 – 8.16 (m, 1H), 8.10 (d, *J* = 9.5 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 4.03 (d, *J* = 6.7 Hz, 2H), 2.04 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 151.34, 149.05, 143.59, 136.44, 132.73, 130.28, 129.23, 128.26, 127.29, 121.86, 119.65, 70.83, 27.86, 19.18. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{18}NO_2^+$ [M+H]$^+$ 256.1338, found 265.1342. IR (film) ν_{max} 2961, 1707, 1636, 1501, 1468, 1380, 1328, 1307, 1280, 1162, 1016, 980, 834 cm^{-1}.



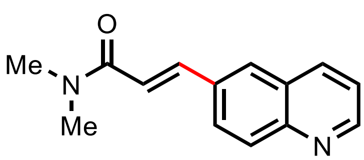
Hexyl (*E*)-3-(quinolin-6-yl)acrylate (2aj) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2aj** as pale yellow oil (19.8 mg, 70%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.91 (dq, *J* = 3.9, 2.0 Hz, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.74 – 1.71 (m, 2H), 1.45 – 1.39 (m, 2H), 1.34 (ddd, *J* = 7.2, 4.5, 3.2 Hz, 4H), 0.93 – 0.90 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.89, 151.34, 149.06, 143.57, 136.45, 132.74, 130.28, 129.22, 128.27, 127.29, 121.86, 119.68, 64.92, 31.48, 28.71, 25.67, 22.57, 14.03. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$ 284.1651, found 284.2643. IR (film) ν_{max} 2954, 2928, 2858, 1710, 1637, 1589, 1501, 1463, 1386, 1329, 1305, 1280, 1171, 982, 835 cm^{-1}.



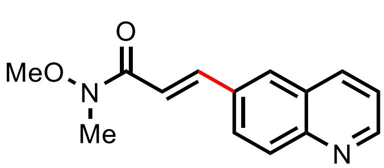
Cyclohexyl (*E*)-3-(quinolin-6-yl)acrylate (2ak) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2ak** as a white solid (12.9 mg, 46%, C6:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 76-78 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (ddd, *J* = 8.3, 1.8, 0.8 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.91 (dq, *J* = 4.6, 2.0 Hz, 2H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.93 (tt, *J* = 9.2, 3.9 Hz, 1H), 1.97 – 1.92 (m, 2H), 1.79 (dp, *J* = 13.4, 4.3 Hz, 2H), 1.59 (dq, *J* = 13.2, 4.9, 4.5 Hz, 1H), 1.55 – 1.48 (m, 2H), 1.46 – 1.40 (m, 2H), 1.32 (ddt, *J* = 13.8, 10.3, 3.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.23, 151.29, 149.03, 143.27, 136.44, 132.83, 130.25, 129.14, 128.27, 127.31, 121.84, 120.28, 72.98, 31.75, 25.44, 23.82. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{20}NO_2^+$ $[M+H]^+$ 282.1494, found 282.1498. IR (film) ν_{max} 2935, 2858, 1706, 1636, 1589, 1501, 1451, 1382, 1329, 1301, 1280, 1174, 1038, 1017, 982, 834 cm^{-1}.



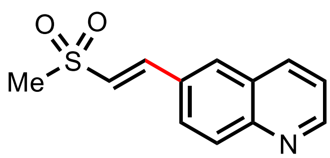
2-Methoxyethyl (*E*)-3-(quinolin-6-yl)acrylate (2al) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 1/1) furnished compound **2al** as pale yellow oil (16.7 mg, 65%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.5, 1.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.85 (m, 3H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 4.42 – 4.39 (m, 2H), 3.71 – 3.68 (m, 2H), 3.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.75, 151.40, 149.09, 144.15, 136.49, 132.63, 130.32, 129.37, 128.25, 127.26, 121.87, 119.19, 70.57, 63.74, 59.08. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ $[M+H]^+$ 258.1130, found 258.1135. IR (film) ν_{max} 2891, 1709, 1636, 1589, 1501, 1455, 1381, 1327, 1304, 1279, 1171, 1127, 1040, 982, 864, 836 cm^{-1}.



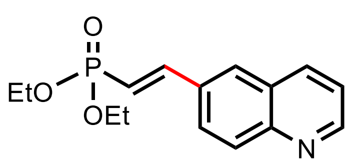
(*E*)-*N,N*-Dimethyl-3-(quinolin-6-yl)acrylamide (2am) The general procedure 2.4 was followed and purification by preparative TLC (EA) furnished compound **2am** as a white solid (12.2 mg, 54%, C6:others = 97:3). TLC: R_f = 0.2 (EA). mp: 151-153 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 – 8.90 (m, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.94 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.89 (s, 1H), 7.84 (d, *J* = 15.4 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.04 (d, *J* = 15.4 Hz, 1H), 3.23 (s, 3H), 3.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.42, 151.03, 148.81, 141.47, 136.38, 133.58, 130.07, 128.79, 128.37, 127.23, 121.77, 118.72, 37.49, 36.02. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{15}N_2O^+$ $[M+H]^+$ 227.1184, found 227.1184. IR (film) ν_{max} 2935, 1649, 1604, 1501, 1397, 1139, 988, 904, 835 cm^{-1}.



(*E*)-*N*-Methoxy-*N*-methyl-3-(quinolin-6-yl)acrylamide (2an)** The general procedure 2.4 was followed and purification by preparative TLC (EA) furnished compound **2an** as a white solid (14.8 mg, 61%, C6:others = 97:3). TLC: R_f = 0.2 (EA). mp: 101-103 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.11 (d, *J* = 9.4 Hz, 1H), 7.98 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.93 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 15.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 (d, *J* = 15.8 Hz, 1H), 3.81 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.69, 151.14, 148.94, 142.51, 136.44, 133.41, 130.10, 129.18, 128.34, 127.39, 121.79, 117.11, 62.01, 32.57. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{15}N_2O_2^+$ $[M+H]^+$ 243.1134, found 243.1140. IR (film) ν_{max} 2935, 1652, 1612, 1501, 1462, 1416, 1385, 1178, 1119, 1097, 999, 833, cm^{-1}.

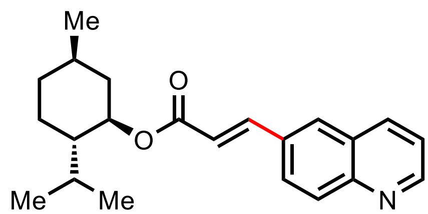


(*E*)-6-(2-(Methylsulfonyl)vinyl)quinoline (2ao) The general procedure 2.4 was followed and purification by preparative TLC (EA/acetone = 10/1) furnished compound **2ao** as a white solid (15.8 mg, 68%, C6:others = 95:5). TLC: R_f = 0.3 (EA/acetone = 10/1). mp: 90-92 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.21 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.81 (d, *J* = 15.4 Hz, 1H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.07 (d, *J* = 15.4 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.04, 149.37, 143.11, 136.64, 130.77, 130.56, 130.29, 128.19, 127.41, 127.04, 122.20, 43.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{12}H_{12}NO_2S^+$ $[M+H]^+$ 234.0589, found 234.0595. IR (film) ν_{max} 1619, 1586, 1502, 1289, 1130, 970, 831, 808 cm^{-1}.

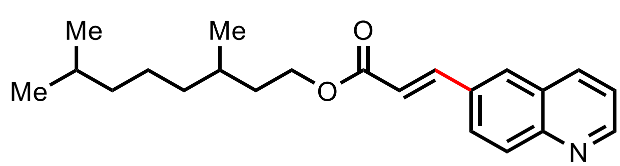


Diethyl (*E*)-(2-(quinolin-6-yl)vinyl)phosphonate (2ap) The general procedure 2.4 was followed and purification by preparative TLC (EA/acetone = 1/1) furnished compound **2ap** as colorless oil (19.3 mg, 66%, C6:others = 96:4). TLC: R_f = 0.5 (EA/acetone = 1/1). ^{1}H NMR (600

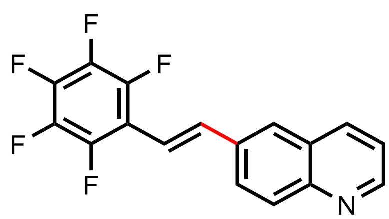
MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.90 (dd, *J* = 11.0, 2.3 Hz, 2H), 7.68 (dd, *J* = 22.4, 17.5 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.42 (t, *J* = 17.2 Hz, 1H), 4.21 – 4.14 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.39, 149.03, 147.70 (d, *J* = 6.8 Hz), 136.54, 133.05 (d, *J* = 23.6 Hz), 130.26, 128.89 (d, *J* = 1.2 Hz), 128.22 (d, *J* = 1.4 Hz), 126.94, 121.89, 115.66 (d, *J* = 191.0 Hz), 62.01, 61.98, 16.47, 16.43. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{19}NO_3P^+$ $[M+H]^+$ 292.1103, found 292.1107. IR (film) ν_{max} 2983, 1614, 1586, 1501, 1386, 1237, 1163, 1048, 1022, 961, 855, 819 cm^{-1}.



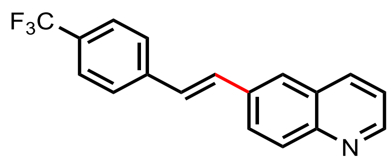
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-3-(quinolin-6-yl)acrylate (2aq) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2aq** as colorless oil (22.6 mg, 67%, C6:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). ^1H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 – 8.16 (m, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.92 (td, *J* = 4.5, 1.9 Hz, 2H), 7.84 (d, *J* = 15.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.86 (td, *J* = 10.9, 4.5 Hz, 1H), 2.09 (dtd, *J* = 12.1, 4.2, 3.7, 1.7 Hz, 1H), 1.95 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.72 (dt, *J* = 12.7, 3.0 Hz, 2H), 1.59 – 1.51 (m, 1H), 1.50 – 1.45 (m, 1H), 1.15 – 1.04 (m, 2H), 0.93 (dd, *J* = 6.8, 2.4 Hz, 7H), 0.81 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.37, 151.30, 149.03, 143.38, 136.44, 132.82, 130.24, 129.16, 128.27, 127.32, 121.84, 120.12, 74.51, 47.23, 41.04, 34.31, 31.45, 26.39, 23.55, 22.06, 20.79, 16.46. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{28}NO_2^+$ $[M+H]^+$ 338.2120, found 338.2120. $[\alpha]_D^{21}$ = – 47.2 (*c* 0.1, $CHCl_3$). IR (film) ν_{max} 2953, 2869, 1705, 1636, 1501, 1456, 1383, 1330, 1303, 1280, 1173, 1013, 983, 835 cm^{-1}.



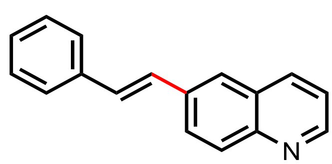
3,7-Dimethyloctyl (*E*)-3-(quinolin-6-yl)acrylate (2ar) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2ar** as colorless oil (23.0 mg, 68%, C6:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.10 (d, *J* = 9.3 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.44 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 4.31 – 4.25 (m, 2H), 1.79 – 1.74 (m, 1H), 1.65 – 1.59 (m, 1H), 1.56 – 1.50 (m, 2H), 1.36 – 1.31 (m, 2H), 1.30 – 1.25 (m, 1H), 1.20 – 1.14 (m, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.88 (dd, *J* = 6.6, 1.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.88, 151.34, 149.05, 143.56, 136.45, 132.74, 130.28, 129.22, 128.26, 127.28, 121.86, 119.69, 63.36, 39.23, 37.17, 35.63, 29.92, 27.97, 24.64, 22.71, 22.62, 19.58. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{30}NO_2^+$ $[M+H]^+$ 340.2277, found 340.2276. IR (film) ν_{max} 2954, 2926, 2868, 1711, 1638, 1501, 1462, 1383, 1329, 1304, 1280, 1173, 981, 835 cm^{-1}.



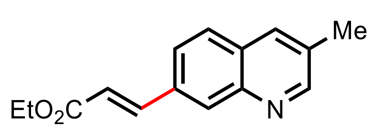
(*E*)-6-(2-(Perfluorophenyl)vinyl)quinoline (2as) The general procedure 2.4 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2as** as a pale yellow solid (26.3 mg, 82%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 108-110 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 16.8 Hz, 1H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.13 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.83, 148.54, 144.92 (dm, *J* = 251.2 Hz), 139.96 (dm, *J* = 255.0 Hz), 137.82 (dm, *J* = 252.4 Hz), 136.34 – 136.14 (m), 136.20, 134.65, 130.15, 128.43, 127.34, 126.70, 121.79, 114.09 (d, *J* = 2.9 Hz), 112.14 (td, *J* = 13.6, 4.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.09 (dd, *J* = 21.4, 8.6 Hz, 2F), -158.42 (t, *J* = 21.0 Hz, 1F), -165.29 (td, *J* = 21.0, 7.3 Hz, 2F). HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_9F_5N^+$ $[M+H]^+$ 322.0655, found 322.0662. IR (film) ν_{max} 1520, 1494, 1130, 1003, 964, 899, 829, 764 cm^{-1}.



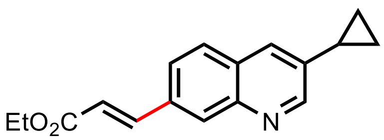
(*E*)-6-(4-(Trifluoromethyl)styryl)quinoline (2at) The general procedure 2.7 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **2at** as a white solid (19.1 mg, 64%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 143-145 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.92 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.63 – 7.53 (m, 4H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.29 (d, *J* = 16.3 Hz, 1H), 7.21 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.52, 148.34, 140.50, 136.05, 134.89, 130.38, 130.04, 129.63 (q, *J* = 3.8 Hz), 128.59, 128.55, 127.13, 126.74, 126.65, 125.75 (q, *J* = 3.8 Hz), 124.18 (q, *J* = 272.0 Hz), 121.70. ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.15. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{13}F_3N^+$ $[M+H]^+$ 300.1000, found 300.1010. IR (film) ν_{max} 1330, 1276, 1164, 1111, 1069, 953, 865, 831, 750 cm^{-1}.



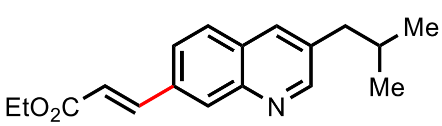
(*E*)-6-Styrylquinoline (2au) The general procedure 2.7 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **2au** as a white solid (14.3 mg, 62%, C6:others = 90:10). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 100-102 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.90 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.23 – 7.21 (m, 1H), 7.19 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.15, 148.12, 137.03, 135.95, 135.61, 130.23, 129.82, 128.81, 128.61, 128.03, 127.87, 127.27, 126.68, 125.94, 121.55. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{14}N^+$ $[M+H]^+$ 232.1126, found 232.1134. IR (film) ν_{max} 3029, 1592, 1500, 1447, 1380, 1325, 1154, 1121, 959, 889, 828, 692 cm^{-1}.



Ethyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3a) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3a** as a white solid (7.7 mg, 64%, C7:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 103-105 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 153.27, 146.55, 144.09, 134.61, 134.43, 131.66, 130.41, 129.10, 127.84, 124.57, 119.51, 60.67, 18.87, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1181, found 242.1185. IR (film) ν_{max} 2981, 1709, 1631, 1368, 1308, 1293, 1282, 1237, 1178, 1151, 1037, 996, 891, 861, 813 cm^{-1}.

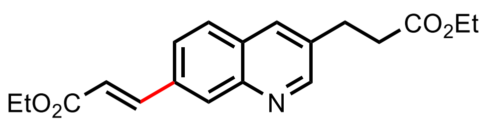


Ethyl (*E*)-3-(3-cyclopropylquinolin-7-yl)acrylate (3b) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **3b** as a white solid (9.5 mg, 71%, C7:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 74-76 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.15 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.8 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.08 (td, *J* = 8.4, 4.2 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.16 – 1.11 (m, 2H), 0.89 – 0.86 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 151.48, 146.67, 144.10, 138.02, 134.43, 130.40, 129.09, 127.85, 124.61, 119.40, 60.66, 14.35, 13.53, 9.54. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{18}NO_2^+$ $[M+H]^+$ 268.1338, found 268.1342. IR (film) ν_{max} 3077, 2983, 2928, 1705, 1632, 1606, 1365, 1307, 1295, 1275, 1171, 1130, 1045, 868, 814 cm^{-1}.

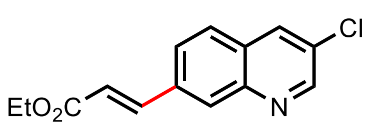


Ethyl (*E*)-3-(3-isobutylquinolin-7-yl)acrylate (3c) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **3c** as a white solid (10.3 mg, 73%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 73-75 ºC. ^{1}H NMR

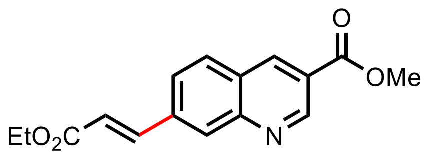
(600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.2 Hz, 1H), 8.17 (s, 1H), 7.90 – 7.85 (m, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.67 (d, *J* = 7.2 Hz, 2H), 2.00 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 153.34, 146.80, 144.10, 135.35, 134.69, 134.66, 130.38, 129.07, 128.04, 124.50, 119.52, 60.67, 42.60, 30.15, 22.27, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$ 284.1651, found 284.1659. IR (film) ν_{max} 2954, 2868, 1707, 1633, 1462, 1367, 1313, 1267, 1179, 994, 911, 819, 749 cm^{-1}.



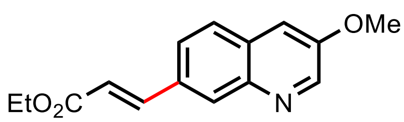
Ethyl (*E*)-3-(3-(3-ethoxy-3-oxopropyl)quinolin-7-yl)acrylate (3d) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **3d** as a white solid (10 mg, 61%, C7:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 85-87 ºC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.2 Hz, 1H), 8.17 (s, 1H), 7.95 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.23, 166.80, 152.57, 147.02, 143.95, 135.04, 134.34, 134.21, 130.36, 128.97, 128.11, 124.72, 119.76, 60.70, 35.24, 28.26, 14.35, 14.20. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{22}NO_4^+$ $[M+H]^+$ 328.1549, found 328.1555. IR (film) ν_{max} 2978, 2934, 1732, 1705, 1632, 1367, 1286, 1166, 1038, 980, 904, 859, 815, 739 cm^{-1}.



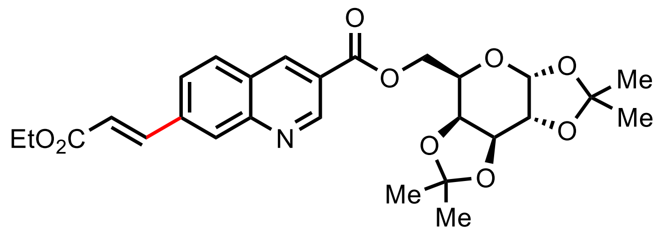
Ethyl (*E*)-3-(3-chloroquinolin-7-yl)acrylate (3e) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10:1) furnished compound **3e** as a white solid (8.1 mg, 62%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 71-73 ºC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.4 Hz, 1H), 8.18 (s, 1H), 8.13 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.76 (s, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 4.30 (t, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.61, 150.54, 146.30, 143.40, 135.80, 133.72, 130.34, 129.42, 129.23, 127.66, 125.75, 120.49, 60.79, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ [M+H]$^+$ 262.0635, found 262.0636. IR (film) ν_{max} 2986, 1715, 1641, 1446, 1371, 1261, 1177, 1088, 902, 764, 750 cm^{-1}.



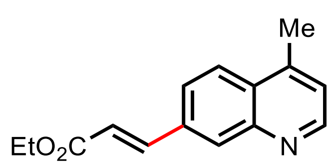
Methyl (*E*)-7-(3-ethoxy-3-oxoprop-1-en-1-yl)quinoline-3-carboxylate (3f) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3f** as a white solid (7.4 mg, 52%, C7:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 121-123 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.47 (d, *J* = 2.1 Hz, 1H), 8.82 (d, *J* = 1.9 Hz, 1H), 8.25 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.49, 165.63, 150.85, 149.97, 143.26, 138.31, 137.86, 130.22, 129.71, 127.68, 125.48, 123.60, 121.32, 60.87, 52.62, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{16}NO_4^+$ [M+H]$^+$ 286.1079, found 286.1084. IR (film) ν_{max} 3006, 1705, 1632, 1445, 1380, 1308, 1276, 1261, 1179, 993, 819, 750 cm^{-1}.



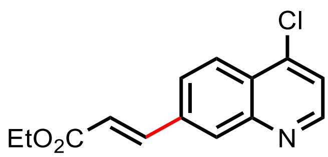
Ethyl (*E*)-3-(3-methoxyquinolin-7-yl)acrylate (3g) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3g** as a white solid (9.4 mg, 73%, C7:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 90-92 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.8 Hz, 1H), 8.14 (s, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.71 (q, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 2.9 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.95, 153.84, 145.49, 144.15, 143.36, 132.92, 130.37, 130.02, 127.33, 125.19, 118.82, 111.94, 60.61, 55.59, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ [M+H]$^+$ 258.1130, found 258.1128. IR (film) ν_{max} 2978, 1708, 1635, 1606, 1458, 1369, 1350, 1282, 1232, 1175, 1152, 1028, 879, 864, 811 cm^{-1}.



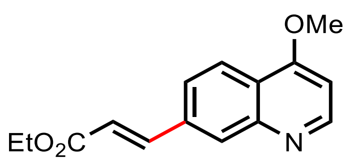
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 7-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)quinoline-3-carboxylate (3h) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3h** as colorless oil (12.8 mg, 50%, C7:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (d, *J* = 2.1 Hz, 1H), 8.83 (d, *J* = 1.8 Hz, 1H), 8.24 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 5.58 (d, *J* = 4.9 Hz, 1H), 4.68 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.62 (dd, *J* = 11.6, 4.5 Hz, 1H), 4.55 (dd, *J* = 11.5, 7.8 Hz, 1H), 4.38 – 4.34 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.25 (ddd, *J* = 7.8, 4.4, 1.9 Hz, 1H), 1.52 (d, *J* = 20.1 Hz, 6H), 1.39 – 1.36 (m, 6H), 1.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.49, 165.02, 150.93, 150.01, 143.28, 138.43, 137.87, 130.22, 129.76, 127.67, 125.44, 123.52, 121.31, 109.84, 108.89, 96.35, 71.16, 70.78, 70.51, 66.13, 64.62, 60.86, 26.07, 26.00, 24.97, 24.50, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{27}H_{32}NO_9^+$ $[M+H]^+$ 514.2077, found 514.2077. $[\alpha]_D^{21}$ = – 60.4 (*c* 0.1, $CHCl_3$). IR (film) ν_{max} 2986, 2932, 1717, 1639, 1620, 1453, 1378, 1289, 1249, 1206, 1173, 1101, 1069, 1005, 896, 763 cm^{-1}.



Ethyl (*E*)-3-(4-methylquinolin-7-yl)acrylate (3i) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3i** as a white solid (6.6 mg, 55%, C7:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 75-77 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.3 Hz, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.25 (s, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 2.72 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79, 151.03, 148.08, 144.24, 143.88, 135.20, 131.03, 129.23, 124.64, 124.27, 122.70, 119.95, 60.71, 18.62, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1181, found 242.1187. IR (film) ν_{max} 2983, 2924, 1709, 1636, 1594, 1448, 1368, 1318, 1266, 1164, 1036, 983, 842, 749 cm^{-1}.

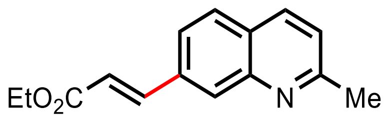


Ethyl (*E*)-3-(4-chloroquinolin-7-yl)acrylate (3j) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3j** as a white solid (5.6 mg, 43%, C7:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 92-94 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.7 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.21 (d, *J* = 1.7 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.82 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.51 (d, *J* = 4.6 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.55, 150.75, 149.28, 143.17, 142.56, 136.53, 130.59, 127.33, 125.59, 124.96, 121.93, 120.97, 60.83, 14.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0639. IR (film) ν_{max} 2925, 1715, 1638, 1584, 1554, 1500, 1371, 1314, 1281, 1205, 1177, 976, 823 cm^{-1}.

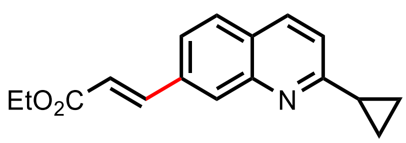


Ethyl (*E*)-3-(4-methoxyquinolin-7-yl)acrylate (3k) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 1/1) furnished compound **3k** as a white solid (6.4 mg, 50%, C7:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 2/1). mp: 103-105 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.2 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 1.7 Hz, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.68 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.76 (d, *J* = 5.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79, 162.15, 152.25, 149.27, 143.99, 135.81, 129.97, 123.61, 122.65, 122.25, 120.01, 100.90, 60.69, 55.82, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ $[M+H]^+$

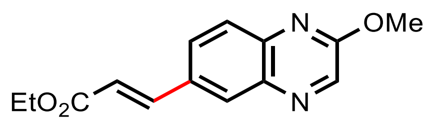
258.1130, found 258.1139. IR (film) ν_{max} 2980, 1708, 1636, 1594, 1567, 1510, 1451, 1388, 1370, 1318, 1267, 1159, 1111, 1038, 985, 818 cm^{-1}.



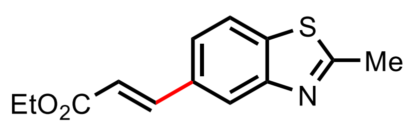
Ethyl (*E*)-3-(2-methylquinolin-7-yl)acrylate (3l) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **3l** as colorless oil (5.4 mg, 45%, C7:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 0.9 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.79 (dd, J = 16.0, 0.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.59 (dd, J = 8.4, 1.7 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 2.69 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.86, 160.01, 147.94, 144.15, 135.82, 135.50, 129.76, 128.17, 127.48, 123.80, 122.90, 119.78, 60.68, 25.41, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$ 242.1181, found 242.1191. IR (film) ν_{max} 2980, 2930, 1710, 1636, 1511, 1451, 1369, 1308, 1286, 1174, 1037, 982, 843 cm^{-1}.



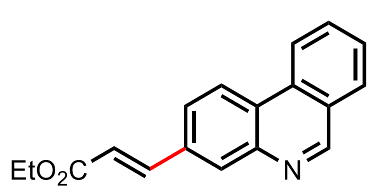
Ethyl (*E*)-3-(2-cyclopropylquinolin-7-yl)acrylate (3m) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 10/1) furnished compound **3m** as colorless oil (5.5 mg, 41%, C7:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 1.0 Hz, 1H), 7.90 (dd, J = 8.6, 0.8 Hz, 1H), 7.77 (d, J = 16.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.53 (dd, J = 8.4, 1.7 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.18 – 2.14 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.12 – 1.10 (m, 1H), 1.05 – 1.03 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.91, 164.45, 148.06, 144.30, 135.38, 135.34, 129.81, 128.11, 127.73, 123.29, 120.55, 119.54, 60.63, 18.09, 14.35, 10.54. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{18}NO_2^+$ $[M+H]^+$ 268.1338, found 268.1349. IR (film) ν_{max} 2926, 1710, 1636, 1604, 1511, 1453, 1367, 1303, 1285, 1173, 1033, 981, 841 cm^{-1}.



Ethyl (*E*)-3-(2-methoxyquinoxalin-6-yl)acrylate (3n) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 20/1) furnished compound **3n** as a white solid (7.5 mg, 58%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 30/1). mp: 81-83 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.12 (d, *J* = 1.8 Hz, 1H), 7.87 – 7.83 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.12 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.81, 158.22, 143.51, 141.63, 140.49, 138.79, 132.85, 129.62, 128.47, 127.83, 119.35, 60.68, 53.95, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{15}N_2O_3^+$ $[M+H]^+$ 259.1083, found 259.1088. IR (film) ν_{max} 2946, 1711, 1638, 1577, 1459, 1391, 1342, 1317, 1271, 1219, 1175, 1142, 1019, 980, 832, 749 cm^{-1}.

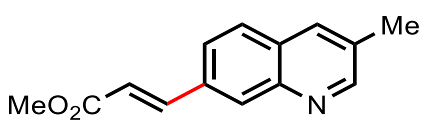


Ethyl (*E*)-3-(2-methylbenzo[d]thiazol-5-yl)acrylate (3o) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 20/1) furnished compound **3o** as a white solid (7.4 mg, 60%, C5:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 30/1). mp: 56-58 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.7 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.53 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.85 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.26, 166.95, 153.90, 144.33, 137.55, 132.71, 123.99, 122.21, 121.76, 118.54, 60.61, 20.25, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0745, found 248.0747. IR (film) ν_{max} 2980, 1709, 1636, 1524, 1454, 1422, 1367, 1274, 1232, 1176, 1157, 1064, 1038, 982, 861, 809 cm^{-1}.

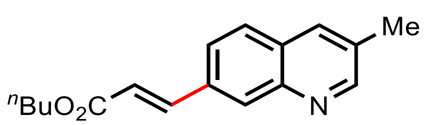


Ethyl (*E*)-3-(phenanthridin-3-yl)acrylate (3p) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3p** as a white solid (10.6

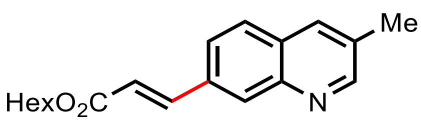
mg, 77%, C_{shown}:others = 93:7). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 85-87 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.59 (dd, *J* = 17.9, 8.4 Hz, 2H), 8.31 (d, *J* = 1.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.85 (m, 3H), 7.76 (t, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.88, 154.42, 144.59, 143.87, 134.81, 132.15, 131.36, 130.63, 128.93, 128.14, 126.68, 125.56, 125.43, 122.97, 122.12, 119.57, 60.68, 14.37. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{16}NO_2^+$ $[M+H]^+$ 278.1181, found 278.1185. IR (film) ν_{max} 2984, 1731, 1708, 1638, 1616, 1480, 1442, 1371, 1252, 1190, 1162, 888, 820, 786, 751, 734 cm^{-1}.



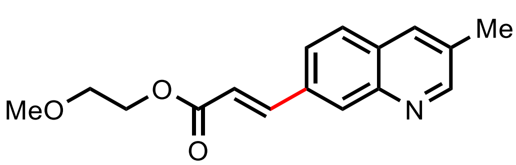
Methyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3q) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3q** as a white solid (6.7 mg, 59%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 150-152 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.91 (s, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.29, 153.30, 146.53, 144.39, 134.52, 134.44, 131.72, 130.46, 129.14, 127.87, 124.57, 119.02, 51.84, 18.87. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$ 228.1025, found 228.1027. IR (film) ν_{max} 2953, 1703, 1629, 1453, 1435, 1316, 1253, 1233, 1173, 1148, 1037, 1005, 880, 813, cm^{-1}.



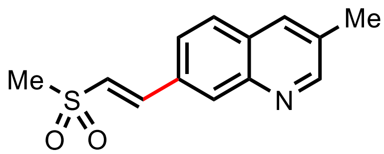
Butyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3r) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3r** as a white solid (8.4 mg, 62%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 68-70 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 2.53 (s, 3H), 1.74 – 1.69 (m, 2H), 1.49 – 1.44 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.96, 153.27, 146.55, 144.07, 134.63, 134.43, 131.66, 130.42, 129.10, 127.83, 124.57, 119.53, 64.60, 30.79, 19.22, 18.87, 13.77. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{20}NO_2^+$ $[M+H]^+$ 270.1494, found 270.1497. IR (film) ν_{max} 2958, 1706, 1633, 1456, 1339, 1309, 1292, 1280, 1065, 993, 888, 862, 811 cm^{-1}.



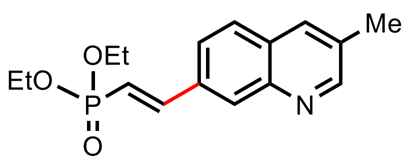
Hexyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3s) The general procedure 2.5 was followed and purification by preparative TLC (DCM) furnished compound **3s** as a white solid (9.0 mg, 61%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 68-70 ºC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 2H), 2.53 (s, 3H), 1.75 – 1.70 (m, 2H), 1.45 – 1.39 (m, 2H), 1.36 – 1.32 (m, 4H), 0.93 – 0.90 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.96, 153.27, 146.55, 144.06, 134.63, 134.43, 131.66, 130.43, 129.10, 127.83, 124.57, 119.54, 64.90, 31.48, 28.71, 25.66, 22.57, 18.87, 14.03. HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{24}NO_2^+$ $[M+H]^+$ 298.1807, found 298.1811. IR (film) ν_{max} 2951, 2924, 2854, 1703, 1633, 1473, 1338, 1312, 1282, 1237, 1173, 1153, 995, 886, 856, 811 cm^{-1}.



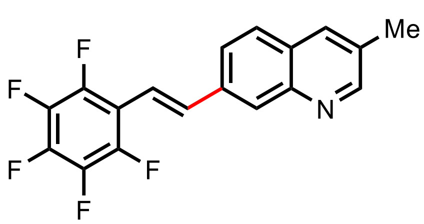
2-Methoxyethyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3t) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 2/1) furnished compound **3t** as a white solid (7.5 mg, 55%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 3/1). mp: 81-83 ºC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.92 – 7.88 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 4.42 – 4.39 (m, 2H), 3.71 – 3.68 (m, 2H), 3.44 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.82, 153.29, 146.54, 144.67, 134.51, 134.43, 131.72, 130.61, 129.16, 127.88, 124.52, 119.02, 70.59, 63.72, 59.09, 18.87. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{18}NO_3^+$ $[M+H]^+$ 272.1287, found 272.1294. IR (film) ν_{max} 2925, 1709, 1635, 1453, 1372, 1309, 1277, 1235, 1172, 1149, 1129, 1042, 983, 863, 814 cm^{-1}.



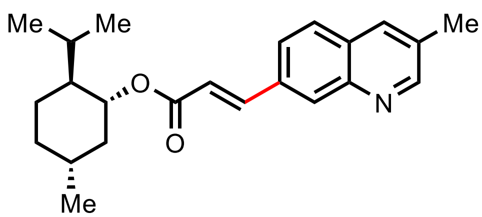
(*E*)-3-Methyl-7-(2-(methylsulfonyl)vinyl)quinoline (3u) The general procedure 2.5 was followed and purification by preparative TLC (EA/acetone = 10/1) furnished compound **3u** as a white solid (5.5 mg, 45%, C7:others > 99:1). TLC: R_f = 0.2 (EA/acetone = 10/1). mp: 180-182 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (d, *J* = 2.3 Hz, 1H), 8.20 (s, 1H), 7.93 (s, 1H), 7.83 – 7.77 (m, 2H), 7.64 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.06 (d, *J* = 15.4 Hz, 1H), 3.08 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.67, 146.34, 143.64, 134.45, 132.44, 132.08, 131.44, 129.67, 128.30, 127.24, 124.56, 43.33, 18.92. HRMS (ESI-TOF) *m/z* Calcd for $C_{13}H_{14}NO_2S^+$ $[M+H]^+$ 248.0745, found 248.0750. IR (film) ν_{max} 2925, 1278, 1127, 990, 971, 890, 800, 763, 750 cm^{-1}.



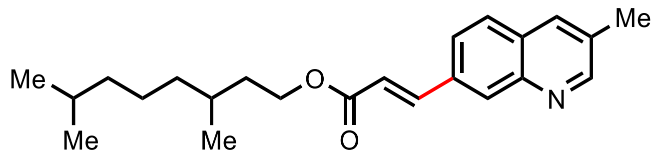
Diethyl (*E*)-(2-(3-methylquinolin-7-yl)vinyl)phosphonate (3v) The general procedure 2.5 was followed and purification by preparative TLC (EA/acetone = 1/1) furnished compound **3v** as a white solid (10.0 mg, 66%, C7:others > 99:1). TLC: R_f = 0.2 (EA/acetone = 1/1). mp: 88-90 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.14 (s, 1H), 7.91 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.72 – 7.65 (m, 2H), 6.42 (t, *J* = 17.3 Hz, 1H), 4.20 – 4.14 (m, 4H), 2.54 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.32, 148.14 (d, *J* = 7.1 Hz), 146.51 (d, *J* = 1.7 Hz), 134.95 (d, *J* = 23.3 Hz), 134.43, 131.69, 129.94, 129.08, 127.83, 124.36, 115.47 (d, *J* = 191.0 Hz), 62.01, 61.97, 18.87, 16.47, 16.42. HRMS (ESI-TOF) *m/z* Calcd for $C_{16}H_{21}NO_3P^+$ $[M+H]^+$ 306.1259, found 306.1258. IR (film) ν_{max} 2982, 2927, 1617, 1454, 1391, 1235, 1049, 1023, 963, 857, 806 cm^{-1}.



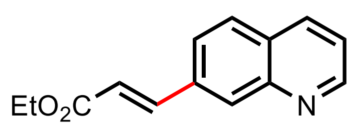
(*E*)-3-methyl-7-(2-(perfluorophenyl)vinyl)quinoline (3w) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3w** as a white solid (11.7 mg, 70%, C7:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 85-87 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.14 (s, 1H), 7.91 (s, 1H), 7.77 – 7.73 (m, 2H), 7.62 (d, *J* = 16.7 Hz, 1H), 7.16 (d, *J* = 16.7 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.17, 146.72, 144.93 (dm, *J* = 247.0 Hz), 139.94 (dm, *J* = 254.8 Hz), 137.83 (dm, *J* = 250.3 Hz), 136.81 – 136.65 (m), 136.66, 134.48, 131.15, 128.43, 127.76, 127.38, 124.20, 114.06 (d, *J* = 3.5 Hz), 112.27 (td, *J* = 13.7, 4.2 Hz), 18.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -145.02 (dd, *J* = 22.1, 8.3 Hz, 2F), -158.61 (t, *J* = 21.5 Hz, 1F), -165.39 (td, *J* = 21.8, 7.9 Hz, 2F). HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{11}F_5N^+$ [M+H]$^+$ 336.0812, found 336.0815. IR (film) ν_{max} 2924, 2852, 1520, 1493, 1276, 1261, 1002, 965, 902, 750 cm^{-1}.



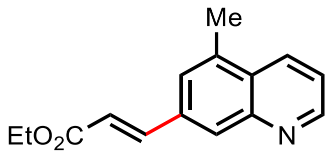
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3x) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3x** as a white solid (10.5 mg, 60%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 135-137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.88 – 4.83 (m, 1H), 2.53 (d, *J* = 1.0 Hz, 3H), 2.11 – 2.07 (m, 1H), 1.95 (ddd, *J* = 11.3, 7.0, 3.5 Hz, 1H), 1.72 (dt, *J* = 14.4, 2.9 Hz, 2H), 1.56 – 1.53 (m, 1H), 1.50 – 1.47 (m, 1H), 1.10 (dd, *J* = 23.4, 11.3 Hz, 2H), 0.93 (dd, *J* = 6.8, 3.6 Hz, 7H), 0.81 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.44, 153.24, 146.56, 143.88, 134.71, 134.43, 131.62, 130.43, 129.06, 127.80, 124.55, 119.97, 74.47, 47.22, 41.04, 34.32, 31.46, 26.41, 23.59, 22.06, 20.78, 18.87, 16.49. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{30}NO_2^+$ [M+H]$^+$ 352.2277, found 352.2281. $[\alpha]_D^{21}$ = – 63.7 (*c* 0.1, $CHCl_3$). IR (film) ν_{max} 2954, 2868, 1701, 1632, 1458, 1308, 1276, 1262, 1176, 993, 812, 751cm^{-1}.



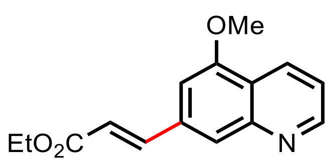
3,7-Dimethyloctyl (*E*)-3-(3-methylquinolin-7-yl)acrylate (3y) The general procedure 2.5 was followed and purification by preparative TLC (DCM) furnished compound **3y** as a white solid (11.5 mg, 65%, C7:others = 95:5). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 53-55 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 4.31 – 4.22 (m, 2H), 2.53 (s, 3H), 1.80 – 1.74 (m, 1H), 1.62 (dd, *J* = 12.3, 6.9 Hz, 1H), 1.56 – 1.49 (m, 2H), 1.33 (ddt, *J* = 9.4, 5.1, 2.8 Hz, 2H), 1.29 – 1.25 (m, 1H), 1.20 – 1.14 (m, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.96, 153.27, 146.55, 144.06, 134.63, 134.43, 131.66, 130.43, 129.10, 127.83, 124.57, 119.55, 63.35, 39.23, 37.18, 35.64, 29.94, 27.97, 24.65, 22.71, 22.62, 19.59, 18.87. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{32}NO_2^+$ $[M+H]^+$ 354.2433, found 354.2430. IR (film) ν_{max} 2954, 2926, 1710, 1636, 1458, 1381, 1308, 1291, 1234, 1170, 1148, 983, 814 cm^{-1}.



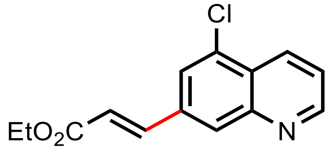
Ethyl (*E*)-3-(quinolin-7-yl)acrylate (3z) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **3z** as a white solid (6.0 mg, 53%, C7:C3 = 90:10). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 55-57 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.20 (s, 1H), 8.15 (d, *J* = 7.4 Hz, 1H), 7.88 (d, *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.43 (dd, *J* = 8.2, 4.2 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.75, 151.27, 148.35, 143.88, 135.76, 135.59, 130.59, 129.20, 128.50, 124.54, 121.93, 120.10, 60.73, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{14}NO_2^+$ $[M+H]^+$ 228.1025, found 228.1026. IR (film) ν_{max} 2982, 1709, 1637, 1503, 1448, 1368, 1307, 1265, 1176, 1036, 985, 836, 764 cm^{-1}.



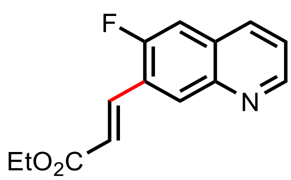
Ethyl (*E*)-3-(5-methylquinolin-7-yl)acrylate (3aa) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3aa** as a white solid (6.3 mg, 52%, C7:C3 = 90:10). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 98-100 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.6 Hz, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.06 (s, 1H), 7.84 (d, J = 16.0 Hz, 1H), 7.57 (s, 1H), 7.45 (dd, J = 8.5, 4.1 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.71 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.83, 150.79, 148.65, 144.04, 135.41, 135.09, 132.32, 129.07, 128.72, 124.80, 121.56, 119.81, 60.68, 18.77, 14.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_2^+$ [M+H]$^+$ 242.1181, found 242.1187. IR (film) ν_{max} 2975, 1701, 1628, 1446, 1368, 1288, 1241, 1182, 1039, 997, 876 cm^{-1}.



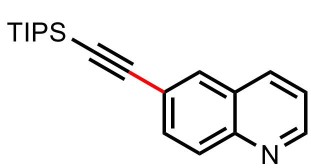
Ethyl (*E*)-3-(5-methoxyquinolin-7-yl)acrylate (3ab) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **3ab** as a white solid (7.2 mg, 56%, C7:C3 = 88:12). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 124-126 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, J = 4.2, 1.8 Hz, 1H), 8.54 (ddd, J = 8.4, 1.7, 0.8 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.40 (dd, J = 8.4, 4.2 Hz, 1H), 7.00 (d, J = 1.4 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.05 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.77, 155.55, 151.48, 149.06, 144.49, 135.52, 130.73, 123.79, 122.16, 121.13, 119.62, 101.46, 60.72, 55.83, 14.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{16}NO_3^+$ [M+H]$^+$ 258.1130, found 258.1142. IR (film) ν_{max} 2924, 1699, 1613, 1589, 1450, 1397, 1373, 1282, 1241, 1148, 1105, 1043, 994, 862 cm^{-1}.



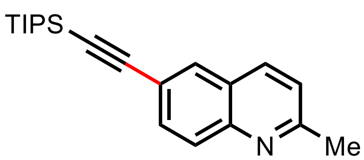
Ethyl (*E*)-3-(5-chloroquinolin-7-yl)acrylate (3ac) The general procedure 2.5 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **3ac** as a white solid (5.9 mg, 45%, C7:C3 = 90:10). TLC: R_f = 0.3 (hexane/EA = 10/1). mp: 100-102 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (dd, J = 4.2, 1.7 Hz, 1H), 8.56 (ddd, J = 8.5, 1.7, 0.9 Hz, 1H), 8.13 (s, 1H), 7.84 – 7.77 (m, 2H), 7.54 (dd, J = 8.5, 4.2 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.41, 151.83, 148.89, 142.55, 135.61, 132.79, 132.29, 129.66, 127.19, 124.45, 122.65, 120.99, 60.86, 14.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}ClNO_2^+$ $[M+H]^+$ 262.0635, found 262.0651. IR (film) ν_{max} 2926, 1711, 1557, 1445, 1365, 1290, 1242, 1177, 1052, 980, 934, 867, 805 cm^{-1}.



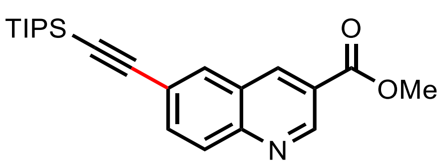
Ethyl (*E*)-3-(6-fluoroquinolin-7-yl)acrylate (3ad) The general procedure 2.5 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **3ad** as a white solid (4.7 mg, 38%, C7:C3 = 88:12). TLC: R_f = 0.3 (hexane/EA = 20/1). mp: 58-60 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (d, J = 3.0 Hz, 1H), 8.30 (d, J = 7.1 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 16.2 Hz, 1H), 7.48 (d, J = 10.8 Hz, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 6.76 (d, J = 16.2 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.60, 158.80 (d, J = 254.9 Hz), 150.59 (d, J = 2.9 Hz), 145.13, 137.09 (d, J = 2.6 Hz), 135.01 (d, J = 5.5 Hz), 131.40 (d, J = 4.9 Hz), 129.58 (d, J = 10.6 Hz), 126.59 (d, J = 16.0 Hz), 123.04 (d, J = 7.1 Hz), 122.47, 111.71 (d, J = 23.0 Hz), 60.85, 14.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.18. HRMS (ESI-TOF) *m/z* Calcd for $C_{14}H_{13}FNO_2^+$ $[M+H]^+$ 246.0930, found 246.0935. IR (film) ν_{max} 2927, 1711, 1631, 1500, 1458, 1369, 1283, 1226, 1179, 1162, 1108, 1037, 982, 862 cm^{-1}.



6-((Triisopropylsilyl)ethynyl)quinoline (4a) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4a** as colorless oil (20.4 mg, 66%, C6:others = 96:4). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.76 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.92, 147.70, 135.70, 132.60, 131.53, 129.45, 127.92, 121.84, 121.71, 106.52, 92.32, 18.70, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{28}NSi^+$ $[M+H]^+$ 310.1991, found 310.1994. IR (film) ν_{max} 2942, 2864, 2153, 1592, 1492, 1462, 1370, 1320, 1213, 1072, 995, 907, 883, 838, 795, 758, 675, 660 cm^{-1}.

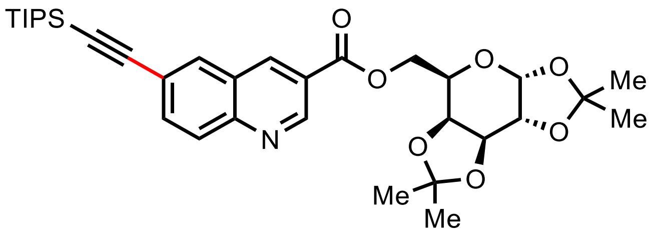


2-Methyl-6-((triisopropylsilyl)ethynyl)quinoline (4b) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4b** as a pale yellow solid (16.1 mg, 50%, C6:others = 98:2). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 86-88 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.72 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 2.74 (s, 3H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.76, 147.32, 135.80, 132.63, 131.30, 128.62, 126.11, 122.65, 120.88, 106.72, 91.67, 25.45, 18.70, 11.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{30}NSi^+$ $[M+H]^+$ 324.2148, found 324.2154. IR (film) ν_{max} 2941, 2864, 2154, 1597, 1491, 1463, 1386, 1276, 1220, 1073, 995, 923, 884, 838, 762, 699, 675, 631 cm^{-1}.

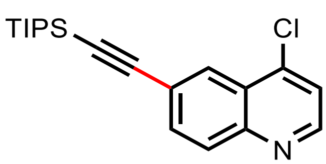


Methyl 6-((triisopropylsilyl)ethynyl)quinoline-3-carboxylate (4c) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4c** as a pale yellow solid (17.2 mg, 47%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 63-65 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (d, *J* = 2.1 Hz, 1H), 8.79 (d, *J* = 1.7 Hz, 1H), 8.08 (d,

J = 8.7 Hz, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.86 (dd, J = 8.7, 1.8 Hz, 1H), 4.02 (s, 3H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.63, 150.47, 149.18, 138.33, 134.90, 132.58, 129.46, 126.59, 123.62, 122.88, 105.87, 93.52, 52.59, 18.68, 11.31. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{30}NO_2Si^+$ $[M+H]^+$ 368.2046, found 368.2043. IR (film) ν_{max} 2943, 2865, 2154, 1727, 1600, 1494, 1462, 1441, 1337, 1278, 1237, 1104, 995, 936, 882, 841, 767, 677, 661 cm^{-1}.

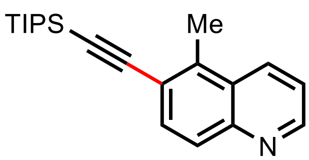


((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 6-((triisopropylsilyl)ethynyl)quinoline-3-carboxylate (4d) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4d** as pale yellow oil (32.7 mg, 55%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.43 (d, J = 2.1 Hz, 1H), 8.79 (d, J = 1.9 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.86 (dd, J = 8.7, 1.8 Hz, 1H), 5.58 (d, J = 4.9 Hz, 1H), 4.68 (dd, J = 7.8, 2.5 Hz, 1H), 4.61 (dd, J = 11.5, 4.7 Hz, 1H), 4.55 (dd, J = 11.5, 7.7 Hz, 1H), 4.38 – 4.35 (m, 2H), 4.24 (ddd, J = 7.0, 4.7, 1.9 Hz, 1H), 1.53 (s, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.17 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.01, 150.55, 149.21, 138.44, 134.93, 132.62, 129.45, 126.57, 123.56, 122.86, 109.82, 108.88, 105.88, 96.34, 93.51, 71.14, 70.78, 70.51, 66.09, 64.52, 29.71, 26.07, 26.00, 24.97, 24.51, 18.69, 11.31. HRMS (ESI-TOF) *m/z* Calcd for $C_{33}H_{46}NO_7Si^+$ $[M+H]^+$ 596.3044, found 596.3060. $[\alpha]_D^{21}$ = – 30.0 (c 0.1, $CHCl_3$). IR (film) ν_{max} 2941, 2865, 1726, 1600, 1495, 1462, 1380, 1277, 1256, 1237, 1214, 1168, 1104, 1071, 1005, 885, 842, 763, 678 cm^{-1}.

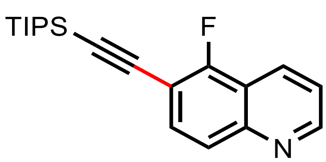


4-Chloro-6-((triisopropylsilyl)ethynyl)quinoline (4e) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4e** as colorless oil

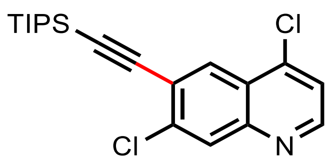
(13.0 mg, 38%, C6:others = 98:2). TLC: R_f = 0.3 (hexane/EA = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.7 Hz, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.80 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.50 (d, *J* = 4.7 Hz, 1H), 1.17 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.30, 148.49, 142.24, 133.61, 129.85, 127.72, 126.32, 123.03, 121.85, 106.19, 93.55, 18.69, 11.32. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{27}ClNSi^+$ $[M+H]^+$ 344.1601, found 344.1609. IR (film) ν_{max} 2942, 2865, 2149, 1579, 1548, 1490, 1463, 1350, 1223, 1161, 992, 911, 884, 846, 678, 659 cm^{-1}.



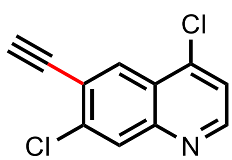
5-Methyl-6-((triisopropylsilyl)ethynyl)quinoline (4f) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 15/1) furnished compound **4f** as a white solid (14.8 mg, 46%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 30/1). mp: 46-48 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.29 (ddd, *J* = 8.6, 1.7, 0.9 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.37 (dd, *J* = 8.5, 4.2 Hz, 1H), 2.78 (s, 3H), 1.10 (d, *J* = 2.9 Hz, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.29, 148.00, 137.84, 132.77, 132.72, 127.48, 127.38, 121.26, 121.24, 106.05, 96.31, 18.73, 16.57, 11.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{30}NSi^+$ $[M+H]^+$ 324.2148, found 324.2160. IR (film) ν_{max} 2940, 2864, 2160, 1565, 1493, 1462, 1382, 1261, 1070, 995, 883, 836, 805, 764, 676, 659 cm^{-1}.



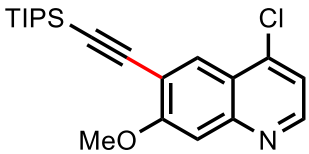
5-Fluoro-6-((triisopropylsilyl)ethynyl)quinoline (4g) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 15/1) furnished compound **4g** as colorless oil (12.8 mg, 39%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.34 (ddd, *J* = 8.4, 1.8, 0.9 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 8.8, 7.4 Hz, 1H), 7.40 (dd, *J* = 8.5, 4.2 Hz, 1H), 1.10 (d, *J* = 3.4 Hz, 16H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.97 (d, *J* = 261.6 Hz), 151.56, 148.44 (d, *J* = 3.3 Hz), 132.35, 129.19 (d, J = 4.5 Hz), 125.05 (d, J = 4.4 Hz), 121.70, 118.90 (d, J = 15.9 Hz), 107.30 (d, J = 14.8 Hz), 99.47, 98.75 (d, J = 4.8 Hz), 18.65, 11.27. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.11. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{27}FNSi^+$ $[M+H]^+$ 328.1897, found 328.1906. IR (film) ν_{max} 2942, 2865, 1971, 1592, 1564, 1489, 1466, 1384, 1232, 1170, 1070, 996, 957, 883, 833, 809, 702, 673, 660 cm^{-1}.



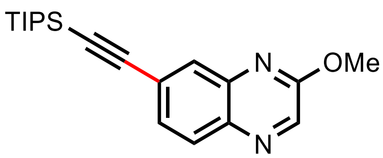
4,7-Dichloro-6-((triisopropylsilyl)ethynyl)quinoline (4h) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 3/1) furnished compound **4h** as a pale yellow solid (23.4 mg, 62%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 65-67 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, J = 4.7 Hz, 1H), 8.37 (s, 1H), 8.17 (s, 1H), 7.48 (d, J = 4.7 Hz, 1H), 1.18 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.34, 148.47, 142.08, 137.78, 129.46, 124.95, 123.38, 121.87, 102.32, 99.28, 18.68, 11.31. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{26}Cl_2NSi^+$ $[M+H]^+$ 378.1212, found 378.1212. IR (film) ν_{max} 2942, 2865, 2153, 1606, 1578, 1543, 1465, 1423, 1327, 1220, 1063, 1025, 996, 886, 846, 778, 679, 662 cm^{-1}.



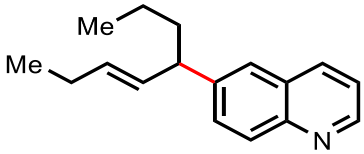
4,7-Dichloro-6-ethynylquinoline (4h') Treating **4h** with TBAF (2 equiv) in THF for 5 min furnished compound **4h'** (white solid, 96%). TLC: R_f = 0.3 (hexane/EA = 5/1). mp: 173-175 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, J = 4.7 Hz, 1H), 8.38 (s, 1H), 8.12 (s, 1H), 7.44 (d, J = 4.7 Hz, 1H), 3.44 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.75, 148.73, 142.23, 137.36, 130.34, 129.67, 124.94, 122.06, 122.01, 83.87, 79.65. HRMS (ESI-TOF) *m/z* Calcd for $C_{11}H_6Cl_2N^+$ $[M+H]^+$ 221.9877, found 221.9885. IR (film) ν_{max} 3189, 2160, 2136, 1546, 1469, 1330, 1276, 1261, 1022, 891, 751, 622 cm^{-1}.



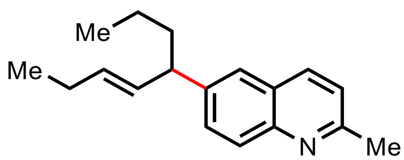
4-Chloro-7-methoxy-6-((triisopropylsilyl)ethynyl)quinoline (4i) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 2/1) furnished compound **4i** as a pale yellow solid (22.4 mg, 60%, C6:others > 99:1). TLC: R_f = 0.3 (hexane/EA = 3/1). mp: 92-94 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, J = 4.8 Hz, 1H), 8.28 (s, 1H), 7.39 (s, 1H), 7.34 (d, J = 4.8 Hz, 1H), 4.00 (s, 3H), 1.18 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.13, 150.64, 150.33, 141.90, 129.43, 121.18, 119.70, 116.62, 107.28, 101.88, 98.02, 56.12, 18.68, 11.36. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{29}ClNOSi^+$ $[M+H]^+$ 374.1707, found 374.1719. IR (film) ν_{max} 2940, 2964, 2149, 1618, 1549, 1466, 1440, 1334, 1290, 1253, 1242, 1138, 1018, 997, 882, 853, 799, 741, 677 cm^{-1}.



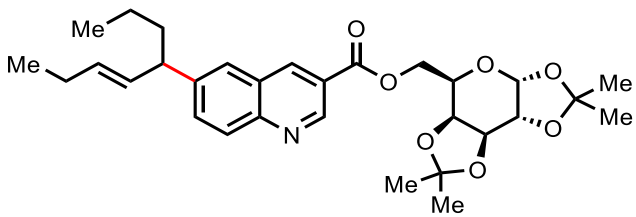
2-Methoxy-7-((triisopropylsilyl)ethynyl)quinoxaline (4j) The general procedure 2.6 was followed and purification by preparative TLC (hexane/EA = 20/1) furnished compound **4j** as colorless oil (8.5 mg, 25%, C7:others = 89:11). TLC: R_f = 0.3 (hexane/EA = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.98 (d, J = 1.7 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.61 (dd, J = 8.5, 1.8 Hz, 1H), 4.09 (s, 3H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.09, 140.14, 139.86, 138.58, 130.82, 129.82, 128.85, 125.38, 106.30, 93.50, 53.80, 18.68, 11.31. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{29}N_2OSi^+$ $[M+H]^+$ 341.2049, found 341.2049. IR (film) ν_{max} 2943, 2865, 2153, 1578, 1499, 1461, 1379, 1341, 1304, 1218, 1020, 987, 912, 884, 834, 751, 677 cm^{-1}.



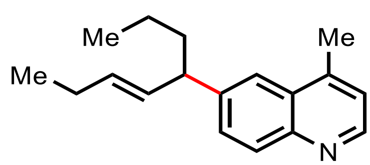
(*E*)-6-(Oct-5-en-4-yl)quinoline (5a) The general procedure 2.7 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **5a** as colorless oil (18.0 mg, 75%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.10 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.60 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.53 (dt, *J* = 15.3, 6.1 Hz, 1H), 3.40 (q, *J* = 7.4 Hz, 1H), 2.03 (p, *J* = 7.1 Hz, 2H), 1.75 (q, *J* = 7.6 Hz, 2H), 1.34 (dt, *J* = 15.0, 7.0 Hz, 1H), 1.24 (dt, *J* = 13.7, 7.1 Hz, 1H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.67, 147.27, 143.99, 135.72, 132.50, 132.40, 130.05, 129.35, 128.35, 125.32, 121.00, 48.46, 38.17, 25.62, 20.72, 14.02, 13.83. HRMS (ESI-TOF) *m/z* Calcd for $C_{17}H_{22}N^+$ $[M+H]^+$ 240.1752, found 240.1758. IR (film) ν_{max} 2960, 2931, 2871, 1678, 1623, 1593, 1501, 1460, 1377, 1172, 1123, 970, 884, 837, 801, 776 cm^{-1}.



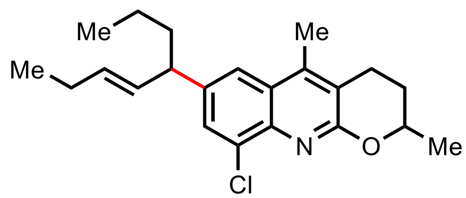
(*E*)-2-Methyl-6-(oct-5-en-4-yl)quinoline (5b) The general procedure 2.7 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **5b** as colorless oil (16.2 mg, 64%, C6:others = 84:16). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 5.59 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.52 (dt, *J* = 15.3, 6.1 Hz, 1H), 3.37 (q, *J* = 7.5 Hz, 1H), 2.72 (s, 3H), 2.02 (q, *J* = 7.1 Hz, 2H), 1.75 – 1.71 (m, 2H), 1.33 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.23 (dd, *J* = 14.3, 7.1 Hz, 1H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.13, 146.80, 143.01, 135.89, 132.65, 132.22, 129.94, 128.51, 126.50, 125.09, 121.88, 48.38, 38.22, 25.62, 25.27, 20.72, 14.03, 13.85. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{24}N^+$ $[M+H]^+$ 254.1909, found 254.1915. IR (film) ν_{max} 2958, 2929, 2870, 1675, 1601, 1497, 1459, 1377, 1310, 1224, 1174, 1122, 968, 890, 836, 814 cm^{-1}.



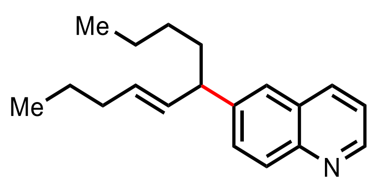
((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 6-((*E*)-oct-5-en-4-yl)quinoline-3-carboxylate (5c) The general procedure 2.7 was followed and purification by preparative TLC (DCM/EA = 5/1) furnished compound **5c** as colorless oil (29.9 mg, 57%, C6:others = 90:10). TLC: R_f = 0.3 (hexane/EA = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (d, J = 2.2 Hz, 1H), 8.81 (d, J = 2.1 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.72 – 7.67 (m, 2H), 5.61 – 5.52 (m, 3H), 4.68 (dd, J = 7.9, 2.5 Hz, 1H), 4.62 (dd, J = 11.5, 4.6 Hz, 1H), 4.53 (dd, J = 11.5, 7.7 Hz, 1H), 4.38 – 4.36 (m, 2H), 4.25 (ddd, J = 6.9, 4.6, 1.9 Hz, 1H), 3.43 (q, J = 7.3 Hz, 1H), 2.07 – 2.01 (m, 2H), 1.76 (q, J = 7.6 Hz, 2H), 1.53 (s, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.34 (m, 4H), 1.26 – 1.23 (m, 1H), 0.98 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.41, 149.38, 148.89, 145.05, 138.59, 132.79, 132.62, 132.14, 129.33, 126.90, 126.64, 122.80, 109.80, 108.88, 96.35, 71.17, 70.78, 70.53, 66.16, 64.37, 48.34, 38.08, 26.07, 26.00, 25.61, 24.98, 24.51, 20.69, 14.00, 13.80. HRMS (ESI-TOF) *m/z* Calcd for $C_{30}H_{40}NO_7^+$ $[M+H]^+$ 526.2805, found 526.2806. $[\alpha]_D^{21}$ = – 83.2 (*c* 0.1, $CHCl_3$). IR (film) ν_{max} 2963, 2932, 1723, 1602, 1501, 1453, 1379, 1281, 1238, 1213, 1168, 1104, 1070, 1004, 895, 763 cm^{-1}.



(*E*)-4-Methyl-6-(oct-5-en-4-yl)quinoline (5d) The general procedure 2.7 was followed and purification by preparative TLC (DCM/EA = 10/1) furnished compound **5d** as colorless oil (15.2 mg, 60%, C6:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 4.4 Hz, 1H), 8.03 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.57 (dd, J = 8.7, 2.0 Hz, 1H), 7.20 (d, J = 4.0 Hz, 1H), 5.61 (dd, J = 15.3, 7.5 Hz, 1H), 5.54 (dt, J = 15.4, 6.1 Hz, 1H), 3.42 (q, J = 7.5 Hz, 1H), 2.70 (s, 3H), 2.04 (p, J = 7.1 Hz, 2H), 1.77 – 1.73 (m, 2H), 1.37 – 1.31 (m, 1H), 1.26 – 1.21 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.41, 146.90, 143.84, 143.73, 132.65, 132.35, 129.95, 129.44, 128.26, 121.85, 121.52, 48.81, 38.32, 25.63, 20.77, 18.73, 14.04, 13.86. HRMS (ESI-TOF) *m/z* Calcd for $C_{18}H_{24}N^+$ $[M+H]^+$ 254.1909, found 254.1911. IR (film) ν_{max} 2960, 2931, 2872, 1681, 1592, 1504, 1461, 1364, 1242, 845 cm^{-1}.

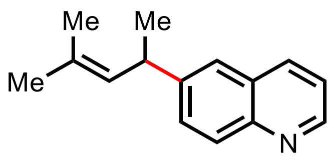


(*E*)-9-Chloro-2,5-dimethyl-7-(oct-5-en-4-yl)-3,4-dihydro-2*H*-pyrano[2,3-b]quinoline (5e) The general procedure 2.7 was followed and purification by preparative TLC (hexane/DCM = 1/1) furnished compound **5e** as a white solid (10.3 mg, 29%, C_{shown}:others = 88:12). TLC: R_f = 0.3 (hexane/DCM = 2/1). mp: 121-123 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.4 Hz, 2H), 5.58 – 5.49 (m, 2H), 4.41 – 4.36 (m, 1H), 3.31 (q, *J* = 7.2 Hz, 1H), 3.01 – 2.97 (m, 1H), 2.87 (td, *J* = 11.6, 5.8 Hz, 1H), 2.55 (s, 3H), 2.16 – 2.12 (m, 1H), 2.04 (p, *J* = 7.3 Hz, 2H), 1.81 (dd, *J* = 12.0, 5.7 Hz, 1H), 1.71 (dd, *J* = 11.5, 4.8 Hz, 2H), 1.53 (d, *J* = 6.3 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 1H), 1.25 – 1.21 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.04, 144.43, 141.04, 140.87, 132.44, 132.40, 131.43, 129.01, 126.13, 120.29, 117.06, 73.33, 48.54, 38.26, 28.87, 25.60, 23.66, 21.32, 20.72, 14.29, 14.01, 13.84. HRMS (ESI-TOF) *m/z* Calcd for $C_{22}H_{29}ClNO^+$ $[M+H]^+$ 358.1938, found 358.1937. IR (film) ν_{max} 2959, 2930, 2872, 1596, 1483, 1446, 1403, 1336, 1264, 1137, 1074, 962, 864, 830, 780, 732 cm^{-1}.

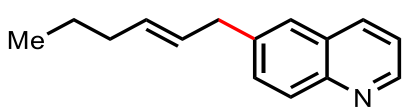


(*E*)-6-(Dec-6-en-5-yl)quinoline (5f) The general procedure 2.7 was followed except using *trans*-5-decene (3 equiv) and purification by preparative TLC (DCM/EA = 10/1) furnished compound **5f** as colorless oil (21.4 mg, 80%, C6:others = 90:10). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.10 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.60 (ddt, *J* = 15.3, 7.7, 1.3 Hz, 1H), 5.48 (dtd, *J* = 15.1, 6.7, 1.0 Hz, 1H), 3.38 (q, *J* = 7.5 Hz, 1H), 2.00 (q, *J* = 7.0 Hz, 2H), 1.79 – 1.75 (m, 2H), 1.38 (q, *J* = 7.3 Hz, 2H), 1.34 – 1.29 (m, 3H), 1.22 – 1.17 (m, 1H), 0.87 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.67, 147.27, 144.06, 135.74, 133.73, 130.70, 130.06, 129.33, 128.36, 125.30, 121.00, 48.78, 35.68, 34.68, 29.84, 22.65, 22.59, 14.04, 13.65.

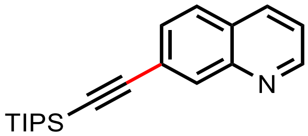
HRMS (ESI-TOF) *m/z* Calcd for $C_{19}H_{26}5N^+$ $[M+H]^+$ 268.2065, found 268.2066. IR (film) ν_{max} 2957, 2927, 2858, 1594, 1572, 1500, 1461, 1377, 1119, 969, 885, 838, 799 cm^{-1}.



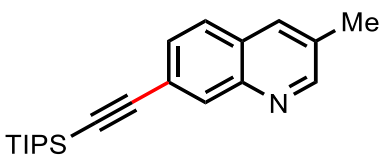
6-(4-Methylpent-3-en-2-yl)quinoline (5g) The general procedure 2.7 was followed except using *trans*-4-methyl-2-pentene (3 equiv) and purification by preparative TLC (hexane/EA = 10/1) furnished compound **5g** as colorless oil (13.1 mg, 62%, C6:others = 85:15). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.30 – 7.28 (m, 1H), 5.27 (dp, *J* = 9.2, 1.4 Hz, 1H), 3.78 (dq, *J* = 9.3, 6.9 Hz, 1H), 1.67 (d, *J* = 1.4 Hz, 3H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.33 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.64, 147.18, 145.63, 135.75, 131.47, 129.91, 129.51, 129.36, 128.36, 124.23, 121.01, 38.12, 25.84, 22.36, 18.08. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{18}N^+$ $[M+H]^+$ 212.1439, found 212.1450. IR (film) ν_{max} 2964, 2925, 1593, 1571, 1499, 1451, 1376, 1322, 1119, 1056, 885, 836, 798 cm^{-1}.



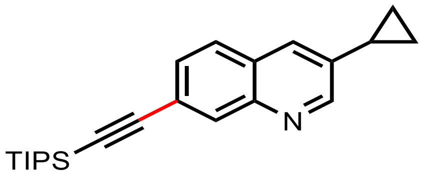
(*E*)-6-(Hex-2-en-1-yl)quinoline (5h) The general procedure 2.7 was followed except using 1-hexene (3 equiv) and purification by preparative TLC (hexane/EA = 10/1) furnished compound **5h** as colorless oil (10.8 mg, 51%, C6:others = 86:14). TLC: R_f = 0.3 (hexane/EA = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.12 – 8.10 (m, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.40 – 7.38 (m, 1H), 5.69 – 5.64 (m, 1H), 5.63 – 5.58 (m, 1H), 3.54 (d, *J* = 6.4 Hz, 2H), 2.09 – 2.04 (m, 2H), 1.46 – 1.42 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.80, 151.34, 149.04, 143.61, 136.48, 132.73, 130.27, 129.23, 128.27, 127.28, 121.87, 119.65, 60.69, 14.34. HRMS (ESI-TOF) *m/z* Calcd for $C_{15}H_{18}N^+$ $[M+H]^+$ 212.1439, found 212.1445. IR (film) ν_{max} 2958, 2928, 2870, 1690, 1593, 1501, 1461, 1378, 1322, 1185, 1119, 969, 888, 835, 799 cm^{-1}.



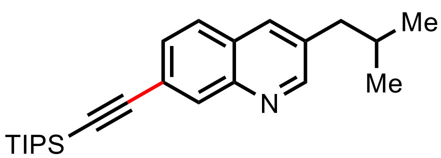
7-((Triisopropylsilyl)ethynyl)quinoline (6a) The general procedure 2.8 was followed except using ***(S,S)*-T25** (0.3 equiv), $Pd(OAc)_2$ (20 mol%), Ac-*L*-Phe-OH (40 mol%), triisopropylsilyl acetylene bromide (4 equiv) at 100 ^{o}C and purification by preparative TLC (hexane/EA = 20/1) furnished compound **6a** as colorless oil (5.5 mg, 36%, C7:others = 88:12). TLC: R_f = 0.3 (hexane/EA = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.27 (dt, *J* = 1.5, 0.7 Hz, 1H), 8.14 (ddd, *J* = 8.3, 1.8, 0.8 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.41 (dd, *J* = 8.2, 4.2 Hz, 1H), 1.19 (d, *J* = 3.0 Hz, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.13, 147.90, 135.71, 133.28, 129.50, 127.98, 127.70, 124.67, 121.47, 106.58, 93.19, 18.69, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{20}H_{28}NSi^{+}$ $[M+H]^{+}$ 310.1991, found 310.1991. IR (film) ν_{max} 2942, 2864, 2152, 1616, 1598, 1493, 1462, 1384, 1318, 1258, 1162, 1072, 1016, 995, 955, 916, 883, 836, 768, 753, 675, 659, 623 cm^{-1}.



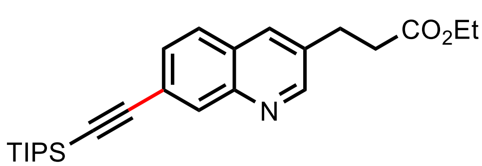
3-Methyl-7-((triisopropylsilyl)ethynyl)quinoline (6b) The general procedure 2.8 was followed and purification by preparative TLC (hexane/EA = 20/1) furnished compound **6b** as a pale yellow solid (7.4 mg, 46%, C7:others = 94:6). TLC: R_f = 0.3 (hexane/EA = 30/1). mp: 47-49 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.2 Hz, 1H), 8.20 (s, 1H), 7.87 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.52 (s, 3H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.14, 146.09, 134.40, 133.04, 131.07, 129.54, 127.85, 127.04, 123.57, 106.77, 92.53, 18.83, 18.68, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{21}H_{30}NSi^{+}$ $[M+H]^{+}$ 324.2148, found 324.2144. IR (film) ν_{max} 2942, 2864, 2154, 1609, 1559, 1462, 1383, 1331, 1203, 1135, 1072, 995, 943, 899, 883, 844, 813, 759, 704, 676, 661, 628 cm^{-1}.



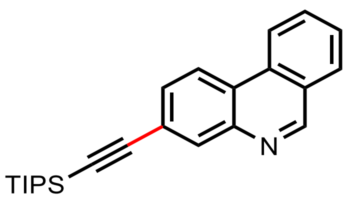
3-Cyclopropyl-7-((triisopropylsilyl)ethynyl)quinoline (6c) The general procedure 2.8 was followed and purification by preparative TLC (hexane/EA = 20/1) furnished compound **6c** as colorless oil (6.8 mg, 39%, C7:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.19 (s, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.07 (td, *J* = 8.5, 4.2 Hz, 1H), 1.16 (m, 21H), 1.12 (dt, *J* = 6.6, 1.6 Hz, 2H), 0.86 (dd, *J* = 5.1, 1.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.36, 146.25, 137.35, 133.01, 130.42, 129.59, 127.83, 127.04, 123.37, 106.82, 92.50, 18.69, 13.47, 11.34, 9.38. HRMS (ESI-TOF) *m/z* Calcd for $C_{23}H_{32}NSi^+$ [M+H]$^+$ 350.2304, found 350.2306. IR (film) ν_{max} 2940, 2864, 2157, 2022, 1607, 1462, 1276, 1019, 994, 949, 917, 884, 814, 756, 676, 626 cm^{-1}.



3-Isobutyl-7-((triisopropylsilyl)ethynyl)quinoline (6d) The general procedure 2.8 was followed and purification by preparative TLC (hexane/EA = 20/1) furnished compound **6d** as colorless oil (6.9 mg, 38%, C7:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.2 Hz, 1H), 8.21 (s, 1H), 7.83 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.66 (d, *J* = 7.2 Hz, 2H), 2.00 (dt, *J* = 13.5, 7.0 Hz, 1H), 1.16 (m, 21H), 0.96 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.20, 146.36, 134.75, 134.62, 133.00, 129.47, 127.81, 127.23, 123.66, 106.80, 92.58, 42.58, 30.12, 22.28, 18.68, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{36}NSi^+$ [M+H]$^+$ 366.2617, found 366.2621. IR (film) ν_{max} 2957, 2865, 2156, 1463, 1383, 1276, 1262, 1199, 994, 910, 883, 751, 674, 629 cm^{-1}.



Ethyl 3-(7-((triisopropylsilyl)ethynyl)quinolin-3-yl)propanoate (6e) The general procedure 2.8 was followed and purification by preparative TLC (hexane/EA = 5/1) furnished compound **6e** as colorless oil (8.6 mg, 42%, C7:others = 91:9). TLC: R_f = 0.3 (hexane/EA = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.16 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.28, 152.42, 146.56, 134.15, 133.74, 133.01, 129.69, 127.72, 127.30, 124.04, 106.65, 92.89, 60.71, 35.26, 28.26, 18.68, 14.19, 11.33. HRMS (ESI-TOF) *m/z* Calcd for $C_{25}H_{36}NO_2Si^+$ $[M+H]^+$ 410.2515, found 410.2528. IR (film) ν_{max} 2939, 2864, 2153, 1735, 1462, 1373, 1333, 1296, 1238, 1190, 1017, 994, 907, 883, 674, 628 cm^{-1}.



3-((Triisopropylsilyl)ethynyl)phenanthridine (6f) The general procedure 2.8 was followed and purification by preparative TLC (hexane/EA = 20/1) furnished compound **6f** as a white solid (5.6 mg, 31%, C_{shown}:others = 92:8). TLC: R_f = 0.3 (hexane/EA = 30/1). mp: 55-57 ºC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 1.7 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.76 – 7.71 (m, 2H), 1.18 (m, 21H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.26, 144.14, 133.89, 132.19, 131.24, 130.15, 128.89, 127.88, 126.53, 124.03, 123.86, 122.22, 122.08, 106.61, 92.64, 18.70, 11.35. HRMS (ESI-TOF) *m/z* Calcd for $C_{24}H_{30}NSi^+$ $[M+H]^+$ 360.2148, found 360.2148. IR (film) ν_{max} 2939, 2864, 2160, 1678, 1612, 1462, 1384, 1249, 1203, 1072, 997, 949, 884, 828, 784, 708, 675, 660, 628 cm^{-1}.

3. Computational Studies

3.1 Computational Methods

All DFT calculations were performed with the Gaussian 16 package[16]. Geometry optimizations were performed in the gas phase with the PBE0[17,18] functional combined with the D3 version of Grimme's dispersion with Becke-Johnson damping(GD3BJ)[19] using the 6-31G(d)[20-22] basis set for all nonmetal atoms and the LANL2DZ[23,24] basis set with effective core potential (ECP) for Pd. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points and to obtain zero-point vibrational energy (ZPVE) and thermal energy corrections at 298.15 K and 1 atm pressure. All transition states were confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. Single-point solvation energies were calculated with 6-311++G(d,p)[25] for all nonmetal atoms and SDD[26,27] for Pd by using the SMD[28,29] solvation model with HFIP (Eps=16.7, EpsInf=1.625625). Detailed methods benchmarks were done for geometry optimization, high basis set energy calculations and SMD solvation model with different HFIP parameters[30-33]. Conformational searches were carried out using MMFF in Spartan 18[34] and the CREST conformer-rotamer ensemble sampling tool, version 2.7.1[35,36] with XTB version 6.2 RC2 (SAW190805)[37-39]. Grimme[40] correction (frequency cut-off is 100 cm^{-1}) for entropy and Head-Gordon[41] correction for enthalpy are performed at 100°C using GoodVibes v3.0.1[42]. Unless otherwise noted, the relative energies reported in the text are Gibbs free energies with solvent effect corrections. Computed structures are illustrated using CYLView[43].

3.2 Methods Benchmark

The popular DFT methods for organometallics are tested for the key CMD TSs. Through the overlay of the optimized CMD TSs with different functionals (**Figure S2**), we could see that the optimized structures are similar at the catalytic center and a little difference in the template portion. PBE0 is one of the popular density functionals for the geometry optimization[44-46] of organometallic systems as well as energy calcualtions[47-49] and have a good performance with adding D3 version of Grimme's dispersion with Becke-Johnson damping. All of the geometries are optimized with PBE0-D3(BJ) functional for the following energy benchmark.

Energy benchmarks are shown in **Table S8** and **Table S9** and the corresponding free energy profiles with different methods are shown in **Figure S3-S12**. The most popular 8 methods for organometallic systems, including GGA functional BP86, meta-GGA functional M06L, hybrid functional B3LYP-D3BJ, B3PW91, PBE0-D3BJ and MN15, hybrid-meta GGA functional M06 and range-separated GGA functional WB97X-D, are tested for the key intermediate and all the TSs. Based on the calculations, we found that these studies require careful benchmarking of methods, attention to the variability of rate-determining step, and exploration of rather complicated surfaces, but ultimately the origins of selectivity can be determined for most of the functionals. M06L, WB97X-D and PBE0-D3BJ were found to be the best three functionals working for both of C6 selective C–H olefination reactions with **T12** and C7 selective C–H olefination reactions with ***cis*-T25**. As shown in **Table S9** and **Figure S7**, solvent effect needs to be considered and HFIP parameters a and b work better than HFIP c parameter.

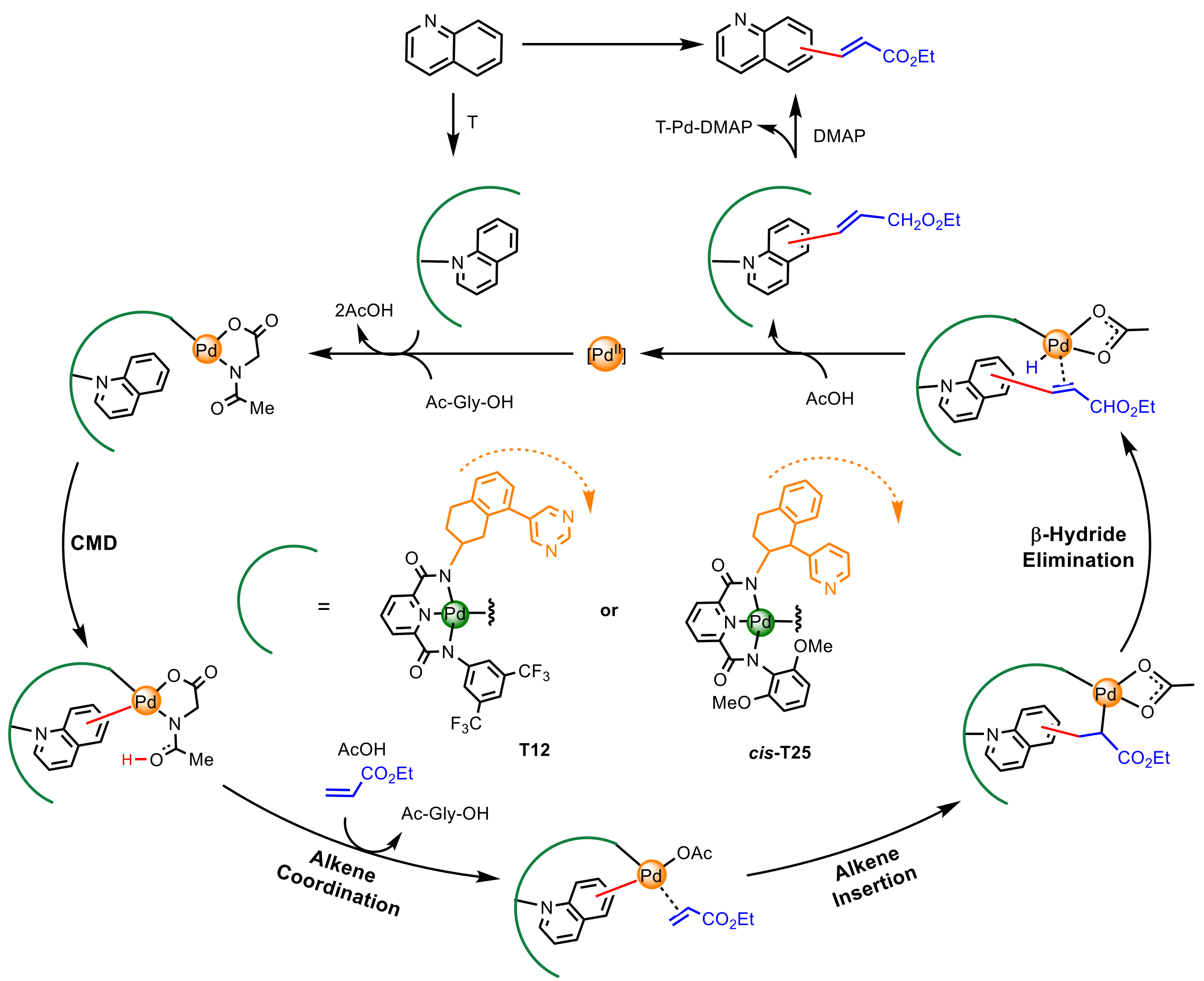


Figure S1. Proposed mechanism.

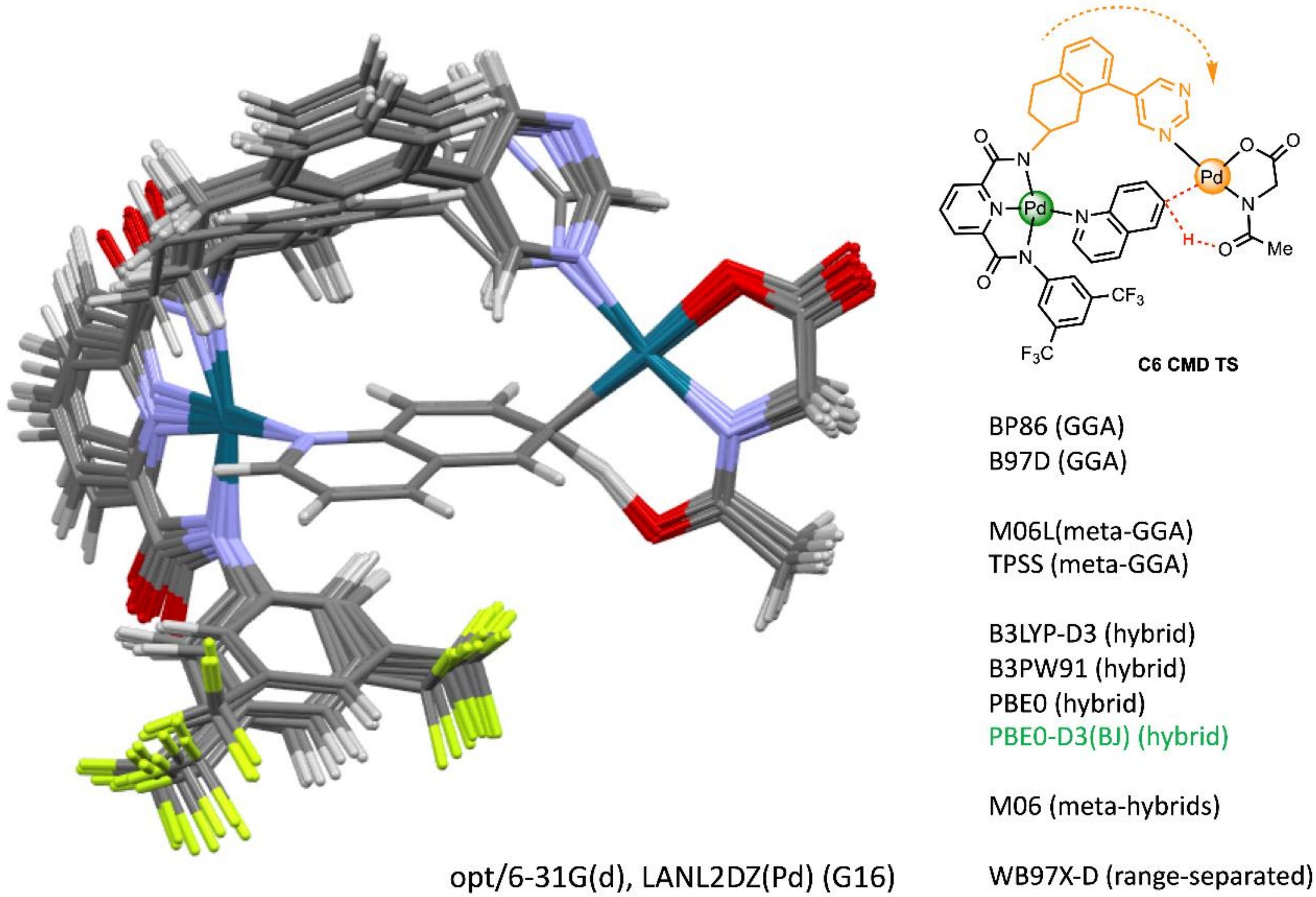
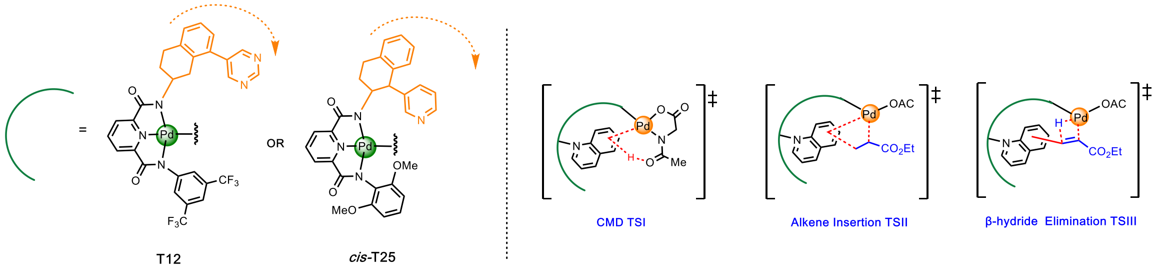


Figure S2. Overlay of optimized structures of C6 CMD TSs with **T12** using different functionals.

Table S8. Methods benchmark for energies.



	B3LYP-D3BJ		M06		MN15		M06L		WB97X-D		B3PW91		BP86		PBE0-D3BJ	
	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}
T12_C5_TSI	-2.0		-1.6		-2.0		-1.1		-1.4		5.4		5.1		-1.5	
T12_C6_TSI	0.0		0.0	19.2	0.0	21.7	0.0		0.0		0.0		0.0		0.0	
T12_C7_TSI	2.4		2.7	21.9	2.4	24.1	1.3	25.7	3.0	22.8	6.4		6.0		2.8	17.6
T12_C5_TSII	1.0	23.3	2.8		0.5		1.3	26.6	1.9	22.0	12.9	36.3	12.5	33.8	2.3	
T12_C6_TSII	0.0	22.2	0.0		0.0		0.0	25.3	0.0	20.0	0.0	23.4	0.0	21.4	0.0	
T12_C7_TSII	-0.7	21.5	0.8		2.1		-0.3		-0.7		7.0	30.3	6.8	28.1	-0.3	
T12_C5_TSIII	5.7		6.4	18.5	7.9	21.2	6.6		6.1		8.6		8.0		6.2	18.3
T12_C6_TSIII	0.0		0.0		0.0		0.0		0.0		0.0		0.0		0.0	15.7
T12_C7_TSIII	-3.1		-2.5		-3.2		-4.4		-3.5		12.2		12.3		-1.9	
Selectivity		**C7**		**C5**		**C5**		**C6**		**C6**		**C6**		**C6**		**C6**

	B3-D3BJ		M06		MN15		M06L		WB97X-D		B3PW91		BP86		PBE0-D3BJ	
	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}
***cis*-T25_C5_TSI**	1.2		0.5		1.1		1.9		1.4		-2.0		-1.4		1.2	
***cis*-T25_C6_TSI**	1.3		0.5		1.4		2.2		1.3		-4.3		-3.5		1.1	
***cis*-T25_C7_TSI**	0.0		0.0		0.0		0.0		0.0		0.0		0.0		0.0	
***cis*-T25_C5_TSII**	4.2	30.6	5.6	25.2	4.0	29.7	5.2	33.6	5.6	29.6	1.4	31.1	1.3	28.6	4.8	
***cis*-T25_C6_TSII**	0.9	28.0	1.9		1.3	27.0	2.7	31.1	2.6	26.6	-5.3	24.3	-5.0	22.3	1.7	

***cis*-T25_C7_TSII**	0.0	25.9	0.0		0.0	25.7	0.0	28.3	0.0	24.1	0.0	29.6	0.0	27.3	0.0	20.5
***cis*-T25_C5_TSIII**	11.1		10.2		12.2		10.0		12.6		0.9		0.9		10.5	24.1
***cis*-T25_C6_TSIII**	7.5		5.8	24.1	9.0		7.2		9.3		-3.6		-3.7		7.2	26.3
***cis*-T25_C7_TSIII**	0.0		0.0	19.7	0.0		0.0		0.0		0.0		0.0		0.0	
Selectivity		**C7**		**C7**		**C7**		**C7**		**C7**		**C6**		**C6**		**C7**

Note: Methods/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3BJ/6-31G(d), LANL2DZ(Pd), with Grimme correction for entropy and Head-Gordon correction for enthalpy at 100°C.

Table S9. Benchmark for HFIP parameters.

	gas		**HFIP[a]**		**HFIP[b]**		**HFIP[c]**	
	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}	$\Delta\Delta G$	ΔG_{Total}
T12_C5_TSI	-3.3		-1.5		-3.8		-8.4	
T12_C6_TSI	0.0	21.4	0.0		0.0		0.0	25.7
T12_C7_TSI	0.0	21.4	2.8	17.6	3.2	18.3	0.6	26.3
T12_C5_TSII	-1.4		2.3		-0.6		-6.3	
T12_C6_TSII	0.0		0.0		0.0		0.0	
T12_C7_TSII	0.7		-0.3		-1.1		-2.5	
T12_C5_TSIII	6.5	22.9	6.2	18.3	6.5	21.6	7.2	27.4
T12_C6_TSIII	0.0		0.0	15.7	0.0	17.4	0.0	
T12_C7_TSIII	-6.3		-1.9		-5.2		-12.4	
Selectivity		**C7**		**C6**		**C6**		**C6**

HFIP[a]	**HFIP[b]**	**HFIP[c]**
Eps=16.7 EpsInf=1.625625	stoichiometry=C3H2O1F6 eps=17.8 solventname=2-propanol epsinf=1.89 molarvolume=94.1 rsolv=2.82 SurfaceTensionAtInterface=23.23 ElectronegativeHalogenicity=0.6 HBondAcidity=0.57 hbondbasicity=0.25	stoichiometry=C3H2F6O1 solventname=1,1,1,3,3,3-hexafluoropropan-2-ol eps=16.7 epsinf=1.625625 HBondAcidity=1.96 HBondBasicity=0.00 SurfaceTensionAtInterface=23.2306248 CarbonAromaticity=0.0 ElectronegativeHalogenicity=0.60

	density=0.158	

Note: PBE0-D3BJ /6-311++G(d,p), SDD(Pd), SMD(HFIP parametes) // PBE0-D3BJ/6-31G(d), LANL2DZ(Pd), with Grimme correction for entropy and Head-Gordon correction for enthalpy at 100℃.

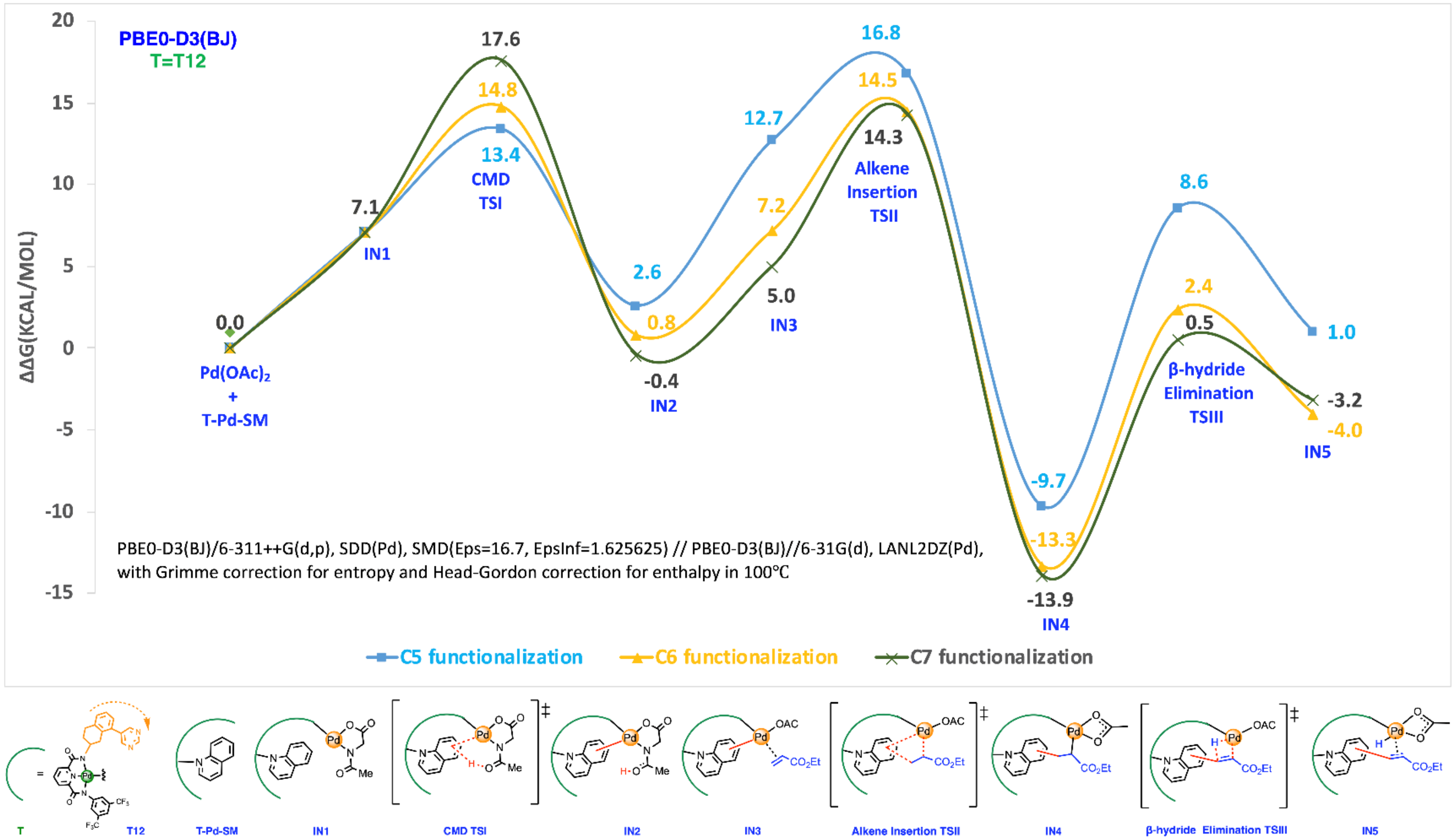
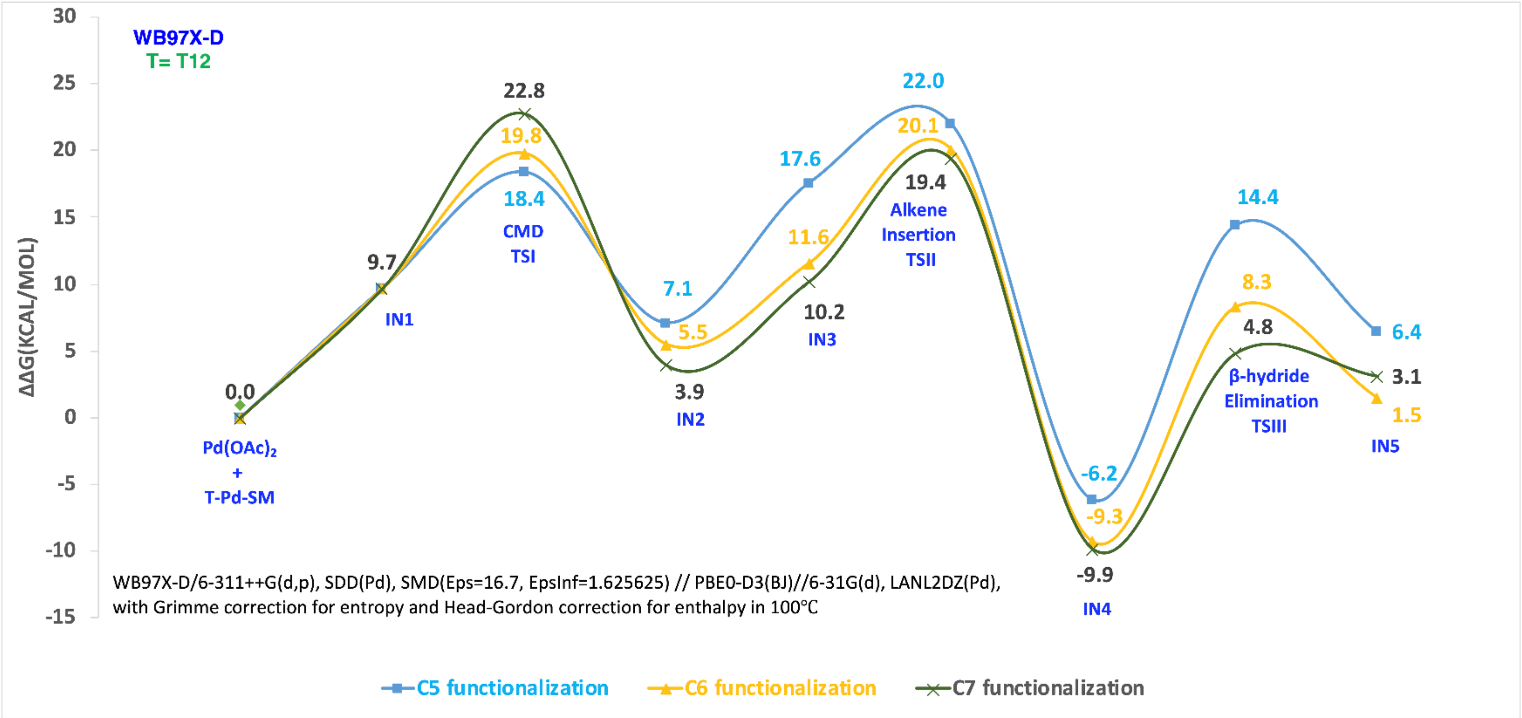


Figure S3. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of PBE0-D3(BJ)/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) //PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.



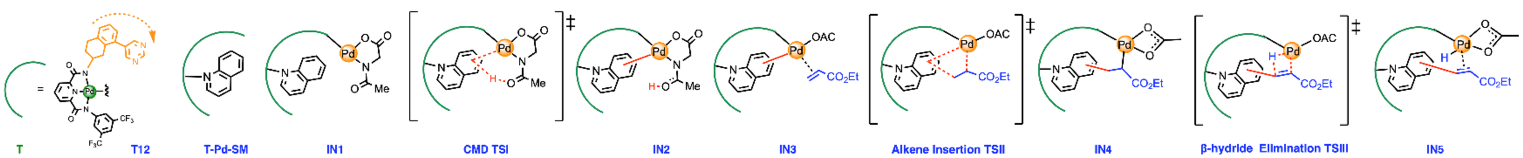


Figure S4. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of WB97X-D/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

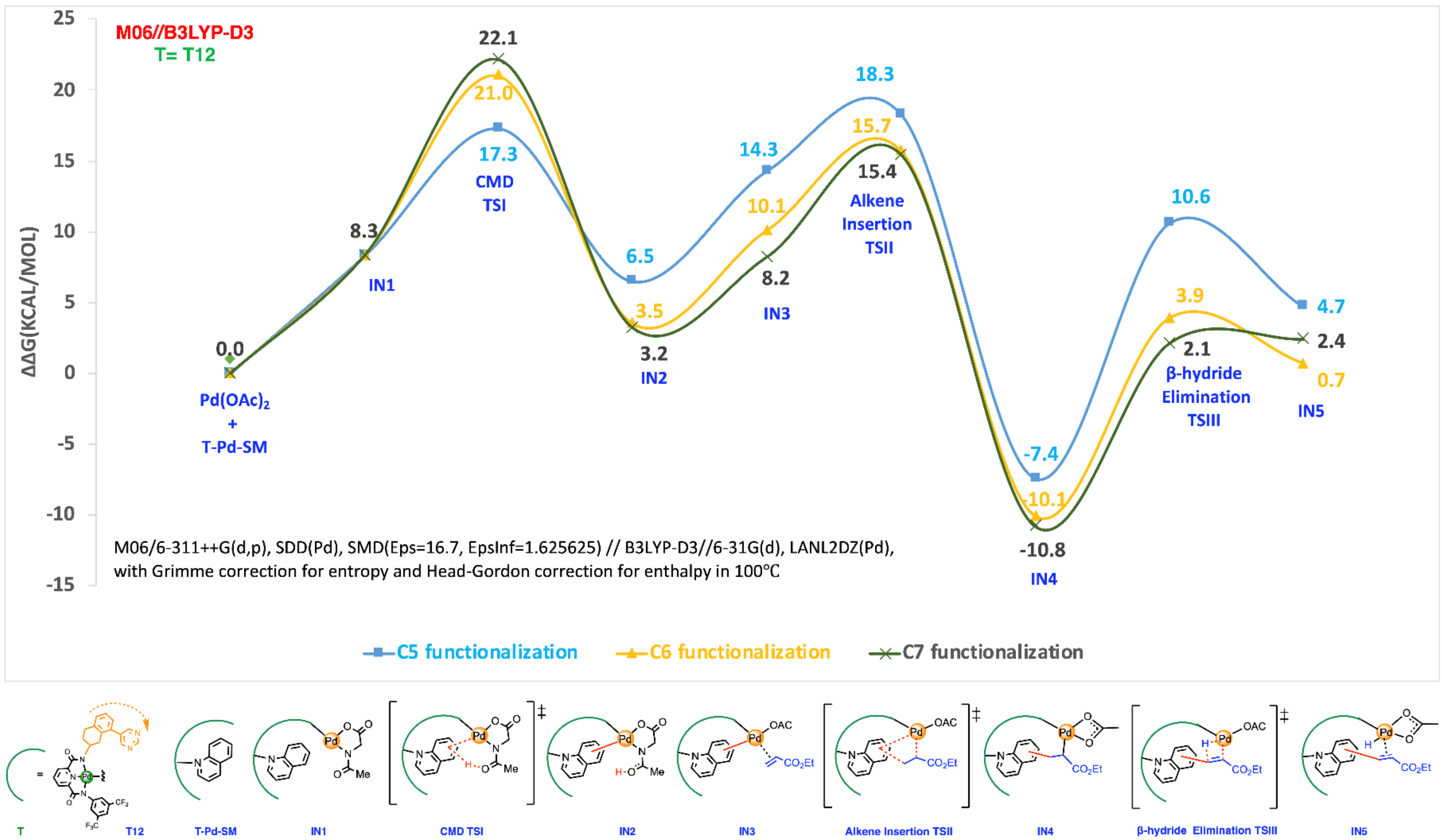


Figure S5. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of M06/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // B3LYP-D3//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

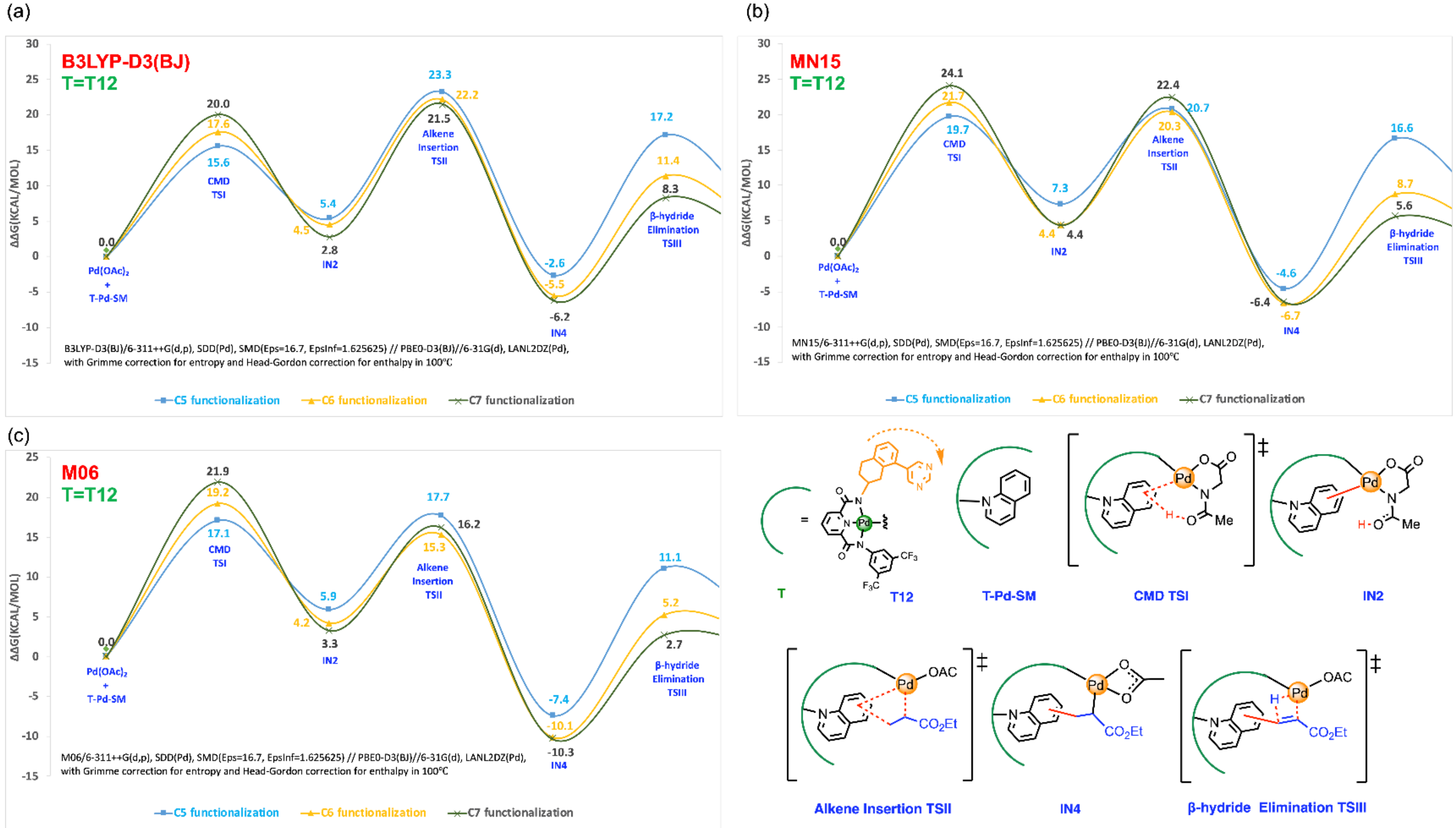


Figure S6A. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of (a) B3LYP-D3(BJ), (b) MN15, (c) M06 /6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

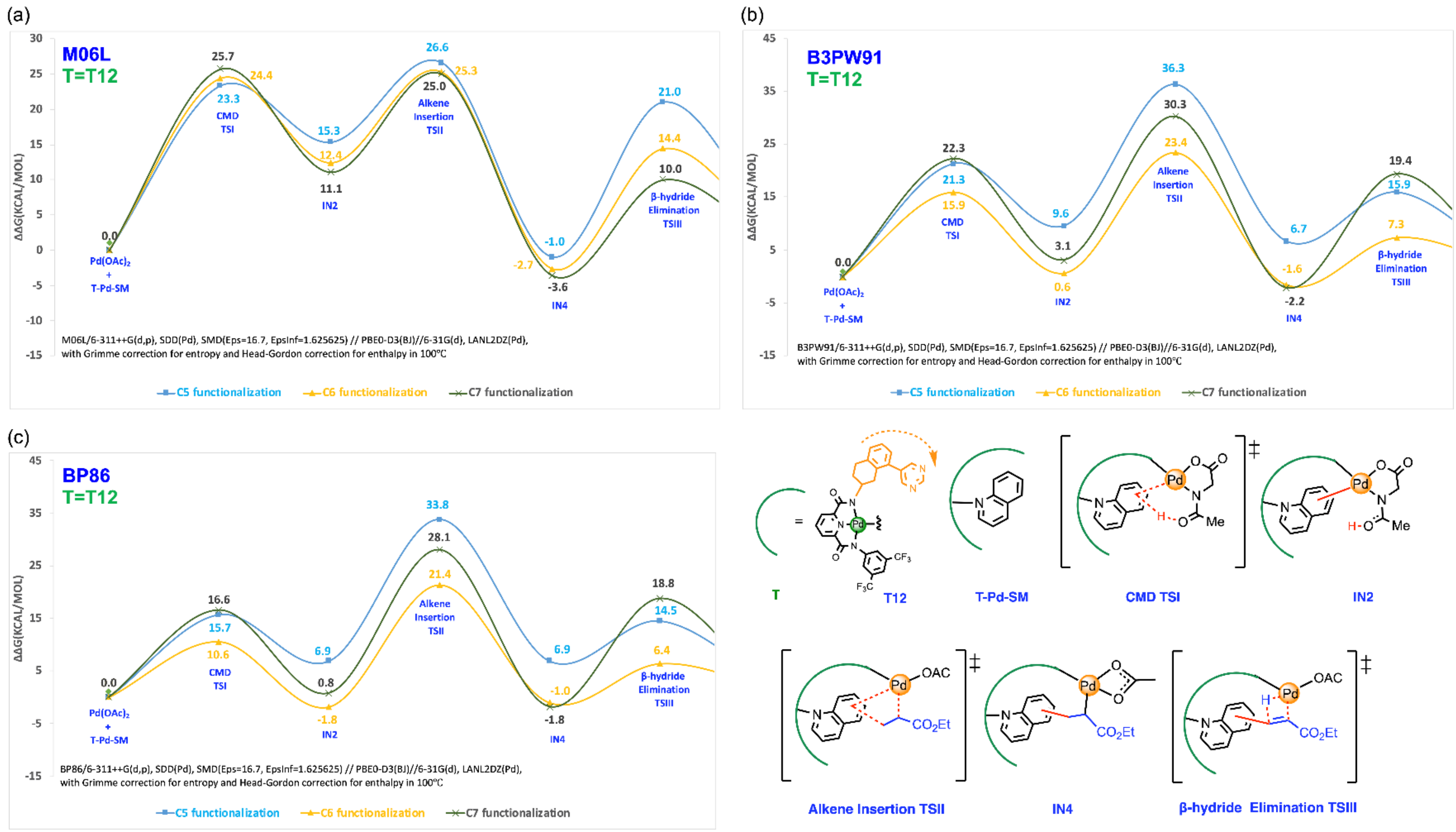
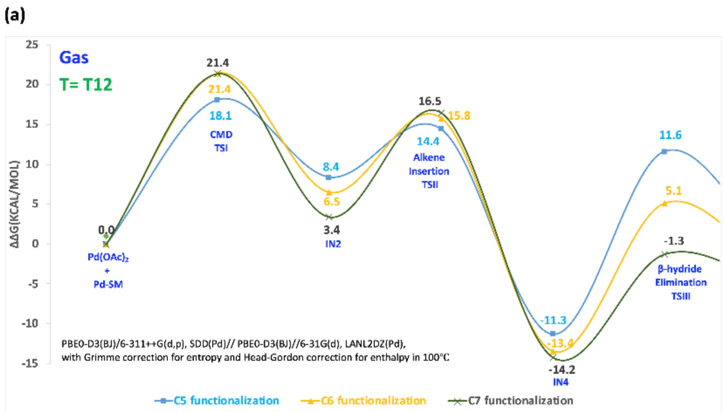
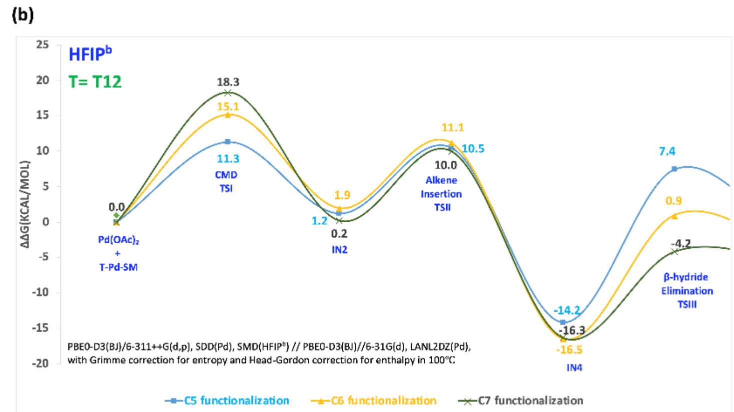


Figure S6B. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of (a) M06L, (b) B3PW91, (c) BP86 /6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

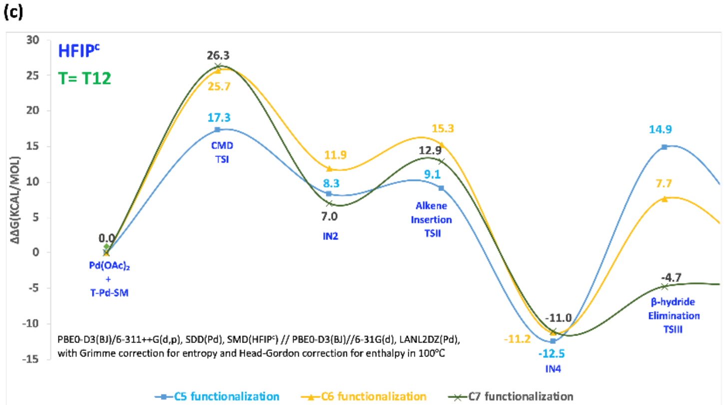
(a)

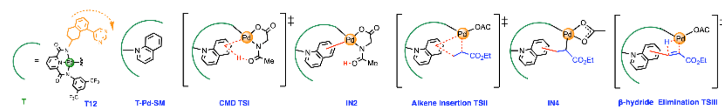


(b)



(c)





HFIP[a]	HFIP[b]	HFIP[c]
Eps=16.7 EpsInf=1.625625	stoichiometry=C3H2O1F6 eps=17.8 solventname=2-propanol epsinf=1.89 molarvolume=94.1 rsolv=2.82 SurfaceTensionAtInterface=23.23 ElectronegativeHalogenicity=0.6 HBondAcidity=0.57 hbondbasicity=0.25 density=0.158	stoichiometry=C3H2F6O1 solventname=1,1,1,3,3,3-hexafluoropropan-2-ol eps=16.7 epsinf=1.625625 HBondAcidity=1.96 HBondBasicity=0.00 SurfaceTensionAtInterface=23.2306248 CarbonAromaticity=0.0 ElectronegativeHalogenicity=0.60

Figure S7. Free energy profiles with template **T12** for C6 selective C–H olefination reactions of quinoline under the level of PBE0-D3(BJ)/6-311++G(d,p), SDD(Pd)// PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd) (a) in gas phase, or (b) and (c) using SMD model with different HFIP parameters. All energies are in kcal/mol.

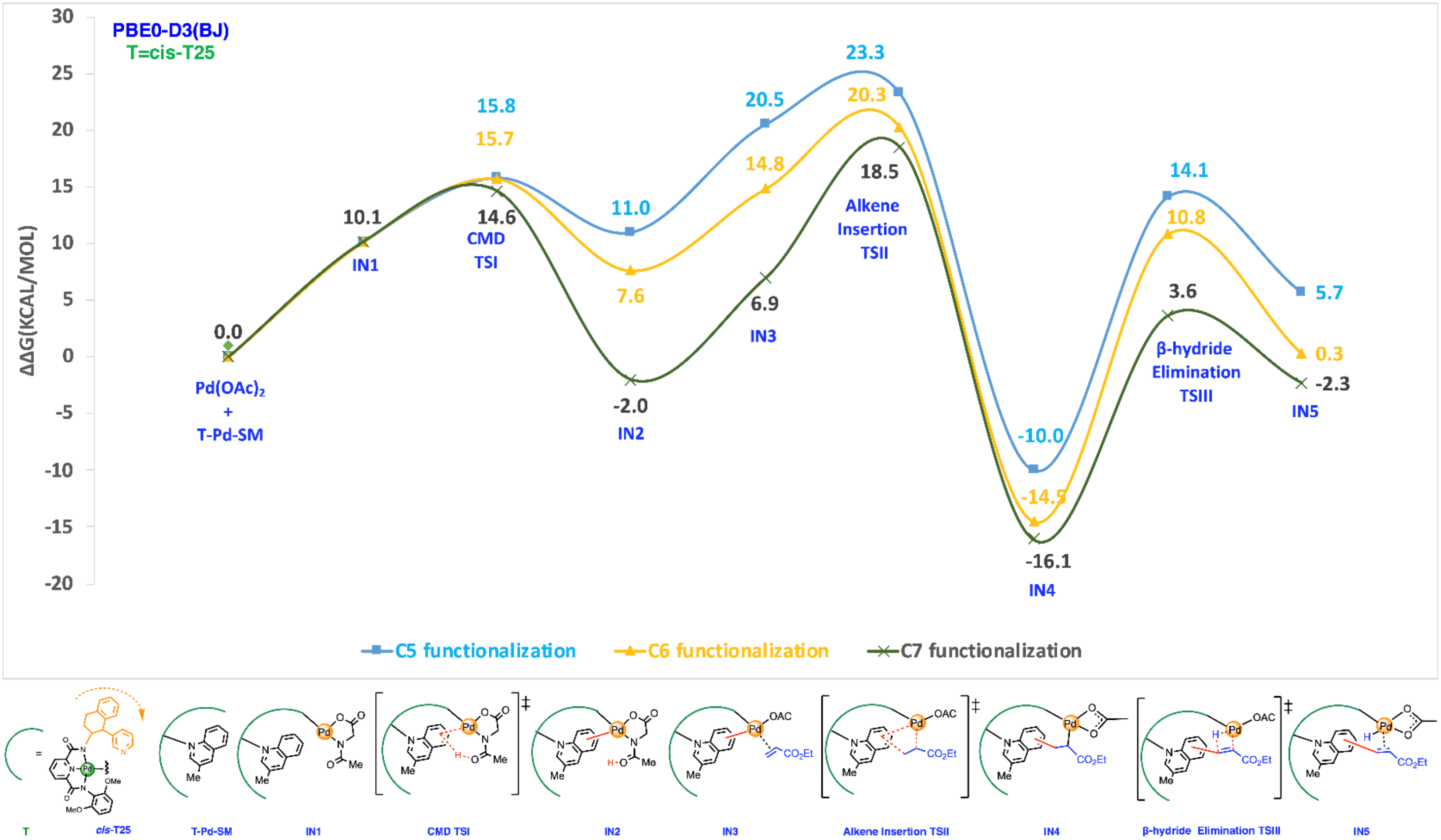


Figure S8. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of 3-methylquinoline under the level of PBE0-D3(BJ)/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) //PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

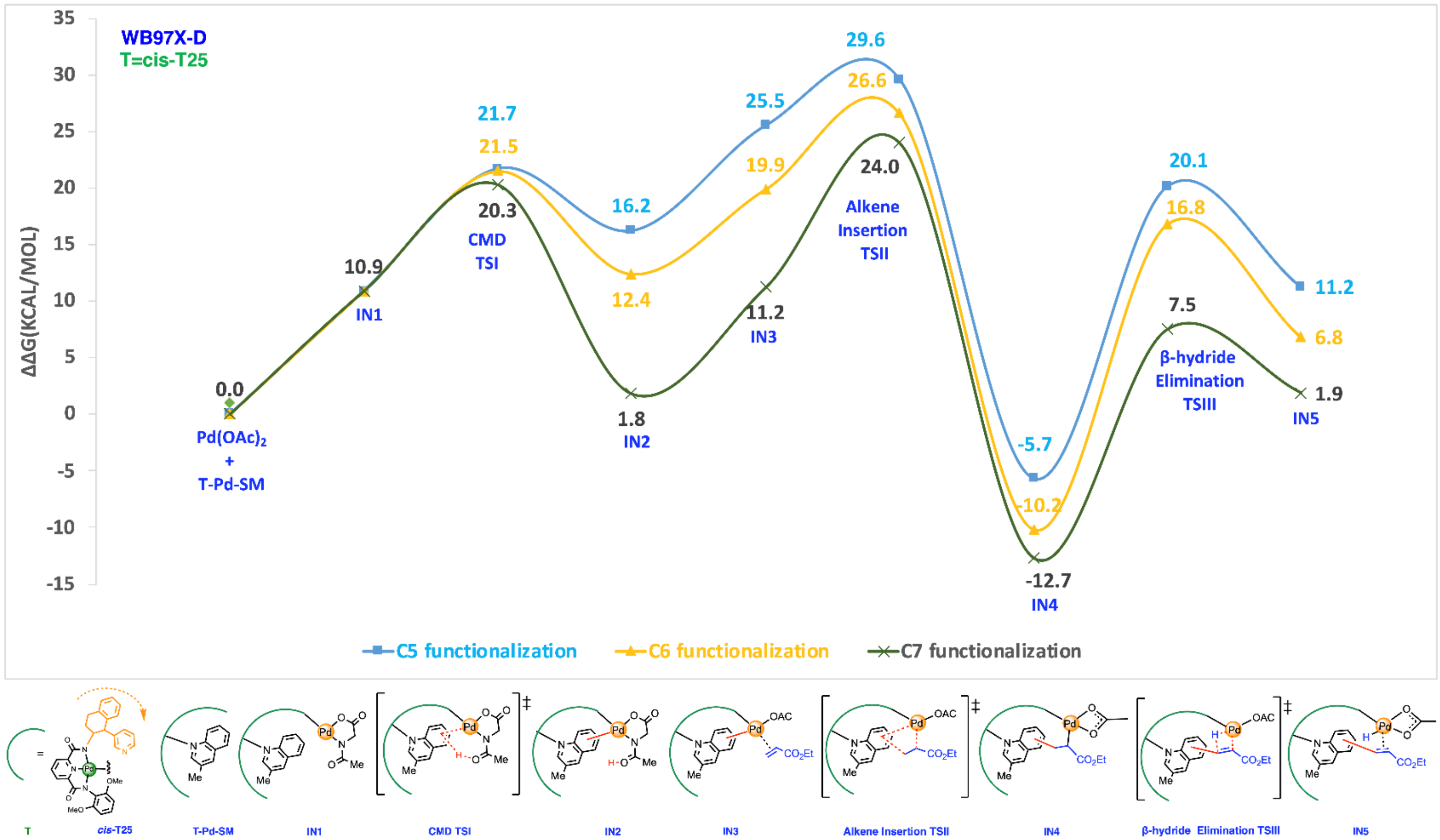


Figure S9. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of 3-methylquinoline under the level of WB97X-D/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

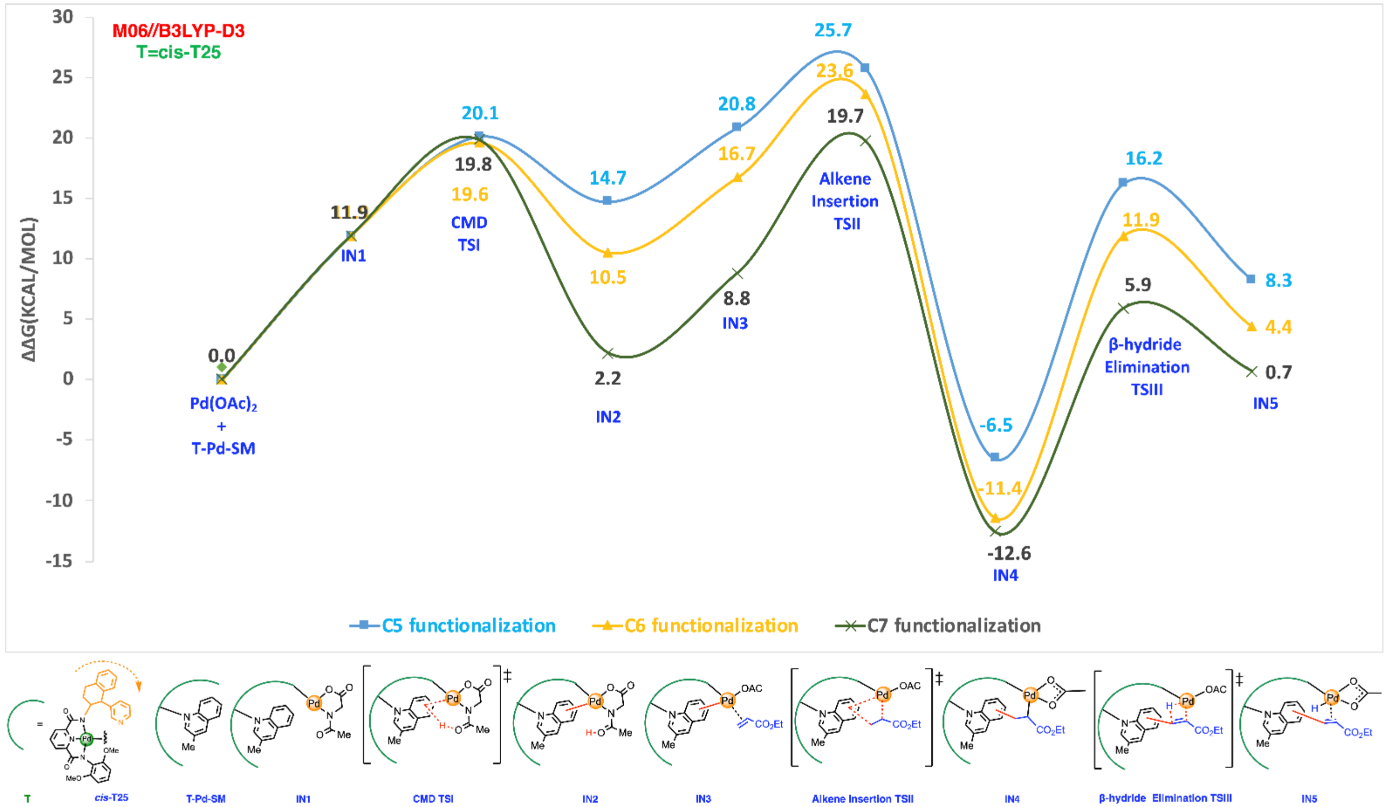


Figure S10. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of 3-methylquinoline under the level of M06/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // B3LYP-D3//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

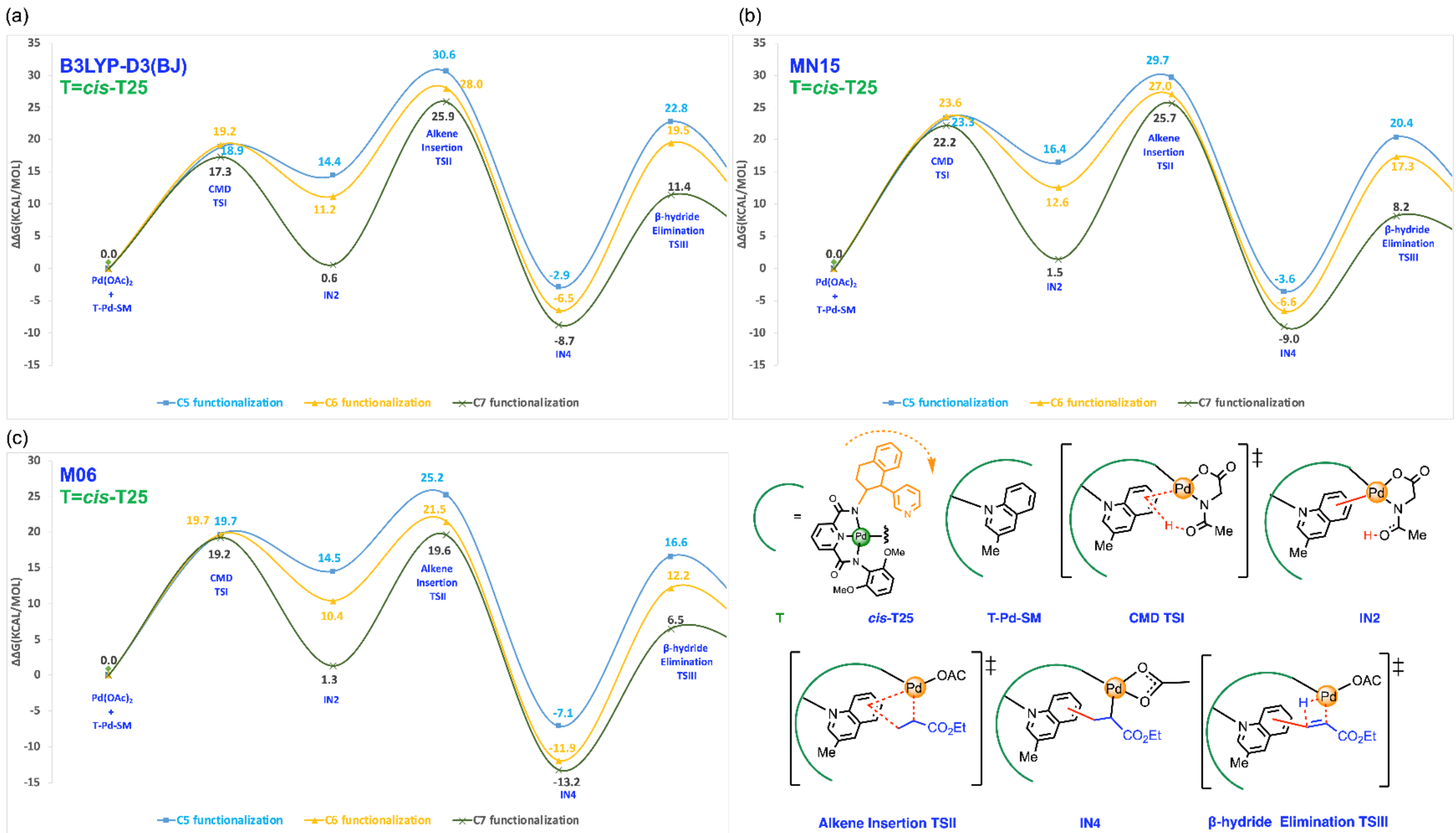


Figure S11A. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of 3-methylquinoline under the level of (a) B3LYP-D3(BJ), (b) MN15, (c) M06 /6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

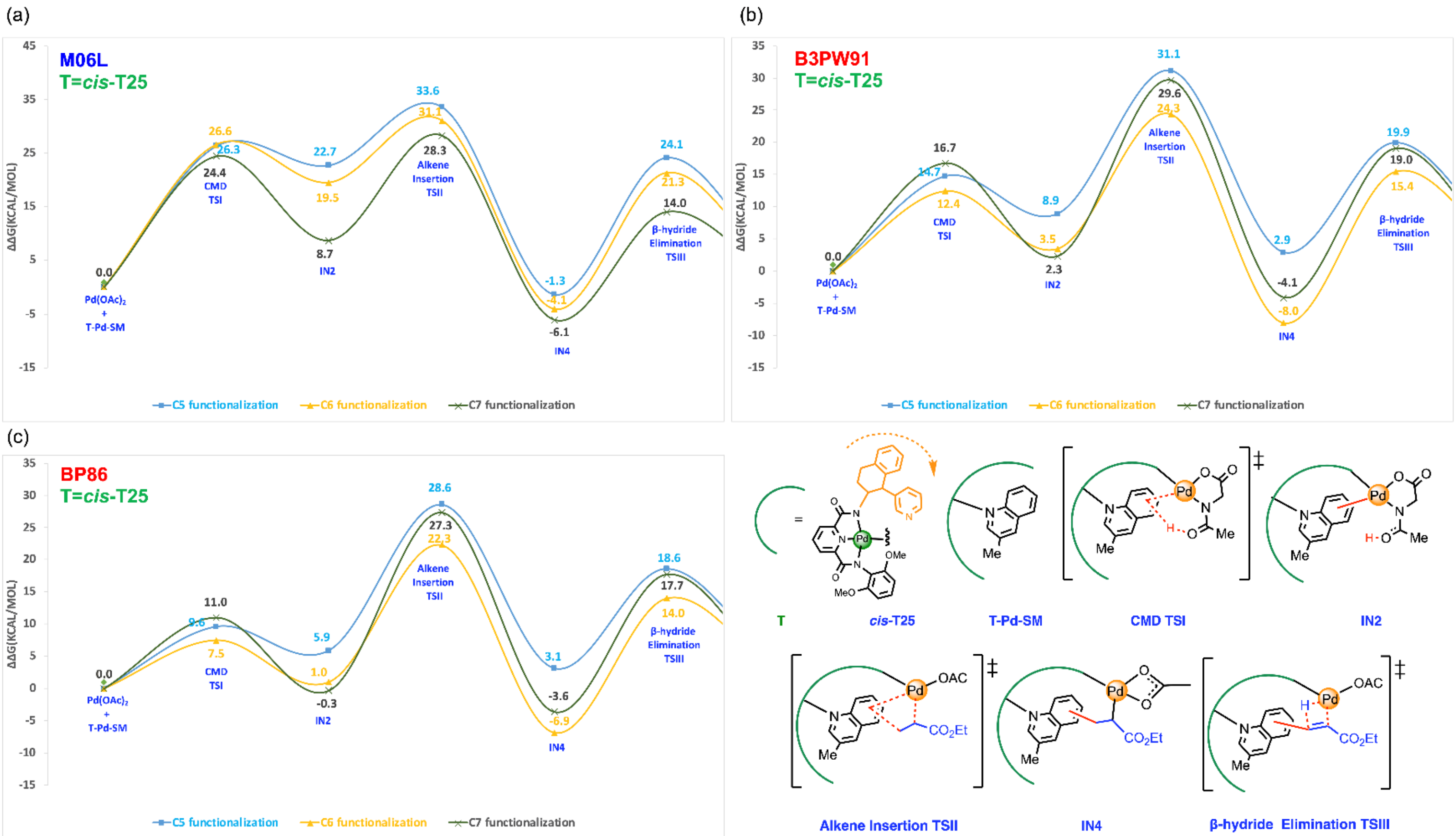


Figure S11B. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of 3-methylquinoline under the level of (a) M06L, (b) B3PW91, (c) BP86 /6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) // PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

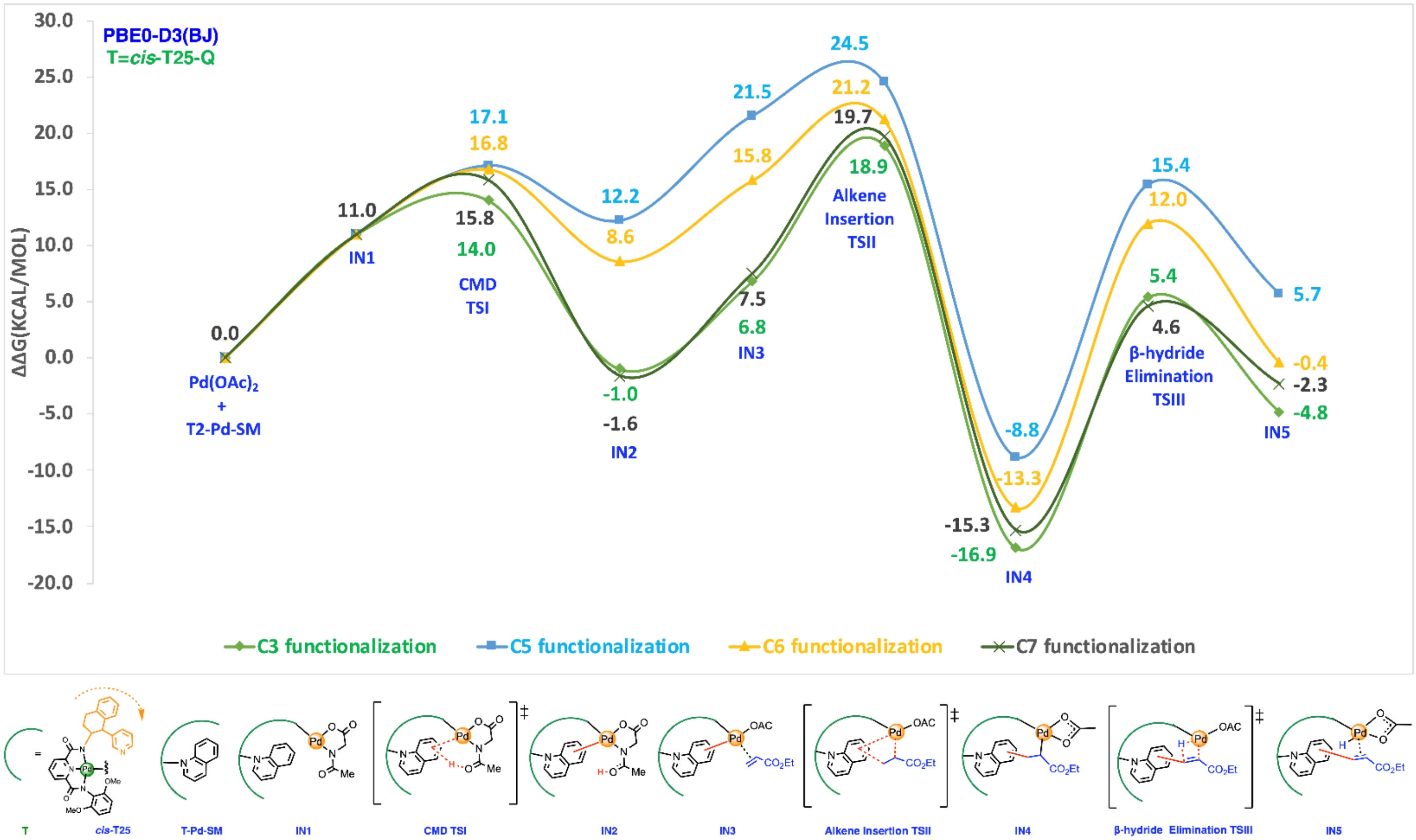
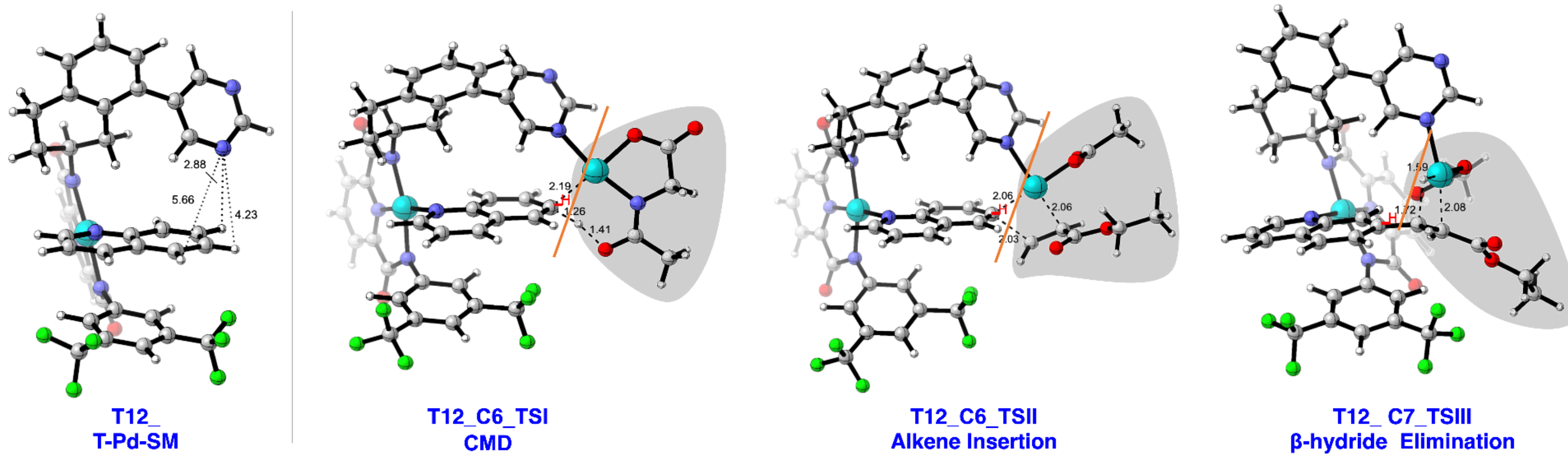


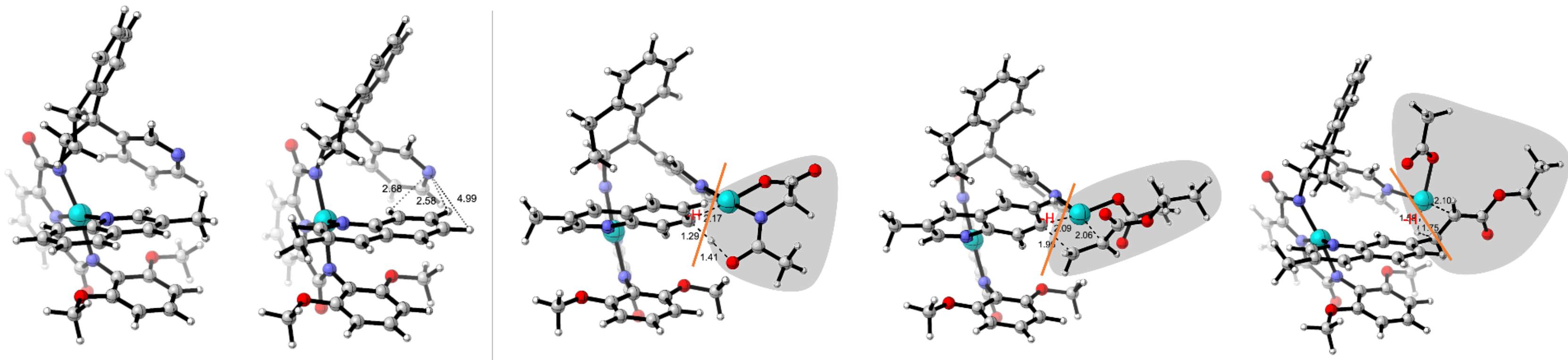
Figure S12. Free energy profiles with template ***cis*-T25** for C7 selective C–H olefination reactions of quinoline under the level of PBE0-D3(BJ)/6-311++G(d,p), SDD(Pd), SMD(Eps=16.7, EpsInf=1.625625) //PBE0-D3(BJ)//6-31G(d), LANL2DZ(Pd). All energies are in kcal/mol.

Table S10. Distortion analysis for C6 selective C–H olefination of quinoline with template **T12**.



	E(distortion) TSI	E(distortion) TSII	E(distortion) TSIII
T12_T-Pd-SM	0.0	0.0	0.0
T12_C7_TS	2.4	1.8	3.4
T12_C6_TS	4.4	3.4	3.1
T12_C5_TS	4.9	4.9	3.9

Table S11. Distortion analysis for C7 selective C–H olefination of 3-methylquinoline with template ***cis*-T25**.



***cis*-T25_ T-Pd-SM_cf1** ΔΔG = 0.0

***cis*-T25_ T-Pd-SM_cf2** ΔΔG = 2.0

***cis*-T25_ C7_TSI CMD**

***cis*-T25_ C7_TSII Alkene Insertion**

***cis*-T25_ C7_TSIII β-hydride Elimination**

	E(distortion) TSI	E(distortion) TSII	E(distortion) TSIII
cis-T25_T-Pd-SM	0.0	0.0	0.0
cis-T25_C7_TS	7.4	9.7	6.9
cis-T25_C6_TS	10.8	12.3	9.9
cis-T25_C5_TS	12.6	15.8	11.0

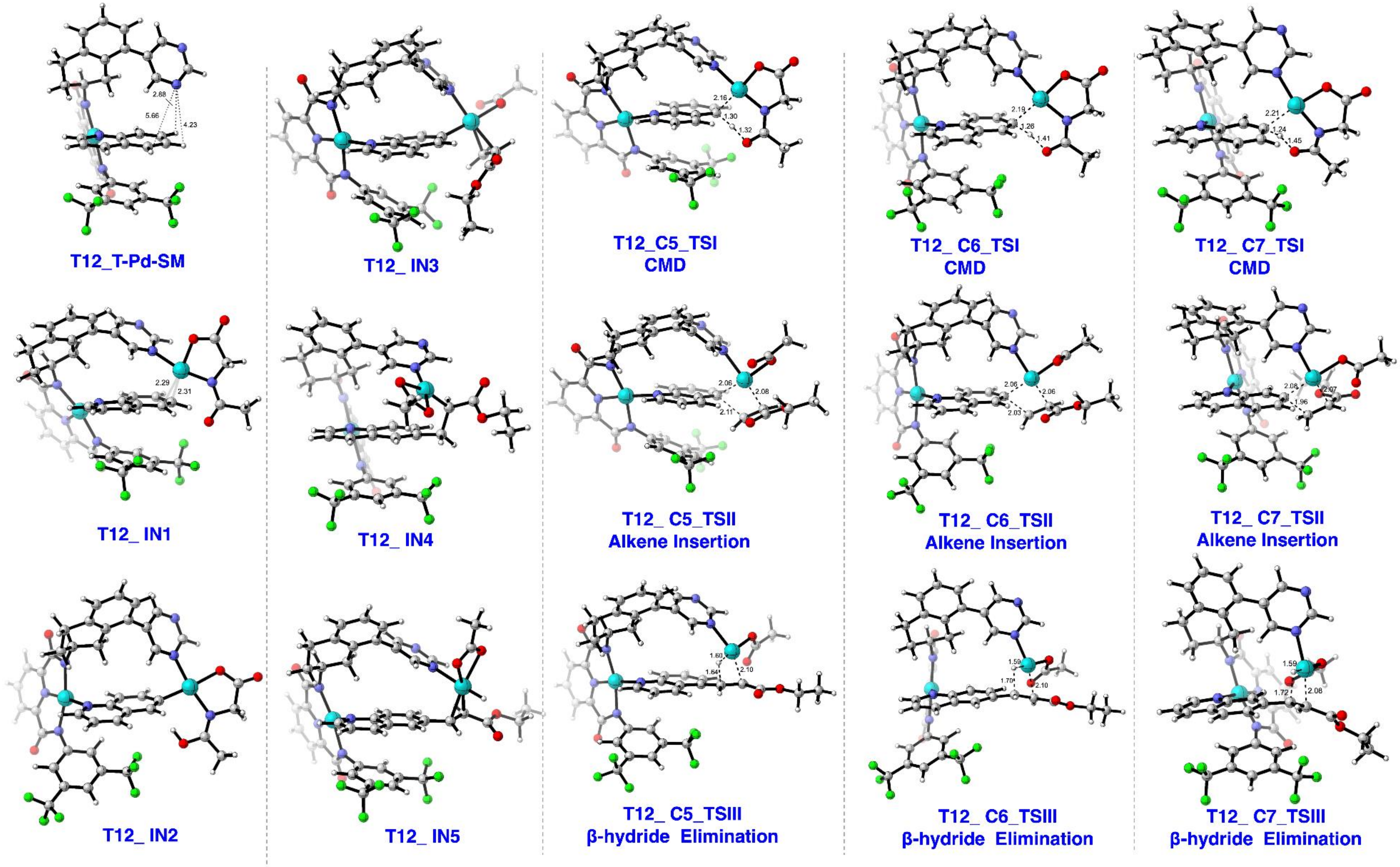


Figure S13. Optimization structures for C6 selective C–H olefination of quinoline with template **T12**.

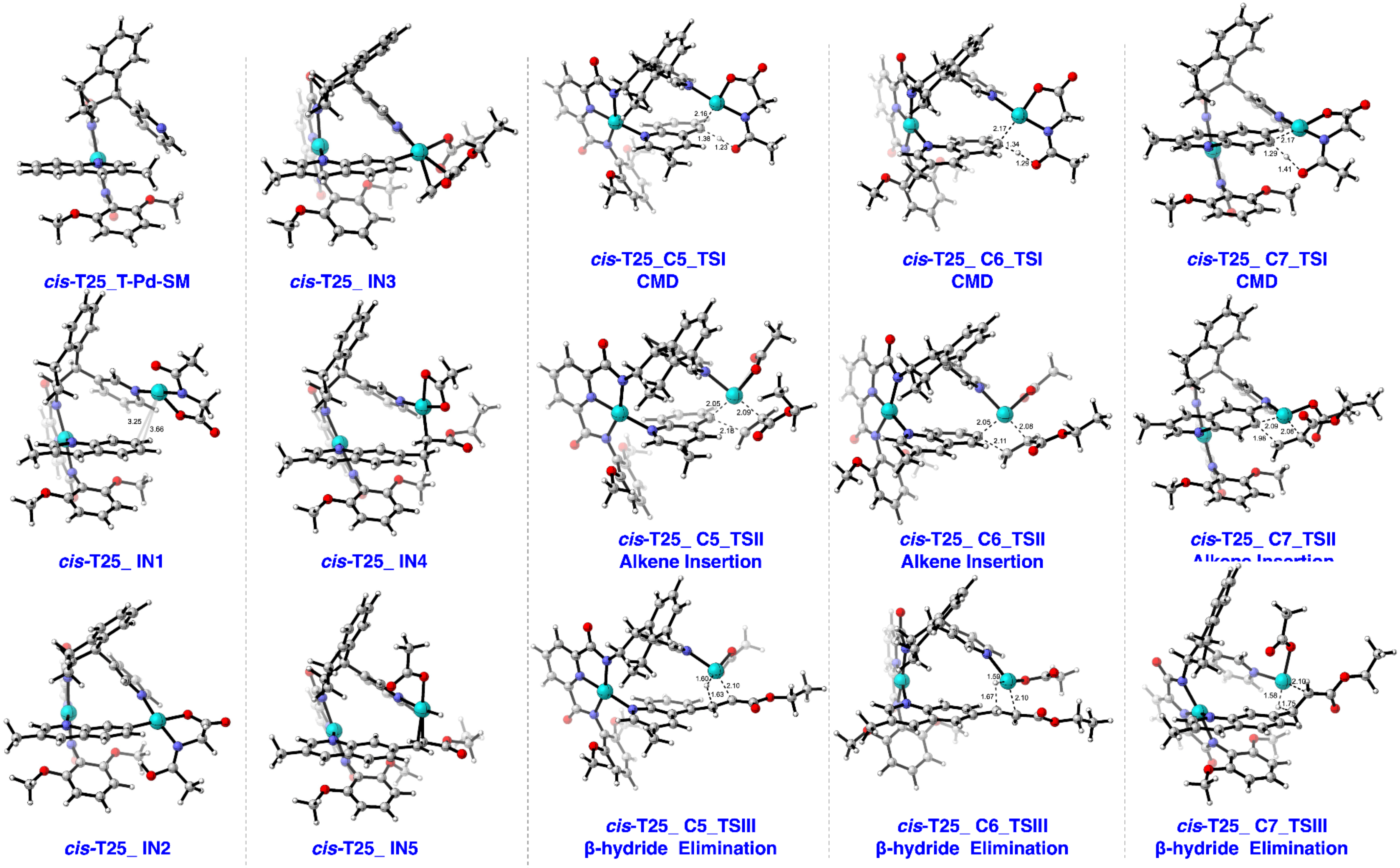


Figure S14. Optimization structures for C7 selective C–H olefination of 3-methylquinoline with template ***cis*-T25**.

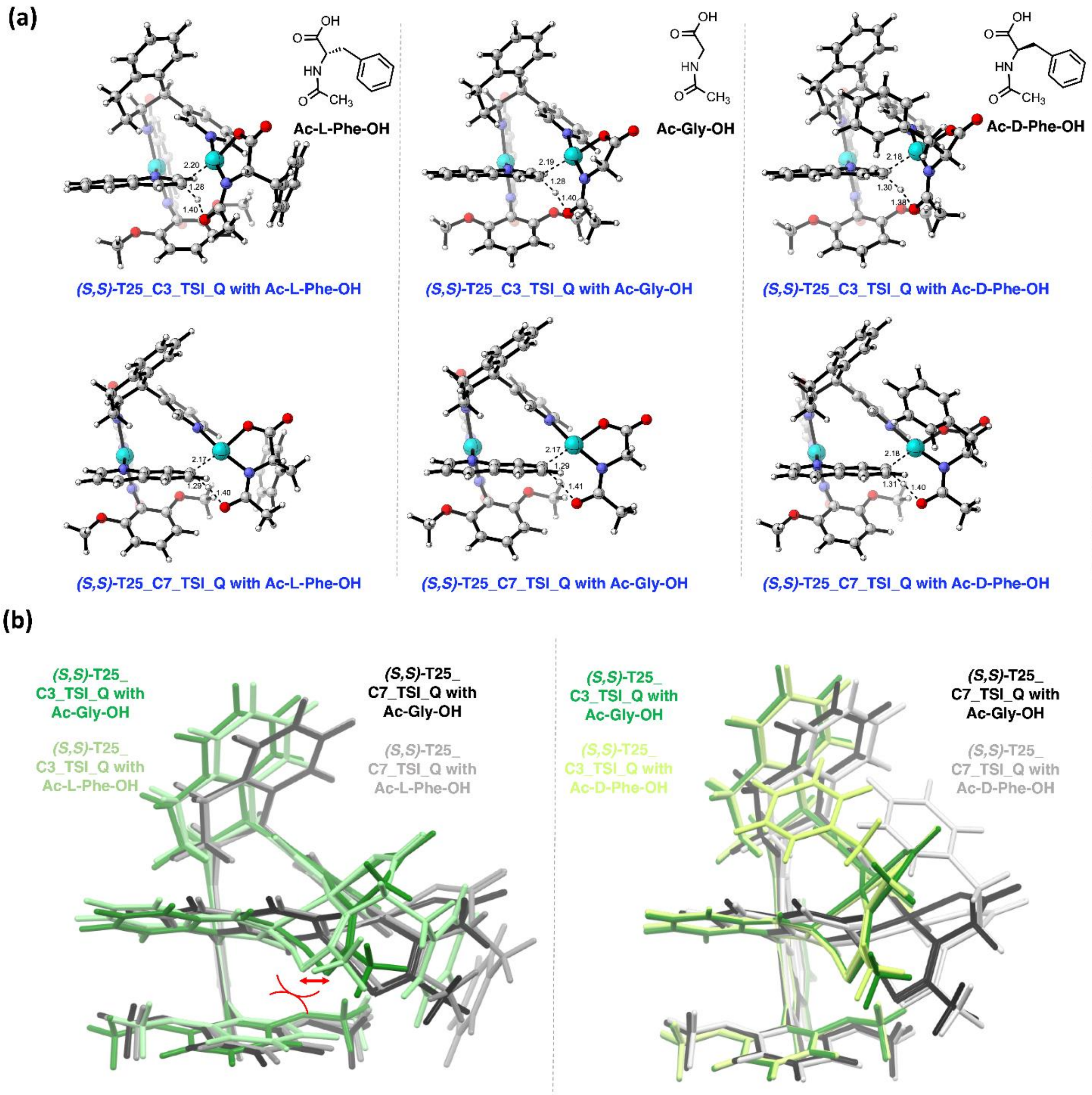


Figure S15. (a) Optimization structures for C7 selective C–H olefination reactions of quinoline with **(*S*,*S*)-T25** and different ligands. (b) Overlay of the CMD TS with different ligands. Distances are in Å.

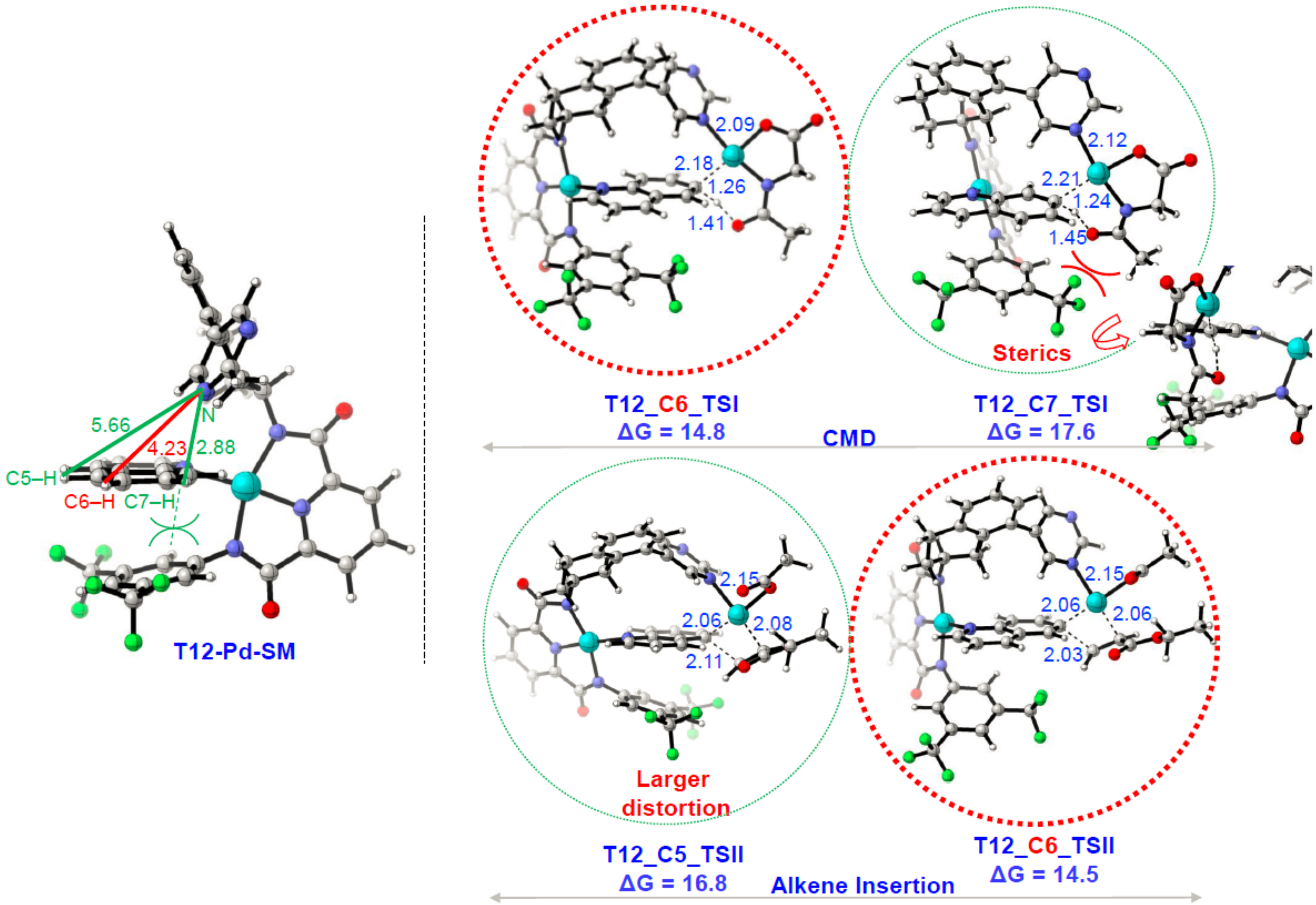


Figure S16. DFT analysis rationalizes the observed C6 selectivity for template **T12**. Bond lengths are denoted in Å.

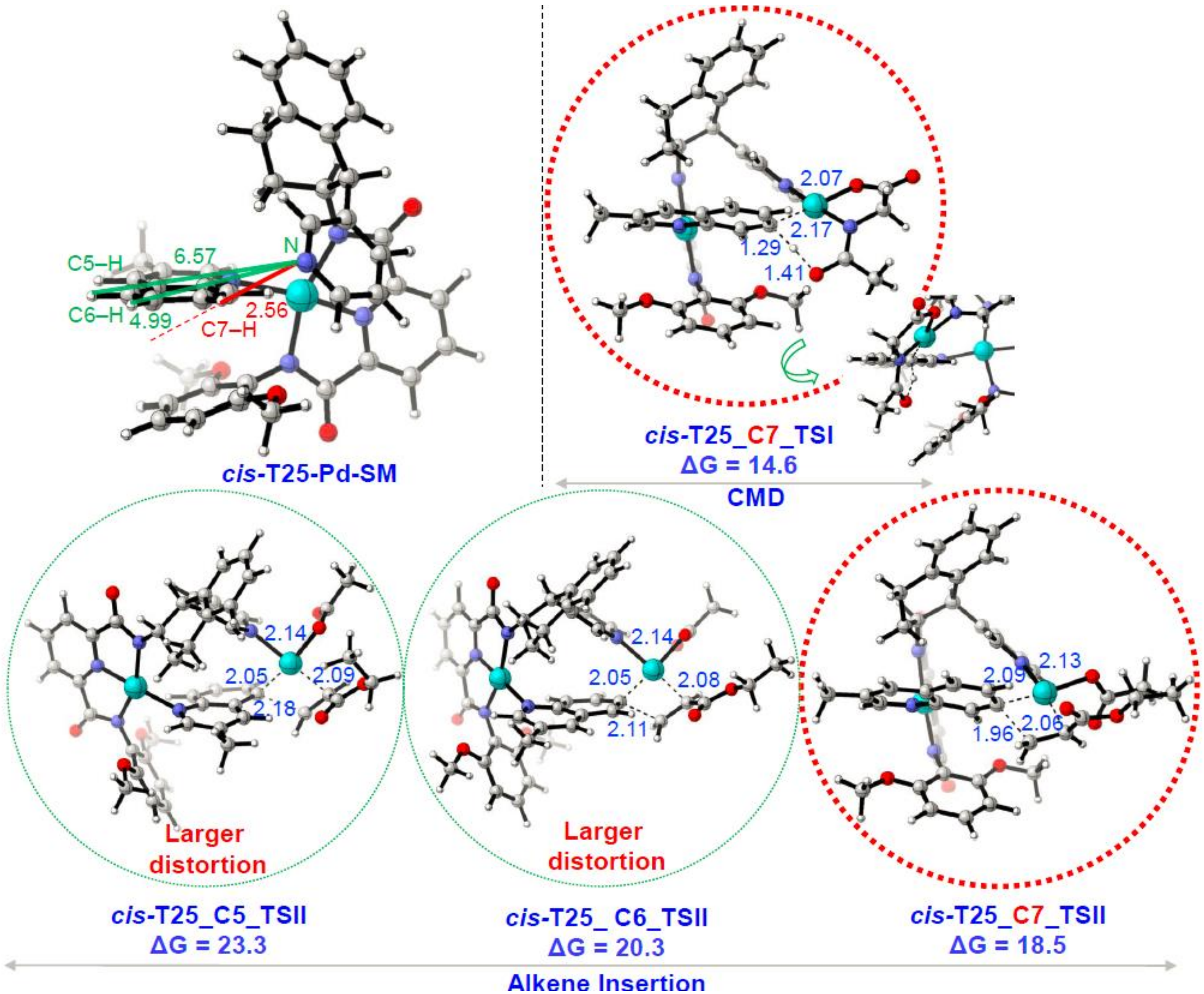


Figure S17. DFT analysis rationalizes the observed C7 selectivity for template ***cis*-T25**. Bond lengths are denoted in Å.

Table S12. Energies.

PBE0-D3(BJ)	E_SPC(PBE0-D3(BJ))	E	ZPE	H_SPC	qh-H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
ACOH	-228.920327	-228.832855	0.062677	-228.850091	-228.850552	0.043143	0.042651	-228.893234	-228.893202
Ac-Gly-OH	-436.779873	-436.622905	0.118963	-436.646938	-436.648782	0.061734	0.058968	-436.708672	-436.707750
CH2CHCO2Et	-345.506216	-345.396184	0.125336	-345.368329	-345.369368	0.056009	0.054949	-345.424338	-345.424317
Cat_3Pd	-1753.704252	-1749.766534	0.319246	-1753.334692	-1753.344552	0.154946	0.138651	-1753.489638	-1753.483203
quinoline	-401.585260	-401.474621	0.137194	-401.436462	-401.436591	0.052910	0.052888	-401.489372	-401.489479
T12_IN1	-3231.292812	-3228.072922	0.687108	-3230.524805	-3230.537446	0.210999	0.192326	-3230.735804	-3230.729772
T12_C5_IN2	-3231.300112	-3228.077183	0.687369	-3230.531892	-3230.544580	0.211396	0.192359	-3230.743288	-3230.736939
T12_C5_IN3	-3368.954828	-3365.707167	0.758301	-3368.108132	-3368.123216	0.229853	0.207416	-3368.337986	-3368.330632
T12_C5_IN4	-3368.994036	-3365.751311	0.760649	-3368.146028	-3368.160888	0.227456	0.205398	-3368.373483	-3368.366286
T12_C5_IN5	-3368.970897	-3365.715238	0.757000	-3368.125804	-3368.141146	0.231836	0.208038	-3368.357640	-3368.349184
T12_C6_IN2	-3231.301852	-3228.078046	0.687647	-3230.533163	-3230.546015	0.214005	0.193745	-3230.747168	-3230.739759
T12_C6_IN3	-3368.964952	-3365.716204	0.758838	-3368.117931	-3368.132802	0.227813	0.206635	-3368.345744	-3368.339437
T12_C6_IN4	-3368.998780	-3365.752965	0.760638	-3368.150661	-3368.165719	0.229221	0.206265	-3368.379882	-3368.371983
T12_C6_IN5	-3368.980417	-3365.720662	0.757053	-3368.135460	-3368.150334	0.229356	0.206921	-3368.364817	-3368.357255
T12_C7_IN2	-3231.307124	-3228.087850	0.688587	-3230.537954	-3230.550233	0.209311	0.191447	-3230.747265	-3230.741680
T12_C7_IN3	-3368.969162	-3365.719186	0.759301	-3368.121883	-3368.136532	0.227909	0.206344	-3368.349791	-3368.342876
T12_C7_IN4	-3369.000785	-3365.755616	0.760735	-3368.152652	-3368.167356	0.227436	0.205576	-3368.380087	-3368.372932
T12_C7_IN5	-3368.978138	-3365.721229	0.756973	-3368.133195	-3368.148262	0.231452	0.207759	-3368.364647	-3368.356021
T12_C5_TSI	-3231.279146	-3228.061730	0.682067	-3230.516746	-3230.529238	0.208206	0.190556	-3230.724952	-3230.719793
T12_C6_TSI	-3231.274664	-3228.052882	0.681960	-3230.512094	-3230.524882	0.212308	0.192562	-3230.724402	-3230.717444
T12_C7_TSI	-3231.274174	-3228.058521	0.683128	-3230.510988	-3230.523212	0.206616	0.189805	-3230.717604	-3230.713017
T12_C5_TSII	-3368.951978	-3365.708411	0.758538	-3368.106451	-3368.120445	0.222767	0.203586	-3368.329218	-3368.324031
T12_C6_TSII	-3368.951406	-3365.700172	0.757798	-3368.106039	-3368.120643	0.229627	0.207056	-3368.335667	-3368.327700
T12_C7_TSII	-3368.955668	-3365.704102	0.758869	-3368.109714	-3368.123943	0.224280	0.204158	-3368.333995	-3368.328100
T12_C5_TSIII	-3368.956809	-3365.695581	0.754978	-3368.114038	-3368.129361	0.231948	0.207791	-3368.345986	-3368.337152
T12_C6_TSIII	-3368.966586	-3365.705527	0.754976	-3368.123858	-3368.139105	0.232140	0.207914	-3368.355998	-3368.347019
T12_C7_TSIII	-3368.974464	-3365.725120	0.755940	-3368.131417	-3368.146115	0.224474	0.203936	-3368.355890	-3368.350050
T12_T-Pd-SM	-2667.805414	-2665.898391	0.588081	-2667.150928	-2667.161384	0.179779	0.164030	-2667.330708	-2667.325413
TC-Pd-SM	-2922.638832	-2920.631879	0.444992	-2922.129133	-2922.139889	0.182231	0.163662	-2922.311364	-2922.303552
cis-T25_C5_IN2	-2809.729384	-2806.643600	0.783468	-2808.865400	-2808.878003	0.208373	0.190586	-2809.073773	-2809.068589
cis-T25_C5_IN3	-2947.387594	-2944.280624	0.855184	-2946.444775	-2946.458781	0.223262	0.204510	-2946.668037	-2946.663291
cis-T25_C5_IN4	-2947.439132	-2944.334563	0.857581	-2946.494832	-2946.508979	0.222841	0.202920	-2946.717672	-2946.711899
cis-T25_C5_IN5	-2947.409871	-2944.296462	0.854023	-2946.468606	-2946.482839	0.223468	0.204079	-2946.692074	-2946.686919
cis-T25_C6_IN2	-2809.734671	-2806.648643	0.783750	-2808.870295	-2808.882877	0.209718	0.191270	-2809.080013	-2809.074146

cis-T25_C6_IN3	-2947.394569	-2944.281548	0.854924	-2946.451684	-2946.466515	0.227010	0.205879	-2946.678694	-2946.672394
cis-T25_C6_IN4	-2947.442626	-2944.331016	0.856674	-2946.498651	-2946.513602	0.228095	0.205386	-2946.726746	-2946.718988
cis-T25_C6_IN5	-2947.417920	-2944.300487	0.853877	-2946.476733	-2946.491003	0.224539	0.204537	-2946.701272	-2946.695540
cis-T25_C7_IN2	-2809.753750	-2806.672827	0.785025	-2808.888650	-2808.900636	0.204677	0.188752	-2809.093326	-2809.089388
cis-T25_C7_IN3	-2947.408388	-2944.298882	0.855594	-2946.464970	-2946.479402	0.226153	0.205477	-2946.691123	-2946.684878
cis-T25_C7_IN4	-2947.448936	-2944.343260	0.857611	-2946.504604	-2946.518908	0.222782	0.202682	-2946.727386	-2946.721590
cis-T25_IN1	-2809.726770	-2806.650932	0.782554	-2808.862844	-2808.876394	0.214083	0.193693	-2809.076927	-2809.070087
cis-T25_C5_TSI	-2809.717630	-2806.635928	0.778464	-2808.859102	-2808.871526	0.206844	0.189548	-2809.065946	-2809.061074
cis-T25_C6_TSI	-2809.717635	-2806.633599	0.778489	-2808.859104	-2808.871501	0.207117	0.189630	-2809.066220	-2809.061131
cis-T25_C7_TSI	-2809.721467	-2806.642501	0.779112	-2808.862621	-2808.874658	0.204498	0.188271	-2809.067119	-2809.062929
cis-T25_C5_TSII	-2947.382109	-2944.272220	0.854588	-2946.440543	-2946.454967	0.224487	0.203847	-2946.665030	-2946.658814
cis-T25_C6_TSII	-2947.385190	-2944.272148	0.854191	-2946.443752	-2946.458471	0.227232	0.205203	-2946.670984	-2946.663674
cis-T25_C7_TSII	-2947.390264	-2944.282757	0.854633	-2946.448643	-2946.462980	0.223102	0.203461	-2946.671744	-2946.666441
cis-T25_C5_TSIII	-2947.393159	-2944.274561	0.851695	-2946.454257	-2946.469138	0.225310	0.204374	-2946.679567	-2946.673511
cis-T25_C6_TSIII	-2947.398282	-2944.278533	0.851441	-2946.459675	-2946.474191	0.225442	0.204550	-2946.685117	-2946.678741
cis-T25_C7_TSIII	-2947.411648	-2944.297196	0.851985	-2946.472823	-2946.487058	0.222883	0.203194	-2946.695706	-2946.690252
cis-T25_T-Pd-SM	-2246.251406	-2244.487608	0.684997	-2245.500898	-2245.510333	0.172373	0.160117	-2245.673271	-2245.670450
cis-T25-Q_C3_IN2	-2770.467462	-2767.395330	0.756934	-2769.632808	-2769.644624	0.201145	0.184658	-2769.833954	-2769.829282
cis-T25-Q_C3_IN3	-2908.127754	-2905.031449	0.828156	-2907.214777	-2907.228418	0.215960	0.198275	-2907.430736	-2907.426693
cis-T25-Q_C3_IN4	-2908.166821	-2905.072899	0.829780	-2907.252777	-2907.266564	0.217062	0.197861	-2907.469839	-2907.464425
cis-T25-Q_C3_IN5	-2908.144831	-2905.040955	0.826655	-2907.233747	-2907.247320	0.215979	0.197867	-2907.449726	-2907.445187
cis-T25-Q_C5_IN2	-2770.444806	-2767.369346	0.755788	-2769.611159	-2769.622973	0.202205	0.185364	-2769.813364	-2769.808336
cis-T25-Q_C5_IN3	-2908.103017	-2905.005521	0.827385	-2907.190612	-2907.203944	0.217493	0.199406	-2907.408106	-2907.403350
cis-T25-Q_C5_IN4	-2908.153403	-2905.057991	0.829646	-2907.239511	-2907.253286	0.217878	0.198203	-2907.457390	-2907.451489
cis-T25-Q_C5_IN5	-2908.126842	-2905.020660	0.826265	-2907.215982	-2907.229518	0.217688	0.198944	-2907.433669	-2907.428461
cis-T25-Q_C6_IN2	-2770.450490	-2767.374937	0.756155	-2769.616414	-2769.628205	0.203085	0.185783	-2769.819499	-2769.813988
cis-T25-	-2908.110282	-2905.007837	0.827285	-2907.197731	-2907.211764	0.220628	0.200535	-2907.418359	-2907.412299

Q_C6_IN3									
cis-T25-Q_C6_IN4	-2908.158632	-2905.057606	0.829089	-2907.244996	-2907.259075	0.220856	0.199650	-2907.465852	-2907.458725
cis-T25-Q_C6_IN5	-2908.135737	-2905.025296	0.826033	-2907.224987	-2907.238672	0.219290	0.199546	-2907.444276	-2907.438218
cis-T25-Q_C7_IN2	-2770.470049	-2767.399603	0.757222	-2769.635371	-2769.646633	0.198702	0.183614	-2769.834074	-2769.830247
cis-T25-Q_C7_IN3	-2908.124764	-2905.025660	0.827881	-2907.211718	-2907.225403	0.219828	0.200152	-2907.431546	-2907.425555
cis-T25-Q_C7_IN4	-2908.165037	-2905.069913	0.829999	-2907.251009	-2907.264509	0.216416	0.197368	-2907.467425	-2907.461877
cis-T25-Q_C7_IN5	-2908.139572	-2905.034747	0.826261	-2907.228631	-2907.242286	0.217866	0.198927	-2907.446497	-2907.441213
cis-T25-Q_IN1	-2770.442759	-2767.377805	0.754835	-2769.609223	-2769.622037	0.207368	0.188198	-2769.816591	-2769.810235
cis-T25-Q_C3_TSI	-2770.437475	-2767.367396	0.751089	-2769.608986	-2769.620855	0.201660	0.184567	-2769.810646	-2769.805422
cis-T25-Q_C5_TSI	-2770.432807	-2767.361484	0.750821	-2769.604603	-2769.616199	0.200504	0.184283	-2769.805107	-2769.800482
cis-T25-Q_C6_TSI	-2770.433260	-2767.359693	0.750838	-2769.605065	-2769.616664	0.200702	0.184283	-2769.805767	-2769.800947
cis-T25-Q_C7_TSI	-2770.436862	-2767.368540	0.751431	-2769.608361	-2769.619612	0.198186	0.182971	-2769.806547	-2769.802583
cis-T25-Q_C3_TSII	-2908.105664	-2905.006829	0.826626	-2907.194542	-2907.208399	0.218841	0.199011	-2907.413382	-2907.407410
cis-T25-Q_C5_TSII	-2908.097385	-2904.997429	0.826879	-2907.186169	-2907.199903	0.218484	0.198604	-2907.404652	-2907.398506
cis-T25-Q_C6_TSII	-2908.100957	-2904.998305	0.826501	-2907.189881	-2907.203819	0.220855	0.199854	-2907.410736	-2907.403674
cis-T25-Q_C7_TSII	-2908.105851	-2905.008989	0.827034	-2907.194536	-2907.208056	0.216613	0.198056	-2907.411148	-2907.406112
cis-T25-Q_C3_TSIII	-2908.127670	-2905.025424	0.824634	-2907.219074	-2907.232108	0.214035	0.196863	-2907.433109	-2907.428971
cis-T25-Q_C5_TSIII	-2908.108528	-2905.000322	0.824046	-2907.199974	-2907.214033	0.218828	0.198999	-2907.418801	-2907.413032
cis-T25-Q_C6_TSIII	-2908.114120	-2905.004845	0.823790	-2907.205887	-2907.219576	0.218399	0.198876	-2907.424286	-2907.418452
cis-T25-Q_C7_TSIII	-2908.127627	-2905.023813	0.824364	-2907.219137	-2907.232568	0.216144	0.197689	-2907.435281	-2907.430257
cis-T25-Q_T-Pd-SM_cf1	-2206.966553	-2205.209402	0.656725	-2206.246566	-2206.255924	0.168870	0.156132	-2206.415436	-2206.412055
cis-T25-Q_T-Pd-SM_cf2	-2206.962936	-2205.207361	0.656840	-2206.242950	-2206.252044	0.168106	0.155839	-2206.411056	-2206.407883
WB97X-D	E_SPC(WB97X-D)	E	ZPE	H_SPC	qh-H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
AcOH	-229.097639	-228.832855	0.062677	-229.027402	-229.027863	0.043143	0.042651	-229.070545	-229.070514
Ac-Gly-OH	-437.115613	-436.622905	0.118963	-436.982678	-436.984522	0.061734	0.058968	-437.044412	-437.043489
CH2CHCO2Et	-345.784031	-345.396184	0.125336	-345.646144	-345.647183	0.056009	0.054949	-345.702153	-345.702133
Cat_3Pd	-1754.853578	-1749.766534	0.319246	-1754.484018	-1754.493878	0.154946	0.138651	-1754.638964	-1754.632529

T12_IN1	-3233.575486	-3228.072922	0.687108	-3232.807479	-3232.820120	0.210999	0.192326	-3233.018478	-3233.012446
T12_C5_IN2	-3233.579782	-3228.077183	0.687369	-3232.811562	-3232.824250	0.211396	0.192359	-3233.022959	-3233.016610
T12_C5_IN3	-3371.353254	-3365.707167	0.758301	-3370.506558	-3370.521641	0.229853	0.207416	-3370.736411	-3370.729057
T12_C5_IN4	-3371.394620	-3365.751311	0.760649	-3370.546612	-3370.561472	0.227456	0.205398	-3370.774067	-3370.766871
T12_C5_IN5	-3371.368578	-3365.715238	0.757000	-3370.523486	-3370.538827	0.231836	0.208038	-3370.755321	-3370.746865
T12_C6_IN2	-3233.581309	-3228.078046	0.687647	-3232.812619	-3232.825471	0.214005	0.193745	-3233.026624	-3233.019215
T12_C6_IN3	-3371.364083	-3365.716204	0.758838	-3370.517062	-3370.531933	0.227813	0.206635	-3370.744875	-3370.738568
T12_C6_IN4	-3371.398688	-3365.752965	0.760638	-3370.550569	-3370.565627	0.229221	0.206265	-3370.779790	-3370.771891
T12_C6_IN5	-3371.377898	-3365.720662	0.757053	-3370.532941	-3370.547814	0.229356	0.206921	-3370.762297	-3370.754736
T12_C7_IN2	-3233.587199	-3228.087850	0.688587	-3232.818029	-3232.830308	0.209311	0.191447	-3233.027339	-3233.021755
T12_C7_IN3	-3371.367141	-3365.719186	0.759301	-3370.519861	-3370.534511	0.227909	0.206344	-3370.747769	-3370.740855
T12_C7_IN4	-3371.400611	-3365.755616	0.760735	-3370.552477	-3370.567182	0.227436	0.205576	-3370.779913	-3370.772758
T12_C7_IN5	-3371.374180	-3365.721229	0.756973	-3370.529237	-3370.544304	0.231452	0.207759	-3370.760688	-3370.752063
T12_C5_TSI	-3233.557898	-3228.061730	0.682067	-3232.795497	-3232.807989	0.208206	0.190556	-3233.003704	-3232.998545
T12_C6_TSI	-3233.553508	-3228.052882	0.681960	-3232.790937	-3232.803726	0.212308	0.192562	-3233.003245	-3232.996288
T12_C7_TSI	-3233.552672	-3228.058521	0.683128	-3232.789486	-3232.801710	0.206616	0.189805	-3232.996102	-3232.991515
T12_C5_TSII	-3371.349915	-3365.708411	0.758538	-3370.504388	-3370.518382	0.222767	0.203586	-3370.727155	-3370.721968
T12_C6_TSII	-3371.348764	-3365.700172	0.757798	-3370.503398	-3370.518002	0.229627	0.207056	-3370.733025	-3370.725058
T12_C7_TSII	-3371.353684	-3365.704102	0.758869	-3370.507731	-3370.521959	0.224280	0.204158	-3370.732011	-3370.726117
T12_C5_TSII	-3371.353786	-3365.695581	0.754978	-3370.511015	-3370.526338	0.231948	0.207791	-3370.742963	-3370.734129
T12_C6_TSII	-3371.363478	-3365.705527	0.754976	-3370.520750	-3370.535997	0.232140	0.207914	-3370.752890	-3370.743911
T12_C7_TSII	-3371.373834	-3365.725120	0.755940	-3370.530786	-3370.545484	0.224474	0.203936	-3370.755260	-3370.749419
T12_TC-Pd-S	-2924.674614	-2920.631879	0.444992	-2924.164915	-2924.175671	0.182231	0.163662	-2924.347146	-2924.339334
T12_T-Pd-SM	-2669.727864	-2665.898391	0.588081	-2669.073378	-2669.083833	0.179779	0.164030	-2669.253157	-2669.247863
cis-T25_C5_IN2	-2811.764817	-2806.643600	0.783468	-2810.900833	-2810.913436	0.208373	0.190586	-2811.109206	-2811.104022
cis-T25_C5_IN3	-2949.542710	-2944.280624	0.855184	-2948.599891	-2948.613897	0.223262	0.204510	-2948.823153	-2948.818408
cis-T25_C5_IN4	-2949.595322	-2944.334563	0.857581	-2948.651021	-2948.665168	0.222841	0.202920	-2948.873862	-2948.868089
cis-T25_C5_IN5	-2949.564076	-2944.296462	0.854023	-2948.622811	-2948.637044	0.223468	0.204079	-2948.846279	-2948.841124
cis-T25_C6_IN2	-2811.770624	-2806.648643	0.783750	-2810.906247	-2810.918829	0.209718	0.191270	-2811.115965	-2811.110099
cis-T25_C6_IN3	-2949.549519	-2944.281548	0.854924	-2948.606634	-2948.621465	0.227010	0.205879	-2948.833644	-2948.827344
cis-T25_C6_IN4	-2949.598843	-2944.331016	0.856674	-2948.654867	-2948.669818	0.228095	0.205386	-2948.882962	-2948.875205
cis-T25_C6_IN5	-2949.570548	-2944.300487	0.853877	-2948.629362	-2948.643631	0.224539	0.204537	-2948.853901	-2948.848168
cis-T25_C7_IN2	-2811.791409	-2806.672827	0.785025	-2810.926309	-2810.938295	0.204677	0.188752	-2811.130985	-2811.127047
cis-T25_C7_IN3	-2949.564726	-2944.298882	0.855594	-2948.621308	-2948.635740	0.226153	0.205477	-2948.847461	-2948.841216
cis-	-2949.606554	-2944.343260	0.857611	-2948.662222	-2948.676526	0.222782	0.202682	-2948.885004	-2948.879208

T25_C7_IN4									
cis-T25_C7_IN5	-2949.578565	-2944.309232	0.853838	-2948.637282	-2948.651691	0.223835	0.204326	-2948.861117	-2948.856018
cis-T25_IN1	-2811.769171	-2806.650932	0.782554	-2810.905246	-2810.918795	0.214083	0.193693	-2811.119328	-2811.112488
cis-T25_C5_TSI	-2811.751840	-2806.635928	0.778464	-2810.893312	-2810.905736	0.206844	0.189548	-2811.100157	-2811.095285
cis-T25_C6_TSI	-2811.752021	-2806.633599	0.778489	-2810.893490	-2810.905887	0.207117	0.189630	-2811.100607	-2811.095517
cis-T25_C7_TSI	-2811.756111	-2806.642501	0.779112	-2810.897265	-2810.909302	0.204498	0.188271	-2811.101763	-2811.097573
cis-T25_C5_TSII	-2949.535141	-2944.272220	0.854588	-2948.593574	-2948.607998	0.224487	0.203847	-2948.818061	-2948.811845
cis-T25_C6_TSII	-2949.538198	-2944.272148	0.854191	-2948.596760	-2948.611479	0.227232	0.205203	-2948.823993	-2948.816682
cis-T25_C7_TSII	-2949.544524	-2944.282757	0.854633	-2948.602903	-2948.617240	0.223102	0.203461	-2948.826004	-2948.820701
cis-T25_C5_TSIII	-2949.546660	-2944.274561	0.851695	-2948.607757	-2948.622638	0.225310	0.204374	-2948.833068	-2948.827012
cis-T25_C6_TSIII	-2949.551772	-2944.278533	0.851441	-2948.613165	-2948.627681	0.225442	0.204550	-2948.838607	-2948.832230
cis-T25_C7_TSIII	-2949.568440	-2944.297196	0.851985	-2948.629615	-2948.643850	0.222883	0.203194	-2948.852498	-2948.847044
cis-T25_T-Pd-SM	-2247.930790	-2244.487608	0.684997	-2247.180282	-2247.189716	0.172373	0.160117	-2247.352655	-2247.349833
M06//B3LYP-D3	E_SPC(M06)	E(B3LYP-D3)	ZPE	H_SPC	qh-H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
ACOH	-229.041568	-229.084786	0.062061	-228.971937	-228.972343	0.043069	0.042682	-229.015006	-229.015025
Ac-Gly-OH	-437.000550	-437.101405	0.117671	-436.868778	-436.870666	0.062233	0.059279	-436.931010	-436.929945
CH2CHCO2Et	-345.671586	-345.795597	0.124421	-345.534603	-345.535622	0.055958	0.054959	-345.590561	-345.590581
Cat_3Pd	-1754.470299	-1751.367791	0.315875	-1754.103668	-1754.113733	0.155727	0.139423	-1754.259395	-1754.253156
T12_IN1	-3232.650724	-3231.326625	0.680444	-3231.888705	-3231.901442	0.212576	0.193742	-3232.101281	-3232.095184
T12_C5_IN2	-3232.655013	-3231.327995	0.680807	-3231.892873	-3231.905424	0.210853	0.192670	-3232.103726	-3232.098094
T12_C5_IN3	-3370.379442	-3369.128313	0.751589	-3369.539068	-3369.553875	0.228549	0.207466	-3369.767617	-3369.761342
T12_C5_IN4	-3370.416951	-3369.169296	0.754084	-3369.575137	-3369.589957	0.227905	0.205951	-3369.803042	-3369.795908
T12_C5_IN5	-3370.391015	-3369.134052	0.750089	-3369.552229	-3369.567687	0.232333	0.208891	-3369.784563	-3369.776578
T12_C6_IN2	-3232.658250	-3231.328890	0.681114	-3231.895560	-3231.908402	0.214377	0.194461	-3232.109936	-3232.102862
T12_C6_IN3	-3370.387850	-3369.139692	0.752392	-3369.546937	-3369.561521	0.226335	0.206518	-3369.773273	-3369.768039
T12_C6_IN4	-3370.420657	-3369.170773	0.754112	-3369.578737	-3369.593735	0.228770	0.206362	-3369.807507	-3369.800097
T12_C6_IN5	-3370.398660	-3369.139340	0.750063	-3369.560110	-3369.575036	0.230146	0.207893	-3369.790255	-3369.782929
T12_C7_IN2	-3232.662527	-3231.341367	0.682150	-3231.899314	-3231.911424	0.209048	0.191863	-3232.108362	-3232.103288
T12_C7_IN3	-3370.390695	-3369.142020	0.752748	-3369.549470	-3369.564067	0.227713	0.206868	-3369.777183	-3369.770935
T12_C7_IN4	-3370.422580	-3369.174179	0.754196	-3369.580615	-3369.595263	0.227500	0.206007	-3369.808115	-3369.801270
T12_C7_IN5	-3370.396147	-3369.140472	0.750150	-3369.557577	-3369.572530	0.230224	0.207778	-3369.787801	-3369.780308
T12_C5_TSI	-3232.633659	-3231.313765	0.675467	-3231.877375	-3231.889751	0.208342	0.191153	-3232.085717	-3232.080903
T12_C6_TSI	-3232.628190	-3231.310620	0.675894	-3231.871607	-3231.883786	0.208425	0.191210	-3232.080031	-3232.074996

T12_C7_TSI	-3232.627329	-3231.312493	0.676310	-3231.870409	-3231.882476	0.207222	0.190741	-3232.077631	-3232.073217
T12_C5_TSII	-3370.376582	-3369.128155	0.751867	-3369.537310	-3369.550997	0.222294	0.203971	-3369.759603	-3369.754969
T12_C6_TSII	-3370.377270	-3369.119555	0.751394	-3369.538017	-3369.552254	0.228086	0.206815	-3369.766103	-3369.759069
T12_C7_TSII	-3370.380640	-3369.125076	0.752340	-3369.540775	-3369.554838	0.223991	0.204624	-3369.764767	-3369.759462
T12_C5_TSIII	-3370.380138	-3369.112421	0.748187	-3369.543697	-3369.558984	0.231817	0.208229	-3369.775514	-3369.767214
T12_C6_TSIII	-3370.390012	-3369.121589	0.747995	-3369.553716	-3369.568951	0.233121	0.208963	-3369.786837	-3369.777913
T12_C7_TSIII	-3370.398412	-3369.147010	0.749137	-3369.561731	-3369.576235	0.224414	0.204568	-3369.786145	-3369.780803
T12_TC-Pd-SM	-2924.008277	-2923.533029	0.440083	-2923.503127	-2923.513777	0.181518	0.163750	-2923.684645	-2923.677527
T12_T-Pd-SM	-2668.932122	-2668.651507	0.582670	-2668.282725	-2668.293063	0.179885	0.164459	-2668.462611	-2668.457522
cis-T25_C5_IN2	-2810.807437	-2809.562966	0.776858	-2809.949601	-2809.962218	0.209174	0.191387	-2810.158775	-2810.153605
cis-T25_C5_IN3	-2948.536834	-2947.371273	0.848309	-2947.600430	-2947.614287	0.223855	0.205276	-2947.824285	-2947.819562
cis-T25_C5_IN4	-2948.583747	-2947.421600	0.851121	-2947.645669	-2947.659802	0.222996	0.203175	-2947.868665	-2947.862977
cis-T25_C5_IN5	-2948.555773	-2947.388045	0.847236	-2947.620854	-2947.634824	0.223319	0.204642	-2947.844173	-2947.839466
cis-T25_C6_IN2	-2810.813973	-2809.567623	0.777112	-2809.955792	-2809.968400	0.210066	0.191840	-2810.165857	-2810.160240
cis-T25_C6_IN3	-2948.541198	-2947.371636	0.848017	-2947.604757	-2947.619596	0.227440	0.206541	-2947.832197	-2947.826137
cis-T25_C6_IN4	-2948.588308	-2947.418057	0.850162	-2947.650645	-2947.665582	0.227652	0.205344	-2947.878297	-2947.870925
cis-T25_C6_IN5	-2948.560267	-2947.387512	0.846760	-2947.625654	-2947.640013	0.225660	0.205637	-2947.851314	-2947.845650
cis-T25_C7_IN2	-2810.831456	-2809.594161	0.778604	-2809.972418	-2809.984256	0.204857	0.189291	-2810.177275	-2810.173547
cis-T25_C7_IN3	-2948.555143	-2947.391781	0.848820	-2947.618067	-2947.632425	0.226847	0.206319	-2947.844914	-2947.838744
cis-T25_C7_IN4	-2948.593905	-2947.432146	0.851281	-2947.655703	-2947.669899	0.222689	0.202815	-2947.878392	-2947.872713
cis-T25_C7_IN5	-2948.567244	-2947.402772	0.847051	-2947.632337	-2947.646591	0.224166	0.204946	-2947.856503	-2947.851538
cis-T25_IN1	-2810.808243	-2809.577514	0.776240	-2809.950352	-2809.963807	0.214754	0.194262	-2810.165106	-2810.158069
cis-T25_C5_TSI	-2810.794864	-2809.556105	0.771971	-2809.942439	-2809.954811	0.207233	0.190120	-2810.149672	-2810.144931
cis-T25_C6_TSI	-2810.795409	-2809.553384	0.771884	-2809.943049	-2809.955448	0.207733	0.190326	-2810.150782	-2810.145774
cis-T25_C7_TSI	-2810.797570	-2809.564316	0.772582	-2809.944898	-2809.956794	0.204496	0.188692	-2810.149393	-2810.145486
cis-T25_C5_TSII	-2948.527918	-2947.359508	0.847639	-2947.592892	-2947.607148	0.224937	0.204606	-2947.817829	-2947.811754
cis-T25_C6_TSII	-2948.530731	-2947.359435	0.847431	-2947.595769	-2947.610440	0.225379	0.204624	-2947.821148	-2947.815064
cis-T25_C7_TSII	-2948.538082	-2947.371649	0.847881	-2947.602825	-2947.617060	0.223658	0.204168	-2947.826483	-2947.821227
cis-T25_C5_TSIII	-2948.539361	-2947.360140	0.844712	-2947.607024	-2947.621912	0.225773	0.205044	-2947.832797	-2947.826956
cis-	-2948.546372	-2947.364122	0.844445	-2947.614377	-2947.628757	0.225426	0.205042	-2947.839803	-2947.833800

T25_C6_TSIII									
cis-T25_C7_TSIII	-2948.557198	-2947.384511	0.844919	-2947.624966	-2947.639202	0.223754	0.204047	-2947.848720	-2947.843249
cis-T25_T-Pd-SM	-2247.101672	-2246.909495	0.679596	-2246.356342	-2246.365684	0.172455	0.160422	-2246.528797	-2246.526107
E-benchmark	E_SPC(B3LYP-D3(BJ))	E_SPC(MN15)	E_SPC(M06)	E_SPC(M06L)	E_SPC(B3PW91)	E_SPC(BP86)	E_SPC(gas)	E_SPC(HFIPb)	E_SPC(HFIPc)
ACOH	-229.182745	-228.920184	-229.041917	-229.139536	-229.083773	-229.176288	-228.909268	-228.917867	-228.892032
Ac-Gly-OH	-437.279601	-436.771130	-437.001079	-437.195861	-437.086169	-437.263260	-436.759502	-436.777895	-436.739858
CH2CHCO2Et	-345.923710	-345.494018	-345.671938	-345.848419	-345.764494	-345.897877	-345.493163	-345.500836	-345.478507
Cat_3Pd	-1755.437937	-1753.001534	-1754.470788	-1755.302221	-1754.874584	-1755.578662	-1753.667988	-1753.696910	-1753.611324
T12_C5_IN2	-3234.802777	-3230.720392	-3232.658741	-3234.246091	-3233.414399	-3234.684598	-3231.207633	-3231.287050	-3231.206599
T12_C5_IN4	-3372.670141	-3368.410072	-3370.420432	-3372.091850	-3371.208887	-3372.523144	-3368.909641	-3368.980024	-3368.898205
T12_C6_IN2	-3234.803095	-3230.723972	-3232.661272	-3234.249728	-3233.427752	-3234.697369	-3231.209676	-3231.284759	-3231.199788
T12_C6_IN4	-3372.673793	-3368.412630	-3370.424589	-3372.093654	-3371.221113	-3372.534852	-3368.912056	-3368.982698	-3368.895130
T12_C7_IN2	-3234.809106	-3230.727323	-3232.665960	-3234.255108	-3233.427004	-3234.696531	-3231.217898	-3231.290936	-3231.211082
T12_C7_IN4	-3372.675896	-3368.413057	-3370.425883	-3372.096128	-3371.223017	-3372.537113	-3368.914309	-3368.983624	-3368.895958
T12_C5_TSI	-3234.782714	-3230.696814	-3232.637132	-3234.229589	-3233.391992	-3234.666747	-3231.188364	-3231.267136	-3231.188513
T12_C6_TSI	-3234.777378	-3230.691557	-3232.632454	-3234.225732	-3233.398499	-3234.672714	-3231.180987	-3231.258928	-3231.172993
T12_C7_TSI	-3234.777440	-3230.691661	-3232.632015	-3234.227585	-3233.392149	-3234.667079	-3231.184850	-3231.257813	-3231.176033
T12_C5_TSII	-3372.629017	-3368.369966	-3370.380693	-3372.048117	-3371.161877	-3372.480444	-3368.868908	-3368.940954	-3368.863986
T12_C6_TSII	-3372.626440	-3368.366498	-3370.380993	-3372.045946	-3371.178179	-3372.496059	-3368.862359	-3368.935773	-3368.849758
T12_C7_TSII	-3372.631401	-3368.366990	-3370.383461	-3372.050229	-3371.170932	-3372.489186	-3368.865149	-3368.941363	-3368.857576
T12_C5_TSIII	-3372.630444	-3368.368220	-3370.382904	-3372.048825	-3371.186155	-3372.503046	-3368.865109	-3368.937516	-3368.846493
T12_C6_TSIII	-3372.639503	-3368.380731	-3370.392943	-3372.059204	-3371.199827	-3372.515753	-3368.875309	-3368.947773	-3368.857809
T12_C7_TSIII	-3372.649268	-3368.390646	-3370.401789	-3372.071133	-3371.185160	-3372.500890	-3368.890271	-3368.960855	-3368.882494
T12_T-Pd-SM	-2670.759637	-2667.475803	-2668.935743	-2670.261454	-2669.561384	-2670.600365	-2667.732398	-2667.789499	-2667.735635
cis-T25_C5_IN2	-2812.893155	-2809.053598	-2810.809556	-2812.380488	-2811.656010	-2812.761362			
cis-T25_C5_IN4	-2950.777010	-2946.758047	-2948.586329	-2950.240502	-2949.457287	-2950.606135			
cis-T25_C6_IN2	-2812.897977	-2809.059310	-2810.815833	-2812.385327	-2811.664334	-2812.768887			

cis-T25_C6_IN4	-2950.779286	-2946.759243	-2948.590359	-2950.241314	-2949.471013	-2950.618570			
cis-T25_C7_IN2	-2812.918751	-2809.080923	-2810.834165	-2812.406380	-2811.670070	-2812.774643			
cis-T25_C7_IN4	-2950.786502	-2946.766731	-2948.596220	-2950.248174	-2949.468469	-2950.616996			
cis-T25_C5_TSI	-2812.881695	-2809.038302	-2810.797044	-2812.370583	-2811.642576	-2812.751161			
cis-T25_C6_TSI	-2812.881202	-2809.037819	-2810.797012	-2812.370056	-2811.646149	-2812.754491			
cis-T25_C7_TSI	-2812.886283	-2809.042033	-2810.799882	-2812.375514	-2811.641297	-2812.750858			
cis-T25_C5_TSII	-2950.719765	-2946.701017	-2948.530959	-2950.180911	-2949.408391	-2950.561638			
cis-T25_C6_TSII	-2950.722152	-2946.703608	-2948.535046	-2950.183047	-2949.417362	-2950.569859			
cis-T25_C7_TSII	-2950.727821	-2946.707911	-2948.540373	-2950.189793	-2949.411194	-2950.564188			
cis-T25_C5_TSIII	-2950.728506	-2946.712137	-2948.540992	-2950.192423	-2949.422502	-2950.573923			
cis-T25_C6_TSIII	-2950.733776	-2946.717102	-2948.547835	-2950.196805	-2949.429575	-2950.581128			
cis-T25_C7_TSIII	-2950.748524	-2946.733405	-2948.558933	-2950.210098	-2949.425629	-2950.577100			
cis-T25_T-Pd-SM	-2248.867740	-2245.826795	-2247.103498	-2248.410952	-2247.805083	-2248.678768			

E_SPC= Single-point solvation energies; E= Electronic energies; ZPE = zero-point vibrational energy; H_SPC = enthalpy; qh-H_SPC = enthalpy with Head-Gordon correction; G(T)_SPC = Gibbs free energy; qh-G(T)_SPC = Gibbs free energy with Head-Gordon correction.

3.3 Cartesian Coordinates

15
Ac-Gly-OH Eopt -436.622905
C 1.809571 -0.166589 -0.000046
O 2.068841 -1.360408 -0.001458
N 0.529409 0.284634 0.002086
H 0.295977 1.267606 0.002247
C 2.878966 0.901976 -0.000453
H 2.483162 1.921609 -0.000051
H 3.513039 0.764760 0.880047
H 3.512027 0.764993 -0.881708
C -0.568134 -0.635187 0.001805
H -0.543908 -1.296657 0.877958
H -0.541832 -1.298089 -0.873175
C -1.856869 0.140576 -0.000139
O -1.934879 1.347416 -0.000998
O -2.921449 -0.670284 -0.000677
H -3.705643 -0.095098 -0.001855
8
AcOH Eopt -228.832855
C -0.092793 0.123421 0.000227
O -0.649099 1.194199 -0.000191
O -0.768308 -1.044866 0.000032
H -1.710144 -0.803630 -0.000147
C 1.390352 -0.103272 0.000020
H 1.906028 0.856453 -0.000253
H 1.678884 -0.684373 -0.881207
H 1.679136 -0.684009 0.881401
15
CH2CHCO2Et Eopt -345.396184
C 1.722369 -0.758071 -0.000018
C 2.981062 -0.323371 0.000068
H 3.823610 -1.007935 0.000119
H 3.187443 0.743544 0.000083
C 0.599786 0.207252 -0.000100
O 0.707339 1.413637 0.000011
O -0.579524 -0.436638 -0.000054
C -1.736282 0.408315 0.000002
C -2.951658 -0.486925 0.000047
H -3.862500 0.120235 0.000090
H -2.964002 -1.127262 0.887275
H -2.964076 -1.127248 -0.887191
H -1.700870 1.056585 0.881985
H -1.700944 1.056599 -0.881972
H 1.467163 -1.813713 -0.000037
45
Cat_3Pd Eopt -1749.766534
Pd 0.357288 -1.770269 -0.011970
C 2.470503 -0.738794 -1.839022
O 2.003770 -1.719408 -1.199180
O 2.223016 0.485137 -1.652572
C -0.469900 2.515387 1.871819
O -1.487007 2.187002 1.202631
O 0.719454 2.131896 1.695556
C -0.711615 3.472774 3.008619
H 0.228876 3.767970 3.474281
H -1.238975 4.353175 2.630633
H -1.361849 2.991495 3.745443
C 3.462122 -1.063410 -2.924704
H 3.162684 -1.974484 -3.446346
H 3.554658 -0.227458 -3.619343
H 4.437638 -1.242193 -2.459196
Pd -1.719191 0.578569 -0.012948
C -0.555461 2.513133 -1.850563
O 0.509023 2.604386 -1.180445
O -1.500850 1.694971 -1.679063
C 2.395963 -0.886089 1.869224
O 1.463373 -1.714913 1.674704
O 2.621144 0.175778 1.228742
C 3.370270 -1.223312 2.966662
H 3.715531 -0.311801 3.457806
H 2.912783 -1.905644 3.684598
H 4.236899 -1.721088 2.517633
C -0.704910 3.493117 -2.983945
H 0.064735 3.285863 -3.733861
H -1.694963 3.418219 -3.434167
H -0.534029 4.506134 -2.609321
Pd 1.352671 1.202838 0.020428
C -1.977403 -1.660442 1.830482
O -1.176285 -2.377405 1.171159
O -2.233652 -0.437567 1.653391
C -2.707641 -2.350436 2.952115
H -1.978394 -2.707276 3.685491
H -3.418948 -1.673900 3.426299
H -3.228951 -3.226062 2.554632
C -1.870622 -1.732878 -1.884465
O -0.687689 -2.133733 -1.698663
O -2.489843 -0.849084 -1.233401
C -2.640472 -2.413456 -2.985093
H -3.238662 -3.217063 -2.541423
H -3.319282 -1.705667 -3.464144
H -1.955726 -2.852607 -3.712133
93
T12_C5_IN2 Eopt -3228.077183
Pd -3.132071 -0.278943 0.173662
C -5.789269 0.098114 -0.701706
C -5.152721 -2.156209 -0.453719
C -7.059098 -0.271744 -1.124860
C -6.396972 -2.591729 -0.885612
H -7.769731 0.508154 -1.375720
H -6.578347 -3.658390 -0.961401
N -4.913716 -0.847027 -0.372284

H	-8.341024	-1.947426	-1.546267
C	-7.356815	-1.631775	-1.212369
N	-2.922230	-2.324198	0.354292
N	-3.963527	1.571388	-0.236868
C	-3.979942	-3.042673	-0.116633
C	-5.280366	1.507432	-0.559776
O	-4.049086	-4.254142	-0.280362
O	-6.058450	2.446204	-0.733466
C	-1.680700	-2.939992	0.554384
C	-1.063886	-3.700289	-0.445154
C	-0.969870	-2.669298	1.728372
C	0.255717	-4.110442	-0.294814
C	0.352268	-3.075387	1.861857
C	0.981775	-3.790482	0.847432
H	2.021677	-4.083887	0.939427
C	-0.192209	-0.154398	-0.236543
C	-0.857878	0.604185	1.866900
C	-0.533267	-0.663629	-1.509932
C	1.177772	0.046361	0.093501
C	0.467391	0.789728	2.281659
H	-1.687994	0.823893	2.529990
C	0.459129	-0.983930	-2.401359
H	-1.581566	-0.810632	-1.752466
C	2.193718	-0.178457	-0.886220
C	1.477996	0.511711	1.392847
H	0.669872	1.135859	3.288589
C	1.814909	-0.730370	-2.095249
H	0.199004	-1.409882	-3.366068
H	2.521900	0.640532	1.667580
H	2.566167	-0.937955	-2.854132
N	-1.176409	0.152541	0.664935
Pd	3.897122	0.903508	-0.716640
C	6.568938	1.645554	-0.051013
O	7.615976	2.230206	0.150407
O	5.500996	2.152383	-0.584489
N	5.193903	-0.443110	0.064320
C	5.009141	-1.697036	0.304157
C	6.050747	-2.591904	0.893387
H	5.638620	-3.590715	1.037823
H	6.397793	-2.197025	1.853569
H	6.921344	-2.651408	0.231546
O	3.873075	-2.305346	0.042961
C	6.487336	0.166819	0.363585
H	6.697936	0.115253	1.439112
H	7.296041	-0.363960	-0.152741
H	-1.456761	-2.106508	2.516338
H	-1.612868	-3.940344	-1.347915
C	0.958691	-4.801763	-1.424954
C	1.141223	-2.748078	3.093363
F	1.828214	-5.722629	-0.983210
F	1.669982	-3.922596	-2.163049
F	0.104455	-5.409159	-2.258493
F	1.479739	-3.850008	3.778679
F	2.296734	-2.123131	2.780700
F	0.471008	-1.942579	3.933260
C	-1.339930	4.315140	0.258196
C	-1.971061	5.079036	1.253519
C	-0.004253	4.631137	-0.071341
C	-1.289901	6.136084	1.863578
C	0.016137	6.449669	1.521144
C	0.662461	5.683665	0.559353
H	-1.801958	6.711422	2.631673
H	0.533679	7.272045	2.005996
H	1.690434	5.902628	0.281698
C	0.783471	3.837100	-1.042815
C	1.886365	3.103678	-0.612660
C	0.538678	3.793152	-2.417370
N	2.630467	2.380509	-1.457242
H	2.161555	3.071741	0.435848
N	1.308611	3.118789	-3.271581
H	-0.298961	4.339649	-2.846241
C	2.316793	2.433834	-2.758600
H	2.941261	1.857337	-3.432525
C	-2.034606	3.136118	-0.398916
H	-1.455459	2.233176	-0.188835
H	-2.014945	3.241417	-1.490630
C	-3.485819	2.917998	0.038993
H	-4.124488	3.597714	-0.539858
C	-3.693187	3.282191	1.505306
H	-4.733175	3.074279	1.775908
H	-3.050576	2.659402	2.143037
C	-3.369904	4.752067	1.707364
H	-4.093994	5.355267	1.139942
H	-3.487967	5.041030	2.758267
H	3.235178	-1.645583	-0.338622

101

T12_C5_IN3 Eopt -3365.707167

Pd	-3.505096	0.047797	0.223706
C	-6.070063	0.841021	-0.643439
C	-5.771490	-1.491010	-0.476001
C	-7.376545	0.675857	-1.084177
C	-7.061787	-1.723845	-0.929094
H	-7.963228	1.559260	-1.311344
H	-7.395645	-2.748839	-1.048942
N	-5.346767	-0.233881	-0.343190
H	-8.885264	-0.778538	-1.571015
C	-7.868632	-0.622326	-1.221859
N	-3.597539	-2.008366	0.334696
N	-4.045003	2.008531	-0.140709
C	-4.736605	-2.549609	-0.178676
C	-5.355694	2.154472	-0.460295
O	-4.967761	-3.729803	-0.407627
O	-5.982465	3.204461	-0.607287
C	-2.441826	-2.785059	0.487256
C	-1.865331	-3.459590	-0.593990
C	-1.747185	-2.738092	1.699743

C	-0.591218	-4.003981	-0.478886
C	-0.475853	-3.289409	1.805136
C	0.116629	-3.919454	0.715037
H	1.122054	-4.319427	0.788597
C	-0.601938	-0.240045	-0.243012
C	-1.095175	0.436155	1.935407
C	-1.042898	-0.552076	-1.547221
C	0.786039	-0.314854	0.071075
C	0.248951	0.355703	2.326067
H	-1.865863	0.735489	2.638257
C	-0.135629	-0.960166	-2.493978
H	-2.101766	-0.477413	-1.775694
C	1.707308	-0.628673	-0.962980
C	1.188081	-0.019069	1.394778
H	0.522465	0.573231	3.351979
C	1.244876	-0.998021	-2.204704
H	-0.479659	-1.229517	-3.488207
H	2.240183	-0.102898	1.664551
H	1.946454	-1.253616	-2.995189
N	-1.504454	0.149873	0.710926
H	-2.197866	-2.222755	2.540405
H	-2.394676	-3.497813	-1.538713
C	0.053316	-4.658813	-1.664222
C	0.294391	-3.205736	3.088117
F	-0.129173	-5.986676	-1.670882
F	1.386915	-4.450255	-1.674634
F	-0.431232	-4.184952	-2.822957
F	0.363495	-4.391307	3.710354
F	1.567498	-2.812733	2.867994
F	-0.246544	-2.331438	3.951597
C	-1.022869	4.294126	0.400170
C	-1.521998	5.119120	1.421882
C	0.339705	4.417034	0.055727
C	-0.685935	6.050963	2.042684
C	0.646938	6.178263	1.684624
C	1.160382	5.347666	0.696675
H	-1.098088	6.676694	2.831275
H	1.286083	6.904593	2.177959
H	2.205996	5.418186	0.408022
C	1.002329	3.545949	-0.946250
C	1.924391	2.586273	-0.537387
C	0.837659	3.657184	-2.329089
N	2.598066	1.834094	-1.413138
H	2.109574	2.403584	0.515829
N	1.545794	2.946826	-3.207504
H	0.121732	4.365886	-2.741921
C	2.406789	2.066081	-2.719321
H	3.020086	1.485258	-3.400850
C	-1.892834	3.249869	-0.274346
H	-1.462585	2.264577	-0.077382
H	-1.852443	3.368486	-1.364552
C	-3.359351	3.253569	0.167739
H	-3.885068	4.043812	-0.383900
C	-3.494227	3.595994	1.647795
H	-4.550746	3.539749	1.928388
H	-2.947095	2.859630	2.253270
C	-2.947710	4.991350	1.891815
H	-3.579579	5.717482	1.359228
H	-3.005018	5.257199	2.953934
Pd	3.581944	0.062857	-0.796588
C	3.585642	-2.088104	-0.140536
C	4.846439	-1.526140	-0.070541
H	2.981479	-2.169347	0.758253
H	3.296683	-2.705835	-0.983489
H	5.581524	-1.676601	-0.855698
C	5.328494	-0.957947	1.220662
O	4.606858	-0.674671	2.156436
O	6.647006	-0.804614	1.207643
C	7.206176	-0.129181	2.343799
C	8.658438	0.137700	2.034426
H	7.078461	-0.762495	3.228063
H	6.642075	0.793984	2.506074
H	8.749720	0.770413	1.146260
H	9.130656	0.652609	2.877155
H	9.199457	-0.796116	1.853445
C	5.840314	1.213187	-1.928818
O	5.275808	0.744298	-2.922429
O	5.388882	1.123706	-0.720059
C	7.161057	1.946669	-2.040134
H	7.453308	2.049917	-3.086302
H	7.084613	2.933380	-1.572837
H	7.931718	1.389341	-1.496494

101

T12_C5_IN4 Eopt -3365.751311

Pd	-3.339938	-0.087847	0.159607
C	-6.079768	0.395344	-0.377055
C	-5.512930	-1.877076	-0.171141
C	-7.408447	0.077374	-0.624115
C	-6.820638	-2.263391	-0.425501
H	-8.109501	0.886583	-0.797146
H	-7.053084	-3.322566	-0.448611
N	-5.204969	-0.580275	-0.150036
H	-8.806385	-1.544276	-0.840583
C	-7.774214	-1.268208	-0.645092
N	-3.215931	-2.137382	0.365032
N	-4.156402	1.791711	-0.165907
C	-4.356127	-2.813179	0.057279
C	-5.498951	1.779493	-0.347208
O	-4.507410	-4.025077	-0.031594
O	-6.242176	2.752121	-0.491106
C	-2.024215	-2.857993	0.530860
C	-1.463774	-3.581866	-0.526159
C	-1.324979	-2.769165	1.735591
C	-0.210412	-4.164677	-0.387074
C	-0.070203	-3.355786	1.864112
C	0.499303	-4.054473	0.805143

H	1.492301	-4.481739	0.896297
C	-0.454237	-0.358650	-0.500800
C	-0.816864	0.453873	1.652801
C	-0.946118	-0.565181	-1.807736
C	0.886000	-0.714859	-0.176454
C	0.511980	0.208726	2.023868
H	-1.526522	0.879431	2.355978
C	-0.141940	-1.163131	-2.745223
H	-1.961055	-0.254480	-2.038576
C	1.698412	-1.350902	-1.161609
C	1.347518	-0.414981	1.127140
H	0.844525	0.457457	3.024726
C	1.164284	-1.571988	-2.413003
H	-0.515956	-1.332780	-3.750086
H	2.351220	-0.692343	1.428561
N	-1.291319	0.161908	0.452317
H	-1.999876	-3.647859	-1.465277
H	-1.763077	-2.214419	2.557697
C	0.699943	-3.241908	3.145420
C	0.396421	-4.919848	-1.532437
F	1.988643	-2.920105	2.911954
F	0.196198	-2.297635	3.958388
F	0.708711	-4.393920	3.830203
F	-0.100074	-4.521079	-2.715500
F	0.177214	-6.238785	-1.435204
F	1.731875	-4.749114	-1.581924
C	-3.593763	3.130331	-0.110175
C	-2.127924	3.146332	-0.514353
H	-4.161555	3.744221	-0.823964
C	-3.778221	3.778385	1.258871
C	-1.404309	4.430620	-0.179755
H	-1.614211	2.321024	-0.013251
H	-2.053845	2.924702	-1.586004
H	-4.823549	3.679791	1.564674
H	-3.155129	3.258752	2.001266
C	-3.388214	5.245627	1.165555
C	-1.997598	5.426445	0.610728
C	-0.069428	4.606216	-0.592322
H	-4.113476	5.762603	0.520013
H	-3.452072	5.732022	2.146190
C	-1.276922	6.582854	0.922094
C	0.638869	5.761124	-0.258596
C	0.656194	3.536115	-1.314233
C	0.027609	6.762836	0.486274
H	-1.753106	7.345941	1.533911
H	1.669253	5.868904	-0.587404
C	1.699262	2.862311	-0.689669
C	0.398877	3.150396	-2.632991
H	0.574696	7.665464	0.741875
N	2.405107	1.906913	-1.317419
H	1.988505	3.081476	0.335489
N	1.105493	2.216279	-3.266319
H	-0.394466	3.630170	-3.203012
C	2.079789	1.632404	-2.585733
H	2.662172	0.871873	-3.090147
C	4.111918	-0.616678	-1.191334
Pd	3.796173	1.044414	-0.061763
H	4.068569	-0.305013	-2.240578
C	5.509797	-1.023290	-0.848810
H	3.261100	-2.054195	0.158989
O	5.812737	-2.002028	-0.203243
O	6.407400	-0.145596	-1.333334
C	7.758762	-0.367703	-0.918377
C	8.580860	0.793524	-1.423120
H	8.105547	-1.324688	-1.323708
H	7.779061	-0.443424	0.173433
H	9.627782	0.669215	-1.127584
H	8.536296	0.859768	-2.514793
H	8.212267	1.735941	-1.005641
O	3.915374	2.446668	1.690247
C	4.726504	1.615429	2.184013
O	5.009803	0.541297	1.546845
C	5.397461	1.866497	3.500265
H	6.406974	2.250875	3.316197
H	4.840052	2.607597	4.076026
H	5.494182	0.933035	4.060032
C	3.122147	-1.732412	-0.877650
H	3.372696	-2.612551	-1.484872
H	1.769778	-2.075432	-3.162077

101

T12_C5_IN5 Eopt -3365.715238

Pd	-3.242948	0.180405	-0.455846
C	-5.677284	1.208063	-1.460056
C	-5.591137	-1.140447	-1.325723
C	-6.957139	1.163987	-1.996950
C	-6.868661	-1.253490	-1.853730
H	-7.453893	2.099843	-2.228489
H	-7.294823	-2.243203	-1.977317
N	-5.060035	0.070171	-1.154632
H	-8.549508	-0.144908	-2.613758
C	-7.548534	-0.083307	-2.196571
N	-3.472141	-1.862598	-0.536672
N	-3.672988	2.199890	-0.611334
C	-4.719173	-2.286552	-0.881958
C	-4.919418	2.452108	-1.086751
O	-5.149030	-3.432484	-0.872270
O	-5.477993	3.545055	-1.185820
C	-2.566580	-2.776236	0.020046
C	-1.341545	-3.015593	-0.611876
C	-2.824883	-3.388339	1.248439
C	-0.387048	-3.821101	-0.003594
C	-1.863522	-4.198780	1.844523
C	-0.636179	-4.415965	1.230839
H	0.111552	-5.043969	1.703026
C	-0.282485	0.022167	-0.763015
C	-0.998752	-0.263261	1.435224

C	-0.581605	0.412952	-2.087971
C	1.030505	-0.404182	-0.422647
C	0.285145	-0.634175	1.858626
H	-1.830104	-0.228580	2.131856
C	0.389808	0.329881	-3.053181
H	-1.581755	0.771668	-2.313478
C	2.024713	-0.482609	-1.447978
C	1.295914	-0.710453	0.931419
H	0.458852	-0.864124	2.903439
C	1.682217	-0.133166	-2.737441
H	0.163257	0.620580	-4.074349
H	2.298595	-0.987577	1.237733
N	-1.272459	0.059127	0.181843
H	-1.147066	-2.556548	-1.574730
H	-3.780409	-3.220578	1.733818
C	-2.124257	-4.759915	3.211484
C	0.941195	-4.069911	-0.652171
F	-1.386899	-5.853126	3.454687
F	-1.818974	-3.858539	4.165852
F	-3.412302	-5.085951	3.380692
F	1.072053	-3.430016	-1.822095
F	1.152240	-5.373945	-0.874747
F	1.953862	-3.651817	0.144264
C	-3.054450	3.345685	0.038271
C	-1.534507	3.317281	-0.033286
H	-3.414525	4.241805	-0.484009
C	-3.514255	3.453551	1.490096
C	-0.855109	4.315113	0.880218
H	-1.189032	2.317305	0.248079
H	-1.214567	3.459084	-1.072626
H	-4.606442	3.391389	1.526390
H	-3.111694	2.604620	2.061861
C	-3.039946	4.770281	2.081499
C	-1.558398	4.979002	1.897689
C	0.532258	4.528522	0.775992
H	-3.584102	5.592990	1.594574
H	-3.286941	4.831492	3.148151
C	-0.879210	5.838827	2.764878
C	1.194761	5.382245	1.659817
C	1.364192	3.842729	-0.240977
C	0.487340	6.047216	2.653928
H	-1.442334	6.342626	3.547494
H	2.267149	5.526501	1.555156
C	2.251521	2.834707	0.127463
C	1.392128	4.205566	-1.588947
H	1.001475	6.714329	3.339648
N	3.095584	2.279699	-0.750964
H	2.309743	2.459176	1.146440
N	2.237269	3.667305	-2.468310
H	0.721310	4.976081	-1.965771
C	3.060310	2.738738	-2.004019
H	3.774375	2.313043	-2.702686
C	4.529310	-0.465666	-1.824630
Pd	4.356092	0.589215	0.001711
H	4.427318	0.251324	-2.634681
C	5.789374	-1.245066	-1.939956
H	5.176309	-0.537746	0.607619
O	6.681887	-0.944372	-2.699803
O	5.816748	-2.312622	-1.132055
C	7.029665	-3.076586	-1.157334
C	6.874153	-4.193889	-0.154955
H	7.865967	-2.413895	-0.911813
H	7.190456	-3.450482	-2.173710
H	7.779313	-4.809205	-0.138543
H	6.710948	-3.792951	0.850248
H	6.025581	-4.834767	-0.413827
O	5.651760	2.053867	1.174160
C	4.854364	1.981226	2.142670
O	3.829020	1.226715	2.097958
C	5.074855	2.819375	3.374982
H	6.034314	3.336046	3.328867
H	4.266961	3.554884	3.458048
H	5.029453	2.186406	4.265798
C	3.393542	-0.919229	-1.115444
H	3.484426	-1.853564	-0.566575
H	2.420522	-0.223313	-3.528101

93

T12_C5_TSI Eopt -3228.061730

Pd	-3.108336	-0.316628	0.096181
C	-5.796942	-0.070812	-0.745904
C	-5.011962	-2.286602	-0.616140
C	-7.043414	-0.501674	-1.179655
C	-6.228887	-2.780965	-1.061984
H	-7.805874	0.241937	-1.384426
H	-6.340476	-3.852741	-1.185713
N	-4.855550	-0.970273	-0.472856
H	-8.216752	-2.234625	-1.679612
C	-7.252327	-1.871951	-1.335936
N	-2.782846	-2.349837	0.197889
N	-4.070570	1.486420	-0.211762
C	-3.790017	-3.113653	-0.306506
C	-5.381421	1.359209	-0.534928
O	-3.786306	-4.321284	-0.506579
O	-6.214402	2.256766	-0.663767
C	-1.523605	-2.918177	0.436520
C	-0.778657	-3.495170	-0.595588
C	-0.934849	-2.776047	1.695215
C	0.551294	-3.842718	-0.388013
C	0.394733	-3.131922	1.893524
C	1.156680	-3.651253	0.850453
H	2.212964	-3.857117	0.985755
C	-0.146749	-0.150912	-0.236202
C	-0.861858	0.489976	1.881603
C	-0.445761	-0.441238	-1.587968
C	1.203909	-0.196095	0.198590
C	0.450993	0.500051	2.379158

H	-1.702206	0.735024	2.522725
C	0.551614	-0.833485	-2.450511
H	-1.479954	-0.370407	-1.914832
C	2.243129	-0.556396	-0.713567
C	1.478915	0.134171	1.544081
H	0.623462	0.751823	3.419143
C	1.886052	-0.915134	-2.005717
H	0.305205	-1.085437	-3.477484
H	2.504672	0.079693	1.896613
H	2.656632	-1.249284	-2.695708
N	-1.157125	0.165023	0.633647
Pd	3.821932	0.921444	-0.701461
H	3.222186	-1.229924	-0.178241
C	6.379033	2.046163	-0.291758
O	7.314591	2.814783	-0.228265
O	5.177987	2.388488	-0.690958
N	5.321232	-0.157207	0.027817
C	5.197127	-1.395730	0.452006
C	6.385165	-2.115729	1.033482
H	6.103118	-3.143562	1.260991
H	6.721816	-1.621338	1.951481
H	7.225827	-2.111379	0.332043
O	4.096392	-2.030146	0.399005
C	6.568920	0.577250	0.100995
H	6.993694	0.560487	1.112528
H	7.324860	0.153735	-0.574345
H	-1.519383	-2.347178	2.501585
H	-1.231549	-3.615753	-1.572623
C	1.355092	-4.411158	-1.520901
C	1.036149	-2.959583	3.237937
F	1.353789	-5.752100	-1.513088
F	2.637377	-4.016640	-1.464400
F	0.871244	-4.023569	-2.716521
F	1.193457	-4.131186	3.870534
F	2.259767	-2.407825	3.132842
F	0.311267	-2.165722	4.047699
C	-1.515386	4.247300	0.347918
C	-2.137092	4.976720	1.372702
C	-0.176824	4.551747	0.028025
C	-1.440592	6.002901	2.017183
C	-0.131402	6.312288	1.679364
C	0.506727	5.571894	0.691317
H	-1.940781	6.556344	2.808823
H	0.396880	7.110911	2.191590
H	1.538372	5.784494	0.422611
C	0.578619	3.751473	-0.962170
C	1.647847	2.961378	-0.551137
C	0.318639	3.735912	-2.335107
N	2.355404	2.224294	-1.414319
H	1.933548	2.903184	0.494061
N	1.037255	3.025500	-3.203526
H	-0.490360	4.334384	-2.749322
C	2.023381	2.295106	-2.708729
H	2.617024	1.701659	-3.395841
C	-2.218584	3.108027	-0.359061
H	-1.629982	2.196828	-0.217480
H	-2.228839	3.278600	-1.442680
C	-3.652708	2.842247	0.098904
H	-4.326018	3.512129	-0.451526
C	-3.843981	3.161808	1.577778
H	-4.877013	2.931706	1.857072
H	-3.183571	2.529490	2.187886
C	-3.534055	4.630648	1.818431
H	-4.263821	5.242328	1.267564
H	-3.653598	4.890324	2.876691

101

T12_C5_TSII Eopt -3365.708411

Pd	-3.373211	0.147722	0.260982
C	-6.035019	0.892016	-0.331122
C	-5.679766	-1.431106	-0.184457
C	-7.377157	0.701974	-0.632328
C	-7.005951	-1.689371	-0.498369
H	-7.999223	1.574750	-0.798203
H	-7.332273	-2.721231	-0.570462
N	-5.262376	-0.166964	-0.106169
H	-8.903003	-0.780612	-0.953233
C	-7.858355	-0.604682	-0.713286
N	-3.434691	-1.907406	0.422771
N	-3.996239	2.096126	-0.032123
C	-4.612784	-2.472540	0.041098
C	-5.333314	2.218514	-0.222086
O	-4.858025	-3.662243	-0.113576
O	-5.990088	3.256699	-0.309364
C	-2.290857	-2.698400	0.579503
C	-1.797939	-3.490597	-0.461845
C	-1.537732	-2.577743	1.751105
C	-0.549143	-4.091026	-0.350477
C	-0.294120	-3.188134	1.854874
C	0.213024	-3.946933	0.804087
H	1.194607	-4.402730	0.877402
C	-0.493819	-0.264131	-0.394531
C	-0.827737	0.650309	1.722777
C	-1.018158	-0.642178	-1.651107
C	0.893972	-0.438753	-0.124877
C	0.527469	0.522931	2.052453
H	-1.538425	1.064405	2.430062
C	-0.200861	-1.231044	-2.585119
H	-2.074496	-0.481381	-1.845285
C	1.732913	-0.963620	-1.152271
C	1.389022	-0.029060	1.134425
H	0.873885	0.839365	3.029317
C	1.173583	-1.411689	-2.330985
H	-0.613163	-1.551437	-3.537095
H	2.440378	-0.168125	1.377264
H	1.802940	-1.855371	-3.098157
N	-1.323891	0.269770	0.556308

H -1.924211 -1.969809 2.561322
H -2.373687 -3.584946 -1.374695
C 0.001686 -4.882535 -1.498571
C 0.535004 -3.037943 3.095379
F -0.262074 -6.191056 -1.388864
F 1.345239 -4.762857 -1.577598
F -0.499526 -4.472506 -2.675300
F 0.567595 -4.170795 3.812953
F 1.811645 -2.734705 2.790967
F 0.073331 -2.067385 3.899946
C -0.891436 4.284761 0.179373
C -1.237125 5.118332 1.254650
C 0.448978 4.289424 -0.263884
C -0.273684 5.946191 1.836937
C 1.038023 5.954632 1.387288
C 1.399650 5.112626 0.343768
H -0.565965 6.581521 2.670092
H 1.778713 6.596652 1.854704
H 2.427014 5.086687 -0.010304
C 0.929559 3.376647 -1.324304
C 1.965621 2.483202 -1.055253
C 0.440995 3.348657 -2.633304
N 2.403383 1.619782 -1.979820
H 2.464589 2.440134 -0.090739
N 0.902960 2.518610 -3.568668
H -0.340589 4.037807 -2.945901
C 1.851927 1.673904 -3.195470
H 2.217526 0.962421 -3.929036
C -1.901569 3.343661 -0.447609
H -1.499989 2.327041 -0.408240
H -2.017873 3.564070 -1.515053
C -3.297143 3.351890 0.185541
H -3.895647 4.129257 -0.306401
C -3.262699 3.718671 1.664902
H -4.287269 3.712362 2.050601
H -2.688968 2.970945 2.229095
C -2.630946 5.091598 1.825211
H -3.260699 5.834296 1.313060
H -2.599537 5.390378 2.879319
Pd 3.566787 -0.042543 -1.264510
C 3.313182 -2.211821 -0.522359
C 4.602178 -1.634621 -0.415187
H 2.767567 -2.373491 0.403725
H 3.115896 -2.924019 -1.315348
H 5.383571 -1.872534 -1.132811
C 5.030659 -1.149449 0.924732
O 4.295681 -1.088023 1.891829
O 6.311462 -0.791795 0.933870
C 6.753044 -0.145121 2.140000
C 8.217688 0.173645 1.968746
H 6.571334 -0.814481 2.986596
H 6.143837 0.754134 2.273848
H 8.373377 0.839453 1.114759
H 8.595147 0.672379 2.867278
H 8.802246 -0.737733 1.808801
C 5.444811 1.866684 -0.517795
O 4.653561 1.974854 0.429190
O 5.311819 1.041700 -1.498780
C 6.671580 2.750948 -0.613846
H 6.852510 3.255157 0.337372
H 7.545196 2.163074 -0.908340
H 6.511445 3.505811 -1.391838
101
T12_C5_TSIII Eopt -3365.695581
Pd 3.168586 -0.525648 -0.664651
C 5.067167 -2.038342 -2.104266
C 5.330516 0.296197 -2.290346
C 6.135224 -2.260617 -2.963183
C 6.408897 0.141462 -3.148947
H 6.419844 -3.283739 -3.183185
H 6.908892 1.028563 -3.522464
N 4.718589 -0.787613 -1.813021
H 7.642797 -1.301648 -4.161714
C 6.803048 -1.154175 -3.488759
N 3.625279 1.433162 -1.091018
N 3.280150 -2.585106 -0.613149
C 4.774688 1.610136 -1.798926
C 4.295160 -3.095051 -1.358476
O 5.340982 2.663760 -2.057218
O 4.661731 -4.267214 -1.434129
C 3.032231 2.523944 -0.439115
C 1.721229 2.893081 -0.757933
C 3.689104 3.193343 0.595715
C 1.070529 3.877500 -0.024531
C 3.032078 4.186841 1.315531
C 1.717759 4.530559 1.021208
H 1.211563 5.304849 1.587364
C 0.292980 0.129525 -0.245603
C 1.559836 0.256807 1.706472
C 0.229924 -0.195108 -1.618055
C -0.848128 0.672595 0.413646
C 0.477612 0.775796 2.431461
H 2.526323 0.104937 2.175101
C -0.919308 0.061737 -2.323423
H 1.104176 -0.632495 -2.091410
C -2.048700 0.873922 -0.336804
C -0.717541 0.979577 1.787329
H 0.606017 1.024222 3.478828
C -2.057686 0.592098 -1.690159
H -0.970131 -0.174032 -3.381875
H -1.550937 1.400404 2.337966
N 1.469580 -0.063622 0.428708
H 1.219322 2.396126 -1.579991
H 4.713634 2.927756 0.833743
C 3.726247 4.823168 2.483554
C -0.354614 4.238534 -0.323144

F	5.039285	4.972863	2.264167
F	3.217330	6.028949	2.775159
F	3.598497	4.064206	3.590479
F	-0.795970	3.681720	-1.458114
F	-0.520114	5.564483	-0.423456
F	-1.179958	3.825920	0.666883
C	2.763558	-3.478675	0.409243
C	1.241942	-3.429944	0.534293
H	3.055391	-4.495599	0.118288
C	3.427130	-3.178418	1.750396
C	0.703173	-4.065182	1.802399
H	0.915226	-2.383624	0.507662
H	0.797720	-3.896322	-0.352829
H	4.513338	-3.148644	1.614354
H	3.112809	-2.184864	2.099660
C	3.043506	-4.239446	2.765379
C	1.550511	-4.415415	2.866694
C	-0.683655	-4.252470	1.970363
H	3.499282	-5.195768	2.469138
H	3.451440	-4.001545	3.755059
C	1.013574	-4.933556	4.048314
C	-1.200832	-4.762171	3.163222
C	-1.670132	-3.907222	0.920125
C	-0.352145	-5.109538	4.206547
H	1.691322	-5.194733	4.858114
H	-2.275078	-4.897043	3.259896
C	-2.561502	-2.855004	1.099153
C	-1.847133	-4.646513	-0.253015
H	-0.755155	-5.509478	5.132325
N	-3.525147	-2.577845	0.210416
H	-2.498497	-2.213289	1.972184
N	-2.816440	-4.395532	-1.131036
H	-1.190851	-5.485994	-0.477067
C	-3.619797	-3.374776	-0.863969
H	-4.424135	-3.137640	-1.553064
C	-4.556082	1.435602	-0.275528
Pd	-4.417209	-0.633313	0.061132
H	-4.658628	1.484767	-1.356090
C	-5.628699	2.039301	0.548966
H	-3.573711	-0.089341	1.306127
O	-5.533823	2.291867	1.733668
O	-6.726356	2.255849	-0.180214
C	-7.853139	2.775127	0.537310
C	-8.996187	2.884350	-0.442020
H	-7.581678	3.745119	0.967281
H	-8.083134	2.098958	1.367427
H	-9.884093	3.278249	0.062850
H	-8.739828	3.556606	-1.266423
H	-9.241845	1.903532	-0.860586
O	-5.708894	-1.301992	-1.406888
C	-5.694117	-0.758031	-2.582138
O	-4.891283	0.087538	-2.983374
C	-6.807750	-1.252177	-3.485642
H	-6.897924	-2.340769	-3.430137
H	-7.758199	-0.830506	-3.139992
H	-6.630184	-0.937058	-4.515119
C	-3.302496	1.233159	0.371297
H	-3.222559	1.727711	1.337769
H	-2.978342	0.683547	-2.262283

93

T12_C6_IN2 Eopt -3228.078046

Pd	-2.538601	1.386261	-0.477066
N	-3.683662	2.238282	-1.801408
C	-3.402697	3.492055	-2.145120
C	-4.189472	4.126912	-3.097008
C	-5.257135	3.420395	-3.650907
C	-5.525304	2.110039	-3.250640
C	-4.695239	1.529814	-2.302674
C	-4.822966	0.128552	-1.763379
O	-5.759807	-0.584747	-2.099367
N	-3.782492	-0.188240	-0.941931
C	-3.702267	-1.464721	-0.376946
C	-4.763101	-2.056970	0.314039
C	-4.584528	-3.289405	0.938120
C	-3.362002	-3.950648	0.893472
C	-2.313385	-3.367941	0.185863
C	-2.486000	-2.151215	-0.456970
H	-1.676371	-1.715027	-1.029325
C	-0.977959	-4.048766	0.155499
F	-0.354175	-3.964123	1.349186
F	-1.086689	-5.354515	-0.126074
F	-0.156527	-3.500047	-0.754643
H	-3.231461	-4.902587	1.396089
C	-5.748455	-3.926650	1.640287
F	-6.521898	-4.616717	0.788990
F	-5.345243	-4.784463	2.592905
F	-6.532391	-3.009073	2.229842
H	-5.719239	-1.549692	0.364202
H	-6.350011	1.527600	-3.646875
H	-5.889623	3.895633	-4.395136
H	-3.952547	5.150676	-3.365175
C	-2.271128	4.120898	-1.377146
O	-2.002077	5.305081	-1.576569
N	-1.698810	3.271869	-0.484398
C	-0.808769	3.895947	0.477542
C	-1.367171	3.822396	1.894364
C	-0.578797	4.765689	2.789152
C	0.916465	4.630589	2.626363
C	1.743359	5.236568	3.576737
C	3.124334	5.183404	3.473083
C	3.696096	4.488373	2.414429
C	2.889048	3.858808	1.464474
C	1.483688	3.941091	1.542446
C	0.610017	3.329003	0.466680
H	1.062003	3.488961	-0.519681
H	0.559654	2.242833	0.602637

C	3.594659	3.084117	0.416138
C	3.536309	1.695260	0.363227
N	4.298460	0.988515	-0.481851
C	5.132577	1.663965	-1.291752
N	5.223962	2.983002	-1.345739
C	4.465045	3.679565	-0.500637
H	4.553900	4.763787	-0.543639
H	5.786257	1.063309	-1.915029
Pd	4.381097	-1.086174	-0.554834
C	2.418435	-1.050910	-0.138284
C	1.890098	-1.337056	1.106974
C	0.591104	-0.906200	1.483927
C	0.026523	-1.172235	2.749984
C	-1.215985	-0.675858	3.060103
C	-1.893644	0.101151	2.106993
N	-1.393826	0.362392	0.910472
C	-0.176795	-0.147199	0.559558
C	0.328530	0.074799	-0.741770
C	1.575887	-0.383354	-1.077101
H	1.952796	-0.187742	-2.077643
H	-0.281292	0.633464	-1.447842
H	-2.872821	0.517819	2.319261
H	-1.683785	-0.867463	4.019269
H	0.583563	-1.772844	3.463872
H	2.479880	-1.874937	1.847142
N	4.767886	-3.083207	-0.672659
C	3.952842	-4.079089	-0.736698
O	2.646193	-3.928700	-0.693960
H	2.431429	-2.972477	-0.580539
C	4.378622	-5.506254	-0.872670
H	4.832237	-5.675077	-1.855635
H	5.126460	-5.763723	-0.116957
H	3.509669	-6.156315	-0.767354
C	6.206849	-3.331894	-0.747445
H	6.444574	-4.072645	-1.517548
H	6.568134	-3.727033	0.211416
C	7.022986	-2.067356	-1.055443
O	8.206005	-2.197744	-1.302597
O	6.371272	-0.946705	-1.002971
H	2.888981	1.131849	1.025733
H	4.776754	4.408218	2.329696
H	3.753508	5.666336	4.214939
H	1.282445	5.765839	4.408118
H	-0.841489	4.614282	3.843790
H	-0.863449	5.801018	2.552234
H	-2.427740	4.096191	1.888984
H	-1.295542	2.791256	2.265737
H	-0.746723	4.955155	0.195919

101

T12_C6_IN3 Eopt -3365.716204

Pd	-3.264870	-0.240348	-0.239109
C	-5.370390	0.708583	-1.866506
C	-4.727361	-1.515662	-2.298329
C	-6.347683	0.652307	-2.851162
C	-5.675849	-1.632356	-3.303770
H	-6.949959	1.535596	-3.033607
H	-5.740486	-2.564968	-3.853726
N	-4.626176	-0.367786	-1.627556
H	-7.251516	-0.602781	-4.346905
C	-6.497520	-0.534966	-3.568023
N	-2.992952	-2.195662	-0.822470
N	-3.975050	1.695439	-0.205033
C	-3.717984	-2.568013	-1.914724
C	-5.021103	1.917107	-1.038751
O	-3.620310	-3.604014	-2.559336
O	-5.659531	2.957701	-1.196087
C	-1.884459	-2.949392	-0.424112
C	-1.749975	-3.299663	0.924214
C	-0.843334	-3.250912	-1.305447
C	-0.582855	-3.892169	1.383913
C	0.321528	-3.848532	-0.833413
C	0.464287	-4.173656	0.509029
H	1.369873	-4.647601	0.868107
C	-0.461898	-0.165305	0.798640
C	-2.056597	-0.413376	2.473699
C	-0.142022	-0.051781	-0.573082
C	0.589609	-0.173992	1.757442
C	-1.073003	-0.498625	3.470854
H	-3.110550	-0.486156	2.721502
C	1.162218	0.120002	-0.960311
H	-0.947410	-0.085619	-1.302240
C	1.920677	0.061668	1.324686
C	0.246896	-0.365034	3.112915
H	-1.371263	-0.658189	4.500852
C	2.207241	0.250256	-0.007892
H	1.389778	0.218540	-2.019015
H	1.035967	-0.404014	3.859140
N	-1.767556	-0.245627	1.193298
H	2.696062	0.137505	2.085089
Pd	3.866417	1.134091	-0.656193
H	-2.566090	-3.084266	1.603793
H	-0.942845	-2.995600	-2.354708
C	1.464256	-4.039900	-1.785090
C	-0.408111	-4.223778	2.834488
F	1.061314	-4.541096	-2.958342
F	2.067366	-2.860866	-2.056331
F	2.408628	-4.857466	-1.292843
F	0.624875	-3.535577	3.374154
F	-0.129920	-5.522249	3.020217
F	-1.493570	-3.928590	3.563376
C	-3.540314	2.830670	0.585858
C	-2.049364	3.103900	0.381688
H	-4.105802	3.698149	0.222030
C	-3.864869	2.672310	2.065717
C	-1.433848	4.042943	1.397009
H	-1.506162	2.151795	0.415403

H	-1.904221	3.481560	-0.637077
H	-4.921538	2.407613	2.179849
H	-3.268044	1.857591	2.493947
C	-3.552982	3.973829	2.787885
C	-2.136814	4.435003	2.547080
C	-0.103983	4.485544	1.240516
H	-4.249938	4.750725	2.440214
H	-3.723058	3.872823	3.866466
C	-1.518018	5.255459	3.494334
C	0.498647	5.295713	2.203867
C	0.720772	4.072254	0.080660
C	-0.211148	5.690036	3.331768
H	-2.079390	5.547300	4.379291
H	1.524786	5.622751	2.056738
C	1.798327	3.210954	0.245462
C	0.508130	4.514756	-1.229084
H	0.256453	6.324314	4.079125
N	2.564292	2.828475	-0.784686
H	2.030617	2.787996	1.217003
N	1.282079	4.162485	-2.252584
H	-0.316469	5.190079	-1.452187
C	2.283641	3.329444	-1.997256
H	2.930172	3.004075	-2.809816
C	4.761977	-0.739898	-1.320317
C	5.280337	-0.415625	-0.080935
H	3.994296	-1.502634	-1.408043
H	5.232940	-0.390760	-2.234574
H	6.167196	0.206624	0.009917
C	4.840214	-1.070241	1.183172
O	5.063535	-0.603234	2.279645
O	4.181115	-2.206389	0.949387
C	3.603281	-2.888980	2.072806
C	3.914336	-4.362042	1.950657
H	2.527329	-2.699359	2.031276
H	4.003018	-2.455860	2.992430
H	3.358191	-4.920027	2.711675
H	3.630085	-4.736367	0.962720
H	4.982538	-4.552243	2.092227
C	5.555026	2.331603	-2.578123
O	4.659671	1.894457	-3.317044
O	5.571652	2.188253	-1.297625
C	6.719459	3.114259	-3.147372
H	6.579485	4.177452	-2.921282
H	7.658119	2.804366	-2.680009
H	6.770671	2.986332	-4.230032

101

T12_C6_IN4 Eopt -3365.752965

Pd	-3.386608	-0.062812	-0.278040
C	-5.511608	0.696976	-1.981862
C	-5.100475	-1.620205	-1.906340
C	-6.546739	0.518099	-2.889509
C	-6.112750	-1.865136	-2.822601
H	-7.079714	1.392973	-3.245577
H	-6.294851	-2.887751	-3.134935
N	-4.855403	-0.366396	-1.524552
H	-7.646653	-0.945729	-4.019782
C	-6.844813	-0.779362	-3.306214
N	-3.353763	-2.121726	-0.379266
N	-3.934990	1.887319	-0.651963
C	-4.181396	-2.659616	-1.315606
C	-5.024917	2.017012	-1.447345
O	-4.237532	-3.825503	-1.685018
O	-5.612951	3.051223	-1.763555
C	-2.335095	-2.900388	0.185217
C	-2.253684	-3.016832	1.574277
C	-1.312110	-3.439914	-0.600597
C	-1.143494	-3.608812	2.165900
C	-0.203696	-4.024274	0.000498
C	-0.105415	-4.108381	1.386078
H	0.779364	-4.530638	1.849923
C	-0.519141	-0.296571	0.471867
C	-1.886315	0.133546	2.302760
C	-0.345236	-0.370142	-0.927197
C	0.575272	-0.615252	1.325038
C	-0.842196	-0.116733	3.207717
H	-2.878244	0.393379	2.656872
C	0.855548	-0.780279	-1.445151
H	-1.182473	-0.116094	-1.571680
C	1.800481	-1.027096	0.751054
C	0.380210	-0.507975	2.719248
H	-1.030614	-0.037080	4.272038
C	1.952914	-1.116593	-0.614030
H	0.976194	-0.849484	-2.523267
H	1.198124	-0.752466	3.390679
N	-1.738298	0.046482	0.991093
H	2.640343	-1.252870	1.403708
Pd	4.105749	1.116384	-0.161563
H	-3.052103	-2.605734	2.181807
H	-1.367921	-3.348008	-1.678806
C	0.916982	-4.552243	-0.846576
C	-1.039139	-3.711912	3.657544
F	0.967919	-3.943529	-2.045356
F	2.110777	-4.364558	-0.254594
F	0.796999	-5.867379	-1.077173
F	0.187201	-3.351284	4.087917
F	-1.245216	-4.963824	4.090508
F	-1.926874	-2.921710	4.285160
C	-3.443900	3.109938	-0.049137
C	-1.924787	3.216939	-0.166919
H	-3.898949	3.940975	-0.603345
C	-3.891731	3.238705	1.402458
C	-1.295867	4.253421	0.738083
H	-1.483737	2.240384	0.067783
H	-1.666659	3.408335	-1.215446
H	-4.975750	3.094326	1.458223
H	-3.420116	2.451562	2.005106

C	-3.501197	4.606997	1.935883
C	-2.032003	4.889843	1.750030
C	0.077099	4.545047	0.625752
H	-4.086928	5.374657	1.408821
H	-3.759422	4.702442	2.997273
C	-1.398361	5.792306	2.608402
C	0.694558	5.440819	1.500706
C	0.942084	3.904339	-0.393301
C	-0.045295	6.073053	2.492453
H	-1.986379	6.272961	3.387248
H	1.756705	5.644296	1.391777
C	1.924209	2.995717	-0.018183
C	0.913712	4.223655	-1.754770
H	0.434026	6.772141	3.171337
N	2.788251	2.483599	-0.906547
H	2.039136	2.673487	1.012860
N	1.785181	3.735656	-2.636158
H	0.172589	4.922500	-2.138878
C	2.698818	2.890877	-2.181165
H	3.440560	2.496517	-2.871363
C	3.285064	-1.399682	-1.249451
C	3.812832	-0.075739	-1.782559
H	3.985761	-1.829052	-0.528251
H	3.164724	-2.128109	-2.064917
H	3.073429	0.404115	-2.428352
C	5.122504	-0.037994	-2.480130
O	5.438627	0.829088	-3.275586
O	5.935912	-1.034908	-2.109439
C	7.269830	-0.975925	-2.623996
C	8.053557	-2.079653	-1.956029
H	7.686213	0.013568	-2.408874
H	7.237753	-1.089994	-3.713092
H	9.089557	-2.073132	-2.310180
H	8.053694	-1.943291	-0.870216
H	7.617819	-3.058316	-2.180176
C	5.383593	0.699951	1.942135
O	5.355796	-0.116955	0.955938
O	4.726178	1.774439	1.889553
C	6.232756	0.365421	3.132122
H	6.251242	-0.714515	3.296627
H	7.259874	0.693879	2.937120
H	5.866593	0.886693	4.018782

101

T12_C6_IN5 Eopt -3365.720662

Pd	3.412383	0.070958	0.466414
C	5.238866	0.814008	2.489492
C	4.856414	-1.504910	2.319579
C	6.130426	0.623881	3.536461
C	5.726248	-1.760586	3.369446
H	6.597255	1.494818	3.983504
H	5.868735	-2.787223	3.689081
N	4.661111	-0.245374	1.927978
H	7.062534	-0.854141	4.791950
C	6.372661	-0.679411	3.971379
N	3.371492	-1.986699	0.531401
N	3.876088	2.013463	0.950874
C	4.042632	-2.537722	1.578976
C	4.806315	2.143300	1.927379
O	4.042679	-3.708346	1.936172
O	5.281327	3.180001	2.389646
C	2.451238	-2.749074	-0.199991
C	2.605157	-2.862573	-1.583936
C	1.297407	-3.264868	0.396458
C	1.597898	-3.424436	-2.359163
C	0.292121	-3.819252	-0.388319
C	0.428558	-3.897107	-1.770359
H	-0.374615	-4.295627	-2.380435
C	0.742447	-0.102994	-0.886898
C	2.499688	0.325256	-2.344970
C	0.252995	-0.225229	0.433247
C	-0.138872	-0.348850	-1.976742
C	1.685357	0.128902	-3.471929
H	3.552812	0.561871	-2.455019
C	-1.045330	-0.596628	0.655961
H	0.935832	-0.046600	1.259729
C	-1.470533	-0.731138	-1.710778
C	0.371017	-0.220188	-3.287742
H	2.115824	0.223547	-4.462054
C	-1.939380	-0.855292	-0.417420
H	-1.390720	-0.718185	1.676615
H	-0.280347	-0.416134	-4.134172
N	2.053617	0.213975	-1.103922
H	-2.140514	-0.915522	-2.546824
Pd	-4.467527	0.572078	-0.056871
H	3.505513	-2.471480	-2.044300
H	1.170237	-3.174610	1.469148
C	-0.968694	-4.316902	0.257171
C	1.745810	-3.524027	-3.847538
F	-2.028665	-4.169157	-0.556908
F	-0.892633	-5.616095	0.575002
F	-1.242581	-3.647966	1.392784
F	0.625781	-3.113435	-4.477295
F	1.971293	-4.783310	-4.246376
F	2.758329	-2.770822	-4.309479
C	3.333981	3.238371	0.398059
C	1.806077	3.215067	0.479665
H	3.709503	4.059000	1.022471
C	3.812334	3.502930	-1.023426
C	1.083392	4.166102	-0.447352
H	1.463425	2.198768	0.254341
H	1.524559	3.388905	1.523548
H	4.907122	3.480203	-1.046278
H	3.447112	2.715479	-1.694199
C	3.285723	4.853692	-1.485039
C	1.782020	4.927409	-1.396287
C	-0.325355	4.232522	-0.433314

H	3.730039	5.642846	-0.860377
H	3.600243	5.065068	-2.513724
C	1.079177	5.741696	-2.288457
C	-1.007963	5.041847	-1.344334
C	-1.143911	3.428373	0.501248
C	-0.306339	5.805964	-2.268553
H	1.638331	6.324007	-3.017552
H	-2.094315	5.073827	-1.315285
C	-2.118274	2.555425	0.021385
C	-1.068151	3.526877	1.894672
H	-0.839259	6.438291	-2.972533
N	-2.907929	1.858282	0.844394
H	-2.288063	2.415294	-1.042155
N	-1.854152	2.838107	2.720769
H	-0.360675	4.209403	2.361302
C	-2.743690	2.033160	2.156571
H	-3.405960	1.472288	2.810739
C	-3.345519	-1.216489	-0.194817
C	-4.008669	-1.166180	1.050075
H	-5.572760	-0.229242	-0.729668
H	-3.802885	-1.841108	-0.959289
H	-3.496058	-0.858122	1.957822
C	-5.211784	-2.011253	1.270940
O	-5.728085	-2.729749	0.445433
O	-5.650633	-1.870139	2.528561
C	-6.840915	-2.604224	2.846998
C	-7.201911	-2.280225	4.276031
H	-6.645784	-3.671756	2.700714
H	-7.629342	-2.313324	2.145306
H	-8.109216	-2.821506	4.562659
H	-6.397027	-2.571583	4.957987
H	-7.387006	-1.208378	4.396121
C	-5.532527	2.785691	-0.885363
O	-5.908667	2.321912	0.222380
O	-4.669346	2.181347	-1.595998
C	-6.124539	4.071820	-1.402213
H	-6.543884	4.660347	-0.584330
H	-5.370649	4.648191	-1.944381
H	-6.928537	3.830868	-2.106483

93

T12_C6_TSI Eopt -3228.052882

Pd	-2.753130	0.851963	-0.699864
C	-4.165697	2.595155	-2.413917
C	-4.720260	0.316716	-2.659060
C	-5.055519	2.953644	-3.417460
C	-5.628827	0.610483	-3.664993
H	-5.157973	4.003724	-3.668726
H	-6.186551	-0.202838	-4.116648
N	-4.037715	1.310709	-2.089384
H	-6.489927	2.199702	-4.832745
C	-5.786230	1.944653	-4.045636
N	-3.416814	-1.022282	-1.200661
N	-2.559749	2.897304	-0.679078
C	-4.433454	-1.057945	-2.102229
C	-3.350003	3.543085	-1.572244
O	-5.074407	-2.032203	-2.471496
O	-3.483683	4.755902	-1.727854
C	-3.052726	-2.164088	-0.473370
C	-3.841500	-2.623071	0.582836
C	-1.805756	-2.757259	-0.695849
C	-3.370807	-3.629678	1.421678
C	-1.347061	-3.762134	0.145787
C	-2.122213	-4.203150	1.215527
H	-1.754466	-4.975555	1.882505
C	-0.143329	-0.212285	0.333912
C	-1.859577	-0.241340	1.900799
C	0.314075	0.120852	-0.963105
C	0.696195	-0.959449	1.208145
C	-1.101264	-0.998920	2.808813
H	-2.879707	0.043321	2.137087
C	1.551715	-0.298316	-1.378326
H	-0.348599	0.683233	-1.616038
C	1.981467	-1.337393	0.755618
C	0.178037	-1.353780	2.462146
H	-1.554141	-1.314195	3.741755
C	2.429357	-1.016249	-0.515984
H	1.879565	-0.072497	-2.389267
H	0.793330	-1.957333	3.123381
N	-1.405876	0.144011	0.718811
H	2.606525	-1.939951	1.410073
H	3.138717	-1.927002	-1.008667
Pd	4.470648	-0.229964	-0.566894
C	7.295955	-0.262004	-0.587857
O	8.457447	0.080765	-0.556225
O	6.289577	0.583873	-0.566608
N	5.491340	-1.917656	-0.793843
C	4.937482	-3.047874	-1.194894
C	5.807373	-4.256663	-1.437588
H	5.167114	-5.125760	-1.588940
H	6.486753	-4.436870	-0.598793
H	6.420462	-4.106679	-2.333733
O	3.696110	-3.163323	-1.390961
C	6.921611	-1.744386	-0.646310
H	7.293664	-2.212637	0.276273
H	7.478418	-2.188286	-1.480151
H	-4.808694	-2.163958	0.760289
H	-1.190432	-2.398457	-1.513256
C	0.013588	-4.365838	-0.049654
C	-4.155100	-3.982175	2.649032
F	0.680629	-3.800349	-1.059516
F	0.763926	-4.216954	1.065574
F	-0.057972	-5.682984	-0.286413
F	-3.878157	-5.215154	3.092934
F	-5.475804	-3.901010	2.447583
F	-3.861000	-3.127814	3.656480
C	-1.930708	3.713768	0.339676

C -0.430730 3.440082 0.431623
H -2.082732 4.761399 0.050984
C -2.600551 3.499738 1.693525
C 0.224866 3.944628 1.697386
H -0.272996 2.357738 0.363240
H 0.068069 3.863877 -0.449118
H -3.682264 3.633925 1.585952
H -2.428197 2.466916 2.025066
C -2.034839 4.474601 2.712496
C -0.529909 4.419796 2.780941
C 1.626810 3.925132 1.814247
H -2.344829 5.494746 2.441880
H -2.452785 4.284593 3.708485
C 0.117914 4.860348 3.937942
C 2.257030 4.377701 2.974072
C 2.500305 3.445460 0.714117
C 1.500864 4.846893 4.041951
H -0.484210 5.221258 4.769013
H 3.341902 4.354827 3.034571
C 2.822757 2.103276 0.543336
C 3.131460 4.330183 -0.164015
H 1.989472 5.194597 4.947389
N 3.719325 1.709123 -0.368816
H 2.376657 1.327406 1.157651
N 4.015495 3.942968 -1.082048
H 2.916615 5.396010 -0.110379
C 4.295291 2.651072 -1.132342
H 5.059859 2.312198 -1.822415
101
T12_C6_TSII Eopt -3365.700172
Pd -3.127590 1.013688 -0.376121
C -4.602417 2.948957 -1.807748
C -5.396411 0.743861 -2.043756
C -5.596329 3.432321 -2.648266
C -6.417078 1.163465 -2.884137
H -5.636363 4.498460 -2.843062
H -7.109201 0.423934 -3.272048
N -4.544693 1.644444 -1.553610
H -7.293747 2.876349 -3.847778
C -6.505387 2.523026 -3.189400
N -4.001941 -0.779471 -0.873502
N -2.751075 3.037694 -0.303934
C -5.145559 -0.677042 -1.605966
C -3.591060 3.782808 -1.066630
O -5.909347 -1.575685 -1.934193
O -3.631956 5.007955 -1.174791
C -3.602815 -2.028316 -0.381597
C -4.407956 -2.780473 0.476994
C -2.334237 -2.513361 -0.713708
C -3.932642 -3.974743 1.011300
C -1.866809 -3.702044 -0.168830
C -2.659994 -4.443141 0.703100
H -2.302114 -5.378256 1.119200
C -0.456200 -0.141267 0.354435
C -1.987302 -0.127624 2.103279
C -0.153814 0.140420 -0.998334
C 0.506382 -0.807053 1.164829
C -1.098741 -0.799839 2.959161
H -2.981925 0.148234 2.437935
C 1.050744 -0.246683 -1.526706
H -0.899573 0.652583 -1.601376
C 1.761633 -1.142713 0.608278
C 0.148518 -1.132207 2.492563
H -1.415776 -1.046036 3.966326
C 2.041782 -0.857785 -0.714542
H 1.266853 -0.047402 -2.572673
H 0.865156 -1.654314 3.120415
N -1.677933 0.200080 0.859581
H 2.498608 -1.667180 1.213317
Pd 3.984100 -0.320881 -1.131973
H -5.405766 -2.429635 0.715955
H -1.723631 -1.950289 -1.409484
C -0.485035 -4.185963 -0.491066
C -4.782444 -4.721775 1.997387
F 0.012089 -3.601611 -1.596501
F 0.381917 -3.916516 0.508410
F -0.449861 -5.511168 -0.681189
F -4.452337 -6.020142 2.062471
F -6.085005 -4.643957 1.693863
F -4.638509 -4.216464 3.238015
C -1.927394 3.780261 0.631533
C -0.443037 3.440835 0.516606
H -2.056721 4.842548 0.387982
C -2.396351 3.571345 2.067759
C 0.397229 4.053378 1.617366
H -0.329482 2.351100 0.537518
H -0.070168 3.760805 -0.464109
H -3.481985 3.706355 2.121996
H -2.176053 2.541378 2.378283
C -1.688588 4.557506 2.981504
C -0.193407 4.575928 2.779125
C 1.798578 4.122573 1.490515
H -2.082588 5.566258 2.789696
H -1.909484 4.341812 4.034285
C 0.606861 5.153665 3.768633
C 2.578025 4.718858 2.483798
C 2.529349 3.578742 0.320588
C 1.983292 5.236188 3.628082
H 0.128427 5.549131 4.662185
H 3.657148 4.755542 2.360107
C 2.694347 2.213554 0.100056
C 3.211852 4.412938 -0.568632
H 2.591960 5.691099 4.404010
N 3.489658 1.750546 -0.868518
H 2.209579 1.472065 0.728408
N 3.995151 3.958532 -1.546614

H	3.123275	5.494066	-0.475296
C	4.120240	2.643832	-1.643740
H	4.802324	2.238023	-2.383135
C	3.040255	-2.386100	-1.599902
C	4.455900	-2.300546	-1.477672
H	2.526212	-3.037948	-0.902562
H	2.600881	-2.339471	-2.592328
H	5.093792	-2.247639	-2.356517
C	5.057317	-2.803924	-0.215900
O	4.411350	-3.079973	0.777402
O	6.381257	-2.892823	-0.306345
C	7.066242	-3.115043	0.936812
C	8.544889	-3.117174	0.638078
H	6.726973	-4.064221	1.363671
H	6.788298	-2.303027	1.614392
H	9.109322	-3.291086	1.559924
H	8.802595	-3.903580	-0.078455
H	8.852503	-2.152450	0.223851
C	6.606914	0.298066	-0.459256
O	6.161350	-0.016134	0.646260
O	5.918074	0.300321	-1.556578
C	8.051471	0.718105	-0.641871
H	8.563002	-0.006419	-1.284510
H	8.102349	1.688138	-1.146119
H	8.556365	0.773740	0.324119

101

T12_C6_TSIII Eopt -3365.705527

Pd	2.453379	1.335368	0.760697
C	2.547130	3.243569	2.837757
C	3.956964	1.383635	3.156035
C	2.933551	3.787175	4.055475
C	4.394087	1.878917	4.375761
H	2.504167	4.735701	4.358911
H	5.126384	1.308797	4.937071
N	3.066571	2.081492	2.451405
H	4.187340	3.496649	5.779600
C	3.866018	3.090811	4.824712
N	3.681857	-0.187208	1.398178
N	1.453657	3.137516	0.718468
C	4.403961	0.092456	2.519076
C	1.617611	3.882899	1.841048
O	5.294402	-0.578095	3.025115
O	1.144011	4.991877	2.086225
C	3.963981	-1.336585	0.651844
C	5.240230	-1.606048	0.152103
C	2.915308	-2.205834	0.329539
C	5.444661	-2.700591	-0.684273
C	3.127567	-3.282932	-0.518968
C	4.394607	-3.539523	-1.038273
H	4.563544	-4.386904	-1.693736
C	0.688505	-0.325565	-0.991947
C	2.681764	0.303434	-2.008784
C	-0.157230	-0.308957	0.141726
C	0.329010	-1.115578	-2.118538
C	2.410377	-0.474467	-3.144345
H	3.602408	0.872025	-1.928664
C	-1.324879	-1.021341	0.147777
H	0.138053	0.279585	1.006296
C	-0.908480	-1.803090	-2.104861
C	1.231738	-1.178578	-3.200576
H	3.135851	-0.511772	-3.949062
C	-1.735123	-1.748016	-1.006407
H	-1.967539	-0.996411	1.030673
H	0.990323	-1.797376	-4.060115
N	1.853620	0.383881	-0.979288
H	-1.201710	-2.366200	-2.987713
Pd	-4.421758	-0.818836	-0.143913
H	6.067177	-0.959504	0.423304
H	1.933565	-2.021893	0.750327
C	1.992288	-4.180225	-0.911907
C	6.804106	-2.916513	-1.281773
F	0.861377	-3.892837	-0.252469
F	1.718968	-4.070498	-2.231119
F	2.278363	-5.471277	-0.691201
F	6.991247	-4.190446	-1.658213
F	7.783561	-2.592898	-0.427330
F	6.974868	-2.153758	-2.380033
C	0.795833	3.812125	-0.383027
C	-0.616495	3.298438	-0.668133
H	0.703768	4.866200	-0.087774
C	1.615127	3.750680	-1.665613
C	-1.247659	4.017102	-1.844609
H	-0.570043	2.216165	-0.857000
H	-1.235885	3.425991	0.227177
H	2.665497	3.974992	-1.448703
H	1.573602	2.736261	-2.080587
C	1.052978	4.749623	-2.664753
C	-0.452640	4.702662	-2.778083
C	-2.647739	4.056433	-2.006038
H	1.342781	5.764569	-2.356699
H	1.495359	4.598346	-3.657680
C	-1.055663	5.402776	-3.827102
C	-3.230112	4.778642	-3.049229
C	-3.570395	3.326293	-1.106772
C	-2.433703	5.454310	-3.965584
H	-0.420107	5.925100	-4.539214
H	-4.312518	4.789641	-3.147958
C	-3.637118	1.937623	-1.092704
C	-4.508741	3.975290	-0.299065
H	-2.886838	6.009277	-4.781790
N	-4.533563	1.280172	-0.346750
H	-2.968819	1.335026	-1.699098
N	-5.397050	3.328216	0.454677
H	-4.535487	5.063070	-0.261945
C	-5.370031	2.004522	0.410255
H	-6.050404	1.440132	1.039410

C	-3.089724	-2.347286	-1.063602
C	-3.792458	-2.807893	0.079914
H	-3.951462	-1.010429	-1.650293
H	-3.379112	-2.808071	-2.008359
H	-3.335024	-2.802265	1.066053
C	-4.950858	-3.705307	-0.138288
O	-5.404312	-4.003650	-1.224305
O	-5.443694	-4.129438	1.028512
C	-6.629592	-4.929341	0.946943
C	-7.094242	-5.183372	2.360241
H	-6.394772	-5.857339	0.414452
H	-7.377383	-4.389724	0.356769
H	-8.004273	-5.791802	2.351413
H	-6.328231	-5.714613	2.933332
H	-7.312976	-4.239075	2.868457
C	-4.470697	-0.824017	2.734425
O	-3.263996	-1.069108	2.652706
O	-5.268845	-0.630369	1.735322
C	-5.157584	-0.752081	4.083513
H	-5.806255	-1.627499	4.199779
H	-4.419377	-0.742259	4.886851
H	-5.795264	0.134678	4.142976

93

T12_C7_IN2 Eopt -3228.087850

Pd	-1.294136	-2.162382	-0.620515
N	-1.580772	-2.921867	-2.393681
C	-2.829066	-2.976489	-2.851175
C	-3.076869	-3.544314	-4.093238
C	-1.995909	-4.038498	-4.823094
C	-0.701274	-3.959429	-4.308957
C	-0.524453	-3.386209	-3.057763
C	0.794089	-3.226153	-2.356691
O	1.828377	-3.562168	-2.921924
N	0.652085	-2.717633	-1.096901
C	1.803561	-2.496168	-0.336174
C	1.804277	-2.829920	1.022784
C	2.910653	-2.566625	1.819423
C	4.061694	-2.003178	1.277808
C	4.073408	-1.698883	-0.077887
C	2.961805	-1.926445	-0.880967
H	2.990452	-1.676826	-1.934087
C	5.309485	-1.138019	-0.713904
F	6.175456	-0.657161	0.197568
F	5.021107	-0.129040	-1.560517
F	5.964712	-2.062917	-1.428273
H	4.927351	-1.803227	1.897933
C	2.855327	-2.834562	3.292237
F	2.597958	-1.704795	3.986403
F	1.892459	-3.713720	3.615876
F	4.017046	-3.313119	3.760072
H	0.933093	-3.312900	1.446084
H	0.171033	-4.324214	-4.840168
H	-2.162018	-4.484382	-5.799435
H	-4.099715	-3.574232	-4.452444
C	-3.856461	-2.341780	-1.958097
O	-5.026022	-2.282771	-2.336026
N	-3.324804	-1.853518	-0.808186
C	-4.214836	-1.020182	-0.022280
C	-4.541142	-1.554558	1.366591
C	-5.666970	-0.718828	1.964576
C	-5.427074	0.769809	1.859573
C	-6.198770	1.642568	2.633075
C	-6.052304	3.018969	2.534931
C	-5.106995	3.546683	1.661329
C	-4.313431	2.692976	0.897060
C	-4.473046	1.294981	0.976967
C	-3.648990	0.389350	0.093429
H	-3.560229	0.818861	-0.911458
H	-2.623681	0.316287	0.478695
C	-3.293707	3.260289	-0.012301
C	-1.939342	3.010356	0.183235
N	-1.003591	3.459356	-0.660318
C	-1.415891	4.206504	-1.704569
N	-2.677534	4.519205	-1.955330
C	-3.603756	4.045062	-1.122630
H	-4.639800	4.290452	-1.350640
H	-0.634639	4.584323	-2.356361
Pd	1.051033	3.148394	-0.463370
C	0.712918	1.741402	0.925080
C	0.104713	0.532235	0.623302
C	-0.297439	-0.364844	1.641337
N	-0.965030	-1.516040	1.323180
C	-1.337201	-2.346930	2.285927
C	-1.072776	-2.118519	3.643485
C	-0.416612	-0.965332	3.999719
C	-0.026655	-0.048940	3.003827
C	0.628734	1.170374	3.300792
C	0.978894	2.035950	2.296570
H	1.476403	2.969227	2.547154
H	0.843143	1.406417	4.340162
H	-0.188373	-0.749105	5.039662
H	-1.386241	-2.850673	4.378733
H	-1.865276	-3.239517	1.965646
H	-0.115586	0.254058	-0.406137
N	3.097372	3.161513	-0.415332
C	3.934167	2.323850	0.092210
O	3.549863	1.200624	0.664287
H	2.572812	1.116910	0.594780
C	5.416312	2.511722	0.098243
H	5.812519	2.375171	-0.913517
H	5.873451	1.764826	0.745697
H	5.682338	3.517564	0.433645
C	3.619429	4.358929	-1.073837
H	4.490059	4.124231	-1.693825
H	3.939210	5.091404	-0.320417
C	2.585388	5.050677	-1.970539

O	2.962057	5.950887	-2.695136
O	1.367546	4.618841	-1.857084
H	-1.599439	2.435190	1.034702
H	-4.967541	4.621654	1.581911
H	-6.666130	3.680406	3.139391
H	-6.934518	1.225494	3.317569
H	-5.830984	-0.985966	3.016047
H	-6.604474	-0.958271	1.441907
H	-4.836992	-2.607517	1.304236
H	-3.655379	-1.493892	2.010070
H	-5.158719	-0.969210	-0.580388

101

T12_C7_IN3 Eopt -3365.719186

Pd	-1.289414	2.376020	0.518580
C	-3.039360	3.309668	2.533235
C	-0.757443	3.507489	3.061712
C	-3.405000	3.879382	3.745251
C	-1.054140	4.074013	4.292999
H	-4.460959	3.992125	3.965201
H	-0.235302	4.348415	4.949077
N	-1.749611	3.155480	2.245871
H	-2.654755	4.709454	5.583531
C	-2.395551	4.264442	4.627254
N	0.607573	2.784291	1.252599
N	-3.345434	2.226711	0.430490
C	0.626121	3.243057	2.538145
C	-3.985038	2.757310	1.504436
O	1.602205	3.471980	3.243174
O	-5.194676	2.783630	1.728987
C	1.822689	2.555415	0.603140
C	1.968052	2.978037	-0.722592
C	2.899628	1.903803	1.217695
C	3.143880	2.741019	-1.419128
C	4.080878	1.689184	0.513603
C	4.220477	2.110669	-0.803031
H	5.146980	1.951649	-1.340833
C	-0.123083	0.426371	-1.500578
C	-0.903331	2.432340	-2.390333
C	0.084549	-0.416420	-0.385643
C	0.284184	-0.008276	-2.796184
C	-0.482708	2.093960	-3.683649
H	-1.394726	3.380589	-2.196111
C	0.621057	-1.675312	-0.549689
H	-0.217637	-0.049591	0.592984
C	0.838162	-1.304612	-2.936655
C	0.105899	0.868135	-3.884072
H	-0.631405	2.797729	-4.494442
H	0.438476	0.563102	-4.872547
N	-0.733048	1.641114	-1.341377
H	1.130147	-1.642830	-3.927907
H	1.154163	3.514417	-1.193149
H	2.813281	1.585362	2.249104
C	5.231341	1.027280	1.214242
C	3.242390	3.103659	-2.868878
F	6.114675	0.504176	0.345601
F	5.904932	1.891084	1.987468
F	4.815418	0.029392	2.014178
F	3.024987	2.026248	-3.656894
F	4.455983	3.572312	-3.190250
F	2.337378	4.028536	-3.227329
C	-4.179332	1.430965	-0.451067
C	-3.723135	-0.022240	-0.421005
H	-5.196095	1.483112	-0.040896
C	-4.249142	1.913397	-1.893855
C	-4.474561	-0.909125	-1.384236
H	-2.647765	-0.047380	-0.642104
H	-3.825673	-0.402960	0.602097
H	-4.462252	2.987682	-1.922353
H	-3.286141	1.750513	-2.391829
C	-5.339511	1.133856	-2.621146
C	-5.240174	-0.361477	-2.422292
C	-4.437844	-2.309207	-1.225550
H	-6.321167	1.469876	-2.256496
H	-5.323660	1.358032	-3.695067
C	-5.953240	-1.215464	-3.269656
C	-5.170978	-3.142248	-2.068038
C	-3.602994	-2.887023	-0.149530
C	-5.930821	-2.592184	-3.095790
H	-6.542620	-0.782963	-4.075527
H	-5.127296	-4.219071	-1.927814
C	-2.218871	-2.739499	-0.166642
C	-4.119560	-3.555724	0.959726
H	-6.496178	-3.237779	-3.761563
N	-1.447952	-3.163174	0.836130
H	-1.722441	-2.263518	-1.003614
N	-3.355088	-4.004305	1.956753
H	-5.191591	-3.722145	1.051749
C	-2.053746	-3.779184	1.864181
H	-1.402770	-4.124790	2.661135
C	0.989340	-2.122579	-1.844781
H	1.384837	-3.128005	-1.969242
Pd	0.717807	-3.010220	0.906827
C	2.284081	-1.751102	1.717397
C	2.835737	-2.947103	1.269707
H	2.391614	-0.840057	1.139270
H	2.008174	-1.645140	2.763769
H	2.941283	-3.781734	1.956607
C	3.606869	-3.138147	0.013512
O	4.037593	-4.217971	-0.322795
O	3.773113	-2.014002	-0.694987
C	4.437552	-2.204728	-1.953968
C	4.664152	-0.850037	-2.571605
H	3.808252	-2.845442	-2.581749
H	5.374832	-2.740291	-1.778039
H	5.135706	-0.966231	-3.553020
H	3.724296	-0.306213	-2.699809

H	5.326388	-0.256247	-1.938356
C	0.649073	-5.607583	1.526798
O	0.504535	-5.467835	0.302220
O	0.758354	-4.598739	2.330357
C	0.696269	-6.972296	2.167474
H	0.584760	-7.752096	1.412762
H	1.648776	-7.098454	2.692016
H	-0.098917	-7.060244	2.915065

101

T12_C7_IN4 Eopt -3365.755616

Pd	3.216180	-0.042079	0.478638
C	4.893493	0.788297	2.597919
C	4.310752	-1.491558	2.651541
C	5.659588	0.654186	3.747777
C	5.049600	-1.689893	3.808815
H	6.161561	1.531983	4.139857
H	5.064781	-2.679374	4.252705
N	4.268823	-0.277578	2.103059
H	6.323369	-0.731395	5.254416
C	5.734594	-0.601339	4.350984
N	2.975449	-2.073558	0.773931
N	3.817899	1.902644	0.790265
C	3.489561	-2.539087	1.946450
C	4.641102	2.071829	1.853642
O	3.357375	-3.655965	2.431185
O	5.143395	3.117446	2.264845
C	2.084656	-2.872315	0.048509
C	2.293489	-3.061052	-1.319586
C	0.924910	-3.393158	0.634391
C	1.333607	-3.700010	-2.096185
C	-0.026408	-4.028749	-0.151894
C	0.161364	-4.179753	-1.523009
H	-0.597226	-4.658464	-2.133969
H	3.202625	-2.679164	-1.769457
H	0.764262	-3.268161	1.698403
C	-1.320433	-4.501332	0.441014
C	1.528410	-3.875539	-3.571780
F	-1.367987	-4.327792	1.770374
F	-2.364653	-3.823441	-0.082706
F	-1.542254	-5.798688	0.189739
F	0.502117	-3.338311	-4.265486
F	1.583618	-5.170039	-3.917073
F	2.652979	-3.291945	-4.014732
C	3.387454	3.109835	0.112986
C	1.862331	3.185987	0.121555
H	3.785708	3.953050	0.691818
C	3.934880	3.238587	-1.302898
C	1.260420	4.171795	-0.850916
H	1.462954	2.190415	-0.112355
H	1.537519	3.392045	1.147528
H	5.024839	3.131089	-1.283388
H	3.530297	2.439981	-1.934653
C	3.533302	4.589103	-1.879559
C	2.041373	4.806981	-1.827034
C	-0.129230	4.399672	-0.840518
H	4.035006	5.385697	-1.310260
H	3.880667	4.689098	-2.914718
C	1.427710	5.643181	-2.763798
C	-0.725500	5.228283	-1.791032
C	-0.987770	3.751947	0.176617
C	0.056186	5.855348	-2.755005
H	2.044815	6.127203	-3.517706
H	-1.800397	5.387335	-1.762150
C	-1.926058	2.786200	-0.163015
C	-0.934919	4.084031	1.534604
H	-0.404676	6.503130	-3.494958
N	-2.705624	2.206788	0.763672
H	-2.063511	2.462265	-1.190156
N	-1.699540	3.507627	2.457353
H	-0.249522	4.855739	1.881451
C	-2.551999	2.580779	2.042067
H	-3.152341	2.059600	2.780811
Pd	-4.157985	0.934574	0.077249
H	-1.582720	-0.070439	1.957385
C	-5.988565	0.944476	-1.610571
O	-5.667615	-0.076687	-0.904606
O	-5.352076	2.024187	-1.481756
C	-7.146407	0.827919	-2.555851
H	-7.166765	-0.165188	-3.011252
H	-8.077780	0.956881	-1.993161
H	-7.090416	1.603750	-3.321687
C	0.776931	-0.187018	-1.308790
N	2.124236	0.054821	-1.288716
C	2.796805	0.096622	-2.428939
C	2.194779	-0.075271	-3.683754
C	0.845582	-0.327693	-3.738530
C	0.101975	-0.403292	-2.544326
C	-1.270190	-0.743498	-2.513554
C	-1.276699	-0.623406	-0.085835
C	0.055575	-0.268407	-0.100446
H	0.589232	-0.087426	0.830564
C	-1.987826	-0.782915	1.231887
C	-3.495007	-0.650670	1.176801
C	-4.117521	-0.462108	2.510957
O	-3.588563	0.078979	3.469116
O	-5.372704	-0.933140	2.546964
C	-6.091806	-0.689842	3.759644
C	-7.481528	-1.249984	3.576038
H	-8.075404	-1.083965	4.480735
H	-7.443782	-2.325738	3.379103
H	-7.985416	-0.764504	2.734595
H	-6.106092	0.388412	3.953619
H	-5.560822	-1.164966	4.591385
H	-3.979049	-1.480184	0.653129
H	-1.738868	-1.778602	1.631979
H	-1.783052	-0.930871	-3.452898

H	0.346701	-0.501049	-4.687557
H	2.805587	-0.033154	-4.578212
H	3.866378	0.259102	-2.344946
C	-1.934124	-0.872570	-1.320666
H	-2.977681	-1.168271	-1.321071

101

T12_C7_IN5 Eopt -3365.721229

Pd	2.773983	-0.923678	0.754134
C	4.054351	-0.404672	3.220138
C	2.954592	-2.482348	3.113603
C	4.475719	-0.656165	4.518700
C	3.333762	-2.790120	4.411991
H	5.063015	0.100743	5.027001
H	3.006300	-3.731411	4.839892
N	3.332648	-1.320885	2.579904
H	4.423713	-2.083867	6.127888
C	4.110805	-1.865143	5.111051
N	1.960281	-2.811689	0.979078
N	3.730481	0.842860	1.216348
C	2.072731	-3.329496	2.234813
C	4.298663	0.862914	2.447664
O	1.550461	-4.346363	2.672795
O	4.936302	1.774119	2.974723
C	1.016031	-3.348552	0.096165
C	1.396448	-3.649937	-1.213373
C	-0.333974	-3.459803	0.451929
C	0.438546	-3.980879	-2.165134
C	-1.281199	-3.790599	-0.507302
C	-0.908467	-4.041284	-1.825218
H	-1.658222	-4.267818	-2.576392
H	2.444471	-3.588517	-1.482659
H	-0.637827	-3.243615	1.469458
C	-2.741670	-3.824845	-0.163691
C	0.829069	-4.259826	-3.585083
F	-3.446842	-3.031576	-0.997944
F	-3.254701	-5.058066	-0.283740
F	-2.983860	-3.402613	1.084160
F	0.156339	-3.461311	-4.440649
F	0.548463	-5.521466	-3.941615
F	2.138414	-4.060861	-3.805843
C	3.848007	2.063601	0.444423
C	2.472780	2.650309	0.127224
H	4.394236	2.779727	1.071708
C	4.636957	1.874131	-0.843879
C	2.522763	3.839186	-0.807795
H	1.862918	1.853731	-0.321568
H	1.973400	2.921296	1.065132
H	5.578247	1.356038	-0.629650
H	4.062116	1.249330	-1.536034
C	4.900503	3.227477	-1.481990
C	3.662262	4.084655	-1.591679
C	1.438322	4.738024	-0.900408
H	5.643097	3.769562	-0.878264
H	5.349167	3.107765	-2.475973
C	3.689118	5.176104	-2.463970
C	1.495414	5.829805	-1.772087
C	0.218735	4.625904	-0.070762
C	2.615175	6.046606	-2.563749
H	4.579132	5.341025	-3.067552
H	0.641404	6.498742	-1.839270
C	-0.597519	3.498104	-0.009356
C	-0.234183	5.722817	0.672776
H	2.647246	6.888471	-3.249122
N	-1.731421	3.494103	0.697439
H	-0.360899	2.585892	-0.548563
N	-1.367084	5.725964	1.371420
H	0.357028	6.636824	0.699632
C	-2.079552	4.609671	1.347799
H	-3.025473	4.585310	1.877600
Pd	-3.044423	1.780725	0.650475
H	-2.718716	1.552709	2.127855
C	-4.530549	3.142571	-1.005226
O	-4.693062	3.418721	0.209031
O	-3.694360	2.255015	-1.386238
C	-5.338413	3.848832	-2.063890
H	-5.868870	4.702875	-1.639608
H	-4.685979	4.172929	-2.879753
H	-6.066872	3.148077	-2.486352
C	0.811350	-0.458694	-1.475287
N	2.139998	-0.645911	-1.206937
C	2.981822	-0.844854	-2.208463
C	2.585322	-0.844827	-3.554534
C	1.260481	-0.636387	-3.856633
C	0.331588	-0.443162	-2.815856
C	-1.058084	-0.274894	-3.036358
C	-1.458854	-0.232008	-0.647191
C	-0.100569	-0.336649	-0.413397
H	0.279867	-0.371286	0.604783
C	-2.347073	-0.196359	0.517818
C	-3.761151	-0.182992	0.486611
C	-4.485479	-0.649393	1.696568
O	-3.976873	-0.890071	2.769187
O	-5.792073	-0.778941	1.438877
C	-6.593818	-1.207242	2.547102
C	-8.024406	-1.270534	2.070531
H	-8.675792	-1.595114	2.888365
H	-8.128514	-1.980252	1.244015
H	-8.363152	-0.288096	1.727600
H	-6.463336	-0.497077	3.370284
H	-6.227916	-2.180684	2.890133
H	-4.314896	-0.232999	-0.445600
H	-1.897616	-0.511846	1.456921
H	-1.422729	-0.243941	-4.059138
H	0.913769	-0.645768	-4.885896
H	3.324900	-1.023109	-4.326634
H	4.017201	-1.019371	-1.934459

C -1.931906 -0.174117 -1.987985
H -2.988716 -0.027883 -2.174543
93
T12_C7_TSI Eopt -3228.058521
Pd 1.926882 -1.461027 1.015559
C 3.225509 -1.271644 3.517928
C 1.283784 -2.605850 3.518887
C 3.426387 -1.503755 4.871549
C 1.422659 -2.867542 4.874184
H 4.277806 -1.038144 5.355873
H 0.677957 -3.486768 5.362424
N 2.186041 -1.837403 2.908645
H 2.645645 -2.507141 6.607551
C 2.513138 -2.313931 5.546960
N 0.342422 -2.739624 1.341342
N 3.577844 -0.290990 1.379106
C 0.159266 -3.098026 2.642697
C 4.059665 -0.372879 2.643195
O -0.759261 -3.751697 3.118541
O 5.034528 0.205117 3.121518
C -0.623197 -3.073433 0.383173
C -0.210583 -3.739144 -0.775356
C -1.963204 -2.688739 0.504658
C -1.101560 -3.964366 -1.815940
C -2.852993 -2.946250 -0.535501
C -2.431478 -3.569258 -1.705451
H -3.131178 -3.754132 -2.513242
C 0.310876 -0.462091 -1.280698
C 2.091528 -1.797821 -1.946474
C -0.367466 0.240166 -0.262522
C -0.244221 -0.500501 -2.591080
C 1.631575 -1.843375 -3.274061
H 2.984266 -2.339311 -1.651907
C -1.602988 0.817959 -0.496407
H 0.073310 0.264501 0.731782
C -1.502661 0.106890 -2.822068
C 0.459730 -1.205394 -3.592256
H 2.185956 -2.416091 -4.008338
H 0.049094 -1.258549 -4.596125
N 1.468176 -1.134342 -0.989224
H -1.934358 0.047245 -3.817557
H -2.324280 0.686574 0.504957
Pd -2.271977 2.781666 0.273986
C -4.385724 4.564668 0.889601
O -5.024954 5.576674 1.069326
O -3.083293 4.556113 0.696115
N -4.076838 2.139154 0.807603
C -4.225962 0.956390 1.381937
C -5.555814 0.562515 1.972050
H -5.567838 -0.519487 2.097818
H -6.390257 0.868597 1.335304
H -5.685581 1.035873 2.952217
O -3.273398 0.130733 1.442834
C -5.065666 3.194232 0.860159
H -5.725326 3.170836 -0.018882
H -5.702938 3.123245 1.747724
H 0.820222 -4.066210 -0.850036
H -2.301018 -2.169608 1.394004
C -4.282417 -2.497615 -0.429755
C -0.659366 -4.650290 -3.071971
F -4.449140 -1.235612 -0.876890
F -5.095978 -3.269959 -1.170532
F -4.730597 -2.534387 0.831039
F -0.980966 -3.923462 -4.163724
F -1.243390 -5.846530 -3.225666
F 0.670495 -4.844971 -3.108107
C 4.246164 0.630346 0.482631
C 3.242352 1.650482 -0.054201
H 5.007592 1.155331 1.073236
C 4.955866 -0.082727 -0.661355
C 3.701710 2.430557 -1.263327
H 2.325407 1.105625 -0.309908
H 2.961740 2.333646 0.756977
H 5.628415 -0.845356 -0.254207
H 4.216349 -0.592596 -1.288512
C 5.724212 0.923679 -1.503496
C 4.861236 2.071519 -1.965882
C 2.963298 3.548018 -1.702021
H 6.558672 1.325438 -0.909855
H 6.179627 0.435188 -2.373479
C 5.245020 2.807980 -3.090135
C 3.374311 4.281245 -2.815894
C 1.780924 4.025704 -0.948993
C 4.512810 3.905268 -3.519530
H 6.142622 2.511930 -3.628827
H 2.789482 5.140761 -3.133234
C 0.597422 3.303414 -0.821734
C 1.794850 5.268492 -0.311522
H 4.825968 4.468113 -4.393985
N -0.439723 3.765691 -0.112399
H 0.471664 2.338278 -1.297453
N 0.762113 5.746995 0.377584
H 2.684784 5.893962 -0.360436
C -0.313633 4.979947 0.456520
H -1.179540 5.347552 0.996050
C -2.183807 0.703174 -1.792306
H -3.182241 1.095619 -1.956499
101
T12_C7_TSII Eopt -3365.704102
Pd 1.132790 -2.128504 0.938972
C 2.047500 -2.479355 3.592418
C -0.174651 -3.157372 3.230852
C 1.977173 -2.844559 4.929896
C -0.314686 -3.533895 4.558664
H 2.852496 -2.694802 5.552486
H -1.269542 -3.928119 4.888912

N	0.985613	-2.655428	2.810575
H	0.698332	-3.667088	6.452732
C	0.780758	-3.377696	5.409130
N	-0.811160	-2.852375	0.957493
N	3.000053	-1.557054	1.613424
C	-1.260437	-3.212143	2.192911
C	3.235859	-1.855544	2.915134
O	-2.397335	-3.545621	2.510510
O	4.262480	-1.658190	3.564032
C	-1.726997	-2.731598	-0.091380
C	-1.375669	-3.201790	-1.360742
C	-2.960229	-2.084502	0.065373
C	-2.197202	-2.967820	-2.455659
C	-3.781719	-1.873399	-1.036285
C	-3.406506	-2.296270	-2.307676
H	-4.043964	-2.106611	-3.164802
C	0.543134	-0.570484	-1.588636
C	1.884440	-2.448596	-1.893995
C	-0.235304	0.245148	-0.740701
C	0.604922	-0.279802	-2.982940
C	1.968054	-2.239943	-3.278055
H	2.368068	-3.303215	-1.432388
C	-0.928915	1.333021	-1.245903
H	-0.302638	-0.013326	0.313988
C	-0.097999	0.847775	-3.477940
C	1.337560	-1.145207	-3.818114
H	2.521972	-2.941900	-3.890567
H	1.378458	-0.945742	-4.885176
N	1.220445	-1.645859	-1.077260
H	-0.042421	1.071708	-4.539954
H	-0.446302	-3.744280	-1.480434
H	-3.260804	-1.732012	1.044087
C	-5.097753	-1.169199	-0.870360
C	-1.768561	-3.383249	-3.830775
F	-5.293517	-0.277465	-1.862754
F	-6.129788	-2.021515	-0.903381
F	-5.165993	-0.495470	0.288337
F	-1.432425	-2.310860	-4.578740
F	-2.748800	-4.016126	-4.489771
F	-0.699750	-4.195492	-3.809884
C	4.082653	-0.884940	0.917160
C	3.582551	0.402107	0.267374
H	4.830694	-0.628050	1.677739
C	4.768961	-1.776445	-0.110453
C	4.541825	1.028352	-0.720111
H	3.321577	1.119972	1.054500
H	2.641096	0.169674	-0.242063
H	5.059808	-2.721568	0.360826
H	4.072155	-2.009640	-0.922666
C	5.982717	-1.060507	-0.680093
C	5.659229	0.322248	-1.190908
C	4.334034	2.347203	-1.178163
H	6.748947	-0.974832	0.104518

H	6.438823	-1.649801	-1.484935
C	6.518385	0.918679	-2.118202
C	5.215425	2.927868	-2.092478
C	3.231310	3.182902	-0.656761
C	6.304211	2.211052	-2.573447
H	7.374392	0.352106	-2.478516
H	5.031062	3.942452	-2.436286
C	1.888490	2.819777	-0.715839
C	3.484646	4.421299	-0.060181
H	6.980105	2.660473	-3.295113
N	0.923053	3.578114	-0.190126
H	1.576598	1.899523	-1.194527
N	2.529665	5.197470	0.445709
H	4.507357	4.787024	0.020319
C	1.287668	4.738184	0.378911
H	0.485019	5.313462	0.827188
C	-0.852774	1.622765	-2.638833
H	-1.408060	2.471626	-3.029663
Pd	-1.168633	3.006146	-0.032020
C	-2.766141	1.404127	-0.570432
C	-3.147908	2.490422	0.269269
H	-3.189405	1.386505	-1.570847
H	-2.688979	0.432552	-0.098893
H	-3.719126	3.317982	-0.141696
C	-3.308326	2.303623	1.732552
O	-3.958189	3.035341	2.440923
O	-2.635909	1.224681	2.184510
C	-2.655305	1.051656	3.607243
C	-1.872542	-0.199001	3.924308
H	-3.694715	0.983547	3.943137
H	-2.215333	1.941947	4.068325
H	-1.795614	-0.324234	5.009494
H	-2.360992	-1.088653	3.515822
H	-0.857889	-0.133570	3.516053
C	-2.282234	5.511488	0.594037
O	-2.701663	5.408222	-0.557348
O	-1.472665	4.667391	1.167055
C	-2.708541	6.644657	1.501912
H	-3.198172	7.430918	0.924973
H	-3.411867	6.242155	2.239400
H	-1.853992	7.049775	2.051337

101

T12_C7_TSIII Eopt -3365.725120

Pd	-0.651847	1.429582	1.675711
C	-1.900274	0.369306	3.978355
C	0.432115	0.123976	3.940163
C	-1.985657	-0.282780	5.201395
C	0.419258	-0.539145	5.159069
H	-2.966785	-0.434337	5.637869
H	1.360578	-0.892211	5.565806
N	-0.710467	0.558669	3.417152
H	-0.844439	-1.245798	6.751764
C	-0.806545	-0.730734	5.796192

N	1.394271	1.154683	2.022780
N	-2.698184	1.363761	1.961386
C	1.655468	0.372597	3.108894
C	-3.068120	0.798986	3.140324
O	2.734141	-0.094927	3.459873
O	-4.209050	0.562726	3.540209
C	2.422448	1.402172	1.113970
C	2.515102	2.670007	0.525224
C	3.342027	0.417299	0.721041
C	3.449958	2.926451	-0.468175
C	4.277042	0.691325	-0.271047
C	4.336056	1.937530	-0.885797
H	5.072508	2.141372	-1.655367
H	1.841267	3.450100	0.859384
H	3.323905	-0.553400	1.200182
C	5.193322	-0.396634	-0.747141
C	3.525287	4.272020	-1.122207
F	4.645945	-1.081361	-1.776668
F	6.360855	0.090836	-1.194082
F	5.466616	-1.292855	0.211016
F	3.193465	4.203174	-2.431031
F	4.765406	4.780949	-1.075453
F	2.699194	5.167381	-0.558149
C	-3.774383	1.488491	0.997772
C	-3.621788	0.443937	-0.104592
H	-4.701014	1.271378	1.544743
C	-3.929912	2.859489	0.356703
C	-4.729754	0.515096	-1.130477
H	-2.640445	0.597133	-0.577638
H	-3.581668	-0.550360	0.353530
H	-3.904564	3.644019	1.121508
H	-3.103585	3.042794	-0.339084
C	-5.250881	2.899997	-0.402435
C	-5.490100	1.686001	-1.272347
C	-5.057206	-0.604540	-1.925352
H	-6.076084	2.967841	0.321192
H	-5.315720	3.805577	-1.019011
C	-6.533752	1.723202	-2.201984
C	-6.116984	-0.551768	-2.831678
C	-4.295073	-1.862592	-1.795969
C	-6.853488	0.617837	-2.977044
H	-7.111035	2.639769	-2.304751
H	-6.346443	-1.425393	-3.436499
C	-2.913284	-1.900792	-1.948627
C	-4.891216	-3.092442	-1.502549
H	-7.670479	0.664591	-3.691153
N	-2.210366	-3.021373	-1.757478
H	-2.349217	-1.014388	-2.218016
N	-4.199002	-4.219462	-1.334621
H	-5.971158	-3.160719	-1.381891
C	-2.881835	-4.134693	-1.439002
H	-2.288820	-5.022058	-1.246591
C	0.060595	1.873792	-1.240740
C	-0.755842	3.744614	-0.126100
C	0.374601	0.501542	-1.226907
C	0.374774	2.666341	-2.382160
C	-0.486781	4.585829	-1.218358
H	-1.187885	4.140111	0.787277
C	1.028195	-0.066732	-2.303877
H	0.111291	-0.098224	-0.352846
C	1.014745	2.050913	-3.482787
C	0.080842	4.045128	-2.344805
H	-0.711553	5.643696	-1.142910
H	0.333055	4.666324	-3.199462
N	-0.501238	2.446794	-0.130491
H	1.267227	2.656864	-4.348021
C	1.338962	0.720383	-3.440800
H	1.852767	0.257663	-4.279028
Pd	-0.143325	-2.773200	-1.469105
C	1.461856	-1.484850	-2.282009
C	1.799035	-2.134687	-1.070101
H	0.076380	-2.256511	-2.953073
H	1.978895	-1.845921	-3.169971
H	1.711397	-1.604708	-0.127626
C	2.768228	-3.253495	-1.113852
O	3.075357	-3.879023	-2.105621
O	3.284970	-3.449080	0.101788
C	4.810404	-4.435231	1.617464
H	5.612086	-5.170881	1.738368
H	5.197612	-3.449191	1.890131
H	3.998377	-4.690187	2.305310
C	-0.436939	-2.745399	1.365989
O	-0.258758	-1.526641	1.222794
O	-0.442167	-3.611056	0.415486
C	-0.647217	-3.308825	2.756500
H	-1.409331	-2.721571	3.277597
H	-0.935691	-4.360861	2.730266
H	0.286569	-3.204077	3.319646
C	4.322531	-4.433202	0.189578
H	3.916053	-5.403073	-0.115324
H	5.114587	-4.163850	-0.516489

93

T12_IN1 Eopt -3228.072922

Pd	2.978416	0.456194	-0.190192
C	5.522899	0.453232	-1.437884
C	4.452333	2.546907	-1.404623
C	6.611423	0.981948	-2.117825
C	5.501269	3.133939	-2.096865
H	7.433735	0.321128	-2.369620
H	5.436101	4.189197	-2.338970
N	4.509847	1.249226	-1.105079
H	7.428454	2.774101	-2.984833
C	6.591653	2.336785	-2.448025
N	2.401048	2.439382	-0.213406
N	4.149520	-1.226135	-0.461160
C	3.206696	3.257115	-0.947292

C	5.360505	-0.979723	-1.017111
O	3.027801	4.436859	-1.220405
O	6.279748	-1.776974	-1.202211
C	1.204666	2.951443	0.306013
C	0.938972	2.813147	1.672213
C	0.230859	3.524081	-0.514605
C	-0.295036	3.185246	2.189395
C	-1.000837	3.897337	0.015007
C	-1.281790	3.721801	1.364205
H	-2.257384	3.983000	1.758820
C	0.017330	0.042731	0.131671
C	1.240288	-0.477839	2.038089
C	-0.030063	0.283709	-1.274219
C	-1.177824	0.097264	0.890424
C	0.091956	-0.513327	2.835855
H	2.219403	-0.659475	2.466361
C	-1.200992	0.644762	-1.873905
H	0.895849	0.203405	-1.837461
C	-2.390199	0.529884	0.257059
C	-1.118774	-0.188338	2.264536
H	0.181796	-0.740458	3.891717
C	-2.397360	0.823614	-1.107318
H	-1.219997	0.861271	-2.937658
H	-2.025721	-0.133469	2.858538
N	1.215820	-0.194612	0.740392
H	-3.220212	0.890803	0.860015
H	-3.237772	1.386748	-1.500843
Pd	-3.589958	-1.129288	-0.761585
C	-5.934367	-2.675538	-0.970338
O	-6.678555	-3.617495	-1.130011
O	-4.624893	-2.777717	-1.088746
N	-5.393523	-0.319542	-0.463096
C	-5.684476	0.967034	-0.184395
C	-7.155265	1.326953	-0.042249
H	-7.212930	2.388290	0.200771
H	-7.642297	0.746024	0.748776
H	-7.707187	1.139021	-0.970068
O	-4.835290	1.854960	-0.038035
C	-6.458060	-1.292274	-0.621228
H	-7.055804	-1.402155	0.294452
H	-7.158998	-1.011351	-1.419544
H	1.704986	2.394845	2.315574
H	0.433308	3.648277	-1.572211
C	-2.027831	4.488272	-0.908055
C	-0.594037	3.021440	3.648776
F	-2.142689	3.752661	-2.035227
F	-3.235592	4.558686	-0.345632
F	-1.681983	5.725556	-1.295296
F	-1.766496	2.379638	3.836877
F	-0.698020	4.200478	4.275418
F	0.351171	2.309401	4.286998
C	3.950769	-2.584298	0.009566
C	2.524458	-3.047131	-0.289710
H	4.650795	-3.216591	-0.551009
C	4.324780	-2.737008	1.480910
C	1.953672	-4.082319	0.650404
H	1.867314	-2.171096	-0.277843
H	2.493699	-3.411579	-1.324064
H	5.367006	-2.427299	1.609079
H	3.706250	-2.075172	2.100846
C	4.128928	-4.182525	1.915667
C	2.705555	-4.626099	1.700687
C	0.608008	-4.471121	0.509878
H	4.810112	-4.824465	1.337543
H	4.401546	-4.316259	2.968785
C	2.113368	-5.550481	2.565627
C	0.028969	-5.387427	1.386774
C	-0.221770	-3.853146	-0.547832
C	0.788839	-5.937619	2.413630
H	2.707329	-5.962753	3.378270
H	-1.012005	-5.671146	1.255201
C	-1.227971	-2.947751	-0.230236
C	-0.046687	-4.101082	-1.911769
H	0.344528	-6.655446	3.096759
N	-1.946376	-2.339190	-1.177930
H	-1.453007	-2.695140	0.800592
N	-0.776974	-3.514729	-2.858909
H	0.706601	-4.811065	-2.247802
C	-1.696649	-2.655264	-2.454575
H	-2.307378	-2.164499	-3.205041

92

T12_T-Pd-P Eopt -3010.123005

Pd	-2.535537	-0.222261	-0.501980
C	-4.316844	0.792571	-2.443549
C	-3.597046	-1.415754	-2.838206
C	-5.099092	0.778008	-3.590397
C	-4.348903	-1.490135	-4.001475
H	-5.661627	1.669862	-3.844196
H	-4.312401	-2.402318	-4.587176
N	-3.621840	-0.294176	-2.117542
H	-5.713045	-0.415280	-5.272267
C	-5.112212	-0.380096	-4.368059
N	-2.168356	-2.160048	-1.096010
N	-3.261262	1.699394	-0.510643
C	-2.683220	-2.493957	-2.310009
C	-4.126034	1.966825	-1.519863
O	-2.483430	-3.516150	-2.952948
O	-4.715018	3.020882	-1.757141
C	-1.186836	-2.963557	-0.500451
C	-1.421899	-3.509718	0.763108
C	0.081447	-3.101720	-1.071997
C	-0.393868	-4.132142	1.462063
C	1.104416	-3.721455	-0.363438
C	0.878952	-4.235236	0.909758
H	1.690291	-4.683483	1.472856
C	0.035474	-0.402764	1.011289

C	-1.844275	-0.697594	2.345227
C	0.605854	-0.021957	-0.224559
C	0.885308	-0.858798	2.058057
C	-1.071777	-1.135531	3.432434
H	-2.925632	-0.641901	2.416626
C	1.960304	-0.083238	-0.408041
H	-0.054245	0.311438	-1.020912
C	2.277258	-0.929101	1.828690
C	0.289715	-1.232480	3.282387
H	-1.564423	-1.422076	4.354243
C	2.828209	-0.525910	0.627764
H	2.384448	0.210393	-1.360353
H	0.915305	-1.604826	4.088213
N	-1.318880	-0.352709	1.180072
H	2.920793	-1.286286	2.628873
H	-2.407862	-3.407073	1.202383
H	0.271985	-2.671070	-2.048240
C	2.477964	-3.818622	-0.961185
C	-0.634838	-4.695461	2.829983
F	2.698531	-2.847813	-1.862763
F	3.430625	-3.712896	-0.016448
F	2.672027	-4.989977	-1.583680
F	-0.700162	-6.033868	2.818993
F	-1.779531	-4.244177	3.370957
F	0.361648	-4.363825	3.677090
C	-2.942218	2.799723	0.375319
C	-1.446006	3.102463	0.353297
H	-3.483019	3.676564	-0.003627
C	-3.389211	2.557022	1.811097
C	-1.030540	4.150041	1.361492
H	-0.907949	2.165121	0.547201
H	-1.154585	3.413573	-0.656799
H	-4.432874	2.224210	1.825664
H	-2.779097	1.758895	2.252651
C	-3.224902	3.840184	2.612420
C	-1.873366	4.490904	2.430328
C	0.201455	4.823543	1.226264
H	-4.000191	4.555224	2.300599
H	-3.397513	3.655740	3.680232
C	-1.481035	5.483829	3.332784
C	0.562035	5.825594	2.128796
C	1.147013	4.507645	0.132265
C	-0.277202	6.156209	3.186473
H	-2.144548	5.733499	4.158233
H	1.516971	6.330128	2.006364
C	1.744888	3.255121	-0.019365
C	1.551247	5.469427	-0.797579
H	0.011369	6.929019	3.893158
N	2.622521	2.980347	-0.984135
H	1.513216	2.446792	0.670796
N	2.432997	5.222926	-1.765742
H	1.137431	6.476380	-0.755758
C	2.919009	3.985333	-1.808454
H	3.638100	3.770611	-2.596561
C	4.275097	-0.538865	0.440742
C	4.934733	0.264774	-0.405129
H	4.858874	-1.221699	1.055995
H	4.430500	1.019542	-1.002771
C	6.404715	0.180007	-0.497206
O	7.109691	-0.573620	0.140066
O	6.874374	1.062091	-1.394013
C	8.296336	1.062488	-1.564303
C	8.627252	2.108203	-2.601518
H	8.616261	0.060783	-1.870475
H	8.768195	1.274244	-0.598835
H	9.709280	2.144087	-2.763792
H	8.143045	1.877586	-3.555452
H	8.294060	3.098631	-2.276380

79

T12_T-Pd-SM Eopt -2665.898391

Pd	0.113540	1.732671	0.276542
C	1.329160	4.143283	-0.555950
C	-0.961741	3.975026	-1.075924
C	1.403535	5.400852	-1.139492
C	-0.951261	5.221486	-1.684304
H	2.359388	5.913280	-1.143109
H	-1.869766	5.592121	-2.126361
N	0.163857	3.501494	-0.540414
H	0.279612	6.918534	-2.170542
C	0.246650	5.938211	-1.703935
N	-1.868759	1.950140	-0.237767
N	2.114810	2.153334	0.489306
C	-2.150126	3.050635	-0.986003
C	2.479307	3.381821	0.047529
O	-3.206361	3.332131	-1.537220
O	3.597042	3.896486	0.067722
C	-2.810108	0.919806	-0.120630
C	-3.202681	0.164948	-1.229302
C	-3.256382	0.541718	1.147599
C	-3.977308	-0.976372	-1.058407
C	-4.032642	-0.600204	1.307992
C	-4.392452	-1.373409	0.208684
H	-4.964854	-2.285356	0.338961
C	-0.440467	-1.217441	0.278412
C	-0.366974	-0.269456	2.401433
C	-0.198540	-1.118394	-1.109475
C	-0.998486	-2.416225	0.808148
C	-0.887456	-1.427661	3.000084
H	-0.132789	0.606147	2.998147
C	-0.524304	-2.161606	-1.942351
H	0.246465	-0.205140	-1.495475
C	-1.331259	-3.467958	-0.078576
C	-1.217430	-2.493141	2.199996
H	-1.053110	-1.445240	4.070944
H	-0.312347	-2.088078	-3.002518
H	-1.661106	-3.390821	2.620587

N -0.154478 -0.160190 1.100133
H -1.773127 -4.372871 0.329404
H -2.852549 0.449728 -2.214586
H -2.958467 1.134228 2.005349
C -4.490889 -1.026391 2.669788
C -4.357714 -1.805760 -2.249302
F -5.798219 -0.796384 2.855656
F -4.301518 -2.349317 2.856871
F -3.829837 -0.390187 3.651754
F -4.405277 -3.114891 -1.940703
F -3.479999 -1.664755 -3.256611
F -5.565627 -1.472823 -2.727330
C 3.175916 1.314026 1.006467
C 3.255270 0.004421 0.228739
H 4.113587 1.866637 0.864323
C 3.029438 1.014346 2.493000
C 4.241738 -0.983661 0.808184
H 2.250430 -0.437603 0.214243
H 3.504468 0.219794 -0.816850
H 2.856615 1.944058 3.046119
H 2.157940 0.366291 2.649501
C 4.287140 0.318529 2.992921
C 4.719288 -0.835871 2.119093
C 4.719992 -2.056541 0.026746
H 5.106432 1.051270 3.031978
H 4.151217 -0.036205 4.022342
C 5.649317 -1.748871 2.624786
C 5.663340 -2.943901 0.547839
C 4.260456 -2.267148 -1.363170
C 6.127205 -2.794797 1.849699
H 6.006208 -1.622910 3.644953
H 6.015757 -3.765567 -0.070355
C 2.921900 -2.475824 -1.702943
C 5.153365 -2.309812 -2.437279
H 6.852787 -3.493918 2.255591
N 2.510953 -2.676835 -2.953811
H 2.152744 -2.490040 -0.933404
N 4.770803 -2.520116 -3.696108
H 6.218905 -2.158495 -2.267200
C 3.463913 -2.685073 -3.885740
H 3.138626 -2.847336 -4.911617
C -1.103718 -3.341261 -1.425899
H -1.367293 -4.147851 -2.102222
80
T12_TC-Pd-P Eopt -3264.856887
Pd -1.545799 1.567557 -0.005409
C -3.450696 3.400693 -1.003479
C -1.359999 4.352828 -0.496300
C -3.958624 4.633858 -1.386825
C -1.800821 5.611962 -0.879359
H -4.988371 4.690021 -1.722757
H -1.110043 6.445792 -0.817083
N -2.189846 3.315713 -0.581970
H -3.487835 6.720019 -1.625188
C -3.116282 5.744708 -1.324921
N 0.118228 2.731259 0.430910
N -3.420936 1.045066 -0.666802
C 0.018532 4.025785 0.010466
C -4.209841 2.100727 -1.022719
O 0.888321 4.887941 0.022173
O -5.386702 2.080919 -1.359883
C 1.364024 2.238650 0.834521
C 2.531619 2.471293 0.100426
C 1.429632 1.389804 1.945366
C 3.706391 1.802776 0.429393
C 2.608804 0.730268 2.262926
C 3.758077 0.916618 1.498518
H 4.668725 0.374186 1.724116
C 0.178927 -0.920151 0.346649
C -1.723369 -0.810682 1.679524
C 0.969086 -0.395582 -0.701171
C 0.617451 -2.089307 1.028355
C -1.385326 -1.989588 2.358464
H -2.634533 -0.272196 1.919179
C 2.191968 -0.941245 -0.979424
H 0.601639 0.467631 -1.248359
C 1.875251 -2.640743 0.701140
C -0.207172 -2.619665 2.042396
H -2.047500 -2.367350 3.129046
H 2.802287 -0.500662 -1.760262
H 0.106923 -3.517140 2.567893
N -0.970664 -0.288310 0.721216
H 2.222460 -3.510373 1.252825
H 2.506602 3.150052 -0.744064
H 0.531536 1.222718 2.529905
C 2.664457 -0.186167 3.448554
C 4.894749 1.982947 -0.466912
F 3.237288 0.402856 4.508636
F 1.439159 -0.587048 3.832759
F 3.381383 -1.292542 3.181934
F 5.188459 3.273356 -0.661500
F 4.652133 1.457004 -1.693659
F 5.990238 1.374872 0.005465
C 2.688717 -2.059213 -0.251253
C -3.937576 -0.253715 -0.680011
C -3.123368 -1.290331 -1.145138
C -5.211750 -0.570703 -0.189335
C -3.544347 -2.612063 -1.073213
H -2.147667 -1.048699 -1.553580
C -5.628024 -1.896527 -0.143345
H -5.867079 0.220811 0.151096
C -4.799715 -2.931496 -0.569475
H -5.127229 -3.962707 -0.510956
C -2.584231 -3.689515 -1.478092
C -7.013555 -2.213092 0.341443
F -7.078751 -3.440717 0.884066

F -7.426213 -1.337823 1.271772
F -7.906174 -2.176768 -0.659393
F -1.914712 -3.366219 -2.594766
F -3.195505 -4.862278 -1.690109
F -1.656117 -3.894468 -0.519358
C 4.035526 -2.577368 -0.451103
C 5.042540 -1.943448 -1.069918
H 4.259090 -3.550851 -0.016394
H 4.952983 -0.951879 -1.500437
C 6.368043 -2.588390 -1.144486
O 6.644315 -3.683184 -0.701062
O 7.245165 -1.791984 -1.772685
C 8.573889 -2.314334 -1.890412
H 8.534638 -3.258432 -2.444283
H 8.954622 -2.539392 -0.888529
C 9.407272 -1.272507 -2.596407
H 9.424075 -0.337654 -2.027919
H 10.436346 -1.629327 -2.706173
H 9.006557 -1.062379 -3.592786
67
T12_TC-Pd-SM Eopt -2920.631879
Pd -0.218894 1.439190 0.126181
C -1.581444 3.892722 -0.192157
C 0.752076 4.096636 0.045937
C -1.727064 5.269820 -0.285808
C 0.677125 5.478576 -0.057269
H -2.723279 5.680397 -0.409648
H 1.594355 6.055088 -0.005345
N -0.364811 3.375728 -0.031301
H -0.666572 7.141894 -0.297722
C -0.580066 6.062047 -0.220600
N 1.752691 1.972989 0.431348
N -2.237709 1.604021 -0.233926
C 2.014934 3.296667 0.232649
C -2.701362 2.887635 -0.263809
O 3.106065 3.851995 0.214158
O -3.860756 3.268710 -0.365911
C 2.805476 1.060660 0.551825
C 3.894860 1.053144 -0.324801
C 2.706602 0.047572 1.511609
C 4.814803 0.010997 -0.280197
C 3.628848 -0.988170 1.542172
C 4.686922 -1.024735 0.637780
H 5.399451 -1.842116 0.650698
C 0.696023 -1.415583 -0.384781
C -0.751982 -1.128707 1.415916
C 1.375654 -0.878181 -1.498952
C 0.864234 -2.790768 -0.057051
C -0.649179 -2.476788 1.788376
H -1.384594 -0.444426 1.972503
C 2.223899 -1.670914 -2.232166
H 1.231520 0.170968 -1.740937
C 1.735628 -3.582789 -0.841646
C 0.169313 -3.302077 1.058427
H -1.205638 -2.835437 2.646631
H 2.773820 -1.243113 -3.063952
H 0.292498 -4.347599 1.326589
N -0.097902 -0.612536 0.387218
H 1.867331 -4.628313 -0.578416
H 4.003596 1.849488 -1.051278
H 1.877125 0.065963 2.209028
C 3.492395 -2.104055 2.534020
C 5.882811 -0.057897 -1.330582
F 4.546265 -2.168376 3.360733
F 2.390839 -1.981781 3.291556
F 3.416059 -3.299537 1.914596
F 6.327904 1.155958 -1.678013
F 5.411126 -0.637616 -2.456281
F 6.936597 -0.785463 -0.932923
C 2.409625 -3.031692 -1.901214
H 3.089759 -3.637813 -2.491468
C -3.127015 0.531106 -0.338765
C -2.739841 -0.583850 -1.088899
C -4.364482 0.498861 0.318758
C -3.538789 -1.718532 -1.140802
H -1.799084 -0.553649 -1.627876
C -5.163097 -0.636881 0.240917
H -4.694343 1.361749 0.882836
C -4.758749 -1.759979 -0.475204
H -5.382276 -2.645384 -0.514977
C -3.025397 -2.928693 -1.860780
C -6.507136 -0.634164 0.910328
F -6.884981 -1.873805 1.266159
F -6.508916 0.122397 2.019057
F -7.460519 -0.149741 0.099765
F -2.339588 -2.600086 -2.966133
F -4.012022 -3.760423 -2.221889
F -2.181283 -3.635909 -1.079930
99
cis-T25_C5_IN2 Eopt -2806.643600
Pd -2.570991 0.616488 0.226577
C -3.661758 2.832084 -1.175533
C -5.061104 0.946102 -1.062226
C -4.583833 3.511218 -1.961346
C -6.026546 1.570977 -1.838094
H -4.340452 4.515158 -2.291548
H -6.932275 1.023483 -2.075780
N -3.944526 1.604200 -0.749783
H -6.519142 3.381360 -2.893470
C -5.779533 2.869842 -2.284008
N -3.994223 -0.821524 0.098670
N -1.629875 2.524226 0.049488
C -5.136559 -0.468122 -0.548326
C -2.341055 3.379297 -0.715174
O -6.136483 -1.147614 -0.736336
O -2.035688 4.538710 -1.022694

C	-3.846526	-2.118565	0.597123
C	-3.692855	-2.329299	1.976692
C	-3.771926	-3.221900	-0.269889
C	-3.477595	-3.612110	2.482840
C	-3.570532	-4.509281	0.232024
C	-3.425843	-4.687273	1.602361
H	-3.266350	-5.687688	1.994455
C	-0.523918	3.173858	0.739600
C	0.688578	3.544879	-0.155808
H	-0.898208	4.146987	1.095932
C	-0.058881	2.388302	1.946807
C	1.864861	4.054711	0.657306
H	0.329852	4.362355	-0.790402
H	-0.934784	2.052842	2.512453
H	0.487153	1.497932	1.618226
C	0.836507	3.248062	2.823928
C	1.953796	3.891577	2.044566
H	0.228185	4.033211	3.297267
H	1.256253	2.652483	3.645052
C	3.094318	4.351528	2.712353
C	4.043487	5.131511	0.646564
C	1.120730	2.441629	-1.090666
C	4.133688	4.964763	2.027967
H	3.161052	4.216521	3.790212
H	4.851570	5.604069	0.095928
C	2.088090	1.499221	-0.741366
C	0.577197	2.357671	-2.372685
H	5.014366	5.305563	2.565038
N	2.498096	0.535695	-1.576841
H	2.562805	1.519629	0.233588
H	-0.184401	3.073529	-2.671376
C	2.004211	0.495721	-2.821296
H	2.388793	-0.285798	-3.465200
H	-3.362712	-3.781580	3.546947
H	-3.518315	-5.364278	-0.431565
O	-3.758361	-1.211357	2.745853
O	-3.878178	-2.927477	-1.587029
C	-3.669787	-1.376342	4.138755
H	-2.697400	-1.794218	4.437842
H	-3.781544	-0.378773	4.567736
H	-4.468233	-2.025038	4.521007
C	-3.825036	-3.993670	-2.502099
H	-3.947282	-3.547027	-3.490278
H	-2.860349	-4.517415	-2.455012
H	-4.636525	-4.711550	-2.329095
C	2.916956	4.678889	-0.023758
H	2.846734	4.795320	-1.103159
C	1.039247	1.389776	-3.254947
H	0.658443	1.320156	-4.268404
C	-0.332464	-1.270410	-0.006519
C	-0.631136	-0.603026	2.197245
C	-0.910506	-1.611388	-1.251434
C	1.032006	-1.567441	0.242280
C	0.662886	-1.021554	2.578205
H	-1.297659	-0.152496	2.925278
C	-0.134543	-2.231734	-2.200382
H	-1.968266	-1.432685	-1.414276
C	1.875637	-1.970481	-0.840164
H	-0.588594	-2.556966	-3.133108
C	1.260909	-2.366738	-2.013288
H	1.866671	-2.718706	-2.846767
Pd	3.690062	-1.028416	-0.889260
C	6.469693	-0.468869	-0.572189
O	7.574407	0.039032	-0.525985
O	5.380284	0.107017	-0.973564
N	4.975957	-2.438292	-0.225819
C	4.709172	-3.668042	0.055018
C	5.733958	-4.653470	0.517498
H	6.487101	-4.810800	-0.262301
H	5.253601	-5.603929	0.750709
H	6.257783	-4.278894	1.402716
O	3.494143	-4.156787	-0.048183
C	6.338451	-1.931500	-0.112010
H	7.030387	-2.531316	-0.715640
C	1.508287	-1.413048	1.564336
H	2.553010	-1.639244	1.767806
N	-1.080755	-0.650496	0.960817
H	6.685182	-1.981751	0.927980
H	2.890806	-3.420360	-0.374310
C	1.083539	-0.930504	4.013830
H	0.567642	-1.679568	4.626886
H	2.159272	-1.095805	4.119535
H	0.849277	0.053969	4.435719

107

cis-T25_C5_IN3 Eopt -2944.280624

Pd	-2.757856	0.671841	0.430655
C	-3.814090	3.147377	-0.481019
C	-5.356475	1.374603	-0.420199
C	-4.769011	4.004430	-1.013070
C	-6.357128	2.178868	-0.945652
H	-4.480134	5.027092	-1.229444
H	-7.335386	1.741848	-1.114769
N	-4.148448	1.892487	-0.195967
H	-6.818605	4.160008	-1.650243
C	-6.052818	3.508770	-1.238304
N	-4.320561	-0.616228	0.336001
N	-1.661254	2.511795	0.352176
C	-5.498008	-0.088291	-0.090291
C	-2.396795	3.522970	-0.156323
O	-6.575489	-0.654590	-0.217922
O	-2.039220	4.694706	-0.336054
C	-4.238799	-1.976662	0.645349
C	-3.939146	-2.383984	1.955056
C	-4.378542	-2.954536	-0.353603
C	-3.786504	-3.736622	2.263976
C	-4.241131	-4.309977	-0.047694

C	-3.946040	-4.683019	1.257818
H	-3.834892	-5.736726	1.497440
C	-0.393653	2.969671	0.908197
C	0.659844	3.396312	-0.145799
H	-0.602711	3.896657	1.466150
C	0.214308	1.969502	1.866992
C	1.978835	3.777238	0.498494
H	0.239581	4.283273	-0.630769
H	-0.560520	1.622824	2.558496
H	0.570086	1.097560	1.310594
C	1.363109	2.590107	2.649489
C	2.330855	3.357180	1.785273
H	0.952724	3.275072	3.406430
H	1.906305	1.812471	3.201064
C	3.596507	3.685062	2.283640
C	4.142055	4.855904	0.255531
C	0.894690	2.371416	-1.227443
C	4.498065	4.426543	1.534293
H	3.872227	3.343630	3.279161
H	4.835622	5.442505	-0.340904
C	1.806479	1.325986	-1.064618
C	0.229592	2.461024	-2.448553
H	5.476470	4.667392	1.941093
N	2.048375	0.426289	-2.025725
H	2.380597	1.197667	-0.151465
H	-0.497002	3.255357	-2.599821
C	1.441268	0.549940	-3.212777
H	1.688972	-0.193007	-3.961560
H	-3.556989	-4.057331	3.273246
H	-4.353016	-5.068461	-0.813413
O	-3.805494	-1.379572	2.859402
O	-4.617658	-2.476483	-1.597966
C	-3.545513	-1.738346	4.193243
H	-2.584915	-2.264224	4.292764
H	-3.504782	-0.802594	4.753955
H	-4.342351	-2.371036	4.604846
C	-4.770915	-3.409499	-2.637941
H	-4.967528	-2.825262	-3.538541
H	-3.859562	-4.006299	-2.781665
H	-5.618556	-4.081392	-2.453118
C	2.893588	4.525712	-0.251476
H	2.612001	4.844998	-1.252865
C	0.523355	1.556040	-3.462225
H	0.044639	1.619933	-4.433823
C	-0.747231	-1.340837	-0.301255
C	-0.733820	-0.923989	1.985658
C	-1.488478	-1.495761	-1.495677
C	0.612133	-1.745750	-0.251026
C	0.557091	-1.465774	2.153932
H	-1.276865	-0.519274	2.833744
C	-0.873294	-2.044912	-2.594305
H	-2.541059	-1.233200	-1.508262
C	1.271664	-2.052540	-1.476158
H	-1.451915	-2.226034	-3.496755
C	0.522161	-2.287467	-2.602637
H	1.003886	-2.562770	-3.538624
C	1.254101	-1.778792	1.008092
H	2.291663	-2.094535	1.073996
N	-1.325847	-0.794962	0.814949
Pd	3.149668	-1.330615	-1.542572
C	3.399826	-3.538685	-1.451544
C	4.562158	-2.897848	-1.061741
H	2.754965	-3.972944	-0.694432
H	3.258939	-3.873698	-2.474080
H	5.364841	-2.682027	-1.760515
C	4.882040	-2.767871	0.388770
O	4.140729	-3.110234	1.288291
O	6.094686	-2.254260	0.564692
C	6.418677	-1.901168	1.919297
C	7.822141	-1.347636	1.914453
H	6.325175	-2.791069	2.549559
H	5.682188	-1.160376	2.245343
H	8.108063	-1.053911	2.929648
H	8.538537	-2.093798	1.556623
H	7.887622	-0.466633	1.269130
C	4.989775	0.418190	-0.400903
O	4.253889	0.167905	0.567302
O	4.881047	-0.132665	-1.560065
C	6.072210	1.469429	-0.291527
H	6.377776	1.586994	0.750465
H	6.928652	1.226282	-0.924924
H	5.656587	2.426907	-0.625574
C	1.163404	-1.578357	3.520054
H	0.647282	-2.335010	4.123652
H	2.216409	-1.863325	3.448423
H	1.100621	-0.627783	4.063357

107

cis-T25_C5_IN4 Eopt -2944.334563

Pd	-2.757313	0.566387	0.215422
C	-4.347764	2.676912	-0.823047
C	-5.486346	0.642533	-0.522321
C	-5.481610	3.272547	-1.359630
C	-6.655567	1.179166	-1.042001
H	-5.419732	4.307295	-1.678351
H	-7.530115	0.541255	-1.111239
N	-4.402024	1.410805	-0.419363
H	-7.547915	2.954337	-1.870247
C	-6.645669	2.510566	-1.458901
N	-4.024590	-1.025508	0.308338
N	-2.091295	2.560072	-0.038693
C	-5.305684	-0.784292	-0.075437
C	-3.022137	3.351951	-0.620558
O	-6.248825	-1.564297	-0.089855
O	-2.897076	4.537582	-0.945004
C	-3.643372	-2.316526	0.683254
C	-3.170080	-2.561625	1.982658

C	-3.639602	-3.368704	-0.248655
C	-2.687035	-3.821363	2.340880
C	-3.177986	-4.636218	0.111119
C	-2.701716	-4.844438	1.399444
H	-2.332861	-5.827568	1.677633
C	-0.920212	3.305995	0.386721
C	0.110799	3.550461	-0.739490
H	-1.268258	4.315617	0.652127
C	-0.233232	2.718596	1.603769
C	1.291082	4.351186	-0.226720
H	-0.413976	4.141916	-1.498646
H	-0.989268	2.466719	2.356541
H	0.281950	1.791263	1.335099
C	0.763914	3.717417	2.178836
C	1.623986	4.384764	1.132779
H	0.213036	4.498883	2.722532
H	1.408971	3.225368	2.917490
C	2.769181	5.083932	1.529958
C	3.230222	5.717651	-0.743836
C	0.586703	2.278953	-1.398502
C	3.569180	5.744444	0.608604
H	3.032490	5.101790	2.585530
H	3.845617	6.233672	-1.475477
C	1.656115	1.554591	-0.876733
C	-0.007971	1.786970	-2.560460
H	4.455509	6.277695	0.941243
N	2.120728	0.422669	-1.430554
H	2.177210	1.887284	0.016446
H	-0.856279	2.311519	-2.991288
C	1.575980	-0.009560	-2.573240
H	1.990687	-0.910901	-3.003062
H	-2.315709	-4.014619	3.340232
H	-3.171570	-5.450193	-0.603983
O	-3.210056	-1.498226	2.826160
O	-4.071045	-3.043494	-1.489538
C	-2.763170	-1.699394	4.143079
H	-1.703164	-1.989970	4.171305
H	-2.890585	-0.742877	4.653725
H	-3.356418	-2.465052	4.659419
C	-4.177925	-4.078323	-2.434202
H	-4.587451	-3.620638	-3.336411
H	-3.198282	-4.520563	-2.662972
H	-4.858204	-4.867096	-2.089213
C	2.100619	5.022133	-1.149442
H	1.833504	4.985955	-2.203651
C	0.505876	0.646059	-3.163047
H	0.078775	0.251300	-4.078532
C	-0.544991	-1.417238	-0.230191
C	-0.490699	-0.425861	1.872283
C	-1.234675	-1.664369	-1.437518
C	0.686811	-2.078654	0.028230
C	0.706637	-1.070632	2.234803
H	-0.987493	0.231028	2.576721
C	-0.706543	-2.542244	-2.350320
H	-2.197364	-1.191690	-1.600740
C	1.283243	-2.876993	-0.994026
H	-1.255075	-2.761523	-3.262072
C	0.560844	-3.122710	-2.141078
H	0.996659	-3.751376	-2.914524
C	1.298692	-1.875539	1.287429
H	2.230491	-2.379138	1.525955
N	-1.070656	-0.552071	0.694927
Pd	3.459322	-0.507361	-0.157597
C	2.715513	-3.314105	-0.884074
C	3.686582	-2.198622	-1.274008
H	2.975618	-3.666569	0.118530
H	2.883081	-4.174304	-1.547185
H	3.572571	-1.893123	-2.319105
C	5.102773	-2.605204	-1.025257
O	5.452183	-3.559218	-0.364533
O	5.967916	-1.760409	-1.618426
C	7.345882	-1.985309	-1.310755
C	8.135605	-0.860825	-1.936551
H	7.645993	-2.964957	-1.699399
H	7.461230	-2.012815	-0.222335
H	9.202548	-0.987007	-1.725076
H	7.998663	-0.843839	-3.022434
H	7.813628	0.104981	-1.534445
C	4.463251	0.023449	2.084819
O	3.695918	0.905669	1.614508
O	4.669325	-1.065048	1.443588
C	5.161922	0.216759	3.398928
H	5.017751	-0.663310	4.032427
H	6.237967	0.318422	3.223019
H	4.791731	1.112519	3.900478
C	1.334682	-0.790931	3.566076
H	0.582924	-0.668514	4.352905
H	2.012986	-1.597274	3.859808
H	1.921209	0.134571	3.511476

107

cis-T25_C5_IN5 Eopt -2944.296462

Pd	-2.890487	0.430432	0.031426
C	-4.273674	2.238977	-1.658302
C	-5.417228	0.231681	-1.217771
C	-5.286337	2.670479	-2.505004
C	-6.466718	0.606735	-2.044114
H	-5.177826	3.633635	-2.991500
H	-7.298140	-0.078933	-2.167212
N	-4.390305	1.064023	-1.046248
H	-7.203231	2.160200	-3.339322
C	-6.394899	1.843507	-2.686266
N	-4.111861	-1.190640	0.154767
N	-2.212106	2.374721	-0.451239
C	-5.297931	-1.088750	-0.501873
C	-3.022433	3.003537	-1.333293
O	-6.200024	-1.913367	-0.562395

O	-2.853670	4.118774	-1.838797
C	-3.772510	-2.380344	0.803789
C	-3.541163	-2.385660	2.189141
C	-3.565972	-3.566237	0.077977
C	-3.113070	-3.545949	2.836501
C	-3.157493	-4.734663	0.723958
C	-2.933314	-4.708322	2.094871
H	-2.608736	-5.614609	2.598151
C	-1.167022	3.246240	0.058724
C	0.048319	3.411014	-0.882620
H	-1.601897	4.256845	0.103842
C	-0.697755	2.893265	1.455615
C	1.089848	4.325969	-0.263841
H	-0.351265	3.917106	-1.769536
H	-1.565662	2.656980	2.081421
H	-0.054445	2.008039	1.426478
C	0.067859	4.068388	2.047114
C	1.097406	4.635911	1.101711
H	-0.644838	4.863570	2.310964
H	0.557321	3.773109	2.983993
C	2.067446	5.517869	1.591608
C	3.027510	5.754036	-0.600241
C	0.662173	2.118703	-1.368417
C	3.022193	6.080458	0.756115
H	2.068097	5.759338	2.652753
H	3.773816	6.178920	-1.265446
C	1.675629	1.454638	-0.672913
C	0.267431	1.576447	-2.591404
H	3.765758	6.762376	1.159682
N	2.296865	0.361944	-1.139924
H	2.018699	1.805129	0.295202
H	-0.528713	2.055847	-3.155176
C	1.940581	-0.106764	-2.339581
H	2.486542	-0.968091	-2.707239
H	-2.932405	-3.555621	3.904820
H	-3.001197	-5.652358	0.169420
O	-3.751451	-1.200868	2.817732
O	-3.755179	-3.464948	-1.258865
C	-3.539858	-1.156973	4.206603
H	-2.494915	-1.381444	4.464591
H	-3.777679	-0.137080	4.514944
H	-4.197698	-1.855957	4.738837
C	-3.631215	-4.635897	-2.026244
H	-3.861952	-4.347815	-3.053307
H	-2.611135	-5.042412	-1.982187
H	-4.341293	-5.406066	-1.699978
C	2.066742	4.884933	-1.096139
H	2.061462	4.629094	-2.153541
C	0.919042	0.456147	-3.089070
H	0.652355	0.027074	-4.049386
C	-0.517135	-1.354982	0.243575
C	-0.880293	-0.115984	2.175067
C	-0.999875	-1.867025	-0.984630
C	0.765918	-1.737415	0.713885
C	0.361146	-0.468430	2.734640
H	-1.555464	0.536185	2.716362
C	-0.214665	-2.718888	-1.717732
H	-2.004176	-1.611487	-1.305189
C	1.619219	-2.499424	-0.144440
C	1.190498	-1.254796	1.967278
C	1.107263	-3.006354	-1.318306
H	-0.600450	-3.143563	-2.639954
H	2.190300	-1.481434	2.323899
N	-1.278549	-0.484829	0.971982
C	4.048380	-2.481862	-0.821016
Pd	3.848497	-0.620168	0.182404
H	3.782939	-2.321303	-1.862517
C	5.397289	-3.068776	-0.600691
O	5.753854	-3.658779	0.394663
O	6.173753	-2.863379	-1.672312
C	7.523112	-3.332495	-1.550309
C	8.250585	-2.947109	-2.815152
H	7.507480	-4.416540	-1.394873
H	7.972065	-2.877907	-0.661298
H	9.290562	-3.285222	-2.764620
H	7.781361	-3.405401	-3.691338
H	8.246150	-1.861012	-2.948326
O	5.048544	1.286634	0.299846
C	4.402277	1.668560	1.311789
O	3.455762	0.968029	1.790345
C	4.727952	2.999523	1.933029
H	5.811112	3.139522	1.971385
H	4.308342	3.793280	1.306287
H	4.297031	3.079929	2.932680
C	3.056346	-2.596289	0.173901
H	3.357627	-3.064477	1.110398
H	1.742537	-3.614785	-1.956173
H	4.885791	-1.184951	1.139392
C	0.804581	0.103249	4.046669
H	1.046063	-0.683902	4.769328
H	1.709341	0.701934	3.888345
H	0.033742	0.743529	4.486526

99

cis-T25_C5_TSI Eopt -2806.635928

Pd	-2.537507	0.628350	0.273006
C	-3.802822	2.832943	-0.992077
C	-5.083007	0.861878	-0.930875
C	-4.790848	3.493550	-1.710248
C	-6.111939	1.465692	-1.639111
H	-4.617948	4.524597	-1.998749
H	-6.992364	0.877255	-1.873982
N	-3.995927	1.569550	-0.623864
H	-6.748774	3.293567	-2.580804
C	-5.958305	2.797888	-2.024428
N	-3.875265	-0.891799	0.108193
N	-1.721679	2.583951	0.157684

C -5.055815 -0.578138 -0.489271
C -2.492745 3.427741 -0.562054
O -6.017469 -1.308364 -0.686203
O -2.239767 4.601353 -0.858857
C -3.633023 -2.203798 0.524028
C -3.421070 -2.483717 1.883697
C -3.518647 -3.248766 -0.408962
C -3.099459 -3.774998 2.304554
C -3.214876 -4.545937 0.008670
C -3.006373 -4.791398 1.360097
H -2.763266 -5.798609 1.686043
C -0.582823 3.247770 0.771786
C 0.585039 3.546434 -0.203895
H -0.929687 4.242606 1.091389
C -0.072206 2.524076 2.000384
C 1.819530 4.059862 0.515060
H 0.210983 4.342452 -0.857851
H -0.924685 2.236638 2.626005
H 0.449198 1.608125 1.703092
C 0.877420 3.422457 2.776473
C 1.973203 3.978473 1.904119
H 0.306682 4.253807 3.216403
H 1.320191 2.877406 3.620178
C 3.162050 4.434170 2.484699
C 4.032531 5.046262 0.329450
C 0.927860 2.383293 -1.102043
C 4.186604 4.962404 1.712606
H 3.279348 4.362797 3.564302
H 4.829130 5.448828 -0.289146
C 1.882216 1.428822 -0.755007
C 0.311730 2.249322 -2.347207
H 5.105771 5.299856 2.183105
N 2.219222 0.411021 -1.559118
H 2.417010 1.488625 0.186833
H -0.440099 2.974998 -2.646624
C 1.658037 0.322537 -2.770963
H 1.993961 -0.495261 -3.396667
H -2.934997 -3.997327 3.352229
H -3.128606 -5.355728 -0.706040
O -3.542025 -1.421155 2.720984
O -3.688745 -2.888124 -1.703019
C -3.374267 -1.657236 4.096010
H -2.360596 -2.017203 4.325409
H -3.537214 -0.696863 4.588804
H -4.103802 -2.384673 4.474214
C -3.659531 -3.905049 -2.673737
H -3.858353 -3.414705 -3.628195
H -2.678004 -4.397368 -2.714202
H -4.434704 -4.658613 -2.487267
C 2.857347 4.598333 -0.254953
H 2.737649 4.649083 -1.335060
C 0.693501 1.221462 -3.198420
H 0.256358 1.112610 -4.185396
C -0.265064 -1.279935 0.057112
C -0.561943 -0.511550 2.224493
C -0.815537 -1.574259 -1.212169
C 1.037636 -1.740728 0.372887
C 0.675402 -1.035138 2.661201
H -1.205033 0.015723 2.920425
C -0.086989 -2.308086 -2.120015
H -1.831169 -1.260893 -1.432227
C 1.860618 -2.319297 -0.645128
H -0.538982 -2.578766 -3.070662
C 1.256831 -2.640441 -1.852430
H 1.847375 -3.126129 -2.627259
Pd 3.576094 -1.025442 -0.890309
H 2.849050 -3.174549 -0.205835
C 6.270433 -0.176157 -0.784457
O 7.292740 0.475866 -0.846795
O 5.085752 0.278288 -1.097372
N 5.020565 -2.240712 -0.257784
C 4.824866 -3.457247 0.181173
C 5.981184 -4.298556 0.649032
H 6.720758 -4.416963 -0.150073
H 5.613904 -5.278553 0.953481
H 6.489872 -3.821134 1.493704
O 3.661849 -3.989597 0.240160
C 6.337509 -1.635847 -0.317505
H 6.993898 -2.172666 -1.015608
C 1.492408 -1.588112 1.702154
H 2.486970 -1.948200 1.954731
N -0.987855 -0.569682 0.979737
H 6.832569 -1.644366 0.662068
C 1.066640 -0.904353 4.102095
H 0.396942 -1.482677 4.749921
H 2.085749 -1.263889 4.266824
H 1.018006 0.140205 4.432334
107
cis-T25_C5_TSII Eopt -2944.272220
Pd -2.822411 0.669287 0.302447
C -3.871311 3.007642 -0.918575
C -5.330553 1.163808 -0.896065
C -4.790460 3.769577 -1.628119
C -6.294259 1.872208 -1.598894
H -4.521873 4.785794 -1.895166
H -7.223636 1.371820 -1.848796
N -4.184360 1.762446 -0.571614
H -6.752904 3.767228 -2.511186
C -6.015244 3.190810 -1.960047
N -4.295388 -0.712605 0.113033
N -1.819340 2.544845 0.219924
C -5.438692 -0.281047 -0.482385
C -2.518997 3.476102 -0.462641
O -6.461861 -0.916412 -0.698258
O -2.179493 4.642297 -0.699057
C -4.169038 -2.050071 0.497158

C	-3.992428	-2.380820	1.850162
C	-4.132082	-3.076347	-0.462165
C	-3.788944	-3.705565	2.240164
C	-3.943352	-4.405053	-0.076393
C	-3.773560	-4.701990	1.270314
H	-3.623706	-5.734685	1.572225
C	-0.658412	3.100897	0.899244
C	0.532755	3.453079	-0.027221
H	-0.968243	4.072979	1.315526
C	-0.190055	2.235960	2.049885
C	1.755200	3.888157	0.761921
H	0.185901	4.305780	-0.620830
H	-1.059352	1.921517	2.637331
H	0.291872	1.333456	1.661104
C	0.784535	3.005602	2.927105
C	1.893984	3.646456	2.133661
H	0.235726	3.789026	3.470753
H	1.213300	2.347183	3.693736
C	3.077227	4.028903	2.775897
C	3.967242	4.893858	0.717589
C	0.908113	2.371009	-1.012371
C	4.108682	4.645571	2.082555
H	3.182686	3.832229	3.841094
H	4.765562	5.376521	0.160882
C	1.811522	1.355551	-0.696972
C	0.406454	2.392784	-2.314010
H	5.020575	4.929453	2.600638
N	2.213559	0.438318	-1.582947
H	2.247312	1.283177	0.294271
H	-0.311647	3.160983	-2.590518
C	1.777810	0.507436	-2.846835
H	2.196091	-0.221565	-3.531250
H	-3.655202	-3.967318	3.283139
H	-3.920035	-5.200831	-0.811453
O	-4.023509	-1.332387	2.713246
O	-4.259174	-2.668653	-1.746867
C	-3.900215	-1.617101	4.083970
H	-2.927077	-2.072538	4.318851
H	-3.984041	-0.658414	4.599314
H	-4.698673	-2.284711	4.432217
C	-4.243486	-3.653382	-2.750091
H	-4.376768	-3.122124	-3.693995
H	-3.287744	-4.195192	-2.768040
H	-5.064223	-4.370215	-2.621871
C	2.799862	4.514654	0.071778
H	2.688368	4.693461	-0.995609
C	0.859523	1.466682	-3.245851
H	0.515695	1.487991	-4.274809
C	-0.663040	-1.299544	-0.061670
C	-0.918227	-0.731859	2.176572
C	-1.252752	-1.498475	-1.330680
C	0.670155	-1.726476	0.181218
C	0.345517	-1.250532	2.532006
H	-1.556267	-0.278364	2.927885
C	-0.523605	-2.107112	-2.324075
H	-2.289485	-1.218562	-1.484110
C	1.453540	-2.145508	-0.932013
H	-0.989405	-2.305669	-3.285668
C	0.843045	-2.406891	-2.138404
H	1.432992	-2.762390	-2.980456
C	1.164317	-1.663585	1.504708
H	2.189843	-1.968913	1.710243
N	-1.369051	-0.686156	0.940020
Pd	3.315405	-1.297606	-0.993264
C	3.094991	-3.516255	-0.508244
C	4.401143	-2.991486	-0.418916
H	2.580523	-3.771813	0.412980
H	2.832056	-4.107427	-1.378222
H	5.117387	-3.140808	-1.222183
C	4.938193	-2.614941	0.909407
O	4.276575	-2.561010	1.932980
O	6.234747	-2.325123	0.836568
C	6.814337	-1.709837	1.997664
C	6.435147	-0.245319	2.071939
H	7.889493	-1.842715	1.859564
H	6.493748	-2.257752	2.888487
H	7.006812	0.249308	2.864766
H	6.635909	0.247157	1.116765
H	5.369921	-0.134677	2.291668
C	5.398990	-0.122873	-2.357248
O	4.790327	-0.667700	-3.282425
O	5.062020	-0.192300	-1.109892
C	6.642489	0.707810	-2.605871
H	7.485350	0.289056	-2.046382
H	6.879751	0.729524	-3.670756
H	6.484728	1.727442	-2.239470
C	0.784523	-1.244131	3.965322
H	0.191376	-1.945075	4.565297
H	1.835286	-1.534059	4.049810
H	0.665806	-0.250375	4.413671

107

cis-T25_C5_TSIIIEopt -2944.274561

Pd	-2.985325	0.246380	0.092986
C	-4.384818	2.131200	-1.505214
C	-5.281779	-0.041628	-1.526332
C	-5.352791	2.576733	-2.395886
C	-6.275838	0.338527	-2.416077
H	-5.330879	3.616098	-2.704696
H	-6.988146	-0.410186	-2.745631
N	-4.396855	0.862895	-1.107104
H	-7.075602	1.988686	-3.543486
C	-6.306756	1.665084	-2.847619
N	-4.005901	-1.490553	-0.153995
N	-2.462412	2.302700	-0.086632
C	-5.081528	-1.431996	-0.982946
C	-3.290330	2.974294	-0.917779

O -5.840437 -2.339042 -1.296039
O -3.238685 4.173385 -1.216107
C -3.614225 -2.717984 0.388028
C -3.662034 -2.923845 1.775760
C -3.094184 -3.734380 -0.431624
C -3.196196 -4.114193 2.336781
C -2.641227 -4.933238 0.122619
C -2.696154 -5.106032 1.500064
H -2.339785 -6.036214 1.933346
C -1.521830 3.182631 0.591584
C -0.394891 3.742273 -0.316432
H -2.084359 4.077801 0.901068
C -0.912744 2.561525 1.831159
C 0.534676 4.643804 0.469692
H -0.906289 4.347718 -1.072753
H -1.706001 2.096291 2.423126
H -0.207053 1.771629 1.545400
C -0.214931 3.625406 2.668483
C 0.658399 4.553302 1.861220
H -0.979149 4.229031 3.180209
H 0.379893 3.155254 3.462557
C 1.586434 5.371607 2.515307
C 2.247800 6.365529 0.428181
C 0.377223 2.670620 -1.048446
C 2.378133 6.269449 1.813266
H 1.683167 5.296173 3.596722
H 2.858508 7.066306 -0.134022
C 1.597054 2.183051 -0.580117
C -0.104002 2.139592 -2.247204
H 3.094812 6.892218 2.341494
N 2.309693 1.247137 -1.221837
H 2.031418 2.567096 0.336515
H -1.044431 2.502848 -2.651618
C 1.840815 0.750123 -2.376774
H 2.441803 -0.023402 -2.844631
H -3.231038 -4.280093 3.407022
H -2.240531 -5.720870 -0.504299
O -4.172056 -1.893045 2.498690
O -3.043792 -3.440506 -1.751713
C -4.279410 -2.068322 3.888666
H -3.294533 -2.210719 4.357325
H -4.734370 -1.153855 4.274025
H -4.919511 -2.923263 4.141171
C -2.575457 -4.438174 -2.626165
H -2.642944 -4.013660 -3.629103
H -1.531189 -4.704255 -2.412765
H -3.197348 -5.340433 -2.573583
C 1.333265 5.555712 -0.229452
H 1.232754 5.616287 -1.311015
C 0.635560 1.174904 -2.917401
H 0.289381 0.748713 -3.853401
C -0.438803 -1.219153 0.613688
C -1.430180 -0.400031 2.550256
C -0.589318 -1.647851 -0.723411
C 0.789611 -1.427195 1.298086
C -0.291134 -0.668742 3.335712
H -2.316951 0.035596 2.998357
C 0.462369 -2.267272 -1.350697
H -1.547043 -1.517419 -1.216382
C 1.920254 -1.884152 0.547737
C 0.829421 -1.121521 2.676606
C 1.728259 -2.347359 -0.738681
H 0.346906 -2.630516 -2.367419
H 1.741816 -1.281458 3.243593
N -1.481752 -0.604543 1.250848
C 4.496916 -1.855052 0.375509
Pd 3.837322 -0.009003 -0.387733
H 4.525703 -2.463229 -0.524155
C 5.746994 -1.722748 1.151921
H 3.165202 0.054654 1.062328
O 5.818035 -1.326815 2.299013
O 6.805349 -2.081713 0.416388
C 8.081388 -1.899246 1.039525
C 9.133343 -2.258053 0.018198
H 8.136038 -2.534307 1.930491
H 8.166460 -0.858961 1.370482
H 10.131945 -2.131864 0.448834
H 9.024702 -3.298025 -0.304761
H 9.051106 -1.612936 -0.862009
O 4.987425 0.027406 -2.102706
C 4.871260 -0.970340 -2.907400
O 4.030419 -1.875835 -2.820239
C 5.896355 -0.978504 -4.025526
H 6.859720 -1.304022 -3.616551
H 5.595552 -1.669960 -4.814746
H 6.036296 0.027868 -4.428899
C 3.278745 -1.570020 1.061802
H 3.405512 -1.436912 2.135427
H 2.577541 -2.644221 -1.346704
C -0.320889 -0.396703 4.809388
H -1.043729 -1.045277 5.318582
H 0.659310 -0.567448 5.262584
H -0.612985 0.639967 5.014755
99
cis-T25_C6_IN2 Eopt -2806.648643
Pd -2.668472 0.567341 -0.075291
C -3.232448 2.703079 -1.858251
C -4.568233 0.787835 -2.148097
C -3.864837 3.345060 -2.915088
C -5.237244 1.371572 -3.213803
H -3.546818 4.348785 -3.175030
H -6.007134 0.797851 -3.718498
N -3.616617 1.476506 -1.517623
H -5.390004 3.147753 -4.420148
C -4.879571 2.666889 -3.590473
N -3.967918 -0.889530 -0.588886

N	-1.653206	2.441106	-0.081547
C	-4.784362	-0.615350	-1.637983
C	-2.122732	3.280250	-1.025392
O	-5.607125	-1.351858	-2.164771
O	-1.746442	4.438340	-1.257020
C	-3.915941	-2.177334	-0.048352
C	-4.446931	-2.433735	1.224361
C	-3.229182	-3.201736	-0.719798
C	-4.309441	-3.693025	1.812404
C	-3.089894	-4.463914	-0.138694
C	-3.635259	-4.692449	1.119213
H	-3.530429	-5.674174	1.572409
C	-0.709888	3.062228	0.837922
C	0.643832	3.491603	0.201231
H	-1.157988	4.013188	1.170234
C	-0.482074	2.211137	2.070444
C	1.677386	3.887514	1.242771
H	0.398766	4.383525	-0.384153
H	-1.452561	1.888132	2.457299
H	0.085424	1.312349	1.804592
C	0.261984	2.995232	3.137016
C	1.518697	3.634115	2.609701
H	-0.399535	3.780204	3.533740
H	0.504523	2.343143	3.985661
C	2.537847	4.004170	3.494869
C	3.852789	4.880423	1.684719
C	1.242456	2.515690	-0.788864
C	3.696956	4.620007	3.045906
H	2.409733	3.798359	4.555893
H	4.754289	5.361085	1.315786
C	2.153659	1.530808	-0.411520
C	0.966486	2.638535	-2.152248
H	4.477728	4.893763	3.750156
N	2.784607	0.745967	-1.295492
H	2.399731	1.366217	0.631613
H	0.247788	3.386783	-2.477836
C	2.562308	0.915405	-2.605967
H	3.143982	0.289998	-3.274143
H	-4.723336	-3.902081	2.791909
H	-2.563479	-5.260270	-0.651379
O	-5.058497	-1.378132	1.821565
O	-2.711627	-2.854061	-1.922103
C	-5.662109	-1.601753	3.071325
H	-4.923326	-1.885612	3.835294
H	-6.127585	-0.656148	3.354640
H	-6.432258	-2.381527	3.014688
C	-1.959134	-3.821928	-2.612858
H	-1.633390	-3.343811	-3.538178
H	-1.078955	-4.133027	-2.034019
H	-2.564751	-4.703461	-2.858059
C	2.849053	4.515329	0.800160
H	2.971659	4.707647	-0.263564
C	1.640285	1.840817	-3.069472
H	1.470238	1.942245	-4.136277
C	-0.449886	-1.074248	0.920271
C	-1.963215	-0.595903	2.613810
C	-0.196246	-1.250732	-0.457891
C	0.569891	-1.353896	1.867115
C	-1.067461	-1.009365	3.624348
H	-2.950388	-0.219332	2.865507
H	-1.021940	-1.164564	-1.158907
C	1.896890	-1.534168	1.391344
C	0.215814	-1.326915	3.234334
H	0.973357	-1.557574	3.980882
N	-1.655045	-0.589213	1.332138
H	2.696790	-1.603236	2.127144
Pd	3.936352	-0.881646	-0.735223
C	6.709986	-0.714626	-1.400297
O	7.812338	-0.398964	-1.808862
O	5.606513	-0.064217	-1.588454
N	5.219819	-2.396851	-0.317497
C	4.937299	-3.604146	0.026878
C	5.954100	-4.680273	0.237960
H	6.748879	-4.338014	0.907149
H	6.421004	-4.953180	-0.714975
H	5.471684	-5.561973	0.660832
O	3.694650	-3.998188	0.220192
C	6.602750	-1.996147	-0.552783
C	2.182305	-1.528643	0.038821
H	7.169758	-2.782113	-1.061805
C	1.080639	-1.520075	-0.869857
H	1.272600	-1.637042	-1.933496
H	7.100537	-1.796300	0.405608
H	3.100622	-3.211315	0.085841
C	-1.517063	-1.024434	5.054509
H	-2.230725	-1.838384	5.231790
H	-0.672302	-1.168781	5.733710
H	-2.016174	-0.087729	5.327236

107

cis-T25_C6_IN3 Eopt -2944.281548

Pd	2.807461	-0.595231	0.029610
C	3.482617	-3.016856	-1.290148
C	4.718155	-1.135148	-1.973416
C	4.150744	-3.827179	-2.199017
C	5.419612	-1.888162	-2.903429
H	3.885451	-4.877649	-2.246802
H	6.159834	-1.390051	-3.520311
N	3.801059	-1.728580	-1.209110
H	5.667816	-3.862394	-3.724701
C	5.130862	-3.249661	-3.006111
N	4.031964	0.791363	-0.779925
N	1.880869	-2.482706	0.404499
C	4.859898	0.351346	-1.761851
C	2.399518	-3.469427	-0.352292
O	5.641241	1.006947	-2.437600
O	2.082740	-4.667861	-0.347043

C	3.905138	2.159505	-0.524268
C	4.397691	2.706377	0.669795
C	3.185119	2.982957	-1.405073
C	4.189989	4.053419	0.974544
C	2.977004	4.331625	-1.108473
C	3.485730	4.848778	0.077174
H	3.328164	5.898369	0.309167
C	0.953345	-2.955051	1.423792
C	-0.371713	-3.563405	0.878981
H	1.438791	-3.800676	1.938357
C	0.667036	-1.889889	2.461613
C	-1.383722	-3.822318	1.981852
H	-0.075555	-4.531531	0.462234
H	1.614487	-1.447734	2.781178
H	0.060531	-1.092791	2.017970
C	-0.052421	-2.481420	3.661117
C	-1.258241	-3.293900	3.271325
H	0.645406	-3.125394	4.217475
H	-0.349656	-1.684088	4.354138
C	-2.259454	-3.552377	4.214816
C	-3.488168	-4.861603	2.618098
C	-1.016516	-2.813874	-0.267453
C	-3.367350	-4.325411	3.899916
H	-2.158598	-3.132126	5.213641
H	-4.348224	-5.471127	2.355582
C	-2.012581	-1.857346	-0.078442
C	-0.685538	-3.134652	-1.586577
H	-4.135042	-4.508701	4.646605
N	-2.672124	-1.281579	-1.094089
H	-2.302314	-1.547206	0.920004
H	0.093287	-3.871471	-1.768157
C	-2.386061	-1.634386	-2.357423
H	-2.995269	-1.164700	-3.126422
H	4.573810	4.485847	1.891110
H	2.426369	4.973950	-1.785560
O	5.047557	1.834186	1.483052
O	2.706351	2.362178	-2.509496
C	5.606443	2.346387	2.666755
H	4.834783	2.745301	3.341569
H	6.109015	1.507004	3.150550
H	6.339943	3.135969	2.459331
C	1.926723	3.123119	-3.400130
H	1.639151	2.442695	-4.203304
H	1.023204	3.511029	-2.910344
H	2.499009	3.958011	-3.823695
C	-2.502723	-4.607824	1.675929
H	-2.597062	-5.015884	0.671773
C	-1.380485	-2.548800	-2.636511
H	-1.162461	-2.804555	-3.668385
C	0.514526	1.098896	0.696666
C	2.030507	1.016535	2.453335
C	0.269618	1.014210	-0.691641
C	-0.535154	1.464391	1.579569
C	1.097028	1.544210	3.373155
H	3.033524	0.747352	2.771160
H	1.106653	0.856230	-1.366192
C	-1.865377	1.463521	1.082387
C	-0.198980	1.700355	2.931619
H	-0.981987	2.001813	3.625029
N	1.740498	0.767031	1.192173
H	-2.679284	1.585351	1.794799
C	-2.110534	1.221560	-0.249980
C	-1.016659	1.123581	-1.150475
H	-1.207690	1.032297	-2.216882
Pd	-3.838249	0.498625	-0.906180
C	-4.491443	2.364548	-1.801635
C	-5.047418	2.275285	-0.538275
H	-3.631951	3.007494	-1.965333
H	-4.990533	1.958326	-2.676718
H	-6.010061	1.795512	-0.381780
C	-4.541502	3.057052	0.622433
O	-4.886691	2.853083	1.766596
O	-3.667389	4.000920	0.254002
C	-3.059419	4.753998	1.312279
C	-3.934853	5.915940	1.728096
H	-2.107671	5.089205	0.893894
H	-2.863777	4.085175	2.154590
H	-3.418922	6.521610	2.480935
H	-4.163977	6.555492	0.870023
H	-4.870961	5.552712	2.160623
C	-5.702087	-0.612536	-2.781376
O	-4.855603	-0.230729	-3.603689
O	-5.629392	-0.425982	-1.509472
C	-6.928999	-1.378115	-3.235762
H	-7.058095	-1.285931	-4.315745
H	-6.801441	-2.436567	-2.981639
H	-7.821192	-1.024596	-2.711673
C	1.523752	1.835865	4.780532
H	2.183500	2.711475	4.817486
H	0.661521	2.041521	5.420922
H	2.075413	0.993941	5.213958

107

cis-T25_C6_IN4 Eopt -2944.331016

Pd	-2.832890	0.608850	-0.075719
C	-3.731372	2.530582	-1.959547
C	-4.886293	0.482065	-2.011296
C	-4.507897	3.034594	-2.994511
C	-5.696079	0.924336	-3.047571
H	-4.312165	4.042069	-3.345076
H	-6.445338	0.247237	-3.443444
N	-3.957229	1.298124	-1.514526
H	-6.124121	2.588578	-4.343650
C	-5.501673	2.217531	-3.534286
N	-4.017844	-1.009489	-0.389202
N	-2.002514	2.536499	-0.307615
C	-4.928220	-0.890731	-1.389701

C	-2.604039	3.254762	-1.279754
O	-5.715137	-1.734386	-1.798086
O	-2.315048	4.397515	-1.656437
C	-3.811400	-2.248881	0.223135
C	-4.136484	-2.431167	1.575986
C	-3.182029	-3.295463	-0.471606
C	-3.833259	-3.628508	2.227184
C	-2.886738	-4.499316	0.171001
C	-3.214044	-4.648292	1.513141
H	-2.980637	-5.582479	2.015984
C	-0.951548	3.263106	0.384660
C	0.302498	3.517519	-0.491610
H	-1.338397	4.270042	0.607894
C	-0.547843	2.613227	1.692996
C	1.412334	4.184317	0.296248
H	-0.030333	4.208473	-1.273641
H	-1.448569	2.374194	2.265725
H	-0.026105	1.668241	1.497962
C	0.337812	3.550308	2.501543
C	1.455183	4.160730	1.694504
H	-0.282749	4.362366	2.909382
H	0.755574	3.021875	3.367621
C	2.544746	4.744835	2.349639
C	3.526447	5.379008	0.248725
C	0.810565	2.281066	-1.194539
C	3.574469	5.347474	1.641972
H	2.579708	4.716667	3.436859
H	4.324678	5.849398	-0.318486
C	1.813860	1.484639	-0.645535
C	0.329324	1.922593	-2.454902
H	4.414262	5.788322	2.171874
N	2.338392	0.421456	-1.276824
H	2.250178	1.719082	0.321680
H	-0.446870	2.524140	-2.920203
C	1.899782	0.116197	-2.504005
H	2.385546	-0.713183	-3.003254
H	-4.080771	-3.776223	3.271688
H	-2.398833	-5.309407	-0.357746
O	-4.732179	-1.369688	2.177672
O	-2.869853	-3.025626	-1.761137
C	-5.118426	-1.521388	3.519789
H	-4.253426	-1.708409	4.172227
H	-5.591085	-0.580077	3.806483
H	-5.839371	-2.339749	3.643694
C	-2.249843	-4.043865	-2.506416
H	-2.100376	-3.635070	-3.507272
H	-1.277703	-4.321832	-2.076601
H	-2.884446	-4.936584	-2.573314
C	2.452189	4.799653	-0.409990
H	2.411791	4.810481	-1.497311
C	0.886677	0.836390	-3.118406
H	0.558330	0.556273	-4.114110
C	-0.681268	-1.127039	1.060403
C	-1.962954	-0.071986	2.685186
C	-0.483877	-1.482306	-0.291122
C	0.201554	-1.634452	2.051950
C	-1.167304	-0.564703	3.741570
H	-2.819602	0.561114	2.893709
C	0.583151	-2.268137	-0.634336
H	-1.199386	-1.144595	-1.034590
C	1.326128	-2.391365	1.646885
C	-0.071395	-1.324576	3.401584
C	1.545639	-2.685467	0.321132
H	0.726829	-2.539483	-1.677084
H	0.597353	-1.699339	4.173655
N	-1.715668	-0.308051	1.411774
H	2.048840	-2.702166	2.397436
Pd	3.709167	-0.565001	-0.088716
C	2.825612	-3.317615	-0.148840
C	3.569432	-2.349580	-1.059401
H	2.622011	-4.257361	-0.686524
H	3.040734	-2.183775	-2.000831
C	4.968783	-2.770261	-1.342583
O	5.598476	-3.603524	-0.727958
O	5.478535	-2.087737	-2.391729
C	6.854118	-2.348666	-2.675553
C	7.260379	-1.439514	-3.810902
H	6.974479	-3.406924	-2.933355
H	7.444541	-2.164125	-1.771715
H	8.313295	-1.600723	-4.064528
H	6.657087	-1.635658	-4.703120
H	7.128445	-0.389744	-3.530399
C	4.962264	-0.033848	2.000417
O	4.996950	-1.173524	1.418349
O	4.257952	0.898485	1.528053
C	5.800098	0.172030	3.227832
H	5.856228	-0.750246	3.810894
H	6.817945	0.437914	2.921169
H	5.395107	0.988499	3.829082
H	3.468597	-3.570248	0.699084
C	-1.508140	-0.208477	5.158187
H	-2.519380	-0.538518	5.422653
H	-0.809249	-0.672491	5.859375
H	-1.470401	0.876339	5.313527

107

cis-T25_C6_IN5 Eopt -2944.300487

Pd	2.831024	0.498374	0.439489
C	3.238264	2.442045	2.454780
C	4.757749	0.643461	2.496014
C	3.828668	3.010921	3.575682
C	5.396244	1.162546	3.613002
H	3.430858	3.946772	3.952591
H	6.244203	0.624412	4.022764
N	3.722452	1.300884	1.974380
H	5.398647	2.783107	5.029252
C	4.916966	2.356661	4.153881

N	4.258239	-0.907078	0.775804
N	1.705669	2.277366	0.620591
C	5.138616	-0.623605	1.770426
C	2.107155	3.037837	1.661439
O	6.127343	-1.261004	2.106685
O	1.678781	4.151303	1.991791
C	4.509623	-1.952613	-0.115603
C	5.527332	-1.839874	-1.078520
C	3.654614	-3.066876	-0.157967
C	5.704226	-2.829912	-2.049762
C	3.813353	-4.048432	-1.139869
C	4.841304	-3.920792	-2.067255
H	4.975767	-4.692593	-2.820154
C	0.816229	2.960366	-0.310613
C	-0.566887	3.352414	0.272350
H	1.284781	3.928154	-0.556755
C	0.625458	2.192985	-1.605815
C	-1.434670	4.016355	-0.778333
H	-0.346647	4.095399	1.044678
H	1.595804	1.842356	-1.968425
H	0.007466	1.305863	-1.422109
C	-0.021574	3.079436	-2.660854
C	-1.203189	3.863215	-2.149340
H	0.729359	3.791008	-3.035768
H	-0.325222	2.476123	-3.525430
C	-2.064520	4.488620	-3.057847
C	-3.355307	5.424512	-1.257832
C	-1.308467	2.232193	0.963192
C	-3.130308	5.264394	-2.625620
H	-1.886358	4.360392	-4.123600
H	-4.183452	6.032473	-0.903995
C	-2.243498	1.428765	0.305374
C	-1.131135	2.017062	2.330831
H	-3.785780	5.741518	-3.349047
N	-2.975220	0.498083	0.929637
H	-2.454325	1.550532	-0.753518
H	-0.412914	2.626831	2.873541
C	-2.837202	0.346310	2.251378
H	-3.494588	-0.377602	2.724827
H	6.499099	-2.756770	-2.783060
H	3.156155	-4.908874	-1.178946
O	6.257671	-0.703095	-1.011639
O	2.684654	-3.089042	0.784841
C	7.370584	-0.588212	-1.864578
H	7.072395	-0.569821	-2.922113
H	7.846734	0.359771	-1.610369
H	8.082943	-1.407266	-1.704857
C	1.759401	-4.149051	0.743425
H	1.062835	-3.971106	1.563501
H	1.201463	-4.159312	-0.202660
H	2.252159	-5.119029	0.887947
C	-2.513901	4.798114	-0.349986
H	-2.687410	4.910550	0.718132
C	-1.912138	1.072054	2.987103
H	-1.824994	0.913963	4.057421
C	0.768186	-1.170601	-0.924212
C	2.589240	-0.664089	-2.271234
C	0.177244	-1.187123	0.358018
C	0.105805	-1.800506	-2.011013
C	2.050639	-1.345404	-3.384653
H	3.560927	-0.183150	-2.339625
C	-1.059930	-1.738312	0.528743
H	0.732386	-0.769924	1.192128
C	-1.201603	-2.298396	-1.811624
C	0.789351	-1.877389	-3.246410
C	-1.812745	-2.229077	-0.573422
H	-1.489648	-1.764601	1.522494
H	0.308920	-2.375483	-4.085818
N	1.972476	-0.563466	-1.109872
H	-1.745818	-2.703351	-2.661414
Pd	-4.339592	-0.771572	-0.295118
C	-3.227060	-2.587538	-0.441070
C	-3.974337	-2.564031	0.757655
H	-3.647769	-3.173829	-1.255459
H	-3.514952	-2.312206	1.709084
C	-5.213153	-3.373979	0.862729
O	-5.678909	-4.073108	-0.009444
O	-5.760487	-3.225793	2.078685
C	-7.008185	-3.902739	2.274302
C	-7.500377	-3.549733	3.656816
H	-6.849515	-4.979823	2.154020
H	-7.706579	-3.583040	1.494238
H	-8.456623	-4.046195	3.850668
H	-6.784720	-3.870234	4.420502
H	-7.646842	-2.469338	3.750736
C	-5.431873	1.425627	-1.127299
O	-5.906639	0.916344	-0.081876
O	-4.471966	0.869763	-1.755027
C	-5.974200	2.722489	-1.665917
H	-6.298244	2.579956	-2.701463
H	-6.809572	3.075585	-1.059398
H	-5.174552	3.469571	-1.674060
H	-5.327638	-1.540549	-1.161832
C	2.862345	-1.458225	-4.638849
H	3.765380	-2.050501	-4.449555
H	2.294277	-1.943393	-5.437143
H	3.182798	-0.473919	-4.998823

99

cis-T25_C6_TSI Eopt -2806.633599

Pd	-2.635373	0.579962	0.005785
C	-3.442572	2.656095	-1.751172
C	-4.629537	0.638510	-1.988988
C	-4.172222	3.245908	-2.774889
C	-5.393836	1.168150	-3.018627
H	-3.946217	4.271042	-3.047379
H	-6.139213	0.535303	-3.488210

N	-3.707415	1.400748	-1.401655
H	-5.746024	2.927477	-4.207588
C	-5.159990	2.488498	-3.405122
N	-3.832895	-0.983798	-0.457729
N	-1.774185	2.516730	-0.043959
C	-4.715236	-0.774509	-1.469116
C	-2.329003	3.310094	-0.982990
O	-5.507859	-1.570222	-1.953980
O	-2.007775	4.471340	-1.268157
C	-3.680835	-2.261303	0.088779
C	-4.060769	-2.511143	1.416290
C	-3.057219	-3.284705	-0.644282
C	-3.830238	-3.757796	2.000966
C	-2.831326	-4.536356	-0.067938
C	-3.222033	-4.755836	1.247377
H	-3.045870	-5.728381	1.698019
C	-0.757131	3.183544	0.754079
C	0.548916	3.505487	-0.026011
H	-1.157487	4.170084	1.036145
C	-0.440445	2.430733	2.029859
C	1.673110	3.969496	0.882439
H	0.280866	4.336712	-0.687232
H	-1.379206	2.159257	2.522098
H	0.092586	1.502083	1.793937
C	0.403267	3.286843	2.959204
C	1.623803	3.843598	2.275270
H	-0.209563	4.119456	3.336065
H	0.704881	2.706390	3.840402
C	2.721433	4.261078	3.036502
C	3.900874	4.927220	1.051003
C	1.011794	2.389697	-0.933595
C	3.852864	4.797038	2.438588
H	2.679080	4.155698	4.118897
H	4.781106	5.339905	0.566862
C	1.954967	1.442003	-0.536770
C	0.543793	2.315373	-2.246732
H	4.696877	5.107682	3.048095
N	2.429475	0.502817	-1.362950
H	2.367955	1.449045	0.466231
H	-0.183647	3.046355	-2.590212
C	1.999397	0.461666	-2.630768
H	2.443619	-0.299691	-3.262933
H	-4.124755	-3.959871	3.024035
H	-2.351581	-5.330512	-0.627462
O	-4.632812	-1.462626	2.063711
O	-2.681161	-2.945593	-1.900170
C	-5.077483	-1.679375	3.379124
H	-4.245546	-1.931167	4.053339
H	-5.532786	-0.741397	3.702306
H	-5.827153	-2.479417	3.426692
C	-2.026818	-3.924207	-2.671223
H	-1.815062	-3.455271	-3.633576
H	-1.084625	-4.240391	-2.203162
H	-2.665061	-4.802034	-2.831824
C	2.817568	4.516421	0.288627
H	2.855789	4.605258	-0.794925
C	1.044523	1.345490	-3.106011
H	0.716836	1.282385	-4.138391
C	-0.370907	-1.066074	0.981999
C	-1.739446	-0.325970	2.706558
C	-0.222384	-1.411567	-0.380064
C	0.669092	-1.354090	1.907447
C	-0.814199	-0.696495	3.707532
H	-2.684442	0.135748	2.975799
H	-1.065042	-1.275257	-1.051739
C	1.914883	-1.789125	1.397157
C	0.411865	-1.154908	3.282328
H	1.195170	-1.380981	4.002973
N	-1.513014	-0.454950	1.414418
H	2.740918	-1.929515	2.092182
Pd	3.792414	-0.946427	-0.758804
C	6.510186	-0.307916	-1.192149
O	7.543217	0.263537	-1.475063
O	5.316297	0.176475	-1.418443
N	5.240683	-2.243222	-0.349624
C	5.015377	-3.515616	-0.125845
C	6.164077	-4.475157	0.041991
H	6.900106	-4.093132	0.756065
H	6.678108	-4.619063	-0.915368
H	5.779927	-5.436004	0.384865
O	3.837289	-3.996075	-0.045339
C	6.567129	-1.685823	-0.518698
C	2.102854	-2.038913	0.046220
H	3.018118	-3.000064	-0.132440
H	7.206348	-2.326877	-1.137393
C	0.968585	-1.935107	-0.810874
H	1.072225	-2.220546	-1.854896
H	7.073738	-1.557762	0.448173
C	-1.169901	-0.514956	5.152500
H	-1.982509	-1.189740	5.447353
H	-0.312836	-0.722822	5.798749
H	-1.506596	0.508451	5.354479

107

cis-T25_C6_TSII Eopt -2944.272148

Pd	-3.000844	0.498334	0.021945
C	-3.767872	2.601330	-1.721220
C	-4.933314	0.581320	-2.031826
C	-4.468687	3.204312	-2.757476
C	-5.666768	1.123479	-3.077069
H	-4.241403	4.235780	-3.003643
H	-6.390506	0.493456	-3.582869
N	-4.036467	1.339152	-1.400915
H	-5.992209	2.900952	-4.246602
C	-5.429883	2.451951	-3.432774
N	-4.170906	-1.064451	-0.508359
N	-2.147403	2.443102	0.029756

C	-5.019550	-0.843430	-1.545725
C	-2.689406	3.252311	-0.902285
O	-5.781676	-1.639123	-2.077590
O	-2.389325	4.430215	-1.140741
C	-4.000702	-2.356883	-0.004634
C	-4.417942	-2.670196	1.297749
C	-3.318879	-3.330579	-0.753263
C	-4.170189	-3.932669	1.840544
C	-3.075285	-4.597659	-0.219511
C	-3.506247	-4.881635	1.070918
H	-3.318279	-5.866592	1.488805
C	-1.185594	3.112263	0.893406
C	0.129476	3.536493	0.181485
H	-1.640343	4.064655	1.210512
C	-0.883023	2.309911	2.141720
C	1.191633	4.009427	1.158563
H	-0.158118	4.391142	-0.439997
H	-1.826670	1.977803	2.583818
H	-0.304290	1.416581	1.880455
C	-0.111850	3.148918	3.146117
C	1.099597	3.805890	2.539846
H	-0.776610	3.927671	3.549473
H	0.190072	2.532008	4.002125
C	2.141856	4.243848	3.365029
C	3.347906	5.089688	1.466640
C	0.700754	2.513320	-0.775749
C	3.258884	4.879048	2.842402
H	2.066397	4.076289	4.437750
H	4.215563	5.585829	1.041051
C	1.664739	1.578239	-0.397124
C	0.333245	2.537404	-2.122882
H	4.058566	5.206470	3.501093
N	2.263901	0.759167	-1.268519
H	1.988450	1.496436	0.635833
H	-0.418388	3.251621	-2.450540
C	1.941946	0.823740	-2.569111
H	2.509261	0.169117	-3.226461
H	-4.493854	-4.184257	2.843649
H	-2.554256	-5.354794	-0.793486
O	-5.043024	-1.665696	1.964666
O	-2.907824	-2.928179	-1.979565
C	-5.517997	-1.944614	3.257540
H	-4.698153	-2.196892	3.946173
H	-6.010261	-1.033003	3.601244
H	-6.244451	-2.767260	3.253735
C	-2.190317	-3.850379	-2.762964
H	-1.956620	-3.334142	-3.695498
H	-1.256487	-4.154310	-2.270183
H	-2.790124	-4.741797	-2.985304
C	2.321193	4.656340	0.641211
H	2.390723	4.808776	-0.433726
C	0.961002	1.690527	-3.027887
H	0.713254	1.712066	-4.084310
C	-0.703324	-1.065971	0.998272
C	-2.153466	-0.499017	2.720562
C	-0.508222	-1.336956	-0.375051
C	0.348360	-1.299295	1.925794
C	-1.216824	-0.843385	3.720791
H	-3.132408	-0.113907	2.989036
H	-1.350924	-1.252252	-1.055266
C	1.642176	-1.581171	1.424881
C	0.049990	-1.183731	3.302852
H	0.836878	-1.373670	4.029841
N	-1.895010	-0.561842	1.429873
H	2.480657	-1.670968	2.113121
C	1.842353	-1.715992	0.066824
C	0.732613	-1.713648	-0.817150
H	0.889533	-1.917058	-1.873256
Pd	3.529317	-0.889369	-0.758070
C	3.350870	-3.133098	-0.317517
C	4.656326	-2.618047	-0.512088
H	3.119265	-3.525811	0.665661
H	2.852788	-3.617416	-1.152205
H	5.152450	-2.709668	-1.474305
C	5.491794	-2.388729	0.688192
O	5.076755	-2.407408	1.832690
O	6.757193	-2.130936	0.354268
C	7.620231	-1.745727	1.430149
C	8.923462	-1.295673	0.816105
H	7.751732	-2.599961	2.103568
H	7.135408	-0.946007	1.998902
H	9.619835	-0.983325	1.601061
H	9.387077	-2.105964	0.244947
H	8.754682	-0.449751	0.142741
C	5.309727	-0.160017	-2.771843
O	4.547615	-0.883348	-3.426189
O	5.177466	0.111940	-1.517922
C	6.518924	0.490564	-3.415451
H	7.430592	0.140030	-2.920381
H	6.561028	0.250385	-4.479144
H	6.474498	1.575738	-3.279008
C	-1.607981	-0.756336	5.165497
H	-2.356007	-1.517557	5.418238
H	-0.744065	-0.908174	5.818250
H	-2.044722	0.220779	5.402073

107

cis-T25_C6_TSIIIEopt -2944.278533

Pd	-2.930591	0.200781	-0.274947
C	-3.648925	1.926453	-2.408546
C	-4.342944	-0.306186	-2.664153
C	-4.237124	2.282942	-3.615068
C	-4.941869	-0.018931	-3.881910
H	-4.168625	3.316109	-3.937664
H	-5.429044	-0.823616	-4.421998
N	-3.727770	0.666796	-1.992405
H	-5.352338	1.546105	-5.301540

C	-4.886967	1.293490	-4.353012
N	-3.702763	-1.598675	-0.784889
N	-2.346769	2.248096	-0.427811
C	-4.292941	-1.661720	-2.007465
C	-2.884772	2.852914	-1.505869
O	-4.752229	-2.645931	-2.569888
O	-2.782923	4.042984	-1.834417
C	-3.413873	-2.777773	-0.091048
C	-4.089767	-3.087659	1.098518
C	-2.372262	-3.617389	-0.520968
C	-3.739764	-4.216678	1.842314
C	-2.022759	-4.751982	0.213779
C	-2.713468	-5.036434	1.385741
H	-2.444146	-5.918598	1.959598
C	-1.583848	3.144319	0.432092
C	-0.338127	3.779894	-0.254867
H	-2.228155	4.003812	0.679340
C	-1.170076	2.476556	1.728193
C	0.514310	4.563068	0.725213
H	-0.746479	4.484121	-0.986239
H	-2.036496	1.979503	2.168698
H	-0.418689	1.704784	1.518758
C	-0.622539	3.495578	2.714548
C	0.415161	4.404583	2.111599
H	-1.454915	4.110473	3.089134
H	-0.206173	2.984478	3.591999
C	1.275787	5.129230	2.944260
C	2.312660	6.167536	1.040826
C	0.504614	2.799233	-1.039697
C	2.219154	6.002518	2.422590
H	1.197345	4.997610	4.021804
H	3.045086	6.848695	0.616951
C	1.621101	2.168930	-0.492962
C	0.211063	2.527124	-2.378045
H	2.881007	6.551108	3.087012
N	2.403189	1.323739	-1.183141
H	1.915831	2.361473	0.532741
H	-0.635608	3.022142	-2.846295
C	2.111585	1.073469	-2.468485
H	2.778828	0.375169	-2.965387
H	-4.260195	-4.466515	2.759355
H	-1.222728	-5.405204	-0.113759
O	-5.062636	-2.212053	1.458970
O	-1.740790	-3.215880	-1.649725
C	-5.798073	-2.504437	2.620256
H	-5.157513	-2.517361	3.514121
H	-6.538008	-1.707895	2.717780
H	-6.315265	-3.469075	2.540082
C	-0.668625	-4.001293	-2.114500
H	-0.302009	-3.505868	-3.014761
H	0.140658	-4.054603	-1.373487
H	-0.995938	-5.017236	-2.367984
C	1.465598	5.451285	0.208314
H	1.540512	5.567217	-0.870863
C	1.022626	1.659974	-3.097148
H	0.823778	1.439311	-4.141123
C	-0.919560	-0.889934	1.636893
C	-2.906864	-0.278368	2.665650
C	-0.221869	-1.235576	0.457006
C	-0.251900	-0.930816	2.888529
C	-2.365806	-0.426728	3.960823
H	-3.935274	0.041244	2.529250
C	1.122601	-1.465903	0.512843
H	-0.767195	-1.297479	-0.480281
C	1.156665	-1.091604	2.896906
C	-1.018503	-0.703657	4.051111
C	1.850096	-1.287790	1.724732
H	1.662552	-1.696673	-0.401284
H	-0.531887	-0.744365	5.023402
N	-2.210102	-0.467700	1.560494
H	1.690439	-0.982478	3.838205
Pd	3.711419	-0.093981	-0.245803
C	3.324483	-1.123839	1.690097
C	4.204263	-1.828385	0.824337
H	3.398588	0.474501	1.205391
H	3.786586	-0.758477	2.608078
H	3.849232	-2.630288	0.182235
C	5.650572	-1.806741	1.150044
O	6.141345	-1.140450	2.037319
O	6.333886	-2.603193	0.327007
C	7.758013	-2.433206	0.361335
C	8.332607	-3.255170	-0.765508
H	8.130417	-2.750567	1.341195
H	7.971223	-1.368659	0.233863
H	9.424132	-3.169446	-0.770150
H	8.069333	-4.312613	-0.659425
H	7.953790	-2.891708	-1.725008
C	5.491364	-0.788113	-2.269582
O	6.243923	-0.227275	-1.472581
O	4.211910	-0.917408	-2.104475
C	6.016623	-1.414576	-3.546488
H	5.393596	-1.130831	-4.399920
H	7.051071	-1.112932	-3.721050
H	5.968048	-2.505781	-3.457465
C	-3.239815	-0.225745	5.162303
H	-3.920395	-1.074817	5.299876
H	-2.643236	-0.127698	6.073392
H	-3.857644	0.673182	5.061345

99

cis-T25_C7_IN2 Eopt -2806.672827

Pd	-2.365446	-0.367882	-0.179026
C	-3.784484	0.927341	-2.267339
C	-3.373811	-1.362132	-2.620464
C	-4.480467	1.022155	-3.464975
C	-4.052802	-1.333993	-3.830281
H	-4.887197	1.985599	-3.752501

H	-4.114888	-2.248052	-4.410944
N	-3.269041	-0.243861	-1.903697
H	-5.153619	-0.078043	-5.187869
C	-4.614474	-0.126337	-4.245974
N	-2.170253	-2.291417	-0.796837
N	-2.789628	1.698527	-0.240680
C	-2.655470	-2.553527	-2.041000
C	-3.474491	2.068868	-1.340762
O	-2.551910	-3.588544	-2.684335
O	-3.796464	3.217125	-1.674610
C	-1.183037	-3.123039	-0.260385
C	-1.400629	-3.826963	0.933002
C	0.094388	-3.158607	-0.848942
C	-0.362431	-4.543538	1.535221
C	1.126930	-3.894730	-0.266191
C	0.886353	-4.570480	0.925329
H	1.694270	-5.129805	1.388085
C	-0.220458	-0.668937	1.947621
C	-2.391229	-0.981760	2.708236
C	0.657632	-0.443555	0.872642
C	0.284957	-0.762609	3.271825
C	-1.976136	-1.152669	4.048490
H	-3.445398	-1.030851	2.451655
C	2.005608	-0.207998	1.074201
H	0.224156	-0.429831	-0.124190
C	1.670836	-0.555458	3.472337
C	-0.630810	-1.021886	4.313010
H	-0.263350	-1.106433	5.333961
N	-1.564482	-0.735969	1.712034
H	2.067490	-0.610499	4.483533
Pd	3.140479	0.279865	-0.495243
C	5.569505	0.461869	-1.995238
O	6.461934	0.674809	-2.794847
O	4.314294	0.741745	-2.140036
N	4.789167	-0.823826	-0.031358
C	4.862102	-2.011723	0.452232
C	6.116635	-2.818977	0.576199
H	5.909130	-3.717326	1.158590
H	6.909101	-2.244201	1.062628
H	6.478001	-3.117421	-0.413940
O	3.792716	-2.656705	0.891264
C	5.944964	-0.171820	-0.634675
H	6.785166	-0.853084	-0.786517
C	-2.329287	2.812398	0.569617
C	-1.250583	3.673474	-0.162683
H	-3.180195	3.493088	0.724707
C	-1.836769	2.362046	1.930571
C	-0.466642	4.579275	0.770054
H	-1.816273	4.306979	-0.854142
H	-2.595297	1.722159	2.392554
H	-0.928673	1.760238	1.817620
C	-1.547722	3.562829	2.814970
C	-0.591215	4.525382	2.163169
H	-2.491180	4.083266	3.039067
H	-1.141637	3.235876	3.780007
C	0.181077	5.387045	2.950024
C	1.183222	6.351471	0.990417
C	-0.324256	2.843056	-1.023202
C	1.061407	6.294424	2.378287
H	0.084844	5.334316	4.032727
H	1.868776	7.055018	0.526485
C	0.795967	2.205534	-0.497376
C	-0.569885	2.678858	-2.387434
H	1.653994	6.951365	3.009062
N	1.613043	1.442214	-1.238247
H	1.050692	2.301261	0.550963
H	-1.445909	3.148645	-2.827617
C	1.394629	1.324694	-2.557195
H	2.134072	0.755168	-3.108713
C	2.496033	-0.264600	2.411114
H	3.552544	-0.085368	2.595196
H	-0.520222	-5.084084	2.460901
H	2.109954	-3.935374	-0.719097
O	-2.654222	-3.736793	1.443811
O	0.236088	-2.402027	-1.960643
C	-2.921440	-4.446463	2.626700
H	-2.296645	-4.094467	3.459590
H	-3.972330	-4.260899	2.858154
H	-2.768355	-5.525440	2.495136
C	1.482833	-2.423723	-2.616114
H	1.366994	-1.794997	-3.499889
H	2.277496	-2.005117	-1.982658
H	1.753713	-3.440049	-2.927963
C	0.424229	5.498881	0.202233
H	0.522178	5.534572	-0.880733
C	0.303750	1.927012	-3.163437
H	0.147966	1.804216	-4.230050
H	6.278727	0.640042	0.024533
H	2.996263	-2.090356	0.780717
C	-2.998459	-1.419446	5.113501
H	-2.525625	-1.535927	6.092626
H	-3.721789	-0.598686	5.185031
H	-3.565983	-2.333071	4.902309

107

cis-T25_C7_IN3 Eopt -2944.298882

Pd	-2.704923	0.208414	0.116160
C	-4.079264	1.725149	-1.849083
C	-4.338261	-0.606847	-2.033076
C	-4.928250	1.938803	-2.926743
C	-5.191071	-0.462158	-3.118413
H	-5.119994	2.958990	-3.241064
H	-5.589442	-1.355662	-3.586948
N	-3.821979	0.479192	-1.459553
H	-6.154498	0.968522	-4.405661
C	-5.487593	0.827810	-3.559672
N	-3.123761	-1.726573	-0.325087

N	-2.587439	2.310206	-0.080278
C	-3.864268	-1.914758	-1.451668
C	-3.328254	2.790233	-1.098858
O	-4.145450	-2.971868	-1.998937
O	-3.385545	3.959906	-1.501611
C	-2.289290	-2.756498	0.122407
C	-2.445498	-3.318101	1.397809
C	-1.199268	-3.158101	-0.671826
C	-1.522317	-4.249855	1.879803
C	-0.286497	-4.104715	-0.203001
C	-0.456792	-4.632203	1.071581
H	0.255926	-5.362245	1.445246
C	-0.450451	-0.548110	2.034547
C	-2.533926	-0.194547	3.001718
C	0.342880	-0.640276	0.873860
C	0.138504	-0.697821	3.318535
C	-2.047792	-0.391278	4.313128
H	-3.582456	0.035646	2.837292
C	1.714929	-0.776209	0.959149
H	-0.174793	-0.575066	-0.078550
C	1.537941	-0.875243	3.388160
C	-0.698490	-0.626028	4.451277
H	-0.261315	-0.748240	5.440487
N	-1.778988	-0.250375	1.922178
H	2.007700	-0.984415	4.362928
C	-1.712632	3.294314	0.530896
C	-0.563534	3.745384	-0.428813
H	-2.301479	4.204863	0.718203
C	-1.146707	2.812621	1.852164
C	0.546204	4.495756	0.281977
H	-1.038914	4.428577	-1.141329
H	-1.962669	2.441699	2.480451
H	-0.464479	1.973097	1.679010
C	-0.408231	3.938405	2.556396
C	0.636500	4.573035	1.676759
H	-1.131737	4.706934	2.867901
H	0.060056	3.568552	3.476749
C	1.709593	5.263468	2.251513
C	2.586944	5.801308	0.079432
C	-0.025711	2.589927	-1.239216
C	2.678987	5.874444	1.468942
H	1.778238	5.314252	3.336387
H	3.337616	6.274234	-0.547576
C	1.008060	1.779422	-0.780591
C	-0.600151	2.258189	-2.468615
H	3.504909	6.402659	1.937515
N	1.432348	0.699090	-1.452381
H	1.505291	1.987983	0.159481
H	-1.404192	2.876064	-2.860086
C	0.871038	0.380870	-2.628034
H	1.249845	-0.511157	-3.115362
C	2.302940	-0.890218	2.246001
H	3.373873	-1.020055	2.348533
H	-1.630621	-4.684401	2.866415
H	0.552824	-4.413242	-0.815620
O	-3.525057	-2.887777	2.099618
O	-1.100887	-2.535567	-1.865489
C	-3.738226	-3.456387	3.366388
H	-2.912182	-3.231568	4.055523
H	-4.658678	-3.008084	3.746457
H	-3.868751	-4.544637	3.305061
C	-0.210520	-3.078380	-2.820667
H	-0.420944	-2.553083	-3.754023
H	0.837873	-2.908172	-2.555997
H	-0.397602	-4.149587	-2.963233
C	1.528716	5.116278	-0.499550
H	1.455938	5.048841	-1.583085
C	-0.149423	1.147781	-3.168496
H	-0.588813	0.861921	-4.118333
Pd	2.802555	-0.699825	-0.727852
C	3.387653	-2.776560	-0.209511
C	4.537708	-2.029796	-0.328190
H	3.008190	-3.061678	0.766882
H	2.969922	-3.251742	-1.092782
H	5.013475	-1.893906	-1.293362
C	5.359740	-1.614393	0.838199
O	5.204770	-1.984638	1.983297
O	6.326904	-0.780836	0.448242
C	7.186029	-0.296542	1.489630
C	8.176548	0.646962	0.853104
H	7.674179	-1.152012	1.968447
H	6.571048	0.199561	2.247883
H	8.853740	1.045280	1.615397
H	8.773923	0.131449	0.095121
H	7.660878	1.485040	0.374666
C	3.629140	-1.239314	-3.453293
O	2.849346	-2.196805	-3.337444
O	3.885480	-0.380785	-2.530126
C	4.343667	-0.982723	-4.765858
H	5.400736	-0.764057	-4.590230
H	4.237575	-1.839862	-5.433201
H	3.907395	-0.098479	-5.244283
C	-2.990001	-0.302441	5.476921
H	-2.461801	-0.451826	6.422760
H	-3.482840	0.675940	5.517432
H	-3.779605	-1.059772	5.409054

107

cis-T25_C7_IN4 Eopt -2944.343260

Pd	-2.224337	0.681531	-0.329655
C	-2.914361	2.120525	-2.674739
C	-3.436107	-0.168525	-2.742714
C	-3.466573	2.320023	-3.932827
C	-3.997070	-0.040261	-4.005784
H	-3.451515	3.320821	-4.350563
H	-4.412750	-0.924127	-4.477448
N	-2.908650	0.899007	-2.147060

H	-4.444467	1.349950	-5.587103
C	-4.008021	1.221201	-4.600621
N	-2.890757	-1.219460	-0.689142
N	-1.750810	2.709096	-0.674979
C	-3.388958	-1.435803	-1.935389
C	-2.216213	3.167273	-1.855884
O	-3.801208	-2.486280	-2.411552
O	-2.048691	4.292050	-2.344261
C	-2.736296	-2.322980	0.154915
C	-3.466339	-2.410431	1.351029
C	-1.824172	-3.345133	-0.160566
C	-3.270973	-3.480320	2.226889
C	-1.660641	-4.440306	0.689450
C	-2.375143	-4.485594	1.880218
H	-2.234956	-5.327009	2.552782
C	-0.820986	3.620794	-0.026034
C	0.488548	3.788800	-0.861176
H	-1.280633	4.620000	-0.004355
C	-0.505528	3.216186	1.400197
C	1.617156	4.442685	-0.089091
H	0.216650	4.442739	-1.696474
H	-1.441214	3.084644	1.950248
H	0.010152	2.247567	1.414124
C	0.339820	4.279076	2.084446
C	1.566362	4.647787	1.293598
H	-0.273518	5.180648	2.234205
H	0.633529	3.941298	3.085690
C	2.668135	5.221800	1.937342
C	3.851920	5.394083	-0.147416
C	0.922375	2.475114	-1.463311
C	3.803395	5.593438	1.231769
H	2.626962	5.370703	3.014487
H	4.735090	5.676912	-0.713119
C	1.703719	1.573306	-0.750032
C	0.518006	2.095010	-2.744654
H	4.650478	6.030522	1.753093
N	2.029804	0.361842	-1.224436
H	2.105993	1.826290	0.225904
H	-0.072994	2.785084	-3.341153
C	1.615781	-0.010739	-2.443869
H	1.912446	-1.003053	-2.766246
H	-3.821464	-3.547792	3.157696
H	-0.974194	-5.240784	0.438800
O	-4.349298	-1.403322	1.571305
O	-1.117118	-3.161644	-1.300092
C	-5.129644	-1.469754	2.738011
H	-4.508573	-1.432550	3.643289
H	-5.782309	-0.594631	2.712877
H	-5.746903	-2.377268	2.760341
C	-0.448659	-4.277485	-1.843675
H	0.357465	-4.634581	-1.189954
H	-1.151971	-5.096117	-2.037133
H	-0.008390	-3.935901	-2.781231
C	2.765643	4.823054	-0.793494
H	2.801924	4.653932	-1.867727
C	0.865632	0.844323	-3.237473
H	0.558822	0.524305	-4.227920
Pd	3.198209	-0.760231	0.004242
C	5.137645	-0.445767	1.538446
O	4.751282	0.574780	0.908313
O	4.536346	-1.564294	1.375408
C	6.320246	-0.388938	2.459685
H	7.215407	-0.695262	1.906742
H	6.468464	0.630117	2.822429
H	6.186752	-1.081710	3.293878
C	-0.920876	-0.437429	2.237787
N	-1.849412	0.410061	1.700975
C	-2.706848	1.028561	2.493003
C	-2.715904	0.912789	3.897452
C	-1.775120	0.079094	4.459230
C	-0.865190	-0.626010	3.647934
C	0.088949	-1.531044	4.169839
C	0.844964	-2.066128	1.918790
C	-0.043163	-1.149445	1.396812
H	-0.124664	-0.984478	0.326971
C	1.700252	-2.952076	1.057543
C	2.028742	-2.394998	-0.308322
C	2.867884	-3.313727	-1.112795
O	3.524898	-4.240941	-0.690288
O	2.818752	-2.995996	-2.437850
C	3.745826	-3.692894	-3.276532
C	5.119946	-3.060516	-3.203992
H	5.806678	-3.564853	-3.892607
H	5.521936	-3.146165	-2.190465
H	5.073506	-2.000428	-3.473913
H	3.320597	-3.620868	-4.281222
H	3.778646	-4.742530	-2.972061
H	1.145762	-2.093981	-0.876188
H	1.166990	-3.912852	0.951859
H	0.148559	-1.667623	5.246511
H	-1.733312	-0.053622	5.538677
H	-3.433320	1.666307	1.996743
C	0.908691	-2.232611	3.327091
H	1.629062	-2.938595	3.731774
H	2.633593	-3.189548	1.578684
C	-3.723948	1.678734	4.701645
H	-3.615287	1.470591	5.769694
H	-3.611585	2.759608	4.556822
H	-4.747914	1.417385	4.409807

107

cis-T25_C7_IN5 Eopt -2944.309232

Pd	-1.139641	-1.974708	0.298503
C	-0.930529	-3.382470	2.743166
C	-2.890993	-2.105585	2.519258
C	-1.346967	-3.869493	3.974992
C	-3.361887	-2.546176	3.748086

H	-0.697756	-4.558559	4.504217
H	-4.323284	-2.183014	4.094738
N	-1.703605	-2.523143	2.084470
H	-2.923418	-3.803958	5.438907
C	-2.575969	-3.439897	4.476153
N	-2.968374	-1.046575	0.399176
N	0.552402	-3.053194	0.899717
C	-3.601662	-1.156421	1.596200
C	0.398332	-3.657906	2.098138
O	-4.633674	-0.600485	1.959441
O	1.239552	-4.309740	2.726569
C	-3.392582	-0.040224	-0.471566
C	-3.819683	-0.347059	-1.776714
C	-3.329159	1.305614	-0.083467
C	-4.155220	0.673627	-2.666609
C	-3.690748	2.327342	-0.959874
C	-4.091997	2.000691	-2.247901
H	-4.357709	2.790496	-2.944531
C	1.934008	-3.004908	0.439231
C	2.800490	-2.134112	1.394612
H	2.353014	-4.019805	0.503589
C	2.064670	-2.518899	-0.991318
C	4.192244	-1.885711	0.853270
H	2.897524	-2.719818	2.314821
H	1.428458	-3.128035	-1.640215
H	1.704803	-1.487550	-1.072651
C	3.504938	-2.603433	-1.479613
C	4.519913	-2.095368	-0.489300
H	3.745895	-3.649914	-1.719088
H	3.604833	-2.037554	-2.413270
C	5.832997	-1.857971	-0.911019
C	6.476633	-1.196731	1.309426
C	2.096999	-0.851244	1.763505
C	6.807930	-1.418795	-0.027531
H	6.083650	-2.018055	-1.957656
H	7.227969	-0.847030	2.012033
C	2.099424	0.249798	0.909200
C	1.383464	-0.733812	2.956031
H	7.820104	-1.238174	-0.379225
N	1.428488	1.377782	1.172381
H	2.645347	0.240856	-0.029219
H	1.366612	-1.568543	3.652998
C	0.739944	1.477852	2.317202
H	0.215294	2.413404	2.487200
H	-4.474071	0.446462	-3.677089
H	-3.623099	3.364510	-0.648036
O	-3.870923	-1.667305	-2.079990
O	-2.808177	1.555601	1.153008
C	-4.328831	-2.021114	-3.361402
H	-3.672163	-1.627825	-4.148624
H	-4.314993	-3.112242	-3.394461
H	-5.353961	-1.668738	-3.534876
C	-3.573947	2.404039	1.990897
H	-3.629305	3.426371	1.598046
H	-4.576467	1.987142	2.123941
H	-3.052109	2.427971	2.949554
C	5.177753	-1.429742	1.736755
H	4.909844	-1.260608	2.777742
C	0.699307	0.442749	3.239455
H	0.136482	0.559840	4.160033
Pd	1.615926	3.014787	-0.293695
H	1.897074	4.207564	-1.220677
C	4.035712	1.900402	-1.189958
O	3.654275	2.797964	-0.338750
O	3.282676	1.181738	-1.855442
C	5.540701	1.757375	-1.275212
H	5.901993	1.261271	-0.368382
H	5.812489	1.147104	-2.138067
H	6.016588	2.740064	-1.333225
C	-0.608288	-0.465016	-2.348271
N	-0.814996	-1.668754	-1.734486
C	-0.940194	-2.760823	-2.463976
C	-0.850199	-2.789932	-3.871980
C	-0.628099	-1.590273	-4.507926
C	-0.508989	-0.397249	-3.767178
C	-0.298779	0.862661	-4.374279
C	-0.315083	1.929404	-2.193718
C	-0.498875	0.704934	-1.578617
H	-0.558287	0.613619	-0.498646
C	-0.217225	3.187148	-1.445521
C	-0.501964	3.343311	-0.091670
C	-0.709791	4.699606	0.461205
O	-0.700653	5.738659	-0.158919
O	-0.928466	4.623275	1.788990
C	-1.103380	5.878080	2.457456
C	-1.334003	5.579315	3.918918
H	-1.474306	6.511897	4.474524
H	-0.477184	5.049675	4.347327
H	-2.226909	4.960511	4.054305
H	-1.949564	6.405255	2.004580
H	-0.209911	6.490232	2.296739
H	-0.902584	2.526869	0.500499
H	-0.168689	4.093700	-2.043380
H	-0.209533	0.916722	-5.455682
H	-0.544771	-1.549372	-5.592089
H	-1.112604	-3.681132	-1.912725
C	-0.207464	1.991435	-3.607626
H	-0.040917	2.957700	-4.074951
C	-0.997535	-4.092865	-4.598599
H	-0.906804	-3.953727	-5.679284
H	-0.230720	-4.810903	-4.285649
H	-1.972735	-4.551727	-4.397192

99

cis-T25_C7_TSI Eopt -2806.642501

Pd	-2.339424	-0.141181	-0.286027
C	-3.504685	1.152959	-2.524323

C	-3.298408	-1.182842	-2.725912
C	-4.102556	1.242342	-3.774216
C	-3.886573	-1.161837	-3.982561
H	-4.392023	2.220964	-4.141362
H	-4.004479	-2.099758	-4.514521
N	-3.133295	-0.038649	-2.063796
H	-4.759122	0.110714	-5.482975
C	-4.293950	0.067326	-4.502213
N	-2.338816	-2.110947	-0.766584
N	-2.578664	1.948115	-0.471710
C	-2.780502	-2.408744	-2.017034
C	-3.149273	2.313245	-1.637839
O	-2.798303	-3.499545	-2.570165
O	-3.333400	3.464860	-2.053488
C	-1.637743	-3.068274	-0.027767
C	-2.148376	-3.539233	1.191481
C	-0.351772	-3.471615	-0.430071
C	-1.393509	-4.397958	1.992641
C	0.404468	-4.337196	0.362212
C	-0.127523	-4.785404	1.564558
H	0.464067	-5.447835	2.189945
C	-0.307124	-0.566058	1.930503
C	-2.508382	-0.331543	2.632847
C	0.610425	-0.798462	0.887627
C	0.153248	-0.487006	3.273312
C	-2.150500	-0.315654	4.000839
H	-3.549840	-0.238349	2.339640
C	1.969759	-0.882794	1.142032
H	0.222425	-0.922311	-0.119696
C	1.546633	-0.545800	3.522265
C	-0.808507	-0.360034	4.299334
H	-0.474268	-0.306255	5.333358
N	-1.637372	-0.417280	1.649714
H	1.899139	-0.462052	4.547171
H	2.650389	-1.841343	0.609188
Pd	3.247851	-0.108752	-0.426887
C	5.773810	0.336057	-1.610963
O	6.687329	0.767084	-2.282939
O	4.522485	0.700344	-1.748908
N	4.818485	-1.250967	-0.003365
C	4.637903	-2.514702	0.310505
C	5.802524	-3.469058	0.378461
H	5.481840	-4.380128	0.884441
H	6.654445	-3.032089	0.906911
H	6.134294	-3.729220	-0.633535
O	3.479674	-2.975147	0.566421
C	6.056096	-0.688051	-0.498270
H	6.731343	-1.448249	-0.903452
C	-2.066208	3.067018	0.300736
C	-0.824414	3.732002	-0.378257
H	-2.840763	3.847886	0.311154
C	-1.772341	2.691956	1.739200
C	0.026453	4.560321	0.568481
H	-1.244035	4.408152	-1.131362
H	-2.655838	2.206223	2.165670
H	-0.947403	1.972052	1.781684
C	-1.407094	3.926469	2.545301
C	-0.238936	4.656197	1.939401
H	-2.277012	4.598720	2.594132
H	-1.173361	3.650155	3.580736
C	0.596093	5.439246	2.743513
C	1.941179	6.033130	0.843060
C	0.012347	2.734499	-1.145657
C	1.677384	6.125229	2.208972
H	0.387916	5.501777	3.809819
H	2.785418	6.560803	0.408559
C	1.002396	1.965785	-0.538603
C	-0.194313	2.547665	-2.513601
H	2.315931	6.724156	2.852429
N	1.739887	1.074917	-1.213989
H	1.226054	2.070265	0.517619
H	-0.966695	3.125596	-3.014487
C	1.545943	0.914212	-2.530641
H	2.205134	0.212485	-3.028352
C	2.423644	-0.726100	2.485332
H	3.489816	-0.799803	2.681314
H	-1.779605	-4.768674	2.934859
H	1.412868	-4.613667	0.080116
O	-3.385767	-3.084329	1.520546
O	0.090898	-2.908100	-1.577847
C	-3.931975	-3.527243	2.736171
H	-3.314495	-3.220416	3.592977
H	-4.916659	-3.061401	2.812647
H	-4.049333	-4.618518	2.755613
C	1.321338	-3.361934	-2.102077
H	1.463486	-2.816082	-3.036434
H	2.154679	-3.151879	-1.421673
H	1.284040	-4.437953	-2.312930
C	1.119932	5.256801	0.038309
H	1.328807	5.177381	-1.026292
C	0.577145	1.630488	-3.213993
H	0.442670	1.474476	-4.279052
H	6.595184	-0.160853	0.301357
C	-3.221565	-0.205089	5.043707
H	-3.916983	-1.050676	4.988270
H	-2.793430	-0.185755	6.049447
H	-3.812109	0.708849	4.909473

107

cis-T25_C7_TSII Eopt -2944.282757

Pd	-2.607653	-0.421970	-0.155828
C	-3.977312	0.328110	-2.527570
C	-3.572346	-1.976255	-2.307674
C	-4.644781	0.130747	-3.728991
C	-4.225862	-2.242680	-3.502250
H	-5.040685	0.996976	-4.247778
H	-4.287400	-3.271864	-3.839122

N	-3.470171	-0.718404	-1.881776
H	-5.284592	-1.352478	-5.151380
C	-4.767219	-1.171667	-4.213429
N	-2.421317	-2.441784	-0.283796
N	-3.059262	1.576846	-0.710677
C	-2.908916	-2.999059	-1.426851
C	-3.699095	1.660336	-1.895076
O	-2.854978	-4.171485	-1.771243
O	-4.005138	2.689467	-2.511793
C	-1.542457	-3.196935	0.496773
C	-1.840015	-3.499769	1.833148
C	-0.298741	-3.592645	-0.034192
C	-0.920949	-4.194437	2.625588
C	0.603760	-4.324954	0.741501
C	0.280822	-4.610826	2.064648
H	0.983440	-5.173360	2.673141
C	-0.579481	-0.062562	2.098952
C	-2.816213	0.006537	2.717056
C	0.410735	-0.503332	1.200153
C	-0.204956	0.563404	3.321056
C	-2.526988	0.507346	4.005409
H	-3.845705	-0.168409	2.417876
C	1.743393	-0.232171	1.450312
H	0.100700	-1.045103	0.311855
C	1.159840	0.887525	3.524806
C	-1.214790	0.833373	4.267274
H	-0.942280	1.295505	5.213992
N	-1.902320	-0.226127	1.795909
H	1.445510	1.410783	4.433888
C	-2.636844	2.871595	-0.200353
C	-1.465270	3.483630	-1.036972
H	-3.477485	3.568012	-0.333915
C	-2.299364	2.837495	1.275072
C	-0.709057	4.584307	-0.315191
H	-1.950585	3.929411	-1.912695
H	-3.129683	2.375965	1.817961
H	-1.408345	2.224357	1.444233
C	-2.048328	4.241811	1.796020
C	-0.971584	4.942242	1.012195
H	-2.981198	4.822859	1.738356
H	-1.771555	4.209226	2.857101
C	-0.222400	5.964279	1.605110
C	1.029499	6.280933	-0.420913
C	-0.533385	2.423944	-1.576373
C	0.769911	6.633246	0.902923
H	-0.427034	6.230469	2.640309
H	1.804167	6.793008	-0.984746
C	0.553370	1.937081	-0.853160
C	-0.759720	1.871006	-2.838410
H	1.342551	7.421331	1.384176
N	1.358168	0.973016	-1.315580
H	0.795524	2.334878	0.127787
H	-1.597316	2.231299	-3.430472
C	1.125853	0.438160	-2.523619
H	1.806181	-0.349805	-2.835069
C	2.105708	0.522055	2.604267
H	3.159573	0.725196	2.778214
H	-1.142645	-4.433335	3.658956
H	1.543615	-4.668109	0.323047
O	-3.050583	-3.073776	2.272996
O	-0.055724	-3.170769	-1.291242
C	-3.363395	-3.295058	3.624555
H	-2.648711	-2.793013	4.292211
H	-4.358984	-2.872740	3.776476
H	-3.390104	-4.365393	3.866873
C	1.149484	-3.568483	-1.914733
H	1.105072	-3.175083	-2.929888
H	2.027843	-3.132604	-1.427018
H	1.232636	-4.661385	-1.948938
C	0.294074	5.266104	-1.015680
H	0.500104	4.982517	-2.045503
C	0.070875	0.866694	-3.314909
H	-0.091130	0.413488	-4.287488
Pd	2.913408	-0.042261	-0.267072
C	3.011330	-1.719638	1.320730
C	4.177866	-1.464742	0.532503
H	3.143063	-1.652826	2.396634
H	2.340873	-2.514516	1.006268
H	4.381279	-2.069426	-0.348451
C	5.320777	-0.779398	1.166659
O	5.292013	-0.227478	2.252477
O	6.399869	-0.814715	0.378948
C	7.526113	-0.054607	0.828647
C	8.536335	-0.048363	-0.292973
H	7.923517	-0.513099	1.741032
H	7.189799	0.955144	1.084482
H	9.423518	0.520467	0.003661
H	8.847100	-1.067176	-0.544597
H	8.109617	0.415134	-1.187908
C	4.376756	-0.601682	-2.643911
O	3.705395	-1.641986	-2.656520
O	4.228578	0.369678	-1.810214
C	5.498855	-0.389496	-3.641013
H	5.520990	0.647016	-3.987632
H	6.451974	-0.590685	-3.138254
H	5.394133	-1.074127	-4.484803
C	-3.639946	0.722167	4.986187
H	-4.095229	-0.230612	5.282038
H	-3.278136	1.216091	5.892062
H	-4.435482	1.342082	4.556779

107

cis-T25_C7_TSIIIEopt -2944.297196

Pd	-2.463868	0.155078	0.050954
C	-3.966821	1.891652	-1.595878
C	-3.932103	-0.345301	-2.317244
C	-4.841676	2.243045	-2.614890

C	-4.797509	-0.058859	-3.364121
H	-5.165639	3.275816	-2.684837
H	-5.091830	-0.865909	-4.026339
N	-3.541101	0.633444	-1.504509
H	-5.934215	1.501962	-4.315219
C	-5.252745	1.251840	-3.506961
N	-2.680774	-1.696064	-0.819907
N	-2.508304	2.237694	0.261888
C	-3.371725	-1.701950	-1.991970
C	-3.333221	2.843618	-0.619525
O	-3.576193	-2.648251	-2.742162
O	-3.521453	4.056619	-0.764125
C	-1.953685	-2.843280	-0.490086
C	-2.236435	-3.557715	0.685484
C	-0.884298	-3.270683	-1.299988
C	-1.462751	-4.661127	1.053531
C	-0.132878	-4.395842	-0.955624
C	-0.424593	-5.069860	0.224893
H	0.167565	-5.937204	0.502641
C	-1.552346	3.134020	0.901495
C	-0.624863	3.800922	-0.161323
H	-2.104630	3.960524	1.372208
C	-0.731607	2.429076	1.965587
C	0.548627	4.533184	0.454620
H	-1.250920	4.532510	-0.682089
H	-1.406556	1.968164	2.692489
H	-0.154312	1.614495	1.514034
C	0.206878	3.385693	2.688374
C	0.954929	4.319672	1.774622
H	-0.370328	3.988677	3.405317
H	0.930525	2.807499	3.274252
C	2.066152	5.016695	2.262144
C	2.360961	6.121178	0.146502
C	-0.167249	2.797109	-1.191583
C	2.764767	5.911903	1.465543
H	2.386393	4.839409	3.286599
H	2.900236	6.816548	-0.490782
C	0.877027	1.919222	-0.913622
C	-0.798163	2.668284	-2.428370
H	3.627056	6.438613	1.865463
N	1.241652	0.938157	-1.749909
H	1.439102	1.978641	0.014091
H	-1.606650	3.346866	-2.689247
C	0.608904	0.797610	-2.921293
H	0.933879	-0.023916	-3.548540
H	-1.670684	-5.208617	1.964989
H	0.676956	-4.739106	-1.589784
O	-3.282673	-3.093056	1.412022
O	-0.631825	-2.501886	-2.384697
C	-3.643811	-3.812963	2.564431
H	-2.835575	-3.821797	3.307305
H	-4.508477	-3.294530	2.983209
H	-3.924704	-4.846218	2.322230

C	0.239689	-3.020002	-3.363619
H	1.277034	-3.068366	-3.004913
H	-0.082760	-4.014831	-3.693084
H	0.187205	-2.329480	-4.207191
C	1.262737	5.432252	-0.346509
H	0.943370	5.584611	-1.375566
C	-0.404773	1.661948	-3.304441
H	-0.888764	1.532600	-4.267056
Pd	2.634655	-0.388996	-0.912291
H	1.648155	-1.574749	-1.254428
C	3.829814	1.669780	0.602693
O	2.976316	1.303267	1.425094
O	3.980060	1.170590	-0.576224
C	4.765276	2.818018	0.919896
H	4.826628	2.967157	1.999799
H	5.757552	2.642206	0.496763
H	4.360429	3.731712	0.470810
C	-0.616789	-1.199208	2.118904
N	-1.763680	-0.492458	1.907704
C	-2.614229	-0.321208	2.902157
C	-2.415776	-0.822302	4.206693
C	-1.265817	-1.543895	4.434549
C	-0.336649	-1.757653	3.395621
C	0.859969	-2.494709	3.560417
C	1.451958	-2.083780	1.243513
C	0.293822	-1.365778	1.062246
H	0.070580	-0.896082	0.109130
C	2.433607	-2.281095	0.140546
C	3.745621	-1.760213	0.229293
C	4.784384	-2.346243	-0.646769
O	4.573284	-3.164352	-1.520387
O	5.991857	-1.847470	-0.363269
C	7.053017	-2.273861	-1.225107
C	8.297355	-1.529138	-0.806654
H	9.139534	-1.820772	-1.442566
H	8.555362	-1.753369	0.233024
H	8.148580	-0.449128	-0.900078
H	6.772596	-2.057015	-2.261051
H	7.169801	-3.359413	-1.135008
H	4.058149	-1.180902	1.093407
H	2.316647	-3.188588	-0.452375
H	1.084390	-2.922509	4.533788
H	-1.063391	-1.957254	5.420671
H	-3.508261	0.250432	2.667985
C	1.726571	-2.658178	2.510676
H	2.645793	-3.221154	2.644049
C	-3.446253	-0.564132	5.265086
H	-3.151812	-1.010520	6.218833
H	-3.590286	0.510428	5.426002
H	-4.419244	-0.982833	4.982049

99

cis-T25_IN1 Eopt -2806.650932

Pd	-2.415971	0.701641	0.032065

C	-3.393623	2.786405	-1.626916
C	-4.392822	0.688002	-1.986678
C	-4.188635	3.372078	-2.602808
C	-5.215474	1.210101	-2.974870
H	-4.064399	4.430188	-2.805889
H	-5.910133	0.543294	-3.474265
N	-3.526613	1.488612	-1.367421
H	-5.741656	3.001270	-4.046053
C	-5.107558	2.567663	-3.277901
N	-3.503860	-0.930368	-0.503813
N	-1.692182	2.677110	0.044984
C	-4.371022	-0.748905	-1.531784
C	-2.323486	3.482841	-0.835117
O	-5.087788	-1.581391	-2.071588
O	-2.079382	4.672131	-1.072313
C	-3.265702	-2.220524	-0.019986
C	-3.723411	-2.597550	1.251337
C	-2.479141	-3.122384	-0.756954
C	-3.391408	-3.843681	1.787683
C	-2.149357	-4.372109	-0.228177
C	-2.606978	-4.713526	1.038563
H	-2.346811	-5.683765	1.452369
C	-0.471148	-1.243444	1.300080
C	-1.940216	-0.213913	2.779064
C	0.056332	-1.365915	-0.001112
C	0.006486	-2.091115	2.338759
C	-1.511524	-0.992731	3.874387
H	-2.724995	0.524837	2.910673
H	-0.334832	-0.722523	-0.784206
C	1.008890	-3.044648	2.039027
C	-0.542595	-1.938648	3.628550
H	-0.185159	-2.579327	4.432305
N	-1.446912	-0.322061	1.560140
H	1.373726	-3.686811	2.836336
Pd	3.843739	-0.756714	-0.731491
C	4.445974	-3.142616	-2.094908
O	4.423426	-4.094272	-2.844262
O	3.549742	-2.171731	-2.134038
N	5.214732	-1.966450	-0.113270
C	5.888173	-1.132183	0.660695
C	7.267990	-1.393776	1.172906
H	7.993738	-0.855961	0.551842
H	7.509788	-2.459933	1.147963
H	7.357494	-1.015236	2.194186
O	5.263105	-0.056928	0.932811
C	5.569255	-3.007775	-1.038051
H	5.683803	-3.979185	-0.542143
C	-0.600514	3.319393	0.751637
C	0.600318	3.649982	-0.179636
H	-0.956925	4.298131	1.108188
C	-0.125831	2.517233	1.947249
C	1.780464	4.197658	0.594936
H	0.234457	4.429457	-0.857097
H	-0.989095	2.227168	2.553634
H	0.351698	1.589313	1.607889
C	0.839645	3.340732	2.787909
C	1.917319	4.013915	1.975837
H	0.271787	4.116605	3.323023
H	1.299209	2.713904	3.562154
C	3.065685	4.497068	2.613347
C	3.920414	5.345675	0.532244
C	0.997691	2.471566	-1.034374
C	4.061941	5.155065	1.906375
H	3.173110	4.346405	3.685665
H	4.690935	5.861663	-0.033632
C	2.024153	1.606084	-0.664581
C	0.340123	2.197955	-2.236864
H	4.947374	5.516411	2.421974
N	2.383584	0.546972	-1.400061
H	2.596021	1.771965	0.244080
H	-0.443214	2.867742	-2.579503
C	1.744239	0.285038	-2.548770
H	2.086568	-0.592614	-3.089060
C	1.509064	-3.146212	0.765689
H	2.285993	-3.868575	0.534683
H	-3.740072	-4.141696	2.769317
H	-1.534006	-5.067983	-0.785666
O	-4.471805	-1.668291	1.900293
O	-2.059061	-2.670437	-1.959486
C	-5.044144	-2.045816	3.126799
H	-4.277803	-2.277585	3.879375
H	-5.632290	-1.189222	3.461943
H	-5.704487	-2.915133	3.012476
C	-1.308108	-3.550534	-2.761927
H	-1.090783	-3.006157	-3.682223
H	-0.364029	-3.832628	-2.278468
H	-1.878259	-4.456515	-3.002924
C	2.787484	4.867298	-0.109616
H	2.672846	5.003556	-1.183042
C	0.712055	1.095196	-2.997324
H	0.215180	0.865298	-3.934074
H	6.505002	-2.798966	-1.577014
C	1.024732	-2.304893	-0.261152
H	1.444396	-2.403248	-1.257196
C	-2.089531	-0.749173	5.237303
H	-1.978425	-1.628949	5.877913
H	-1.583577	0.087962	5.734192
H	-3.153850	-0.498393	5.183421

98

cis-T25_T-Pd-P Eopt -2588.707048

Pd	1.410578	-1.306578	0.217285
N	2.061157	-1.958277	1.938347
C	3.209858	-1.467838	2.397896
C	3.745972	-1.974130	3.574049
C	3.058675	-2.996437	4.229176
C	1.862544	-3.489612	3.707997

C	1.382762	-2.941081	2.526773
C	0.107975	-3.334320	1.832993
O	-0.652825	-4.140050	2.353809
N	-0.038168	-2.696245	0.639710
C	-1.292612	-2.748040	0.025413
C	-2.413261	-2.178238	0.660578
C	-3.662748	-2.177923	0.039593
C	-3.781171	-2.710579	-1.238760
C	-2.688430	-3.259536	-1.900434
C	-1.446884	-3.289938	-1.259826
O	-0.323587	-3.815970	-1.810255
C	-0.438442	-4.404083	-3.081025
H	-1.149252	-5.240787	-3.076842
H	-0.745925	-3.672762	-3.840598
H	0.555919	-4.781300	-3.328637
H	-2.812371	-3.668208	-2.896278
H	-4.747945	-2.694502	-1.734080
H	-4.522877	-1.734814	0.527844
O	-2.165215	-1.600661	1.856438
C	-3.268697	-1.268618	2.674197
H	-3.919534	-2.138885	2.821784
H	-3.849528	-0.431817	2.267869
H	-2.843967	-0.969745	3.634128
H	1.288344	-4.278552	4.181600
H	3.456485	-3.409018	5.152078
H	4.673563	-1.550497	3.943355
C	3.764040	-0.316827	1.607445
O	4.723819	0.314267	2.063231
N	3.062487	-0.048125	0.484277
C	3.401516	1.228423	-0.119927
C	2.887526	1.381572	-1.537619
C	3.484621	2.627302	-2.176230
C	3.357241	3.855694	-1.311832
C	3.126438	3.752824	0.064750
C	3.048614	4.921492	0.831180
C	3.195103	6.174615	0.254986
C	3.421217	6.277360	-1.117314
C	3.499491	5.124492	-1.885315
H	3.674061	5.199071	-2.957107
H	3.532531	7.252289	-1.584245
H	3.131067	7.068088	0.869952
H	2.860388	4.832909	1.899021
C	2.926720	2.420931	0.759183
C	1.508352	2.256430	1.258533
C	0.399433	2.751683	0.566084
N	-0.864466	2.625515	0.974336
C	-1.082239	1.982260	2.123073
C	-0.059534	1.444418	2.898980
C	1.250246	1.592471	2.460513
H	2.079623	1.211896	3.051916
H	-0.286065	0.928613	3.827390
H	-2.123016	1.900550	2.435566
H	0.545332	3.299543	-0.363619
H	3.577131	2.400823	1.641514
H	3.020359	2.813898	-3.152832
H	4.551550	2.446924	-2.376943
H	3.162190	0.499992	-2.124966
H	1.792288	1.441522	-1.534284
H	4.498710	1.304358	-0.144567
N	0.847064	-0.960842	-1.757763
C	1.642698	-1.476500	-2.674797
C	1.384954	-1.430078	-4.061551
C	0.217673	-0.820007	-4.463782
C	-0.673454	-0.283760	-3.513279
C	-1.910341	0.315839	-3.860953
C	-2.757838	0.776611	-2.891352
C	-2.412220	0.685620	-1.514985
C	-1.194276	0.138192	-1.159652
C	-0.321791	-0.367851	-2.137960
H	-0.902473	0.070801	-0.115523
C	-3.298338	1.106500	-0.443026
C	-4.492249	1.709345	-0.544721
C	-5.231909	2.028486	0.684616
O	-4.893657	1.733009	1.816233
O	-6.361392	2.699174	0.409625
C	-7.150011	3.065280	1.547524
C	-8.358963	3.812408	1.038475
H	-8.992884	4.113385	1.878712
H	-8.058938	4.712380	0.492976
H	-8.951861	3.183732	0.366918
H	-6.539012	3.677498	2.219113
H	-7.425953	2.157338	2.094543
H	-4.948756	1.996543	-1.486516
H	-2.941071	0.891957	0.558630
H	-3.712229	1.210061	-3.173448
H	-2.179797	0.386412	-4.911436
H	-0.032842	-0.756869	-5.520925
H	2.546887	-1.951790	-2.304833
C	2.365217	-2.039226	-5.018459
H	2.030856	-1.923307	-6.053043
H	3.352252	-1.571050	-4.928190
H	2.495639	-3.110207	-4.823327

85

cis-T25_T-Pd-SM Eopt -2244.487608

Pd	0.511936	0.824649	-0.647903
C	-0.301910	3.439623	-1.367736
C	1.942773	3.259869	-0.677353
C	-0.158261	4.801455	-1.597552
C	2.151392	4.615736	-0.886516
H	-1.019833	5.362736	-1.942417
H	3.130307	5.028827	-0.668266
N	0.741965	2.739985	-0.929775
H	1.225321	6.448277	-1.531731
C	1.086723	5.384731	-1.358757
N	2.467507	1.020844	-0.108202
N	-1.426301	1.337831	-1.218655

C	2.957094	2.286035	-0.129155
C	-1.581774	2.655839	-1.480843
O	4.059479	2.677141	0.232915
O	-2.632450	3.252923	-1.734199
C	3.177317	0.002415	0.531377
C	3.705396	-1.065470	-0.212639
C	3.247248	-0.046644	1.934042
C	4.284341	-2.163219	0.430113
C	3.844328	-1.132347	2.581388
C	4.350920	-2.179062	1.818321
H	4.811771	-3.026240	2.318631
C	0.630754	-2.134259	-1.324671
C	0.514489	-1.614006	0.938110
C	0.642483	-1.711415	-2.671284
C	0.756550	-3.514903	-1.016088
C	0.633411	-2.964342	1.340186
H	0.432196	-0.831295	1.684587
H	0.560795	-0.647538	-2.876186
C	0.883977	-4.442760	-2.078809
C	0.751601	-3.902209	0.343809
H	0.846789	-4.957261	0.592324
N	0.499252	-1.217980	-0.319245
H	0.978016	-5.499139	-1.840436
C	-2.671418	0.602005	-1.141576
C	-3.406405	0.842983	0.204560
H	-3.341677	1.011756	-1.910989
C	-2.521978	-0.887166	-1.385967
C	-4.682505	0.030172	0.279007
H	-3.677468	1.906296	0.202722
H	-1.901430	-1.060339	-2.270409
H	-2.012820	-1.356282	-0.536321
C	-3.897452	-1.510454	-1.581806
C	-4.896795	-1.092754	-0.530549
H	-4.285556	-1.213958	-2.567701
H	-3.821635	-2.604890	-1.604033
C	-6.082406	-1.820828	-0.377917
C	-6.832659	-0.329196	1.351925
C	-2.519616	0.610611	1.408601
C	-7.044864	-1.450516	0.550746
H	-6.245154	-2.694784	-1.005894
H	-7.578149	-0.025591	2.081697
C	-2.512338	-0.592600	2.123670
C	-1.655402	1.611115	1.860991
H	-7.956839	-2.032745	0.651768
N	-1.751465	-0.833127	3.194832
H	-3.175926	-1.400647	1.822310
H	-1.630549	2.571666	1.354263
C	-0.941105	0.144441	3.605787
H	-0.335815	-0.072312	4.485135
C	0.883933	-4.013475	-3.383328
H	0.978595	-4.731215	-4.192924
H	4.688040	-2.992278	-0.138715
H	3.915332	-1.168626	3.662394

O	3.586737	-0.948534	-1.554918
O	2.667343	0.994456	2.577306
C	4.059442	-2.012479	-2.344822
H	3.528435	-2.947070	-2.120766
H	3.859328	-1.729483	-3.378892
H	5.138632	-2.163381	-2.210833
C	2.780086	1.037604	3.977270
H	2.296264	1.964194	4.291048
H	2.272229	0.186326	4.452130
H	3.829878	1.054075	4.296272
C	-5.658972	0.397019	1.211573
H	-5.480408	1.267923	1.838827
C	-0.850879	1.378812	2.970631
H	-0.168432	2.140095	3.334647
C	0.763658	-2.636980	-3.679275
H	0.769928	-2.307734	-4.714208
C	0.628780	-3.292180	2.800191
H	-0.261851	-2.870364	3.281479
H	0.646002	-4.373354	2.963877
H	1.511296	-2.857460	3.284700

80

cis-T25_TC-Pd-P Eopt -3264.861611

Pd	0.538156	1.390687	-0.510666
C	1.538514	4.027629	-0.299530
C	-0.695798	3.889343	-1.021399
C	1.515420	5.412977	-0.378709
C	-0.790229	5.271301	-1.108440
H	2.414156	5.963086	-0.121837
H	-1.730495	5.708538	-1.426337
N	0.447079	3.335820	-0.621612
H	0.287106	7.115922	-0.849468
C	0.333026	6.032818	-0.784527
N	-1.385173	1.621524	-1.251985
N	2.421071	1.869782	0.191555
C	-1.801310	2.918677	-1.336861
C	2.722966	3.199553	0.120067
O	-2.912477	3.334249	-1.641252
O	3.792207	3.742230	0.368645
C	-2.300575	0.582172	-1.449412
C	-3.599180	0.608491	-0.921357
C	-1.865153	-0.574053	-2.103614
C	-4.394411	-0.528286	-0.984733
C	-2.663214	-1.708718	-2.141884
C	-3.932317	-1.702276	-1.572357
H	-4.547641	-2.596063	-1.579871
C	-0.139320	-1.450642	0.322138
C	1.690079	-1.239794	-1.098936
C	-1.173552	-0.853987	1.060669
C	0.002379	-2.865785	0.311088
C	1.942194	-2.626779	-1.116214
H	2.336497	-0.566497	-1.655035
C	-2.107429	-1.628756	1.725139
H	-1.240418	0.228915	1.059679

C	-0.940079	-3.644266	1.024329
C	1.071334	-3.428425	-0.413981
H	1.204713	-4.507507	-0.406304
N	0.709940	-0.672229	-0.417684
H	-0.840259	-4.725691	1.013565
H	-3.969258	1.505846	-0.443105
H	-0.872209	-0.587609	-2.536887
C	-2.157992	-2.967841	-2.779613
C	-5.764903	-0.536821	-0.371396
F	-2.794675	-3.241735	-3.927882
F	-0.843754	-2.902041	-3.057514
F	-2.339959	-4.029078	-1.971778
F	-6.055698	0.617876	0.247917
F	-5.880728	-1.521625	0.537010
F	-6.715956	-0.748587	-1.294642
C	-1.969103	-3.043683	1.698394
H	-2.703958	-3.648768	2.221961
C	3.416337	0.949136	0.532129
C	3.074892	-0.138141	1.346597
C	4.718545	1.020201	0.021982
C	3.984978	-1.157448	1.584528
H	2.075772	-0.188863	1.763481
C	5.631527	0.006078	0.296425
H	5.008934	1.864017	-0.590868
C	5.275576	-1.096750	1.064209
H	5.986498	-1.894950	1.248294
C	3.577491	-2.379187	2.351538
C	7.033906	0.122331	-0.228145
F	7.600754	-1.084925	-0.393954
F	7.068815	0.750946	-1.413542
F	7.818049	0.815130	0.610633
F	2.322239	-2.298568	2.814896
F	4.385619	-2.610602	3.395202
F	3.639758	-3.477618	1.566513
C	-3.263602	-1.049557	2.398369
C	-3.586496	0.250684	2.442171
H	-3.962164	-1.743995	2.862062
H	-2.980352	1.030990	1.992966
C	-4.866790	0.665822	3.042486
O	-5.644146	-0.060317	3.621871
O	-5.077586	1.975771	2.834447
C	-6.344122	2.449734	3.279442
H	-6.356255	3.516464	3.055904
H	-7.147132	1.936128	2.743551
H	-6.466558	2.277644	4.352047
C	3.143620	-3.156179	-1.836196
H	3.343854	-2.595791	-2.754646
H	4.029180	-3.072940	-1.194535
H	3.016967	-4.210191	-2.097688

70

cis-T25_TC-Pd-SM Eopt -2959.907072

Pd	-0.119884	1.501679	0.058040
C	-1.397245	4.010447	-0.206128
C	0.921531	4.131063	0.178189
C	-1.497291	5.394209	-0.249850
C	0.892984	5.517677	0.130083
H	-2.472226	5.840171	-0.413961
H	1.822039	6.061994	0.260350
N	-0.209277	3.448536	0.007223
H	-0.384761	7.231182	-0.118437
C	-0.334372	6.146903	-0.082533
N	1.843158	1.962480	0.504547
N	-2.125432	1.747047	-0.379445
C	2.149402	3.287279	0.399298
C	-2.542756	3.047165	-0.370246
O	3.252475	3.812924	0.480872
O	-3.684948	3.472490	-0.492078
C	2.858782	1.012016	0.645820
C	4.027973	1.037665	-0.120965
C	2.638641	-0.074047	1.500065
C	4.904971	-0.041558	-0.084385
C	3.515365	-1.148120	1.518110
C	4.653676	-1.149561	0.715943
H	5.331639	-1.995863	0.716255
C	0.766951	-1.306021	-0.677507
C	-0.809705	-1.170141	1.029614
C	1.565708	-0.677228	-1.656555
C	0.831911	-2.717848	-0.517487
C	-0.847072	-2.565090	1.221616
H	-1.445199	-0.524153	1.629190
C	2.436669	-1.423115	-2.412050
H	1.494464	0.399784	-1.776026
C	1.731066	-3.458356	-1.321350
C	-0.000276	-3.323139	0.446118
H	3.078901	-0.930249	-3.134538
H	0.030172	-4.403665	0.564228
N	-0.047726	-0.565133	0.133994
H	1.784630	-4.534812	-1.185821
H	4.232272	1.888527	-0.759509
H	1.747009	-0.082547	2.115832
C	3.237027	-2.344819	2.377159
C	6.067623	-0.058681	-1.031311
F	4.187981	-2.527029	3.305305
F	2.060572	-2.249530	3.018170
F	3.196322	-3.472448	1.640244
F	6.596853	1.159395	-1.201818
F	5.685455	-0.492208	-2.252380
F	7.044933	-0.878298	-0.617404
C	2.525365	-2.822591	-2.241138
H	3.225757	-3.392001	-2.844294
C	-3.062921	0.714098	-0.464952
C	-2.733489	-0.431102	-1.201403
C	-4.282072	0.737105	0.224598
C	-3.562157	-1.543469	-1.190061
H	-1.804538	-0.447559	-1.759030
C	-5.118682	-0.374817	0.199977

H -4.567510 1.621523 0.779562
C -4.766190 -1.528814 -0.490395
H -5.413357 -2.399060 -0.480268
C -3.143783 -2.809993 -1.873588
C -6.440016 -0.311546 0.910666
F -6.856637 -1.531932 1.289465
F -6.374986 0.452678 2.012098
F -7.397098 0.206024 0.126119
F -2.007978 -2.666017 -2.570623
F -4.085536 -3.262857 -2.713164
F -2.930806 -3.792938 -0.970437
C -1.814314 -3.157352 2.199536
H -1.927379 -2.527871 3.087616
H -2.801294 -3.258203 1.732385
H -1.492685 -4.151138 2.522545
96
cis-T25-Q_C3_IN2 Eopt -2767.395330
Pd -2.345765 -0.097724 0.020312
C -4.281822 1.406856 -1.397805
C -4.423508 -0.926810 -1.693634
C -5.351292 1.614937 -2.258575
C -5.498763 -0.786269 -2.559218
H -5.662858 2.633453 -2.463135
H -5.924292 -1.678093 -3.006670
N -3.887048 0.162030 -1.142461
H -6.808701 0.636662 -3.503222
C -5.967667 0.500410 -2.829204
N -2.691762 -2.019301 -0.502718
N -2.495380 1.995156 0.073792
C -3.713917 -2.222355 -1.370041
C -3.459598 2.480799 -0.736170
O -4.064365 -3.270597 -1.894936
O -3.702817 3.668238 -0.981702
C -1.749602 -3.016389 -0.232482
C -1.787935 -3.723488 0.978907
C -0.642801 -3.179728 -1.082147
C -0.743156 -4.582530 1.332987
C 0.403501 -4.037255 -0.734921
C 0.337818 -4.726926 0.471982
H 1.155456 -5.386202 0.748000
C -1.737067 3.012305 0.775120
C -0.723313 3.762939 -0.134763
H -2.447158 3.789728 1.096591
C -1.048456 2.468252 2.012034
C 0.225987 4.642576 0.658658
H -1.336669 4.405105 -0.777007
H -1.758431 1.866330 2.588395
H -0.226815 1.803829 1.725320
C -0.508900 3.612258 2.854120
C 0.347742 4.557734 2.051374
H -1.352031 4.171762 3.286096
H 0.065997 3.222953 3.703276
C 1.272078 5.382835 2.702183
C 1.937888 6.367295 0.612562
C 0.039722 2.839276 -1.054596
C 2.062376 6.280564 1.998629
H 1.367389 5.310045 3.783761
H 2.549888 7.064565 0.047486
C 1.188369 2.168676 -0.640045
C -0.394907 2.605719 -2.360523
H 2.775554 6.908299 2.525760
N 1.860820 1.318744 -1.430220
H 1.578401 2.296900 0.363086
H -1.305268 3.086813 -2.709462
C 1.480448 1.159375 -2.706522
H 2.107256 0.512957 -3.310892
H -0.762365 -5.127698 2.269129
H 1.261674 -4.168924 -1.383317
O -2.865299 -3.476242 1.759230
O -0.652122 -2.408296 -2.198319
C -2.942451 -4.147683 2.993071
H -2.103902 -3.879988 3.649660
H -3.877391 -3.822215 3.452550
H -2.967918 -5.236724 2.858067
C 0.474890 -2.467989 -3.038690
H 0.277025 -1.771208 -3.854920
H 1.389081 -2.157590 -2.510883
H 0.620570 -3.474417 -3.450914
C 1.027052 5.551804 -0.042789
H 0.930747 5.609268 -1.125117
C 0.346693 1.784828 -3.203194
H 0.049134 1.619196 -4.233259
C -0.429267 -0.753548 2.374841
C -1.379155 -1.077927 4.562644
C 0.882580 -0.864475 2.912469
C -0.081658 -1.188678 5.110936
H -2.245296 -1.166728 5.212051
C 1.988720 -0.722130 2.034561
C 1.025017 -1.083682 4.303380
H 0.037360 -1.358236 6.177113
H 2.026087 -1.167154 4.718794
H 2.990756 -0.757361 2.459881
Pd 3.189396 -0.085050 -0.711413
C 5.746989 -0.074662 -1.961248
O 6.728115 0.111401 -2.655104
O 4.556469 0.395887 -2.164386
N 4.622710 -1.441478 -0.231726
C 4.486473 -2.660081 0.153951
C 5.603164 -3.646166 0.298099
H 6.422475 -3.229949 0.890241
H 6.003444 -3.915611 -0.685359
H 5.225749 -4.547663 0.781838
O 3.305827 -3.170477 0.459523
C 5.908950 -0.918877 -0.676961
C 1.804955 -0.545862 0.676936
H 6.640912 -1.706811 -0.868225

C	0.455284	-0.511541	0.243487
H	0.218076	-0.422213	-0.810774
N	-0.597034	-0.539618	1.037985
C	-1.554957	-0.860387	3.216354
H	-2.540867	-0.790642	2.765473
H	6.314852	-0.258693	0.100614
H	2.613433	-2.478173	0.359050

104

cis-T25-Q_C3_IN3 Eopt -2905.031449

Pd	-2.327783	-0.599106	0.228217
C	-4.734050	0.435533	-0.860986
C	-4.299976	-1.822176	-1.370441
C	-5.916534	0.407383	-1.588547
C	-5.469640	-1.916557	-2.110705
H	-6.502009	1.317401	-1.661650
H	-5.697236	-2.856050	-2.602791
N	-4.000874	-0.670681	-0.769187
H	-7.208445	-0.837229	-2.777007
C	-6.286562	-0.788831	-2.204312
N	-2.225213	-2.503826	-0.443195
N	-2.987584	1.394627	0.458445
C	-3.245432	-2.896182	-1.249567
C	-4.136027	1.649486	-0.203460
O	-3.361514	-3.950742	-1.858654
O	-4.693384	2.744918	-0.343200
C	-1.026546	-3.222417	-0.420403
C	-0.633713	-3.914375	0.735901
C	-0.127121	-3.127798	-1.497320
C	0.617957	-4.532412	0.803342
C	1.120449	-3.756560	-1.440438
C	1.474463	-4.452283	-0.289510
H	2.442713	-4.943287	-0.242073
C	-2.401416	2.565351	1.084726
C	-1.722383	3.529353	0.068149
H	-3.223115	3.153738	1.520087
C	-1.434204	2.208326	2.193896
C	-0.927792	4.624883	0.753406
H	-2.547301	3.993079	-0.484913
H	-1.885740	1.453565	2.844572
H	-0.527313	1.766010	1.768234
C	-1.065496	3.447442	2.992146
C	-0.593582	4.576837	2.112638
H	-1.942936	3.782914	3.564892
H	-0.292462	3.205713	3.732089
C	0.176556	5.610287	2.658251
C	0.270900	6.727536	0.531702
C	-0.880413	2.792326	-0.945455
C	0.608492	6.677571	1.883711
H	0.438934	5.566276	3.713427
H	0.600715	7.557055	-0.087423
C	0.456759	2.477357	-0.715562
C	-1.440877	2.352403	-2.146972
H	1.208269	7.466539	2.329076
N	1.199291	1.767938	-1.580658
H	0.947996	2.784541	0.201167
H	-2.487125	2.564711	-2.352061
C	0.664789	1.386539	-2.753183
H	1.320623	0.828410	-3.417167
H	0.923707	-5.079004	1.687451
H	1.806767	-3.705745	-2.277873
O	-1.531713	-3.907885	1.748853
O	-0.542170	-2.359747	-2.530539
C	-1.164764	-4.548967	2.945744
H	-0.273257	-4.088474	3.392588
H	-2.009862	-4.423359	3.624716
H	-0.983411	-5.620475	2.790811
C	0.325333	-2.216085	-3.636282
H	-0.209360	-1.589449	-4.351777
H	1.265699	-1.720957	-3.363600
H	0.540101	-3.185656	-4.102140
C	-0.488881	5.706326	-0.019871
H	-0.749725	5.735010	-1.075923
C	-0.658112	1.666243	-3.065623
H	-1.065321	1.328391	-4.012828
C	-0.129424	-0.674801	2.411944
C	-0.787038	-1.066184	4.694615
C	1.163584	-0.267679	2.839181
C	0.489407	-0.649115	5.134631
H	-1.528665	-1.380998	5.423013
C	2.106161	0.134410	1.856447
C	1.442906	-0.254005	4.227285
H	0.714290	-0.641035	6.197170
H	2.424628	0.074389	4.559668
H	3.066106	0.522930	2.191481
C	1.804645	0.025477	0.518601
C	0.498278	-0.400868	0.193624
H	0.182054	-0.480865	-0.841599
N	-0.442590	-0.650723	1.085042
C	-1.099324	-1.070933	3.355735
H	-2.070258	-1.389293	2.987185
Pd	2.911199	0.635862	-1.021970
C	3.835645	-1.324726	-1.270373
C	4.693594	-0.555355	-0.506406
H	3.219772	-2.082807	-0.794010
H	3.874437	-1.314199	-2.357195
H	5.441574	0.083778	-0.968473
C	4.885754	-0.787934	0.951344
O	5.492377	-0.034888	1.681508
O	4.316924	-1.929270	1.352657
C	4.390961	-2.223944	2.753033
C	3.404092	-3.331173	3.029844
H	4.160650	-1.318008	3.320820
H	5.420530	-2.510409	2.993672
H	3.414576	-3.581786	4.095495
H	2.392829	-3.019833	2.751996
H	3.654701	-4.230286	2.458447

C	3.898120	0.873764	-3.766264
O	3.113195	-0.049380	-4.035712
O	4.074757	1.379892	-2.595765
C	4.732806	1.516816	-4.854831
H	4.684509	0.926471	-5.771401
H	4.347193	2.522980	-5.053614
H	5.769989	1.628293	-4.526517

104

cis-T25-Q_C3_IN4 Eopt -2905.072899

Pd	-2.358464	0.342289	-0.032473
C	-4.030527	1.813515	-1.792832
C	-4.317734	-0.519489	-1.879947
C	-5.024706	2.006966	-2.742475
C	-5.319412	-0.395482	-2.832434
H	-5.249909	3.019924	-3.057912
H	-5.782935	-1.298331	-3.215286
N	-3.728195	0.576869	-1.405080
H	-6.458819	1.009109	-3.999391
C	-5.675962	0.885057	-3.256481
N	-2.860576	-1.608468	-0.361426
N	-2.278884	2.419571	-0.288718
C	-3.782279	-1.818463	-1.335116
C	-3.154345	2.885322	-1.207643
O	-4.185311	-2.887224	-1.776786
O	-3.244795	4.038985	-1.640404
C	-2.160165	-2.699911	0.158851
C	-2.356840	-3.092750	1.493140
C	-1.174712	-3.349593	-0.604207
C	-1.593512	-4.121922	2.050293
C	-0.425379	-4.395150	-0.059408
C	-0.645969	-4.766595	1.262478
H	-0.060424	-5.575632	1.690341
C	-1.285288	3.393645	0.115599
C	-0.230070	3.627551	-1.003799
H	-1.792926	4.361607	0.235864
C	-0.601367	3.047044	1.423051
C	0.896318	4.528707	-0.541824
H	-0.770059	4.126194	-1.817313
H	-1.355082	2.804032	2.177893
H	0.020907	2.153201	1.297817
C	0.247307	4.220147	1.892267
C	1.147024	4.771569	0.814313
H	-0.417888	5.025148	2.238824
H	0.849762	3.929946	2.761688
C	2.242674	5.567642	1.166759
C	2.820176	5.882227	-1.146237
C	0.297385	2.321515	-1.547181
C	3.075533	6.119365	0.203770
H	2.440553	5.749471	2.221185
H	3.463986	6.307624	-1.910802
C	1.411698	1.705349	-0.986908
C	-0.336234	1.650200	-2.596252
H	3.923935	6.728795	0.502418
N	1.861077	0.504686	-1.384898
H	1.978687	2.184742	-0.194898
H	-1.204834	2.098211	-3.070991
C	1.258902	-0.126045	-2.402786
H	1.682273	-1.081719	-2.692449
H	-1.740207	-4.430339	3.078543
H	0.332465	-4.902794	-0.645147
O	-3.304524	-2.399441	2.164464
O	-0.989834	-2.857738	-1.853981
C	-3.492990	-2.702492	3.525728
H	-2.576243	-2.532266	4.105541
H	-4.268610	-2.021942	3.878781
H	-3.826689	-3.739044	3.664778
C	-0.195740	-3.613569	-2.741192
H	-0.284056	-3.122224	-3.712410
H	0.860090	-3.625589	-2.441019
H	-0.566243	-4.642516	-2.824187
C	1.739019	5.091547	-1.506722
H	1.538561	4.892319	-2.557539
C	0.155745	0.426727	-3.036139
H	-0.317998	-0.108607	-3.851915
C	-1.244374	-0.039756	2.782652
C	-2.642289	0.765392	4.574684
C	-0.343675	-0.602232	3.728191
C	-1.745816	0.223280	5.523939
H	-3.532302	1.287082	4.914246
C	0.776917	-1.316937	3.249328
C	-0.622374	-0.448015	5.109347
H	-1.952398	0.336819	6.584060
H	0.069927	-0.873996	5.830963
H	1.461596	-1.767326	3.965327
C	0.994679	-1.467839	1.899139
C	0.063412	-0.845276	1.040012
H	0.172116	-0.916720	-0.033104
N	-0.993469	-0.164688	1.447396
C	-2.400258	0.637338	3.228689
H	-3.081600	1.037704	2.482830
Pd	3.351590	-0.243080	-0.213457
C	2.117148	-2.313931	1.358393
C	2.437139	-2.055874	-0.098471
H	3.021285	-2.172263	1.961071
H	1.826843	-3.368315	1.485682
H	1.546235	-2.053970	-0.729861
C	3.410935	-3.017529	-0.669684
O	4.173816	-3.730580	-0.057742
O	3.341756	-3.013013	-2.028941
C	4.303326	-3.834885	-2.693750
C	4.076125	-3.681480	-4.178790
H	4.180161	-4.871908	-2.363291
H	5.308226	-3.514954	-2.398240
H	4.796107	-4.289834	-4.735546
H	3.067412	-4.005926	-4.455903
H	4.198843	-2.637268	-4.483718

C	5.373598	0.577299	0.981377
O	4.930455	-0.621151	1.073497
O	4.770808	1.415530	0.258059
C	6.628435	0.943550	1.715448
H	6.720397	0.356122	2.631708
H	7.490254	0.715898	1.077967
H	6.637321	2.012772	1.936896

104

cis-T25-Q_C3_IN5 Eopt -2905.040955

Pd	2.390625	-0.113174	-0.106604
C	4.080435	-1.361262	-2.009808
C	4.127227	0.992232	-2.038969
C	5.018940	-1.427111	-3.031027
C	5.066145	0.995306	-3.060744
H	5.318552	-2.402936	-3.397475
H	5.406655	1.949579	-3.447993
N	3.689647	-0.171704	-1.559690
H	6.254840	-0.255748	-4.346925
C	5.518372	-0.231450	-3.548689
N	2.657480	1.886241	-0.406434
N	2.505067	-2.184165	-0.412923
C	3.487756	2.214684	-1.430009
C	3.352648	-2.531675	-1.407384
O	3.738260	3.328940	-1.870786
O	3.523979	-3.656247	-1.889000
C	1.838955	2.866595	0.159831
C	1.989165	3.216737	1.513236
C	0.774676	3.425412	-0.569451
C	1.103020	4.110283	2.119559
C	-0.094239	4.344961	0.023589
C	0.078006	4.669666	1.363939
H	-0.606631	5.370841	1.832519
C	1.649043	-3.269315	0.029791
C	0.521571	-3.563389	-0.999939
H	2.259413	-4.183307	0.058182
C	1.060083	-3.048848	1.408665
C	-0.486461	-4.568098	-0.480140
H	1.026757	-3.993874	-1.872759
H	1.853853	-2.762905	2.105133
H	0.341669	-2.221765	1.383320
C	0.372037	-4.317647	1.891672
C	-0.586525	-4.890918	0.878332
H	1.137231	-5.074452	2.120545
H	-0.158334	-4.127108	2.832543
C	-1.584061	-5.781450	1.290677
C	-2.356879	-6.038150	-0.972004
C	-0.160714	-2.297269	-1.457767
C	-2.464103	-6.352758	0.382680
H	-1.667371	-6.022042	2.348471
H	-3.035054	-6.482300	-1.695593
C	-1.250578	-1.761135	-0.771920
C	0.301465	-1.590538	-2.569543
H	-3.233213	-7.038373	0.727386
N	-1.834718	-0.608961	-1.120577
H	-1.696898	-2.272007	0.076508
H	1.147536	-1.975359	-3.133105
C	-1.400662	0.044348	-2.204022
H	-1.930573	0.956300	-2.461593
H	1.211438	4.379974	3.163297
H	-0.914937	4.776343	-0.538380
O	3.017755	2.615295	2.154316
O	0.630728	2.961757	-1.835555
C	3.179288	2.888153	3.525441
H	2.299639	2.575469	4.104186
H	4.042335	2.304212	3.847192
H	3.373581	3.953709	3.703272
C	-0.217000	3.682675	-2.703183
H	-0.090372	3.229206	-3.688088
H	-1.271184	3.612813	-2.405165
H	0.076459	4.738393	-2.751524
C	-1.376521	-5.149339	-1.390127
H	-1.294552	-4.887958	-2.443190
C	-0.330735	-0.414956	-2.957320
H	0.003977	0.145837	-3.823524
C	1.284804	0.003081	2.748147
C	2.800195	-0.659914	4.499198
C	0.283830	0.296980	3.713870
C	1.811129	-0.377969	5.468351
H	3.772718	-1.025074	4.815869
C	-0.960973	0.788163	3.264946
C	0.579221	0.091891	5.084517
H	2.030620	-0.532694	6.520534
H	-0.187430	0.313164	5.822311
H	-1.741881	1.004164	3.990490
C	-1.184506	1.010643	1.922477
C	-0.124088	0.702406	1.037566
H	-0.229379	0.872277	-0.025202
N	1.027219	0.193226	1.419124
C	2.545136	-0.473785	3.161421
H	3.293819	-0.673129	2.399744
Pd	-3.454688	0.170962	0.158936
C	-2.458647	1.546383	1.436581
C	-2.657658	2.116276	0.157999
H	-4.652914	0.642796	0.976768
H	-3.149117	1.863068	2.215082
H	-1.840196	2.159920	-0.554335
C	-3.699044	3.149055	-0.034833
O	-4.511846	3.511205	0.784603
O	-3.610885	3.660759	-1.278171
C	-4.599680	4.644032	-1.609905
C	-4.315894	5.110486	-3.017057
H	-4.544074	5.461301	-0.883518
H	-5.590622	4.187681	-1.518846
H	-5.055822	5.858237	-3.319542
H	-3.322059	5.565190	-3.085756
H	-4.364538	4.273826	-3.720915

C -4.694047 -2.014865 -0.468095
O -4.836380 -1.047773 -1.256399
O -4.027678 -1.893450 0.611773
C -5.282932 -3.364393 -0.784099
H -4.473316 -4.098455 -0.855409
H -5.936035 -3.679777 0.035325
H -5.845193 -3.334921 -1.718563
96
cis-T25-Q_C3_TSI Eopt -2767.367396
Pd -2.276062 0.194404 -0.091679
C -4.025118 1.917331 -1.514260
C -4.463316 -0.381771 -1.774364
C -5.062457 2.247551 -2.376021
C -5.519493 -0.118324 -2.634566
H -5.244867 3.294863 -2.590817
H -6.067931 -0.955880 -3.052154
N -3.783980 0.636500 -1.246658
H -6.638883 1.445151 -3.601475
C -5.818072 1.212844 -2.928827
N -2.875656 -1.673447 -0.585587
N -2.202556 2.299685 -0.021427
C -3.969427 -1.754595 -1.381857
C -3.089037 2.889825 -0.850752
O -4.538141 -2.759406 -1.786961
O -3.186220 4.095665 -1.106929
C -2.253059 -2.822409 -0.085021
C -2.594888 -3.302523 1.189523
C -1.172430 -3.405832 -0.766170
C -1.880125 -4.352386 1.769695
C -0.447025 -4.450027 -0.187288
C -0.813409 -4.908486 1.072349
H -0.246408 -5.716715 1.525389
C -1.343274 3.231747 0.682865
C -0.215026 3.815626 -0.213470
H -1.957860 4.099767 0.964671
C -0.765949 2.631983 1.948251
C 0.843650 4.558626 0.579536
H -0.714793 4.527182 -0.880705
H -1.569257 2.160846 2.522360
H -0.049367 1.843039 1.694687
C -0.079173 3.704762 2.776918
C 0.927689 4.488744 1.975480
H -0.839099 4.394953 3.172777
H 0.410390 3.256963 3.650464
C 1.957703 5.175279 2.628221
C 2.803778 5.994191 0.532230
C 0.401600 2.757839 -1.093130
C 2.889873 5.922212 1.922028
H 2.022828 5.113680 3.712727
H 3.527648 6.572417 -0.034776
C 1.443689 1.944826 -0.651938
C -0.087064 2.529756 -2.380192
H 3.684026 6.442788 2.449986
N 1.967136 0.968517 -1.402907
H 1.873803 2.072330 0.335687
H -0.911936 3.134746 -2.747999
C 1.522540 0.786395 -2.655045
H 2.011255 0.005676 -3.227931
H -2.137588 -4.728934 2.752578
H 0.413181 -4.879030 -0.686054
O -3.617855 -2.651429 1.795718
O -0.870690 -2.849057 -1.966927
C -4.002412 -3.095631 3.073340
H -3.186074 -2.984859 3.800212
H -4.840184 -2.462677 3.371444
H -4.331136 -4.142633 3.054252
C 0.220739 -3.392015 -2.677348
H 0.297048 -2.807303 -3.596108
H 1.157786 -3.313486 -2.110063
H 0.045258 -4.444183 -2.934781
C 1.787963 5.315268 -0.124590
H 1.721201 5.360175 -1.209680
C 0.489959 1.548743 -3.177410
H 0.144051 1.366898 -4.189338
C -0.462963 -0.642359 2.273214
C -1.419176 -0.529078 4.479519
C 0.787526 -1.029764 2.831231
C -0.175299 -0.884881 5.047356
H -2.272082 -0.351925 5.128470
C 1.847530 -1.323634 1.946622
C 0.906217 -1.132782 4.238585
H -0.082017 -0.971445 6.125672
H 1.864338 -1.423251 4.661278
H 2.809097 -1.629823 2.353974
Pd 3.258411 -0.494003 -0.687619
C 5.954046 -0.279734 -1.476325
O 7.002531 0.115914 -1.939039
O 4.794990 0.296219 -1.690077
N 4.572529 -1.931892 -0.302649
C 4.166838 -3.183273 -0.246520
C 5.164495 -4.313626 -0.245713
H 5.994899 -4.121330 0.439549
H 5.583760 -4.445595 -1.250014
H 4.653318 -5.232723 0.041935
O 2.933241 -3.484460 -0.186569
C 5.933920 -1.516313 -0.562942
C 1.659079 -1.294437 0.573981
H 2.268461 -2.273551 0.014676
H 6.526439 -2.299146 -1.046894
C 0.375949 -0.895511 0.124567
H 0.147730 -0.875998 -0.935078
N -0.605960 -0.517063 0.918075
C -1.564900 -0.404209 3.117290
H -2.516650 -0.149545 2.659701
H 6.447985 -1.243215 0.369107
104

cis-T25-Q_C3_TSII Eopt -2905.006829

Pd	-2.634457	-0.058382	0.148917
C	-4.622642	1.399631	-1.265885
C	-4.809760	-0.938315	-1.423527
C	-5.735780	1.577790	-2.076913
C	-5.929347	-0.830372	-2.235430
H	-6.042659	2.589799	-2.317465
H	-6.390200	-1.740289	-2.604445
N	-4.223468	0.167438	-0.964874
H	-7.272677	0.557733	-3.185415
C	-6.397194	0.445574	-2.552107
N	-3.053392	-2.008982	-0.240467
N	-2.762896	2.056225	0.081134
C	-4.119468	-2.225598	-1.056435
C	-3.755895	2.497464	-0.720187
O	-4.522230	-3.293849	-1.496633
O	-3.991530	3.666227	-1.049366
C	-2.166004	-3.057708	0.008886
C	-1.990724	-3.552191	1.311458
C	-1.342551	-3.548971	-1.019968
C	-1.041224	-4.544971	1.573252
C	-0.412931	-4.562440	-0.770654
C	-0.279127	-5.049847	0.526288
H	0.440988	-5.838629	0.725616
C	-1.935847	3.130497	0.605157
C	-0.943401	3.691432	-0.449477
H	-2.605719	3.971436	0.837731
C	-1.212143	2.748206	1.876954
C	0.102801	4.610759	0.154002
H	-1.559256	4.277992	-1.140915
H	-1.921047	2.291228	2.572313
H	-0.443997	1.998645	1.662227
C	-0.567948	3.970963	2.508360
C	0.298395	4.727265	1.535284
H	-1.356603	4.640214	2.883751
H	0.025542	3.677177	3.382846
C	1.307023	5.573521	2.009119
C	1.911872	6.185807	-0.235159
C	-0.297210	2.601995	-1.269671
C	2.109667	6.298902	1.140392
H	1.460595	5.654580	3.083354
H	2.534035	6.745140	-0.928090
C	0.811879	1.886384	-0.817518
C	-0.806703	2.261221	-2.522687
H	2.890693	6.945242	1.531139
N	1.388791	0.914265	-1.530674
H	1.260476	2.097686	0.148058
H	-1.686968	2.779596	-2.895103
C	0.929171	0.637672	-2.759395
H	1.480479	-0.116574	-3.311323
H	-0.906823	-4.937035	2.574279
H	0.196581	-4.971343	-1.568658
O	-2.777647	-2.988721	2.255399
O	-1.493671	-2.934020	-2.216394
C	-2.605187	-3.413811	3.586261
H	-1.587100	-3.211573	3.944260
H	-3.313015	-2.833874	4.180151
H	-2.827906	-4.482544	3.699300
C	-0.663670	-3.344765	-3.275555
H	-0.935276	-2.720315	-4.127970
H	0.398754	-3.191324	-3.038078
H	-0.828760	-4.398357	-3.532968
C	0.917066	5.346751	-0.714995
H	0.764415	5.246518	-1.787691
C	-0.178091	1.284062	-3.285962
H	-0.538787	1.022174	-4.275351
C	-0.655900	-0.326108	2.504128
C	-1.494821	0.123244	4.715563
C	0.676070	-0.343545	3.004151
C	-0.173867	0.144816	5.218311
H	-2.327975	0.289625	5.392317
C	1.727771	-0.644001	2.110345
C	0.890183	-0.084433	4.381086
H	-0.004700	0.334315	6.274125
H	1.909393	-0.085737	4.757732
H	2.758090	-0.669721	2.461872
C	1.443788	-1.006879	0.806554
C	0.092447	-0.936077	0.391857
H	-0.181591	-1.164839	-0.633214
N	-0.889710	-0.524525	1.171784
C	-1.735893	-0.099822	3.380420
H	-2.741349	-0.120445	2.969627
Pd	2.728652	-0.579216	-0.783009
C	2.500742	-2.614346	0.314452
C	3.750518	-2.304519	-0.308390
H	2.541983	-2.864021	1.368676
H	1.760532	-3.182533	-0.243383
H	3.992482	-2.692057	-1.295098
C	4.879242	-1.932202	0.574617
O	4.761059	-1.674426	1.759401
O	6.029754	-1.888185	-0.093020
C	7.114529	-1.248168	0.594988
C	8.254069	-1.125338	-0.385597
H	7.381540	-1.846922	1.472192
H	6.764527	-0.268366	0.930537
H	9.114729	-0.655219	0.101249
H	8.562091	-2.106695	-0.760529
H	7.954133	-0.502072	-1.232800
C	4.953942	0.529239	-1.978629
O	5.114420	0.890018	-0.810737
O	3.961698	-0.188693	-2.397571
C	5.950860	0.890547	-3.062109
H	6.673166	1.617220	-2.685710
H	6.478385	-0.014151	-3.384285
H	5.433515	1.294227	-3.937403

104

cis-T25-Q_C3_TSIII Eopt -2905.025424

Pd	-2.130757	-1.091103	-0.034401
C	-4.242124	-0.962148	-1.926069
C	-2.997500	-2.958410	-1.965571
C	-5.077250	-1.422282	-2.935199
C	-3.794825	-3.476989	-2.976031
H	-5.870027	-0.771745	-3.288209
H	-3.563242	-4.463422	-3.363168
N	-3.255855	-1.741087	-1.489717
H	-5.487986	-3.080493	-4.244213
C	-4.848069	-2.697018	-3.454520
N	-1.248940	-2.893298	-0.359898
N	-3.381509	0.580732	-0.320958
C	-1.777543	-3.621932	-1.380526
C	-4.288235	0.405451	-1.304686
O	-1.368554	-4.679112	-1.839447
O	-5.074920	1.245233	-1.758806
C	0.059599	-3.149470	0.056931
C	1.134266	-2.906953	-0.820324
C	0.331119	-3.523267	1.382950
C	2.454111	-3.057647	-0.384509
C	1.649003	-3.660009	1.826845
C	2.691884	-3.432831	0.933664
H	3.717397	-3.546797	1.274912
C	-3.323629	1.938531	0.188537
C	-2.710719	2.934431	-0.842987
H	-4.357436	2.284825	0.337613
C	-2.602301	2.029714	1.518618
C	-2.390035	4.284963	-0.232039
H	-3.488378	3.074835	-1.602113
H	-3.002388	1.272070	2.199227
H	-1.536178	1.813538	1.382288
C	-2.775629	3.417183	2.114843
C	-2.393260	4.509629	1.150010
H	-3.826903	3.551733	2.410487
H	-2.186742	3.513904	3.035299
C	-2.052647	5.778321	1.632903
C	-1.719648	6.591439	-0.604389
C	-1.513845	2.347171	-1.553171
C	-1.718125	6.813972	0.772170
H	-2.050624	5.946287	2.708108
H	-1.459605	7.391946	-1.291206
C	-0.228037	2.446411	-1.031377
C	-1.664544	1.633406	-2.744540
H	-1.453148	7.789588	1.170221
N	0.842581	1.854730	-1.589142
H	-0.043679	3.016863	-0.128222
H	-2.653545	1.538460	-3.186015
C	0.684917	1.175790	-2.734801
H	1.583355	0.706980	-3.122077
H	3.283170	-2.855056	-1.052397
H	1.866778	-3.952225	2.847254
O	0.784049	-2.501730	-2.056958
O	-0.758134	-3.712679	2.165136
C	1.798740	-2.442262	-3.041620
H	2.293685	-3.415860	-3.147515
H	1.285030	-2.201367	-3.974673
H	2.530028	-1.660645	-2.807772
C	-0.541857	-4.058231	3.511194
H	-0.007681	-5.012801	3.601463
H	0.018226	-3.277073	4.043260
H	-1.531928	-4.152672	3.959069
C	-2.052210	5.336412	-1.092679
H	-2.046475	5.153537	-2.165250
C	-0.554355	1.058592	-3.348166
H	-0.642846	0.501233	-4.274997
C	-1.246307	-0.716308	2.860783
C	-2.904457	-1.290159	4.511814
C	-0.349746	-0.321039	3.890715
C	-2.019779	-0.902282	5.543743
H	-3.890613	-1.667792	4.765180
C	0.343532	-0.217990	1.244173
C	0.915296	0.189301	3.521661
C	-0.768473	-0.426330	5.239915
H	-2.334974	-0.982230	6.579775
C	1.284660	0.237876	2.197498
H	0.595221	-0.194703	0.188295
H	-0.081866	-0.122298	6.025591
H	1.591146	0.545612	4.296011
Pd	2.524336	1.295143	-0.393816
C	2.577124	0.835543	1.781975
C	3.576686	0.166852	1.045753
H	1.965858	2.197587	0.758383
H	2.948356	1.639256	2.418653
H	3.432597	-0.855833	0.705721
C	4.966109	0.684094	1.143909
O	5.281760	1.689275	1.743085
O	5.813127	-0.116272	0.493893
C	7.138696	0.409829	0.329497
C	7.940777	-0.623029	-0.423184
H	7.561173	0.623840	1.316333
H	7.053266	1.347864	-0.226294
H	8.964799	-0.264300	-0.569139
H	7.981650	-1.568925	0.126591
H	7.499881	-0.810678	-1.406789
C	4.510956	0.705545	-2.270229
O	3.355201	0.192374	-1.978274
O	4.984343	1.700825	-1.723834
C	5.258252	-0.037491	-3.359669
H	5.481464	-1.055054	-3.020229
H	4.635157	-0.124376	-4.255805
H	6.187551	0.478769	-3.606212
C	-2.529492	-1.198570	3.193223
H	-3.188522	-1.502705	2.384978
N	-0.870159	-0.621895	1.550426

96

cis-T25-Q_C5_IN2 Eopt -2767.369346

Pd	-2.553094	0.618703	0.273171
C	-3.614021	2.821496	-1.172454
C	-5.026819	0.946601	-1.048355
C	-4.523915	3.496417	-1.975854
C	-5.980362	1.567423	-1.841963
H	-4.270577	4.494449	-2.316327
H	-6.887043	1.022428	-2.081743
N	-3.908931	1.601187	-0.733303
H	-6.450894	3.367193	-2.925237
C	-5.720636	2.858810	-2.302038
N	-3.983932	-0.812762	0.146479
N	-1.595086	2.514947	0.073106
C	-5.116257	-0.460695	-0.518660
C	-2.294116	3.365898	-0.706985
O	-6.117069	-1.137403	-0.711930
O	-1.978723	4.519668	-1.025276
C	-3.850372	-2.106826	0.656749
C	-3.722616	-2.308804	2.040170
C	-3.769014	-3.216683	-0.201298
C	-3.526894	-3.589807	2.558794
C	-3.586381	-4.501977	0.312758
C	-3.467676	-4.671361	1.686755
H	-3.322945	-5.670159	2.088563
C	-0.489972	3.163137	0.765611
C	0.728316	3.525937	-0.125065
H	-0.861365	4.138879	1.117928
C	-0.033677	2.376247	1.974624
C	1.898802	4.041123	0.692793
H	0.375150	4.337708	-0.769796
H	-0.913176	2.046865	2.538036
H	0.505836	1.481311	1.647808
C	0.865012	3.228504	2.855351
C	1.983216	3.875747	2.080055
H	0.259117	4.012336	3.333924
H	1.282636	2.625858	3.671969
C	3.119816	4.338945	2.752368
C	4.073175	5.126145	0.691078
C	1.167804	2.413326	-1.045225
C	4.159169	4.957250	2.072503
H	3.183383	4.202541	3.830217
H	4.881231	5.603088	0.144167
C	2.126134	1.469815	-0.674173
C	0.641855	2.320020	-2.333829
H	5.036623	5.300572	2.613244
N	2.542449	0.496186	-1.494525
H	2.587985	1.497850	0.306751
H	-0.112803	3.036013	-2.649379
C	2.066387	0.447428	-2.745688
H	2.456397	-0.341636	-3.377098
H	-3.431773	-3.752649	3.625858
H	-3.529348	-5.362061	-0.343841
O	-3.793292	-1.185038	2.800031
O	-3.851269	-2.930739	-1.522255
C	-3.748698	-1.342578	4.196386
H	-2.790343	-1.767969	4.527371
H	-3.864003	-0.341411	4.615885
H	-4.565022	-1.981265	4.557030
C	-3.800369	-4.004662	-2.428340
H	-3.905415	-3.564450	-3.421390
H	-2.842891	-4.539956	-2.365847
H	-4.622575	-4.711172	-2.259321
C	2.950718	4.670272	0.016139
H	2.883410	4.788365	-1.063295
C	1.112320	1.342331	-3.200998
H	0.745937	1.265716	-4.219270
C	-0.319897	-1.274699	0.088817
C	-0.645890	-0.607594	2.289633
C	-0.889419	-1.618887	-1.159772
C	1.042685	-1.582242	0.346984
C	0.636635	-1.043666	2.664226
H	-1.319206	-0.159103	3.010959
C	-0.110573	-2.249470	-2.099025
H	-1.944978	-1.436233	-1.331895
C	1.892196	-1.994608	-0.728118
H	0.941006	-0.983543	3.703445
H	-0.560916	-2.577478	-3.032606
C	1.282967	-2.392908	-1.902811
H	1.891268	-2.753052	-2.730834
Pd	3.714475	-1.067827	-0.773332
C	6.494158	-0.522571	-0.438634
O	7.601668	-0.021307	-0.392422
O	5.412335	0.053357	-0.860956
N	4.984847	-2.477121	-0.079259
C	4.709932	-3.704392	0.204438
C	5.724131	-4.690971	0.686993
H	6.482484	-4.862302	-0.084818
H	5.235533	-5.635615	0.926634
H	6.242993	-4.309757	1.572218
O	3.494587	-4.189404	0.086051
C	6.347506	-1.974320	0.049988
H	7.048391	-2.589971	-0.526515
C	1.505352	-1.439703	1.674807
H	2.542810	-1.679620	1.893592
N	-1.078293	-0.648124	1.044122
H	6.672863	-2.003383	1.097718
H	2.899130	-3.452631	-0.251400

104

cis-T25-Q_C5_IN3 Eopt -2905.005521

Pd	-2.744463	0.672013	0.452028
C	-3.775597	3.120437	-0.557962
C	-5.325667	1.356079	-0.466052
C	-4.718202	3.963359	-1.132738
C	-6.314332	2.146519	-1.033486
H	-4.421556	4.977535	-1.376795
H	-7.291265	1.707441	-1.204911

N	-4.119373	1.876411	-0.238316
H	-6.756475	4.105750	-1.808291
C	-6.000141	3.465350	-1.363239
N	-4.310858	-0.613424	0.370340
N	-1.639285	2.503367	0.327846
C	-5.478498	-0.095060	-0.093176
C	-2.362195	3.501103	-0.222994
O	-6.555502	-0.661783	-0.222896
O	-1.996579	4.665041	-0.434164
C	-4.242307	-1.964410	0.721864
C	-3.975473	-2.333777	2.049681
C	-4.367700	-2.971027	-0.250087
C	-3.841501	-3.677583	2.402791
C	-4.248209	-4.317490	0.099562
C	-3.985883	-4.652803	1.422254
H	-3.888842	-5.699525	1.696126
C	-0.377855	2.970600	0.889807
C	0.692396	3.368161	-0.158910
H	-0.590414	3.910520	1.424278
C	0.210981	1.987289	1.876782
C	2.005334	3.754359	0.494428
H	0.284600	4.246149	-0.669980
H	-0.574645	1.660863	2.565715
H	0.565430	1.101058	1.342325
C	1.355725	2.613117	2.660316
C	2.339328	3.356234	1.792965
H	0.942525	3.315721	3.399339
H	1.884339	1.840927	3.232907
C	3.601810	3.684117	2.299339
C	4.179200	4.812191	0.255773
C	0.934576	2.316553	-1.212802
C	4.517513	4.404202	1.546264
H	3.863749	3.359514	3.304137
H	4.883907	5.382303	-0.343608
C	1.841021	1.272547	-1.014707
C	0.280803	2.377113	-2.441793
H	5.493199	4.645149	1.959489
N	2.087484	0.347071	-1.949679
H	2.408041	1.166989	-0.094274
H	-0.441058	3.170178	-2.620016
C	1.491382	0.441971	-3.145021
H	1.742974	-0.320996	-3.872142
H	-3.637242	-3.969201	3.426192
H	-4.349435	-5.098105	-0.645122
O	-3.854404	-1.303189	2.925782
O	-4.576681	-2.529161	-1.513264
C	-3.646012	-1.623535	4.278765
H	-2.696240	-2.156574	4.428575
H	-3.614301	-0.671375	4.811715
H	-4.464757	-2.234459	4.680032
C	-4.725983	-3.492357	-2.525945
H	-4.902166	-2.934336	-3.447177
H	-3.820124	-4.104244	-2.637504

H	-5.584378	-4.148052	-2.332941
C	2.933971	4.481849	-0.259092
H	2.666096	4.784158	-1.269486
C	0.580039	1.444890	-3.428915
H	0.110611	1.485529	-4.406293
C	-0.724676	-1.362104	-0.185595
C	-0.753598	-0.901384	2.092210
C	-1.454641	-1.545589	-1.383201
C	0.634725	-1.772831	-0.112619
C	0.524601	-1.452184	2.271371
H	-1.309863	-0.484334	2.924137
C	-0.832966	-2.127506	-2.460551
H	-2.506094	-1.280247	-1.412249
C	1.303351	-2.112015	-1.325577
H	0.948058	-1.519959	3.267350
H	-1.405331	-2.331328	-3.362173
C	0.561050	-2.375210	-2.450616
H	1.049243	-2.676998	-3.374932
C	1.257270	-1.791875	1.157865
H	2.289861	-2.117572	1.250832
N	-1.322409	-0.788129	0.906474
Pd	3.182055	-1.400108	-1.419098
C	3.432891	-3.607322	-1.293155
C	4.594783	-2.959385	-0.915344
H	2.788465	-4.027832	-0.528003
H	3.290444	-3.958677	-2.310012
H	5.397296	-2.754778	-1.617612
C	4.909641	-2.799562	0.533049
O	4.161982	-3.118444	1.435317
O	6.123098	-2.285802	0.702711
C	6.441667	-1.901519	2.050360
C	7.846744	-1.352203	2.038891
H	6.342441	-2.775887	2.701062
H	5.705785	-1.151333	2.355364
H	8.128610	-1.034722	3.048043
H	8.562781	-2.108719	1.702706
H	7.917860	-0.487252	1.372727
C	5.029832	0.371791	-0.341116
O	4.291116	0.152517	0.632276
O	4.920035	-0.213160	-1.483620
C	6.115750	1.421750	-0.260098
H	6.430624	1.556373	0.777096
H	6.966129	1.165932	-0.896528
H	5.698777	2.374477	-0.605947

104

cis-T25-Q_C5_IN4 Eopt -2905.057991

Pd	-2.724041	0.570144	0.256153
C	-4.288827	2.691033	-0.800114
C	-5.444391	0.664485	-0.511881
C	-5.413749	3.295460	-1.345520
C	-6.605025	1.209912	-1.041508
H	-5.341707	4.330238	-1.662026
H	-7.483222	0.578096	-1.119784

N	-4.355491	1.424798	-0.398720
H	-7.477628	2.992487	-1.874893
C	-6.582178	2.541832	-1.456253
N	-4.003419	-1.013871	0.334592
N	-2.038891	2.554460	-0.001711
C	-5.277568	-0.764458	-0.066652
C	-2.959605	3.355448	-0.586793
O	-6.224277	-1.539639	-0.097670
O	-2.822556	4.540551	-0.908046
C	-3.634255	-2.310411	0.702712
C	-3.187142	-2.572445	2.008044
C	-3.618940	-3.352479	-0.240438
C	-2.717219	-3.838723	2.361033
C	-3.170541	-4.626291	0.113517
C	-2.719379	-4.851173	1.408157
H	-2.360751	-5.839232	1.682233
C	-0.860245	3.286514	0.426494
C	0.165716	3.536804	-0.703517
H	-1.197939	4.295666	0.706750
C	-0.172613	2.674067	1.630234
C	1.344026	4.338214	-0.188731
H	-0.362297	4.129134	-1.459486
H	-0.926950	2.431758	2.387882
H	0.316942	1.737220	1.348290
C	0.853329	3.642149	2.209461
C	1.692654	4.341858	1.167112
H	0.329060	4.409127	2.797982
H	1.514053	3.113883	2.907925
C	2.836180	5.042342	1.567010
C	3.263267	5.735339	-0.696356
C	0.645945	2.267992	-1.364418
C	3.618465	5.732531	0.652239
H	3.112409	5.037239	2.619400
H	3.864620	6.275172	-1.422493
C	1.707122	1.540438	-0.830684
C	0.065425	1.778867	-2.534576
H	4.503620	6.266421	0.987058
N	2.172920	0.405072	-1.376128
H	2.218456	1.871074	0.068550
H	-0.775743	2.305782	-2.976493
C	1.641453	-0.025676	-2.525576
H	2.057008	-0.930283	-2.948169
H	-2.365134	-4.044636	3.364799
H	-3.155494	-5.432502	-0.610221
O	-3.237997	-1.518540	2.862489
O	-4.026616	-3.011532	-1.485308
C	-2.832507	-1.740412	4.189973
H	-1.773883	-2.031344	4.246943
H	-2.975748	-0.791740	4.710767
H	-3.442326	-2.513330	4.675000
C	-4.131480	-4.037202	-2.440186
H	-4.525216	-3.567960	-3.343488
H	-3.153413	-4.487155	-2.660717

H	-4.823452	-4.822250	-2.110388
C	2.135357	5.038871	-1.104999
H	1.854968	5.025807	-2.156291
C	0.583741	0.636253	-3.130808
H	0.167750	0.244111	-4.052615
C	-0.515074	-1.424155	-0.152375
C	-0.511356	-0.467185	1.967723
C	-1.184273	-1.651921	-1.375106
C	0.707141	-2.101918	0.118444
C	0.655215	-1.152015	2.334462
H	-1.012775	0.190071	2.666913
C	-0.650443	-2.527955	-2.286018
H	-2.139034	-1.167925	-1.550950
C	1.314412	-2.893463	-0.903201
H	1.061475	-1.021378	3.331167
H	-1.187015	-2.733786	-3.207987
C	0.607616	-3.122925	-2.062929
H	1.049201	-3.749082	-2.835038
C	1.287436	-1.933680	1.398443
H	2.211380	-2.442407	1.651479
N	-1.055074	-0.562234	0.768829
Pd	3.464785	-0.534743	-0.062292
C	2.742084	-3.341405	-0.779365
C	3.717495	-2.229446	-1.167389
H	2.993883	-3.688907	0.226919
H	2.908980	-4.205962	-1.436967
H	3.615404	-1.932896	-2.216285
C	5.130427	-2.631160	-0.896651
O	5.472925	-3.576076	-0.219184
O	6.002131	-1.793835	-1.491115
C	7.377371	-2.020057	-1.172141
C	8.176036	-0.910502	-1.813063
H	7.674490	-3.007759	-1.542221
H	7.487557	-2.029755	-0.082828
H	9.241176	-1.038436	-1.593763
H	8.044800	-0.911757	-2.899778
H	7.857148	0.063835	-1.429549
C	4.353437	-0.009471	2.223621
O	3.625497	0.878256	1.705238
O	4.586955	-1.101991	1.597140
C	4.986972	0.193506	3.568474
H	5.051692	-0.754336	4.108093
H	6.006796	0.568426	3.426386
H	4.424796	0.931367	4.144484

104

cis-T25-Q_C5_IN5 Eopt -2905.020660

Pd	-2.900620	0.448611	0.106955
C	-4.230972	2.311217	-1.565778
C	-5.404846	0.307351	-1.195094
C	-5.226459	2.777975	-2.414100
C	-6.437142	0.716673	-2.026734
H	-5.099825	3.752799	-2.872159
H	-7.274185	0.044278	-2.180958

N	-4.370289	1.121761	-0.987599
H	-7.136633	2.313384	-3.289472
C	-6.341663	1.969484	-2.633794
N	-4.142624	-1.161165	0.169611
N	-2.178017	2.381147	-0.338758
C	-5.310625	-1.033337	-0.514319
C	-2.973566	3.049080	-1.205411
O	-6.214164	-1.851386	-0.622915
O	-2.785197	4.176656	-1.674923
C	-3.823614	-2.377735	0.778238
C	-3.645536	-2.445752	2.169464
C	-3.591602	-3.530664	0.008309
C	-3.244507	-3.635431	2.780034
C	-3.208774	-4.727917	0.615848
C	-3.037472	-4.763711	1.994253
H	-2.733639	-5.692614	2.468380
C	-1.114320	3.215076	0.194420
C	0.088246	3.409073	-0.758137
H	-1.533940	4.228385	0.294119
C	-0.626132	2.786981	1.563101
C	1.123679	4.319572	-0.124095
H	-0.323663	3.931192	-1.629565
H	-1.486966	2.538874	2.193775
H	-0.005291	1.889341	1.479879
C	0.172964	3.917240	2.198904
C	1.163173	4.555286	1.255513
H	-0.523299	4.693206	2.549246
H	0.701427	3.555423	3.089926
C	2.124139	5.436028	1.765037
C	3.009286	5.819835	-0.437747
C	0.713907	2.133600	-1.273165
C	3.036518	6.071031	0.934353
H	2.150197	5.620336	2.837245
H	3.721711	6.303647	-1.099941
C	1.728206	1.462095	-0.585430
C	0.334344	1.615912	-2.511429
H	3.772955	6.751413	1.353279
N	2.357434	0.380985	-1.068460
H	2.073251	1.800069	0.386978
H	-0.459858	2.101795	-3.072482
C	2.014508	-0.064912	-2.280597
H	2.569006	-0.916349	-2.659911
H	-3.105399	-3.693902	3.853006
H	-3.033195	-5.620500	0.027112
O	-3.878648	-1.289559	2.842013
O	-3.733565	-3.369625	-1.328757
C	-3.748925	-1.316414	4.241592
H	-2.721015	-1.556551	4.549102
H	-4.004983	-0.312943	4.586846
H	-4.436330	-2.040158	4.697748
C	-3.599056	-4.508719	-2.141267
H	-3.797052	-4.175233	-3.161396
H	-2.584866	-4.928357	-2.085640

H	-4.325852	-5.283791	-1.867913
C	2.058829	4.950222	-0.952717
H	2.026984	4.752694	-2.022106
C	0.998797	0.511268	-3.028226
H	0.744660	0.103848	-4.001383
C	-0.527757	-1.325678	0.338189
C	-0.989260	-0.211839	2.324150
C	-0.979897	-1.791897	-0.919005
C	0.747973	-1.718608	0.822774
C	0.224586	-0.618796	2.897537
H	-1.689762	0.401956	2.876824
C	-0.178832	-2.621507	-1.659853
H	-1.977786	-1.528371	-1.252567
C	1.621599	-2.449487	-0.041455
C	1.119996	-1.314333	2.123462
H	0.463702	-0.323174	3.912852
C	1.131422	-2.924115	-1.238930
H	-0.544671	-3.018573	-2.602271
H	2.105589	-1.555659	2.507003
N	-1.325061	-0.497081	1.080280
C	4.052189	-2.498344	-0.694406
Pd	3.893797	-0.617311	0.262984
H	3.796293	-2.356097	-1.741040
C	5.383838	-3.114191	-0.453479
O	5.719783	-3.691629	0.556538
O	6.172226	-2.949222	-1.523348
C	7.510363	-3.443773	-1.381105
C	8.257260	-3.092021	-2.644458
H	7.471220	-4.524880	-1.209848
H	7.960155	-2.985073	-0.494690
H	9.289747	-3.449964	-2.579005
H	7.787084	-3.553797	-3.518321
H	8.275600	-2.008129	-2.793392
O	5.212448	1.236577	0.223277
C	4.588224	1.697924	1.213501
O	3.625833	1.053104	1.742511
C	4.946499	3.055042	1.753189
H	6.028123	3.202943	1.709898
H	4.473991	3.817874	1.125398
H	4.582276	3.177212	2.774876
C	3.050756	-2.568280	0.298031
H	3.331897	-3.030966	1.243083
H	1.776335	-3.521609	-1.876906
H	4.907953	-1.185668	1.241508

96

cis-T25-Q_C5_TSI Eopt -2767.361484

Pd	-2.519801	0.630677	0.326145
C	-3.766897	2.824090	-0.976752
C	-5.054948	0.858953	-0.901727
C	-4.747852	3.480524	-1.708261
C	-6.077005	1.458675	-1.623259
H	-4.569001	4.507652	-2.006941
H	-6.957841	0.870659	-1.857631

N	-3.967025	1.565626	-0.595595
H	-6.701146	3.278506	-2.588763
C	-5.916050	2.785990	-2.022072
N	-3.861043	-0.888095	0.164489
N	-1.693794	2.578935	0.187264
C	-5.035065	-0.576855	-0.447144
C	-2.456961	3.418198	-0.545983
O	-5.995754	-1.307147	-0.648509
O	-2.196940	4.587166	-0.854487
C	-3.624084	-2.200269	0.583014
C	-3.427618	-2.481274	1.944778
C	-3.503020	-3.245335	-0.349158
C	-3.115032	-3.774020	2.368266
C	-3.208370	-4.543700	0.070907
C	-3.015304	-4.790316	1.424488
H	-2.779183	-5.798456	1.752697
C	-0.554231	3.242887	0.799466
C	0.617097	3.529732	-0.175291
H	-0.897617	4.241419	1.111248
C	-0.049555	2.524289	2.033035
C	1.848253	4.051137	0.543417
H	0.246198	4.317573	-0.840721
H	-0.904402	2.244594	2.658858
H	0.467143	1.603581	1.742673
C	0.902628	3.422205	2.806457
C	1.998934	3.976134	1.933135
H	0.333664	4.255552	3.244911
H	1.344010	2.877205	3.650343
C	3.185419	4.437853	2.513891
C	4.058602	5.042981	0.357605
C	0.964902	2.355275	-1.056584
C	4.209974	4.965612	1.741449
H	3.300790	4.371646	3.594001
H	4.855204	5.445507	-0.261039
C	1.911815	1.401247	-0.687705
C	0.362796	2.209096	-2.307094
H	5.127140	5.307908	2.212367
N	2.253541	0.372454	-1.475545
H	2.436683	1.470964	0.259033
H	-0.383368	2.933507	-2.623303
C	1.707140	0.273001	-2.693452
H	2.047671	-0.552756	-3.306184
H	-2.961918	-3.997130	3.417455
H	-3.117547	-5.353539	-0.643208
O	-3.554811	-1.419077	2.781057
O	-3.658141	-2.883683	-1.645088
C	-3.412725	-1.658617	4.159067
H	-2.404552	-2.021284	4.405905
H	-3.582867	-0.698785	4.650488
H	-4.151574	-2.384563	4.521573
C	-3.636540	-3.902161	-2.614362
H	-3.827074	-3.411144	-3.570177
H	-2.660250	-4.405157	-2.651279
H	-4.420159	-4.647190	-2.429120
C	2.885941	4.588937	-0.227153
H	2.767931	4.634739	-1.307699
C	0.751567	1.170756	-3.142556
H	0.326355	1.052880	-4.133712
C	-0.251357	-1.284062	0.157438
C	-0.574986	-0.512411	2.320868
C	-0.791839	-1.579362	-1.117077
C	1.045377	-1.759306	0.484298
C	0.645360	-1.059518	2.753332
H	-1.221742	0.018754	3.008507
C	-0.063074	-2.324997	-2.013995
H	-1.802434	-1.258181	-1.348431
C	1.872437	-2.348133	-0.525044
H	0.923415	-0.981203	3.798786
H	-0.510510	-2.596257	-2.966647
C	1.275959	-2.669458	-1.734950
H	1.867630	-3.163706	-2.503406
Pd	3.596446	-1.062206	-0.773750
H	2.855763	-3.201814	-0.073330
C	6.292544	-0.222293	-0.659098
O	7.317129	0.425325	-0.725275
O	5.111597	0.231742	-0.988038
N	5.030962	-2.274266	-0.113539
C	4.827609	-3.485830	0.335827
C	5.977036	-4.325086	0.823660
H	6.722038	-4.456815	0.031689
H	5.603721	-5.299636	1.138040
H	6.481152	-3.838422	1.665756
O	3.662642	-4.014607	0.388467
C	6.350231	-1.673840	-0.166958
H	7.013977	-2.223938	-0.847435
C	1.483610	-1.620280	1.820426
H	2.466698	-1.996506	2.089537
N	-0.981841	-0.564570	1.066662
H	6.832652	-1.666879	0.818933

104

cis-T25-Q_C5_TSII Eopt -2904.997429

Pd	-2.817599	0.662423	0.338975
C	-3.852867	2.964055	-0.962023
C	-5.312280	1.121571	-0.902288
C	-4.764952	3.705757	-1.701439
C	-6.268856	1.809703	-1.634354
H	-4.493544	4.714220	-1.993842
H	-7.195428	1.301939	-1.879735
N	-4.169260	1.729012	-0.583177
H	-6.718633	3.678516	-2.603403
C	-5.986452	3.117837	-2.029215
N	-4.287974	-0.725921	0.169474
N	-1.811535	2.532517	0.206344
C	-5.423986	-0.311637	-0.451770
C	-2.505002	3.445210	-0.506726
O	-6.443065	-0.954413	-0.665008

O	-2.163386	4.604662	-0.771274
C	-4.165830	-2.054983	0.583293
C	-4.013597	-2.358225	1.945559
C	-4.113917	-3.100581	-0.354303
C	-3.820642	-3.675356	2.365804
C	-3.934978	-4.421486	0.061407
C	-3.790201	-4.691228	1.416802
H	-3.648194	-5.717840	1.742314
C	-0.656297	3.104889	0.881484
C	0.540471	3.440912	-0.043597
H	-0.970144	4.084212	1.277344
C	-0.194173	2.260608	2.049133
C	1.753224	3.900646	0.746330
H	0.195061	4.277050	-0.660943
H	-1.066456	1.956266	2.637292
H	0.288166	1.351033	1.677943
C	0.776132	3.042995	2.919441
C	1.884920	3.681054	2.122480
H	0.223468	3.830145	3.453691
H	1.204424	2.393297	3.693293
C	3.060178	4.084982	2.766292
C	3.955619	4.926888	0.700636
C	0.930779	2.336657	-0.997862
C	4.090178	4.700987	2.070187
H	3.160438	3.905866	3.835060
H	4.752913	5.408876	0.141875
C	1.832052	1.330946	-0.646390
C	0.446293	2.325839	-2.306075
H	4.995717	5.001850	2.589840
N	2.247048	0.393126	-1.504351
H	2.255299	1.284076	0.351787
H	-0.269854	3.085330	-2.610343
C	1.828210	0.431153	-2.775541
H	2.257678	-0.313026	-3.436545
H	-3.705644	-3.916131	3.416012
H	-3.900710	-5.232128	-0.656805
O	-4.057717	-1.292447	2.786295
O	-4.218538	-2.718802	-1.649197
C	-3.975005	-1.551235	4.165697
H	-3.011483	-2.006155	4.436898
H	-4.069357	-0.582378	4.659740
H	-4.786639	-2.208462	4.502938
C	-4.199119	-3.724683	-2.631128
H	-4.318464	-3.212765	-3.587517
H	-3.247233	-4.273590	-2.627438
H	-5.026245	-4.432894	-2.496483
C	2.796264	4.526435	0.053188
H	2.689837	4.688012	-1.017479
C	0.913852	1.378841	-3.209526
H	0.584053	1.375112	-4.243297
C	-0.647656	-1.305871	0.057600
C	-0.939621	-0.703172	2.282230
C	-1.225984	-1.530936	-1.212723
C	0.685689	-1.730231	0.318695
C	0.314835	-1.222905	2.641629
H	-1.589156	-0.243918	3.018363
C	-0.490194	-2.160742	-2.187255
H	-2.261481	-1.254968	-1.380384
C	1.477156	-2.172536	-0.781020
H	0.624144	-1.206591	3.681044
H	-0.949632	-2.379064	-3.147637
C	0.874212	-2.458676	-1.985557
H	1.469484	-2.833062	-2.815529
C	1.163284	-1.651812	1.647964
H	2.184354	-1.955363	1.875671
N	-1.370278	-0.673871	1.035710
Pd	3.340012	-1.330940	-0.865005
C	3.107782	-3.539393	-0.327687
C	4.416696	-3.018287	-0.257588
H	2.597978	-3.771680	0.602191
H	2.838741	-4.150797	-1.181627
H	5.128118	-3.191222	-1.060386
C	4.959854	-2.613061	1.059710
O	4.298091	-2.521912	2.080158
O	6.260330	-2.343972	0.979136
C	6.849963	-1.708361	2.124386
C	6.500057	-0.235191	2.156450
H	7.922514	-1.866848	1.993111
H	6.515967	-2.224420	3.029118
H	7.076979	0.269064	2.939331
H	6.716550	0.227584	1.189927
H	5.436074	-0.097357	2.366444
C	5.437871	-0.235046	-2.268745
O	4.825203	-0.813029	-3.171273
O	5.096042	-0.245470	-1.021003
C	6.692536	0.567951	-2.549345
H	7.528846	0.161121	-1.971503
H	6.931407	0.542437	-3.613762
H	6.548413	1.603770	-2.225303

104

cis-T25-Q_C5_TSIII Eopt -2905.000322

Pd	-2.993250	0.244442	0.187807
C	-4.401517	2.113905	-1.420790
C	-5.295039	-0.060293	-1.421471
C	-5.374698	2.551458	-2.309688
C	-6.294146	0.311771	-2.308989
H	-5.355786	3.588530	-2.626315
H	-7.006370	-0.440706	-2.630031
N	-4.409568	0.848580	-1.013106
H	-7.102592	1.952486	-3.443954
C	-6.329642	1.635148	-2.749757
N	-4.008923	-1.498212	-0.046577
N	-2.472556	2.297810	-0.013451
C	-5.087284	-1.447253	-0.872745
C	-3.304620	2.962419	-0.846052
O	-5.842147	-2.359126	-1.181477

O	-3.254375	4.158825	-1.154859
C	-3.603959	-2.725200	0.486749
C	-3.639629	-2.939162	1.873681
C	-3.083718	-3.733761	-0.342637
C	-3.161926	-4.129984	2.423898
C	-2.619761	-4.933210	0.200786
C	-2.662860	-5.114099	1.577684
H	-2.297616	-6.044557	2.002908
C	-1.528247	3.182275	0.653222
C	-0.406369	3.735597	-0.264868
H	-2.088879	4.079700	0.959572
C	-0.912930	2.569239	1.893487
C	0.525970	4.644045	0.509919
H	-0.921742	4.334375	-1.023772
H	-1.702690	2.108248	2.493123
H	-0.209257	1.776781	1.609314
C	-0.210076	3.638563	2.719532
C	0.657503	4.562251	1.901269
H	-0.971463	4.245042	3.232050
H	0.388957	3.173412	3.512898
C	1.588118	5.386025	2.544803
C	2.236198	6.367889	0.447708
C	0.364202	2.659360	-0.991801
C	2.374487	6.280578	1.832602
H	1.691044	5.317564	3.626089
H	2.842592	7.066114	-0.122293
C	1.585321	2.175216	-0.522907
C	-0.118640	2.121257	-2.186691
H	3.093193	6.907705	2.352870
N	2.297715	1.236391	-1.160696
H	2.020848	2.564861	0.390798
H	-1.060353	2.481195	-2.591153
C	1.827803	0.733674	-2.312789
H	2.429227	-0.040899	-2.778177
H	-3.186437	-4.301636	3.493476
H	-2.219541	-5.714894	-0.433858
O	-4.150764	-1.916392	2.606430
O	-3.043898	-3.431476	-1.661447
C	-4.249873	-2.102334	3.996396
H	-3.261542	-2.237298	4.459075
H	-4.712862	-1.195196	4.389458
H	-4.880889	-2.965005	4.245138
C	-2.589740	-4.426161	-2.546683
H	-2.669773	-3.997004	-3.546722
H	-1.543281	-4.695919	-2.348955
H	-3.212926	-5.327198	-2.489465
C	1.319149	5.552610	-0.199623
H	1.212281	5.606350	-1.280954
C	0.621206	1.154323	-2.853541
H	0.274239	0.723508	-3.787149
C	-0.443873	-1.210806	0.717061
C	-1.438561	-0.397703	2.655647
C	-0.596922	-1.638714	-0.620689
C	0.788450	-1.426464	1.396705
C	-0.299845	-0.688604	3.420589
H	-2.322910	0.037351	3.105936
C	0.450952	-2.261826	-1.249784
H	-1.554810	-1.505444	-1.112475
C	1.917333	-1.880587	0.640911
C	0.828767	-1.139095	2.778409
H	-0.310534	-0.509331	4.490031
C	1.720137	-2.344319	-0.643761
H	0.330528	-2.625576	-2.265781
H	1.736253	-1.312125	3.347748
N	-1.486929	-0.594600	1.352226
C	4.492699	-1.850887	0.459118
Pd	3.827157	-0.013336	-0.319997
H	4.517896	-2.468628	-0.434140
C	5.746254	-1.708751	1.228498
H	3.161117	0.063773	1.132281
O	5.821190	-1.300740	2.370996
O	6.801558	-2.073768	0.491965
C	8.080345	-1.883433	1.107526
C	9.128108	-2.250956	0.085040
H	8.139703	-2.509616	2.004427
H	8.165325	-0.839809	1.427760
H	10.128422	-2.119231	0.509977
H	9.019456	-3.294211	-0.227131
H	9.041165	-1.614615	-0.801085
O	4.970437	0.006588	-2.039168
C	4.854716	-1.000454	-2.832332
O	4.016285	-1.906947	-2.732799
C	5.877070	-1.018926	-3.952665
H	6.841178	-1.341118	-3.542785
H	5.574401	-1.717604	-4.734766
H	6.016469	-0.016341	-4.365456
C	3.277382	-1.560166	1.147917
H	3.407576	-1.416060	2.219832
H	2.566439	-2.640071	-1.256841

96

cis-T25-Q_C6_IN2 Eopt -2767.374937

Pd	-2.698699	0.552037	0.058815
C	-3.306157	2.623854	-1.786030
C	-4.622366	0.686232	-2.000427
C	-3.960439	3.226950	-2.852335
C	-5.312812	1.230103	-3.073550
H	-3.657028	4.225762	-3.146419
H	-6.081760	0.632030	-3.550641
N	-3.670542	1.403682	-1.403452
H	-5.503893	2.967997	-4.329291
C	-4.976421	2.517826	-3.493088
N	-3.982267	-0.938426	-0.400734
N	-1.697715	2.433497	-0.026901
C	-4.811639	-0.704794	-1.450192
C	-2.188400	3.236541	-0.991127
O	-5.625623	-1.468803	-1.950683

O	-1.821560	4.386985	-1.270956
C	-3.897503	-2.217966	0.155445
C	-4.391835	-2.465937	1.444424
C	-3.223584	-3.244808	-0.525639
C	-4.231180	-3.719436	2.038787
C	-3.061749	-4.501164	0.061616
C	-3.571179	-4.721424	1.336020
H	-3.448497	-5.698430	1.794853
C	-0.732051	3.089661	0.843698
C	0.605439	3.490893	0.155771
H	-1.171188	4.053945	1.148083
C	-0.473494	2.289300	2.103394
C	1.665010	3.928330	1.153494
H	0.345811	4.358017	-0.459878
H	-1.433778	1.984410	2.528095
H	0.086174	1.379250	1.859936
C	0.298053	3.115222	3.117636
C	1.541155	3.730464	2.533112
H	-0.353012	3.916680	3.498260
H	0.561274	2.498344	3.986032
C	2.582526	4.135143	3.376298
C	3.850735	4.936479	1.499200
C	1.178457	2.473658	-0.807419
C	3.729704	4.731306	2.873315
H	2.481500	3.972746	4.447713
H	4.742377	5.401234	1.088313
C	2.101580	1.506687	-0.413104
C	0.864531	2.536731	-2.166711
H	4.528094	5.032719	3.545797
N	2.708484	0.683757	-1.279204
H	2.377782	1.388972	0.628846
H	0.136858	3.270609	-2.504757
C	2.448783	0.795040	-2.589039
H	3.011826	0.140640	-3.245307
H	-4.615687	-3.921787	3.031502
H	-2.545567	-5.299264	-0.458699
O	-4.996176	-1.409921	2.047572
O	-2.740954	-2.904826	-1.745029
C	-5.573852	-1.629778	3.310710
H	-4.818513	-1.903955	4.061286
H	-6.040653	-0.685598	3.596784
H	-6.339766	-2.414838	3.273164
C	-2.015371	-3.879709	-2.454198
H	-1.719605	-3.409027	-3.393299
H	-1.117190	-4.190560	-1.903386
H	-2.631892	-4.760739	-2.672368
C	2.824795	4.536830	0.656007
H	2.920066	4.686153	-0.417388
C	1.513090	1.699367	-3.066595
H	1.313122	1.753952	-4.131631
C	-0.465550	-1.045199	1.090186
C	-1.944359	-0.490861	2.792626
C	-0.242782	-1.281600	-0.284956
C	0.580696	-1.286577	2.021880
C	-1.014509	-0.858956	3.779962
H	-2.926219	-0.108450	3.050285
H	-1.083565	-1.227592	-0.971139
C	1.896295	-1.486662	1.522112
C	0.261335	-1.200676	3.394688
H	-1.296669	-0.804901	4.825876
H	1.033265	-1.400217	4.133906
N	-1.663270	-0.542324	1.503127
H	2.713108	-1.525477	2.241345
Pd	3.881272	-0.914310	-0.679252
C	6.636766	-0.761785	-1.416811
O	7.726628	-0.457543	-1.865187
O	5.524674	-0.126094	-1.606025
N	5.183353	-2.404011	-0.228834
C	4.916264	-3.597387	0.171805
C	5.943994	-4.658463	0.404452
H	6.752067	-4.284170	1.039688
H	6.390145	-4.969383	-0.546783
H	5.476736	-5.523742	0.875517
O	3.680576	-3.989289	0.409380
C	6.557938	-2.006052	-0.512746
C	2.149655	-1.534498	0.164608
H	7.118433	-2.810003	-1.000387
C	1.024627	-1.565568	-0.715088
H	1.190159	-1.728036	-1.777241
H	7.075945	-1.762067	0.424462
H	3.079375	-3.211881	0.255256

104

cis-T25-Q_C6_IN3 Eopt -2905.007837

Pd	2.836782	-0.549321	0.140215
C	3.559267	-2.892407	-1.292933
C	4.778452	-0.963830	-1.863830
C	4.251219	-3.648075	-2.230615
C	5.503290	-1.660588	-2.819395
H	4.000335	-4.698050	-2.334330
H	6.244807	-1.122612	-3.400185
N	3.858732	-1.605738	-1.143230
H	5.790498	-3.588354	-3.733146
C	5.234991	-3.018936	-2.993349
N	4.048974	0.893310	-0.587945
N	1.925728	-2.464407	0.401268
C	4.894388	0.512255	-1.580094
C	2.467168	-3.404556	-0.397722
O	5.671571	1.211270	-2.215888
O	2.162369	-4.604386	-0.461802
C	3.893718	2.248465	-0.282776
C	4.357245	2.758933	0.938643
C	3.181280	3.094230	-1.148692
C	4.129346	4.092745	1.284421
C	2.952849	4.429639	-0.810821
C	3.433700	4.911062	0.401294
H	3.260450	5.950412	0.665879

C	0.981726	-3.000017	1.373140
C	-0.326503	-3.586750	0.766667
H	1.463685	-3.869912	1.848955
C	0.665200	-1.998559	2.463945
C	-1.359508	-3.915057	1.830838
H	-0.013016	-4.527562	0.302741
H	1.601870	-1.569165	2.828917
H	0.061329	-1.181192	2.054711
C	-0.074061	-2.663973	3.611808
C	-1.265307	-3.460194	3.150602
H	0.617529	-3.334816	4.143588
H	-0.390800	-1.910727	4.344142
C	-2.284182	-3.778751	4.056106
C	-3.468461	-5.003220	2.361478
C	-0.953481	-2.778879	-0.349600
C	-3.378999	-4.540037	3.673965
H	-2.207682	-3.415588	5.079171
H	-4.317809	-5.602759	2.046371
C	-1.962076	-1.842439	-0.128907
C	-0.591848	-3.022350	-1.677228
H	-4.160753	-4.770798	4.392366
N	-2.604833	-1.215247	-1.124760
H	-2.275972	-1.591777	0.878917
H	0.196967	-3.741957	-1.883027
C	-2.288593	-1.493856	-2.399460
H	-2.885367	-0.986280	-3.153986
H	4.490174	4.497263	2.222745
H	2.408465	5.089180	-1.476310
O	5.002842	1.866931	1.733092
O	2.730739	2.506686	-2.283204
C	5.544612	2.347521	2.938422
H	4.762381	2.718531	3.616288
H	6.050133	1.498075	3.401176
H	6.273113	3.149256	2.762509
C	1.968361	3.292451	-3.167080
H	1.704838	2.637632	-3.999272
H	1.050690	3.659243	-2.687306
H	2.545599	4.144173	-3.548212
C	-2.465410	-4.689482	1.456672
H	-2.535212	-5.040552	0.429229
C	-1.269312	-2.383471	-2.707476
H	-1.027103	-2.578971	-3.747098
C	0.520781	1.085271	0.870113
C	2.007677	0.917258	2.646855
C	0.304727	1.078293	-0.526070
C	-0.554400	1.394859	1.747104
C	1.041021	1.380654	3.556371
H	3.007564	0.645821	2.968139
H	1.156483	0.966611	-1.191373
C	-1.873662	1.411972	1.221036
C	-0.250277	1.558925	3.116833
H	1.310742	1.519985	4.597733
H	-1.046840	1.817188	3.810593
N	1.741776	0.735893	1.366263
H	-2.703492	1.489296	1.921198
C	-2.088113	1.240708	-0.127064
C	-0.972311	1.202504	-1.005577
H	-1.138447	1.171224	-2.079618
Pd	-3.792993	0.540600	-0.862837
C	-4.448792	2.447627	-1.666922
C	-5.028247	2.283028	-0.421917
H	-3.593153	3.106873	-1.777472
H	-4.926041	2.085792	-2.573101
H	-5.988598	1.786137	-0.311468
C	-4.553150	3.004282	0.790002
O	-4.917706	2.733619	1.914144
O	-3.682580	3.975529	0.491268
C	-3.105359	4.677495	1.600890
C	-4.002719	5.806312	2.058949
H	-2.149095	5.044517	1.221278
H	-2.919765	3.966806	2.410575
H	-3.509538	6.376234	2.853761
H	-4.221260	6.488306	1.231336
H	-4.943385	5.410866	2.451544
C	-5.603128	-0.478994	-2.838890
O	-4.743425	-0.042615	-3.619168
O	-5.559505	-0.364466	-1.557013
C	-6.811575	-1.229294	-3.362539
H	-6.918867	-1.076652	-4.438048
H	-6.677650	-2.299256	-3.166515
H	-7.718451	-0.915169	-2.838568

104

cis-T25-Q_C6_IN4 Eopt -2905.057606

Pd	-2.857664	0.607287	0.055282
C	-3.793674	2.524516	-1.814084
C	-4.945211	0.473352	-1.842494
C	-4.590602	3.026092	-2.834560
C	-5.775109	0.913165	-2.863825
H	-4.403657	4.033658	-3.189646
H	-6.529641	0.233963	-3.245833
N	-4.008975	1.292016	-1.363827
H	-6.231166	2.575673	-4.152500
C	-5.592778	2.206532	-3.354767
N	-4.042201	-1.016338	-0.236842
N	-2.035844	2.534181	-0.193675
C	-4.968727	-0.901026	-1.223089
C	-2.655102	3.251099	-1.155573
O	-5.755135	-1.749279	-1.622517
O	-2.374450	4.394006	-1.537696
C	-3.803012	-2.259989	0.354727
C	-4.086806	-2.463662	1.714044
C	-3.174251	-3.287249	-0.369275
C	-3.742654	-3.662303	2.342334
C	-2.840463	-4.493115	0.250081
C	-3.126380	-4.662810	1.599284
H	-2.861925	-5.598050	2.084500

C	-0.976412	3.261488	0.484298
C	0.263081	3.523601	-0.410176
H	-1.362670	4.266353	0.717762
C	-0.550751	2.606870	1.783265
C	1.381347	4.193214	0.363273
H	-0.084304	4.214867	-1.185532
H	-1.441344	2.361640	2.368972
H	-0.029332	1.664442	1.575261
C	0.344436	3.543196	2.582222
C	1.445837	4.163138	1.760583
H	-0.272775	4.350325	3.004576
H	0.778043	3.012021	3.438512
C	2.542412	4.750048	2.401420
C	3.487992	5.399496	0.288519
C	0.767732	2.291702	-1.123598
C	3.557761	5.361587	1.680700
H	2.594393	4.717004	3.487800
H	4.274708	5.877062	-0.288706
C	1.778802	1.495821	-0.587797
C	0.276237	1.937658	-2.381209
H	4.403250	5.804578	2.199654
N	2.301180	0.437685	-1.229203
H	2.222546	1.726403	0.376971
H	-0.507396	2.537944	-2.835644
C	1.854474	0.138630	-2.455135
H	2.340621	-0.684968	-2.963672
H	-3.955888	-3.824900	3.392130
H	-2.353353	-5.288208	-0.301682
O	-4.683870	-1.420704	2.345228
O	-2.899217	-2.995620	-1.662632
C	-5.017317	-1.589714	3.700222
H	-4.123864	-1.752676	4.319867
H	-5.507094	-0.663860	4.007678
H	-5.710033	-2.428665	3.844624
C	-2.290470	-3.996931	-2.439310
H	-2.175267	-3.573646	-3.438663
H	-1.302938	-4.269671	-2.042316
H	-2.916823	-4.895945	-2.498989
C	2.406727	4.817416	-0.356212
H	2.349233	4.833326	-1.442715
C	0.832919	0.858064	-3.056313
H	0.497451	0.582848	-4.051020
C	-0.693378	-1.134650	1.159229
C	-1.968452	-0.104761	2.806095
C	-0.499632	-1.458018	-0.201322
C	0.187614	-1.680163	2.135095
C	-1.179464	-0.651328	3.830892
H	-2.815439	0.533234	3.030981
C	0.560717	-2.241903	-0.566285
H	-1.213332	-1.095815	-0.934974
C	1.307916	-2.432251	1.707570
C	-0.087489	-1.414126	3.493104
H	-1.428097	-0.438893	4.865100

C	1.525023	-2.689424	0.374430
H	0.698882	-2.487476	-1.616012
H	0.568623	-1.822510	4.257446
N	-1.719521	-0.312315	1.525763
H	2.028500	-2.768639	2.449032
Pd	3.675028	-0.559170	-0.053184
C	2.799884	-3.314364	-0.118594
C	3.527677	-2.338099	-1.033489
H	2.591034	-4.251238	-0.659401
H	2.985807	-2.168562	-1.966677
C	4.924343	-2.751884	-1.338766
O	5.566466	-3.584876	-0.736794
O	5.415342	-2.063032	-2.392673
C	6.787613	-2.317028	-2.698555
C	7.172397	-1.402342	-3.836909
H	6.908426	-3.373889	-2.961732
H	7.391059	-2.132919	-1.803274
H	8.221943	-1.558191	-4.107248
H	6.556307	-1.598156	-4.720410
H	7.040410	-0.354075	-3.550870
C	4.935364	-0.044890	2.035044
O	4.964533	-1.181313	1.446140
O	4.232734	0.892234	1.569574
C	5.777139	0.151463	3.261125
H	5.837027	-0.775770	3.835831
H	6.793301	0.422193	2.953090
H	5.372927	0.961926	3.870972
H	3.455547	-3.570745	0.718394

104

cis-T25-Q_C6_IN5 Eopt -2905.025296

Pd	-2.958359	0.543663	-0.100555
C	-3.636494	2.194135	-2.300279
C	-4.794319	0.147095	-2.206863
C	-4.303811	2.558028	-3.462447
C	-5.492521	0.448493	-3.367279
H	-4.068493	3.514287	-3.916771
H	-6.200168	-0.279044	-3.750004
N	-3.914526	1.026506	-1.728756
H	-5.779171	1.933232	-4.898890
C	-5.243157	1.671928	-3.990836
N	-4.108364	-1.110952	-0.319601
N	-2.064063	2.409855	-0.509432
C	-4.894135	-1.140318	-1.427525
C	-2.572638	3.002396	-1.611217
O	-5.611178	-2.051092	-1.818842
O	-2.243945	4.091120	-2.098335
C	-3.913065	-2.274115	0.430775
C	-4.386250	-2.357392	1.749090
C	-3.141226	-3.330411	-0.082167
C	-4.101223	-3.473384	2.538866
C	-2.861265	-4.453235	0.698797
C	-3.345993	-4.508955	2.000121
H	-3.128013	-5.380382	2.610965

C	-1.061996	3.211987	0.173994
C	0.255539	3.380789	-0.627554
H	-1.461161	4.235753	0.255517
C	-0.750852	2.717025	1.572532
C	1.265750	4.197803	0.151602
H	-0.028045	3.958804	-1.513625
H	-1.685927	2.519804	2.103852
H	-0.198324	1.771127	1.518515
C	0.056171	3.757925	2.336659
C	1.191905	4.349741	1.540481
H	-0.615301	4.575676	2.638145
H	0.443655	3.325734	3.267779
C	2.169347	5.109569	2.192951
C	3.264648	5.576779	0.103634
C	0.855485	2.090255	-1.138692
C	3.195987	5.722890	1.489611
H	2.112935	5.221006	3.273912
H	4.061787	6.052595	-0.460820
C	1.862596	1.398542	-0.459401
C	0.462829	1.586047	-2.380303
H	3.941869	6.311448	2.016890
N	2.469971	0.313496	-0.957873
H	2.241395	1.742309	0.499189
H	-0.307674	2.104374	-2.944976
C	2.114338	-0.125123	-2.169696
H	2.672188	-0.971493	-2.560031
H	-4.465208	-3.545980	3.556862
H	-2.268241	-5.271888	0.308732
O	-5.099463	-1.285443	2.178791
O	-2.681425	-3.146632	-1.343378
C	-5.620039	-1.335742	3.483741
H	-4.821079	-1.398757	4.236526
H	-6.175698	-0.406489	3.622545
H	-6.301843	-2.185651	3.614976
C	-1.900225	-4.171365	-1.906762
H	-1.644929	-3.835432	-2.913268
H	-0.978553	-4.336752	-1.331717
H	-2.459016	-5.113343	-1.972656
C	2.308150	4.814107	-0.550113
H	2.358414	4.688736	-1.629602
C	1.101364	0.469669	-2.906608
H	0.840733	0.080783	-3.885848
C	-0.869887	-0.845854	1.492191
C	-2.456860	0.206623	2.821008
C	-0.478265	-1.323873	0.221984
C	-0.040016	-1.098165	2.620120
C	-1.739460	-0.083843	3.993755
H	-3.393196	0.752042	2.853634
C	0.738752	-1.924102	0.069883
H	-1.162284	-1.217622	-0.614548
C	1.232481	-1.674738	2.414955
C	-0.517682	-0.703445	3.889590
H	-2.140947	0.223116	4.953417
C	1.658061	-2.029391	1.149459
H	1.022512	-2.294808	-0.908330
H	0.091309	-0.892772	4.769668
N	-2.025025	-0.135879	1.620754
H	1.905523	-1.780910	3.262192
Pd	4.071151	-0.673089	0.253054
C	3.054860	-2.415907	0.934680
C	3.646415	-2.660794	-0.324625
H	3.590359	-2.795673	1.802486
H	3.065829	-2.630295	-1.241927
C	4.887524	-3.470755	-0.405671
O	5.483901	-3.948380	0.533705
O	5.267491	-3.608521	-1.684740
C	6.499690	-4.312543	-1.884073
C	6.796542	-4.291416	-3.363792
H	6.391595	-5.331868	-1.498066
H	7.283295	-3.819903	-1.299507
H	7.734555	-4.819219	-3.563777
H	5.998136	-4.781337	-3.930033
H	6.895519	-3.262708	-3.723590
C	5.223909	1.636803	0.463627
O	5.533094	0.928129	-0.527086
O	4.374409	1.233162	1.323101
C	5.860880	2.984698	0.670740
H	6.502347	2.942424	1.557511
H	6.459723	3.267712	-0.196402
H	5.085582	3.731932	0.858565
H	5.215514	-1.237680	1.082512

96

cis-T25-Q_C6_TSI Eopt -2767.359693

Pd	-2.656950	0.574566	0.133070
C	-3.499764	2.626344	-1.636198
C	-4.681398	0.601503	-1.832289
C	-4.249421	3.202147	-2.653398
C	-5.465542	1.116791	-2.854257
H	-4.032311	4.225160	-2.940683
H	-6.215440	0.475426	-3.304684
N	-3.752851	1.373709	-1.268708
H	-5.846318	2.861956	-4.055228
C	-5.244599	2.434015	-3.258433
N	-3.851028	-1.002131	-0.298608
N	-1.802229	2.512736	0.043872
C	-4.749128	-0.807222	-1.299344
C	-2.374942	3.292591	-0.895863
O	-5.541346	-1.613186	-1.767562
O	-2.060599	4.450188	-1.202413
C	-3.674529	-2.278500	0.243424
C	-4.023156	-2.534228	1.578391
C	-3.060124	-3.295902	-0.505904
C	-3.771281	-3.781044	2.154053
C	-2.813966	-4.547756	0.061227
C	-3.173947	-4.773175	1.384352
H	-2.981628	-5.745719	1.828327

C	-0.770659	3.191593	0.812613
C	0.519922	3.502623	0.002896
H	-1.166260	4.182101	1.087244
C	-0.428996	2.458860	2.093484
C	1.659098	3.985027	0.882506
H	0.237702	4.321125	-0.668217
H	-1.357372	2.193451	2.607715
H	0.101542	1.527418	1.862283
C	0.430145	3.331295	2.993112
C	1.635998	3.880686	2.277803
H	-0.177854	4.168154	3.368294
H	0.749286	2.765630	3.877475
C	2.746313	4.313380	3.011683
C	3.886366	4.951919	0.994236
C	0.968874	2.371271	-0.892098
C	3.864612	4.843281	2.384329
H	2.724496	4.224972	4.096185
H	4.756047	5.359687	0.487394
C	1.922166	1.433706	-0.495196
C	0.476035	2.270222	-2.194372
H	4.718800	5.165998	2.973033
N	2.382873	0.479262	-1.311693
H	2.354765	1.461996	0.499151
H	-0.259671	2.992736	-2.538098
C	1.929056	0.412782	-2.570203
H	2.362929	-0.359788	-3.195985
H	-4.040783	-3.987373	3.183099
H	-2.341902	-5.337350	-0.511152
O	-4.589033	-1.492189	2.240692
O	-2.712564	-2.950338	-1.768524
C	-5.005224	-1.716807	3.564833
H	-4.157536	-1.962395	4.220788
H	-5.463064	-0.783962	3.899185
H	-5.746921	-2.523398	3.624225
C	-2.084410	-3.927825	-2.562283
H	-1.898850	-3.455597	-3.528426
H	-1.130184	-4.249876	-2.123370
H	-2.730304	-4.802671	-2.707611
C	2.790359	4.525991	0.258773
H	2.807916	4.598026	-0.826571
C	0.963162	1.285217	-3.044236
H	0.616284	1.201533	-4.068851
C	-0.379198	-1.056654	1.105415
C	-1.726244	-0.296681	2.839622
C	-0.250551	-1.414641	-0.255887
C	0.676497	-1.345096	2.016315
C	-0.782110	-0.670868	3.811059
H	-2.665836	0.167080	3.118548
H	-1.101521	-1.280430	-0.917331
C	1.913448	-1.787727	1.490040
C	0.439974	-1.140164	3.393432
H	-1.011562	-0.529525	4.861510
H	1.227795	-1.368149	4.106959
N	-1.514186	-0.436641	1.543654
H	2.749041	-1.926335	2.173870
Pd	3.756904	-0.958054	-0.703166
C	6.467337	-0.316066	-1.171615
O	7.494729	0.256218	-1.472084
O	5.269114	0.161086	-1.392206
N	5.213408	-2.245287	-0.293902
C	4.993977	-3.516709	-0.058122
C	6.147179	-4.471384	0.106516
H	6.889859	-4.080649	0.808856
H	6.651035	-4.623141	-0.855036
H	5.769384	-5.429942	0.462599
O	3.818203	-3.999868	0.037091
C	6.536149	-1.685080	-0.481564
C	2.080326	-2.046496	0.138693
H	2.994194	-3.005664	-0.048202
H	7.172440	-2.331261	-1.097859
C	0.931611	-1.946334	-0.699838
H	1.016876	-2.242020	-1.742652
H	7.050625	-1.542867	0.479137

104

cis-T25-Q_C6_TSII Eopt -2904.998305

Pd	-3.026916	0.484083	0.152708
C	-3.838533	2.542294	-1.623846
C	-4.993858	0.508063	-1.870229
C	-4.563104	3.118286	-2.659109
C	-5.750795	1.022660	-2.912654
H	-4.347976	4.145859	-2.931123
H	-6.478503	0.376562	-3.391768
N	-4.091290	1.285274	-1.272046
H	-6.111987	2.772835	-4.112503
C	-5.531089	2.345097	-3.300274
N	-4.190333	-1.100596	-0.327830
N	-2.184366	2.433188	0.099191
C	-5.057885	-0.907333	-1.355399
C	-2.748527	3.217526	-0.841068
O	-5.819447	-1.720837	-1.860377
O	-2.458540	4.390454	-1.113841
C	-3.994137	-2.384873	0.187477
C	-4.381185	-2.688548	1.501396
C	-3.320058	-3.360474	-0.565894
C	-4.111700	-3.943816	2.050674
C	-3.055259	-4.620379	-0.025647
C	-3.456715	-4.895020	1.276342
H	-3.252105	-5.874304	1.699699
C	-1.205749	3.126874	0.923818
C	0.091006	3.536466	0.170895
H	-1.656484	4.085933	1.226095
C	-0.871631	2.359368	2.185831
C	1.171581	4.042511	1.110247
H	-0.214805	4.371066	-0.468861
H	-1.802913	2.035371	2.658561
H	-0.294263	1.461689	1.936107

C	-0.082116	3.229238	3.149153
C	1.111661	3.875633	2.498168
H	-0.741984	4.015458	3.545905
H	0.241705	2.637613	4.014691
C	2.169512	4.341504	3.287500
C	3.327338	5.142865	1.340307
C	0.646867	2.488055	-0.767770
C	3.270546	4.968656	2.722854
H	2.119134	4.202657	4.365761
H	4.182014	5.632470	0.882126
C	1.624045	1.569495	-0.382463
C	0.250021	2.469617	-2.106675
H	4.082727	5.318234	3.354304
N	2.208396	0.727021	-1.241591
H	1.971048	1.521320	0.645048
H	-0.512086	3.170254	-2.439388
C	1.857921	0.750932	-2.536259
H	2.414644	0.079764	-3.185912
H	-4.411362	-4.187787	3.063024
H	-2.540660	-5.379075	-0.603359
O	-5.001461	-1.683340	2.170999
O	-2.937673	-2.966604	-1.804470
C	-5.453063	-1.956143	3.474221
H	-4.619993	-2.195338	4.150861
H	-5.948386	-1.046205	3.818024
H	-6.172395	-2.784872	3.487811
C	-2.240446	-3.895028	-2.598641
H	-2.032279	-3.386949	-3.541646
H	-1.293399	-4.194248	-2.128615
H	-2.845135	-4.788843	-2.796666
C	2.285045	4.681711	0.550208
H	2.329325	4.805884	-0.529710
C	0.862675	1.598928	-2.999346
H	0.592153	1.587607	-4.050326
C	-0.708634	-1.046651	1.134357
C	-2.134129	-0.445912	2.867222
C	-0.537491	-1.346529	-0.236763
C	0.363879	-1.263944	2.045129
C	-1.171551	-0.774224	3.837721
H	-3.109156	-0.061399	3.145234
H	-1.391816	-1.276145	-0.903901
C	1.648390	-1.555236	1.525158
C	0.091550	-1.125361	3.425008
H	-1.421766	-0.684924	4.889312
H	0.887553	-1.304379	4.143261
N	-1.894590	-0.534114	1.571759
H	2.499663	-1.632750	2.199060
C	1.823004	-1.715834	0.166807
C	0.694792	-1.731868	-0.693979
H	0.830490	-1.958097	-1.748403
Pd	3.490758	-0.901750	-0.707996
C	3.324342	-3.136176	-0.221308
C	4.627188	-2.619365	-0.431941

H	3.101443	-3.518466	0.767955
H	2.822422	-3.632917	-1.046427
H	5.119253	-2.728382	-1.394371
C	5.466963	-2.368450	0.761019
O	5.054906	-2.365915	1.906906
O	6.731833	-2.118890	0.419798
C	7.599142	-1.723160	1.488766
C	8.911628	-1.310448	0.868385
H	7.713911	-2.563296	2.182546
H	7.126721	-0.901948	2.037073
H	9.611089	-0.992376	1.648260
H	9.362411	-2.141966	0.317865
H	8.760510	-0.477511	0.174990
C	5.225100	-0.217322	-2.774172
O	4.453783	-0.963038	-3.391673
O	5.119802	0.085249	-1.524609
C	6.411526	0.428302	-3.463267
H	7.337980	0.116241	-2.970215
H	6.440367	0.146923	-4.517240
H	6.347439	1.517134	-3.369883

104

cis-T25-Q_C6_TSIII Eopt -2905.004845

Pd	-2.995971	0.180095	-0.093186
C	-3.805342	1.882170	-2.212545
C	-4.477632	-0.361051	-2.432148
C	-4.439436	2.223819	-3.399926
C	-5.121909	-0.088787	-3.630067
H	-4.395433	3.255761	-3.730622
H	-5.615762	-0.903101	-4.149248
N	-3.853162	0.623994	-1.787181
H	-5.602565	1.462553	-5.042632
C	-5.101304	1.221597	-4.109489
N	-3.755092	-1.634970	-0.569231
N	-2.441392	2.231669	-0.278669
C	-4.382298	-1.712818	-1.772814
C	-3.020237	2.822942	-1.343140
O	-4.839512	-2.707383	-2.318207
O	-2.938557	4.010690	-1.684938
C	-3.406928	-2.807359	0.108679
C	-4.013552	-3.130540	1.331772
C	-2.370143	-3.624569	-0.373718
C	-3.600597	-4.250877	2.056375
C	-1.959957	-4.751658	0.340692
C	-2.582912	-5.049657	1.546816
H	-2.265717	-5.925414	2.105823
C	-1.654402	3.140432	0.545537
C	-0.435945	3.774019	-0.190359
H	-2.294199	3.999527	0.805236
C	-1.193221	2.489267	1.834098
C	0.443242	4.574637	0.751113
H	-0.872567	4.466158	-0.917024
H	-2.041183	1.992415	2.309348
H	-0.444252	1.719737	1.607758

C	-0.619038	3.522941	2.789716
C	0.391653	4.431533	2.141768
H	-1.442369	4.136708	3.185337
H	-0.169893	3.024901	3.658416
C	1.274743	5.171384	2.936686
C	2.240241	6.194052	0.987704
C	0.386341	2.787635	-0.989507
C	2.194168	6.044518	2.373615
H	1.233256	5.052011	4.017695
H	2.953366	6.874956	0.531735
C	1.525748	2.172785	-0.473062
C	0.048163	2.493869	-2.312666
H	2.874095	6.605105	3.009138
N	2.289358	1.322822	-1.177999
H	1.854791	2.382539	0.538750
H	-0.817557	2.976681	-2.758235
C	1.954900	1.052084	-2.448778
H	2.610070	0.352116	-2.959236
H	-4.066179	-4.509692	2.999958
H	-1.164187	-5.387936	-0.028023
O	-4.985469	-2.276853	1.742314
O	-1.802119	-3.207403	-1.530385
C	-5.642274	-2.576376	2.948936
H	-4.948578	-2.562560	3.801876
H	-6.396206	-1.798409	3.082811
H	-6.138409	-3.554341	2.907681
C	-0.743595	-3.974350	-2.053455
H	-0.431521	-3.470008	-2.969163
H	0.103827	-4.018225	-1.355658
H	-1.068114	-4.994300	-2.293991
C	1.370590	5.462781	0.192355
H	1.408398	5.566671	-0.889986
C	0.840343	1.621811	-3.047243
H	0.606925	1.384774	-4.080410
C	-0.922322	-0.880954	1.769096
C	-2.884013	-0.276895	2.852000
C	-0.259114	-1.225127	0.568296
C	-0.212332	-0.923898	2.999565
C	-2.288956	-0.428160	4.114893
H	-3.917073	0.034968	2.747324
C	1.086908	-1.449978	0.582270
H	-0.831817	-1.288639	-0.352418
C	1.196796	-1.079465	2.963402
C	-0.942993	-0.704201	4.186222
H	-2.883489	-0.267347	5.007600
C	1.853491	-1.268811	1.769803
H	1.598030	-1.679846	-0.348558
H	-0.431730	-0.748936	5.144428
N	-2.216076	-0.464091	1.726215
H	1.758954	-0.970241	3.887980
Pd	3.640072	-0.075214	-0.270089
C	3.324703	-1.094486	1.684848
C	4.179886	-1.798863	0.794776
H	3.367871	0.500476	1.186875
H	3.814650	-0.719907	2.584500
H	3.809338	-2.607123	0.169591
C	5.636321	-1.764589	1.071486
O	6.151098	-1.089365	1.938074
O	6.297456	-2.560400	0.230092
C	7.720678	-2.378837	0.214736
C	8.265731	-3.221070	-0.911833
H	8.127102	-2.671606	1.188603
H	7.919876	-1.315537	0.057131
H	9.355600	-3.125547	-0.954523
H	8.016559	-4.278134	-0.773091
H	7.852365	-2.883961	-1.866743
C	5.362084	-0.764767	-2.340872
O	6.129243	-0.187420	-1.569859
O	4.089932	-0.909866	-2.136961
C	5.858308	-1.392757	-3.628347
H	5.213813	-1.112133	-4.466802
H	6.887105	-1.088047	-3.828812
H	5.814622	-2.483877	-3.536465

96

cis-T25-Q_C7_IN2 Eopt -2767.399603

Pd	-2.407508	-0.439173	0.070109
C	-3.979425	0.750288	-1.971018
C	-3.543233	-1.542821	-2.266092
C	-4.748565	0.787528	-3.126329
C	-4.294531	-1.572203	-3.432343
H	-5.192010	1.731858	-3.422855
H	-4.372618	-2.508180	-3.974916
N	-3.418981	-0.396931	-1.597630
H	-5.501654	-0.388304	-4.764065
C	-4.905552	-0.391502	-3.855870
N	-2.215403	-2.380908	-0.486025
N	-2.876976	1.614861	-0.040079
C	-2.768094	-2.698939	-1.687967
C	-3.636860	1.931169	-1.107237
O	-2.683486	-3.756109	-2.297116
O	-4.003350	3.059939	-1.460898
C	-1.190974	-3.179627	0.030066
C	-1.340794	-3.841465	1.257695
C	0.056352	-3.220844	-0.618983
C	-0.263617	-4.519585	1.835500
C	1.126975	-3.920550	-0.060216
C	0.954466	-4.552833	1.166588
H	1.791967	-5.083899	1.609749
C	-0.126125	-0.632312	2.067325
C	-2.237750	-0.977427	2.970345
C	0.676200	-0.416203	0.932156
C	0.472264	-0.688333	3.356863
C	-1.714733	-1.114366	4.268492
H	-3.303754	-1.054878	2.786023
C	2.029542	-0.150974	1.038012
H	0.178325	-0.437945	-0.034029

C	1.863980	-0.448436	3.459690
C	-0.363325	-0.950059	4.461806
H	-2.388422	-1.315624	5.094345
H	0.070126	-1.010194	5.457156
N	-1.480723	-0.730148	1.917653
H	2.327818	-0.474218	4.443064
Pd	3.054938	0.311184	-0.612311
C	5.387863	0.510680	-2.254123
O	6.227044	0.725111	-3.108840
O	4.118302	0.749420	-2.335393
N	4.756589	-0.736349	-0.214180
C	4.886601	-1.910938	0.289304
C	6.165295	-2.686021	0.357670
H	6.013718	-3.575188	0.970588
H	6.970288	-2.082020	0.784439
H	6.475921	-2.998884	-0.645155
O	3.859714	-2.570234	0.803219
C	5.857748	-0.071142	-0.899549
H	6.707889	-0.733052	-1.079061
C	-2.391117	2.765489	0.700814
C	-1.381563	3.622422	-0.128282
H	-3.245369	3.433551	0.888890
C	-1.800860	2.371710	2.040305
C	-0.561835	4.577345	0.720821
H	-2.004140	4.218037	-0.804365
H	-2.512210	1.731712	2.571834
H	-0.888141	1.785888	1.886655
C	-1.482927	3.607609	2.864474
C	-0.594396	4.568210	2.120136
H	-2.421859	4.114621	3.133630
H	-1.007180	3.322402	3.810699
C	0.206338	5.473039	2.825978
C	1.055638	6.391696	0.774262
C	-0.492094	2.779871	-1.015229
C	1.025581	6.379384	2.168259
H	0.181760	5.455364	3.913800
H	1.692410	7.093917	0.243612
C	0.672897	2.185896	-0.538220
C	-0.819411	2.557519	-2.353852
H	1.641789	7.070381	2.736954
N	1.457708	1.409628	-1.300117
H	0.991419	2.328539	0.487065
H	-1.731423	2.992723	-2.754701
C	1.158933	1.235114	-2.596776
H	1.873579	0.657495	-3.172043
C	2.609773	-0.165161	2.340326
H	3.672136	0.039312	2.448344
H	-0.368578	-5.025281	2.788024
H	2.086983	-3.967442	-0.559550
O	-2.569859	-3.749349	1.823587
O	0.131668	-2.506034	-1.764496
C	-2.777132	-4.429097	3.036611
H	-2.133901	-4.035404	3.835949
H	-3.823132	-4.261419	3.300200
H	-2.601407	-5.507255	2.930390
C	1.345022	-2.535427	-2.479158
H	1.176986	-1.941957	-3.378821
H	2.162997	-2.082171	-1.901663
H	1.616596	-3.558921	-2.766035
C	0.267784	5.496296	0.065895
H	0.294211	5.497127	-1.021765
C	0.019535	1.792433	-3.154808
H	-0.200674	1.624471	-4.203747
H	6.203344	0.769038	-0.283427
H	3.045427	-2.024331	0.728186

104

cis-T25-Q_C7_IN3 Eopt -2905.025660

Pd	-2.739583	0.223298	0.317854
C	-4.178290	1.759525	-1.585345
C	-4.465467	-0.569456	-1.766485
C	-5.066943	1.984600	-2.628129
C	-5.358423	-0.413276	-2.817359
H	-5.261774	3.007583	-2.931261
H	-5.782893	-1.301511	-3.272817
N	-3.917549	0.509970	-1.209968
H	-6.358659	1.030541	-4.061136
C	-5.660449	0.880877	-3.242383
N	-3.200373	-1.704794	-0.107501
N	-2.609382	2.324006	0.122149
C	-3.983251	-1.883726	-1.206148
C	-3.387963	2.815004	-0.862416
O	-4.295900	-2.936929	-1.743726
O	-3.451941	3.986937	-1.257436
C	-2.369068	-2.746008	0.318933
C	-2.502943	-3.305249	1.598008
C	-1.302873	-3.160010	-0.500306
C	-1.578876	-4.246421	2.059665
C	-0.388461	-4.114511	-0.050816
C	-0.535489	-4.639363	1.227873
H	0.178575	-5.375801	1.586096
C	-0.413284	-0.572130	2.136740
C	-2.455459	-0.220315	3.191347
C	0.330982	-0.653506	0.942479
C	0.231675	-0.753202	3.391927
C	-1.902526	-0.451941	4.462342
H	-3.506765	0.019856	3.075836
C	1.703986	-0.805300	0.966259
H	-0.226150	-0.569617	0.014108
C	1.631240	-0.945187	3.398164
C	-0.554381	-0.699839	4.560634
H	-2.541017	-0.403216	5.337720
H	-0.080685	-0.847424	5.528150
N	-1.742227	-0.259466	2.080396
H	2.140415	-1.077569	4.349975
C	-1.701468	3.297338	0.701293
C	-0.592123	3.746567	-0.304793

H	-2.274286	4.210844	0.921058
C	-1.081528	2.800722	1.992479
C	0.552896	4.484626	0.361414
H	-1.092865	4.436872	-0.992611
H	-1.871555	2.431077	2.653720
H	-0.414663	1.957241	1.782070
C	-0.303185	3.915065	2.671737
C	0.705878	4.549627	1.751348
H	-1.006117	4.686099	3.021637
H	0.202869	3.534283	3.567287
C	1.808433	5.228125	2.282982
C	2.591565	5.778269	0.078152
C	-0.098386	2.591219	-1.142661
C	2.746127	5.839142	1.462700
H	1.925751	5.269645	3.364068
H	3.316683	6.251557	-0.577980
C	0.946620	1.770219	-0.730713
C	-0.726900	2.269005	-2.347931
H	3.595763	6.358064	1.898084
N	1.331808	0.688222	-1.422900
H	1.485391	1.971471	0.187818
H	-1.541265	2.895197	-2.703146
C	0.718591	0.378644	-2.574751
H	1.068636	-0.515207	-3.080047
C	2.346172	-0.946518	2.224893
H	3.419208	-1.087932	2.278885
H	-1.669799	-4.679117	3.048873
H	0.434445	-4.431334	-0.681241
O	-3.560743	-2.861334	2.323148
O	-1.227846	-2.540631	-1.697406
C	-3.761674	-3.434474	3.590659
H	-2.924189	-3.220796	4.269050
H	-4.670762	-2.977711	3.986762
H	-3.904329	-4.520783	3.524230
C	-0.359265	-3.087595	-2.669565
H	-0.588488	-2.565720	-3.600258
H	0.694580	-2.916292	-2.428776
H	-0.549116	-4.159334	-2.804144
C	1.503743	5.105104	-0.458357
H	1.382044	5.047250	-1.538058
C	-0.316307	1.156854	-3.069495
H	-0.797746	0.878333	-4.000947
Pd	2.722719	-0.719393	-0.763546
C	3.336480	-2.799117	-0.283272
C	4.478152	-2.048181	-0.445418
H	2.999192	-3.091620	0.706354
H	2.883869	-3.270570	-1.151316
H	4.911531	-1.903764	-1.429117
C	5.348148	-1.636219	0.687189
O	5.243536	-2.013473	1.835758
O	6.294781	-0.797528	0.260711
C	7.196644	-0.315637	1.266760
C	8.153955	0.636633	0.593615
H	7.709091	-1.171911	1.717918
H	6.613070	0.172524	2.054379
H	8.862148	1.033190	1.328132
H	8.719800	0.128900	-0.193252
H	7.614025	1.475348	0.143934
C	3.430634	-1.242727	-3.523647
O	2.652604	-2.197698	-3.380066
O	3.730687	-0.391663	-2.606284
C	4.087868	-0.978884	-4.864266
H	5.151779	-0.762030	-4.733575
H	3.951824	-1.831962	-5.531363
H	3.631960	-0.091572	-5.318075

104

cis-T25-Q_C7_IN4 Eopt -2905.069913

Pd	-2.236394	0.879758	-0.040768
C	-2.982449	2.513215	-2.236441
C	-3.666609	0.273013	-2.407696
C	-3.605445	2.832205	-3.435454
C	-4.303236	0.521827	-3.615692
H	-3.549492	3.855643	-3.790103
H	-4.811466	-0.299454	-4.109330
N	-3.025489	1.261373	-1.787411
H	-4.761149	2.041077	-5.070227
C	-4.267341	1.818312	-4.128566
N	-3.057899	-0.945373	-0.467827
N	-1.641343	2.888293	-0.297419
C	-3.653620	-1.045346	-1.685752
C	-2.155798	3.454396	-1.409229
O	-4.170123	-2.032585	-2.194389
O	-1.942878	4.595147	-1.839071
C	-2.928413	-2.109784	0.294555
C	-3.584686	-2.225571	1.530404
C	-2.116951	-3.169649	-0.146233
C	-3.411233	-3.361819	2.323601
C	-1.978955	-4.327160	0.621808
C	-2.615602	-4.401225	1.854664
H	-2.494167	-5.292962	2.463000
C	-0.600757	3.688105	0.331018
C	0.650986	3.821519	-0.594146
H	-0.982437	4.712736	0.451657
C	-0.208265	3.166881	1.698974
C	1.877596	4.348448	0.123497
H	0.364765	4.543510	-1.366186
H	-1.105892	3.061202	2.313656
H	0.236603	2.167569	1.610117
C	0.760848	4.121714	2.378481
C	1.946358	4.463056	1.515863
H	0.226495	5.049036	2.635101
H	1.105556	3.696807	3.328964
C	3.131109	4.920573	2.103111
C	4.162023	5.155701	-0.055513
C	0.942957	2.521668	-1.302225
C	4.232417	5.264873	1.332794

H	3.182423	4.999443	3.187197
H	5.017065	5.418620	-0.671785
C	1.706201	1.525875	-0.703685
C	0.417816	2.249556	-2.567144
H	5.144910	5.610842	1.810327
N	1.904575	0.325381	-1.268075
H	2.198057	1.690577	0.249865
H	-0.162735	3.014203	-3.076596
C	1.374722	0.057587	-2.470059
H	1.571731	-0.931586	-2.869099
H	-3.904194	-3.452565	3.284204
H	-1.371873	-5.155444	0.275044
O	-4.376357	-1.177760	1.871274
O	-1.475341	-2.961096	-1.319744
C	-5.095856	-1.273541	3.075197
H	-4.426069	-1.337816	3.943139
H	-5.686493	-0.358216	3.145779
H	-5.770848	-2.139166	3.073313
C	-0.933394	-4.083412	-1.978694
H	-0.114526	-4.541136	-1.408909
H	-1.709294	-4.833962	-2.170555
H	-0.532940	-3.712446	-2.922898
C	2.992728	4.700362	-0.646201
H	2.935114	4.601768	-1.728270
C	0.634133	1.010005	-3.154199
H	0.231967	0.773099	-4.133816
Pd	3.067509	-0.948322	-0.191623
C	5.121649	-0.862246	1.217553
O	4.769516	0.218737	0.674094
O	4.430691	-1.924681	1.035154
C	6.363841	-0.942835	2.054611
H	7.196128	-1.273155	1.422885
H	6.608152	0.039279	2.464240
H	6.237204	-1.675947	2.854685
C	-0.852370	-0.490118	2.359054
N	-1.748089	0.453541	1.939578
C	-2.502373	1.080532	2.827943
C	-2.408946	0.861447	4.209739
C	-1.503588	-0.066029	4.668093
C	-0.709798	-0.777280	3.748858
C	0.208665	-1.779722	4.142133
C	0.763586	-2.213351	1.812986
C	-0.088462	-1.204990	1.414737
H	-0.230005	-0.964942	0.365542
C	1.492306	-3.096031	0.839691
C	1.763927	-2.476849	-0.511756
C	2.479122	-3.397281	-1.426606
O	3.095265	-4.391188	-1.106459
O	2.364779	-2.993545	-2.723722
C	3.187285	-3.691638	-3.664414
C	4.602364	-3.152542	-3.646715
H	5.208369	-3.651273	-4.410994
H	5.062102	-3.330625	-2.670436

H	4.609127	-2.075862	-3.845515
H	2.704486	-3.527597	-4.631545
H	3.168908	-4.758844	-3.427298
H	0.867402	-2.082361	-0.994728
H	0.886857	-4.011109	0.718430
H	0.332580	-1.990698	5.201138
H	-1.398050	-0.269384	5.730975
H	-3.048221	1.421455	4.883422
H	-3.209869	1.799239	2.427116
C	0.913061	-2.478649	3.200065
H	1.605861	-3.258328	3.505181
H	2.440545	-3.426803	1.276223

104

cis-T25-Q_C7_IN5 Eopt -2905.034747

Pd	-1.289958	-1.879284	0.237132
C	-1.045126	-3.175821	2.742341
C	-2.936837	-1.795100	2.535303
C	-1.418644	-3.554295	4.025038
C	-3.361737	-2.124641	3.814522
H	-0.784743	-4.250526	4.563330
H	-4.282323	-1.684834	4.182705
N	-1.803673	-2.316611	2.067823
H	-2.901752	-3.293176	5.562676
C	-2.588615	-3.015053	4.560265
N	-3.060750	-0.870168	0.359503
N	0.358260	-3.048666	0.814642
C	-3.668666	-0.897185	1.574128
C	0.217887	-3.590398	2.042649
O	-4.696548	-0.326048	1.916701
O	1.030808	-4.296072	2.652494
C	-3.590847	-0.056091	-0.644236
C	-4.101711	-0.628527	-1.821381
C	-3.577414	1.342460	-0.521132
C	-4.552487	0.179044	-2.867102
C	-4.055049	2.153720	-1.551566
C	-4.525029	1.561830	-2.717045
H	-4.883698	2.191065	-3.526639
C	1.695478	-3.192931	0.255419
C	2.751244	-2.445341	1.124042
H	1.975665	-4.256027	0.302841
C	1.770717	-2.745186	-1.191426
C	4.096266	-2.305801	0.440078
H	2.889540	-3.069688	2.012525
H	1.006714	-3.272801	-1.769365
H	1.548881	-1.674779	-1.269518
C	3.140388	-3.036171	-1.786164
C	4.280701	-2.571556	-0.919954
H	3.240237	-4.119981	-1.949181
H	3.220895	-2.565854	-2.773209
C	5.558984	-2.432721	-1.472129
C	6.455869	-1.766654	0.656564
C	2.226082	-1.116587	1.608914
C	6.641725	-2.040956	-0.698653

H	5.695943	-2.634390	-2.532530
H	7.292698	-1.453060	1.274518
C	2.213797	0.005691	0.782539
C	1.698292	-0.974654	2.891798
H	7.624827	-1.937420	-1.149749
N	1.693461	1.179211	1.159824
H	2.627106	-0.019759	-0.221315
H	1.693461	-1.829871	3.563307
C	1.180608	1.304128	2.391628
H	0.771519	2.276712	2.649626
H	-4.938494	-0.255650	-3.781552
H	-4.044178	3.233484	-1.456869
O	-4.121446	-1.985336	-1.848648
O	-3.044480	1.823150	0.629089
C	-4.709869	-2.602746	-2.966332
H	-4.153742	-2.385766	-3.888770
H	-4.675248	-3.675965	-2.769707
H	-5.754890	-2.292619	-3.093695
C	-3.429255	3.120710	1.025243
H	-3.026171	3.892700	0.356303
H	-4.521249	3.206164	1.065292
H	-3.009179	3.267258	2.021534
C	5.191244	-1.897789	1.211490
H	5.037444	-1.683478	2.267138
C	1.171573	0.248633	3.290701
H	0.755211	0.386519	4.283526
Pd	1.846999	2.869143	-0.240321
H	2.124074	4.095462	-1.125986
C	4.057663	1.624332	-1.414586
O	3.848894	2.515796	-0.498728
O	3.175989	1.024766	-2.038132
C	5.523679	1.318525	-1.634544
H	5.884330	0.705144	-0.801969
H	5.654967	0.756351	-2.560681
H	6.112674	2.239251	-1.654755
C	-0.754607	-0.305991	-2.342199
N	-1.027337	-1.530804	-1.798089
C	-1.268615	-2.558016	-2.592312
C	-1.232953	-2.471280	-3.993940
C	-0.939051	-1.261152	-4.573217
C	-0.694575	-0.139571	-3.756353
C	-0.401337	1.140919	-4.280981
C	-0.278405	2.044125	-2.033907
C	-0.542129	0.797687	-1.499505
H	-0.602381	0.638458	-0.427231
C	-0.064360	3.231924	-1.199910
C	-0.221768	3.287839	0.182873
C	-0.303062	4.602621	0.856322
O	-0.303633	5.684738	0.314701
O	-0.389392	4.433642	2.190139
C	-0.430109	5.641267	2.961700
C	-0.509052	5.243157	4.415304
H	-0.549025	6.136943	5.045857
H	0.368260	4.656875	4.706608
H	-1.405340	4.645083	4.608606
H	-1.296904	6.231487	2.646540
H	0.466781	6.229168	2.741539
H	-0.603919	2.438387	0.738848
H	-0.017075	4.182625	-1.724830
H	-0.340652	1.265284	-5.358462
H	-0.893468	-1.152344	-5.653755
H	-1.428996	-3.357722	-4.587222
H	-1.492514	-3.498173	-2.099447
C	-0.198424	2.201231	-3.442231
H	0.034792	3.182370	-3.845387

96

cis-T25-Q_C7_TSI Eopt -2767.368540

Pd	-2.403860	-0.132591	-0.042227
C	-3.710307	1.167740	-2.197613
C	-3.521266	-1.167818	-2.416931
C	-4.388959	1.260562	-3.405284
C	-4.190620	-1.143378	-3.632202
H	-4.700503	2.240382	-3.750519
H	-4.344762	-2.080064	-4.157023
N	-3.310993	-0.025249	-1.764857
H	-5.158184	0.133409	-5.069429
C	-4.629513	0.087373	-4.121517
N	-2.438680	-2.101413	-0.525848
N	-2.647379	1.957174	-0.210499
C	-2.960666	-2.396018	-1.745711
C	-3.294324	2.325753	-1.334903
O	-3.015912	-3.485662	-2.298587
O	-3.502546	3.478430	-1.735794
C	-1.694810	-3.061631	0.165695
C	-2.129793	-3.533605	1.413786
C	-0.438548	-3.468739	-0.317991
C	-1.327979	-4.395031	2.164968
C	0.363260	-4.338270	0.423579
C	-0.092889	-4.785837	1.657053
H	0.535036	-5.450847	2.243075
C	-0.235987	-0.582862	2.038882
C	-2.387727	-0.349887	2.884263
C	0.610275	-0.802956	0.933294
C	0.317811	-0.533295	3.349547
C	-1.923686	-0.368350	4.211936
H	-3.444477	-0.247132	2.663086
C	1.982118	-0.900562	1.094953
H	0.155172	-0.908299	-0.047671
C	1.724634	-0.604848	3.502814
C	-0.570967	-0.424982	4.440844
H	-2.637731	-0.302788	5.025752
H	-0.172061	-0.396763	5.451609
N	-1.579798	-0.420458	1.844127
H	2.145388	-0.542888	4.503199
H	2.623920	-1.848891	0.500019
Pd	3.162350	-0.115939	-0.547624

C	5.614126	0.344570	-1.870867
O	6.485687	0.785357	-2.590176
O	4.355887	0.707408	-1.932439
N	4.756102	-1.258710	-0.225763
C	4.591643	-2.526029	0.083595
C	5.756860	-3.481881	0.074548
H	5.465444	-4.397004	0.590826
H	6.639362	-3.050290	0.555011
H	6.027290	-3.733760	-0.957604
O	3.449025	-2.987499	0.399863
C	5.962319	-0.690973	-0.787844
H	6.611245	-1.447038	-1.240946
C	-2.078544	3.072361	0.526948
C	-0.885318	3.735188	-0.236054
H	-2.847773	3.855630	0.594379
C	-1.684659	2.691087	1.939573
C	0.029539	4.562105	0.650138
H	-1.354185	4.411212	-0.959615
H	-2.536335	2.205716	2.426358
H	-0.860795	1.968793	1.920396
C	-1.260110	3.921897	2.722036
C	-0.137805	4.653392	2.036754
H	-2.123337	4.594792	2.836074
H	-0.953274	3.641389	3.736977
C	0.752345	5.434126	2.781868
C	1.959040	6.034314	0.792470
C	-0.105069	2.734226	-1.056277
C	1.792948	6.121973	2.173972
H	0.620429	5.493419	3.860442
H	2.770279	6.563547	0.300770
C	0.923393	1.966121	-0.516156
C	-0.407656	2.540594	-2.405352
H	2.475590	6.719034	2.772313
N	1.608013	1.068179	-1.236222
H	1.221718	2.076718	0.520791
H	-1.211120	3.118732	-2.854394
C	1.320939	0.899853	-2.534687
H	1.939459	0.190983	-3.072899
C	2.528334	-0.770656	2.406591
H	3.604735	-0.854453	2.527804
H	-1.654735	-4.764686	3.129774
H	1.350429	-4.618327	0.077123
O	-3.343350	-3.077524	1.818944
O	-0.067974	-2.905647	-1.491344
C	-3.824117	-3.535314	3.057427
H	-3.169582	-3.226005	3.884960
H	-4.808400	-3.080695	3.185666
H	-3.928533	-4.627813	3.072897
C	1.114496	-3.377181	-2.103206
H	1.195114	-2.834791	-3.046917
H	1.998374	-3.177851	-1.486370
H	1.046770	-4.452829	-2.308139
C	1.082578	5.260428	0.045699
H	1.215182	5.184455	-1.031340
C	0.309396	1.616356	-3.152685
H	0.099583	1.454534	-4.204615
H	6.548919	-0.172201	-0.016723

104

cis-T25-Q_C7_TSII Eopt -2905.008989

Pd	-2.670658	-0.376338	0.052485
C	-4.151478	0.472023	-2.217415
C	-3.760944	-1.842145	-2.102029
C	-4.883182	0.324635	-3.388212
C	-4.478778	-2.058999	-3.269377
H	-5.296386	1.212793	-3.853694
H	-4.569142	-3.074670	-3.639143
N	-3.622410	-0.601688	-1.637241
H	-5.612841	-1.099856	-4.827291
C	-5.045005	-0.958016	-3.912111
N	-2.514296	-2.392202	-0.157575
N	-3.124535	1.645853	-0.408970
C	-3.064627	-2.902341	-1.294247
C	-3.825210	1.777778	-1.553881
O	-3.040058	-4.061578	-1.683632
O	-4.150913	2.831114	-2.117284
C	-1.606308	-3.185621	0.548376
C	-1.842687	-3.541589	1.883958
C	-0.395762	-3.573133	-0.059620
C	-0.895297	-4.280029	2.600051
C	0.533651	-4.348011	0.639062
C	0.271803	-4.686014	1.963471
H	0.995486	-5.282148	2.512381
C	-0.530070	-0.119057	2.215658
C	-2.732254	-0.056463	2.951620
C	0.406448	-0.538717	1.250439
C	-0.077982	0.457008	3.438552
C	-2.350901	0.390014	4.227923
H	-3.776636	-0.214532	2.704157
C	1.754364	-0.294162	1.438255
H	0.042663	-1.046270	0.362386
C	1.300338	0.759051	3.578154
C	-1.029601	0.699351	4.449525
H	-3.108179	0.538496	4.989884
H	-0.703838	1.120333	5.397408
N	-1.868020	-0.259173	1.973468
H	1.641443	1.245556	4.488515
C	-2.657131	2.917720	0.120166
C	-1.529466	3.545630	-0.763099
H	-3.495465	3.627083	0.060881
C	-2.232622	2.828997	1.570523
C	-0.721422	4.616183	-0.052300
H	-2.058642	4.022281	-1.596014
H	-3.033091	2.356829	2.147257
H	-1.339642	2.202546	1.664067
C	-1.935037	4.212199	2.122922
C	-0.900474	4.930744	1.299705

H -2.863493 4.802696 2.142424
H -1.595172 4.140362 3.163513
C -0.107296 5.926440 1.880146
C 1.024007 6.301944 -0.205944
C -0.640731 2.494275 -1.384779
C 0.847552 6.611205 1.142135
H -0.247077 6.159119 2.934040
H 1.768364 6.826978 -0.797987
C 0.474488 1.971295 -0.733802
C -0.938137 1.985444 -2.650541
H 1.455469 7.378253 1.614025
N 1.241542 1.013077 -1.266774
H 0.771421 2.334949 0.245335
H -1.800071 2.374292 -3.187004
C 0.941540 0.520926 -2.478129
H 1.594926 -0.263997 -2.849202
C 2.189527 0.416774 2.595417
H 3.254041 0.600837 2.717866
H -1.069493 -4.559859 3.632214
H 1.446731 -4.684689 0.160357
O -3.024500 -3.121802 2.399779
O -0.209404 -3.102387 -1.309135
C -3.288136 -3.424136 3.746835
H -2.547299 -2.965356 4.416577
H -4.274450 -3.008244 3.961461
H -3.311124 -4.507314 3.922957
C 0.952380 -3.497065 -2.011876
H 0.861538 -3.063578 -3.007435
H 1.864230 -3.096377 -1.556500
H 1.011485 -4.589112 -2.091860
C 0.244500 5.313453 -0.788844
H 0.385593 5.063318 -1.838114
C -0.146039 0.987579 -3.200636
H -0.362945 0.568287 -4.177713
Pd 2.834447 -0.054007 -0.333202
C 2.986427 -1.785186 1.187916
C 4.117508 -1.517240 0.351799
H 3.174875 -1.763579 2.257435
H 2.291961 -2.561499 0.878890
H 4.269376 -2.094542 -0.557490
C 5.299954 -0.869131 0.951786
O 5.332238 -0.355437 2.056179
O 6.338064 -0.889865 0.110674
C 7.496185 -0.160553 0.529920
C 8.449972 -0.127749 -0.639584
H 7.931099 -0.656169 1.404995
H 7.187537 0.843744 0.836938
H 9.358935 0.418602 -0.367713
H 8.732949 -1.140946 -0.941585
H 7.986766 0.372786 -1.495579
C 4.172417 -0.540158 -2.796982
O 3.491461 -1.573996 -2.811909
O 4.075699 0.402091 -1.922949
C 5.244686 -0.300766 -3.841460
H 5.260262 0.747645 -4.150538
H 6.219804 -0.528967 -3.395661
H 5.090050 -0.952709 -4.703260
104
cis-T25-Q_C7_TSIII Eopt -2905.023813
Pd -2.508123 0.106509 0.271134
C -4.133999 1.787755 -1.314858
C -4.092226 -0.458314 -2.006503
C -5.071357 2.106253 -2.288044
C -5.020444 -0.205035 -3.007083
H -5.420416 3.131096 -2.353725
H -5.334249 -1.027688 -3.640526
N -3.677092 0.540009 -1.230436
H -6.241111 1.318076 -3.914227
C -5.510482 1.093865 -3.142131
N -2.731555 -1.761761 -0.563220
N -2.583251 2.190401 0.454769
C -3.486370 -1.798307 -1.694838
C -3.467218 2.766661 -0.388625
O -3.711876 -2.759190 -2.419978
O -3.686959 3.973362 -0.540238
C -1.962104 -2.889135 -0.262354
C -2.161376 -3.594891 0.935568
C -0.933389 -3.305832 -1.128767
C -1.345352 -4.678590 1.269718
C -0.140524 -4.411728 -0.816448
C -0.349196 -5.077065 0.386440
H 0.275150 -5.929647 0.638233
C -1.610787 3.114760 1.026199
C -0.756680 3.780661 -0.097295
H -2.152347 3.938627 1.513583
C -0.718973 2.444001 2.054607
C 0.434789 4.544824 0.440356
H -1.424541 4.491674 -0.594169
H -1.343613 1.984095 2.825618
H -0.150839 1.632742 1.585680
C 0.238497 3.431008 2.708445
C 0.916912 4.362278 1.739330
H -0.310577 4.035613 3.445742
H 1.004312 2.877084 3.263295
C 2.039366 5.088411 2.153084
C 2.196518 6.160027 0.006041
C -0.337729 2.767519 -1.134705
C 2.675853 5.981959 1.304212
H 2.418389 4.935650 3.161307
H 2.686516 6.853665 -0.671636
C 0.736420 1.913449 -0.900107
C -1.033584 2.604839 -2.331996
H 3.548220 6.531732 1.647181
N 1.072102 0.923249 -1.737680
H 1.346872 1.999777 -0.005900
H -1.867675 3.264202 -2.559319

C	0.378330	0.750161	-2.869550
H	0.683079	-0.077141	-3.499227
H	-1.489536	-5.219378	2.197320
H	0.637289	-4.747285	-1.493391
O	-3.172012	-3.142029	1.717059
O	-0.760541	-2.546722	-2.235668
C	-3.459200	-3.863147	2.889829
H	-2.612148	-3.855926	3.588122
H	-4.307516	-3.356647	3.353312
H	-3.734766	-4.901779	2.665447
C	0.062279	-3.061028	-3.257830
H	1.119779	-3.082886	-2.960582
H	-0.257838	-4.066892	-3.554315
H	-0.054939	-2.384224	-4.105999
C	1.086430	5.442332	-0.413988
H	0.708180	5.570477	-1.426256
C	-0.670674	1.589478	-3.210800
H	-1.204681	1.433816	-4.142571
Pd	2.530269	-0.366537	-0.954802
H	1.549498	-1.575076	-1.228358
C	3.761688	1.730926	0.473072
O	2.957733	1.357873	1.341329
O	3.861250	1.221390	-0.706854
C	4.690603	2.899115	0.730446
H	4.799445	3.065168	1.804095
H	5.665080	2.733324	0.264068
H	4.250046	3.799226	0.287616
C	-0.535242	-1.185627	2.261131
N	-1.700974	-0.497086	2.099396
C	-2.498858	-0.317050	3.138183
C	-2.202924	-0.797511	4.423897
C	-1.040433	-1.504803	4.616585
C	-0.172304	-1.724430	3.527988
C	1.041755	-2.444520	3.633557
C	1.496509	-2.052304	1.283349
C	0.319736	-1.353282	1.158163
H	0.038637	-0.897328	0.213718
C	2.420744	-2.246313	0.131198
C	3.725862	-1.701031	0.143406
C	4.726378	-2.280953	-0.780114
O	4.482634	-3.114213	-1.630603
O	5.938156	-1.757928	-0.568698
C	6.958864	-2.177728	-1.481377
C	8.210936	-1.407497	-1.139224
H	9.022615	-1.693374	-1.816080
H	8.528117	-1.614354	-0.112398
H	8.039088	-0.331330	-1.237236
H	6.619561	-1.978529	-2.503150
H	7.098689	-3.259985	-1.384916
H	4.073694	-1.104568	0.981954
H	2.289301	-3.164475	-0.441832
H	1.326244	-2.856411	4.598014
H	-0.778633	-1.897076	5.596159
H	-2.895718	-0.605265	5.235826
H	-3.410693	0.239738	2.947287
C	1.849753	-2.609618	2.539177
H	2.782847	-3.158542	2.626340

96

cis-T25-Q_IN1 Eopt -2767.377805

Pd	-2.448264	0.685114	0.164664
C	-3.464308	2.737465	-1.511150
C	-4.471358	0.632786	-1.807232
C	-4.280260	3.304038	-2.480995
C	-5.315193	1.135640	-2.787475
H	-4.160365	4.357843	-2.707701
H	-6.020708	0.459442	-3.258204
N	-3.592231	1.445332	-1.222566
H	-5.864514	2.905437	-3.882250
C	-5.213807	2.486859	-3.119682
N	-3.548672	-0.956537	-0.314241
N	-1.725820	2.659681	0.123731
C	-4.440535	-0.794774	-1.324049
C	-2.377594	3.448974	-0.756245
O	-5.171727	-1.636707	-1.828520
O	-2.140941	4.634300	-1.019298
C	-3.305662	-2.234241	0.198833
C	-3.733194	-2.570858	1.492059
C	-2.540468	-3.160906	-0.529842
C	-3.391005	-3.800908	2.058299
C	-2.201066	-4.395012	0.028927
C	-2.628033	-4.695899	1.316668
H	-2.360340	-5.654038	1.753301
C	-0.473200	-1.248202	1.399342
C	-1.911320	-0.217942	2.909420
C	0.023893	-1.368183	0.085644
C	0.031116	-2.102542	2.422381
C	-1.457329	-1.016124	3.972089
H	-2.686937	0.524349	3.062640
H	-0.384016	-0.721321	-0.685899
C	1.026523	-3.054511	2.095510
C	-0.491859	-1.960566	3.724250
H	-1.878751	-0.875391	4.961525
H	-0.121501	-2.604107	4.518210
N	-1.439925	-0.322116	1.679840
H	1.409771	-3.699434	2.881835
Pd	3.801682	-0.760845	-0.721069
C	4.375463	-3.168097	-2.058841
O	4.335533	-4.132862	-2.790475
O	3.479566	-2.196699	-2.095915
N	5.184953	-1.961359	-0.112606
C	5.872809	-1.115466	0.635734
C	7.262527	-1.368301	1.124768
H	7.975261	-0.837178	0.483230
H	7.505803	-2.434285	1.108808
H	7.370772	-0.976602	2.139258
O	5.251852	-0.036796	0.903967

C	5.521539	-3.015758	-1.029243
H	5.649219	-3.979400	-0.521582
C	-0.624227	3.316384	0.801080
C	0.556983	3.642819	-0.156416
H	-0.979294	4.297208	1.153309
C	-0.122608	2.530375	1.996471
C	1.749455	4.203538	0.589548
H	0.174681	4.413588	-0.834687
H	-0.972567	2.242071	2.622134
H	0.354146	1.601589	1.658238
C	0.853601	3.368635	2.809574
C	1.912960	4.036574	1.969675
H	0.291506	4.148250	3.345264
H	1.329829	2.753651	3.583129
C	3.071102	4.531720	2.579741
C	3.883089	5.359074	0.473093
C	0.942916	2.457523	-1.006652
C	4.051147	5.185265	1.846468
H	3.199177	4.394186	3.651543
H	4.640667	5.871435	-0.113185
C	1.978351	1.598573	-0.646745
C	0.264857	2.170493	-2.194539
H	4.944551	5.556223	2.341062
N	2.327697	0.533222	-1.378121
H	2.565703	1.774932	0.249988
H	-0.526532	2.834870	-2.529220
C	1.669213	0.258802	-2.513055
H	2.004600	-0.622851	-3.051181
C	1.494559	-3.152993	0.810165
H	2.264729	-3.874900	0.556538
H	-3.714775	-4.066307	3.057687
H	-1.602189	-5.110110	-0.522179
O	-4.461388	-1.618415	2.129607
O	-2.149075	-2.747108	-1.755423
C	-4.982897	-1.941742	3.394033
H	-4.184813	-2.127785	4.126567
H	-5.567525	-1.075558	3.709385
H	-5.637054	-2.821758	3.347179
C	-1.420945	-3.653974	-2.548924
H	-1.225672	-3.139079	-3.490849
H	-0.465538	-3.923917	-2.080862
H	-1.999213	-4.565162	-2.747126
C	2.740290	4.868747	-0.141680
H	2.604917	4.992078	-1.214263
C	0.626858	1.061708	-2.951063
H	0.114623	0.821630	-3.876924
H	6.444697	-2.813106	-1.591776
C	0.984139	-2.307710	-0.200767
H	1.378703	-2.403830	-1.207184

82

cis-T25-Q_T-Pd-SM Eopt -2205.209402

Pd	0.545931	0.692252	-0.654739
C	-0.214300	3.238152	-1.632634
C	2.027377	3.081236	-0.926483
C	-0.042538	4.566943	-1.997080
C	2.263877	4.404801	-1.269689
H	-0.892667	5.108856	-2.396926
H	3.251379	4.817212	-1.092755
N	0.815637	2.564045	-1.126852
H	1.375280	6.182710	-2.095169
C	1.214759	5.144869	-1.817005
N	2.504446	0.900091	-0.134064
N	-1.379941	1.184044	-1.279566
C	3.020564	2.146470	-0.280252
C	-1.509621	2.472681	-1.670754
O	4.130070	2.549158	0.045159
O	-2.547670	3.061401	-1.987101
C	3.184957	-0.059756	0.618517
C	3.696008	-1.212168	-0.000523
C	3.240012	0.040145	2.019125
C	4.244571	-2.246342	0.762537
C	3.801091	-0.984420	2.786005
C	4.293344	-2.115996	2.145689
H	4.727607	-2.915485	2.739538
C	0.612217	-2.326008	-1.015660
C	0.465172	-1.568346	1.177850
C	0.654244	-2.043773	-2.398660
C	0.701999	-3.673346	-0.569716
C	0.537259	-2.873363	1.695246
H	0.389367	-0.713434	1.839100
H	0.599489	-1.004885	-2.711740
C	0.825900	-4.706650	-1.530783
C	0.658782	-3.922050	0.821883
H	0.490045	-3.014567	2.768459
H	0.721314	-4.946508	1.180058
N	0.485708	-1.305536	-0.115692
H	0.891987	-5.735106	-1.185194
C	-2.637863	0.479839	-1.142973
C	-3.372049	0.847614	0.173970
H	-3.298622	0.833836	-1.947454
C	-2.516137	-1.027475	-1.257706
C	-4.668138	0.073784	0.302716
H	-3.618029	1.913258	0.083460
H	-1.891678	-1.288377	-2.117713
H	-2.025187	-1.431819	-0.365191
C	-3.902912	-1.637062	-1.412824
C	-4.901852	-1.108026	-0.412227
H	-4.276142	-1.419920	-2.424774
H	-3.850884	-2.730623	-1.338415
C	-6.106503	-1.792368	-0.213460
C	-6.837165	-0.143047	1.375825
C	-2.499202	0.693780	1.401278
C	-7.068903	-1.322438	0.669045
H	-6.284483	-2.711985	-0.767802
H	-7.582242	0.238495	2.068484
C	-2.534514	-0.441551	2.219679

C	-1.610874	1.705504	1.775778
H	-7.995960	-1.872250	0.807470
N	-1.794521	-0.609636	3.318980
H	-3.217435	-1.254333	1.979933
H	-1.551343	2.616529	1.187073
C	-0.963963	0.379207	3.655161
H	-0.379394	0.227627	4.562121
C	0.855759	-4.411604	-2.871213
H	0.946827	-5.208636	-3.603212
H	4.637833	-3.138818	0.290515
H	3.850947	-0.910606	3.866108
O	3.592029	-1.237521	-1.349468
O	2.680245	1.158249	2.539652
C	4.064472	-2.382473	-2.016210
H	3.519755	-3.283899	-1.705446
H	3.884299	-2.206913	-3.077502
H	5.139520	-2.529522	-1.848938
C	2.794234	1.357518	3.926157
H	2.340540	2.329006	4.129996
H	2.259331	0.583150	4.493635
H	3.844134	1.376971	4.244556
C	-5.644585	0.540796	1.189303
H	-5.450871	1.456881	1.743395
C	-0.828188	1.549609	2.914103
H	-0.129089	2.321163	3.220257
C	0.770256	-3.069147	-3.305012
H	0.799596	-2.846162	-4.367548

4. X-ray Crystallographic Data

Table S13. Crystal data and structure refinement for **2ab**

Identification code	yu135_0m_a	
No. in paper	**2ab**	
CCDC	2078170	
Empirical formula	C14 H14 N2 O3	
Formula weight	258.27	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 15.4115(4) Å	α= 90°.
	b = 12.0140(3) Å	β= 92.765(2)°.
	c = 20.1556(5) Å	γ = 90°.
Volume	3727.54(16) Å^3	
Z	12	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	0.813 mm^{-1}	
F(000)	1632	
Crystal size	0.18 x 0.07 x 0.07 mm^3	
Theta range for data collection	2.871 to 70.166°.	
Index ranges	-18<=h<=18, -14<=k<=14, -24<=l<=24	
Reflections collected	80899	
Independent reflections	7008 [R(int) = 0.0819]	
Completeness to theta = 67.679°	99.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5220 and 0.3247
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7008 / 0 / 520
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1269
R indices (all data)	R1 = 0.0677, wR2 = 0.1346
Largest diff. peak and hole	0.227 and -0.211 e.Å^{-3}

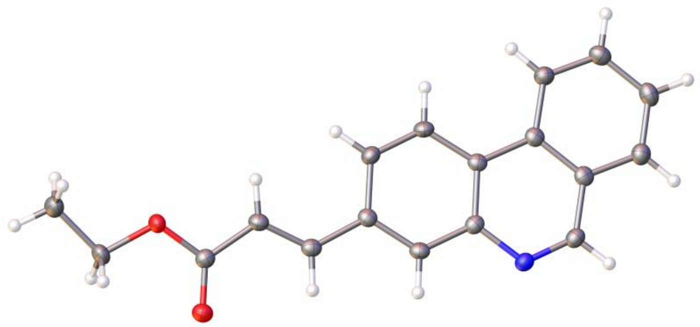


Table S14. Crystal data and structure refinement for **3p**

Identification code	yu137_0m_a	
No. in paper	**3p**	
CCDC	2078172	
Empirical formula	C18 H15 N O2	
Formula weight	277.31	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4675(4) Å	α = 86.655(2)°.
	b = 11.4554(6) Å	β = 83.006(2)°.
	c = 15.7719(9) Å	λ = 84.612(2)°.
Volume	1331.72(13) Å^3	
Z	4	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	584	

Crystal size	0.22 x 0.2 x 0.075 mm^3
Theta range for data collection	2.261 to 26.427°.
Index ranges	-9<=h<=9, -14<=k<=14, -19<=l<=19
Reflections collected	45896
Independent reflections	5485 [R(int) = 0.0801]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4908 and 0.4180
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5485 / 0 / 381
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0900
R indices (all data)	R1 = 0.0619, wR2 = 0.1026
Largest diff. peak and hole	0.209 and -0.210 e.$Å^{-3}$

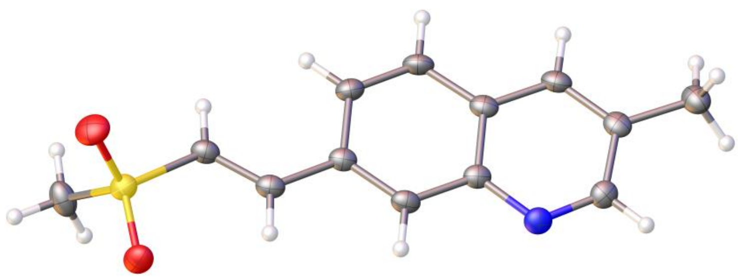


Table S15. Crystal data and structure refinement for **3u**

Identification code	yu136	
No. in paper	**3u**	
CCDC	2078171	
Empirical formula	C13 H13 N O2 S	
Formula weight	247.30	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.6345(9) Å	α = 90°.
	b = 8.5567(5) Å	β = 104.257(3)°.
	c = 11.2183(9) Å	γ = 90°.

Volume	1175.45(14) $Å^3$
Z	4
Density (calculated)	1.397 Mg/m^3
Absorption coefficient	0.263 mm^{-1}
F(000)	520
Crystal size	0.2 x 0.2 x 0.2 mm^3
Theta range for data collection	2.904 to 26.769°.
Index ranges	-15<=h<=15, -10<=k<=10, -14<=l<=14
Reflections collected	20192
Independent reflections	2500 [R(int) = 0.0458]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6466 and 0.6025
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2500 / 0 / 156
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0810
R indices (all data)	R1 = 0.0434, wR2 = 0.0852
Largest diff. peak and hole	0.296 and -0.354 e.$Å^{-3}$

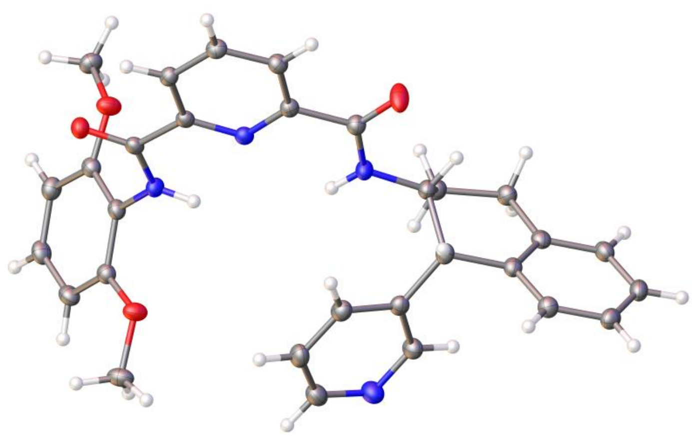


Table S16. Crystal data and structure refinement for ***cis*-T25**

Identification code	yu138_a
No. in paper	***cis*-T25**
CCDC	2078173
Empirical formula	C31 H32 N4 O5

Formula weight	540.60	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 25.5684(9) Å	α = 90°.
	b = 7.7587(3) Å	β = 90°.
	c = 26.7946(9) Å	γ = 90°.
Volume	5315.4(3) $Å^3$	
Z	8	
Density (calculated)	1.351 Mg/m^3	
Absorption coefficient	0.756 mm^{-1}	
F(000)	2288	
Crystal size	0.23 x 0.08 x 0.04 mm^3	
Theta range for data collection	3.299 to 68.993°.	
Index ranges	-30<=h<=30, -9<=k<=9, -31<=l<=26	
Reflections collected	86534	
Independent reflections	4918 [R(int) = 0.0558]	
Completeness to theta = 67.679°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5213 and 0.3698	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4918 / 0 / 366	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0968	
R indices (all data)	R1 = 0.0419, wR2 = 0.0988	
Extinction coefficient	0.00023(5)	
Largest diff. peak and hole	0.277 and -0.246 e.$Å^{-3}$	

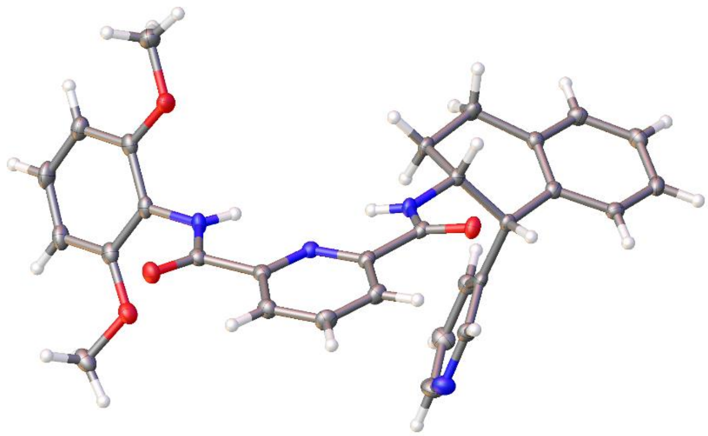


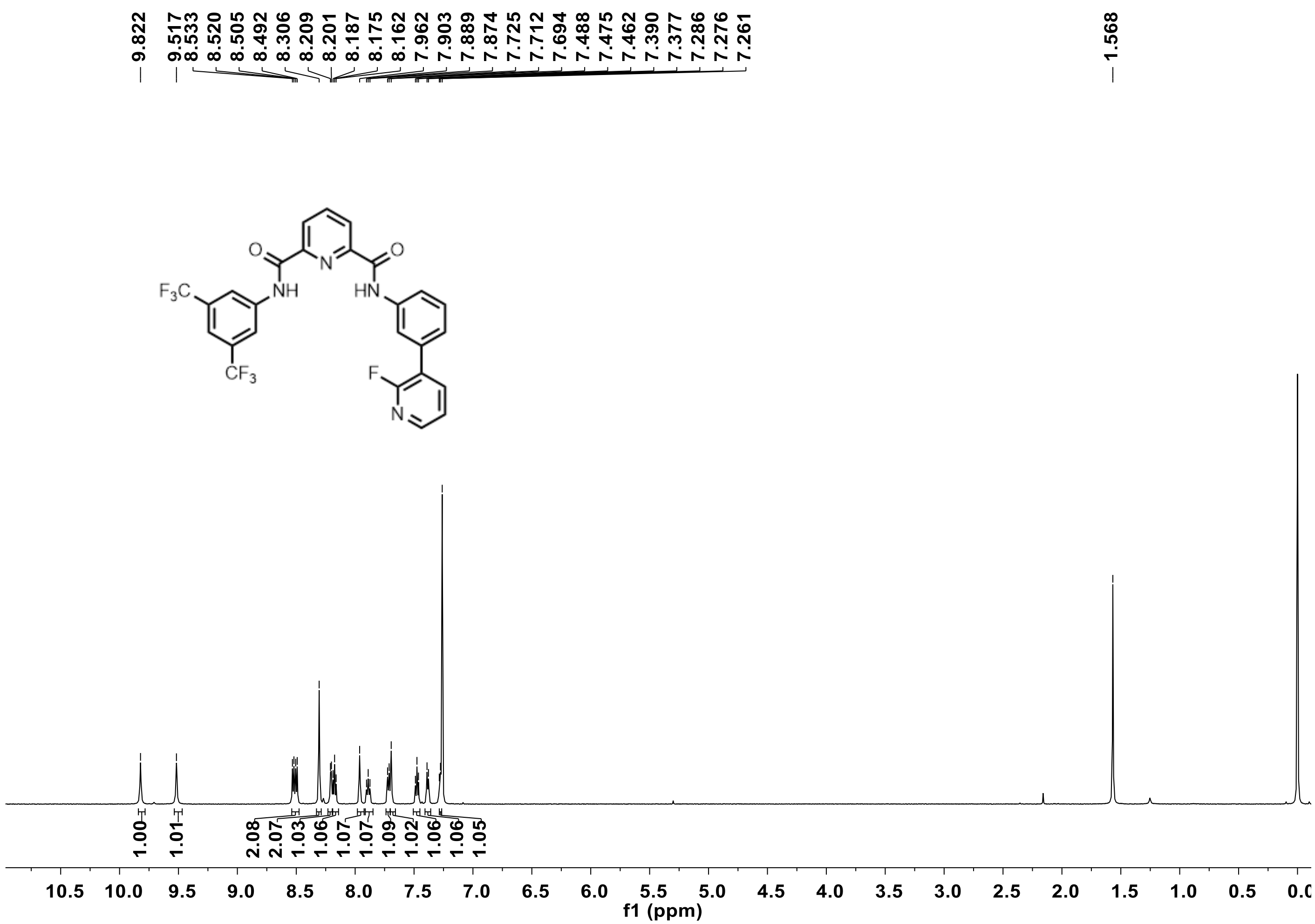
Table S17. Crystal data and structure refinement for **(*R*,*R*)-T25**

Identification code	Yu149	
No. in paper	**(*R*,*R*)-T25**	
CCDC	2132680	
Empirical formula	C30 H28 N4 O4	
Molecular formula	C30 H28 N4 O4	
Formula weight	508.56	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_5$	
Unit cell dimensions	a = 11.5894(4) Å	α = 90°.
	b = 11.5894(4) Å	β = 90°.
	c = 31.8918(18) Å	γ = 120°.
Volume	3709.6(3) $Å^3$	
Z	6	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	0.748 mm^{-1}	
F(000)	1608	
Crystal size	0.2 x 0.08 x 0.08 mm^3	
Crystal color, habit	colorless plank	
Theta range for data collection	4.405 to 70.391°.	
Index ranges	-14<=h<=14, -14<=k<=14, -38<=l<=38	
Reflections collected	143001	
Independent reflections	4707 [R(int) = 0.0364]	

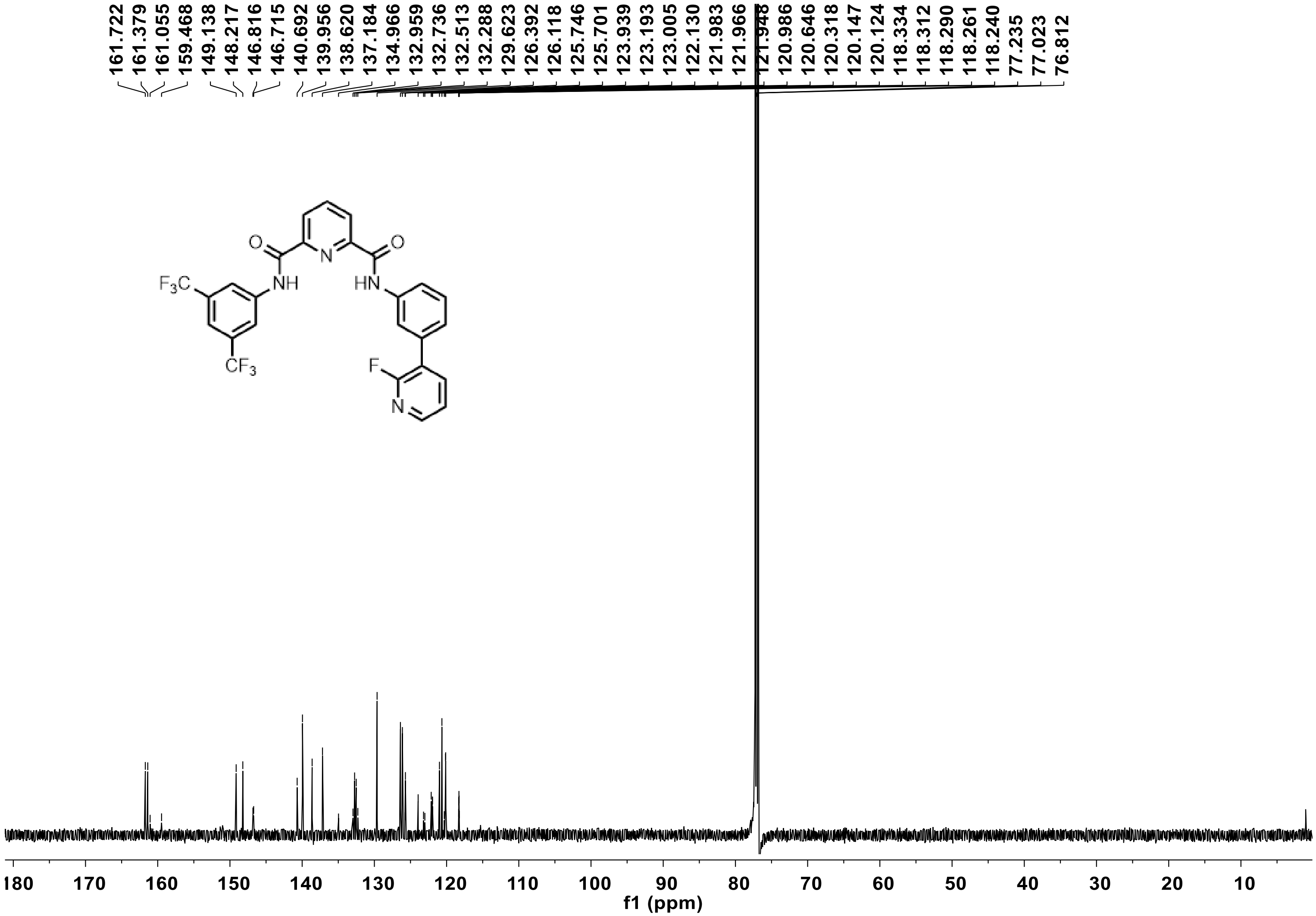
Completeness to theta = 67.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.6868
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4707 / 1 / 345
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0218, wR2 = 0.0560
R indices (all data)	R1 = 0.0219, wR2 = 0.0561
Absolute structure parameter	-0.020(19)
Largest diff. peak and hole	0.168 and -0.123 e.Å^{-3}

5. NMR Spectra

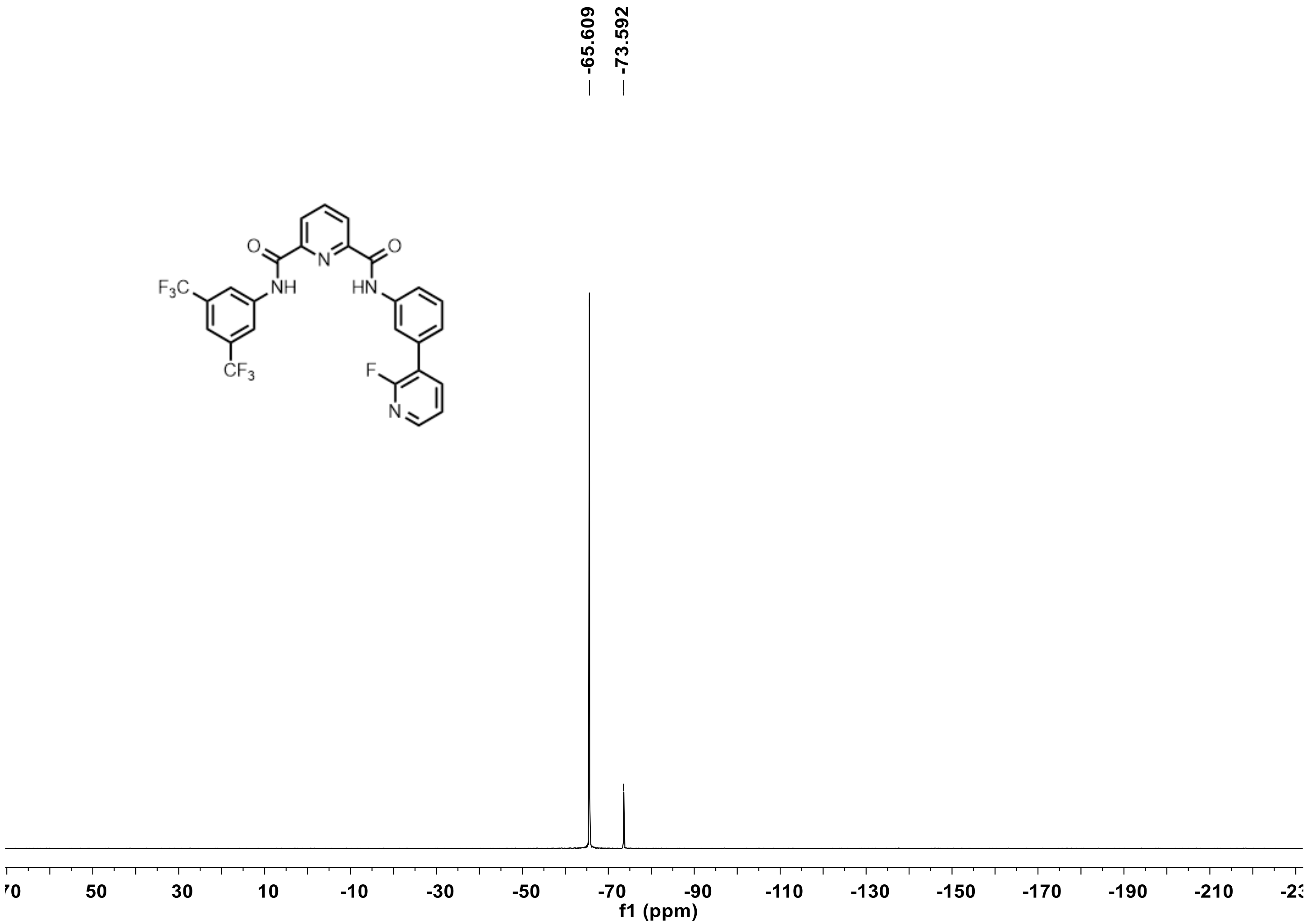
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T1**



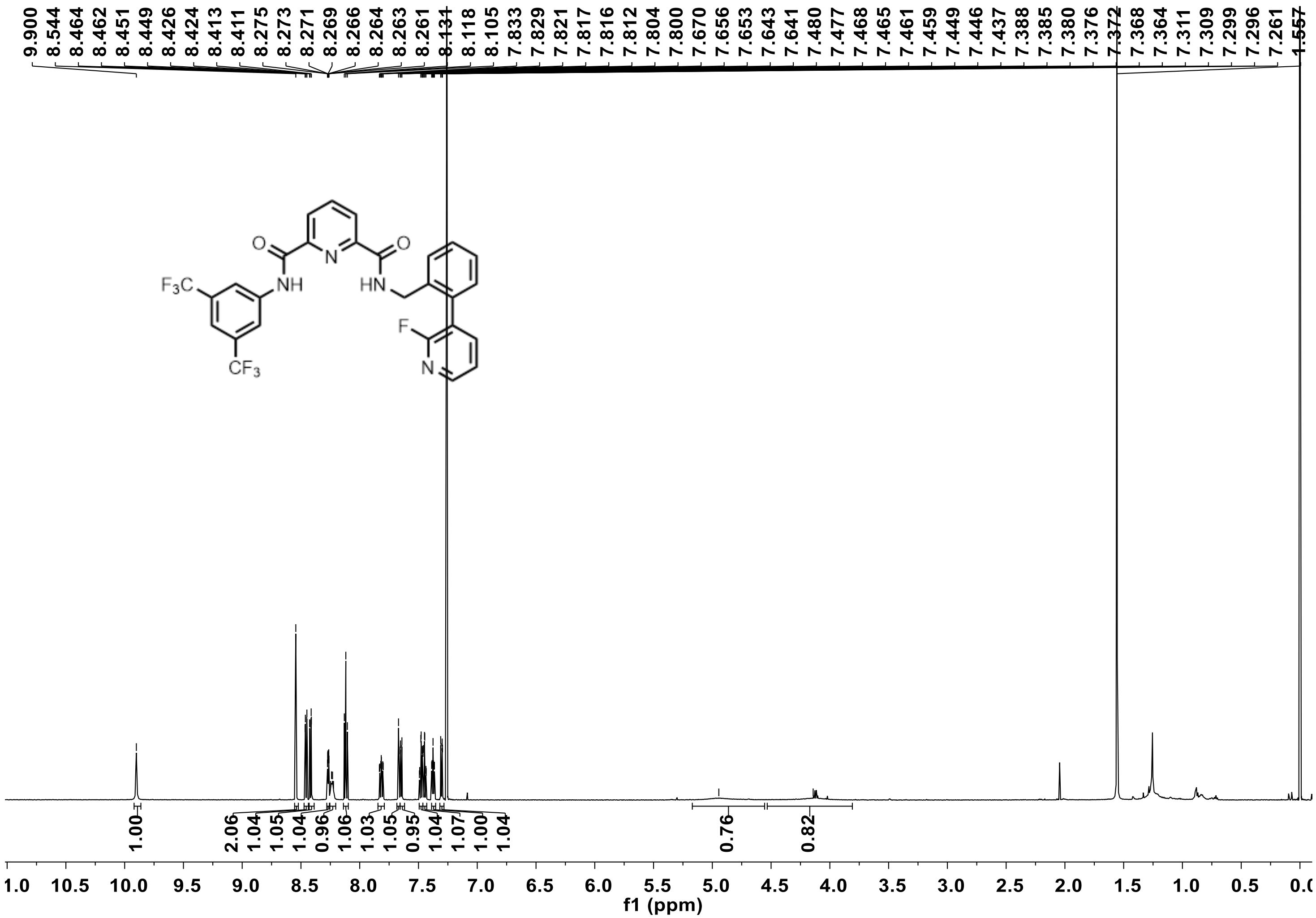
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T1**



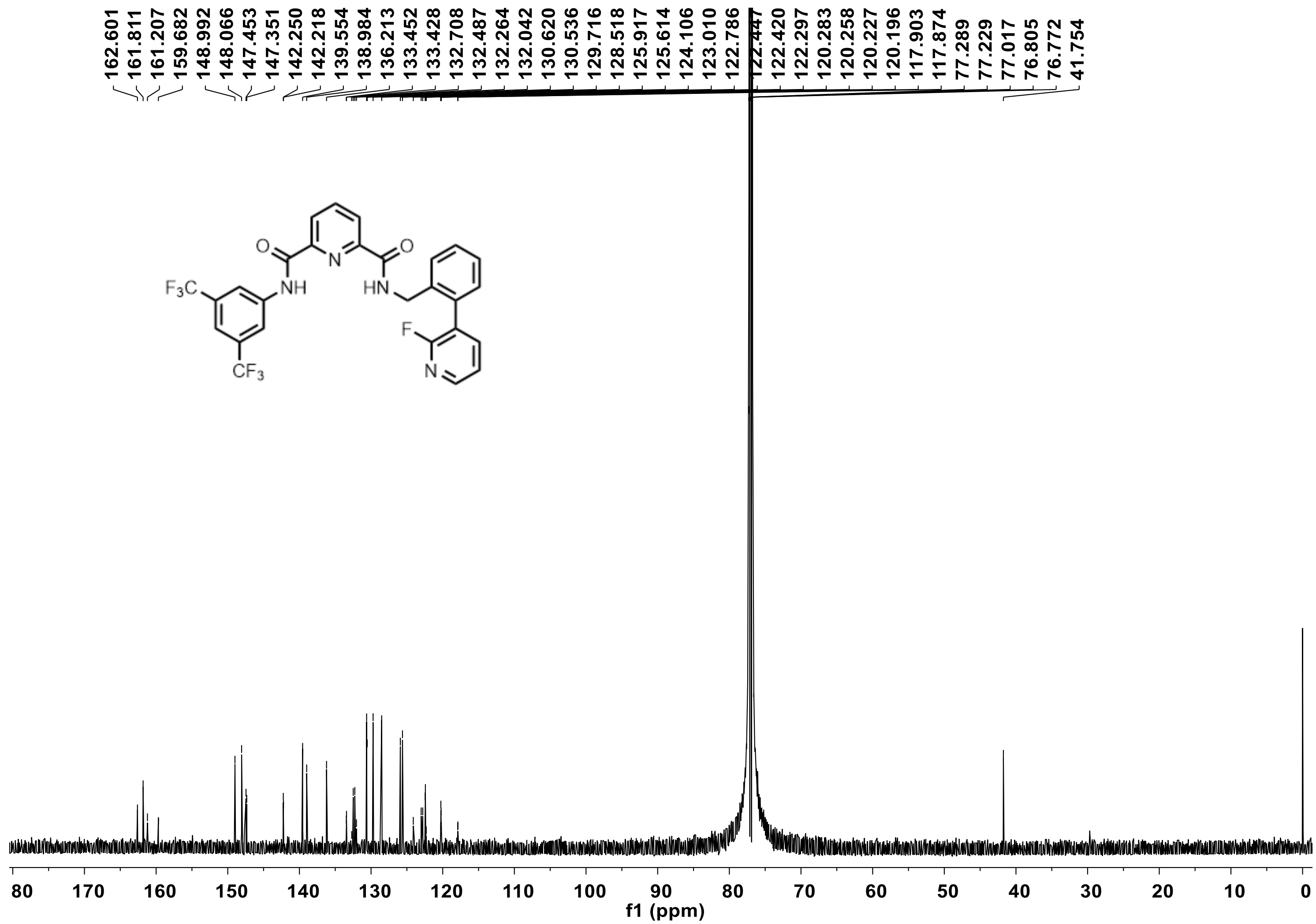
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T1**



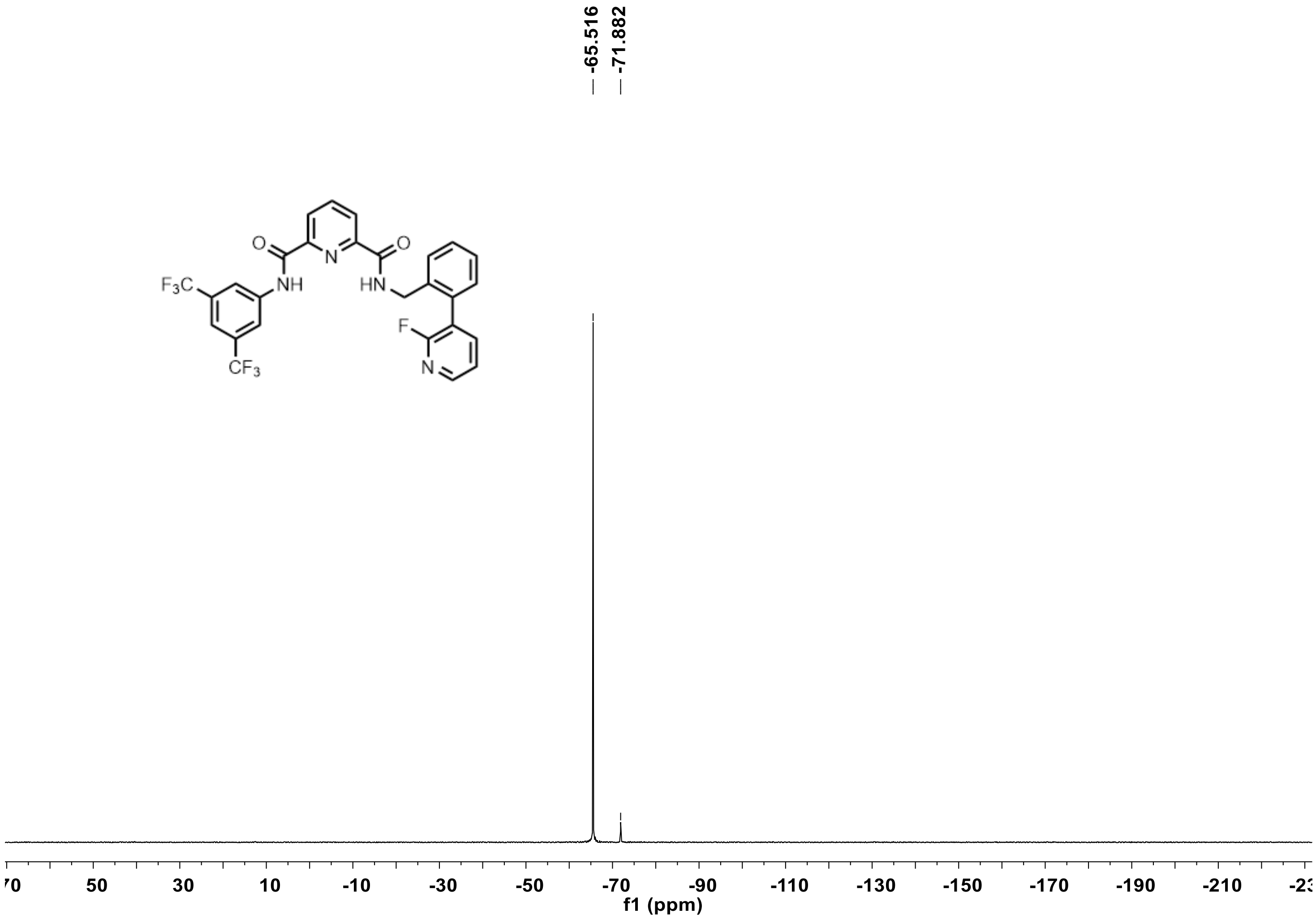
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T2**



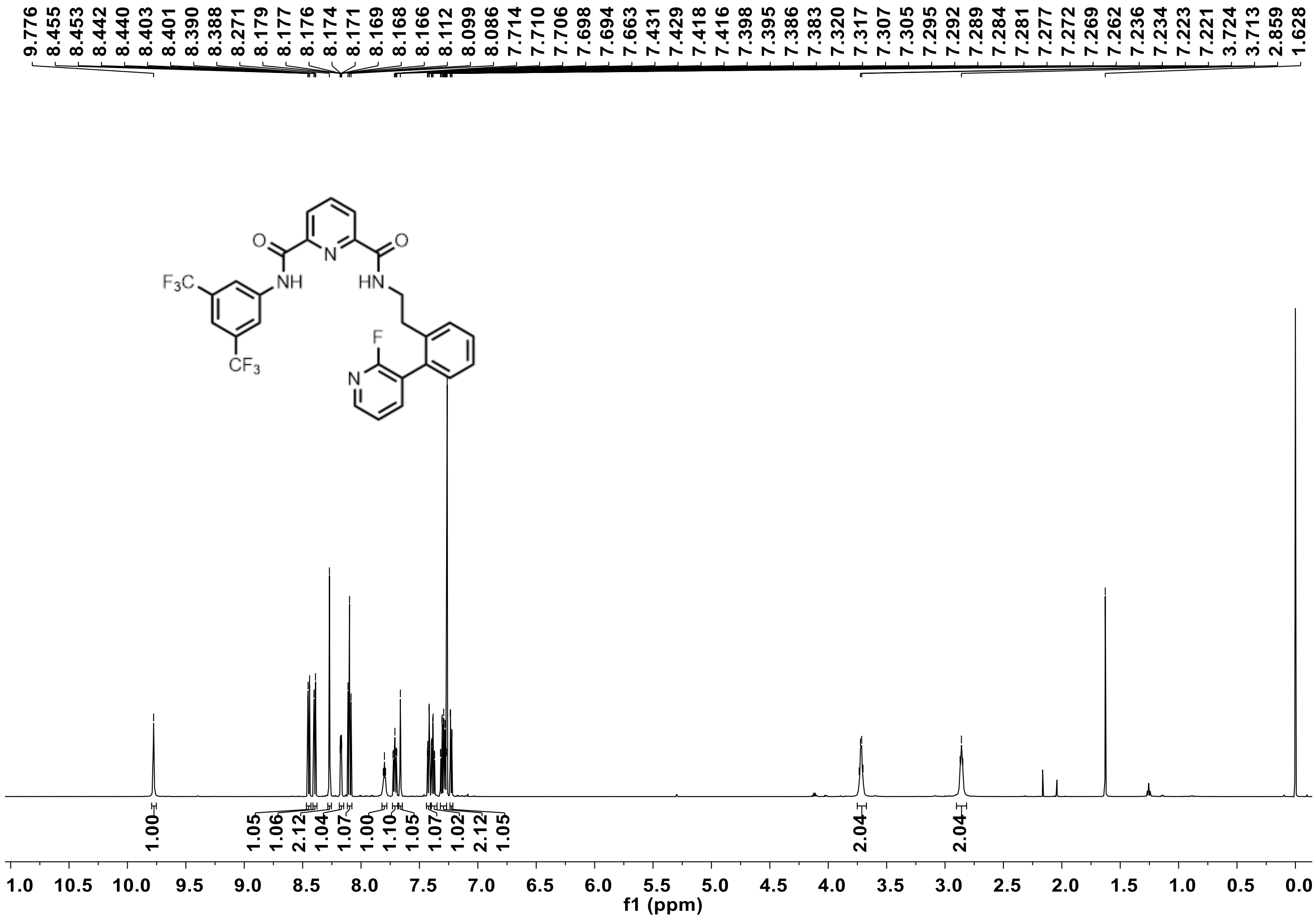
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T2**



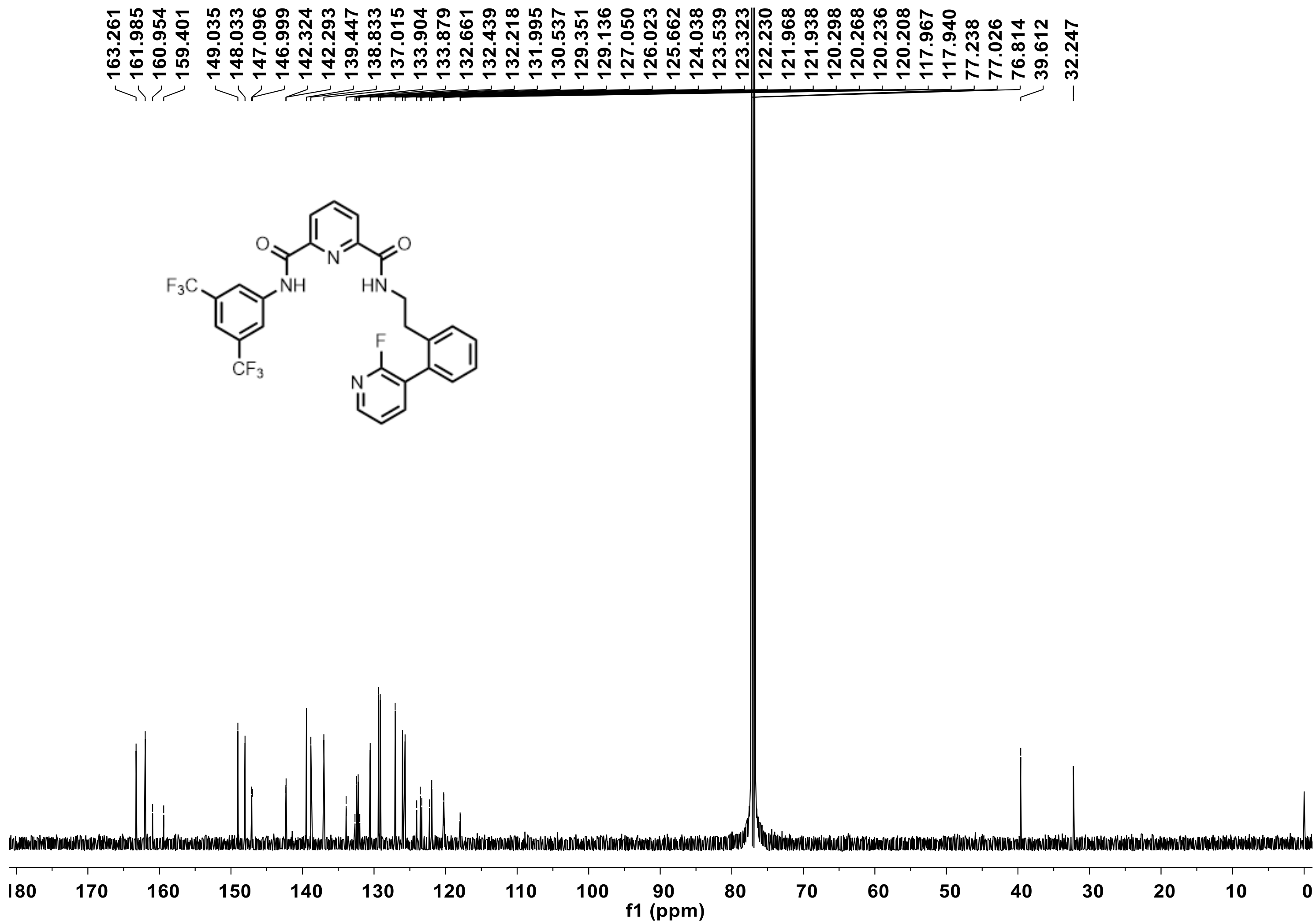
[19]F NMR (376 MHz, $CDCl_3$) spectrum of **T2**



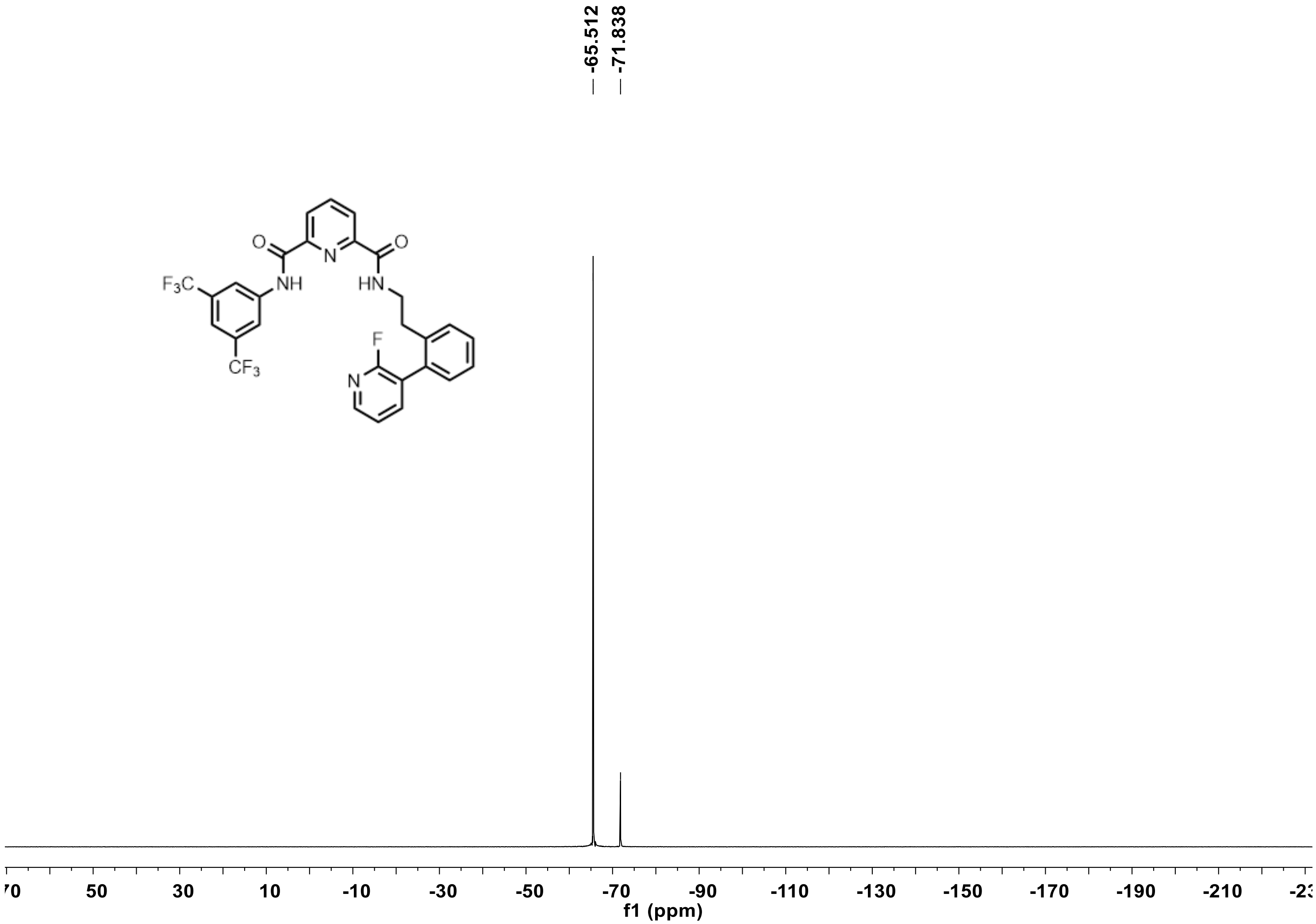
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T3**



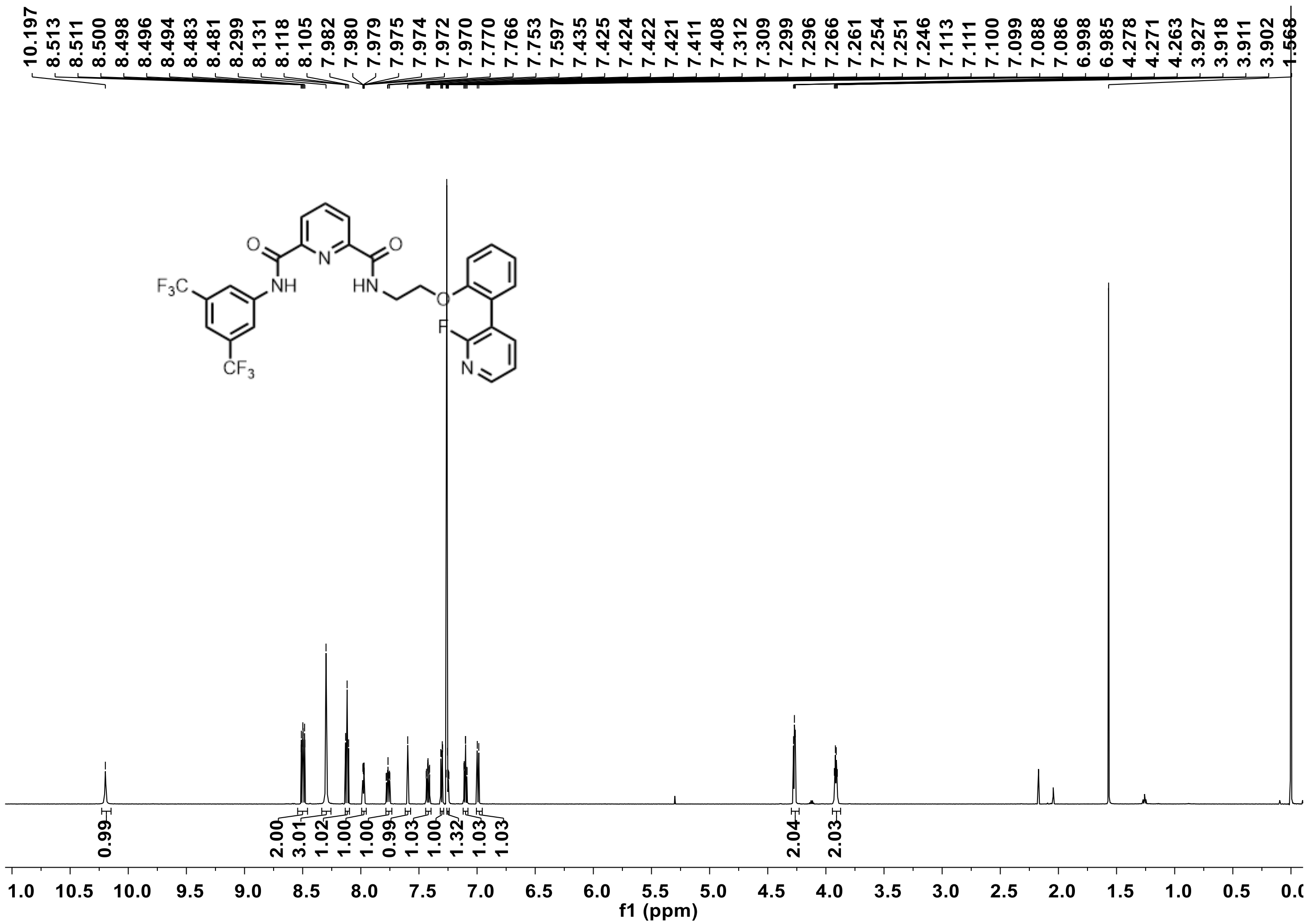
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T3**



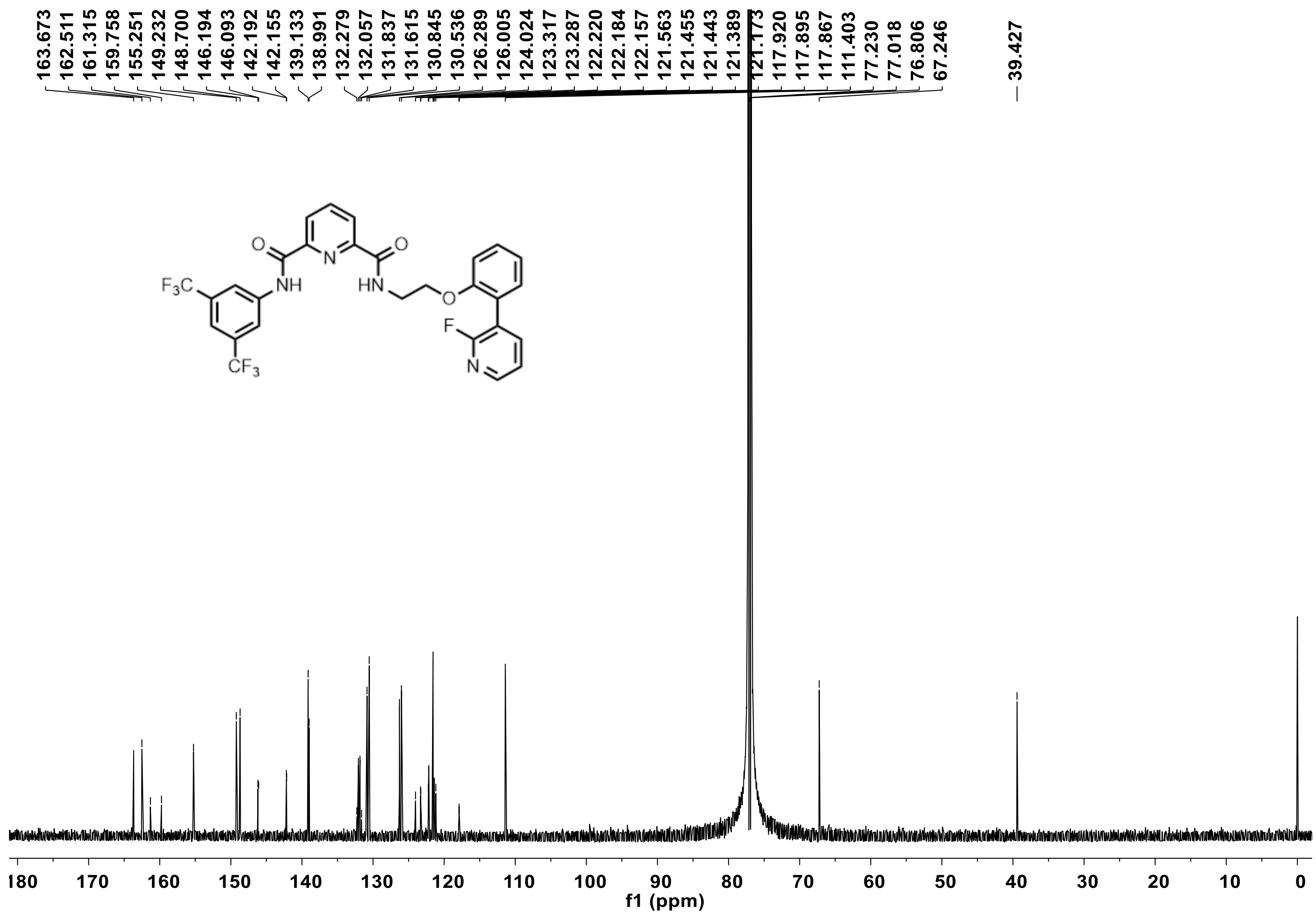
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T3**



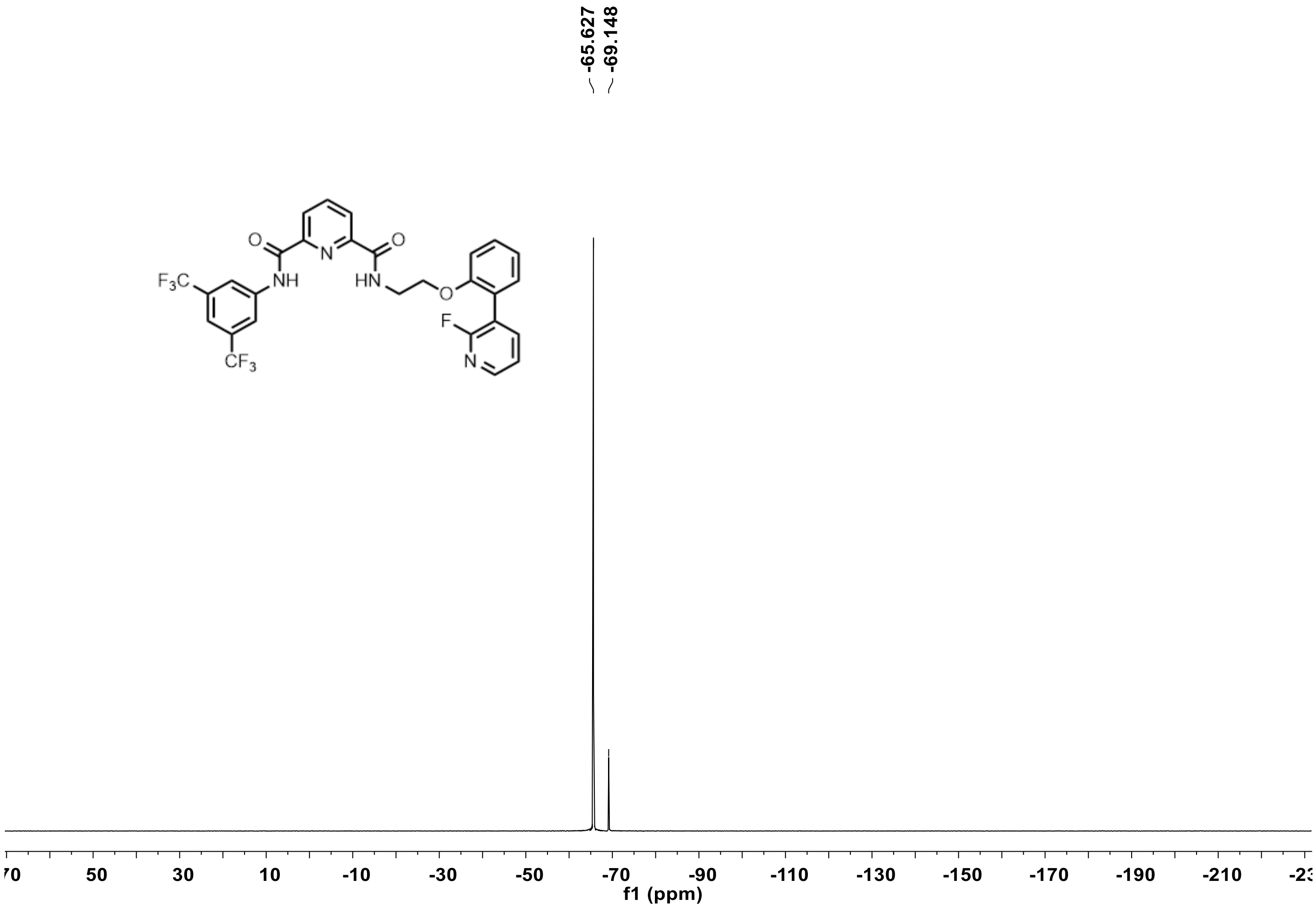
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T4**



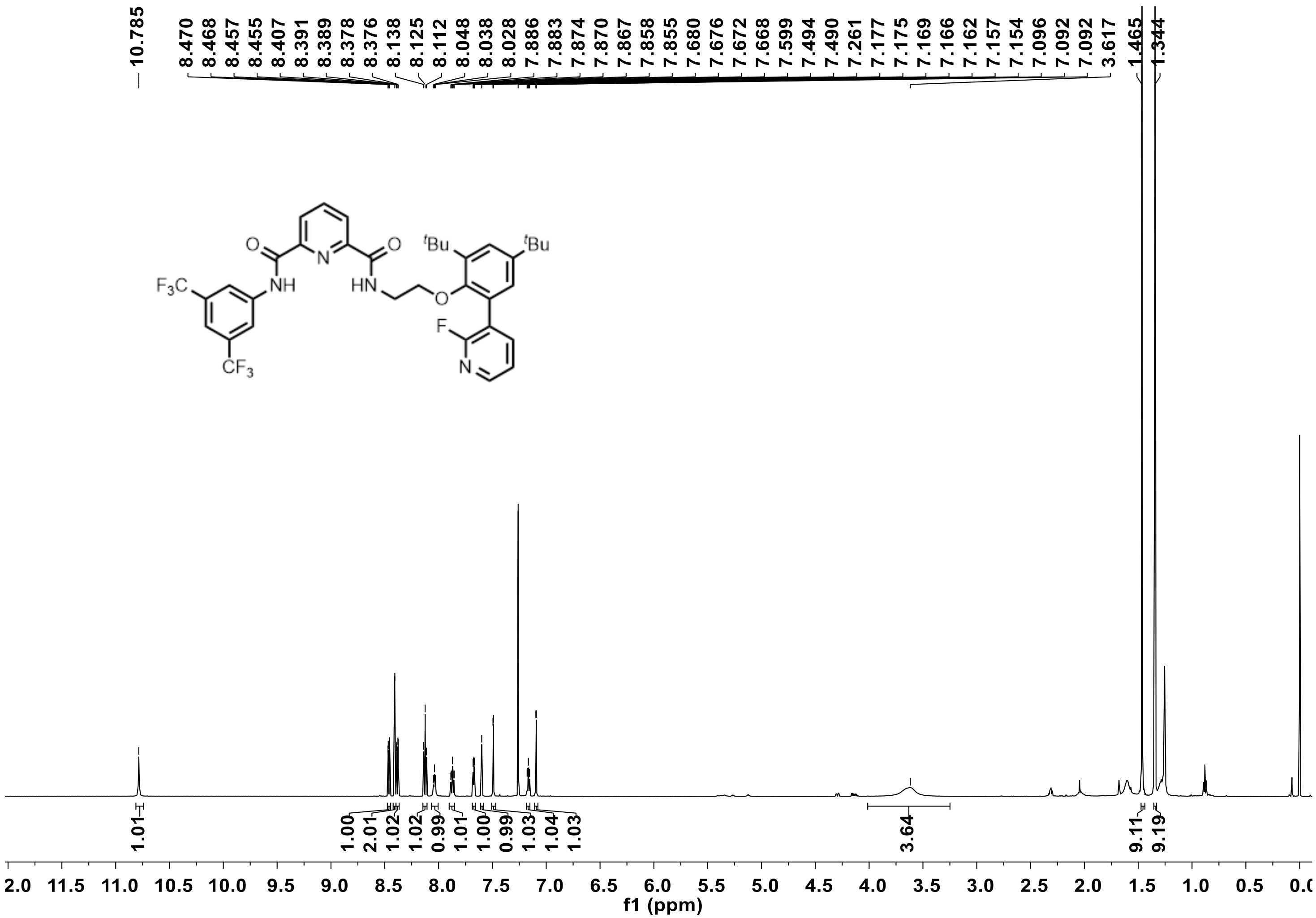
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T4**



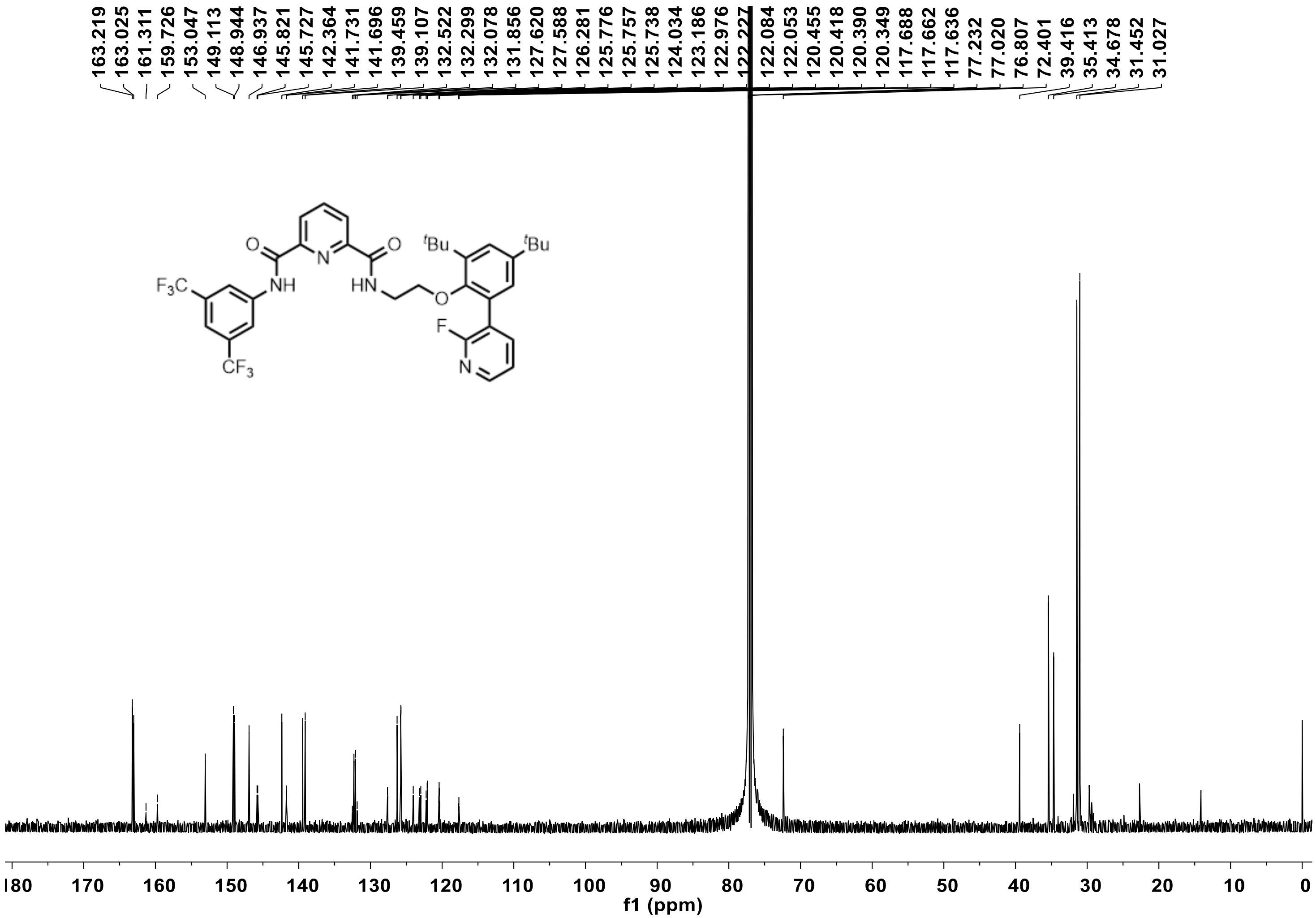
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T4**



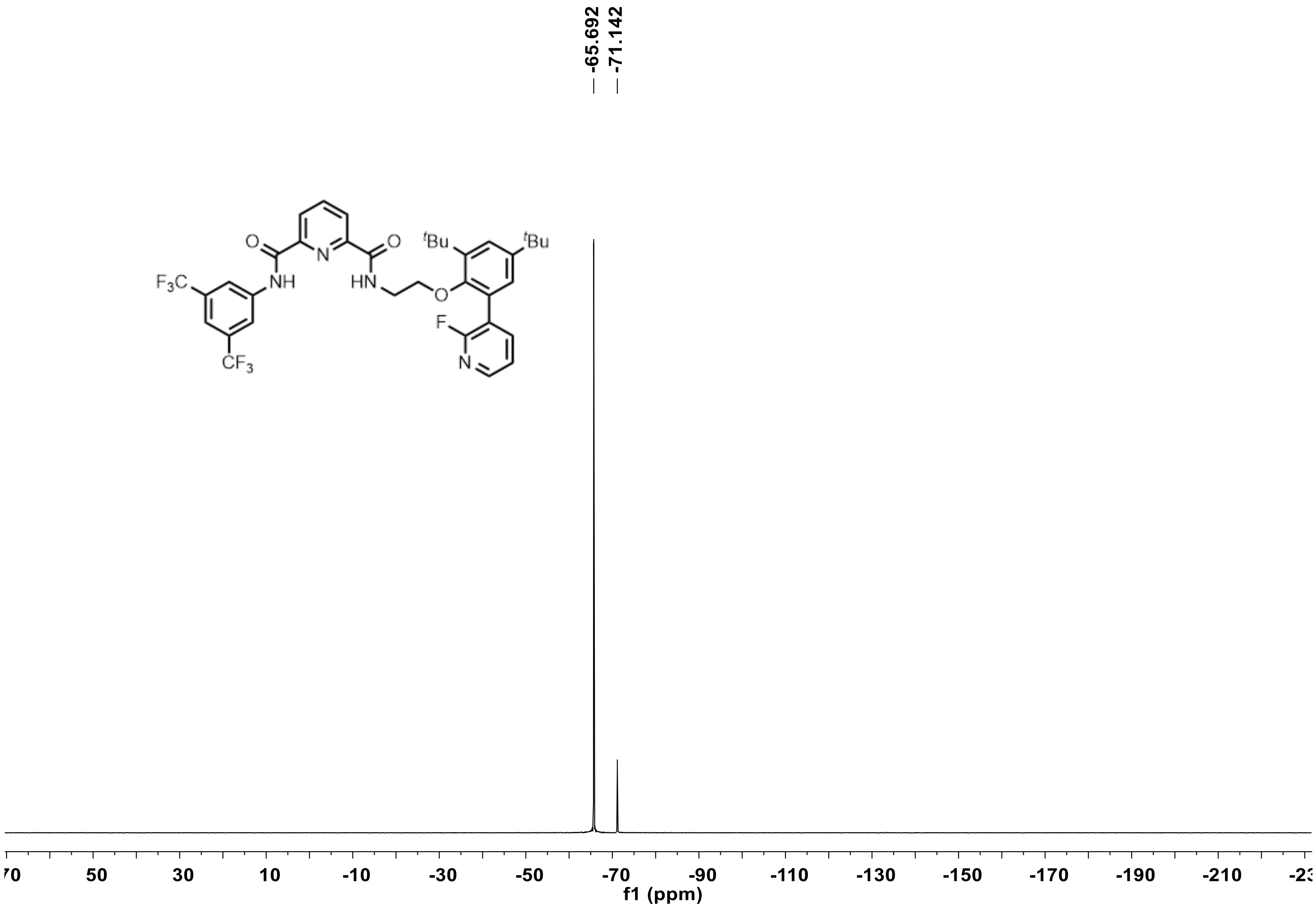
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T5**



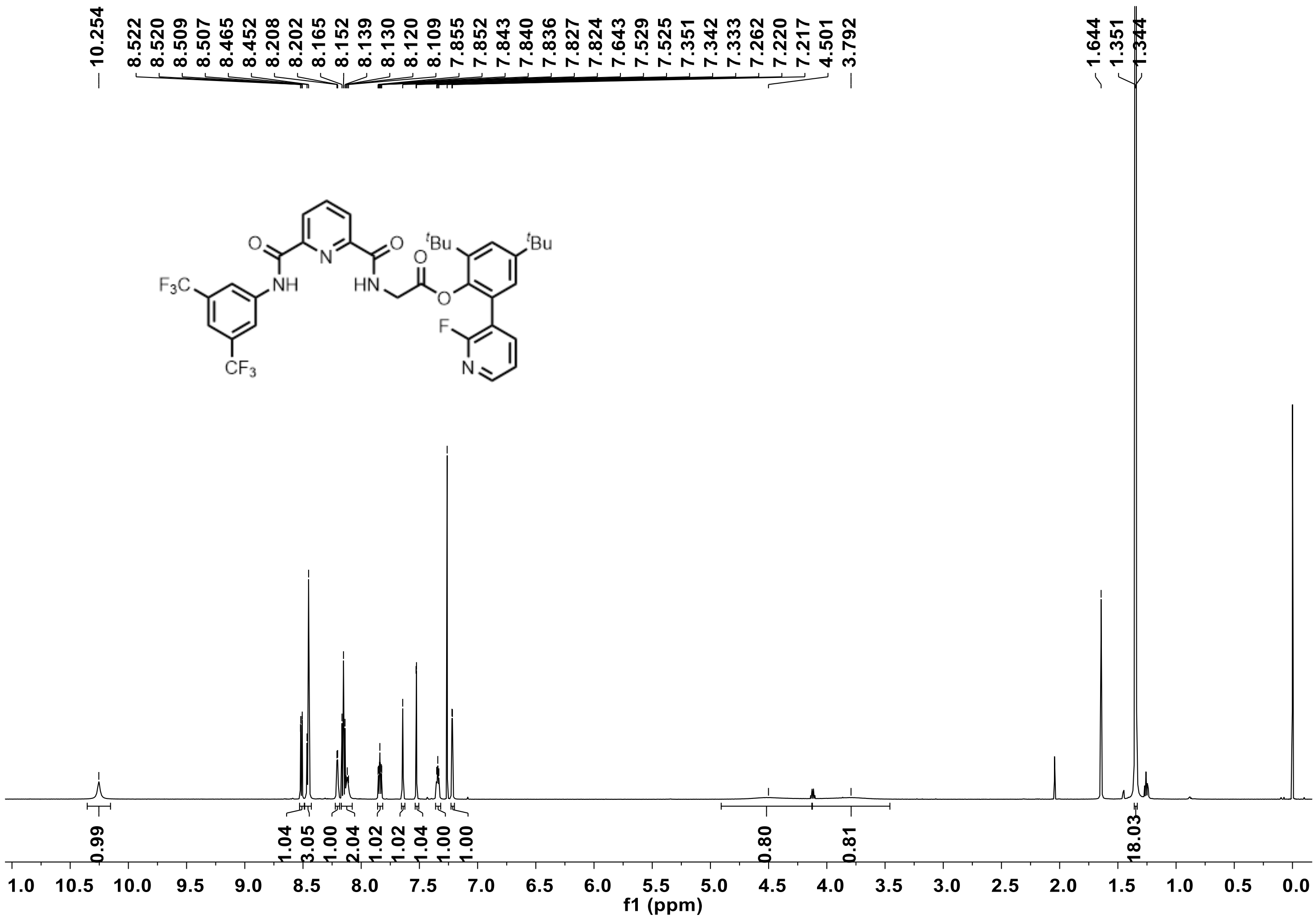
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T5**



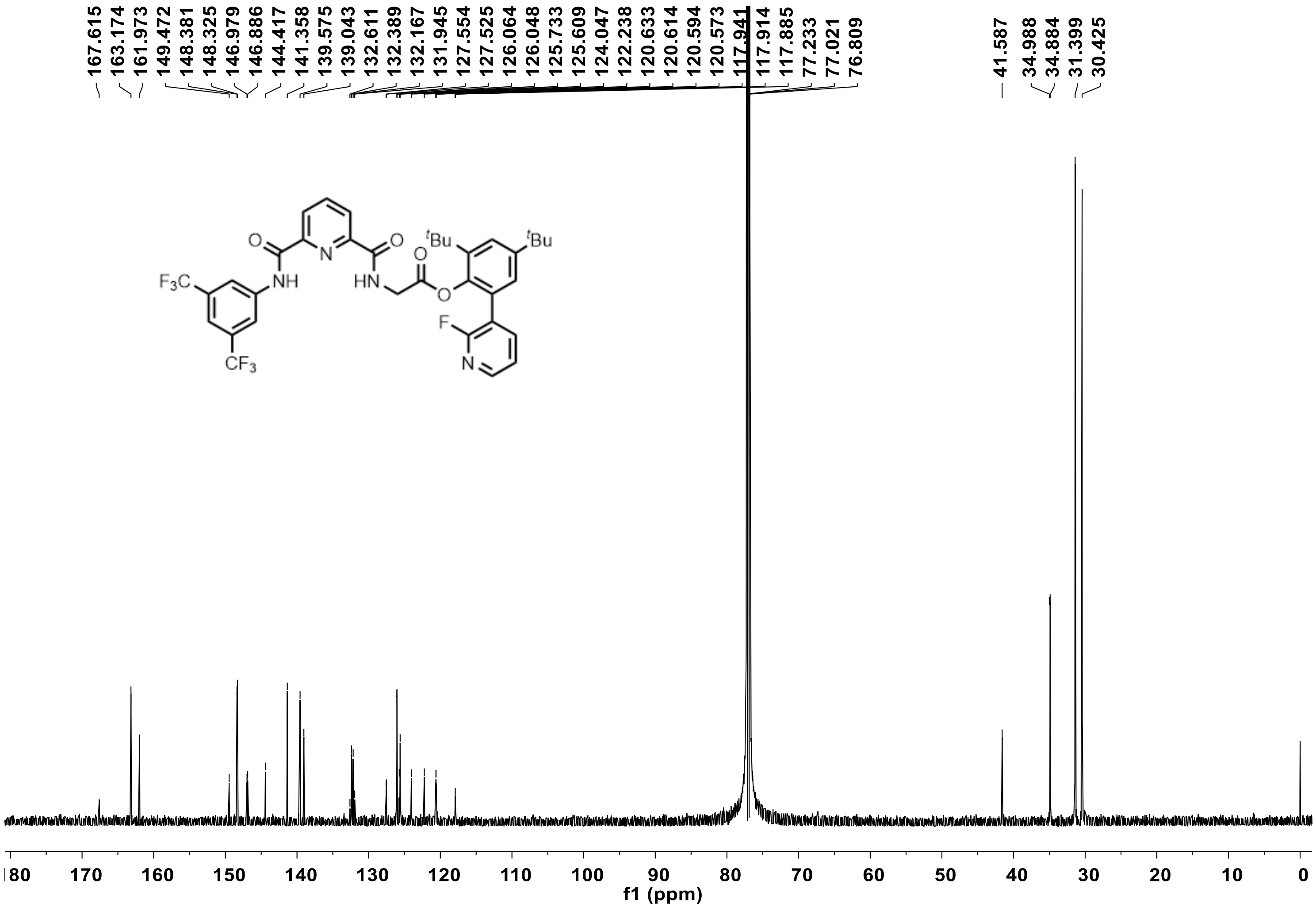
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T5**



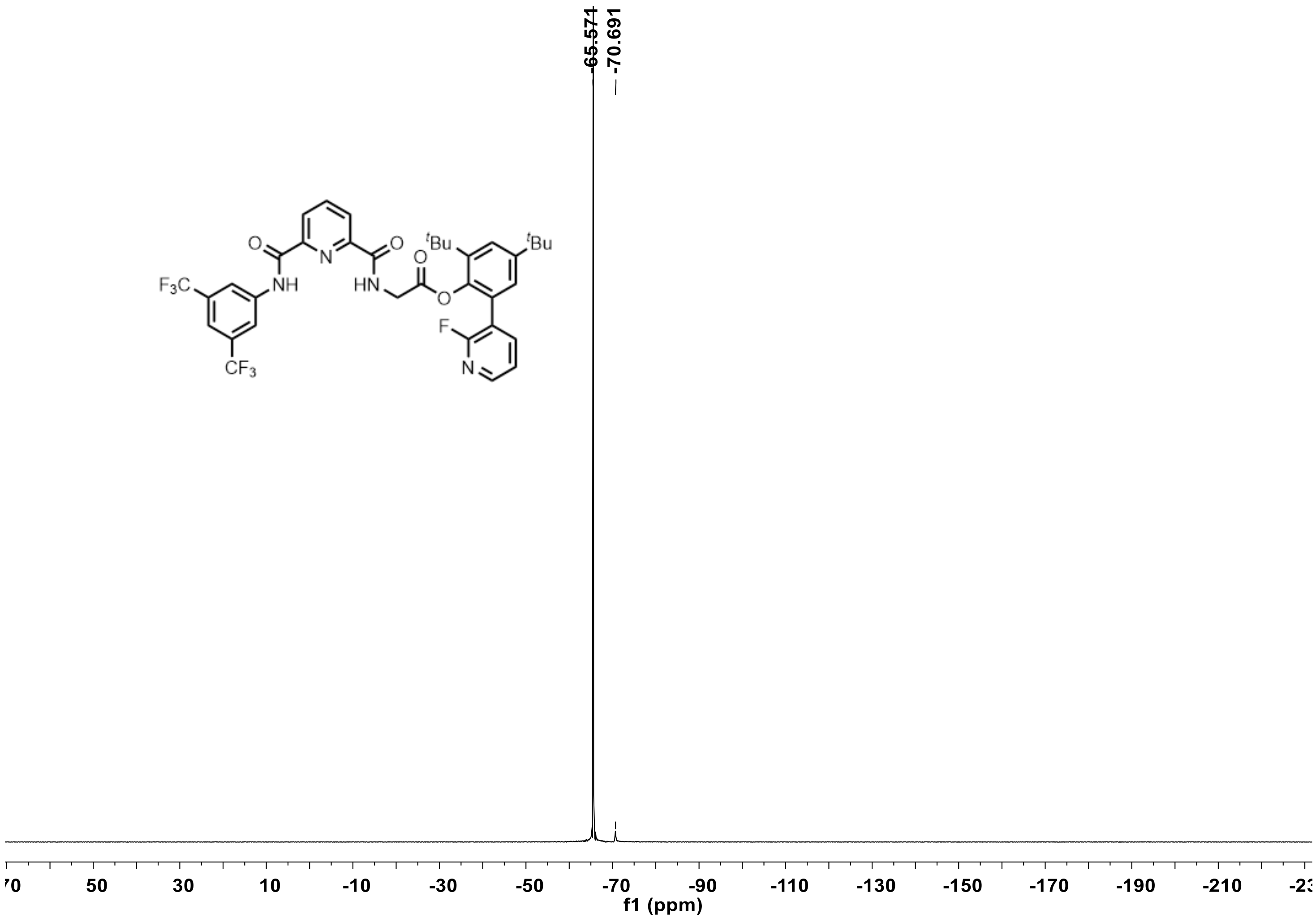
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T6**



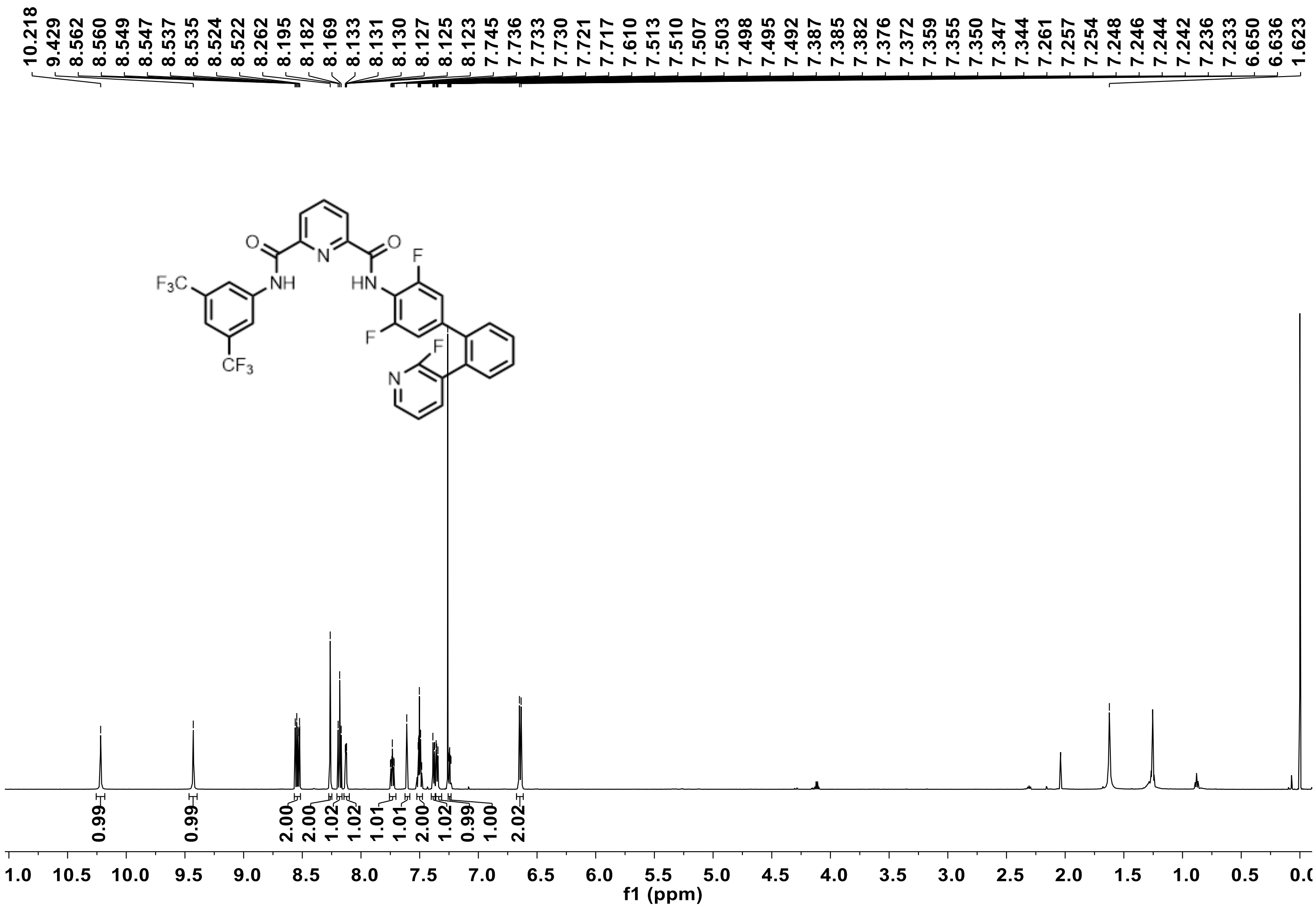
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T6**



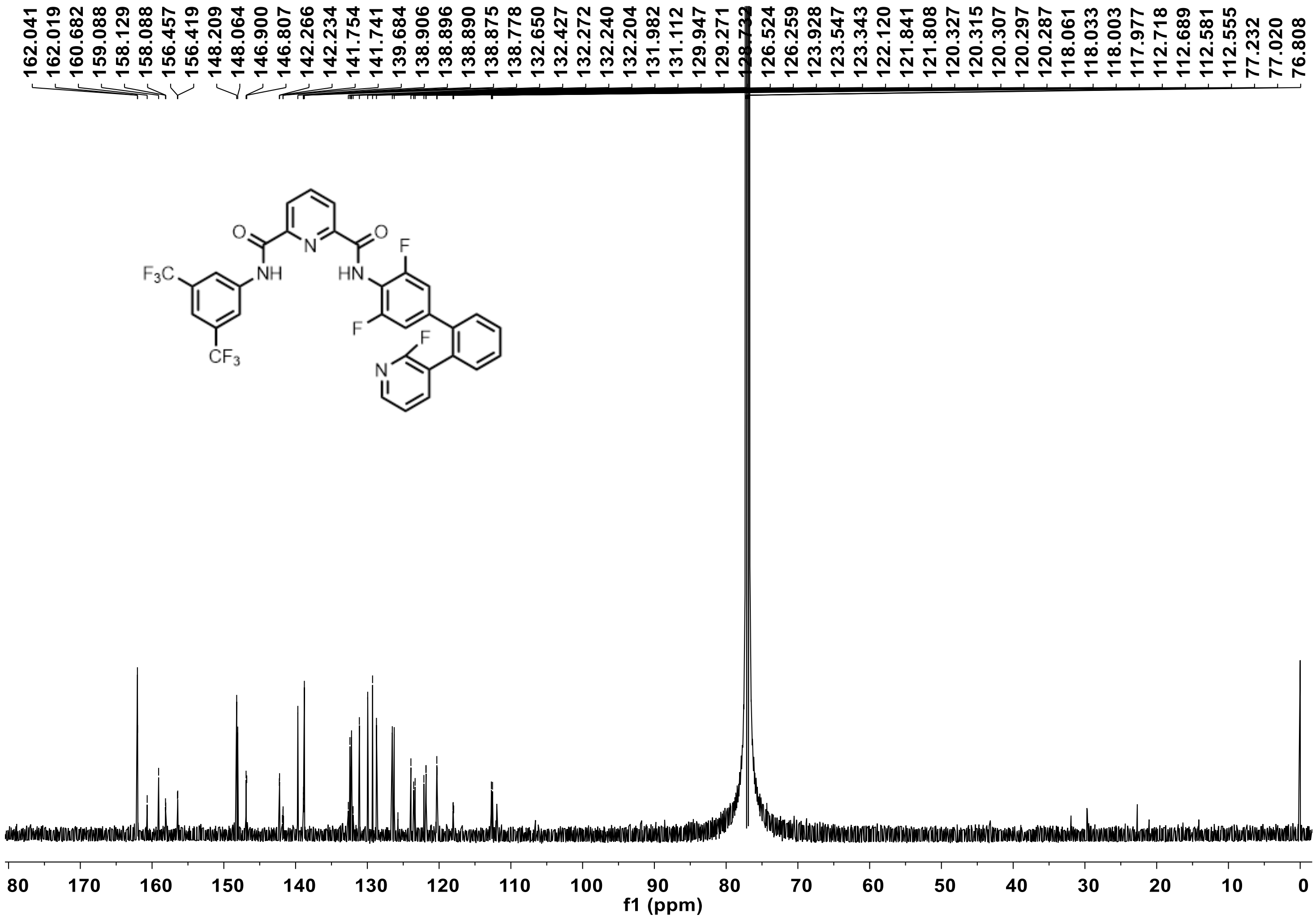
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T6**



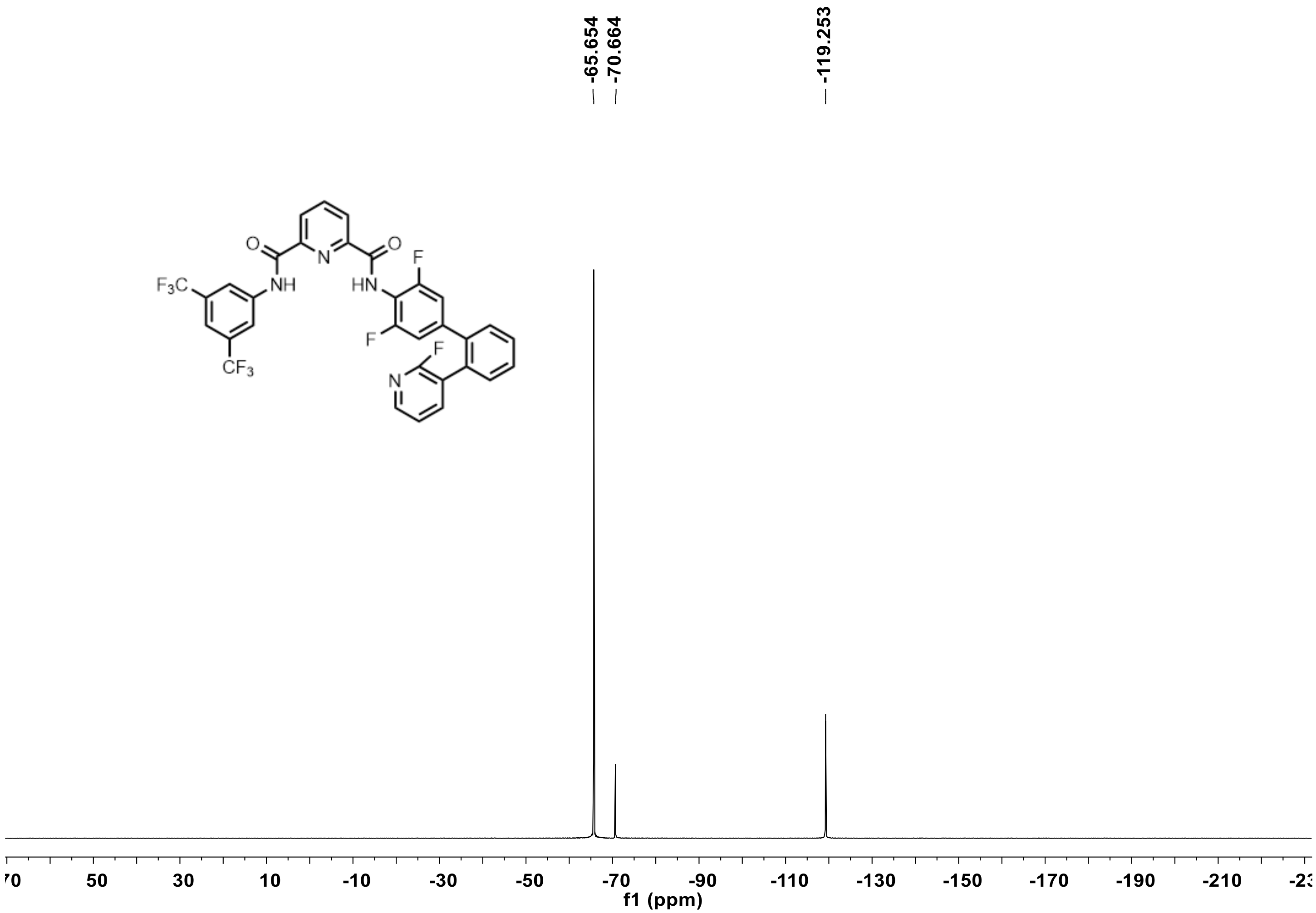
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T7**



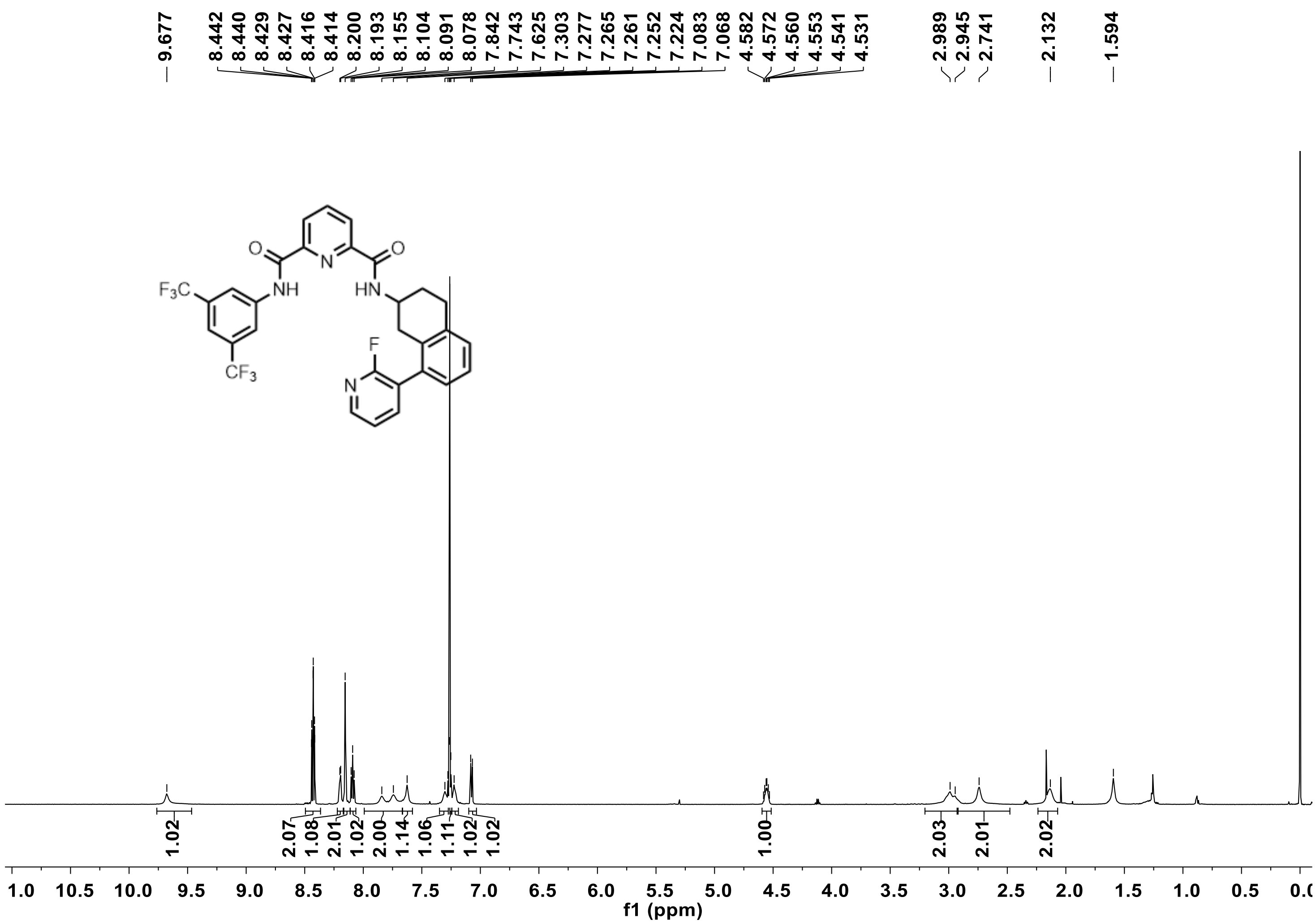
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T7**



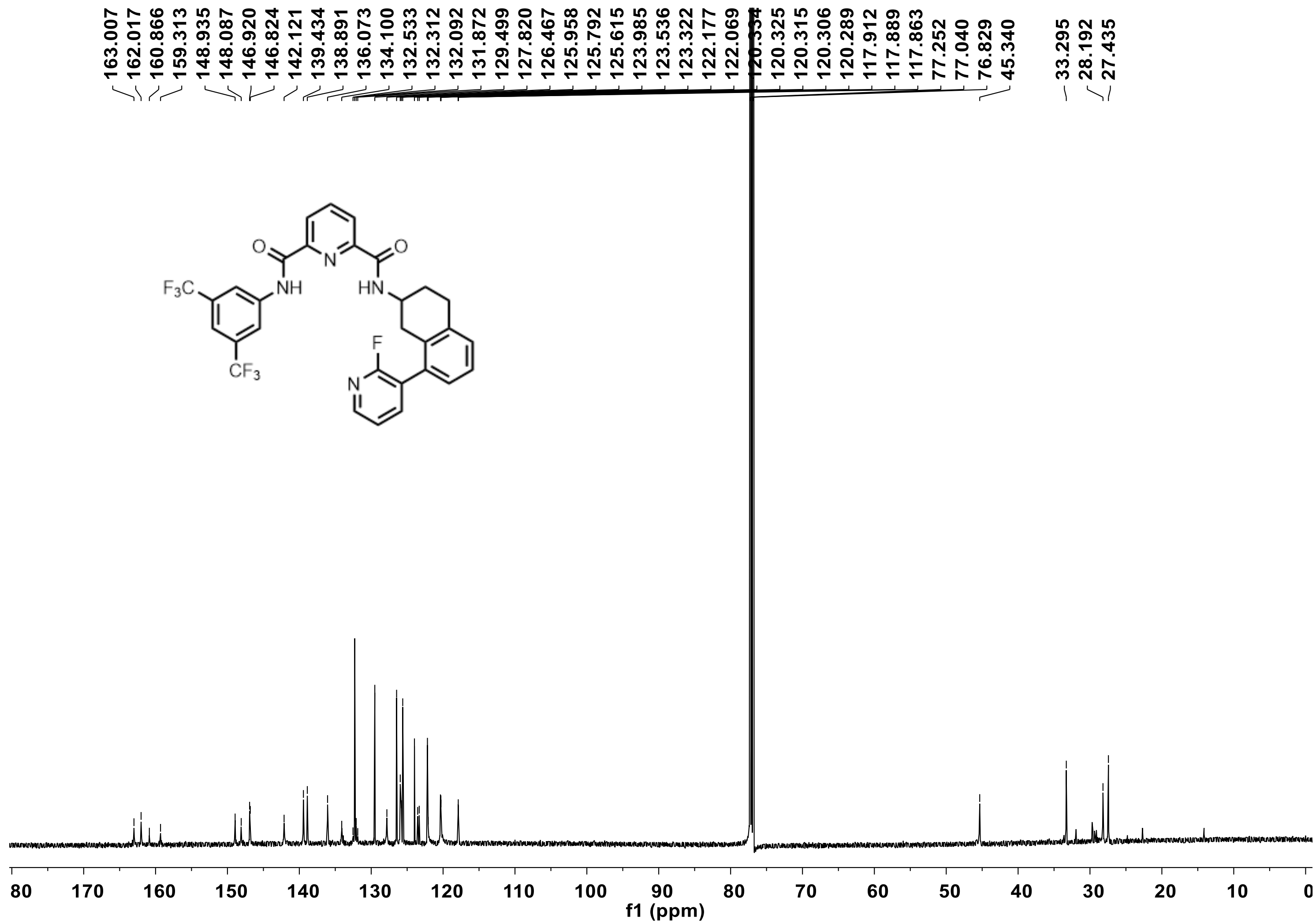
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T7**



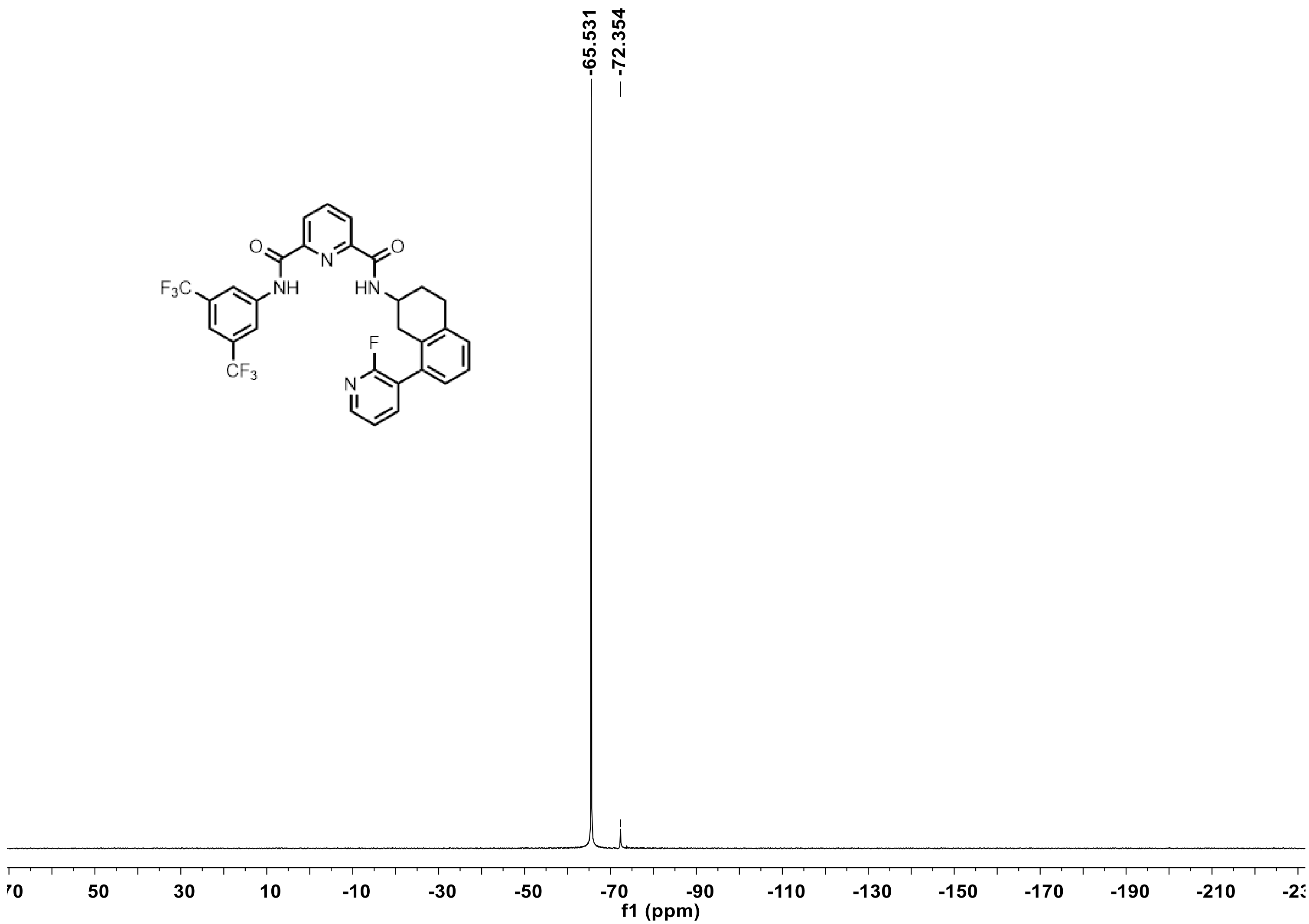
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **T8**



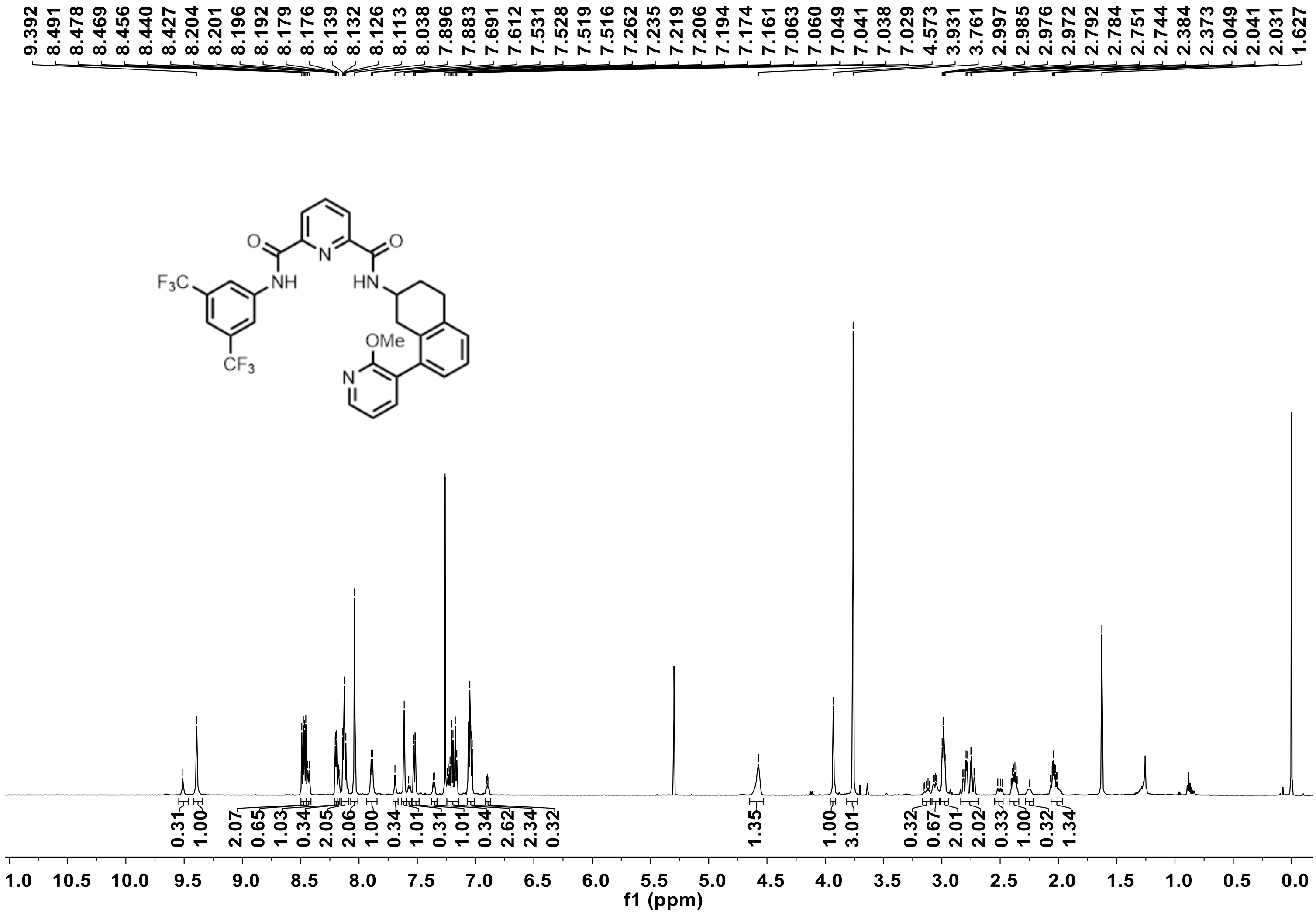
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T8**



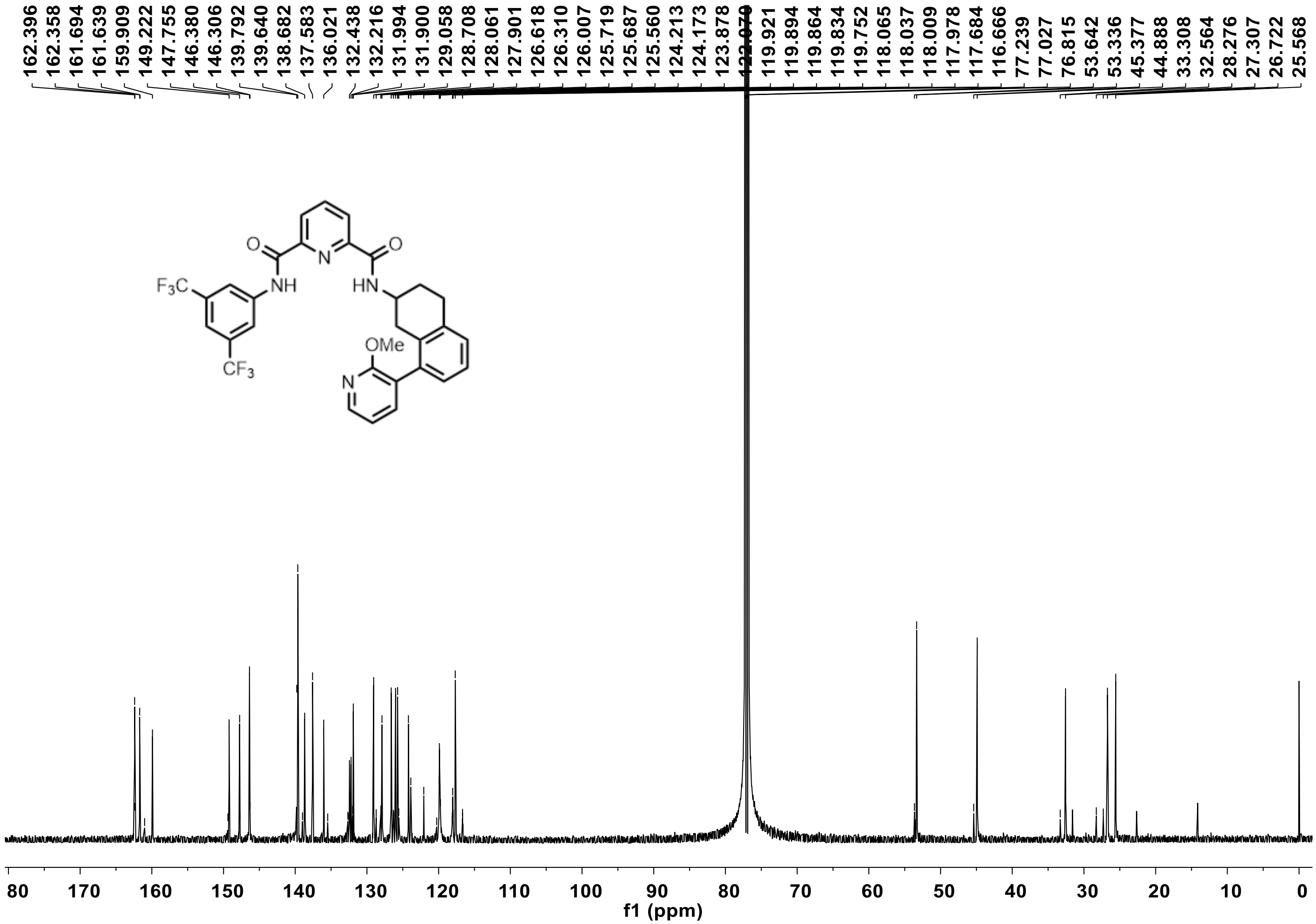
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T8**



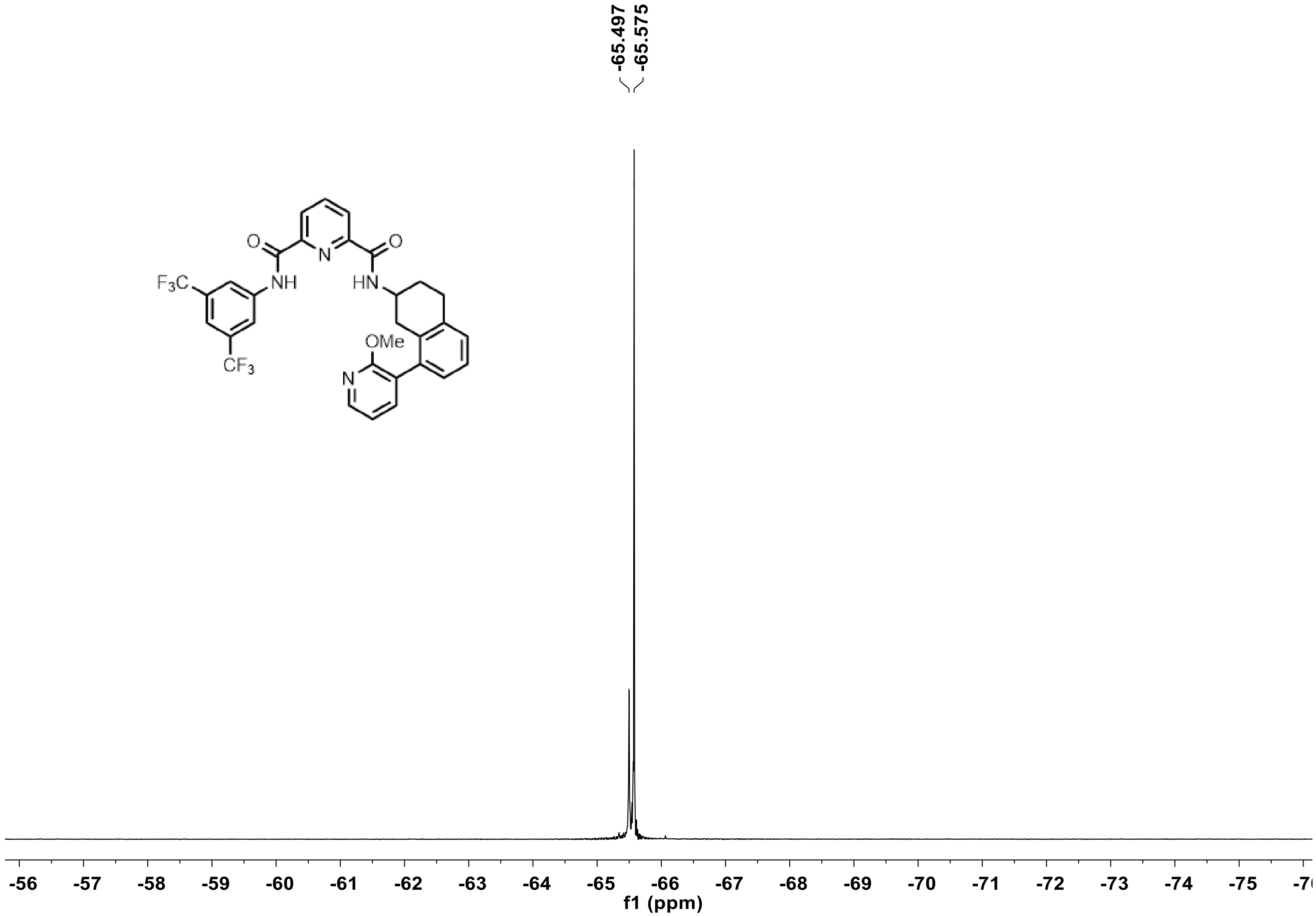
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T9**



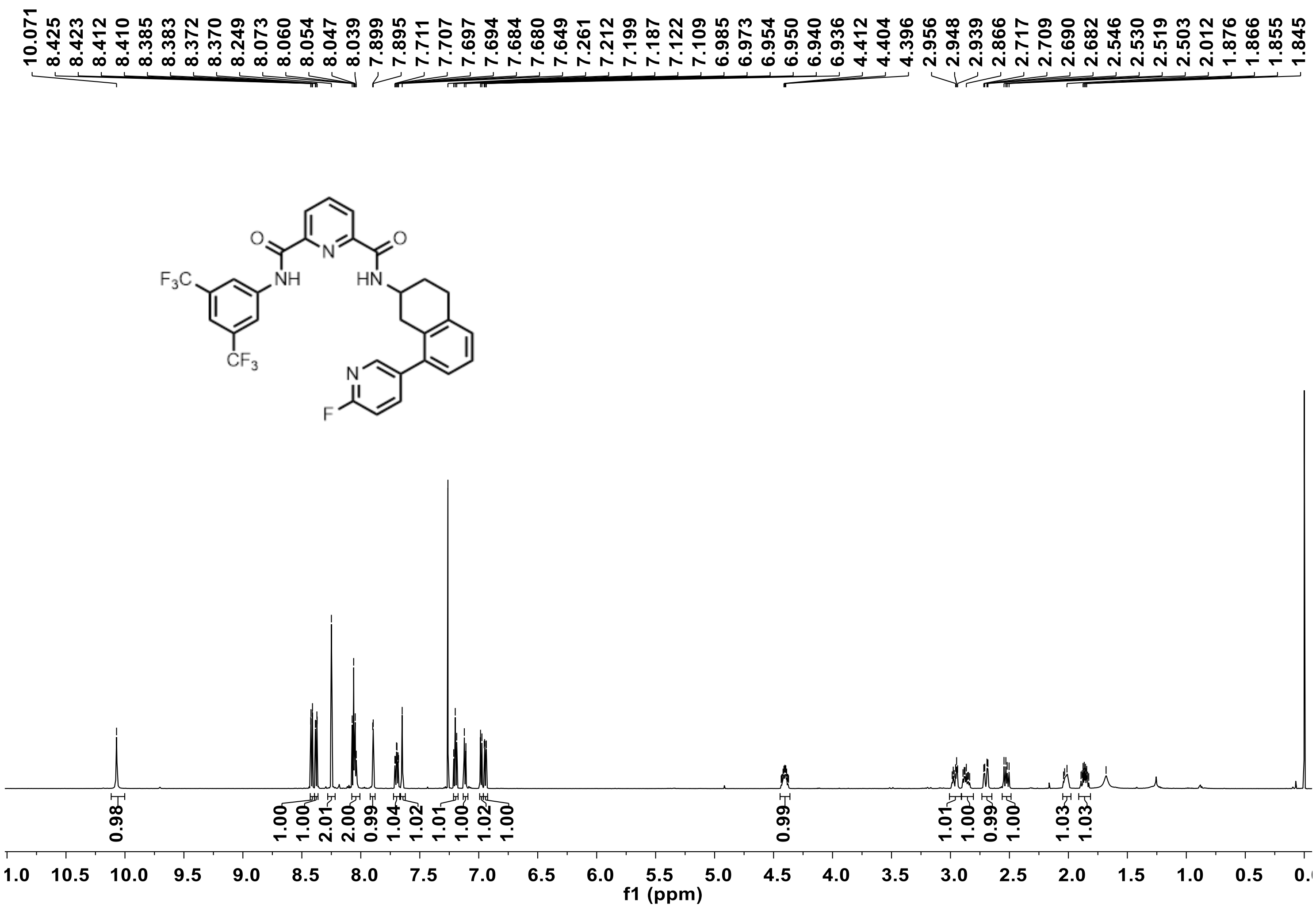
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T9**



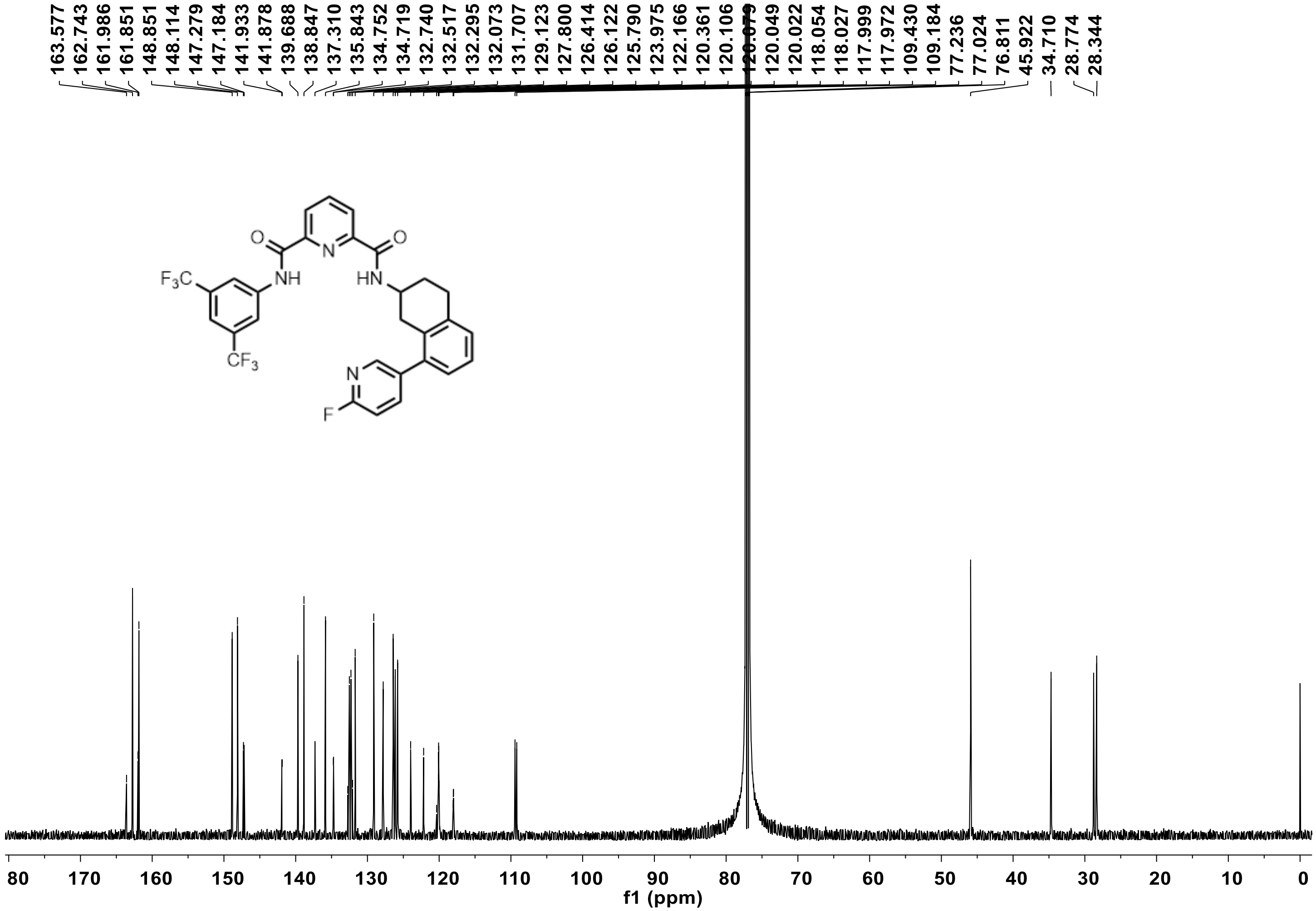
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T9**



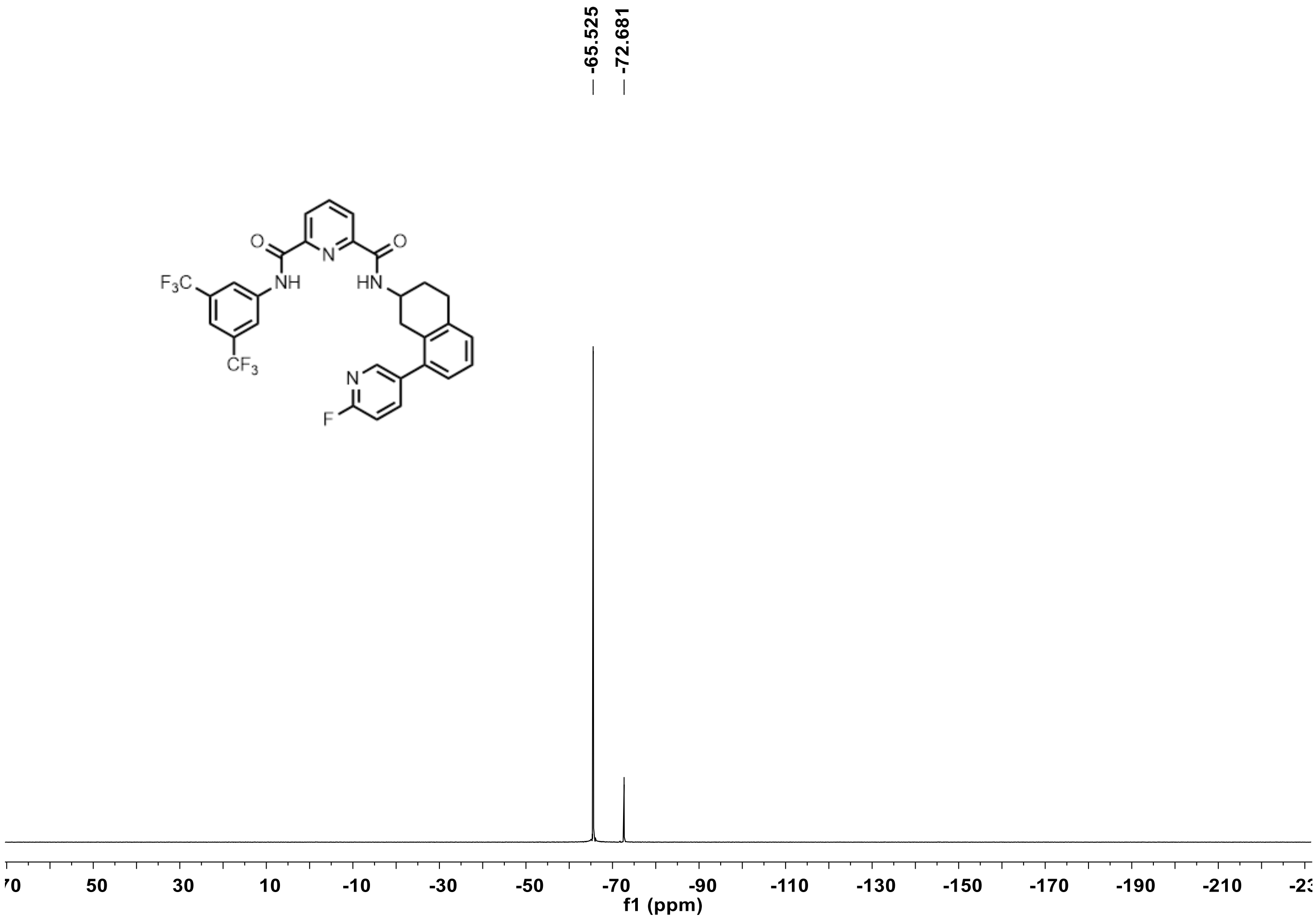
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T10**



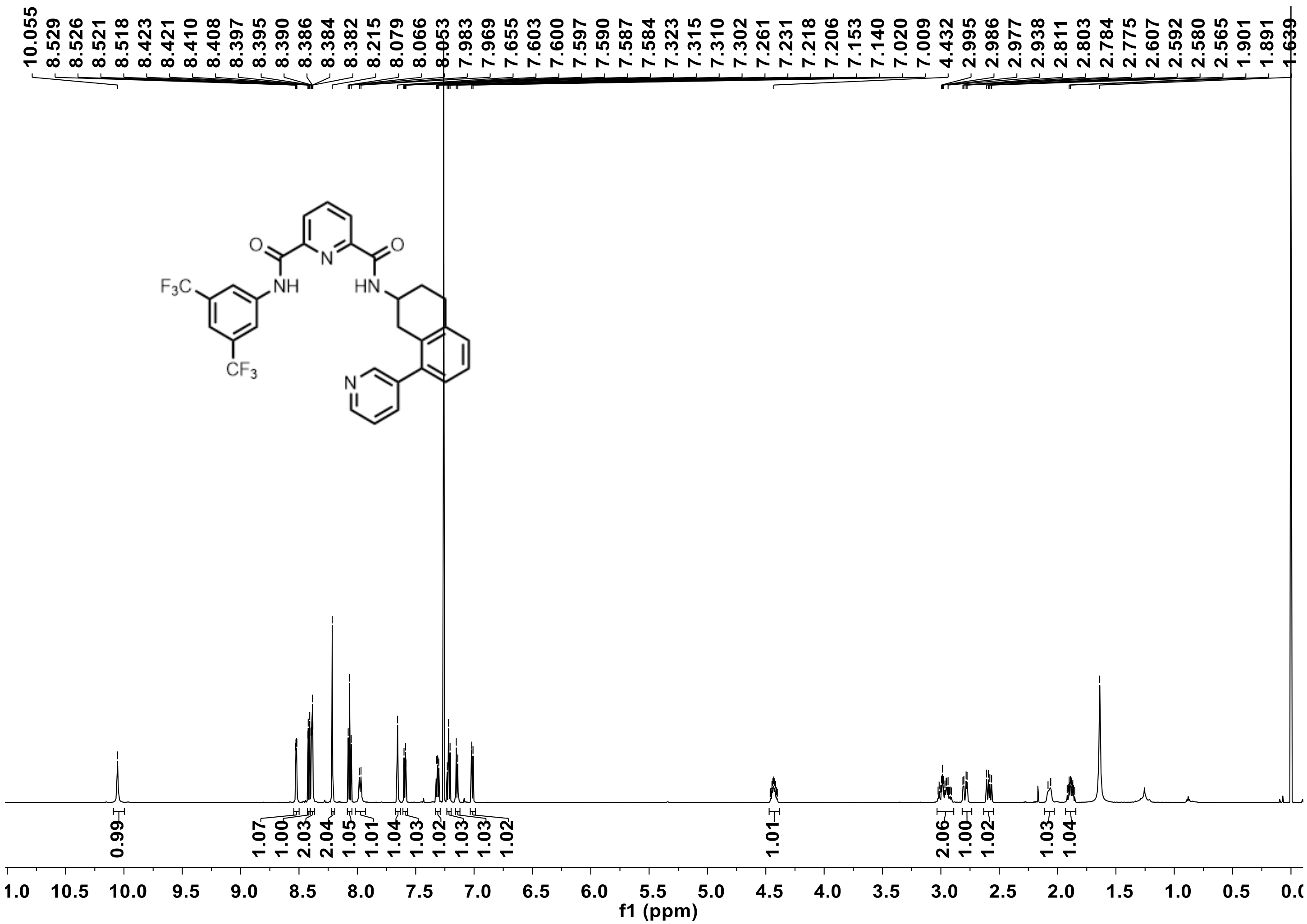
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T10**



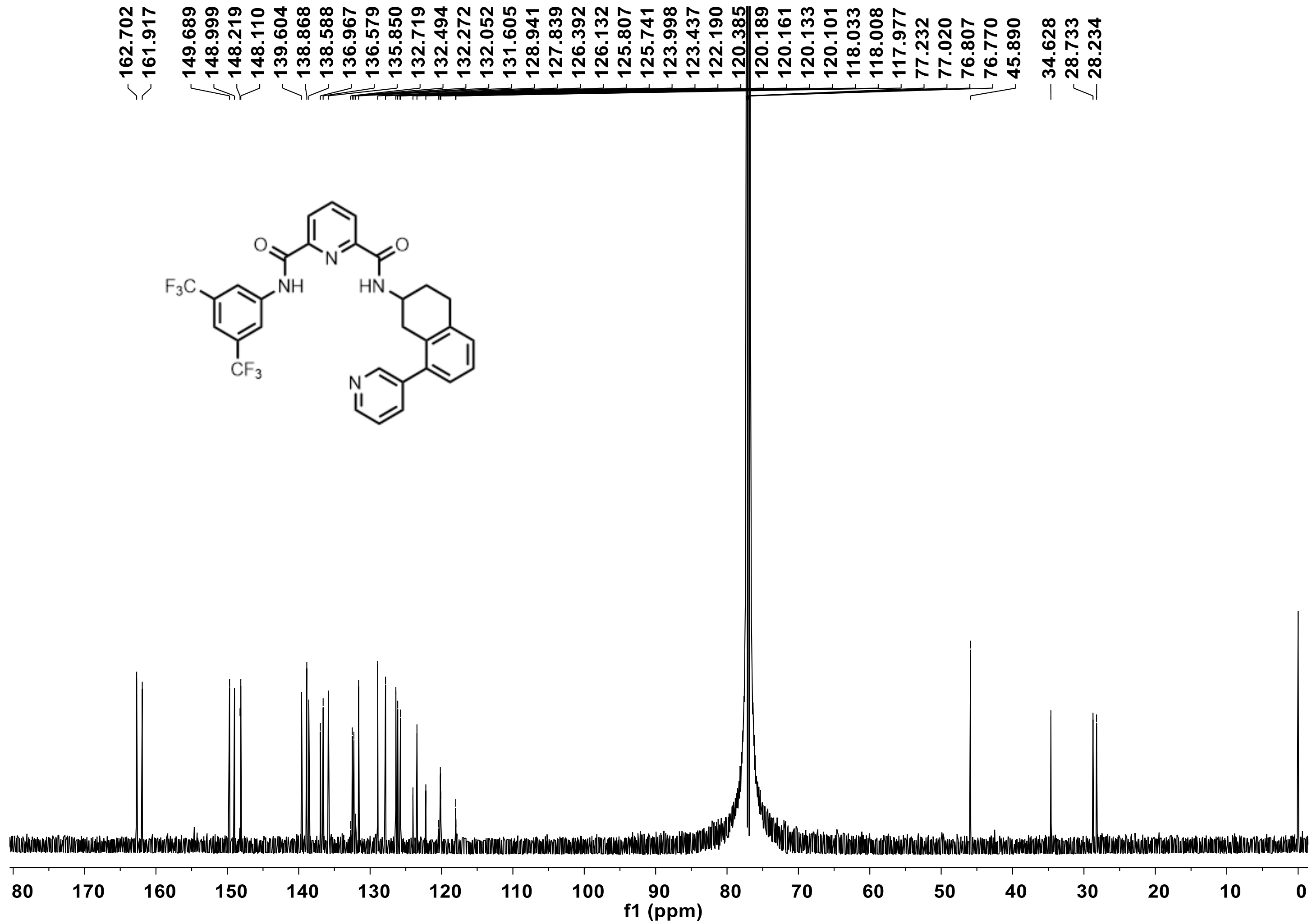
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T10**



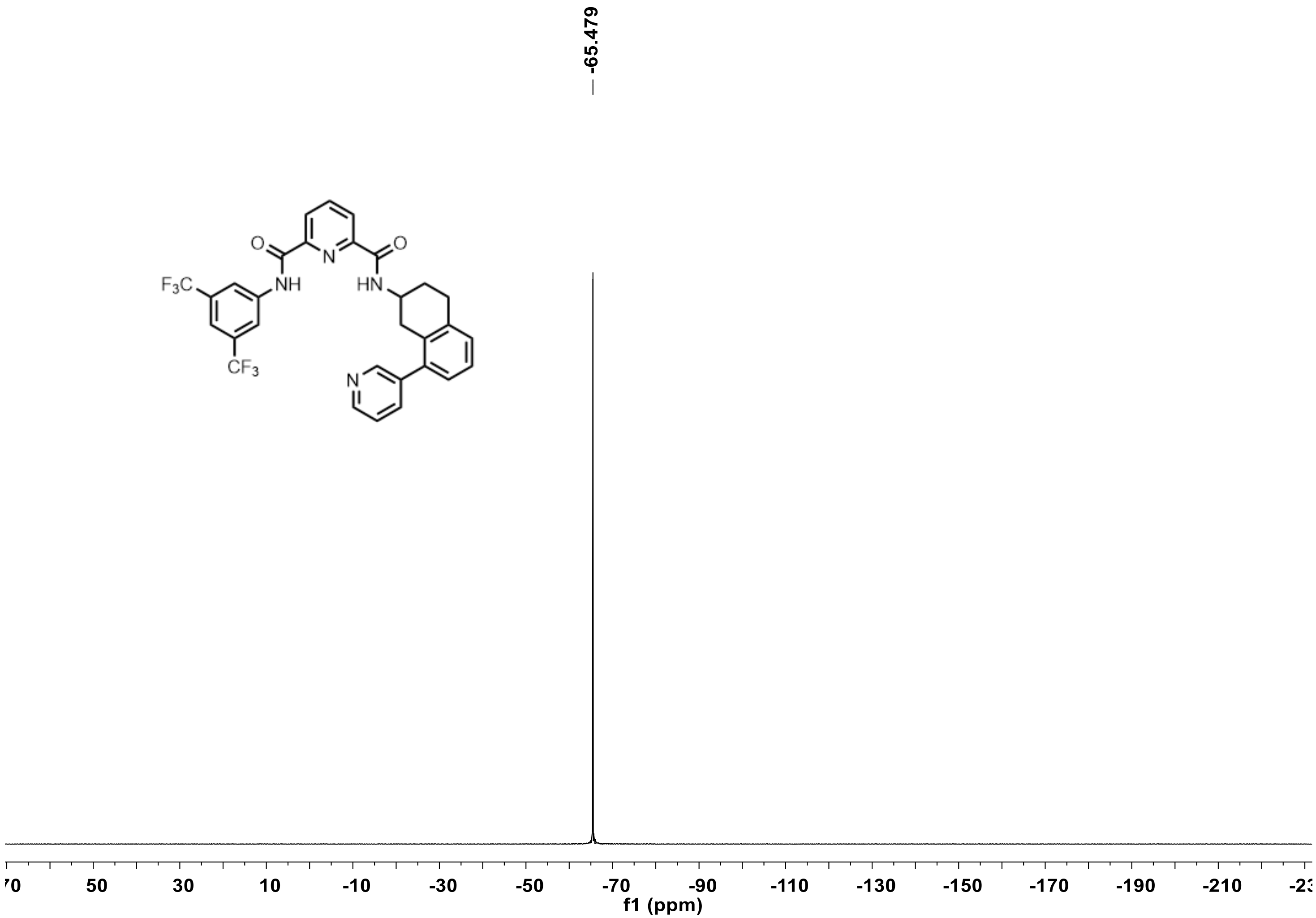
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T11**



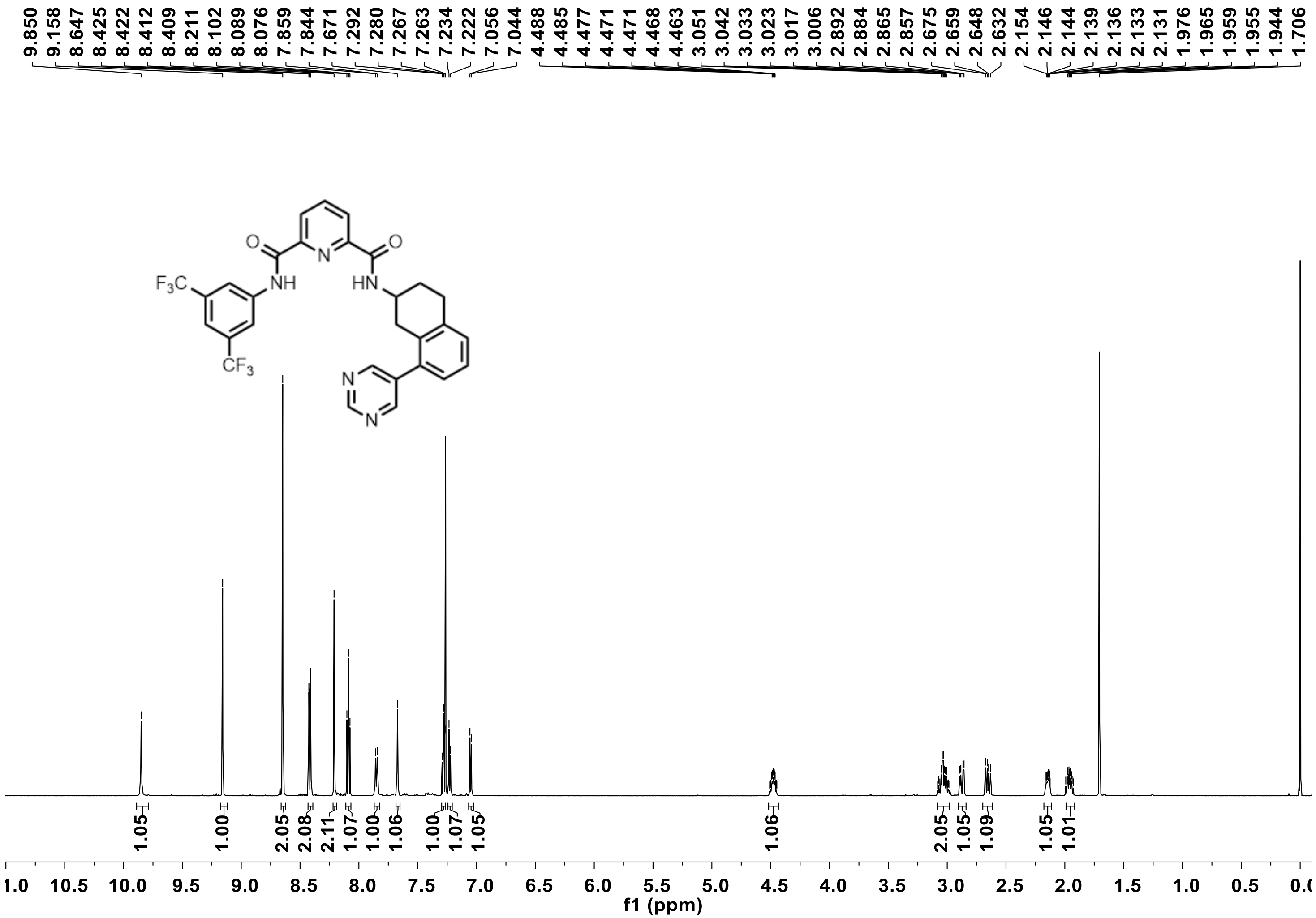
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T11**



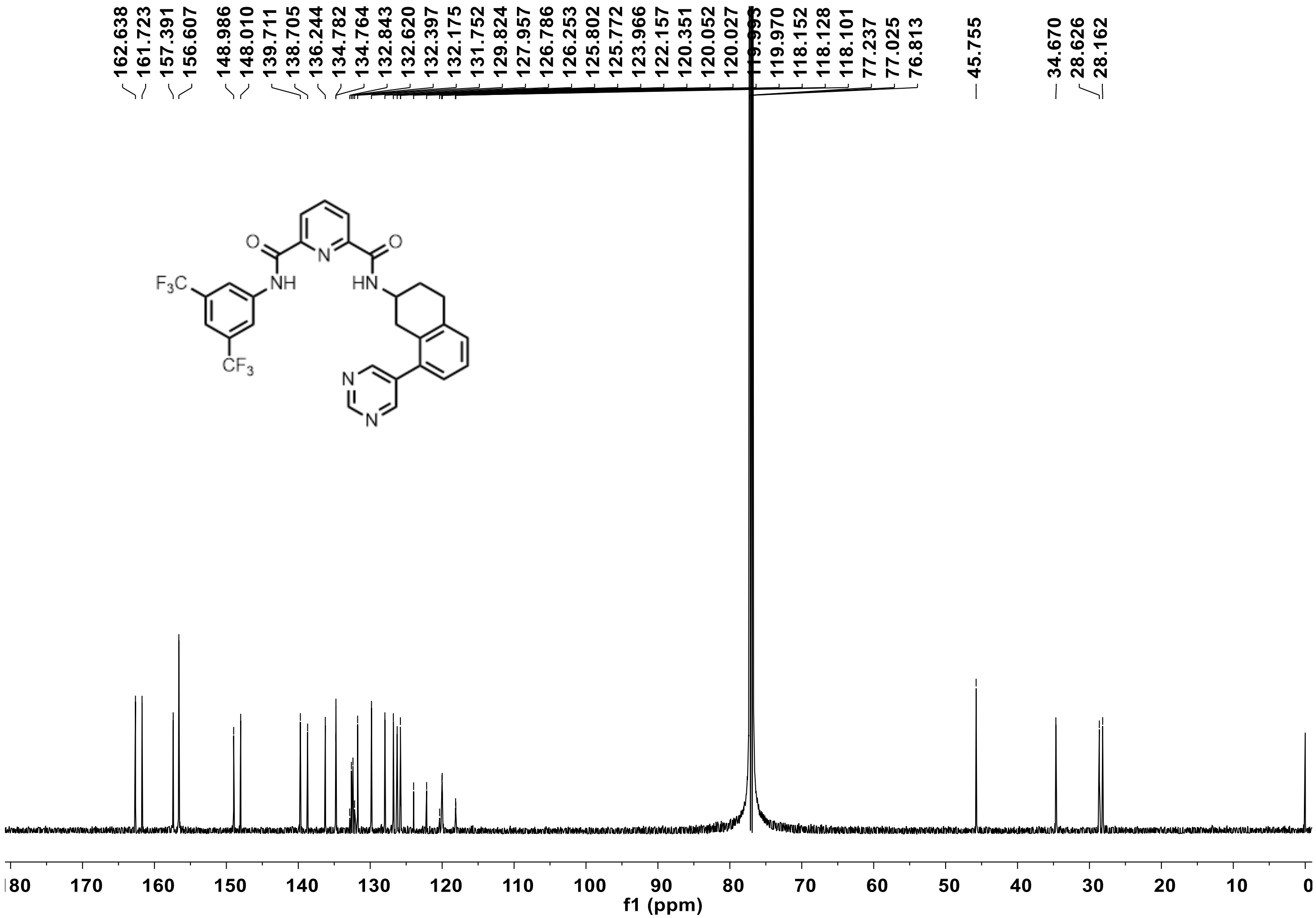
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T11**



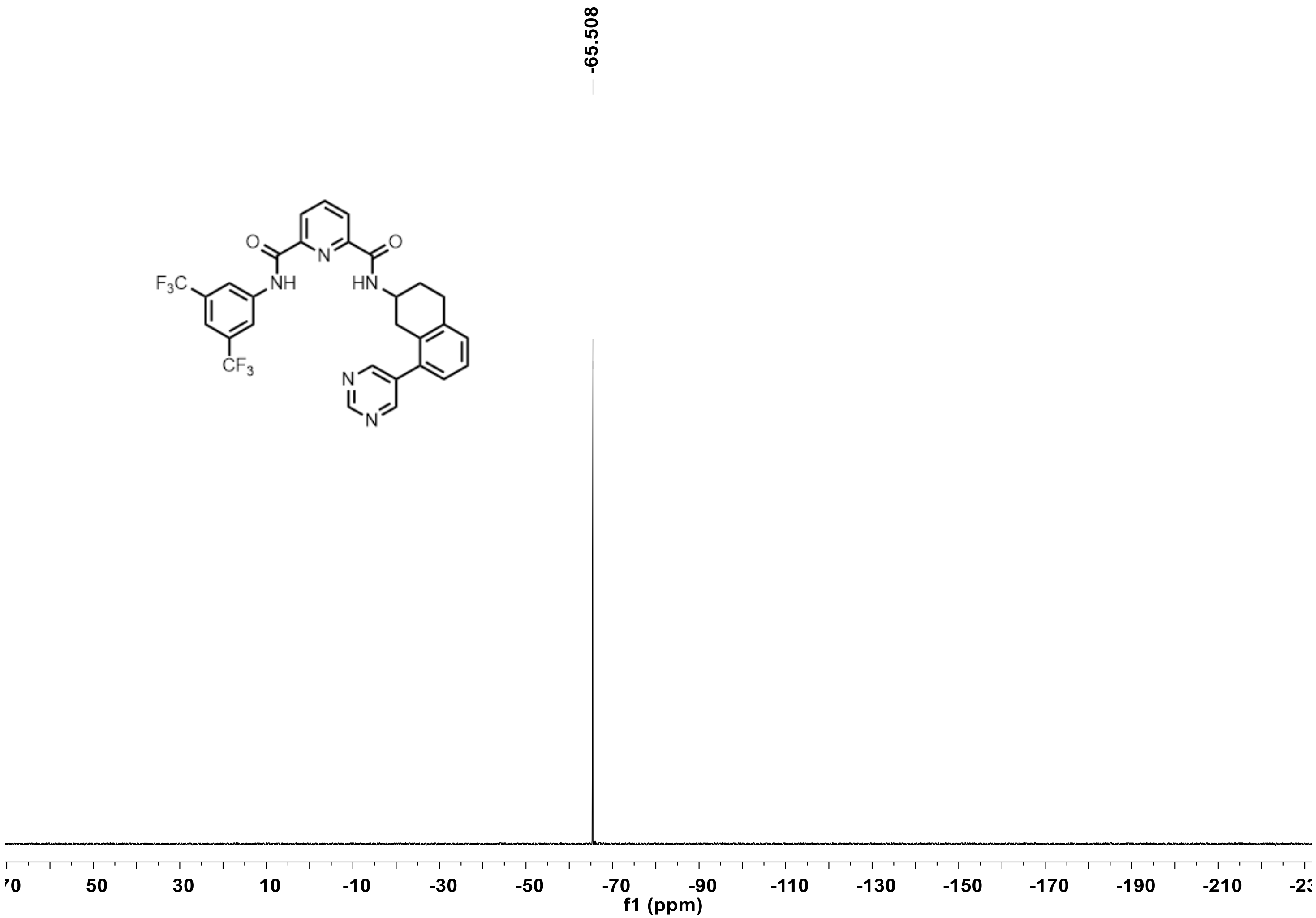
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T12**



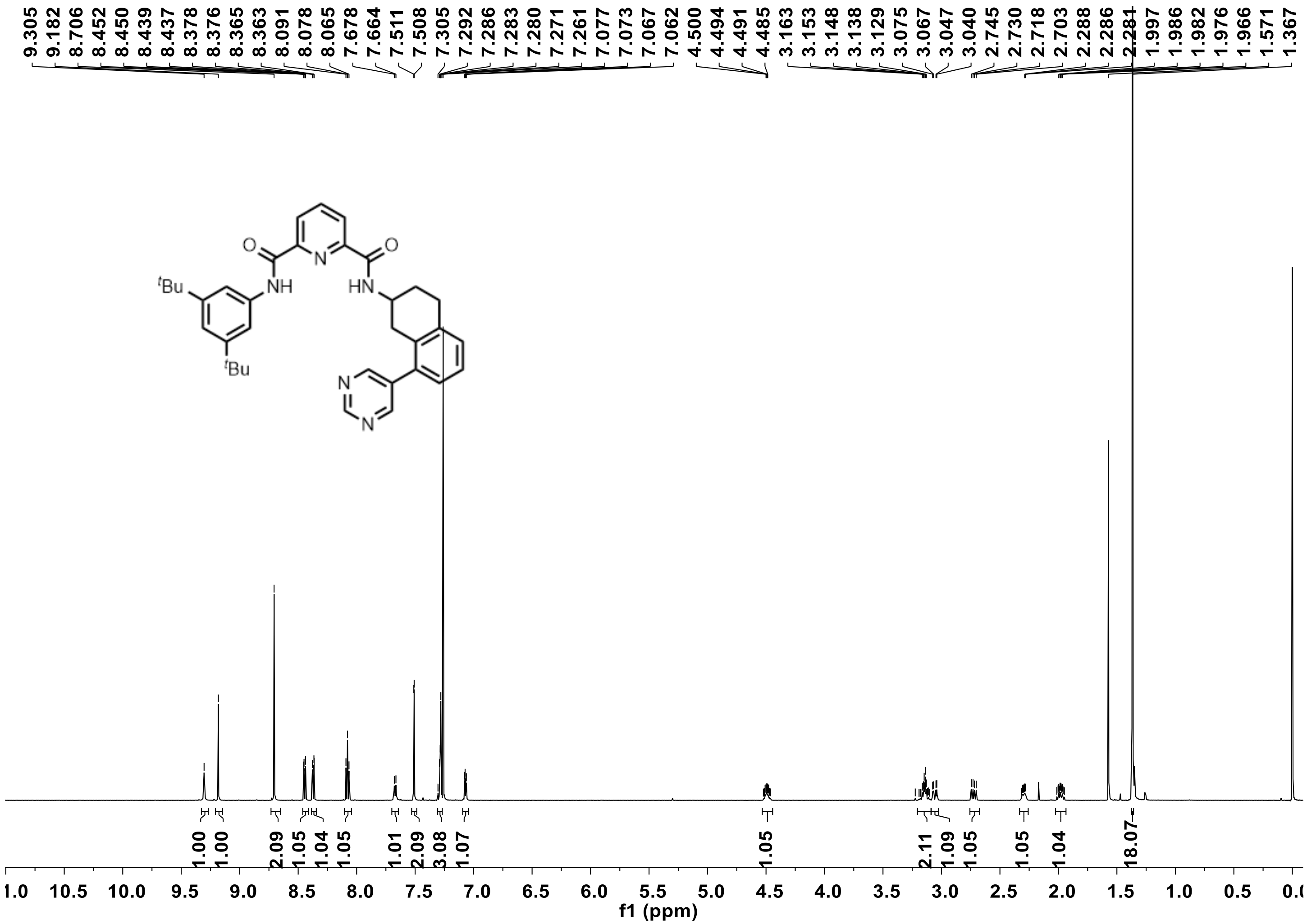
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T12**



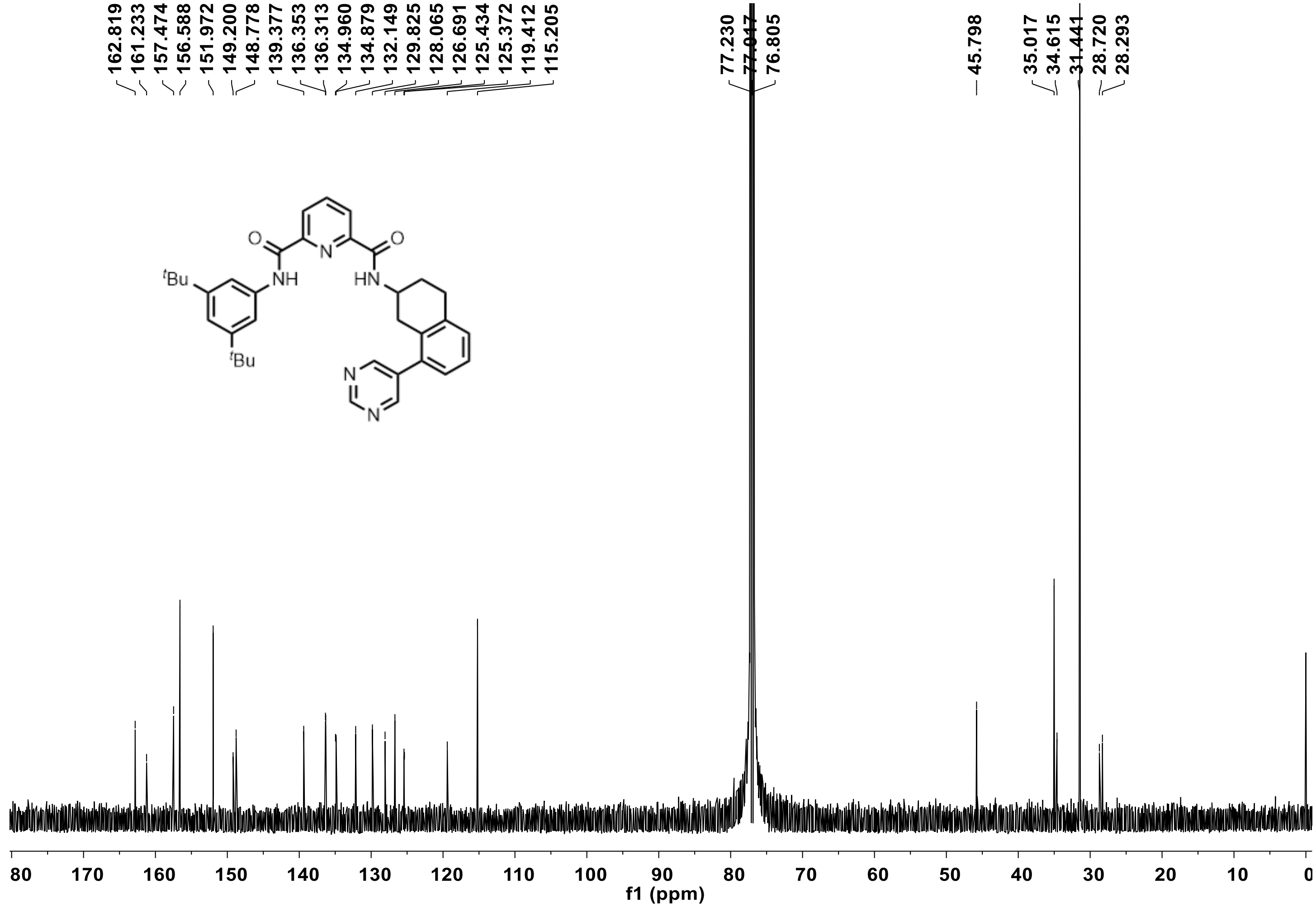
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T12**



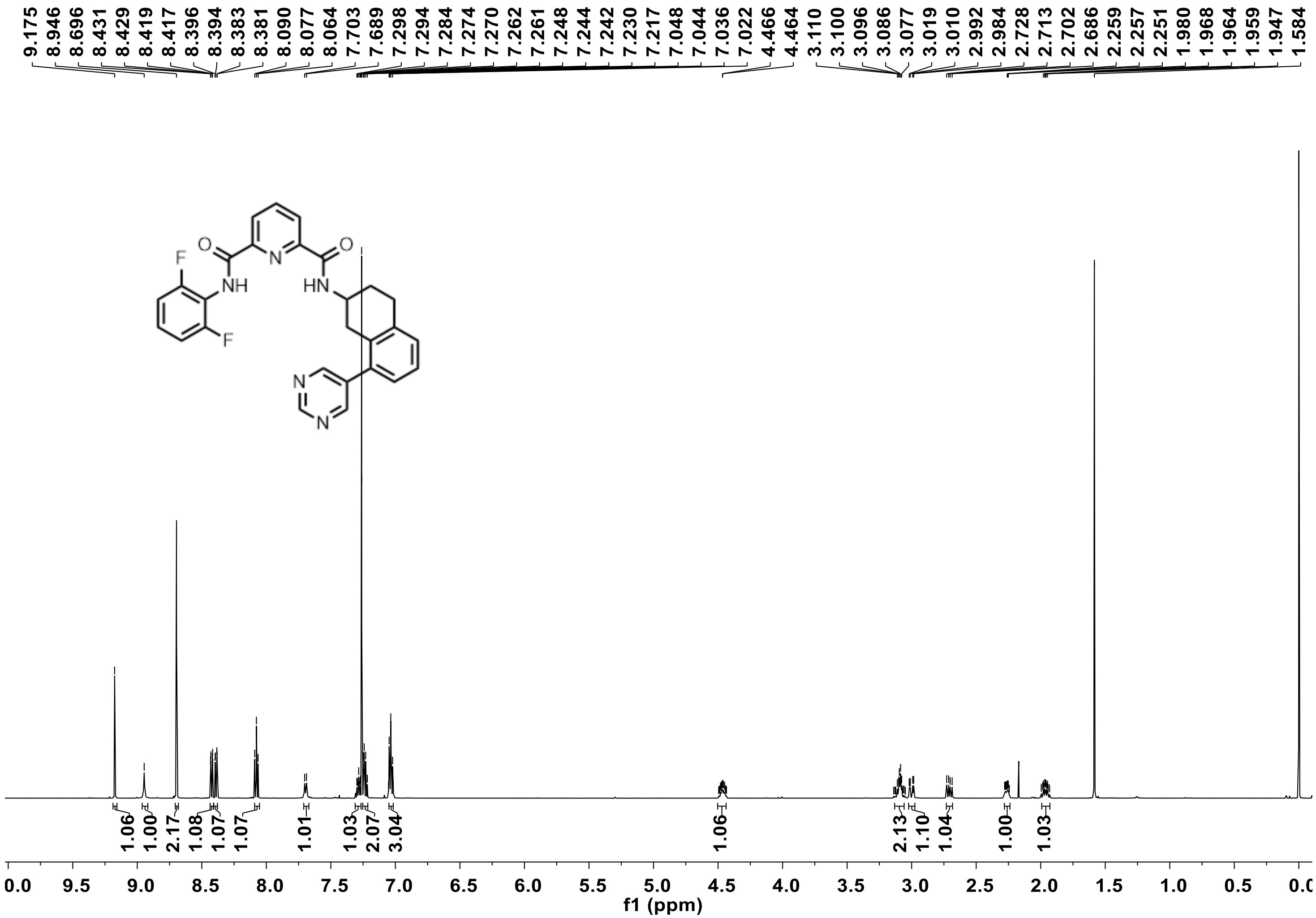
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T13**



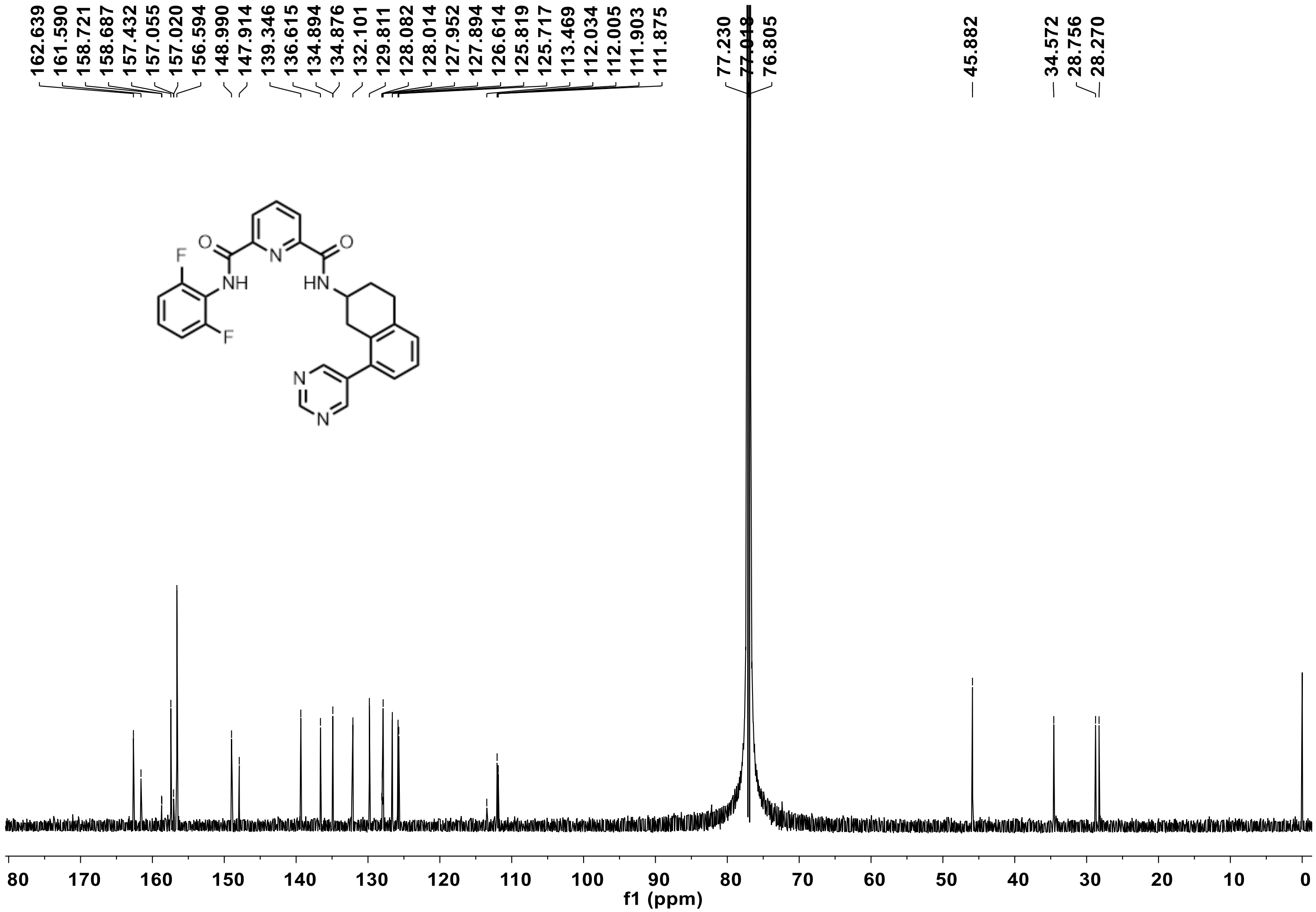
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T13**



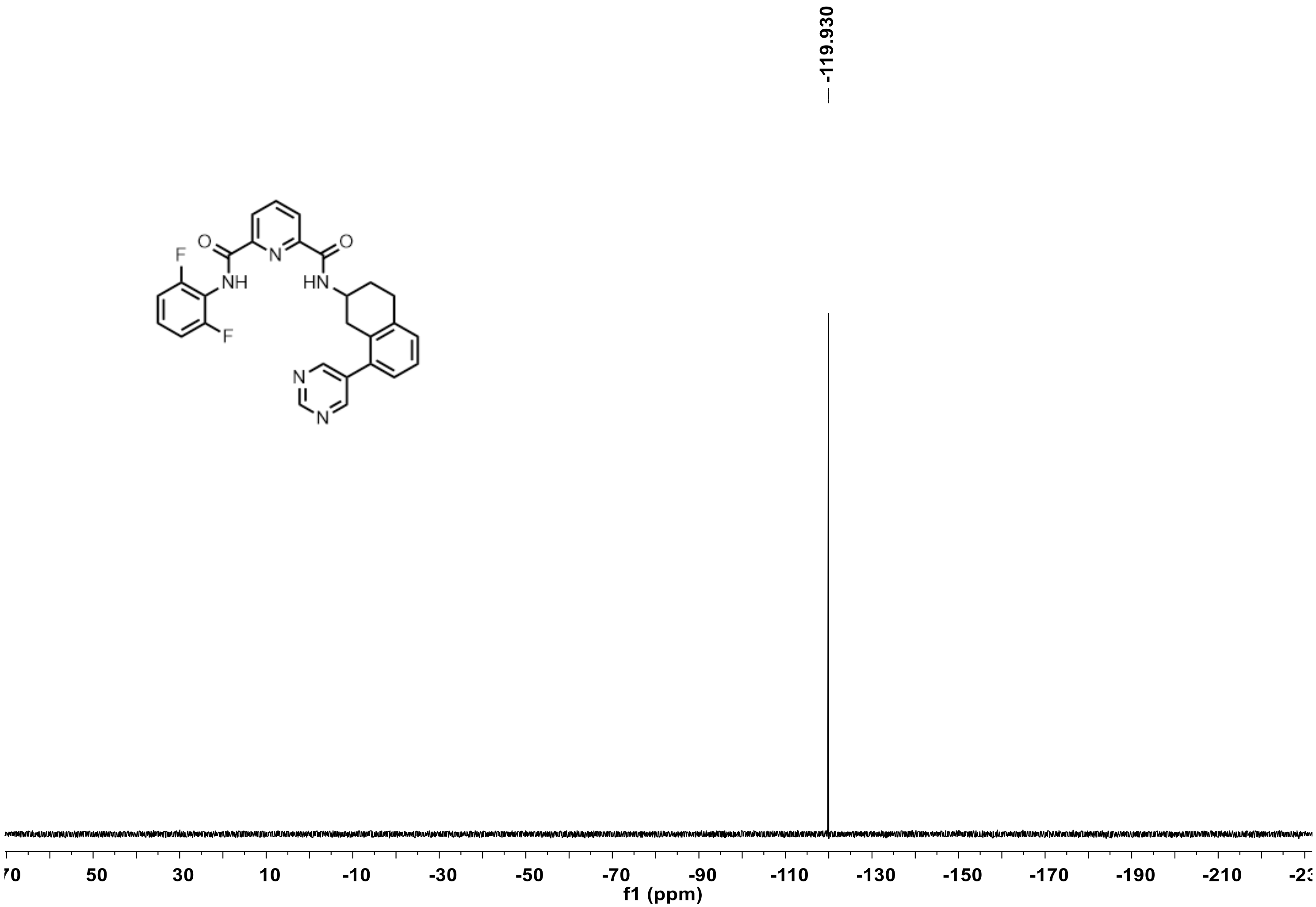
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T14**



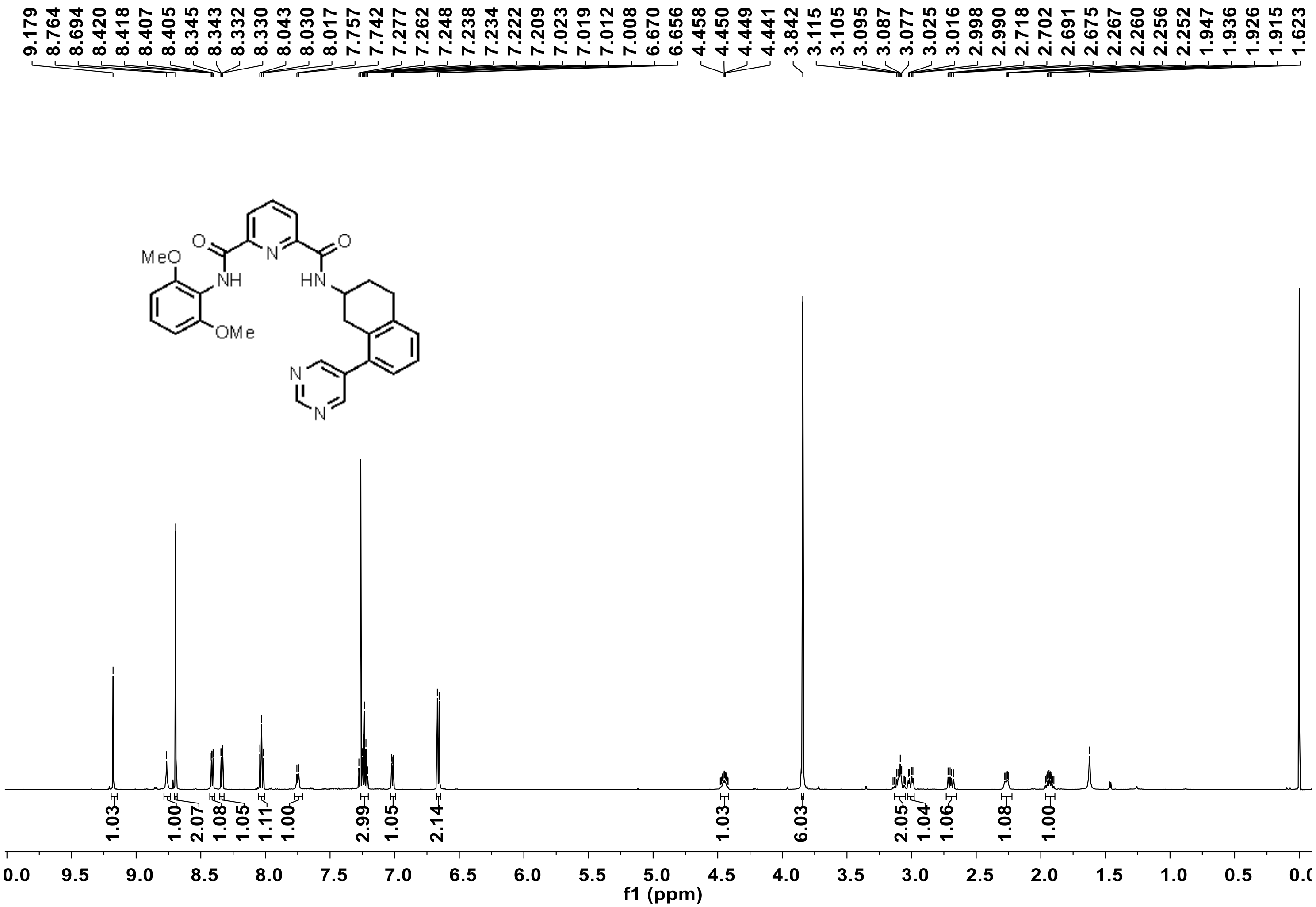
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T14**



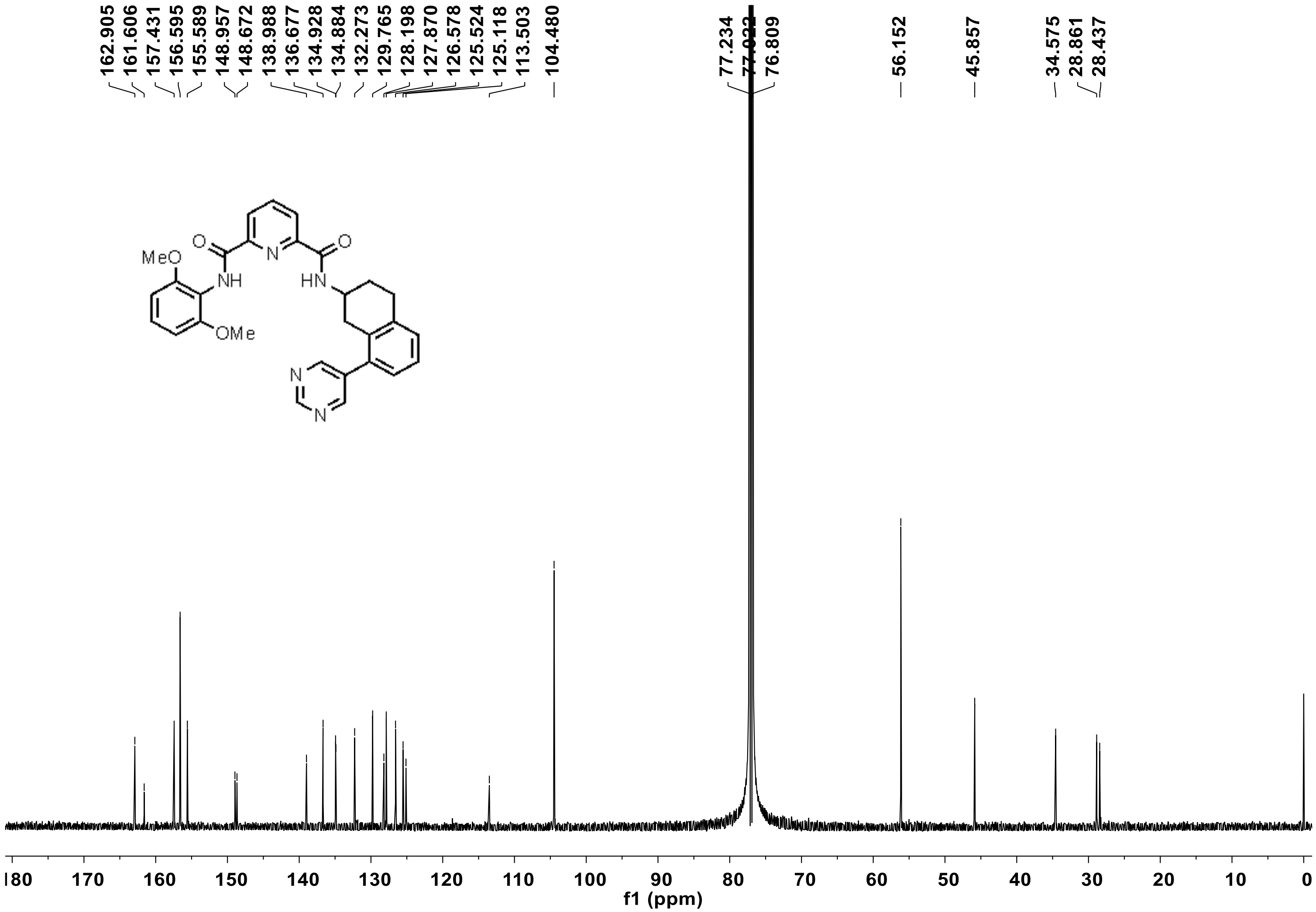
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T14**



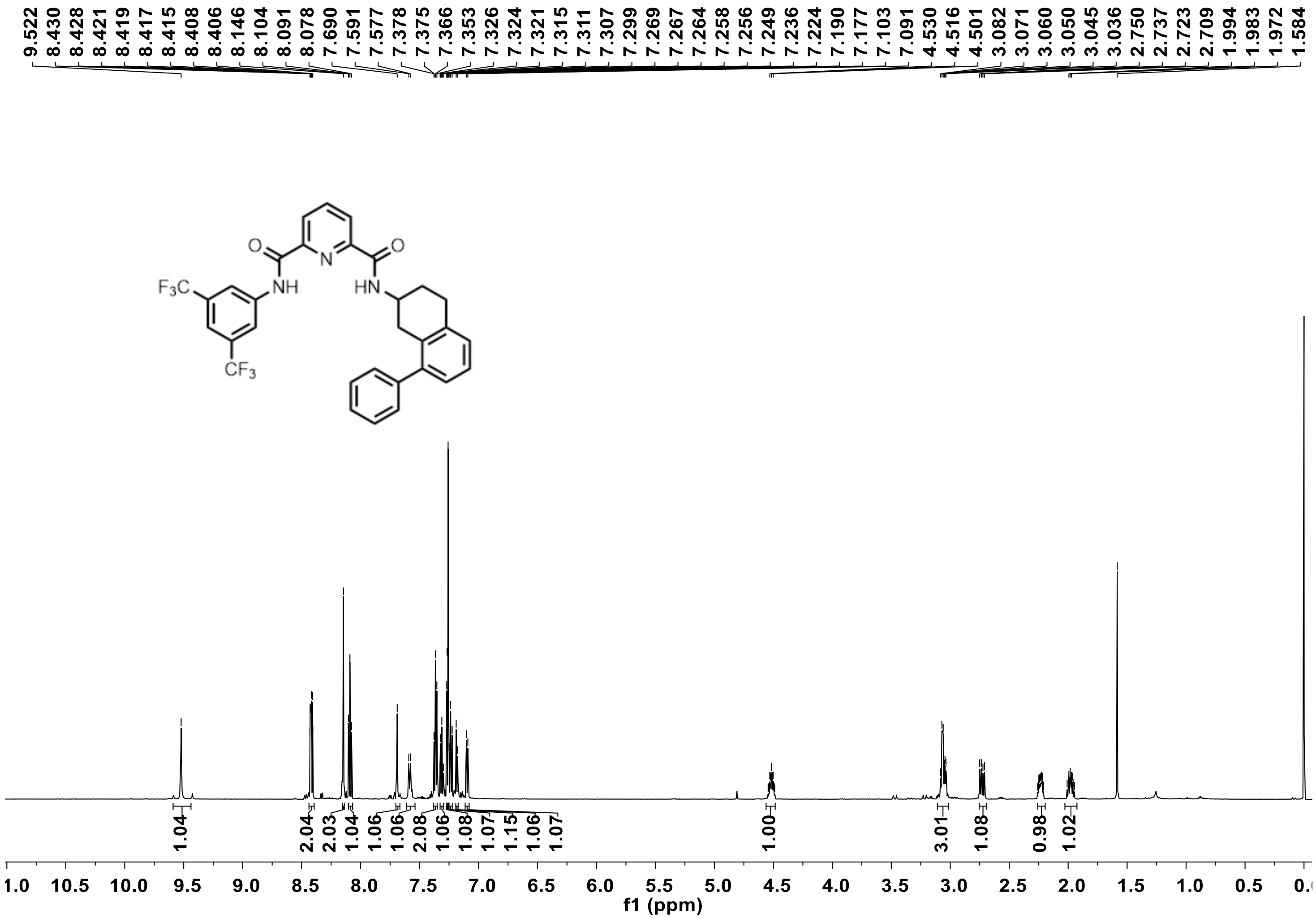
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T15**



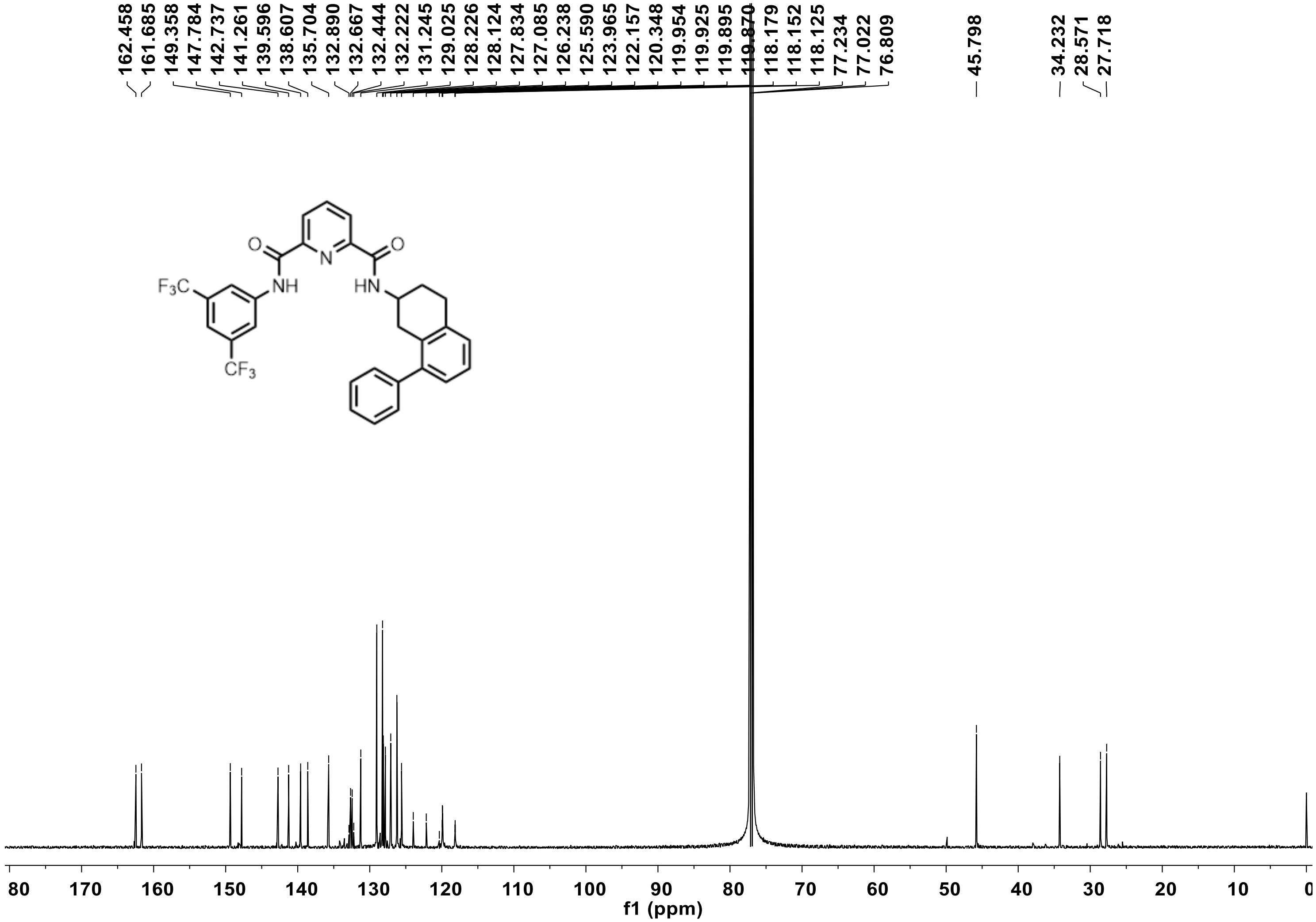
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T15**



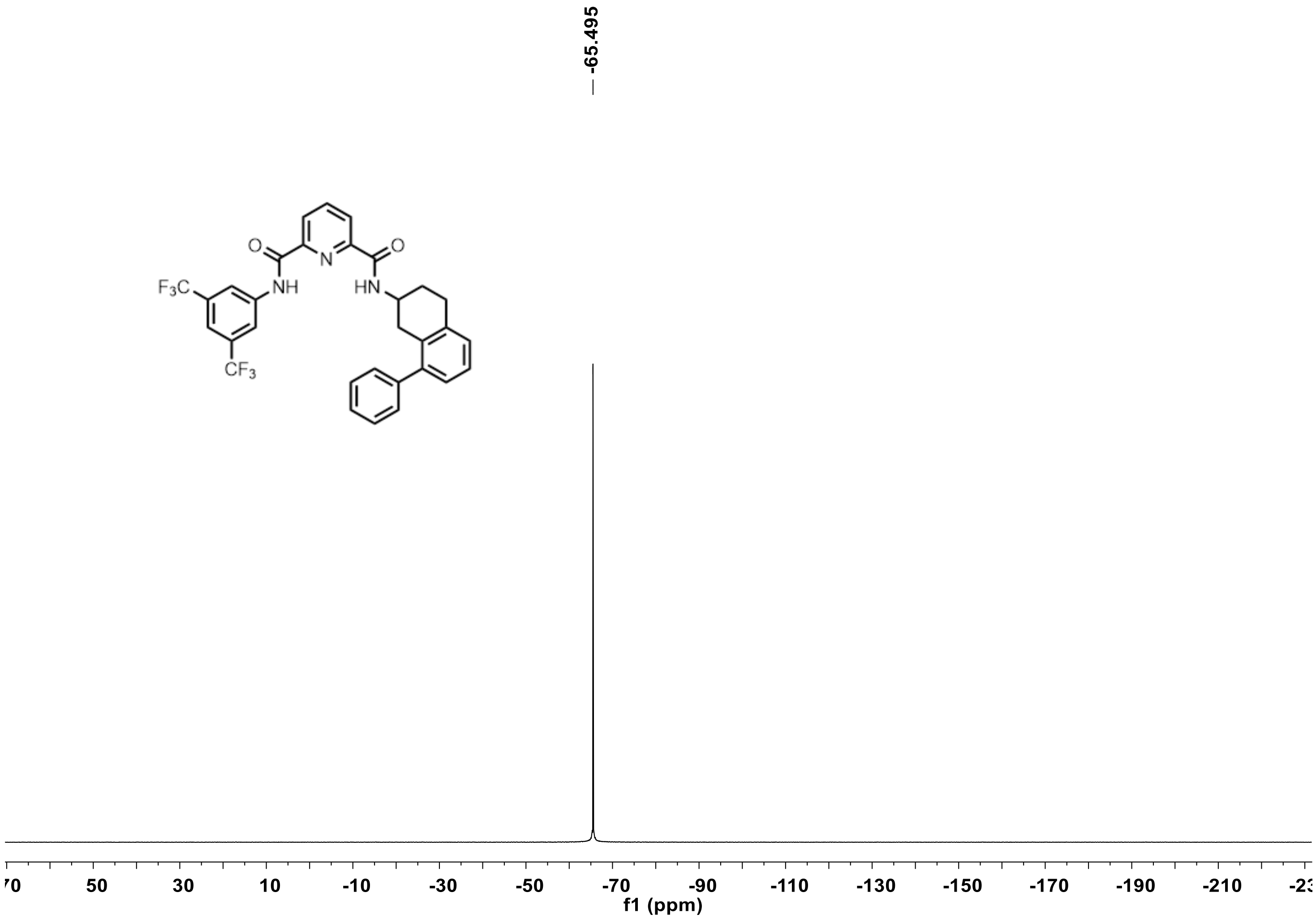
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T16**



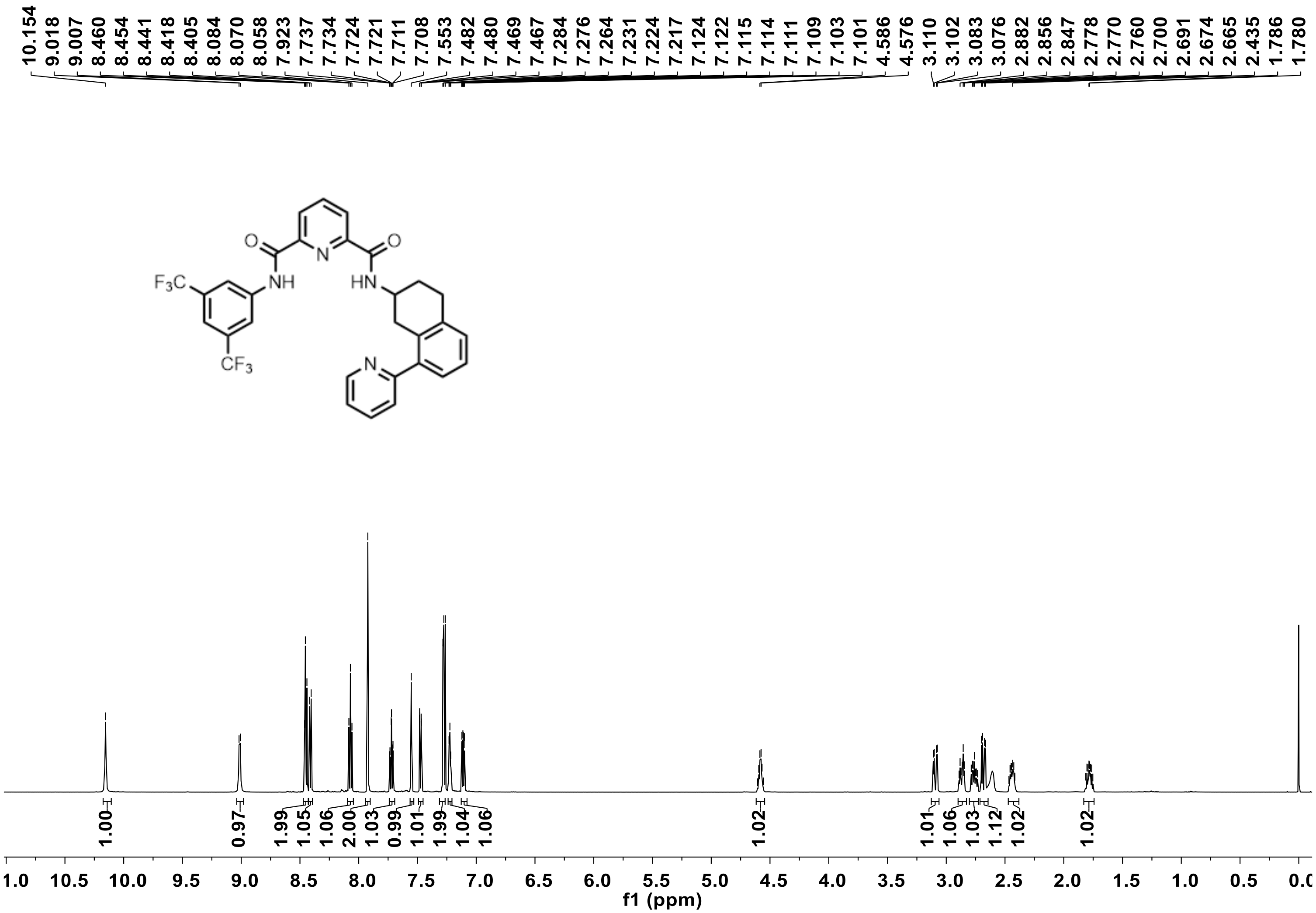
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T16**



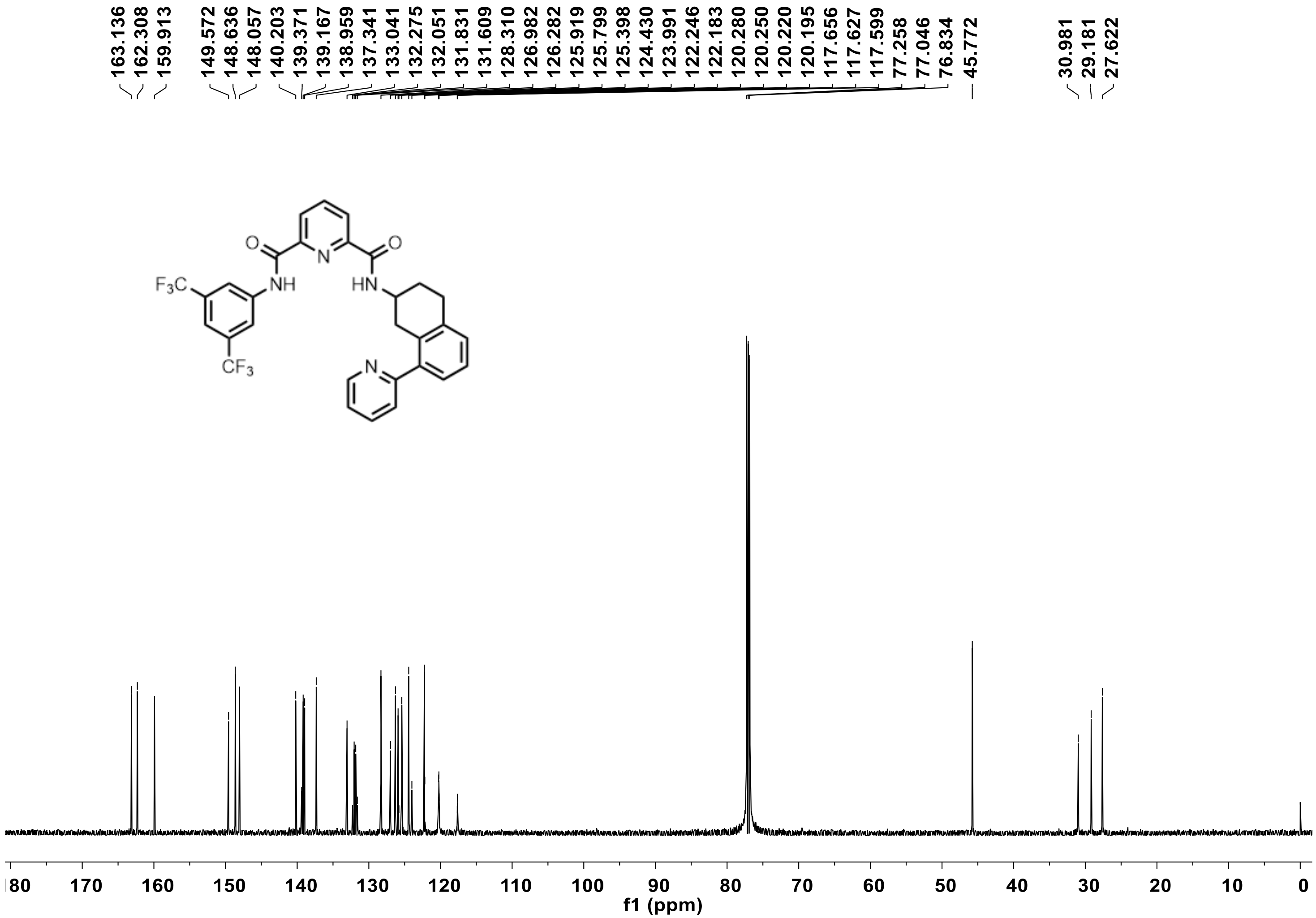
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T16**



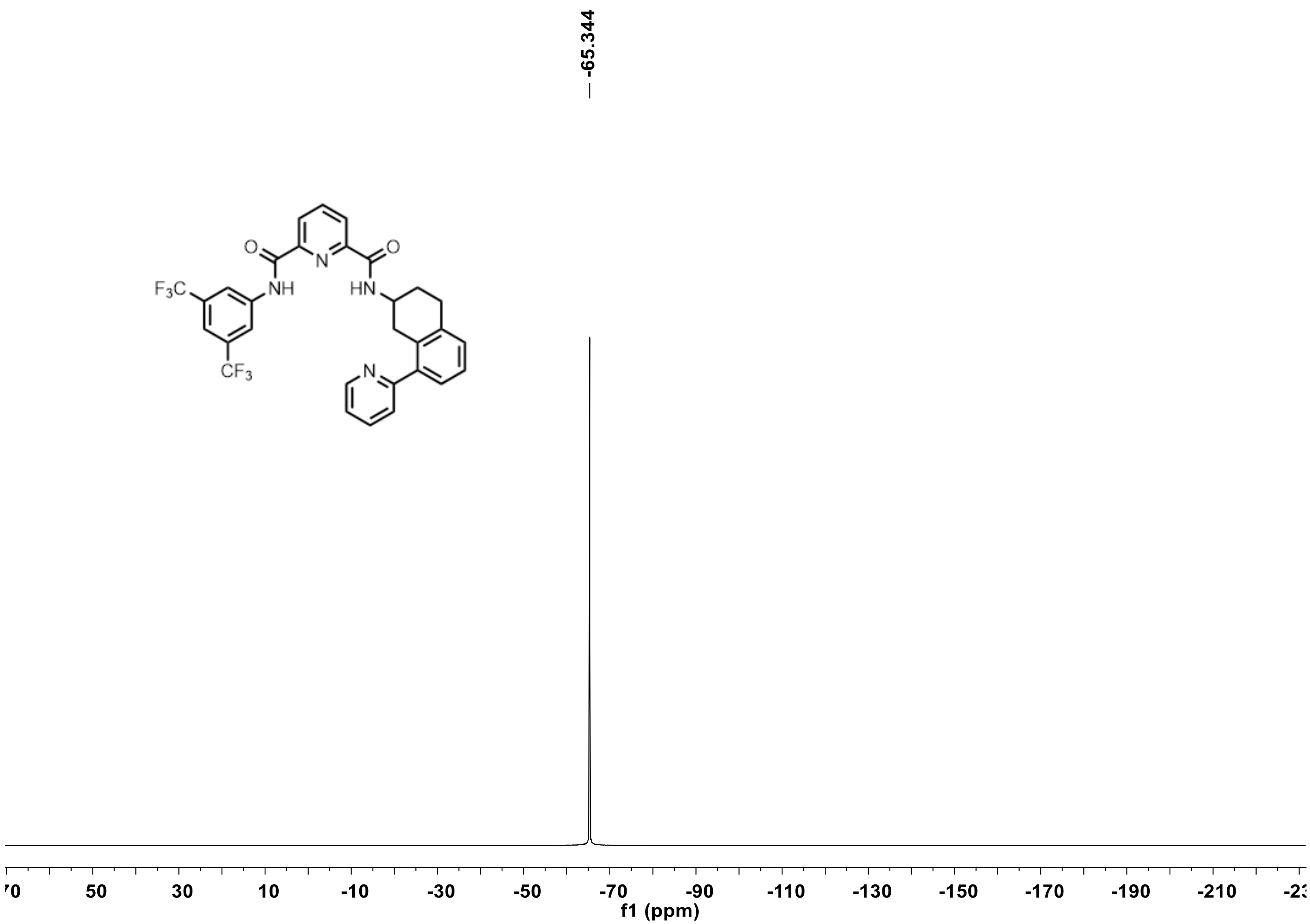
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T17**



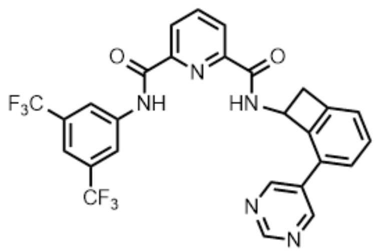
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T17**

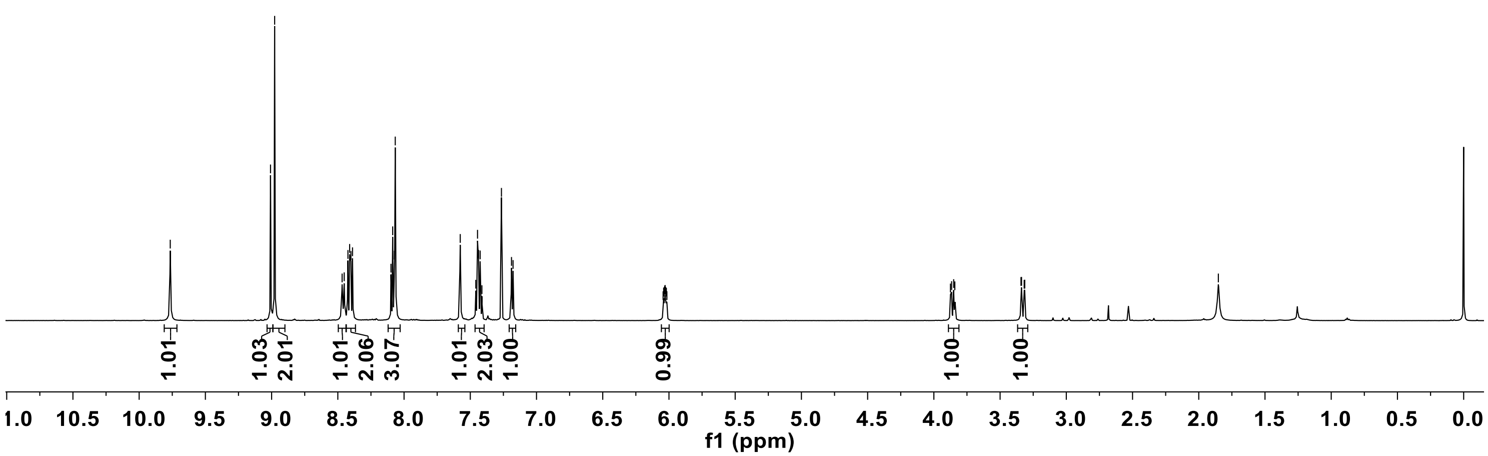


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T17**

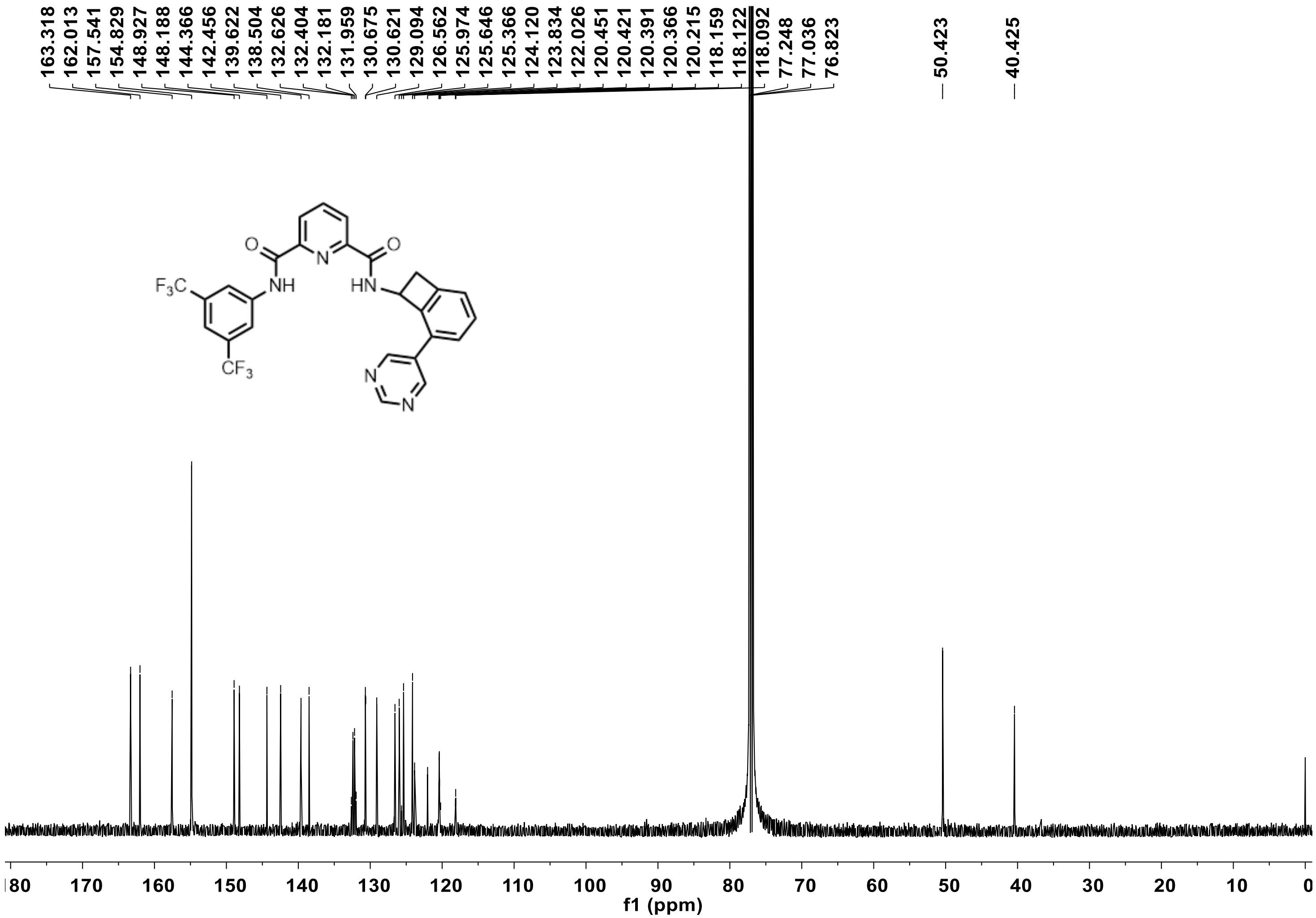


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T18**

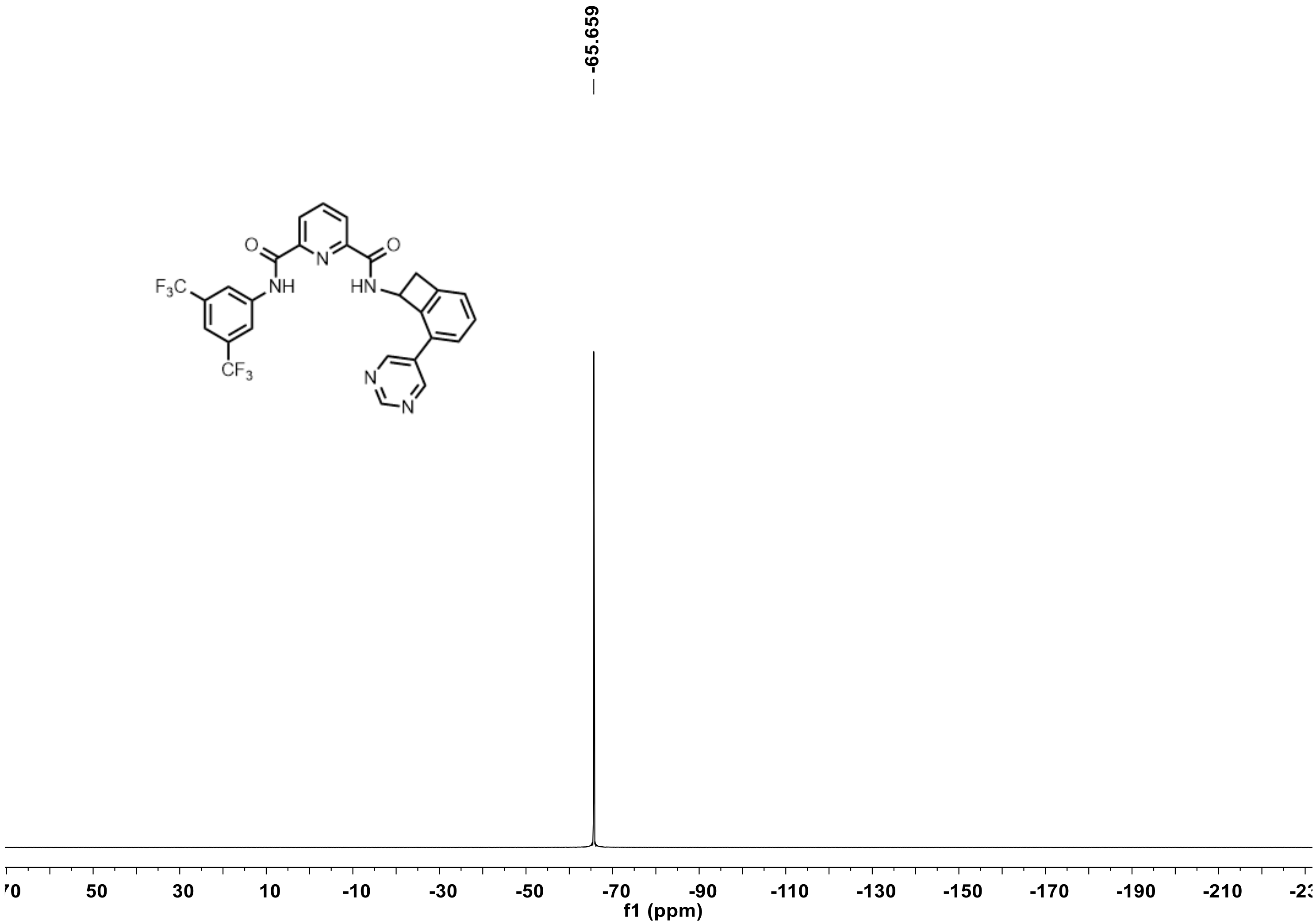




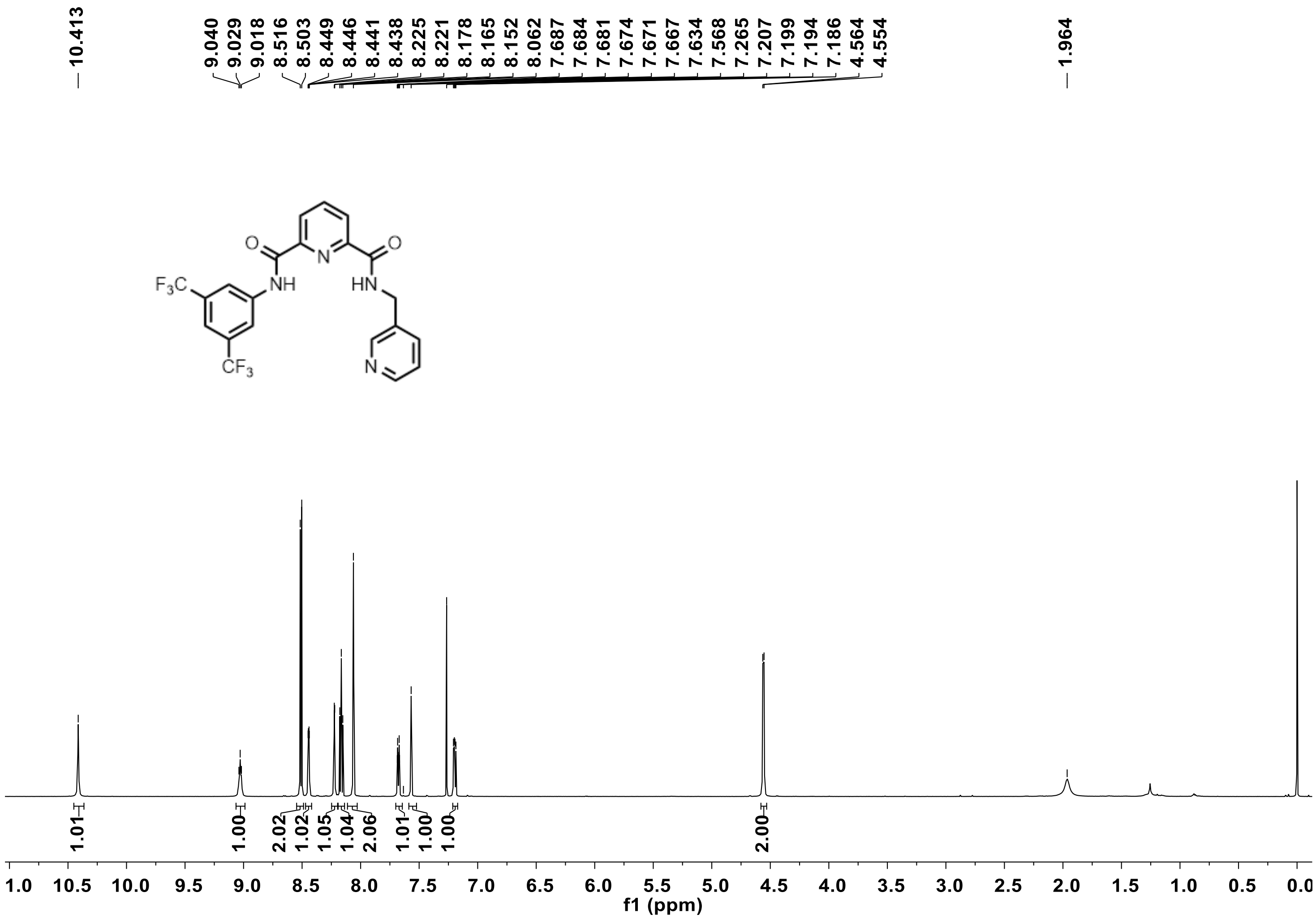
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T18**



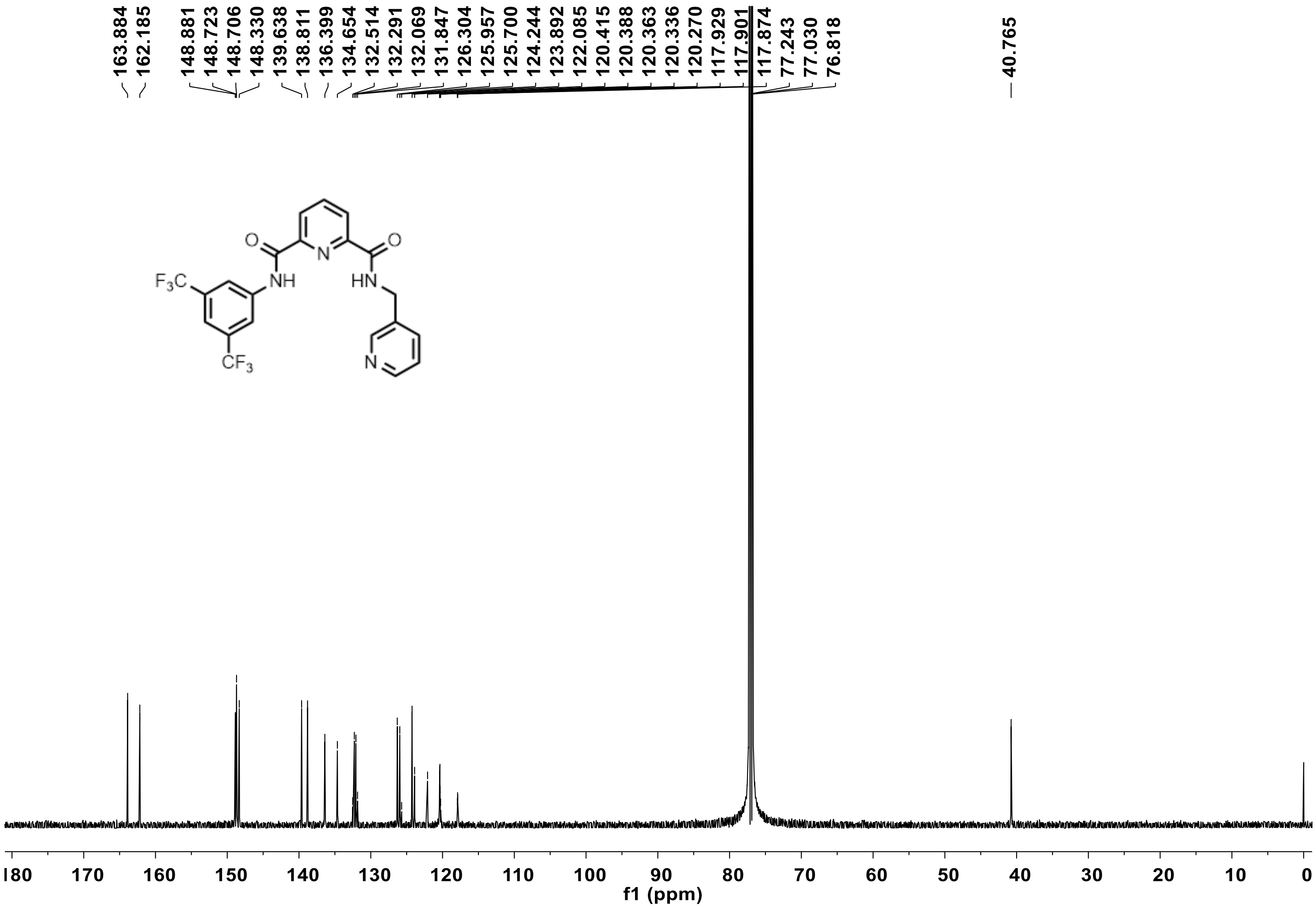
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T18**



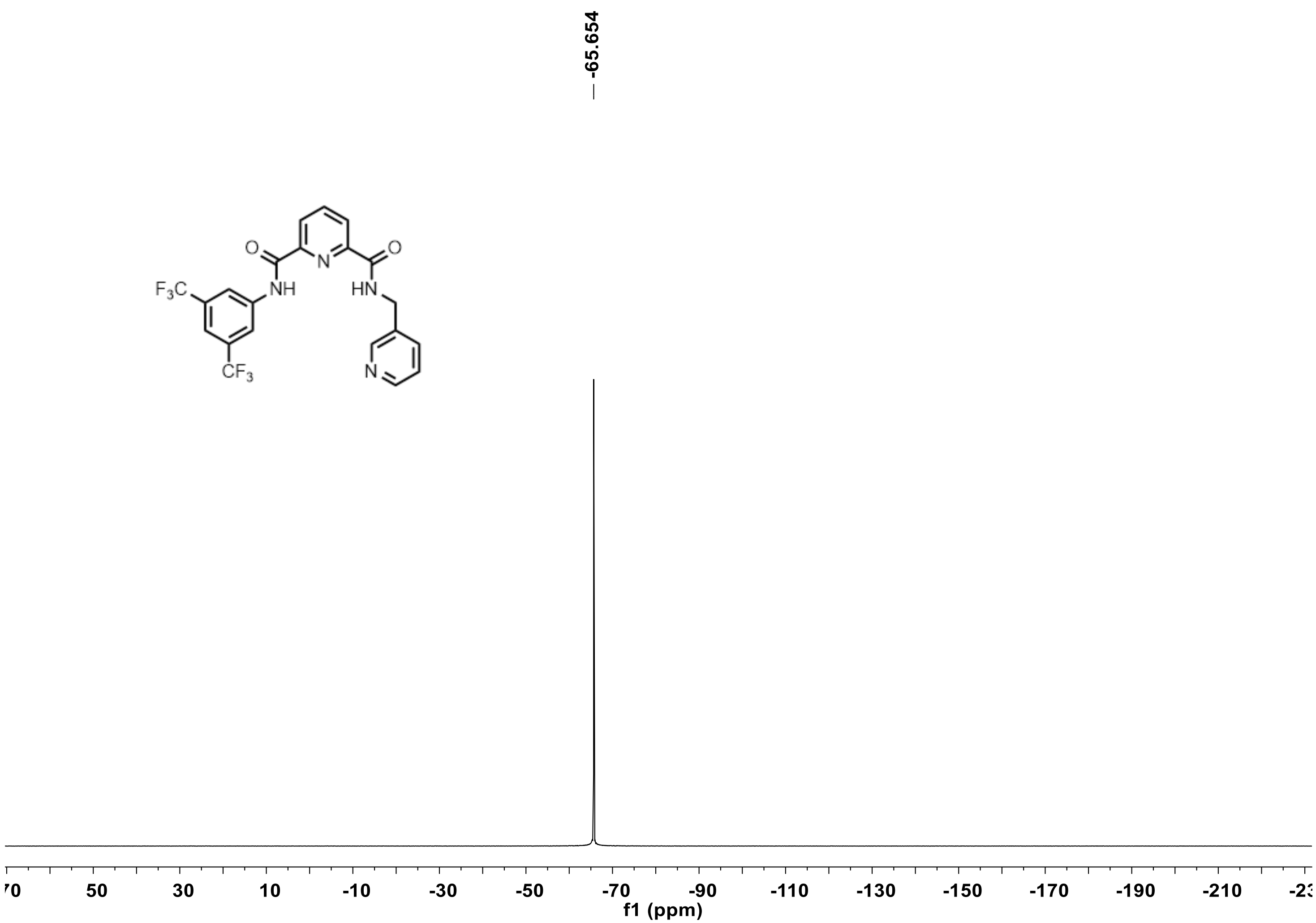
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T19**



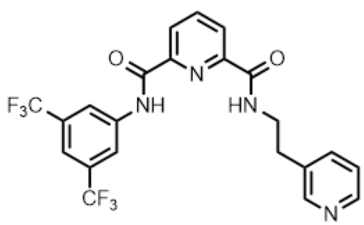
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T19**

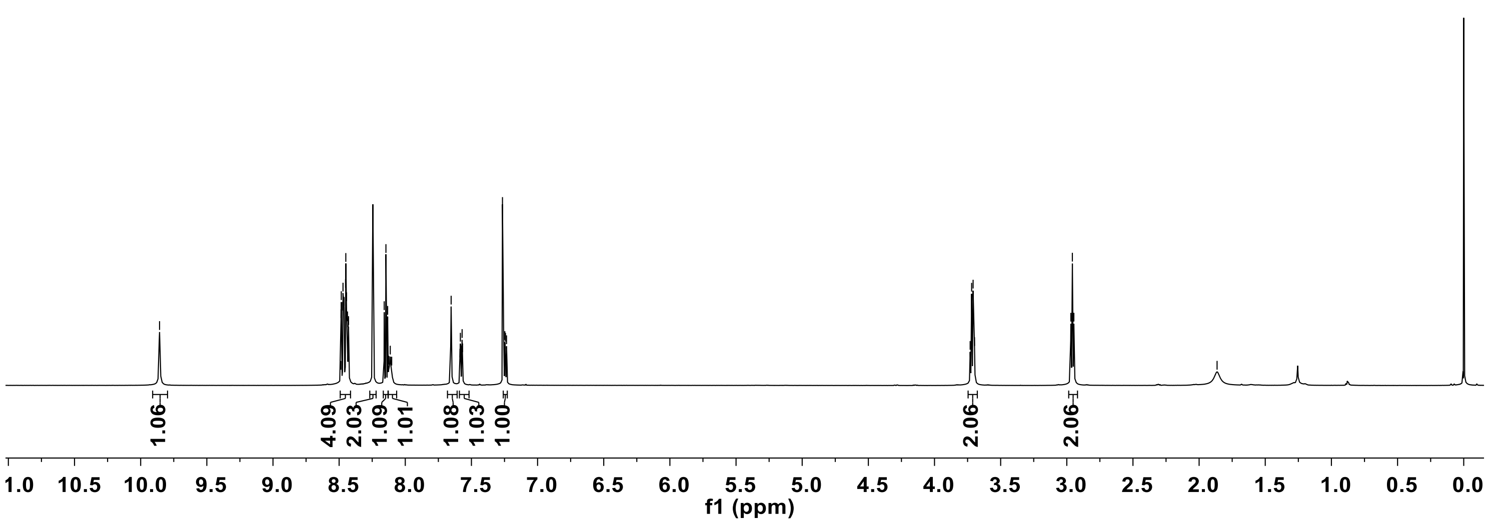


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T19**

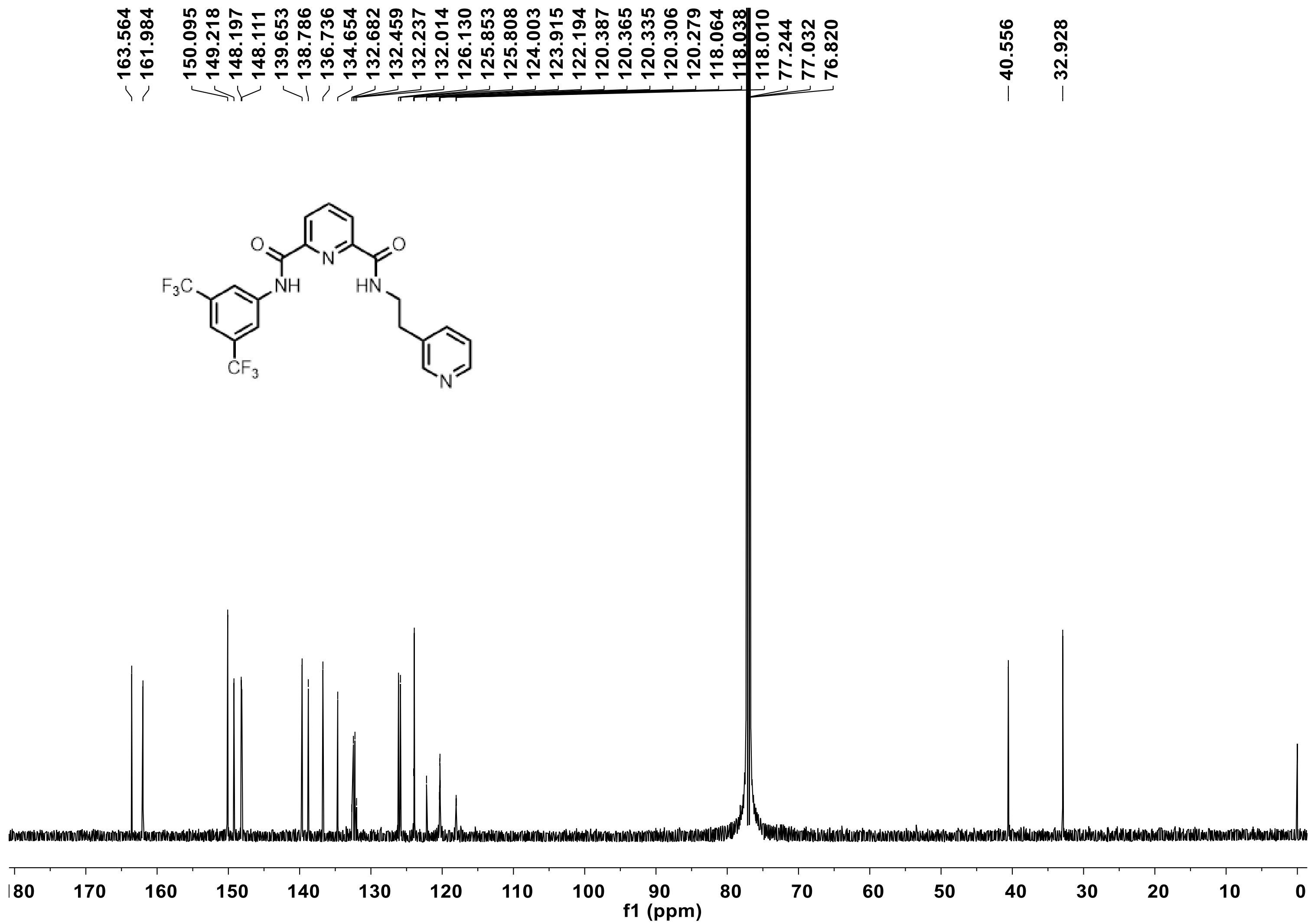


^1H NMR (600 MHz, $CDCl_3$) spectrum of **T20**

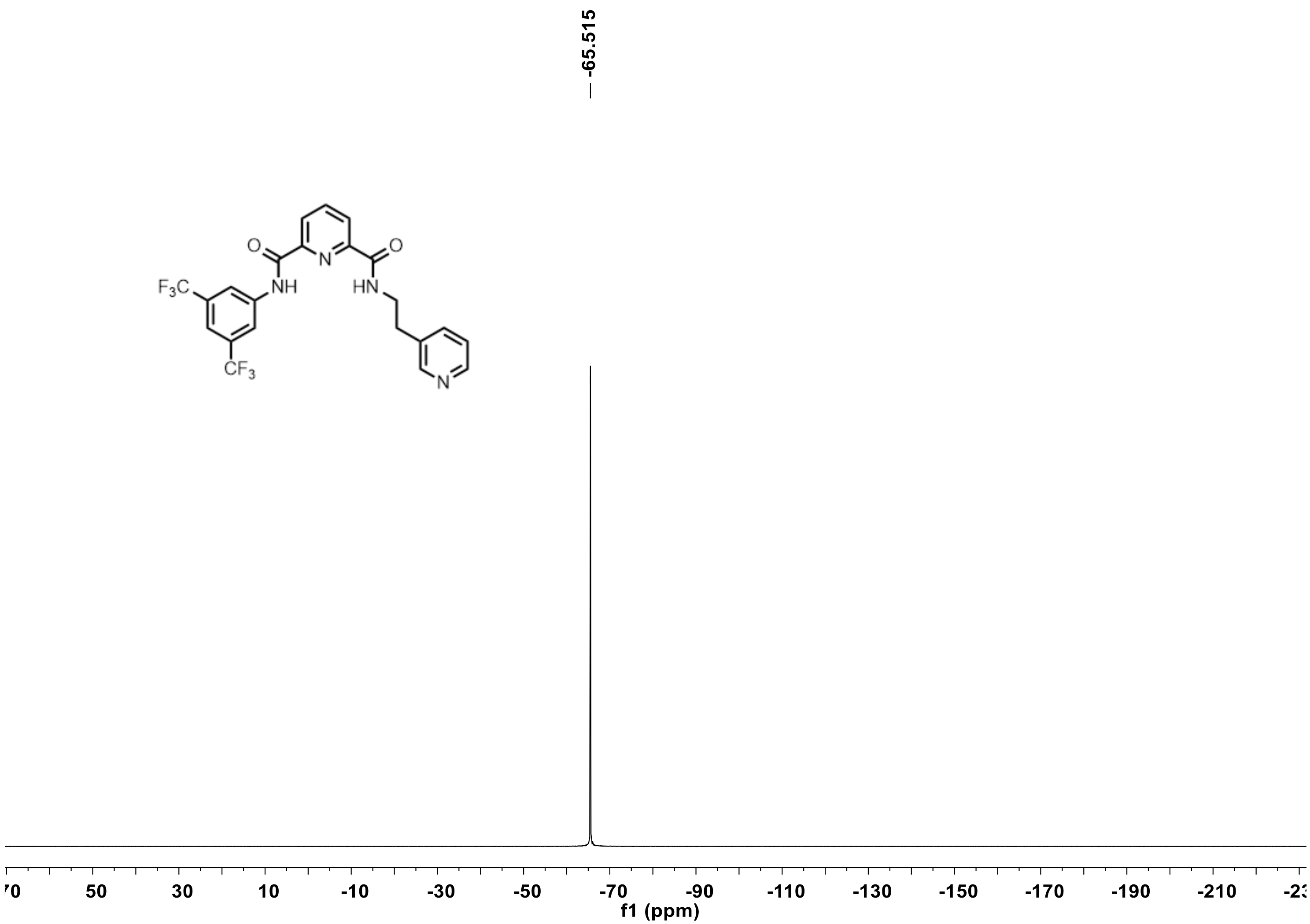




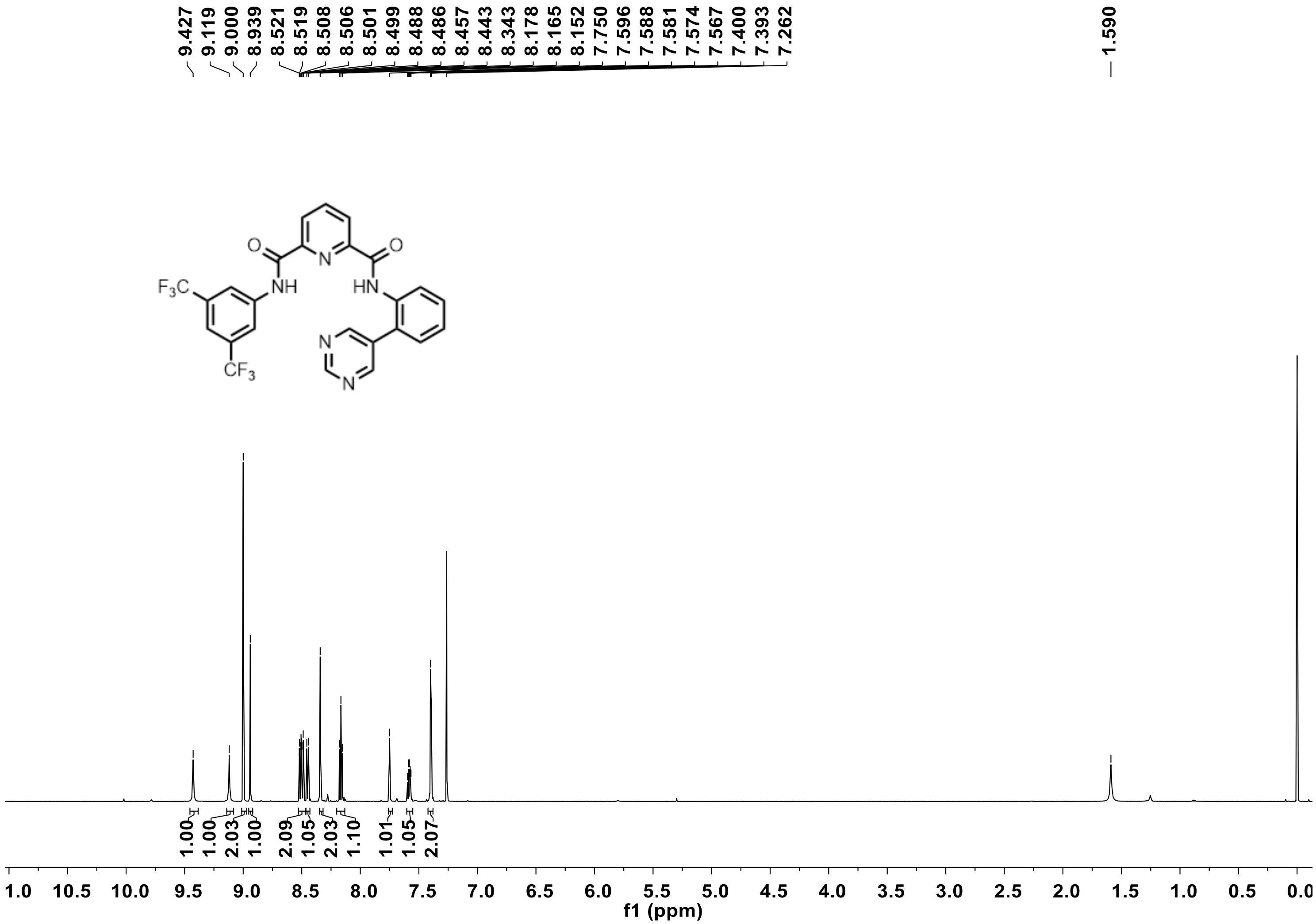
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T20**



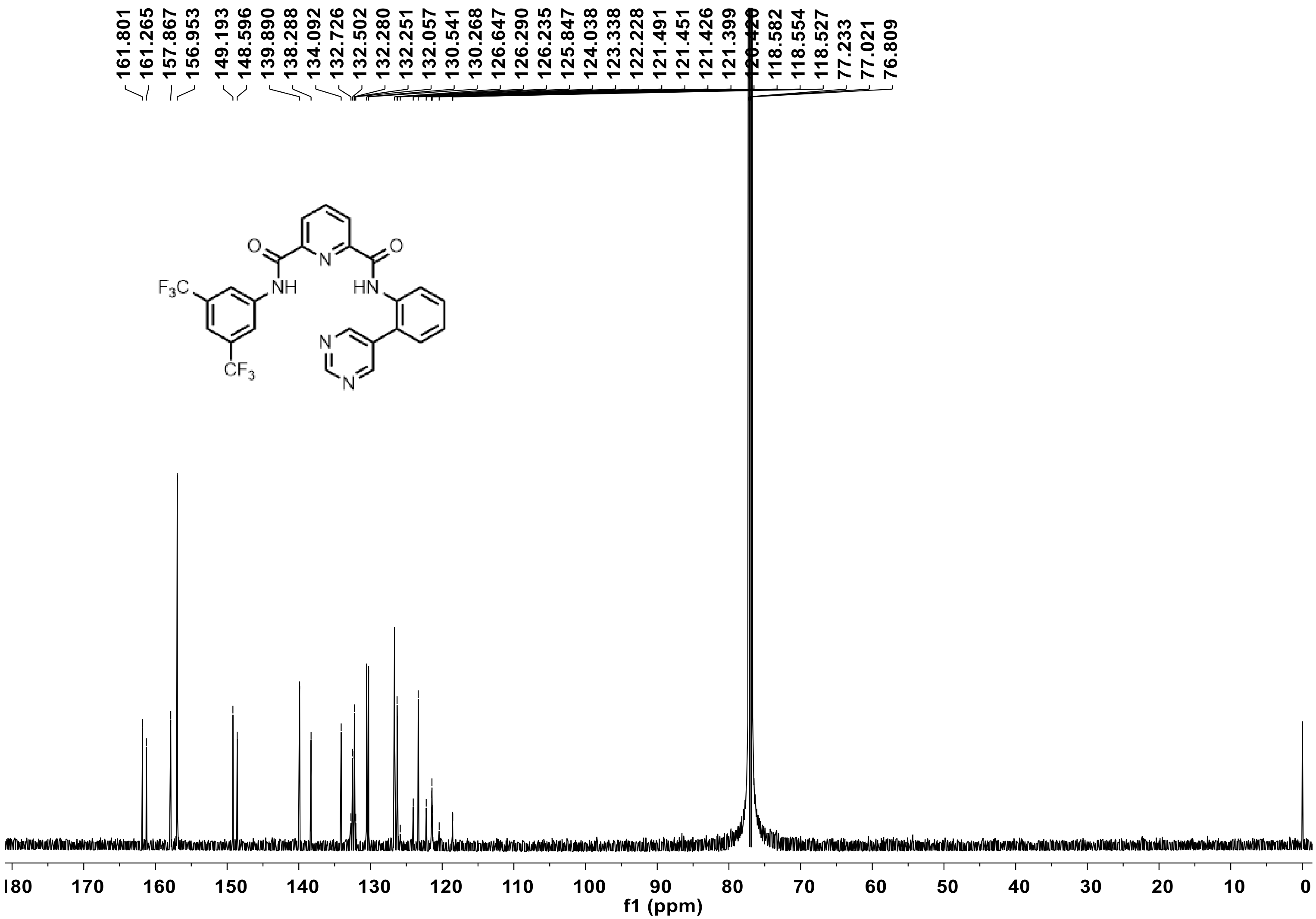
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T20**



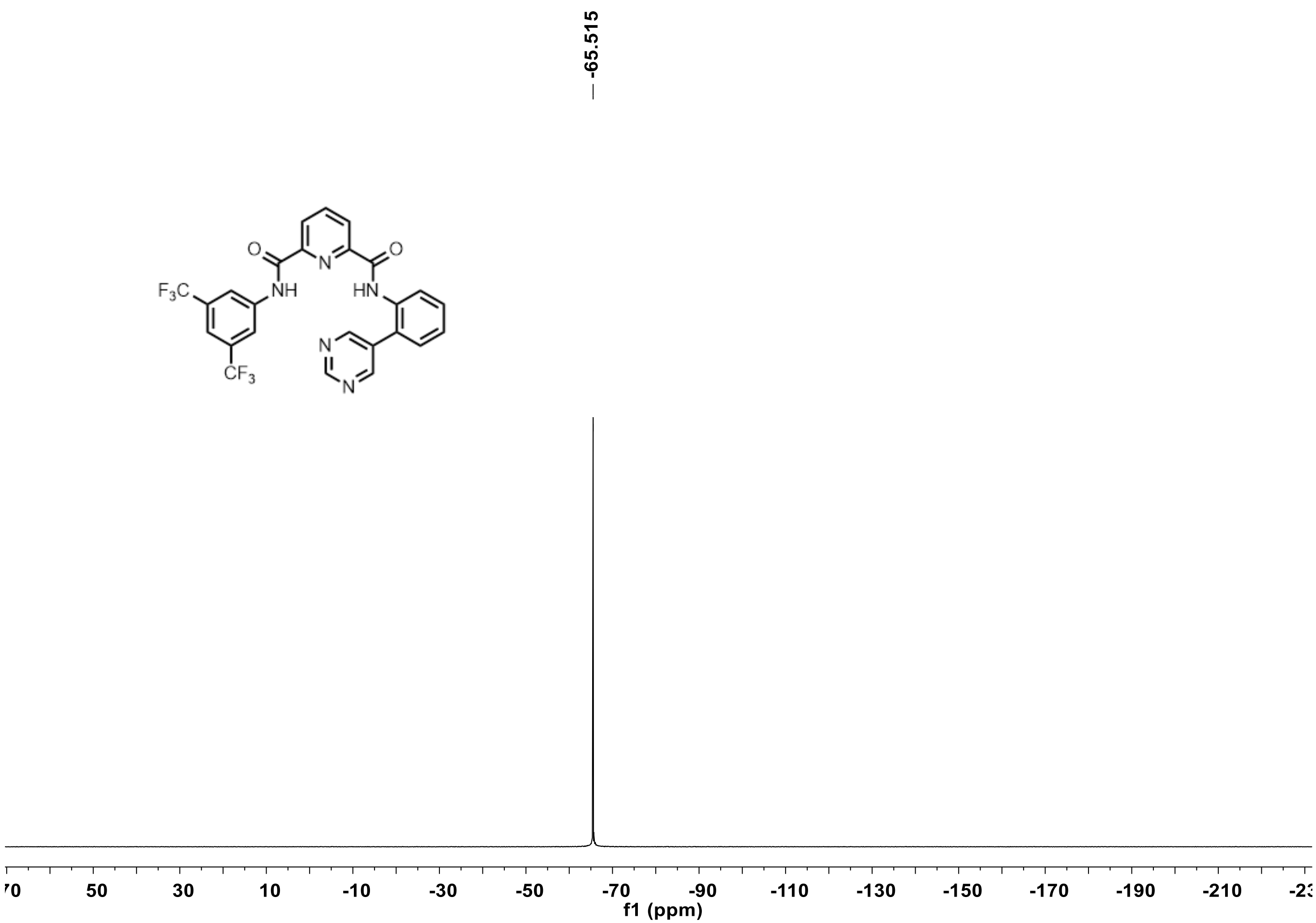
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T21**



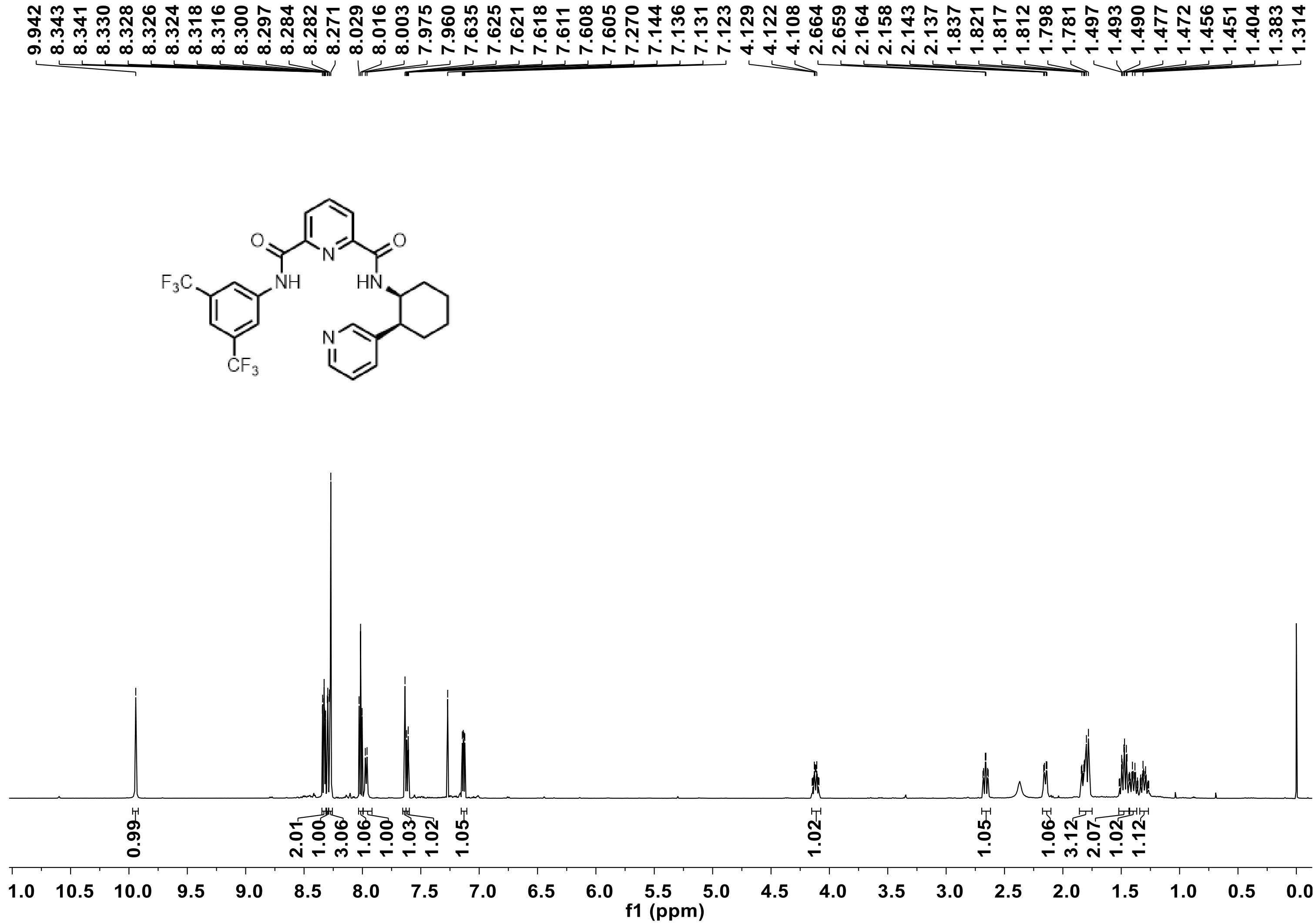
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T21**



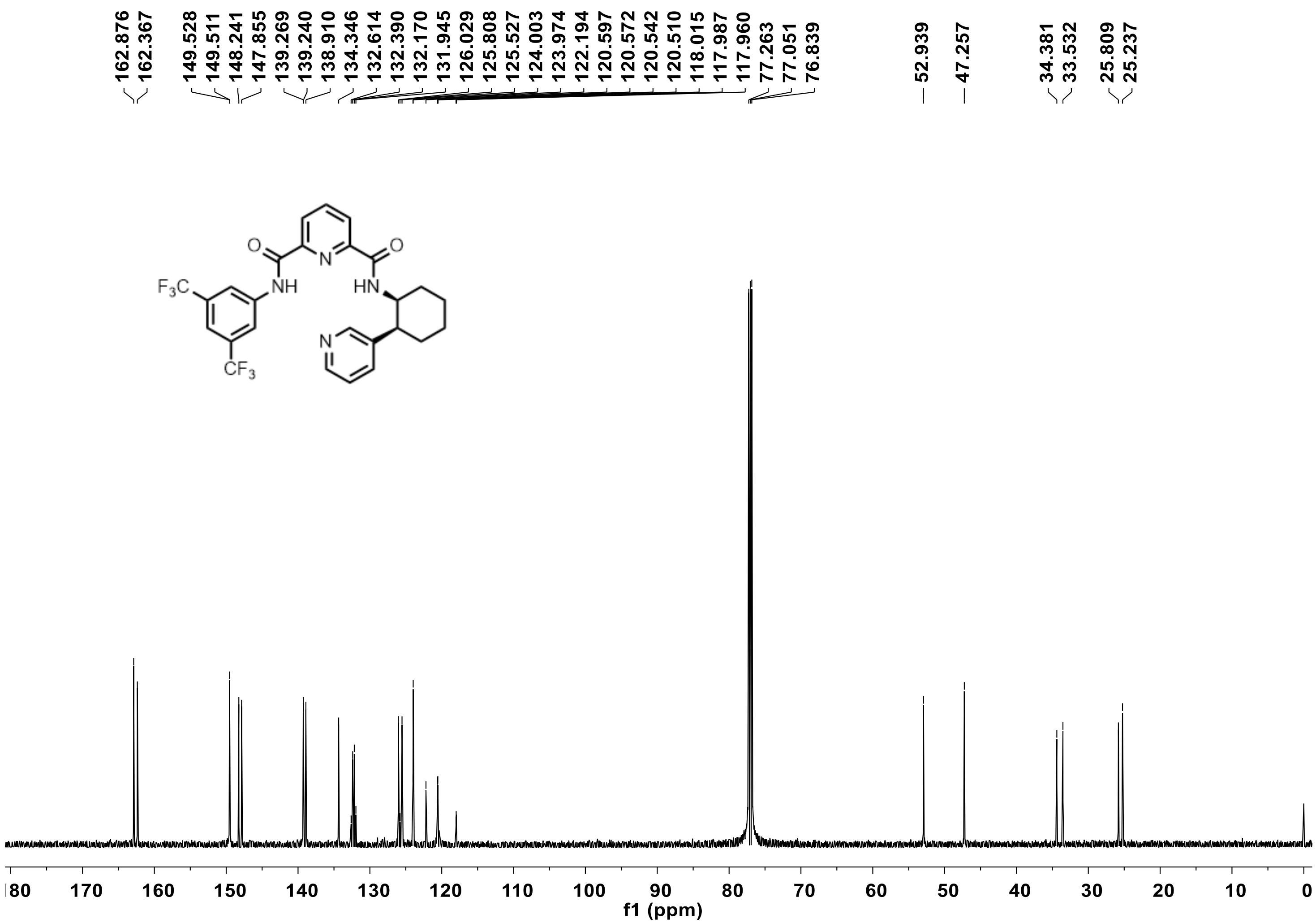
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T21**



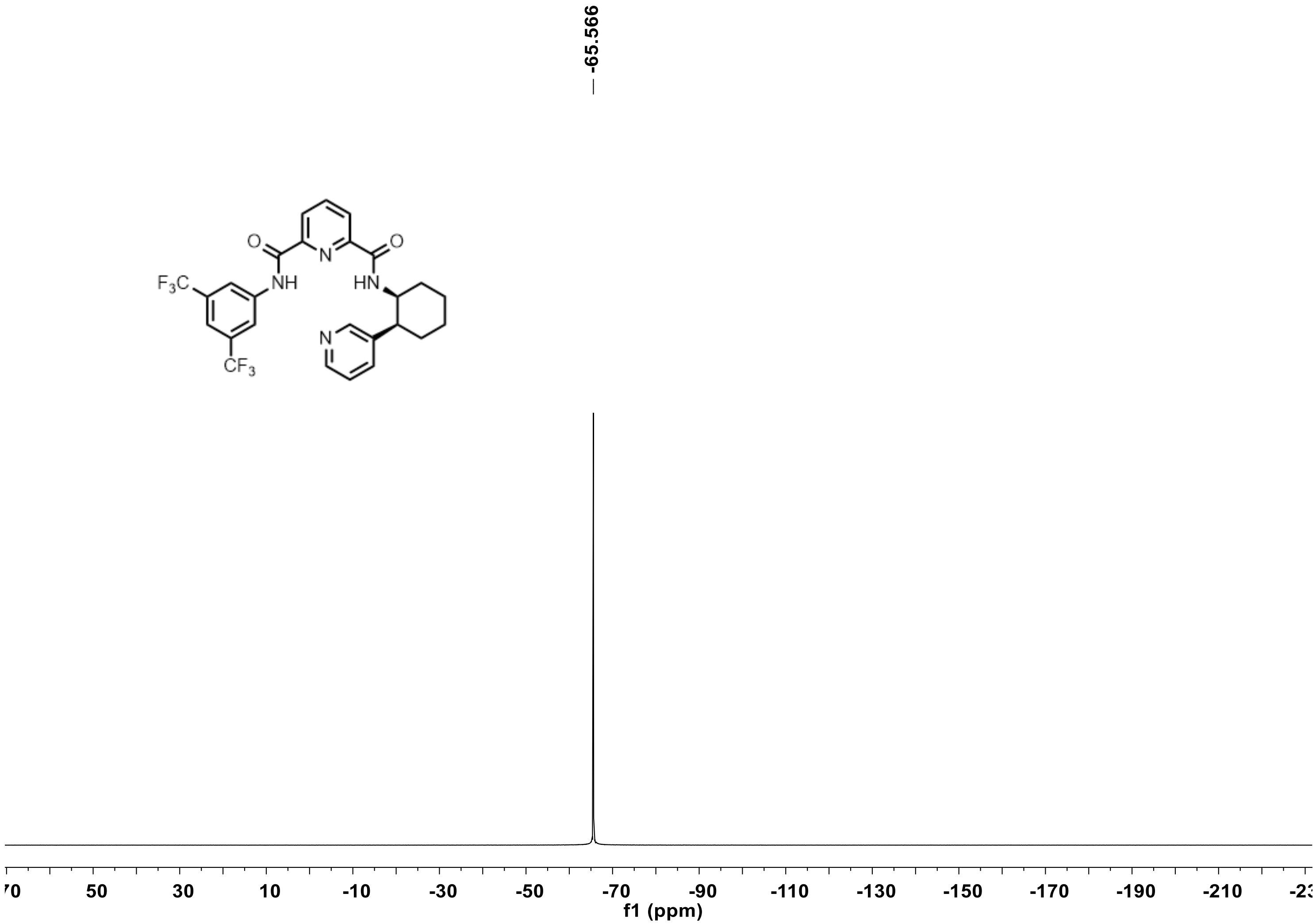
[1]H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T22**



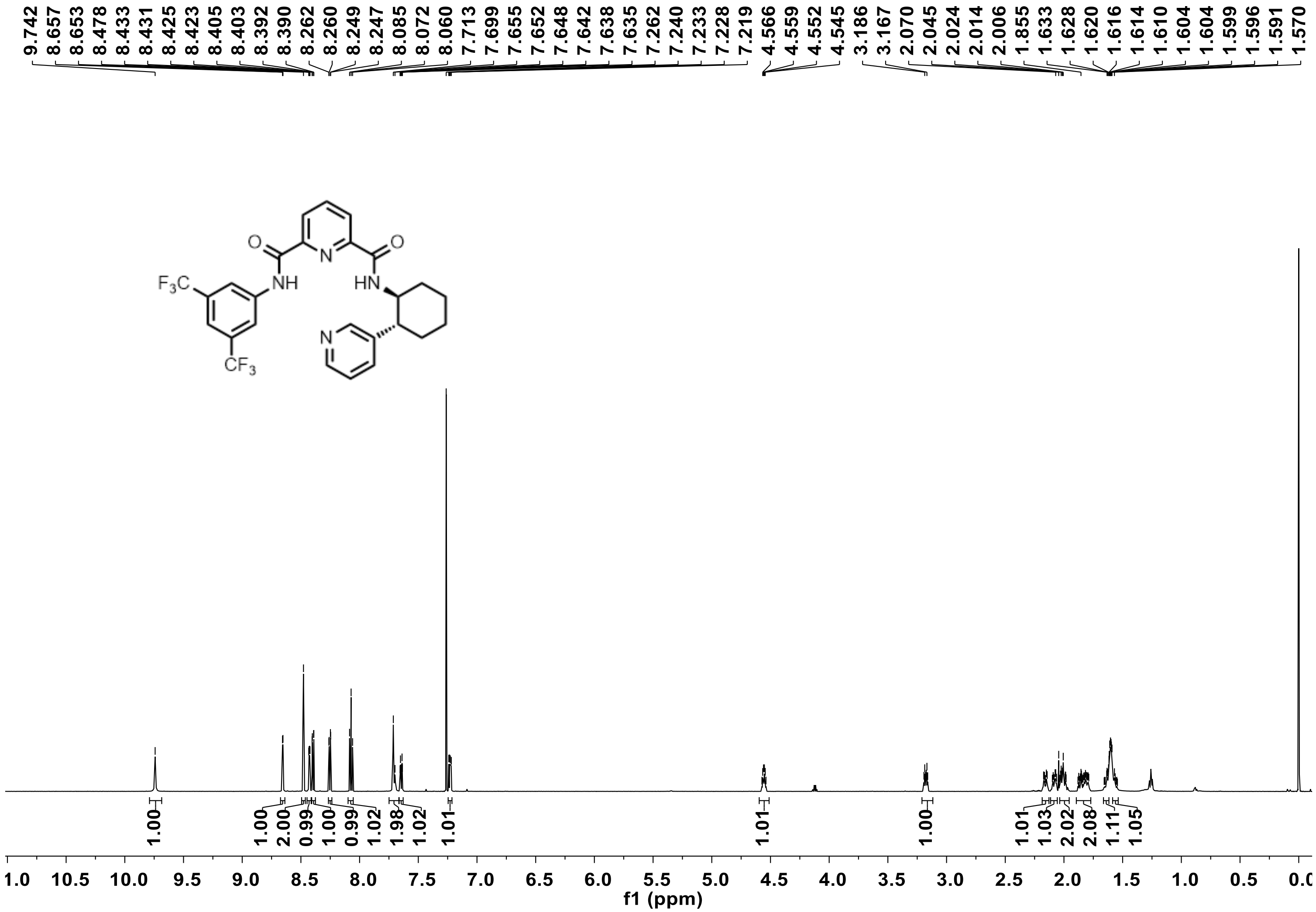
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-T22**



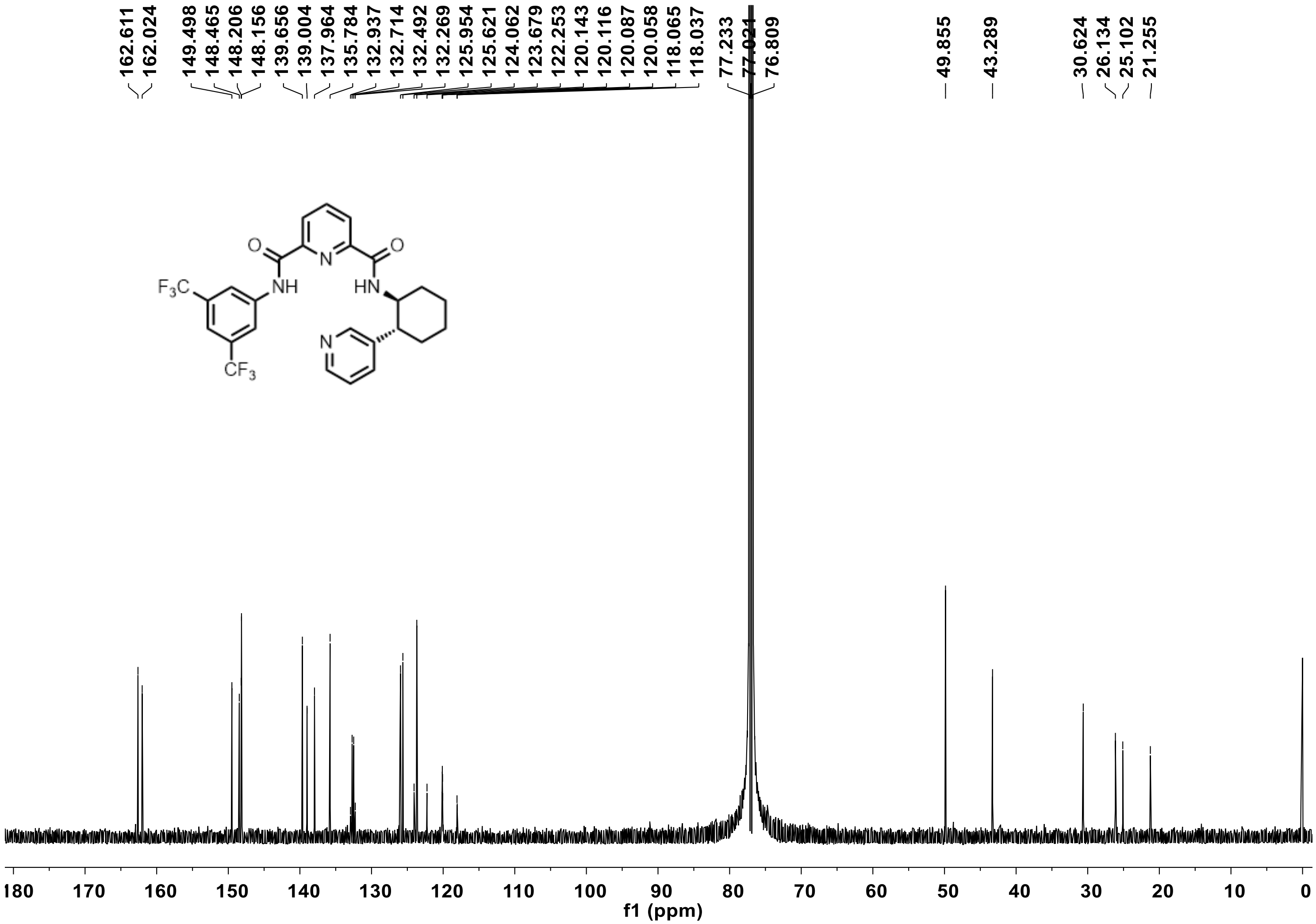
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ***cis*-T22**



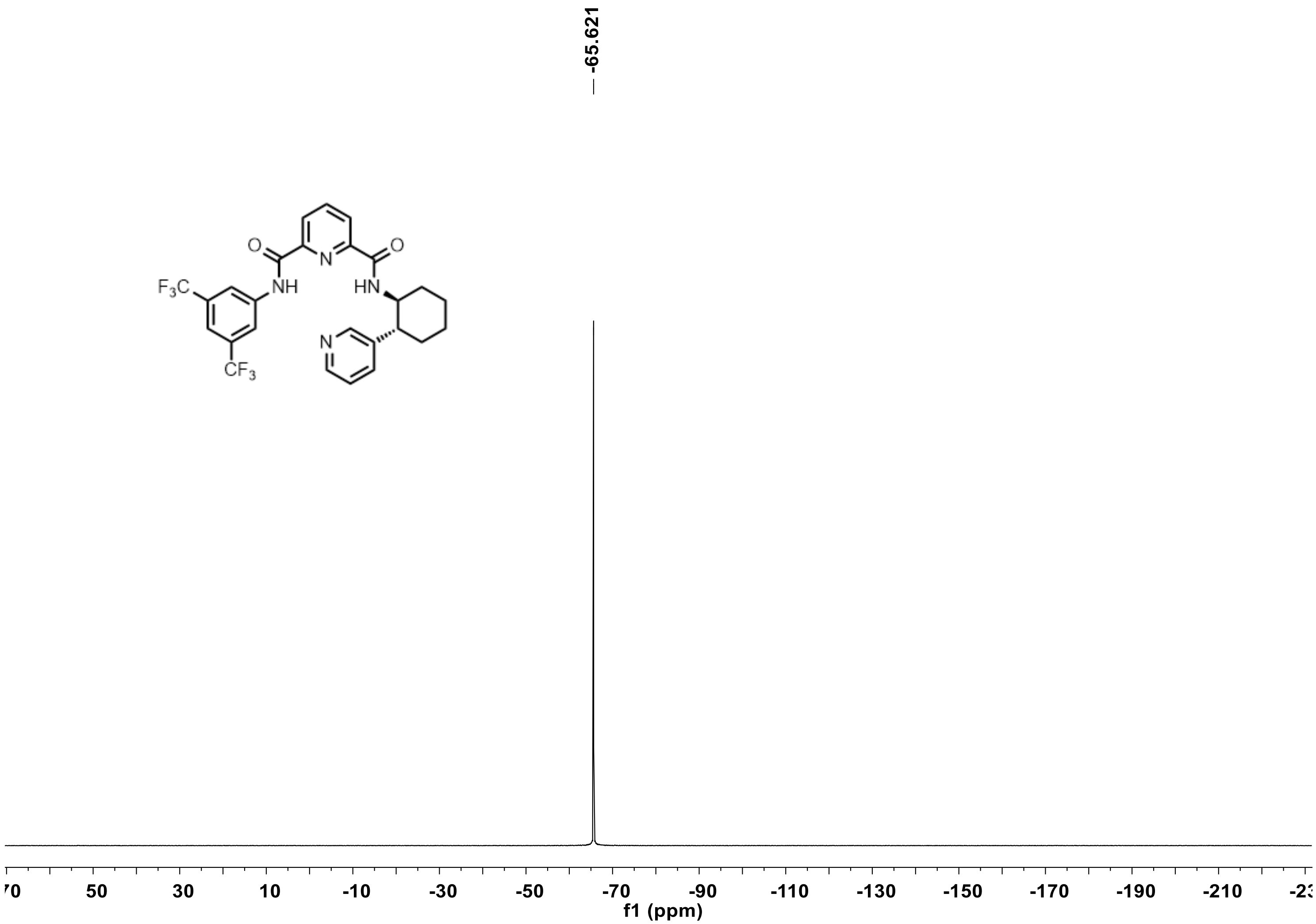
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***trans*-T22**



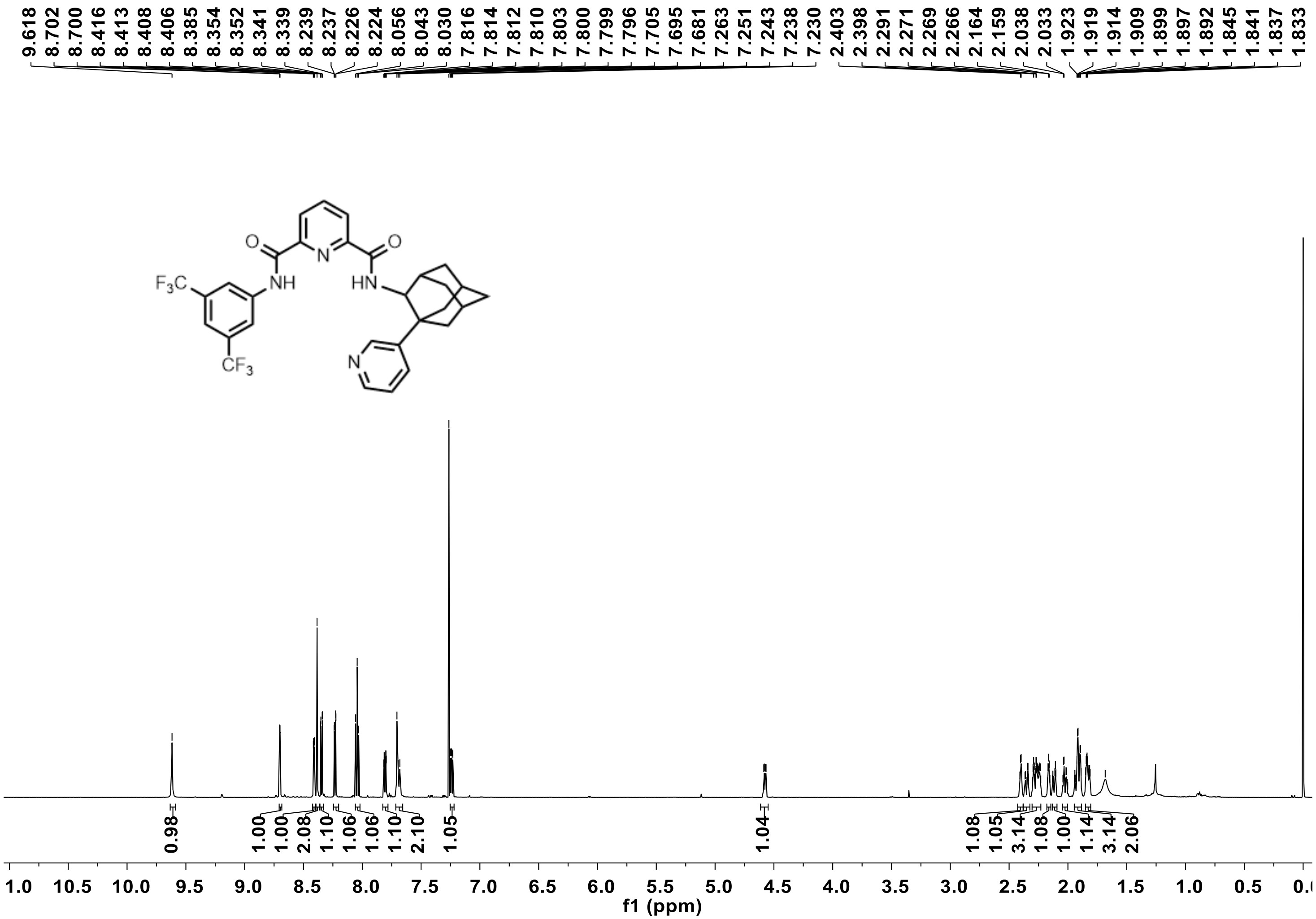
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***trans*-T22**



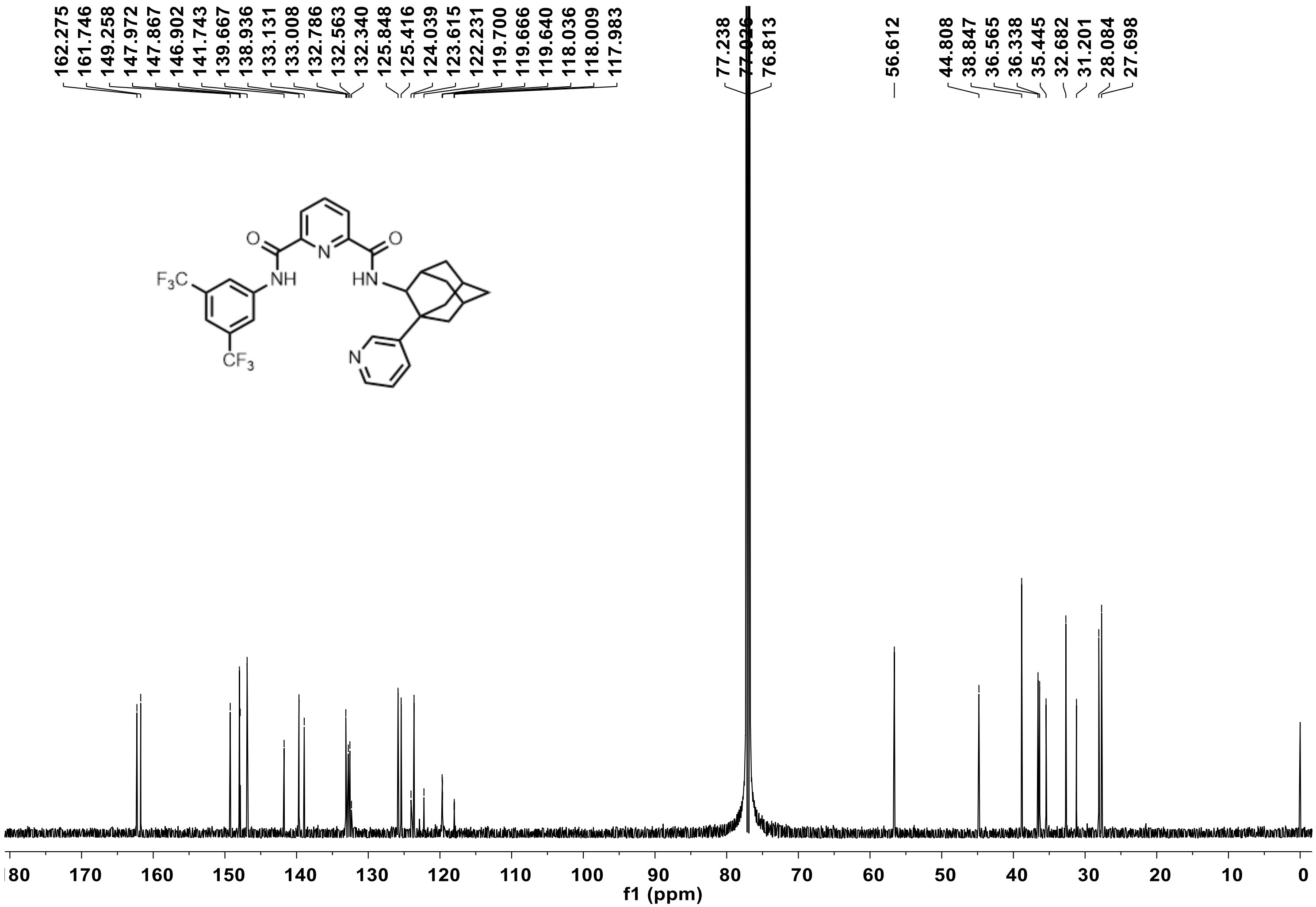
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ***trans*-T22**



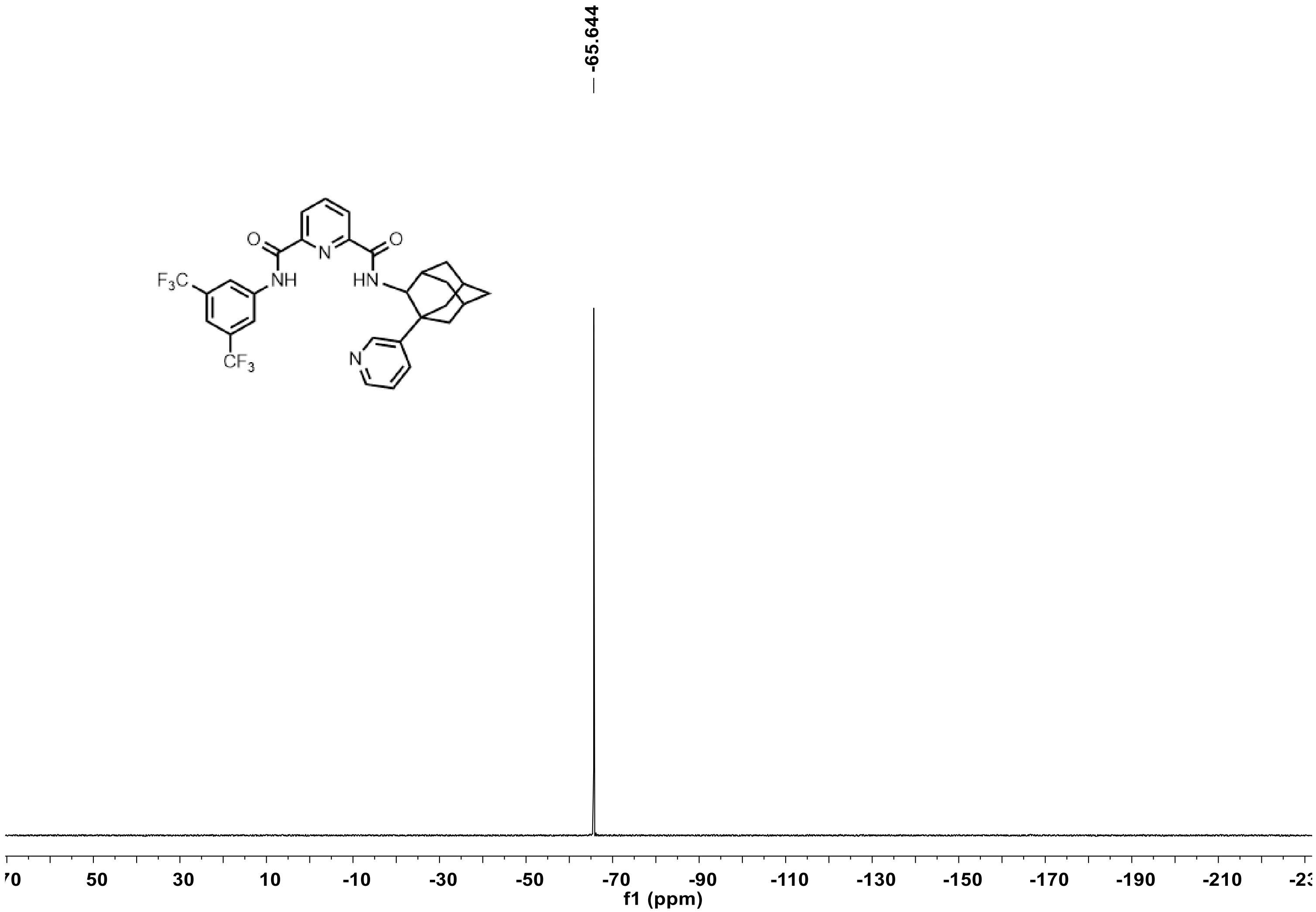
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **T23**



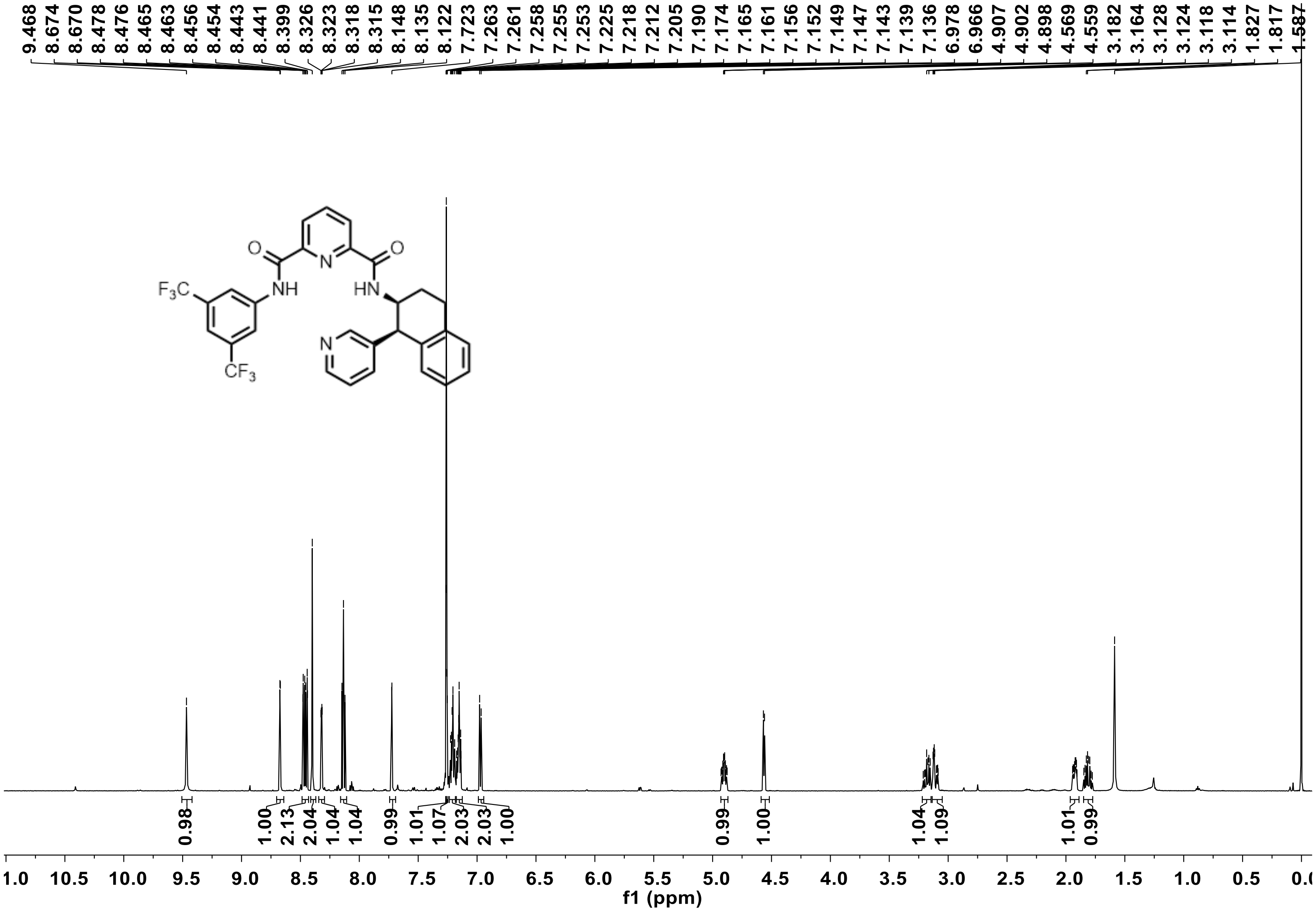
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **T23**



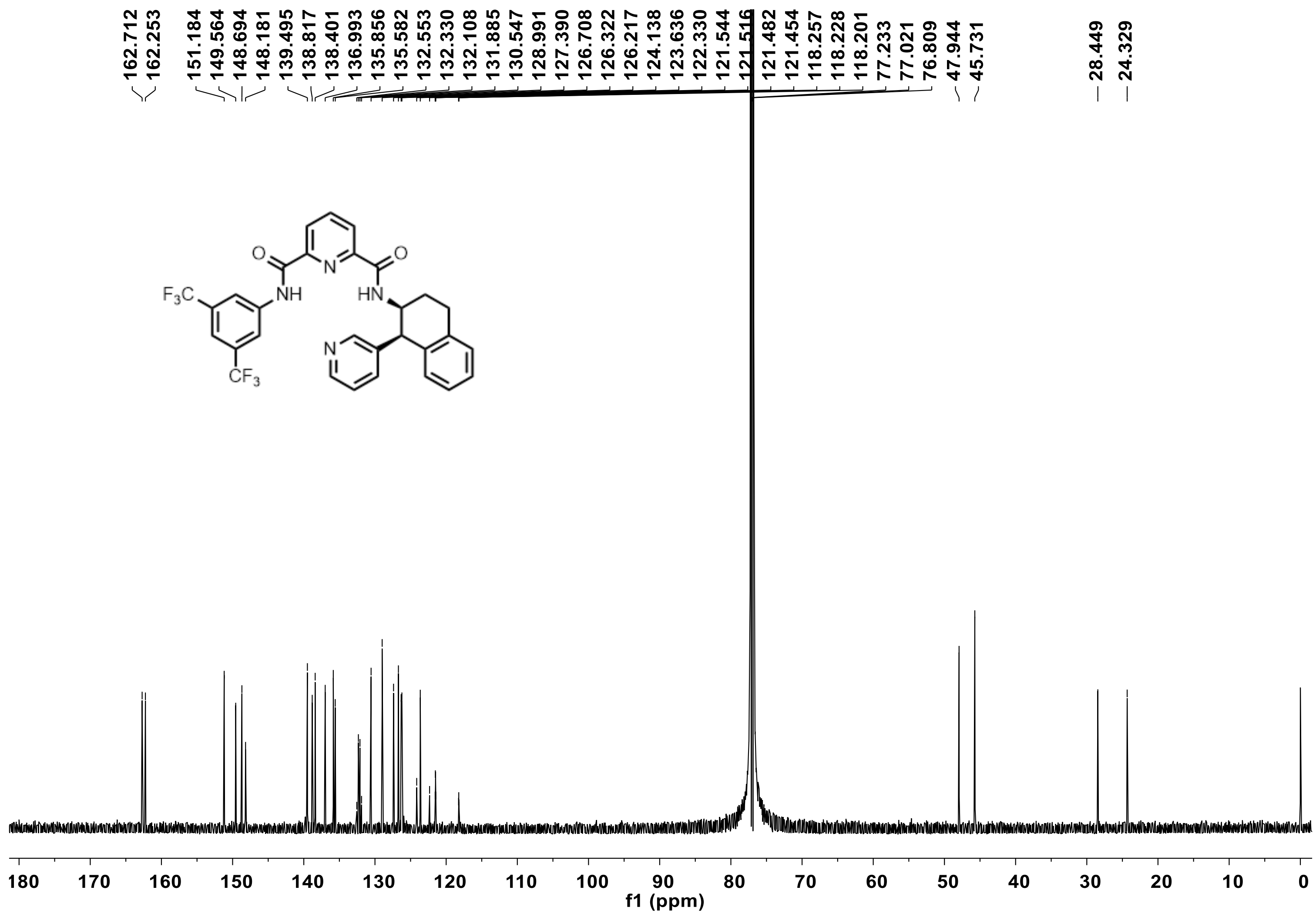
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **T23**



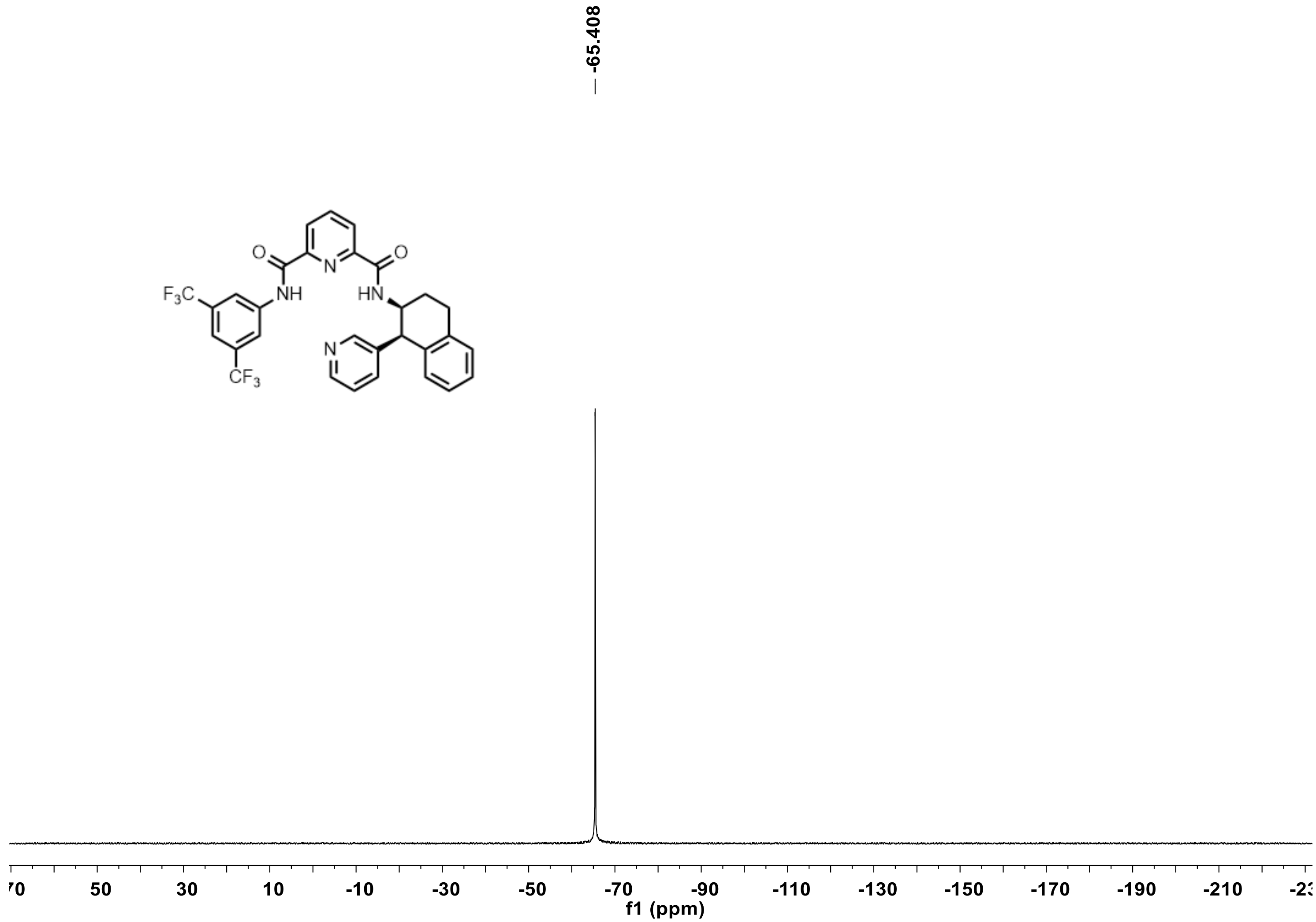
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T24**



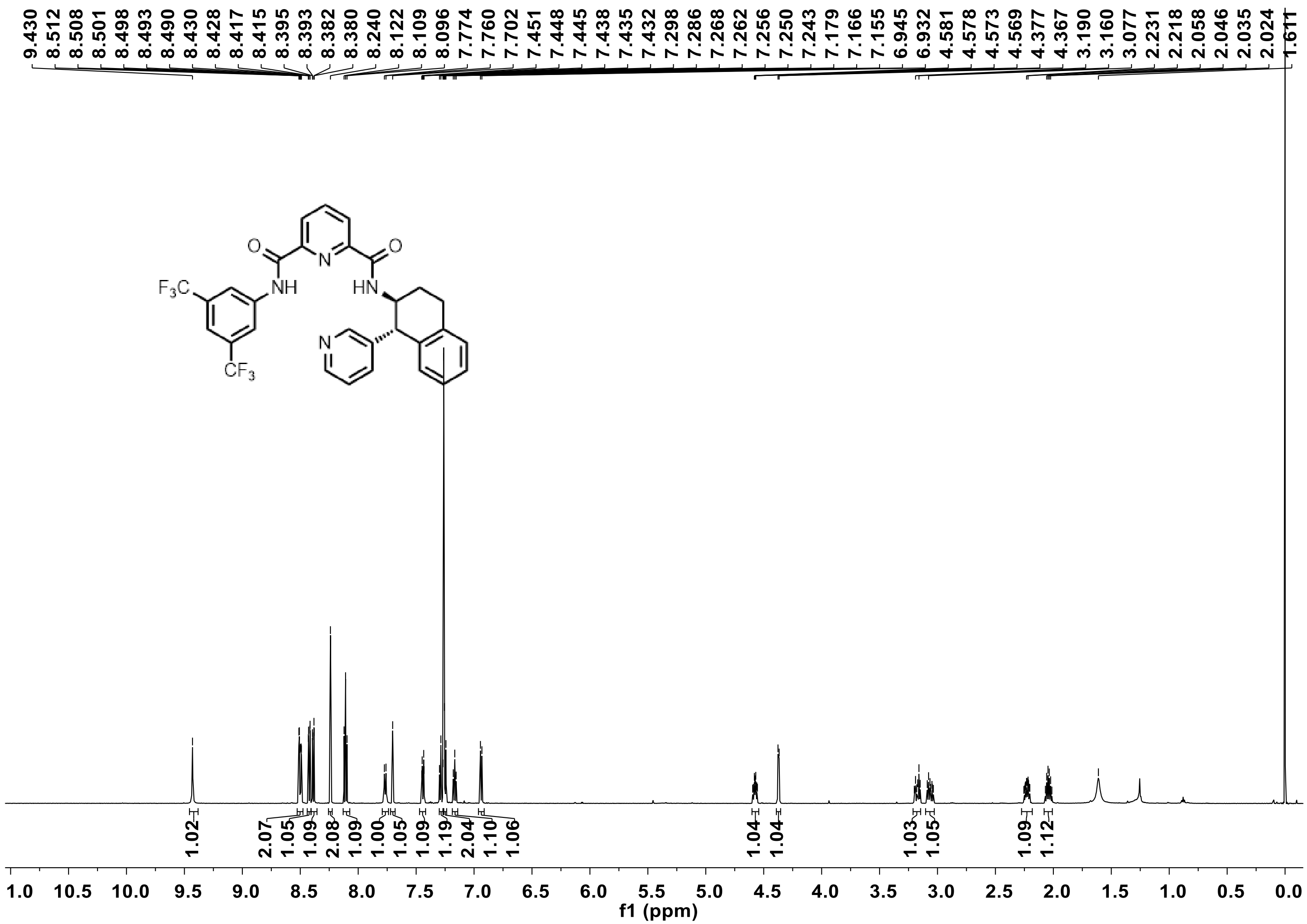
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-T24**



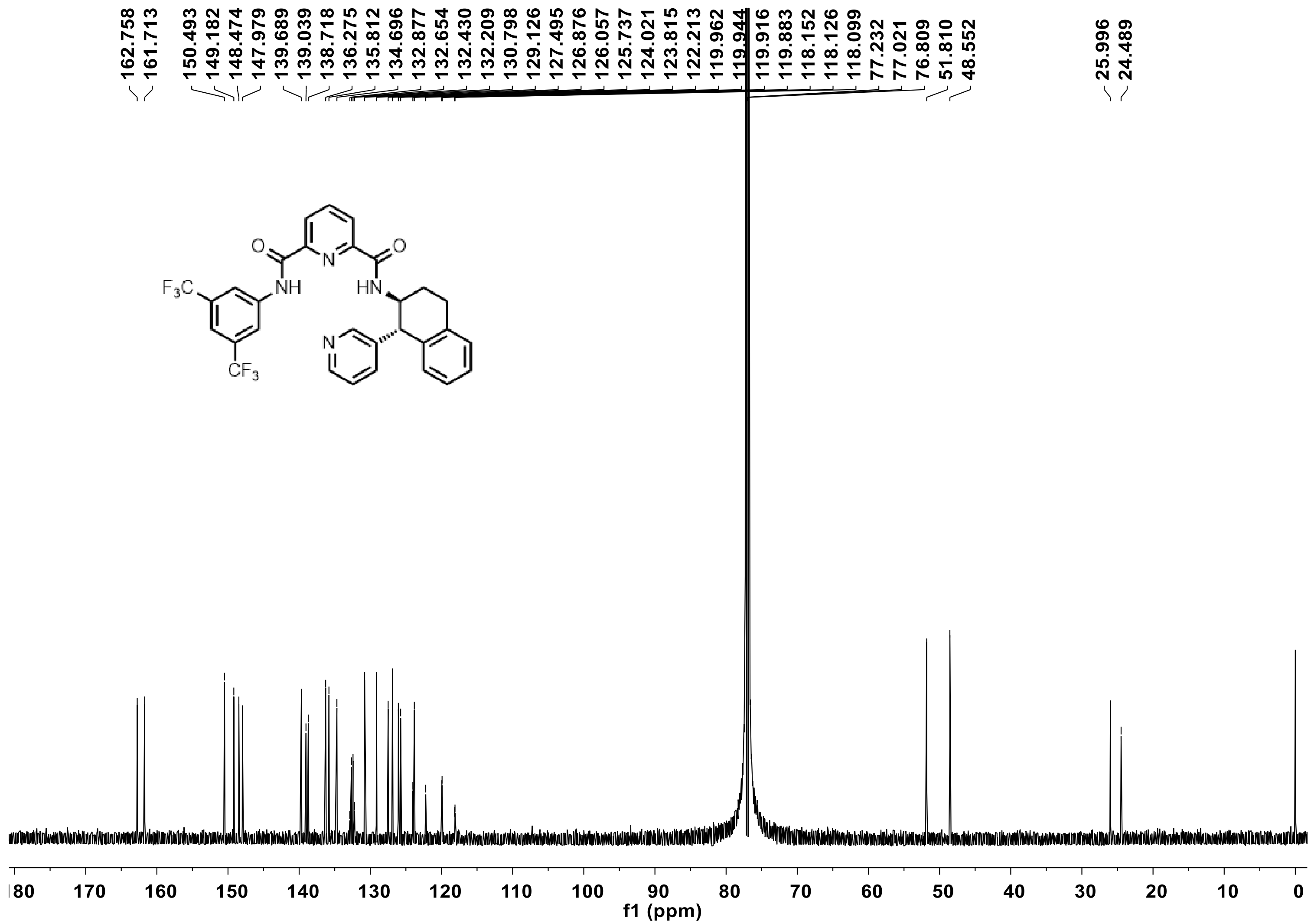
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ***cis*-T24**



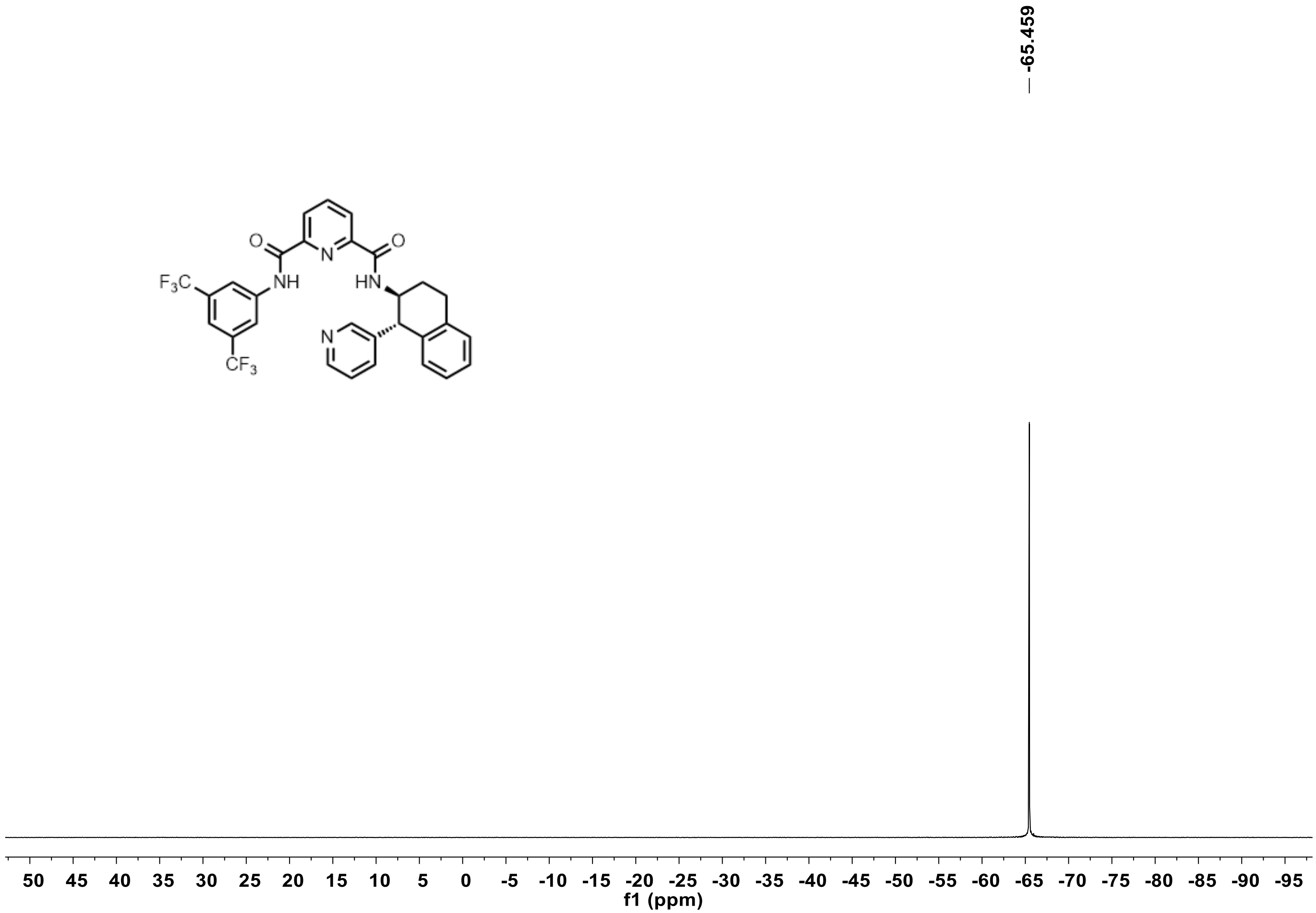
[1]H NMR (600 MHz, $CDCl_3$) spectrum of ***trans*-T24**



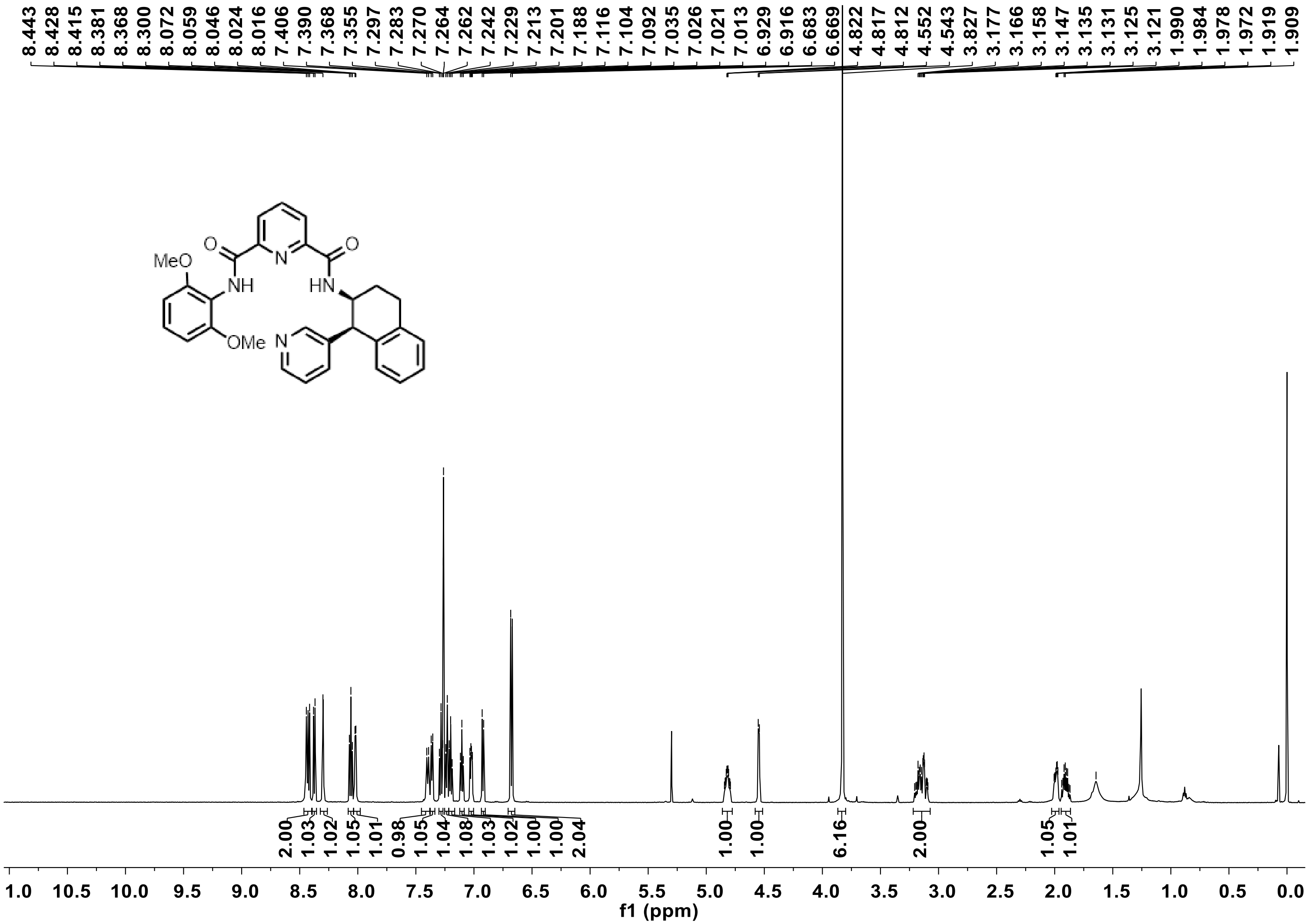
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***trans*-T24**



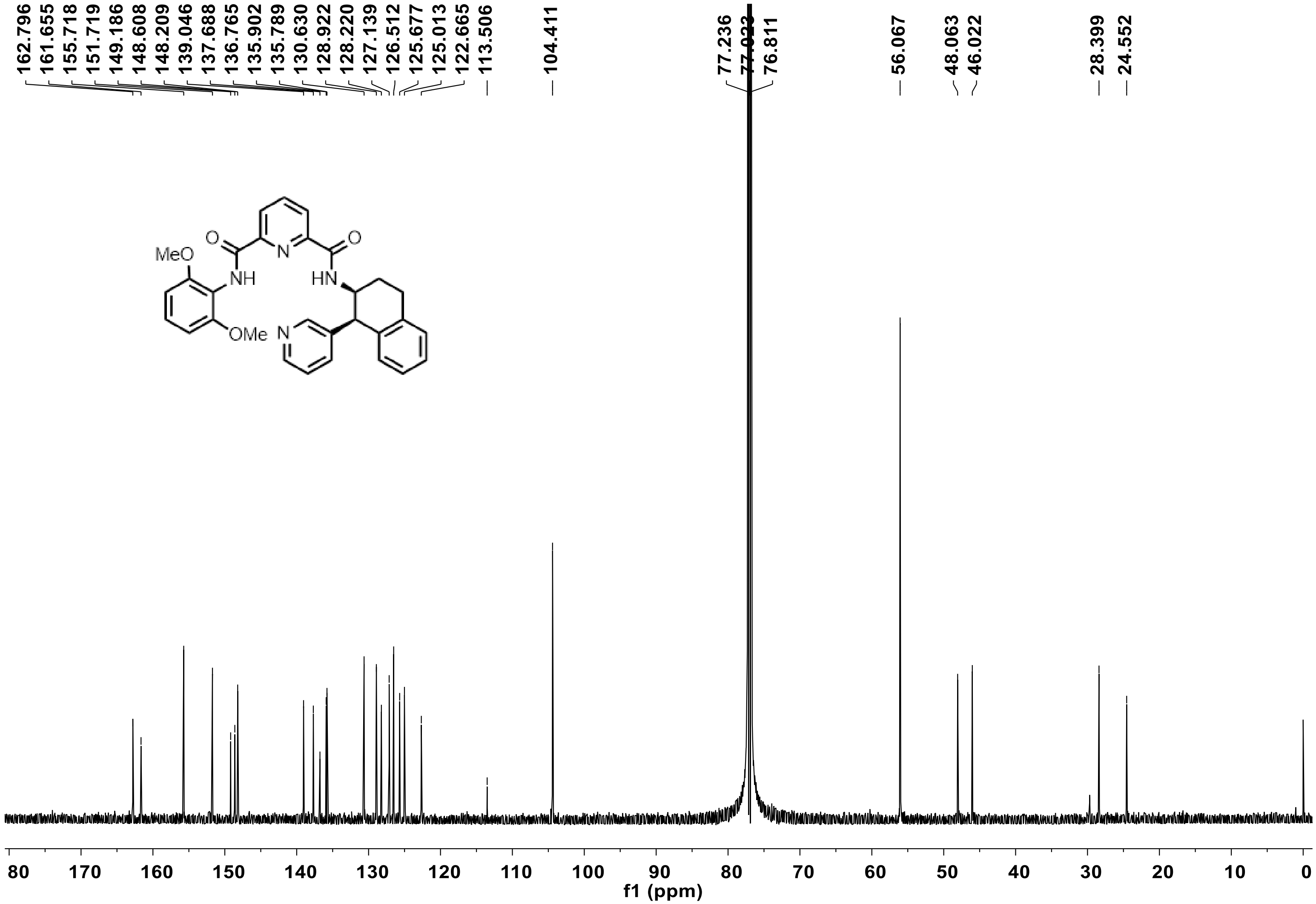
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ***trans*-T24**



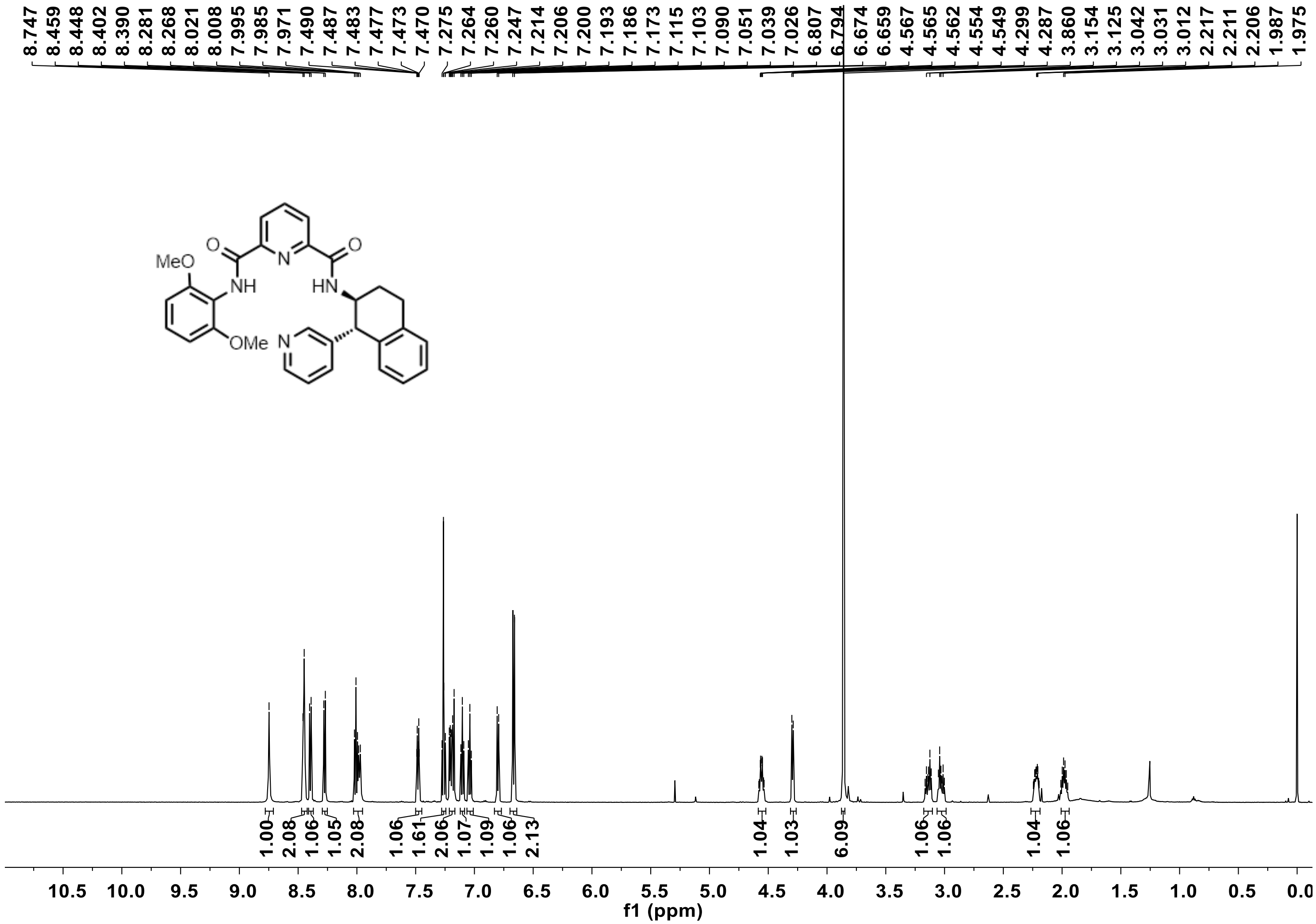
[1]H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T25**



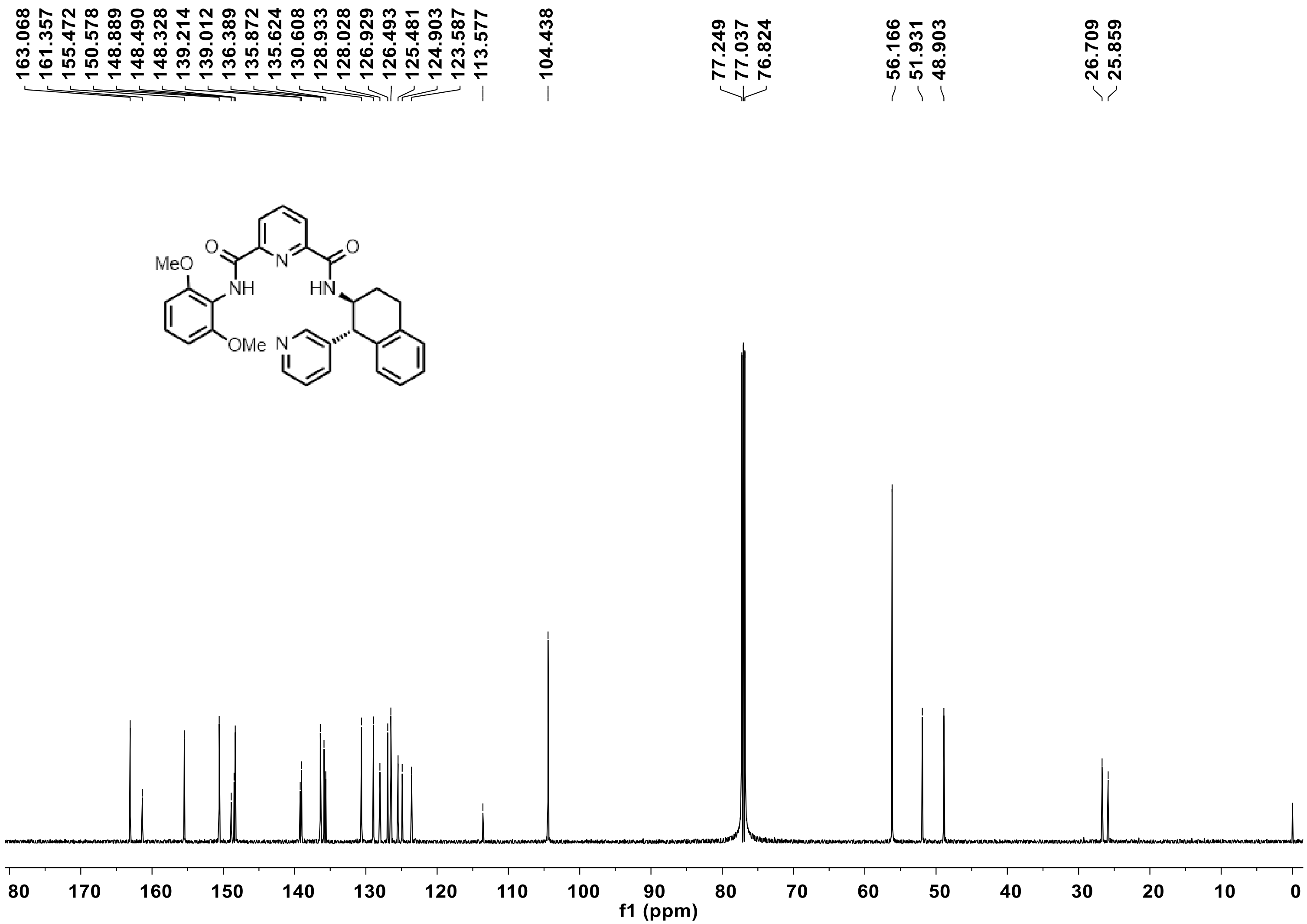
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-T25**



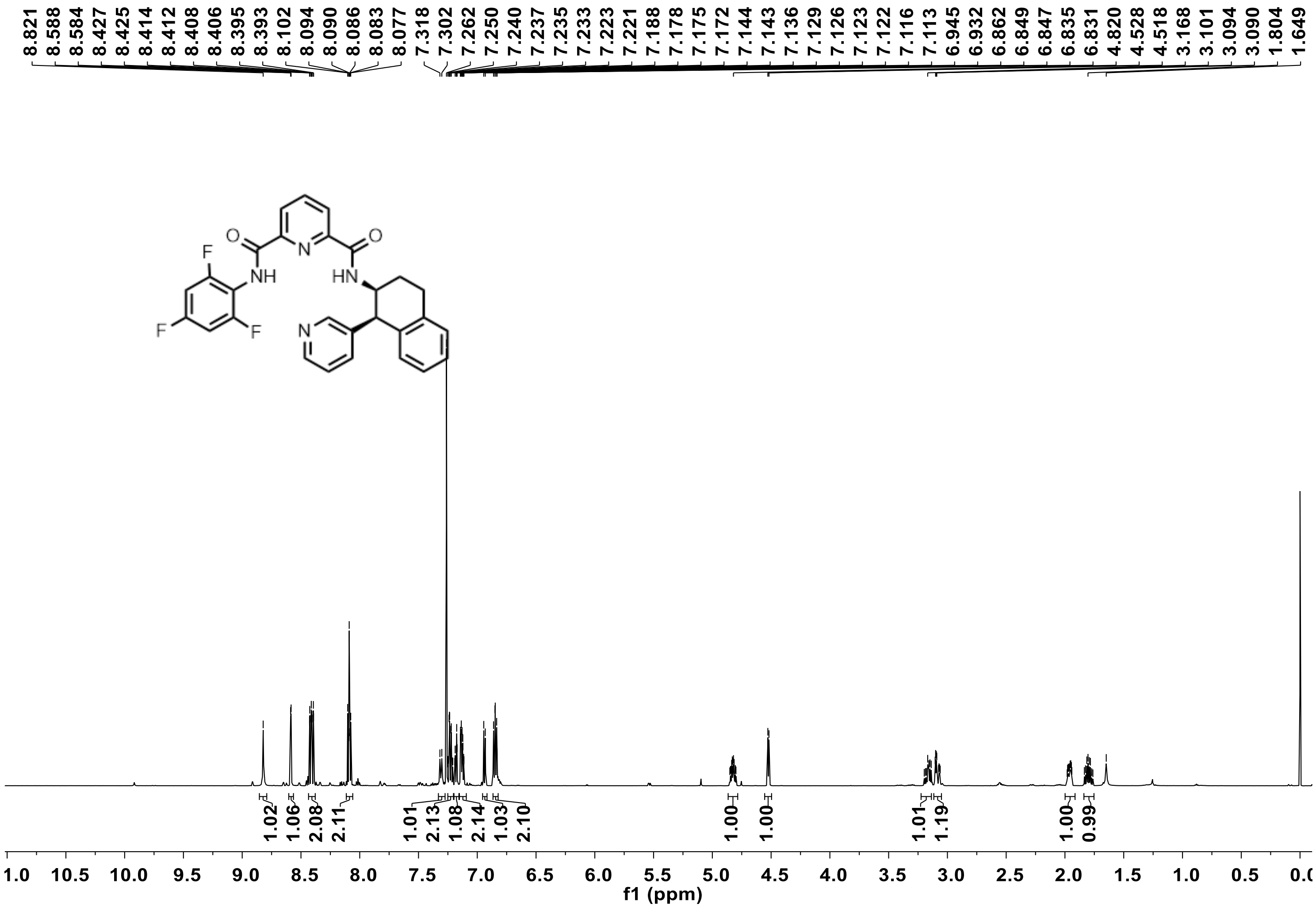
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***trans*-T25**



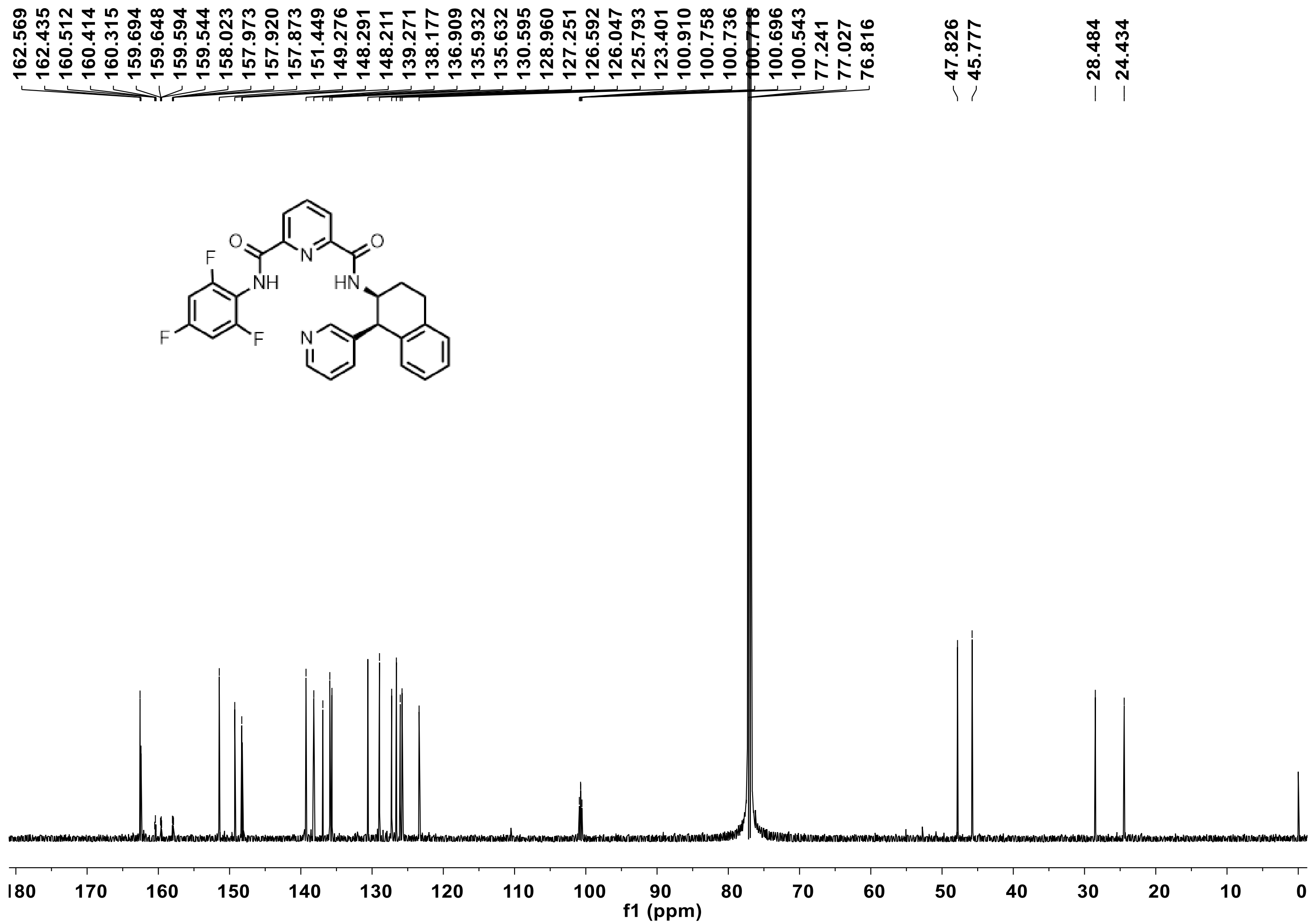
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***trans*-T25**



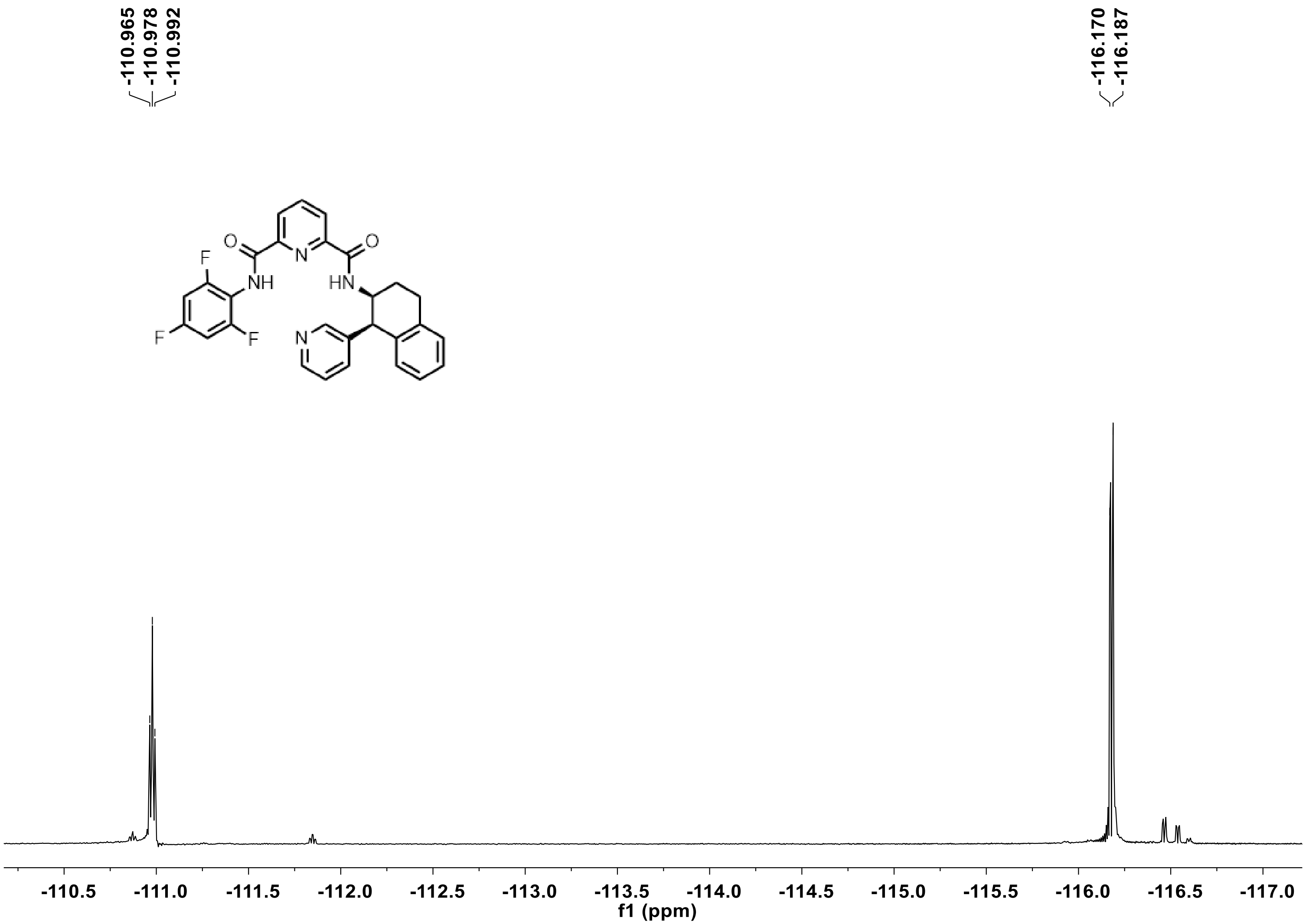
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T26**



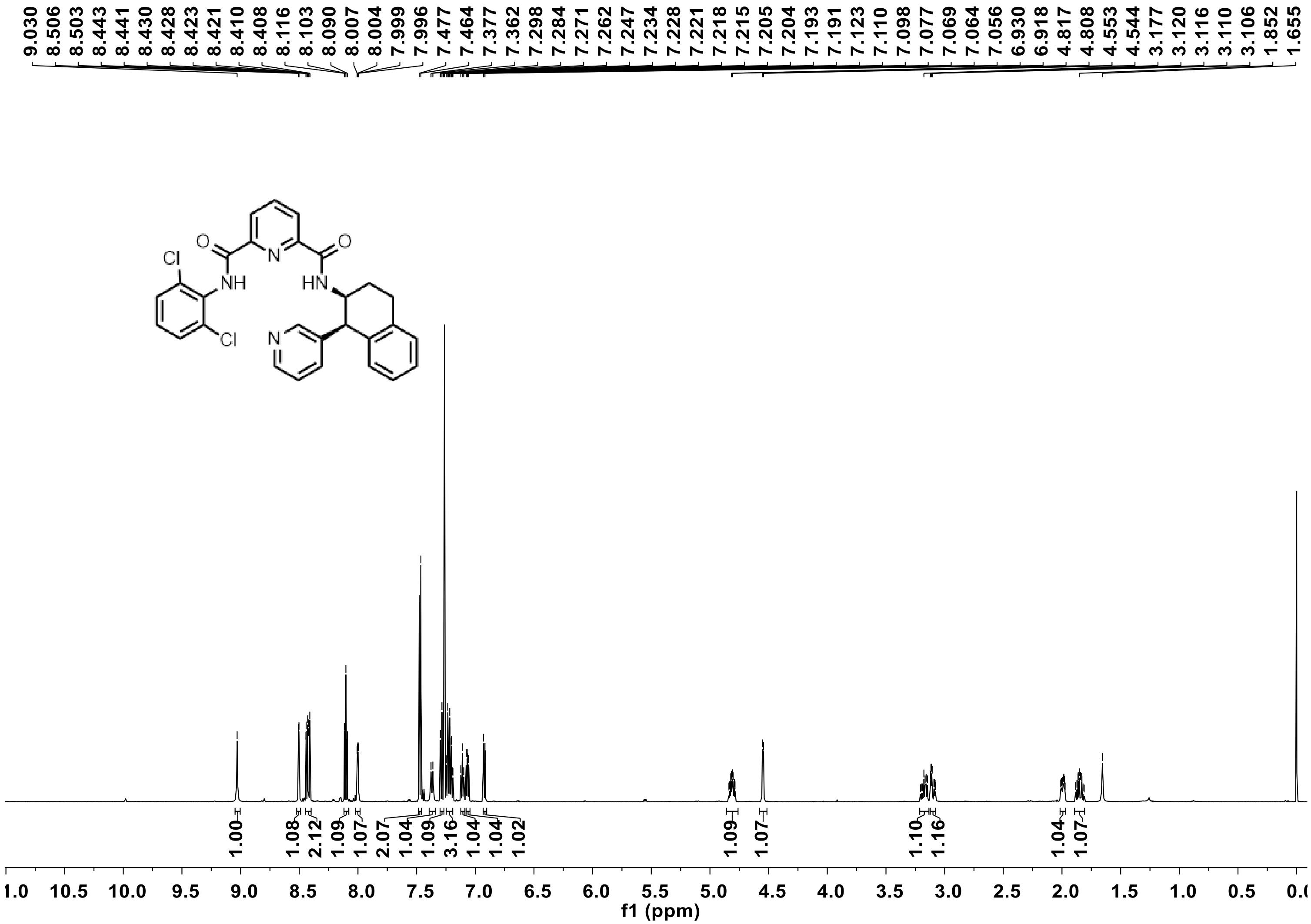
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-T26**



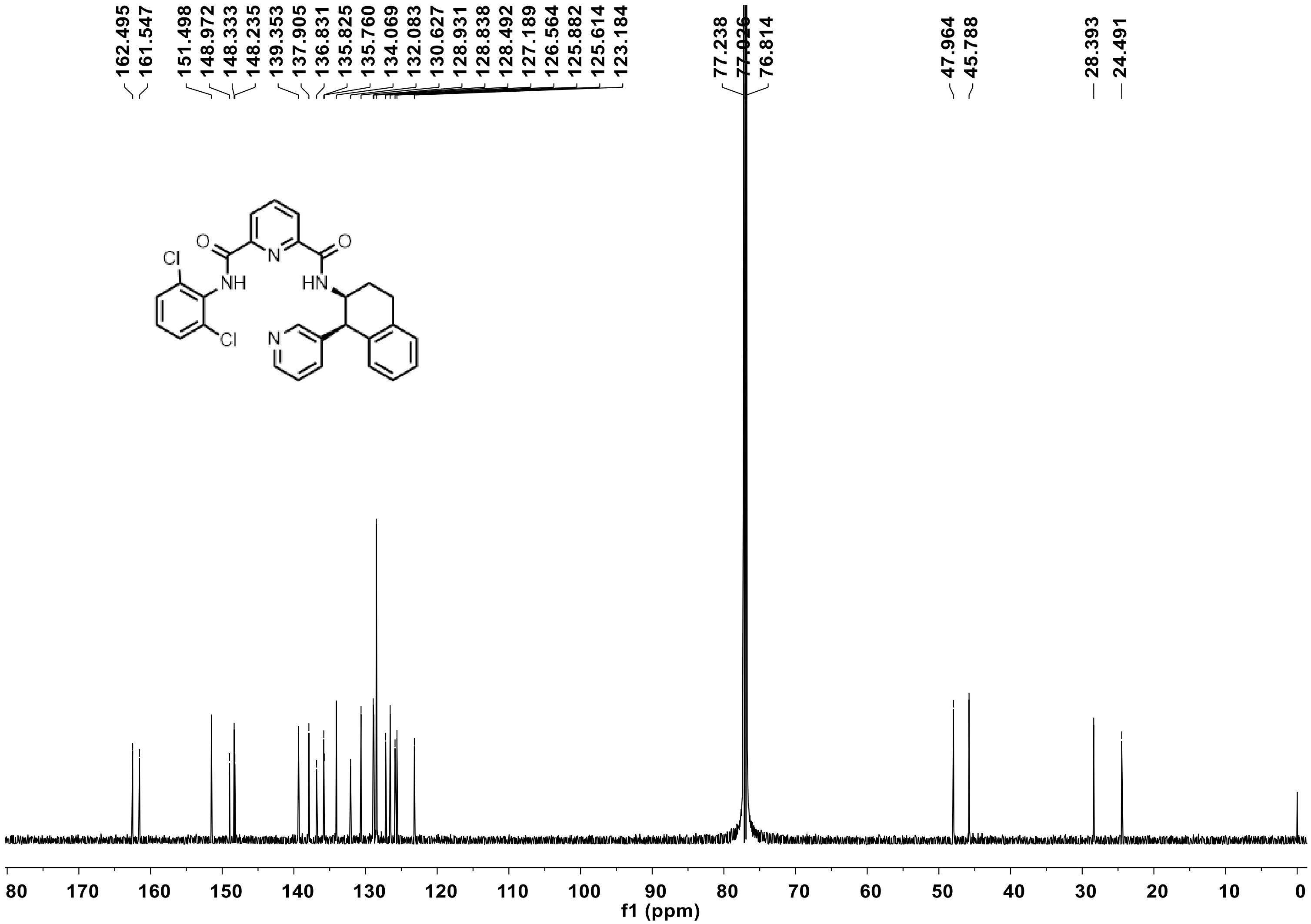
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ***cis*-T26**



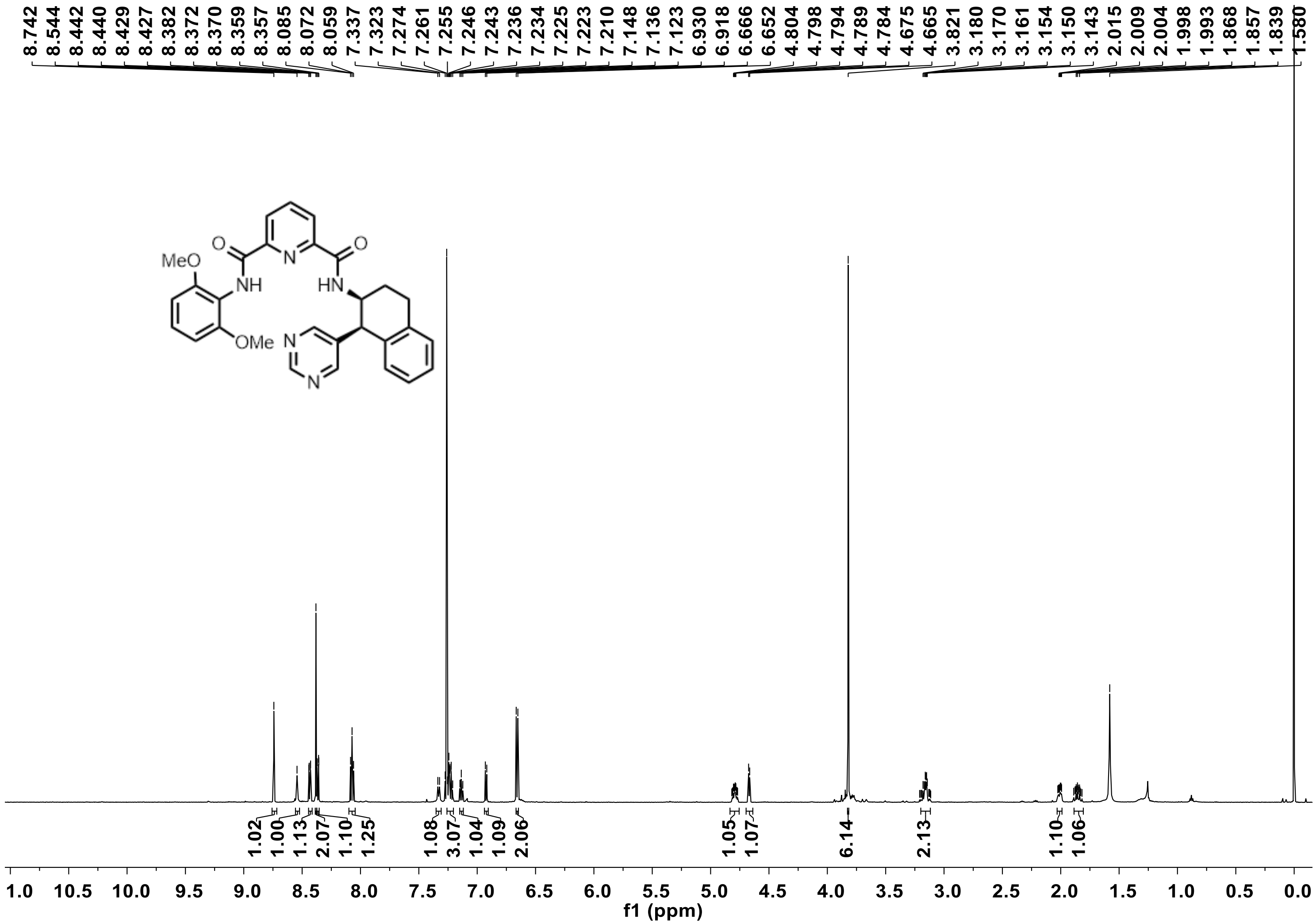
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T27**



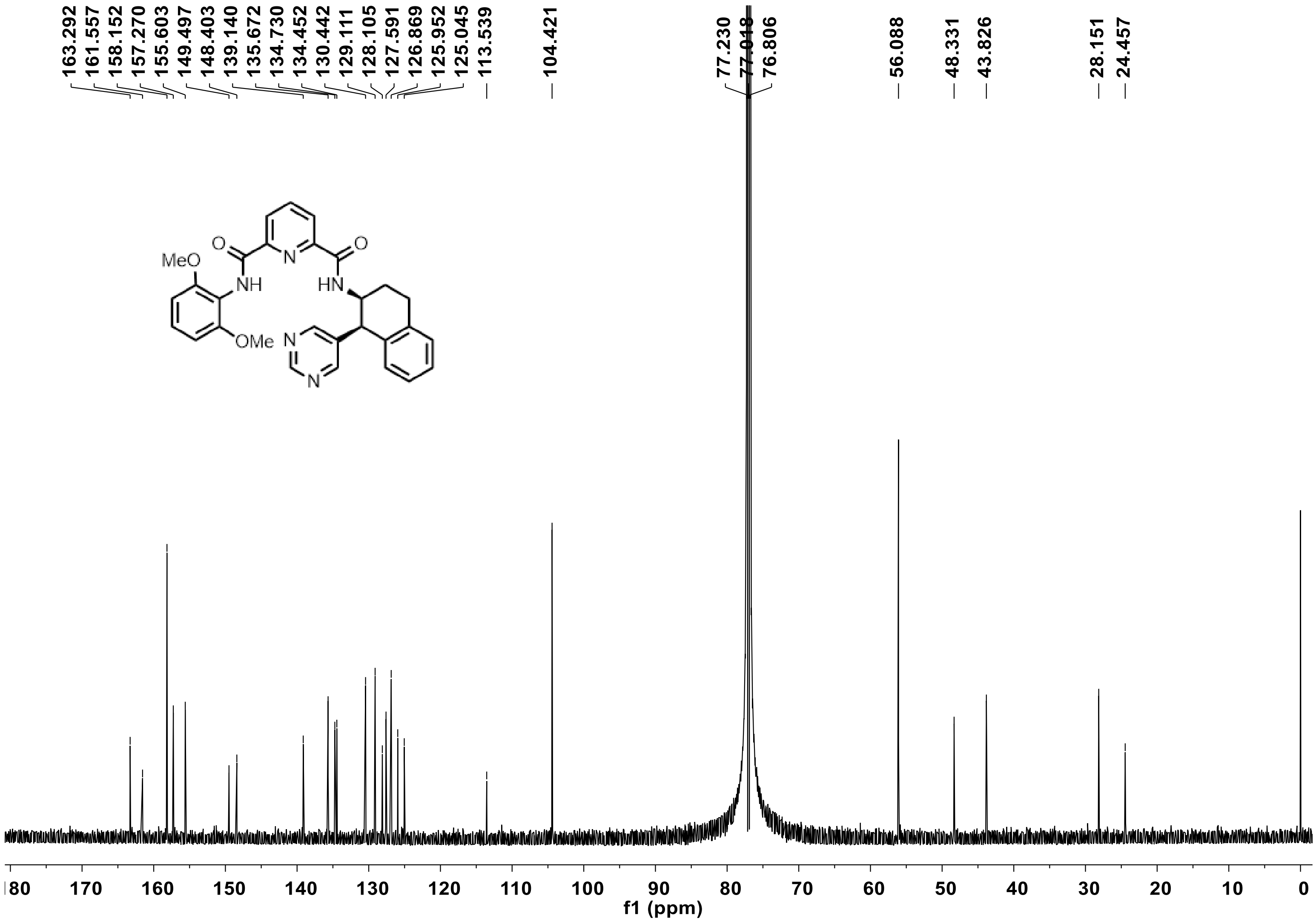
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of ***cis*-T27**



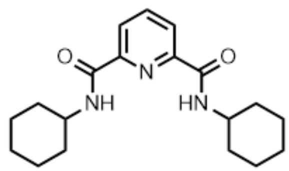
^1H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-T28**

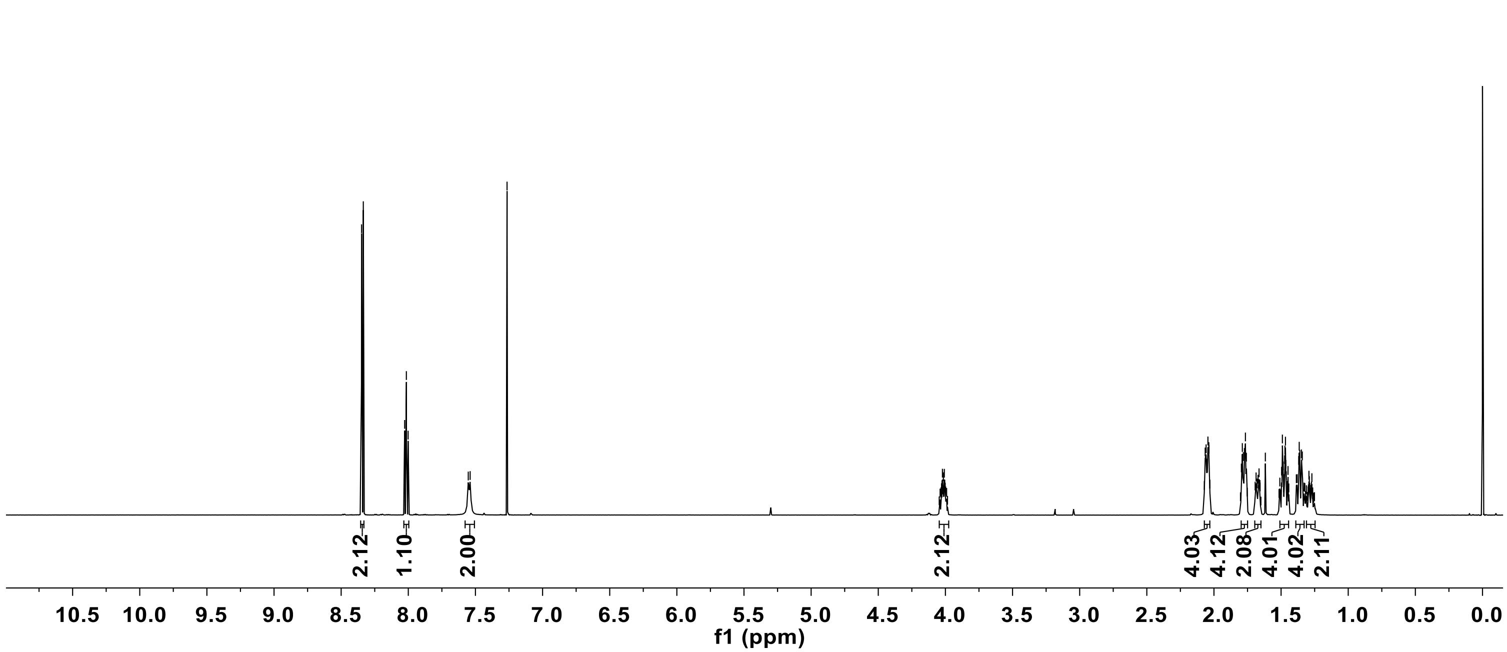


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-T28**

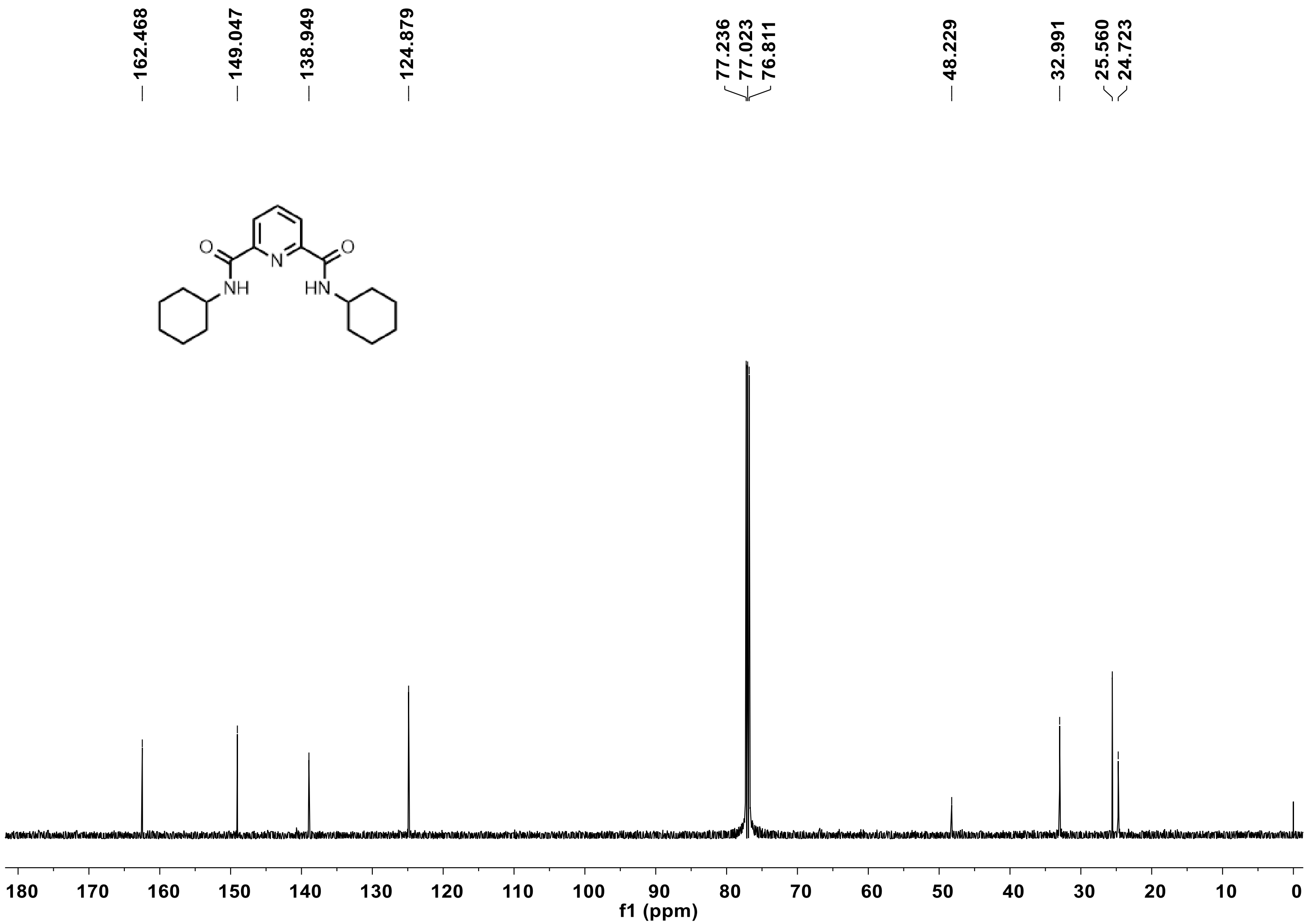


^1H NMR (600 MHz, $CDCl_3$) spectrum of **TC1**

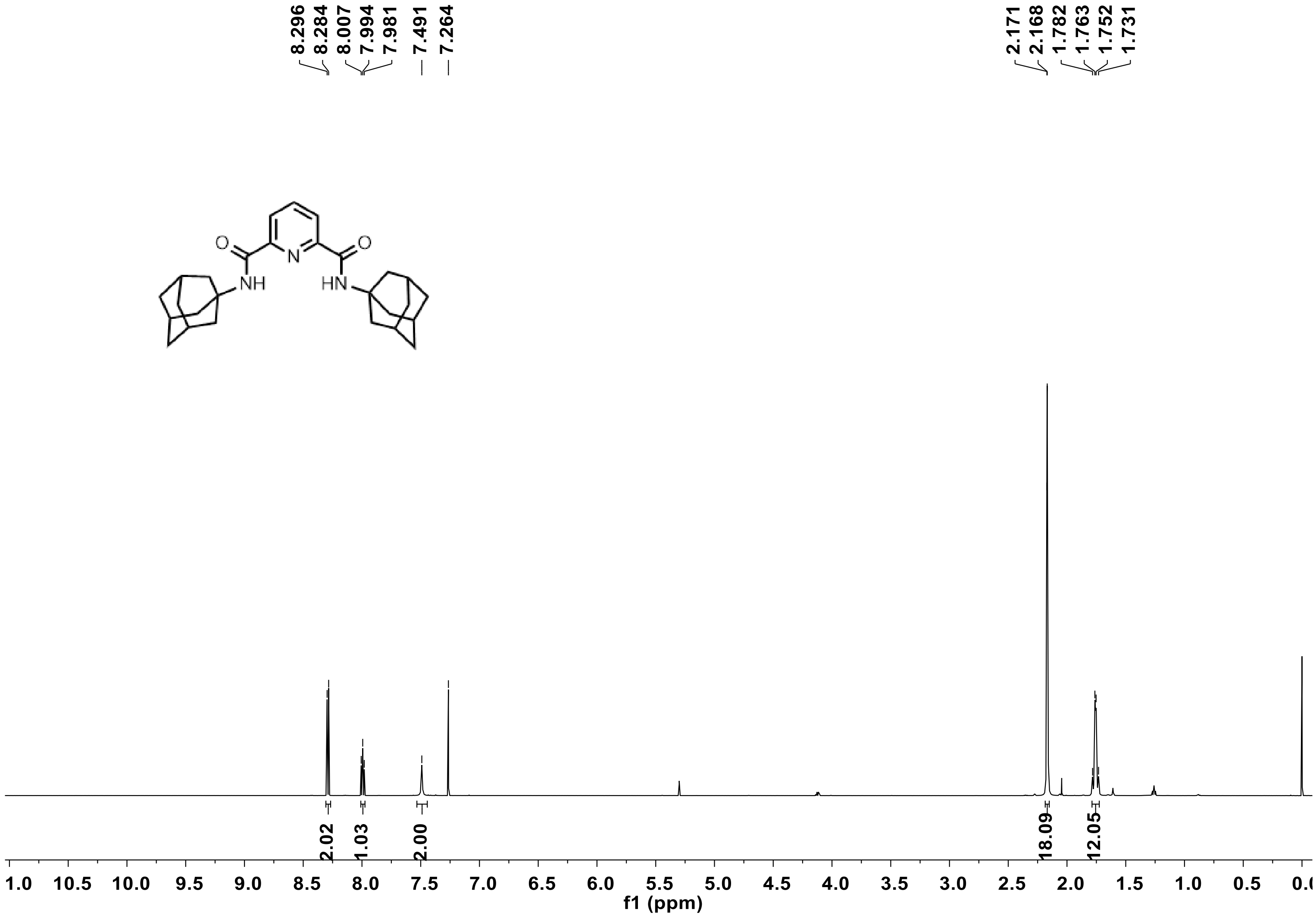




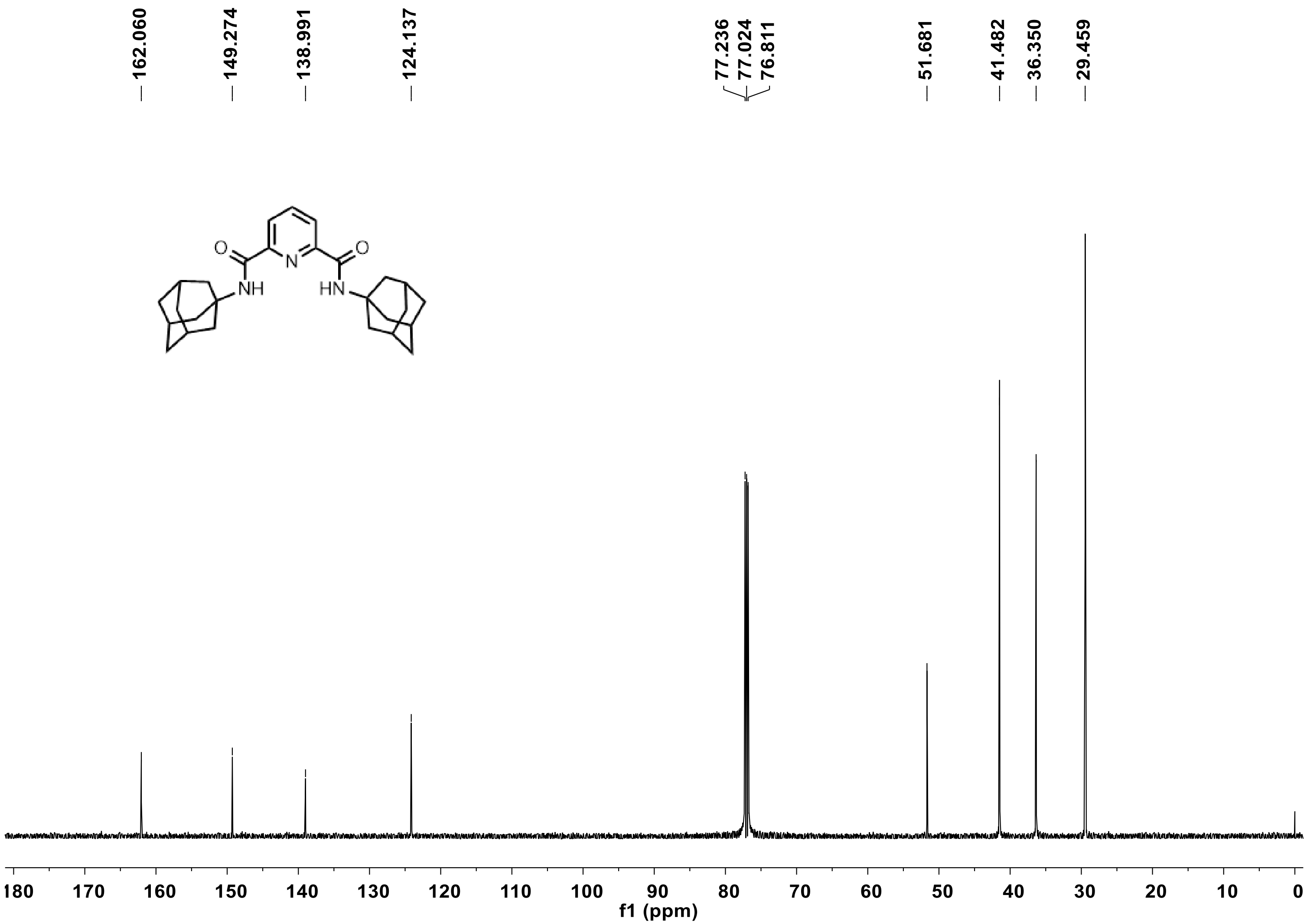
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **TC1**



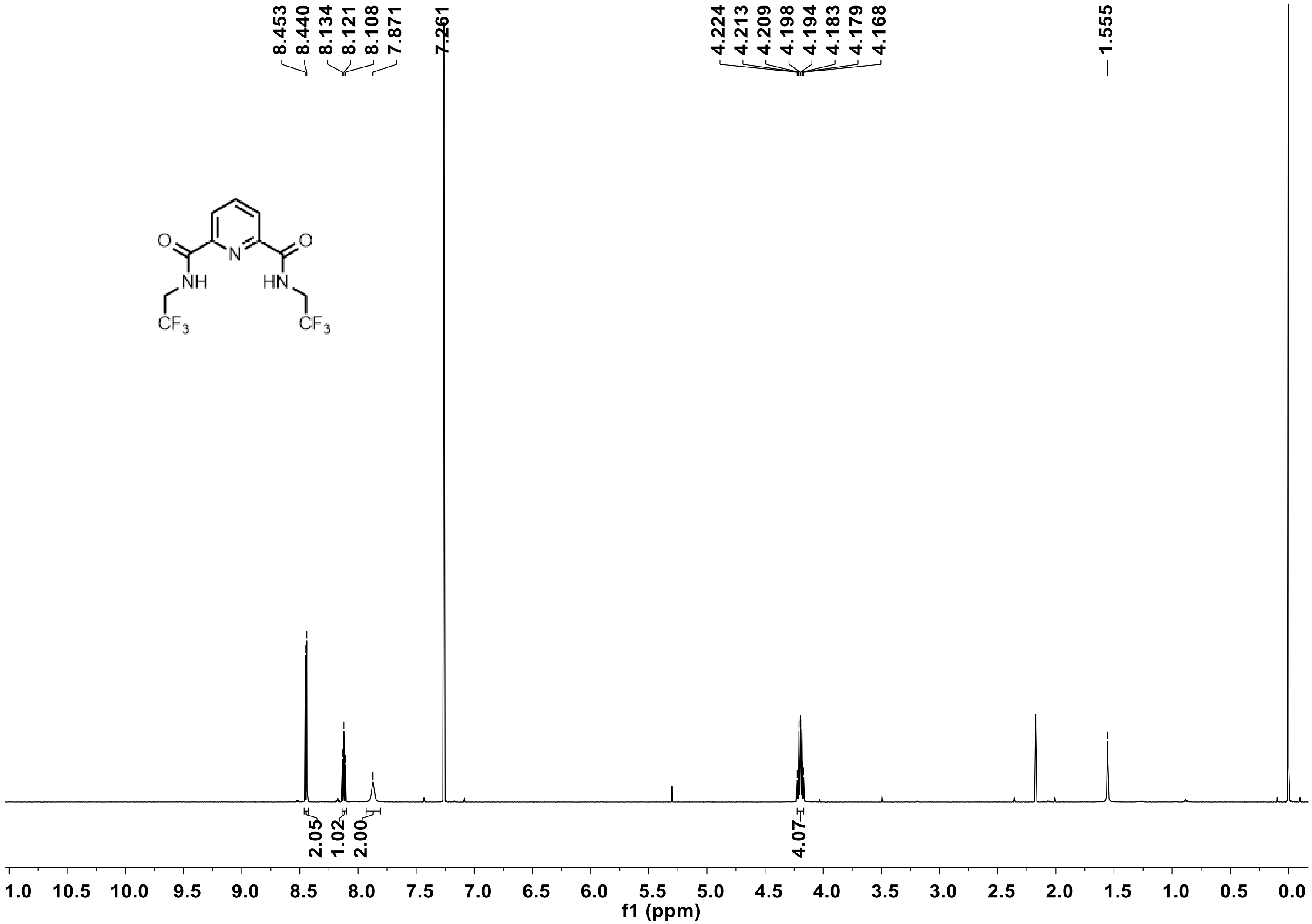
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **TC2**



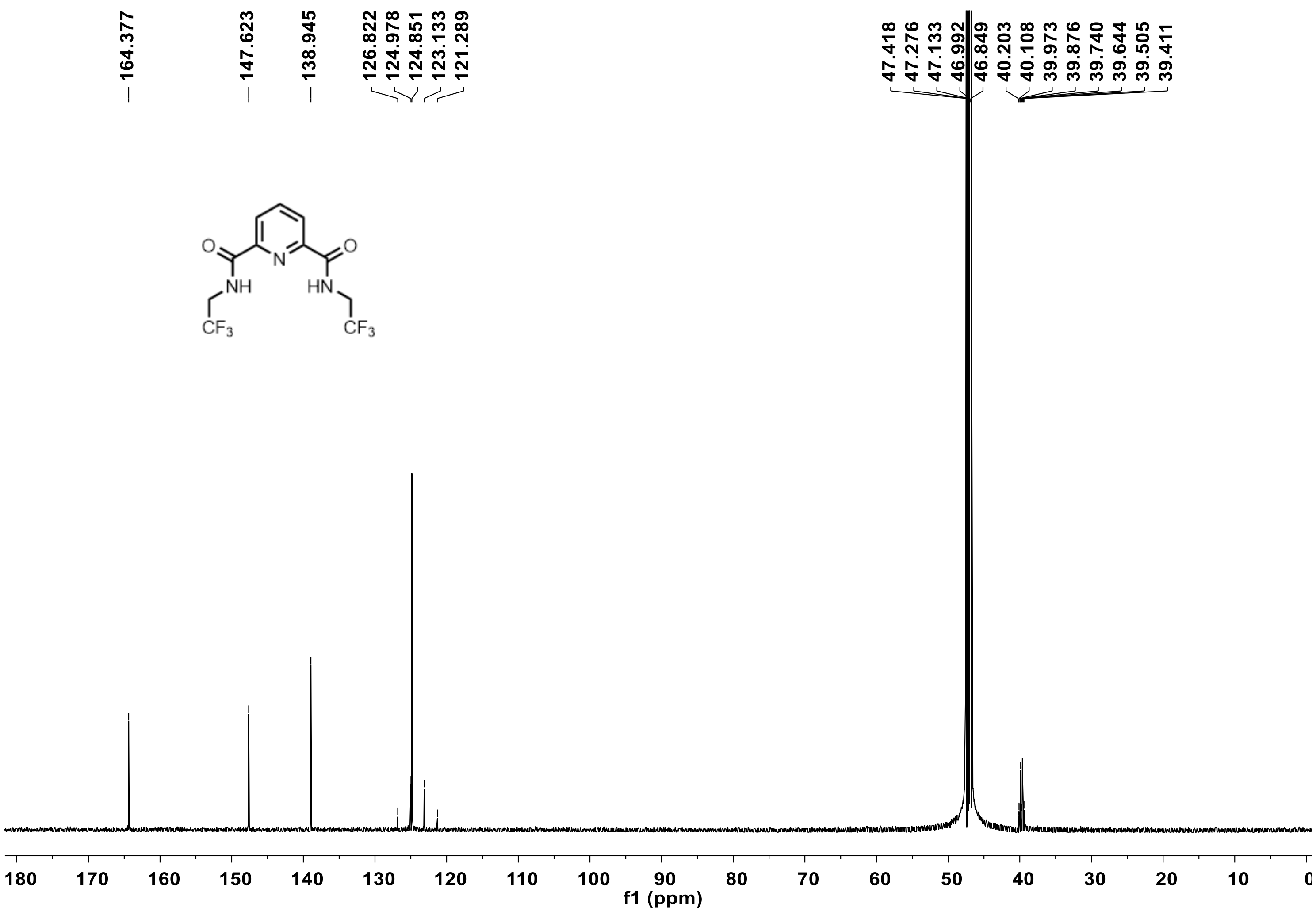
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **TC2**



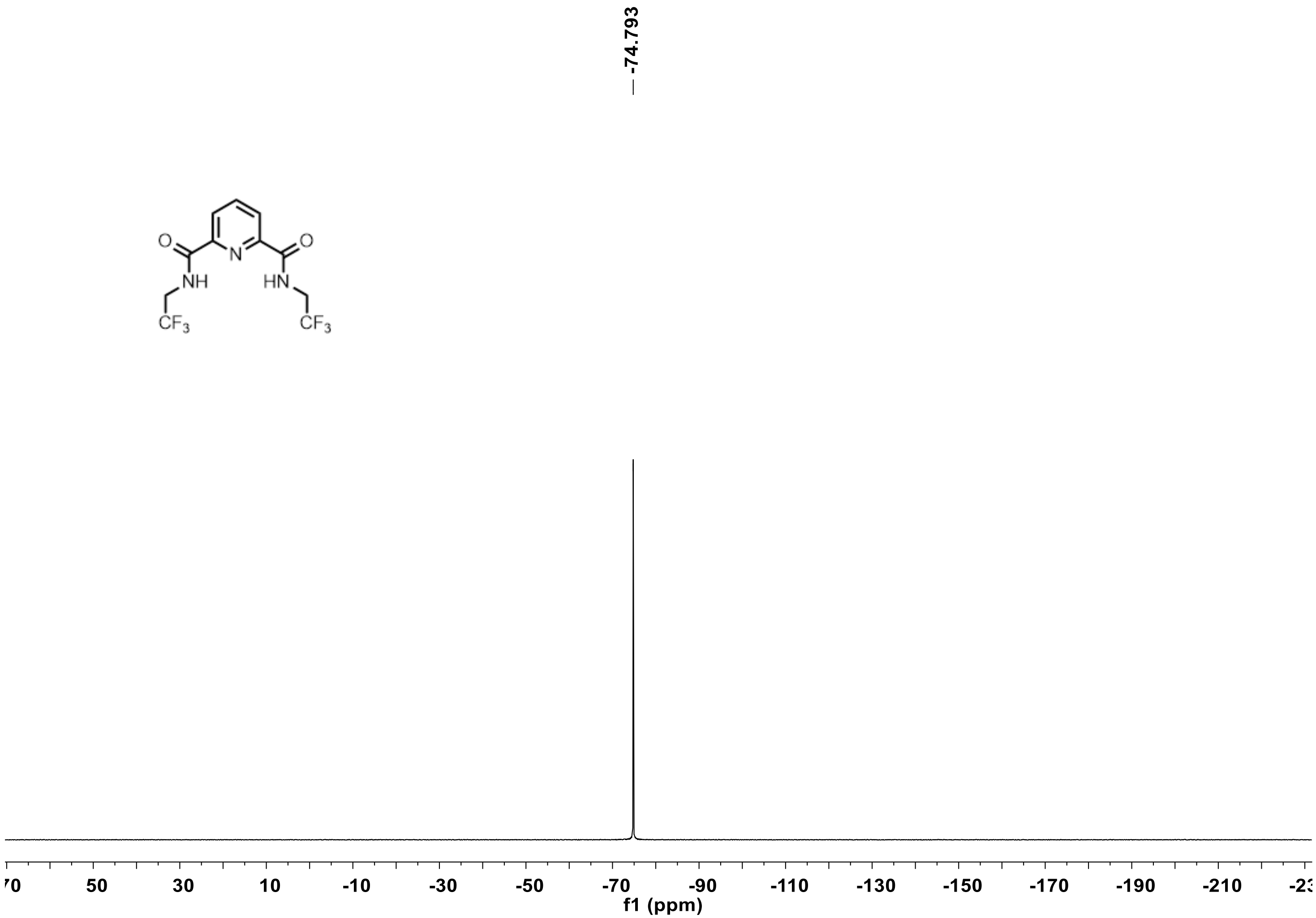
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **TC3**



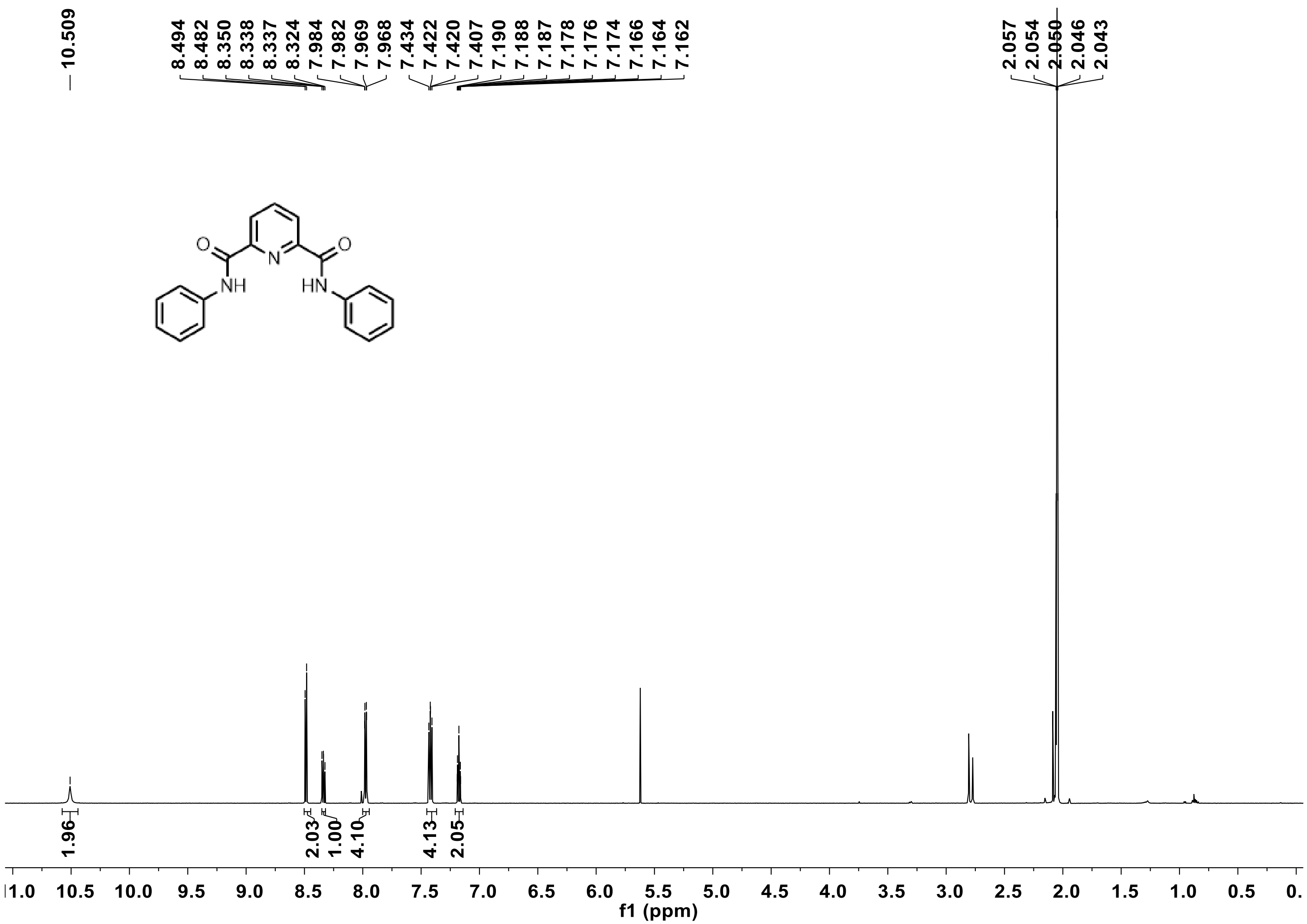
^{13}C NMR (151 MHz, CD_3OD) spectrum of **TC3**



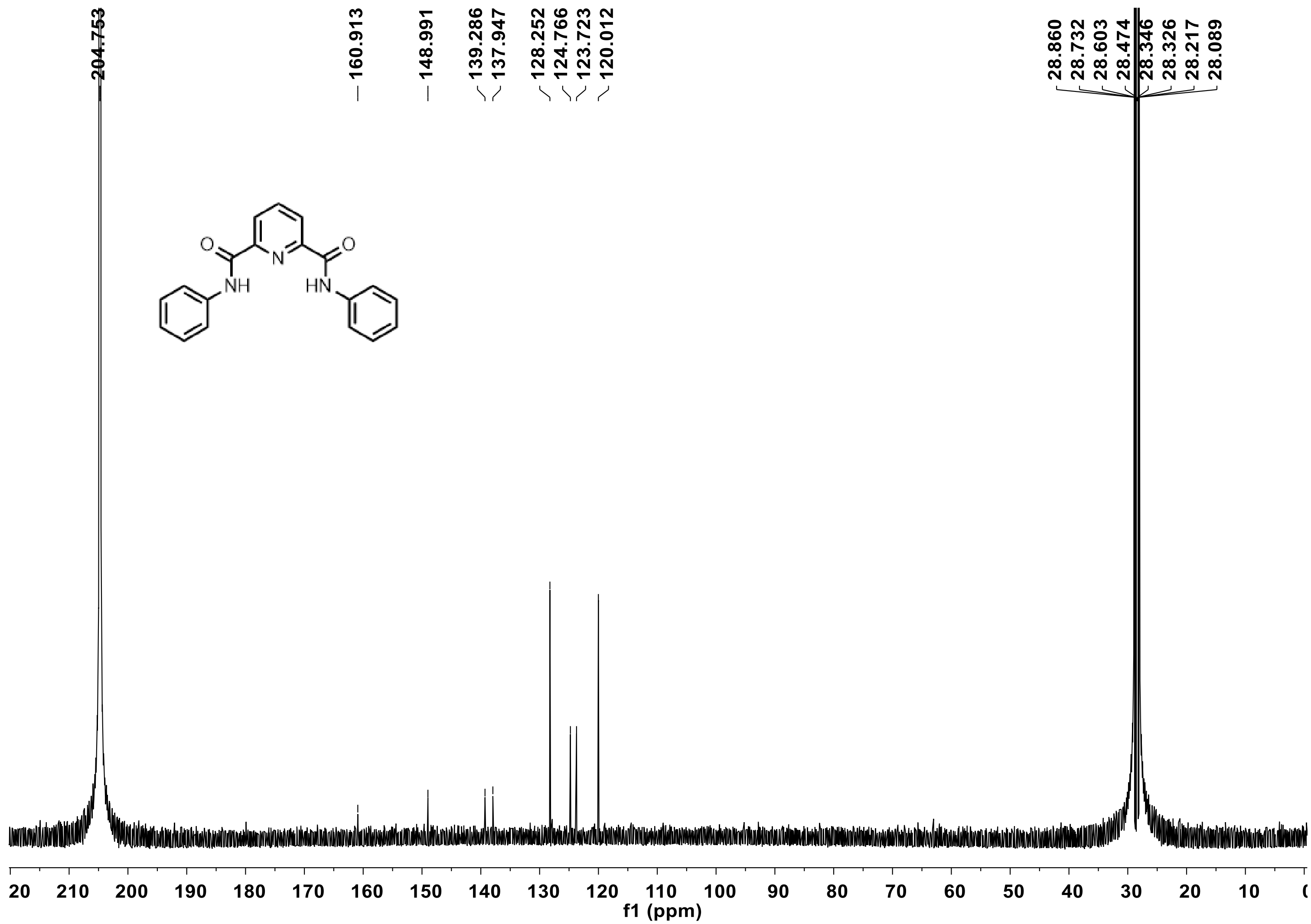
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **TC3**



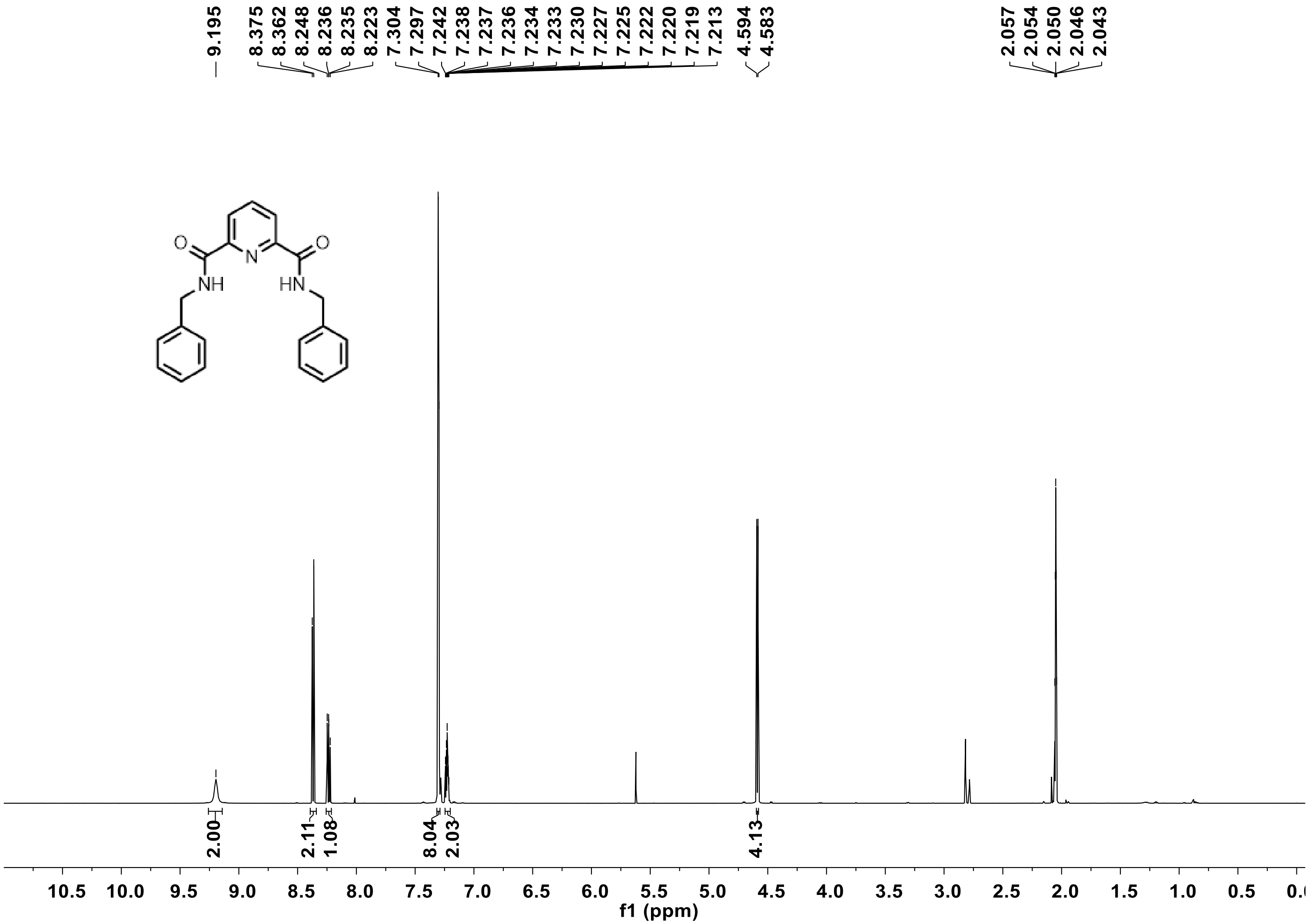
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC4**



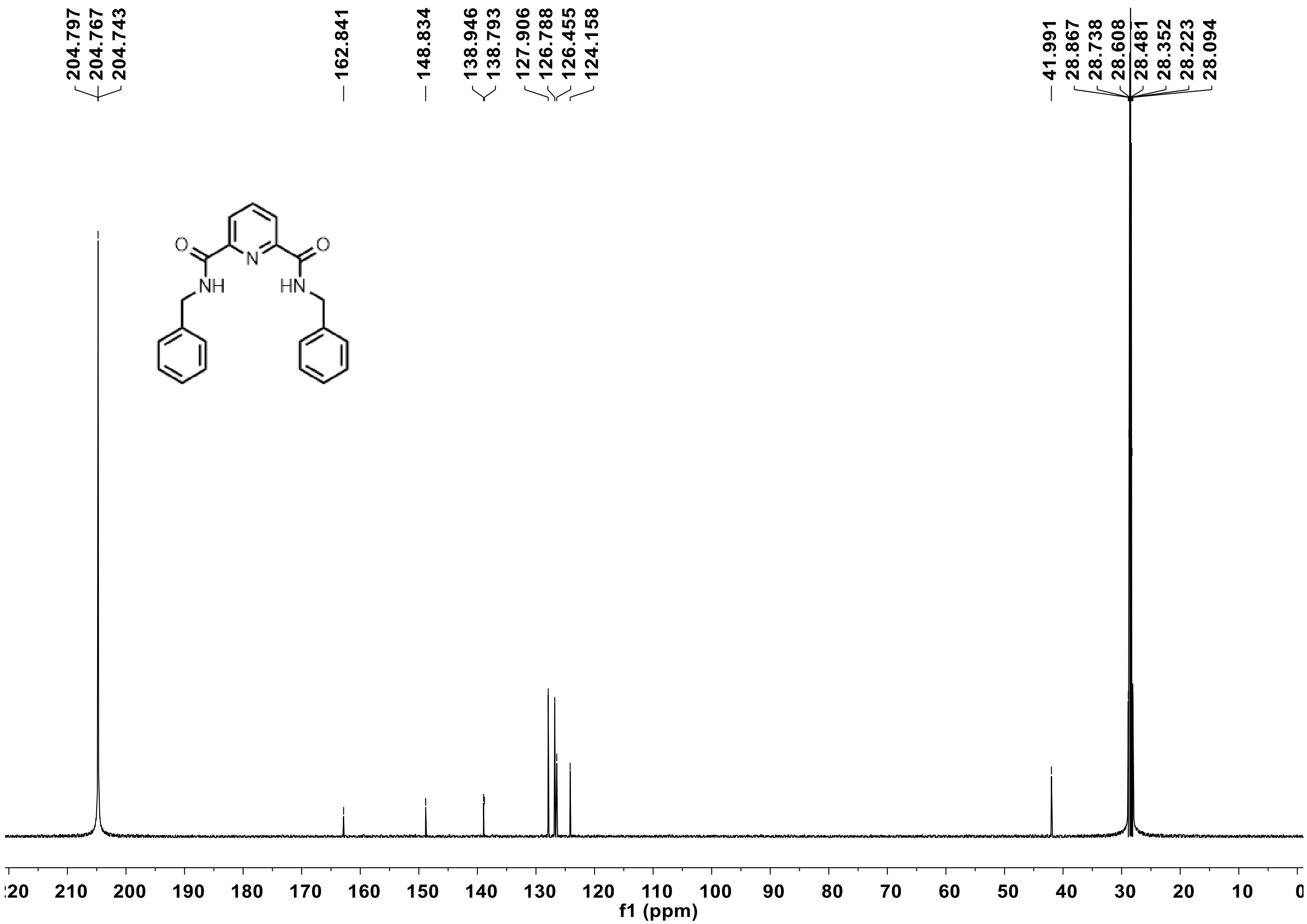
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC4**



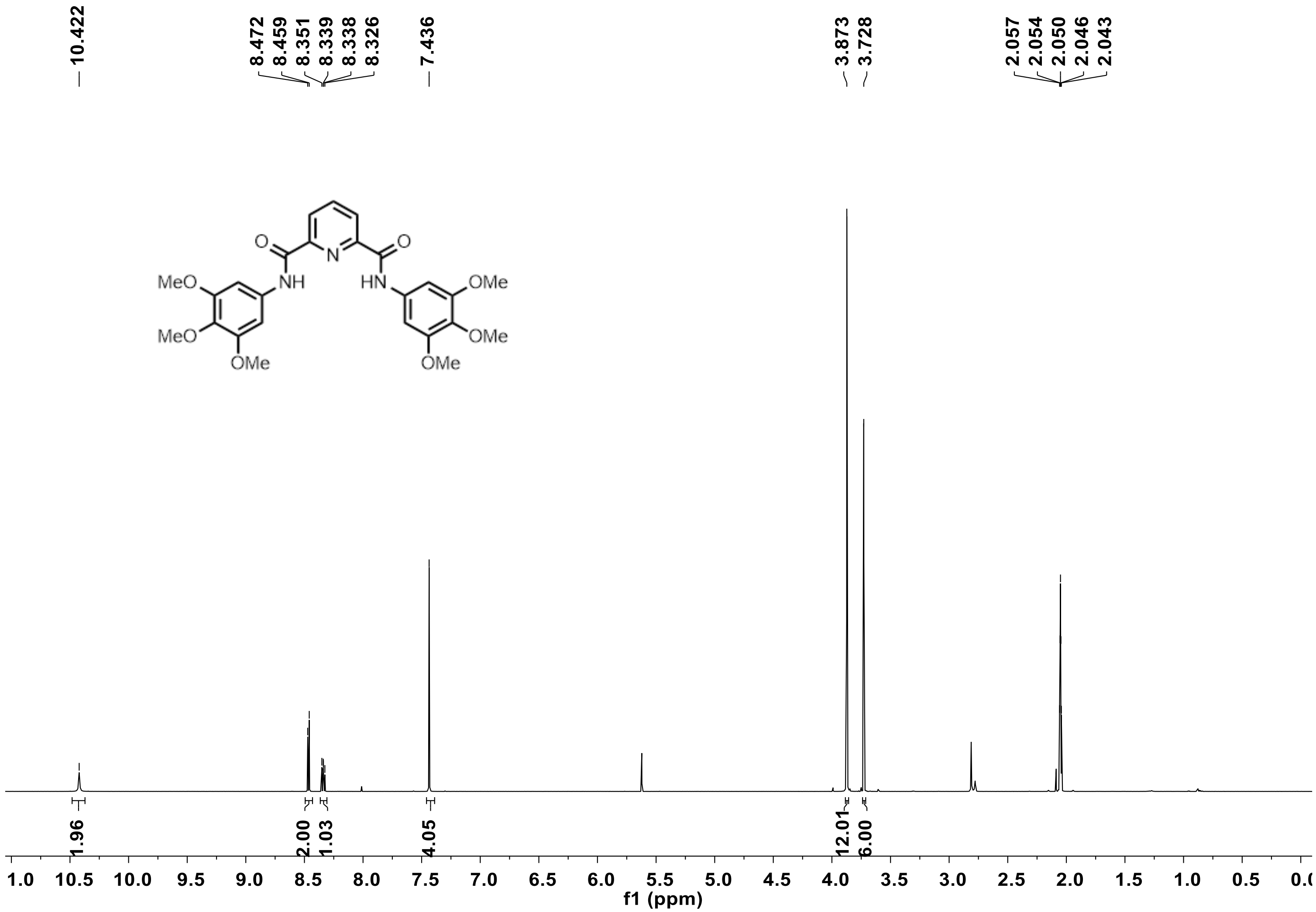
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC5**



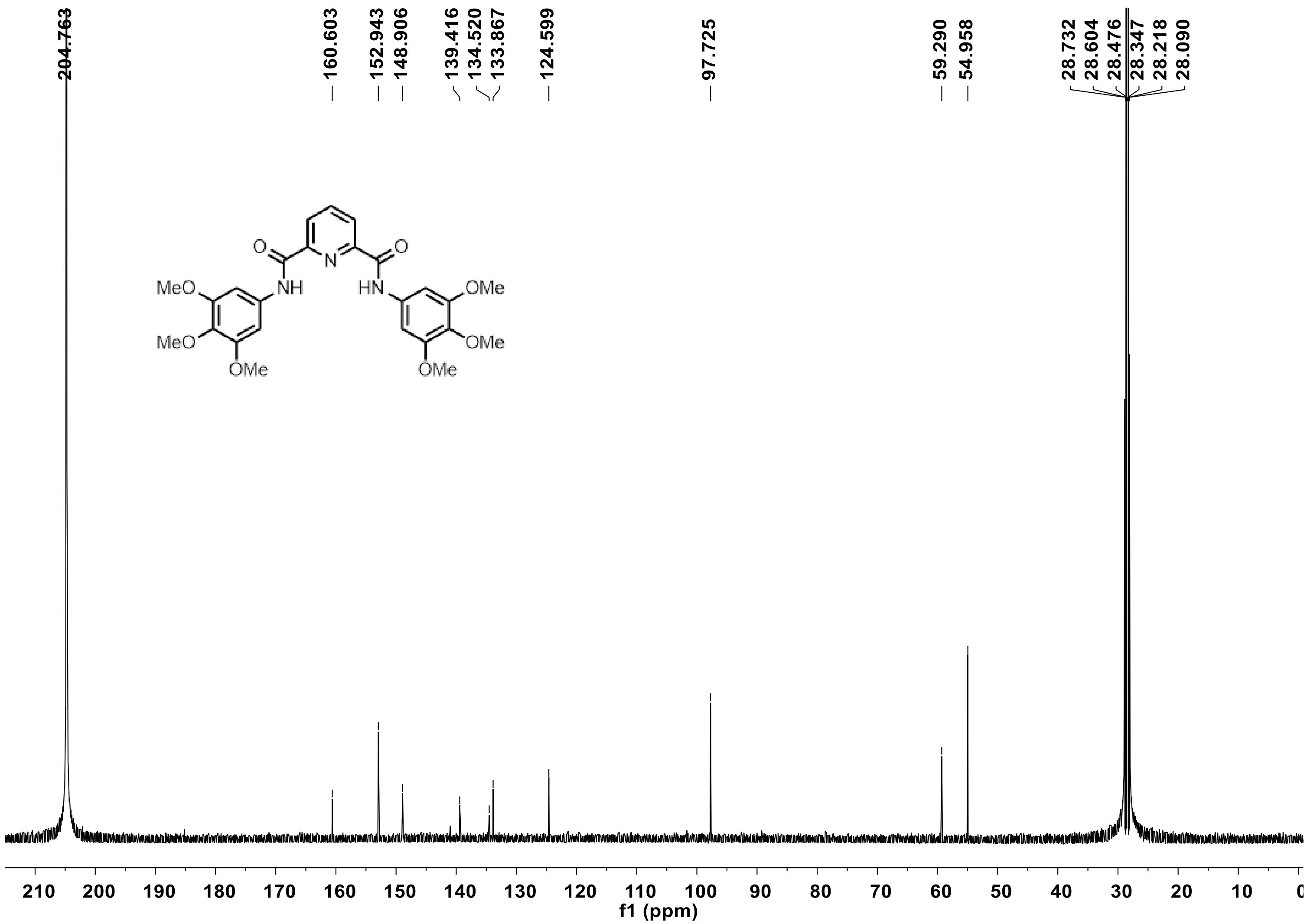
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC5**



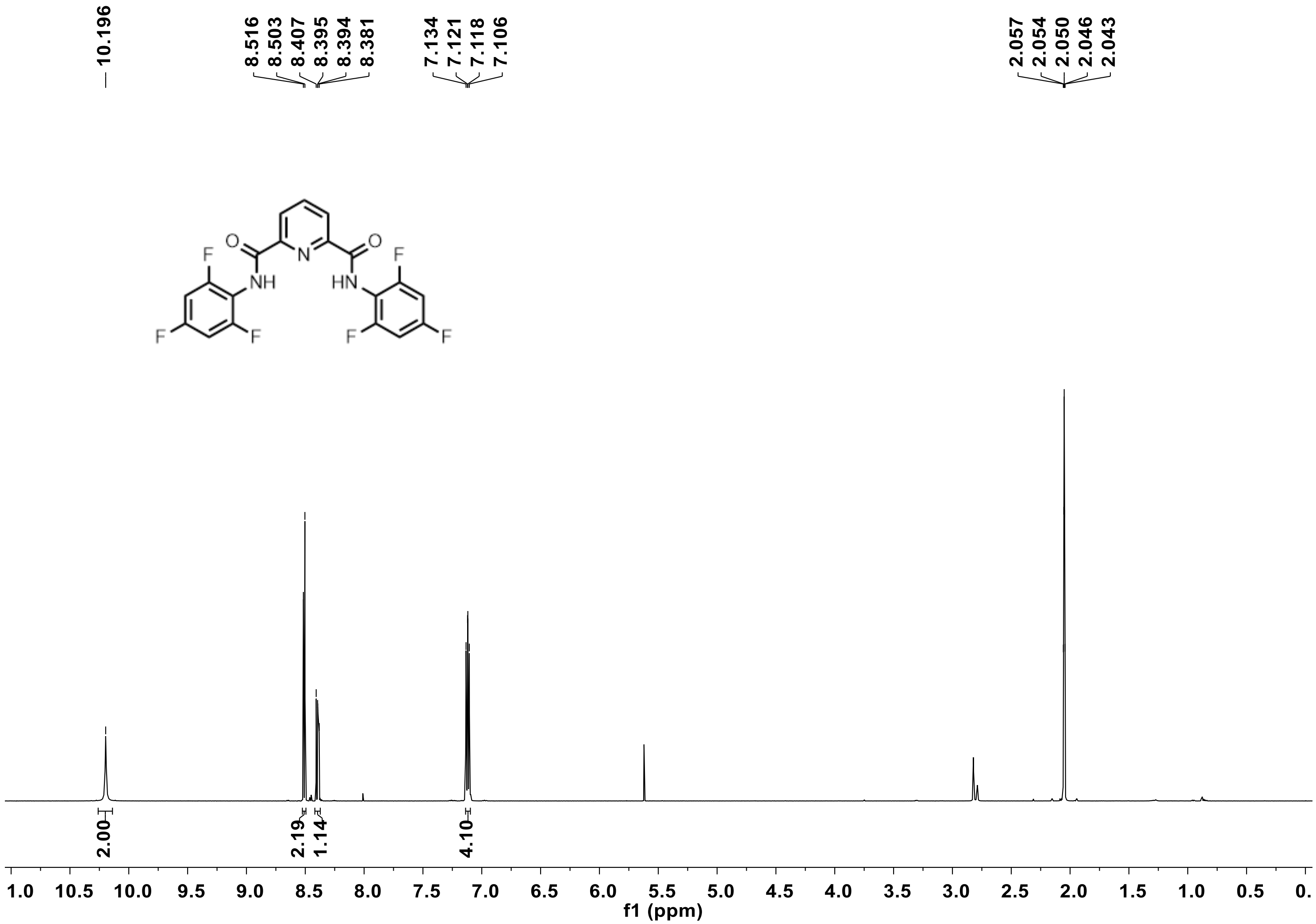
[1]H NMR (600 MHz, Acetone-d_6) spectrum of **TC6**



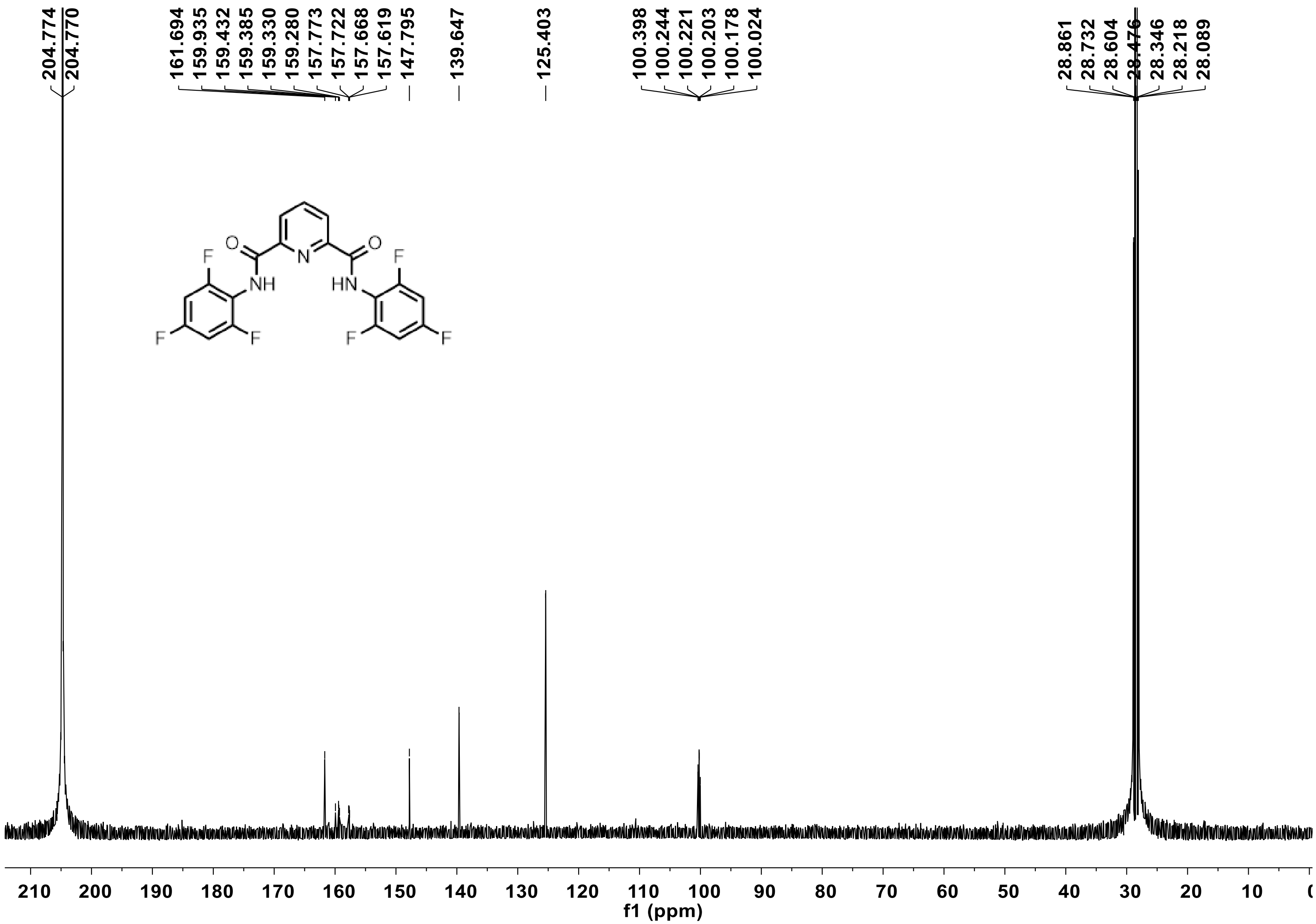
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC6**



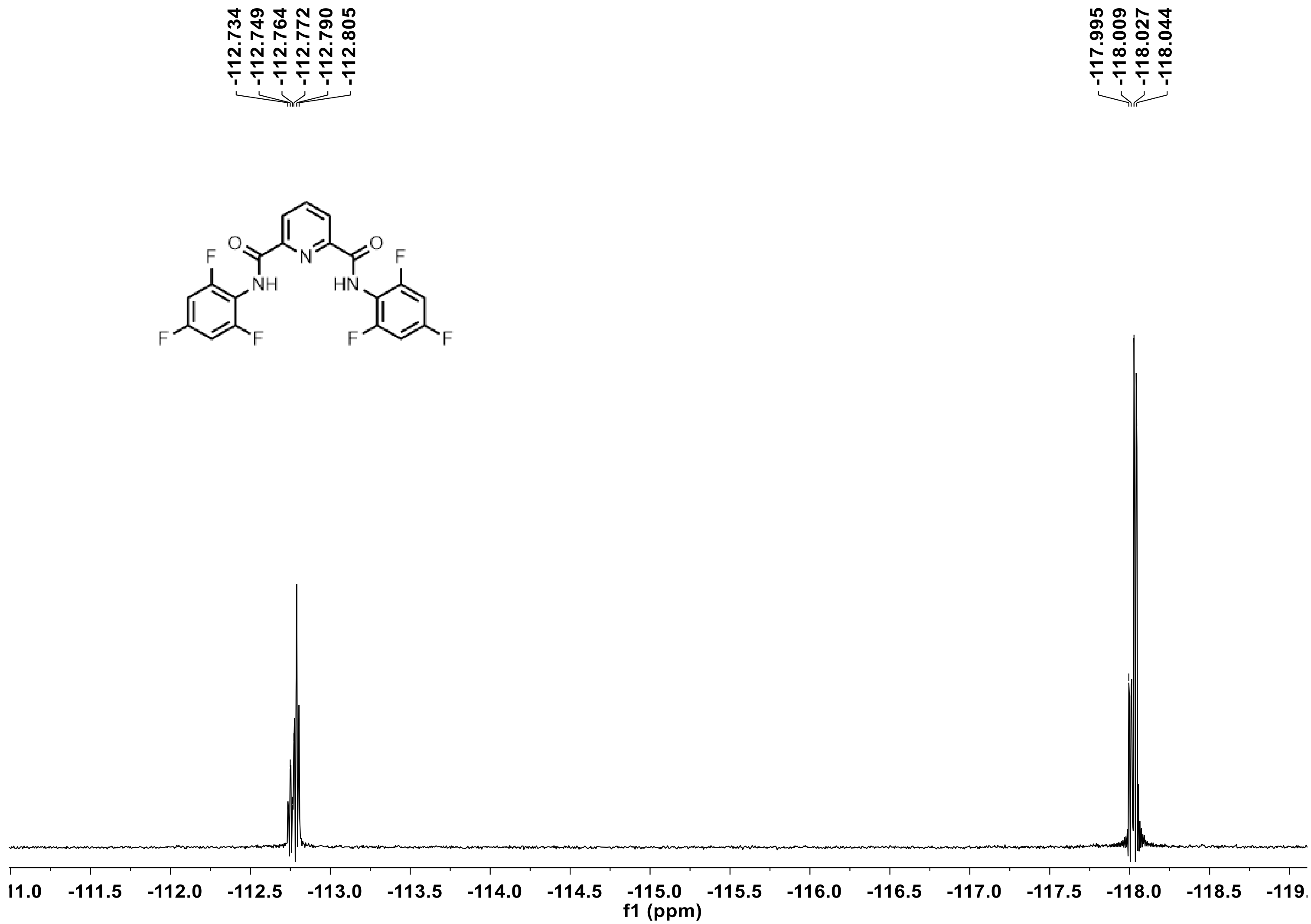
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC7**



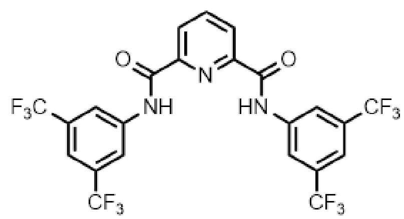
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC7**

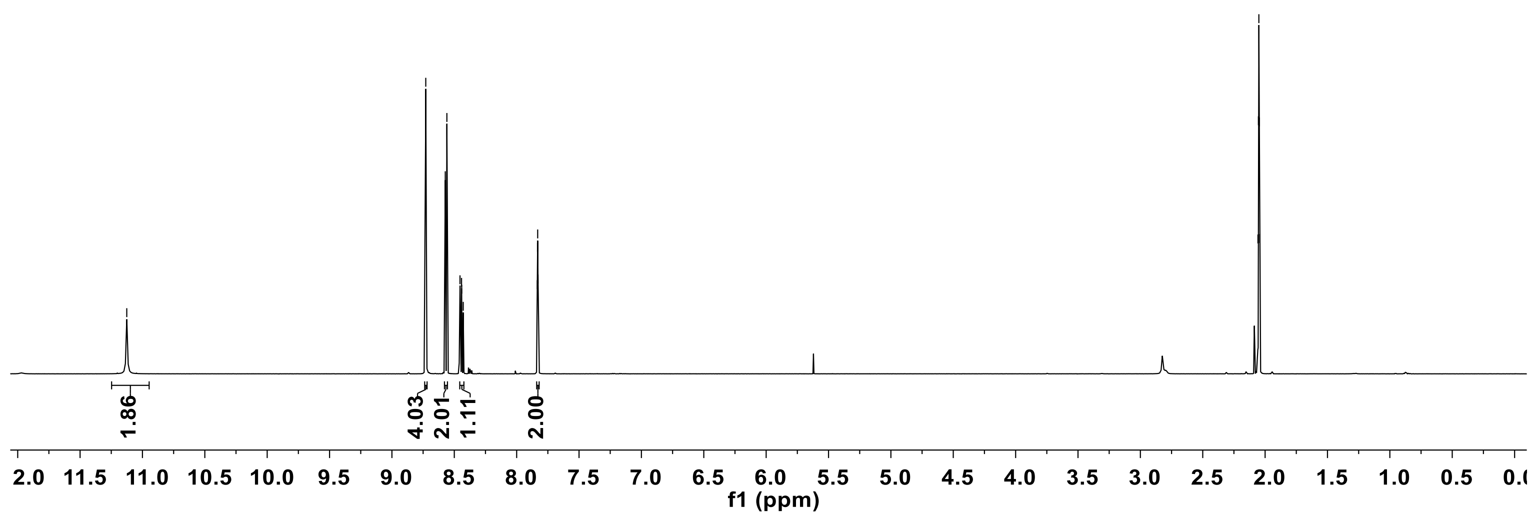


^{19}F NMR (376 MHz, Acetone-d_6) spectrum of **TC7**

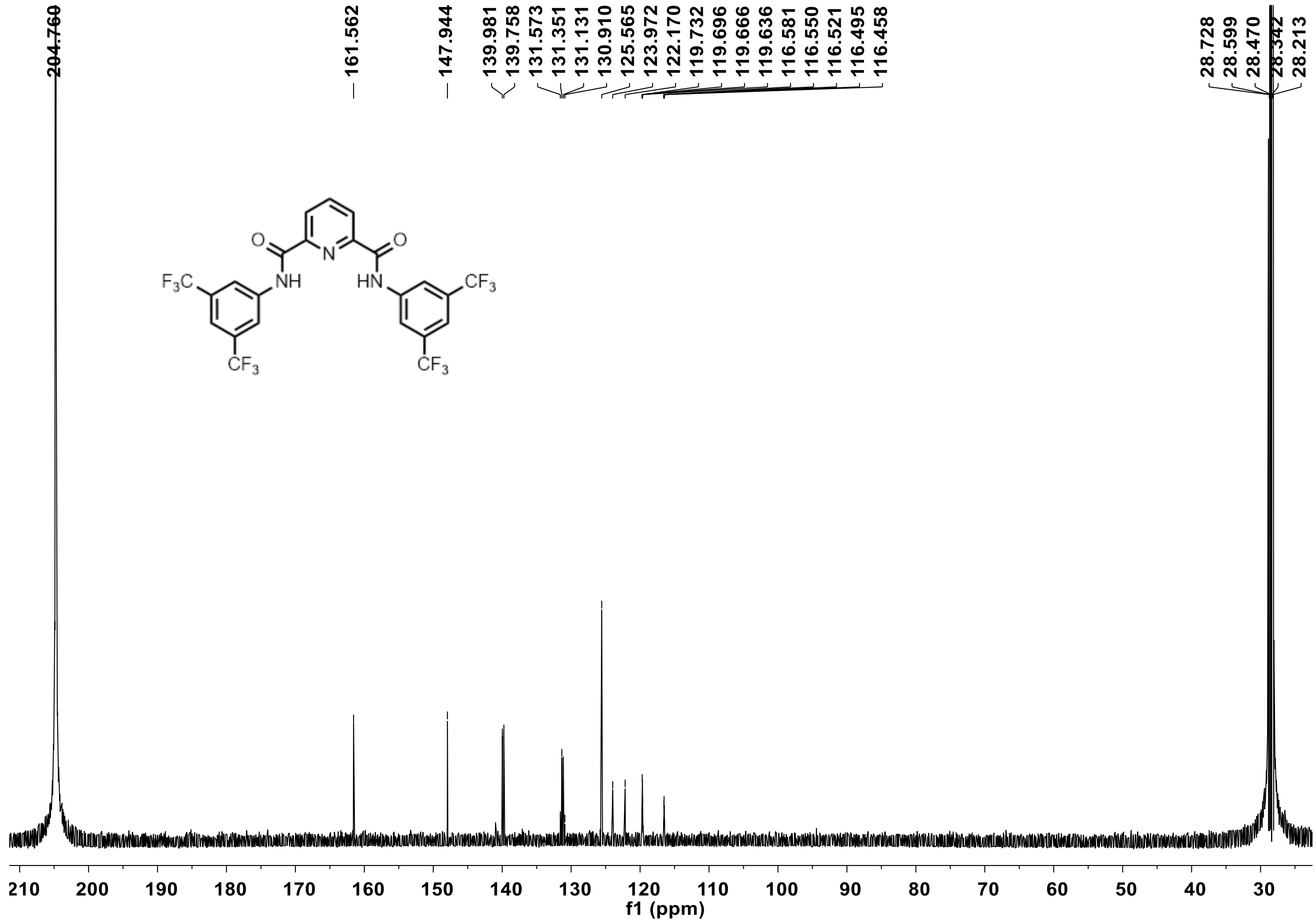


^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC8**

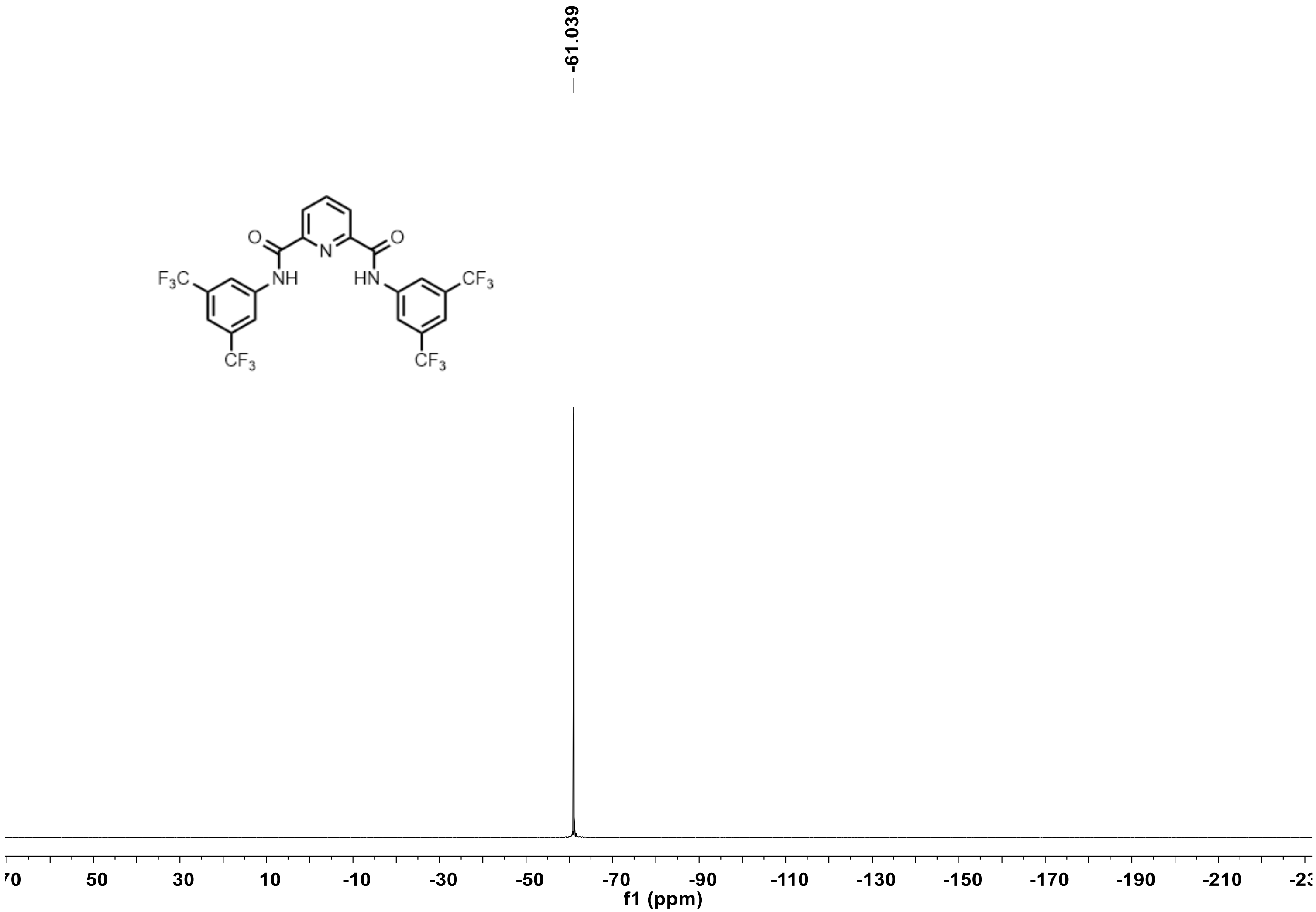




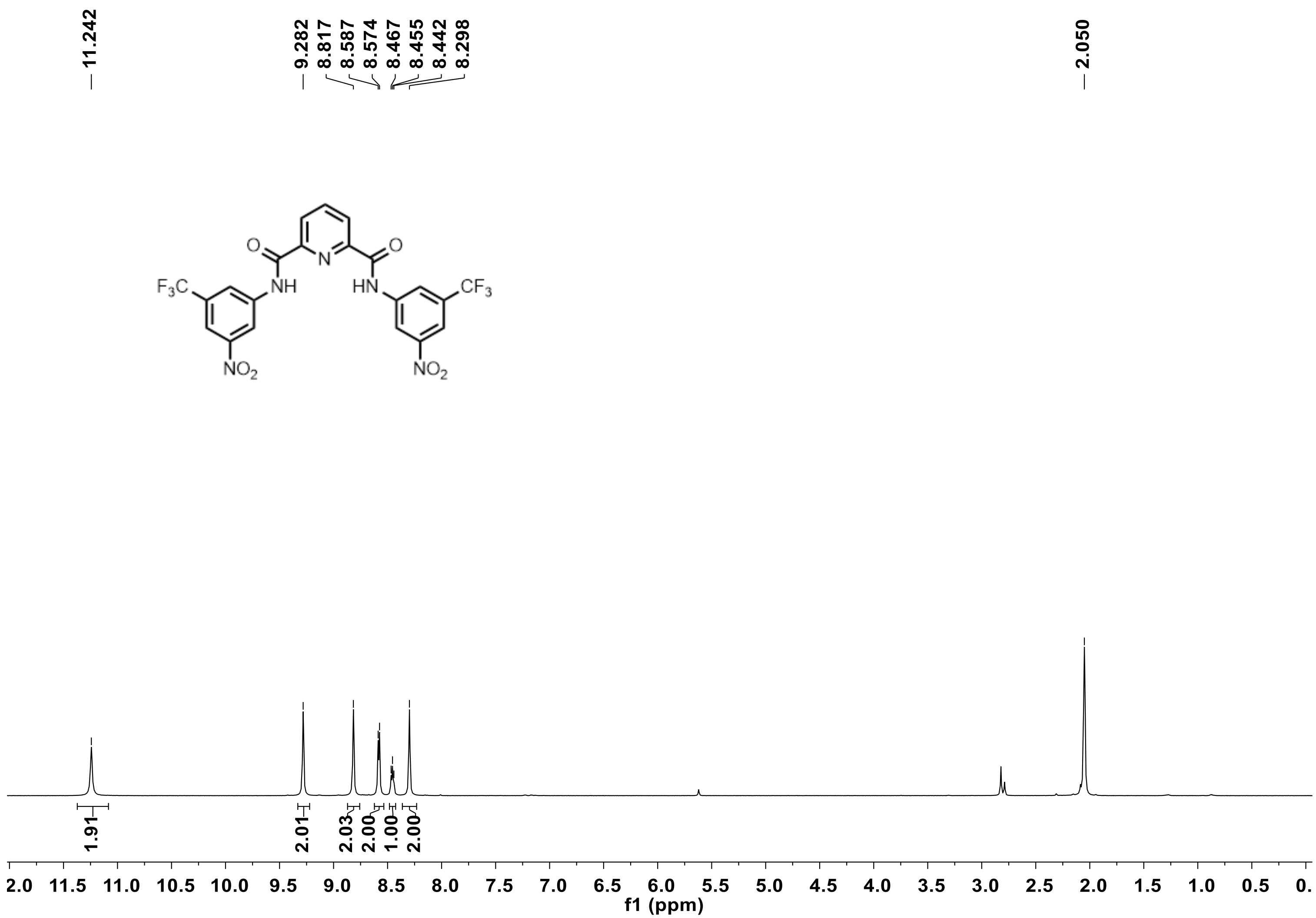
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC8**



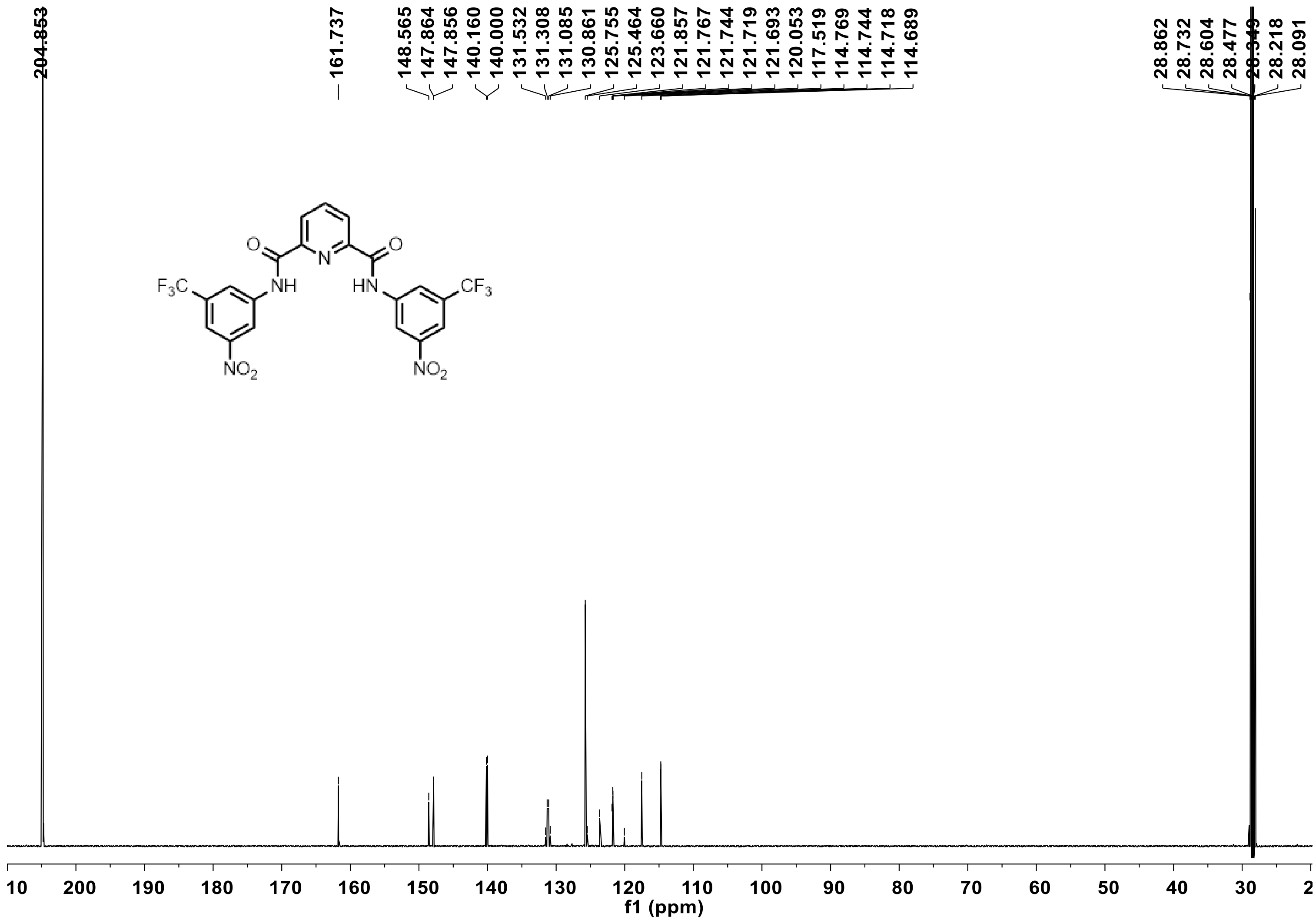
^{19}F NMR (376 MHz, Acetone-d_6) spectrum of **TC8**



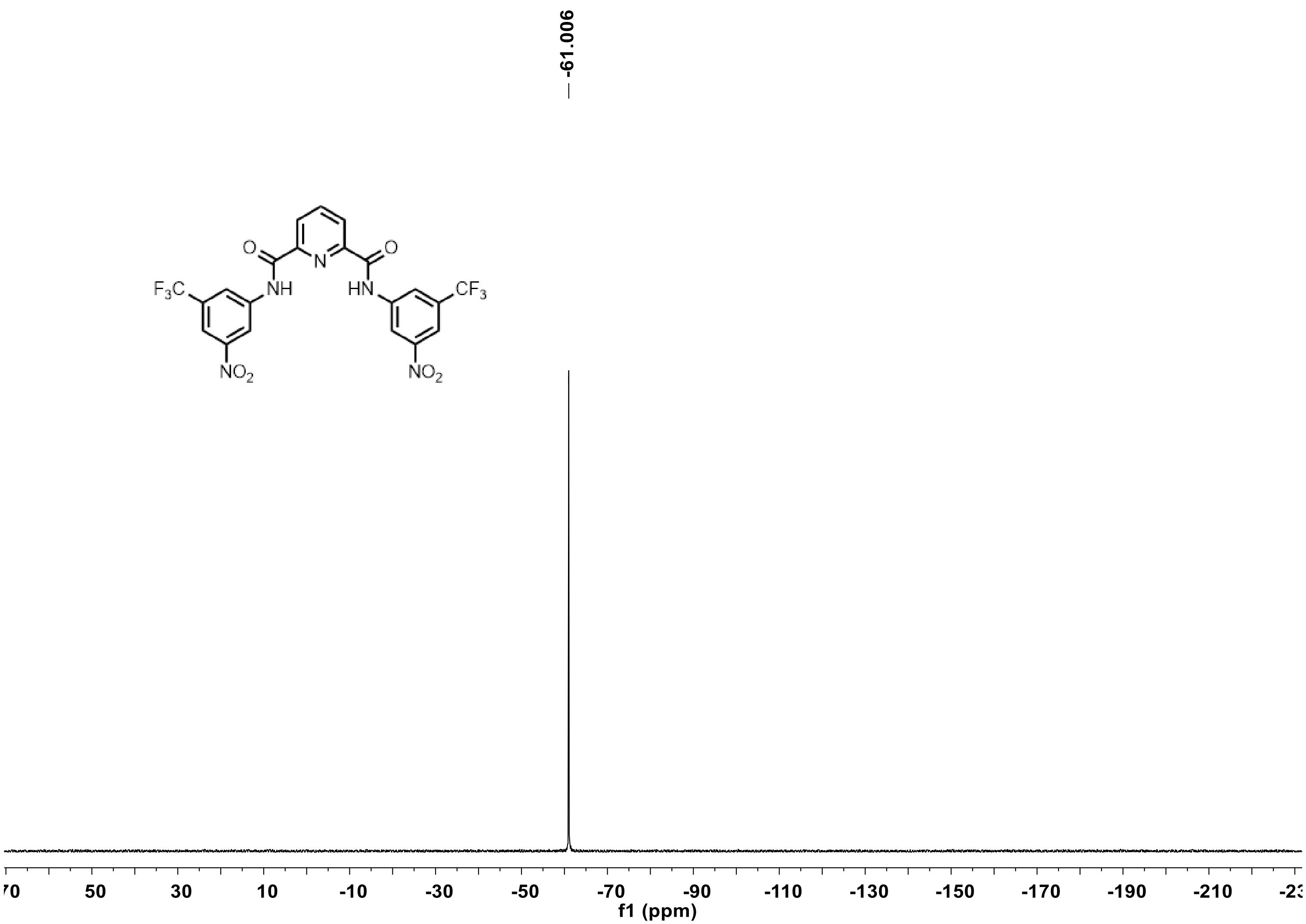
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC9**



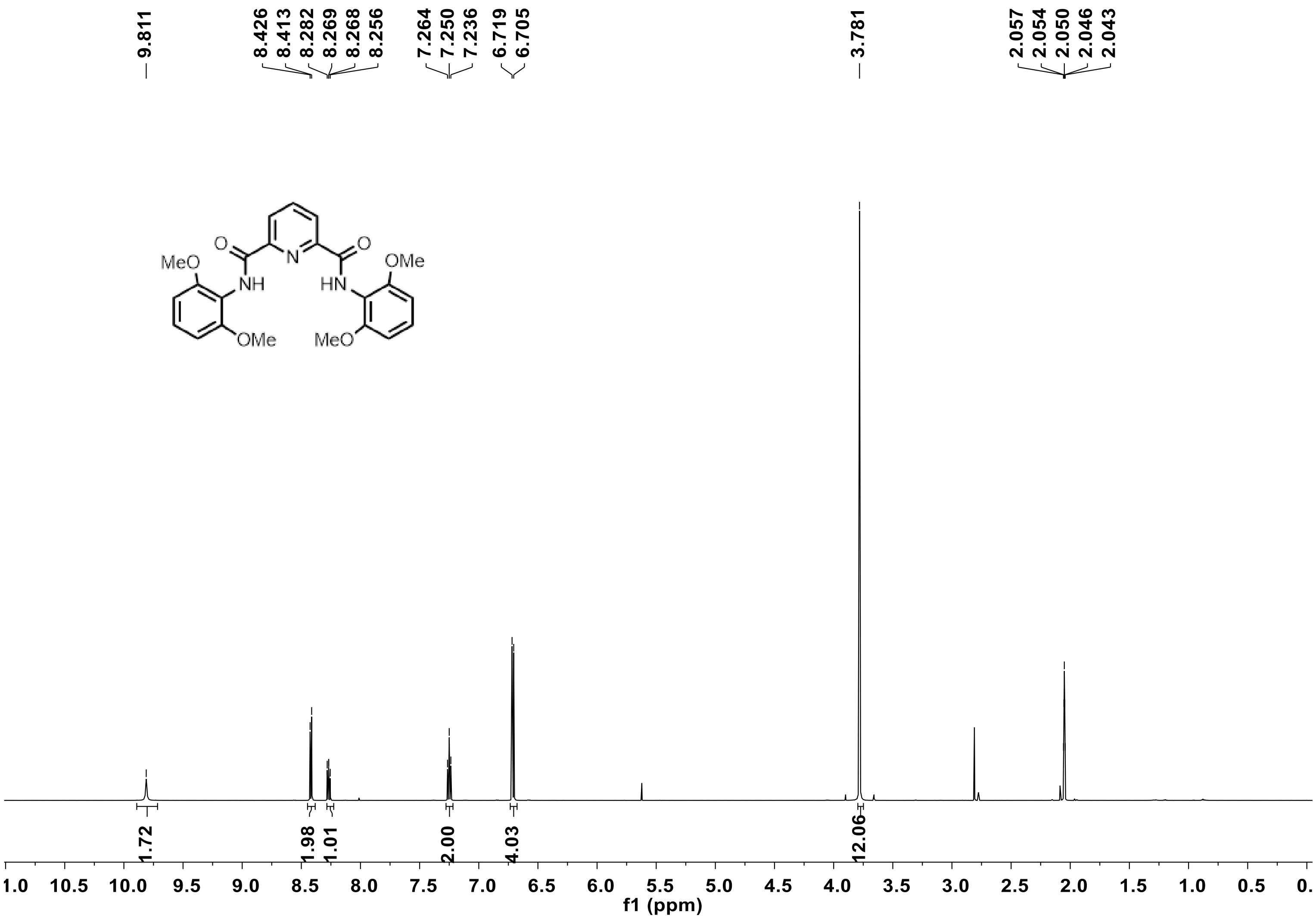
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC9**



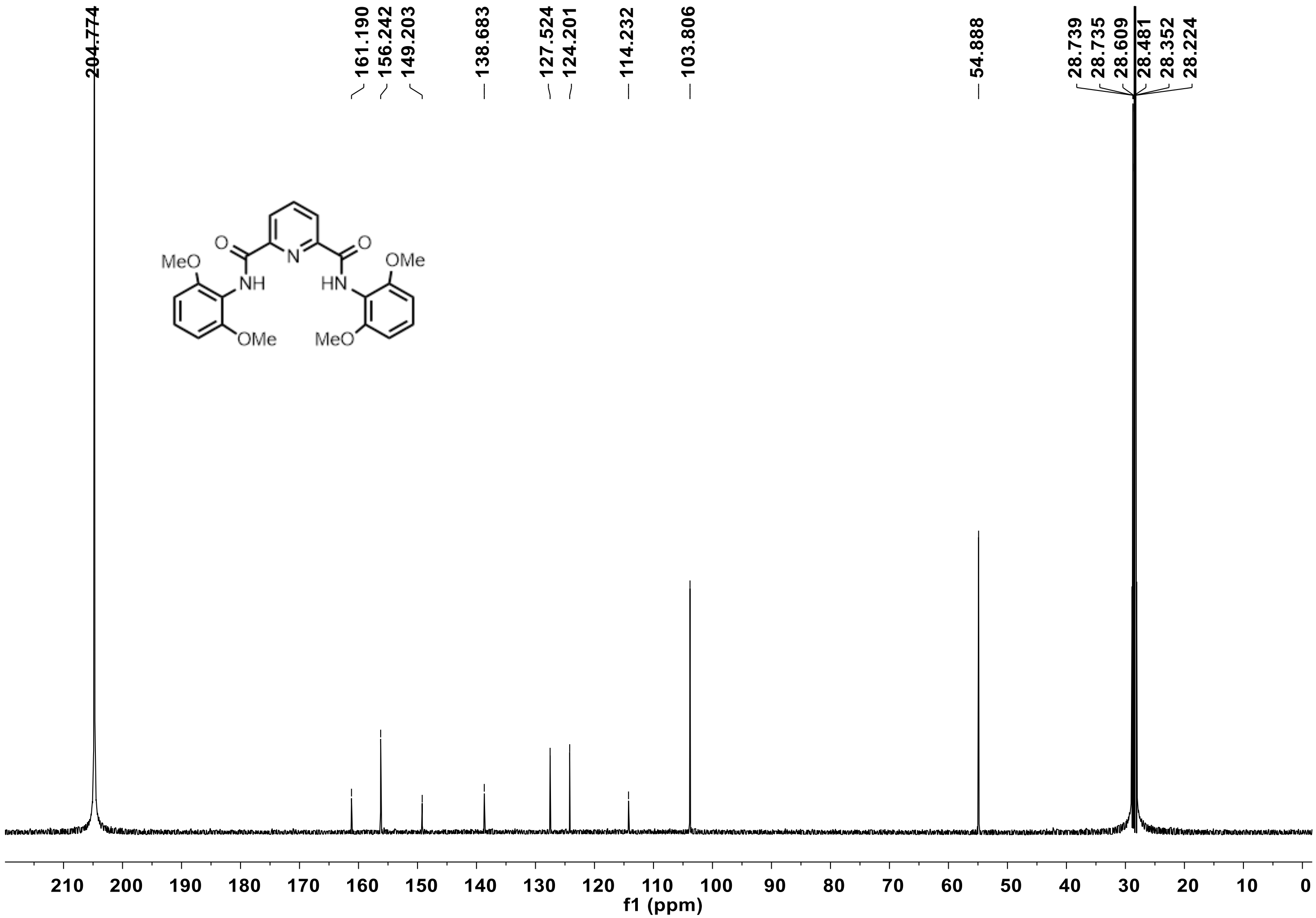
^{19}F NMR (376 MHz, Acetone-d_6) spectrum of **TC9**



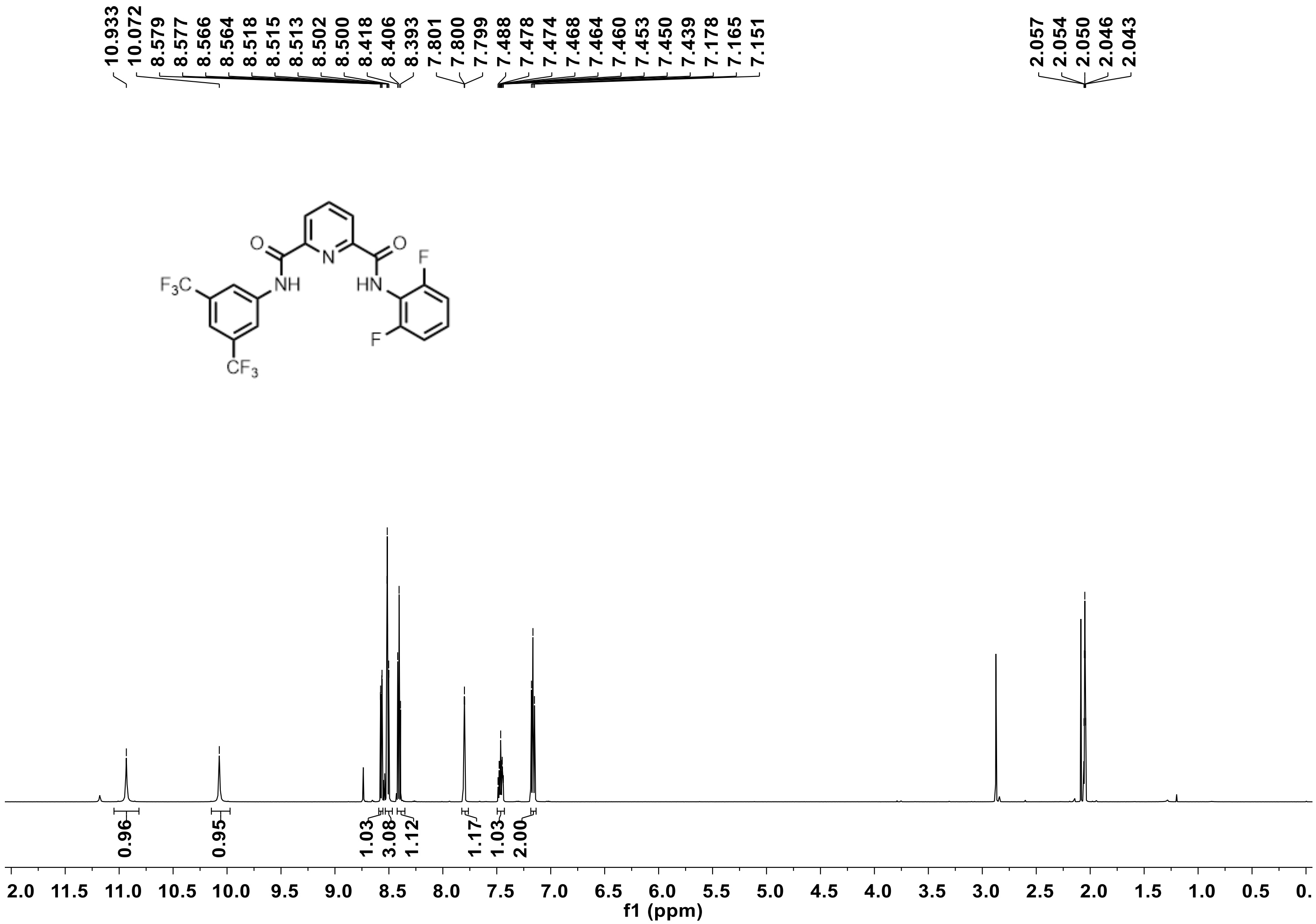
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC10**



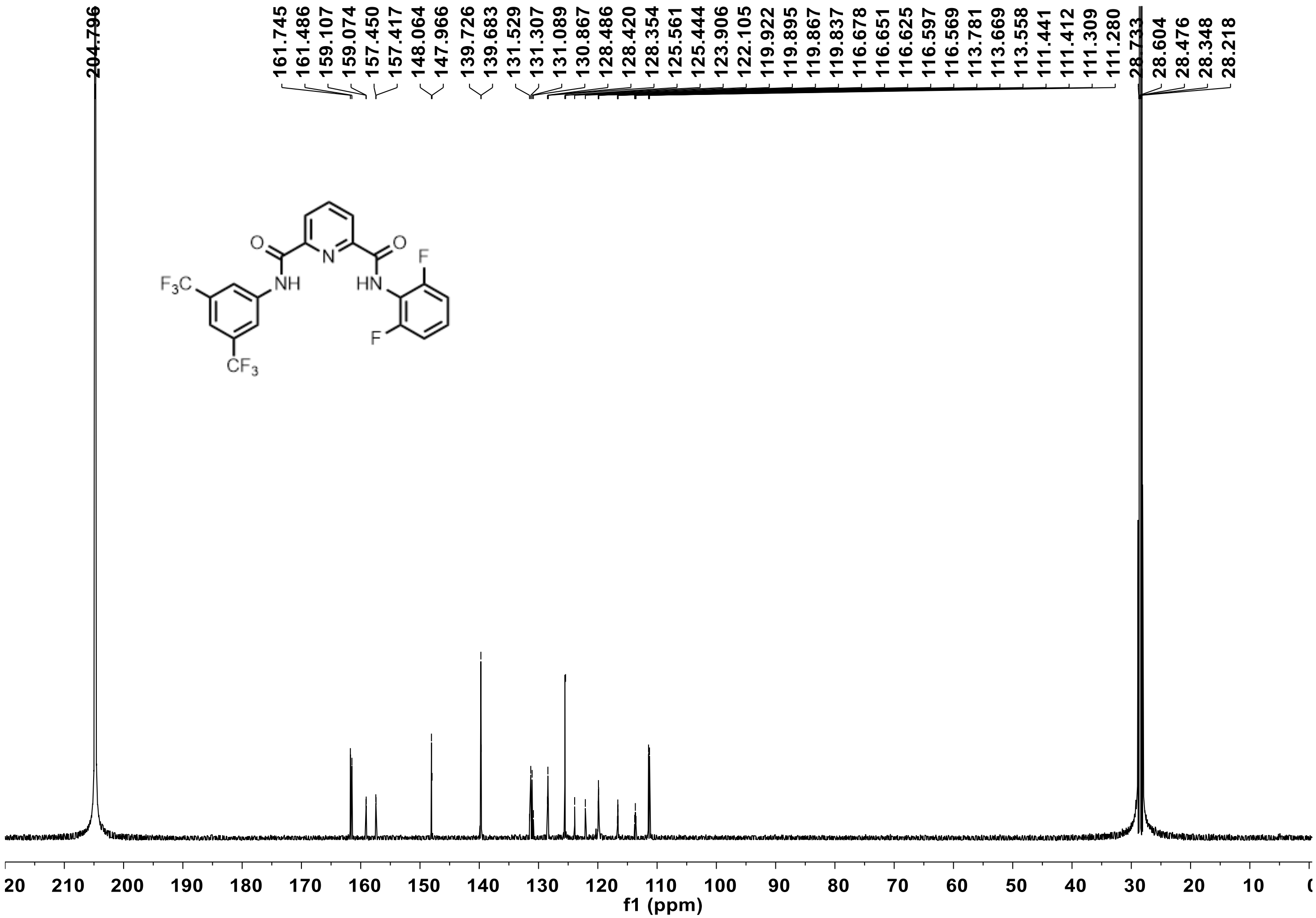
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC10**



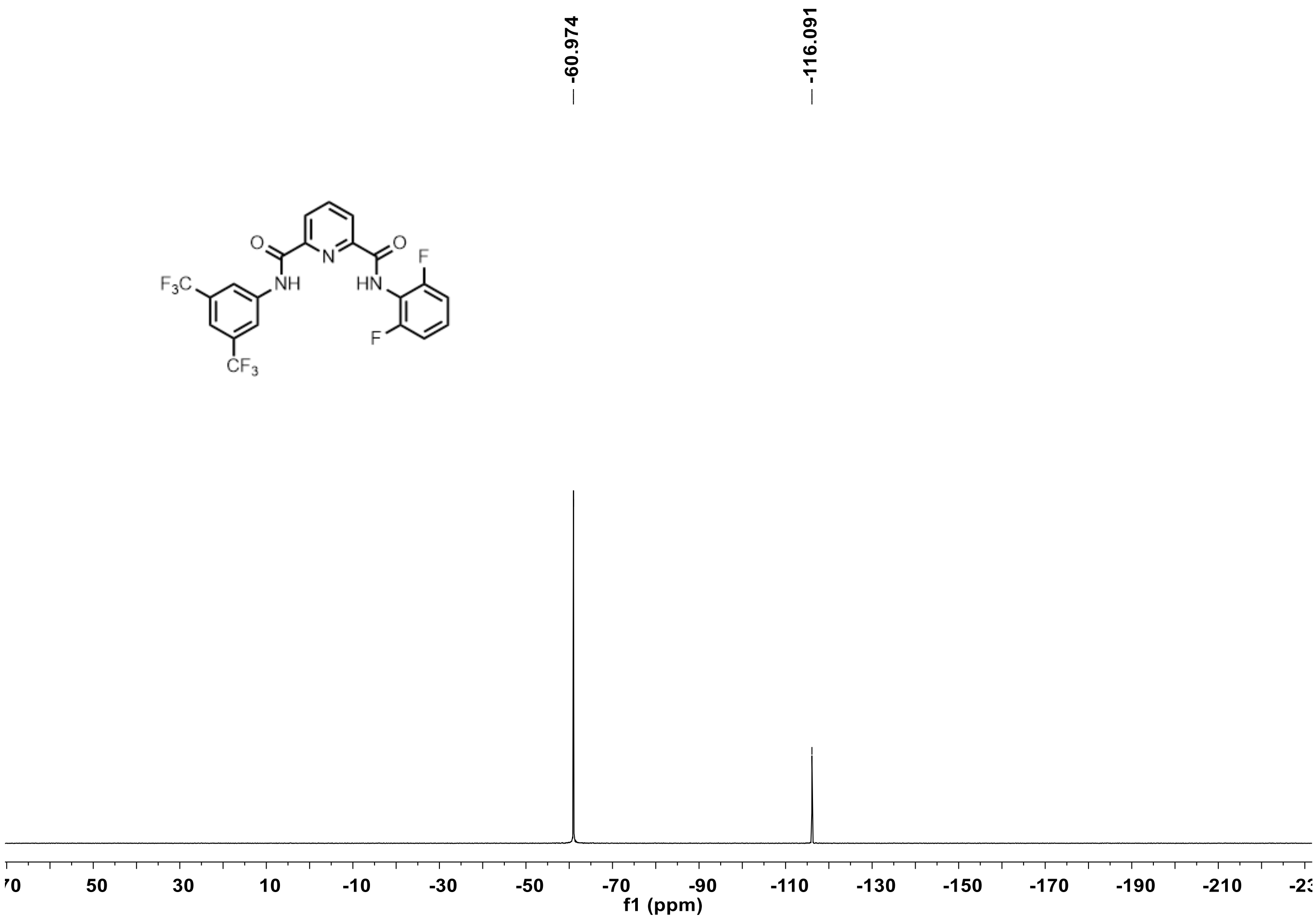
^{1}H NMR (600 MHz, Acetone-d_6) spectrum of **TC11**



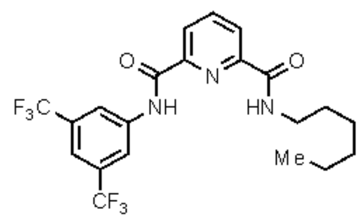
^{13}C NMR (151 MHz, Acetone-d_6) spectrum of **TC11**

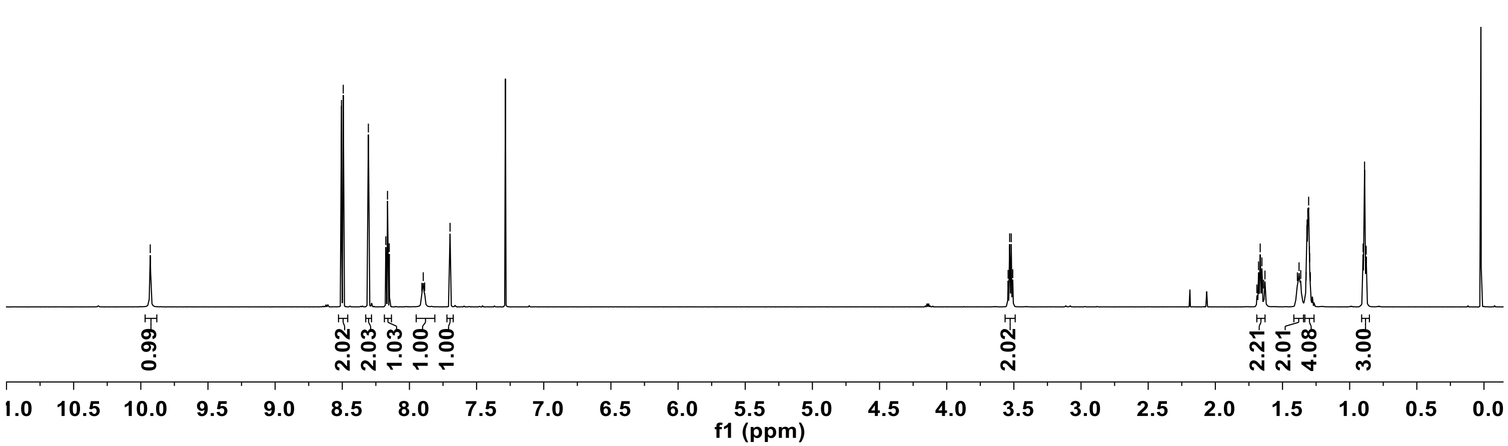


^{19}F NMR (376 MHz, Acetone-d_6) spectrum of **TC11**

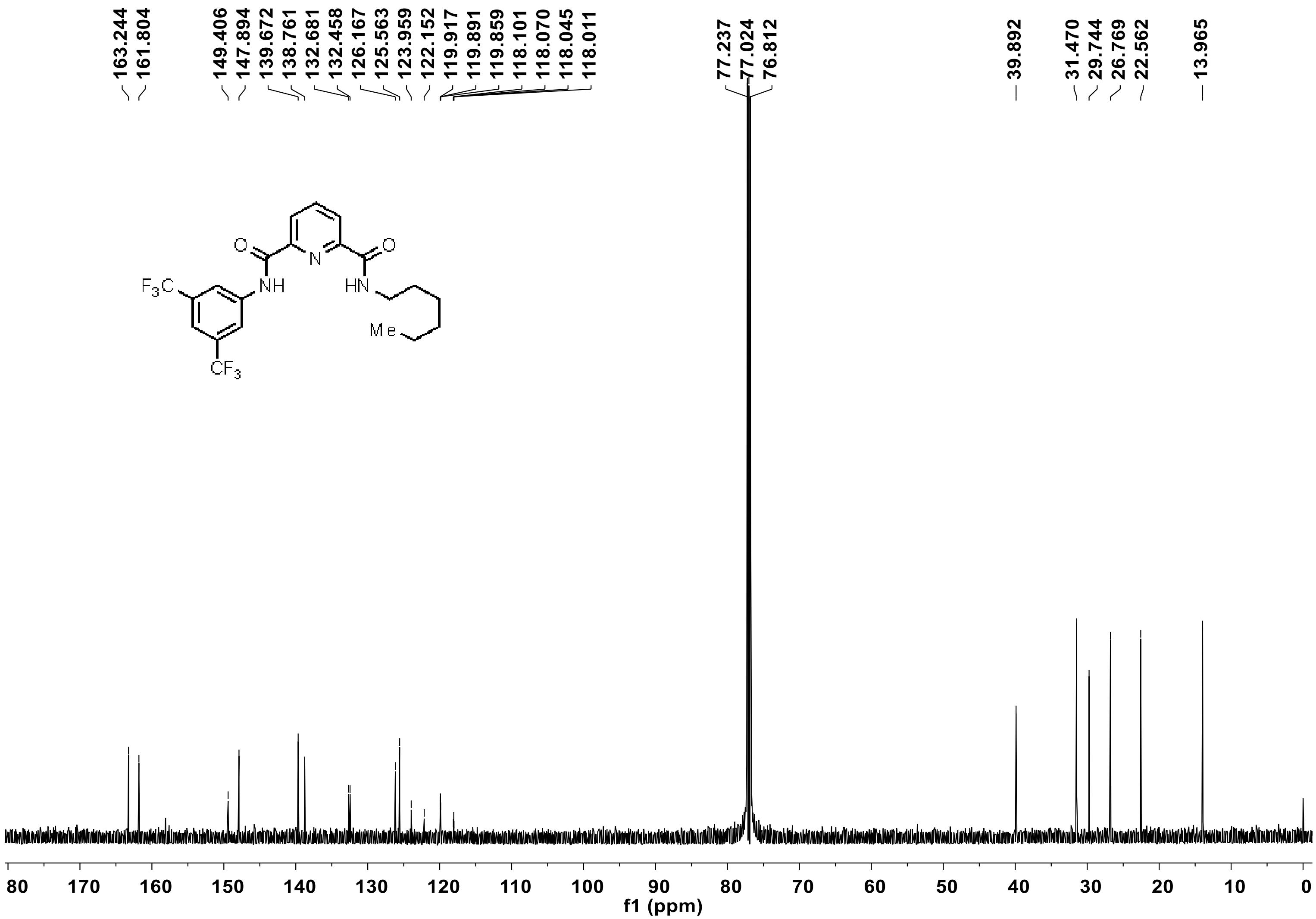


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **TC12**

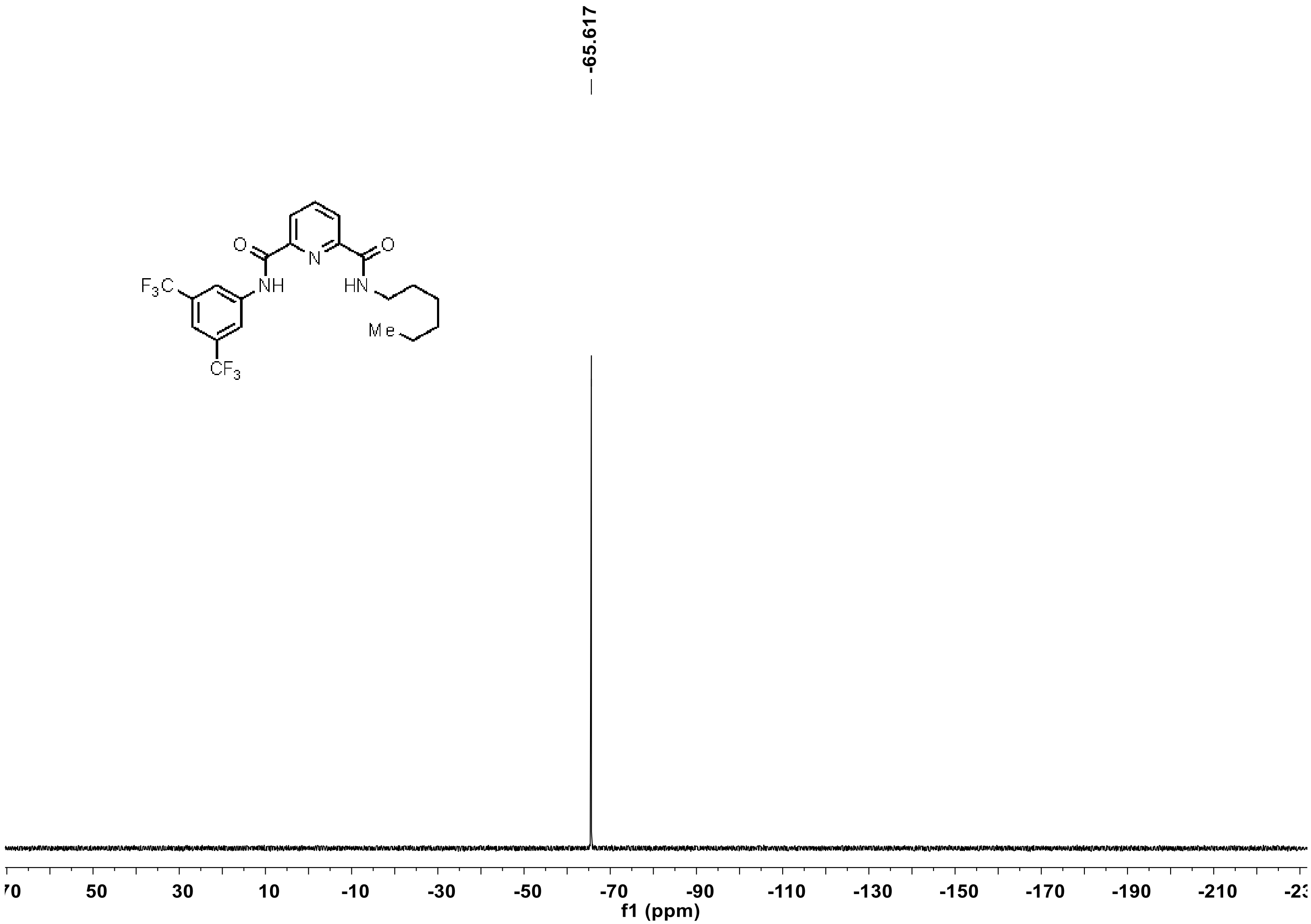




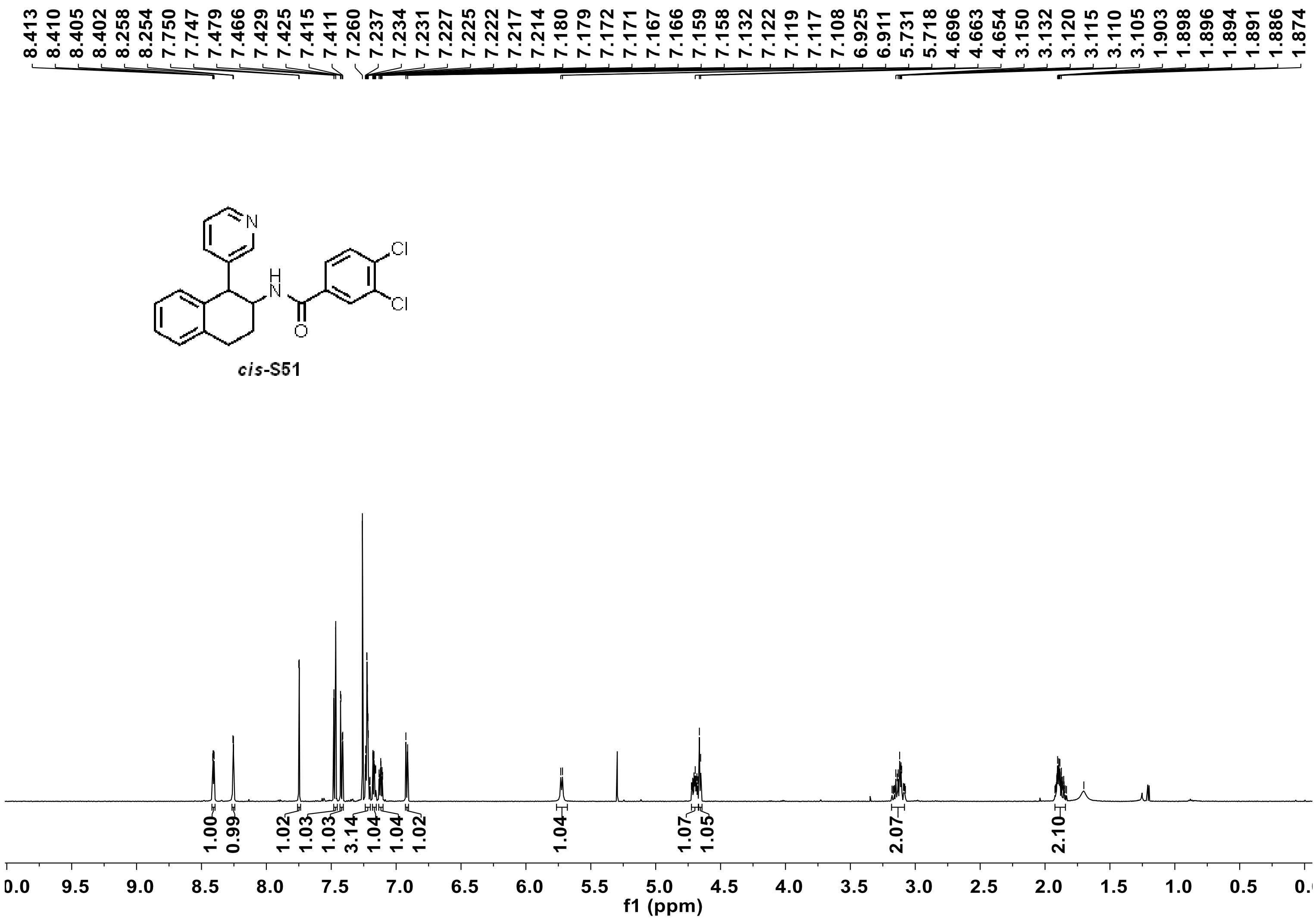
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **TC12**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **TC12**

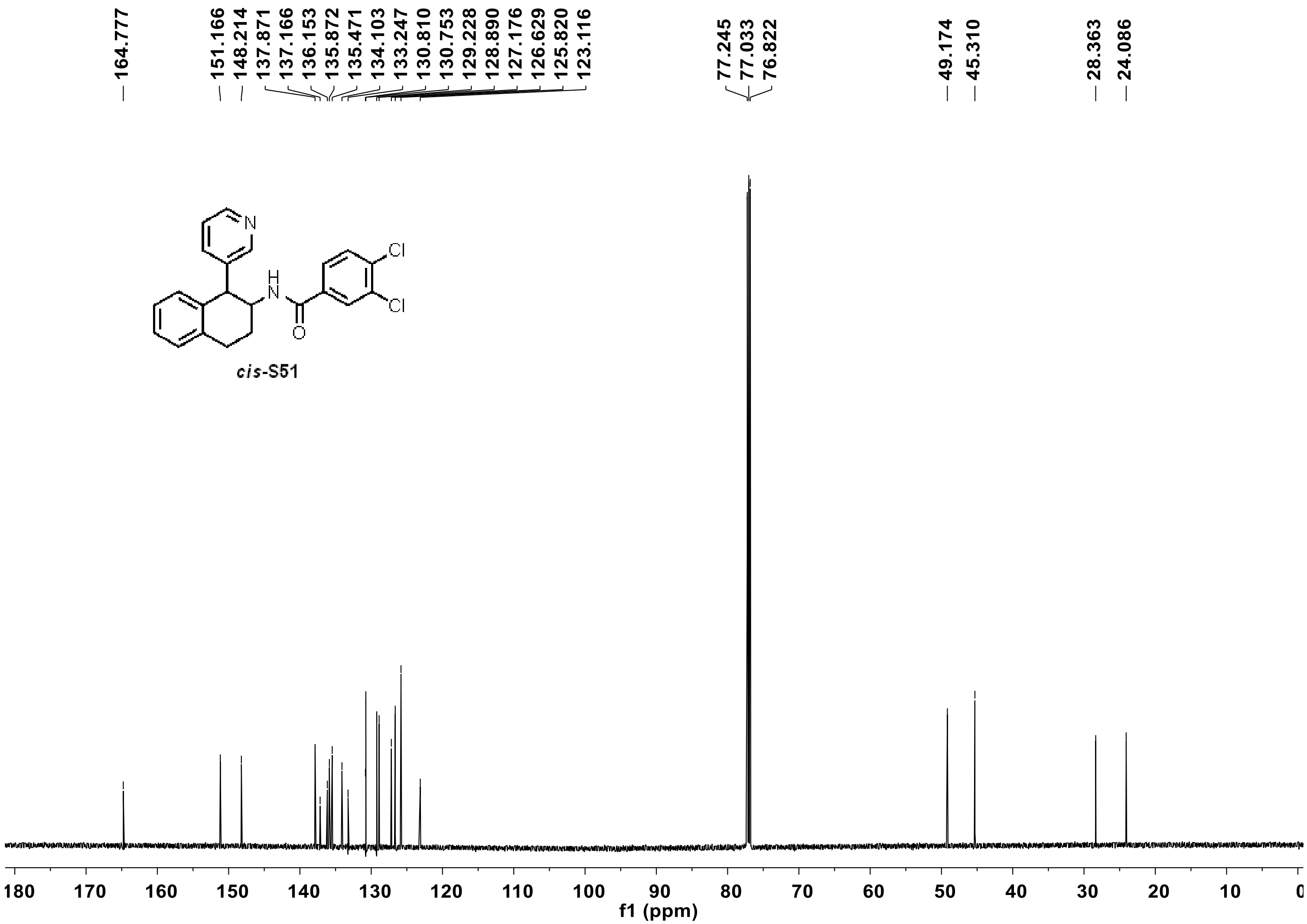


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***cis*-S51**

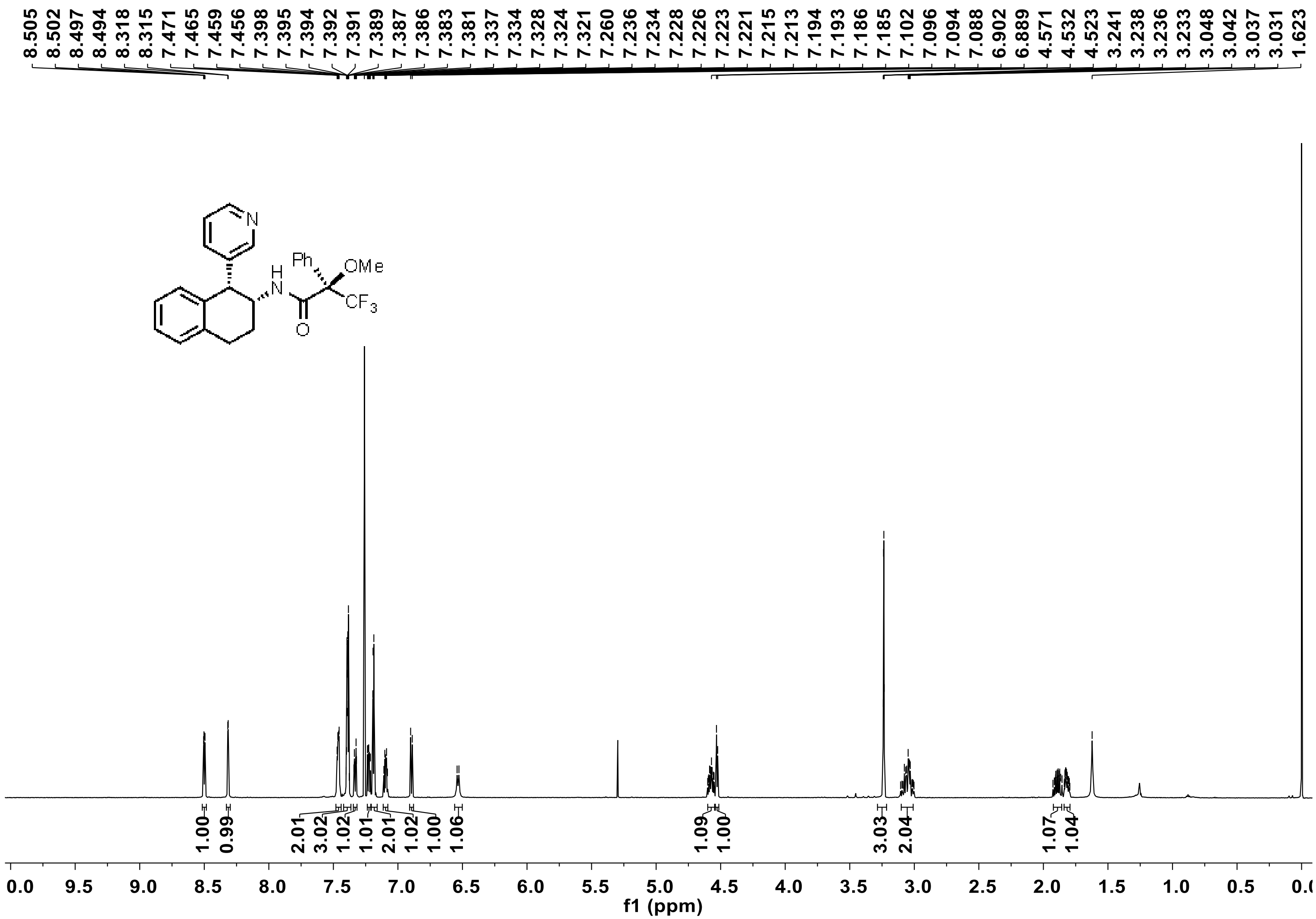


cis-S51

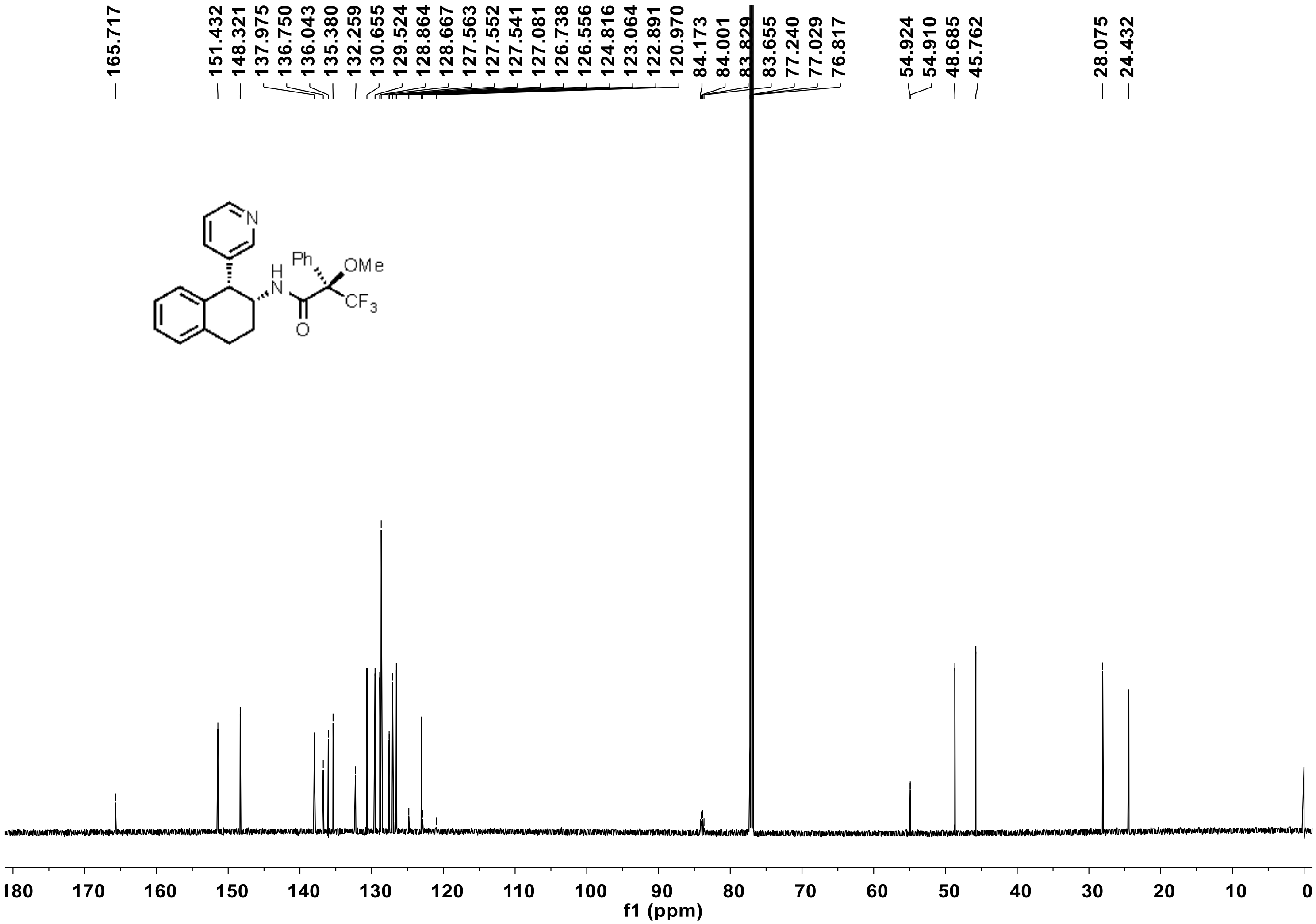
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***cis*-S51**



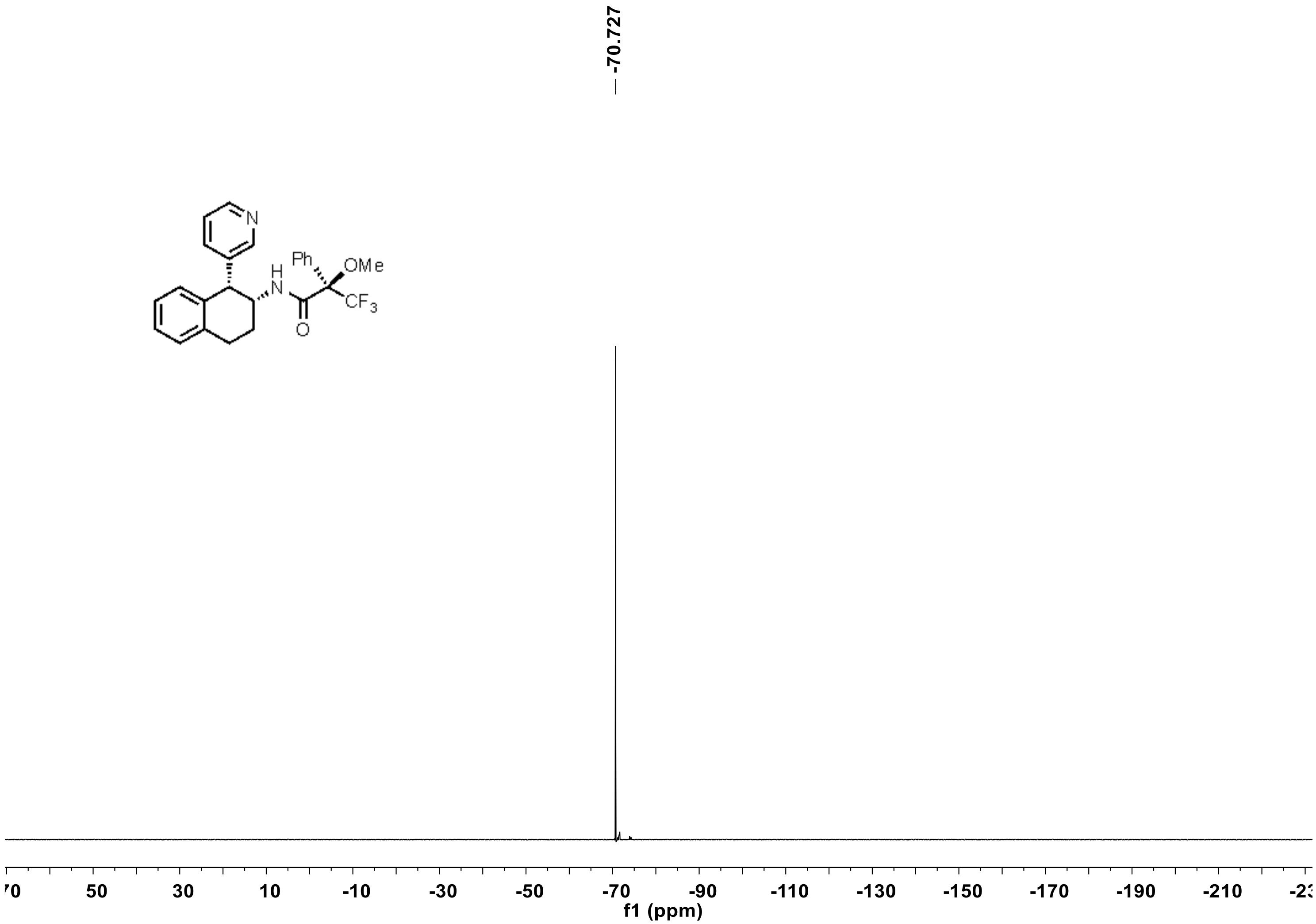
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **(*R*,*R*)-S39-(*R*)-MTPA**



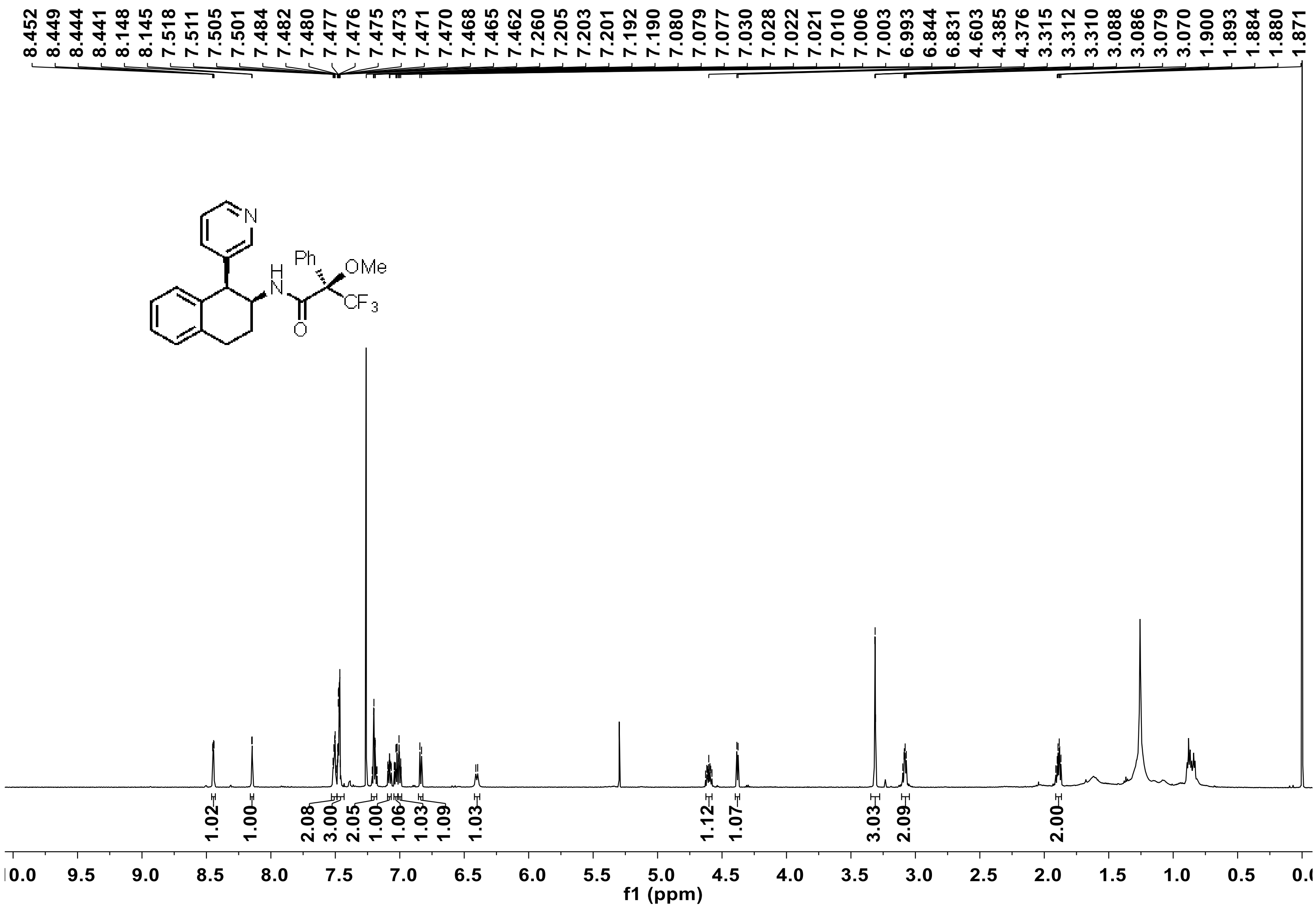
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ***(R,R)*-S39-(*R*)-MTPA**



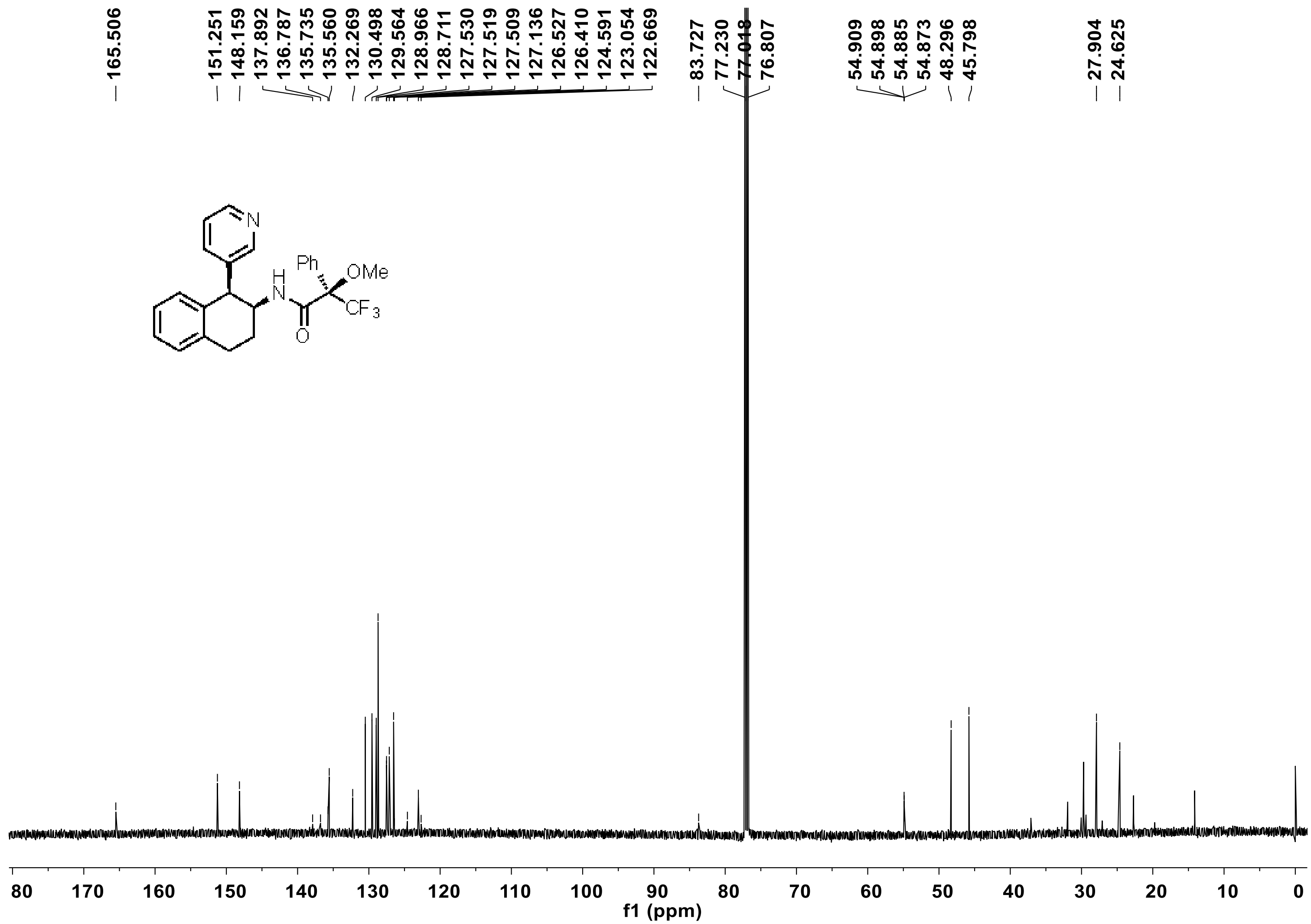
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **(*R*,*R*)-S39-(*R*)-MTPA**



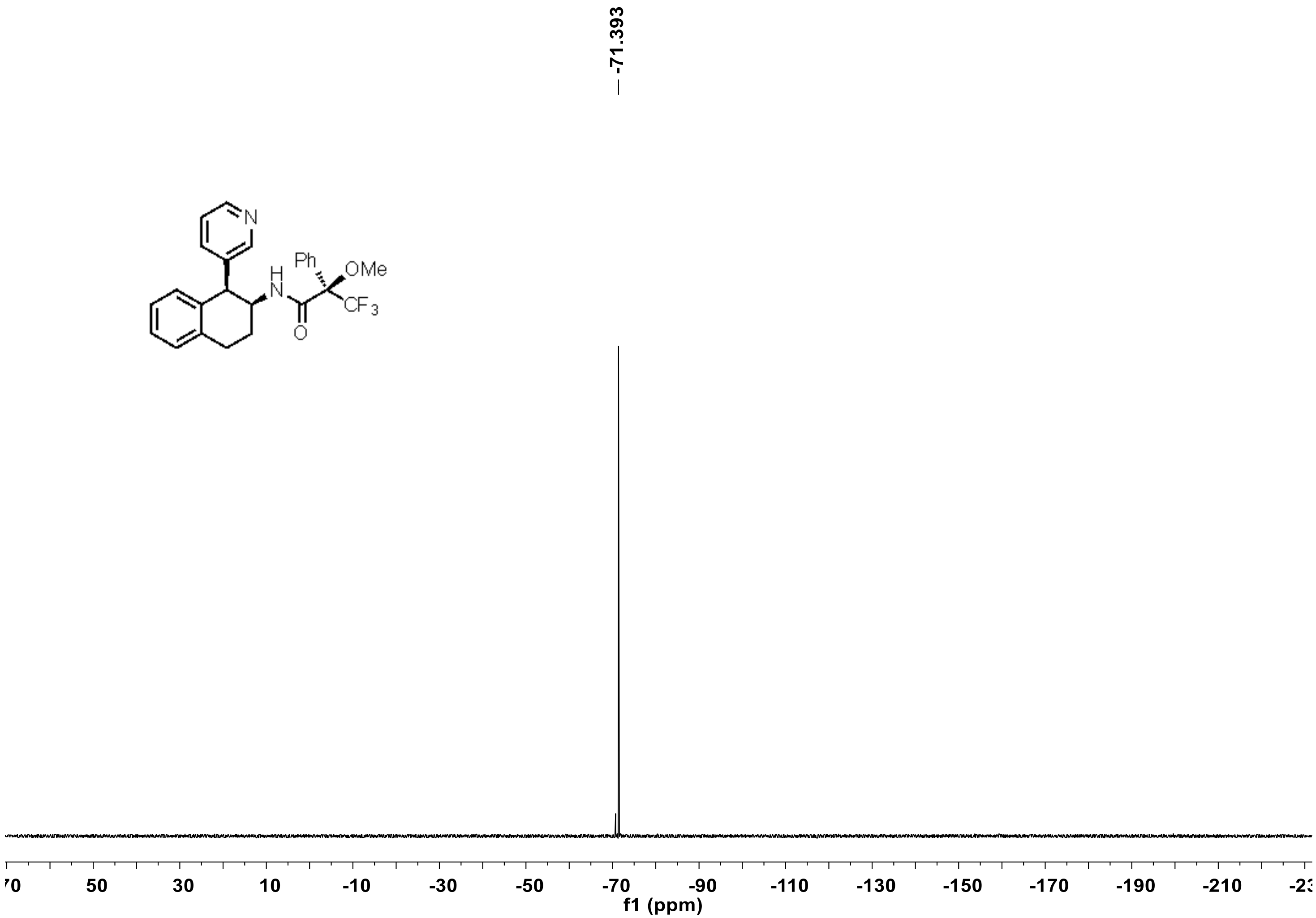
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **(*S*,*S*)-S39-(*R*)-MTPA**



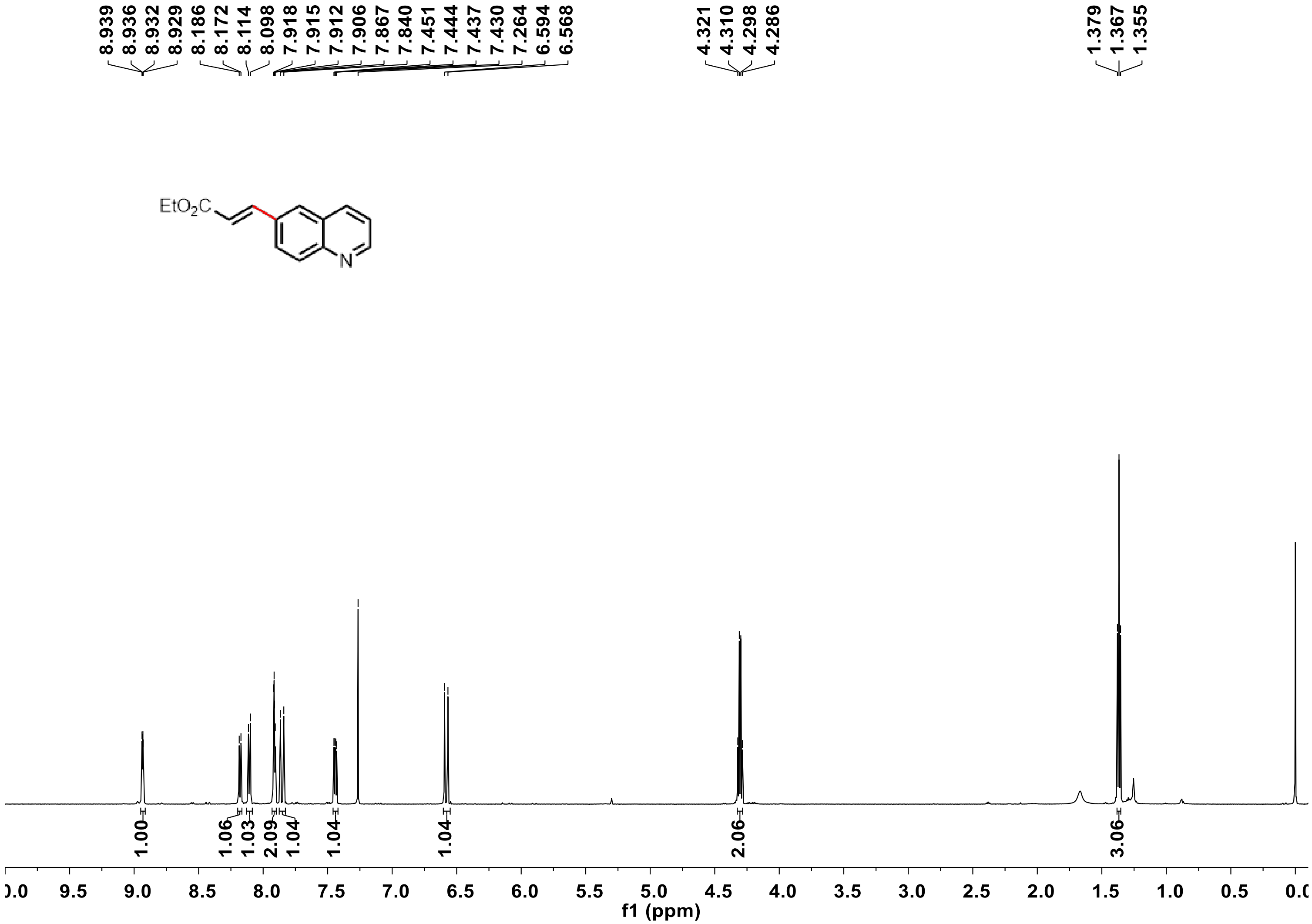
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **(*S*,*S*)-S39-(*R*)-MTPA**



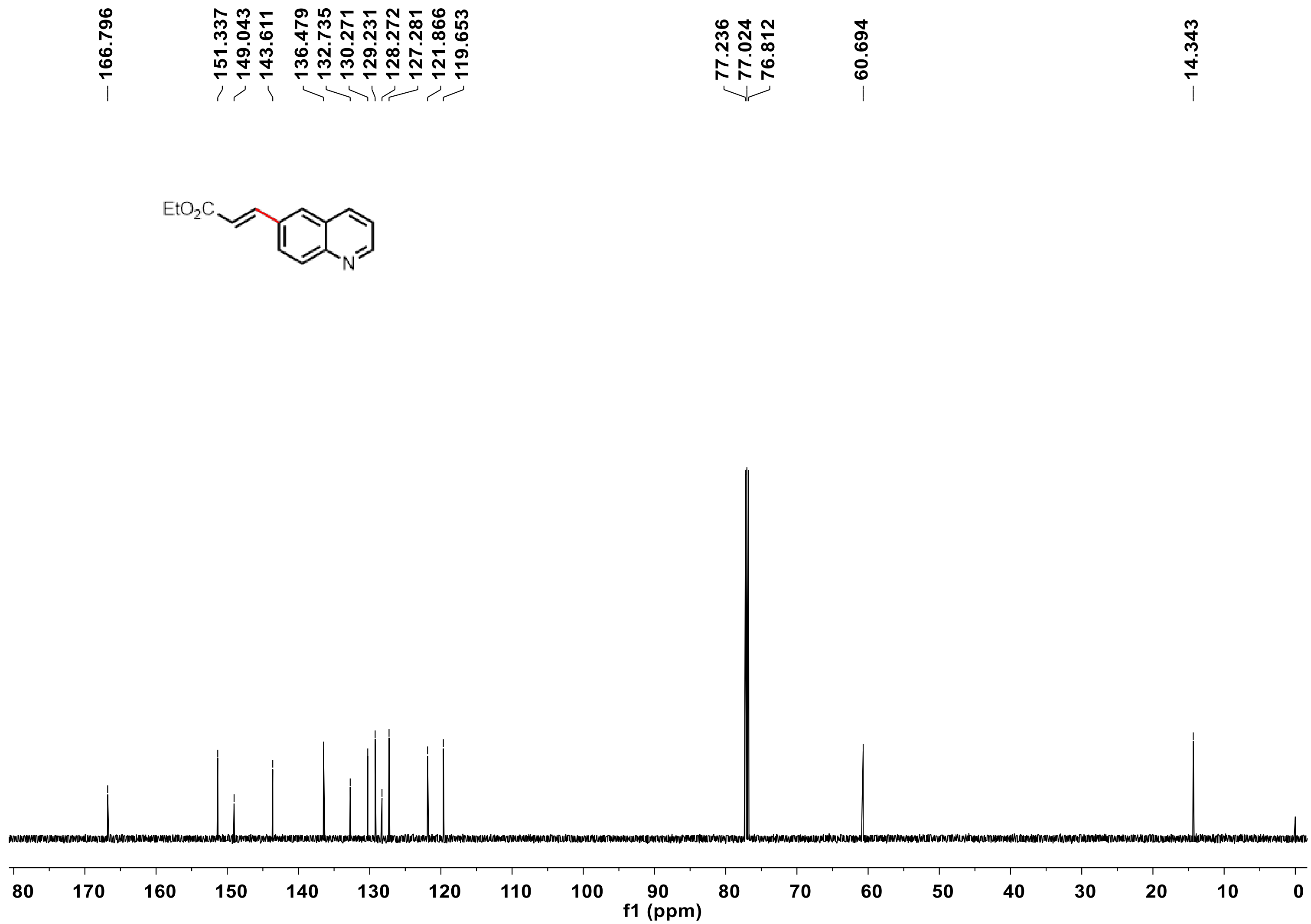
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **(*S*,*S*)-S39-(*R*)-MTPA**



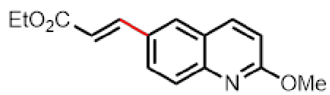
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a**

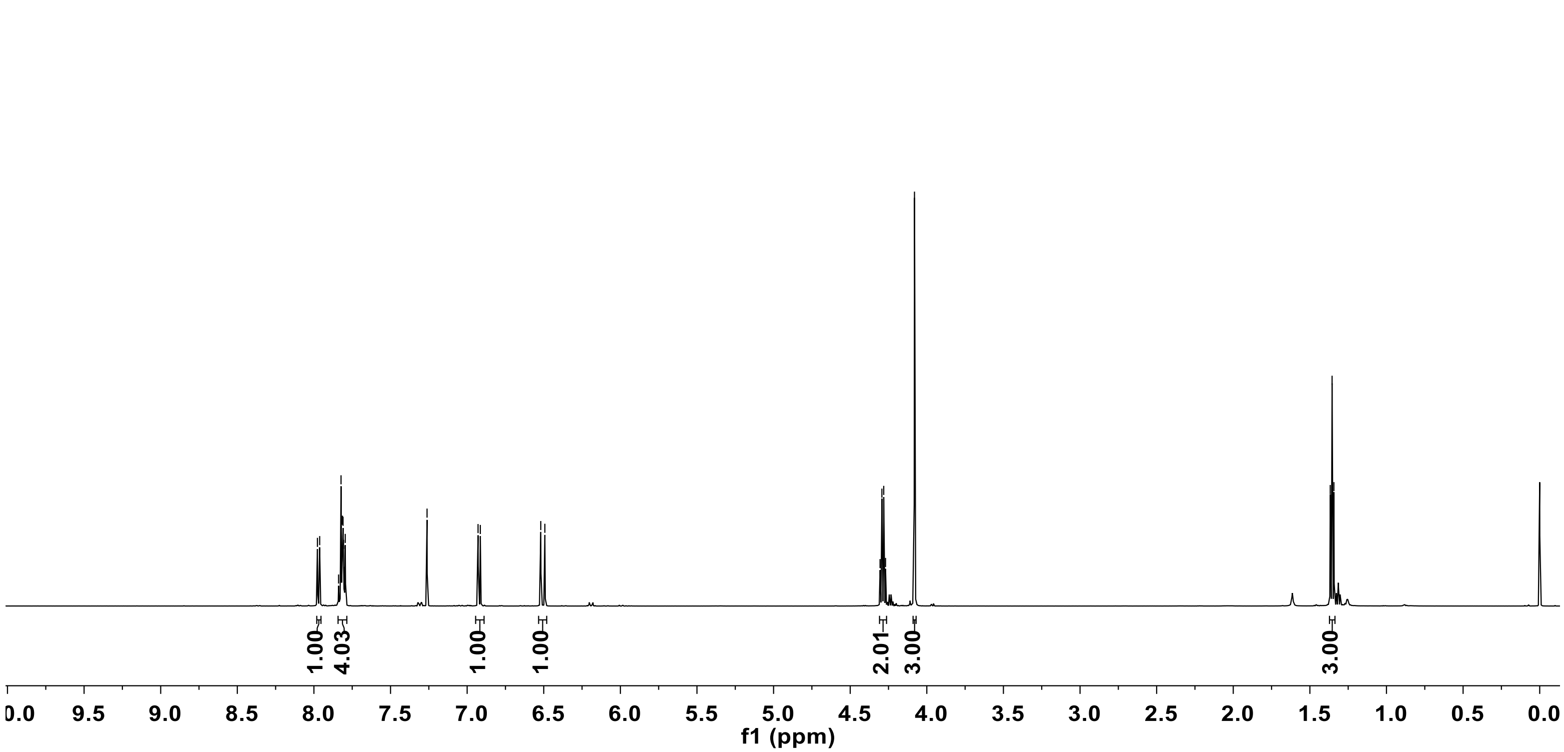


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2a**

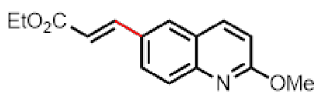


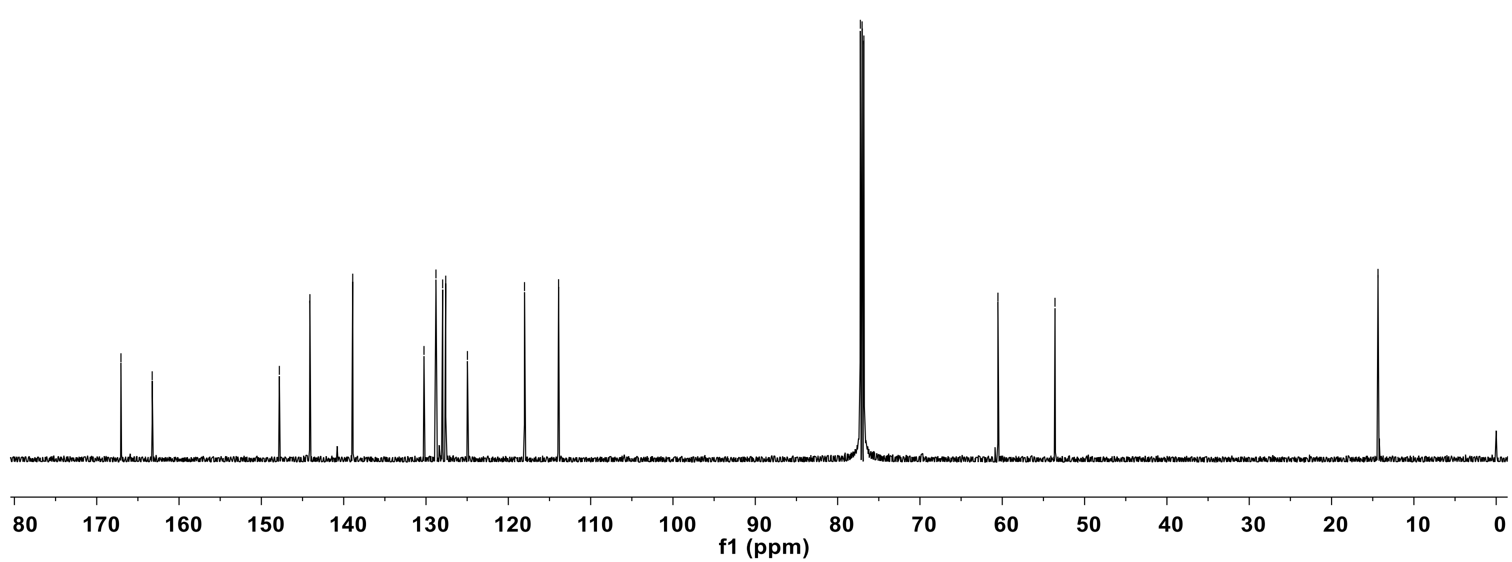
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b**



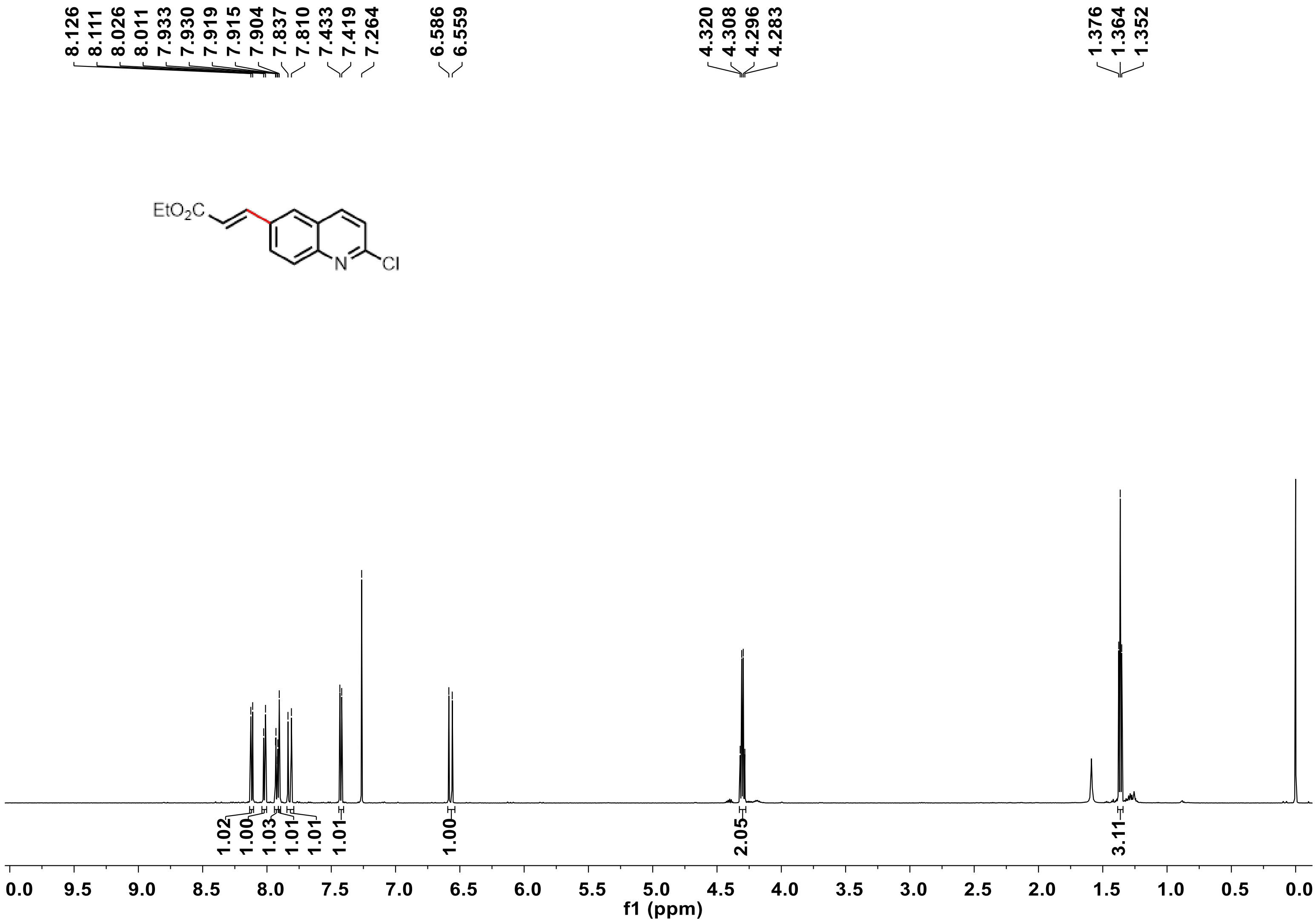


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2b**

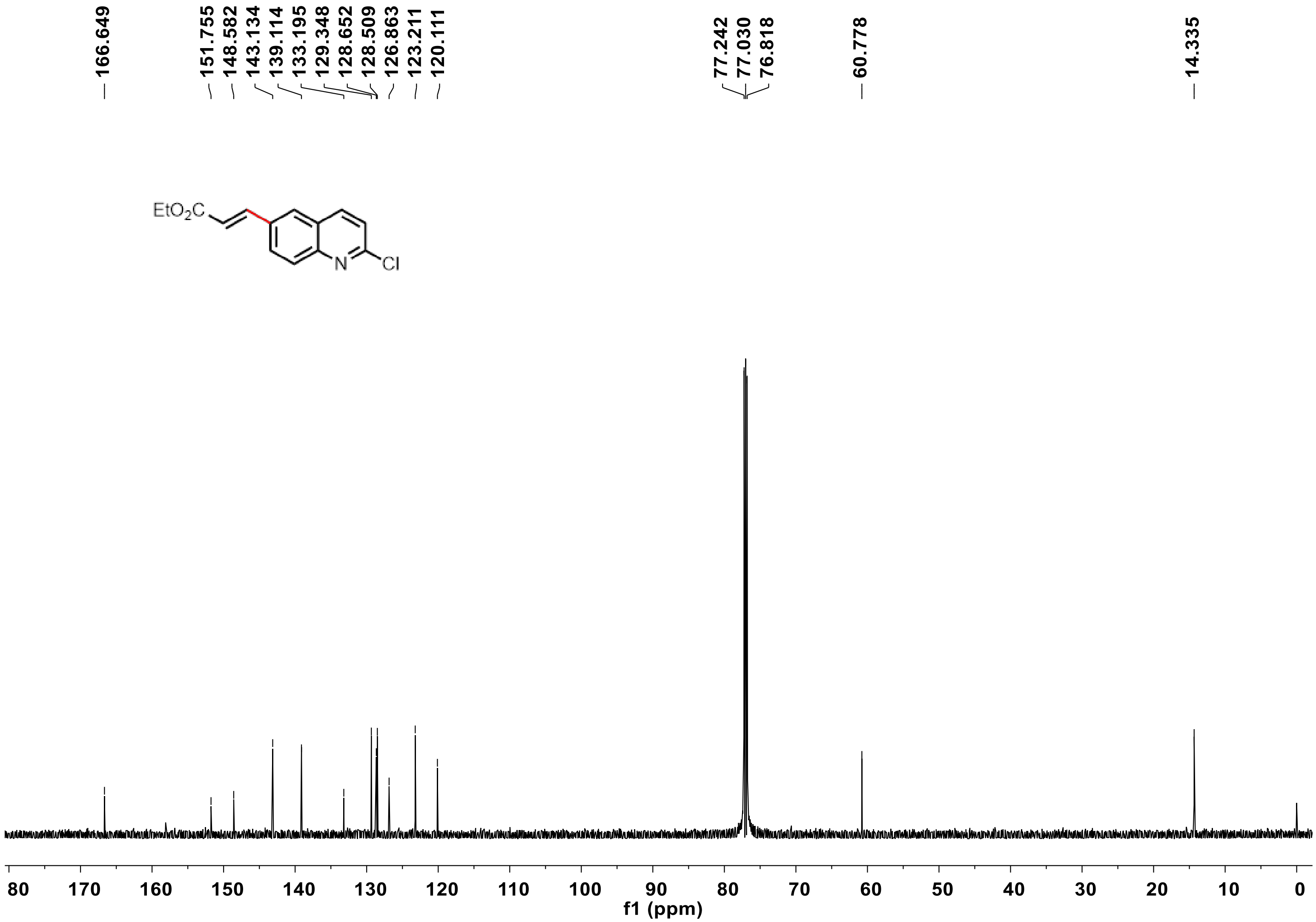




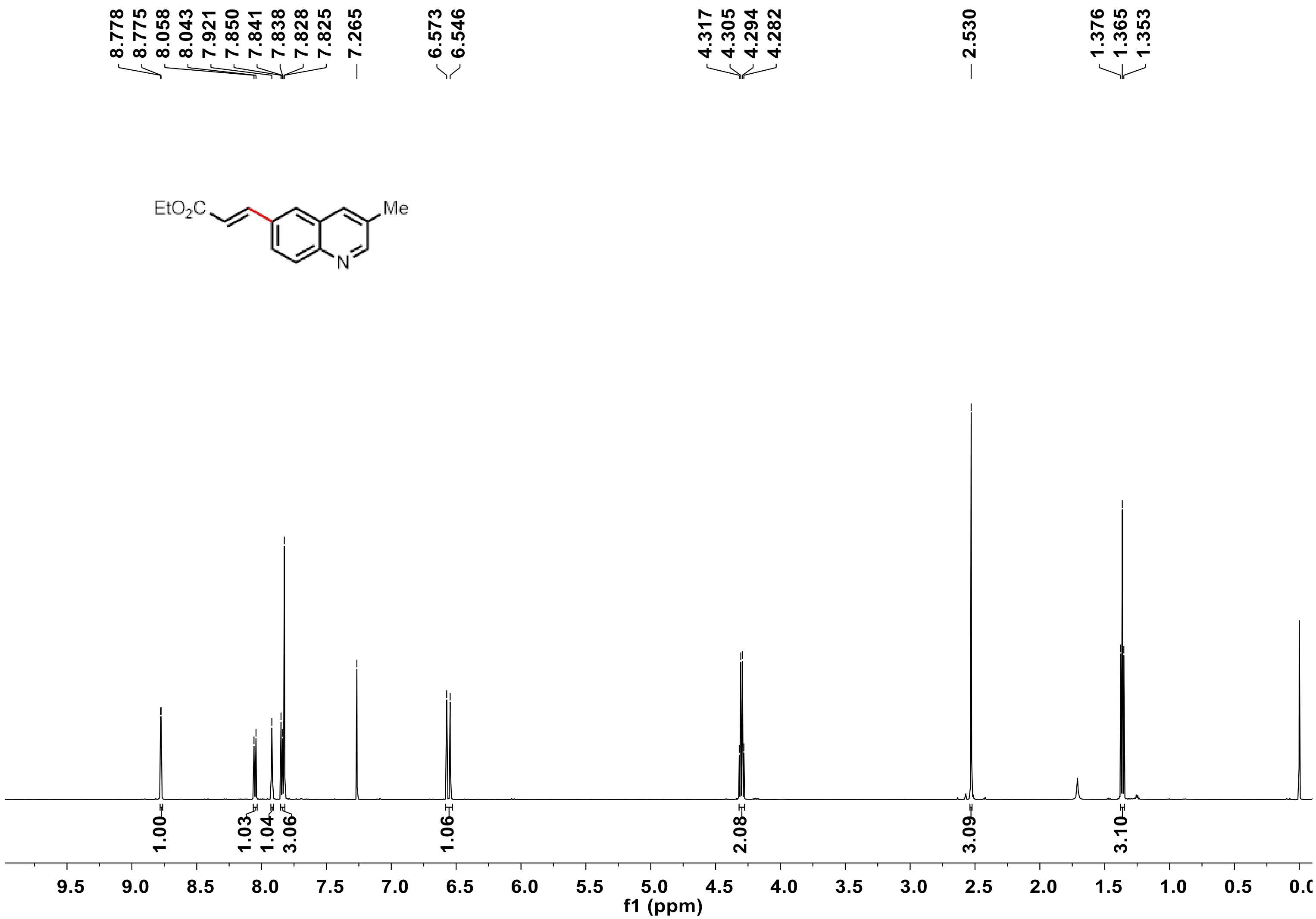
^1H NMR (600 MHz, $CDCl_3$) spectrum of **2c**



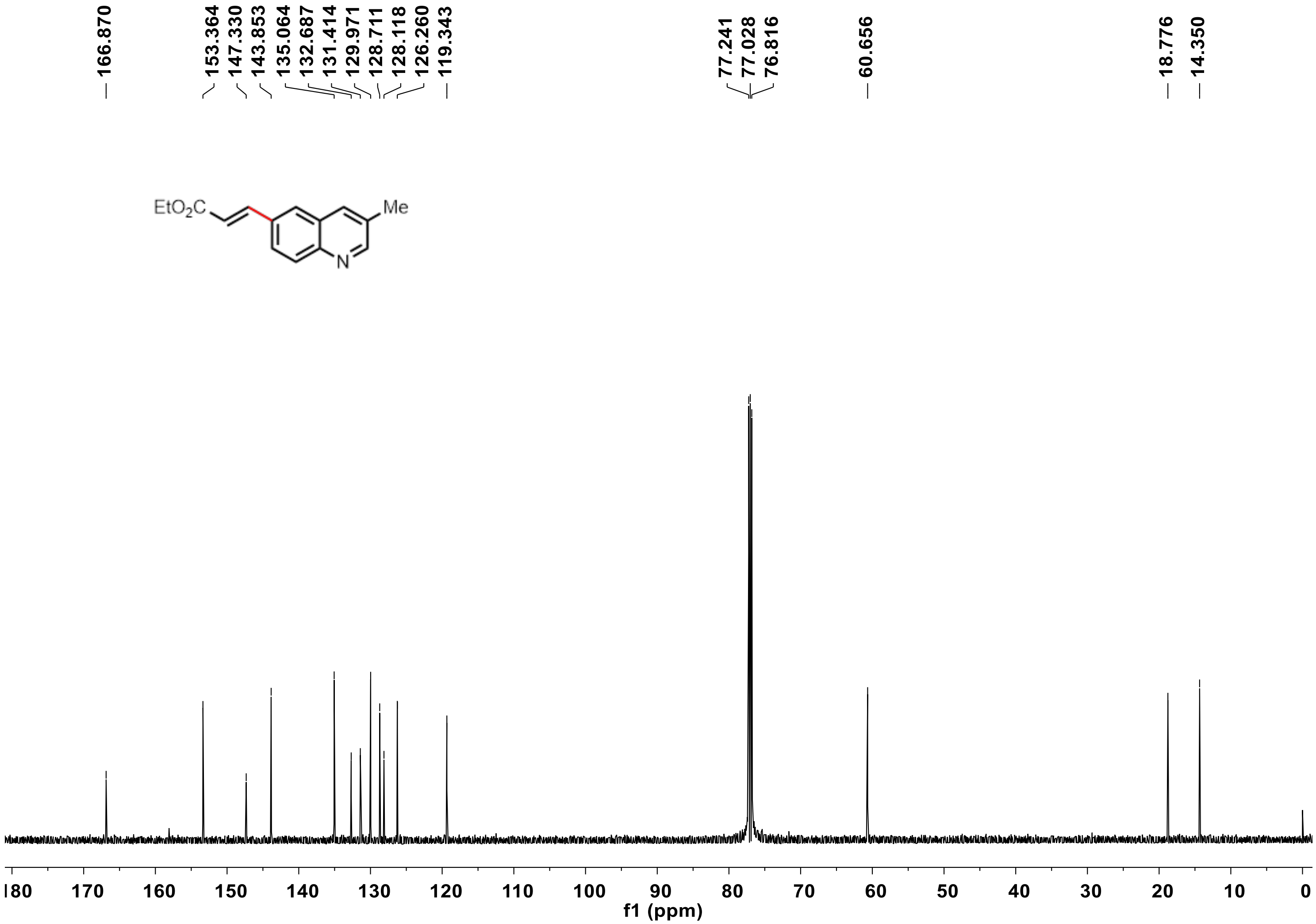
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2c**



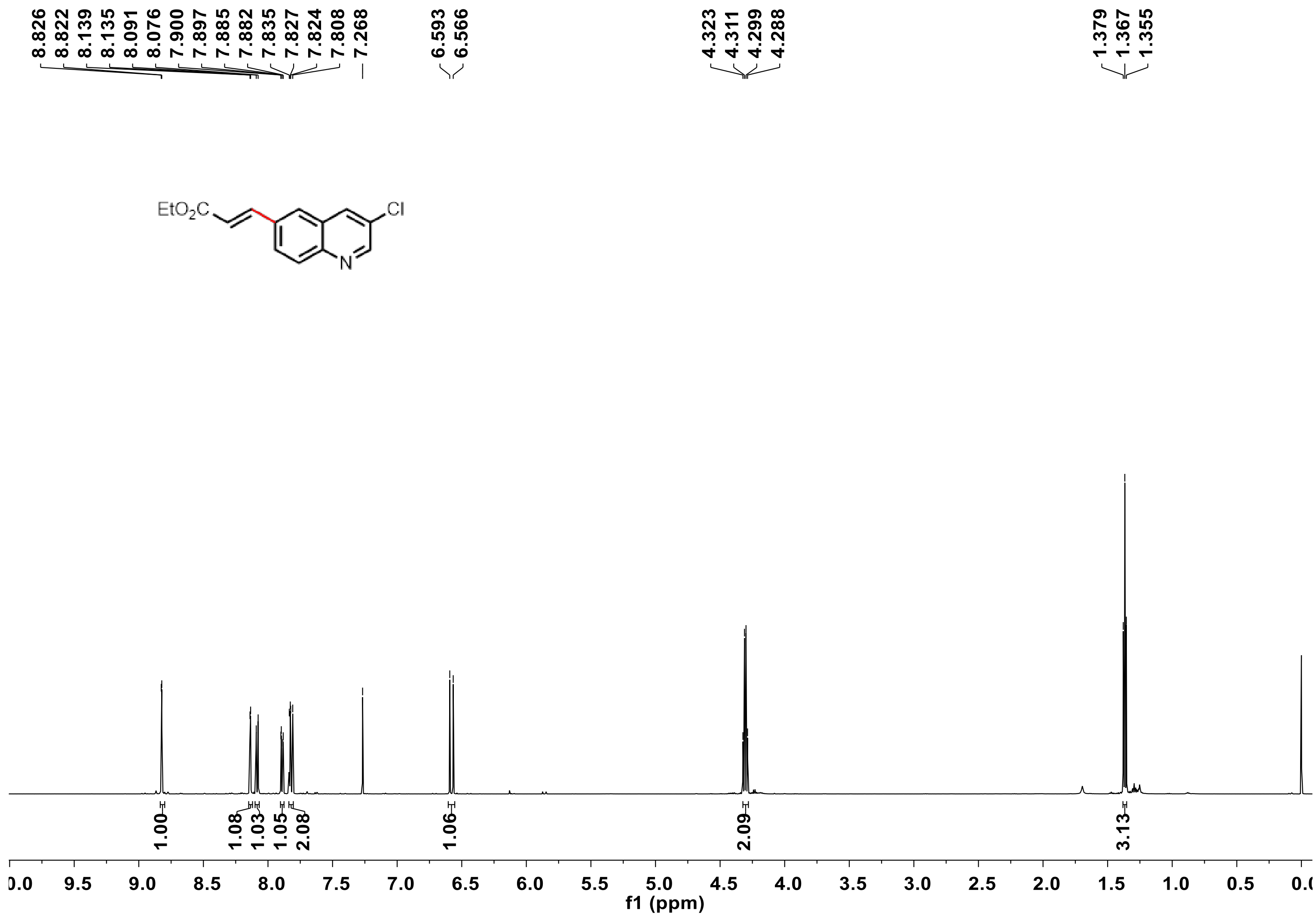
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2d**



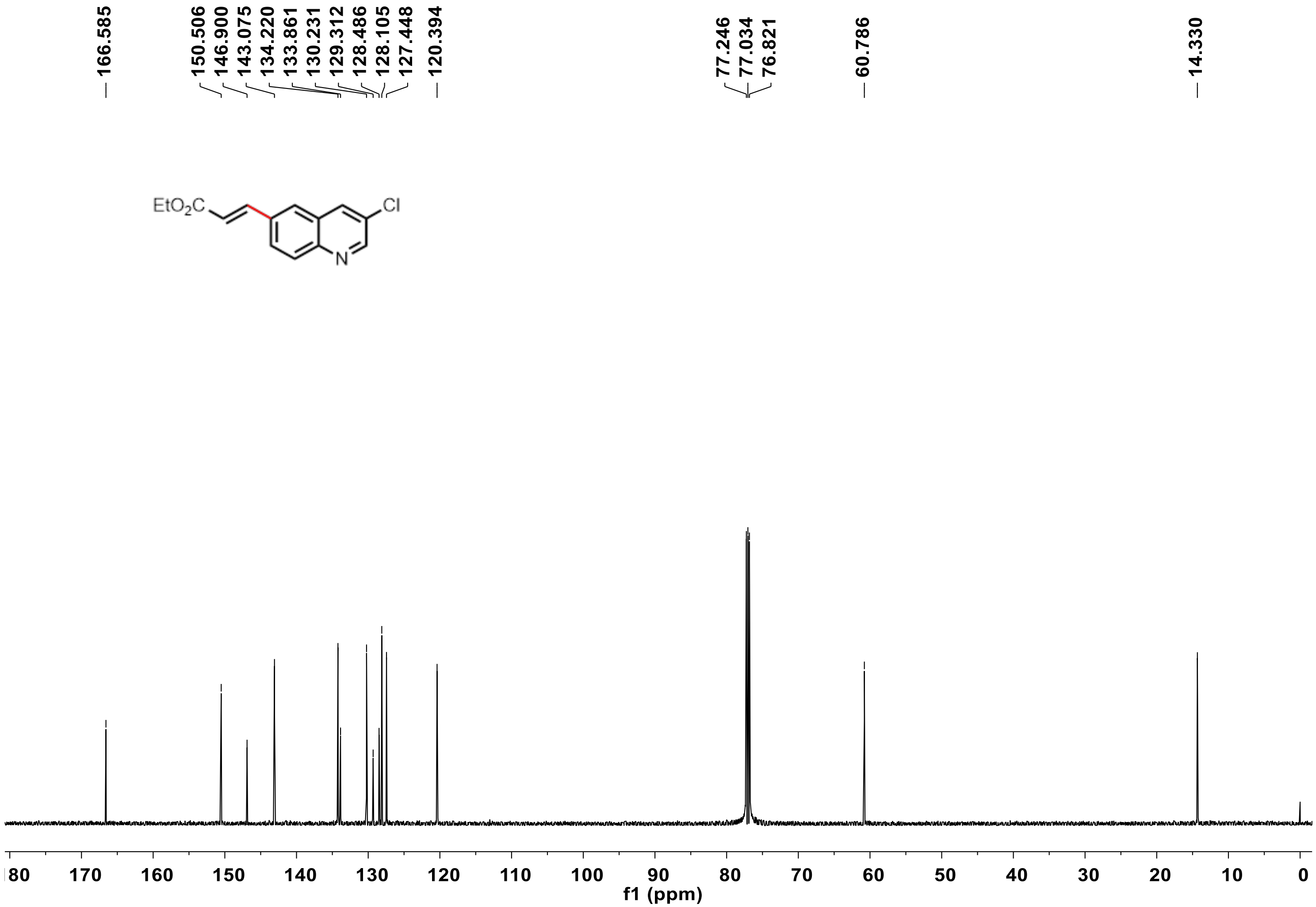
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2d**



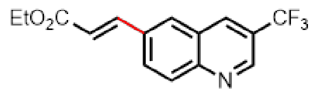
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2e**

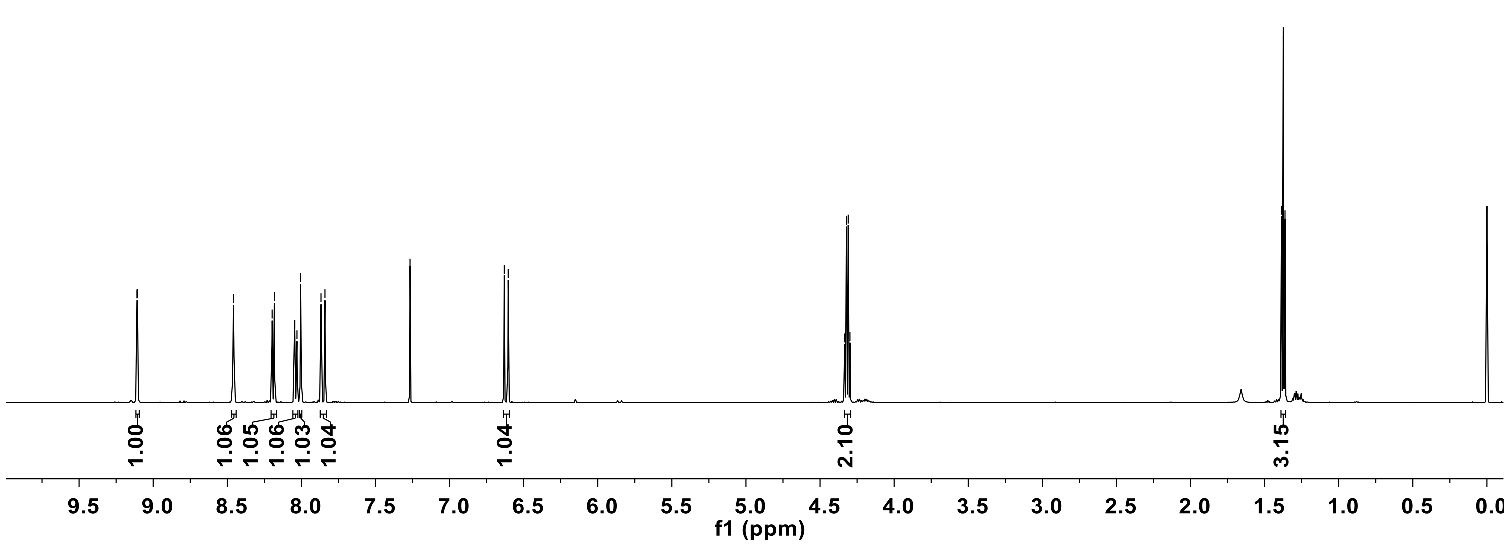


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2e**

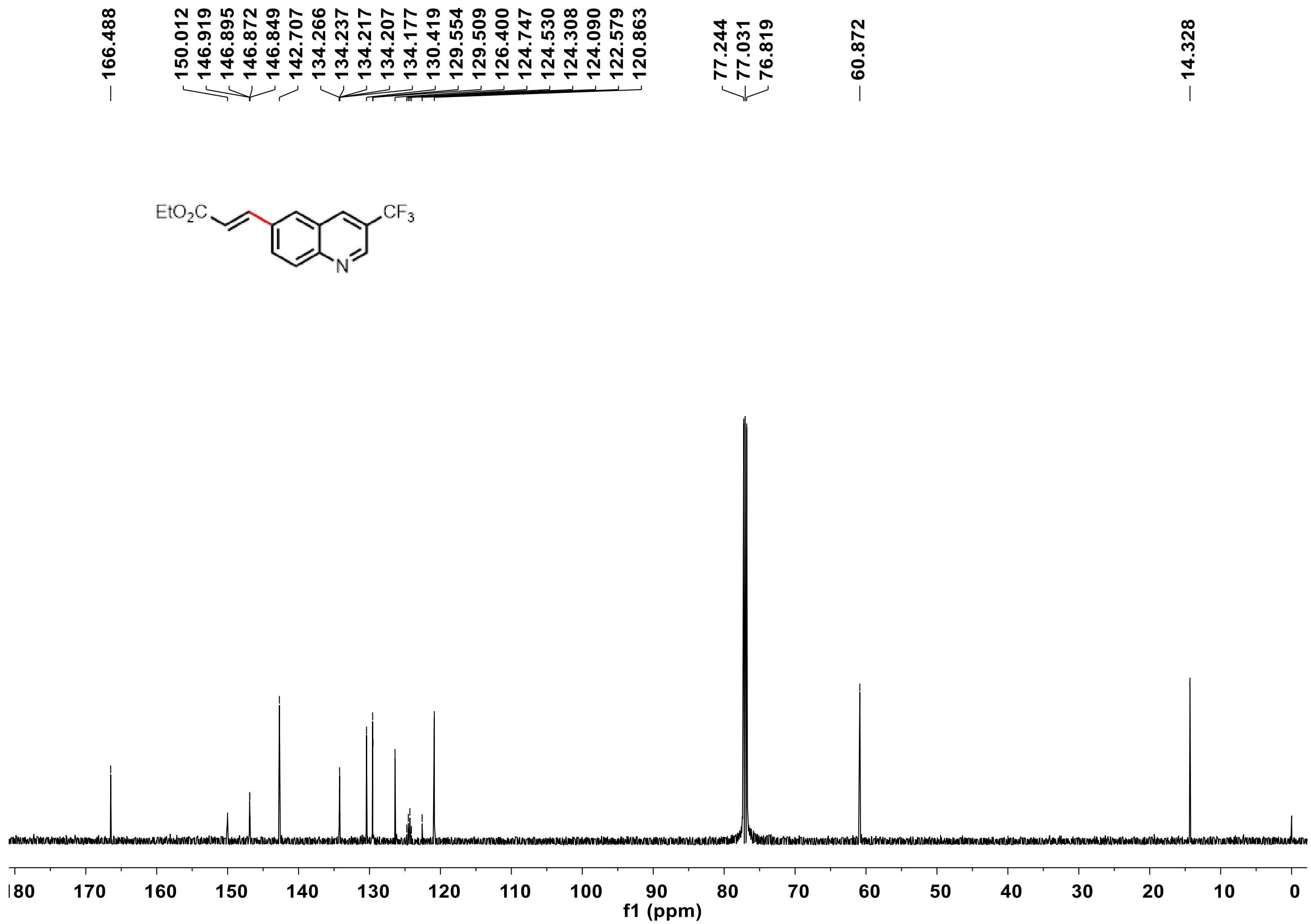


[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2f**

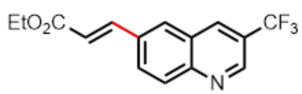


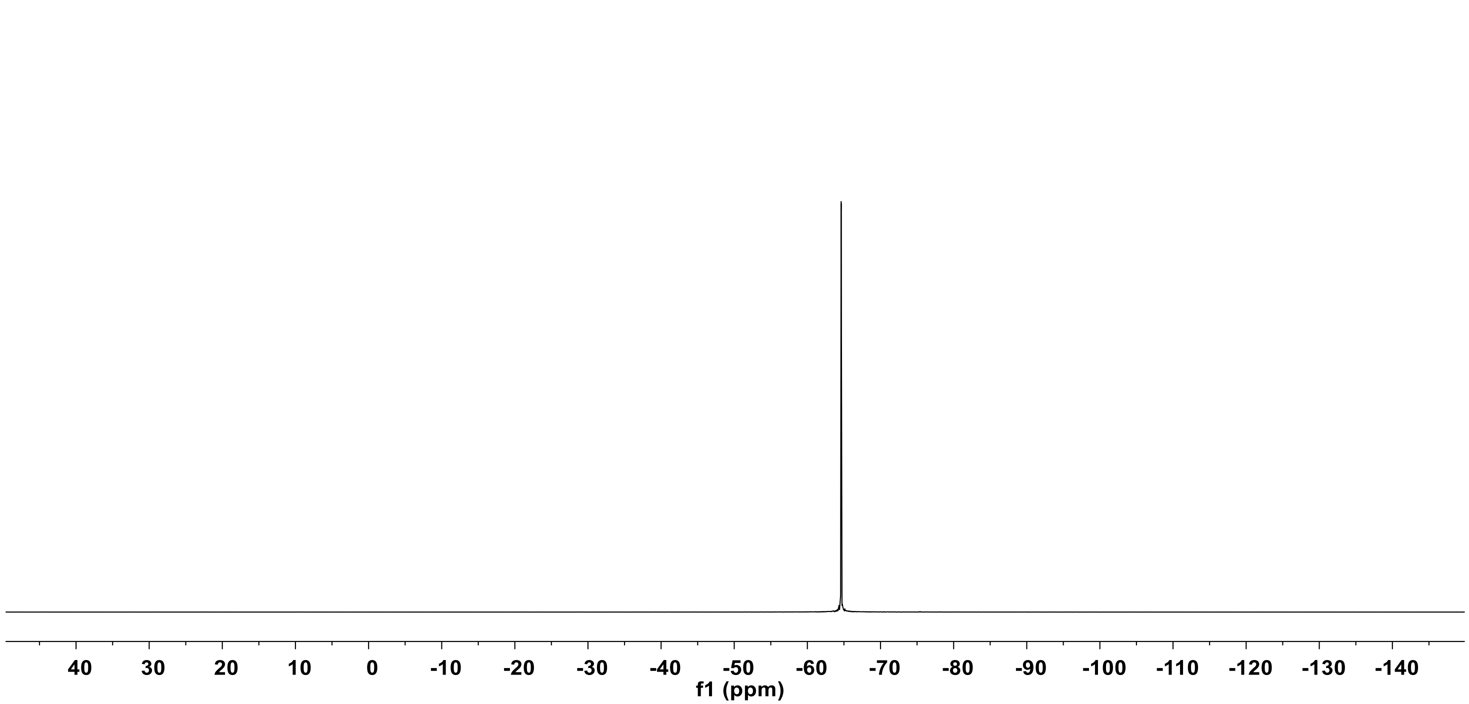


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2f**

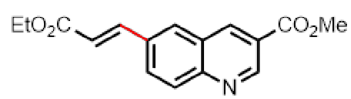


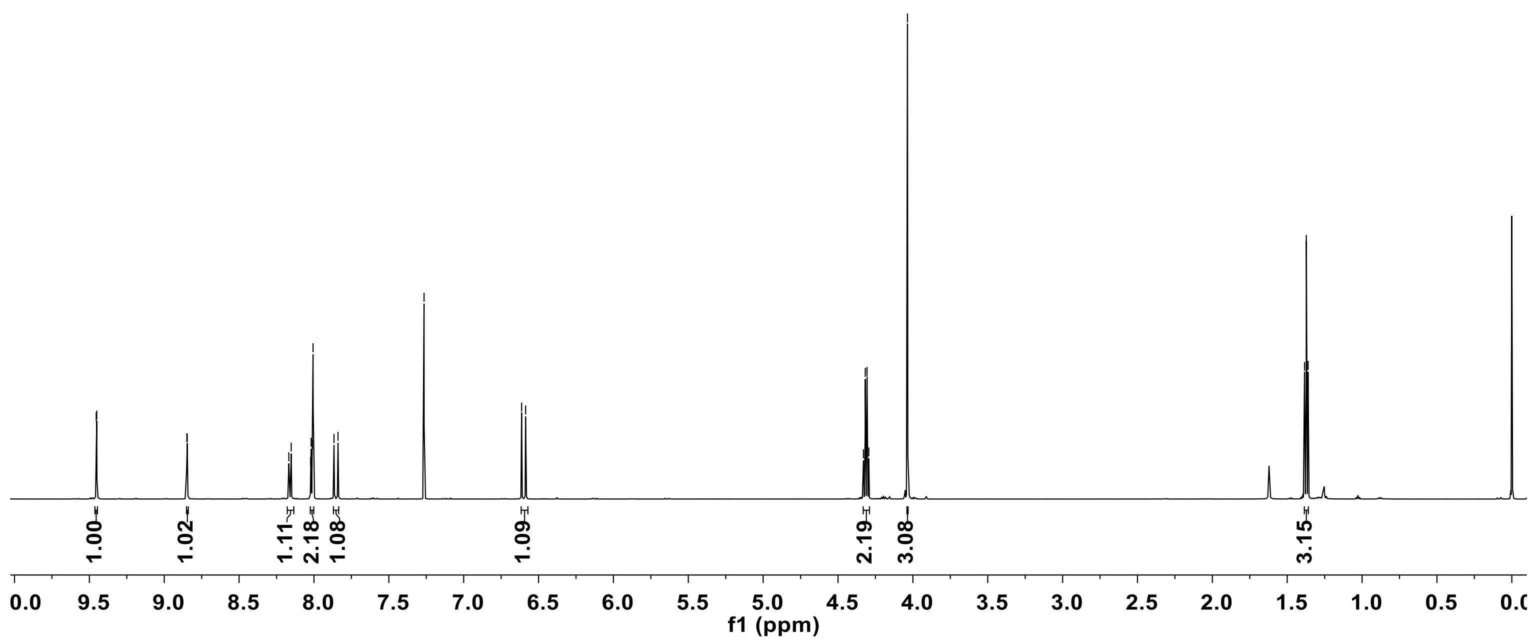
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2f**



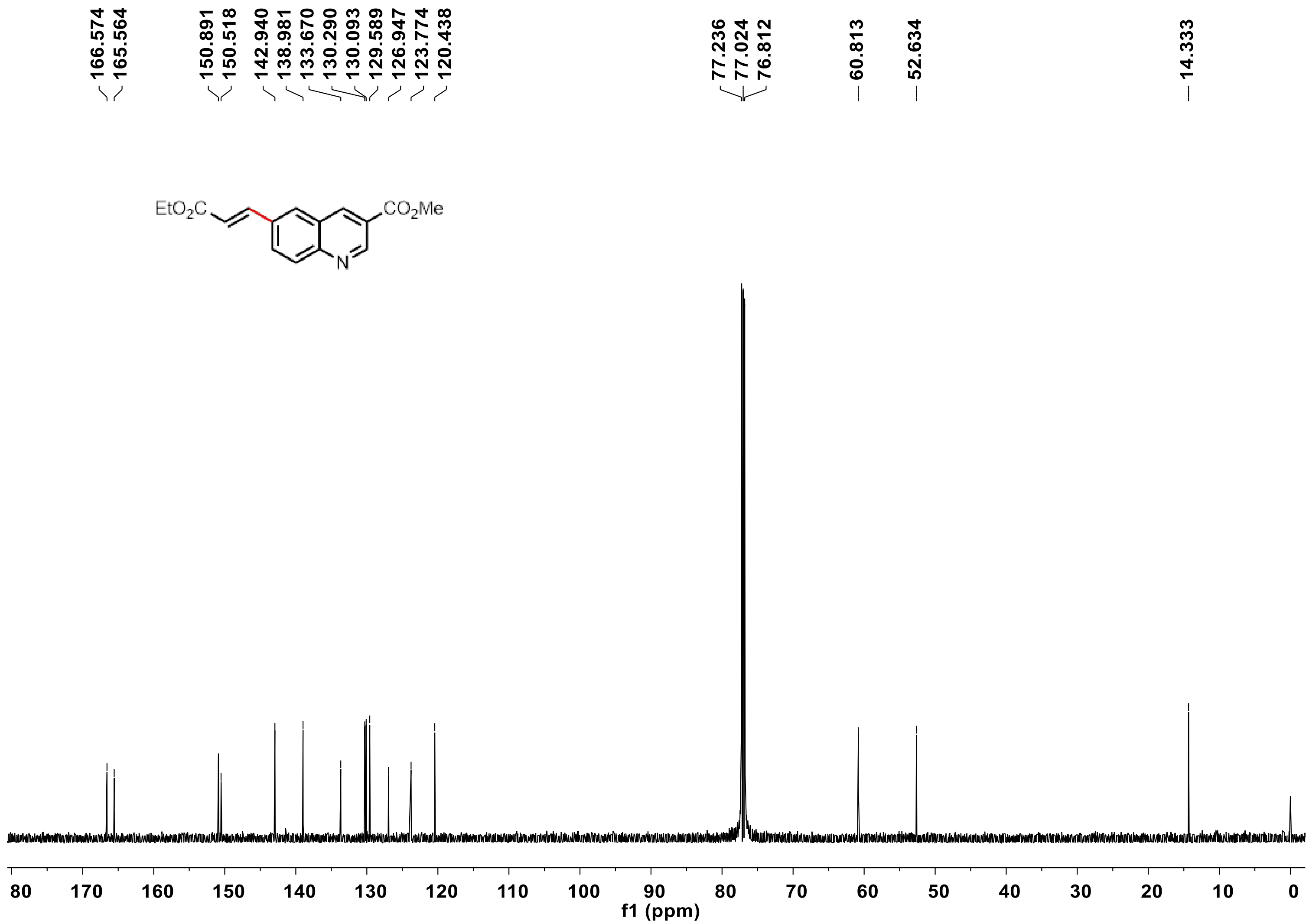


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2g**

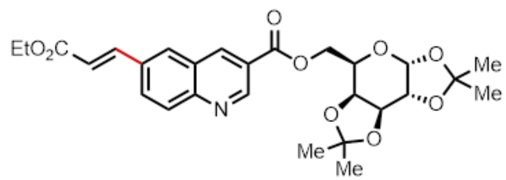


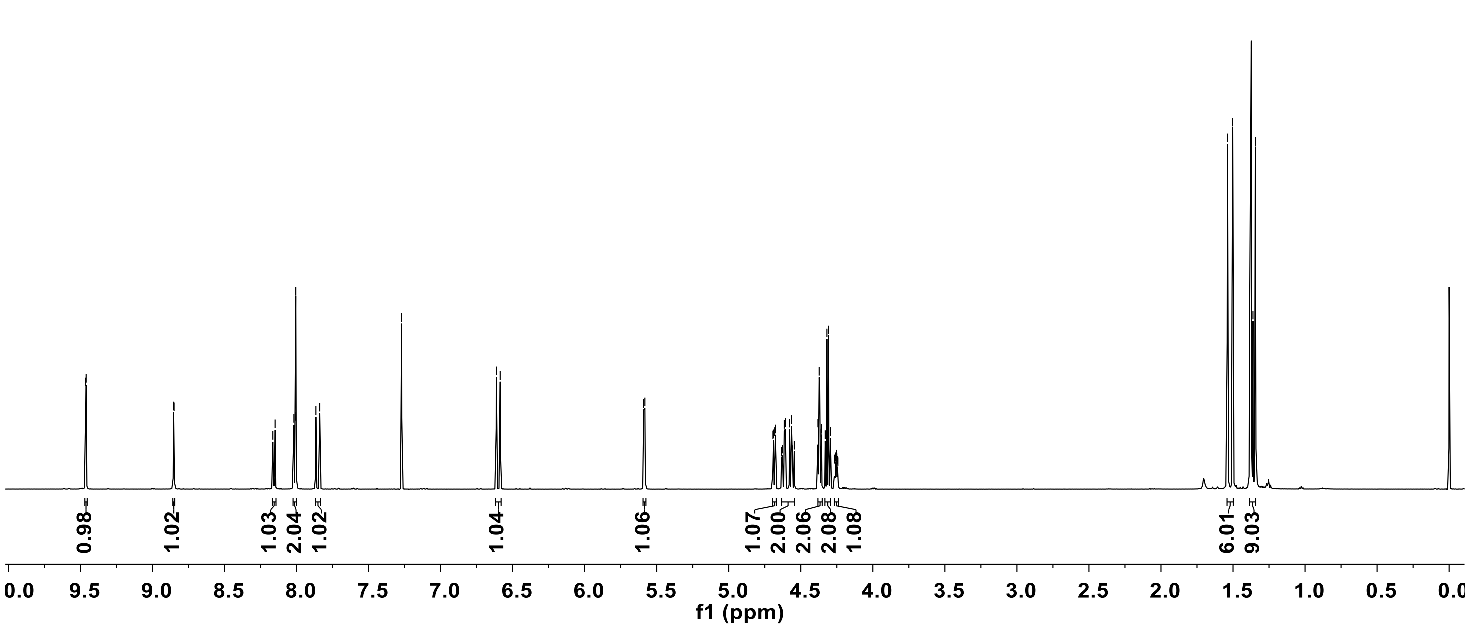


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2g**

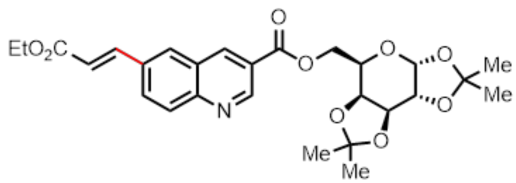


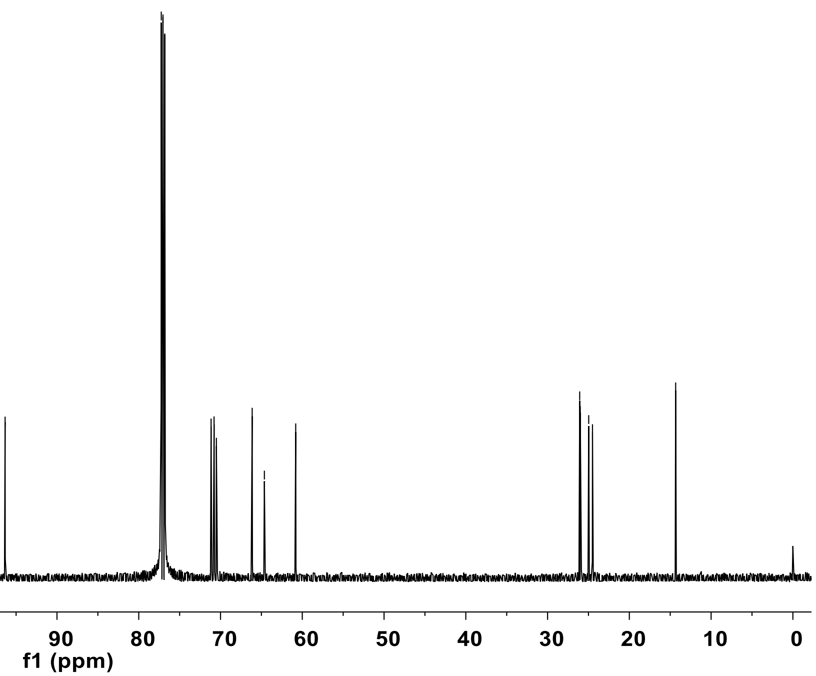
^1H NMR (600 MHz, $CDCl_3$) spectrum of **2h**



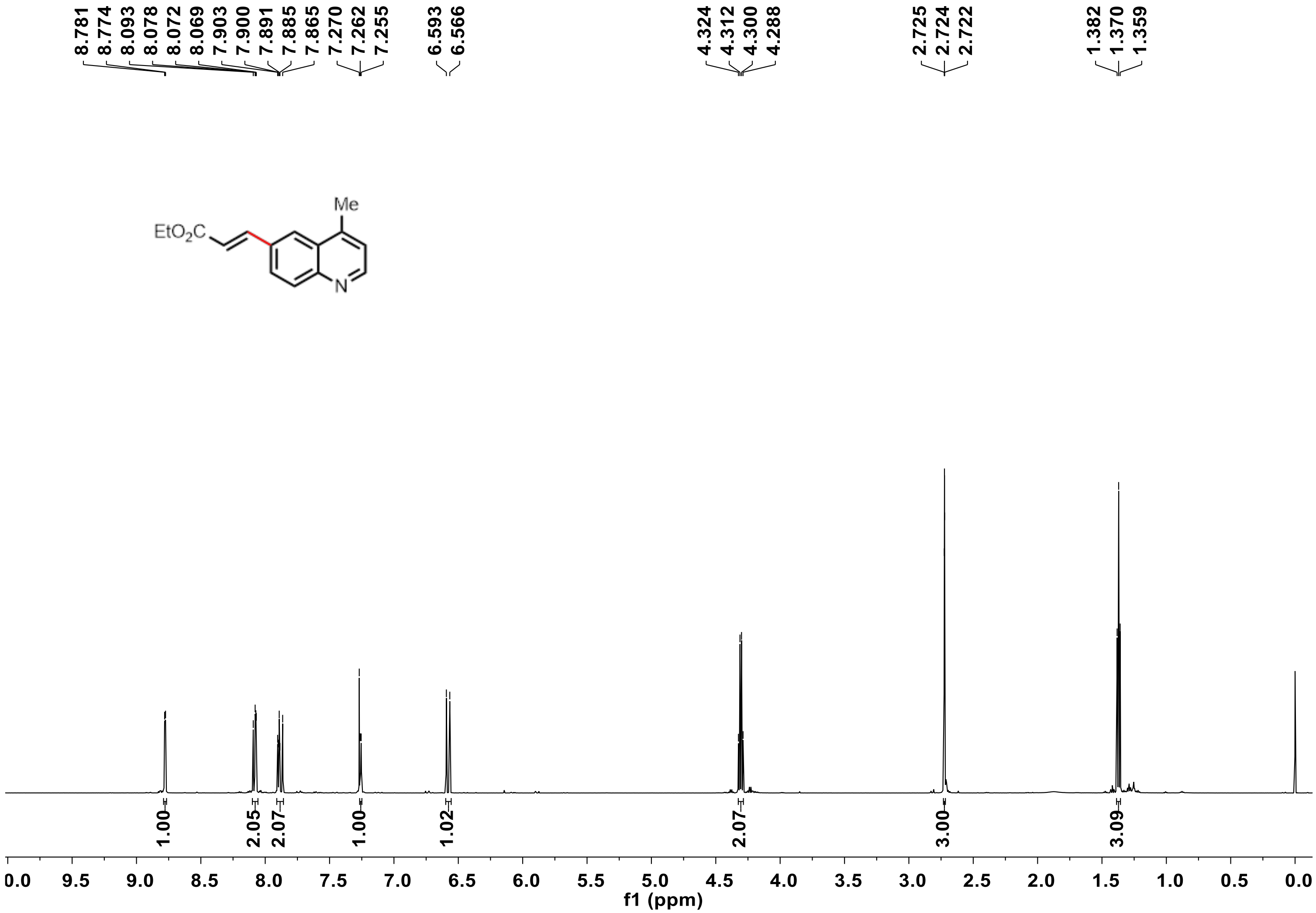


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2h**

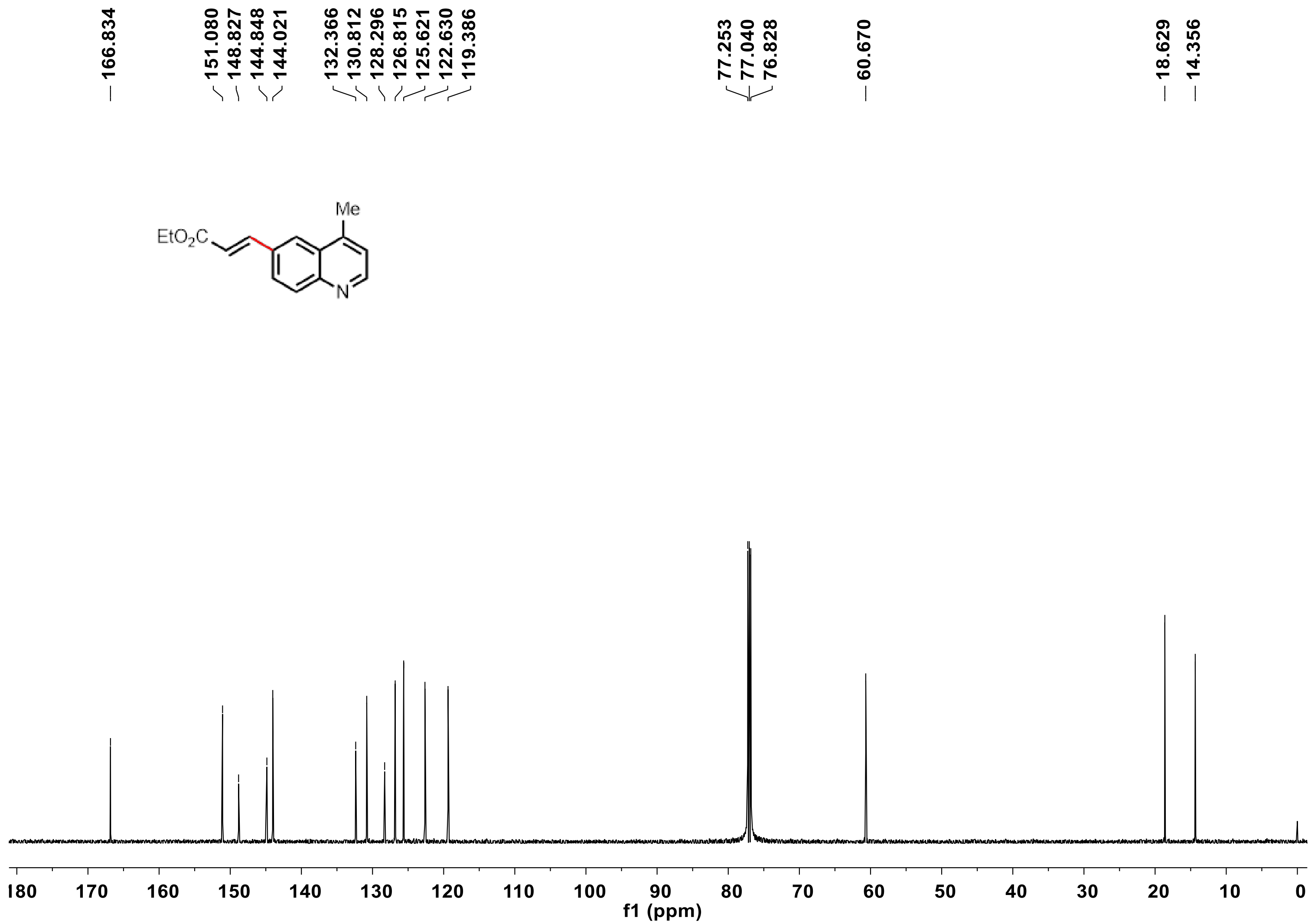




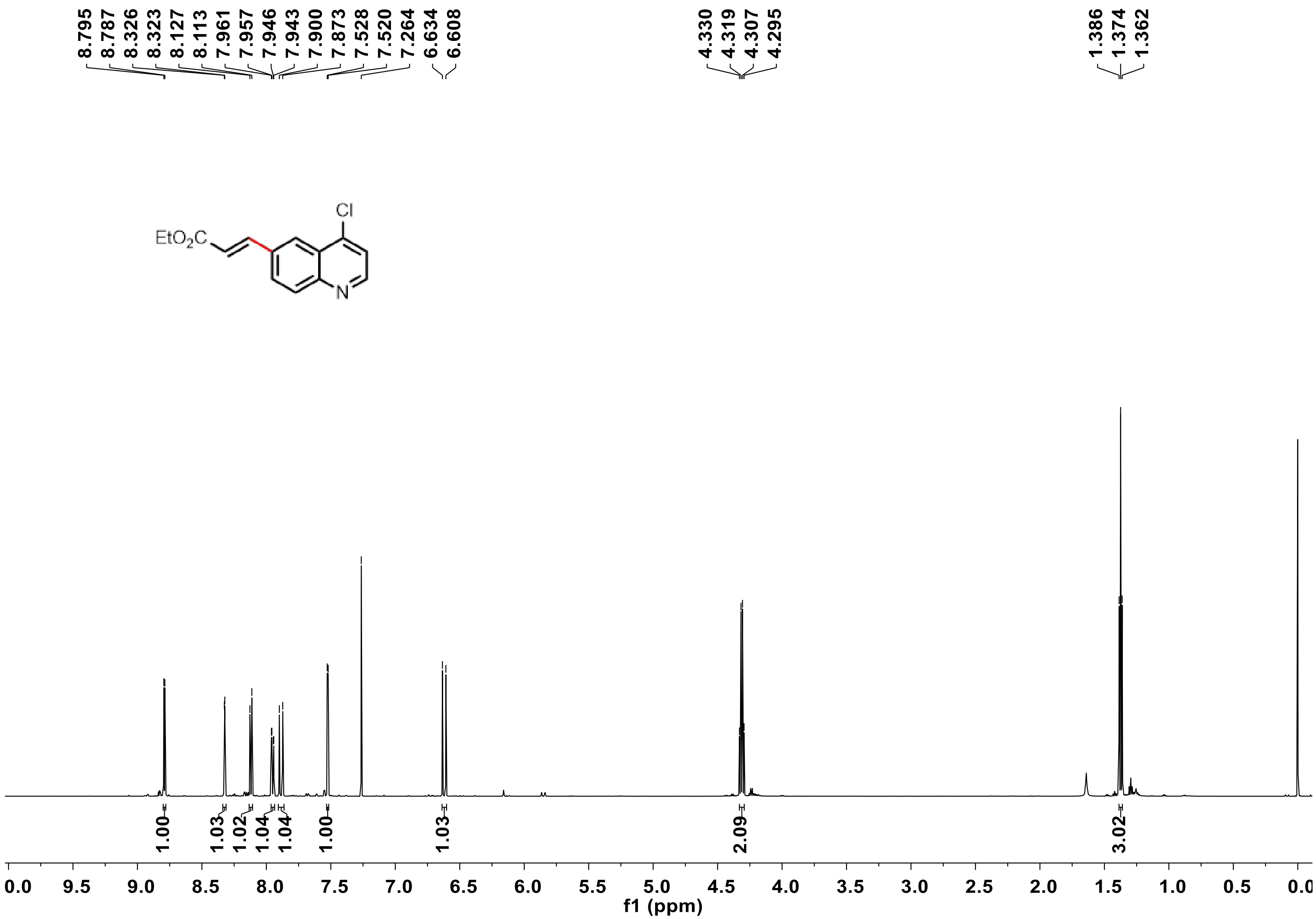
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2i**



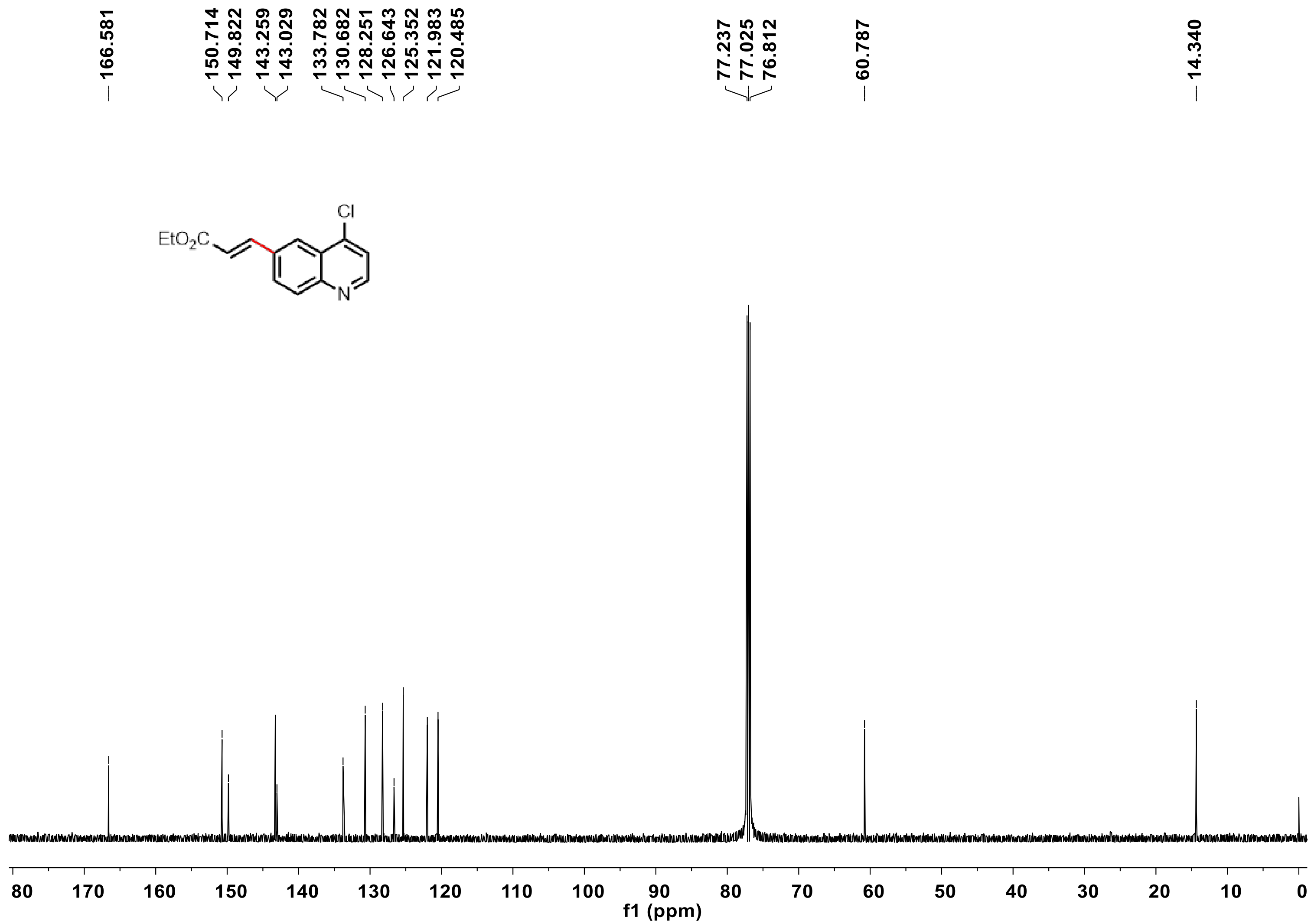
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2i**



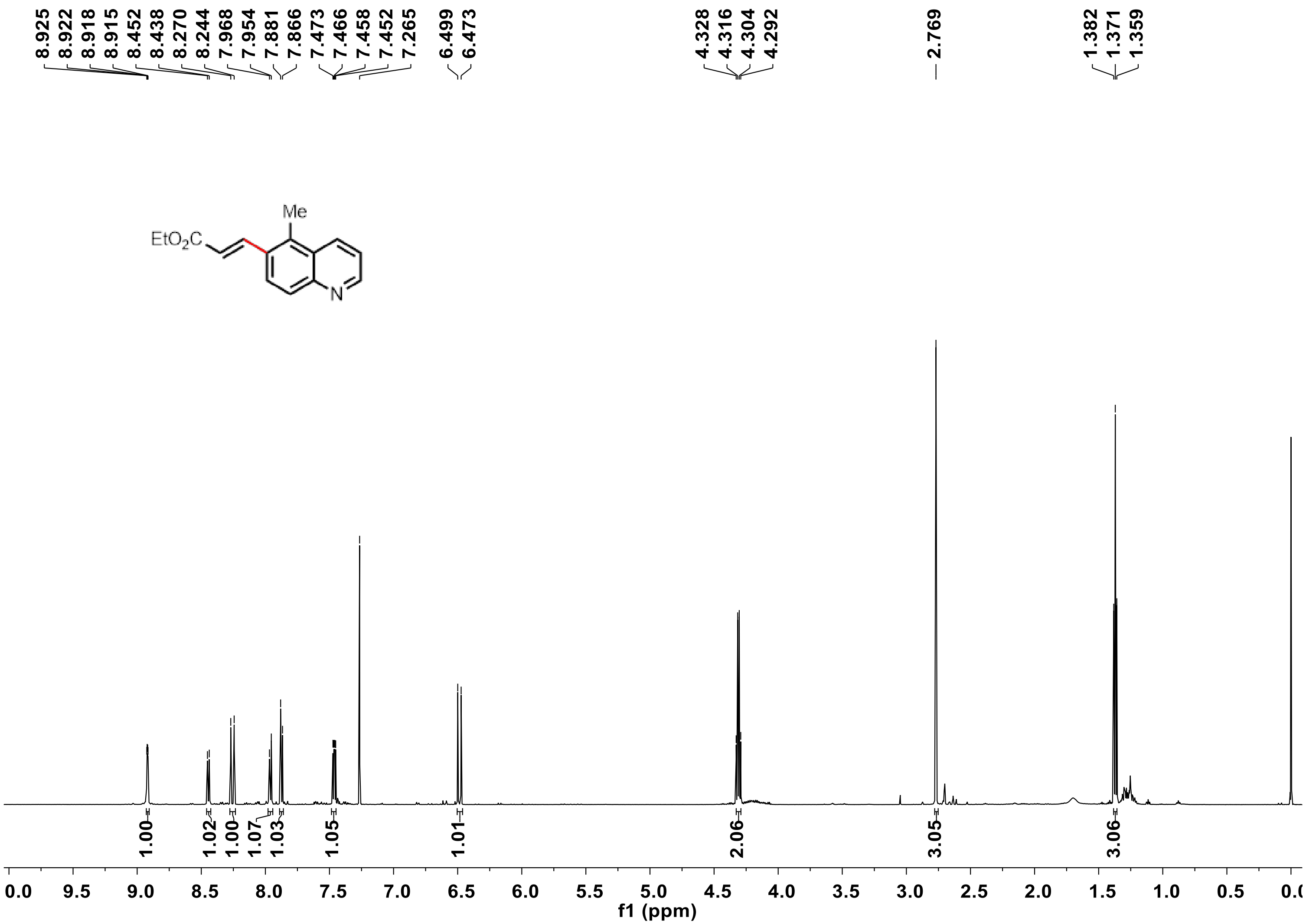
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2j**



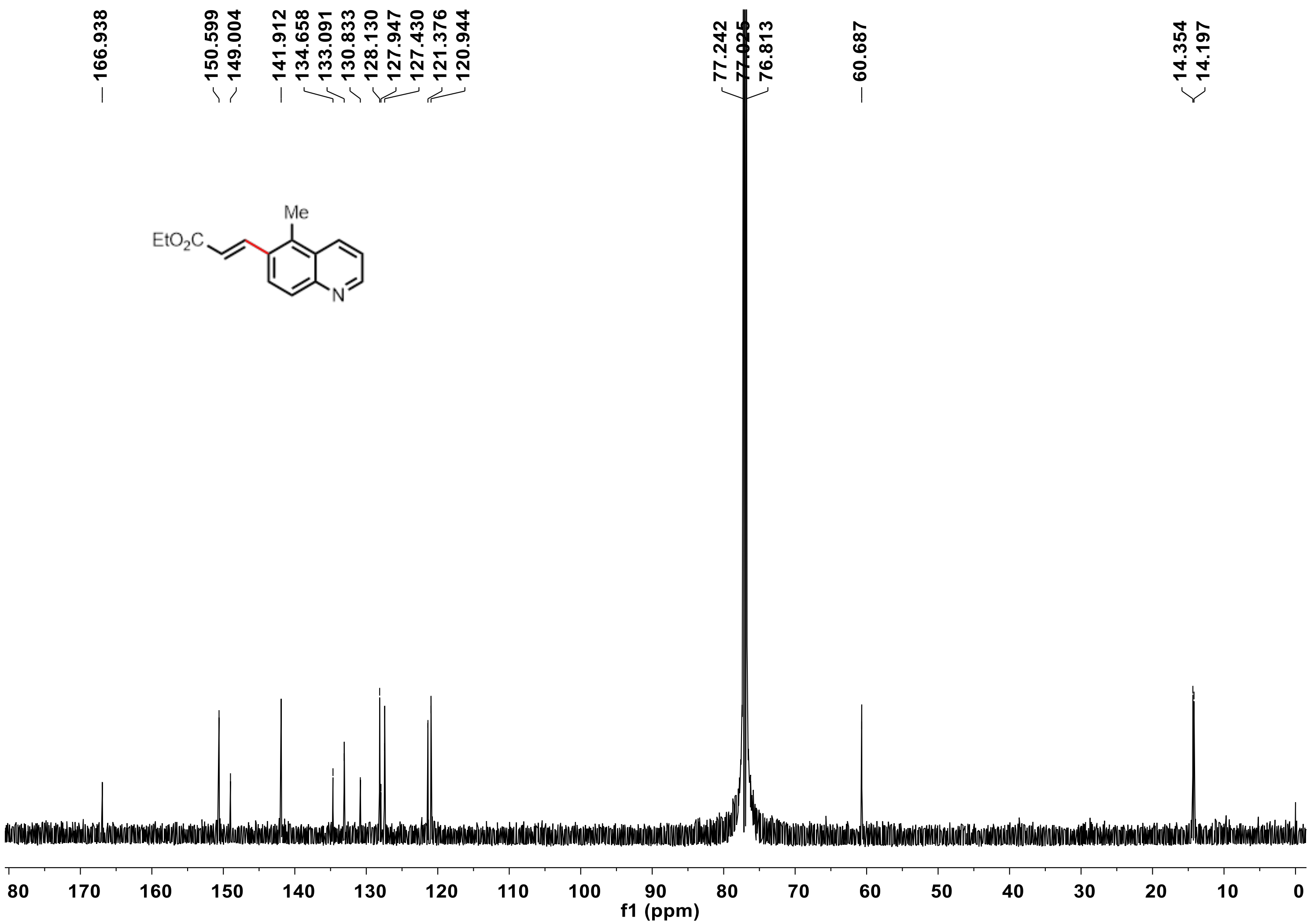
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2j**



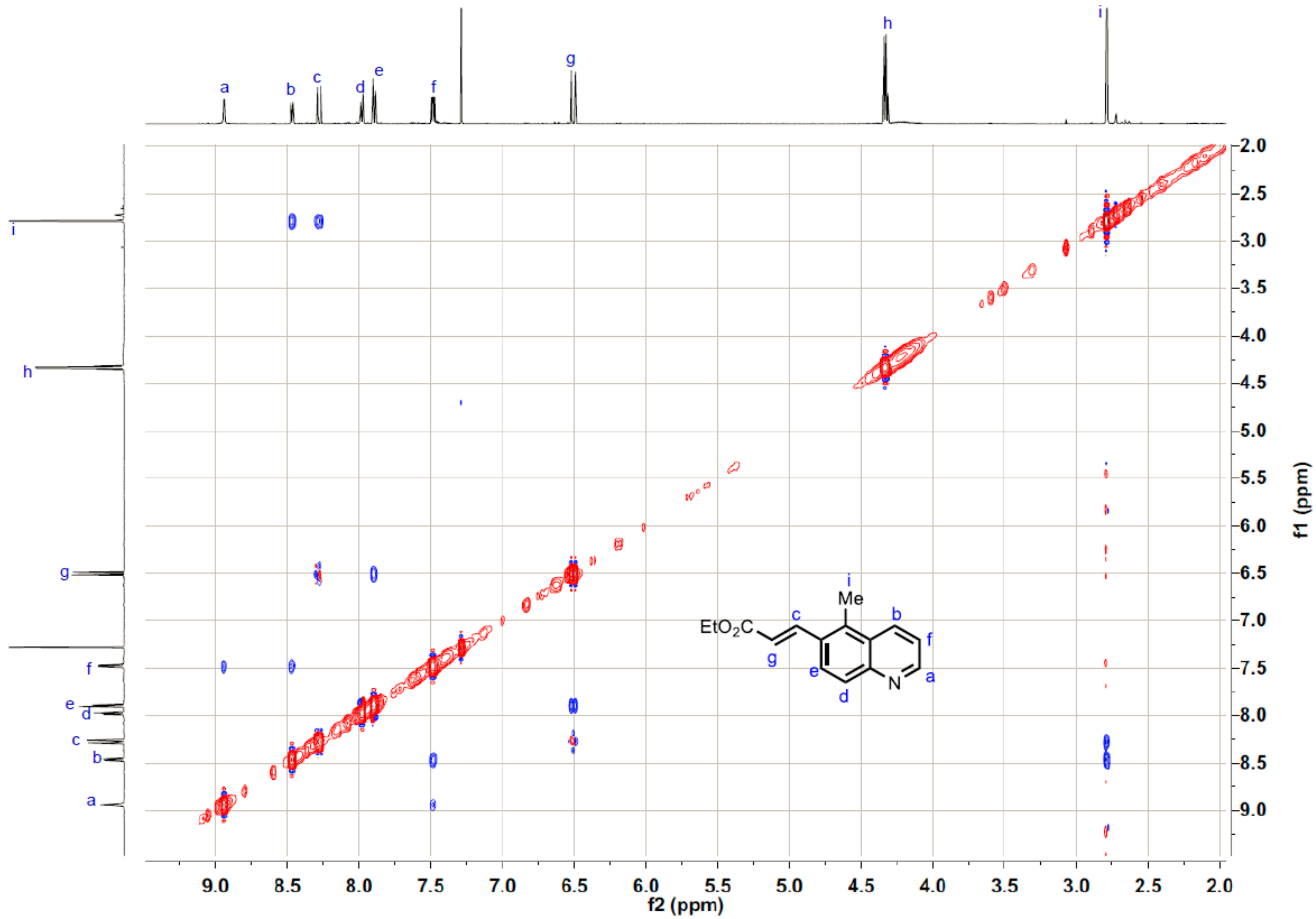
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2k**



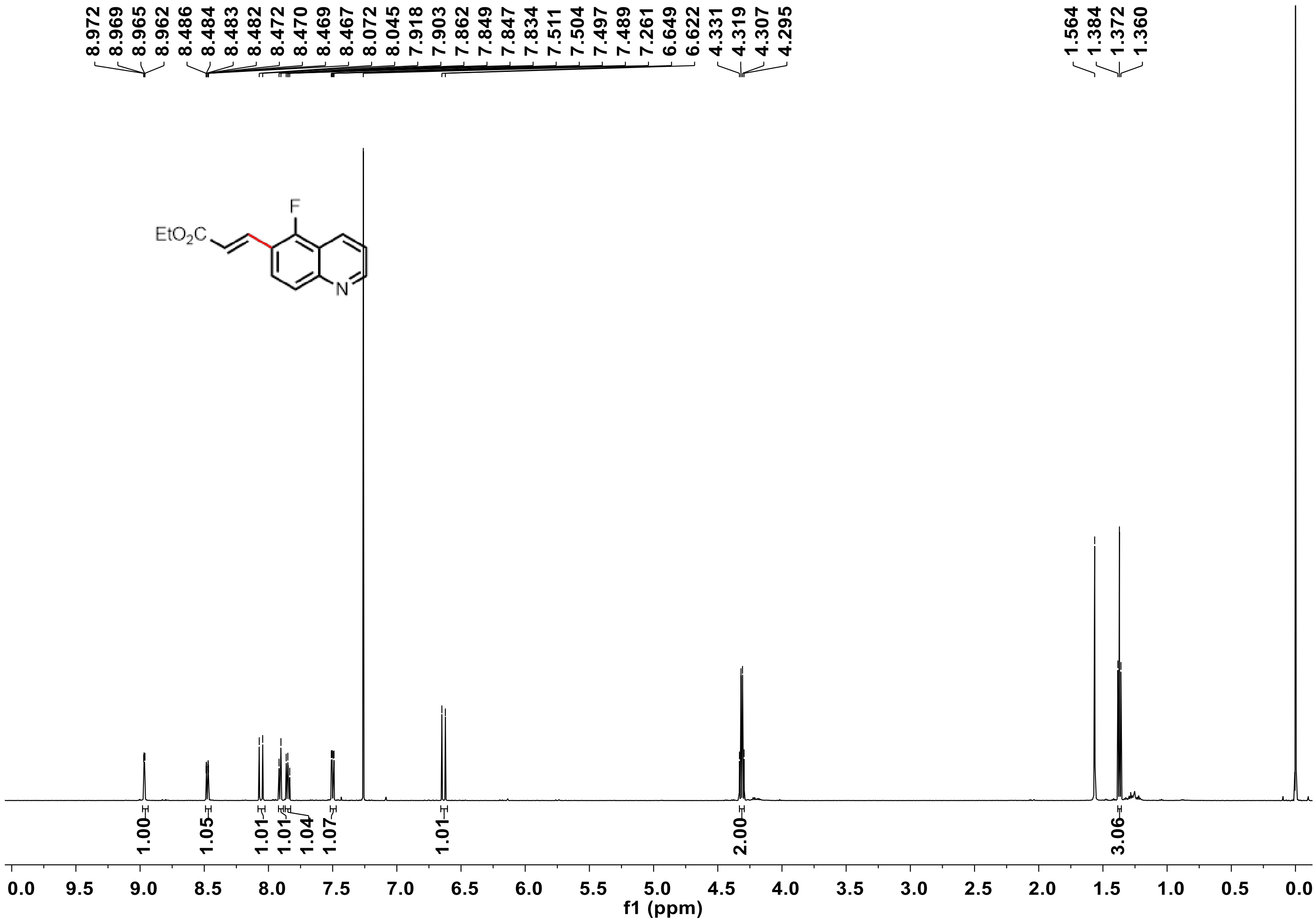
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2k**



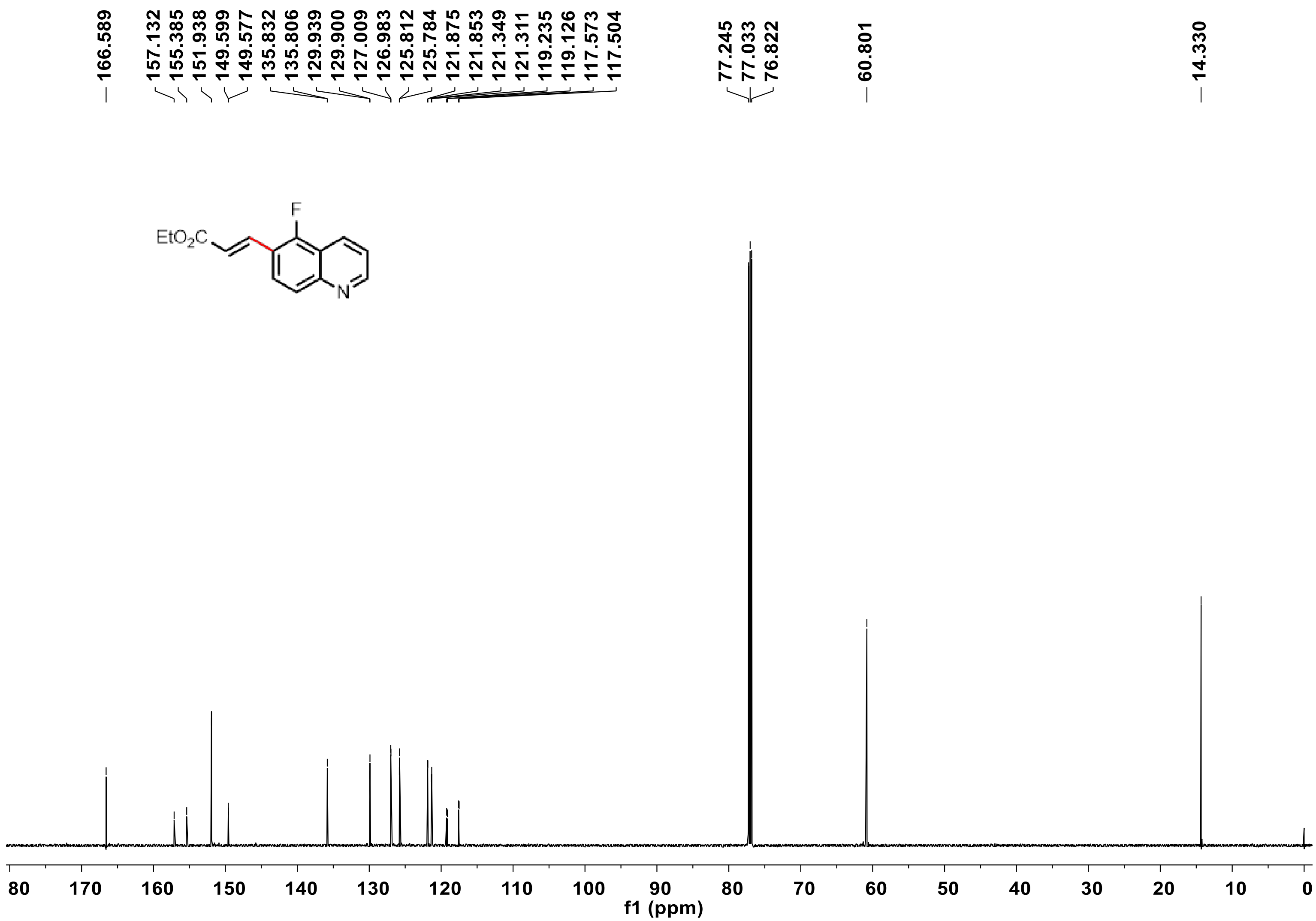
NOESY spectrum of **2k**



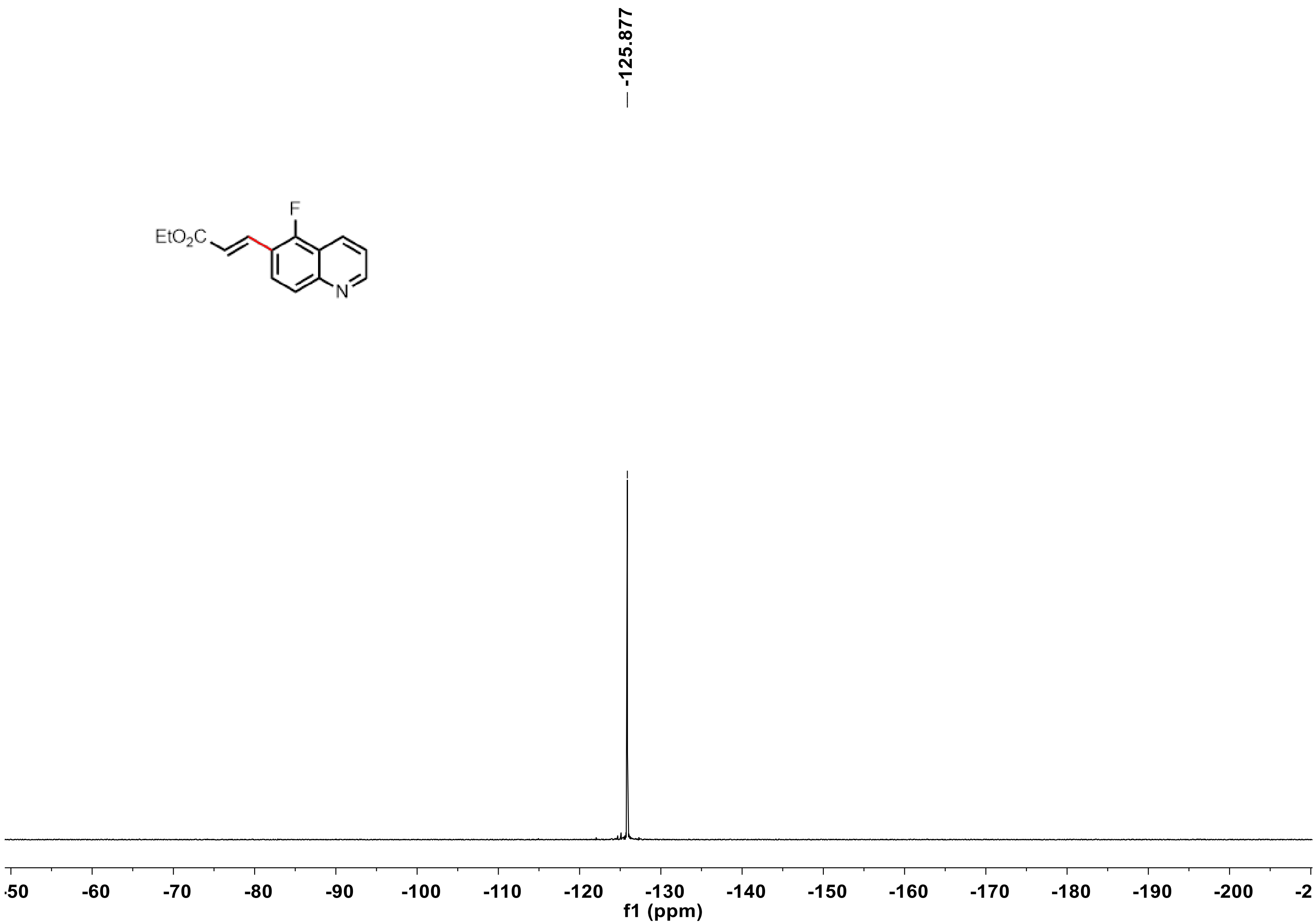
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2l**



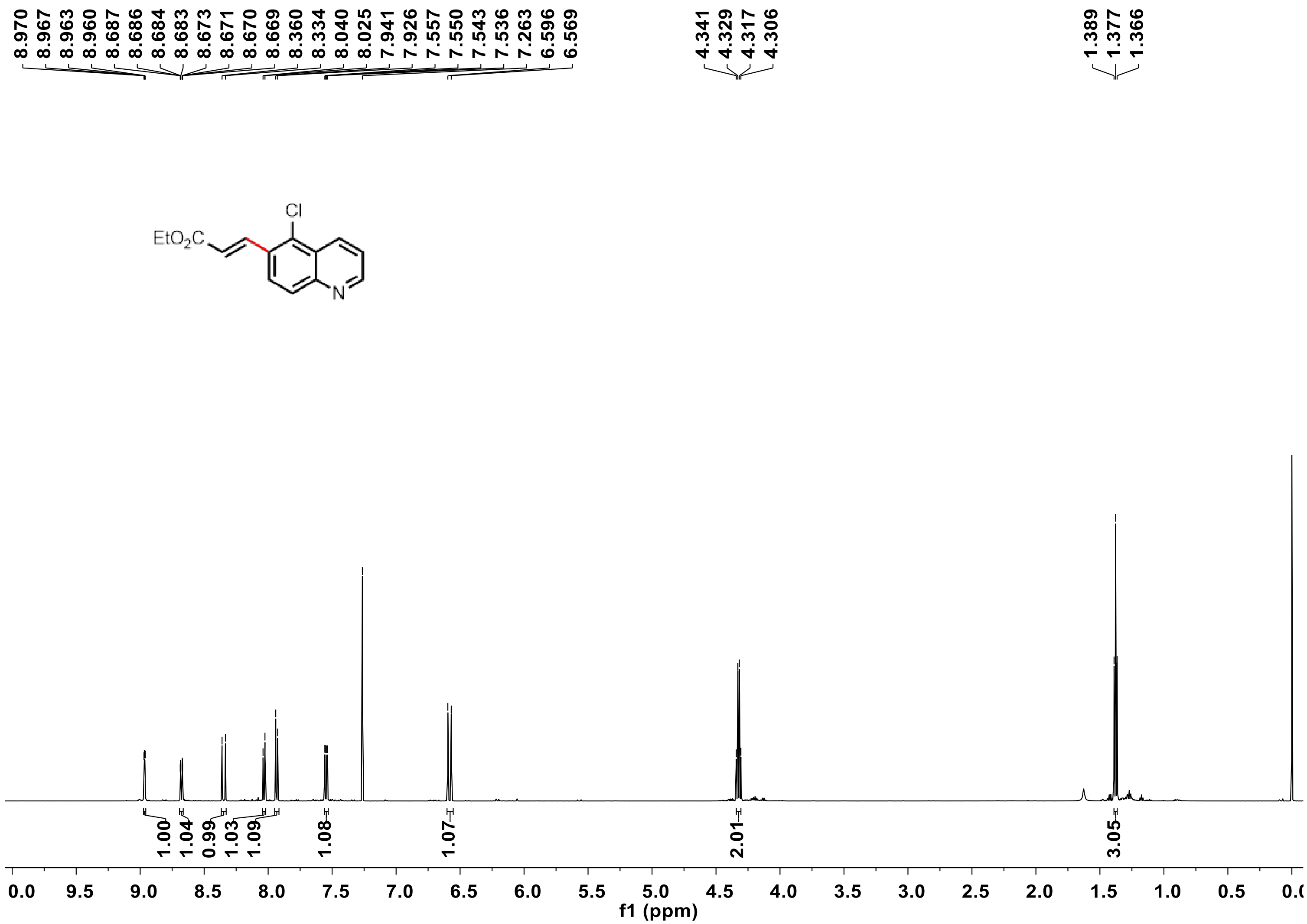
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2l**



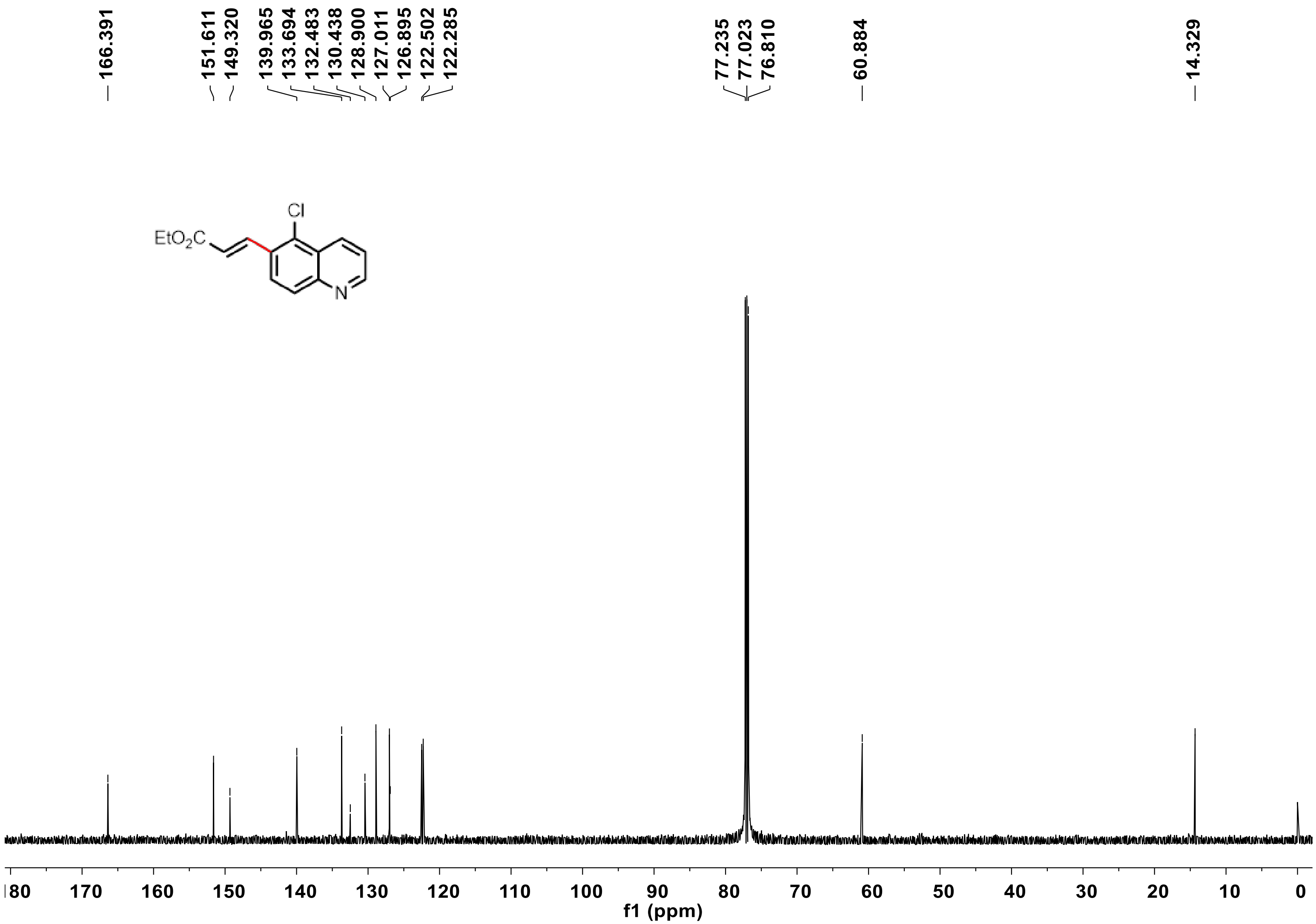
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2l**



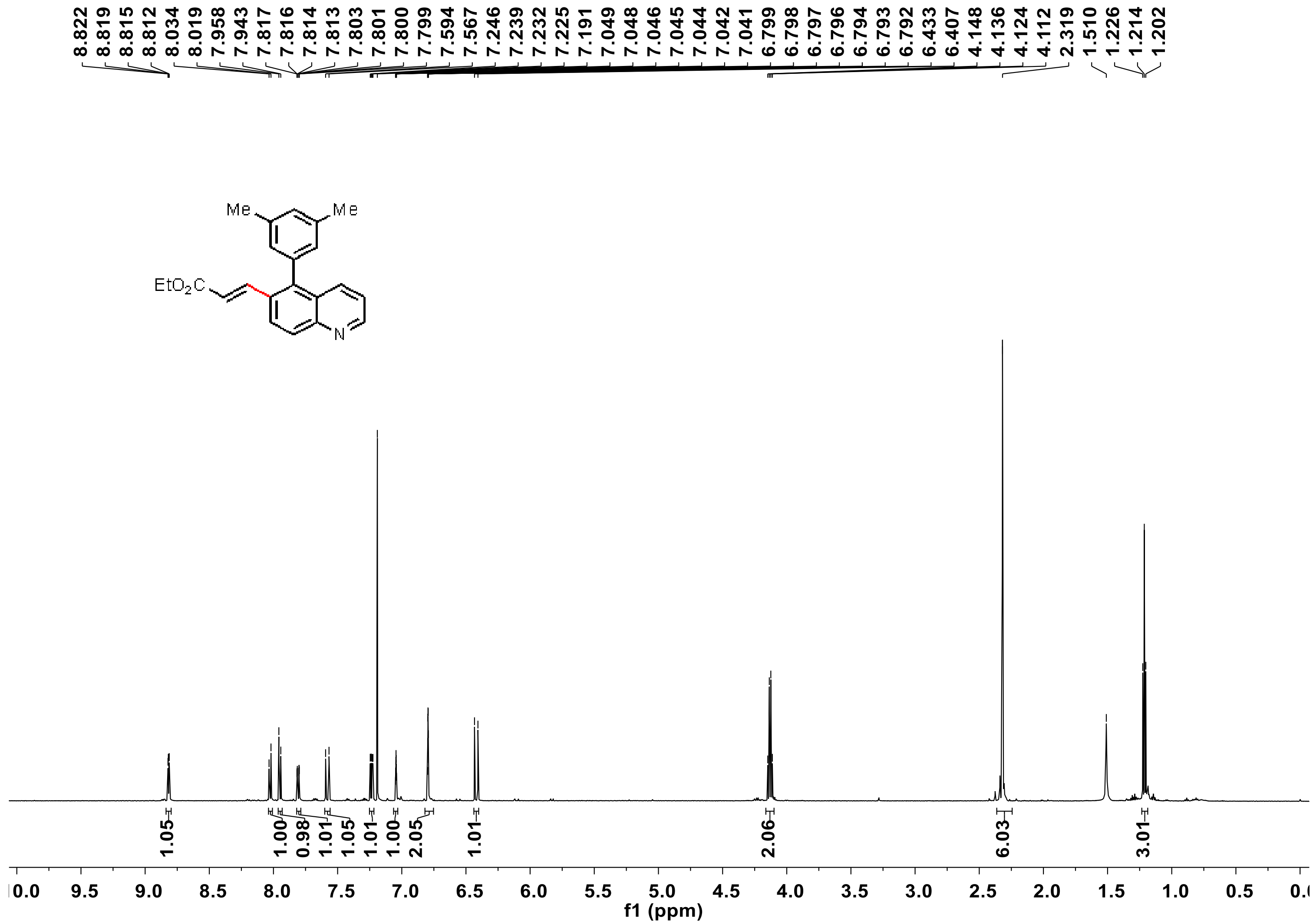
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2m**



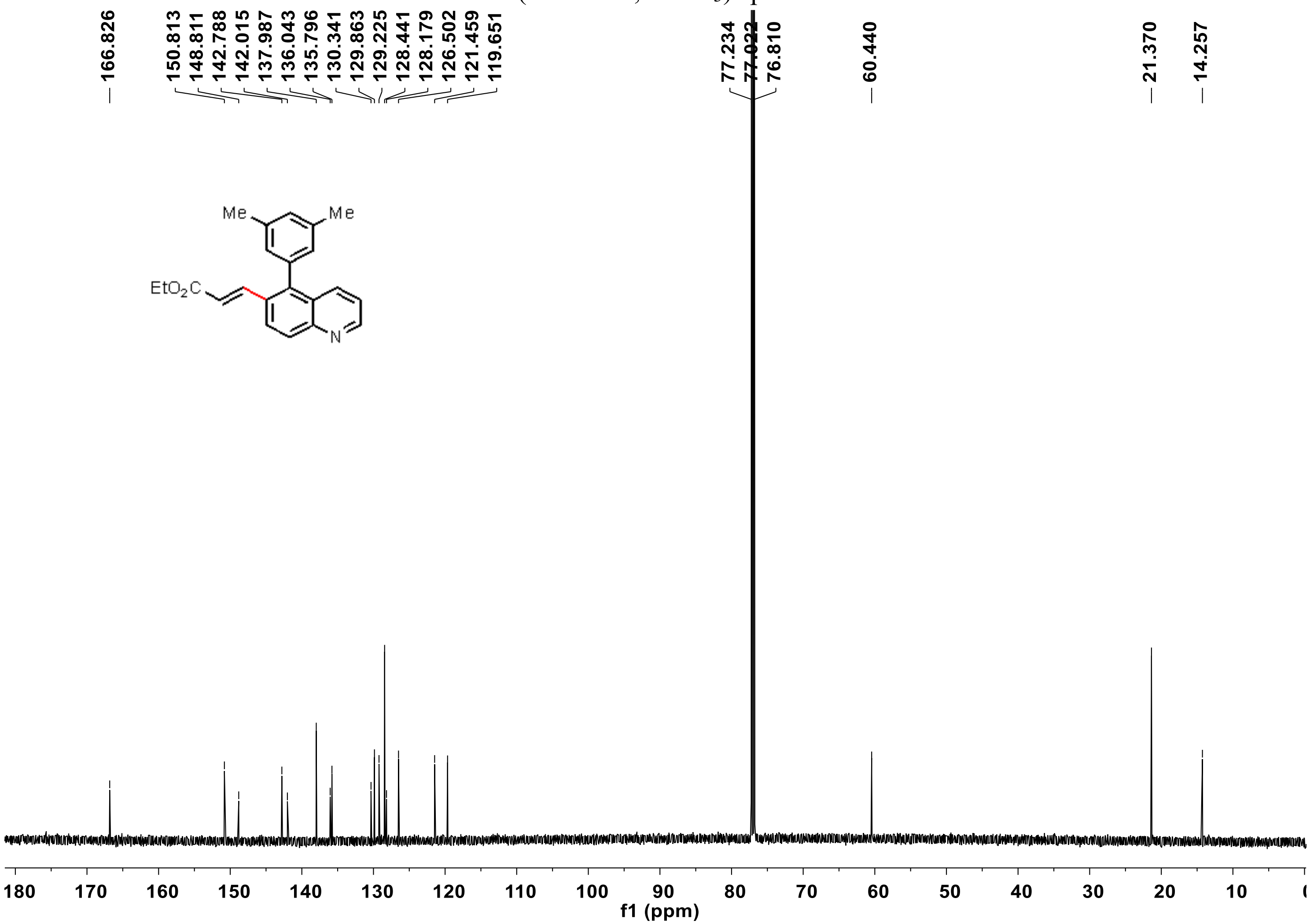
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2m**



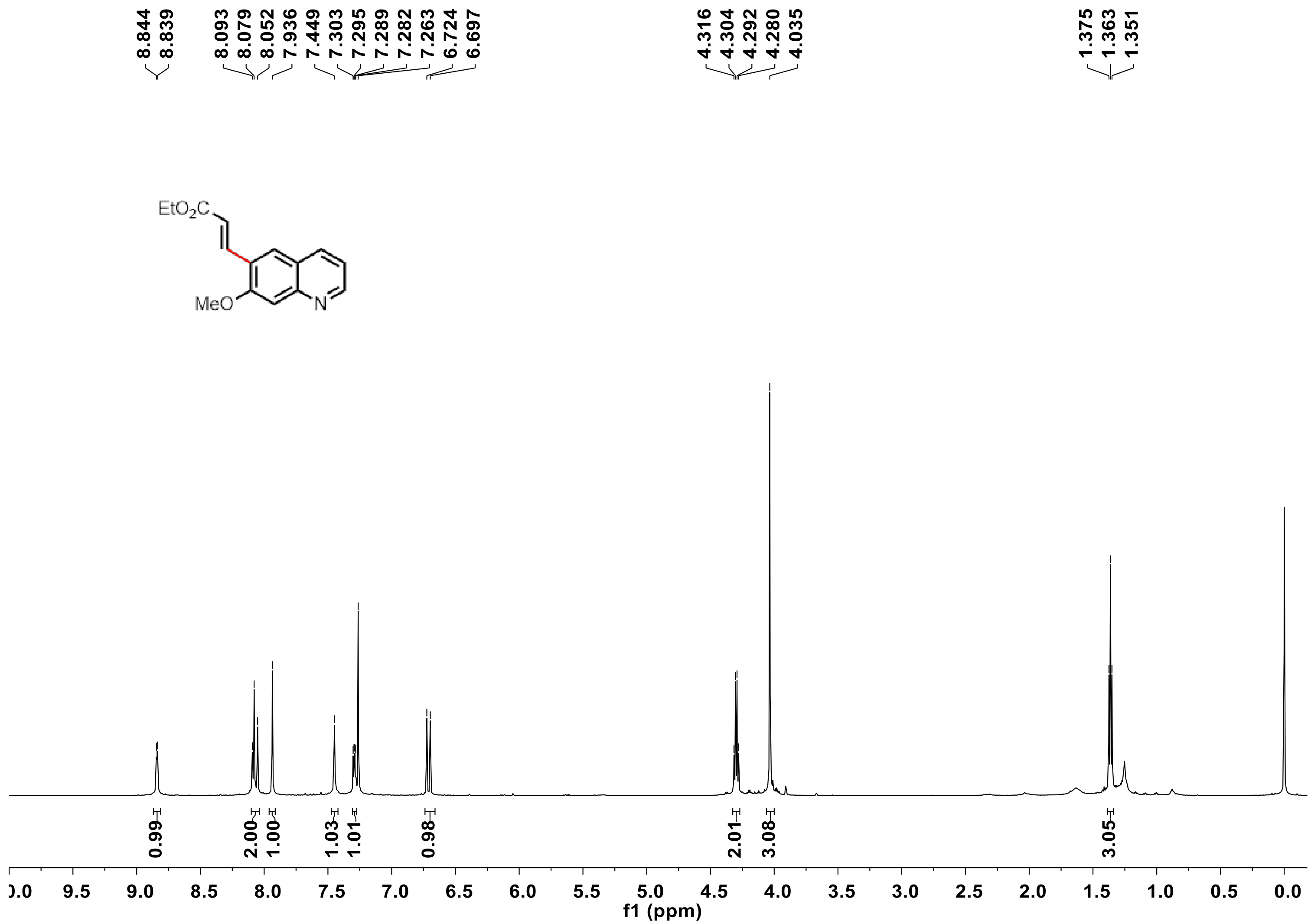
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2n**



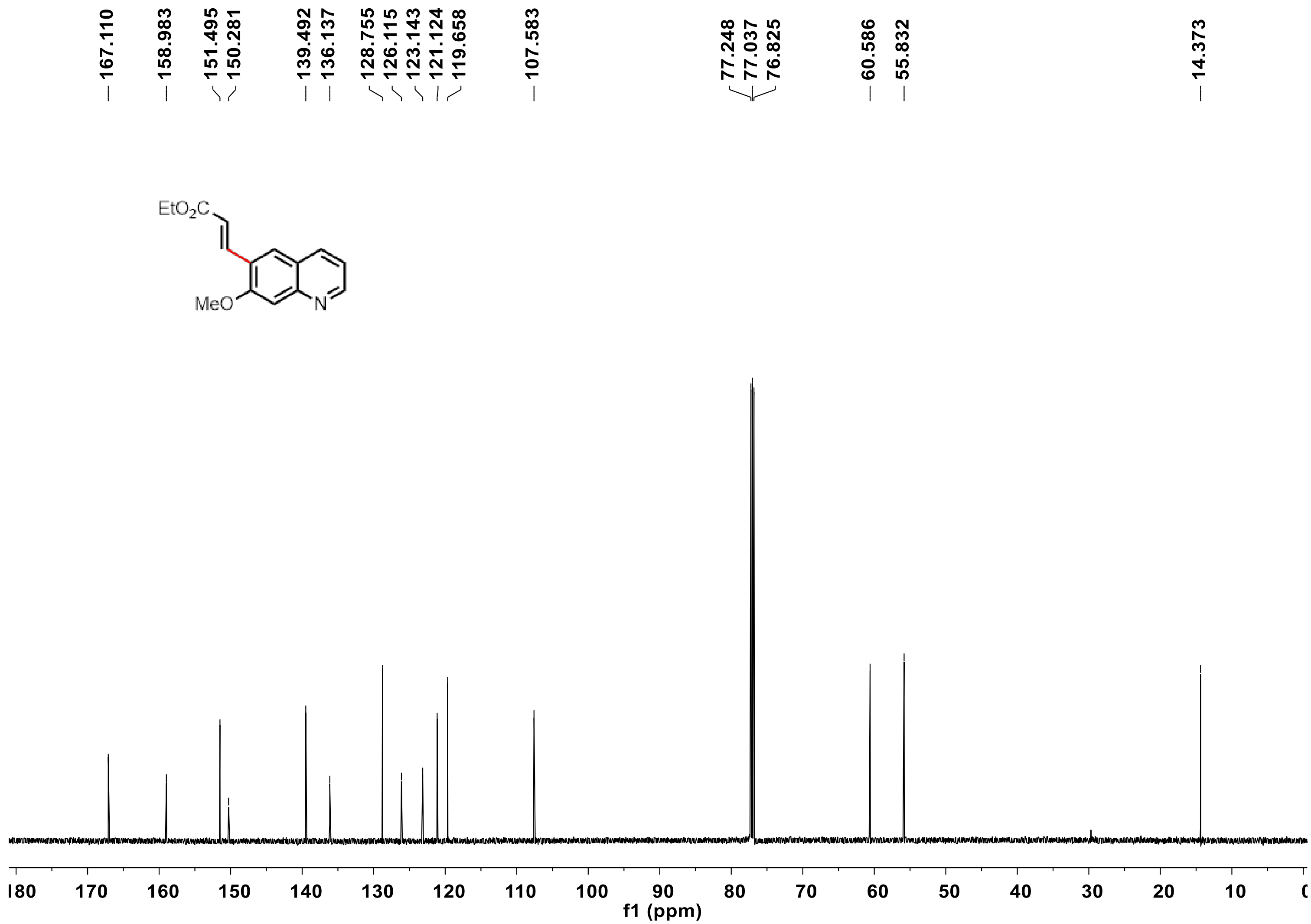
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2n**



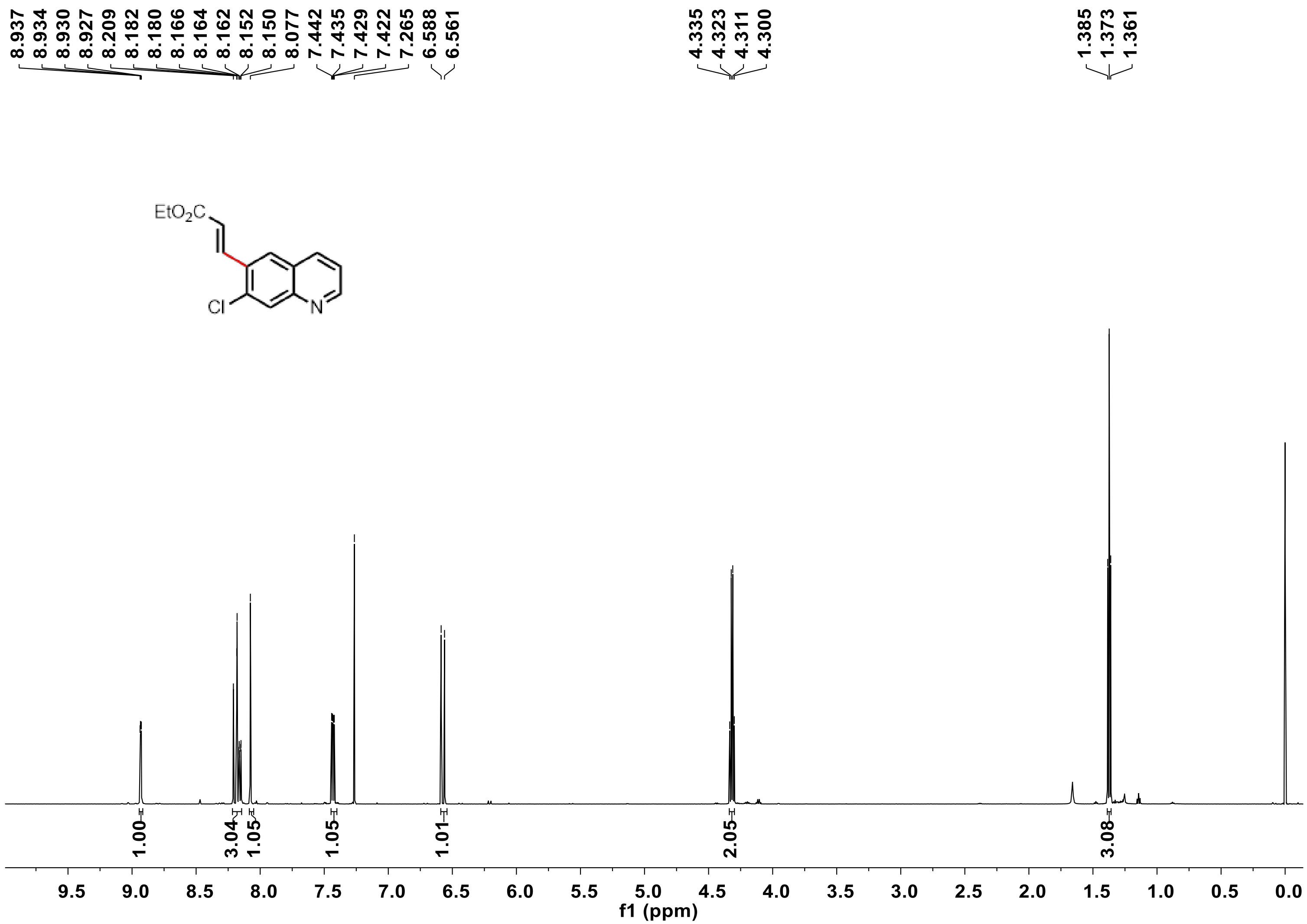
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2o**



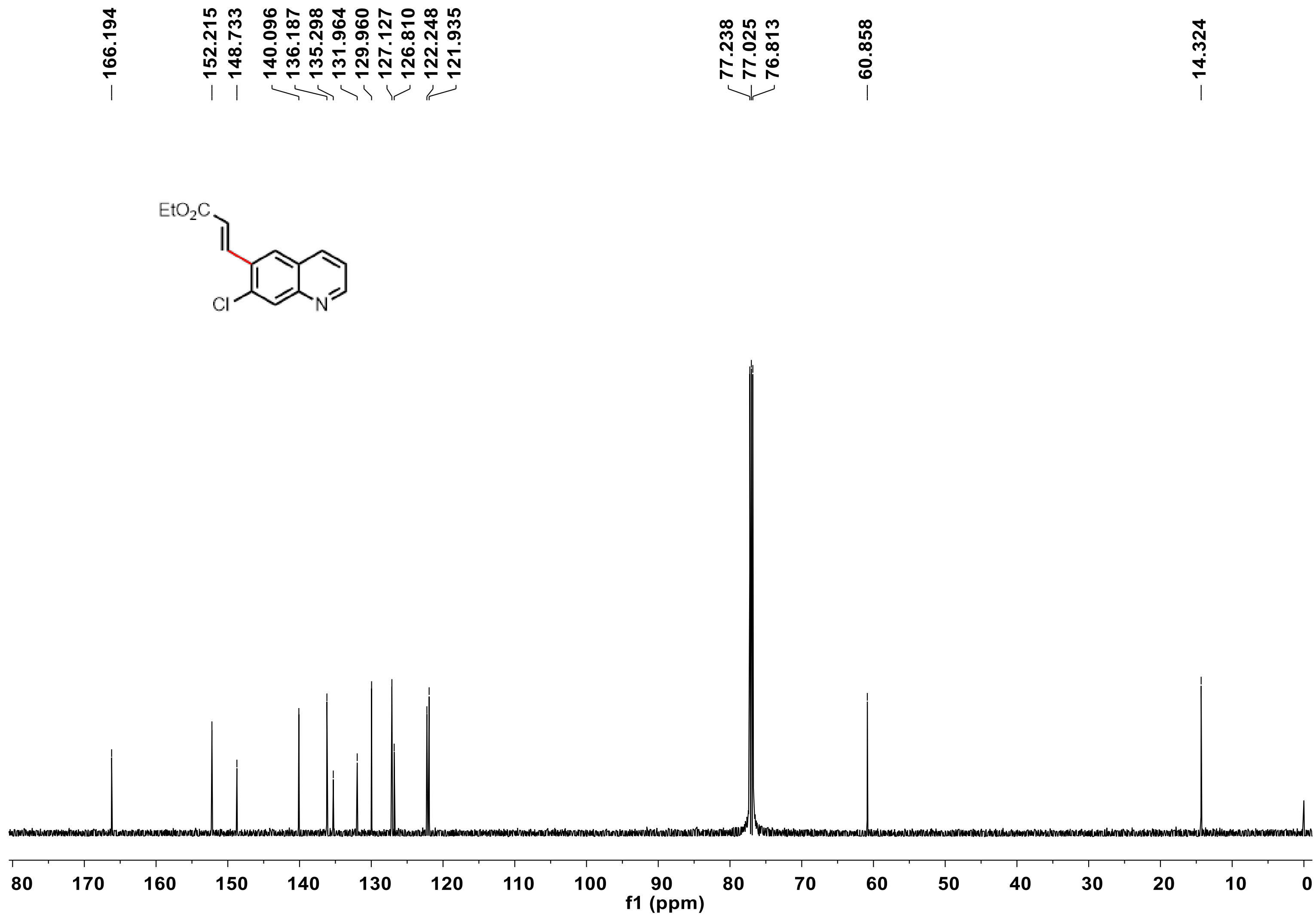
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2o**



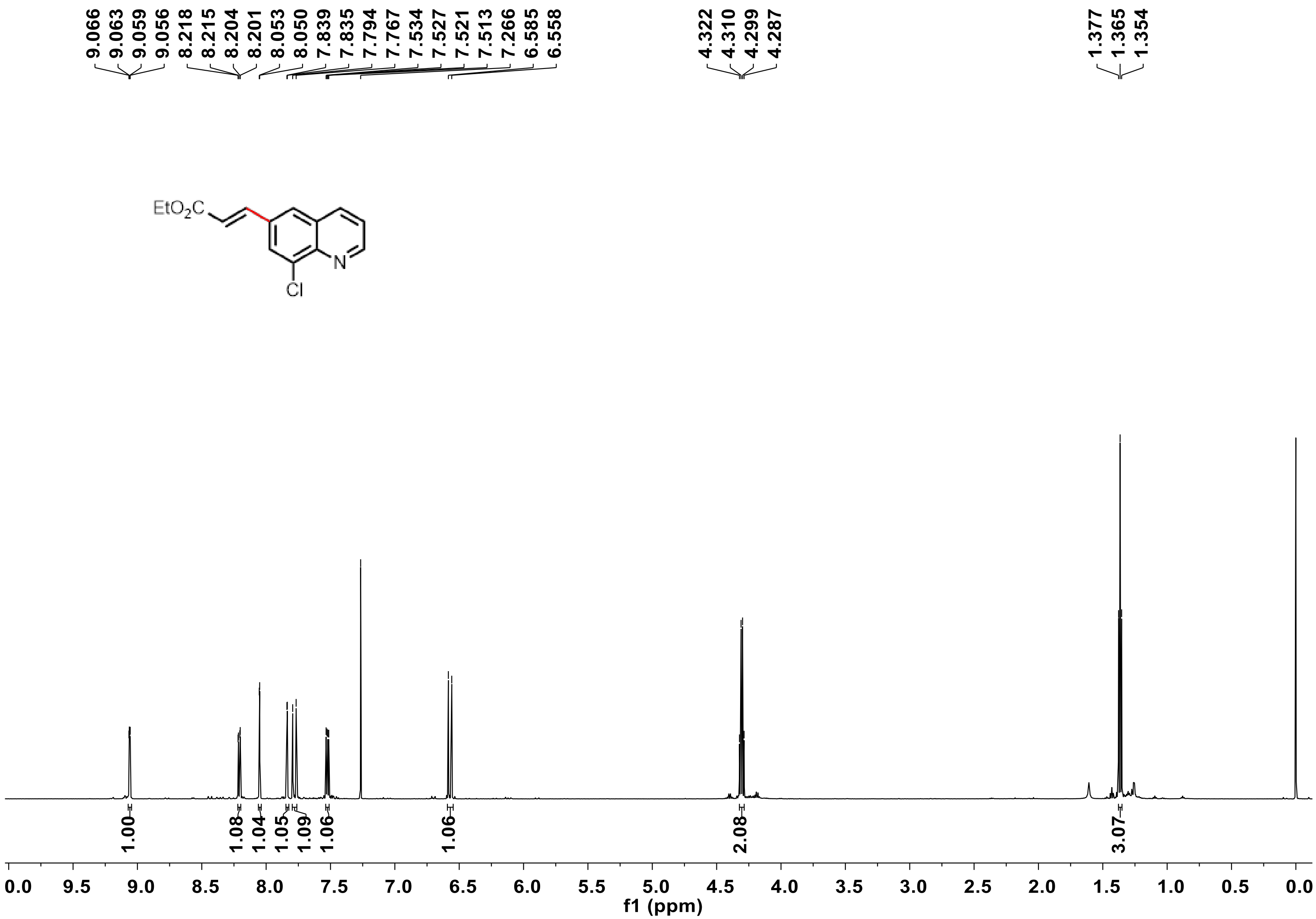
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2p**



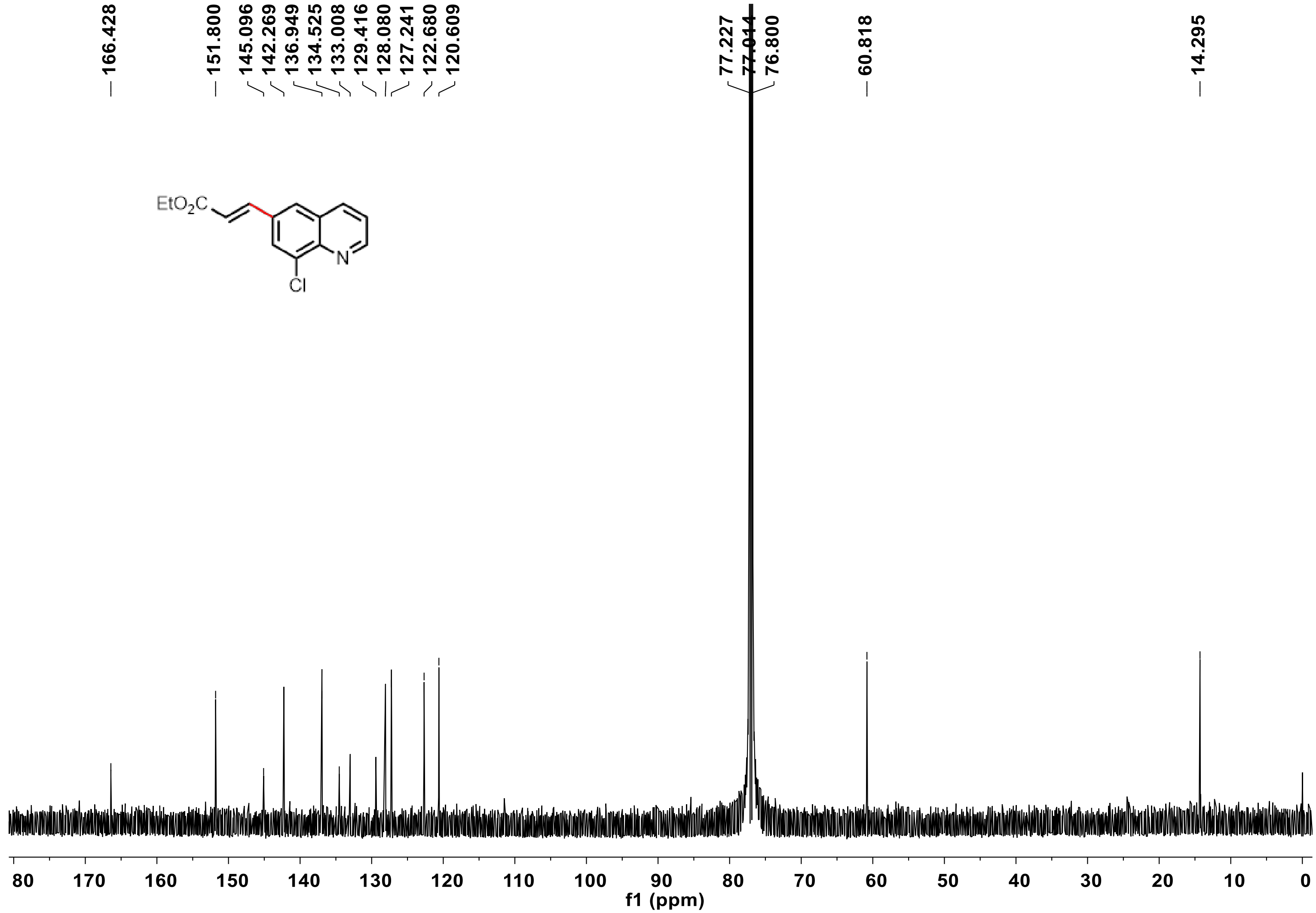
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2p**



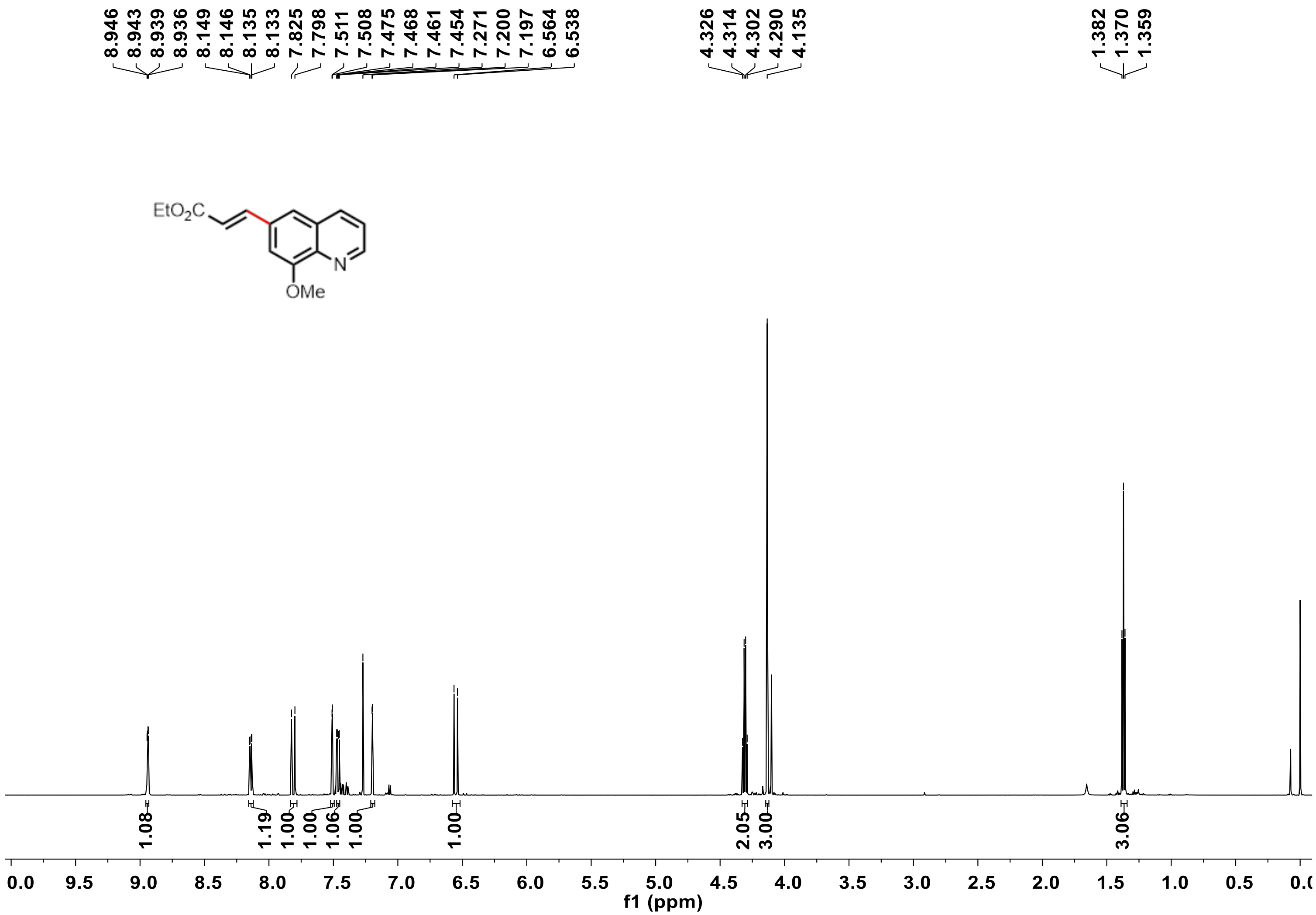
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2q**



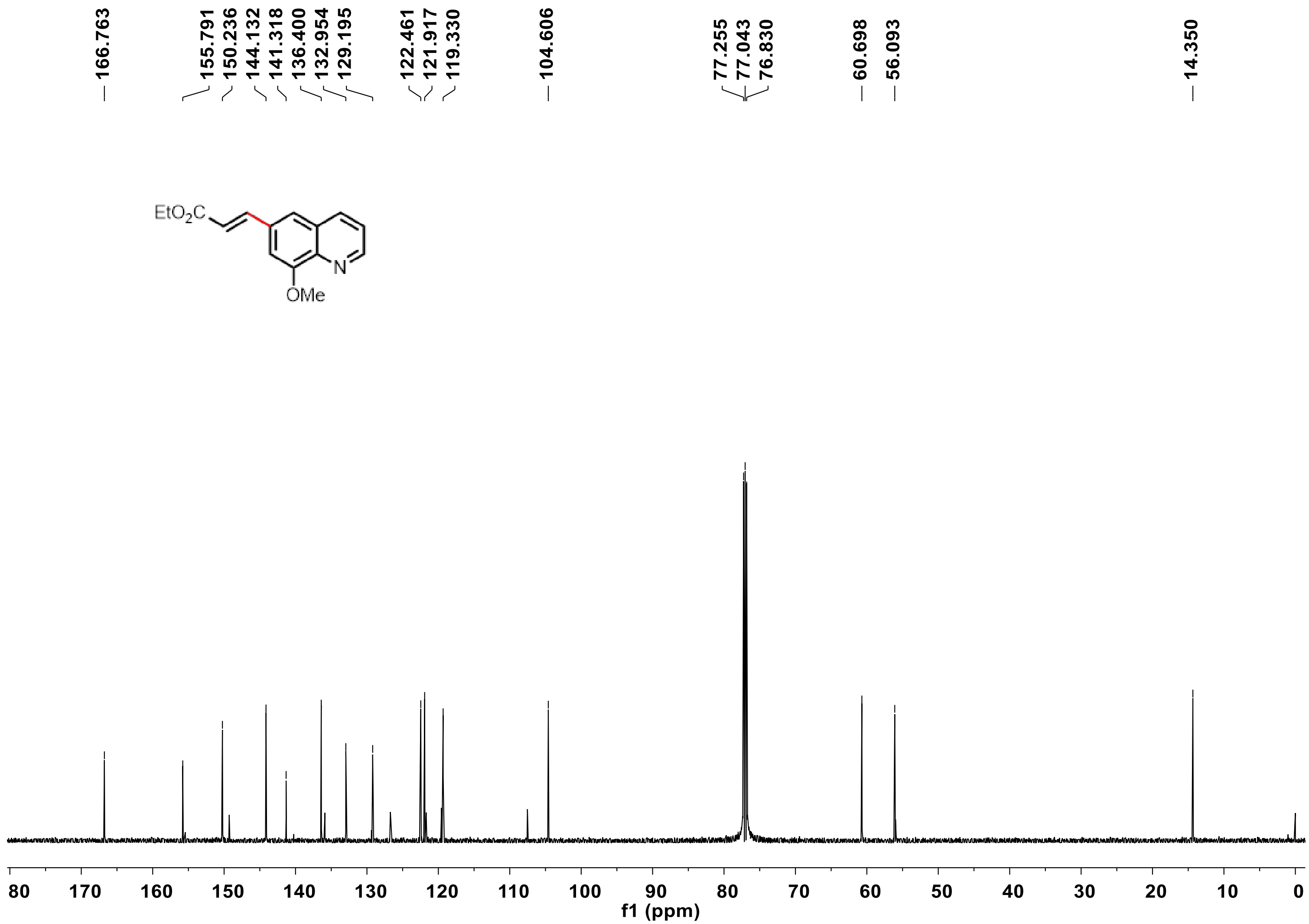
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2q**



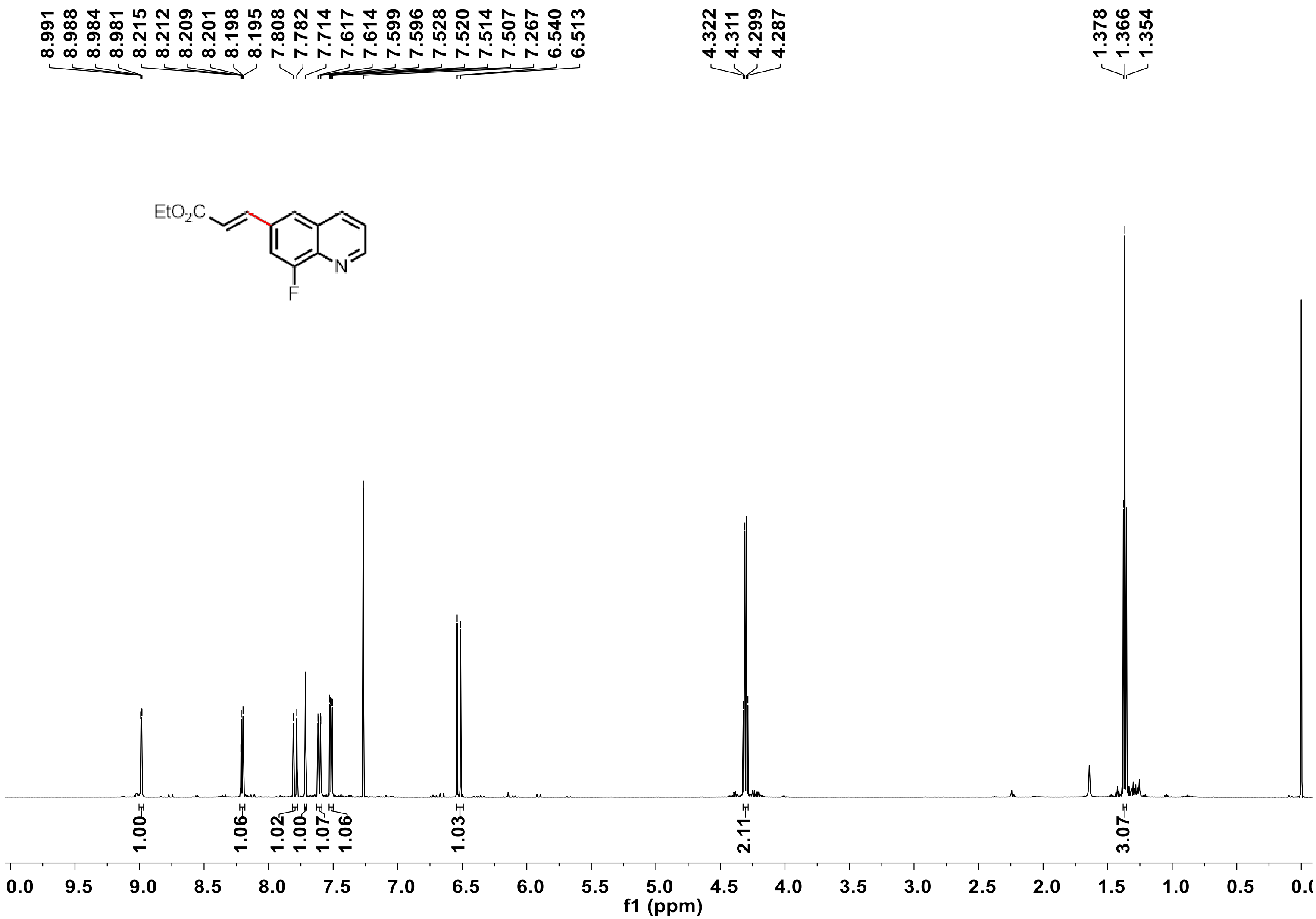
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2r**



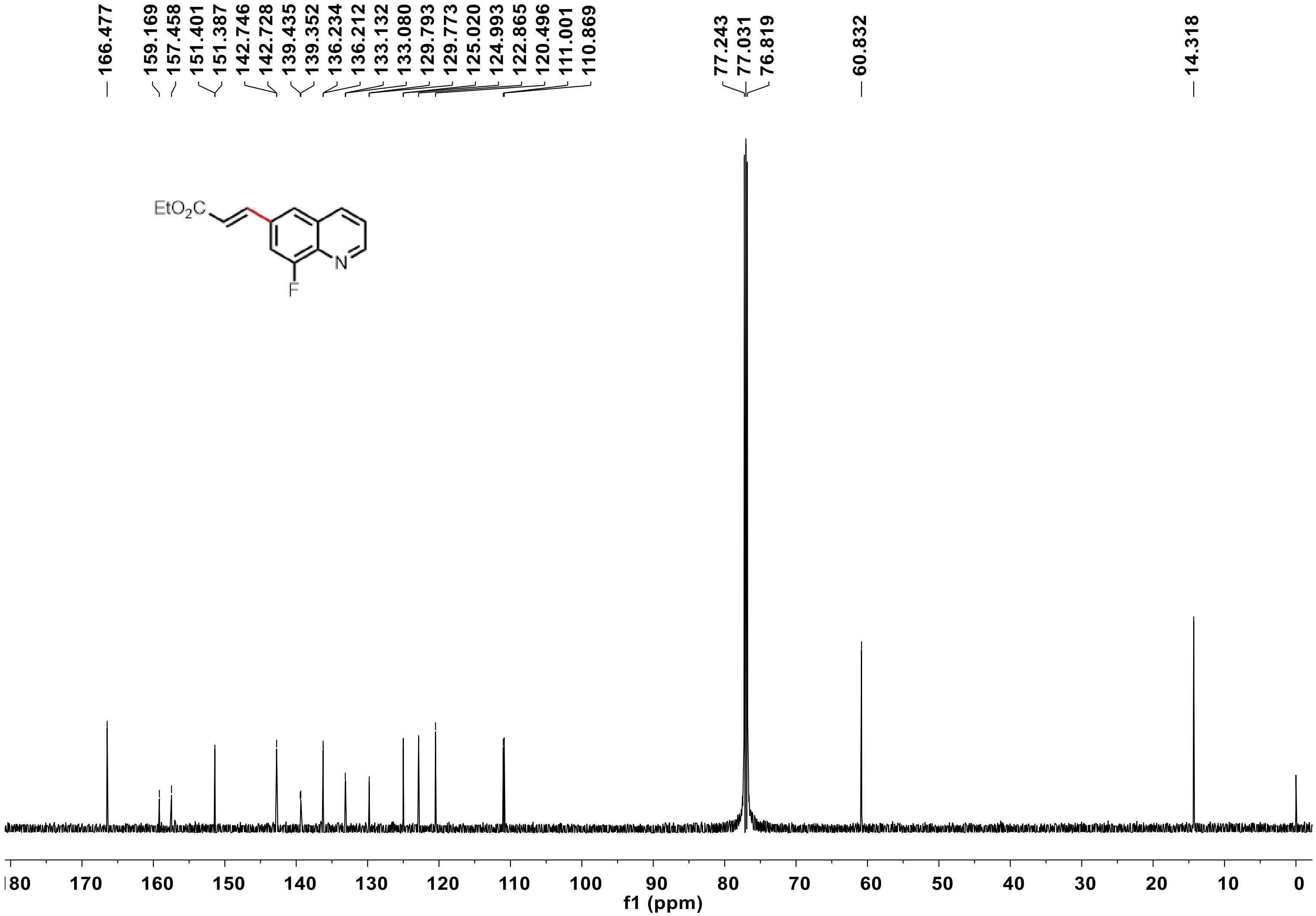
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2r**



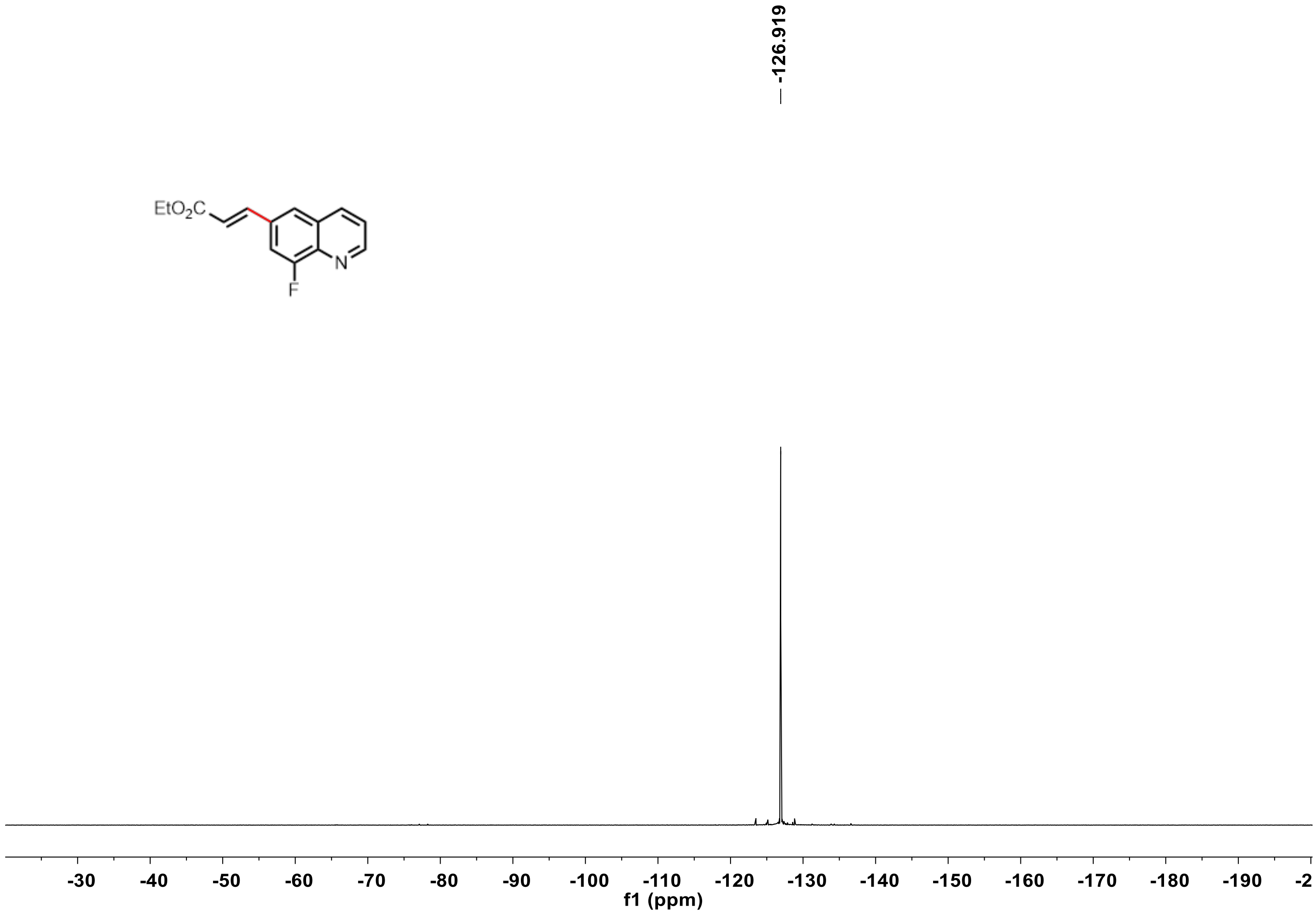
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2s**



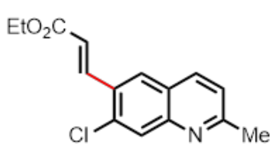
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2s**

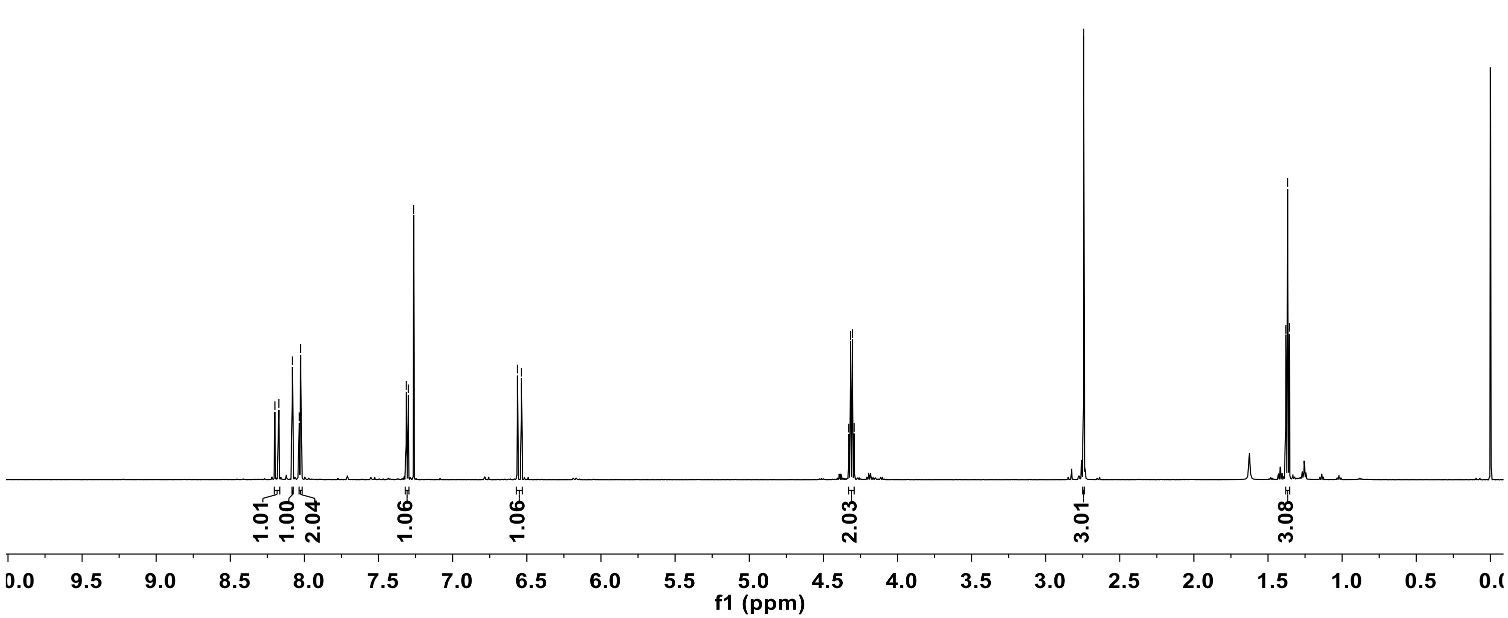


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2s**

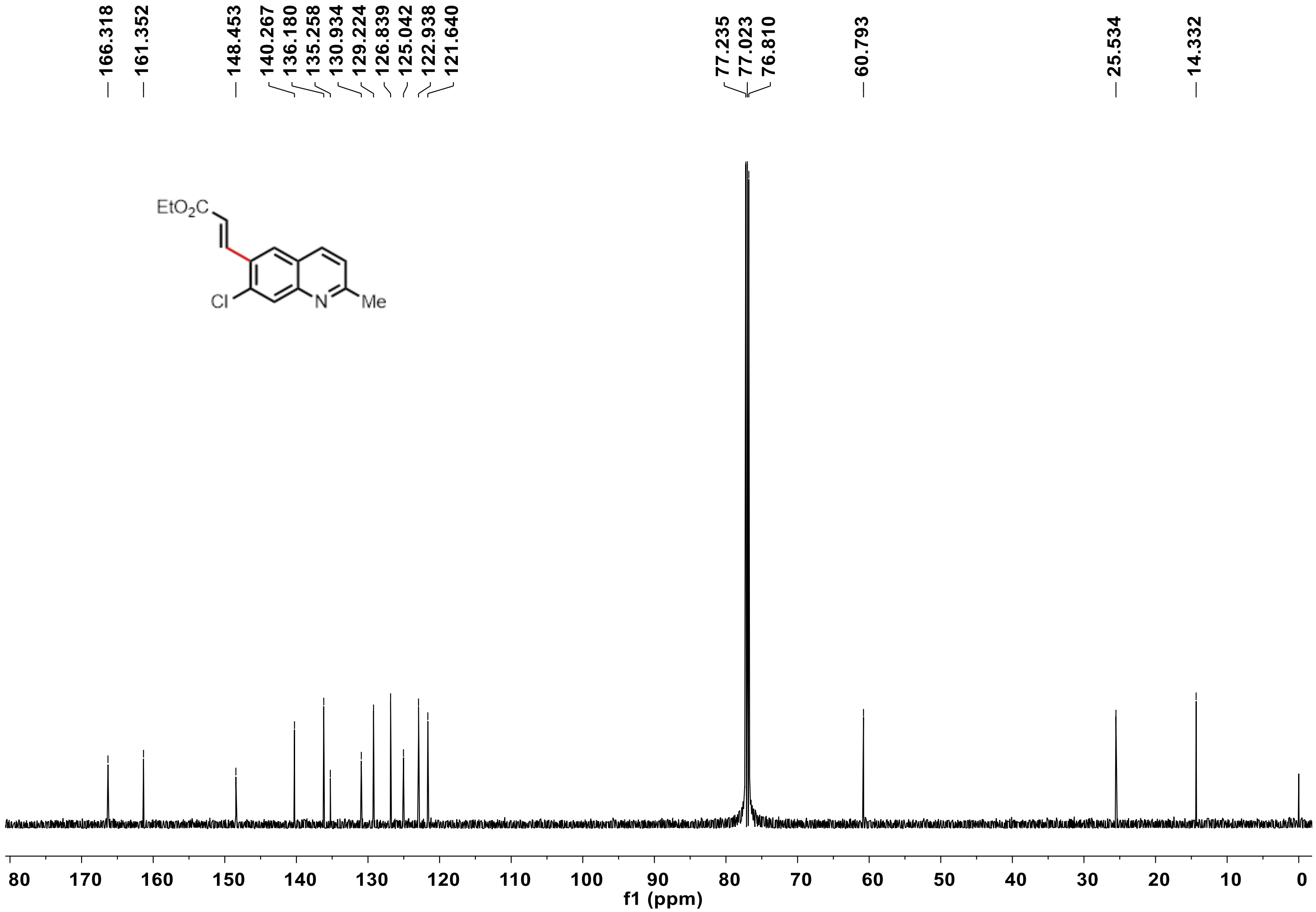


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2t**

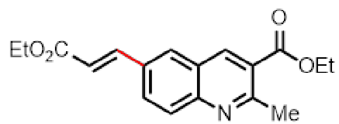


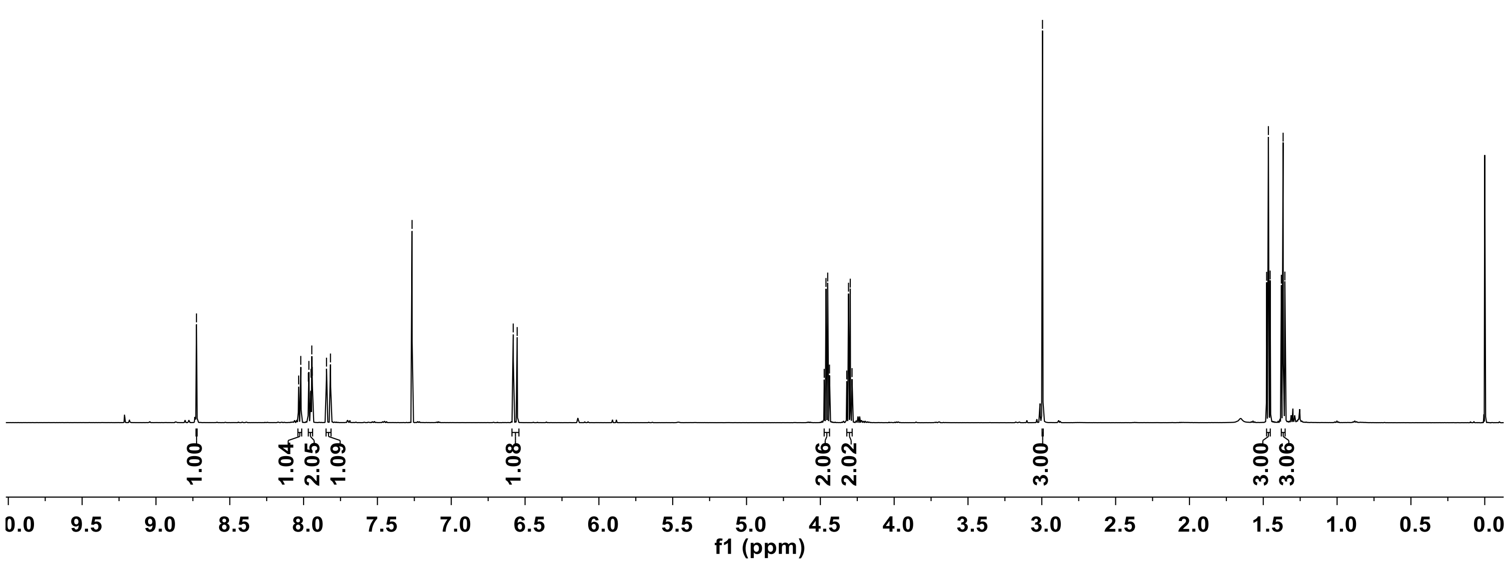


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2t**

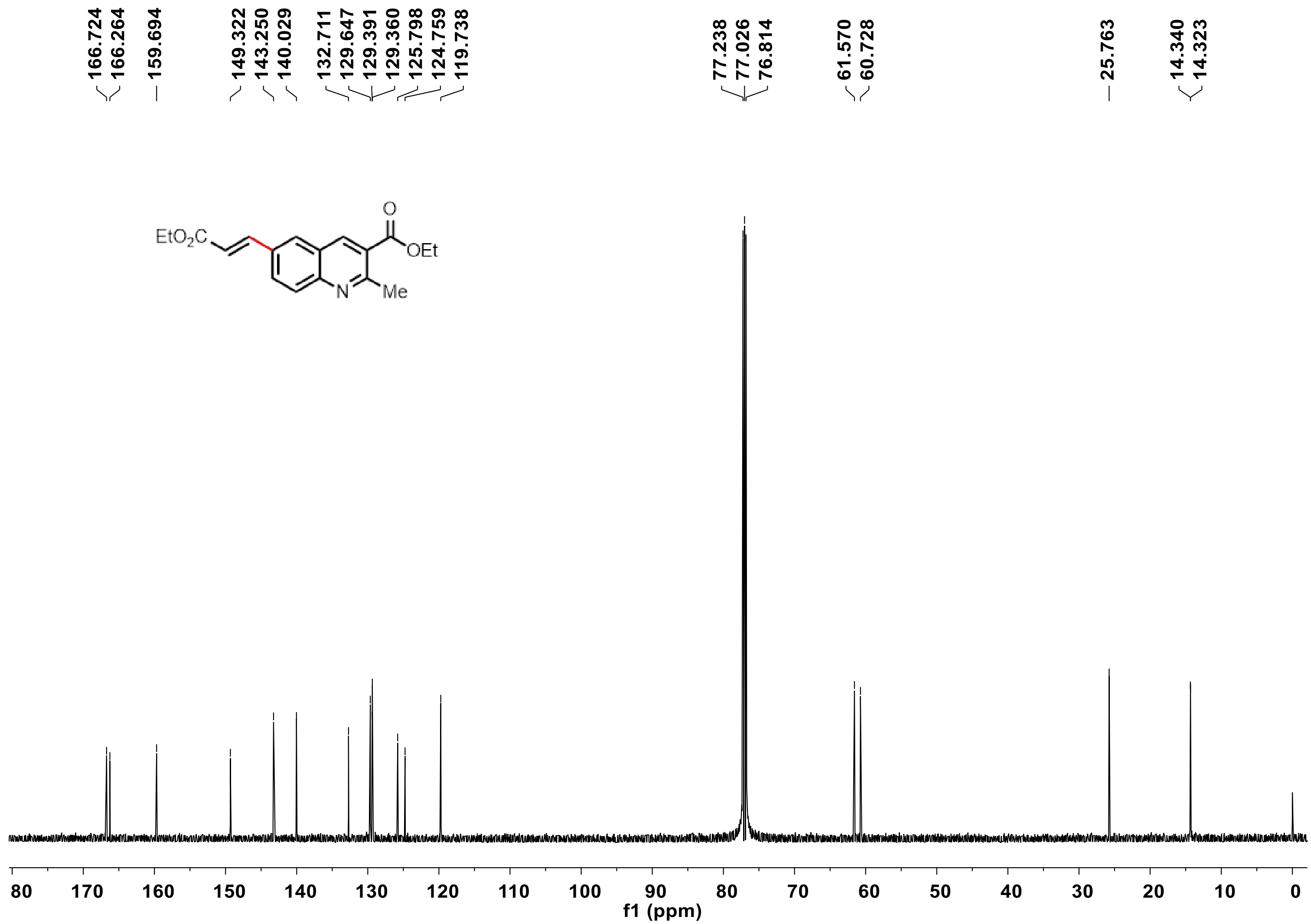


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2u**

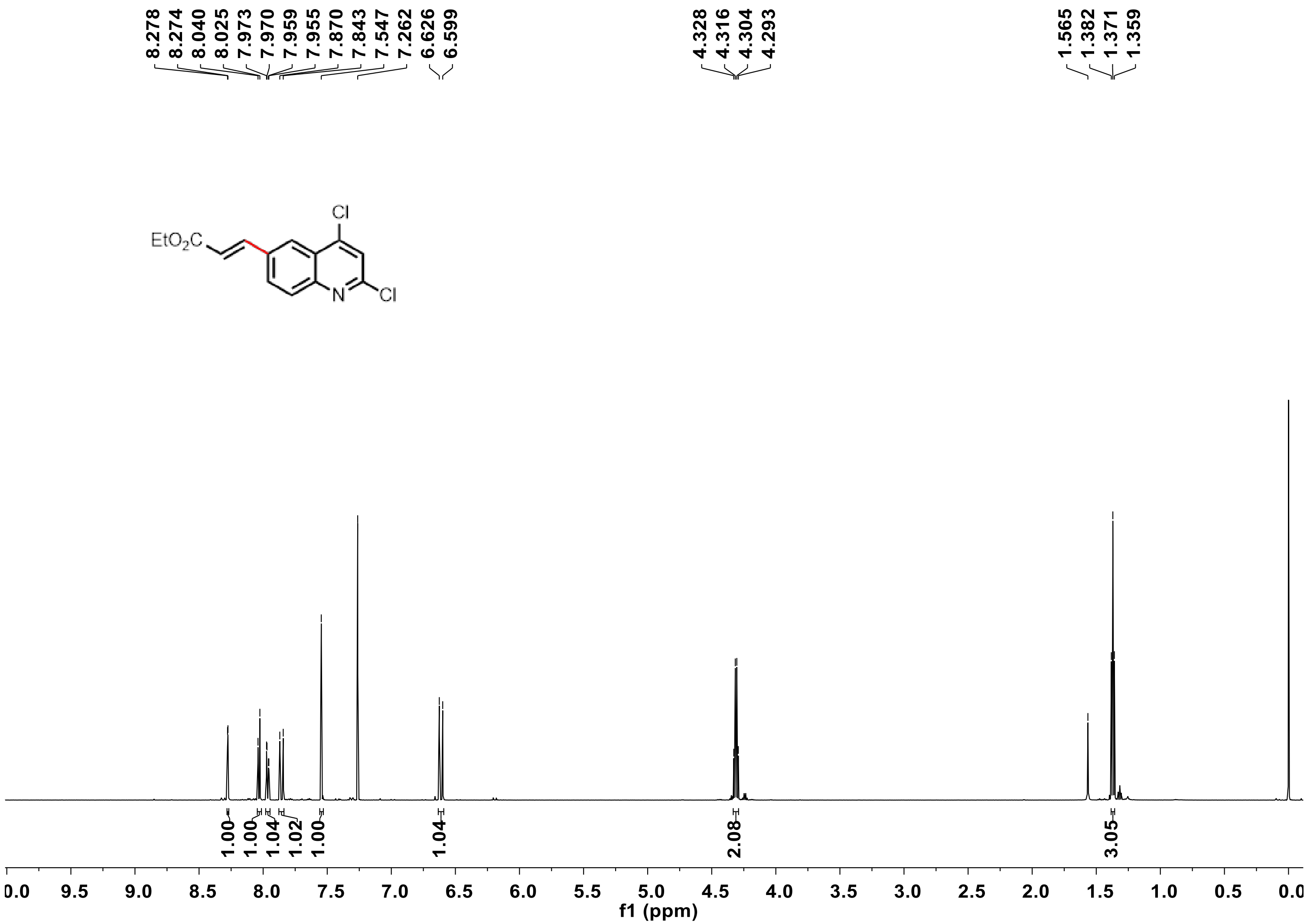




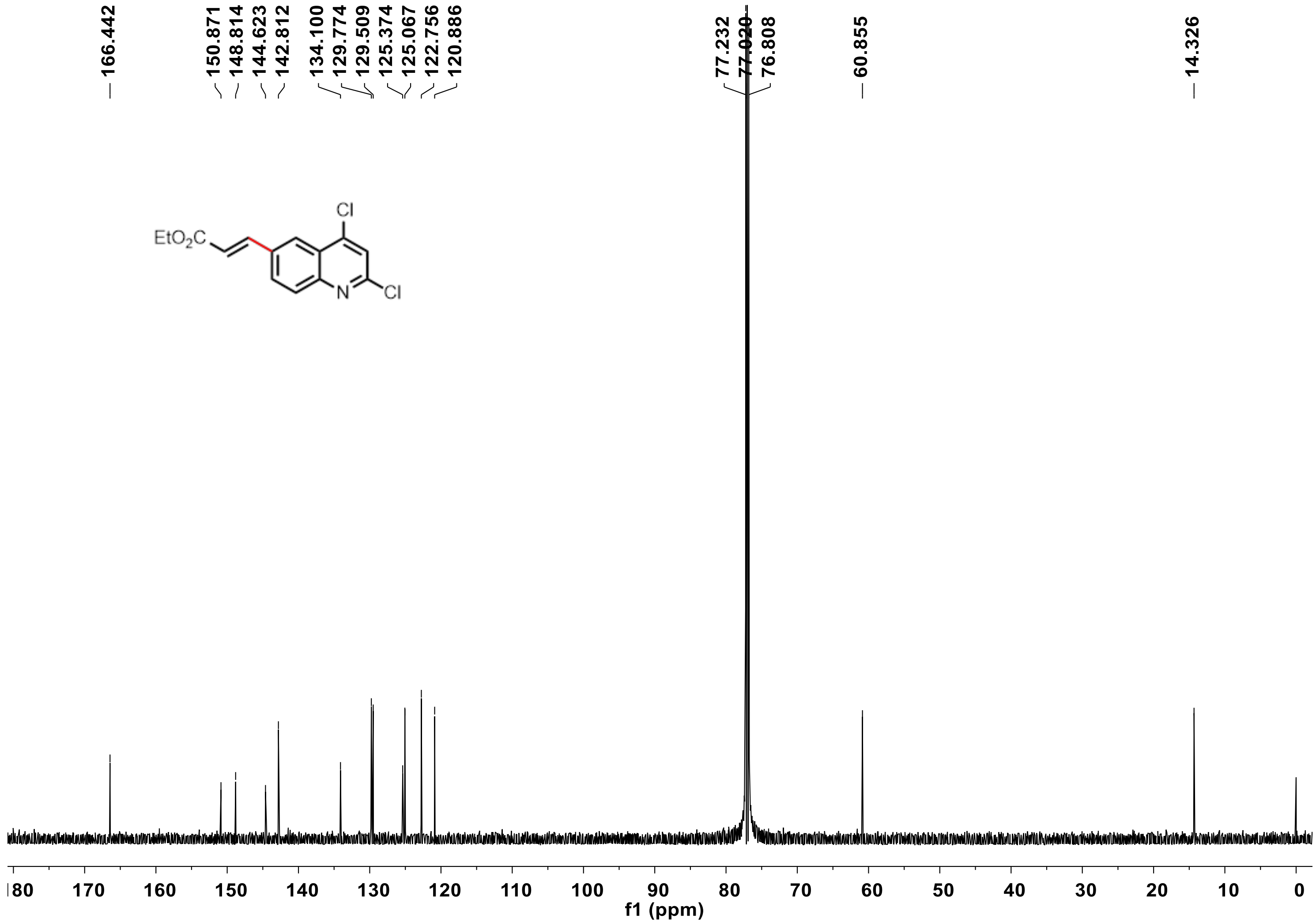
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2u**



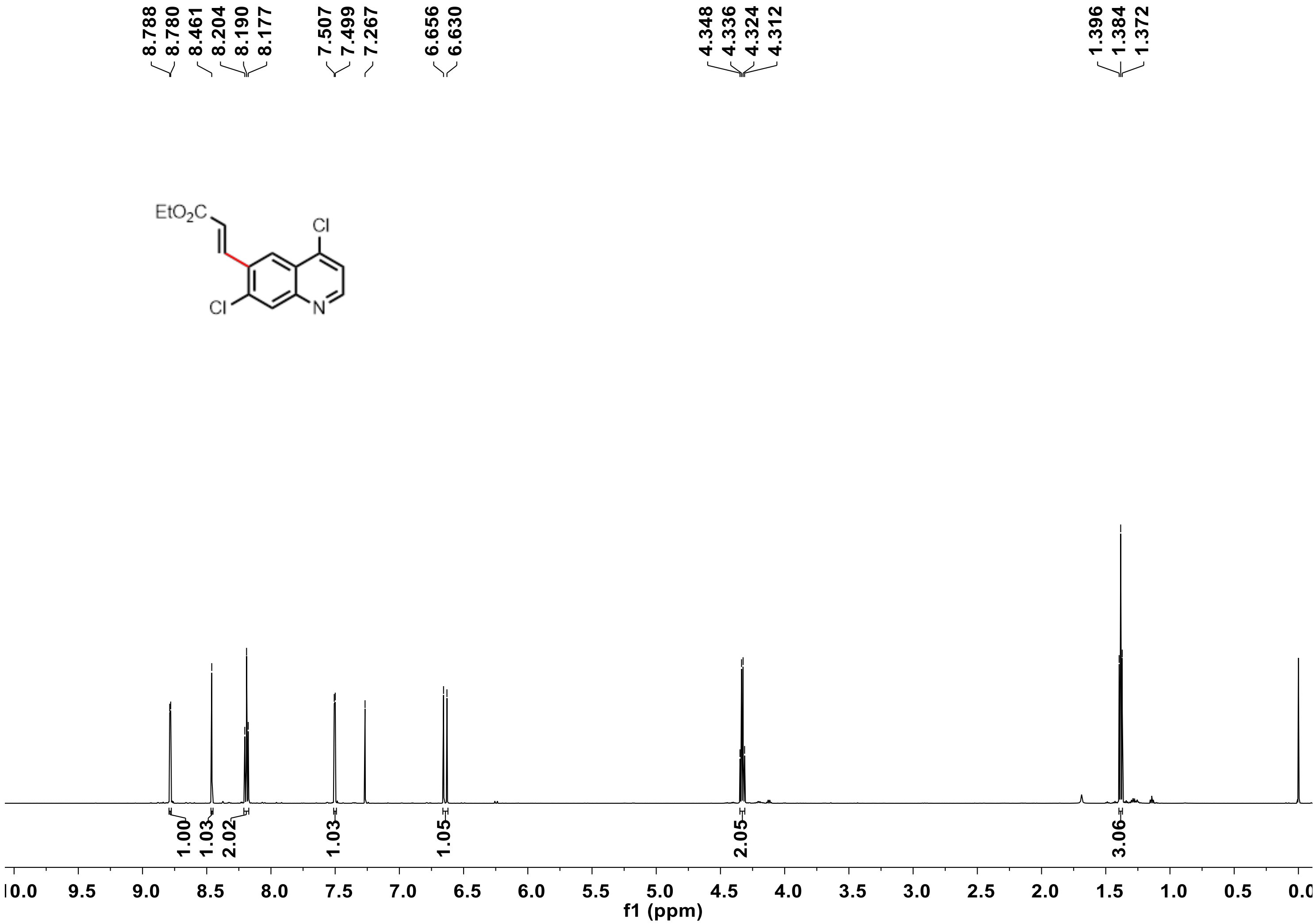
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2v**



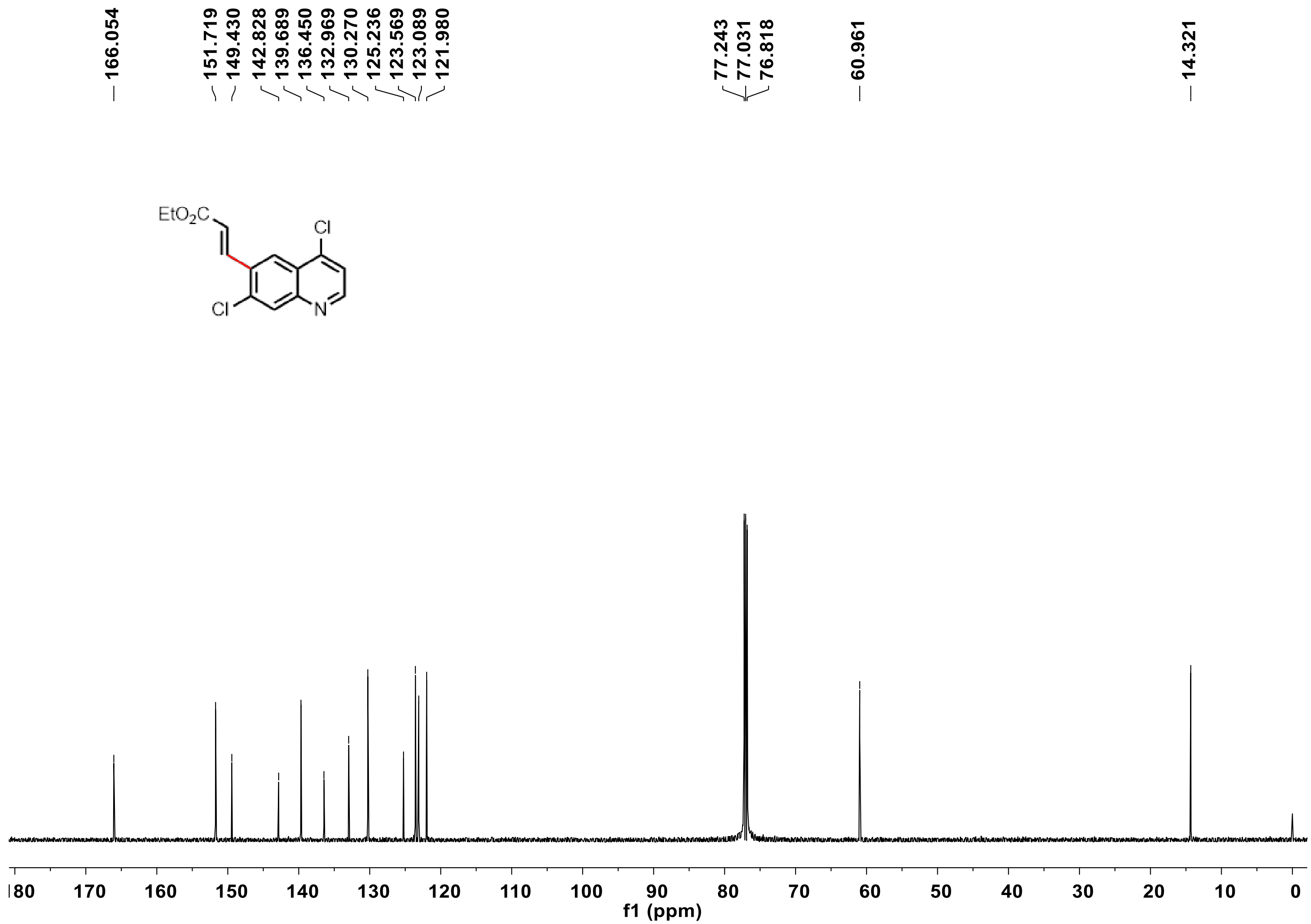
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2v**



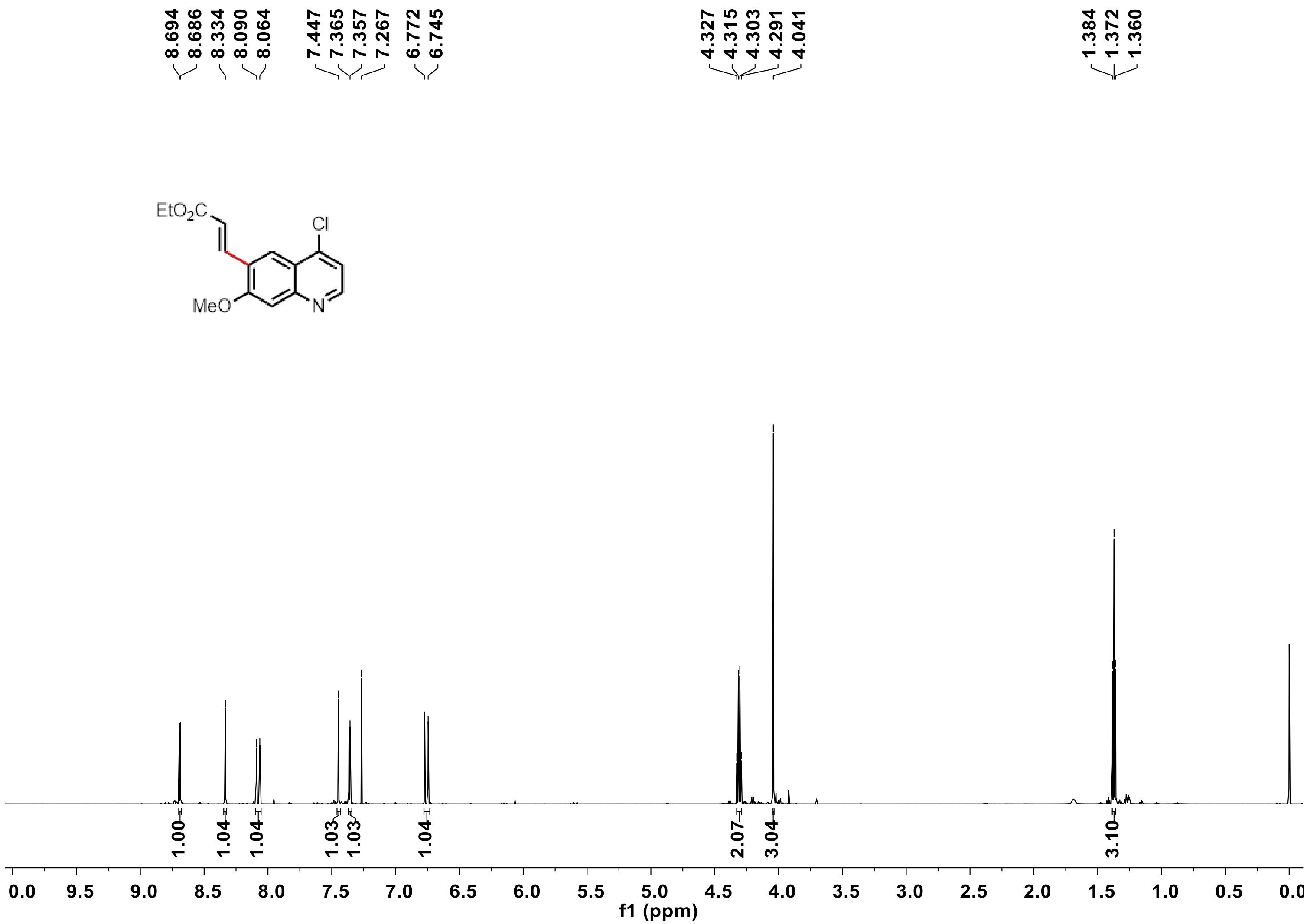
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2w**



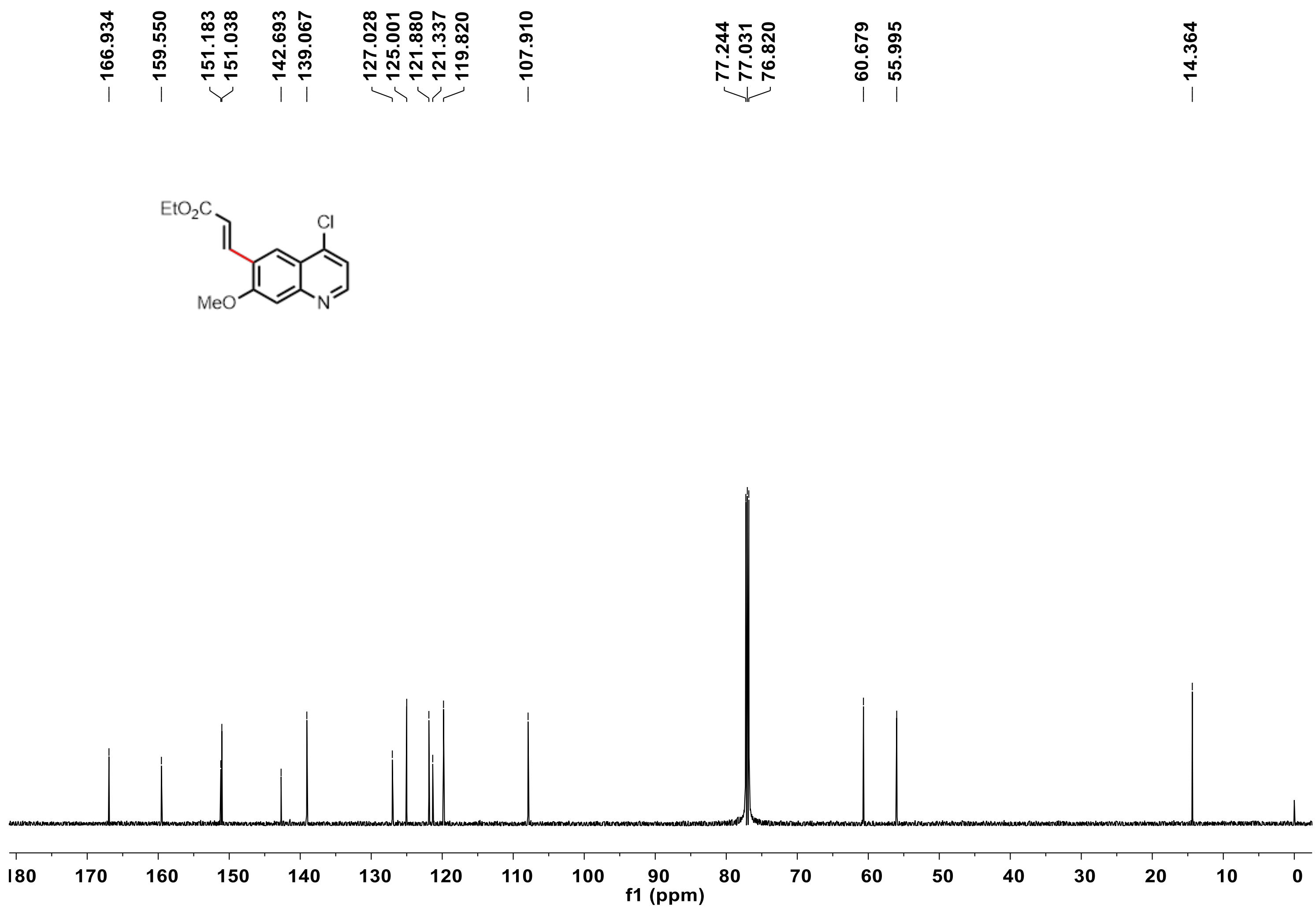
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2w**



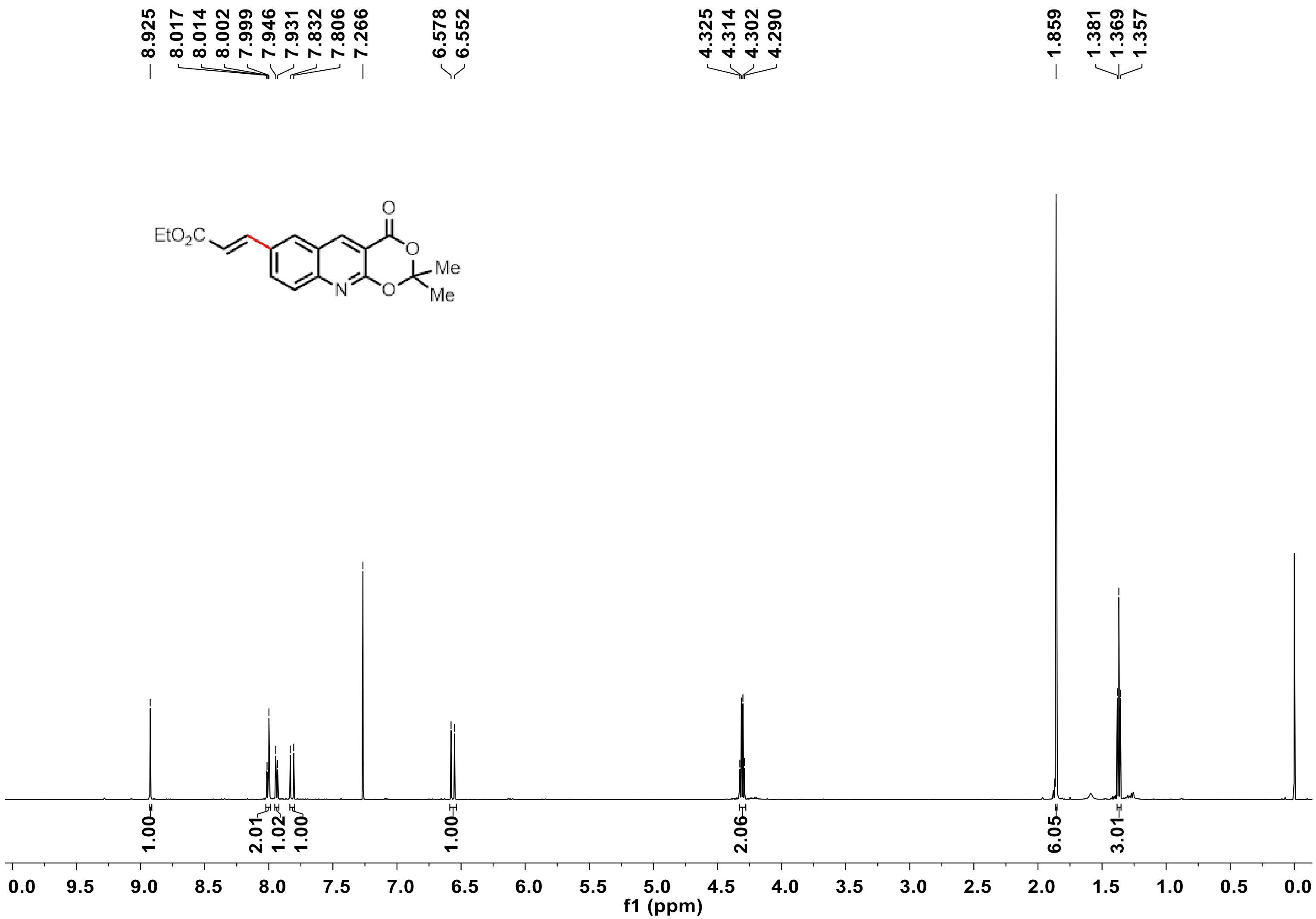
^1H NMR (600 MHz, $CDCl_3$) spectrum of **2x**



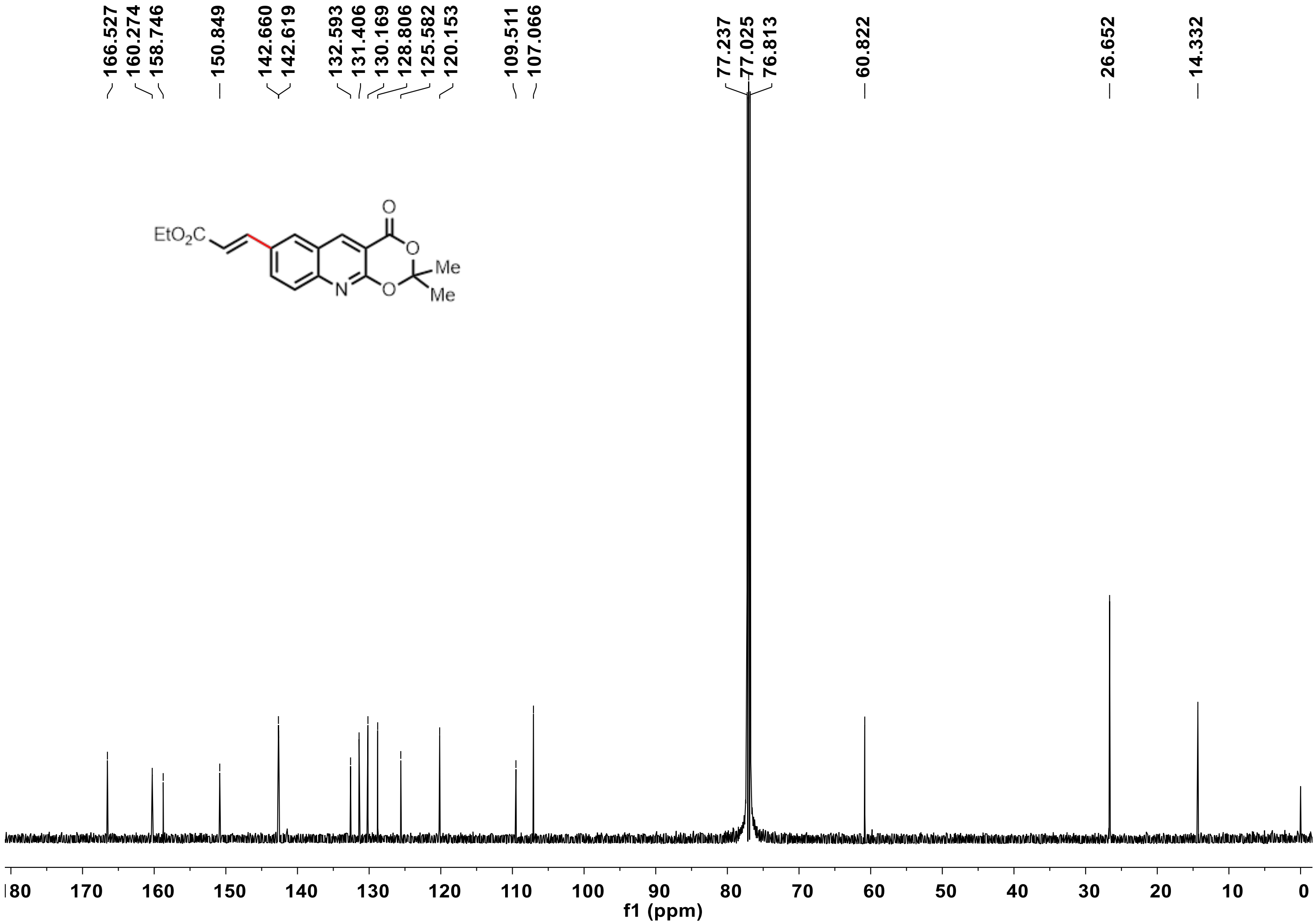
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2x**



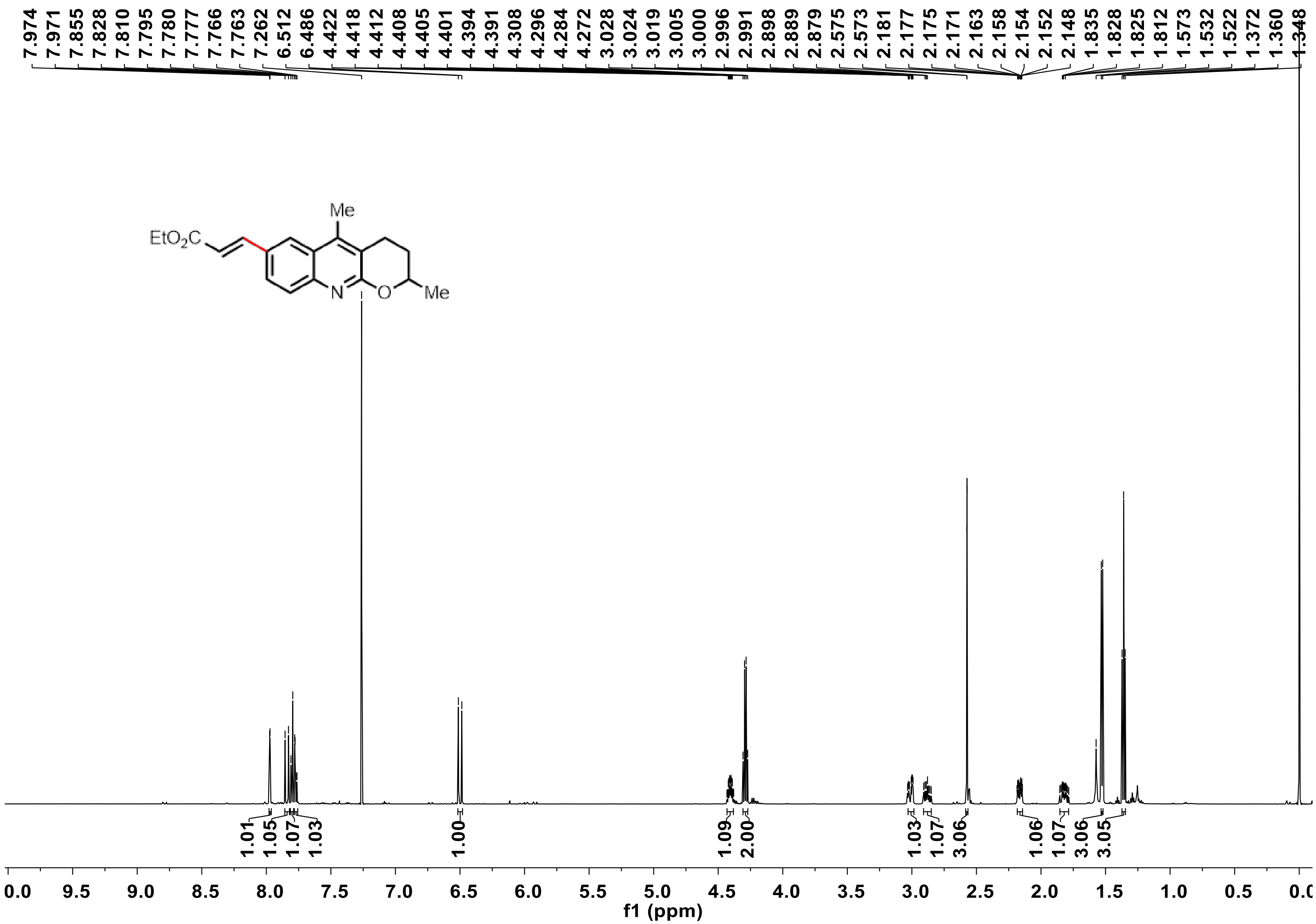
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2y**



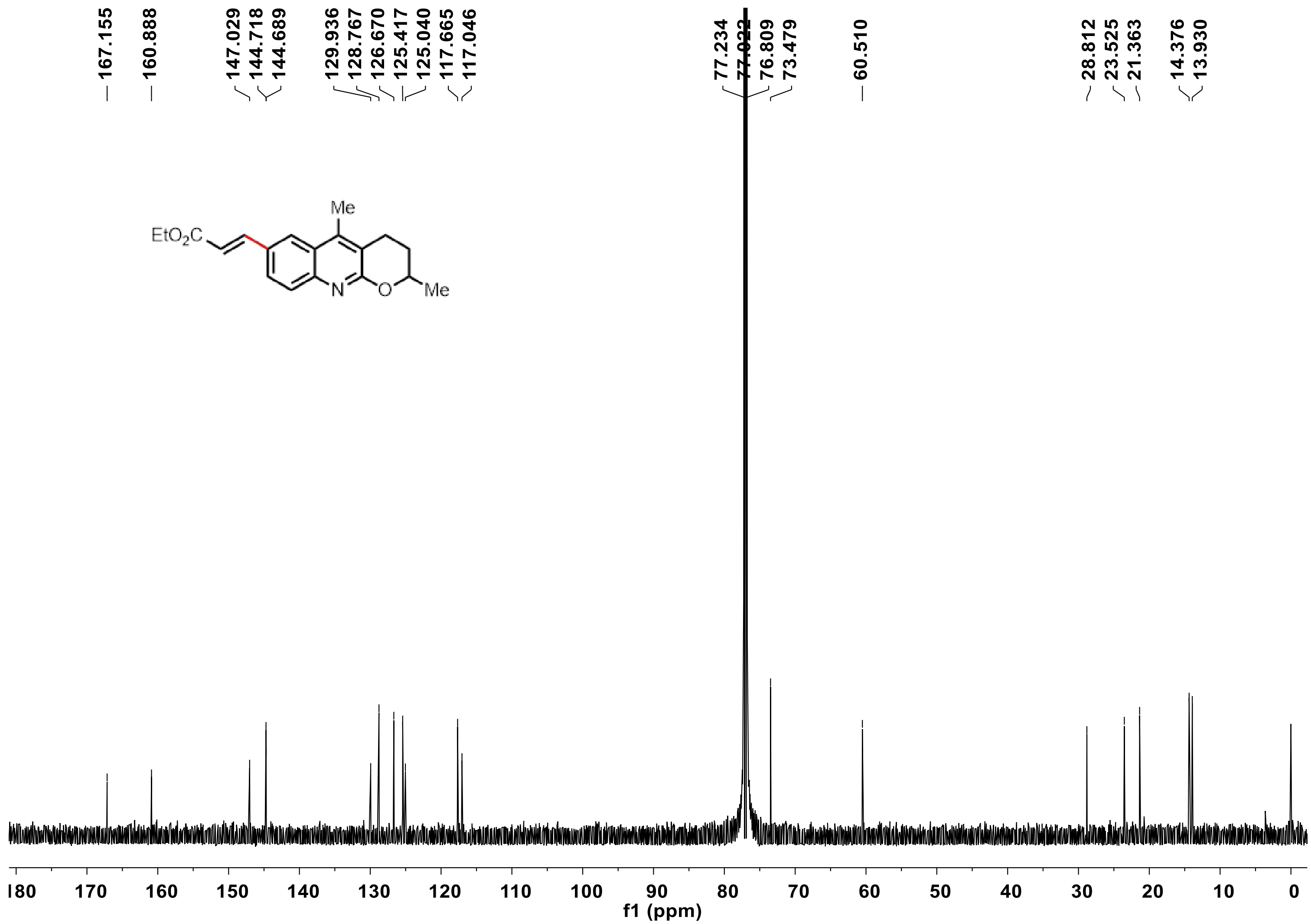
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2y**



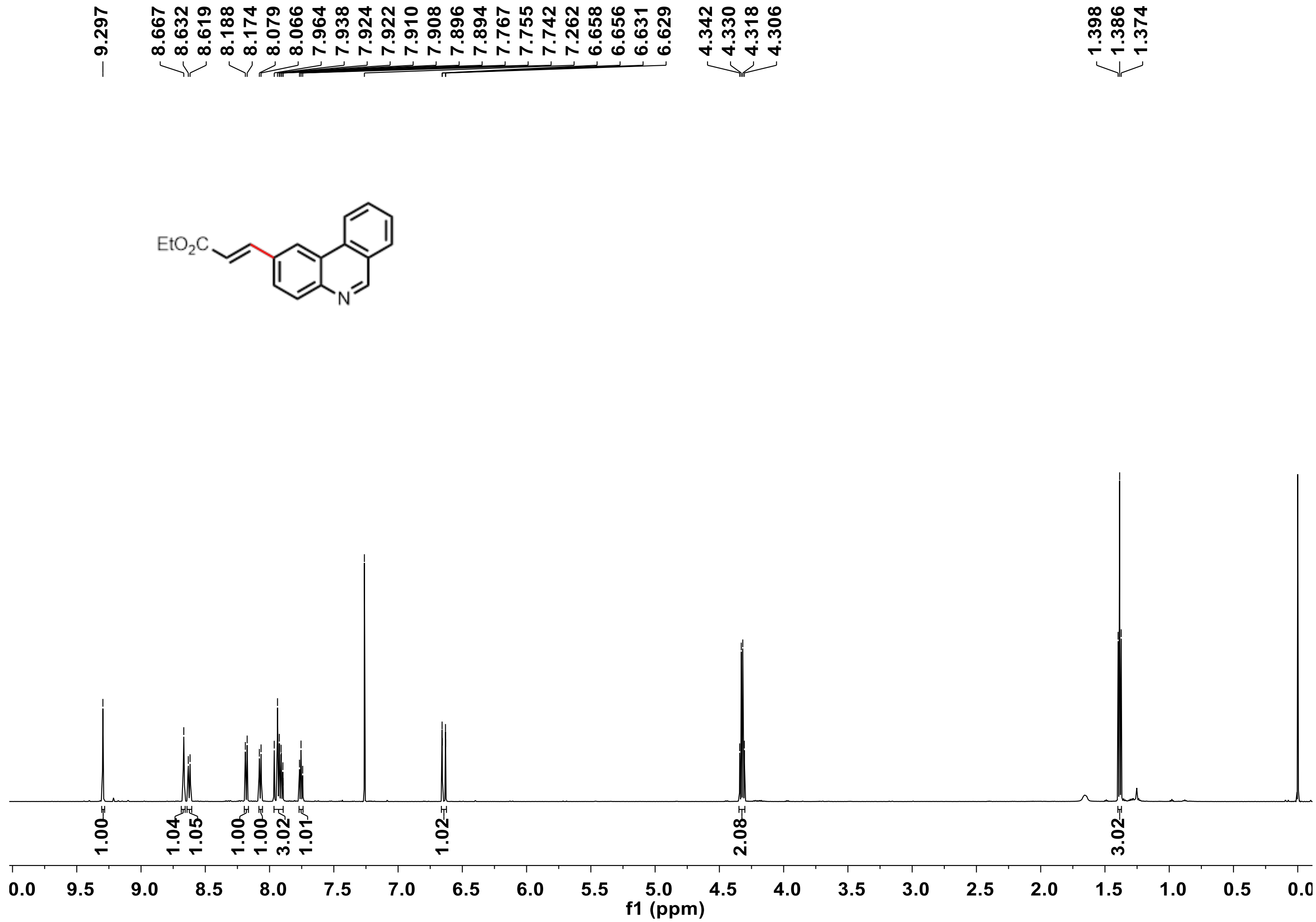
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2z**



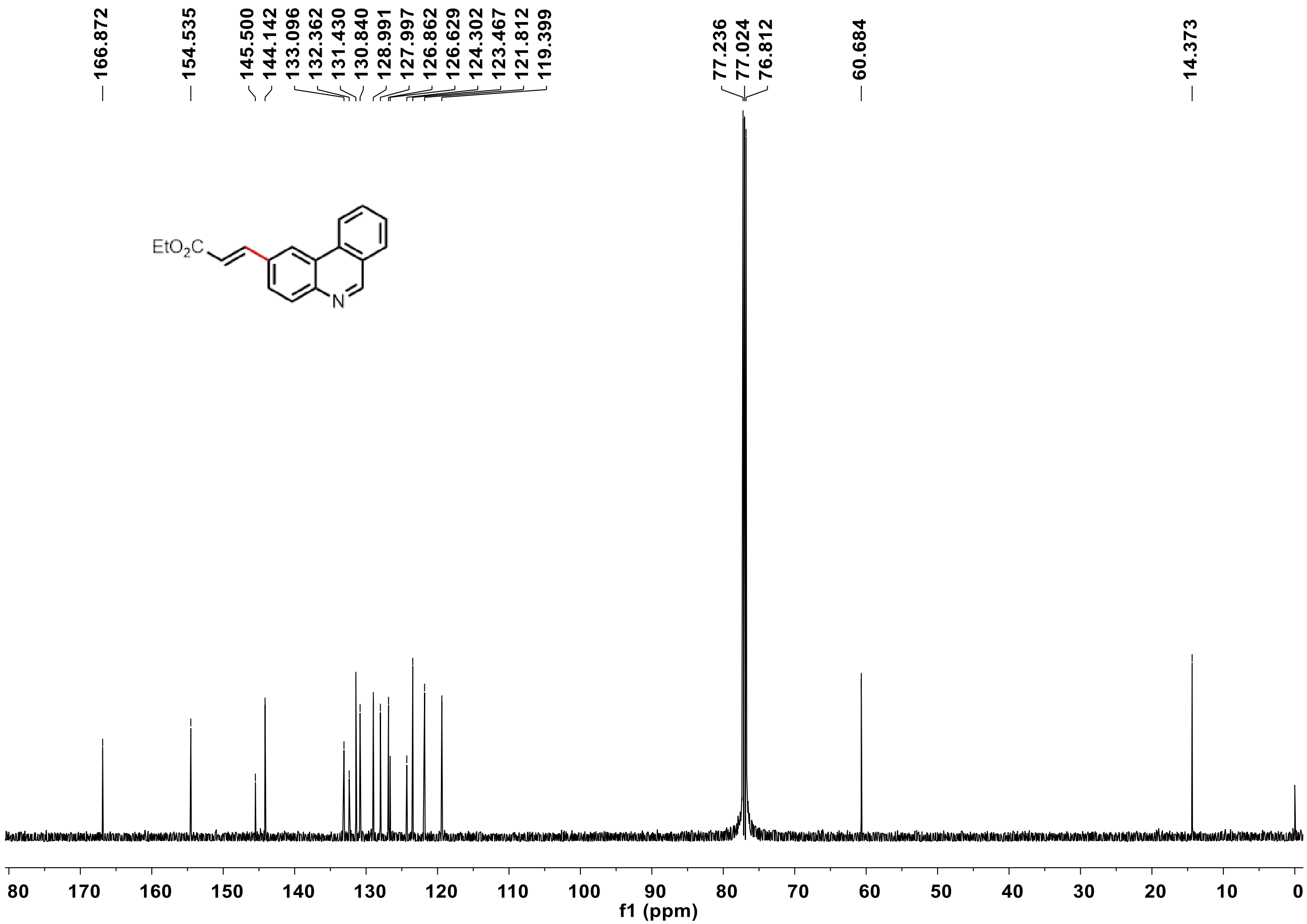
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2z**



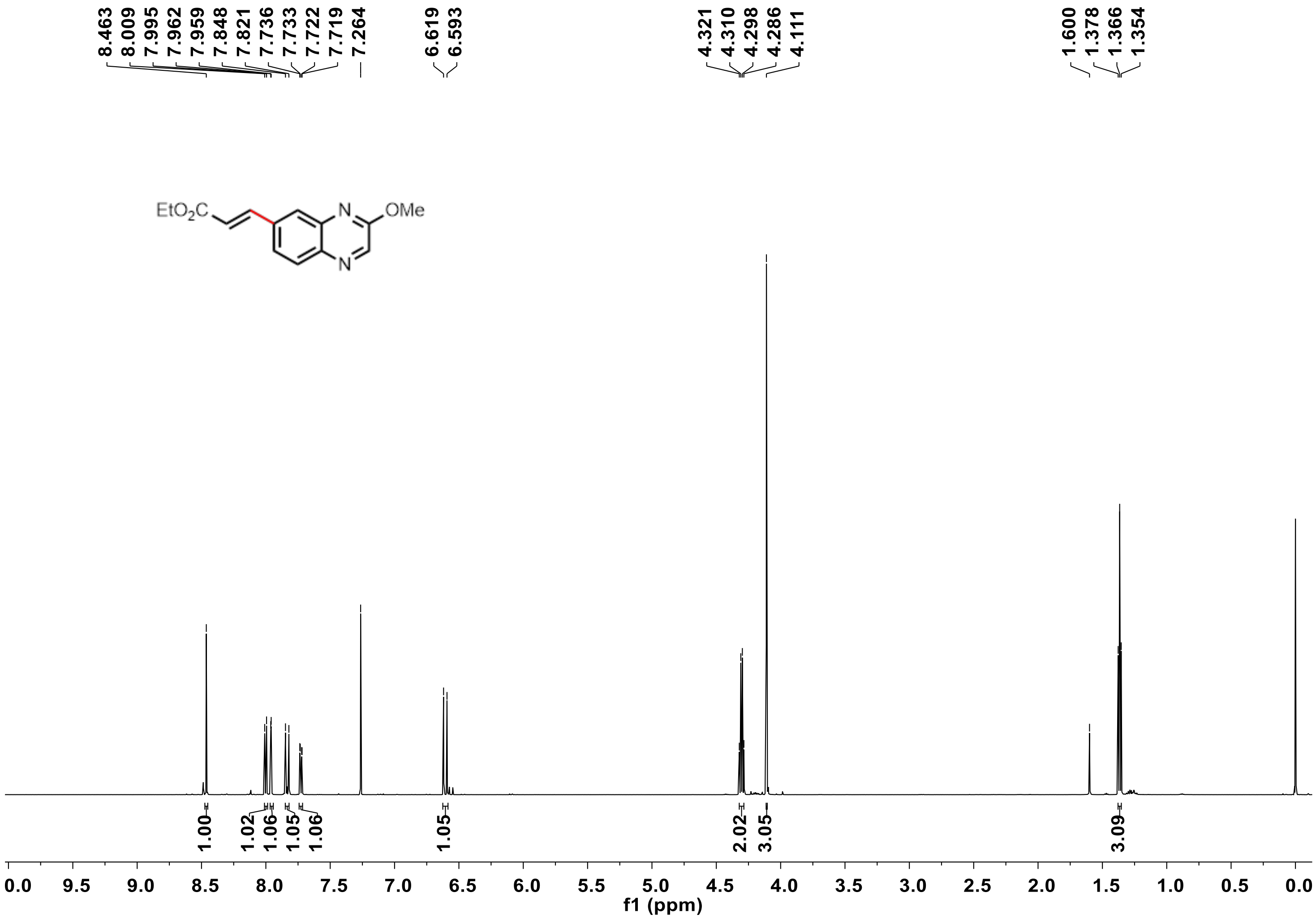
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aa**



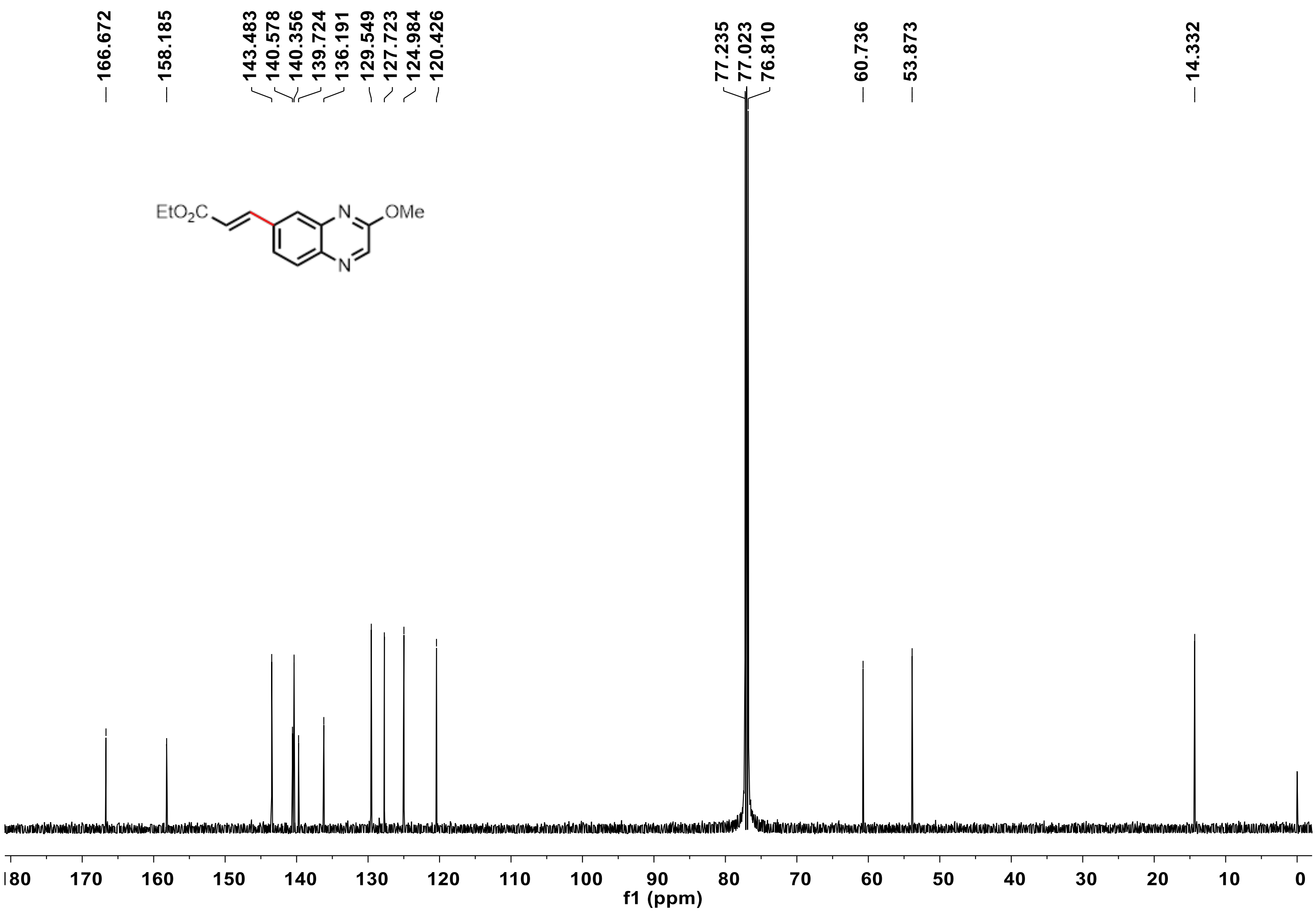
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2aa**



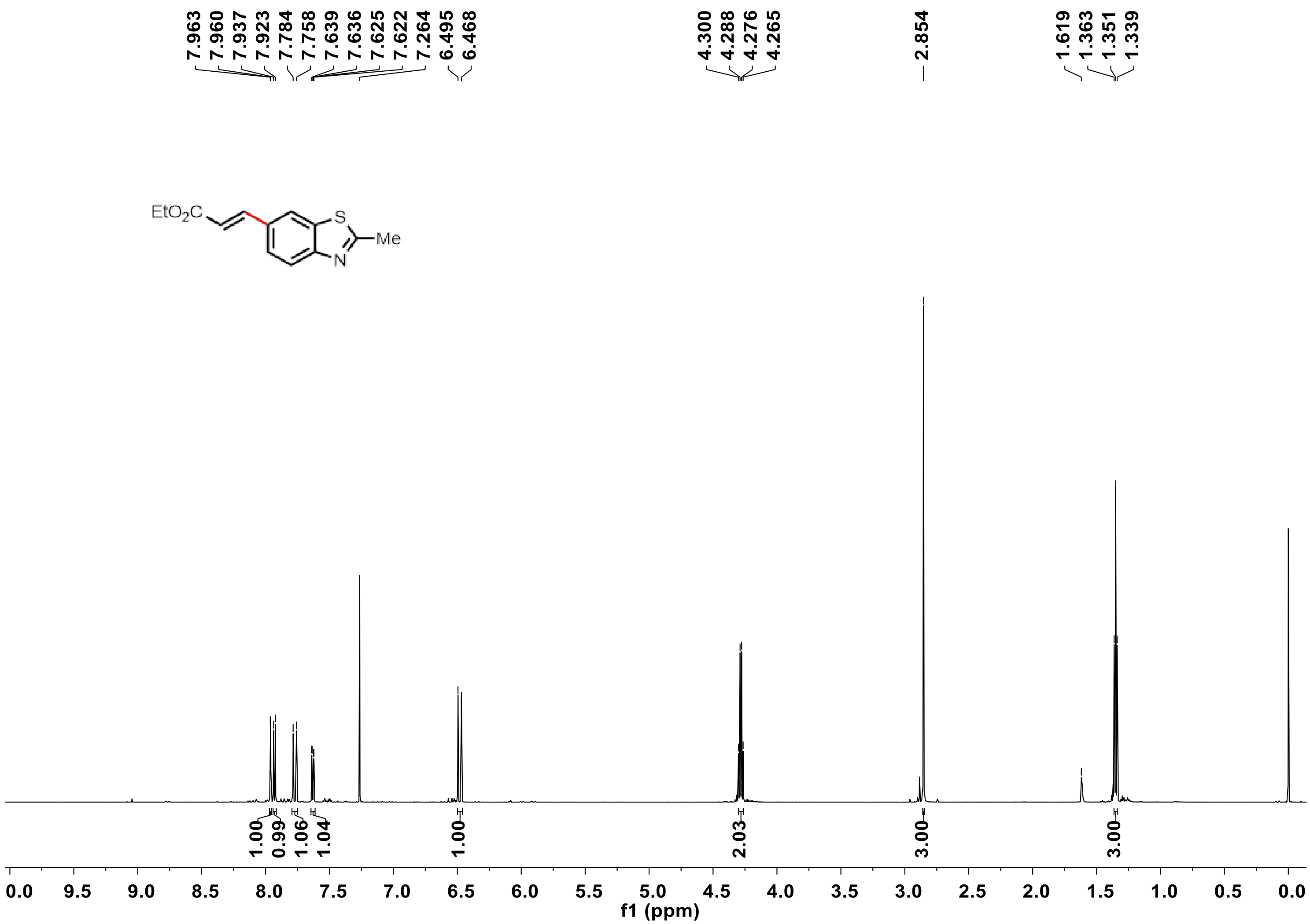
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ab**



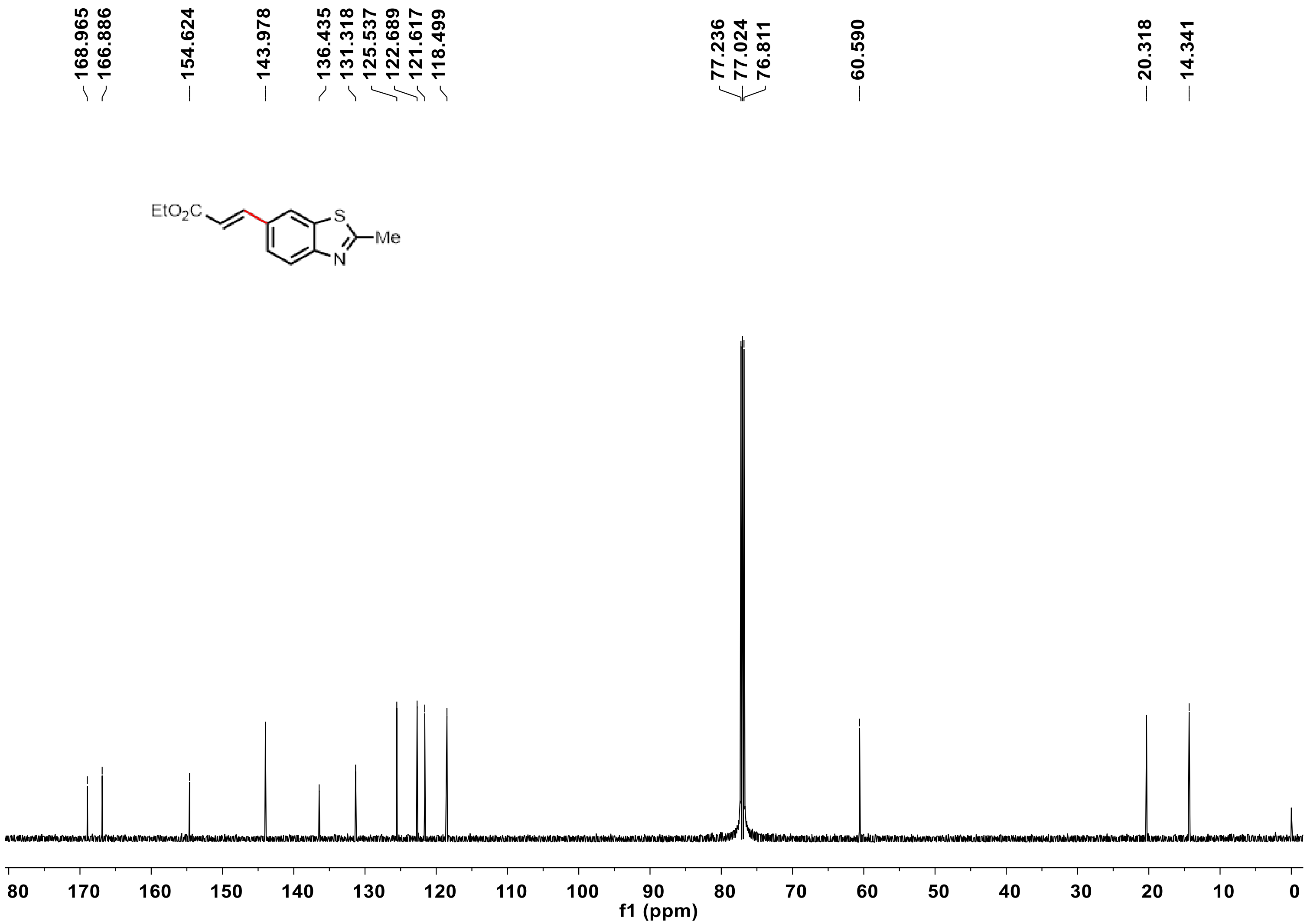
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ab**



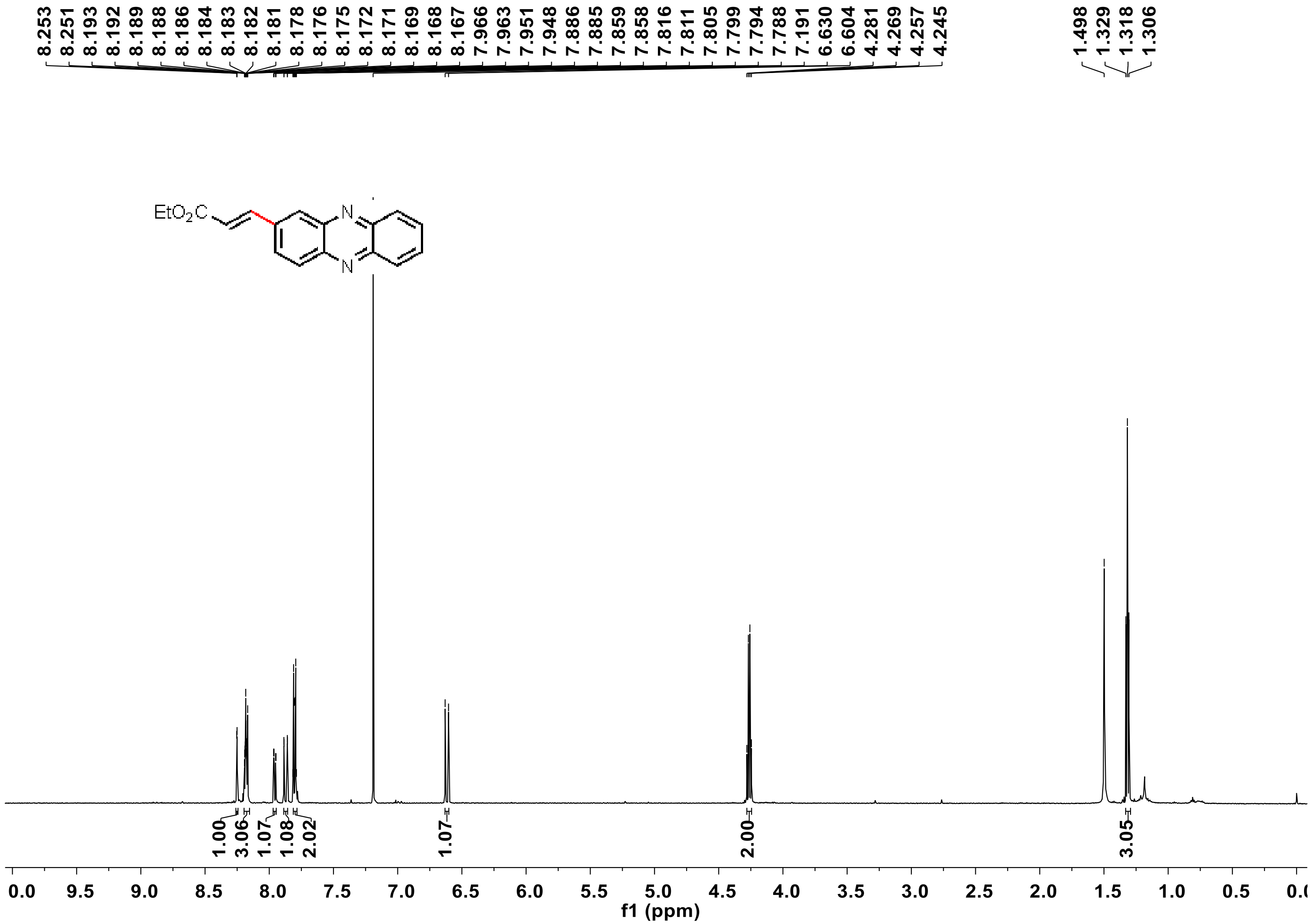
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ac**



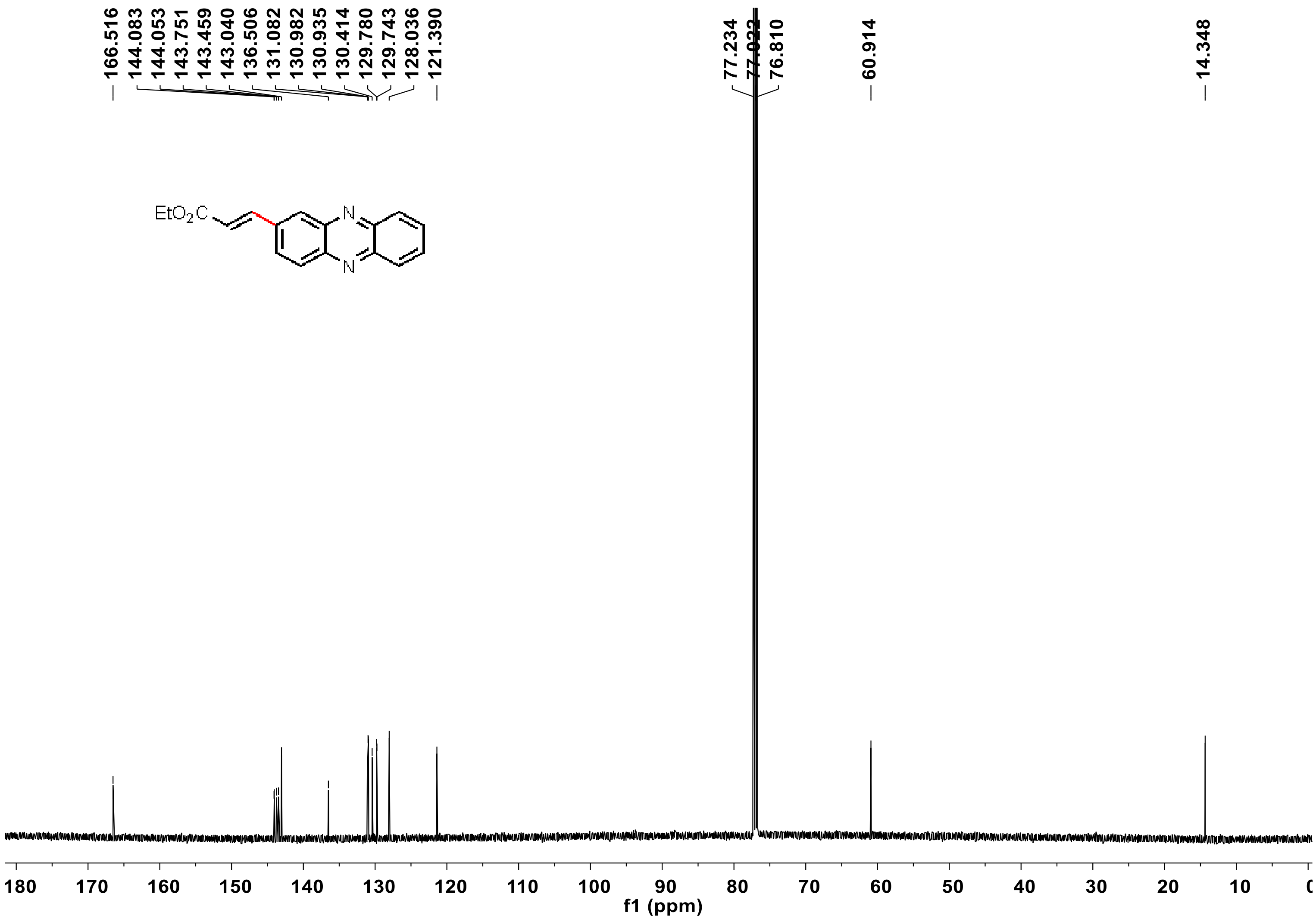
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ac**



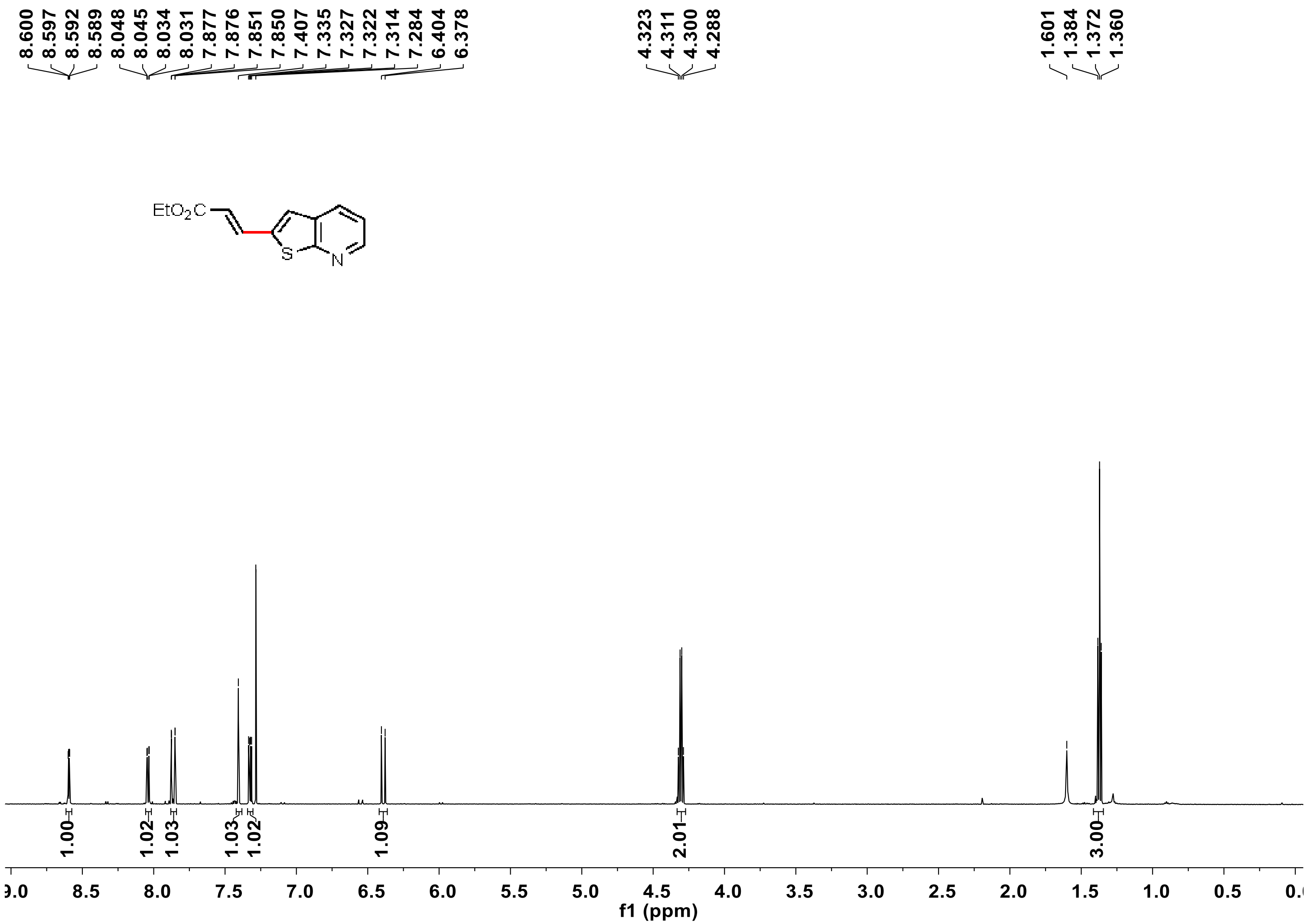
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2ad**



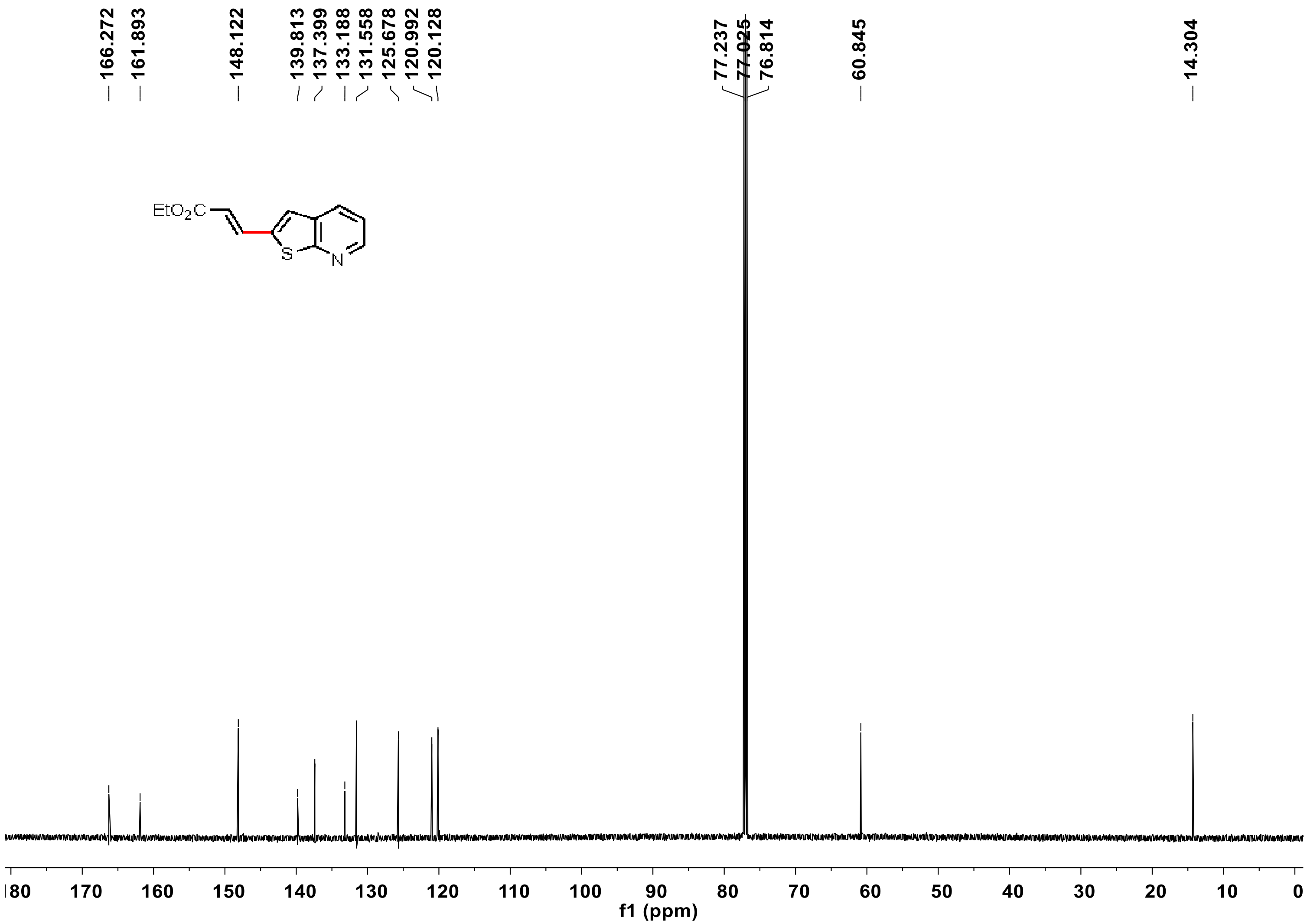
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ad**



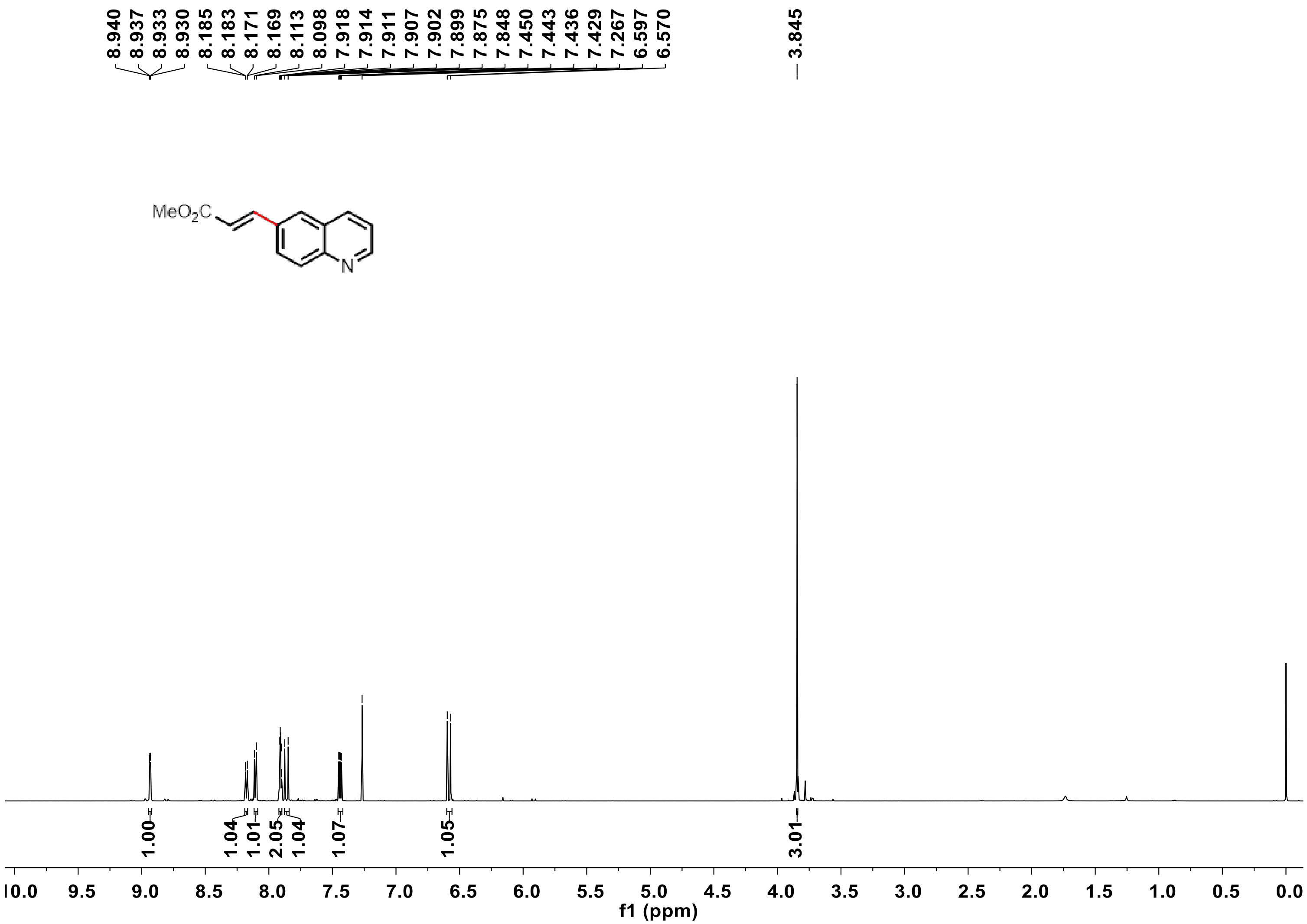
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **2ae**



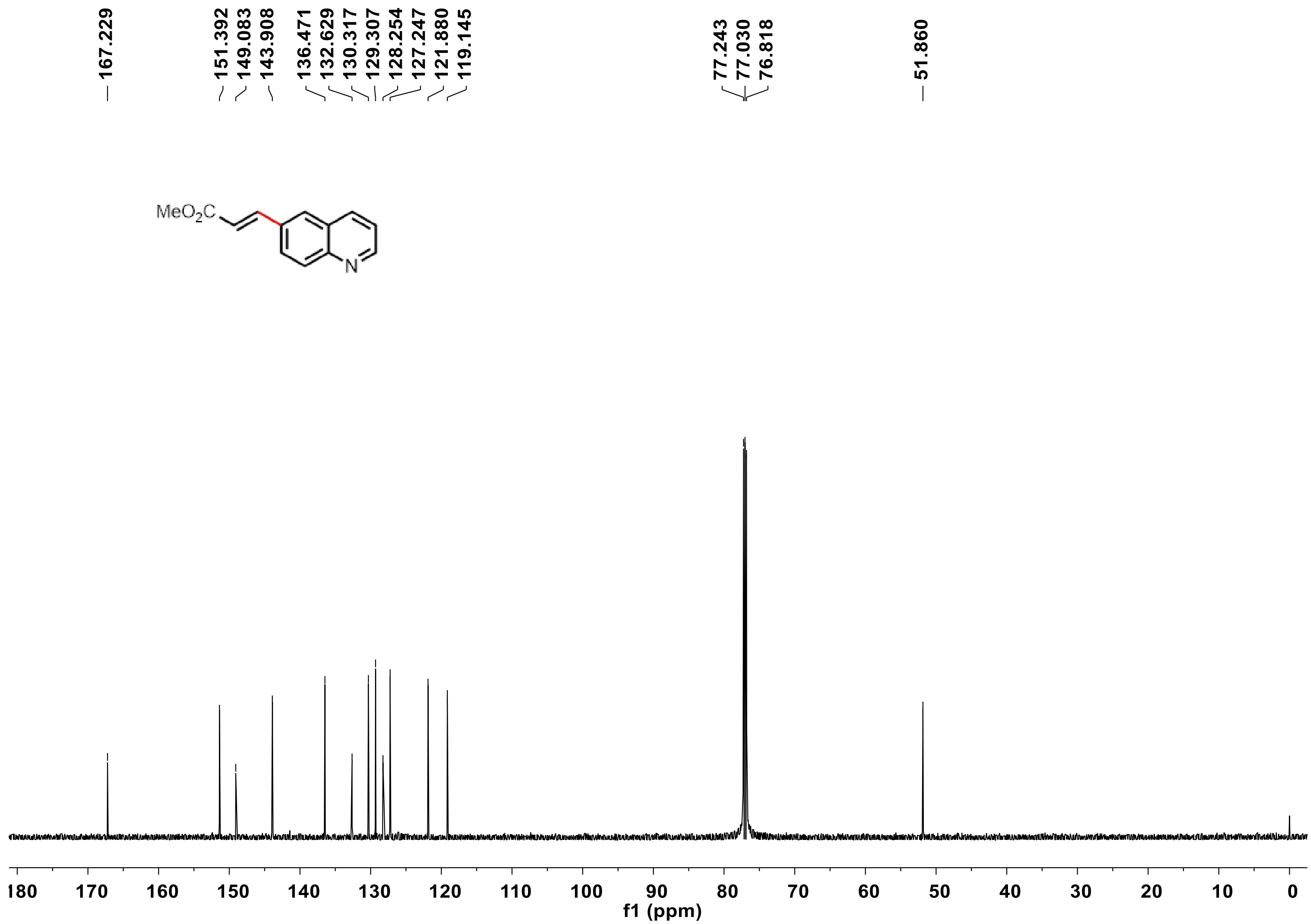
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ae**



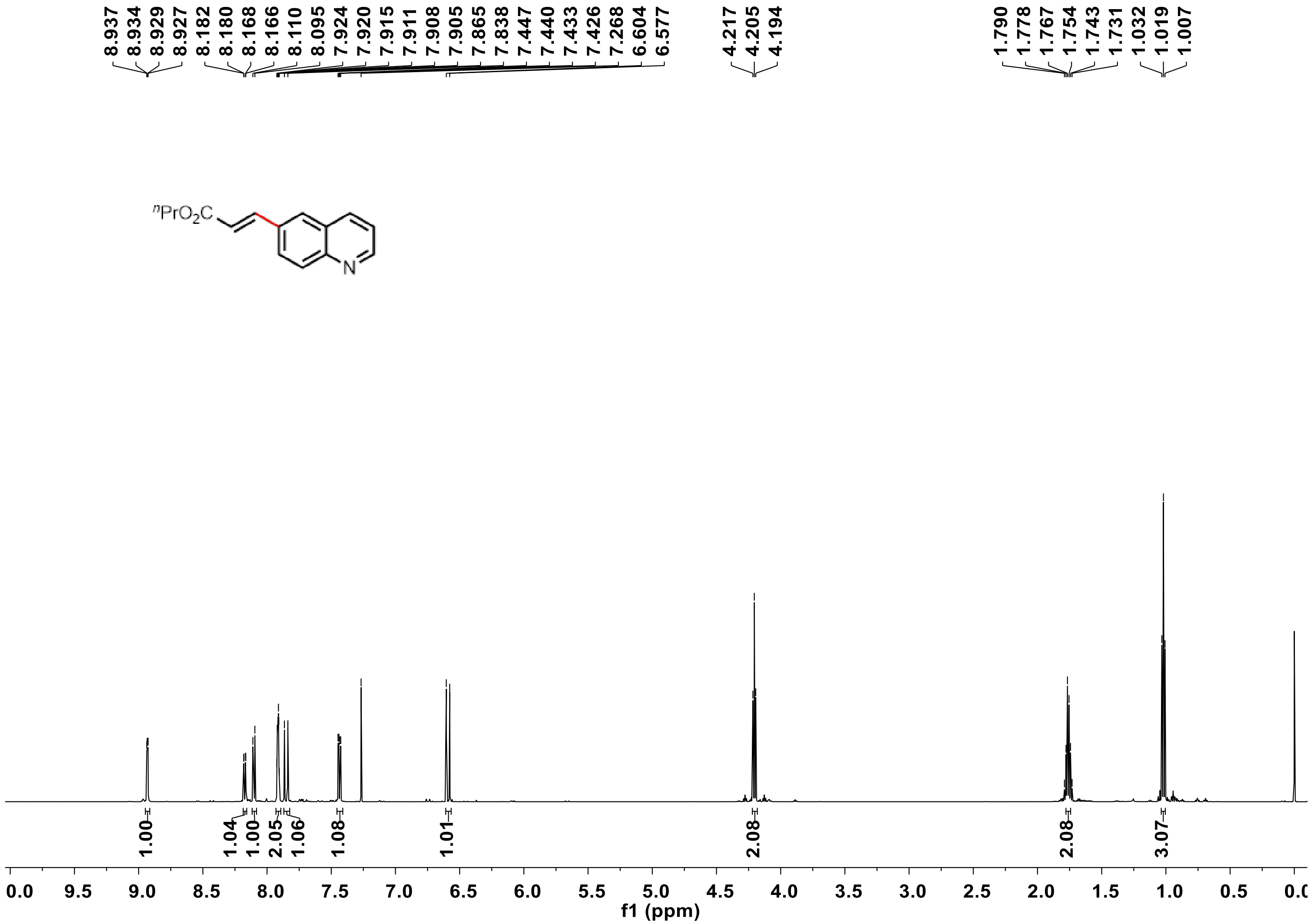
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2af**



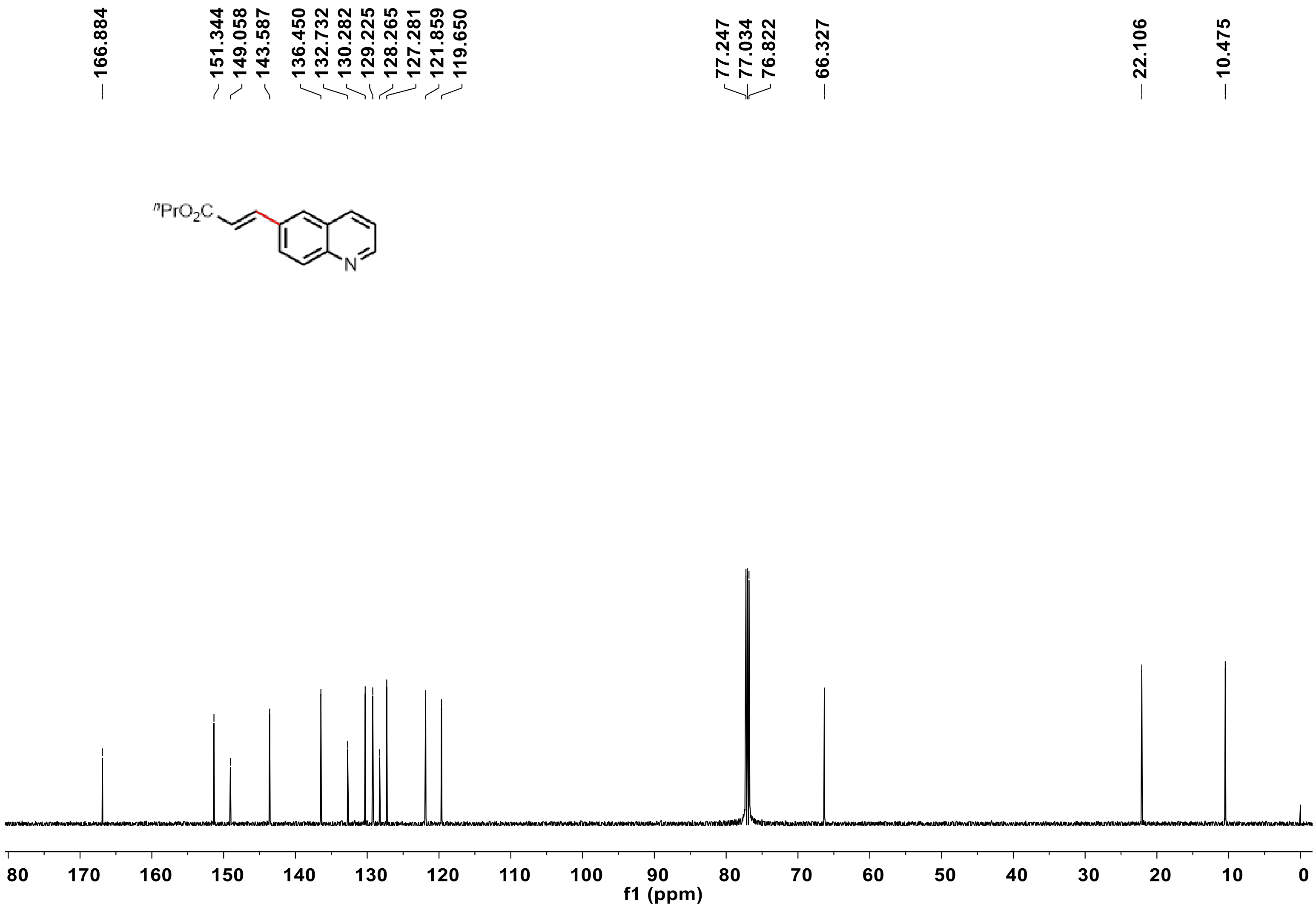
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2af**



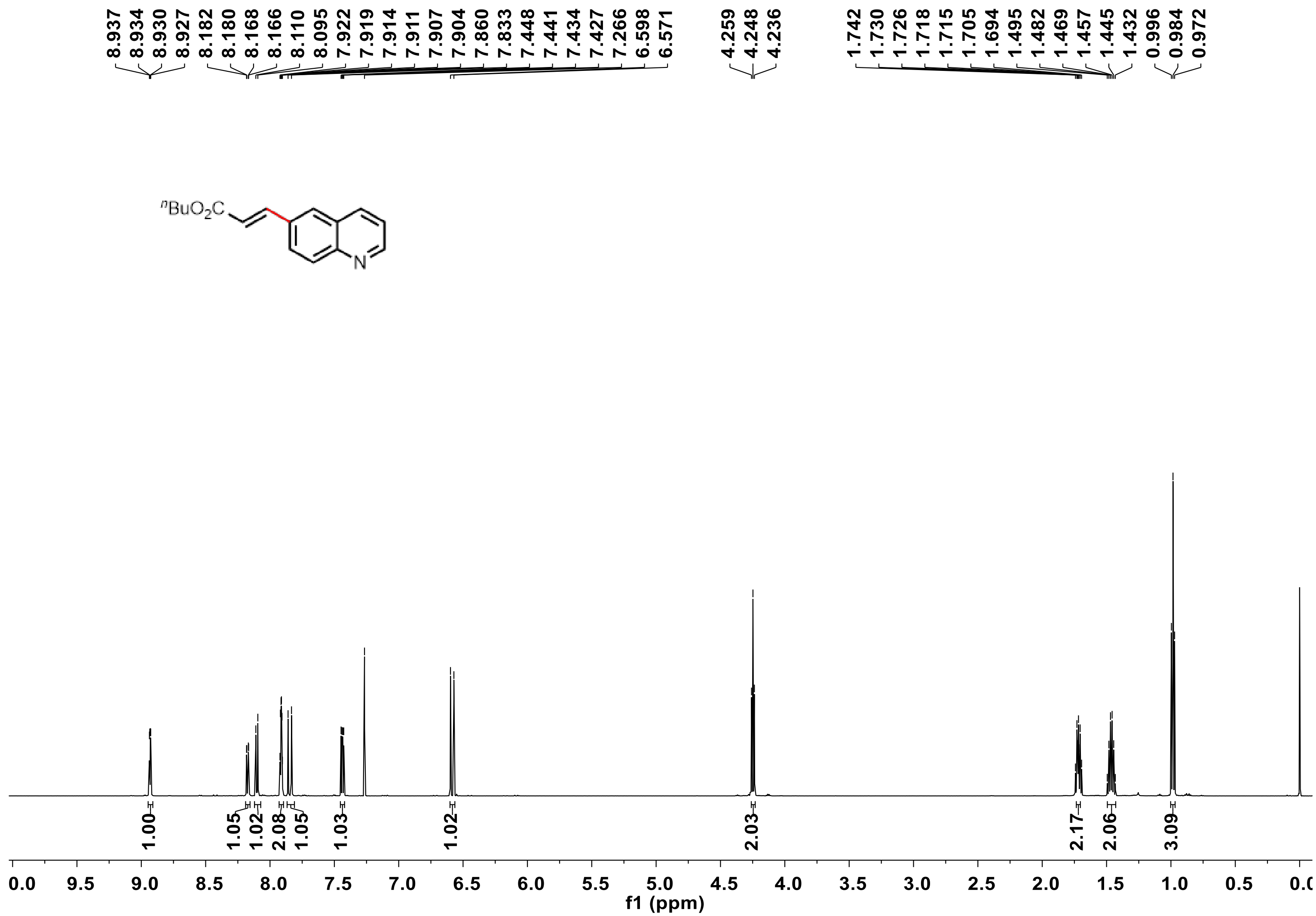
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ag**



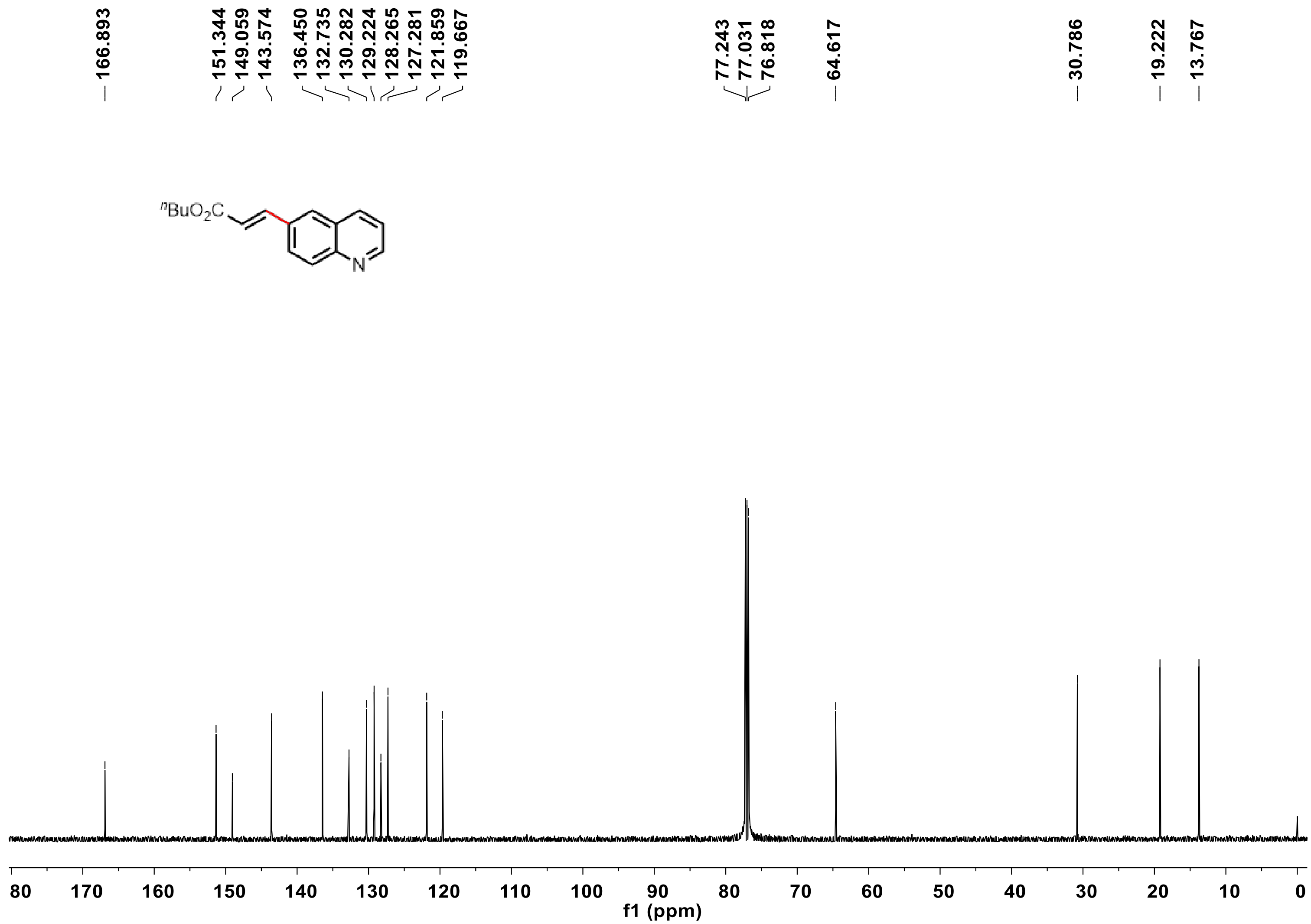
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ag**



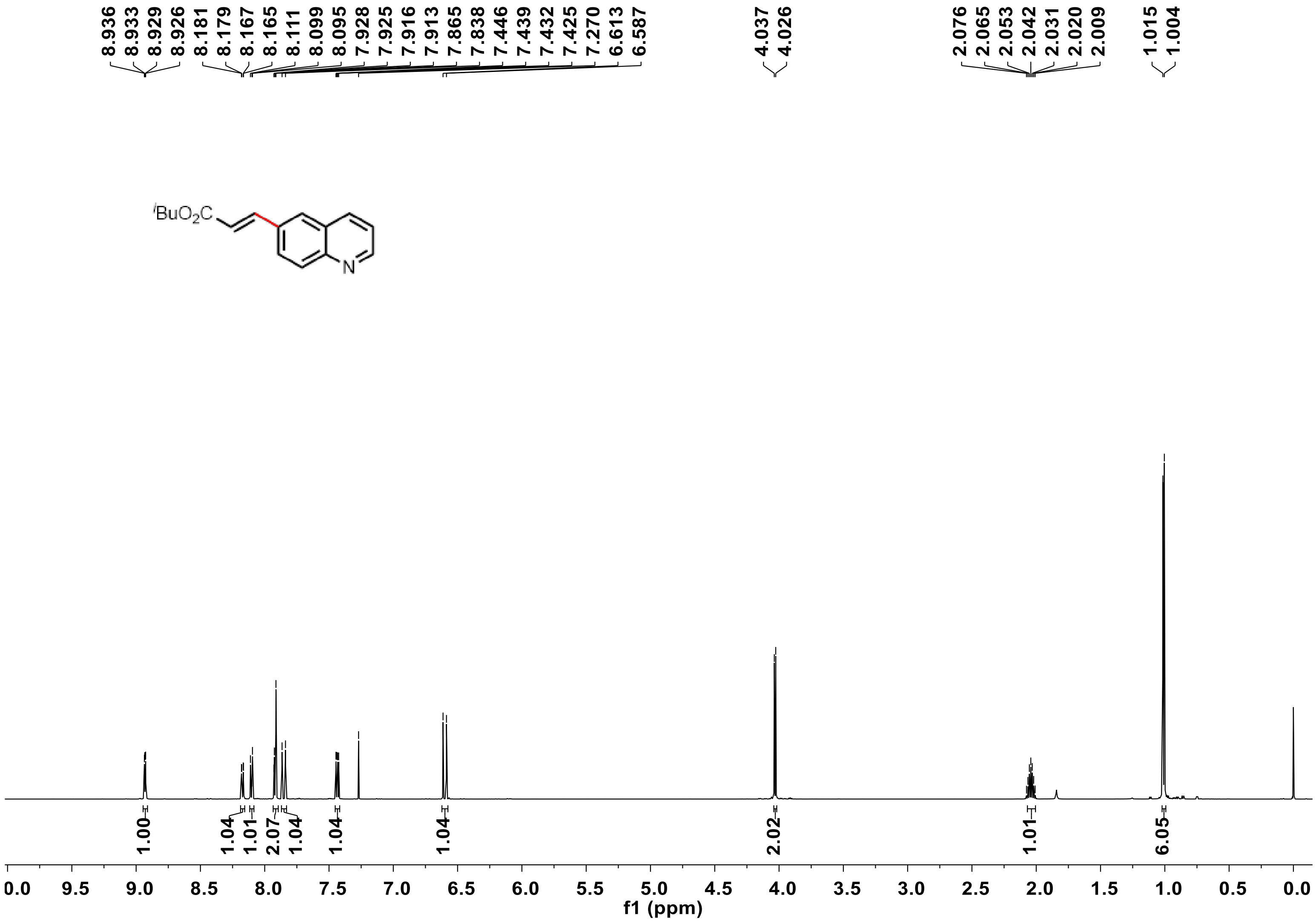
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ah**



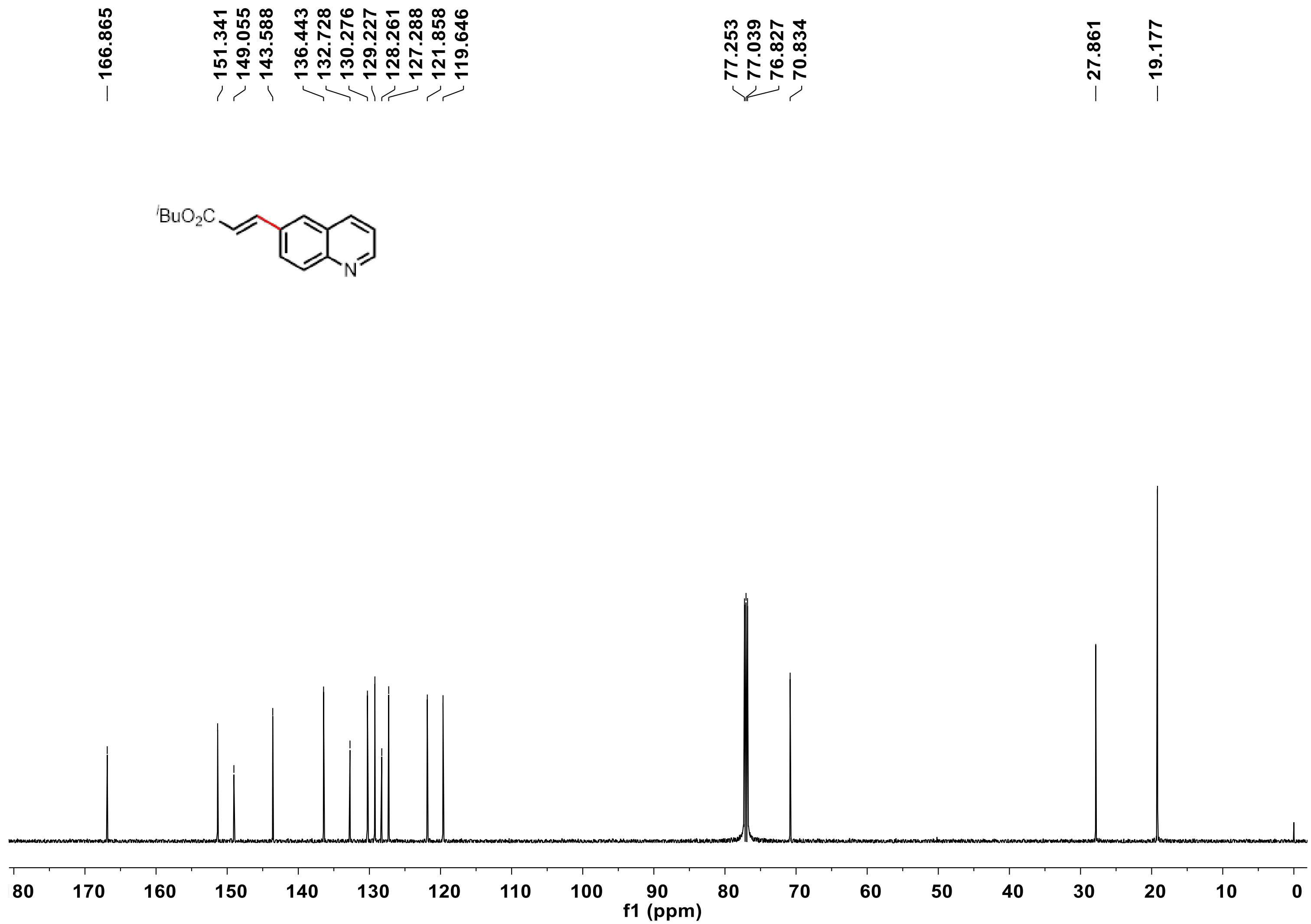
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ah**



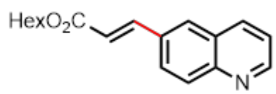
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ai**

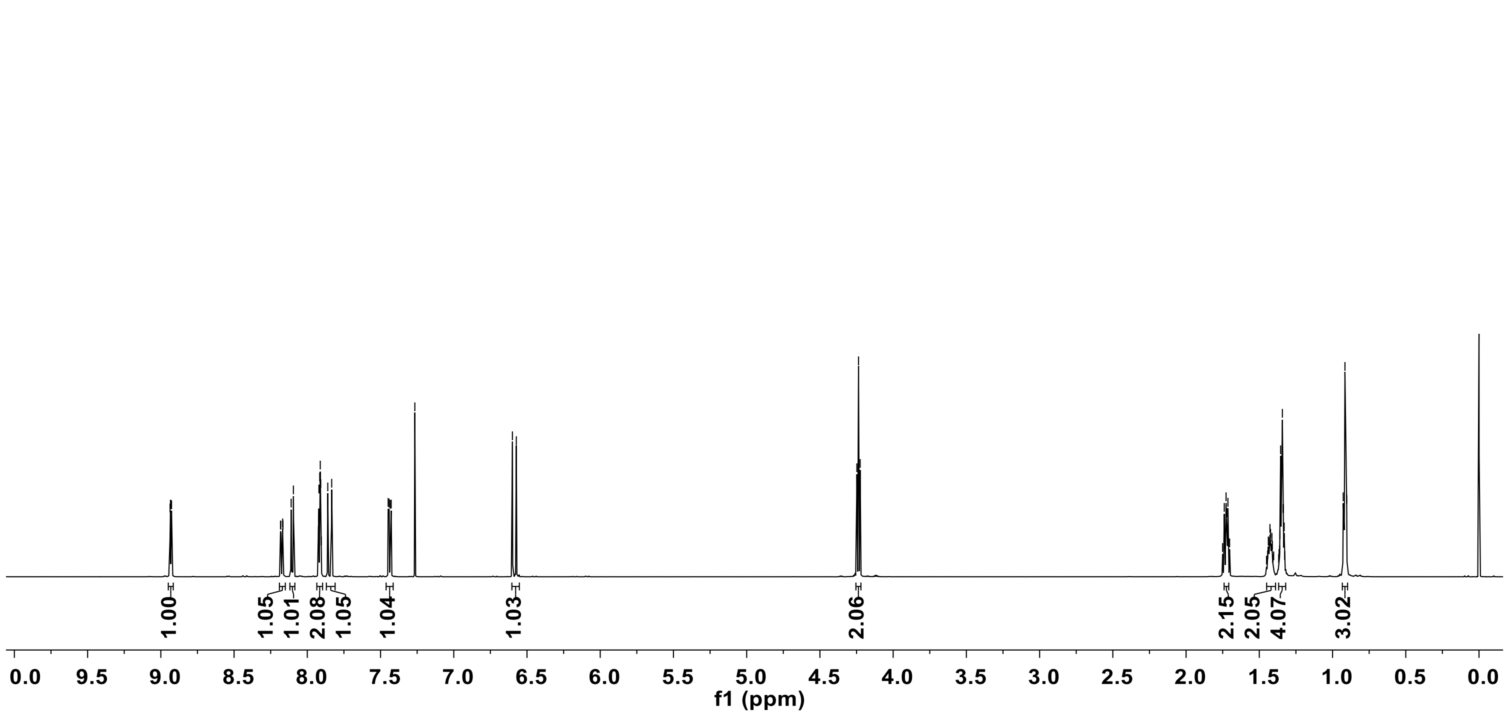


^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2ai**

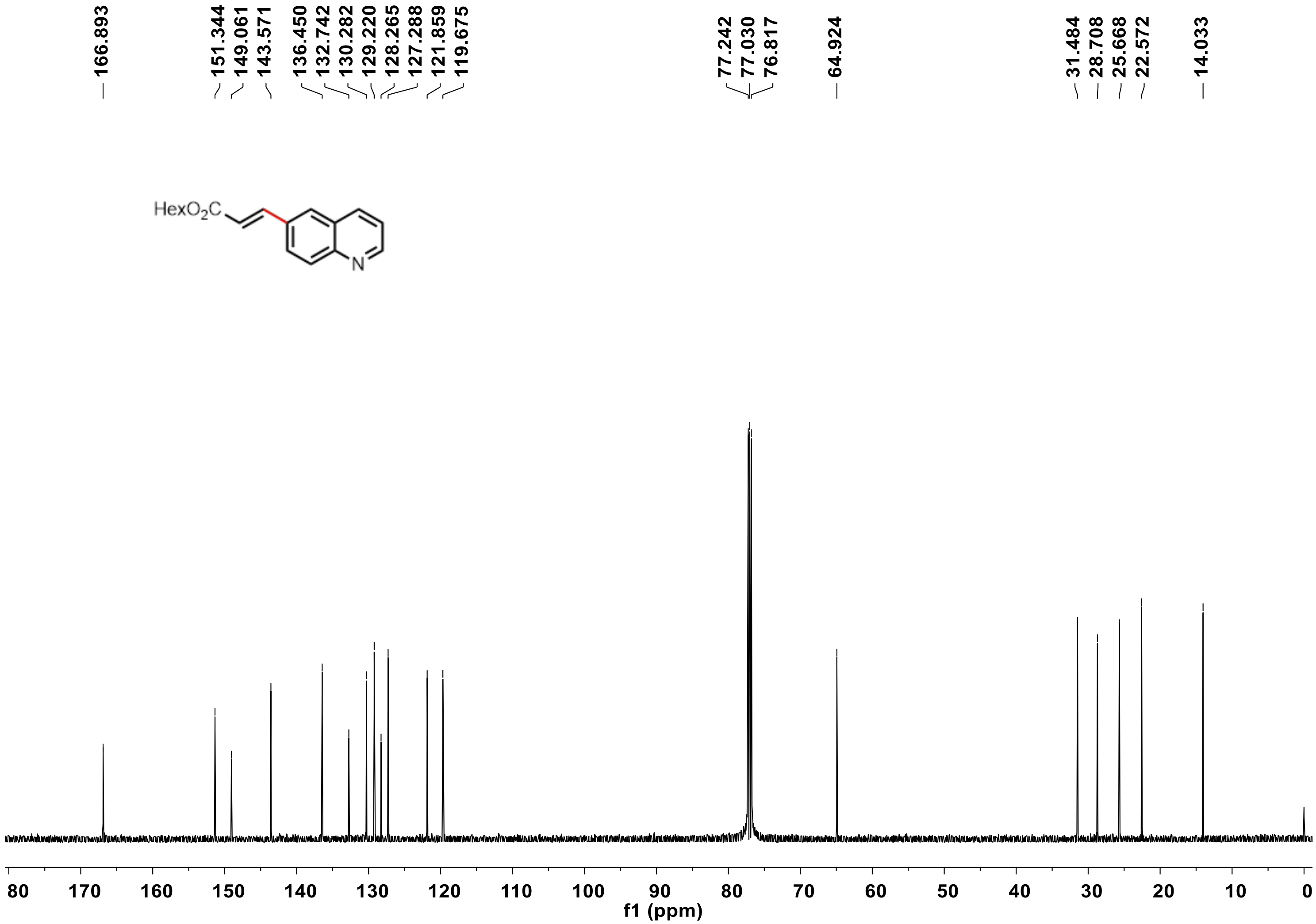


^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2aj**

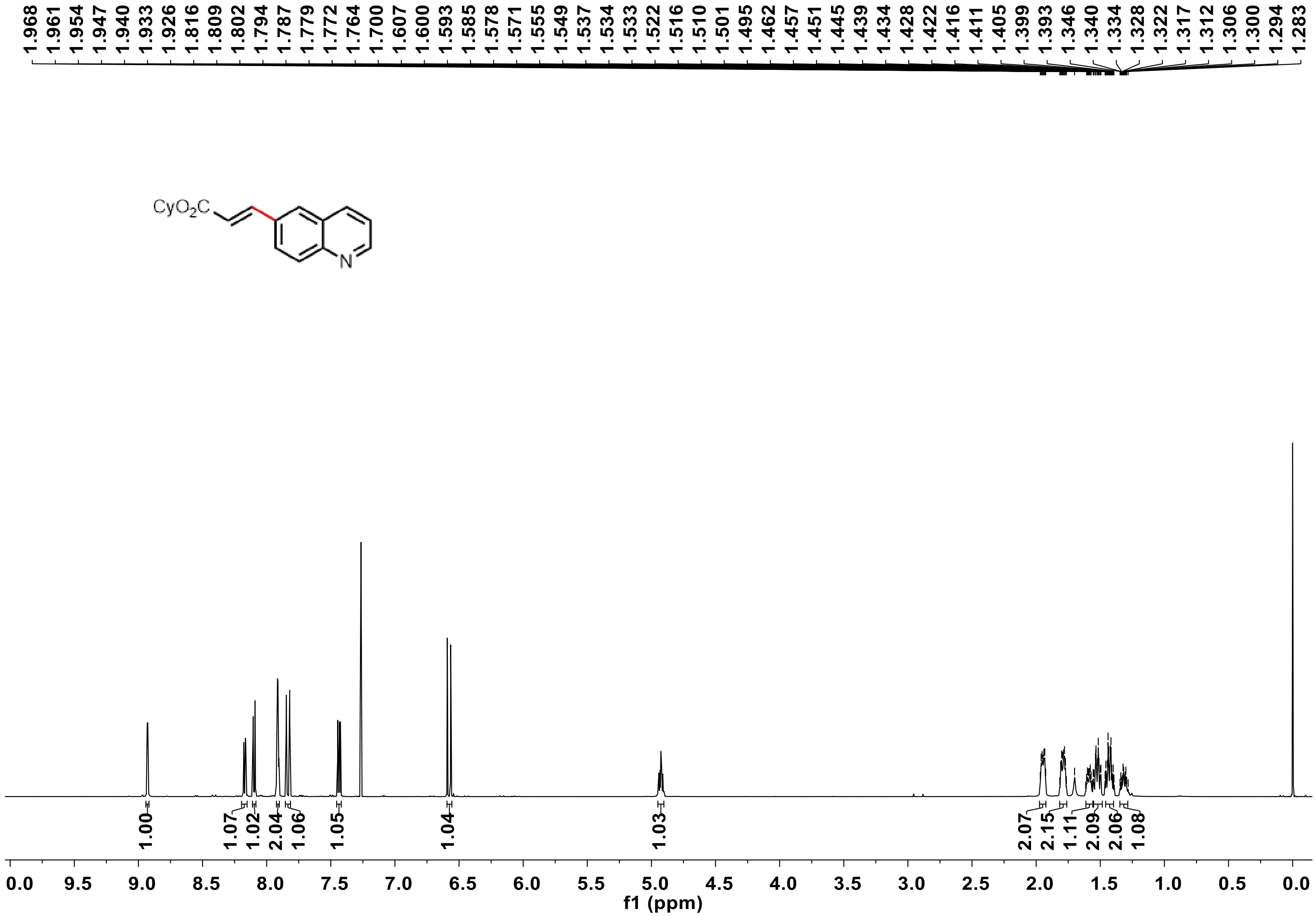




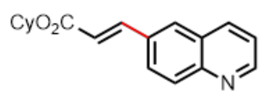
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2aj**

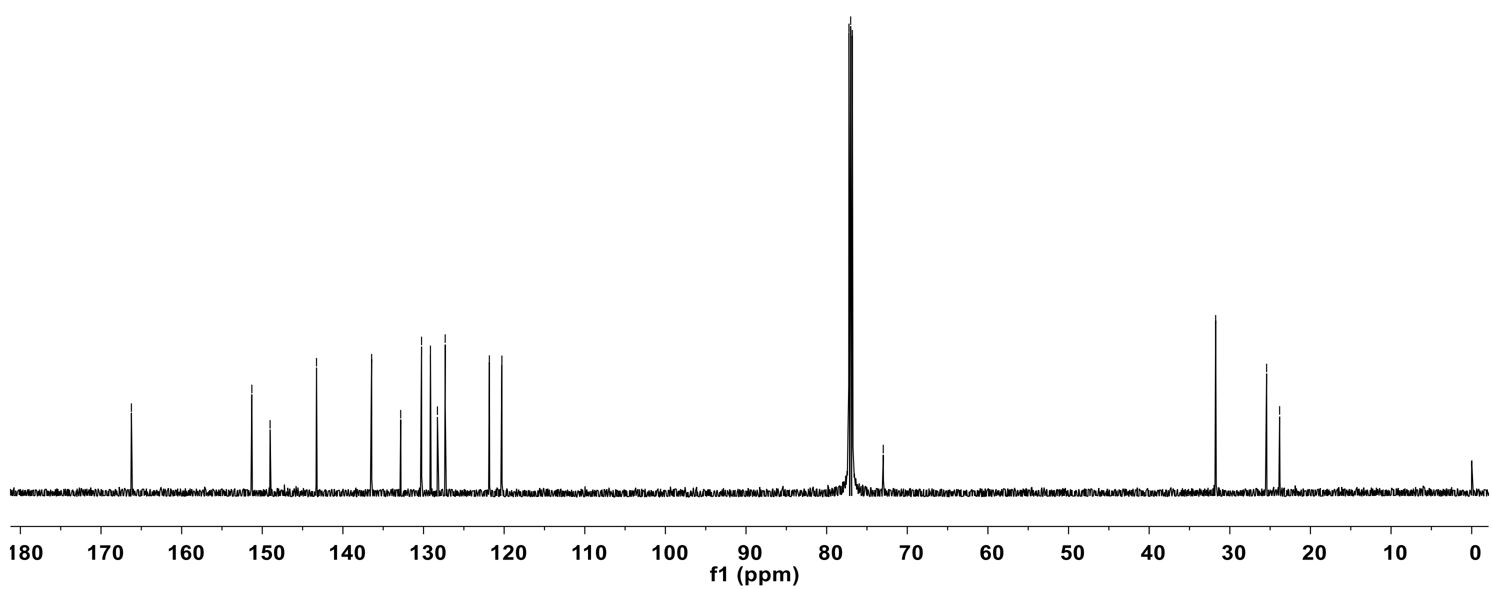


^1H NMR (600 MHz, $CDCl_3$) spectrum of **2ak**

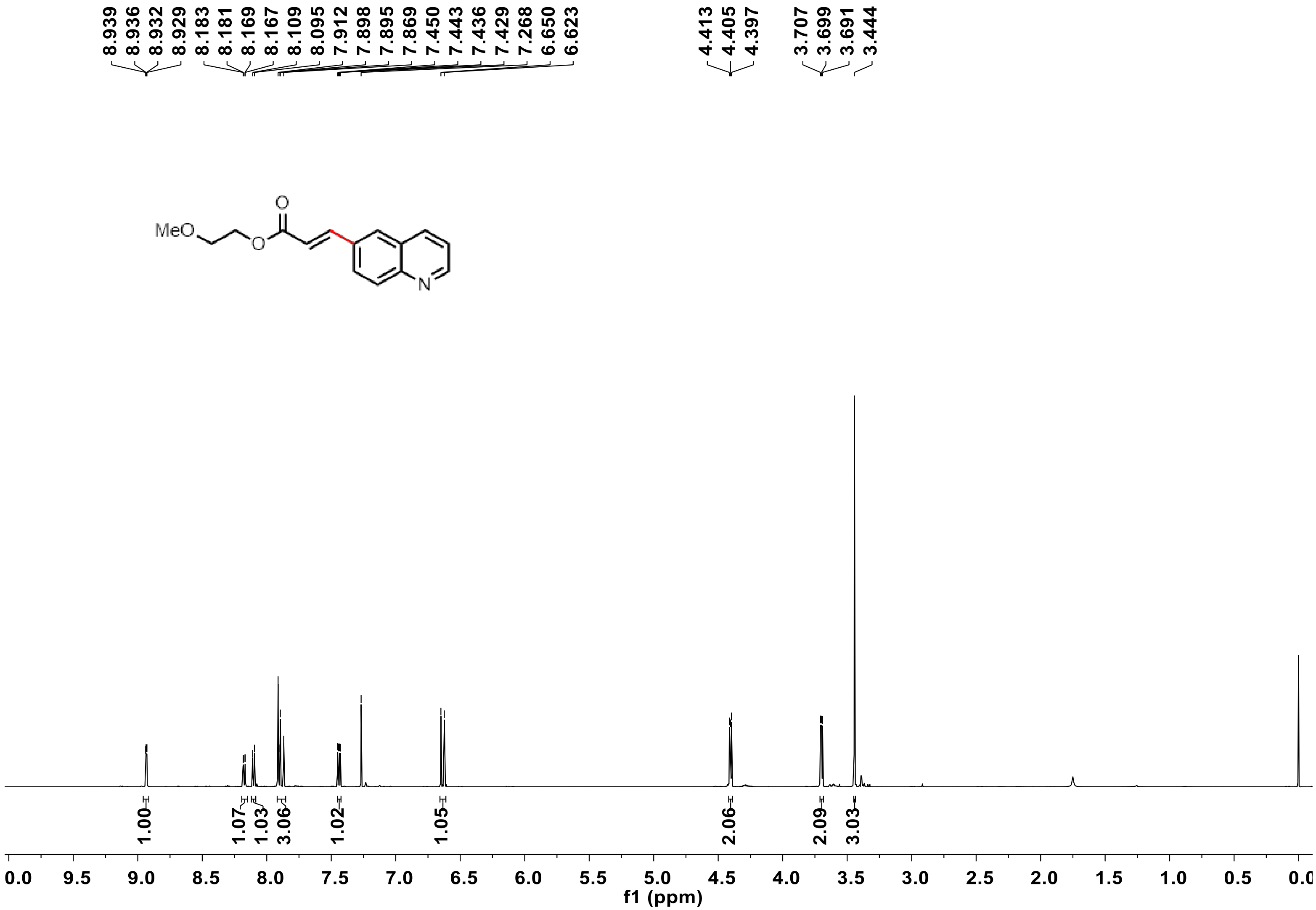


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ak**

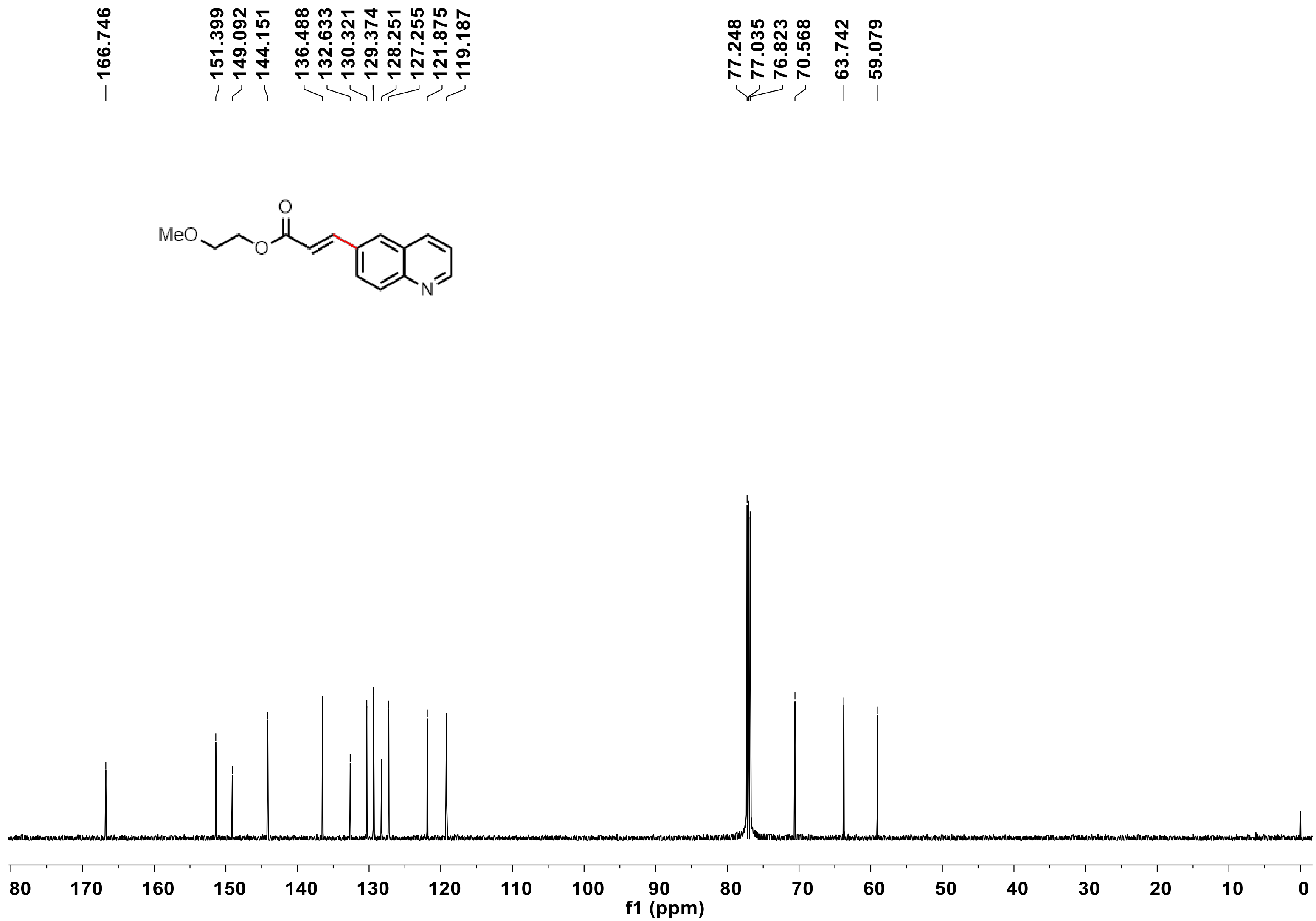




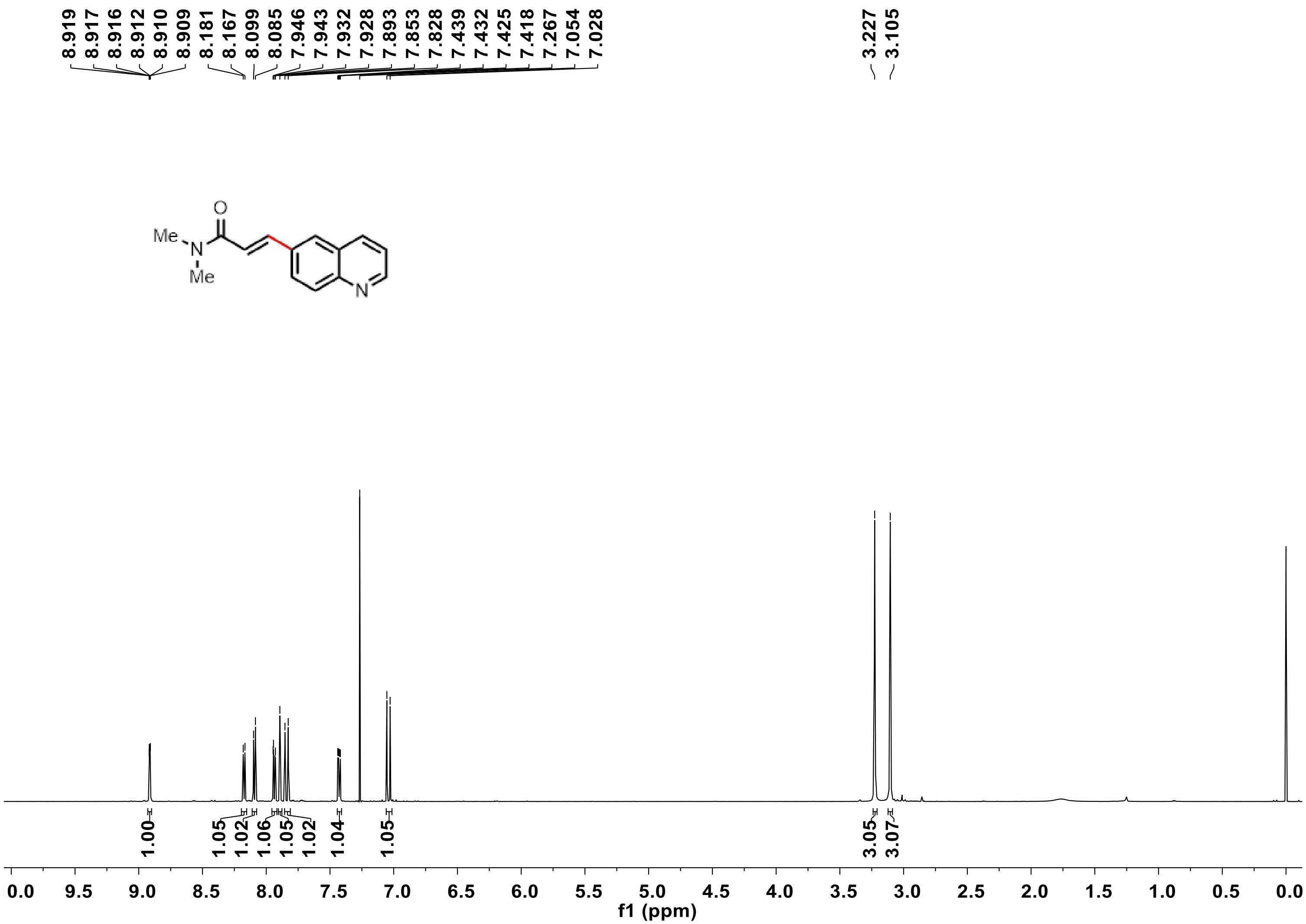
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2al**



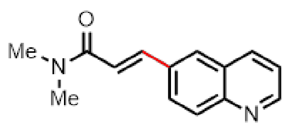
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2al**

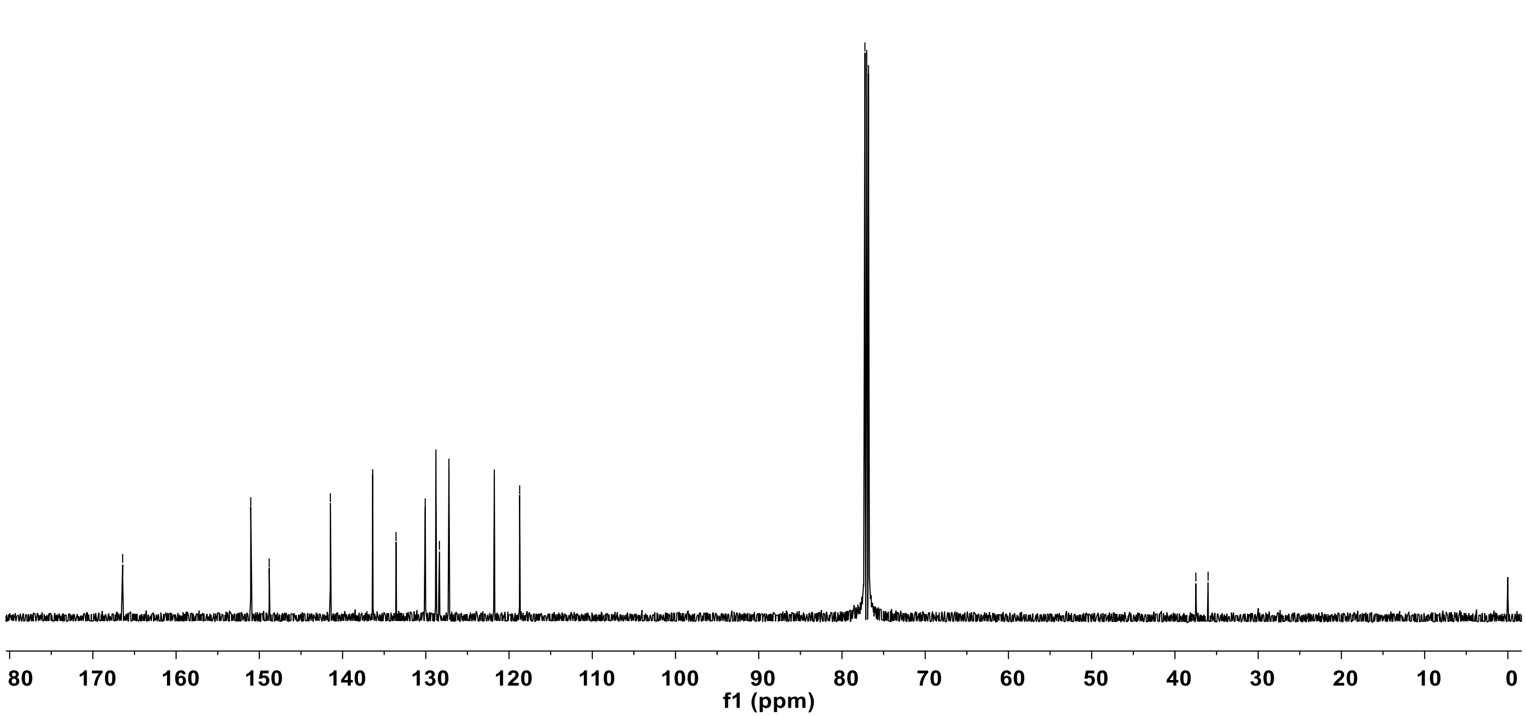


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2am**

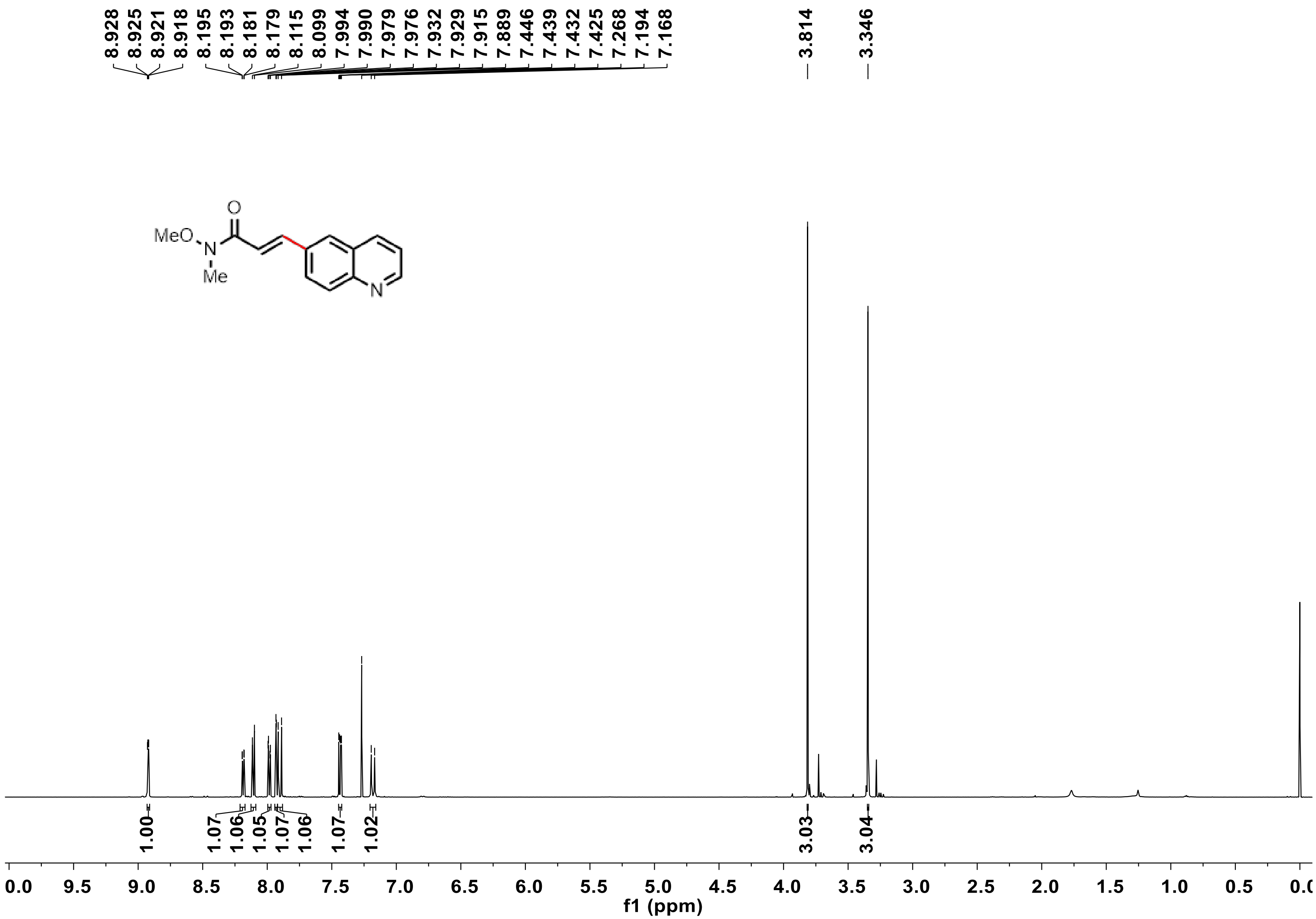


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2am**

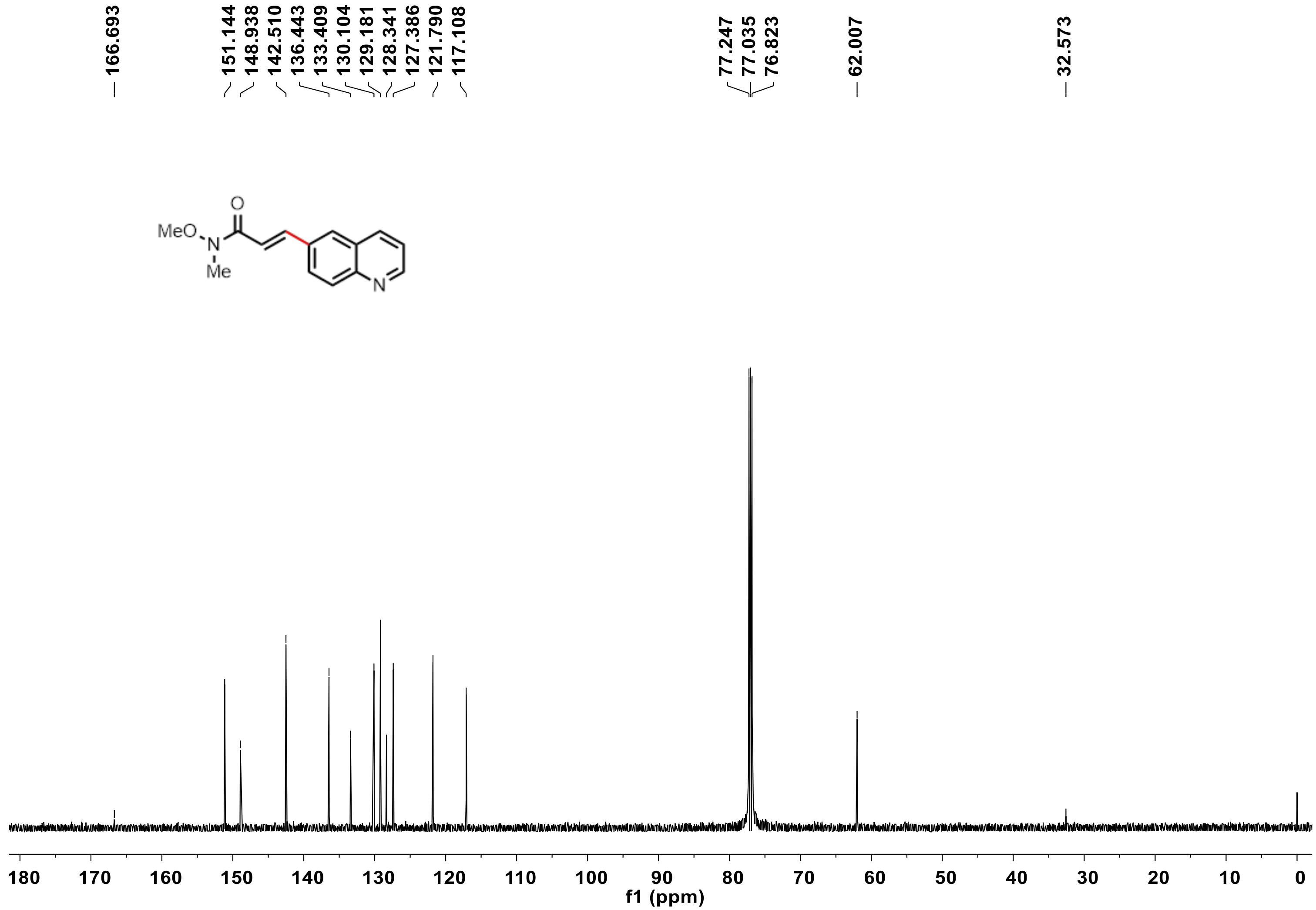




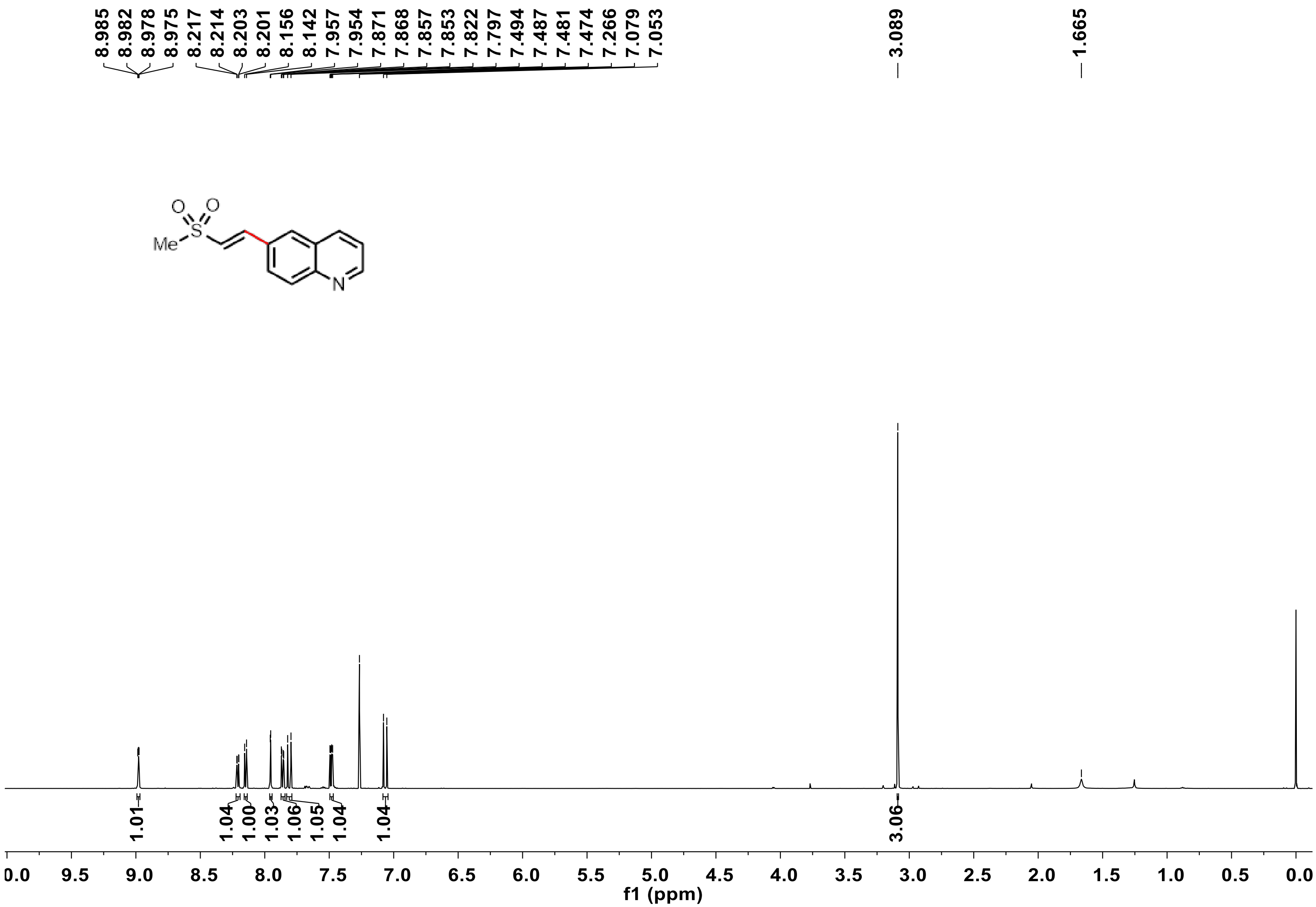
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2an**



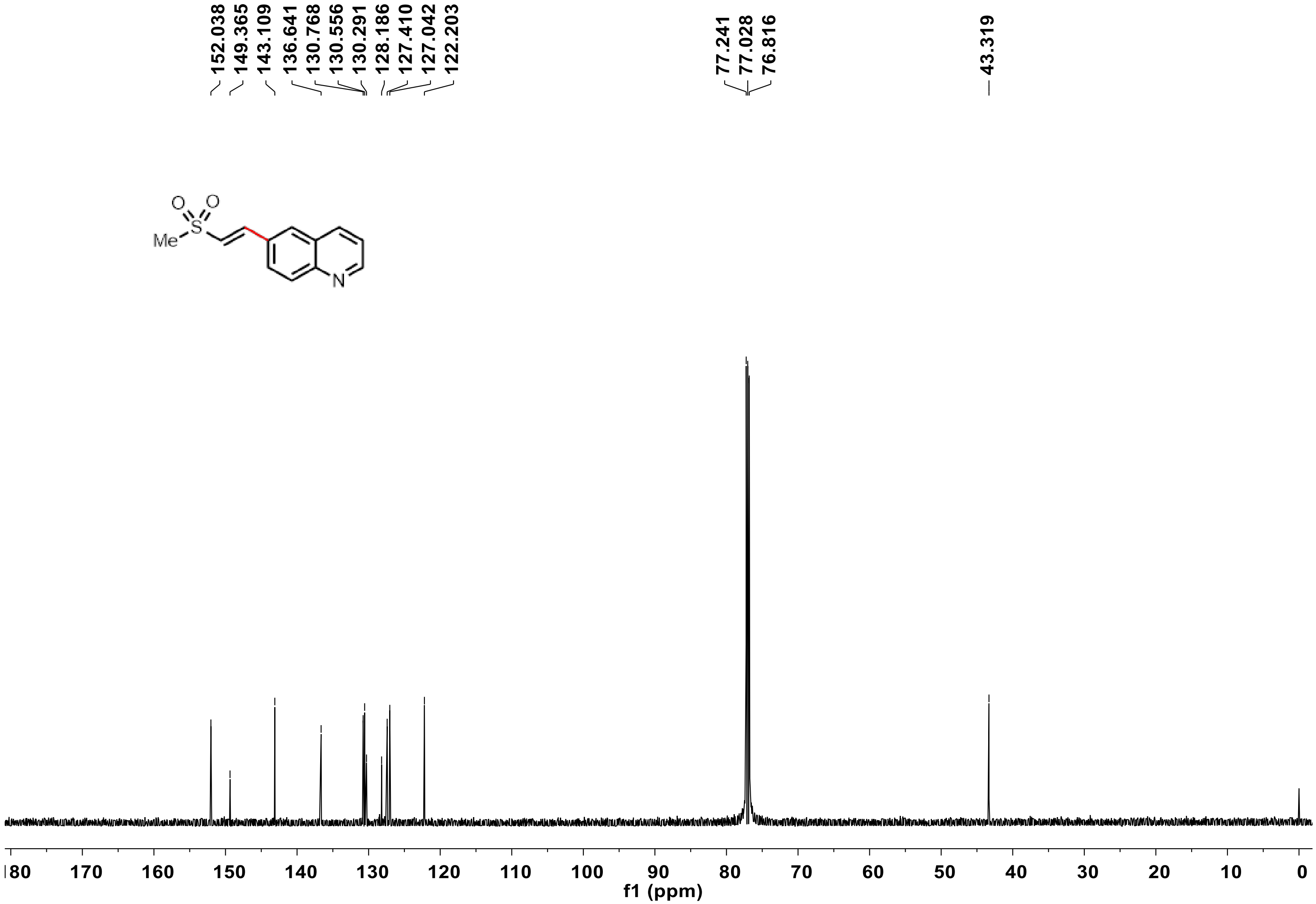
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2an**



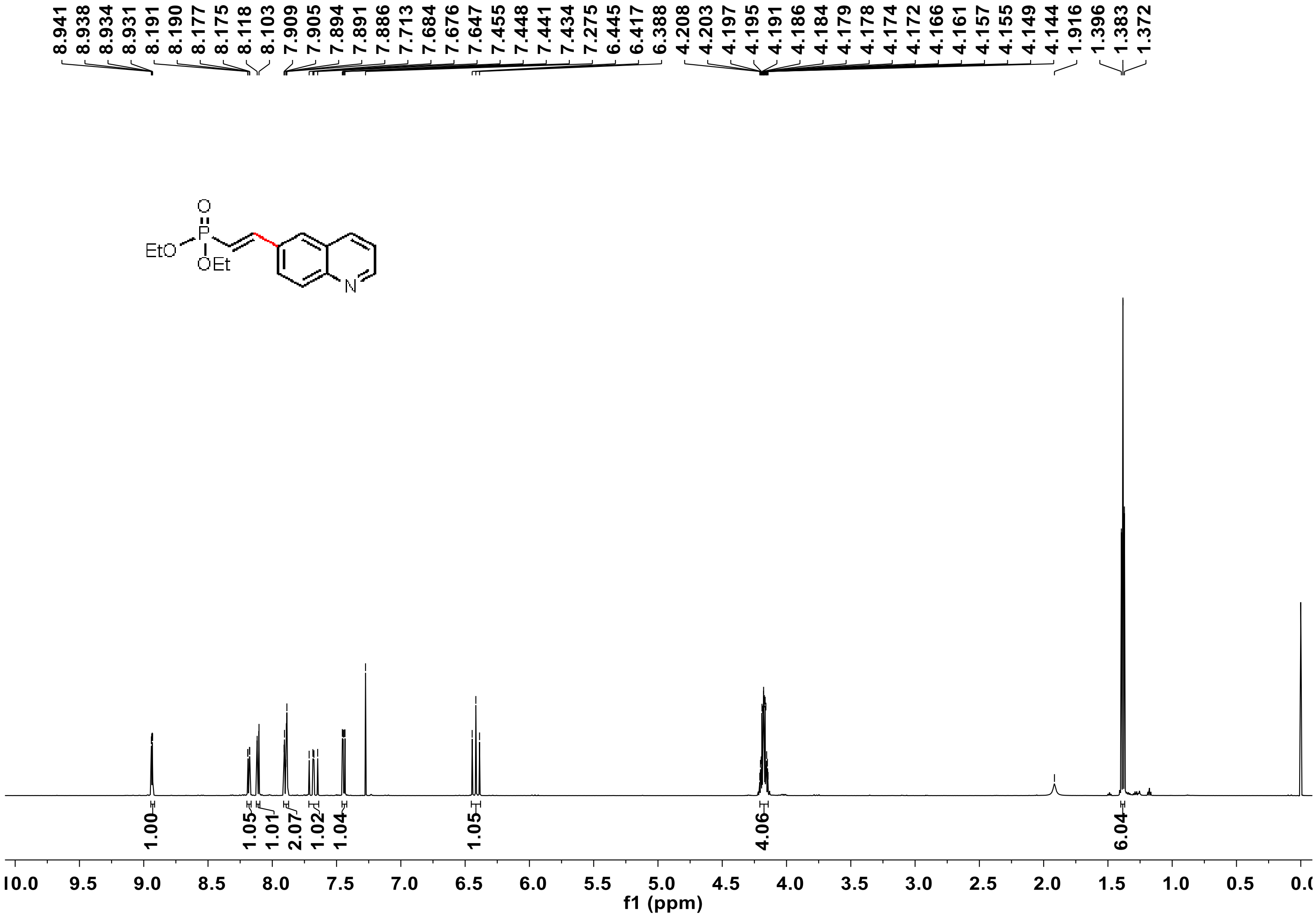
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ao**



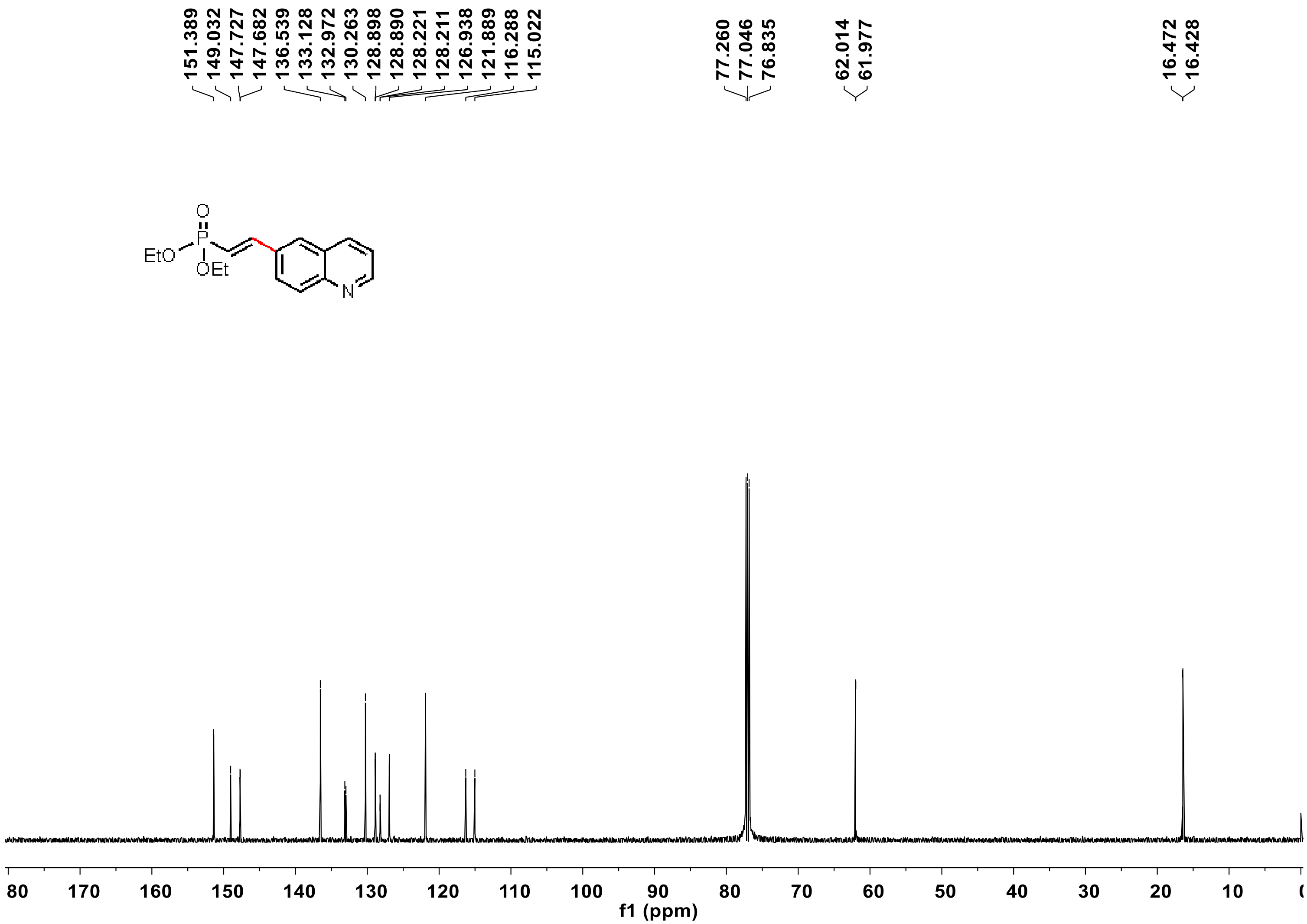
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ao**



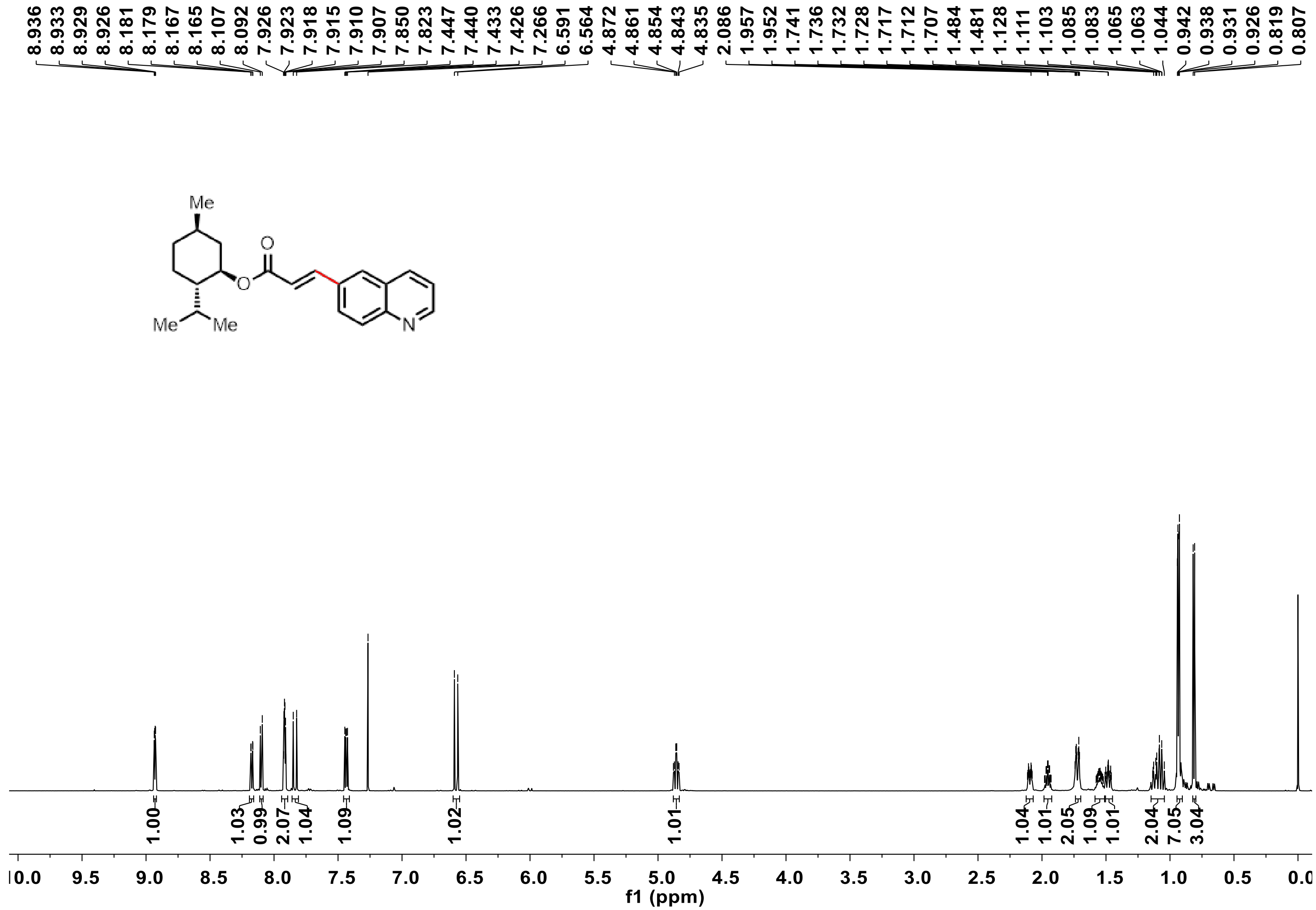
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ap**



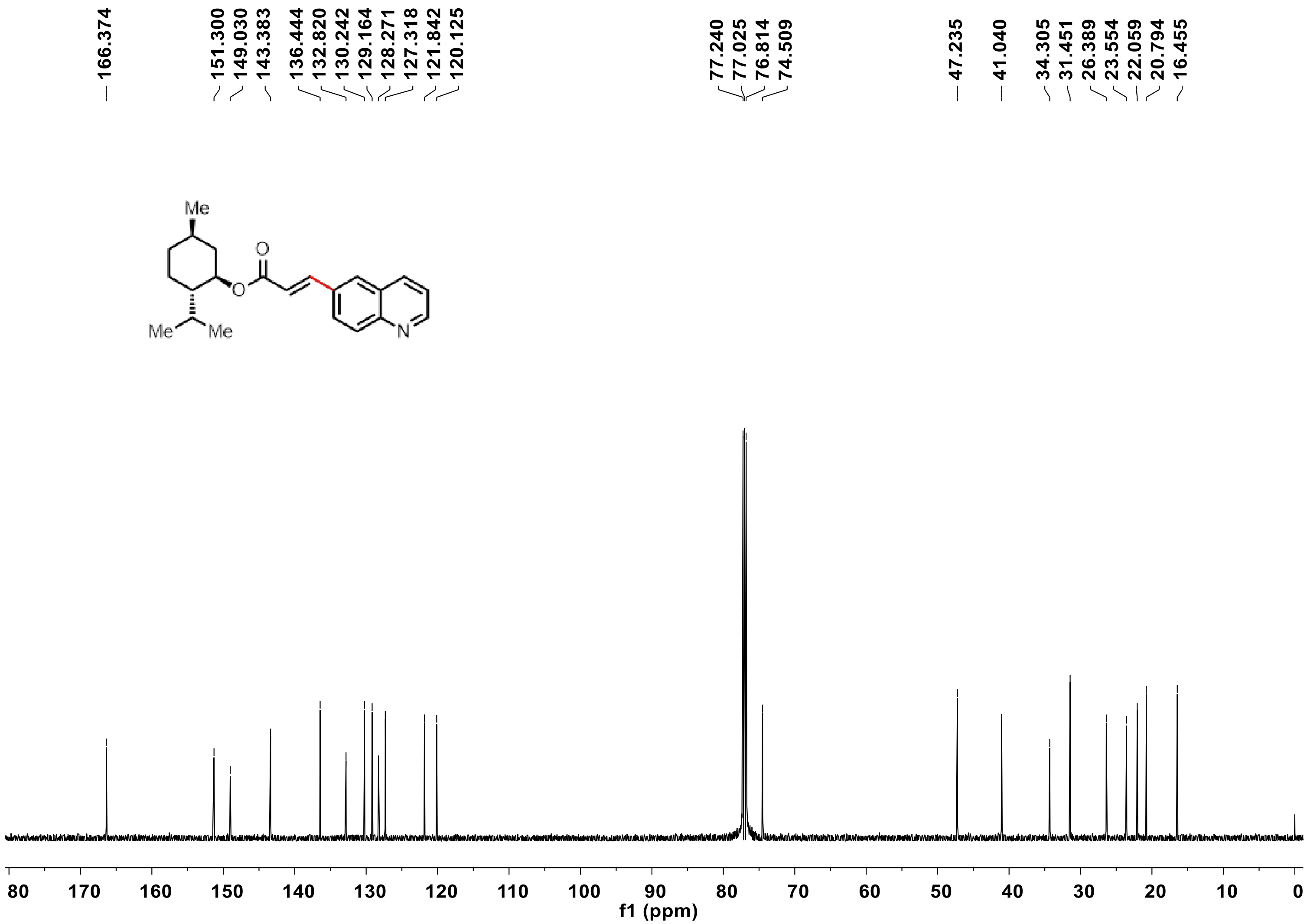
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ap**



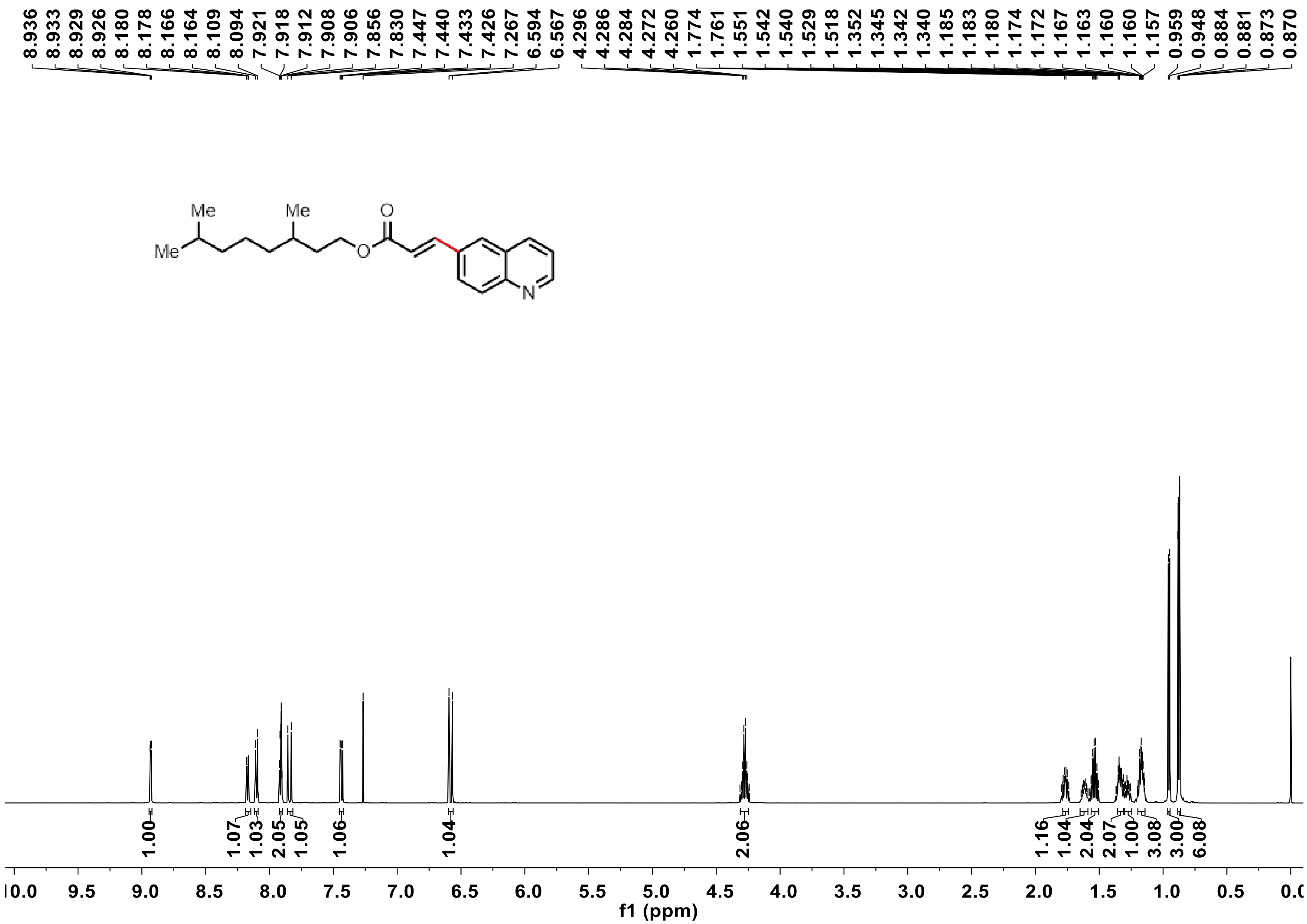
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aq**



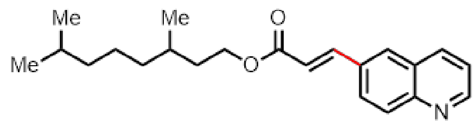
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2aq**

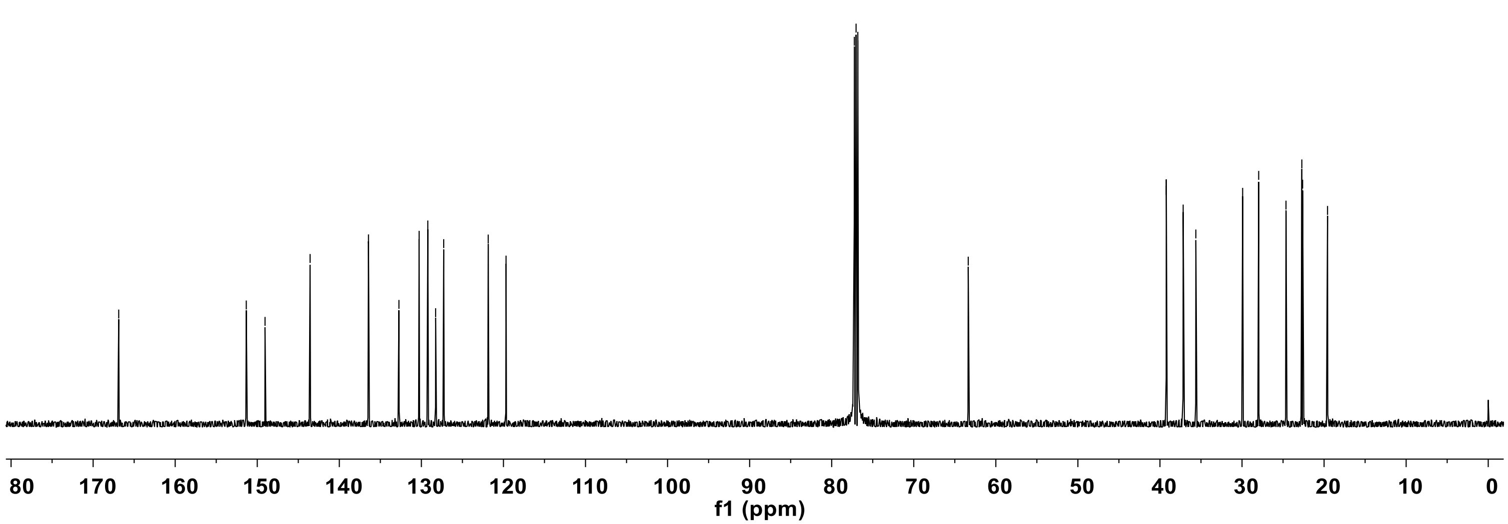


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ar**

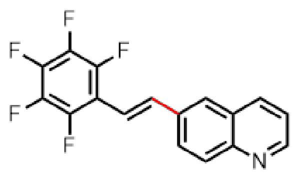


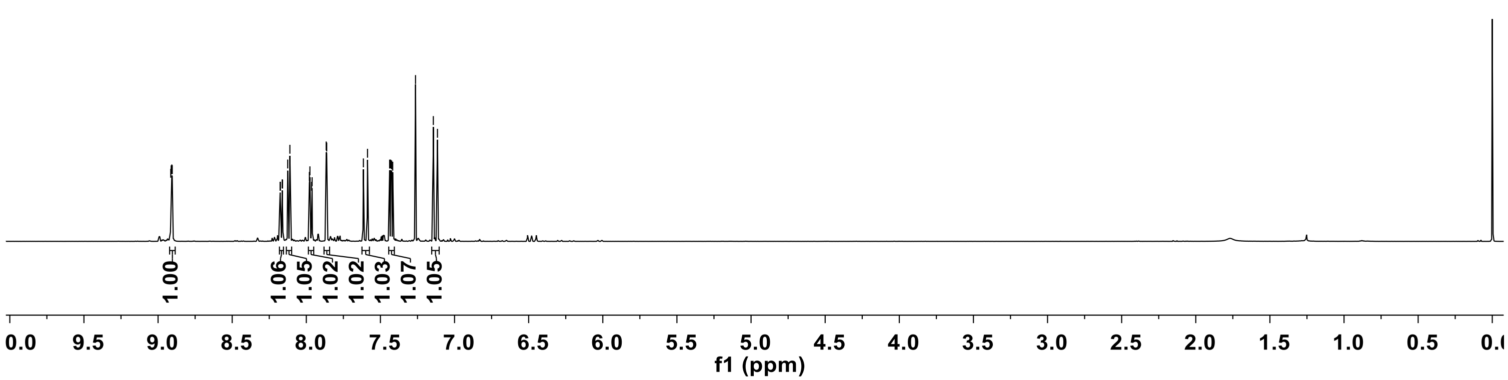
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2ar**



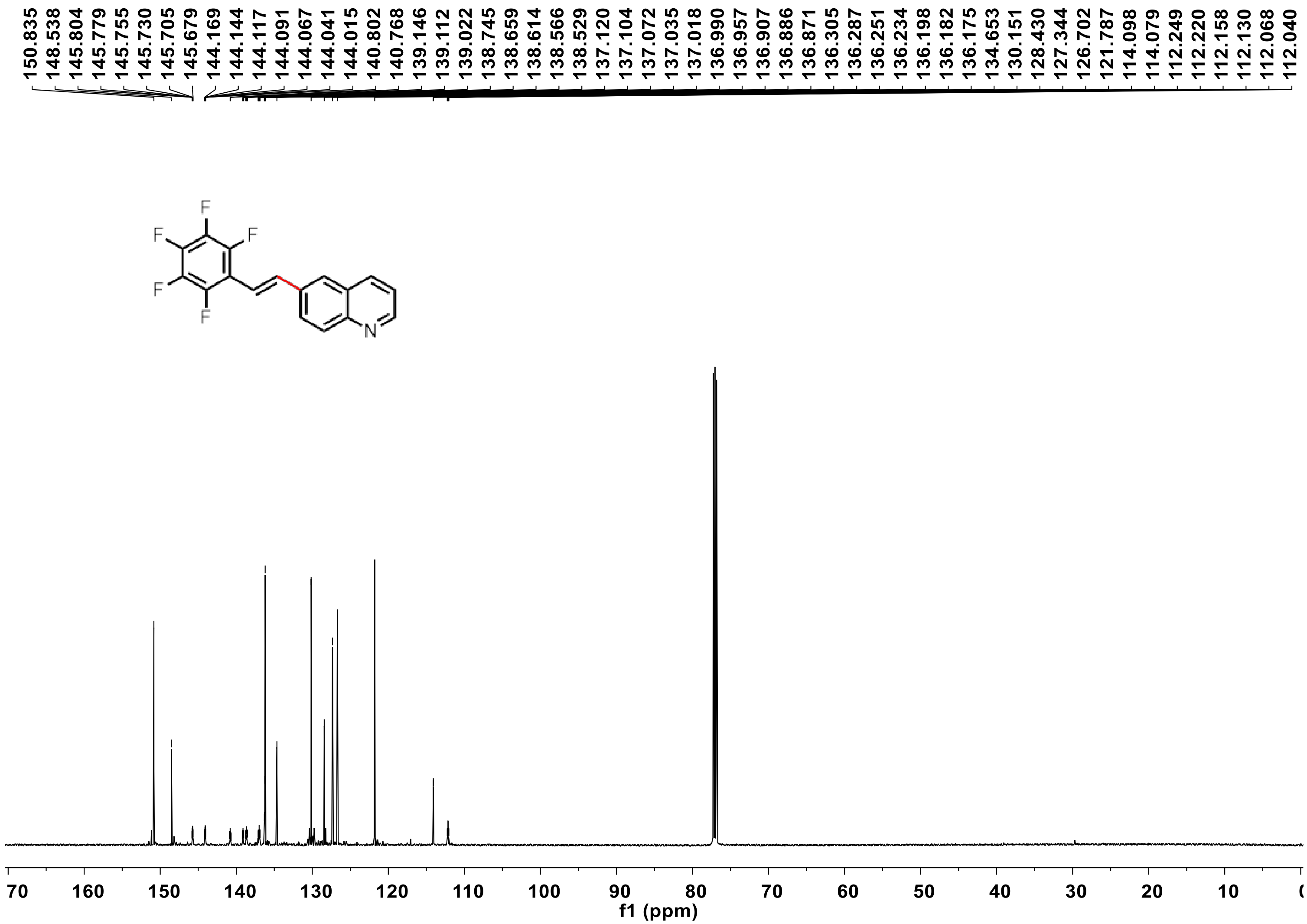


^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **2as**

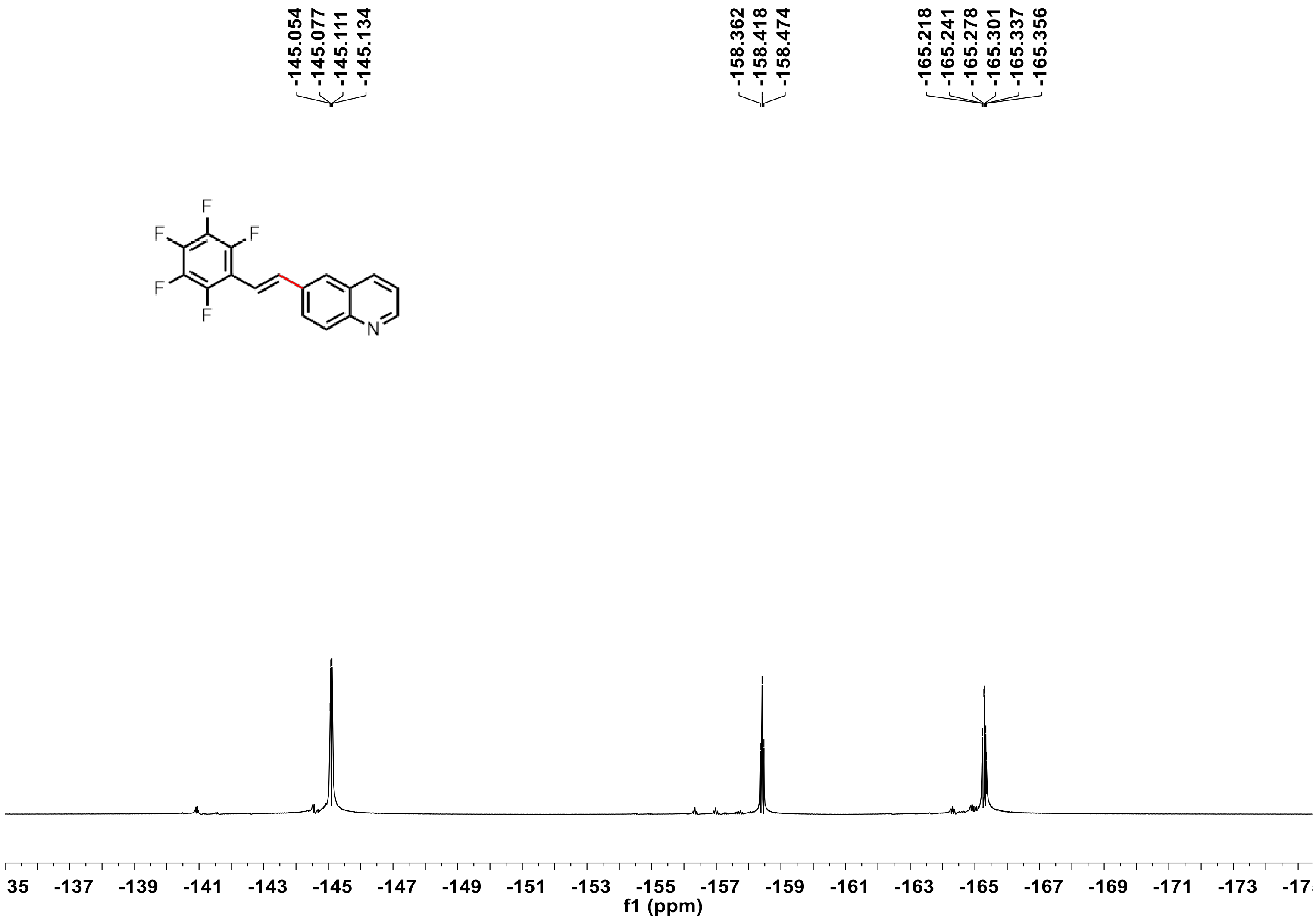




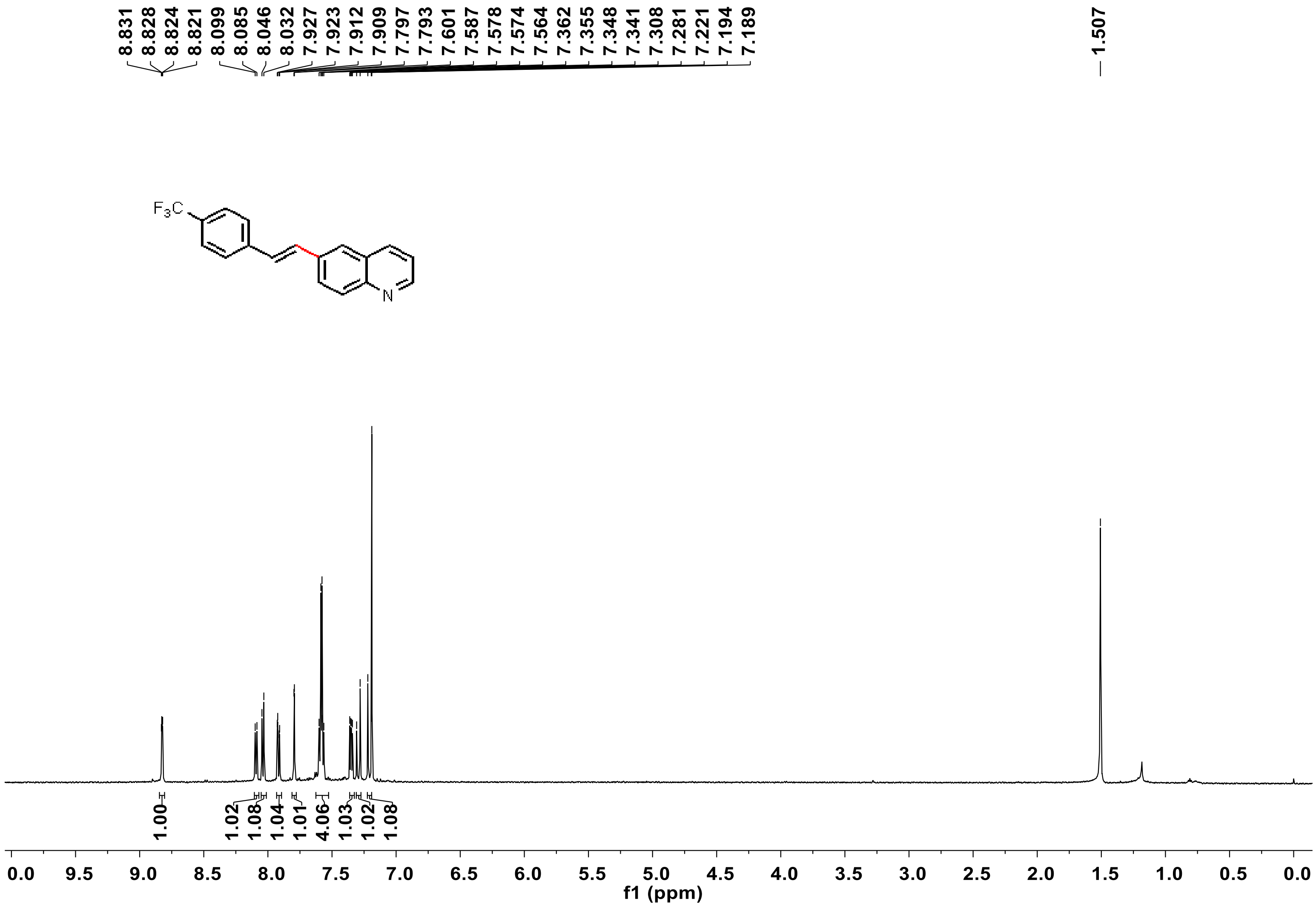
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2as**



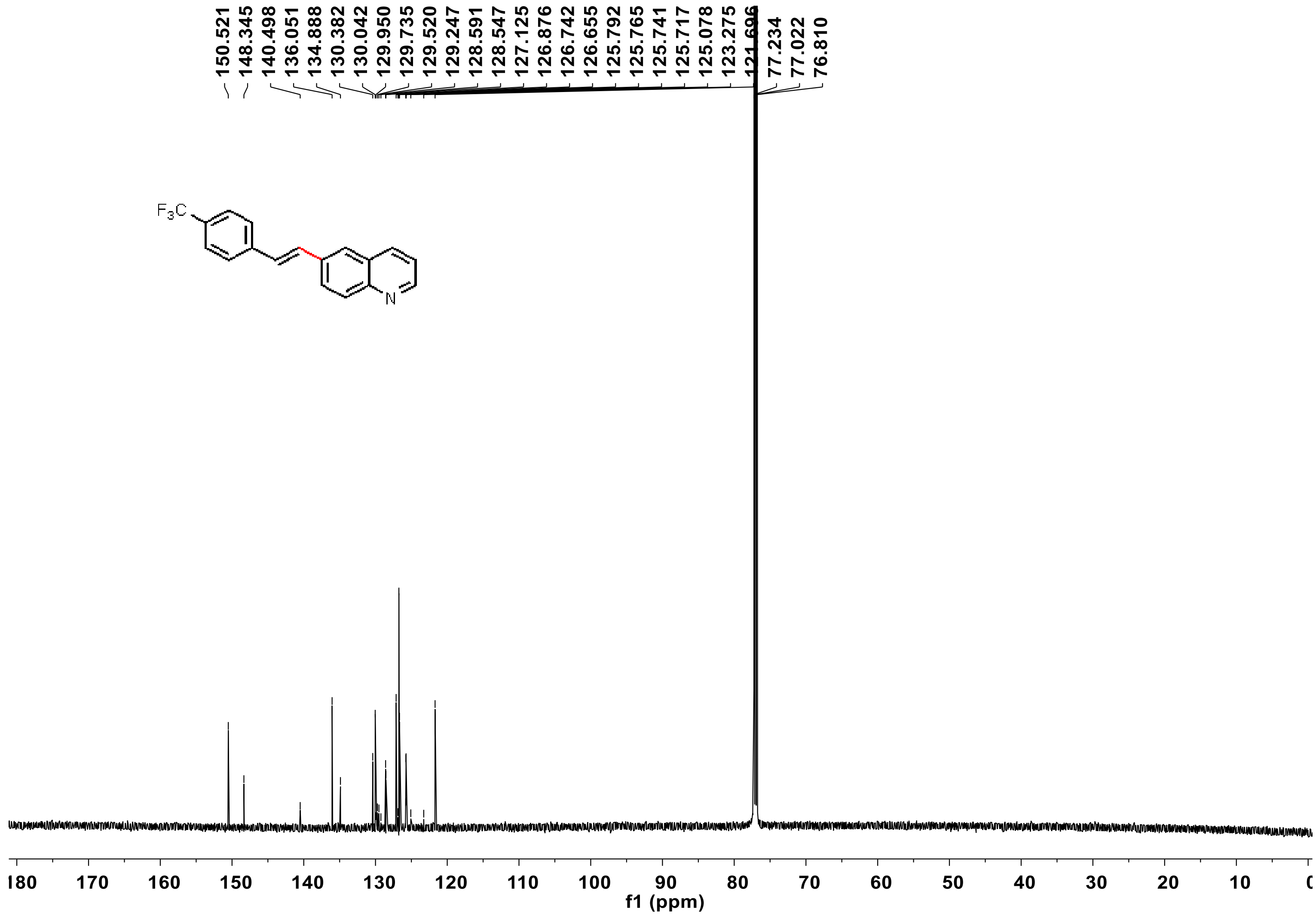
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2as**



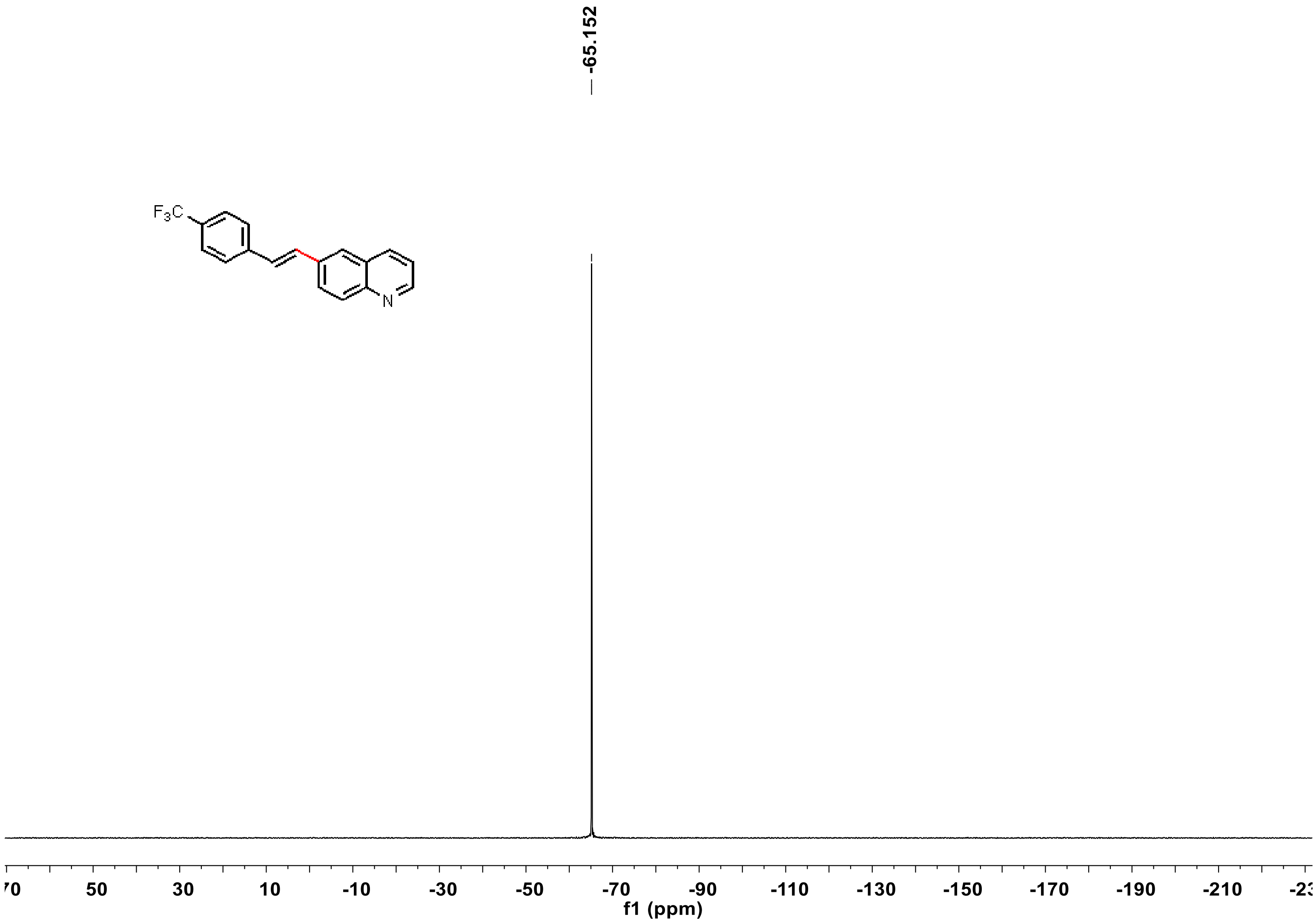
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2at**



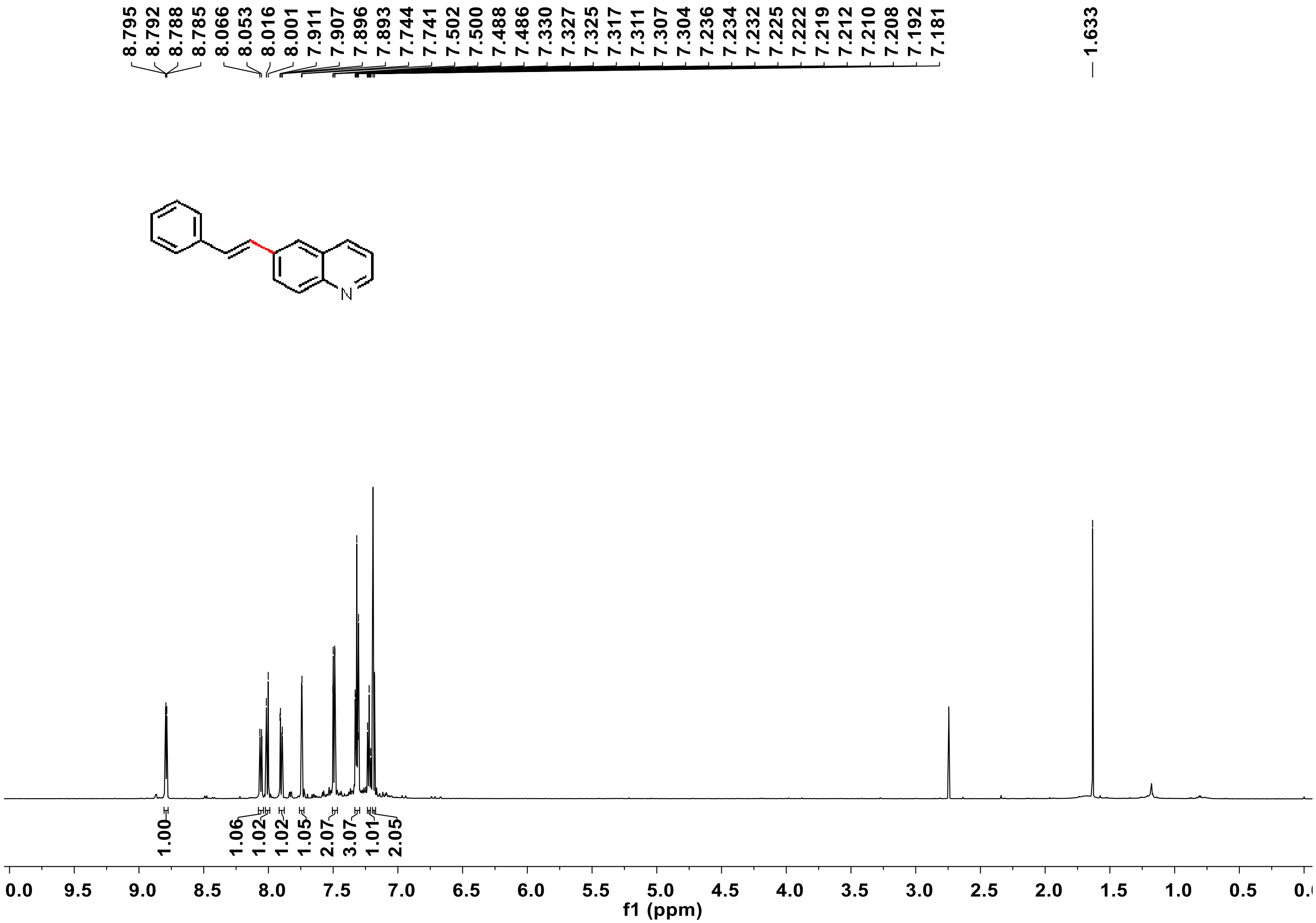
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2at**



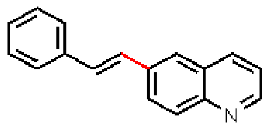
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2at**

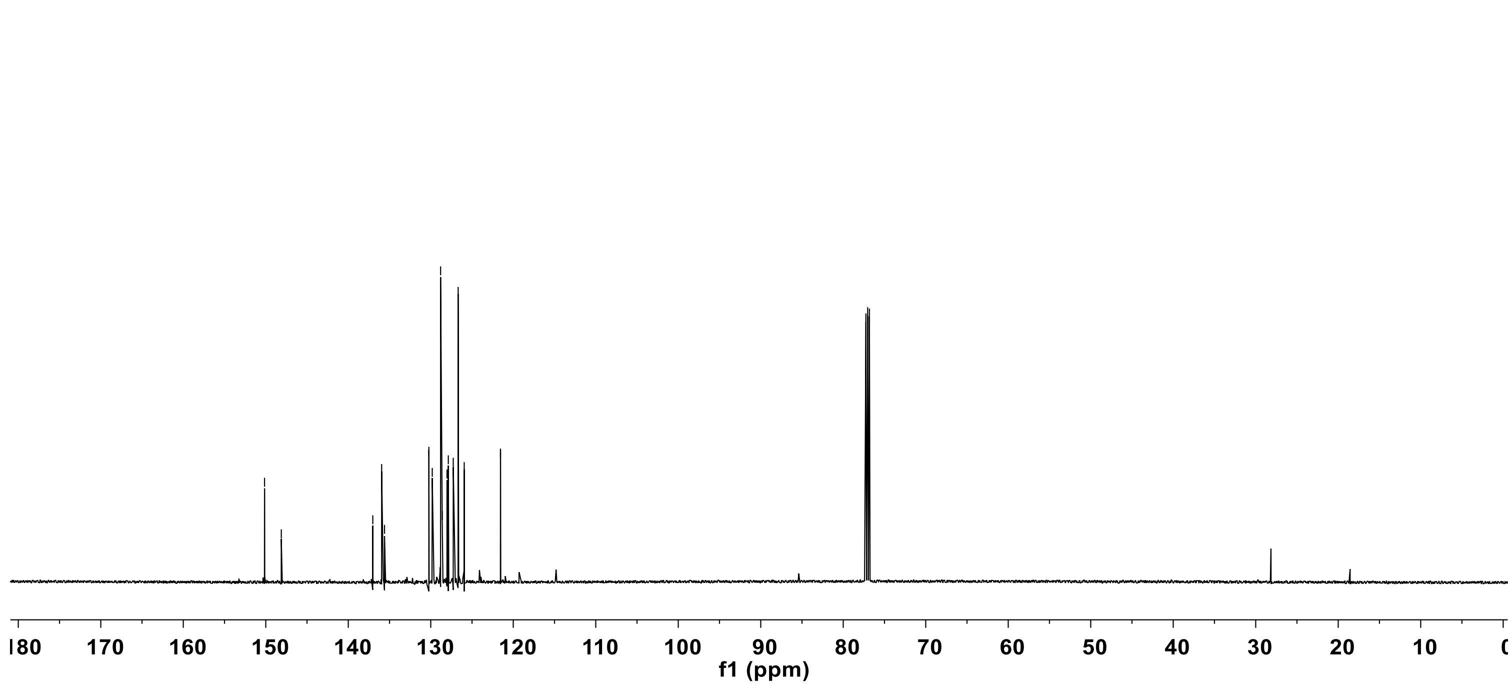


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2au**

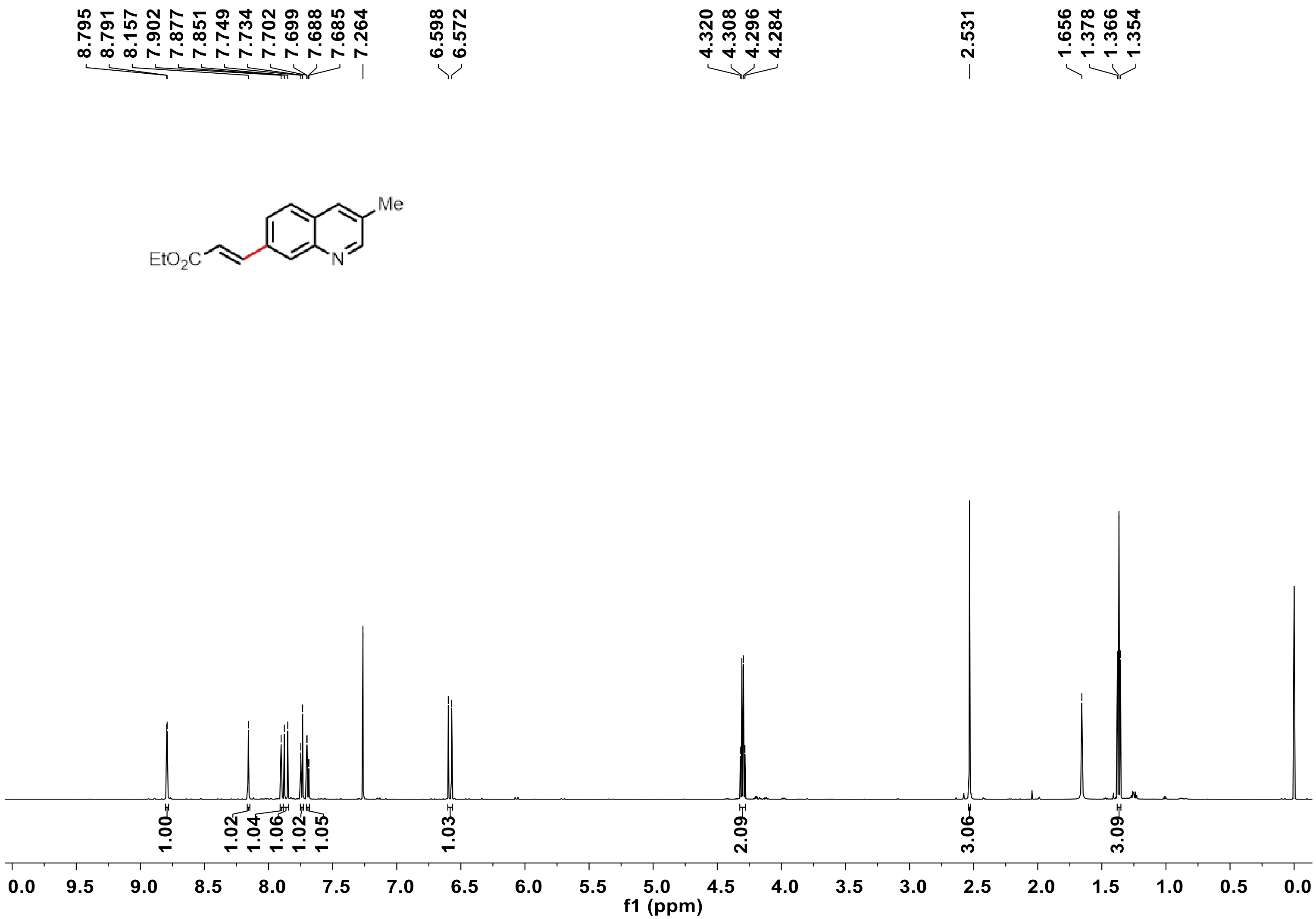


^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **2au**

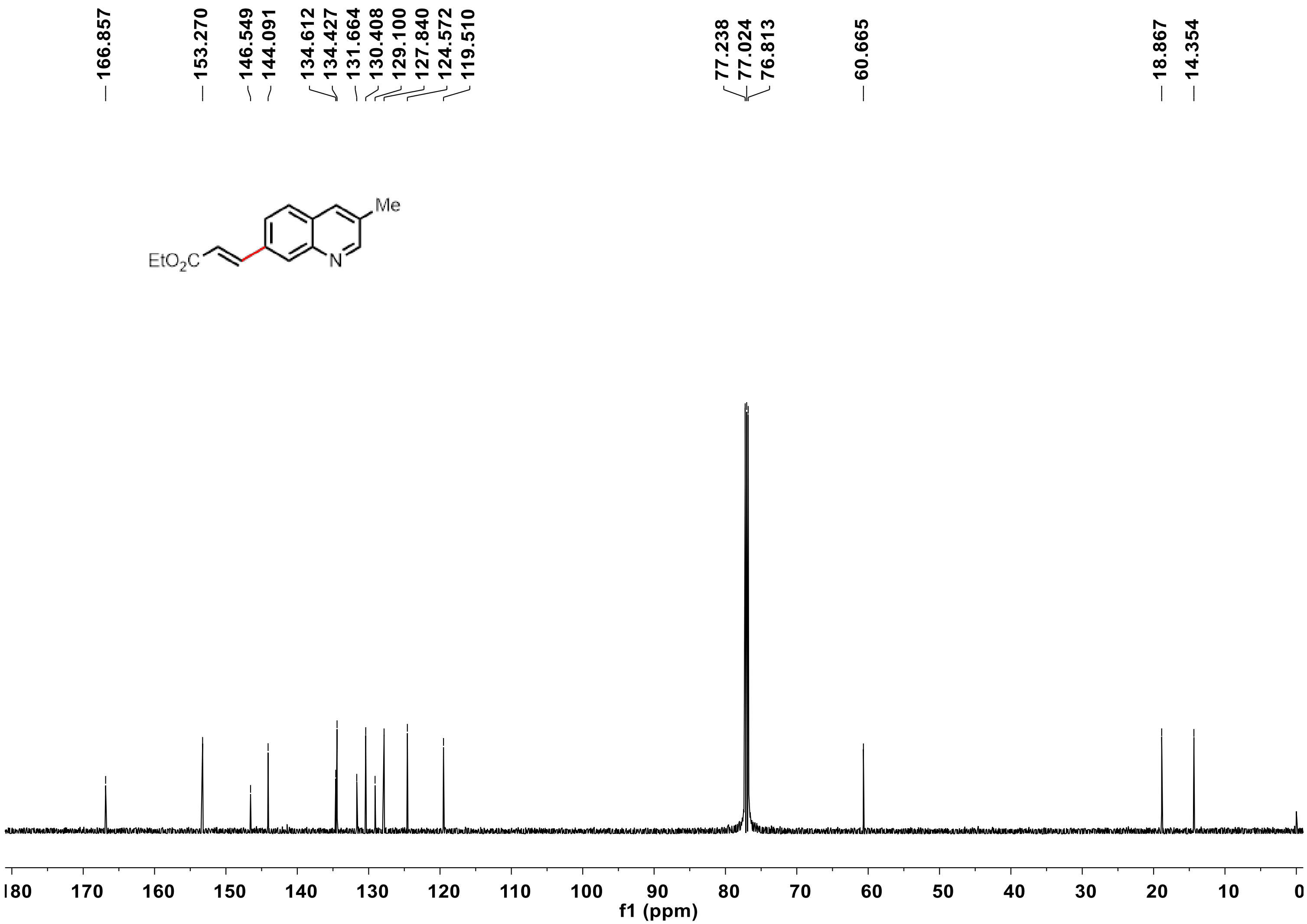




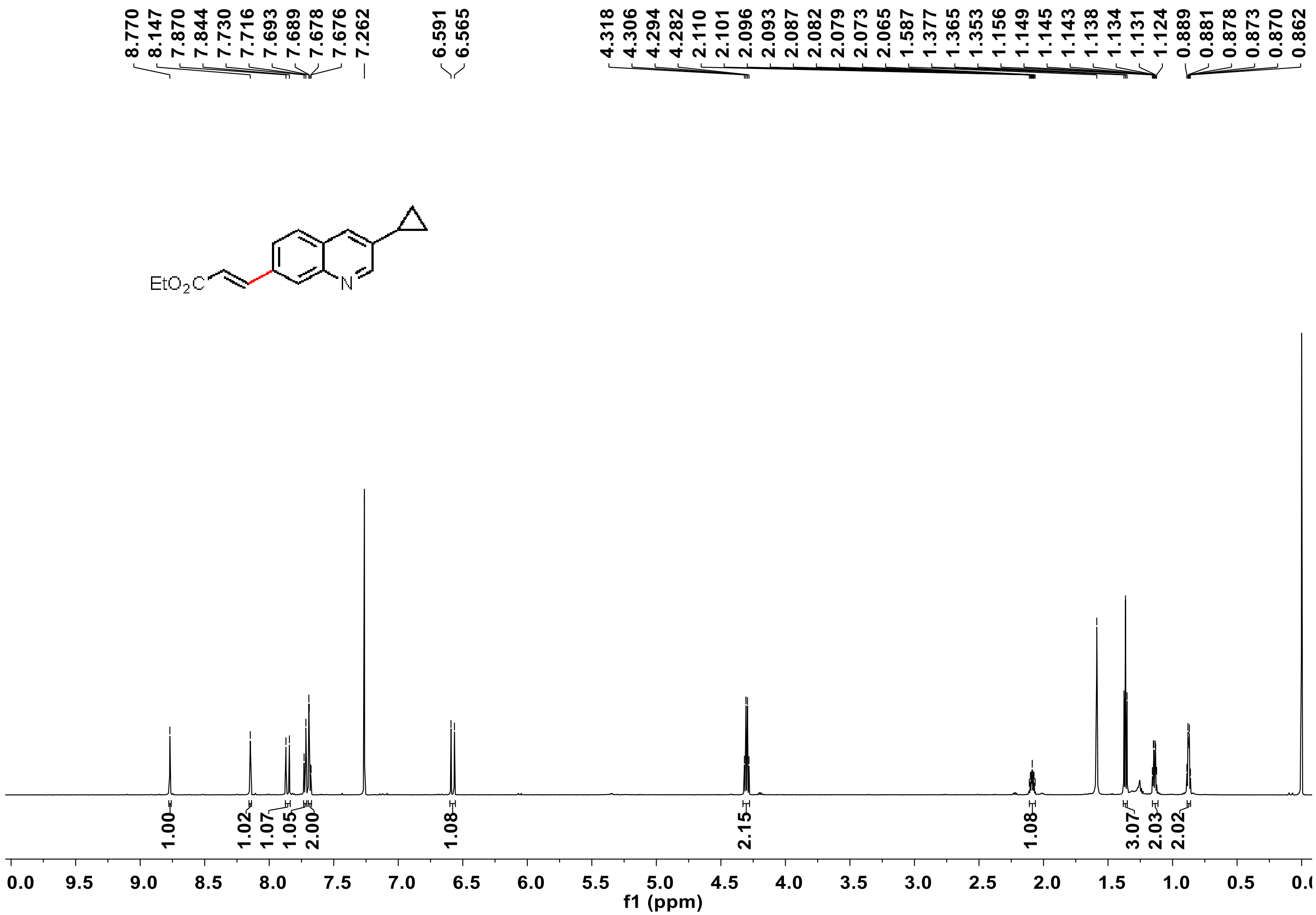
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3a**



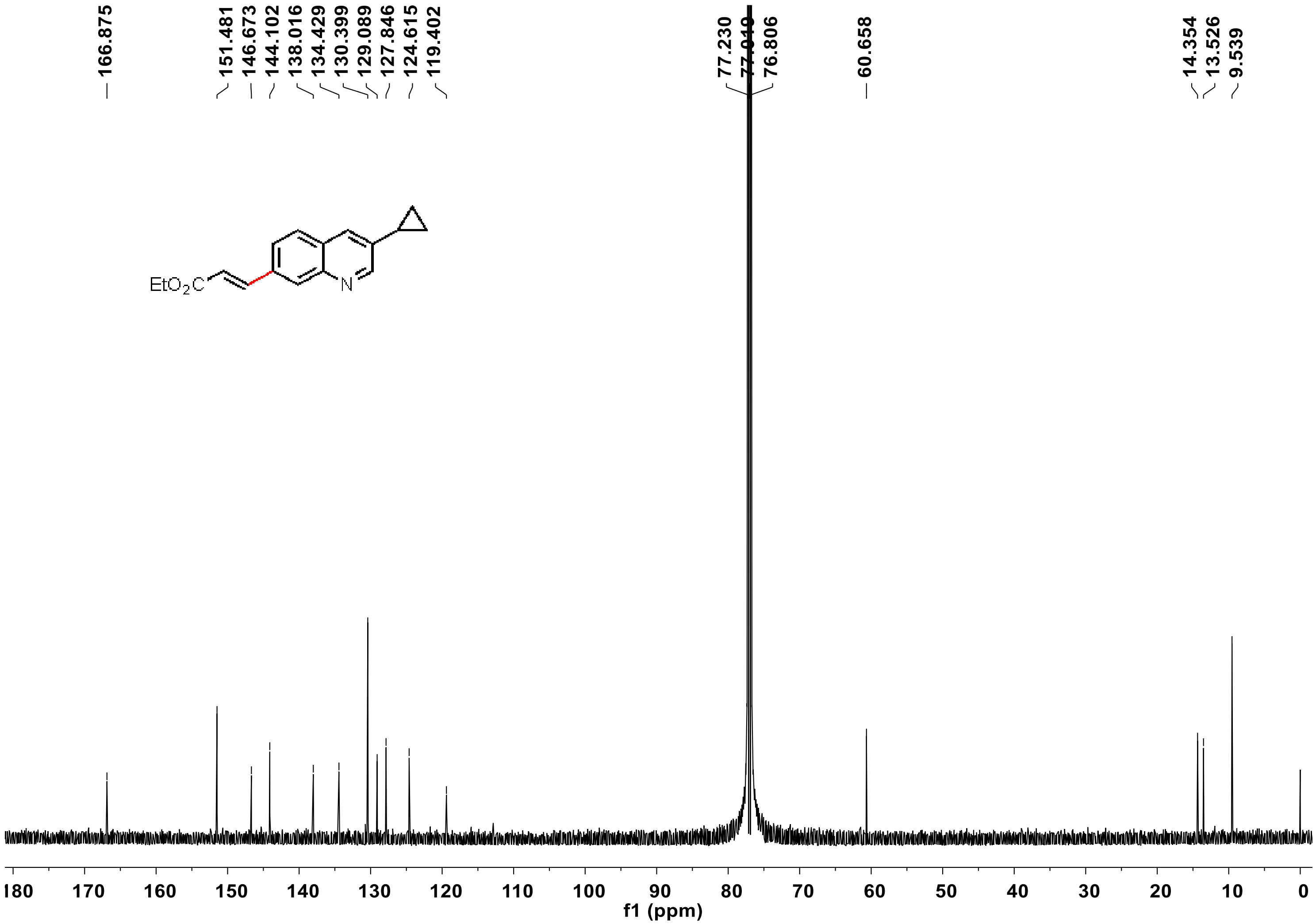
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3a**



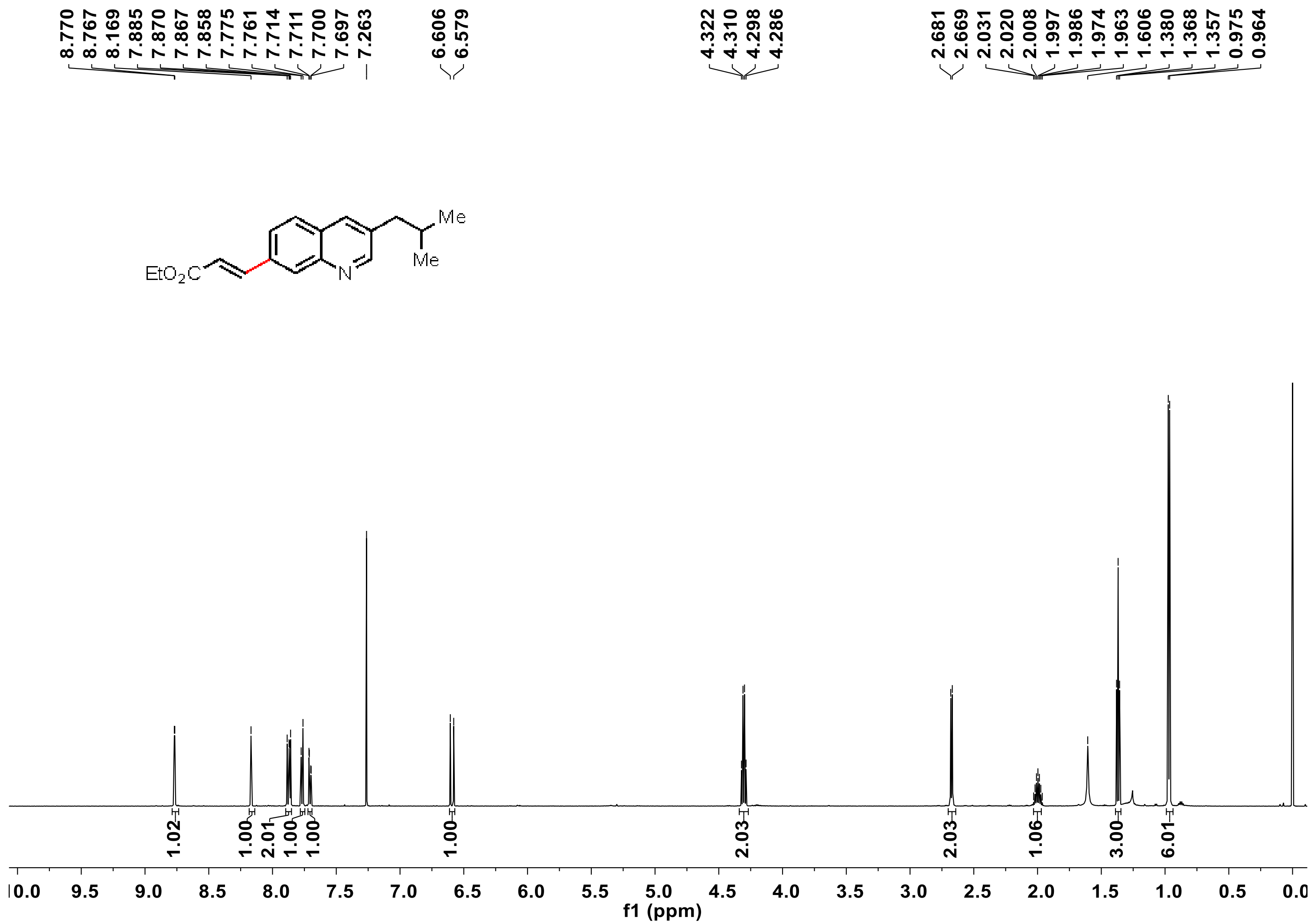
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3b**



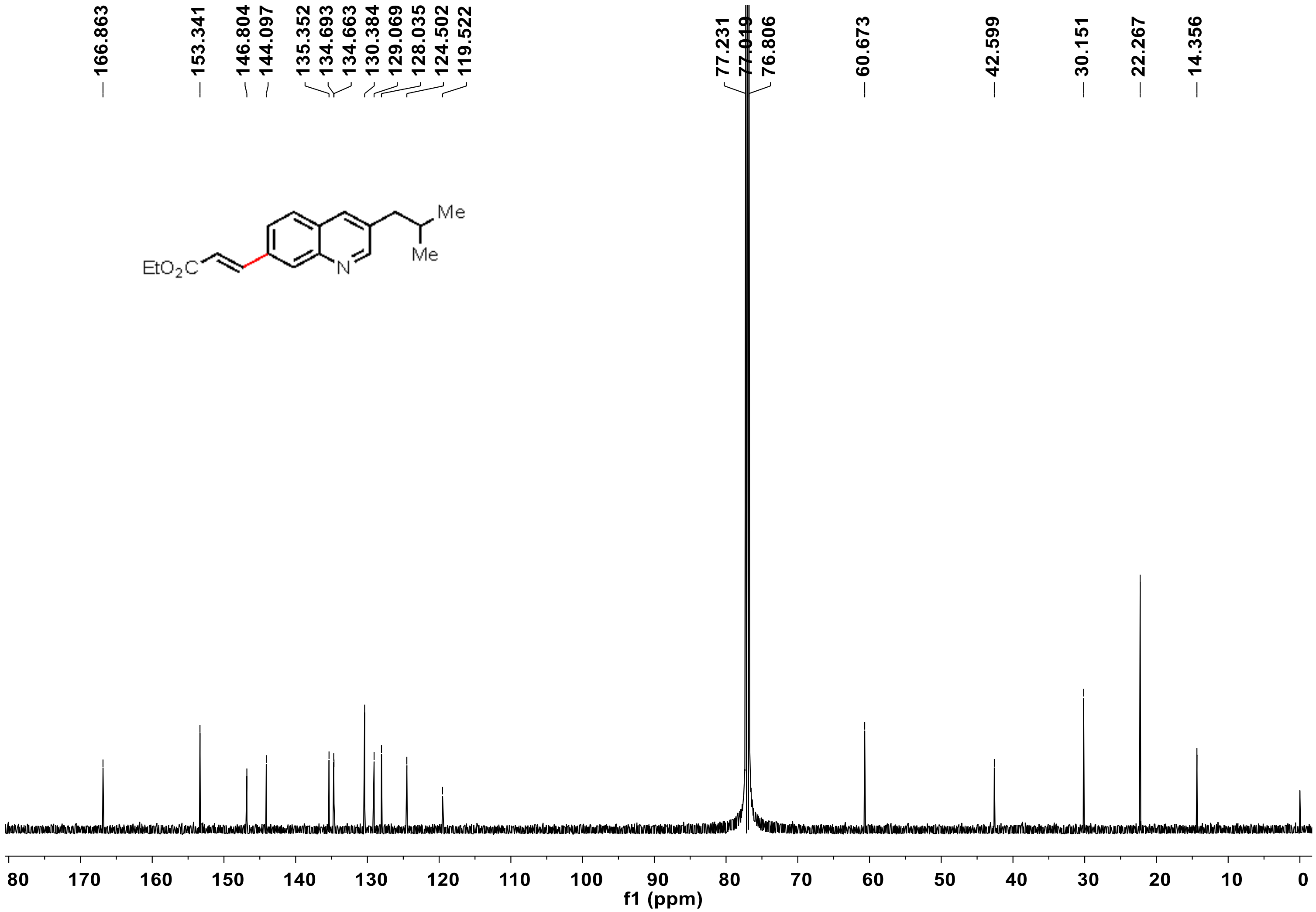
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3b**



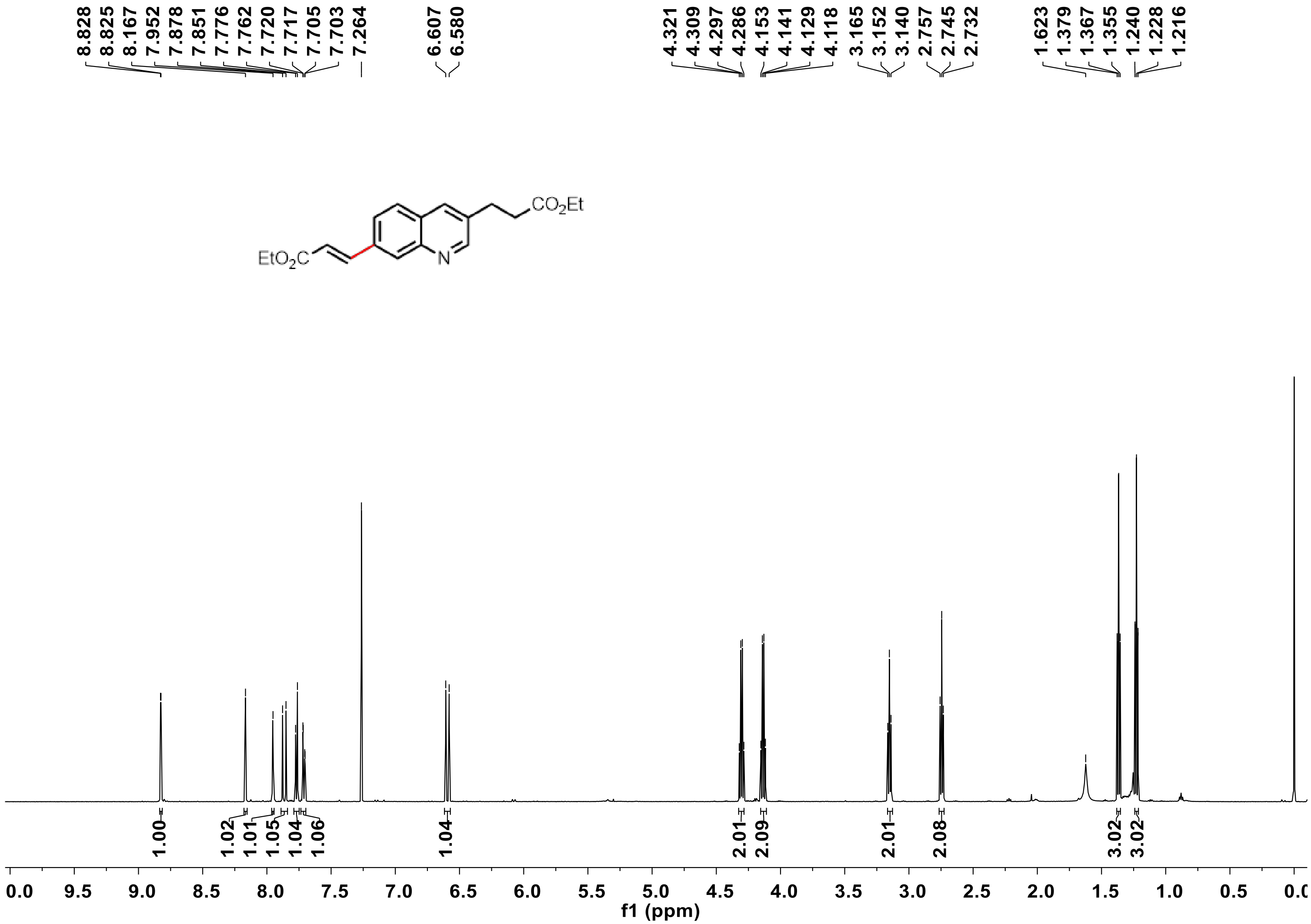
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3c**



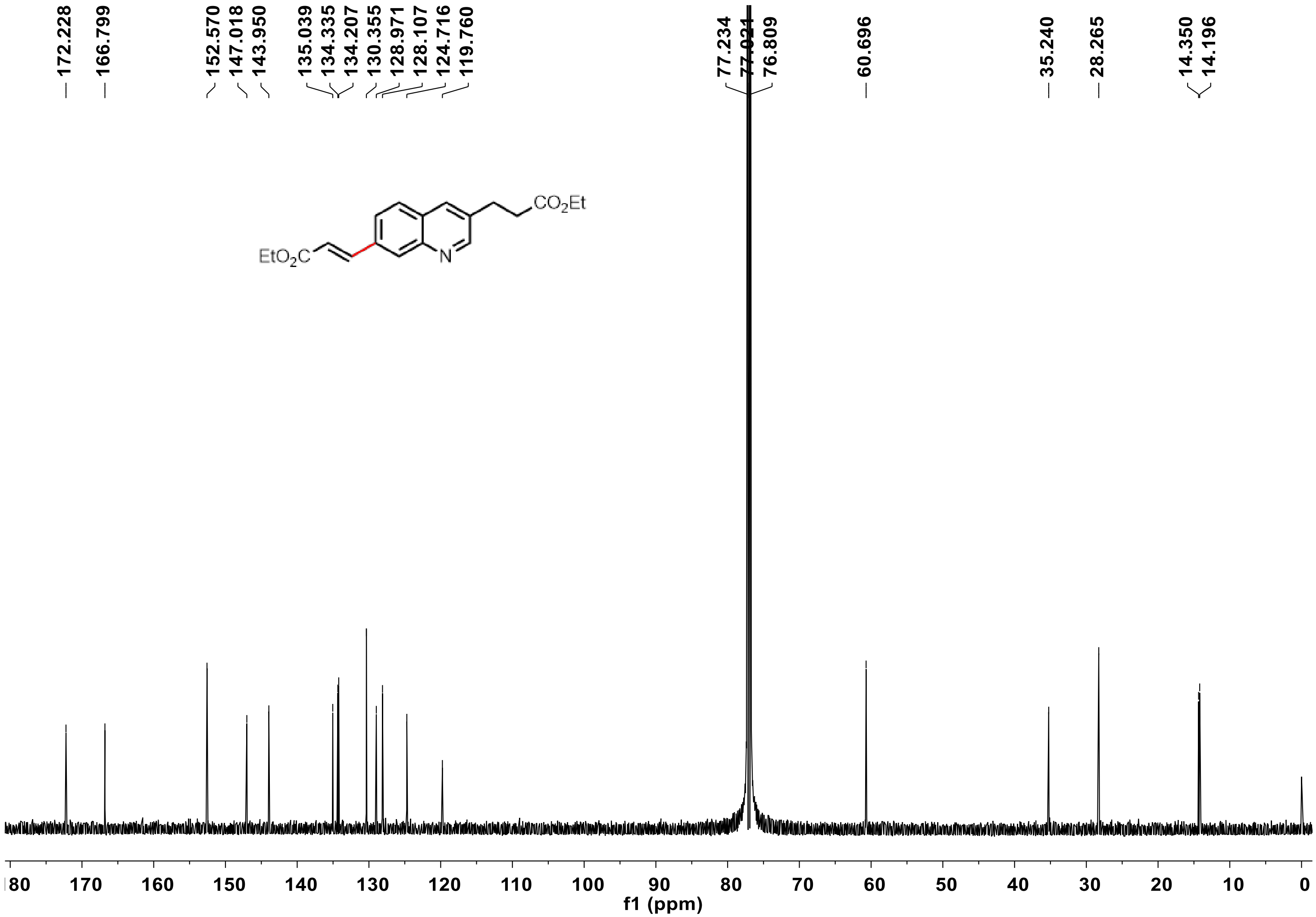
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3c**



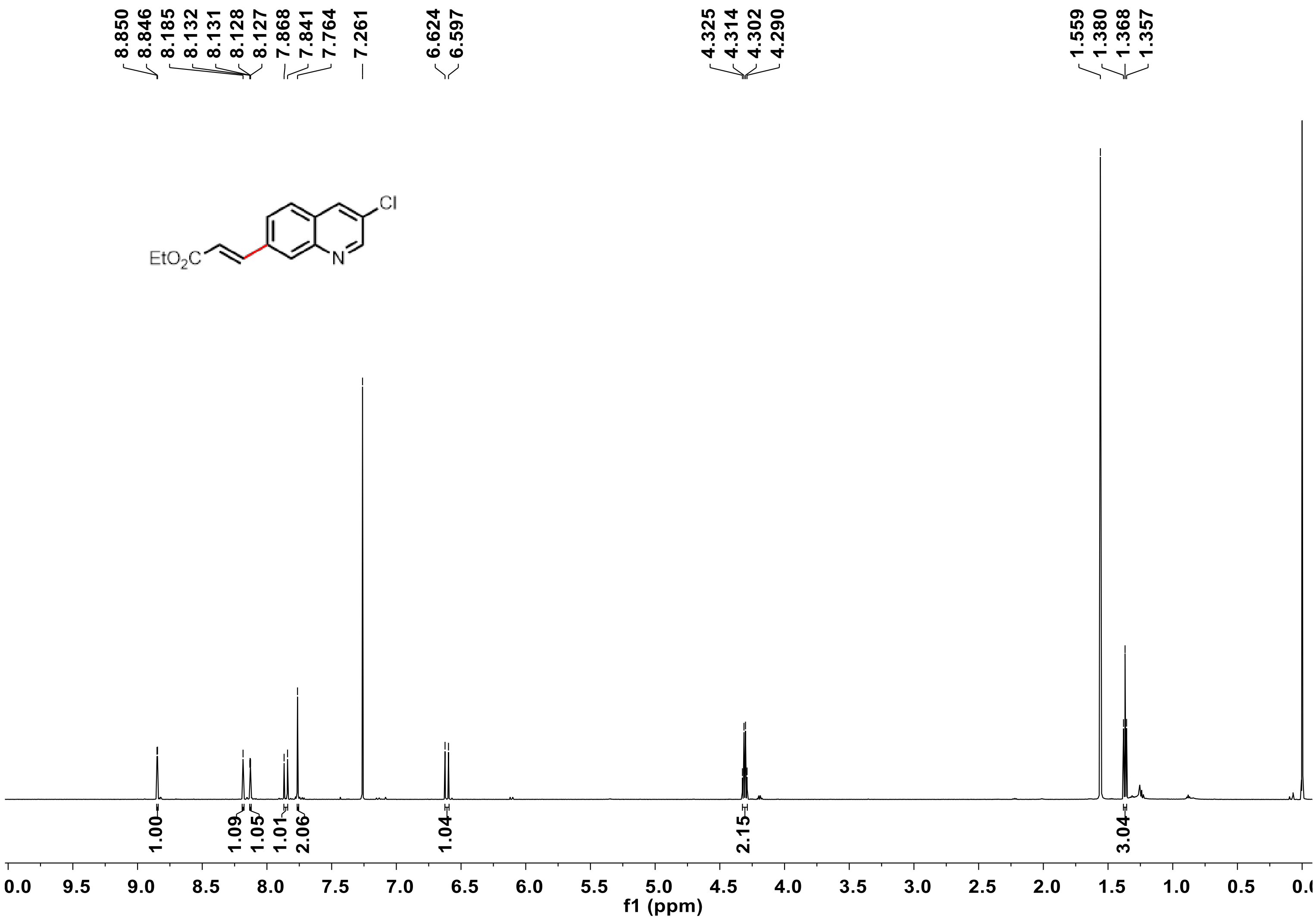
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **3d**



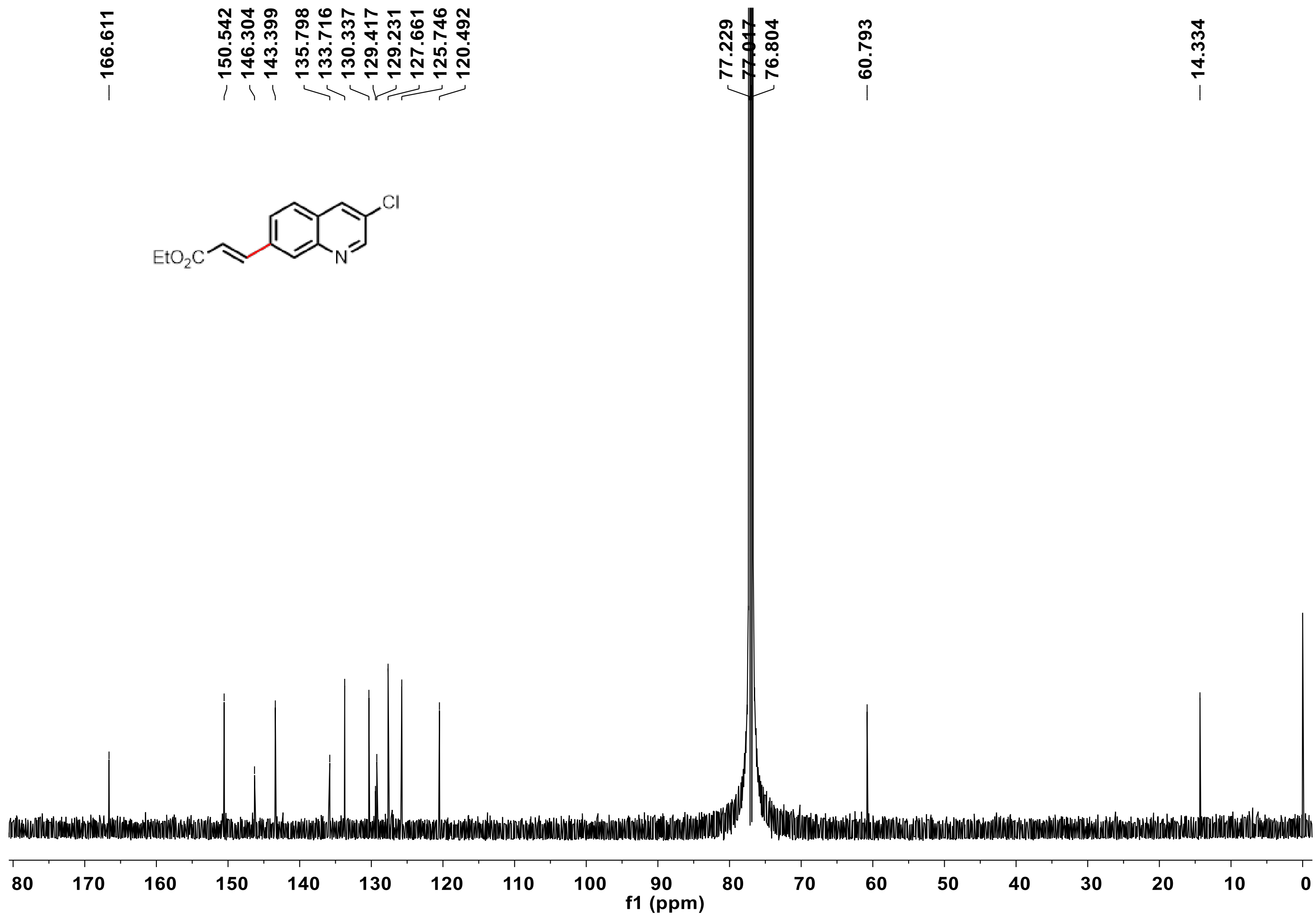
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3d**



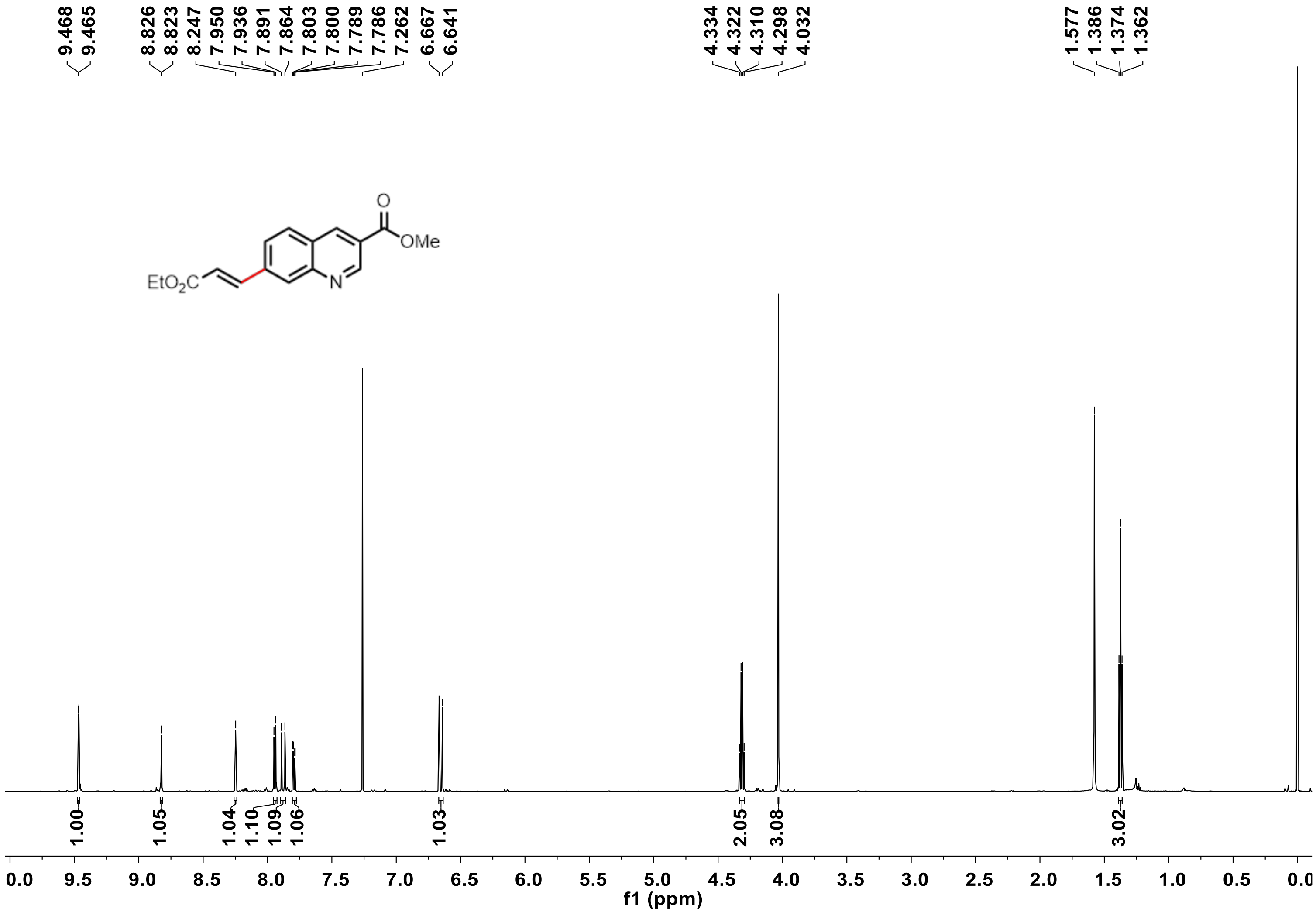
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3e**



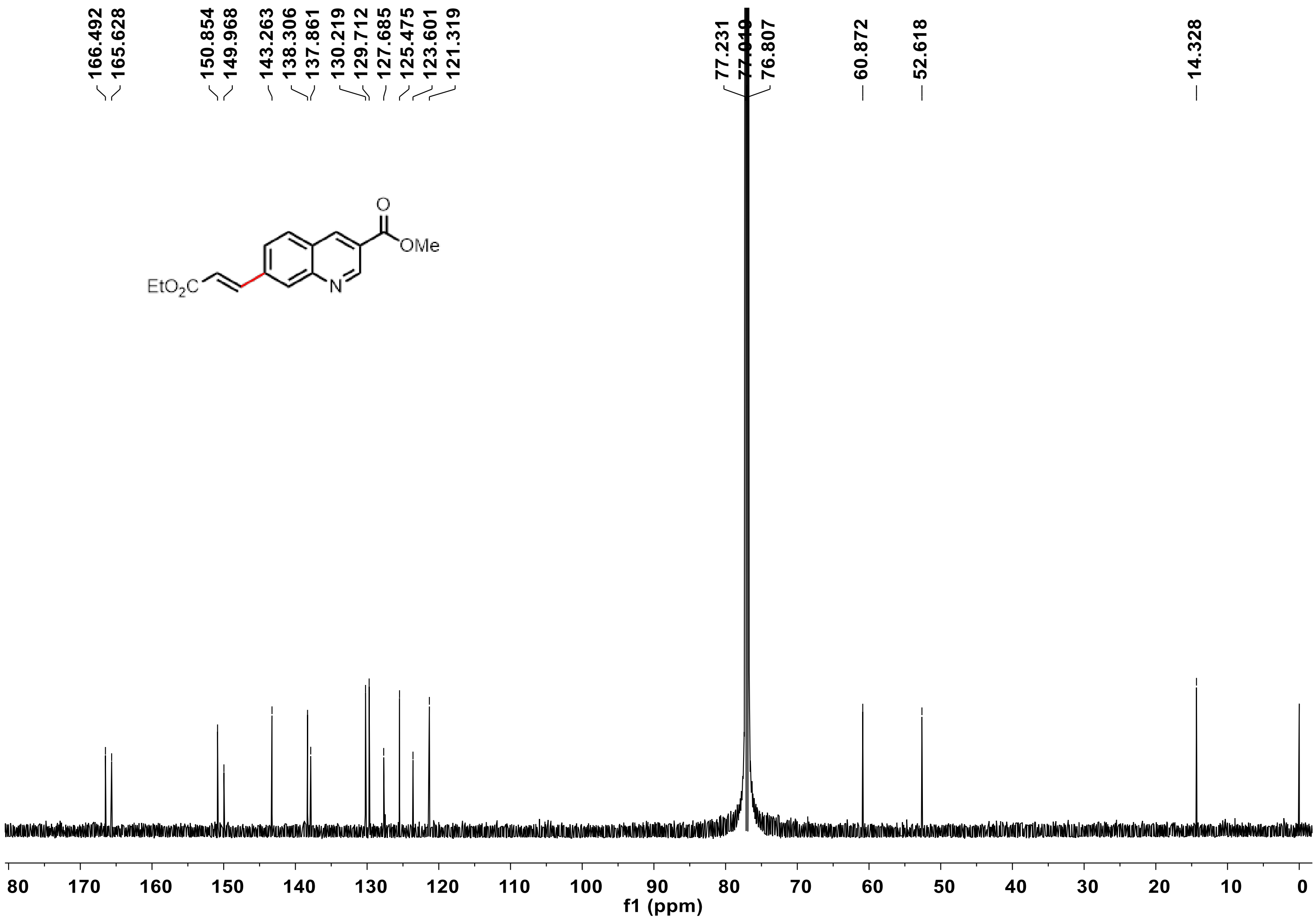
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3e**



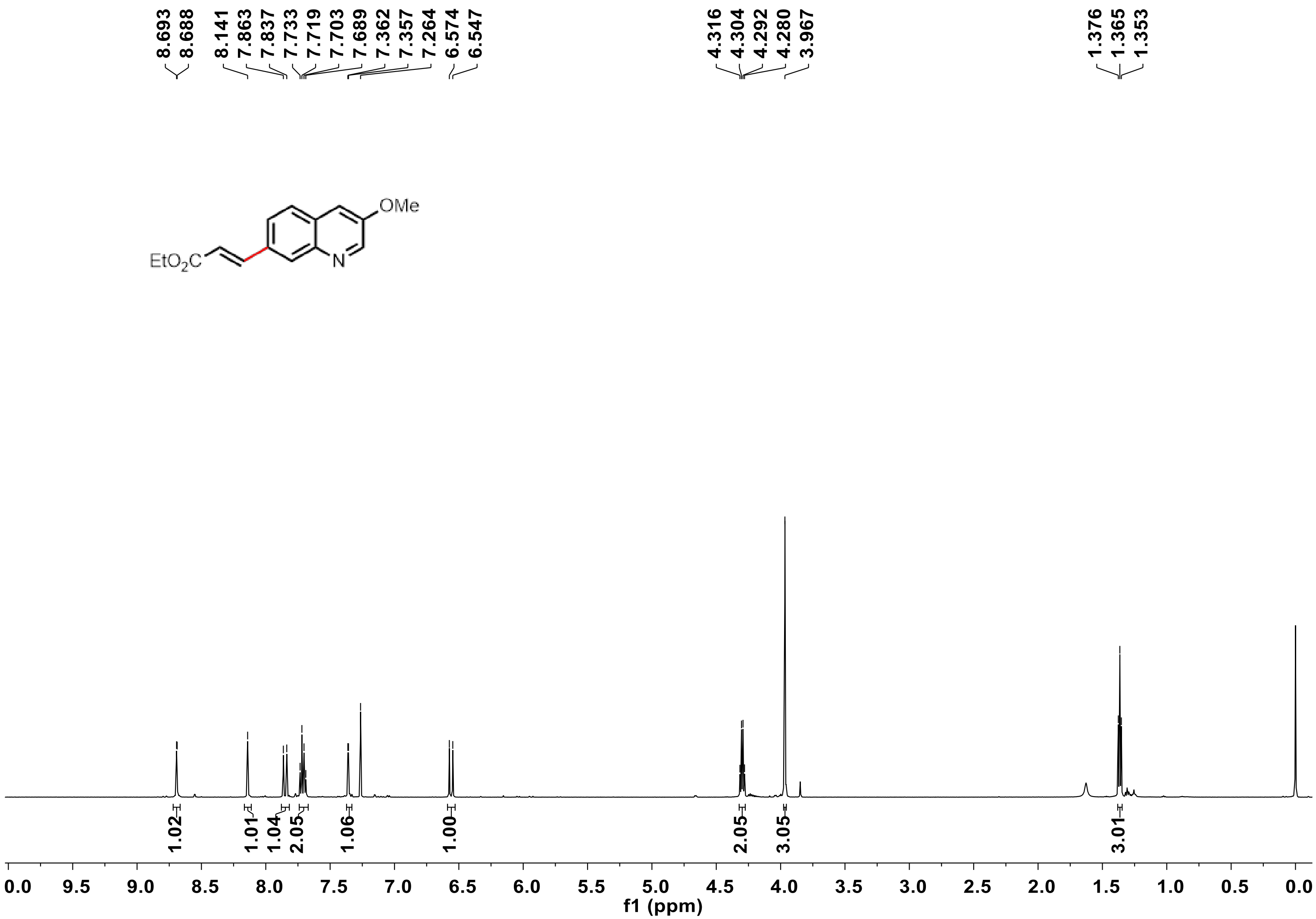
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3f**



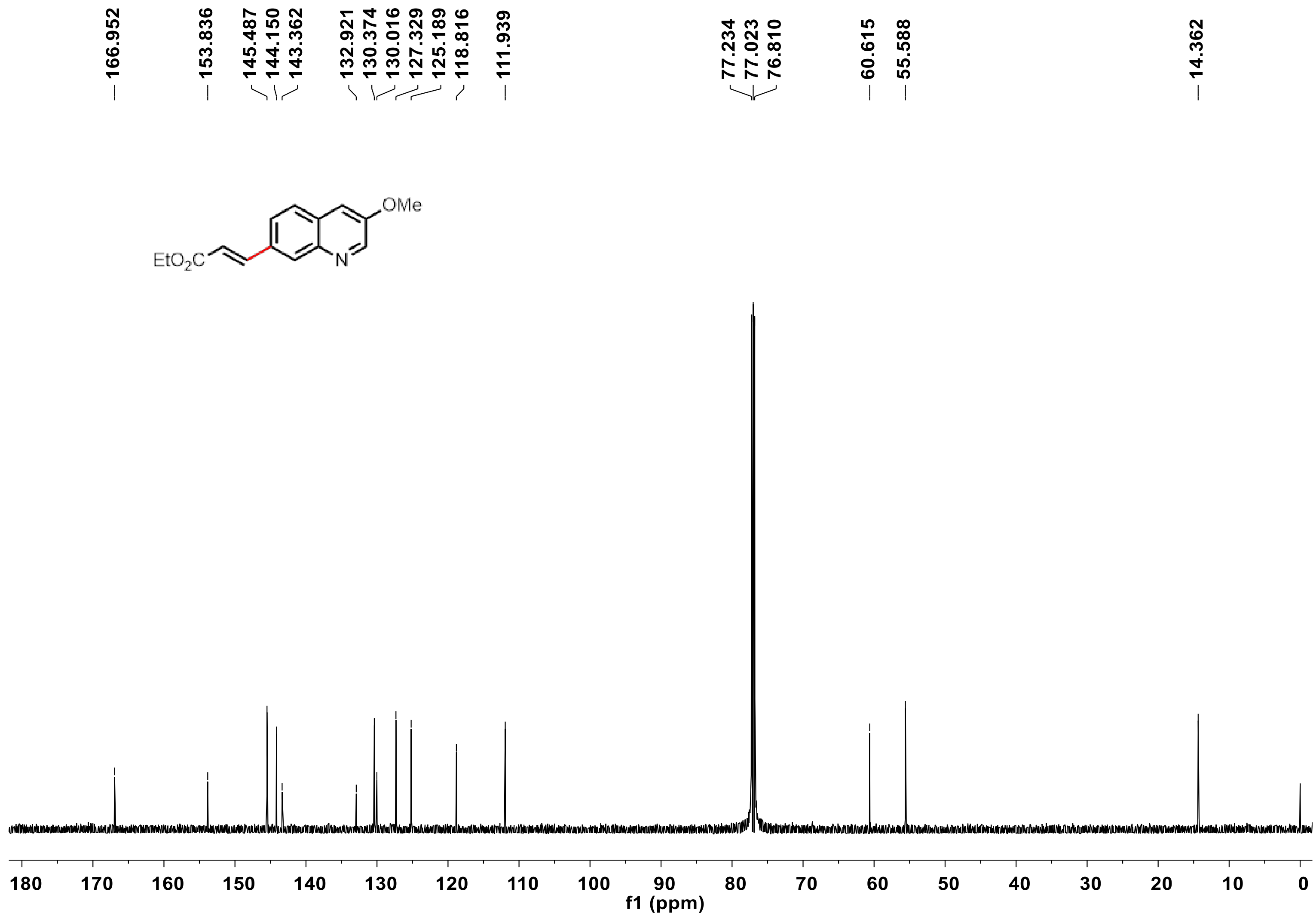
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3f**



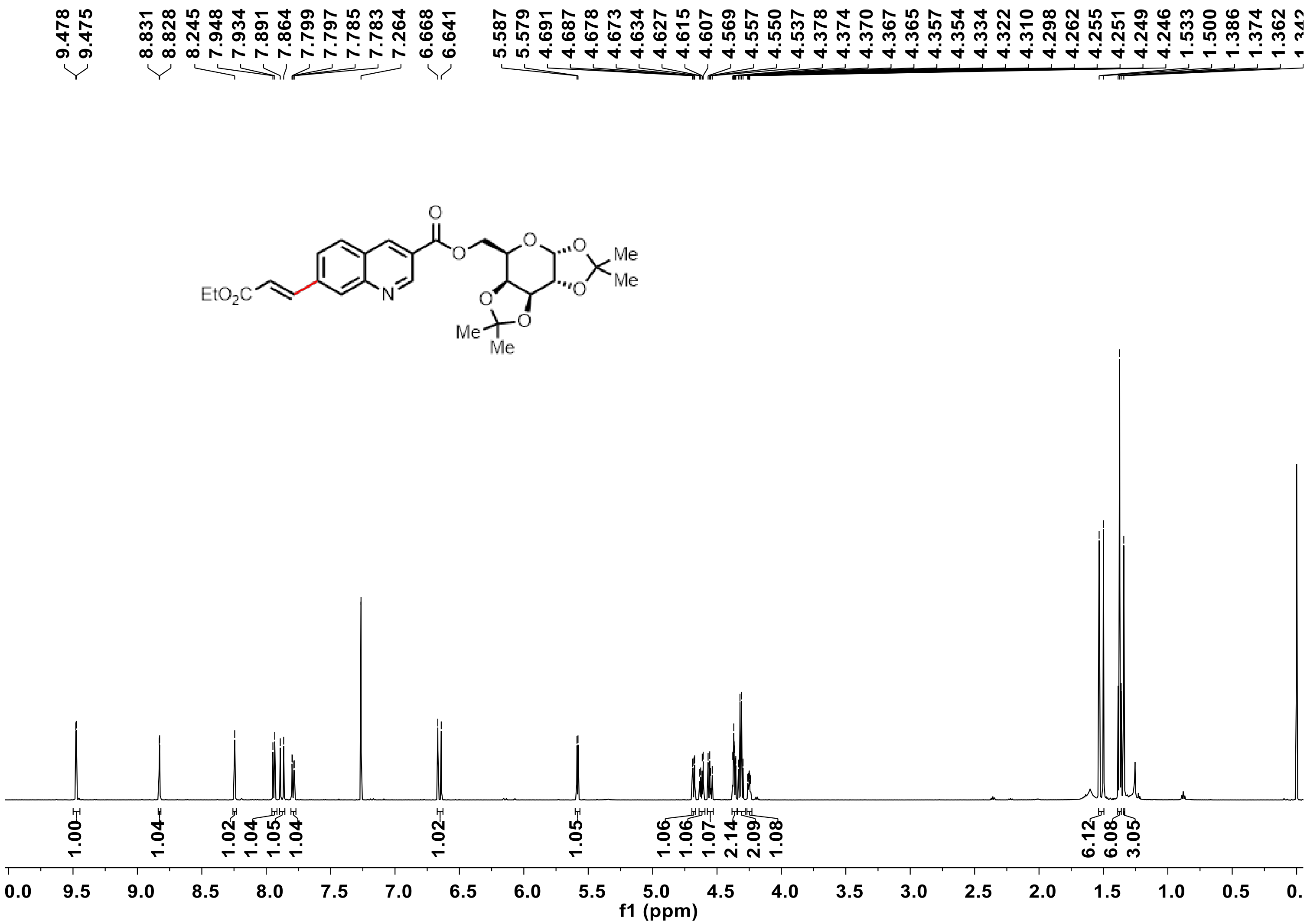
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3g**



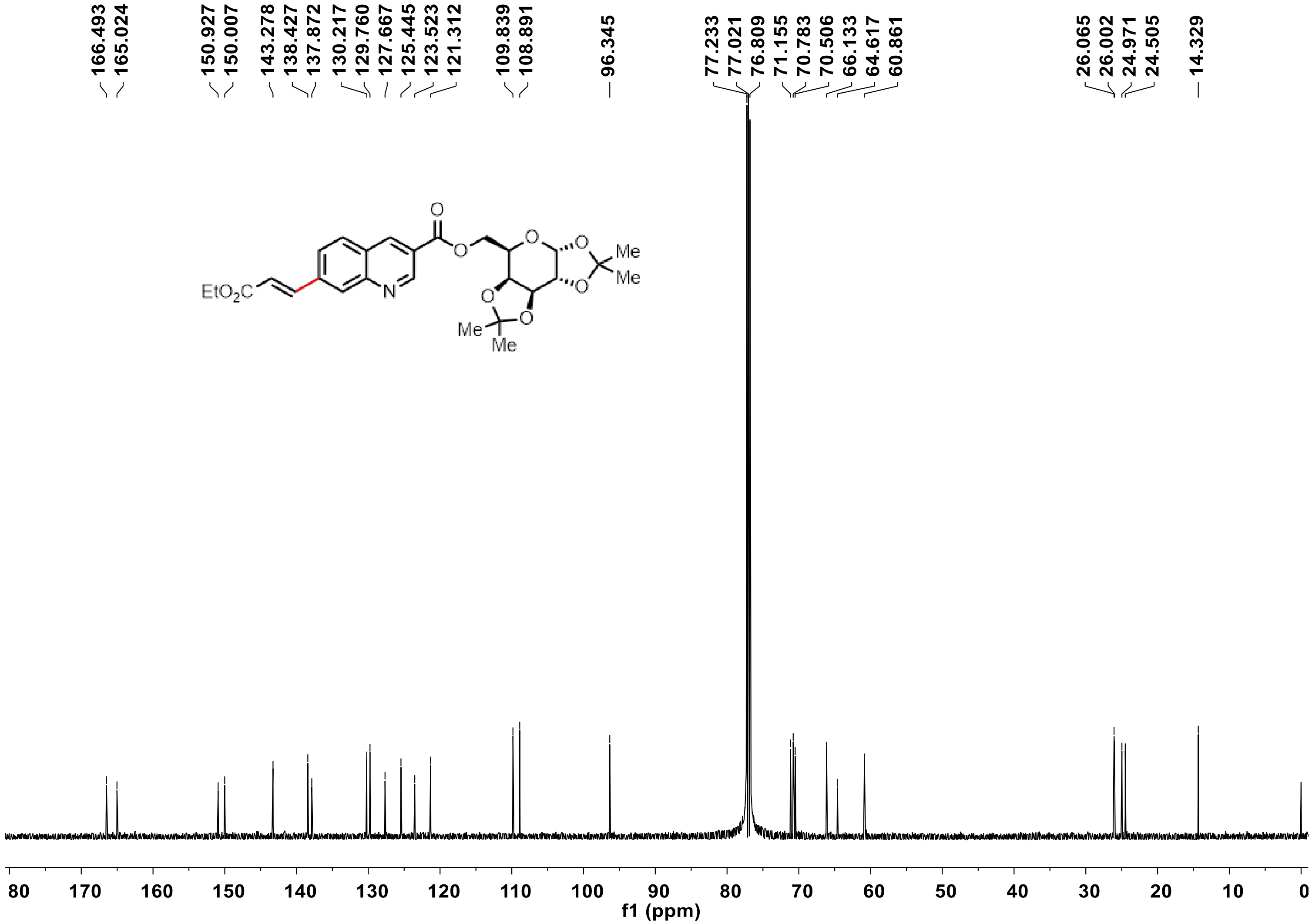
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3g**



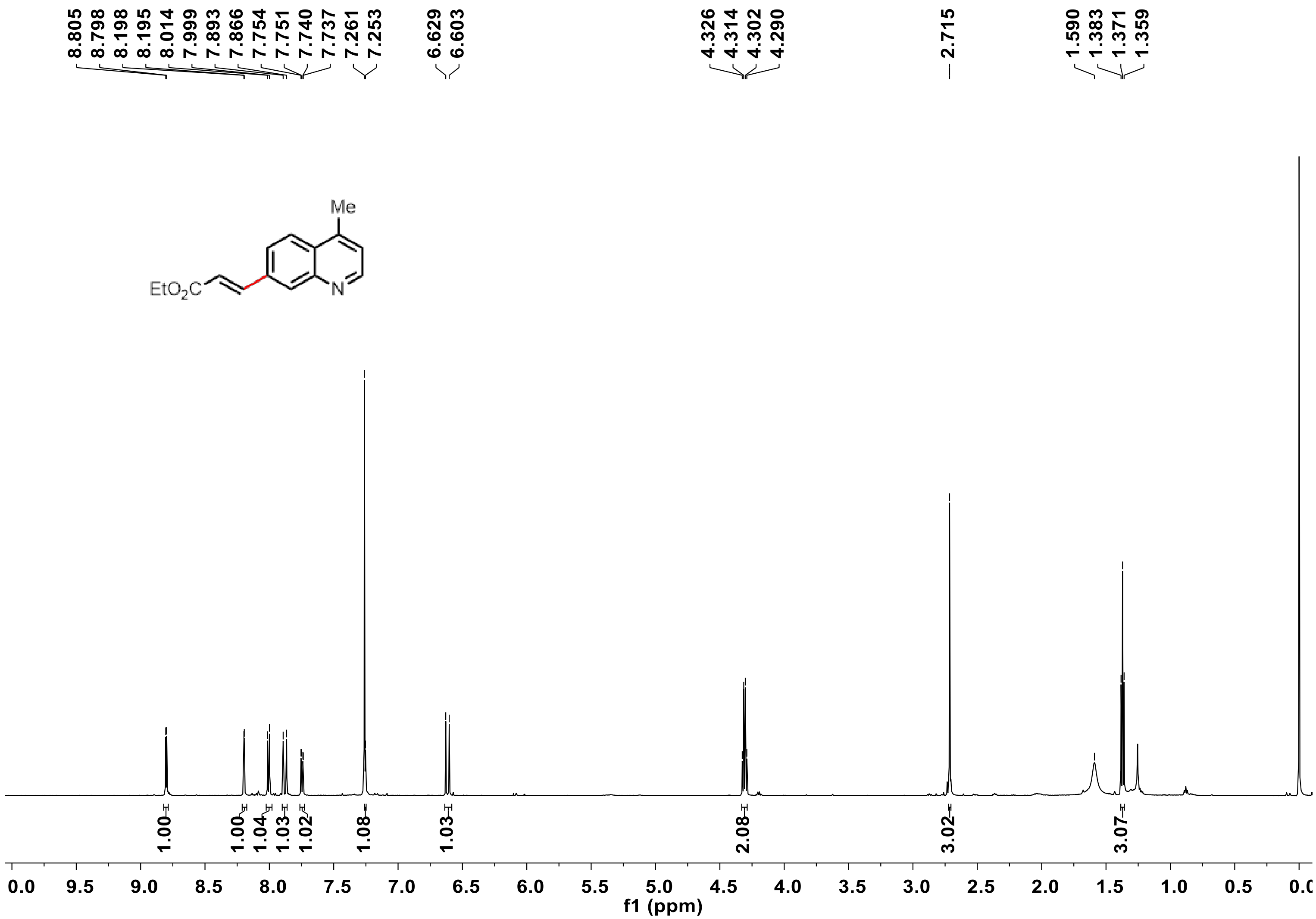
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3h**



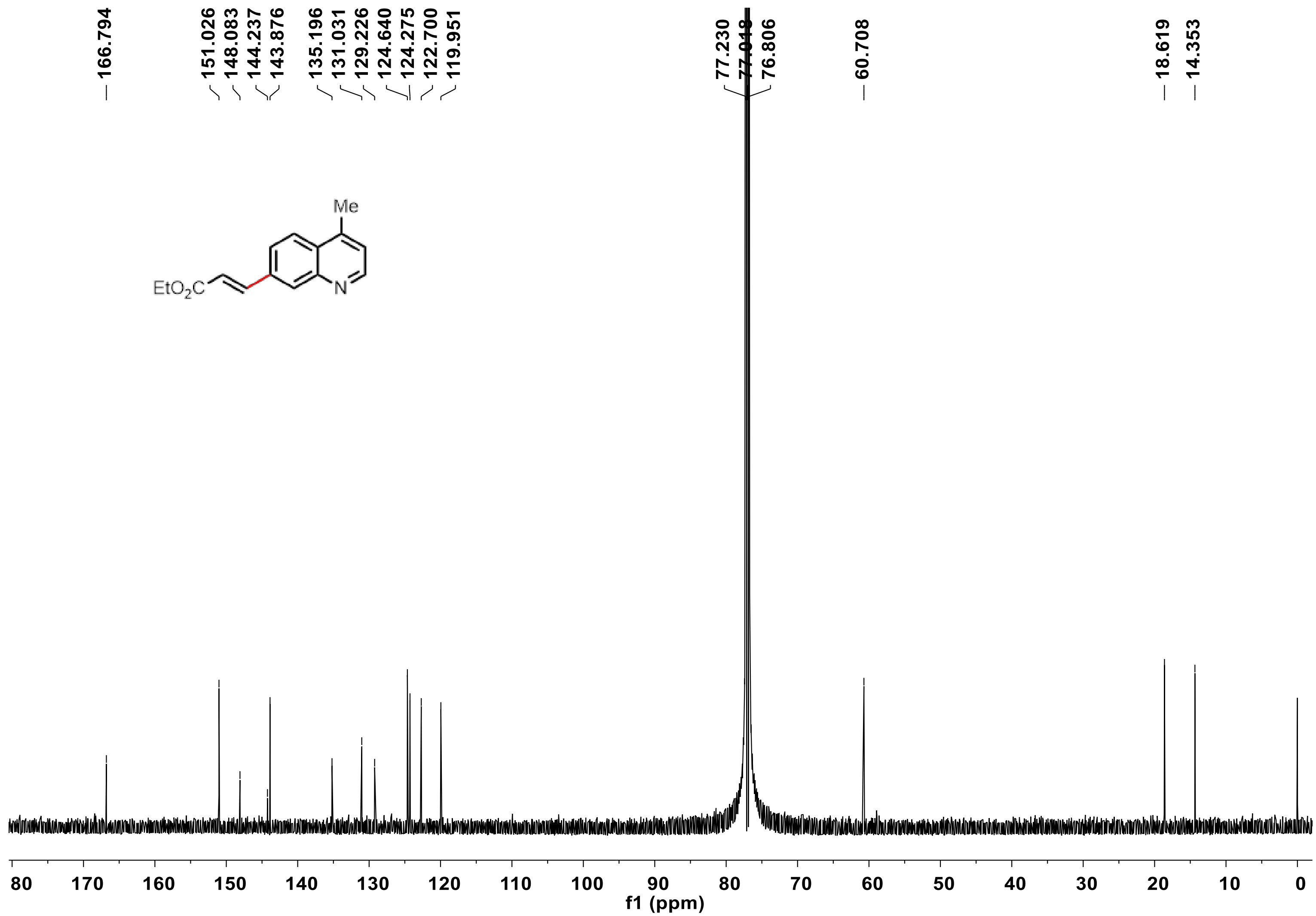
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3h**



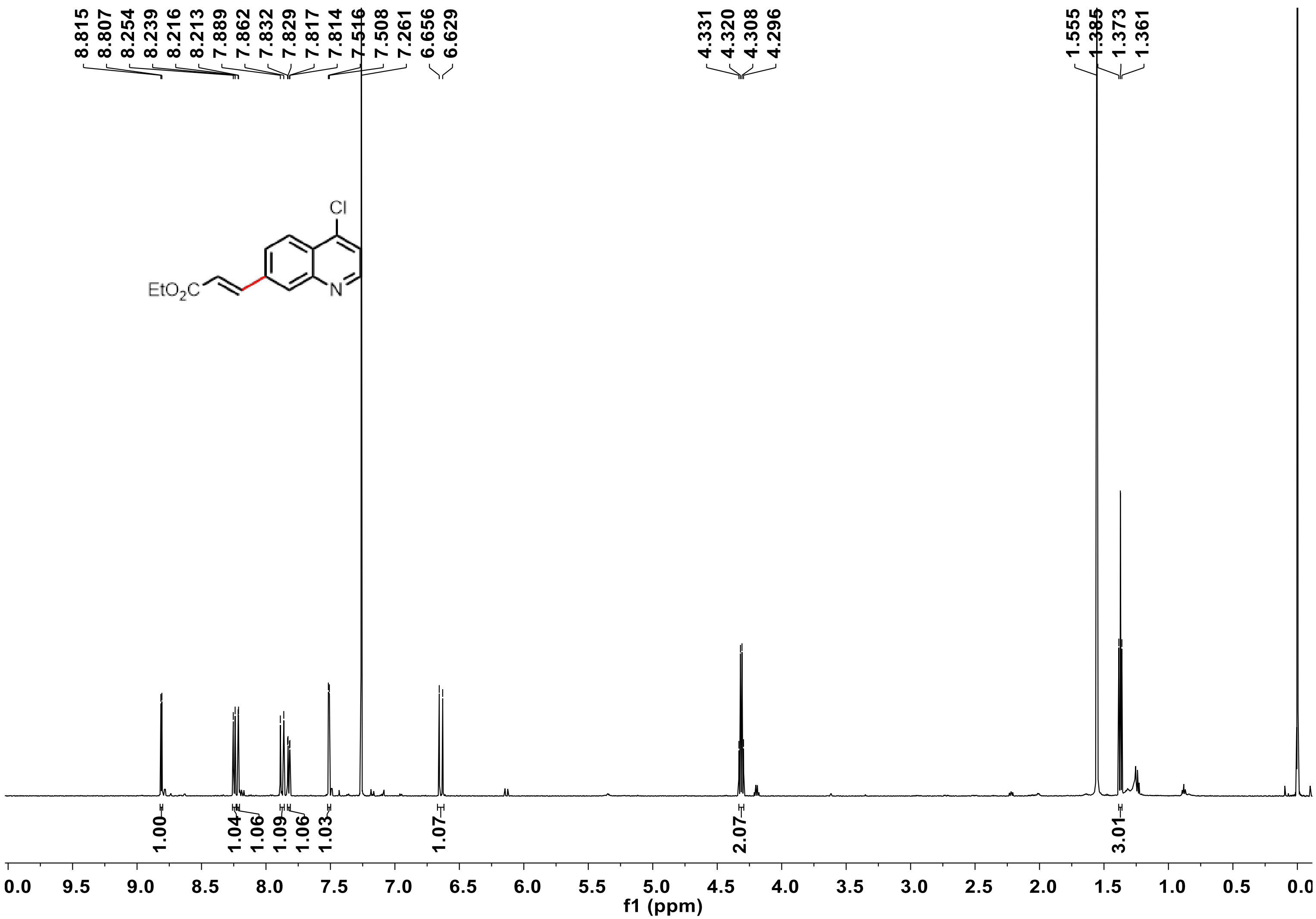
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3i**



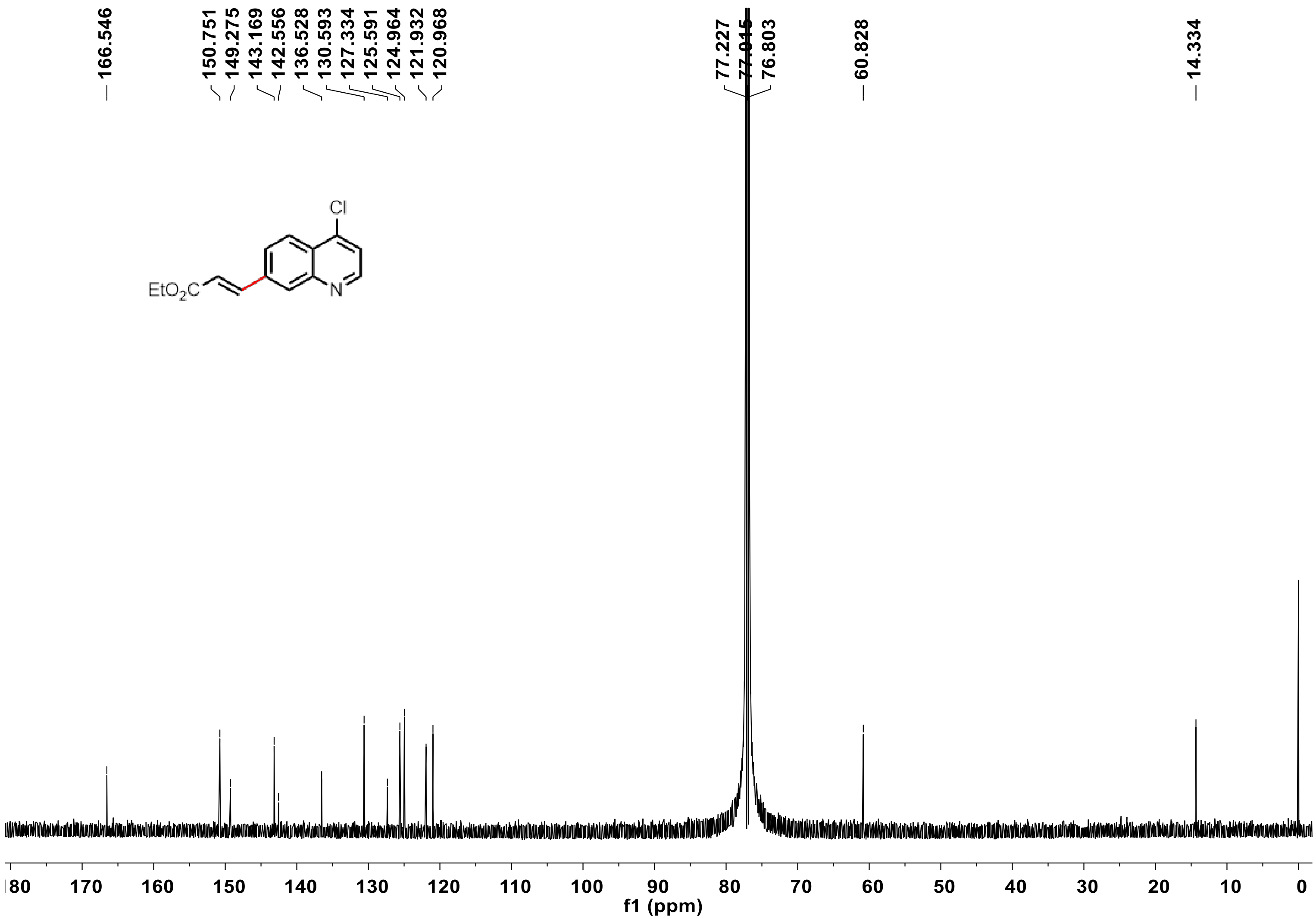
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3i**



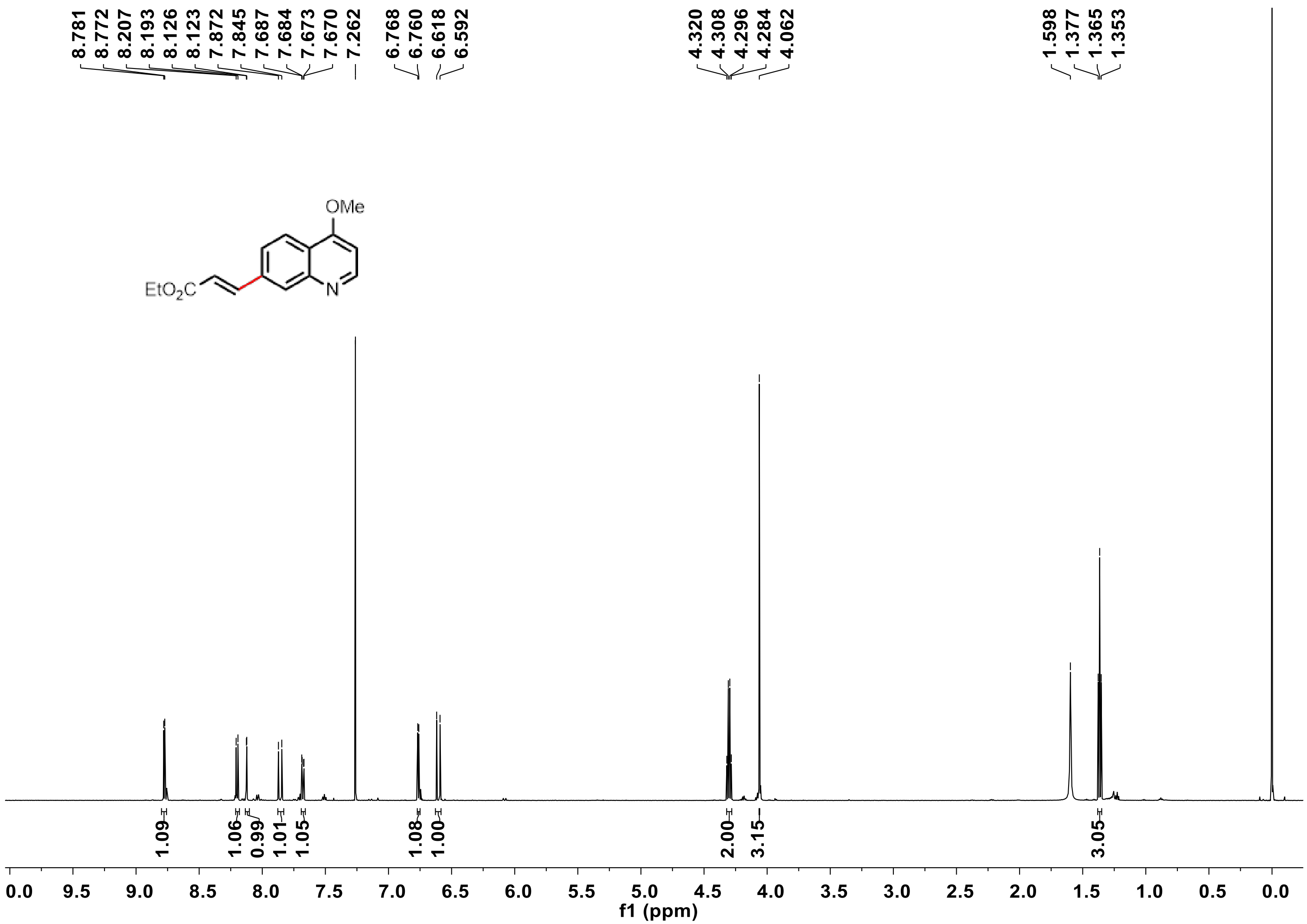
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3j**



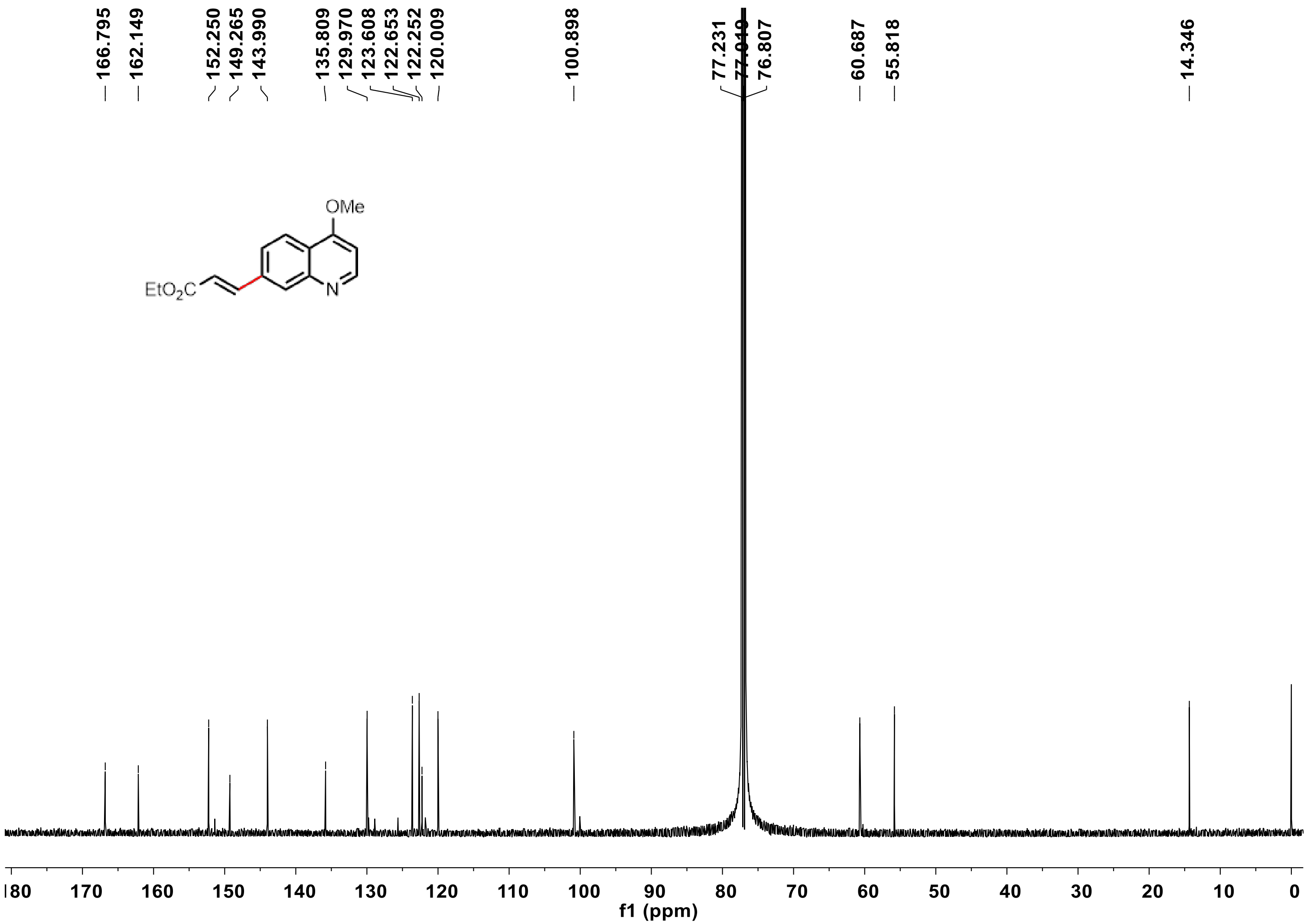
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3j**



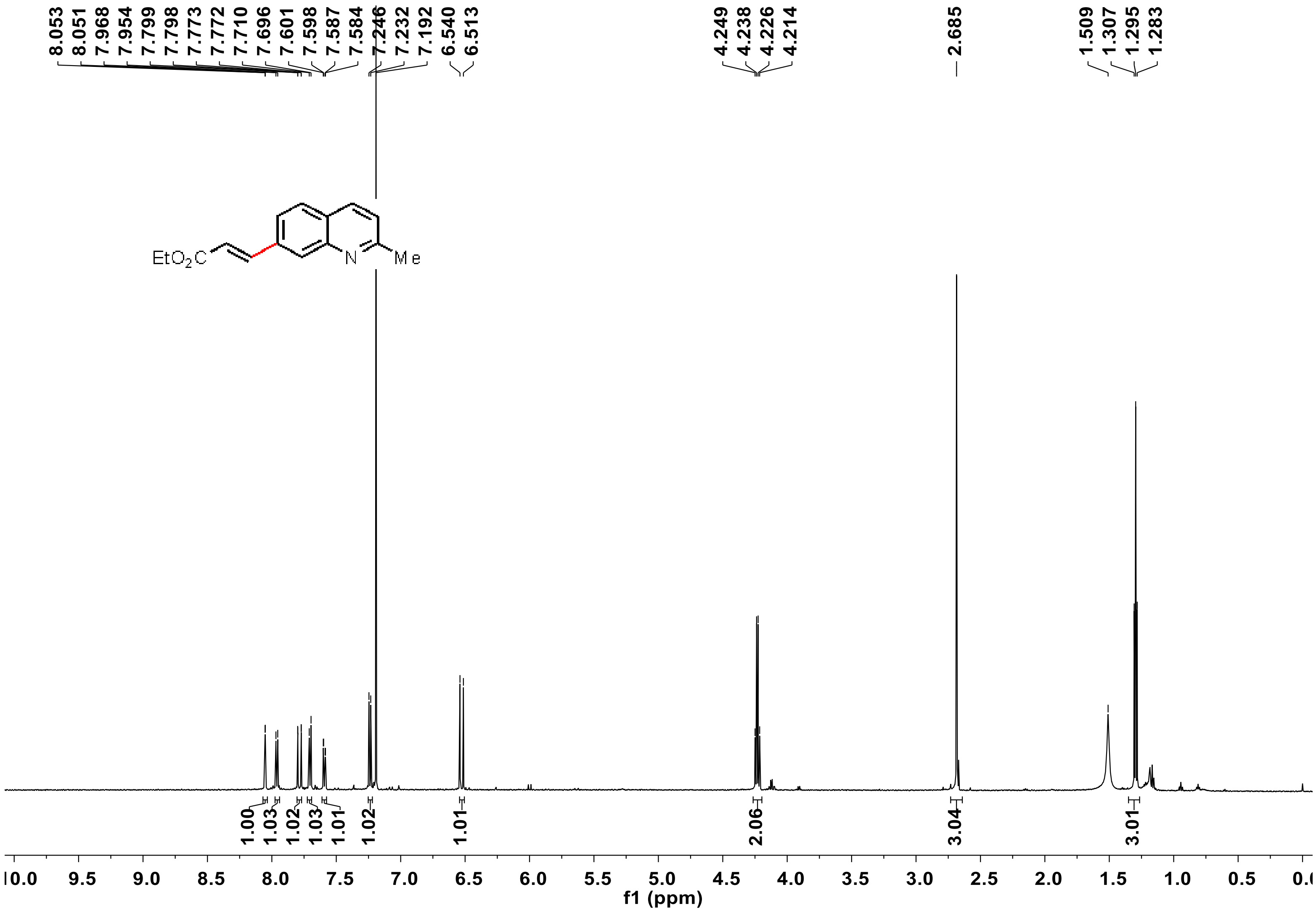
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3k**



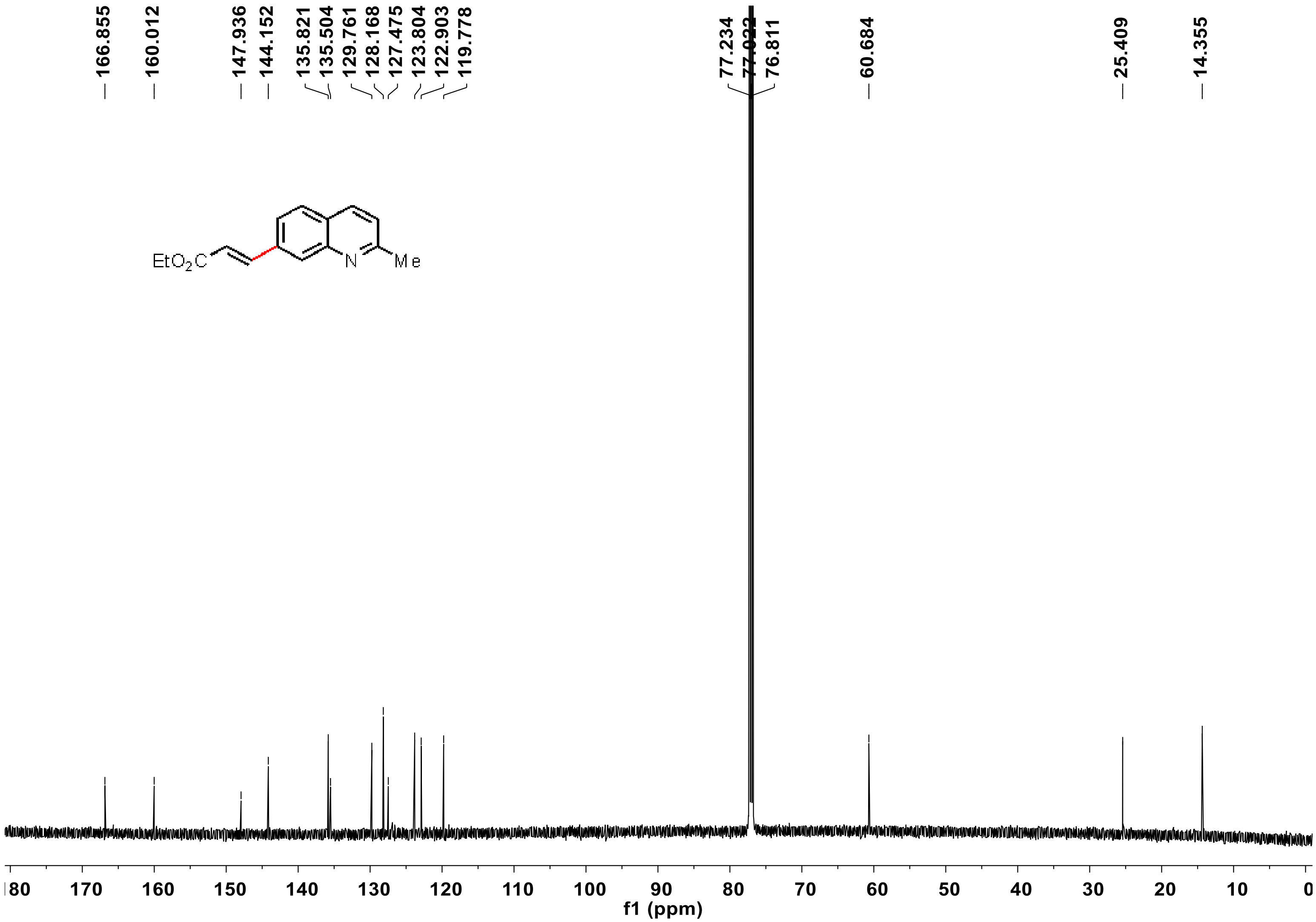
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3k**



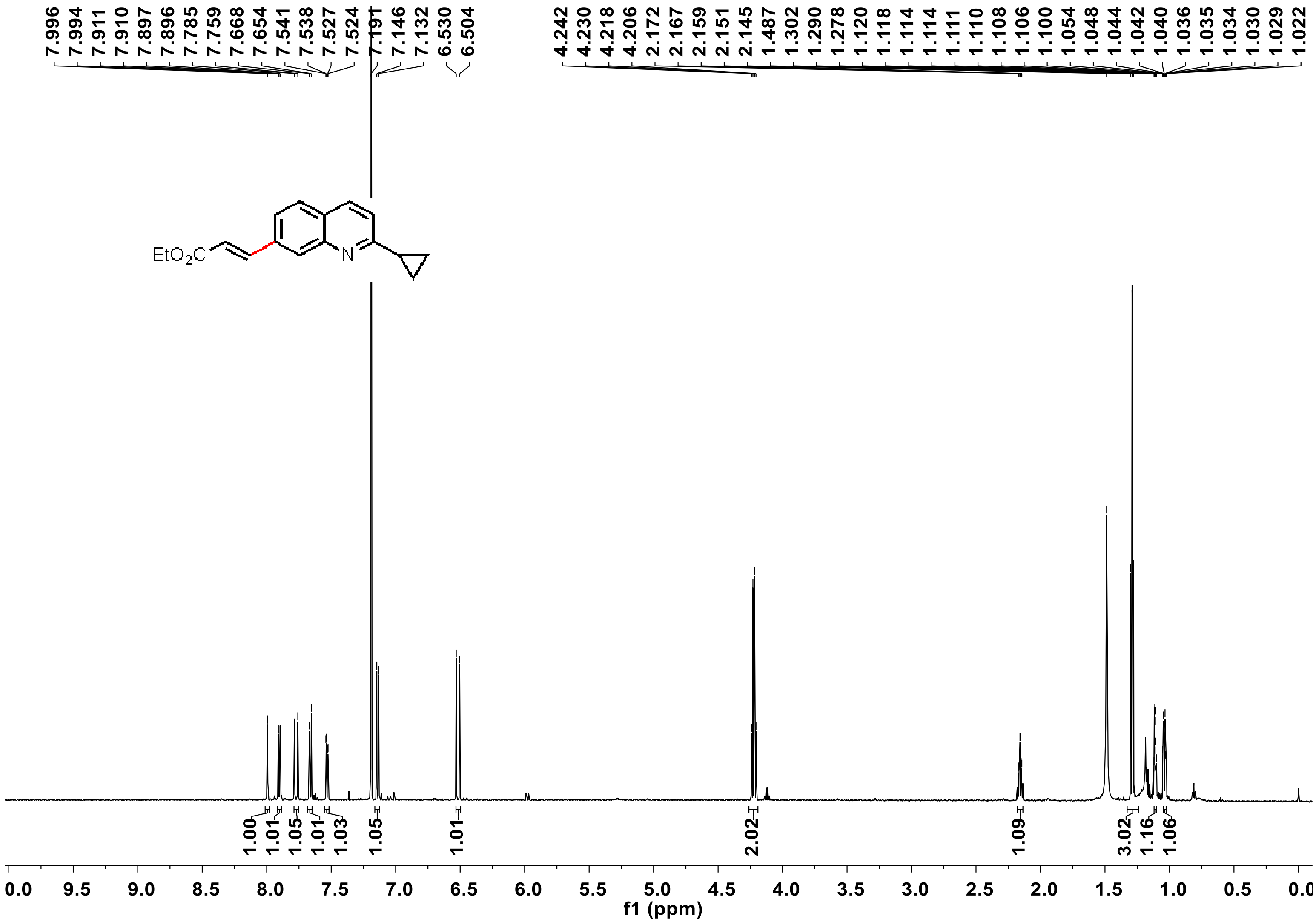
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **3l**



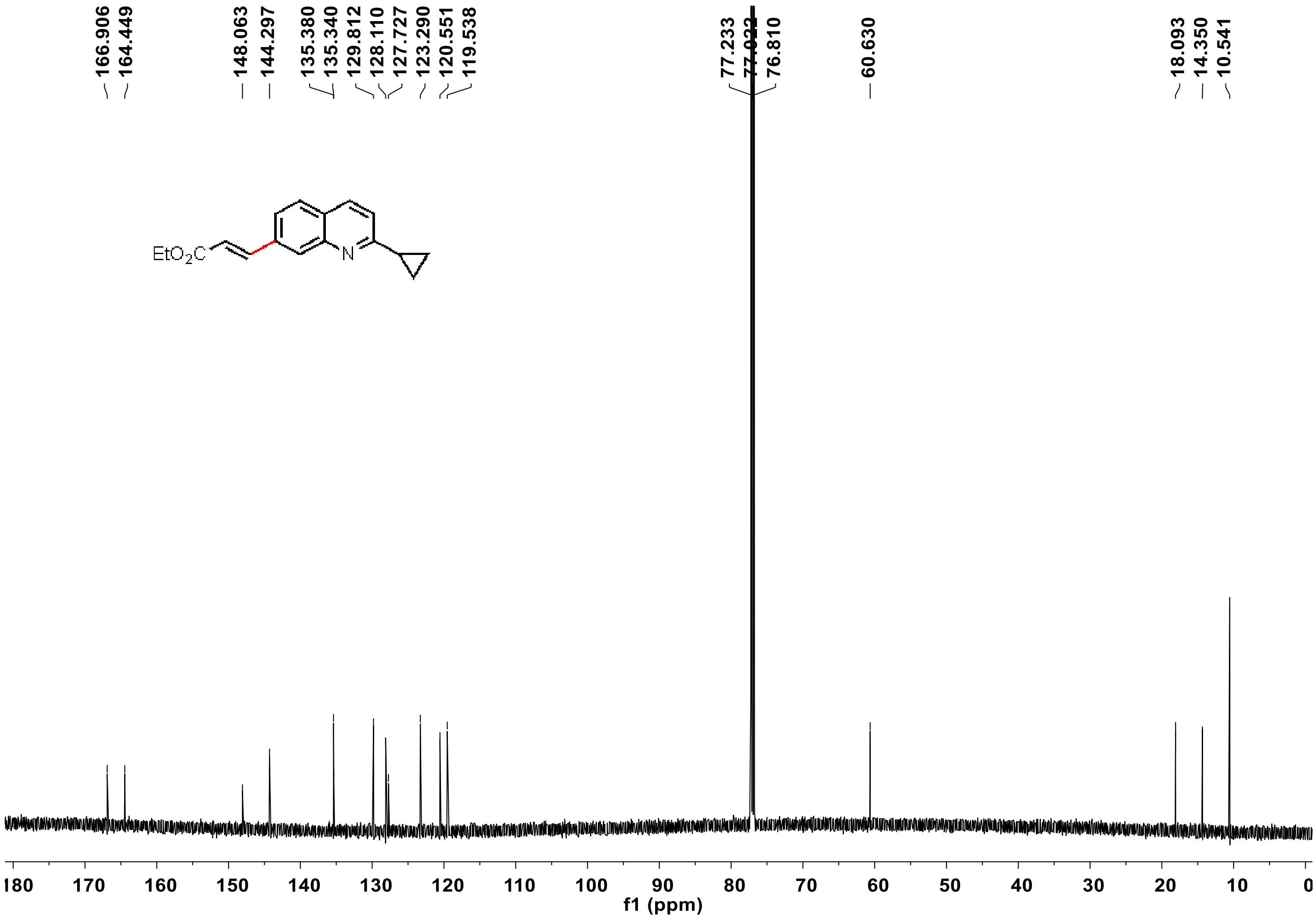
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3l**



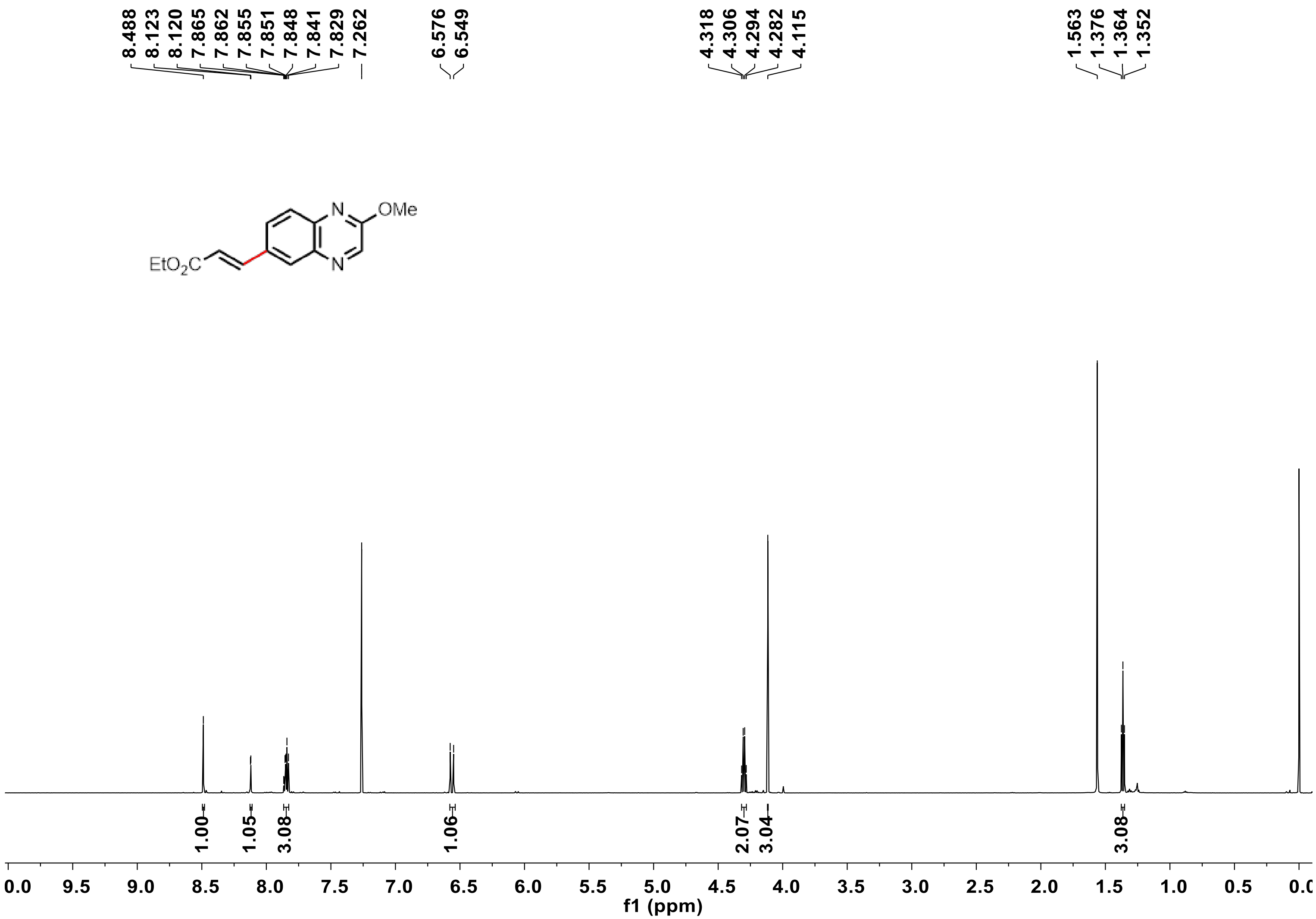
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3m**



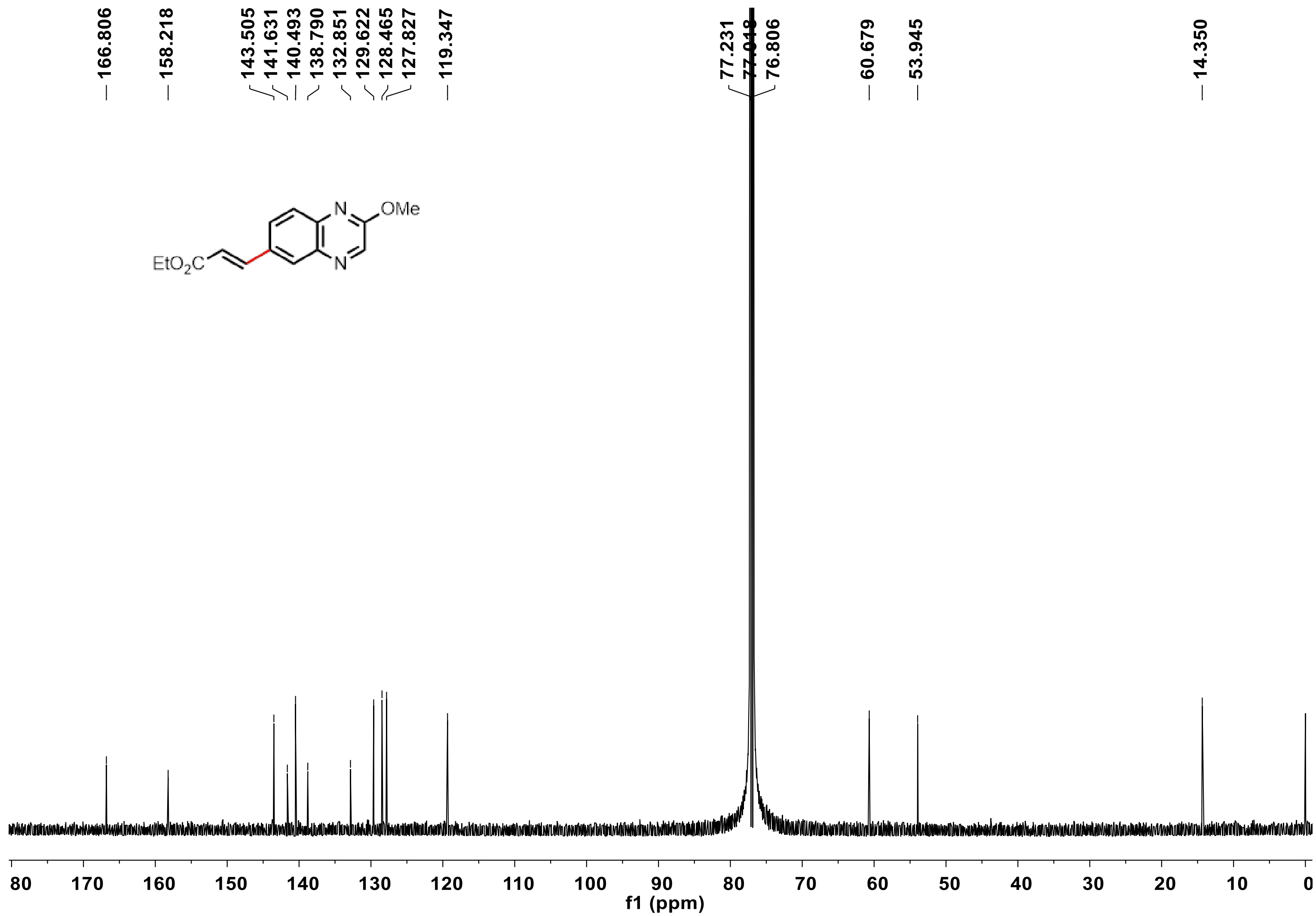
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3m**



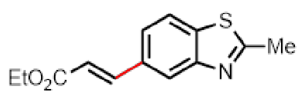
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3n**

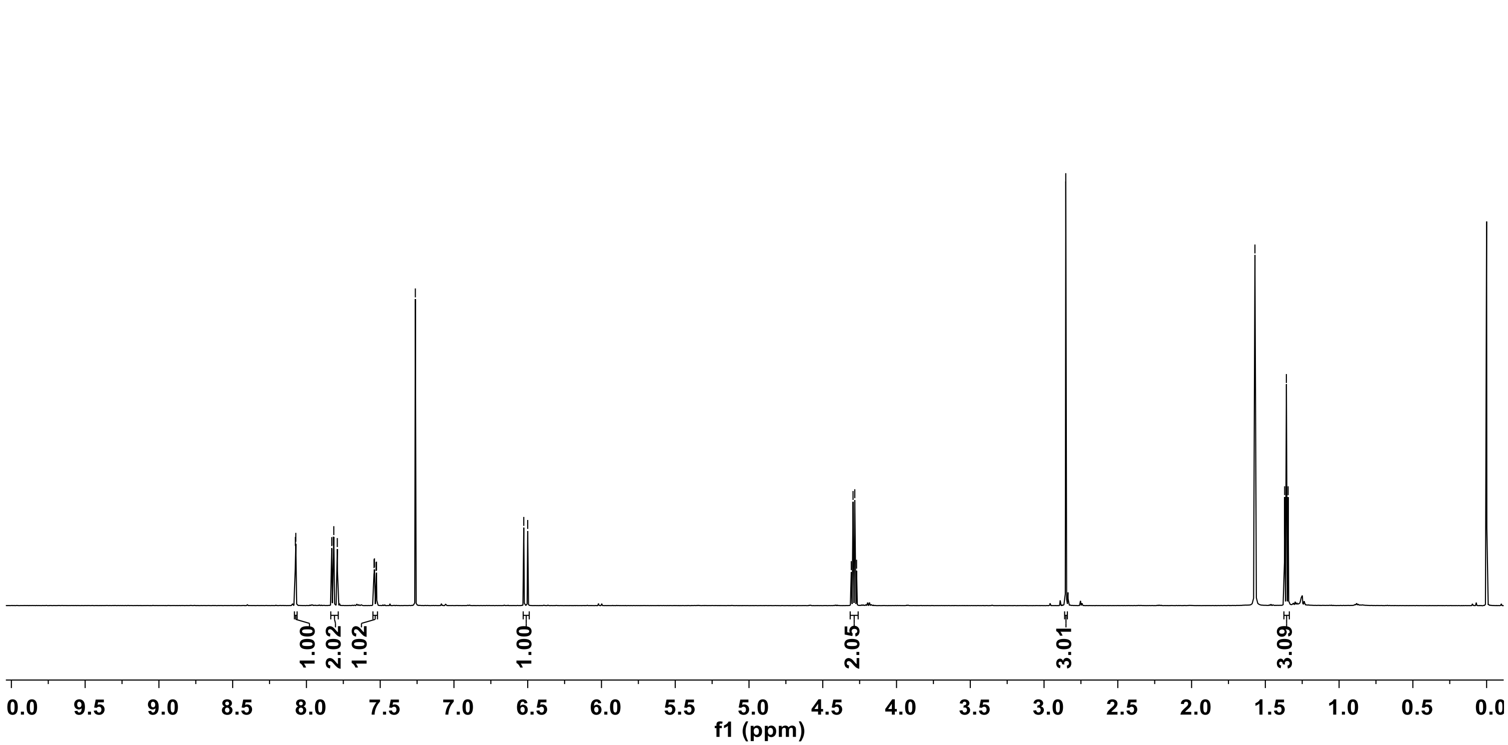


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3n**

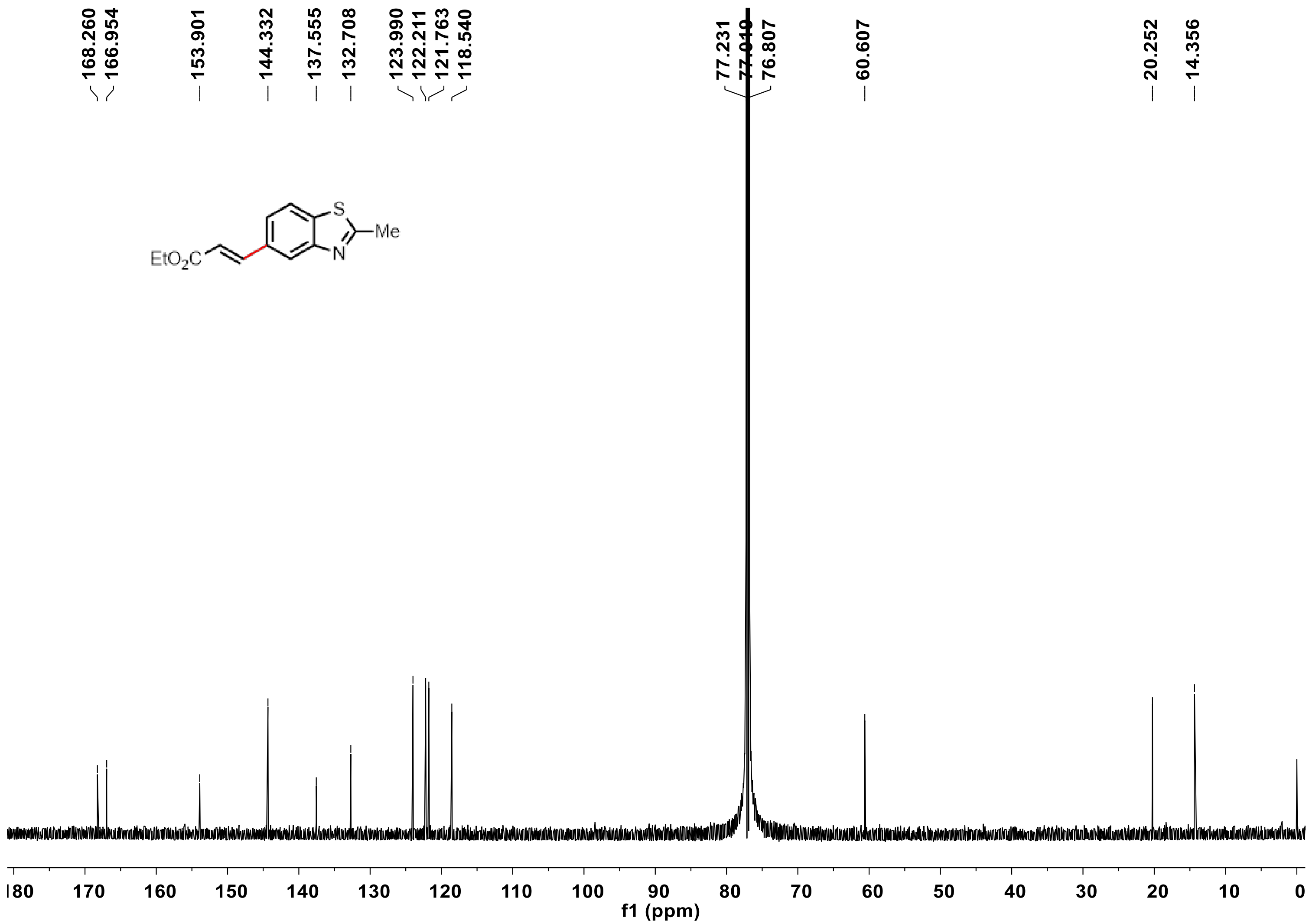


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3o**

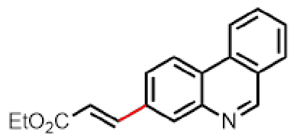


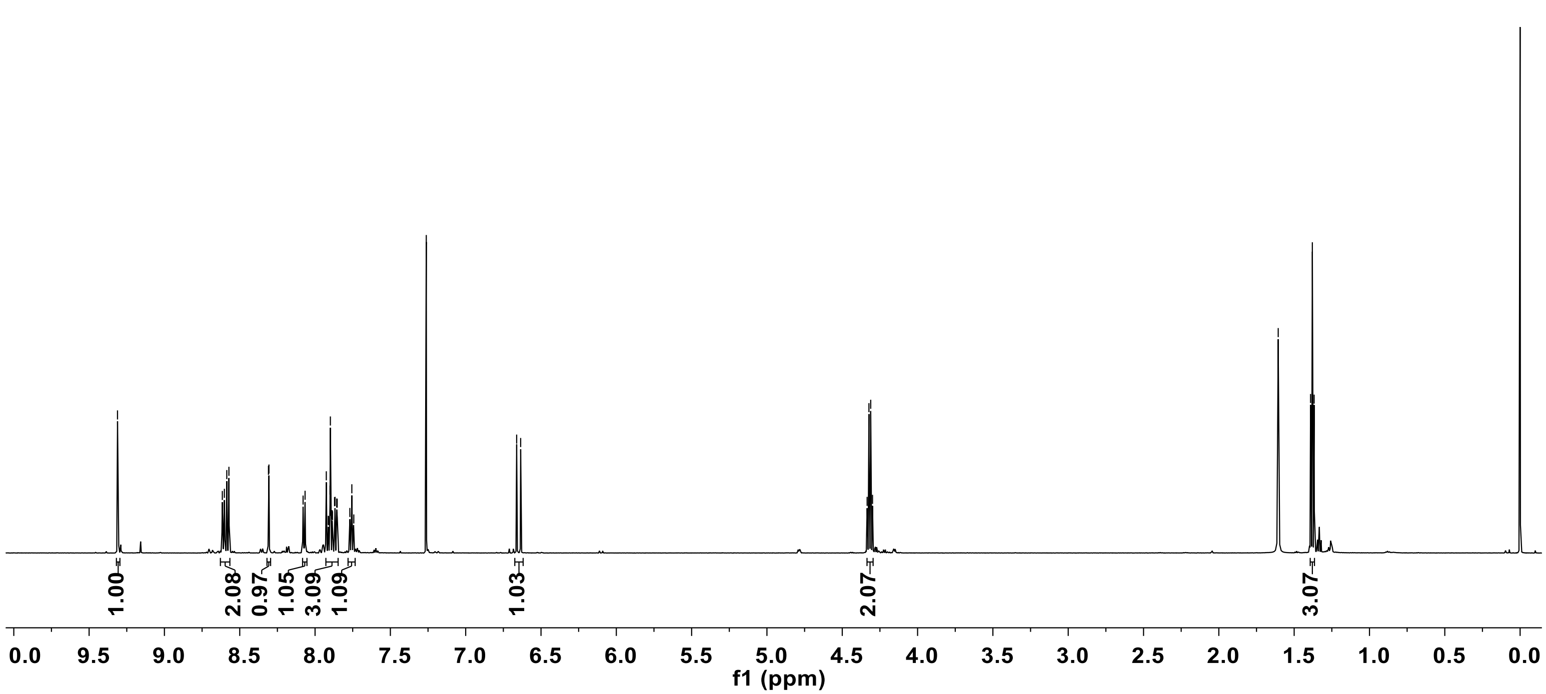


^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3o**

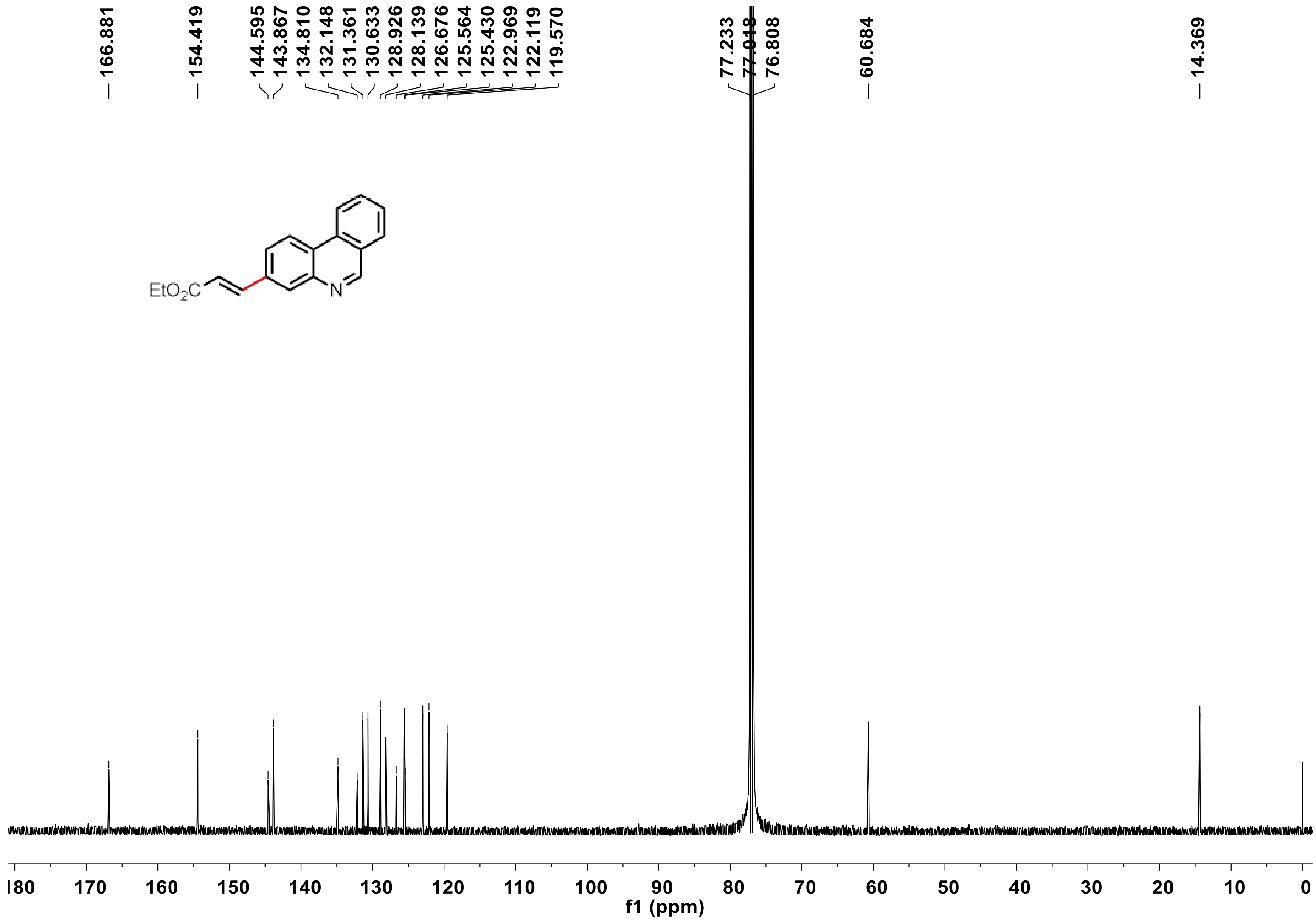


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3p**

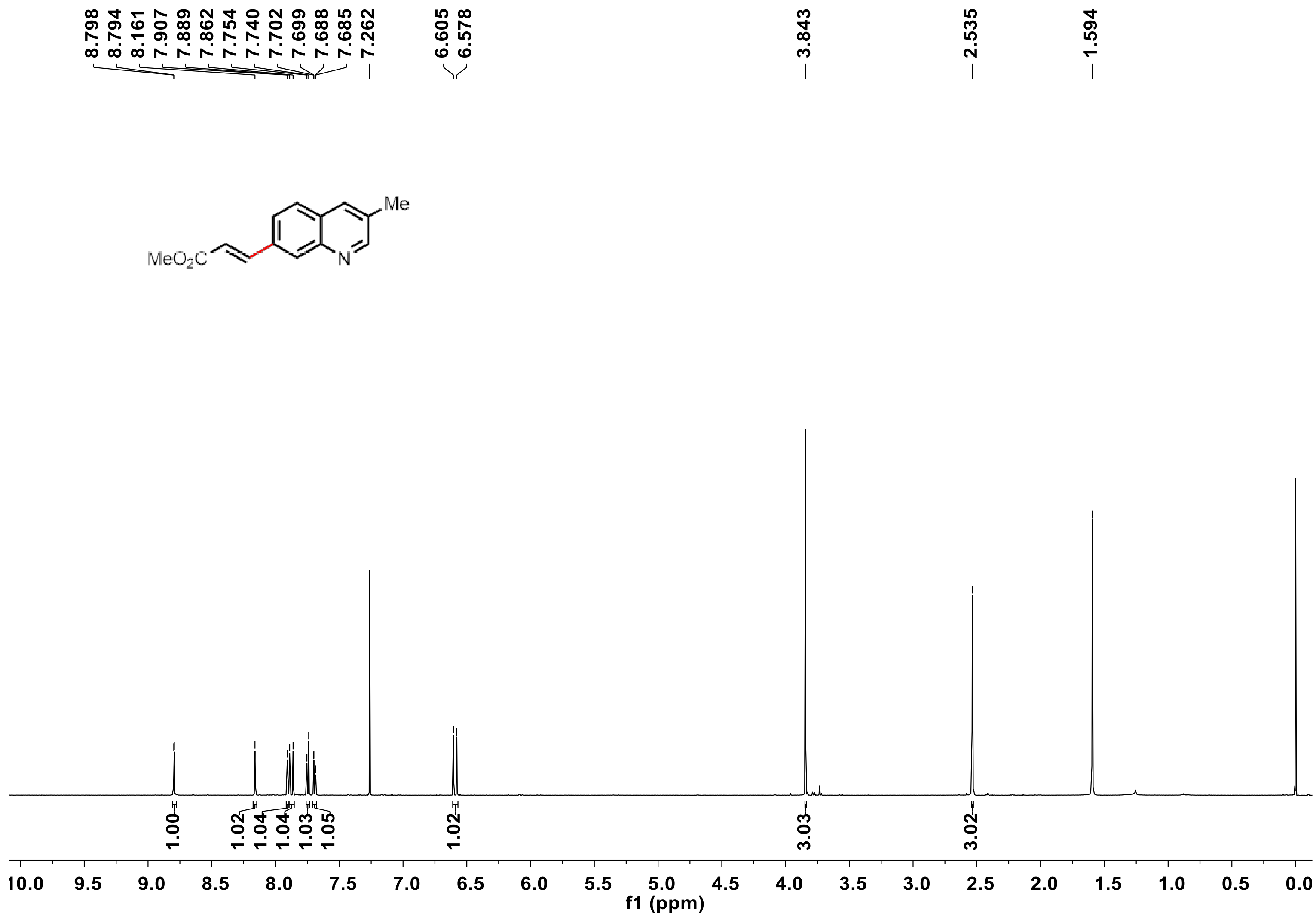




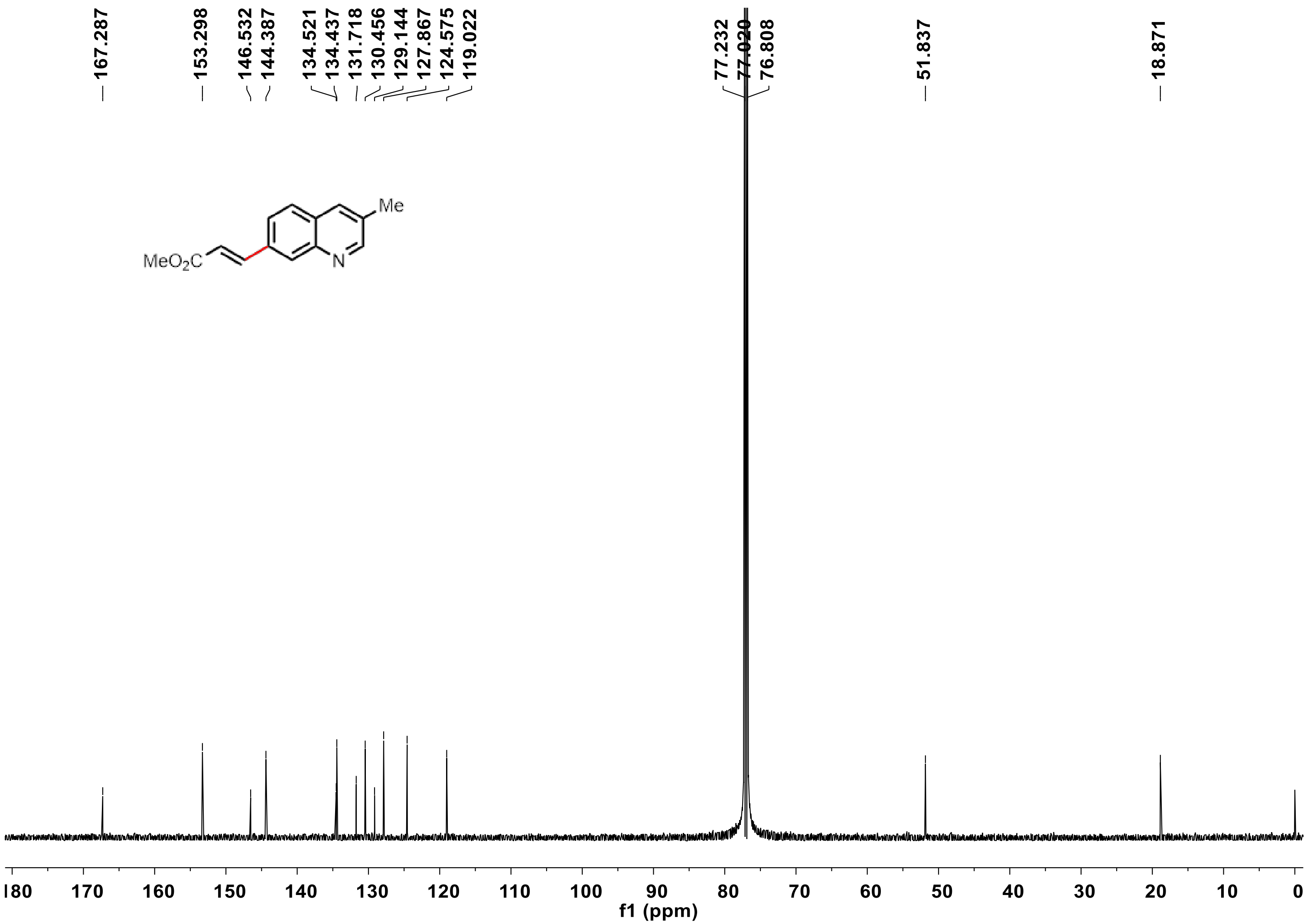
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3p**



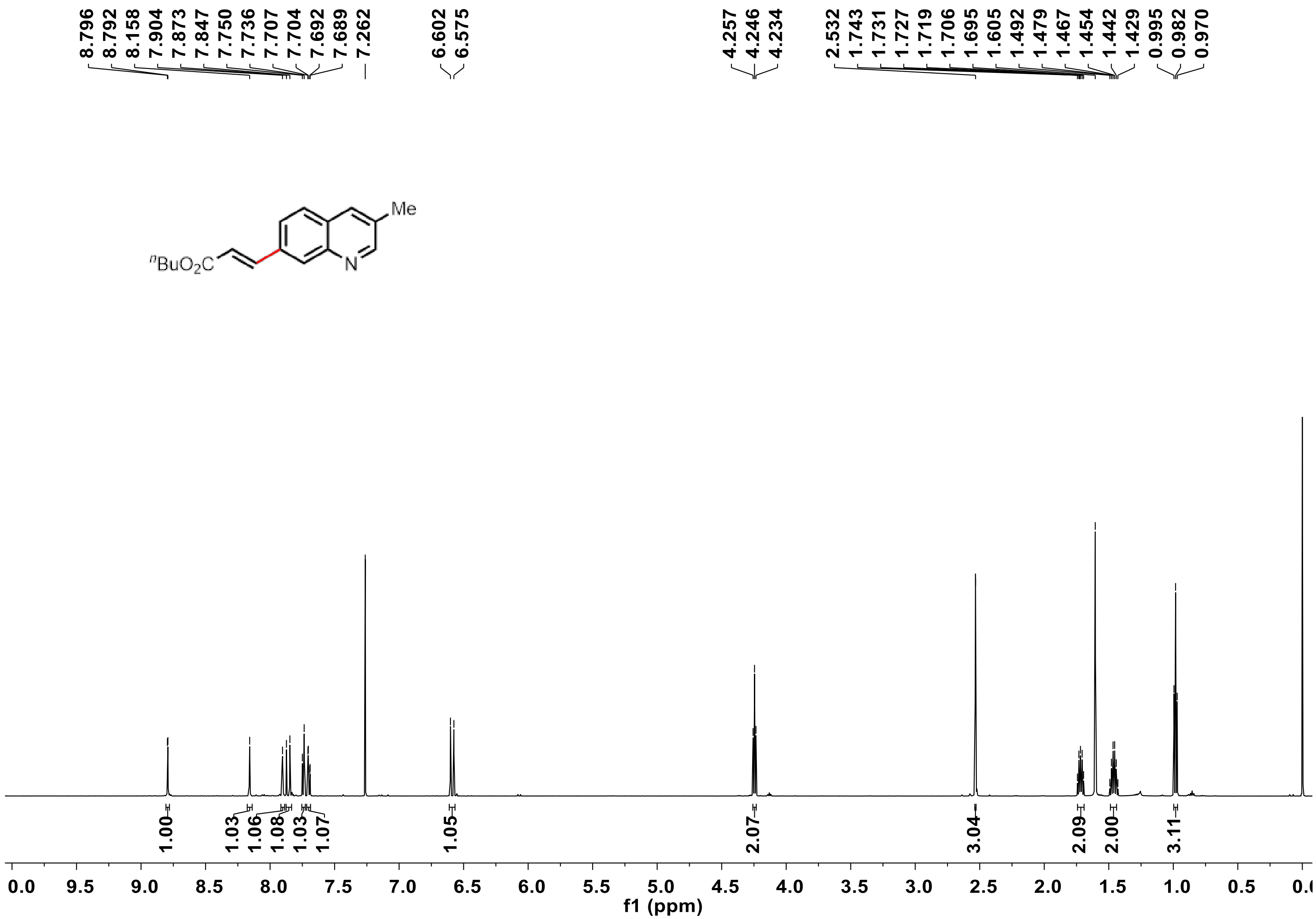
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3q**



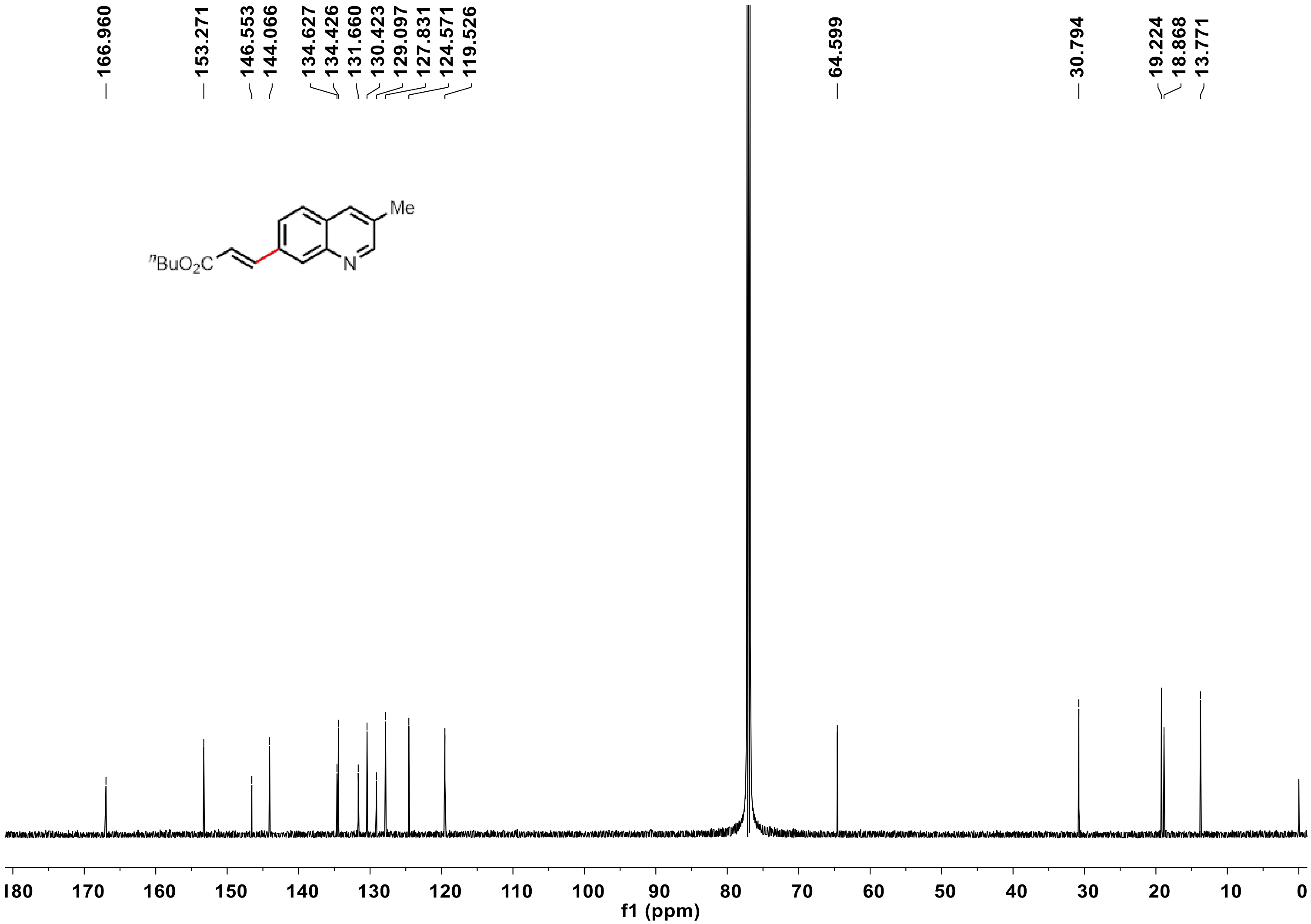
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3q**



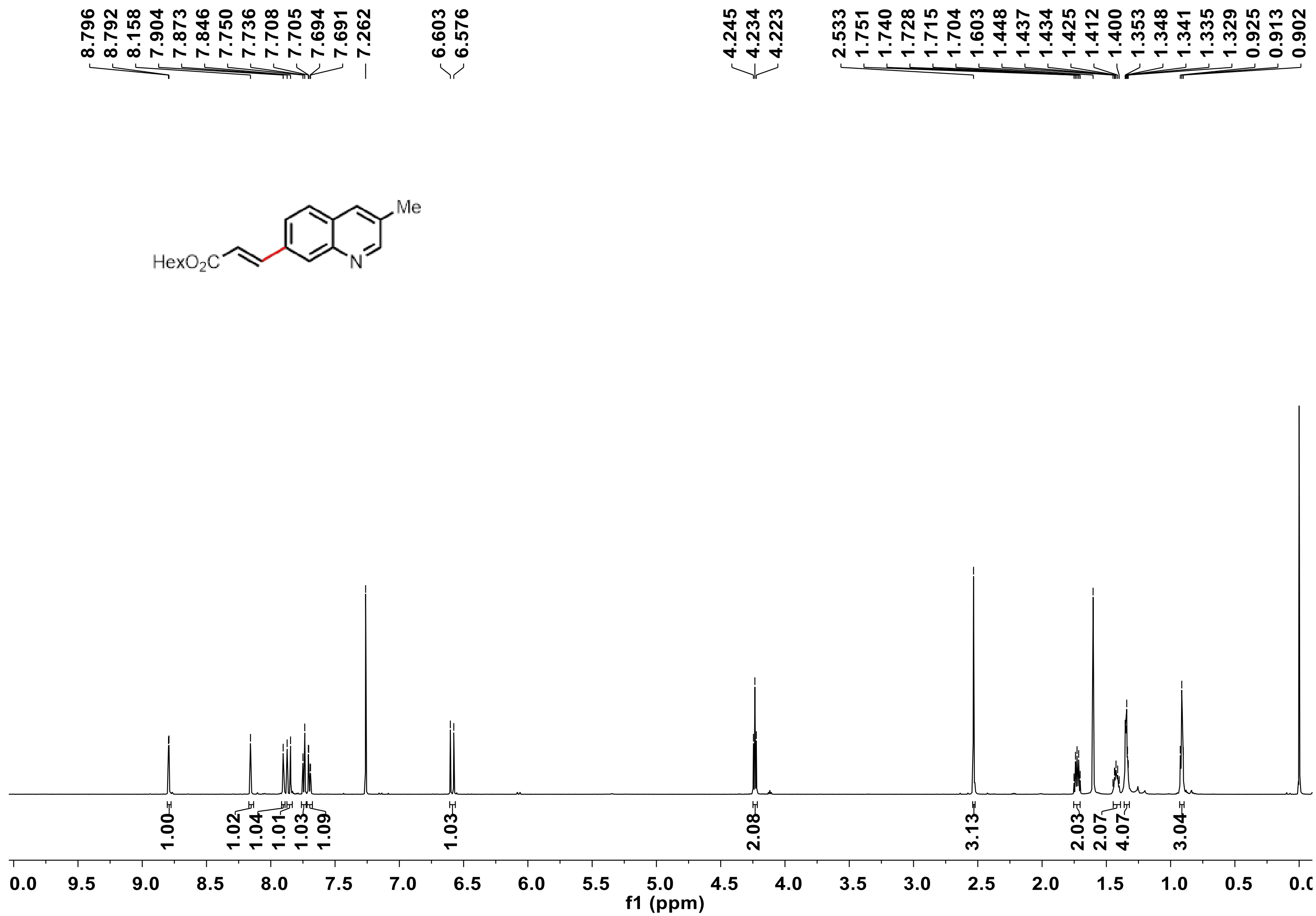
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3r**



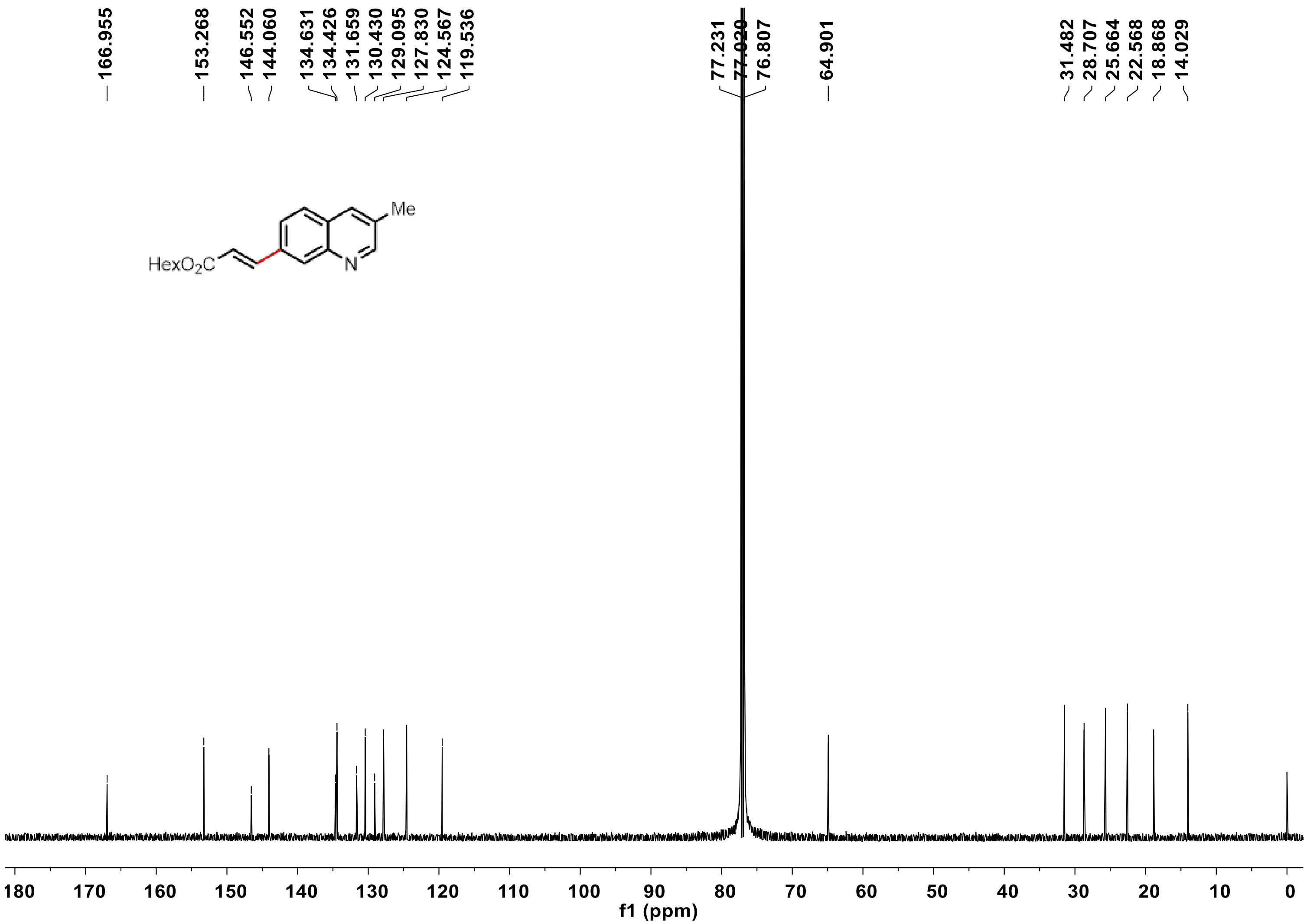
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3r**



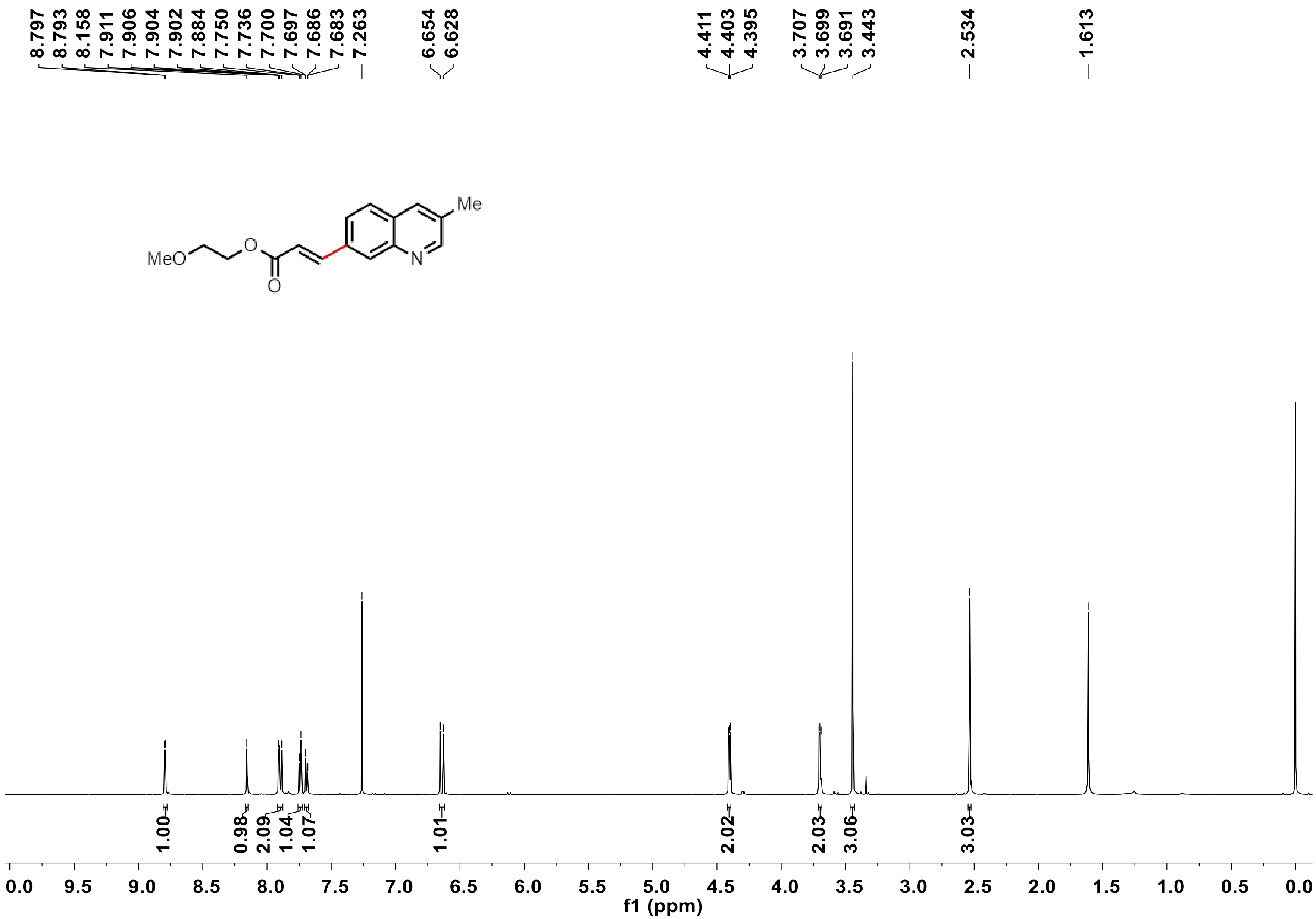
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **3s**



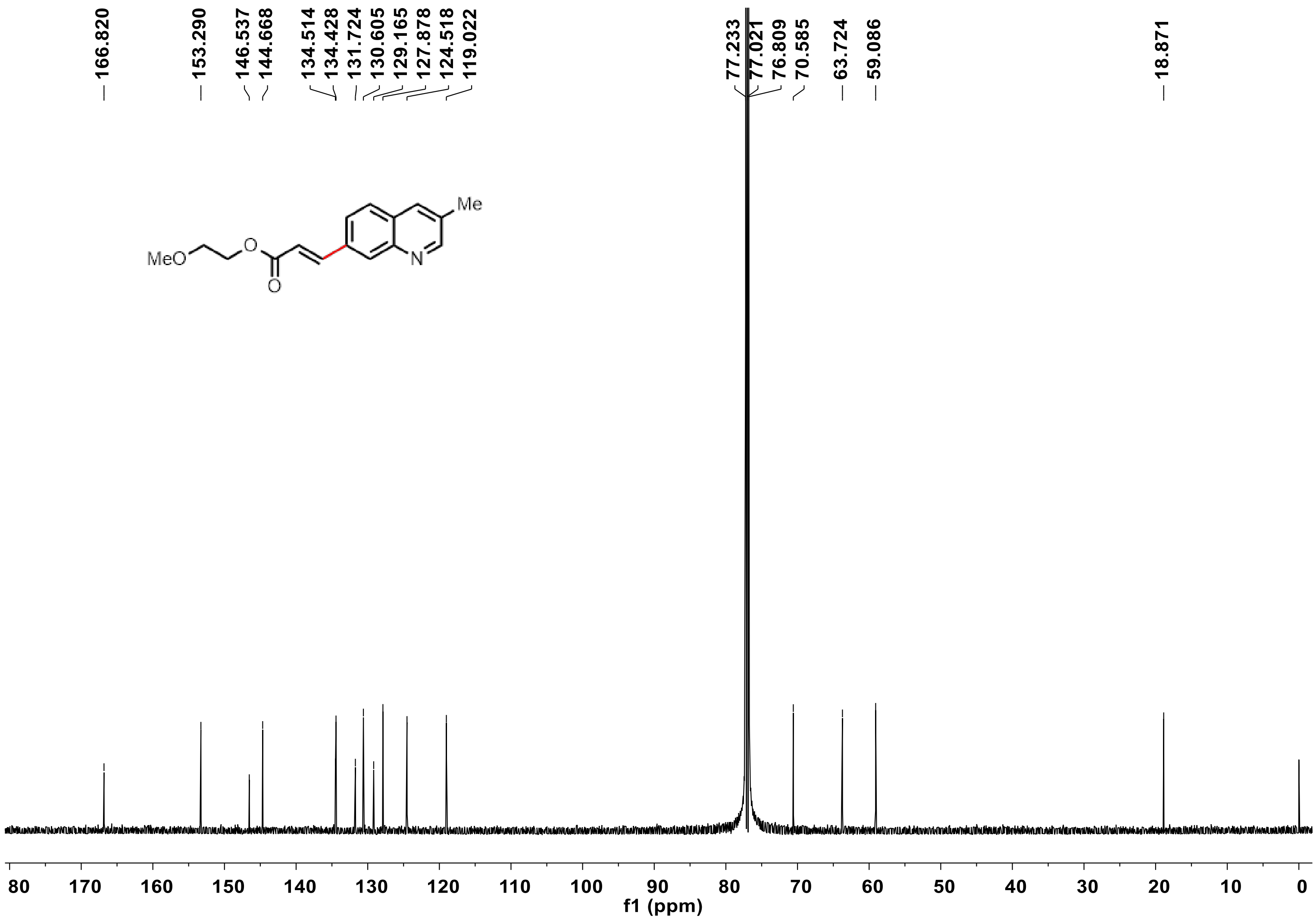
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3s**



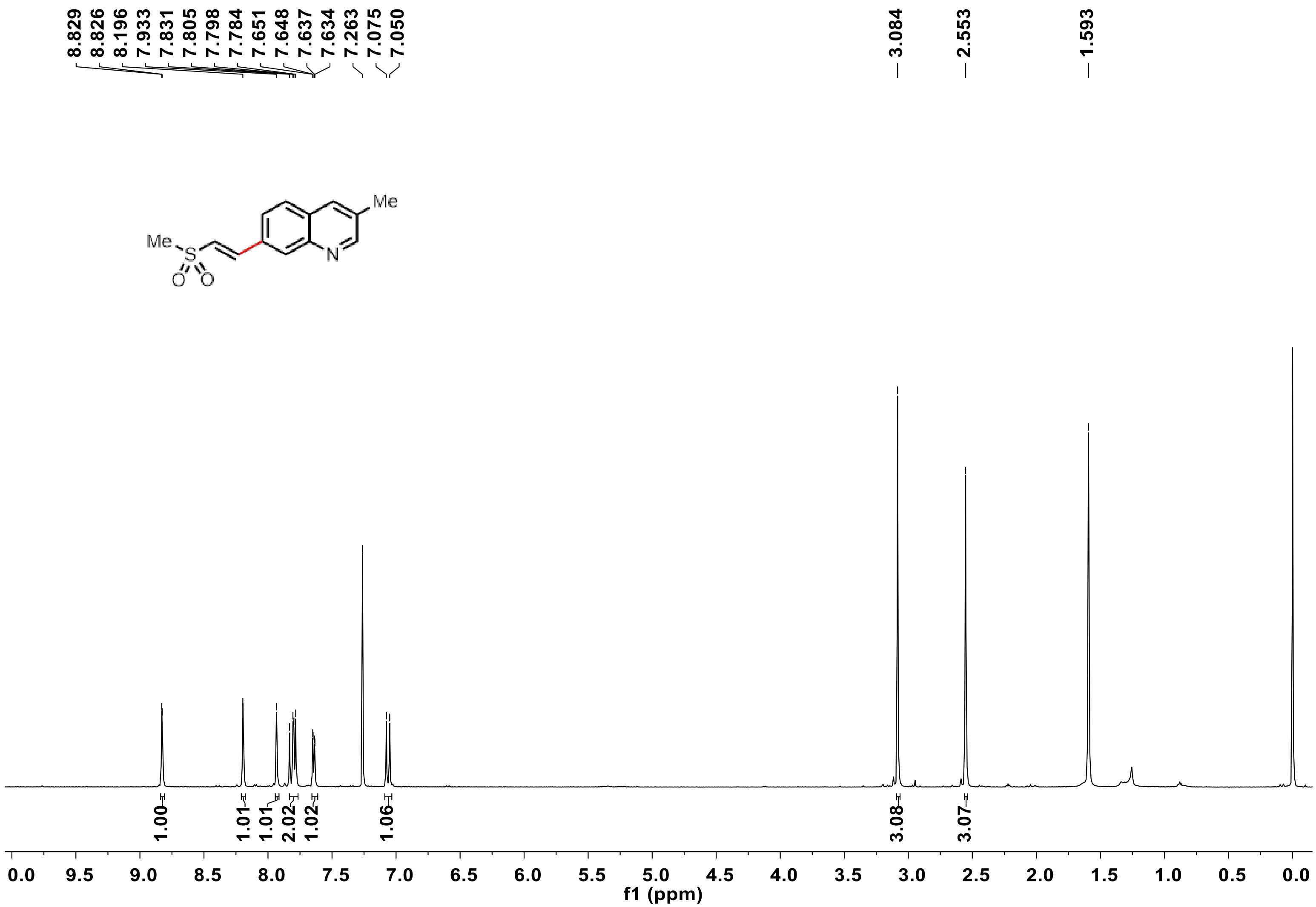
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3t**



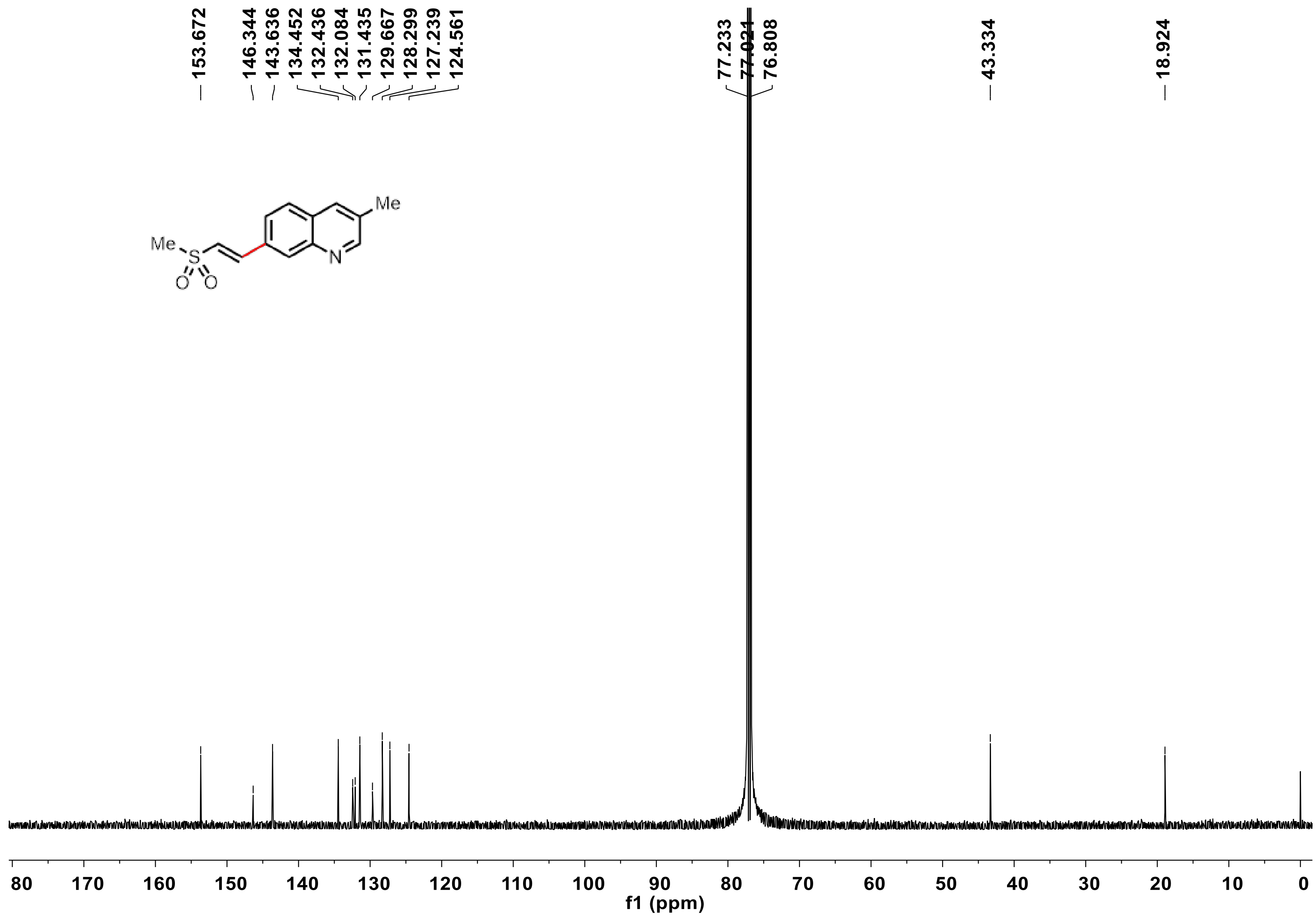
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **3t**



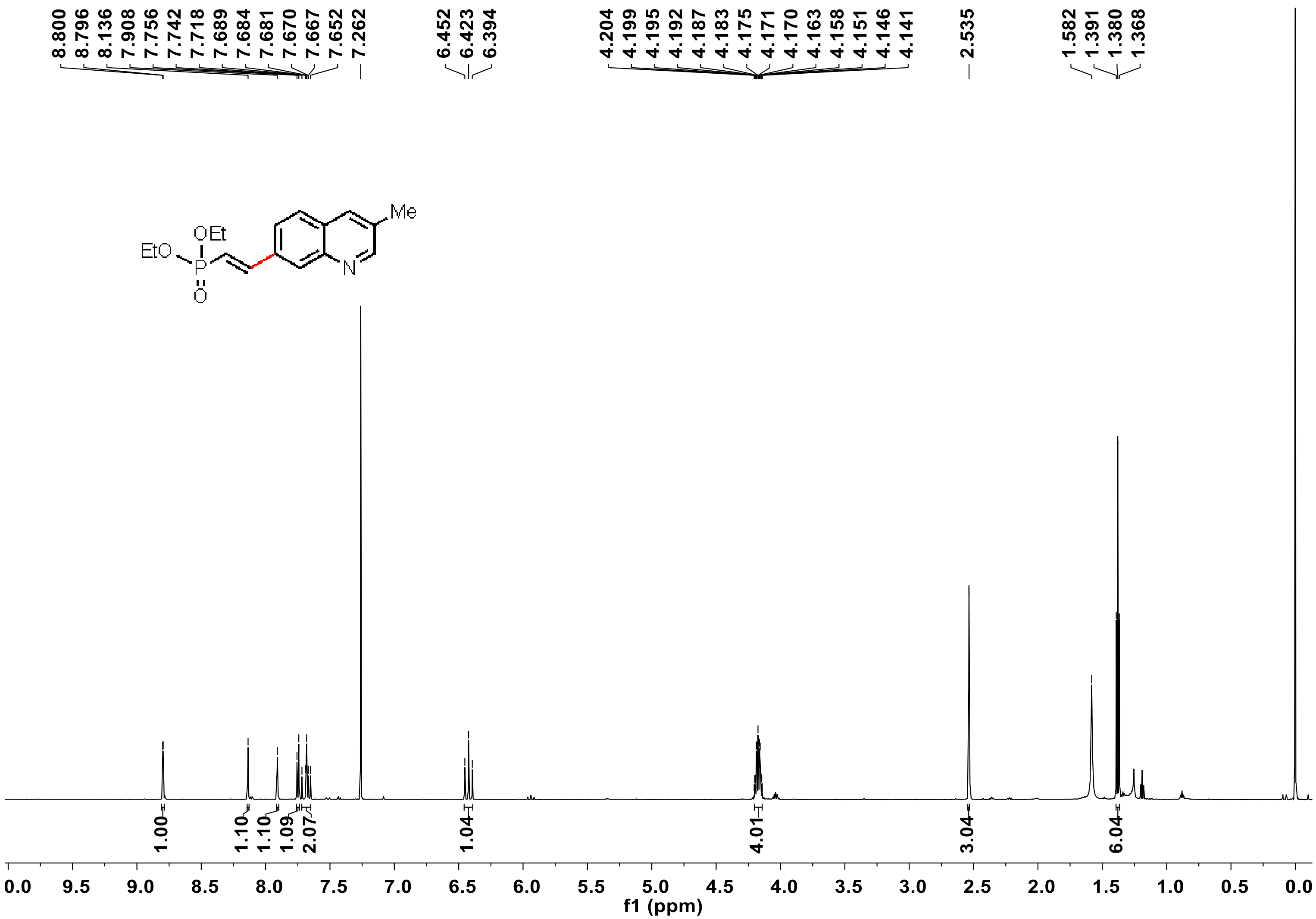
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3u**



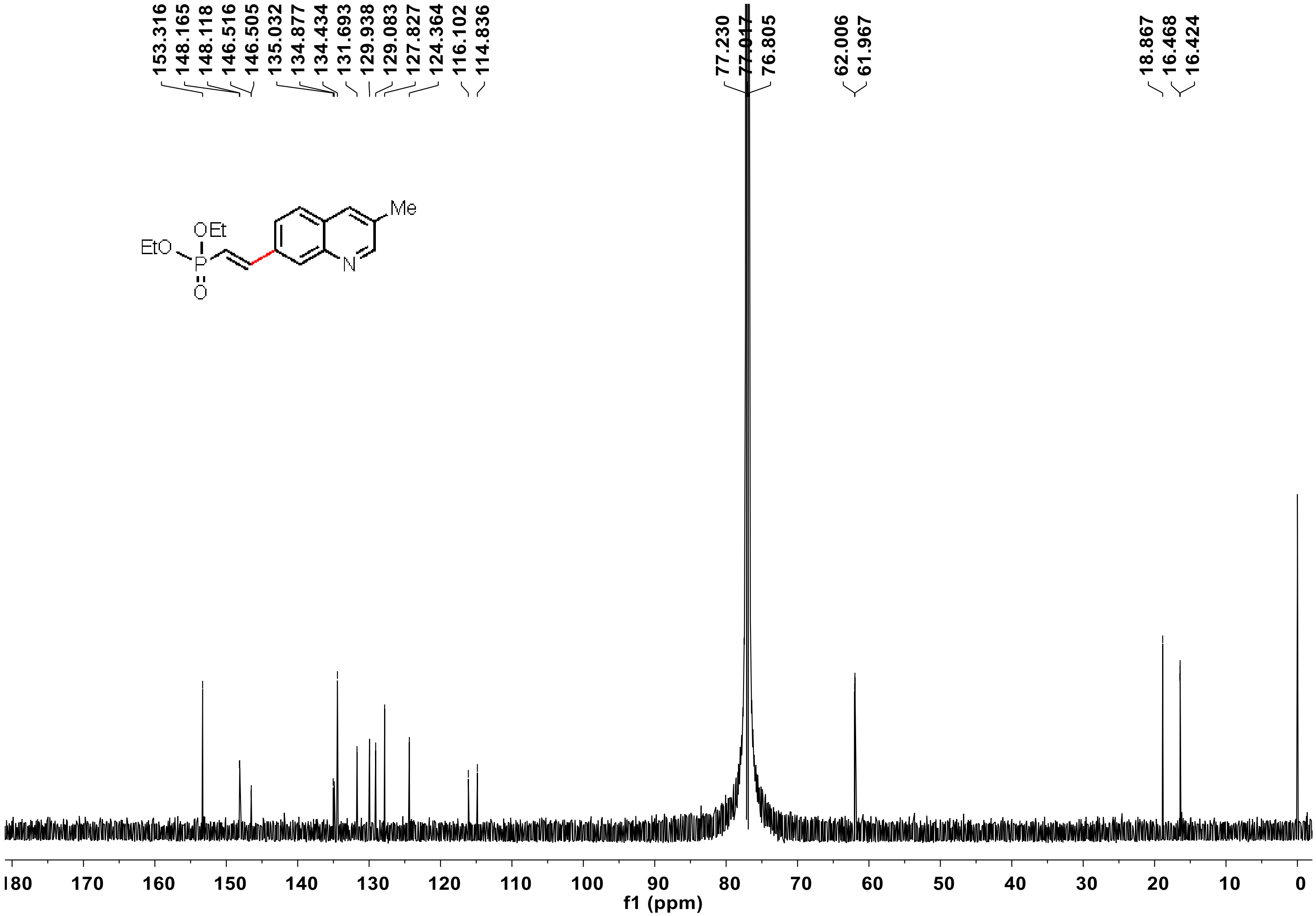
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3u**



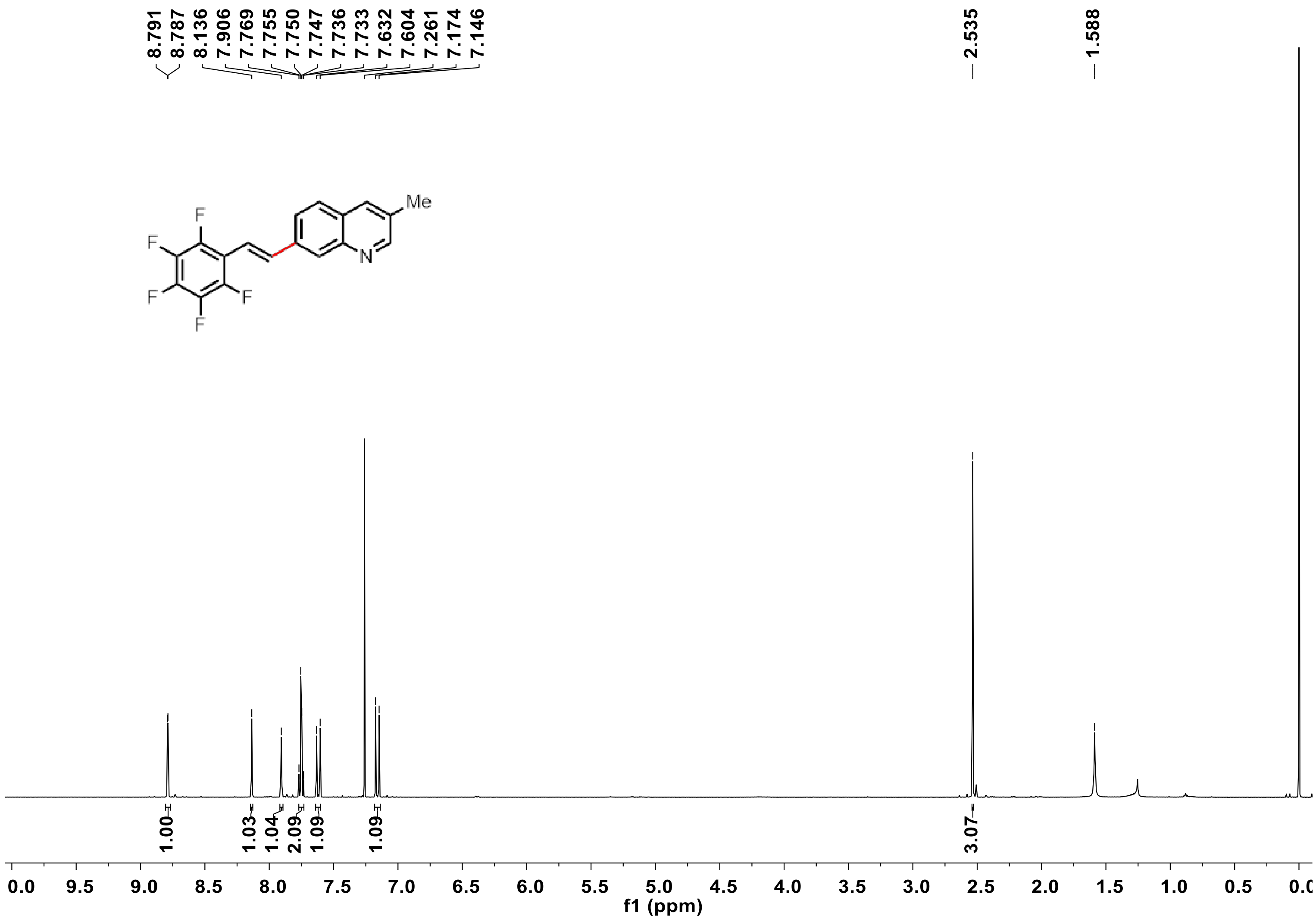
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3v**



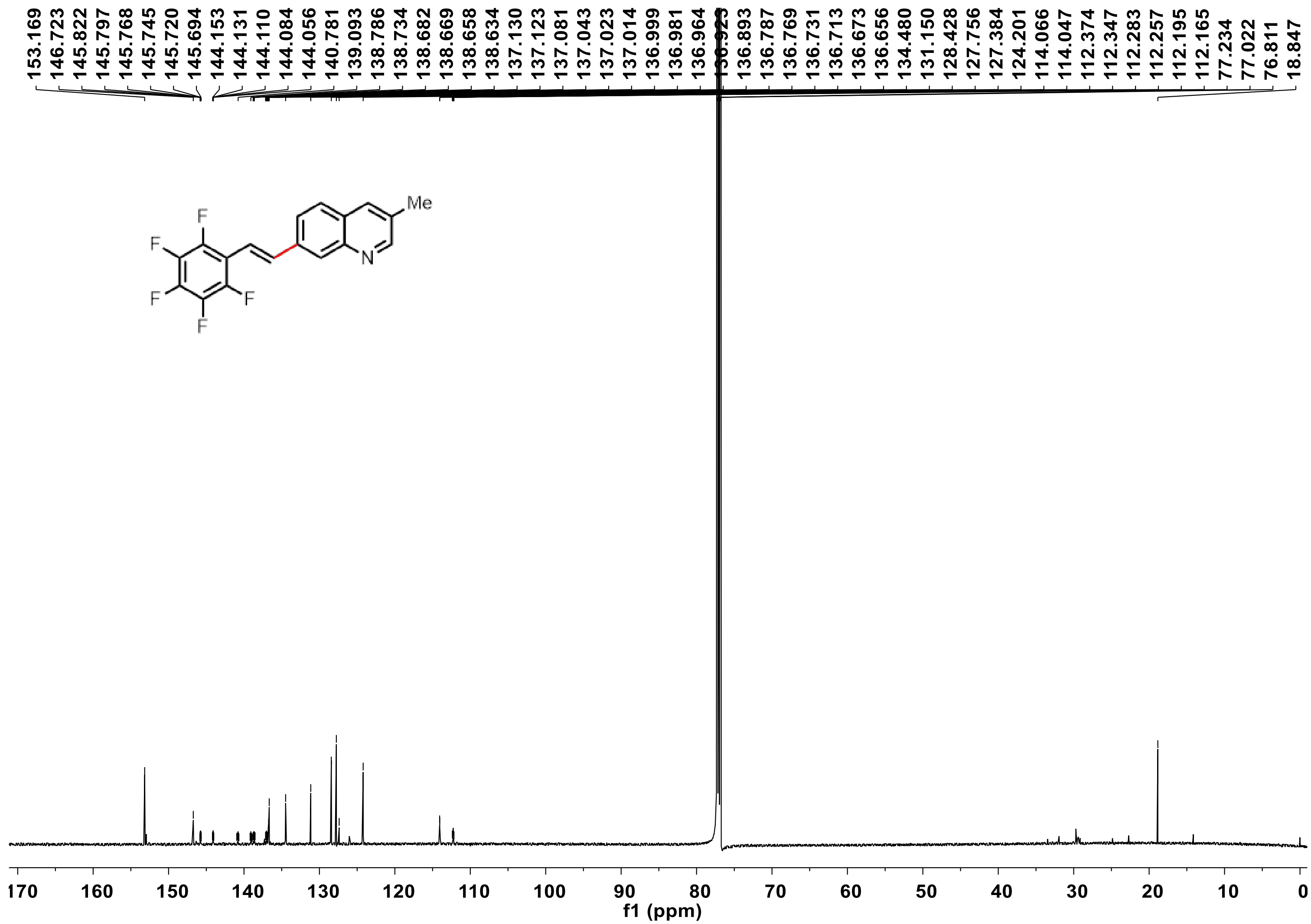
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3v**



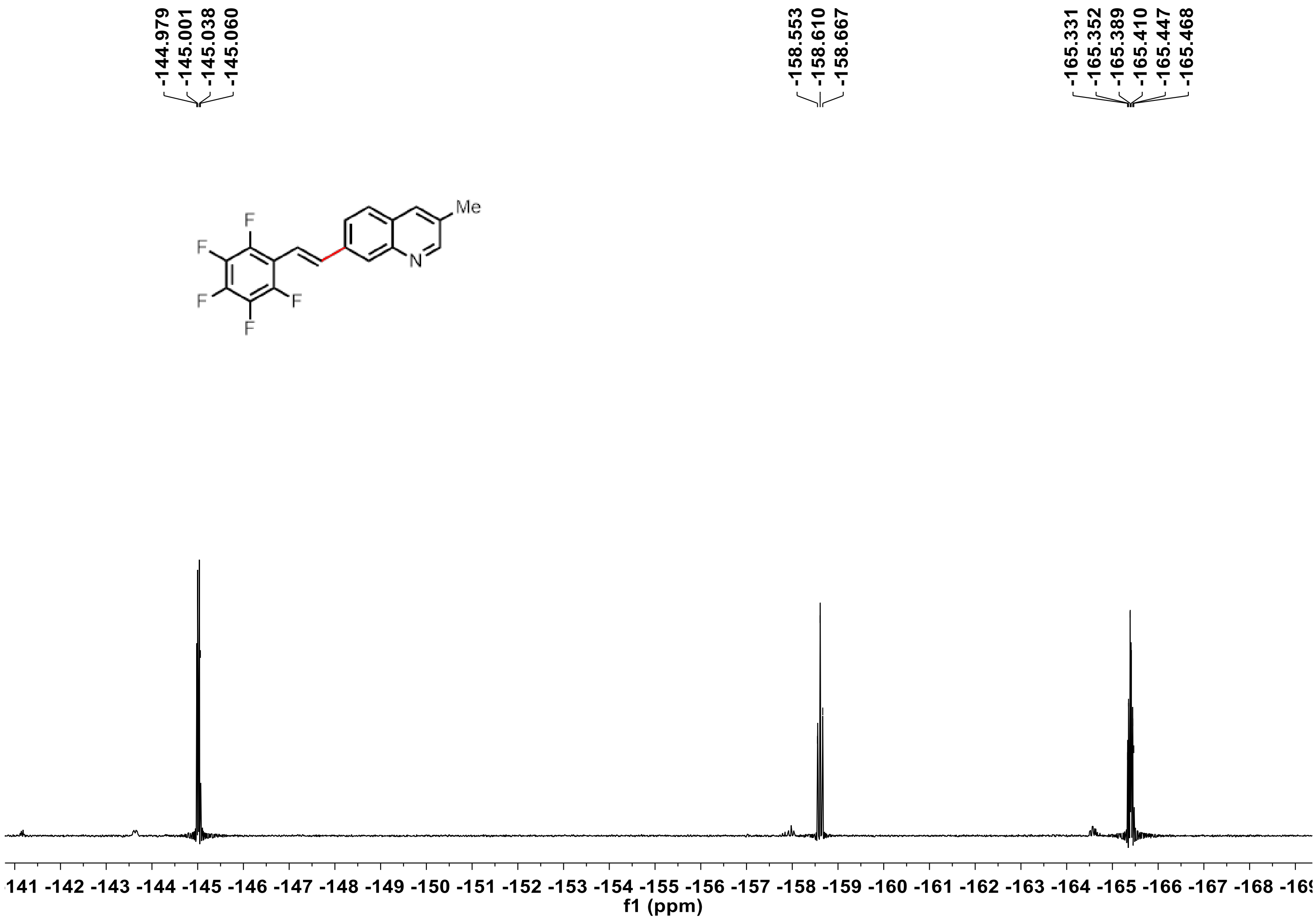
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3w**



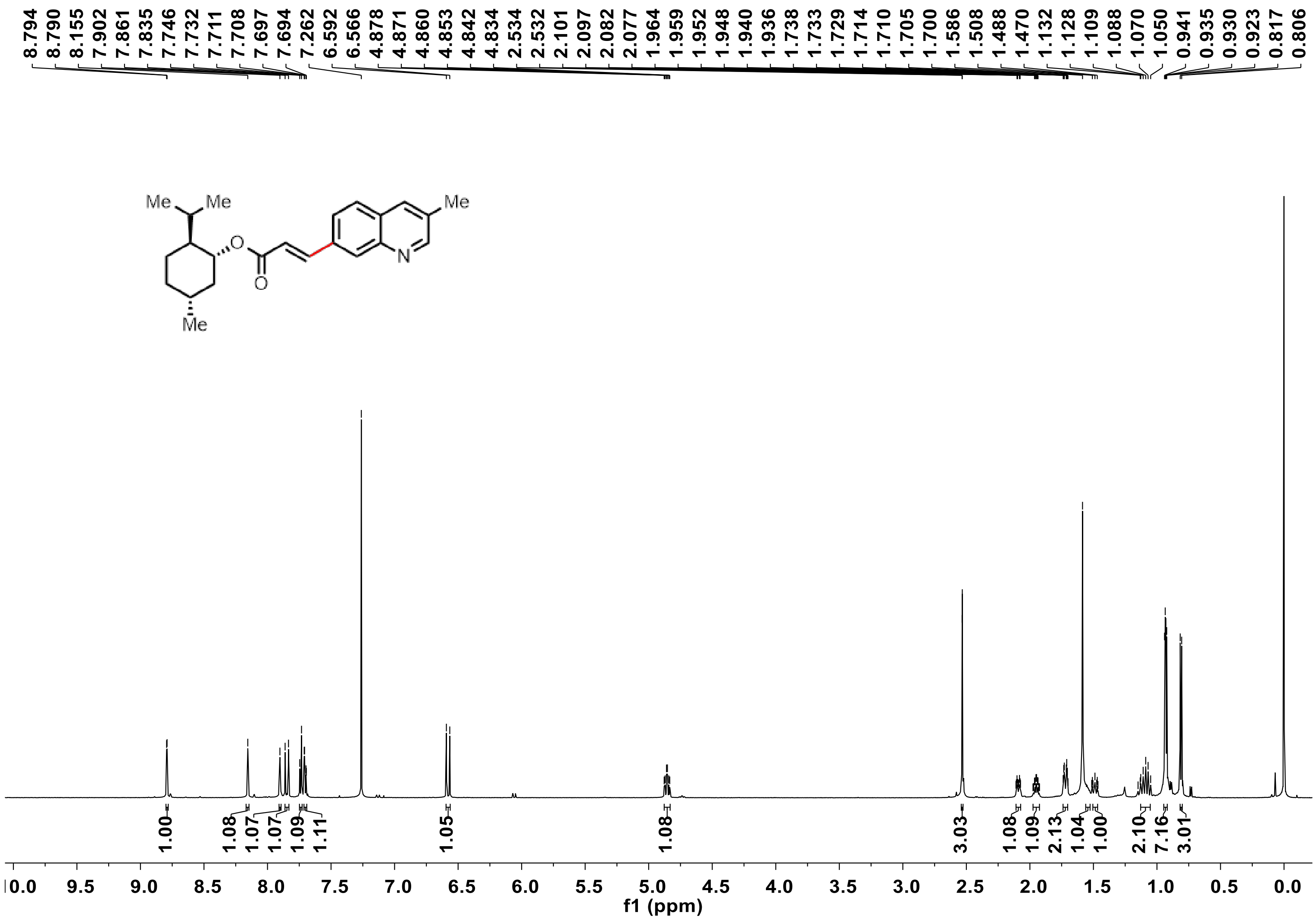
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3w**



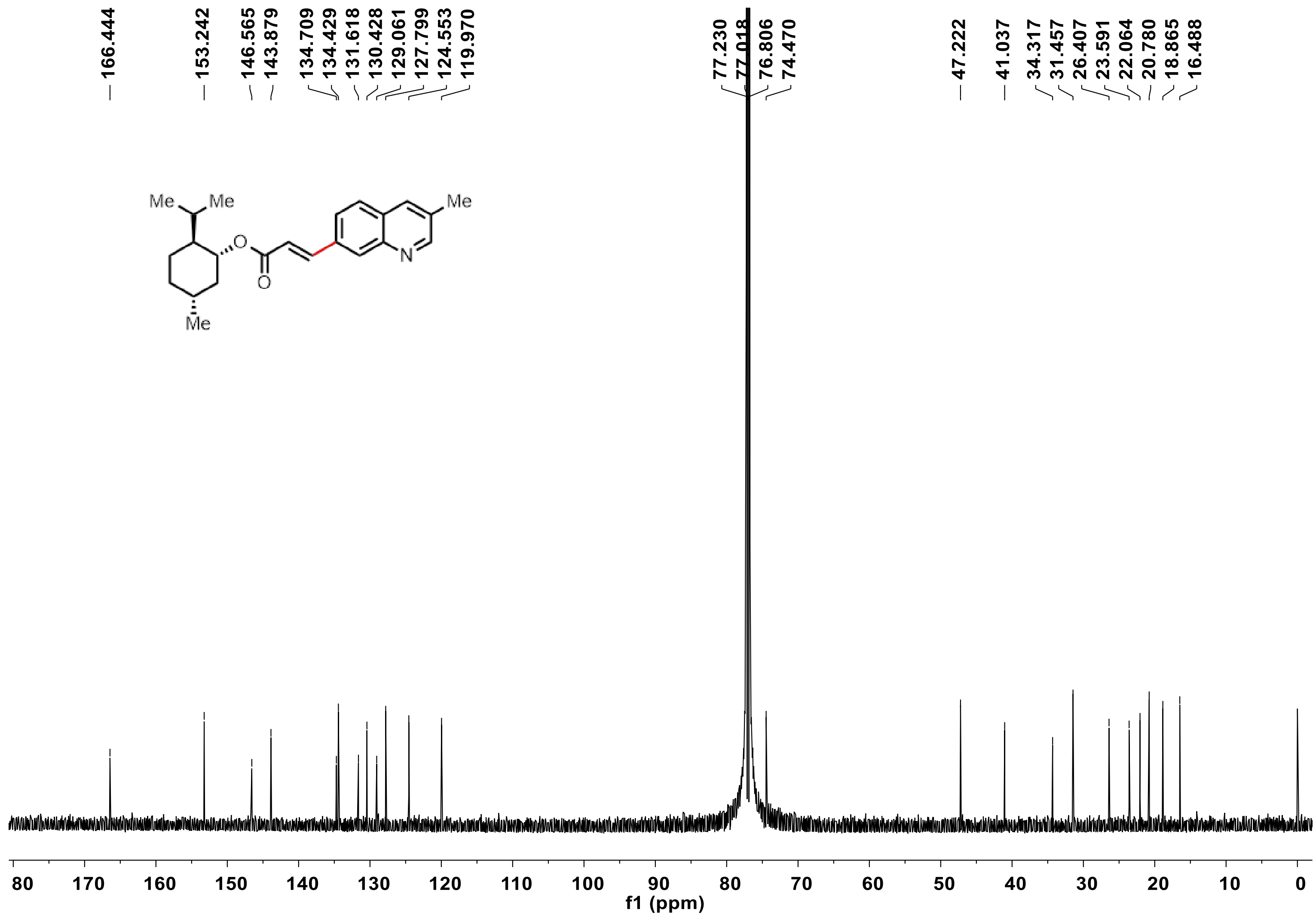
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3w**



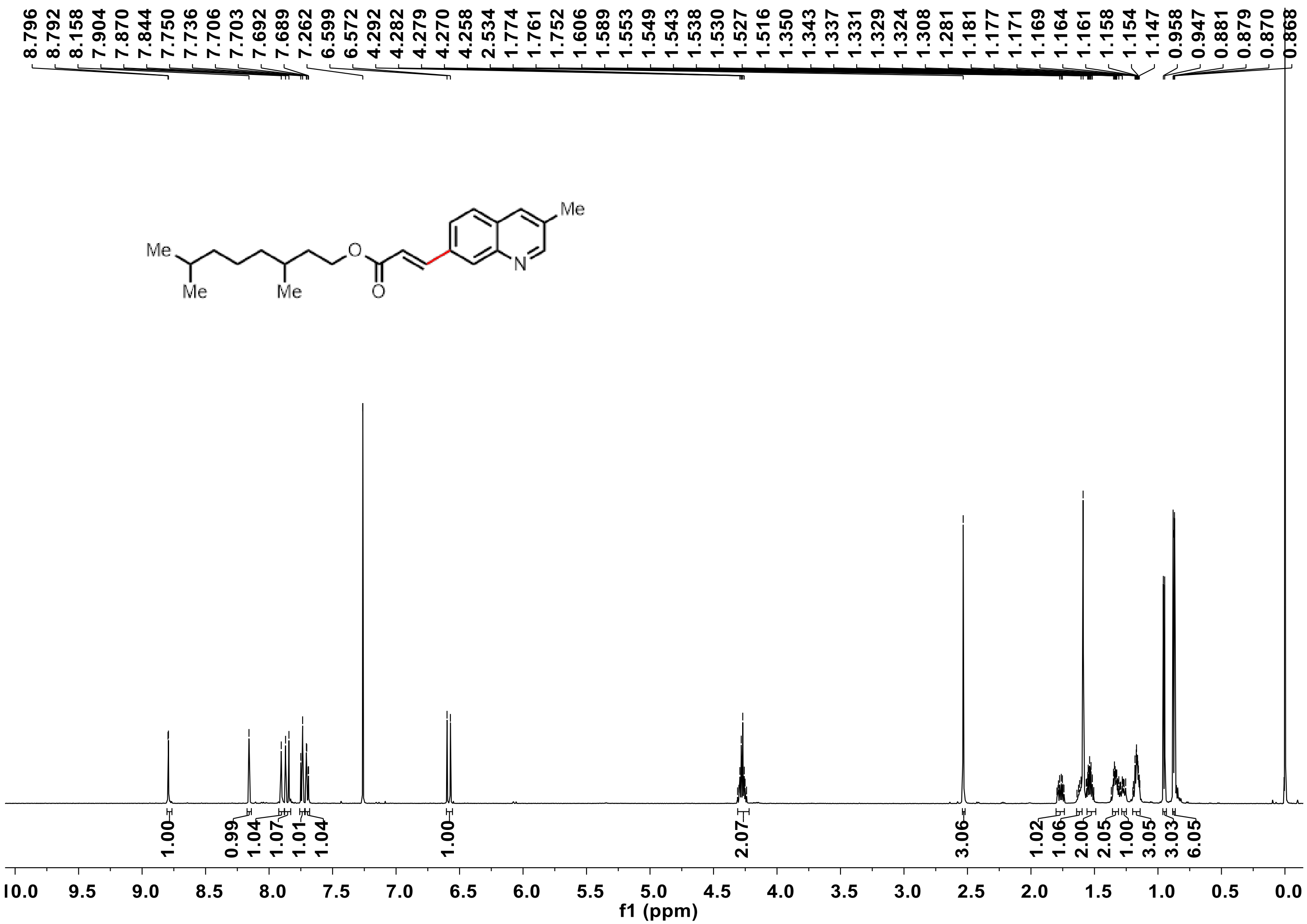
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **3x**



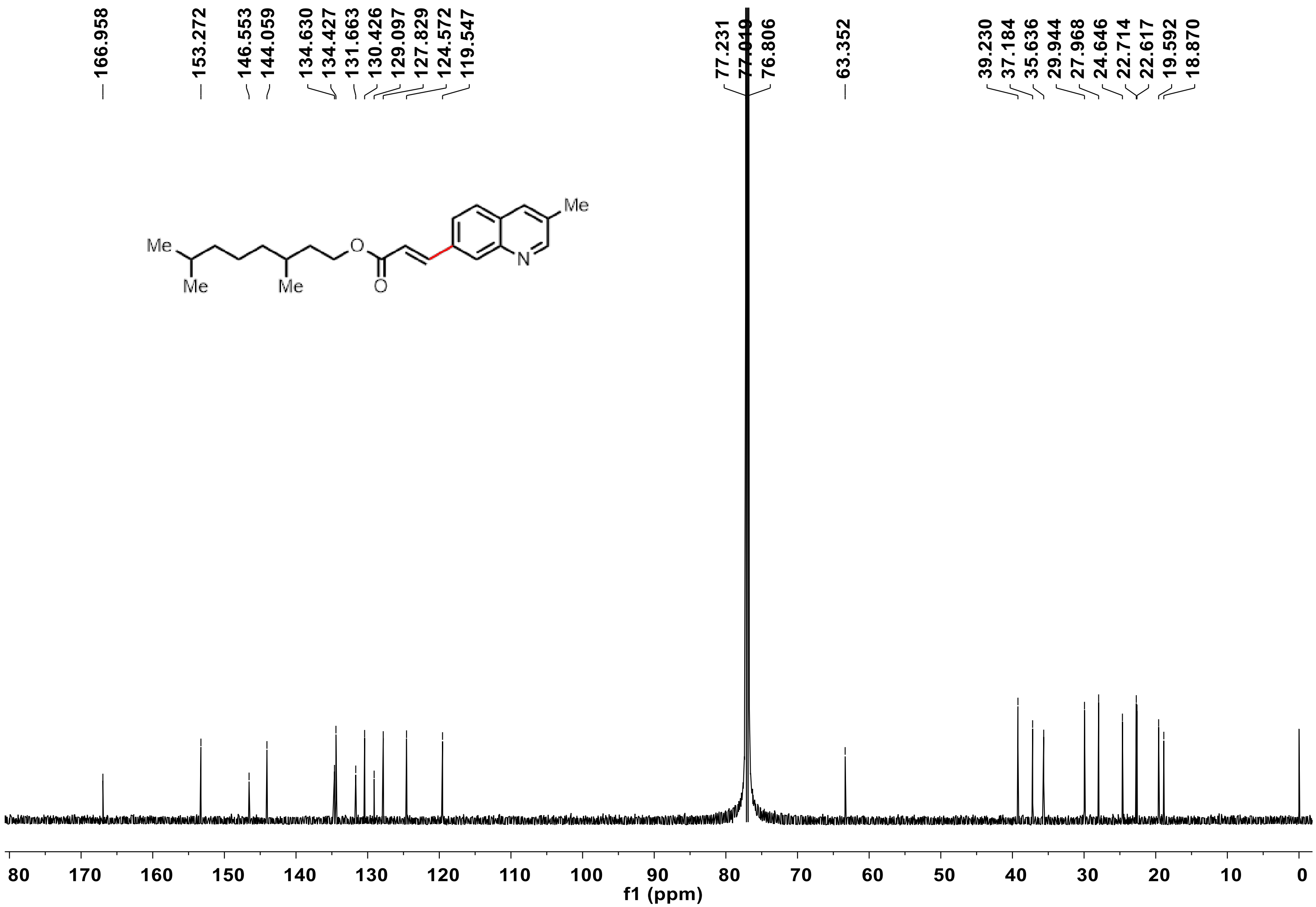
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3x**



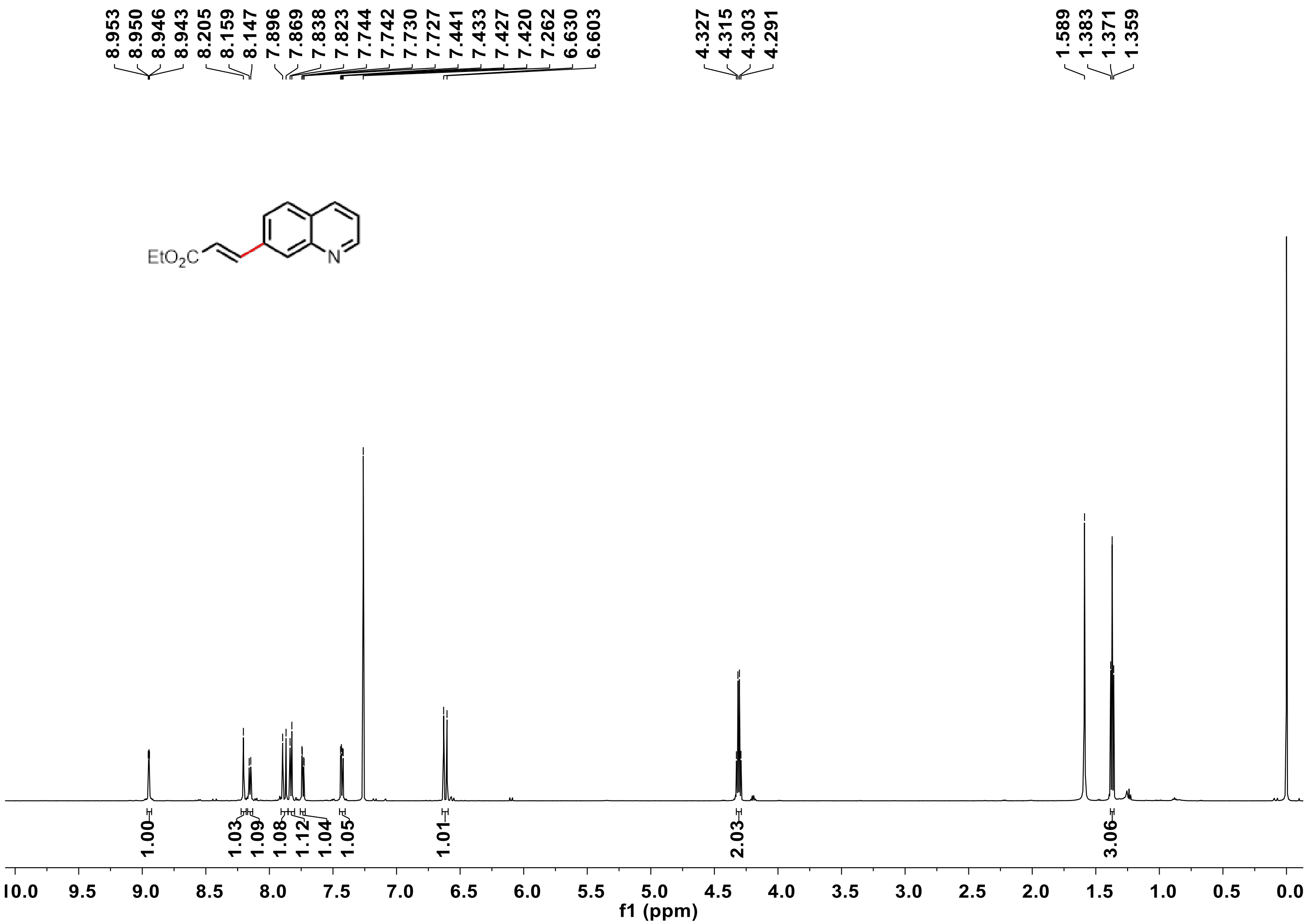
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3y**



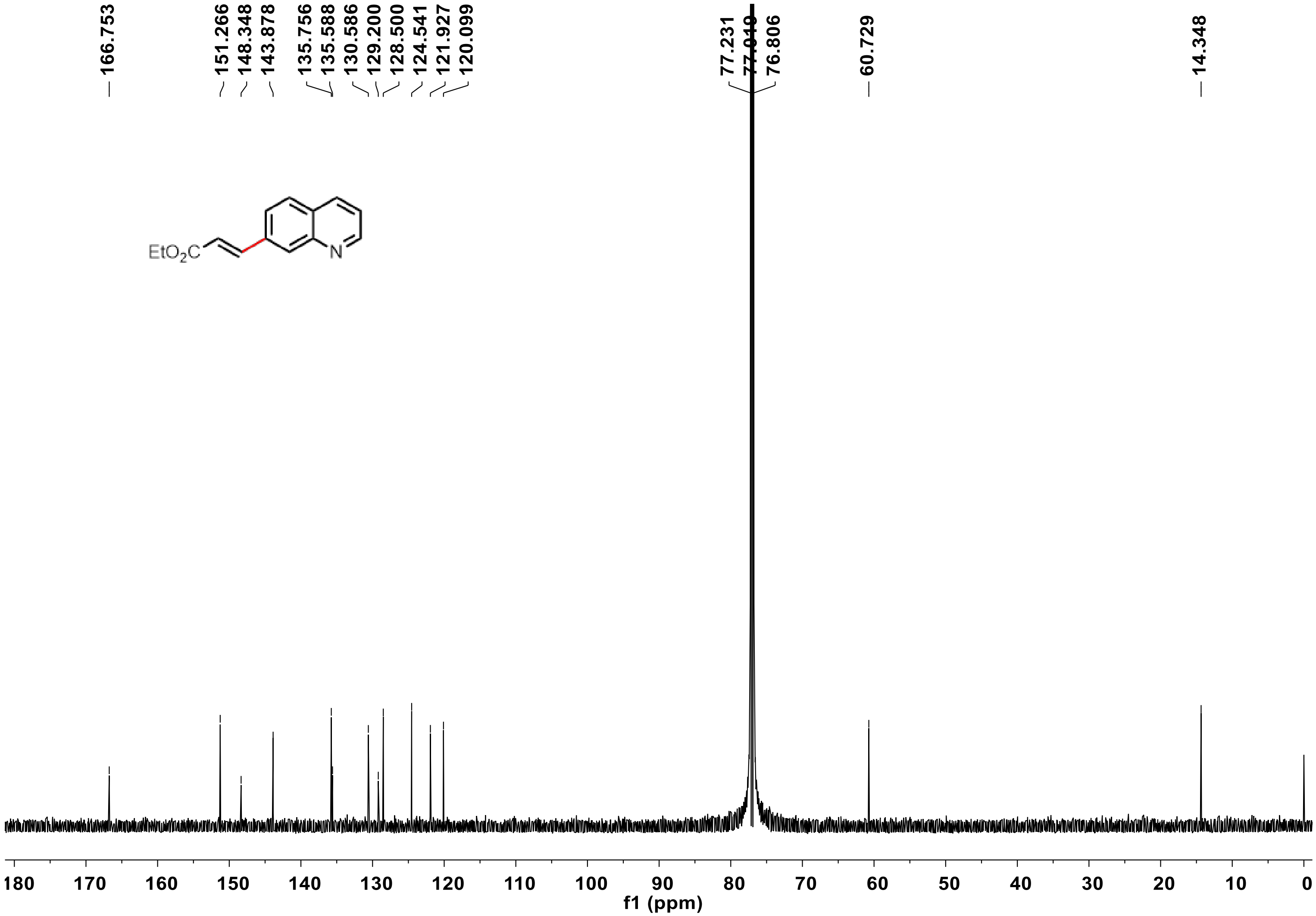
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3y**



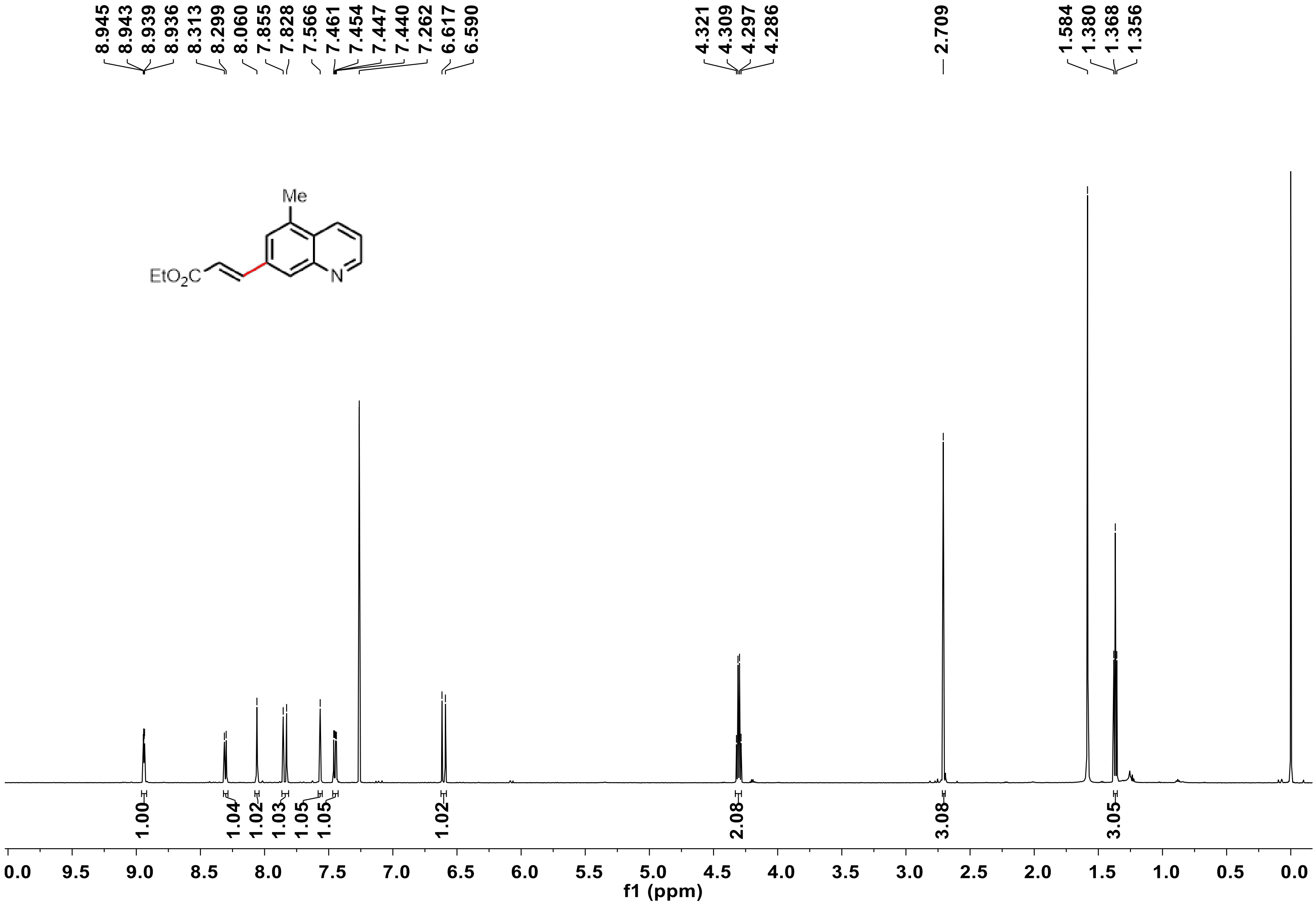
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3z**



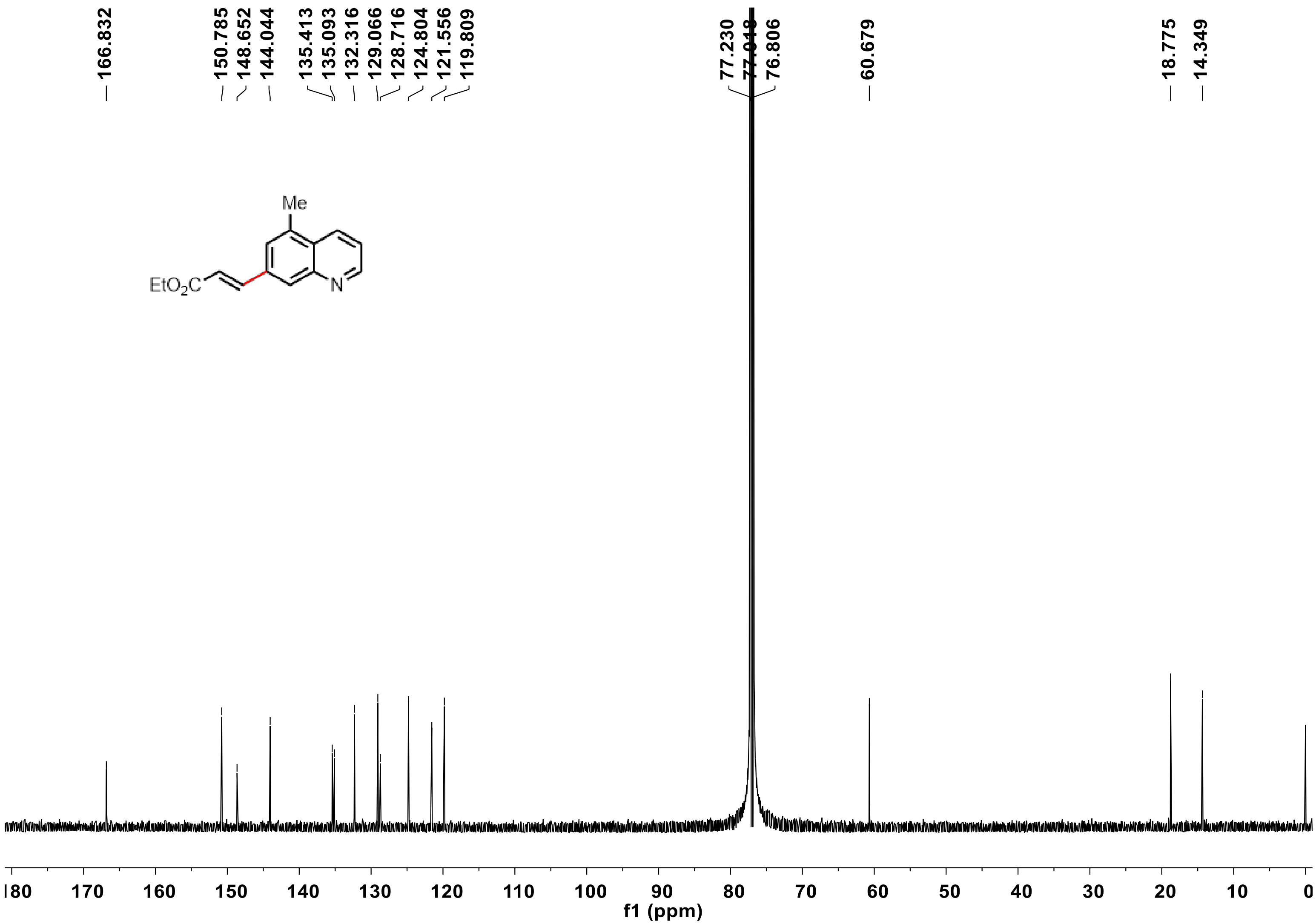
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3z**



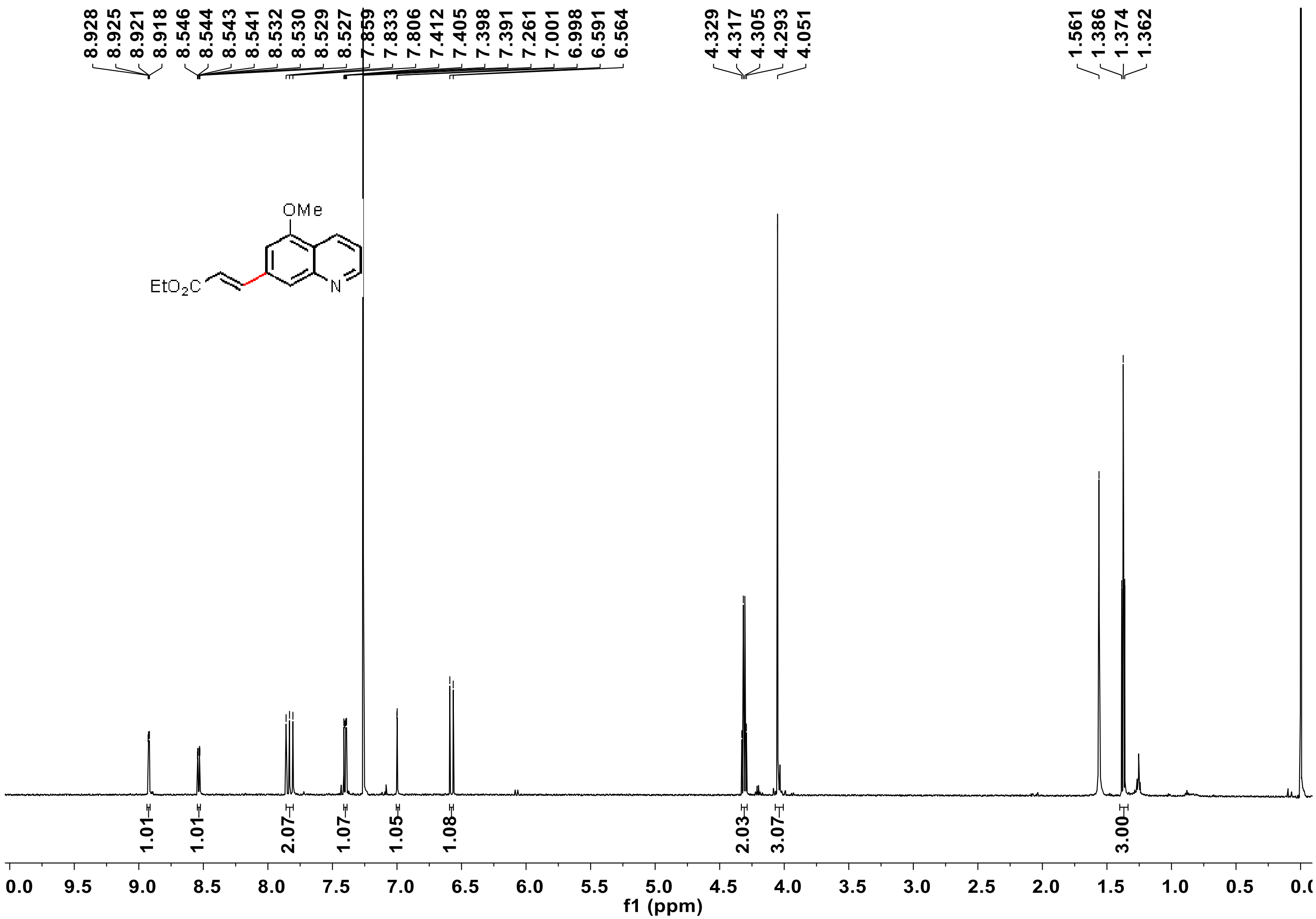
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aa**



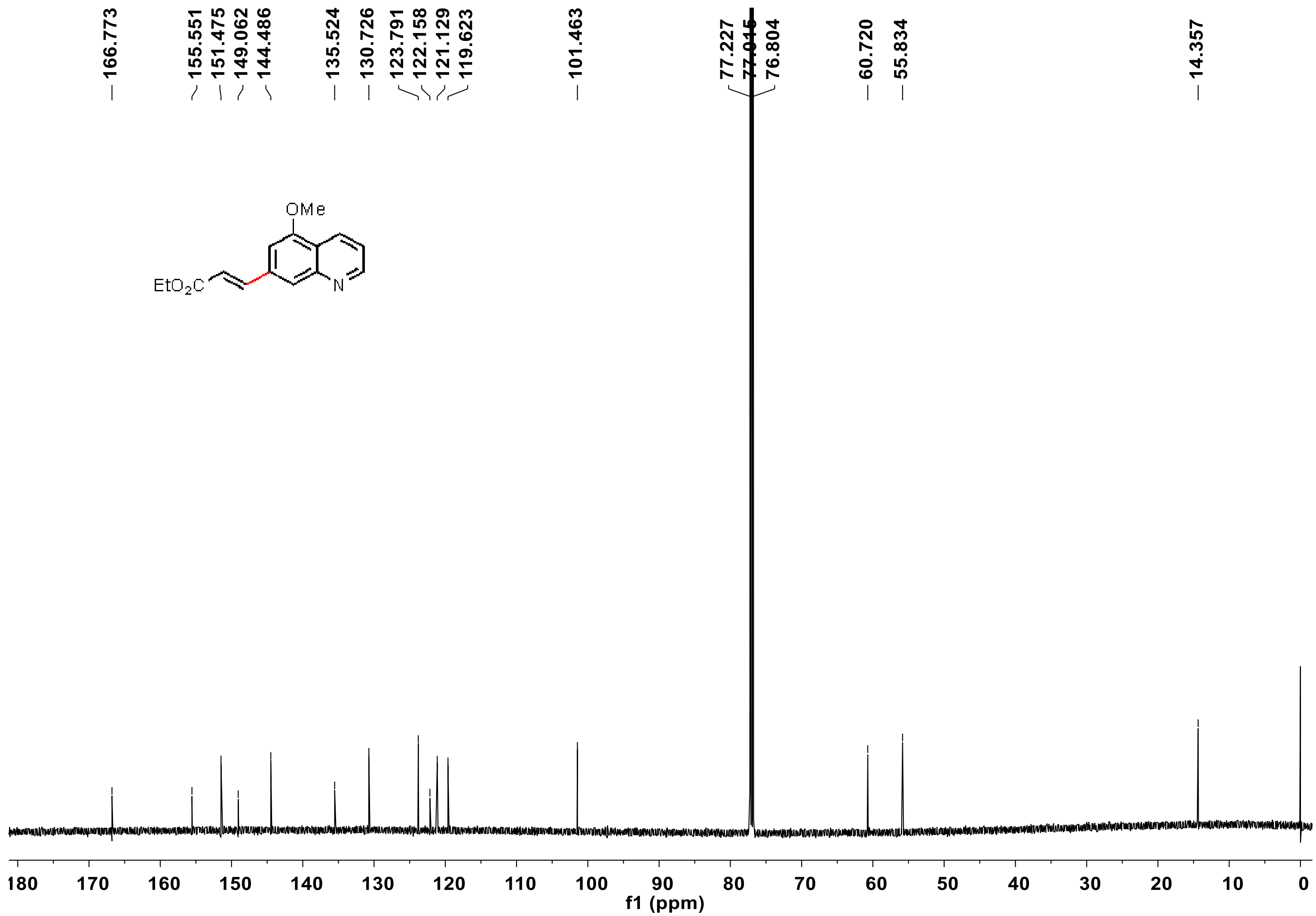
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3aa**



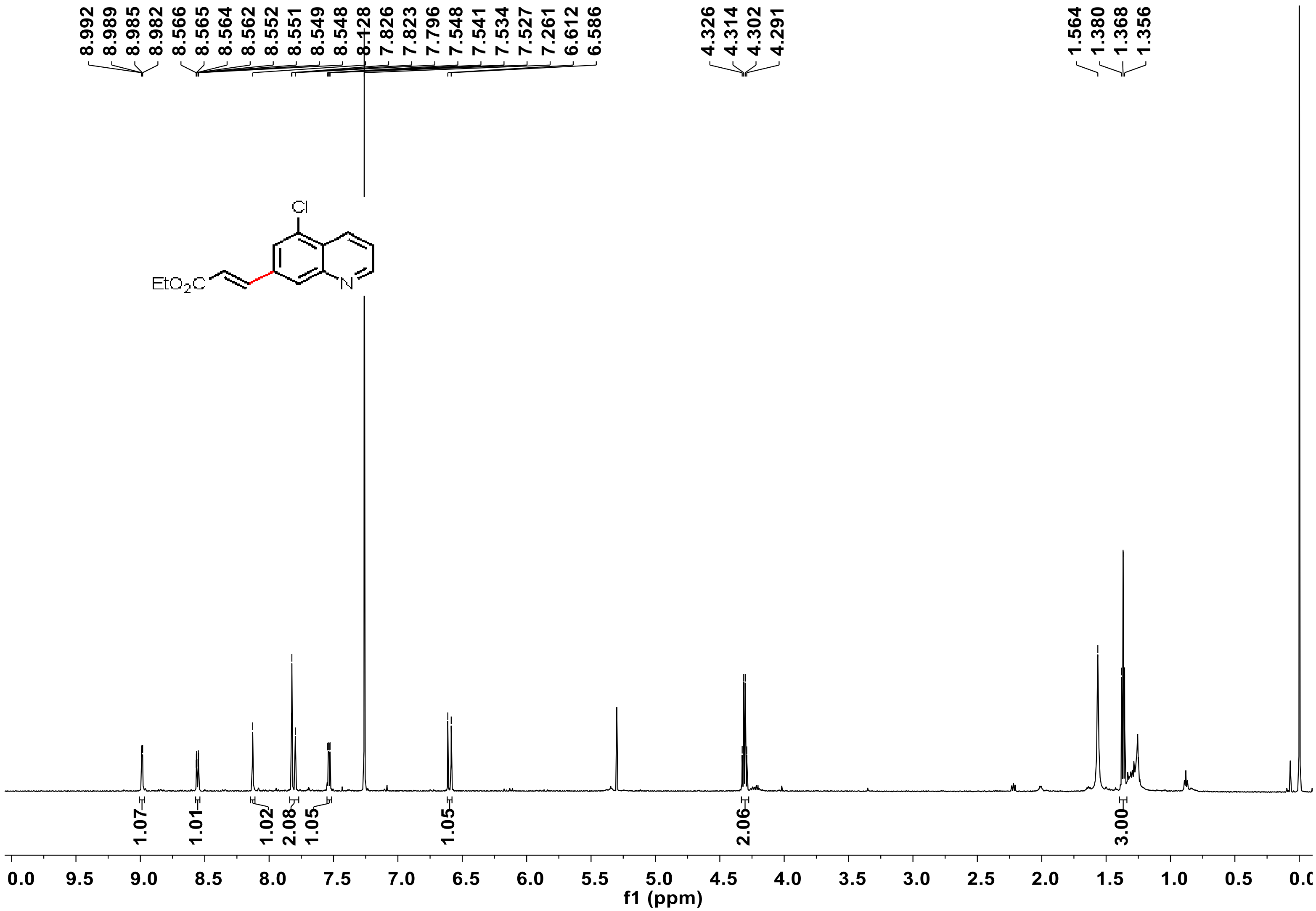
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ab**



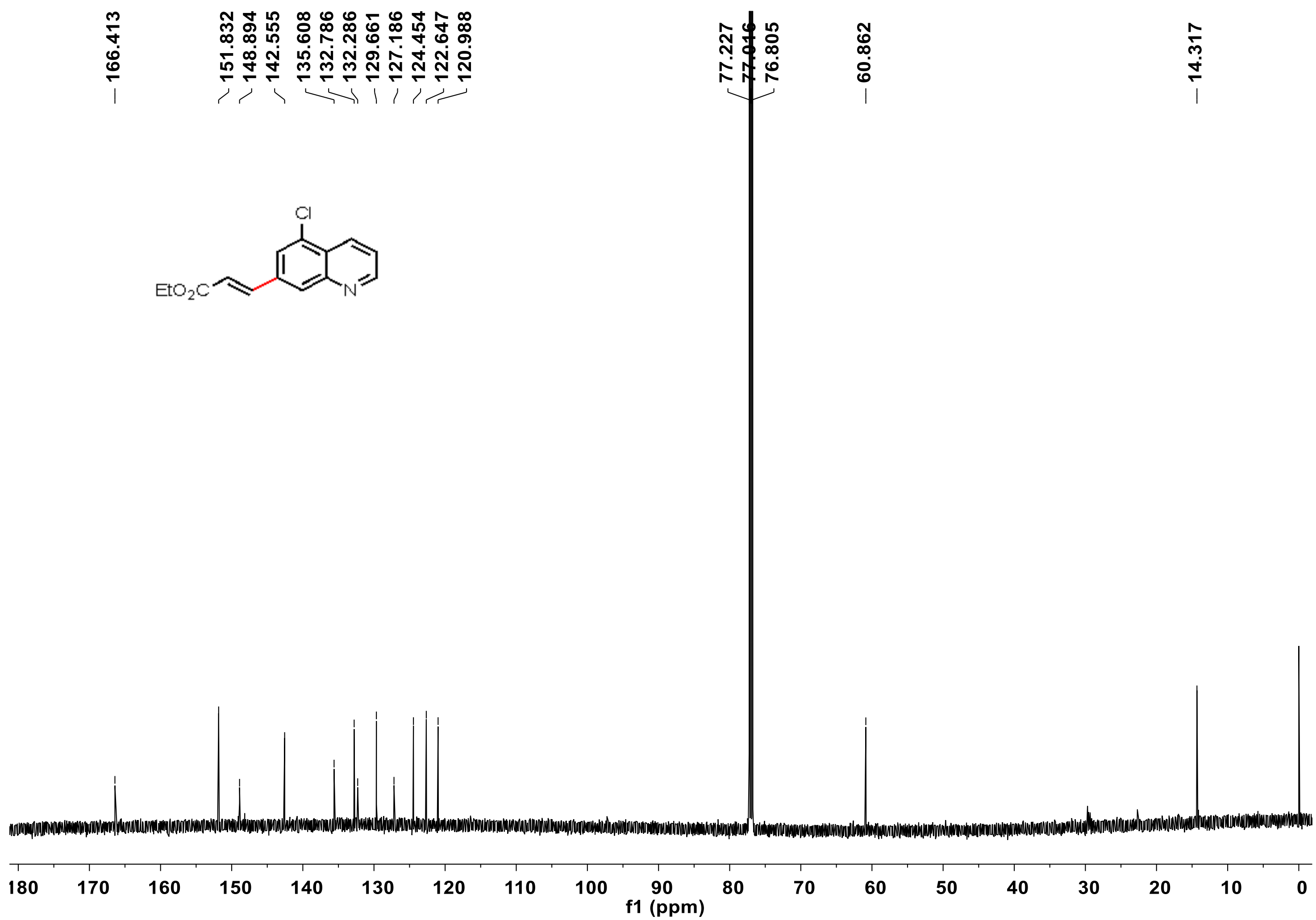
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ab**



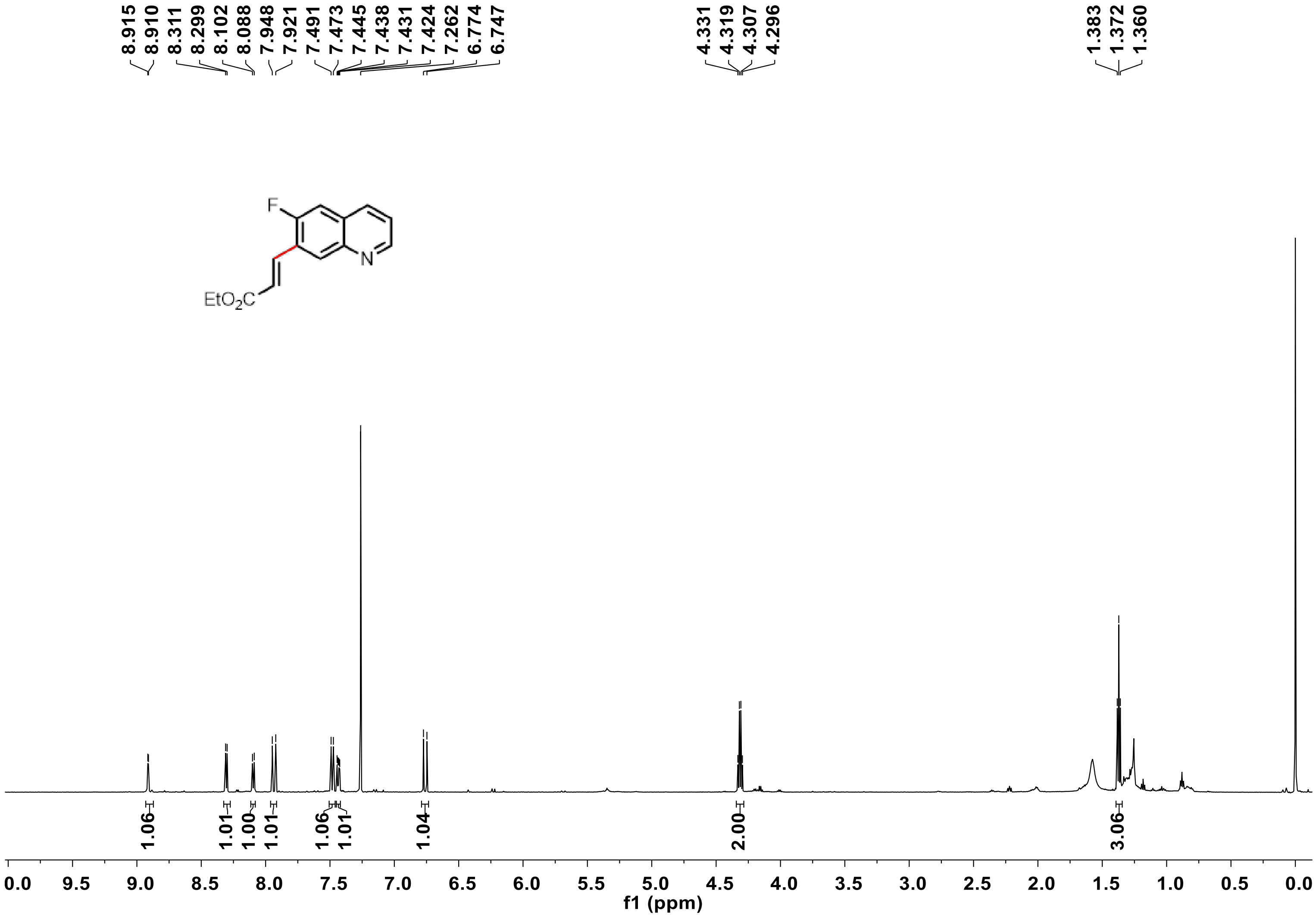
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ac**



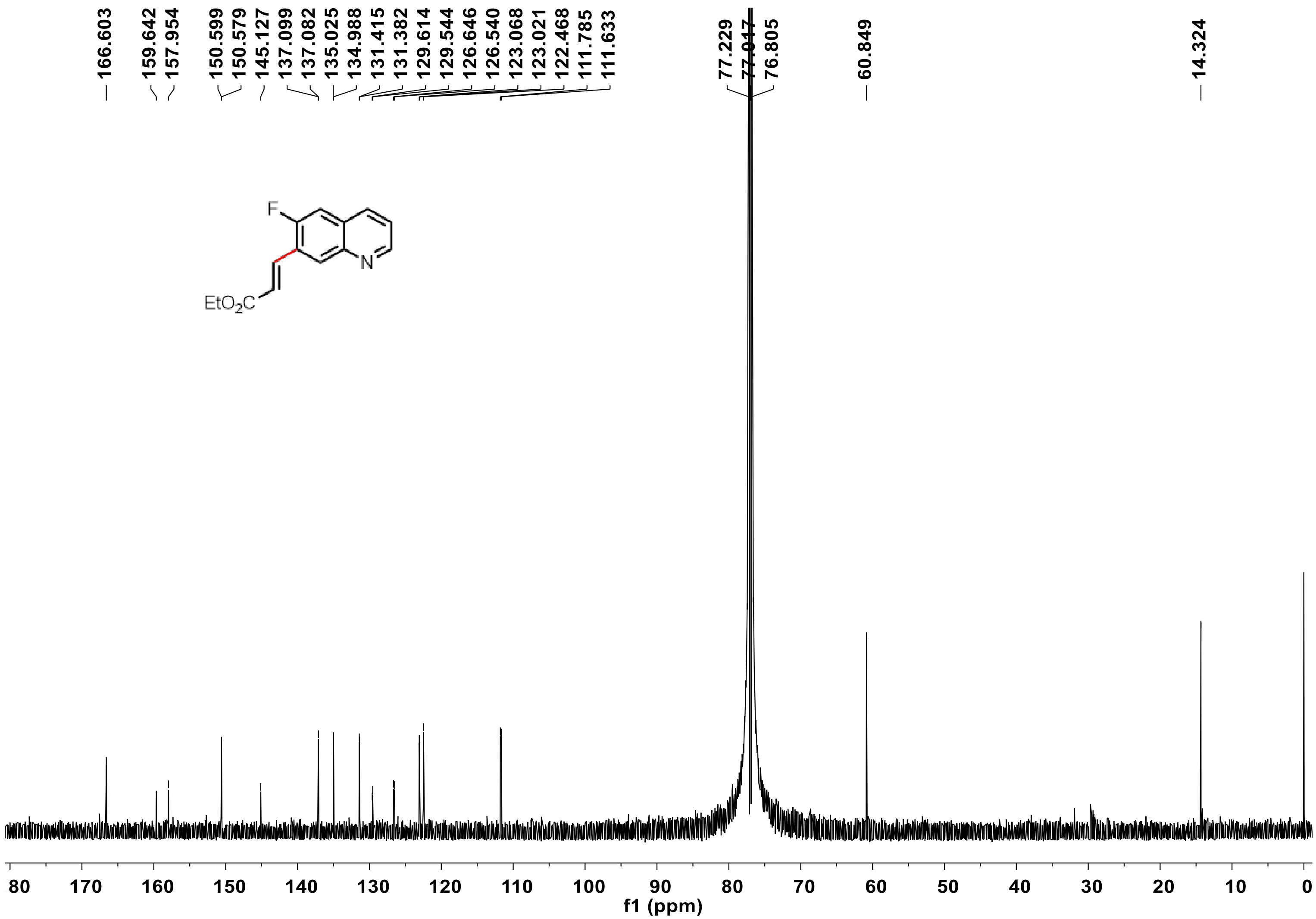
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ac**



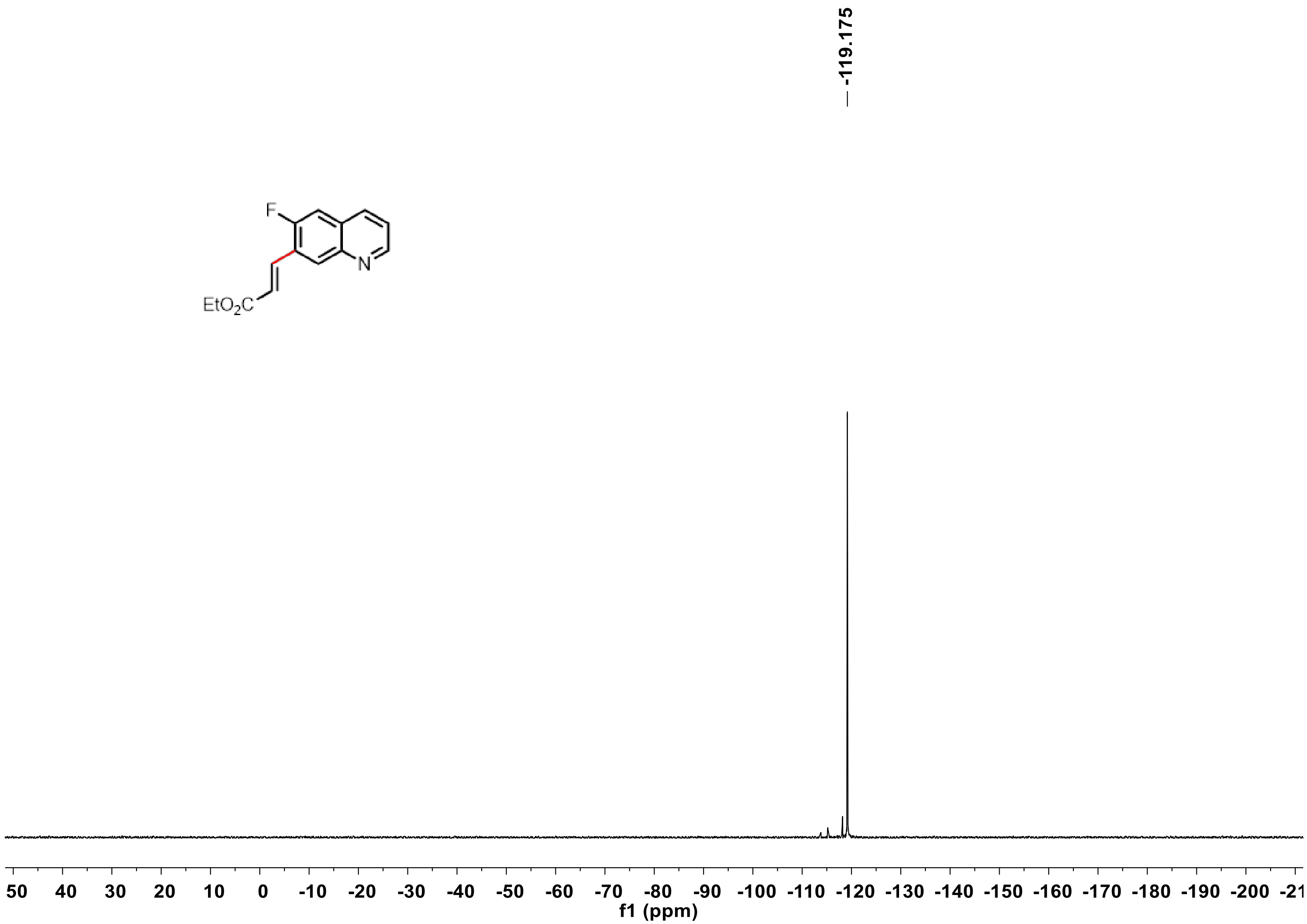
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ad**



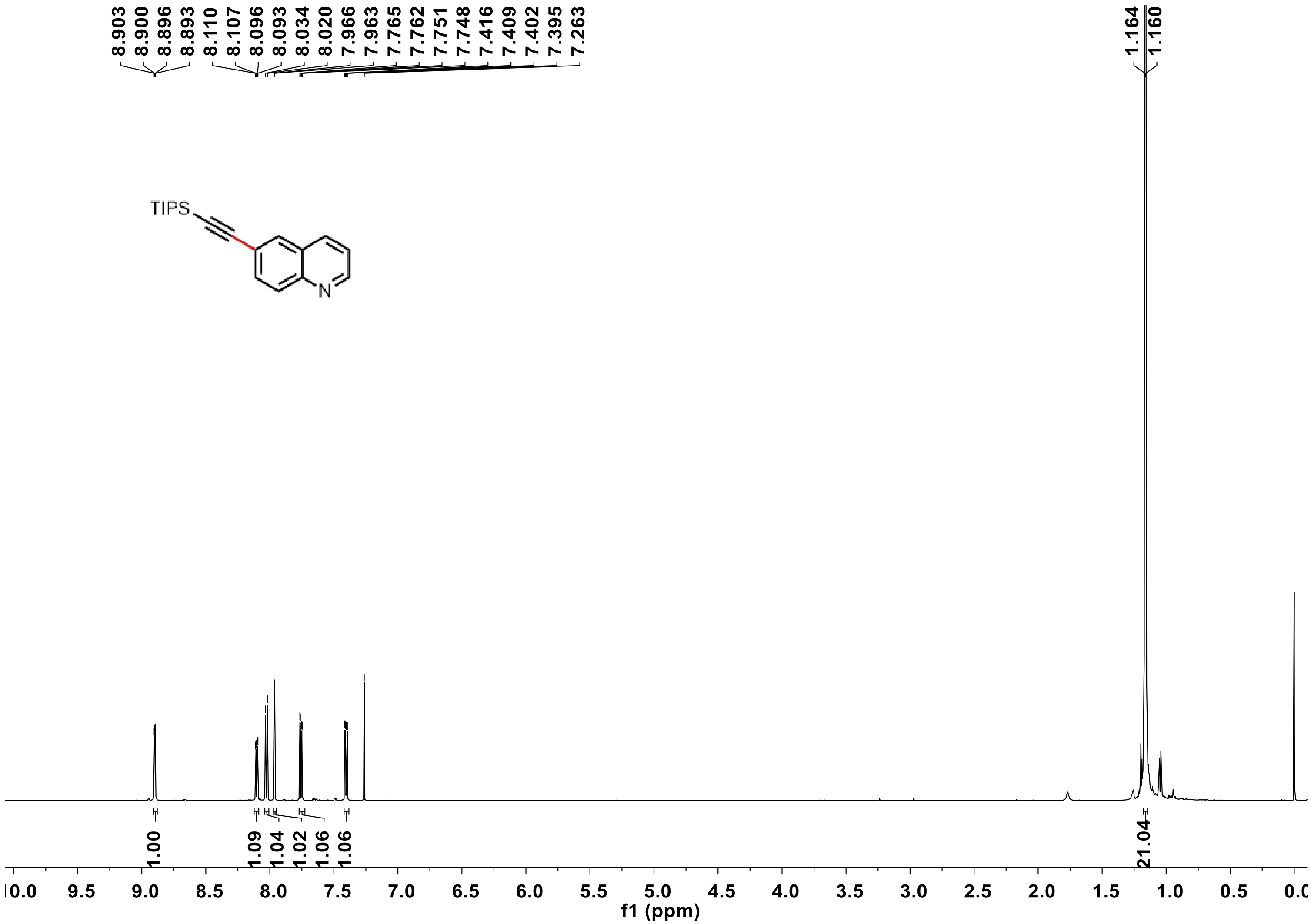
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ad**



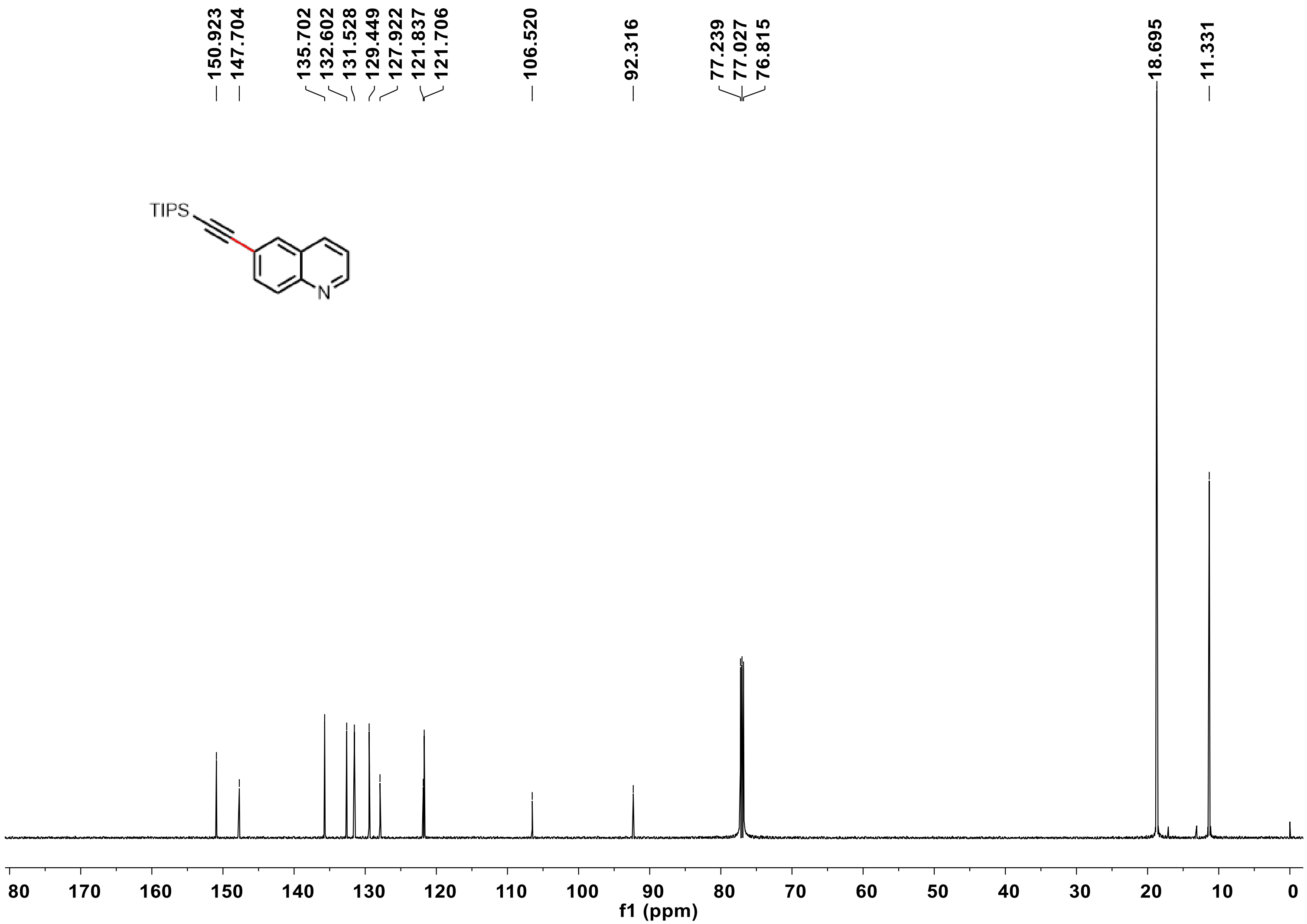
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3ad**



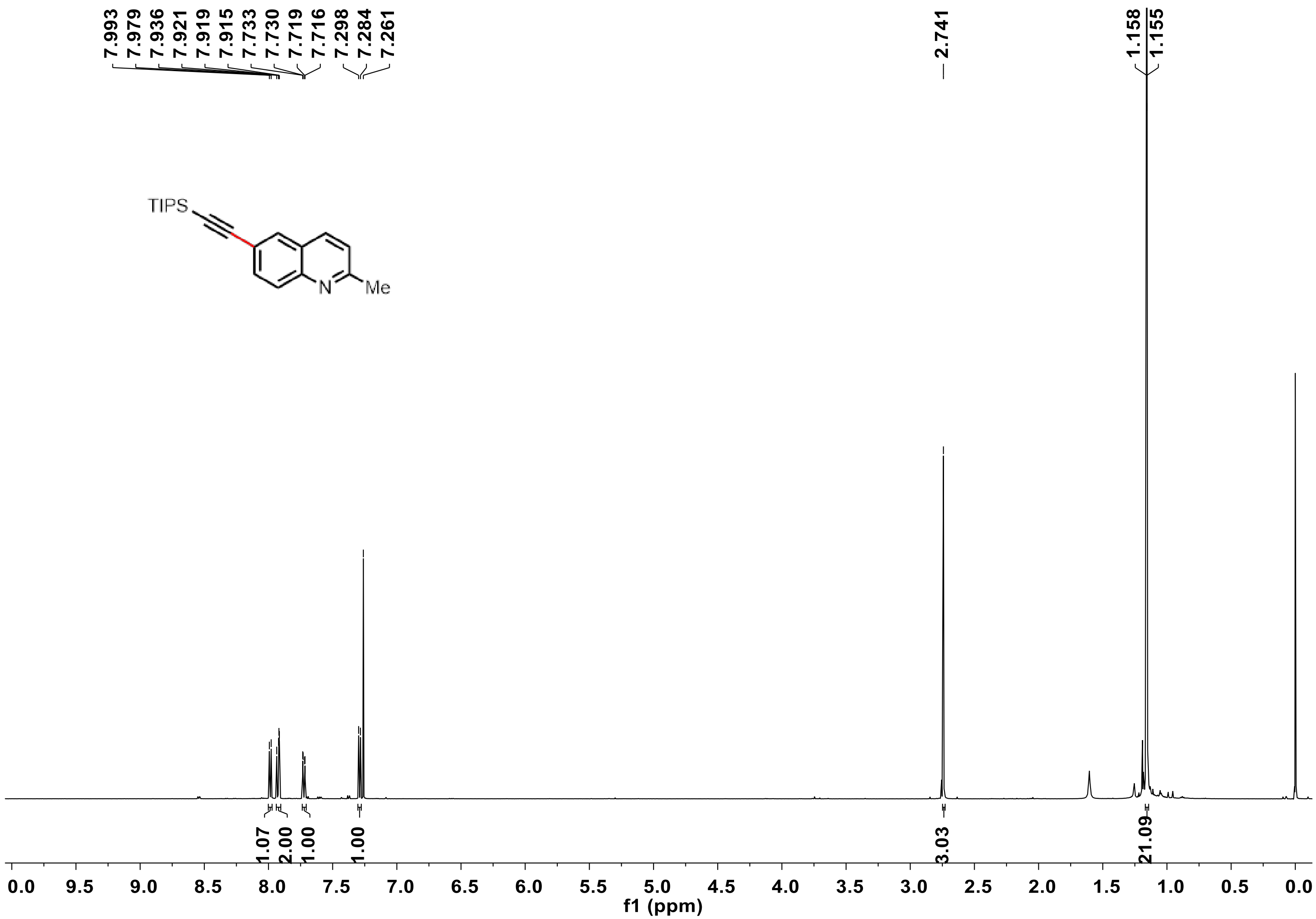
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4a**



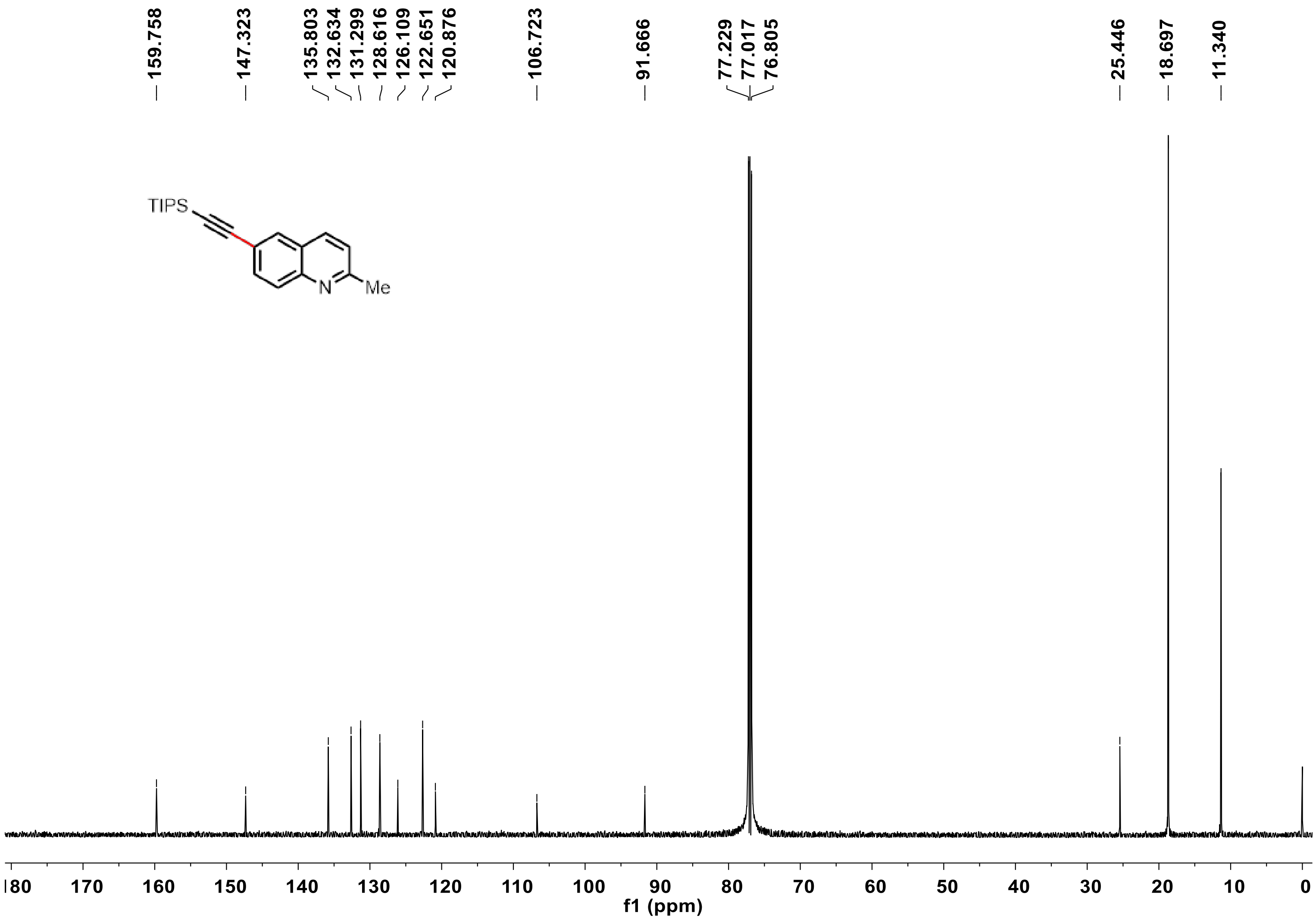
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4a**



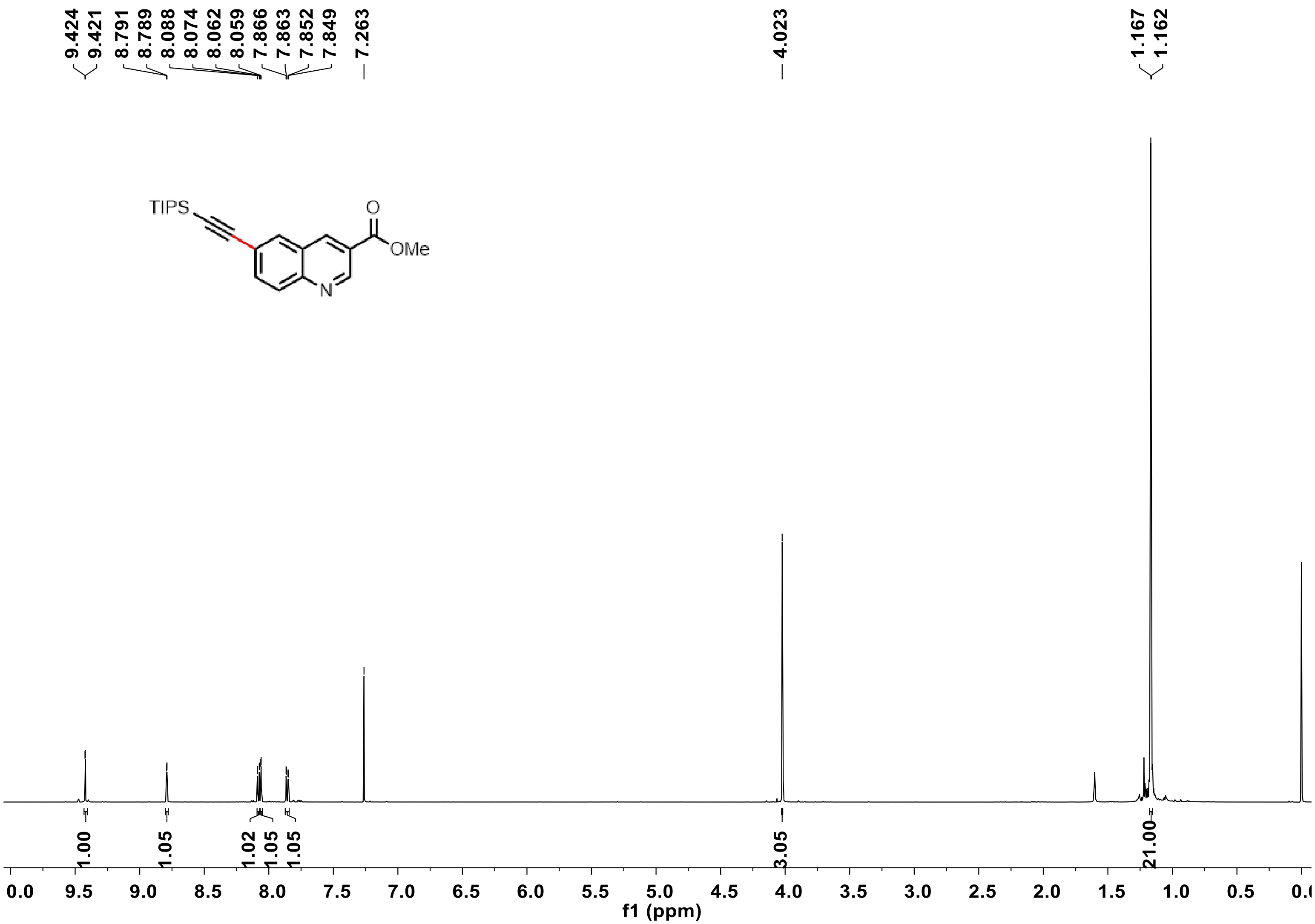
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **4b**



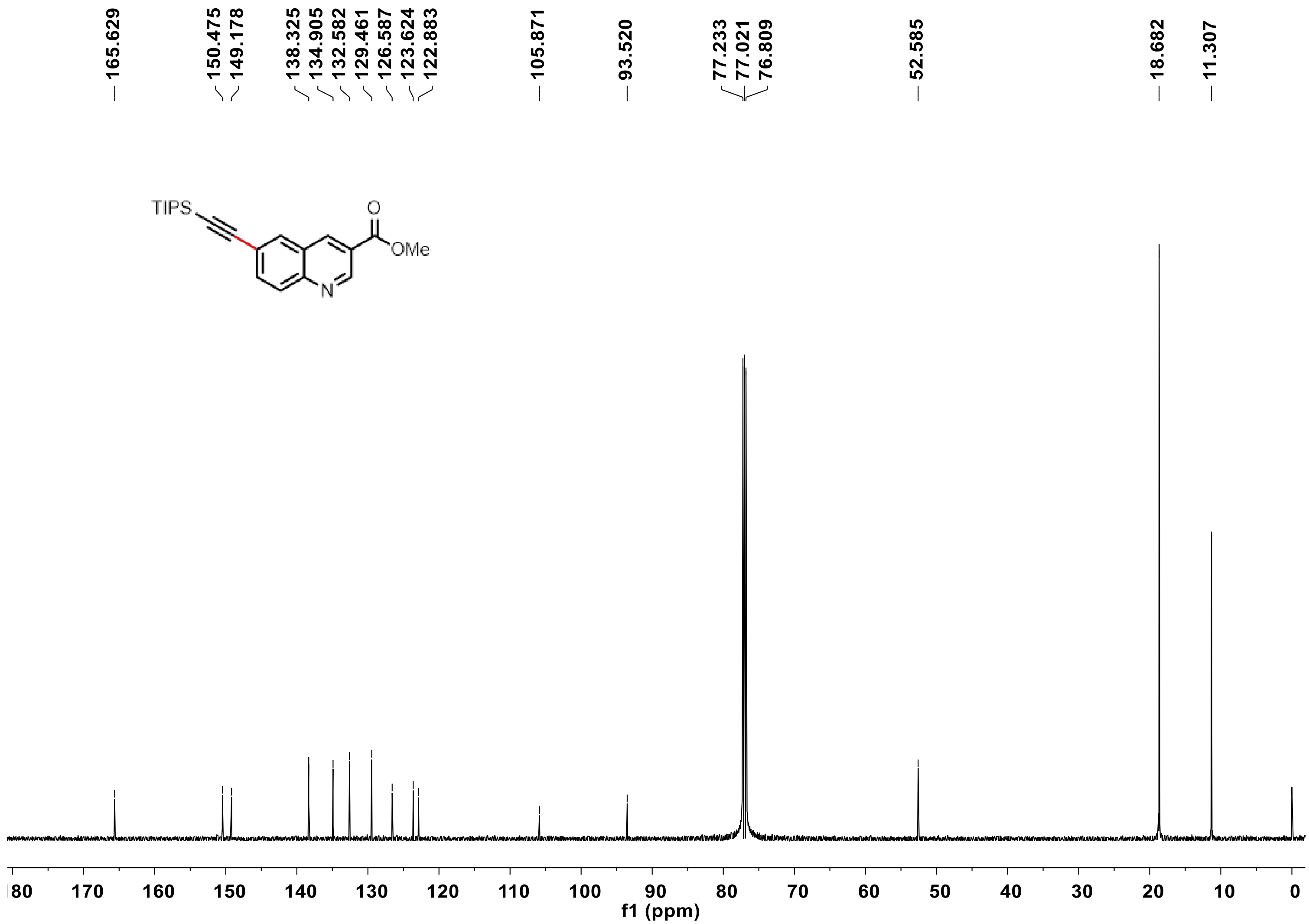
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4b**



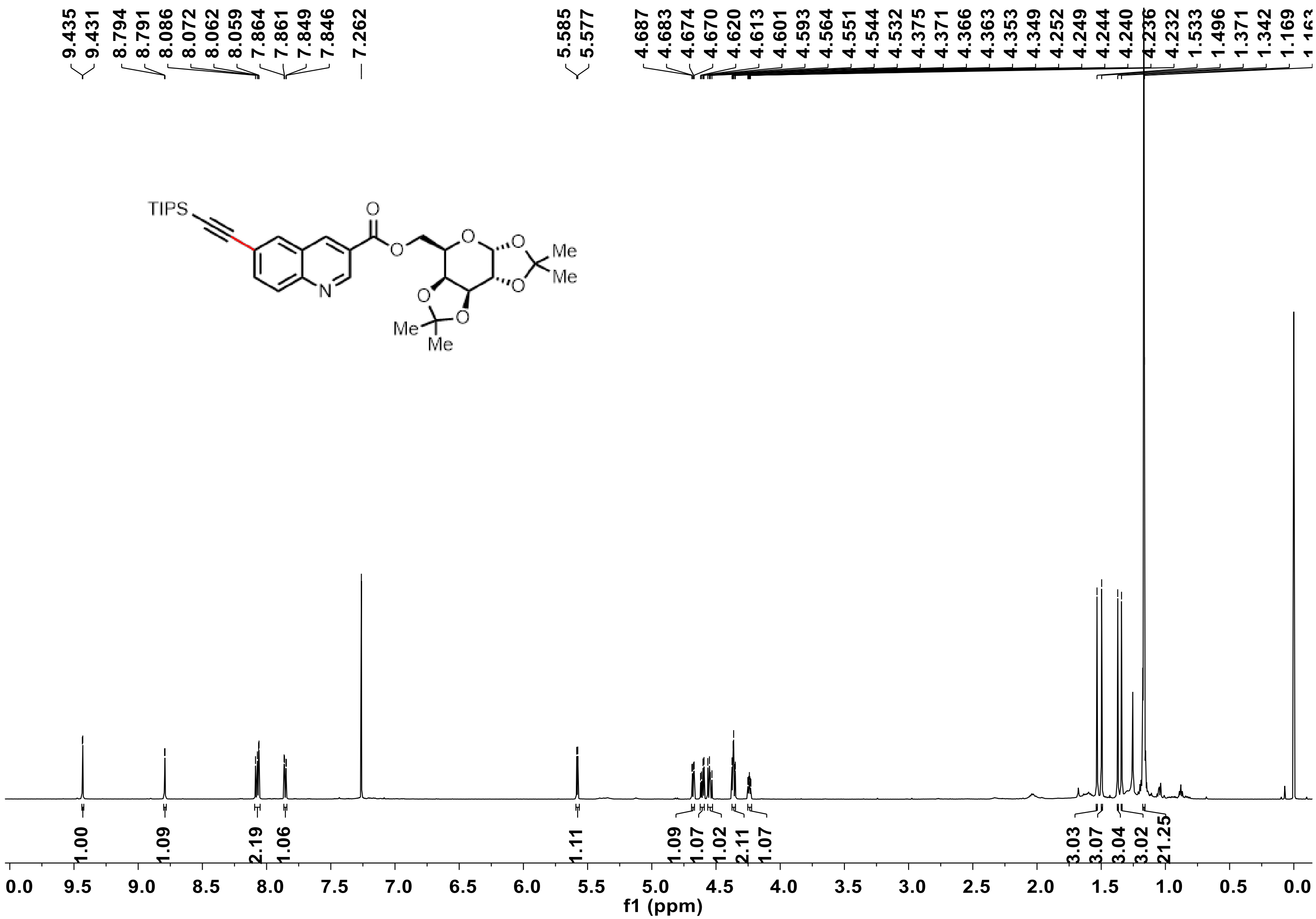
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **4c**



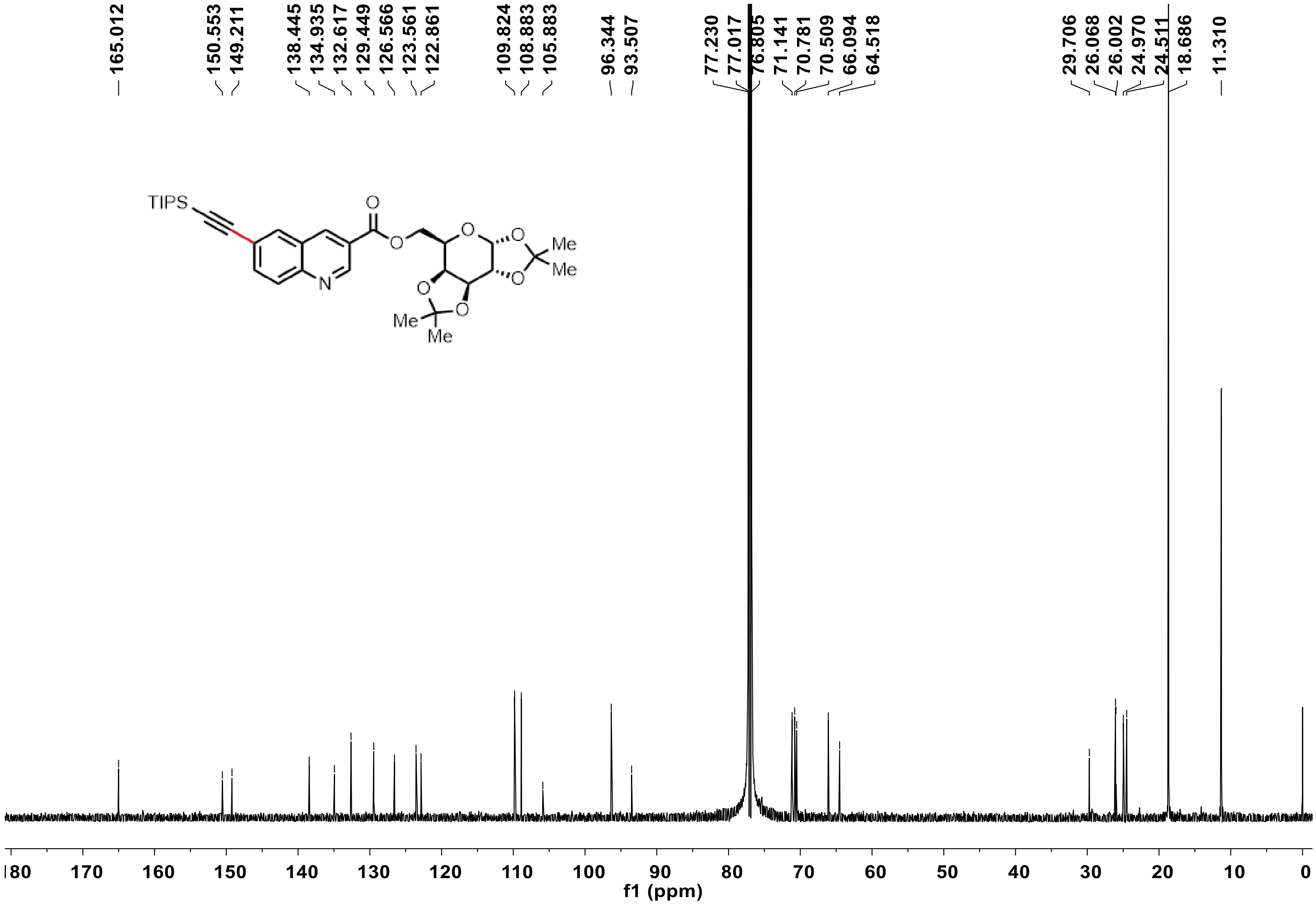
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4c**



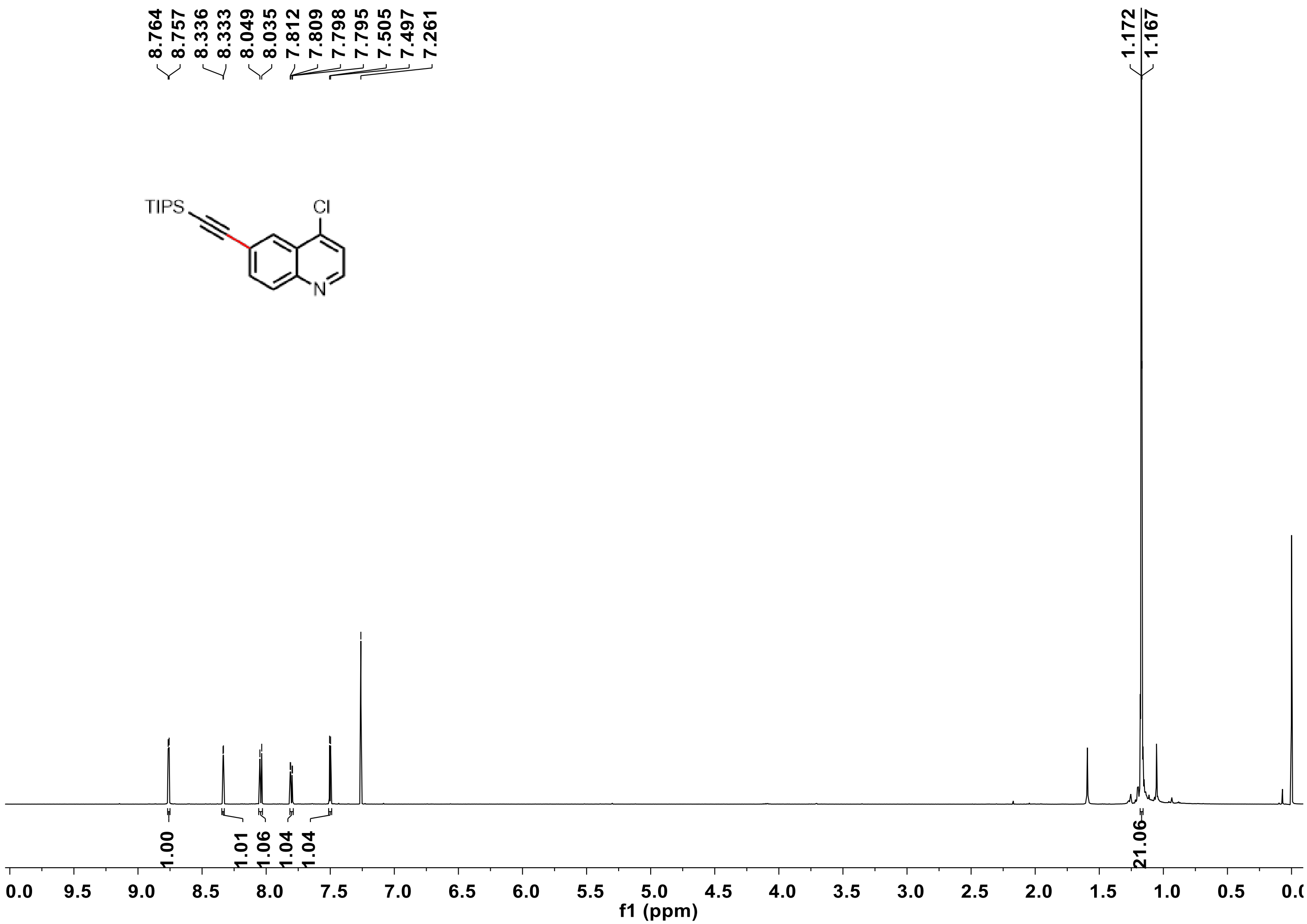
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **4d**



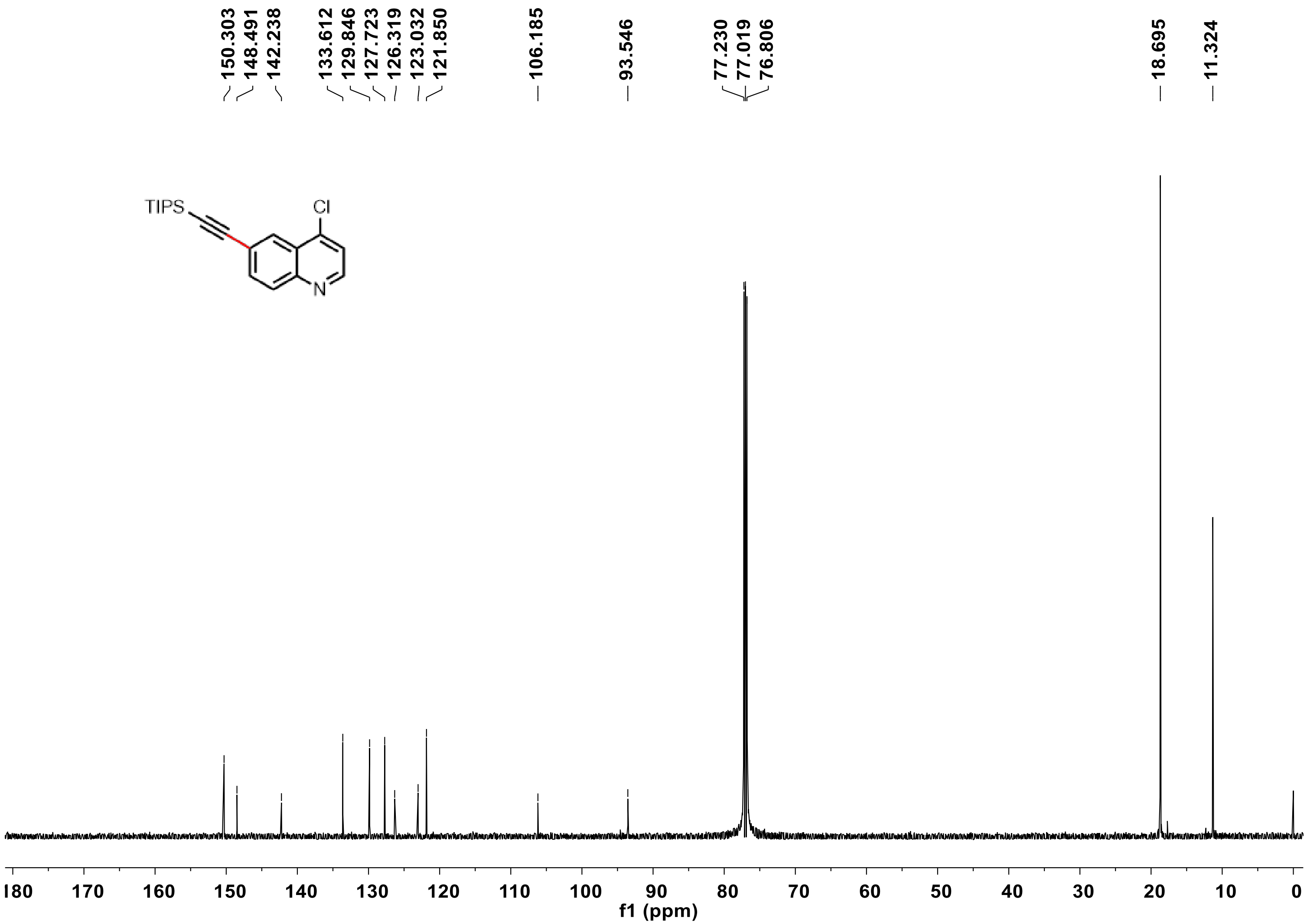
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4d**



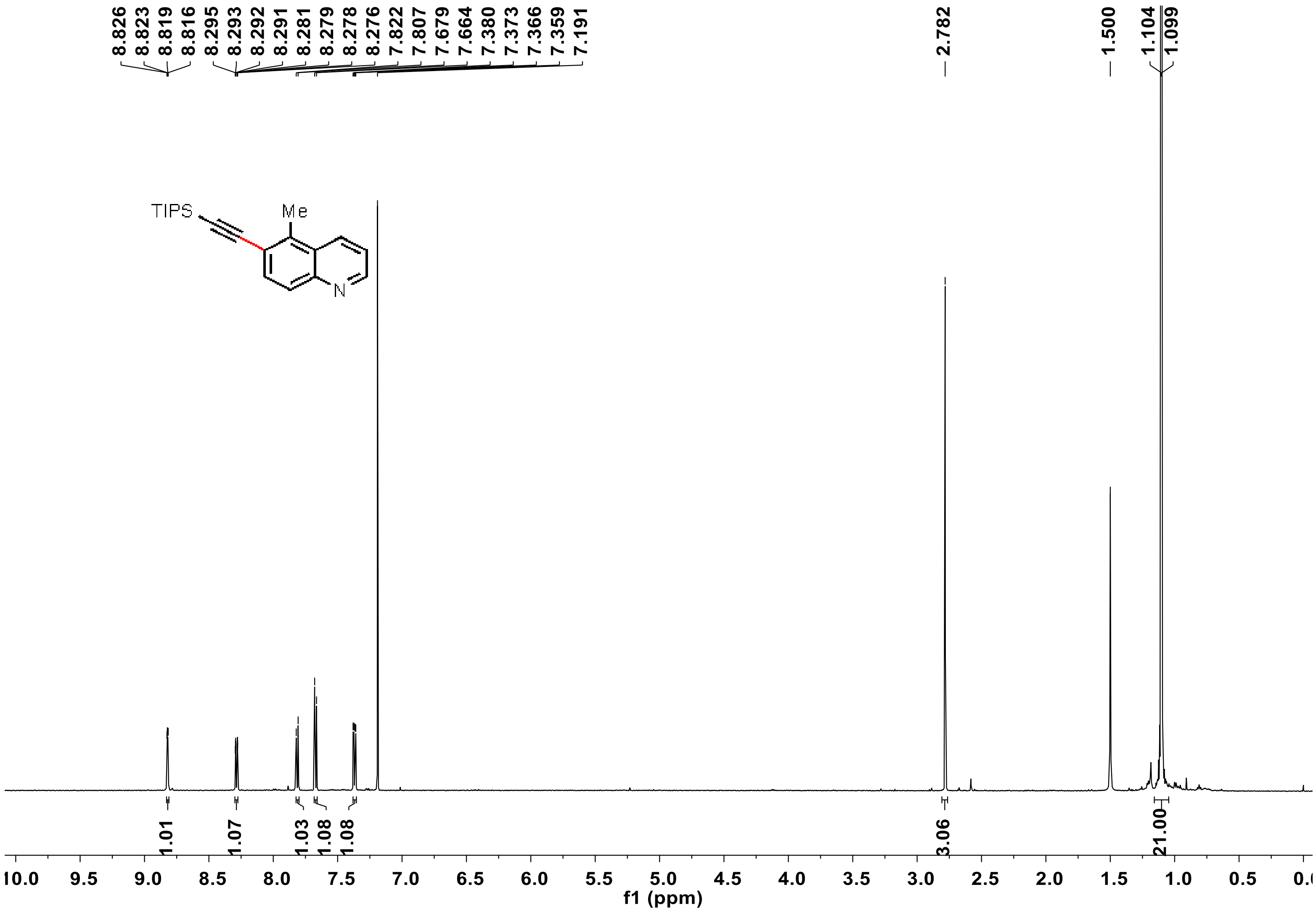
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4e**



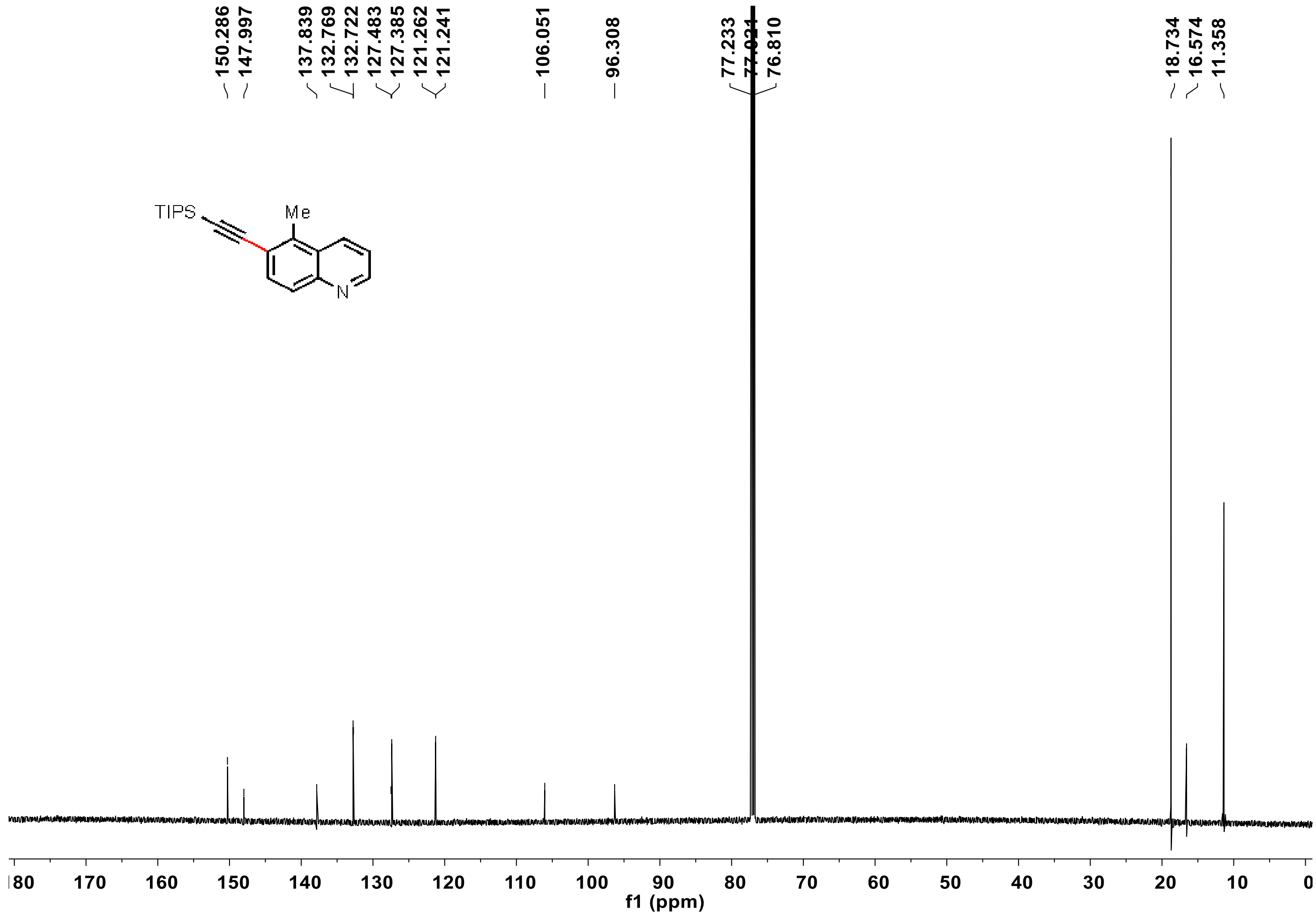
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4e**



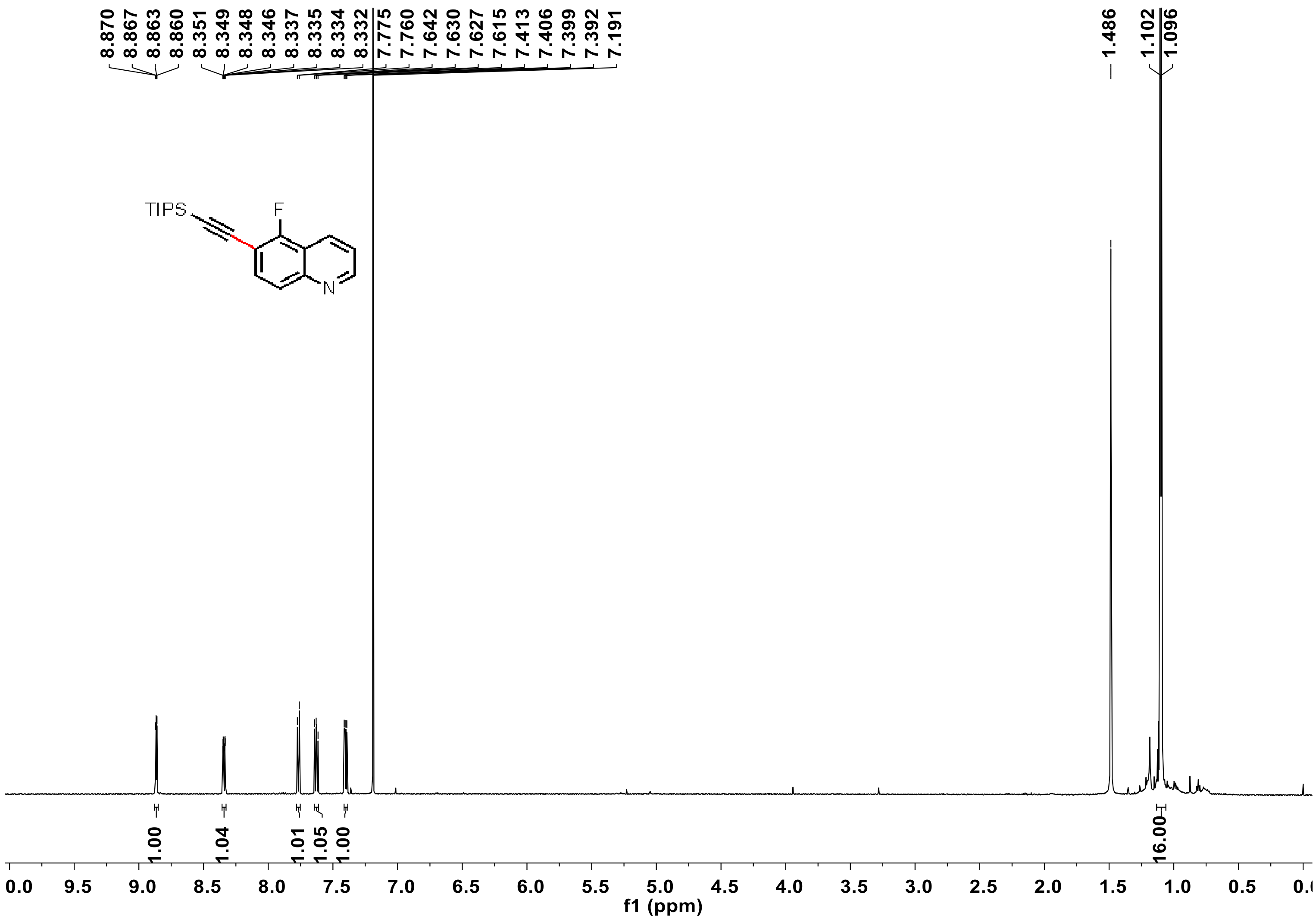
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **4f**



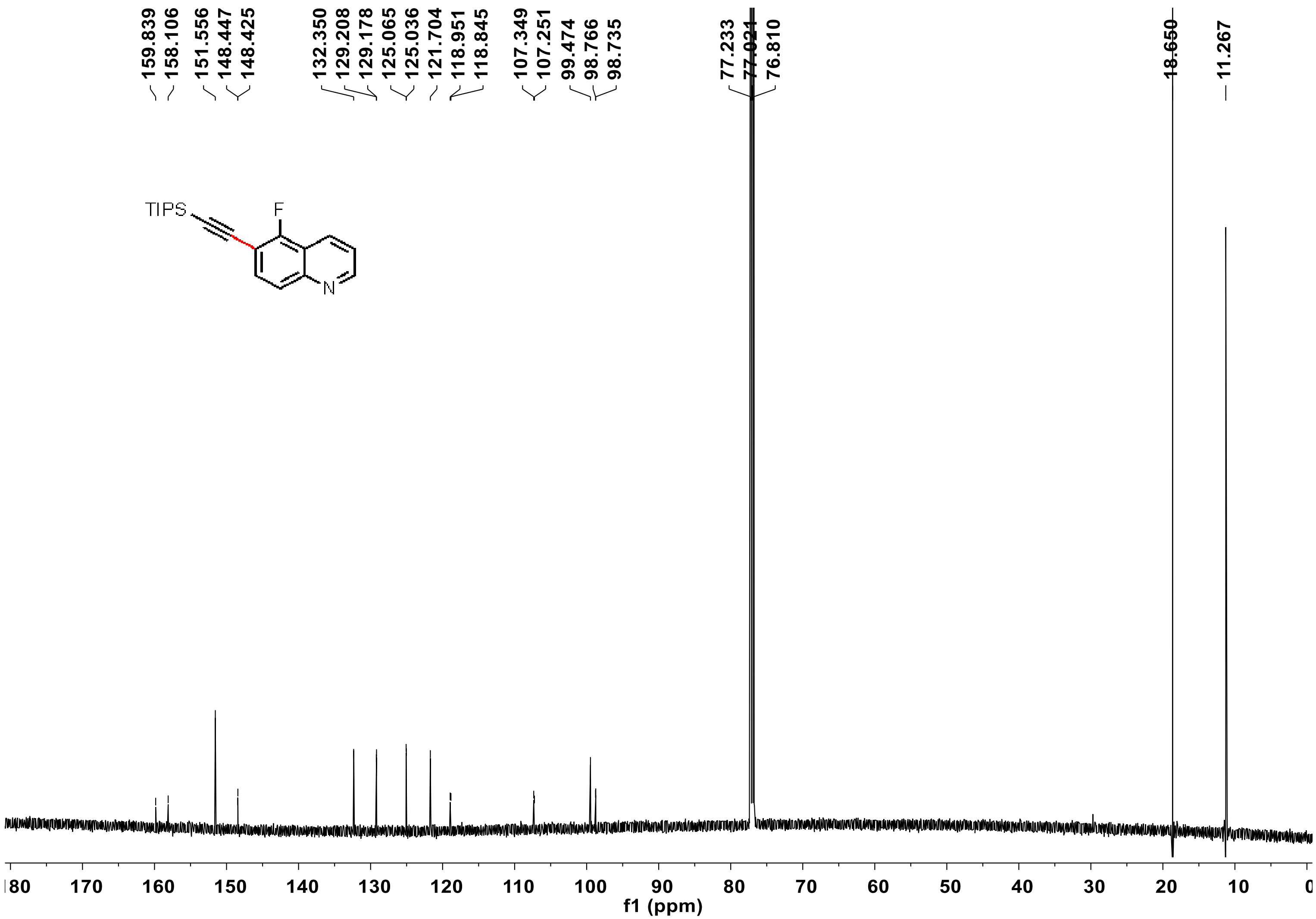
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4f**



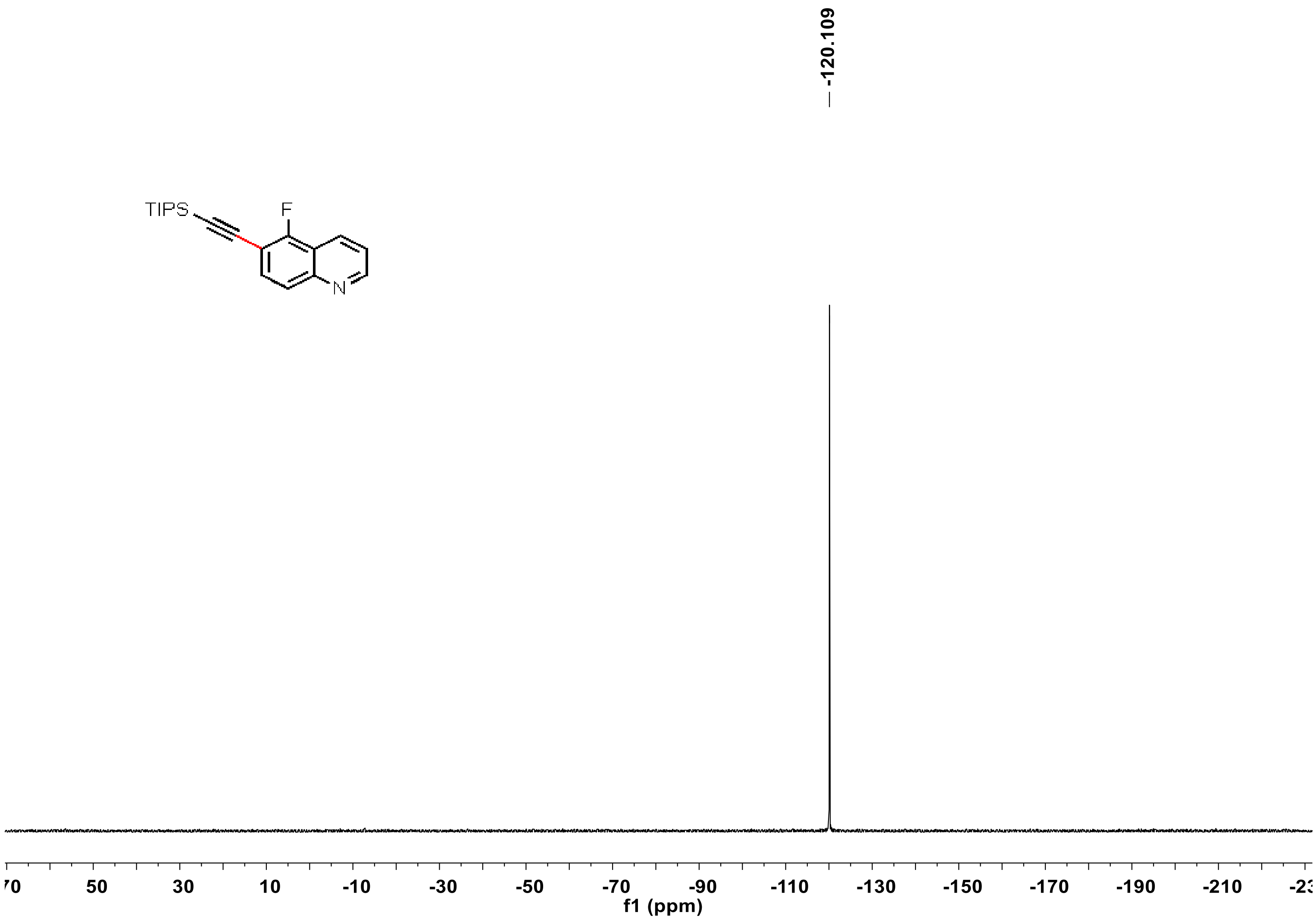
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4g**



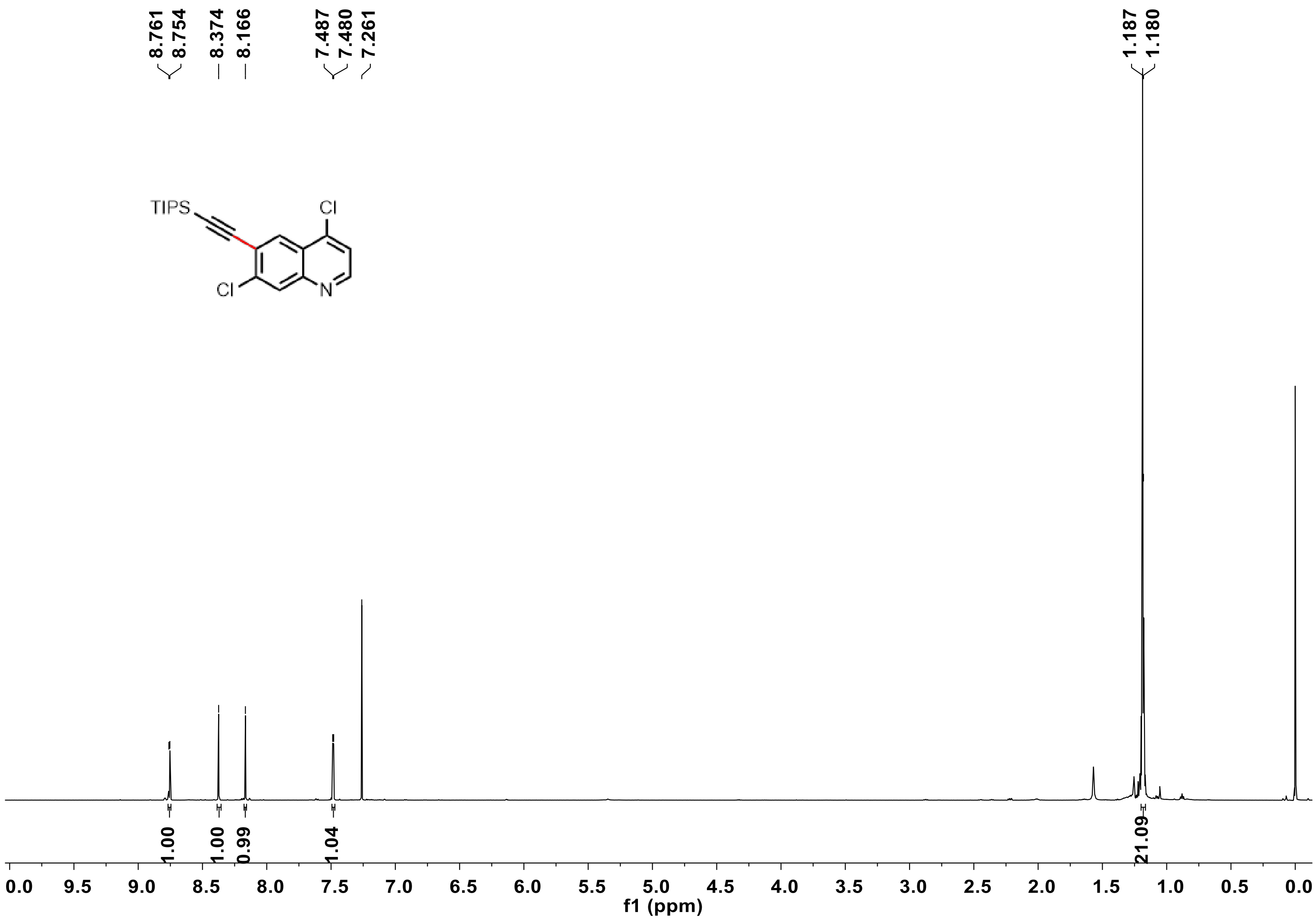
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4g**



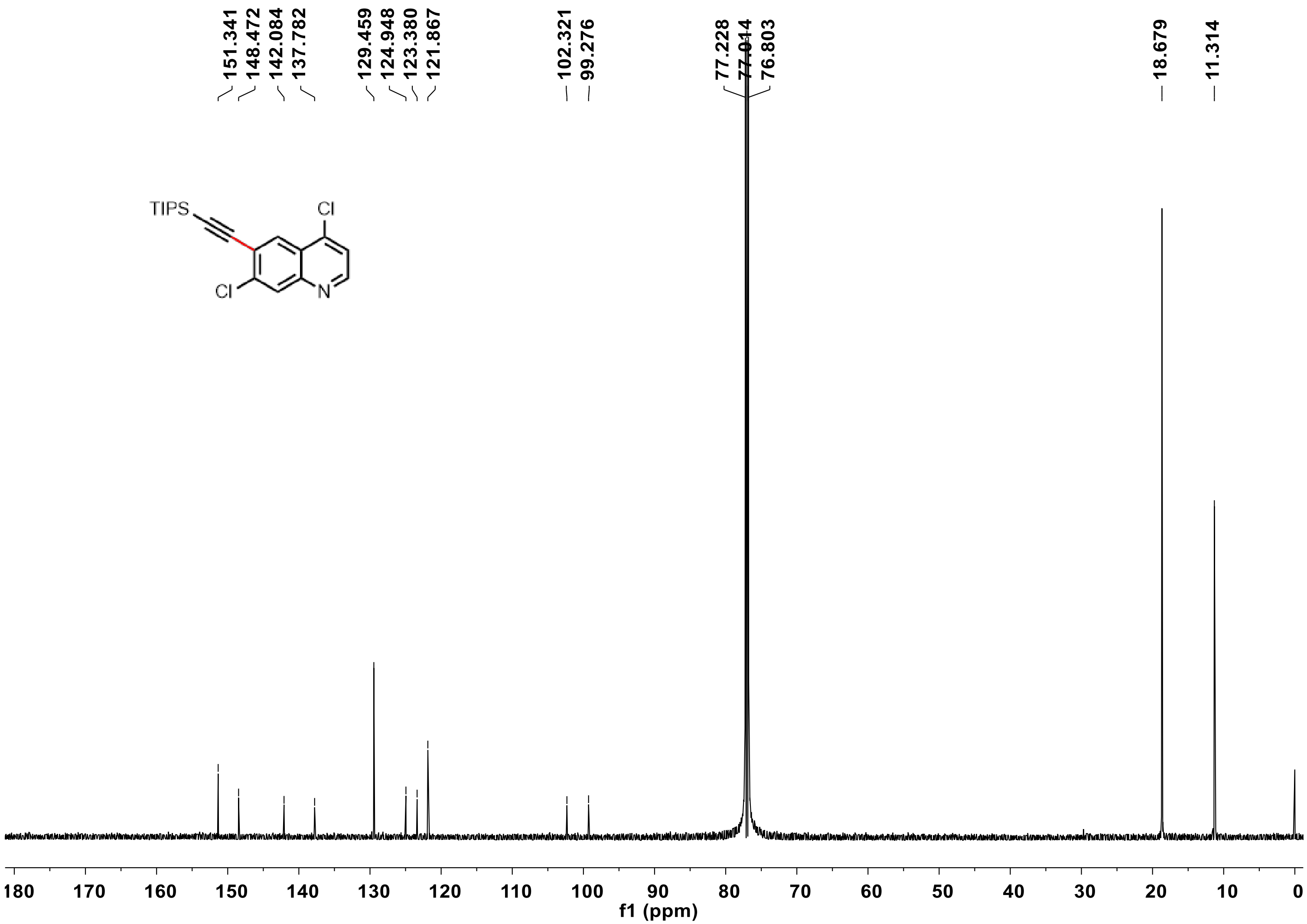
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4g**



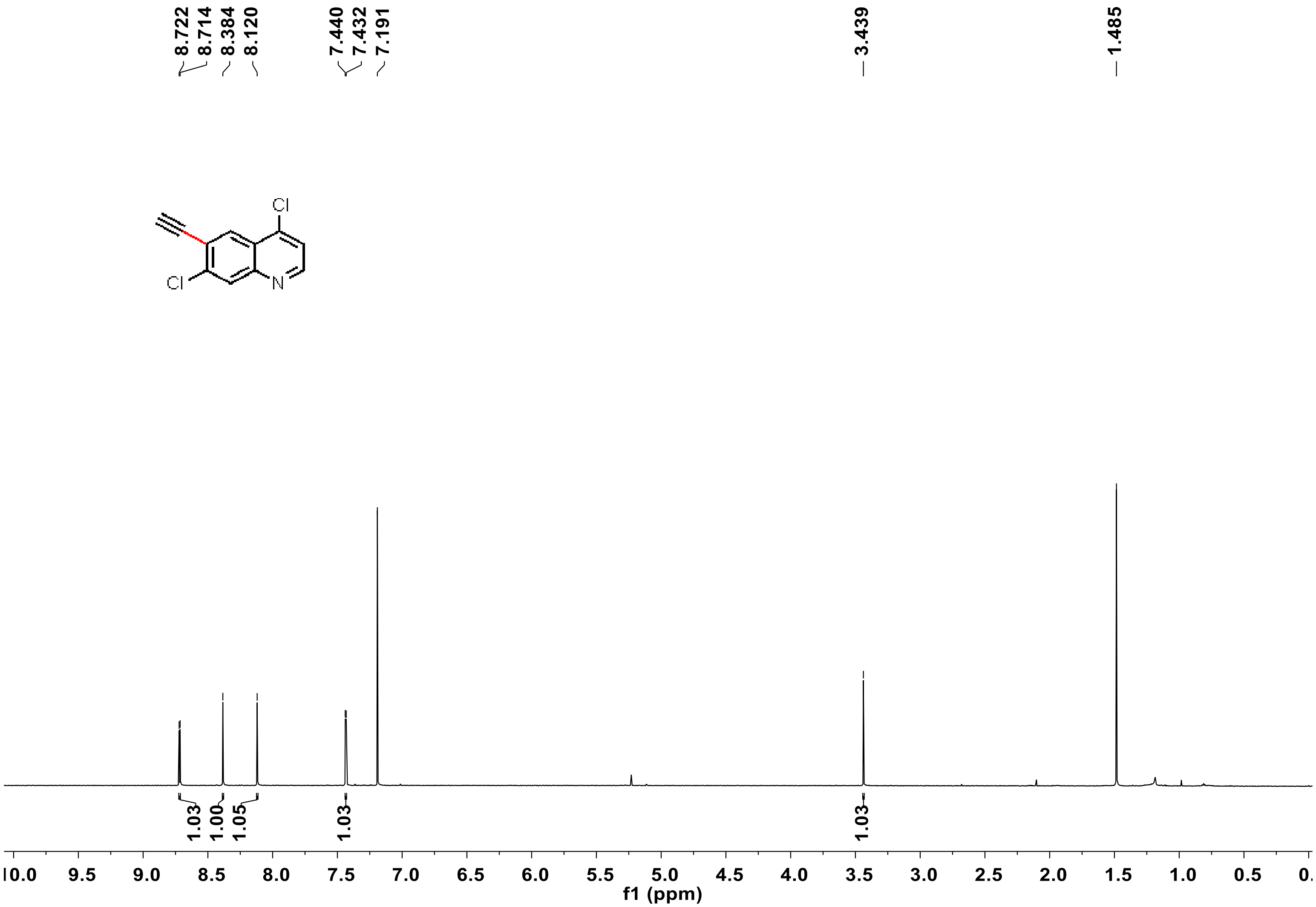
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **4h**



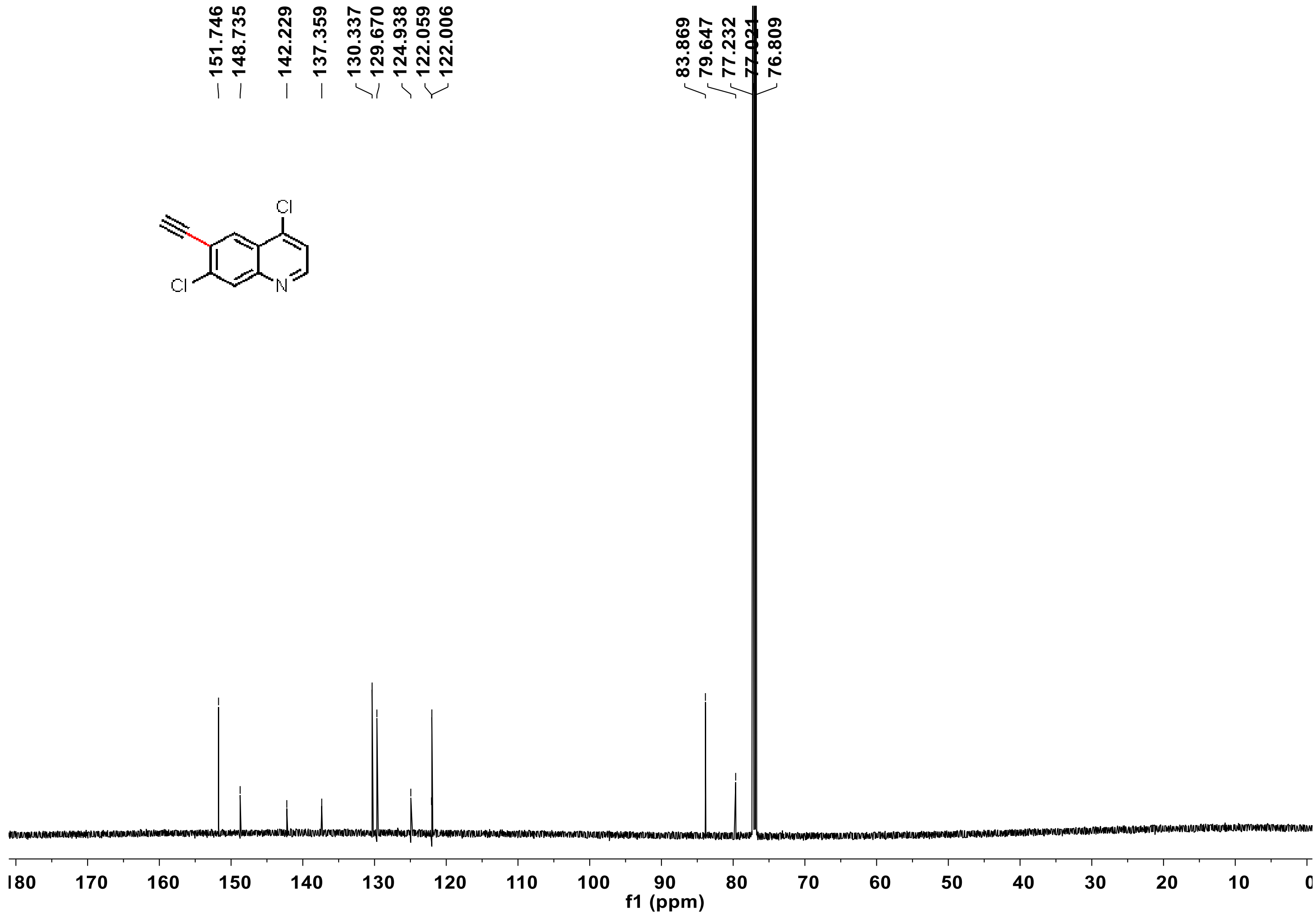
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4h**



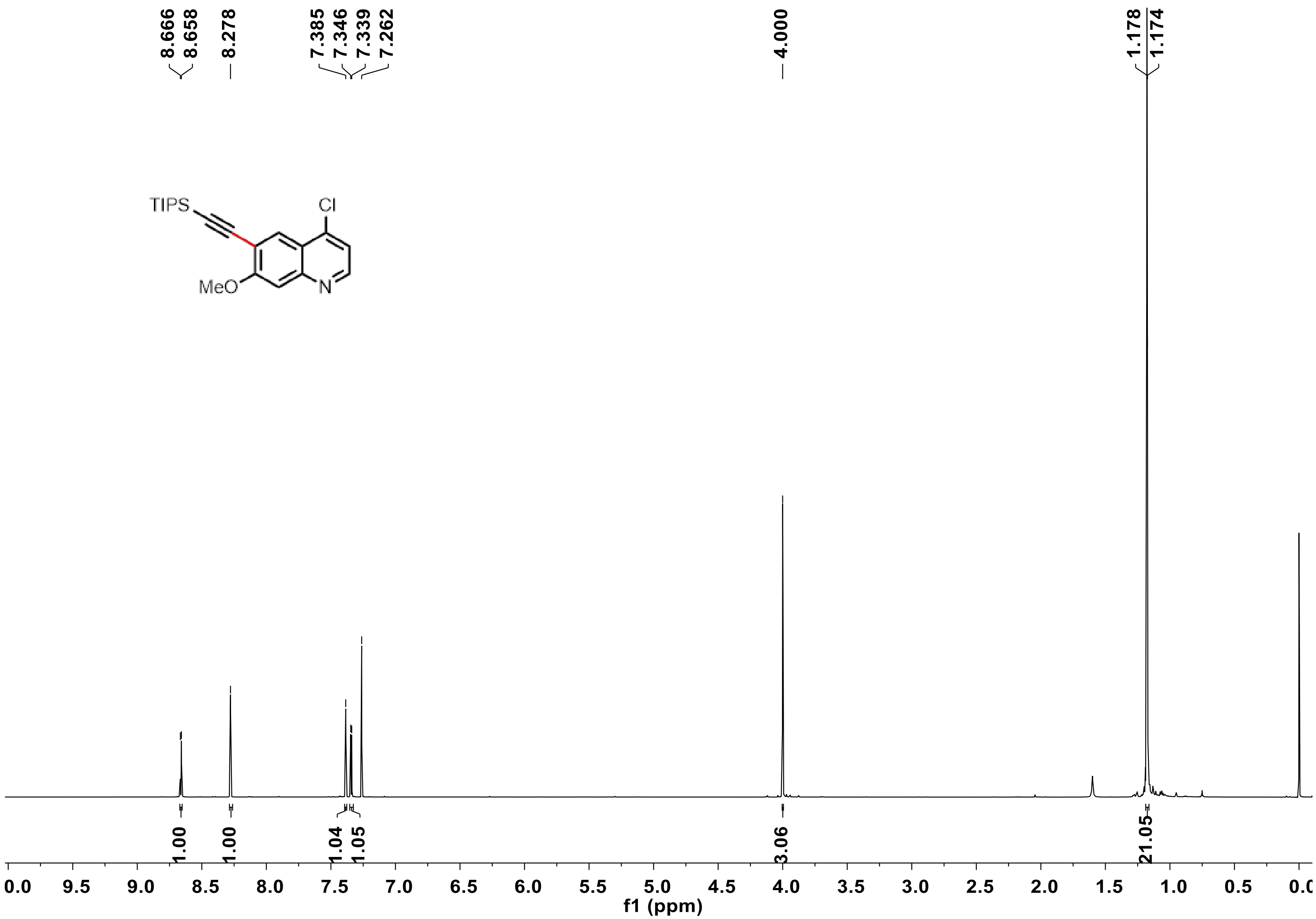
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4h'**



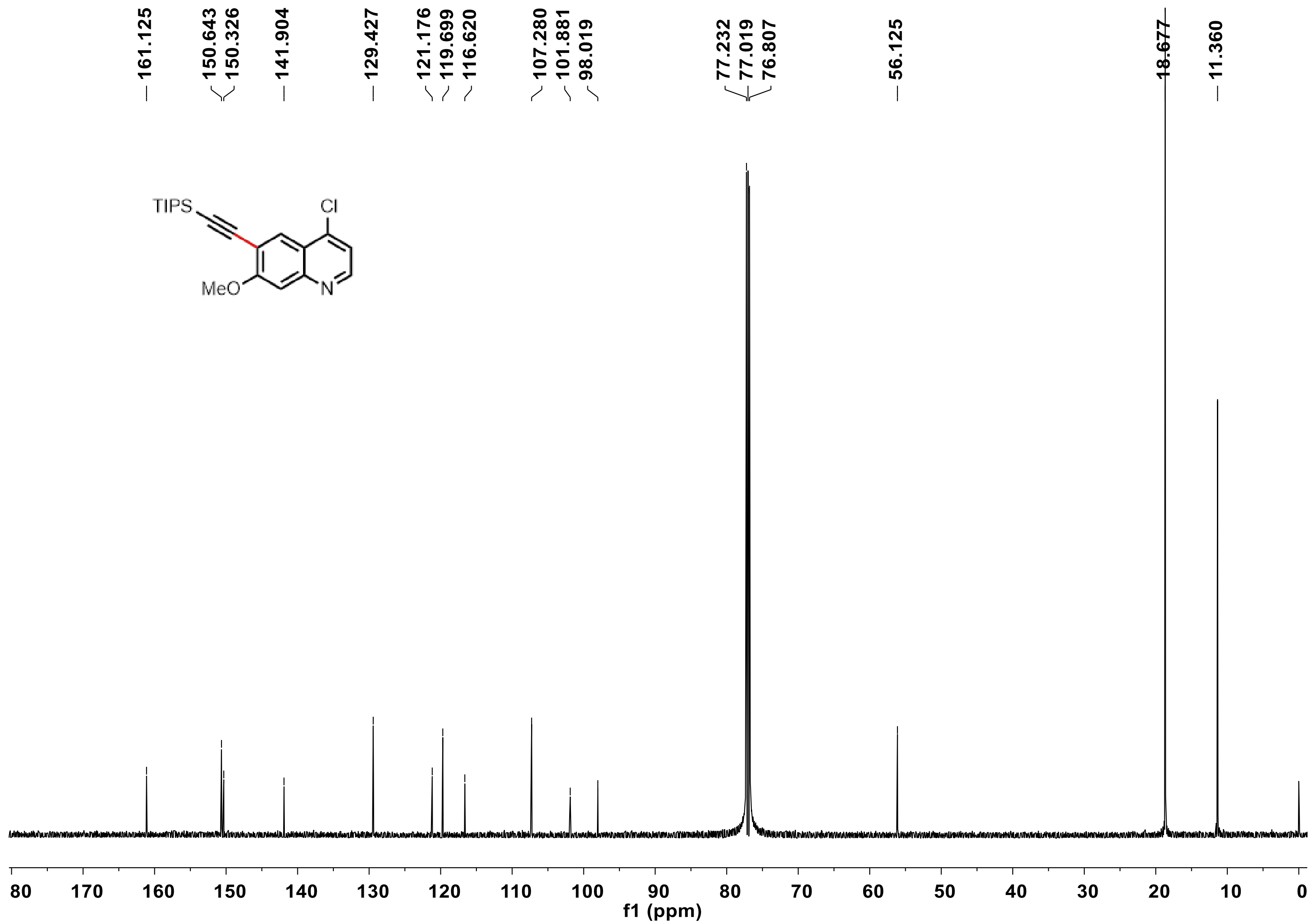
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4h’**



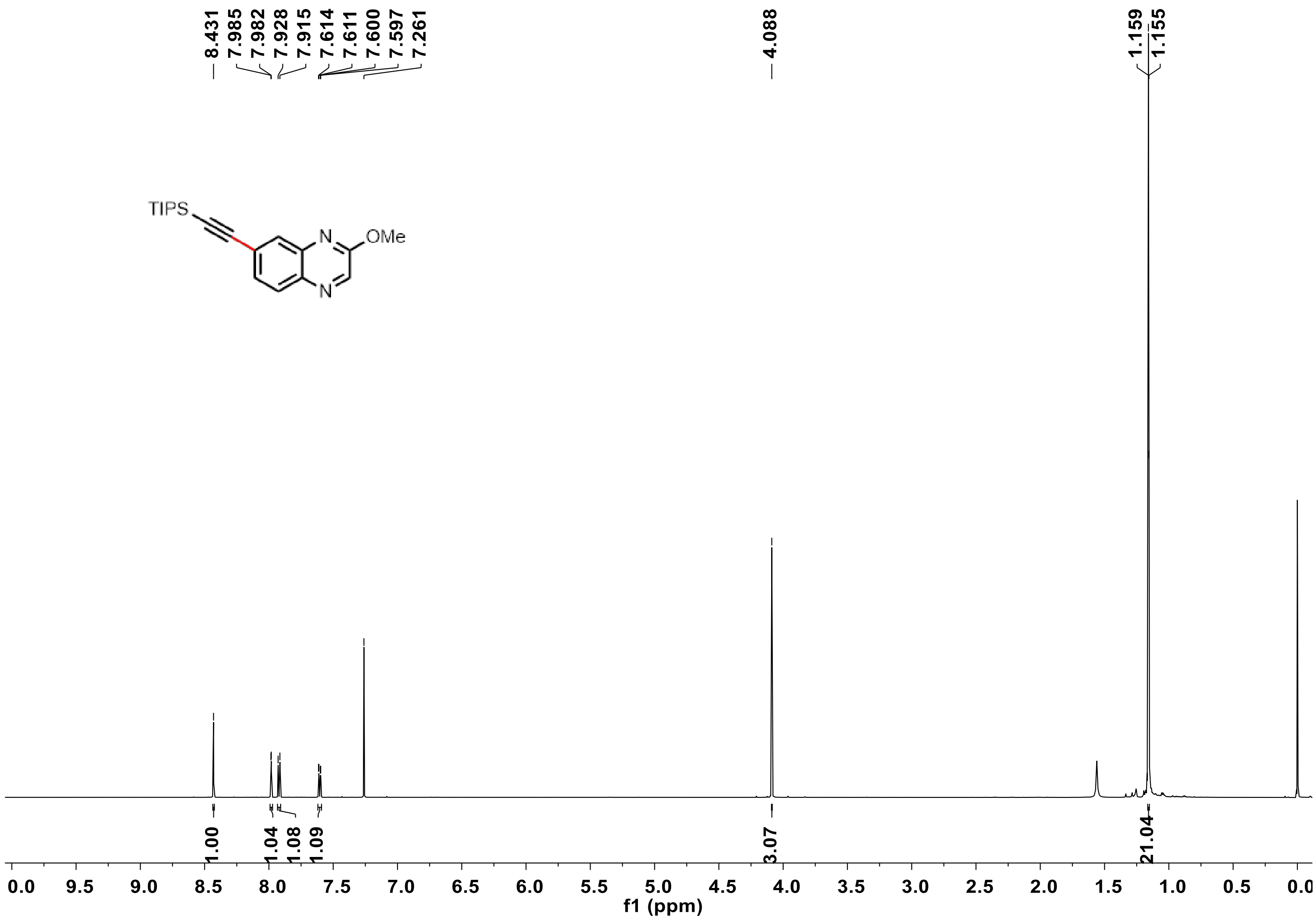
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **4i**



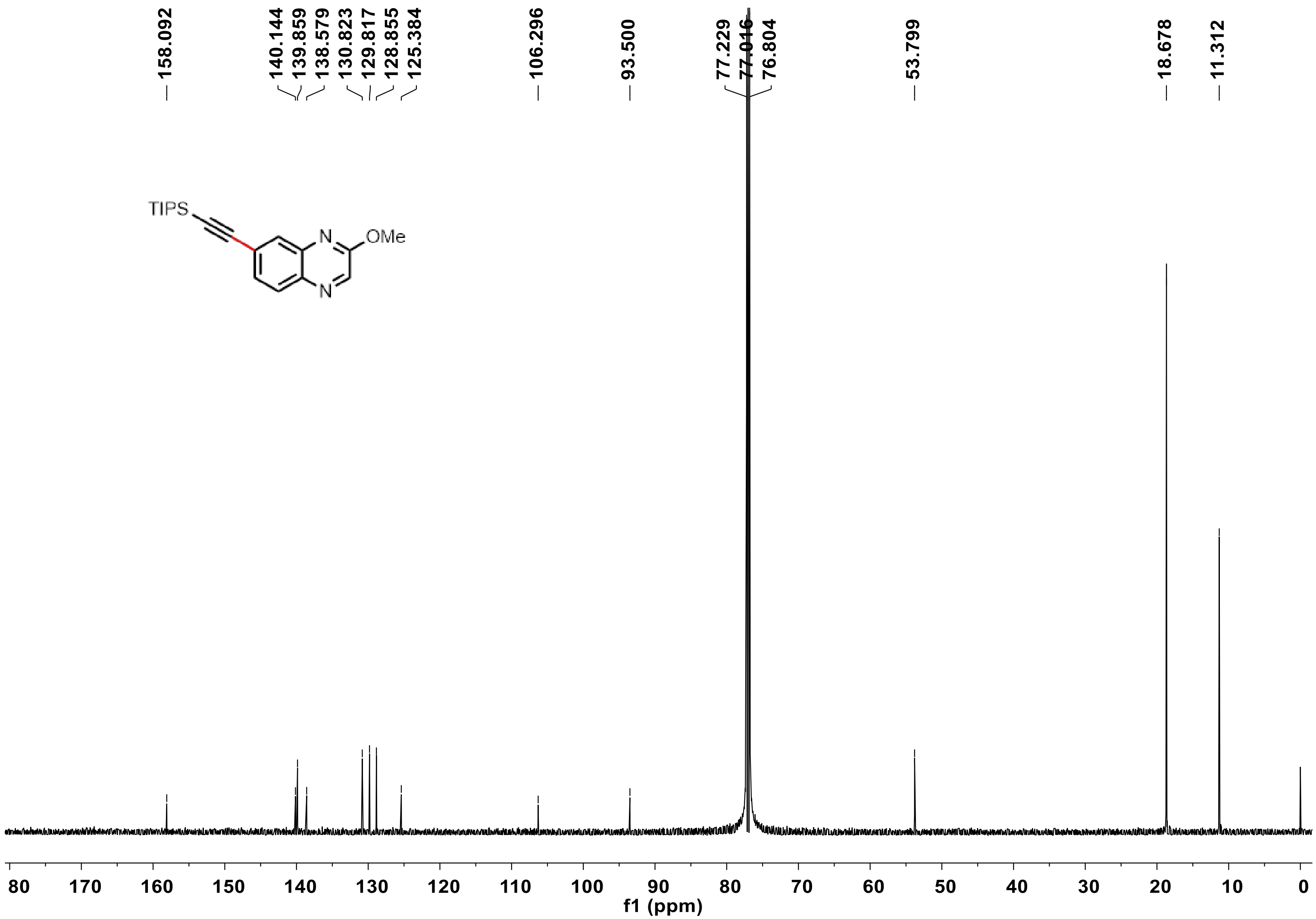
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4i**



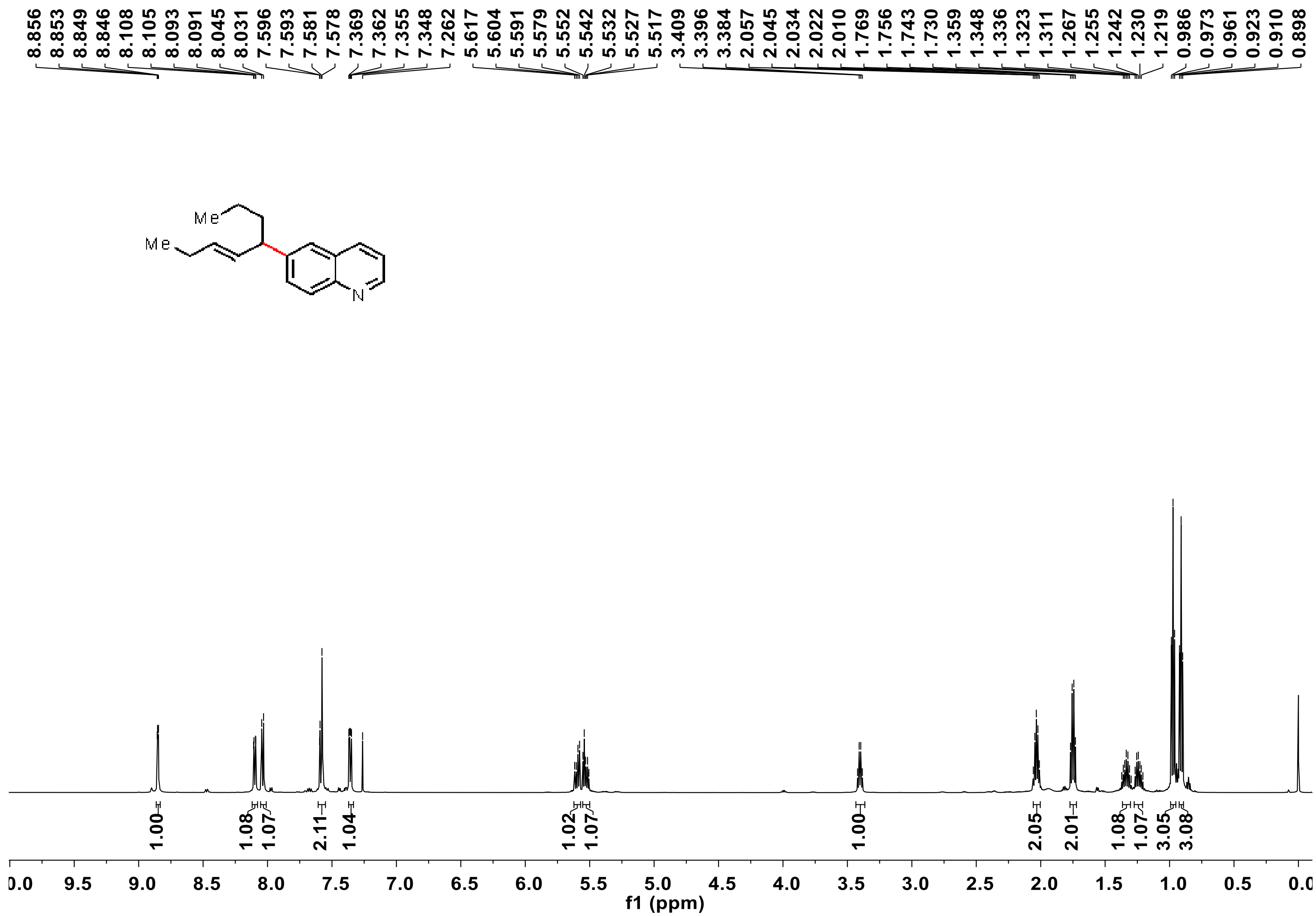
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **4j**



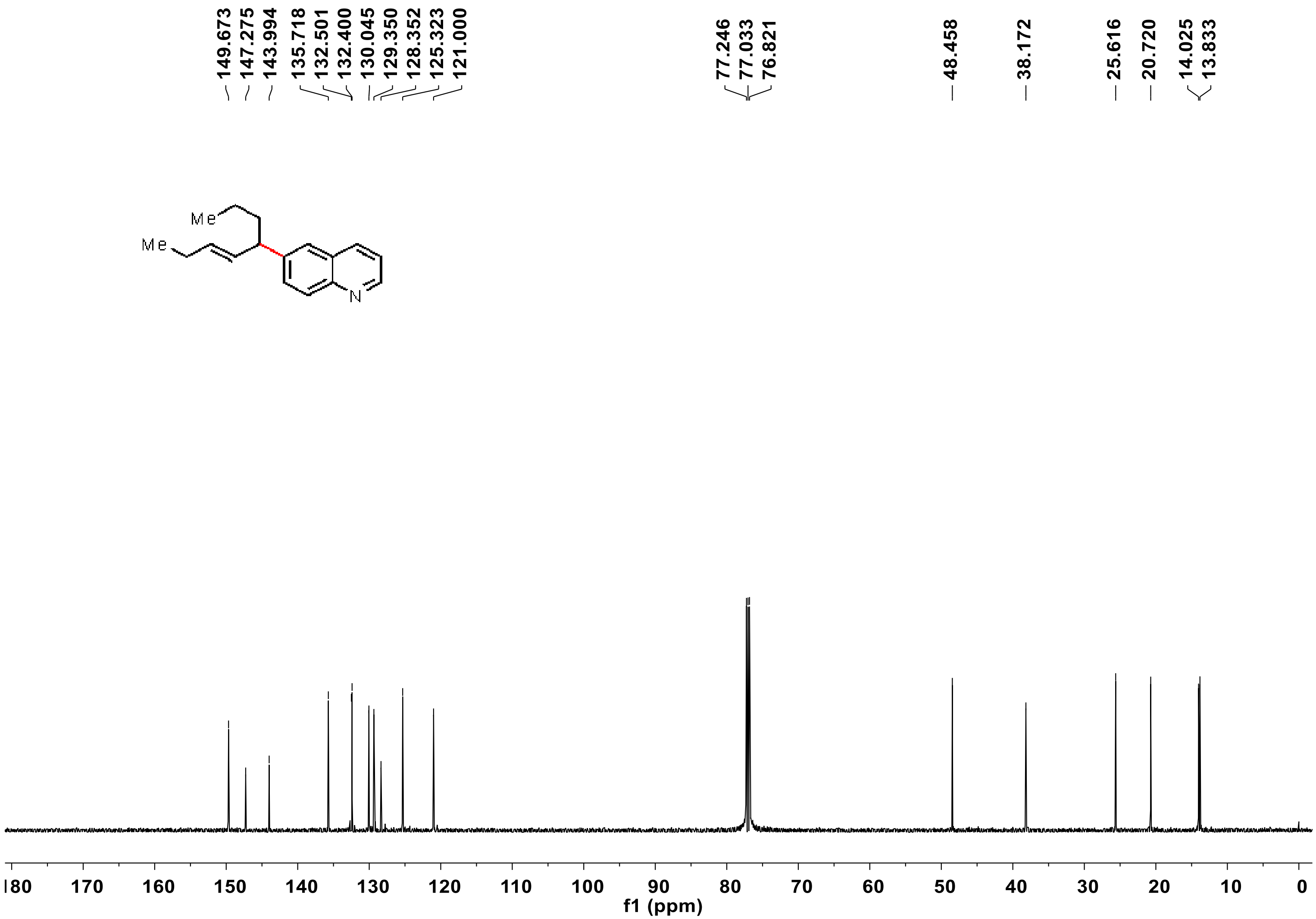
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **4j**



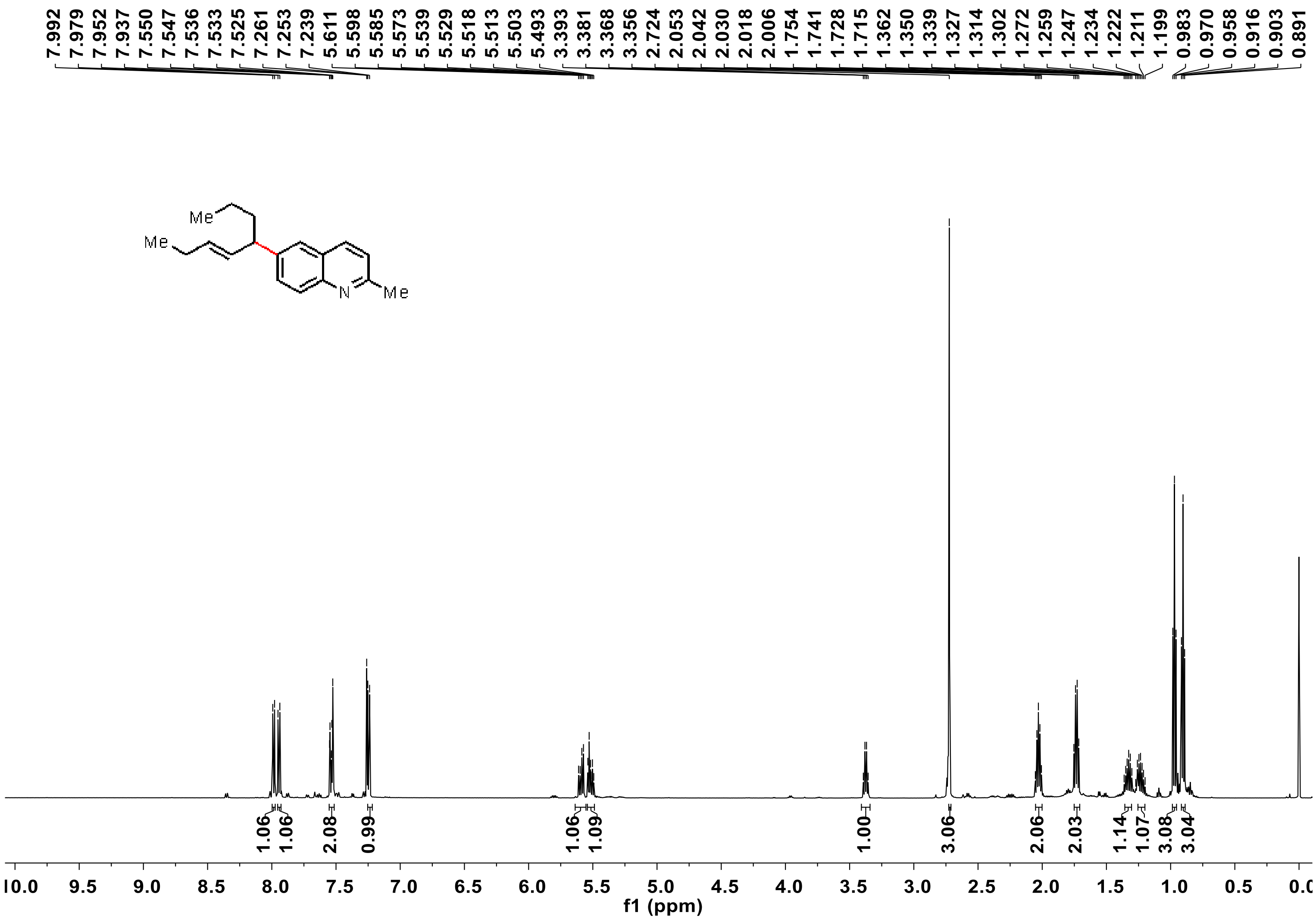
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5a**



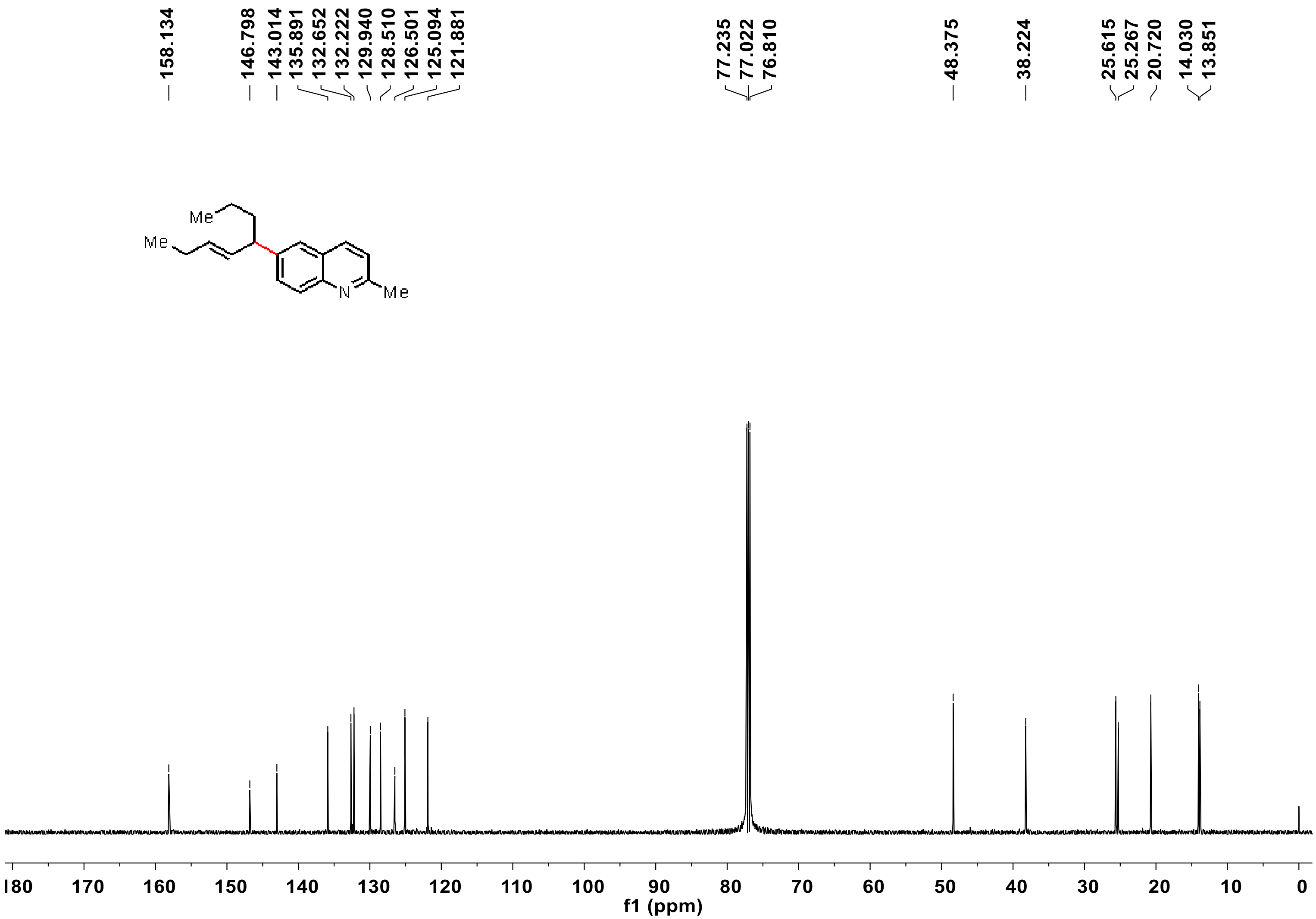
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5a**



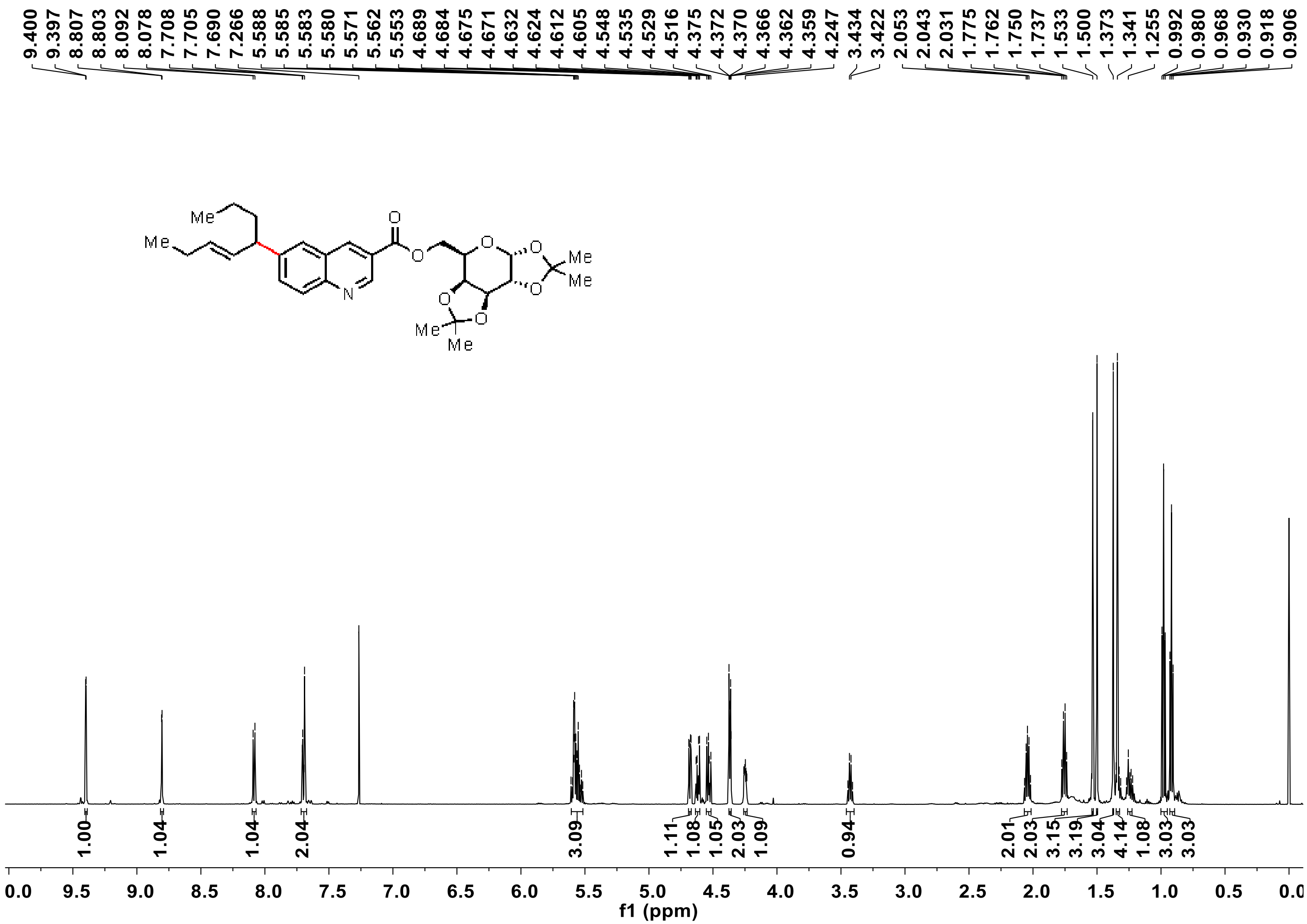
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **5b**



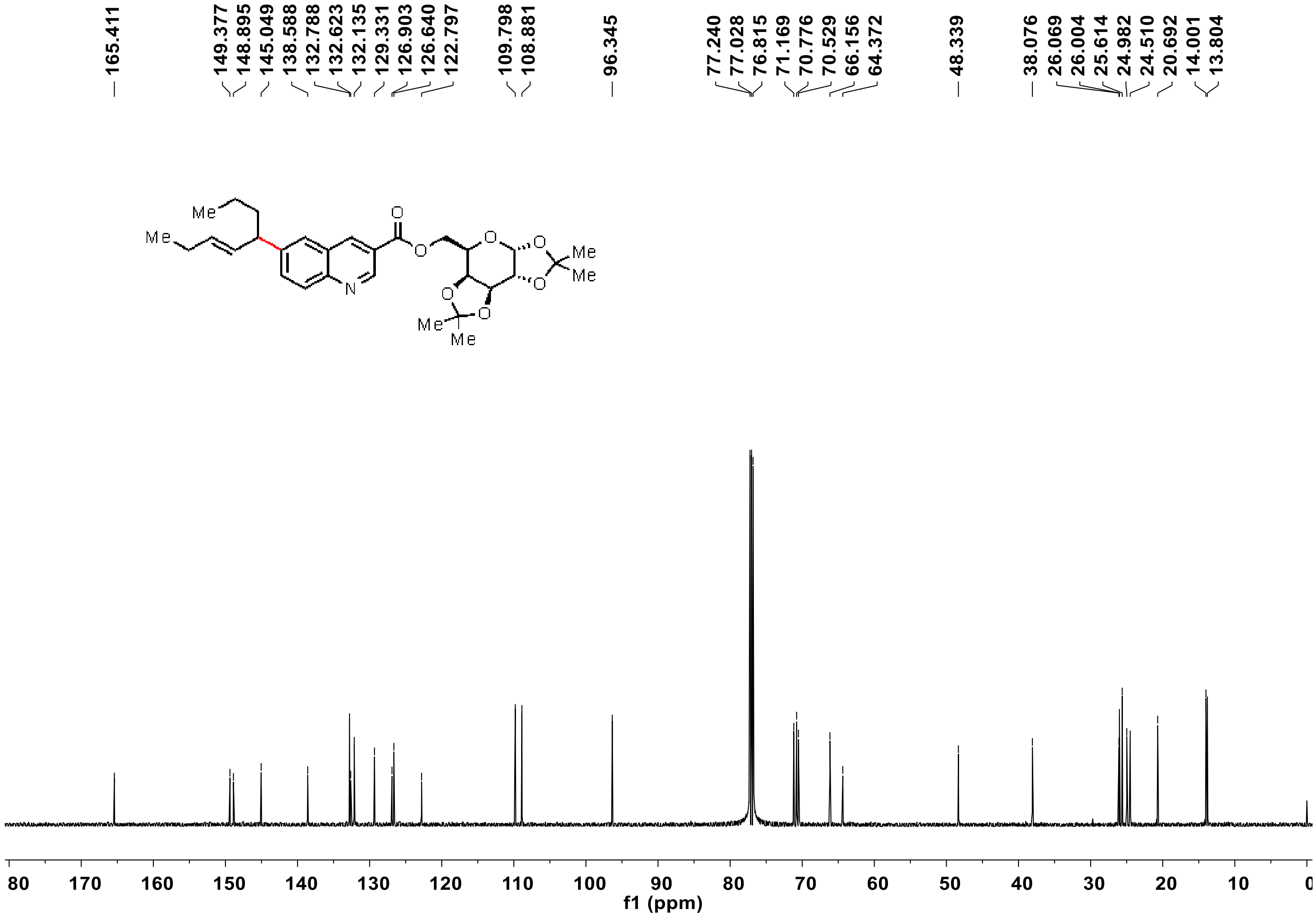
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5b**



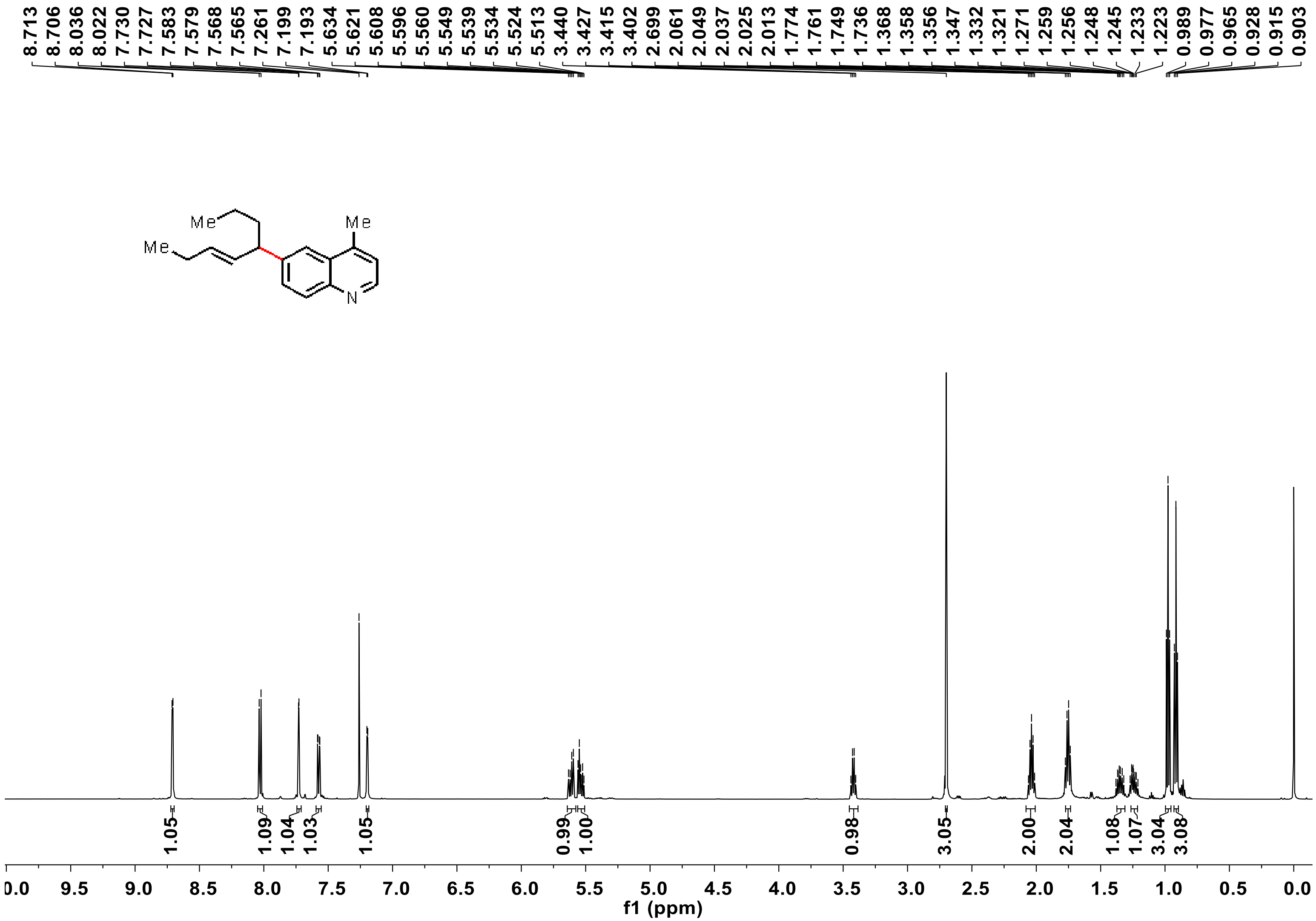
^1H NMR (600 MHz, $CDCl_3$) spectrum of **5c**



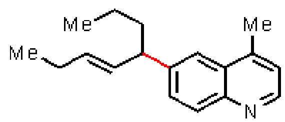
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5c**

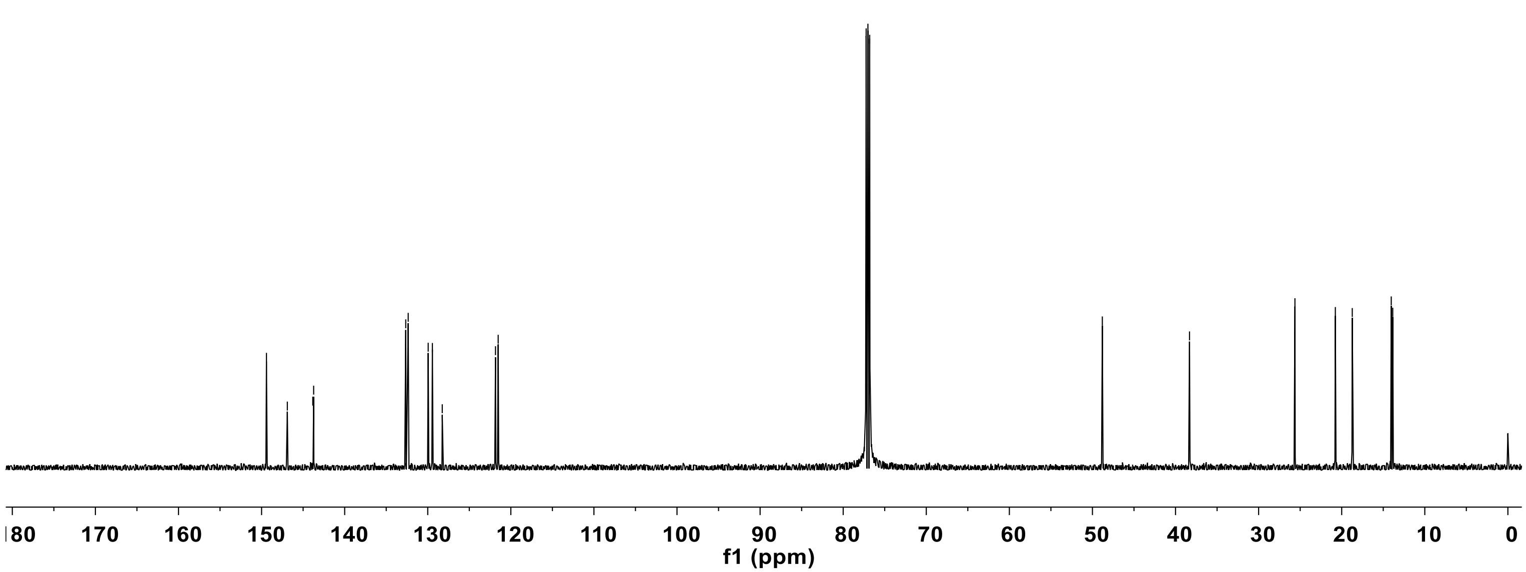


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5d**

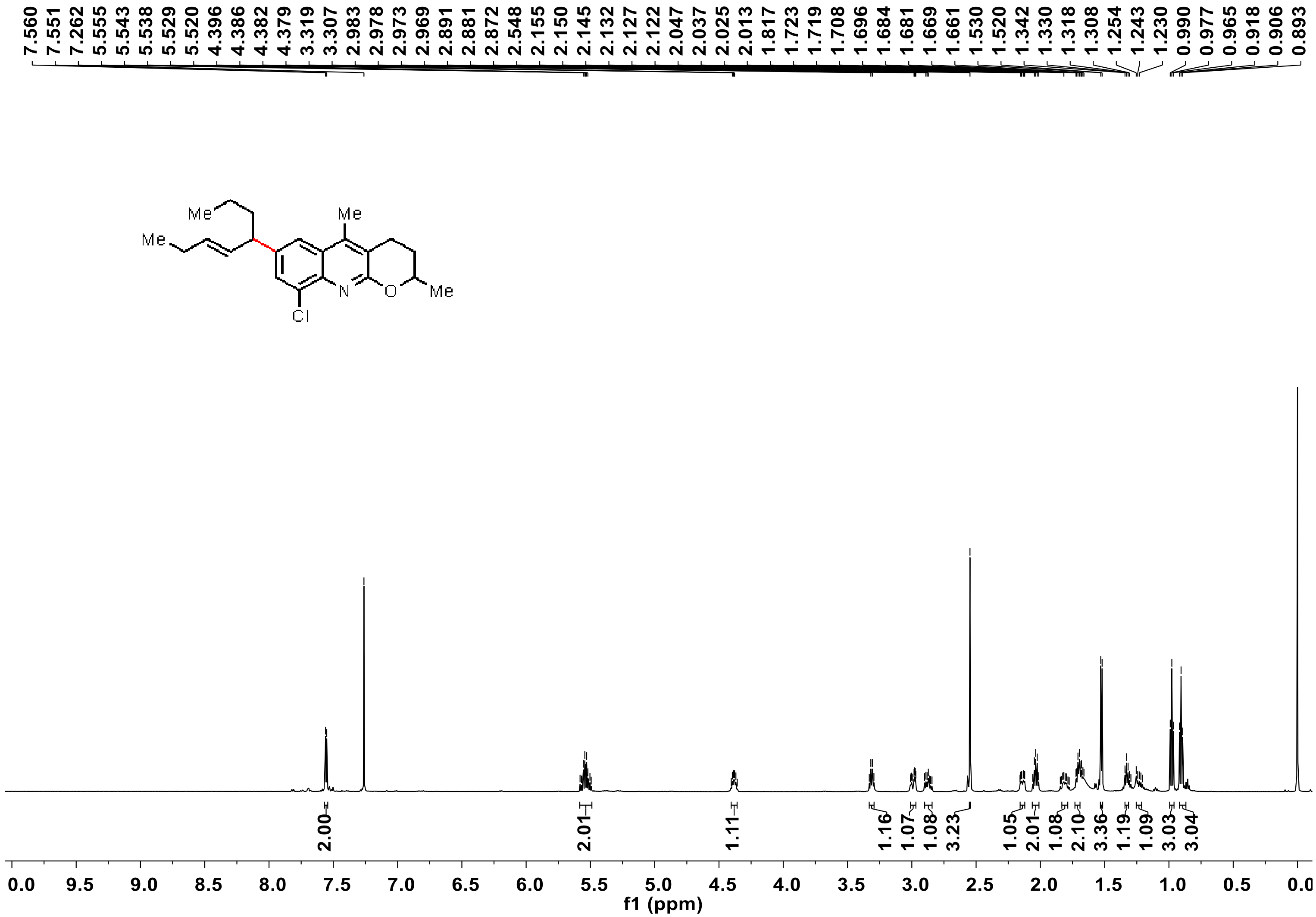


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5d**

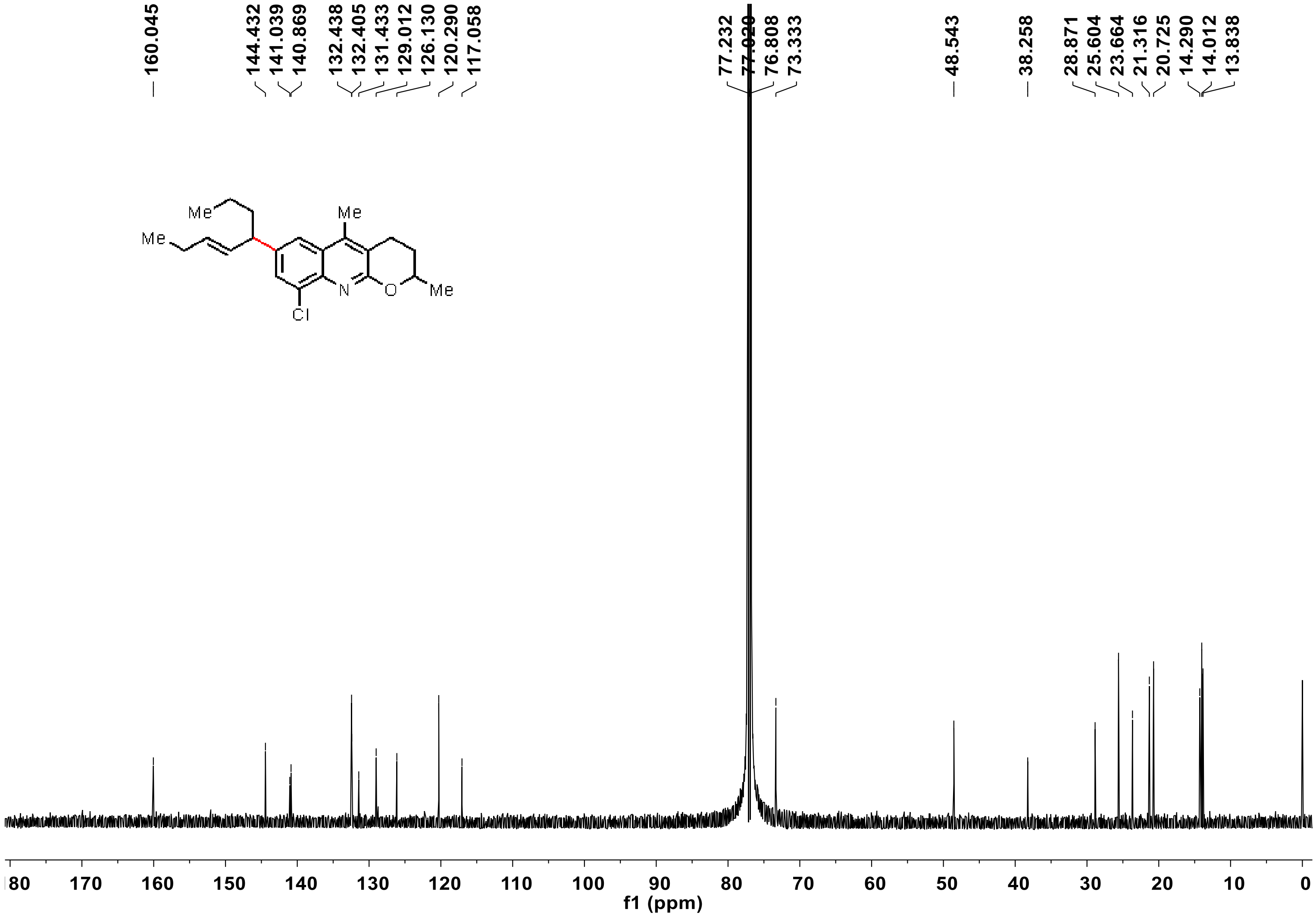




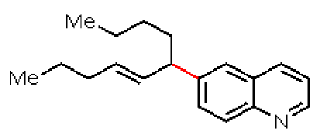
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **5e**

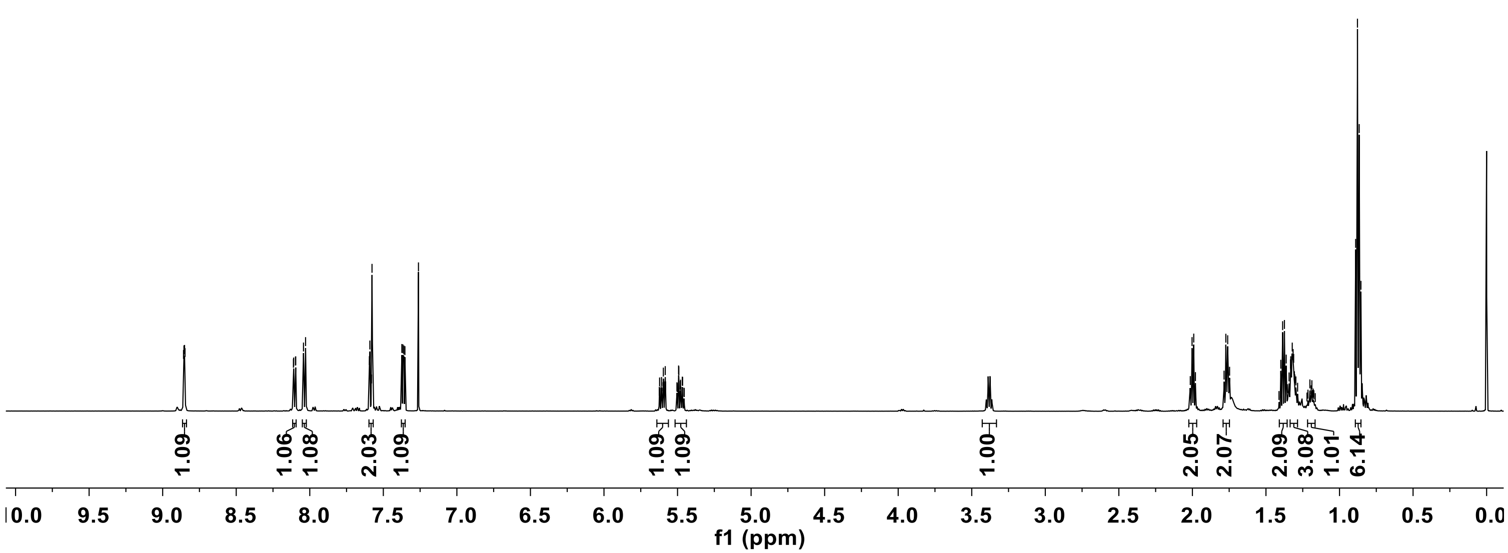


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5e**

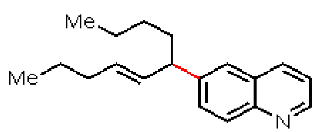


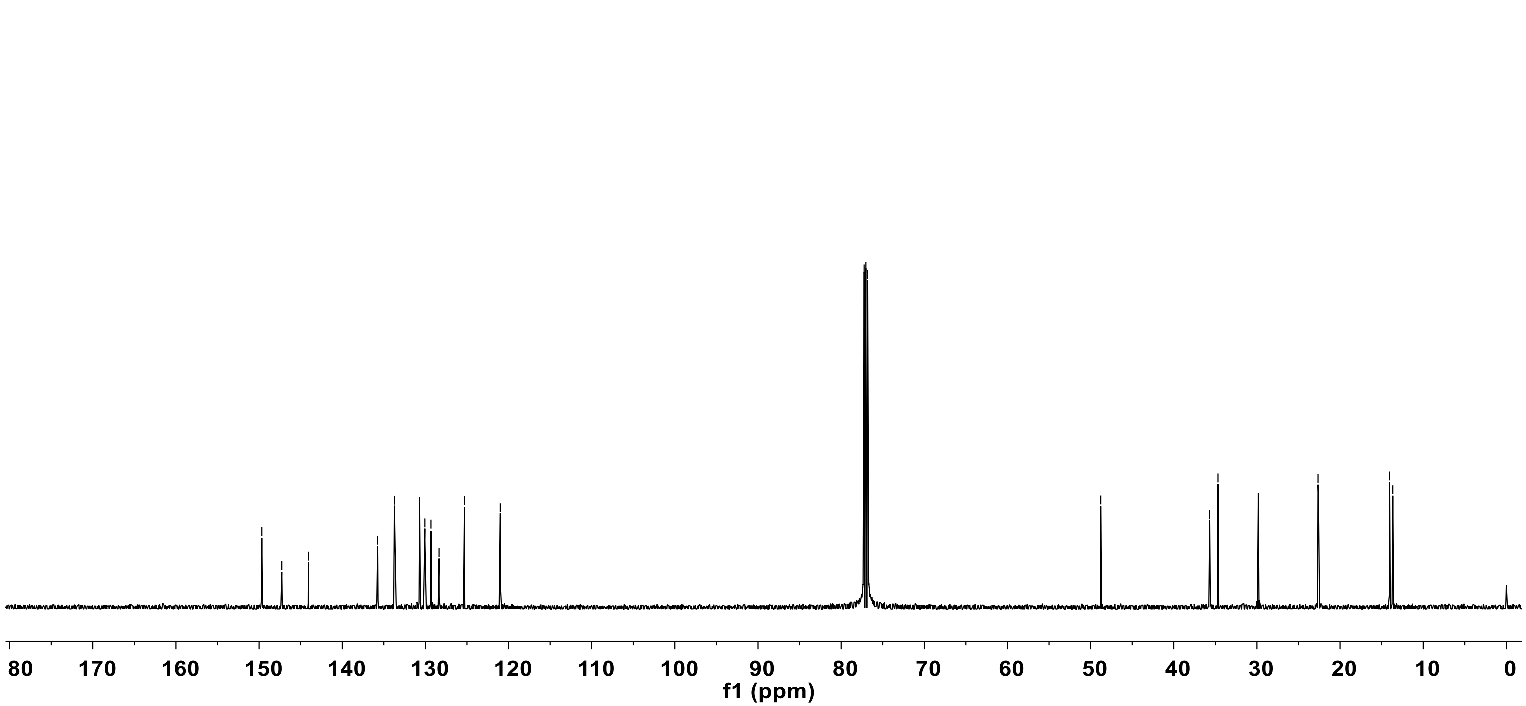
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5f**



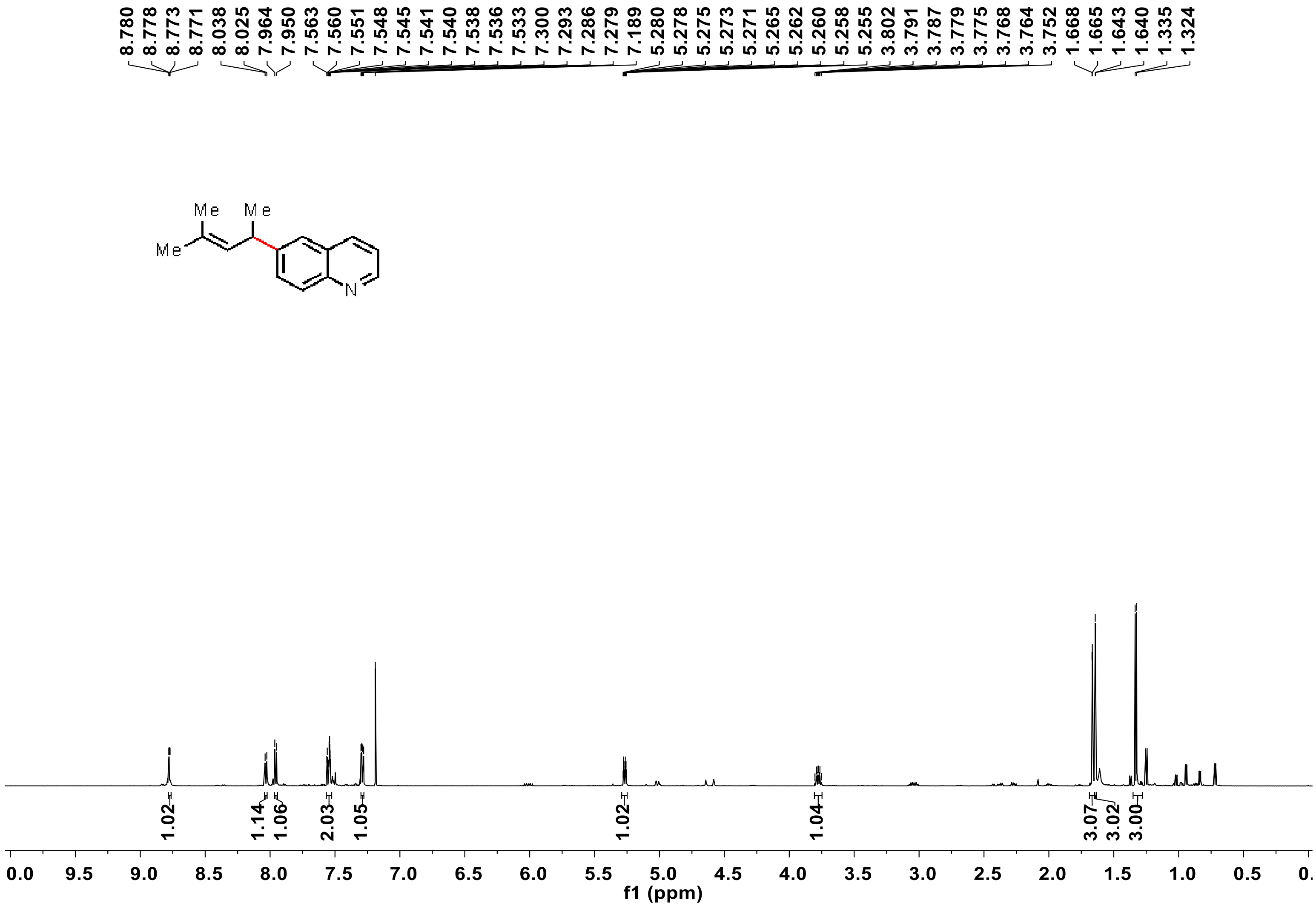


^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5f**

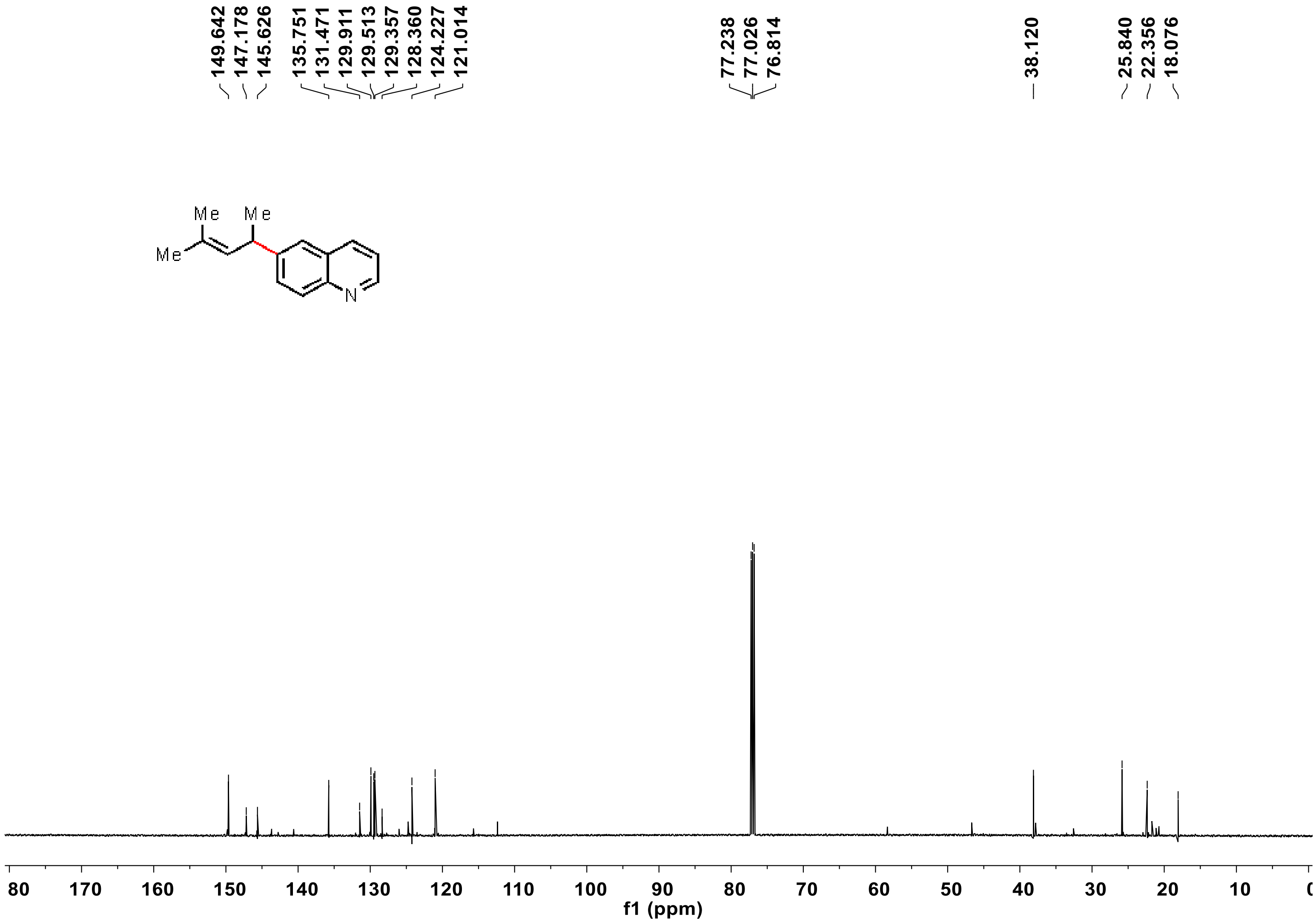




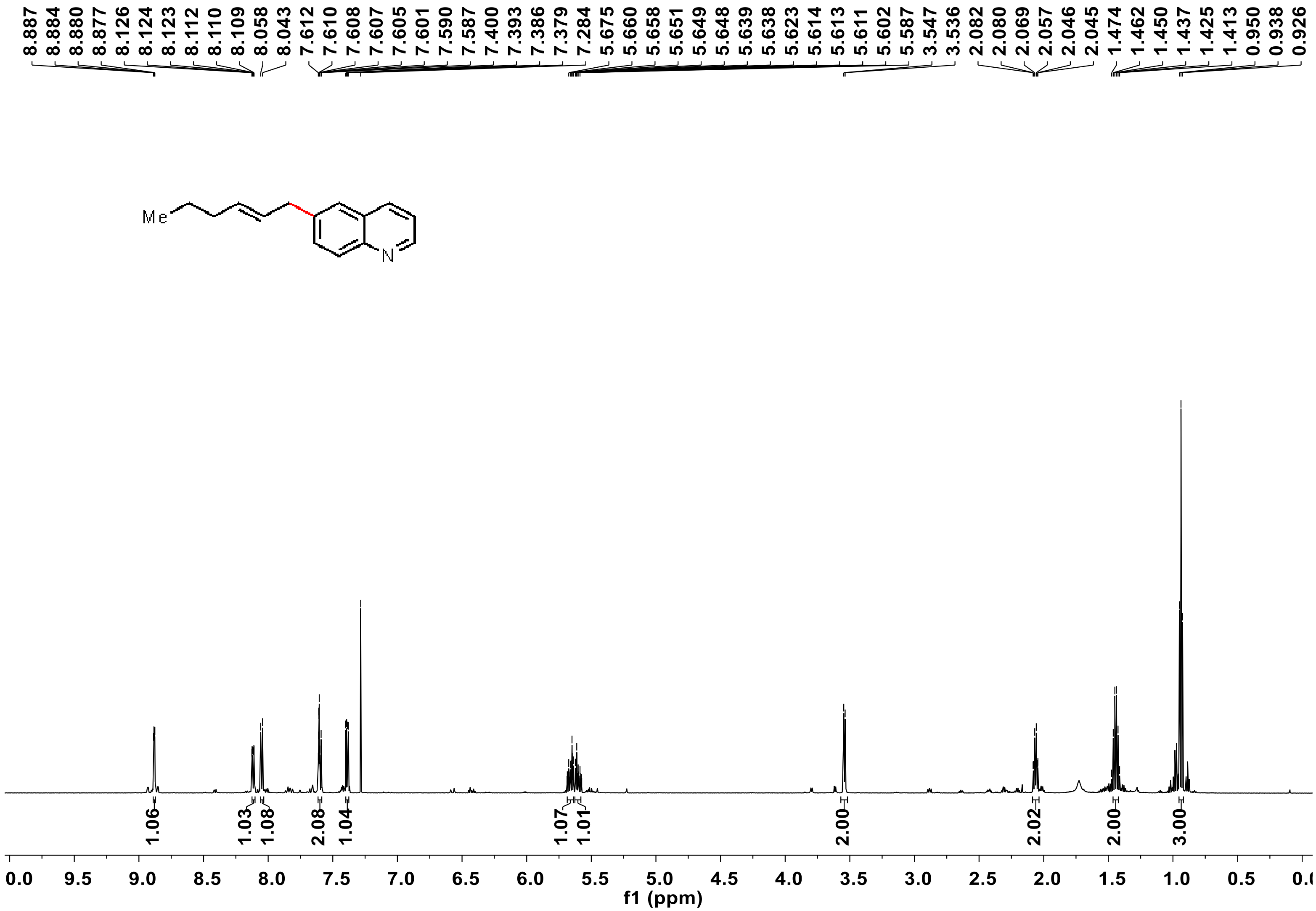
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5g**



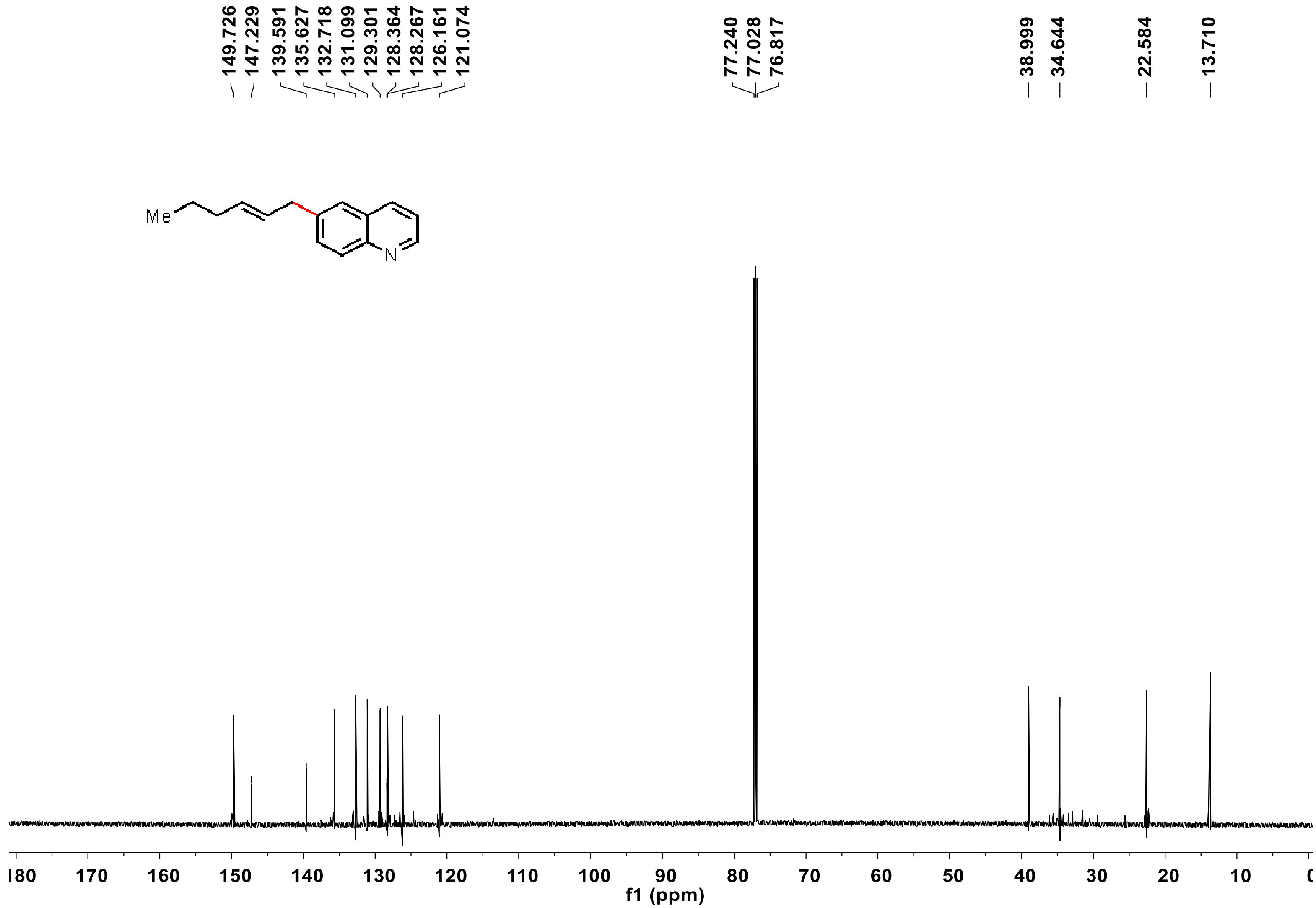
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5g**



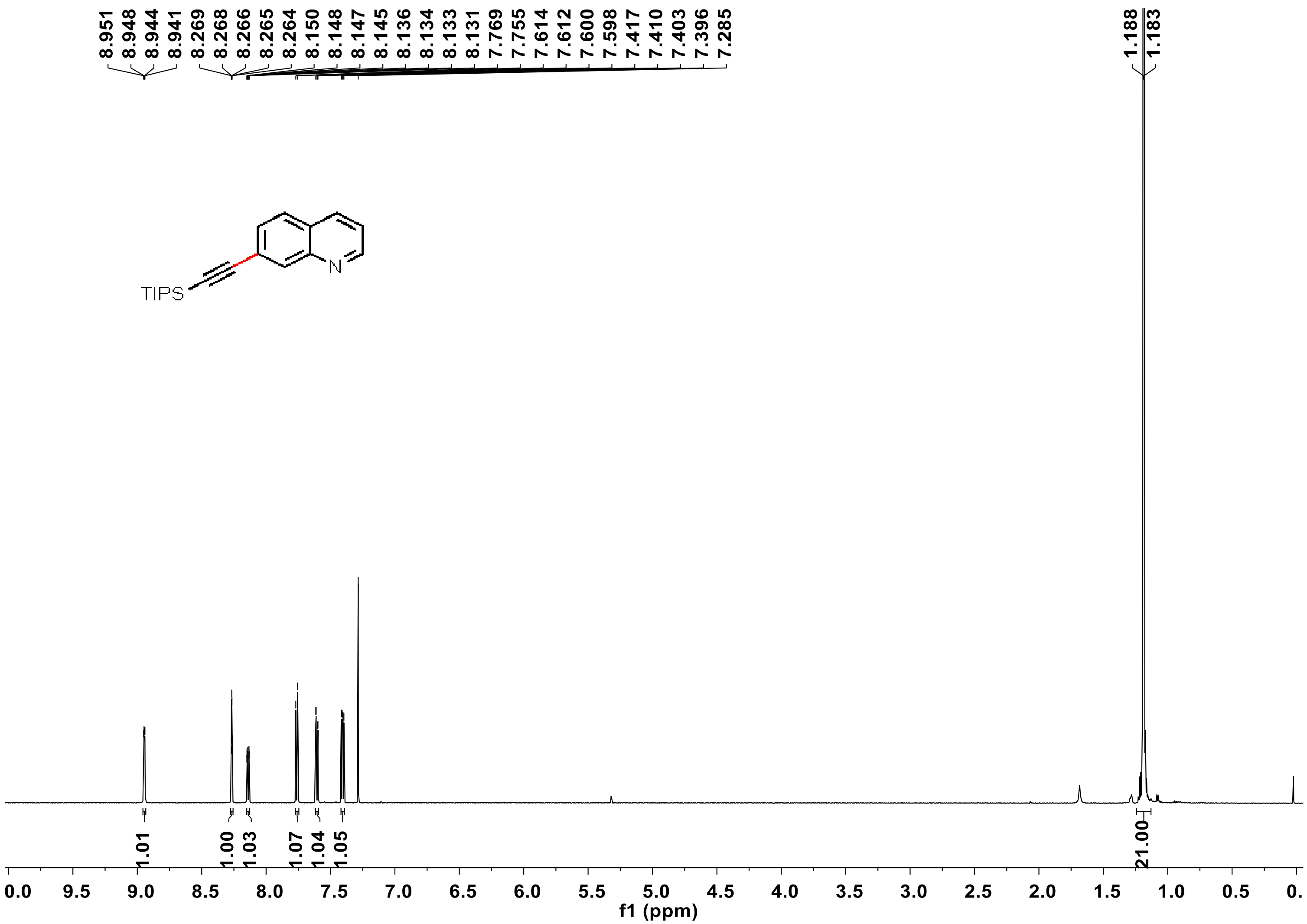
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5h**



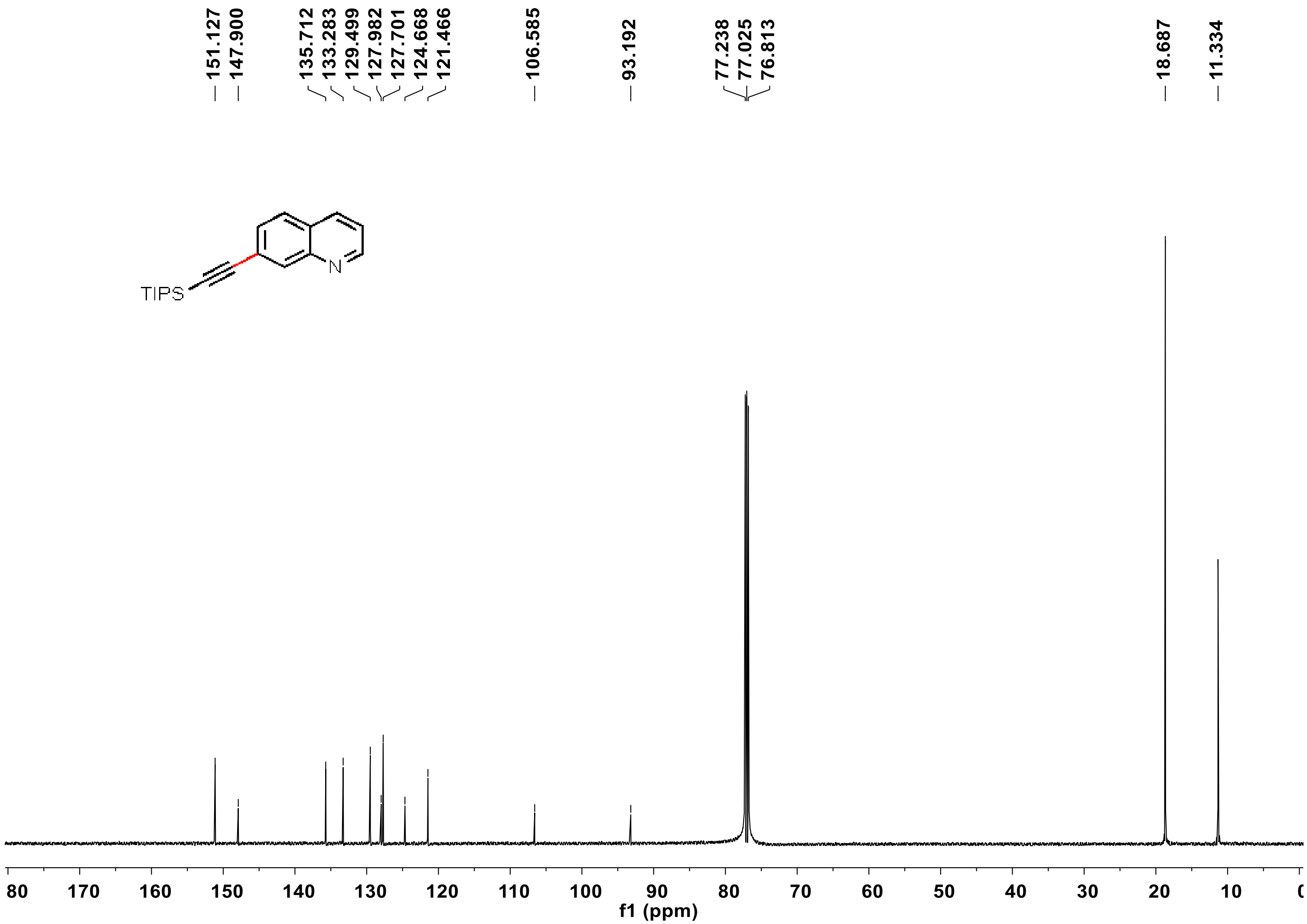
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5h**



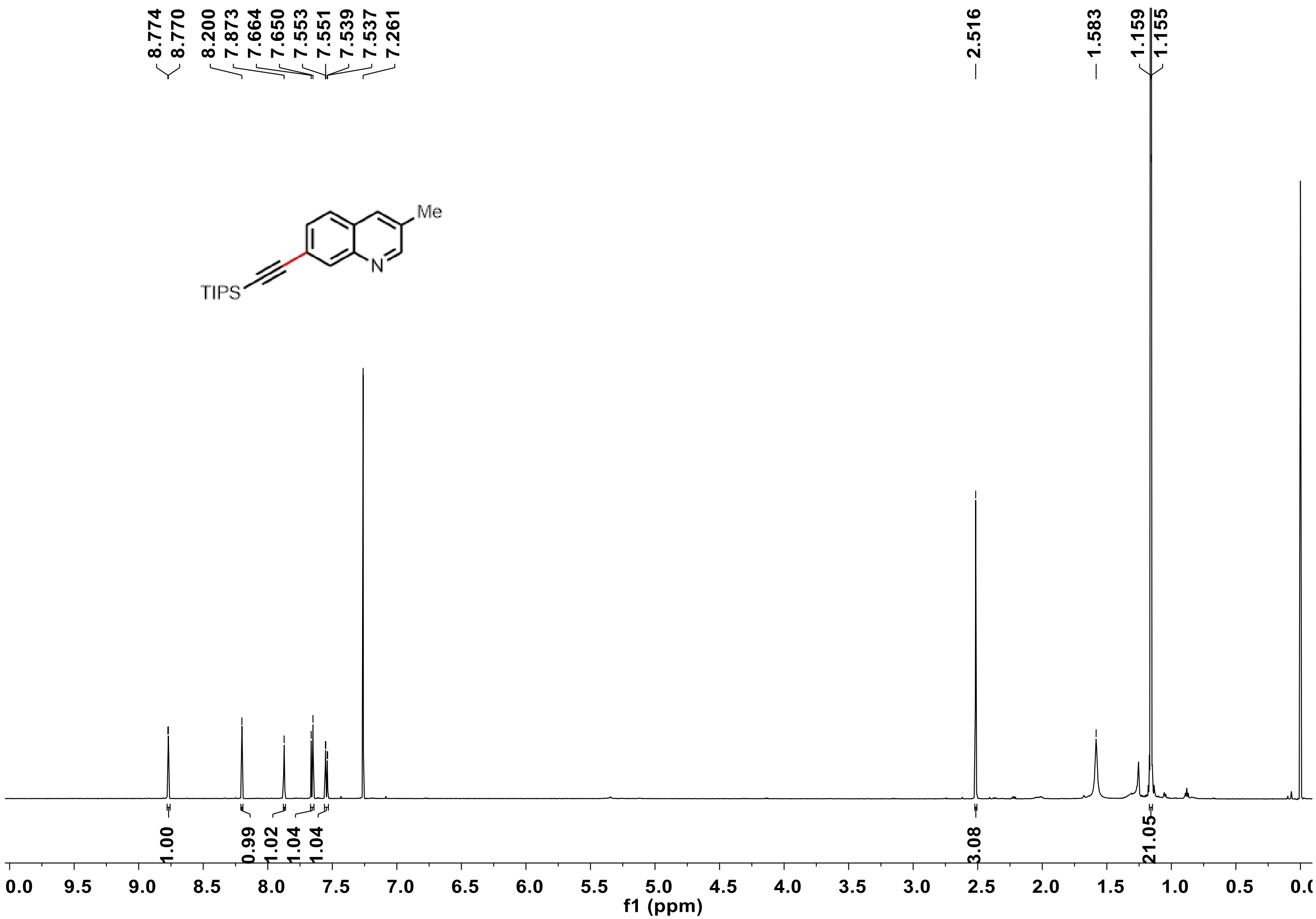
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6a**



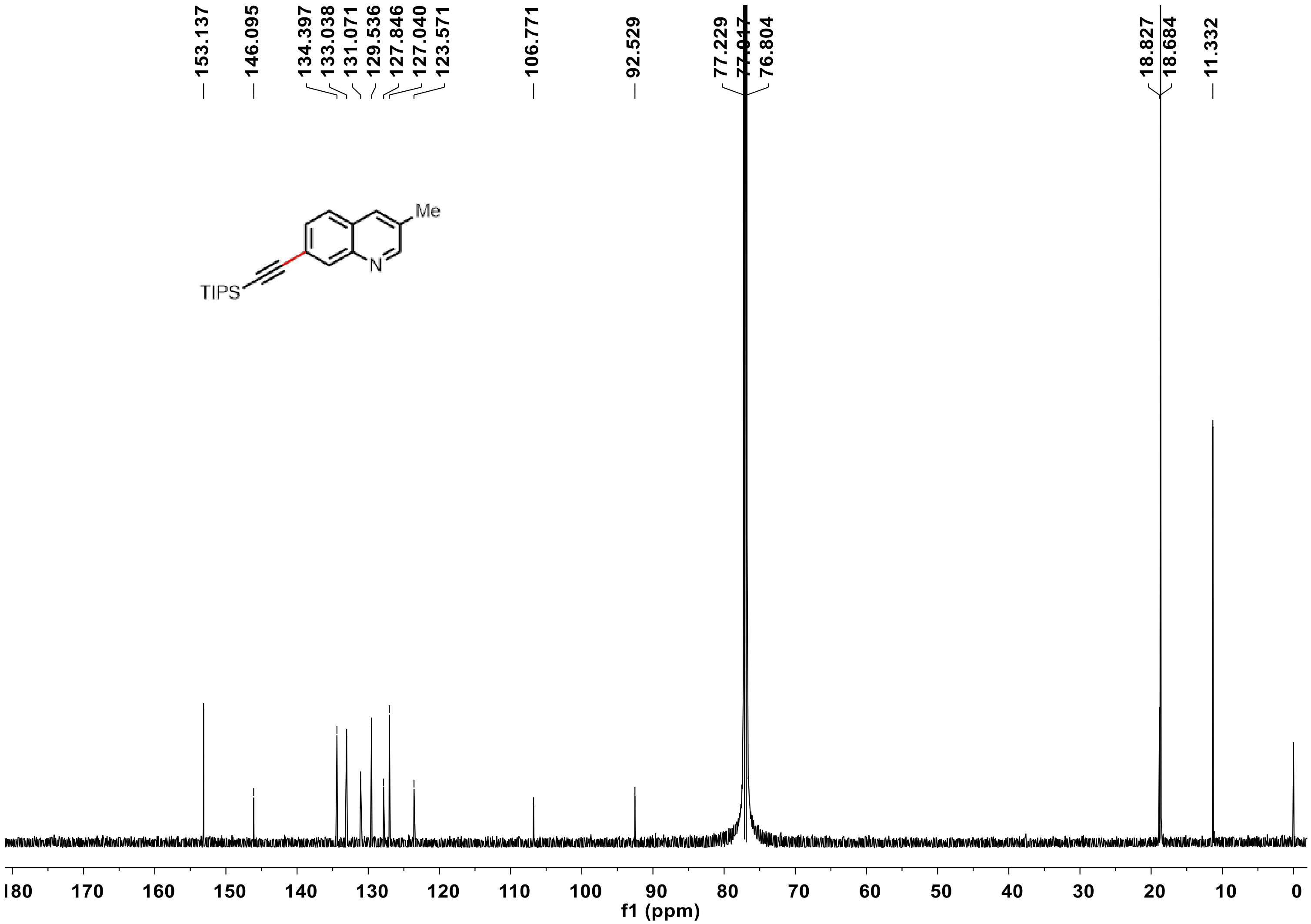
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6a**



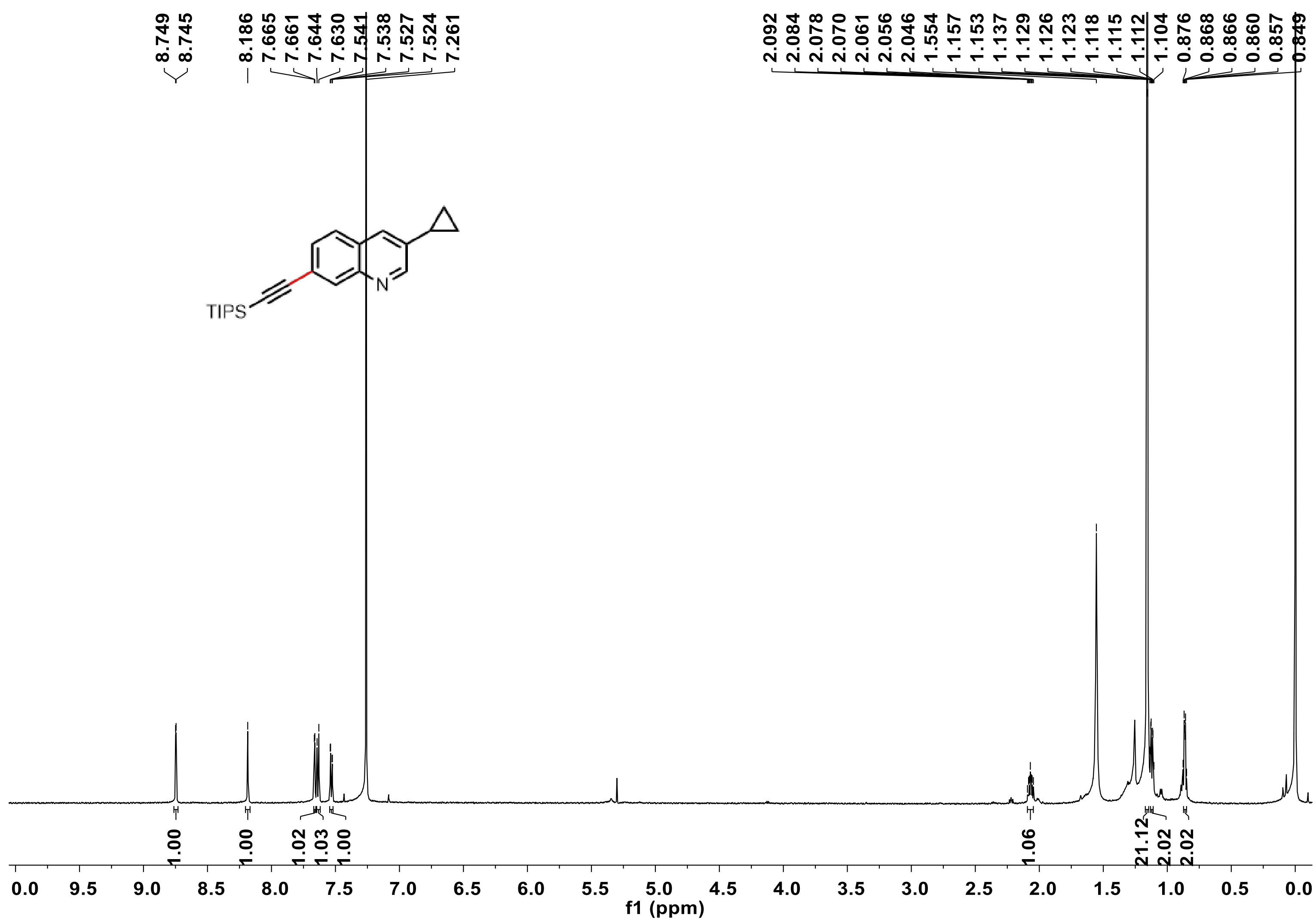
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6b**



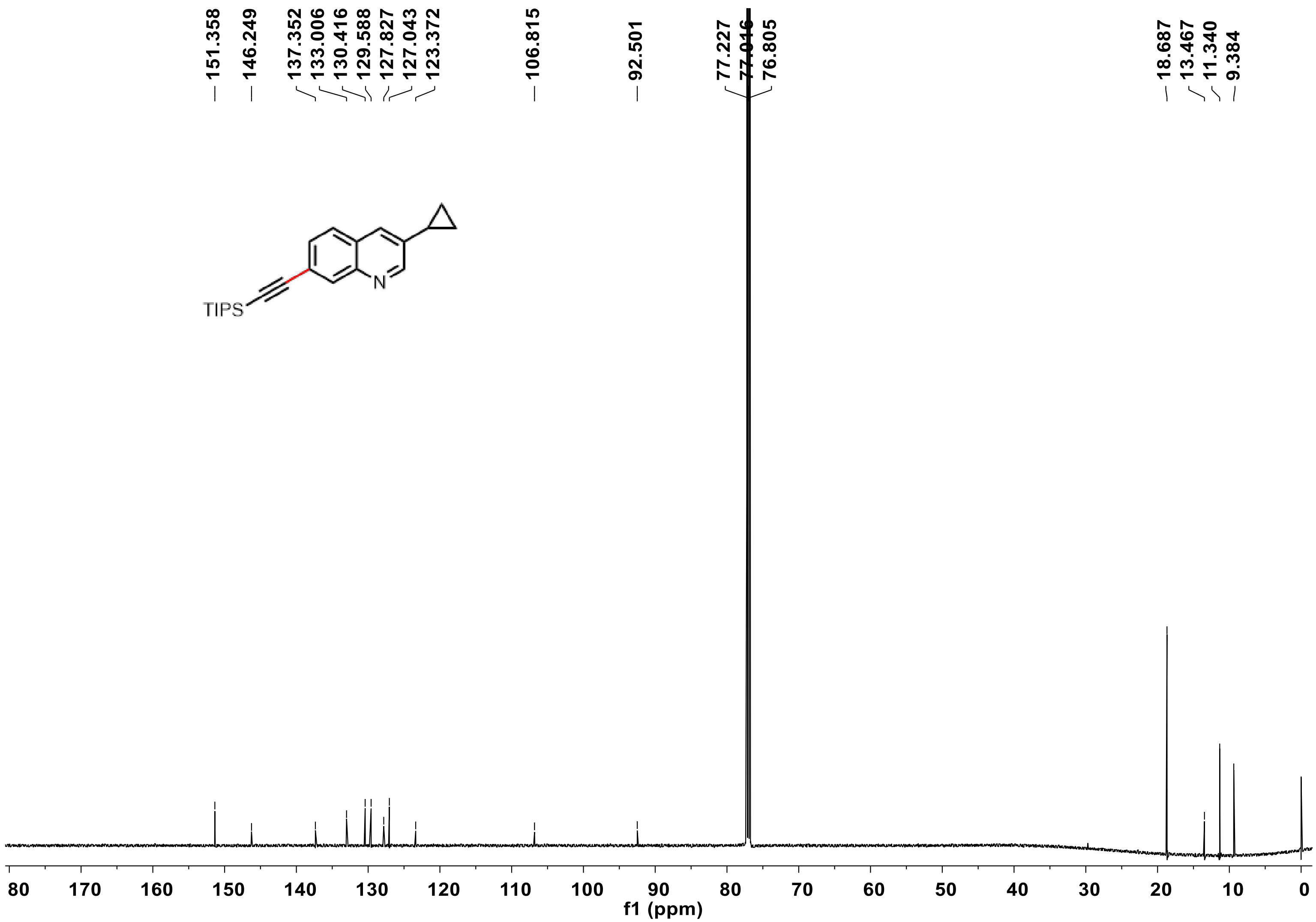
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **6b**



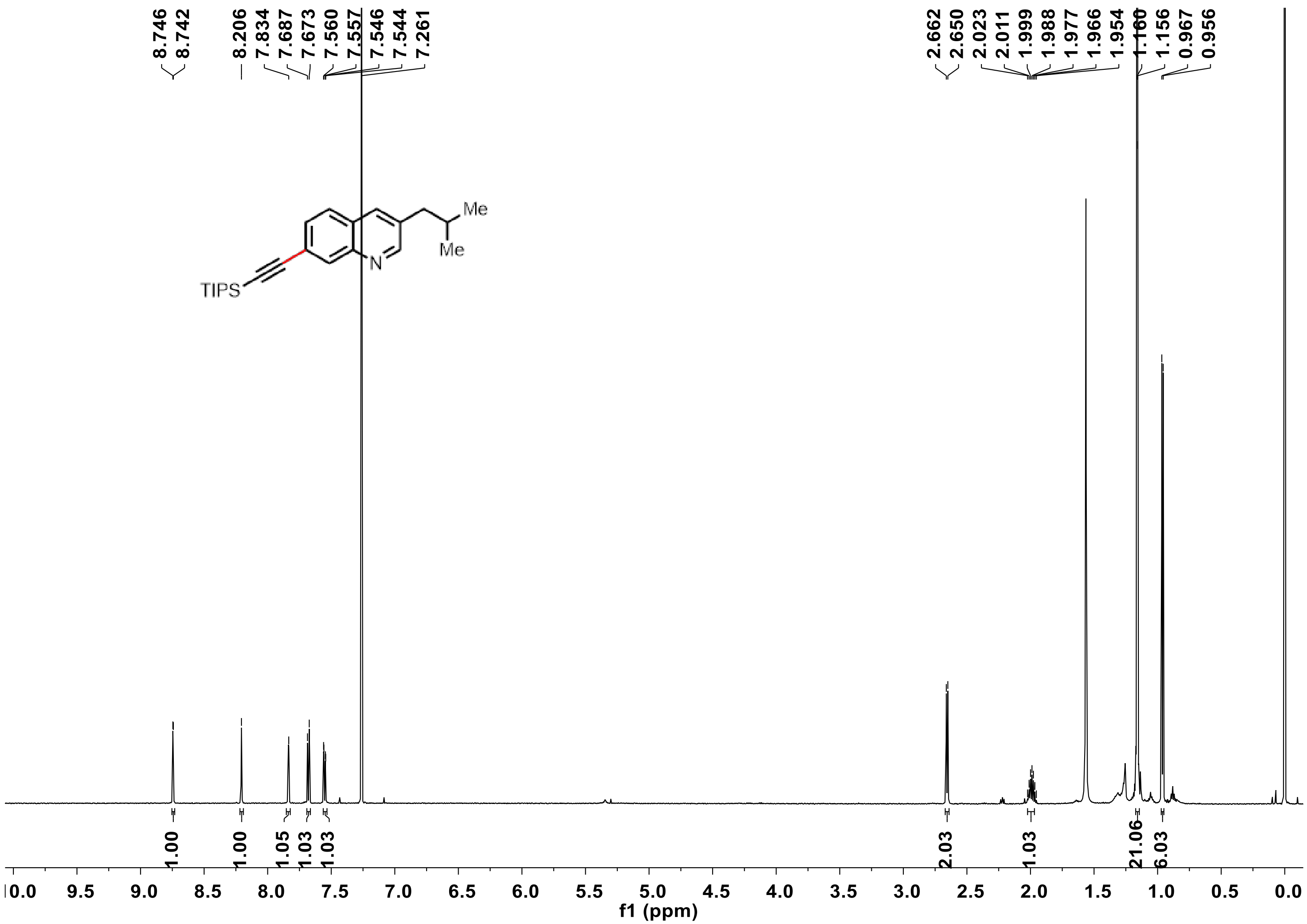
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6c**



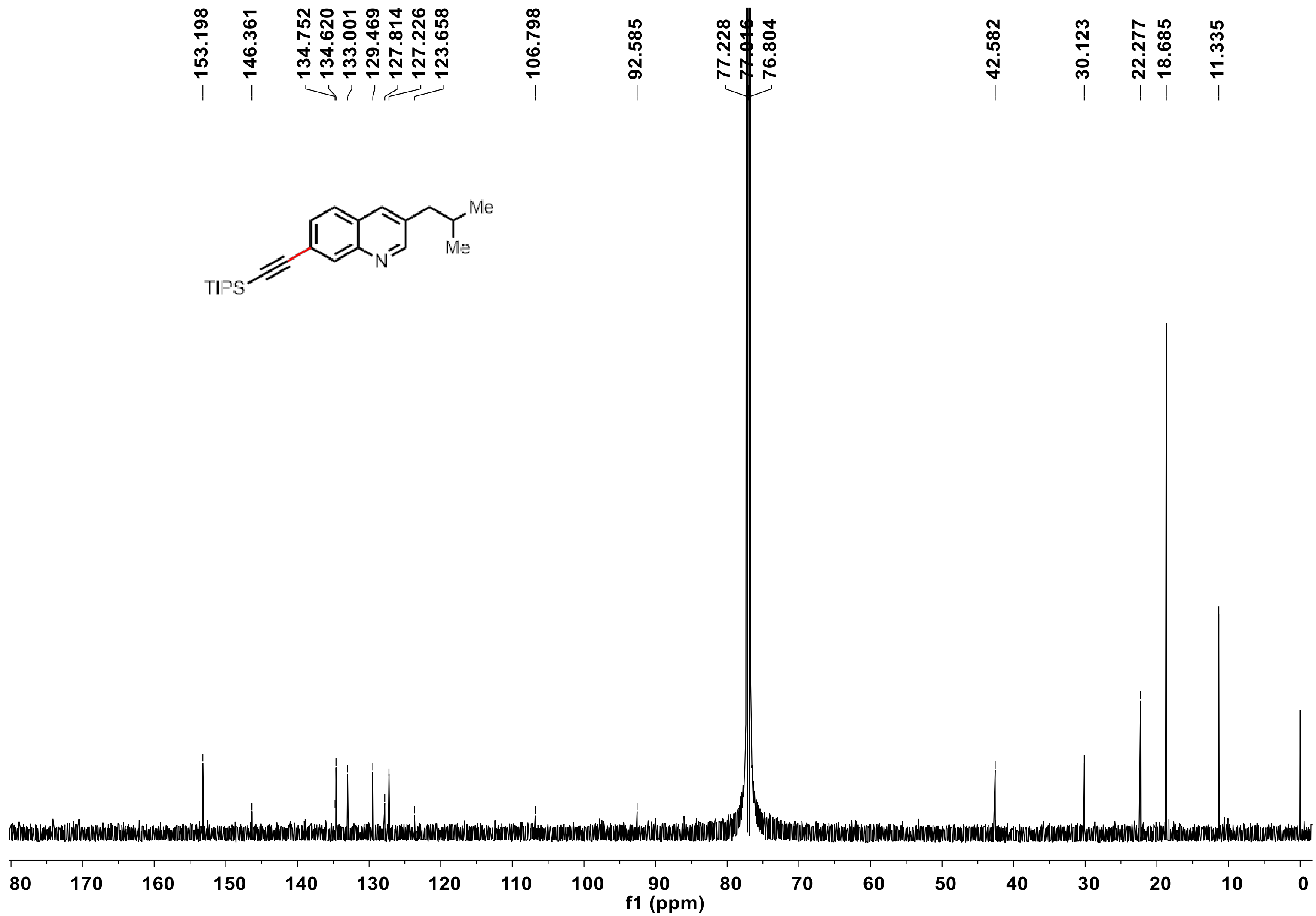
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6c**



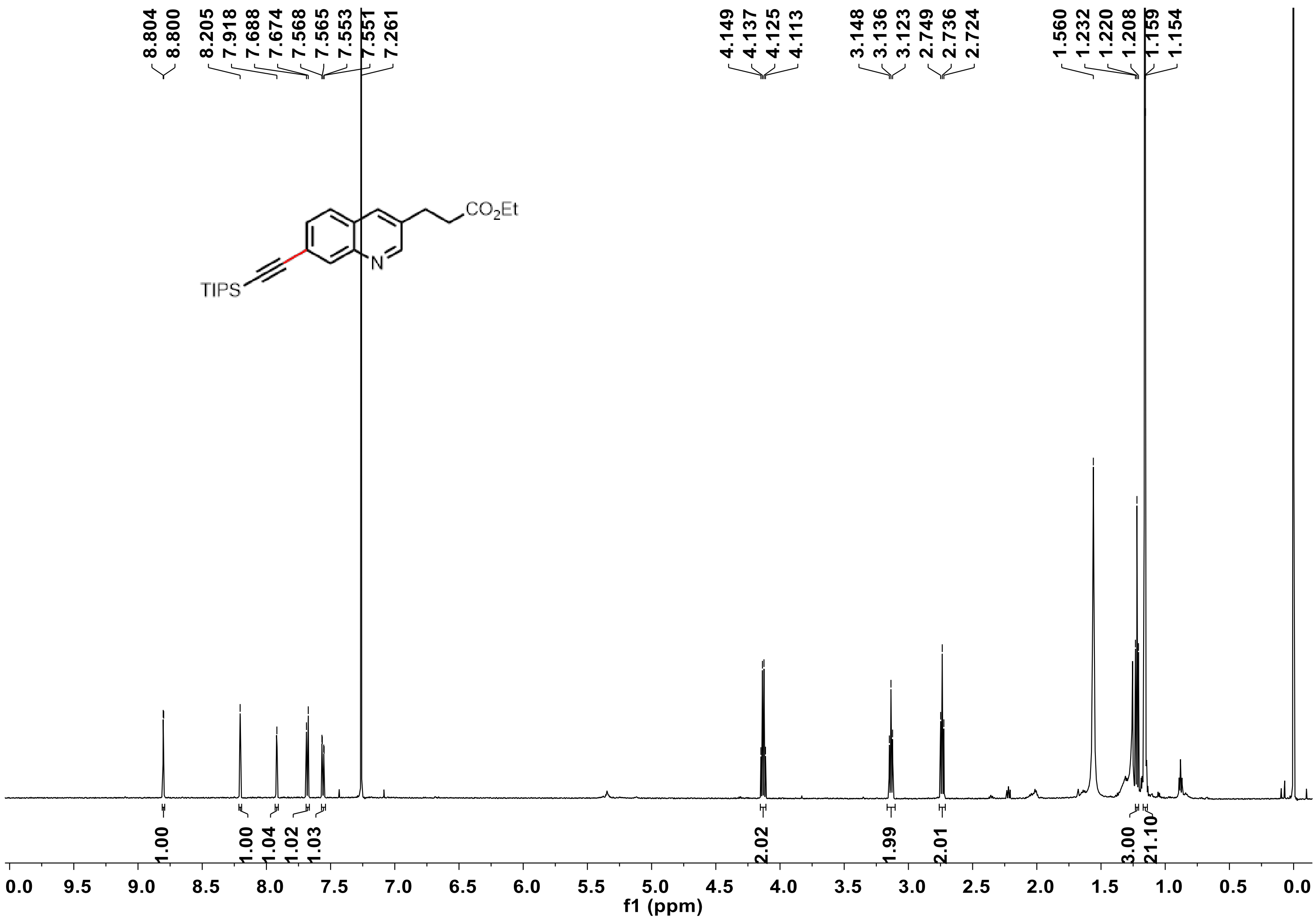
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6d**



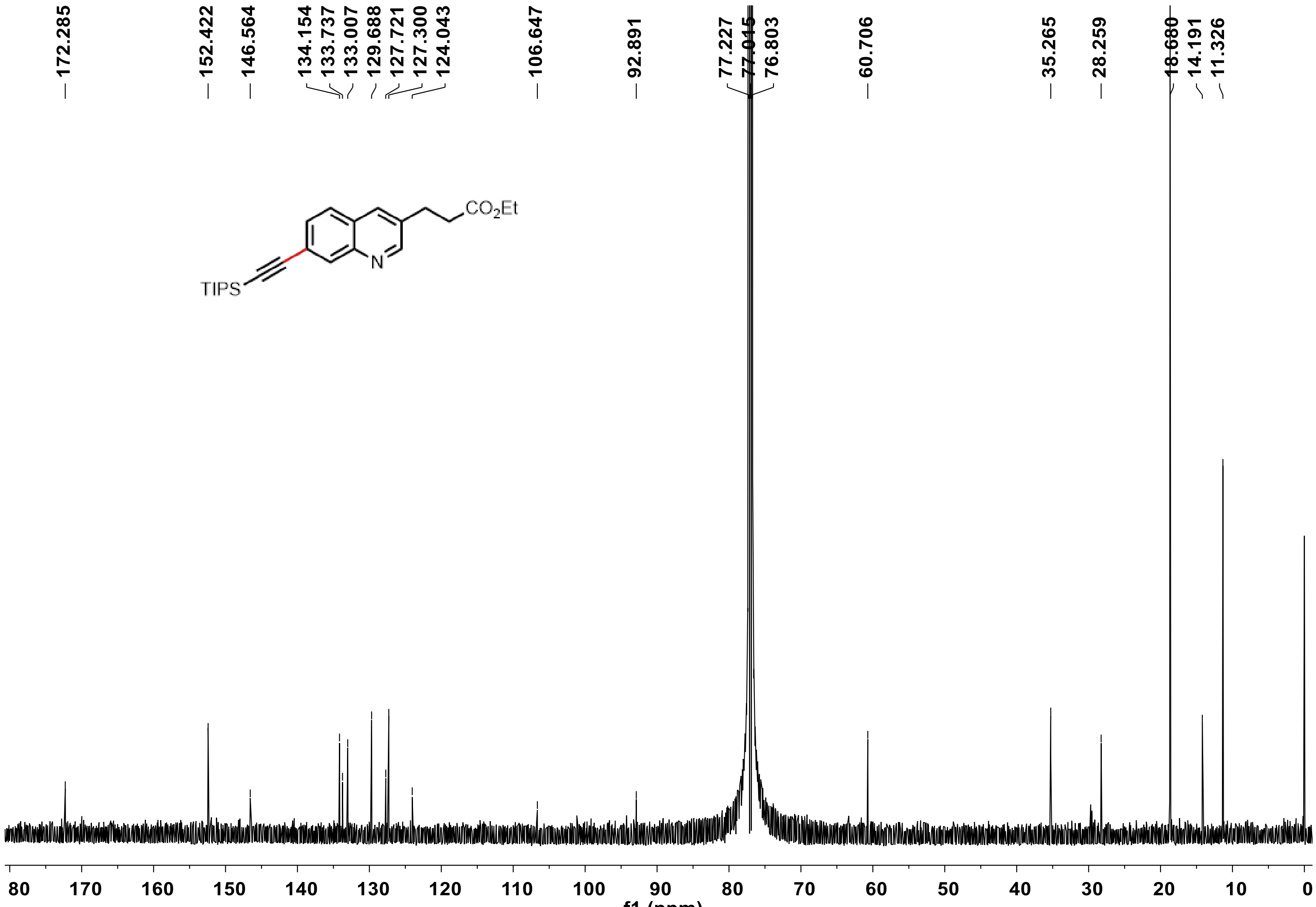
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6d**



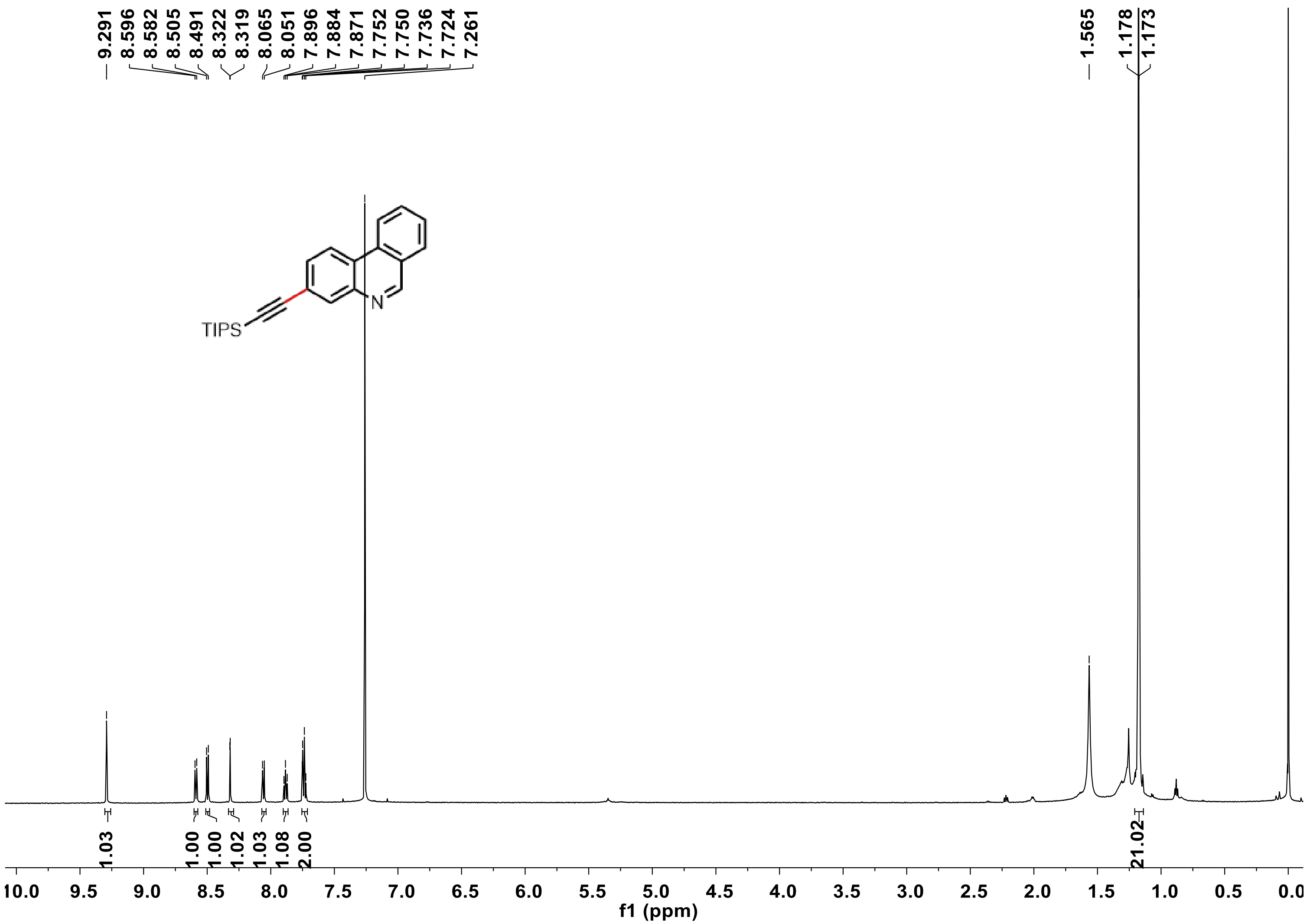
^1H NMR (600 MHz, $CDCl_3$) spectrum of **6e**



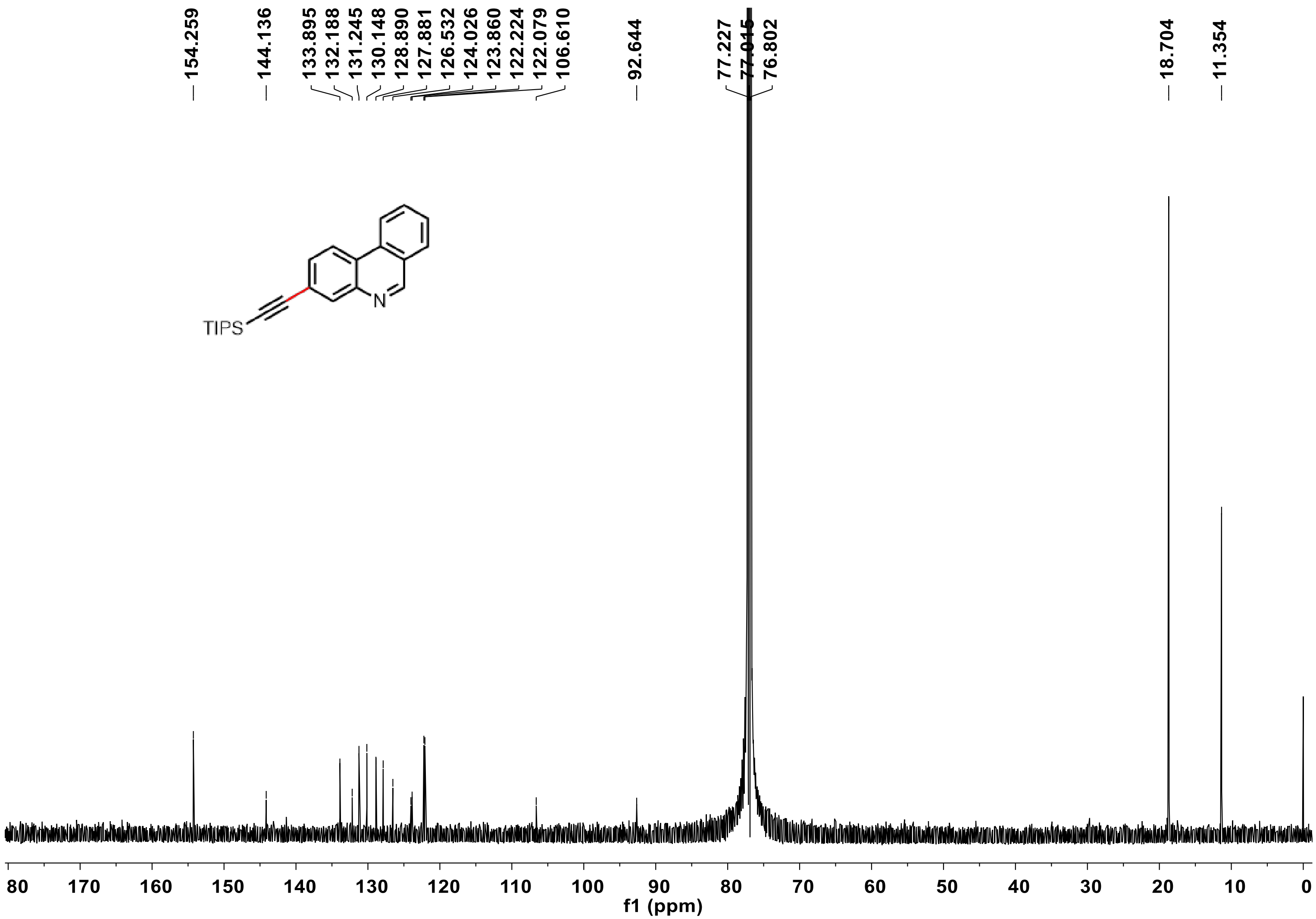
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6e**



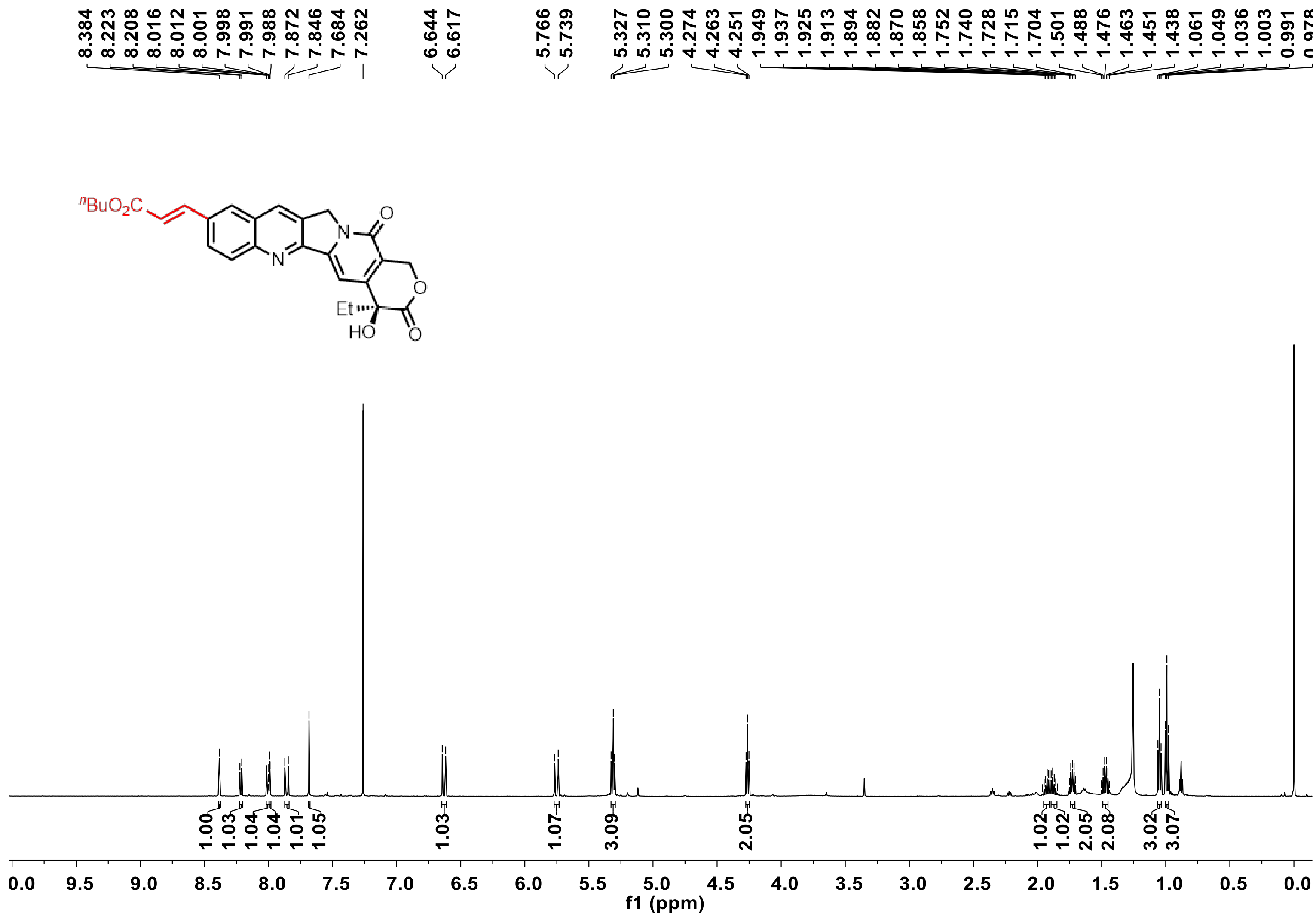
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6f**



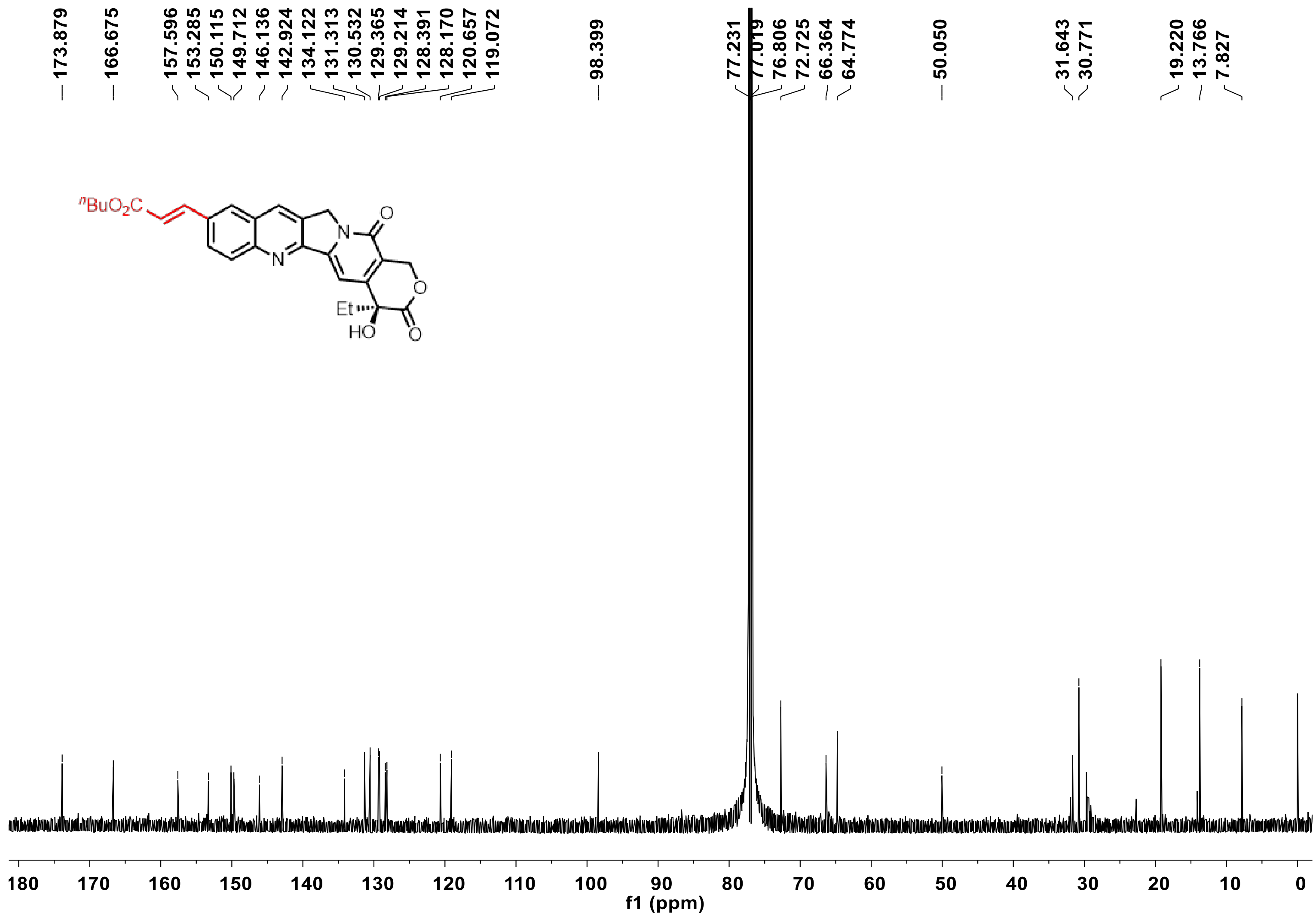
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **6f**



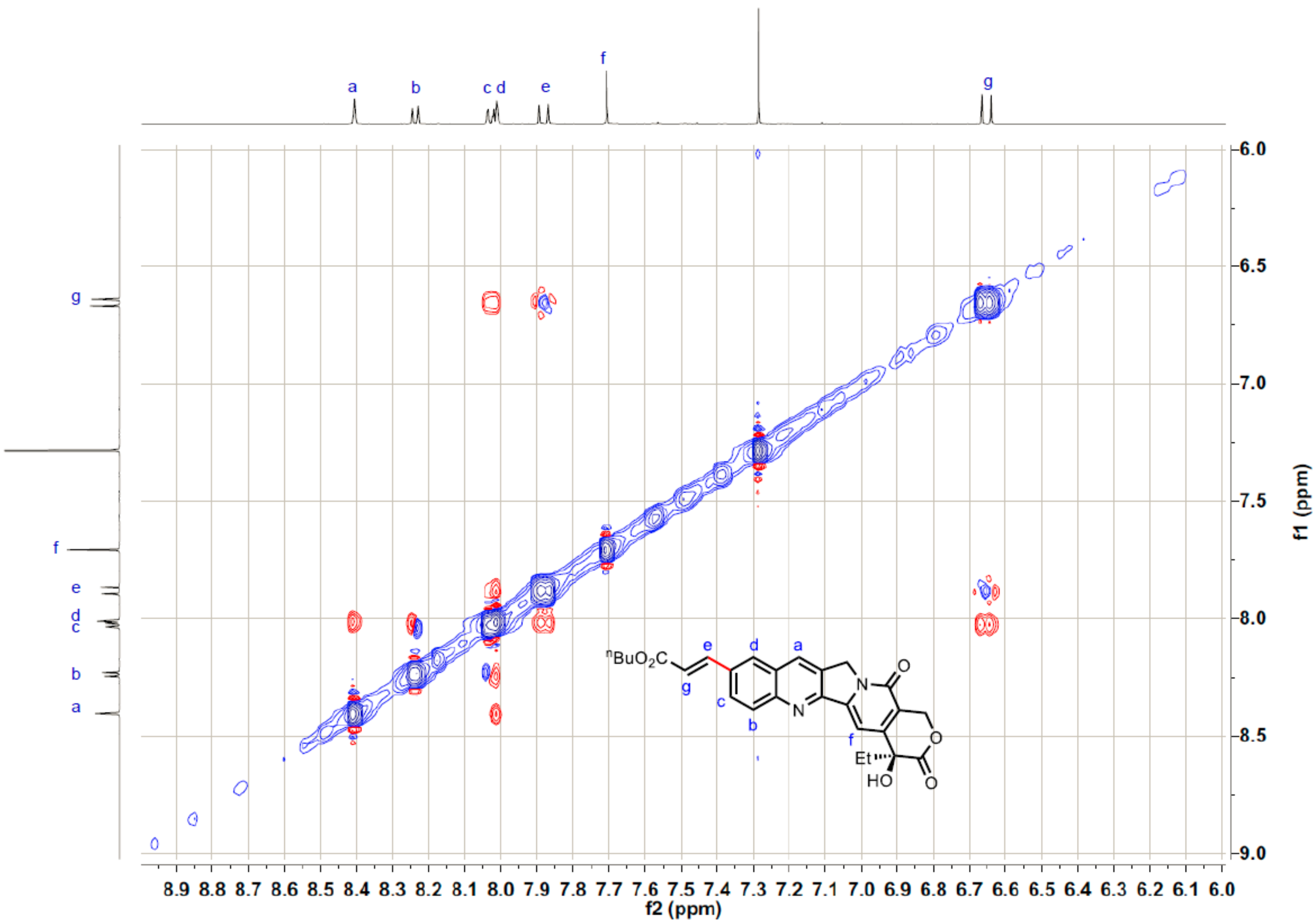
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **8**



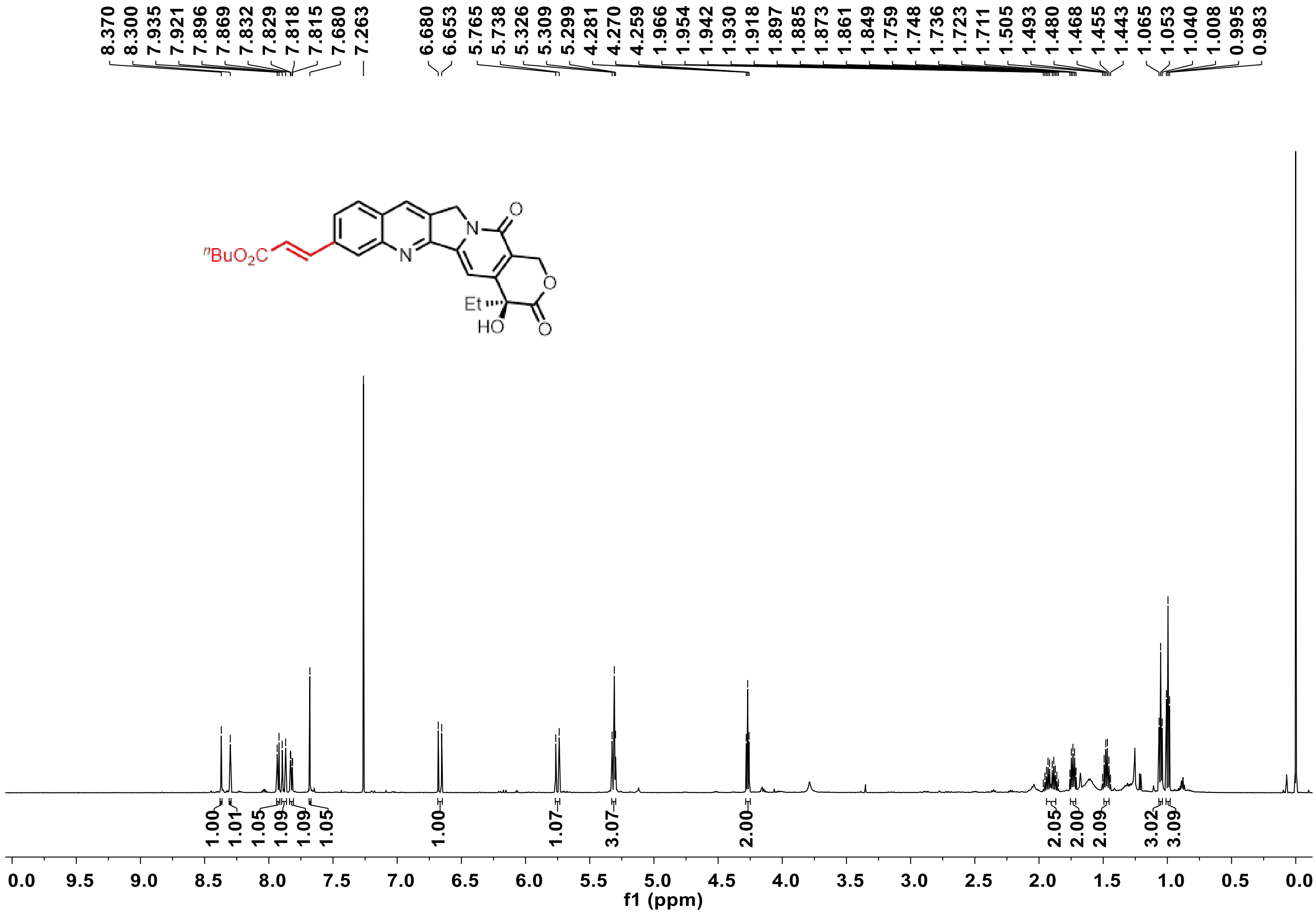
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **8**



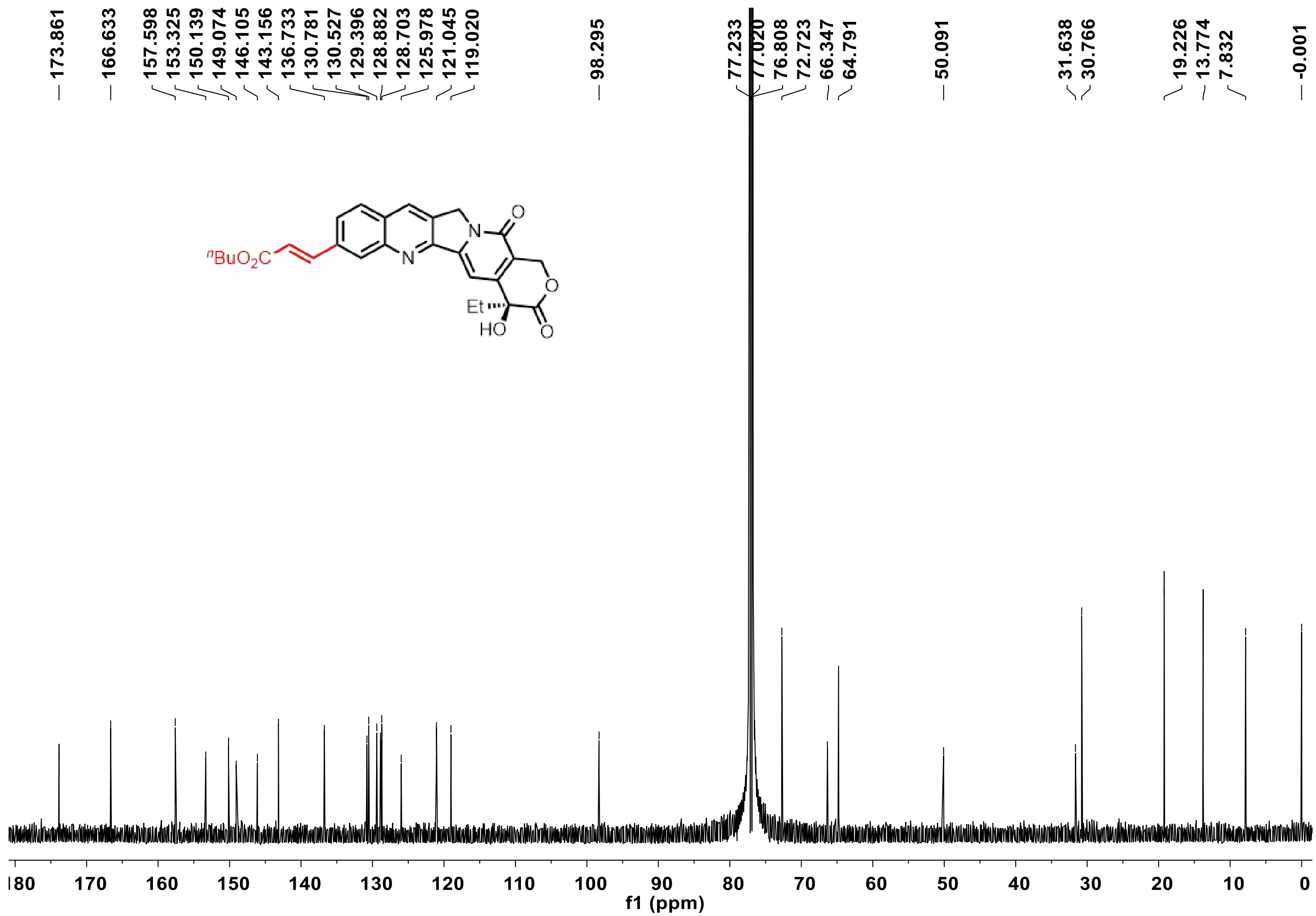
NOESY spectrum of **8**



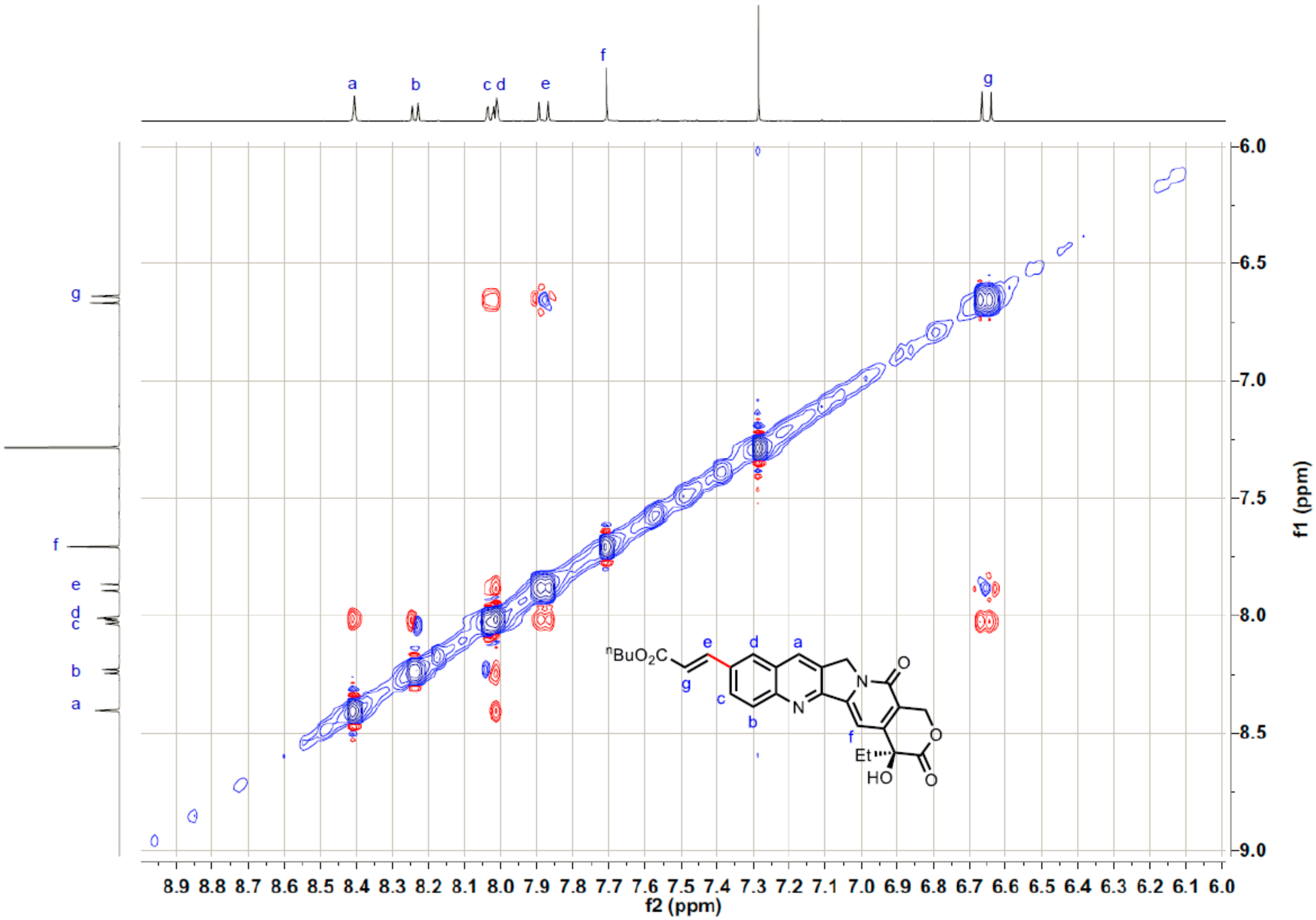
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **9**



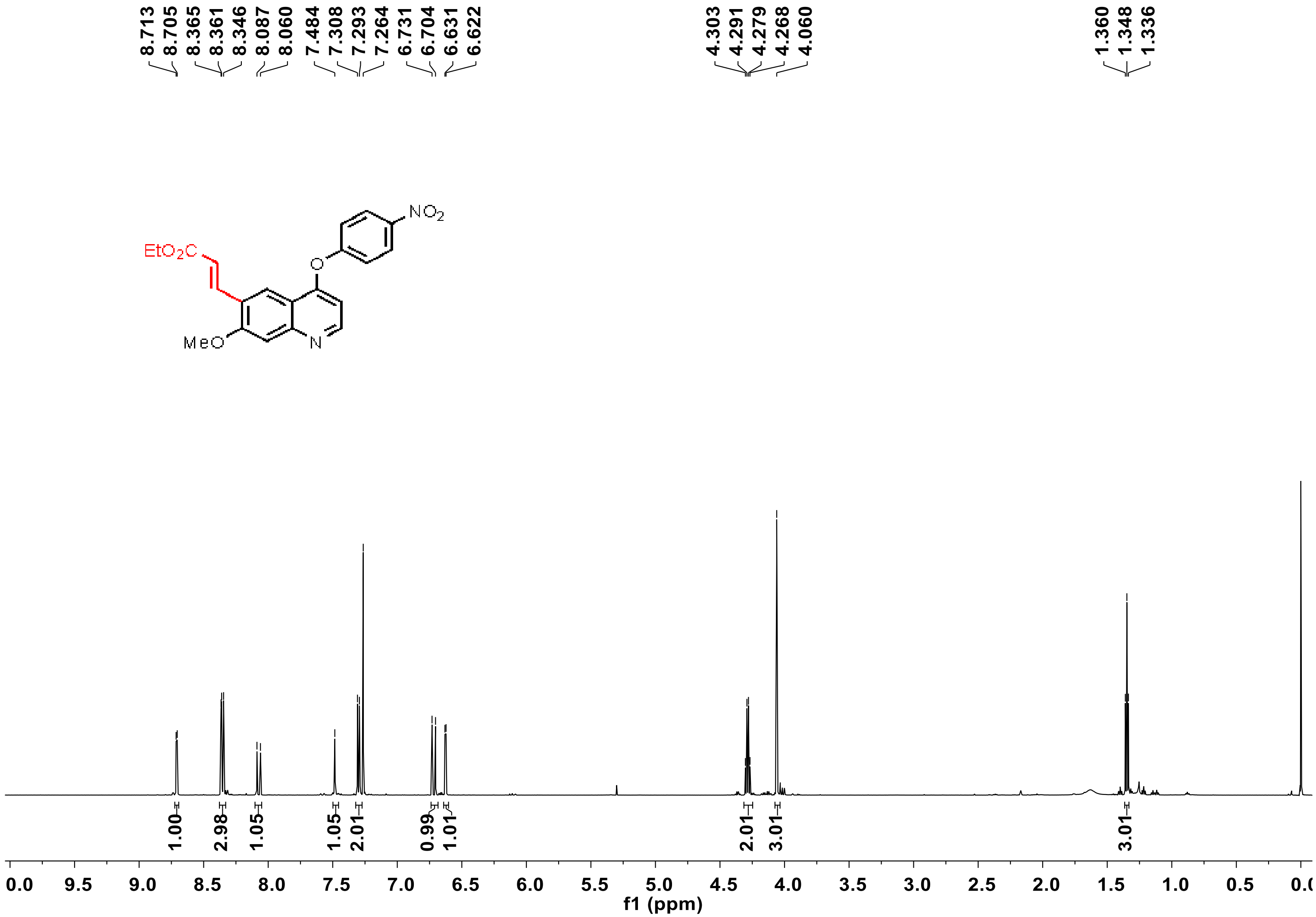
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9**



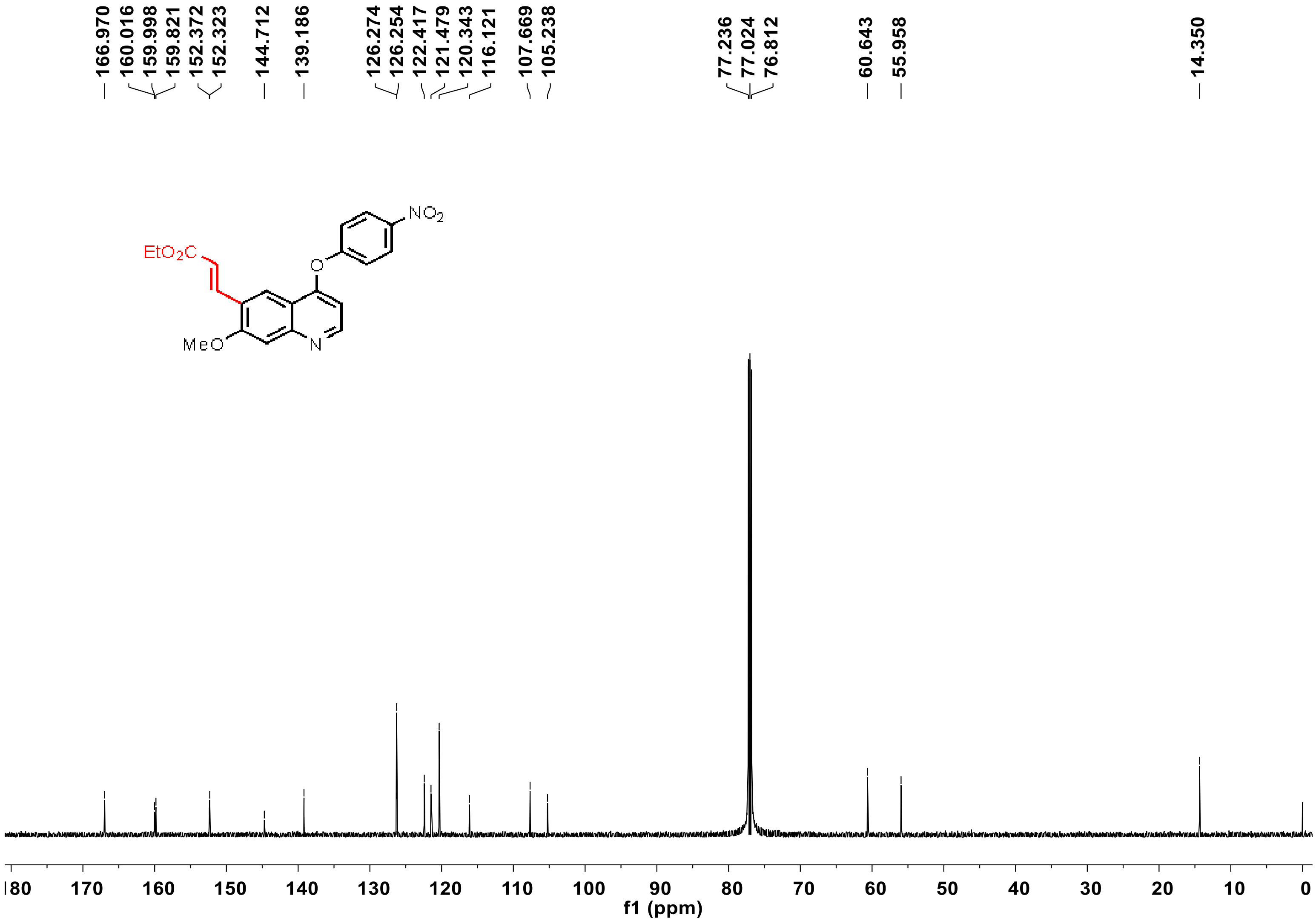
NOESY spectrum of **9**



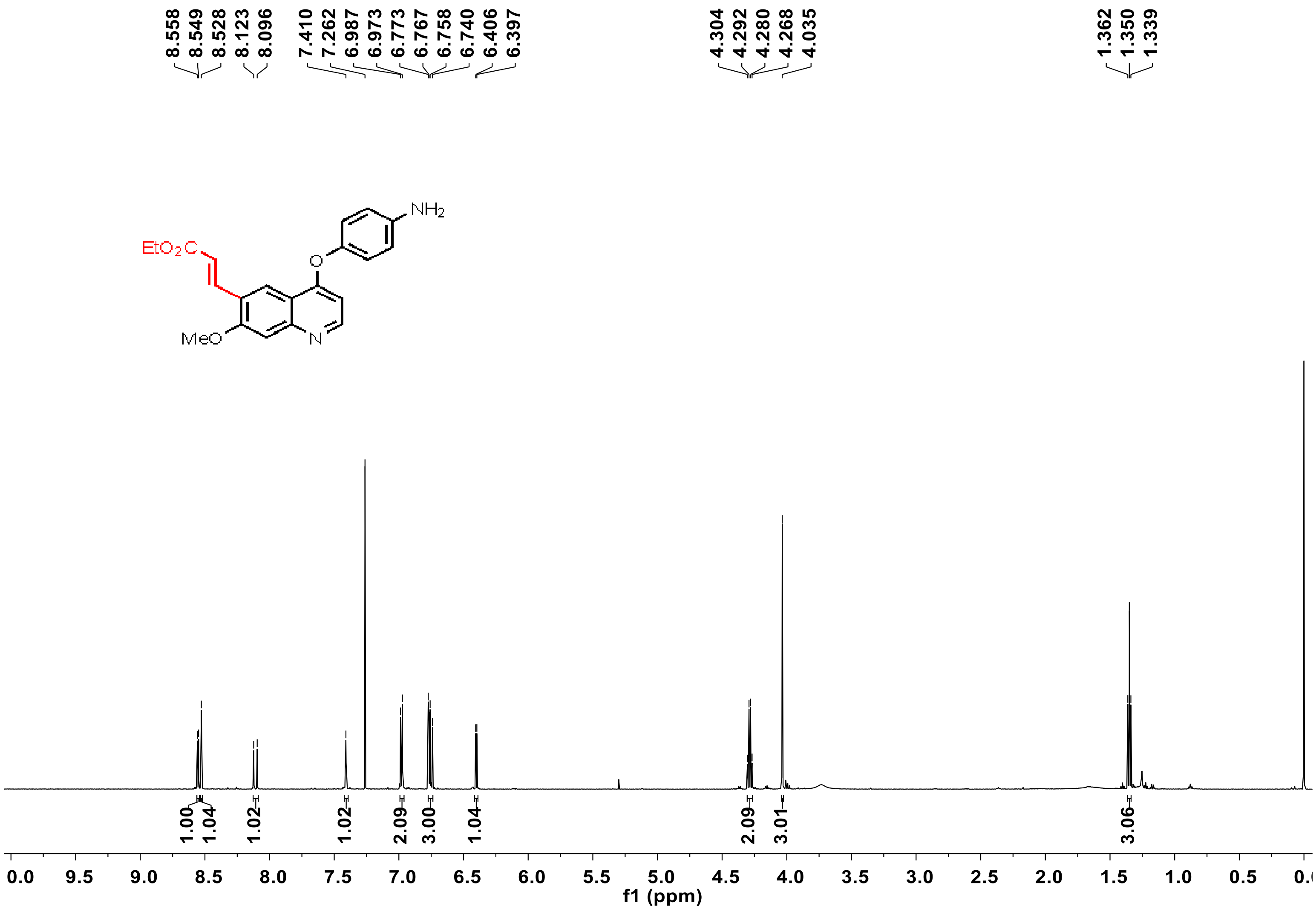
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **10**



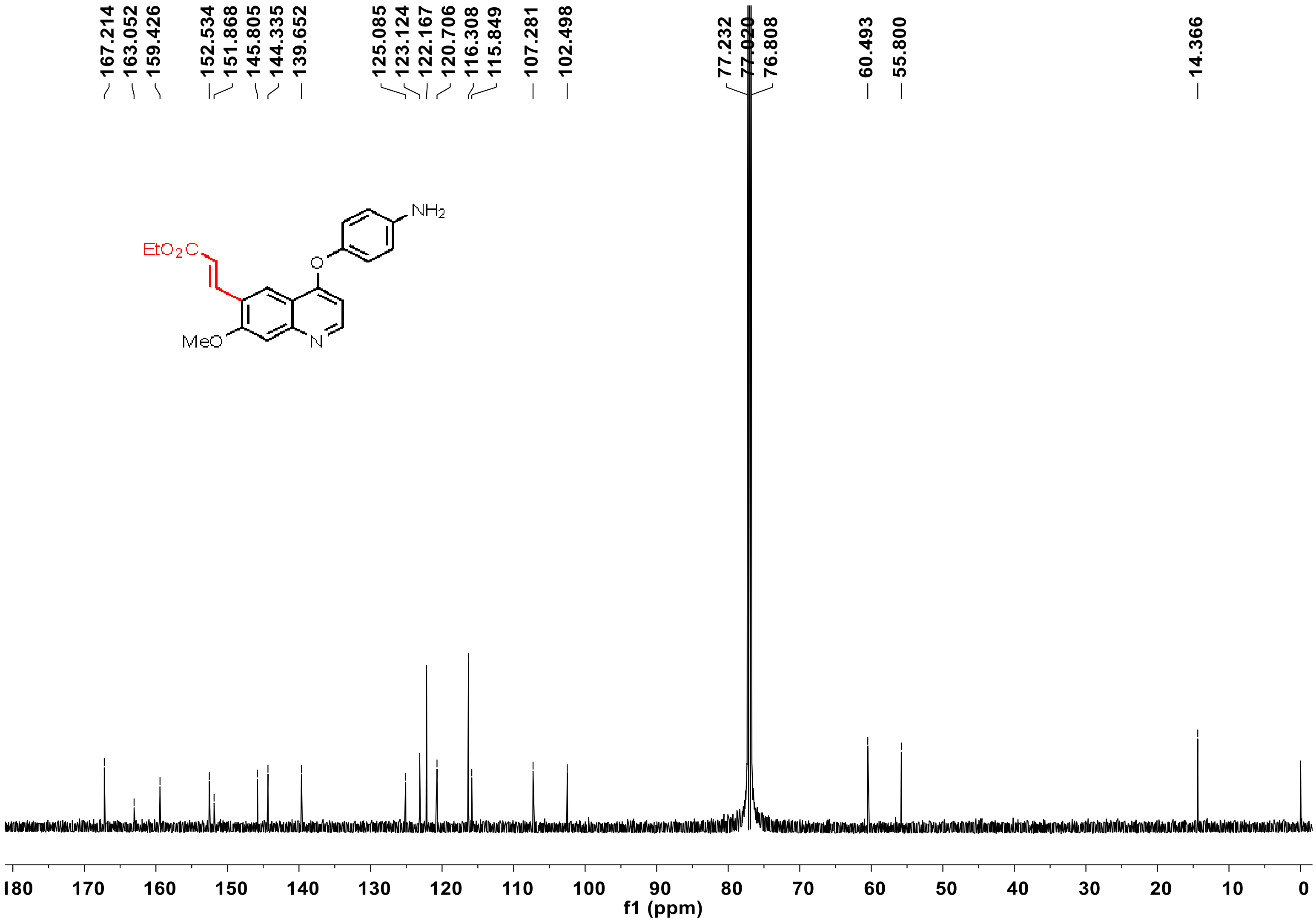
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **10**



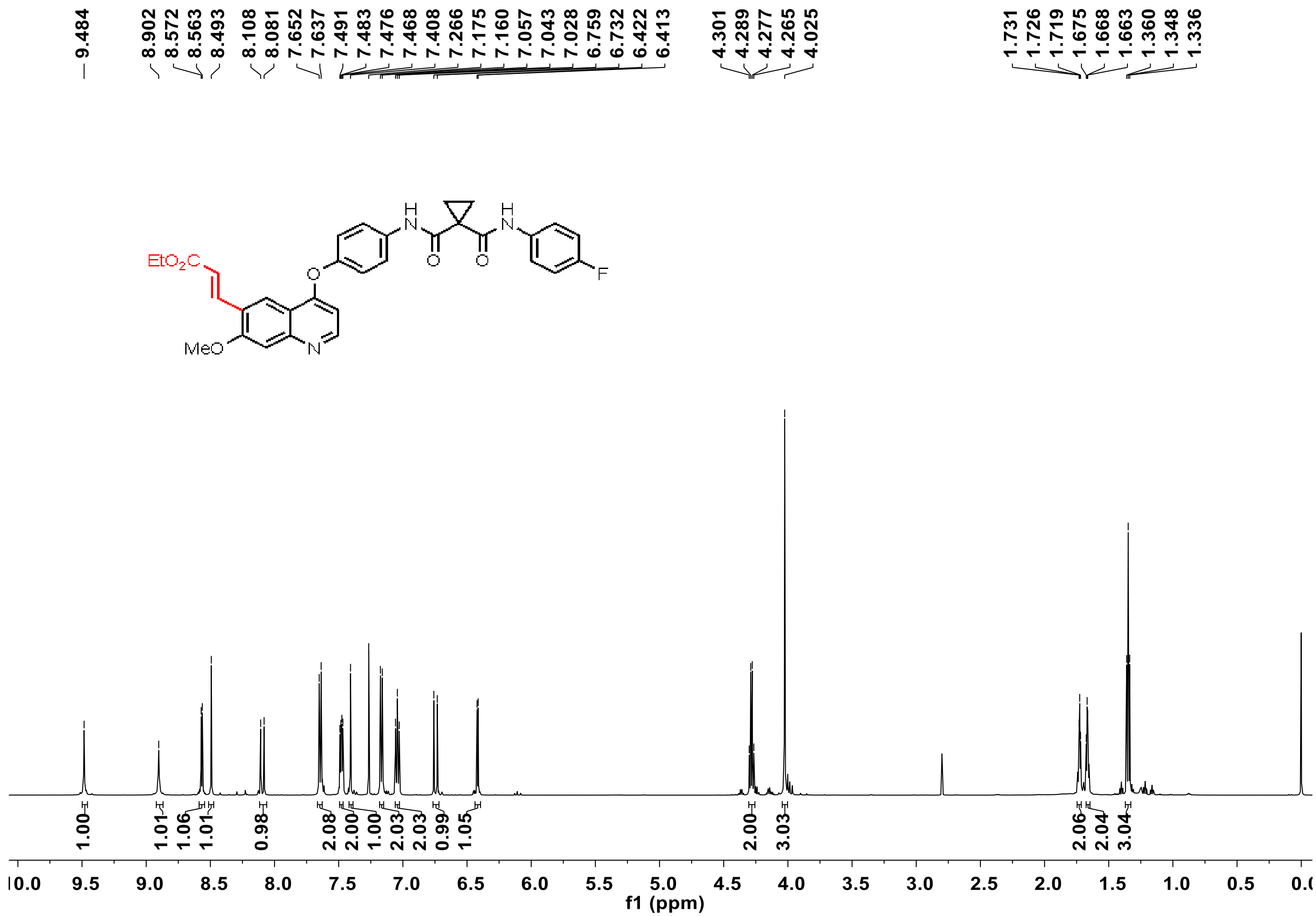
^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **11**



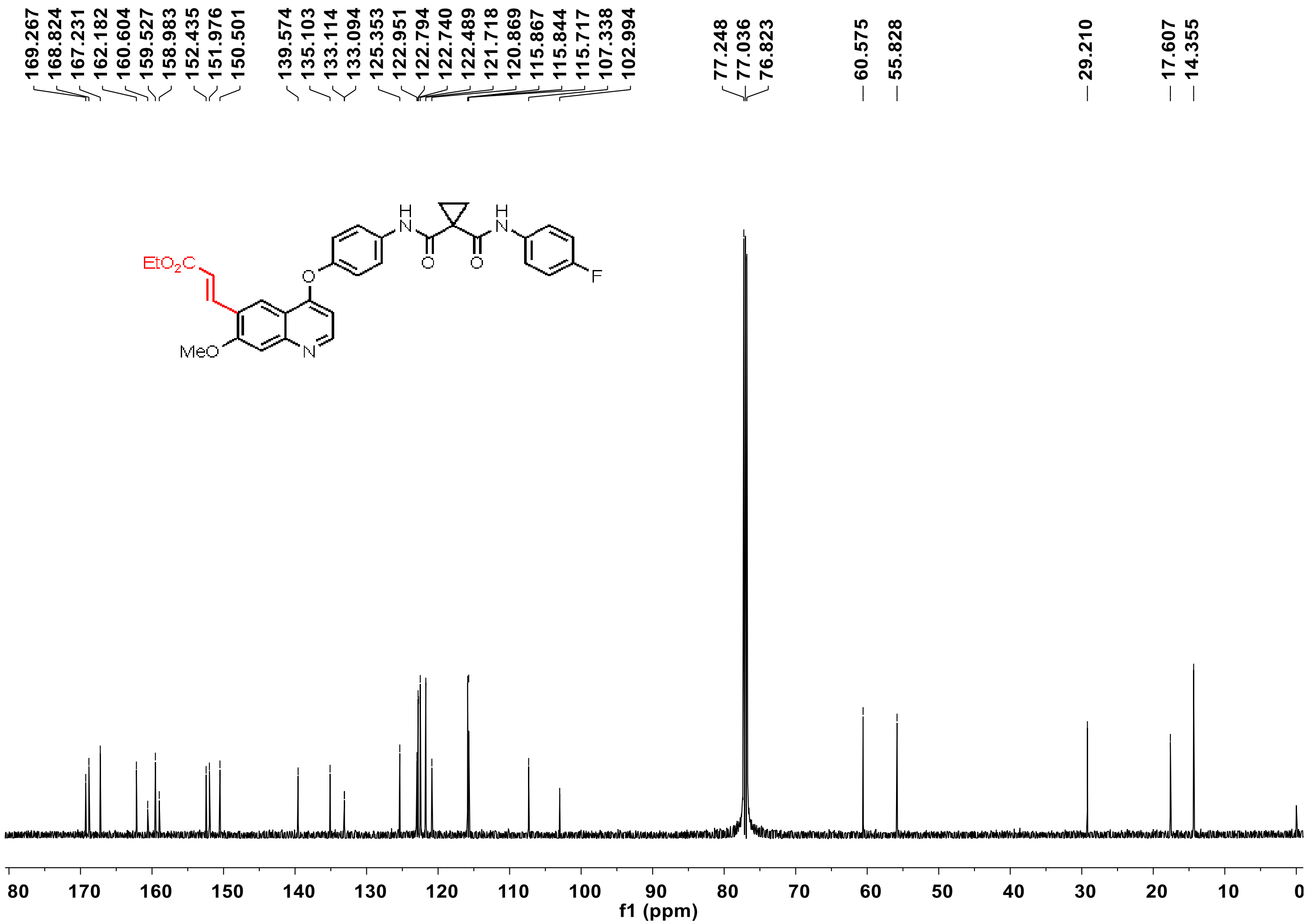
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **11**



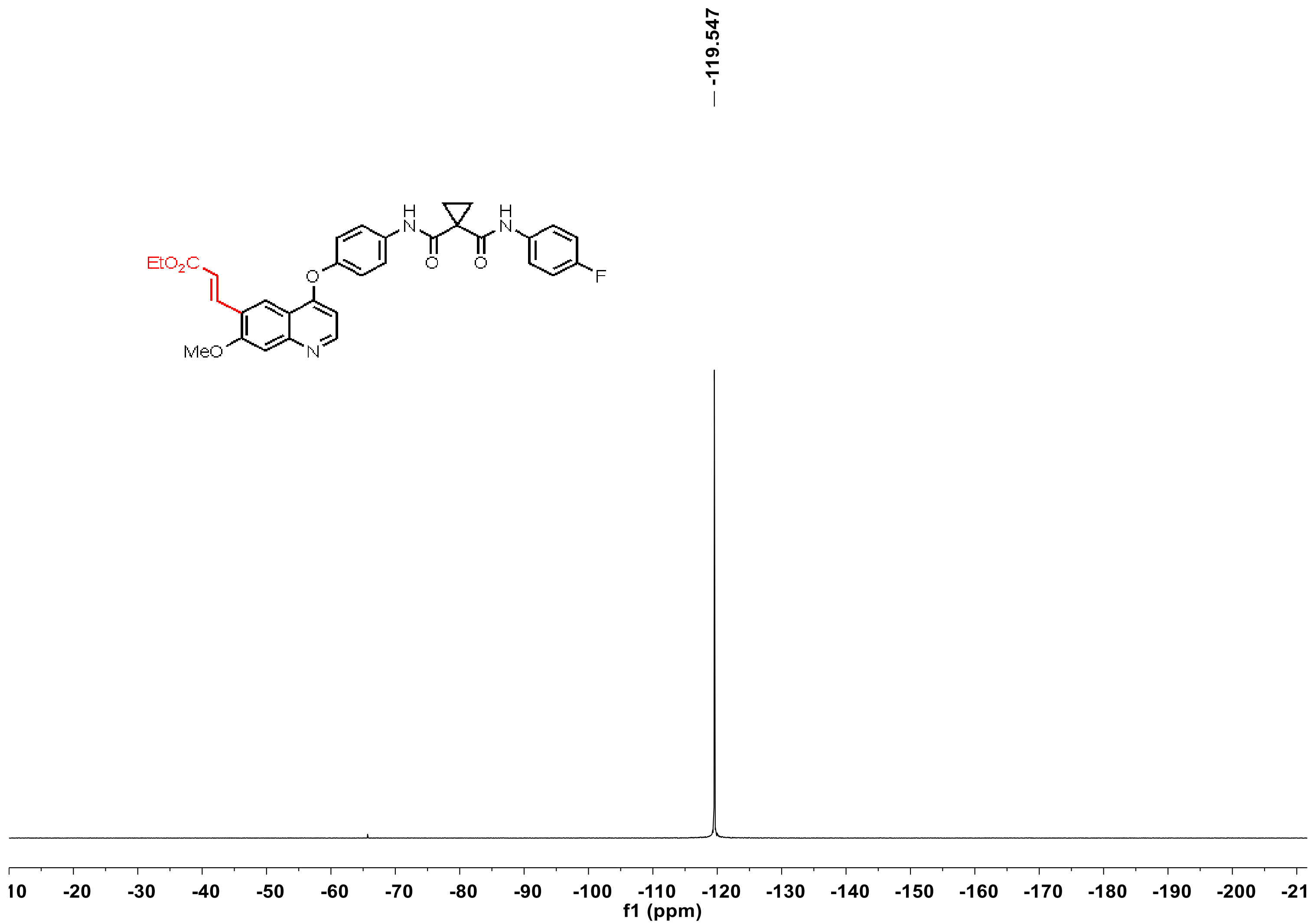
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **12**



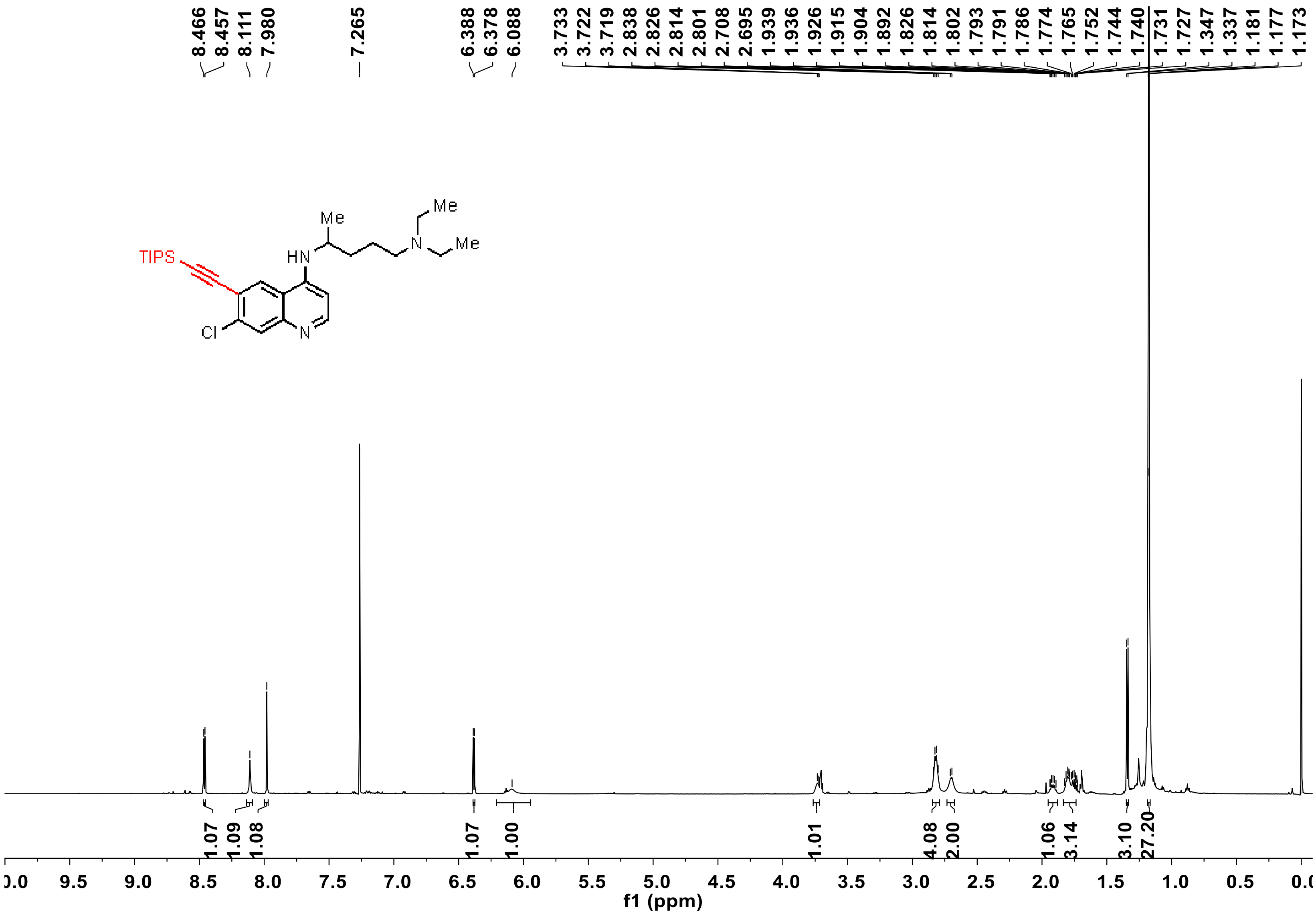
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **12**



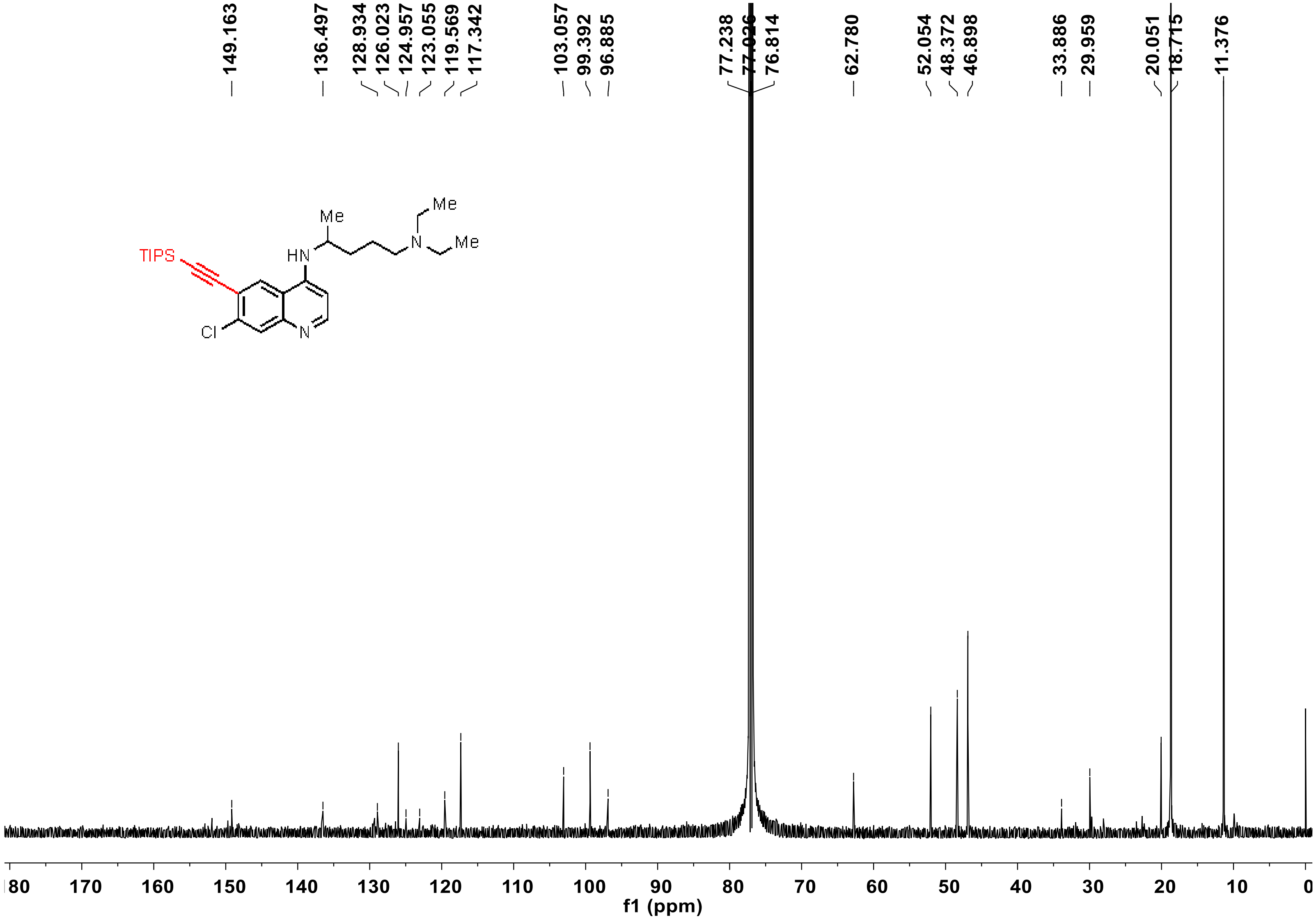
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **12**



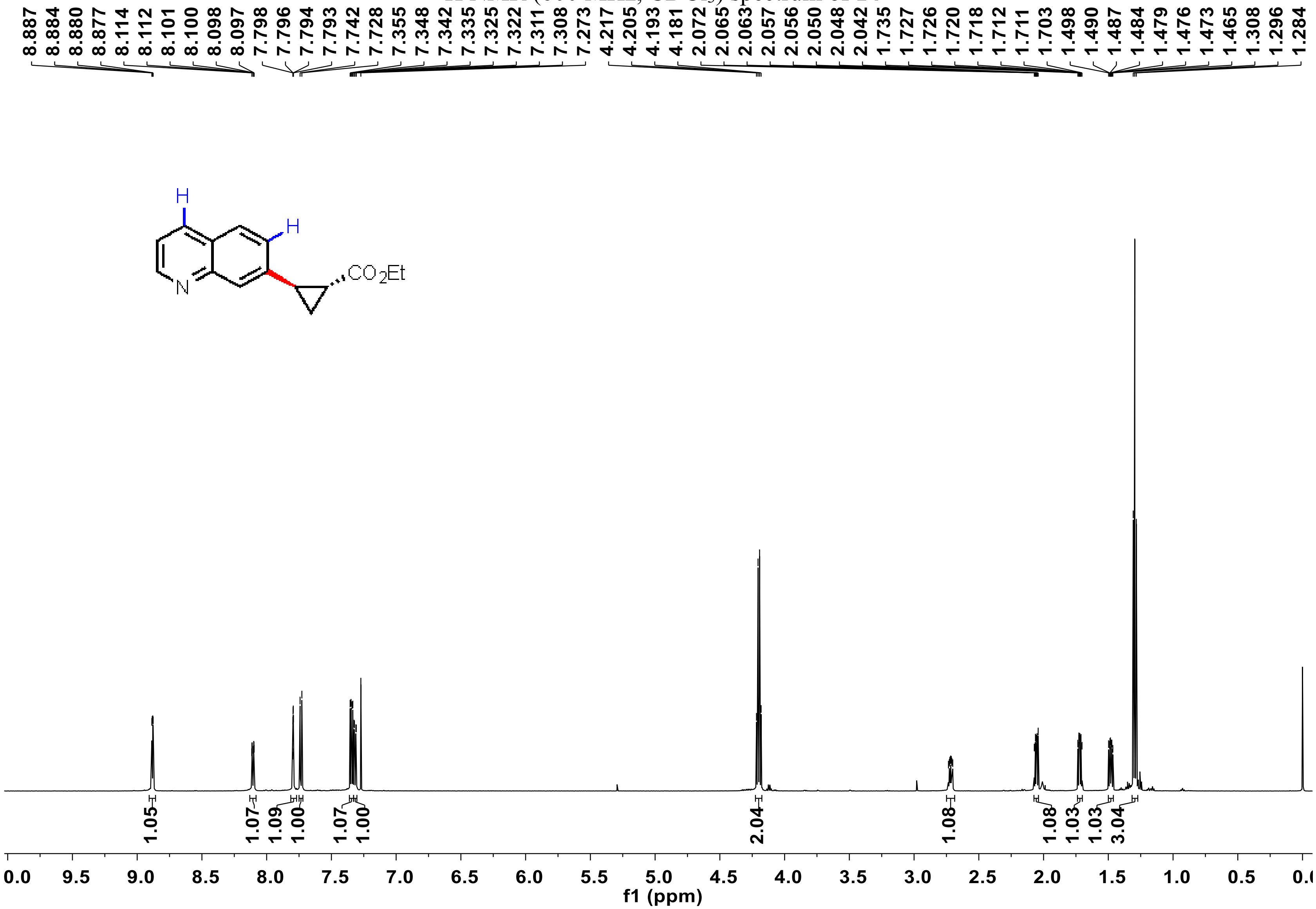
^1H NMR (600 MHz, $CDCl_3$) spectrum of **13**



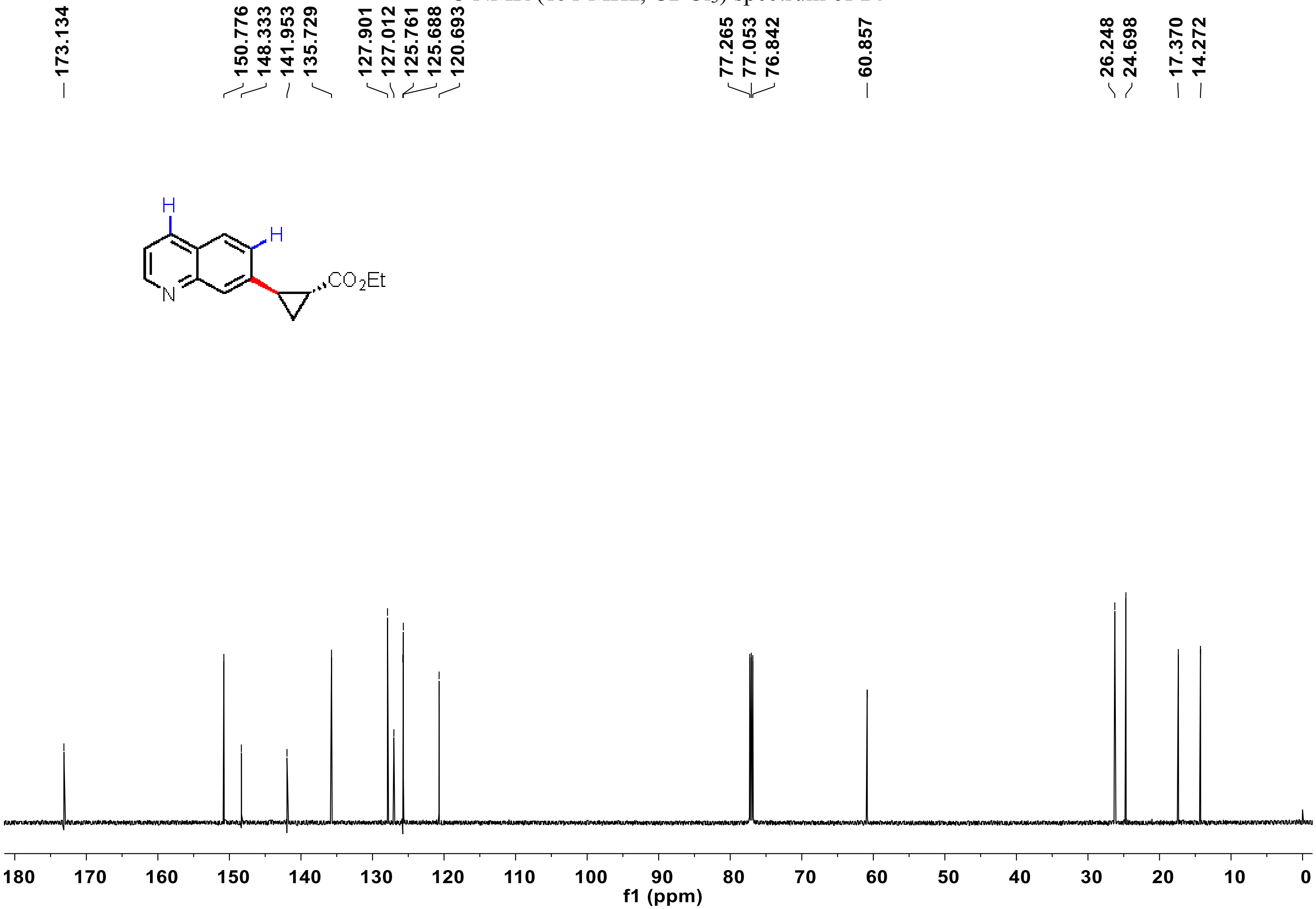
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **13**



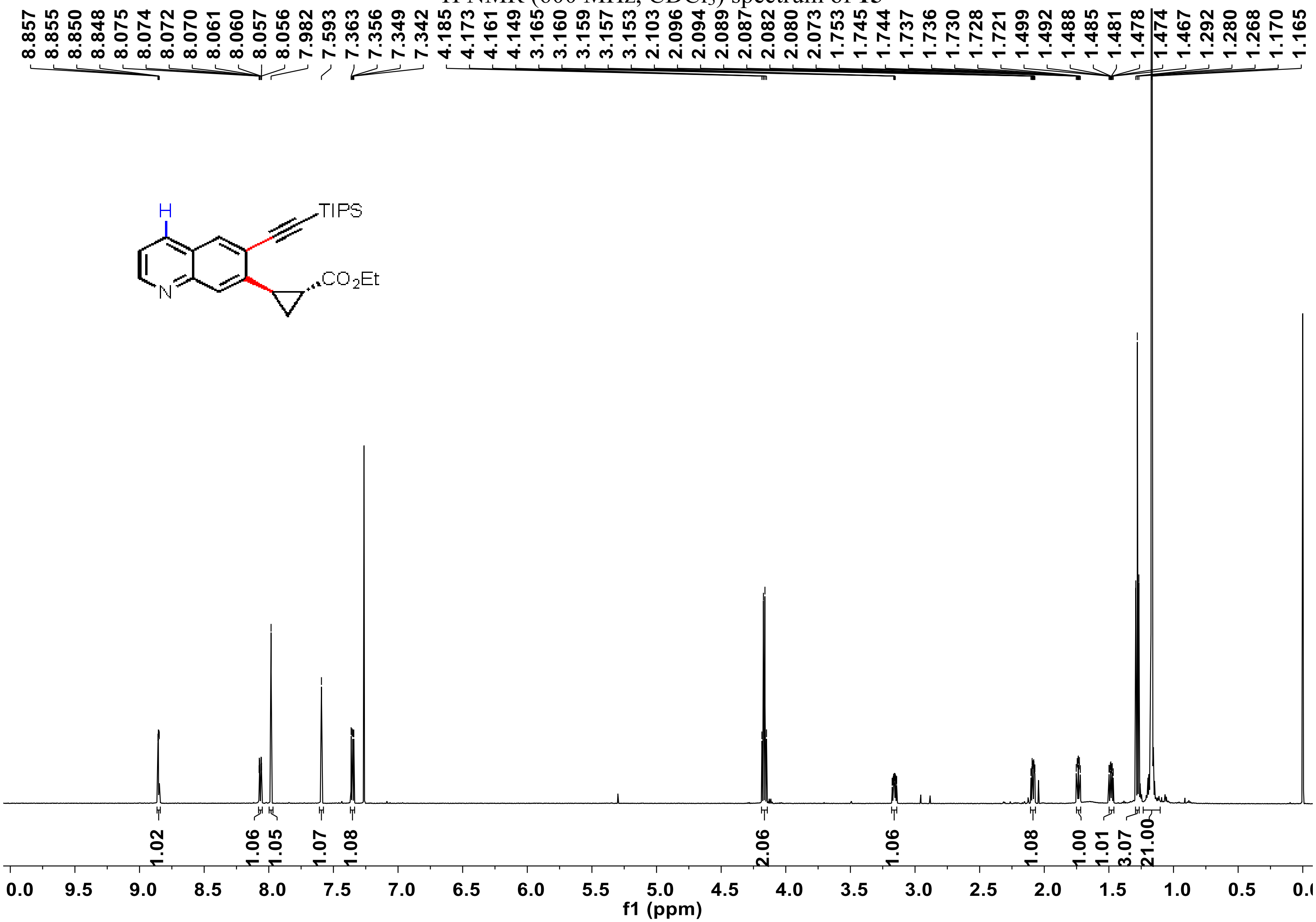
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14**



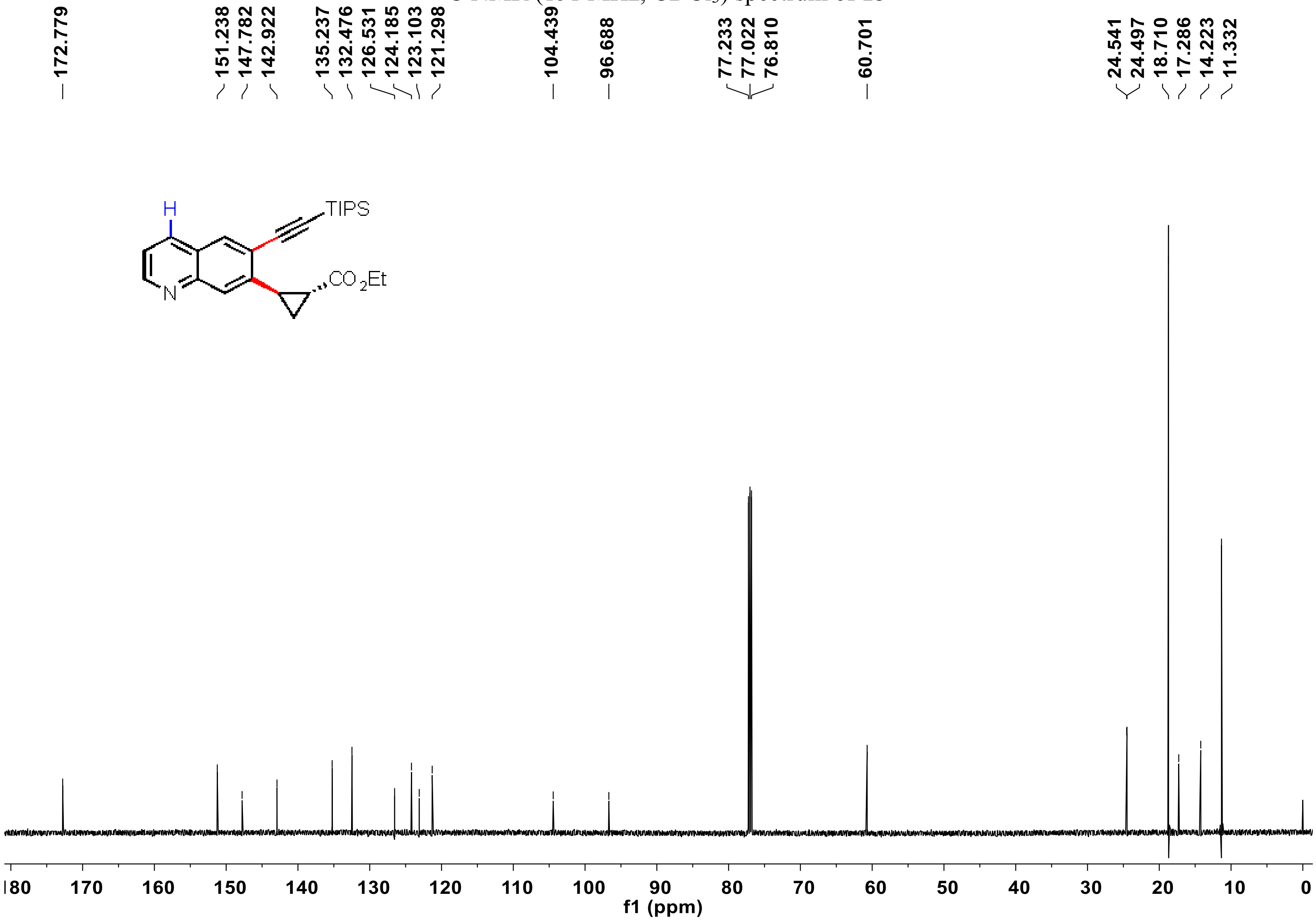
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **14**



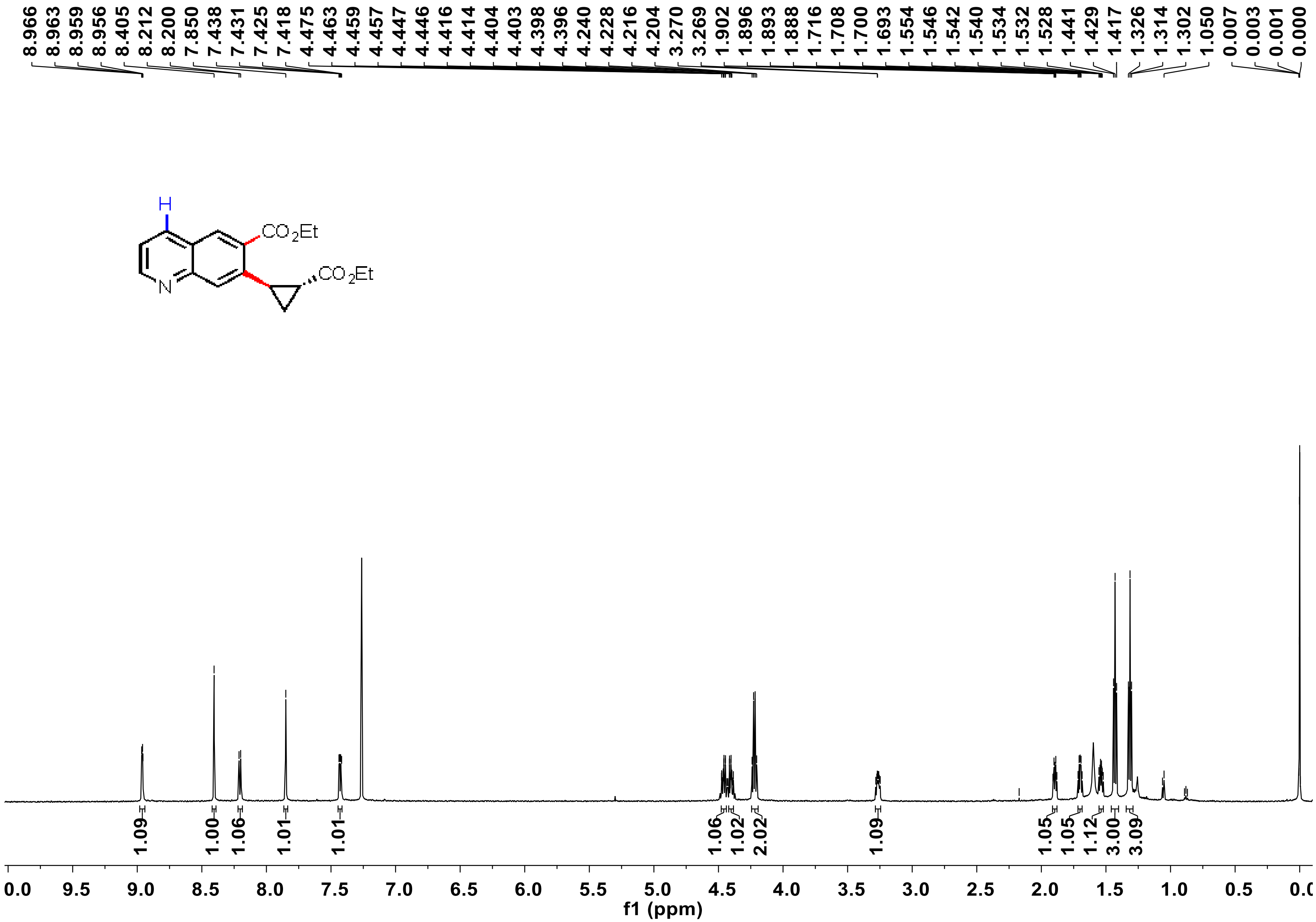
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **15**



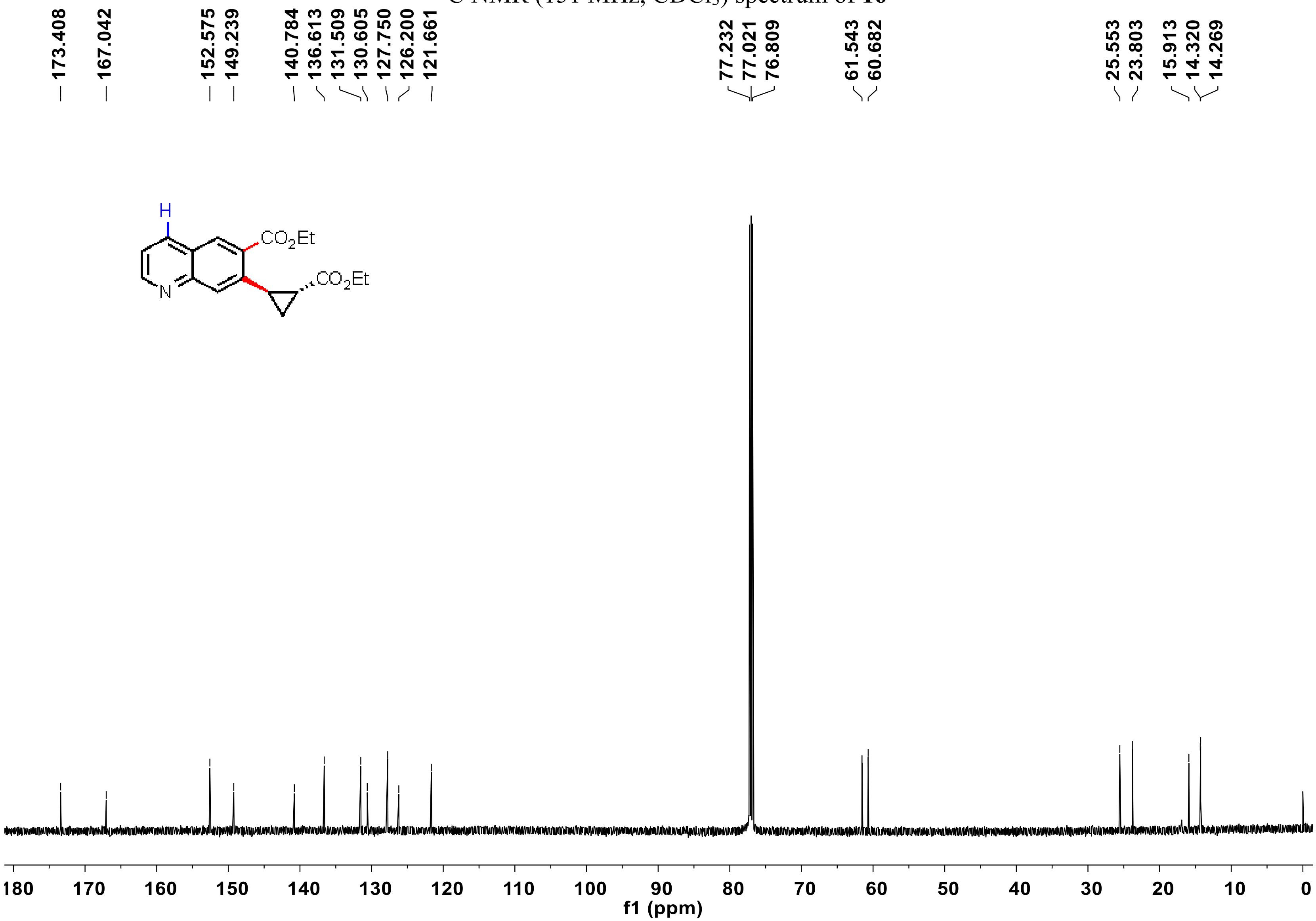
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **15**



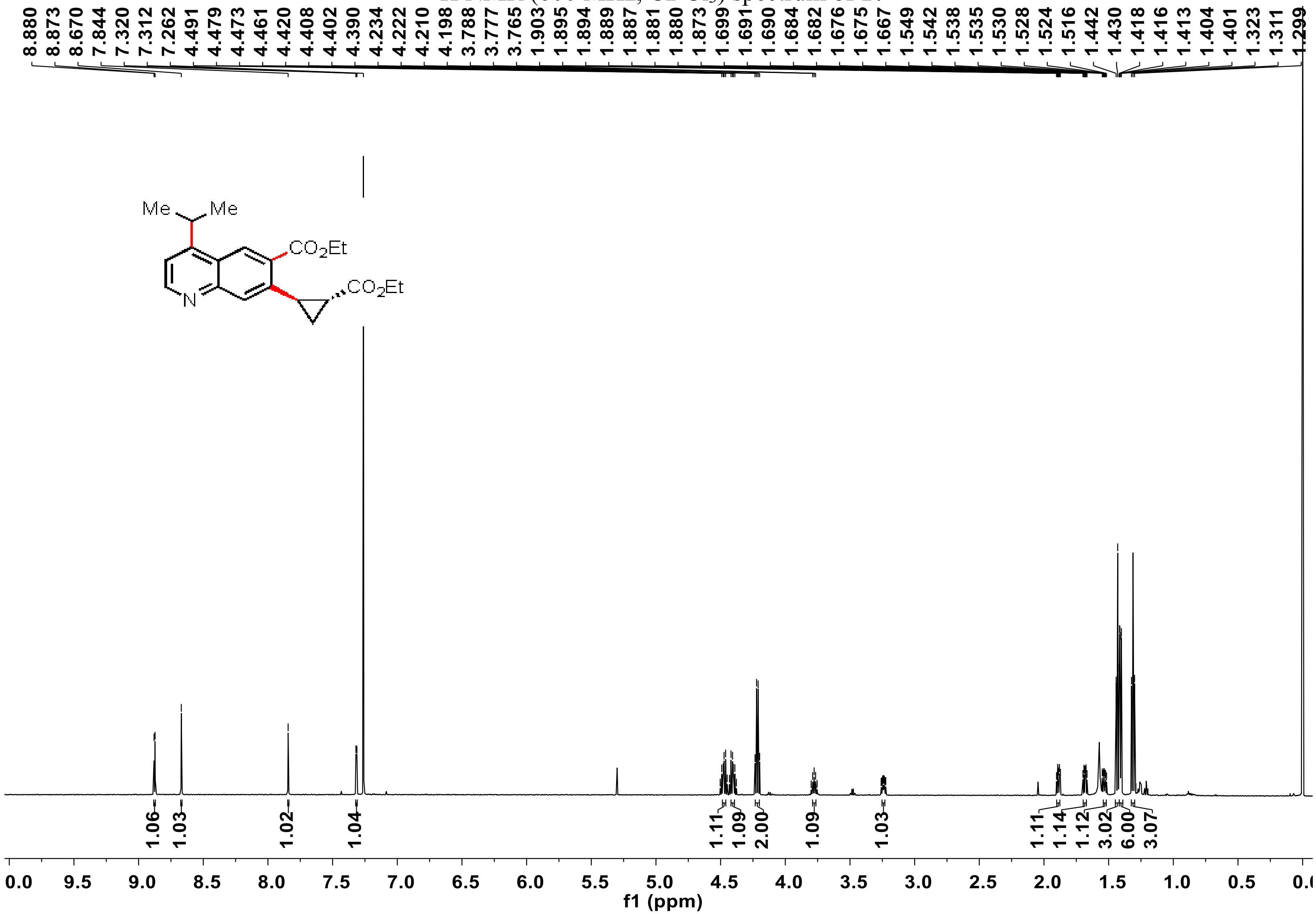
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **16**



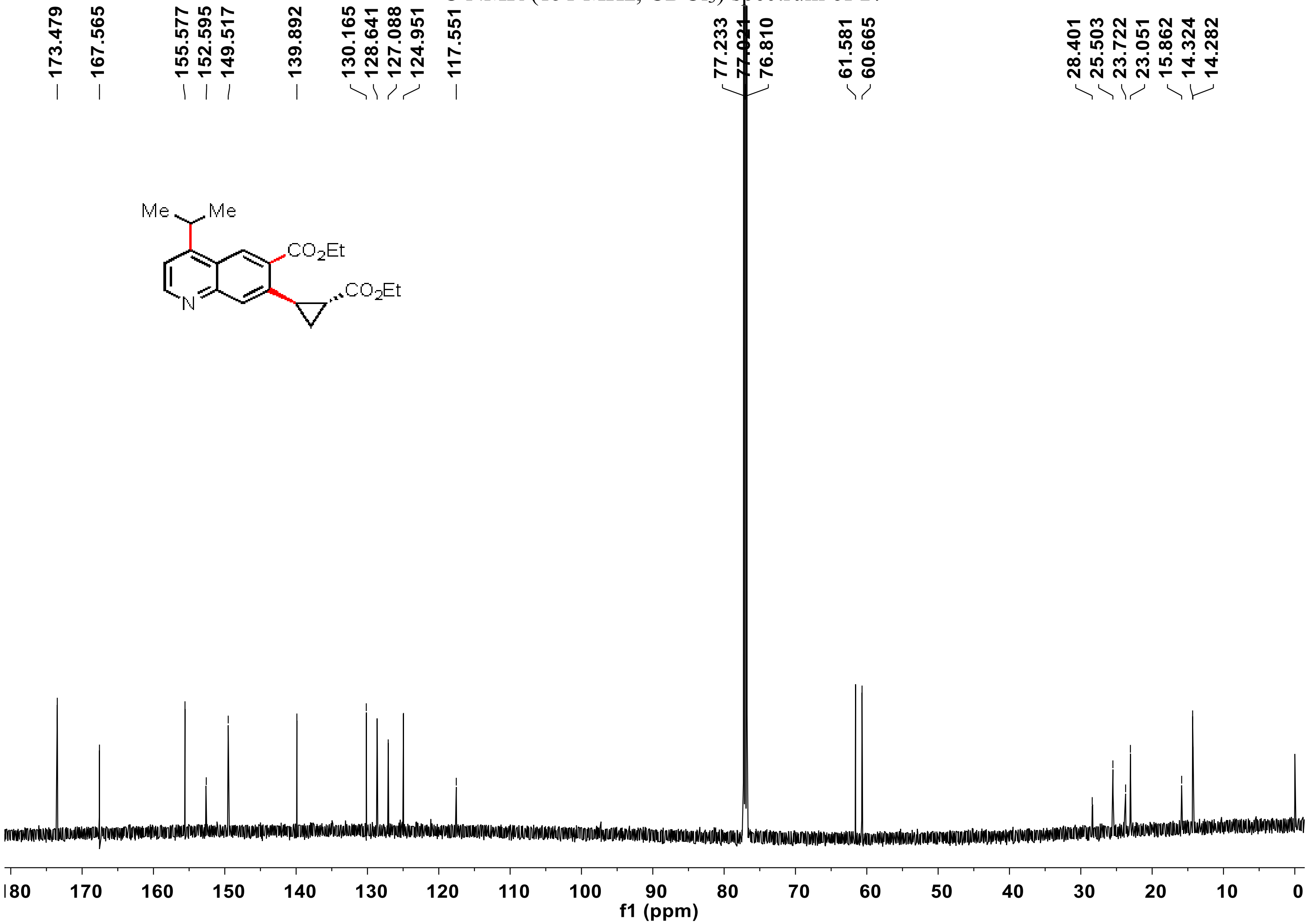
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **16**



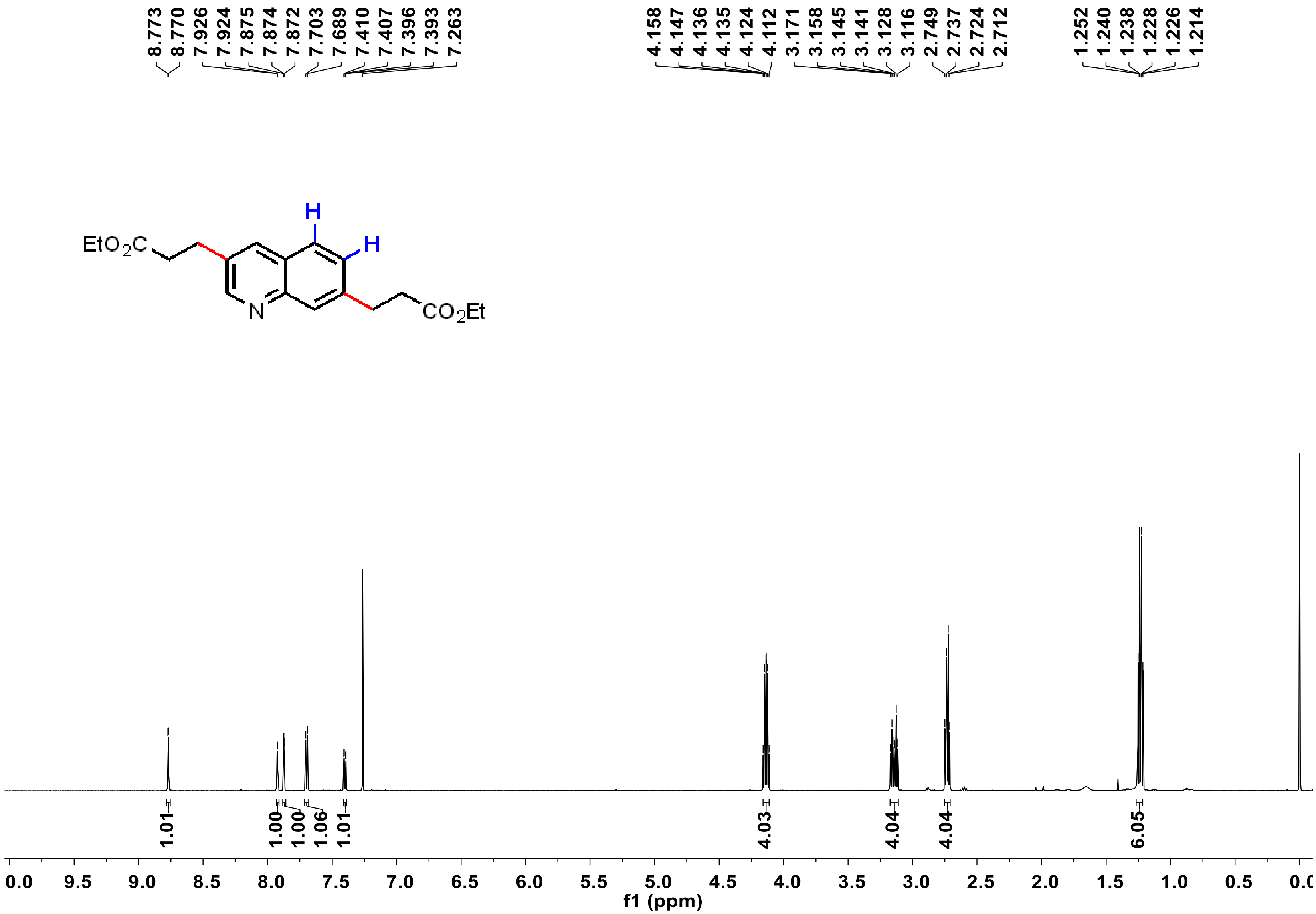
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **17**



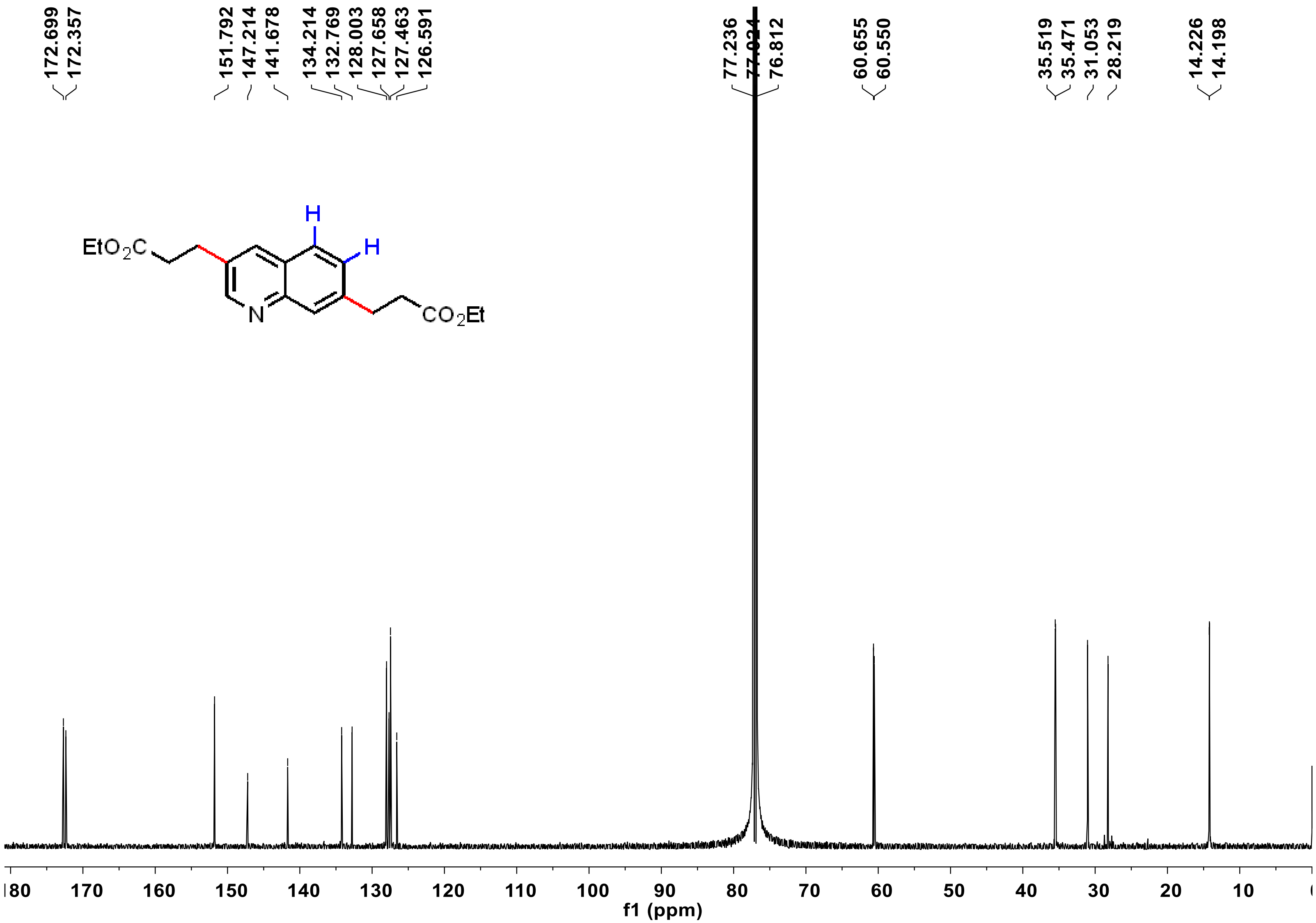
^{13}C NMR (151 MHz, CDCl$_3$) spectrum of **17**



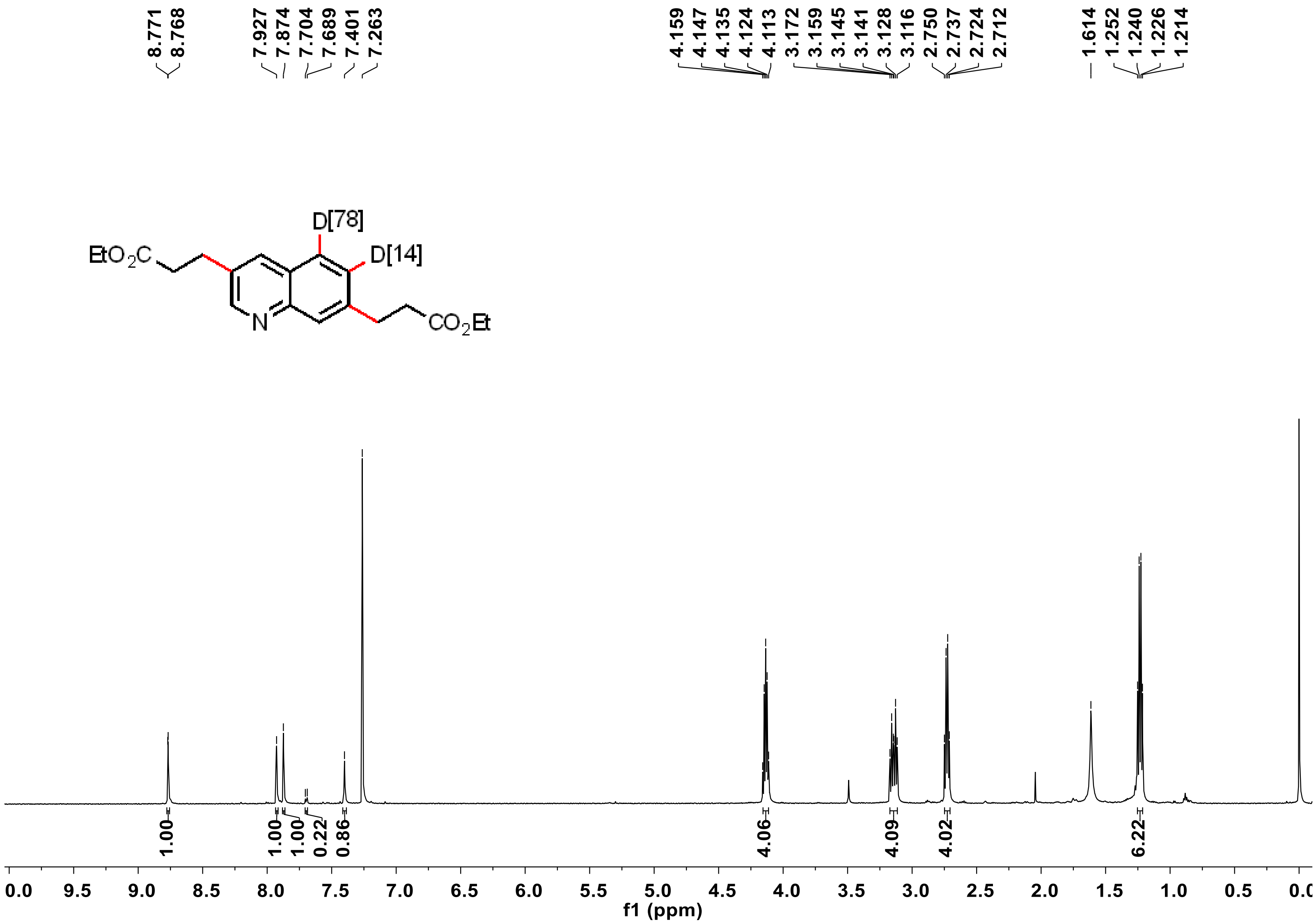
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **18**



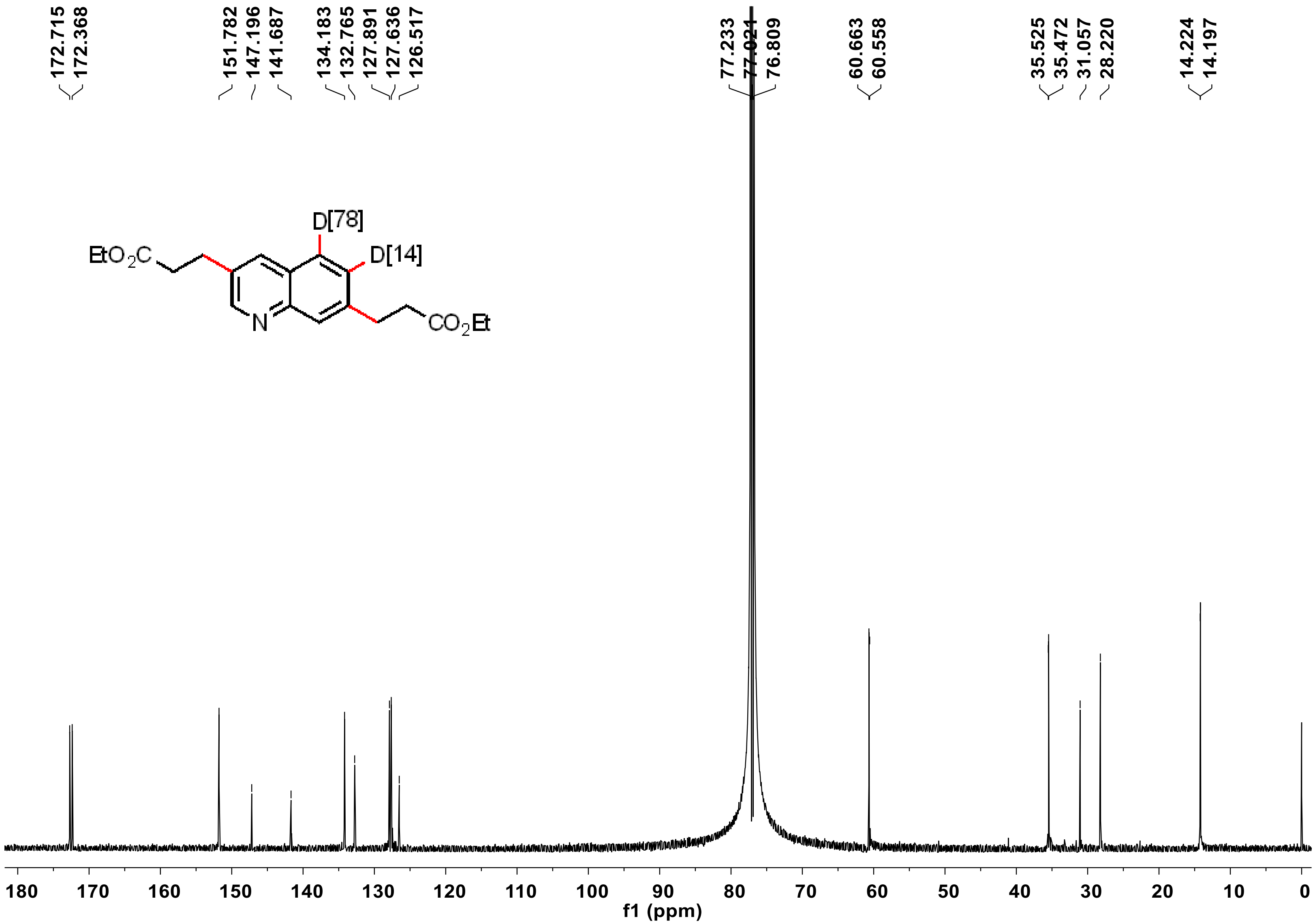
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **18**



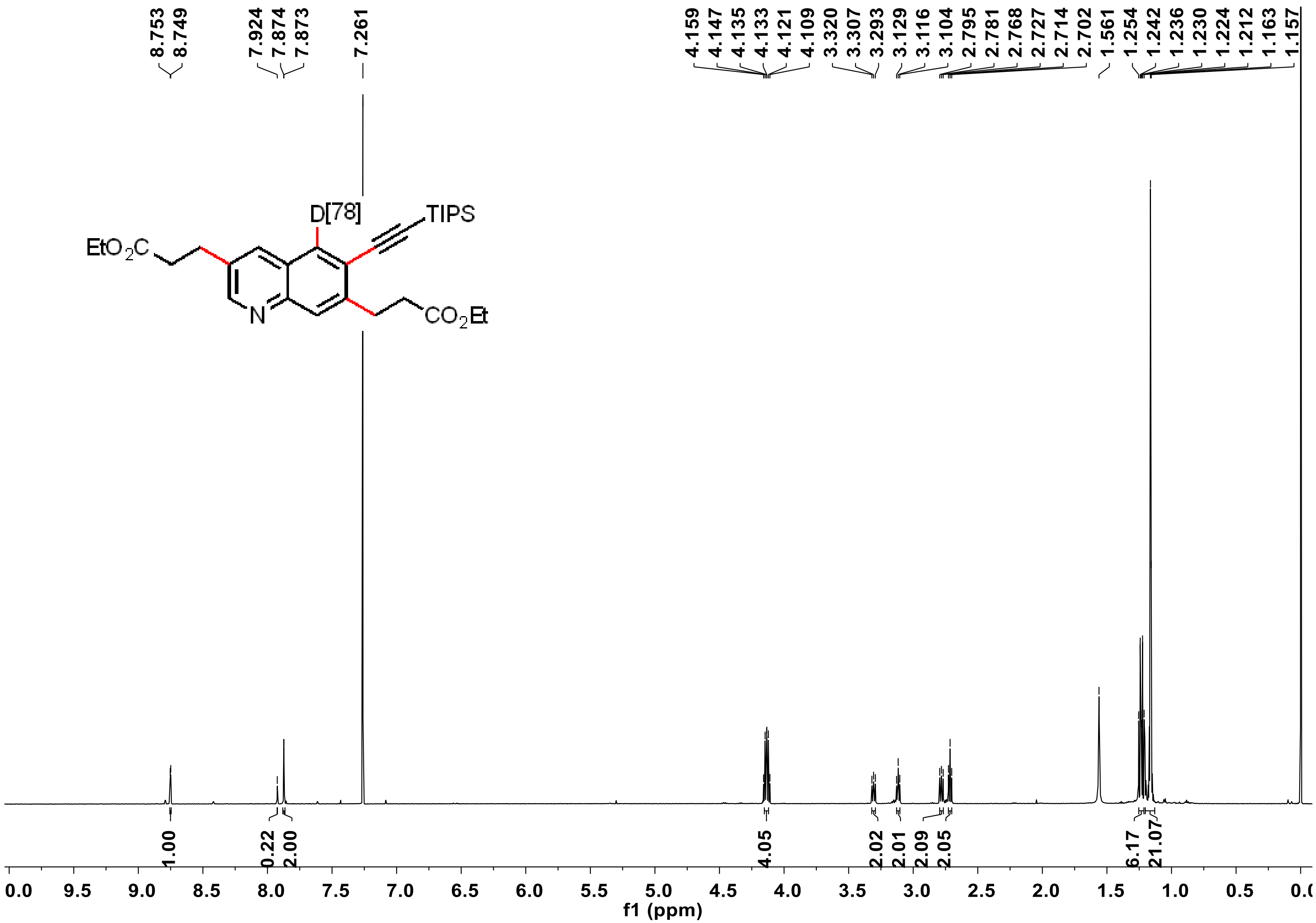
[1]H NMR (600 MHz, $CDCl_3$) spectrum of **19**



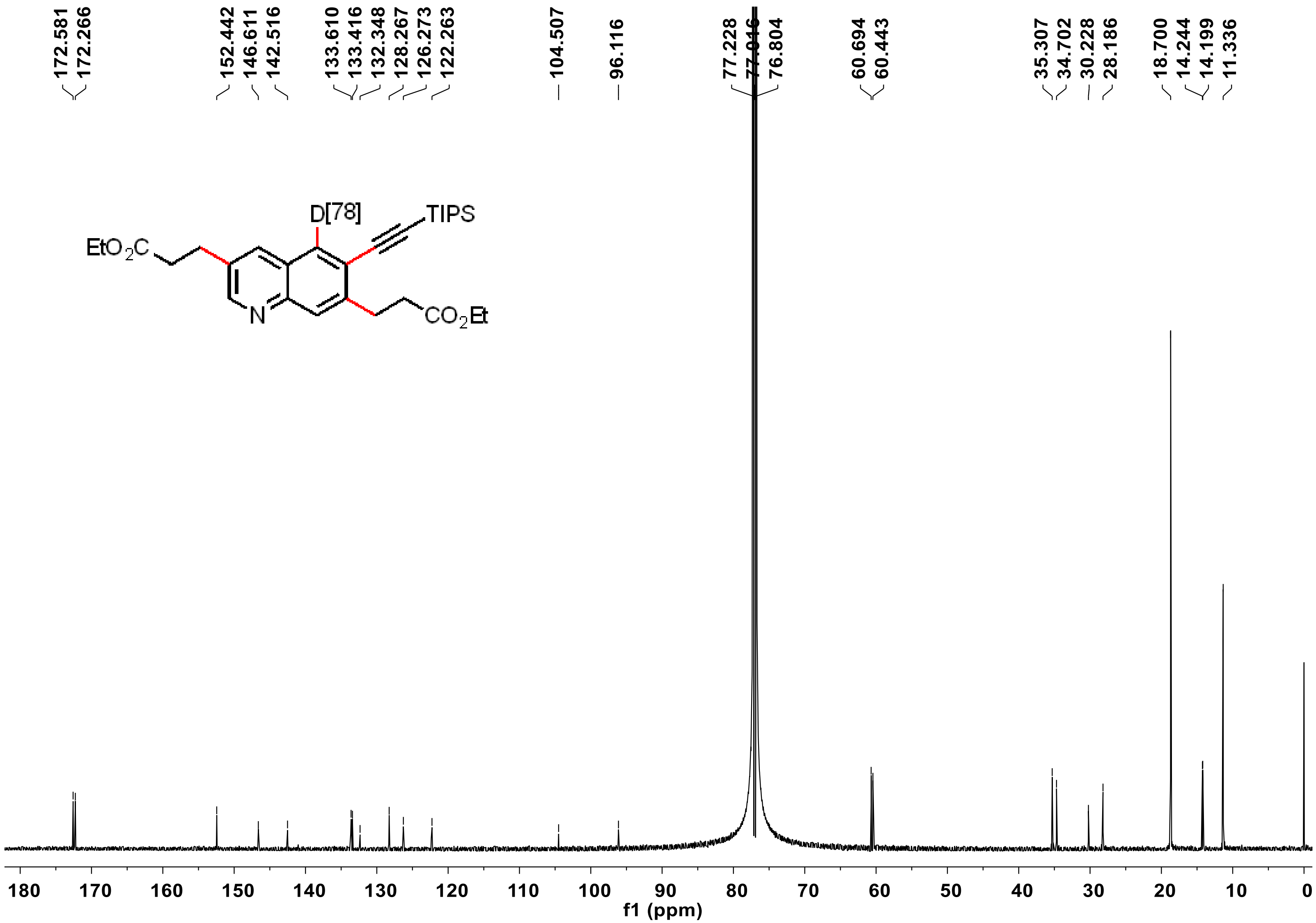
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **19**



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20**



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **20**



6. References

1 Ellingboe, J. W. *et al.* Antihyperglycemic activity of novel naphthalenyl 3H-l,2,3,5-Oxathiadiazole 2-Oxides. *J. Med. Chem.* **36**, 2485-2493 (1993).

2 Aguilar Izquierdo, N., Carrascal Riera, M., Castro Palomino Laria, J. C. & Erra Sola, M. Oxadiazole derivatives as slpl receptor agonists. WO 2010081692A1 (2010).

3 Xu, T. & Dong, G. Rhodium-catalyzed regioselective carboacylation of olefins: a C-C bond activation approach for accessing fused-ring systems. *Angew. Chem. Int. Ed.* **51**, 7567-7571 (2012).

4 Chen, P.-H., Savage, N. A. & Dong, G. Concise synthesis of functionalized benzocyclobutenones. *Tetrahedron* **70**, 4135-4146 (2014).

5 Willis, M. C., Brace, G. N. & Holmes, I. P. Palladium-catalyzed tandem alkenyl and aryl C-N bond formation: a cascade *N*-annulation route to 1-functionalized indoles. *Angew. Chem. Int. Ed.* **44**, 403-406 (2005).

6 Lenoir, D., Glaser, R., Mison, P. & Schleyer, P. V. R. Synthesis of 1,2- and 2,4-disubstituted adamantanes. The protoadamantane route. *J. Org. Chem.* **36**, 1821-1826 (1971).

7 Jolliffe, J. D., Armstrong, R. J. & Smith, M. D. Catalytic enantioselective synthesis of atropisomeric biaryls by a cation-directed *O*-alkylation. *Nat. Chem.* **9**, 558-562 (2017).

8 Clark, A. H., McCorvy, J. D., Watts, V. J. & Nichols, D. E. Assessment of dopamine D1 receptor affinity and efficacy of three tetracyclic conformationally-restricted analogs of SKF38393. *Bioorg. Med. Chem.* **19**, 5420-5431 (2011).

9 Beves, J. E. *et al.* Toward metal complexes that can directionally walk along tracks: controlled stepping of a molecular biped with a palladium(II) foot. *J. Am. Chem. Soc.* **136**, 2094-2100 (2014).

10 Zhao, Y. & Swager, T. M. Simultaneous chirality sensing of multiple amines by ^{19}F NMR. *J. Am. Chem. Soc.* **137**, 3221-3224 (2015).

11 Chen, Q., du Jourdin, X. M. & Knochel, P. Transition-metal-free BF_3-mediated regioselective direct alkylation and arylation of functionalized pyridines using Grignard or organozinc reagents. *J. Am. Chem. Soc.* **135**, 4958-4961 (2013).

12 Ye, M., Gao, G.-L. & Yu, J.-Q. Ligand-promoted C-3 selective C–H olefination of pyridines with Pd catalysts. *J. Am. Chem. Soc.* **133**, 6964-6967 (2011).

13 Zhang, Z., Tanaka, K. & Yu, J.-Q. Remote site-selective C–H activation directed by a catalytic bifunctional template. *Nature* **543**, 538-542 (2017).

14 Wang, X. *et al.* General and practical potassium methoxide/disilane-mediated dehalogenative deuteration of (hetero)arylhalides. *J. Am. Chem. Soc.* **140**, 10970-10974 (2018).

15 Monrad, R. N. & Madsen, R. Ruthenium-catalysed synthesis of 2- and 3-substituted quinolines from anilines and 1,3-diols. *Org. Biomol. Chem.* **9**, 610-615 (2011).

16 Gaussian 16 Rev. B.01 (Wallingford, CT, 2016).

17 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865-3868 (1996).

18 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **78**, 1396-1396 (1997).

19 Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456-1465 (2011).

20 Ditchfield, R., Hehre, W. J. & Pople, J. A. Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **54**, 724-728 (1971).

21 Hehre, W. J., Ditchfield, R. & Pople, J. A. Self—consistent molecular orbital methods. XII. Further extensions of Gaussian—type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **56**, 2257-2261 (1972).

22 Hariharan, P. C. & Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **28**, 213-222 (1973).

23 Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **82**, 299-310 (1985).

24 Roy, L. E., Hay, P. J. & Martin, R. L. Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.* **4**, 1029-1031 (2008).

25 Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **72**, 650-654 (1980).

26 Dolg, M., Wedig, U., Stoll, H. & Preuss, H. Energy-adjustedabinitiopseudopotentials for the first row transition elements. *J. Chem. Phys.* **86**, 866-872 (1987).

27 Nicklass, A., Dolg, M., Stoll, H. & Preuss, H. Ab initioenergy-adjusted pseudopotentials for the noble gases Ne through Xe: Calculation of atomic dipole and quadrupole polarizabilities. *J. Chem. Phys.* **102**, 8942-8952 (1995).

28 Tomasi, J., Mennucci, B. & Cammi, R. Quantum mechanical continuum solvation models. *Chem. Rev.* **105**, 2999-3094 (2005).

29 Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378-6396 (2009).

30 Richmond, E. *et al.* Ring-opening hydroarylation of monosubstituted cyclopropanes enabled by hexafluoroisopropanol. *Chem. Sci.* **9**, 6411-6416 (2018).

31 Fioroni, M., Burger, K., Mark, A. E. & Roccatano, D. Model of 1,1,1,3,3,3-hexafluoro-propan-2-ol for molecular dynamics simulations. *J. Phys. Chem. B* **105**, 10967-10975 (2001).

32 Park, H., Chekshin, N., Shen, P.-X. & Yu, J.-Q. Ligand-enabled, palladium-catalyzed beta-C(sp(3))-H arylation of Weinreb amides. *ACS Catal* **8**, 9292-9297 (2018).

33 Shi, H. *et al.* Differentiation and functionalization of remote C–H bonds in adjacent positions. *Nat. Chem.* **12**, 399-404 (2020).

34 Spartan’18 (Wavefunction, Inc. Irvine, CA, 2019).

35 Grimme, S. *et al.* Fully automated quantum-chemistry-based computation of spin-spin-coupled nuclear magnetic resonance spectra. *Angew. Chem. Int. Ed.* **56**, 14763-14769 (2017).

36 Grimme, S. Exploration of chemical compound, conformer, and reaction space with meta-dynamics simulations based on tight-binding quantum chemical calculations. *J. Chem. Theory Comput.* **15**, 2847-2862 (2019).

37 Grimme, S., Ehlert, S., Caldeweyher, E. & Pracht, P. A Robust non-self-consistent tight-binding quantum chemistry method for large molecules. *ChemRxiv* **preprint**, doi:10.26434/chemrxiv.8326202.v1 (2019).

38 Bannwarth, C., Ehlert, S. & Grimme, S. GFN2-xTB-An accurate and broadly parametrized self-consistent tight-binding quantum chemical method with multipole

electrostatics and density-dependent dispersion contributions. *J. Chem. Theory Comput.* **15**, 1652-1671 (2019).

39 Grimme, S., Bannwarth, C. & Shushkov, P. A robust and accurate tight-binding quantum chemical method for structures, vibrational frequencies, and noncovalent interactions of large molecular systems parametrized for all spd-block elements (Z = 1-86). *J. Chem. Theory Comput.* **13**, 1989-2009 (2017).

40 Grimme, S. Supramolecular binding thermodynamics by dispersion-corrected density functional theory. *Chemistry* **18**, 9955-9964 (2012).

41 Li, Y.-P., Gomes, J., Mallikarjun Sharada, S., Bell, A. T. & Head-Gordon, M. Improved Force-Field parameters for QM/MM simulations of the energies of adsorption for molecules in Zeolites and a free rotor correction to the rigid rotor Harmonic Oscillator model for adsorption enthalpies. *J. Phys. Chem. C* **119**, 1840-1850 (2015).

42 Luchini, G. A.-R. J. V. G., Y.; Funes-Ardoiz, I.; Paton, R. S. (2019). *GoodVibes v3.0.1* (2019).

43 CYLView, 1.0b (Université de Sherbrooke, http://www.cylview.org, Canada, 2009).

44 Buhl, M., Reimann, C., Pantazis, D. A., Bredow, T. & Neese, F. Geometries of third-row transition-metal complexes from density-functional theory. *J. Chem. Theory Comput.* **4**, 1449-1459 (2008).

45 Jimenez-Hoyos, C. A., Janesko, B. G. & Scuseria, G. E. Evaluation of range-separated hybrid and other density functional approaches on test sets relevant for transition metal-based homogeneous catalysts. *J Phys Chem A* **113**, 11742-11749 (2009).

46 Waller, M. P., Braun, H., Hojdis, N. & Buhl, M. Geometries of second-row transition-metal complexes from density-functional theory. *J. Chem. Theory Comput.* **3**, 2234-2242 (2007).

47 Dohm, S., Hansen, A., Steinmetz, M., Grimme, S. & Checinski, M. P. Comprehensive thermochemical benchmark set of realistic closed-shell metal organic reactions. *J. Chem. Theory Comput.* **14**, 2596-2608 (2018).

48 Husch, T., Freitag, L. & Reiher, M. Calculation of ligand dissociation energies in large transition-metal complexes. *J. Chem. Theory Comput.* **14**, 2456-2468 (2018).

49 Steinmetz, M. & Grimme, S. Benchmark study of the performance of density functional theory for bond activations with (ni,pd)-based transition-metal catalysts. *ChemistryOpen* **2**, 115-124 (2013).