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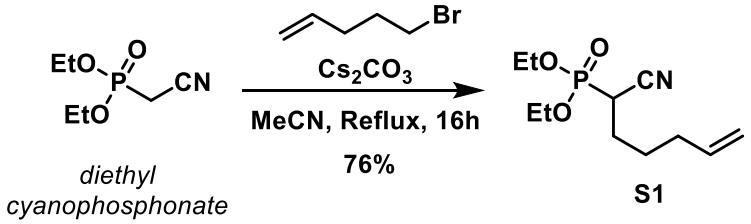
A. General Experimental Information

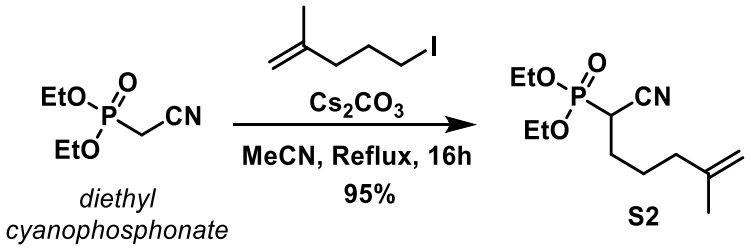
All reactions were performed in oven-dried (120 °C) or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Reaction solvents including dichloromethane (CH_2Cl_2, Fisher, HPLC Grade), hexanes (Fisher, HPLC Grade), diethyl ether (Et_2O, Fisher, BHT stabilized, HPLC Grade), benzene (C_6H_6, Fisher, HPLC Grade), tetrahydrofuran (THF, Fisher, HPLC Grade), and toluene ($PhCH_3$, Fisher, HPLC Grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Solvents for workup and chromatography were: hexanes (Fisher or EMD, ACS Grade), EtOAc (Fisher, ACS Grade), dichloromethane (CH_2Cl_2, Fisher, ACS Grade), and diethyl ether (Fisher, ACS Grade). Column chromatography was performed using EMD Millipore 60 Å (0.040–0.063 mm) mesh silica gel (SiO_2). Analytical and preparatory thin-layer chromatography was performed on Merck silica gel 60 F254 TLC plates. Visualization was accomplished with UV (254 or 210 nm), and *p*-anisaldehyde, vanillin, potassium permanganate, 2,4-dinitrophenylhydrazine, or ceric ammonium molybdate and heat as developing agents. Chloroform-d ($CDCl_3$, D 99.8%, DLM-7) was purchased from Cambridge Isotope Laboratories. K_2CO_3 (anhydrous, 99%, Alfa Aesar), $NaHCO_3$ (ACS grade, Fisher), NaOH (ACS grade, Macron or Fisher), $Na_2S_2O_3$ (ACS grade, Fisher), triethylamine (Et_3N, EMD, CaH_2) and pyridine (Alfa Aesar, CaH_2),were distilled from the indicated drying agents prior to use. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded at 298K on a Bruker CRYO500 (500 MHz, ^1H; 125 MHz, ^{13}C) or a Bruker AVANCE600 (600 MHz, ^1H; 151 MHz, ^{13}C) spectrometer with solvent resonance as the internal standard (^1H NMR: $CHCl_3$ at 7.26 ppm, ^{13}C NMR: $CDCl_3$ at 77.16 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tdd = triplet of doublet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz), and integration. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier spectrometer using ESI-TOF (electrospray ionization-time of flight) and data

are reported in the form of (m/z). To quantify the extent of deuterium incorporation, the purified samples were analyzed by isotope ratio mass spectrometry modeling (flow injection analysis). Catalysts **C1**[1], **C2**[2], **C3**[3], **C4**[4] and **C5**[5] were prepared as described in the literature and used without further purification.

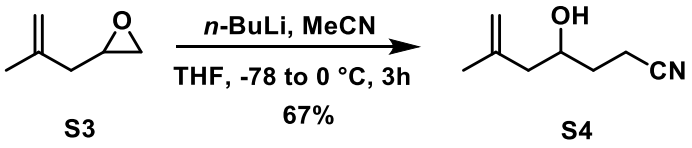
B. α,β-Unsaturated Nitrile Substrate Synthesis and Characterization



To a solution of diethyl cyanophosphonate (1.77 g, 10.0 mmol, 1.0 equiv.) in MeCN (36 mL) was added Cs_2CO_3 (3.26 g, 10 mmol, 1.0 equiv.) followed by 5-bromo-1-pentene (1.80 g, 12.1 mmol, 1.2 equiv.). The resulting suspension was heated to reflux for 16 h, cooled to ambient temperature and the volatiles were removed *in vacuo*. The resulting residue was partitioned between H_2O (20 mL) and EtOAc (40 mL) and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo.* The resulting crude residue was purified via flash column chromatography using a mixture of MeOH/ DCM (2:98) as eluent to give **S1** as a colorless oil (1.86 g, 7.60 mmol, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 4.28 – 4.15 (m, 4H), 2.89 (ddd, *J* = 23.7, 10.3, 4.7 Hz, 1H), 2.17 – 2.04 (m, 2H), 1.96 – 1.82 (m, 2H), 1.81 – 1.73 (m, 1H), 1.63 – 1.52 (m, 1H), 1.37 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.3, 116.3 (d, *J* = 9.3 Hz), 115.8, 64.2 (d, *J* = 7.0 Hz), 63.8 (d, *J* = 6.8 Hz), 32.8, 30.0 (d, *J* = 143.8 Hz), 27.1 (d, *J* = 12.2 Hz), 26.5 (d, *J* = 4.3 Hz), 16.50 (d, *J* = 2.5 Hz), 16.46 (d, *J* = 2.5 Hz); **HRMS** (ES+) *m/z* calc'd for $C_{11}H_{20}NO_3PH$ $[M+H]^+$: 246.1259, found 246.1259.

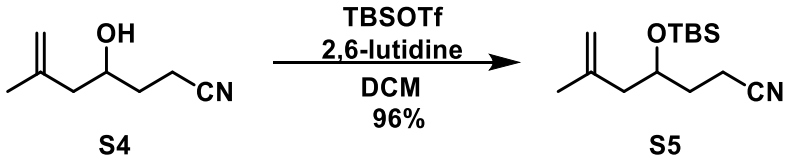


To a solution of diethyl cyanophosphonate (1.32 g, 7.48 mmol, 1.0 equiv.) in MeCN (30 mL) was added Cs_2CO_3 (2.44 g, 7.48 mmol, 1.0 equiv.) followed by 5-iodo-2-methylpent-1-ene[6] (1.90 g, 9.05 mmol, 1.2 equiv.). The resulting suspension was heated to reflux for 16 h, then the volatiles were removed *in vacuo*. The resulting residue was partitioned between H_2O (20 mL) and EtOAc (40 mL) and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo.* The resulting crude residue was purified via flash column chromatography using a mixture of EtOAc/ hexanes (35:65) as eluent to give **S2** as a colorless oil (1.84 g, 7.09 mmol, 95% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.69 (s, 1H), 4.28 – 4.18 (m, 4H), 2.91 (ddd, *J* = 23.7, 10.1, 4.6 Hz, 1H), 2.14 – 2.02 (m, 2H), 1.93 – 1.79 (m, 3H), 1.71 (s, 3H), 1.65 – 1.58 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.4, 116.4 (d, *J* = 9.3 Hz), 111.1, 64.2 (d, *J* = 7.0 Hz), 63.8 (d, *J* = 6.8 Hz), 36.9, 30.1 (d, *J* = 143.7 Hz), 26.6 (d, *J* = 4.3 Hz), 25.7 (d, *J* = 12.2 Hz), 22.3, 16.53 (d, *J* = 3.3 Hz), 16.50 (d, *J* = 3.3 Hz); **HRMS** (ES+) *m/z* calc'd for $C_{12}H_{22}NO_3PNa$ $[M+Na]^+$: 282.1235, found 282.1233.

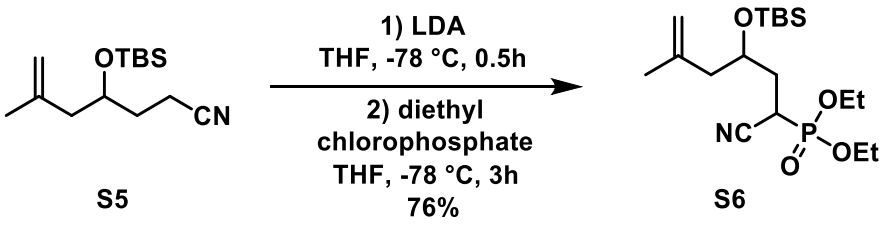


To a solution of acetonitrile (2.24 mL, 41.1 mmol, 2.0 equiv.) in THF (70 mL) was added a 1.6 M solution of *n*-butyllithium (18.7 mL, 30.0 mmol, 1.4 equiv.) in hexanes at –78 °C. The resulting solution was stirred for 1 h, then a solution of epoxide **S3**[7] (2.1 g, 21.4 mmol, 1.0 equiv.) in THF (10 mL) was added over a period of 3 minutes. The mixture was warmed to 0 °C, stirred for 3 hours and then quenched with satd. $NH_4Cl_{(aq)}$ (30 mL). The aqueous phase was extracted with EtOAc (3 x 20 mL), the combined

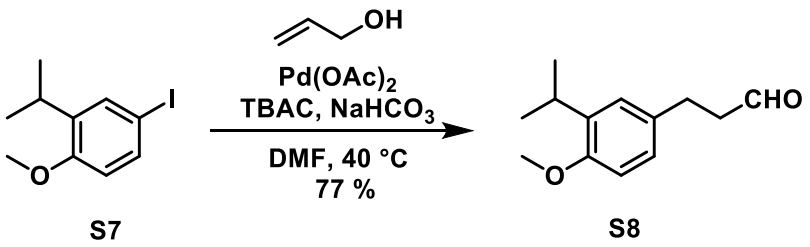
organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography using a mixture of EtOAc/ hexanes (30:70) as eluent to give **S4** as a colorless oil (2.00 g, 14.3 mmol, 67% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.82 (s, 1H), 3.84 (tt, *J* = 9.2, 3.4 Hz, 1H), 2.54 (td, *J* = 7.1, 3.9 Hz, 2H), 2.21 (dd, *J* = 13.6, 3.6 Hz, 1H), 2.14 (dd, *J* = 13.6, 9.3 Hz, 1H), 1.89 – 1.82 (m, 2H), 1.77 (s, 3H), 1.75 – 1.68 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.8, 120.0, 114.5, 66.6, 46.2, 32.5, 22.5, 13.9; **HRMS** (ES+) *m/z* calc'd for $C_{16}H_{26}N_2O_2Na$ $[2M+Na]^+$: 301.1892, found 301.1892.



To a solution of alcohol **S4** (2.00 g, 14.3 mmol, 1.0 equiv.) and 2,6-lutidine (5.00 mL, 43.2 mmol, 3.0 equiv.) in DCM (20 mL) was added TBSOTf (4.96 mL, 21.6 mmol, 1.5 equiv.). The mixture stirred for 1 hour at ambient temperature, then methanol (5.0 mL) was added. The volatiles were removed *in vacuo*, and the resulting crude residue was directly purified via flash chromatography using a mixture of EtOAc/hexanes (10:90) as eluent to give silyl ether **S5** as a colorless oil (3.52 g, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.72 (s, 1H), 4.01 – 3.82 (m, 1H), 2.46 – 2.34 (m, 2H), 2.28 (dd, *J* = 13.6, 4.9 Hz, 1H), 2.12 (dd, *J* = 13.6, 8.3 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.73 (s, 3H), 1.66 (td, *J* = 14.1, 6.9 Hz, 1H), 0.89 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 120.1, 113.9, 68.8, 46.0, 32.0, 25.9, 23.0, 18.1, 13.2, –4.2, –4.7; **HRMS** (ES+) *m/z* calc'd for $C_{14}H_{27}NOSiNa$ $[M+Na]^+$: 276.1760, found 276.1764.



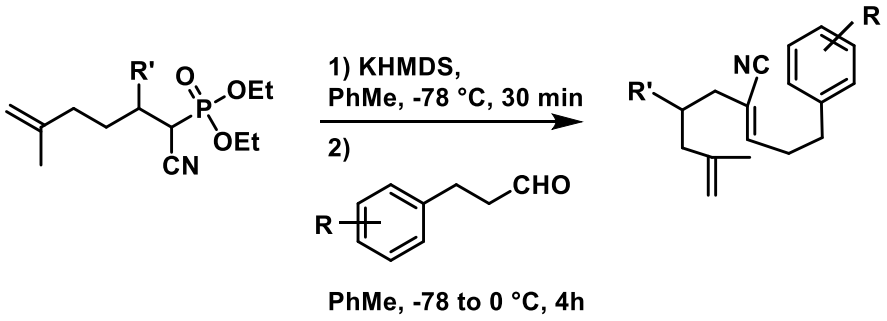
To a solution of diisopropylamine (2.08 mL, 14.7 mmol, 2.2 equiv.) in THF (25 mL) was added a 1.6 M solution of *n*-butyllithium (8.79 mL, 14.1 mmol, 2.1 equiv.) at –78 °C. The mixture was allowed to warm to 0 °C, stirred for 30 minutes and cooled back down to –78 °C. A solution of nitrile **S5** (1.7 g, 6.7 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise and the mixture was stirred for 30 minutes at –78 °C. Diethyl chlorophosphate (1.07 mL, 7.37 mmol, 1.1 equiv.) was added dropwise (neat). After stirring for 3 hours at –78 °C, satd. $NH_4Cl_{(aq)}$ (30 mL) was added to the reaction mixture. The aqueous phase was extracted with EtOAc (3 x 20 mL), the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography, using a mixture of EtOAc/hexanes (30:70) as eluent to give an inconsequential mixture (2:1) of cyanophosphonate **S6** diastereomers as a colorless oil (1.98 g, 5.1 mmol, 76% yield). *Note: signals are reported for the major diastereomer only*. **^{1}H NMR** (600 MHz, $CDCl_3$) δ4.81 (*major*-s, 1H), 4.74 (*major*-s, 1H), 4.29 – 4.18 (*overlapping* m, 4H), 4.05 – 3.99 (*major*-m, 1H), 3.17 (*overlapping* -ddd, J = 23.2, 12.4, 3.3 Hz, 1H), 2.38 (*major*-dd, J = 13.6, 4.0 Hz, 1H), 2.27 (*major*-qd, J = 13.7, 6.5 Hz, 1H), 2.15 (*overlapping*- dd, J = 13.6, 9.0 Hz, 1H), 2.03 – 1.92 (*overlapping* m, 1H), 1.83 – 1.76 (*major*-m, 1H), 1.74 (*major*- s, 3H), 1.37 (*overlapping*- t, J = 7.1 Hz, 6H), 0.89 (*overlapping*- s, 9H), 0.14 (*major*-s, 3H), 0.12 (*major*-s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ141.19 (*major*), 116.24 (*major*-d, J = 9.3 Hz), 114.07 (*major*), 67.93 (d, J = 13.8 Hz), 64.04 (*major*-d, J = 6.9 Hz), 63.72 (*major*-d, J = 6.8 Hz), 46.48 (*major*), 33.78 (*major*-d, J = 4.0 Hz), 26.96 (*major*-d, J = 145.5 Hz), 25.85 (*overlapping*), 22.85 (*major*), 18.01 (*major*), 16.41 (*overlapping*-d, J = 3.2 Hz), 16.37 (*overlapping*-d, J = 3.2 Hz), –4.05 (*major*), –4.77 (*major*); **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{36}NO_4PSiNa$ $[M+Na]^+$: 412.2044, found 412.2036.



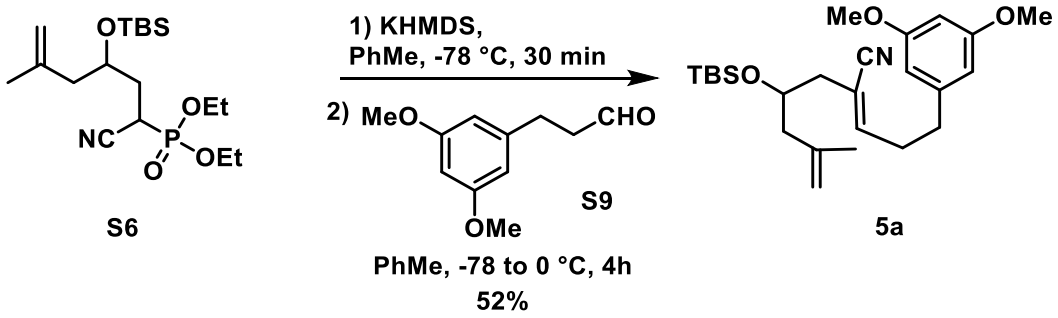
S7 **S8**

To a solution of iodoanisole **S7**[8] (3.50 g, 12.7 mmol, 1.0 equiv.) in degassed DMF (50 mL) was added tetrabutylammonium chloride (3.53 g, 12.7 mmol, 1.0 equiv.), allyl alcohol (1.72 mL, 25.4 mmol, 2.0 equiv.), sodium bicarbonate (2.67 g, 31.8 mmol, 2.5 equiv.), and finally $Pd(OAc)_2$ (144 mg, 0.64 mmol, 0.05 equiv.). The resulting mixture was stirred at 40 °C for 6 hours, then Et_2O (80 mL) was added and the organic phases were washed with DI H_2O (3x 30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified via flash column chromatography (EtOAc/hexanes 4:96) to give aldehyde **S8** as a clear yellow oil (2.02 g, 9.78 mmol, 77% yield).**^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.03 (s, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 3.81 (s, 3H), 3.30 (septet, J = 6.9 Hz, 1H), 2.91 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 1.21 (d, J = 7.0 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.1, 155.5, 137.3, 132.2, 126.2, 126.1, 110.6, 55.6, 45.8, 27.7, 26.9, 22.8 (2C); **HRMS** (ES+) *m/z* calc'd for $C_{13}H_{18}O_2Na$ $[M + Na]^+$: 229.1205, found 229.1209.

General Procedure A (HWE reaction for the synthesis of α,β-unsaturated nitrile substrates):

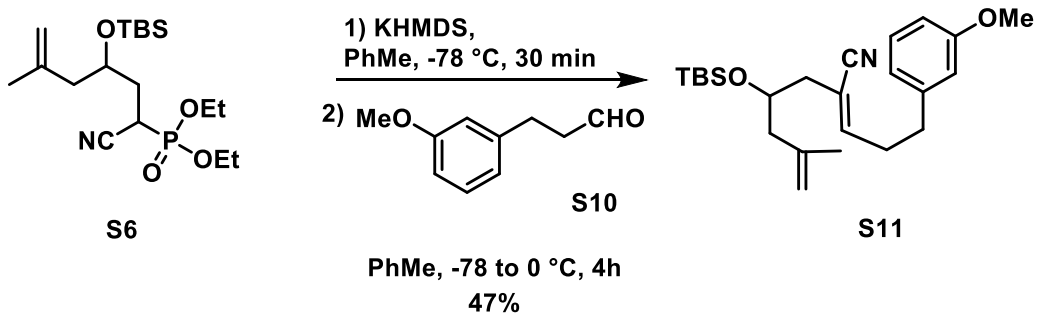


To a cooled (−78 °C) solution of cyanophosphonate **S1**, **S2** or **S6** (1.5 mmol, 1.0 equiv.) in dry toluene (15 mL) was added dropwise a solution of KHMDS (3.0 mL, 1.0 equiv., 0.5 M in toluene). After stirring for at least 30 min at −78 °C, a solution of aldehyde (1.5 mmol, 1.0 equiv.) was added dropwise in dry toluene (15 mL). The resulting solution was stirred at −78 °C for 1 h then allowed to warm to 0 °C and stirred for 3 h. Then, satd. $NH_4Cl_{(aq)}$ (10 mL) was added and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of Et_2O/hexanes or EtOAc/hexanes as eluent.

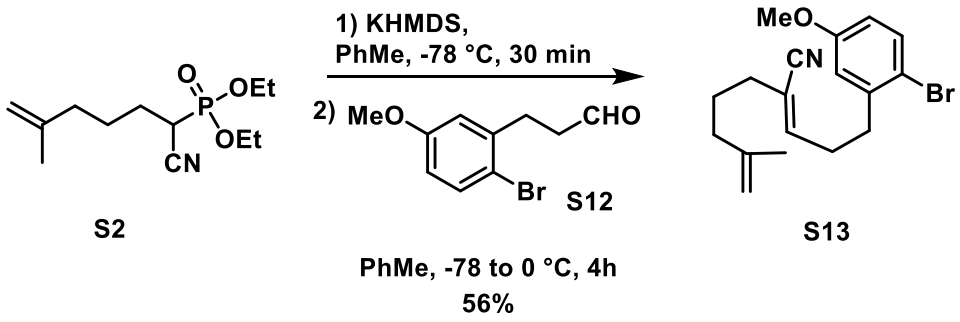


Prepared according to general procedure A, using cyanophosphonate **S6** *(2.62 mmol) and aldehyde* **S9**[9] *(2.75 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield of **5a**: 52% (586 mg, 1.36 mmol, colorless oil) of Z ; R_f= 0.15 (3:97 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.34 (d, *J* = 2.1 Hz, 2H), 6.32 (t, *J* = 2.2 Hz, 1H), 6.16 (t, *J* = 6.0 Hz, 1H), 4.79 (s, 1H), 4.69 (s, 1H), 3.98 (tt, *J* = 7.4,

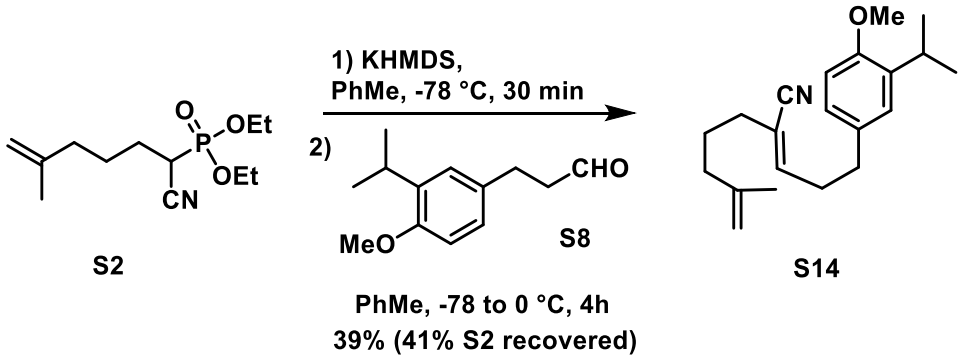
5.3 Hz, 1H), 3.78 (s, 6H), 2.75 – 2.62 (m, 4H), 2.37 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.20 (dd, *J* = 13.9, 5.0 Hz, 1H), 2.17 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.10 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.73 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 149.1, 142.7, 142.1, 117.8, 113.9, 112.8, 106.6, 98.4, 69.0, 55.4, 46.0, 41.7, 35.0, 33.0, 26.0, 23.1, 18.2, –4.4, –4.5; **HRMS** (ES+) *m/z* calc'd for $C_{25}H_{39}NO_3SiNa$ $[M + Na]^+$: 452.2597, found 452.2599.



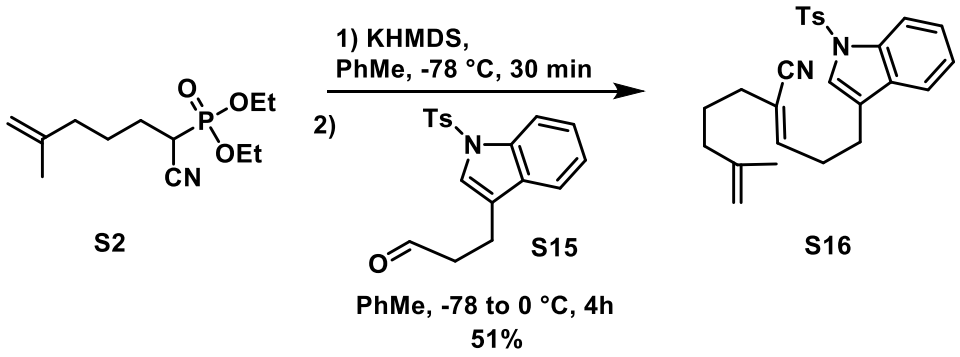
Prepared according to general procedure A, using cyanophosphonate **S6** *(1.16 mmol) and aldehyde* **S10**[10] *(1.22 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield of **S11**: 47% (218 mg, 0.545 mmol, colorless oil) of Z ; R_f=0.15 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.80 – 6.72 (m, 3H), 6.16 (t, *J* = 7.0 Hz, 1H), 4.80 (s, 1H), 4.69 (s, 1H), 3.98 (tt, *J* = 7.5, 4.9 Hz, 1H), 3.80 (s, 3H), 2.77 – 2.65 (m, 4H), 2.37 (dd, *J* = 14.0, 4.1 Hz, 1H), 2.21 (dd, *J* = 13.9, 5.6 Hz, 1H), 2.17 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.11 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.73 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 149.1, 142.1, 142.0, 129.7, 120.9, 117.8, 114.3, 113.9, 112.8, 111.8, 69.0, 55.3, 46.0, 41.7, 34.8, 33.1, 26.0, 23.1, 18.2, –4.4, –4.5; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{37}NO_2SiNa$ $[M + Na]^+$: 422.2491, found 422.2484.



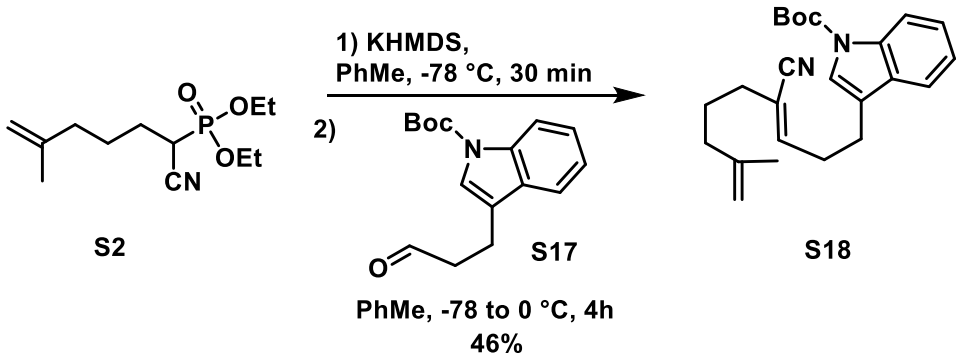
Prepared according to general procedure A, using cyanophosphonate **S2***(2.06 mmol) and aldehyde* **S12**[11]*(2.06 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield of **S13**: 56% (401 mg, 1.15 mmol, colorless oil) of Z ; R_f=0.15 (3:97 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 6.65 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.17 (t, *J* = 7.6 Hz, 1H), 4.73 (s, 1H), 4.66 (s, 1H), 3.78 (s, 3H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.66 (m, 2H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.68 – 1.61 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.2, 146.1, 144.8, 140.6, 133.6, 117.5, 116.2, 115.7, 114.9, 113.9, 110.8, 55.6, 36.7, 35.2, 33.8, 31.7, 25.9, 22.3; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{22}BrNONa$ $[M + Na]^+$: 370.0782, found 370.0775.



Prepared according to general procedure A, using cyanophosphonate **S2***(4.12 mmol) and aldehyde* **S8***(4.12 mmol) to give a 1:4 (E: Z) mixture of α, β-unsaturated nitriles*. Yield of **S14**: 39% (41% recovered SM) of Z (500 mg, 1.61 mmol, colorless oil); R_f= 0.15 (2:98 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.14 (t, *J* = 7.2 Hz, 1H), 4.73 (s, 1H), 4.65 (s, 1H), 3.81 (s, 3H), 3.31 (septet, *J* = 6.9 Hz, 1H), 2.73 – 2.63 (m, 4H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.97 (t, *J* = 7.5 Hz, 2H), 1.70 (s, 3H), 1.67 – 1.61 (m, 2H), 1.21 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.4, 147.1, 144.8, 137.2, 132.2, 126.3, 126.2, 117.7, 115.1, 110.8, 110.5, 55.6, 36.6, 34.3, 33.7, 33.4, 26.9, 25.9, 22.8, 22.3; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{29}NONa$ $[M + Na]^+$: 334.2147, found 334.2153.

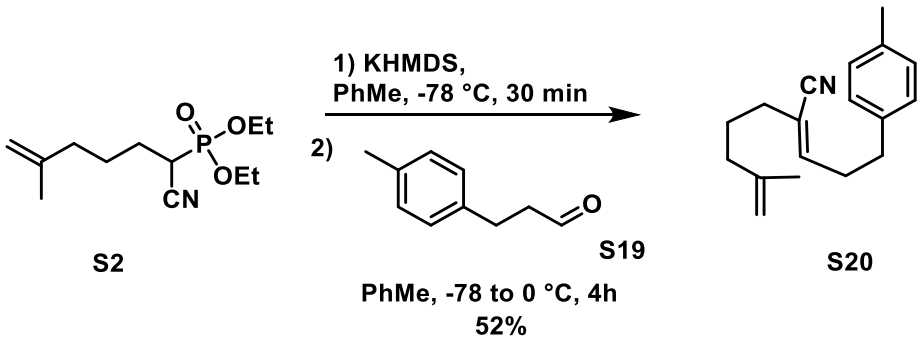


Prepared according to general procedure A, using cyanophosphonate **S2***(0.77 mmol) and aldehyde* **S15**[12]*(0.77 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 51% of **S16** (170 mg, 0.39 mmol, off-white solid); R_f=0.15 (8:92 EtOAc/hexanes) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.05 (t, *J* = 7.4 Hz, 1H), 4.63 (s, 1H), 4.55 (s, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.66 – 2.61 (m, 2H), 2.23 (s, 3H), 2.06 (t, *J* = 7.6 Hz, 2H), 1.89 (t, *J* = 7.4 Hz, 2H), 1.60 (s, 3H), 1.53 – 1.50 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.2, 145.0, 144.7, 135.4, 130.7, 130.0, 126.9, 125.0, 123.3, 123.0, 121.4, 119.4, 117.5, 115.8, 113.9, 110.9, 36.7, 33.7, 31.0, 25.9, 24.2, 22.3, 21.7; **HRMS** (ES+) *m/z* calc'd for $C_{26}H_{28}N_2O_2SNa$ $[M + Na]^+$: 455.1769, found 455.1774.

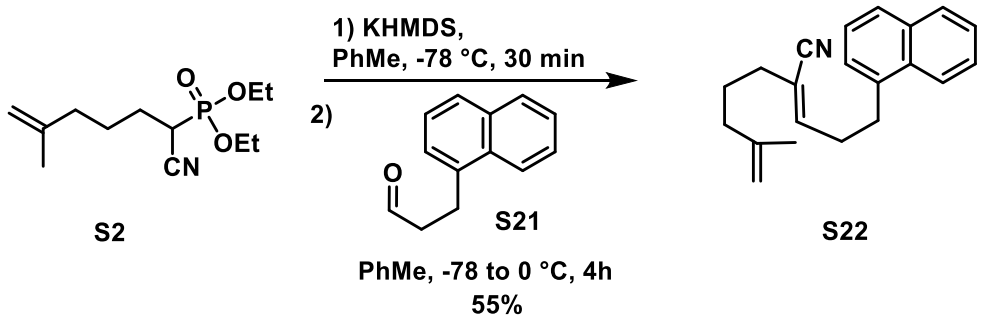


Prepared according to general procedure A, using cyanophosphonate **S2** *(1.16 mmol) and aldehyde* **S17**[13] *(1.16 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 46% of **S18** (200 mg,

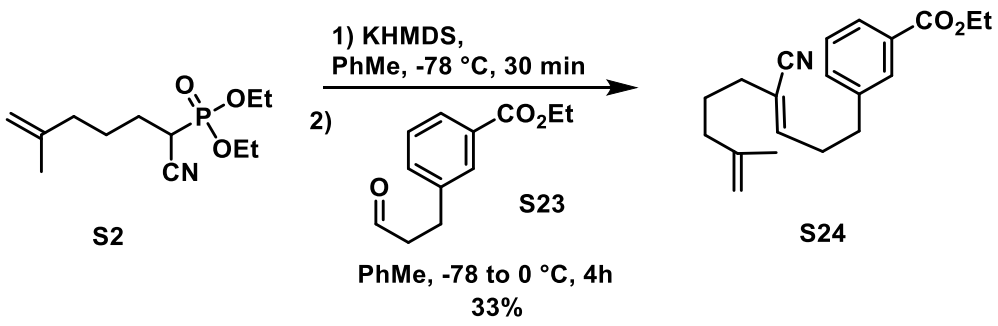
0.53 mmol, off-white solid); R_f=0.15 (5:95 EtOAc/hexanes) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.39 (s, 1H), 7.32 (ddd, , *J* = 7.2, 7.2, 1.1 Hz, 1H), 7.25 (ddd, 7.2, 7.2, 1.1, 1H), 6.20 (t, *J* = 7.3 Hz, 1H), 4.72 (s, 1H), 4.65 (s, 1H), 2.85 (dd, *J* = 7.8, 6.8 Hz, 2H), 2.78 (dd, *J* = 14.5, 7.0 Hz, 2H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.70 (s, 3H), 1.67 (s, 9H), 1.69-1.62 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) (Note: *mixture of rotamers*) δ 149.8 (broad), 146.8 (broad), 144.7, 135.7 (broad), 130.4, 124.6, 122.8, 122.6, 119.3, 118.9, 117.6, 115.53, 115.45, 110.9, 83.7, 36.7, 33.7, 31.1, 28.4, 25.9, 24.2, 22.3; **HRMS** (ES+) m/z calc'd for $C_{24}H_{31}N_2O_2$ [M + H]$^+$: 379.2386, found 379.2373.



Prepared according to general procedure A, using cyanophosphonate **S2***(1.54 mmol) and aldehyde* **S19**[14]*(1.54 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 52% of **S20** (203 mg, 0.80 mmol, colorless oil); R_f=0.15 (2:97 Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.13 (t, *J* = 7.3 Hz, 1H), 4.74 (s, 1H), 4.66 (s, 1H), 2.73 (dd, *J* = 11.0, 4.3 Hz, 2H), 2.67 (dd, *J* = 14.4, 7.1 Hz, 2H), 2.33 (s, 3H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.98 (t, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.68 – 1.60 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.9, 144.8, 137.2, 135.9, 129.3, 128.4, 117.7, 115.3, 110.8, 36.6, 34.5, 33.7, 33.2, 25.9, 22.3, 21.1; **HRMS** (ES+) m/z calc'd for $C_{18}H_{23}NNa$ [M + Na]+: 276.1728, found 276.1731.

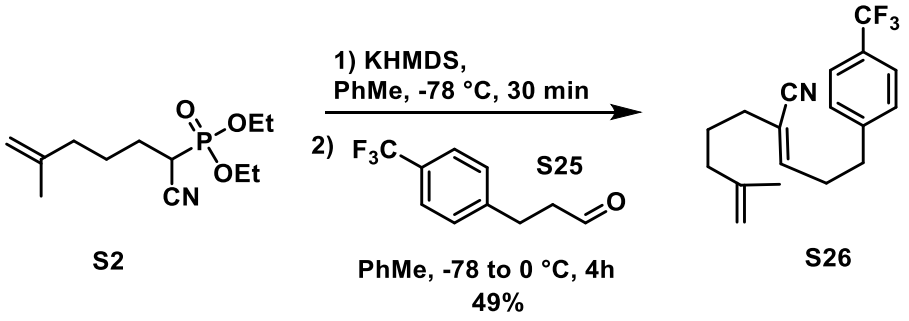


Prepared according to general procedure A, using cyanophosphonate **S2***(1.16 mmol) and aldehyde* **S21**[15]*(1.05 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 55% of **S22** (183 mg, 0.63 mmol, colorless oil); R_f=0.15 (2:98 Et_2O/Hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 6.21 (t, *J* = 7.6 Hz, 1H), 4.75 (s, 1H), 4.67 (s, 1H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.84 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.72 (s, 3H), 1.68 – 1.61 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.7, 144.8, 136.4, 134.0, 131.8, 129.0, 127.3, 126.3, 126.2, 125.8, 125.6, 123.6, 117.6, 115.4, 110.8, 36.7, 33.8, 32.4, 32.0, 25.9, 22.3; **HRMS** (ES+) m/z calc'd for $C_{21}H_{23}NNa$ [M + Na]+: 312.1728, found 312.1729.

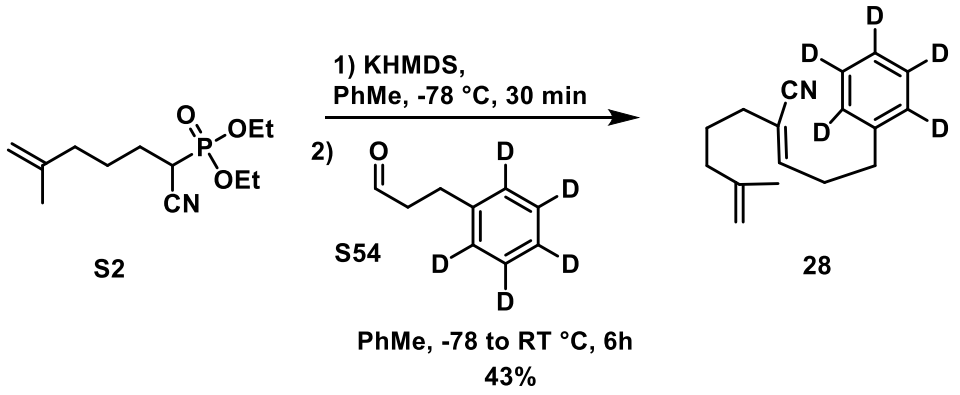


Prepared according to general procedure A, using cyanophosphonate **S2***(1.54 mmol) and aldehyde* **S23**[16]*(1.54 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 33% of **S24** (157 mg, 0.50 mmol, colorless oil); R_f=0.15 (15:85 Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 1H), 7.86 (s, 1H), 7.41 – 7.36 (m, 2H), 6.12 (t, *J* = 7.5 Hz, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.73 – 2.68 (m, 2H), 2.16 (t, *J* = 7.6 Hz, 2H), 1.96 (t, *J* = 7.5 Hz, 2H),

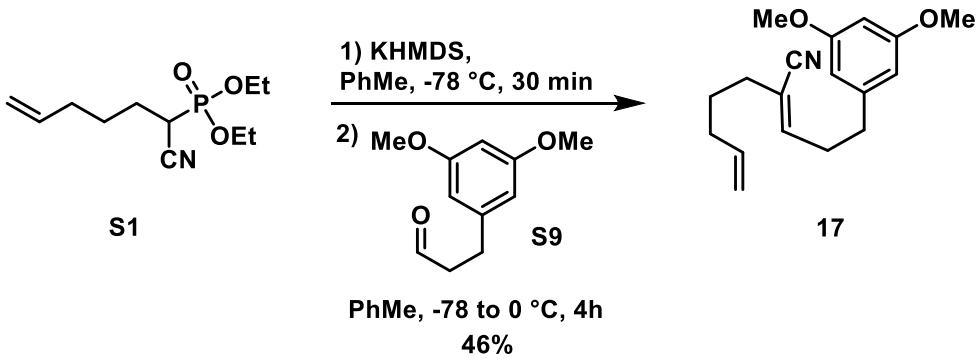
1.69 (s, 3H), 1.67 – 1.59 (m, 2H), 1.40 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 146.1, 144.7, 140.6, 133.0, 130.9, 129.6, 128.7, 127.8, 117.5, 115.9, 110.9, 61.1, 36.6, 34.7, 33.7, 32.9, 25.9, 22.3, 14.5; **HRMS** (ES+) m/z calc'd for $C_{20}H_{25}NO_2H$ [M + H]+: 312.1964, found 312.1961.



Prepared according to general procedure A, using cyanophosphonate **S2***(1.16 mmol) and aldehyde* **S25***[17](1.05 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 49% of **S26** (174 mg, 0.57 mmol, colorless oil) ; R_f=0.15 (4:96 Et_2O/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.11 (t, J = 7.5 Hz, 1H), 4.73 (s, 1H), 4.64 (s, 1H), 2.83 (t, J = 7.5 Hz, 2H), 2.72 – 2.69 (m, 2H), 2.17 (t, J = 7.5 Hz, 2H), 1.97 (t, J = 7.5 Hz, 2H), 1.69 (s, 3H), 1.66 – 1.60 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.8, 144.7, 144.4, 128.9 (q, J = 32.4 Hz), 128.9 (2C), 125.6 (q, J = 3.7 Hz, 2C), 124.4 (q, J = 271.8 Hz), 117.5, 116.1, 110.9, 36.6, 34.7, 33.7, 32.7, 25.8, 22.3; **HRMS** (ES+) m/z calc'd for $C_{18}H_{20}F_3NNa$ [M + Na]+: 330.1446, found 330.1442.

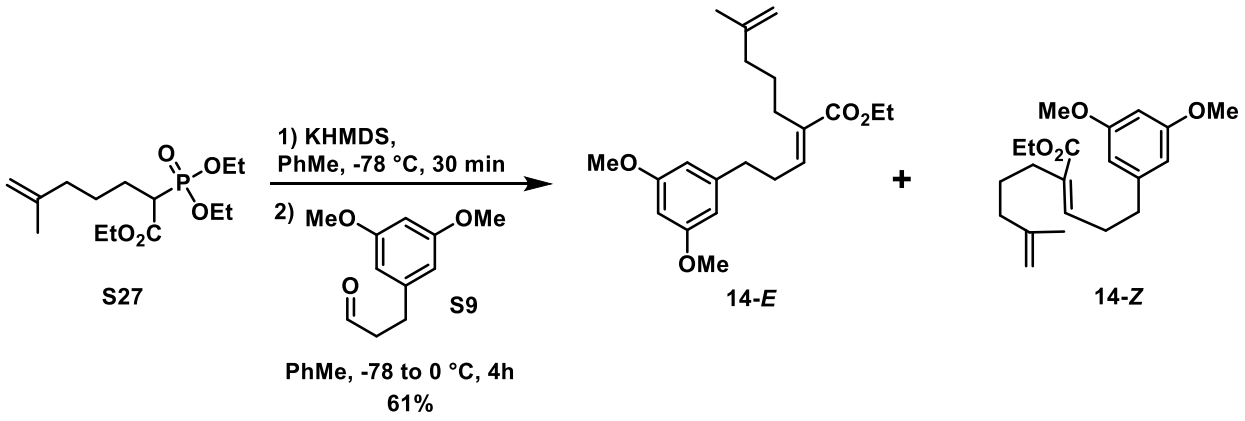


Prepared according to general procedure A, using cyanophosphonate **S2** *(1.44 mmol) and aldehyde* **S54**[18] *(1.44 mmol) to give a 1:8 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 43% of **28** (151 mg, 0.62 mmol, colorless oil); R_f=0.15 (1.5:98.5 EtOAc/Hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.13 (t, *J* = 7.5 Hz, 1H), 4.73 (s, 1H), 4.65 (s, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.69 (dd, *J* = 14.9, 7.4 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.98 (t, *J* = 7.5 Hz, 2H), 1.70 (s, 3H), 1.67 – 1.61 (m, 2H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 146.7, 144.8, 140.1, 128.1(t, *J* = 24.3 Hz, 2C), 128.1(t, *J* = 24.3 Hz, 2C), 125.9 (t, *J* = 24.3 Hz), 117.6, 115.4, 110.8, 36.6, 34.8, 33.7, 33.1, 25.9, 22.3; **HRMS** (ES+) *m/z* calc'd for $C_{17}H_{16}D_5NNa$ [M + Na]$^+$: 267.1885, found 267.1884.



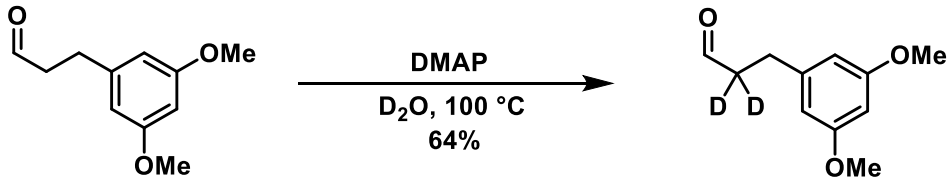
Prepared according to general procedure A, using cyanophosphonate **S1** *(1.63 mmol) and aldehyde* **S9**[9] *(1.48 mmol) to give a 1:4 (E: Z) mixture of α,β-unsaturated nitriles*. Yield: 46% of **17** (215 mg, 0.75 mmol, colorless oil); R_f=0.15 (3:97 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.35 – 6.31 (m, 3H), 6.11 (t, *J* = 6.8 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.03 – 4.95 (m, 2H), 3.78 (s, 6H), 2.75 –

2.64 (m, 4H), 2.18 (t, *J* = 7.5 Hz, 2H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.65 – 1.54 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 146.7, 142.7, 137.8, 117.7, 115.5, 115.3, 106.6, 98.4, 55.4, 35.1, 33.6, 32.7, 32.6, 27.2; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}NO_2H$ $[M + H]^+$: 286.1807, found 286.1805. Yield: 14% of *E*-isomer (64 mg, 0.22 mmol, colorless oil); R_f=0.15 (4:96 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.35 (t, *J* = 7.6 Hz, 1H), 6.33 (s, 1H), 6.30 (s, 2H), 5.75 (td, *J* = 16.7, 6.9 Hz, 1H), 5.04– 4.96 (m, 2H), 3.78 (s, 6H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.48 (q, *J* = 7.5 Hz, 2H), 2.14 (t, *J* = 7.6 Hz, 2H), 2.04 (q, *J* = 6.9 Hz, 2H), 1.59 – 1.52 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.1, 146.9, 142.7, 137.7, 120.0, 115.5, 115.3, 106.7, 98.3, 55.4, 34.9, 32.9, 30.2, 28.0, 27.1; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}NO_2Na$ $[M + Na]^+$: 308.1627, found 308.1631.



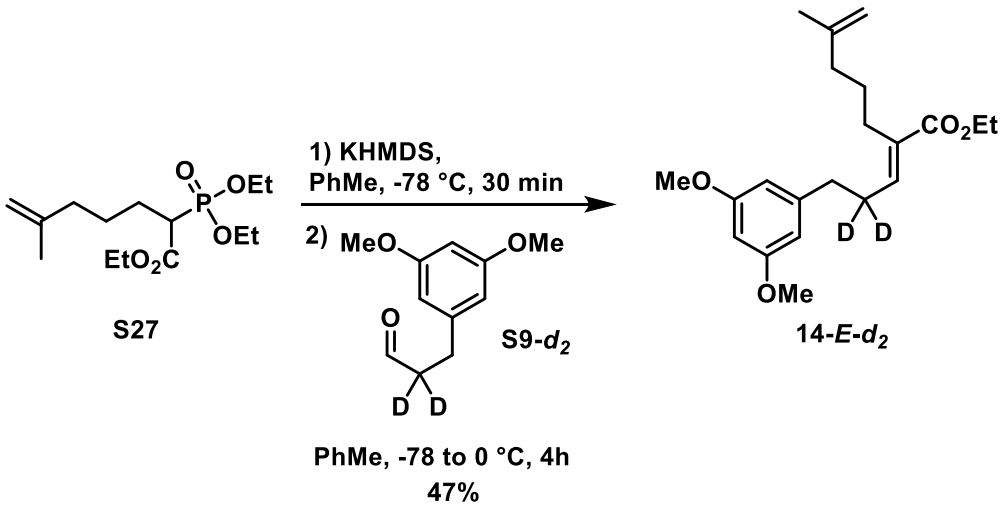
Prepared according to general procedure A, using phosphonoacetate **S27**[19] *(0.849 mmol) and aldehyde* **S9**[9] *(1.02 mmol) to give a 1:4 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 48% of **14-*E*** (140 mg, 0.40 mmol, colorless oil) of E; R_f=0.15 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.78 (t, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 2.1 Hz, 2H), 6.32 (t, *J* = 2.2 Hz, 1H), 4.70 (s, 1H), 4.67 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.50 – 2.48 (m, 2H), 2.28 – 2.23 (m, 2H), 2.00 (t, *J* = 7.6 Hz, 2H), 1.70 (s, 3H), 1.51 – 1.44 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.0, 161.0, 145.7, 143.8, 141.3, 133.2, 110.1, 106.6, 98.2, 60.5, 55.4, 37.8, 35.5, 30.5, 27.2, 26.6, 22.5, 14.4; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{31}O_4$ $[M + H]^+$: 347.2222, found 347.2217.

Yield: 13% of **14-*Z*** (38 mg, 0.11 mmol, colorless oil); R_f=0.16 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.36 (d, *J* = 2.2 Hz, 2H), 6.30 (t, *J* = 2.2 Hz, 1H), 5.87 (t, *J* = 7.1 Hz, 1H), 4.70 (s, 1H), 4.65 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 2.76 – 2.70 (m, 2H), 2.70 – 2.64 (m, 2H), 2.25 – 2.19 (m, 2H), 1.99 (t, *J* = 7.6 Hz, 2H), 1.70 (s, 3H), 1.58 – 1.50 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 160.9, 145.7, 144.1, 140.3, 132.9, 110.2, 106.7, 98.1, 60.2, 55.4, 37.3, 36.0, 34.3, 31.0, 27.1, 22.5, 14.5; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{30}O_4Na$ $[M + Na]^+$: 369.2042, found 369.2029.

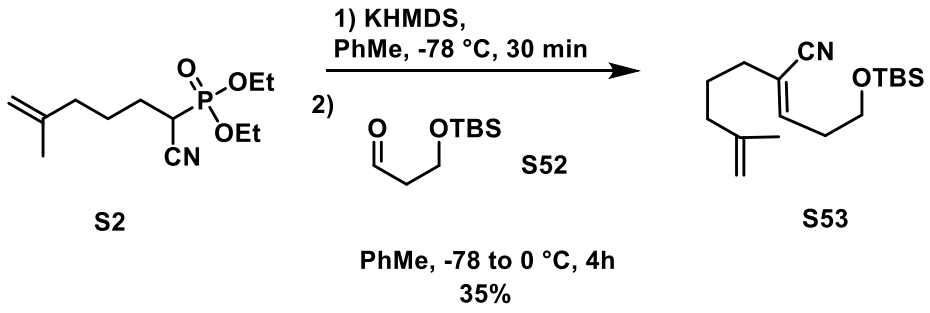


S9 **S9-*d*$_2$**

A sealed tube charged with a magnetic stirring bar, aldehyde **S9** (250 mg, 1.29 mmol), DMAP (16 mg, 0. 13 mmol), and heavy water (0.50 ml) was heated to 100 °C for 2h. After cooling to room temperature, the suspension was extracted with diethyl ether (3 x 2 mL), the combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of EtOAc/ hexanes (2:8) as eluent to give α-d_2 aldehyde **S9– *d*$_2$** as a colorless oil (161 mg, 0.82 mmol, 64% yield – *ca. ~90% deuteration at the α-position estimated by ^{1}H NMR*); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 6.34 (d, *J* = 2.2 Hz, 2H), 6.32 (t, *J* = 2.2 Hz, 1H), 3.77 (s, 6H), 2.88 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.8, 161.1, 142.8, 106.5, 98.2, 55.4, 44.6 (pent, *J* = 19.5 Hz), 28.4; **HRMS** (ES+) *m/z* calc'd for $C_{11}H_{13}D_2O_3$ $[M + H]^+$: 197.1147, found 197.1149.

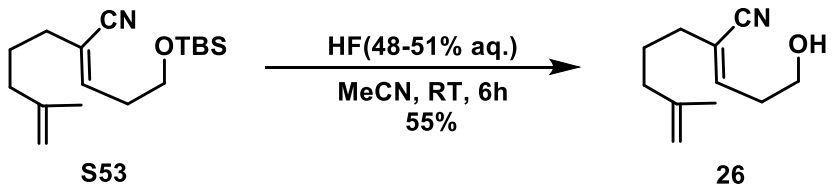


Prepared according to general procedure A, using phosphonoacetate **S27**[19] *(0. 97 mmol) and aldehyde* **S9–*d*$_2$** *(0.97 mmol) to give a 5:1 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 47% of **14–*E*–*d*$_2$** (160 mg, 0.46 mmol, colorless oil) of E; R_f=0.15 (2:98 EtOAc/hexanes - *ca. ~90% deuteration at the α-position estimated by ^{1}H NMR*); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.40 (s, 2H), 6.37 (s, 1H), 4.76 (s, 1H), 4.73 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 6H), 2.73 (s, 2H), 2.34 – 2.29 (m, 2H), 2.06 (t, *J* = 7.6 Hz, 2H), 1.76 (s, 3H), 1.54 (dd, *J* = 15.4, 7.7 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.9, 160.9, 145.6, 143.7, 141.1, 133.2, 110.1, 106.5, 98.1, 60.4, 55.3, 37.7, 35.3, 29.7 (pent, *J* = 19.5 Hz) 27.1, 26.5, 22.4, 14.4; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{28}D_2O_4Na$ $[M + Na]^+$: 371.2167, found 371.2171.



Prepared according to general procedure A, using cyanophosphonate **S2***(0.77 mmol) and aldehyde* **S52**[20] *(0.77 mmol) to give a 1:8 (E:Z) mixture of α,β-unsaturated nitriles*. Yield: 35% of **S53** (80 mg,

0.27 mmol, colorless oil); R_f=0.15 (1:99 EtOAc/hexanes);**^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.23 (t, *J* = 7.5 Hz, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.55 (dd, *J* = 13.3, 6.3 Hz, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 2.03 (t, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.71 – 1.64 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 145.0, 144.8, 117.7, 116.0, 110.8, 61.6, 36.7, 35.1, 33.8, 26.1, 26.0, 25.9, 22.3, -5.3; **HRMS** (GG-CI) *m/z* calc'd for $C_{17}H_{32}NOSiH$ $[M + H]^+$: 294.2253, found 294.2263.

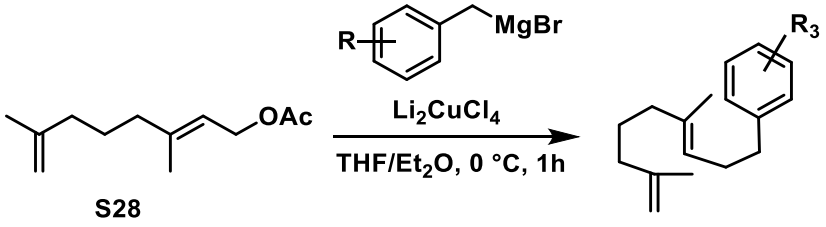


S53 **26**

To a solution of silyl ether **S53** (80 mg, 0.27 mmol) in acetonitrile (1.0 mL) was added a solution of HF in water (48-51%, 0.10 mL). After stirring for 6 hours at room temperature, the mixture was diluted with water (3 mL) and extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4, filtered and carefully concentrated *in vacuo (caution: the product is volatile)*. The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of EtOAc/ hexanes (3:7) as eluent to give alcohol **26** as a colorless oil (27 mg, 0.15 mmol, 55% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.25 (t, *J* = 7.5 Hz, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 3.74 (t, *J* = 6.1 Hz, 1H), 2.60 (q, *J* = 6.6 Hz, 1H), 2.22 (t, *J* = 7.6 Hz, 1H), 2.02 (t, *J* = 7.5 Hz, 1H), 1.78 (s, 1H), 1.70 (s, 1H), 1.71 – 1.65 (m, 1H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 144.7, 144.3, 117.7, 116.8, 110.9, 61.3, 36.7, 34.9, 33.8, 25.8, 22.3; **HRMS** (ES+) *m/z* calc'd for $C_{11}H_{17}NONa$ $[M + Na]^+$: 202.1208, found 202.1208.

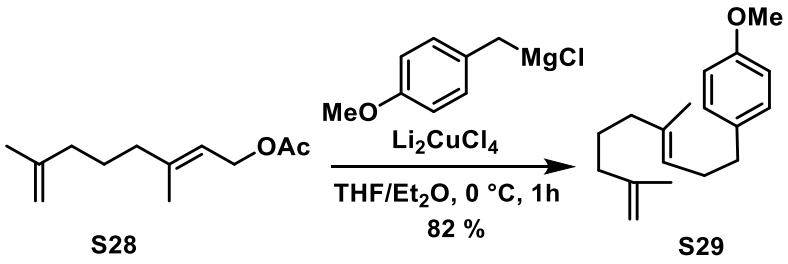
C. C-20 Methyl Substrate Synthesis and Characterization

General Procedure B (copper catalyzed allylic substitution):

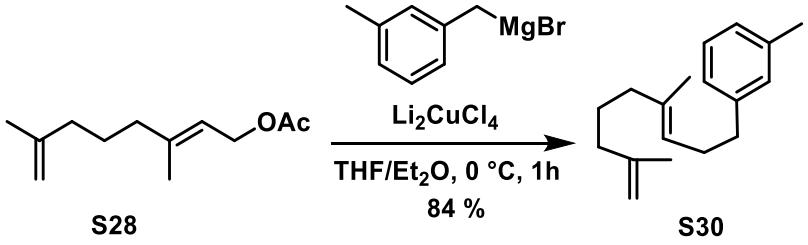


Grignard reagents were prepared from corresponding benzylic chlorides (or bromides) as follows: A suspension of activated Mg^0 turnings (2.0 equiv.) in Et_2O was cooled to 0 °C, and the benzyl halide (1.0 equiv., ~1.0M) was added slowly enough to maintain the reaction temperature under 20 °C. The resulting suspension was stirred vigorously at ambient temperature for 1 hour prior to use. Concentrations were determined using salicylaldehyde phenylhydrazone as titrant, and generally gave 1.0–1.2M solutions.

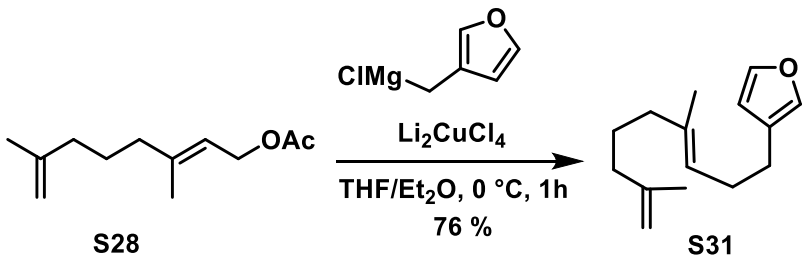
To an ice-cold solution of allylic acetate **S28**[21] (1.00 mmol, 1 equiv.) in THF (0.5 mL) was added a 1.0 M solution of Li_2CuCl_4 (0.10 mmol, 0.1 equiv.). The resulting mixture was stirred for 10 minutes and a solution of freshly prepared benzylic Grignard reagent (2.0 mmol, 2.0 equiv., ~ 1.0M in Et_2O) was added dropwise. After stirring for 2 hours at 0 °C, the reaction mixture was quenched with satd. $NH_4Cl_{(aq)}$ (10 mL) and stirred for 1 hour while warming to ambient temperature. The aqueous phase was extracted with Et_2O (3 x 20 mL), then the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo.* The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of Et_2O/ hexanes as eluent (NOTE: *the products contained ~11% of the inseparable trisubstituted alkene isomer, since* **S28** *contained ~11% of geraniol acetate*).



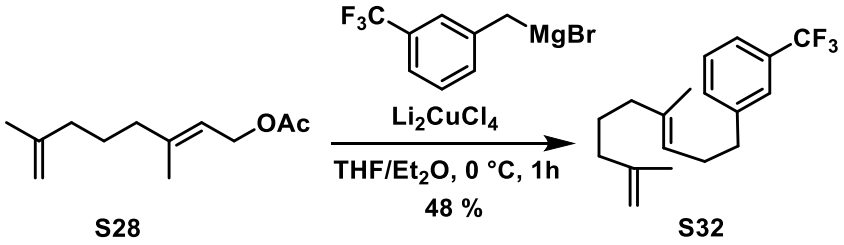
Prepared according to general procedure B, using allylic acetate **S28** *(2.36 mmol) and p-methoxybenzyl chloride (4.71 mmol) to give a 89:11 mixture of alkene isomers*. Yield: 82% of **S29** (501 mg, 1.94 mmol, colorless oil); R_f=0.30 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.17 (td, *J* = 7.0, 1.2 Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 3.79 (s, 3H), 2.60 – 2.56 (m, 2H), 2.27 (dd, *J* = 15.2, 7.4 Hz, 2H), 1.98-1.93 (m, 4H), 1.71 (s, 3H), 1.54 (s, 3H), 1.53 – 1.49 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.8, 146.3, 135.8, 134.7, 129.5, 124.0, 113.8, 109.8, 55.4, 39.4, 37.5, 35.4, 30.3, 26.1, 22.6, 16.0; ; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{26}O$ $[M]^+$: 258.1984, found 258.1991.



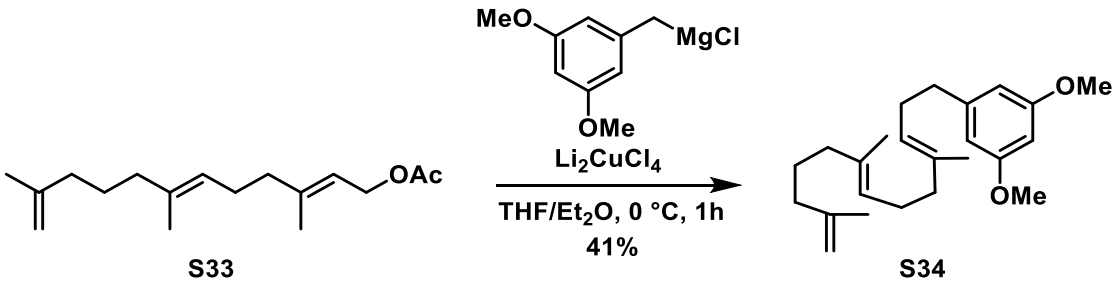
Prepared according to general procedure B, using allylic acetate **S28** *(1.18 mmol) and 3-methylbenzyl bromide (2.36 mmol) to give a 89:11 mixture of alkene isomers*. Yield: 84% of **S30** (241 mg, 0.99 mmol, colorless oil); R_f=0.73 (hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 1H), 7.02 – 6.98 (m, 3H), 5.19 (t, *J* = 6.5 Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H), 2.31 – 2.26 (m, 2H), 2.01 – 1.91 (m, 4H), 1.71 (s, 3H), 1.56 (s, 3H), 1.54 – 1.48 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.2, 142.5, 137.8, 135.8, 129.4, 128.3, 126.5, 125.6, 124.0, 109.9, 39.4, 37.5, 36.2, 30.1, 26.1, 22.6, 21.6, 16.0; ; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{26}$ $[M]^+$: 242.2034, found 242.2045.



Prepared according to general procedure B, using allylic acetate **S28** *(1.00 mmol) and 3-chloromethylfuran (2.00 mmol) to give a 89:11 mixture of alkene isomers*. Yield: 76% of **S31** (165 mg, 0.76 mmol, colorless oil); R_f=0.40 (hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 1.6 Hz, 1H), 7.21 (d, *J* = 0.9 Hz, 1H), 6.28 (s, 1H), 5.19 – 5.15 (m, 1H), 4.70 (d, *J* = 0.7 Hz, 1H), 4.66 (d, *J* = 0.8 Hz, 1H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.25 (q, *J* = 7.4 Hz, 2H), 2.01 – 1.94 (m, 4H), 1.71 (s, 3H), 1.59 (s, 3H), 1.56 – 1.48 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.2, 142.7, 139.0, 135.9, 125.1, 124.0, 111.2, 109.9, 39.4, 37.5, 28.6, 26.0, 25.2, 22.6, 16.1; **HRMS** (ES+) *m/z* calc'd for $C_{15}H_{22}OH$ $[M + H]^+$: 219.1749, found 219.1656.

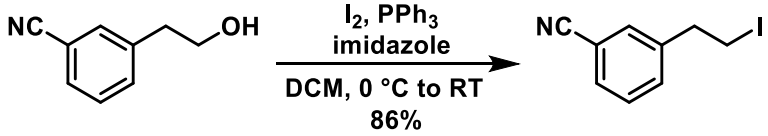


Prepared according to general procedure B, using allylic acetate **S28** *(1.18 mmol) and 3-(trifluoromethyl)benzyl bromide (2.95 mmol) to give a 89:11 mixture of alkene isomers*. Yield: 48% of **S32** (168 mg, 0.57 mmol, colorless oil); R_f=0.65 (hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 5.15 (td, *J* = 7.1, 1.1 Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 2.00 – 1.91 (m, 4H), 1.71 (s, 3H), 1.52 (s, 3H), 1.53 – 1.49 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.1, 143.2, 136.5, 132.0, 130.5 (q, *J* = 31.9 Hz), 128.6, 125.3 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.8 Hz), 123.0, 122.6 (q, *J* = 3.8 Hz), 109.8, 39.3, 37.4, 35.9, 29.6, 25.9, 22.4, 15.9; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}F_3NH_4$ $[M + NH_4]^+$: 314.2096, found 314.2093.



S33 S34

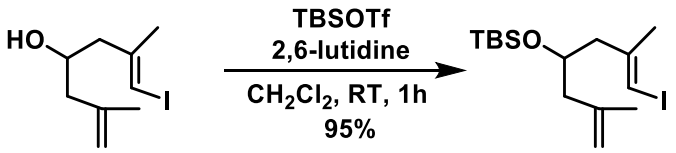
Prepared according to general procedure B, using allylic acetate **S33**[22] *(0.340 mmol, 1.0 equiv.) and 3,5-dimethoxybenzyl chloride (0.6.80 mmol, 2.0 equiv) to give a 89:11 mixture of alkene isomers*. Yield: 41% of **S34** (55 mg, 0.15 mmol, colorless oil); R_f=0.21 (2:98 Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.37 (d, *J* = 2.0 Hz, 2H), 6.32 (d, *J* = 1.9 Hz, 1H), 5.20 (t, *J* = 7.0 Hz, 1H), 5.12 (t, *J* = 6.7 Hz, 1H), 4.71 (s, 1H), 4.68 (s, 1H), 3.79 (s, 6H), 2.62 – 2.56 (m, 2H), 2.33 – 2.30 (m, 2H), 2.13 – 2.04 (m, 4H), 2.03 – 1.95 (m, 4H), 1.73 (s, 3H), 1.60 (s, 3H), 1.60 (s, 3H), 1.53 (dt, *J* = 15.2, 7.7 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.8, 146.2, 145.0, 135.9, 135.1, 124.5, 123.7, 109.9, 106.7, 97.8, 55.4, 39.9, 39.4, 37.5, 36.6, 29.9, 26.9, 26.8, 26.1, 22.6, 16.2, 16.0; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{37}O_2$ $[M + H]^+$: 357.2794, found 357.2787.



S35 S36

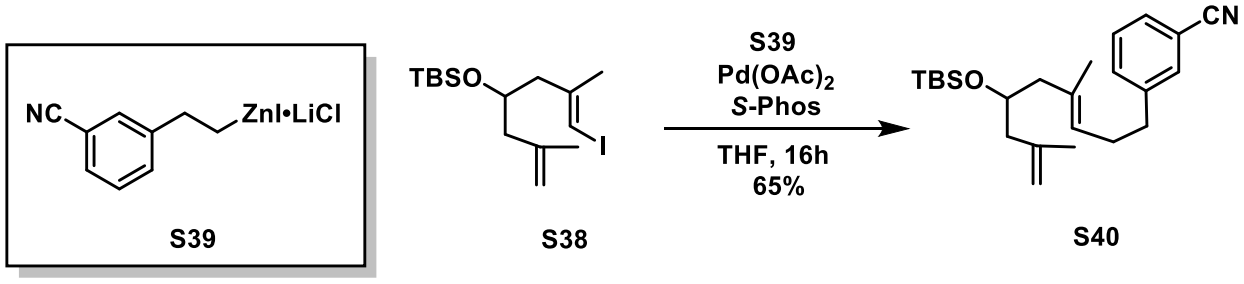
To an ice-cold solution of triphenylphosphine (5.88 g, 22.4 mmol, 1.5 equiv.) in CH_2Cl_2 (35 mL) was added iodine (5.69 g, 22.4 mmol, 1.5 equiv.). After 10 min., imidazole (2.54 g, 37.4 mmol, 2.5 equiv.) was added and the mixture was stirred for 10 min. A solution of alcohol **S35** (2.20 g, 15.0 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise over approximately 5 min. After 90 min., satd. $Na_2SO_{3(aq)}$ (40 mL) was added in one portion and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified via flash column chromatography (EtOAc/hexanes 5:95) to give

iodide **S36** as a crystalline white solid (3.32 g, 12.9 mmol, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.50 (s, 1H), 7.46 – 7.43 (m, 2H), 3.35 (t, *J* = 7.4 Hz, 2H), 3.21 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 133.1, 132.1, 130.8, 129.6, 118.8, 112.9, 39.4, 4.4. **HRMS** (ES+) *m/z* calc'd for C_9H_8IN $[M]^+$: 256.9702, found 256.9713.



S37 **S38**

To a solution of alcohol **S37**[23] (100 mg, 0.376 mmol, 1.0 equiv.) and 2,6-lutidine (200 µL, 1.73 mmol, 4.6 equiv.) in CH_2Cl_2 (1 mL) was added TBSOTf (130 µL, 0.564 mmol, 1.5 equiv.). The mixture was stirred for 1 h at ambient temperature, then methanol (5.0 mL) was added. Volatiles were removed *in vacuo*, and the resulting crude residue was directly purified via flash chromatography using a mixture of EtOAc/hexanes (1:99) as eluent to give silyl ether **S38** as a colorless oil (3.52 g, 95%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.90 (d, *J* = 0.8 Hz, 1H), 4.79 (s, 1H), 4.70 (s, 1H), 3.90 (tdd, *J* = 7.4, 5.6, 4.5 Hz, 1H), 2.35 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.27 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.19 (dd, *J* = 13.6, 5.5 Hz, 1H), 2.12 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.83 (d, *J* = 0.9 Hz, 3H), 1.73 (s, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H): **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 142.5, 113.5, 77.6, 69.0, 47.0, 46.4, 26.0, 24.6, 23.2, 18.2, –4.4(2C); **HRMS** (ES+) *m/z* calc'd for $C_{15}H_{29}IOSiH$ $[M+H]^+$: 381.1111, found 381.1109.

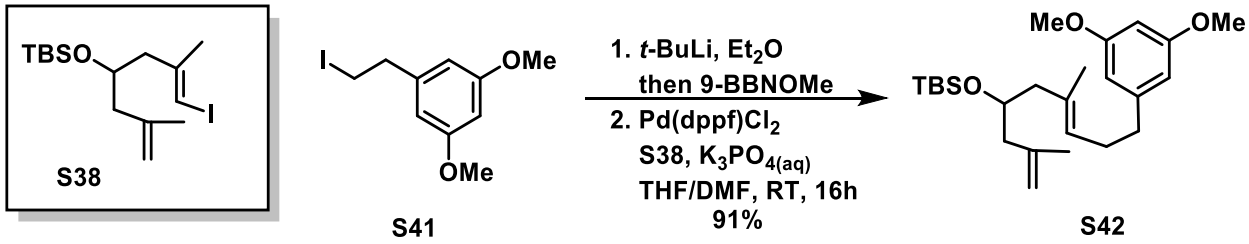


Preparation of the homobenzylic zinc reagent **S39**: LiCl (53 mg, 1.25 mmol, 1.9 equiv.) was dried under high-vacuum for 2 h at 170 °C, then Zn^0 dust (82 mg, 1.25 mmol, 1.9 equiv.) was added and the mixture

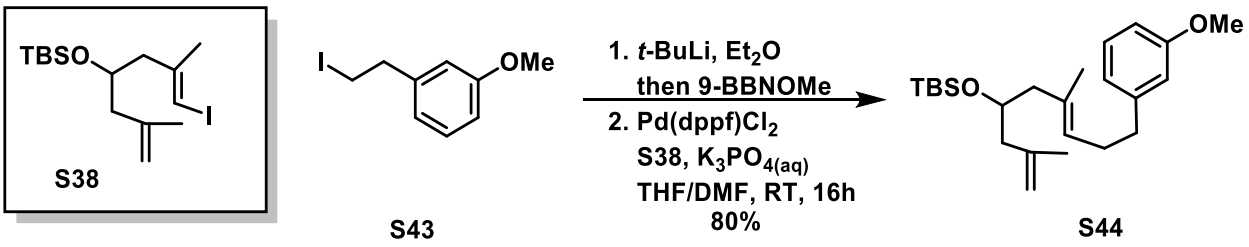
was dried for another 2 h. The flask was cooled to ambient temperature, the contents were suspended in THF (0.5 mL). The zinc dust was activated by adding 5 drops of a saturated I_2 solution in THF and sonicating the suspension until the brown color faded. A THF (4 mL) solution of homobenzylic iodide **S36** (169 mg, 0.66 mmol, 1.25 equiv.) was added and the mixture was stirred at 50 °C for 4 h.

Negishi Cross-Coupling: To a solution of $Pd(OAc)_2$ (15 mg, 65.8 μmol, 0.1 equiv.) and S-Phos (59 mg, 0.132 mmol, 0.2 equiv.) in THF (1 mL) was added a solution of vinyl iodide **S38** (200 mg, 0.526 mmol, 1.0 equiv.) in THF (0.5 mL). The aforementioned solution of homobenzylic zinc reagent **S39** was quickly added and the resulting suspension was stirred at room temperature for 16 h. Then, satd. $NH_4Cl_{(aq)}$ (10 mL) was added and the reaction mixture was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography using a mixture of Et_2O/ hexanes (2:98) as eluent to give **S40** as a colorless oil (131 mg, 0.341 mmol, 65% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 5.15 (t, *J* = 6.6 Hz, 1H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.67 (s, 1H), 3.86 (p, *J* = 6.3 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.36 – 2.25 (m, 2H), 2.13 – 2.03 (m, 4H), 1.71 (s, 3H), 1.55 (s, 3H), 0.86 (s, 9H), 0.01 (s, 3H), -0.00 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.7, 143.0, 133.9, 133.3, 132.1, 129.7, 129.1, 125.8, 119.3, 113.2, 112.3, 69.5, 47.7, 46.0, 35.6, 29.7, 26.0, 23.1, 18.2, 16.7, –4.4, –4.5; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{37}NOSiNa$ $[M + Na]^+$: 406.2542, found 406.2540.

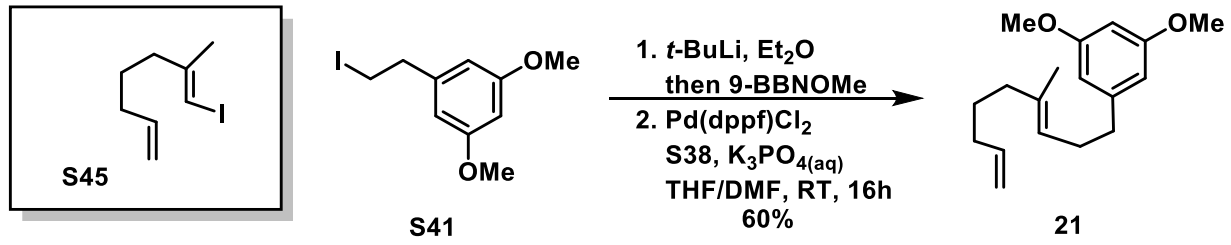
General Procedure C (B-alkyl Suzuki coupling):



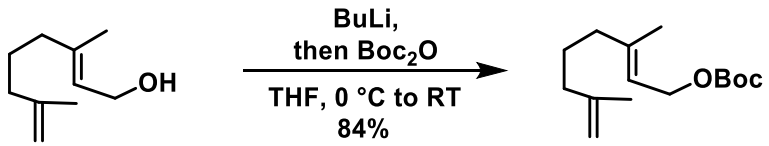
To a solution of homobenzylic iodide **S41**[24] (200 mg, 0.684 mmol, 1.3 equiv.) in Et_2O (2 mL) was added a 1.7 M solution of *tert*-butylithium (1.24 mL, 2.1 mmol, 4.0 equiv.) in pentane at –78 °C. The resulting mixture was stirred for 10 minutes and a 1.0 M solution of 9-BBN-OMe (2.4 mL, 4.5 equiv.) was added dropwise and the reaction flask was allowed to warm to ambient temperature over 30 min. THF (2 mL) followed by 3.0 M $K_3PO_{4(aq)}$ (0.44 mL, 1.3 mmol, 2.5 equiv.) were added, then the mixture was stirred for 1 h at room temperature. A solution of vinyl iodide **S38** (200 mg, 0.526 mmol, 1.0 equiv.) in DMF (2.0 mL), followed by Pd(dppf)Cl_2 (43 mg, 0.053 mmol, 0.1 equiv.) were finally added and the resulting suspension was stirred overnight under Ar. Next, the mixture was diluted with Et_2O (30 mL) and the organic phases were washed with DI H_2O (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo.* The crude residue was purified via flash column chromatography (Et_2O/ hexanes 4:96) to give **S42** as a colorless oil (200 mg, 0.479 mmol, 91 % yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.35 (d, *J* = 2.2 Hz, 2H), 6.30 (t, *J* = 2.1 Hz, 1H), 5.20 (t, *J* = 6.9 Hz, 1H), 4.76 (s, 1H), 4.68 (s, 1H), 3.91 – 3.85 (m, 1H), 3.78 (s, 6H), 2.62 – 2.55 (m, 2H), 2.34 – 2.24 (m, 2H), 2.12 – 2.06 (m, 4H), 1.71 (s, 3H), 1.60 (s, 3H), 0.87 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.7, 144.8, 143.1, 132.9, 126.7, 112.9, 106.5, 97.7, 69.7, 55.3, 47.8, 45.9, 36.3, 29.9, 29.3, 25.9, 23.05, 18.17, 16.69, –4.49; **HRMS** (ES+) *m/z* calc'd for $C_{25}H_{42}O_3SiNa$ $[M + Na]^+$: 441.2801, found 441.2818.



Prepared according to general procedure C, using vinyl iodide **S38** *(0.71 mmol) and homobenzylic iodide* **S43**[25] *(0.92 mmol)*. Yield: 80% of **S44** (220 mg, 0.57 mmol, colorless oil); R_f=0.38 (3:97 Et_2O/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.76 – 6.71 (m, 2H), 5.22 (t, *J* = 6.8 Hz, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 3.88 (p, *J* = 6.2 Hz, 1H), 3.80 (s, 3H), 2.68 – 2.58 (m, 2H), 2.31 (dt, *J* = 14.7, 7.2 Hz, 2H), 2.16 – 2.06 (m, 4H), 1.72 (s, 3H), 1.59 (s, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 144.2, 143.2, 133.0, 129.3, 126.9, 121.0, 114.4, 113.0, 111.1, 69.8, 55.3, 47.9, 46.0, 36.1, 30.1, 26.0(3C), 23.2, 18.3, 16.8, –4.4(2C); **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{40}O_2SiNa$ $[M + Na]^+$: 411.2695, found 411.2702.



Prepared according to general procedure C, using vinyl iodide **S45**[26] *(0.53 mmol) and homobenzylic iodide* **S41**[21] *(0.68 mmol)*. Yield: 60% of **21** (86 mg, 0.31 mmol, colorless oil); R_f=0.28 (2:98 Et_2O/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.36 (d, *J* = 2.0 Hz, 2H), 6.31 (d, *J* = 2.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.18 (t, *J* = 7.0 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 3.78 (s, 6H), 2.63 – 2.55 (m, 2H), 2.30 (dd, *J* = 15.3, 7.5 Hz, 2H), 2.03 – 1.96 (m, 4H), 1.57 (s, 3H), 1.52 – 1.44 (m, 2H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 160.8, 145.0, 139.1, 135.8, 123.9, 114.5 (2C), 106.7 (2C), 97.8, 55.4 (2C), 39.2, 36.6, 33.5, 29.8, 27.3, 16.0; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{27}O_2$ $[M + H]^+$: 275.2011, found 275.2010.

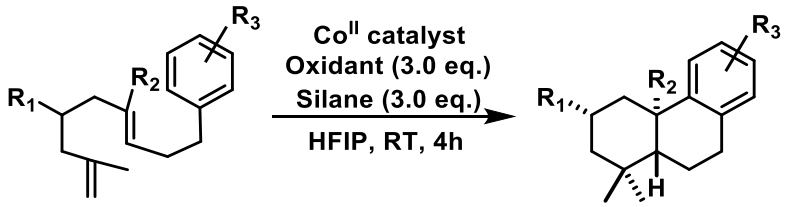


S47 **22**

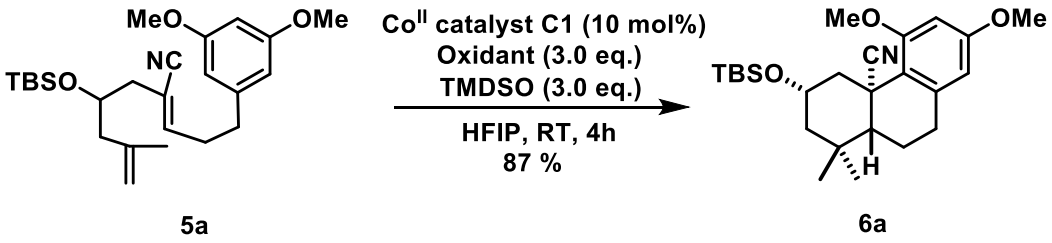
To an ice-cold solution of alcohol **S47**[27] (700 mg, 4.54 mmol, 1.0 equiv.) in THF (12 mL) was added a 2.4M solution of *n*-butyllithium (1.9 mL, 4.54 mmol, 1.0 equiv.) in hexanes. The resulting solution was stirred for 15 minutes, and a solution of Boc_2O (990 mg, 4.54 mmol, 1.0 equiv.) in THF (6 mL) added dropwise. After stirring for 1 hour, satd. $NH_4Cl_{(aq)}$ (10 mL) was added. The aqueous phase was extracted with EtOAc (3 x 10 mL), the combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude residue was purified via flash column chromatography, using a mixture of EtOAc/ hexanes (5:95) as eluent to give carbonate **22** as a colorless oil (969 mg, 3.81 mmol, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.37 (t, *J* = 7.1 Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 4.58 (d, *J* = 7.2 Hz, 2H), 2.04 – 2.00 (m, 2H), 2.00 – 1.95 (m, 2H), 1.70 (s, 6H), 1.57 – 1.52 (m, 2H), 1.48 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.8, 145.8, 142.7, 118.3, 110.1, 82.0, 63.9, 39.2, 37.4, 28.0, 25.6, 22.5, 16.5; ; **HRMS** (ES+) *m/z* calc'd for $C_{15}H_{26}O_3Na$ $[M + Na]^+$: 277.1780, found 277.1782.

D. Cobalt Catalyzed Bicyclizations and Product Characterization

General Procedure D (Cobalt catalyzed bicyclization):



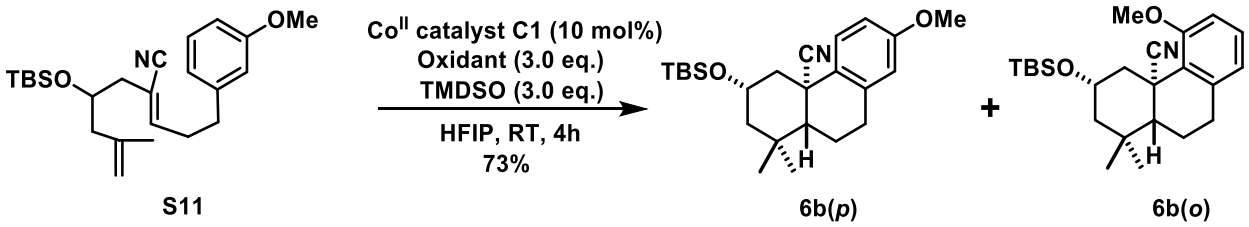
A dry round-bottom flask was charged with a magnetic stirring bar, bicyclization substrate (0.20 mmol, 1.0 equiv.) cobalt catalyst (0.02 mmol, 0.1 equiv.) and 1-fluoro-2,4,6-trimethylpyridinium triflate (0.60 mmol, 3.0 equiv.). The reagents were dissolved in HFIP (1.0 mL, 0.2 M based on substrate), and the flask was capped with a rubber septum. A balloon equipped with a syringe needle was used to bubble Ar through the solution for 10 minutes (a syringe needle was used as an outlet). Then, the flask was sealed from the atmosphere and TMDSO (0.60 mmol, 3 equiv.) was added dropwise at a rate of 1 drop per 3 seconds. The resulting solution gradually turned dark red or tan from its initial, dark green color. After 4-9 hours, TLC indicated complete starting material consumption and the volatiles were removed *in vacuo*. The resulting residue was directly purified via flash column chromatography. *Note: if ^{1}H NMR spectrum of the crude reaction mixture is desired, the crude residue should be passed through a short silica plug (using EtOAc as eluent) to remove paramagnetic cobalt complexes*.



5a **6a**

Prepared according to general procedure D, using α,β-unsaturated nitrile **5a** *(0.12 mmol), cobalt catalyst* **C1** *(0.012 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.36 mmol), and 1,1,3,3-tetramethyldisiloxane (0.36 mmol)*. Yield: 87% of **6a** (44 mg, 0.10 mmol, white crystalline solid);

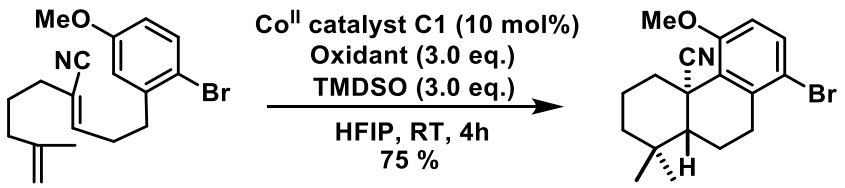
R_f=0.15 (5:95 Et_2O/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.32 (d, *J* = 2.1 Hz, 1H), 6.23 (d, *J* = 1.8 Hz, 1H), 4.22 (tt, *J* = 11.3, 4.0 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.68 (d, *J* = 12.6 Hz, 1H), 2.90 – 2.82 (m, 2H), 1.98 (d, *J* = 13.2 Hz, 1H), 1.80 (d, *J* = 11.3 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.34 – 1.28 (m, 2H), 1.20 (s, 3H), 1.20 – 1.14 (m, 4H), 0.94 (s, 10H), 0.15 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 159.9, 139.8, 122.8, 118.6, 105.4, 97.8, 66.2, 55.6, 55.4, 52.5, 50.5, 43.3, 39.4, 34.9, 33.0, 32.8, 26.1, 21.6, 21.0, 18.5, –4.5; **HRMS** (ES+) *m/z* calc'd for $C_{25}H_{39}NO_3SiNa$ $[M + Na]^+$: 452.2597, found 452.2600.



Prepared according to general procedure D, using α,β-unsaturated nitrile **S11** *(0.38 mmol), cobalt catalyst* **C1***(0.038 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (1.13 mmol), and 1,1,3,3-tetramethyldisiloxane (1.13 mmol)*. Combined yield: 73%; *p*-regioisomer **6b(*p*)**: Yield: 46% (69 mg, 0.17 mmol, white solid); R_f=0.15 (2:2:96 benzene/EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 1H), 6.77 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.24 (tt, *J* = 11.3, 4.0 Hz, 1H), 3.78 (s, 3H), 3.01 (dd, *J* = 17.3, 5.2 Hz, 1H), 2.92 – 2.82 (m, 2H), 2.05 (dd, *J* = 13.1, 7.3 Hz, 1H), 1.90 – 1.86 (m, 1H), 1.79 (ddd, *J* = 12.9, 3.9, 2.1 Hz, 1H), 1.51 – 1.45 (m, 1H), 1.32 – 1.25 (m, 2H), 1.17 (s, 3H), 1.03 (s, 3H), 0.93 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.2, 137.6, 129.8, 126.7, 123.5, 114.2, 113.0, 65.9, 55.4, 50.5, 50.0, 45.2, 39.8, 35.0, 32.2, 30.4, 26.1, 21.3, 21.1, 18.3, –4.4(2C); ; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{37}NO_2SiNa$ $[M + Na]^+$: 422.2491, found 422.2490.

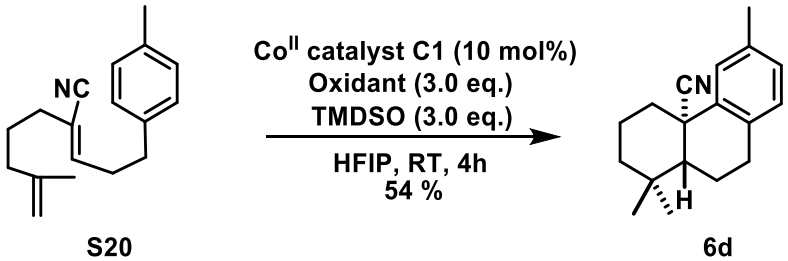
o-regioisomer **6b(o)**: Yield: 27% (41 mg, 0.10 mmol, white solid); R_f=0.20 (2:2:96 benzene/EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.76 – 6.70 (m, 2H), 4.24 (ddd, *J* = 15.3, 7.7, 4.0 Hz, 1H), 3.88 (s, 3H), 3.73 (d, *J* = 12.6 Hz, 1H), 2.94 – 2.83 (m, 2H), 2.03 – 1.97 (m, 1H), 1.82 (ddd, *J* = 12.8, 3.9, 2.1 Hz, 1H), 1.70 – 1.63 (m, 1H), 1.38 – 1.29 (m, 2H), 1.21 (s,

3H), 1.20 – 1.16 (m, 1H), 1.05 (s, 3H), 0.94 (s, 9H), 0.15 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.9, 139.0, 128.8, 125.7, 122.6, 122.4, 109.5, 66.3, 55.6, 52.5, 50.6, 43.0, 39.7, 35.0, 33.0, 32.4, 26.1, 21.6, 20.9, 18.5, –4.48, –4.50; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{37}NO_2SiNa$ $[M + Na]^+$: 422.2491, found 422.2489.



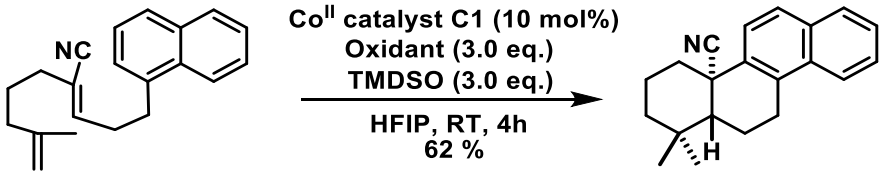
S13 **6c**

Prepared according to general procedure D, using α,β-unsaturated nitrile **S13** *(0.11 mmol), cobalt catalyst* **C1** *(0.011 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.33 mmol), and 1,1,3,3-tetramethyldisiloxane (0.33 mmol)*. Yield: 75% (30 mg, 0.57 mmol, white solid); R_f=0.15 (3:97 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 3H), 3.48 (d, *J* = 13.1 Hz, 1H), 2.93 (dd, *J* = 17.7, 3.6 Hz, 1H), 2.74 – 2.56 (m, 1H), 2.08 (dd, *J* = 13.4, 6.1 Hz, 1H), 1.99 (qt, *J* = 13.7, 3.3 Hz, 1H), 1.71 – 1.58 (m, 3H), 1.31 (d, *J* = 11.8 Hz, 1H), 1.26 (td, *J* = 13.4, 3.8 Hz, 1H), 1.18 (s, 3H), 1.13 (td, *J* = 13.3, 3.3 Hz, 1H), 1.02 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.4, 138.3, 132.5, 129.1, 122.6, 117.0, 111.2, 55.9, 52.3, 40.9, 40.2, 35.0, 34.2, 34.2, 32.7, 21.2, 20.6, 20.5; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{22}BrNONa$ $[M + Na]^+$: 370.0782, found 370.0783.



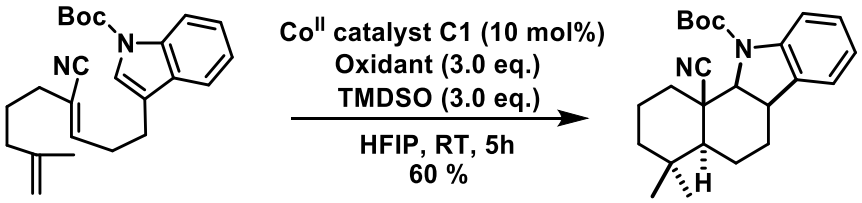
S20 **6d**

Prepared according to general procedure D, using α,β-unsaturated nitrile **S20** *(0.20 mmol), cobalt catalyst* **C1** *(0.020 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.59 mmol), and 1,1,3,3-tetramethyldisiloxane (0.59 mmol)*. Yield: 54% of **6d** (27 mg, 0.57 mmol, white solid); R_f=0.15 (2:98 Et_2O/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.05 – 7.01 (m, 2H), 2.98 (dd, *J* = 16.9, 5.0 Hz, 1H), 2.87 – 2.81 (m, 2H), 2.32 (s, 3H), 2.09 – 1.99 (m, 2H), 1.92 – 1.83 (m, 1H), 1.82 – 1.77 (m, 1H), 1.60 (ddd, *J* = 13.5, 4.6, 3.2 Hz, 1H), 1.49 (td, *J* = 13.4, 3.5 Hz, 1H), 1.35 (dd, *J* = 12.1, 1.9 Hz, 1H), 1.26 (td, *J* = 13.7, 3.8 Hz, 1H), 1.16 (s, 3H), 1.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 137.9, 136.1, 133.1, 129.8, 128.8, 126.2, 123.9, 50.6, 40.8, 40.1, 36.8, 33.8, 32.1, 30.0, 21.7, 21.3, 20.11, 20.08; **HRMS** (ES+) m/z calc'd for $C_{18}H_{23}NNa$ [M + Na]+: 276.1728, found 276.1739.



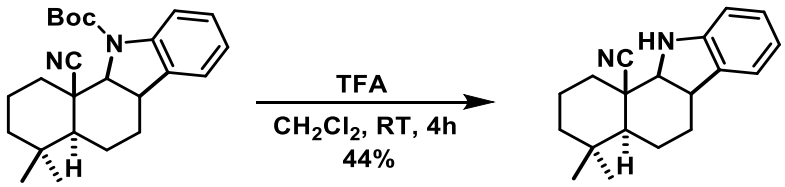
S22 **6e**

Prepared according to general procedure D, using α,β-unsaturated nitrile **S22** *(0.17 mmol), cobalt catalyst* **C1** *(0.017 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.52 mmol), and 1,1,3,3-tetramethyldisiloxane (0.52 mmol)*. Yield: 62% of **6e** (31 mg, 0.11 mmol, white crystalline solid); R_f=0.15 (2:98 Et_2O/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 3.46 (dd, *J* = 17.3, 5.6 Hz, 1H), 3.22 – 3.13 (m, 1H), 2.93 (d, *J* = 13.0 Hz, 1H), 2.30 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.15 – 2.05 (m, 1H), 2.03 – 1.96 (m, 1H), 1.86 – 1.82 (m, 1H), 1.63 (d, *J* = 13.5 Hz, 1H), 1.53 – 1.46 (m, 2H), 1.33 – 1.25 (m, 1H), 1.22 (s, 3H), 1.07 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 135.1, 132.7, 132.4, 132.1, 128.5, 127.5, 126.7, 126.3, 123.7, 123.6, 123.2, 50.5, 40.8, 40.7, 37.2, 33.7, 32.1, 27.7, 21.5, 20.3, 20.1; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{23}NNa$ $[M + Na]^+$: 312.1728, found 312.1724.



S18 **6f**

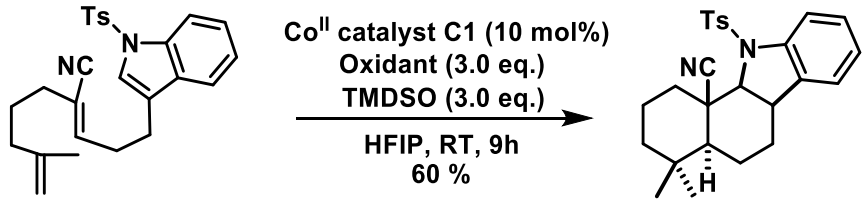
Prepared according to general procedure D, using α,β-unsaturated nitrile **S18** *(0.13 mmol), cobalt catalyst* **C1** *(0.013 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.40 mmol), and 1,1,3,3-tetramethyldisiloxane (0.40 mmol)*. Yield: 60% of **6f** (30 mg, 0.08 mmol, white crystalline solid); R_f=0.18 (2.5:97.5 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) (Note: *mixture of rotamers, integrations are relative*) δ 7.48 – 7.30 (m (br), 1H), 7.24 (t (br), *J* = 7.3 Hz, 1H), 7.16 – 7.11 (m(br), 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.63 – 4.18 (m(br), 2H), 3.63 (t (br), *J* = 7.0 Hz, 2H), 2.51 (d, *J* = 14.1 Hz, 1H), 2.45 – 2.29 (m (br), 2H), 1.95 – 1.80 (m , 2H), 1.78 – 1.64 (m(br), 5H), 1.60 (s(br), 3H), 1.57 (s(br), 15H), 1.29 – 1.16 (m(br), 4H), 1.03 – 0.98 (m, 3H), 0.95 (s(br), 6H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.3, 153.4(br), 143.4(br), 133.9(br), 131.6(br), 128.0(br), 123.8, 123.8, 121.62br), 118.7(br), 117.7, 82.0(br), 69.1(br), 60.6(br), 49.4(br), 45.5, 44.0(br), 41.0, 40.8, 39.7(br), 38.1, 37.9, 33.4, 32.4, 28.5, 28.5, 24.3, 21.2, 21.1, 20.6, 20.6(br), 20.36, 19.2(br), 19.0(br), 14.34. **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{32}N_2O_2Na$ $[M + Na]^+$: 403.2361, found 403.2367.



6f **S49**

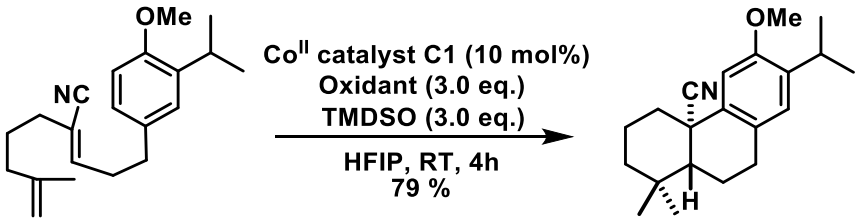
To a solution of indoline **6f** (30 mg, 0.079 mmol) in CH_2Cl_2 (1 mL) was added trifluoroacetic acid (100 µL, 1.3 mmol, ~16 equiv.). The mixture was stirred for 4 h at ambient temperature, then a satd. $NaHCO_{3(aq)}$ solution (2.0 mL) was added. The resulting biphasic mixture was vigorously stirred for 1h then the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic phases were washed with brine (3 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting crude

residue was directly purified via flash chromatography using a mixture of EtOAc/ hexanes (15:85) as eluent to give N-H indoline **S49** as a crystalline white solid (13 mg, 44%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 – 7.05 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 4.34 (s, 1H), 3.47 – 3.44 (m, 2H), 2.49 – 2.42 (m, 1H), 2.27 (d, *J* = 13.0 Hz, 1H), 1.90 (ddd, *J* = 16.2, 11.3, 5.6 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.64 – 1.49 (m, 3H), 1.27 (td, *J* = 13.2, 3.5 Hz, 1H), 1.20 (td, *J* = 13.5, 3.5 Hz, 1H), 1.00 (s, 3H), 1.00 – 0.97 (m, 1H), 0.95 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.7, 130.0, 128.0, 122.4, 122.3, 119.4, 109.6, 69.3, 48.2, 42.7, 41.2, 40.6, 38.0, 33.4, 32.2, 24.7, 20.7, 20.6, 19.0. **HRMS** (ES+) *m/z* calc'd for $C_{19}H_{24}N_2Na$ $[M + Na]^+$: 303.1936, found 303.1939.



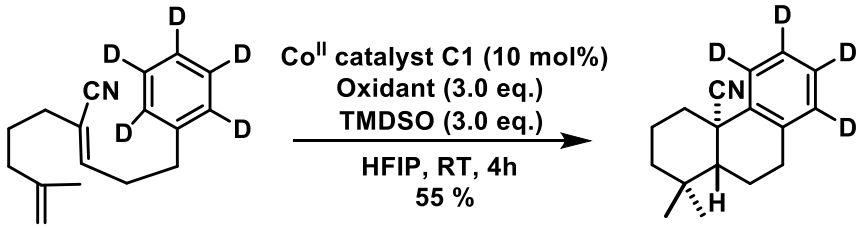
S16 **6g**

Prepared according to general procedure D, using α,β-unsaturated nitrile **S16** *(0.23 mmol), cobalt catalyst* **C1** *(0.023 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.69 mmol), and 1,1,3,3-tetramethyldisiloxane (0.69 mmol)*. Yield: 60% of **6g** (60 mg, 0.14 mmol, white crystalline solid); R_f=0.15 (1:9 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 1H), 3.99 (d, *J* = 7.5 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.71 (t, *J* = 6.8 Hz, 1H), 2.35 (s, 3H), 2.26 (d, *J* = 15.1 Hz, 1H), 1.75 (q, *J* = 13.6 Hz, 1H), 1.70 – 1.61 (m, 3H), 1.50 (d, *J* = 13.4 Hz, 1H), 1.43 (td, *J* = 13.5, 3.0 Hz, 1H), 1.37 (q, *J* = 12.2 Hz, 1H), 1.22 (td, *J* = 13.3, 2.7 Hz, 1H), 0.97 (d, *J* = 11.8 Hz, 1H), 0.93 (s, 3H), 0.92 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.2, 142.9, 135.9, 135.8, 129.8, 128.5, 127.1, 126.3, 122.0, 121.2, 120.3, 72.2, 49.7, 43.1, 41.2, 39.5, 37.1, 33.5, 32.3, 24.4, 21.7, 20.6, 20.1, 18.9; **HRMS** (ES+) *m/z* calc'd for $C_{26}H_{30}N_2O_2SNa$ $[M + Na]^+$: 457.1926, found 457.1926.



S14 **6h**

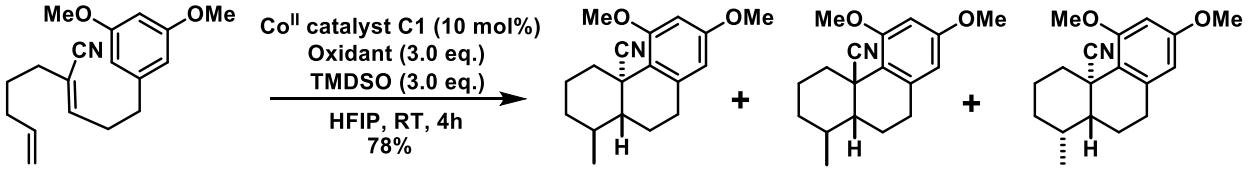
Prepared according to general procedure D, using α,β-unsaturated nitrile **S14** *(1.00 mmol), cobalt catalyst* **C1** *(0.10 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (3.00 mmol), and 1,1,3,3-tetramethyldisiloxane (3.00 mmol)*. Yield: 79% of **6h** (245 mg, 0.79 mmol, white crystalline solid, *spectral data were in accordance with that reported in the literature* [28]); R_f=0.20 (2:2.5:95.5 benzene/EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.83 (s, 1H), 3.81 (s, 3H), 3.25 (sept, *J* = 6.9 Hz, 1H), 3.00 – 2.88 (m, 1H), 2.85 – 2.75 (m, 2H), 2.10 – 1.98 (m, 2H), 1.89 – 1.83 (m, 1H), 1.82 – 1.77 (m, 1H), 1.59 (dd, *J* = 13.5, 1.3 Hz, 1H), 1.52 (td, *J* = 13.3, 3.5 Hz, 1H), 1.37 (dd, *J* = 12.1, 1.7 Hz, 1H), 1.26 (td, *J* = 13.7, 3.7 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 6H), 1.16 (s, 3H), 1.01 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.63, 137.31, 135.70, 127.98, 127.35, 123.97, 107.22, 55.63, 50.65, 40.83, 40.26, 36.85, 33.76, 32.14, 29.77, 26.65, 22.73, 21.89, 20.121, 20.116; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{29}NONa$ $[M + Na]^+$: 334.2147, found 334.2153.



28 **29**

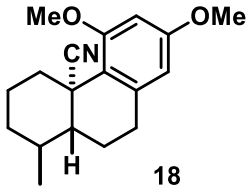
Prepared according to general procedure D, using α,β-unsaturated nitrile **28** *(0.53 mmol), cobalt catalyst* **C1** *(0.053 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (1.60 mmol), and 1,1,3,3-tetramethyldisiloxane (1.60 mmol)*. Yield: 55% of **29** (72 mg, 0.29 mmol, white crystalline solid); R_f=0.15 (1.5:98.5 EtOAc/hexanes- recrystallized from a mixture of methanol/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.09 (ddd, *J* = 17.1, 6.0, 1.7 Hz, 1H), 2.95 (ddd, *J* = 18.6,12.0, 6.7 Hz, 1H), 2.89 (d, *J* =

13.1 Hz, 1H), 2.14 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.08 (tt, *J* = 13.9, 3.3 Hz, 1H), 1.95 (ddd, *J* = 25.6, 12.2, 6.0 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.66 (d, *J* = 13.5 Hz, 1H), 1.56 (td, *J* = 13.4, 3.5 Hz, 1H), 1.43 (dd, *J* = 12.1, 1.7 Hz, 1H), 1.32 (td, *J* = 13.6, 3.7 Hz, 1H), 1.22 (s, 3H), 1.07 (s, 3H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 137.9, 136.1, 129.4 (t, *J* = 24.0 Hz), 127.3 (t, *J* = 24.4 Hz), 126.1 (t, *J* = 24.8 Hz), 125.2 (t, *J* = 24.0 Hz), 123.6, 50.4, 40.7, 40.1, 36.7, 33.7, 32.0, 30.1, 21.5, 20.0, 20.0; **HRMS** (ES+) *m/z* calc'd for $C_{17}H_{17}D_4NNa$ $[M + Na]^+$: 266.1823, found 266.1826. *To quantify the extent of deuterium incorporation (~5% D_2), the purified samples were analyzed by isotope ratio mass spectrometry modeling (flow injection analysis)- see the attached spectra*.



17 18 19 20

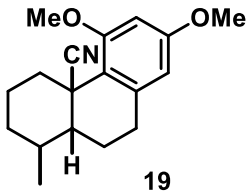
Prepared according to general procedure D, using α,β-unsaturated nitrile **17** *(0.31 mmol), cobalt catalyst* **C1** *(0.031 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.92 mmol), and 1,1,3,3-tetramethyldisiloxane (0.92 mmol)*. Combined yield: 78% (69 mg, 0.24 mmol) - individual yields were determined from crude ^{1}H NMR spectra, using an internal standard (CH_2Br_2). Pure samples of each stereoisomer were obtained via extensive preparatory TLC (multiple developments using 5:1:4 benzene /chloroform /hexanes mixture as eluent).



18

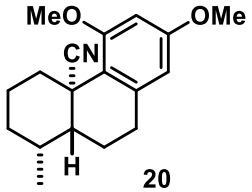
Stereoisomer **18**: white crystalline solid; R_f=0.15 (5:1:4 benzene/chloroform/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.33 (d, *J* = 2.5 Hz, 1H), 6.23 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.32 (d, *J* =

13.1 Hz, 1H), 2.87 – 2.75 (m, 2H), 2.08 – 2.03 (m, 1H), 1.99 – 1.87 (m, 2H), 1.86 – 1.82 (m, 1H), 1.80 – 1.74 (m, 1H), 1.49 (ddd, *J* = 18.2, 12.7, 6.2 Hz, 1H), 1.26 – 1.22 (m, 1H), 1.21 – 1.17 (m, 1H), 1.07 (ddd, *J* = 24.9, 13.2, 4.4 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.2, 159.9, 140.3, 122.2, 117.6, 105.3, 97.8, 55.6, 55.4, 51.8, 42.3, 35.7, 34.7, 33.1, 32.1, 23.5, 22.7, 20.1; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}NO_2Na$ $[M + Na]^+$: 308.1627, found 308.1637.



19

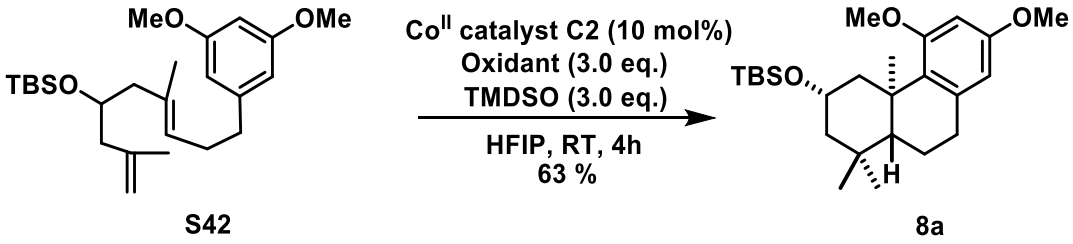
Stereoisomer **19**: white crystalline solid; R_f=0.13 (5:1:4 benzene/chloroform/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.35 (d, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.85 – 2.74 (m, 2H), 2.43 (d, *J* = 13.9 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.03 (d, *J* = 13.1 Hz, 1H), 1.85 – 1.75 (m, 2H), 1.72 – 1.66 (m, 1H), 1.60 – 1.54 (m, 1H), 1.52 – 1.49 (m, 1H), 1.46 (td, *J* = 13.8, 3.9 Hz, 1H), 1.13 (qd, *J* = 13.1, 3.9 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8, 158.8, 138.4, 124.3, 118.3, 105.3, 97.9, 55.8, 55.4, 45.3, 40.1, 31.9, 30.9, 30.3, 28.5, 23.6, 19.8, 16.9; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}NO_2Na$ $[M + Na]^+$: 308.1627, found 308.1620.



20

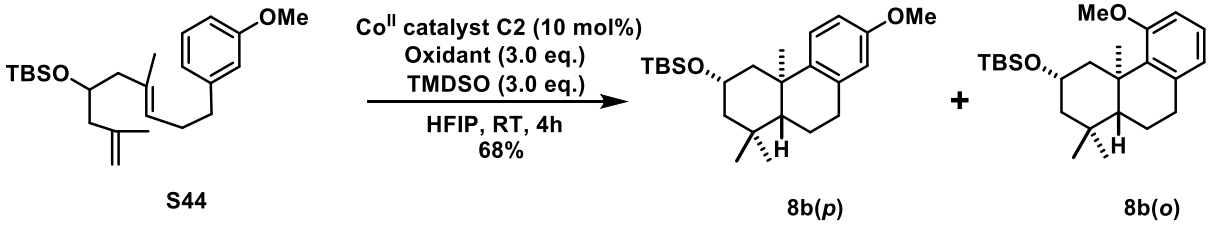
Stereoisomer **20**: white crystalline solid; R_f=0.14 (5:1:4 benzene/chloroform/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.31 (d, *J* = 2.5 Hz, 1H), 6.22 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 3.44 (d, *J* = 13.3 Hz, 1H), 2.92 (ddd, *J* = 18.2, 12.6, 5.9 Hz, 1H), 2.82 (dd, *J* = 16.5, 4.3 Hz, 1H), 2.14 – 2.07 (m, 1H), 2.07 – 2.00 (m, 2H), 1.98 – 1.95 (m, 1H), 1.72 (ddd, *J* = 12.3, 4.5, 1.4 Hz, 1H), 1.69 – 1.61 (m, 3H), 1.25

([*overlapping with silicone grease signal*] d, *J* = 6.5 Hz, 3H), 1.18 (td, *J* = 13.4, 3.0 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.2, 159.8, 139.9, 123.7, 118.9, 105.4, 97.7, 55.5, 55.3, 47.1, 38.3, 35.3, 34.4, 32.6, 32.2, 26.3, 19.3, 13.7. **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{23}NO_2Na$ $[M + Na]^+$: 308.1627, found 308.1628.



S42 8a

Prepared according to general procedure D, using terminal alkene **S42** *(0.12 mmol), cobalt catalyst* **C2** *(0.012 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.36 mmol), and 1,1,3,3-tetramethyldisiloxane (0.36 mmol)*. Yield: 63% of **8a** (32 mg, 0.08 mmol, white solid); R_f=0.20 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 2.5 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 4.01 (tt, *J* = 11.3, 4.1 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.45 – 3.34 (m, 1H), 2.89 – 2.80 (m, 2H), 1.83 – 1.76 (m, 1H), 1.75 – 1.68 (m, 1H), 1.55 – 1.49 (m, 1H), 1.29 (s, 3H), 1.27 – 1.21 (m, 2H), 1.15 – 1.08 (m, 1H), 0.99 (s, 3H), 0.95 (s, 3H), 0.94 (s, 9H), 0.12 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 158.0, 138.6, 129.8, 105.1, 97.7, 66.5, 55.2, 55.1, 52.9, 51.1, 46.1, 40.4, 34.8, 34.2, 33.6, 26.3(3C), 23.1, 20.9, 18.8, 18.6, –4.3(2C); **HRMS** (ES+) *m/z* calc'd for $C_{25}H_{42}O_3SiNa$ $[M + Na]^+$: 441.2801, found 441.2818.

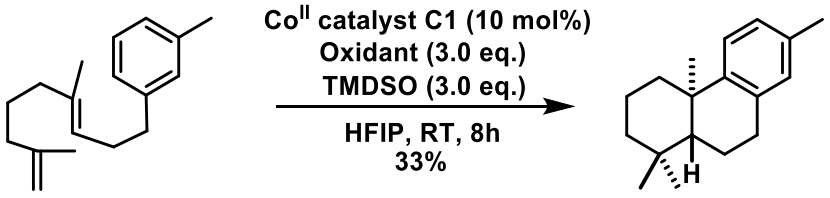


S44 8b(*p*) 8b(*o*)

Prepared according to general procedure D, using terminal alkene **S44** *(0.13 mmol), cobalt catalyst* **C2** *(0.013 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.39 mmol), and 1,1,3,3-tetramethyldisiloxane*

(0.39 mmol). Combined yield: 68%; *p*-regioisomer **8b(*p*)** : Yield: 41% (21 mg, 0.053 mmol, white solid); R_f=0.14 (5:1:94 benzene/EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.7 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.03 (tt, *J* = 11.3, 4.0 Hz, 1H), 3.76 (s, 3H), 2.93 (dd, *J* = 17.2, 6.6 Hz, 1H), 2.89 – 2.81 (m, 1H), 2.44 (ddd, *J* = 12.2, 3.6, 2.2 Hz, 1H), 1.87 (dd, *J* = 13.3, 7.7 Hz, 1H), 1.75 – 1.70 (m, 1H), 1.70 – 1.64 (m, 1H), 1.38 (t, *J* = 11.7 Hz, 1H), 1.30 (dd, *J* = 12.6, 2.3 Hz, 1H), 1.26 (t, *J* = 12.1 Hz, 1H), 1.18 (s, 3H), 0.99 (s, 3H), 0.96 (s, 3H), 0.94 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.3, 142.1, 136.4, 125.4, 113.4, 112.0, 66.4, 55.3, 51.3, 49.9, 48.4, 39.0, 34.8, 33.5, 30.6, 26.2, 26.0, 22.7, 18.9, 18.5, –4.30, –4.33; **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{40}O_2SiNa$ $[M + Na]^+$: 411.2695, found 411.2693.

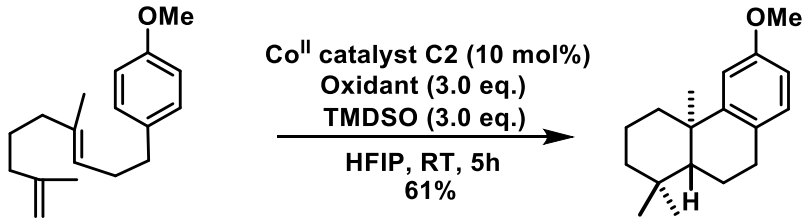
o-regioisomer **8b(*o*)**: Yield: 27% (14 mg, 0.035 mmol, white solid); R_f=0.15 (5:1:94 benzene/EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 (t, *J* = 7.8 Hz, 1H), 6.70 – 6.65 (m, 2H), 4.02 (tt, *J* = 11.3, 4.2 Hz, 1H), 3.79 (s, 3H), 3.45 (ddd, *J* = 12.6, 3.7, 2.2 Hz, 1H), 2.88-2.66 (m, 2H), 1.83 – 1.77 (m, 1H), 1.72 (ddd, *J* = 12.5, 4.2, 2.2 Hz, 1H), 1.32 (s, 3H), 1.27 – 1.22 (m, 3H), 1.15 (t, *J* = 12.0 Hz, 1H), 1.00 (s, 3H), 0.96 (s, 3H), 0.94 (s, 9H), 0.12 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.6, 138.0, 136.9, 126.3, 122.4, 109.3, 66.5, 55.1, 52.7, 51.0, 45.8, 40.9, 34.8, 34.2, 33.1, 26.3(3C), 23.2, 20.7, 18.8, 18.7, –4.3(2C); **HRMS** (ES+) *m/z* calc'd for $C_{24}H_{40}O_2SiNa$ $[M + Na]^+$: 411.2695, found 411.2697.



S30 **8c**

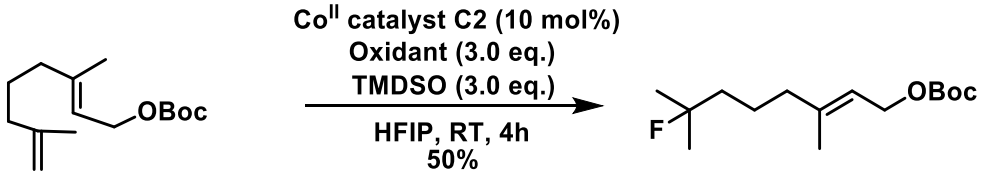
Prepared according to general procedure D, using terminal alkene **S30** *(0.21 mmol), cobalt catalyst* **C1***(0.021 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.62 mmol), and 1,1,3,3-tetramethyldisiloxane (0.62 mmol)*. Yield: 33% of **8c**(17 mg, 0.07 mmol, white solid, ~80% purity by ^{1}H NMR); R_f=0.64 (hexanes); *spectral data were in accordance with that reported in the literature*[29]: **^{1}H**

NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.86 (s, 1H), 2.90 (dd, *J* = 16.4, 6.5 Hz, 1H), 2.86 – 2.78 (m, 1H), 2.27 (s, 4H), 1.90 – 1.83 (m, 1H), 1.77 – 1.72 (m, 1H), 1.71 – 1.66 (m, 1H), 1.63 – 1.57 (m, 2H), 1.48 (d, *J* = 13.3 Hz, 1H), 1.38 (td, *J* = 13.3, 3.7 Hz, 1H), 1.32 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.23 (dd, *J* = 13.7, 3.8 Hz, 1H), 1.18 (s, 3H), 0.94 (s, 3H), 0.93 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 135.3, 134.7, 129.7, 126.6, 124.5, 77.4, 77.2, 77.0, 50.7, 41.9, 39.1, 37.6, 33.6, 33.5, 30.5, 25.0, 21.8, 20.9, 19.5, 19.2.



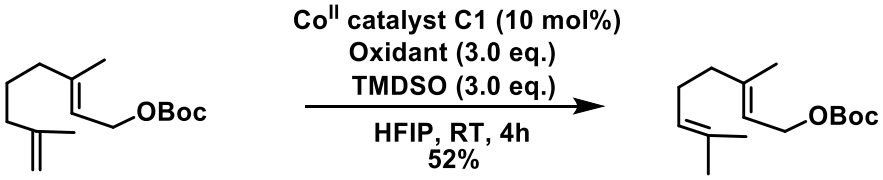
S29 **8d**

Prepared according to general procedure D, using terminal alkene **S29** *(0.39 mmol), cobalt catalyst* **C2** *(0.039 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (1.16 mmol), and 1,1,3,3-tetramethyldisiloxane (1.16 mmol)*. Yield: 61% of **8d** (61 mg, 0.24 mmol, white crystalline solid, *spectral data were in accordance with that reported in the literature*[30]); R_f=0.15 (1:99 EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.66 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.78 (s, 3H), 2.89 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.25 (d, *J* = 12.7 Hz, 1H), 1.87 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.70 – 1.65 (m, 1H), 1.64 – 1.59 (m, 1H), 1.48 (dd, *J* = 13.2, 1.2 Hz, 1H), 1.41 (td, *J* = 12.9, 3.5 Hz, 1H), 1.33 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.22 (td, *J* = 13.5, 4.0 Hz, 1H), 1.19 (s, 3H), 0.95 (s, 3H), 0.93 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.8, 151.6, 129.9, 127.6, 110.8, 110.3, 55.4, 50.5, 41.8, 39.0, 38.2, 33.6, 33.5, 29.7, 24.9, 21.8, 19.5, 19.3; **HRMS** (ES+) *m/z* calc'd for $C_{18}H_{26}O_3$ $[M]^+$: 258.19484, found 258.1978.



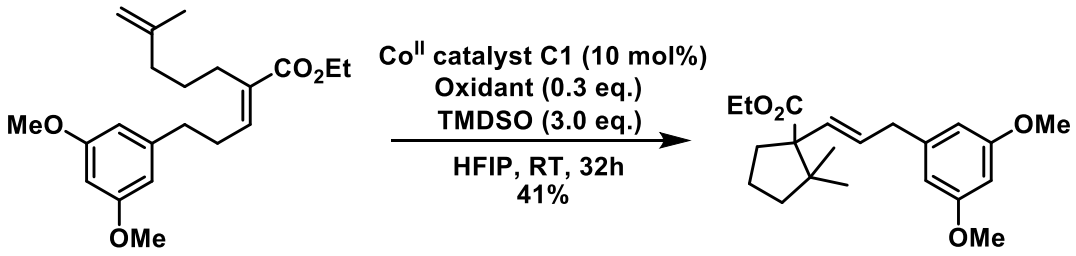
22 **24**

Prepared according to general procedure D, using terminal alkene **22** *(0.20 mmol), cobalt catalyst* **C2** *(0.020 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.60 mmol), and 1,1,3,3-tetramethyldisiloxane (0.60 mmol)*. Yield: 50% of **24** (25 mg, 0.10 mmol, clear colorless oil); R_f=0.40 (1:9 EtOAc/hexanes); *Note: The sample contained other regio- and sterioisomers, which could not be separated (~70% purity).* **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.37 (t, *J* = 7.1 Hz, 1H), 4.58 (d, *J* = 7.1 Hz, 2H), 2.04 (t, *J* = 7.0 Hz, 2H), 1.70 (s, 3H), 1.59 – 1.55 (m, 2H), 1.55 – 1.50 (m, 2H), 1.48 (s, 9H), 1.33 (d, *J* = 21.4 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.8, 142.4, 118.6, 95.7 (d, *J* = 164.6 Hz), 82.0, 63.8, 41.0 (d, *J* = 23.0 Hz), 39.7, 27.9, 26.8 (d, *J* = 24.9 Hz), 21.93, 21.91(d, *J* = 5.1 Hz), 16.4; **HRMS** (ES+) *m/z* calc'd for $C_{15}H_{27}FO_3Na$ $[M + Na]^+$: 297.1841, found 297.1836.



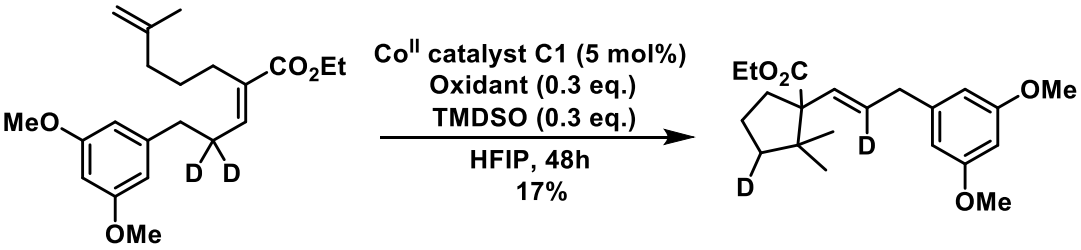
22 **25**

Prepared according to general procedure D, using terminal alkene **22** *(0.20 mmol), cobalt catalyst* **C1** *(0.020 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.60 mmol), and 1,1,3,3-tetramethyldisiloxane (0.60 mmol)*. Yield: 52% of **25** (26 mg, 0.10 mmol, clear colorless oil); R_f=0.40 (1:9 EtOAc/hexanes); *spectral data were in accordance with that reported in the literature[31]* ; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.37 (td, *J* = 7.1, 1.1 Hz, 1H), 5.08 (t, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 7.1 Hz, 2H), 2.13 – 2.06 (m, 2H), 2.06 – 2.01 (m, 2H), 1.70 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.48 (s, 9H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.8, 142.7, 132.0, 123.9, 118.2, 82.0, 63.9, 39.7, 28.0, 26.4, 25.8, 17.8, 16.7; **HRMS** (ES+) *m/z* calc'd for $C_{15}H_{26}O_3Na$ $[M + Na]^+$: 277.1780, found 277.1784.



14-*E* **16**

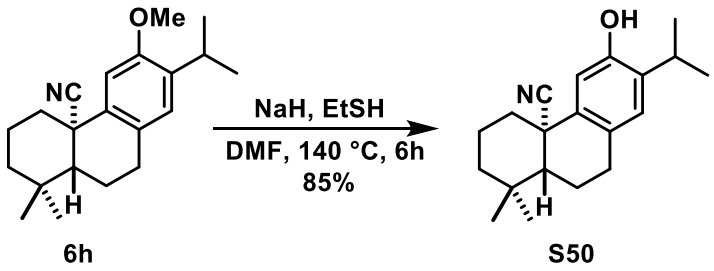
Prepared according to general procedure D, using α,β-unsaturated ethyl ester **14–*E*** *(0.14 mmol), cobalt catalyst* **C1** *(0.014 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.05 mmol), and 1,1,3,3-tetramethyldisiloxane (0.42 mmol)*. Yield: 41% of **16** (21 mg, 0.06 mmol, clear colorless oil); R_f=0.15 (2:98 EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 1.9 Hz, 2H), 6.31 (t, *J* = 2.1 Hz, 1H), 5.90 (d, *J* = 15.7 Hz, 1H), 5.62 – 5.50 (m, 1H), 4.19 – 4.09 (m, 2H), 3.76 (s, 6H), 3.34 (d, *J* = 6.9 Hz, 2H), 2.44 – 2.35 (m, 1H), 1.98 – 1.91 (m, 1H), 1.82 – 1.71 (m, 1H), 1.67 – 1.57 (m, 2H), 1.54 – 1.48 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.0, 160.9, 143.3, 133.1, 127.8, 106.6, 98.3, 60.9, 60.4, 55.4, 46.1, 39.7, 39.5, 30.7, 25.3, 24.6, 19.9, 14.4; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{30}O_4Na$ $[M + Na]^+$: 369.2042, found 369.2045.



14-*E*-*d*$_2$ **16-*d*$_2$**

Prepared according to general procedure D, using α,β-unsaturated ethyl ester **14–*E*–*d*$_2$** *(0.066 mmol), cobalt catalyst* **C1** *(0.0033 mmol), 1-fluoro-2,4,6-trimethylpyridinium triflate (0.02 mmol), and 1,1,3,3-tetramethyldisiloxane (0.020 mmol). Note: the reaction time was 48h. The crude reaction mixture contained a considerable amount of isomerized starting material*. Yield: 17% of **16–*d*$_2$** (4 mg, 0.011 mmol, clear colorless oil); R_f=0.15 (2:98 EtOAc/hexanes – purified via PTLC); **^{1}H NMR** (600 MHz,

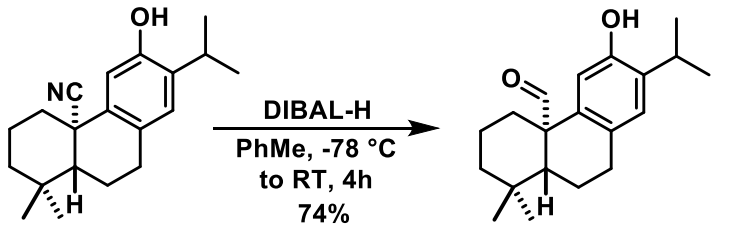
$CDCl_3$) δ 6.33 (d, *J* = 2.0 Hz, 2H), 6.31 (t, *J* = 2.0 Hz, 1H), 5.90 (s, 1H), 4.17 – 4.09 (m, 2H), 3.76 (s, 6H), 3.34 (s, 2H), 2.47 – 2.32 (m, 1H), 1.98 – 1.90 (m, 1H), 1.80 – 1.72 (m, 1H), 1.65 – 1.58 (m, 2H), 1.53 – 1.47 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.0, 160.9 (2C), 143.3, 132.9, 127.5 (t, *J* = 23.0 Hz), 106.6 (2C), 98.3, 60.9, 60.4, 55.4 (2C), 46.1, 39.6, 39.4, 30.6, 25.3, 24.6, 19.9, 14.4; **HRMS** (ES+) *m/z* calc'd for $C_{21}H_{28}D_2O_4Na$ $[M + Na]^+$: 371.2167, found 371.2175. *To quantify the extent of deuterium incorporation (~38% D_2), the purified samples were analyzed by isotope ratio mass spectrometry modeling (flow injection analysis)- see the attached spectra*.



6h **S50**

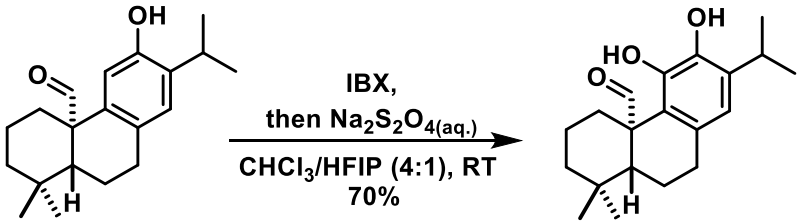
To a cooled (4 °C) suspension of sodium hydride (60% in mineral oil, 167 mg, 4.18 mmol, 10 equiv.) in DMF (2.0 mL), ethanethiol (0.6 mL, 8.36 mmol, 20 equiv.) was added dropwise. The resulting mixture was stirred for 30 min. while warming to ambient temperature, then a solution of **6h (**130 mg, 0.42 mmol, 1.0 equiv.) in DMF (1.0 mL) was added and the mixture was heated to 140 °C. After stirring for 6 hours, the mixture was cooled to ambient temperature, diluted with Et_2O (20 mL) and a solution of 2N $HCl_{(aq.)}$ (5 mL) was added. After stirring vigorously for 15 min., the organic phase was washed with DI H_2O (3 x 10 mL), then brine (10 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo.* The crude residue was purified via flash column chromatography (EtOAc/ hexanes 15:85, R_f= 0.34) to give **S50** as a white solid (106 mg, 0.355 mmol, 85 % yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.80 (s, 1H), 5.15 (s (broad), 1H), 3.15 (hept, *J* = 6.9 Hz, 1H), 2.93 (dd, *J* = 16.7, 4.9 Hz, 1H), 2.84 – 2.75 (m, 1H), 2.69 (d, *J* = 13.1 Hz, 1H), 2.06 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.00 (qt, *J* = 13.9, 3.2 Hz, 1H), 1.83 (qd, *J* = 12.3, 5.9 Hz,

1H), 1.79 – 1.74 (m, 1H), 1.58 (d, *J* = 13.4 Hz, 1H), 1.48 (td, *J* = 13.4, 3.5 Hz, 1H), 1.35 (dd, *J* = 12.1, 1.5 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.15 (s, 3H), 1.00 (s, 3H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 151.7, 135.8, 135.0, 128.1, 127.6, 123.9, 112.1, 50.5, 40.8, 40.0, 36.8, 33.7, 32.1, 29.7, 27.0, 22.7, 22.6, 21.9, 20.08, 20.07; **HRMS** (ES+) *m/z* calc'd for $C_{20}H_{27}NONa$ $[M + Na]^+$: 320.1990, found 320.1992.



S50 **S51** ***pisiferal***

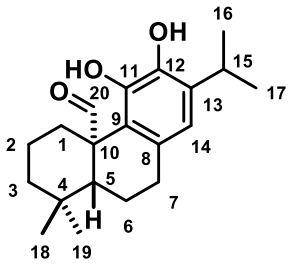
To a cooled (–78 °C) solution of nitrile **S50** (8 mg, 0.027 mmol, 1 equiv.) in toluene (0.5 mL), a 1.0 M solution of diisobutylaluminum hydride (0.8 mL, 0.80 mmol, 30 equiv.) was added dropwise. The resulting mixture was stirred at –78 °C for 2 hours, warmed to ambient temperature, quenched with a saturated aqueous solution of sodium potassium tartrate (2.0 mL) and stirred vigorously for 1 h. The aqueous phase was extracted with EtOAc (3 x 3 mL), then the combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo.* The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of EtOAc/ hexanes (6:94) as eluent to give **S51** (+/- ***pisiferal***) as a white solid (6 mg, 0.020 mmol, 74% yield, *spectral data are in agreement with that reported in the literature*[32]); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 6.92 (s, 1H), 6.60 (s, 1H), 5.40 (s (broad), 1H), 3.16 (hept, *J* = 6.8 Hz, 1H), 2.99 – 2.85 (m, 3H), 2.14 – 2.01 (m, 2H), 1.76 – 1.57 (m, 3H), 1.46 (d, *J* = 13.2 Hz, 1H), 1.27 (td, *J* = 13.5, 4.3 Hz, 1H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.20 – 1.16 (m, 1H), 1.00 (s, 3H), 0.83 (s, 3H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 201.5, 152.0, 134.5, 133.2, 130.4, 127.4, 113.9, 53.4, 51.9, 41.4, 34.0, 32.7, 31.7, 30.2, 27.0, 22.7, 22.5, 20.7, 19.7, 18.5; **HRMS** (ES+) *m/z* calc'd for $C_{20}H_{27}O_2$ $[M – H]^–$: 299.2011, found 299.2023.



S51 ***carnosaldehyde***

To a solution of **S51** (8 mg, 0.027 mmol, 1 equiv.) in a mixture of $CHCl_3$ and HFIP (4:1, 0.5 mL) was added 2-Iodoxybenzoic acid (14 mg, 0.049 mmol, 1.5 equiv.). The resulting suspension was stirred in the dark for 3 hours or until **S51** was consumed as determined via TLC. Then, a saturated solution of $Na_2S_2O_4$(aq.) (2.0 mL) was added and the biphasic mixture was stirred vigorously for 3 hours. The aqueous phase was extracted with $CHCl_3$ (3 x 3.0 mL), then the combined organic extracts were washed with satd. $NaHCO_{3(aq)}$ (5.0 mL), brine (5.0 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo.* The resulting crude residue was purified via flash column chromatography on SiO_2, using a mixture of EtOAc/ hexanes (7:93) as eluent to give +/- ***carnosaldehyde*** as a white solid (6 mg, 0.019 mmol, 70% yield, *spectral data are in agreement with that reported in the literature- only ^1H NMR data[33] is known*); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.13 (s, 1H), 6.60 (s, 1H), 5.78 (s, 1H), 3.28 – 3.19 (m, 2H), 2.87 (dd, *J* = 8.5, 3.5 Hz, 2H), 2.03 (d, *J* = 13.3 Hz, 1H), 1.86 (tt, *J* = 13.2, 8.9 Hz, 1H), 1.62 (d, *J* = 12.1 Hz, 1H), 1.60 – 1.52 (m, 2H), 1.48 (d, *J* = 13.4 Hz, 1H), 1.33 (td, *J* = 13.1, 4.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.14 (td, *J* = 13.0, 3.1 Hz, 1H), 1.04 (s, 3H), 0.90 (s, 3H); **^{13}C DEPTQ NMR** (151 MHz, $CDCl_3$) δ 203.7, 143.4, 142.5, 134.7, 130.1, 119.5, 116.4, 116.3, 54.1, 53.1, 41.5, 34.4, 32.0, 31.7, 30.6, 27.3, 22.5, 22.3, 21.7, 19.8, 19.0; **HRMS** (ES+) *m/z* calc'd for $C_{20}H_{28}O_3$ $[M - H]^-$: 315.1960, found 315.1950.

Comparison table of ^{1}H NMR data [δ_H (J, Hz)] for natural[33] and synthetic ***carnosaldehyde***:



Note: some signals have been reassigned based on 2D NMR data (highlighted in green). Aside from minor impurities in the natural sample, the spectra are practically identical. *Overlapping signals.

^{1}H Signal	natural carnosaldehyde	synthetic carnosaldehyde
1α	1.13 m	1.14 td (13.0, 3.1)
1β	3.22 m*	3.28 – 3.19 m*
2α	1.48 – 1.59 m*	1.60 – 1.52 m*
2β	1.48 – 1.59 m*	1.60 – 1.52 m*
3α	1.15 – 1.36 m*	1.33 td (13.1, 4.9)
3β	1.15 – 1.36 m*	1.48 d, (13.4)
5	1.62 dd (12.7, 1.7)	1.62 d (12.1)
6α	2.03 m	1.86 tt, (13.2, 8.9)
6β	1.86 tt (13.2, 8.7)	2.03 d (13.3)
7α	2.87 dd (8.5, 3.6)	2.87 dd (8.5, 3.5)
7β	2.87 dd (8.5, 3.6)	2.87 dd (8.5, 3.5)
14	6.60 s	6.60 s
15	3.23 m*	3.28 – 3.19 m*
16	1.21 d (6.9)	1.21 d (6.9)
17	1.21 d (6.9)	1.21 d (6.9)
18	1.04 s	1.04 s
19	0.9 s	0.90 s
20	9.9 d (1.5)	9.90 s
11-OH	7.13 s	7.13 s
12-OH	5.78 s	5.78 s

E. X-Ray Crystallographic Data

X-ray Data Collection, Structure Solution and Refinement for cdv56 (**6e**)

A colorless crystal of approximate dimensions 0.198 x 0.243 x 0.417 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.1161 and Goof = 1.047 for 291 variables refined against 3705 data (0.74 Å), R1 = 0.0393 for those 3247 data with $I > 2.0\sigma(I)$.

References.

1. APEX2 Version 2014.11-0, Bruker AXS, Inc.; Madison, WI 2014.

2. SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.

3. Sheldrick, G. M. SADABS, Version 2014/5, Bruker AXS, Inc.; Madison, WI 2014.

4. Sheldrick, G. M. SHELXTL, Version 2014/7, Bruker AXS, Inc.; Madison, WI 2014.

5. International Tables for Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Definitions:

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

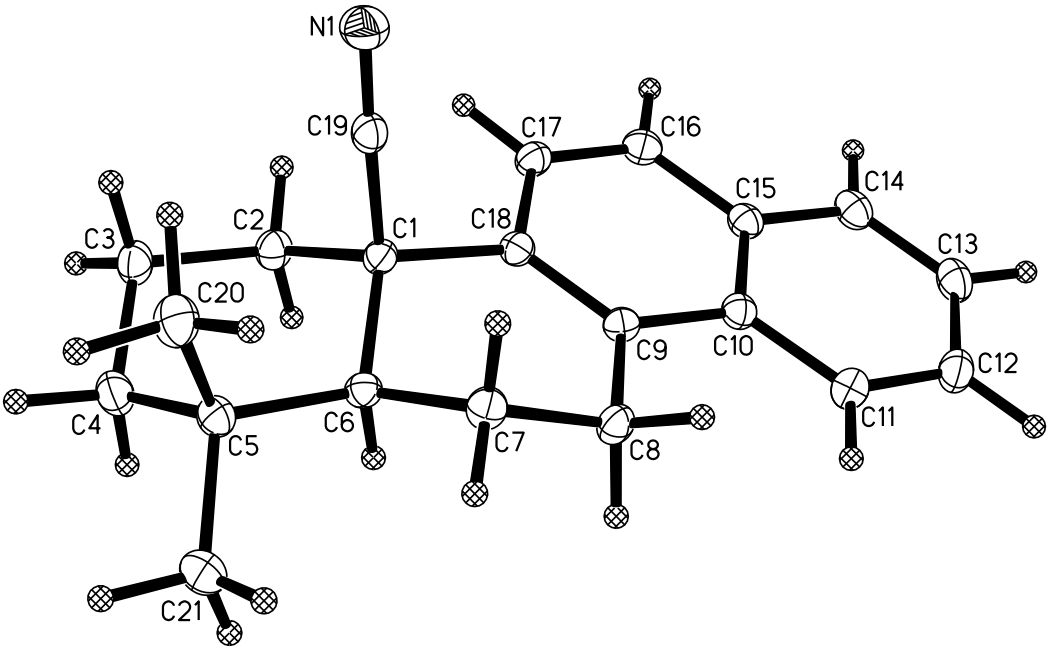

N1
C19
C17
C16
C15
C14
C2
C1
C18
C3
C13
C20
C9
C10
C12
C4
C5
C6
C7
C8
C11
C21

Table 1. Crystal data and structure refinement for cdv56.

Identification code	cdv56 (Darius Vrubliauskas)	
Empirical formula	C_{21} H_{23} N	
Formula weight	289.40	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.0668(10) Å	α = 108.7911(14)°.
	b = 8.2309(10) Å	β = 96.3755(15)°.
	c = 12.7071(15) Å	γ = 97.8034(14)°.
Volume	780.50(16) Å^3	
Z	2	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	312	
Crystal color	colorless	
Crystal size	0.417 x 0.243 x 0.198 mm^3	
Theta range for data collection	1.716 to 28.741°	
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 11$, $-16 \le l \le 16$	
Reflections collected	9432	
Independent reflections	3705 [R(int) = 0.0275]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6770	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3705 / 0 / 291	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I) = 3247 data]	R1 = 0.0393, wR2 = 0.1111	
R indices (all data, 0.74 Å)	R1 = 0.0443, wR2 = 0.1161	
Largest diff. peak and hole	0.364 and -0.222 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for cdv56. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6114(1)	6143(1)	8157(1)	24(1)
C(1)	6249(1)	2836(1)	7150(1)	14(1)
C(2)	4434(1)	1777(1)	6952(1)	17(1)
C(3)	3882(1)	1745(1)	8057(1)	19(1)
C(4)	5119(1)	1014(1)	8703(1)	20(1)
C(5)	6968(1)	1983(1)	8947(1)	16(1)
C(6)	7481(1)	2091(1)	7825(1)	14(1)
C(7)	9289(1)	3027(1)	7918(1)	16(1)
C(8)	9826(1)	2568(1)	6761(1)	16(1)
C(9)	8494(1)	2670(1)	5860(1)	14(1)
C(10)	8968(1)	2658(1)	4800(1)	15(1)
C(11)	10616(1)	2450(1)	4548(1)	18(1)
C(12)	11052(1)	2482(1)	3540(1)	20(1)
C(13)	9864(1)	2705(1)	2720(1)	20(1)
C(14)	8260(1)	2898(1)	2930(1)	19(1)
C(15)	7778(1)	2882(1)	3969(1)	15(1)
C(16)	6128(1)	3103(1)	4201(1)	17(1)
C(17)	5685(1)	3061(1)	5197(1)	16(1)
C(18)	6852(1)	2821(1)	6034(1)	14(1)
C(19)	6202(1)	4702(1)	7756(1)	16(1)
C(20)	7176(1)	3774(1)	9872(1)	21(1)
C(21)	8088(1)	893(2)	9386(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for cdv56.

N(1)-C(19)	1.1464(13)
C(1)-C(19)	1.4877(13)
C(1)-C(18)	1.5459(12)
C(1)-C(2)	1.5484(13)
C(1)-C(6)	1.5544(12)
C(2)-C(3)	1.5268(13)
C(3)-C(4)	1.5263(14)
C(4)-C(5)	1.5399(14)
C(5)-C(20)	1.5342(14)
C(5)-C(21)	1.5369(13)
C(5)-C(6)	1.5543(12)
C(6)-C(7)	1.5271(13)
C(7)-C(8)	1.5232(13)
C(8)-C(9)	1.5120(12)
C(9)-C(18)	1.3828(13)
C(9)-C(10)	1.4374(13)
C(10)-C(11)	1.4208(13)
C(10)-C(15)	1.4210(13)
C(11)-C(12)	1.3732(14)
C(12)-C(13)	1.4090(15)
C(13)-C(14)	1.3694(14)
C(14)-C(15)	1.4200(13)
C(15)-C(16)	1.4180(13)
C(16)-C(17)	1.3625(13)
C(17)-C(18)	1.4219(13)

C(19)-C(1)-C(18)	104.44(7)
C(19)-C(1)-C(2)	107.95(7)
C(18)-C(1)-C(2)	112.23(7)
C(19)-C(1)-C(6)	112.47(7)
C(18)-C(1)-C(6)	110.72(7)
C(2)-C(1)-C(6)	108.99(7)
C(3)-C(2)-C(1)	111.63(8)
C(4)-C(3)-C(2)	111.57(8)

C(3)-C(4)-C(5)	113.98(8)
C(20)-C(5)-C(21)	108.02(8)
C(20)-C(5)-C(4)	110.41(8)
C(21)-C(5)-C(4)	107.52(8)
C(20)-C(5)-C(6)	113.33(8)
C(21)-C(5)-C(6)	108.80(8)
C(4)-C(5)-C(6)	108.59(7)
C(7)-C(6)-C(5)	115.41(7)
C(7)-C(6)-C(1)	108.53(7)
C(5)-C(6)-C(1)	115.28(7)
C(8)-C(7)-C(6)	110.29(8)
C(9)-C(8)-C(7)	113.23(8)
C(18)-C(9)-C(10)	119.12(8)
C(18)-C(9)-C(8)	122.07(8)
C(10)-C(9)-C(8)	118.79(8)
C(11)-C(10)-C(15)	117.81(9)
C(11)-C(10)-C(9)	122.20(9)
C(15)-C(10)-C(9)	119.98(8)
C(12)-C(11)-C(10)	121.17(9)
C(11)-C(12)-C(13)	120.62(9)
C(14)-C(13)-C(12)	119.86(9)
C(13)-C(14)-C(15)	120.70(9)
C(16)-C(15)-C(14)	121.18(9)
C(16)-C(15)-C(10)	118.99(9)
C(14)-C(15)-C(10)	119.82(9)
C(17)-C(16)-C(15)	120.26(9)
C(16)-C(17)-C(18)	121.56(9)
C(9)-C(18)-C(17)	120.00(8)
C(9)-C(18)-C(1)	122.01(8)
C(17)-C(18)-C(1)	117.91(8)
N(1)-C(19)-C(1)	175.50(10)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for cdv56. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	31(1)	20(1)	22(1)	8(1)	8(1)	9(1)
C(1)	13(1)	15(1)	13(1)	4(1)	3(1)	4(1)
C(2)	13(1)	20(1)	18(1)	7(1)	2(1)	2(1)
C(3)	16(1)	23(1)	20(1)	9(1)	6(1)	2(1)
C(4)	20(1)	21(1)	20(1)	10(1)	5(1)	2(1)
C(5)	18(1)	19(1)	14(1)	7(1)	3(1)	4(1)
C(6)	14(1)	15(1)	13(1)	5(1)	2(1)	4(1)
C(7)	15(1)	20(1)	14(1)	6(1)	1(1)	3(1)
C(8)	12(1)	21(1)	16(1)	7(1)	3(1)	5(1)
C(9)	14(1)	13(1)	14(1)	4(1)	2(1)	3(1)
C(10)	16(1)	13(1)	15(1)	4(1)	3(1)	2(1)
C(11)	16(1)	20(1)	19(1)	6(1)	4(1)	4(1)
C(12)	19(1)	20(1)	22(1)	6(1)	9(1)	3(1)
C(13)	26(1)	19(1)	17(1)	6(1)	8(1)	2(1)
C(14)	23(1)	17(1)	15(1)	6(1)	3(1)	2(1)
C(15)	18(1)	13(1)	15(1)	4(1)	3(1)	2(1)
C(16)	17(1)	18(1)	16(1)	7(1)	0(1)	4(1)
C(17)	14(1)	17(1)	17(1)	6(1)	3(1)	4(1)
C(18)	15(1)	13(1)	13(1)	4(1)	2(1)	3(1)
C(19)	16(1)	20(1)	15(1)	8(1)	4(1)	4(1)
C(20)	25(1)	23(1)	14(1)	5(1)	4(1)	4(1)
C(21)	24(1)	28(1)	21(1)	14(1)	4(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for cdv56.

	x	y	z	U(eq)
H(2A)	3611(17)	2300(17)	6554(11)	27(3)
H(2B)	4431(15)	584(16)	6445(10)	18(3)
H(3A)	3780(16)	2977(17)	8537(11)	22(3)
H(3B)	2727(16)	975(16)	7872(10)	19(3)
H(4A)	5053(16)	-240(17)	8252(11)	23(3)
H(4B)	4733(17)	1026(18)	9438(12)	30(3)
H(6)	7365(15)	835(16)	7305(10)	16(3)
H(7A)	9364(16)	4313(17)	8239(10)	22(3)
H(7B)	10104(17)	2710(17)	8440(11)	26(3)
H(8A)	10911(17)	3370(17)	6808(11)	25(3)
H(8B)	10080(16)	1358(17)	6532(11)	23(3)
H(11)	11459(18)	2273(18)	5090(12)	29(3)
H(12)	12228(17)	2335(17)	3380(11)	26(3)
H(13)	10200(17)	2714(18)	2002(11)	28(3)
H(14)	7394(18)	3057(18)	2358(12)	33(4)
H(16)	5311(18)	3281(18)	3625(11)	30(3)
H(17)	4523(17)	3234(16)	5337(11)	24(3)
H(20A)	8343(18)	4440(18)	10006(11)	31(3)
H(20B)	6942(17)	3585(18)	10574(12)	32(3)
H(20C)	6359(18)	4520(19)	9691(12)	32(3)
H(21A)	8029(18)	-290(19)	8806(12)	33(4)
H(21B)	7696(17)	683(18)	10058(12)	32(4)
H(21C)	9278(19)	1454(18)	9612(12)	31(3)

X-ray Data Collection, Structure Solution and Refinement for cdv64 (**8g**)

A colorless crystal of approximate dimensions 0.128 x 0.159 x 0.298 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.
Hydrogen atoms were included using a riding model. There were three molecules of the formula-unit present and one-half molecule of dichloromethane solvent (1/6 molecule of solvent per formula-unit). The solvent atoms were included with site-occupancy-factors = 0.50.

Least-squares analysis yielded wR2 = 0.1143 and Goof = 1.019 for 873 variables refined against 17282 data (0.75 Å), R1 = 0.0467 for those 13089 data with $I > 2.0\sigma(I)$.

References.

6. APEX2 Version 2014.11-0, Bruker AXS, Inc.; Madison, WI 2014.

7. SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.

8. Sheldrick, G. M. SADABS, Version 2014/5, Bruker AXS, Inc.; Madison, WI 2014.

9. Sheldrick, G. M. SHELXTL, Version 2014/7, Bruker AXS, Inc.; Madison, WI 2014

10. International Tables for Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

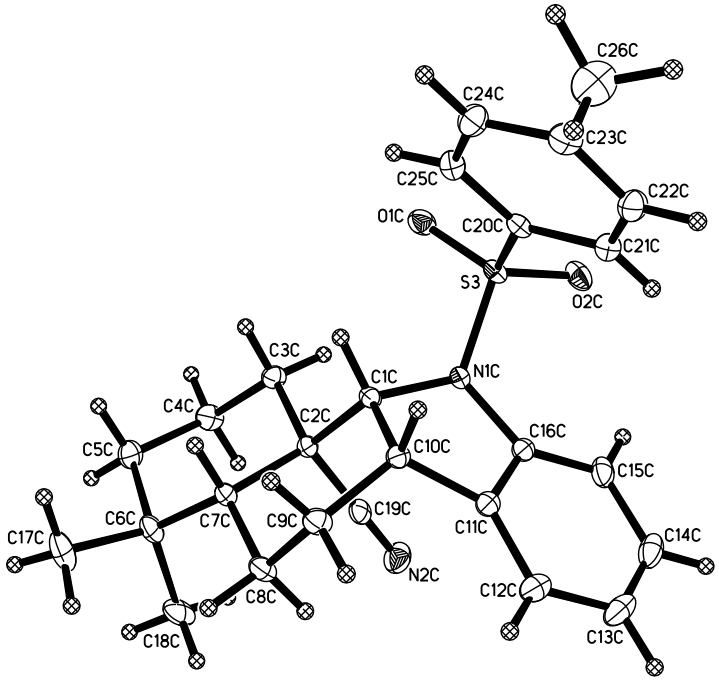
Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.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S3
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C3C
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C4C
C2C
C16C
C5C
C10C
C15C
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C12C
C18C
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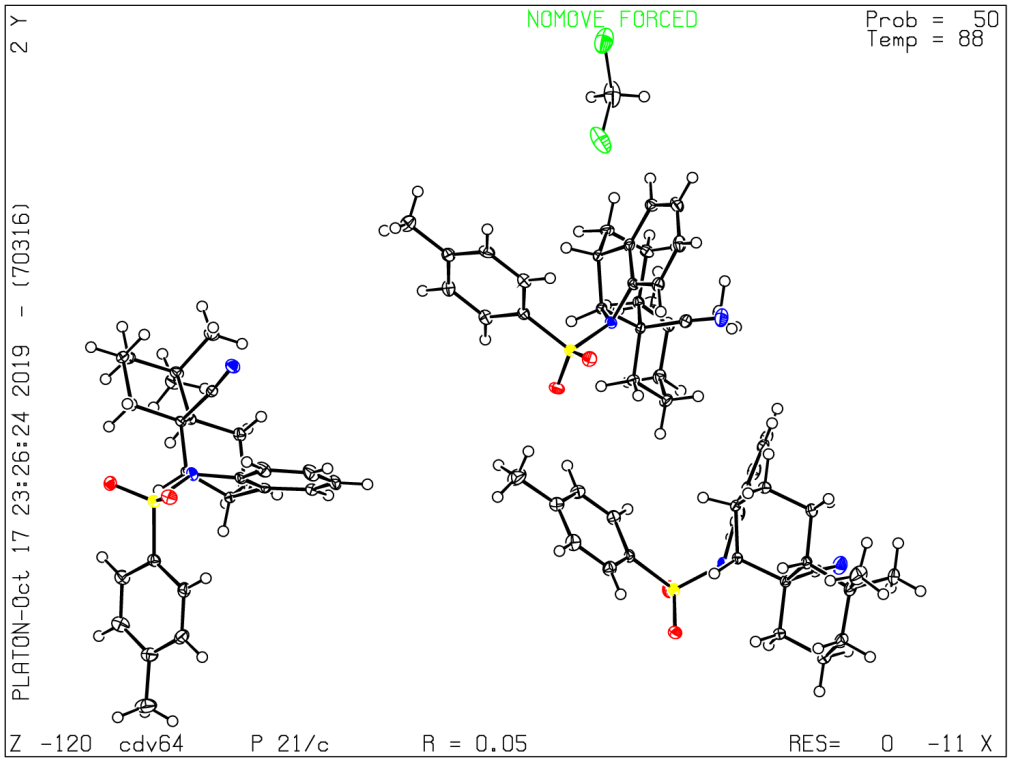
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2 Y
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Z -120 cdv64 P 21/c R = 0.05 RES= 0 -11 X

Three molecules and one-half dichloromethane solvent

Table 1. Crystal data and structure refinement for cdv64.

Identification code	cdv64 (Darius Vrubliauskas)	
Empirical formula	$C_{26}\ H_{30}\ N_2\ O_2\ S \bullet 1/6(CH_2Cl_2)$	
Formula weight	448.73	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 25.696(2) Å	α = 90°.
	b = 24.774(2) Å	β = 97.6915(14)°.
	c = 11.0354(9) Å	γ = 90°.
Volume	6961.8(10) Å^3	
Z	12	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.204 mm^{-1}	
F(000)	2868	
Crystal color	colorless	
Crystal size	0.298 x 0.159 x 0.128 mm^3	
Theta range for data collection	1.147 to 28.281°	
Index ranges	$-34 \le h \le 34$, $-33 \le k \le 33$, $-14 \le l \le 14$	
Reflections collected	96678	
Independent reflections	17282 [R(int) = 0.0631]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17282 / 0 / 873	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I) = 13089 data]	R1 = 0.0467, wR2 = 0.1035	
R indices (all data, 0.75 Å)	R1 = 0.0700, wR2 = 0.1143	
Largest diff. peak and hole	0.406 and -0.428 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for cdv64. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-2066(1)	2379(1)	695(1)	12(1)
O(1)	-2420(1)	2675(1)	-173(1)	18(1)
O(2)	-2162(1)	2338(1)	1943(1)	18(1)
N(1)	-2063(1)	1753(1)	192(1)	12(1)
N(2)	-2691(1)	533(1)	-355(1)	23(1)
C(1)	-1968(1)	1658(1)	-1104(1)	11(1)
C(2)	-2433(1)	1318(1)	-1762(1)	10(1)
C(3)	-2921(1)	1682(1)	-2021(2)	13(1)
C(4)	-3367(1)	1396(1)	-2818(2)	15(1)
C(5)	-3189(1)	1222(1)	-4024(2)	16(1)
C(6)	-2717(1)	833(1)	-3869(2)	15(1)
C(7)	-2264(1)	1085(1)	-2964(1)	12(1)
C(8)	-1784(1)	720(1)	-2635(2)	15(1)
C(9)	-1312(1)	1053(1)	-2078(2)	14(1)
C(10)	-1422(1)	1387(1)	-974(1)	11(1)
C(11)	-1405(1)	1104(1)	246(2)	12(1)
C(12)	-1107(1)	675(1)	754(2)	15(1)
C(13)	-1158(1)	511(1)	1940(2)	18(1)
C(14)	-1504(1)	772(1)	2606(2)	17(1)
C(15)	-1818(1)	1194(1)	2101(2)	14(1)
C(16)	-1757(1)	1352(1)	925(2)	12(1)
C(17)	-2524(1)	782(1)	-5126(2)	22(1)
C(18)	-2887(1)	269(1)	-3491(2)	22(1)
C(19)	-2564(1)	873(1)	-957(2)	14(1)
C(20)	-1432(1)	2647(1)	709(2)	13(1)
C(21)	-1042(1)	2524(1)	1676(2)	15(1)
C(22)	-544(1)	2740(1)	1684(2)	17(1)
C(23)	-425(1)	3078(1)	750(2)	17(1)
C(24)	-823(1)	3197(1)	-206(2)	18(1)
C(25)	-1324(1)	2984(1)	-238(2)	16(1)
C(26)	116(1)	3313(1)	778(2)	26(1)

S(2)	-1394(1)	7325(1)	-2582(1)	12(1)
O(1B)	-1007(1)	7626(1)	-3117(1)	17(1)
O(2B)	-1342(1)	7250(1)	-1281(1)	17(1)
N(1B)	-1392(1)	6715(1)	-3169(1)	12(1)
N(2B)	-578(1)	5643(1)	-3288(1)	18(1)
C(1B)	-1446(1)	6652(1)	-4532(1)	10(1)
C(2B)	-940(1)	6378(1)	-4895(1)	10(1)
C(3B)	-489(1)	6794(1)	-4814(2)	13(1)
C(4B)	-9(1)	6562(1)	-5301(2)	16(1)
C(5B)	-152(1)	6394(1)	-6631(2)	16(1)
C(6B)	-590(1)	5966(1)	-6835(2)	14(1)
C(7B)	-1071(1)	6152(1)	-6220(1)	11(1)
C(8B)	-1510(1)	5733(1)	-6248(2)	14(1)
C(9B)	-2021(1)	6004(1)	-6023(2)	14(1)
C(10B)	-1963(1)	6326(1)	-4830(1)	11(1)
C(11B)	-1979(1)	6014(1)	-3656(2)	12(1)
C(12B)	-2250(1)	5549(1)	-3428(2)	16(1)
C(13B)	-2222(1)	5368(1)	-2227(2)	20(1)
C(14B)	-1920(1)	5636(1)	-1282(2)	22(1)
C(15B)	-1630(1)	6093(1)	-1503(2)	19(1)
C(16B)	-1674(1)	6277(1)	-2698(2)	13(1)
C(17B)	-764(1)	5930(1)	-8222(2)	21(1)
C(18B)	-379(1)	5412(1)	-6384(2)	18(1)
C(19B)	-758(1)	5947(1)	-4002(2)	12(1)
C(20B)	-2006(1)	7640(1)	-3020(2)	14(1)
C(21B)	-2414(1)	7564(1)	-2325(2)	17(1)
C(22B)	-2882(1)	7843(1)	-2635(2)	20(1)
C(23B)	-2946(1)	8199(1)	-3623(2)	19(1)
C(24B)	-2535(1)	8262(1)	-4316(2)	21(1)
C(25B)	-2064(1)	7987(1)	-4022(2)	18(1)
C(26B)	-3447(1)	8518(1)	-3920(2)	30(1)
S(3)	-5374(1)	2321(1)	-4274(1)	13(1)
O(1C)	-5754(1)	2616(1)	-3701(1)	17(1)
O(2C)	-5440(1)	2260(1)	-5579(1)	19(1)
N(1C)	-5363(1)	1704(1)	-3710(1)	12(1)
N(2C)	-6030(1)	523(1)	-3504(1)	23(1)

C(1C)	-5285(1)	1638(1)	-2346(1)	11(1)
C(2C)	-5755(1)	1309(1)	-1955(1)	11(1)
C(3C)	-6239(1)	1683(1)	-2013(2)	14(1)
C(4C)	-6692(1)	1403(1)	-1501(2)	17(1)
C(5C)	-6522(1)	1234(1)	-177(2)	18(1)
C(6C)	-6051(1)	843(1)	-17(2)	17(1)
C(7C)	-5595(1)	1090(1)	-633(1)	12(1)
C(8C)	-5112(1)	726(1)	-613(2)	15(1)
C(9C)	-4638(1)	1058(1)	-870(2)	15(1)
C(10C)	-4740(1)	1364(1)	-2079(2)	12(1)
C(11C)	-4716(1)	1053(1)	-3250(2)	13(1)
C(12C)	-4420(1)	607(1)	-3489(2)	18(1)
C(13C)	-4449(1)	422(1)	-4690(2)	23(1)
C(14C)	-4776(1)	673(1)	-5621(2)	23(1)
C(15C)	-5091(1)	1109(1)	-5387(2)	18(1)
C(16C)	-5050(1)	1292(1)	-4192(2)	13(1)
C(17C)	-5866(1)	795(1)	1363(2)	27(1)
C(18C)	-6222(1)	280(1)	-502(2)	22(1)
C(19C)	-5895(1)	859(1)	-2826(2)	14(1)
C(20C)	-4755(1)	2620(1)	-3838(2)	13(1)
C(21C)	-4339(1)	2499(1)	-4487(2)	16(1)
C(22C)	-3857(1)	2747(1)	-4154(2)	19(1)
C(23C)	-3783(1)	3117(1)	-3197(2)	19(1)
C(24C)	-4203(1)	3228(1)	-2557(2)	19(1)
C(25C)	-4689(1)	2980(1)	-2867(2)	16(1)
C(26C)	-3263(1)	3396(1)	-2864(2)	29(1)
C(27)	-272(2)	-102(2)	-5556(4)	36(1)
Cl(1)	-586(1)	368(1)	-4642(1)	46(1)
Cl(2)	351(1)	-278(1)	-4844(1)	44(1)

Table 3. Bond lengths [Å] and angles [°] for cdv64.

S(1)-O(1)	1.4326(12)
S(1)-O(2)	1.4345(12)
S(1)-N(1)	1.6473(14)
S(1)-C(20)	1.7578(17)
N(1)-C(16)	1.445(2)
N(1)-C(1)	1.501(2)
N(2)-C(19)	1.147(2)
C(1)-C(10)	1.545(2)
C(1)-C(2)	1.558(2)
C(2)-C(19)	1.483(2)
C(2)-C(3)	1.541(2)
C(2)-C(7)	1.560(2)
C(3)-C(4)	1.523(2)
C(4)-C(5)	1.526(2)
C(5)-C(6)	1.540(2)
C(6)-C(18)	1.537(2)
C(6)-C(17)	1.539(2)
C(6)-C(7)	1.560(2)
C(7)-C(8)	1.532(2)
C(8)-C(9)	1.526(2)
C(9)-C(10)	1.530(2)
C(10)-C(11)	1.513(2)
C(11)-C(12)	1.385(2)
C(11)-C(16)	1.392(2)
C(12)-C(13)	1.394(2)
C(13)-C(14)	1.386(3)
C(14)-C(15)	1.392(2)
C(15)-C(16)	1.384(2)
C(20)-C(25)	1.394(2)
C(20)-C(21)	1.396(2)
C(21)-C(22)	1.386(2)
C(22)-C(23)	1.395(2)
C(23)-C(24)	1.400(2)
C(23)-C(26)	1.503(2)

C(24)-C(25)	1.385(2)
S(2)-O(1B)	1.4316(12)
S(2)-O(2B)	1.4360(12)
S(2)-N(1B)	1.6438(14)
S(2)-C(20B)	1.7640(17)
N(1B)-C(16B)	1.440(2)
N(1B)-C(1B)	1.500(2)
N(2B)-C(19B)	1.141(2)
C(1B)-C(10B)	1.553(2)
C(1B)-C(2B)	1.563(2)
C(2B)-C(19B)	1.487(2)
C(2B)-C(3B)	1.545(2)
C(2B)-C(7B)	1.560(2)
C(3B)-C(4B)	1.523(2)
C(4B)-C(5B)	1.523(2)
C(5B)-C(6B)	1.540(2)
C(6B)-C(18B)	1.536(2)
C(6B)-C(17B)	1.539(2)
C(6B)-C(7B)	1.555(2)
C(7B)-C(8B)	1.532(2)
C(8B)-C(9B)	1.524(2)
C(9B)-C(10B)	1.530(2)
C(10B)-C(11B)	1.515(2)
C(11B)-C(12B)	1.385(2)
C(11B)-C(16B)	1.392(2)
C(12B)-C(13B)	1.392(2)
C(13B)-C(14B)	1.384(3)
C(14B)-C(15B)	1.394(3)
C(15B)-C(16B)	1.385(2)
C(20B)-C(21B)	1.393(2)
C(20B)-C(25B)	1.393(2)
C(21B)-C(22B)	1.389(2)
C(22B)-C(23B)	1.396(3)
C(23B)-C(24B)	1.393(3)
C(23B)-C(26B)	1.508(3)
C(24B)-C(25B)	1.388(2)

S(3)-O(1C)	1.4316(12)
S(3)-O(2C)	1.4356(12)
S(3)-N(1C)	1.6497(14)
S(3)-C(20C)	1.7623(17)
N(1C)-C(16C)	1.445(2)
N(1C)-C(1C)	1.500(2)
N(2C)-C(19C)	1.142(2)
C(1C)-C(10C)	1.549(2)
C(1C)-C(2C)	1.564(2)
C(2C)-C(19C)	1.484(2)
C(2C)-C(3C)	1.545(2)
C(2C)-C(7C)	1.560(2)
C(3C)-C(4C)	1.528(2)
C(4C)-C(5C)	1.526(2)
C(5C)-C(6C)	1.541(2)
C(6C)-C(18C)	1.537(2)
C(6C)-C(17C)	1.539(2)
C(6C)-C(7C)	1.557(2)
C(7C)-C(8C)	1.531(2)
C(8C)-C(9C)	1.525(2)
C(9C)-C(10C)	1.527(2)
C(10C)-C(11C)	1.513(2)
C(11C)-C(12C)	1.387(2)
C(11C)-C(16C)	1.388(2)
C(12C)-C(13C)	1.395(3)
C(13C)-C(14C)	1.384(3)
C(14C)-C(15C)	1.394(3)
C(15C)-C(16C)	1.384(2)
C(20C)-C(25C)	1.387(2)
C(20C)-C(21C)	1.398(2)
C(21C)-C(22C)	1.387(2)
C(22C)-C(23C)	1.393(2)
C(23C)-C(24C)	1.394(3)
C(23C)-C(26C)	1.506(3)
C(24C)-C(25C)	1.391(2)
C(27)-Cl(2)	1.741(5)

C(27)-Cl(1)	1.801(6)

O(1)-S(1)-O(2)	120.22(7)
O(1)-S(1)-N(1)	106.74(7)
O(2)-S(1)-N(1)	105.47(7)
O(1)-S(1)-C(20)	108.48(8)
O(2)-S(1)-C(20)	107.21(8)
N(1)-S(1)-C(20)	108.22(7)
C(16)-N(1)-C(1)	106.29(12)
C(16)-N(1)-S(1)	119.00(11)
C(1)-N(1)-S(1)	118.53(10)
N(1)-C(1)-C(10)	103.89(12)
N(1)-C(1)-C(2)	108.51(12)
C(10)-C(1)-C(2)	115.99(13)
C(19)-C(2)-C(3)	107.50(13)
C(19)-C(2)-C(1)	110.12(13)
C(3)-C(2)-C(1)	108.92(13)
C(19)-C(2)-C(7)	110.22(13)
C(3)-C(2)-C(7)	111.80(13)
C(1)-C(2)-C(7)	108.27(12)
C(4)-C(3)-C(2)	111.47(13)
C(3)-C(4)-C(5)	110.10(13)
C(4)-C(5)-C(6)	113.85(14)
C(18)-C(6)-C(17)	107.88(14)
C(18)-C(6)-C(5)	110.64(14)
C(17)-C(6)-C(5)	107.14(14)
C(18)-C(6)-C(7)	113.83(14)
C(17)-C(6)-C(7)	107.88(14)
C(5)-C(6)-C(7)	109.20(13)
C(8)-C(7)-C(6)	115.09(13)
C(8)-C(7)-C(2)	108.89(13)
C(6)-C(7)-C(2)	115.08(13)
C(9)-C(8)-C(7)	110.40(13)
C(8)-C(9)-C(10)	113.05(13)
C(11)-C(10)-C(9)	118.21(14)
C(11)-C(10)-C(1)	101.62(12)

C(9)-C(10)-C(1)	115.02(13)
C(12)-C(11)-C(16)	119.05(15)
C(12)-C(11)-C(10)	131.55(15)
C(16)-C(11)-C(10)	109.39(14)
C(11)-C(12)-C(13)	119.10(16)
C(14)-C(13)-C(12)	120.69(16)
C(13)-C(14)-C(15)	121.14(16)
C(16)-C(15)-C(14)	117.06(16)
C(15)-C(16)-C(11)	122.92(15)
C(15)-C(16)-N(1)	126.70(15)
C(11)-C(16)-N(1)	110.21(14)
N(2)-C(19)-C(2)	176.70(18)
C(25)-C(20)-C(21)	120.58(16)
C(25)-C(20)-S(1)	119.87(13)
C(21)-C(20)-S(1)	119.55(13)
C(22)-C(21)-C(20)	119.25(16)
C(21)-C(22)-C(23)	121.41(16)
C(22)-C(23)-C(24)	118.18(16)
C(22)-C(23)-C(26)	120.82(16)
C(24)-C(23)-C(26)	121.00(16)
C(25)-C(24)-C(23)	121.48(16)
C(24)-C(25)-C(20)	119.11(16)
O(1B)-S(2)-O(2B)	120.21(7)
O(1B)-S(2)-N(1B)	106.08(7)
O(2B)-S(2)-N(1B)	105.69(7)
O(1B)-S(2)-C(20B)	107.38(8)
O(2B)-S(2)-C(20B)	106.96(8)
N(1B)-S(2)-C(20B)	110.35(7)
C(16B)-N(1B)-C(1B)	107.40(12)
C(16B)-N(1B)-S(2)	121.45(11)
C(1B)-N(1B)-S(2)	119.18(10)
N(1B)-C(1B)-C(10B)	103.23(12)
N(1B)-C(1B)-C(2B)	109.53(12)
C(10B)-C(1B)-C(2B)	115.98(13)
C(19B)-C(2B)-C(3B)	105.86(13)
C(19B)-C(2B)-C(7B)	111.87(13)

C(3B)-C(2B)-C(7B)	111.01(13)
C(19B)-C(2B)-C(1B)	109.91(13)
C(3B)-C(2B)-C(1B)	109.84(12)
C(7B)-C(2B)-C(1B)	108.32(12)
C(4B)-C(3B)-C(2B)	111.47(13)
C(5B)-C(4B)-C(3B)	109.92(14)
C(4B)-C(5B)-C(6B)	114.00(14)
C(18B)-C(6B)-C(17B)	108.26(14)
C(18B)-C(6B)-C(5B)	110.32(14)
C(17B)-C(6B)-C(5B)	107.15(14)
C(18B)-C(6B)-C(7B)	113.00(13)
C(17B)-C(6B)-C(7B)	108.01(13)
C(5B)-C(6B)-C(7B)	109.90(13)
C(8B)-C(7B)-C(6B)	114.66(13)
C(8B)-C(7B)-C(2B)	109.08(13)
C(6B)-C(7B)-C(2B)	115.58(13)
C(9B)-C(8B)-C(7B)	110.34(13)
C(8B)-C(9B)-C(10B)	112.56(13)
C(11B)-C(10B)-C(9B)	117.30(14)
C(11B)-C(10B)-C(1B)	101.81(12)
C(9B)-C(10B)-C(1B)	115.81(13)
C(12B)-C(11B)-C(16B)	119.87(15)
C(12B)-C(11B)-C(10B)	130.66(15)
C(16B)-C(11B)-C(10B)	109.43(14)
C(11B)-C(12B)-C(13B)	118.53(16)
C(14B)-C(13B)-C(12B)	120.98(16)
C(13B)-C(14B)-C(15B)	121.10(17)
C(16B)-C(15B)-C(14B)	117.23(17)
C(15B)-C(16B)-C(11B)	122.21(16)
C(15B)-C(16B)-N(1B)	127.72(15)
C(11B)-C(16B)-N(1B)	109.84(14)
N(2B)-C(19B)-C(2B)	173.79(17)
C(21B)-C(20B)-C(25B)	120.79(16)
C(21B)-C(20B)-S(2)	119.85(13)
C(25B)-C(20B)-S(2)	119.25(13)
C(22B)-C(21B)-C(20B)	119.14(16)

C(21B)-C(22B)-C(23B)	121.07(17)
C(24B)-C(23B)-C(22B)	118.67(16)
C(24B)-C(23B)-C(26B)	120.62(17)
C(22B)-C(23B)-C(26B)	120.70(17)
C(25B)-C(24B)-C(23B)	121.18(17)
C(24B)-C(25B)-C(20B)	119.13(16)
O(1C)-S(3)-O(2C)	120.13(8)
O(1C)-S(3)-N(1C)	106.48(7)
O(2C)-S(3)-N(1C)	105.93(7)
O(1C)-S(3)-C(20C)	108.02(8)
O(2C)-S(3)-C(20C)	107.41(8)
N(1C)-S(3)-C(20C)	108.42(7)
C(16C)-N(1C)-C(1C)	106.67(12)
C(16C)-N(1C)-S(3)	119.94(11)
C(1C)-N(1C)-S(3)	118.28(10)
N(1C)-C(1C)-C(10C)	103.49(12)
N(1C)-C(1C)-C(2C)	109.28(12)
C(10C)-C(1C)-C(2C)	115.57(13)
C(19C)-C(2C)-C(3C)	107.44(13)
C(19C)-C(2C)-C(7C)	110.80(13)
C(3C)-C(2C)-C(7C)	110.94(13)
C(19C)-C(2C)-C(1C)	109.99(13)
C(3C)-C(2C)-C(1C)	108.86(13)
C(7C)-C(2C)-C(1C)	108.79(13)
C(4C)-C(3C)-C(2C)	111.19(13)
C(5C)-C(4C)-C(3C)	110.04(14)
C(4C)-C(5C)-C(6C)	113.76(14)
C(18C)-C(6C)-C(17C)	108.15(15)
C(18C)-C(6C)-C(5C)	110.31(14)
C(17C)-C(6C)-C(5C)	107.26(15)
C(18C)-C(6C)-C(7C)	113.70(14)
C(17C)-C(6C)-C(7C)	108.07(14)
C(5C)-C(6C)-C(7C)	109.13(13)
C(8C)-C(7C)-C(6C)	114.75(13)
C(8C)-C(7C)-C(2C)	109.27(13)
C(6C)-C(7C)-C(2C)	115.16(13)

C(9C)-C(8C)-C(7C)	110.22(13)
C(8C)-C(9C)-C(10C)	112.50(13)
C(11C)-C(10C)-C(9C)	118.10(14)
C(11C)-C(10C)-C(1C)	101.55(13)
C(9C)-C(10C)-C(1C)	115.37(13)
C(12C)-C(11C)-C(16C)	119.76(16)
C(12C)-C(11C)-C(10C)	130.90(16)
C(16C)-C(11C)-C(10C)	109.32(14)
C(11C)-C(12C)-C(13C)	118.77(17)
C(14C)-C(13C)-C(12C)	120.50(17)
C(13C)-C(14C)-C(15C)	121.35(17)
C(16C)-C(15C)-C(14C)	117.21(17)
C(15C)-C(16C)-C(11C)	122.35(16)
C(15C)-C(16C)-N(1C)	127.35(16)
C(11C)-C(16C)-N(1C)	110.07(14)
N(2C)-C(19C)-C(2C)	176.35(18)
C(25C)-C(20C)-C(21C)	120.69(15)
C(25C)-C(20C)-S(3)	119.63(13)
C(21C)-C(20C)-S(3)	119.67(13)
C(22C)-C(21C)-C(20C)	119.15(16)
C(21C)-C(22C)-C(23C)	121.21(16)
C(22C)-C(23C)-C(24C)	118.53(16)
C(22C)-C(23C)-C(26C)	120.86(17)
C(24C)-C(23C)-C(26C)	120.61(17)
C(25C)-C(24C)-C(23C)	121.28(16)
C(20C)-C(25C)-C(24C)	119.12(16)
Cl(2)-C(27)-Cl(1)	111.2(3)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for cdv64. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	13(1)	10(1)	15(1)	-3(1)	2(1)	1(1)
O(1)	15(1)	14(1)	23(1)	-3(1)	-2(1)	4(1)
O(2)	20(1)	17(1)	17(1)	-5(1)	7(1)	-1(1)
N(1)	12(1)	10(1)	12(1)	-2(1)	1(1)	0(1)
N(2)	22(1)	22(1)	23(1)	5(1)	1(1)	-7(1)
C(1)	10(1)	10(1)	12(1)	-1(1)	2(1)	-1(1)
C(2)	10(1)	10(1)	11(1)	0(1)	2(1)	-2(1)
C(3)	10(1)	13(1)	15(1)	-1(1)	3(1)	1(1)
C(4)	11(1)	17(1)	17(1)	0(1)	1(1)	-2(1)
C(5)	15(1)	17(1)	15(1)	0(1)	0(1)	-3(1)
C(6)	17(1)	14(1)	13(1)	-2(1)	-1(1)	-2(1)
C(7)	14(1)	11(1)	11(1)	-1(1)	3(1)	0(1)
C(8)	18(1)	13(1)	14(1)	-1(1)	3(1)	3(1)
C(9)	13(1)	16(1)	15(1)	0(1)	4(1)	3(1)
C(10)	10(1)	11(1)	14(1)	-1(1)	2(1)	-2(1)
C(11)	11(1)	12(1)	13(1)	-1(1)	0(1)	-3(1)
C(12)	13(1)	13(1)	18(1)	-2(1)	1(1)	1(1)
C(13)	20(1)	13(1)	19(1)	2(1)	-2(1)	0(1)
C(14)	21(1)	16(1)	14(1)	2(1)	0(1)	-4(1)
C(15)	15(1)	14(1)	13(1)	-3(1)	1(1)	-3(1)
C(16)	12(1)	9(1)	14(1)	-1(1)	-2(1)	-1(1)
C(17)	25(1)	25(1)	15(1)	-6(1)	1(1)	3(1)
C(18)	25(1)	15(1)	25(1)	-5(1)	-3(1)	-6(1)
C(19)	13(1)	14(1)	14(1)	-1(1)	0(1)	-2(1)
C(20)	14(1)	10(1)	15(1)	-4(1)	3(1)	0(1)
C(21)	18(1)	13(1)	14(1)	0(1)	1(1)	1(1)
C(22)	16(1)	15(1)	18(1)	-2(1)	-3(1)	4(1)
C(23)	16(1)	13(1)	22(1)	-4(1)	2(1)	0(1)
C(24)	21(1)	16(1)	17(1)	2(1)	3(1)	-3(1)
C(25)	19(1)	15(1)	14(1)	0(1)	-1(1)	-1(1)
C(26)	17(1)	26(1)	36(1)	2(1)	1(1)	-3(1)

S(2)	14(1)	10(1)	12(1)	-4(1)	2(1)	0(1)
O(1B)	16(1)	13(1)	21(1)	-4(1)	4(1)	-3(1)
O(2B)	20(1)	18(1)	12(1)	-4(1)	-1(1)	1(1)
N(1B)	16(1)	10(1)	10(1)	-1(1)	3(1)	0(1)
N(2B)	19(1)	16(1)	18(1)	3(1)	2(1)	3(1)
C(1B)	13(1)	9(1)	9(1)	-1(1)	2(1)	1(1)
C(2B)	11(1)	9(1)	11(1)	1(1)	2(1)	1(1)
C(3B)	12(1)	12(1)	15(1)	1(1)	2(1)	-2(1)
C(4B)	10(1)	15(1)	22(1)	4(1)	2(1)	0(1)
C(5B)	14(1)	17(1)	18(1)	5(1)	7(1)	3(1)
C(6B)	16(1)	14(1)	13(1)	1(1)	6(1)	4(1)
C(7B)	13(1)	10(1)	10(1)	0(1)	2(1)	1(1)
C(8B)	17(1)	12(1)	12(1)	-3(1)	3(1)	0(1)
C(9B)	13(1)	15(1)	14(1)	-2(1)	0(1)	-1(1)
C(10B)	10(1)	10(1)	13(1)	0(1)	2(1)	0(1)
C(11B)	11(1)	12(1)	15(1)	1(1)	4(1)	3(1)
C(12B)	13(1)	12(1)	22(1)	0(1)	4(1)	1(1)
C(13B)	22(1)	13(1)	27(1)	6(1)	11(1)	2(1)
C(14B)	31(1)	19(1)	19(1)	7(1)	11(1)	6(1)
C(15B)	25(1)	16(1)	15(1)	1(1)	4(1)	4(1)
C(16B)	15(1)	10(1)	15(1)	0(1)	6(1)	2(1)
C(17B)	25(1)	24(1)	14(1)	-1(1)	8(1)	4(1)
C(18B)	20(1)	16(1)	22(1)	1(1)	7(1)	5(1)
C(19B)	11(1)	12(1)	13(1)	-3(1)	3(1)	-1(1)
C(20B)	14(1)	11(1)	14(1)	-4(1)	1(1)	0(1)
C(21B)	18(1)	15(1)	19(1)	-1(1)	3(1)	-3(1)
C(22B)	15(1)	20(1)	25(1)	-5(1)	6(1)	-3(1)
C(23B)	16(1)	20(1)	21(1)	-8(1)	-3(1)	1(1)
C(24B)	24(1)	22(1)	16(1)	-1(1)	-1(1)	4(1)
C(25B)	20(1)	18(1)	15(1)	-2(1)	4(1)	2(1)
C(26B)	18(1)	34(1)	37(1)	-5(1)	-2(1)	7(1)
S(3)	14(1)	12(1)	13(1)	4(1)	2(1)	-1(1)
O(1C)	16(1)	16(1)	21(1)	5(1)	5(1)	3(1)
O(2C)	22(1)	21(1)	13(1)	4(1)	1(1)	-3(1)
N(1C)	16(1)	11(1)	10(1)	1(1)	4(1)	0(1)
N(2C)	25(1)	21(1)	24(1)	-6(1)	9(1)	-6(1)

C(1C)	12(1)	10(1)	11(1)	2(1)	2(1)	0(1)
C(2C)	12(1)	10(1)	12(1)	0(1)	4(1)	-1(1)
C(3C)	12(1)	13(1)	17(1)	1(1)	3(1)	1(1)
C(4C)	12(1)	18(1)	23(1)	2(1)	4(1)	0(1)
C(5C)	17(1)	19(1)	20(1)	1(1)	9(1)	-2(1)
C(6C)	17(1)	18(1)	16(1)	4(1)	6(1)	-3(1)
C(7C)	14(1)	12(1)	12(1)	2(1)	3(1)	-1(1)
C(8C)	16(1)	14(1)	17(1)	4(1)	3(1)	0(1)
C(9C)	12(1)	15(1)	19(1)	3(1)	2(1)	2(1)
C(10C)	10(1)	11(1)	15(1)	0(1)	4(1)	-1(1)
C(11C)	11(1)	11(1)	17(1)	-2(1)	6(1)	-4(1)
C(12C)	12(1)	14(1)	28(1)	-4(1)	7(1)	-3(1)
C(13C)	17(1)	16(1)	38(1)	-11(1)	14(1)	-6(1)
C(14C)	25(1)	22(1)	24(1)	-10(1)	13(1)	-10(1)
C(15C)	20(1)	20(1)	16(1)	-2(1)	8(1)	-7(1)
C(16C)	13(1)	10(1)	18(1)	-1(1)	8(1)	-3(1)
C(17C)	27(1)	37(1)	18(1)	9(1)	9(1)	-2(1)
C(18C)	20(1)	17(1)	29(1)	7(1)	8(1)	-3(1)
C(19C)	11(1)	15(1)	15(1)	2(1)	5(1)	-1(1)
C(20C)	13(1)	12(1)	13(1)	4(1)	2(1)	-1(1)
C(21C)	19(1)	15(1)	15(1)	-1(1)	5(1)	0(1)
C(22C)	16(1)	18(1)	23(1)	-1(1)	7(1)	1(1)
C(23C)	16(1)	18(1)	21(1)	2(1)	1(1)	1(1)
C(24C)	22(1)	19(1)	14(1)	-4(1)	1(1)	-2(1)
C(25C)	18(1)	18(1)	15(1)	1(1)	5(1)	-1(1)
C(26C)	17(1)	33(1)	36(1)	-7(1)	1(1)	-4(1)
C(27)	48(3)	34(3)	21(2)	8(2)	-10(2)	-17(2)
Cl(1)	70(1)	23(1)	41(1)	4(1)	-6(1)	0(1)
Cl(2)	36(1)	52(1)	42(1)	20(1)	-10(1)	-15(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for cdv64.

	x	y	z	U(eq)
H(1A)	-1953	2012	-1530	13
H(3A)	-3040	1788	-1237	15
H(3B)	-2827	2015	-2438	15
H(4A)	-3672	1642	-2984	18
H(4B)	-3478	1075	-2383	18
H(5A)	-3093	1548	-4465	19
H(5B)	-3486	1045	-4535	19
H(7A)	-2136	1401	-3403	14
H(8A)	-1864	442	-2045	18
H(8B)	-1700	535	-3380	18
H(9A)	-1207	1299	-2709	17
H(9B)	-1014	807	-1823	17
H(10A)	-1155	1682	-865	14
H(12A)	-871	494	299	18
H(13A)	-954	218	2296	21
H(14A)	-1527	661	3421	21
H(15A)	-2064	1367	2544	17
H(17A)	-2813	655	-5730	33
H(17B)	-2234	523	-5072	33
H(17C)	-2404	1135	-5376	33
H(18A)	-3151	123	-4130	34
H(18B)	-3036	295	-2721	34
H(18C)	-2581	29	-3381	34
H(21A)	-1118	2295	2321	19
H(22A)	-278	2655	2340	20
H(24A)	-749	3428	-848	21
H(25A)	-1589	3066	-896	19
H(26A)	127	3540	54	39
H(26B)	200	3533	1517	39
H(26C)	373	3021	783	39

H(1BA)	-1490	7015	-4925	12
H(3BA)	-610	7119	-5292	16
H(3BB)	-392	6904	-3951	16
H(4BA)	274	6836	-5237	19
H(4BB)	123	6245	-4805	19
H(5BA)	166	6249	-6934	19
H(5BB)	-265	6718	-7122	19
H(7BA)	-1227	6461	-6726	13
H(8BA)	-1561	5550	-7053	16
H(8BB)	-1411	5456	-5611	16
H(9BA)	-2294	5724	-5995	17
H(9BB)	-2139	6248	-6714	17
H(10B)	-2259	6592	-4899	13
H(12B)	-2450	5358	-4077	19
H(13B)	-2414	5055	-2054	24
H(14B)	-1910	5507	-469	27
H(15B)	-1413	6271	-862	22
H(17D)	-922	6274	-8519	31
H(17E)	-1023	5641	-8393	31
H(17F)	-459	5853	-8639	31
H(18D)	-256	5430	-5505	28
H(18E)	-86	5309	-6822	28
H(18F)	-659	5142	-6538	28
H(21B)	-2373	7324	-1647	21
H(22B)	-3162	7790	-2166	23
H(24B)	-2577	8498	-5001	25
H(25B)	-1786	8035	-4498	21
H(26D)	-3716	8372	-3461	46
H(26E)	-3569	8494	-4798	46
H(26F)	-3381	8897	-3693	46
H(1CA)	-5271	2002	-1949	13
H(3CA)	-6142	2015	-1537	16
H(3CB)	-6353	1789	-2872	16
H(4CA)	-6996	1651	-1540	21
H(4CB)	-6803	1081	-2001	21
H(5CA)	-6822	1060	143	22

H(5CB)	-6428	1561	319	22
H(7CA)	-5473	1412	-127	15
H(8CA)	-5035	551	197	18
H(8CB)	-5184	440	-1239	18
H(9CA)	-4335	814	-891	18
H(9CB)	-4547	1319	-197	18
H(10C)	-4471	1657	-2047	14
H(12C)	-4201	431	-2847	21
H(13C)	-4243	121	-4871	27
H(14C)	-4786	546	-6436	27
H(15C)	-5324	1274	-6021	22
H(17G)	-5732	1145	1681	40
H(17H)	-5585	525	1504	40
H(17I)	-6161	685	1784	40
H(18G)	-5916	41	-439	32
H(18H)	-6379	308	-1359	32
H(18I)	-6481	132	-16	32
H(21C)	-4385	2251	-5149	19
H(22C)	-3571	2662	-4586	23
H(24C)	-4157	3477	-1897	23
H(25C)	-4971	3057	-2420	20
H(26G)	-3318	3745	-2486	43
H(26H)	-3097	3452	-3603	43
H(26I)	-3034	3171	-2286	43
H(27A)	-490	-431	-5696	43
H(27B)	-242	63	-6362	43

Table 6. Torsion angles [°] for cdv64.

O(1)-S(1)-N(1)-C(16)	-176.85(12)
O(2)-S(1)-N(1)-C(16)	-47.90(13)
C(20)-S(1)-N(1)-C(16)	66.57(13)
O(1)-S(1)-N(1)-C(1)	51.35(13)
O(2)-S(1)-N(1)-C(1)	-179.71(11)
C(20)-S(1)-N(1)-C(1)	-65.23(13)
C(16)-N(1)-C(1)-C(10)	-26.01(15)
S(1)-N(1)-C(1)-C(10)	111.21(12)
C(16)-N(1)-C(1)-C(2)	97.97(14)
S(1)-N(1)-C(1)-C(2)	-124.82(12)
N(1)-C(1)-C(2)-C(19)	-43.81(17)
C(10)-C(1)-C(2)-C(19)	72.61(17)
N(1)-C(1)-C(2)-C(3)	73.84(15)
C(10)-C(1)-C(2)-C(3)	-169.74(13)
N(1)-C(1)-C(2)-C(7)	-164.39(12)
C(10)-C(1)-C(2)-C(7)	-47.97(17)
C(19)-C(2)-C(3)-C(4)	-68.57(17)
C(1)-C(2)-C(3)-C(4)	172.13(13)
C(7)-C(2)-C(3)-C(4)	52.52(17)
C(2)-C(3)-C(4)-C(5)	-58.08(18)
C(3)-C(4)-C(5)-C(6)	59.87(18)
C(4)-C(5)-C(6)-C(18)	72.91(18)
C(4)-C(5)-C(6)-C(17)	-169.73(14)
C(4)-C(5)-C(6)-C(7)	-53.14(18)
C(18)-C(6)-C(7)-C(8)	50.9(2)
C(17)-C(6)-C(7)-C(8)	-68.83(18)
C(5)-C(6)-C(7)-C(8)	175.05(14)
C(18)-C(6)-C(7)-C(2)	-77.02(18)
C(17)-C(6)-C(7)-C(2)	163.30(14)
C(5)-C(6)-C(7)-C(2)	47.18(18)
C(19)-C(2)-C(7)-C(8)	-59.50(17)
C(3)-C(2)-C(7)-C(8)	-179.00(13)
C(1)-C(2)-C(7)-C(8)	61.01(16)
C(19)-C(2)-C(7)-C(6)	71.42(17)

C(3)-C(2)-C(7)-C(6)	-48.08(18)
C(1)-C(2)-C(7)-C(6)	-168.07(13)
C(6)-C(7)-C(8)-C(9)	162.98(14)
C(2)-C(7)-C(8)-C(9)	-66.11(17)
C(7)-C(8)-C(9)-C(10)	54.96(18)
C(8)-C(9)-C(10)-C(11)	79.42(18)
C(8)-C(9)-C(10)-C(1)	-40.75(19)
N(1)-C(1)-C(10)-C(11)	28.59(15)
C(2)-C(1)-C(10)-C(11)	-90.39(15)
N(1)-C(1)-C(10)-C(9)	157.53(13)
C(2)-C(1)-C(10)-C(9)	38.56(19)
C(9)-C(10)-C(11)-C(12)	32.2(2)
C(1)-C(10)-C(11)-C(12)	159.04(17)
C(9)-C(10)-C(11)-C(16)	-149.03(14)
C(1)-C(10)-C(11)-C(16)	-22.14(16)
C(16)-C(11)-C(12)-C(13)	-1.5(2)
C(10)-C(11)-C(12)-C(13)	177.18(16)
C(11)-C(12)-C(13)-C(14)	0.2(3)
C(12)-C(13)-C(14)-C(15)	1.6(3)
C(13)-C(14)-C(15)-C(16)	-2.0(2)
C(14)-C(15)-C(16)-C(11)	0.7(2)
C(14)-C(15)-C(16)-N(1)	175.48(15)
C(12)-C(11)-C(16)-C(15)	1.1(2)
C(10)-C(11)-C(16)-C(15)	-177.90(15)
C(12)-C(11)-C(16)-N(1)	-174.46(14)
C(10)-C(11)-C(16)-N(1)	6.56(18)
C(1)-N(1)-C(16)-C(15)	-162.62(15)
S(1)-N(1)-C(16)-C(15)	60.4(2)
C(1)-N(1)-C(16)-C(11)	12.71(17)
S(1)-N(1)-C(16)-C(11)	-124.26(13)
O(1)-S(1)-C(20)-C(25)	-15.38(15)
O(2)-S(1)-C(20)-C(25)	-146.61(13)
N(1)-S(1)-C(20)-C(25)	100.07(14)
O(1)-S(1)-C(20)-C(21)	164.15(13)
O(2)-S(1)-C(20)-C(21)	32.92(15)
N(1)-S(1)-C(20)-C(21)	-80.39(14)

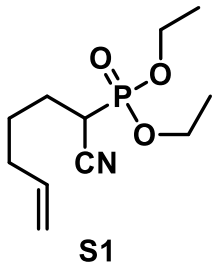
C(25)-C(20)-C(21)-C(22)	-0.1(2)
S(1)-C(20)-C(21)-C(22)	-179.67(13)
C(20)-C(21)-C(22)-C(23)	0.3(3)
C(21)-C(22)-C(23)-C(24)	-0.1(3)
C(21)-C(22)-C(23)-C(26)	179.36(17)
C(22)-C(23)-C(24)-C(25)	-0.3(3)
C(26)-C(23)-C(24)-C(25)	-179.69(17)
C(23)-C(24)-C(25)-C(20)	0.4(3)
C(21)-C(20)-C(25)-C(24)	-0.2(2)
S(1)-C(20)-C(25)-C(24)	179.35(13)
O(1B)-S(2)-N(1B)-C(16B)	170.11(12)
O(2B)-S(2)-N(1B)-C(16B)	41.42(14)
C(20B)-S(2)-N(1B)-C(16B)	-73.88(14)
O(1B)-S(2)-N(1B)-C(1B)	-51.89(13)
O(2B)-S(2)-N(1B)-C(1B)	179.43(11)
C(20B)-S(2)-N(1B)-C(1B)	64.12(13)
C(16B)-N(1B)-C(1B)-C(10B)	25.09(15)
S(2)-N(1B)-C(1B)-C(10B)	-118.17(12)
C(16B)-N(1B)-C(1B)-C(2B)	-99.03(14)
S(2)-N(1B)-C(1B)-C(2B)	117.71(12)
N(1B)-C(1B)-C(2B)-C(19B)	39.76(16)
C(10B)-C(1B)-C(2B)-C(19B)	-76.54(16)
N(1B)-C(1B)-C(2B)-C(3B)	-76.33(15)
C(10B)-C(1B)-C(2B)-C(3B)	167.37(13)
N(1B)-C(1B)-C(2B)-C(7B)	162.27(12)
C(10B)-C(1B)-C(2B)-C(7B)	45.97(17)
C(19B)-C(2B)-C(3B)-C(4B)	67.97(16)
C(7B)-C(2B)-C(3B)-C(4B)	-53.64(17)
C(1B)-C(2B)-C(3B)-C(4B)	-173.41(13)
C(2B)-C(3B)-C(4B)-C(5B)	59.40(17)
C(3B)-C(4B)-C(5B)-C(6B)	-59.26(18)
C(4B)-C(5B)-C(6B)-C(18B)	-73.88(18)
C(4B)-C(5B)-C(6B)-C(17B)	168.48(14)
C(4B)-C(5B)-C(6B)-C(7B)	51.37(18)
C(18B)-C(6B)-C(7B)-C(8B)	-50.25(19)
C(17B)-C(6B)-C(7B)-C(8B)	69.47(17)

C(5B)-C(6B)-C(7B)-C(8B)	-173.95(13)
C(18B)-C(6B)-C(7B)-C(2B)	77.94(18)
C(17B)-C(6B)-C(7B)-C(2B)	-162.33(14)
C(5B)-C(6B)-C(7B)-C(2B)	-45.75(18)
C(19B)-C(2B)-C(7B)-C(8B)	60.65(17)
C(3B)-C(2B)-C(7B)-C(8B)	178.66(13)
C(1B)-C(2B)-C(7B)-C(8B)	-60.66(16)
C(19B)-C(2B)-C(7B)-C(6B)	-70.26(17)
C(3B)-C(2B)-C(7B)-C(6B)	47.75(18)
C(1B)-C(2B)-C(7B)-C(6B)	168.43(13)
C(6B)-C(7B)-C(8B)-C(9B)	-161.37(13)
C(2B)-C(7B)-C(8B)-C(9B)	67.23(16)
C(7B)-C(8B)-C(9B)-C(10B)	-55.48(18)
C(8B)-C(9B)-C(10B)-C(11B)	-80.28(18)
C(8B)-C(9B)-C(10B)-C(1B)	40.07(19)
N(1B)-C(1B)-C(10B)-C(11B)	-28.01(15)
C(2B)-C(1B)-C(10B)-C(11B)	91.76(15)
N(1B)-C(1B)-C(10B)-C(9B)	-156.44(13)
C(2B)-C(1B)-C(10B)-C(9B)	-36.67(19)
C(9B)-C(10B)-C(11B)-C(12B)	-32.2(2)
C(1B)-C(10B)-C(11B)-C(12B)	-159.71(17)
C(9B)-C(10B)-C(11B)-C(16B)	149.95(14)
C(1B)-C(10B)-C(11B)-C(16B)	22.48(16)
C(16B)-C(11B)-C(12B)-C(13B)	2.2(2)
C(10B)-C(11B)-C(12B)-C(13B)	-175.40(16)
C(11B)-C(12B)-C(13B)-C(14B)	-1.7(3)
C(12B)-C(13B)-C(14B)-C(15B)	-0.6(3)
C(13B)-C(14B)-C(15B)-C(16B)	2.3(3)
C(14B)-C(15B)-C(16B)-C(11B)	-1.8(3)
C(14B)-C(15B)-C(16B)-N(1B)	-175.71(16)
C(12B)-C(11B)-C(16B)-C(15B)	-0.5(2)
C(10B)-C(11B)-C(16B)-C(15B)	177.64(15)
C(12B)-C(11B)-C(16B)-N(1B)	174.42(14)
C(10B)-C(11B)-C(16B)-N(1B)	-7.50(18)
C(1B)-N(1B)-C(16B)-C(15B)	162.83(16)
S(2)-N(1B)-C(16B)-C(15B)	-54.9(2)

C(1B)-N(1B)-C(16B)-C(11B)	-11.68(17)
S(2)-N(1B)-C(16B)-C(11B)	130.57(13)
O(1B)-S(2)-C(20B)-C(21B)	-157.48(13)
O(2B)-S(2)-C(20B)-C(21B)	-27.19(16)
N(1B)-S(2)-C(20B)-C(21B)	87.32(14)
O(1B)-S(2)-C(20B)-C(25B)	18.84(15)
O(2B)-S(2)-C(20B)-C(25B)	149.14(13)
N(1B)-S(2)-C(20B)-C(25B)	-96.35(14)
C(25B)-C(20B)-C(21B)-C(22B)	-0.5(3)
S(2)-C(20B)-C(21B)-C(22B)	175.73(13)
C(20B)-C(21B)-C(22B)-C(23B)	-0.4(3)
C(21B)-C(22B)-C(23B)-C(24B)	1.3(3)
C(21B)-C(22B)-C(23B)-C(26B)	-177.33(17)
C(22B)-C(23B)-C(24B)-C(25B)	-1.3(3)
C(26B)-C(23B)-C(24B)-C(25B)	177.35(17)
C(23B)-C(24B)-C(25B)-C(20B)	0.4(3)
C(21B)-C(20B)-C(25B)-C(24B)	0.6(3)
S(2)-C(20B)-C(25B)-C(24B)	-175.73(13)
O(1C)-S(3)-N(1C)-C(16C)	174.33(12)
O(2C)-S(3)-N(1C)-C(16C)	45.36(14)
C(20C)-S(3)-N(1C)-C(16C)	-69.66(14)
O(1C)-S(3)-N(1C)-C(1C)	-52.38(13)
O(2C)-S(3)-N(1C)-C(1C)	178.65(11)
C(20C)-S(3)-N(1C)-C(1C)	63.63(13)
C(16C)-N(1C)-C(1C)-C(10C)	25.64(15)
S(3)-N(1C)-C(1C)-C(10C)	-113.18(12)
C(16C)-N(1C)-C(1C)-C(2C)	-98.02(14)
S(3)-N(1C)-C(1C)-C(2C)	123.16(12)
N(1C)-C(1C)-C(2C)-C(19C)	41.14(17)
C(10C)-C(1C)-C(2C)-C(19C)	-75.04(17)
N(1C)-C(1C)-C(2C)-C(3C)	-76.32(15)
C(10C)-C(1C)-C(2C)-C(3C)	167.49(13)
N(1C)-C(1C)-C(2C)-C(7C)	162.67(12)
C(10C)-C(1C)-C(2C)-C(7C)	46.48(17)
C(19C)-C(2C)-C(3C)-C(4C)	67.46(17)
C(7C)-C(2C)-C(3C)-C(4C)	-53.79(18)

C(1C)-C(2C)-C(3C)-C(4C)	-173.47(13)
C(2C)-C(3C)-C(4C)-C(5C)	58.75(18)
C(3C)-C(4C)-C(5C)-C(6C)	-59.60(19)
C(4C)-C(5C)-C(6C)-C(18C)	-72.60(18)
C(4C)-C(5C)-C(6C)-C(17C)	169.83(15)
C(4C)-C(5C)-C(6C)-C(7C)	52.99(19)
C(18C)-C(6C)-C(7C)-C(8C)	-52.71(19)
C(17C)-C(6C)-C(7C)-C(8C)	67.35(19)
C(5C)-C(6C)-C(7C)-C(8C)	-176.32(14)
C(18C)-C(6C)-C(7C)-C(2C)	75.45(18)
C(17C)-C(6C)-C(7C)-C(2C)	-164.49(14)
C(5C)-C(6C)-C(7C)-C(2C)	-48.16(19)
C(19C)-C(2C)-C(7C)-C(8C)	61.26(17)
C(3C)-C(2C)-C(7C)-C(8C)	-179.49(13)
C(1C)-C(2C)-C(7C)-C(8C)	-59.77(16)
C(19C)-C(2C)-C(7C)-C(6C)	-69.59(17)
C(3C)-C(2C)-C(7C)-C(6C)	49.66(18)
C(1C)-C(2C)-C(7C)-C(6C)	169.38(13)
C(6C)-C(7C)-C(8C)-C(9C)	-162.77(14)
C(2C)-C(7C)-C(8C)-C(9C)	66.16(17)
C(7C)-C(8C)-C(9C)-C(10C)	-56.31(18)
C(8C)-C(9C)-C(10C)-C(11C)	-77.92(18)
C(8C)-C(9C)-C(10C)-C(1C)	42.38(19)
N(1C)-C(1C)-C(10C)-C(11C)	-29.10(15)
C(2C)-C(1C)-C(10C)-C(11C)	90.32(15)
N(1C)-C(1C)-C(10C)-C(9C)	-158.07(13)
C(2C)-C(1C)-C(10C)-C(9C)	-38.65(19)
C(9C)-C(10C)-C(11C)-C(12C)	-30.9(2)
C(1C)-C(10C)-C(11C)-C(12C)	-158.09(17)
C(9C)-C(10C)-C(11C)-C(16C)	150.79(14)
C(1C)-C(10C)-C(11C)-C(16C)	23.57(16)
C(16C)-C(11C)-C(12C)-C(13C)	2.6(2)
C(10C)-C(11C)-C(12C)-C(13C)	-175.57(16)
C(11C)-C(12C)-C(13C)-C(14C)	-1.2(3)
C(12C)-C(13C)-C(14C)-C(15C)	-1.2(3)
C(13C)-C(14C)-C(15C)-C(16C)	2.1(3)

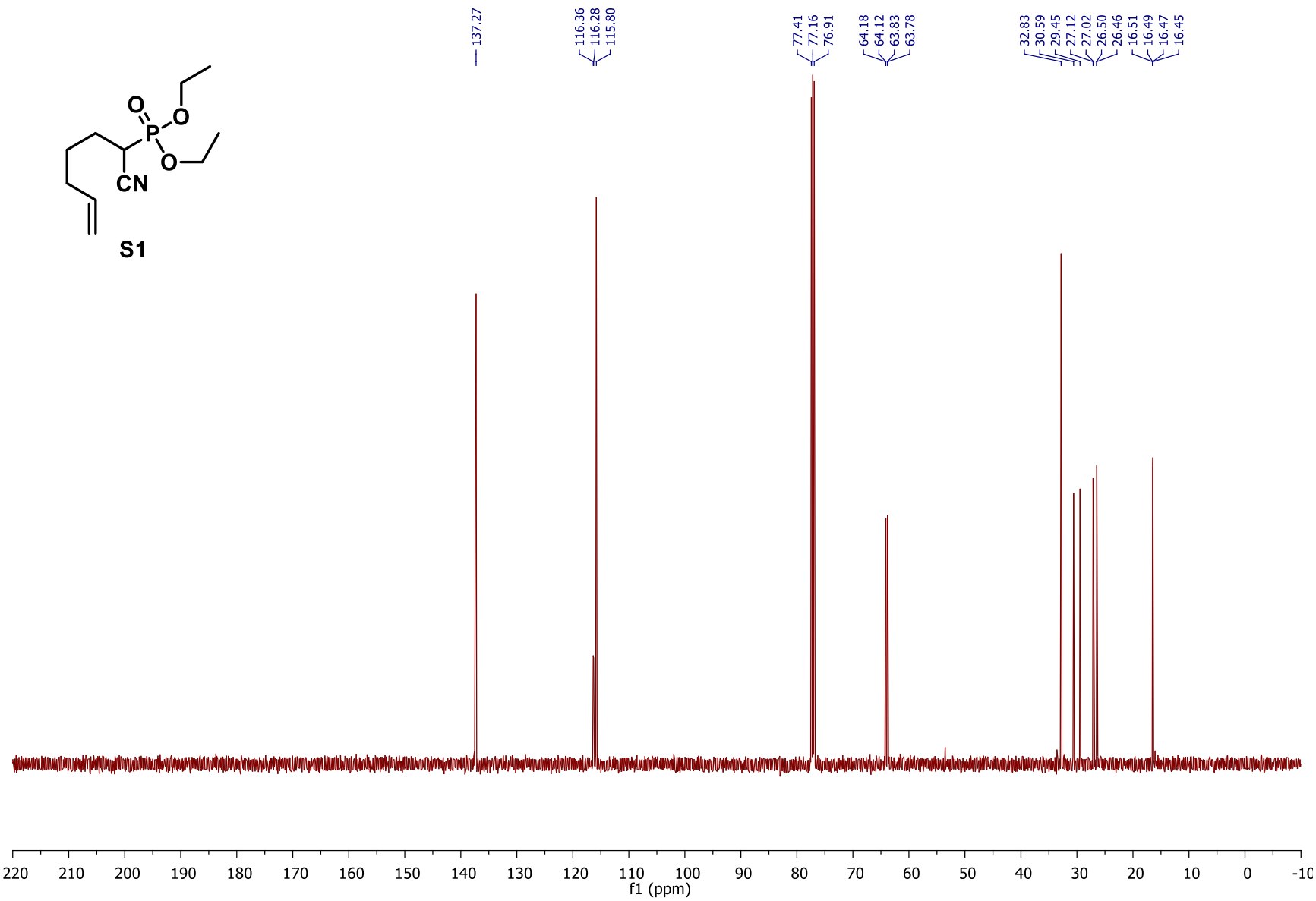
C(14C)-C(15C)-C(16C)-C(11C)	-0.6(2)
C(14C)-C(15C)-C(16C)-N(1C)	-174.61(15)
C(12C)-C(11C)-C(16C)-C(15C)	-1.7(2)
C(10C)-C(11C)-C(16C)-C(15C)	176.82(15)
C(12C)-C(11C)-C(16C)-N(1C)	173.17(14)
C(10C)-C(11C)-C(16C)-N(1C)	-8.27(18)
C(1C)-N(1C)-C(16C)-C(15C)	163.09(16)
S(3)-N(1C)-C(16C)-C(15C)	-58.9(2)
C(1C)-N(1C)-C(16C)-C(11C)	-11.50(17)
S(3)-N(1C)-C(16C)-C(11C)	126.50(13)
O(1C)-S(3)-C(20C)-C(25C)	14.21(16)
O(2C)-S(3)-C(20C)-C(25C)	145.15(13)
N(1C)-S(3)-C(20C)-C(25C)	-100.80(14)
O(1C)-S(3)-C(20C)-C(21C)	-164.59(13)
O(2C)-S(3)-C(20C)-C(21C)	-33.65(16)
N(1C)-S(3)-C(20C)-C(21C)	80.40(15)
C(25C)-C(20C)-C(21C)-C(22C)	-0.3(3)
S(3)-C(20C)-C(21C)-C(22C)	178.47(13)
C(20C)-C(21C)-C(22C)-C(23C)	-0.8(3)
C(21C)-C(22C)-C(23C)-C(24C)	1.3(3)
C(21C)-C(22C)-C(23C)-C(26C)	-178.26(17)
C(22C)-C(23C)-C(24C)-C(25C)	-0.7(3)
C(26C)-C(23C)-C(24C)-C(25C)	178.91(17)
C(21C)-C(20C)-C(25C)-C(24C)	1.0(3)
S(3)-C(20C)-C(25C)-C(24C)	-177.83(13)
C(23C)-C(24C)-C(25C)-C(20C)	-0.5(3)

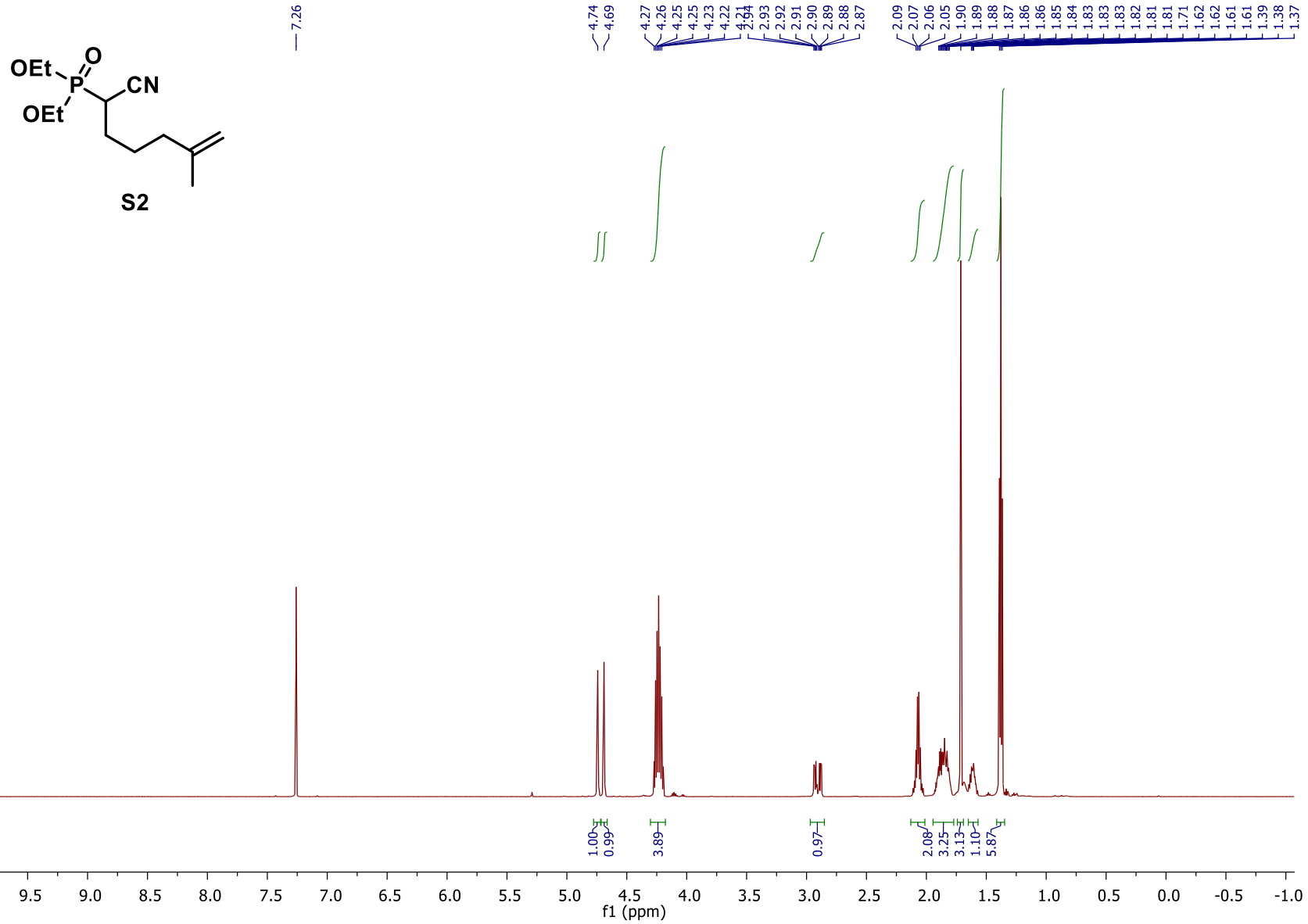

O
O
P
O
CN

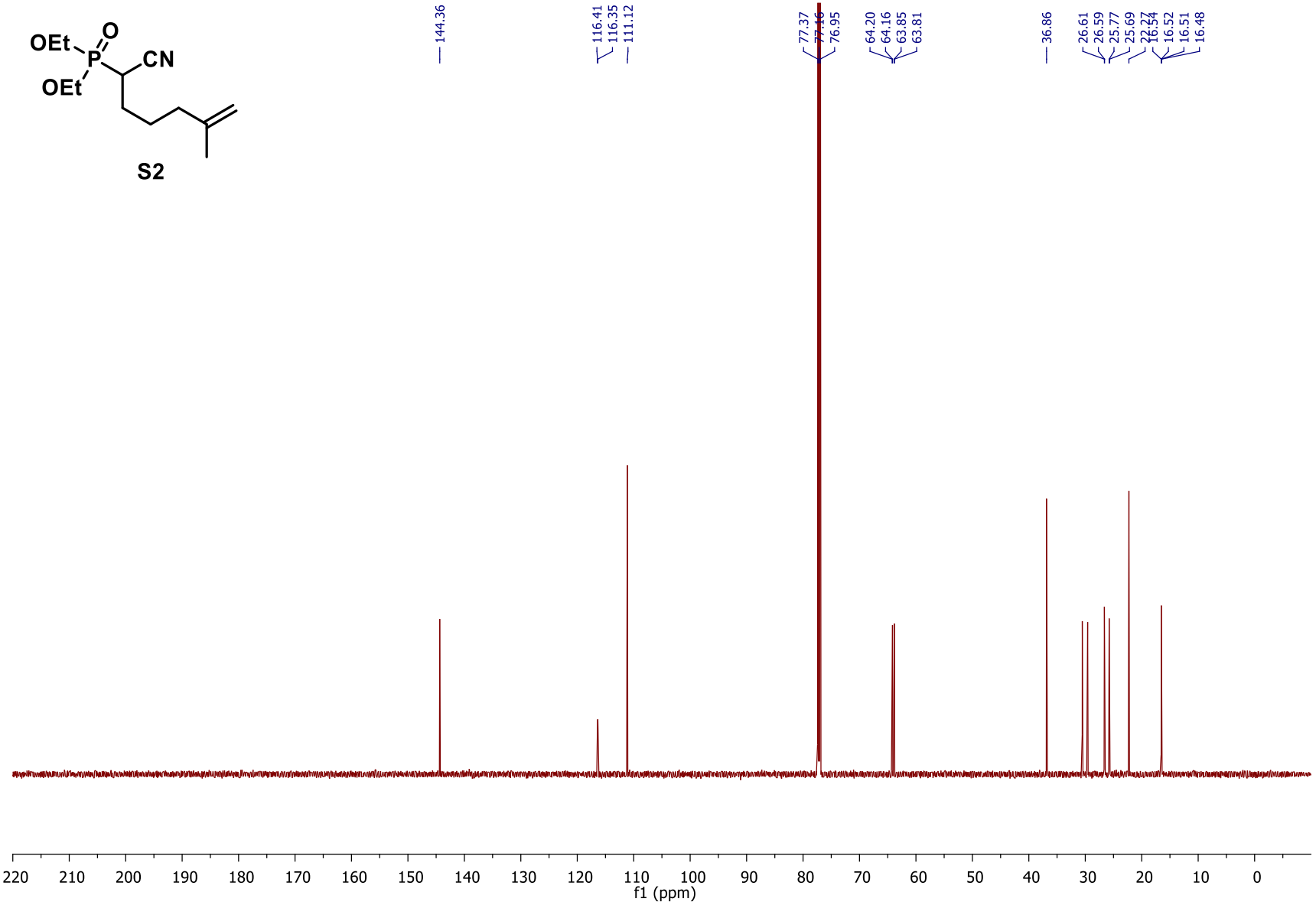
S1

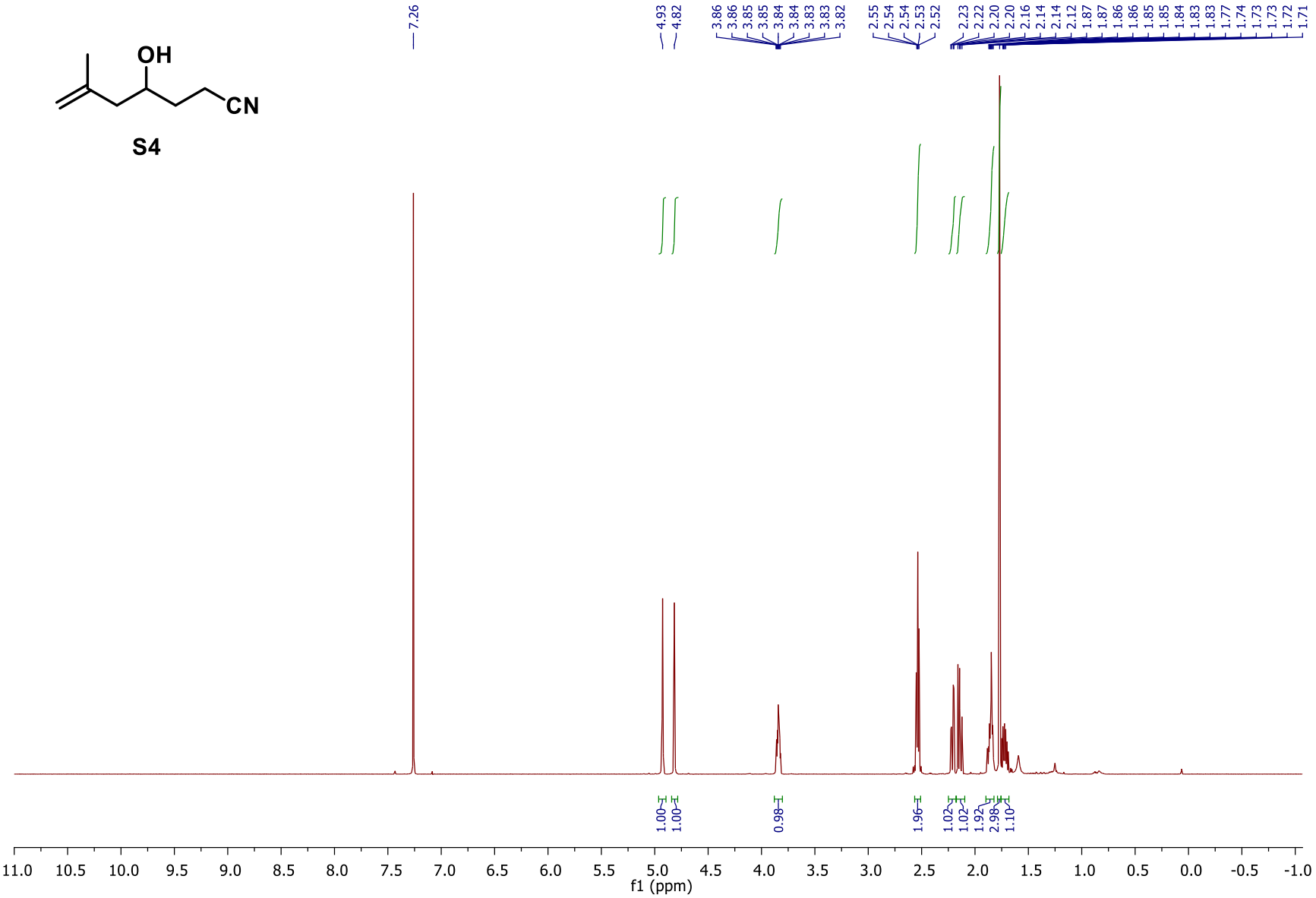
7.26
5.79
5.77
5.75
5.73
5.05
5.04
5.01
5.01
5.00
4.98
4.26
4.25
4.24
4.23
4.22
4.22
4.21
4.19
2.93
2.92
2.90
2.90
2.88
2.87
2.86
2.85
2.14
2.12
2.11
2.09
2.08
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.85
1.81
1.79
1.78
1.77
1.77
1.76
1.58
1.39
1.38
1.37
1.35
1.00
1.03
0.98
4.14
1.04
2.18
2.09
1.32
1.05
6.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

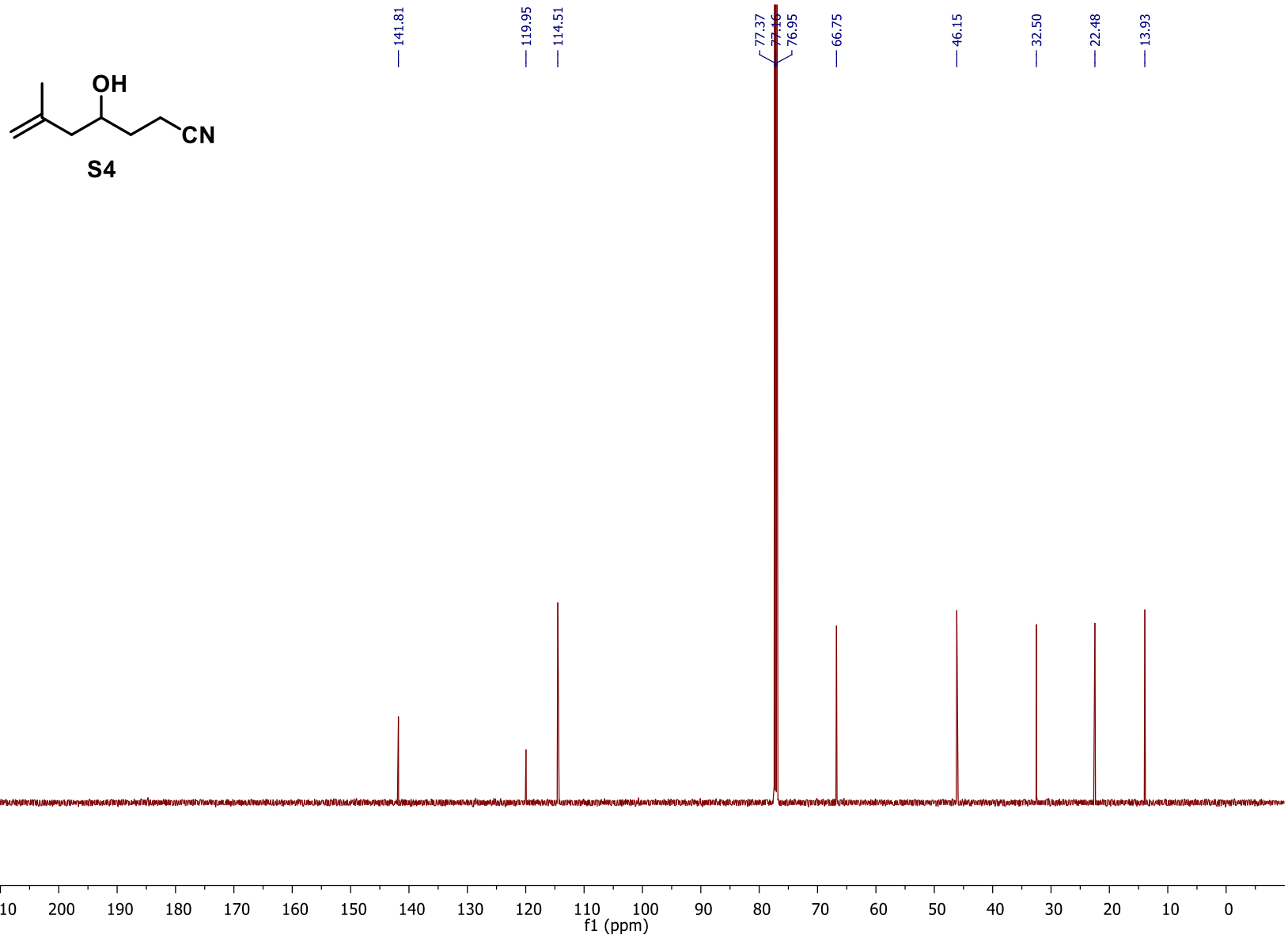
F. ^{1}H, ^{13}C and 2D NMR Spectra

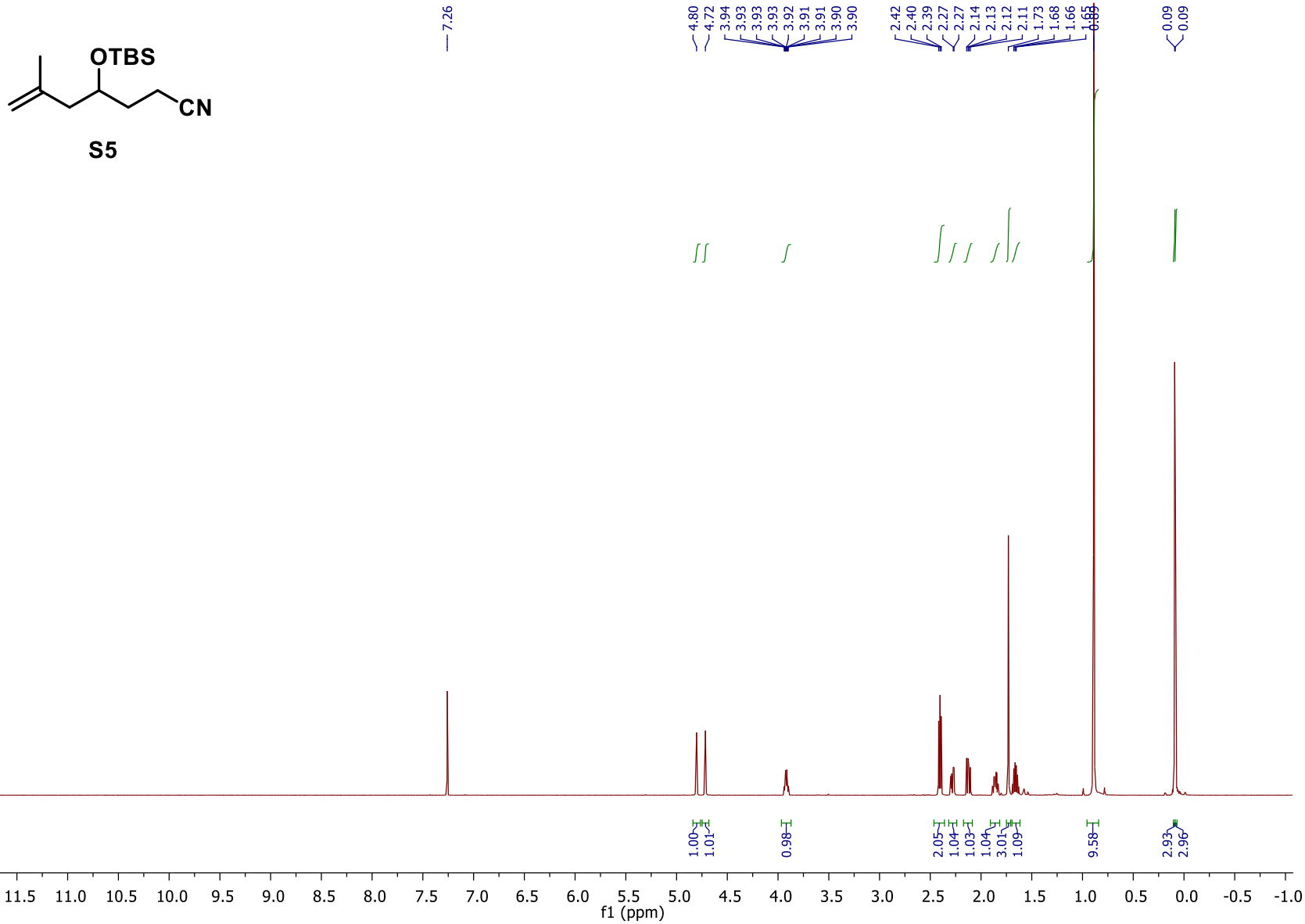


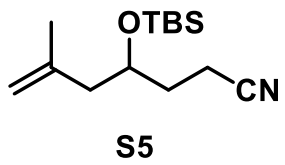

OEt
O
P
CN
OEt
S2
7.26
4.74
4.69
4.27
4.26
4.25
4.25
4.23
4.22
2.94
2.93
2.92
2.91
2.90
2.89
2.88
2.87
2.09
2.07
2.06
2.05
1.90
1.89
1.88
1.87
1.86
1.86
1.85
1.84
1.83
1.83
1.83
1.82
1.81
1.81
1.71
1.62
1.62
1.61
1.61
1.39
1.38
1.37
1.00
0.99
3.89
0.97
2.08
3.25
3.13
1.10
5.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


OEt
O
P
CN
OEt
S2
144.36
116.41
116.35
111.12
77.37
77.16
76.95
64.20
64.16
63.85
63.81
36.86
26.61
26.59
25.77
25.69
22.27
22.24
16.52
16.51
16.48
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
CN
S4
7.26
4.93
4.82
3.86
3.86
3.85
3.85
3.84
3.84
3.83
3.83
3.82
2.55
2.54
2.54
2.53
2.52
2.23
2.22
2.20
2.20
2.16
2.14
2.14
2.12
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.83
1.83
1.77
1.74
1.73
1.73
1.72
1.71
1.00
1.00
0.98
1.96
1.02
1.02
1.92
2.98
1.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

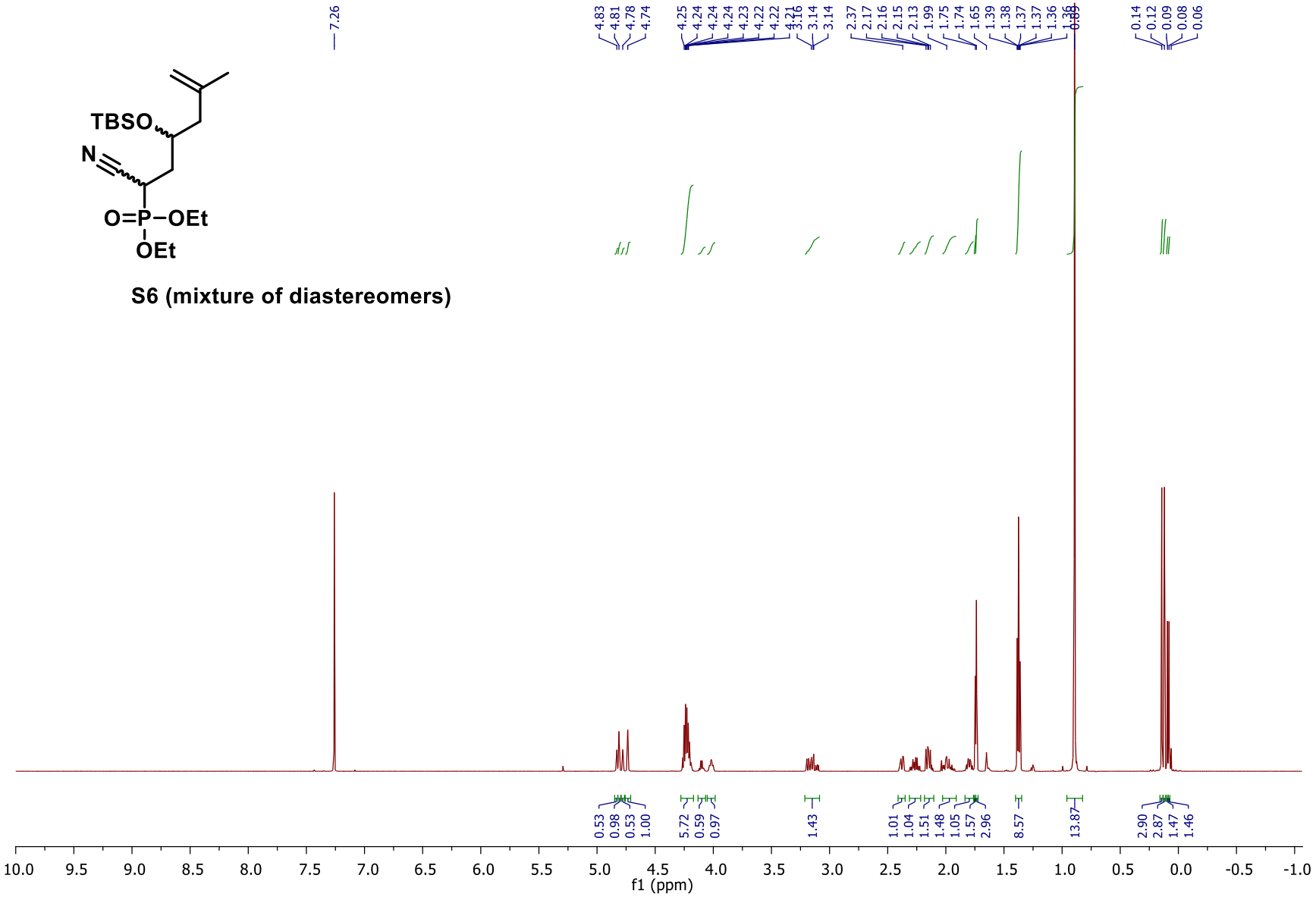

OH
CN
S4
141.81
119.95
114.51
77.37
77.16
76.95
66.75
46.15
32.50
22.48
13.93
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

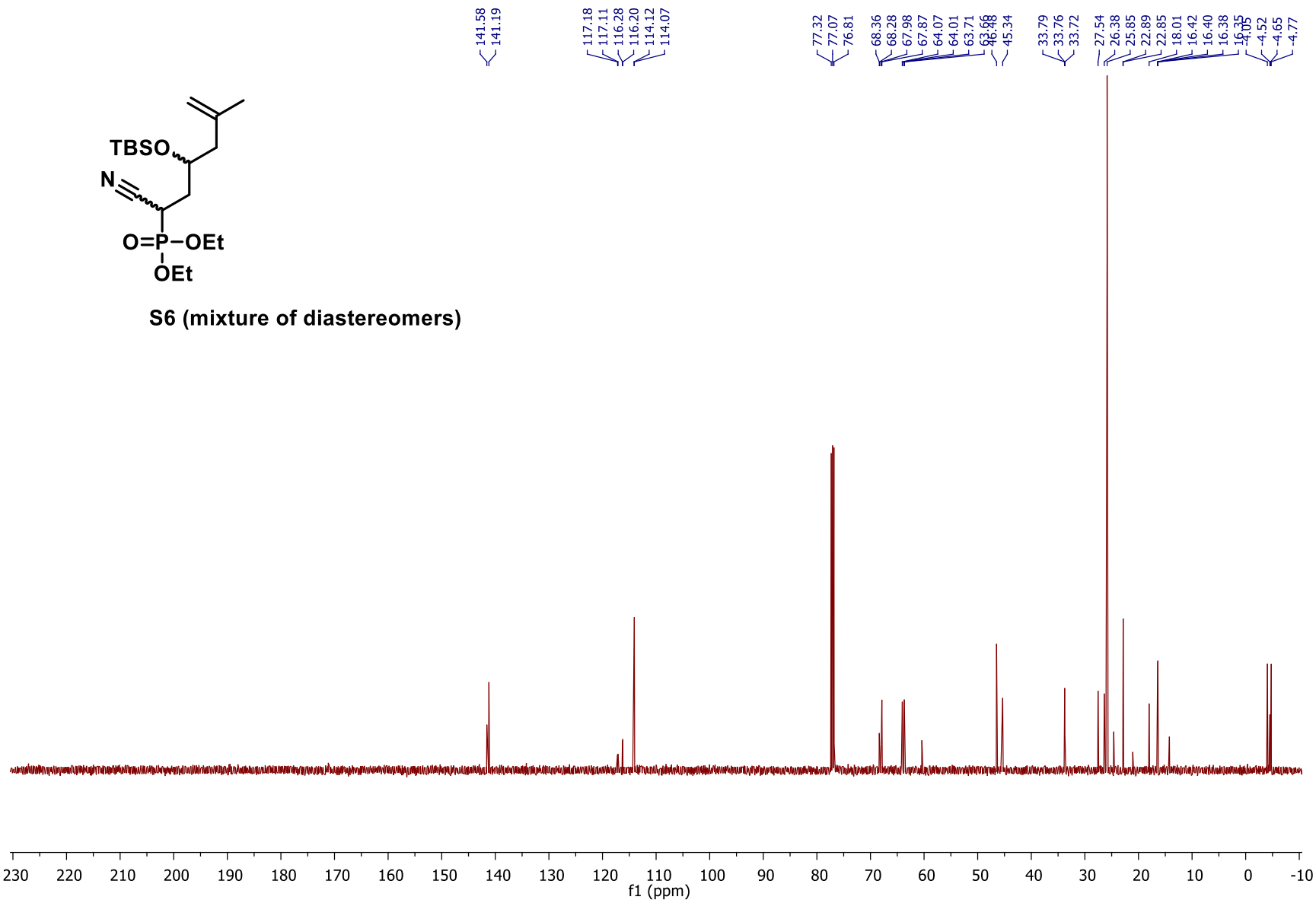

OTBS
CN
S5
7.26
4.80
4.72
3.94
3.93
3.93
3.93
3.92
3.91
3.91
3.90
3.90
2.42
2.40
2.39
2.27
2.27
2.14
2.13
2.12
2.11
1.73
1.68
1.66
1.65
0.89
0.09
0.09
1.00
1.01
0.98
2.05
1.04
1.03
1.04
3.01
1.09
9.58
2.93
2.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

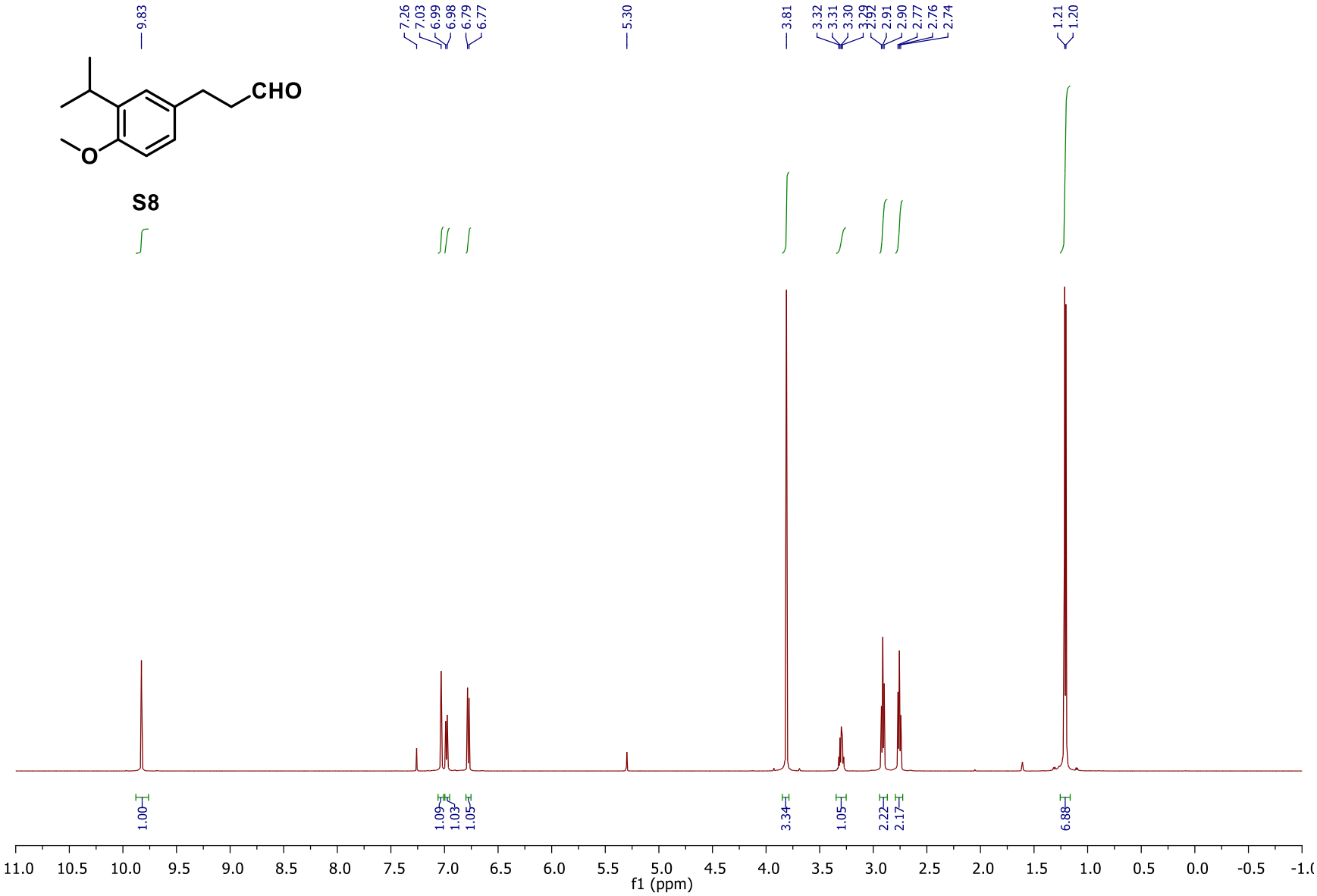

OTBS
CN

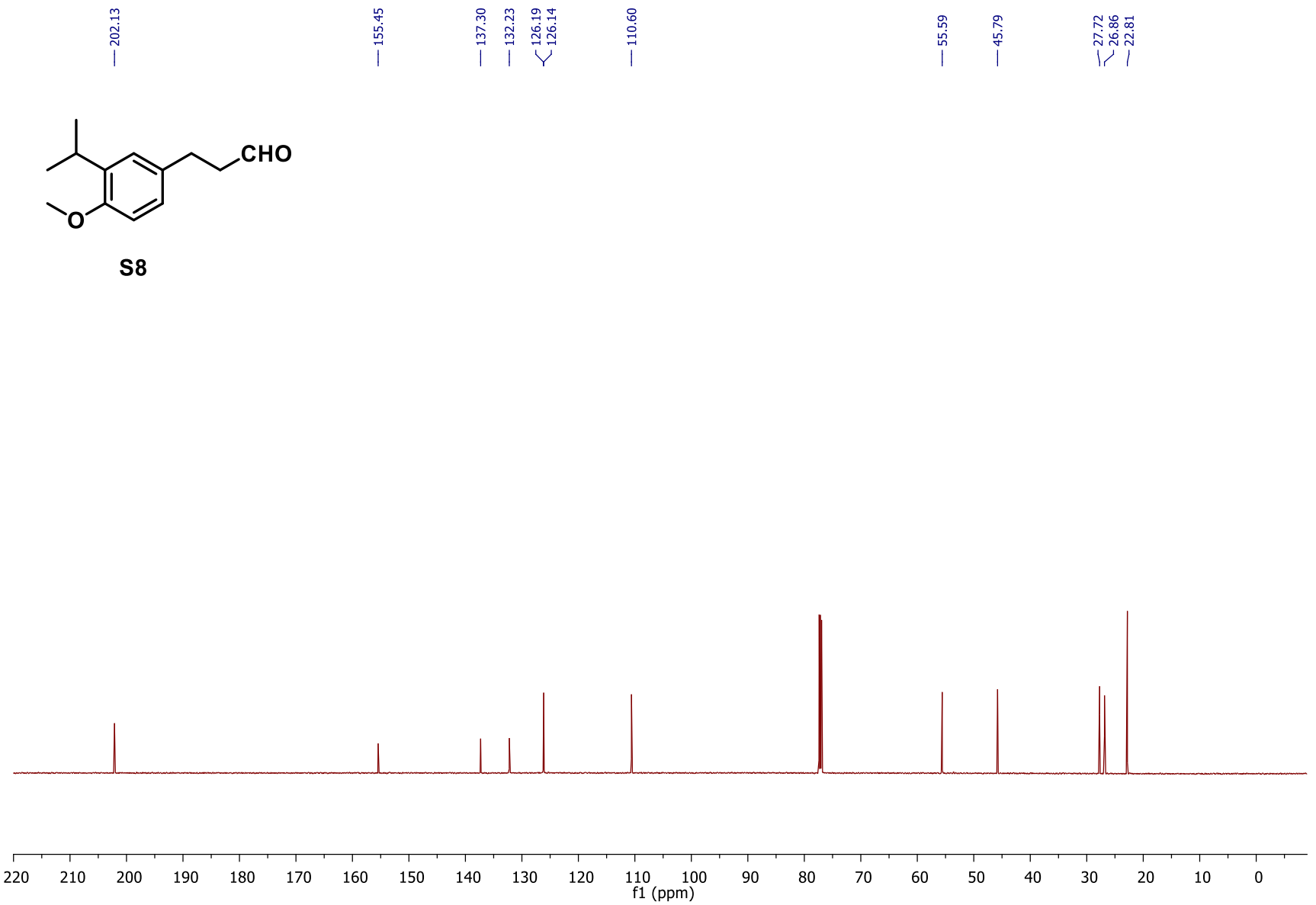
S5

141.77
120.13
113.88
77.41
77.16
76.91
68.81
45.95
32.04
25.93
22.96
18.13
13.22
-4.20
-4.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

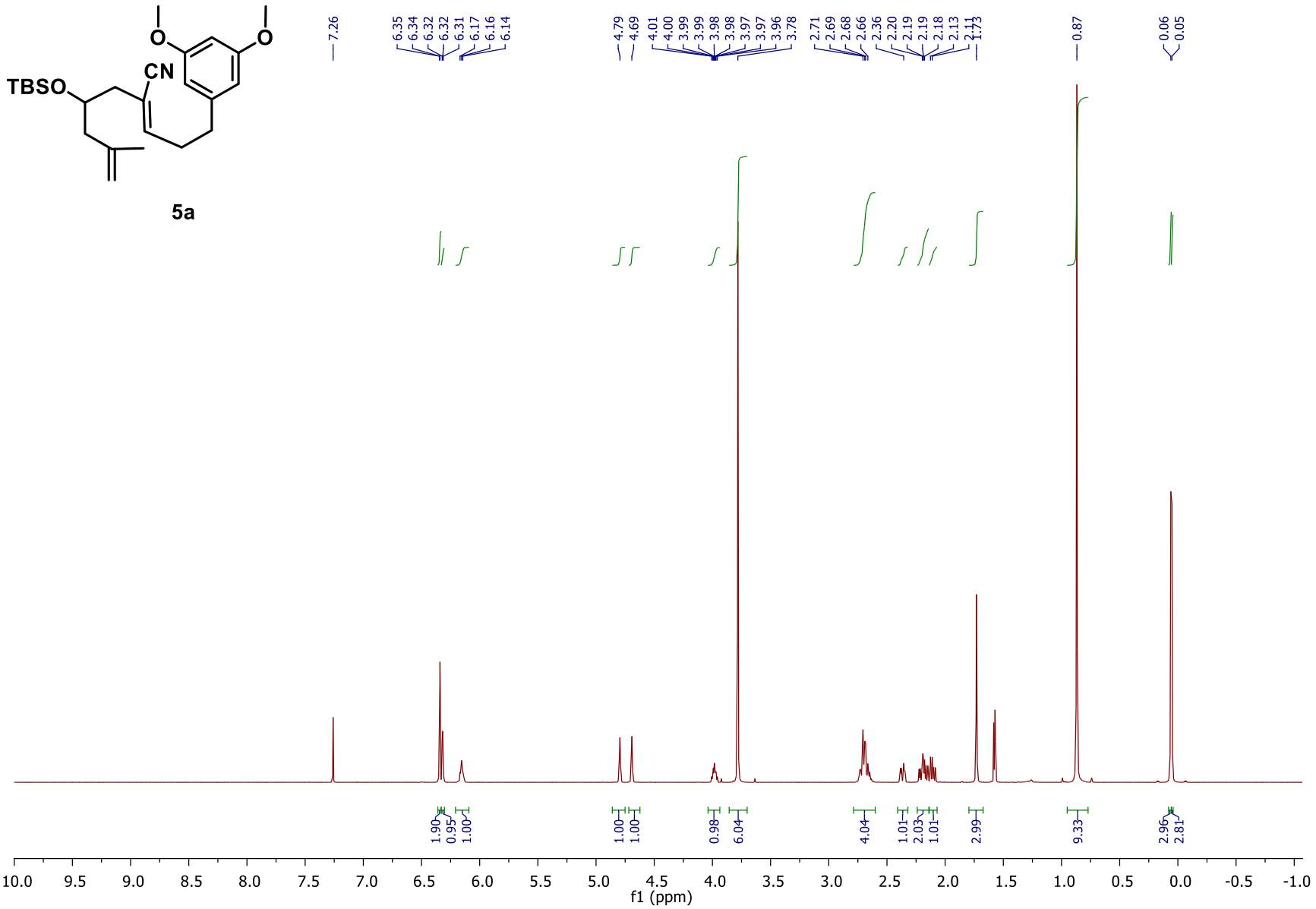

TBSO
N
O=P−OEt
OEt
S6 (mixture of diastereomers)
f1 (ppm)

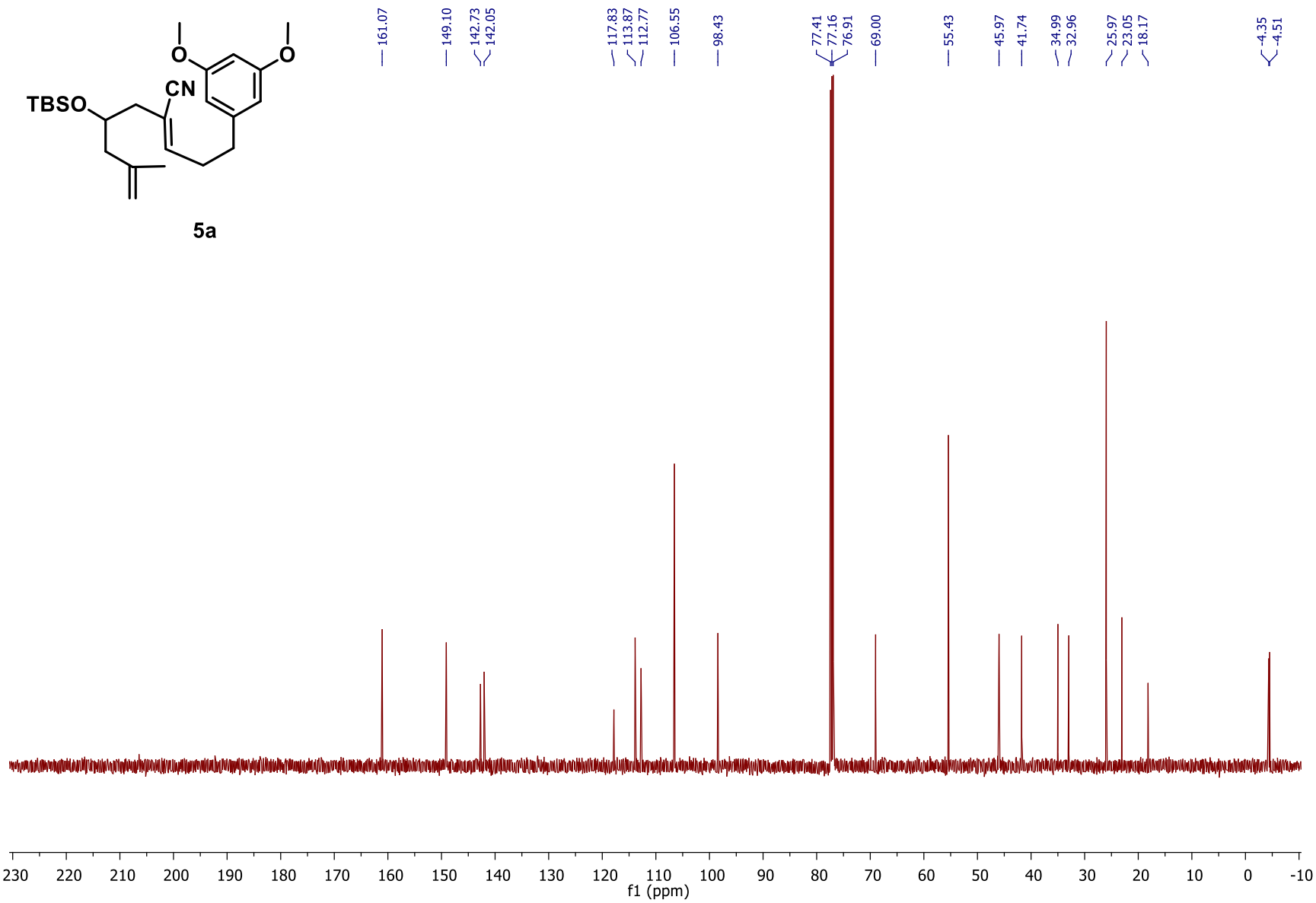

141.58
141.19
117.18
117.11
116.28
116.20
114.12
114.07
77.32
77.07
76.81
68.36
68.28
67.98
67.87
64.07
64.01
63.71
63.66
46.48
45.34
33.79
33.76
33.72
27.54
26.38
25.85
22.89
22.85
18.01
16.42
16.40
16.38
16.35
16.05
-4.52
-4.65
-4.77
TBSO
N
O=P−OEt
OEt
S6 (mixture of diastereomers)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

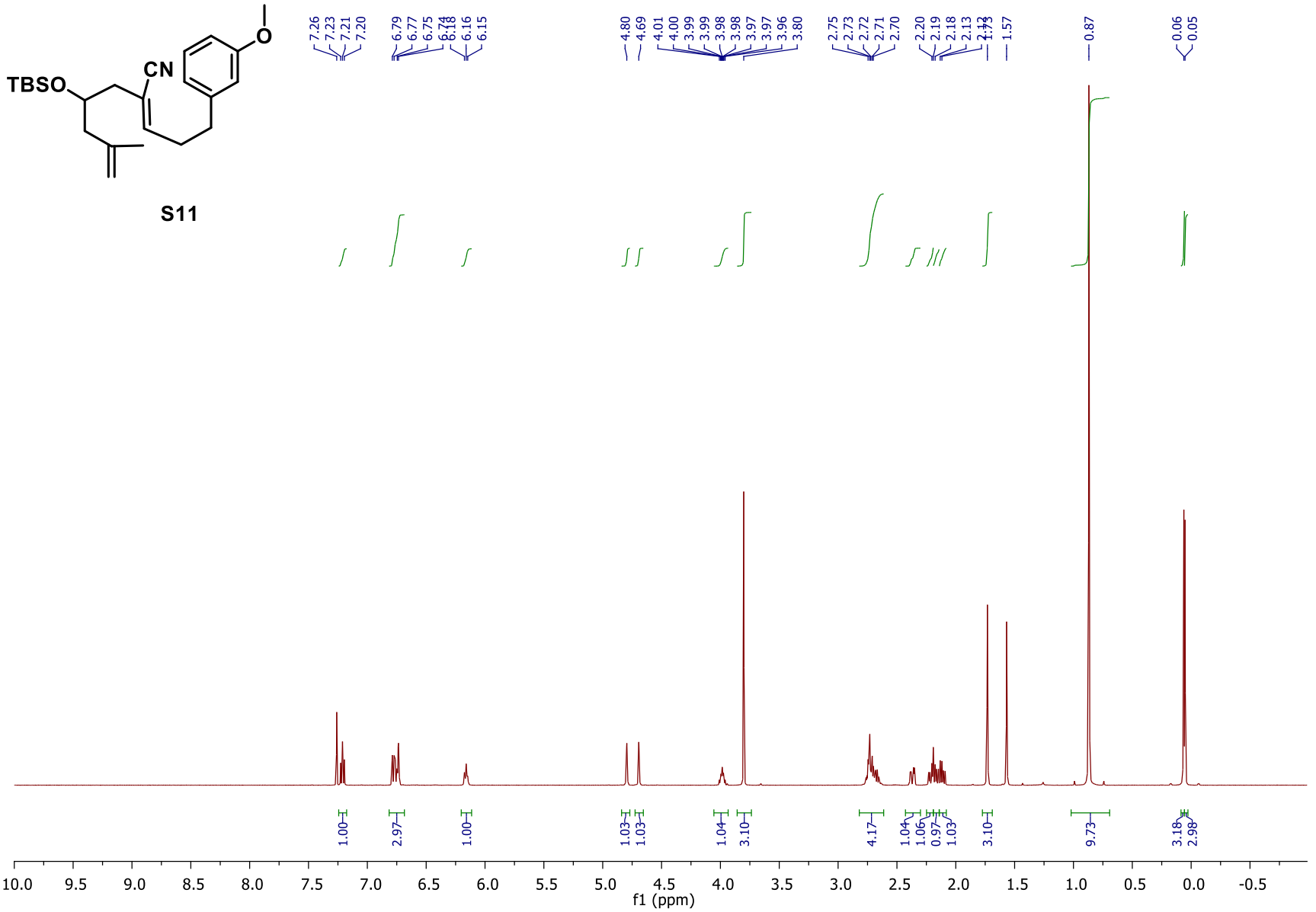

9.83
7.26
7.03
6.99
6.98
6.79
6.77
5.30
3.81
3.32
3.31
3.30
2.91
2.90
2.77
2.76
2.74
1.21
1.20
CHO
O
S8
1.00
1.09
1.03
1.05
3.34
1.05
2.22
2.17
6.88
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

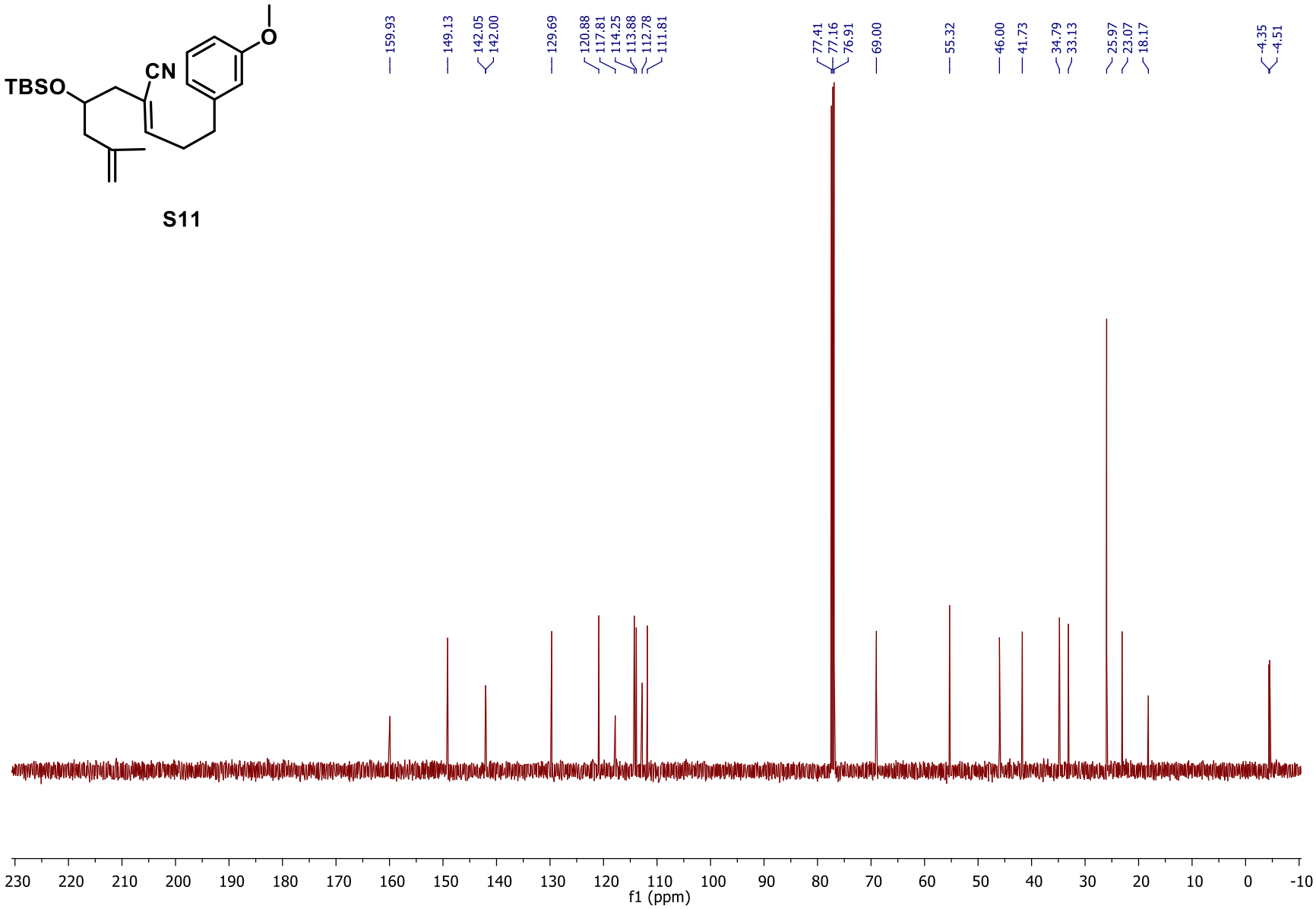

202.13
155.45
137.30
132.23
126.19
126.14
110.60
55.59
45.79
27.72
26.86
22.81
CHO
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

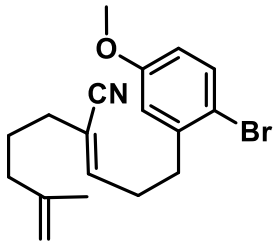
S8


TBSO
CN
O
O
5a
7.26
6.35
6.34
6.32
6.32
6.31
6.17
6.16
6.14
4.79
4.69
4.01
4.00
3.99
3.99
3.98
3.98
3.97
3.97
3.96
3.78
2.71
2.69
2.68
2.66
2.36
2.20
2.19
2.19
2.18
2.13
2.11
1.73
0.87
0.06
0.05
1.90
0.95
1.00
1.00
1.00
0.98
6.04
4.04
1.01
2.03
1.01
2.99
9.33
2.96
2.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

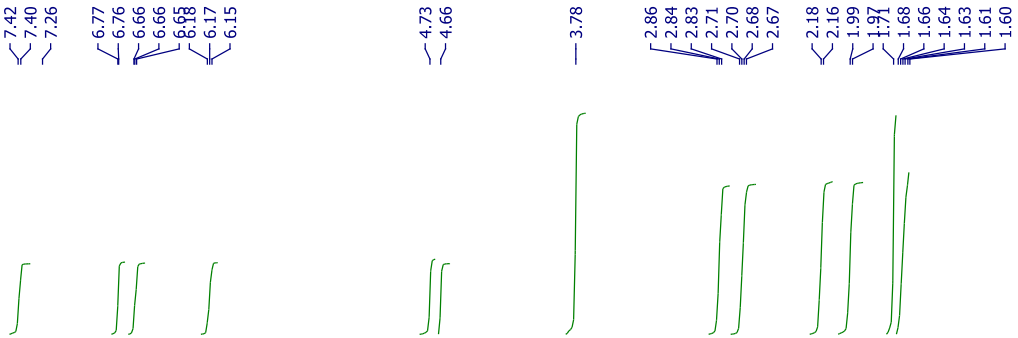

TBSO
CN
O
O
5a
161.07
149.10
142.73
142.05
117.83
113.87
112.77
106.55
98.43
77.41
77.16
76.91
69.00
55.43
45.97
41.74
34.99
32.96
25.97
23.05
18.17
-4.35
-4.51
f1 (ppm)


TBSO
CN
O
S11
7.26
7.23
7.21
7.20
6.79
6.77
6.75
6.74
6.18
6.16
6.15
4.80
4.69
4.01
4.00
3.99
3.99
3.98
3.98
3.97
3.97
3.96
3.80
2.75
2.73
2.72
2.71
2.70
2.20
2.19
2.18
2.13
1.57
0.87
0.06
0.05
1.00
2.97
1.00
1.03
1.03
1.04
3.10
4.17
1.04
1.06
0.97
1.03
3.10
9.73
3.18
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


TBSO
CN
O
S11
159.93
149.13
142.05
142.00
129.69
120.88
117.81
114.25
113.88
112.78
111.81
77.41
77.16
76.91
69.00
55.32
46.00
41.73
34.79
33.13
25.97
23.07
18.17
-4.35
-4.51
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
CN
Br

S13


7.42
7.40
7.26
6.77
6.76
6.66
6.66
6.65
6.18
6.17
6.15
4.73
4.66
3.78
2.86
2.84
2.83
2.71
2.70
2.68
2.67
2.18
2.16
1.99
1.97
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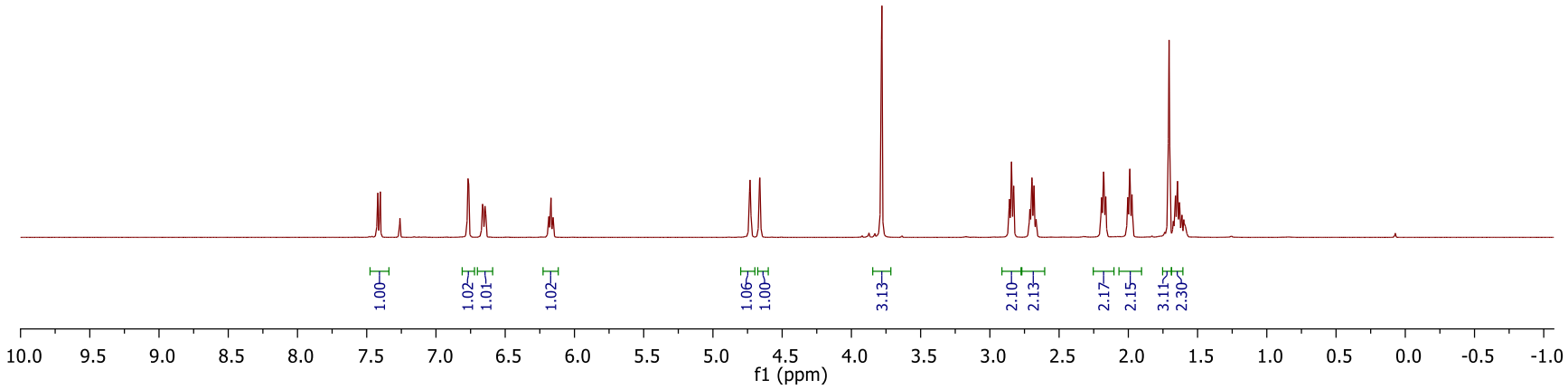
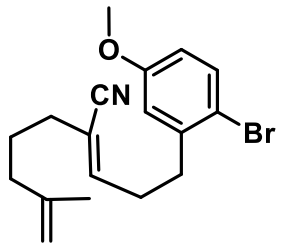
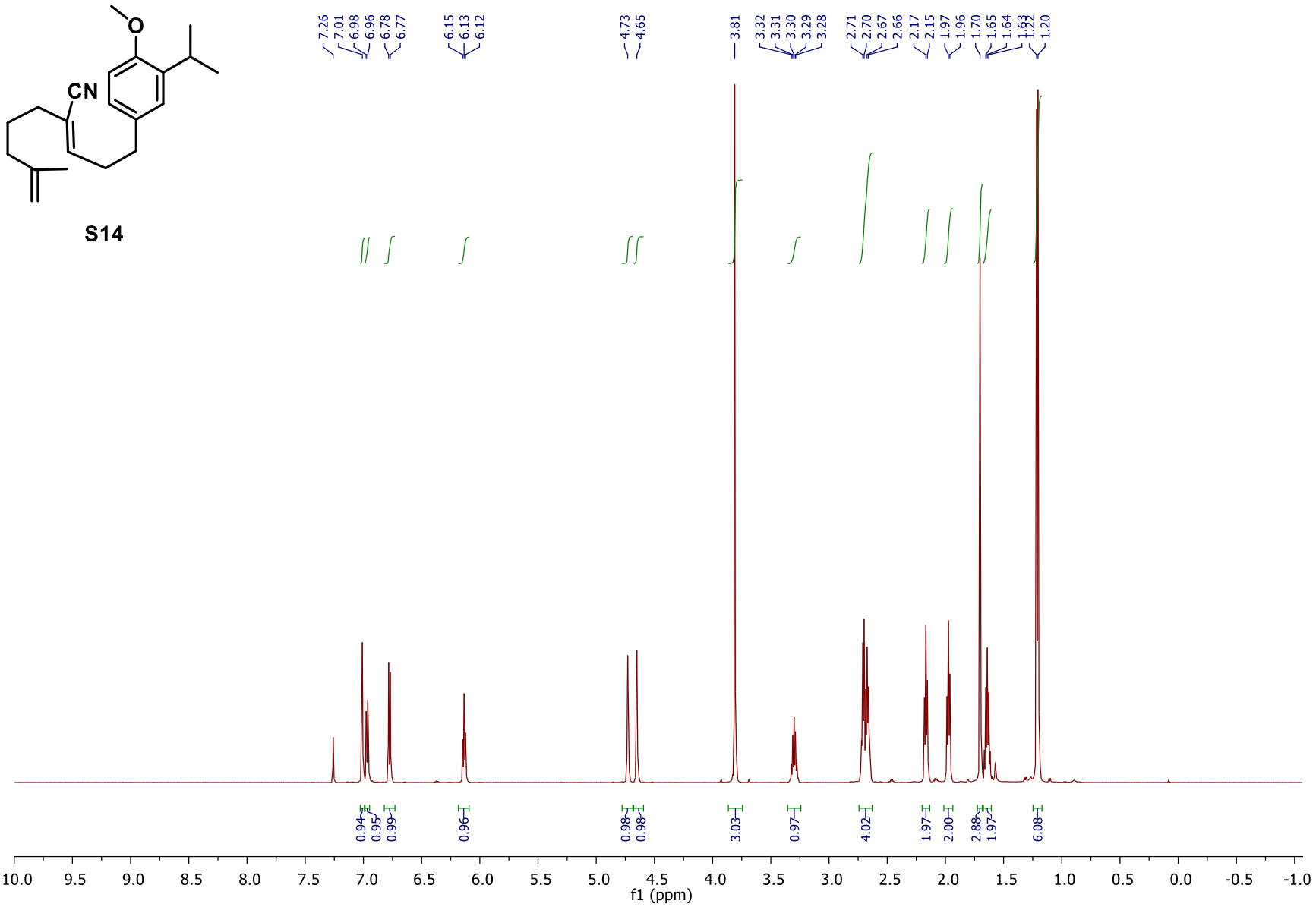
1.68
1.66
1.64
1.63
1.61
1.60


1.00
1.02
1.01
1.02
1.06
1.00
3.13
2.10
2.13
2.17
2.15
3.11
2.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


O
CN
Br

S13

159.17
146.05
144.79
140.59
133.55
117.54
116.16
115.67
114.93
113.89
110.80
77.41
77.16
76.91
55.58
36.69
35.18
33.78
31.69
25.91
22.33
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
CN
S14
7.26
7.01
6.98
6.96
6.78
6.77
6.15
6.13
6.12
4.73
4.65
3.81
3.32
3.31
3.30
3.29
3.28
2.71
2.70
2.67
2.66
2.17
2.15
1.97
1.96
1.70
1.65
1.64
1.63
1.22
1.20
0.94
0.95
0.99
0.96
0.98
0.98
3.03
0.97
4.02
1.97
2.00
2.88
1.97
6.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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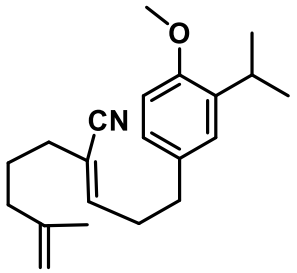
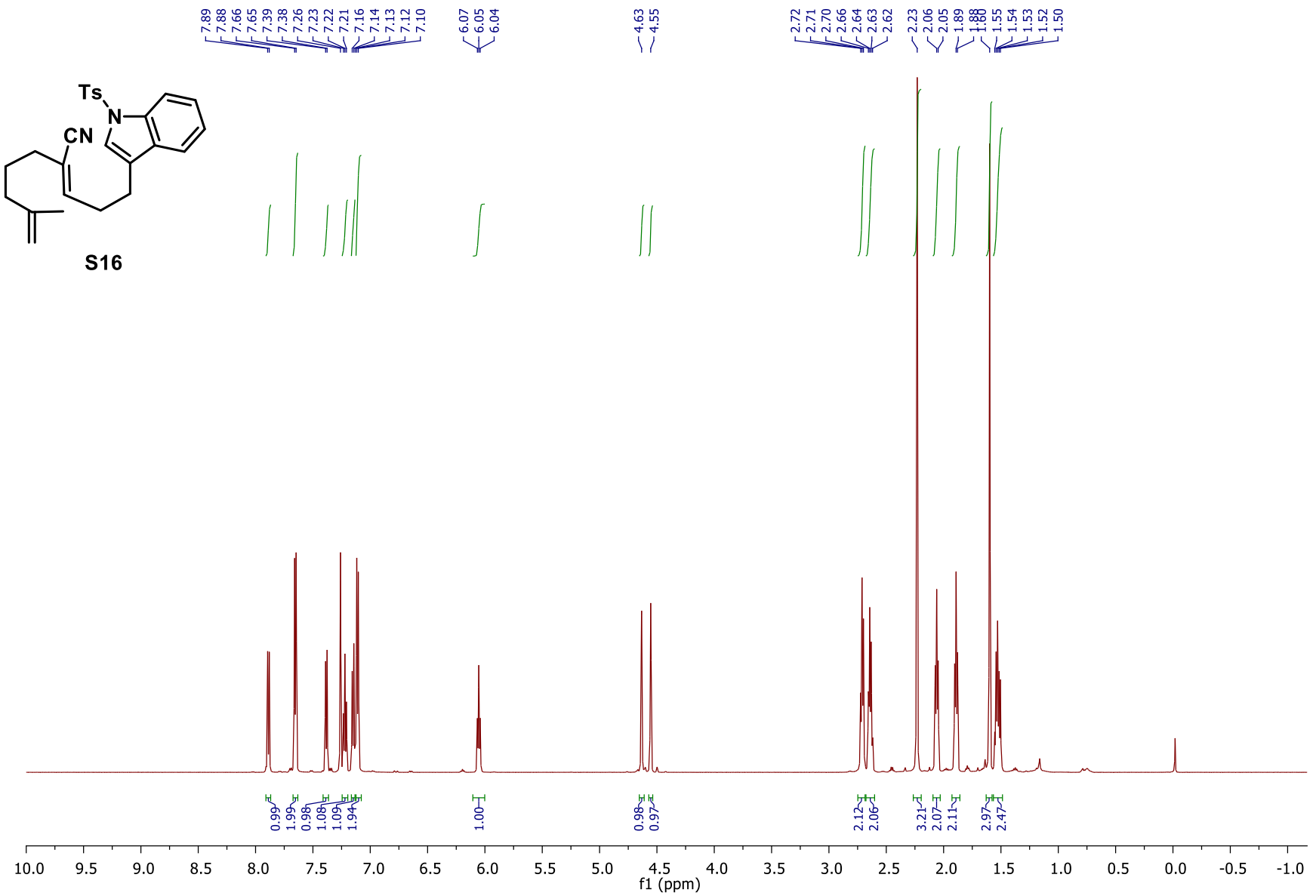
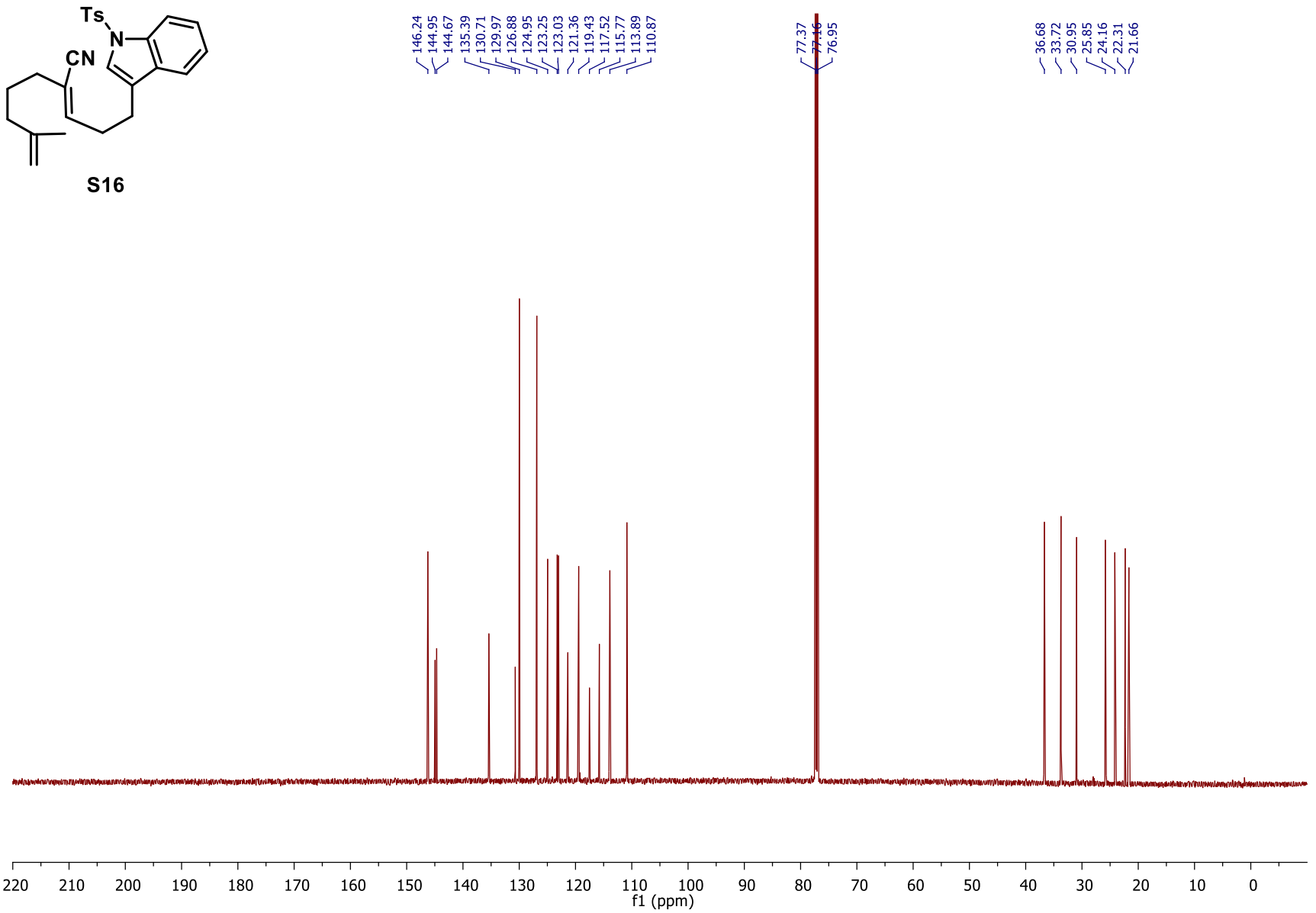
0.0
-0.5
-1.0
f1 (ppm)

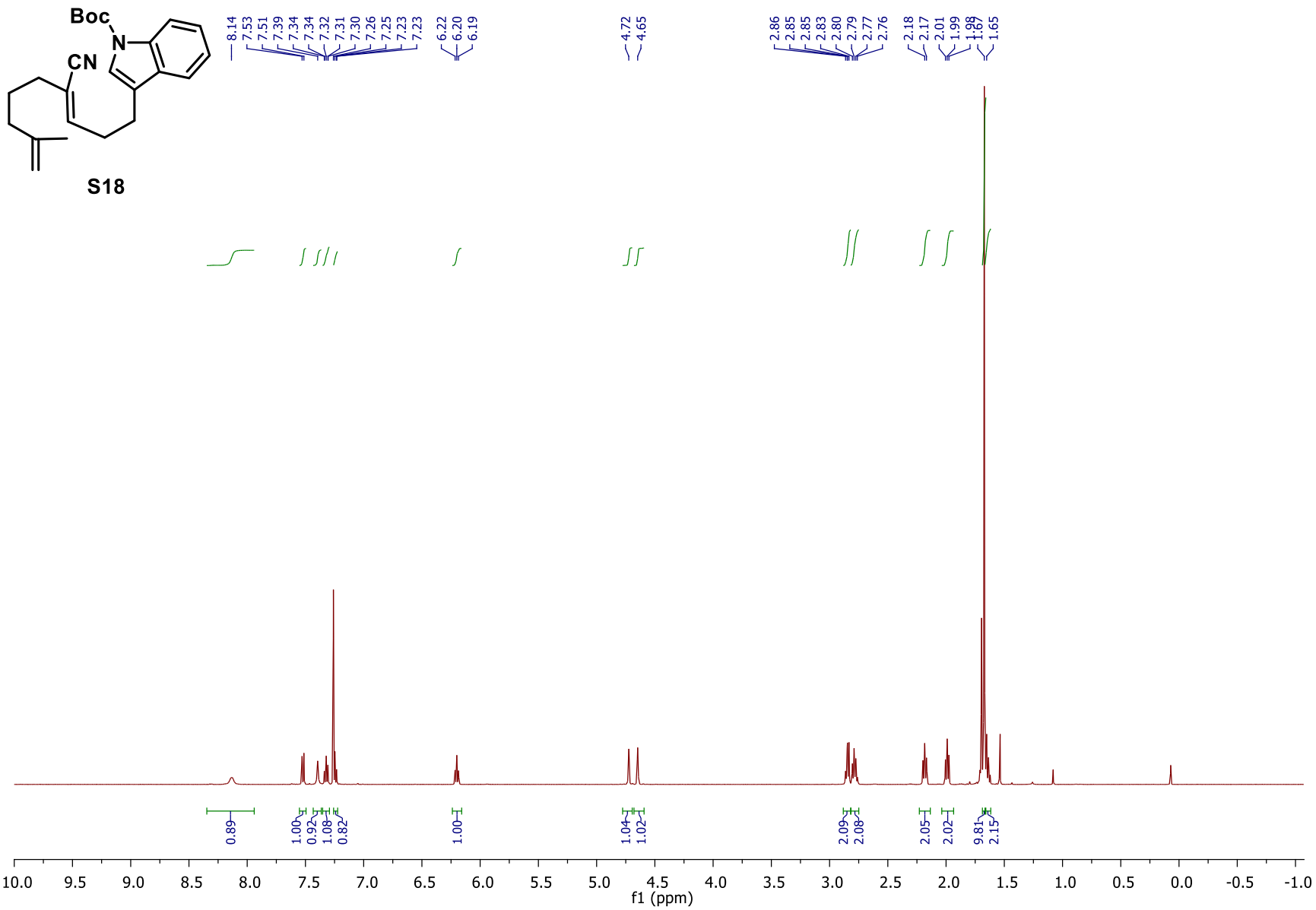

O
CN

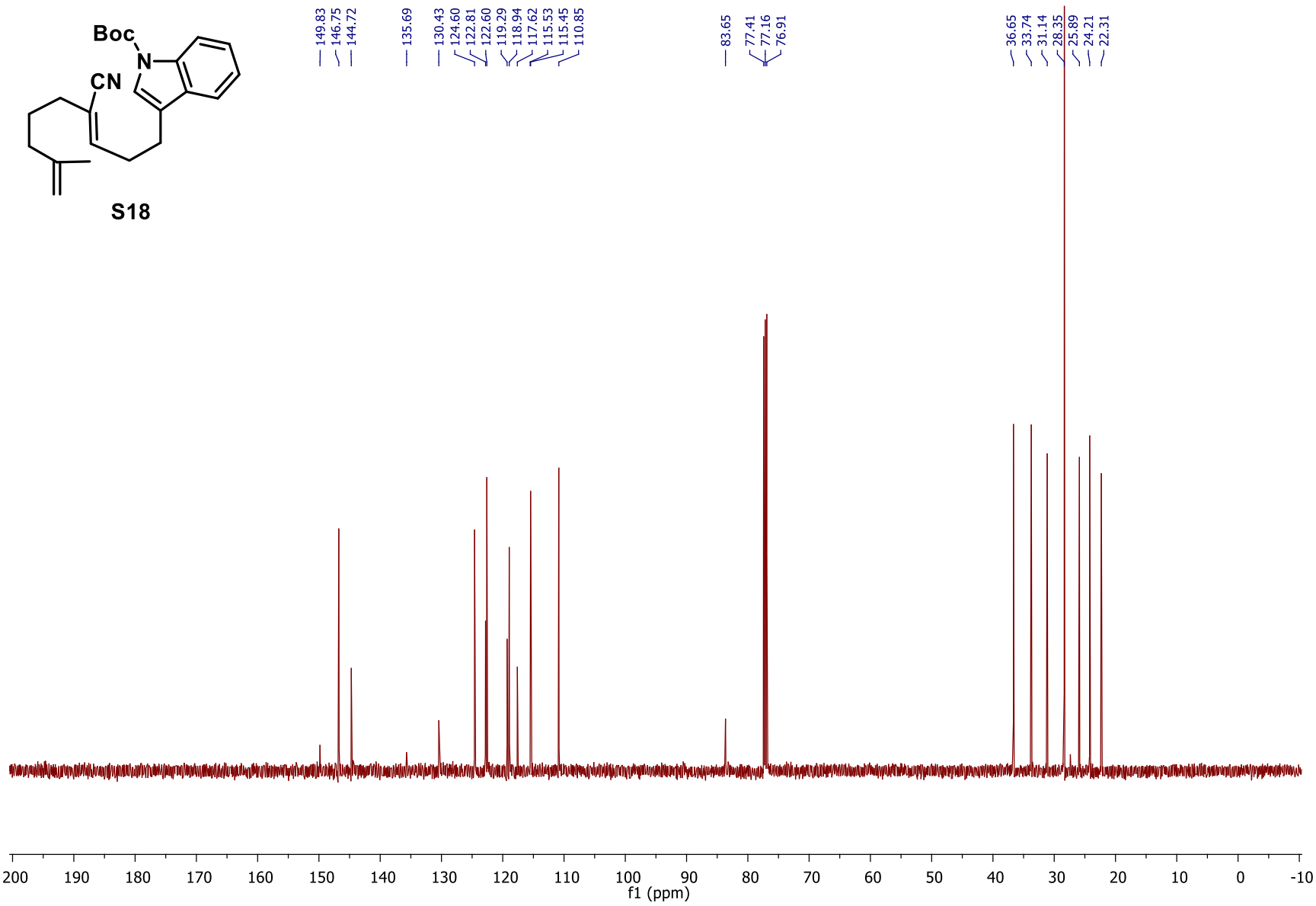
S14

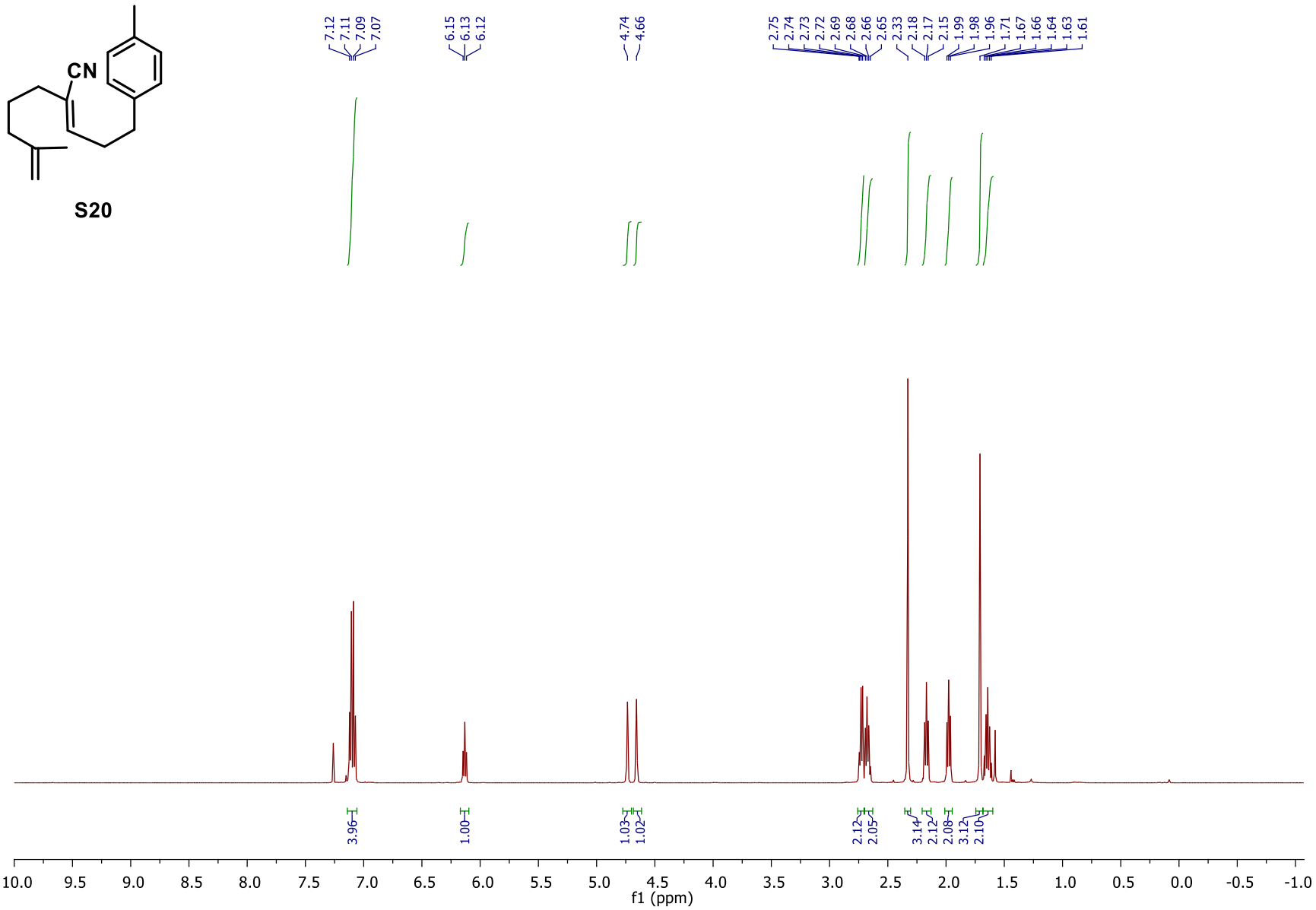
155.42
147.12
144.81
137.16
132.18
126.28
126.24
117.73
115.08
110.79
110.53
77.37
77.16
76.95
55.57
36.63
34.29
33.74
33.35
26.85
25.92
22.83
22.32
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

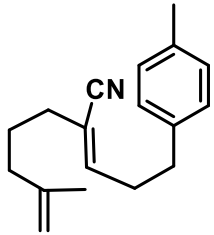

Ts
N
CN
S16
7.89
7.88
7.66
7.65
7.39
7.38
7.26
7.23
7.22
7.21
7.16
7.14
7.13
7.12
7.10
6.07
6.05
6.04
4.63
4.55
2.72
2.71
2.70
2.66
2.64
2.63
2.62
2.23
2.06
2.05
1.89
1.88
1.60
1.55
1.54
1.53
1.52
1.50
0.99
1.99
0.98
1.08
1.09
1.94
1.00
0.98
0.97
2.12
2.06
3.21
2.07
2.11
2.97
2.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


Ts
N
CN
S16
146.24
144.95
144.67
135.39
130.71
129.97
126.88
124.95
123.25
123.03
121.36
119.43
117.52
115.77
113.89
110.87
77.37
77.16
76.95
36.68
33.72
30.95
25.85
24.16
22.31
21.66
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Boc
N
CN
S18
8.14
7.53
7.51
7.39
7.34
7.34
7.32
7.31
7.30
7.26
7.25
7.23
7.23
6.22
6.20
6.19
4.72
4.65
2.86
2.85
2.85
2.83
2.80
2.79
2.77
2.76
2.18
2.17
2.01
1.99
1.98
1.67
1.65
0.89
1.00
0.92
1.08
0.82
1.00
1.04
1.02
2.09
2.08
2.05
2.02
9.81
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

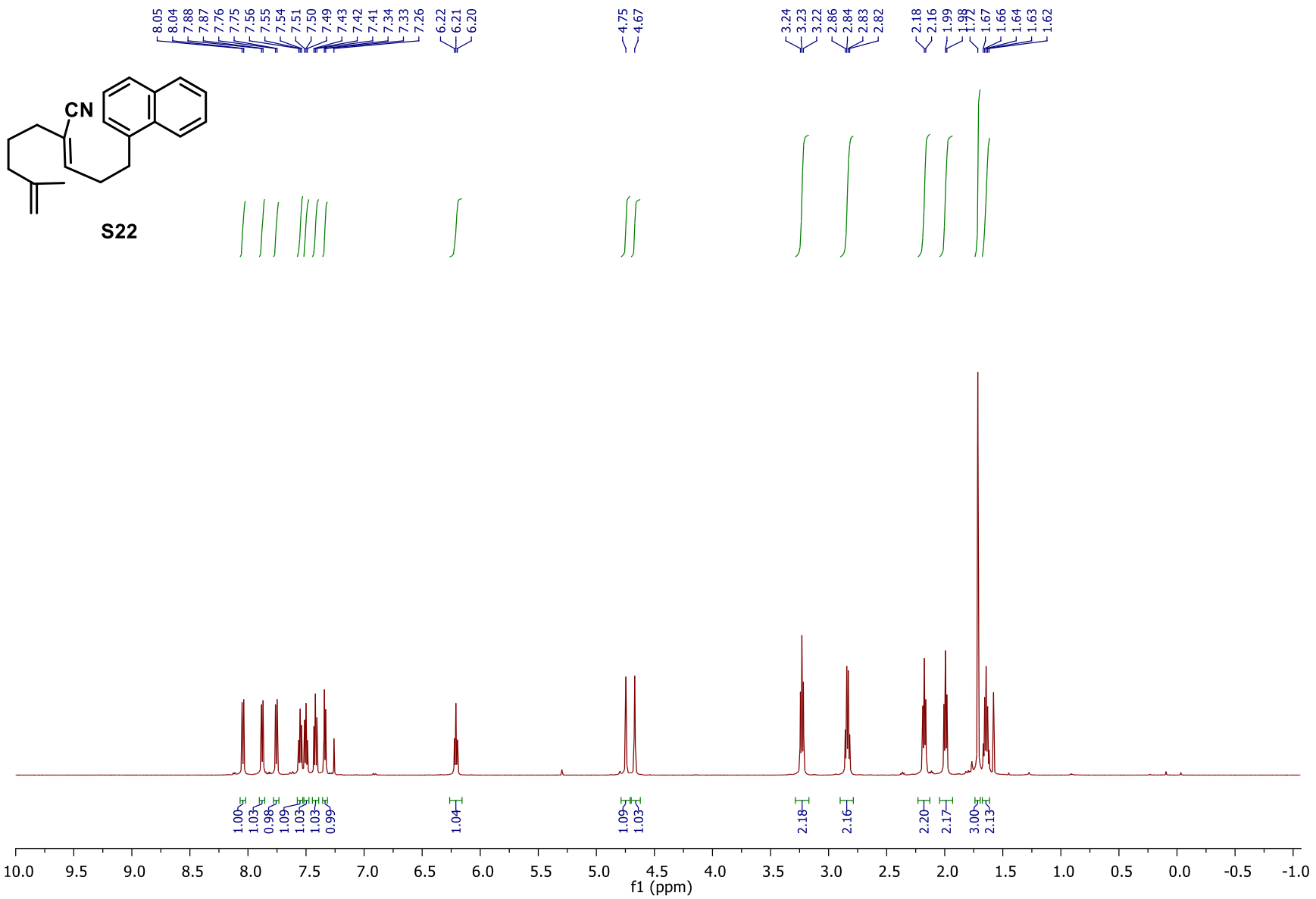

Boc
N
CN
S18
149.83
146.75
144.72
135.69
130.43
124.60
122.81
122.60
119.29
118.94
117.62
115.53
115.45
110.85
83.65
77.41
77.16
76.91
36.65
33.74
31.14
28.35
25.89
24.21
22.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

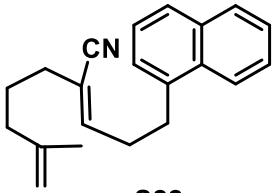

CN
S20
7.12
7.11
7.09
7.07
6.15
6.13
6.12
4.74
4.66
2.75
2.74
2.73
2.72
2.69
2.68
2.66
2.65
2.33
2.18
2.17
2.15
1.99
1.98
1.96
1.71
1.67
1.66
1.64
1.63
1.61
3.96
1.00
1.03
1.02
2.12
2.05
3.14
2.12
2.08
3.12
2.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


CN

S20

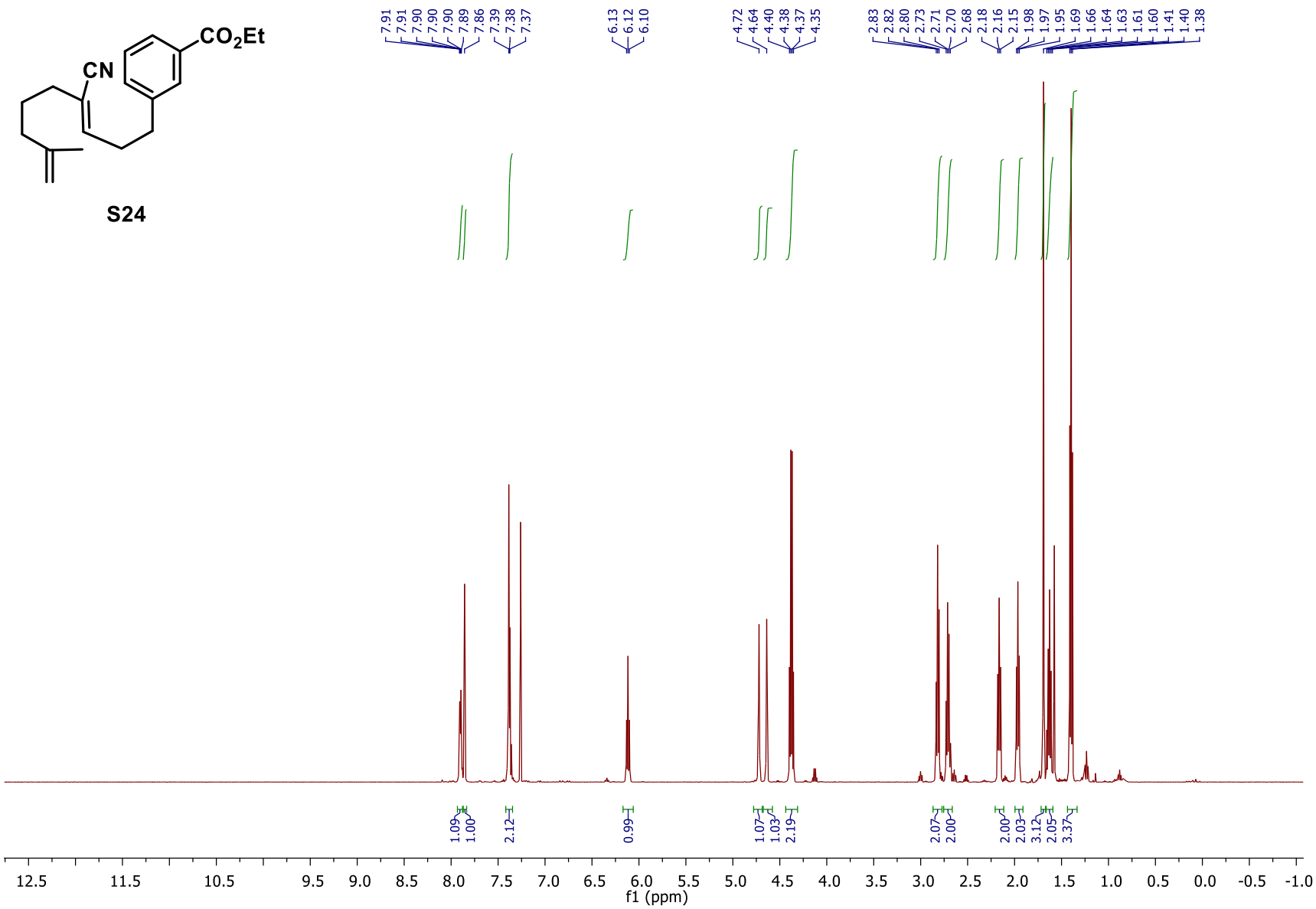
146.86
144.81
137.24
135.90
129.32
128.41
117.66
115.26
110.77
77.41
77.16
76.91
36.61
34.48
33.73
33.18
25.90
22.32
21.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

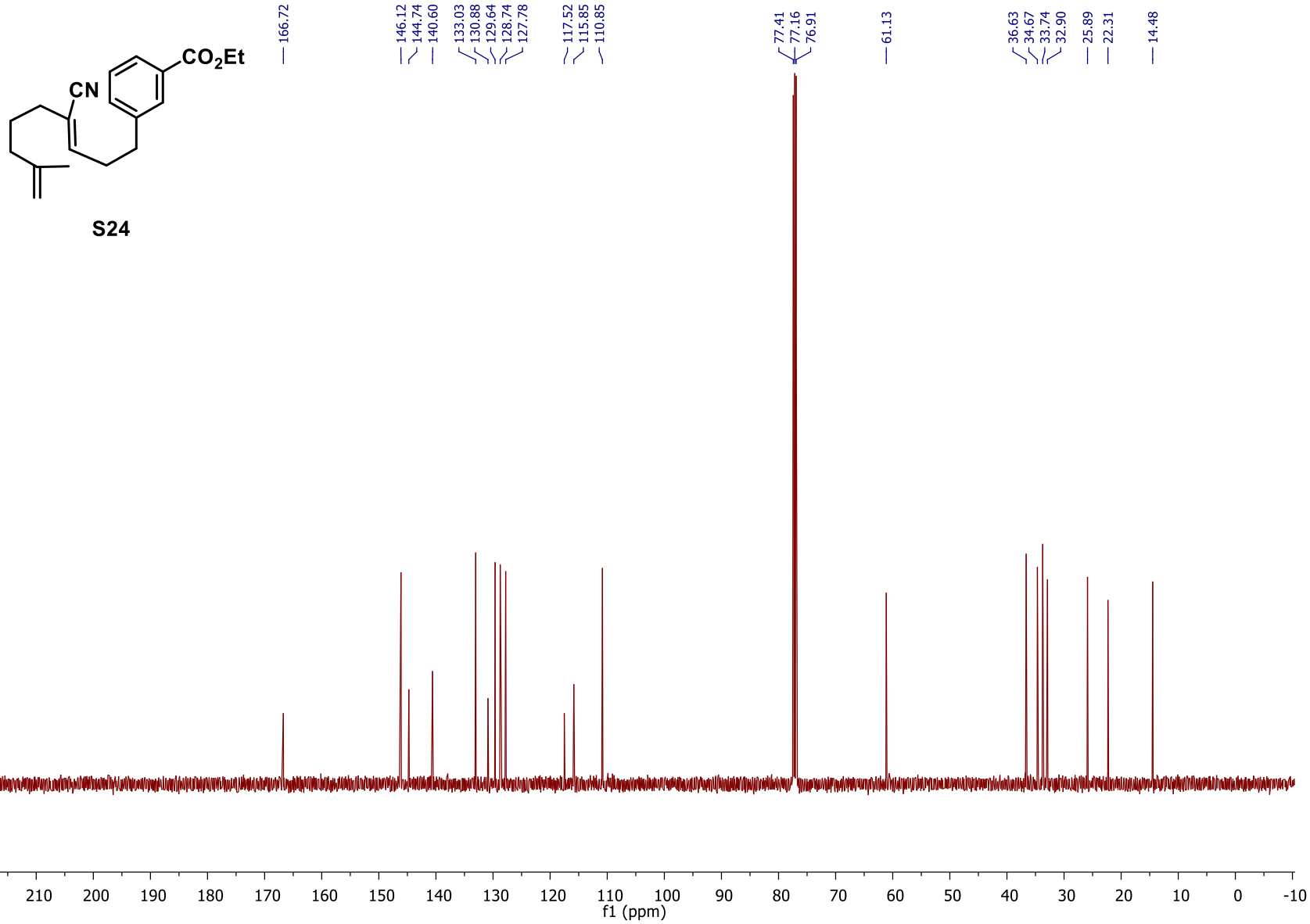

8.05
8.04
7.88
7.87
7.76
7.75
7.56
7.55
7.54
7.51
7.50
7.49
7.43
7.42
7.41
7.34
7.33
7.26
6.22
6.21
6.20
4.75
4.67
3.24
3.23
3.22
2.86
2.84
2.83
2.82
2.18
2.16
1.99
1.98
1.72
1.67
1.66
1.64
1.63
1.62
CN
S22
1.00
1.03
0.98
1.09
1.03
1.03
0.99
1.04
1.09
1.03
2.18
2.16
2.20
2.17
3.00
2.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

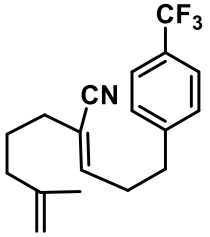

CN

S22

146.69
144.78
136.39
129.01
127.32
126.29
126.21
125.77
125.60
123.55
117.60
115.38
110.81
36.67
33.75
32.41
31.98
25.89
22.34
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

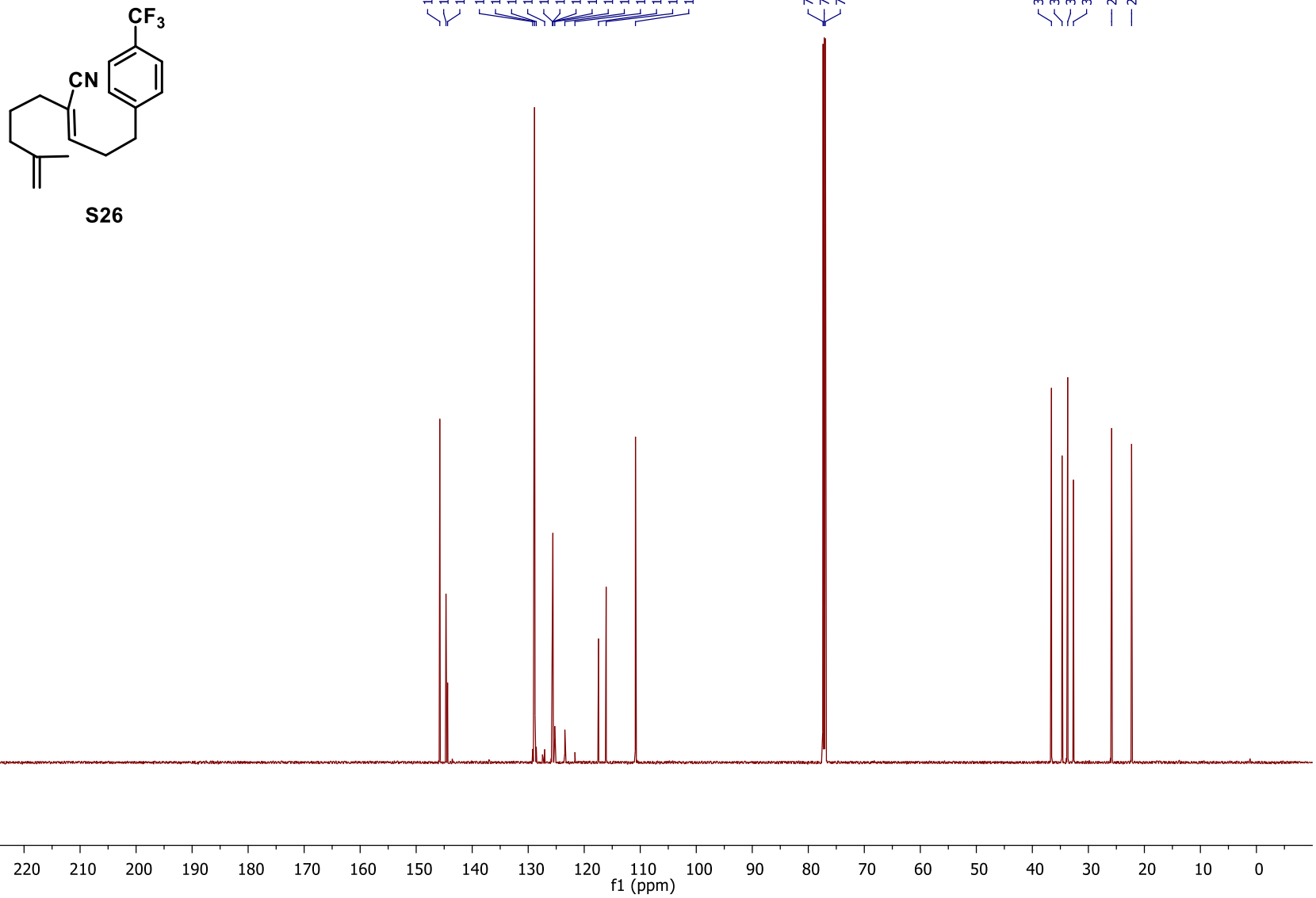

CO2Et
CN
S24
7.91
7.91
7.90
7.90
7.90
7.89
7.86
7.39
7.38
7.37
6.13
6.12
6.10
4.72
4.64
4.40
4.38
4.37
4.35
2.83
2.82
2.80
2.73
2.71
2.70
2.68
2.18
2.16
2.15
1.98
1.97
1.95
1.69
1.66
1.64
1.63
1.61
1.60
1.41
1.40
1.38
1.09
1.00
2.12
0.99
1.07
1.03
2.19
2.07
2.00
2.00
2.03
3.12
2.05
3.37
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

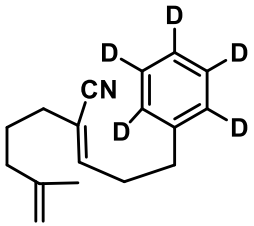

CO2Et
CN
S24
166.72
146.12
144.74
140.60
133.03
130.88
129.64
128.74
127.78
117.52
115.85
110.85
77.41
77.16
76.91
61.13
36.63
34.67
33.74
32.90
25.89
22.31
14.48
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CF3
CN

S26

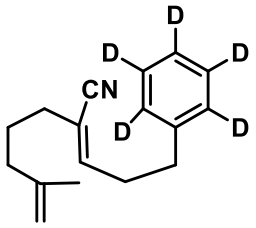
7.56
7.55
7.31
7.30
7.26
6.12
6.11
6.10
4.73
4.64
2.84
2.83
2.81
2.72
2.71
2.70
2.69
2.18
2.17
2.16
1.98
1.97
1.96
1.69
1.66
1.64
1.63
1.62
1.61
1.97
1.97
1.00
1.07
0.99
2.10
2.08
2.09
2.03
3.03
2.07
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


CF3
CN
S26
145.78
144.68
144.39
129.21
128.88
128.56
127.06
125.64
125.62
125.59
125.57
125.26
123.46
121.66
117.45
116.09
110.85
77.37
77.16
76.95
36.59
34.69
33.68
32.66
25.84
22.28
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


D
D
D
CN
D
D

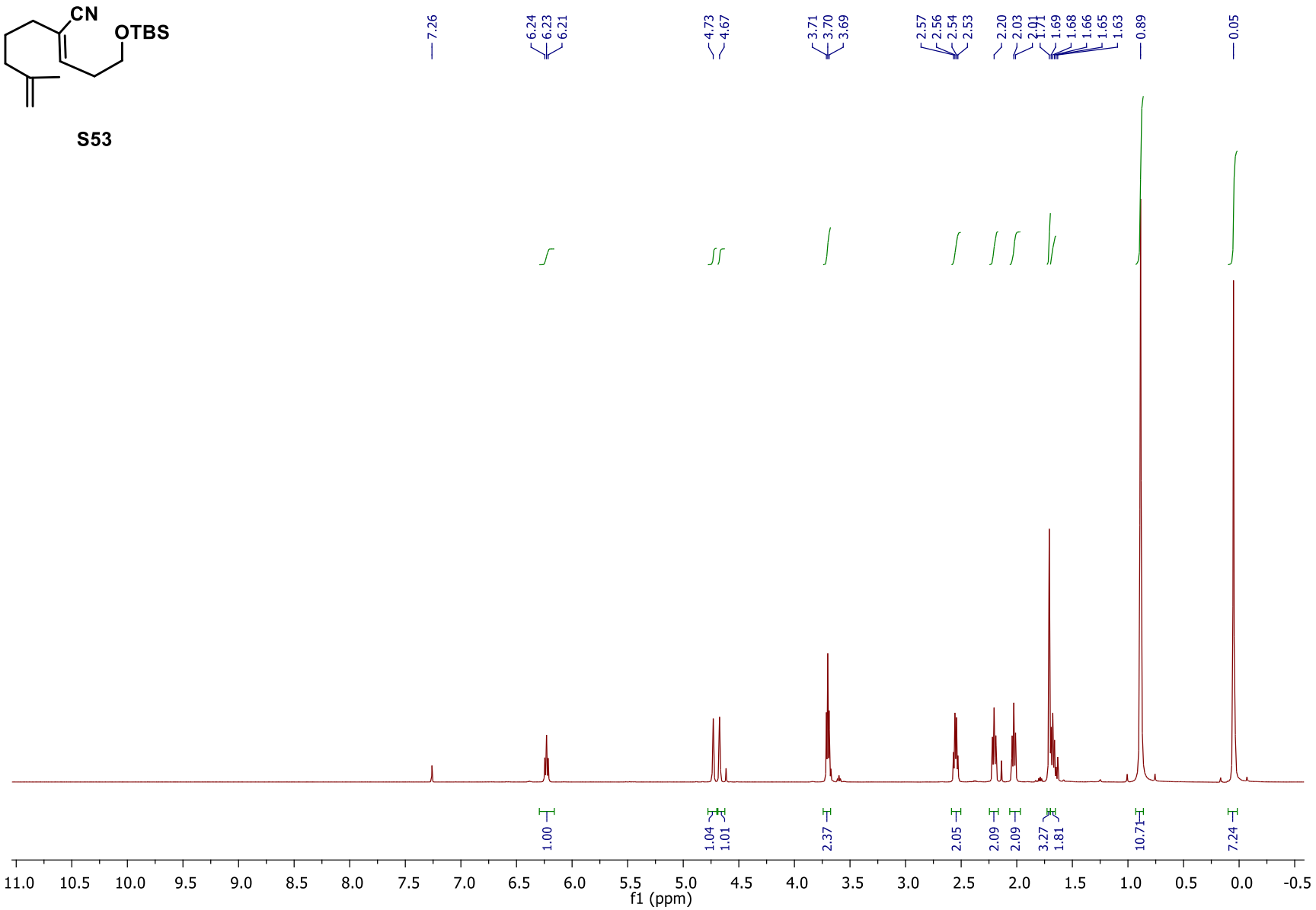
28

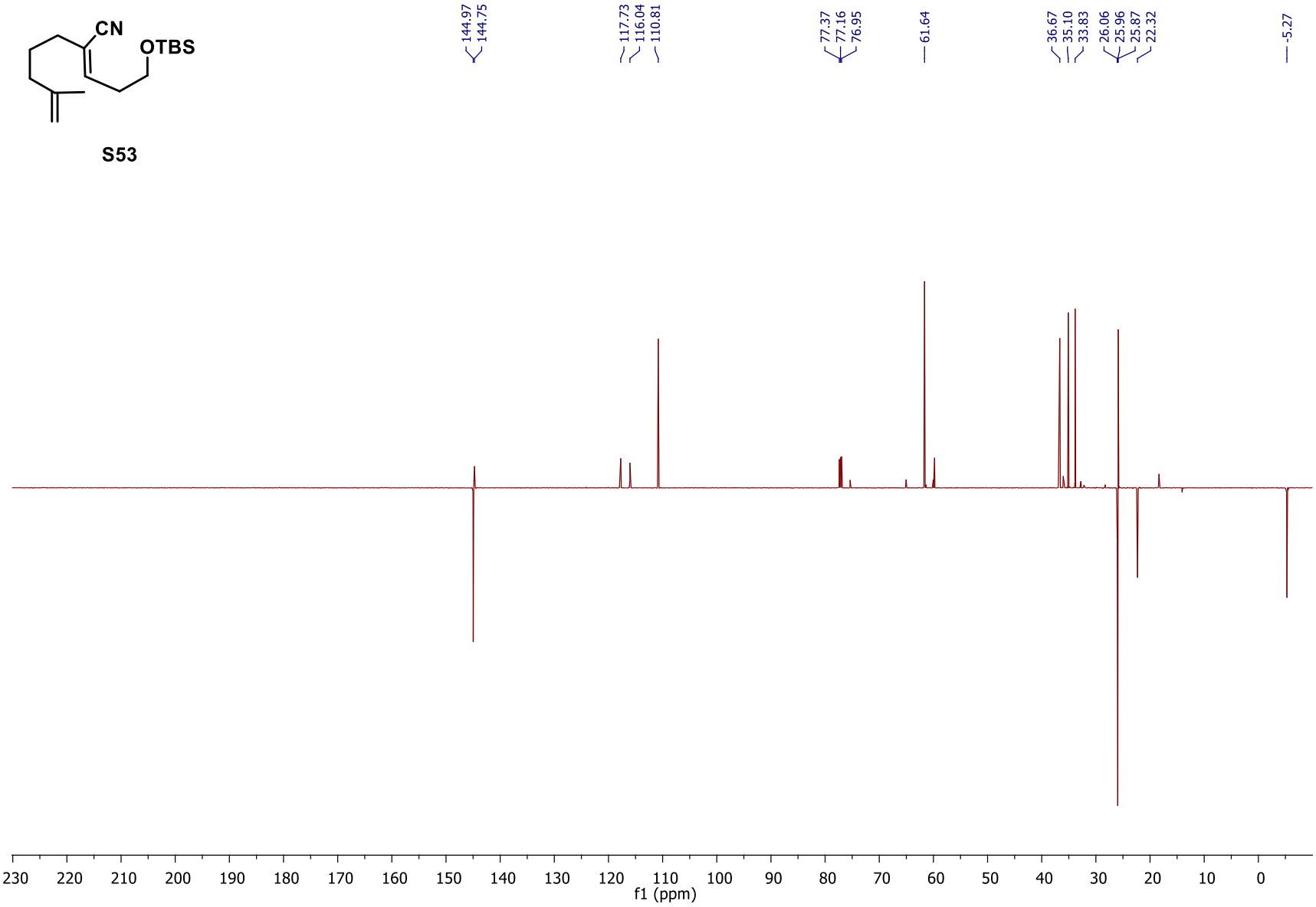
7.26
6.15
6.13
6.12
4.73
4.65
2.78
2.77
2.76
2.71
2.70
2.69
2.68
2.18
2.17
2.15
1.99
1.98
1.96
1.70
1.66
1.65
1.64
1.63
1.61
1.00
0.97
0.99
2.03
2.01
2.02
2.01
2.93
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

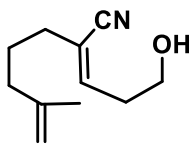

D
D
D
CN
D
D

28

146.69
144.79
140.13
128.29
128.26
128.13
127.97
126.07
125.91
125.75
117.63
115.38
110.79
77.37
77.16
76.95
36.60
34.79
33.70
33.06
25.87
22.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

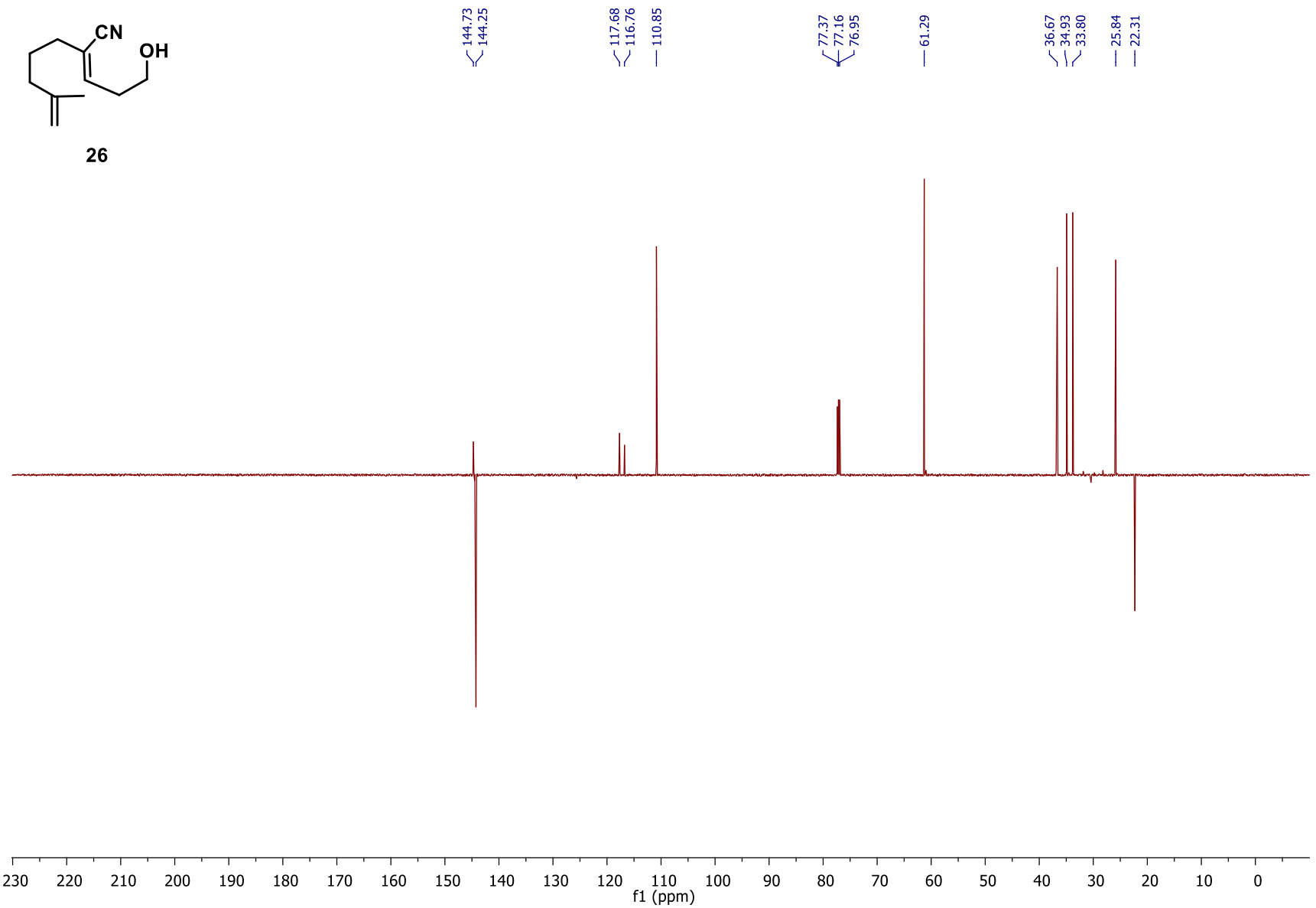

CN
OTBS
S53
7.26
6.24
6.23
6.21
4.73
4.67
3.71
3.70
3.69
2.57
2.56
2.54
2.53
2.20
2.03
2.01
1.71
1.69
1.68
1.66
1.65
1.63
0.89
0.05
1.00
1.04
1.01
2.37
2.05
2.09
2.09
3.27
1.81
10.71
7.24
f1 (ppm)

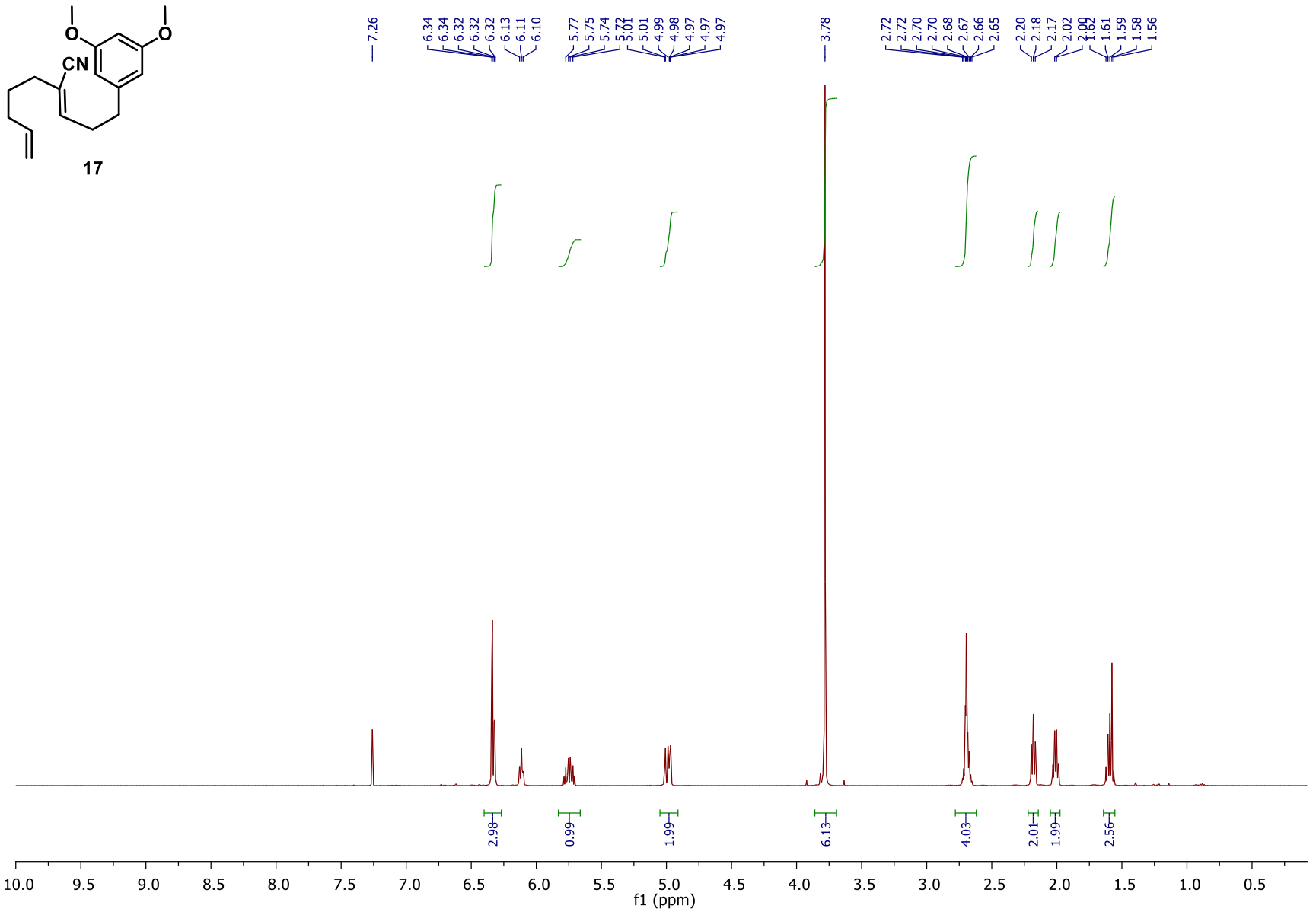

CN
OTBS
S53
144.97
144.75
117.73
116.04
110.81
77.37
77.16
76.95
61.64
36.67
35.10
33.83
26.06
25.96
25.87
22.32
-5.27
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CN
OH

26

7.26
6.26
6.25
6.24
4.73
4.67
3.75
3.74
3.73
2.62
2.61
2.60
2.59
2.23
2.22
2.20
2.04
2.02
2.01
1.78
1.70
1.69
1.68
1.67
1.65
1.00
1.00
0.99
2.05
2.02
2.08
2.03
1.30
3.13
1.91
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CN
OH
26
144.73
144.25
117.68
116.76
110.85
77.37
77.16
76.95
61.29
36.67
34.93
33.80
25.84
22.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
CN
O
17
7.26
6.34
6.34
6.32
6.32
6.32
6.13
6.11
6.10
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5.75
5.74
5.72
5.01
4.99
4.98
4.97
4.97
4.97
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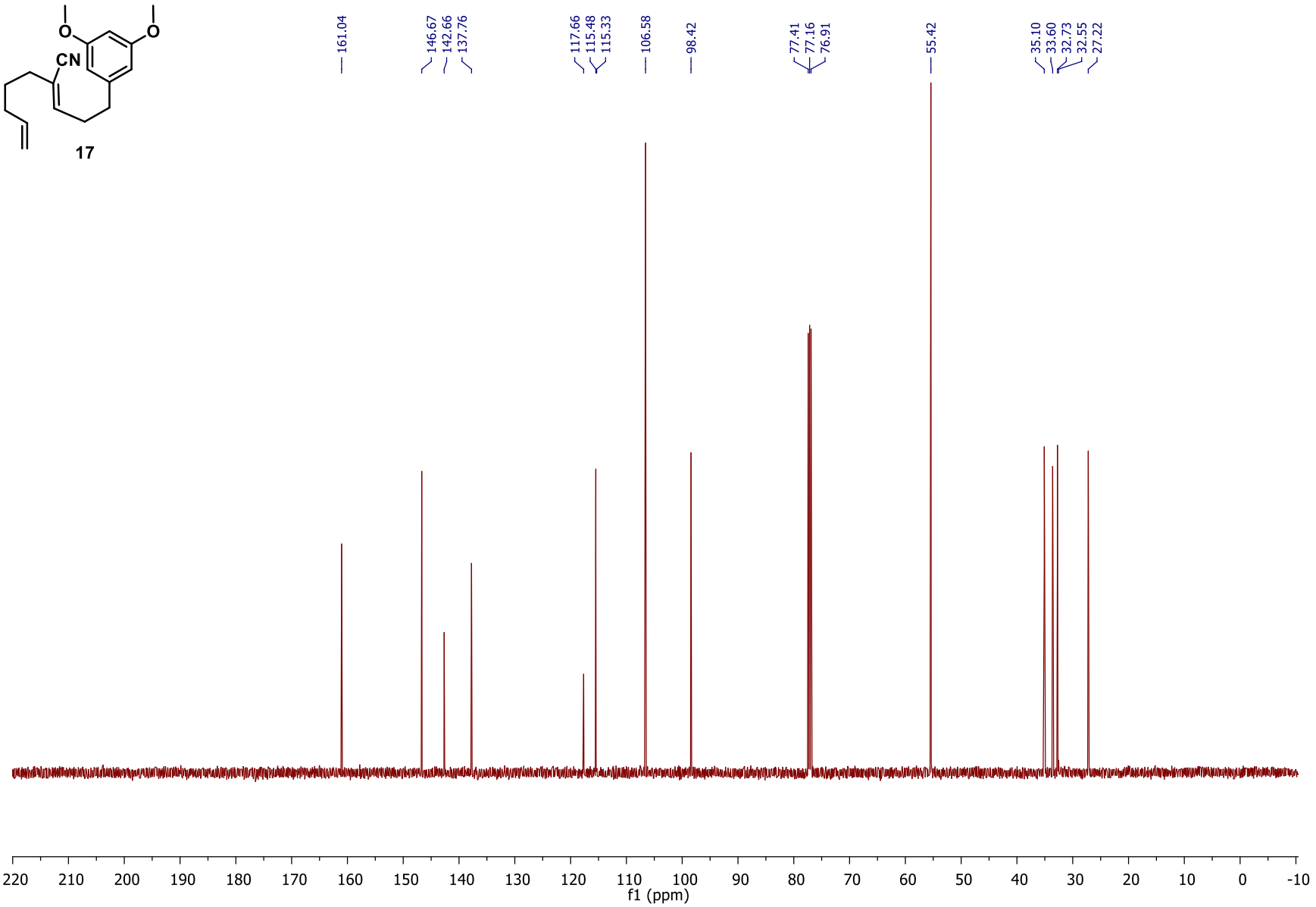
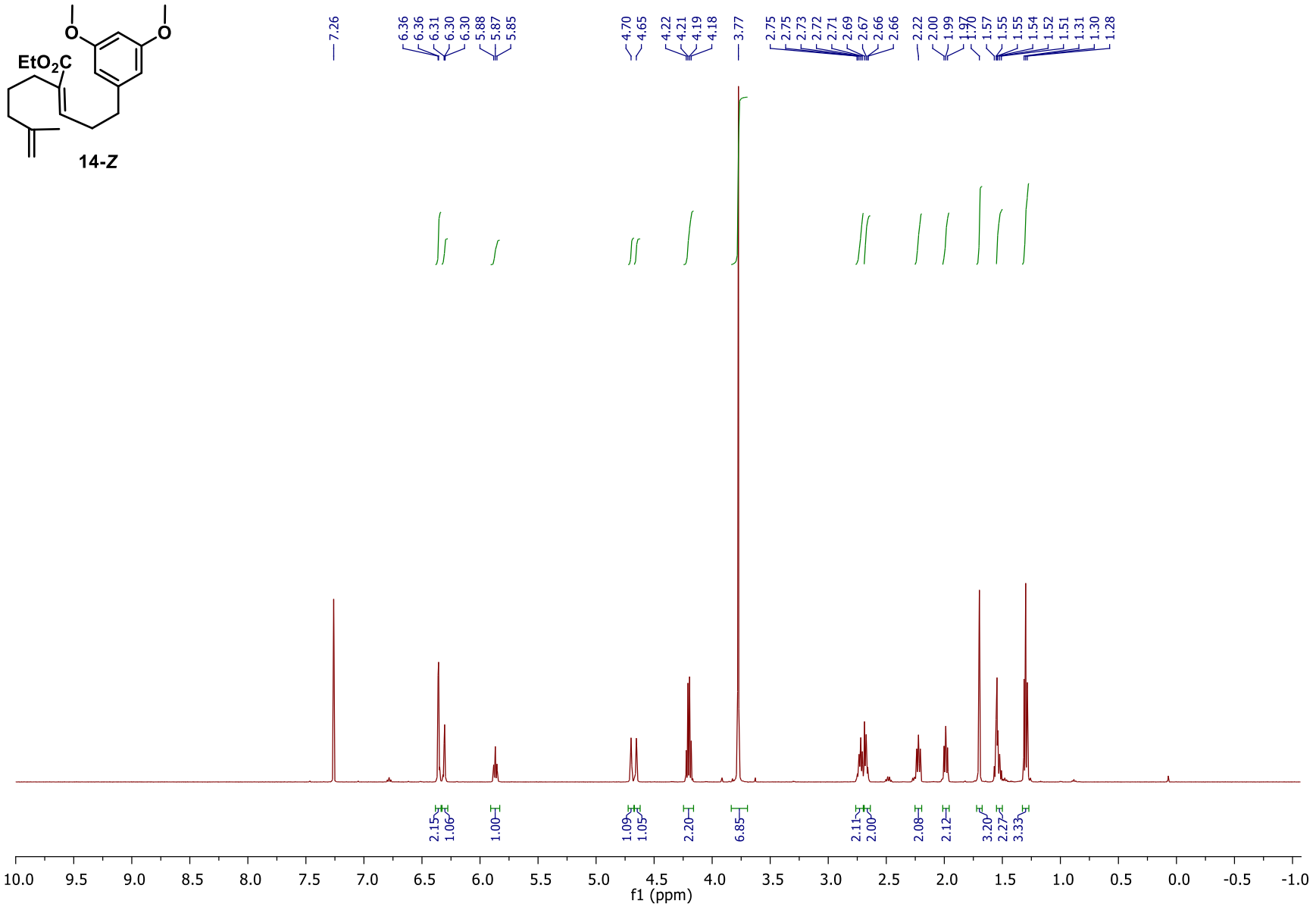
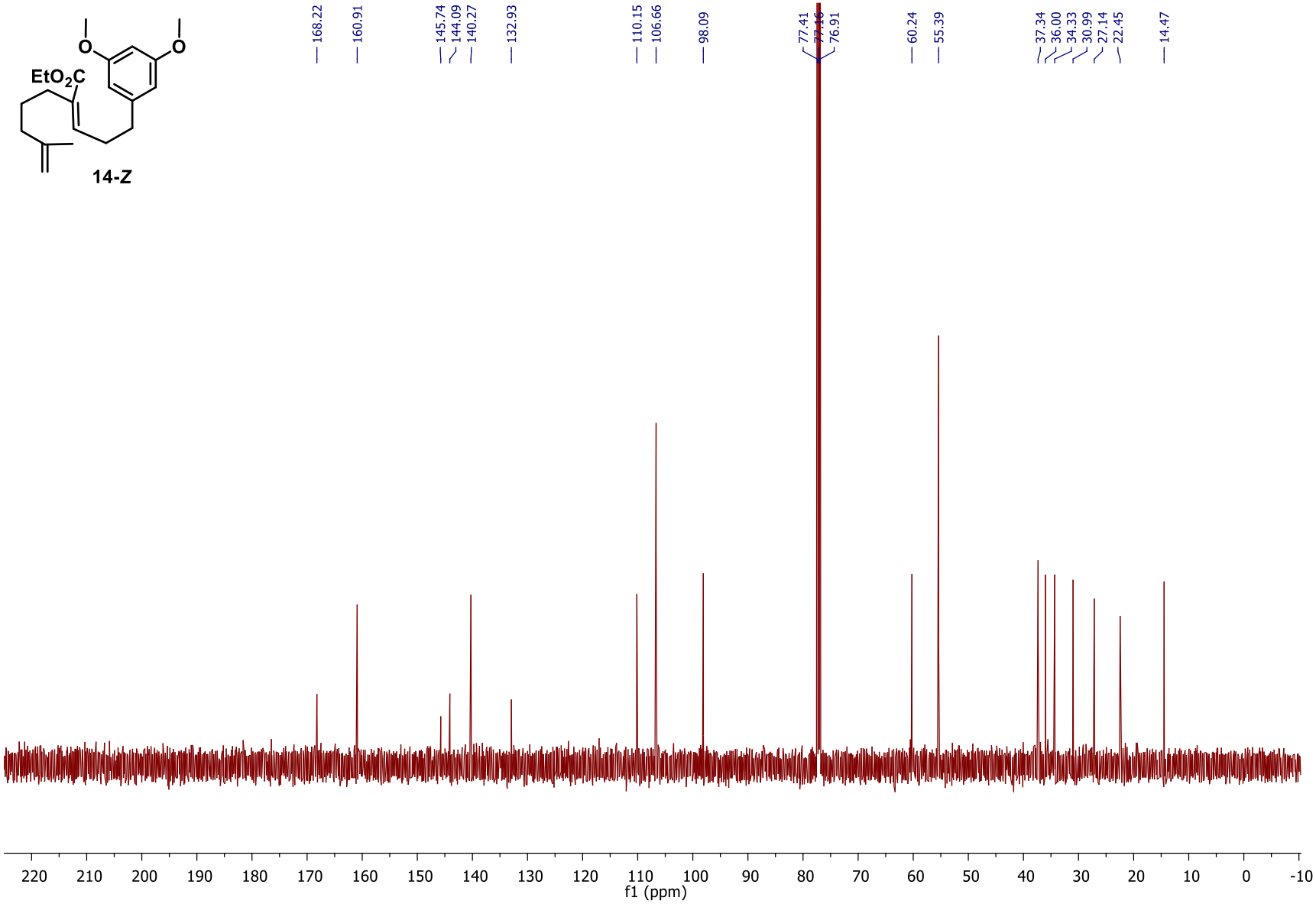
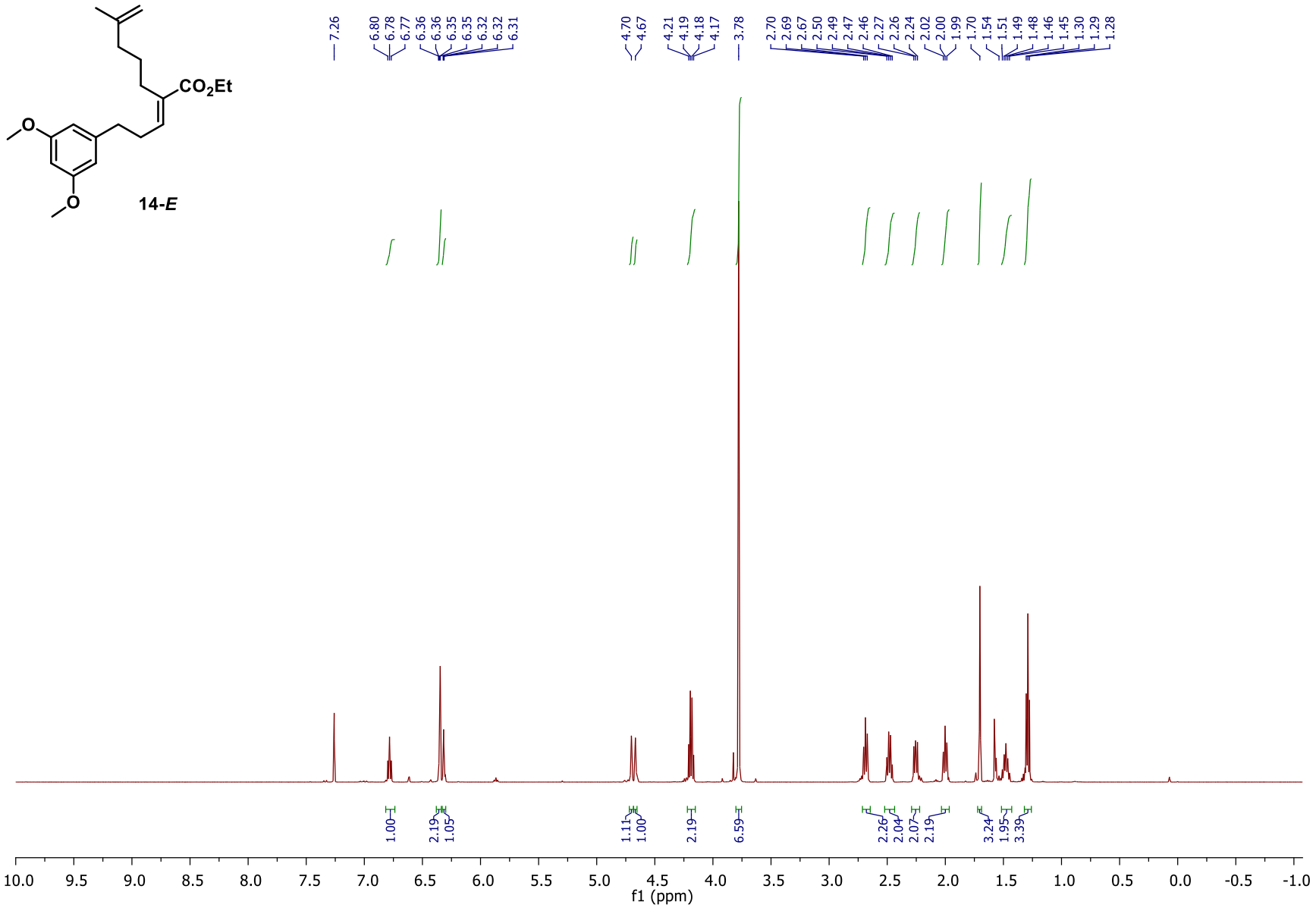
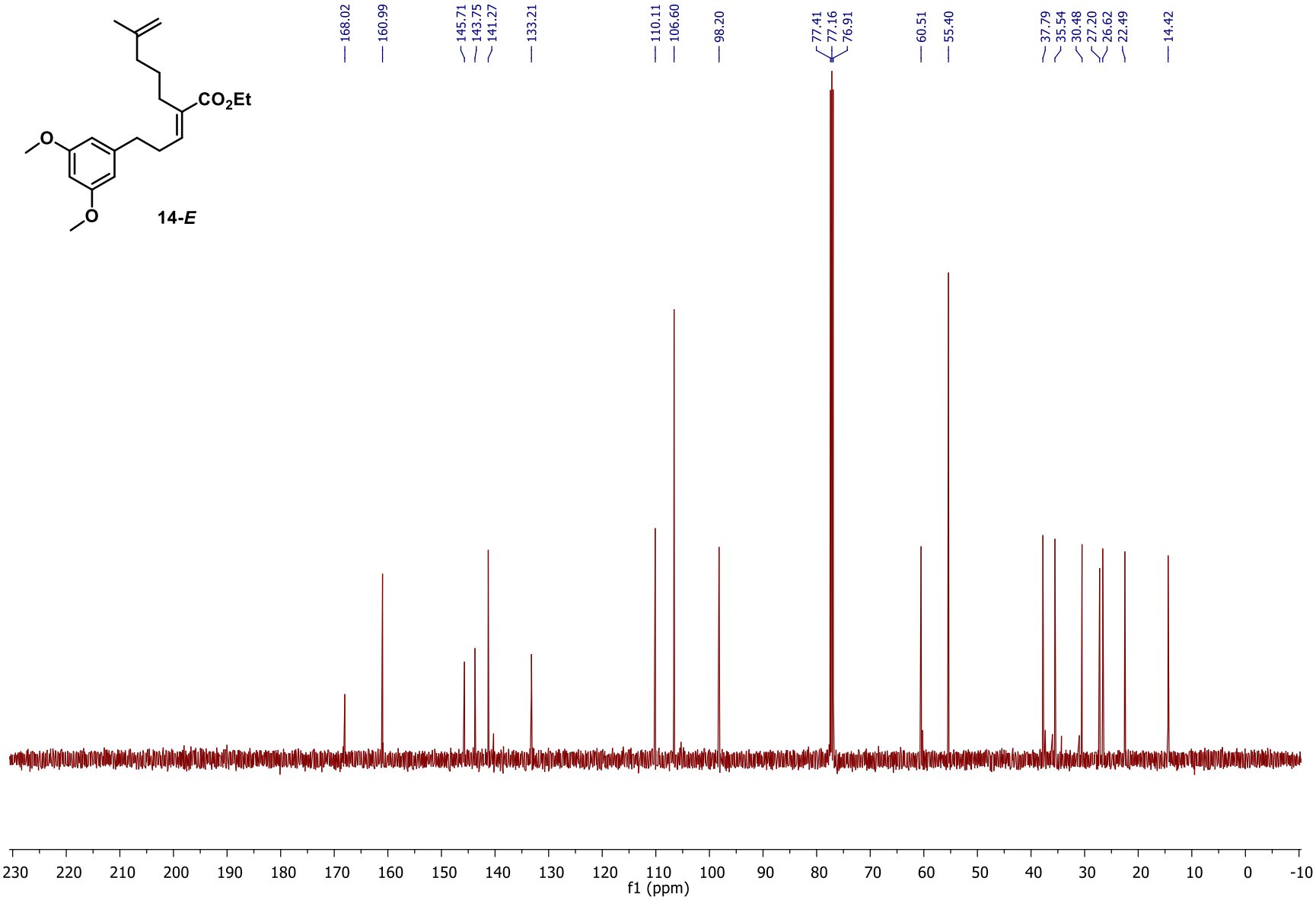
2.65
2.20
2.18
2.17
2.02
2.00
1.62
1.61
1.59
1.58
1.56
2.98
0.99
1.99
6.13
4.03
2.01
1.99
2.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

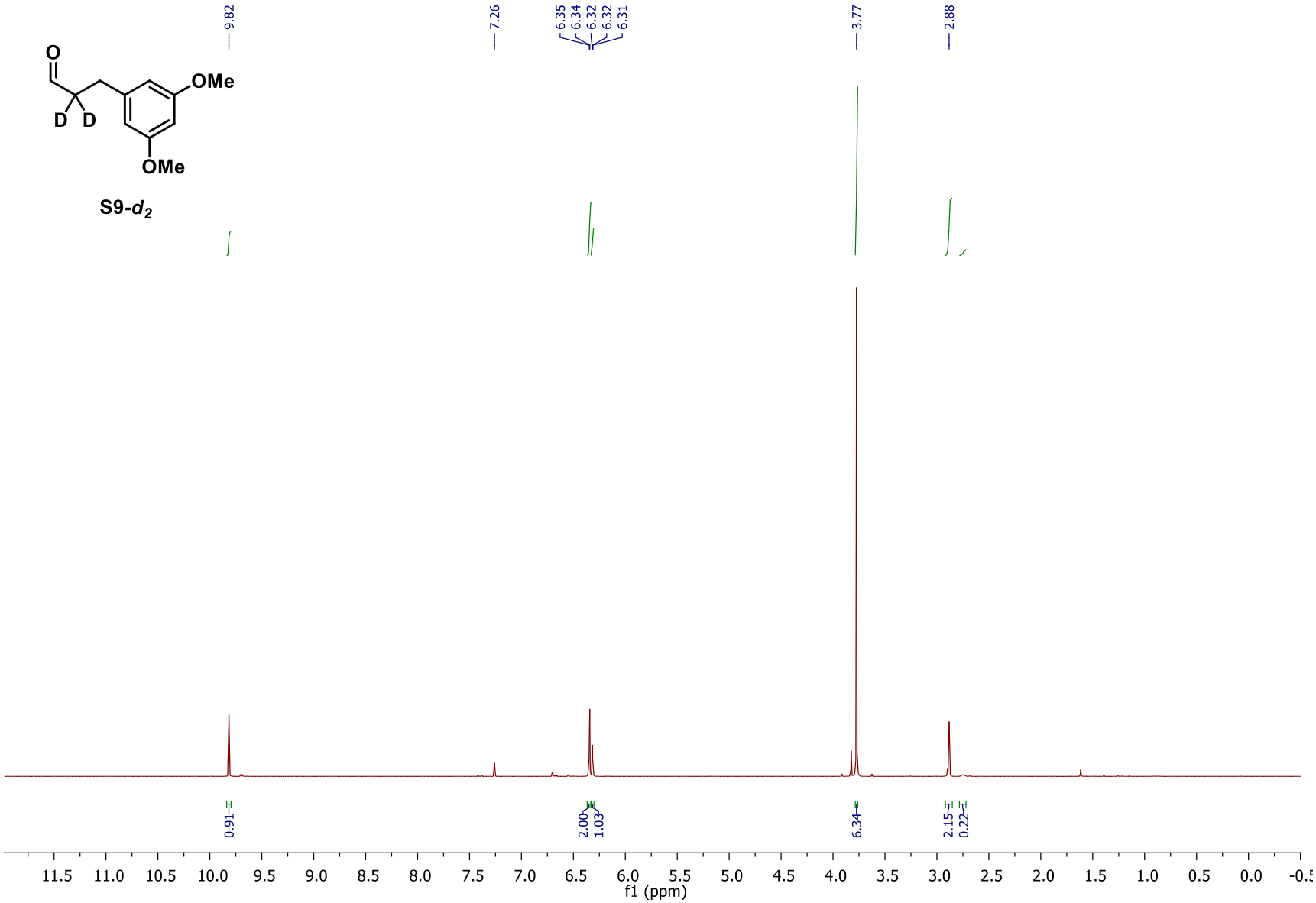

O
CN
O
17
161.04
146.67
142.66
137.76
117.66
115.48
115.33
106.58
98.42
77.41
77.16
76.91
55.42
35.10
33.60
32.73
32.55
27.22
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

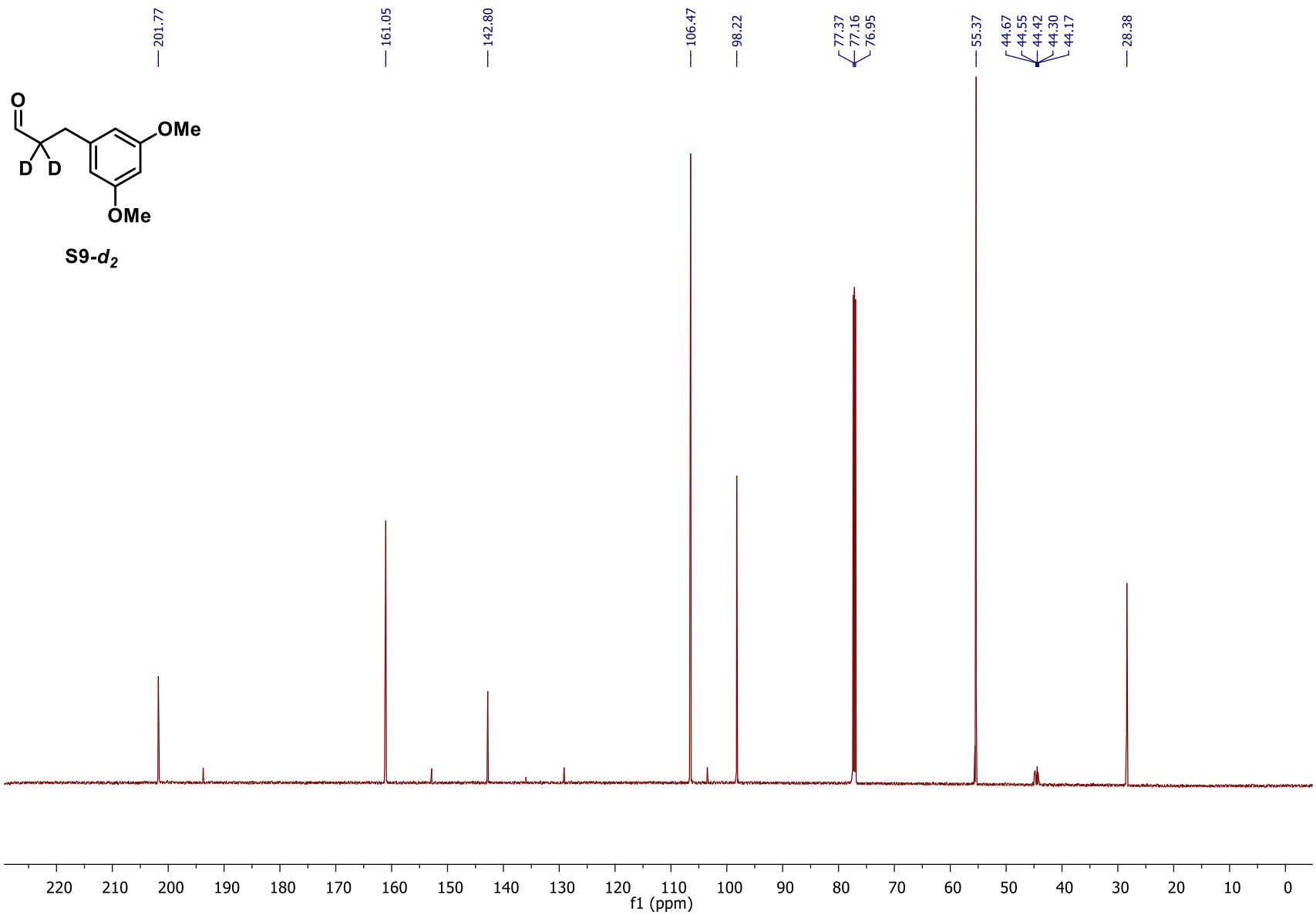

EtO2C
14-Z
7.26
6.36
6.36
6.31
6.30
6.30
5.88
5.87
5.85
4.70
4.65
4.22
4.21
4.19
4.18
3.77
2.75
2.75
2.73
2.72
2.71
2.69
2.67
2.66
2.66
2.22
2.00
1.99
1.97
1.70
1.57
1.55
1.55
1.54
1.52
1.51
1.31
1.30
1.28
2.15
1.06
1.00
1.09
1.05
2.20
6.85
2.11
2.00
2.08
2.12
3.20
2.27
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

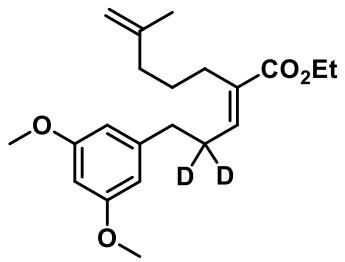

EtO2C
O
O
14-Z
168.22
160.91
145.74
144.09
140.27
132.93
110.15
106.66
98.09
77.41
77.16
76.91
60.24
55.39
37.34
36.00
34.33
30.99
27.14
22.45
14.47
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2Et
O
O
14-E
7.26
6.80
6.78
6.77
6.36
6.36
6.35
6.35
6.32
6.32
6.31
4.70
4.67
4.21
4.19
4.18
4.17
3.78
2.70
2.69
2.67
2.50
2.49
2.47
2.46
2.27
2.26
2.24
2.02
2.00
1.99
1.70
1.54
1.51
1.49
1.48
1.46
1.45
1.30
1.29
1.28
1.00
2.19
1.05
1.11
1.00
2.19
6.59
2.26
2.04
2.07
2.19
3.24
1.95
3.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


168.02
160.99
145.71
143.75
141.27
133.21
110.11
106.60
98.20
77.41
77.16
76.91
60.51
55.40
37.79
35.54
30.48
27.20
26.62
22.49
14.42
CO2Et
O
O
14-E
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

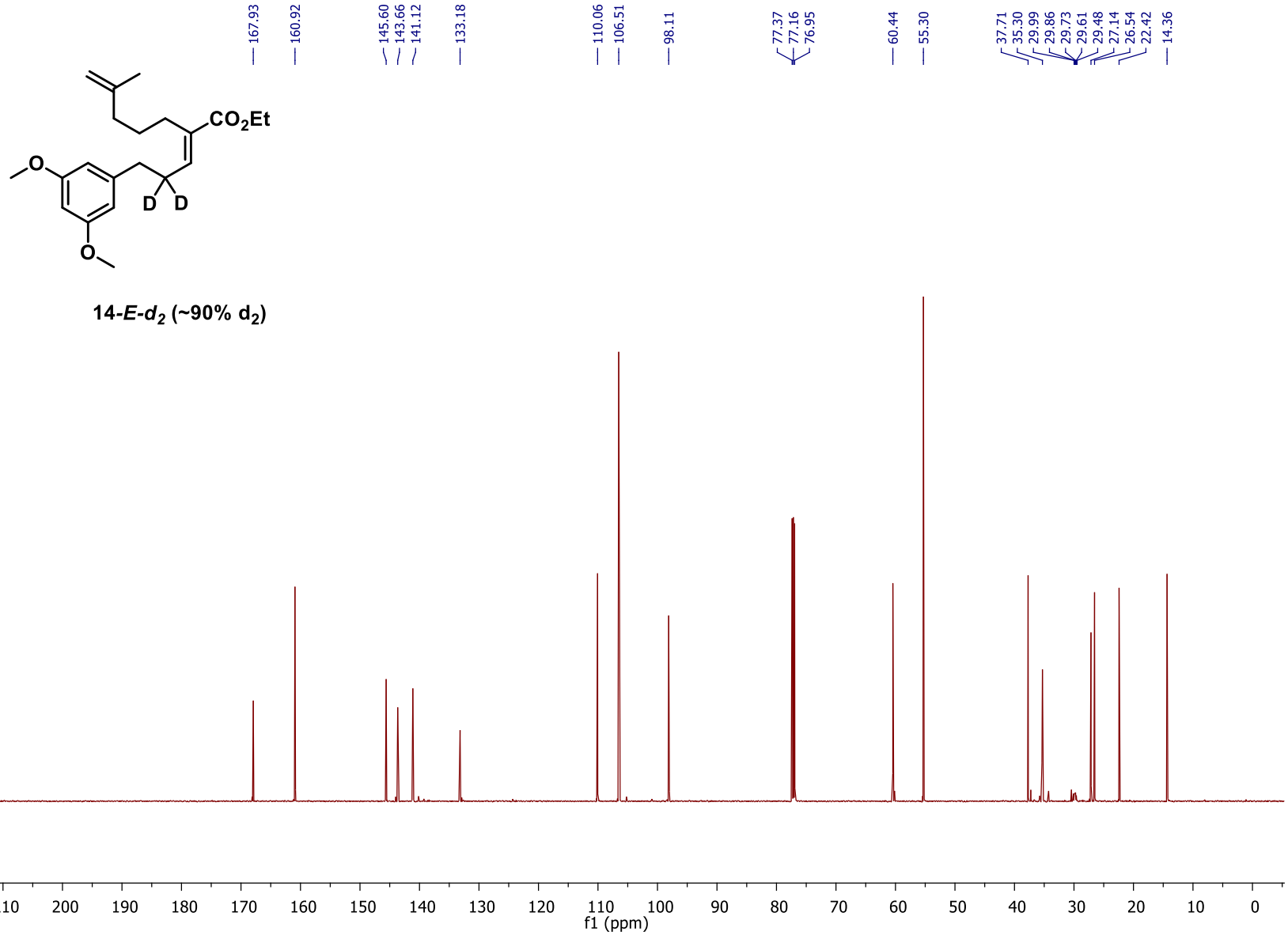

O
D D
OMe
OMe
S9-d_2
9.82
7.26
6.35
6.34
6.32
6.32
6.31
3.77
2.88
0.91
2.00
1.03
6.34
2.15
0.22
f1 (ppm)

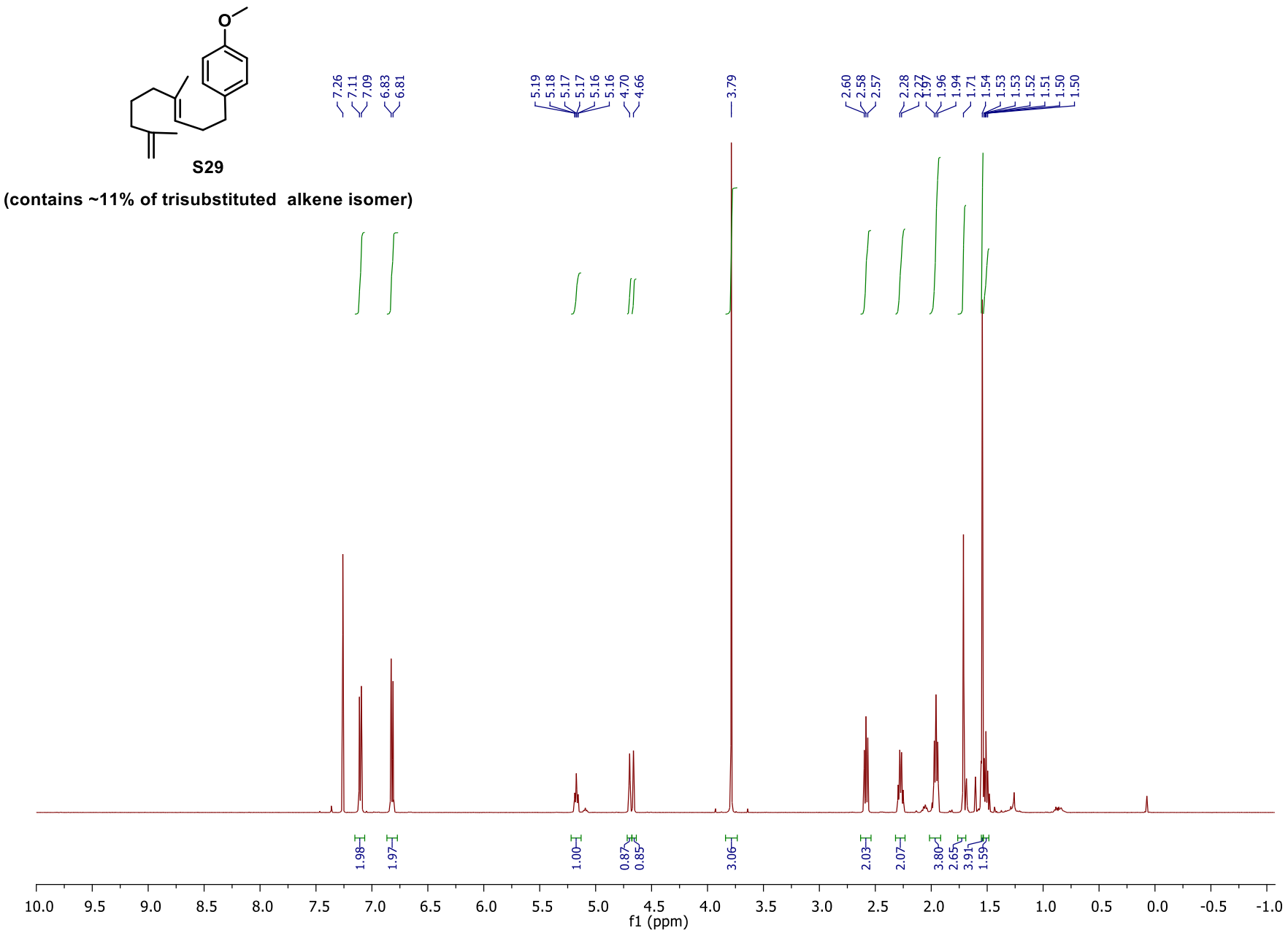

201.77
161.05
142.80
106.47
98.22
77.37
77.16
76.95
55.37
44.67
44.55
44.42
44.30
44.17
28.38
O
D D
OMe
OMe
S9-d_2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

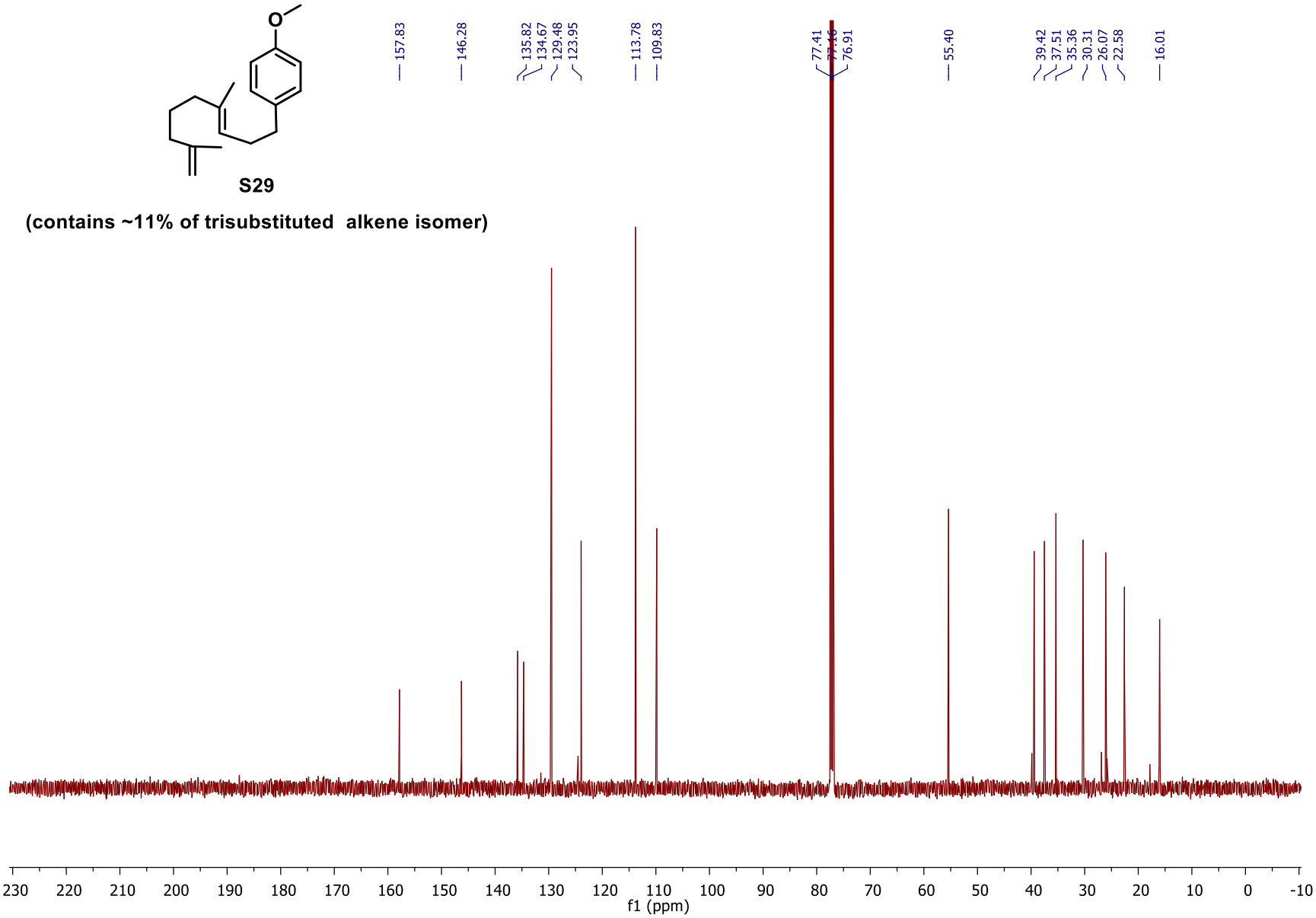

CO2Et
O
D
D
O

14-*E*-d_2 (~90% d_2)

7.26
6.78
6.35
6.32
4.70
4.67
4.20
4.19
4.18
4.17
3.77
2.67
2.27
2.26
2.24
2.02
2.00
1.99
1.70
1.50
1.49
1.48
1.47
1.30
1.29
1.28
1.00
2.06
0.97
1.08
1.05
2.11
6.62
2.24
0.34
2.20
2.16
3.29
2.12
3.37
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

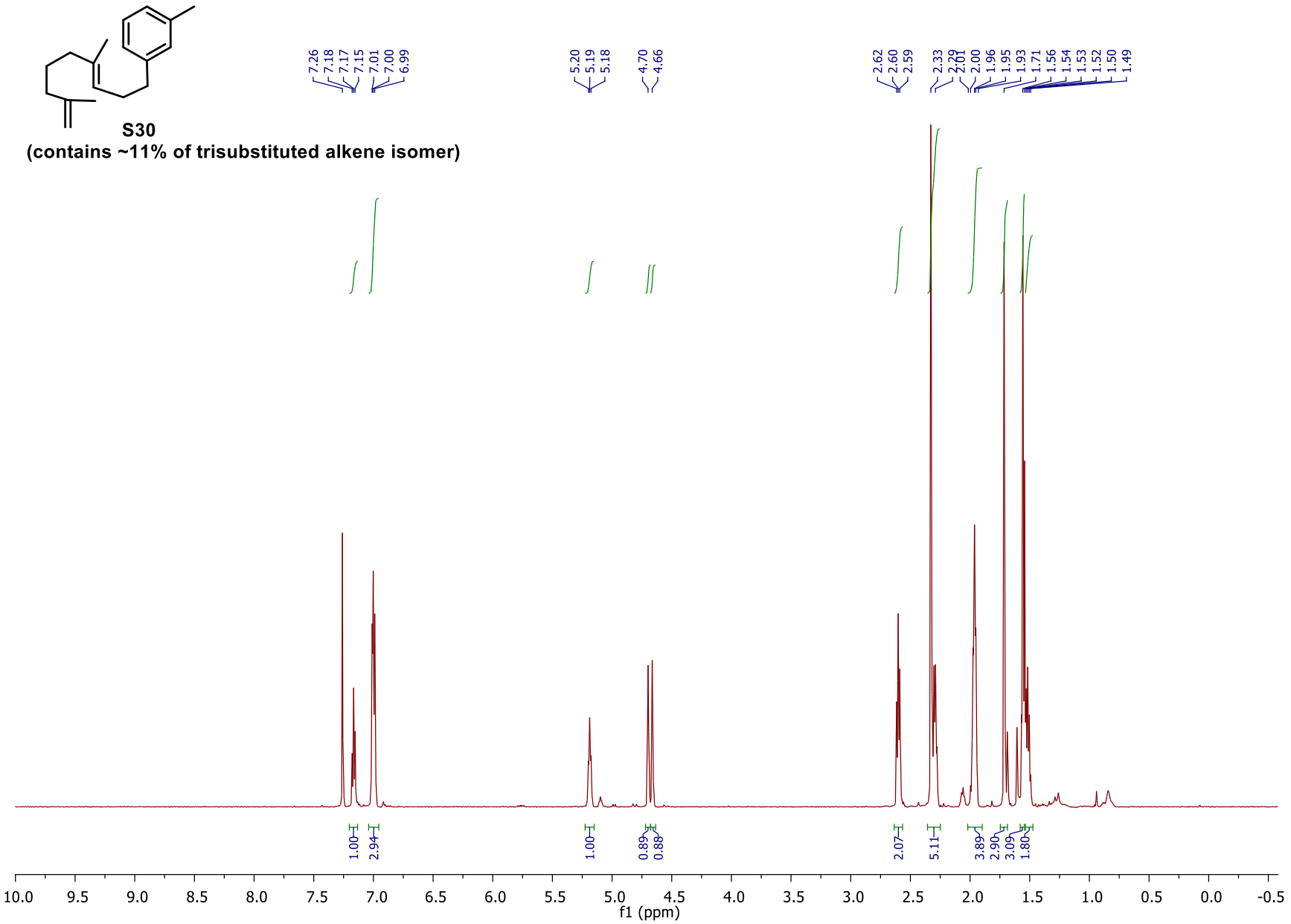

167.93
160.92
145.60
143.66
141.12
133.18
110.06
106.51
98.11
77.37
77.16
76.95
60.44
55.30
37.71
35.30
29.99
29.86
29.73
29.61
29.48
27.14
26.54
22.42
14.36
CO2Et
O
O
D
D
14-E-d2 (~90% d2)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

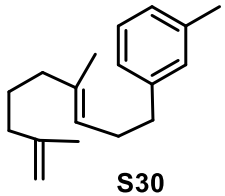

S29
(contains ~11% of trisubstituted alkene isomer)
7.26
7.11
7.09
6.83
6.81
5.19
5.18
5.17
5.17
5.16
5.16
4.70
4.66
3.79
2.60
2.58
2.57
2.28
2.27
2.27
1.97
1.96
1.94
1.71
1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.98
1.97
1.00
0.87
0.85
3.06
2.03
2.07
3.80
2.65
3.91
1.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



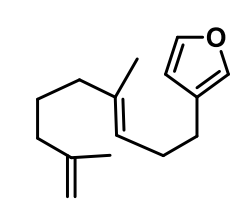
S29

(contains ~11% of trisubstituted alkene isomer)

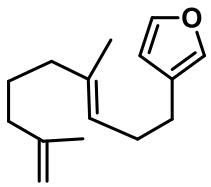

S30
(contains ~11% of trisubstituted alkene isomer)
7.26
7.18
7.17
7.15
7.01
7.00
6.99
5.20
5.19
5.18
4.70
4.66
2.62
2.60
2.59
2.33
2.29
2.01
2.00
1.96
1.95
1.93
1.71
1.56
1.54
1.53
1.52
1.50
1.49
1.00
2.94
1.00
0.89
0.88
2.07
5.11
3.89
2.90
3.09
1.80
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



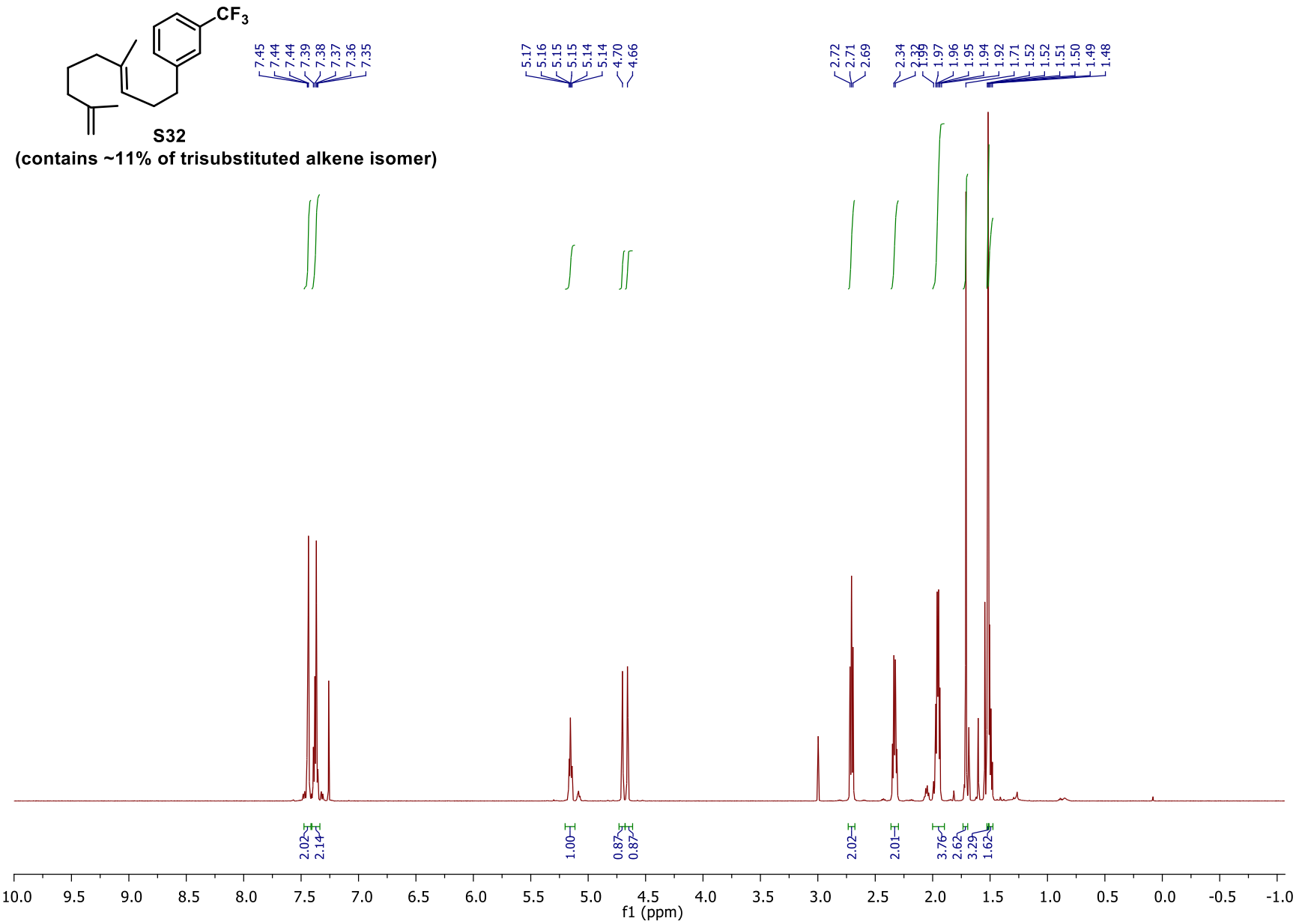
S30
(contains ~11% of trisubstituted alkene isomer)



S31
(contains ~11% of trisubstituted alkene isomer)

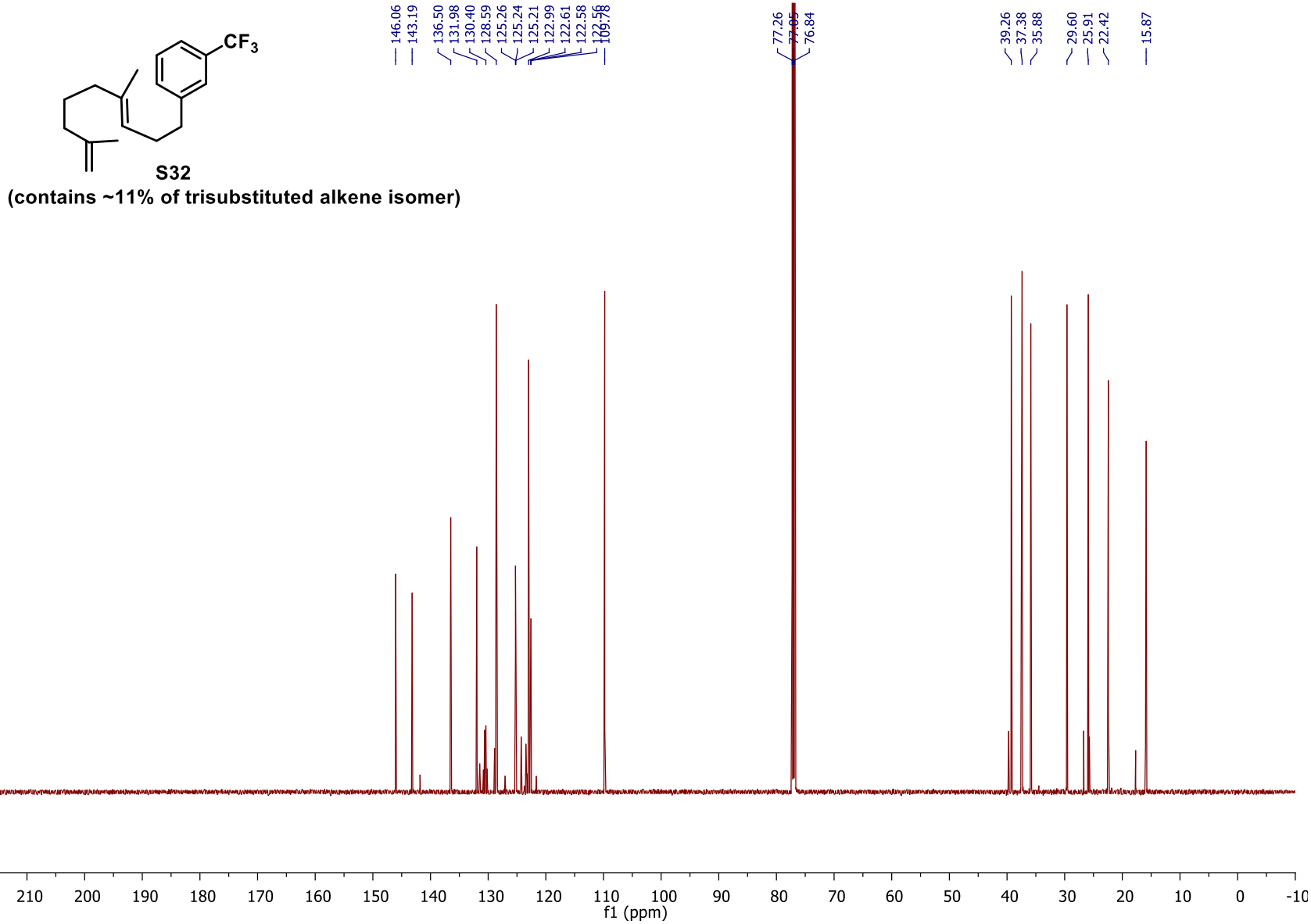


S31
(contains ~11% of trisubstituted alkene isomer)



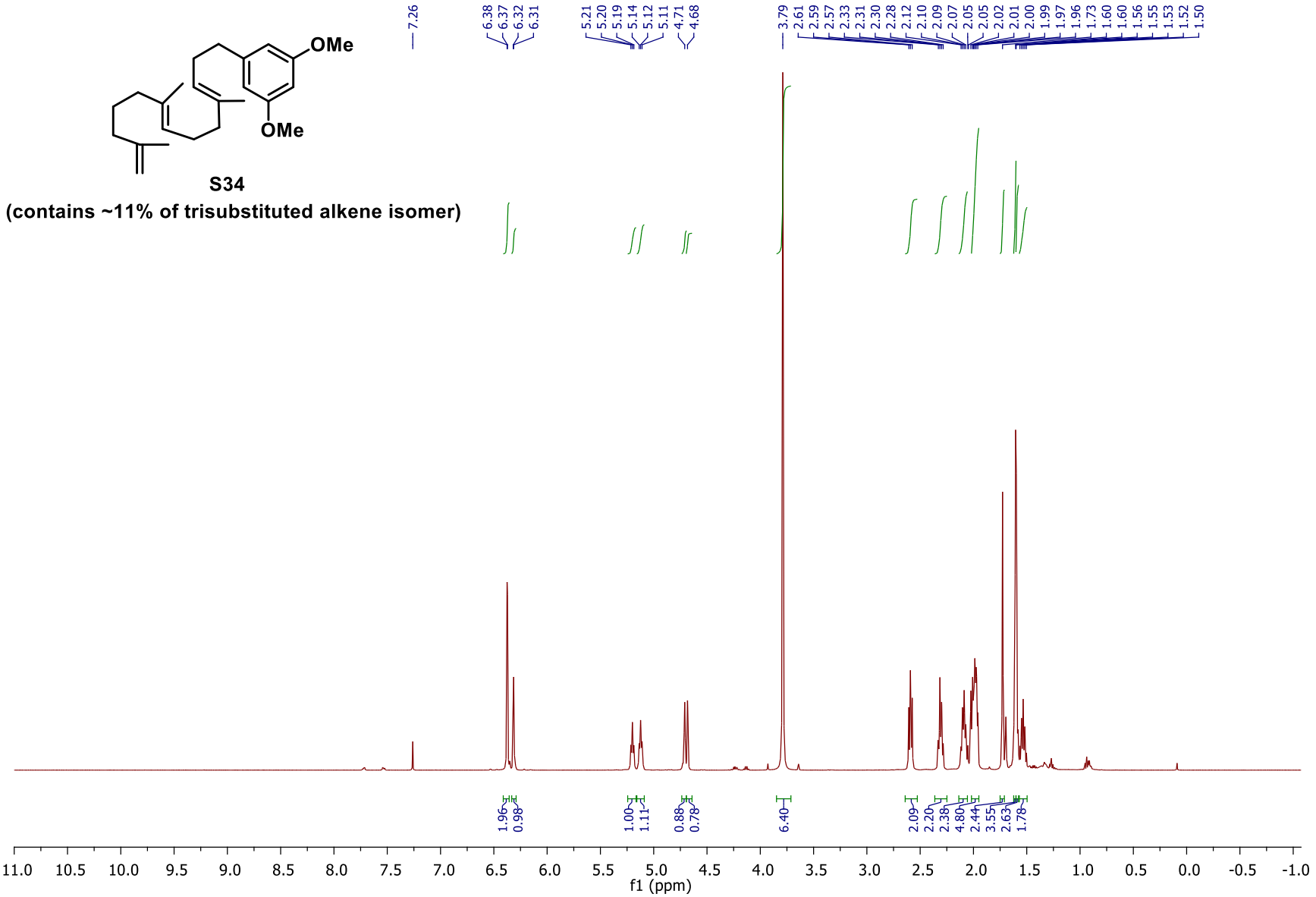
S32

(contains ~11% of trisubstituted alkene isomer)



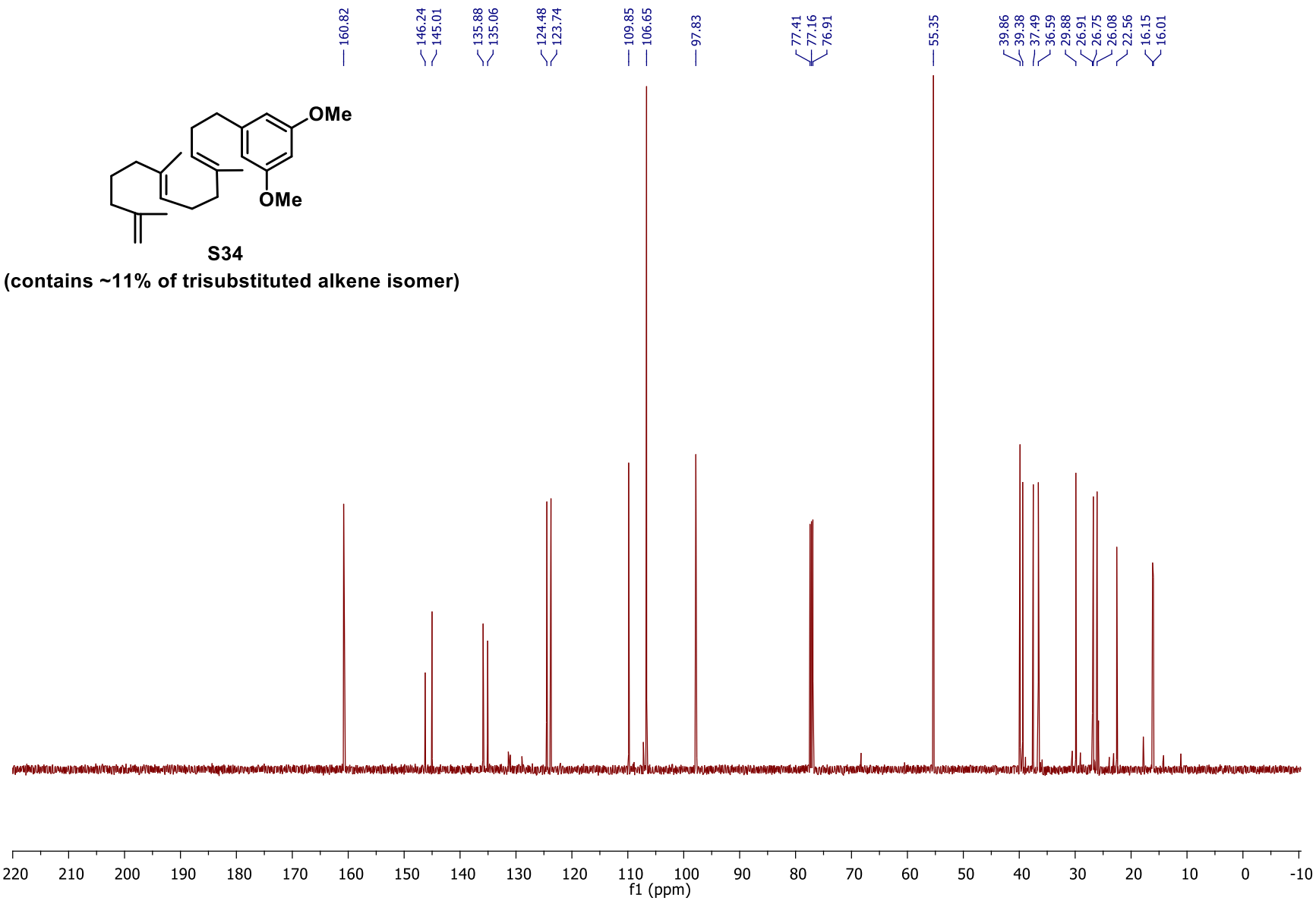
S32

(contains ~11% of trisubstituted alkene isomer)



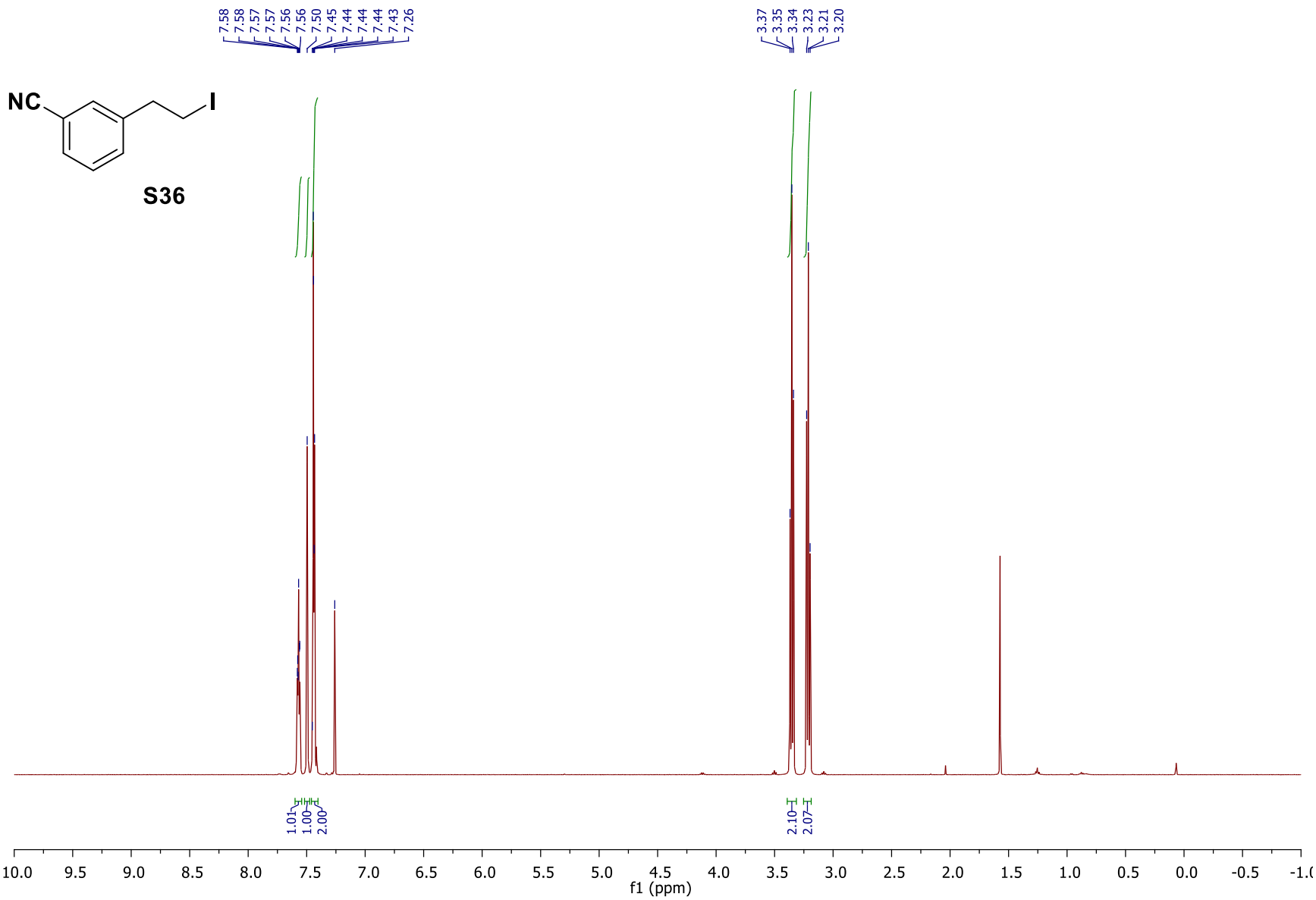
S34

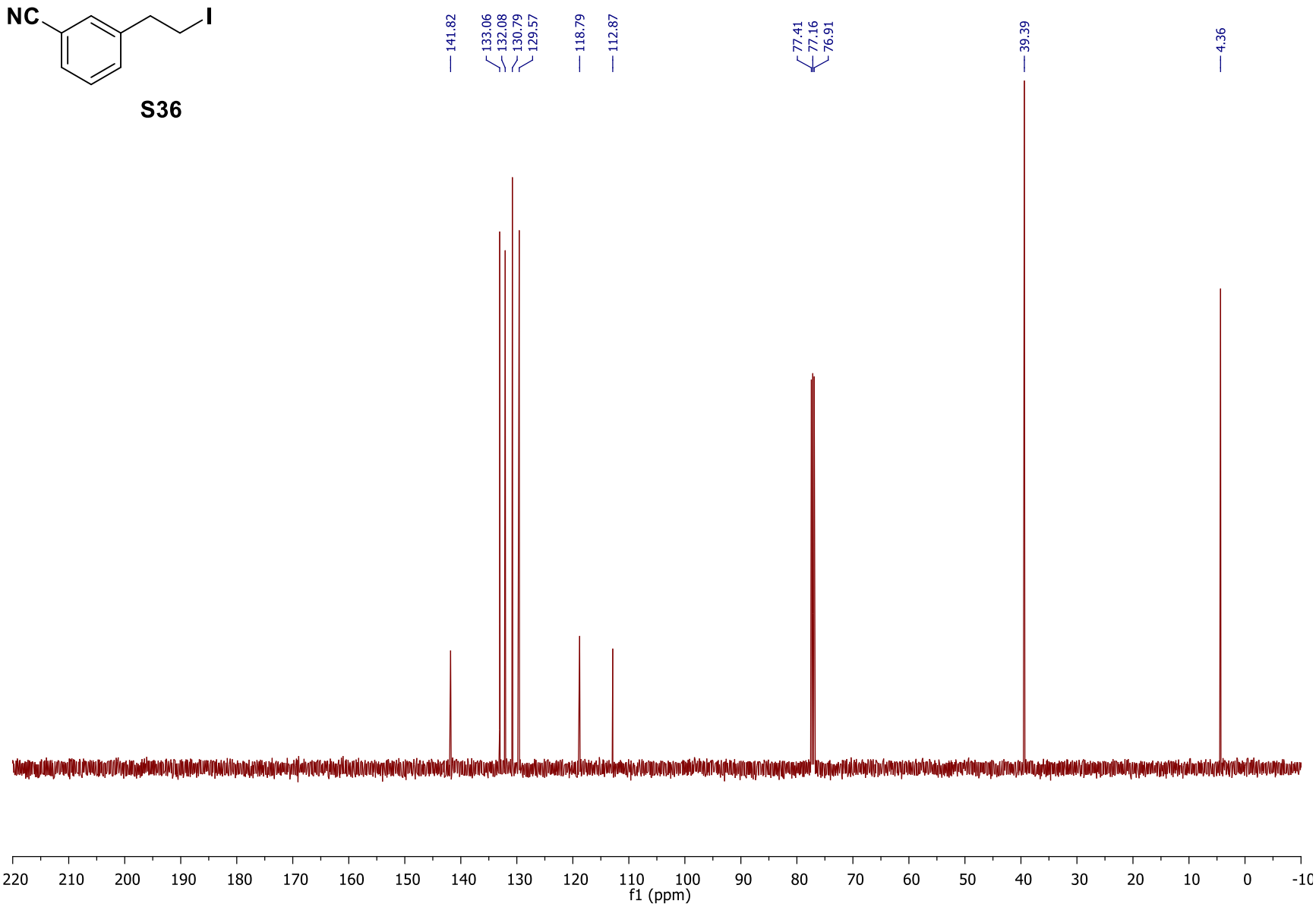
(contains ~11% of trisubstituted alkene isomer)

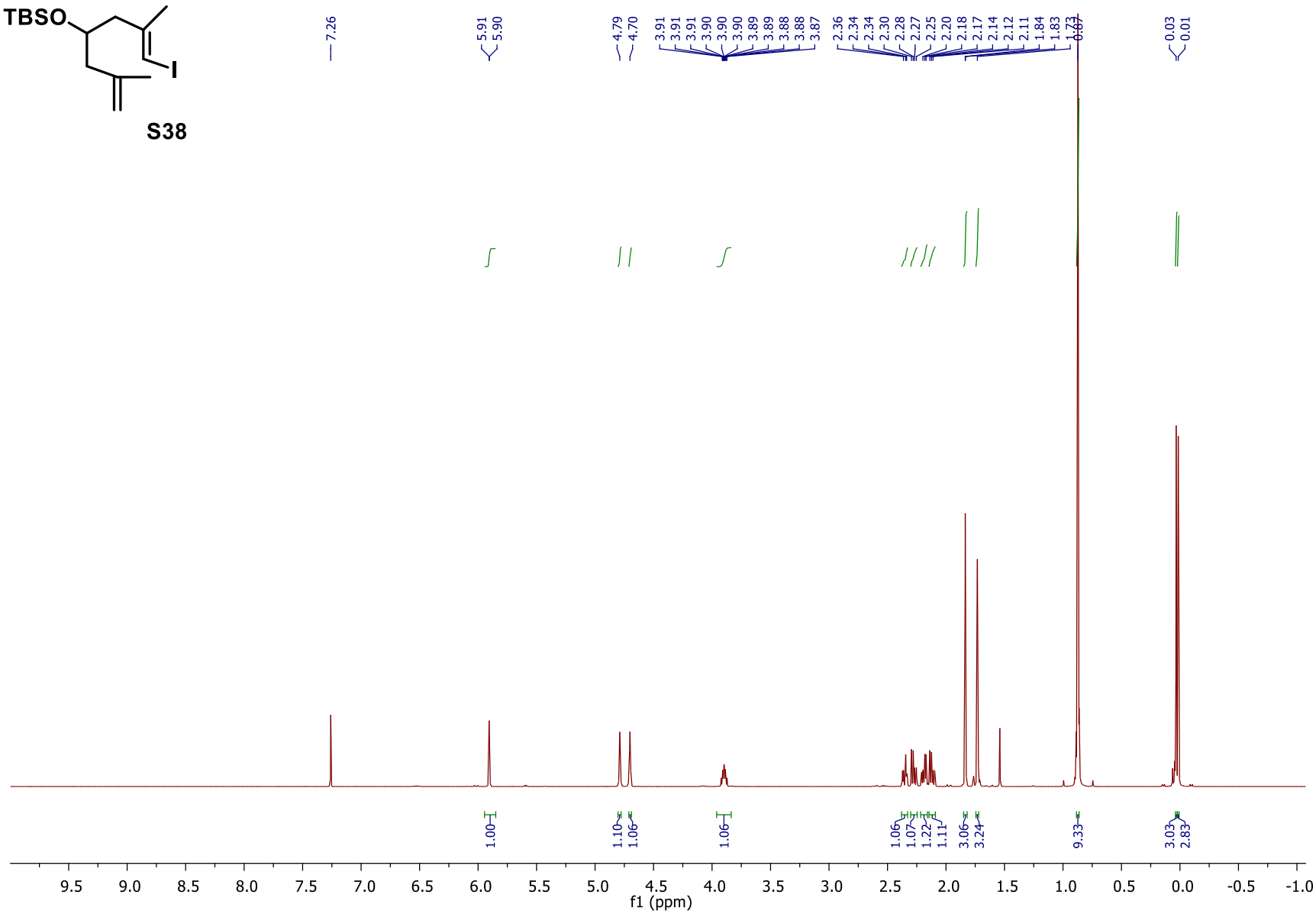


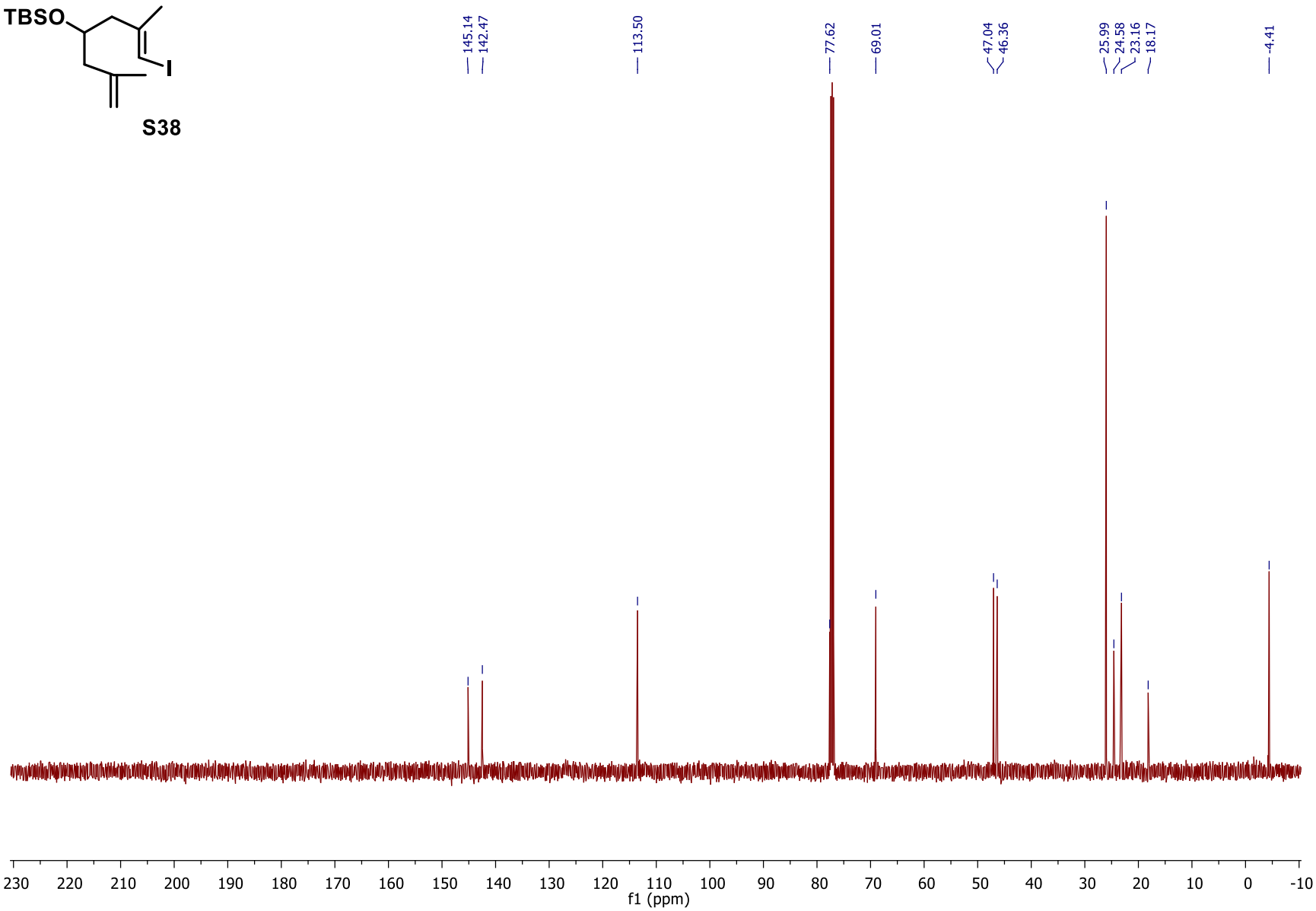
S34

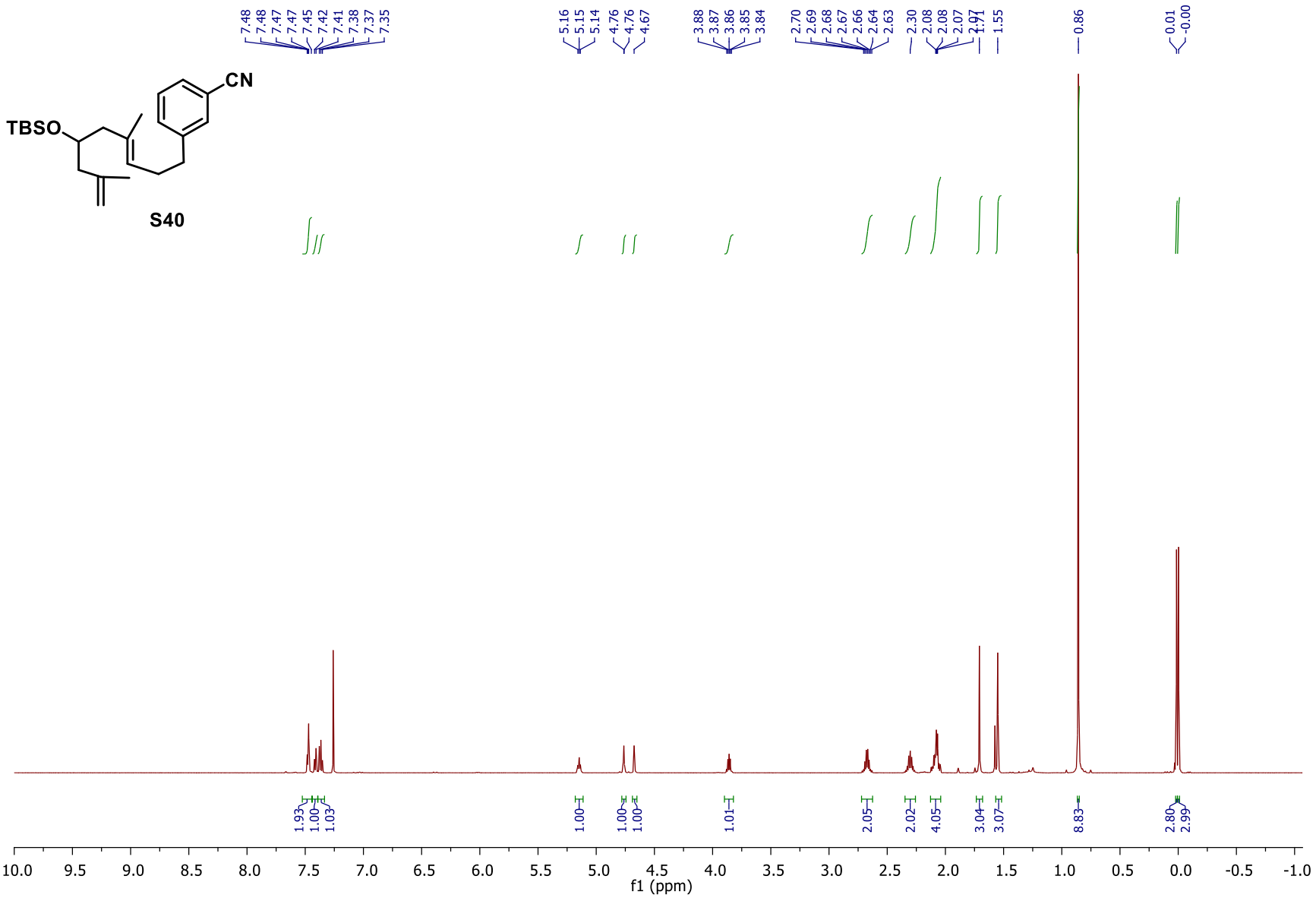
(contains ~11% of trisubstituted alkene isomer)

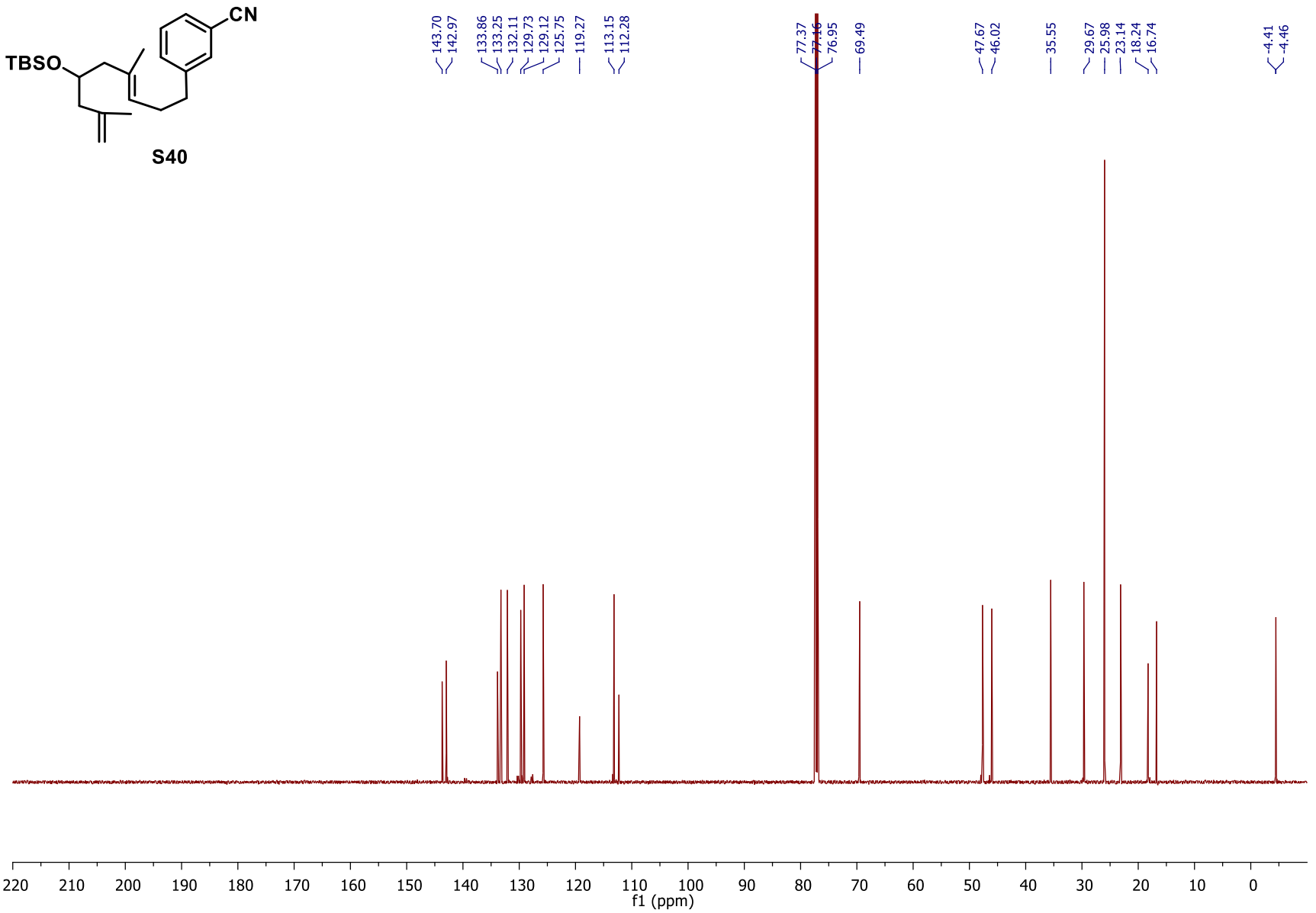

7.58
7.58
7.57
7.57
7.56
7.56
7.50
7.45
7.44
7.44
7.44
7.43
7.26
3.37
3.35
3.34
3.23
3.21
3.20
NC
I
S36
1.01
1.00
2.00
2.10
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

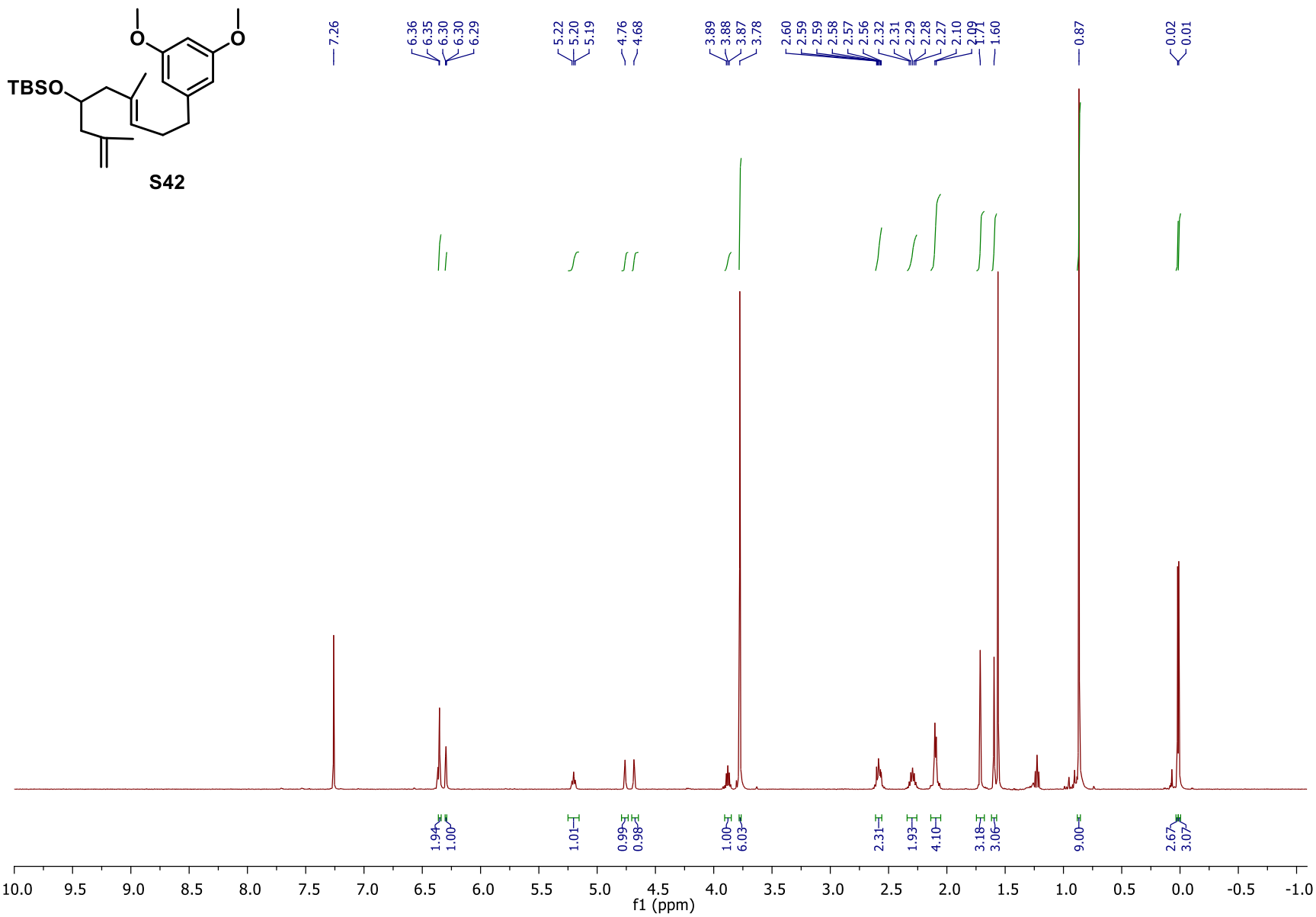

NC
I
S36
141.82
133.06
132.08
130.79
129.57
118.79
112.87
77.41
77.16
76.91
39.39
4.36
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

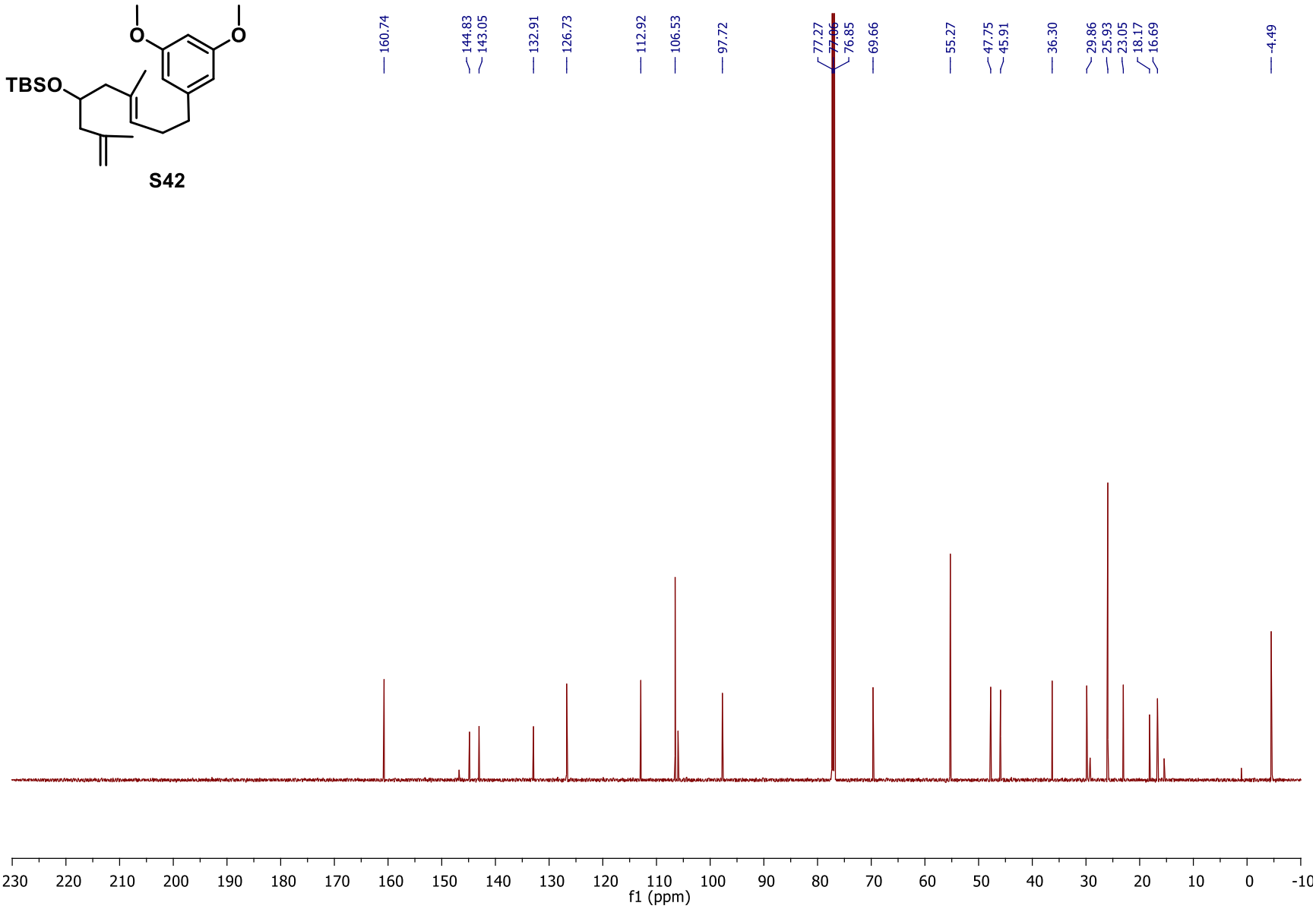

TBSO
I
S38
7.26
5.91
5.90
4.79
4.70
3.91
3.91
3.91
3.90
3.90
3.90
3.89
3.89
3.88
3.88
3.87
2.36
2.34
2.34
2.30
2.28
2.27
2.25
2.20
2.18
2.17
2.14
2.12
2.11
1.84
1.83
1.73
0.87
0.03
0.01
1.00
1.10
1.06
1.06
1.06
1.07
1.22
1.11
3.06
3.24
9.33
3.03
2.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

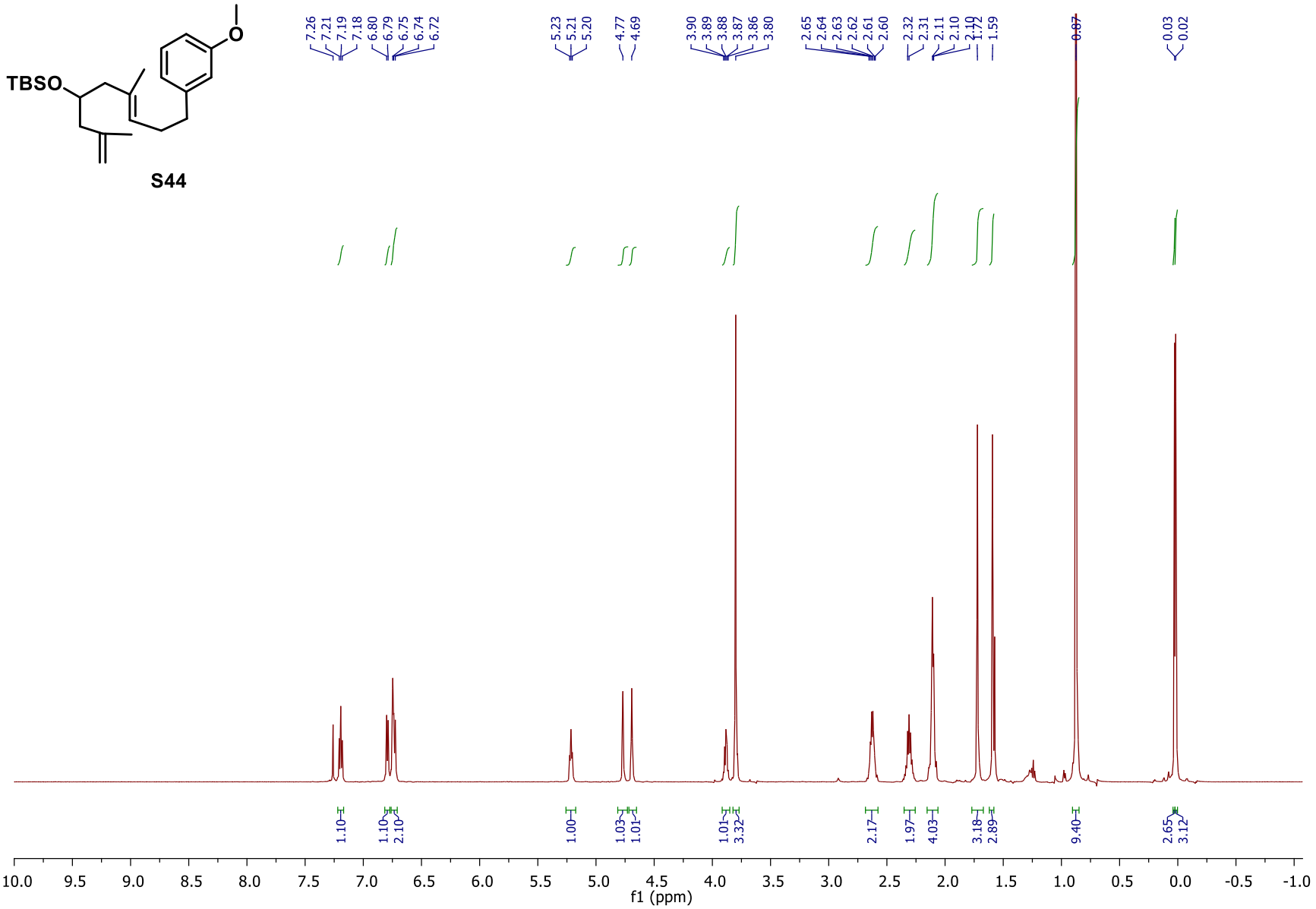

TBSO
I
S38
145.14
142.47
113.50
77.62
69.01
47.04
46.36
25.99
24.58
23.16
18.17
-4.41
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

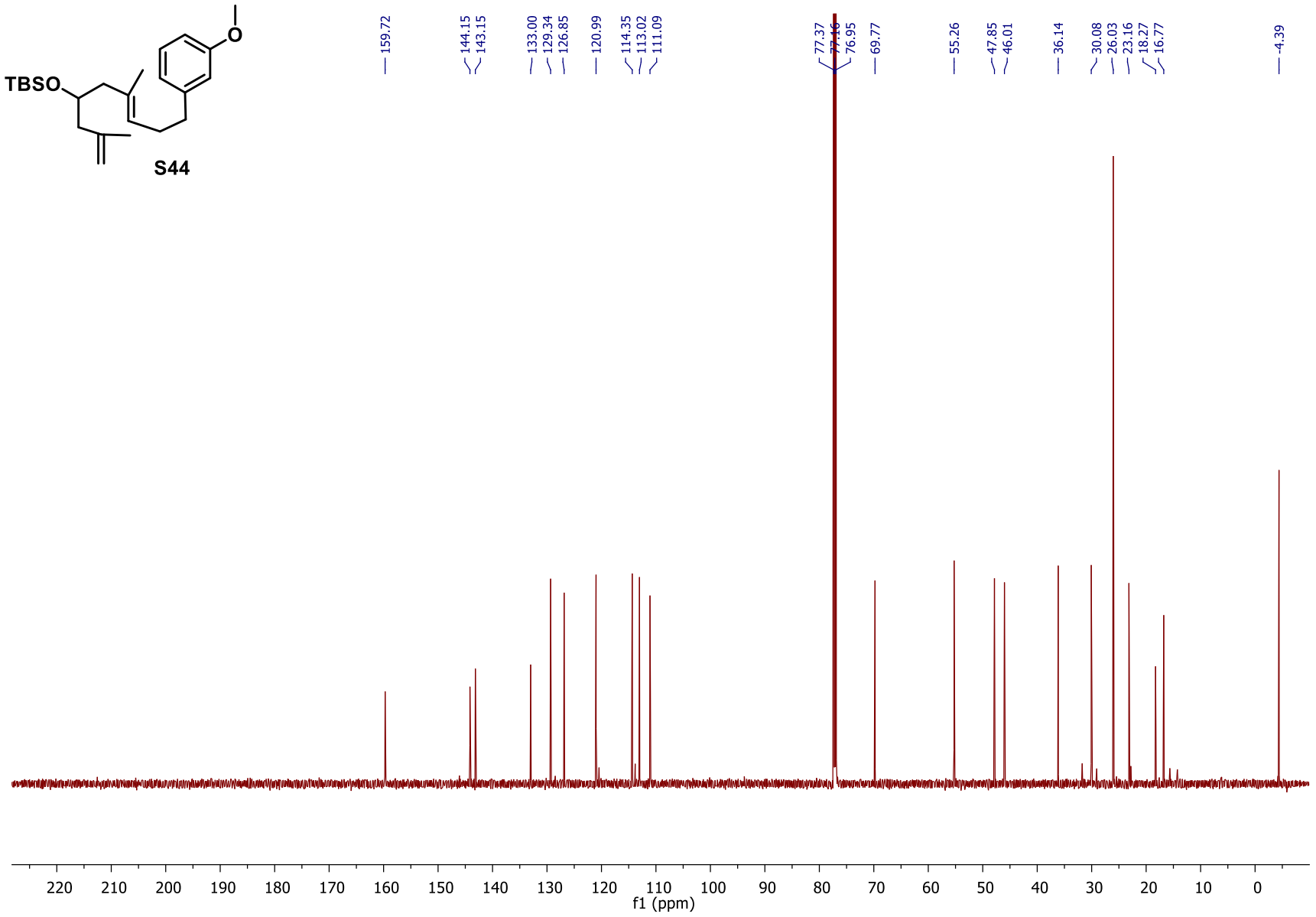

CN
TBSO
S40
7.48
7.48
7.47
7.47
7.45
7.42
7.41
7.38
7.37
7.35
5.16
5.15
5.14
4.76
4.76
4.67
3.88
3.87
3.86
3.85
3.84
2.70
2.69
2.68
2.67
2.66
2.64
2.63
2.30
2.08
2.08
2.07
1.91
1.55
0.86
0.01
-0.00
1.93
1.00
1.03
1.00
1.00
1.00
1.01
2.05
2.02
4.05
3.04
3.07
8.83
2.80
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

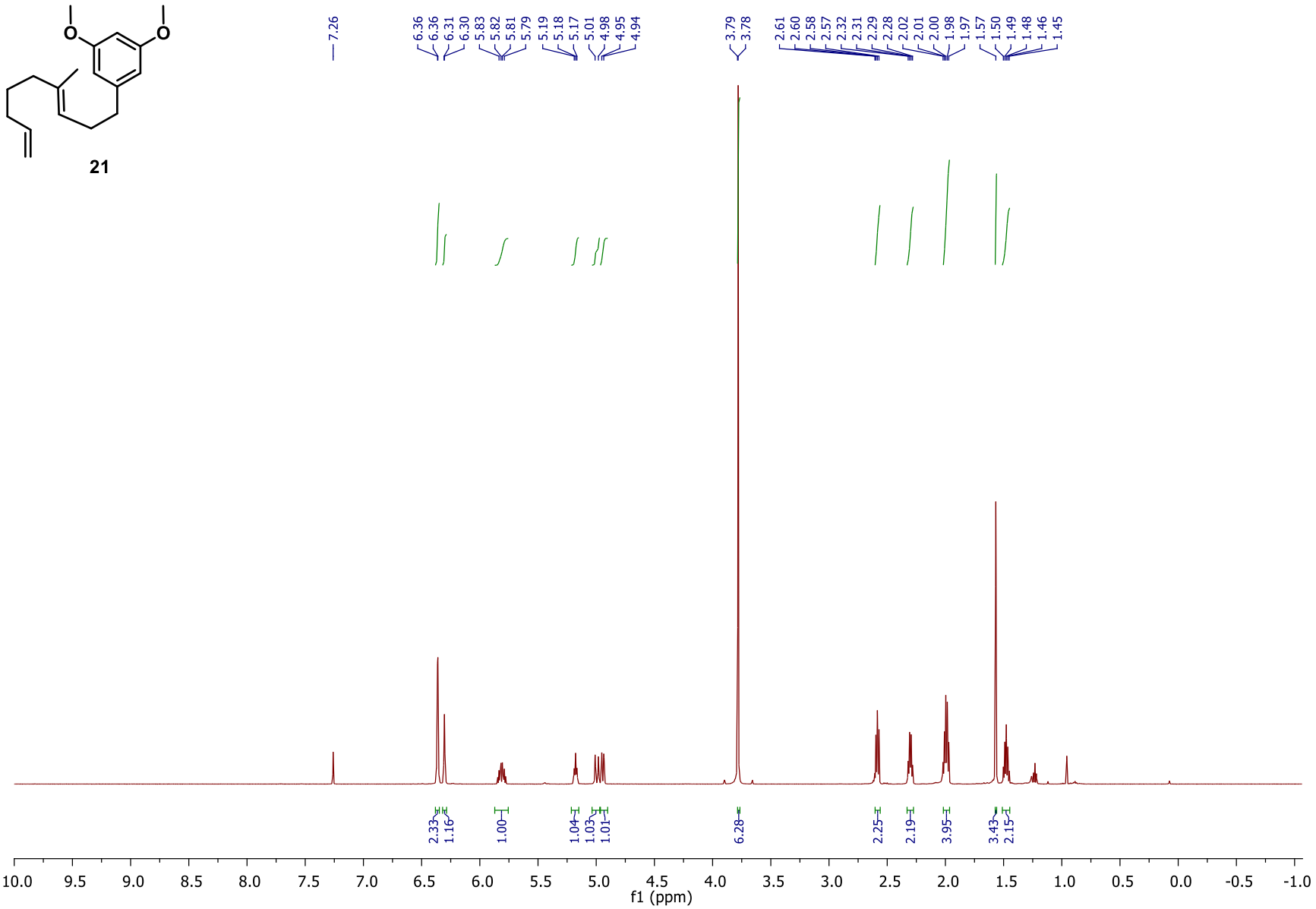

CN
TBSO
S40
143.70
142.97
133.86
133.25
132.11
129.73
129.12
125.75
119.27
113.15
112.28
77.37
77.16
76.95
69.49
47.67
46.02
35.55
29.67
25.98
23.14
18.24
16.74
-4.41
-4.46
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

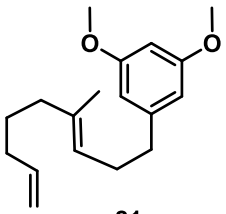

TBSO
O
O
S42
7.26
6.36
6.35
6.30
6.30
6.29
5.22
5.20
5.19
4.76
4.68
3.89
3.88
3.87
3.78
2.60
2.59
2.59
2.58
2.57
2.56
2.32
2.31
2.29
2.28
2.27
2.10
2.09
1.71
1.60
0.87
0.02
0.01
1.94
1.00
1.01
0.99
0.98
1.00
6.03
2.31
1.93
4.10
3.18
3.06
9.00
2.67
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


TBSO
O
O
S42
160.74
144.83
143.05
132.91
126.73
112.92
106.53
97.72
77.27
77.06
76.85
69.66
55.27
47.75
45.91
36.30
29.86
25.93
23.05
18.17
16.69
-4.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


TBSO
O
S44
7.26
7.21
7.19
7.18
6.80
6.79
6.75
6.74
6.72
5.23
5.21
5.20
4.77
4.69
3.90
3.89
3.88
3.87
3.86
3.80
2.65
2.64
2.63
2.62
2.61
2.60
2.32
2.31
2.11
2.10
1.72
1.59
0.87
0.03
0.02
1.10
1.10
2.10
1.00
1.03
1.01
1.01
3.32
2.17
1.97
4.03
3.18
2.89
9.40
2.65
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

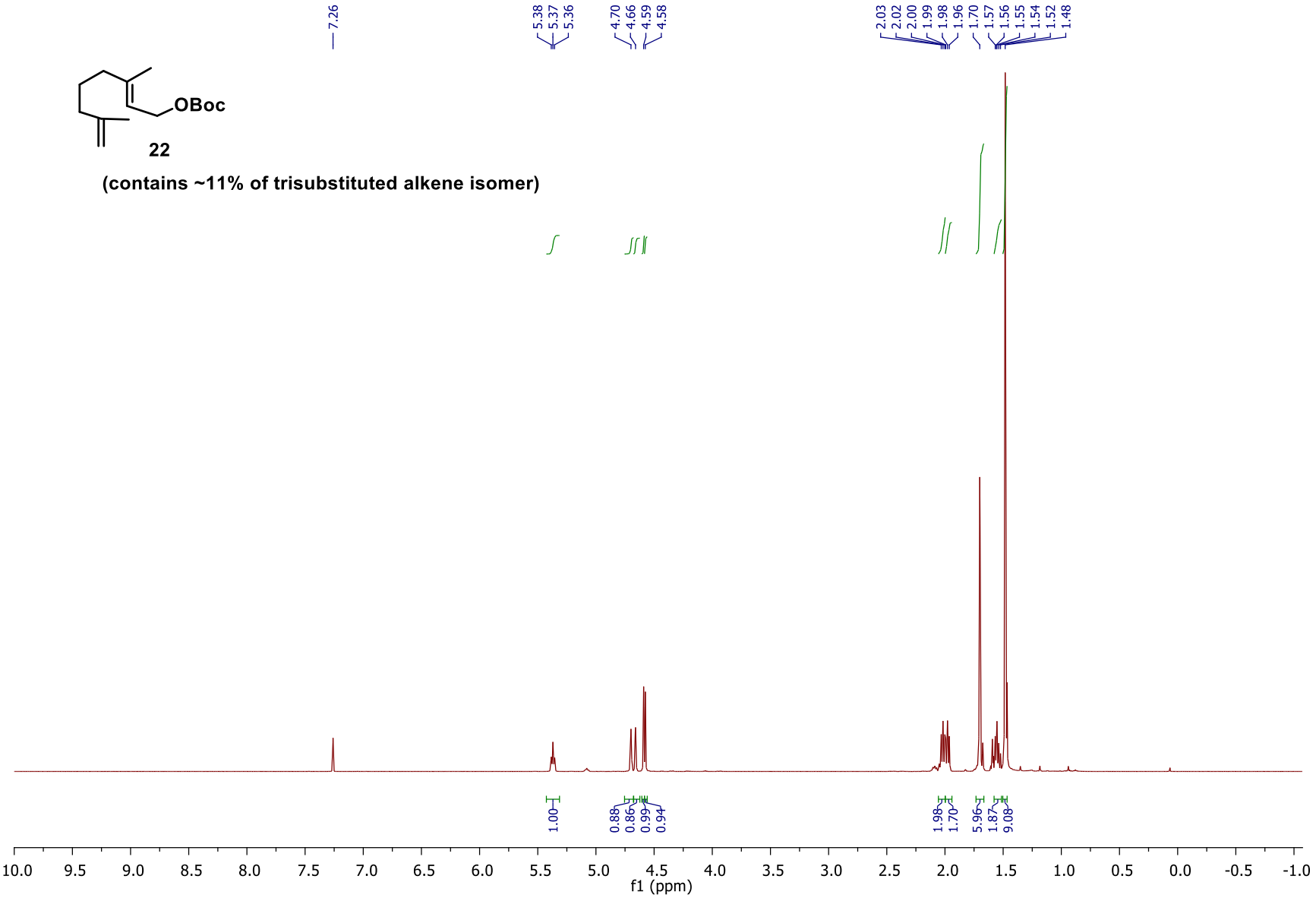

TBSO
O
S44
159.72
144.15
143.15
133.00
129.34
126.85
120.99
114.35
113.02
111.09
77.37
77.16
76.95
69.77
55.26
47.85
46.01
36.14
30.08
26.03
23.16
18.27
16.77
-4.39
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

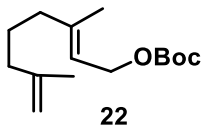

21
7.26
6.36
6.36
6.31
6.30
5.83
5.82
5.81
5.79
5.19
5.18
5.17
5.01
4.98
4.95
4.94
3.79
3.78
2.61
2.60
2.58
2.57
2.32
2.31
2.29
2.28
2.02
2.01
2.00
1.98
1.97
1.57
1.50
1.49
1.48
1.46
1.45
2.33
1.16
1.00
1.04
1.03
1.01
6.28
2.25
2.19
3.95
3.43
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


O
O

21

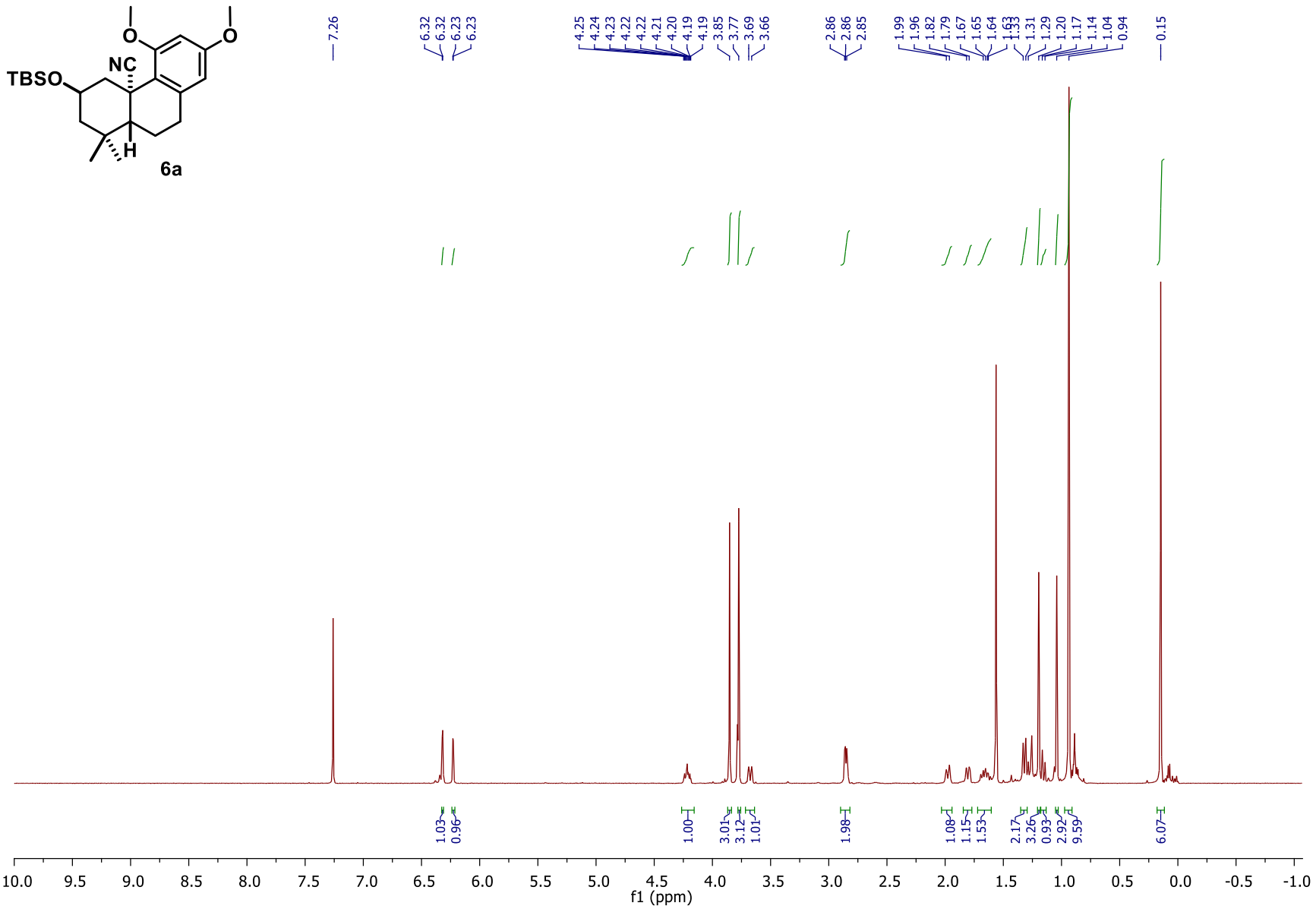
160.71
144.88
139.05
135.73
123.78
114.37
106.56
97.74
77.28
77.06
76.85
55.28
39.12
36.48
33.35
29.73
27.22
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

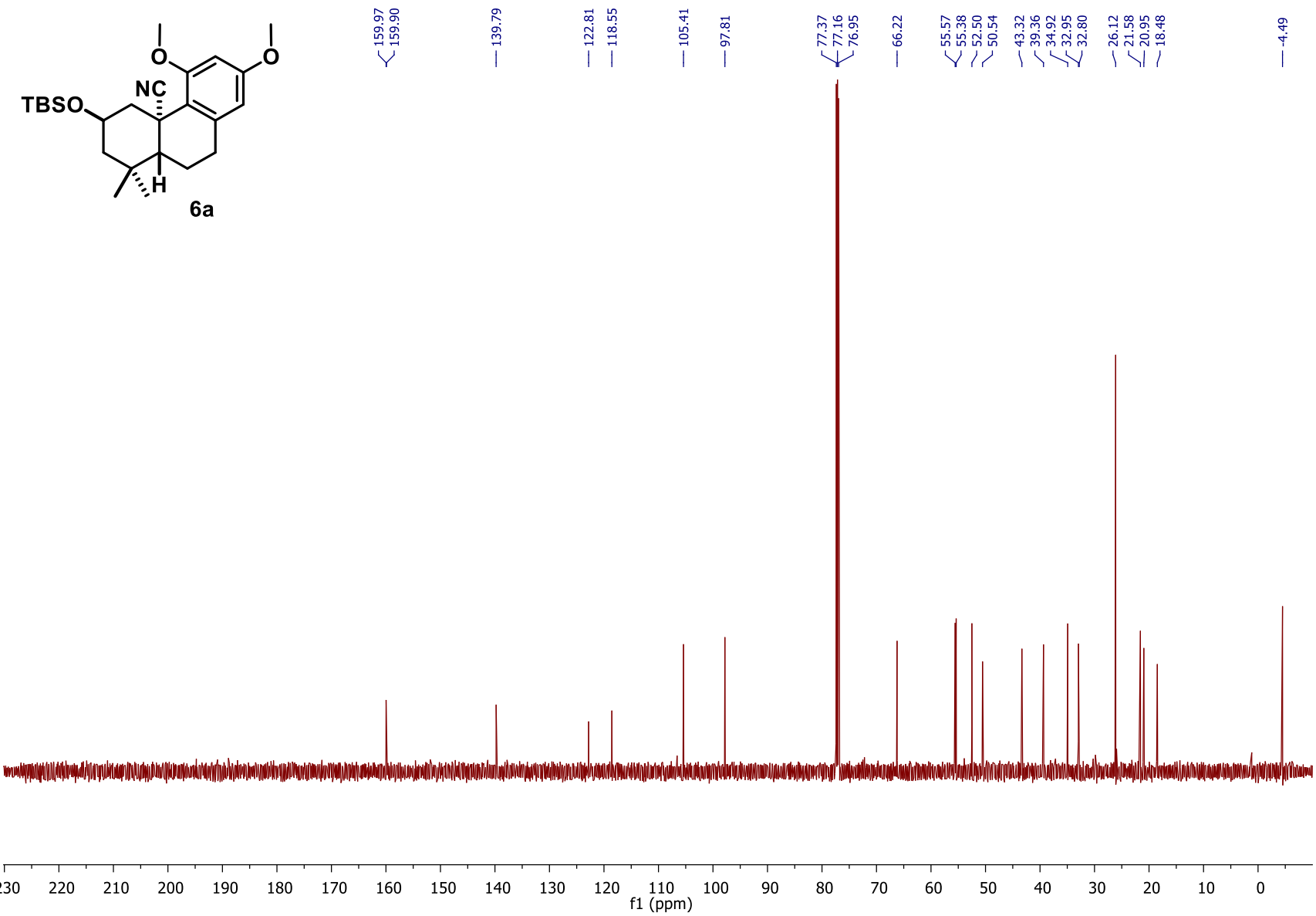

7.26
5.38
5.37
5.36
4.70
4.66
4.59
4.58
2.03
2.02
2.00
1.99
1.98
1.96
1.70
1.57
1.56
1.55
1.54
1.52
1.48
OBoc
22
(contains ~11% of trisubstituted alkene isomer)
1.00
0.88
0.86
0.99
0.94
1.98
1.70
5.96
1.87
9.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

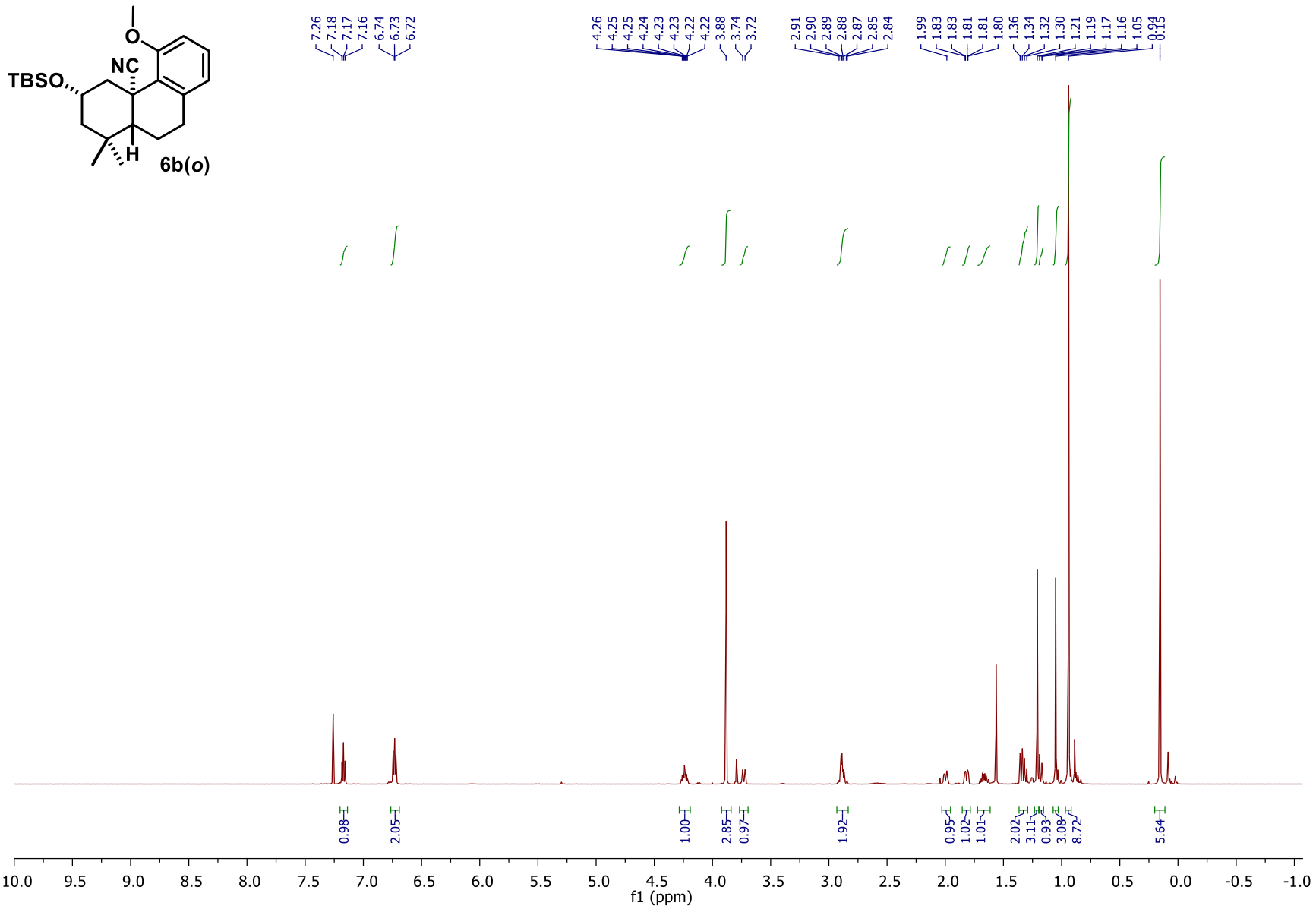


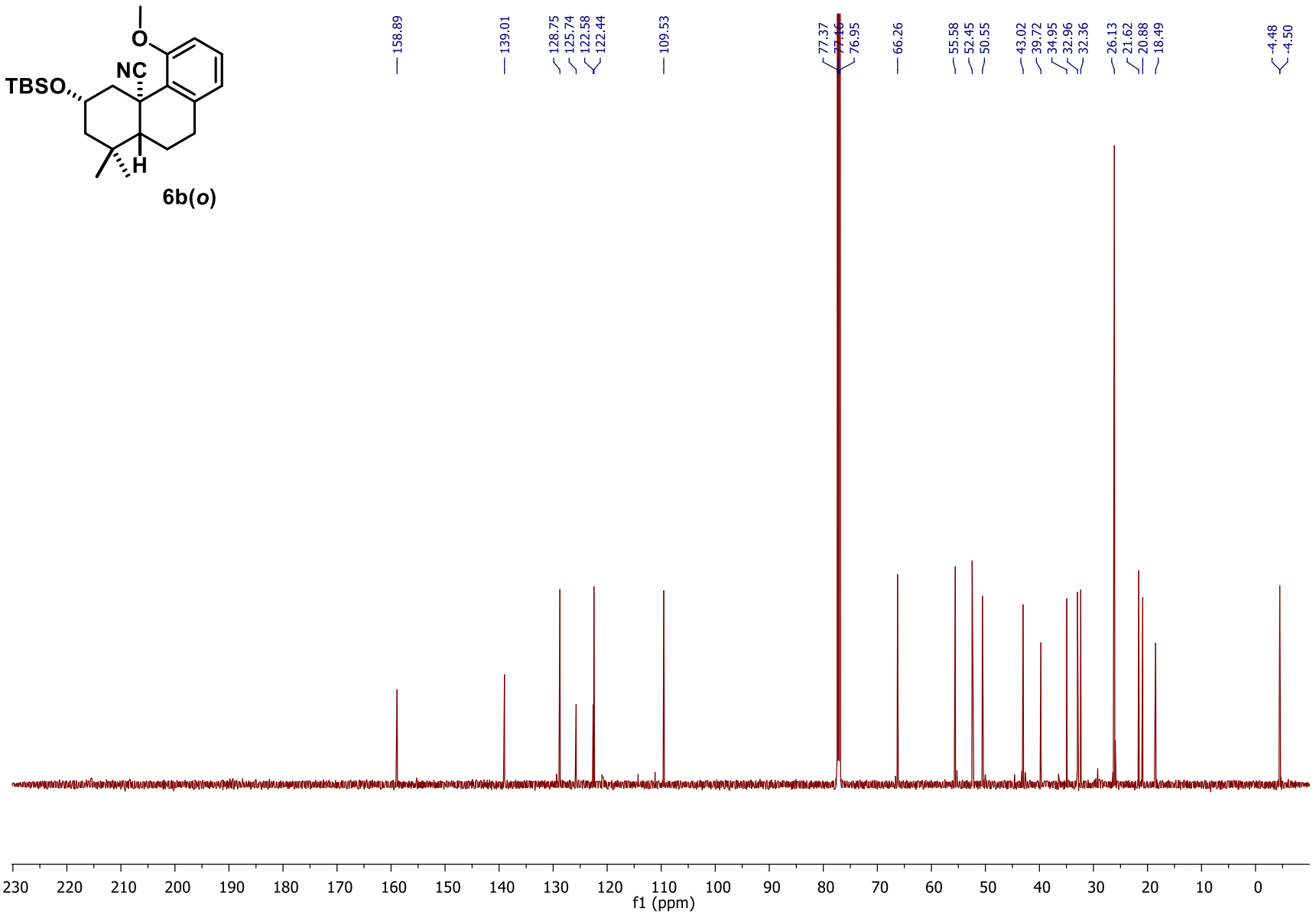
22

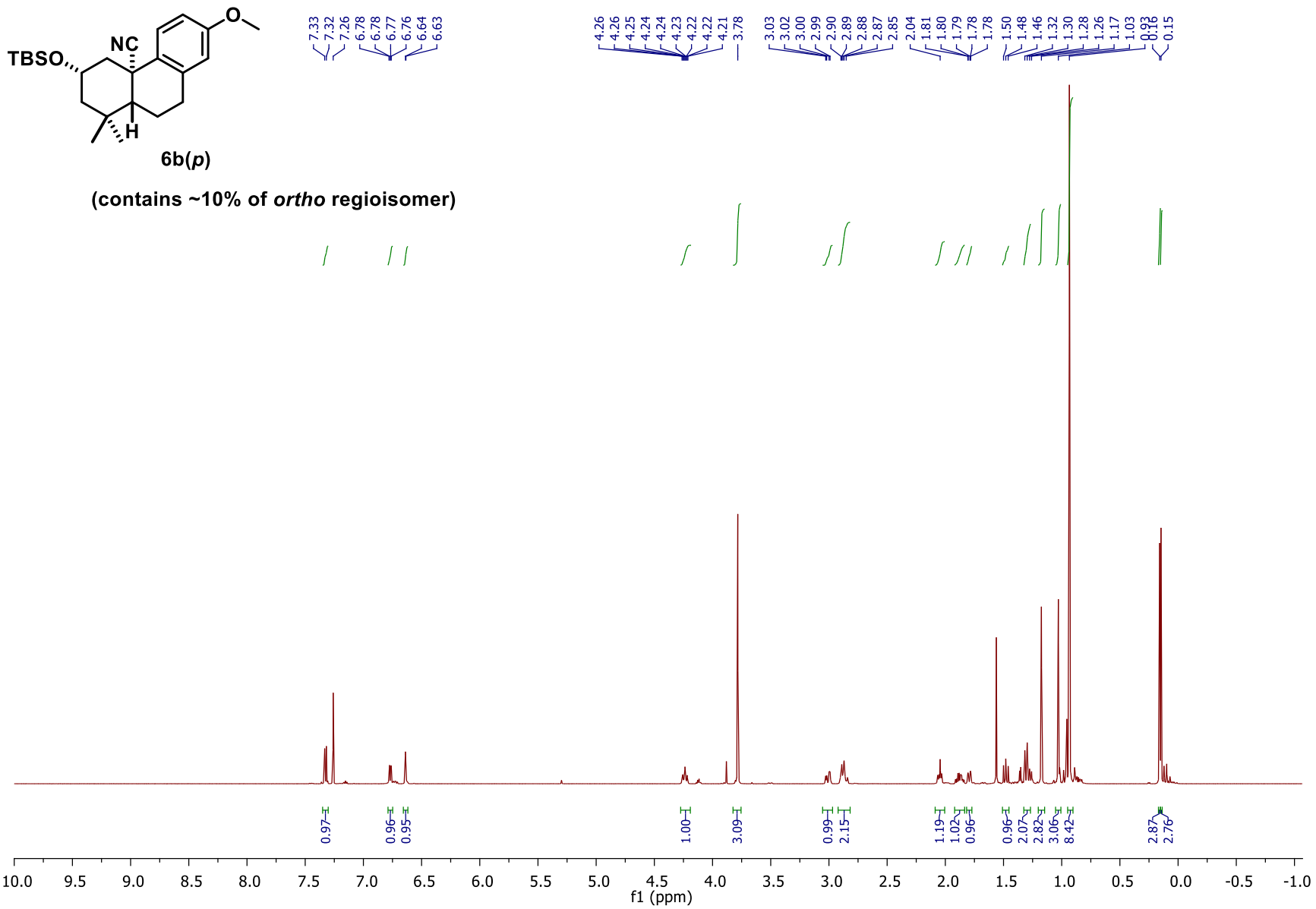
(contains ~11% of trisubstituted alkene isomer)

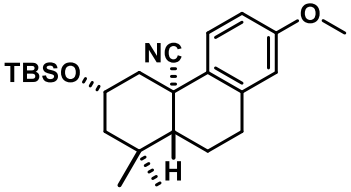

TBSO
NC
O
O
H
6a
7.26
6.32
6.32
6.23
6.23
4.25
4.24
4.23
4.22
4.22
4.21
4.20
4.19
4.19
3.85
3.77
3.69
3.66
2.86
2.86
2.85
1.99
1.96
1.82
1.79
1.67
1.65
1.64
1.53
1.31
1.29
1.20
1.17
1.14
1.04
0.94
0.15
1.03
0.96
1.00
3.01
3.12
1.01
1.98
1.08
1.15
1.53
2.17
3.26
0.93
2.92
9.59
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


TBSO
NC
O
O
H
6a
159.97
159.90
139.79
122.81
118.55
105.41
97.81
77.37
77.16
76.95
66.22
55.57
55.38
52.50
50.54
43.32
39.36
34.92
32.95
32.80
26.12
21.58
20.95
18.48
-4.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TBSO
NC
O
H
6b(o)
7.26
7.18
7.17
7.16
6.74
6.73
6.72
4.26
4.25
4.25
4.24
4.23
4.23
4.22
4.22
3.88
3.74
3.72
2.91
2.90
2.89
2.88
2.87
2.85
2.84
1.99
1.83
1.83
1.81
1.81
1.80
1.36
1.34
1.32
1.30
1.21
1.19
1.17
1.16
1.05
0.94
0.15
0.98
2.05
1.00
2.85
0.97
1.92
0.95
1.02
1.01
2.02
3.11
0.93
3.08
8.72
5.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

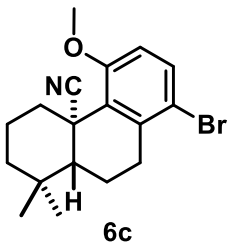

TBSO
NC
O
H
6b(o)
158.89
139.01
128.75
125.74
122.58
122.44
109.53
77.37
77.16
76.95
66.26
55.58
52.45
50.55
43.02
39.72
34.95
32.96
32.36
26.13
21.62
20.88
18.49
-4.48
-4.50
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TBSO
NC
O
H
6b(p)
(contains ~10% of ortho regioisomer)
7.33
7.32
7.26
6.78
6.78
6.77
6.76
6.64
6.63
4.26
4.26
4.25
4.24
4.24
4.23
4.22
4.22
4.21
3.78
3.03
3.02
3.00
2.99
2.90
2.89
2.88
2.87
2.85
2.04
1.81
1.80
1.79
1.78
1.78
1.50
1.48
1.46
1.32
1.30
1.28
1.26
1.17
1.03
0.16
0.15
0.97
0.96
0.95
1.00
3.09
0.99
2.15
1.19
1.02
0.96
0.96
2.07
2.82
3.06
8.42
2.87
2.76
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



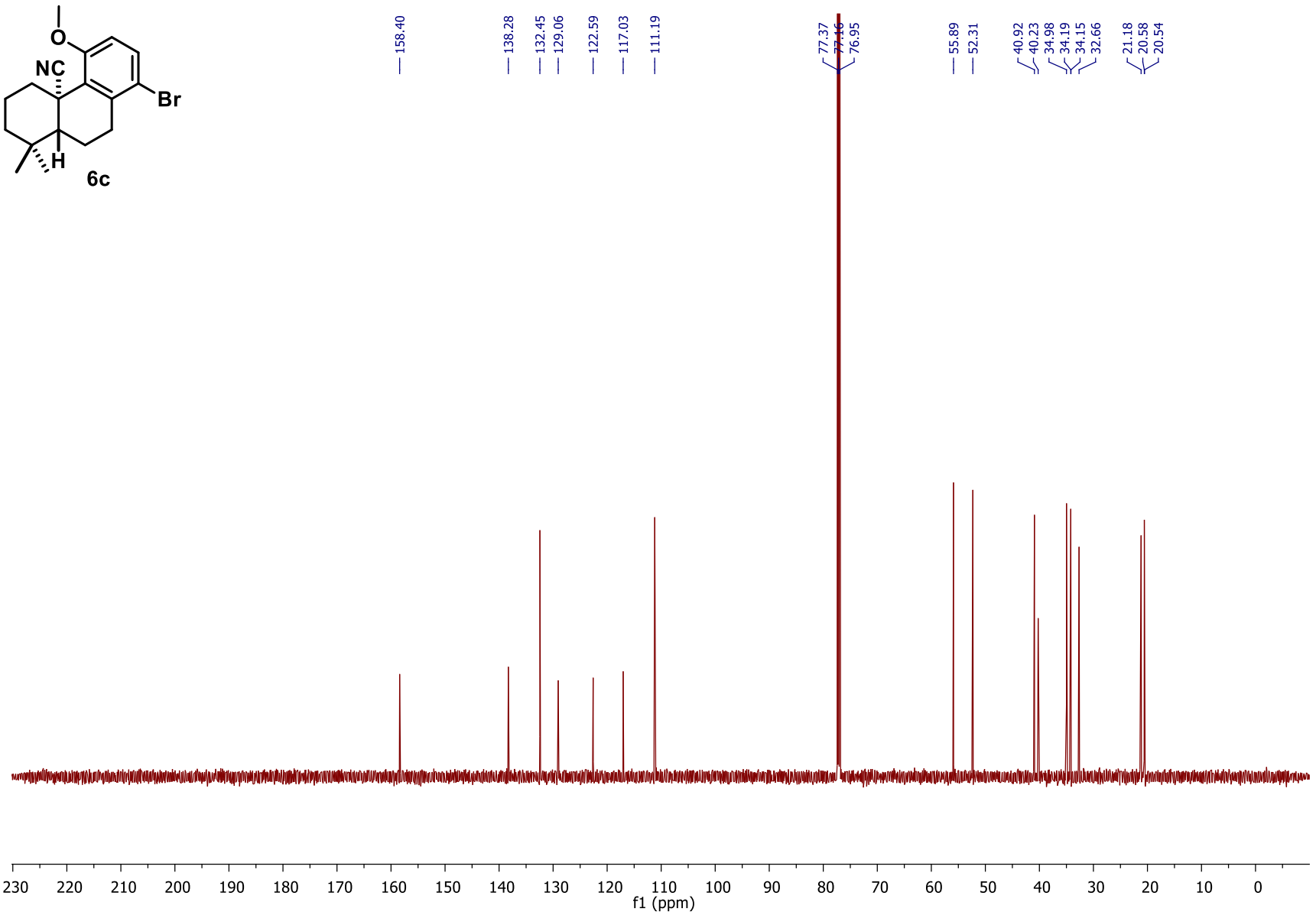
6b(*p*)

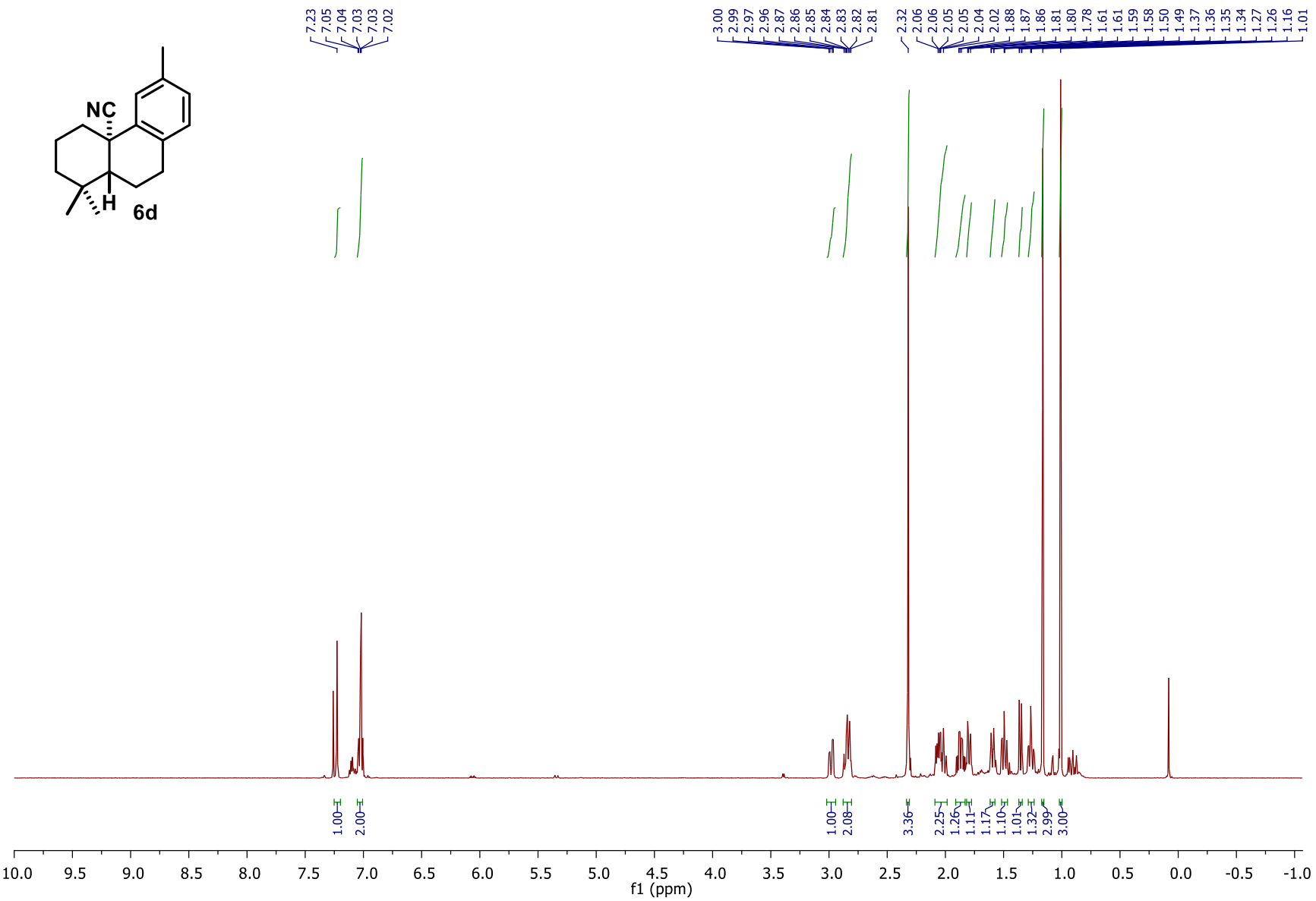
(contains ~10% of the *ortho* regioisomer)

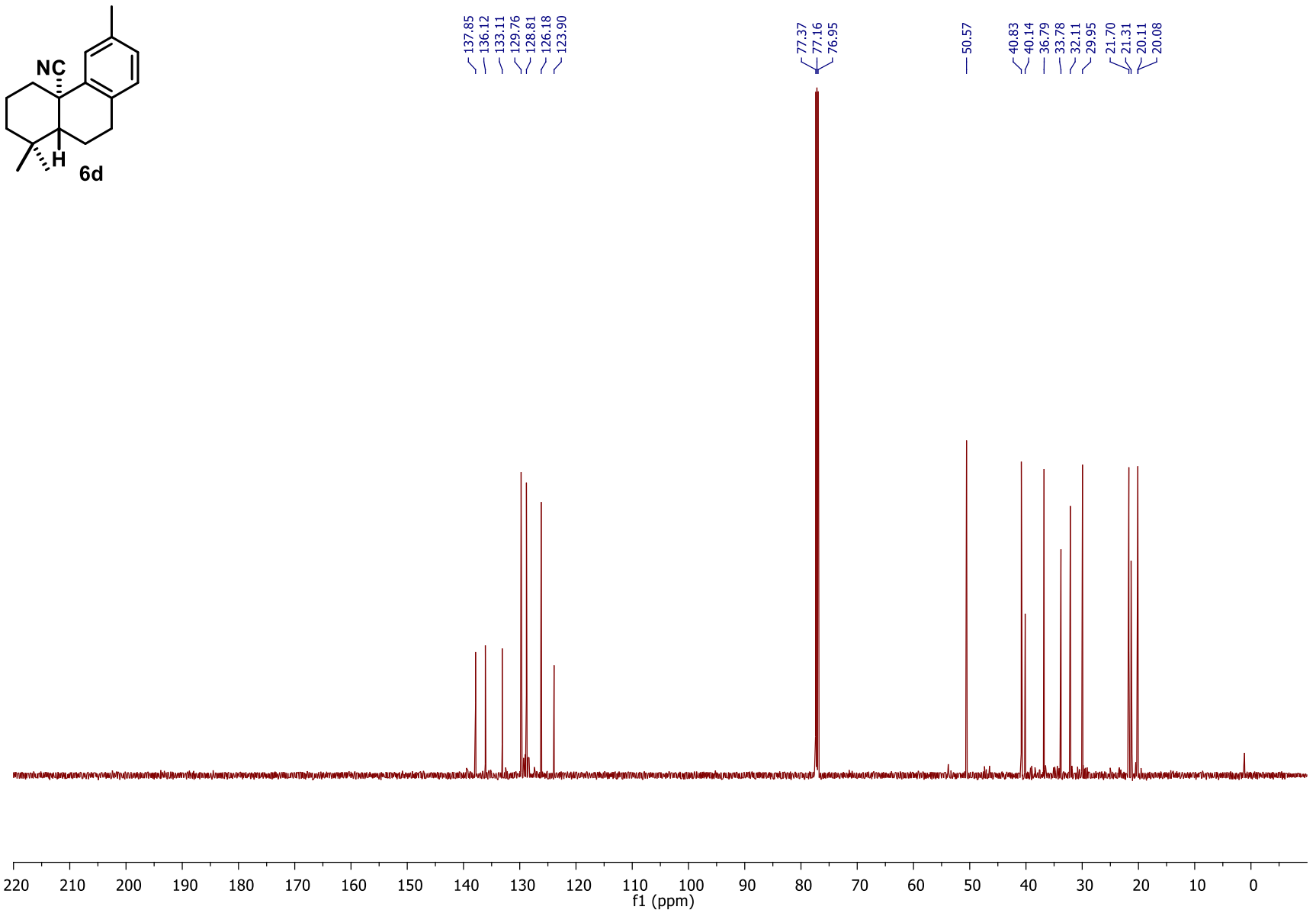

O
NC
Br
H

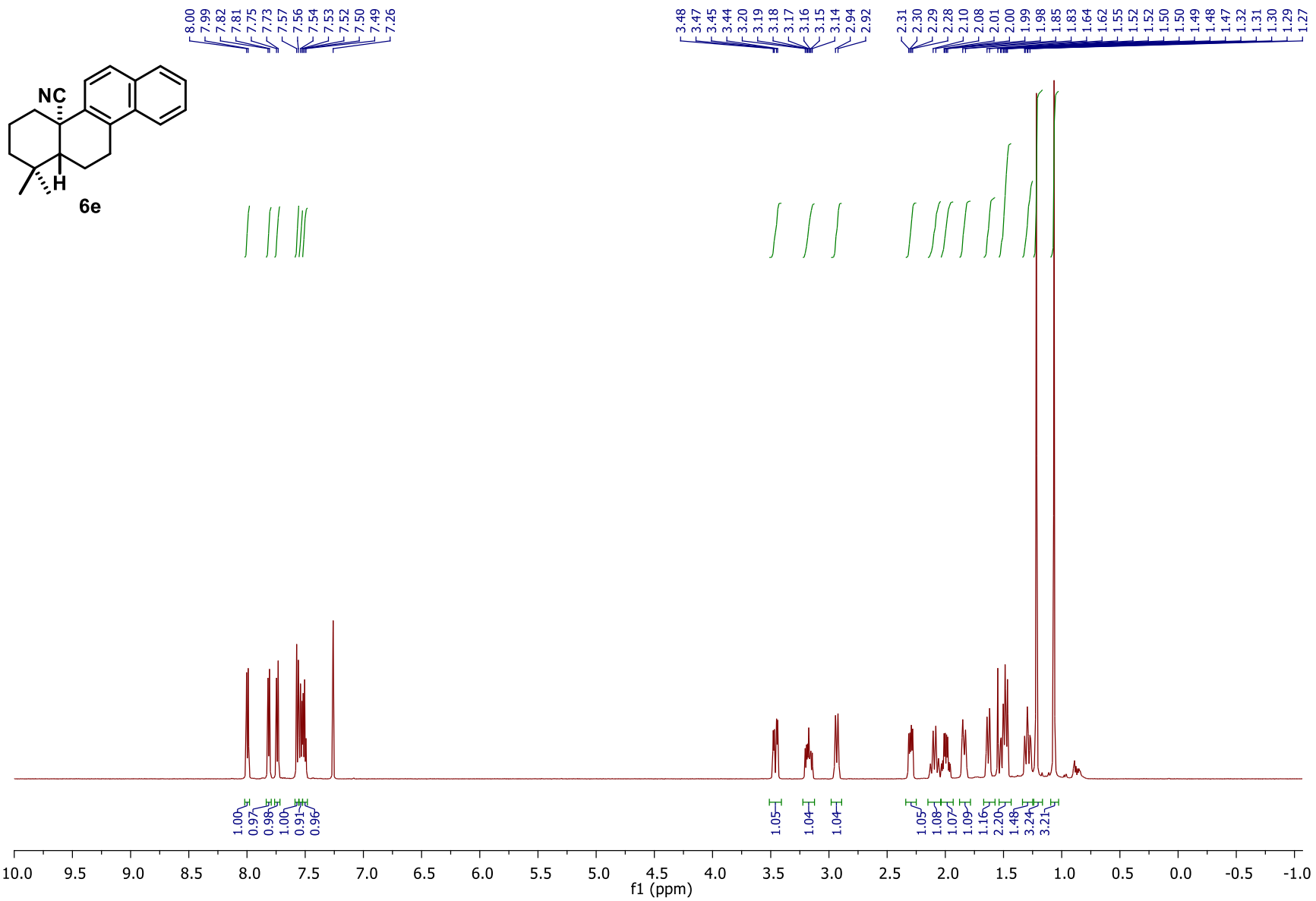
6c

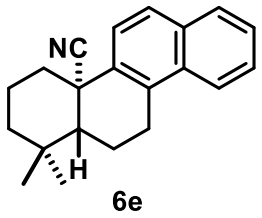
7.45
7.43
7.26
6.68
6.66
3.87
3.49
3.47
2.95
2.95
2.92
2.92
2.69
2.68
2.67
2.66
2.07
2.06
2.00
1.98
1.69
1.67
1.57
1.32
1.30
1.26
1.26
1.18
1.16
1.15
1.13
1.13
1.02
1.00
1.01
3.17
1.02
1.01
1.01
1.01
1.04
2.59
1.07
1.22
3.03
1.07
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
NC
Br
H
6c
158.40
138.28
132.45
129.06
122.59
117.03
111.19
77.37
77.16
76.95
55.89
52.31
40.92
40.23
34.98
34.19
34.15
32.66
21.18
20.58
20.54
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
H
6d
7.23
7.05
7.04
7.03
7.03
7.02
3.00
2.99
2.97
2.96
2.87
2.86
2.85
2.84
2.83
2.82
2.81
2.32
2.06
2.06
2.05
2.05
2.04
2.02
1.88
1.87
1.86
1.81
1.80
1.78
1.61
1.61
1.59
1.58
1.50
1.49
1.37
1.36
1.35
1.34
1.27
1.26
1.16
1.01
1.00
2.00
1.00
2.08
3.36
2.25
1.26
1.11
1.17
1.10
1.01
1.32
2.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

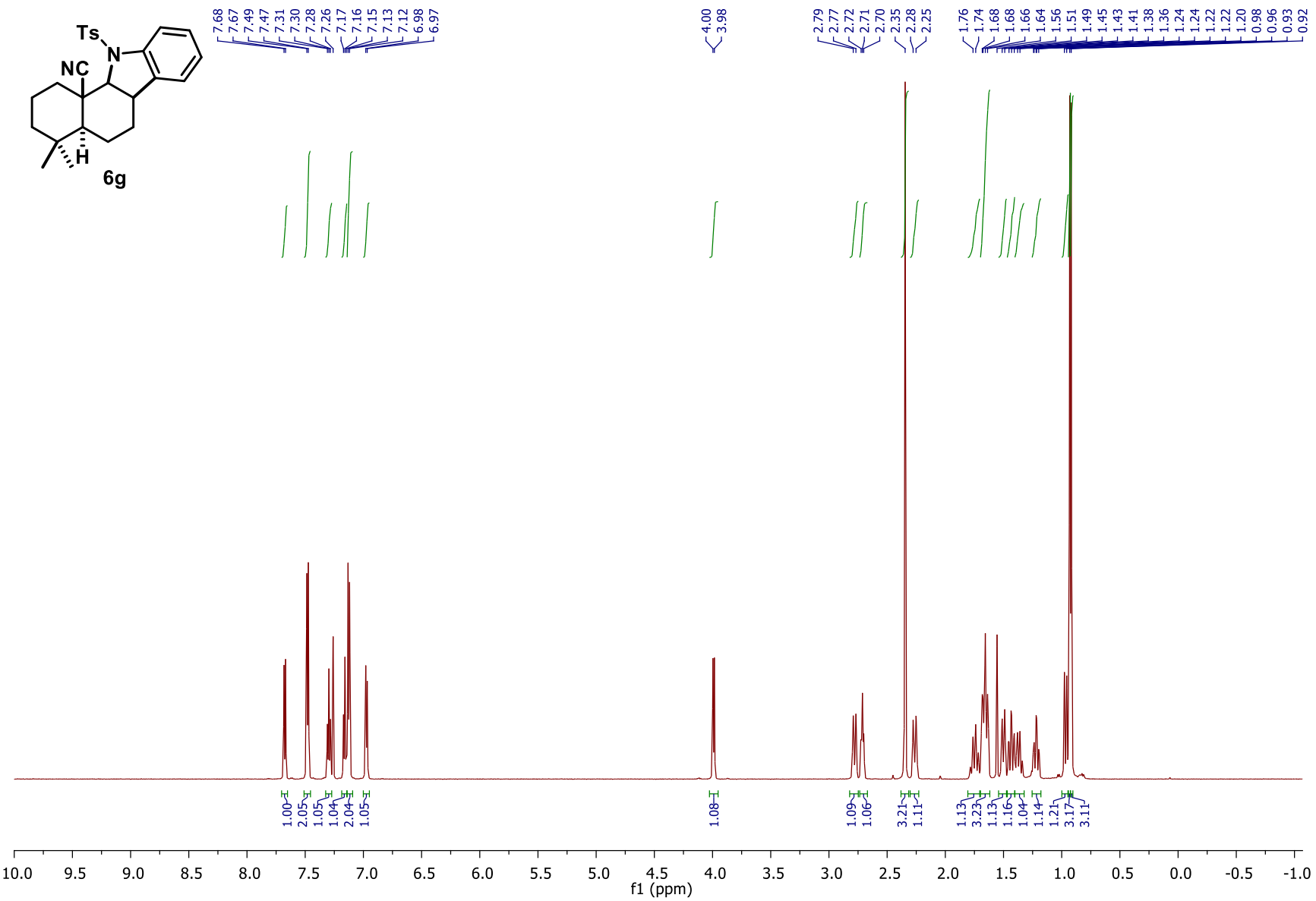

NC
H
6d
137.85
136.12
133.11
129.76
128.81
126.18
123.90
77.37
77.16
76.95
50.57
40.83
40.14
36.79
33.78
32.11
29.95
21.70
21.31
20.11
20.08
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

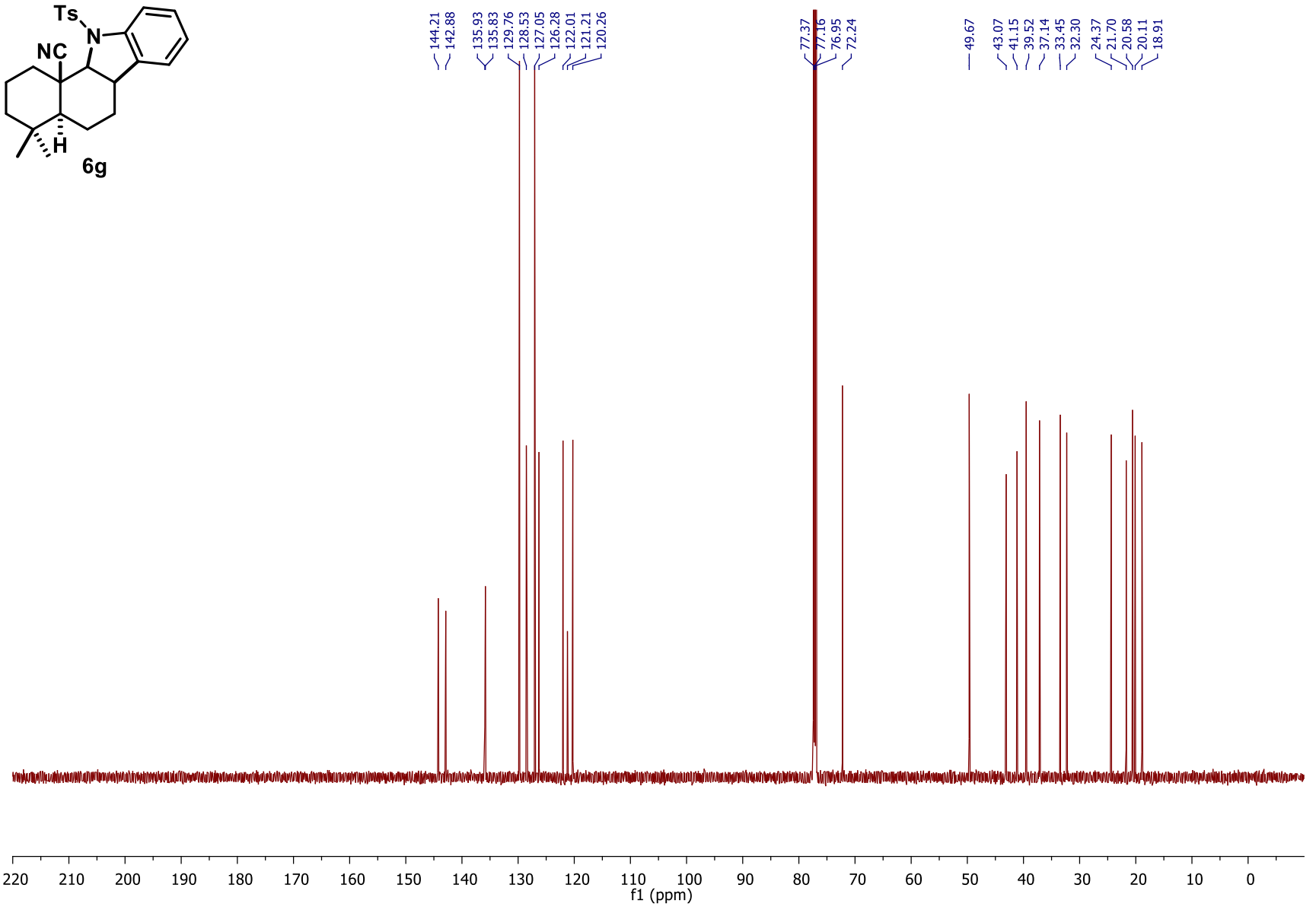

NC
H
6e
f1 (ppm)

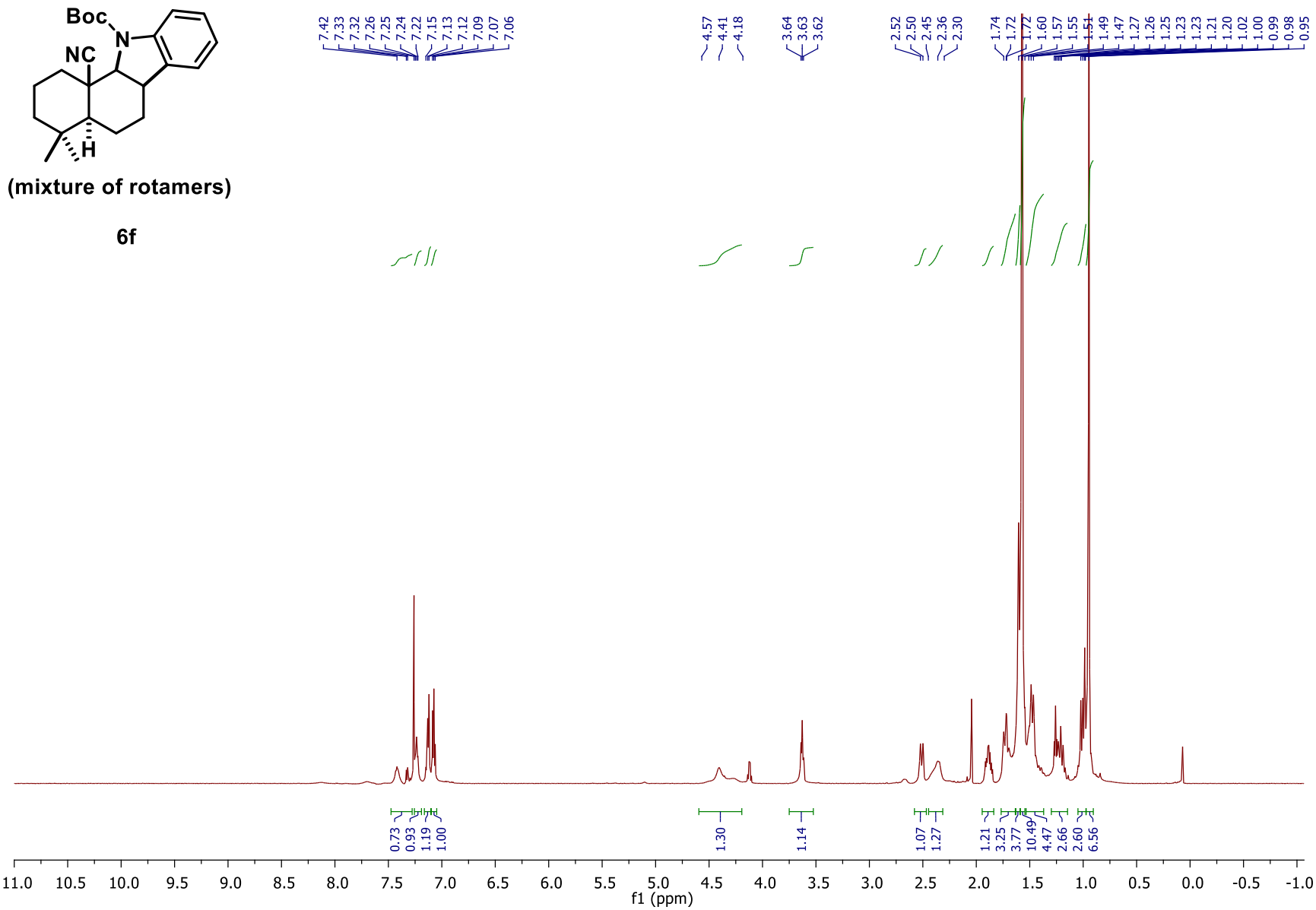

NC
H

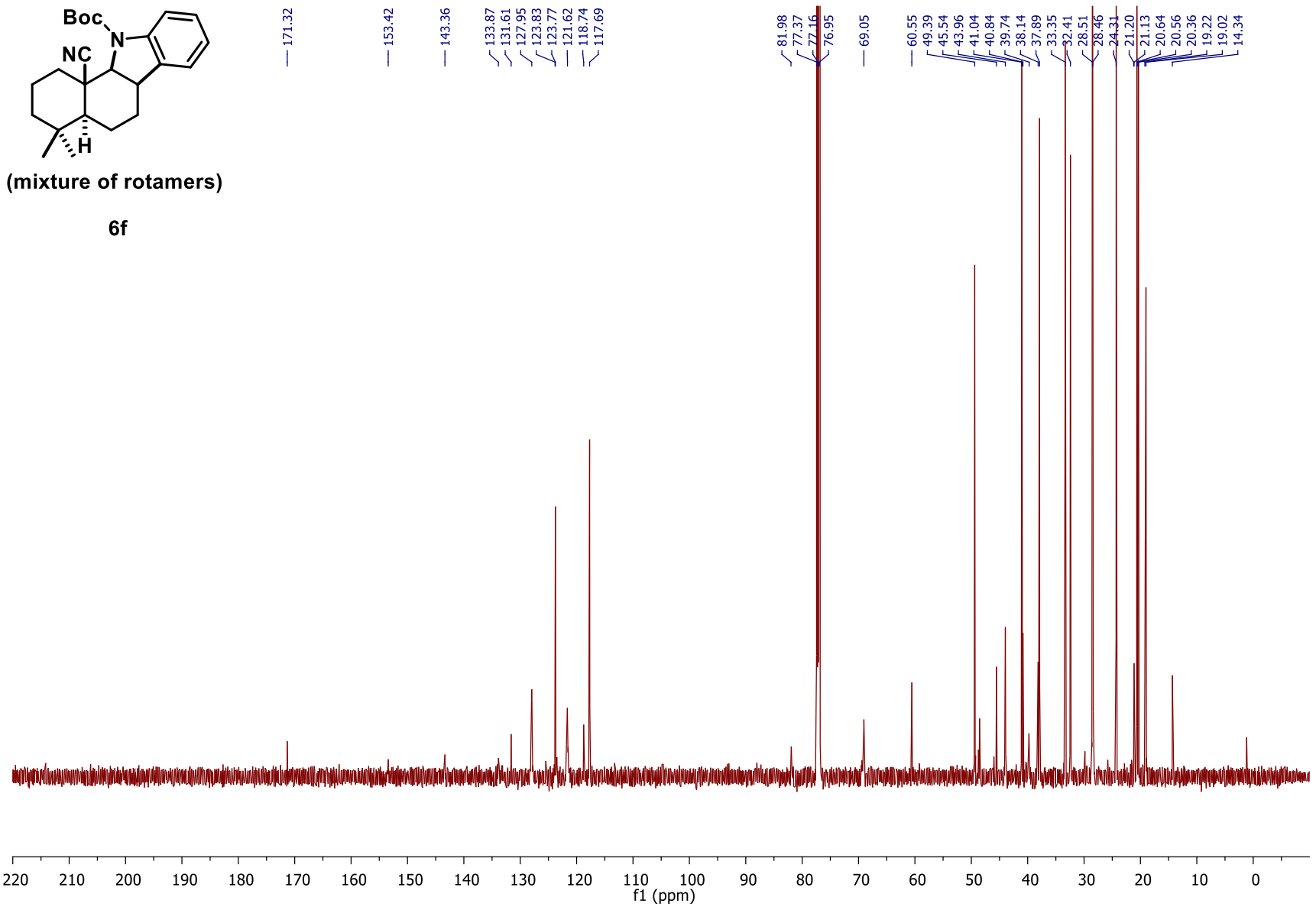
6e

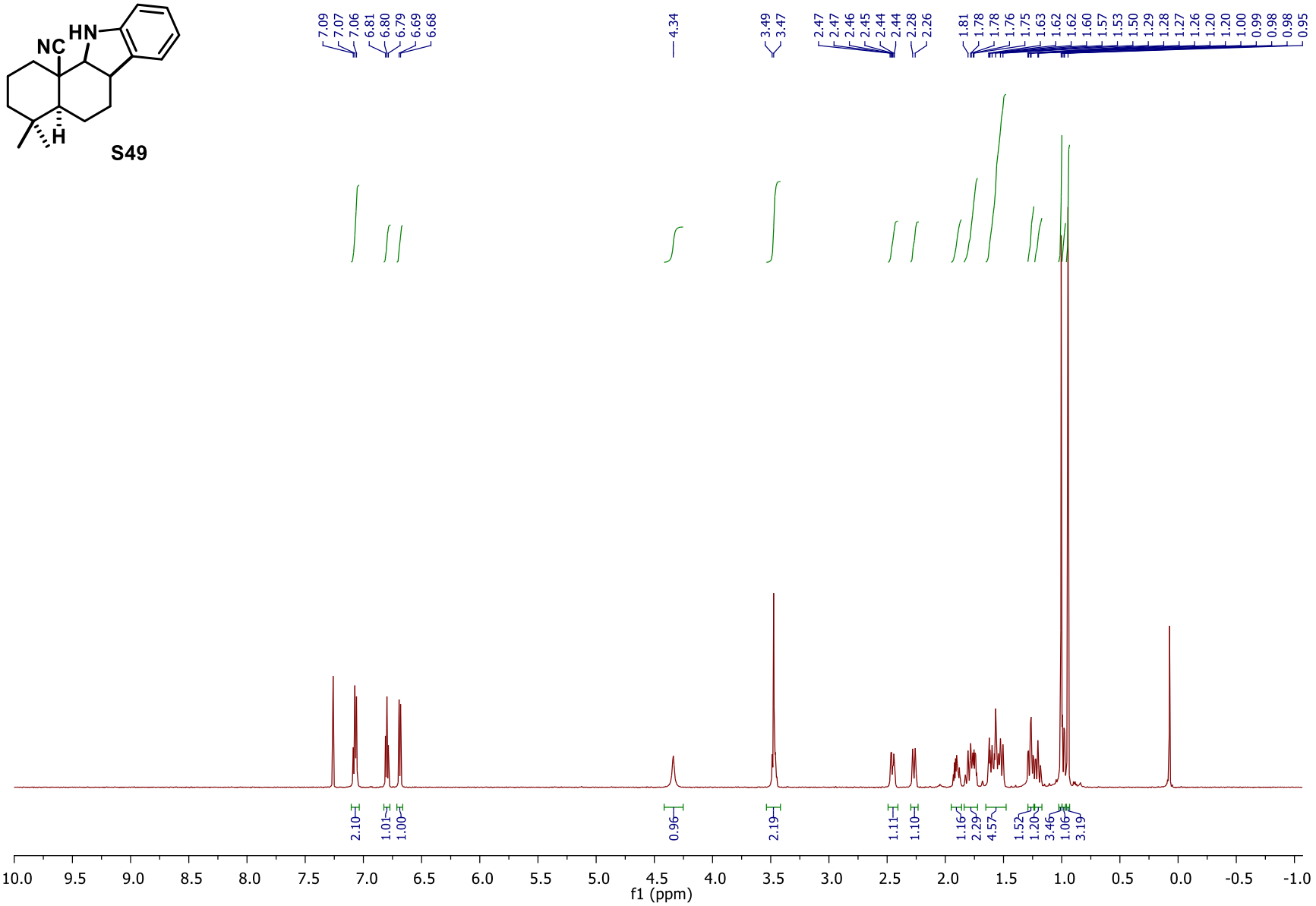
135.07
132.67
132.37
132.16
128.48
127.46
126.66
126.34
123.69
123.57
123.19
77.37
77.16
76.95
50.52
40.76
40.74
37.18
33.74
32.11
27.72
21.52
20.27
20.14
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

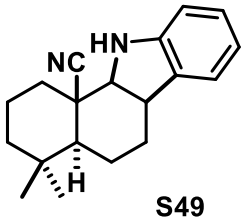

Ts
N
NC
H
6g
7.68
7.67
7.49
7.47
7.31
7.30
7.28
7.26
7.17
7.16
7.15
7.13
7.12
6.98
6.97
4.00
3.98
2.79
2.77
2.72
2.71
2.70
2.35
2.28
2.25
1.76
1.74
1.68
1.68
1.66
1.64
1.56
1.51
1.49
1.45
1.43
1.41
1.38
1.36
1.24
1.24
1.22
1.22
1.20
0.98
0.96
0.93
0.92
1.00
2.05
1.05
1.04
2.04
1.05
1.08
1.09
1.06
3.21
1.11
1.13
3.23
1.13
1.16
1.04
1.14
1.21
3.17
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


Ts
N
NC
H
6g
144.21
142.88
135.93
135.83
129.76
128.53
127.05
126.28
122.01
121.21
120.26
77.37
77.16
76.95
72.24
49.67
43.07
41.15
39.52
37.14
33.45
32.30
24.37
21.70
20.58
20.11
18.91
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Boc
N
NC
H
(mixture of rotamers)
6f
7.42
7.33
7.32
7.26
7.25
7.24
7.22
7.15
7.13
7.12
7.09
7.07
7.06
4.57
4.41
4.18
3.64
3.63
3.62
2.52
2.50
2.45
2.36
2.30
1.74
1.72
1.72
1.60
1.57
1.55
1.51
1.49
1.47
1.27
1.26
1.25
1.23
1.23
1.21
1.20
1.02
1.00
0.99
0.98
0.95
0.73
0.93
1.19
1.00
1.30
1.14
1.07
1.27
1.21
3.25
3.77
10.49
4.47
2.66
2.60
6.56
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

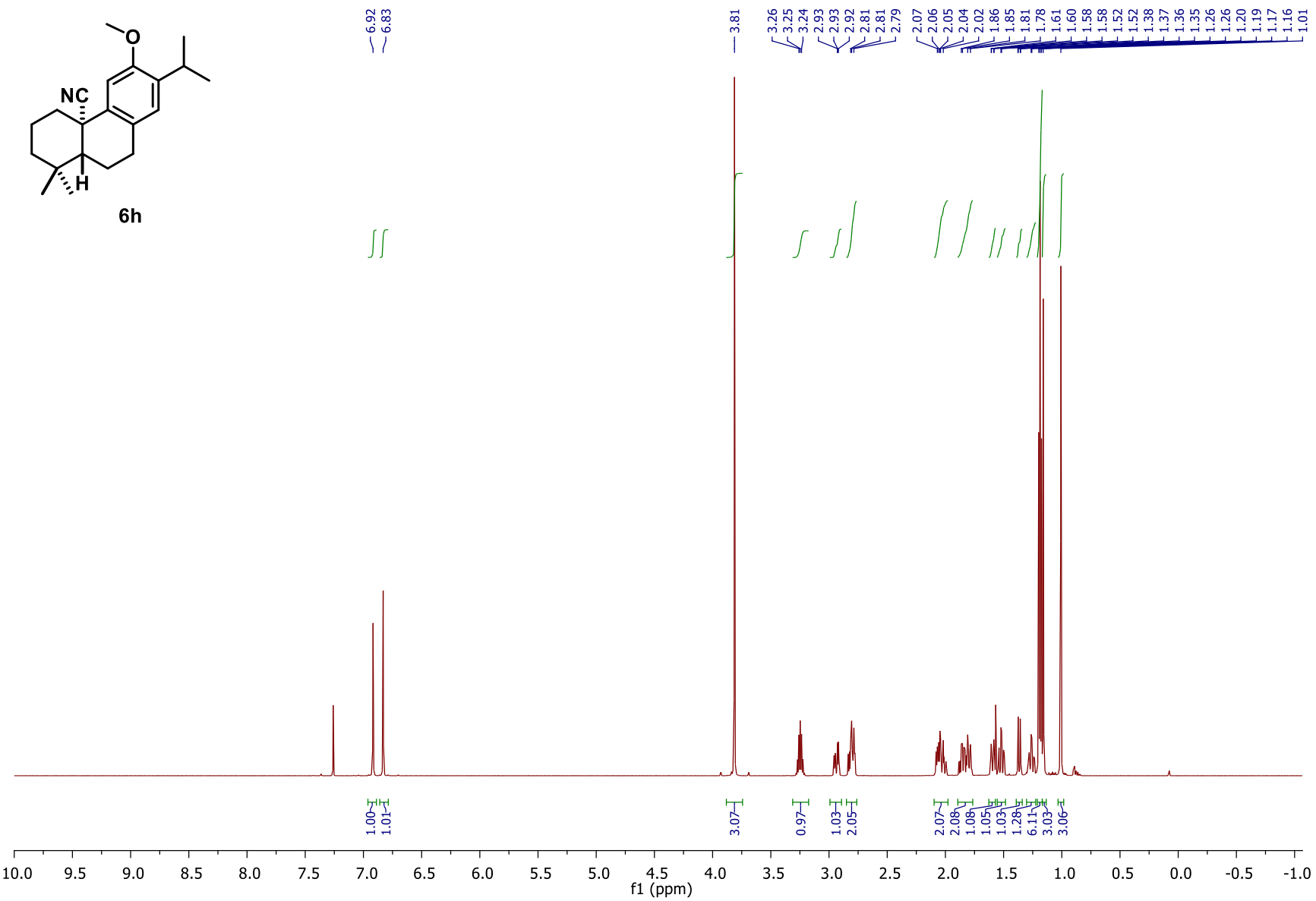

Boc
N
NC
H
(mixture of rotamers)
6f
171.32
153.42
143.36
133.87
131.61
127.95
123.83
123.77
121.62
118.74
117.69
81.98
77.37
77.16
76.95
69.05
60.55
49.39
45.54
43.96
41.04
40.84
39.74
38.14
37.89
33.35
32.41
28.51
28.46
24.31
21.20
21.13
20.64
20.56
20.36
19.22
19.02
14.34
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

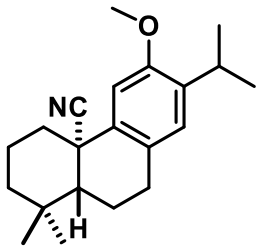

NC
HN
H
S49
7.09
7.07
7.06
6.81
6.80
6.79
6.69
6.68
4.34
3.49
3.47
2.47
2.47
2.46
2.45
2.44
2.44
2.28
2.26
1.81
1.78
1.78
1.76
1.75
1.63
1.62
1.62
1.60
1.57
1.53
1.50
1.29
1.28
1.27
1.26
1.20
1.20
1.00
0.99
0.98
0.98
0.95
2.10
1.01
1.00
0.96
2.19
1.11
1.10
1.16
2.29
4.57
1.52
1.20
3.46
1.06
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


NC
HN
H

S49

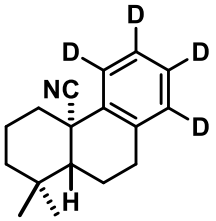
150.66
129.98
128.01
122.39
122.27
119.36
109.63
77.37
77.16
76.95
69.32
48.18
42.68
41.20
40.56
37.95
33.37
32.16
24.67
20.65
20.56
19.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NC
O
H
6h
6.92
6.83
3.81
3.26
3.25
3.24
2.93
2.92
2.81
2.81
2.79
2.07
2.06
2.05
2.04
2.02
1.86
1.85
1.81
1.78
1.61
1.60
1.58
1.58
1.52
1.52
1.38
1.37
1.36
1.35
1.26
1.26
1.20
1.19
1.17
1.16
1.01
1.00
1.01
3.07
0.97
1.03
2.05
2.07
2.08
1.08
1.05
1.03
1.28
6.11
3.03
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


O
NC
H

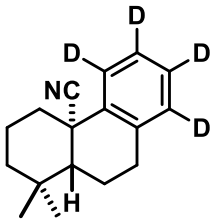
6h

155.63
137.31
135.70
127.98
127.35
123.97
107.22
77.37
77.16
76.95
55.63
50.65
40.83
40.26
36.85
33.76
32.14
29.77
26.65
22.73
21.89
20.12
20.12
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


D
D
D
NC
D
H

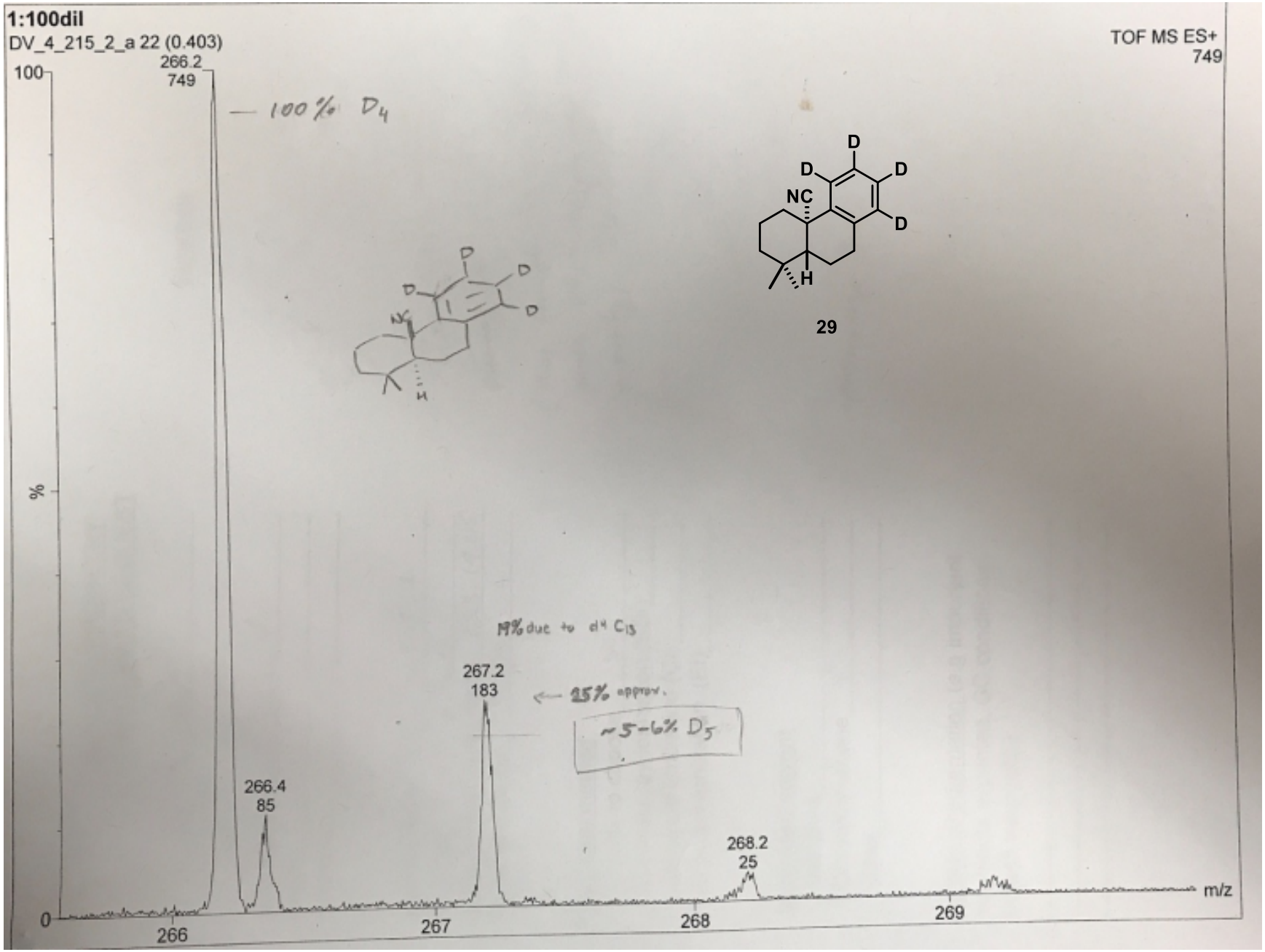
29

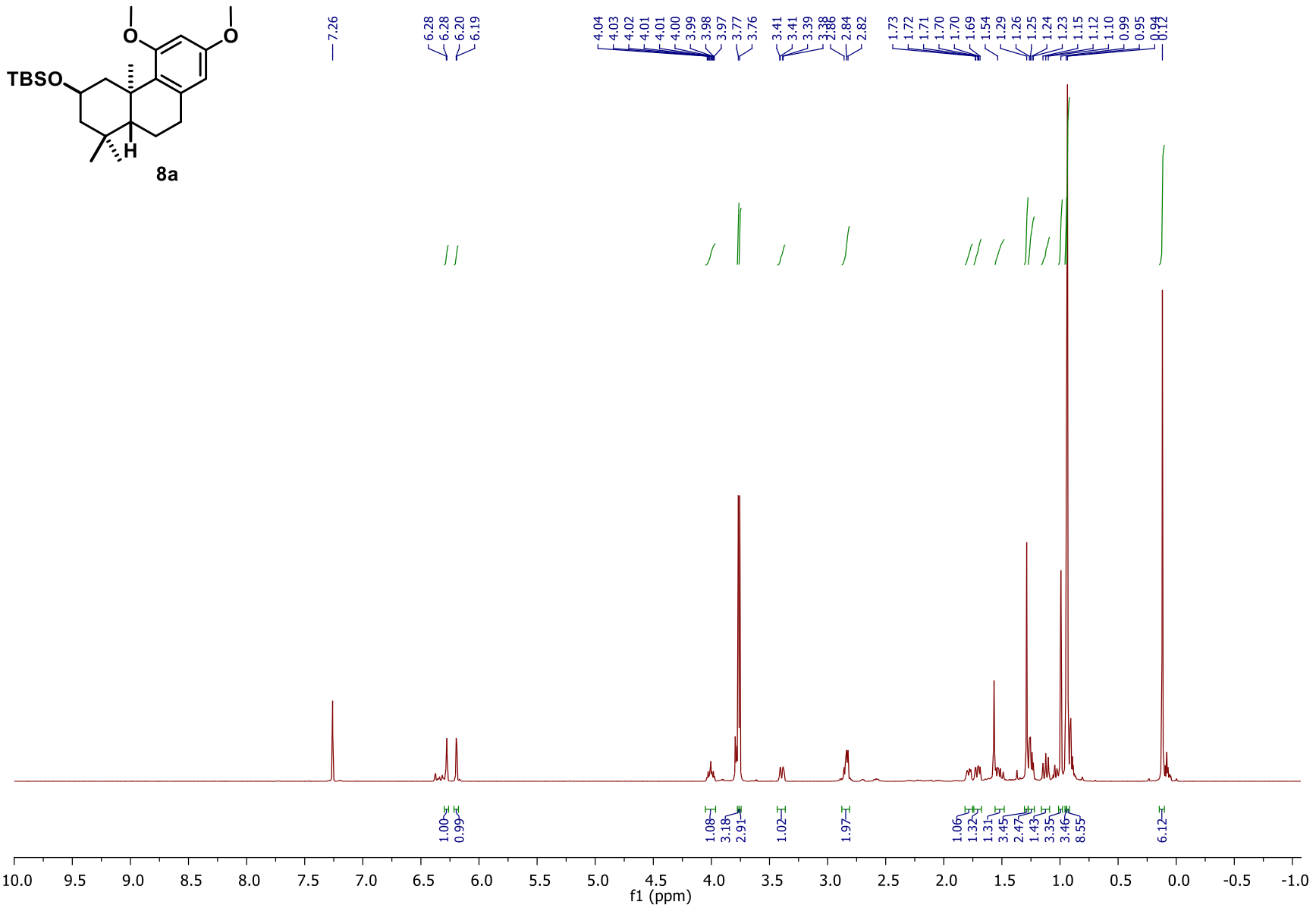
7.32
3.11
3.11
3.10
3.10
3.08
3.08
3.07
3.07
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.90
2.88
2.13
2.12
2.10
2.08
1.97
1.96
1.87
1.87
1.86
1.85
1.67
1.65
1.57
1.56
1.44
1.44
1.42
1.42
1.34
1.33
1.32
1.31
1.22
1.07
1.00
1.06
0.98
1.16
0.92
1.02
1.01
1.12
1.03
0.98
2.05
3.17
3.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

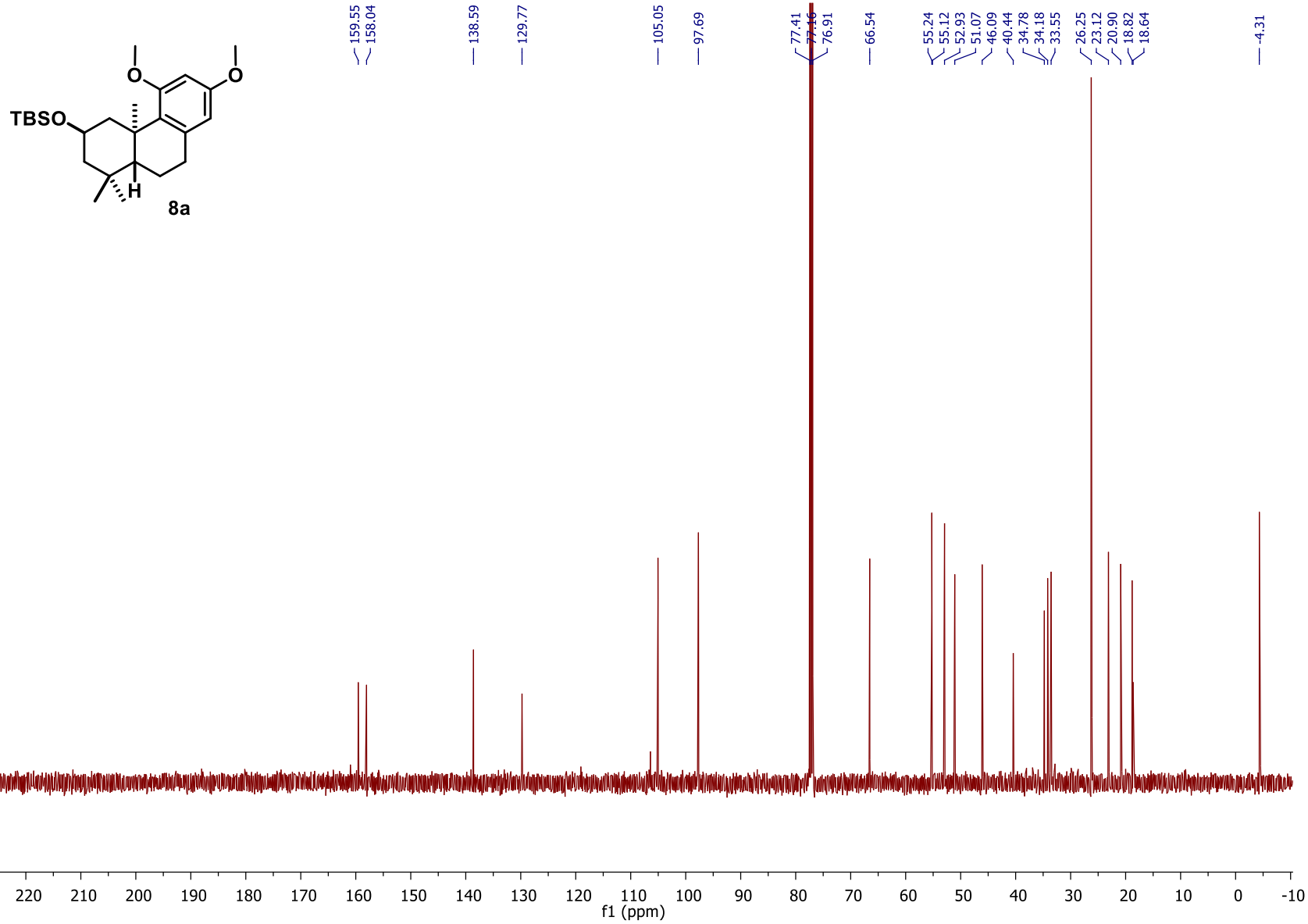

D
D
D
NC
D
H

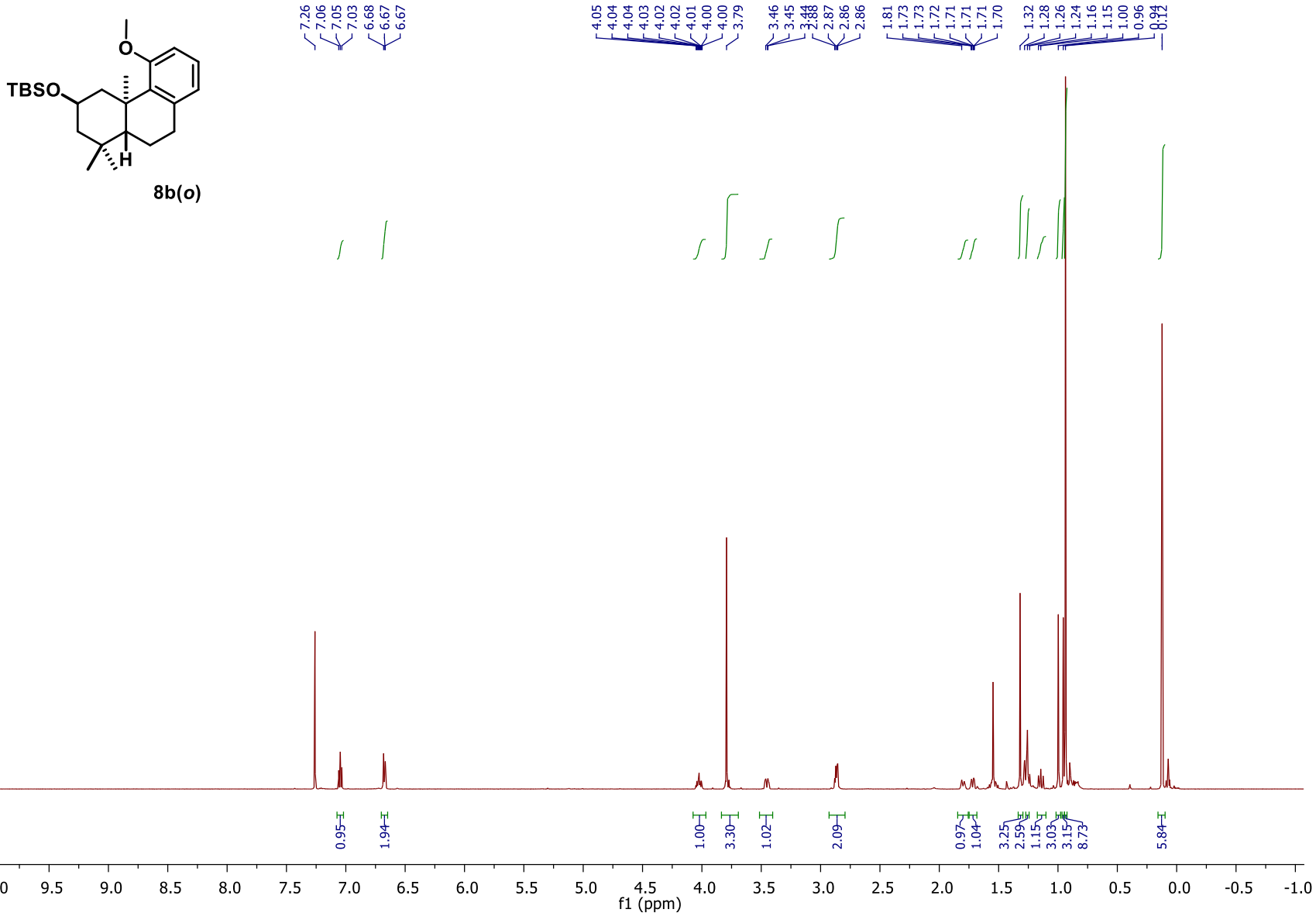
29

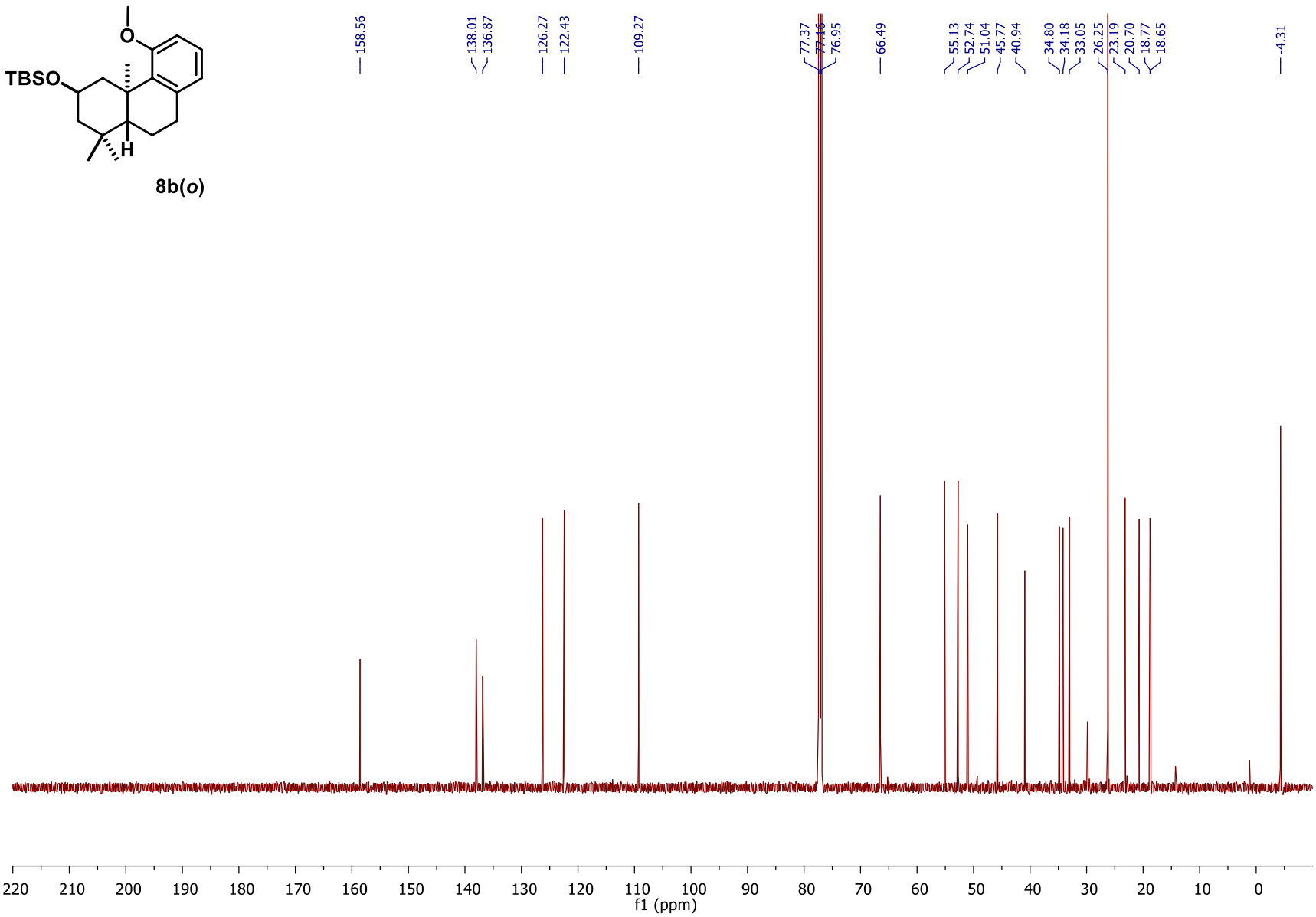
137.93
136.11
129.53
129.37
129.21
127.49
127.32
127.16
126.23
126.07
125.90
125.35
125.20
125.04
123.64
77.28
77.07
76.86
50.36
40.73
40.06
36.65
33.69
32.00
30.13
21.51
20.02
19.97
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

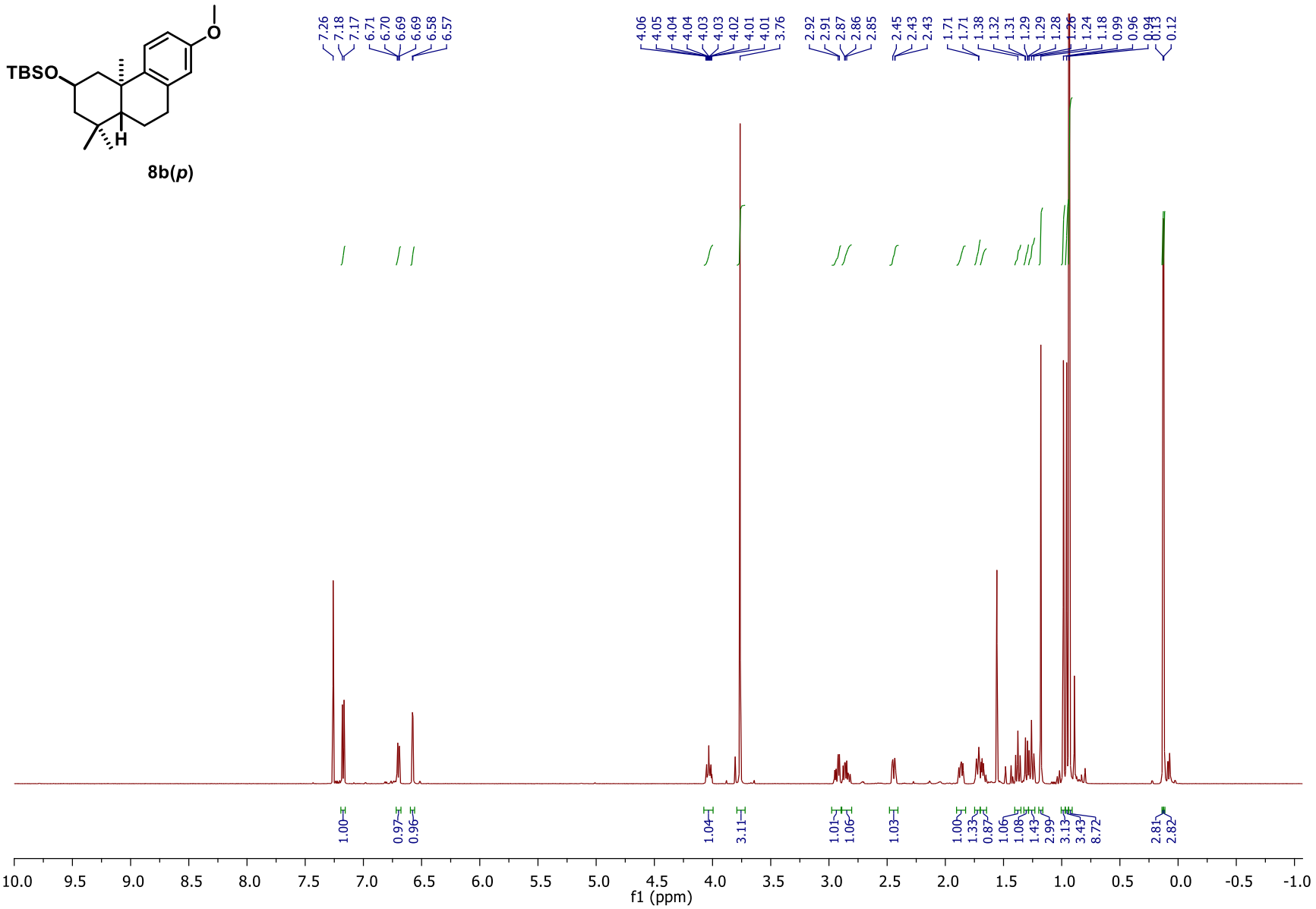

1:100dil
DV_4_215_2_a 22 (0.403)
TOF MS ES+
749
100
266.2
749
— 100% D4
D
D
D
D
NC
H
29
%
M% due to d4 C13
267.2
183
25% approx.
~5-6% D5
266.4
85
268.2
25
0
266
267
268
269
m/z

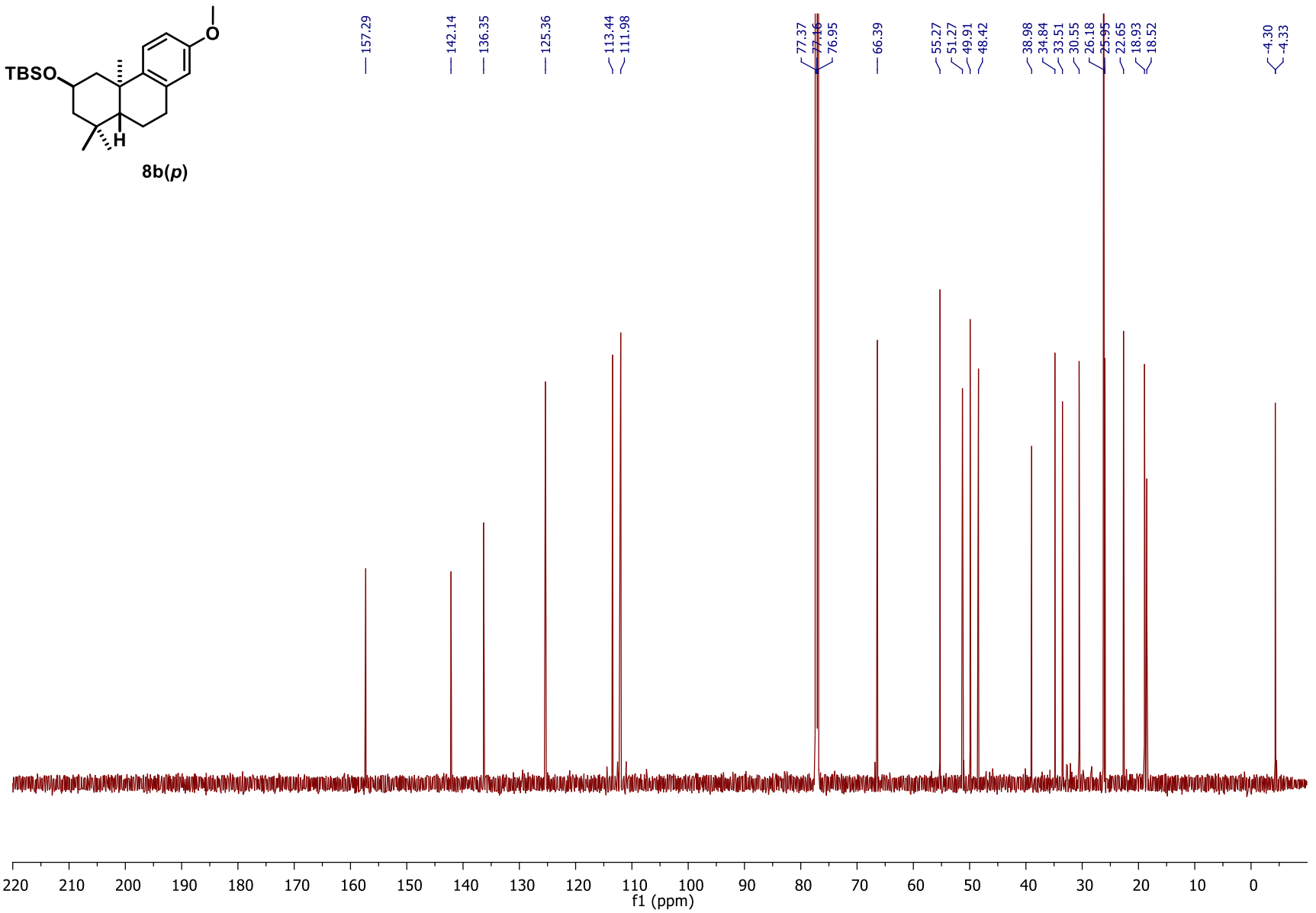

TBSO
O
O
H
8a
7.26
6.28
6.28
6.20
6.19
4.04
4.03
4.02
4.01
4.01
4.00
3.99
3.98
3.97
3.77
3.76
3.41
3.41
3.39
2.88
2.86
2.84
2.82
1.73
1.72
1.71
1.70
1.70
1.69
1.54
1.29
1.26
1.25
1.24
1.23
1.15
1.12
1.10
0.99
0.95
0.94
0.12
1.00
0.99
1.08
3.18
2.91
1.02
1.97
1.06
1.32
1.31
3.45
2.47
1.43
3.35
3.46
8.55
6.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

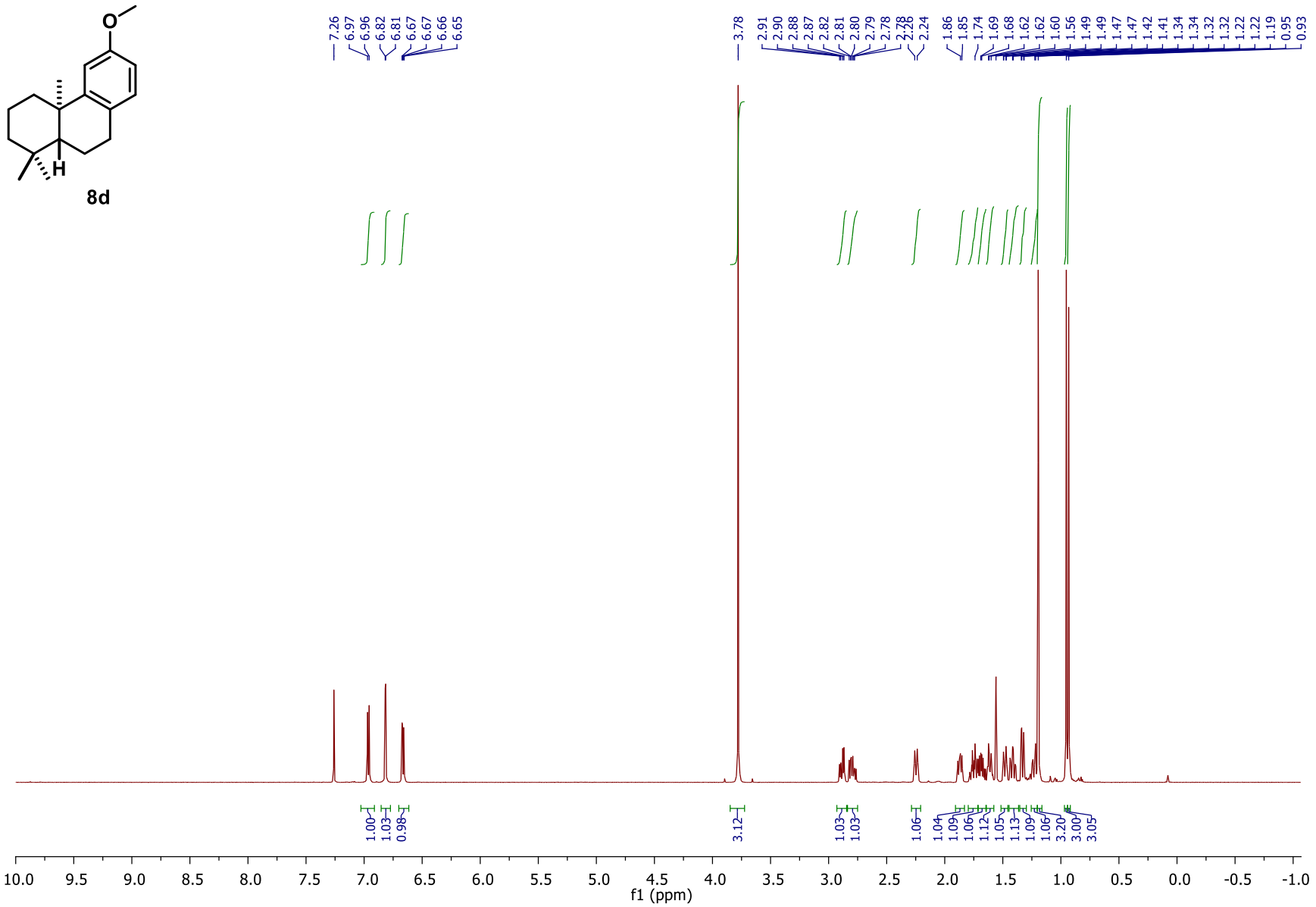

TBSO
O
O
H
8a
159.55
158.04
138.59
129.77
105.05
97.69
77.41
77.16
76.91
66.54
55.24
55.12
52.93
51.07
46.09
40.44
34.78
34.18
33.55
26.25
23.12
20.90
18.82
18.64
-4.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

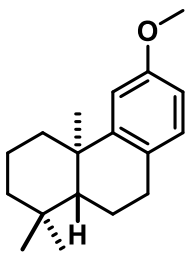

TBSO
O
H
8b(o)
7.26
7.06
7.05
7.03
6.68
6.67
6.67
4.05
4.04
4.04
4.03
4.02
4.02
4.01
4.00
4.00
3.79
3.46
3.45
3.44
2.88
2.87
2.86
2.86
1.81
1.73
1.73
1.72
1.71
1.71
1.71
1.70
1.32
1.28
1.26
1.24
1.16
1.15
1.00
0.96
0.12
0.95
1.94
1.00
3.30
1.02
2.09
0.97
1.04
3.25
2.59
1.15
3.03
3.15
8.73
5.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


TBSO
O
H
8b(o)
158.56
138.01
136.87
126.27
122.43
109.27
77.37
77.16
76.95
66.49
55.13
52.74
51.04
45.77
40.94
34.80
34.18
33.05
26.25
23.19
20.70
18.77
18.65
-4.31
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBSO
O
H
8b(p)
7.26 7.18 7.17 6.71 6.70 6.69 6.69 6.58 6.57
4.06 4.05 4.04 4.04 4.03 4.03 4.02 4.01 4.01 3.76
2.92 2.91 2.87 2.86 2.85
2.45 2.43 2.43
1.71 1.71 1.38 1.32 1.31 1.29 1.29 1.28 1.26 1.24 1.18 0.99 0.96 0.94 0.13 0.12
1.00 0.97 0.96 1.04 3.11 1.01 1.06 1.03 1.00 1.33 0.87 1.06 1.08 1.43 2.99 3.13 3.43 8.72 2.81 2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

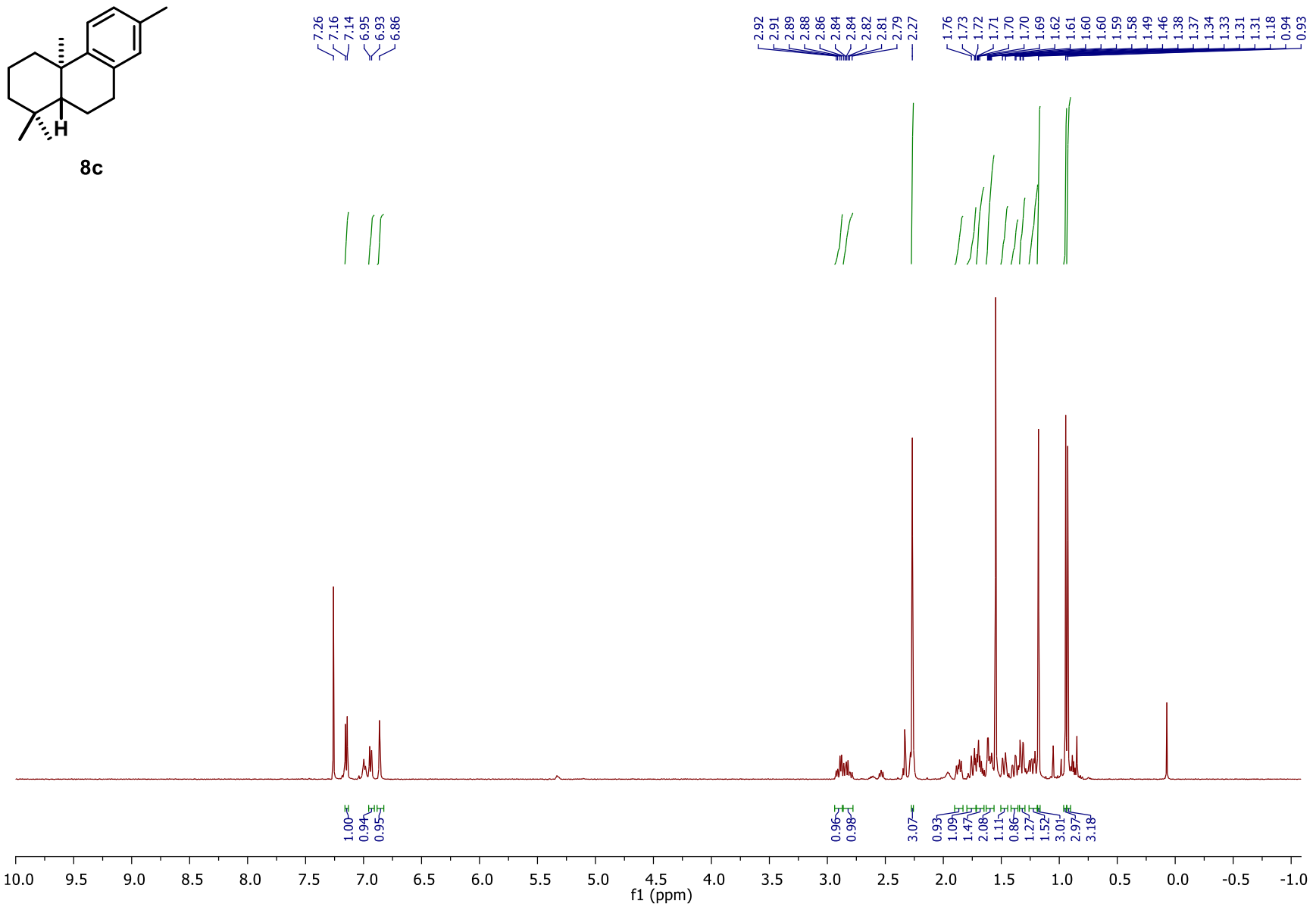

TBSO
O
H
8b(p)
157.29
142.14
136.35
125.36
113.44
111.98
77.37
77.16
76.95
66.39
55.27
51.27
49.91
48.42
38.98
34.84
33.51
30.55
26.18
25.95
22.65
18.93
18.52
-4.30
-4.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

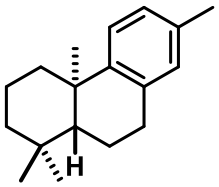

O
H
8d
7.26
6.97
6.96
6.82
6.81
6.67
6.67
6.66
6.65
3.78
2.91
2.90
2.88
2.87
2.82
2.81
2.80
2.79
2.78
2.24
1.86
1.85
1.74
1.69
1.68
1.62
1.62
1.60
1.56
1.49
1.49
1.47
1.47
1.42
1.41
1.34
1.32
1.32
1.22
1.22
1.19
0.95
0.93
1.00
1.03
0.98
3.12
1.03
1.03
1.06
1.04
1.09
1.06
1.12
1.05
1.13
1.09
1.06
3.20
3.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


O
H

8d

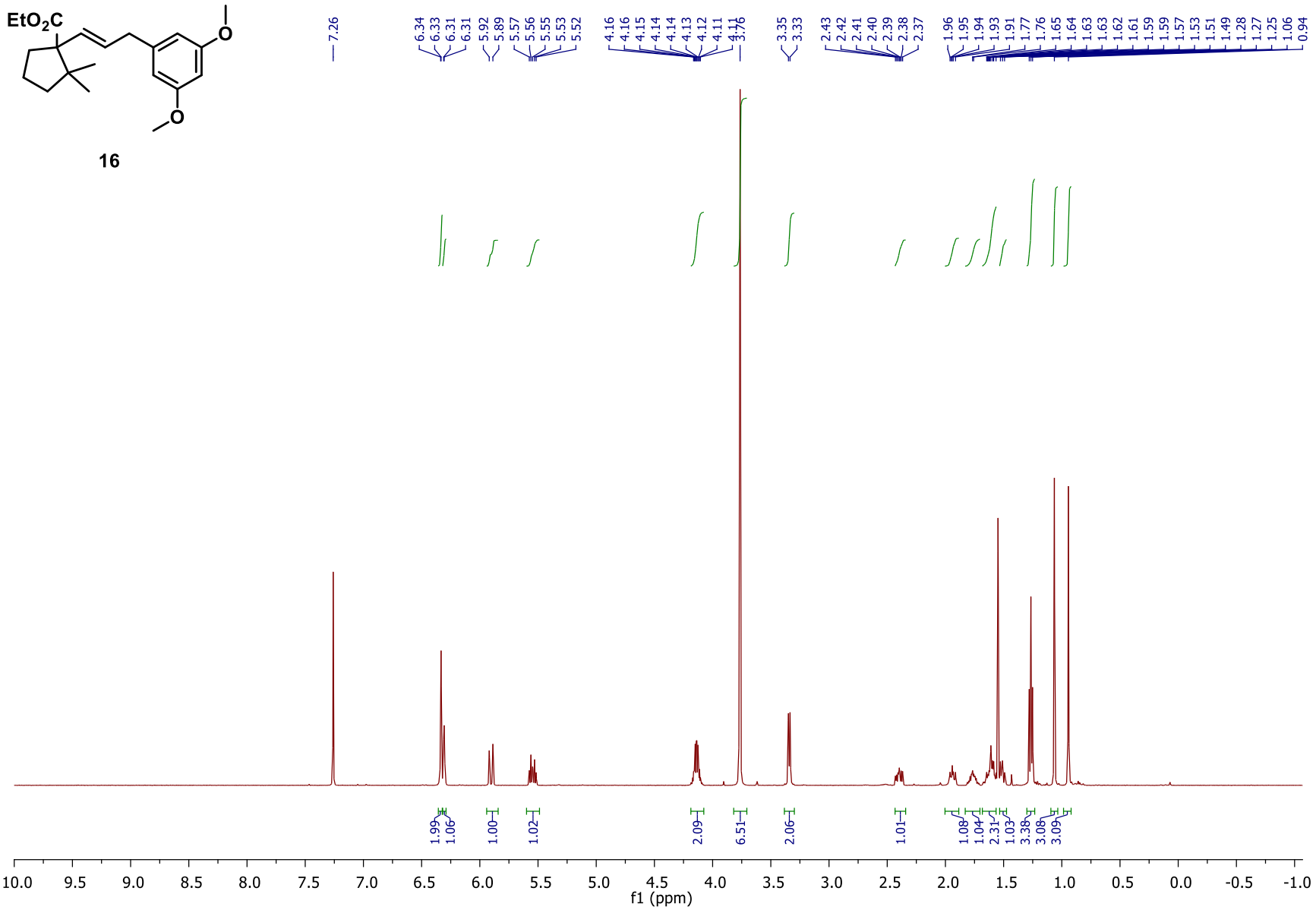
157.77
151.61
129.88
127.63
110.83
110.29
77.37
77.16
76.95
55.39
50.45
41.81
38.97
38.16
33.63
33.46
29.70
24.89
21.80
19.45
19.28
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

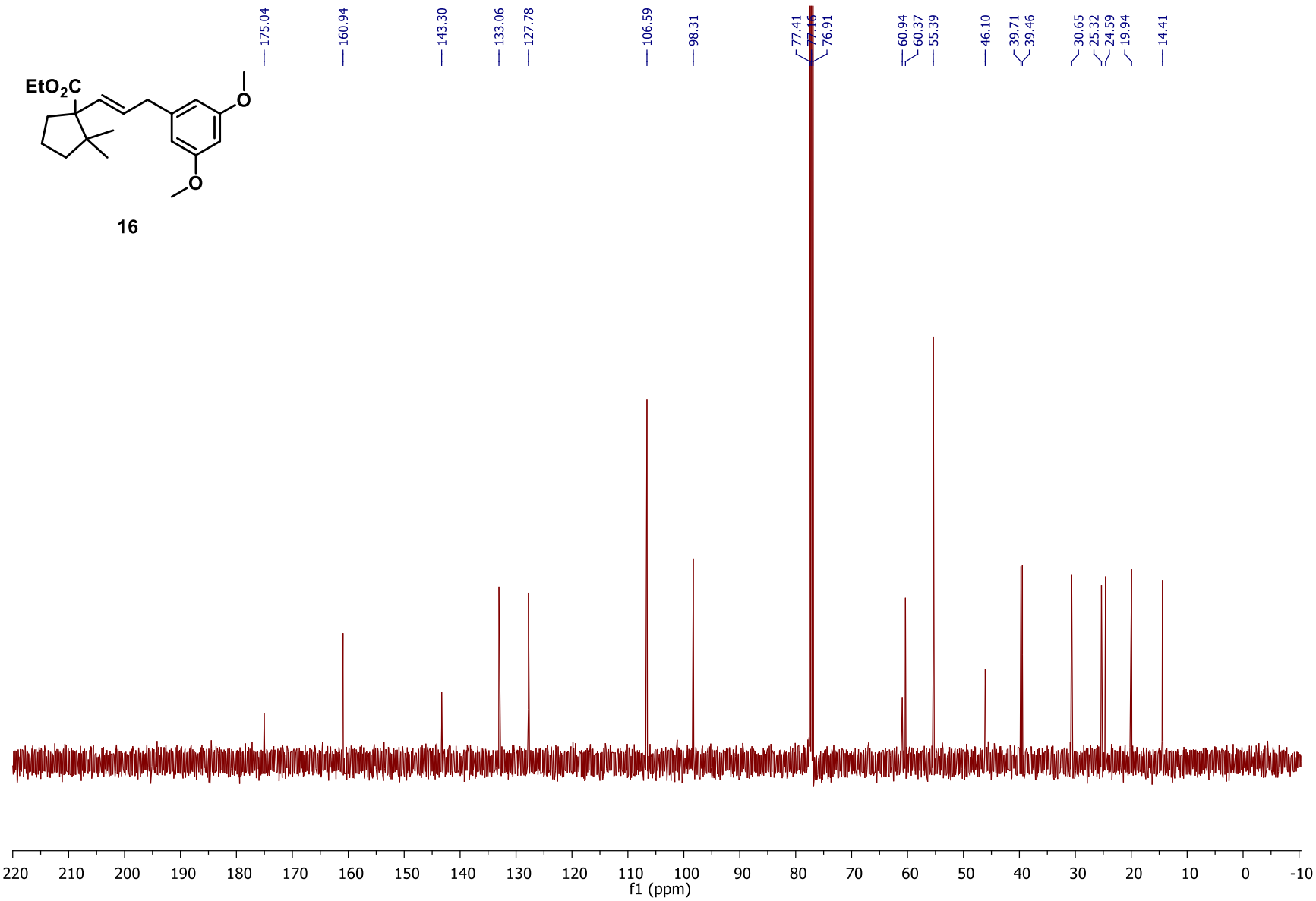

8c
7.26
7.16
7.14
6.95
6.93
6.86
2.92
2.91
2.89
2.88
2.86
2.84
2.84
2.82
2.81
2.79
2.27
1.76
1.73
1.72
1.71
1.70
1.70
1.69
1.62
1.61
1.60
1.60
1.59
1.58
1.49
1.46
1.38
1.37
1.34
1.33
1.31
1.31
1.18
0.94
0.93
1.00
0.94
0.95
0.96
0.98
3.07
0.93
1.09
1.47
2.08
1.11
0.86
1.27
1.52
3.01
2.97
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

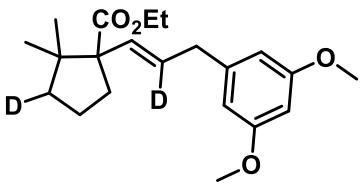

H

8c

147.51
135.26
134.68
129.70
126.61
124.47
77.37
77.16
76.95
50.65
41.87
39.05
37.63
33.58
33.47
30.49
25.03
21.76
20.94
19.47
19.19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

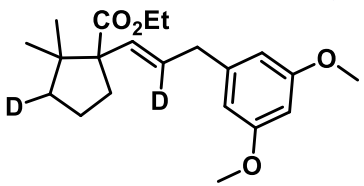

EtO2C
O
O
16
7.26
6.34
6.33
6.31
6.31
5.92
5.89
5.57
5.56
5.55
5.53
5.52
4.16
4.16
4.15
4.14
4.14
4.13
4.12
4.11
4.11
3.76
3.35
3.33
2.43
2.42
2.41
2.40
2.39
2.38
2.37
1.96
1.95
1.94
1.93
1.91
1.77
1.76
1.65
1.64
1.63
1.63
1.62
1.61
1.59
1.59
1.57
1.53
1.51
1.49
1.28
1.27
1.25
1.06
0.94
1.99
1.06
1.00
1.02
2.09
6.51
2.06
1.01
1.08
1.04
2.31
1.03
3.38
3.08
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


175.04
160.94
143.30
133.06
127.78
106.59
98.31
77.41
77.16
76.91
60.94
60.37
55.39
46.10
39.71
39.46
30.65
25.32
24.59
19.94
14.41
EtO2C
O
O
16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2Et
D
D
O
O

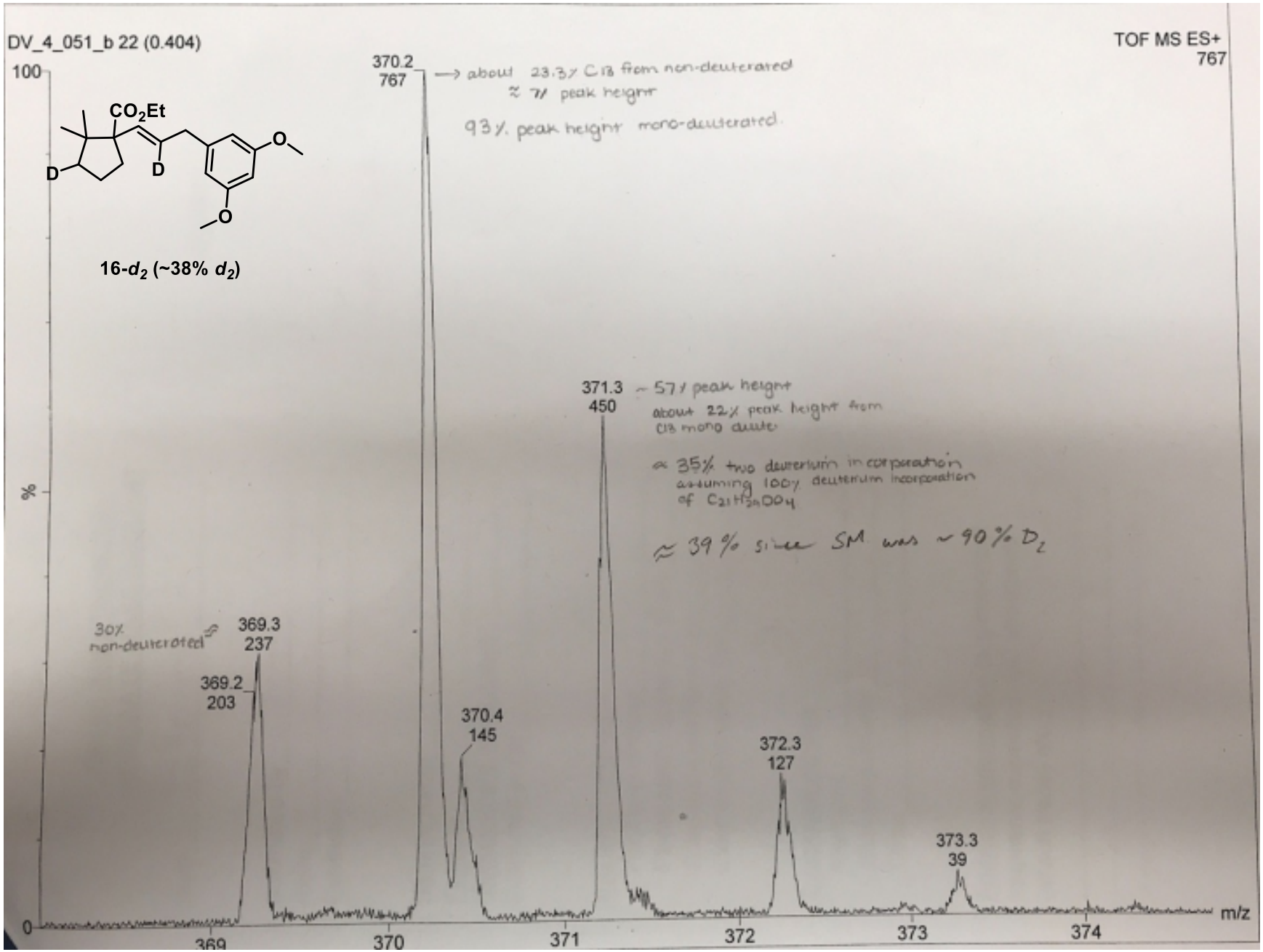
16-d_2 (~38% d_2)

7.26
6.34
6.33
6.31
6.31
5.90
4.18
4.17
4.16
4.15
4.14
4.13
4.11
3.76
3.34
2.42
2.42
2.40
2.38
2.37
1.95
1.94
1.93
1.92
1.77
1.76
1.61
1.60
1.59
1.52
1.51
1.49
1.28
1.27
1.25
1.06
0.94
1.77
1.01
1.00
1.96
6.37
2.04
0.99
0.92
0.94
2.04
0.96
3.74
3.12
2.97
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

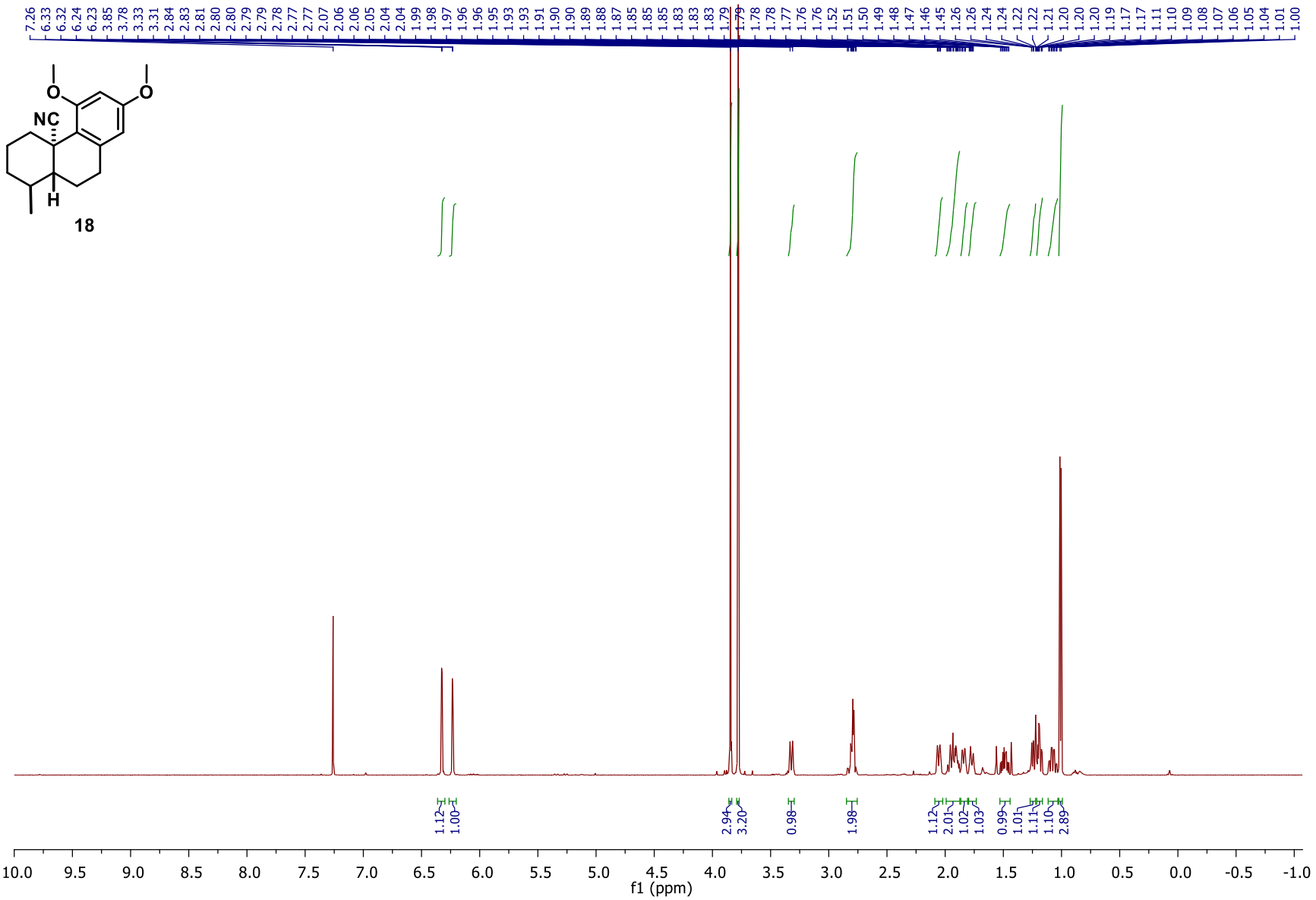

CO2Et
D
D
O
O

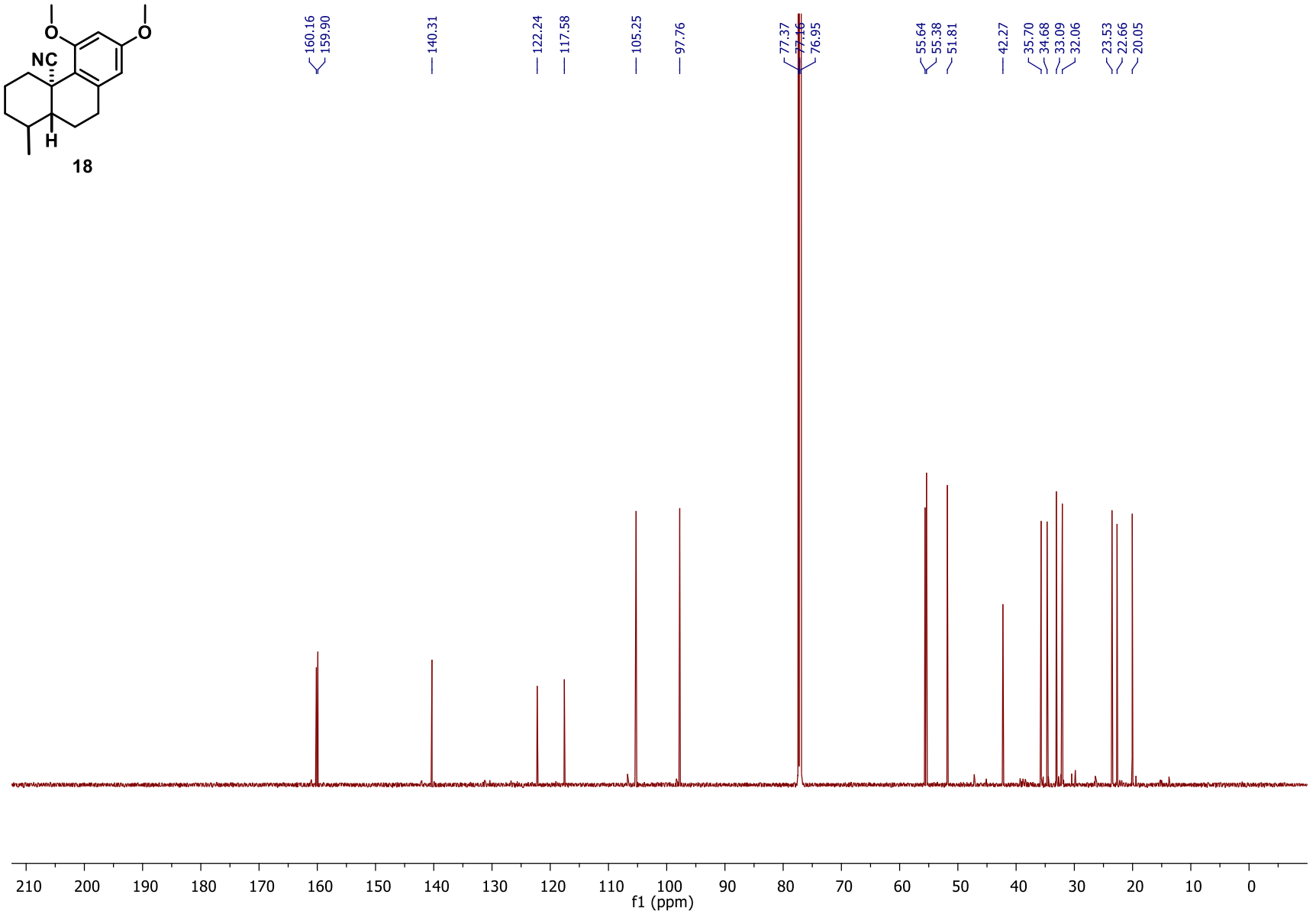
16-d_2 (~38% d_2)

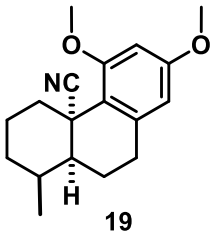
175.04
160.92
143.29
132.94
127.60
127.45
127.30
106.56
98.28
77.37
77.16
76.95
60.91
60.37
55.38
46.10
39.59
39.43
30.62
25.31
24.58
19.92
14.41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


DV_4_051_b 22 (0.404)
TOF MS ES+
767
100
%
0
370.2
767
→ about 23.3% C13 from non-deuterated
≈ 7% peak height
93% peak height mono-deuterated
371.3
450
~57% peak height
about 22% peak height from C13 mono deute
≈ 35% two deuterium incorporation assuming 100% deuterium incorporation of C21H32D2O4
≈ 39% since SM was ~90% D2
30% non-deuterated
369.3
237
369.2
203
370.4
145
372.3
127
373.3
39
369
370
371
372
373
374
m/z
CO2Et
D
D
O
O

16-d_2 (~38% d_2)

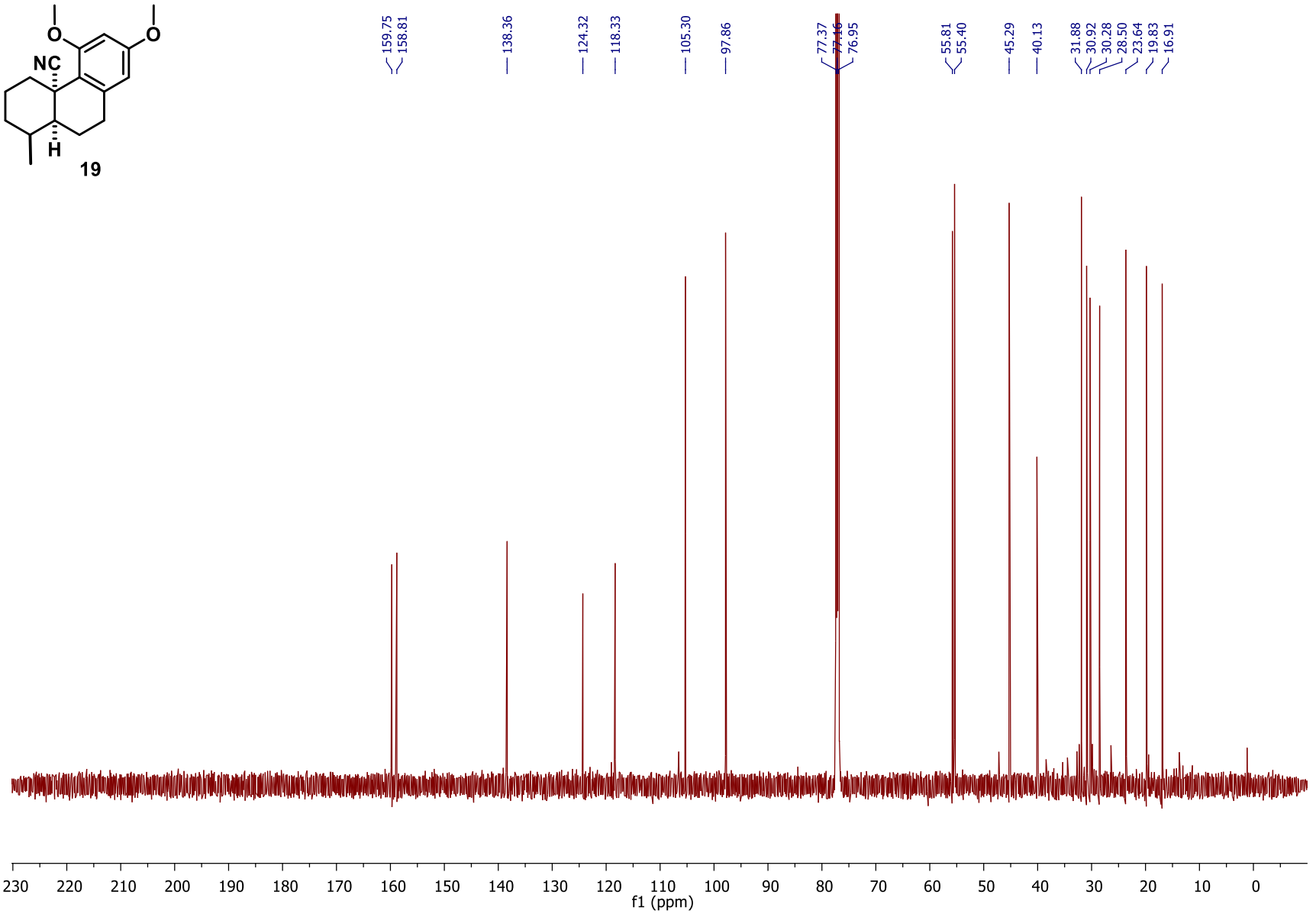

7.26 6.33 6.32 6.24 6.23 3.85 3.78 3.33 3.31 2.84 2.83 2.81 2.80 2.80 2.79 2.79 2.78 2.77 2.77 2.07 2.06 2.06 2.05 2.04 2.04 1.99 1.98 1.97 1.96 1.96 1.95 1.93 1.93 1.91 1.90 1.90 1.89 1.88 1.87 1.85 1.85 1.85 1.83 1.83 1.79 1.79 1.78 1.78 1.77 1.76 1.76 1.52 1.51 1.50 1.49 1.48 1.47 1.46 1.45 1.26 1.26 1.24 1.24 1.22 1.22 1.21 1.20 1.20 1.20 1.19 1.17 1.17 1.11 1.10 1.09 1.08 1.07 1.06 1.05 1.04 1.01 1.00
O
O
NC
H
18
1.12 1.00 2.94 3.20 0.98 1.98 1.12 2.01 1.02 1.03 0.99 1.01 1.11 1.10 2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

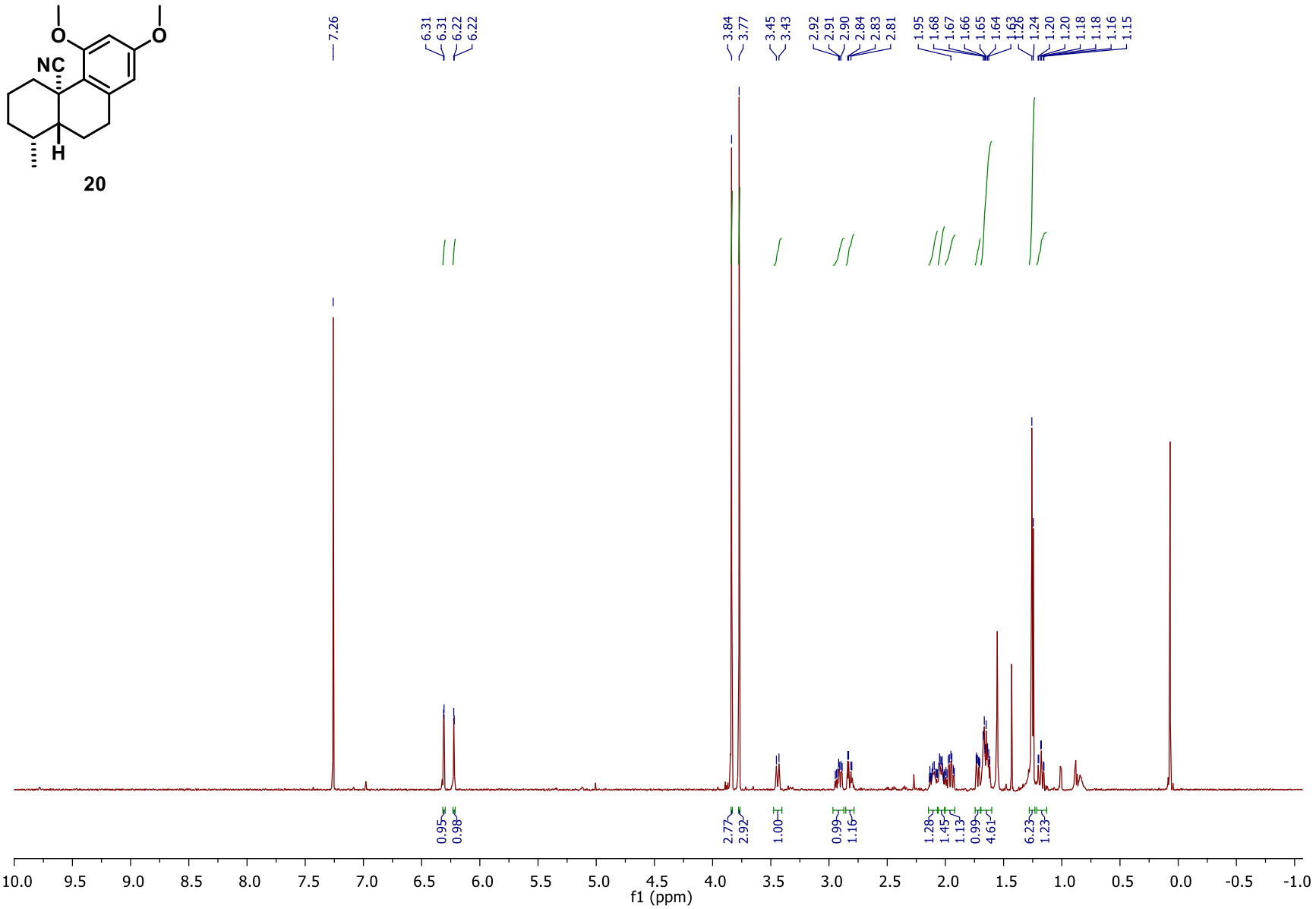

O
O
NC
H
18
160.16
159.90
140.31
122.24
117.58
105.25
97.76
77.37
77.16
76.95
55.64
55.38
51.81
42.27
35.70
34.68
33.09
32.06
23.53
22.66
20.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

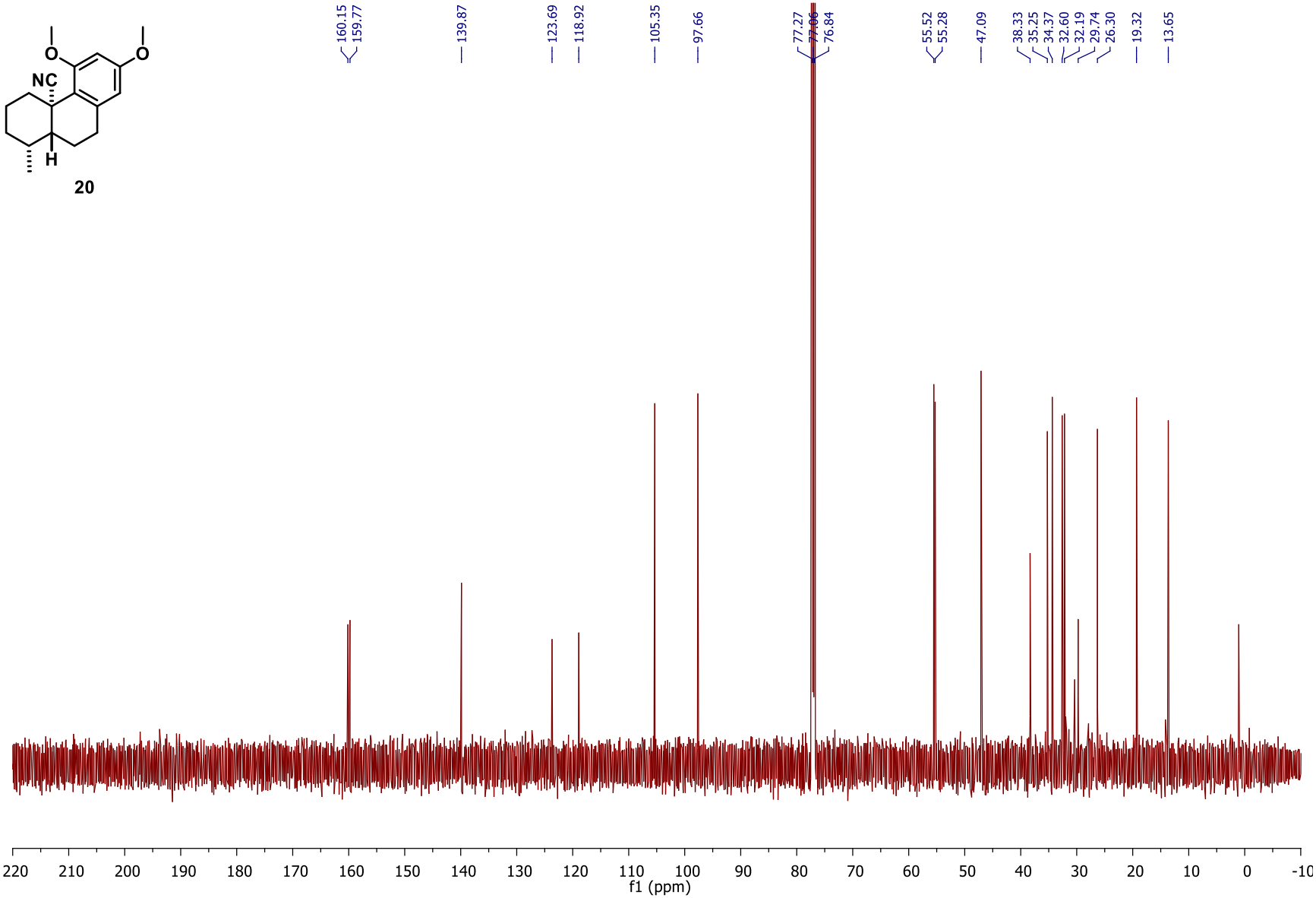

O
O
NC
H

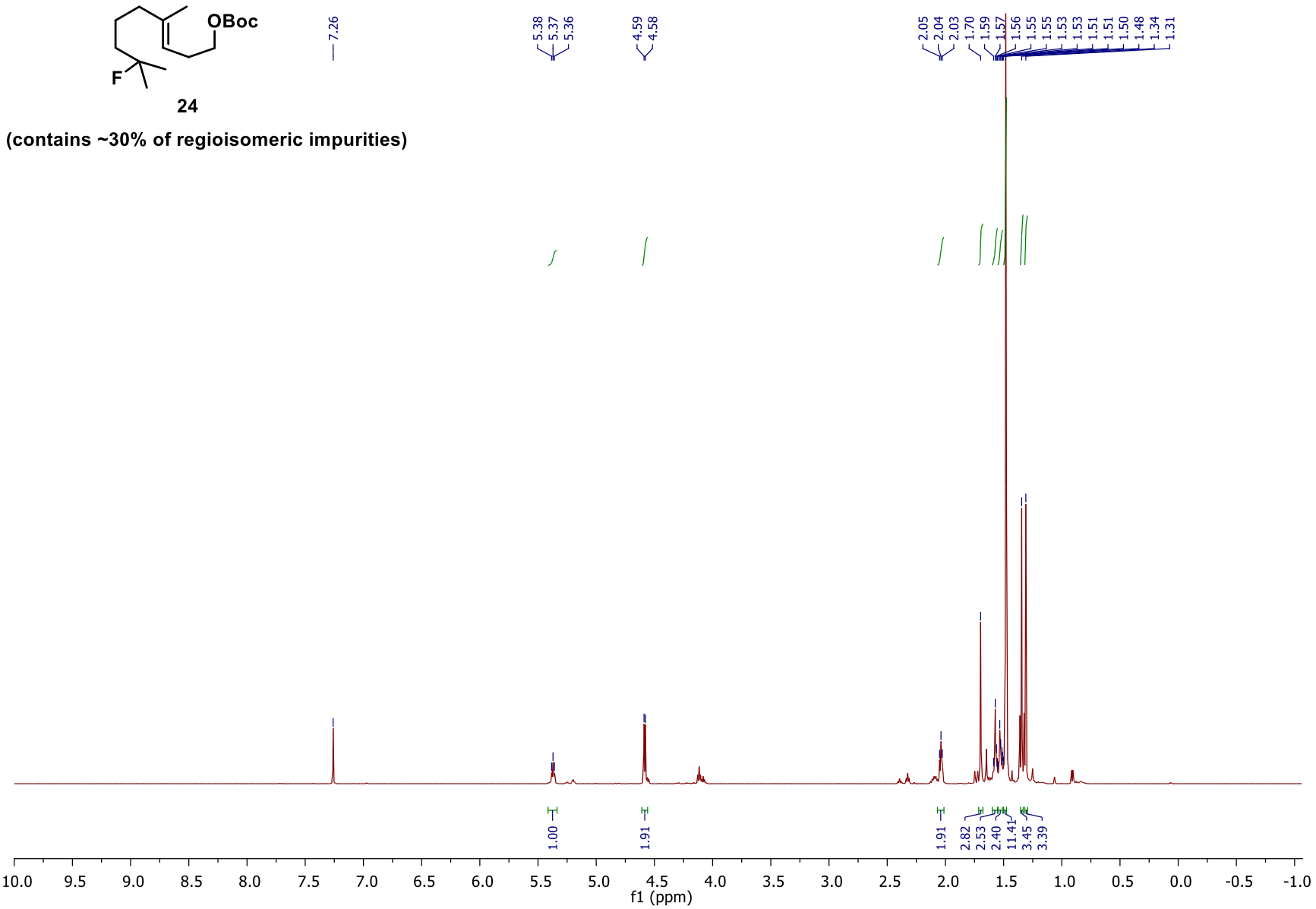
19

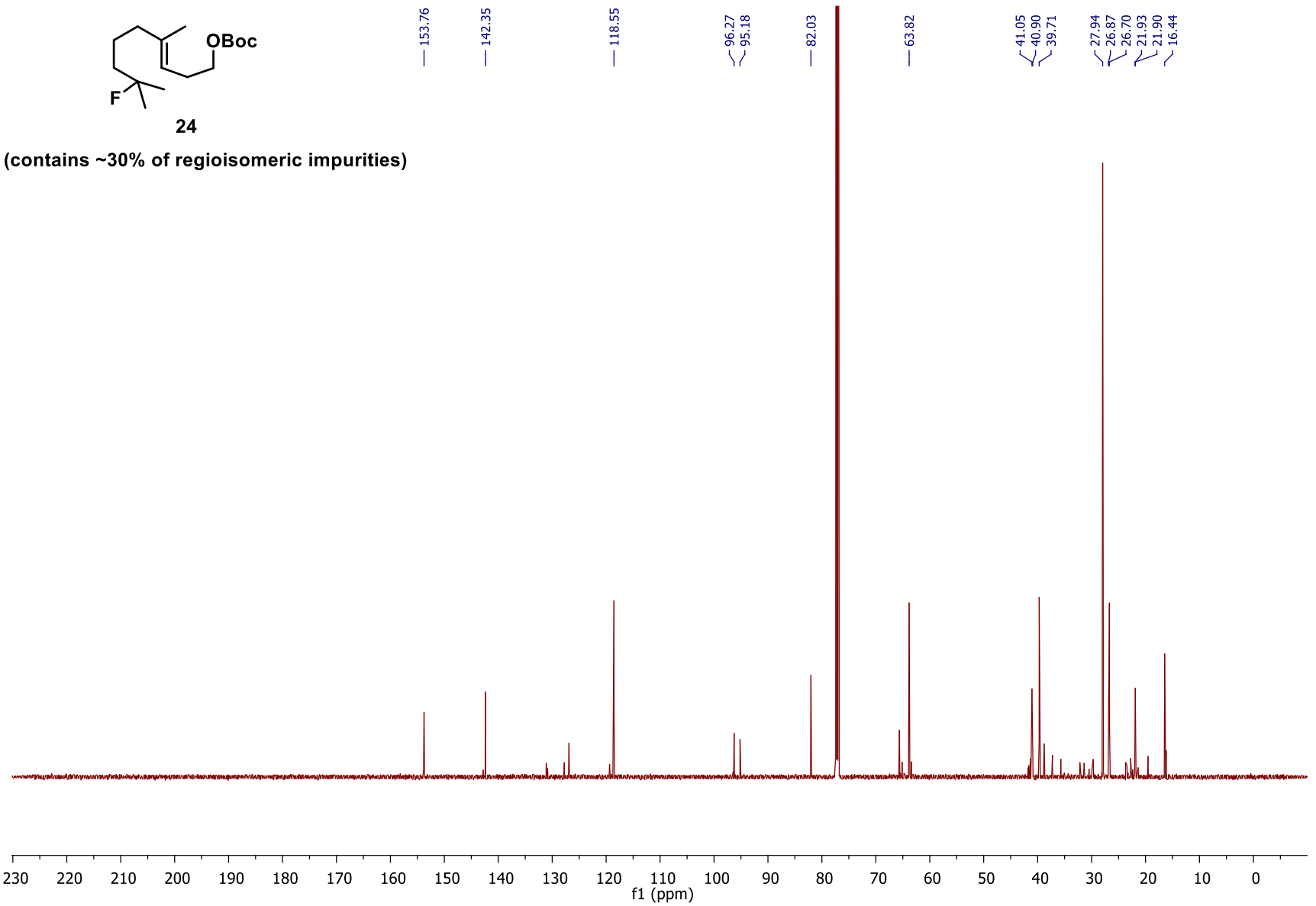
7.26
6.35
6.35
6.24
6.23
3.88
3.78
2.83
2.82
2.81
2.80
2.79
2.78
2.77
2.75
2.45
2.42
2.36
2.04
2.02
1.83
1.83
1.82
1.81
1.81
1.80
1.80
1.79
1.70
1.68
1.58
1.56
1.55
1.48
1.46
1.45
1.14
1.14
1.12
1.12
1.02
1.01
1.03
0.99
3.00
3.18
2.05
1.00
1.00
1.18
2.09
1.30
0.93
1.06
1.07
0.99
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

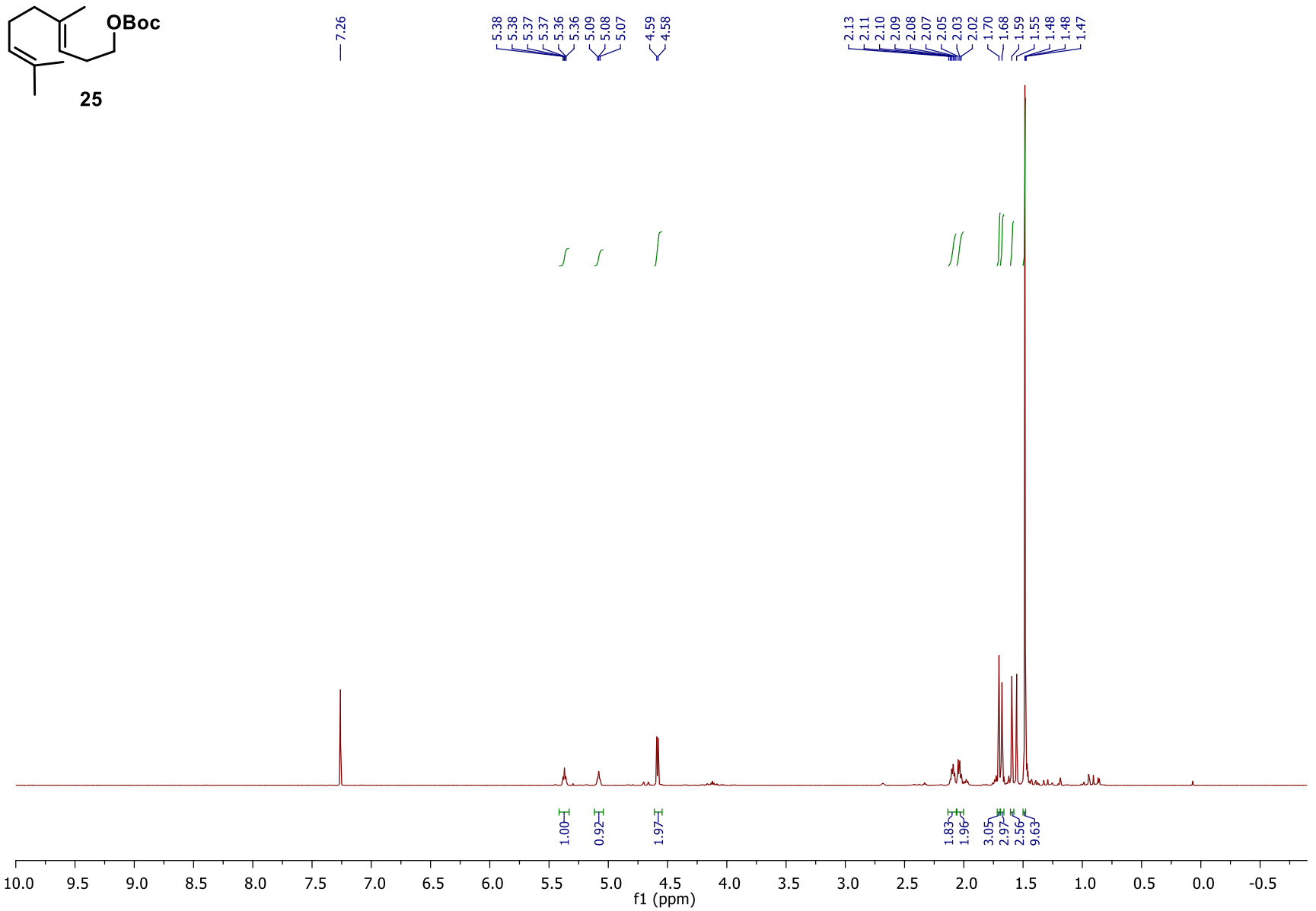

O
O
NC
H
19
159.75
158.81
138.36
124.32
118.33
105.30
97.86
77.37
77.16
76.95
55.81
55.40
45.29
40.13
31.88
30.92
30.28
28.50
23.64
19.83
16.91
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

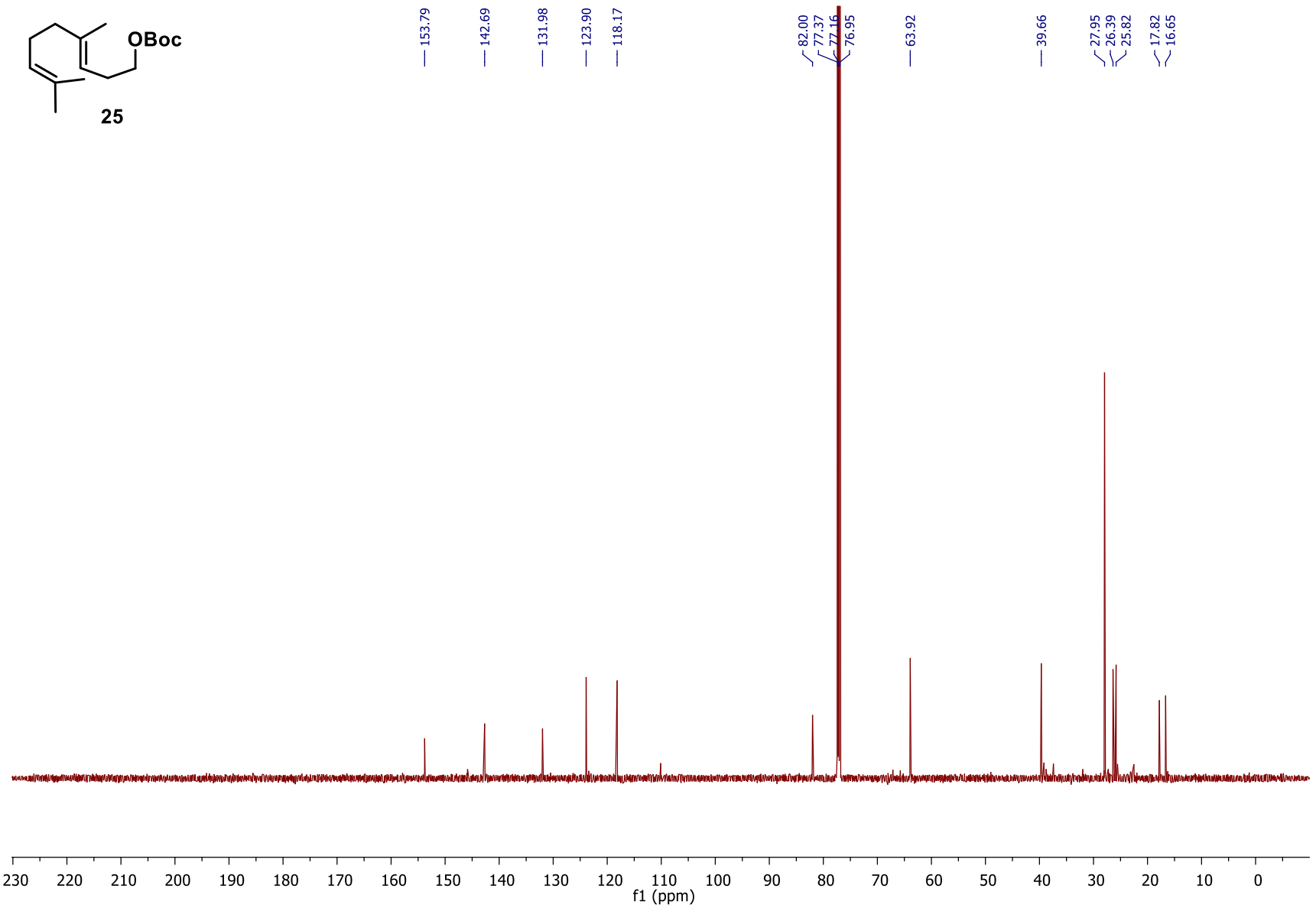

O
O
NC
H
20
7.26
6.31
6.31
6.22
6.22
3.84
3.77
3.45
3.43
2.92
2.91
2.90
2.84
2.83
2.81
1.95
1.68
1.67
1.66
1.65
1.64
1.63
1.26
1.24
1.20
1.20
1.18
1.18
1.16
1.15
0.95
0.98
2.77
2.92
1.00
0.99
1.16
1.28
1.45
1.13
0.99
4.61
6.23
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

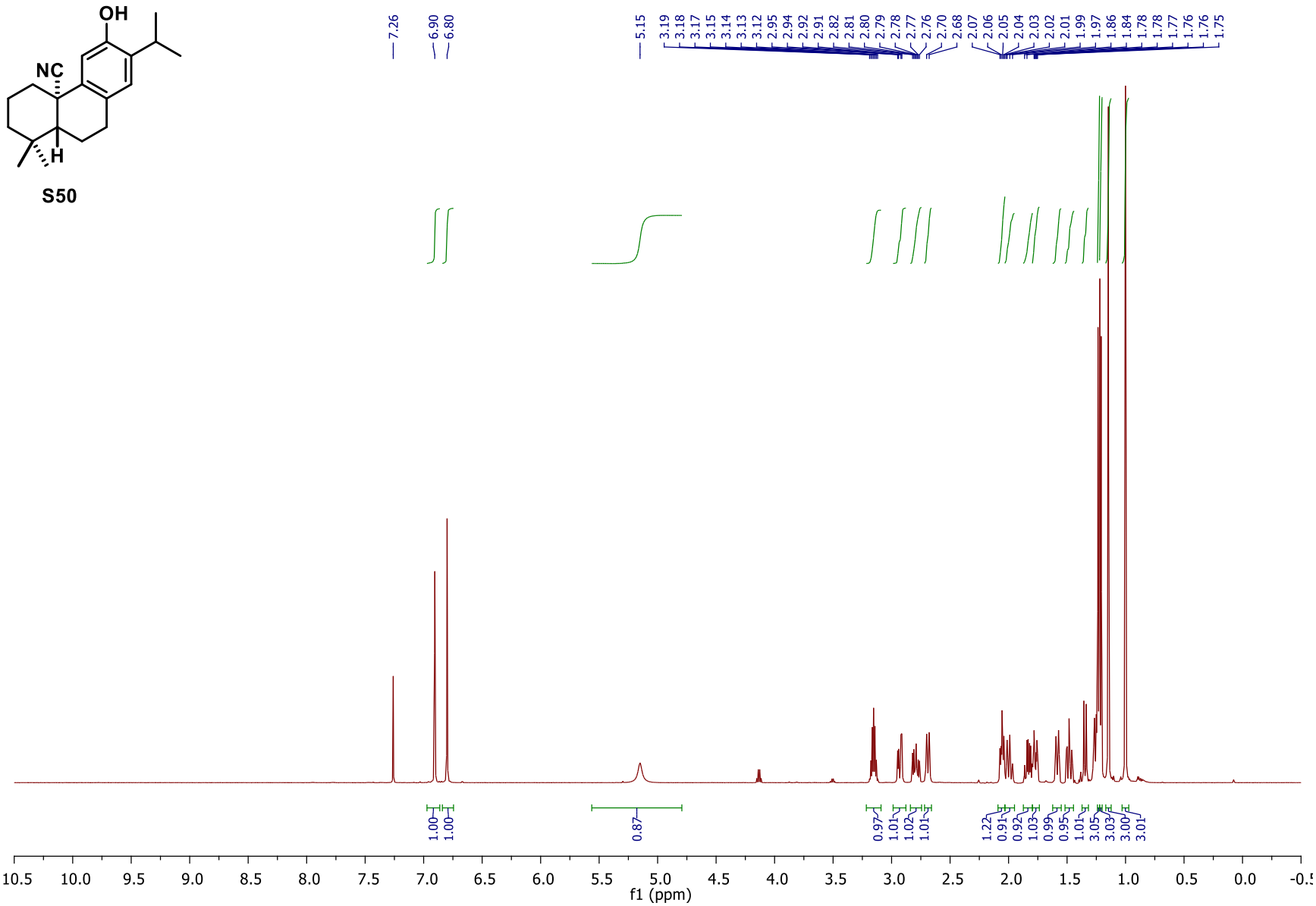

O
O
NC
H
20
160.15
159.77
139.87
123.69
118.92
105.35
97.66
77.27
77.06
76.84
55.52
55.28
47.09
38.33
35.25
34.37
32.60
32.19
29.74
26.30
19.32
13.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

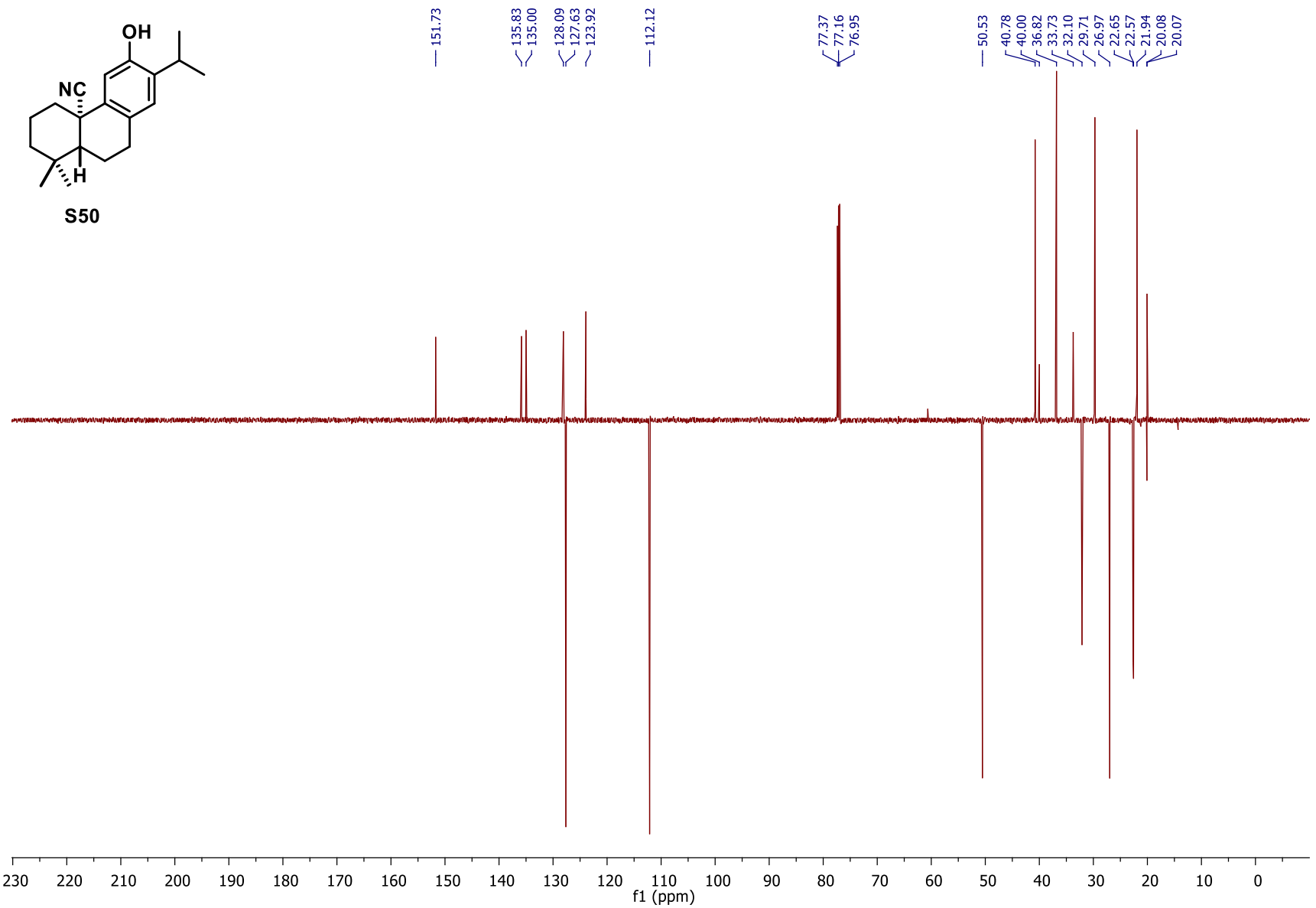

OBoc
F
24
(contains ~30% of regioisomeric impurities)
7.26
5.38
5.37
5.36
4.59
4.58
2.05
2.04
2.03
1.70
1.59
1.57
1.56
1.55
1.55
1.53
1.53
1.51
1.51
1.50
1.48
1.34
1.31
1.00
1.91
1.91
2.82
2.53
2.40
11.41
3.45
3.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

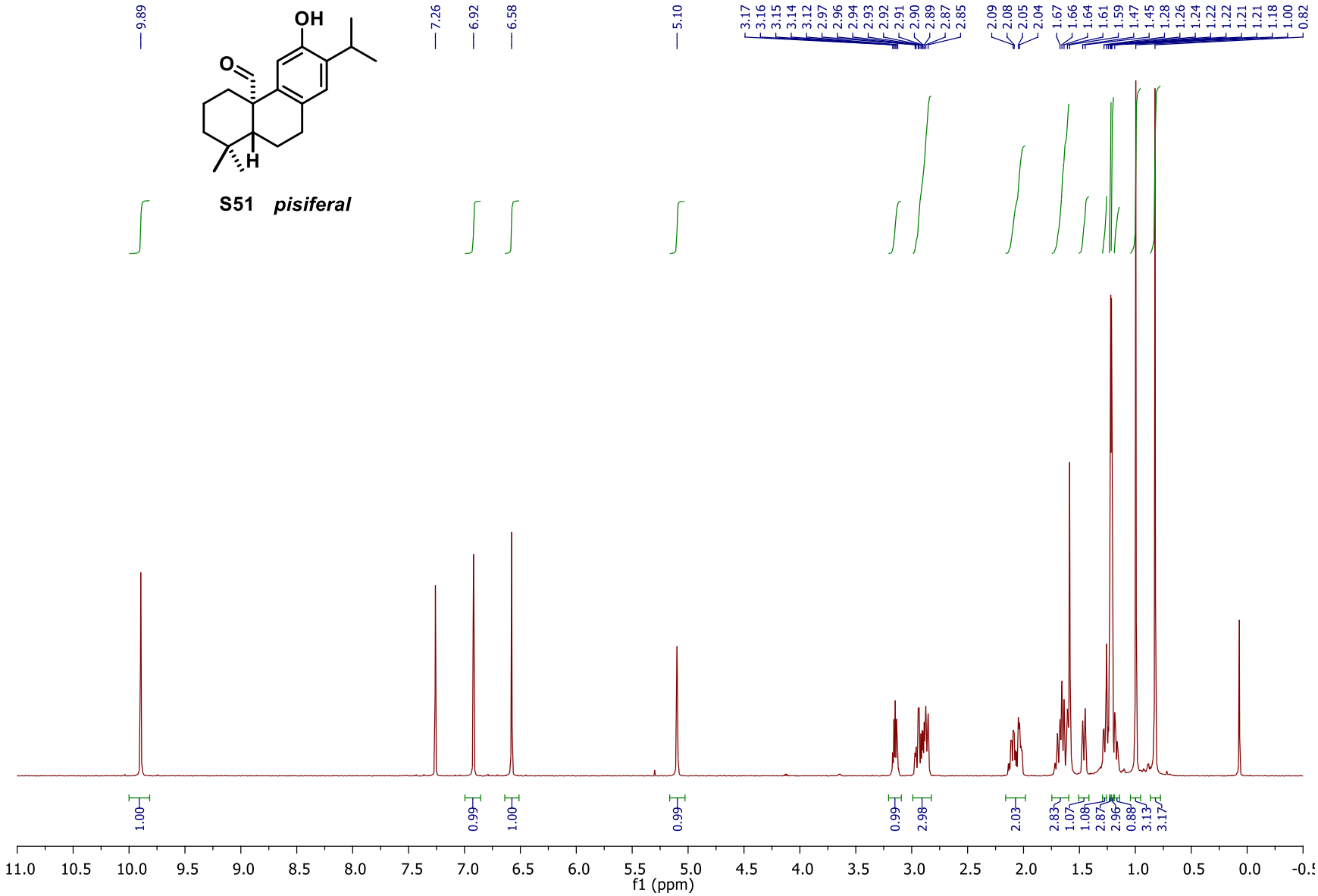

OBoc
F
24
(contains ~30% of regioisomeric impurities)
153.76
142.35
118.55
96.27
95.18
82.03
63.82
41.05
40.90
39.71
27.94
26.87
26.70
21.93
21.90
16.44
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OBoc
25
7.26
5.38
5.38
5.37
5.37
5.36
5.36
5.09
5.08
5.07
4.59
4.58
2.13
2.11
2.10
2.09
2.08
2.07
2.05
2.03
2.02
1.70
1.68
1.59
1.55
1.48
1.48
1.47
1.00
0.92
1.97
1.83
1.96
3.05
2.97
2.56
9.63
f1 (ppm)

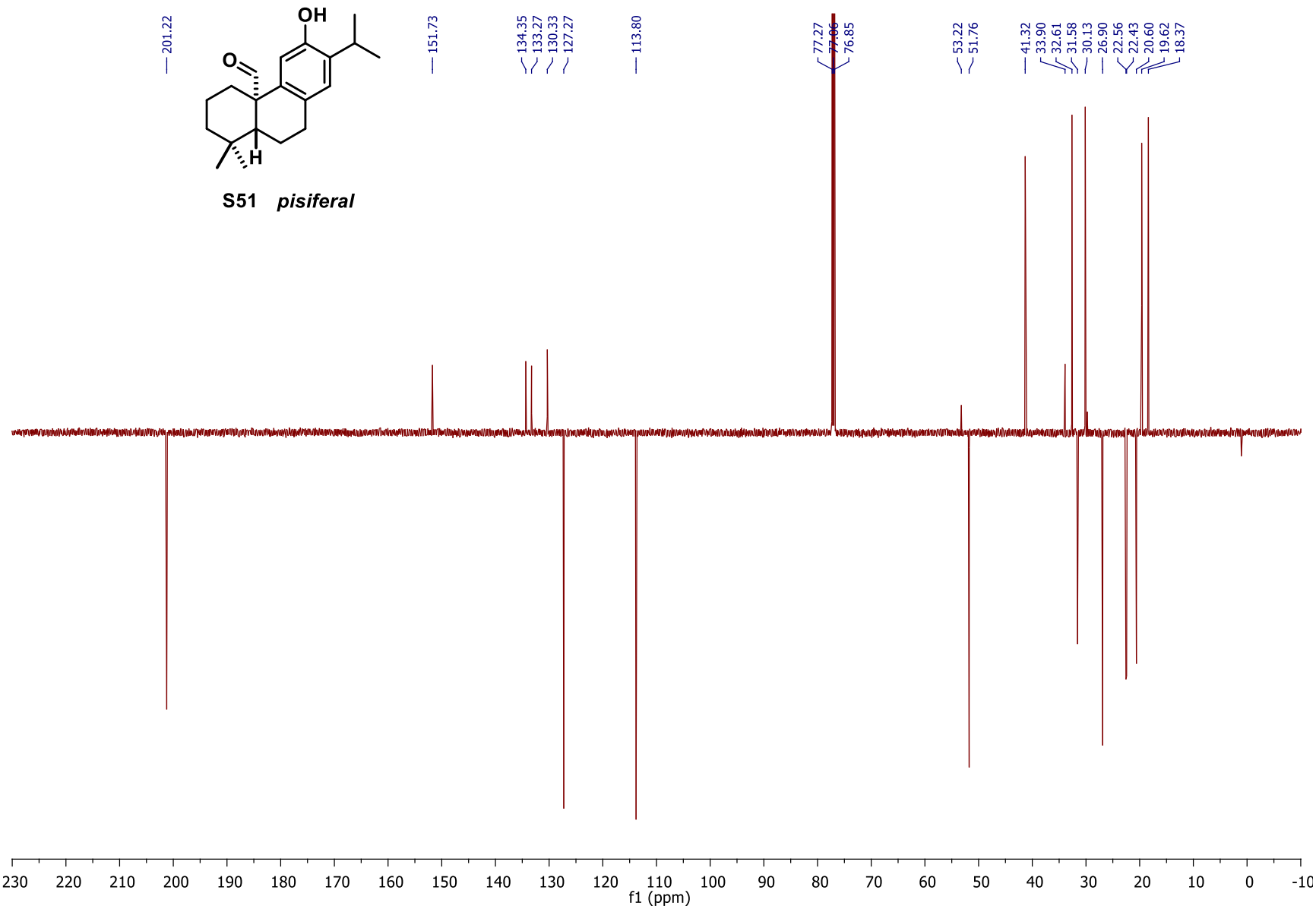

OBoc
25
153.79
142.69
131.98
123.90
118.17
82.00
77.37
77.16
76.95
63.92
39.66
27.95
26.39
25.82
17.82
16.65
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
NC
H
S50
7.26
6.90
6.80
5.15
3.19
3.18
3.17
3.15
3.14
3.13
3.12
2.95
2.94
2.92
2.91
2.82
2.81
2.80
2.79
2.78
2.77
2.76
2.70
2.68
2.07
2.06
2.05
2.04
2.03
2.02
2.01
1.99
1.97
1.86
1.84
1.78
1.77
1.76
1.76
1.75
1.00
1.00
0.87
0.97
1.01
1.02
1.01
1.22
0.91
0.92
1.03
0.99
0.95
1.01
3.05
3.03
3.00
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

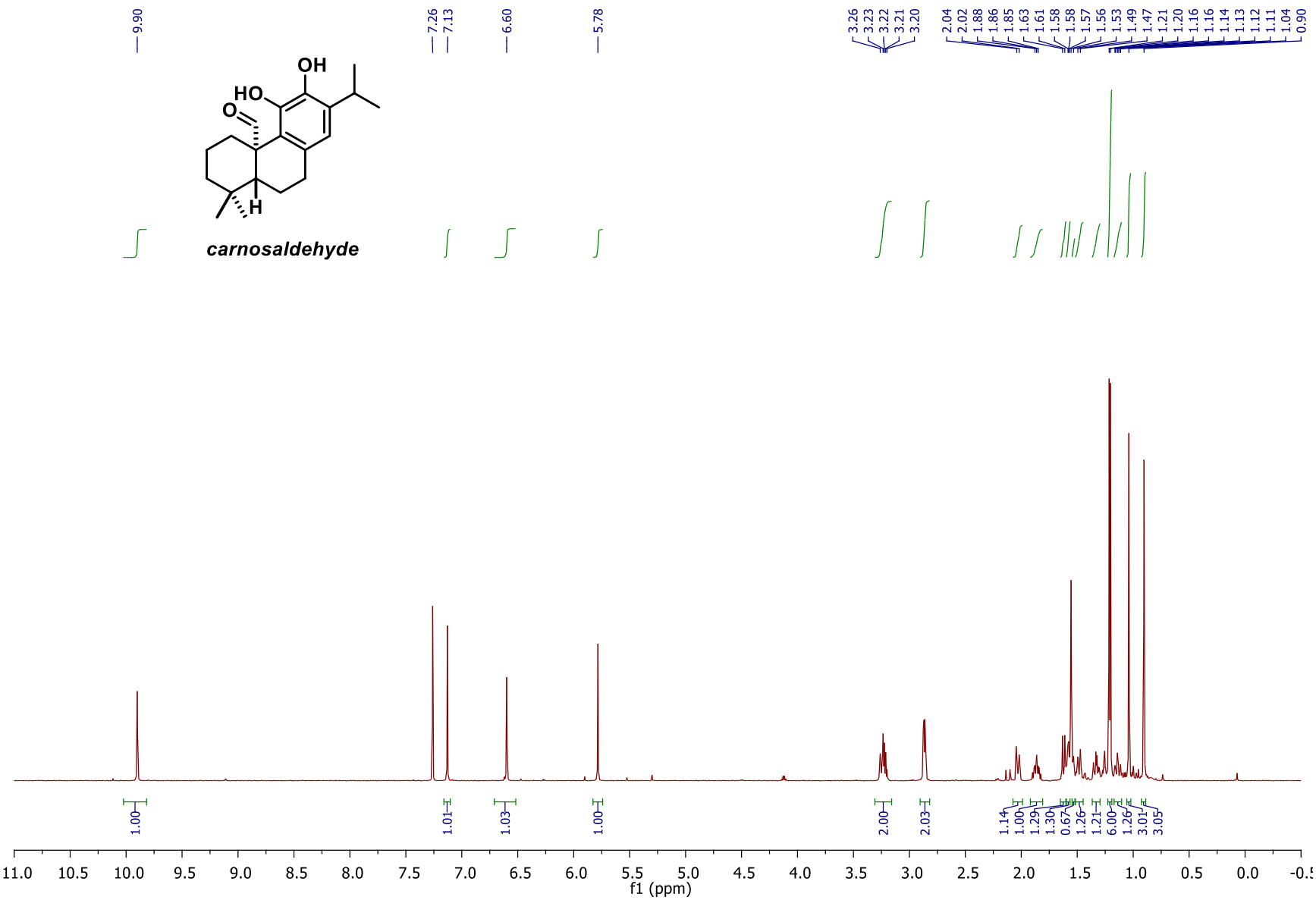

OH
NC
H
S50
151.73
135.83
135.00
128.09
127.63
123.92
112.12
77.37
77.16
76.95
50.53
40.78
40.00
36.82
33.73
32.10
29.71
26.97
22.65
22.57
21.94
20.08
20.07
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

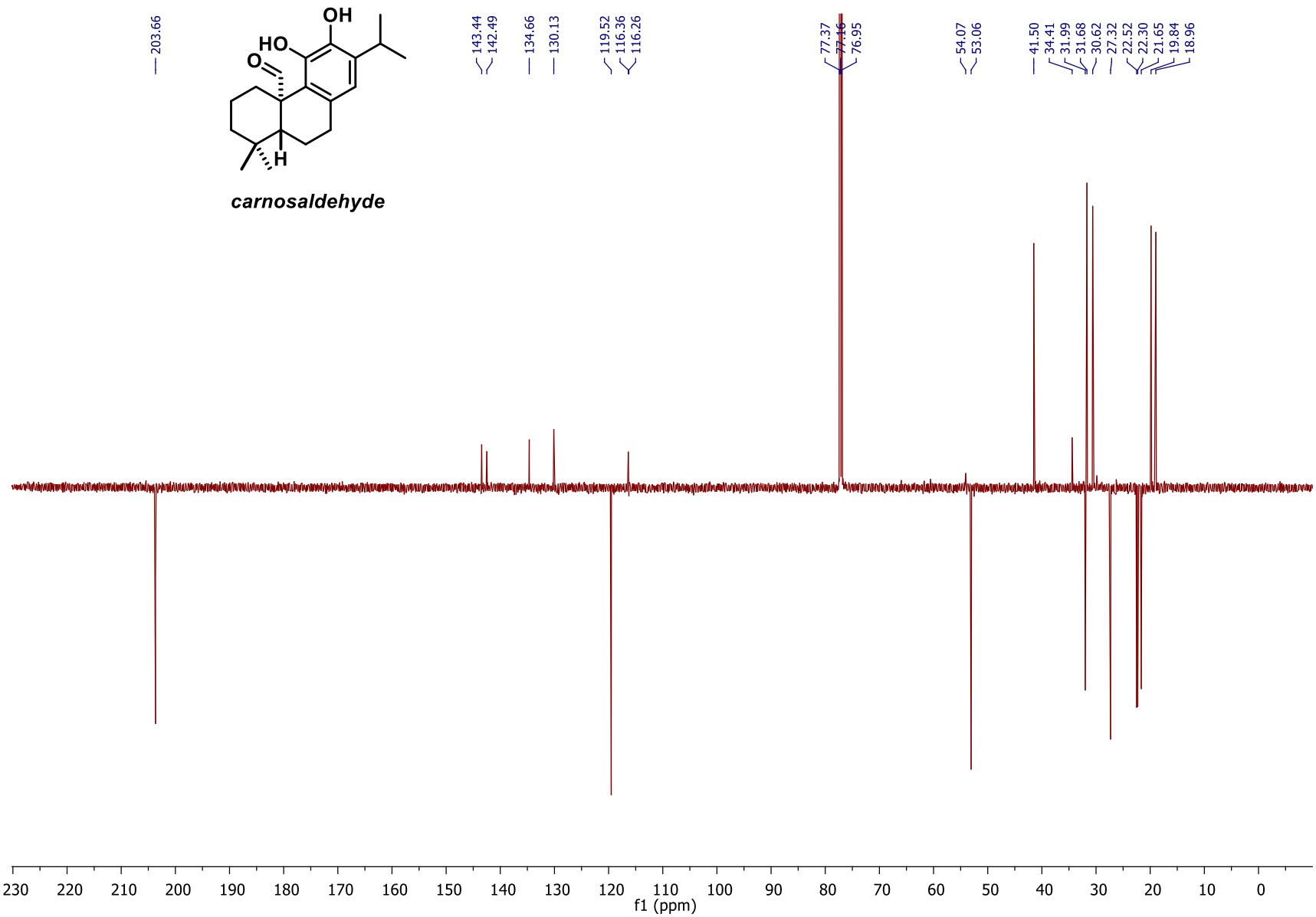


S51 ***pisiferal***

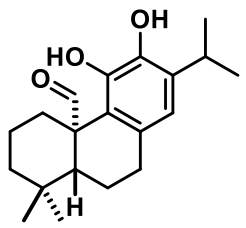


S51 ***pisiferal***


9.90
7.26
7.13
6.60
5.78
3.26
3.23
3.22
3.21
3.20
2.04
2.02
1.88
1.86
1.85
1.63
1.61
1.58
1.58
1.57
1.56
1.53
1.49
1.47
1.21
1.20
1.16
1.16
1.14
1.13
1.12
1.11
1.04
0.90
OH
HO
O
H
carnosaldehyde
1.00
1.01
1.03
1.00
2.00
2.03
1.14
1.00
1.29
1.30
0.67
1.26
1.21
6.00
1.26
3.01
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

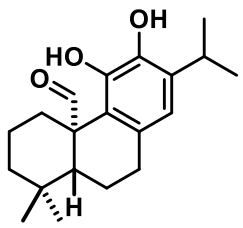

203.66
143.44
142.49
134.66
130.13
119.52
116.36
116.26
77.37
77.16
76.95
54.07
53.06
41.50
34.41
31.99
31.68
30.62
27.32
22.52
22.30
21.65
19.84
18.96
OH
HO
O
H
carnosaldehyde
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H COSY



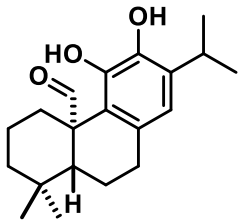
carnosaldehyde

^{1}H COSY



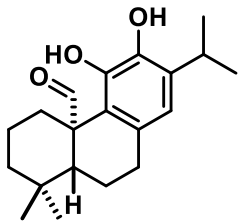
carnosaldehyde

HSQC



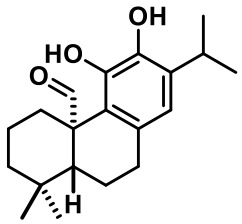
carnosaldehyde

HSQC



carnosaldehyde

^{1}H NOESY



carnosaldehyde

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