# Supporting Information

# Photoactive Electron Donor-Acceptor Complex Platform for Ni-Mediated C($sp^3$)–C($sp^2$) Bond Formation

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# I. General Considerations:

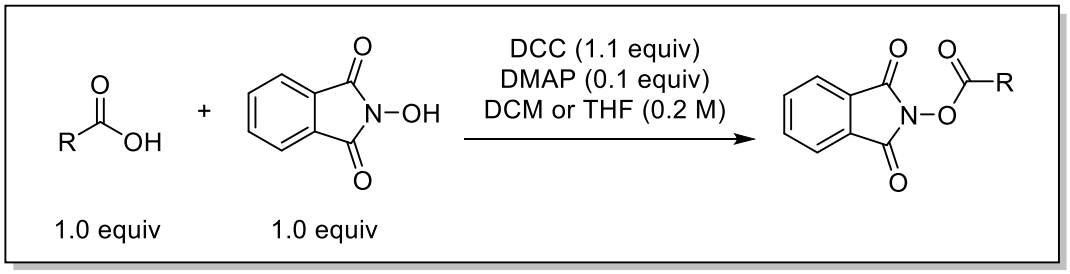
**General:** All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For purple and blue light irradiation, two Kessil PR160-purple LED lamps (30 W High Luminous DEX 2100 LED, $\lambda_{max}$ = 390 nm) or two Kessil A160WE Tuna Blue LED lamps (40 W, $\lambda_{max}$ = 456 nm) were placed 1.5 inches away from the reaction vials. NMR spectra ($^{1}$H, $^{13}$C, $^{19}$F) were obtained at 298 ºK using 300, 400 and 500 MHz spectrometers. $^{1}$H NMR spectra were referenced to residual, $CHCl_3$ (δ 7.26) in $CDCl_3$ or DMSO-*d*$_6$ (δ 2.50). $^{13}$C NMR spectra were referenced to $CDCl_3$ (δ 77.3) or DMSO-*d*$_6$ (δ 39.5). Reactions were monitored by LCMS, GC/MS, $^{1}$H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using ninhydrin, *p*-anisaldehyde stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® $R_f$ silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep $R_f$ Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

**Chemicals:** Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. $CH_2Cl_2$, EtOAc, hexanes, MeOH, $Et_2O$, and toluene were obtained from commercial suppliers and used as purchased. DMAP and DCC were purchased from commercial suppliers and used without further purification. THF and $CH_2Cl_2$ were purchased and dried *via* a solvent delivery system. Redox-active esters were prepared according to the literature.[1] Synthesis of all new redox-active esters is outlined here. Hantzsch-ester was obtained commercially or prepared according to the literature.[2] Aryl bromides were purchased from commercial suppliers. The Ni complex **46** was synthesized according to Martin et al. [3] All other reagents were purchased commercially and used as received. Photoredox-catalyzed reactions were performed using 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa). DMA

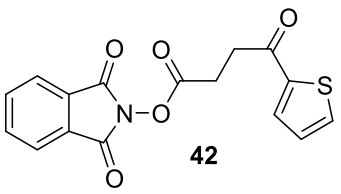
99.5% extra pure over molecular sieves was purchased from Acros Organics and used as received.

## II. Preparation of Redox-Active Esters

*General Procedure I:*



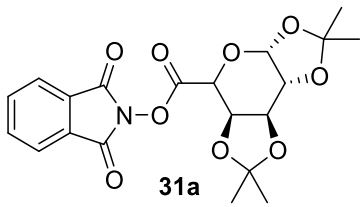

To a round-bottom flask equipped with a stir bar was added the corresponding carboxylic acid (if solid) (1.0 equiv), *N*-hydroxyphthalimide (1.0 equiv), and DMAP (0.1 equiv). The flask was then charged with $CH_2Cl_2$ or THF (0.2 M). At this point, carboxylic acid (1.0 equiv) was added via syringe (if liquid). DCC (1.1 equiv) was added, and the reaction was allowed to stir at rt until full consumption of the starting material. The mixture was then filtered over Celite and rinsed with additional $CH_2Cl_2$. The solvent was removed under reduced pressure, and the crude material was purified via flash chromatography.



**42**

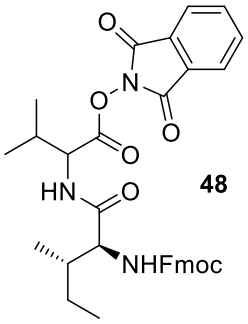
**1,3-Dioxoisoindolin-2-yl 4-oxo-4-(thiophen-2-yl)butanoate**, (20 mmol scale, 6.5 g, 70%) was prepared following procedure I. The product was obtained as a brown solid. **Mp** = 115 – 117 °C). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.81 – 7.73 (m, 3H), 7.64 (d, *J* = 4.9 Hz, 1H), 7.12 (t, *J* = 4.4 Hz, 1H), 3.39 (t, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 7.0 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 189.4, 169.2, 161.8 (2C), 143.1, 134.9 (2C), 134.2, 132.4, 128.9 (2C), 128.3, 124.0 (2C), 33.6, 25.4. **FT-IR** ($cm^{-1}$, neat, ATR) 1816, 1787, 1741, 1666, 1518,

1467, 1415, 1356, 1250, 1219, 1186. **HRMS** (ESI) calc for $C_{16}H_{12}NO_5S$ $[M+H]^+$: 330.0436, found: 330.0452.



31a

**1,3-Dioxoisoindolin 2 yl (3a*R*,5a*R*,8a*S*,8b*R*) 2,2,7,7 tetramethyltetrahydro 5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-carboxylate**, (20 mmol scale, 6.0 g, 72%) was prepared following General Procedure I. The product was obtained as a white solid. **Mp** = 176 – 178 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.82 – 7.76 (m, 2H), 5.70 (d, *J* = 5.0 Hz, 1H), 4.83 (d, *J* = 2.3 Hz, 1H), 4.73 (qd, *J* = 7.5, 2.5 Hz, 2H), 4.45 (dd, *J* = 5.1, 2.7 Hz, 1H), 1.54 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.9 (2C), 161.4, 134.9 (2C), 129.0, 128.9, 124.1 (2C), 111.0, 109.6, 96.6, 72.0, 70.9, 70.3, 68.4, 26.2, 26.0, 25.1, 24.9. **FT-IR** ($cm^{-1}$, neat, ATR) 2989, 2933, 1833, 1792, 1624, 1374, 1256, 1213, 1186, 1071. **HRMS** (ESI) calcd for $C_{20}H_{21}NO_9Na$ $[M+Na]^+$: 442.1114, found: 442.1118.



48

**1,3-Dioxoisoindolin-2-yl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-isoleucylvalinate**, (1.73 mmol scale, 383 mg, 37%) was prepared following the general procedure. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.81 – 7.70 (m, 4H), 7.59 – 7.56 (m, 2H), 7.44 – 7.27 (m, 4H), 6.50 – 6.43 (m, 1H), 5.43 – 5.33 (m, 1H), 4.96 (dd, *J* = 8.8, 5.0 Hz, 1H), 4.39 (q, *J* = 10.6, 8.1 Hz, 2H), 4.27 – 4.01 (m, 2H), 2.38 (dd, *J* = 12.9, 6.6 Hz, 1H), 2.04 – 1.84 (m, 1H), 1.62 (brs, 2H), 1.09 (dd, *J* = 6.9, 2.7 Hz, 6H), 0.93 (d, *J* = 10.3 Hz, 6H).**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 183.0, 172.8, 168.4, 161.6, 141.5 (2C), 135.0 (3C), 129.0 (2C), 127.9 (2C), 127.2 (4C), 125.2 (2C), 124.2 (2C), 120.1 (2C), 67.3, 55.7, 47.3, 37.5, 31.6, 18.9, 17.7, 15.8, 15.5, 11.6, 11.4. **FT-IR** ($cm^{-1}$, neat, ATR) 3298, 2966, 1789, 1746,

1661, 1537, 1467, 758, 696. **HRMS** (ESI) calc for $C_{34}H_{35}N_3NaO_7$ $[M+Na]^+$: 620.2367, found: 620.2370.

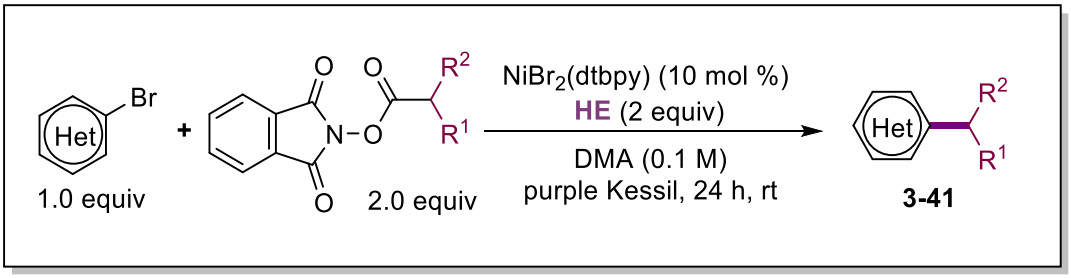
## III. Decarboxylative Arylation and Reaction Workflow

*Reaction Workflow:*

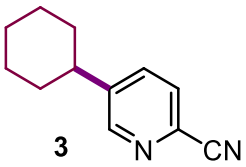
All photoredox reactions were performed with two Kessil PR160-purple LED lamps (30 W High Luminous DEX 2100 LED, 390 nm). The lamps were placed 1.5 inches away from the reaction vials within a ventilated fume hood. A typical reaction setup is shown below.

**Figure S1:** Typical reaction setup for the decarboxylative arylation.

*General Procedure II:*

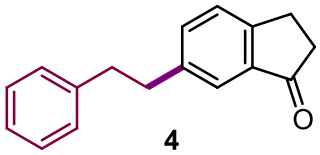


To an 8 mL vial equipped with a magnetic stir bar and a rubber septum was added $NiBr_2$(dtbpy) (10 mol %), Hantzsch-ester (2.0 equiv, 1.0 mmol), redox-active ester (2.0 equiv, 1.0 mmol), and aryl bromide (1.0 equiv, 0.50 mmol, if solid). The vial was evacuated three times via an inlet needle then purged with argon. The vial was then charged with dry, degassed DMA (0.1 M, 5 mL) via syringe. At this point, aryl bromide (1.0 equiv, 0.50 mmol) was added via syringe (if liquid). The reaction mixture was irradiated for 24 h with two Kessil PR160-purple LED lamps (30 W High Luminous DEX 2100 LED, $\lambda_{max}$ = 390 nm) as described in the "Workflow" section. The temperature of the reaction was maintained at approximately 24 °C via a fan. Upon completion, the reaction mixture was poured into a separatory funnel containing an aq 5% LiCl soln (15 mL) and extracted with $Et_2O$ or MTBE (methyl-*tert*-butyl ether, 3 x 15 mL). The combined organic layers were dried ($MgSO_4$), and all volatiles were removed under reduced pressure. The crude mixture was purified using automatic flash column chromatography.




3

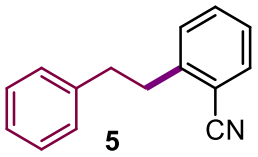
**5-Cyclohexylpicolinonitrile**, (74 mg, 79%) was prepared following the General Procedure II. The product was obtained as a yellow oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 8.55 (pseudo t, *J* = 1.6 Hz, 1H), 7.62 (pseudo t, *J* = 1.6 Hz, 2H), 2.60 (tt, *J* = 9.0, 2.5 Hz, 1H), 1.93 – 1.69 (m, 5H), 1.49 – 1.17 (m, 5H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 150.7, 147.2, 135.0, 131.3, 128.4, 117.6, 42.2, 33.8 (2C), 26.5 (2C), 25.8. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2927, 2853, 2234, 1720, 1566, 1470, 1397, 1024, 999. **HRMS** (ESI) calc for $C_{12}H_{15}N_2$ $[M+H]^+$: 187.1230, found 187.1226.




4

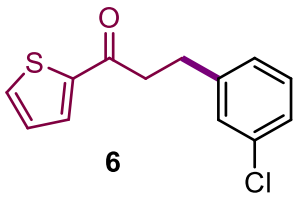
**6-Phenethyl-2,3-dihydro-1*H*-inden-1-one**, (87.4 mg, 74%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 87-88 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.82 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.29 (m, 4H), 7.19 (t, *J* = 6.9 Hz, 3H),

5.27 (br s, 2H), 2.78 (t, $J$ = 7.8 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.01 (q, $J$ = 7.8 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 171.2, 149.7, 147.2, 141.7, 129.8 (2C), 128.5 (2C), 126.1, 125.7 (2C), 123.7, 121.9, 69.6, 35.9, 35.4, 32.9. **FT-IR** ($cm^{-1}$, neat, ATR) 3025, 2930, 1757, 1619, 1601, 1495, 1357, 1282, 1209, 1118. **HRMS** (EI) calc for $C_{17}H_{16}O_7$ $[M]^+$: 236.1201, found: 236.1203.



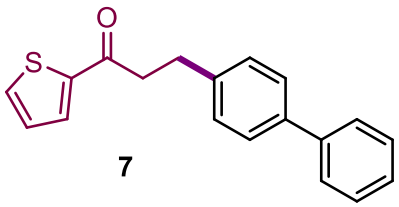

**5**

**2-Phenethylbenzonitrile**, (75.7 mg, 73%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.63 (d, $J$ = 7.7 Hz, 1H), 7.49 (t, $J$ = 7.6 Hz, 1H), 7.33 – 7.18 (m, 7H), 3.16 (dd, $J$ = 9.6, 6.6 Hz, 2H), 2.99 (dd, $J$ = 9.5, 6.5 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 145.6, 140.6, 132.9, 132.8 (2C), 129.8 (2C), 128.6 (2C), 126.7, 126.4, 118.1, 112.5, 37.3, 36.9. **FT-IR** ($cm^{-1}$, neat, ATR) 3062, 2929, 2862, 2223, 1600, 1494, 1485, 1452, 1311, 1163, 1072. **HRMS** (EI) calc for $C_{15}H_{13}N$ $[M]^+$: 207.1048, found: 207.1050.



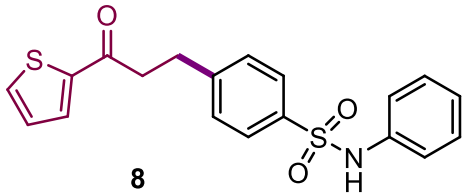

**6**

**3-(3-Chlorophenyl)-1-(thiophen-2-yl)propan-1-one**, (109.1 mg, 87%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.68 – 7.64 (m, 2H), 7.30 – 7.05 (m, 5H), 3.22 (t, $J$ = 7.7 Hz, 2H), 3.05 (t, $J$ = 7.7 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 191.7, 144.1, 143.1, 134.4, 133.8, 132.0, 129.9, 128.7, 128.2, 126.8, 126.5, 40.8, 30.0. **FT-IR** ($cm^{-1}$, neat, ATR) 1659, 1597, 1518, 1477, 1414, 1355, 1289, 1237, 1207, 1079. **HRMS** (EI) calc for $C_{13}H_{11}OSCl$ $[M]^+$: 250.0219, found: 250.0218.



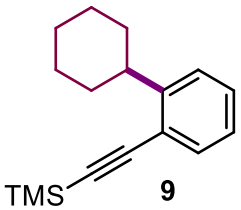
7

**3-([1,1'-Biphenyl]-4-yl)-1-(thiophen-2-yl)propan-1-one**, (93.6 mg, 64%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.72 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.67 – 7.50 (m, 5H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (dd, *J* = 7.7, 6.1 Hz, 3H), 7.13 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.28 (dd, *J* = 8.5, 6.8 Hz, 2H), 3.13 (t, *J* = 7.7 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 192.2, 144.3, 141.1, 140.3, 139.4, 133.7, 132.0, 129.0 (2C), 128.9, 128.3 (2C), 127.4 (2C), 127.3 (2C), 127.2, 41.2, 30.1. **FT-IR** ($cm^{-1}$, neat, ATR) 2980, 1662, 1518, 1486, 1415, 1238, 1205, 1063, 933, 827. **HRMS** (EI) calc for $C_{19}H_{16}OS$ $[M]^+$: 292.0922, found: 292.0912.



8

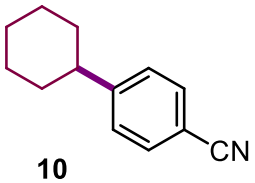
**4-(3-Oxo-3-(thiophen-2-yl)propyl)-*N*-phenylbenzenesulfonamide**, (154.2 mg, 83%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.83 – 7.57 (m, 4H), 7.36 – 7.20 (m, 4H), 7.18 – 7.01 (m, 4H), 6.71 (d, *J* = 6.8 Hz, 1H), 3.21 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 191.5, 146.9, 143.9, 137.1, 136.6, 134.0, 132.1 (2C), 129.4, 129.3 (2C), 128.3 (2C), 127.6 (2C), 125.4, 121.6, 40.3, 30.1. **FT-IR** ($cm^{-1}$, neat, ATR) 3253, 1657, 1598, 1518, 1495, 1415, 1300, 1219, 1092, 920. **HRMS** (ESI) calc for $C_{19}H_{17}NNaO_3S_2$ $[M+Na]^+$: 394.0548, found: 394.0558.



9

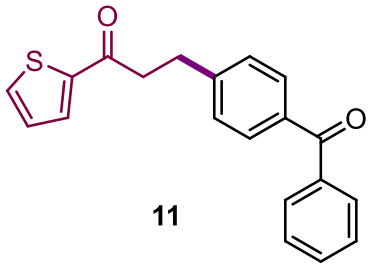
**((2-Cyclohexylphenyl)ethynyl)trimethylsilane**, (100 mg, 78%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^{1}$H NMR** (300 MHz,

$CDCl_3$): δ /ppm 7.44 (ddd, $J$ = 7.6, 1.5, 0.6 Hz, 1H), 7.32 – 7.19 (m, 2H), 7.11 (ddd, $J$ = 7.6, 7.0, 1.7 Hz, 1H), 3.08 – 3.04 (m, 1H), 2.15 – 1.68 (m, 5H), 1.54 – 1.19 (m, 5H), 0.28 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 150.3, 132.5, 128.9 (2C), 125.5 (2C), 122.2, 104.2, 98.0, 42.2, 33.0 (2C), 27.2 (3C), 26.4, 0.2. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2925, 2851, 2155, 1447, 1248, 861, 841, 756. **HRMS** (EI), calc for $C_{17}H_{24}Si$ $[M]^+$ 256.1647, found 256.1645.



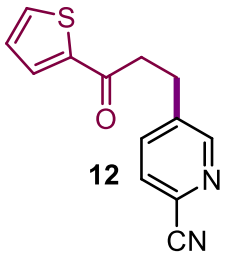

**10**

**4-Cyclohexylbenzonitrile**, (64.5 mg, 70%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.61 – 7.46 (m, 2H), 7.35 – 7.21 (m, 2H), 2.58 – 2.51 (m, 1H), 1.96 – 1.71 (m, 5H), 1.49 – 1.16 (m, 5H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 153.6, 132.3 (2C), 127.8 (2C), 119.3, 109.6, 44.8, 34.1 (2C), 26.7 (2C), 26.0. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2924, 2851, 2226, 1606, 1504, 1448, 1415, 1175, 999, 827. **HRMS** (ESI) calc for $C_{13}H_{16}N$ $[M+H]^+$: 186.1277, found 186.1271.



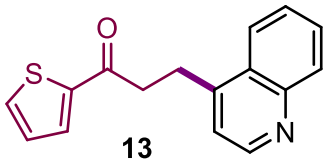

**11**

**3-(4-Benzoylphenyl)-1-(thiophen-2-yl)propan-1one**, (116.9 mg, 73%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 119-120 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.83 – 7.68 (m, 5H), 7.64 (d, $J$ = 5.0 Hz, 1H), 7.58 (t, $J$ = 7.5 Hz, 1H), 7.47 (t, $J$ = 7.7 Hz, 2H), 7.36 (d, $J$ = 7.7 Hz, 2H), 7.12 (t, $J$ = 4.4 Hz, 1H), 3.28 (t, $J$ = 7.5 Hz, 2H), 3.16 (t, $J$ = 7.5 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 196.5, 191.7, 146.2, 144.1, 137.9, 135.8, 133.9, 132.4, 132.0, 130.6 (2C), 130.1 (2C), 128.6 (2C), 128.4 (2C), 128.3, 40.6, 30.4. **FT-IR** ($cm^{-1}$, neat, ATR) 2970, 1655, 1518, 1446, 1415, 1355, 1316, 1278, 1177, 1063. **HRMS** (EI) calc for $C_{20}H_{16}O_2S$ $[M]^+$: 320.0871, found: 320.0883.



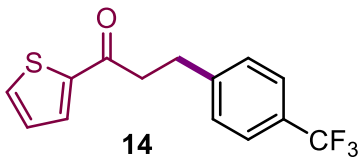

12

**5-(4-Oxo-4-(thiophen-2-yl)butyl)picolinonitrile**, (0.30 mmol scale, 52 mg, 72%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 8.63 (s, 1H), 7.83 – 7.50 (m, 4H), 7.13 (t, *J* = 4.4 Hz, 1H), 3.30 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.1 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 190.6, 151.7, 143.6, 140.9, 137.2, 134.3, 132.2, 131.9, 128.4, 128.3, 117.4, 39.7, 27.3. **FT-IR** ($cm^{-1}$, neat, ATR) 2835, 2473, 1651, 1414, 1250, 1089, 722.




13

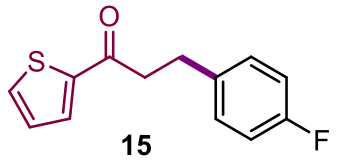
**3-(Quinoline-4-yl)-1-(thiophen-2-yl)propan-1-one**, (61.5 mg, 46%) was prepared following General Procedure II. The product was obtained as a yellow solid. **Mp** = 104-105 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.93 – 7.72 (m, 7H), 7.66 (d, *J* = 4.9 Hz, 1H), 7.14 (t, *J* = 4.4 Hz, 1H), 3.41 (t, *J* = 7.0 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 189.5, 169.3, 168.0, 161.9, 143.2, 134.9, 134.5, 134.2, 132.8, 132.4, 129.0, 128.3, 124.1, 123.7, 33.8, 25.5. **FT-IR** ($cm^{-1}$, neat, ATR) 1816, 1787, 1774, 1739, 1665, 1415, 1373, 1303, 1250, 1219, 1185.




14

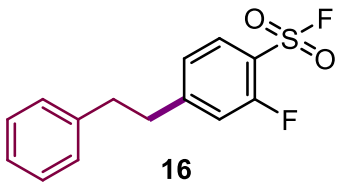
**1-(Thiophen-2-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one**, (0.30 mmol scale, 65.9 mg, 77%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.68 – 7.63 (m, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 4.4 Hz, 1H), 3.26 (t, *J* = 7.5 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 191.5, 145.3, 144.0, 133.8, 132.0, 128.6 (d, *J* = 32.3 Hz),

128.9 (2C), 128.3, 125.5 (q, $J$ = 3.8 Hz, 2C), 124.4 (q, $J$ = 271.9 Hz), 40.5, 30.0. **$^{19}$F NMR** (471 MHz, $C_6D_6$) δ -62.3. **FT-IR** ($cm^{-1}$, neat, ATR) 1662, 1618, 1518, 1415, 1354, 1322, 1240, 1209, 1161, 1118, 1107. **HRMS** (EI) calc for $C_{14}H_{11}OSF_3$ $[M]^+$: 284.0483, found: 284.0502.



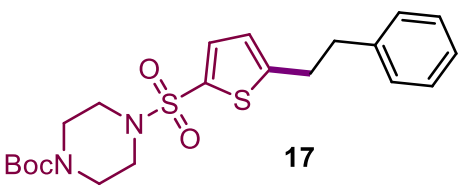

**15**

**1-(Thiophen-2-yl)-3-(4-fluoro)phenyl)propan-1-one**, (50.4 mg, 43%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.68 (dd, $J$ = 3.8, 1.1 Hz, 1H), 7.63 (dd, $J$ = 4.9, 1.1 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.11 (dd, $J$ = 4.9, 3.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 3.21 (t, $J$ = 7.6 Hz, 2H), 3.04 (t, $J$ = 7.6 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 192.1, 161.6 (d, $J$ = 243.9 Hz), 144.2, 136.73, 136.71, 133.8, 132.0, 130.01, 130.0, 128.2, 115.4 (d, $J$ = 21.3 Hz), 41.3, 29.7. **$^{19}$F NMR** (471 MHz, $C_6D_6$) δ -117.11. **FT-IR** ($cm^{-1}$, neat, ATR) 2925, 2854, 1661, 1601, 1509, 1415, 1355, 1296, 1219, 1157. **HRMS** (EI) calc for $C_{13}H_{11}OSF$ $[M]^+$: 234.0515, found: 234.0520.



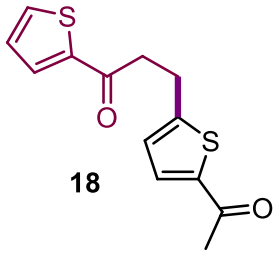

**16**

**2-Fluoro-4-phenethylbenzenesulfonyl fluoride**, (120 mg, 85%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.84 (t, $J$ = 7.5 Hz, 1H), 7.36 – 7.00 (m, 7H), 3.04 – 2.99 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 159.6 (d, $J$ = 261.8 Hz), 154.0 (d, $J$ = 8.1 Hz), 140.0, 130.8, 128.8 (2C), 128.5 (2C), 126.7, 125.16 (d, $J$ = 3.6 Hz), 117.8, 117.7, 37.8, 36.8. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ /ppm -107.04, -107.07. **FT-IR** ($cm^{-1}$, neat, ATR) 1607, 1574, 1496, 1453, 1260, 1245, 1212, 1154, 1074, 779. **HRMS** (EI) calc for $C_{14}H_{12}O_2F_2S$ $[M]^+$: 282.0526, found: 282.0510.



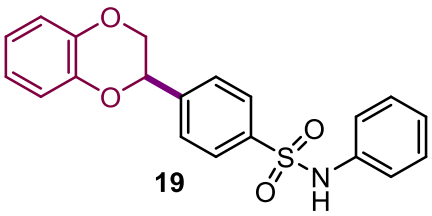

**17**

***tert*-Butyl 4-((5-phenethylthiophen-2-yl)sulfonyl)piperazine-1-carboxylate**, (152.8 mg, 70%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 87-88 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.40 – 7.06 (m, 6H), 6.77 (d, *J* = 3.8 Hz, 1H), 3.51 (pseudo t, *J* = 5.1 Hz, 4H), 3.14 (t, *J* = 7.7 Hz, 2H), 2.99 – 2.94 (m, 6H), 1.43 (s, 9H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 154.3, 152.7, 140.0, 133.0, 132.5 (2C), 128.6 (2C), 128.5 (2C), 126.6, 125.5, 80.5, 46.0 (2C), 42.8, 37.5, 32.1, 28.4 (3C). **FT-IR** ($cm^{-1}$, neat, ATR) 2979, 1736, 1694, 1454, 1421, 1355, 1310, 1249, 1221, 1162. **HRMS** (ESI) calc for $C_{21}H_{29}N_2O_4S_2$ $[M+H]^+$: 437.1569, found: 437.1578.



**18**

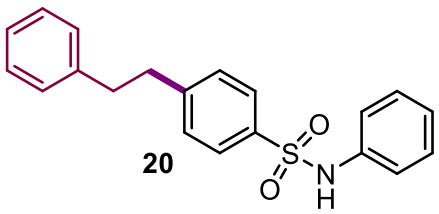
**4-(5-Acetylthiophen-2-yl)-1-(thiophen-2-yl)butan-1-one**, (86 mg, 65%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 89-90 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.72 (d, *J* = 3.9 Hz, 1H), 7.65 (d, *J* = 4.6 Hz, 1H), 7.52 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 4.6 Hz, 1H), 6.90 (d, *J* = 3.9 Hz, 1H), 3.31 (s, 4H), 2.51 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 190.9, 190.6, 153.6, 143.8, 142.8, 134.1, 133.0, 132.2 (2C), 126.6, 40.6, 26.7, 25.1. **FT-IR** ($cm^{-1}$, neat, ATR) 3088, 2980, 1742, 1654, 1518, 1415, 1358, 1252, 1233, 852. **HRMS** (ESI) calc for $C_{13}H_{13}O_2S_2$ $[M+H]^+$: 265.0338, found: 265.0337.



**19**

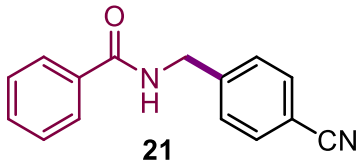
**4-(2,3.Dihydrobenzo[*b*][1,4]dioxin-2-yl)-*N*-phenylbenzenesulfonamide**, (137.8 mg, 75%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 171-172 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.83 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.21 (m, 2H), 7.14 – 7.09 (m, 3H), 7.00 – 6.80 (m, 4H), 6.73 (s, 1H), 5.17 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.34 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.95 (dd, *J* = 11.6, 8.6 Hz, 1H). **$^{13}$C NMR**

(126 MHz, $CDCl_3$) δ /ppm 143.4, 143.0, 141.9, 139.6, 136.3, 129.6 (2C), 127.8 (2C), 127.2 (2C), 125.8, 122.1 (2C), 122.0, 121.9, 117.6, 117.4, 74.4, 69.0. **FT-IR** ($cm^{-1}$, neat, ATR) 2980, 1493, 1382, 1263, 1159, 1078, 954, 751. **HRMS** (ESI) calc for $C_{20}H_{18}NO_4S$ $[M+H]^+$: 368.0965, found: 368.0957.



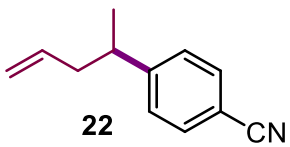
**20**

**4-Phenethyl-*N*-phenylbenzenesulfonamide**, (133.9 mg, 71%) was prepared following General Procedure II. The product was obtained as a colorless solid. **Mp** = 128-129 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.71 (d, $J$ = 7.9 Hz, 2H), 7.40 – 6.88 (m, 12H), 5.45 (s, 1H), 3.16 – 2.64 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 147.5, 140.8, 136.6, 129.4 (2C), 129.3 (2C), 128.5 (4C), 127.5 (2C), 126.3 (2C), 125.5, 121.8 (2C), 37.8, 37.4. **FT-IR** ($cm^{-1}$, neat, ATR) 3257, 2980, 1598, 1410, 1221, 1092, 1030, 920, 820, 752. **HRMS** (ESI) calc for $C_{20}H_{20}NO_2S$ $[M+H]^+$: 338.1214, found: 338.1215.



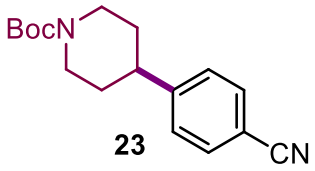
**21**

***N*-(4-Cyanobenzyl)benzamide**, (114 mg, 96%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.88 – 7.71 (m, 2H), 7.63 – 7.47 (m, 3H), 7.47 – 7.34 (m, 4H), 6.96 (t, $J$ = 6.3 Hz, 1H), 4.66 (d, $J$ = 6.3 Hz, 2H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 167.8, 144.1, 133.9, 132.6 (2C), 132.0, 128.8 (2C), 128.3 (2C), 127.1 (2C), 118.8, 111.3, 43.6. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 3319, 2930, 2228, 1725, 1641, 1577, 1415, 1077, 880. **HRMS** (ESI) calc for $C_{15}H_{13}N_2O$ $[M+H]^+$: 237.1022, found 237.1017.



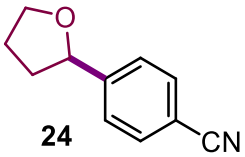
**22**

**4-(Pent-4-en-2-yl)benzonitrile**, (67 mg, 78%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.67 – 7.55 (m, 2H), 7.36 – 7.28 (m, 2H), 5.68 (ddt, *J* = 17.7, 9.6, 7.1 Hz, 1H), 5.15 – 4.76 (m, 2H), 2.92 – 2.88 (m, 1H), 2.38 – 2.33 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 152.6, 136.2, 132.3 (2C), 128.0 (2C), 119.2, 116.9, 109.9, 42.3, 40.1, 21.2. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2964, 2927, 2227, 1640, 1607, 1504, 1416, 1178, 993, 834. **HRMS** (ESI) calc for $C_{12}H_{14}N$ $[M+H]^+$: 172.1121, found 172.1114.



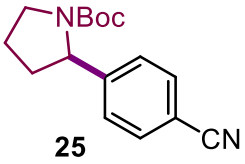

**23**

***tert*-Butyl 4-(4-cyanophenyl)piperidine-1-carboxylate**, (111 mg, 79%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.55 (pseudo dt, *J* = 8.2, 1.9 Hz, 2H), 7.27 (pseudo dt, *J* = 8.4, 1.5 Hz, 2H), 4.22 (br d, *J* = 12.8 Hz, 2H), 2.87 – 2.54 (m, 3H), 1.83 – 1.69 (m, 2H), 1.66 – 1.51 (m, 2H), 1.47 – 1.41 (m, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 154.8, 154.7, 151.2, 132.4, 127.7 (2C), 127.6, 118.9, 110.2, 79.6, 42.8, 41.0, 32.7, 28.4 (3C), 26.9. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2939, 2225, 2167, 2029, 1691, 1422, 1365, 1279, 1170, 1014. **HRMS** (ESI) calc for $C_{17}H_{23}N_2O_2$ $[M+H]^+$: 287.1754, found 287.1766.



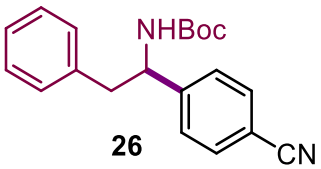

**24**

**4-(Tetrahydrofuran-2-yl)benzonitrile**, (76 mg, 88%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.70 – 7.53 (m, 2H), 7.48 – 7.36 (m, 2H), 4.93 (t, *J* = 7.2 Hz, 1H), 4.11 – 4.00 (m, 2H), 2.50 – 2.28 (m, 1H), 2.12 – 1.91 (m, 2H), 1.75 – 1.72 (m, 1H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 149.4, 132.3 (2C), 126.3 (2C), 119.1, 111.0, 80.0, 69.1, 34.9, 26.1. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2953, 2923, 2852, 1726, 1609, 1459, 1261, 1066, 836. **HRMS** (ESI) calc for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0913, found 174.0907.



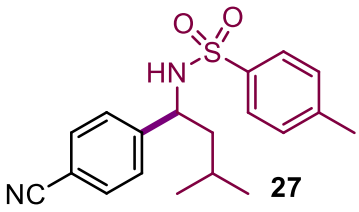

25

***tert*-Butyl 2-(4-cyanophenyl)pyrrolidine-1-carboxylate**, (115 mg, 85%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.55 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.89 – 4.75 (m, 1H), 3.59 – 3.32 (m, 2H), 2.41 – 2.22 (m, 1H), 1.91 – 1.67 (m, 3H), 1.40 (s, 4H), 1.13 (s, 5H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 155.3, 132.2, 126.3 (2C), 124.9, 119.7, 110.4, 79.7, 61.2, 47.2, 35.9, 28.4, 28.1 (3C), 23.3. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2975, 2227, 1693, 1608, 1477, 1454, 1365, 1249, 1111. **HRMS** (APCI) calc for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1598, found 273.1592.




26

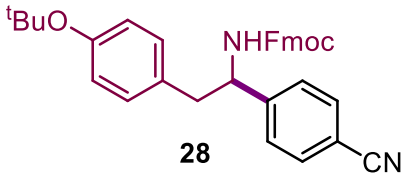
***tert*-Butyl (1-(4-cyanophenyl)-2-phenylethyl)carbamate**, (113 mg, 70%) was prepared following the general procedure. The product was obtained as a colorless oil. **$^{1}$H NMR** (300 MHz, DMSO-*d*$_6$): δ /ppm 7.78 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.45 (m, 2H), 7.30 – 7.12 (m, 5H), 4.79 (q, *J* = 8.1 Hz, 1H), 2.89 (d, *J* = 8.6 Hz, 1H), 1.39 (s, 2H), 1.27 (s, 9H). **$^{13}$C NMR** (75 MHz, DMSO-*d*$_6$): δ /ppm 160.2, 143.5, 137.4 (2C), 134.4, 133.3 (2C), 132.7 (2C), 131.4 (2C), 124.1, 114.7, 83.2, 61.0, 47.1, 33.4 (2C), 31.6 (2C). **FT-IR** (ATR): ṽ ($cm^{-1}$) 2976, 2926, 2229, 1698, 1505, 1455, 1366, 1168, 1018, 700. **HRMS** (ESI) calc for $C_{20}H_{22}NaN_2O_2$ $[M+Na]^+$: 345.1573, found 345.1566.




27

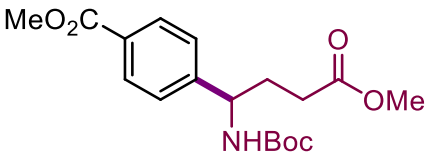
***N*-(1-(4-Cyanophenyl)-3-methylbutyl)-4-methylbenzenesulfonamide**, (130 mg, 76%) was prepared following the general procedure. The product was obtained as a yellow oil. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.53 – 7.46 (m, 2H), 7.45 – 7.39 (m, 2H), 7.16 – 7.10 (m, 4H), 5.25

(d, $J$ = 7.1 Hz, 1H), 4.38 (dt, $J$ = 8.1, 6.6 Hz,1H), 2.37 (s, 3H), 1.70 – 1.35 (m, 3H), 0.82 (dd, $J$ = 18.4, 6.1 Hz, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 147.0, 143.7, 137.4, 134.5, 132.3, 129.9, 129.5, 127.5, 127.1, 126.6, 123.8, 118.7, 111.1, 56.2, 46.9, 24.7, 22.6, 22.0, 21.6. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 3200, 2957, 2228, 1773, 1605, 1468, 1386, 1160, 815, 714. **HRMS** (APCI) calc for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1475, found 343.1475.



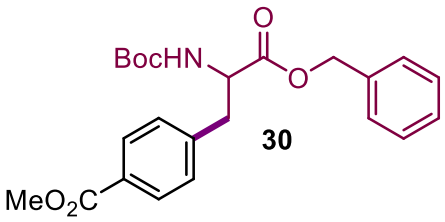

**28**

**(9*H*-Fluoren-9-yl)methyl (2-(4-(*tert*-butoxy)phenyl)-1-(4-cyanophenyl)ethyl)carbamate**, (145 mg, 56%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.88 – 7.70 (m, 2H), 7.67 – 7.49 (m, 2H), 7.40 – 7.30 (m, 5H), 7.17 (d, $J$ = 8.4 Hz, 4H), 6.91 (d, $J$ = 8.4 Hz, 3H), 6.70 (d, $J$ = 10.9 Hz, 1H), 5.94 (d, $J$ = 14.6 Hz, 1H), 4.53 (d, $J$ = 6.7 Hz, 2H), 4.48 – 4.36 (m, 1H), 4.25 (t, $J$ = 6.7 Hz, 1H), 1.34 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 154.1, 153.7, 143.7 (2C), 141.5 (2C), 131.5 (2C), 128.0 (2C), 127.3 (4C), 125.9 (2C), 125.0 (4C), 124.6 (4C), 123.1, 120.2 (2C), 110.8, 78.7, 67.3, 47.2, 29.0 (3C). **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2978, 1721, 1661, 1596, 1542, 1447, 1284, 1105, 951. **HRMS** (ESI) calc for $C_{34}H_{33}N_2O_3$ $[M+H]^+$: 517.2486, found 517.2478.



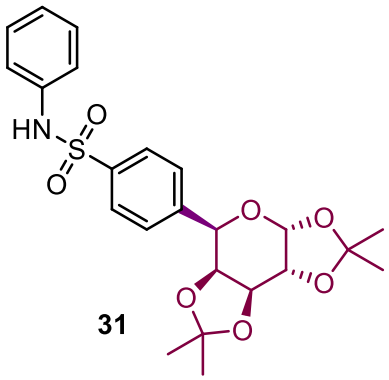

**29**

**Methyl 4-(1-((*tert*-butoxycarbonyl)amino)-4-methoxy-4-oxobutyl)benzoate,** (170 mg, 97%) was prepared following General Procedure II. The product was obtained as a colorless foam. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 8.12 – 7.85 (m, 2H), 7.32 (d, $J$ = 8.1 Hz, 2H), 5.27 – 5.15 (m, 1H), 4.67 (br s, 1H), 3.87 (s, 3H), 3.63 (s, 3H), 2.34 (td, $J$ = 7.4, 4.1 Hz, 2H), 2.03 (d, $J$ = 7.4 Hz, 2H), 1.44 – 1.29 (m, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 173.6, 166.9, 155.3, 147.7, 134.2, 130.0, 129.2, 126.3, 123.5, 79.8, 54.3, 52.1, 51.8, 51.7, 31.5, 30.9, 30.8, 28.4. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2977, 1717, 1611, 1513, 1437, 1366, 1278, 1164, 1113, 859. **HRMS** (ESI) calc for $C_{18}H_{25}NaNO_6$ $[M+Na]^+$: 374.1574, found 374.1569.



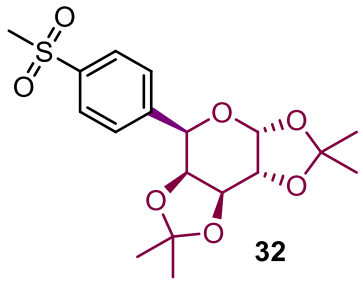

**30**

**Methyl 4-(3-(benzyloxy)-2-((tert-butoxycarbonyl)amino)-3-oxopropyl)benzoate**, (188 mg, 91%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (300 MHz, $CDCl_3$): δ /ppm 7.88 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.31 – 7.22 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 5.26 – 4.93 (m, 3H), 4.71 – 4.56 (m, 1H), 3.90 (s, 3H), 3.18 – 3.10 (m, 2H), 1.41 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 171.5, 167.0, 155.1, 141.5, 135.1, 129.9, 129.5 (2C), 129.0 (2C), 128.8 (2C), 128.7 (2C), 80.2, 67.4, 54.3, 52.2, 38.4, 28.4 (3C). **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2977, 1715, 1611, 1498, 1366, 1277, 1161, 1105, 1055, 1020. **HRMS** (ESI) calc for $C_{22}H_{27}NaNO_6$ $[M+Na]^+$: 436.1731, found 436.1741.



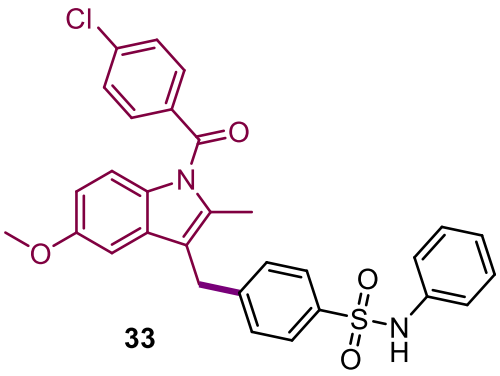

**31**

***N*-Phenyl-4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)benzenesulfonamide**, (127 mg, 55%, dr >20:1) was prepared following General Procedure II. The product was obtained as a yellow solid. **Mp** = 85-86 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.73 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.11 – 7.07 (m, 3H), 6.76 (d, *J* = 8.9 Hz, 1H), 5.69 (d, *J* = 5.0 Hz, 1H), 4.88 (s, 1H), 4.71 (d, *J* = 7.8 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 2H), 1.54 (s, 3H), 1.40 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 143.4, 138.1, 136.5 129.5 (2C), 127.7 (2C), 127.1 (2C), 125.6 (2C), 121.9, 109.6, 109.0, 96.9, 73.5, 71.1, 70.7, 69.2, 26.3, 26.0, 25.0, 24.4. **FT-IR** ($cm^{-1}$, neat, ATR) 2980, 1495, 1382, 1300, 1254, 1211, 1161, 1092, 1000, 961. **HRMS** (ESI) calc for $C_{23}H_{28}NO_7S$ $[M+H]^+$: 462.1586, found: 462.1593.



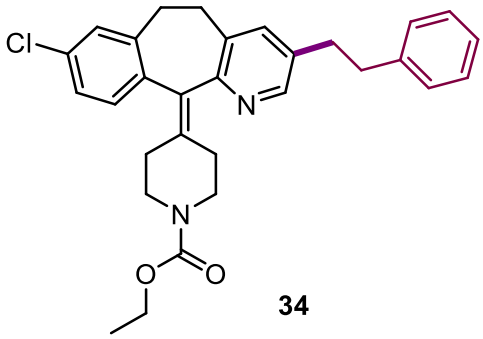
32

**4-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methylsulfonamide**, (125 mg, 65%, dr. >20:1) was prepared following General Procedure II. The product was obtained as a yellow solid. **Mp** = 108-110 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.91 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 4.9 Hz, 1H), 4.95 (s, 1H), 4.74 (dd, *J* = 7.7, 2.5 Hz, 1H), 4.54 – 4.33 (m, 2H), 3.04 (s, 3H), 1.56 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.29 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 144.3, 139.5, 127.9 (2C), 127.3, 109.7, 109.0, 97.0, 73.5, 71.2, 70.7, 69.2, 44.7, 26.3, 26.0, 25.0, 24.4. **FT-IR** ($cm^{-1}$, neat, ATR) 2981, 1730, 1382, 1255, 1210, 1149, 1068, 1001, 957, 867.



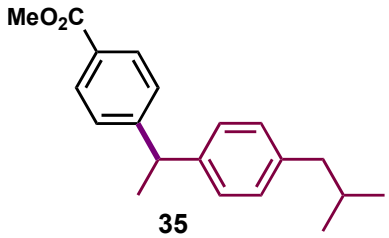
33

**4-((1-(4-Chlorobenzoyl)5-methoxy-2-methyl-1*H*-indol-3yl)methyl-*N* phenylbenzenesulfonamide**, (190.1 mg, 70%) was prepared following General Procedure II. The product was obtained as a yellow foam. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.63 (dd, *J* = 14.9, 8.2 Hz, 4H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.00 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 8.7 Hz, 2H), 4.32 (s, 1H), 3.99 (s, 2H), 3.66 (s, 3H), 2.29 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 168.5, 156.1, 145.7, 139.4, 137.1, 136.6, 135.6, 134.0, 131.3 (2C), 131.2 (2C), 130.9 (2C), 129.4 (2C), 129.3 (2C), 128.9 (2C), 127.7, 125.5, 121.7, 116.9, 115.2, 111.4, 101.7, 55.8, 30.0, 13.5. **FT-IR** ($cm^{-1}$, neat, ATR): $\tilde{\nu}$ ($cm^{-1}$) 3253, 2927, 1678, 1596, 1401, 1352, 1224, 1090, 1066, 832. **HRMS** (ESI) calc for $C_{30}H_{26}ClN_2O_4S$ $[M+H]^+$: 545.1302, found 545.1293.



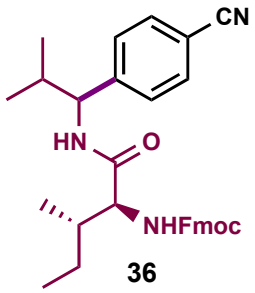

**34**

**Ethyl 4-(8-chloro-3-phenethyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine-11-ylidene)piperidine-1-carboxylate**, (153.4 mg, 63%) was prepared following General Procedure II. The product was obtained as a yellow oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 8.23 (s, 1H), 7.33 – 7.06 (m, 9H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.81 – 3.78 (m, 2H), 3.39 – 3.30 (m, 2H), 3.17 – 3.01 (m, 2H), 2.94 – 2.68 (m, 5H), 2.57 – 2.40 (m, 1H), 2.31 – 2.29 (m, 3H), 1.25 (t, *J* = 7.0 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 155.6, 154.5, 146.6, 141.0, 139.7, 138.0, 135.7, 133.0, 130.6 (2C), 129.0 (2C), 128.6 (2C), 128.5 (4C), 126.3 (2C), 61.4, 44.9 (2C), 37.5, 34.6, 31.7, 31.6, 30.9, 30.7, 14.8. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ ($cm^{-1}$) 2923, 2856, 1693, 1470, 1385, 1277, 1227, 1172, 1115, 1029, 997. **HRMS** (ESI) calc for $C_{30}H_{32}ClN_2O_2$ $[M+H]^+$: 487.2152, found 487.2148.



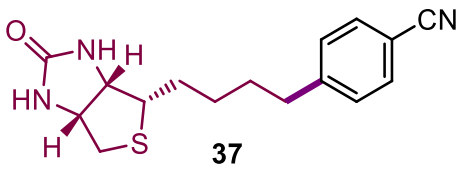

**35**

**Methyl 4-(1-(4-isobutylphenyl)ethyl)benzoate**, (0.29 mmol, 86 mg, 58%) was prepared following General Procedure II. The product was obtained as a colorless foam. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ /ppm 8.03 – 7.83 (m, 2H), 7.32 – 7.26 (m, 2H), 7.14 – 7.01 (m, 4H), 4.17 (q, *J* = 7.3 Hz, 1H), 3.89 (s, 3H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.88 – 1.81 (m, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H). **$^{13}$C NMR** (75 MHz, $CDCl_3$): δ /ppm 167.2, 152.2, 142.8, 139.8, 129.9 (2C), 129.3 (2C), 128.0 (2C), 127.8 (2C), 127.4 (2C), 52.1, 45.1, 44.6, 30.3, 22.5, 21.8. **FT-IR** ($cm^{-1}$, neat, ATR): ṽ 2953, 1724, 1608, 1434, 1278, 1179, 1112, 1014, 848. **HRMS** (ESI, *m/z*) calc for $C_{20}H_{25}O_2$ $[M+H]^+$: 297.1849, found 297.1853.



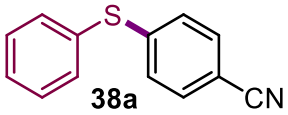

**36**

**(9*H*-Fluoren-9-yl)methyl (1-((1-(4-cyanophenyl)-2-methylpropyl)amino)-4-methyl-1-oxopentan-2-yl)carbamate**, (168 mg, 65%, dr: 1.1:1) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^{1}$H NMR** (300 MHz, DMSO-$d_6$): δ /ppm 7.95 – 7.84 (m, 3H), 7.80 – 7.65 (m, 4H), 7.54 – 7.20 (m, 5H), 4.60 (q, $J$ = 8.6 Hz, 1H), 4.36 – 4.10 (m, 3H), 3.99 – 3.90 (m, 1H), 2.02 – 1.87 (m, 1H), 1.70 – 1.65 m, 1H), 1.51 – 1.00 (m, 3H), 0.93 – 0.53 (m, 13H). **$^{13}$C NMR** (75 MHz, DMSO-$d_6$): δ /ppm 171.1, 156.0, 148.6, 143.9, 143.8, 140.7, 132.0, 128.9 128.2, 128.1, 127.6, 127.3, 127.0, 125.4, 120.1, 118.9, 109.5, 65.6 59.0, 58.5, 46.7, 46.0, 36.0, 32.6, 32.5, 20.1, 19.6, 19.6, 18.9, 18.5, 15.5, 15.2. **FT-IR** (cm$^{-1}$, neat, ATR): ṽ 3296, 3064, 2963, 1770, 1723, 1655, 1533, 1129, 1008. **HRMS** (ESI, *m/z*) calc for $C_{32}H_{35}NaN_3O_3$ $[M+H]^+$: 532.2570, found 532.2566.



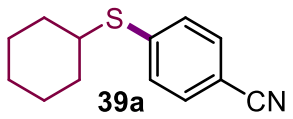

**37**

**4-(4-((3a*S*,4*S*,6a*R*)-2-Oxohexahydro-1*H*-thieno[3,4-*d*]imidazole-4-yl)butyl)benzonitrile/ biotin derivative**, (130 mg, 86%) was prepared following General Procedure II. The product was obtained as a pale yellow oil. **$^{1}$H NMR** (600 MHz, $CDCl_3$): δ /ppm 7.42 – 7.37 (m, 2H), 7.15 – 7.09 (m, 2H), 5.88 (s, 1H), 5.56 (s, 1H), 4.33 (dd, $J$ = 8.0, 4.9 Hz, 1H), 4.11 (ddd, $J$ =8.0, 4.7, 1.7 Hz, 1H), 2.72 (dd, $J$ = 12.7, 5.0 Hz, 1H), 2.62 (d, $J$ = 12.7 Hz, 1H), 2.51 (t, $J$ = 7.7 Hz, 3H), 1.55 – 1.46 (m, 3H), 1.33 – 1.21 (m, 3H). **$^{13}$C NMR** (151 MHz, $CDCl_3$): δ /ppm 163.3, 147.9, 131.9 (2C), 129.0 (2C), 118.9, 109.3, 61.8, 60.0, 55.4, 40.3, 35.6, 30.6, 28.4, 28.3. **FT-IR** (cm$^{-1}$, neat, ATR): ṽ 2961, 2864, 1703, 1449, 1346, 1204, 1125, 1077, 1009, 576. **HRMS** (ESI) calc for $C_{16}H_{20}N_3OS$ $[M+H]^+$: 302.1322, found 302.1318.



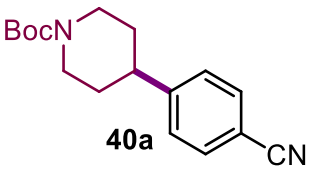

**38a**

**4-(Phenylthio)benzonitrile**, (90 mg, 85%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.54 – 7.37 (m, 7H), 7.16 (d, *J* = 8.2 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 145.8, 134.6 (2C), 132.5 (2C), 130.9, 130.0, 129.5 (2C), 127.4 (2C), 118.9, 108.8. **FT-IR** ($cm^{-1}$, neat, ATR) 2226, 1592, 1484, 1440, 1401, 1080, 1016, 822, 749, 691, 543. **HRMS** (EI) calc for $C_{13}H_9NS$ $[M]^+$: 211.0456, found: 211.0450.



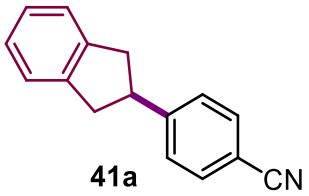
**39a**

**4-(Cyclohexylthio)benzonitrile**, (56 mg, 51%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ /ppm 7.54 – 7.49 (m, 2H), 7.36 – 7.31 (m, 2H), 3.29 (tt, *J* = 10.3, 3.7 Hz, 1H), 2.12 – 1.95 (m, 2H), 1.83 – 1.79 (m, 2H), 1.72 – 1.60 (m, 1H), 1.51 – 1.19 (m, 5H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ /ppm 144.1, 132.3 (2C), 128.7 (2C), 119.1, 108.5, 45.0, 33.1 (2C), 26.0 (2C), 25.7. **FT-IR** ($cm^{-1}$, neat, ATR) 2931, 2854, 2225, 1592, 1485, 1449, 1088, 820, 544. **HRMS** (EI) calc for $C_{13}H_{15}NS$ $[M]^+$: 217.0925, found: 217.0923.



**40a**

***tert*-Butyl 4-(4-cyanophenyl)piperidine-1-carboxylate**, (121 mg, 84%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) δ /ppm 7.72 – 7.51 (m, 2H), 7.32 – 7.27 (m, 2H), 4.26 (s, 2H), 2.92 – 2.63 (m, 3H), 1.87 – 1.74 (m, 2H), 1.60 (qd, *J* = 12.7, 4.4 Hz, 2H), 1.47 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ /ppm 154.9, 151.3, 132.5 (2C), 128.8, 127.8 (2C), 119.1, 110.4, 79.8, 43.0 (2C), 32.9, 29.8, 28.6 (3C). **FT-IR** ($cm^{-1}$, neat, ATR) 1476, 1465, 1392, 1125, 1107, 986, 884, 860. **HRMS** (ES+) calcd for $C_{17}H_{23}N_2O_2$ $[M+H]^+$: 287.1760, found: 287.1747.




41a

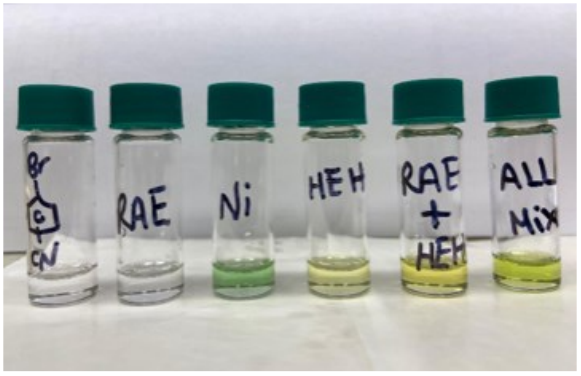
**4-(2,3-Dihydro-1*H*-inden-2-yl)benzonitrile**, (77 mg, 70%) was prepared following General Procedure II. The product was obtained as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.70 – 7.50 (m, 2H), 7.40 – 7.35 (m, 2H), 7.28 – 7.17 (m, 4H), 3.75 – 3.72 (m, 1H), 3.39 (dd, *J* = 15.6, 8.2 Hz, 2H), 3.06 (dd, *J* = 15.6, 8.2 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 151.4, 142.2 (2C), 132.5 (2C), 128.0 (2C), 126.9 (2C), 124.5 (2C), 119.2, 110.2, 45.4, 40.8 (2C). **FT-IR** ($cm^{-1}$, neat, ATR) 2945, 2905, 2840, 2222, 1607, 1475, 1457, 1178, 1006, 852, 829, 754. **HRMS** (EI) calc for $C_{16}H_{13}NS$ $[M]^+$: 219.1048, found: 219.1044.

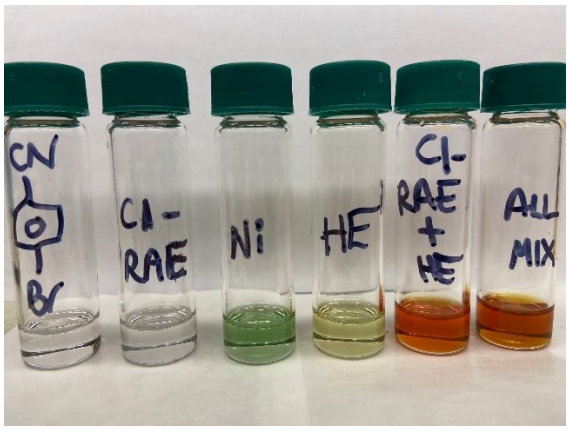
## IV. Mechanistic Studies

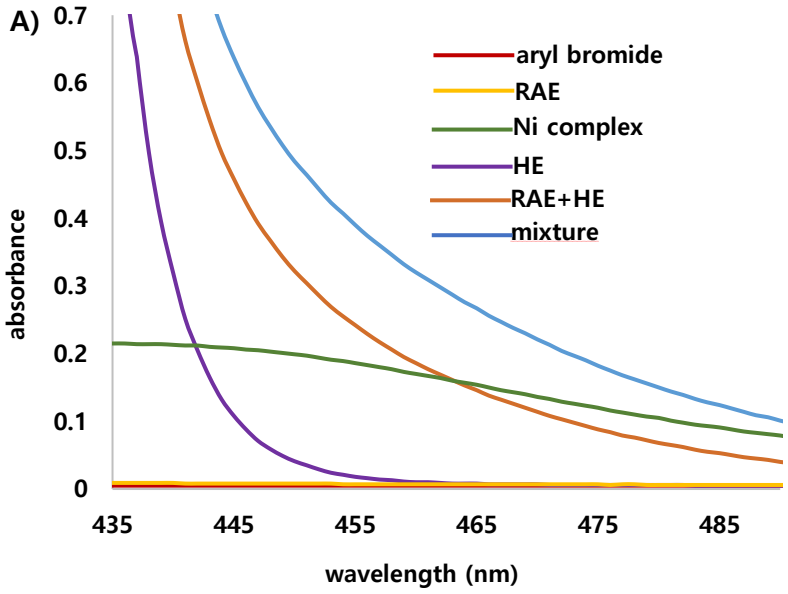
***UV-vis studies:***

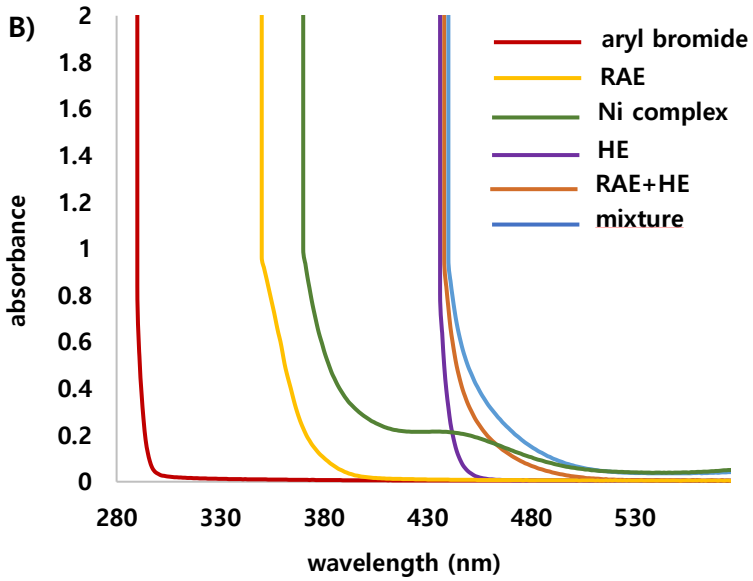
UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific. Absorption spectra of individual reaction components and mixtures thereof were recorded. A bathochromic shift was observed for a mixture of alkyl redox-active esters and Hantzsch-ester in DMA (0.2 M), which was visibly yellow in color. This indicates the formation of an electron donor-acceptor (EDA) complex (**A**, orange band). Notably, concentration is a crucial parameter for effective cross-coupling. A dilute reaction mixture ($10^{-4}$ M) exhibits a blue-shifted absorption band, indicating the inhibition of EDA complex formation (**C**, black band).

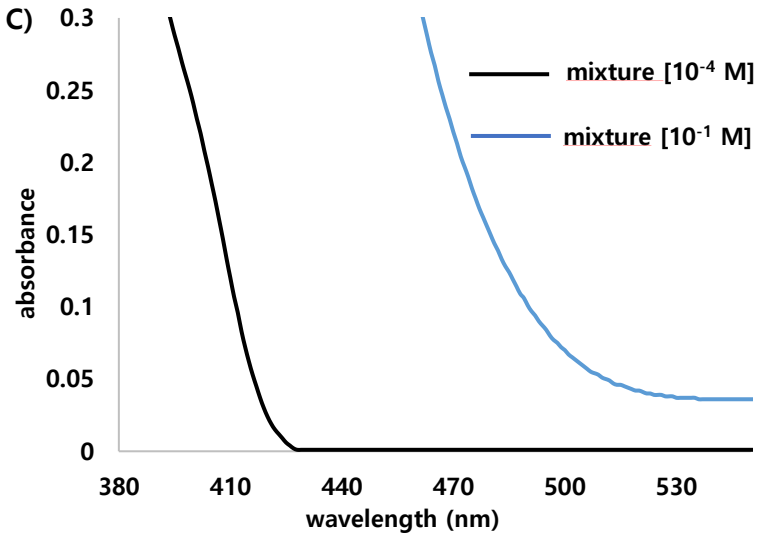
To underline the formation of EDA complexes between redox-active esters with Hantzsch-ester, we further recorded the corresponding UV-vis absorption spectra using the more electron deficient tetrachloro *N*-hydroxyphthalimide ester derivative (**E** & **F**). As expected, this species functions as a potent electron acceptor, and a more significant bathochromic shift was detected in this case (see **E** and **F**).

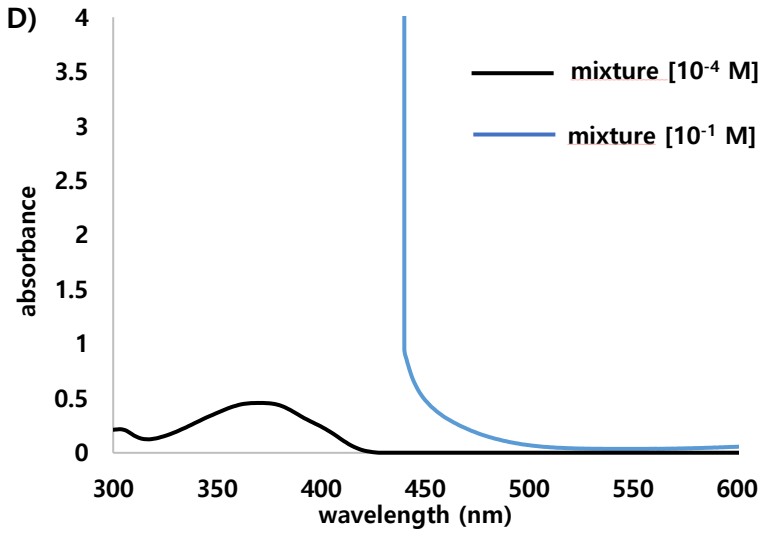



A)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
absorbance
435
445
455
465
475
485
wavelength (nm)
aryl bromide
RAE
Ni complex
HE
RAE+HE
mixture


B)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
absorbance
280
330
380
430
480
530
wavelength (nm)
aryl bromide
RAE
Ni complex
HE
RAE+HE
mixture


C)
0.3
0.25
0.2
0.15
0.1
0.05
0
absorbance
380
410
440
470
500
530
wavelength (nm)
mixture [10-4 M]
mixture [10-1 M]


D)
4
3.5
3
2.5
2
1.5
1
0.5
0
absorbance
300
350
400
450
500
550
600
wavelength (nm)
mixture [10-4 M]
mixture [10-1 M]

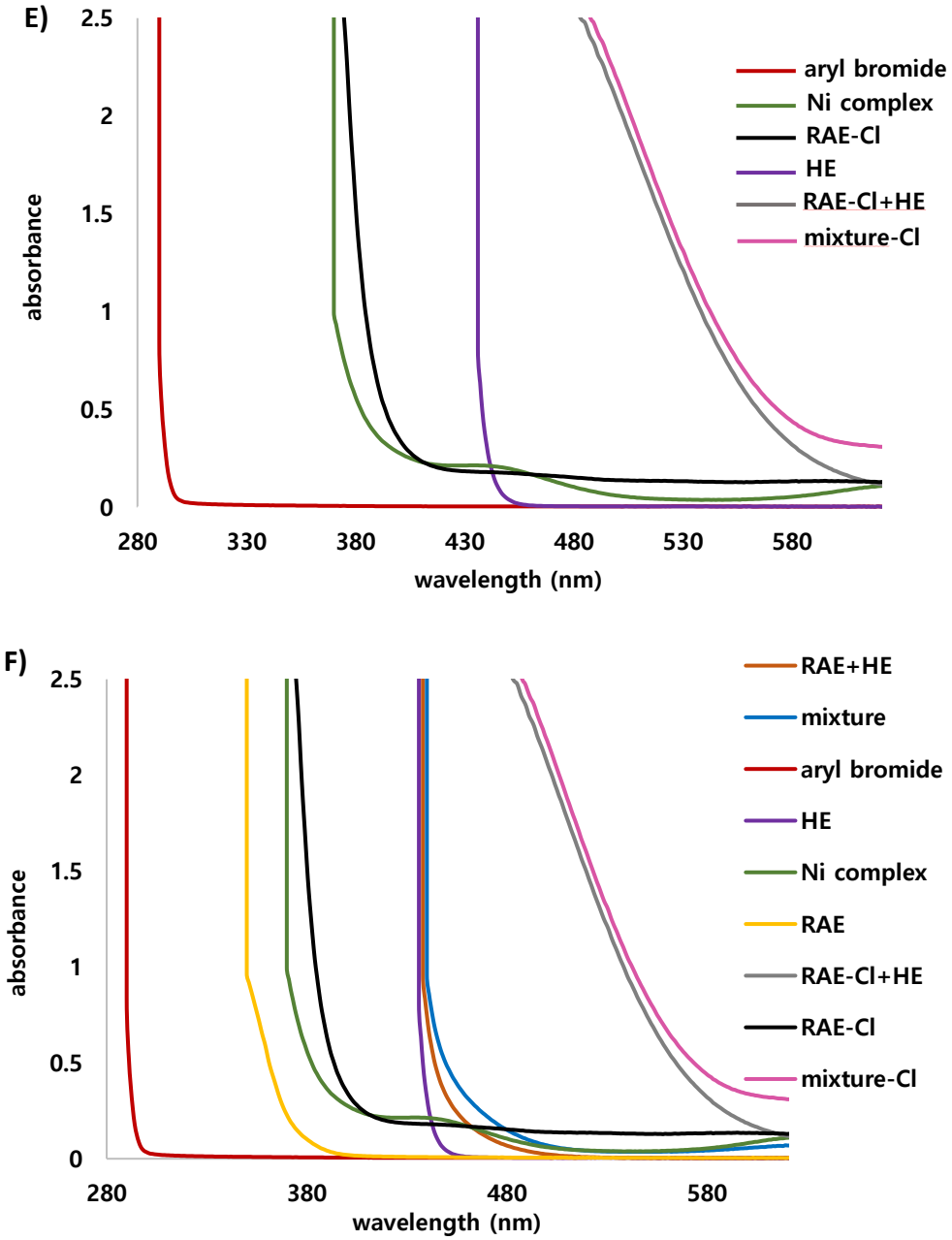
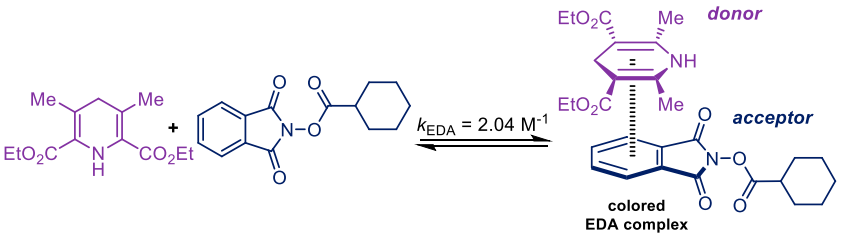



**Figure S2:** UV/vis absorption spectra of individual reaction components and a combination thereof (A–F). All spectra were measured in DMA and with a concentration of: 0.1 M aryl bromide, 0.2 M RAE/RAE-Cl, 0.2 M HE and 0.01 M Ni complex. The stoichiometry and concentration of sample "mixture" reflects the reaction conditions. The stoichiometry and concentration of sample "mixture-Cl" reflects the reaction conditions, and instead of RAE, RAE-Cl was used. Ni complex = $NiBr_2$(dtbpy), aryl bromide = 4-bromobenzonitrile, and RAE = cyclohexyl-*N*-hydroxyphthalimide-ester, RAE-Cl = cyclohexyl-*N*-hydroxy-3,4,5,6-tetra-chlorophthalimide-ester.

***Job's method experiment:***

The stoichiometry of the EDA complex was determined using Job's method with varying ratios of redox-active ester **2** and Hantzsch-ester (**HE**) in DMA (0.2 M) at 455 nm. The absorbance was plotted against the molar fraction of **HE**. Maximum absorbance was detected at 50% molar fraction of **HE**, indicating a 1:1 stoichiometry of the EDA complex.



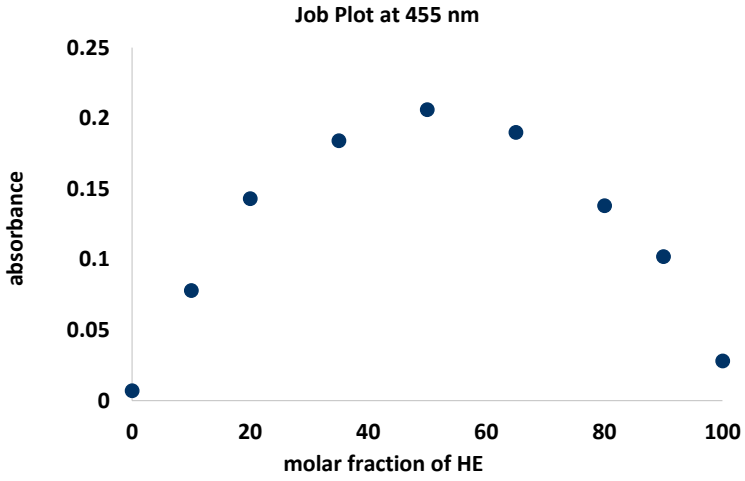




**Figure S3**: Job plot of the EDA complex (0.2 M total concentration in DMA) between Hantzsch-ester **HE** and *N*-cyclohexyl-hydroxyphthalimide-ester (**2**) recorded at 455 nm.

***Determination of association constant (k*EDA)**

The association constant for the EDA complex formed between *N*-hydroxyphthalimide ester **2** and Hantzsch-ester was determined by UV-vis measurements in DMA employing the Benesi-Hildebrand[4] method. The absorbance of a constant concentration of **2** (0.02 M) and an increasing concentration of HE (0.02-0.07 M) was recorded at 445 nm. The absorption spectra shown in Figure S4 were recorded in 1 cm path quartz cuvette.

To determine the $k_{EDA}$, the reciprocal concentration of HE was plotted against the reciprocal absorbance (A) of HE at 445 nm (Table S2 and Figure S4). A straight line was obtained, and by dividing the intercept through the slope: $k_{EDA}$ = 2.04 $M^{-1}$ for **2**/HE.

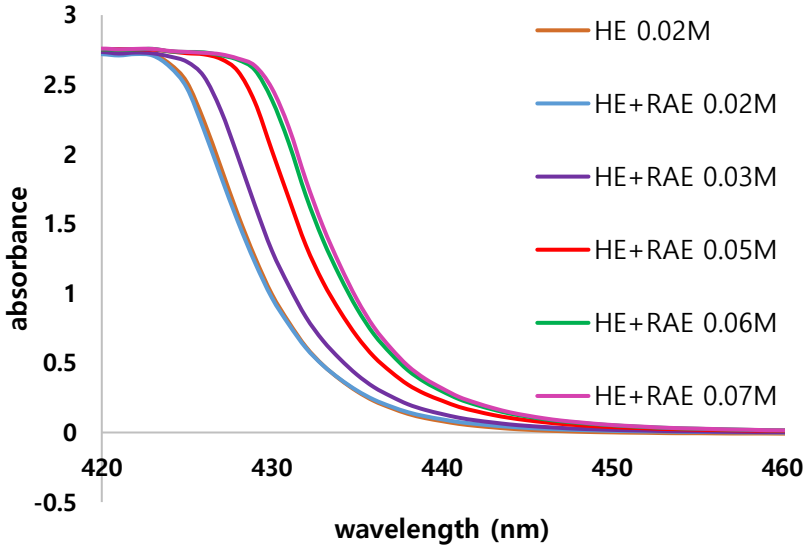



**Figure S4:** UV-vis absorption spectra of *N*-cyclohexyl hydroxyphthalimide ester (**2**, 0.02 M in DMA) in combination with increasing concentrations of HE (0.02 M up to 0.07 M in DMA).

**Table S1:** Data obtained from the UV-vis absorption spectra of the EDA complex between **2** and **HE** in DMA. The concentration of **2** was kept at 0.02 M in DMA.

| HE (M) | 1/HE ($M^{-1}$) | $Abs_{EDA}$ | $1/Abs_{EDA}$-$A_0$ |
|---|---|---|---|
| 0.02 | 50 | 0.033 | 30.3 |
| 0.03 | 33.3 | 0.048 | 20.8 |
| 0.05 | 20 | 0.088 | 11.4 |
| 0.06 | 16.7 | 0.115 | 8. 7 |
| 0.07 | 14.3 | 0.122 | 8.2 |

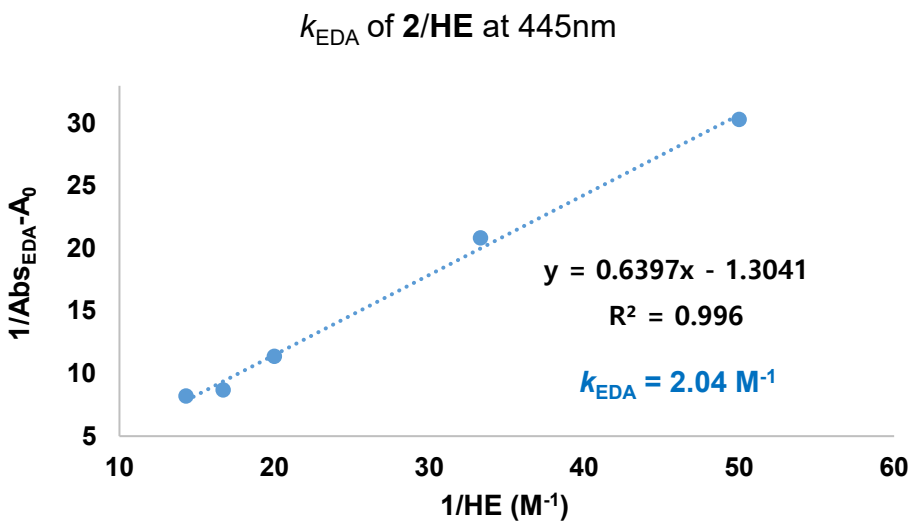
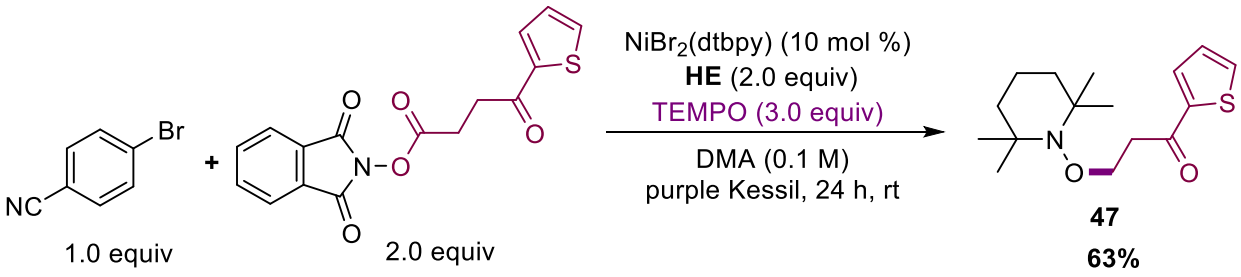



**Figure S5:** Benesi-Hildebrand[4] plot for the EDA complex generated in DMA upon association of *N*-cyclohexyl hydroxyphthalimide ester **2** with HE.

***TEMPO trapping experiment:***

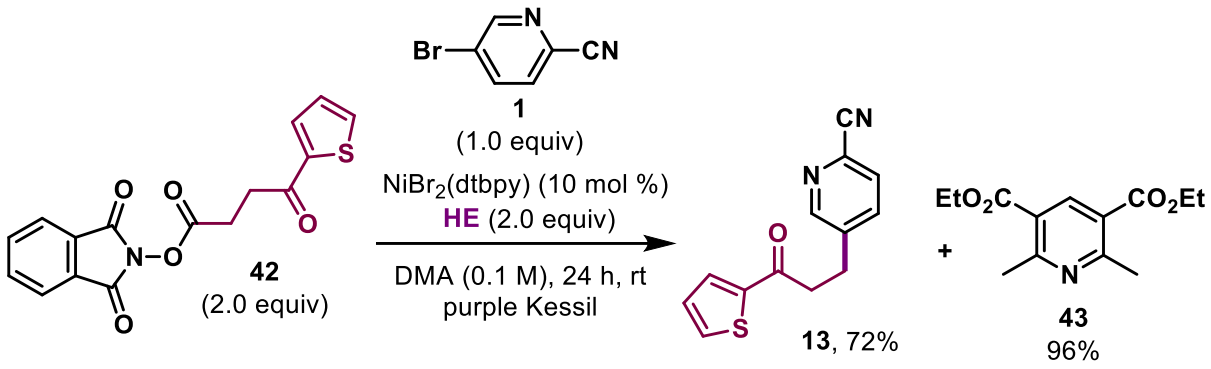



**Scheme S1:** TEMPO trapping experiment. All values correspond to isolated yields after purification. Reaction conditions as described in the general procedure for decarboxylative arylation.

To probe the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger (Scheme S1). The reaction was performed according to General Procedure II (0.3 mmol scale) in the presence of TEMPO (0.9 mmol, 3.0 equiv). The corresponding TEMPO adduct **47** was isolated in 63% yield via flash column chromatography. The product was obtained as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.77 (d, $J$ = 3.8 Hz, 1H), 7.64 (d, $J$ = 4.6 Hz, 1H), 7.13 (t, $J$ = 4.4 Hz, 1H), 3.30 (t, $J$ = 7.0 Hz, 2H), 2.81 (t, $J$ = 7.0 Hz, 2H), 1.77 – 1.47 (m, 6H), 1.14 (s, 6H), 1.06 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 191.0, 143.8, 133.7, 132.1, 128.2, 60.2, 39.1 (2C), 34.1, 32.0 (2C), 26.8 (2C), 20.6 (2C), 17.1. **FT-IR** (cm$^{-1}$, neat, ATR) 2977, 2937, 1756,

1666, 1380, 1245, 1131, 1083, 904, 854. **HRMS** (EI) calc for $C_{16}H_{25}NO_2S$ $[M]^+$: 295.1606, found: 295.1557.

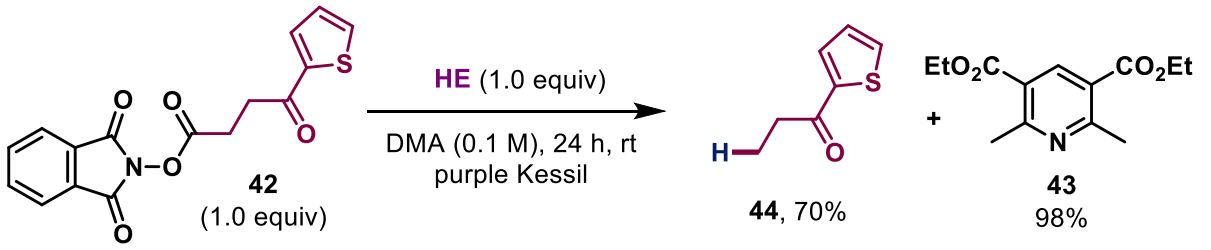
***Investigation of Hantzsch-ester backbone:***




**Scheme S2:** Formation of pyridine **43**. All values correspond to isolated yields after purification. Reaction conditions as described in General Procedure II for decarboxylative arylation.

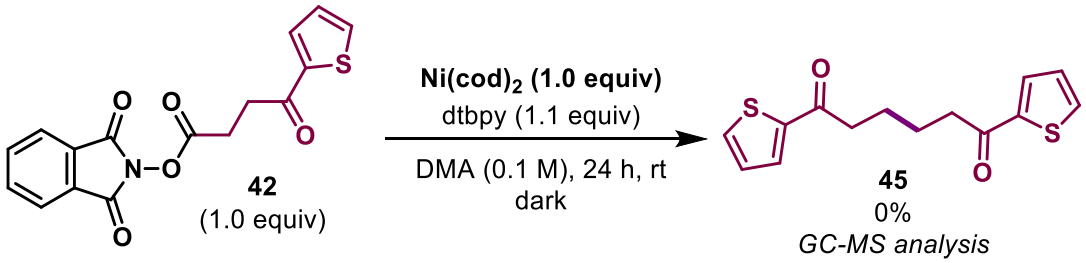
The reaction was performed according to General Procedure II (0.3 mmol scale), and the corresponding (by-)products **13** & **43** were isolated via flash column chromatography. For characterization of compound **13** see Section **III.** The product **43** was obtained as a colorless solid. **Mp** = 72-74 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 8.66 (s, 1H), 4.39 (q, $J$ = 7.1 Hz, 4H), 2.84 (s, 6H), 1.41 (t, $J$ = 7.1 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 166.1 (2C), 162.4, 141.0 (2C), 123.2 (2C), 61.5 (2C), 25.1 (2C), 14.4 (2C). **FT-IR** ($cm^{-1}$, neat, ATR) 2977, 2931, 1716, 1590, 1474, 1442, 1378, 1293, 1222, 1045. **HRMS** (ESI) calc for $C_{13}H_{18}NO_4$ $[M+H]^+$: 252.1236, found: 252.1234.

***Investigation of radical intermediates and stoichiometric Ni experiments:***




**Scheme S3:** Hydroalkylation experiment. Isolated yields after purification. Reaction conditions as described in General Procedure II for decarboxylative arylation.

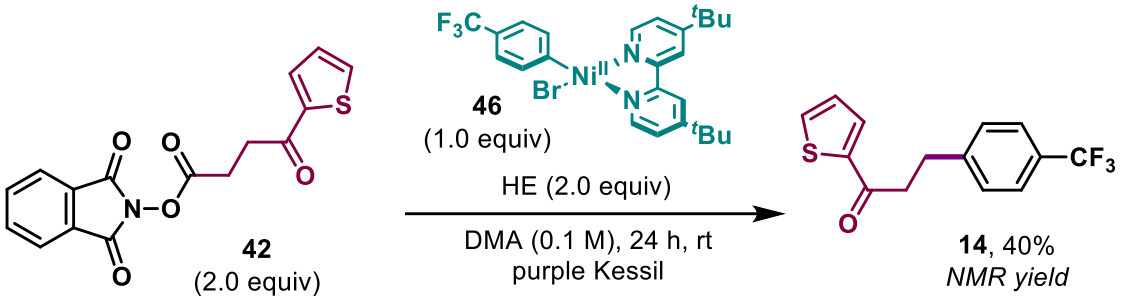
The reaction was performed according to General Procedure II using **42** (1.0 equiv, 0.3 mmol), Hantzsch ester (1.0 equiv, 0.3 mmol) in DMA (0.1 M, 3 mL). The corresponding products (**43** & **44**) were isolated via automated flash column chromatography. For characterization of compound **43** see above. Product **44** was obtained as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ /ppm 7.71 (d, $J$ = 3.7 Hz, 1H), 7.61 (d, $J$ = 4.9 Hz, 1H), 7.12 (t, $J$ = 4.4 Hz, 1H), 2.94 (q, $J$ = 7.4 Hz, 2H), 1.24 (t, $J$ = 7.4 Hz, 3H).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ /ppm 194.0, 144.3, 133.3, 131.7, 128.1, 32.7, 8.7. **FT-IR** ($cm^{-1}$, neat, ATR) 2978, 2937, 1660, 1518, 1459, 1376, 1277, 1225, 1085, 799. The spectroscopic data is consistent with those reported in literature.[5]




**Scheme S4:** Investigating SET events from Ni(0) to the corresponding redox-active ester in the presence of stoichiometric amounts of $Ni(COD)_2$ as reductant.

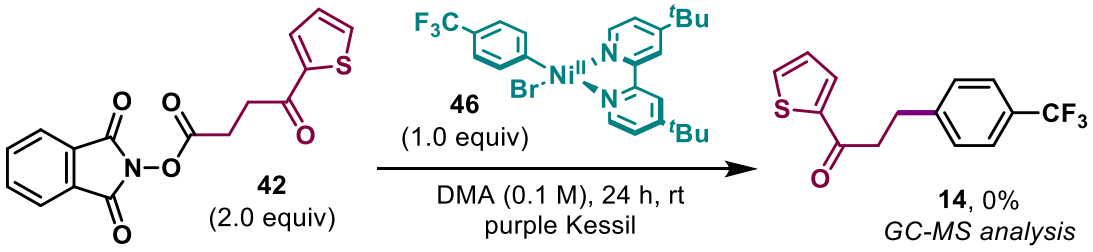
The reaction was performed according to General Procedure II using **42** (1.0 equiv, 0.3 mmol), $Ni(COD)_2$ (1.0 equiv, 0.3 mmol), and 4,4'-di-*tert*-butyl-2,2'-dipyridine (dtbpy, 1.1 equiv, 0.33 mmol) in DMA (0.1 M, 3 mL). The crude reaction mixture was analyzed using GC-MS analysis whereby no homocoupling or alkene product formation was observed, ruling out a plausible SET event from Ni(0) to the redox-active ester.

**Stoichiometric experiments with Ni-complex 46**




**Scheme S5:** Stoichiometric experiments with Ni-complex **46**. Yield was determined using $^{1}$H-NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. Reaction conditions as described in General Procedure II for decarboxylative arylation.

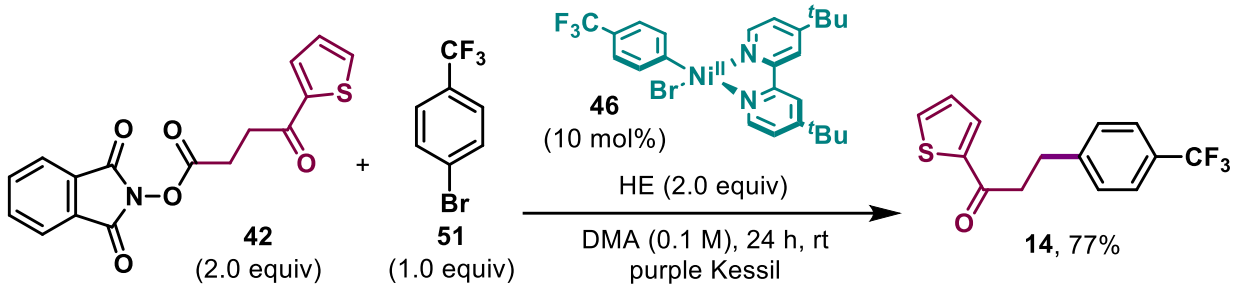
The reaction was performed in a nitrogen-filled glove box according to General Procedure II using **42** (2.0 equiv, 0.6 mmol), Ni-complex **46** (1.0 equiv, 0.3 mmol), and HE (2.0 equiv, 0.6 mmol) in DMA (0.1 M). The reaction vial was removed from the glove box and irradiated for 24 h. After the work-up, the desired product was obtained in 40% yield as determined by $^{1}$H-NMR spectroscopy using 1,3,5-trimethoxybenzene (0.3 mmol) as an internal standard. For characterization of compound **14** see Section **III.**




**Scheme S6:** Stoichiometric experiment with Ni-complex **46**. Reaction conditions as described in General Procedure II for decarboxylative arylation.

The reaction was performed in a nitrogen-filled glove box according to General Procedure II using **42** (2.0 equiv, 0.6 mmol) and Ni-complex **46** (1.0 equiv, 0.3 mmol) in DMA (0.1 M). No aryl bromide or HE were added to the reaction mixture. The tube was removed from the glove box and irradiated for 24 h. The crude reaction mixture was analyzed by GC-MS. The C($sp^3$)–C($sp^2$) product was not observed, highlighting the necessity for EDA complexation for effective coupling.

**Catalytic competence of Ni-complex 46**




**Scheme S7:** Catalytic competence of Ni-complex **46**. Isolated yield after purification. Reaction conditions as described in the general procedure for decarboxylative arylation.

The reaction was set up in a nitrogen-filled glove box and performed according to General Procedure II using **42** (2.0 equiv, 0.6 mmol) and Ni-complex **46** (10 mol %, 0.03 mmol). The reaction vial was removed from the glove box, and the reaction mixture was irradiated for 24 h. After automated flash column chromatography, the desired product (**14**) was isolated in 77% yield. For characterization of compound **14** see Section **III.**

## V. X-Ray Structure Determination of 32

Product **32** was obtained with a diastereomeric ratio of >20:1. The relative configuration of the major diastereomer was elucidated based X-ray crystallography with the aryl group *cis* with respect to the dimethyl acetal protecting group. Supplementary crystallographic data is provided free of charge by The Cambridge Crystallographic Data Centre (CCDC deposition number: CCDC 2062315).

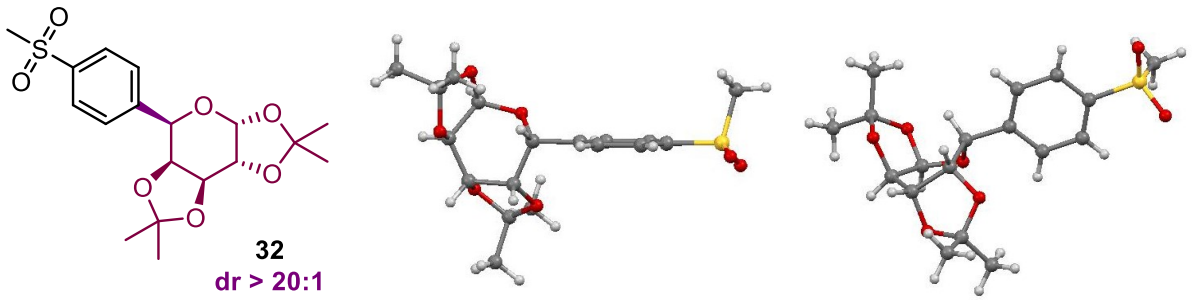


**Figure S6**: Molecular crystal structure obtained for product **32**. CCDC deposition number: CCDC 2062315.

Compound **32**, $C_{18}H_{24}O_7S$, crystallizes in the monoclinic space group $P2_1$ (systematic absences 0k0: k=odd) with a=13.1341(2)Å, b=5.53710(10)Å, c=15.0402(3)Å, β=113.768(2)°, V=1001.03(3)Å$^3$, Z=2, and $d_{calc}$=1.275 g/cm$^3$. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[1] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 seconds for θ = ±47.2° and 1 second for θ = 107.75°. A total of 4592 frames (36 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.05 seconds for θ = ±47.2° and 0.1 seconds for θ = 107.75° and -86.25°.

Rotation frames were integrated using CrysAlisPro[1], producing a listing of unaveraged $F^2$ and $\sigma(F^2)$ values. A total of 16678 reflections were measured over the ranges $6.422 \leq 2\theta \leq 148.994°$, $-16 \leq h \leq 13$, $-6 \leq k \leq 6$, $-18 \leq l \leq 18$ yielding 3995 unique reflections ($R_{int}$ = 0.0397). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[6] (minimum and maximum transmission 0.7948, 1.0000). The structure was solved by direct methods - SHELXT.[7] There was a region of disordered solvent for which a reliable disorder model could not be devised; the X-ray data were corrected for the presence of disordered solvent using SQUEEZE.[8] Refinement was by full-matrix least squares based on $F^2$ using SHELXL-2018. [7]All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0347P)^2 + 0.1843P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0280 and wR2=0.0702 for 3923 observed reflections for which $F > 4\sigma(F)$ and R1=0.0283 and wR2=0.0704 and GOF =1.049 for all 3995 unique, non-zero reflections and 240 variables. The maximum $\Delta/\sigma$ in the final cycle of least squares was 0.003 and the two most prominent peaks in the final difference Fourier were +0.14 and -0.30 e/Å$^3$.

[1] CrysAlisPro 1.171.40.53: Rigaku Oxford Diffraction, Rigaku Corporation, Oxford, UK. (2019).

Table S3 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables S4 and S5 Anisotropic thermal parameters are in Table S6 Tables S7 and S8 list bond distances and bond angles. Figure S7 is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

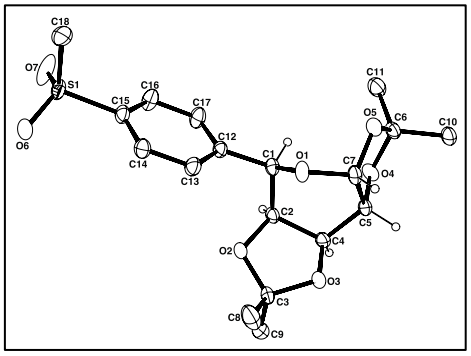



**Figure S7:** ORTEP drawing of the title compound with 50% thermal ellipsoids.

**Table S2:** Summary of Structure Determination of Compound **32**

| | |
|---|---|
| Empirical formula | $C_{18}H_{24}O_7S$ |
| Formula weight | 384.43 |
| Diffractometer | Rigaku XtaLAB Synergy-S (HyPix-6000HE) |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| a | 13.1341(2)Å |
| b | 5.53710(10)Å |
| c | 15.0402(3)Å |
| β | 113.768(2)° |
| Volume | 1001.03(3)$Å^3$ |
| Z | 2 |
| $d_{calc}$ | 1.275 g/$cm^3$ |
| μ | 1.745 $mm^{-1}$ |
| F(000) | 408.0 |
| Crystal size, mm | 0.28 × 0.14 × 0.11 |
| 2θ range for data collection | 6.422 - 148.994° |
| Index ranges | $-16 \leq h \leq 13$, $-6 \leq k \leq 6$, $-18 \leq l \leq 18$ |

| | |
|---|---|
| Reflections collected | 16678 |
| Independent reflections | 3995[R(int) = 0.0397] |
| Data/restraints/parameters | 3995/1/240 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0280, $wR_2$ = 0.0702 |
| Final R indexes [all data] | $R_1$ = 0.0283, $wR_2$ = 0.0704 |
| Largest diff. peak/hole | 0.14/-0.30 eÅ$^{-3}$ |
| Flack parameter | -0.007(7) |

**Table S3:** Refined Positional Parameters for Compound **32**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| S1 | 0.16085(3) | 0.31441(9) | 0.09277(3) | 0.02334(12) |
| O1 | 0.67026(10) | 0.7869(3) | 0.29088(10) | 0.0214(3) |
| O2 | 0.62767(10) | 0.5682(3) | 0.45493(10) | 0.0222(3) |
| O3 | 0.78219(11) | 0.8023(3) | 0.51346(11) | 0.0277(3) |
| O4 | 0.90168(11) | 0.5048(3) | 0.36468(10) | 0.0230(3) |
| O5 | 0.81365(10) | 0.7583(3) | 0.23828(10) | 0.0228(3) |
| O6 | 0.10102(12) | 0.4190(4) | 0.14457(12) | 0.0346(4) |
| O7 | 0.15139(12) | 0.0583(3) | 0.07414(15) | 0.0425(5) |
| C1 | 0.65134(14) | 0.5365(3) | 0.30366(14) | 0.0185(4) |
| C2 | 0.69851(14) | 0.4755(4) | 0.41199(14) | 0.0188(4) |
| C3 | 0.68882(15) | 0.7280(4) | 0.53276(15) | 0.0234(4) |
| C4 | 0.81061(16) | 0.6040(4) | 0.46796(14) | 0.0221(4) |
| C5 | 0.86462(15) | 0.7047(4) | 0.40413(14) | 0.0211(4) |
| C6 | 0.90418(15) | 0.5892(4) | 0.27568(15) | 0.0213(4) |
| C7 | 0.78333(14) | 0.8370(4) | 0.31361(14) | 0.0210(4) |
| C8 | 0.6182(2) | 0.9445(4) | 0.5276(2) | 0.0368(6) |
| C9 | 0.72689(18) | 0.5945(5) | 0.62913(16) | 0.0309(5) |
| C10 | 1.01337(15) | 0.7176(4) | 0.29485(15) | 0.0247(4) |
| C11 | 0.8825(2) | 0.3825(4) | 0.20581(18) | 0.0315(5) |
| C12 | 0.52820(14) | 0.4847(4) | 0.25296(14) | 0.0189(4) |
| C13 | 0.44858(16) | 0.6501(4) | 0.25354(15) | 0.0230(4) |
| C14 | 0.33596(16) | 0.5995(4) | 0.20498(15) | 0.0235(4) |
| C15 | 0.30412(15) | 0.3815(4) | 0.15685(14) | 0.0214(4) |
| C16 | 0.38174(16) | 0.2119(4) | 0.15755(16) | 0.0275(4) |
| C17 | 0.49423(16) | 0.2648(4) | 0.20660(16) | 0.0265(4) |
| C18 | 0.12218(17) | 0.4673(5) | -0.01841(16) | 0.0307(5) |

**Table S4:** Positional Parameters for Hydrogens in Compound **32**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1 | 0.690532 | 0.439102 | 0.272957 | 0.022 |
| H2 | 0.707104 | 0.300378 | 0.421532 | 0.023 |
| H4 | 0.862142 | 0.495639 | 0.517054 | 0.027 |
| H5 | 0.927293 | 0.809685 | 0.441795 | 0.025 |
| H7 | 0.795868 | 1.011435 | 0.32264 | 0.025 |
| H8a | 0.594348 | 1.016763 | 0.464393 | 0.055 |
| H8b | 0.660765 | 1.059593 | 0.576076 | 0.055 |
| H8c | 0.554362 | 0.895874 | 0.538989 | 0.055 |
| H9a | 0.663094 | 0.540266 | 0.639473 | 0.046 |
| H9b | 0.770323 | 0.701124 | 0.680864 | 0.046 |
| H9c | 0.771285 | 0.457872 | 0.627874 | 0.046 |
| H10a | 1.015597 | 0.764352 | 0.234194 | 0.037 |
| H10b | 1.074316 | 0.610869 | 0.328815 | 0.037 |
| H10c | 1.019142 | 0.858795 | 0.333663 | 0.037 |
| H11a | 0.81248 | 0.308913 | 0.195753 | 0.047 |
| H11b | 0.940851 | 0.265158 | 0.232031 | 0.047 |
| H11c | 0.88019 | 0.441093 | 0.144965 | 0.047 |
| H13 | 0.470988 | 0.795408 | 0.286703 | 0.028 |
| H14 | 0.282787 | 0.710638 | 0.204829 | 0.028 |
| H16 | 0.359091 | 0.064864 | 0.125759 | 0.033 |
| H17 | 0.547177 | 0.151329 | 0.208282 | 0.032 |
| H18a | 0.044884 | 0.438392 | -0.057658 | 0.046 |
| H18b | 0.166177 | 0.409631 | -0.051785 | 0.046 |
| H18c | 0.13434 | 0.637408 | -0.006555 | 0.046 |

**Table S5:** Refined Thermal Parameters (U's) for Compound **32**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S1 | 0.01192(19) | 0.0285(2) | 0.0248(2) | 0.0021(2) | 0.00246(15) | -0.00080(17) |
| O1 | 0.0124(5) | 0.0225(7) | 0.0291(7) | 0.0042(6) | 0.0081(5) | 0.0011(5) |
| O2 | 0.0132(6) | 0.0335(8) | 0.0219(7) | -0.0043(6) | 0.0092(5) | -0.0024(5) |
| O3 | 0.0210(6) | 0.0374(8) | 0.0308(7) | -0.0128(7) | 0.0168(5) | -0.0099(7) |
| O4 | 0.0192(6) | 0.0300(8) | 0.0239(7) | 0.0039(6) | 0.0129(5) | 0.0060(5) |
| O5 | 0.0159(6) | 0.0305(8) | 0.0231(7) | 0.0027(6) | 0.0091(5) | 0.0018(5) |
| O6 | 0.0160(6) | 0.0604(11) | 0.0283(8) | -0.0016(7) | 0.0098(6) | -0.0038(7) |
| O7 | 0.0181(7) | 0.0276(9) | 0.0633(12) | 0.0011(8) | -0.0029(7) | -0.0049(6) |
| C1 | 0.0136(8) | 0.0201(9) | 0.0220(9) | 0.0022(7) | 0.0074(7) | 0.0013(7) |
| C2 | 0.0134(8) | 0.0244(9) | 0.0196(9) | 0.0014(7) | 0.0078(7) | 0.0020(7) |
| C3 | 0.0182(8) | 0.0295(11) | 0.0276(10) | -0.0065(8) | 0.0143(8) | -0.0067(7) |
| C4 | 0.0152(8) | 0.0337(11) | 0.0182(9) | -0.0017(8) | 0.0076(7) | 0.0002(7) |
| C5 | 0.0120(7) | 0.0305(10) | 0.0220(9) | -0.0029(8) | 0.0082(7) | -0.0009(7) |
| C6 | 0.0183(8) | 0.0256(10) | 0.0235(10) | 0.0007(8) | 0.0120(7) | 0.0009(7) |
| C7 | 0.0149(8) | 0.0236(10) | 0.0271(9) | 0.0001(8) | 0.0112(7) | -0.0008(7) |
| C8 | 0.0378(12) | 0.0304(13) | 0.0556(16) | -0.0047(11) | 0.0329(12) | -0.0025(10) |
| C9 | 0.0231(10) | 0.0478(14) | 0.0234(10) | -0.0061(10) | 0.0108(8) | -0.0045(9) |
| C10 | 0.0164(8) | 0.0339(11) | 0.0260(10) | 0.0006(9) | 0.0109(7) | -0.0009(8) |
| C11 | 0.0364(11) | 0.0297(11) | 0.0369(12) | -0.0069(9) | 0.0236(10) | -0.0062(8) |
| C12 | 0.0135(8) | 0.0245(9) | 0.0175(8) | 0.0028(7) | 0.0048(7) | 0.0007(7) |
| C13 | 0.0158(8) | 0.0269(10) | 0.0243(10) | -0.0025(8) | 0.0058(7) | 0.0007(7) |
| C14 | 0.0149(8) | 0.0292(11) | 0.0250(10) | 0.0013(8) | 0.0066(7) | 0.0047(8) |
| C15 | 0.0130(8) | 0.0279(10) | 0.0209(9) | 0.0042(8) | 0.0042(7) | 0.0003(7) |
| C16 | 0.0184(9) | 0.0248(10) | 0.0345(12) | -0.0034(9) | 0.0056(8) | -0.0016(8) |
| C17 | 0.0158(8) | 0.0272(11) | 0.0328(11) | -0.0004(9) | 0.0059(8) | 0.0025(7) |
| C18 | 0.0208(9) | 0.0448(13) | 0.0221(10) | 0.0028(9) | 0.0040(8) | 0.0073(9) |

**Table S6:** Bond Distances in Compound **32**, Å

| | | | | | |
|---|---|---|---|---|---|
| S1-O6 | 1.4331(17) | S1-O7 | 1.4414(19) | S1-C15 | 1.7736(18) |
| S1-C18 | 1.757(2) | O1-C1 | 1.435(2) | O1-C7 | 1.411(2) |
| O2-C2 | 1.425(2) | O2-C3 | 1.428(2) | O3-C3 | 1.430(2) |
| O3-C4 | 1.421(3) | O4-C5 | 1.431(2) | O4-C6 | 1.431(2) |
| O5-C6 | 1.438(2) | O5-C7 | 1.413(2) | C1-C2 | 1.529(3) |
| C1-C12 | 1.512(2) | C2-C4 | 1.544(3) | C3-C8 | 1.498(3) |
| C3-C9 | 1.521(3) | C4-C5 | 1.512(3) | C5-C7 | 1.536(3) |
| C6-C10 | 1.521(3) | C6-C11 | 1.502(3) | C12-C13 | 1.393(3) |
| C12-C17 | 1.385(3) | C13-C14 | 1.389(3) | C14-C15 | 1.383(3) |
| C15-C16 | 1.383(3) | C16-C17 | 1.391(3) | | |

**Table S7:** Bond Angles in Compound **32, °**

| | | | | | |
|---|---|---|---|---|---|
| O6-S1-O7 | 118.70(12) | O6-S1-C15 | 108.30(10) | O6-S1-C18 | 108.13(11) |
| O7-S1-C15 | 107.53(9) | O7-S1-C18 | 108.66(13) | C18-S1-C15 | 104.64(10) |
| C7-O1-C1 | 112.32(15) | C2-O2-C3 | 109.90(13) | C4-O3-C3 | 106.77(16) |
| C6-O4-C5 | 105.98(15) | C7-O5-C6 | 110.06(14) | O1-C1-C2 | 109.78(16) |
| O1-C1-C12 | 108.87(15) | C12-C1-C2 | 112.78(15) | O2-C2-C1 | 110.19(15) |
| O2-C2-C4 | 103.89(15) | C1-C2-C4 | 111.53(16) | O2-C3-O3 | 104.89(15) |
| O2-C3-C8 | 108.74(18) | O2-C3-C9 | 109.89(17) | O3-C3-C8 | 108.82(18) |
| O3-C3-C9 | 110.72(16) | C8-C3-C9 | 113.41(19) | O3-C4-C2 | 103.94(15) |
| O3-C4-C5 | 107.59(18) | C5-C4-C2 | 114.34(16) | O4-C5-C4 | 107.64(17) |
| O4-C5-C7 | 103.44(15) | C4-C5-C7 | 113.74(15) | O4-C6-O5 | 104.57(14) |
| O4-C6-C10 | 110.54(16) | O4-C6-C11 | 109.65(18) | O5-C6-C10 | 109.74(17) |
| O5-C6-C11 | 109.20(17) | C11-C6-C10 | 112.82(16) | O1-C7-O5 | 110.76(15) |
| O1-C7-C5 | 114.13(16) | O5-C7-C5 | 104.12(15) | C13-C12-C1 | 121.72(18) |
| C17-C12-C1 | 118.87(17) | C17-C12-C13 | 119.40(17) | C14-C13-C12 | 120.51(19) |
| C15-C14-C13 | 118.97(19) | C14-C15-S1 | 119.88(15) | C14-C15-C16 | 121.49(17) |
| C16-C15-S1 | 118.63(16) | C15-C16-C17 | 118.9(2) | C12-C17-C16 | 120.69(19) |

This report has been created with Olex2 [9], compiled on 2018.05.29 svn.r3508 for OlexSys.

## VI. References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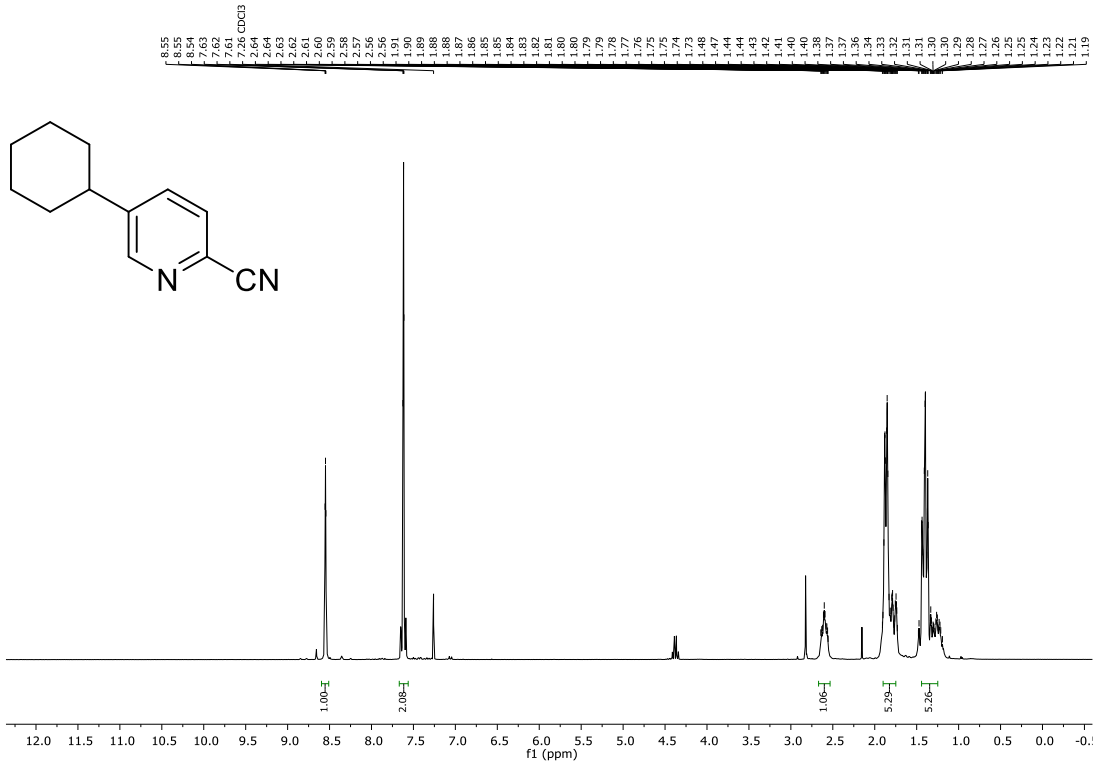
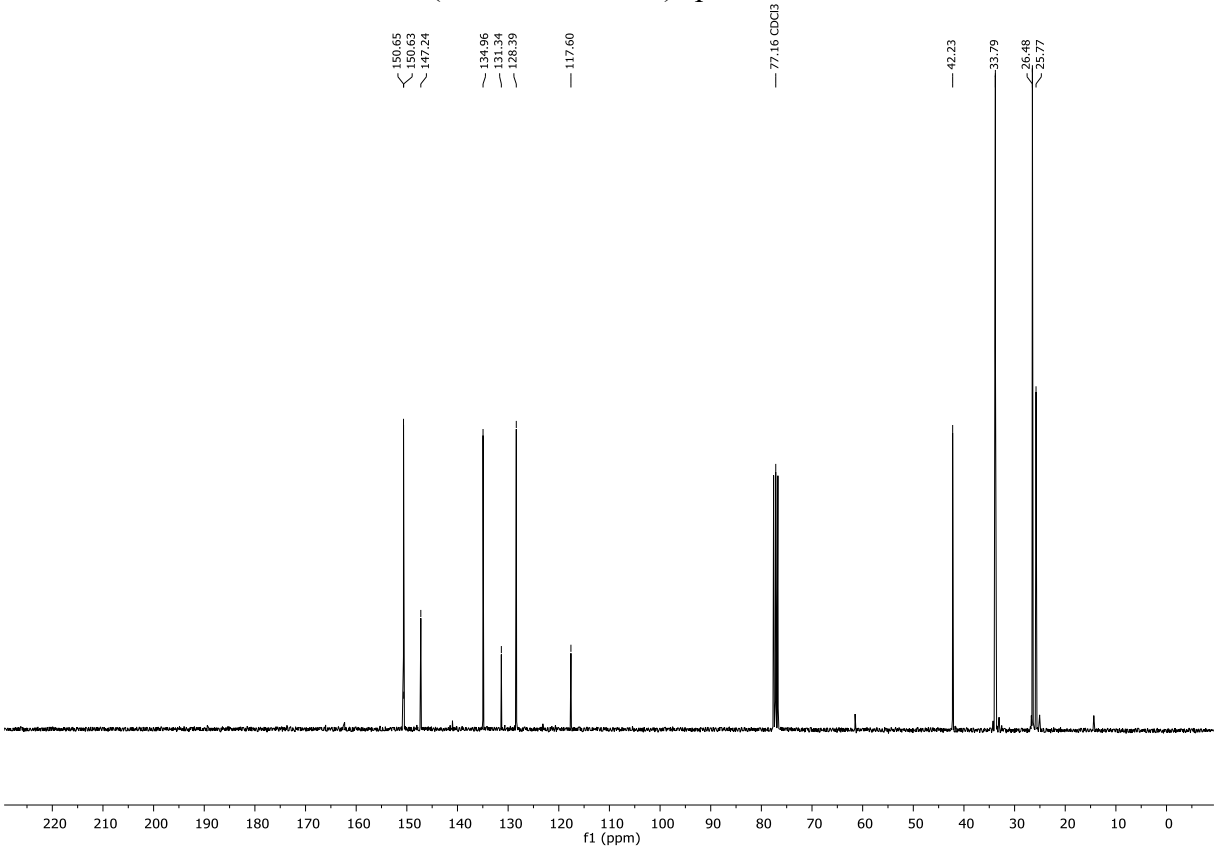
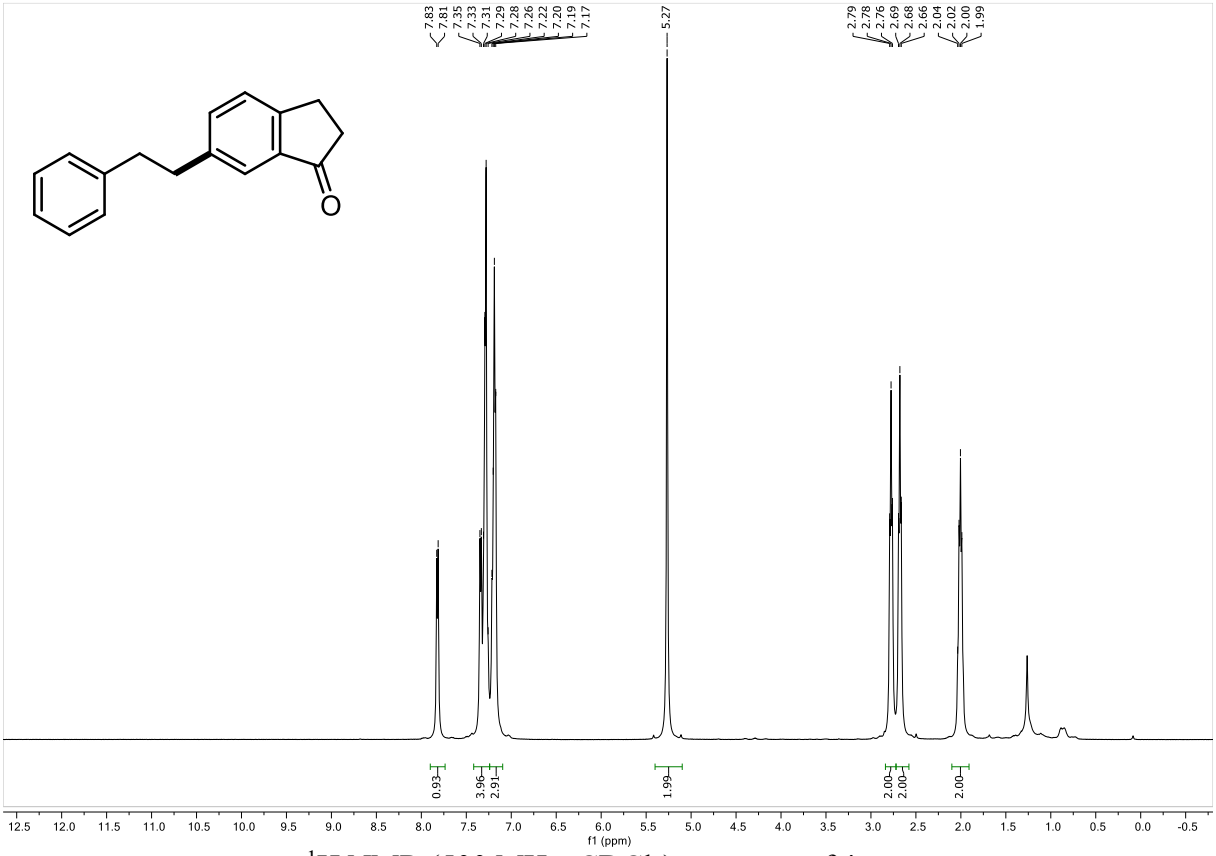
# VII. NMR Spectra of Synthesized Compounds



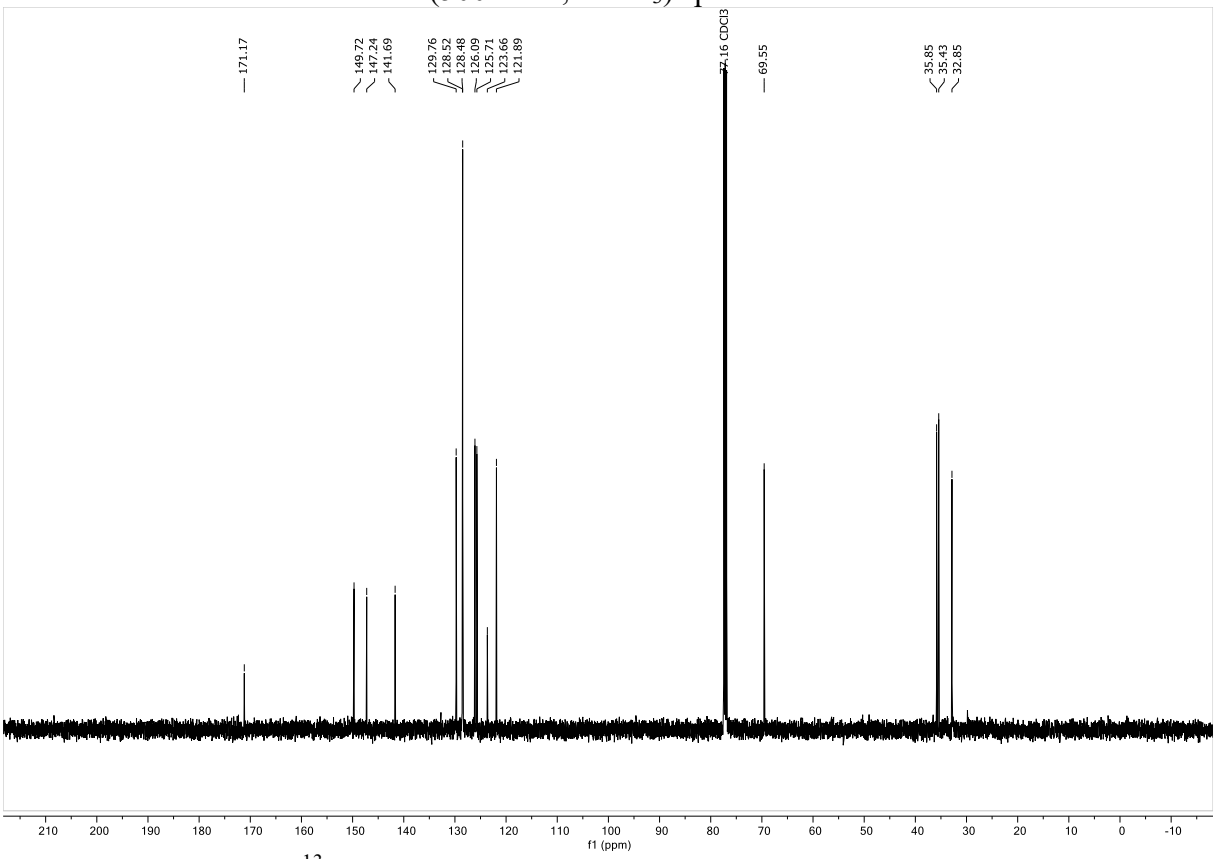

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **3**



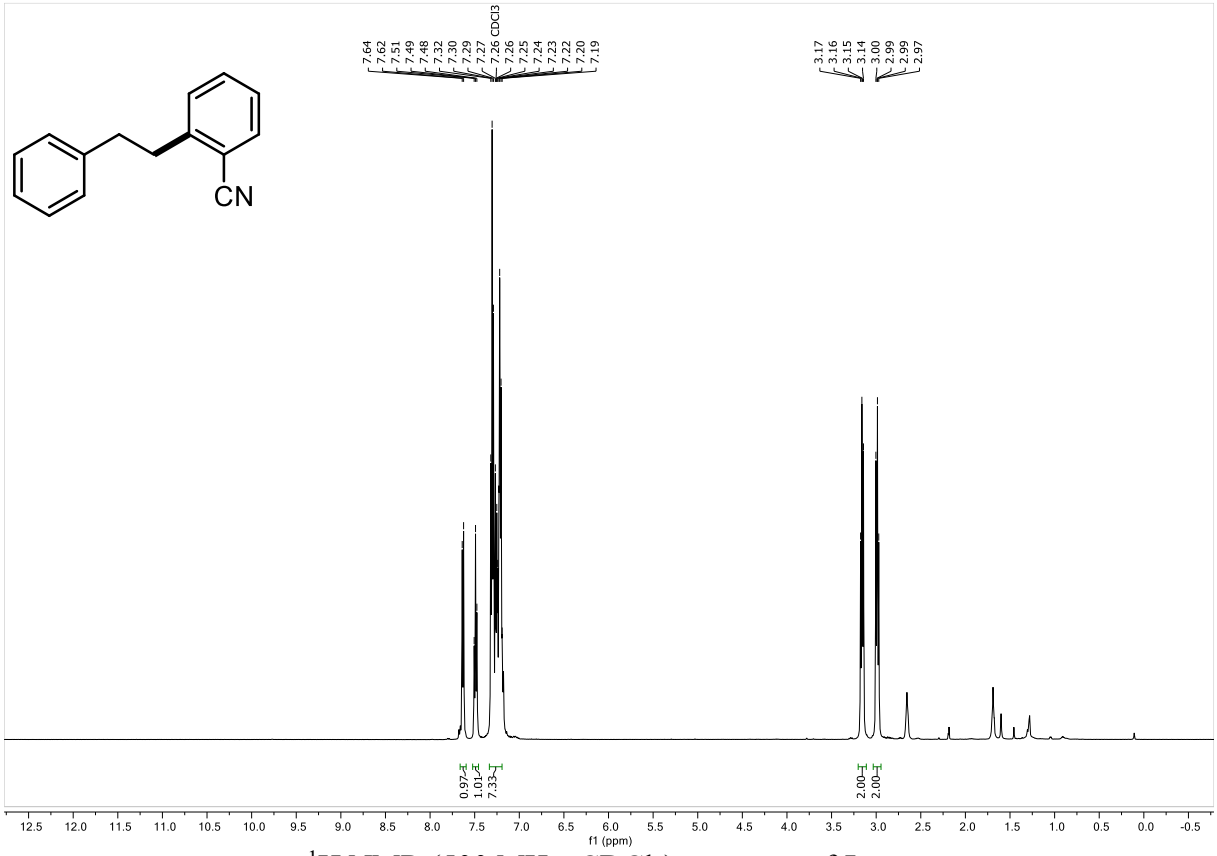

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **3**



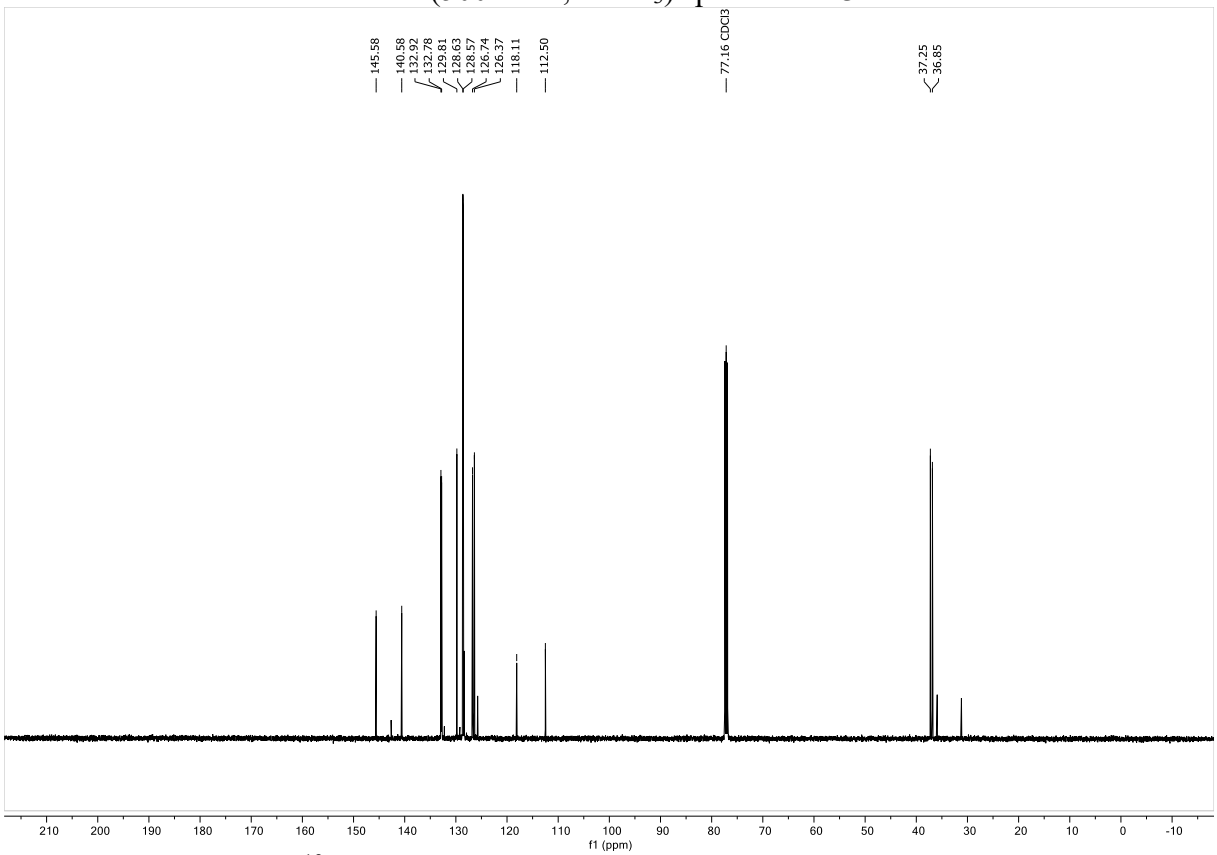

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **4**



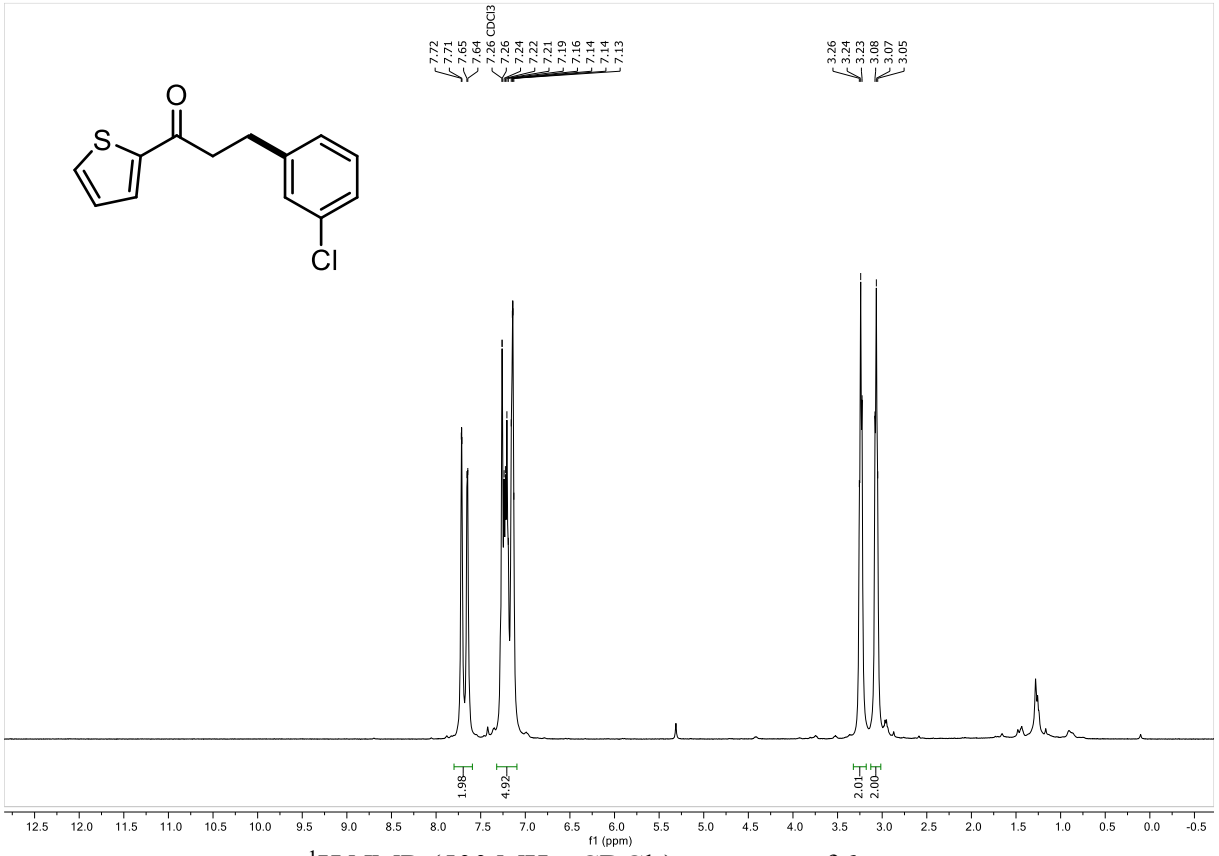

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **4**



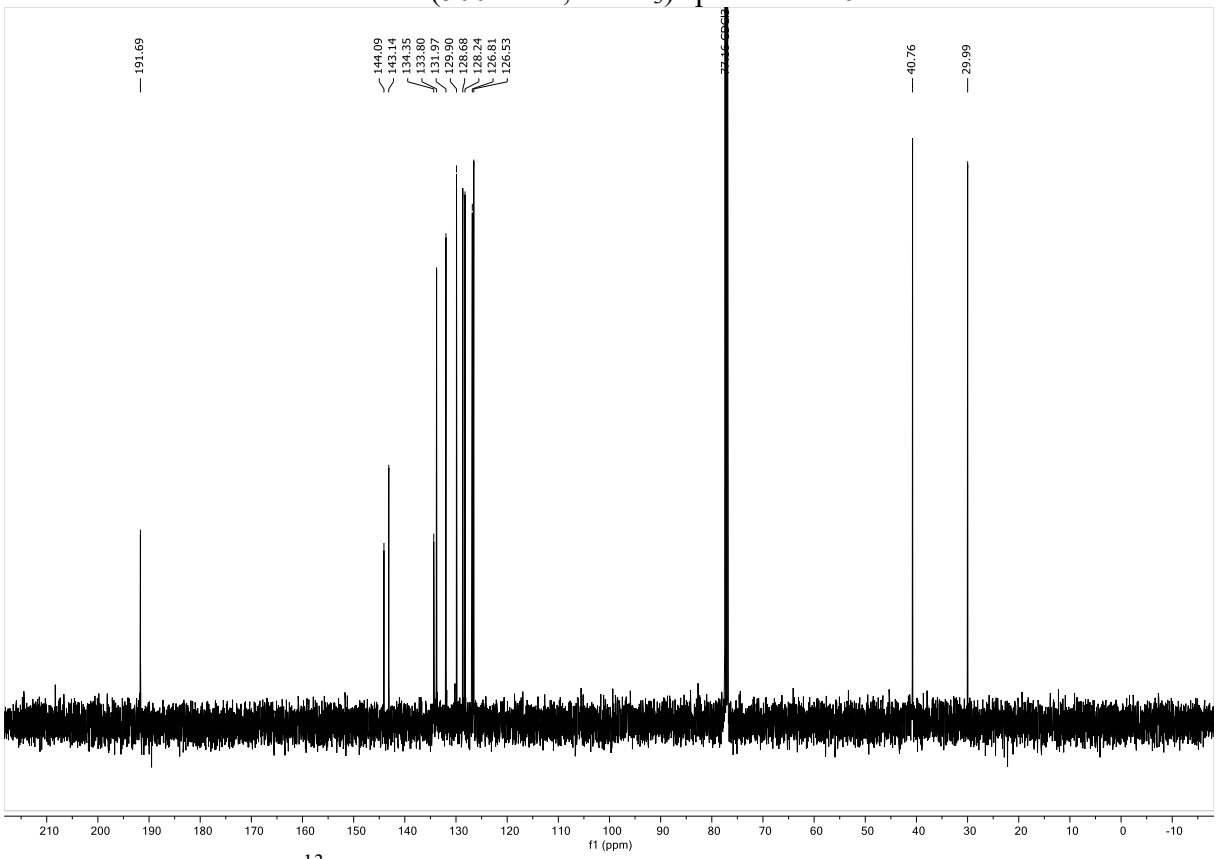

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **5**



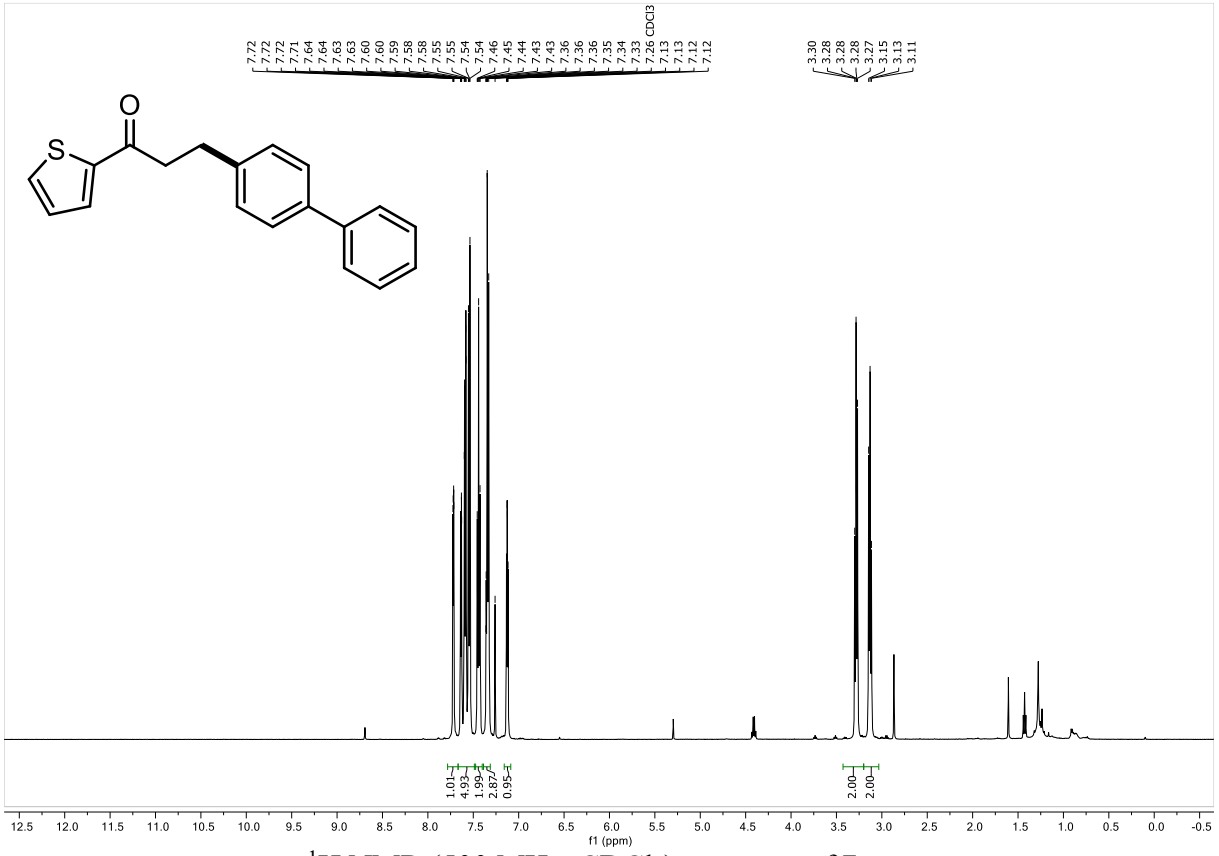

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **5**



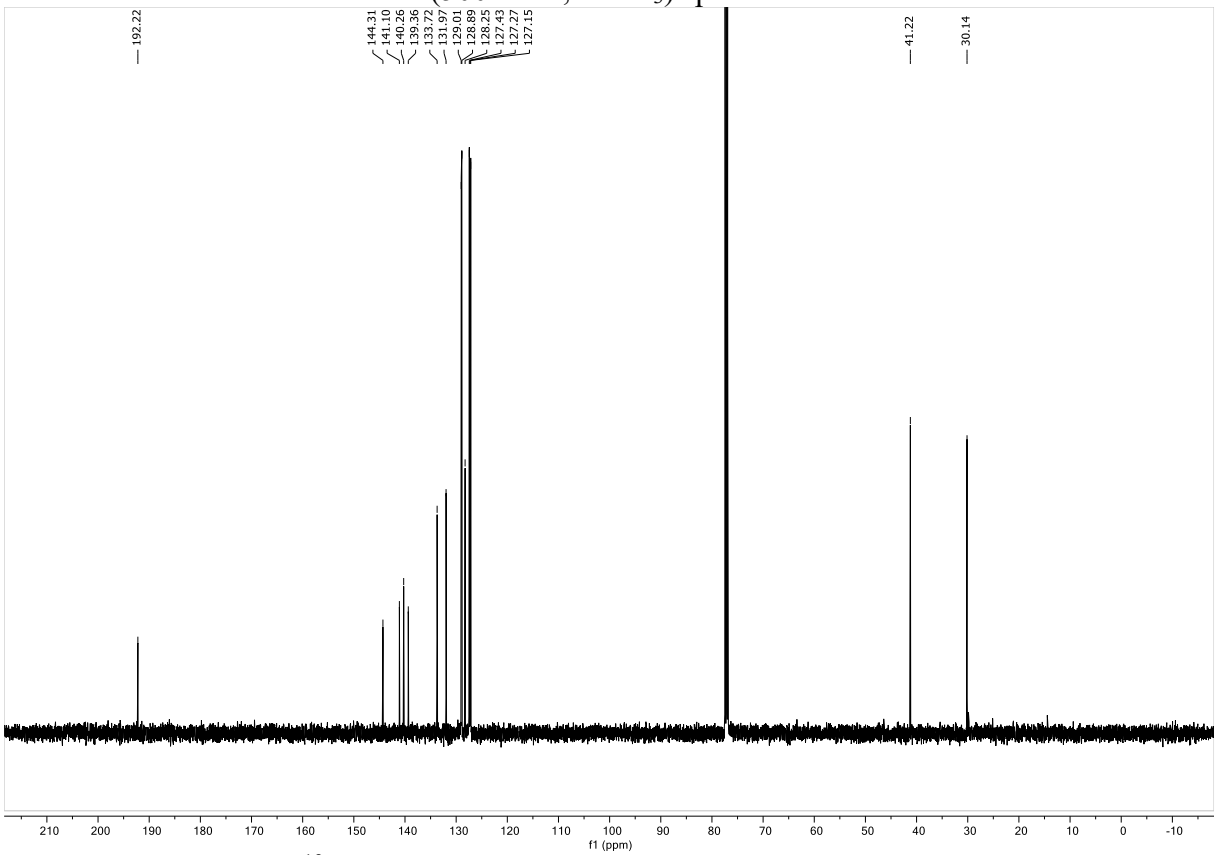

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **6**



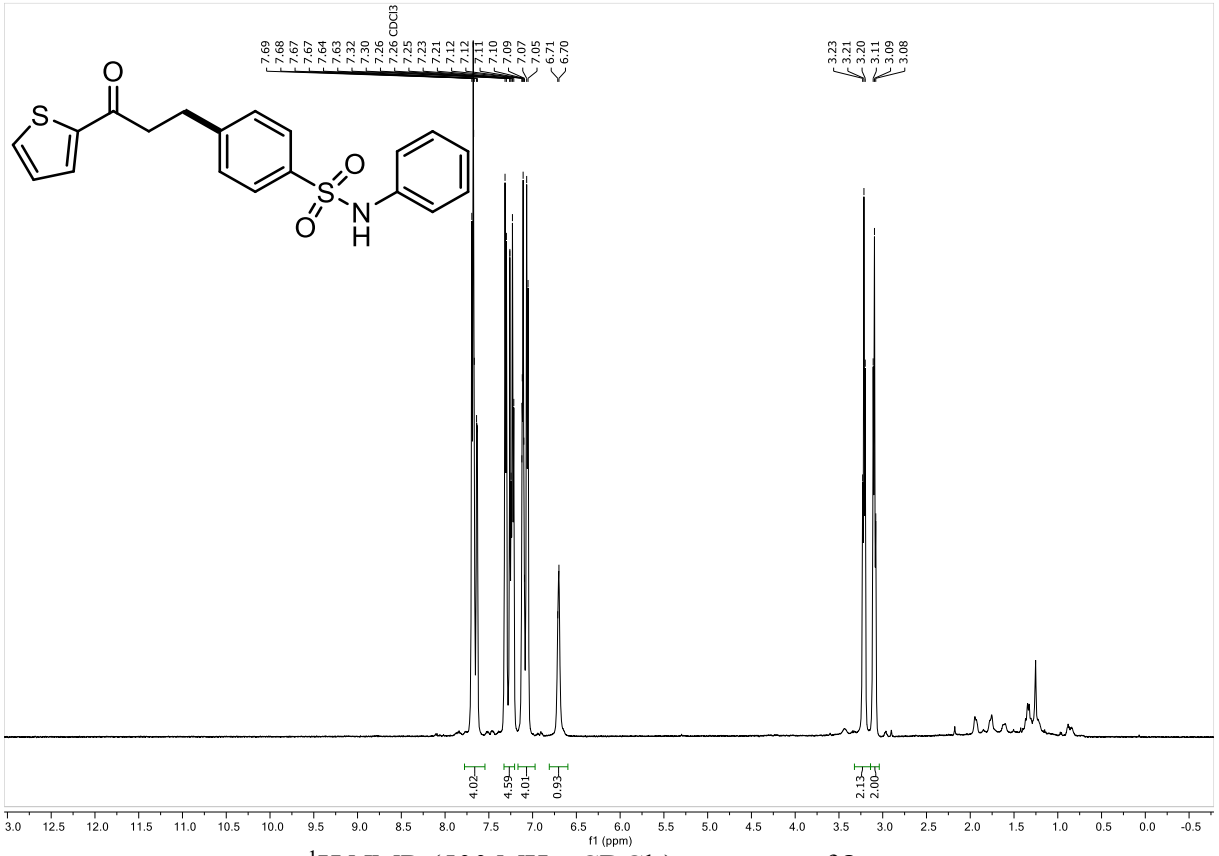

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **6**



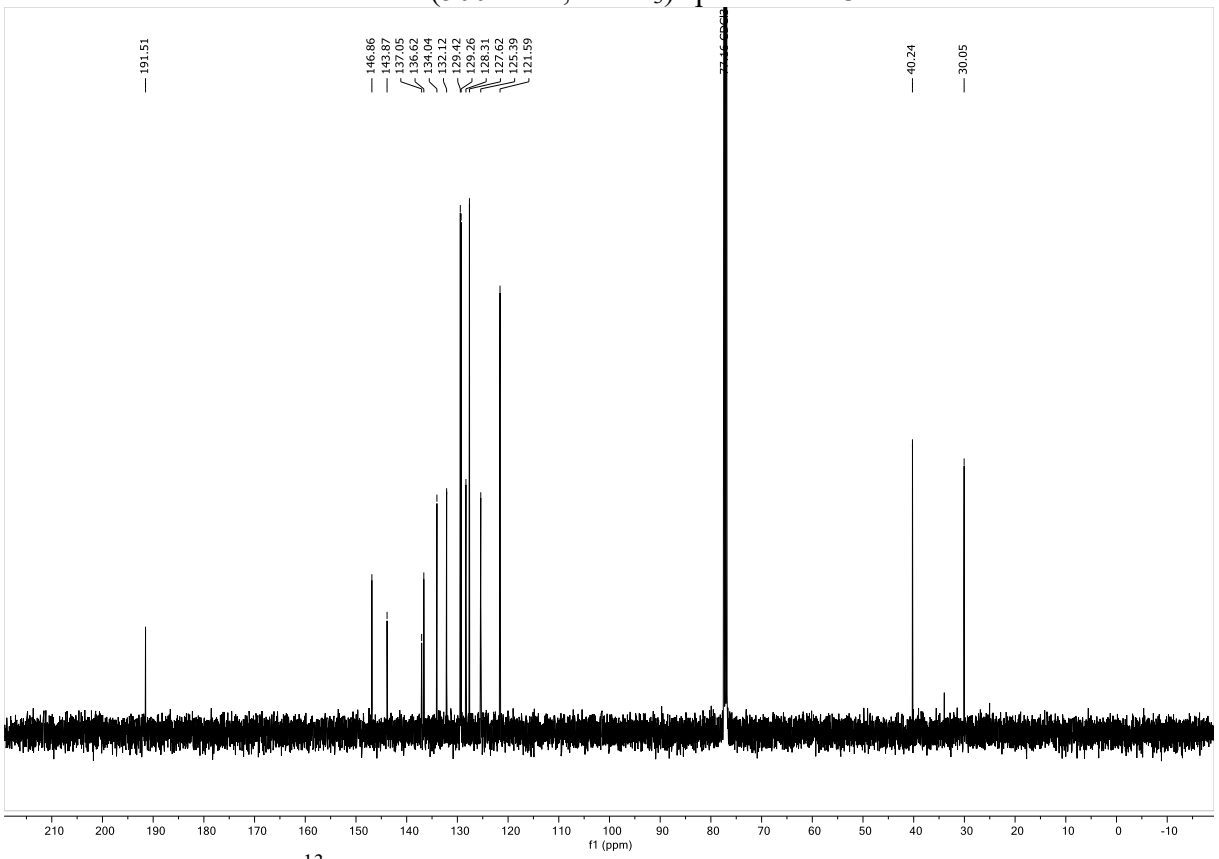

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **7**



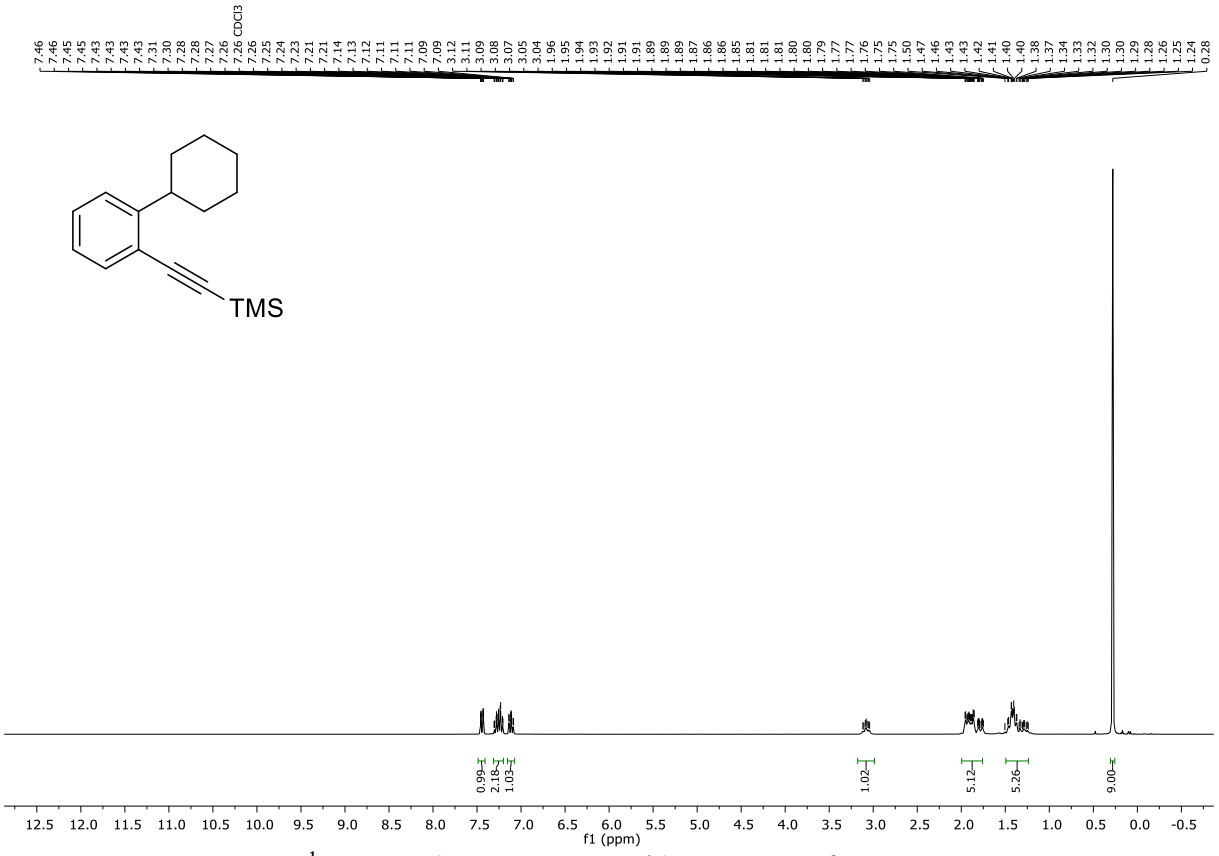

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **7**



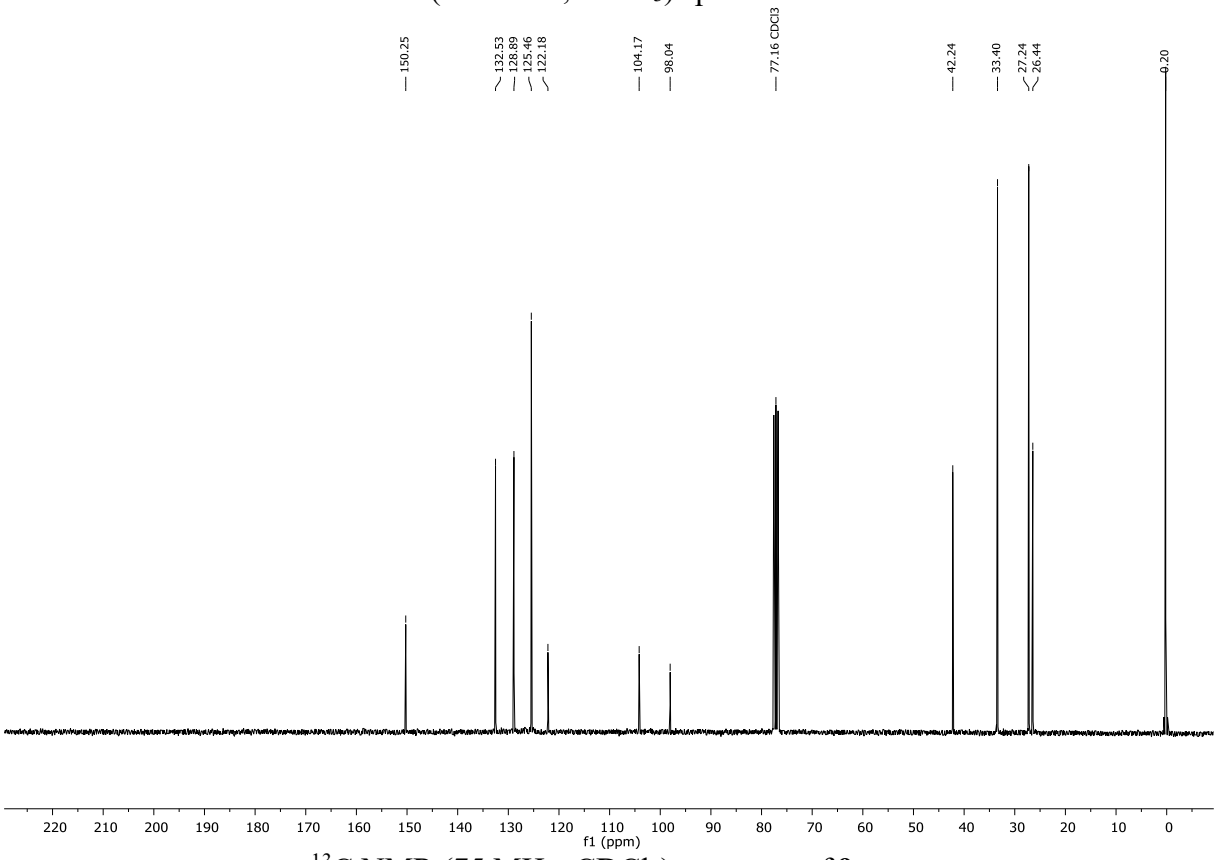

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **8**



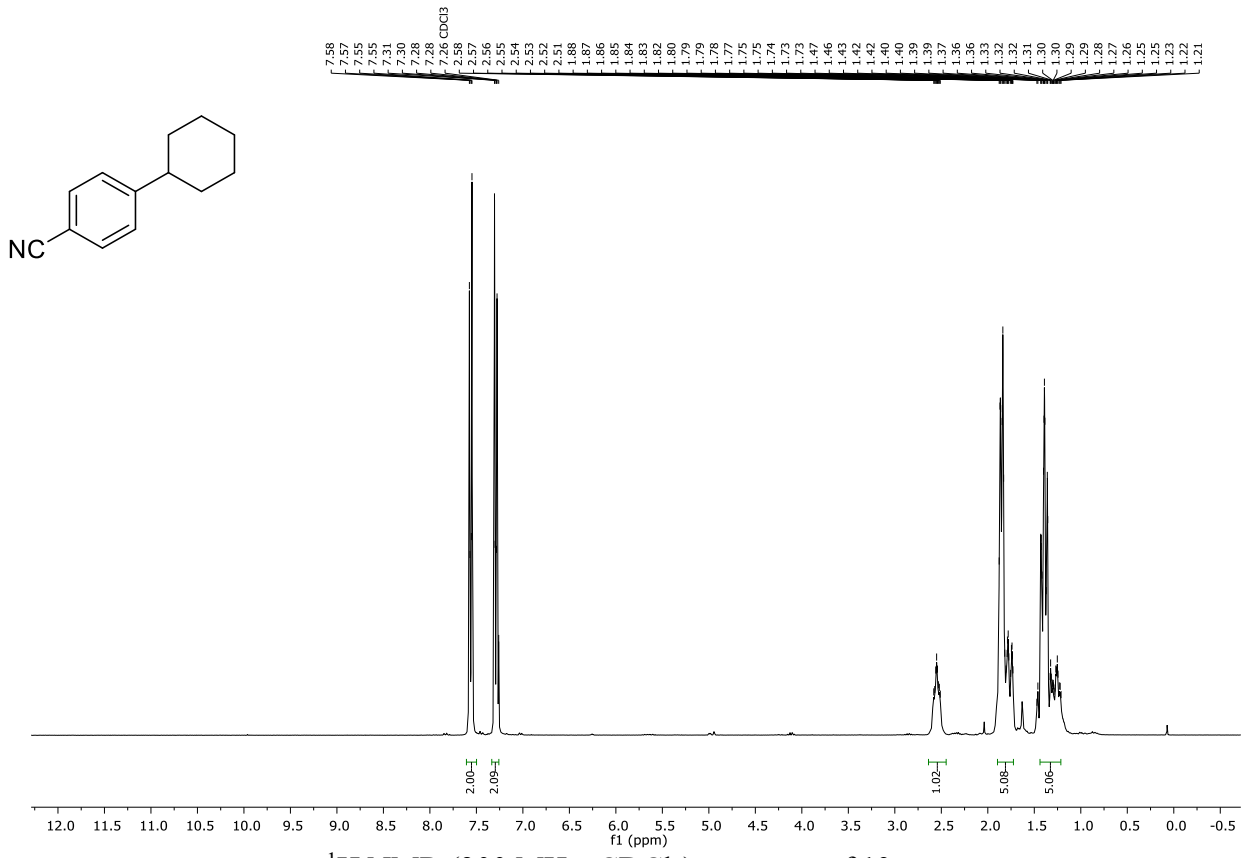

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **8**



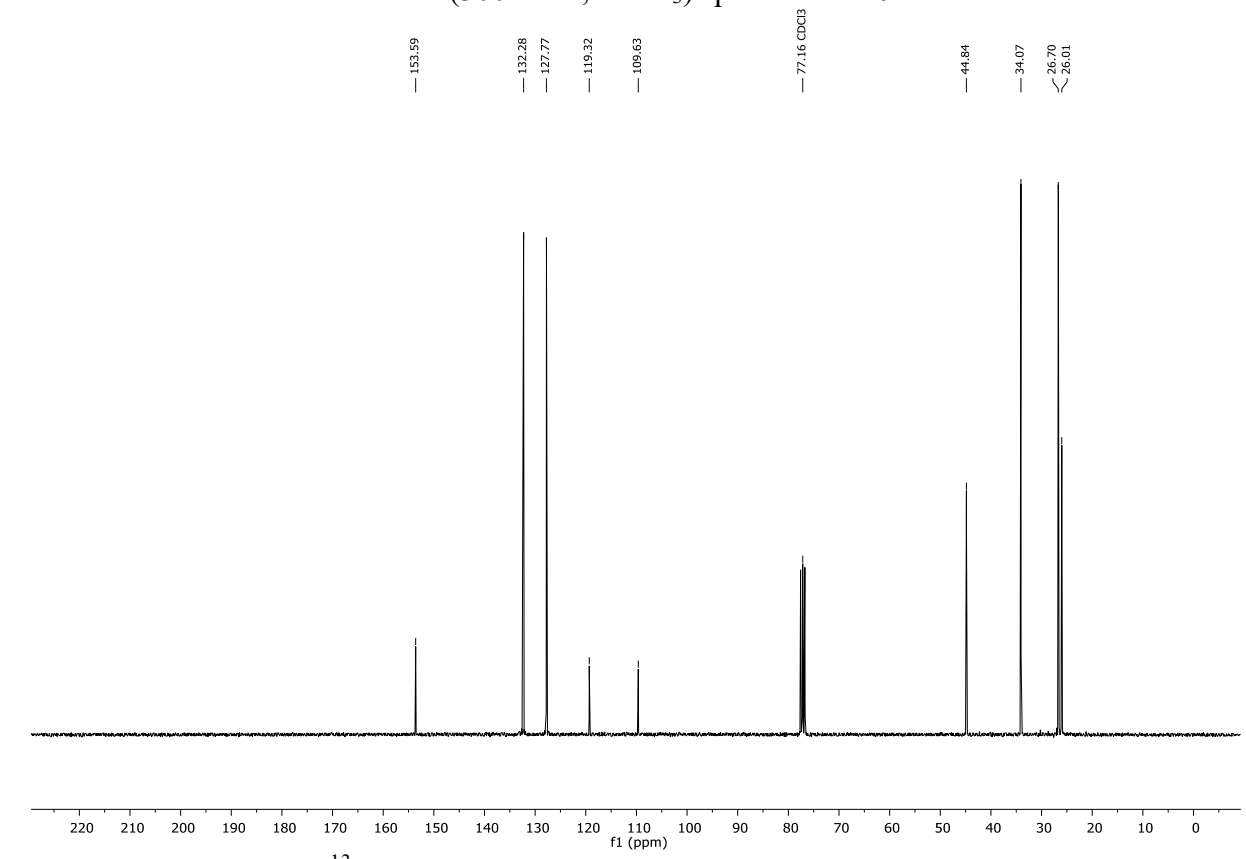

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **9**



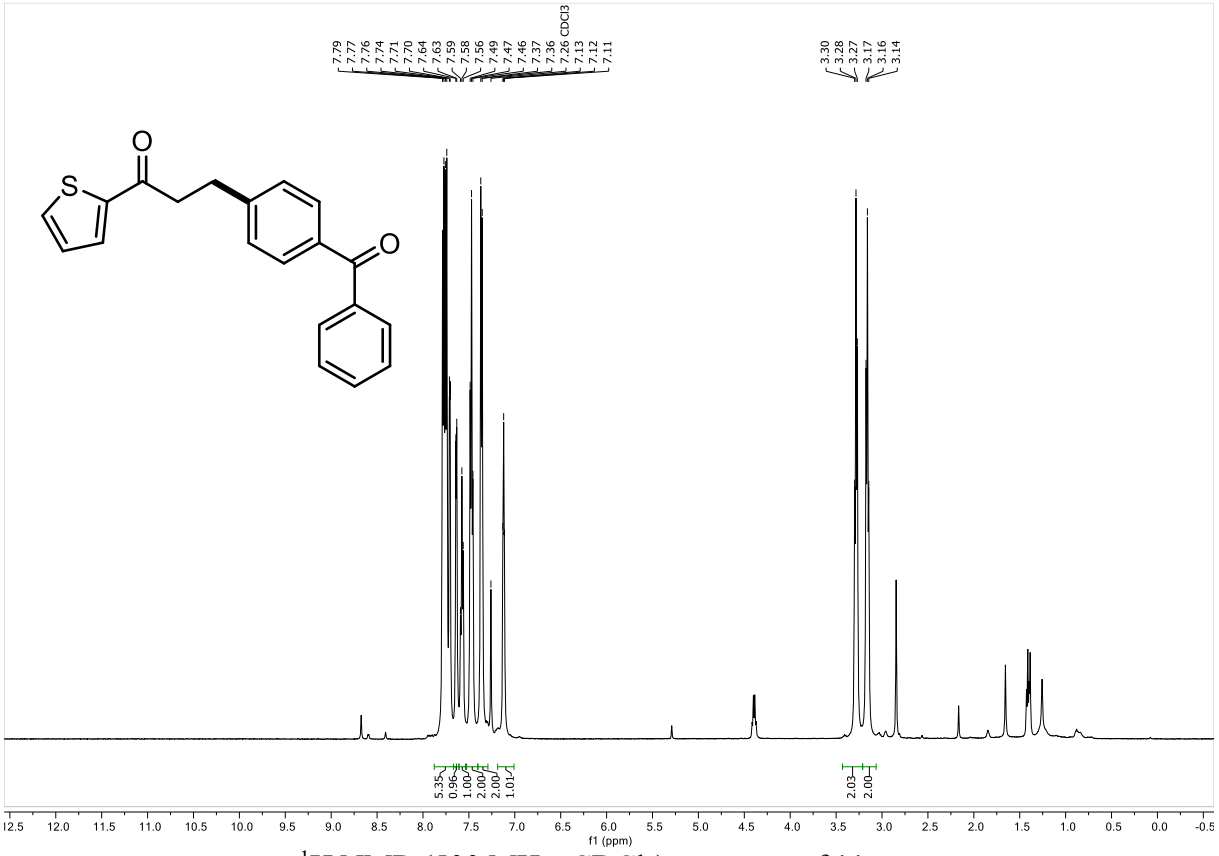

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **9**



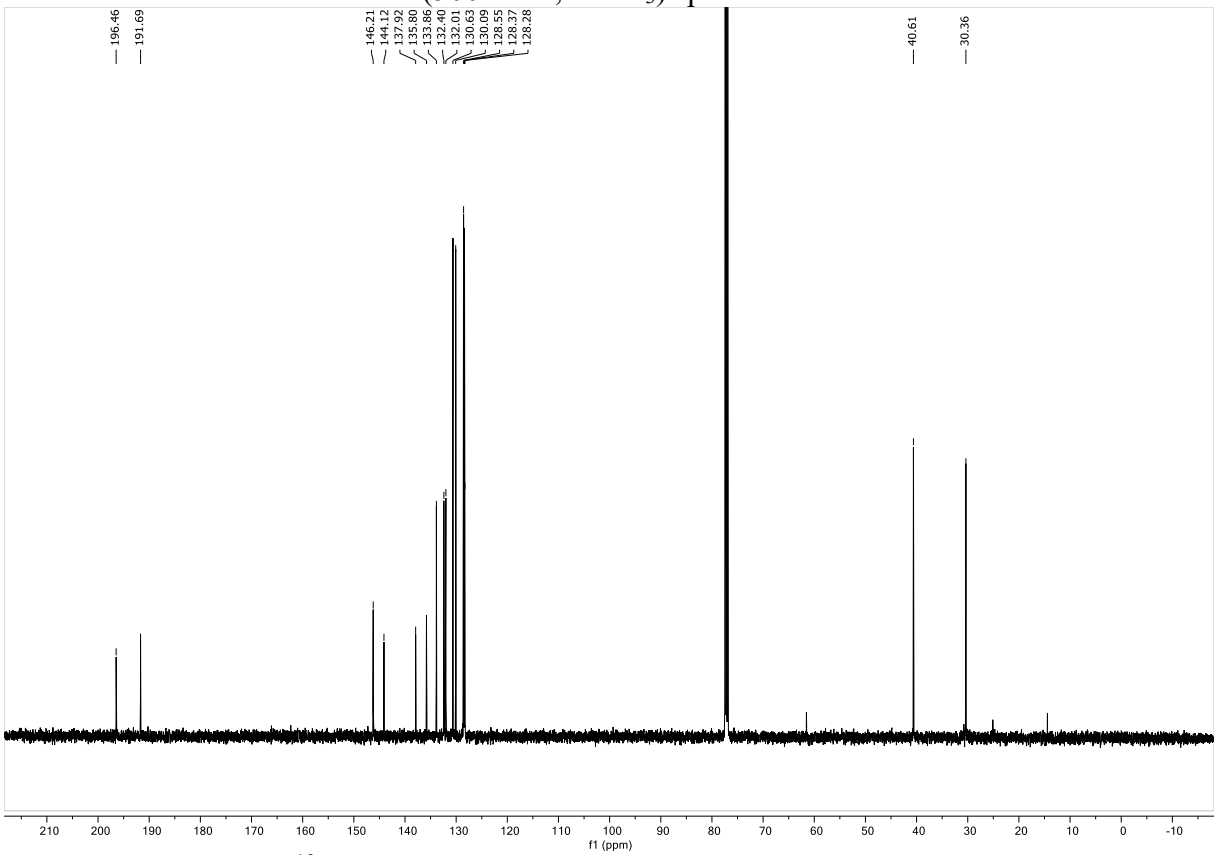

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **10**



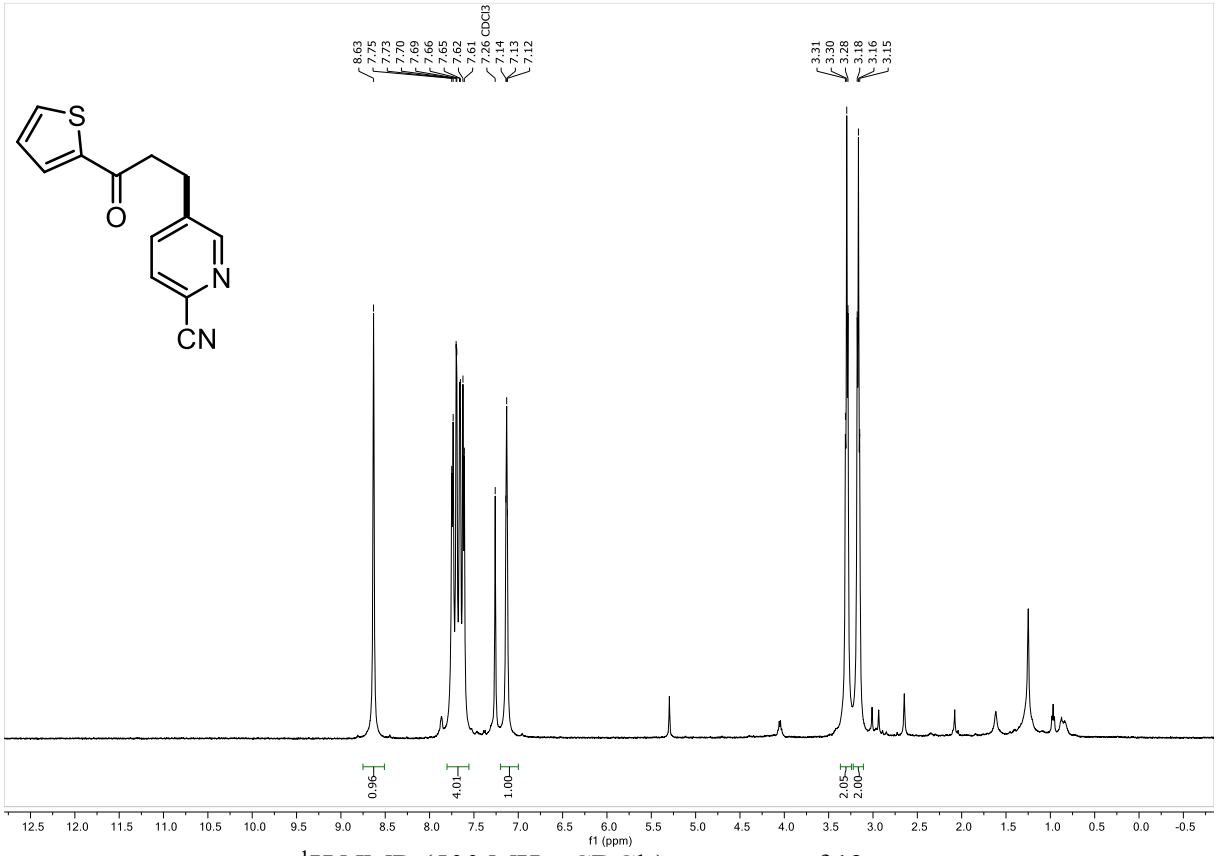

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **10**



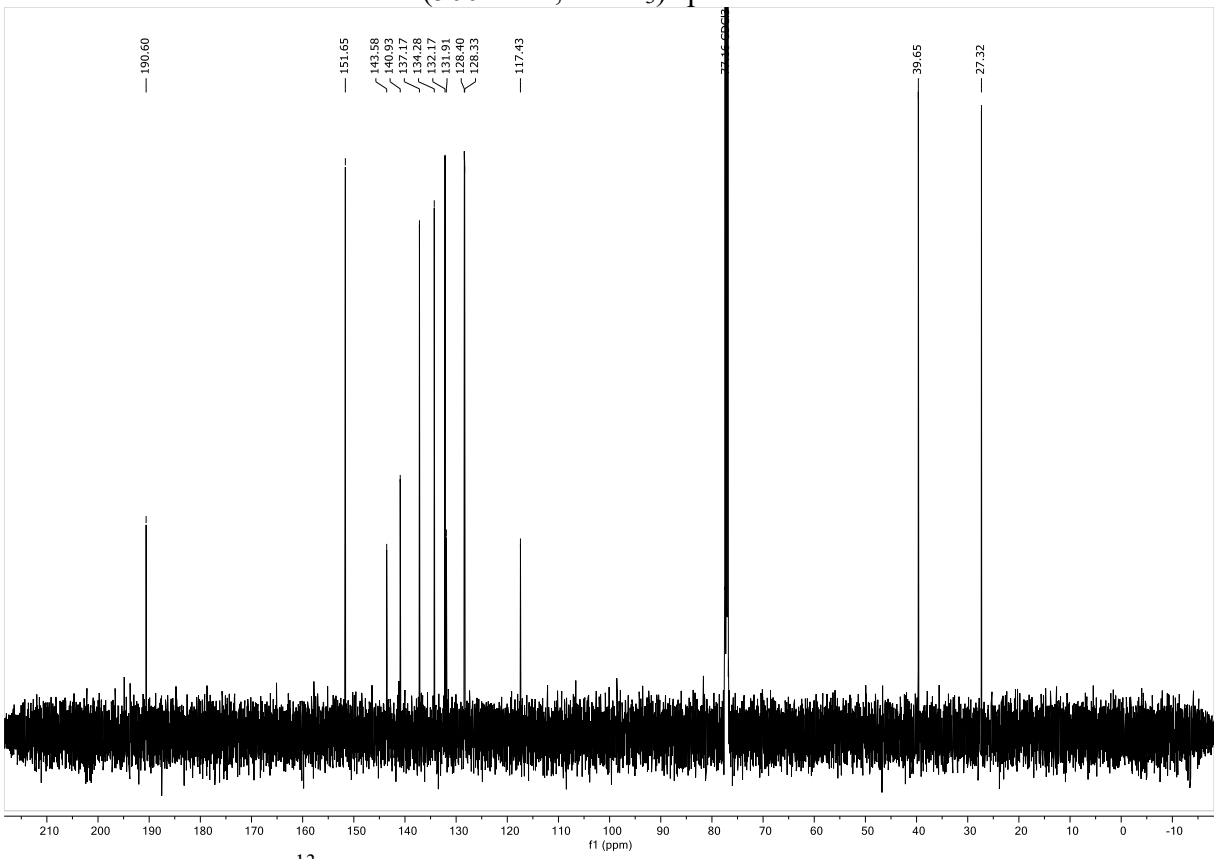

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **11**



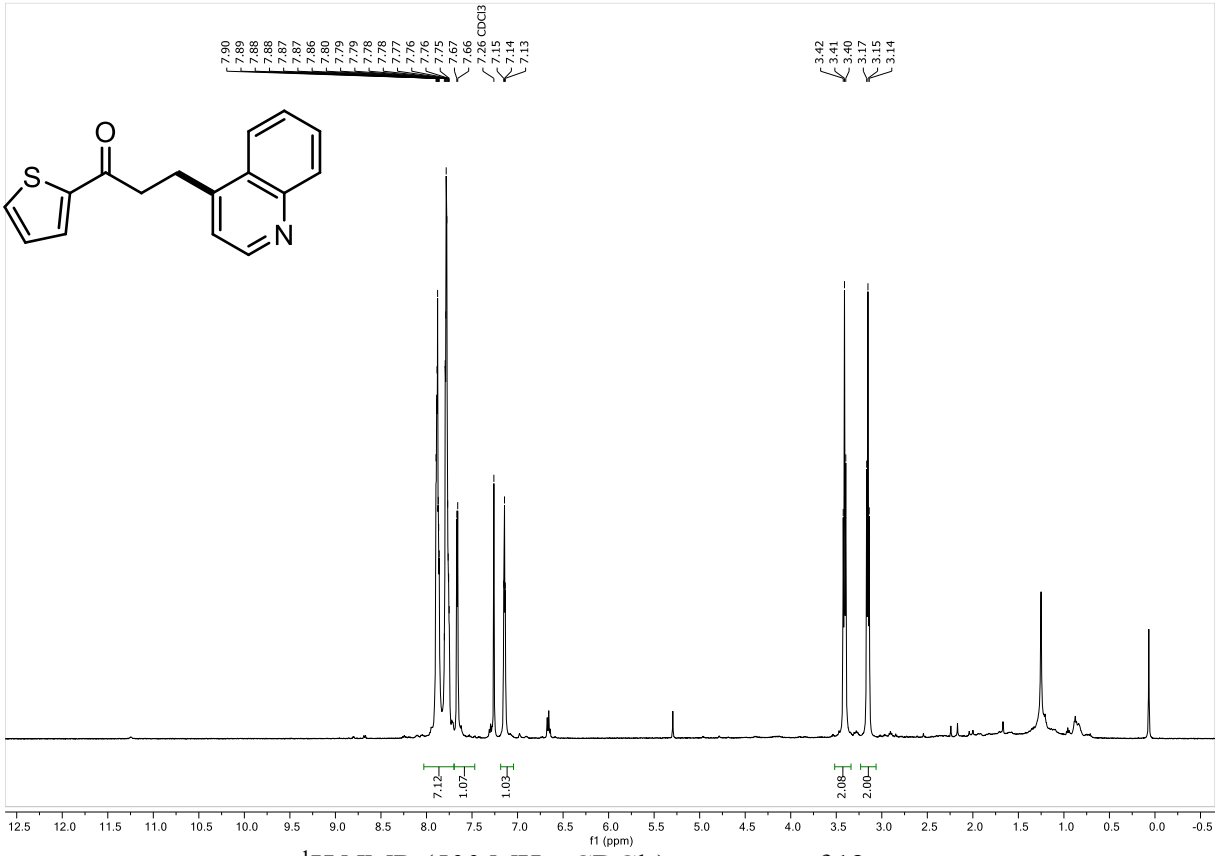

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **11**



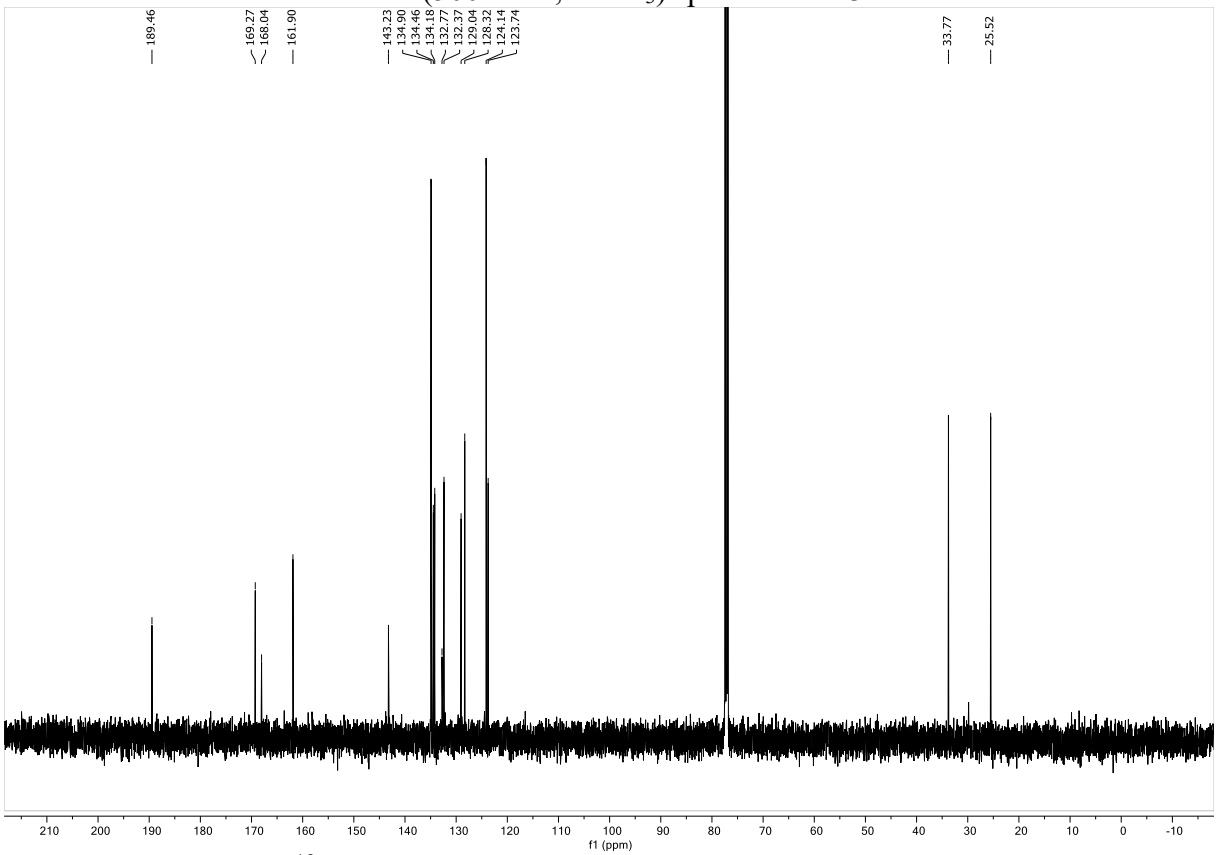

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **12**



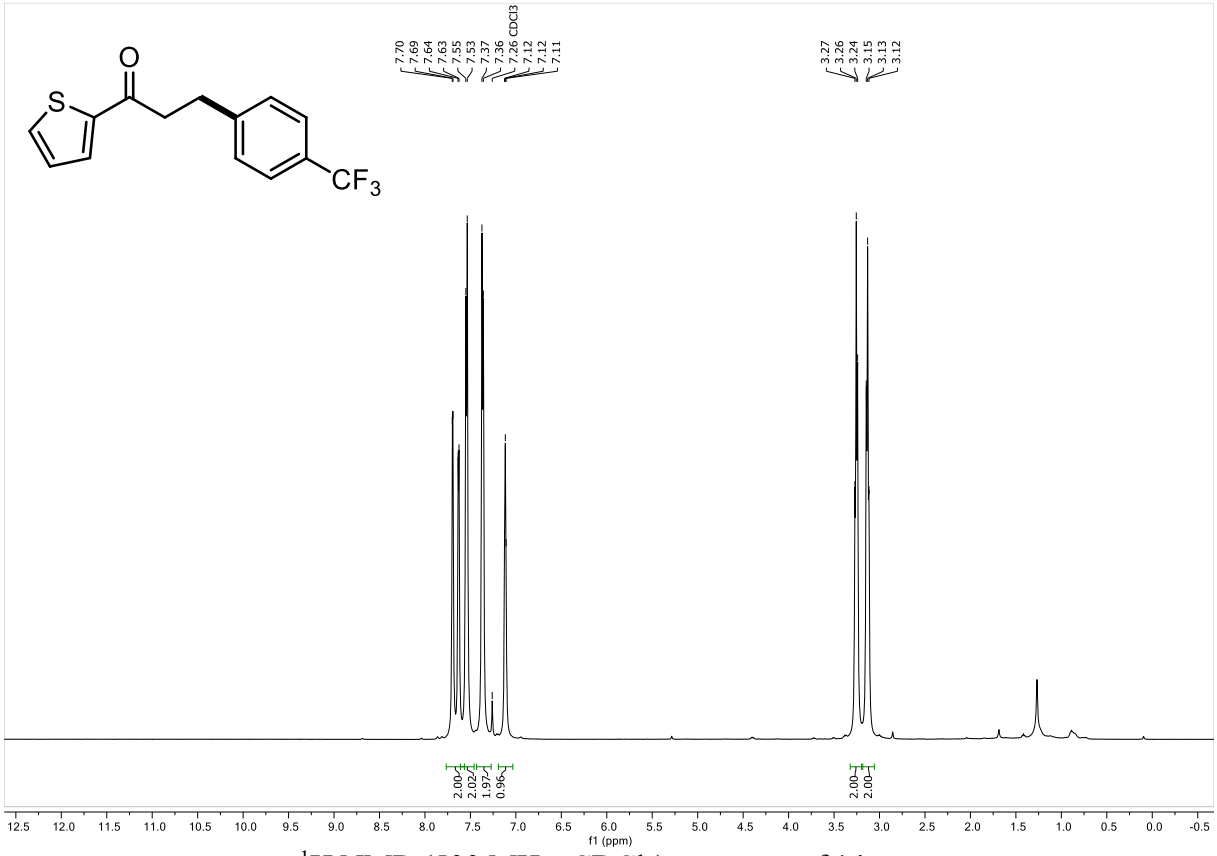

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **12**



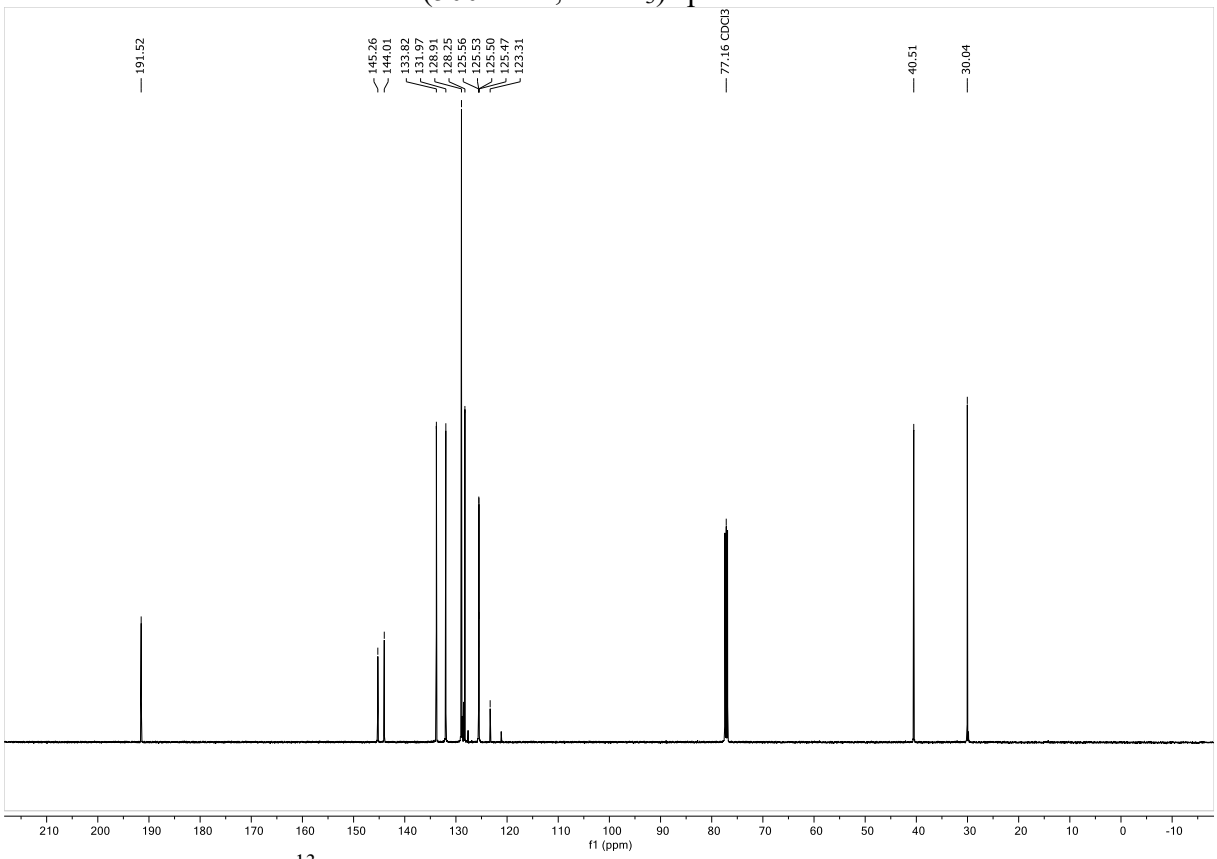

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **13**



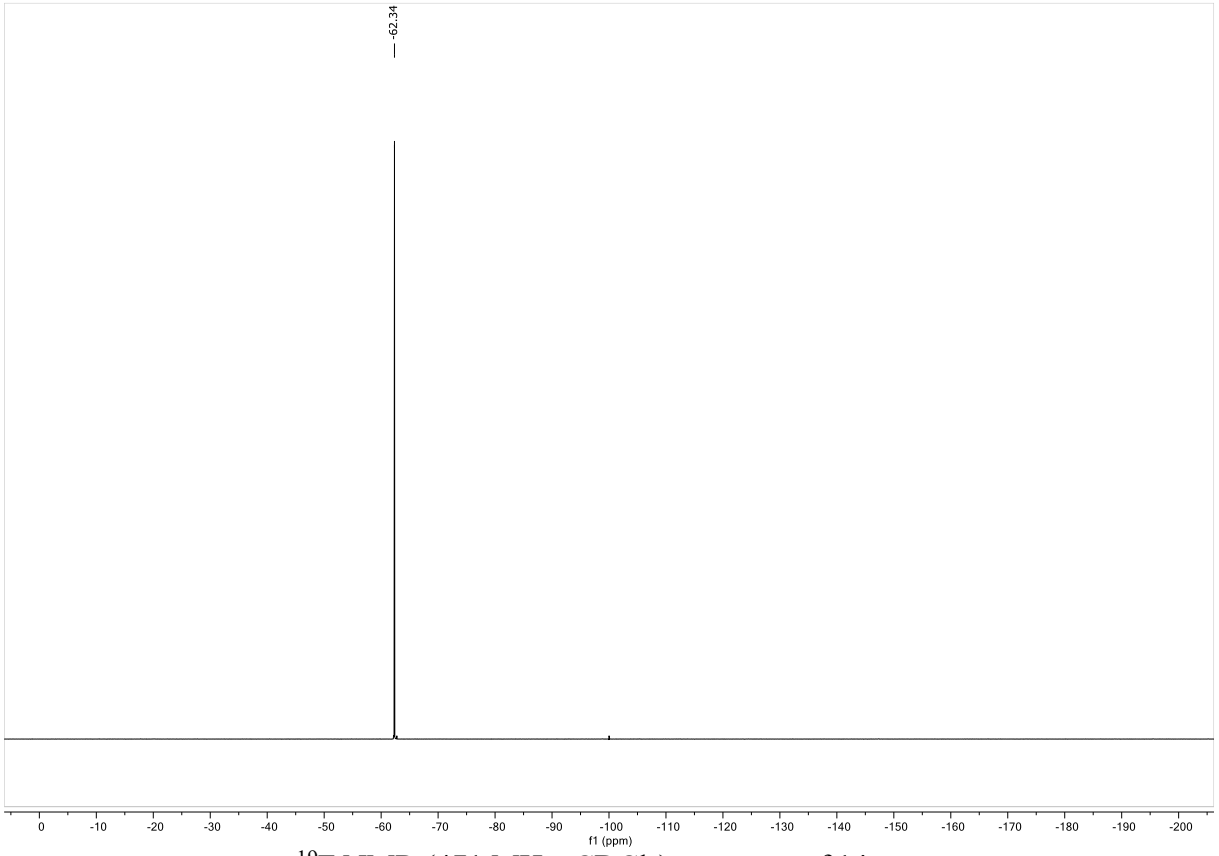

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **13**



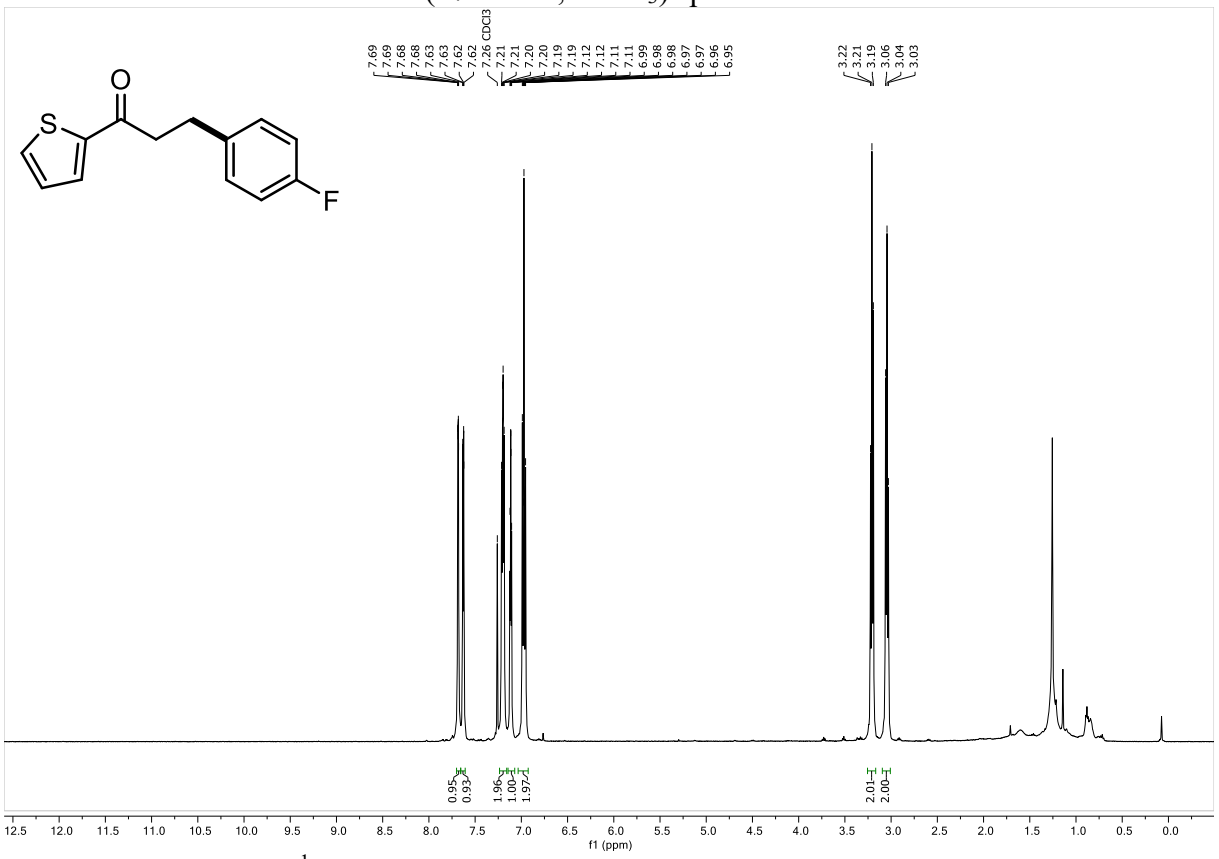

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **14**



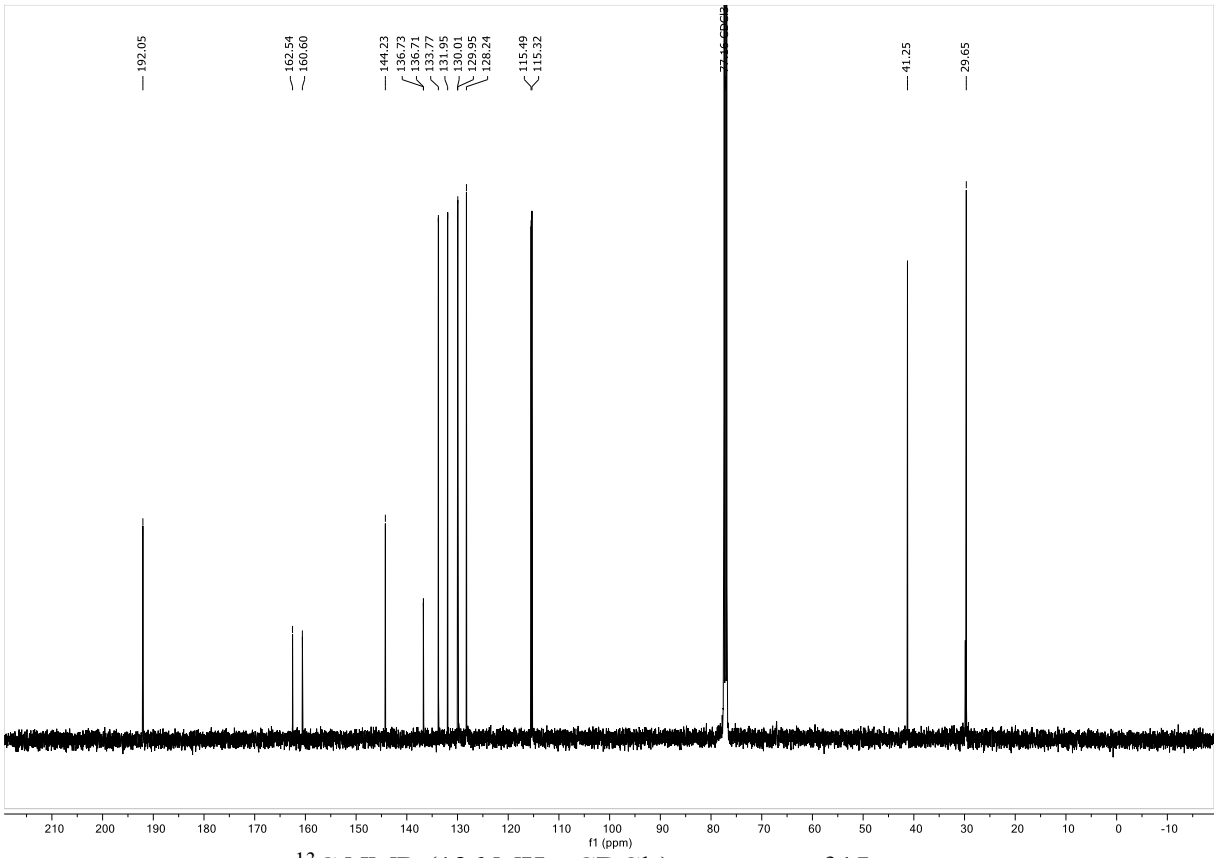

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **14**



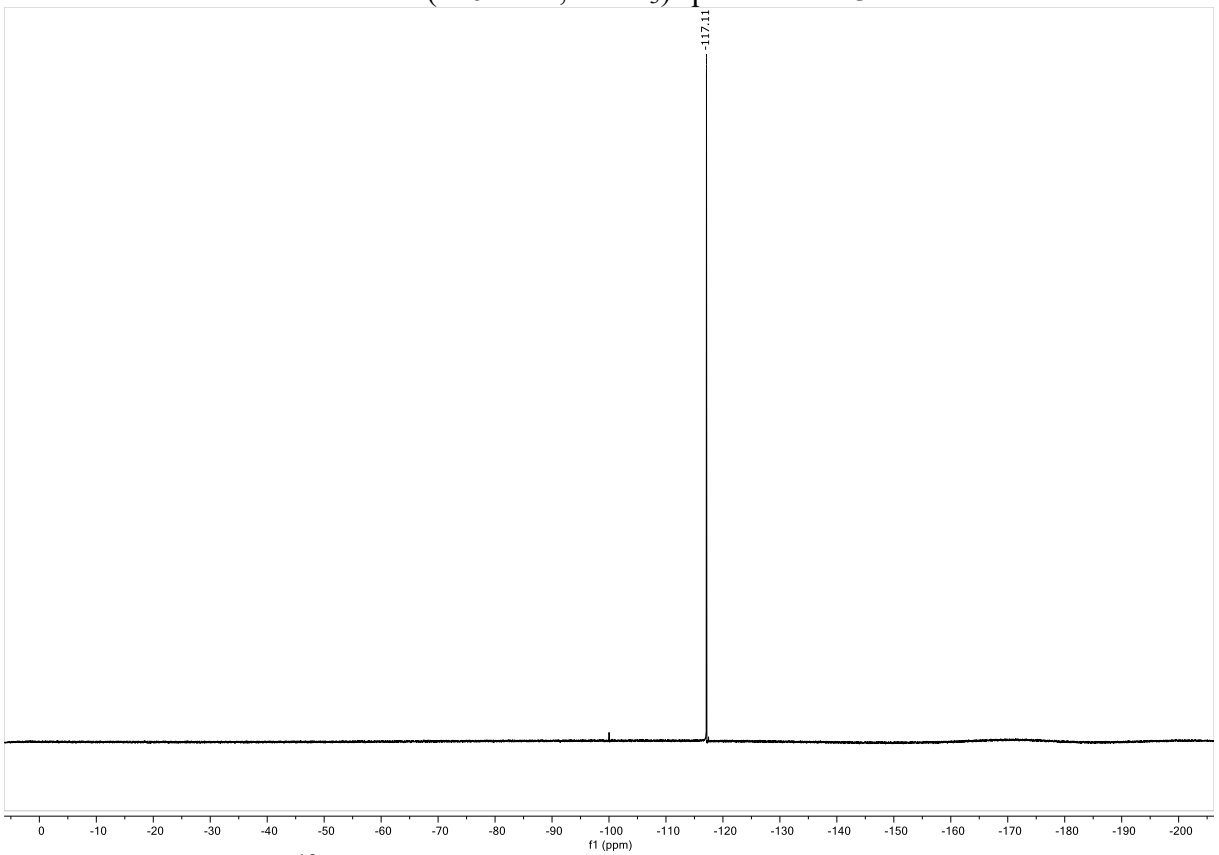

$^{19}F$ NMR (471 MHz, $CDCl_3$) spectrum of **14**



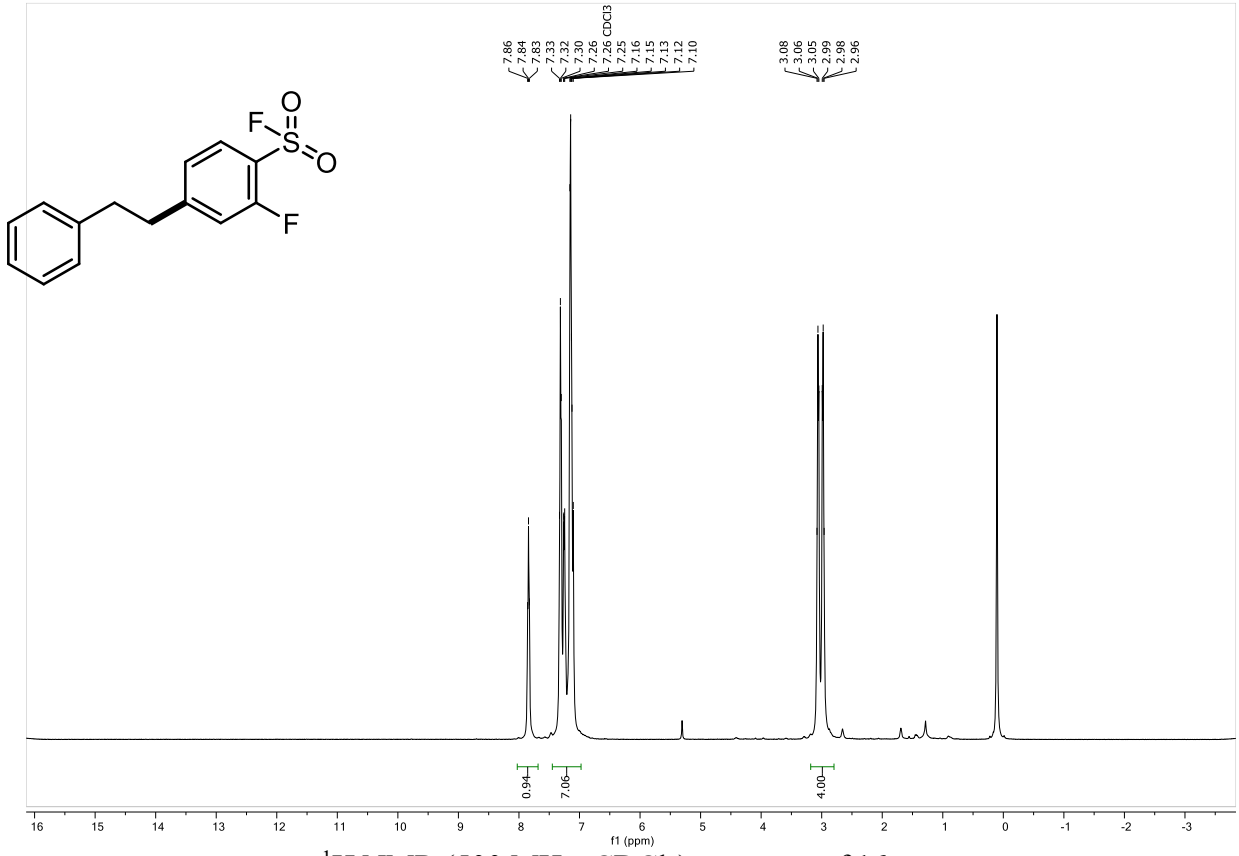

$^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **15**



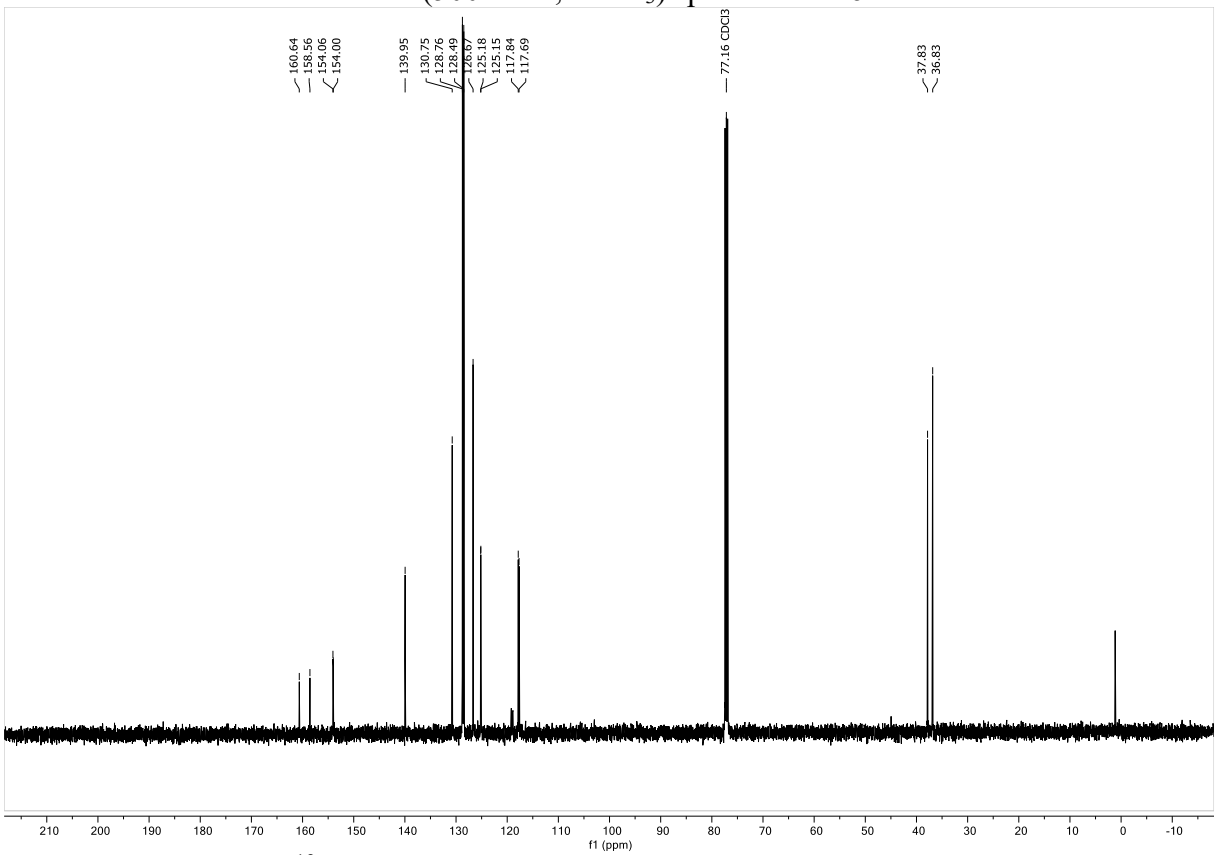

$^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **15**



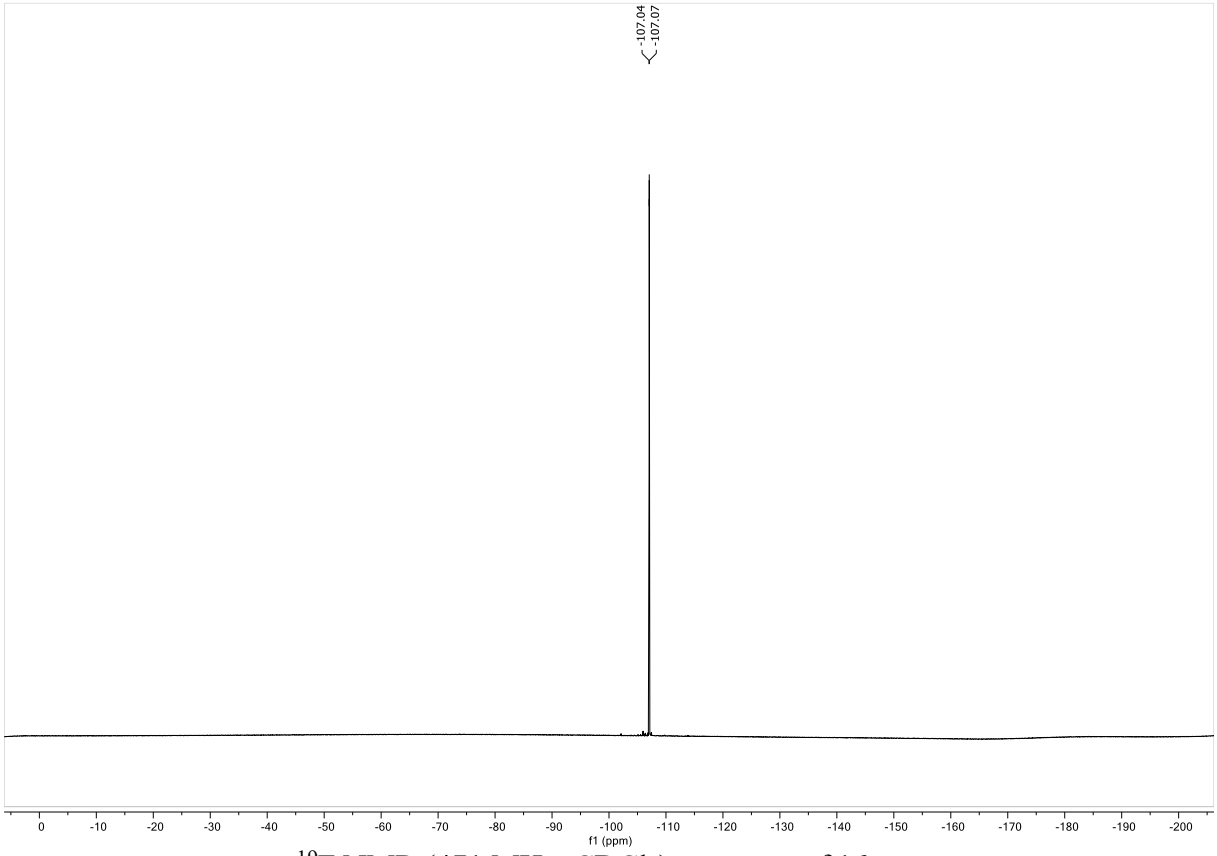

$^{19}F$ NMR (471 MHz, $CDCl_3$) spectrum of **15**



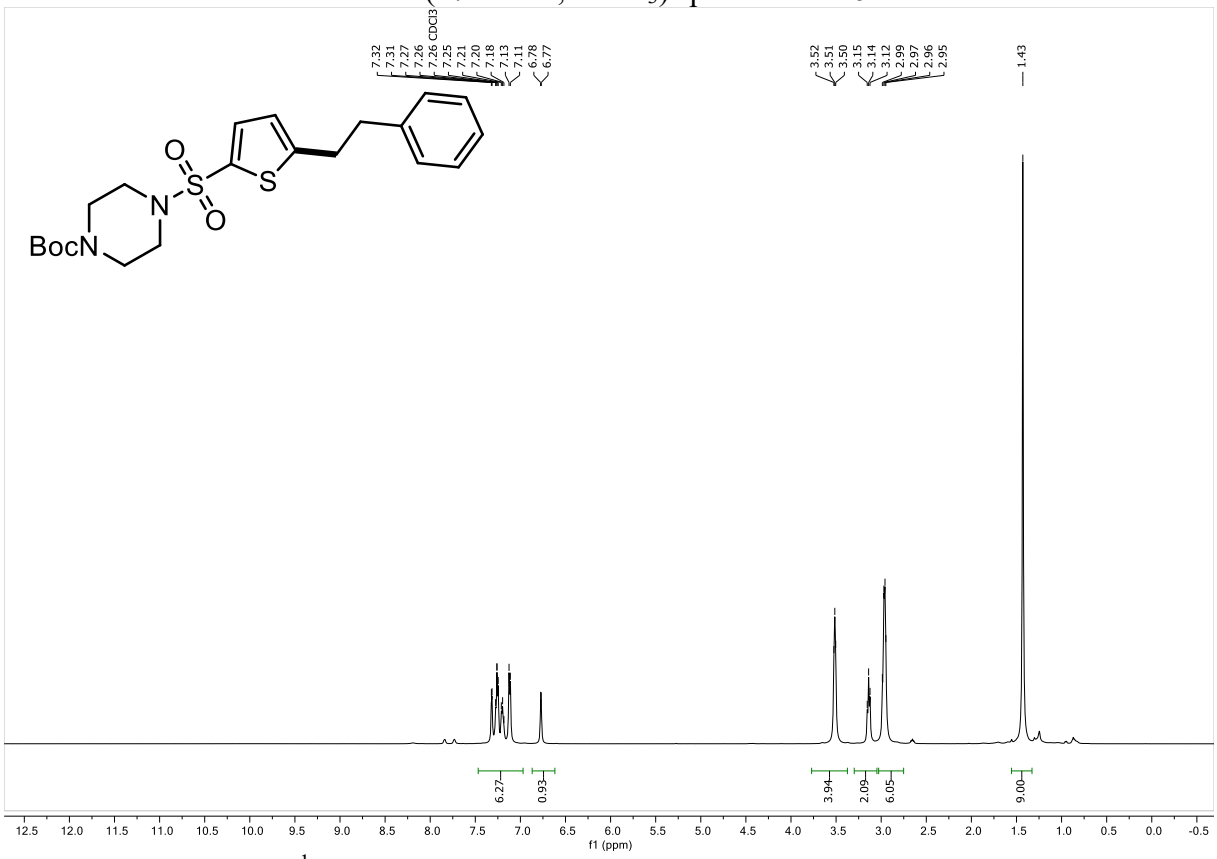

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **16**



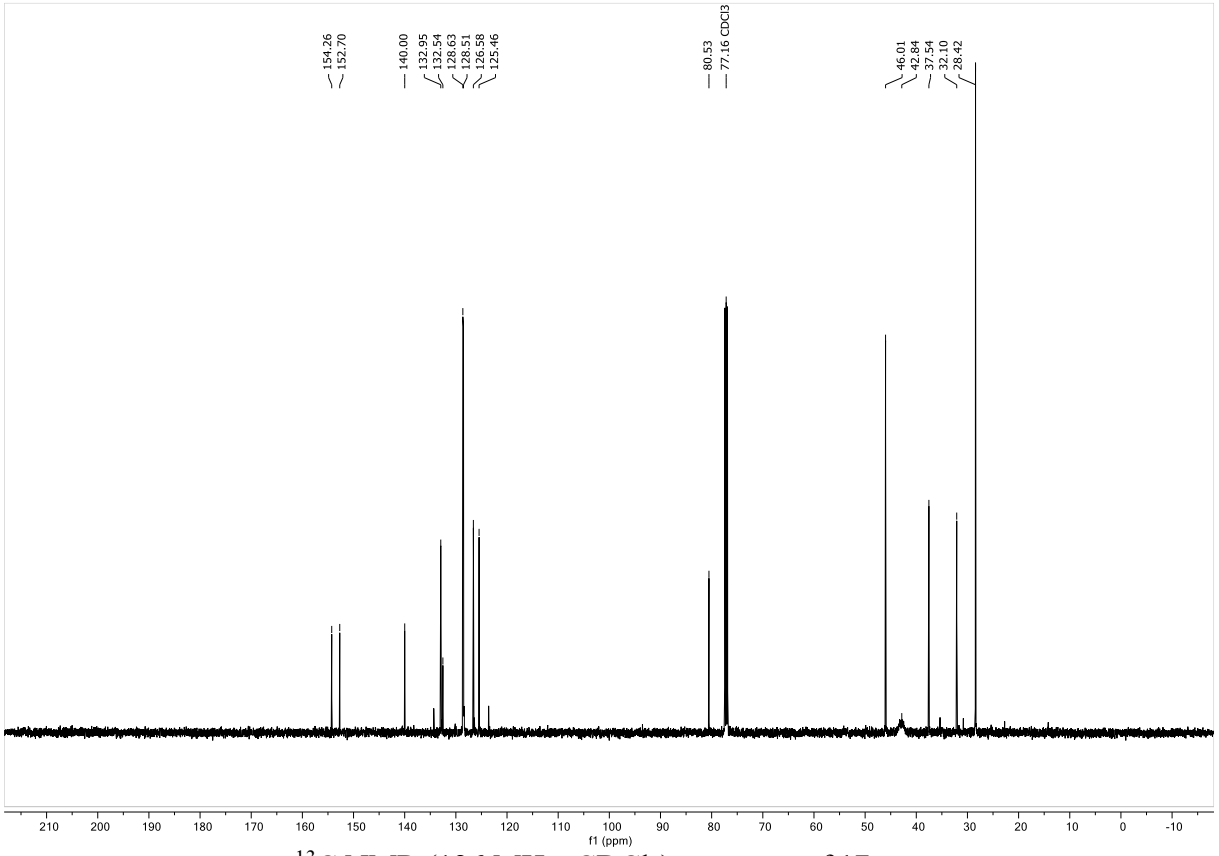

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **16**



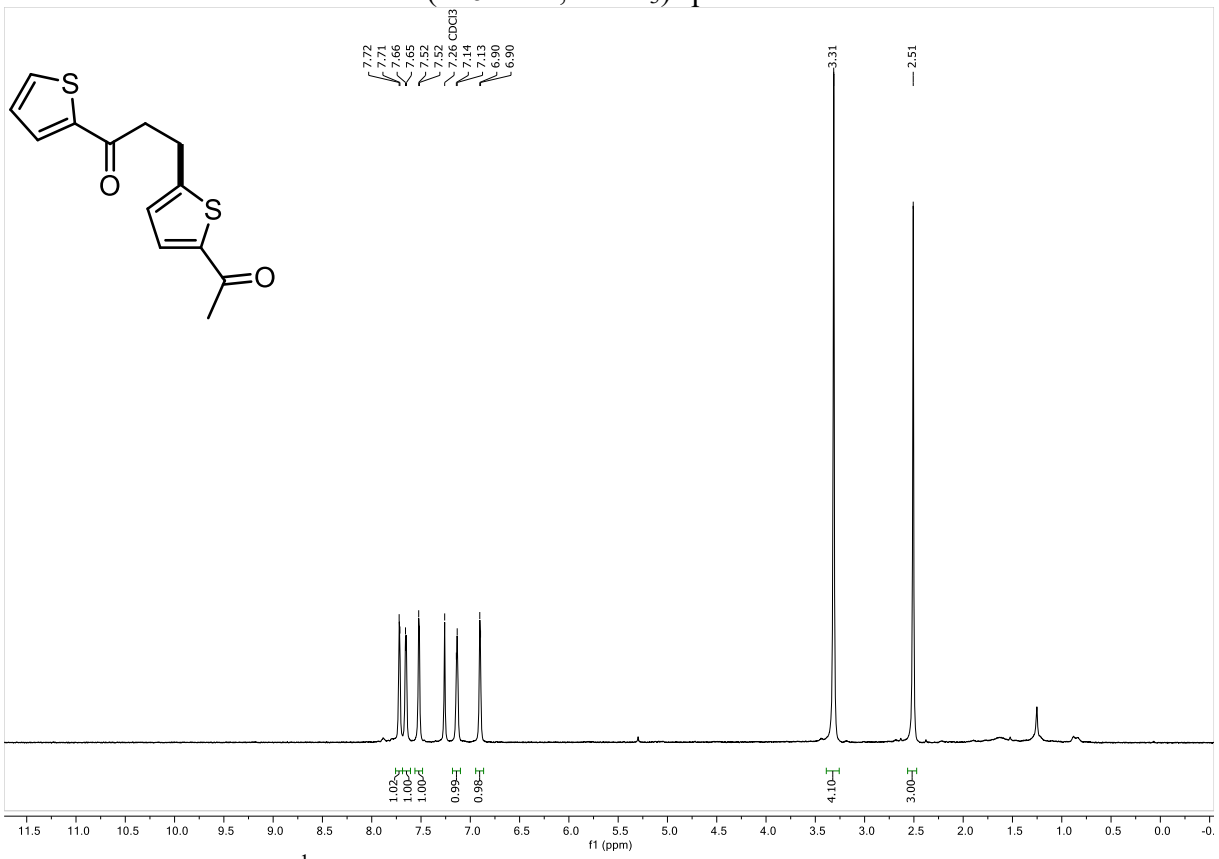

$^{19}F$ NMR (471 MHz, $CDCl_3$) spectrum of **16**



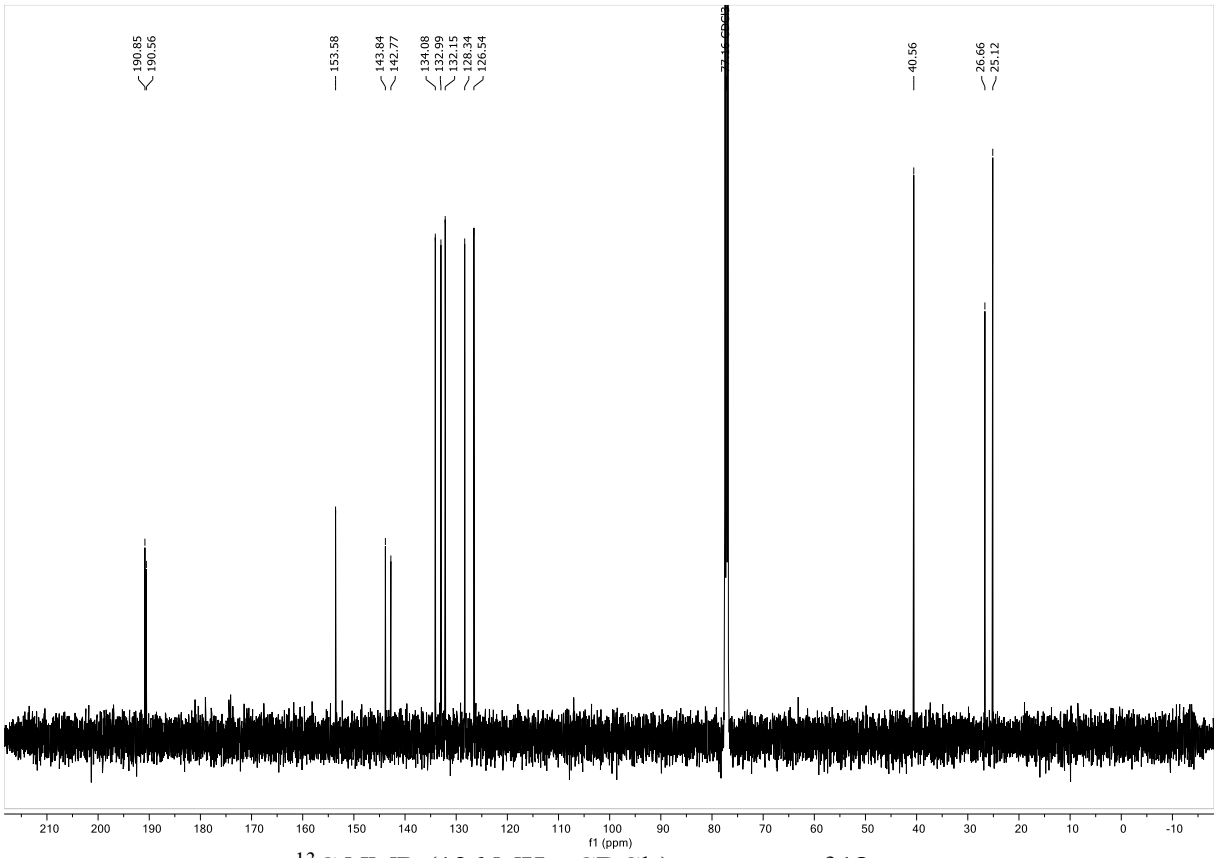

$^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **17**



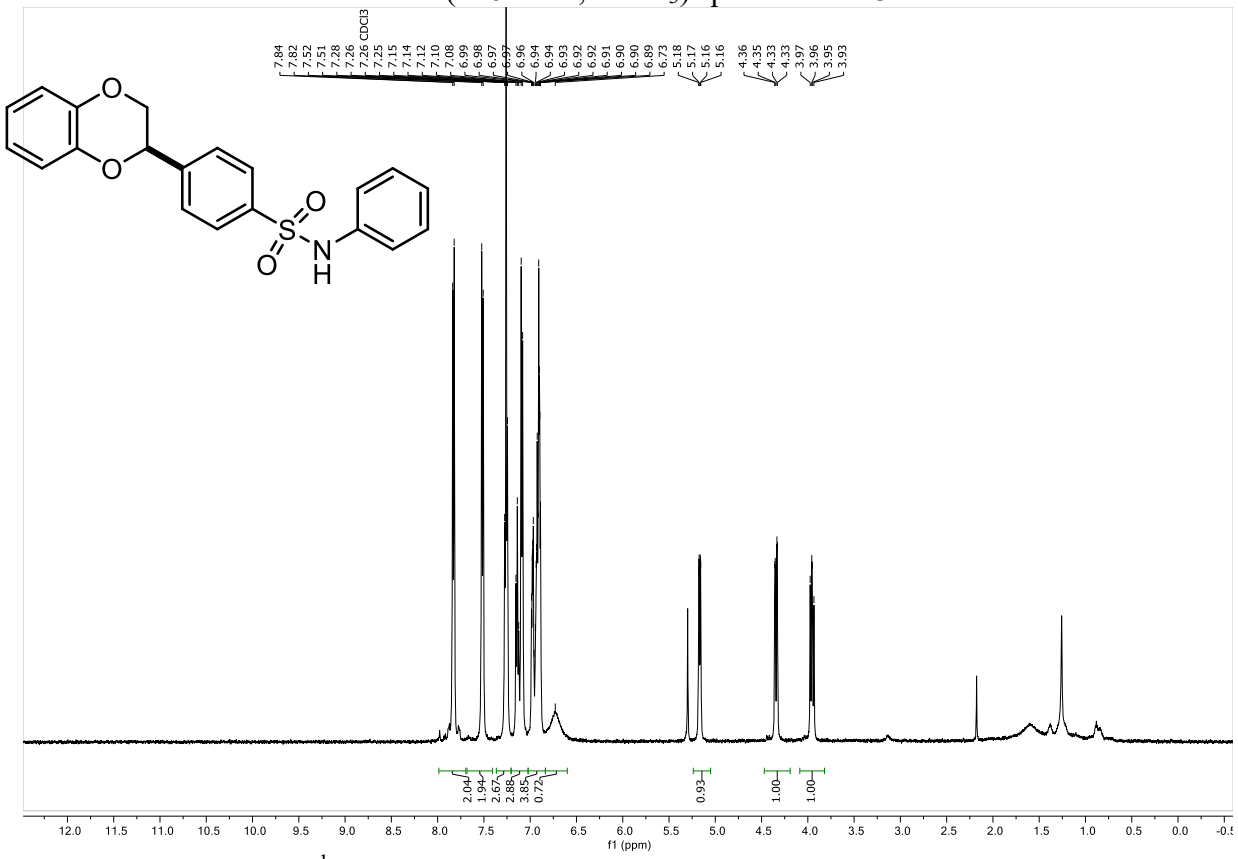

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **17**



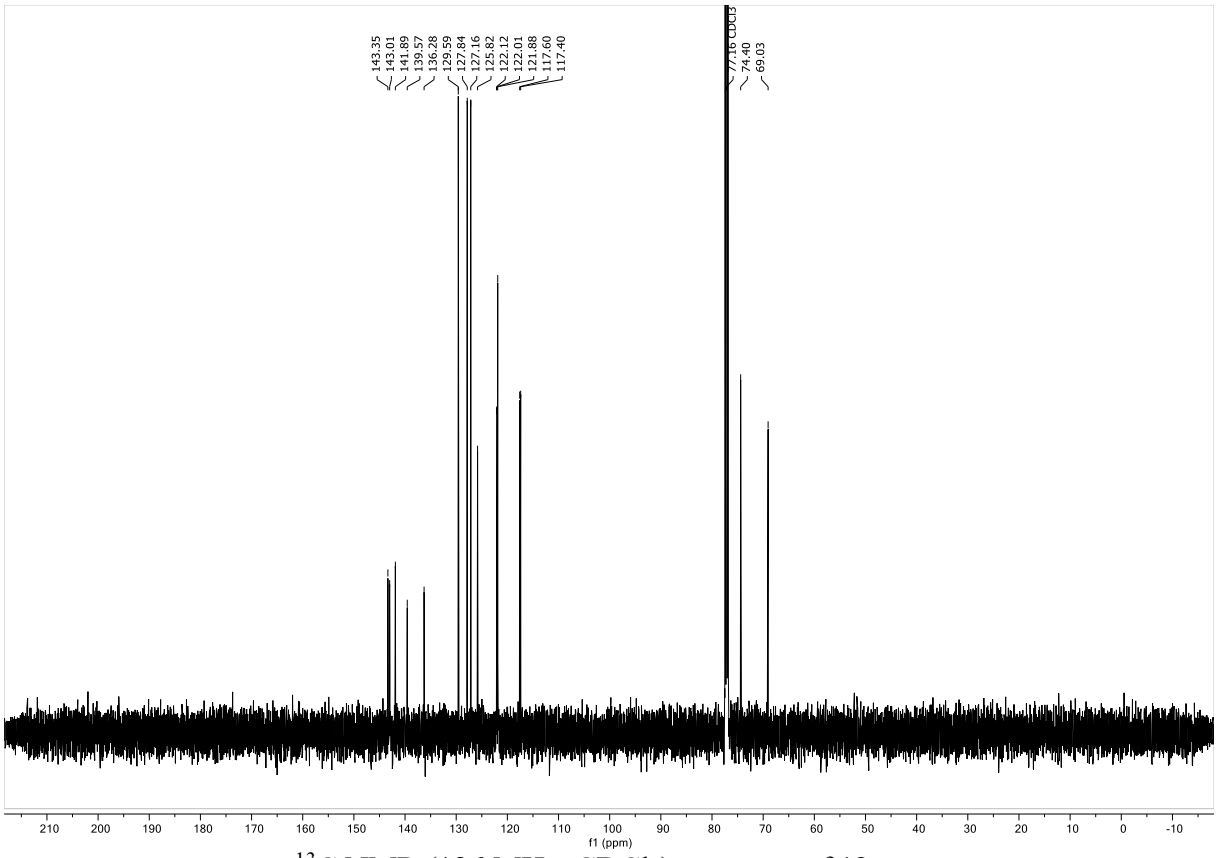

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **18**



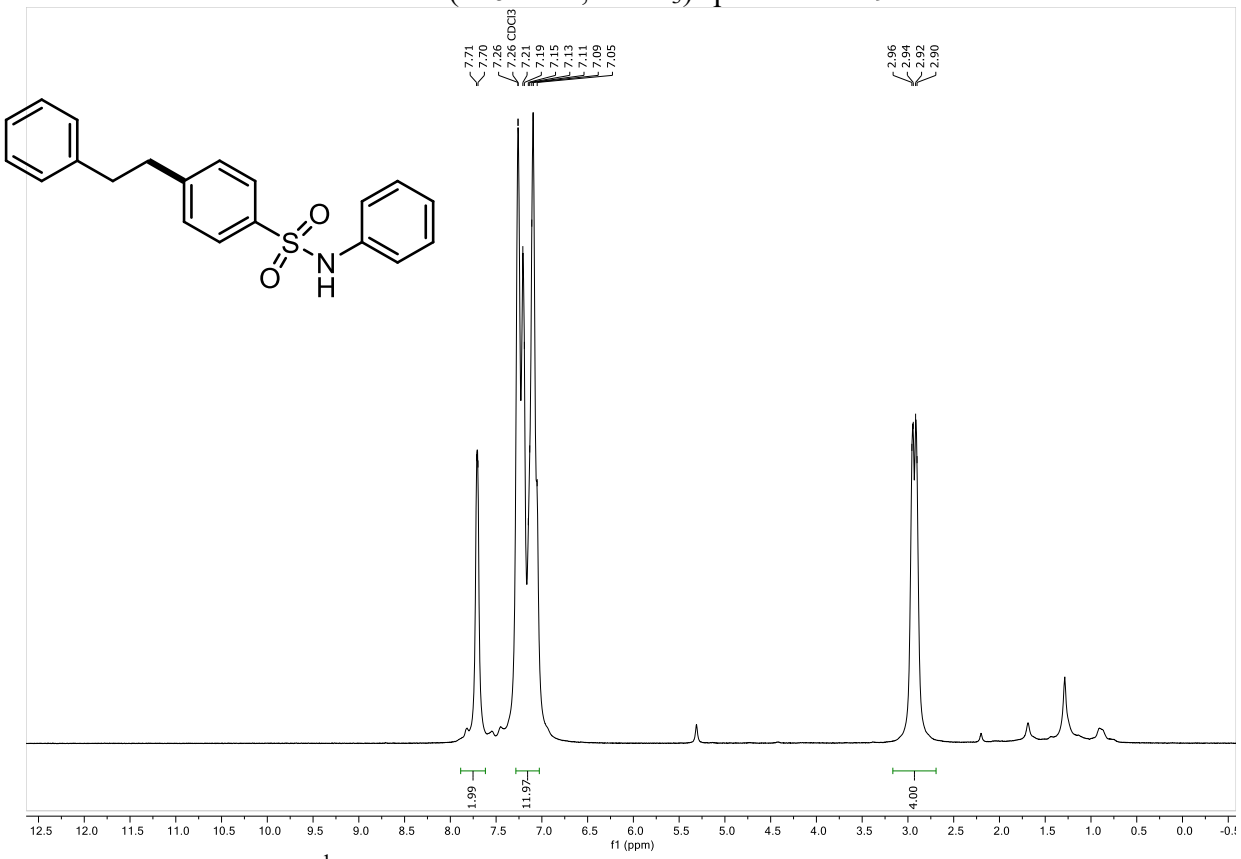

$^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **18**



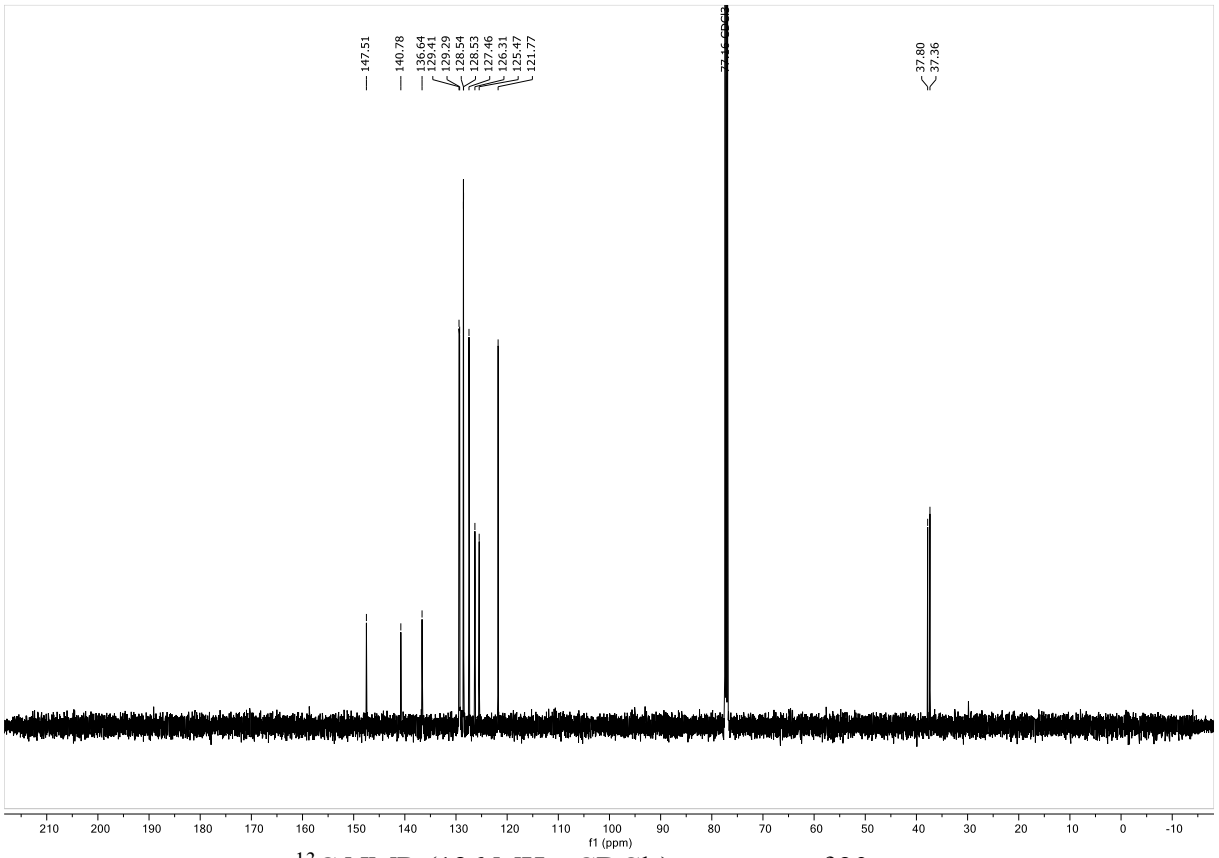

$^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **19**



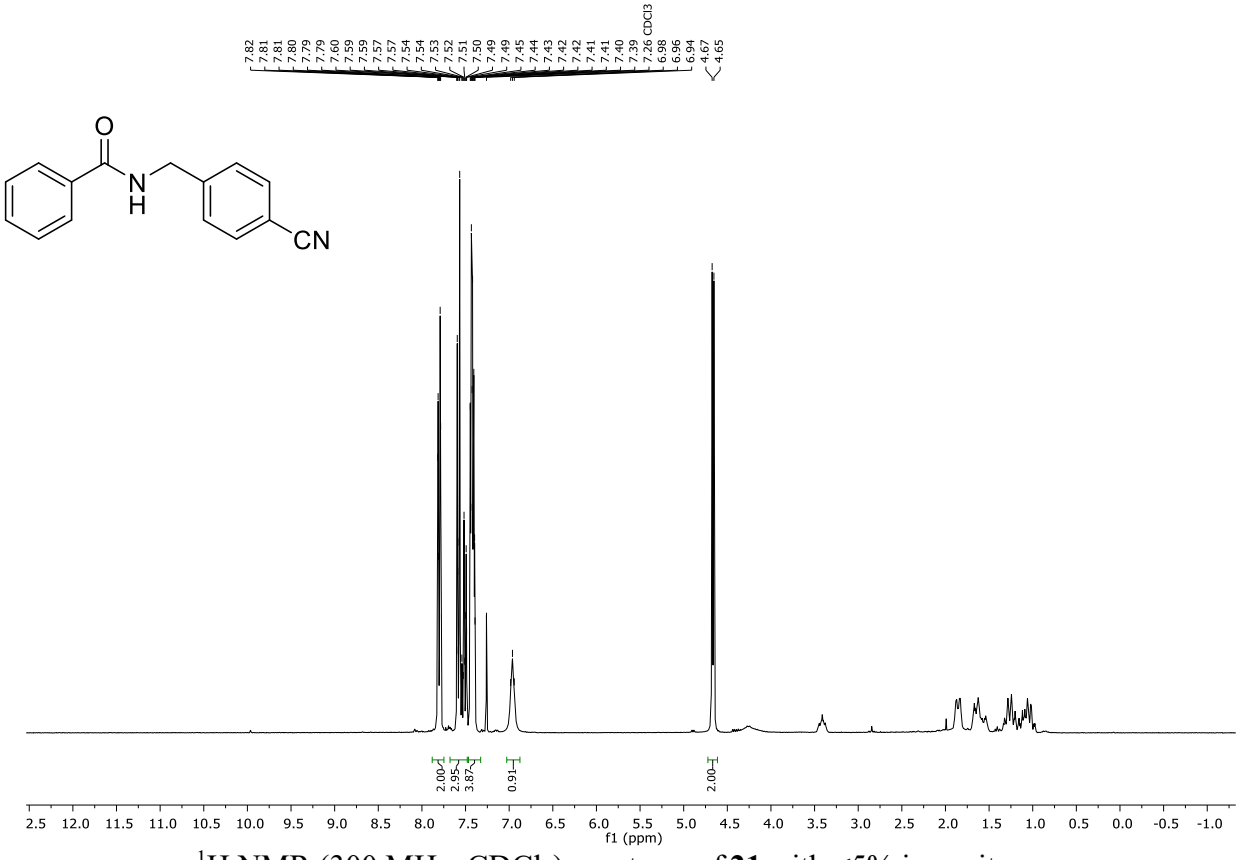

$^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **19**



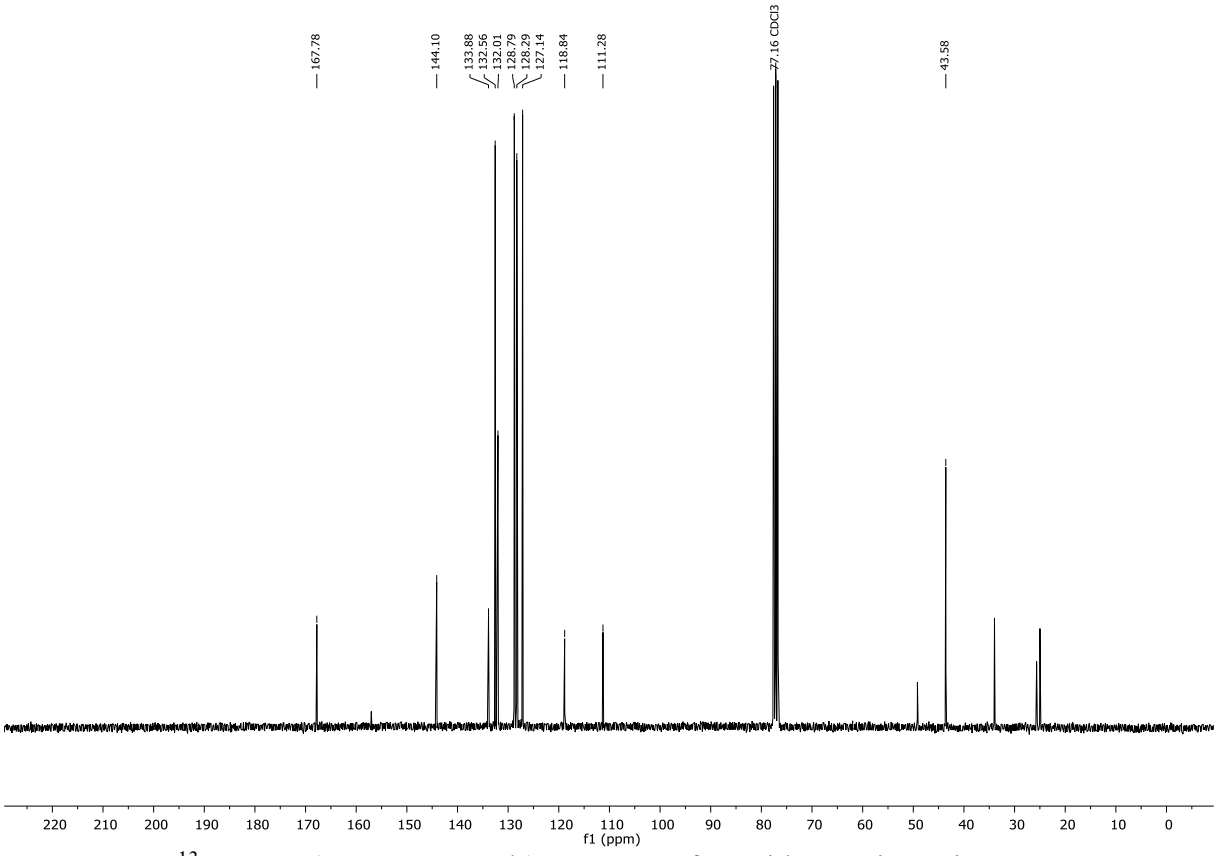

$^{1}H$ NMR (500 MHz, $CDCl_3$) spectrum of **20**



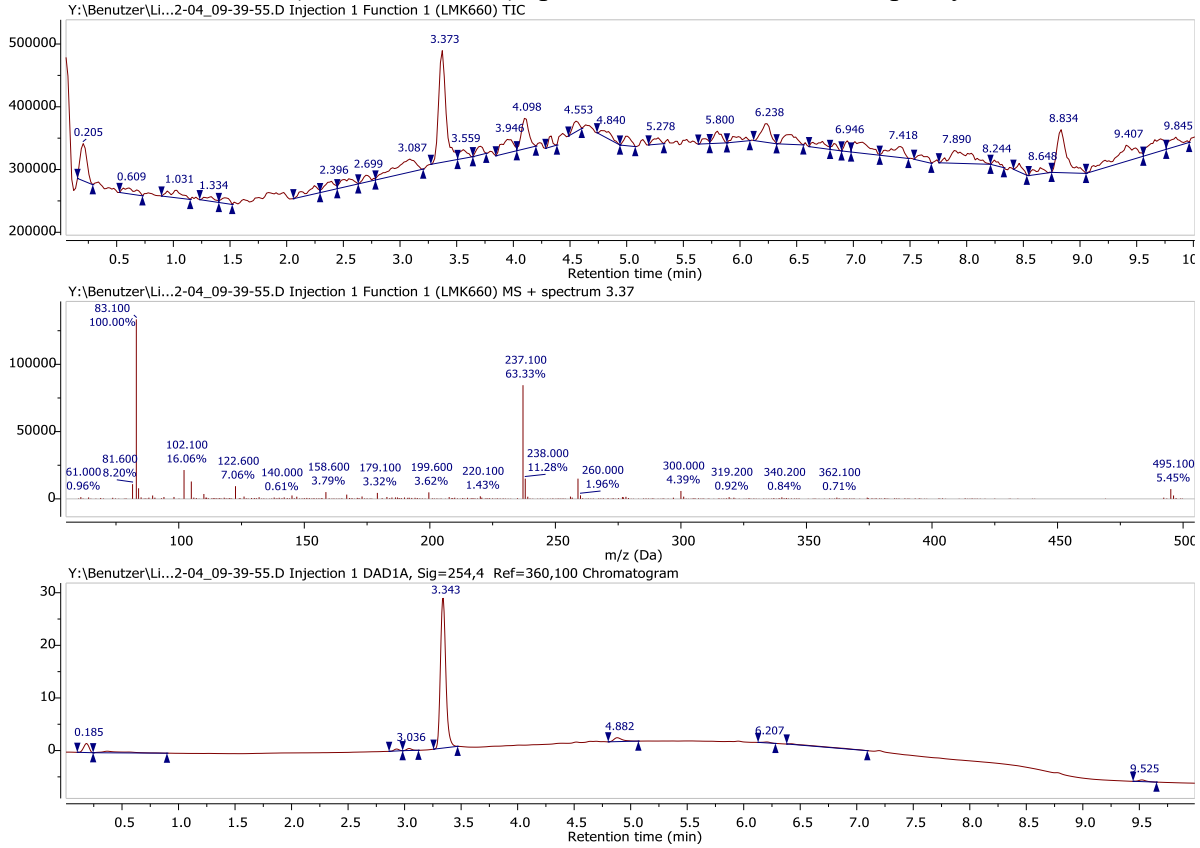

$^{13}C$ NMR (126 MHz, $CDCl_3$) spectrum of **20**



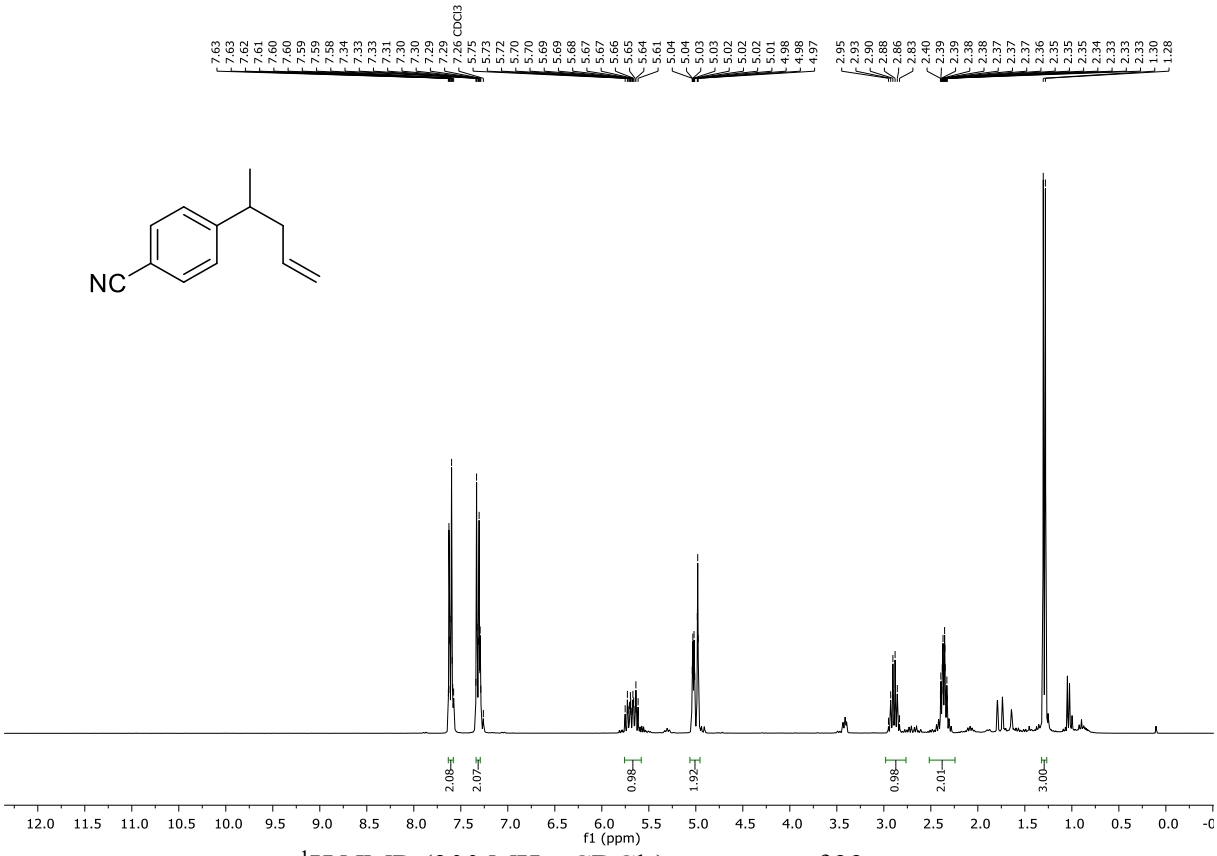

$^{1}H$ NMR (300 MHz, $CDCl_3$) spectrum of **21** with <5% impurity



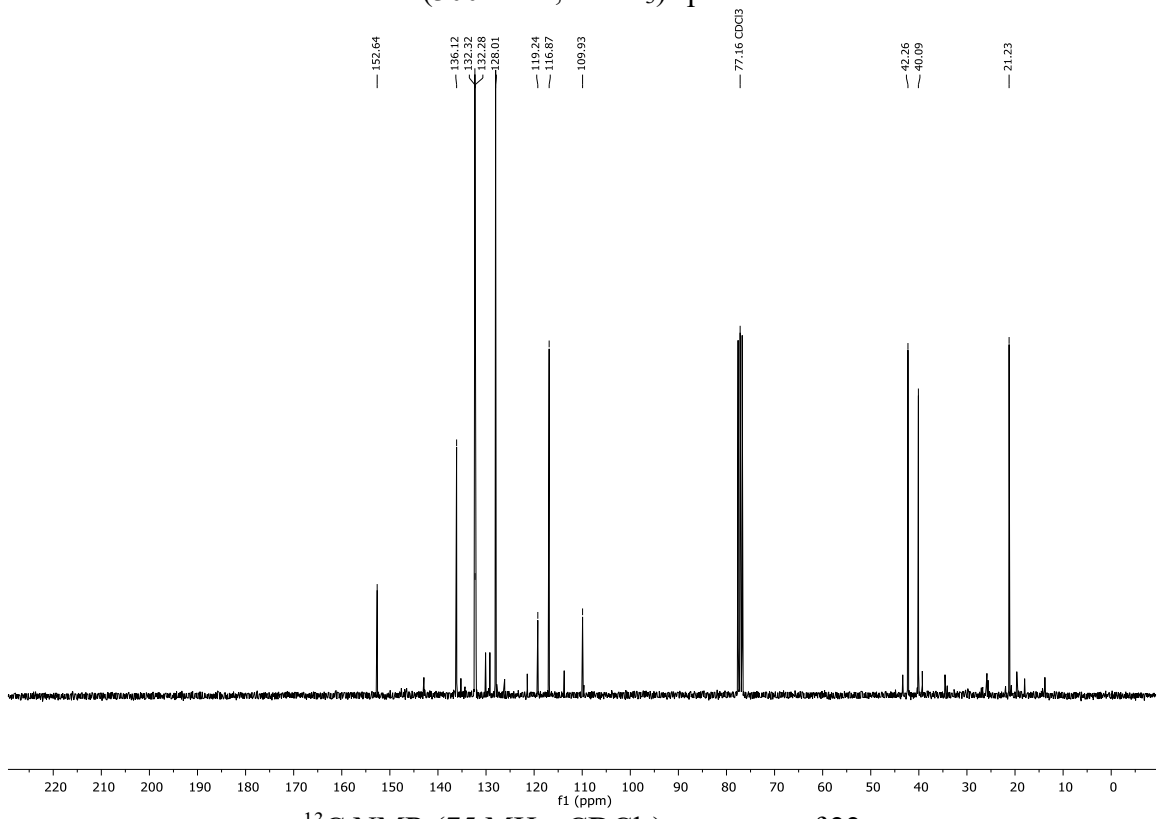

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **21** with <5% impurity



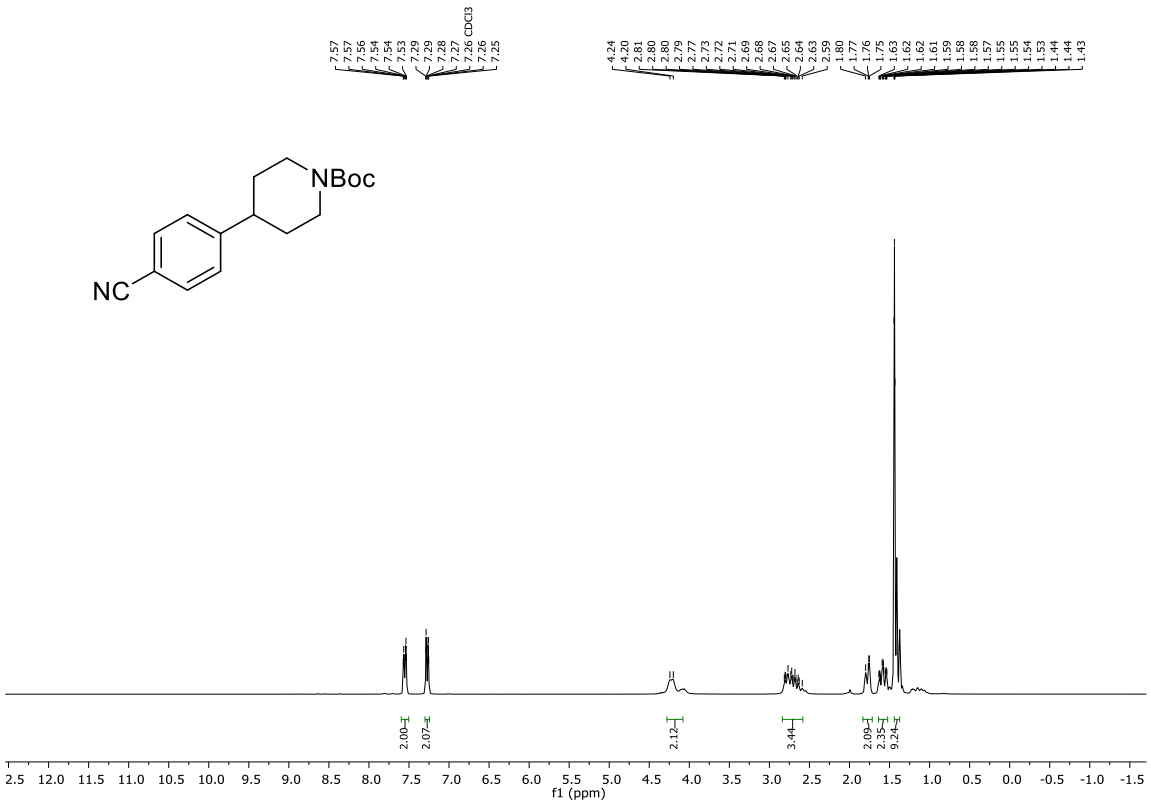

LC-MS chromatogram of **21**



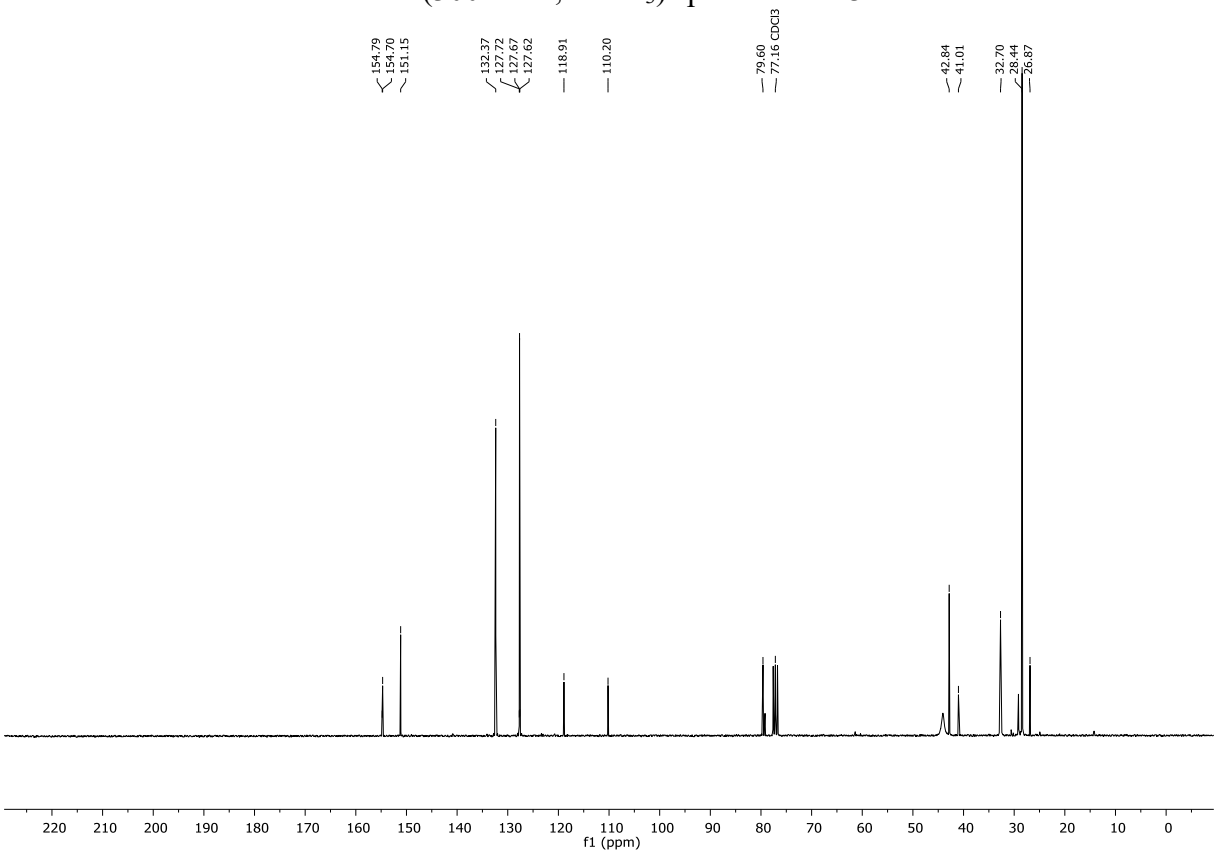

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **22**



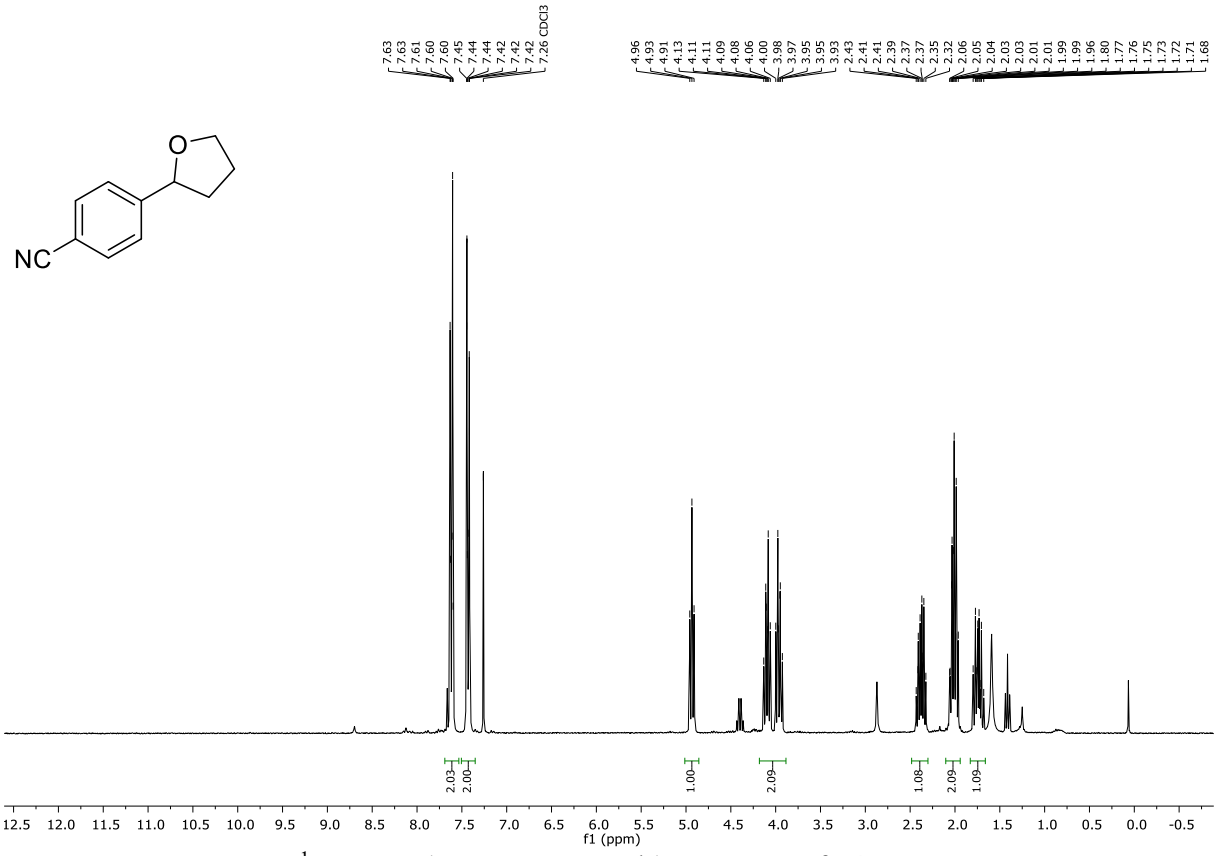

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **22**



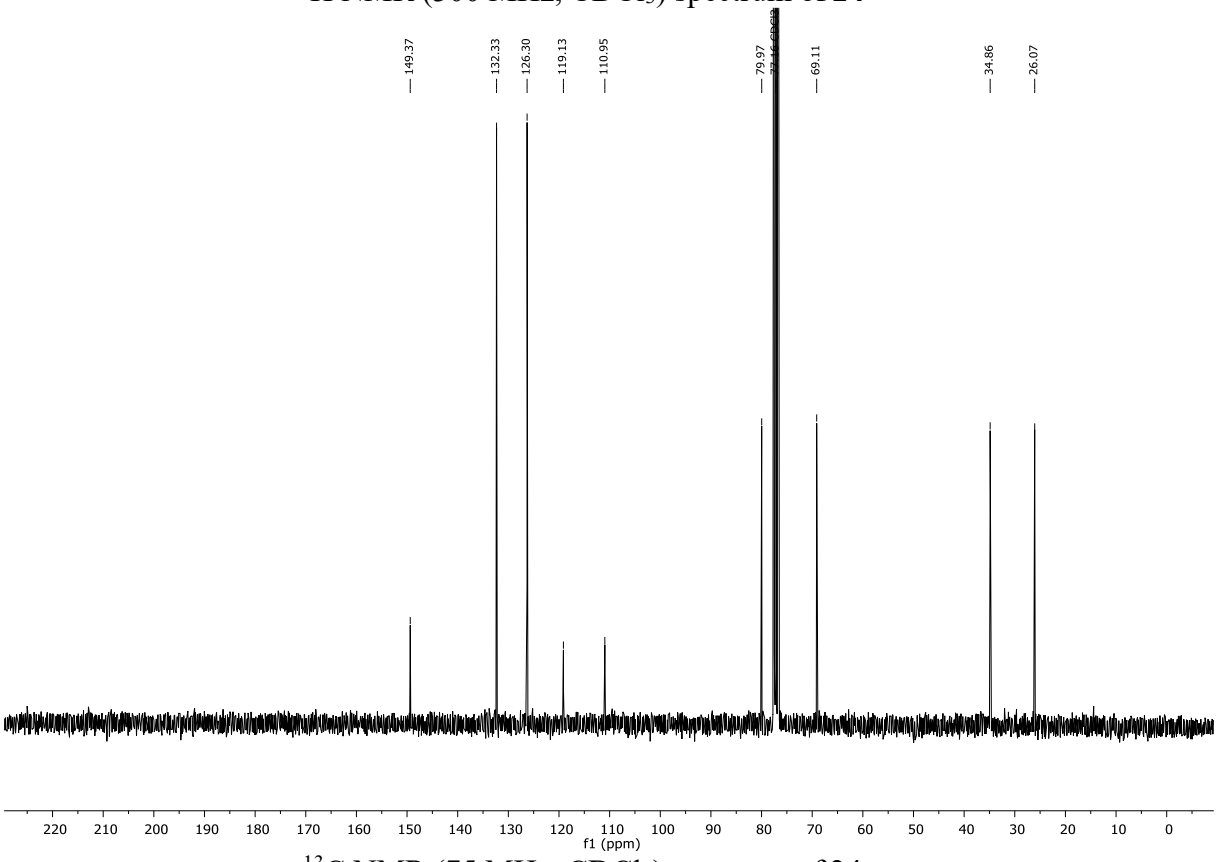

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **23**



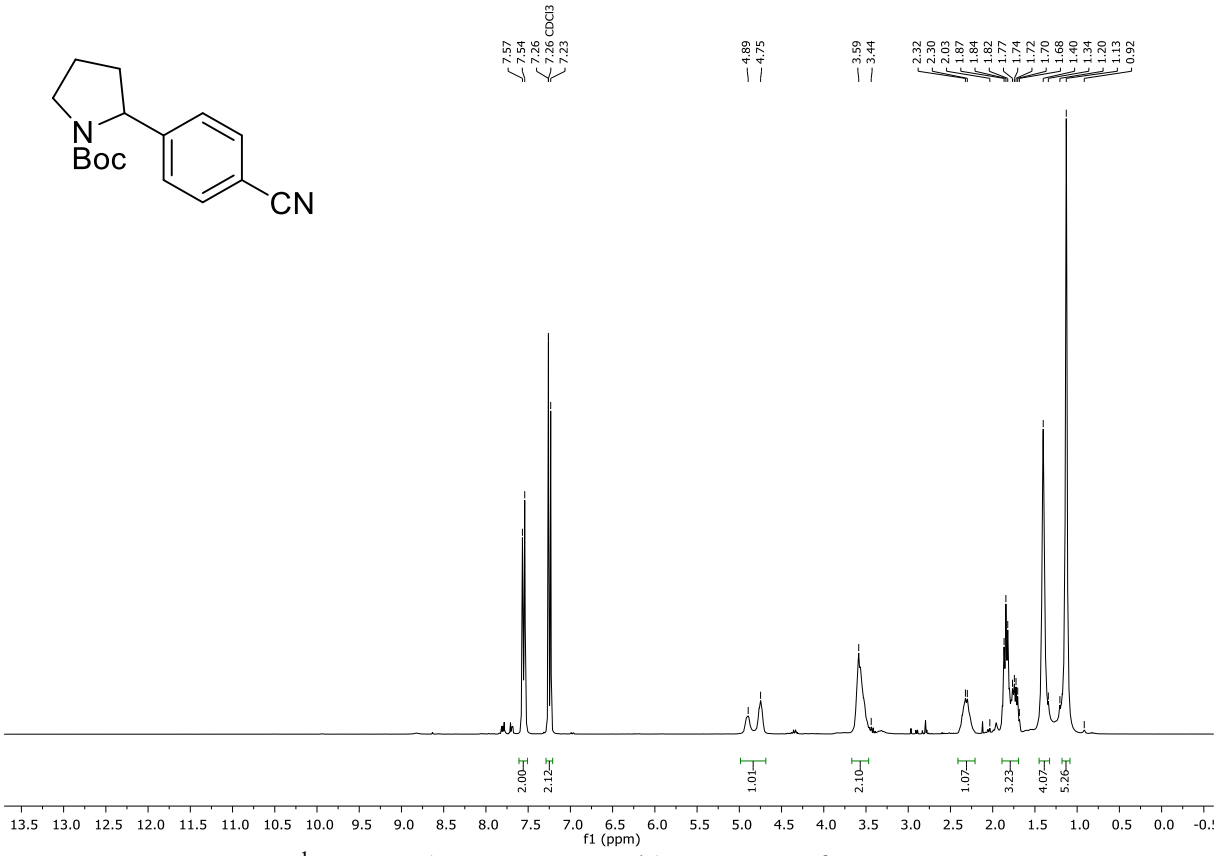

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **23**



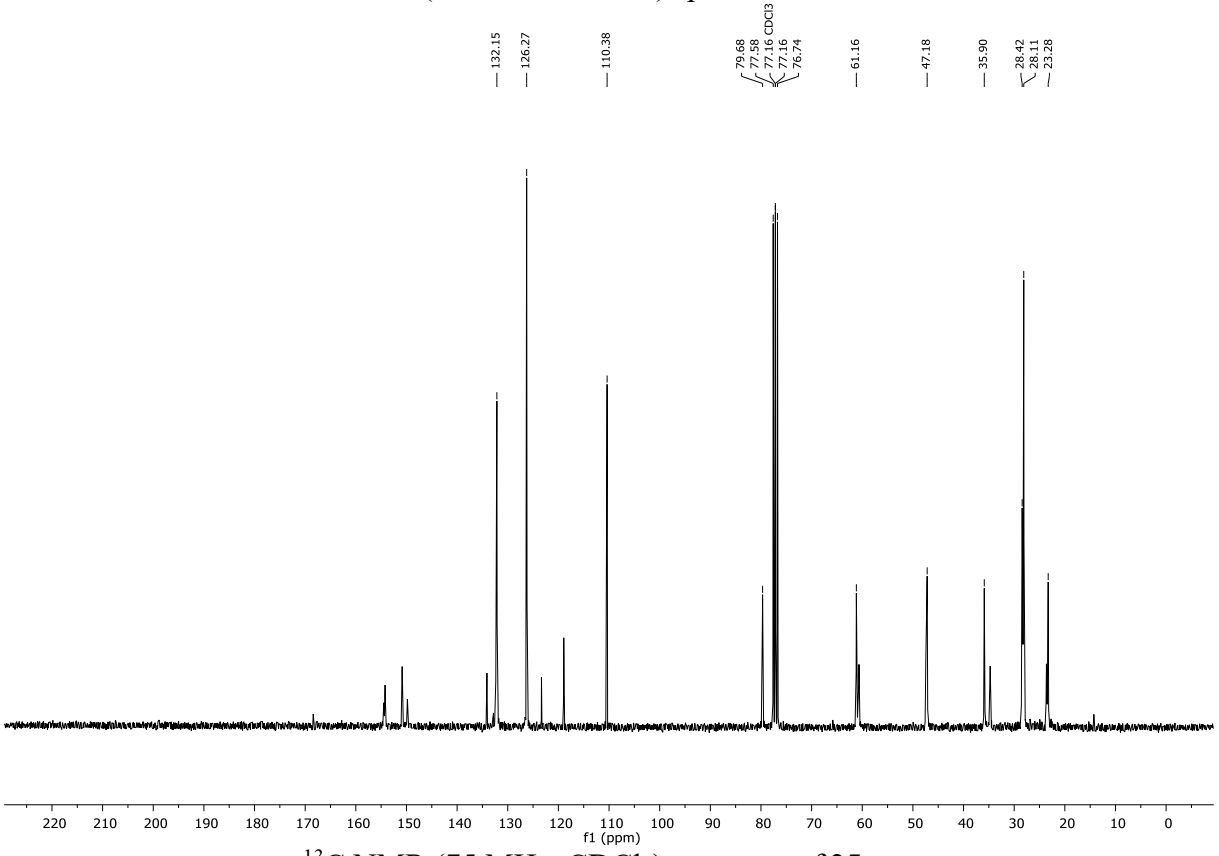

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **24**



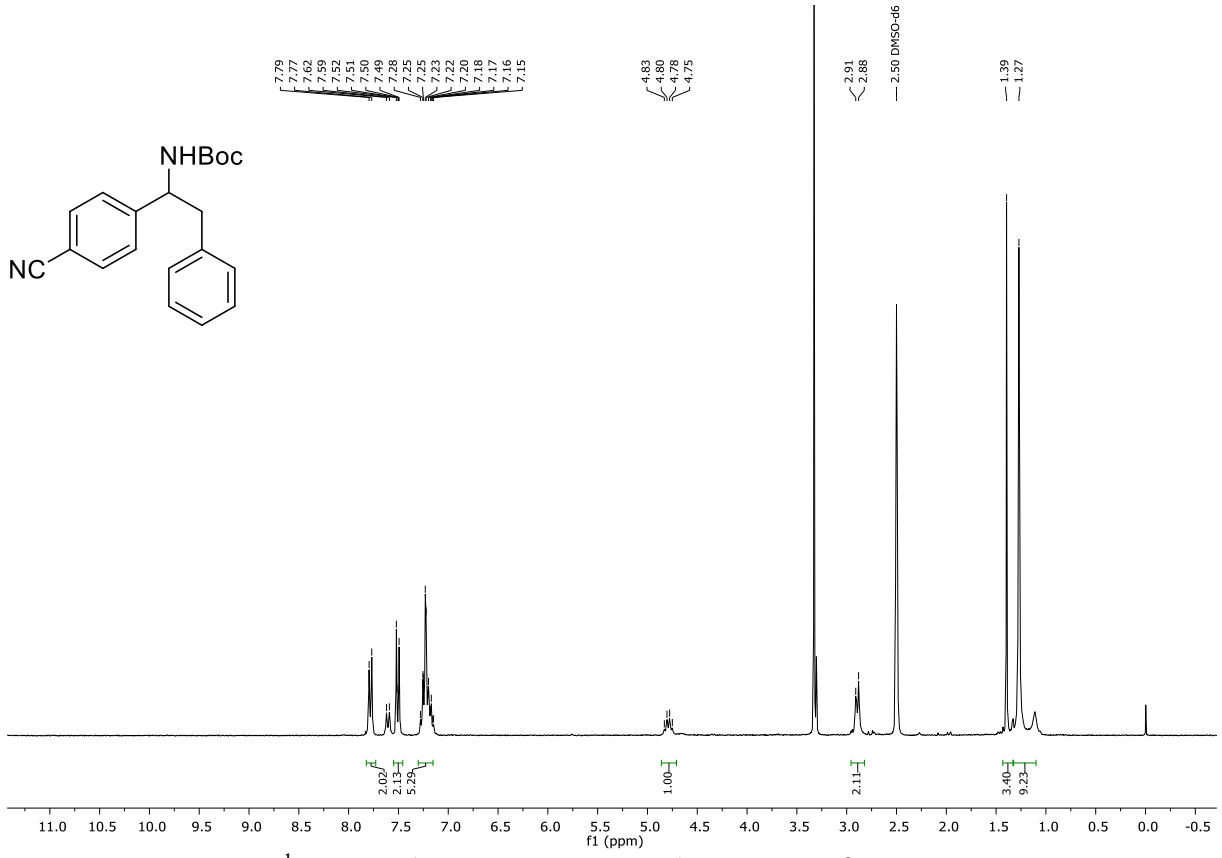

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **24**



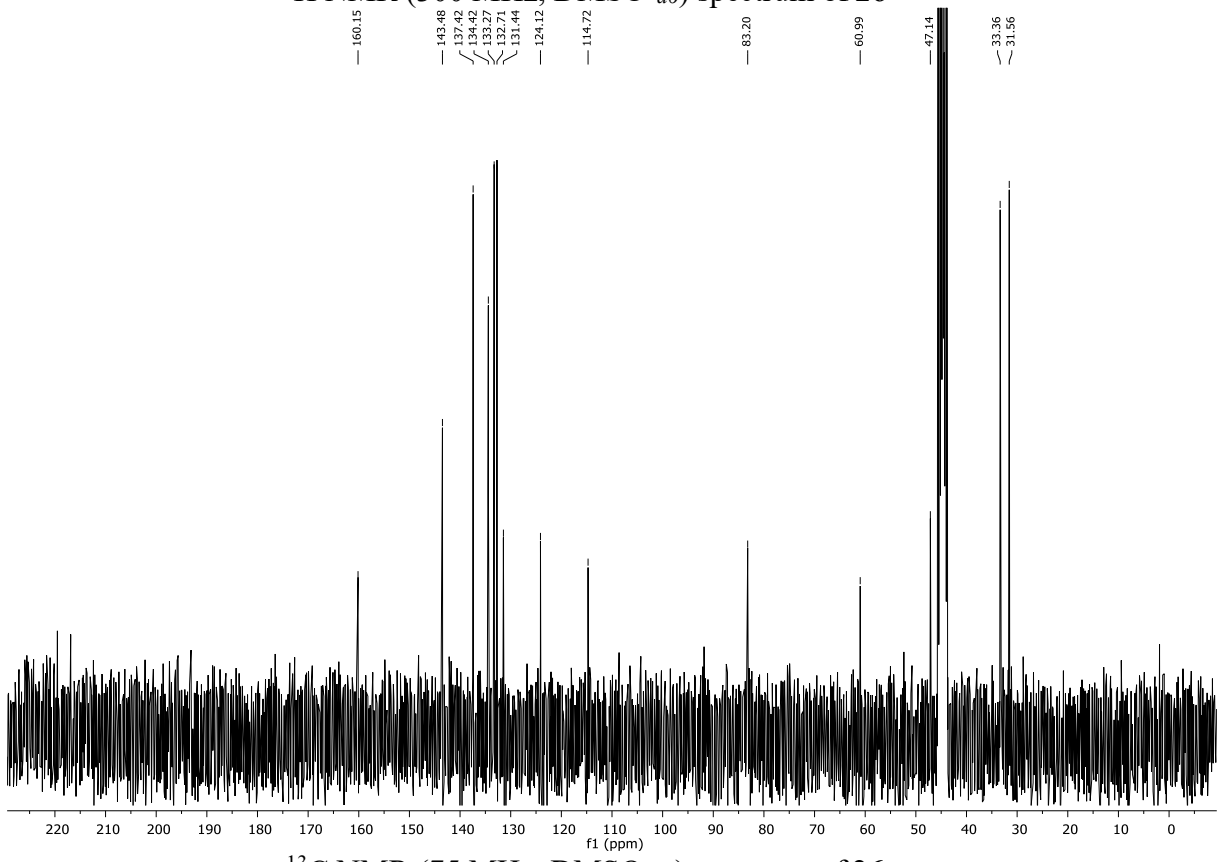

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **25**



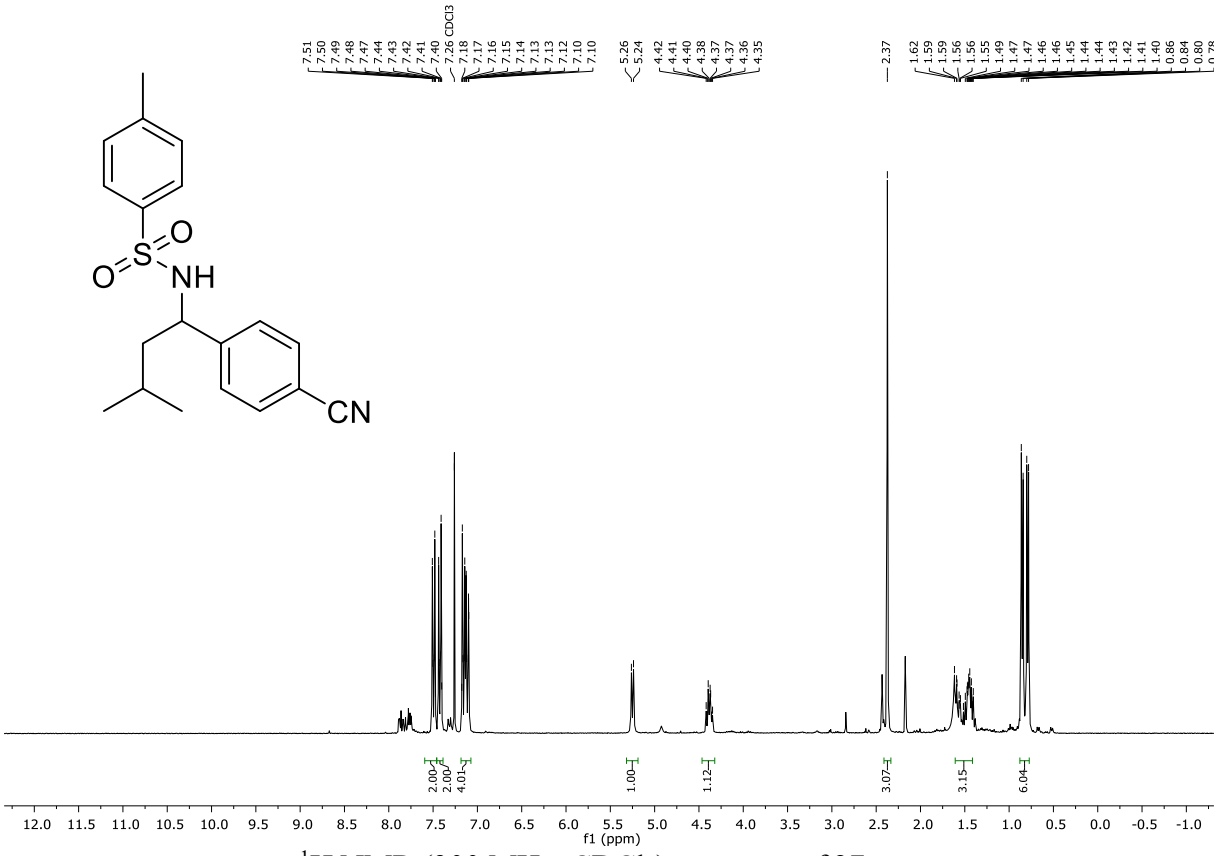

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **25**



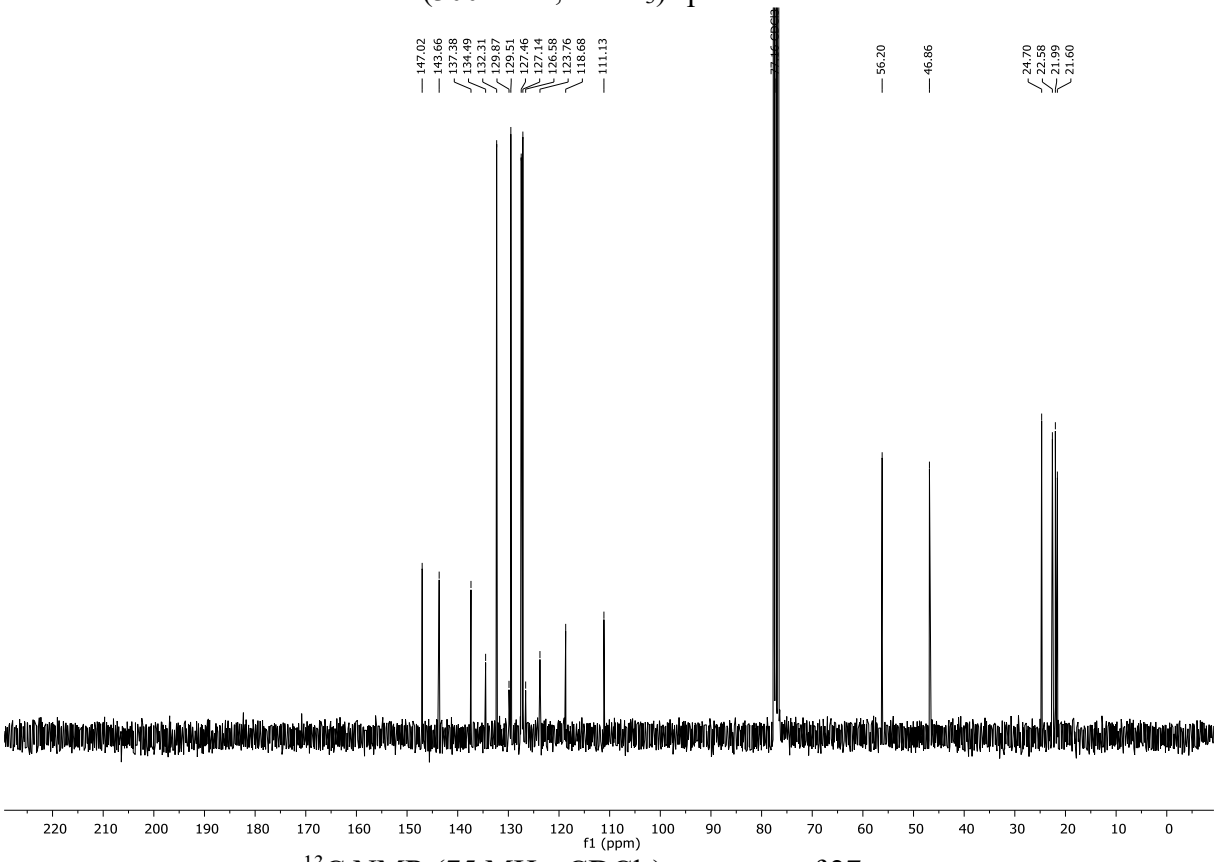

$^{1}$H NMR (300 MHz, DMSO-*d6*) spectrum of **26**



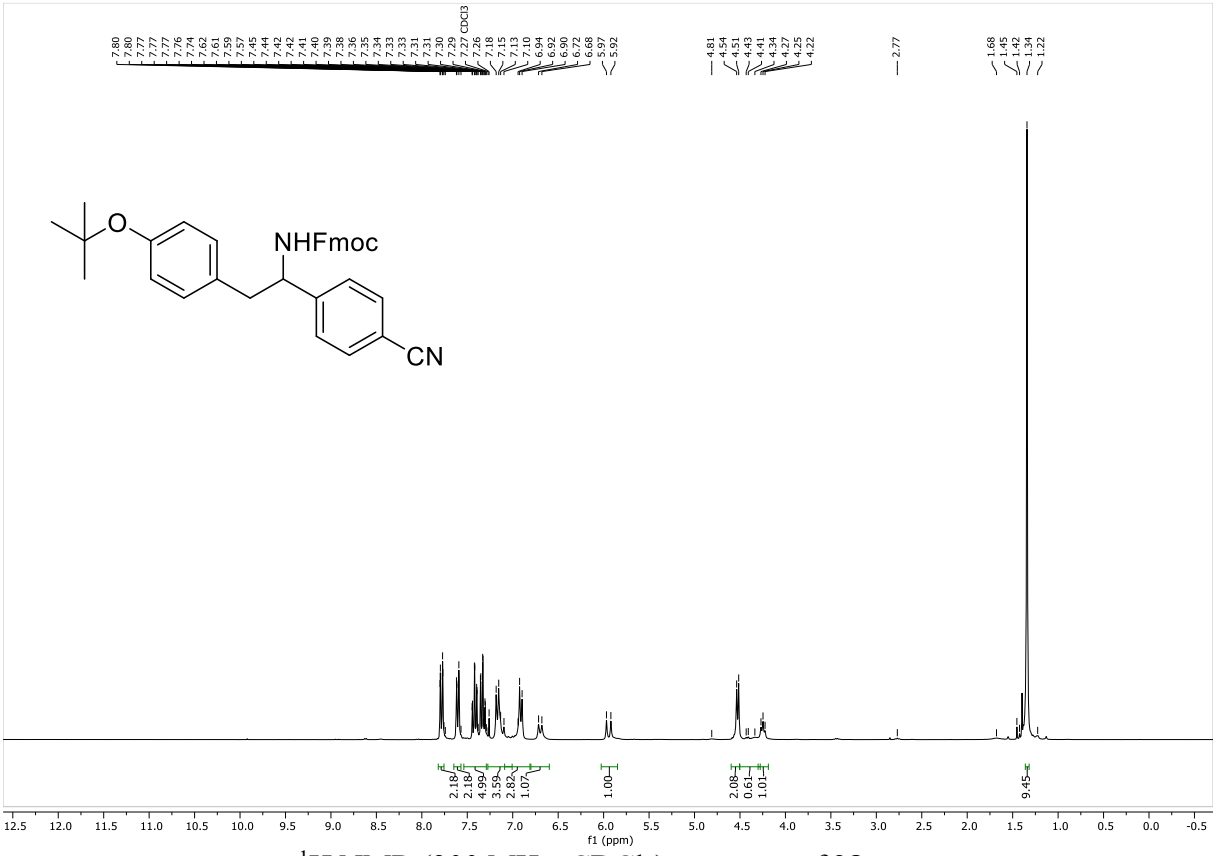

$^{13}$C NMR (75 MHz, DMSO-*d6*) spectrum of **26**



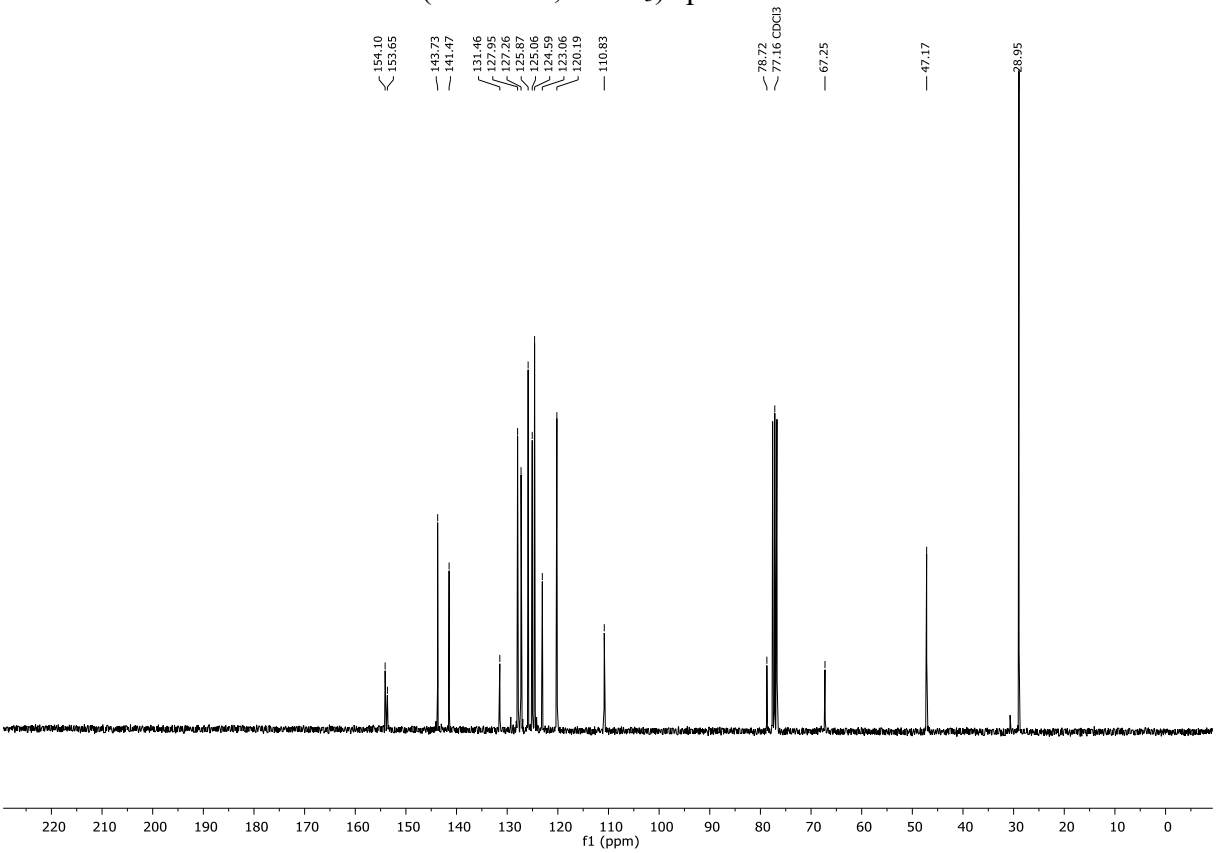

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **27**



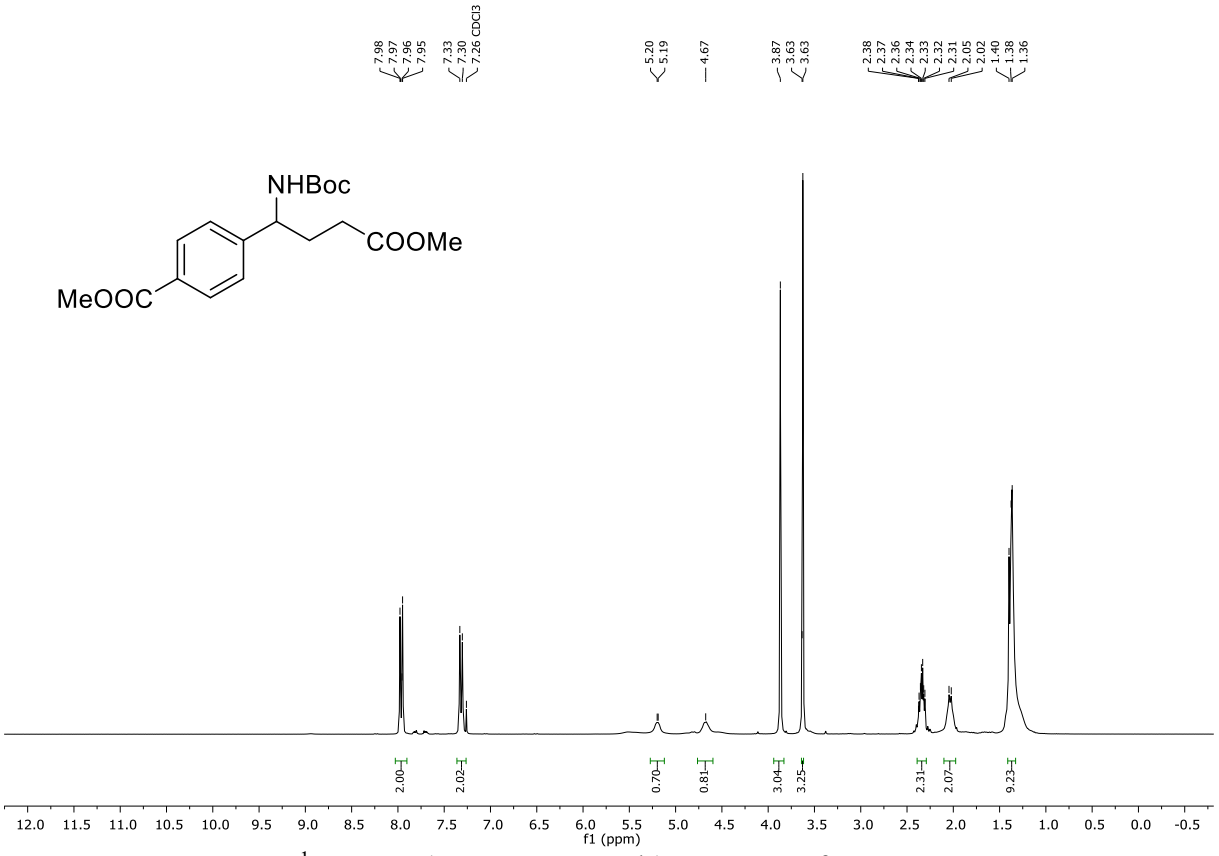

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **27**



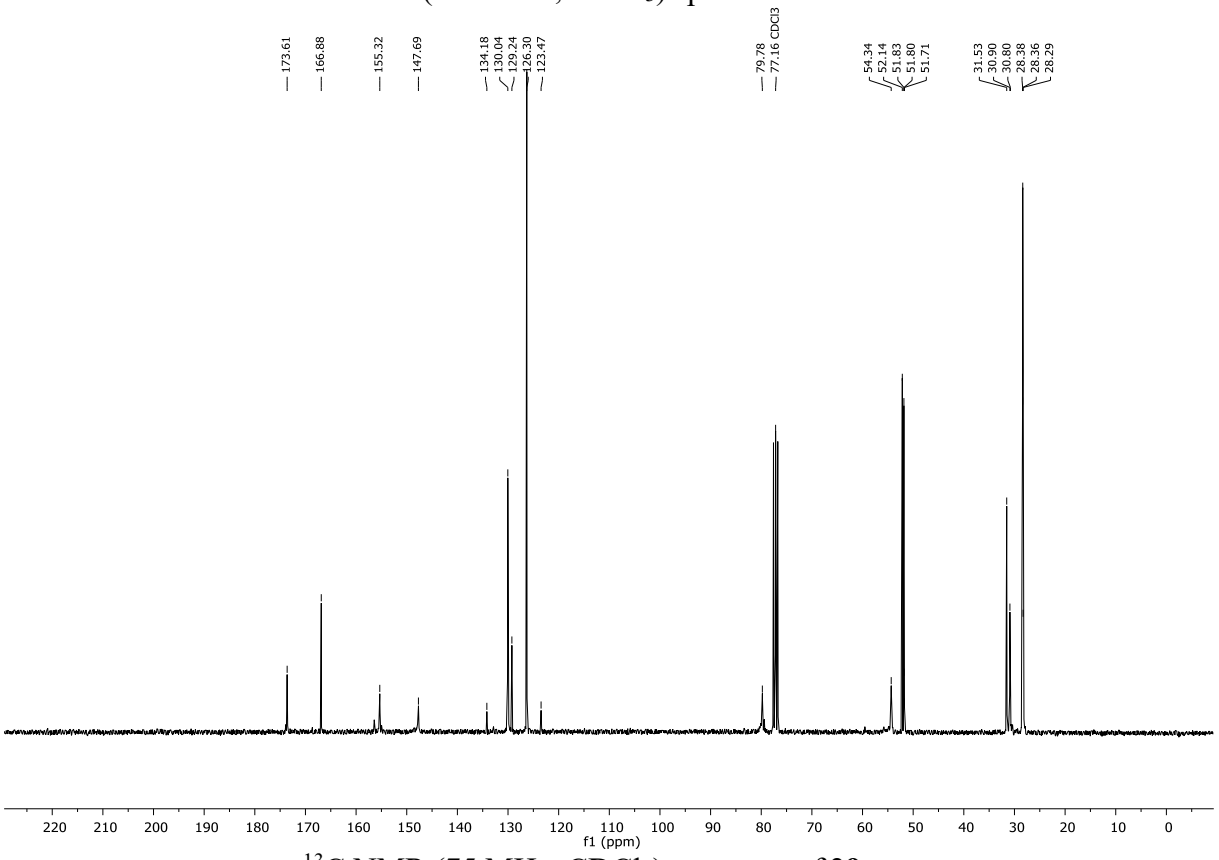

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **28**



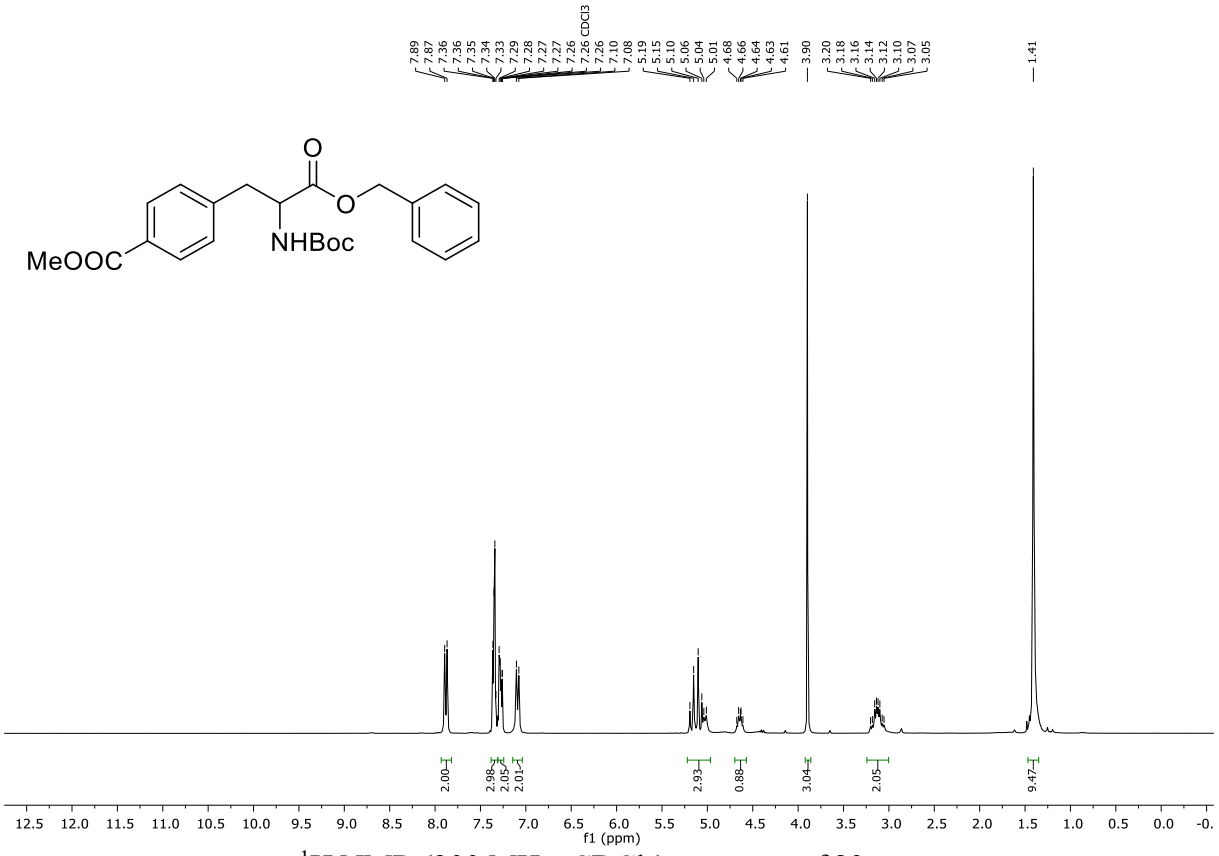

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **28**



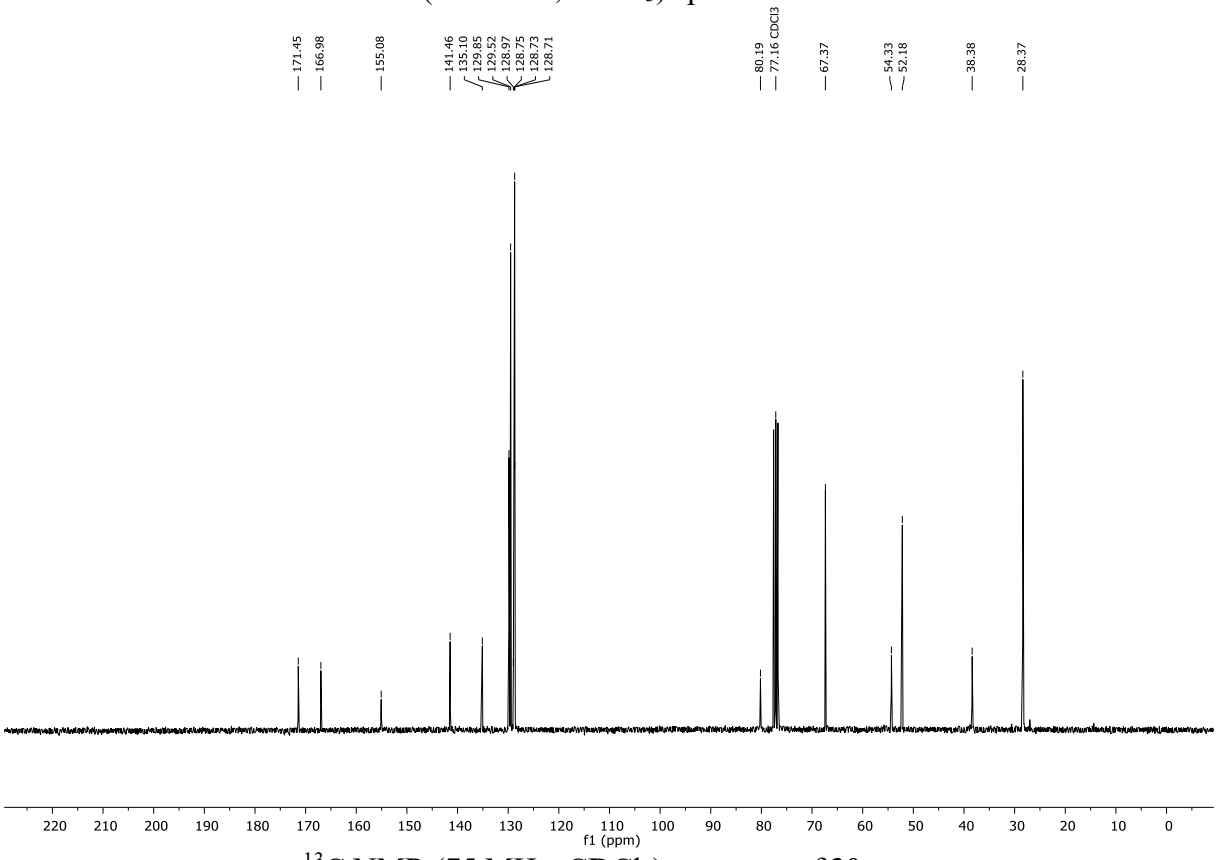

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **29**



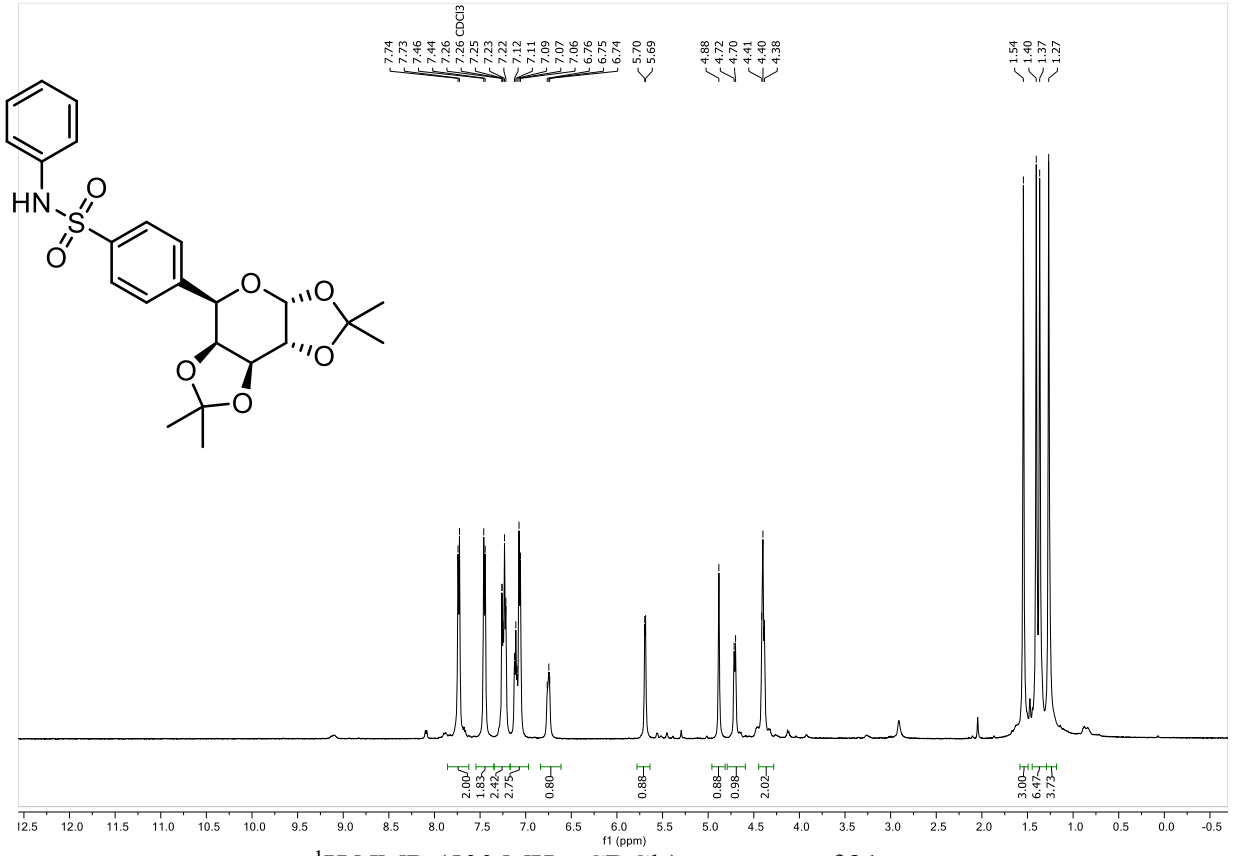

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **29**



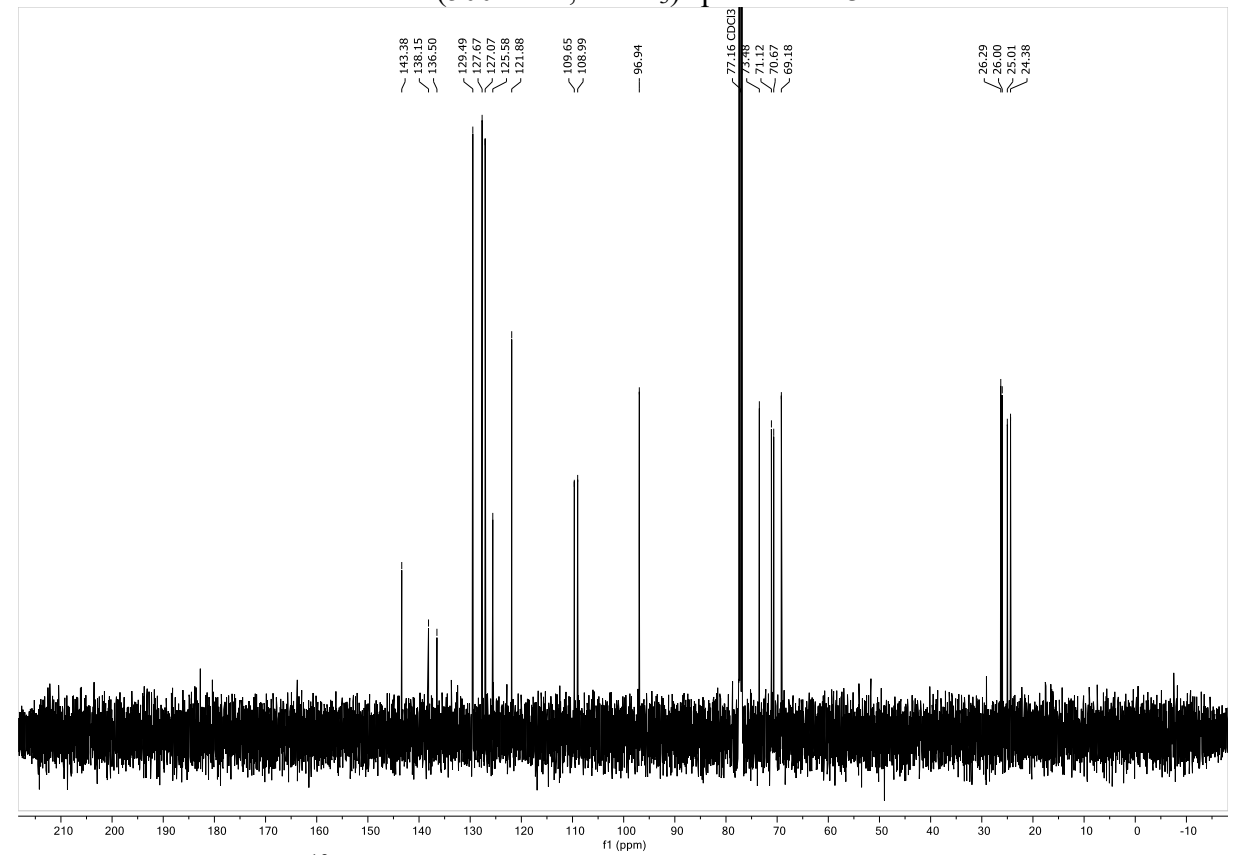

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **30**



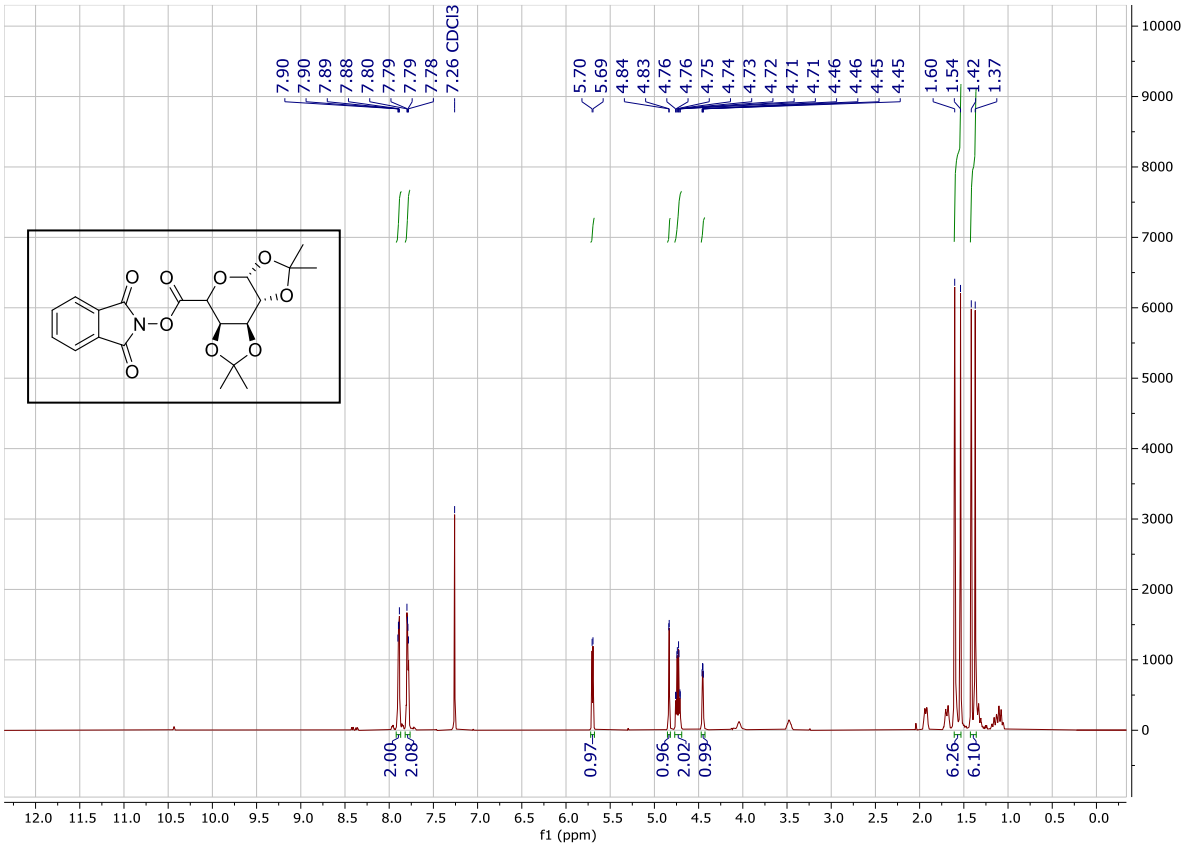

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **30**



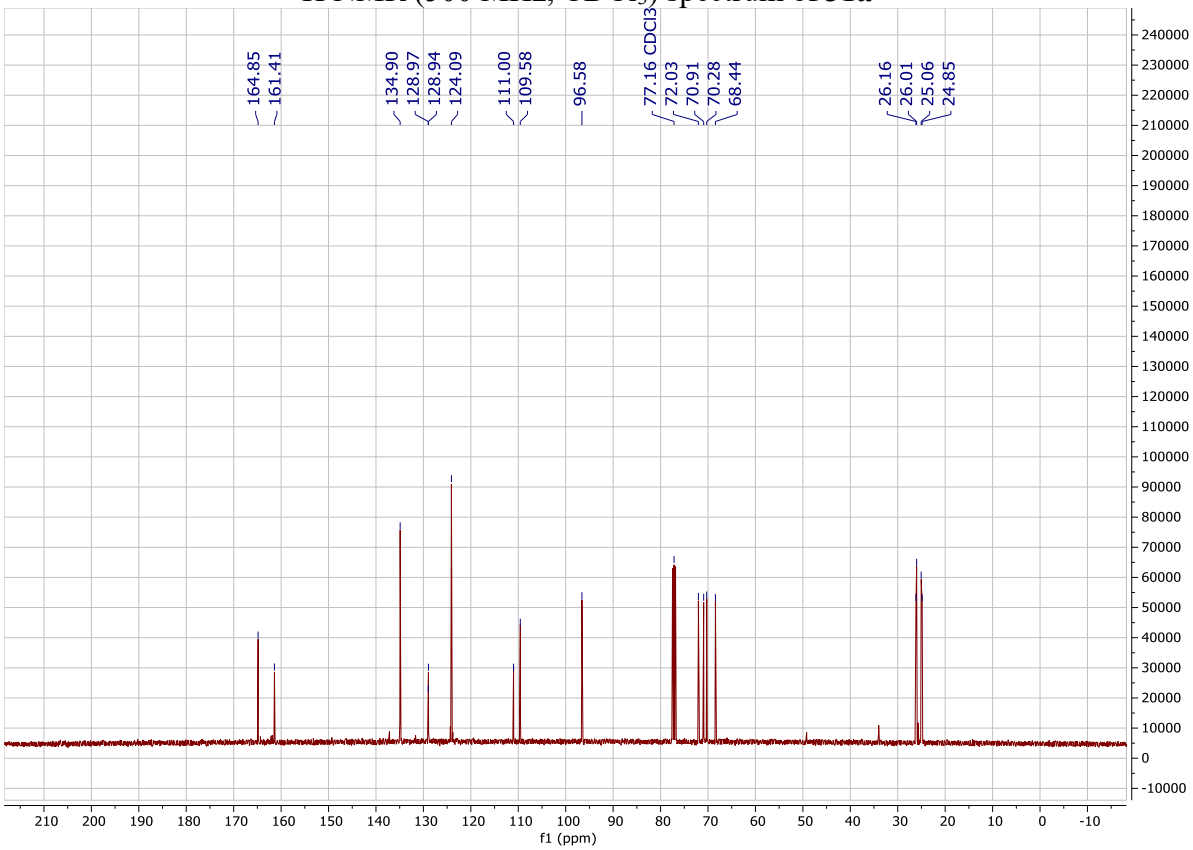

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **31**



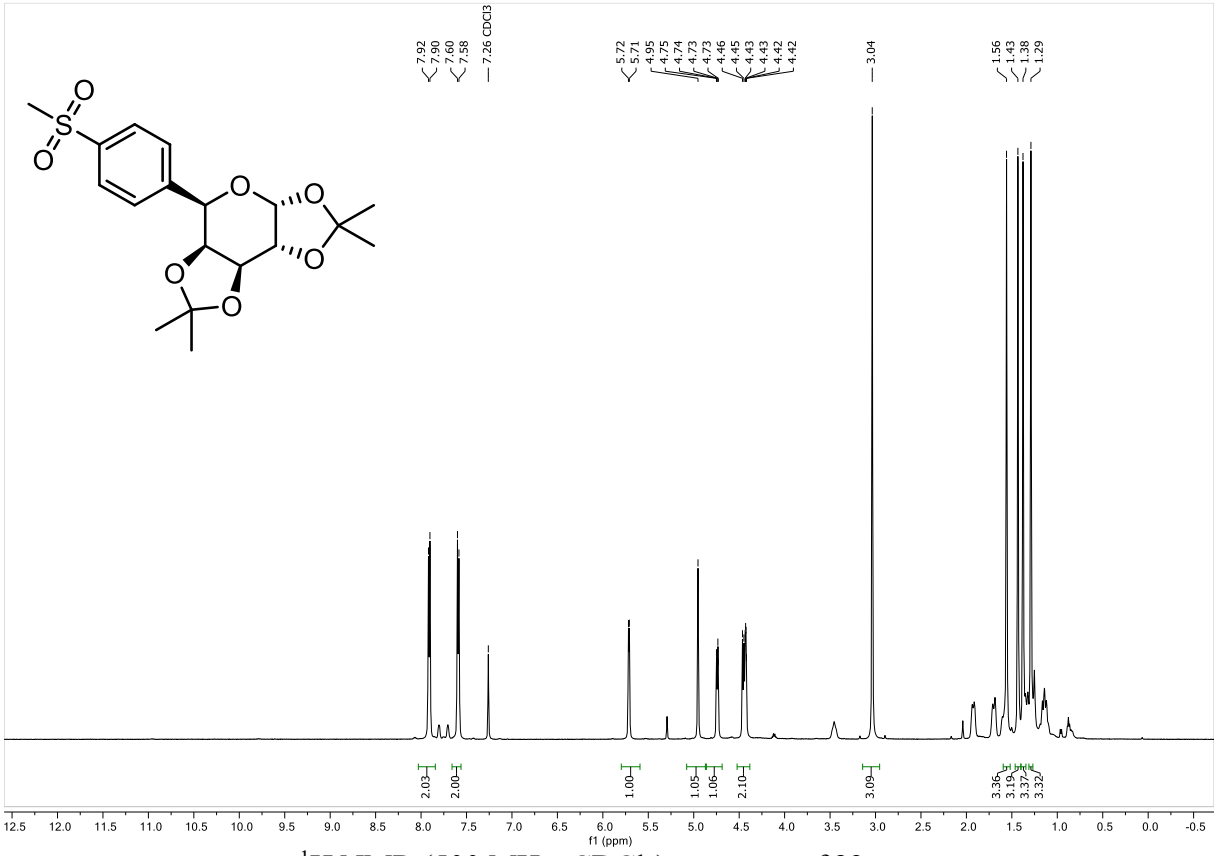

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **31**



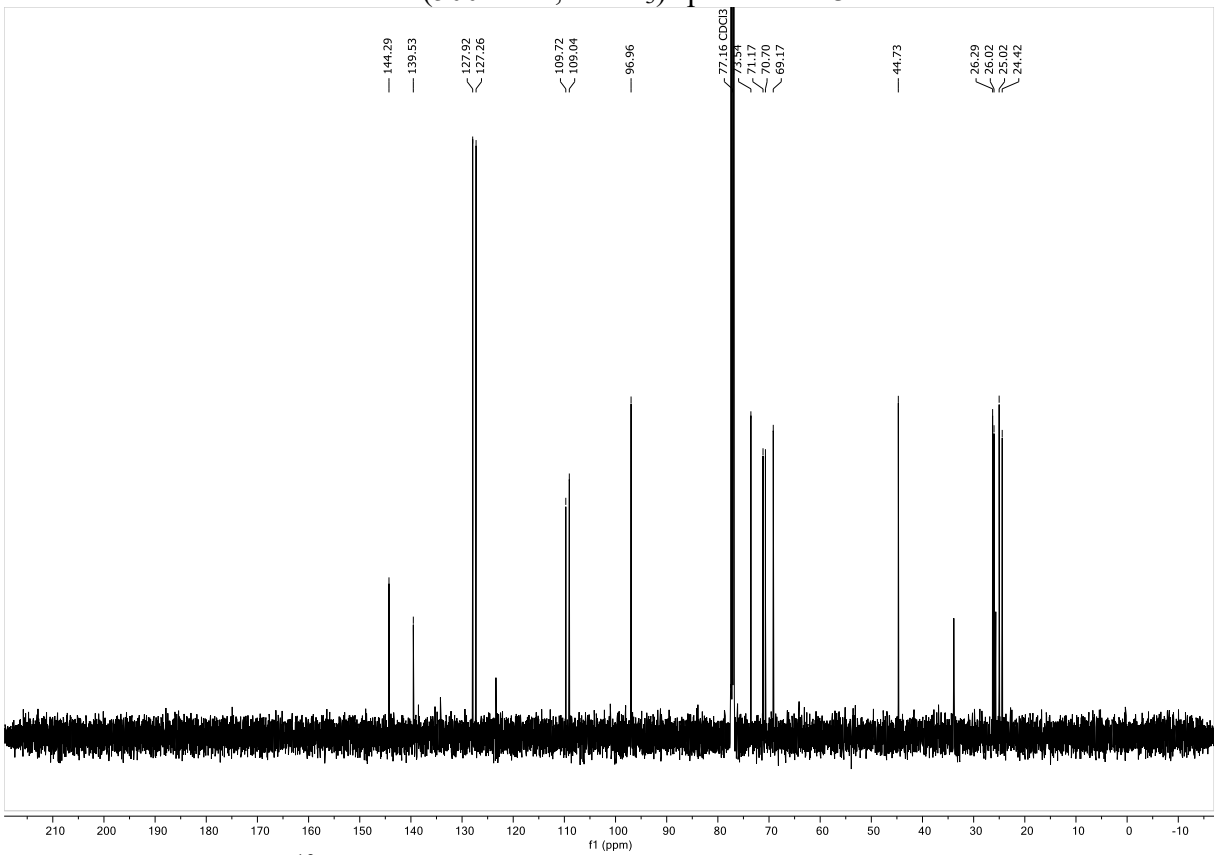

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **31a**



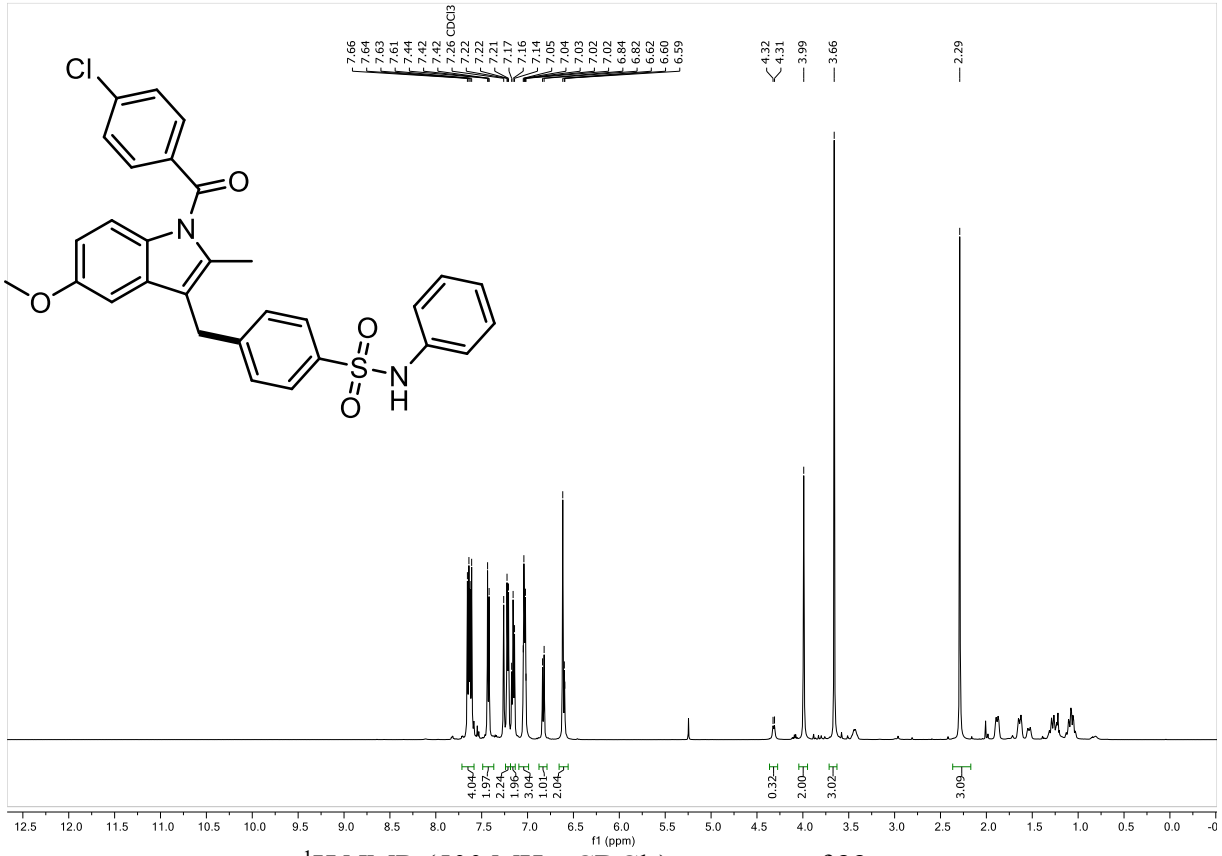

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **31a**



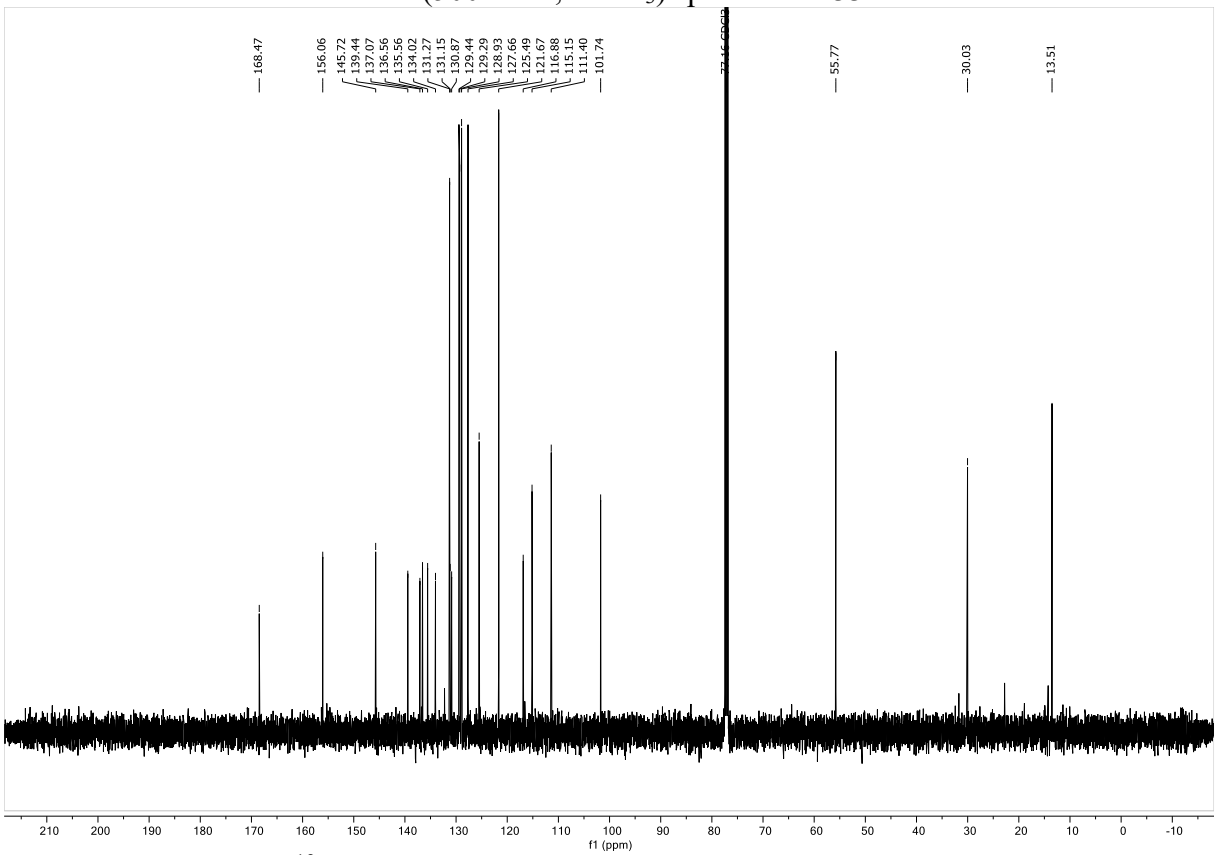

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **32**



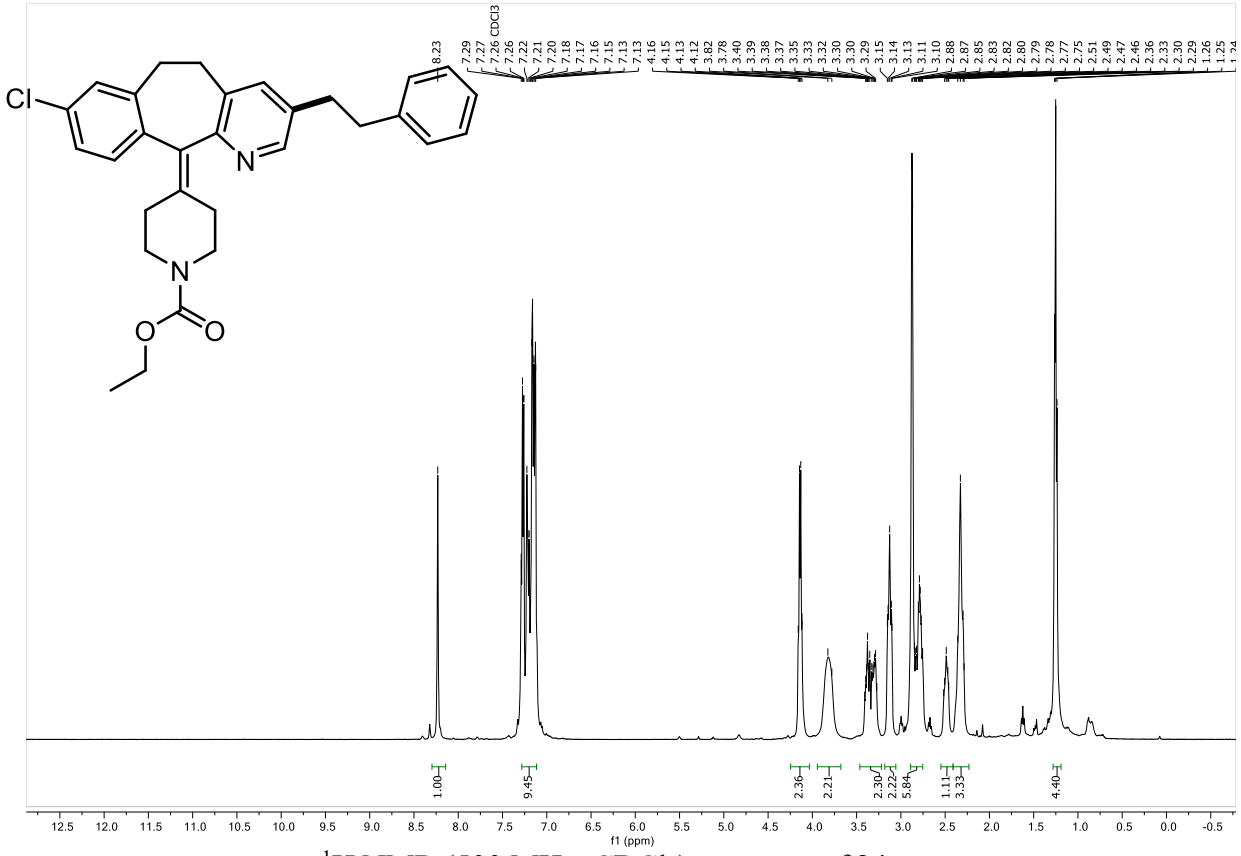

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **32**



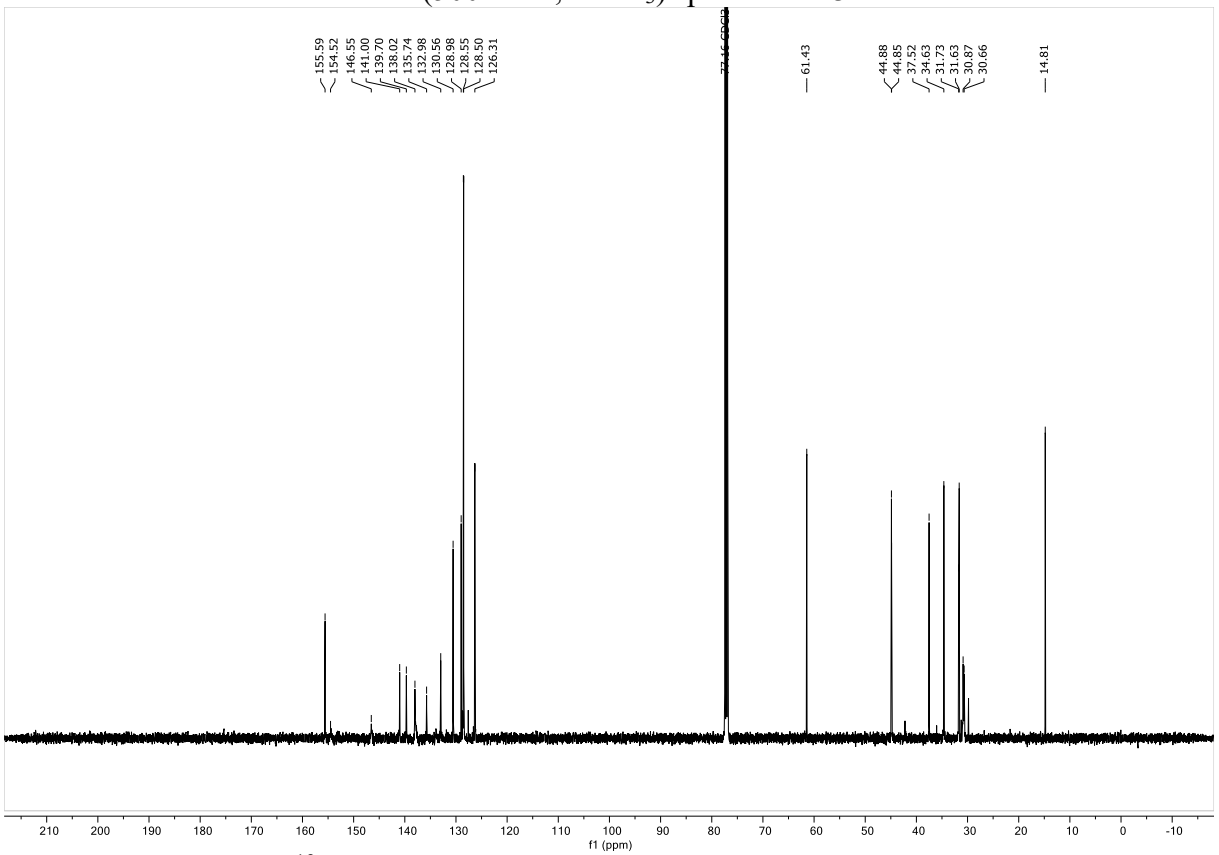

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **33**



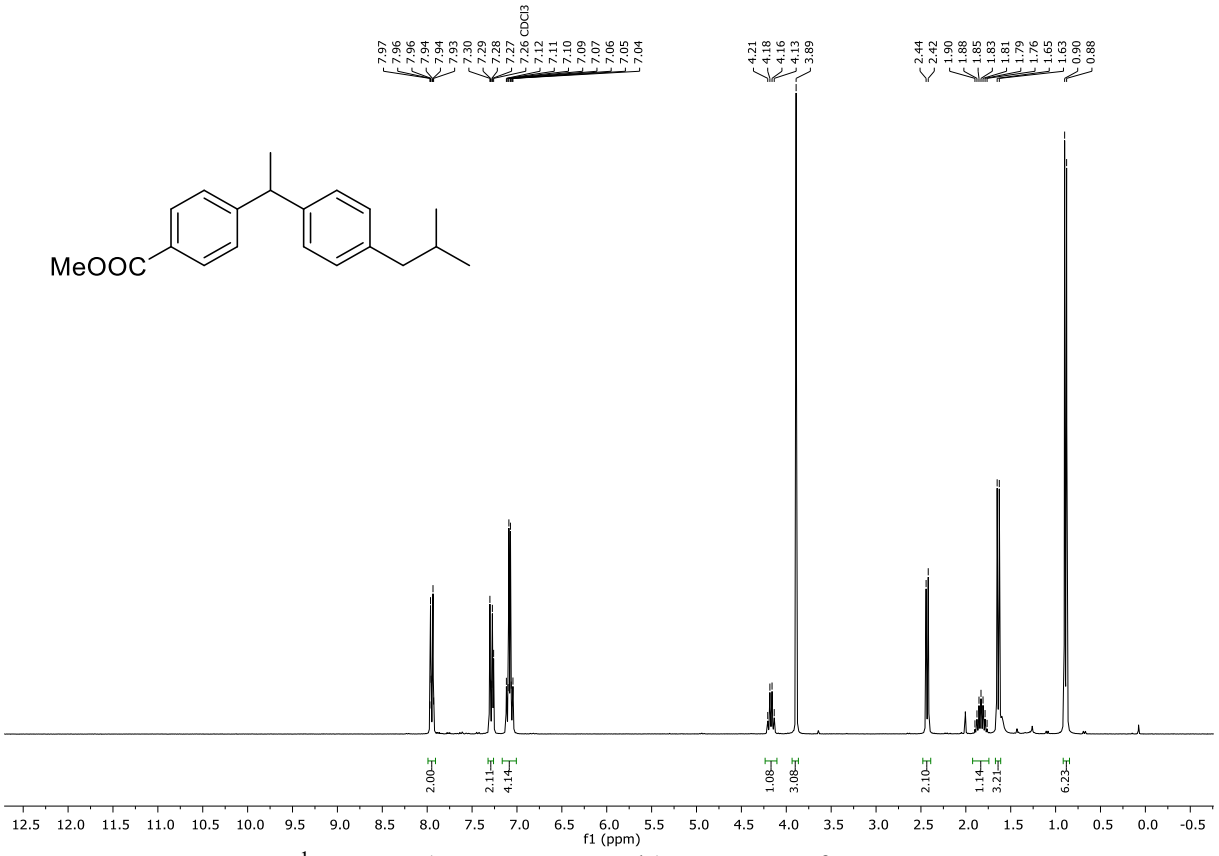

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **33**



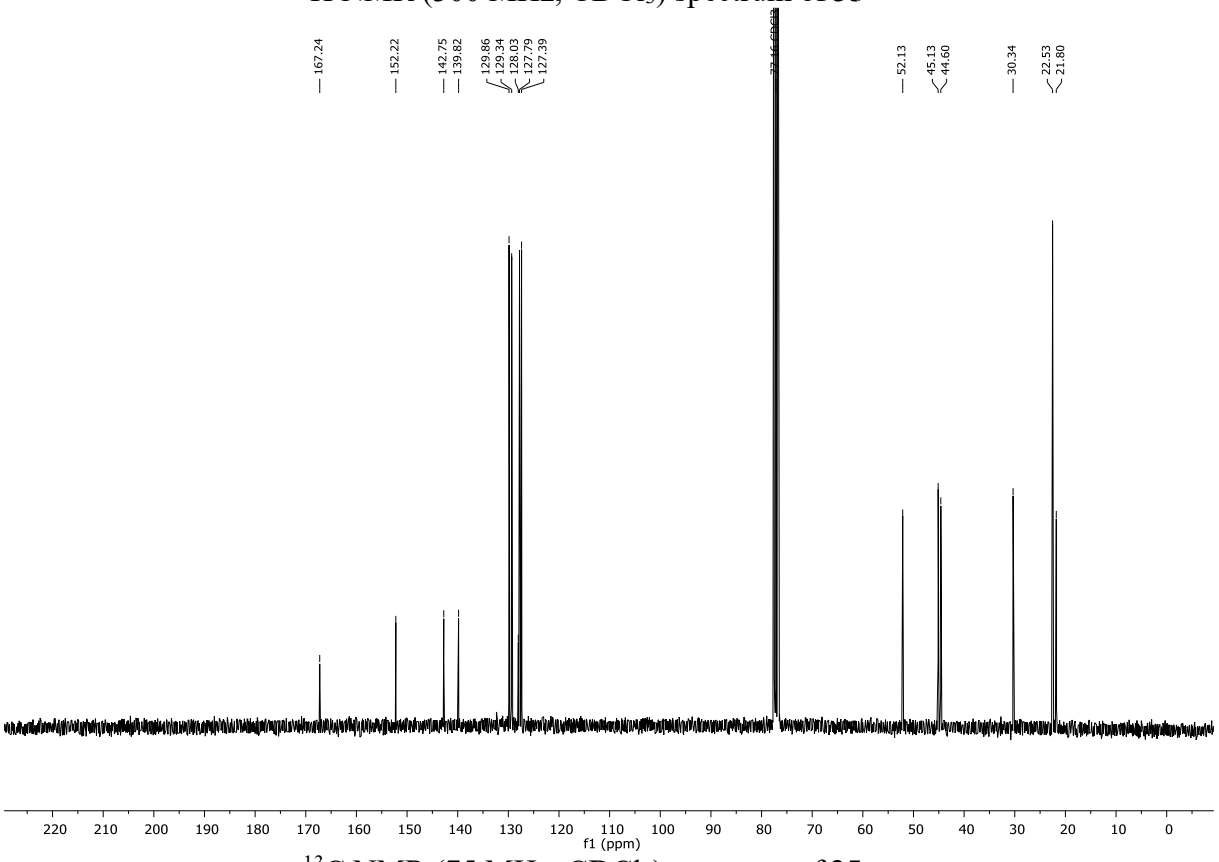

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **34**



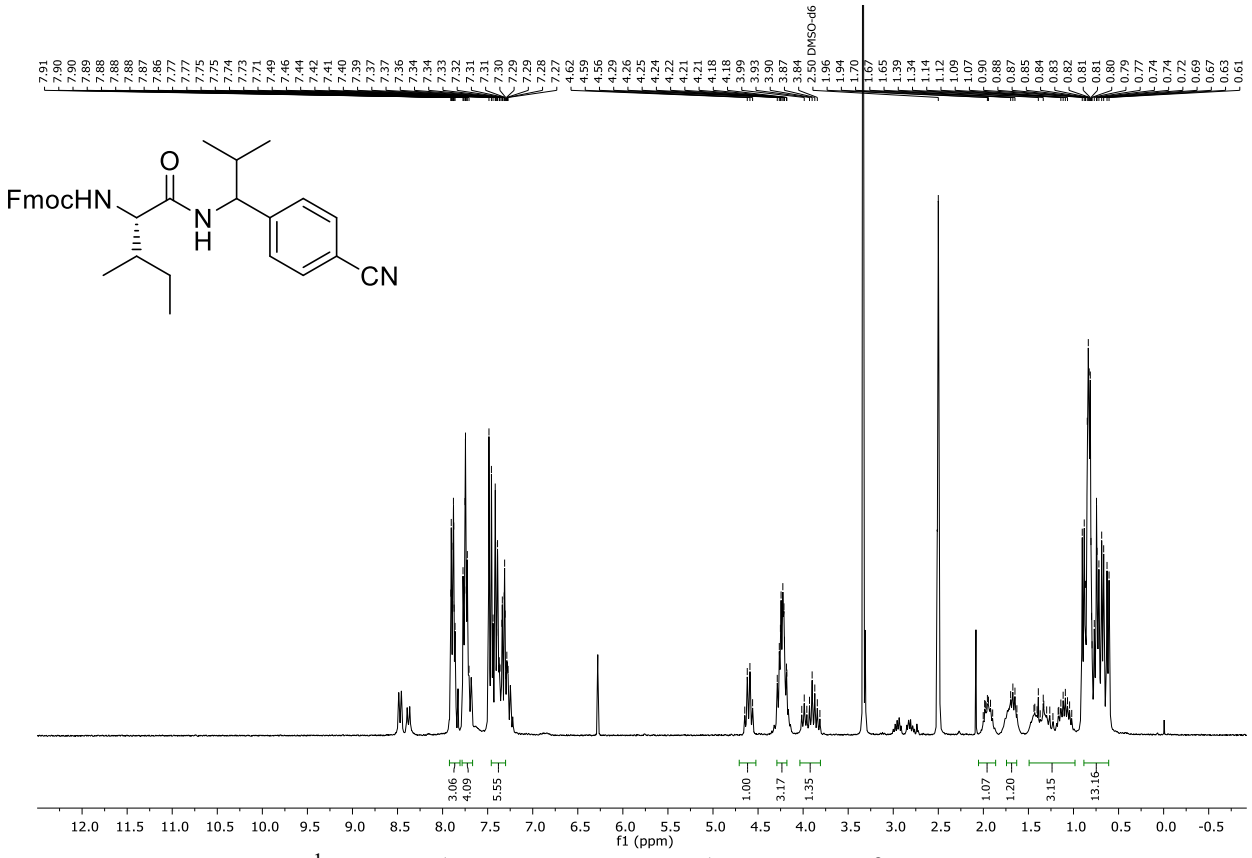

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **34**



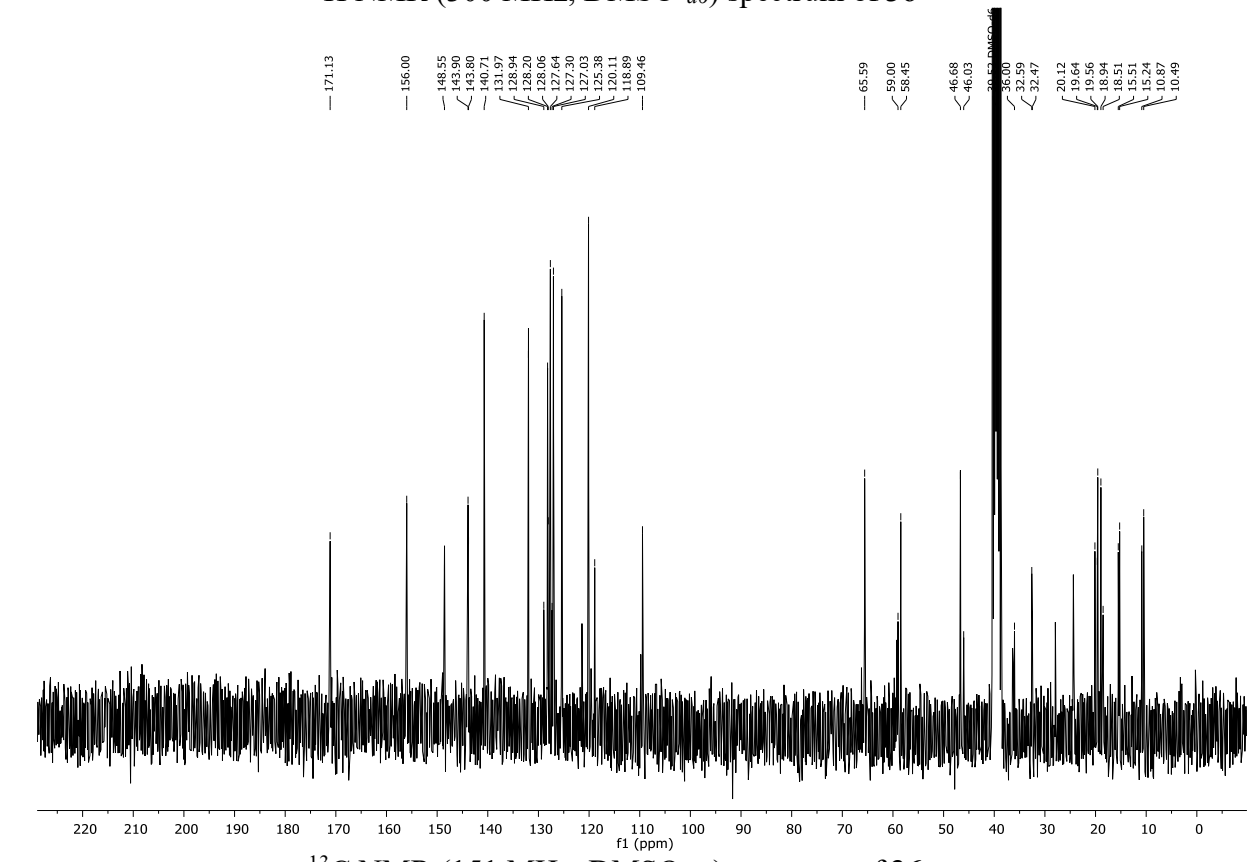

$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **35**



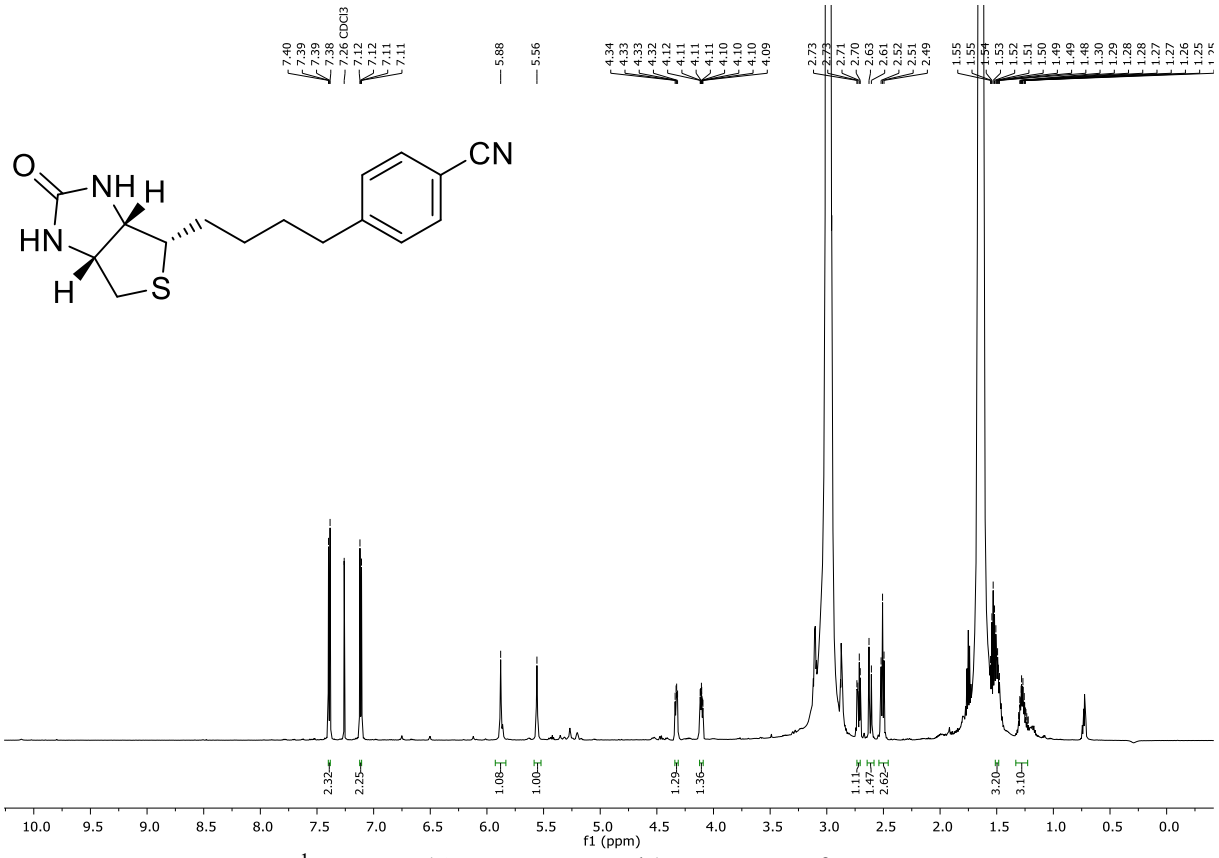

$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **35**



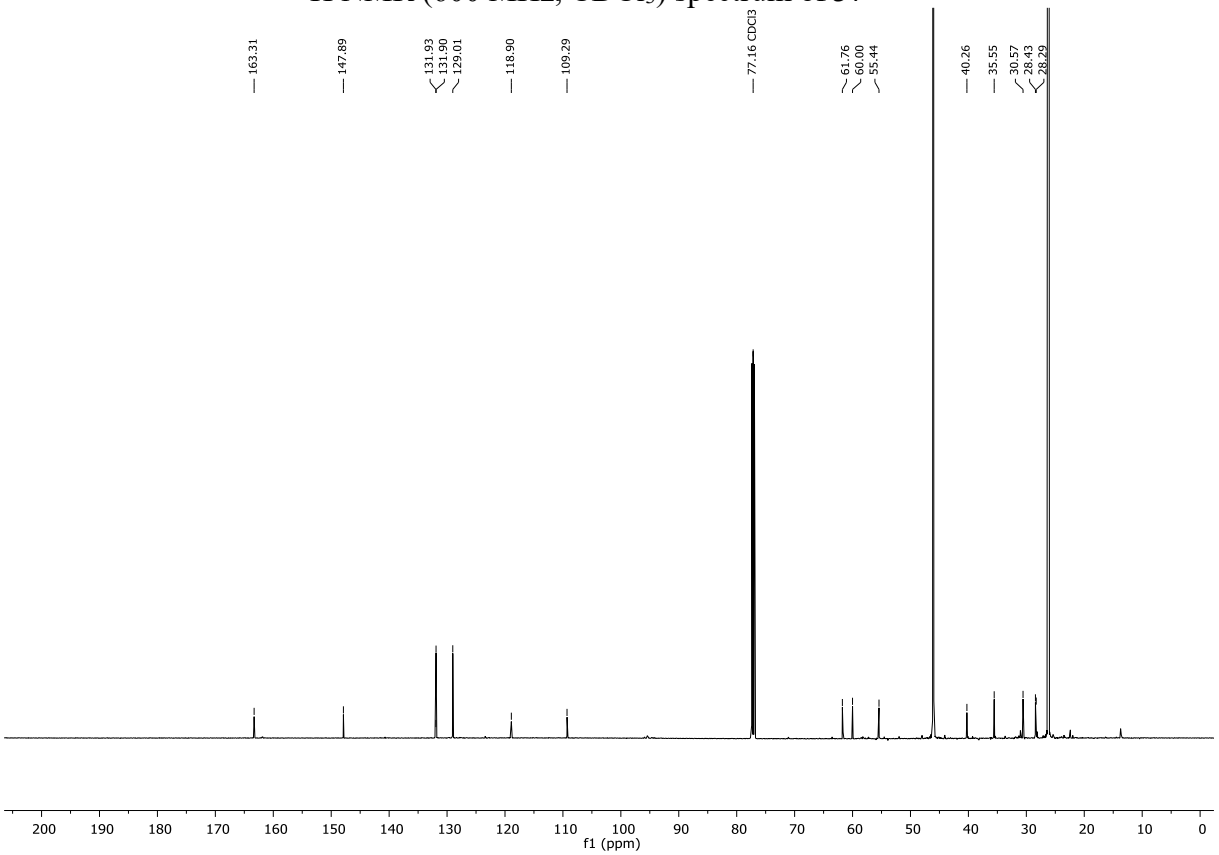

$^{1}$H NMR (300 MHz, DMSO-*d6*) spectrum of **36**



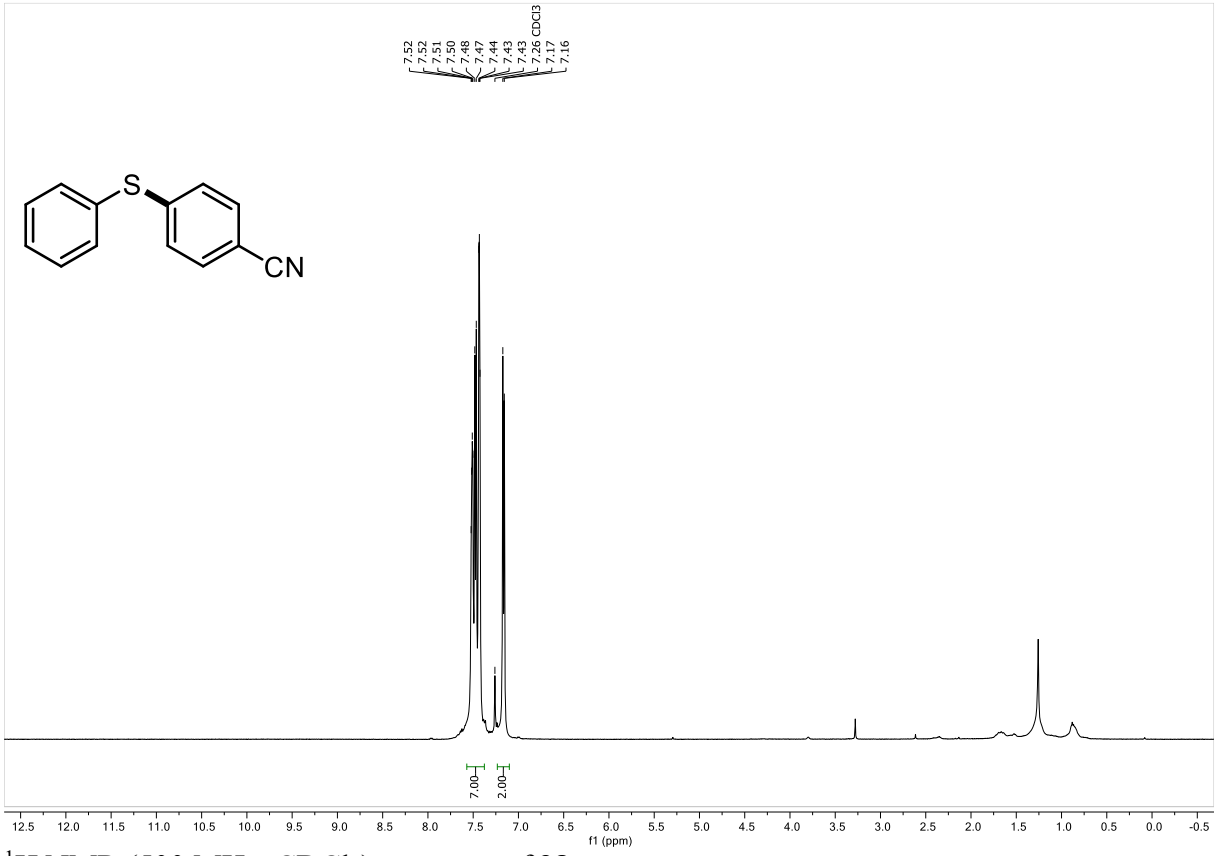

$^{13}$C NMR (151 MHz, DMSO-*d6*) spectrum of **36**



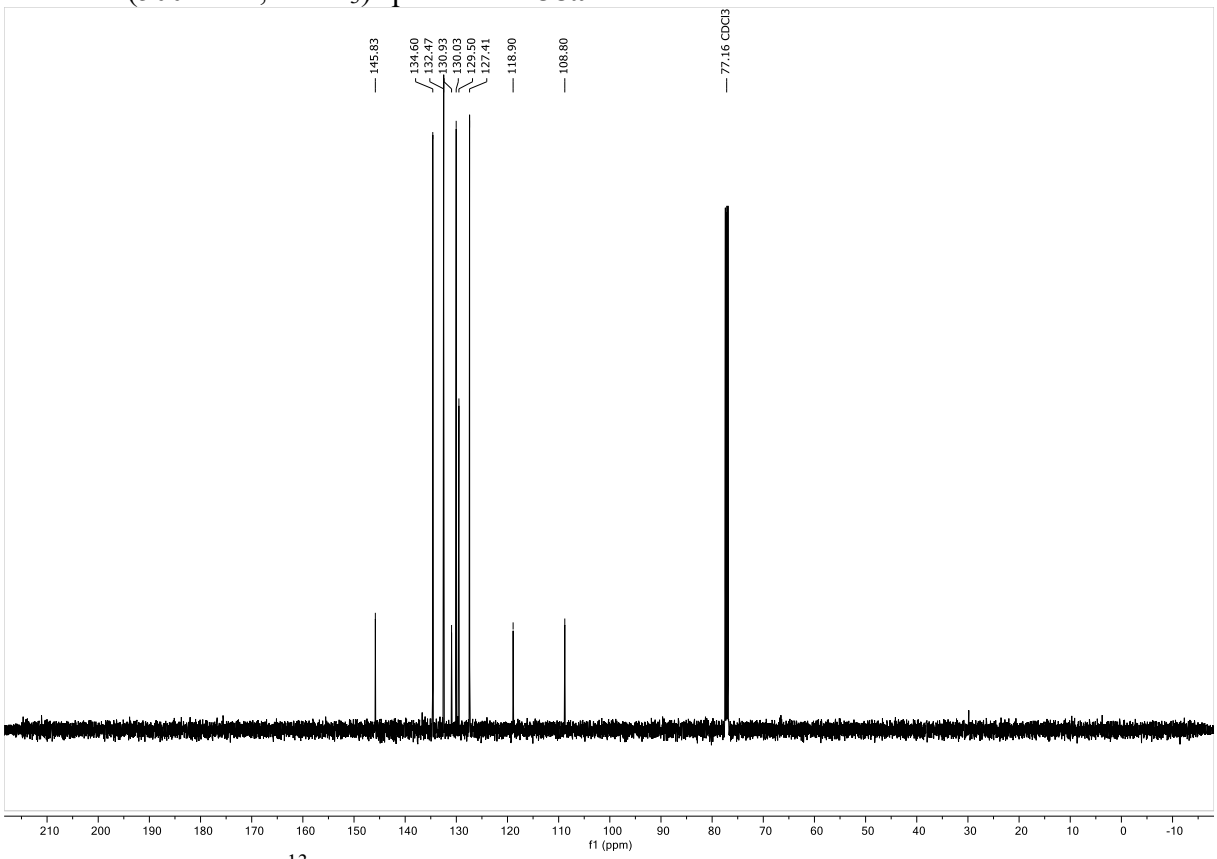

$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **37**



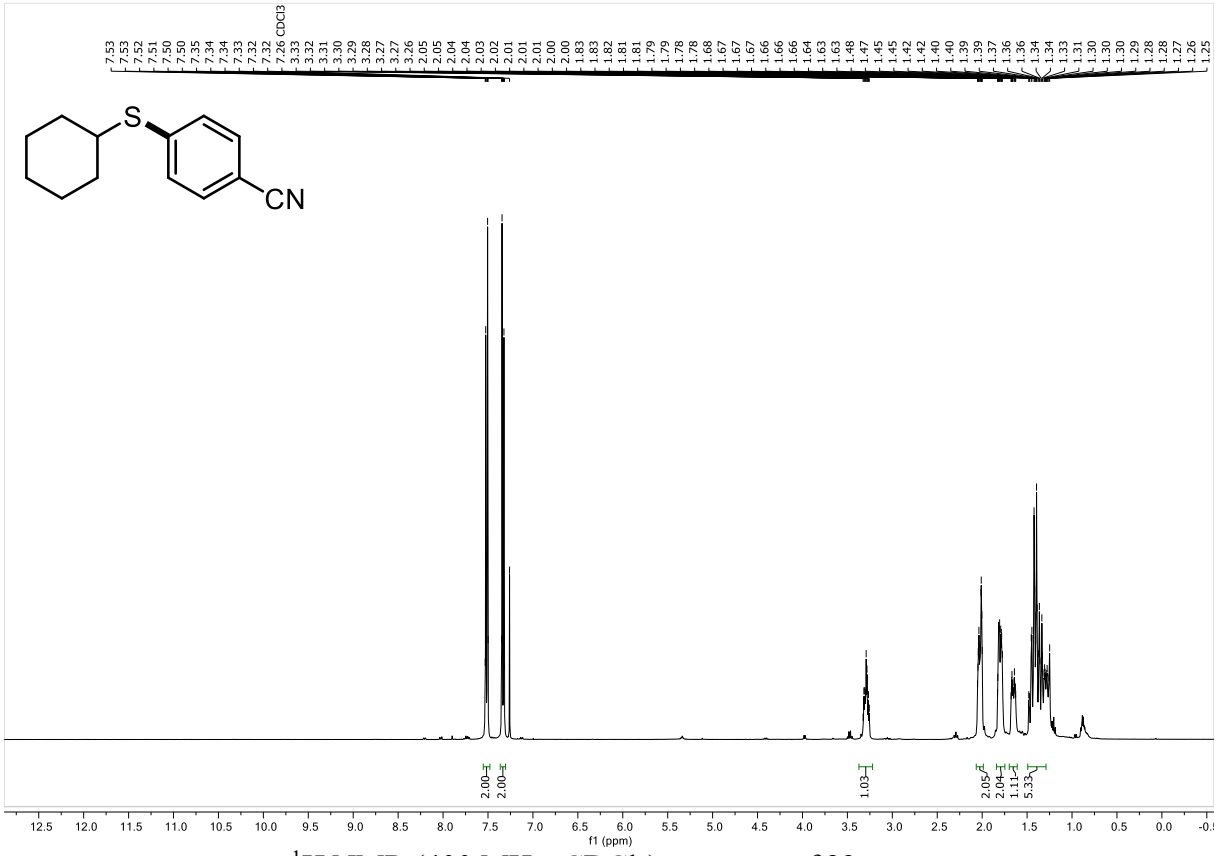

$^{13}$C NMR (151 MHz, $CDCl_3$) spectrum of **37**



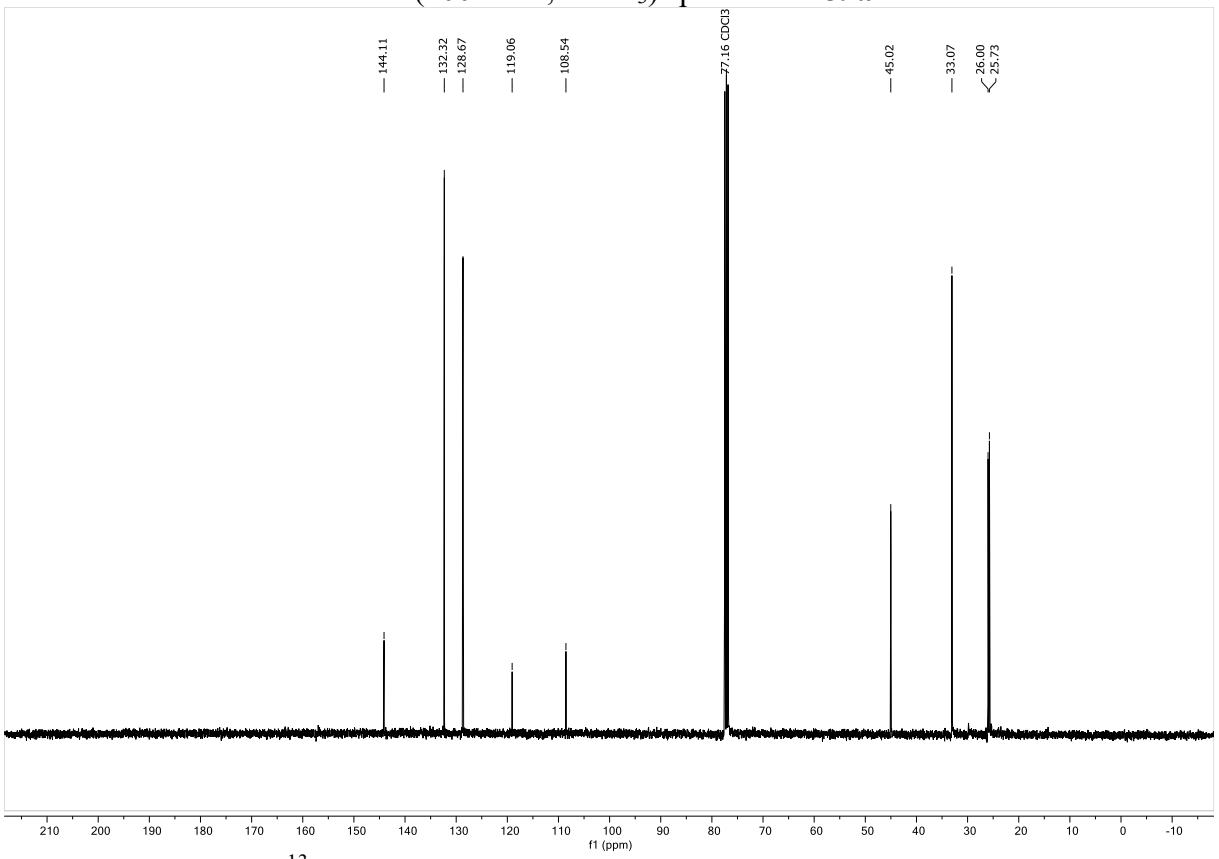

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **38a**



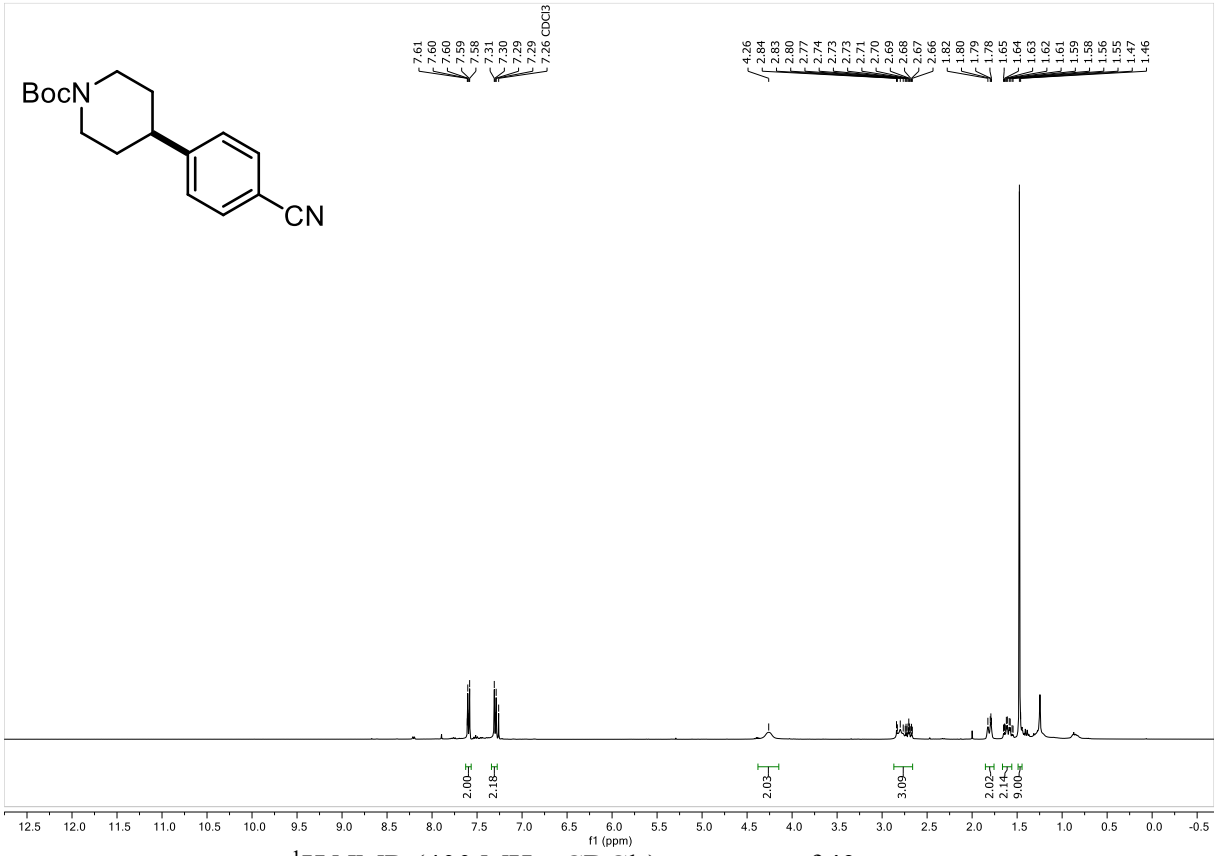

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **38a**



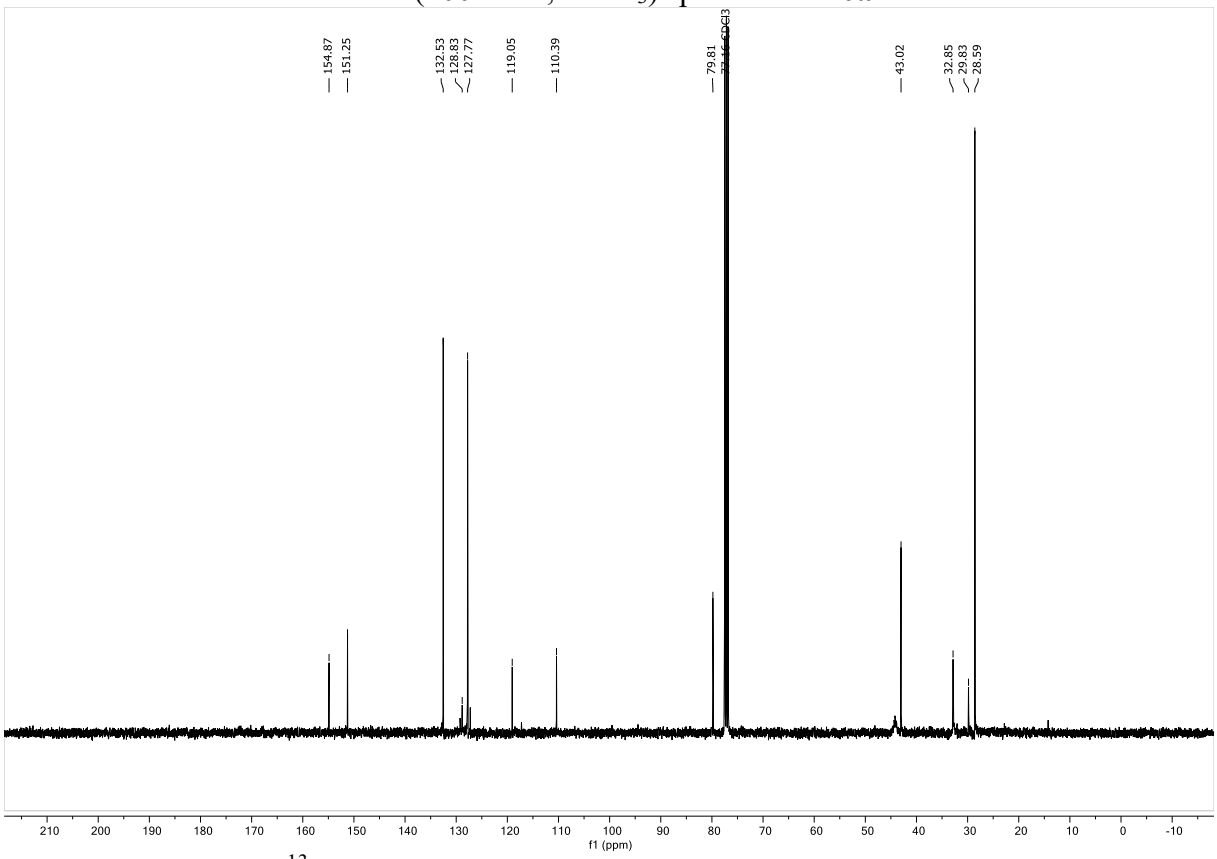

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **39a**



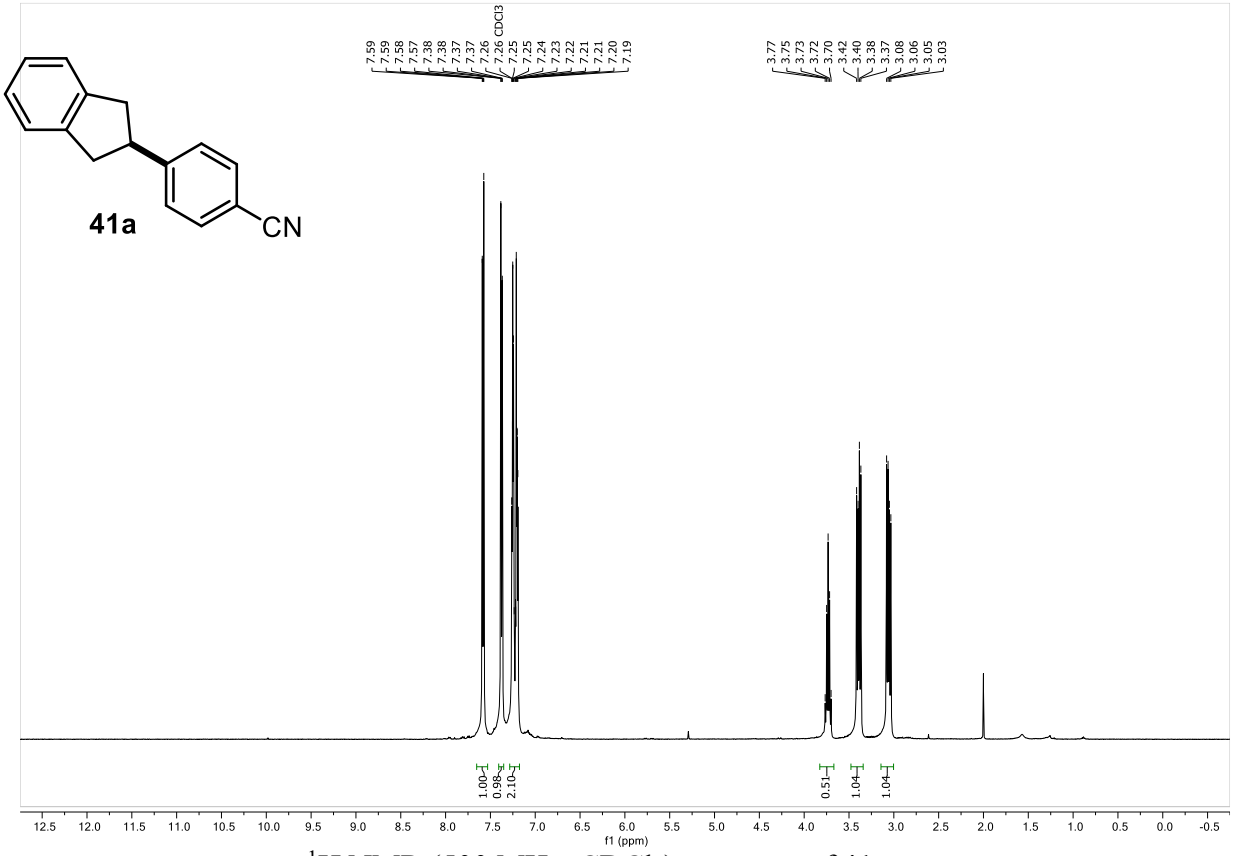

$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **39a**



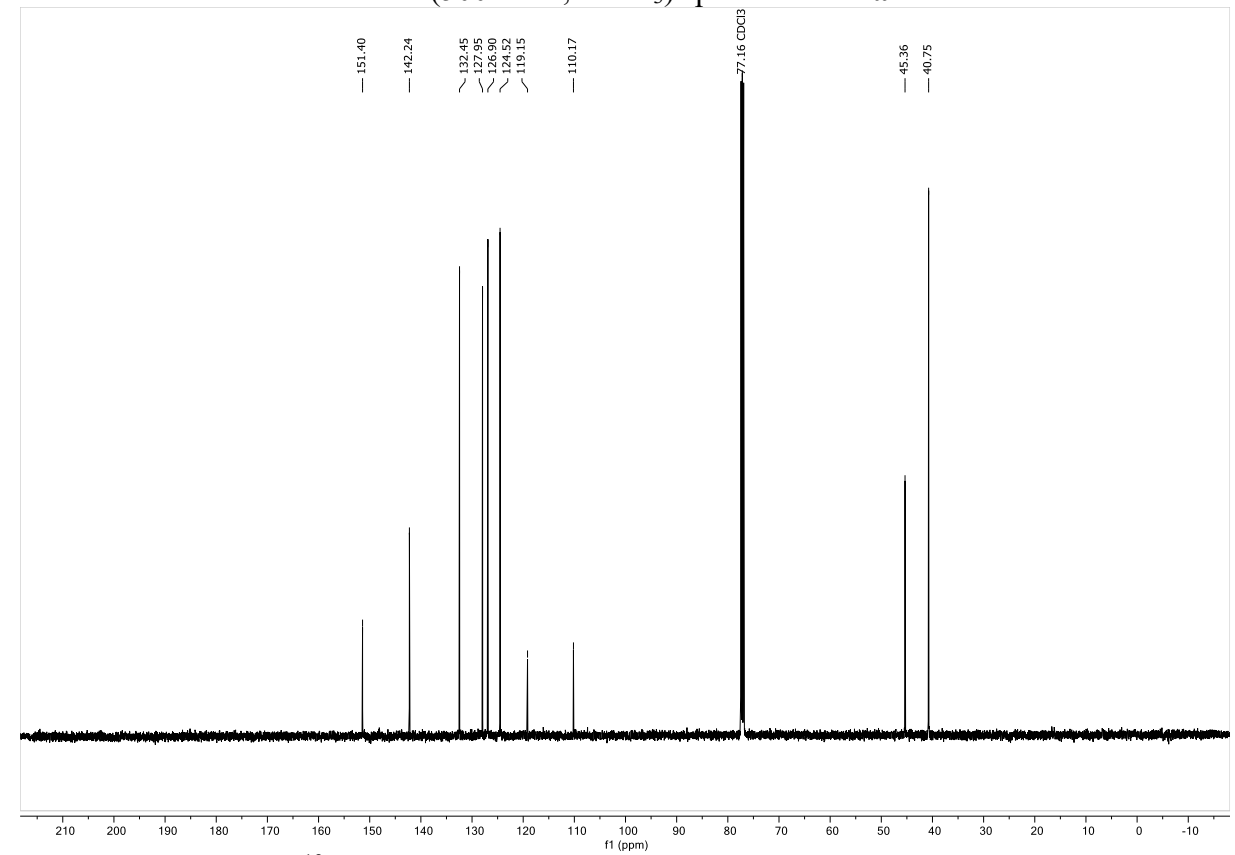

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **40a**



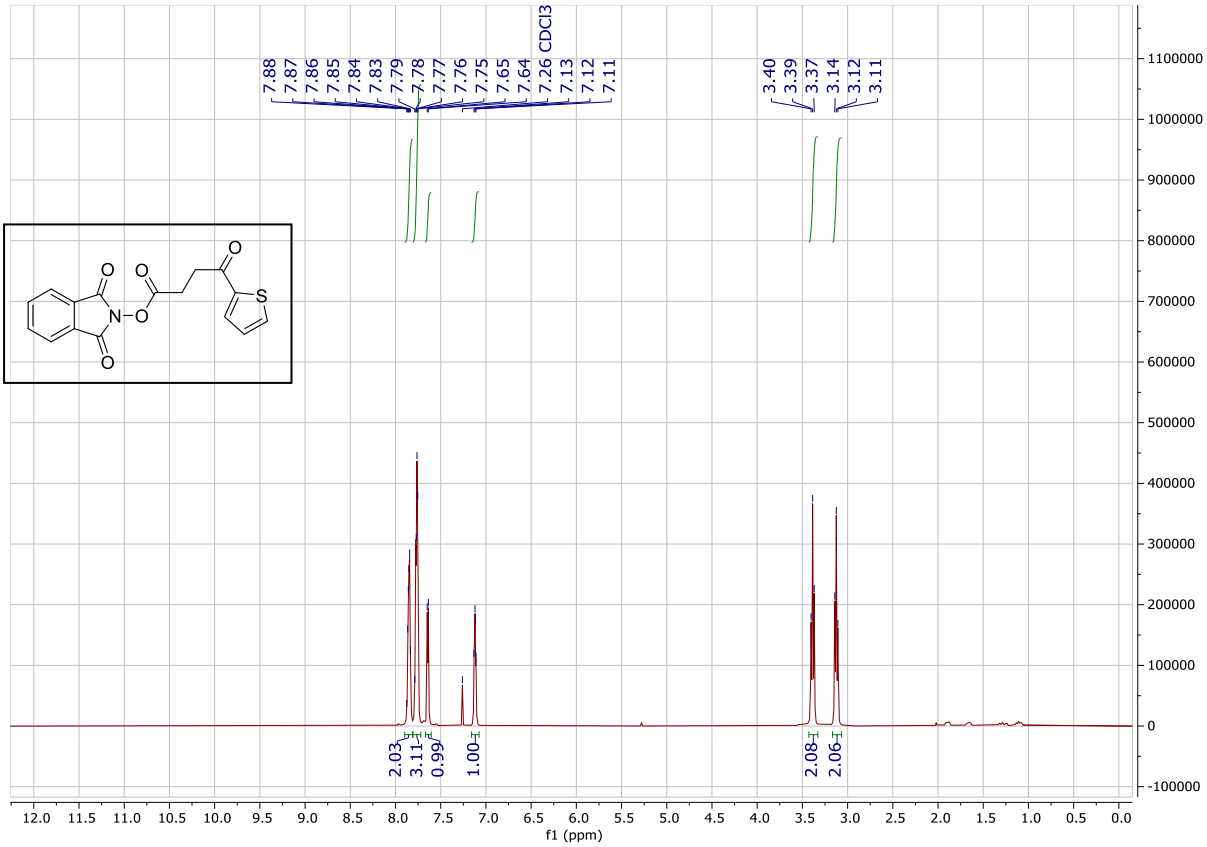

$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **40a**



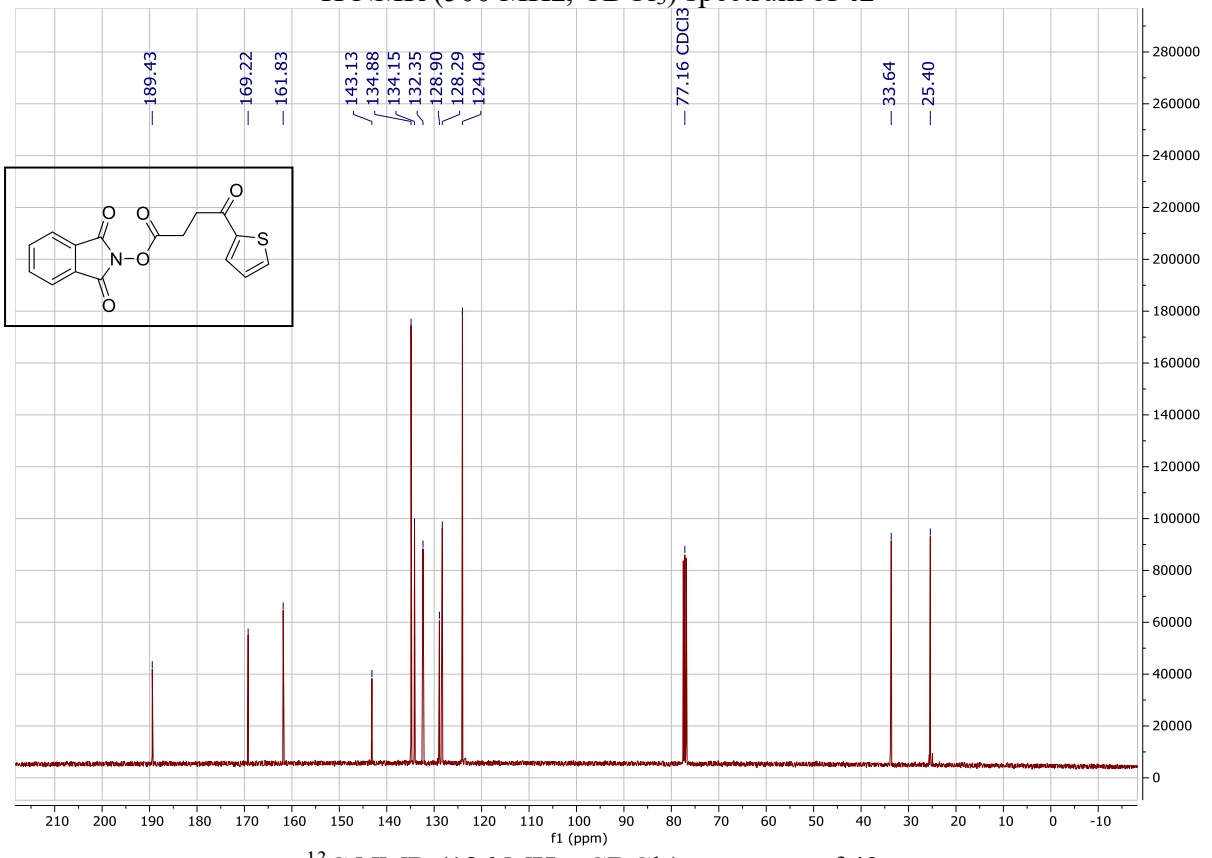

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **41a**



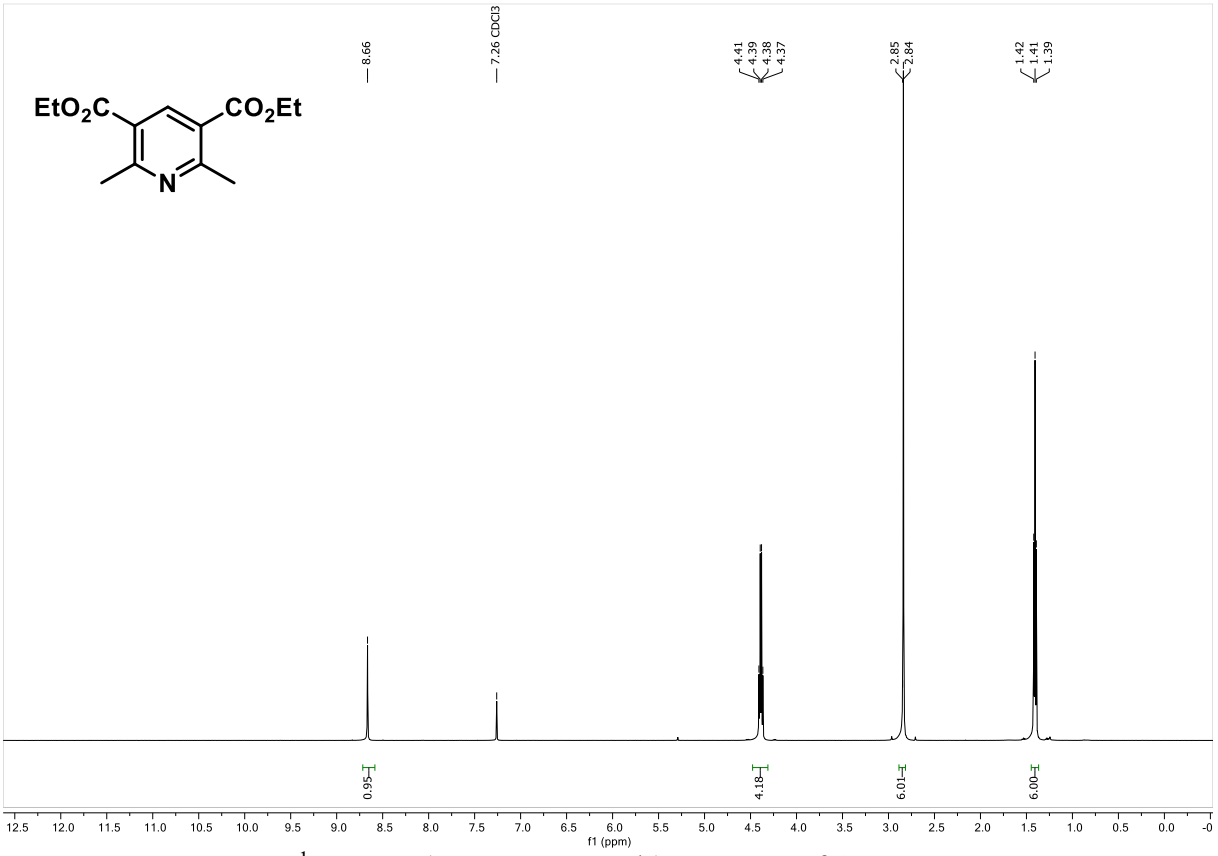

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **41a**



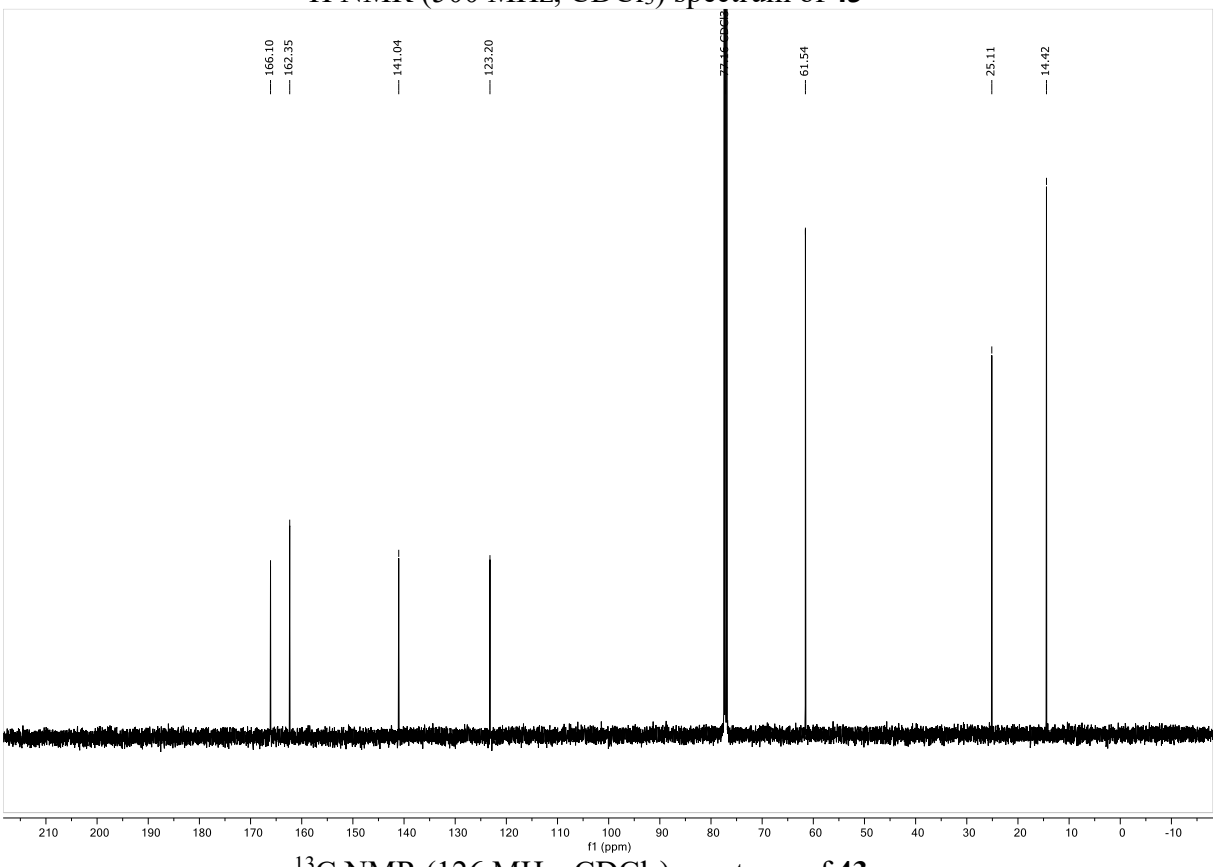

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **42**



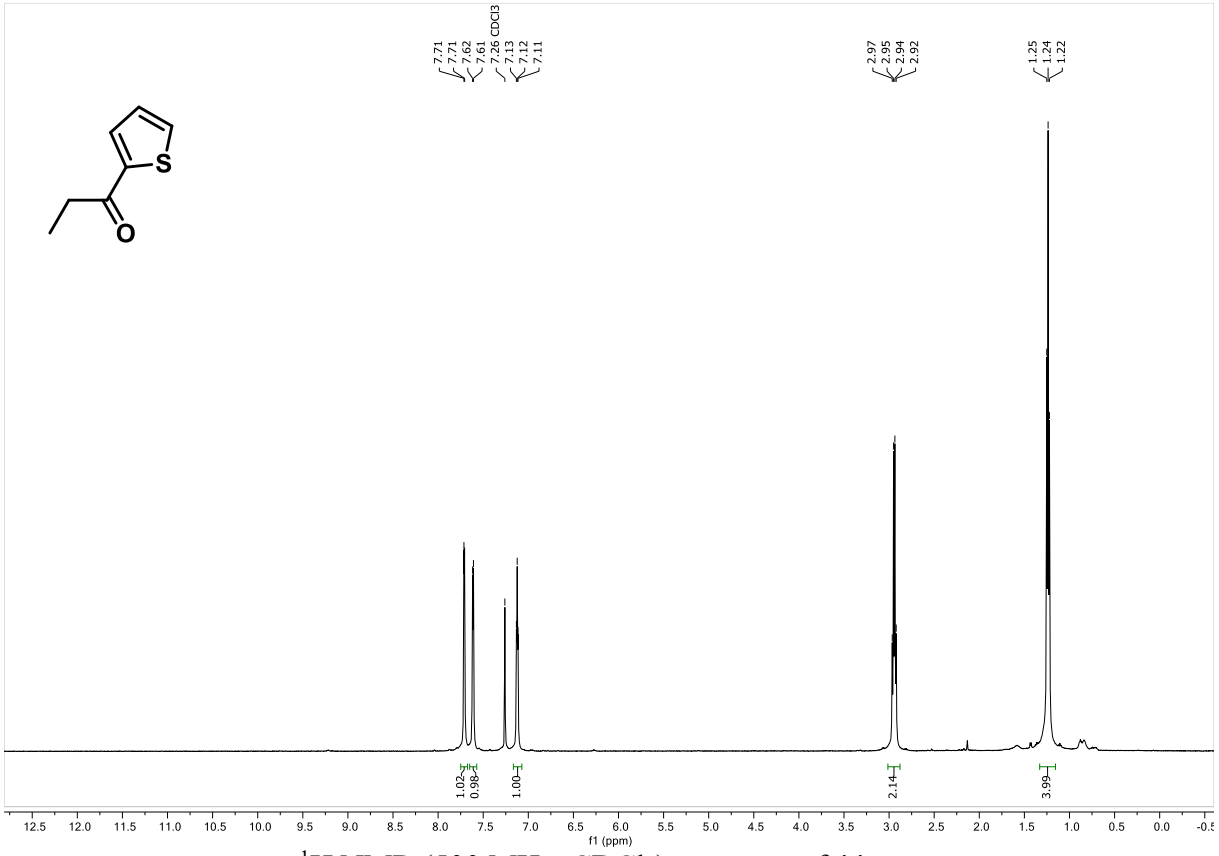

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **42**



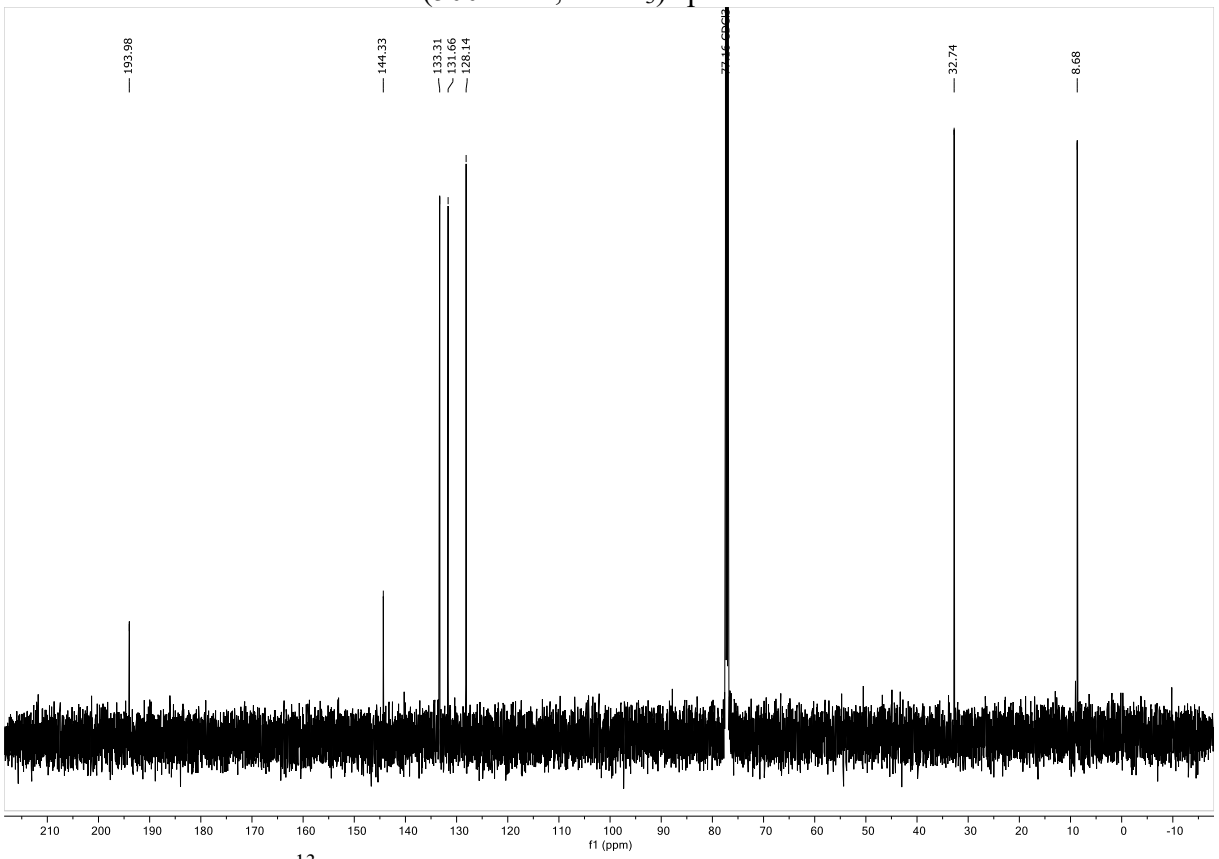

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **43**



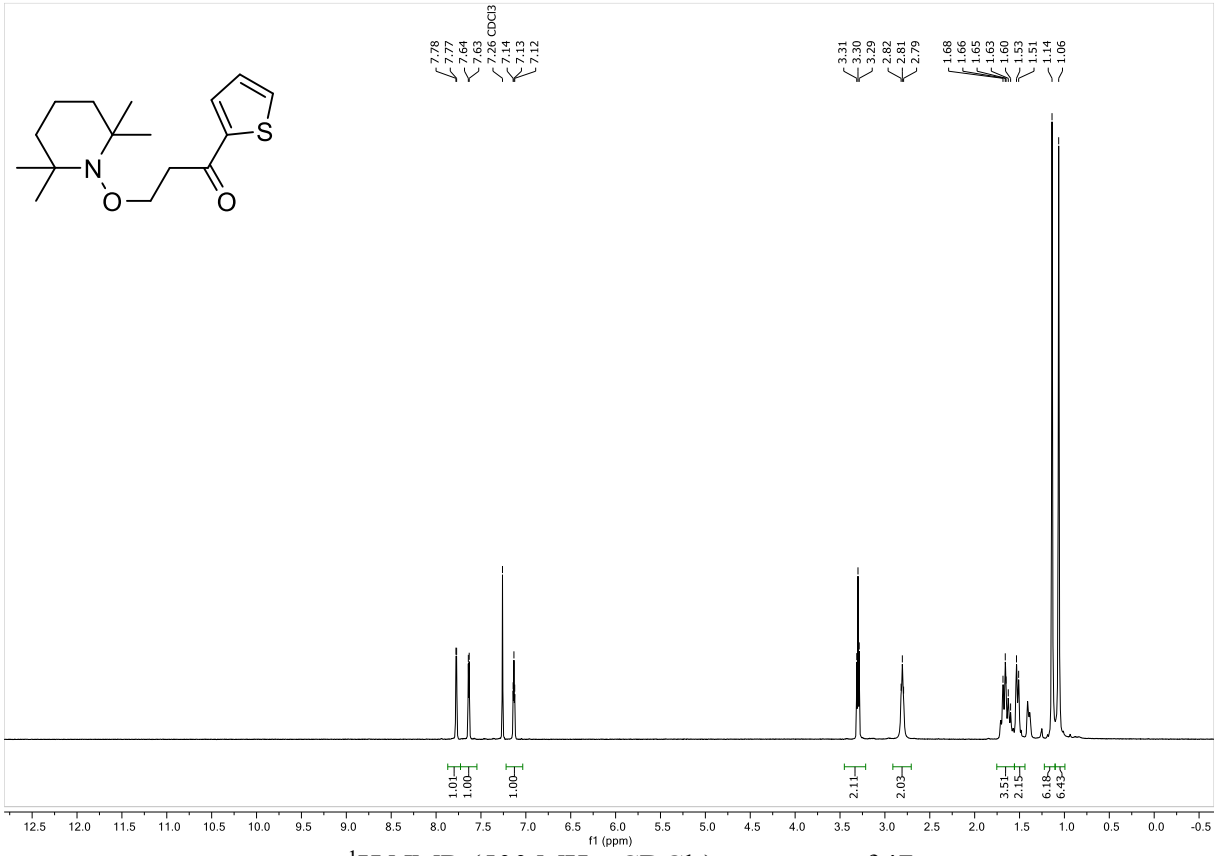

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **43**



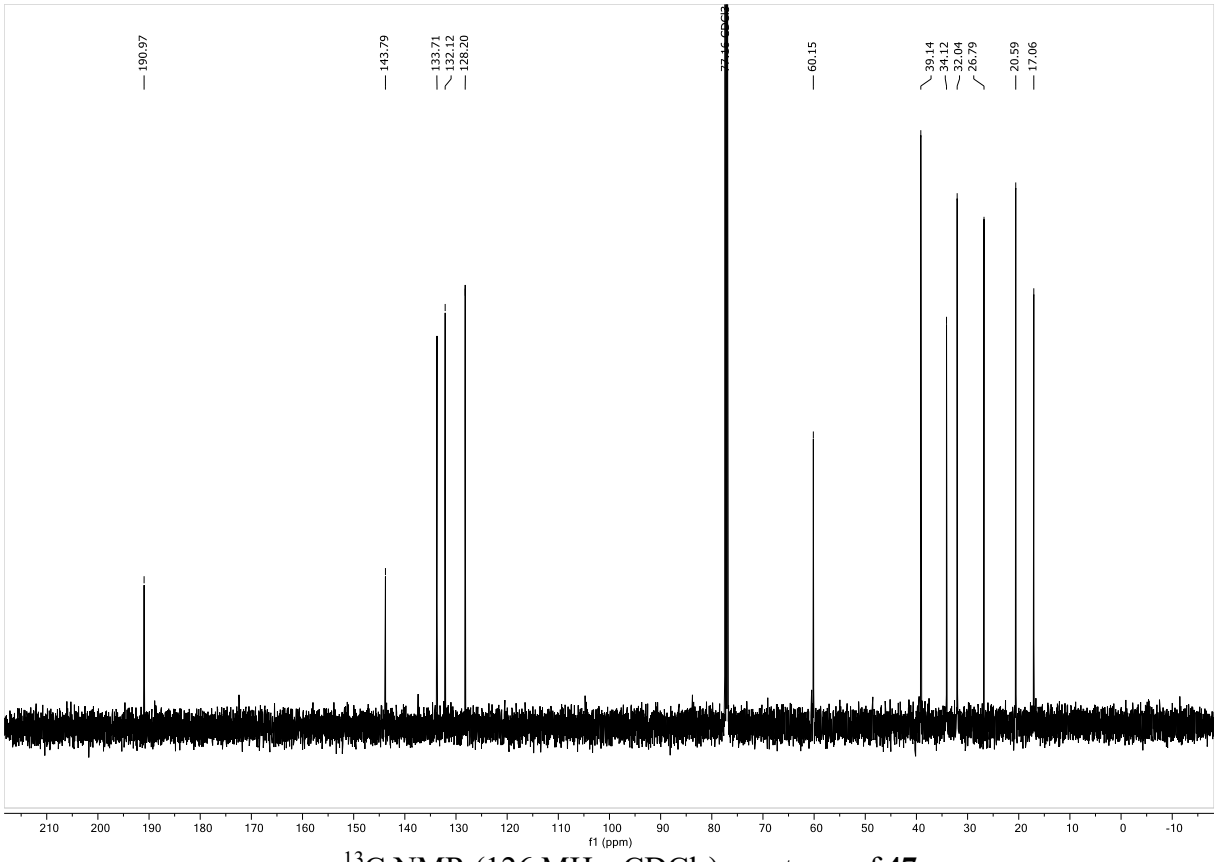

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **44**



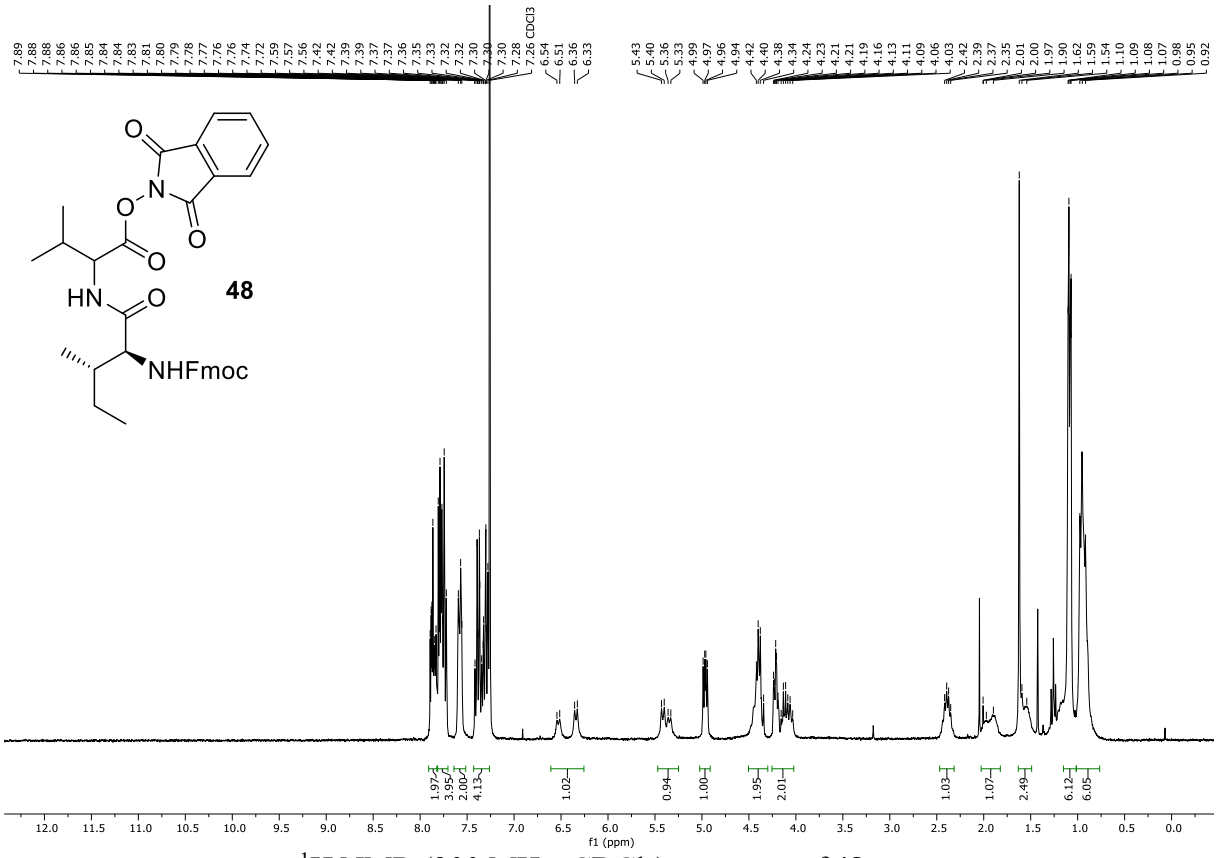

$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **44**



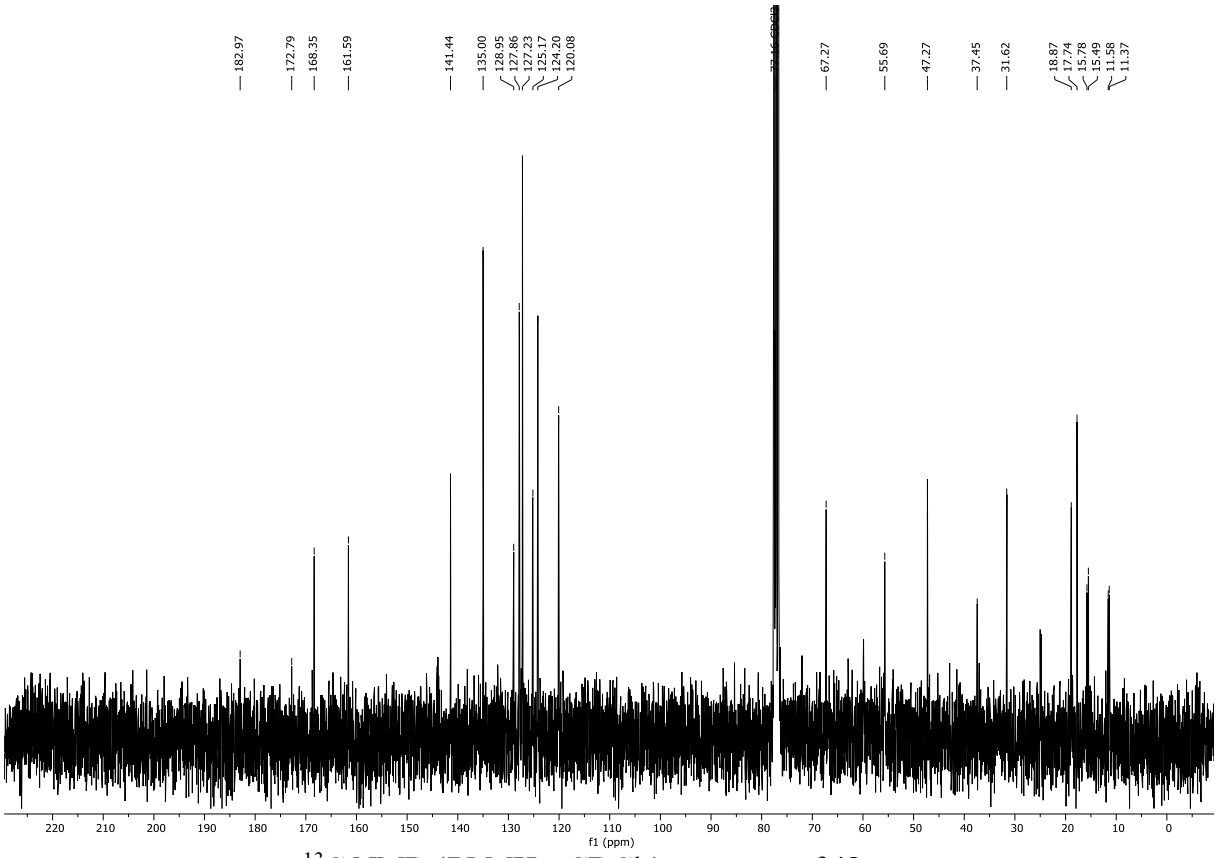

$^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of **47**




$^{13}$C NMR (126 MHz, $CDCl_3$) spectrum of **47**




$^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of **48**




$^{13}$C NMR (75 MHz, $CDCl_3$) spectrum of **48**