Supporting Information for:

Nickel-Catalyzed Decarbonylative Amination of Carboxylic Acid Esters

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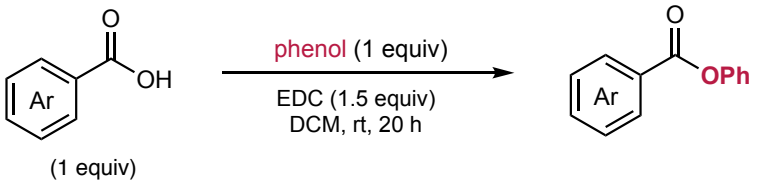
I. General information

All NMR experiments were recorded using Varian MR400 (400.52 MHz for ^{1}H, 100.71 MHz for ^{13}C, 376.87 MHz for ^{19}F), Varian vnmrs 500 (500.01 MHz for ^{1}H, 125.75 MHz for ^{13}C, 470.56 MHz for 19F), or Varian nmrs 700 (699.76 MHz for ^{1}H, 175.95 MHz for ^{13}C) spectrometers. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are reported in Hz. The 7.26 resonance of residual $CHCl_3$ for proton spectra and the 77.23 ppm resonance of $CDCl_3$ for carbon spectra were used as internal references. High-resolution mass spectrometry data (HRMS) were obtained on a Micromass AutoSpec Ultima Magnetic Sector instrument. GCMS analyses were performed on a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer. Melting points were determined with a Mel-Temp 3.0 (Laboratory Devices, Inc.) and are uncorrected. Chromatographic purifications were performed using 40-63 micron flash silica gel or a CombiFlash Torrent® system using RediSep® Rf columns packed with silica gel. X-ray crystallographic data were obtained on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer.

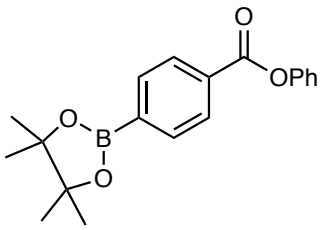
II. Materials and methods

All commercially available reagents were used as received unless otherwise stated. $Ni(cod)_2$ and dcype were purchased from Sigma Aldrich and stored in a glovebox. Carboxylic acids were purchased from commercial sources (Sigma, Alfa Aesar, Matrix Scientific, Frontier Scientific, Synquest) and used as received. Silyl amines (TMS-morpholine, TMS-indole, TMS-aniline) were purchased from commercial sources (Sigma, Alfa Aesar) and used as received. TMS-transfer reagents (MSTFA, BSA, TMS-phenol, TMSCl, TMSOTf) were purchased from commercial sources and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc.

III. Synthesis of carboxylic acid phenyl esters

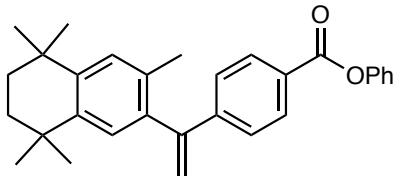


General procedure for the synthesis of phenyl esters from commercial carboxylic acids: A 20 mL vial equipped with a magnetic stir bar was charged with the corresponding carboxylic acid (2.0 mmol, 1.0 equiv), phenol (2.0 mmol, 1.0 equiv), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (3.0 mmol, 1.5 equiv) in DCM (8 mL). The reaction mixture was stirred at rt for 20 h. The reaction mixture was then diluted with dichloromethane (10 mL) and washed with ice-cold water (10 mL x 2). The organic extracts were collected, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes.



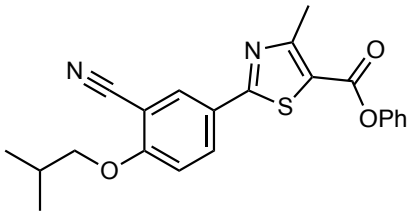
10-OPh

Phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (10-OPh). The general procedure was followed using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (0.81 mmol, 200 mg). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **10-OPh** as a white solid (141 mg, 79% yield): **mp** 53–55 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.28 (m, 1H), 7.23 (dd, *J* = 8.6, 1.2 Hz, 2H), 1.38 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.44, 151.17, 135.04, 131.94, 129.70, 129.36, 126.11, 121.92, 84.50, 25.12; **HRMS** (ESI) calcd. For $C_{19}H_{22}BO_4$ $[M+H]^+$ *m/z* 325.1611, found 325.1618.



19-OPh

Phenyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (19-OPh). The general procedure was followed using bexarotene (0.57 mmol, 200 mg). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **19-OPh** as a white solid (151 mg, 82% yield): **mp** 103–105 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.9 Hz, 2H), 7.43–7.41 (multiple peaks, 4H), 7.28 (m, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.14 (s, 1H), 7.09 (s, 1H), 5.85 (s, 1H), 5.36 (s, 1H), 1.97 (s, 3H), 1.70 (s, 4H), 1.31 (s, 6H), 1.28 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.22, 151.21, 149.31, 146.48, 144.64, 142.58, 138.12, 132.91, 130.46, 129.66, 128.54, 128.28, 126.96, 126.03, 121.93, 117.36, 35.42, 35.41, 34.22, 34.12, 32.16, 32.11, 20.18; **HRMS** (ESI) calcd. for $C_{30}H_{33}O_2$ $[M+H]^+$ *m/z* 425.2481, found 425.2479.



20-OPh

Phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (20-OPh). The general procedure was followed using febuxostat (0.32 mmol, 100 mg). Purification by flash chromatography on silica gel (hexanes/EtOAc, 30:70) afforded **20-OPh** as a white solid (57 mg, 63% yield): **mp:** 95–97 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 1H), 3.44 (d, *J* = 6.5 Hz, 2H), 2.35 (s, 3H), 1.74 (dt, *J* = 13.4, 6.7 Hz, 1H), 0.62 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.11, 162.99, 162.65, 160.43, 150.22, 132.64, 132.22, 129.53, 126.21, 125.86, 121.59, 120.64, 115.32, 112.66, 103.09, 75.73, 28.15, 19.04, 17.68; **HRMS** (ESI) calcd. for $C_{22}H_{21}N_2O_3S$ $[M+H]^+$ *m/z* 393.1273, found 393.1276.

Preparation of known phenyl esters based on literature procedures. The following phenyl esters were prepared based on literature procedures. Spectral data matched those in the literature: phenyl 4-(trifluoromethyl)benzoate (**1-OPh**)[1], methyl phenyl terephthalate (**5-OPh**)[2], phenyl 4-benzoylbenzoate (**6-OPh**)[3], phenyl 4-cyanobenzoate (**7-OPh**)[1], phenyl benzoate (**8-OPh**)[1], phenyl 4-phenoxybenzoate (**9-OPh**)[3], phenyl 1-naphthoate (**11-OPh**)[1], phenyl nicotinate (**12-OPh**)[4], phenyl quinoline-3-carboxylate (**13-OPh**)[1], phenyl quinoxaline-2-carboxylate (**14-OPh**)[5], phenyl benzo[b]thiophene-2-carboxylate (**15-OPh**)[2], phenyl benzo[b]furan-2-carboxylate (**16-OPh**)[6], phenyl 4-oxo-4H-chromene-2-carboxylate (**17-OPh**)[2], phenyl 4-(*N*,*N*-dipropylsulfamoyl)-benzoate (**18-OPh**)[3].

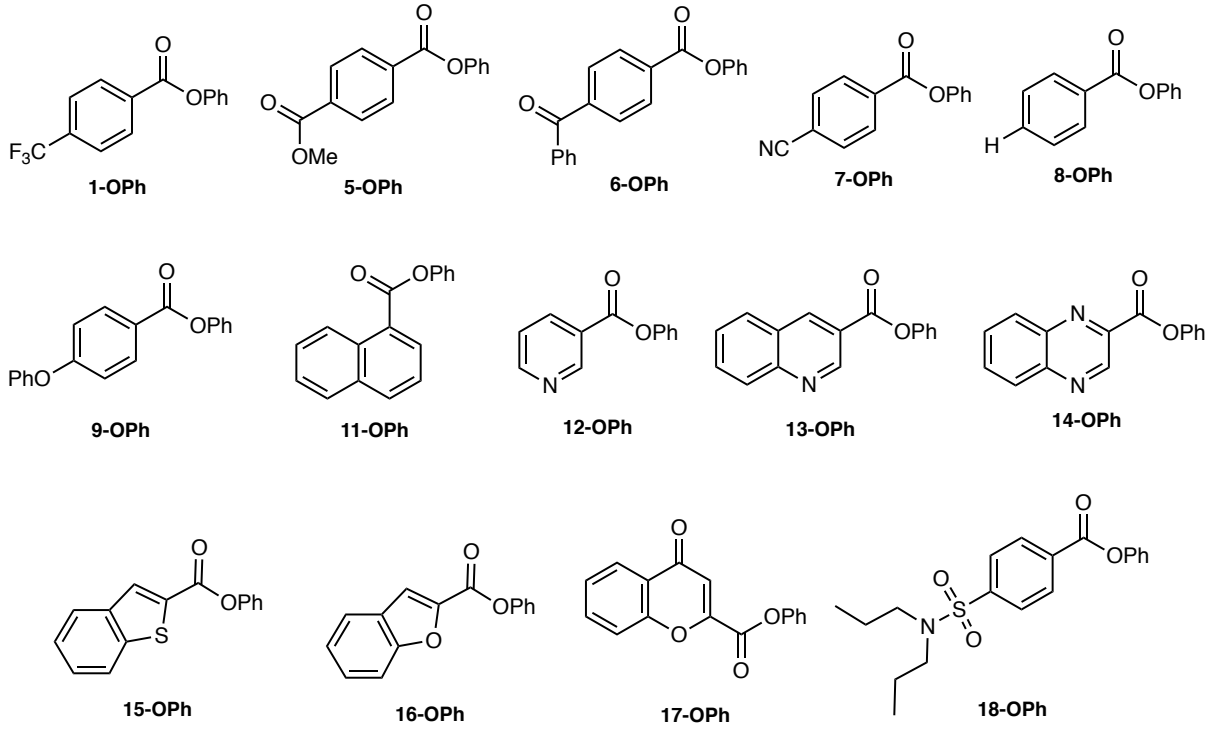


Fig. S1. List of known carboxylic acid phenyl esters synthesized and used in this study.

IV. Development of catalytic decarbonylative amination

IV-A. Uncatalyzed reactions of carboxylic acid derivatives with amines

General procedure for uncatalyzed reactions: In a nitrogen-filled glovebox, the corresponding carboxylic acid derivative (0.1 mmol, 1.0 equiv) and amine or TMS-amine (0.1 mmol, 1.0 equiv) were weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. 4-Fluorotoluene (0.1 mmol, 1.0 equiv) in a toluene stock solution (0.5 mL) was added as the ^{19}F NMR standard, and the reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 100 ºC for 1 h and then analyzed by ^{19}F NMR spectroscopy.

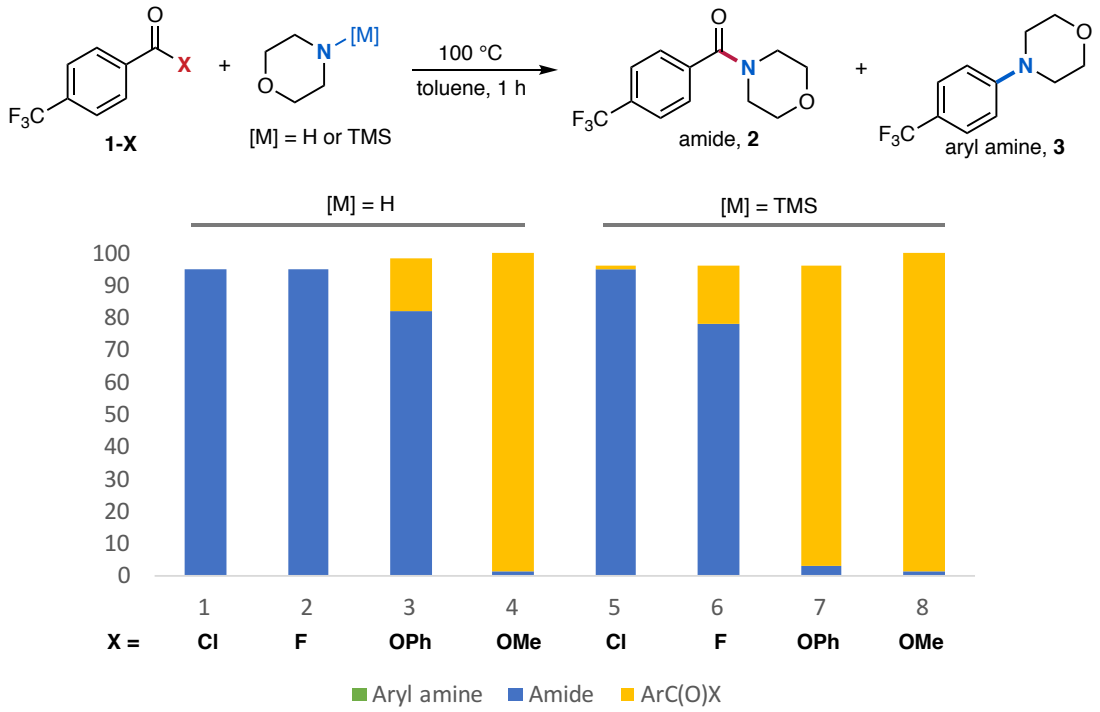
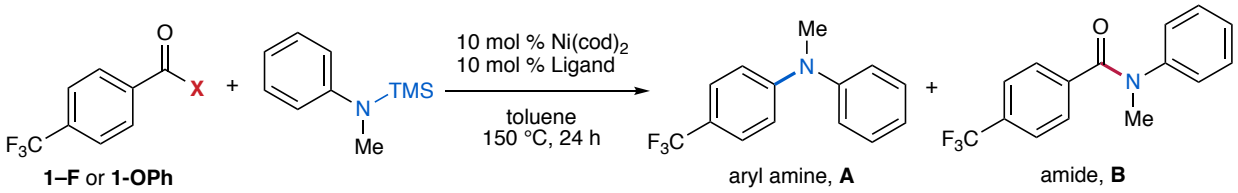


Fig. S2. Reaction of morpholine and TMS-morpholine with carboxylic acid derivatives.

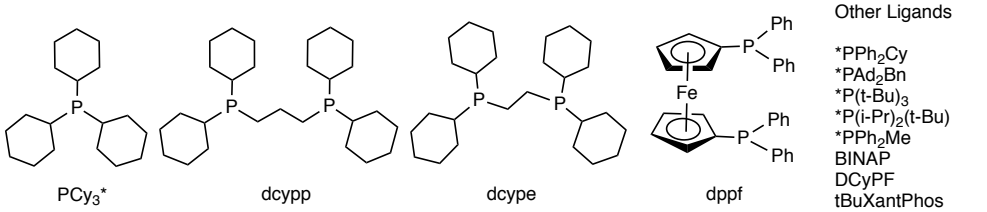
IV-B. Ni-catalyzed decarbonylative amination: Ligand screen

General procedure for decarbonylative amination: In a nitrogen-filled glovebox, carboxylic acid derivative **1-F** or **1-OPh** (0.1 mmol, 1.0 equiv) and TMS-amine (0.1 mmol, 1.0 equiv) were weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Ni(cod)_2$ (0.01 mmol, 0.1 equiv) and ligand (0.01 mmol, 0.1 equiv) in toluene (0.3 mL) was added. 4-Fluorotoluene (0.1 mmol, 1 equiv) in a toluene stock solution (0.2 mL) was added as the ^{19}F NMR standard, and the reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h and then analyzed by ^{19}F NMR spectroscopy.

Various ligands were investigated for this reaction, and the results are summarized in Fig. S3. Of all the ligands screened, 1,2-bis(dicyclohexylphosphino)ethane (dcype) was found to be the most effective. 1,3-Bis(dicyclohexylphosphino)propane (dcypp) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) were also found to yield products but with low yields and poor selectivites. Other ligands investigated for this transformation gave product in <5% yield; in these cases, the mass balance was either starting material or amide.



1–X	Ligand	PCy_3	dcypp	dcype	dppf	other ligands
1-F	**A**, % yield	<5%	12%	42%	8%	0 to <5%
	selectivity (**A**:**B**)	---	1:5	25:1	1:4	---
1-OPh	**A**, % yield	<2%	50%	89%	35%	0 to <5%
	selectivity (A:**B**)	---	1:1	25:1	1:1.3	---



*20 mol % ligand was used

Fig. S3. Investigation of various ligands.

IV-C. Ni-catalyzed decarbonylative amination of carboxylic acid derivatives

General procedure for decarbonylative amination: In a nitrogen-filled glovebox, the corresponding carboxylic acid derivative **1-X** (0.1 mmol, 1.0 equiv) and TMS-amine (0.1 mmol, 1.0 equiv) were weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Ni(cod)_2$ (0.01 mmol, 0.1 equiv) and ligand (0.01 mmol, 0.1 equiv) in toluene (0.3 mL) was added. 4-Fluorotoluene (0.1 mmol, 1 equiv) in a toluene stock solution (0.2 mL) was added as the ^{19}F NMR standard, and the reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h and then analyzed by ^{19}F NMR spectroscopy.

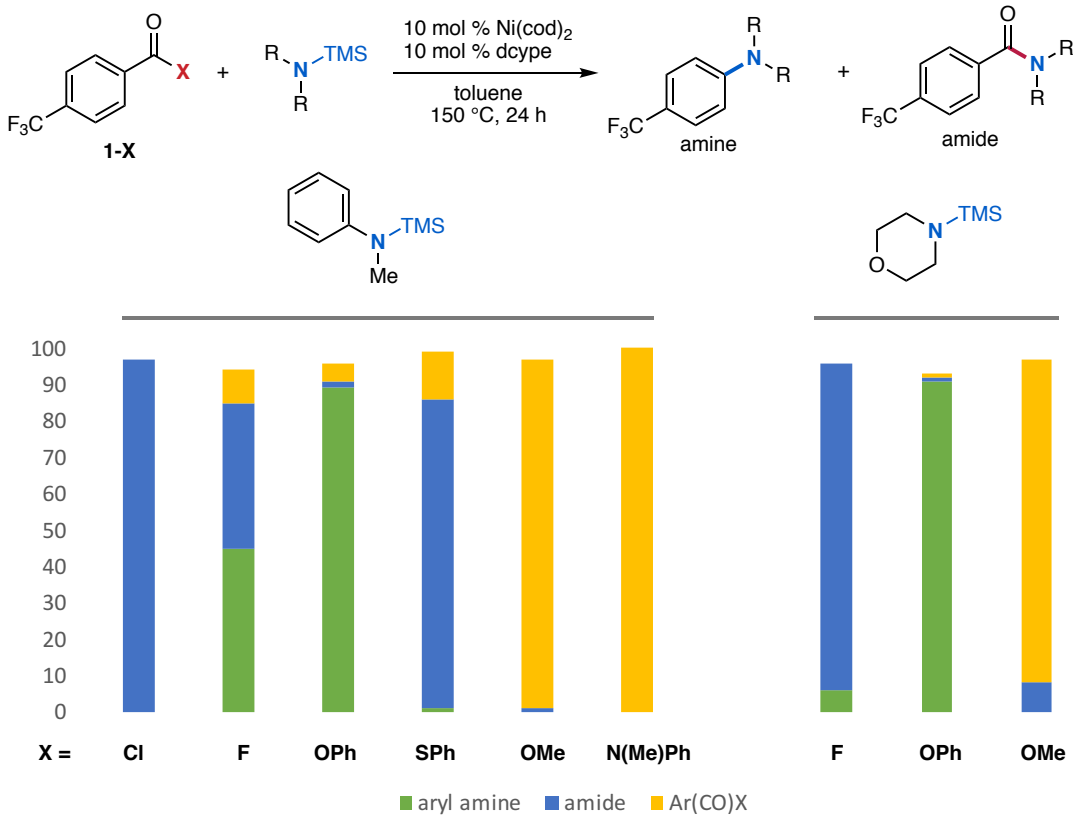
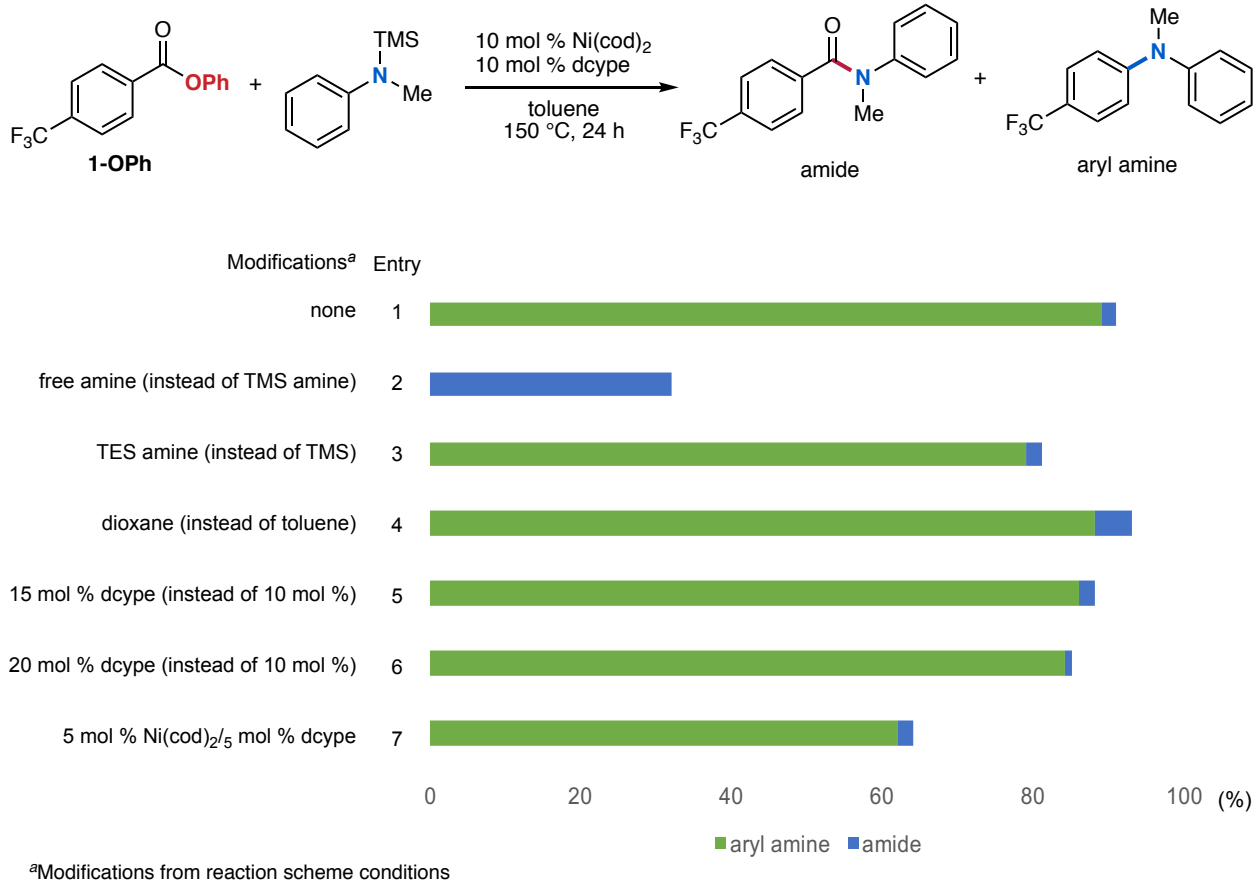


Fig. S4. Ni-catalyzed amination of various carboxylic acid derivatives.

IV-D. Investigation of other conditions

General procedure for decarbonylative amination: In a nitrogen-filled glovebox, the phenyl ester **1-OPh** (0.1 mmol, 1.0 equiv) and TMS-amine (0.1 mmol, 1.0 equiv) were weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Ni(cod)_2$ (0.01 mmol, 0.1 equiv) and ligand (0.01 mmol, 0.1 equiv) in toluene (0.3 mL) was added. 4-Fluorotoluene (0.1 mmol, 1 equiv) in a toluene stock solution (0.2 mL) was added as the ^{19}F NMR standard, and the reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h and then analyzed by ^{19}F NMR spectroscopy. Modifications from this general procedure were performed and results are summarized in Fig. S5.



[a]Modifications from reaction scheme conditions

Fig. S5. Other conditions for Ni-catalyzed amination of phenyl esters.

V. Optimization of Ni-catalyzed decarbonylative amination using free amines

General procedure for decarbonylative amination: In a nitrogen-filled glovebox, carboxylic acid ester **1-OPh** (0.1 mmol, 1.0 equiv) and the corresponding free amine (0.1–0.2 mmol, 1.0–2.0 equiv) were weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. The corresponding TMS-reagent (0.1–0.2 mmol, 1.0–2.0 equiv) was added via a microsyringe. (*Note: the free amine and the TMS-reagent are always added in equimolar quantities*). A pre-mixed solution of $Ni(cod)_2$ (0.01 mmol, 0.1 equiv) and ligand (0.01 mmol, 0.1 equiv) in toluene (0.3 mL) was added. 4-Fluorotoluene (0.1 mmol, 1 equiv) in a toluene stock solution (0.2 mL) was added as the ^{19}F NMR standard, and the reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h and then analyzed by ^{19}F NMR spectroscopy. Different TMS-transfer reagents, different amines, and different equivalents were investigated. Results are summarized in Fig. S6. MSTFA was found to be the most effective; and in most cases, only 1 equiv of free amine and MSTFA were required.

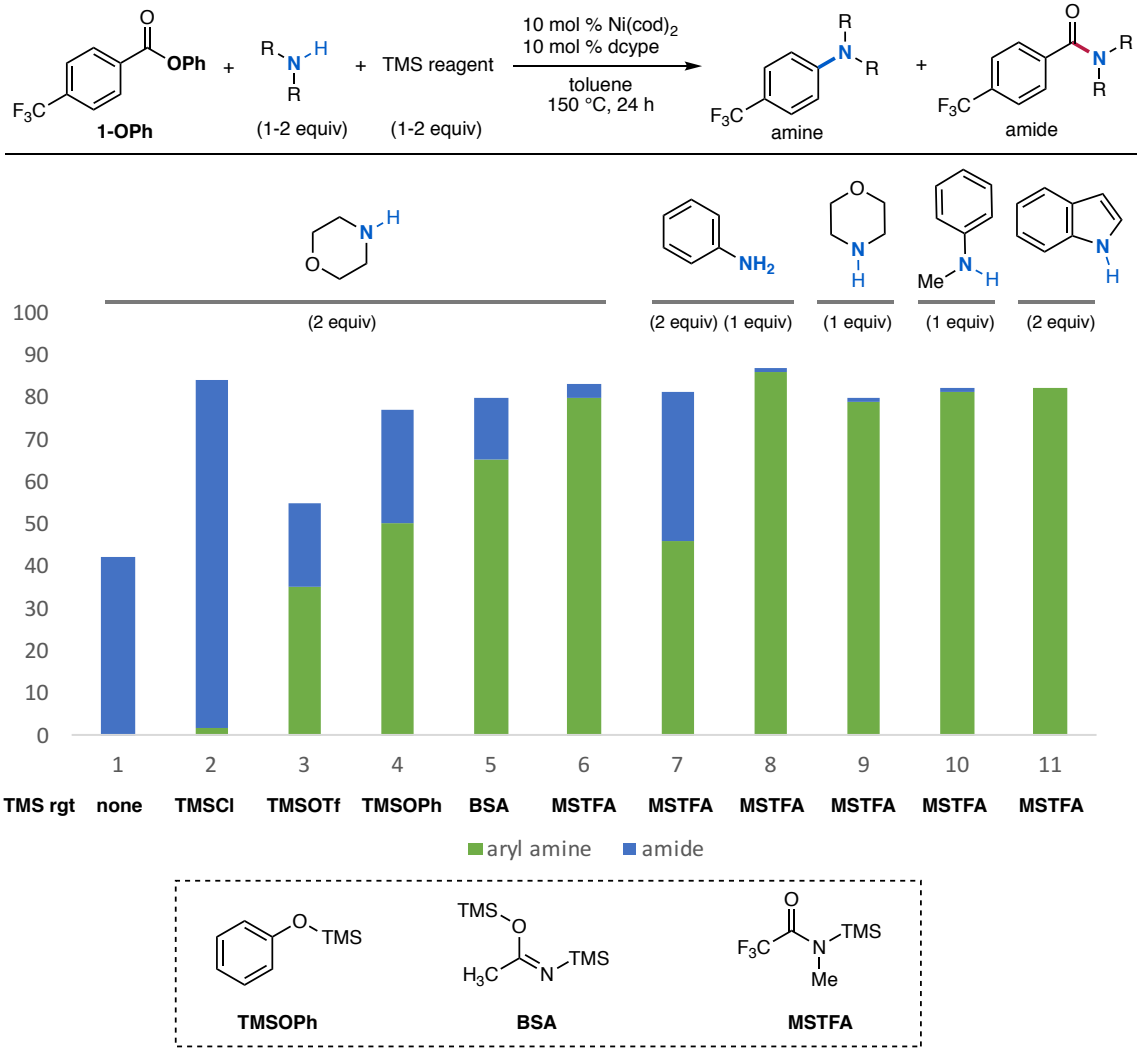
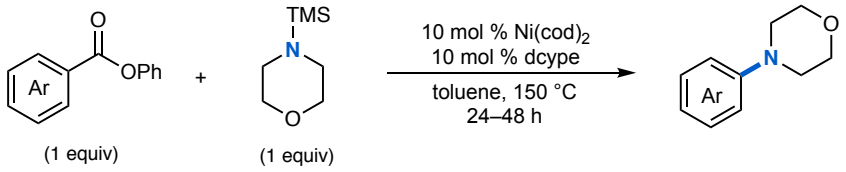
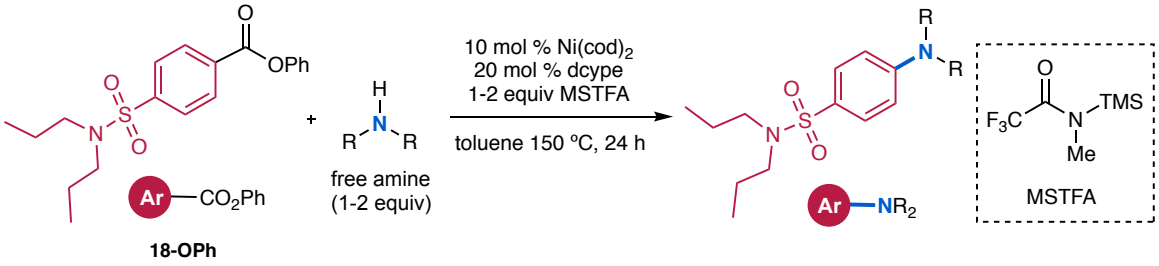


Fig. S6. Decarbonylative amination using free amines.

VI. Scope of Ni-catalyzed decarbonylative amination

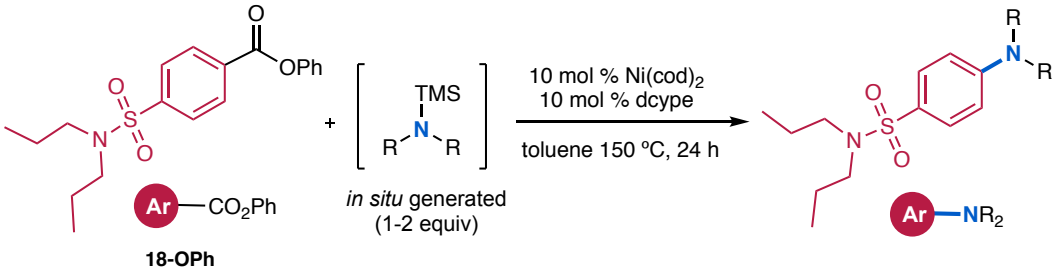


General procedure for decarbonylative amination of esters (Method A, using TMS-amine): In a nitrogen-filled glovebox, the corresponding carboxylic acid ester (0.2 mmol, 1.0 equiv) and TMS-morpholine (0.2 mmol, 1.0 equiv) were weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Ni(cod)_2$ (0.02 mmol, 0.1 equiv) and dcype (0.02 mmol, 0.1 equiv) in toluene (0.3 mL) was added. The resulting solution was diluted further with toluene (0.7 mL). The reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h. The reaction was then cooled to rt, and Et_2O (10 mL) and saturated $NaHCO_3$ (10 mL) were added. The organic layer was collected, and the aqueous solution was further extracted with Et_2O (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes.

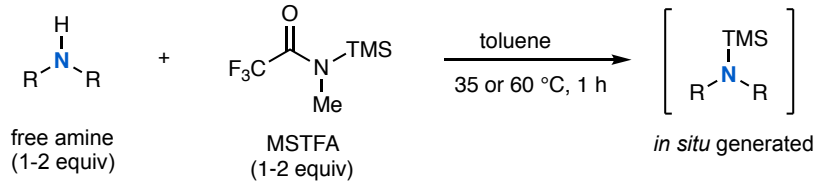


General procedure for decarbonylative amination of esters (Method B, using free amine): In a nitrogen-filled glovebox, phenyl ester **18-OPh** (0.2 mmol, 1.0 equiv) was weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. Pre-mixed solutions of $Ni(cod)_2$ (0.02 mmol, 0.1 equiv) and dcype (0.02 mmol, 0.1 equiv) in toluene (0.3 mL) and free amine (0.2–0.4 mmol, 1.0–2.0 equiv) in toluene (0.3 mL) were added. *N*-Methyl-*N*-(trimethylsilyl) trifluoroacetamide, MSTFA (0.2–0.4 mmol, 0.2–0.4 equiv) was added using a microsyringe, and the resulting solution was diluted with toluene (0.4 mL). The reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h. The reaction was then cooled to rt, and Et_2O (10 mL) and saturated $NaHCO_3$ (10 mL) were added. The organic layer was collected, and the

aqueous solution was further extracted with Et_2O (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes.



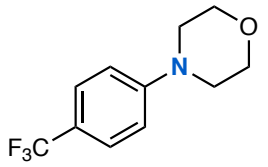
in situ generation of TMS-amine:



General procedure for decarbonylative amination of esters (Method C, via in situ formation of TMS-amine):

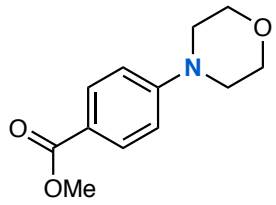
In situ formation of TMS-amine: In a nitrogen-filled glovebox, free amine (0.2–0.4 mmol, 0.2–0.4 equiv) was weighed into a 4 mL vial. MSTFA (0.2–0.4 mmol, 0.2–0.4 equiv) was added using a microsyringe and diluted with toluene (0.5 mL). The reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 35 or 60 ºC for 1 h and brought back into the glovebox.

Decarbonylative amination: In a nitrogen-filled glovebox, phenyl ester **18-OPh** (0.2 mmol, 1.0 equiv) was weighed into a 10 mL tall vial equipped with a 10 μm magnetic stir bar. Pre-mixed solutions of $Ni(cod)_2$ (0.02 mmol, 0.1 equiv) and dcype (0.02 mmol, 0.1 equiv) in toluene (0.3 mL) and the *in situ* generated TMS-amine (0.2–0.4 mmol, 1.0–2.0 equiv) in toluene (0.5 mL) were added. The resulting solution was then further diluted with toluene (0.2 mL). The reaction vial was capped and removed from the glovebox. The reaction mixture was stirred at 150 ºC for 24 h. The reaction was then cooled to rt, and Et_2O (10 mL) and saturated $NaHCO_3$ (10 mL) were added. The organic layer was collected, and the aqueous solution was further extracted with Et_2O (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel using EtOAc in hexanes.



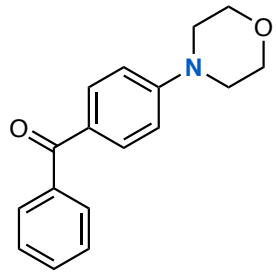
4

4-(4-(Trifluoromethyl)phenyl)morpholine (4) Method A was followed using phenyl ester **1-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **4** as a white solid (35 mg, 77% yield): **mp** 66–67 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.24 (t, *J* = 4.8 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.55, 126.64 (q, *J* = 7.3 Hz), 124.87 (q, *J* = 270.7 Hz), 121.22 (q, *J* = 32.7 Hz), 114.53, 66.86, 48.38; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –61.44; **HRMS** (ESI) calcd. for $C_{11}H_{13}F_3NO$ $[M+H]^+$ *m/z* 232.0949, found 232.0953.



5

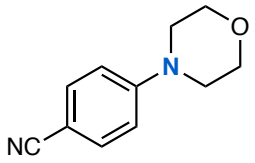
Methyl 4-morpholinobenzoate (5). Method A was followed using phenyl ester **5-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 70:30) afforded **5** as a colorless oil (28 mg, 64% yield): **mp** 153–155 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 3.86 (br s, 8H), 3.28 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.03, 154.18, 131.19, 120.29, 113.45, 66.59, 51.68, 47.70; **HRMS** (ESI) calcd. for $C_{12}H_{16}NO_3$ $[M+H]^+$ *m/z* 222.1130, found 222.1129.



6

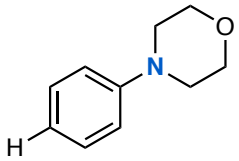
(4-Morpholinophenyl)(phenyl)methanone (6). Method A was followed using phenyl ester **6-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 70:30) afforded **6** as a white solid (36 mg, 68% yield): **mp** 137–139 °C; **^{1}H NMR** (500 MHz, $CDCl_3$)

δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 3.86 (t, *J* = 4.6 Hz, 4H), 3.32 (t, *J* = 4.6 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.25, 154.02, 138.68, 132.45, 131.54, 129.57, 128.10, 127.76, 113.17, 66.57, 47.55; **HRMS** (ESI) calcd. for $C_{17}H_{18}NO_2$ $[M+H]^+$ *m/z* 268.1338, found 268.1342.



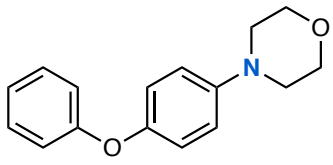
7

4-Morpholinobenzonitrile (7). Method A was followed using phenyl ester **7-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 80:20) afforded **7** as a white solid (29 mg, 78% yield): **mp** 82–83 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 3.85 (t, *J* = 4.8 Hz, 4H), 3.28 (t, *J* = 4.8 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.47, 133.50, 119.84, 114.05, 100.96, 66.44, 47.29; **HRMS** (ESI) calcd. for $C_{11}H_{13}N_2O$ $[M+H]^+$ *m/z* 189.1028, found 189.1033.



8

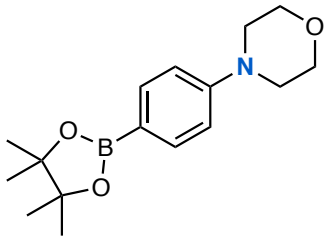
4-Phenylmorpholine (8). Method A was followed using phenyl ester **8-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **8** as a white solid (22 mg, 66% yield): **mp** 52–53 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.28 (multiple peaks, 2H), 6.94–6.92 (multiple peaks, 3H), 3.88 (t, *J* = 4.5 Hz, 4H), 3.17 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.25, 129.18, 120.10, 115.75, 66.94, 49.39; **HRMS** (ESI) calcd. for $C_{10}H_{14}NO$ $[M+H]^+$ *m/z* 164.1075, found 164.1080.



9

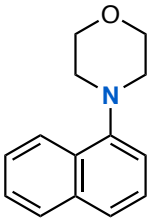
4-(4-Phenoxyphenyl)morpholine (9). Method A was followed using phenyl ester **9-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 80:20) afforded **9** as a white solid (36 mg, 71% yield): **mp** 50–52 °C; **^{1}H NMR** ($CDCl_3$, 700 MHz) δ 7.30

(t, *J* = 7.6 Hz, 2H), 7.04 (m, 1H), 6.97–6.98 (multiple peaks, 4H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.87 (t, *J* = 4.5 Hz, 4H), 3.12 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.39, 150.06, 147.76, 129.53, 122.44, 120.52, 117.67, 117.27, 66.96, 50.10; **HRMS** (ESI) calcd. for $C_{16}H_{18}NO_2$ $[M+H]^+$ *m/z* 256.1338, found 256.1341.



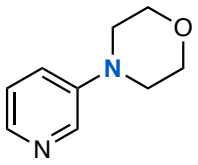
10

4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (10). Method A was followed using phenyl ester **10-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **10** as a white solid (43 mg, 74% yield): **mp** 90–92 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 3.85 (t, *J* = 4.5 Hz, 4H), 3.23 (t, *J* = 4.5 Hz, 4H), 1.33 (s, 12H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.34, 136.13, 114.07, 83.40, 66.77, 48.35, 24.83, *the carbon-bound boron was not observed due to quadrupolar coupling*; **HRMS** (ESI) calcd. for $C_{18}H_{25}BNO_3$ $[M+H]^+$ *m/z* 290.1927, found 290.1930.



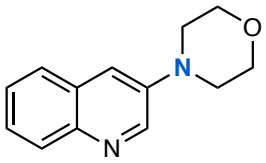
11

4-(Naphthalen-1-yl)morpholine (11). Method A was followed using phenyl ester **11-OPh** and TMS-morpholine. The reaction was allowed to stir for 48 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **11** as a white solid (27 mg, 63% yield): **mp** 81–83 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.52–7.49 (multiple peaks, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 3.99 (t, *J* = 4.5 Hz, 4H), 3.13 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.41, 134.77, 128.77, 128.45, 125.87, 125.83, 125.44, 123.78, 123.37, 114.66, 67.47, 53.49; **HRMS** (ESI) calcd. for $C_{14}H_{16}NO$ $[M+H]^+$ *m/z* 214.1232, found 214.1229.



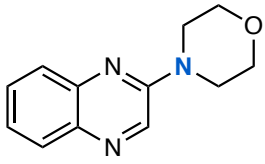
12

4-(Pyridin-3-yl)morpholine (12). Method A was followed using phenyl ester **12-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/MeOH, 95:5) afforded **12** as a yellow solid (26 mg, 77% yield): **mp** 37–38 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 8.13 (br s, 1H), 7.18–7.19 (multiple peaks, 2H), 3.85 (t, *J* = 4.5 Hz, 4H), 3.18 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.91, 141.02, 138.23, 123.50, 122.09, 66.66, 48.59; **HRMS** (ESI) calcd. for $C_9H_{13}N_2O$ $[M+H]^+$ *m/z* 165.1028, found 165.1032.



13

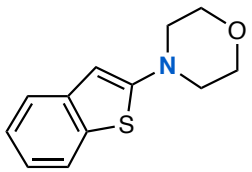
4-(Quinolin-3-yl)morpholine (13). Method A was followed using phenyl ester **13-OPh**, TMS-morpholine, and 20 mol % catalyst loading. Purification by flash chromatography on silica gel (hexanes/EtOAc, 35:65) afforded **13** as a white solid (28 mg, 66% yield): **mp** 84–86 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.9 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.52 (m, 1H), 7.47 (m, 1H), 7.34 (d, *J* = 2.9 Hz, 1H), 3.93 (t, *J* = 4.5 Hz, 4H), 3.28 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.71, 144.50, 143.12, 128.93, 128.71, 127.00, 126.59, 126.58, 116.69, 66.70, 49.38; **HRMS** (ESI) calcd. for $C_{13}H_{15}N_2O$ $[M+H]^+$ *m/z* 215.1184, found 215.1189.



14

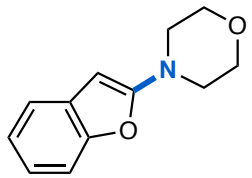
4-(Quinoxalin-2-yl)morpholine (14). Method A was followed using phenyl ester **14-OPh**, TMS-morpholine, and 20 mol % catalyst loading. Purification by flash chromatography on silica gel (hexanes/EtOAc, 65:35) afforded **14** as a white solid (36 mg, 84% yield): **mp** 88–90 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 3.87 (t, *J* = 4.6 Hz, 4H), 3.76 (t, *J* = 4.6 Hz, 4H); **^{13}C NMR** (126

MHz, $CDCl_3$) δ 152.30, 141.49, 137.10, 135.42, 130.17, 128.71, 126.58, 125.06, 66.63, 45.03; **HRMS** (ESI) calcd. for $C_{12}H_{14}N_3O$ $[M+H]^+$ *m/z* 216.1137, found 216.1141.



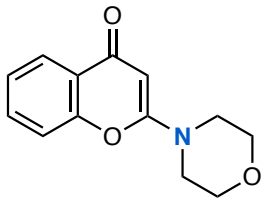
15

4-(Benzo[b]thiophen-2-yl)morpholine (15). Method A was followed using phenyl ester **15-OPh** and TMS-morpholine. The reaction was allowed to stir for 48 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **15** as a white solid (33 mg, 75% yield): **mp** 63–64 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.9 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.68 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 3.93 (t, *J* = 4.5 Hz, 4H), 3.28 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.71, 144.50, 143.12, 128.93, 128.71, 127.00, 126.58, 116.69, 66.70, 49.38; **HRMS** (ESI) calcd. for $C_{12}H_{14}NOS$ $[M+H]^+$ *m/z* 220.0796, found 220.0801.



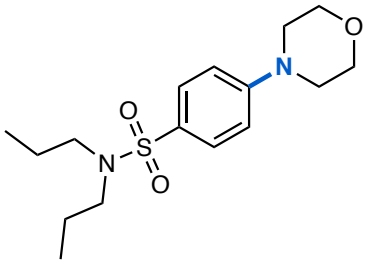
16

4-(Benzo[b]furan-2-yl)morpholine (16). Method A was followed using phenyl ester **16-OPh** and TMS-morpholine. The reaction was allowed to stir for 48 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **16** as a white solid (21 mg, 52% yield): **mp** 63–64 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36–7.28 (multiple peaks, 2H), 7.14 (m, 1H), 7.00 (m, 1H), 5.19 (d, *J* = 1.0 Hz, 1H), 3.39 (t, *J* = 4.6 Hz, 4H), 3.82 (t, *J* = 4.6 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.01, 150.82, 130.40, 122.83, 120.62, 118.29, 109.71, 79.80, 66.13, 47.50; **HRMS** (ESI) calcd. for $C_{12}H_{14}NO_2$ $[M+H]^+$ *m/z* 204.1025, found 204.1031.



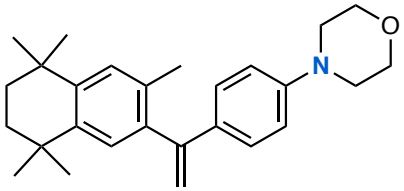
17

2-Morpholino-4H-chromen-4-one (17). Method A was followed using phenyl ester **17-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (EtOAc/MeOH, 95:5) afforded **17** as a white solid (37 mg, 80% yield): **mp** 145–147 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.53 (s, 1H), 3.83 (t, *J* = 4.5 Hz, 4H), 3.52 (t, *J* = 4.5 Hz, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) 177.32, 162.69, 153.68, 132.52, 125.61, 125.03, 122.85, 116.46, 87.34, 65.98, 44.67; **HRMS** (EI) calcd. for $C_{13}H_{13}NO_3$ $[M]^+$ *m/z* 231.0895, found 231.0898.



18

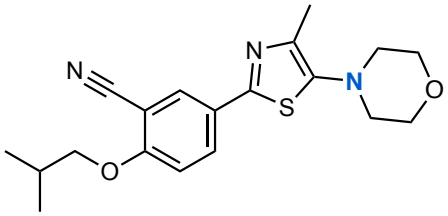
4-Morpholino-N,N-dipropylbenzenesulfonamide (18). Method A was followed using phenyl ester **18-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **18** as a white solid (76 mg, 77% yield). Compound **18** was also obtained using Method B (70 mg, 72% yield): **mp** 78–79 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.87 (t, *J* = 4.9 Hz, 4H), 3.28 (t, *J* = 4.9 Hz, 4H), 3.04 (t, *J* = 7.7 Hz, 4H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.47, 129.35, 128.76, 113.80, 66.64, 50.05, 47.70, 22.07, 11.23; **HRMS** (ESI) calcd. for $C_{16}H_{27}N_2O_3S$ $[M+H]^+$ *m/z* 327.1742, found 327.1744.



19

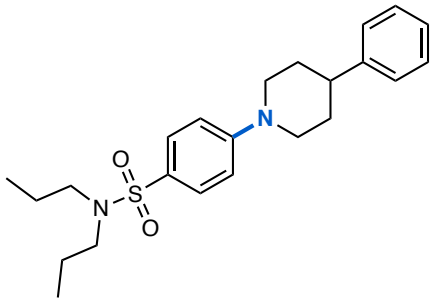
4-(4-(1-(3,5,5,8,8-Pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)phenyl)morpholine (19). Method A was followed using phenyl ester **19-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **19** as a colorless thick oil (49 mg, 63% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.06 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 5.07 (s, 1H), 3.86 (t, *J* = 4.4 Hz, 4H), 3.16 (t, *J* = 4.4 Hz, 4H), 1.99 (s, 3H), 1.70.–1.69 (multiple peaks, 4H), 1.30 (s, 6H), 1.27 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.46, 149.08, 143.70, 141.96, 138.96, 132.82, 132.53, 127.95, 127.71, 127.42,

115.02, 112.20, 66.87, 49.05, 49.04, 35.26, 33.94, 33.85, 31.91, 31.90, 20.18; **HRMS** (ESI) calcd. for $C_{27}H_{36}NO$ $[M+H]^+$ *m/z* 390.2797, found 390.2799.



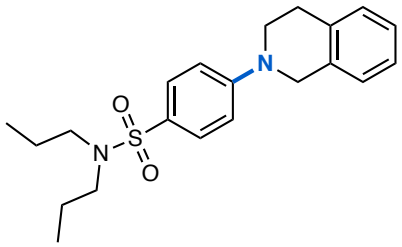
20

2-Isobutoxy-5-(4-methyl-5-morpholinothiazol-2-yl)benzonitrile (20). Method A was followed using phenyl ester **20-OPh** and TMS-morpholine. Purification by flash chromatography on silica gel (EtOAc) afforded **20** as a white solid (30 mg, 41% yield): **mp** 74–76 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.87–3.84 (multiple peaks, 6H), 2.89 (t, *J* = 4.5 Hz, 4H), 2.36 (s, 3H), 2.19 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.63, 158.00, 147.56, 144.10, 131.75, 131.29, 127.80, 115.98, 112.66, 102.82, 75.75, 67.17, 55.29, 28.40, 19.29, 14.83; **HRMS** (ESI) calc for $C_{19}H_{24}N_3O_2S$ $[M+H]^+$ *m/z* 358.1589, found 358.1592.



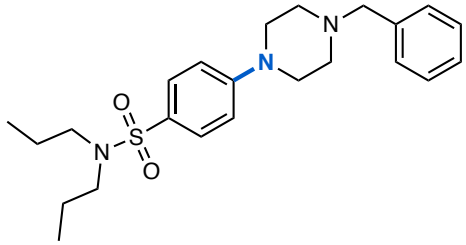
21

4-(4-Phenylpiperidin-1-yl)-*N*,*N*-dipropylbenzenesulfonamide (21). Method B was followed using phenyl ester **18-OPh**, 4-phenylpiperidine (1.0 equiv), and MSTFA (1.0 equiv). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **21** as a light brown solid (70 mg, 88% yield): **mp** 126–128 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.32 (m, 2H), 7.25–7.23 (multiple peaks, 3H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.98 (multiple peaks, 2H), 3.05 (t, *J* = 7.7 Hz, 4H), 2.97 (multiple peaks, 2H), 2.74 (m, 1H), 1.98 (multiple peaks, 2H), 1.83 (multiple peaks, 2H), 1.57 (m, 4H), 0.88 (t, *J* = 6.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.72, 145.65, 129.02, 128.74, 128.20, 126.93, 126.64, 114.36, 50.28, 48.89, 42.57, 32.96, 22.29, 11.45; **HRMS** (ESI) calcd. for $C_{23}H_{33}N_2O_2S$ $[M+H]^+$ *m/z* 401.2263, found 401.2268.



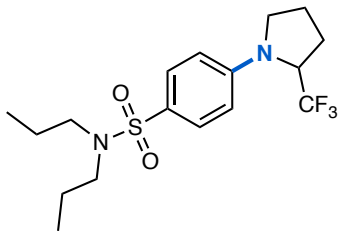
22

4-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-*N*,*N*-dipropylbenzenesulfonamide (22). Method B was followed using phenyl ester **18-OPh**, 1,2,3,4-tetrahydroisoquinoline (1.0 equiv), and MSTFA (1.0 equiv). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **22** as a colorless thick oil (63 mg, 85% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.22–7.19 (multiple peaks, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 2H), 3.64 (t, *J* = 5.9 Hz, 2H), 3.04 (t, *J* = 7.9 Hz, 4H), 2.99 (t, *J* = 5.9 Hz, 2H), 1.56 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.44, 135.13, 133.80, 129.09, 128.38, 127.14, 126.98, 126.65, 126.60, 112.46, 50.29, 49.21, 45.01, 29.17, 22.29, 11.46; **HRMS** (ESI) calcd. for $C_{21}H_{29}N_2O_2S$ $[M+H]^+$ *m/z* 373.1950, found 373.1954.



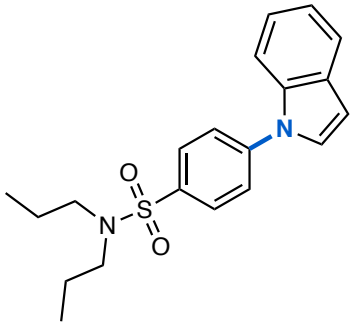
23

4-(4-Benzylpiperazin-1-yl)-*N*,*N*-dipropylbenzenesulfonamide (23). Method B was followed using phenyl ester **18-OPh**, 1-benzylpiperazine (1.0 equiv), and MSTFA (1.0 equiv). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **23** as a light brown thick oil (60 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.43–7.32 (multiple peaks, 4H), 7.27 (m, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.57 (s, 2H), 3.32 (t, *J* = 4.8 Hz, 4H), 3.02 (t, *J* = 7.9 Hz, 4H), 2.60 (t, *J* = 4.8 Hz, 4H), 1.54 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.64, 137.76, 129.36, 128.92, 128.70, 128.52, 127.48, 114.08, 63.11, 52.85, 50.27, 47.66, 22.28, 11.44; **HRMS** (ESI) calcd. for $C_{23}H_{34}N_3O_2S$ $[M+H]^+$ *m/z* 416.2372, found 416.2375.



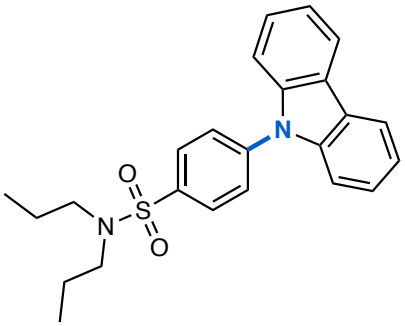
24

***N,N*-Dipropyl-4-(2-(trifluoromethyl)pyrrolidin-1-yl)benzenesulfonamide (24).** Method C was followed using phenyl ester **18-OPh**, 2-(trifluoromethyl)pyrrolidine (1.5 equiv), and MSTFA (1.5 equiv). TMS-amine was generated *in situ* at 60 °C for 1 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **24** as a colorless oil (58 mg, 77% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.30 (m, 1H), 3.66 (m, 1H), 3.30 (m, 1H), 3.03 (t, *J* = 8.9 Hz, 4H), 2.26–2.65 (multiple peaks, 2H), 2.10–2.09 (multiple peaks, 2H), 1.54 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 150.15, 128.93, 128.33, 126.61 (q, *J* = 284.8 Hz), 112.72, 59.81 (q, *J* = 30.8 Hz), 50.35, 49.80, 26.98, 23.34, 22.35, 11.46; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –75.22 (d, *J* = 6.8 Hz); **HRMS** (ESI) calcd. for $C_{17}H_{26}F_3N_2O_2S$ $[M+H]^+$ *m/z* 379.1667, found 379.1670.



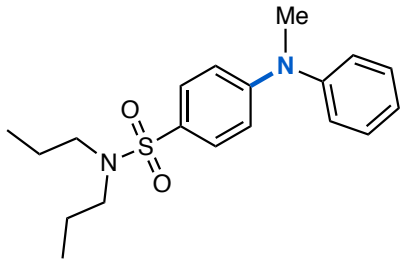
25

4-(1H-Indol-1-yl)-N,N-dipropylbenzenesulfonamide (25). Method A was followed using phenyl ester **18-OPh** and TMS-indole. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **25** as a white solid (51 mg, 70% yield). Compound **25** was also obtained using TES-indole and TIPPS-indole (63% and 41% yield, respectively): **mp** 124–126 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.34–7.32 (multiple peaks, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.01–7.00 (multiple peaks, 2H), 6.26 (m, 1H), 3.05 (t, *J* = 8.1 Hz, 4H), 1.56 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.69, 140.63, 129.59, 129.50, 129.41, 129.01, 128.96, 123.30, 120.60, 118.45, 114.90, 114.70, 50.11, 22.10, 11.25; **HRMS** (ESI) calcd. for $C_{20}H_{25}N_2O_2S$ $[M+H]^+$ *m/z* 357.1637, found 357.1639.



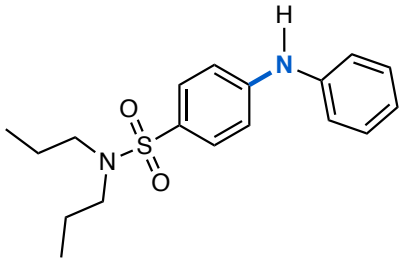
26

4-(9H-carbazol-9-yl)-N,N-dipropylbenzenesulfonamide (26). Method B was followed using phenyl ester **18-OPh** and carbazole. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **26** as a white solid (72 mg, 87% yield): **mp** 101–103 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.46–7.41 (multiple peaks, 4H), 7.33 (t, *J* = 7.1 Hz, 2H), 3.20 (t, *J* = 8.2 Hz, 4H), 1.64 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.43, 140.14, 138.64, 128.87, 126.92, 126.26, 123.84, 120.73, 120.51, 109.55, 50.15, 22.16, 11.23; **HRMS** (ESI) calcd. for $C_{24}H_{27}N_2O_2S$ $[M+H]^+$ *m/z* 407.1793, found 407.1793.



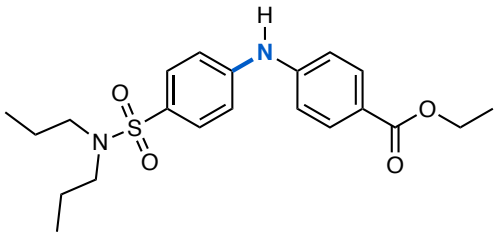
27

4-(Methyl(phenyl)amino)-N,N-dipropylbenzenesulfonamide (27). Method A was followed using phenyl ester **18-OPh** and TMS-*N*-methylaniline. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **27** as a light brown oil (57 mg, 82% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.24–7.21 (multiple peaks, 3H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.35 (s, 3H), 3.02 (t, *J* = 8.5 Hz, 4H), 1.56 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.81, 147.22, 129.91, 128.56, 127.72, 126.04, 125.67, 113.70, 50.15, 40.22, 22.15, 11.26; **HRMS** (ESI) calcd. for $C_{19}H_{27}N_2O_2S$ $[M+H]^+$ *m/z* 347.1793, found 347.1797.



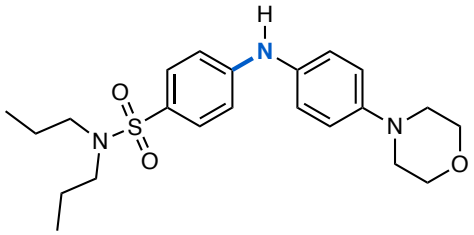
28

4-(Phenylamino)-N,N-dipropylbenzenesulfonamide (28). Method A was followed using phenyl ester **18-OPh** and TMS-aniline. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **28** as a light brown oil (54 mg, 81% yield). Compound **28** was also obtained using Method B (56 mg, 83% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64–7.59 (multiple peaks, 2H), 7.37–7.29 (multiple peaks, 2H), 7.19–7.14 (m, 2H), 7.07 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.04–6.97 (multiple peaks, 2H), 6.26 (s, 1H), 3.05 (t, *J* = 8.4 Hz, 4H), 1.56 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.69, 140.63, 129.59, 129.50, 128.96, 123.30, 120.60, 114.70, 50.11, 22.10, 11.25; **HRMS** (EI) calcd. for $C_{18}H_{24}N_2O_2S$ $[M]^+$ *m/z* 333.1637, found 333.1641.



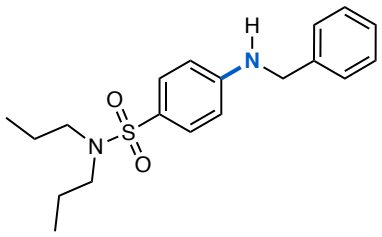
29

Ethyl 4-((4-(*N*,*N*-dipropylsulfamoyl)phenyl)amino)benzoate (29). Method B was followed using phenyl ester **18-OPh**, benzocaine (2.0 equiv), and MSTFA (2.0 equiv). Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **29** as a white solid (57 mg, 70% yield): **mp** 125–127 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.39 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 3H), 3.07 (t, *J* = 7.9 Hz, 4H), 1.57 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.38, 145.61, 145.59, 132.31, 131.63, 129.19, 124.05, 117.34, 117.21, 60.96, 50.29, 22.30, 14.60, 11.45; **HRMS** (EI) calcd. for $C_{21}H_{29}N_2O_4S$ $[M]^+$ *m/z* 405.1848, found 405.1851.



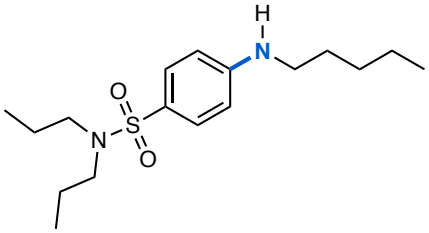
30

4-(4-Benzylpiperazin-1-yl)-*N*,*N*-dipropylbenzenesulfonamide (30). Method B was followed using phenyl ester **18-OPh**, 4-morpholinoaniline (2.0 equiv), and MSTFA (2.0 equiv). Purification by flash chromatography on silica gel (hexanes/EtOAc, 60:40) afforded **30** as a light brown solid (66 mg, 79% yield): **mp** 81–83 °C; **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 3.87 (t, *J* = 4.4 Hz, 4H), 3.14 (t, *J* = 4.4 Hz, 4H), 3.03 (t, *J* = 8.2 Hz, 4H), 1.54 (m, 4H), 0.86 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.37, 148.55, 132.88, 129.23, 128.78, 124.24, 116.98, 113.64, 67.09, 50.29, 49.88, 22.30, 11.45; **HRMS** (ESI) calcd. for $C_{22}H_{32}N_3O_3S$ $[M+H]^+$ *m/z* 418.2164, found 418.2165.



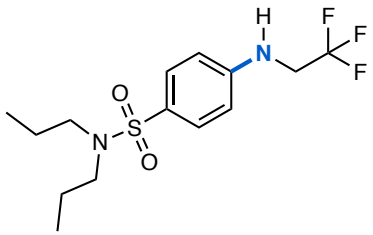
31

4-(Benzylamino)-*N*,*N*-dipropylbenzenesulfonamide (31). Method C was followed using phenyl ester **18-OPh**, benzylamine (1.0 equiv), and MSTFA (1.0 equiv). TMS-amine was generated *in situ* at 60 °C for 1 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 85:15) afforded **31** as a colorless oil (43 mg, 62% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.41–7.29 (multiple peaks, 5H), 6.61 (d, *J* = 8.6 Hz, 2H), 4.56 (t, *J* = 5.5 Hz, 1H), 4.37 (d, *J* = 5.5 Hz, 2H), 3.02 (t, *J* = 8.1 Hz, 4H), 1.54 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 151.22, 138.33, 129.29, 129.00, 127.79, 127.60, 127.54, 112.07, 50.29, 47.91, 22.31, 11.46; **HRMS** (ESI) calcd. for $C_{19}H_{27}N_2O_2S$ $[M+H]^+$ *m/z* 347.1793, found 347.1797.



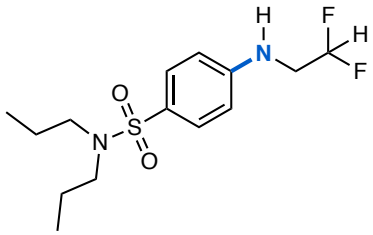
32

4-(Pentylamino)-*N*,*N*-dipropylbenzenesulfonamide (32). Method C was followed using phenyl ester **18-OPh**, 1-pentylamine (1.0 equiv), and MSTFA (1.0 equiv). TMS-amine was generated *in situ* at 35 °C for 1 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 85:15) afforded **32** as a colorless oil (54 mg, 83% yield): **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.28 (br. s, 1H), 3.12 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.9 Hz, 4H), 1.63–1.61 (multiple peaks, 2H), 1.53 (m, 4H), 1.37–1.34 (multiple peaks, 4H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.58, 129.24, 126.63, 111.69, 50.25, 43.59, 29.37, 29.06, 22.60, 22.26, 14.16, 11.43; **HRMS** (ESI) calcd. for $C_{17}H_{31}N_2O_2S$ $[M+H]^+$ *m/z* 327.2106, found 327.2110.



33

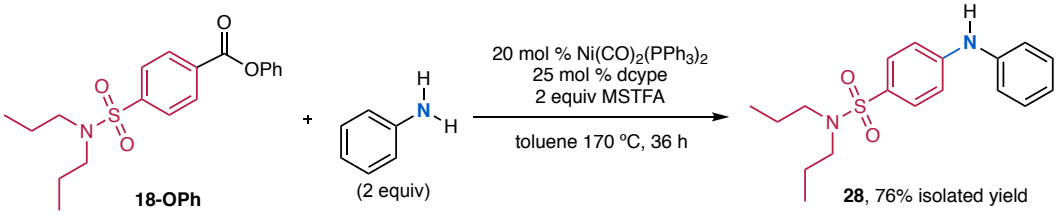
***N*,*N*-Dipropyl-4-((2,2,2-trifluoroethyl)amino)benzenesulfonamide (33).** Method C was followed using phenyl ester **18-OPh**, 2,2,2-trifluoroethan-1-amine (2.0 equiv), and MSTFA (2.0 equiv). TMS-amine was generated *in situ* at 35 °C for 1 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **33** as a colorless oil (49 mg, 72% yield): **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 7.6 Hz, 2H), 4.48 (t, *J* = 7.1 Hz, 1H), 3.83–3.81 (multiple peaks, 2H), 3.03 (t, *J* = 7.9 Hz, 4H), 1.54 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.64, 129.59, 129.31, 124.86 (q, *J* = 280.1 Hz), 112.52, 77.41, 77.23, 77.05, 50.26, 45.48 (q, *J* = 34.2 Hz), 22.27, 11.43; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –72.31 (t, *J* = 8.9 Hz); **HRMS** (ESI) calcd. for $C_{14}H_{22}F_3N_2O_2S$ $[M+H]^+$ *m/z* 339.1354, found 339.1360.



34

4-((2,2-Difluoroethyl)amino)-*N*,*N*-dipropylbenzenesulfonamide (34). Method C was followed using phenyl ester **18-OPh**, 2,2-difluoroethan-1-amine (2.0 equiv), and MSTFA (2.0 equiv). TMS-amine was generated *in situ* at 35 °C for 1 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **34** as a colorless oil (52 mg, 81% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.92 (tt, *J* = 55.7, 3.6 Hz, 1H), 4.38 (t, *J* = 6.7 Hz, 1H), 3.59 (ddt, *J* = 14.5, 10.8, 3.0 Hz, 2H), 3.03 (dd, *J* = 8.5, 6.8 Hz, 4H), 1.54 (m, 4H), 0.87 (t, *J* = 7.7 Hz, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 150.21, 129.39, 129.03, 114.28 (t, *J* = 242.4 Hz), 112.32, 50.26, 45.95 (t, *J* = 26.0 Hz), 22.28, 11.45; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –122.70 (dt, *J* = 55.7, 14.5 Hz); **HRMS** (ESI) calcd. for $C_{14}H_{23}F_2N_2O_2S$ $[M+H]^+$ *m/z* 321.1448, found 321.1451.

Ni-catalyzed decarbonylation using air-stable Ni source



All catalysts/reagents were handled on the benchtop. Into an oven-dried 15 mL Schlenk tube equipped with a stir bar was weighed $Ni(CO)_2(PPh_3)_2$ (0.06 mmol, 0.2 equiv), dcype (0.0075 mmol, 0.25 equiv), and phenyl ester **18-OPh** (0.3 mmol, 1.0 equiv). The tube was sealed and was evacuated (~2 min) and backfilled with nitrogen (1 min). This cycle was repeated 3 times. Using a syringe, the aniline (0.6 mmol, 2.0 equiv), MSTFA (0.6 mmol, 2.0 equiv), and toluene (0.4 mL) were added. The reaction mixture was stirred at 170 °C for 36 h. Purification by flash chromatography on silica gel (hexanes/EtOAc, 90:10) afforded **28** as a light brown oil (51 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64–7.59 (multiple peaks, 2H), 7.37–7.29 (multiple peaks, 2H), 7.19–7.14 (m, 2H), 7.07 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.04–6.97 (multiple peaks, 2H), 6.26 (s, 1H), 3.05 (t, *J* = 8.4 Hz, 4H), 1.56 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$)

δ 147.69, 140.63, 129.59, 129.50, 128.96, 123.30, 120.60, 114.70, 50.11, 22.10, 11.25; **HRMS** (EI) calcd. for $C_{18}H_{24}N_2O_2S$ $[M]^+$ *m/z* 333.1637, found 333.1641.

Substrate scope limitation

The following esters and amines were also conducted under the standard catalytic conditions but failed to give significant amount of isolable products.

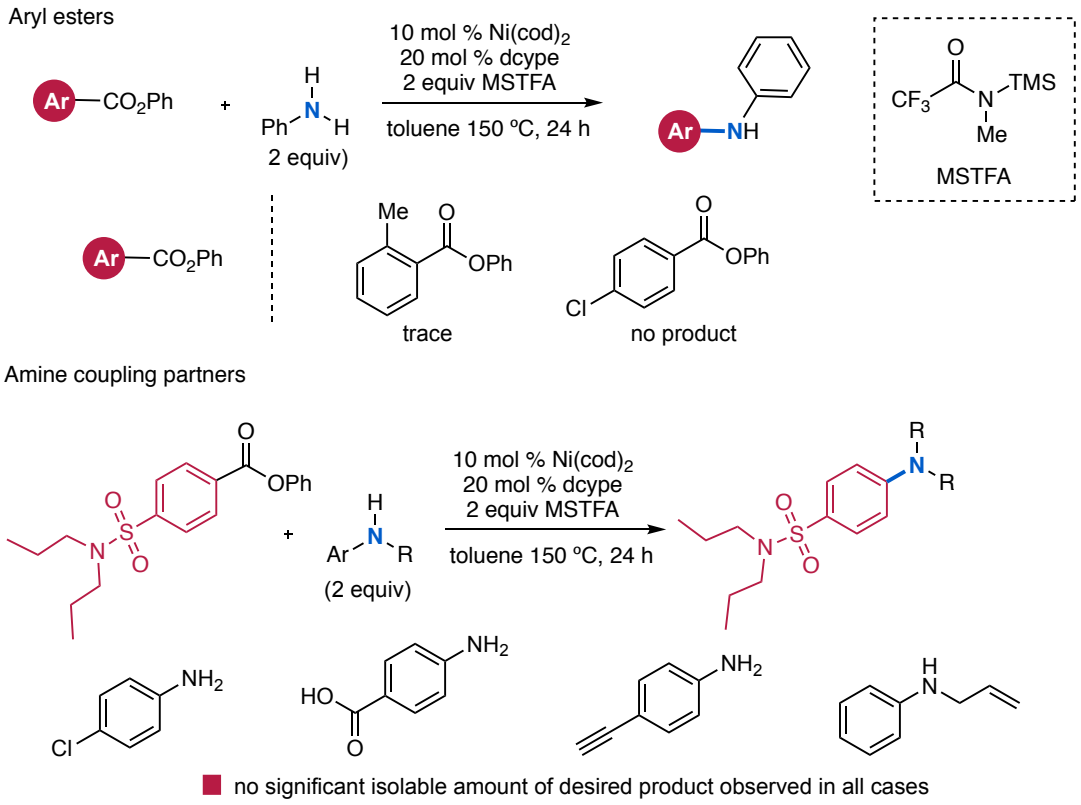
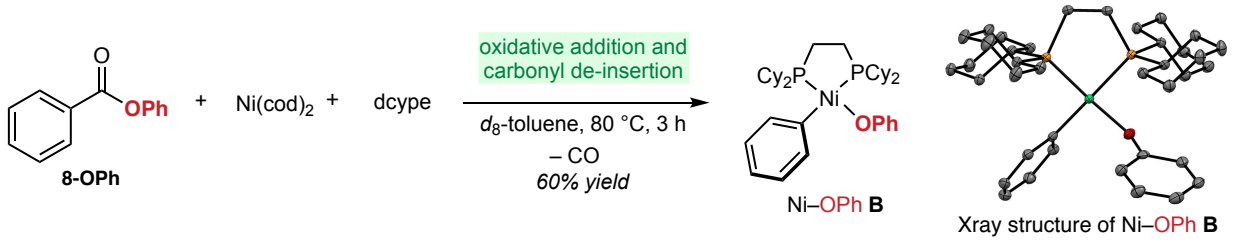


Fig. S7. Current limitations on substrate scope.

VII. Mechanistic studies: oxidative addition and carbonyl deinsertion



In a glovebox, a solution of $Ni(cod)_2$ (0.03 mmol, 1 equiv) and dcype (0.03 mmol, 1 equiv) in toluene (0.25 mL) was stirred in a 4 mL vial at rt for 10 min. In a separate 4 mL vial, a solution of phenyl ester **8-OPh** (0.02 mmol) in toluene (0.25 mL) was stirred for 5 min. Both solutions were combined, and the resulting solution was transferred to a J. Young tube. The tube was then sealed and removed from the glovebox. The reaction mixture was analyzed by ^{31}P NMR spectroscopy at 80 °C. As summarized in Fig. S8, Ni–OPh **B** was observed with concomitant consumption of $Ni(cod)_2$/dcype and formation of $(dcype)Ni(CO)_2$. Reactions performed at 60 °C or lower showed no significant conversions. In a separate reaction, Ni–OPh **B** was synthesized, isolated, and characterized by NMR spectroscopy and X-ray crystallography (see Sections **IX** and **X**).

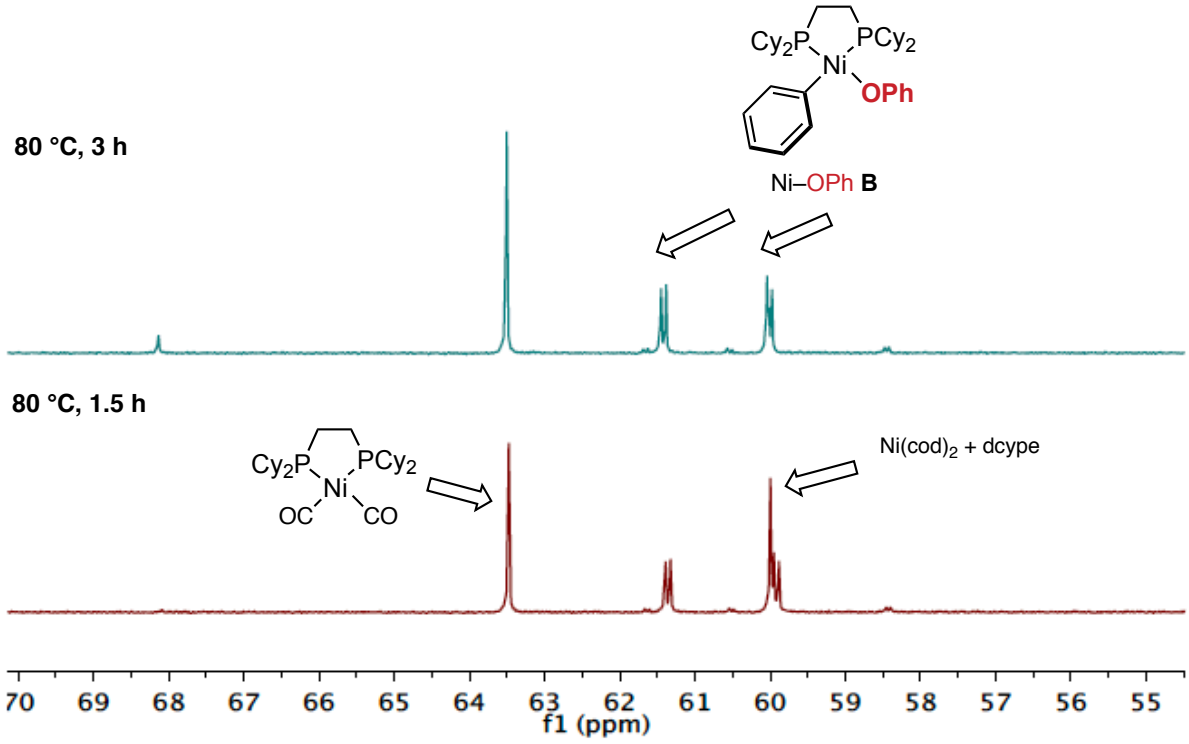
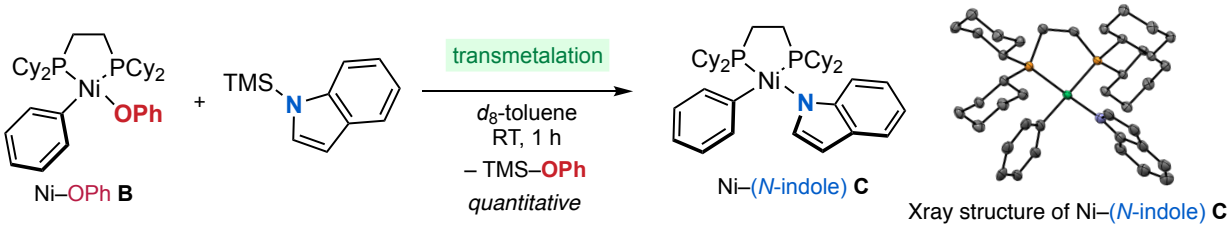


Fig. S8. Stoichiometric decarbonylation of phenyl ester **34** with $Ni(cod)_2$/dcype in toluene at 80 °C. Analysis by ^{31}P NMR spectroscopy.

VIII. Mechanistic studies: transmetallation and reductive elimination



Transmetallation studies: In a glovebox, Ni–OPh **B** (0.02 mmol, 1.0 equiv) was weighed in a 4 mL vial and dissolved in toluene (0.3 mL). In a separate 4 mL vial, TMS-indole (0.022 mmol, 1.2 equiv) in toluene (0.2 mL) was added. Both vials were placed in the glovebox freezer (–35 °C) for 20 min. The vials were then removed from the freezer, the solutions were combined, and the resulting solution was transferred to a J. Young tube. The tube was sealed and removed from the glovebox. After 5 min from the time of mixing, the reaction mixture was analyzed by ^{31}P NMR spectroscopy at a number of time points at room temperature (Fig. S9).

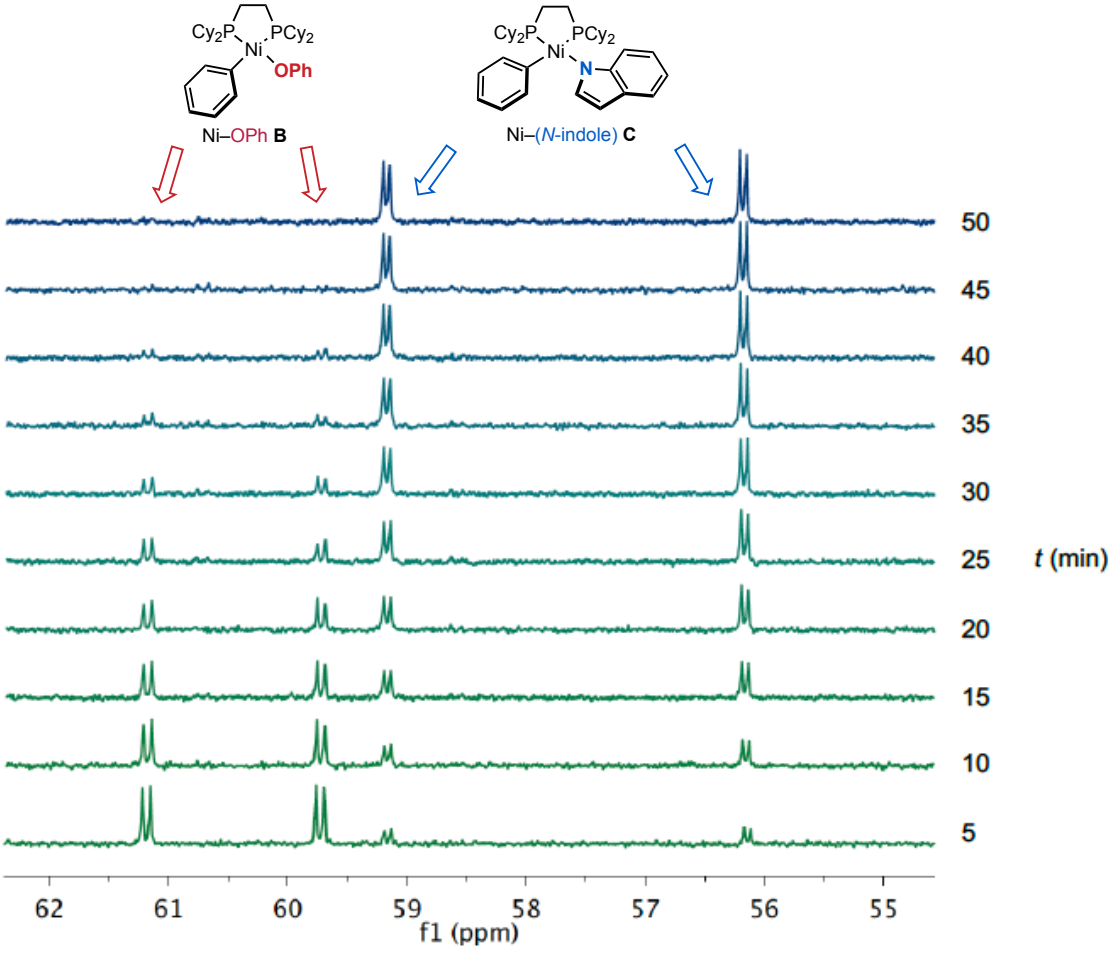
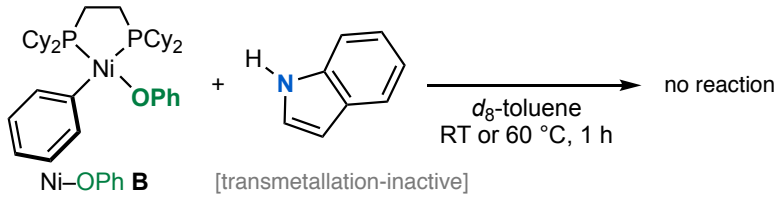
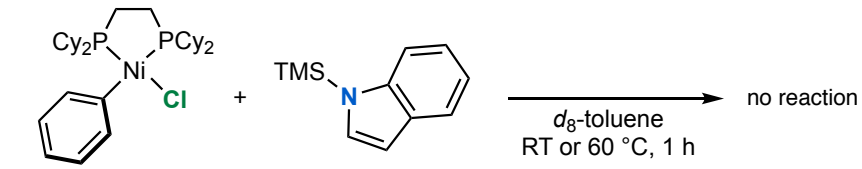


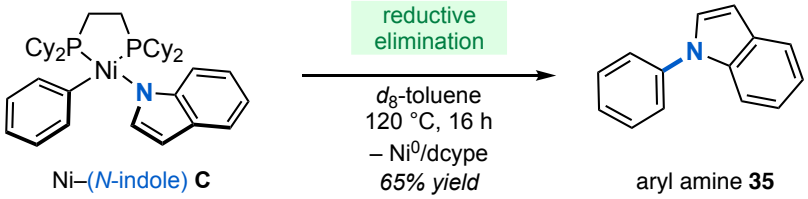
Fig. S9. Transmetallation of Ni–OPh **B** with TMS-indole in toluene at room temperature. Analysis by ^{31}P NMR spectroscopy.

As shown in Fig. S8, quantitative conversion of Ni–OPh **B** to Ni–indole **C** was observed after 1 h. In a separate reaction, the Ni-indole **C** complex was synthesized, isolated, and characterized by NMR spectroscopy and X-ray crystallography (see Sections **IX** and **X**).



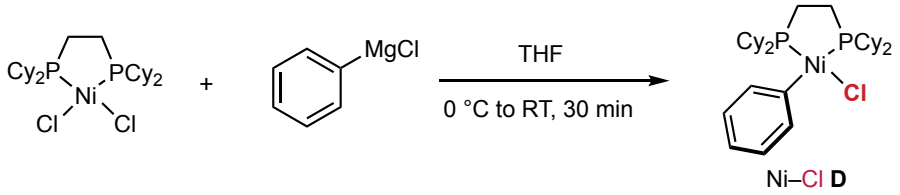


Following the same procedure as the transmetallation studies above, the reaction of Ni–OPh **B** with free indole (M = H) and the Ni–Cl D with TMS-indole were also investigated. At room temperature and at 60 °C for 1 h, no transmetallation activities were observed.



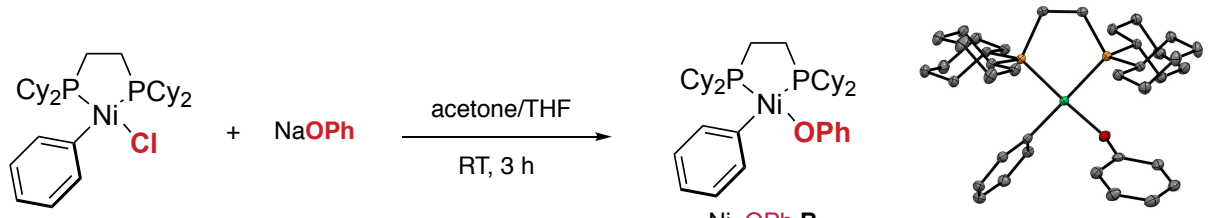
Reductive elimination studies: In a glovebox, Ni–indole **C** (0.02 mmol, 1.0 equiv) was weighed in a 4 mL vial and dissolved in toluene (0.3 mL). Neopentylbenzene (0.02 mmol, 1.0 equiv) in toluene (0.2 mL) was added. The vial was sealed and removed from the glovebox. The reaction was heated in an oil bath at 120 °C for 16 h. The reaction mixture was then cooled and analyzed by gas chromatography (GC). Reactions performed at 100 °C or below did not show any observed reactivity. Aryl amine **35** was obtained in 65% GC yield via C–N reductive elimination.

IX. Synthesis of Ph(dcype)NiOPh B and Ph(dcype)Ni(N-indole) C complexes



Ni–Cl **D**

[Ni(dcype)(Ph)(Cl)] (D). Ni(dcype)$(Cl)_2$ (552 mg, 1 mmol) was suspended in 50 mL of dry THF and cooled to 0 °C. With vigorous stirring, PhMgCl (1M in THF, 1.02 mL, 1.02 mmol) was added dropwise over 1 min. Following the addition, the now homogenous reaction mixture was allowed to warm to rt. Solvent was removed *in vacuo* and anhydrous MeOH (5 mL) was added. The suspension was sonicated for 5 min before being filtered over a frit. The obtained solid was washed with cold MeOH (1 mL x 2) to yield the Ni–Cl **D** complex as a bright yellow solid in 78% yield (460 mg):[7] **^{1}H NMR** (700 MHz, CD_2Cl_2) δ 7.43 (d, *J* = 5.5 Hz, 2H), 6.94 (t, *J* = 7.0 Hz, 2H), 6.78 (t, *J* = 7.0 Hz, 1H), 2.38 (d, *J* = 10.0 Hz, 2H), 2.15–2.02 (multiple peaks, 4H), 1.91–1.10 (multiple peaks, 40H), 0.78 (multiple peaks, 2H); **^{13}C NMR** (176 MHz, CD_2Cl_2) δ 161.61 (dd, *J* = 88.4, 39.1 Hz), 138.94, 127.68 (dd, *J* = 5.7, 1.8 Hz), 123.66, 36.36 (d, *J* = 26.7 Hz), 35.62 (d, *J* = 17.6 Hz), 31.50–20.19 (multiple overlapping peaks, 24 carbons); **^{31}P NMR** (202 MHz, CD_2Cl_2) δ 65.02 (d, *J* = 20.6 Hz), 62.80 (d, *J* = 20.6 Hz); spectral data matched that from the literature[7].

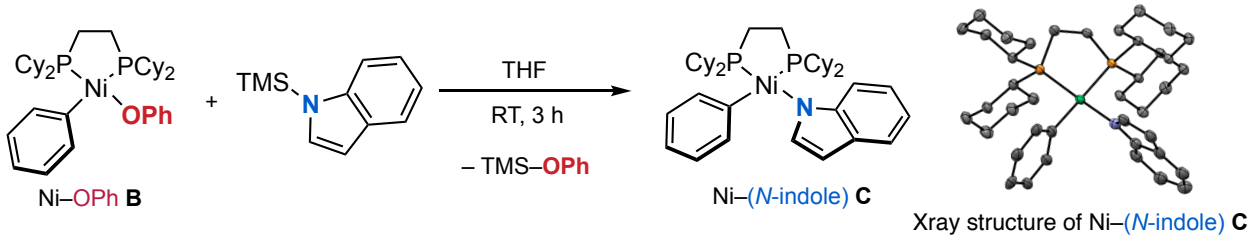


Ni–Cl **D** Ni–OPh **B** Xray structure of Ni–OPh **B**

[Ni(dcype)(Ph)(OPh)] (B). [Ni(dcype)(Ph)(Cl)] **D** (118 mg, 0.2 mmol) and NaOPh (26 mg, 0.22 mmol) were added to a 20 mL scintillation vial. Acetone (5 mL) and THF (5 mL) were added to the vial, and the reaction was stirred for 3 h at rt. Following removal of solvent *in vacuo*, the resulting solid was redissolved in THF (5 mL) and passed through a Celite plug. Removal of solvent yielded Ni–OPh complex **B** as a light orange solid (124 mg, 95% yield): **^{1}H NMR** (700 MHz, CD_2Cl_2)δ 7.58 (t, *J* = 6.3 Hz, 2H), 6.88 (t, *J* = 7.0 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.19 (t, *J* = 7.1 Hz, 1H), 2.28 (d, *J* = 11.7 Hz, 2H), 2.17

(d, *J* = 11.3 Hz, 2H), 1.87–1.18 (multiple peaks, 42H), 0.85–0.77 (multiple peaks, 2H); **^{13}C NMR** (176 MHz, CD_2Cl_2) δ 168.58, 158.84 (dd, *J* = 89.1, 39.7 Hz), 137.23, 127.92, 125.23 (dd, *J* = 5.8, 1.9 Hz), 121.91, 120.40 (d, *J* = 1.7 Hz), 111.17, 34.02 (d, *J* = 26.4 Hz), 33.34 (d, *J* = 14.8 Hz), 33.35–17.32 (multiple overlapping peaks, 24 carbons); **^{31}P NMR** (202 MHz, CD_2Cl_2) δ 61.20 (d, *J* = 13.5 Hz), 59.75 (d, *J* = 13.5 Hz).

Orange blocks of Ni-OPh complex **B** were grown from a THF/pentane solution of the compound at 22 °C for X-ray crystallographic analysis (see Section **X**). Crystallographic parameters for compound **B** are available free of charge from the Cambridge Crystallographic Data Centre under CCDC 1962368.



Ni–OPh **B** Ni–(*N*-indole) **C**

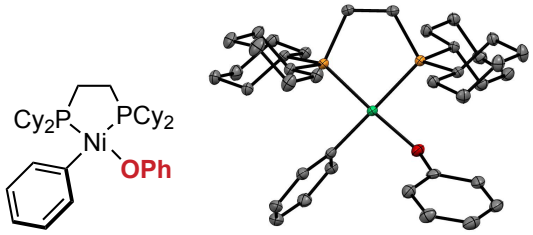
Xray structure of Ni–(*N*-indole) **C**

[Ni(dcype)(Ph)(indole)] (C). [Ni(dcype)(Ph)(OPh)] **B** (98 mg, 0.15 mmol) was dissolved in THF (5 mL) and stirred in a 20 mL scintillation vial. *N*-(trimethylsilyl)-indole (90 mg, 0.45 mmol) was dissolved in THF (1 mL) and added to the reaction solution. The reaction was stirred for 3 h at rt before solvent was removed *in vacuo*. The resulting solid was suspended in Et_2O/pentane (50:50, 10 mL) and stirred. The precipitate was collected on a frit and washed once with cold Et_2O (2 mL) to obtain the product as yellow solid (63 mg, 62% yield): **^{1}H NMR** (700 MHz, CD_2Cl_2) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.5 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 2.2 Hz, 1H), 6.87 (m, 1H), 6.82 (t, *J* = 6.8 Hz, 2H), 6.71 (t, *J* = 6.8 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 1.92–1.56 (multiple peaks, 36H), 1.32–0.52 (multiple peaks, 12H); **^{13}C NMR** (176 MHz, CD_2Cl_2) δ 160.06 (dd, *J* = 87.3, 37.1 Hz), 144.45, 135.66, 133.76, 131.33 (dd, *J* = 2.7, 0.9 Hz), 125.52 (dd, *J* = 5.7, 2.4 Hz), 121.52, 118.89, 116.51, 115.58, 115.13, 100.30 (dd, *J* = 2.1, 0.8 Hz), 33.85–18.16 (multiple overlapping peaks, 26 carbons); **^{31}P NMR** (202 MHz, CD_2Cl_2) δ 60.24 (d, *J* = 13.2 Hz), 57.77 (d, *J* = 13.2 Hz).

Yellow needles of Ni–(*N*-indole) **C** were grown from a dichloromethane/pentane solution of the compound at rt for X-ray crystallographic analysis (see Section **X**). Crystallographic parameters for compound **C** are available free of charge from the Cambridge Crystallographic Data Centre under CCDC 1962368.

X. X-Ray crystallographic data of [Ni(dcype)(Ph)(OPh)] B and [Ni(dcype)(Ph)(N-indole)] C complexes

Structure determination of [Ni(dcype)(Ph)(OPh)] B



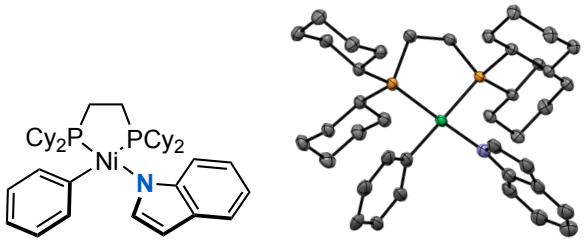
[Ni(dcype)(Ph)(OPh)] B

Orange blocks of Ni-OPh **B** were grown from a THF/pentane solution of the compound at 22 °C. A crystal of dimensions 0.16 x 0.14 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 s for the low angle images, 3 s for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 24996 reflections to a maximum 2θ value of 138.61º of which 6173 were independent and 6073 were greater than 2σ(I). The final cell constants (Table S1) were based on the xyz centroids of 20405 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P-1 with Z = 2 for the formula $C_{38}H_{58}OP_2Ni$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0407 and wR2 = 0.1111 [based on I > 2sigma(I)], R1 = 0.0411 and wR2 = 0.1115 for all data. Additional details are presented in Table S1[8–12].

Table S1. Crystal data and structural refinement for **[Ni(dcype)(Ph)(OPh)] B**

Empirical Formula	$C_{38}H_{58}OP_2Ni$
Formula Weight	651.49
Temperature	85(2) K
Wavelength	1.54184 A
Crystal System	Triclinic
Space Group	P-1
Unit Cell Dimensions	a = 8.8378(2) A alpha = 76.737(2)º b = 12.4920(3) A beta= 78.709(2)º c = 16.4162(3) A gamma = 79.504(2)º
Volume	1711.92(7) $Å^3$
Z	2
Calculated Density	1.264 mg/m^3
Absorption Coefficient	1.902 mm^{-1}
F(000)	704
Crystal Size	0.160 x 0.140 x 0.100 mm
Theta Range for Data Collection	2.802 to 69.305 deg.
Limiting Indicies	-10<=h<=10, -15<=k<=14, -19<=l<=19
Reflections Collected	24996
Independent Reflections	6173 [R(int) = 0.0469]
Completeness to Theta	67.684 (97.8%)
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 and 0.72810
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6173 / 0 / 380
Goodness-of-Fit on F^2	1.062
Final R Indices [I>2σ(I)]	R1 = 0.0407, wR2 = 0.1111
R indices (all data)	R1 = 0.0411, wR2 = 0.1115
Largest Difference Peak and Hole	0.621 and -0.510 e $Å^{-3}$

Structure determination of [Ni(dcype)(Ph)(N-indole)] C



[Ni(dcype)(Ph)(N-indole)] C

Yellow needles of Ni–(*N*-indole) **C** were grown from a dichloromethane/pentane solution of the compound at 25 °C. A crystal of dimensions 0.20 x 0.15 x 0.05 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 s for the low angle images, 6 s for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 58757 reflections to a maximum 2θ value of 138.50º of which 7263 were independent and 6152 were greater than 2σ(I). The final cell constants (Table S2) were based on the xyz centroids of 17216 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{40}H_{59}NP_2Ir$ + [solvent]. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0808 and wR2 = 0.2179 [based on I > 2sigma(I)], R1 = 0.0915 and wR2 = 0.2327 for all data. The SQUEEZE subroutine of the PLATON program suite was used to address the disordered solvent in four large cavities present in the structure. Additional details are presented in Table S2[8–12].

Table S2. Crystal data and structural refinement for **[Ni(dcype)(Ph)(N-indole)] C**

Empirical Formula	$C_{40}H_{59}NP_2Ni$
Formula Weight	674.53
Temperature	85(2) K
Wavelength	1.54184 A
Crystal System	Monoclinic
Space Group	P2(1)/c
Unit Cell Dimensions	a = 13.1407(2) Å alpha = 90º b = 18.4231(4) Å beta = 106.562(2)º c = 16.9248(3) Å gamma = 90º
Volume	3927.37(13) $Å^3$
Z	4
Calculated Density	1.141 mg/m^3
Absorption Coefficient	1.663 mm^{-1}
F(000)	1456
Crystal Size	0.200 x 0.150 x 0.050 mm
Theta Range for Data Collection	3.630 to 69.251 deg.
Limiting Indicies	-15<=h<=15, -18<=k<=21, -20<=l<=20
Reflections Collected	58787
Independent Reflections	7263 [R(int) = 0.0825]
Completeness to Theta	67.684 (99.5%)
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 and 0.52352
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	7263 / 105 / 398
Goodness-of-Fit on F^2	1.050
Final R Indices [I>2σ(I)]	R1 = 0.0808, wR2 = 0.2179
R indices (all data)	R1 = 0.0915, wR2 = 0.2327
Largest Difference Peak and Hole	1.043 and -0.644 e $Å^{-3}$

XI. References

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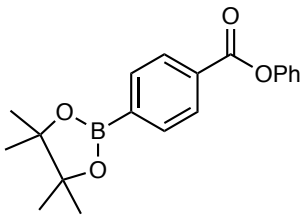
(9) CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

(10) CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015)

(11) Spek, A.L. Single-crystal structure validation with the program PLATON. *J. Appl. Cryst.* **36**, 7–13 (2003).

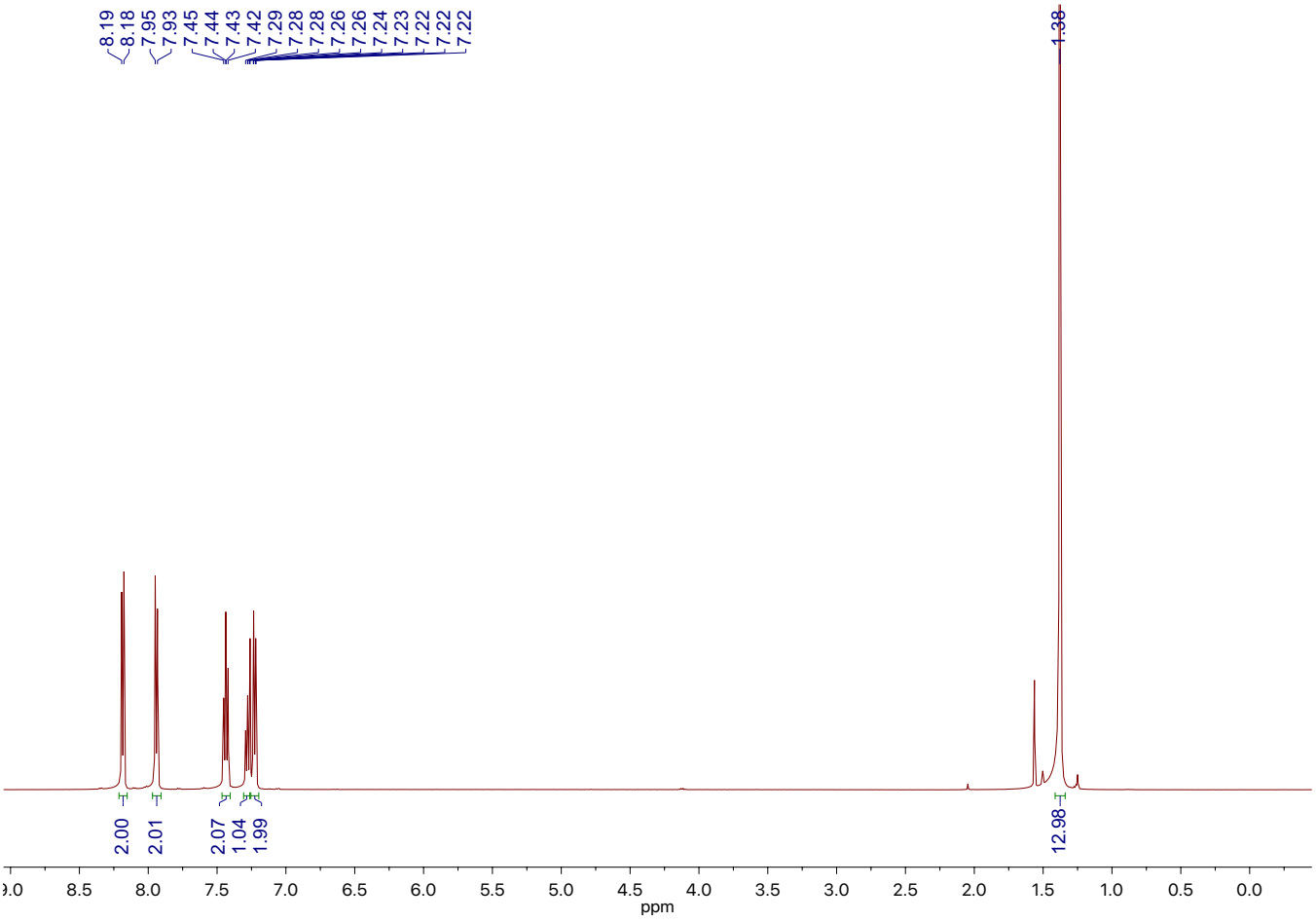
(12) Spek, A.L. Structure validation in chemical crystallography *Acta Crystallogr. D.* **65**, 148–155 (2009).

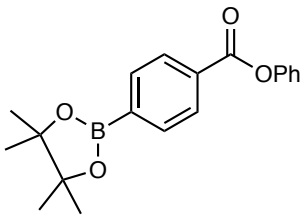
XII. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR Spectra



9-OPh

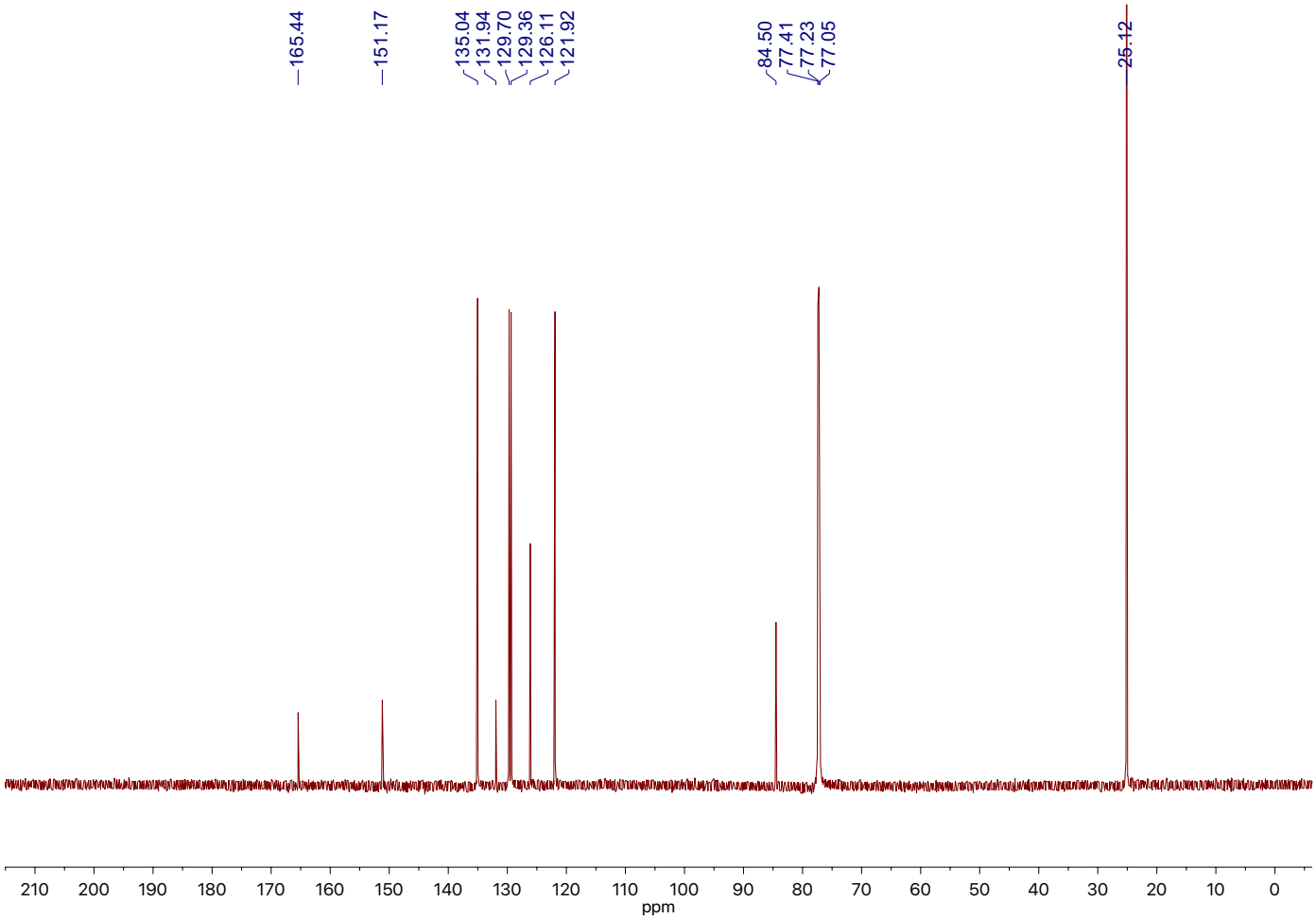
^{1}H NMR




O
OPh
O
B
O

9-OPh

^{13}C NMR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77.41
77.23
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210
200
190
180
170
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140
130
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110
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90
80
70
60
50
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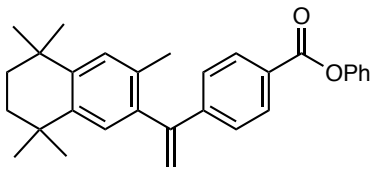
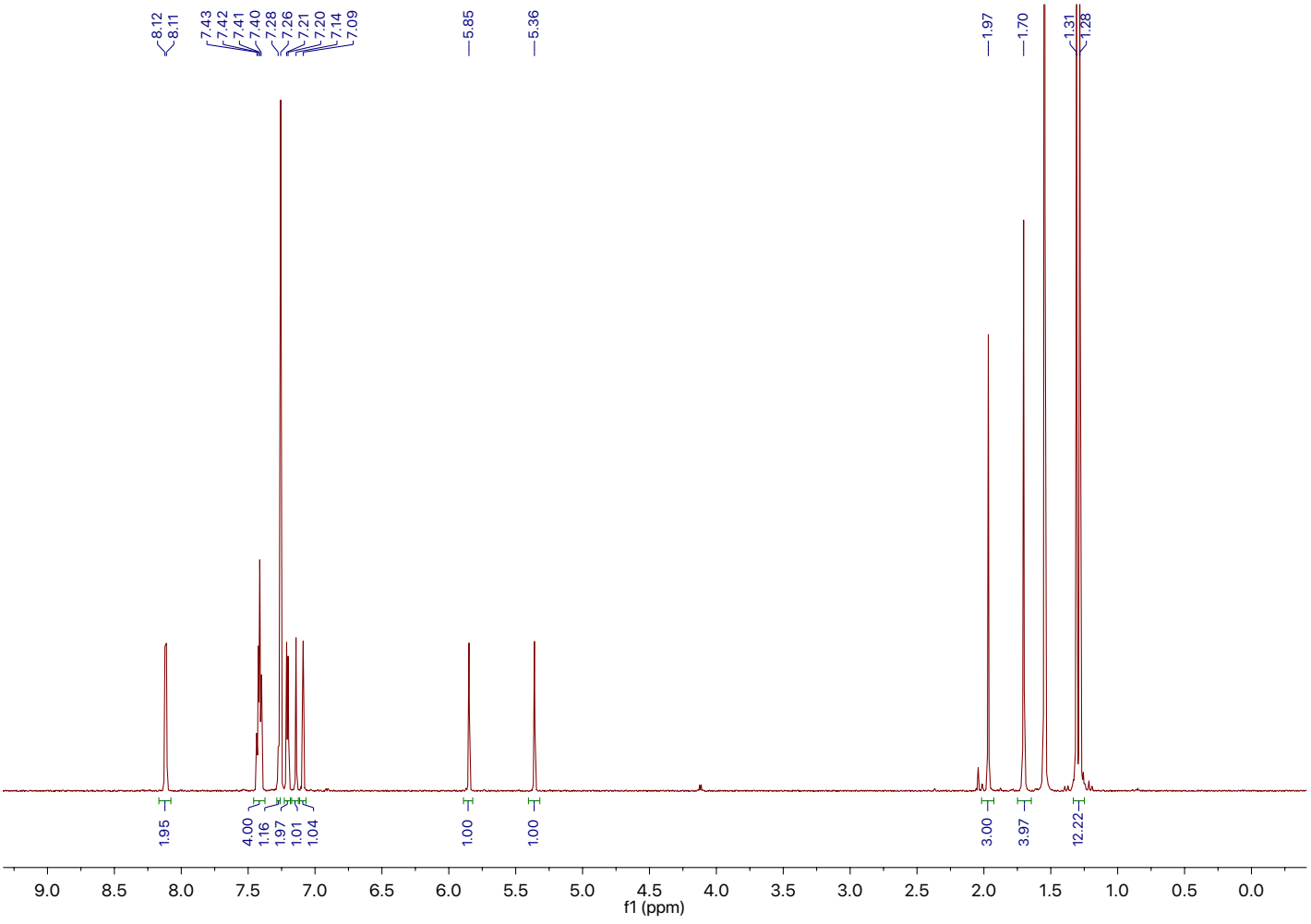
ppm


O
OPh

18-OPh

^{1}H NMR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7.14
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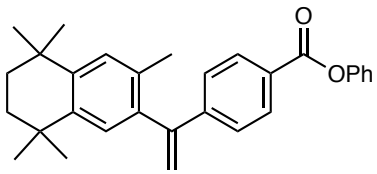
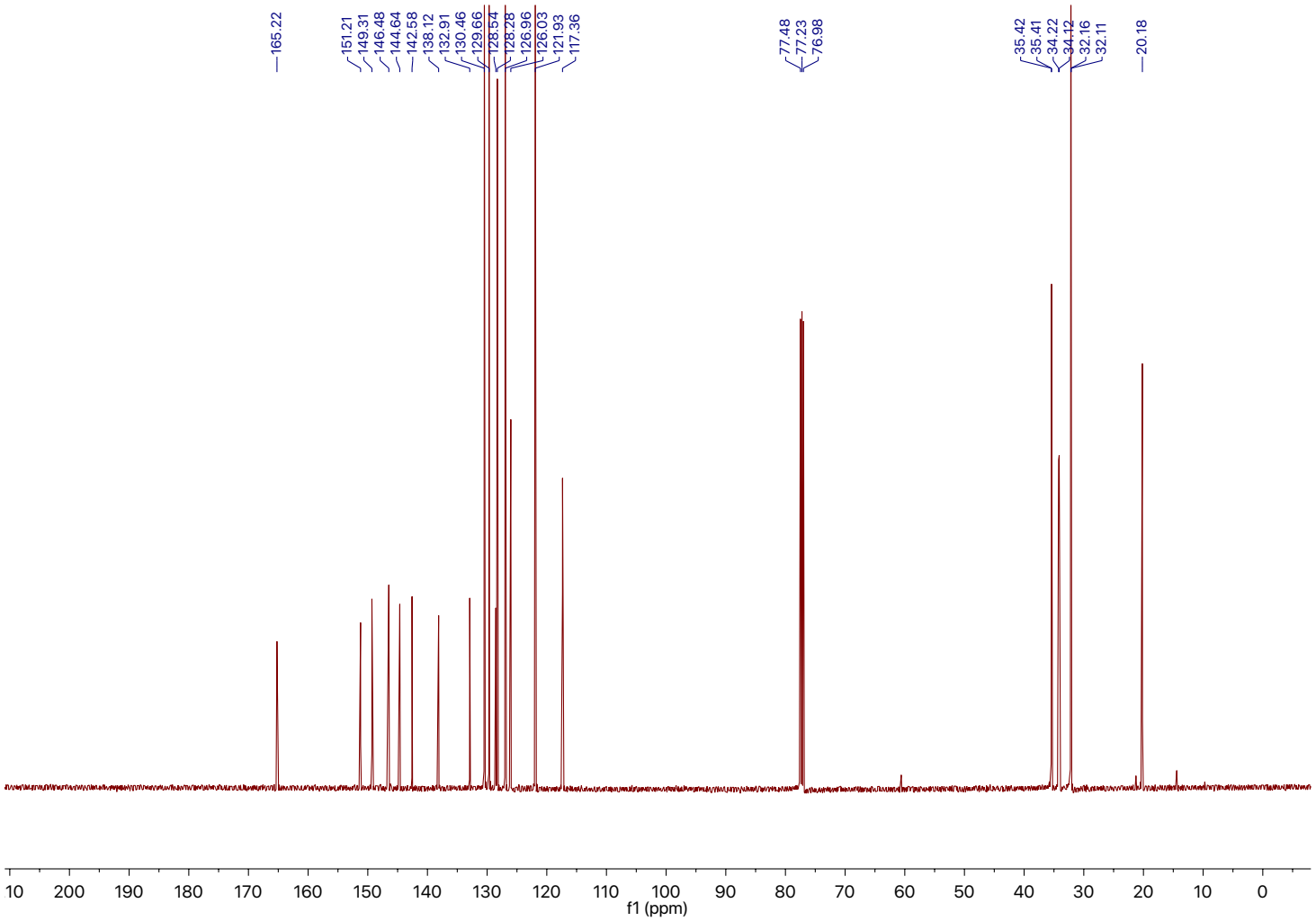
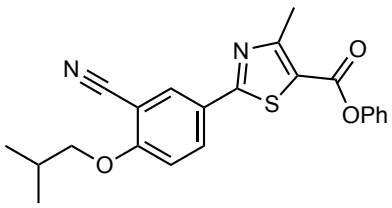
f1 (ppm)



18-OPh

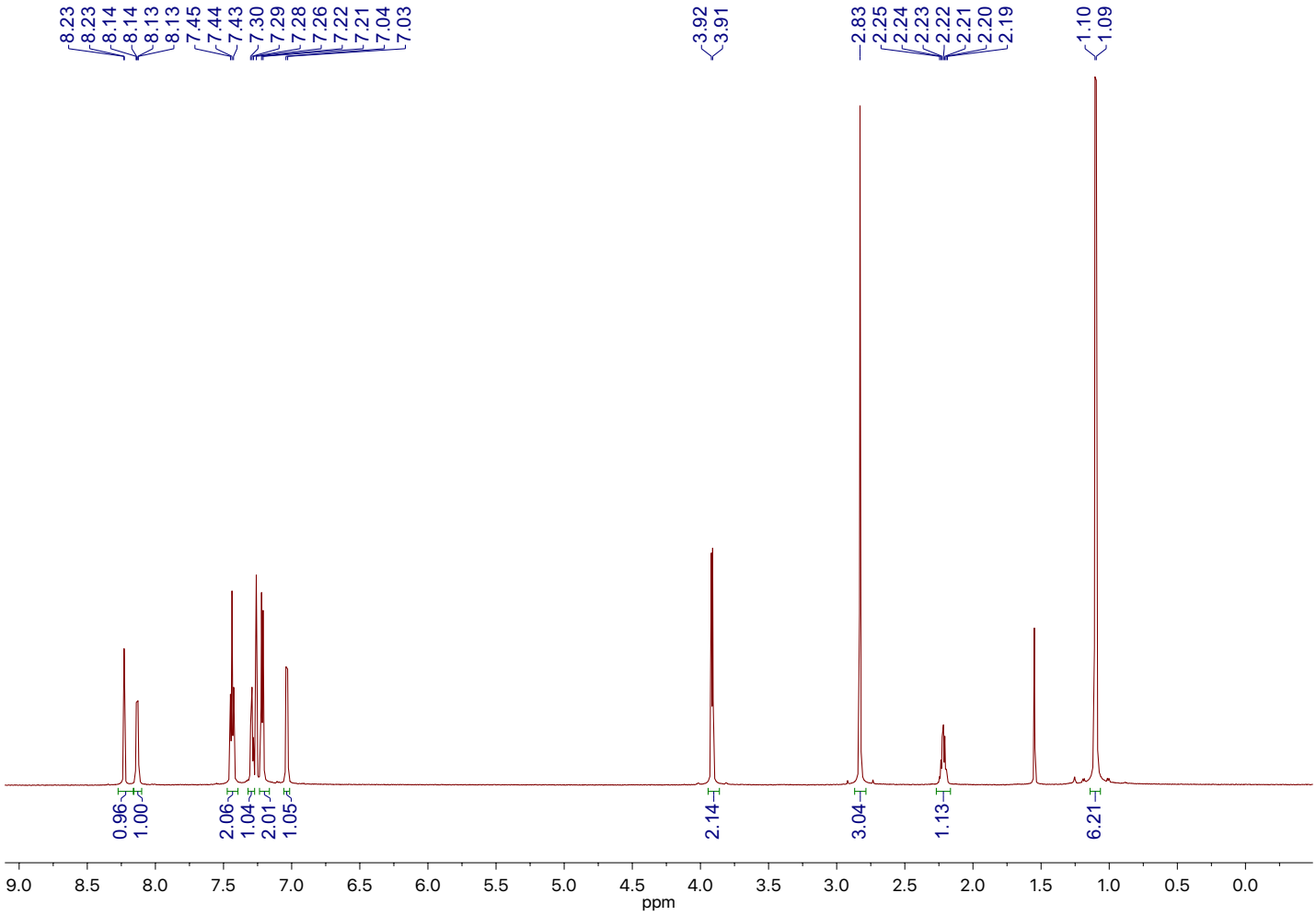
^{13}C NMR




N
N
S
O
OPh
O

19-OPh

^{1}H NMR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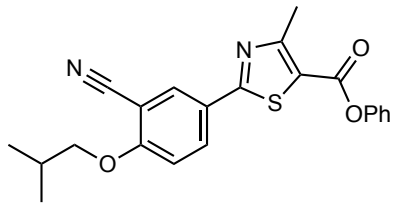
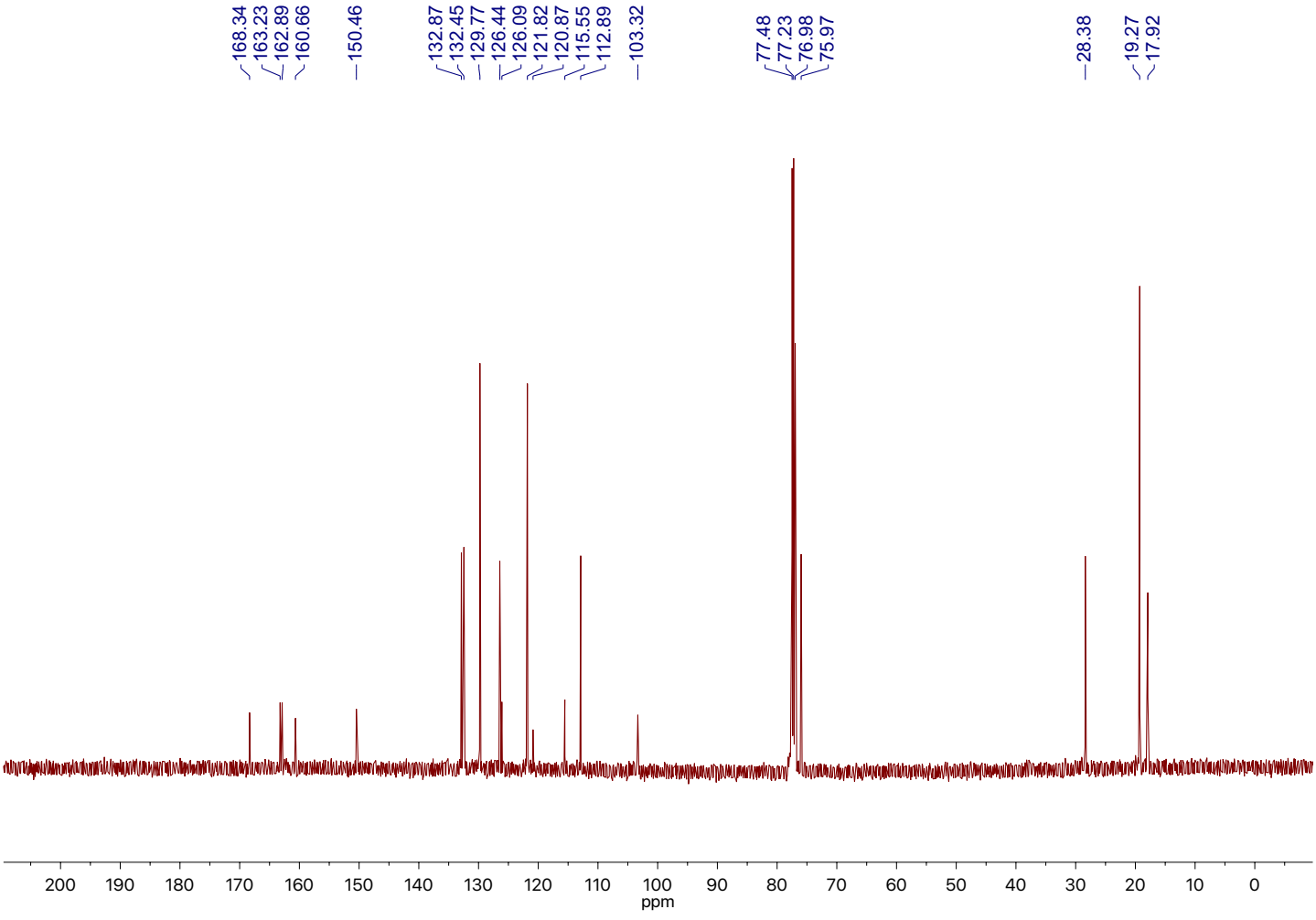
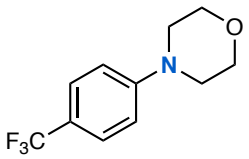
7.22
7.21
7.04
7.03
3.92
3.91
2.83
2.25
2.24
2.23
2.22
2.21
2.20
2.19
1.10
1.09
0.96
1.00
2.06
1.04
2.01
1.05
2.14
3.04
1.13
6.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



19-OPh

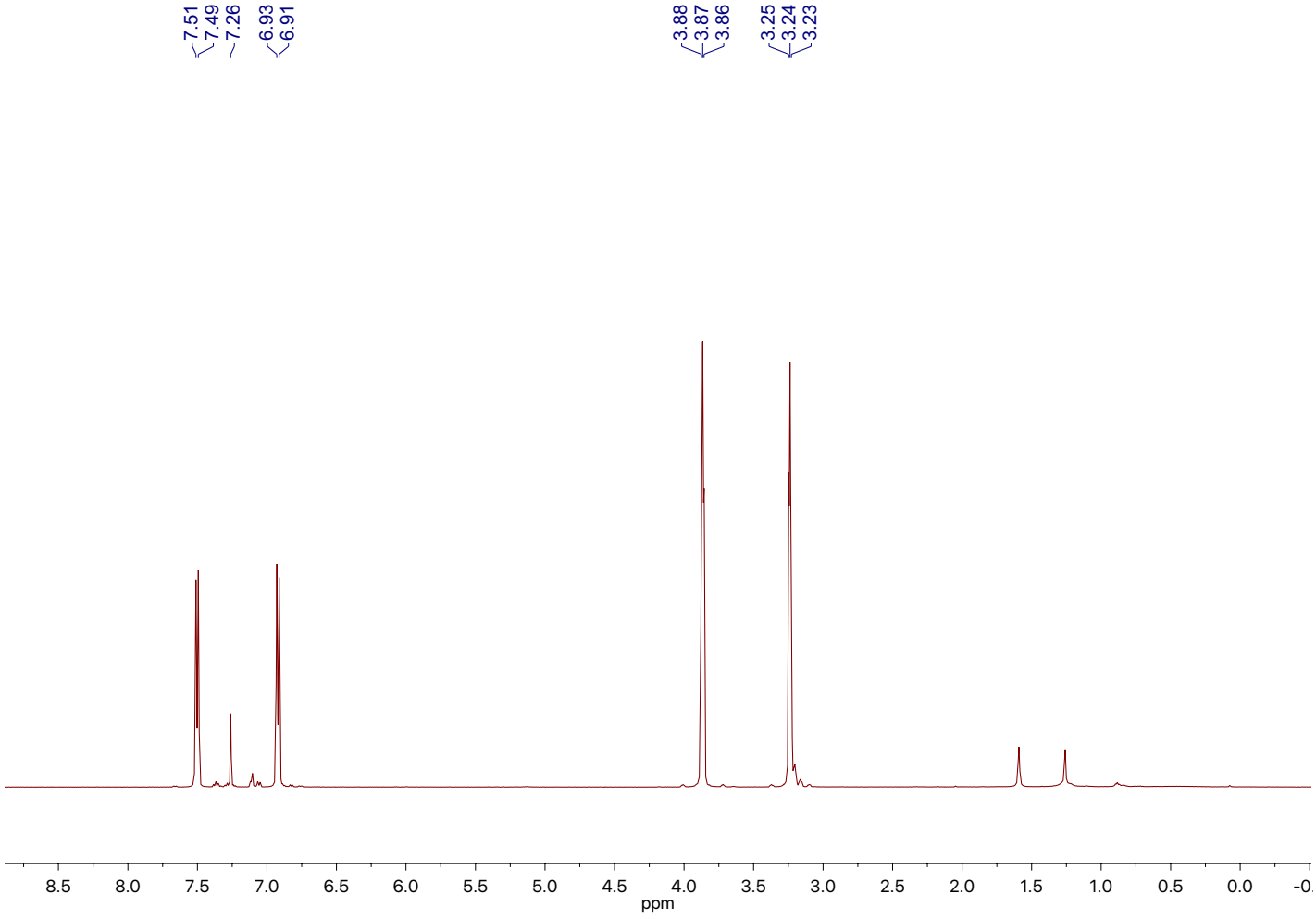
^{13}C NMR

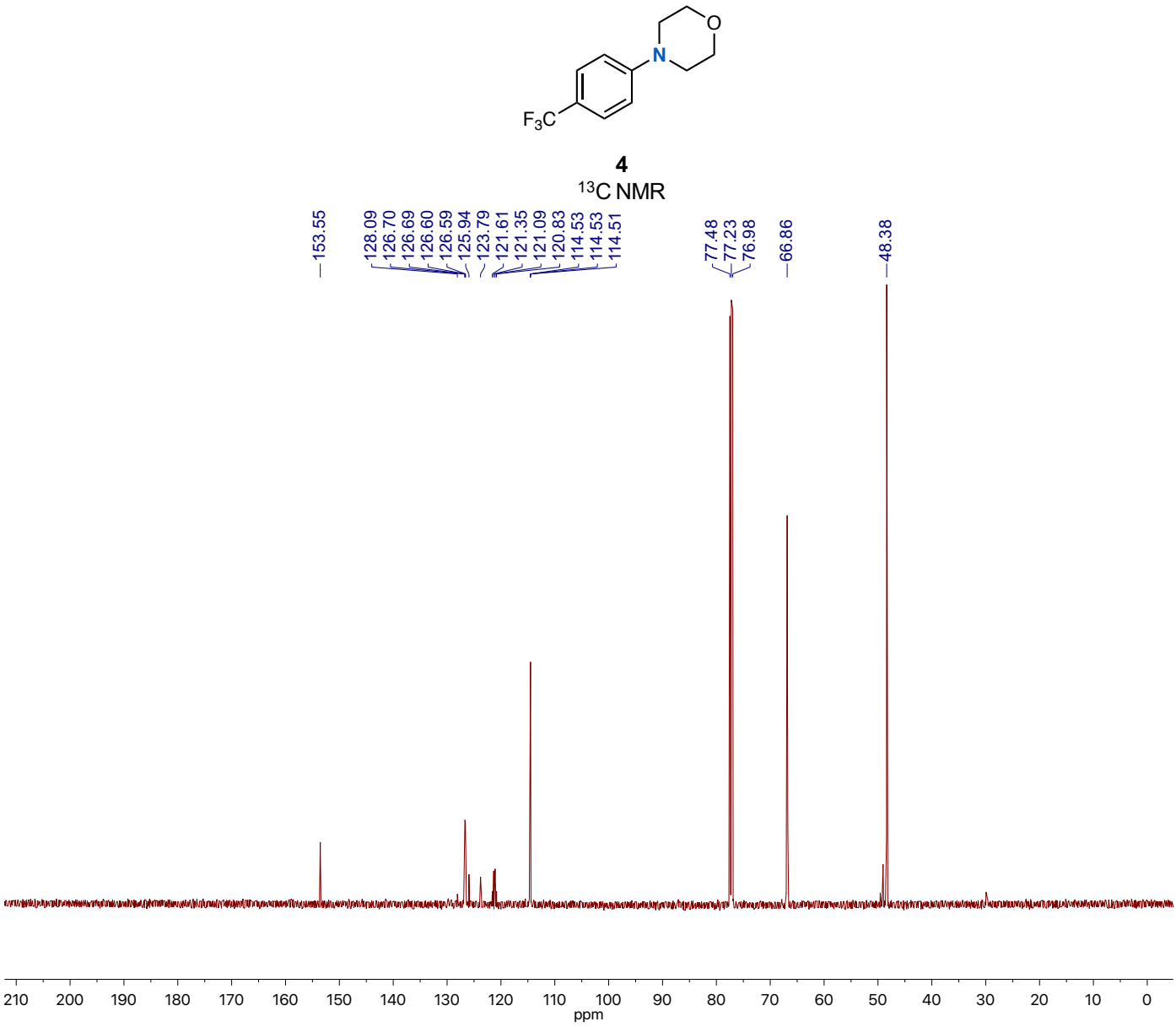


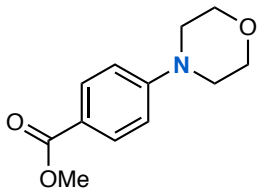

O
N
F3C

4

^{1}H NMR

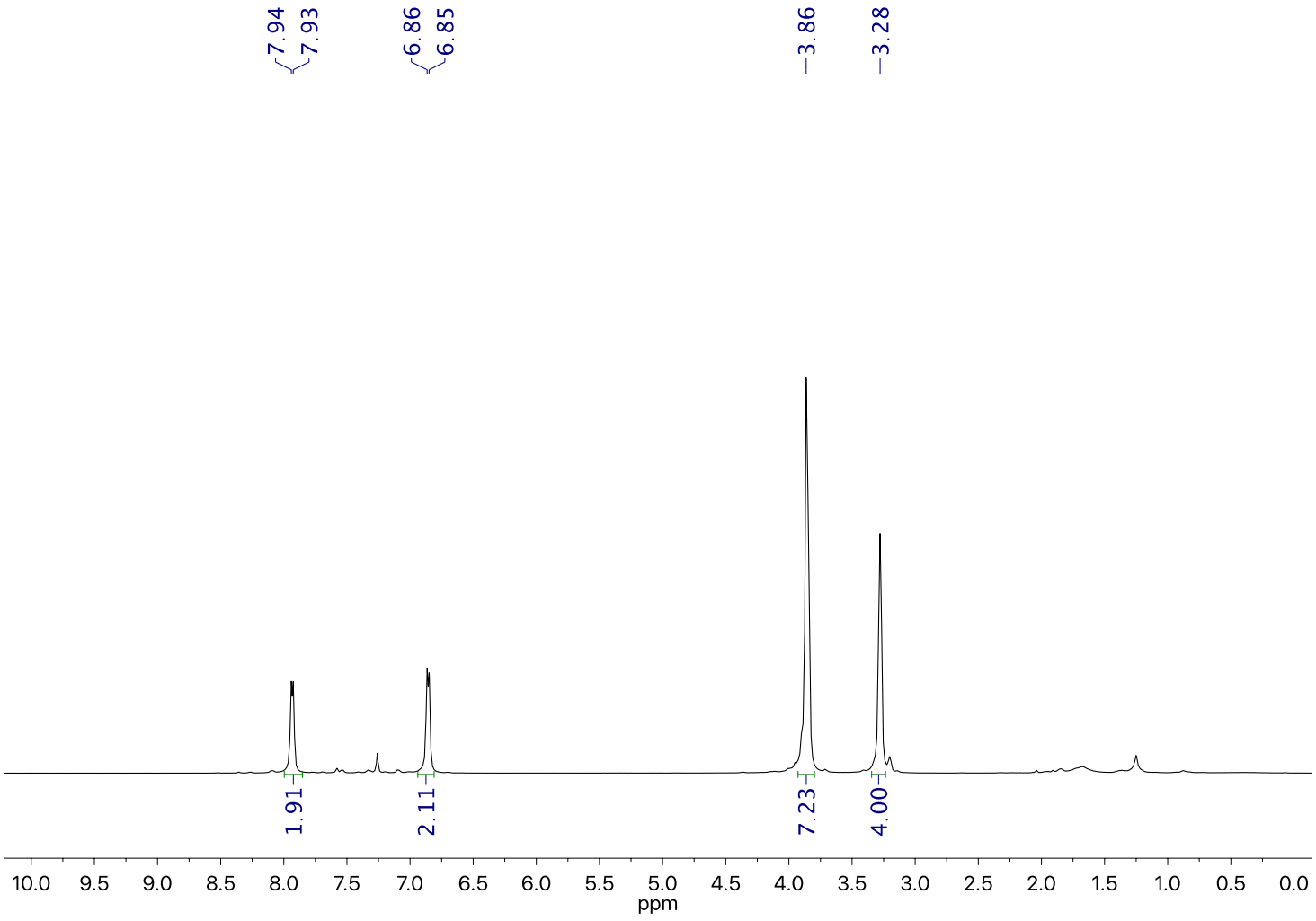

7.51
7.49
7.26
6.93
6.91
3.88
3.87
3.86
3.25
3.24
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

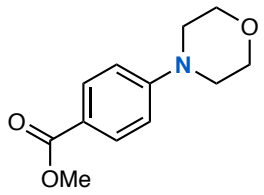

O
N
F3C
4
13C NMR
153.55
128.09
126.70
126.69
126.60
126.59
125.94
123.79
121.61
121.35
121.09
120.83
114.53
114.53
114.51
77.48
77.23
76.98
66.86
48.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
O
OMe

5

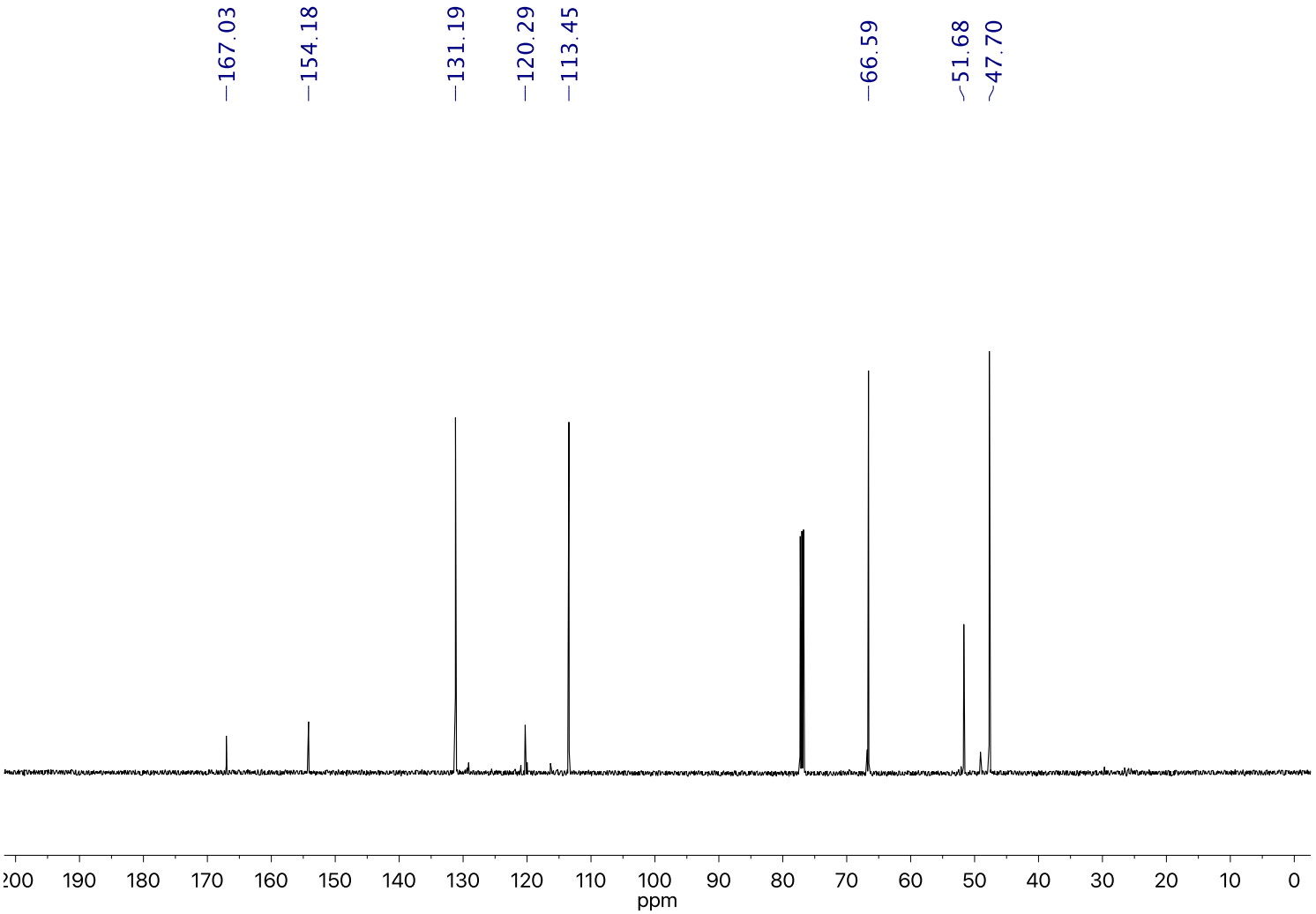
^{1}H NMR

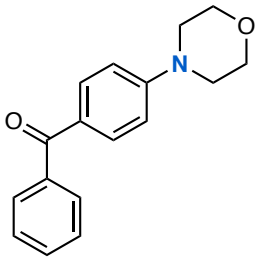

7.94
7.93
6.86
6.85
3.86
3.28
1.91
2.11
7.23
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


O
N
O
OMe

5

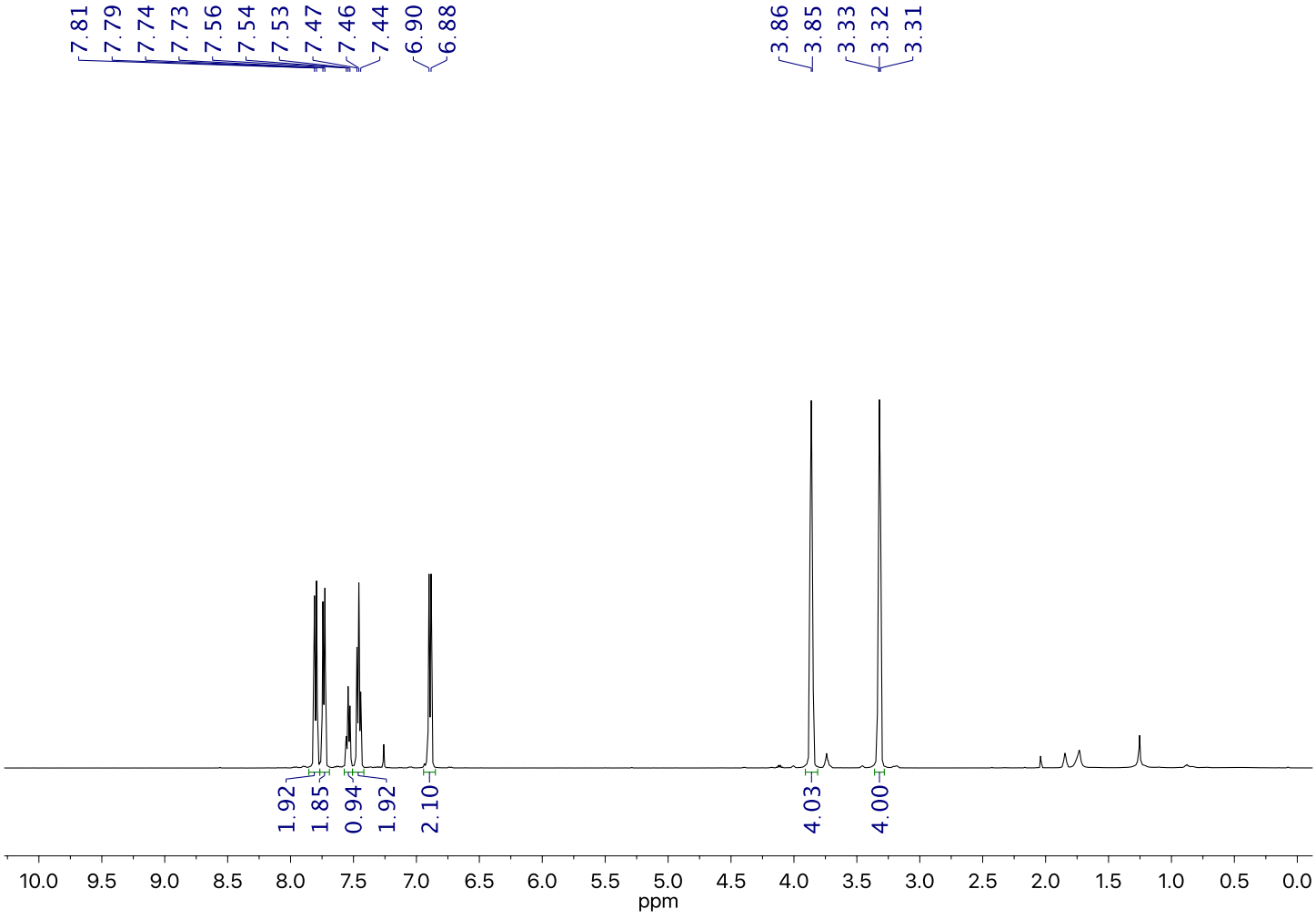
^{13}C NMR

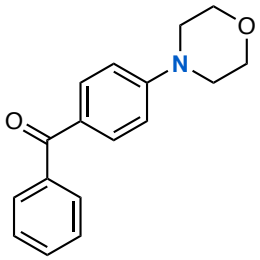

167.03
154.18
131.19
120.29
113.45
66.59
51.68
47.70
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
O

6

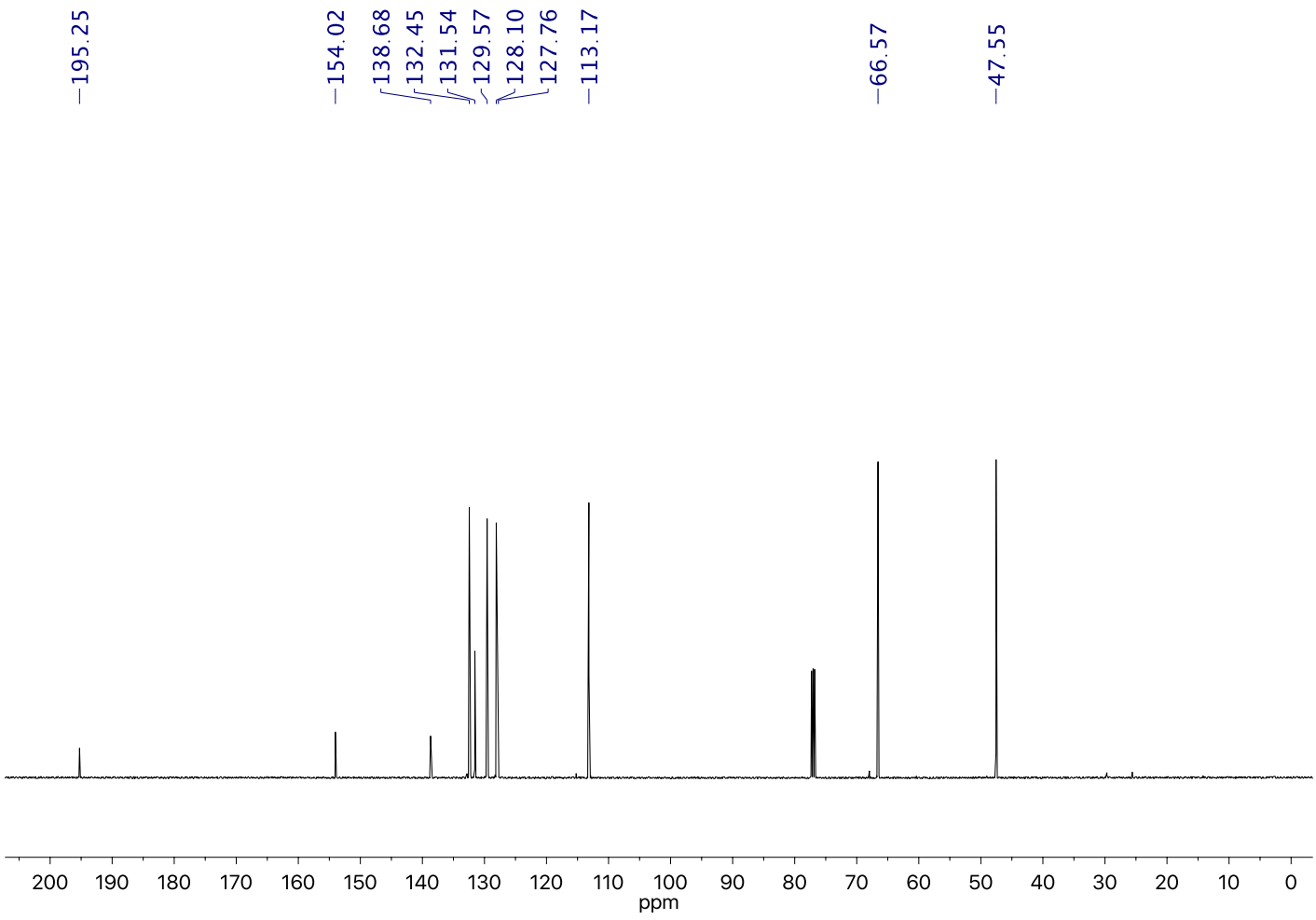
^{1}H NMR

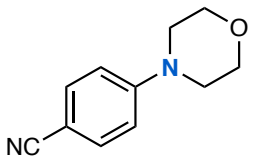

7.81
7.79
7.74
7.73
7.56
7.54
7.53
7.47
7.46
7.44
6.90
6.88
3.86
3.85
3.33
3.32
3.31
1.92
1.85
0.94
1.92
2.10
4.03
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N
O

6

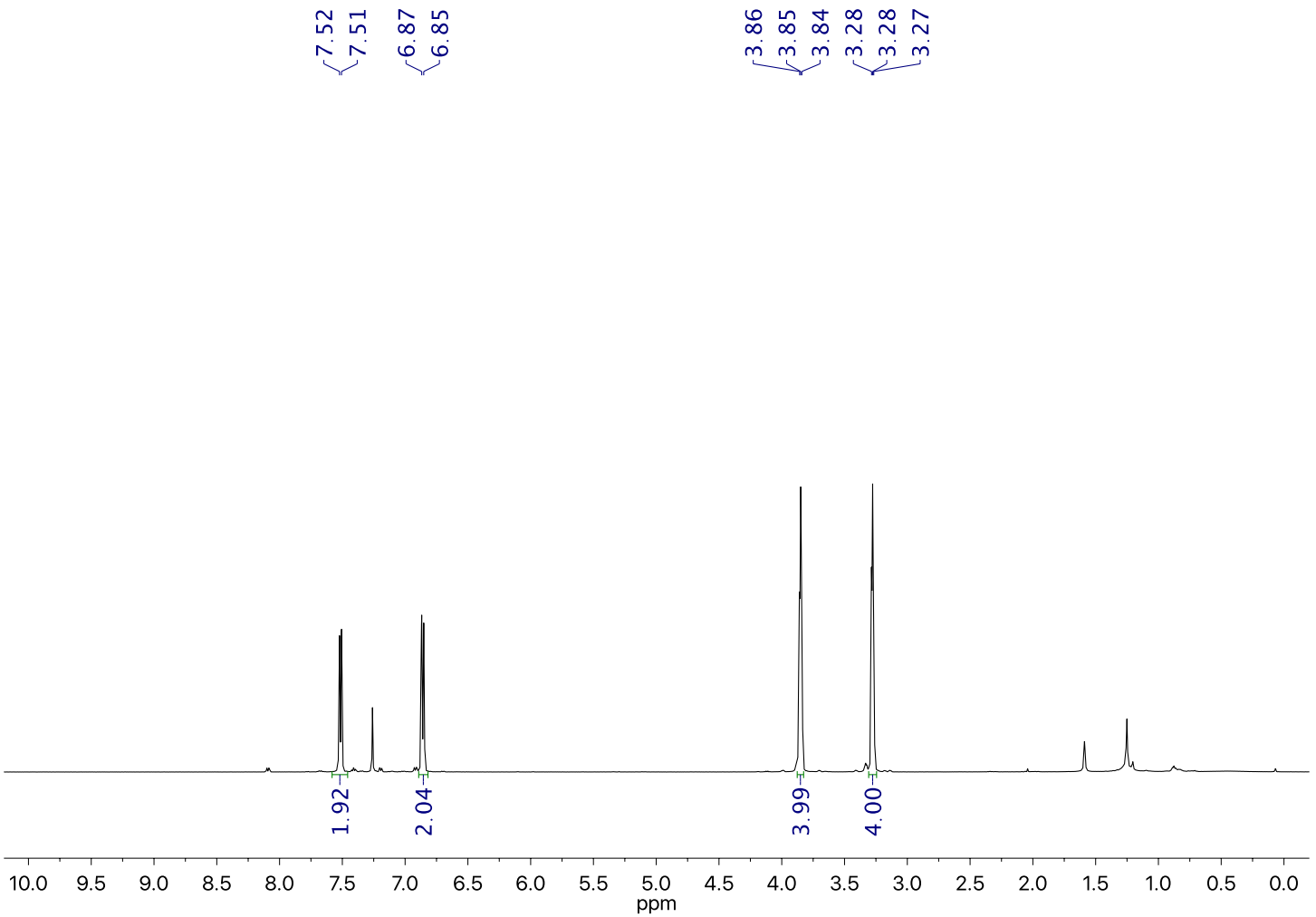
^{13}C NMR

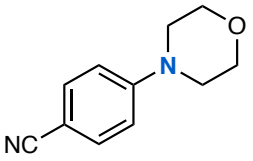

195.25
154.02
138.68
132.45
131.54
129.57
128.10
127.76
113.17
66.57
47.55
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
NC

7

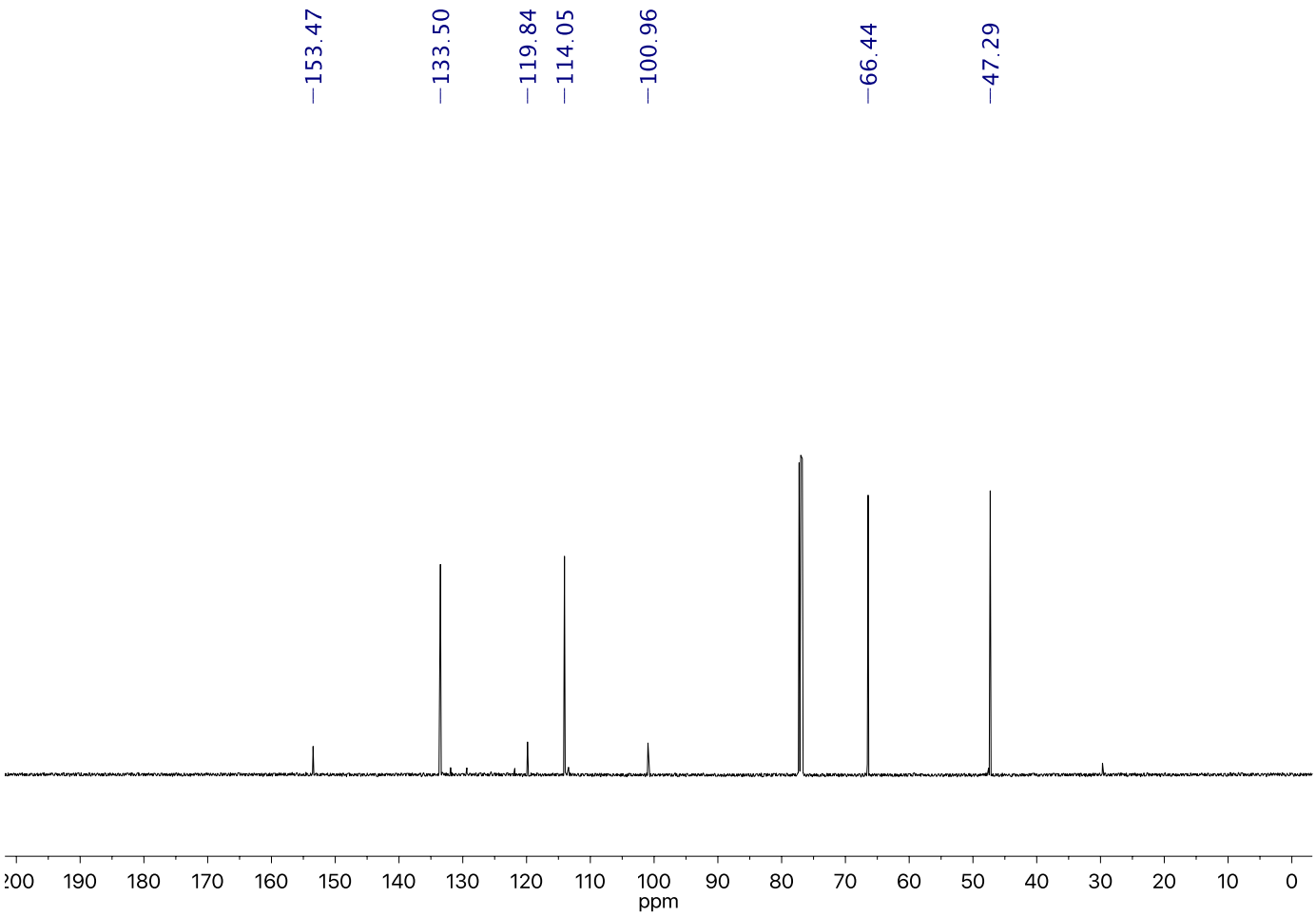
^{1}H NMR

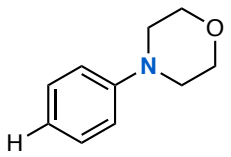

7.52
7.51
6.87
6.85
3.86
3.85
3.84
3.28
3.28
3.27
1.92
2.04
3.99
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N
NC

7

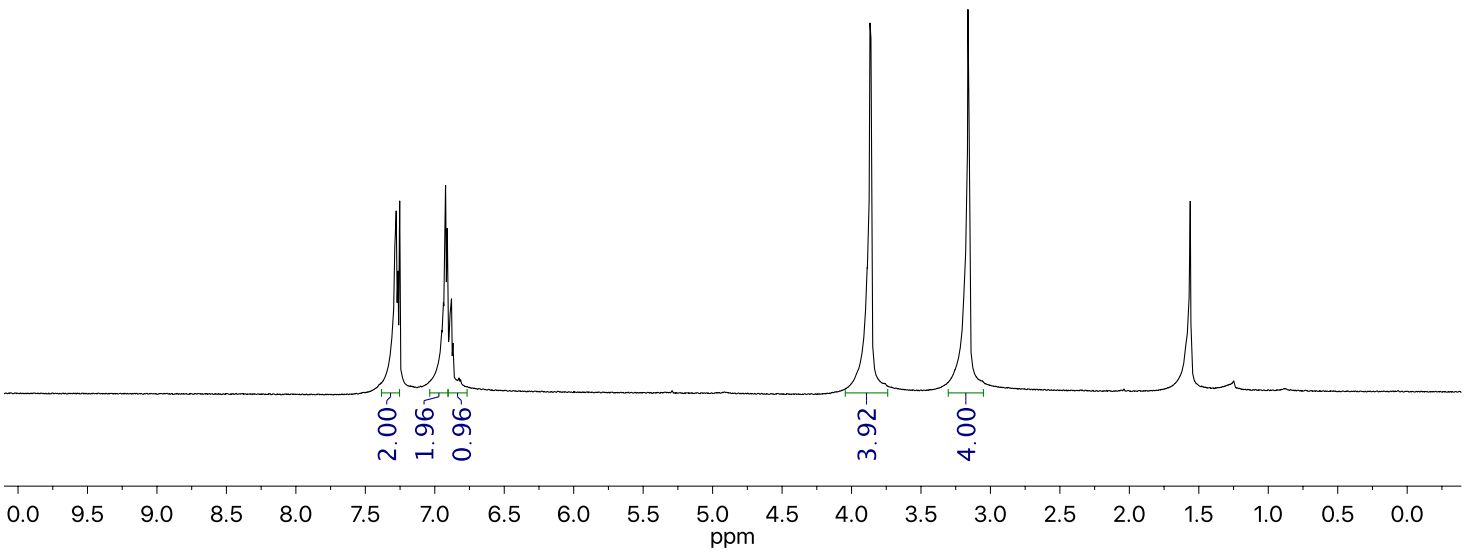
^{13}C NMR

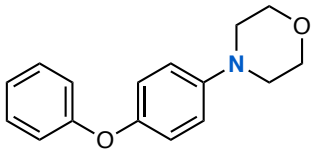

153.47
133.50
119.84
114.05
100.96
66.44
47.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
N
H

8

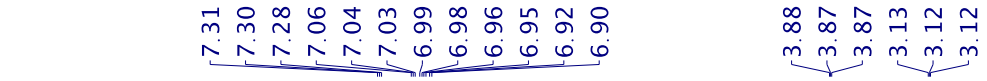
^{1}H NMR

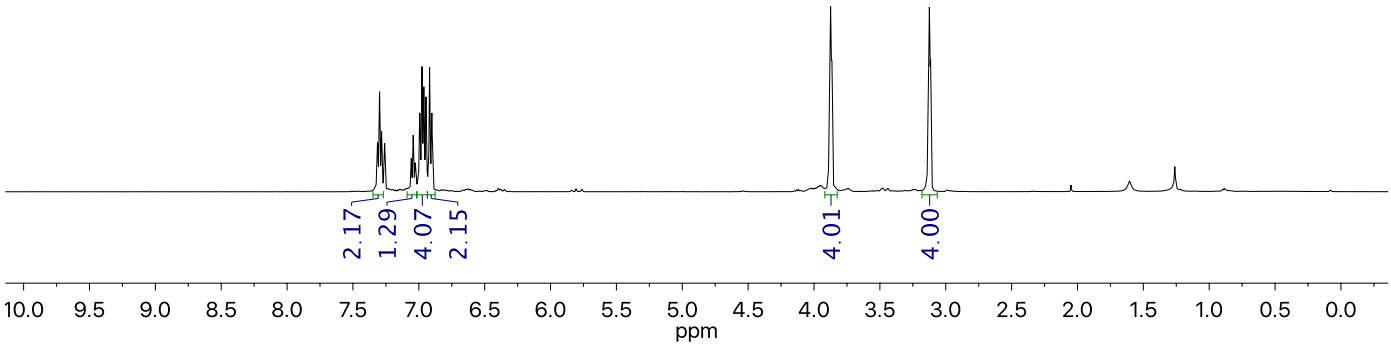

7.29
7.28
7.27
6.94
6.92
6.91
6.89
6.88
6.87
3.89
3.88
3.87
3.86
3.85
3.18
3.18
3.16
3.16
3.15
2.00
1.96
0.96
3.92
4.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

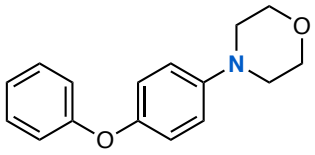

O
N
O

9

^{1}H NMR

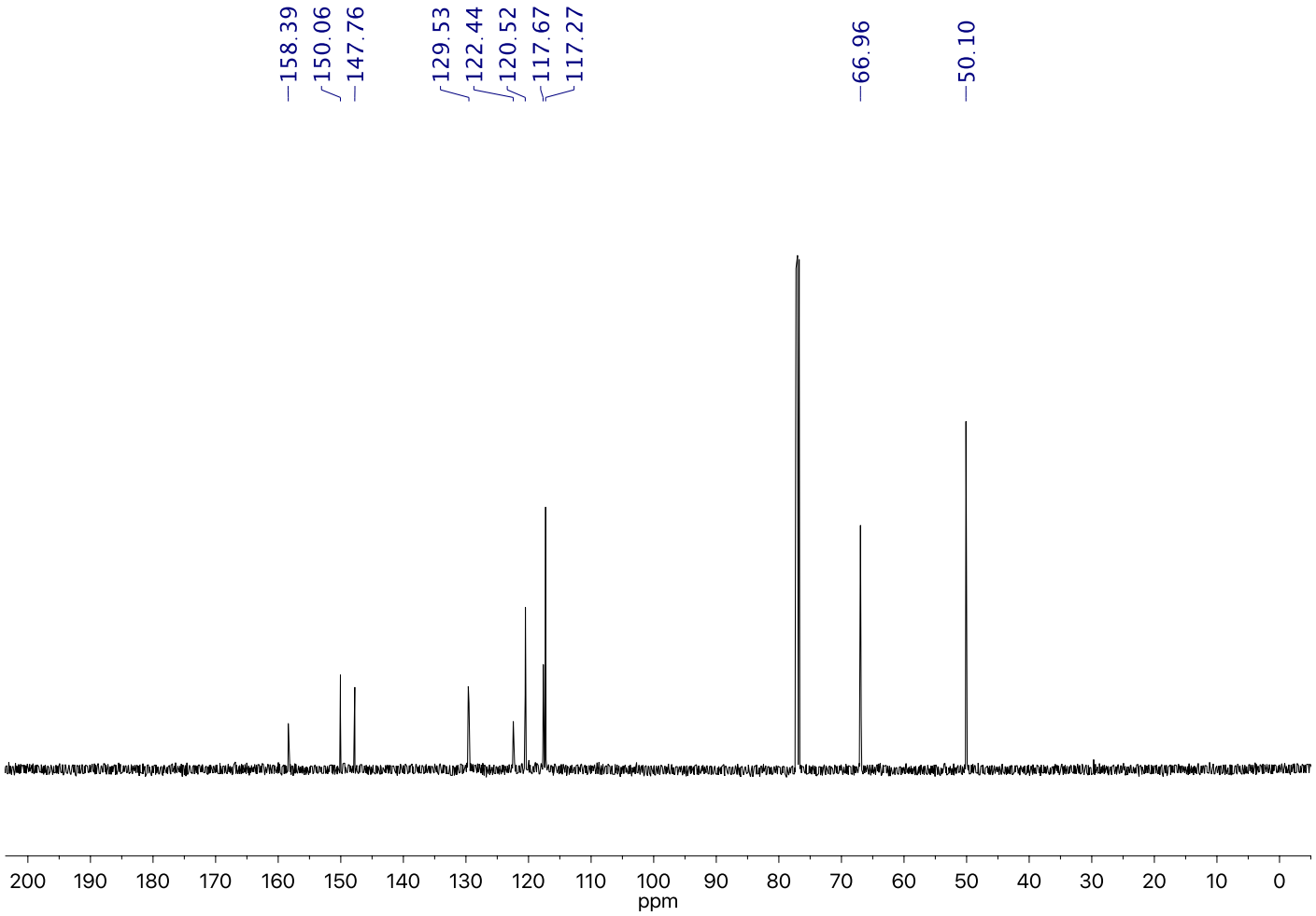

7.31
7.30
7.28
7.06
7.04
7.03
6.99
6.98
6.96
6.95
6.92
6.90
3.88
3.87
3.87
3.13
3.12
3.12

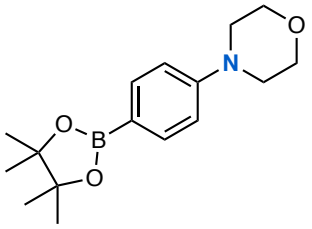

2.17
1.29
4.07
2.15
4.01
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N
O

9

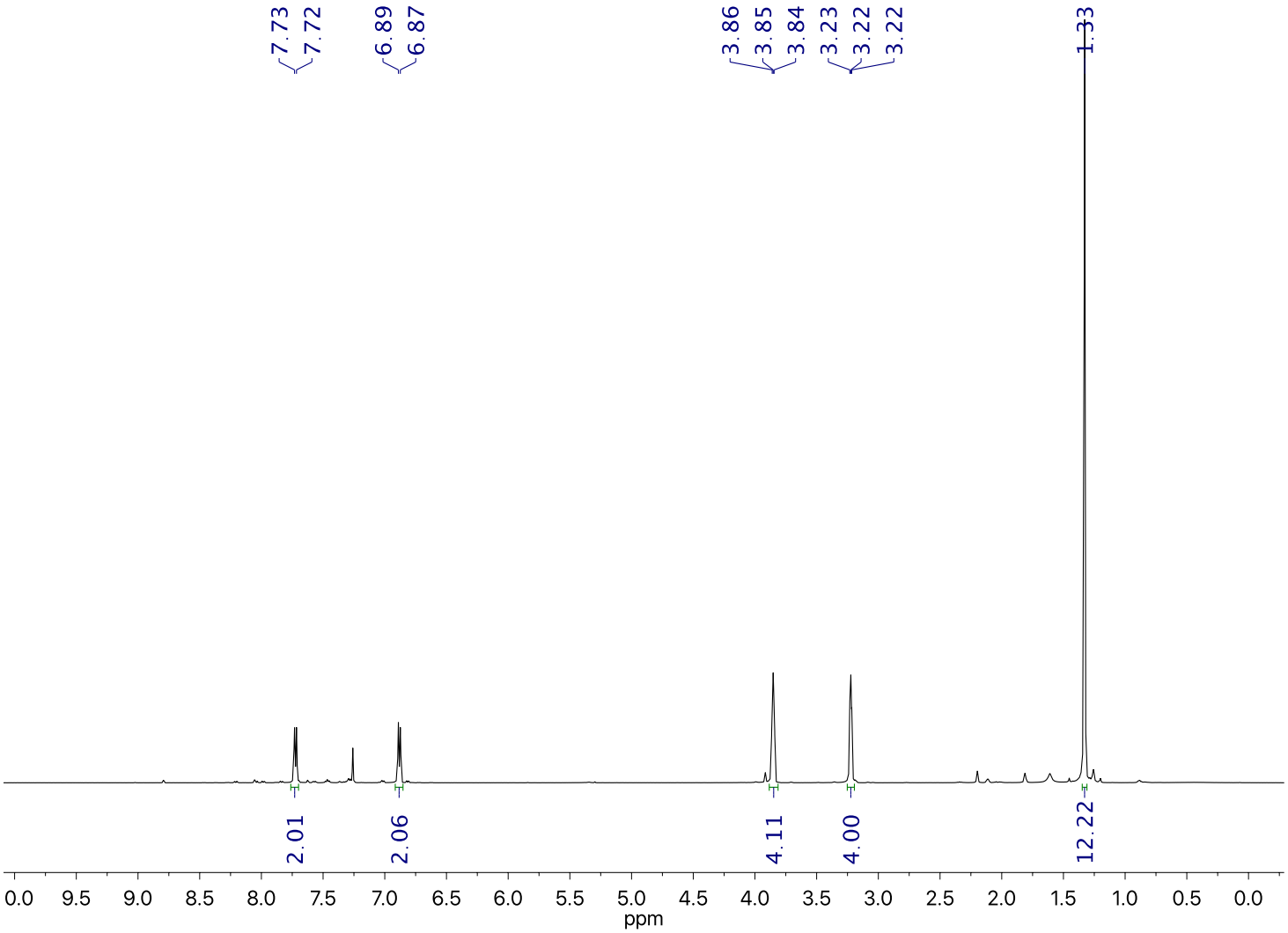
^{13}C NMR

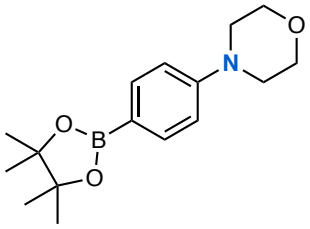

158.39
150.06
147.76
129.53
122.44
120.52
117.67
117.27
66.96
50.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
N
O
B
O

10

^{1}H NMR

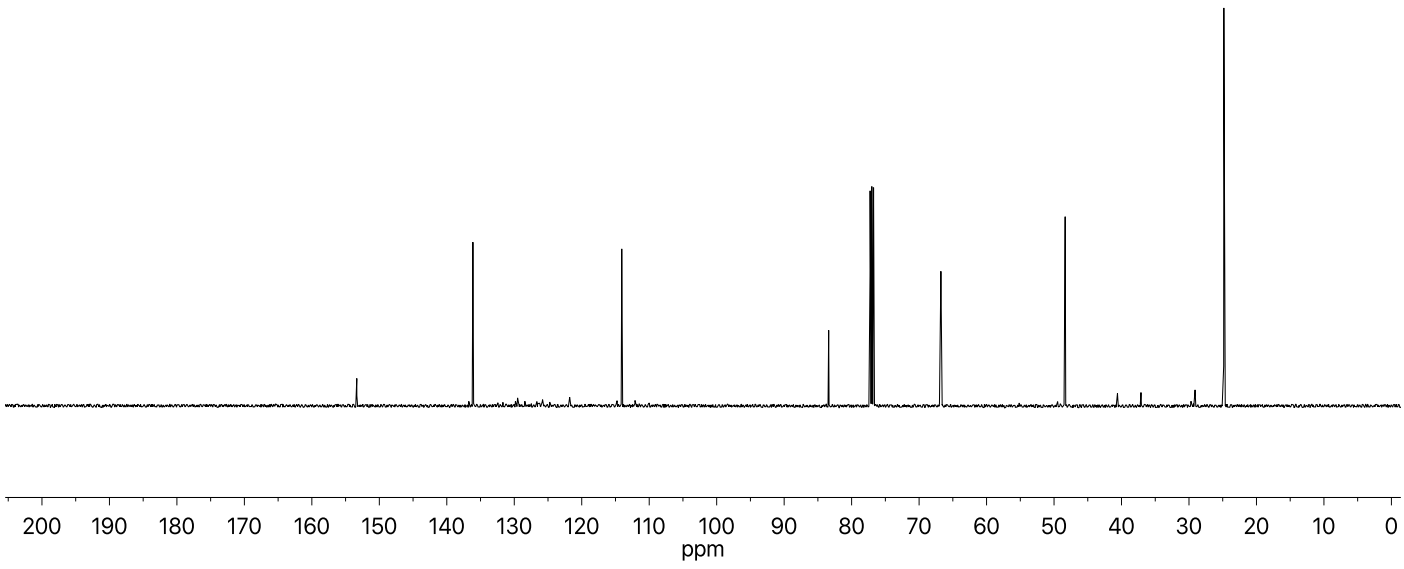

7.73
7.72
6.89
6.87
3.86
3.85
3.84
3.23
3.22
3.22
1.33
2.01
2.06
4.11
4.00
12.22
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

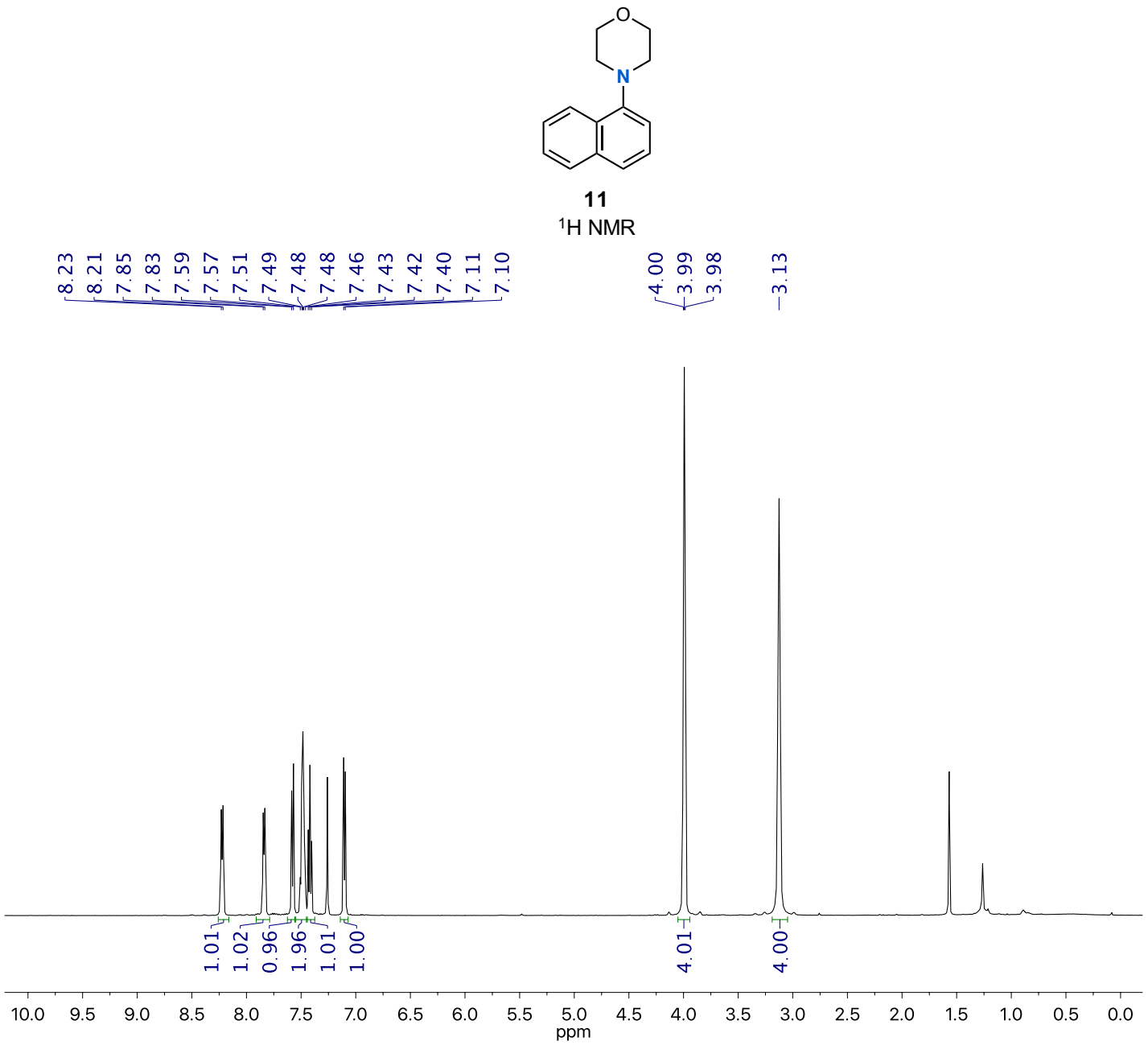


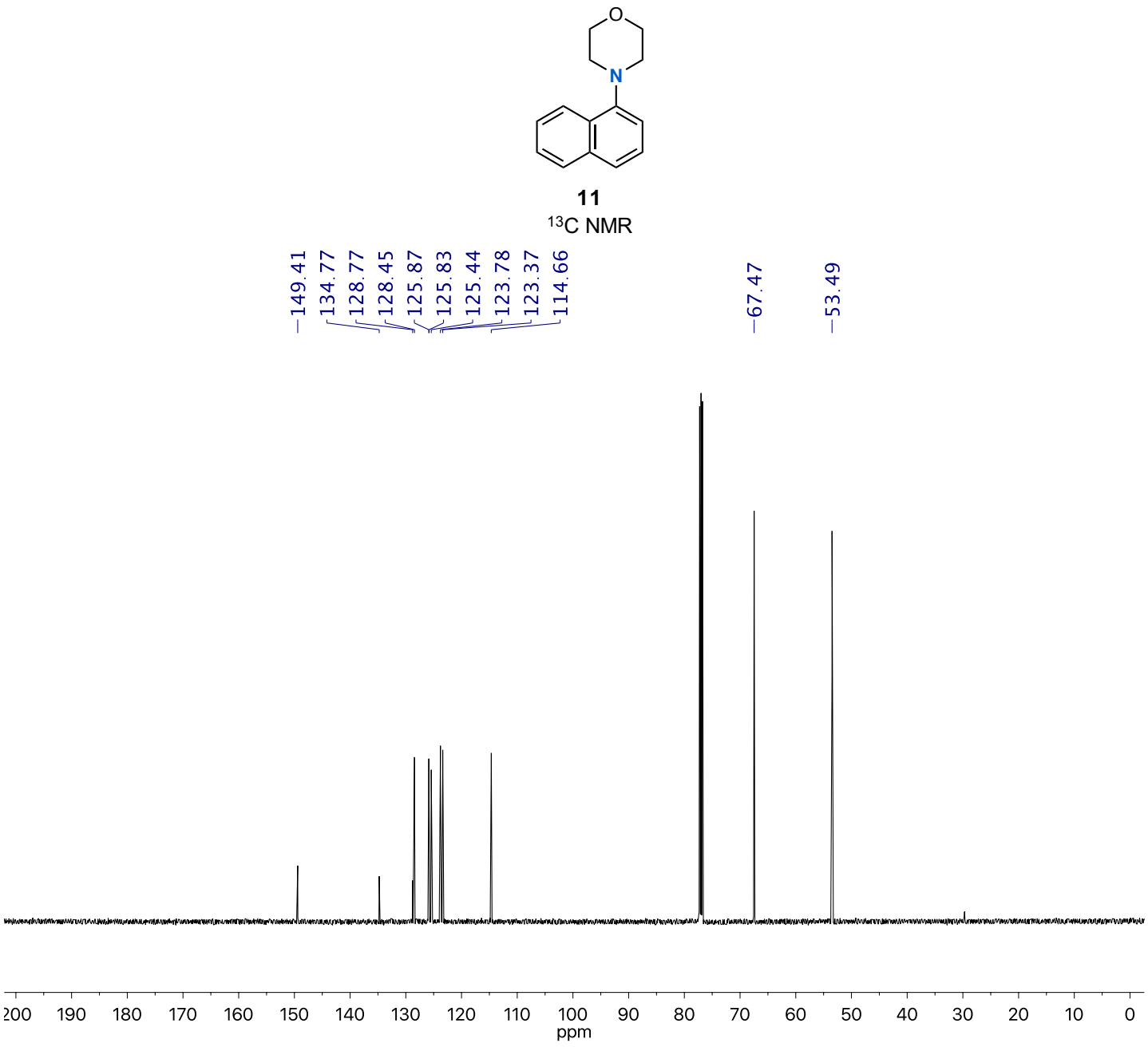
10

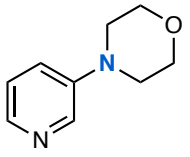
^{13}C NMR

153.34
136.13
114.07
83.40
66.77
48.35
24.83



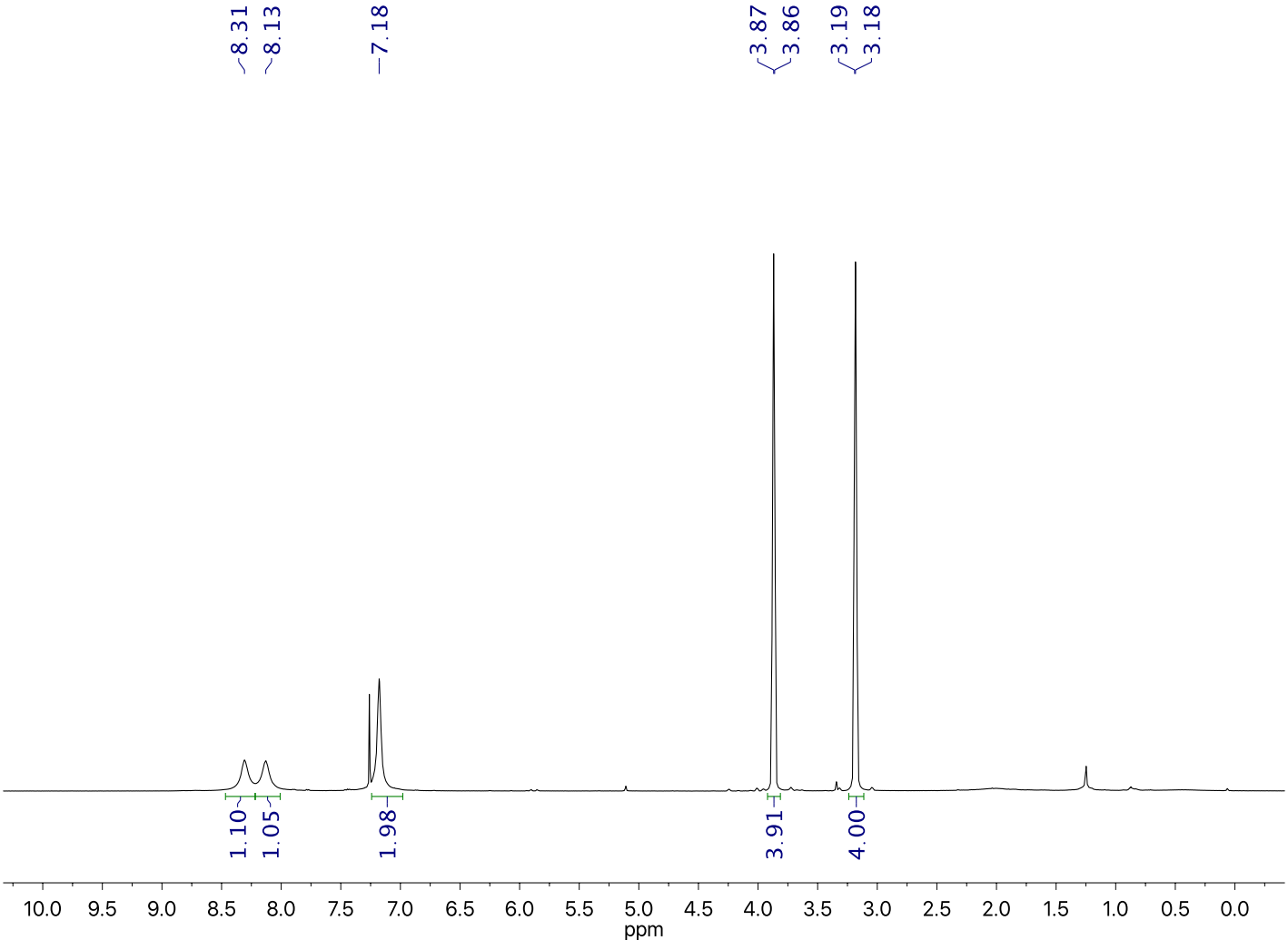

O
N
11
1H NMR
8.23
8.21
7.85
7.83
7.59
7.57
7.51
7.49
7.48
7.48
7.46
7.43
7.42
7.40
7.11
7.10
4.00
3.99
3.98
3.13
1.01
1.02
0.96
1.96
1.01
1.00
4.01
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

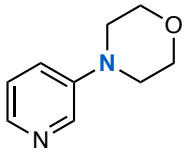

O
N
11
13C NMR
149.41
134.77
128.77
128.45
125.87
125.83
125.44
123.78
123.37
114.66
67.47
53.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
N
N

12

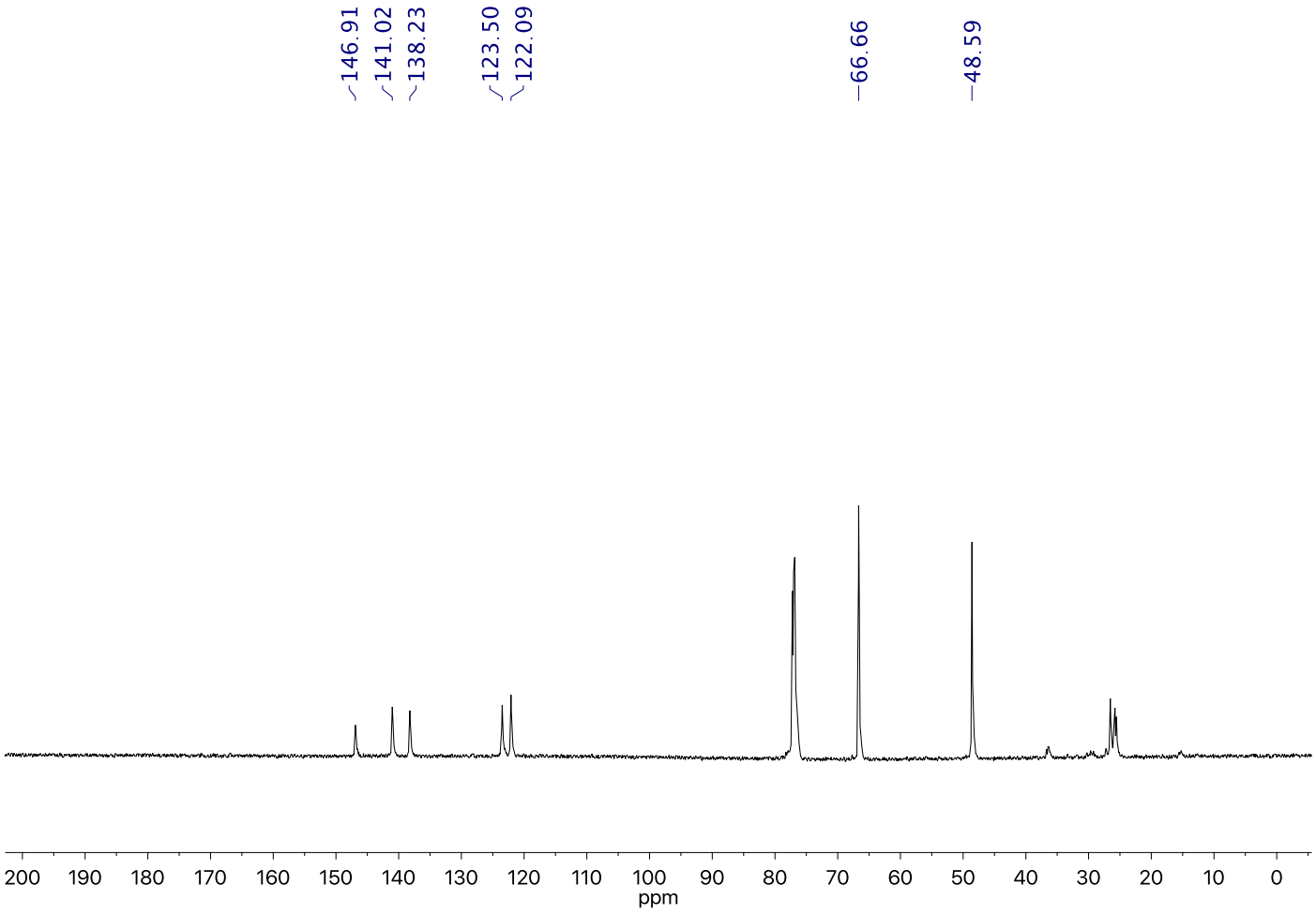
^{1}H NMR

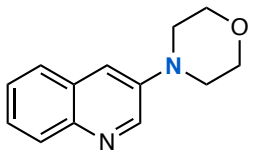

8.31
8.13
7.18
3.87
3.86
3.19
3.18
1.10
1.05
1.98
3.91
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


O
N
N

12

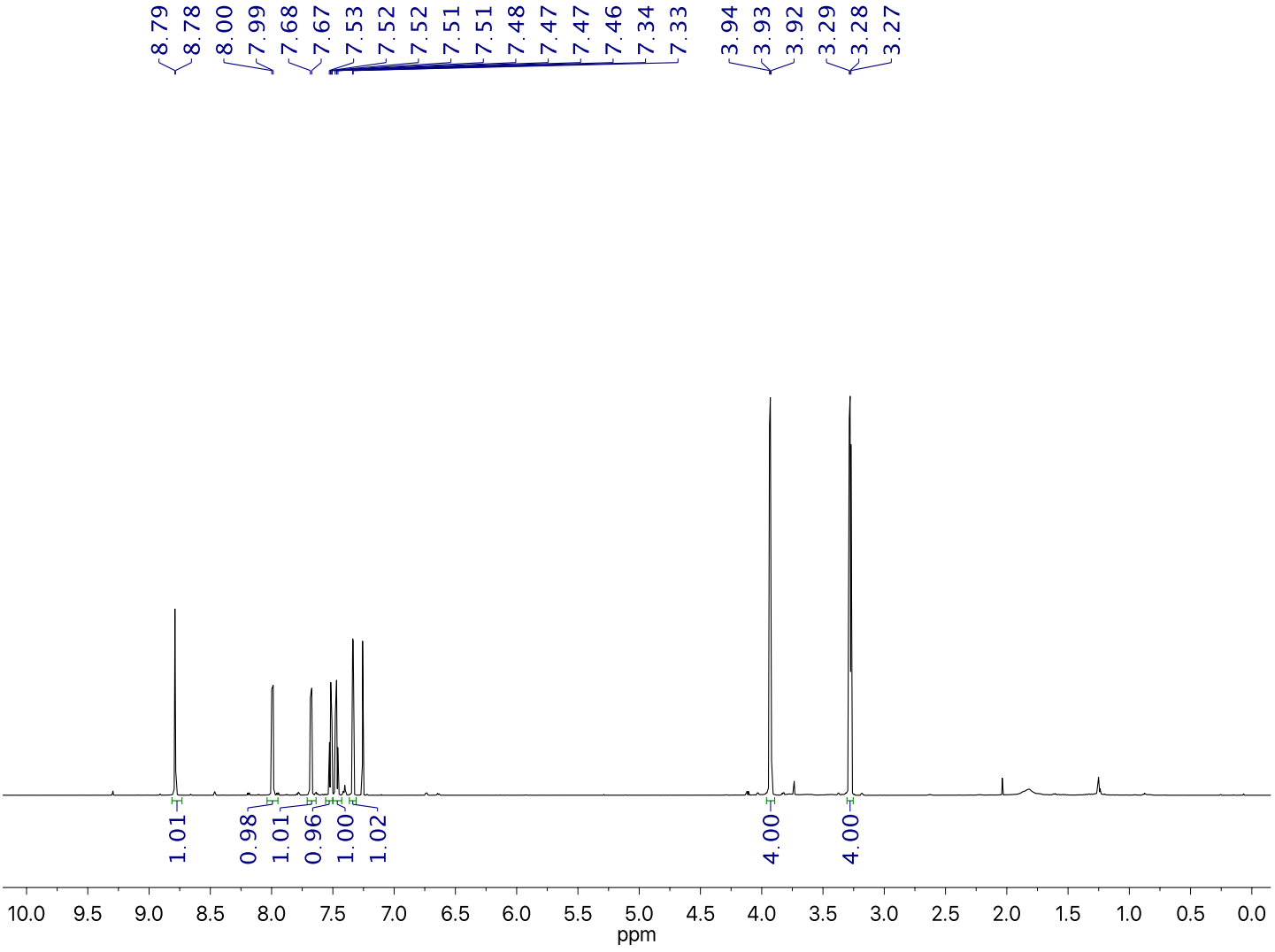
^{13}C NMR

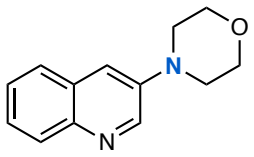

146.91
141.02
138.23
123.50
122.09
66.66
48.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
N
N

13

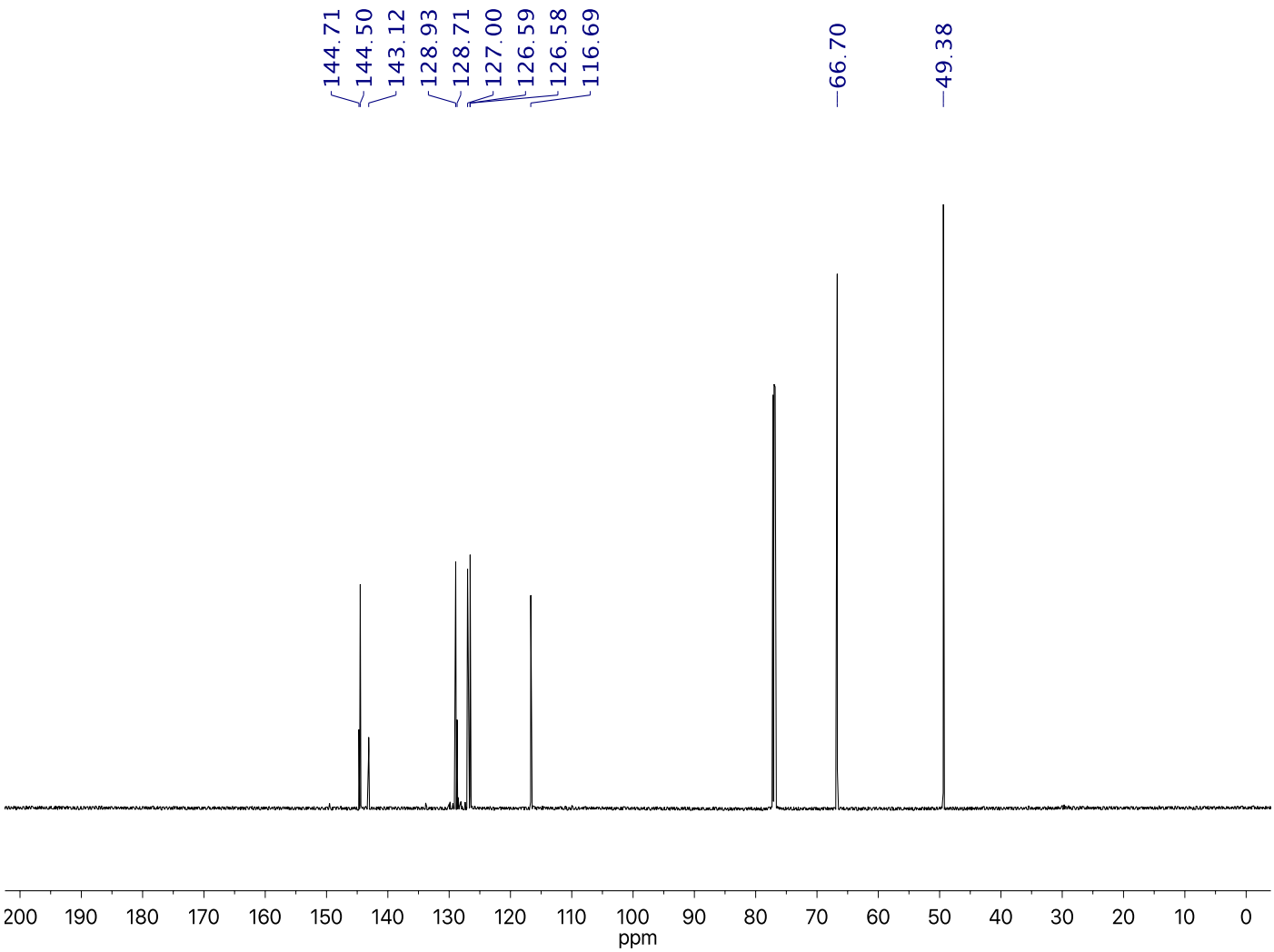
^{1}H NMR

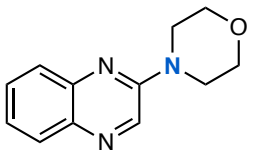

8.79
8.78
8.00
7.99
7.68
7.67
7.53
7.52
7.52
7.51
7.51
7.48
7.47
7.47
7.46
7.34
7.33
3.94
3.93
3.92
3.29
3.28
3.27
1.01
0.98
1.01
0.96
1.00
1.02
4.00
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N
N

13

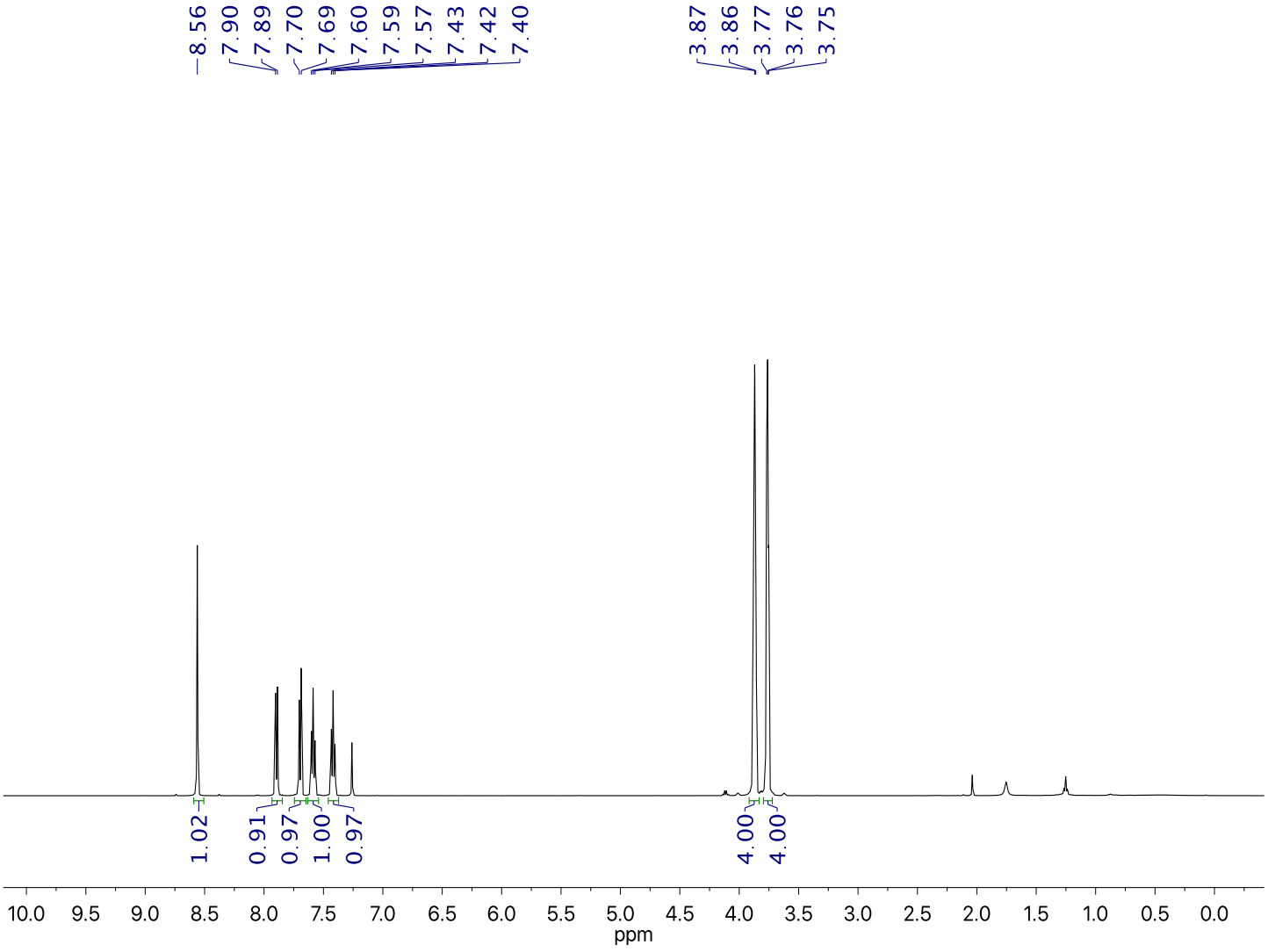
^{13}C NMR

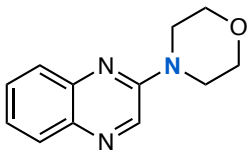

144.71
144.50
143.12
128.93
128.71
127.00
126.59
126.58
116.69
66.70
49.38
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



14

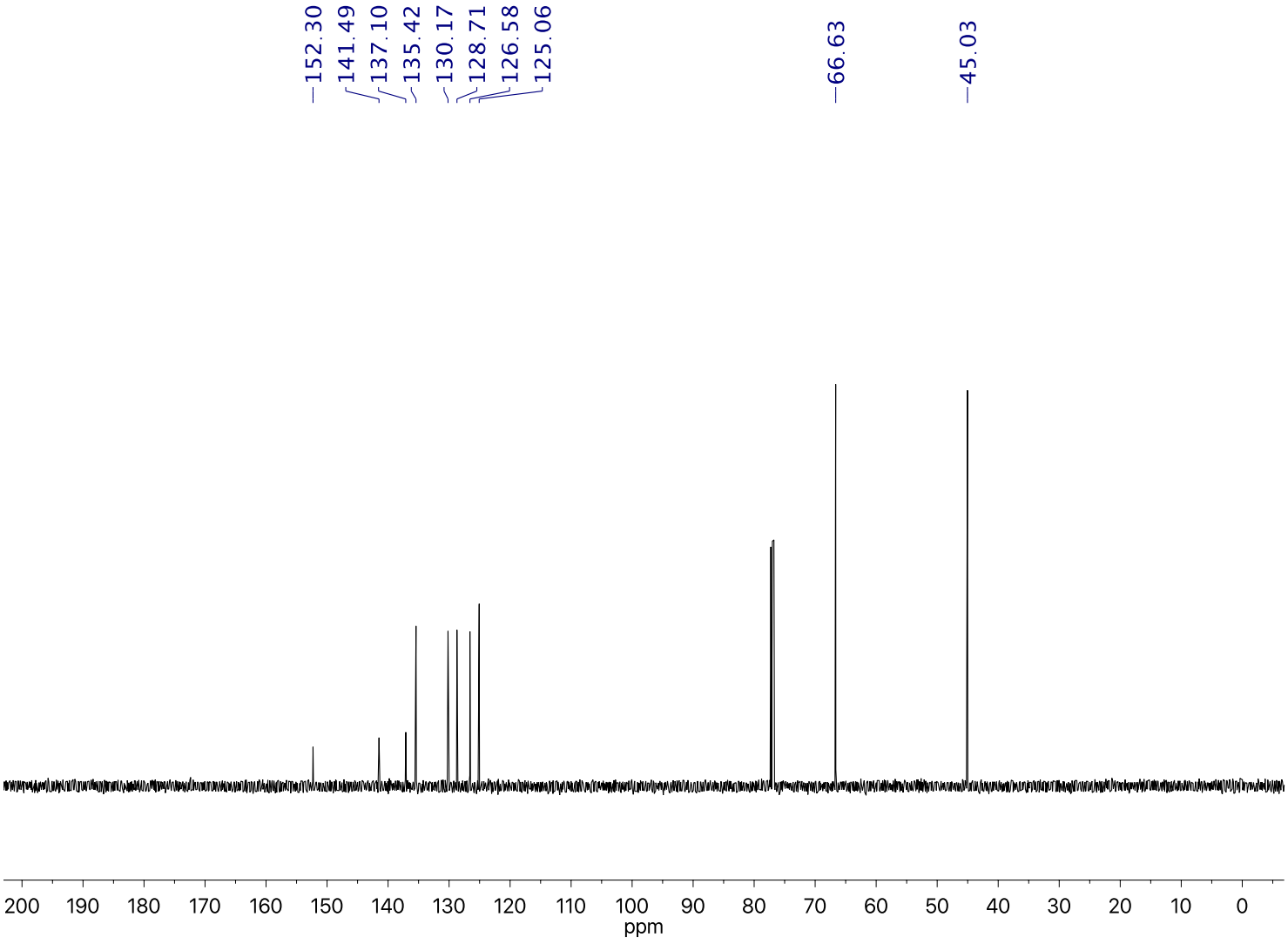
^{1}H NMR

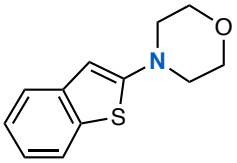

8.56
7.90
7.89
7.70
7.69
7.60
7.59
7.57
7.43
7.42
7.40
3.87
3.86
3.77
3.76
3.75
1.02
0.91
0.97
1.00
0.97
4.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm



14

^{13}C NMR

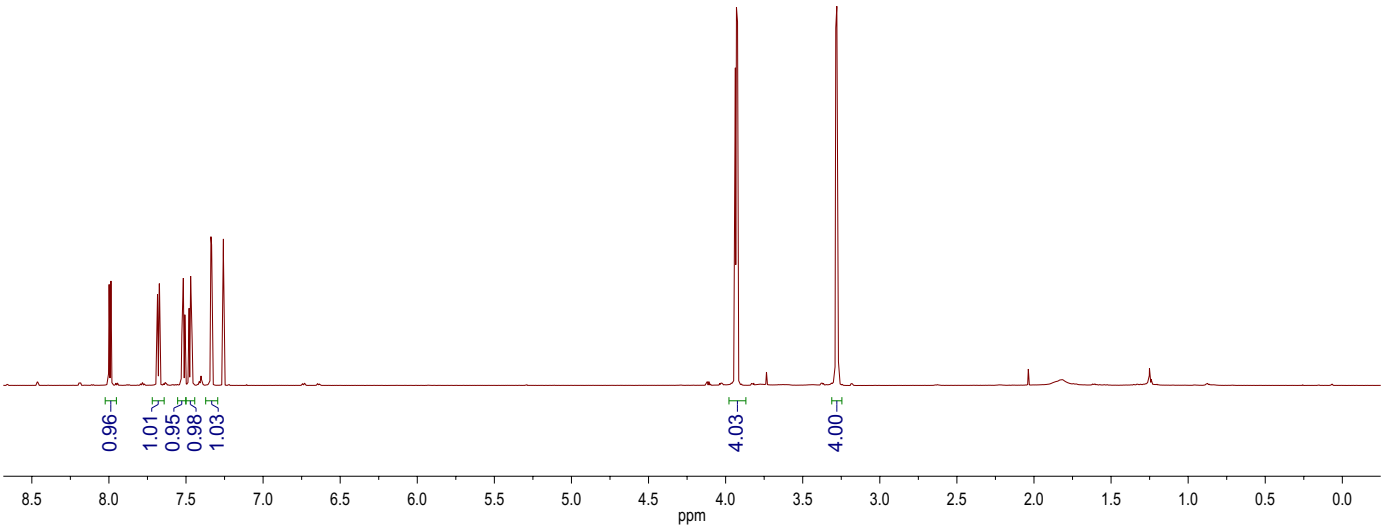

152.30
141.49
137.10
135.42
130.17
128.71
126.58
125.06
66.63
45.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

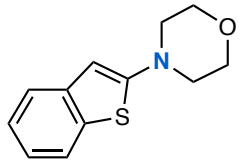

O
N
S

15

^{1}H NMR

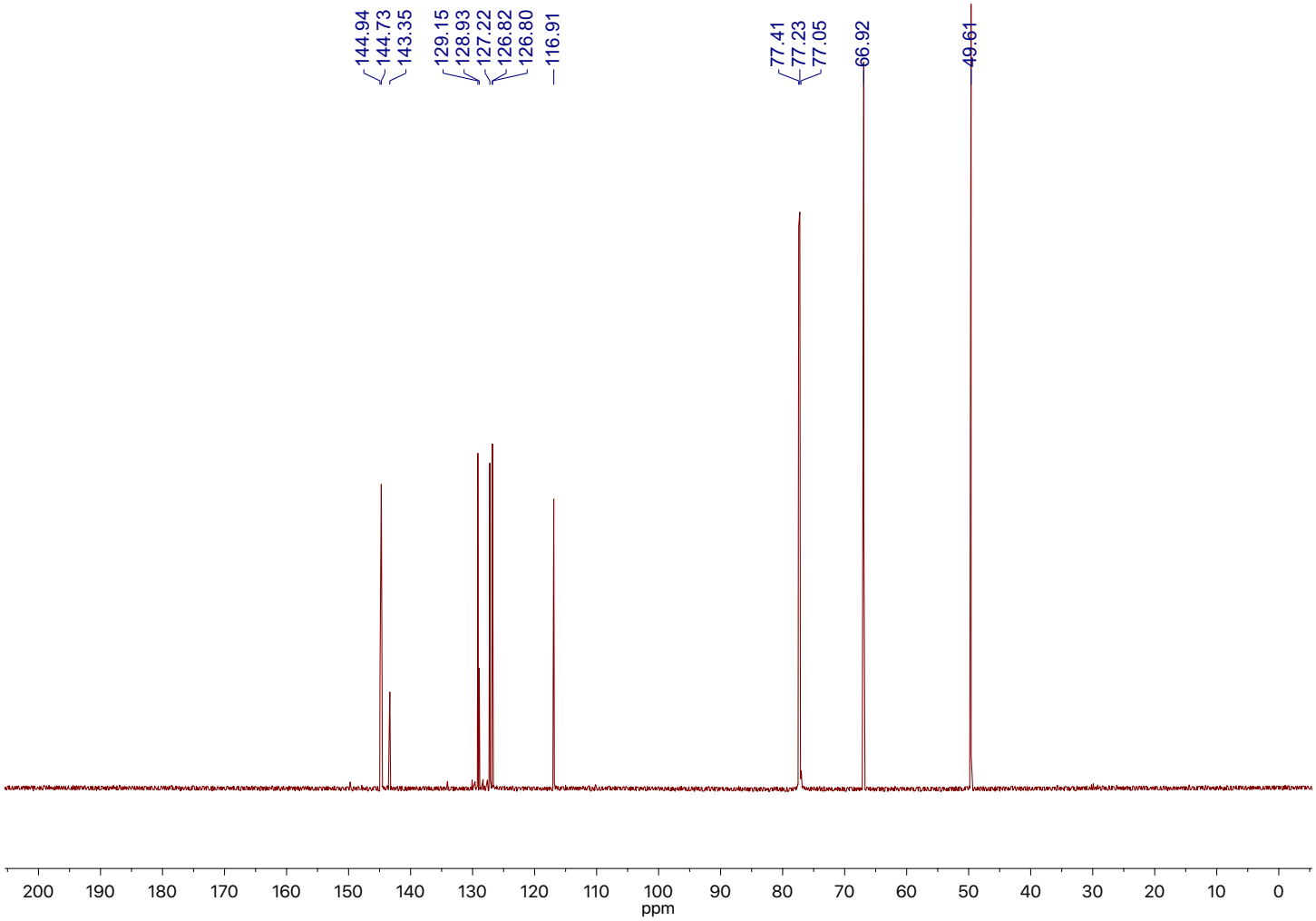

8.00
8.00
7.99
7.99
7.69
7.68
7.67
7.67
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.34
7.33
7.26
3.94
3.93
3.93
3.93
3.92
3.29
3.28
3.28
3.28
3.27

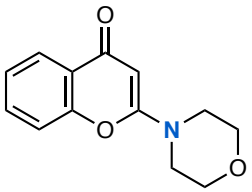

0.96
1.01
0.95
0.98
1.03
4.03
4.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N
S

15

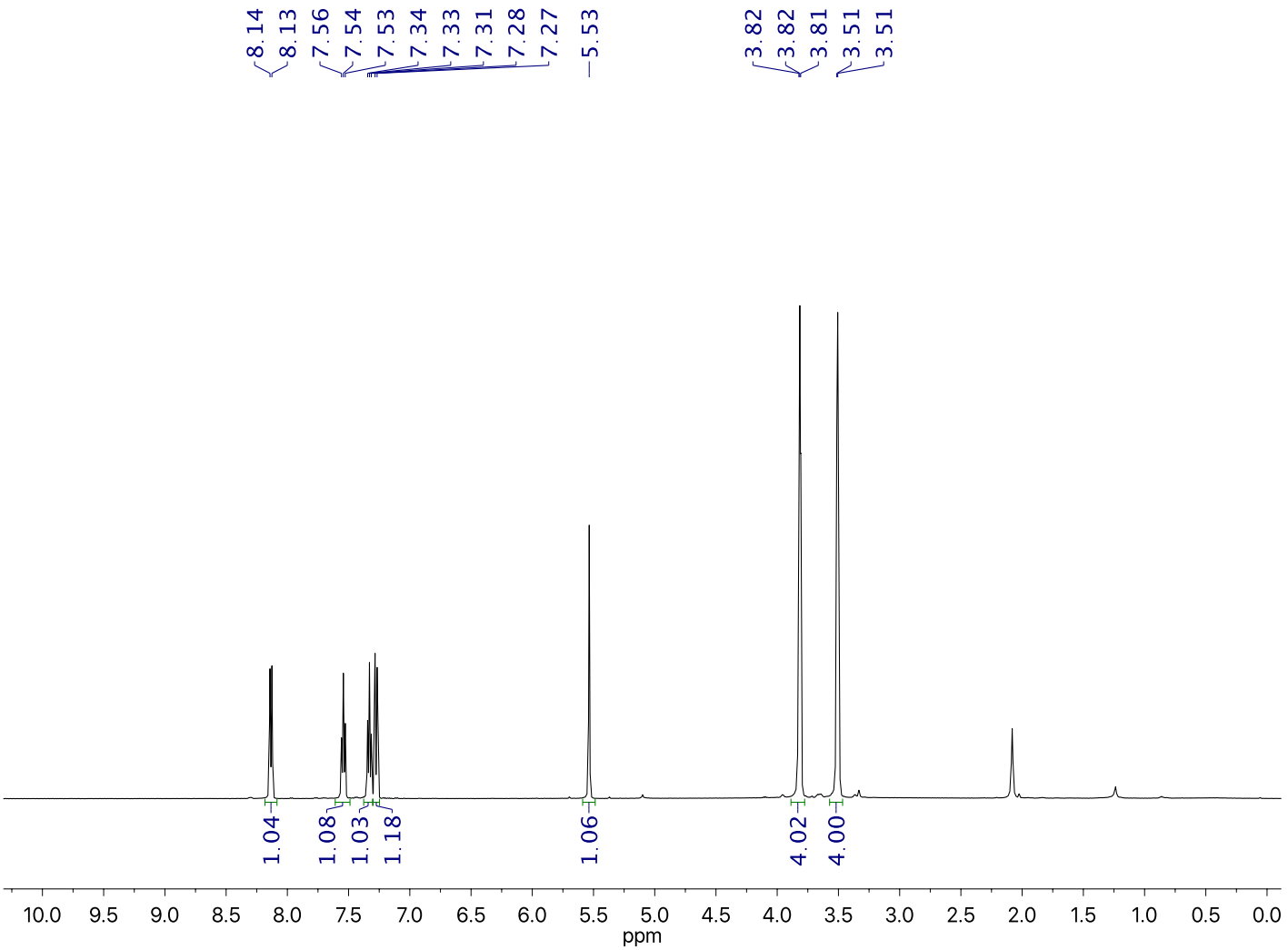
^{13}C NMR

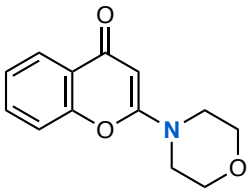

144.94
144.73
143.35
129.15
128.93
127.22
126.82
126.80
116.91
77.41
77.23
77.05
66.92
49.61
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
O
N
O

17

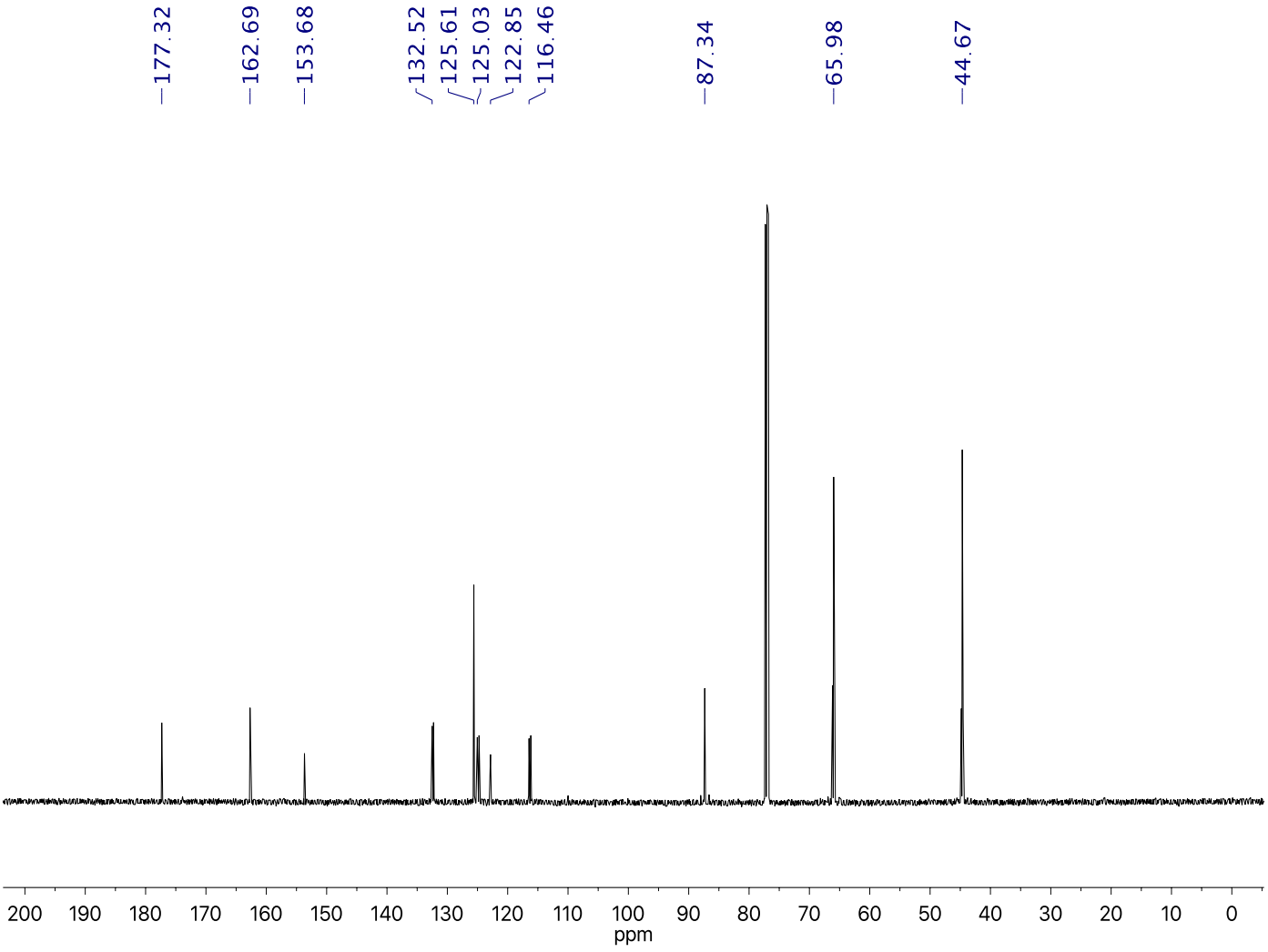
^{1}H NMR

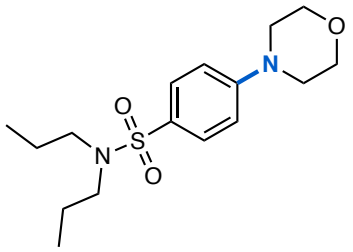

8.14
8.13
7.56
7.54
7.53
7.34
7.33
7.31
7.28
7.27
5.53
3.82
3.82
3.81
3.51
3.51
1.04
1.08
1.03
1.18
1.06
4.02
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
O
N
O

17

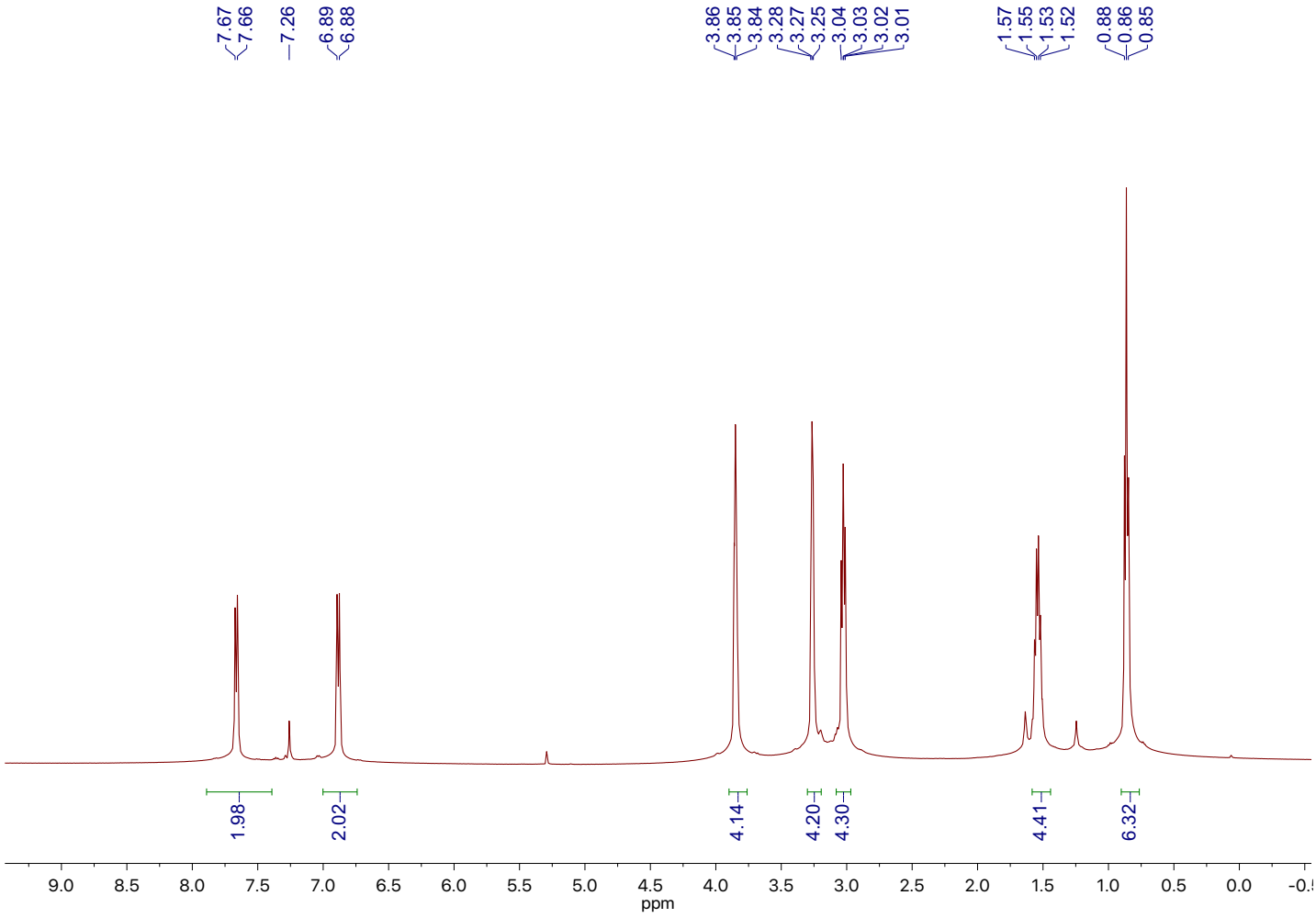
^{13}C NMR

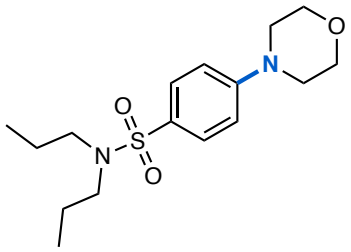

177.32
162.69
153.68
132.52
125.61
125.03
122.85
116.46
87.34
65.98
44.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



18

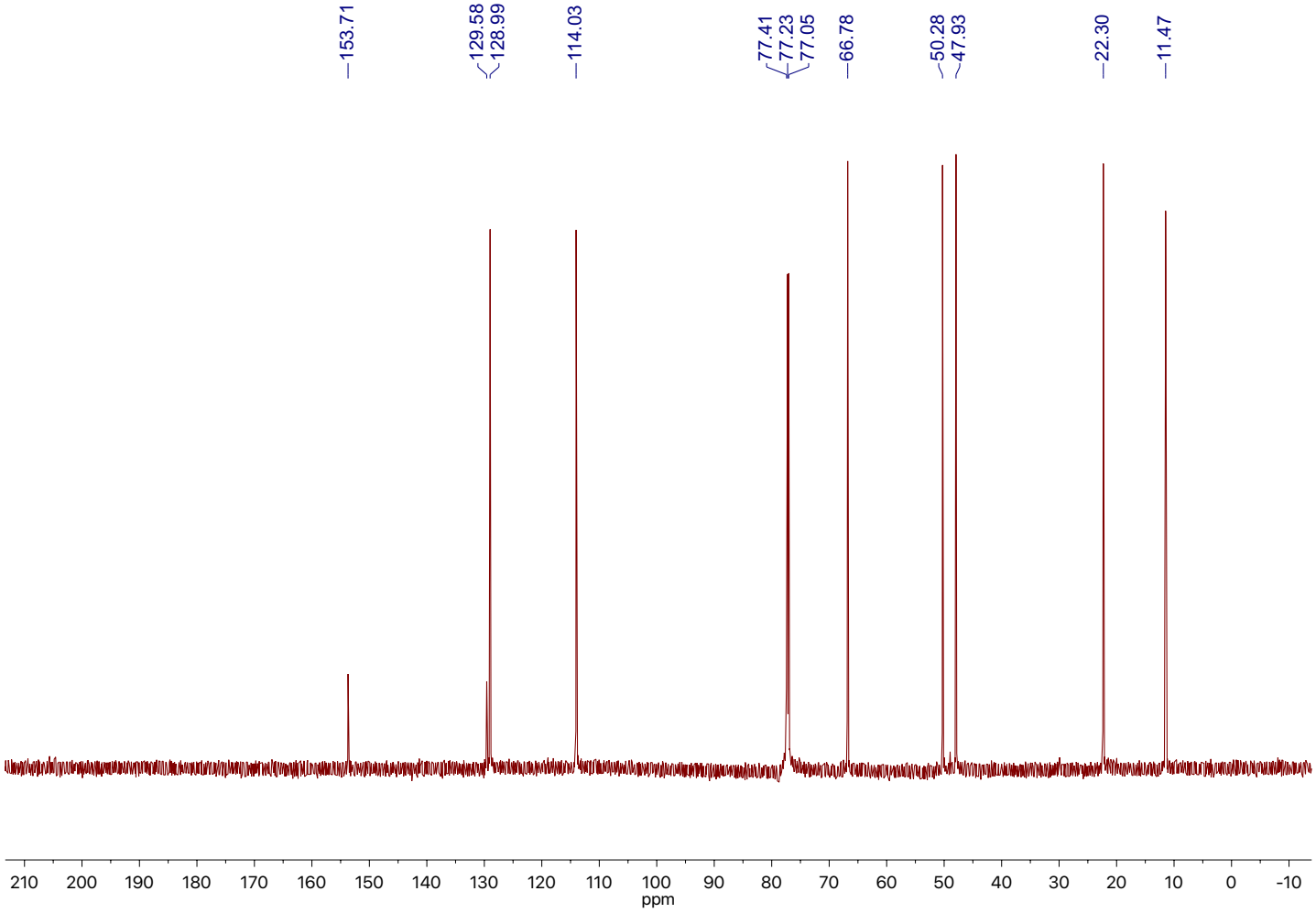
^{1}H NMR

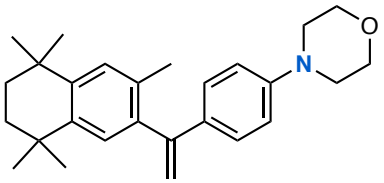

7.67
7.66
7.26
6.89
6.88
3.86
3.85
3.84
3.28
3.27
3.25
3.04
3.03
3.02
3.01
1.57
1.55
1.53
1.52
0.88
0.86
0.85
1.98
2.02
4.14
4.20
4.30
4.41
6.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



18

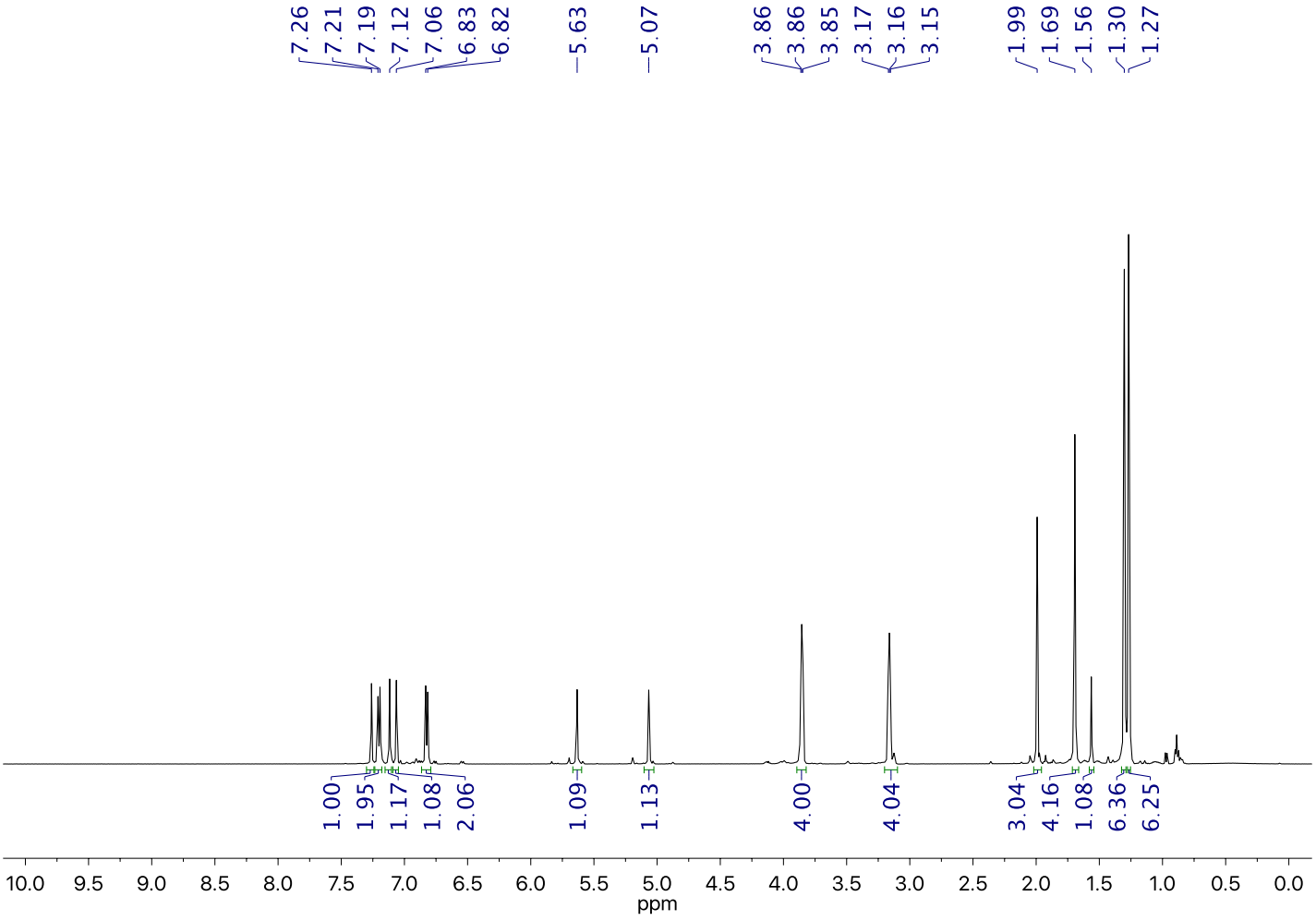
^{13}C NMR

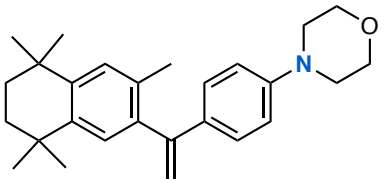

153.71
129.58
128.99
114.03
77.41
77.23
77.05
66.78
50.28
47.93
22.30
11.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


O
N

19

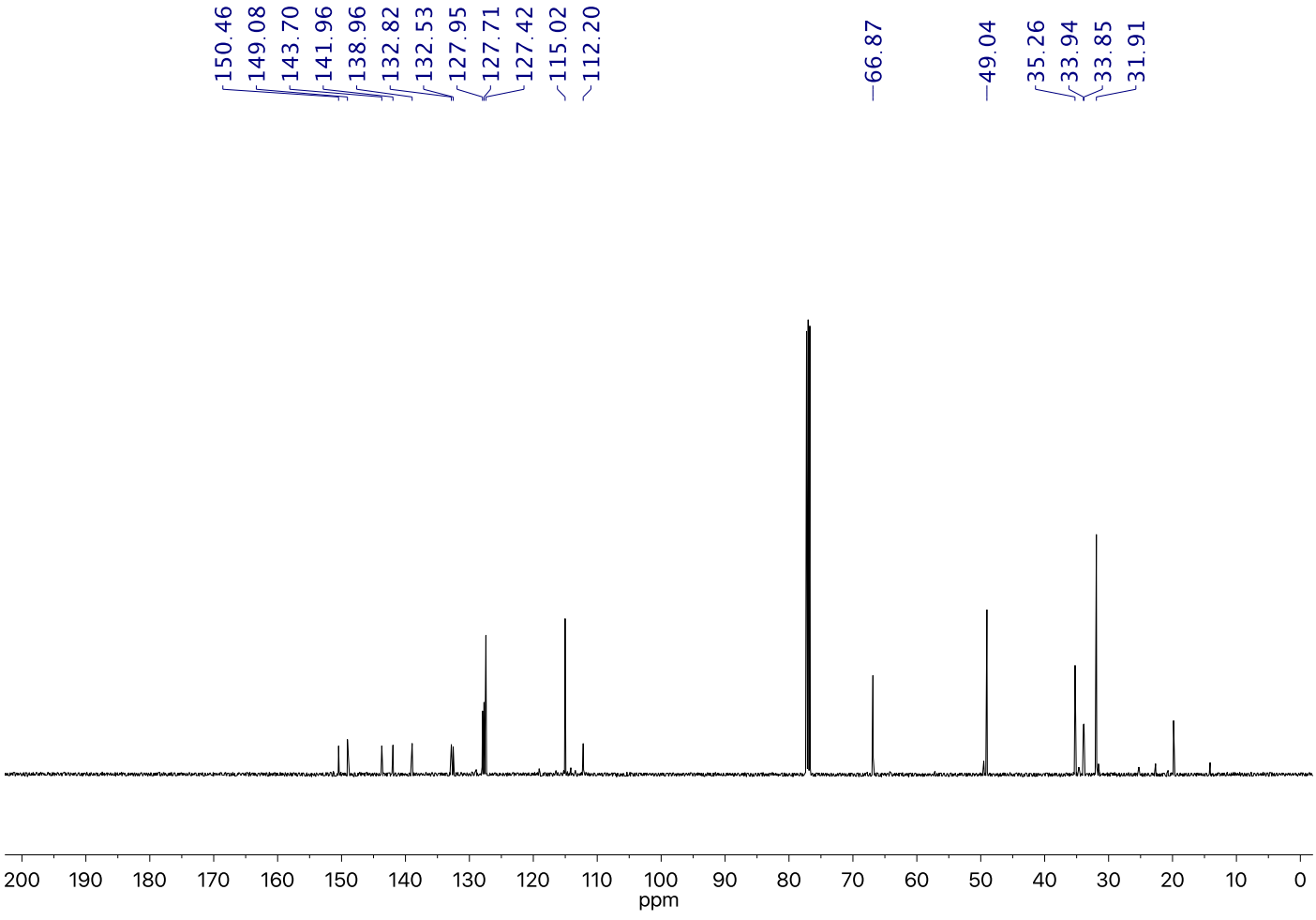
^{1}H NMR

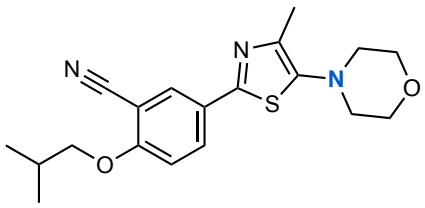

7.26
7.21
7.19
7.12
7.06
6.83
6.82
5.63
5.07
3.86
3.86
3.85
3.17
3.16
3.15
1.99
1.69
1.56
1.30
1.27
1.00
1.95
1.17
1.08
2.06
1.09
1.13
4.00
4.04
3.04
4.16
1.08
6.36
6.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
N

19

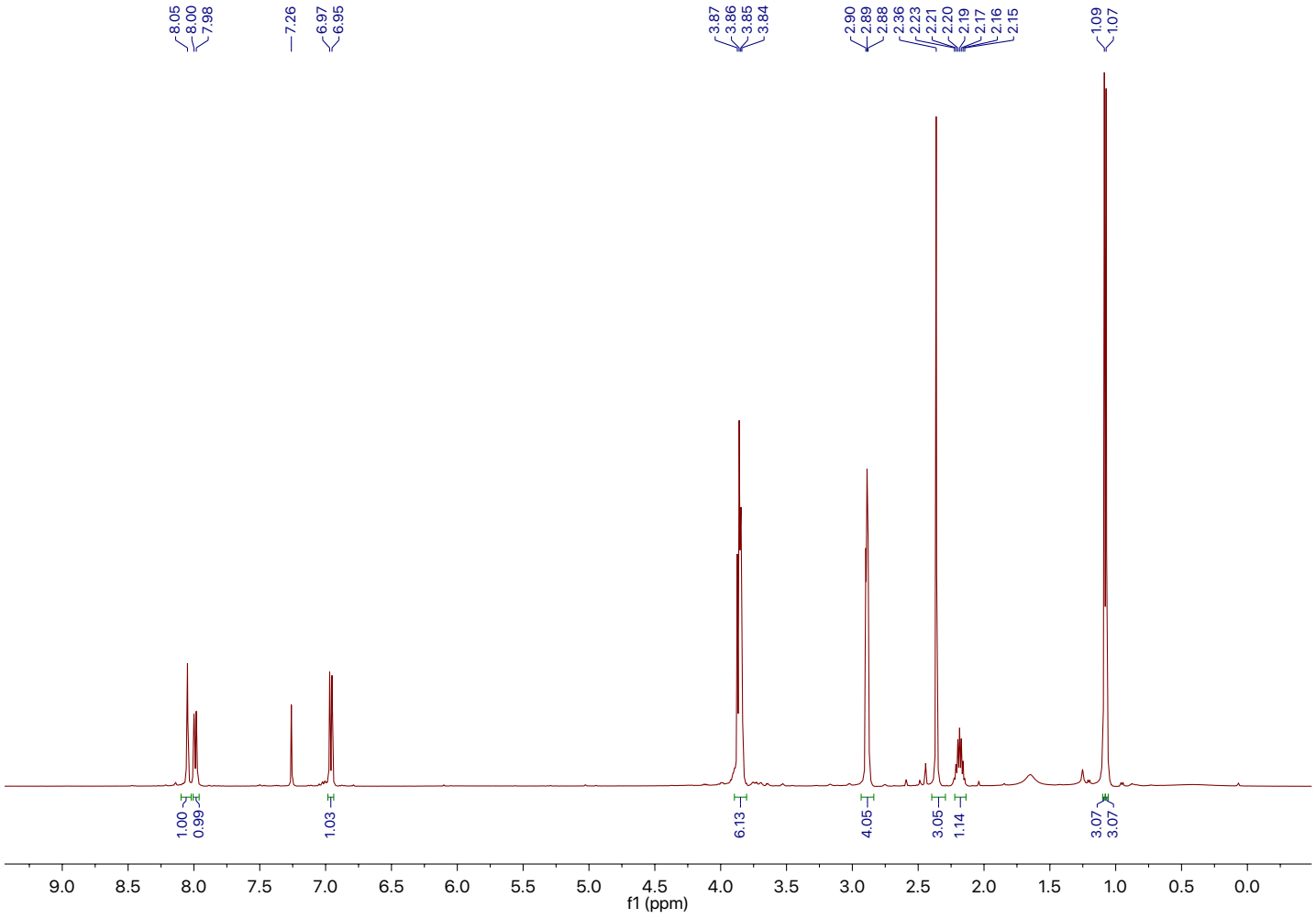
^{13}C NMR

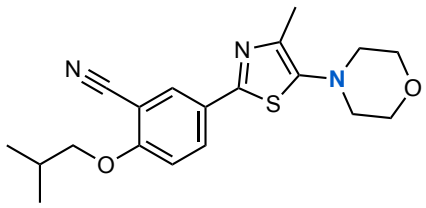

150.46
149.08
143.70
141.96
138.96
132.82
132.53
127.95
127.71
127.42
115.02
112.20
66.87
49.04
35.26
33.94
33.85
31.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



20

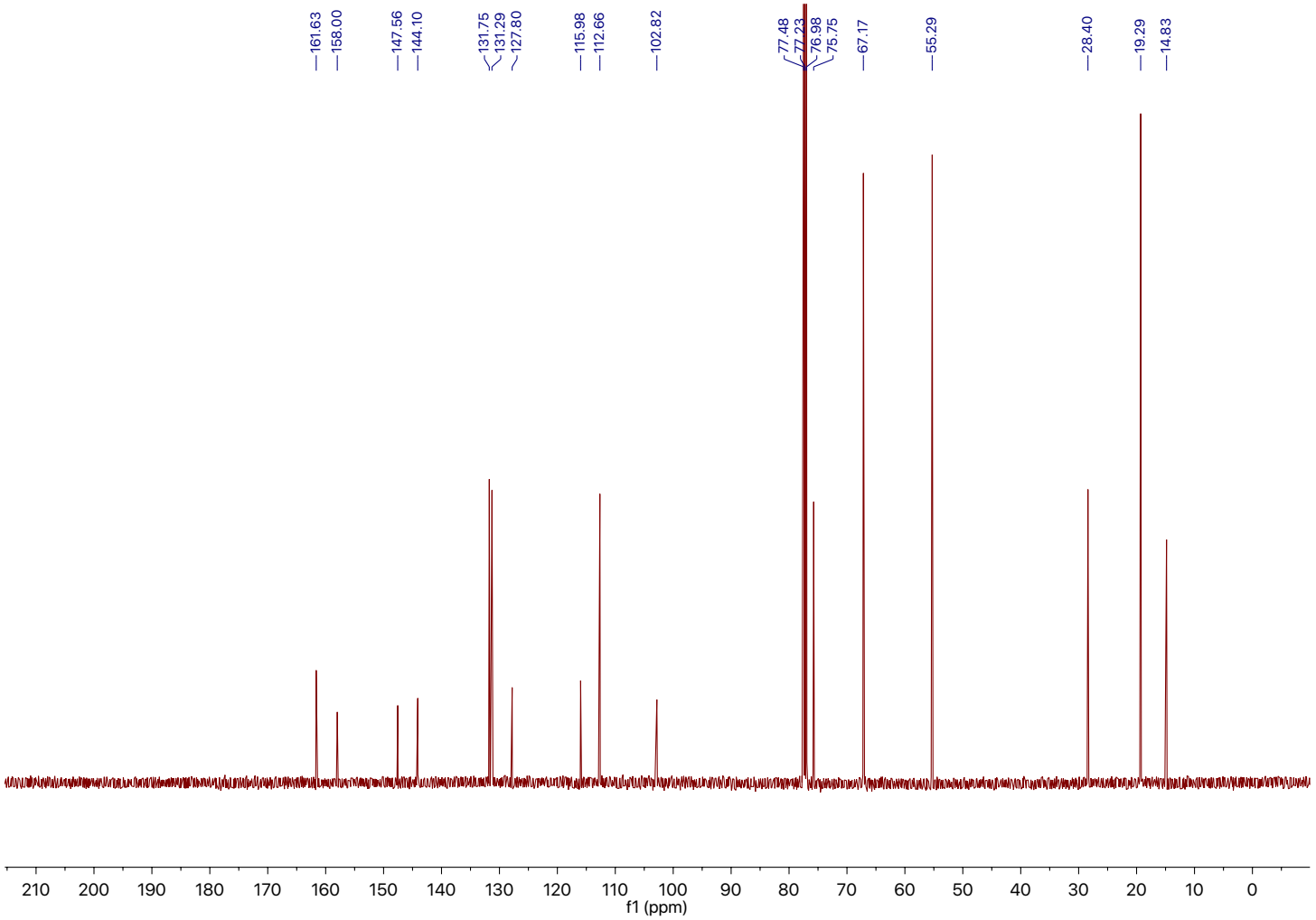
^{1}H NMR

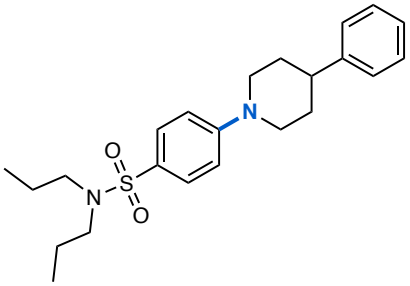

8.05
8.00
7.98
7.26
6.97
6.95
3.87
3.86
3.85
3.84
2.90
2.89
2.88
2.36
2.23
2.21
2.20
2.19
2.17
2.16
2.15
1.09
1.07
1.00
0.99
1.03
6.13
4.05
3.05
1.14
3.07
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
N
S
N
O
O

20

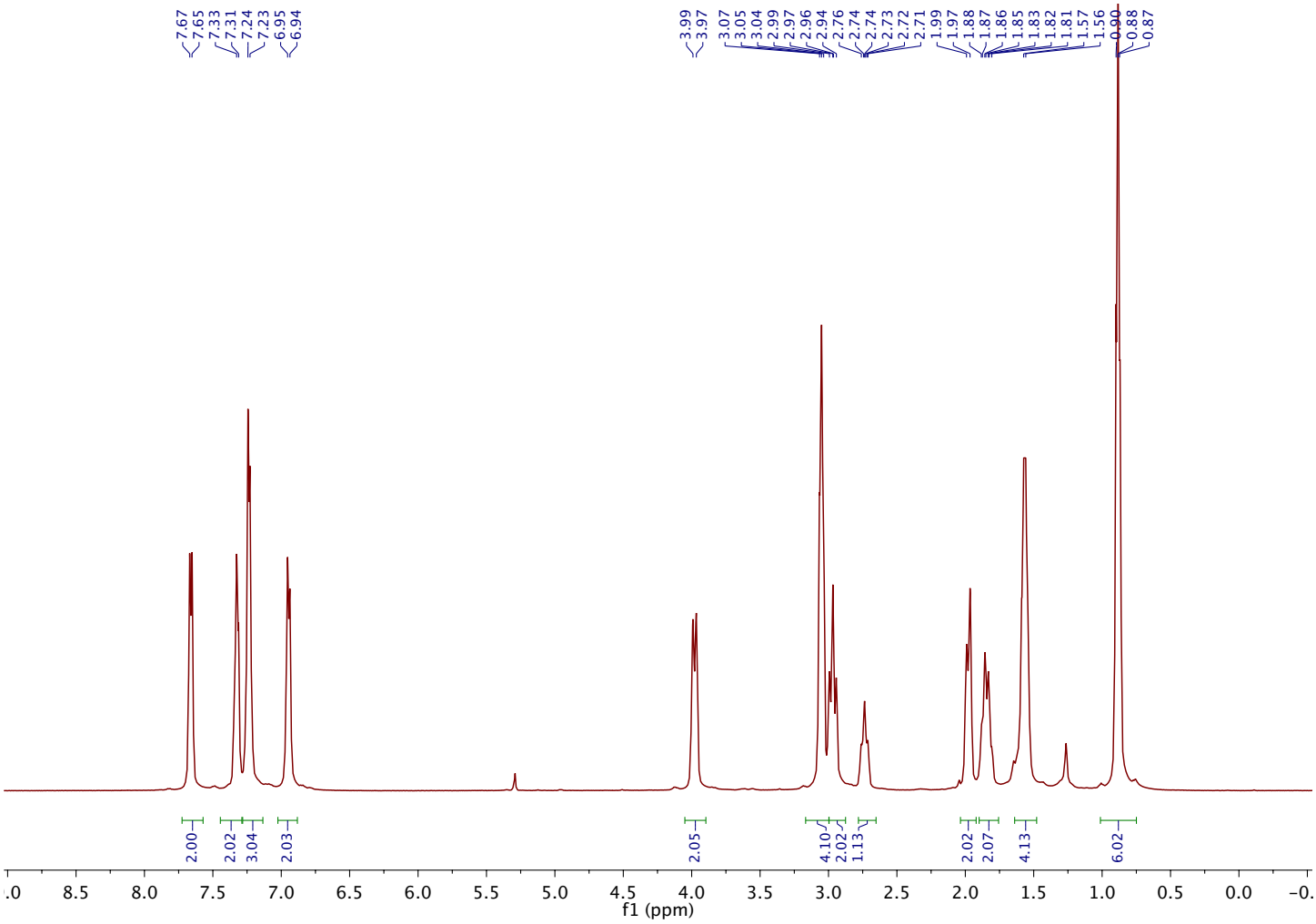
^{13}C NMR

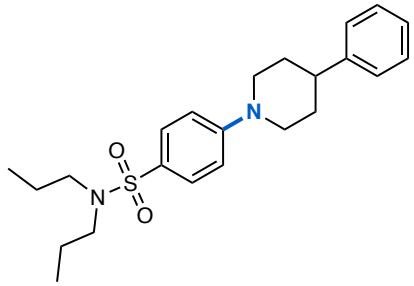

161.63
158.00
147.56
144.10
131.75
131.29
127.80
115.98
112.66
102.82
77.48
77.23
76.98
75.75
67.17
55.29
28.40
19.29
14.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
S
O
N

21

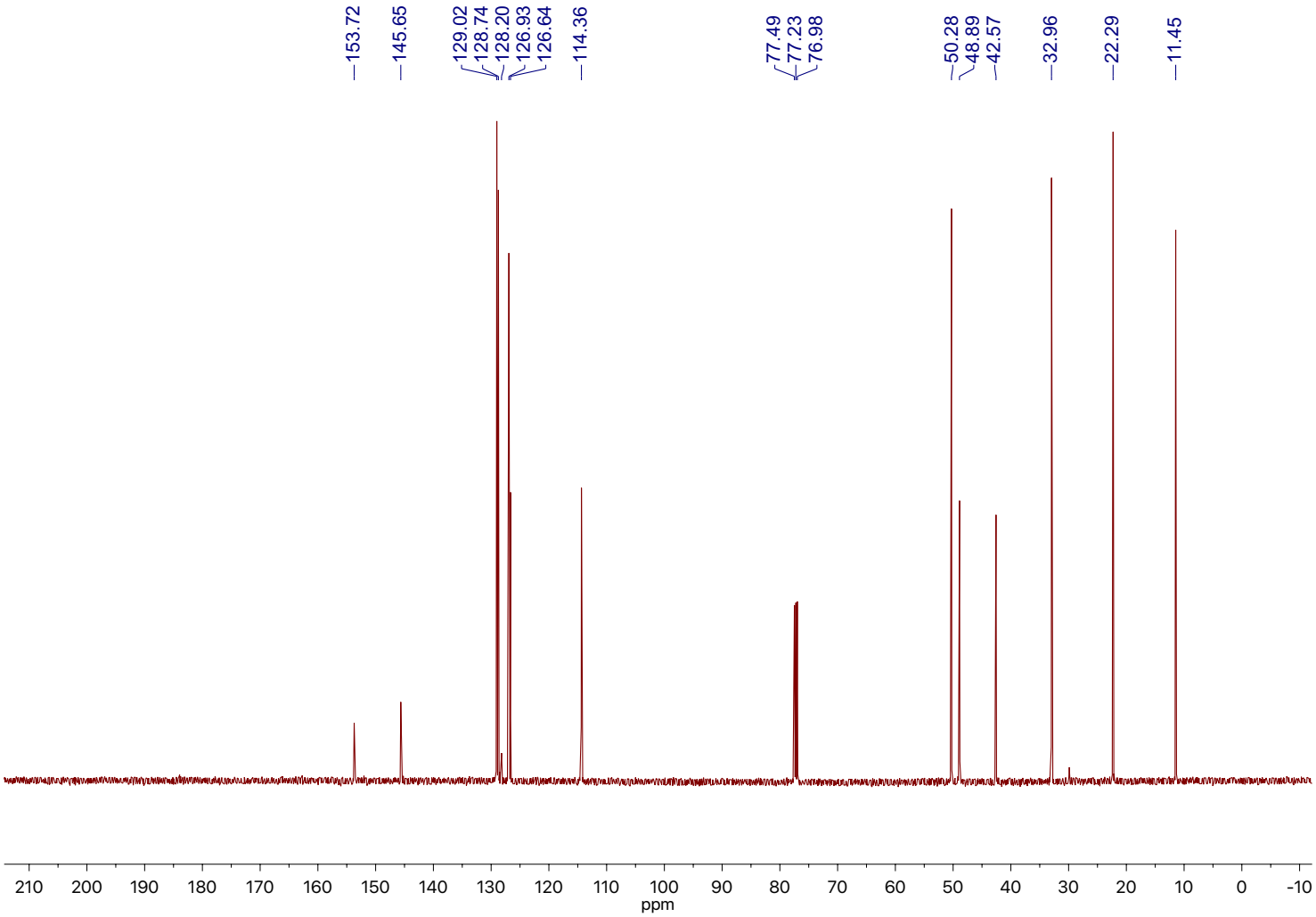
^{1}H NMR

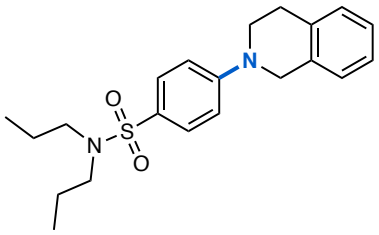

7.67
7.65
7.33
7.31
7.24
7.23
6.95
6.94
3.99
3.97
3.07
3.05
3.04
2.99
2.97
2.96
2.94
2.76
2.74
2.74
2.73
2.72
2.71
1.99
1.97
1.88
1.87
1.86
1.85
1.83
1.82
1.81
1.57
1.56
0.90
0.88
0.87
2.00
2.02
3.04
2.03
2.05
4.10
2.02
1.13
2.02
2.07
4.13
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



21

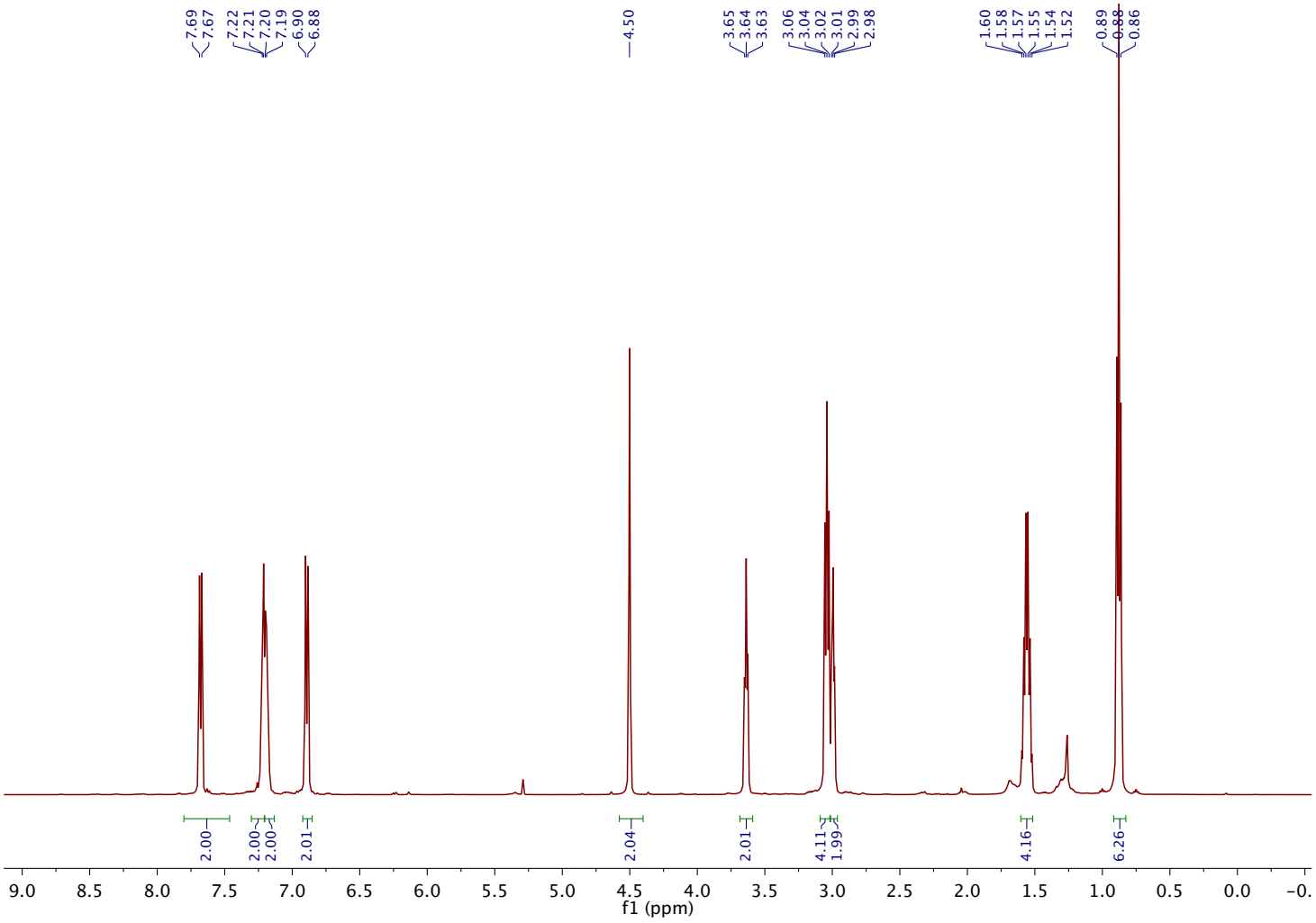
^{13}C NMR

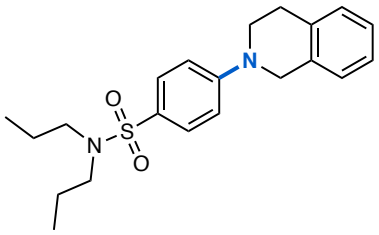

153.72
145.65
129.02
128.74
128.20
126.93
126.64
114.36
77.49
77.23
76.98
50.28
48.89
42.57
32.96
22.29
11.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



22

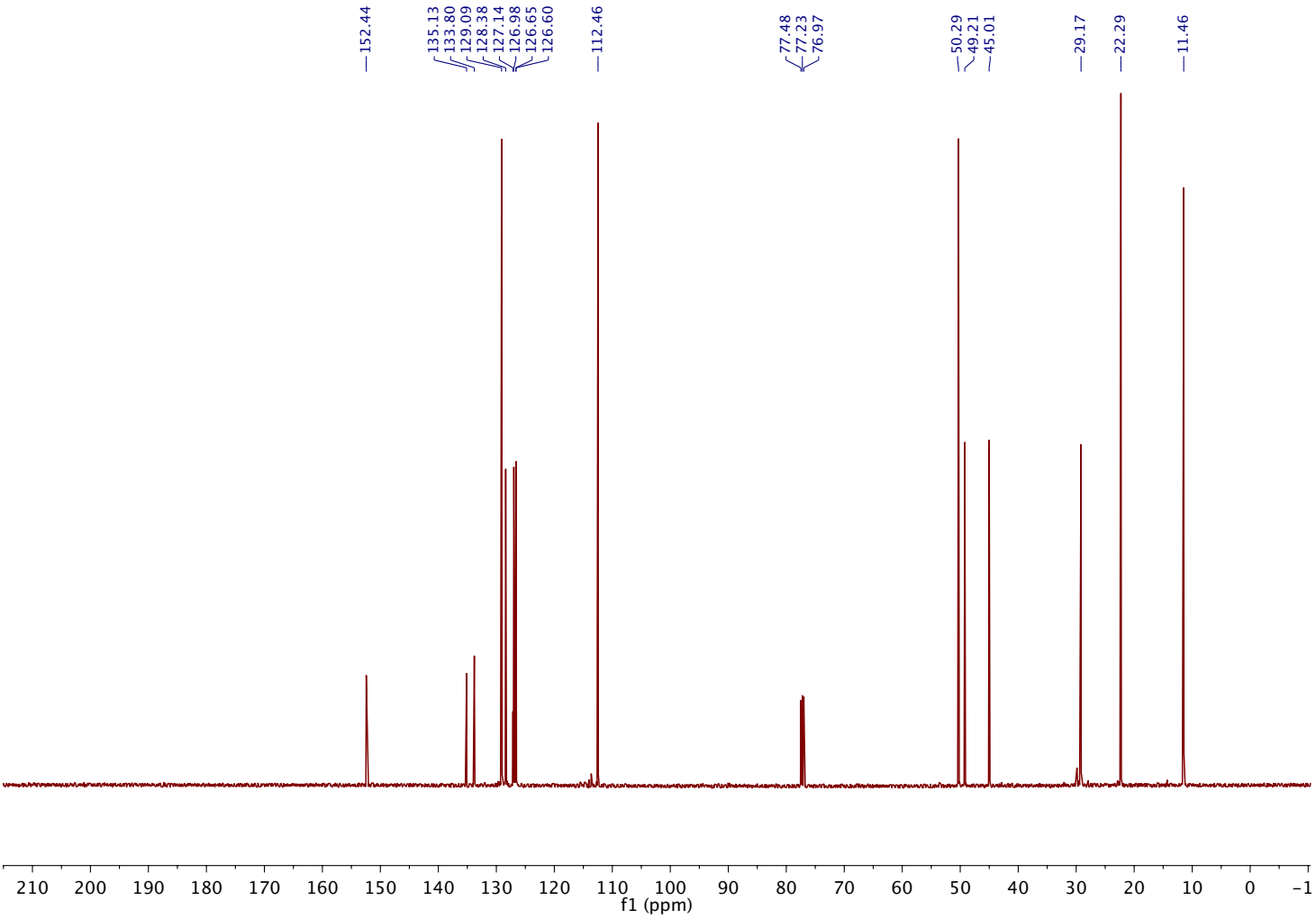
^{1}H NMR

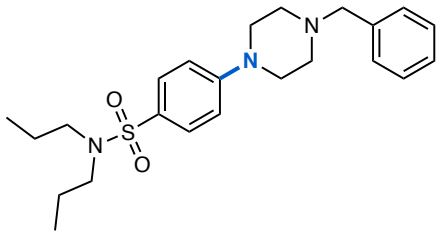

7.69
7.67
7.22
7.21
7.20
7.19
6.90
6.88
4.50
3.65
3.64
3.63
3.06
3.04
3.02
3.01
2.99
2.98
1.60
1.58
1.57
1.55
1.54
1.52
0.89
0.88
0.86
2.00
2.00
2.00
2.01
2.04
2.01
4.11
1.99
4.16
6.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)



22

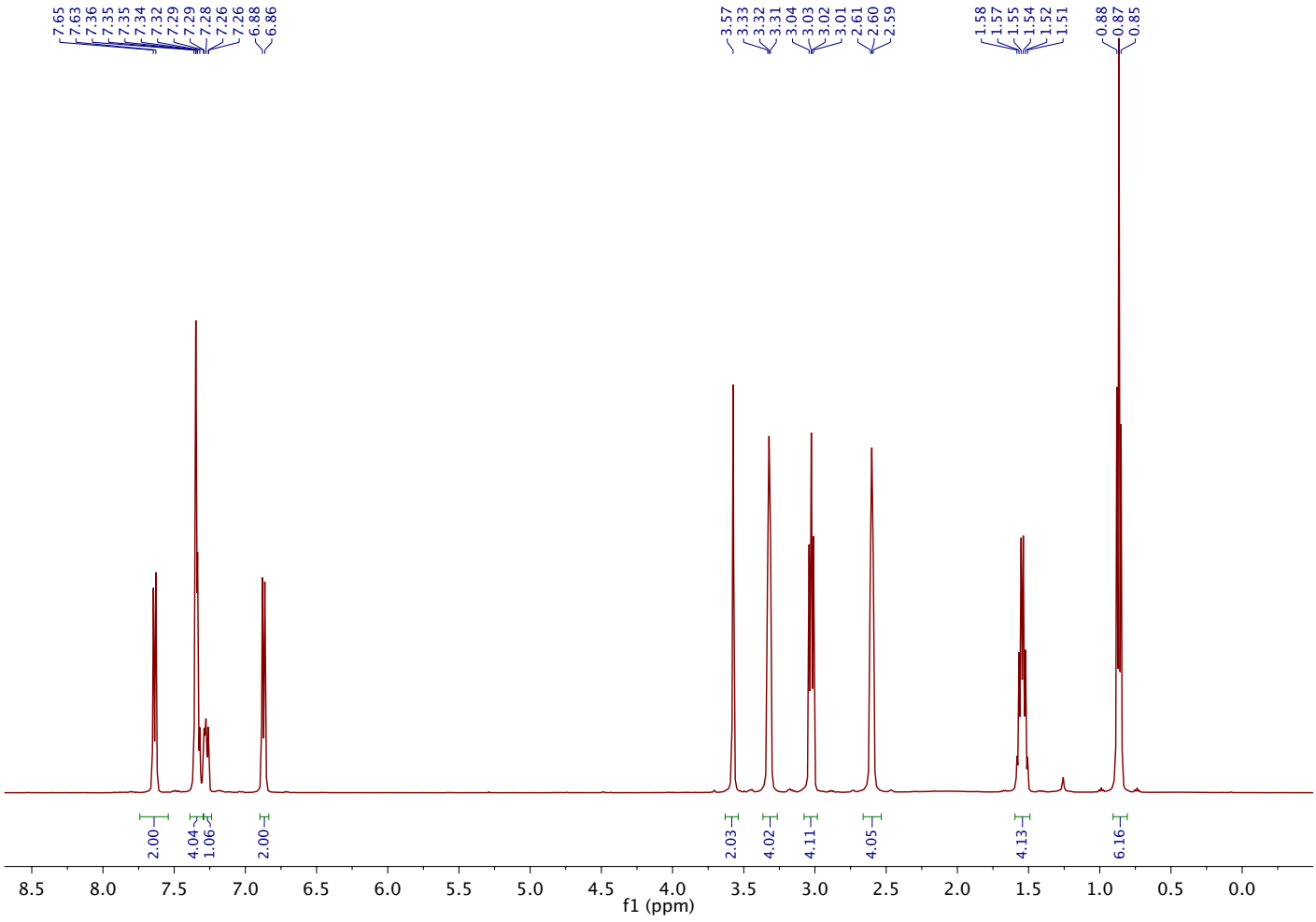
^{13}C NMR

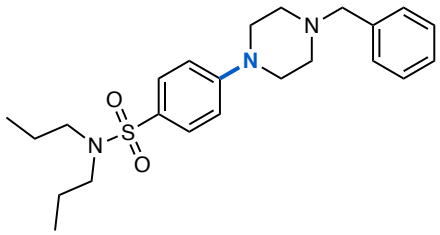

152.44
135.13
133.80
129.09
128.38
127.14
126.98
126.65
126.60
112.46
77.48
77.23
76.97
50.29
49.21
45.01
29.17
22.29
11.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



23

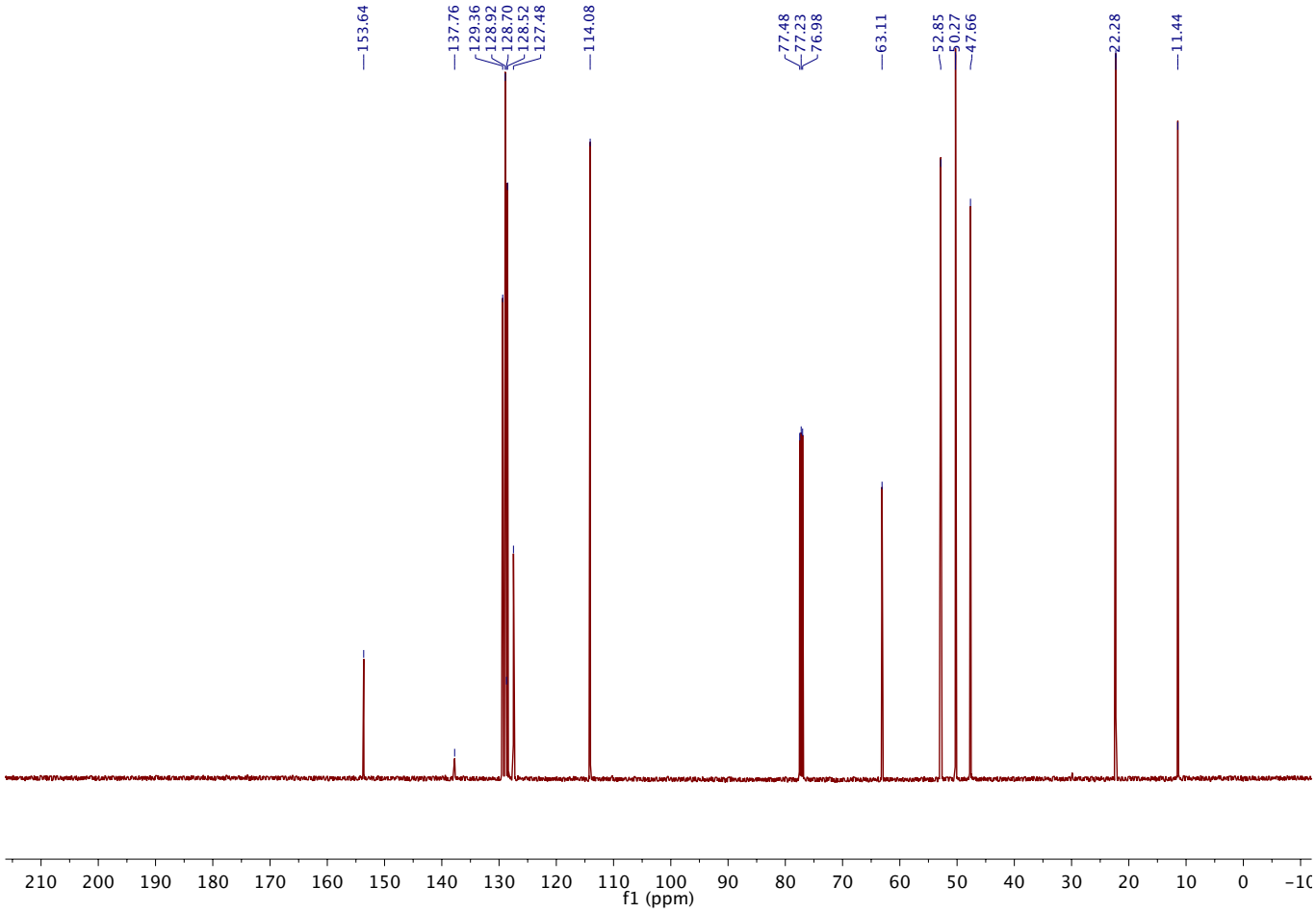
^{1}H NMR

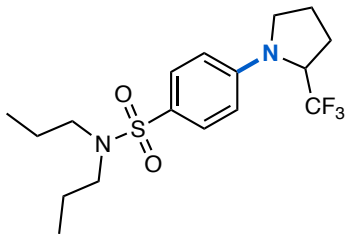

7.65
7.63
7.36
7.35
7.35
7.34
7.32
7.29
7.29
7.28
7.26
7.26
6.88
6.86
3.57
3.33
3.32
3.31
3.04
3.03
3.02
3.01
2.61
2.60
2.59
1.58
1.57
1.55
1.54
1.52
1.51
0.88
0.87
0.85
2.00
4.04
1.06
2.00
2.03
4.02
4.11
4.05
4.13
6.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



23

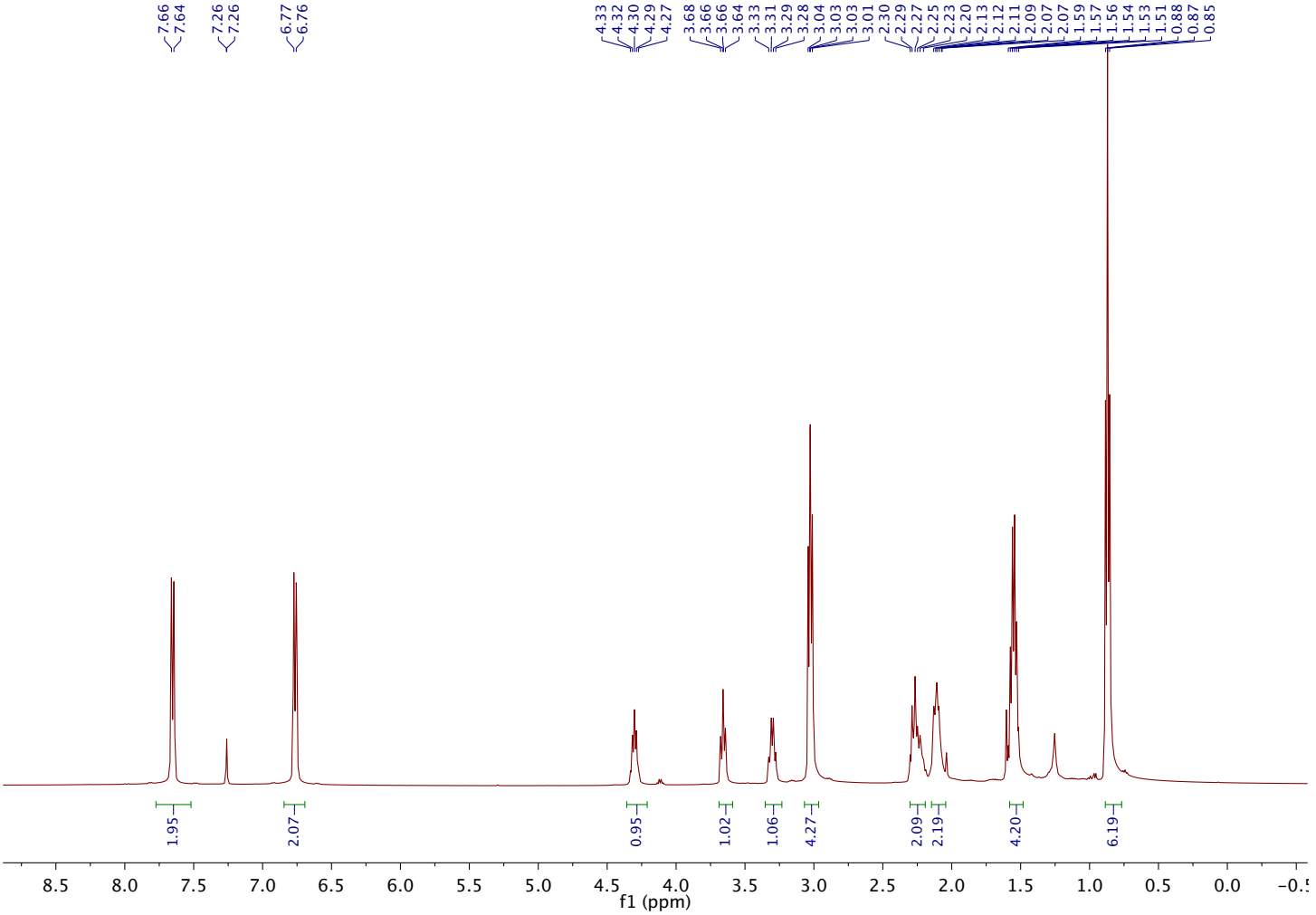
^{13}C NMR

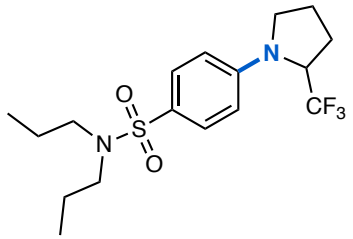

153.64
137.76
129.36
128.92
128.70
128.52
127.48
114.08
77.48
77.23
76.98
63.11
52.85
50.27
47.66
22.28
11.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
O
S
O
N
CF3

24

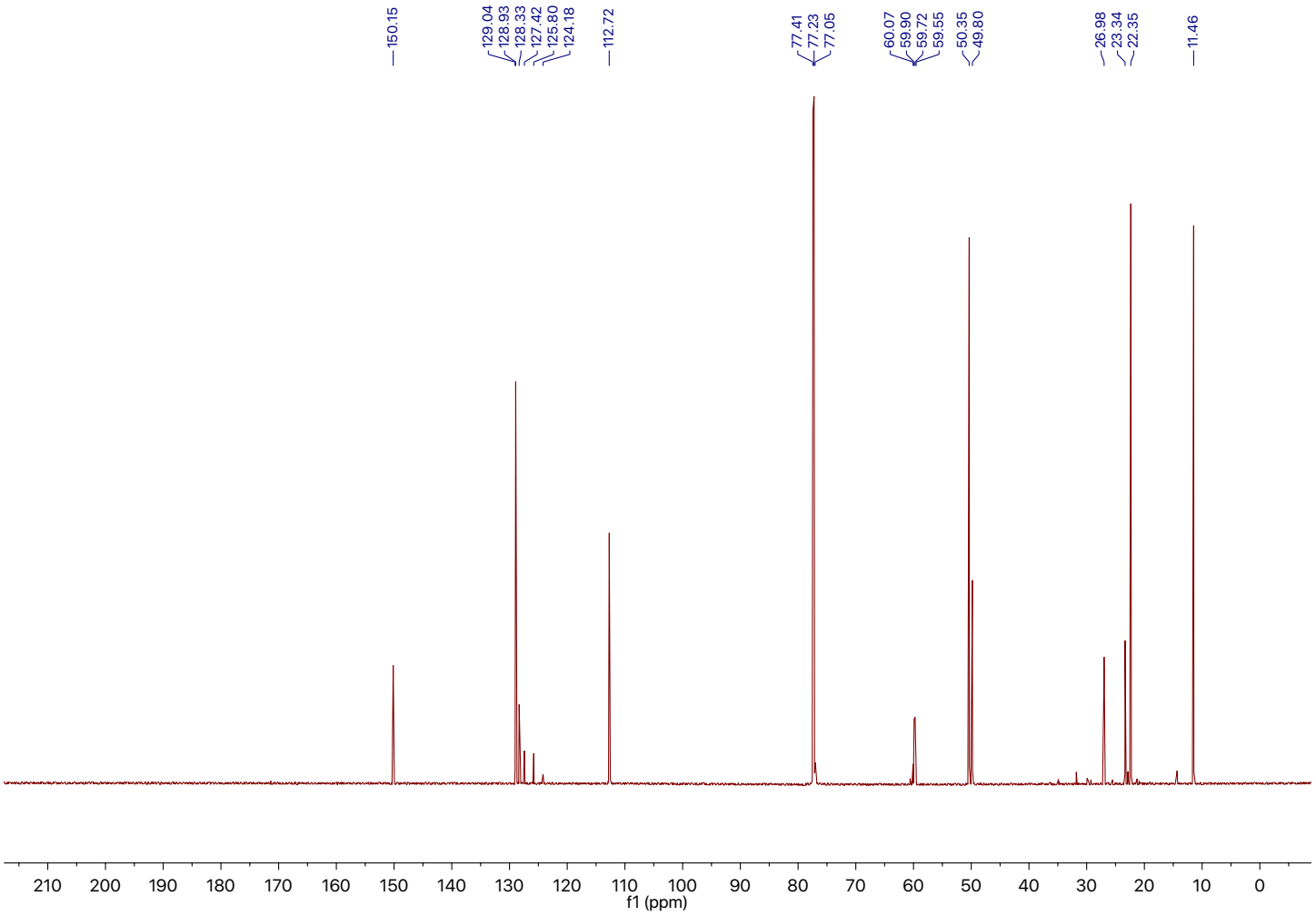
^{1}H NMR

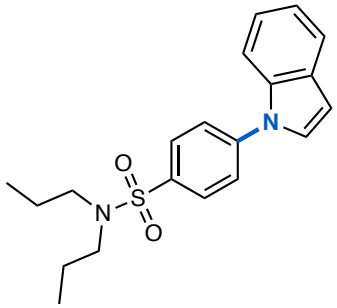

7.66
7.64
7.26
7.26
6.77
6.76
4.33
4.32
4.30
4.29
4.27
3.68
3.66
3.66
3.64
3.33
3.31
3.29
3.28
3.04
3.03
3.03
3.01
2.30
2.29
2.27
2.25
2.23
2.20
2.13
2.12
2.11
2.09
2.07
2.07
1.59
1.57
1.56
1.54
1.53
1.51
0.88
0.87
0.85
1.95
2.07
0.95
1.02
1.06
4.27
2.09
2.19
4.20
6.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



24

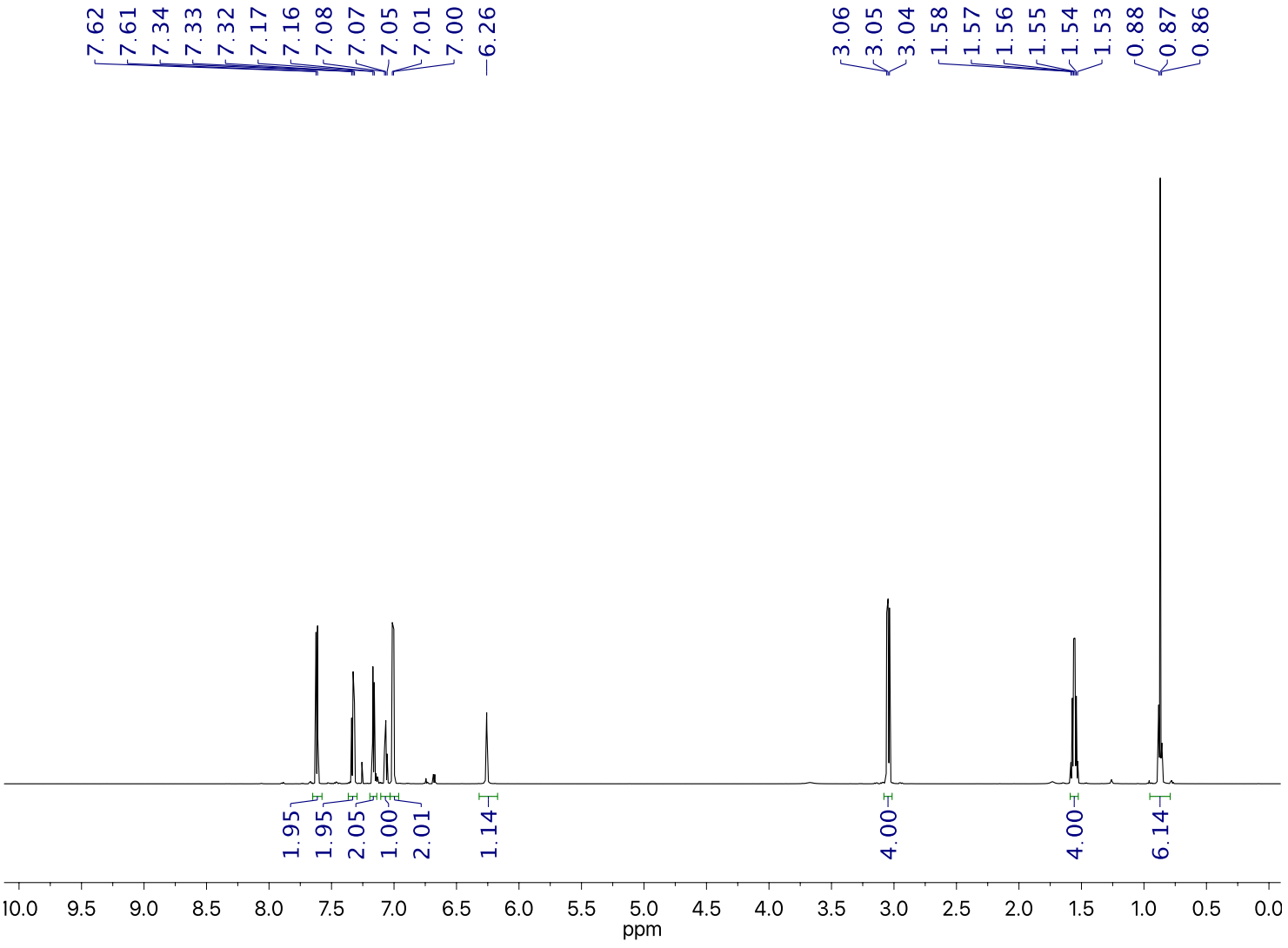
^{13}C NMR

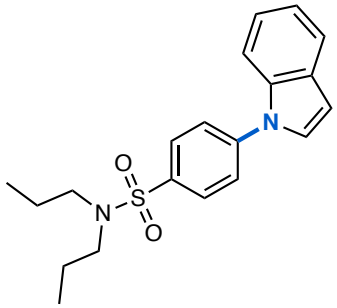

150.15
129.04
128.93
128.33
127.42
125.80
124.18
112.72
77.41
77.23
77.05
60.07
59.90
59.72
59.55
50.35
49.80
26.98
23.34
22.35
11.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



25

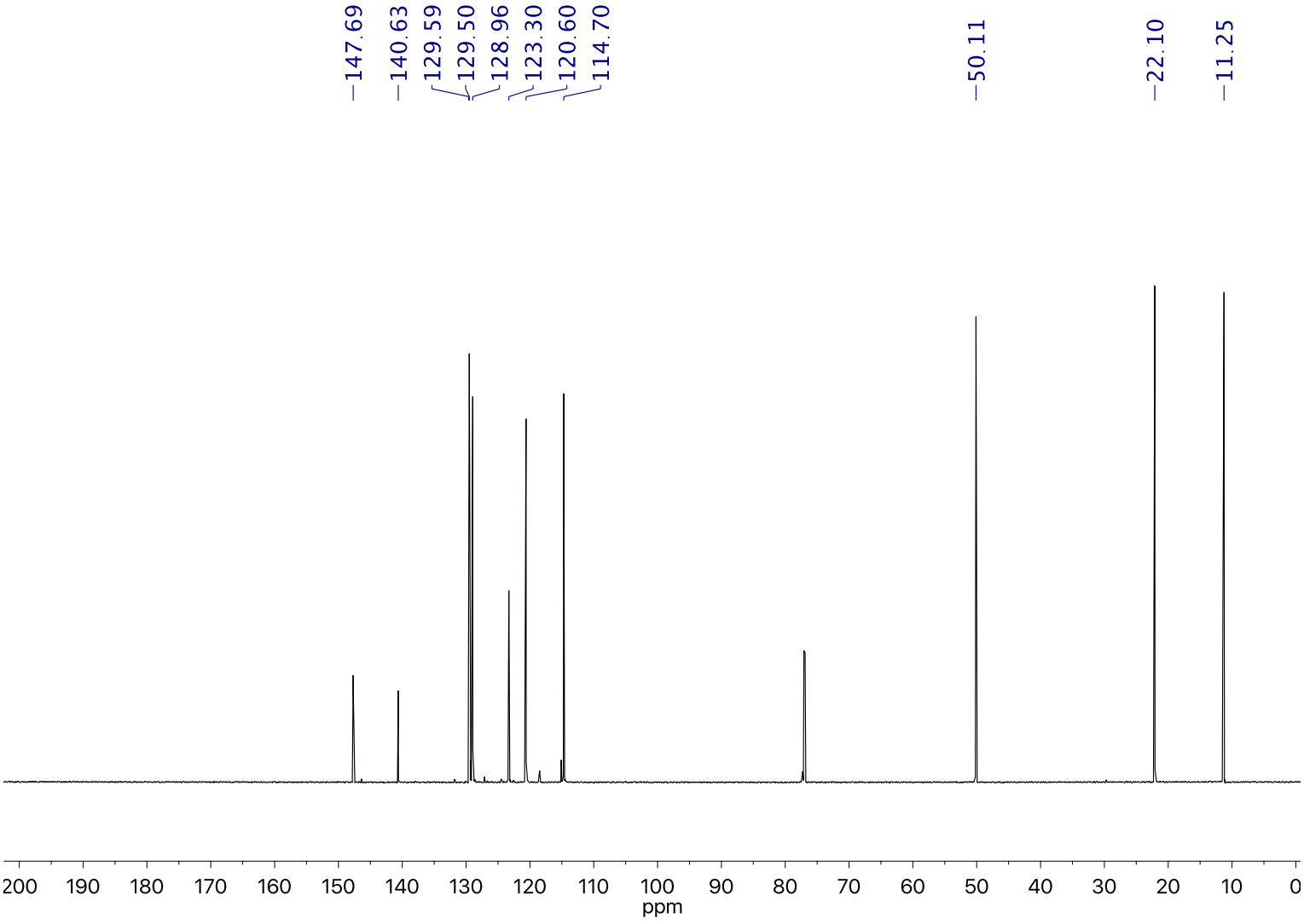
^{1}H NMR

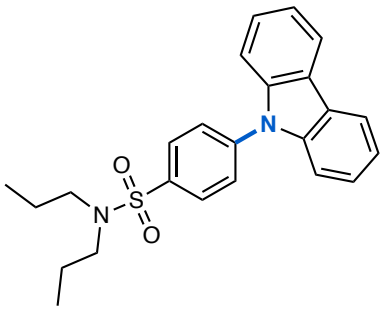

7.62
7.61
7.34
7.33
7.32
7.17
7.16
7.08
7.07
7.05
7.01
7.00
6.26
3.06
3.05
3.04
1.58
1.57
1.56
1.55
1.54
1.53
0.88
0.87
0.86
1.95
1.95
2.05
1.00
2.01
1.14
4.00
4.00
6.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



25

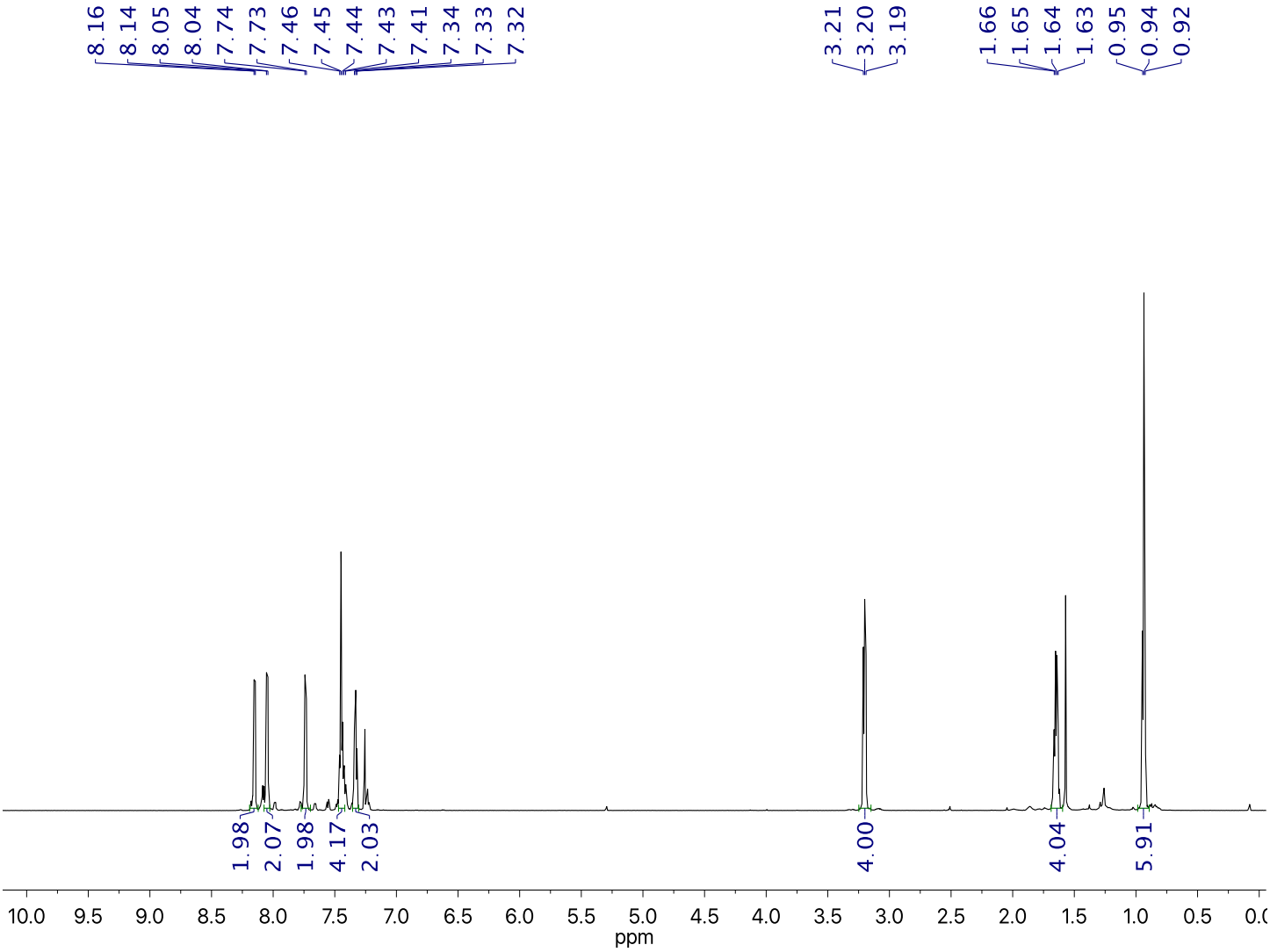
^{13}C NMR

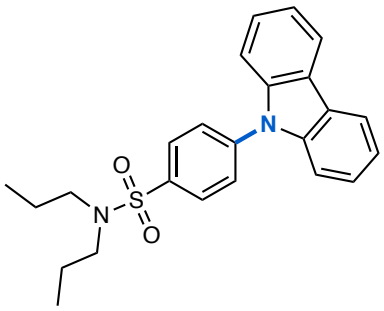

147.69
140.63
129.59
129.50
128.96
123.30
120.60
114.70
50.11
22.10
11.25
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



26

^{1}H NMR

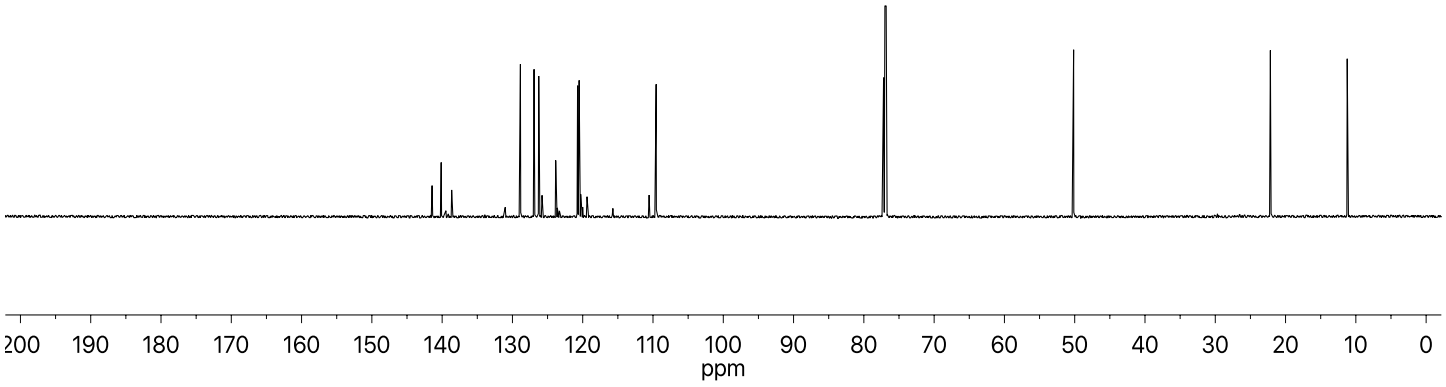

8.16
8.14
8.05
8.04
7.74
7.73
7.46
7.45
7.44
7.43
7.41
7.34
7.33
7.32
3.21
3.20
3.19
1.66
1.65
1.64
1.63
0.95
0.94
0.92
1.98
2.07
1.98
4.17
2.03
4.00
4.04
5.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

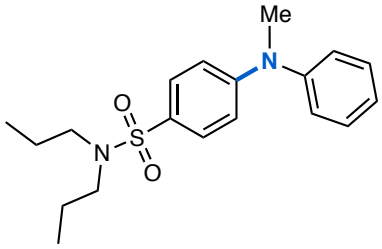


26

^{13}C NMR

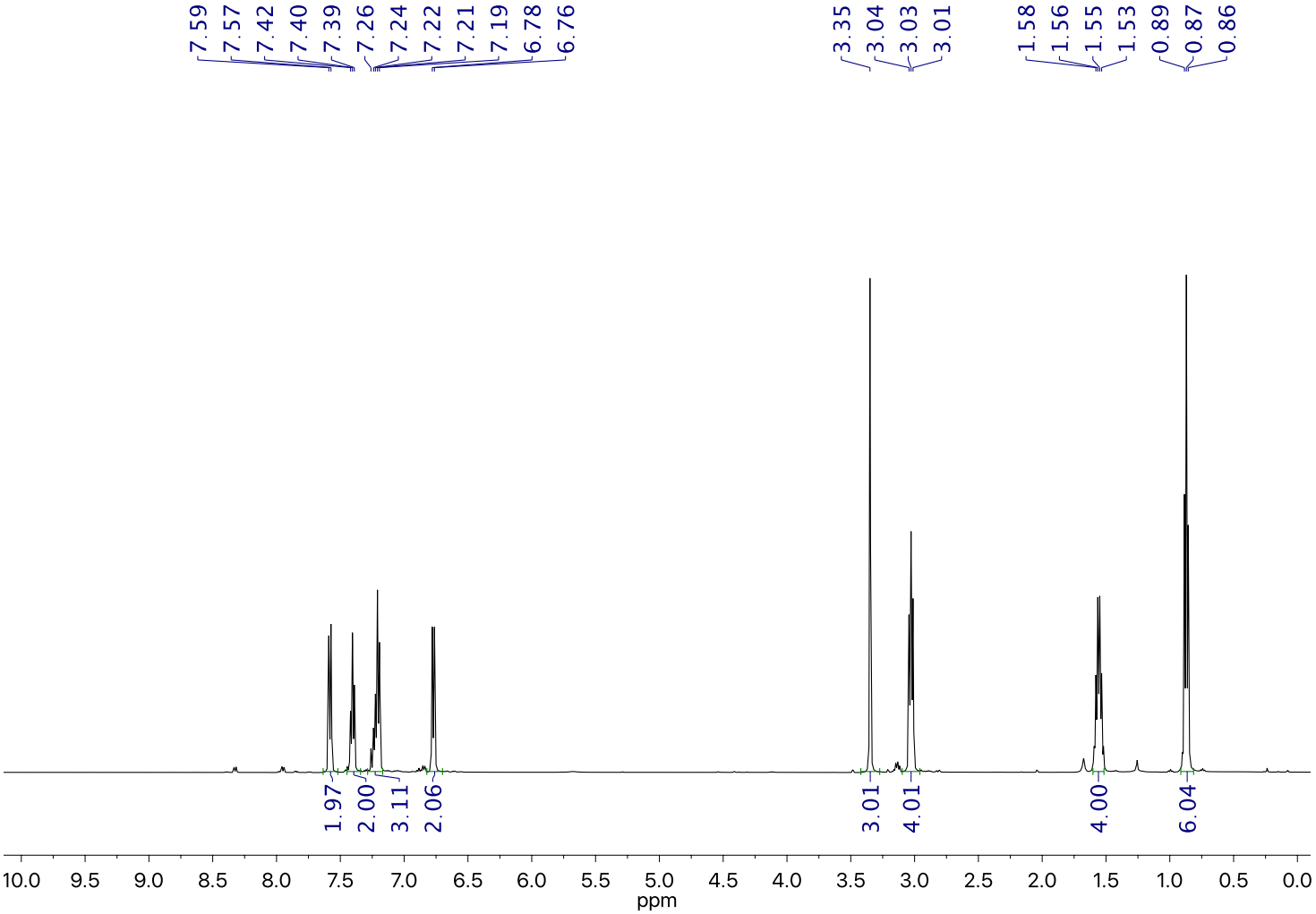

141.43
140.14
138.64
128.87
126.92
126.26
123.84
120.73
120.51
109.55
50.15
22.16
11.23

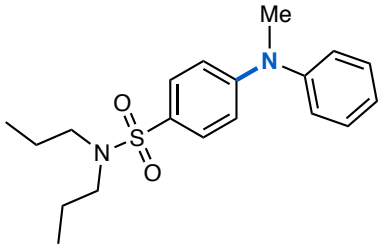

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me
N
O
S
O
N

27

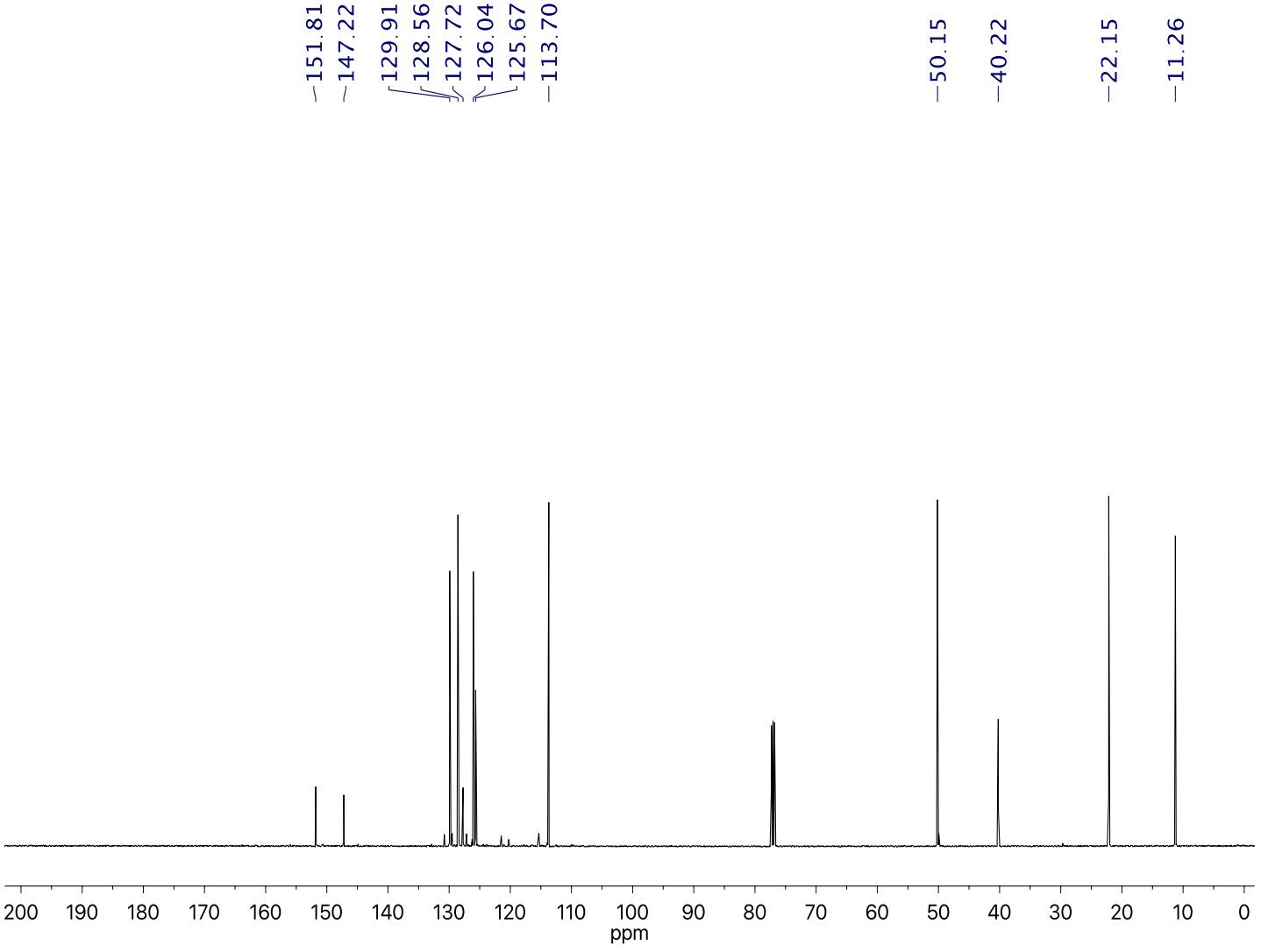
^{1}H NMR

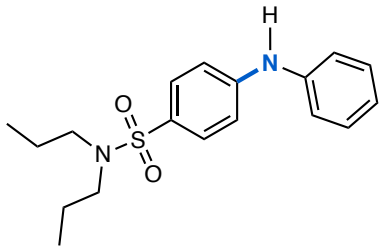

7.59
7.57
7.42
7.40
7.39
7.26
7.24
7.22
7.21
7.19
6.78
6.76
3.35
3.04
3.03
3.01
1.58
1.56
1.55
1.53
0.89
0.87
0.86
1.97
2.00
3.11
2.06
3.01
4.01
4.00
6.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Me
N
O
S
O
N

27

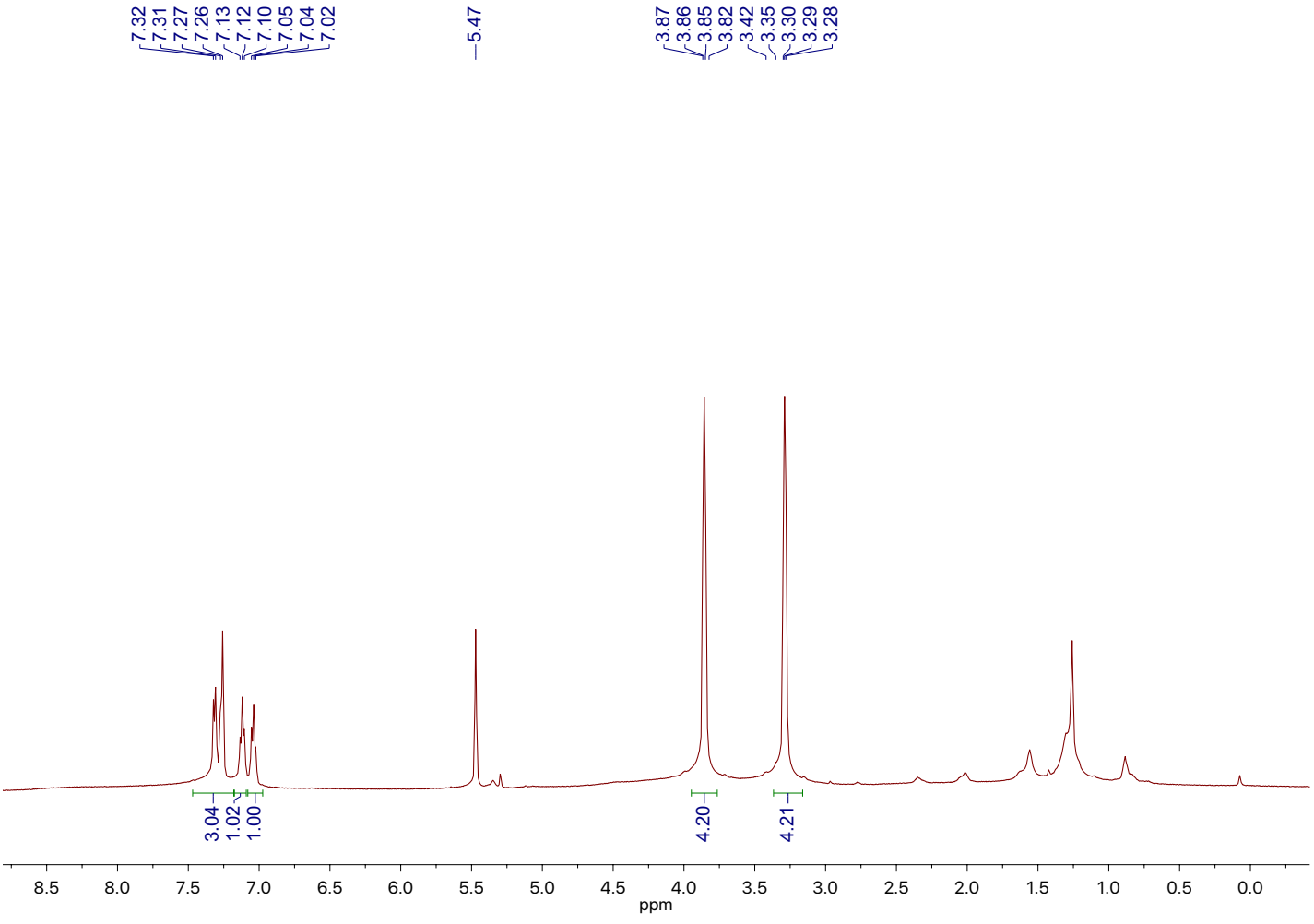
^{13}C NMR

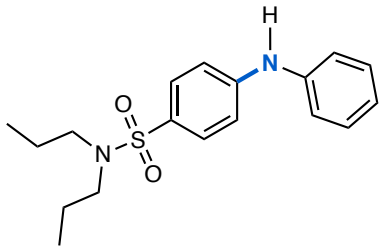

151.81
147.22
129.91
128.56
127.72
126.04
125.67
113.70
50.15
40.22
22.15
11.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



28

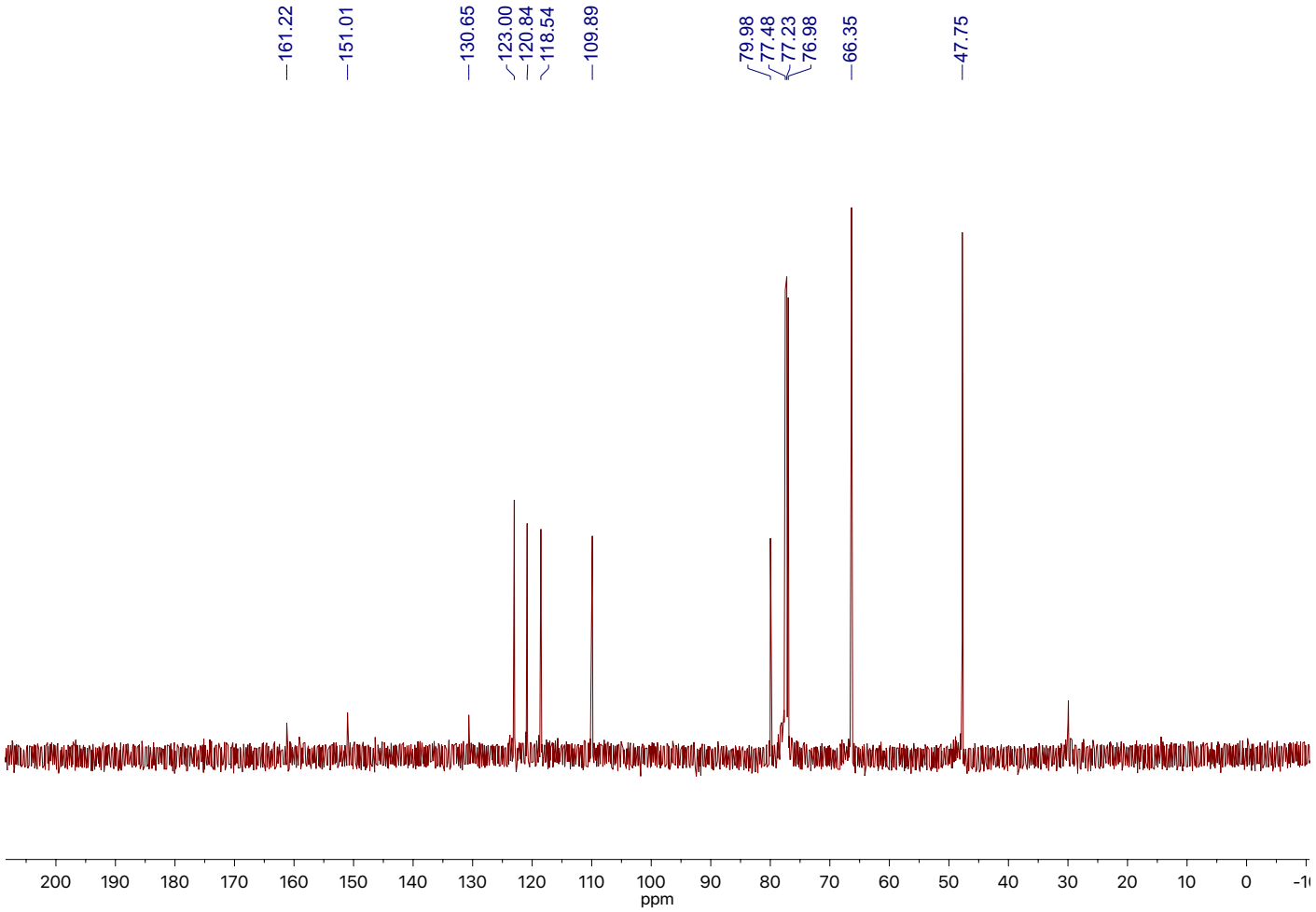
^{1}H NMR

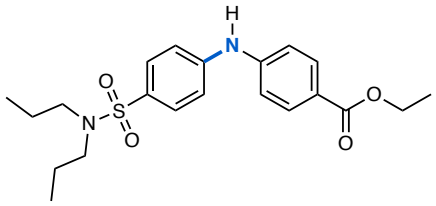

7.32
7.31
7.27
7.26
7.13
7.12
7.10
7.05
7.04
7.02
5.47
3.87
3.86
3.85
3.82
3.42
3.35
3.30
3.29
3.28
3.04
1.02
1.00
4.20
4.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



28

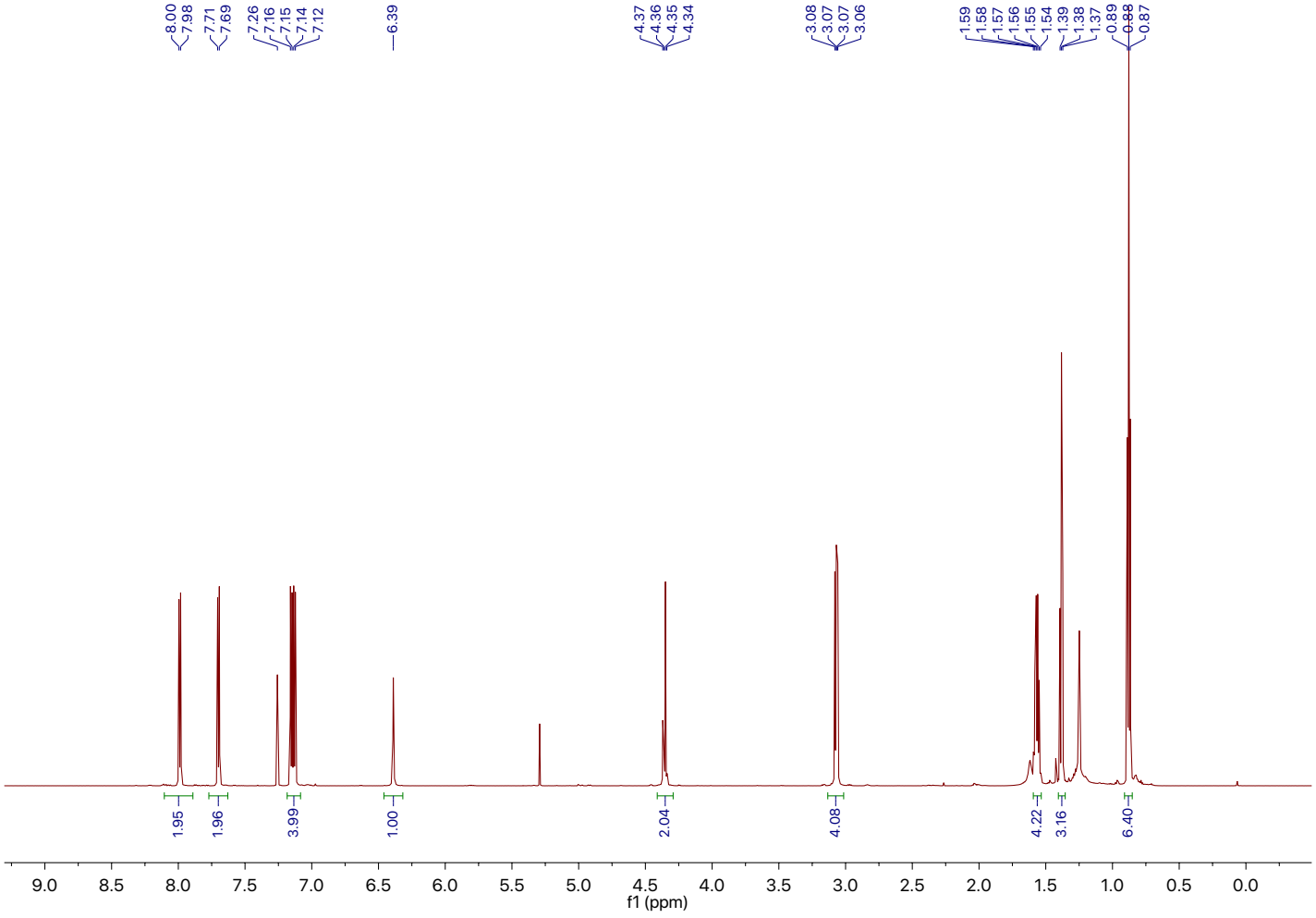
^{13}C NMR

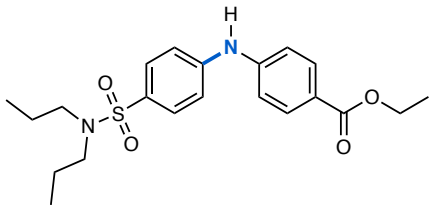

161.22
151.01
130.65
123.00
120.84
118.54
109.89
79.98
77.48
77.23
76.98
66.35
47.75
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



29

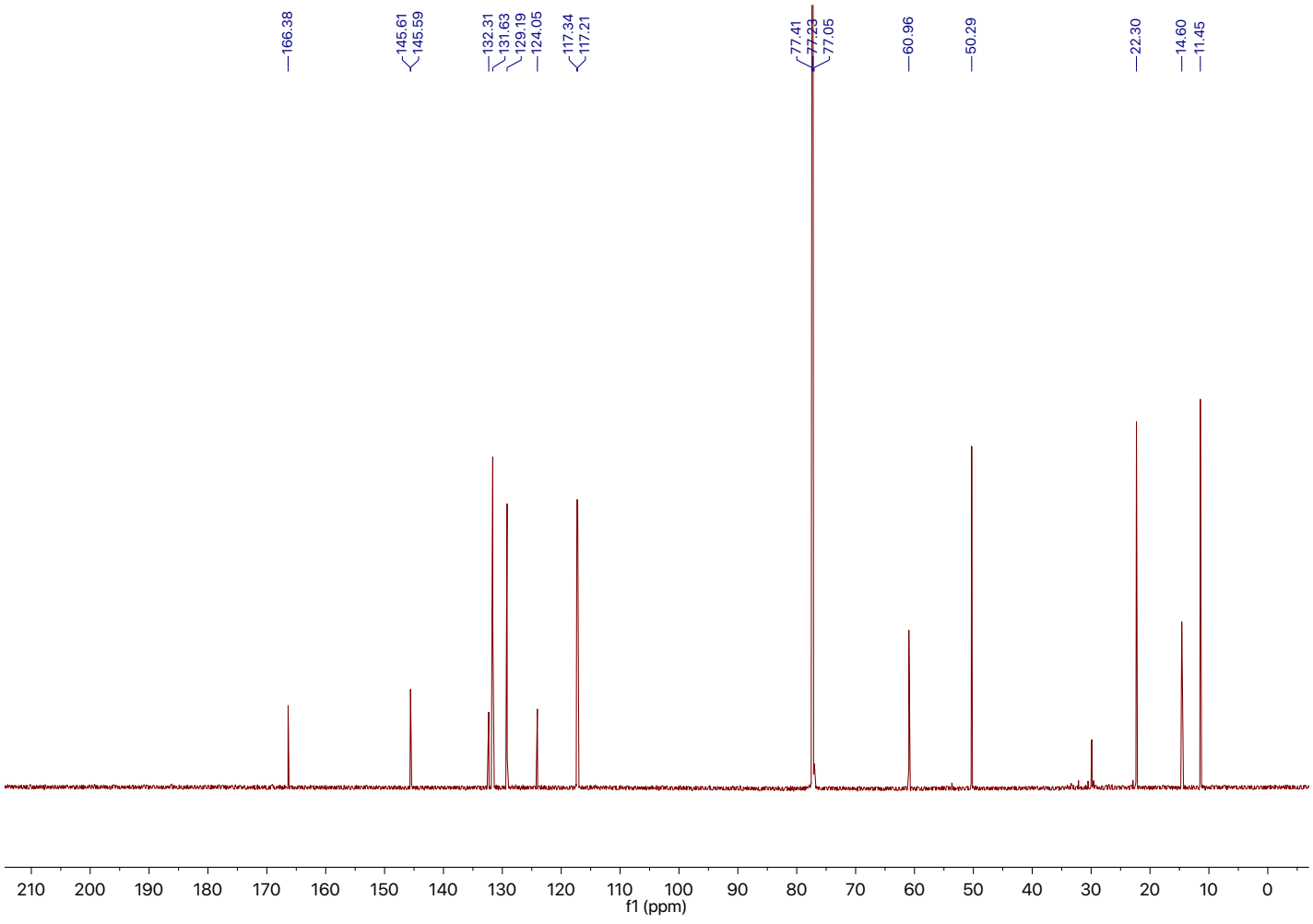
^{1}H NMR

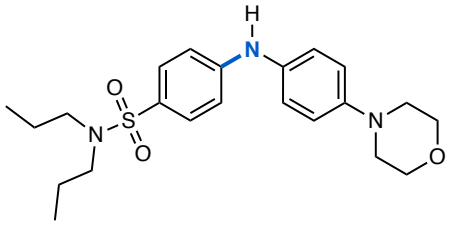

8.00
7.98
7.71
7.69
7.26
7.16
7.15
7.14
7.12
6.39
4.37
4.36
4.35
4.34
3.08
3.07
3.07
3.06
1.59
1.58
1.57
1.56
1.55
1.54
1.39
1.38
1.37
0.89
0.88
0.87
1.95
1.96
3.99
1.00
2.04
4.08
4.22
3.16
6.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



29

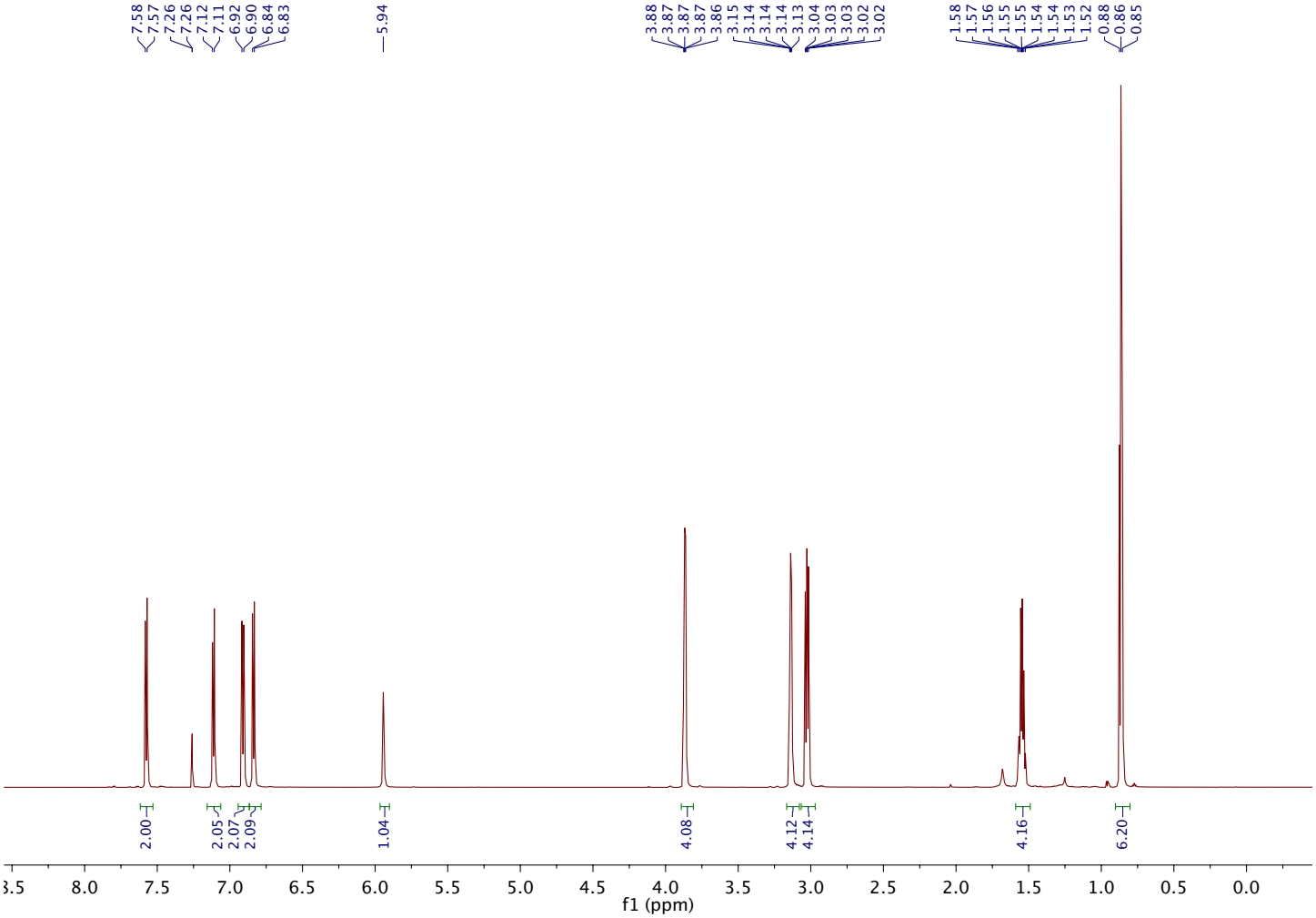
^{13}C NMR

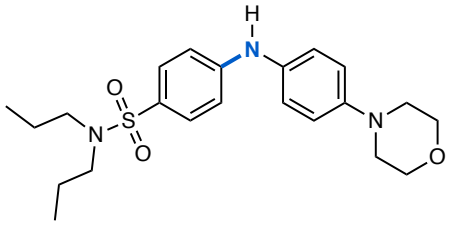

166.38
145.61
145.59
132.31
131.63
129.19
124.05
117.34
117.21
77.41
77.23
77.05
60.96
50.29
22.30
14.60
11.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



30

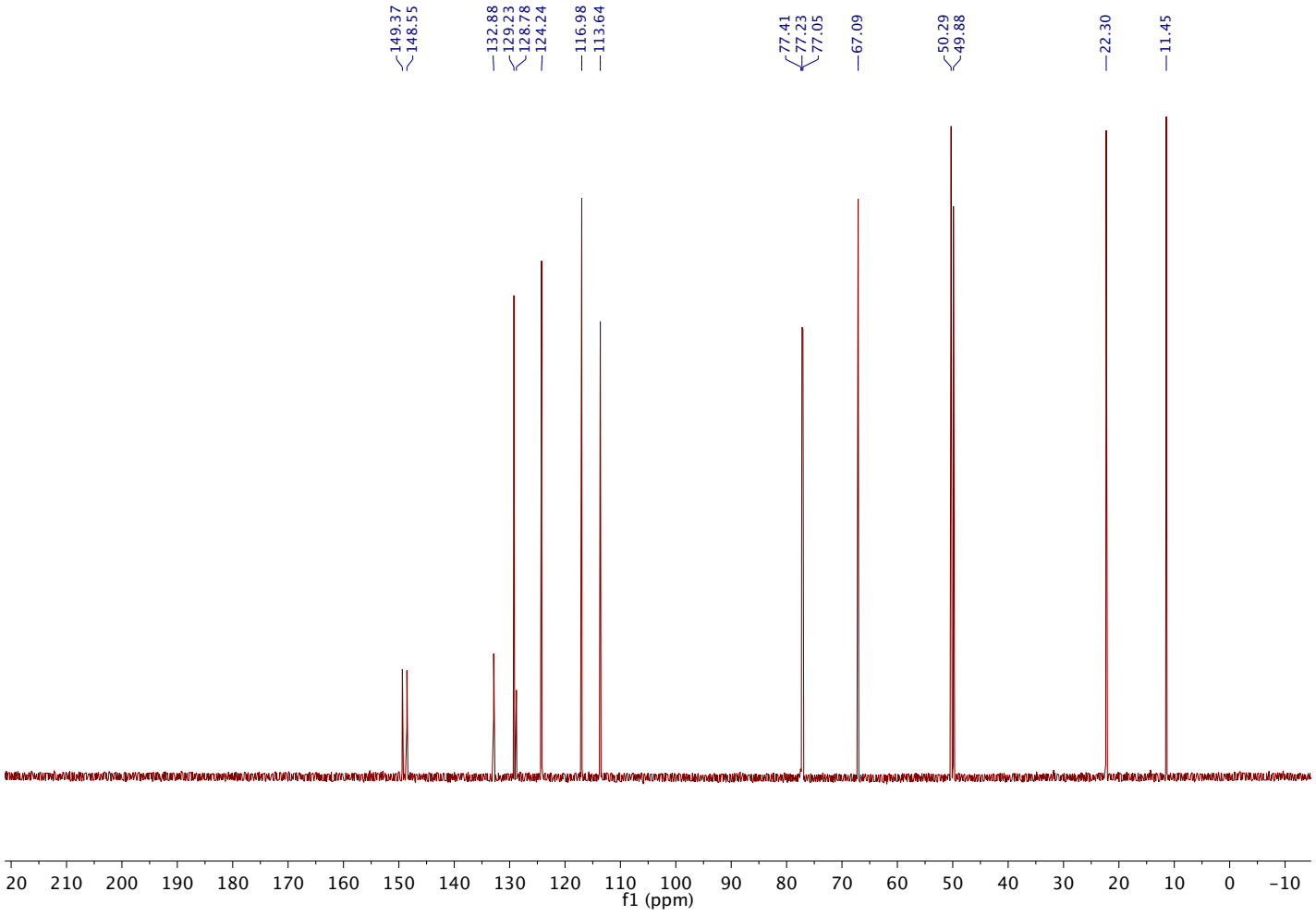
^{1}H NMR

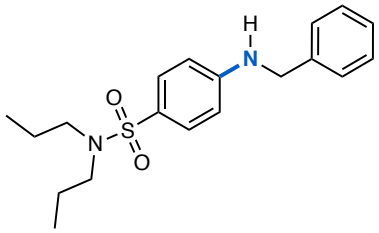

7.58
7.57
7.26
7.26
7.12
7.11
6.92
6.90
6.84
6.83
5.94
3.88
3.87
3.87
3.87
3.86
3.15
3.14
3.14
3.14
3.13
3.04
3.03
3.03
3.02
3.02
1.58
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.52
0.88
0.86
0.85
2.00
2.05
2.07
2.09
1.04
4.08
4.12
4.14
4.16
6.20
f1 (ppm)



30

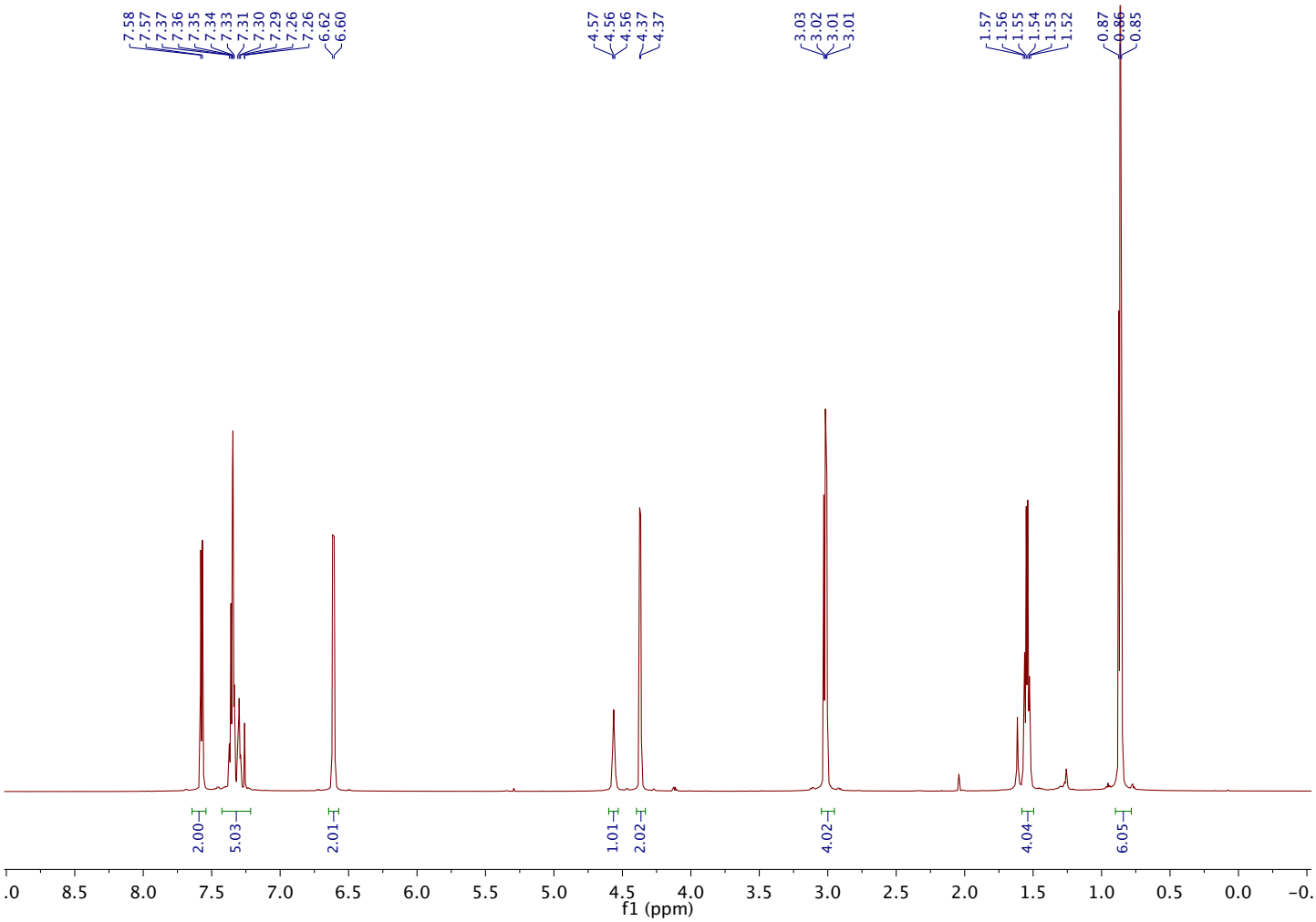
^{13}C NMR

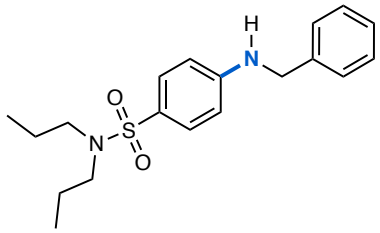

149.37
148.55
132.88
129.23
128.78
124.24
116.98
113.64
77.41
77.23
77.05
67.09
50.29
49.88
22.30
11.45
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



31

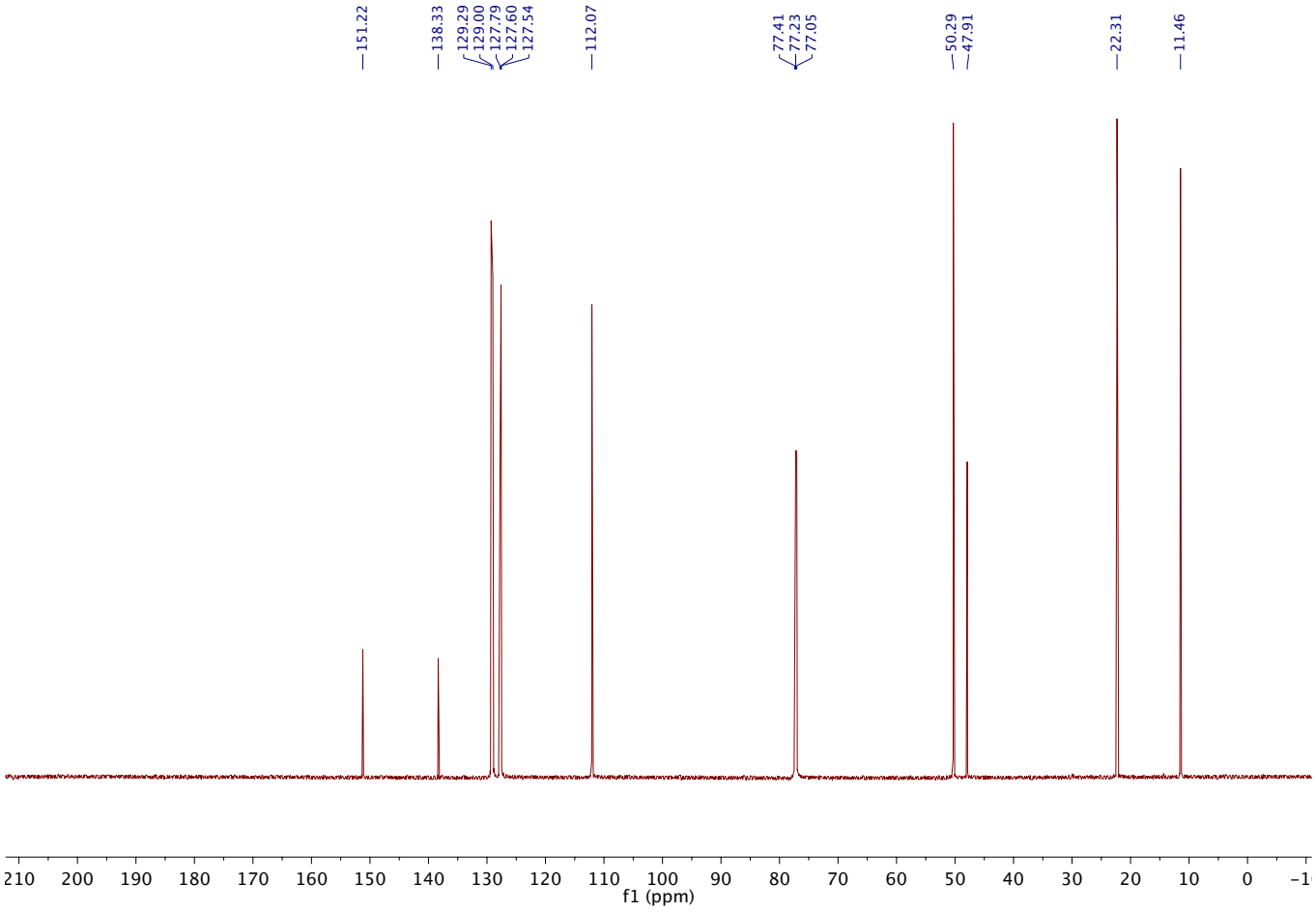
^{1}H NMR

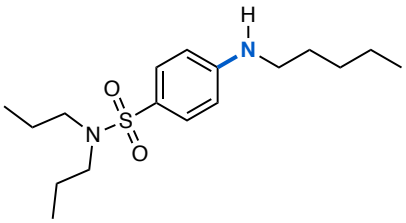

7.58
7.57
7.37
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.26
7.26
6.62
6.60
4.57
4.56
4.56
4.37
4.37
3.03
3.02
3.01
3.01
1.57
1.56
1.55
1.54
1.53
1.52
0.87
0.86
0.85
2.00
5.03
2.01
1.01
2.02
4.02
4.04
6.05
f1 (ppm)



31

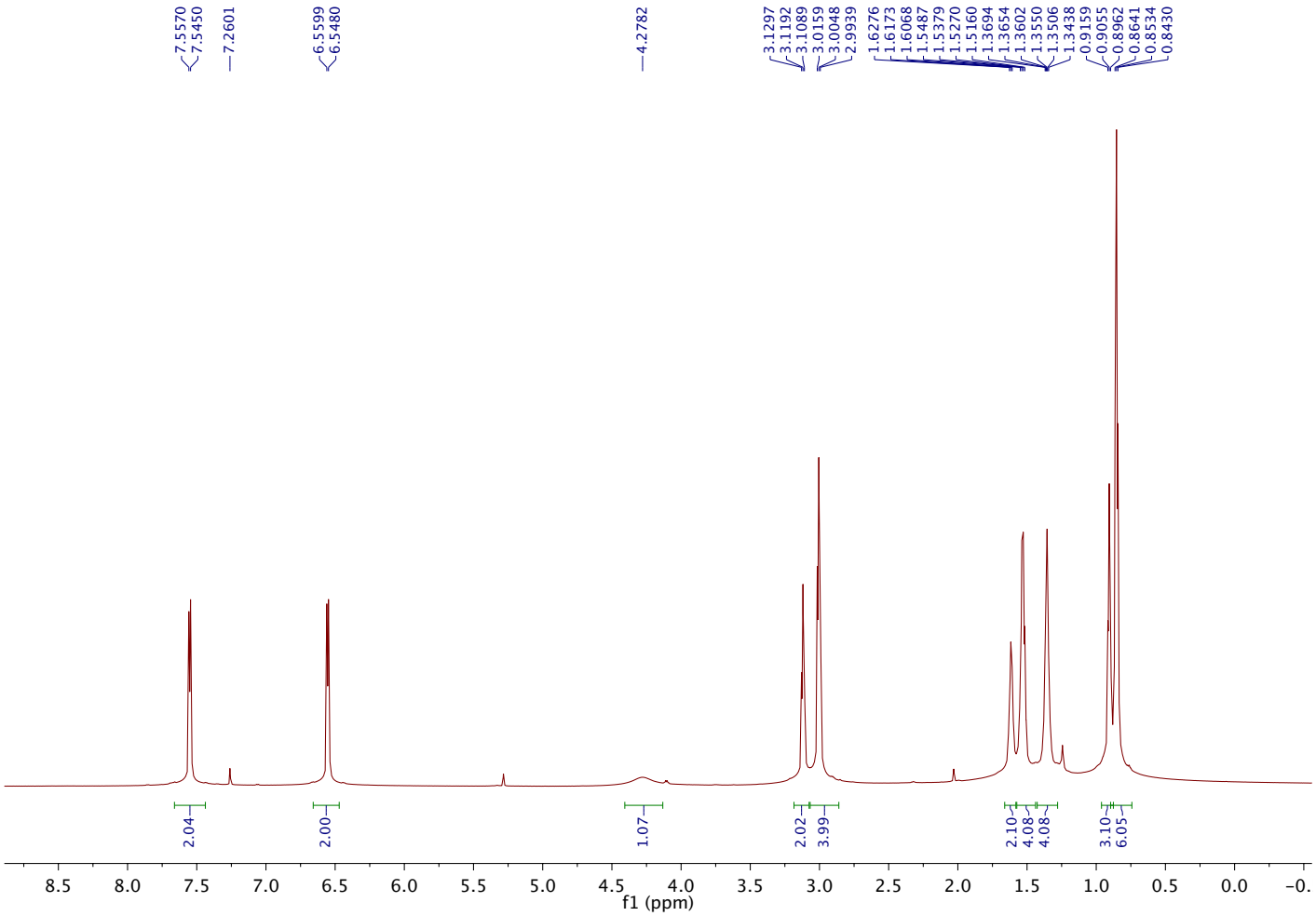
^{13}C NMR

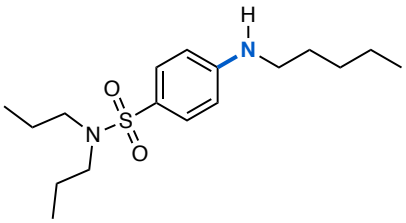

151.22
138.33
129.29
129.00
127.79
127.60
127.54
112.07
77.41
77.23
77.05
50.29
47.91
22.31
11.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



32

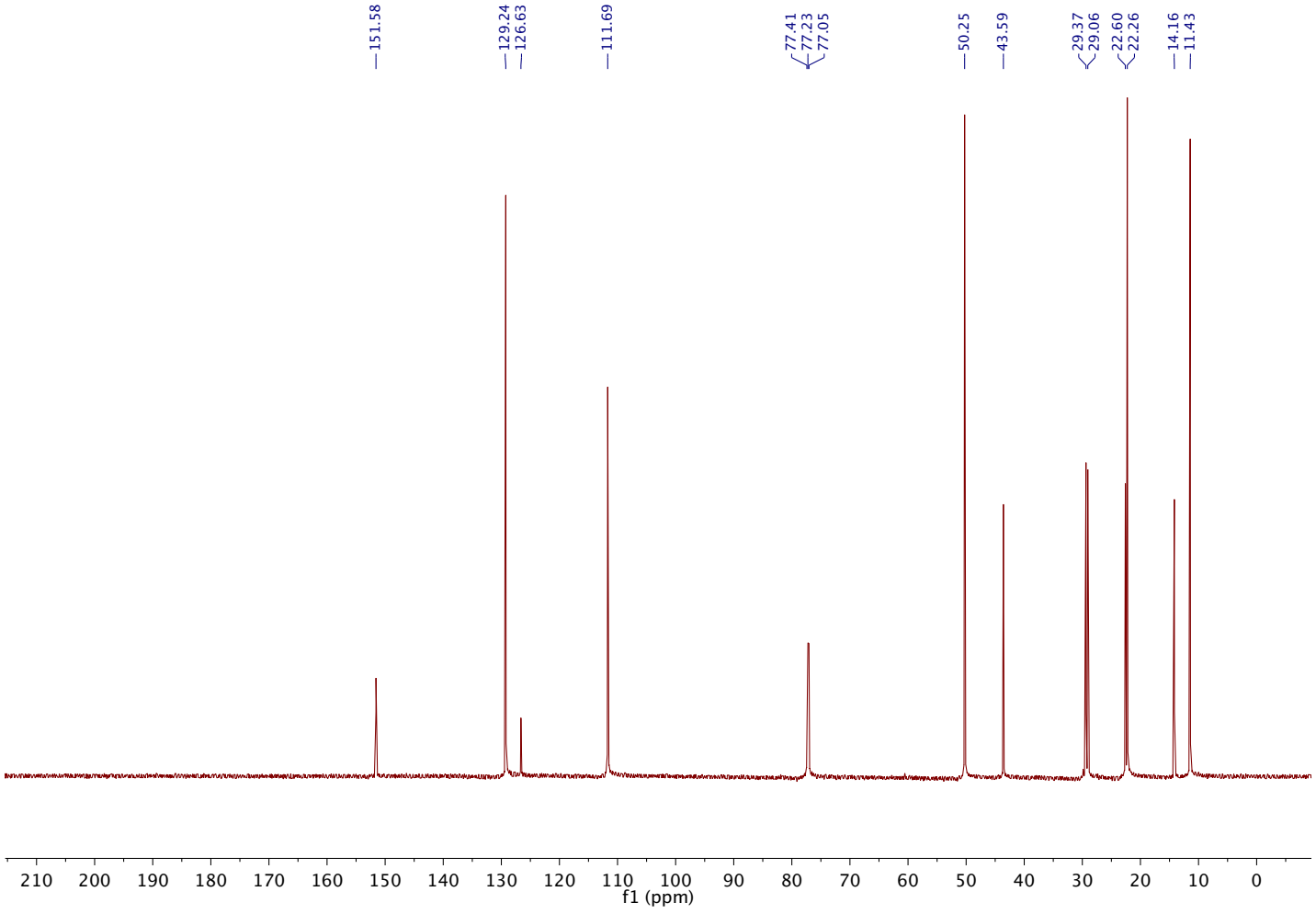
^{1}H NMR

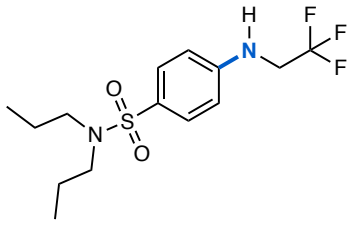

7.5570
7.5450
7.2601
6.5599
6.5480
4.2782
3.1297
3.1192
3.1089
3.0159
3.0048
2.9939
1.6276
1.6173
1.6068
1.5487
1.5379
1.5270
1.5160
1.3694
1.3654
1.3602
1.3550
1.3506
1.3438
0.9159
0.9055
0.8962
0.8641
0.8534
0.8430
2.04
2.00
1.07
2.02
3.99
2.10
4.08
4.08
3.10
6.05
f1 (ppm)



32

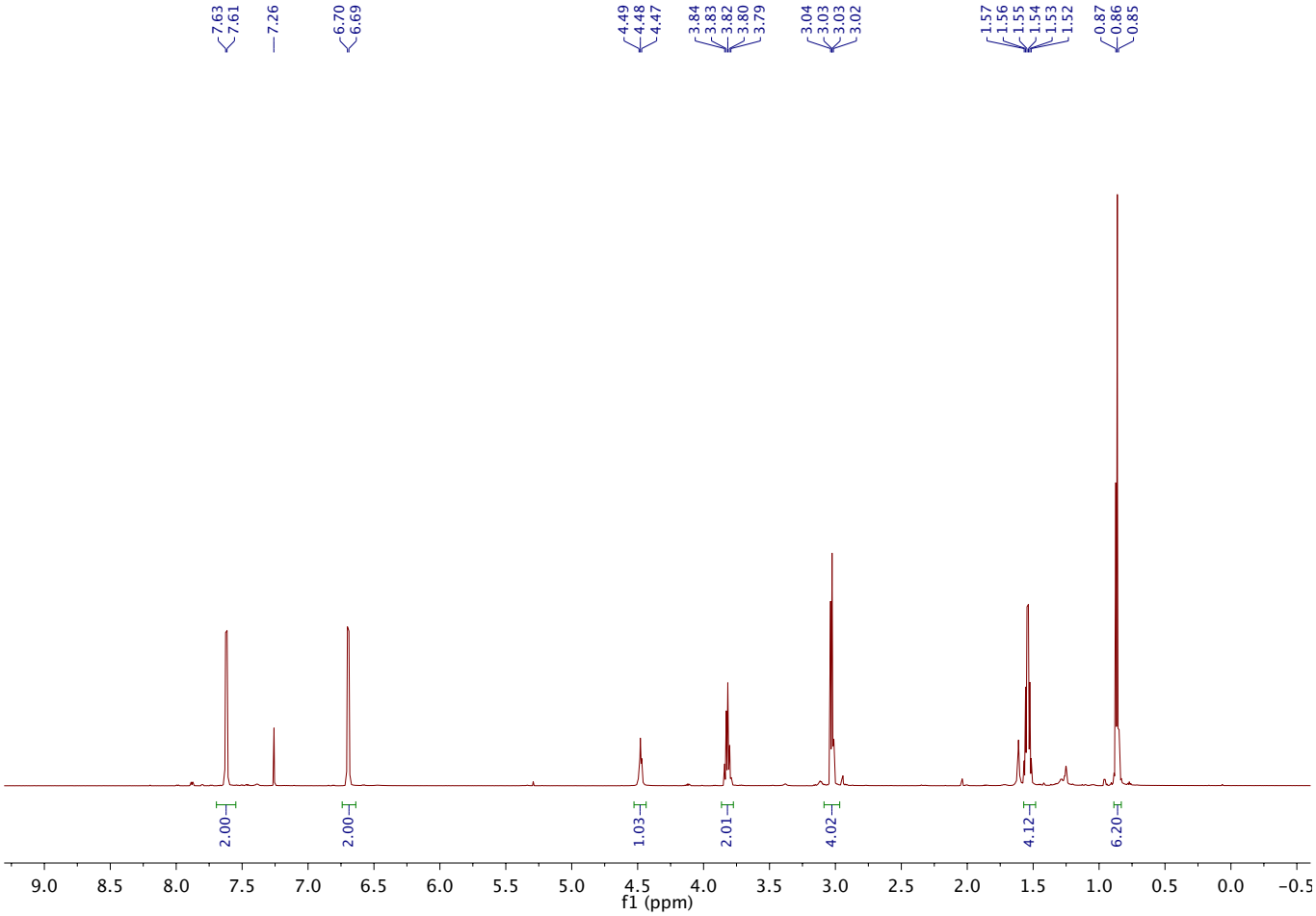
^{13}C NMR

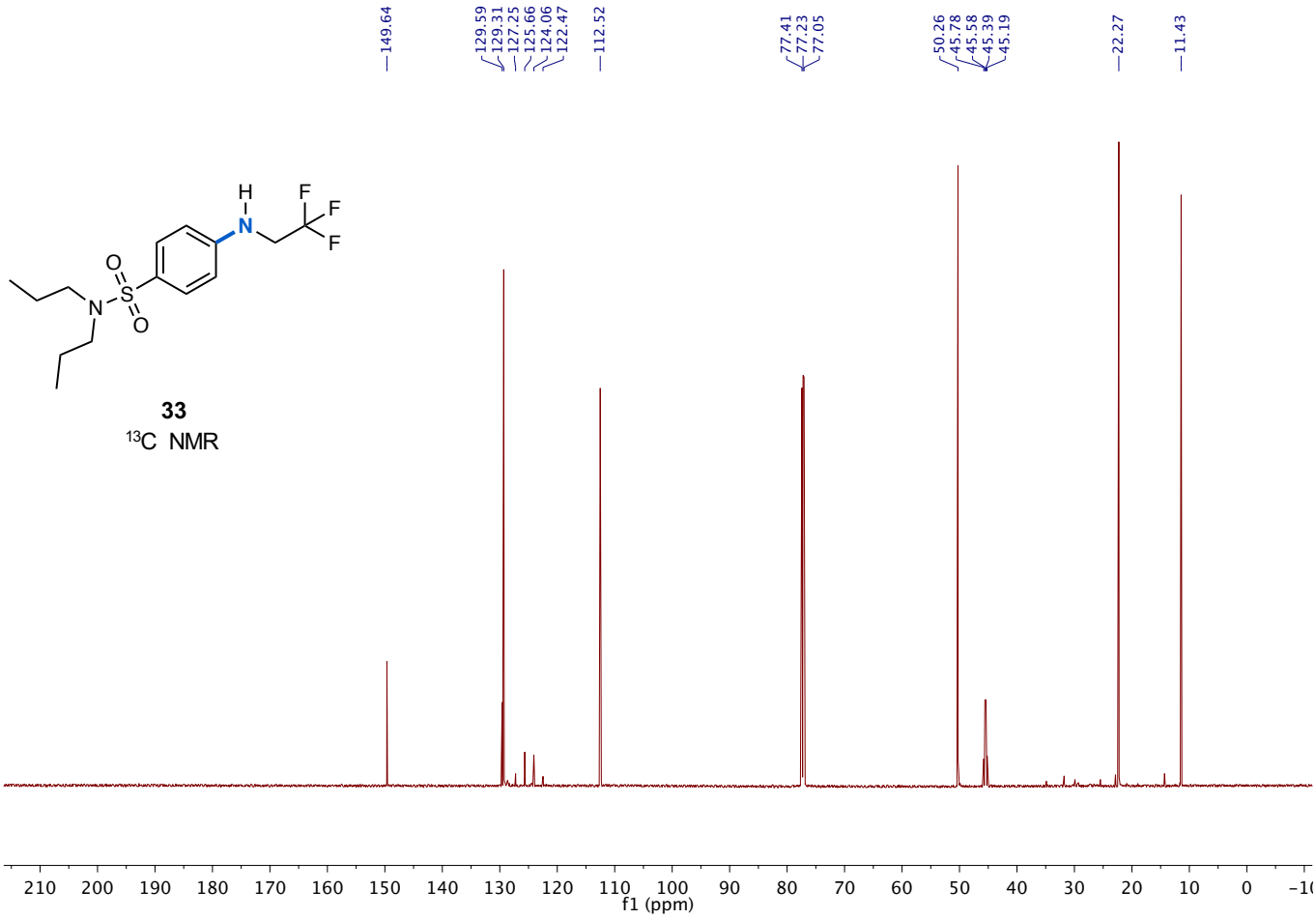

151.58
129.24
126.63
111.69
77.41
77.23
77.05
50.25
43.59
29.37
29.06
22.60
22.26
14.16
11.43
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

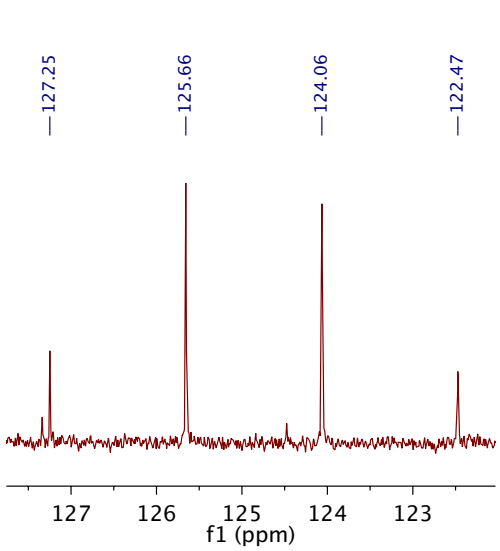


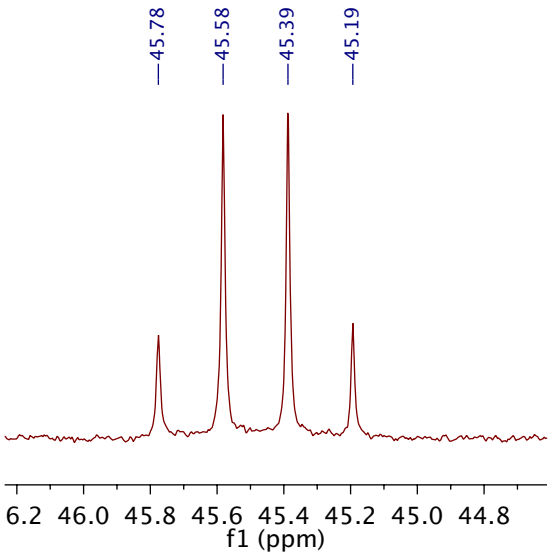
33

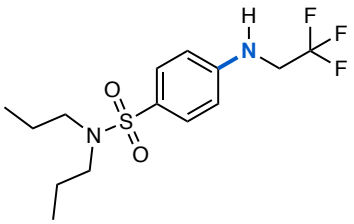
^{1}H NMR


7.63
7.61
7.26
6.70
6.69
4.49
4.48
4.47
3.84
3.83
3.82
3.80
3.79
3.04
3.03
3.03
3.02
1.57
1.56
1.55
1.54
1.53
1.52
0.87
0.86
0.85
2.00
2.00
1.03
2.01
4.02
4.12
6.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


149.64
129.59
129.31
127.25
125.66
124.06
122.47
112.52
77.41
77.23
77.05
50.26
45.78
45.58
45.39
45.19
22.27
11.43
H
N
F
F
F
O
S
O
N
33
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

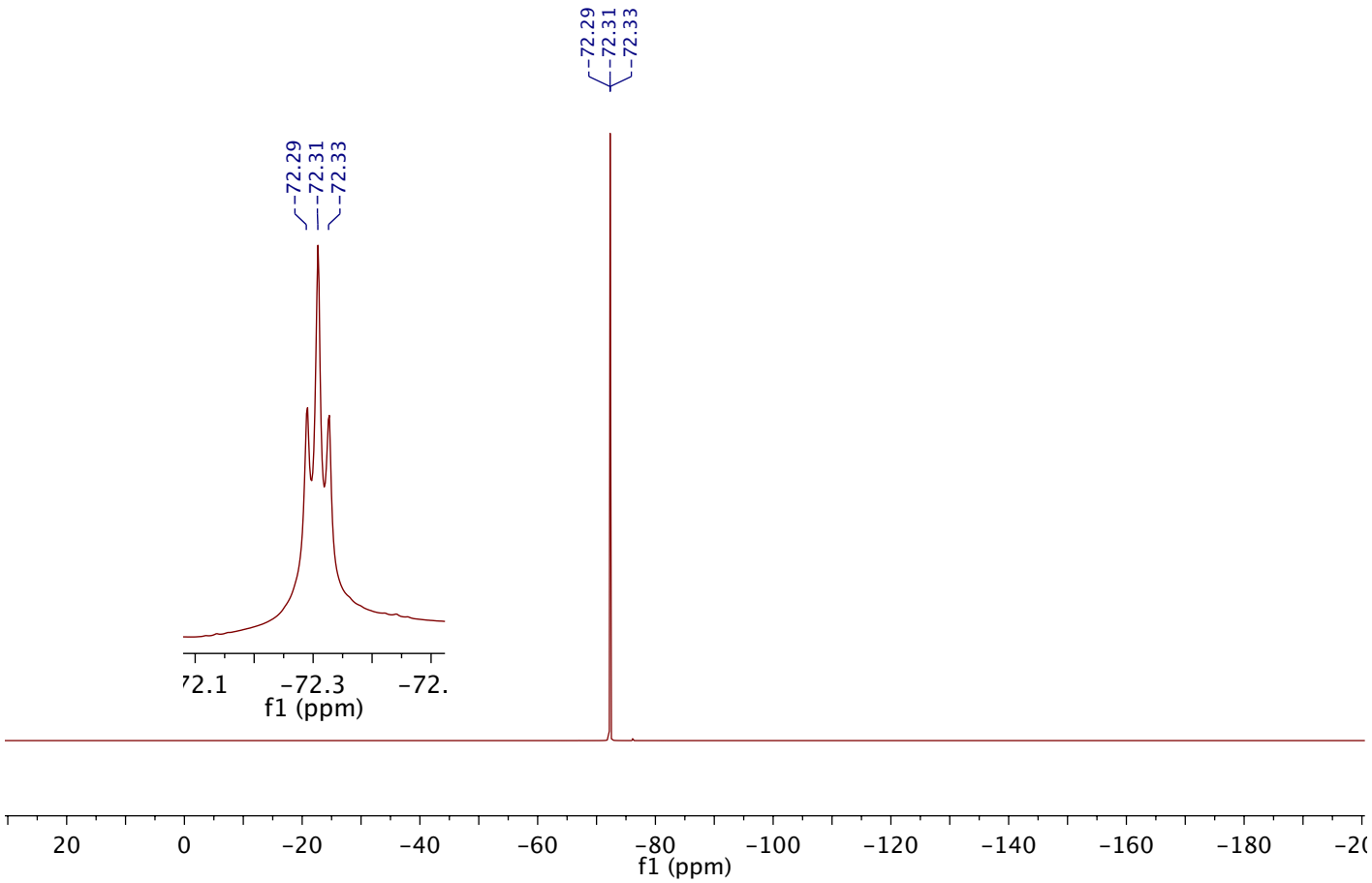

127.25
125.66
124.06
122.47
127 126 125 124 123
f1 (ppm)

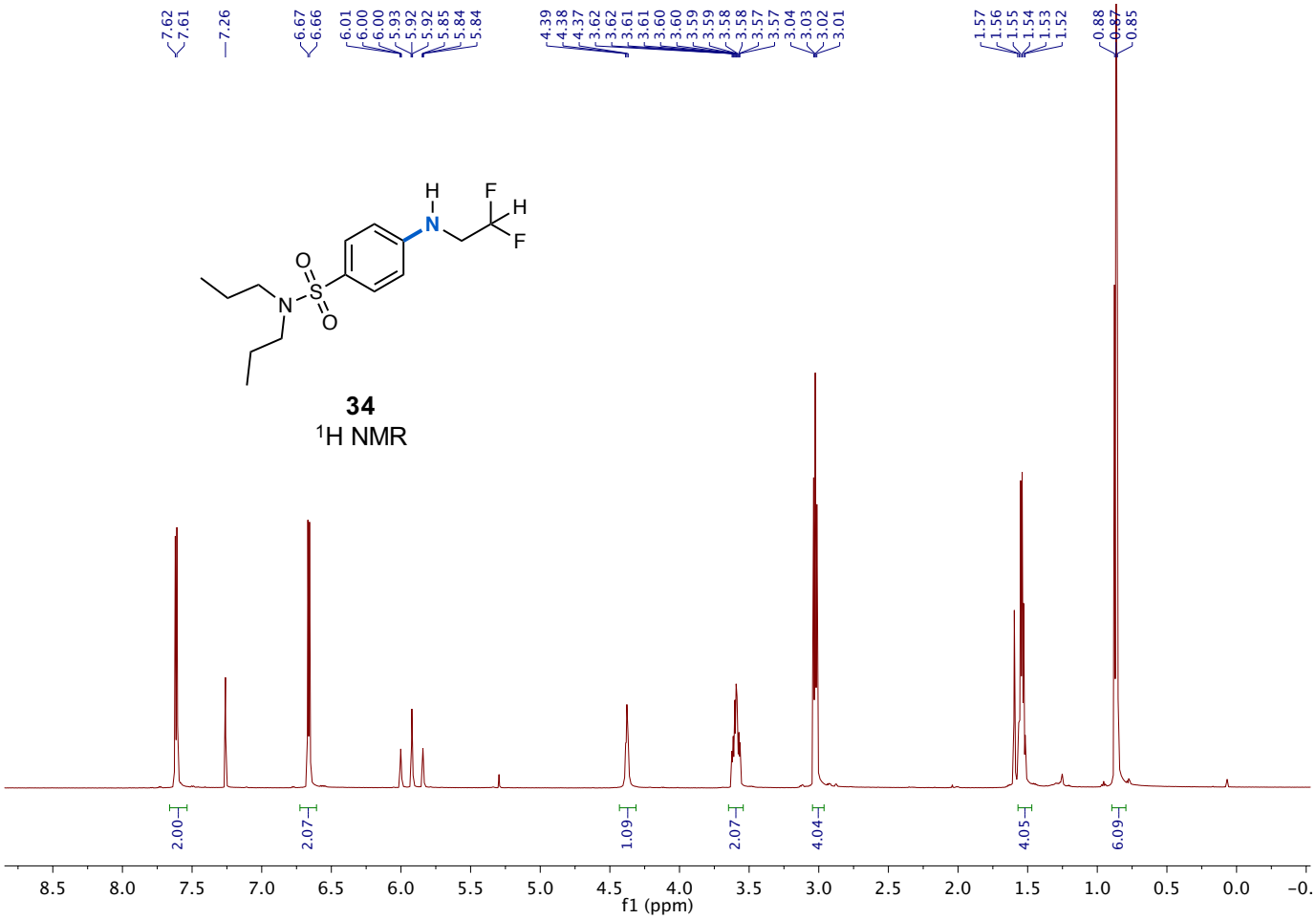

45.78
45.58
45.39
45.19
6.2 46.0 45.8 45.6 45.4 45.2 45.0 44.8
f1 (ppm)

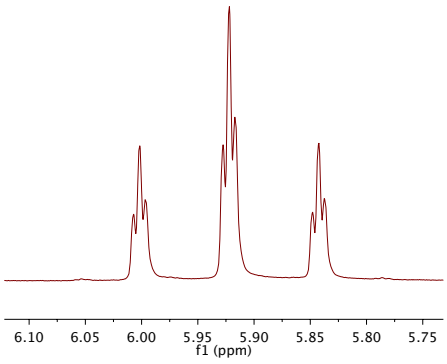

H
F
F
F
N
O
S
O
N
O

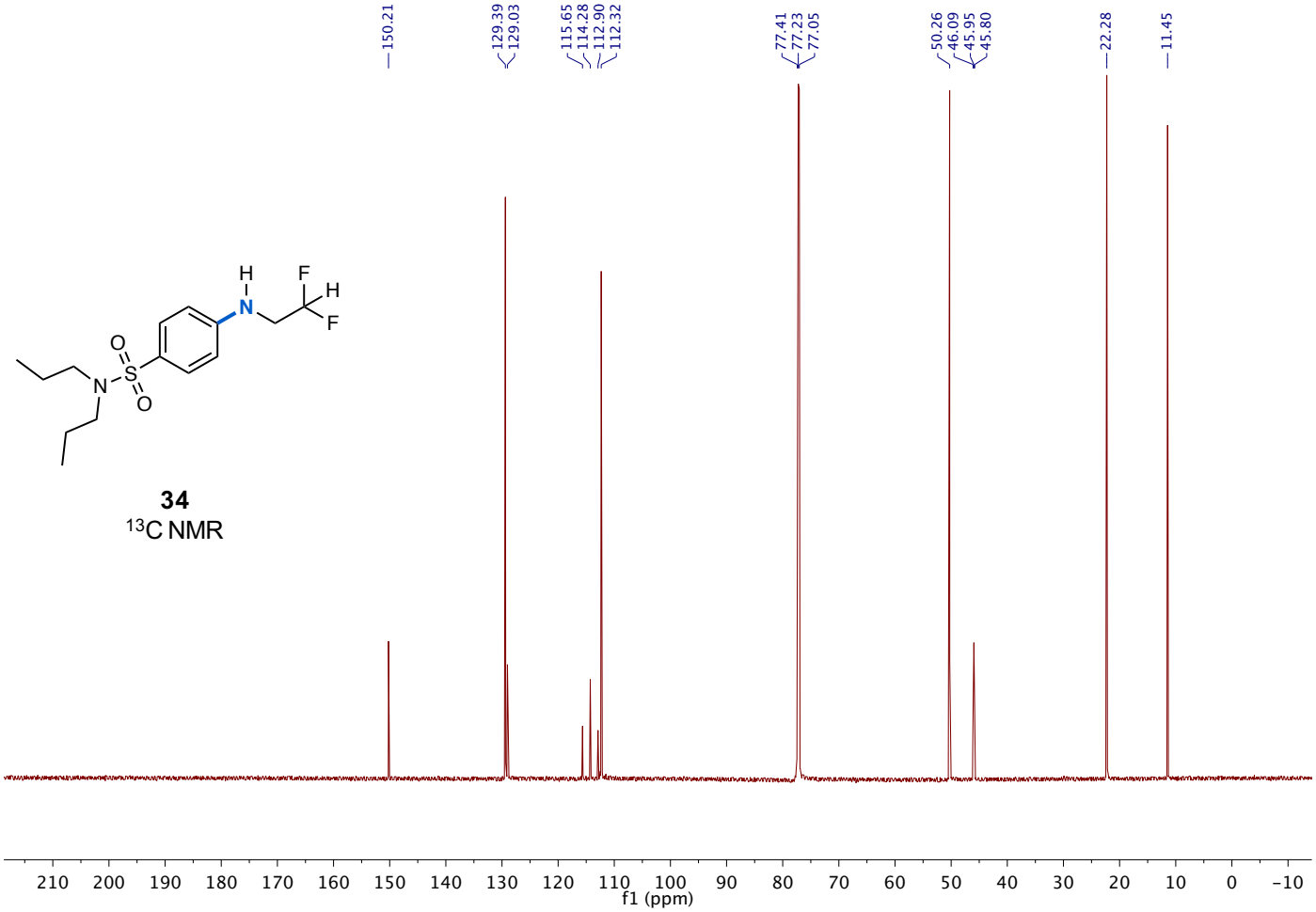
33

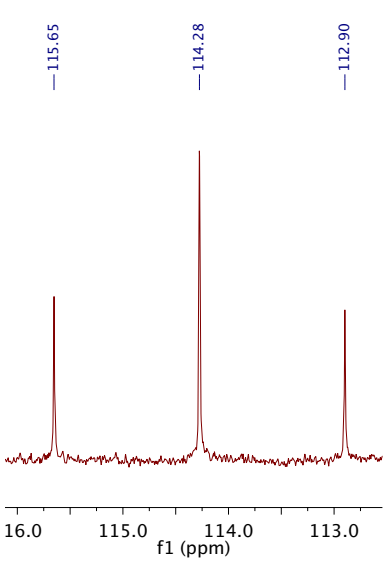
^{19}F NMR

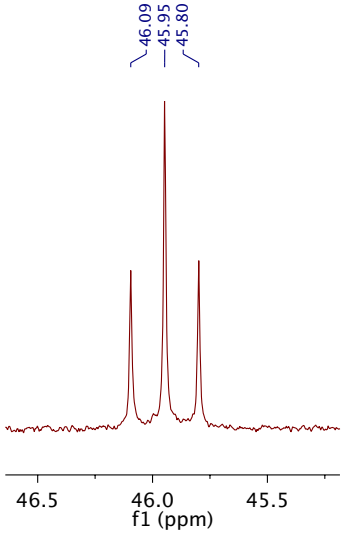

-72.29
-72.31
-72.33
-72.29
-72.31
-72.33
72.1
-72.3
-72.
f1 (ppm)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

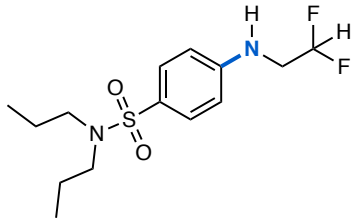

7.62
7.61
7.26
6.67
6.66
6.01
6.00
6.00
5.93
5.92
5.92
5.85
5.84
5.84
4.39
4.38
4.37
3.62
3.62
3.61
3.61
3.60
3.60
3.59
3.59
3.58
3.58
3.57
3.57
3.04
3.03
3.02
3.01
1.57
1.56
1.55
1.54
1.53
1.52
0.88
0.87
0.85
H
N
F
H
F
O
S
O
N
34
1H NMR
2.00
2.07
1.09
2.07
4.04
4.05
6.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
f1 (ppm)


150.21
129.39
129.03
115.65
114.28
112.90
112.32
77.41
77.23
77.05
50.26
46.09
45.95
45.80
22.28
11.45
H
N
F
H
F
O
S
O
N
34
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

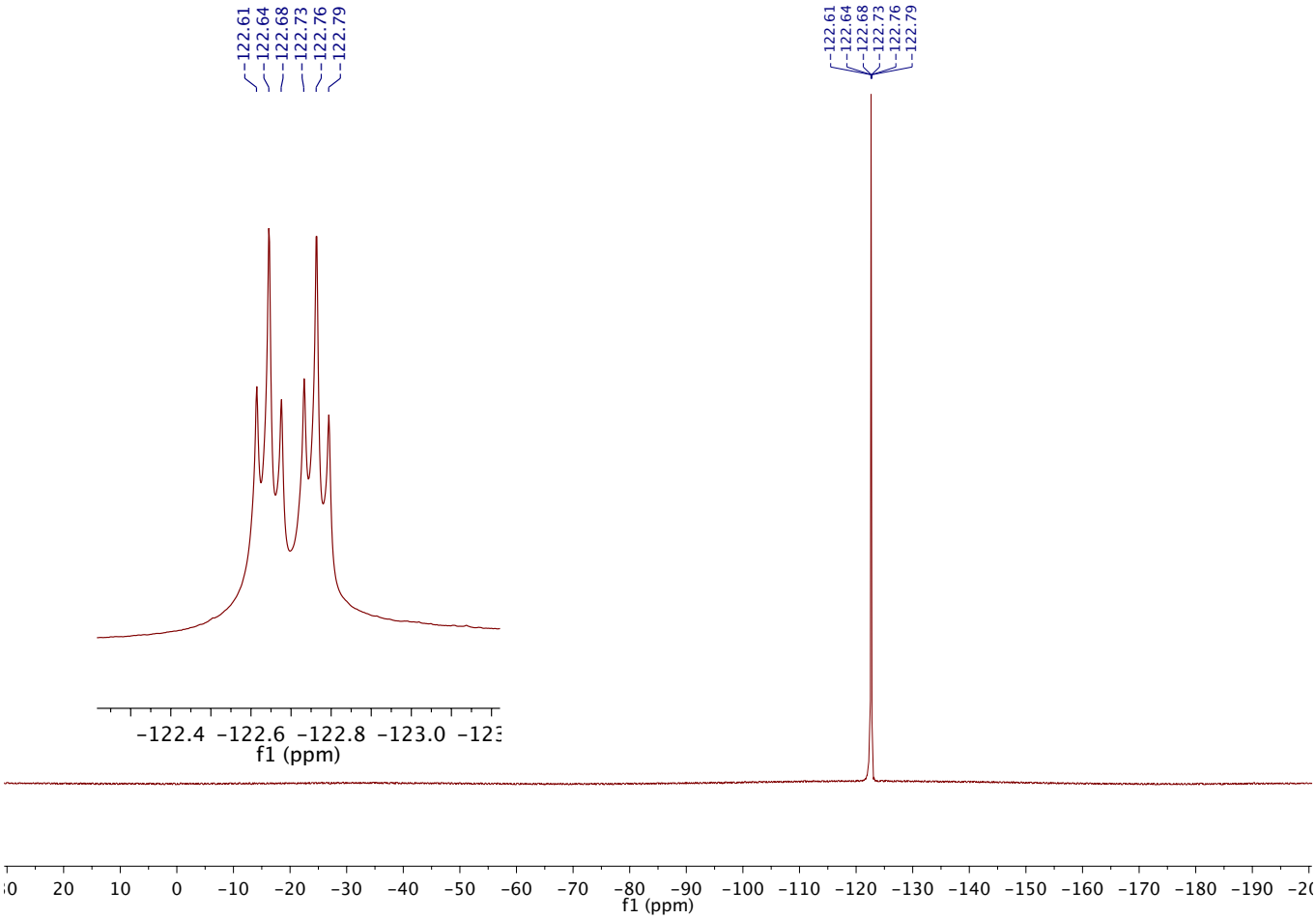

115.65
114.28
112.90
16.0 115.0 114.0 113.0
f1 (ppm)

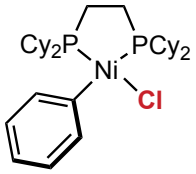

46.09
45.95
45.80
46.5 46.0 45.5
f1 (ppm)


H
F
H
F
N
O
S
O
N
O

34

^{19}F NMR

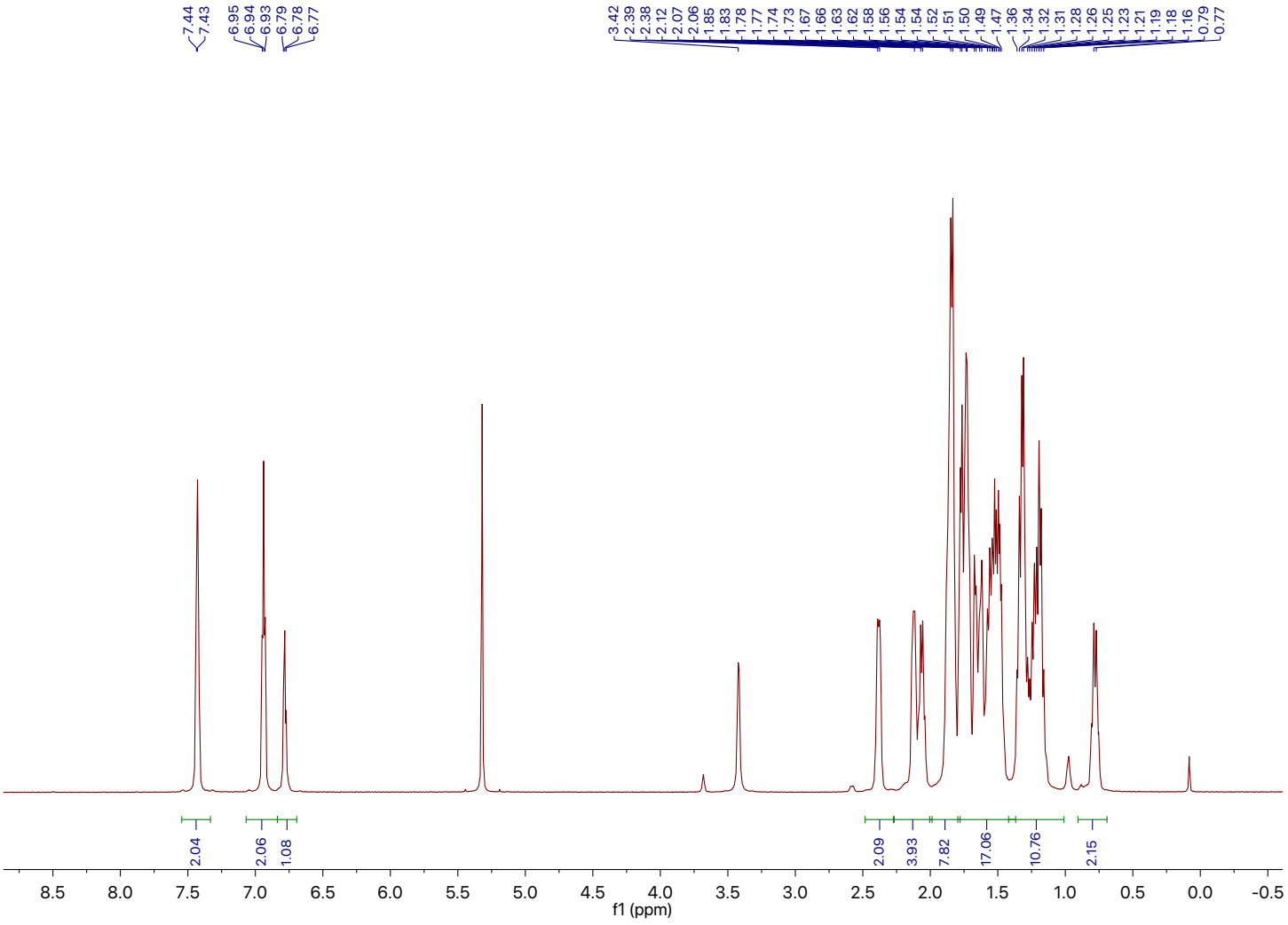

-122.61
-122.64
-122.68
-122.73
-122.76
-122.79
-122.4 -122.6 -122.8 -123.0 -123
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

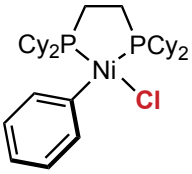


Ni–Cl **D**

Complex D

^{1}H NMR

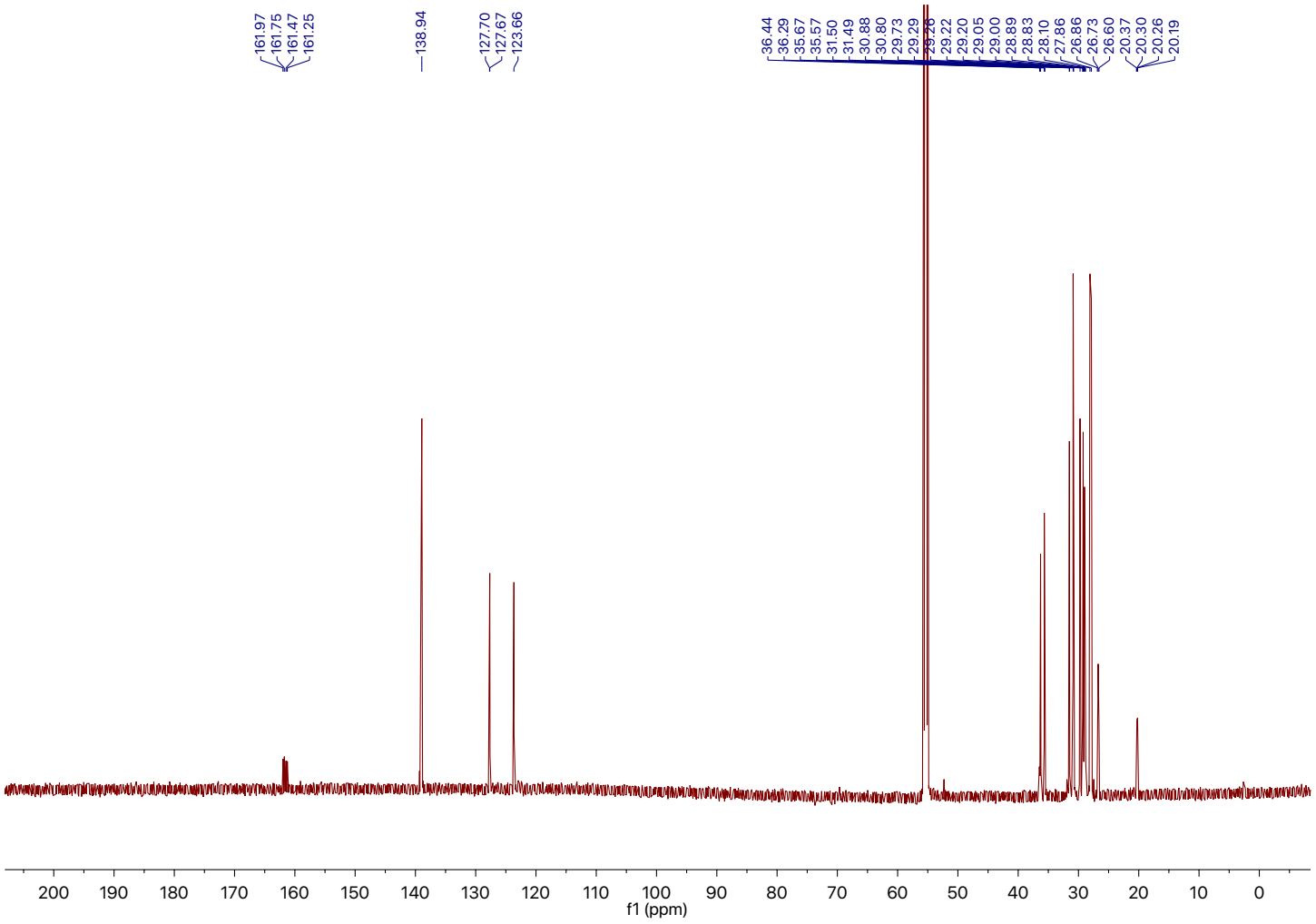


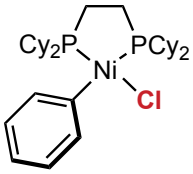


Ni–Cl **D**

Complex D

^{13}C NMR

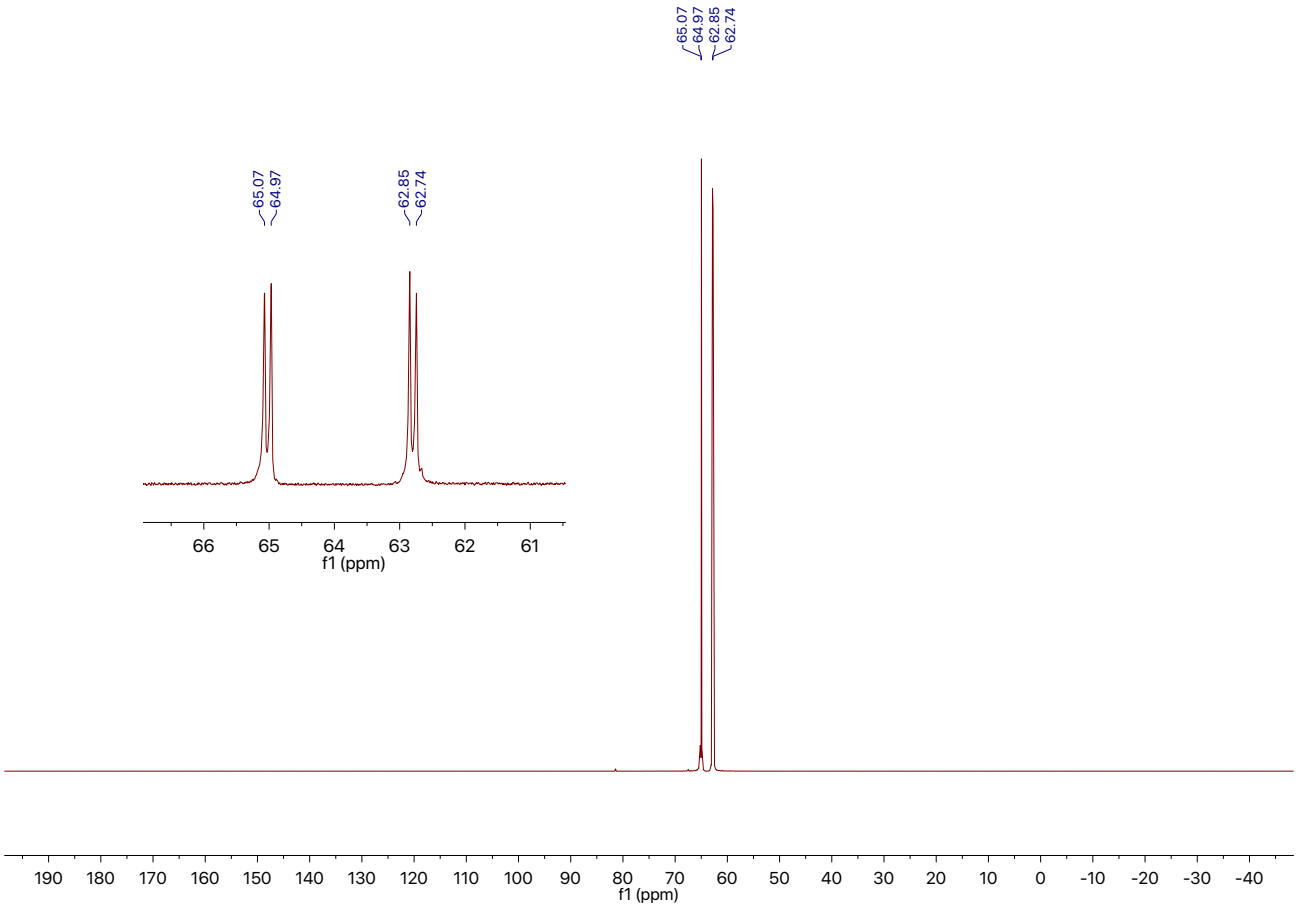


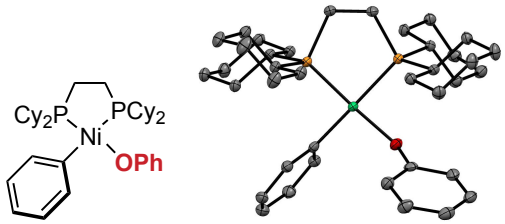


Ni–Cl **D**

Complex D

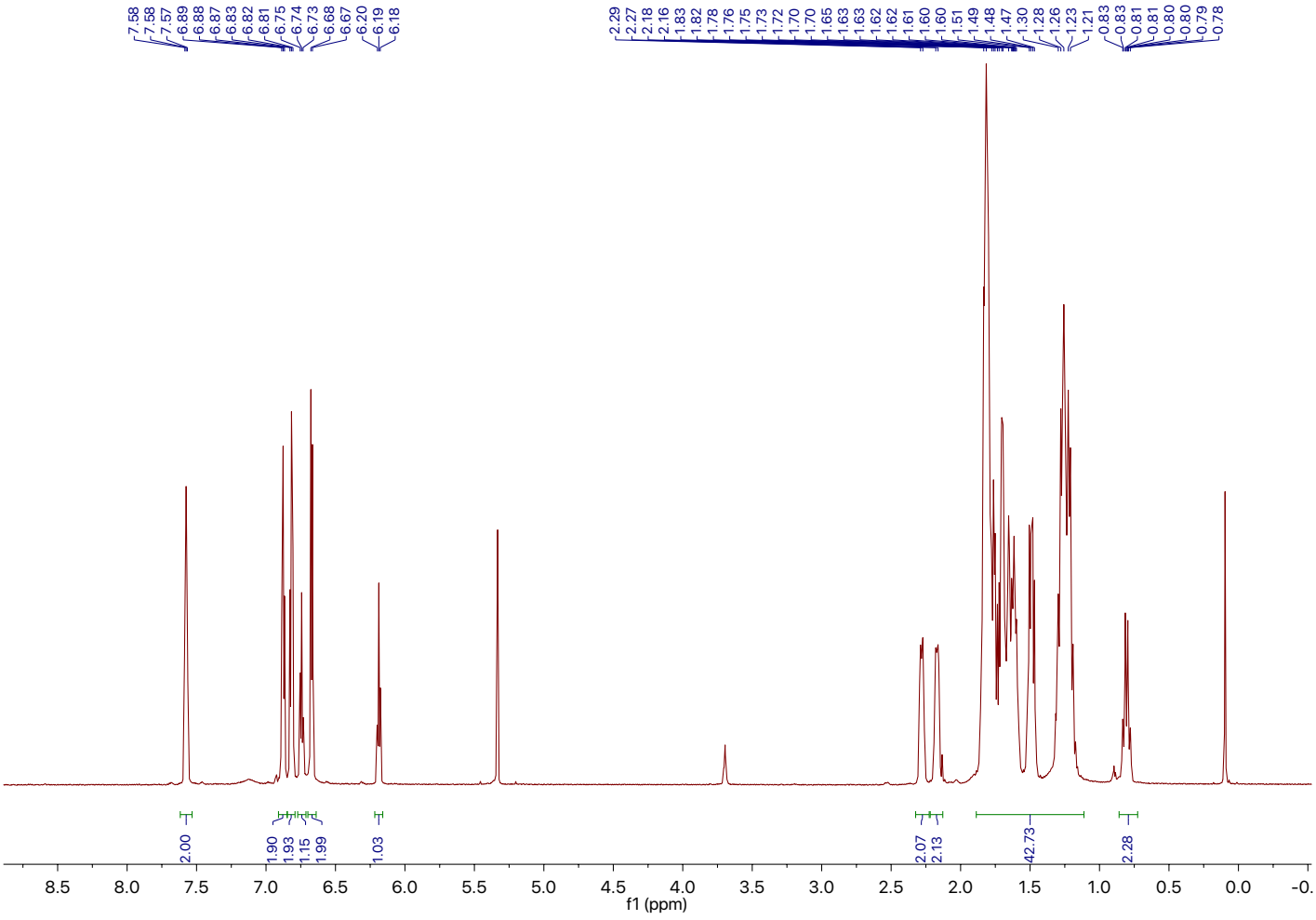
^{31}P NMR

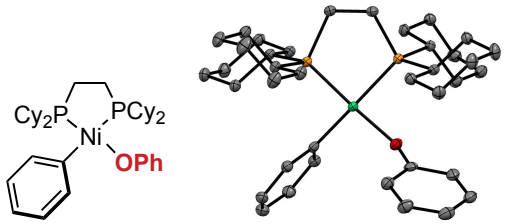




Complex B

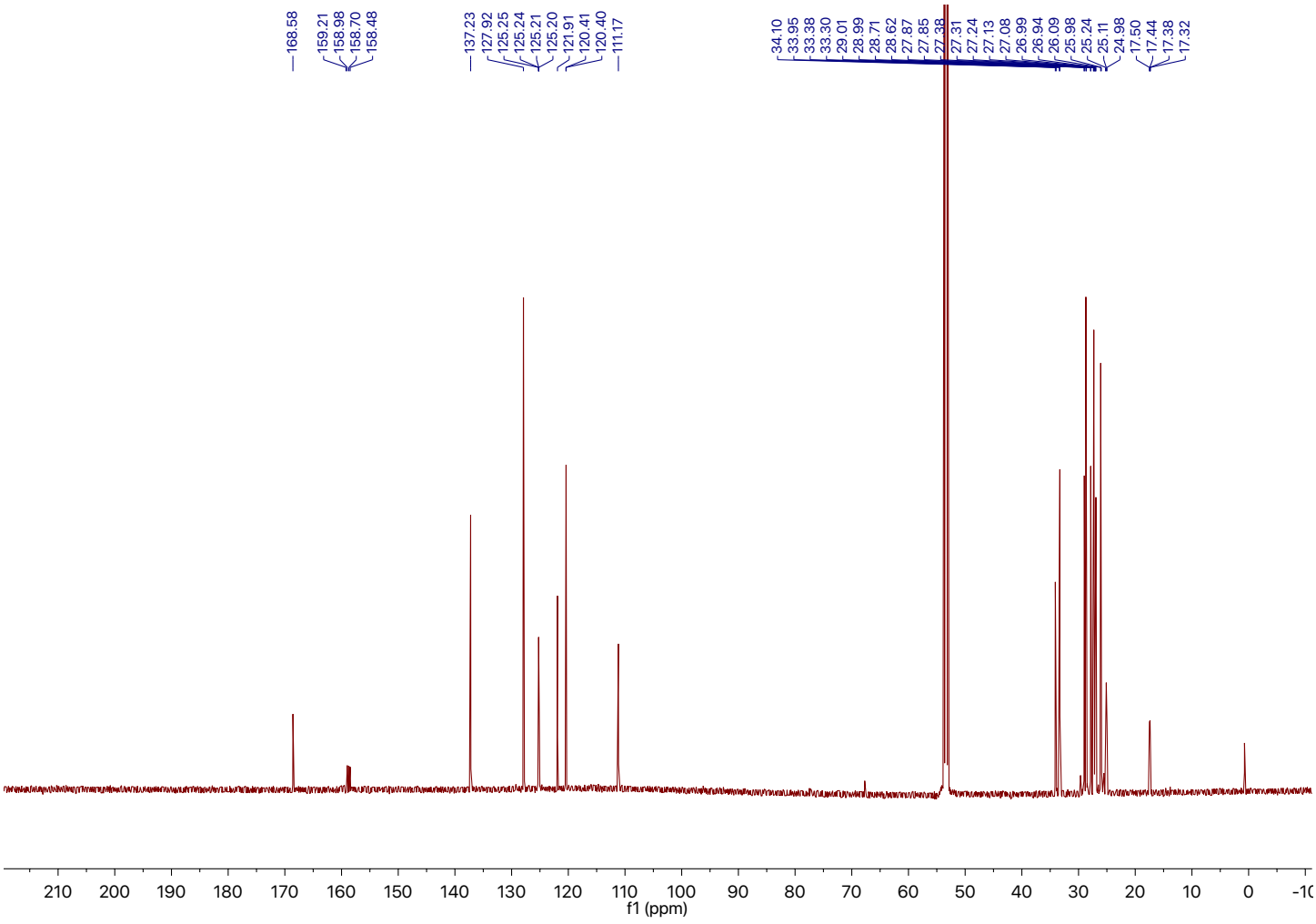
^{1}H NMR

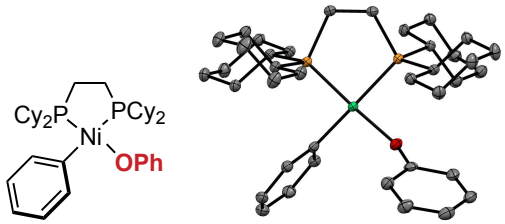




Complex B

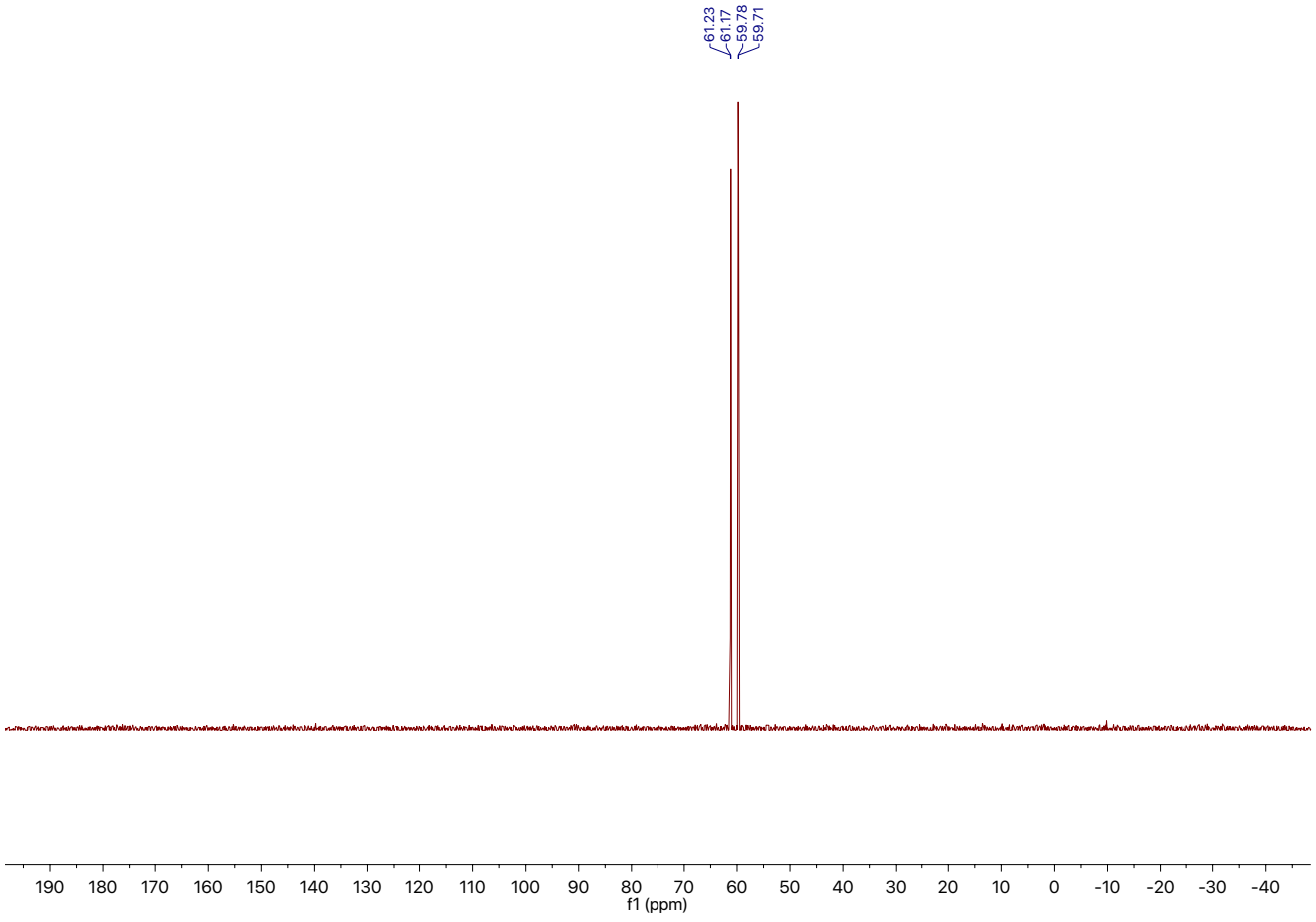
^{13}C NMR

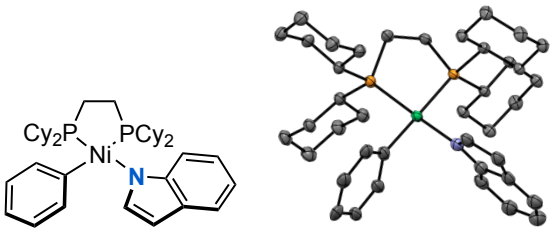




Complex B

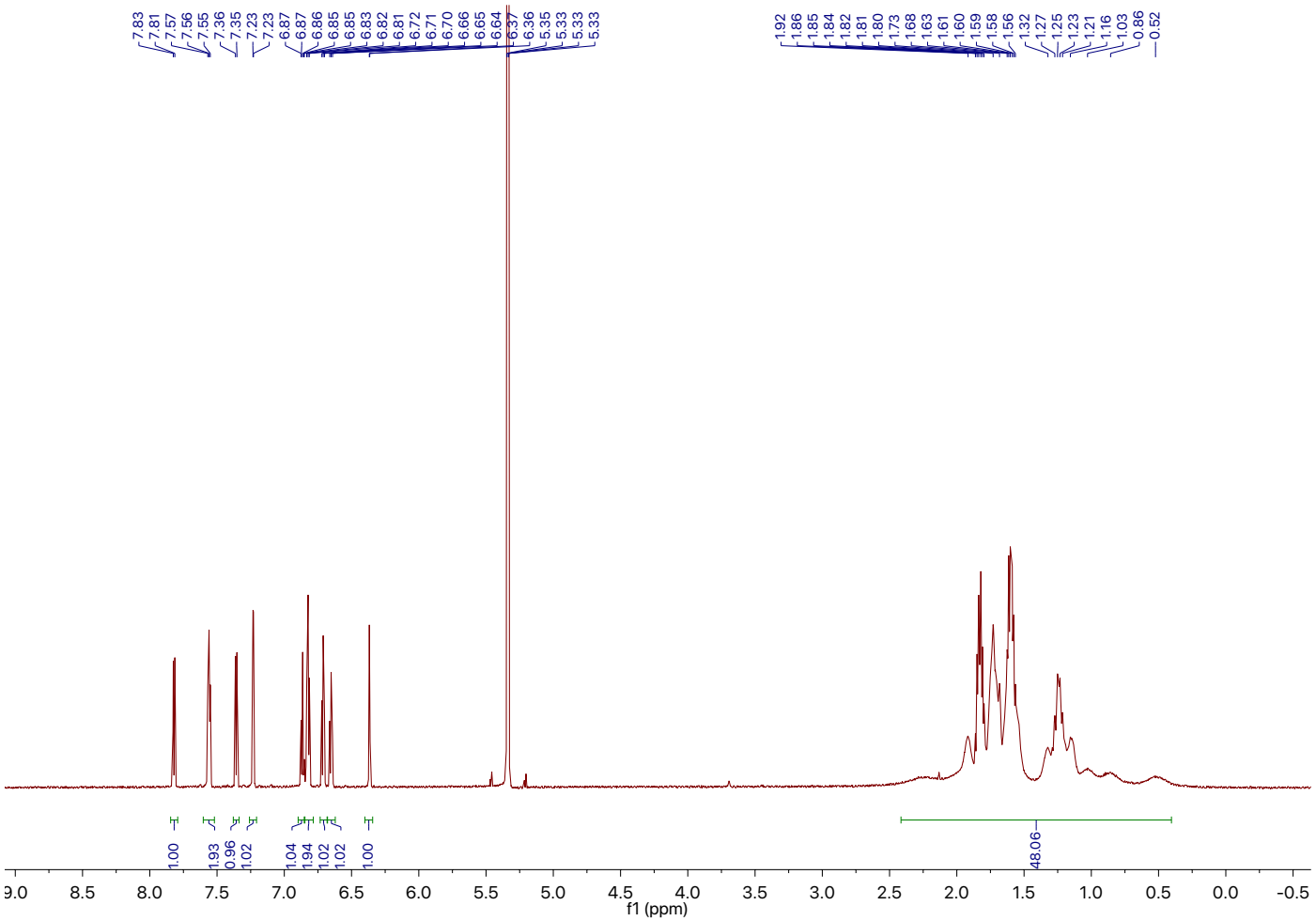
^{31}P NMR

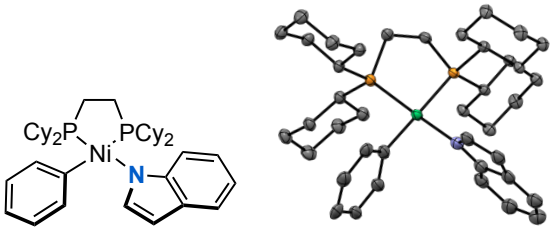




Complex C

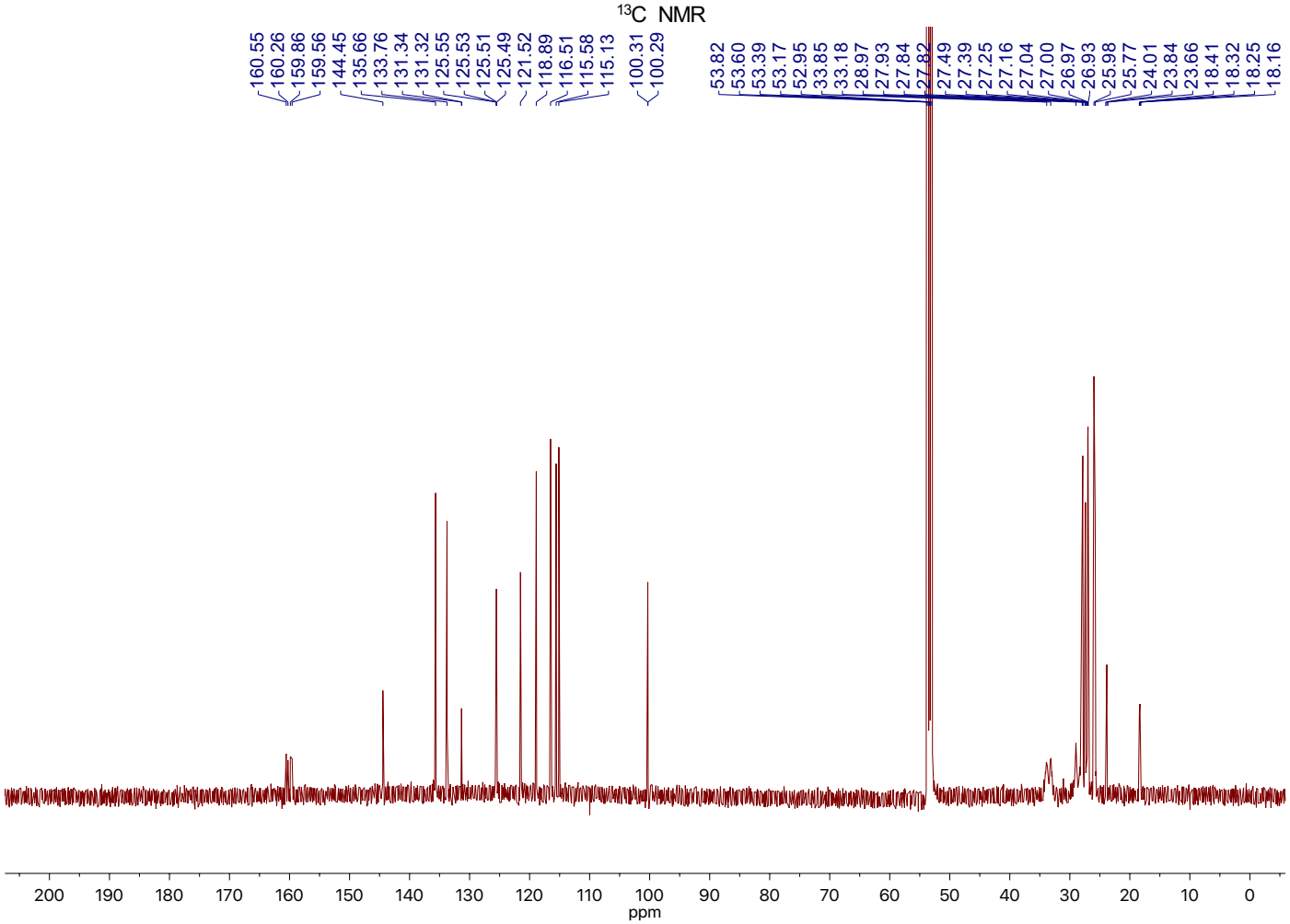
^{1}H NMR

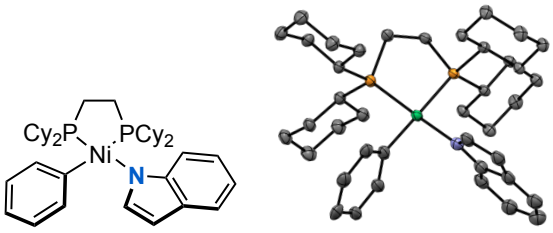




Complex C

^{13}C NMR





Complex C

^{31}P NMR