Supporting Information

Pd-Catalyzed Decarbonylative Cross-Couplings of Aroyl Chlorides

Christian A. Malapit, Naoko Ichiishi, and Melanie S. Sanford*

Department of Chemistry, University of Michigan
930 North University Avenue, Ann Arbor, MI 48109 United States

**Email: mssanfor@umich.edu*

Table of Contents

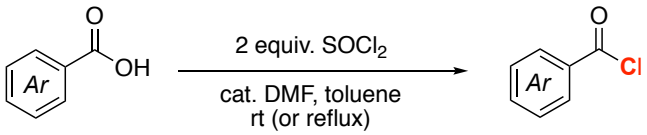
I. General Information

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 spectra (HRMS) were obtained on a Micromass AutoSpec Ultima Magnetic Sector instrument. GCMS analyses were performed on a Shimadzu GCMS-QP2010 gas chromatograph mass spectrometer. Infrared spectroscopy was performed on a Perkin-Elmer Spectrum BX FT-IR spectrometer, and peaks are reported in cm^{-1}. Melting points were determined with a Mel-Temp 3.0 (Laboratory Devices, Inc.) and are uncorrected. Chromatographic purifications were performed by column chromatography using 40–63 micron flash silica gel or a CombiFlash Torrent® system using RediSep® Rf columns packed with silica gel.

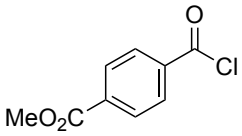
II. Materials and Methods

All commercially available reagents were used as received unless otherwise stated. The commercial acid chlorides 4-nitrobenzoyl chloride, 1-naphthoyl chloride (**1e**), 4-biphenylcarbonyl chloride, 4-*n*-butylbenzoyl chloride, and 4-anisoyl chloride were purchased from Sigma-Aldrich. Trimellitic anhydride chloride was purchased from Alfa Aesar. 4-Phenoxybenzoyl chloride was purchased from MayBridge. Quinaldoyl chloride was purchased from Acros Organics. $Pd[P(o\text{-}tol)_3]_2$ was purchased from Alfa Aesar. $Pd(dba)_2$ was purchased from Frontier Scientific. BrettPhos was purchased from Sigma Aldrich. Dioxane, purchased from Acros Organics (99.5% extra dry, with molecular sieves), was purified by distillation and then stored over molecular sieves in the glove box. Toluene was purchased from VWR International and purified by an Innovative Technologies solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, Inc. Triethyl(trifluoromethyl)silane ($TESCF_3$) and trimethyl(pentafluoromethyl)silane ($TMSCF_2CF_3$) were purchased from SynQuest Labs, Inc. Trimethyl(difluoromethyl)silane ($TMSCF_2H$) was purchased from Oakwood. Spray-dried KF and CsF (Chemetall) were provided by The Dow Chemical Company (Midland, MI) and were stored in the glove box.

III. Synthesis of Acid Chlorides

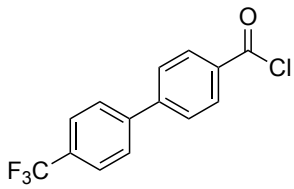


General procedure for the synthesis of acid chlorides: A round bottomed flask with a stir bar was charged with carboxylic acid (1.0 equiv), anhydrous DCM (0.25 M), and DMF (1-5 mol %). Thionyl chloride (2.0 equiv) was added dropwise using a syringe. The reaction mixture was stirred overnight at room temperature or refluxed for 4 h. The solvent and unreacted thionyl chloride were removed under reduced pressure to afford the acid chloride. The obtained acid chlorides were used without additional purification.



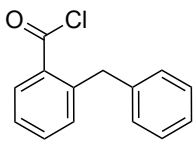
1a

Methyl 4-(chlorocarbonyl)benzoate (1a).[1] Compound **1a** was prepared according to the general procedure using 4-(methoxycarbonyl)benzoic acid (1.80 g, 10.0 mmol). Methyl 4-(chlorocarbonyl)-benzoate (**1a**) was obtained as a white solid (1.88 g, 95% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19–8.14 (multiple peaks, 4H), 3.97 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1, 165.8, 136.8, 136.1, 131.4, 130.2, 53.0.



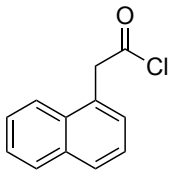
1d

4'-(Trifluoromethyl)-4-biphenylcarbonyl chloride (1d). Compound **1d** was prepared according to the general procedure using 4'-(trifluoromethyl)-4-biphenylcarboxylic acid (713 mg, 2.5 mmol). 4'-(Trifluoromethyl)-4-biphenylcarbonyl chloride (**1d**) was obtained as a yellow powder (683 mg, 92% yield): **^{1}H NMR** (700 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.0 Hz, 2H), 7.76-7.73 (multiple peaks, 6H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 167.7, 145.9, 142.5, 132.7, 132.1, 130.8 (q, *J* = 33.0 Hz), 127.8, 127.7, 126.1 (q, *J* = 3.8 Hz), 126.0 (q, *J* = 272.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.7; **HRMS** (EI) calcd for $C_{14}H_8ClF_3O$ $[M+H]^+$ *m/z* 284.0216, found 284.0214.



1h

2-Benzylbenzoyl chloride (1h).[2] Compound **1h** was prepared according to the general procedure using 2-benzylbenzoic acid (2.12 g, 10.0 mmol). 2-Benzylbenzoyl chloride (**1h**) was obtained as a yellowish oil (2.19 g, 95% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (t, *J* = 6.7 Hz, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.34-7.20 (multiple peaks, 5H), 7.14 (d, *J* = 6.7 Hz, 2H), 4.32 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.9, 143.5, 139.6, 134.4, 134.0, 132.9, 131.9, 129.2, 128.7, 127.0, 126.5, 39.8.



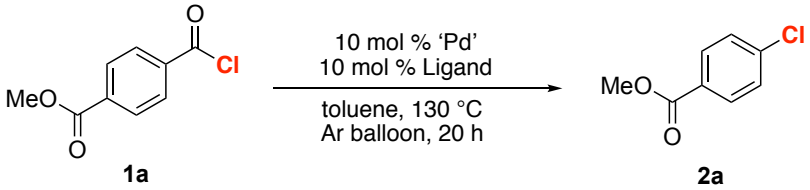
1k

1-Naphthylacetyl chloride (1k).[3] Compound **1k** was prepared according to the general procedure using 1-naphthylacetic acid (0.93 g, 5.0 mmol). 1-Naphthylacetyl chloride (**1k**) was obtained as a light brown oil (1.03 g, 100% yield): **^{1}H NMR** 400 MHz, 7.97–7.95 (multiple peaks, 2H), 7.93–7.91 (m, 1H), 7.66-7.58 (multiple peaks, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 4.56 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 133.9, 131.7, 129.3, 129.0, 128.9, 127.9, 127.0, 126.2, 125.5, 123.2, 50.7.

IV. Optimization Studies for Pd-Catalyzed Decarbonylative Chlorination

In a nitrogen-filled glovebox, acid chloride **1a** (1 equiv, 0.1 mmol) was weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of Pd catalyst and ligand in toluene (0.3 mL) was added. The vial was connected to a reflux condenser, capped with a rubber septum, and this assembly was removed from the glovebox. An argon balloon was placed on top of the condenser and the reaction mixture was stirred at 130 ºC (see Fig. S1, set-up A). After 20 h, the reaction mixture was cooled to room temperature and diluted with DCM (2 mL). The crude mixture was analyzed by GC using neopentyl benzene (0.05 mmol) as a standard. Alternatively, selected reactions were also set up without a condenser in a 4 mL (B) or 10 mL vial (C) under a nitrogen atmosphere. Representative results are summarized in Tables S1 and S2.

Table S1. Catalyst and Ligand Screen



entry	Pd cat.	ligand	yield of **2a** (%)
1	$Pd[P(o\text{-tol})_3]_2$	none	4
2	$Pd[P(o\text{-tol})_3]_2$	$P(o\text{-tol})_3$ (20 mol %)mol%)	5
3	$Pd[P(o\text{-tol})_3]_2$	P^tBu_3 (20 mol %)	<2
4	$Pd[P(o\text{-tol})_3]_2$	P^tBu_3 (10 mol %)	<2
5	$Pd[P(o\text{-tol})_3]_2$	$PAd_2{}^nBu$ (20 mol%)	10
6	$Pd[P(o\text{-tol})_3]_2$	PCy_3 (20 mol%)	0
7	$Pd[P(o\text{-tol})_3]_2$	*rac*-BINAP	0
8	$Pd[P(o\text{-tol})_3]_2$	Xantphos	41
9	$Pd[P(o\text{-tol})_3]_2$	DavePhos	14
10	$Pd[P(o\text{-tol})_3]_2$	SPhos	12
11	$Pd[P(o\text{-tol})_3]_2$	XPhos	13
12	$Pd[P(o\text{-tol})_3]_2$	RuPhos	22
13	$Pd[P(o\text{-tol})_3]_2$	BrettPhos	84
14	$Pd[P(o\text{-tol})_3]_2$	^{t}BuBrettPhos	5
15	$Pd[P(o\text{-tol})_3]_2$	AdBrettPhos	0
16	$Pd(OAc)_2$	BrettPhos	0
17	$Pd(PPh_3)_4$	BrettPhos	10
18	$[Pd(cinnamyl)Cl]_2$	BrettPhos	26
19	$[Pd(allyl)Cl]_2$	BrettPhos	15
20	$Pd(dba)_2$	BrettPhos	56

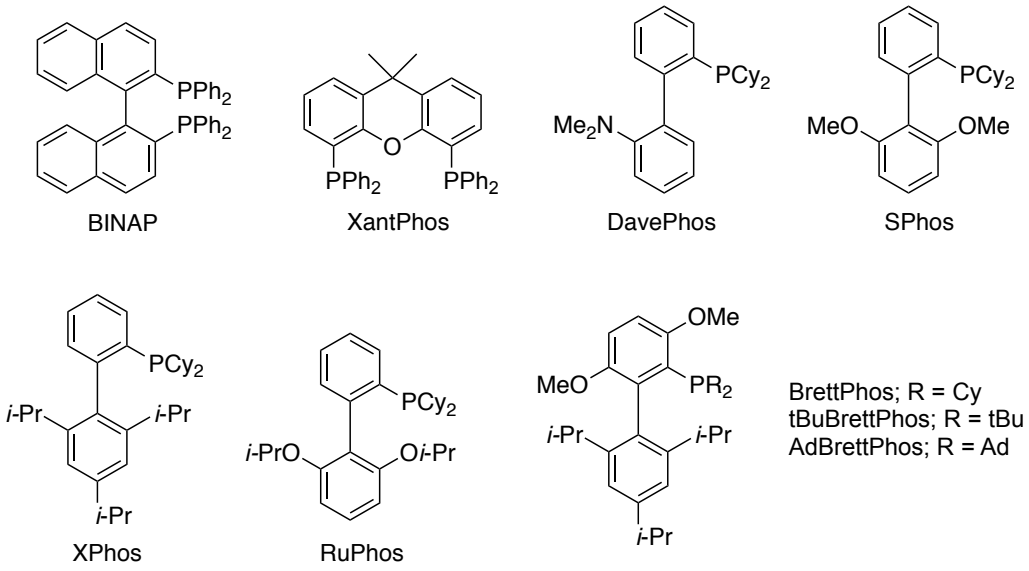
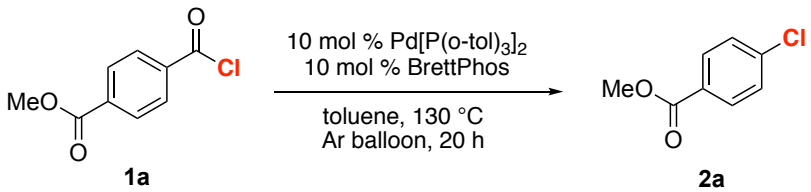


Table S2. Reaction Set-up and Other Conditions



1a **2a**

entry	Variations from scheme	yield of **2a** (%)
1	none	84
2	Dioxane (as solvent)	42
3	100 °C (instead of 130 °C)	28
4	$Pd(dba)_2$ in dioxane	59
5	5 mol% $Pd[P(o\text{-}tol)_3]_2$, 5 mol % BrettPhos	55
6	0 mol % $Pd[P(o\text{-}tol)_3]_2$	0
7	0 mol% $Pd[P(o\text{-}tol)_3]_2$, 0 mol % BrettPhos	0
8	Set-up **B** (4 mL vial)	32
9	Set-up **C** (10 mL vial)	91

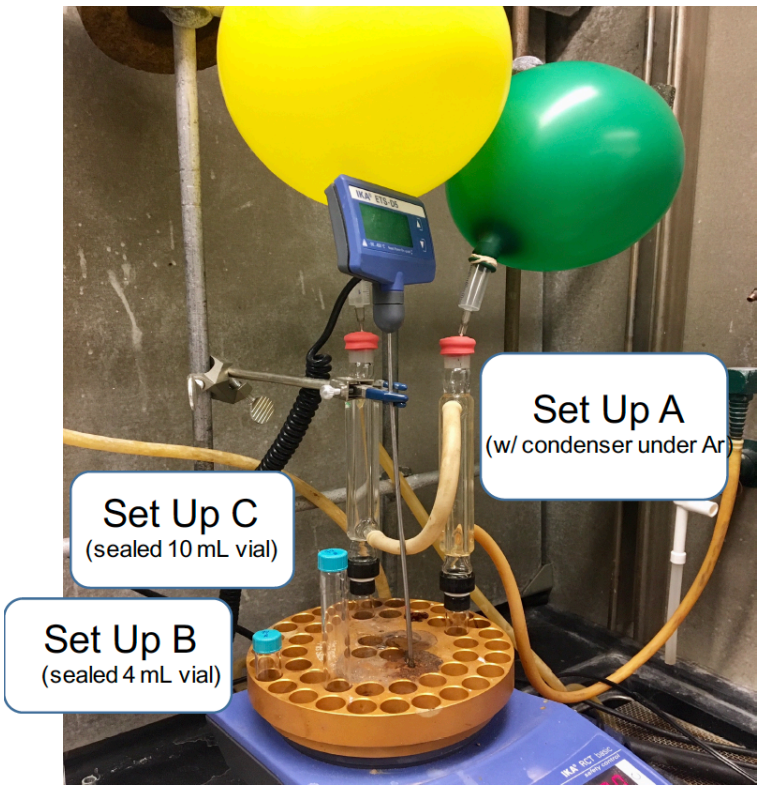
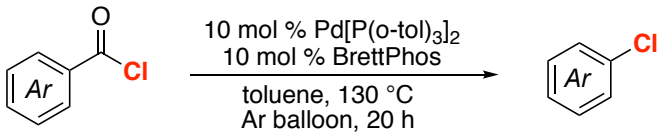
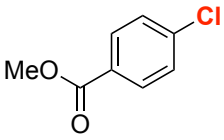


Figure S1. Reaction set up. Set up **A**: A 4 mL vial equipped with a condenser under Ar balloon. Set up **B**: A sealed 4 mL vial under N_2 atmosphere. Set up **C**: A sealed 10 mL vial under N_2 atmosphere.

V. Pd-Catalyzed Decarbonylative Chlorination



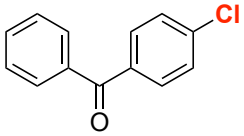
General procedure for the Pd-catalyzed decarbonylative chlorination: In a nitrogen-filled glovebox, acid chloride (1 equiv, 0.5 mmol) was weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of Pd[P(*o*-tol)$_3$]$_2$ (0.1 equiv, 0.05 mmol) and BrettPhos (0.1 equiv, 0.05 mmol) in toluene (1.5 mL) was added. The vial was connected to a reflux condenser, capped with a rubber septum, and this assembly was removed from the glovebox. An argon balloon was placed on top of the condenser and the reaction mixture was stirred at 130 ºC (see **Fig. S1**, set up **A**). After 20 h, the reaction mixture was cooled to room temperature and diluted with diethyl ether. The resulting solution was filtered through a silica plug and concentrated under reduced pressure. The products were purified via flash column chromatography on silica gel (hexanes/Et_2O).



2a

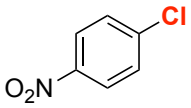
Methyl 4-chlorobenzoate (2a).[4] Compound **2a** was prepared using methyl 4-(chlorocarbonyl)-benzoate (**1a**) (100 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2a** as a colorless oil (60 mg, 70% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 168.4, 139.5, 131.2, 128.9, 128.8, 52.4; **HRMS** (ESI) calcd for $C_8H_8ClO_2$ $[M+H]^+$ *m/z* 171.0213, found 171.0219.

Method for 1.0 mmol scale: Using the general procedure with methyl 4-(chlorocarbonyl)-benzoate (**1a**) (200 mg, 1.0 mmol), Pd[P(*o*-tol)$_3$]$_2$ (0.10 mmol) and BrettPhos (0.10 mmol) in toluene (3.0 mL) performed in a 4 mL vial (see **Fig. S1**, set up **A**). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2a** as a colorless oil (123 mg, 72% yield). Spectral data matches that of compound **2a** obtained from 0.5 mmol scale. *The Pd-catalyzed decarbonylative chlorination using acid chloride **2a** at larger scale (1.0 mmol) did not affect the outcome of the reaction as well as the general set-up used in this methodology.*



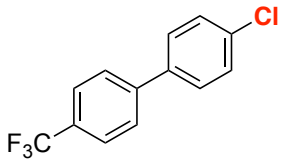
2b

(4-Chlorophenyl)(phenyl)methanone (2b). Compound **2b** was prepared using 4-benzoylbenzoyl chloride (122 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2b** as a white solid (70 mg, 65% yield): **mp** 73–74 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.78–7.74 (multiple peaks, 4H), 7.59 (m, 1H), 7.50–7.45 (multiple peaks, 4H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 195.5, 139.0, 137.4, 136.0, 132.8, 131.6, 130.0, 128.7, 128.5; GCMS analysis $[M]^+$ *m/z* 216 matched that of authentic sample (Alfa Aesar).



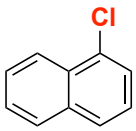
2c

1-Chloro-4-nitrobenzene (2c). Compound **2c** was prepared using 4-nitrobenzoyl chloride (93 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2c** as a yellowish solid (65 mg, 82% yield): **mp** 83–84 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.16 (d, *J* = 9.1 Hz, 2H), 7.50 (d, *J* = 9.1 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.6, 141.5, 129.7, 125.1; GCMS analysis $[M]^+$ *m/z* 157 matched that of authentic sample (Sigma).



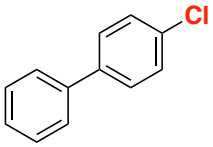
2d

4-Chloro-4'-(trifluoromethyl)biphenyl (2d). Compound **2d** was prepared using acid chloride **1d** (122 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2d** as a yellowish powder (114 mg, 89% yield): **mp** 98–99 °C; **^{1}H NMR** ($CDCl_3$, 700 MHz) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.53–7.52 (multiple peaks, 2H), 7.45–7.44 (multiple peaks, 2H); **^{13}C NMR** ($CDCl_3$, 176 MHz) δ 143.5, 138.2, 134.4, 129.7 (q, *J* = 32.5 Hz), 129.2, 128.5, 127.3, 125.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.5; **HRMS** (EI) calcd for $C_{13}H_8ClF_3$ $[M]^+$ *m/z* 256.0267, found 256.0262.



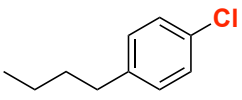
2e

1-Chloronaphthalene (2e). Compound **2e** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2e** as a colorless oil (85 mg, 89% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.68–7.52 (multiple peaks, 3H), 7.40 (m, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 134.8, 132.1, 131.0, 128.4, 127.3, 127.2, 126.9, 126.3, 125.9, 124.6; GCMS analysis $[M]^+$ *m/z* 162 matched that of authentic sample (Alfa Aesar).



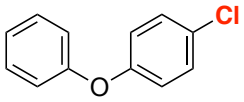
2f

4-Chlorobiphenyl (2f). Compound **2f** was prepared using 4-biphenylcarbonyl chloride (108 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2f** as a white solid (60 mg, 64% yield): **mp** 76–77 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.57–7.51 (multiple peaks, 4H), 7.46–7.36 (multiple peaks, 5H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 140.2, 139.9, 133.6, 129.11, 129.13, 128.6, 127.8, 127.2; GCMS analysis (*m/z* 188) matched that of authentic sample (Alfa Aesar).



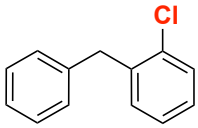
2g

1-Butyl-4-chlorobenzene (2g). Compound **2g** was prepared using 4-butylbenzoyl chloride (98 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2g** as a colorless oil (57 mg, 67% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.9 Hz, 2H), 1.58 (tt, *J* = 8.9, 6.9 Hz, 2H), 1.35 (tq, *J* = 7.3, 6.9 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.5, 131.5, 129.9, 128.5, 35.2, 33.8, 22.5, 14.1; GCMS analysis $[M]^+$ *m/z* 168 matched that of authentic sample (Alfa Aesar).



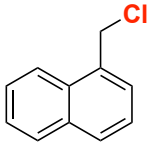
2i

1-chloro-4-phenoxybenzene (2i). Compound **2i** was prepared using 4-phenoxybenzoyl chloride (115 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2i** as a colorless oil (85 mg, 55% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.35 (ddd, *J* = 8.8, 6.2, 2.0 Hz, 2H), 7.29 (ddd, *J* = 8.8, 6.2, 2.0 Hz, 2H), 7.13 (m, 1H), 7.47 (dd, *J* = 6.8, 1.4 Hz, 2H), 6.94 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 157.1, 156.2, 130.1, 129.9, 128.4, 123.8, 120.2, 119.2; GCMS analysis $[M]^+$ *m/z* 188 matched that of authentic sample (Alfa Aesar).



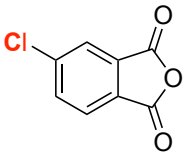
2j

1-Benzyl-2-chlorobenzene (2j).[5] Compound **2j** was prepared using 2-benzylbenzoyl chloride (115 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2j** as a colorless oil (85 mg, 84% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.41 (m, 1H), 7.35–7.31 (multiple peaks, 2H), 7.27–7.17 (multiple peaks, 6H), 4.15 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 139.7, 138.9, 134.4, 131.2, 129.7, 129.2, 128.7, 127.9, 127.0, 126.4, 39.4; **HRMS** (EI) calcd for $C_{13}H_{11}Cl$ $[M]^+$ *m/z* 202.0549, found 202.0558.



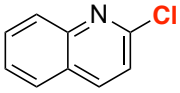
2k

1-(Chloromethyl)naphthalene (2k).[6] Compound **2k** was prepared using 1-naphthylacetyl chloride (**1k**) (102 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **2k** as a colorless oil (81 mg, 92% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.19 (d, *J* = 8.6 Hz, 1H), 7.93–7.87 (multiple peaks, 2H), 7.64 (m, 1H), 7.58–7.54 (multiple peaks, 2H), 7.45 (m, 1H), 5.07 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 134.0, 133.0, 131.1, 129.8, 128.9, 127.7, 126.7, 126.2, 125.3, 123.7, 44.6; **HRMS** (EI) calcd for $C_{11}H_9Cl$ $[M]^+$ *m/z* 176.0393, found 176.0398.



2l

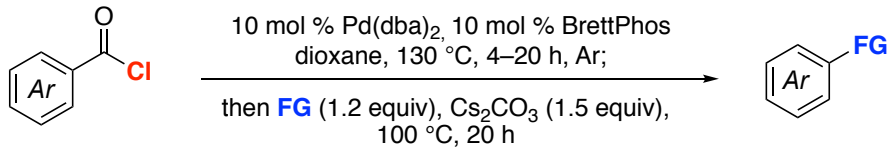
5-Chloroisobenzofuran-1,3-dione (2l).[7] Compound **2l** was prepared using trimellitic anhydride chloride (105 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **2l** as a white solid (77 mg, 84% yield): **mp** 96–97 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 161.9, 161.7, 143.4, 136.6, 133.2, 129.5, 127.0, 126.1; **HRMS** (ESI) calcd for $C_8H_4ClO_3$ $[M+H]^+$ *m/z* 182.9849, found 182.9852.



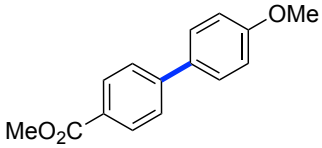
2m

2-Chloroquinoline (2m). Compound **2m** was prepared using quinaldoyl chloride (96 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **2m** as a low melting colorless solid (34 mg, 42% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (m, 1H), 7.54 (m, 1H), 7.36 (d, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 150.8, 148.0, 139.1, 130.7, 128.7, 127.7, 127.2, 127.0, 122.5; GCMS analysis $[M]^+$ *m/z* 163 matched that of authentic sample (Sigma Aldrich).

VI. Pd-Catalyzed Decarbonylative Chlorination and Cross Coupling Reactions

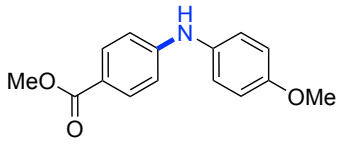


General procedure for the Pd-catalyzed decarbonylative chlorination/cross-coupling reaction: In a nitrogen-filled glovebox, acid chloride (1 equiv, 0.5 mmol) was weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Pd(dba)_2$ (0.1 equiv, 0.05 mmol) and BrettPhos (0.1 equiv, 0.05 mmol) in dioxane (1.5 mL) was added. The vial was connected to a reflux condenser, capped with a rubber septum, and the assembly was removed from the glovebox. An argon balloon was placed on top of the condenser and the reaction mixture was stirred at 130 ºC (see Fig. S1, set-up A). After 4 or 20 h, the reaction mixture was cooled to room temperature. The condenser was removed, and the vial was immediately capped. In a glovebox, the cross-coupling partner (FG) (1.2 equiv, 0.6 mmol) and Cs_2CO_3 (1.5 equiv, 0.75 mmol) were added, and the reaction vial was recapped and taken out from the glovebox. The reaction mixture was stirred at 100 ºC. After 20 h, the reaction mixture was cooled to room temperature and diluted with diethyl ether. The resulting solution was filtered through a plug of silica and concentrated under reduced pressure. The porducts were purified by flash column chromatography on silica gel (hexanes/Et_2O).



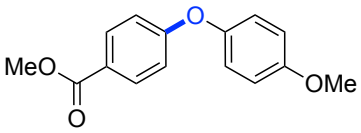
3

Methyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (3).[8] Compound **3** was prepared using methyl 4-(chlorocarbonyl)-benzoate (**1a**) (100 mg, 0.5 mmol). 4-Methoxyphenylboronic acid (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **3** as a white solid (94 mg, 78% yield): **mp** 170–172 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.08 (dd, *J* = 6.6, 1.6 Hz, 2H), 7.62 (dd, *J* = 6.6, 1.6 Hz, 2H), 7.57 (dd, *J* = 6.7, 2.0 Hz, 2H), 6.99 (dd, *J* = 6.7, 2.0 Hz, 2H), 3.93 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 189.4, 167.3, 160.0, 145.4, 132.6, 130.3, 128.6, 126.7, 114.6, 55.6, 52.3; **HRMS** (ESI) calcd for $C_{15}H_{15}O_3$ $[M+H]^+$ *m*/*z* 243.1021, found 243.1020.



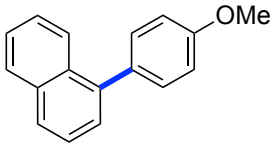
4

Methyl 4-((4-methoxyphenyl)amino)benzoate (4).[9] Compound **4** was prepared using methyl 4-(chlorocarbonyl)-benzoate (**1a**) (100 mg, 0.5 mmol). *p*-Anisidine (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **4** as a beige solid (93 mg, 72% yield): **mp** 85-86 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.99 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.3, 156.6, 150.0, 133.6, 131.7, 124.5, 120.0, 114.9, 113.3, 55.7, 51.8; **HRMS** (ESI) calcd for $C_{15}H_{16}NO_3$ $[M+H]^+$ *m*/*z* 258.1130, found 258.1134.



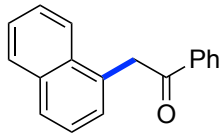
5

Methyl 4-(4-methoxyphenoxy)benzoate (5).[10] Compound **5** was prepared using methyl 4-(chlorocarbonyl)-benzoate (**1a**) (100 mg, 0.5 mmol). *p*-Methoxyphenol (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **5** as a white solid (84 mg, 65% yield): **mp** 102–103 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.91–6.89 (multiple peaks, 4H), 3.87 (s, 3H), 3.80 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 166.8, 163.0, 156.8, 148.8, 131.8, 124.1, 121.8, 116.5, 115.3, 55.8, 52.1; **HRMS** (ESI) calcd for $C_{15}H_{15}O_4$ $[M+H]^+$ *m*/*z* 259.0970, found 259.0968.



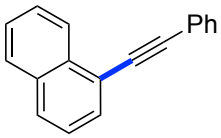
6

1-(4-Methoxyphenyl)naphthalene (6).[11] Compound **6** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). 4-Methoxyphenylboronic acid (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **6** as a white solid (84 mg, 75% yield): **mp** 113–114 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.95 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.85 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.56–7.48 (multiple peaks, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.47–7.41 (multiple peaks, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 159.2, 140.1, 134.1, 133.3, 132.0, 131.3, 128.5, 127.5, 127.1, 126.3, 126.1, 125.9, 125.6, 113.9, 55.6; **HRMS** (EI) calcd for $C_{17}H_{14}O$ $[M]^+$ *m*/*z* 234.1045, found 234.1047.



7

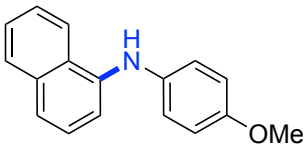
2-(Naphthalen-1-yl)-1-phenylethanone (7).[12] Compound **7** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). Acetophenone (1.2 equiv) and NaO^{t}Bu (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **7** as a white solid (110 mg, 89% yield): **mp** 105–107 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.94–7.86 (multiple peaks, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 8.3, 6.6 Hz, 1H), 7.51–7.42 (multiple peaks, 4H), 7.44 (m, 1H), 7.37 (d, *J* = 6.6 Hz, 1H), 4.75 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 197.8, 136.9, 134.1, 133.5, 132.5, 131.5, 129.0, 128.9, 128.7, 128.2, 128.1, 126.5, 125.9, 125.7, 124.1, 43.3; **HRMS** (ESI) calcd for $C_{18}H_{15}O$ $[M+H]^+$ *m*/*z* 247.1117, found 247.1114.



8

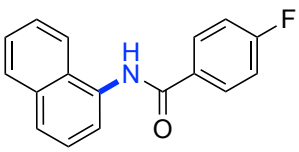
1-(Phenylethynyl)naphthalene (8).[13] Compound **8** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). Phenylacetylene (1.2 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 98:2) afforded **8** as a yellow oil (104 mg, 91% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.46 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.9, 2H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.61 (m, 1H), 7.55 (m, 1H), 7.47 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.42–7.38 (multiple peaks, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 133.5, 133.4, 131.9, 130.6, 129.0, 128.7, 128.6,

128.5, 127.0, 126.6, 126.4, 125.5, 123.6, 121.1, 94.5, 87.7; **HRMS** (EI) calcd for $C_{18}H_{12}$ $[M]^+$ *m*/*z* 228.0939, found 228.0944.



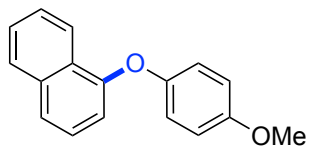
9

***N*-(4-Methoxyphenyl)naphthalen-1-amine (9).**[14] Compound **9** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). *p*-Anisidine (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **9** as a light brown solid (112 mg, 90% yield): **mp** 57–58 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.03 (m, 1H), 7.88 (m, 1H), 7.53–7.49 (multiple peaks, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.13 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.88 (s, 1H), 3.83 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.3, 141.1, 137.1, 134.8, 128.8, 126.4, 126.2, 126.1, 125.5, 122.0, 121.3, 121.1, 115.0, 111.9, 55.8; **HRMS** (ESI) calcd for $C_{17}H_{16}NO$ $[M+H]^+$ m/z 250.1232, found 250.1234.



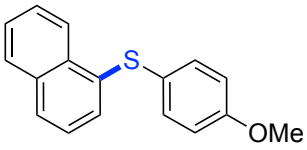
10

4-Fluoro-*N*-(naphthalen-1-yl)benzamide (10). Compound **10** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). 4-Fluorobenzamide (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **10** as a white solid (102 mg, 80% yield): **mp** 166–168 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.15 (br s, 1H), 8.00-7.96 (multiple peaks, 3H), 7.92–7.86 (multiple peaks, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.58-7.47 (multiple peaks, 3H), 7.20 (td, *J* = 8.6, 2.6 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 165.5, 165.2 (d, *J* = 253.0 Hz), 134.4, 132.4, 131.2 (d, *J* = 1.9 Hz), 129.8 (d, *J* = 9.0 Hz), 129.1, 127.8, 126.7, 126.6, 126.3, 126.0, 121.7, 120.9, 116.2 (d, *J* = 22.1 Hz); **HRMS** (ESI) calcd for $C_{17}H_{13}FNO$ $[M+H]^+$ m/z 266.0981, found 266.0979.



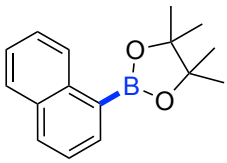
11

1-(4-Methoxyphenoxy)naphthalene (11).[15] Compound **11** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). *p*-Methoxyphenol (1.5 equiv) and Cs_2CO_3 (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **11** as a colorless solid (95 mg, 76% yield): **mp** 77–78 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.29 (m, 1H), 7.85 (m, 1H), 7.54–7.49 (multiple peaks, 3H), 7.32 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.78 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 156.1, 154.7, 150.9, 135.0, 127.9, 126.8, 126.6, 126.0, 125.9, 122.6, 122.3, 120.8, 115.1, 111.5, 55.9; **HRMS** (EI) calcd for $C_{17}H_{14}O_2$ $[M]^+$ *m*/*z* 250.0994, found 250.0996.



12

(4-Methoxyphenyl)(naphthalen-1-yl)sulfane (12).[16] Compound **12** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). *p*-Methoxythiophenol (1.5 equiv) and KO^{t}Bu (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 90:10) afforded **12** as a white solid (113 mg, 85% yield): **mp** 106–107 °C **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.38 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.73 (m, 1H), 7.57–7.48 (multiple peaks, 3H), 7.41–7.23 (multiple peaks, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 159.6, 134.8, 134.2, 134.1, 134.0, 132.4, 128.7, 127.6, 126.7, 126.5, 125.9, 125.4, 125.1, 115.2, 55.6; **HRMS** (EI) calcd for $C_{17}H_{14}OS$ $[M]^+$ *m*/*z* 266.0765, found 266.0764.



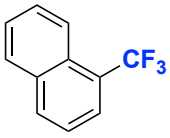
13

Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (13). Compound **13** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). B_2pin_2 (1.5 equiv) and KOAc (1.5 equiv) were used as cross-coupling partner and base, respectively. Purification by flash chromatography on silica gel (hexanes/Et_2O, 95:5) afforded **13** as a white solid (104 mg, 82% yield): **mp** 51–52 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.83 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 6.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.58 (m, 1H), 7.53-7.50 (multiple peaks, 2H), 1.46 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 137.1, 135.9, 133.4, 131.8, 128.6, 128.5, 126.5, 125.7, 125.2, 83.9, 25.2 (the carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation); **HRMS** (EI) calcd for $C_{16}H_{19}BO_2$ $[M]^+$ *m*/*z* 254.1478, found 254.1490.

VII. Pd-Catalyzed Decarbonylative Chlorination/Trifluoromethylation

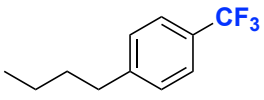
General procedure for Pd-catalyzed decarbonylative chlorination/trifluoromethylation: In a nitrogen-filled glovebox, the acid chloride (1 equiv, 0.5 mmol) was weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Pd(dba)_2$ (0.1 equiv, 0.05 mmol) and BrettPhos (0.1 equiv, 0.05 mmol) in dioxane (1.5 mL) was added. The vial was connected to a reflux condenser, capped with a rubber septum, and this assembly was removed from the glovebox. An argon balloon was placed on top of the condenser and the reaction mixture was stirred at 130 ºC (see Fig. S1, set-up A). After 4 or 20 h, the reaction mixture was cooled to rt. The condenser was removed and the vial was immediately capped. In a glovebox, $TESCF_3$ (2.0 equiv, 1.0 mmol), and KF (2.0 equiv, 1.0 mmol) were added, and the reaction vial was recapped and taken out from the glovebox. The reaction mixture was stirred at 130 ºC. After 20 h, the reaction mixture was cooled to rt and diluted with diethyl ether. The resulting solution was filtered through a plug of silica gel and concentrated under reduced pressure. The products were purified by flash column chromatography on silica gel (hexanes/Et_2O).

One-pot decarbonylative trifluoromethylation procedure: In a nitrogen-filled glovebox, acid chloride (1 equiv, 0.5 mmol) was weighed into a 4 mL vial equipped with a 10 μm magnetic stir bar. A pre-mixed solution of $Pd(dba)_2$ (0.1 equiv, 0.05 mmol) and BrettPhos (0.1 equiv, 0.05 mmol) in dioxane (1.5 mL), $TESCF_3$ (2.0 equiv, 1.0 mmol), and KF (2.0 equiv, 1.0 mmol) were added. The vial was connected to a reflux condenser, capped with a rubber septum, and this assembly was removed from the glovebox. An argon balloon was placed on top of the condenser, and the reaction mixture was stirred at 130 ºC (see Fig. S1, set-up A). After 20 h, the reaction mixture cooled to rt and diluted with diethyl ether. The resulting solution was filtered through a plug of silica gel and concentrated under reduced pressure. The products were purified by flash column chromatography on silica gel (hexanes/Et_2O).



14

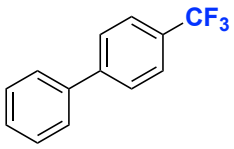
1-(Trifluoromethyl)naphthalene (14).[17] Compound **14** was prepared using 1-naphthoyl chloride (96 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **14** as a colorless oil (71 mg, 72% yield). Compound **14** was also obtained using the one pot decarbonylative trifluoromethylation procedure (80 mg, 81% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.24 (m, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.98–7.90 (multiple peaks, 2H), 7.72–7.39 (multiple peaks, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 134.1, 132.9, 129.1 (q, *J* = 1.2 Hz), 128.9, 127.8, 126.8, 126.2 (q, *J* = 29.9 Hz), 125.0 (q, *J* = 273.4 Hz), 124.8 (q, *J* = 6.0 Hz), 124.4 (q, *J* = 2.3 Hz), 124.3; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –59.7 (s, 3F); **HRMS** (EI) calcd for $C_{11}H_7F_3$ $[M]^+$ *m*/*z* 196.0500, found 196.0500.



15

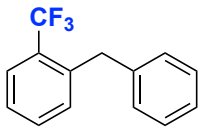
1-Butyl-4-(trifluoromethyl)benzene (15).[18] Compound **15** was prepared using 4-butylbenzoyl chloride (98 mg, 0.5 mmol). Purification by flash chromatography on silica gel (pentane) afforded **15** as a colorless oil (66 mg, 65% yield, contains ~5% inseparable 1-butyl-4-chlorobenzene): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.60 (tt, *J* = 7.8, 6.9 Hz, 2H), 1.36 (tq, *J* = 7.3, 6.9 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.0 (q, *J* = 1.1 Hz), 128.9, 128.0 (q, *J* = 32.2 Hz), 125.4 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 271.7 Hz), 35.7, 33.6, 22.5, 14.1; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –62.5 (s,

3F); **HRMS** (EI) calcd for $C_{11}H_{13}F_3$ $[M]^+$ *m*/*z* 202.0969, found 202.0975.



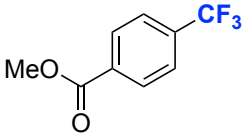
16

4-(Trifluoromethyl)biphenyl (16).[17] Compound **16** was prepared using 4-biphenylcarbonyl chloride (108 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **16** as a white solid (64 mg, 58% yield): **mp** 70 ºC; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71–7.66 (multiple peaks, 4H), 7.63–7.53 (multiple peaks, 2H), 7.52–7.41 (multiple peaks, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 144.9, 140.0, 129.6, (*J* = 32.1 Hz), 129.2, 128.4, 127.6, 127.5, 125.9 (*J* = 4.1 Hz), 124.5 (*J* = 272.0 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –62.4 (s, 3F); **HRMS** (EI) calcd for $C_{13}H_9F_3$ $[M]^+$ *m*/*z* 222.0656, found 222.0660.



17

1-Benzyl-2-(trifluoromethyl)benzene (17). Compound **17** was prepared using 2-benzylbenzoyl chloride (115 mg, 0.5 mmol). Purification by flash chromatography on silica gel (hexanes) afforded **17** as a colorless oil (73 mg, 62% yield). Compound **17** was also obtained using the one pot decarbonylative trifluoromethylation procedure (61 mg, 52% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.70–7.62 (multiple peaks, 2H), 7.47–7.43 (multiple peaks, 2H), 7.34–7.17 (multiple peaks, 5H), 4.22 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.5, 140.1, 139.7 (br), 131.9, 129.4, 128.7, 127.5 (d, *J* = 32.0 Hz), 126.5, 126.4, 126.1 (q, *J* = 5.7 Hz), 124.8 (q, *J* = 274.2 Hz), 38.0 (q, *J* = 2.2 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –59.6 (s, 3F); **HRMS** (EI) calcd for $C_{14}H_{11}F_3$ $[M]^+$ *m*/*z* 236.0813, found 236.0824.



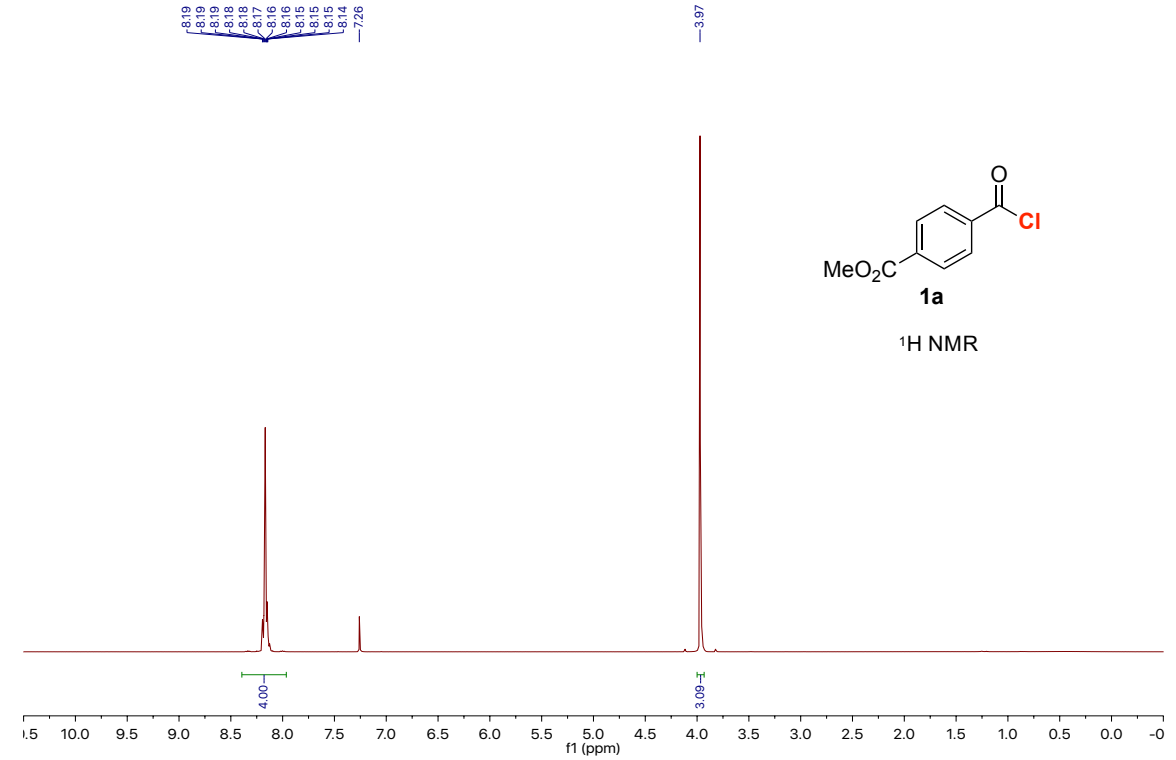
18

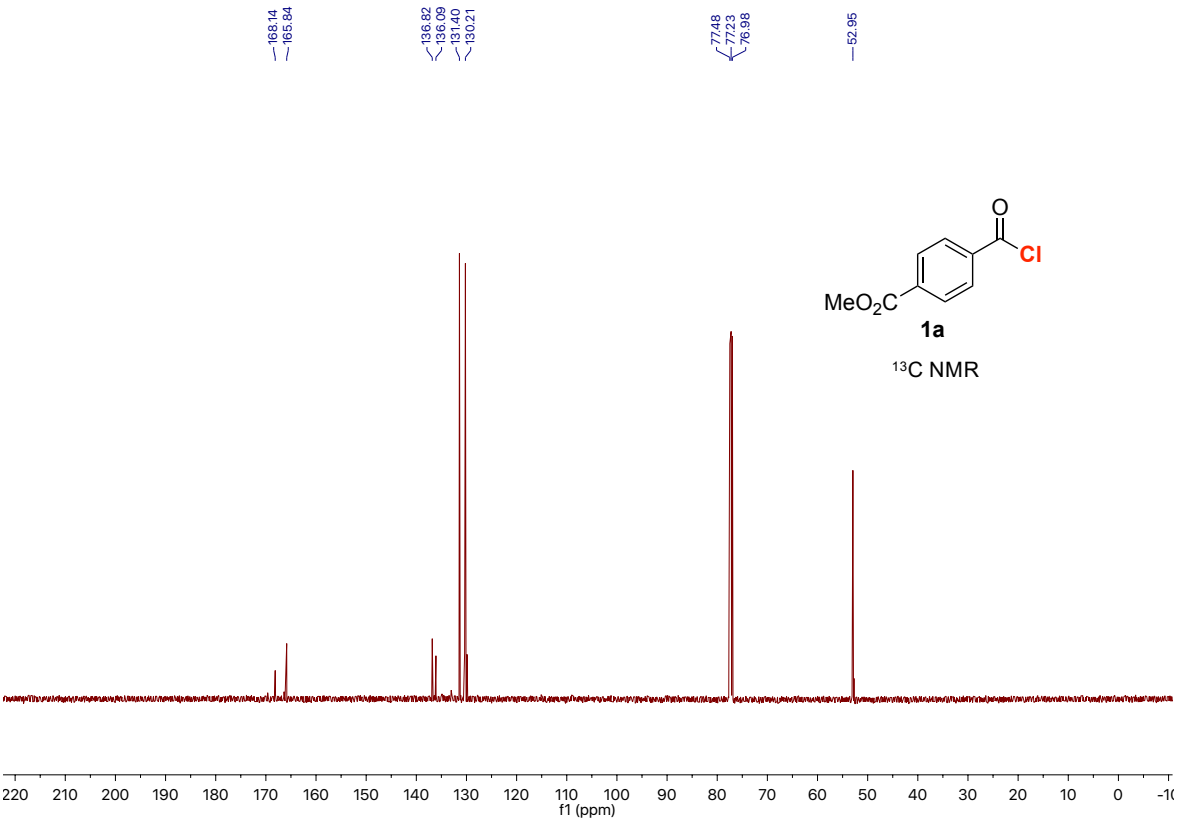
Methyl 4-(trifluoromethyl)benzoate (18). Compound **18** was prepared using methyl 4-(chlorocarbonyl)-benzoate (**1a**) (100 mg, 0.5 mmol) using $Pd[P(o\text{-}tol)_3]_2$ (0.05 mmol) as catalyst. Purification by flash chromatography on silica gel (hexanes/Et_2O, 98:2) afforded **18** as a colorless oil (56 mg, 55% yield): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 166.1, 134.7 (q, *J* = 32.4 Hz), 133.6, 130.2, 125.6, (q, *J* = 3.9 Hz), 123.9 (q, *J* = 272.8 Hz), 52.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ –63.2 (s, 3F); **HRMS** (EI) calcd for $C_9H_7O_2F_3$ $[M]^+$ *m*/*z* 204.0398, found 204.0405.

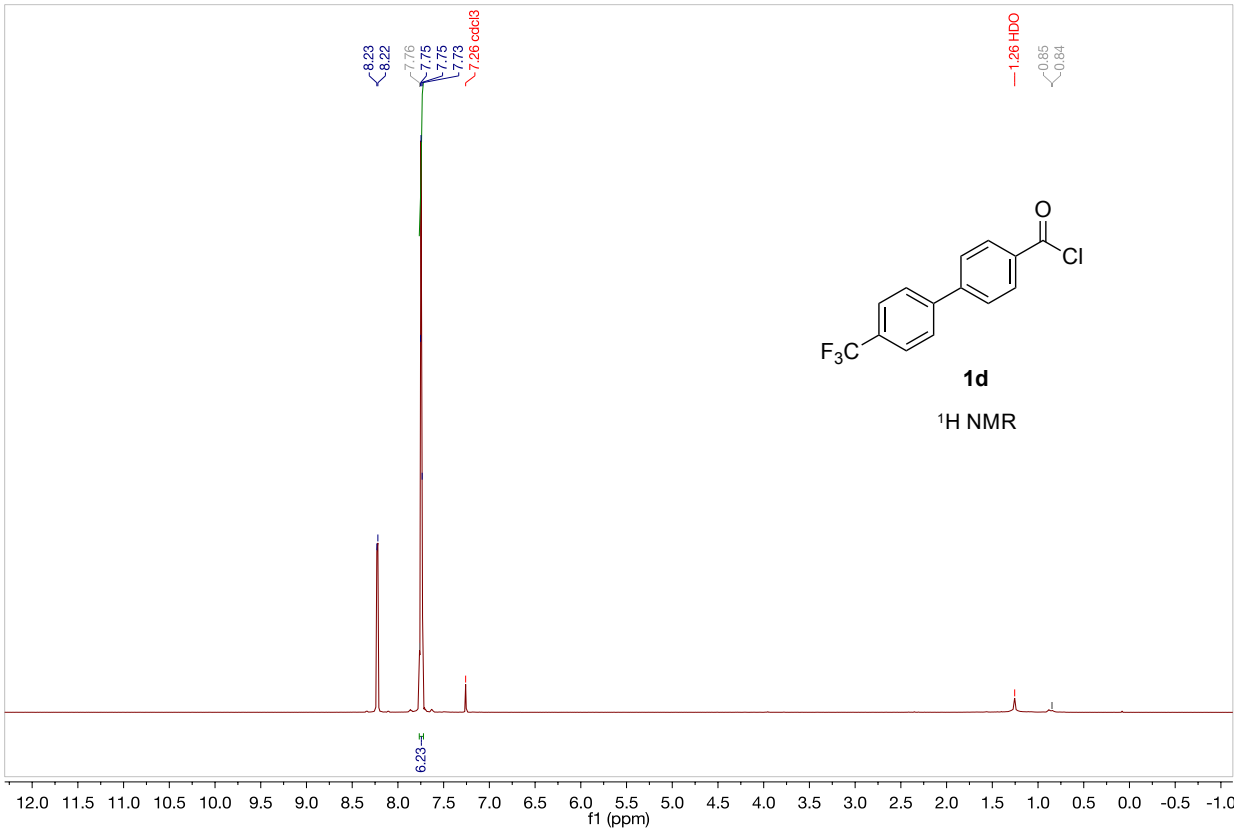
VIII. References

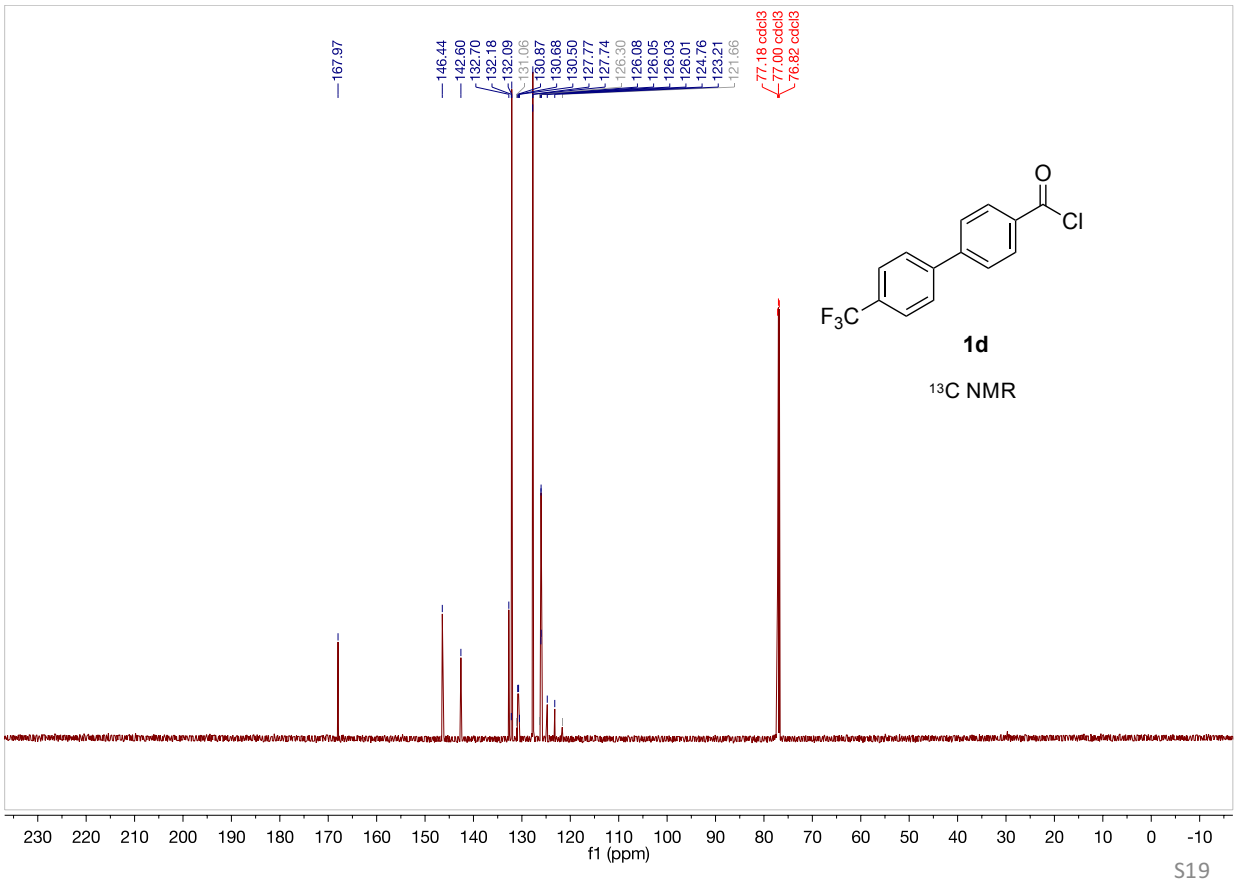
(1) Yli-Kauhaluoma, J. T.; Ashley, J. A.; Lo, C. H.; Tucker, L.; Wolfe, M. M.; Janda, K. D. *J. Am. Chem. Soc.* **1995**, *117*, 7041.
(2) Fisher, L. E.; Caroon, J. M.; Jahangir; Stabler, S. R.; Lundberg, S.; Muchowski, J. M. *J. Org. Chem.* **1993**, *58*, 3643.
(3) Burckhalter, J. H.; Campbell, J. R. *J. Org. Chem.* **1961**, *26*, 4232.
(4) Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052.
(5) Srimani, D.; Bej, A.; Sarkar, A. *J. Org. Chem.* **2010**, *75*, 4296.
(6) Nakamura, H.; Usui, T.; Kuroda, H.; Ryu, I.; Matsubara, H.; Yasuda, S.; Curran, D. P. *Org. Lett.* **2003**, *5*, 1167.
(7) Nandhikonda, P.; Heagy, M. D. *Org. Lett.* **2010**, *12*, 4796.
(8) Razler, T. M.; Hsiao, Y.; Qian, F.; Khan, R.; Fu, R. K.; Doubleday, W. *J. Org. Chem.* **2008**, *74*, 1381.
(9) Pompeo, M.; Farmer, J. L.; Froese, R. D. J.; Organ, M. G. *Angew. Chem., Int. Ed.* **2014**, *53*, 3223.
(10) Kim, H. J.; Kim, M.; Chang, S. *Org. Lett.* **2011**, *13*, 2368.
(11) Stibingerova, I.; Voltrova, S.; Kocova, S.; Lindale, M.; Srogl, J. *Org. Lett.* **2016**, *18*, 312.
(12) Fu, W. C.; So, C. M.; Yuen, O. Y.; Lee, I. T. C.; Kwong, F. Y. *Org. Lett.* **2016**, *18*, 1872.
(13) Gallop, C. W. D.; Chen, M.-T.; Navarro, O. *Org. Lett*. **2014**, *16*, 3724.
(14) Fang, W.; Jiang, J.; Xu, Y.; Zhou, J.; Tu, T. *Tetrahedron* **2013**, *69*, 673.
(15) Bhadra, S.; Sreedhar, B.; Ranu, B. C*. Adv. Synth. Catal.* **2009**, *351*, 2369.
(16) Prasad, D. J. C.; Sekar, G. *Org. Lett.* **2011**, *13*, 1008.
(17) Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A. Buchwald, S. L. *Science* **2010**, *328*, 1679.
(18) Senecal, T. D.; Parsons, A. T.; Buchwald, S. L. *J. Org. Chem.* **2011**, *76*, 1174.

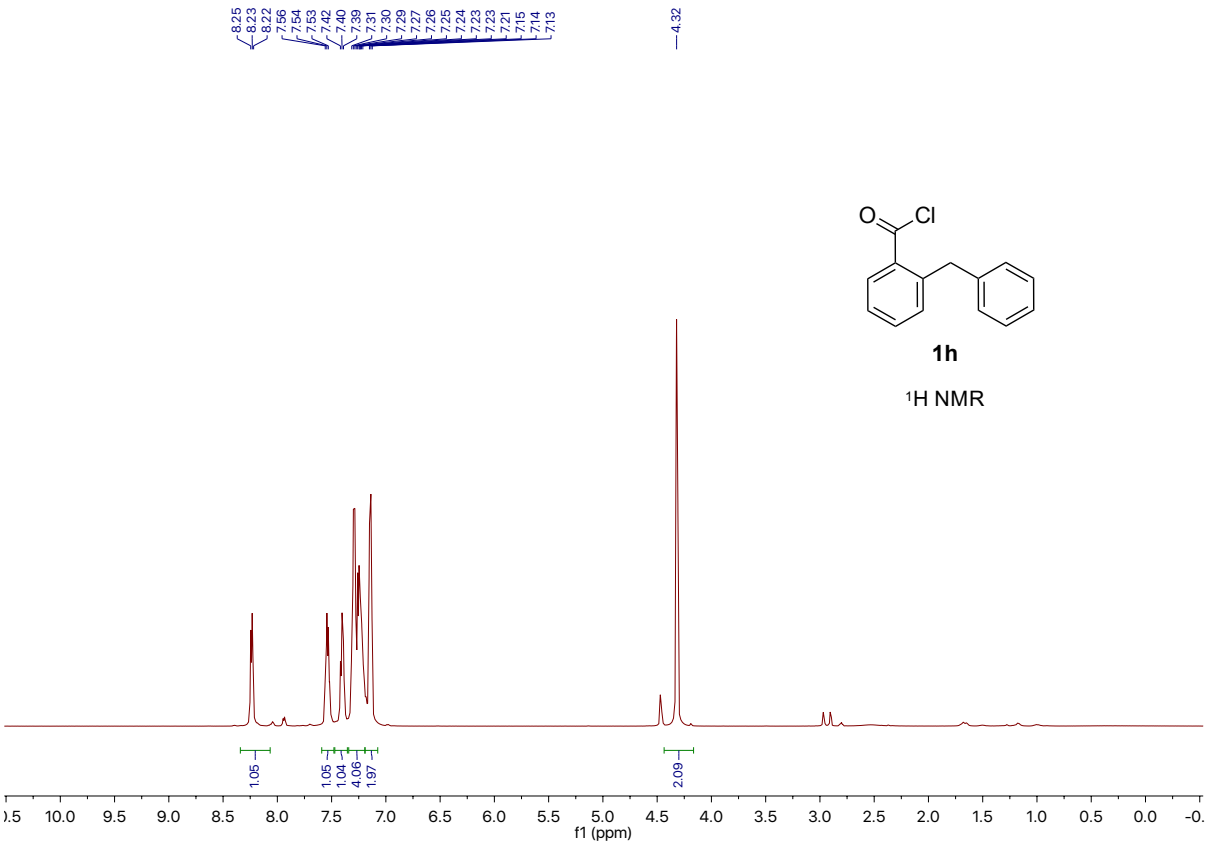
IX. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

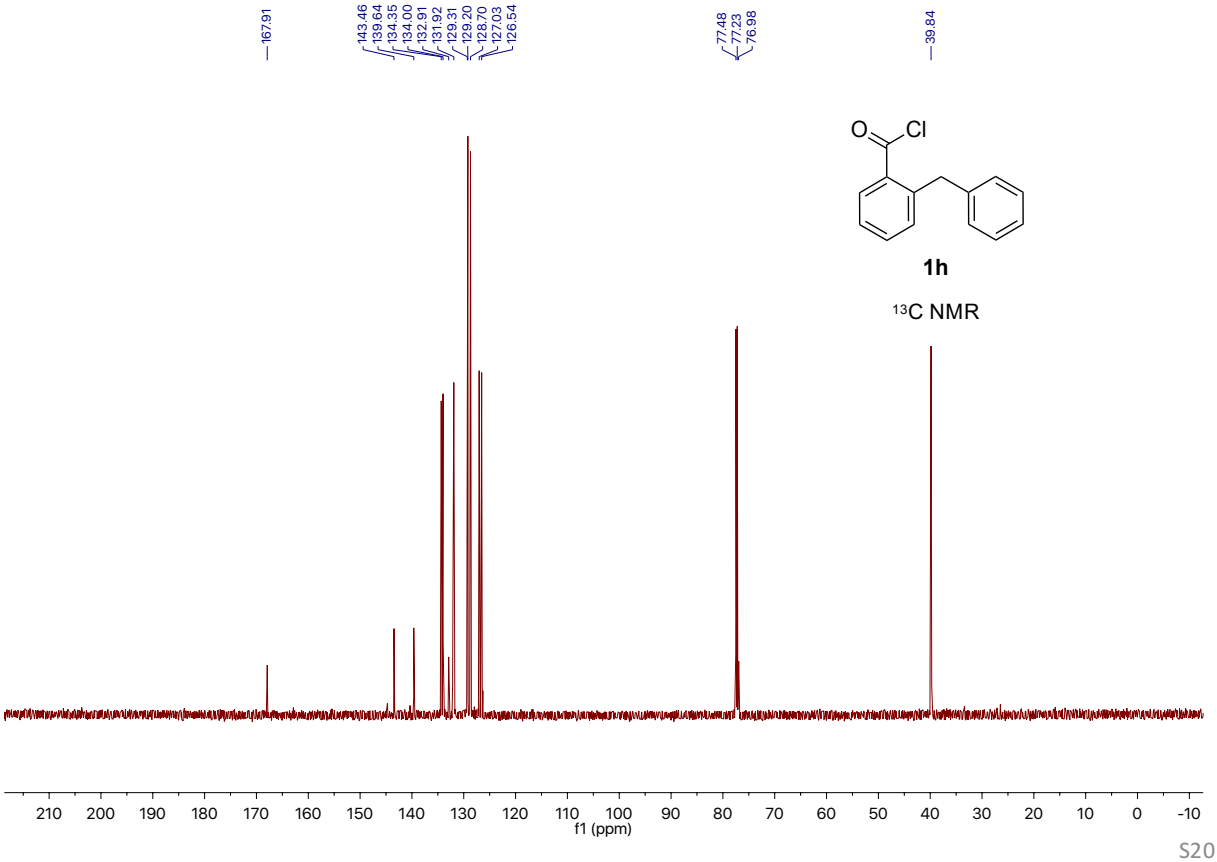

8.19
8.19
8.19
8.18
8.18
8.17
8.16
8.16
8.15
8.15
8.15
8.14
7.26
3.97
O
Cl
MeO2C
1a
1H NMR
4.00
3.09
f1 (ppm)

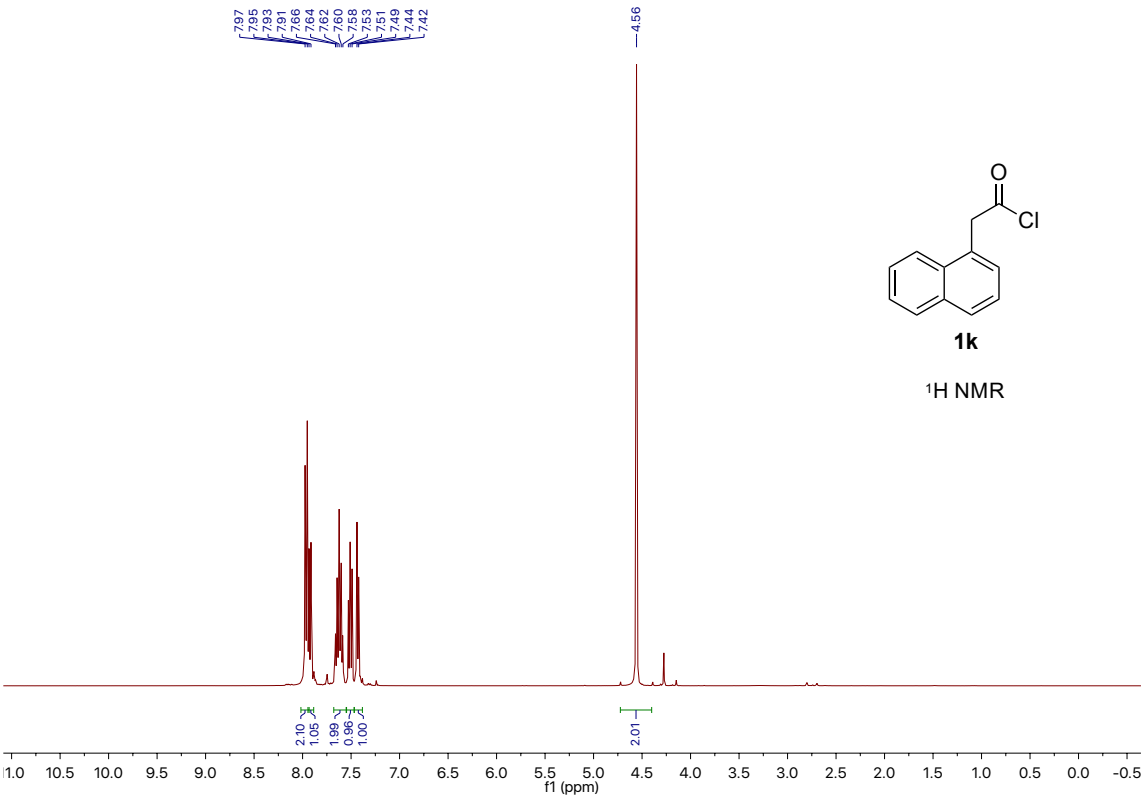

168.14
165.84
136.82
136.09
131.40
130.21
77.48
77.23
76.98
52.95
O
Cl
MeO2C
1a
13C NMR
f1 (ppm)

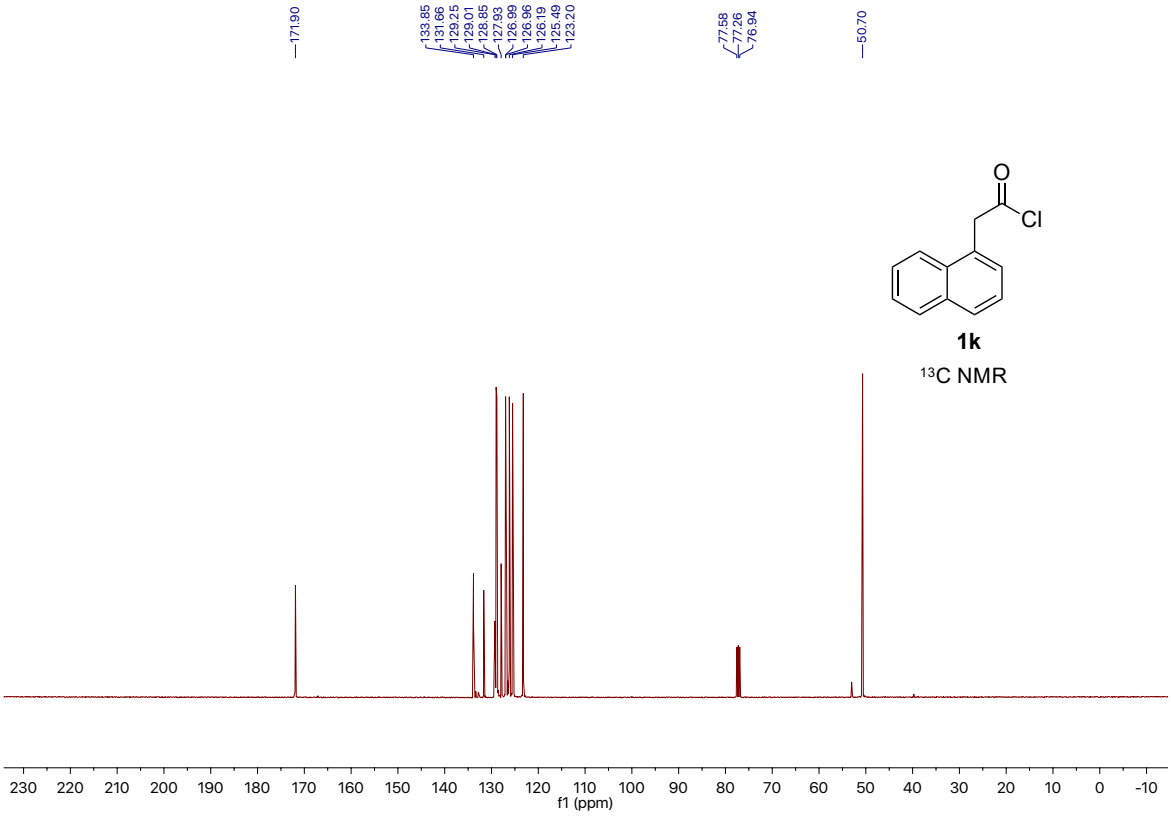

8.23
8.22
7.76
7.75
7.75
7.73
7.26 cdcl3
1.26 HDO
0.85
0.84
O
Cl
F3C
1d
1H NMR
6.23
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

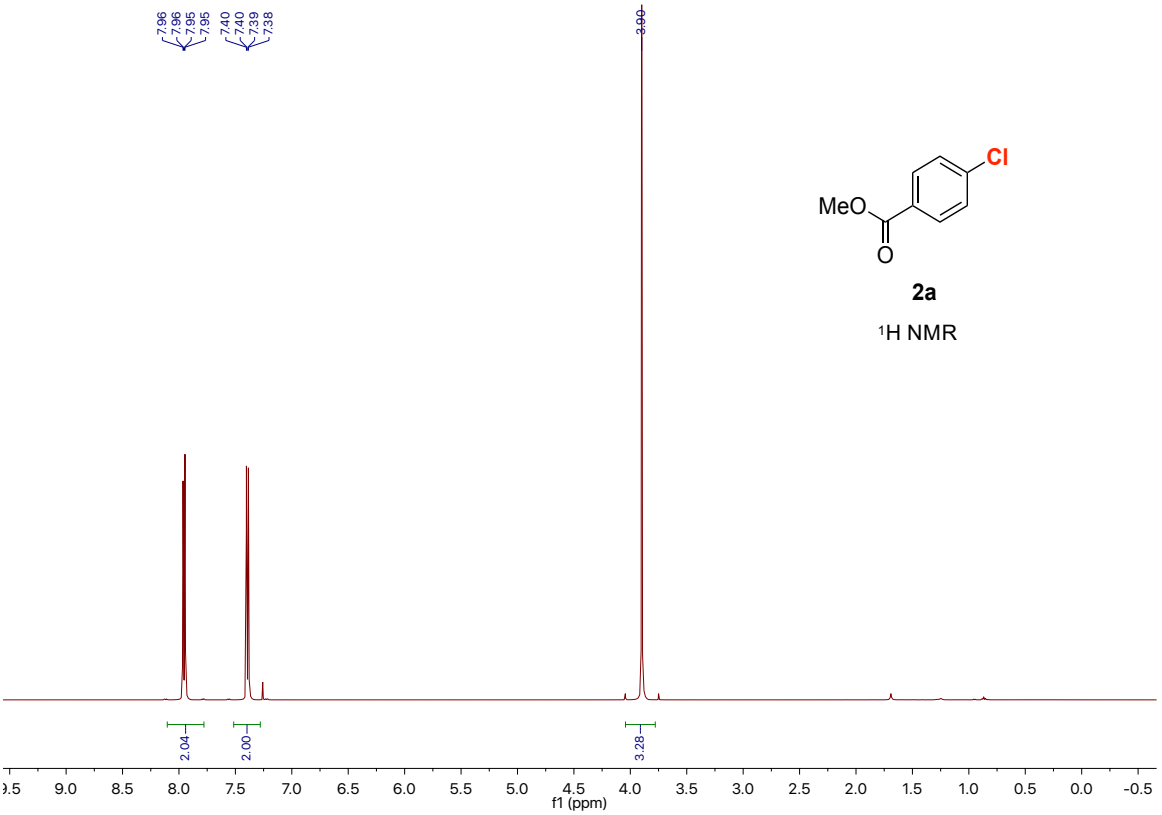

167.97
146.44
142.60
132.70
132.18
132.09
131.06
130.87
130.68
130.50
127.77
127.74
126.30
126.08
126.05
126.03
126.01
124.76
123.21
121.66
77.18 cdcl3
77.00 cdcl3
76.82 cdcl3
O
Cl
F3C
1d
13C NMR
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.25
8.23
8.22
7.56
7.54
7.53
7.42
7.40
7.39
7.31
7.30
7.29
7.27
7.26
7.25
7.24
7.23
7.23
7.21
7.15
7.14
7.13
4.32
O
Cl
1h
1H NMR
1.05
1.05
1.04
4.06
1.97
2.09
f1 (ppm)


167.91
143.46
139.64
134.35
134.00
132.91
131.92
129.31
129.20
128.70
127.03
126.54
77.48
77.23
76.98
39.84
O
Cl
1h
13C NMR
f1 (ppm)

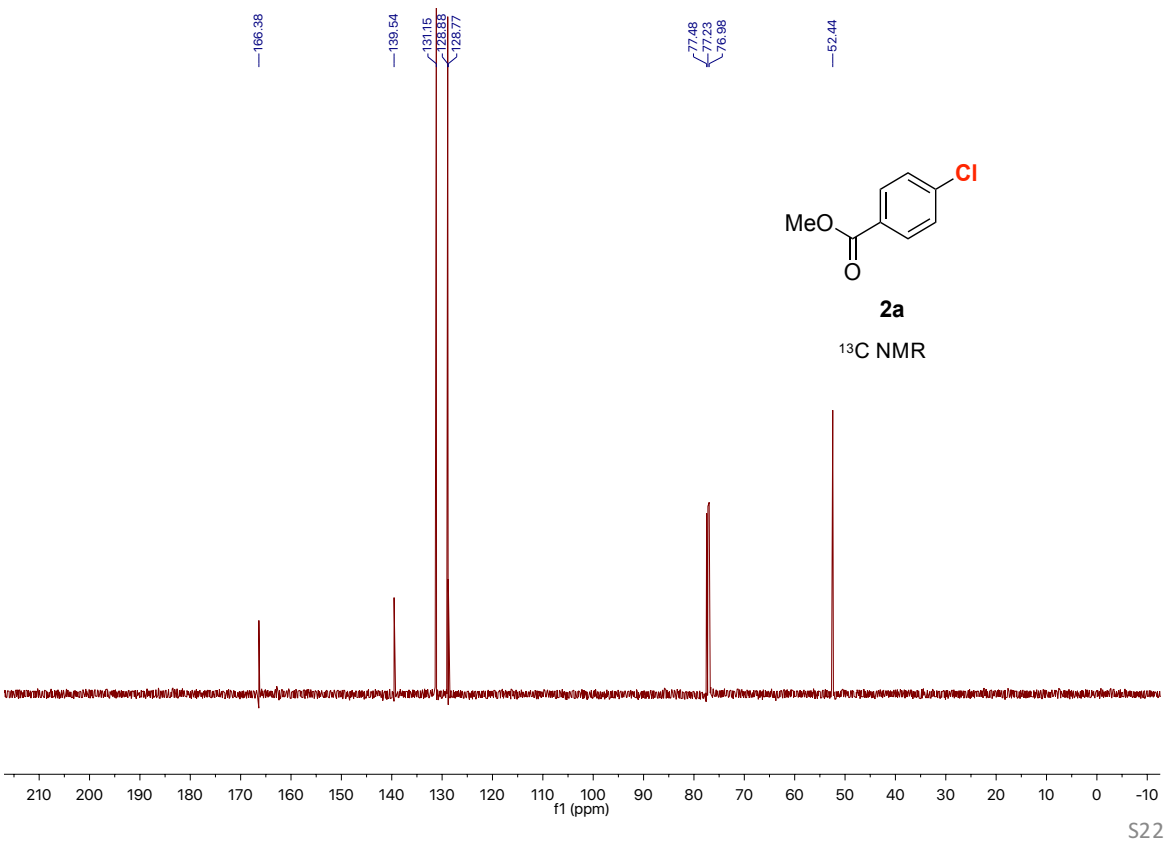

7.97
7.95
7.93
7.91
7.66
7.64
7.62
7.60
7.58
7.53
7.51
7.49
7.44
7.42
4.56
O
Cl
1k
1H NMR
2.10
1.05
1.99
0.96
1.00
2.01
f1 (ppm)


171.90
133.85
131.66
129.25
129.01
128.85
127.93
126.99
126.96
126.19
125.49
123.20
77.58
77.26
76.94
50.70
O
Cl
1k
13C NMR
f1 (ppm)



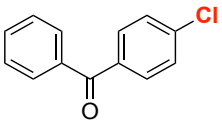
2a

^{1}H NMR



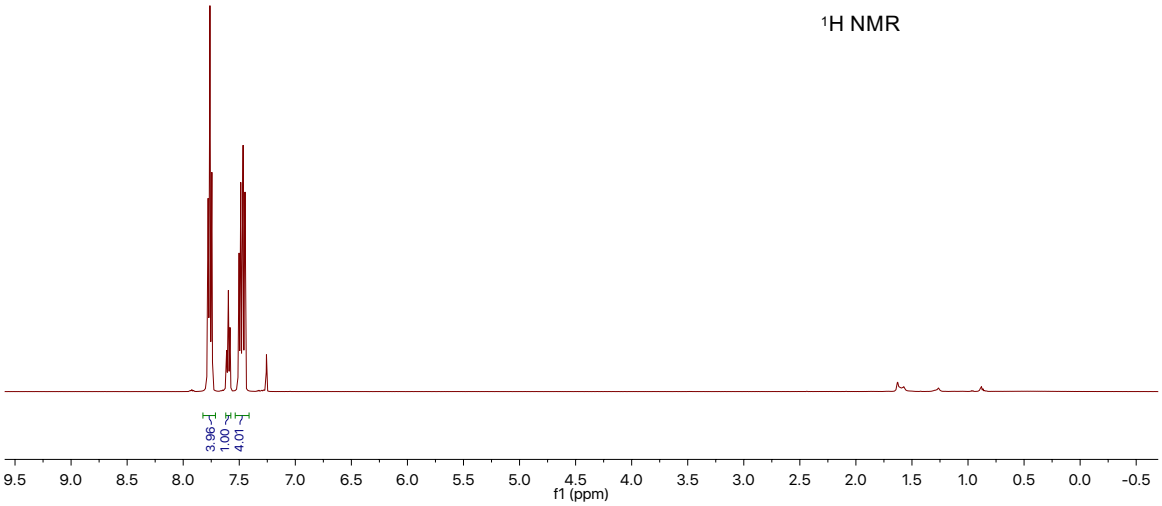
2a

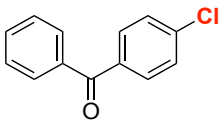
^{13}C NMR



2b

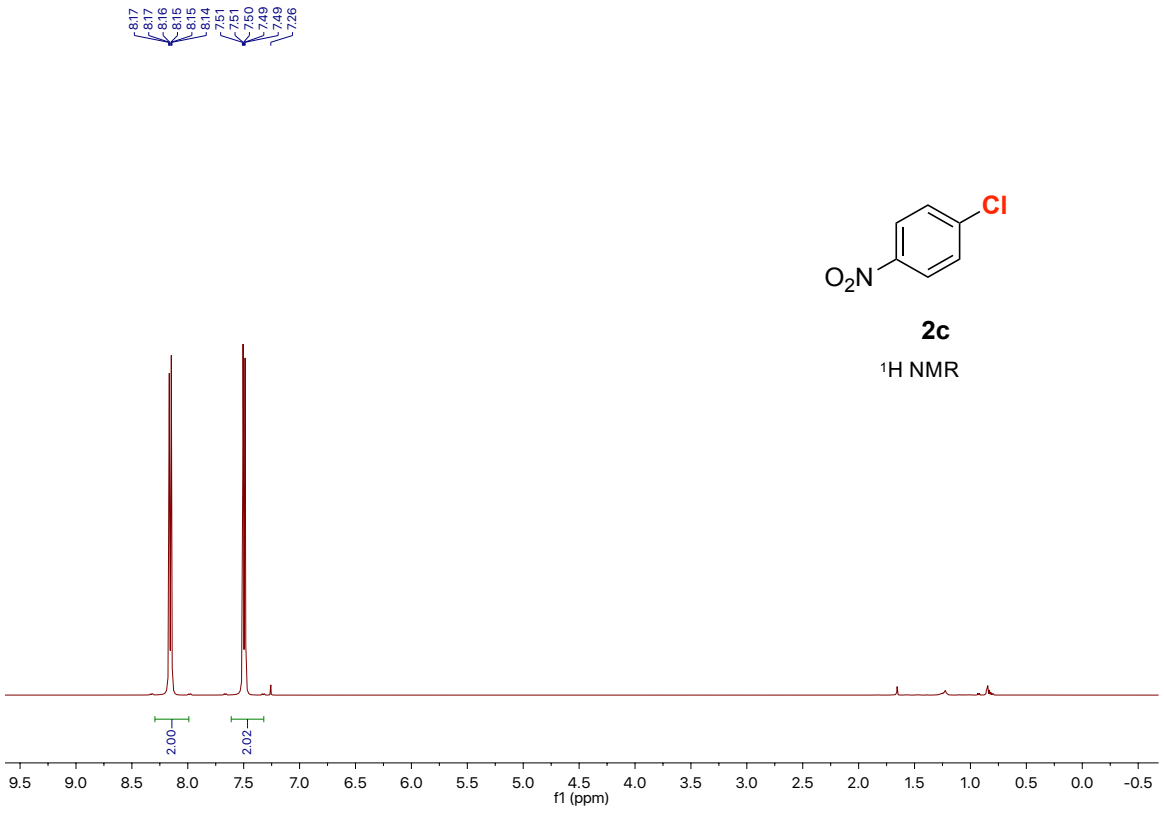
^{1}H NMR

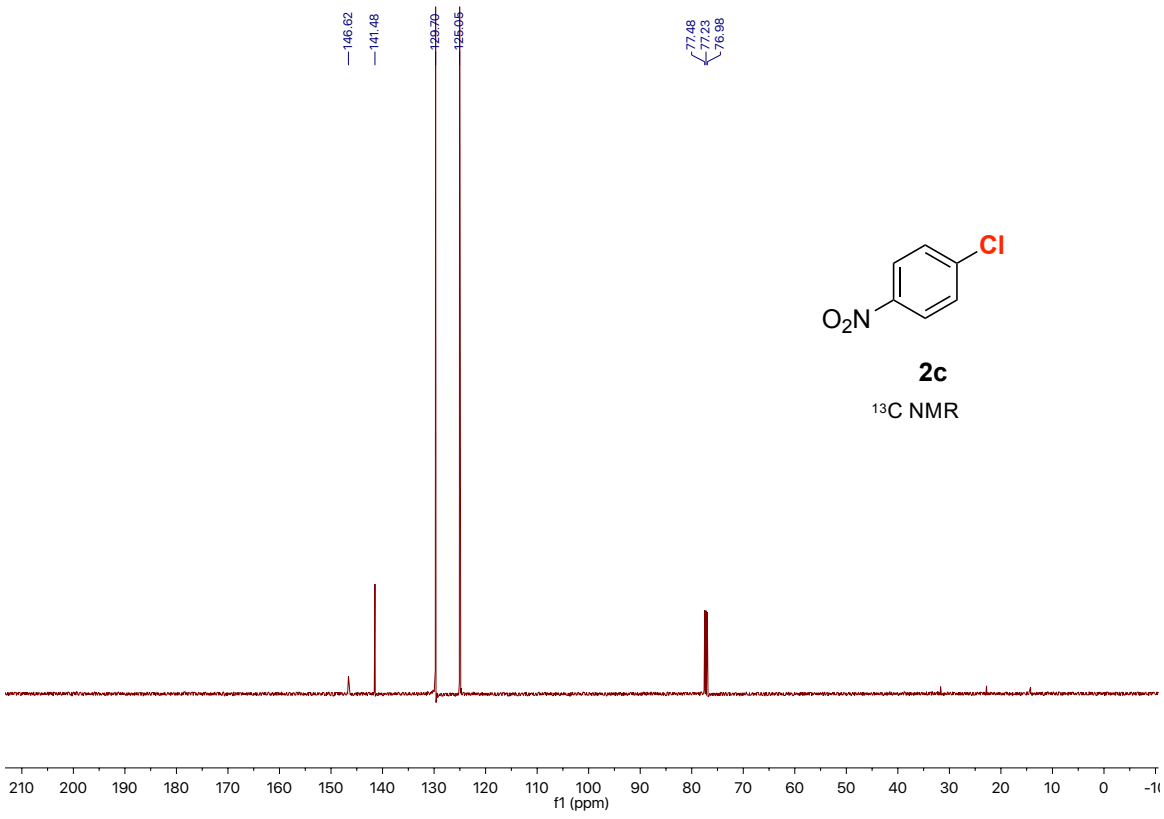


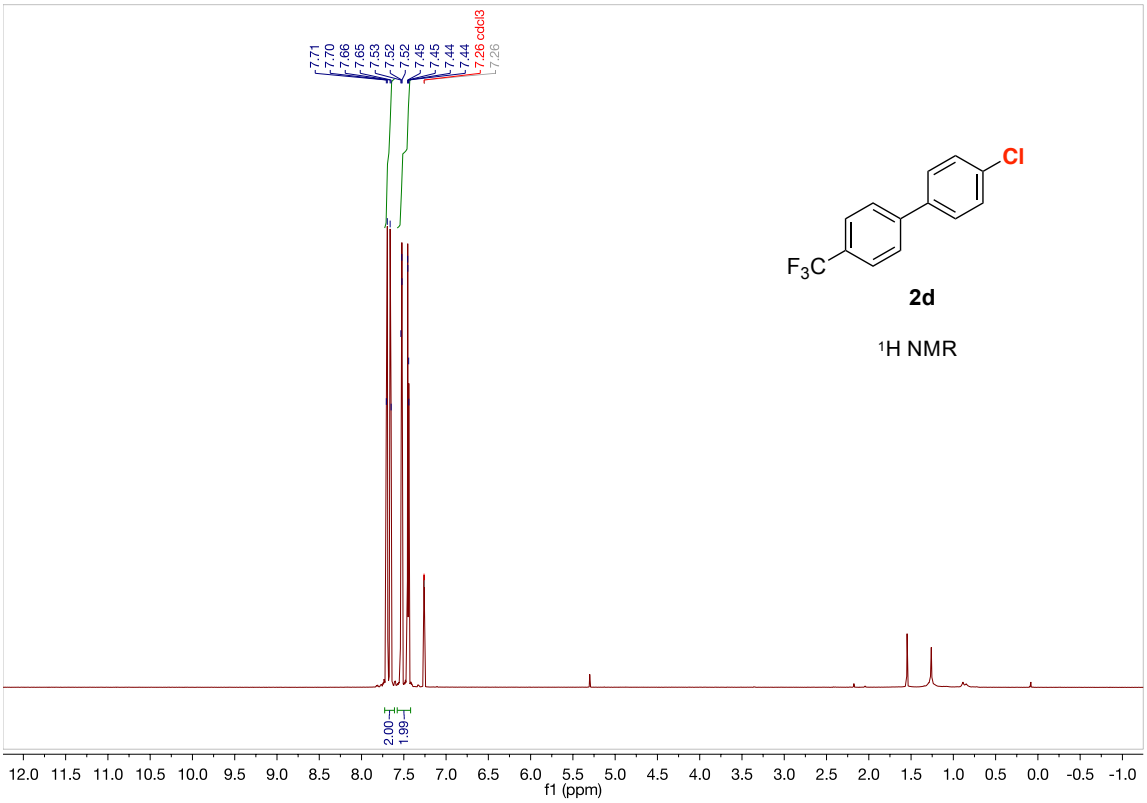


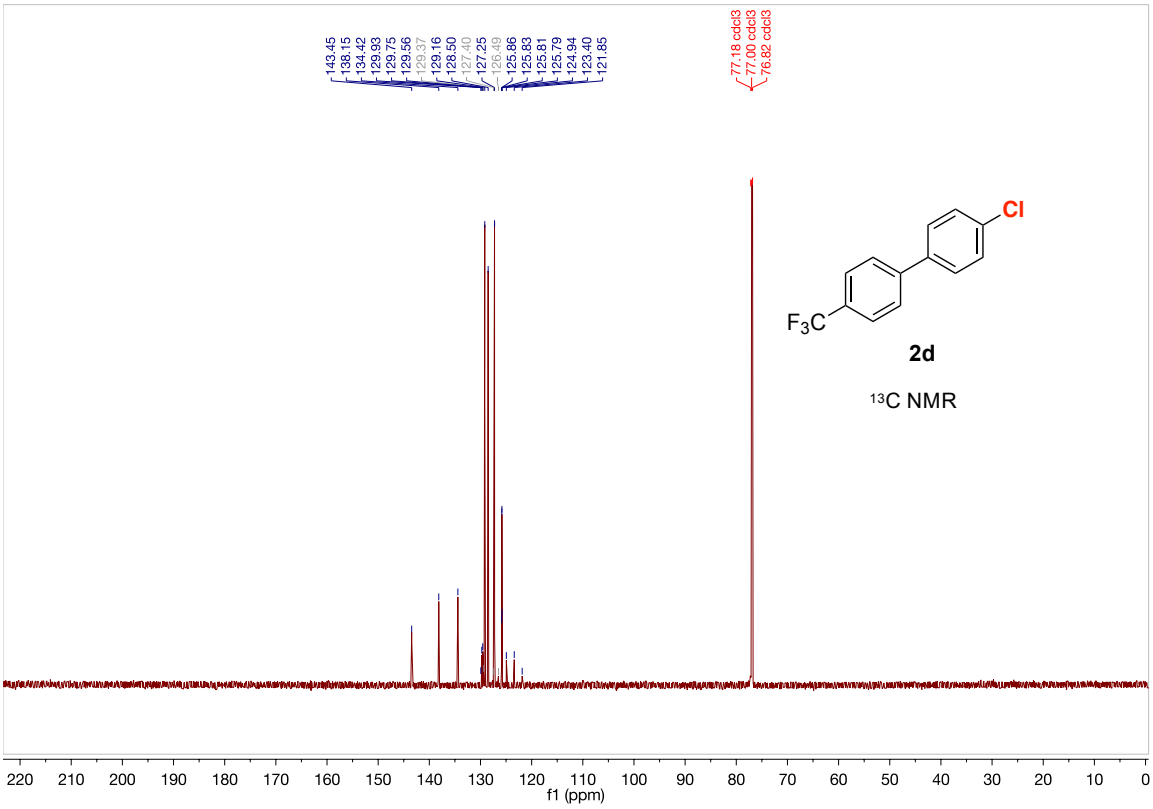
2b

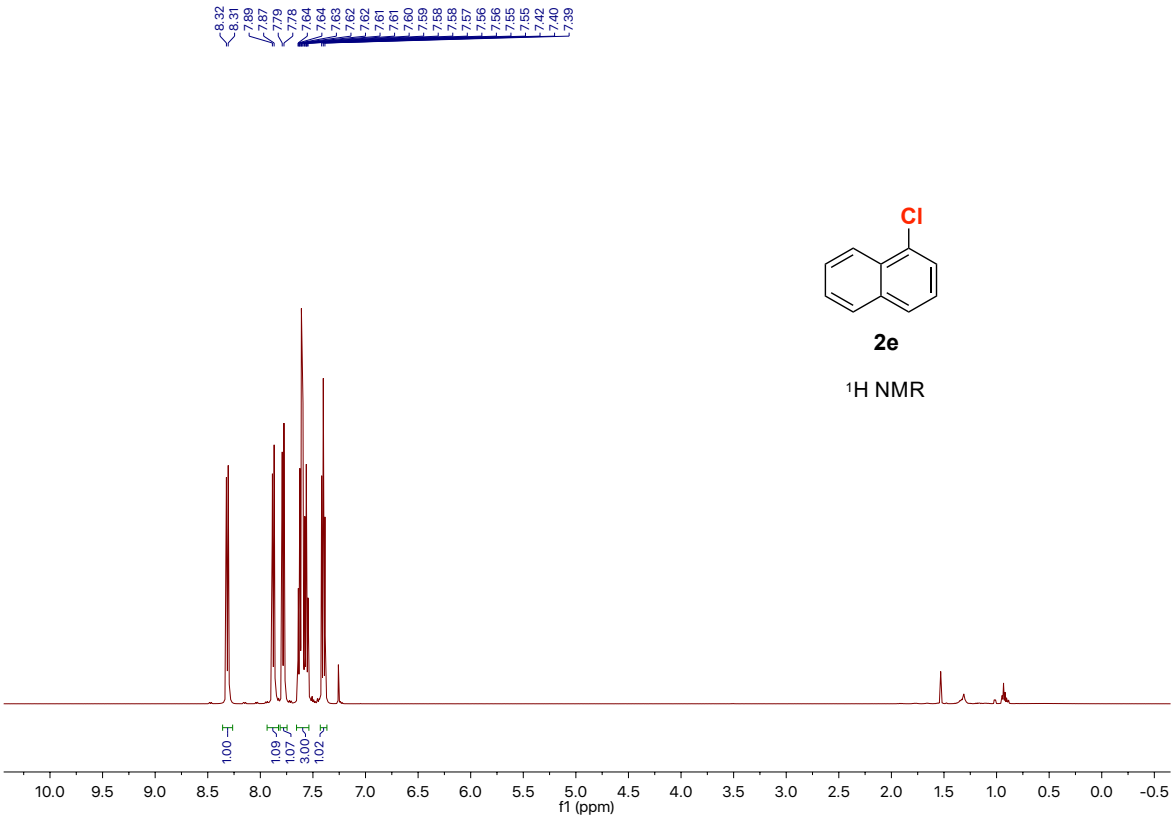
^{13}C NMR

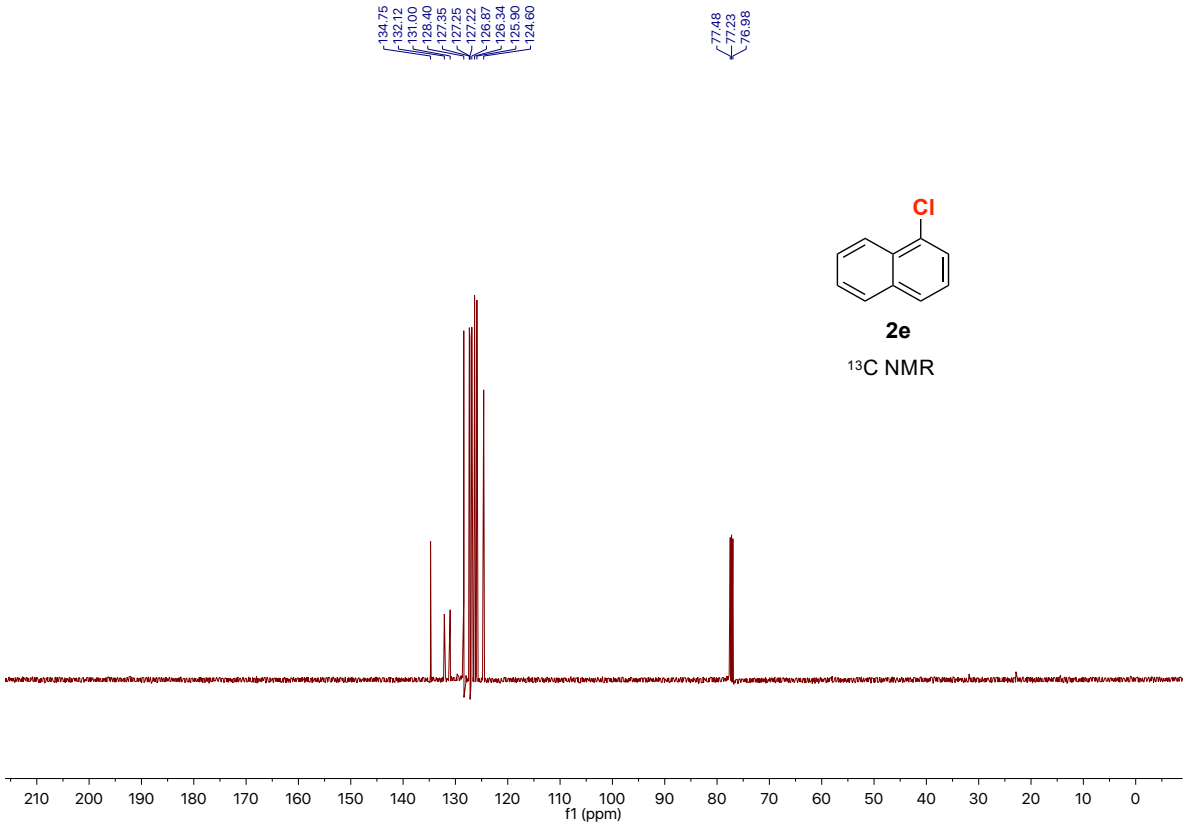

8.17
8.17
8.16
8.15
8.15
8.14
7.51
7.51
7.50
7.49
7.49
7.26
Cl
O2N
2c
1H NMR
2.00
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

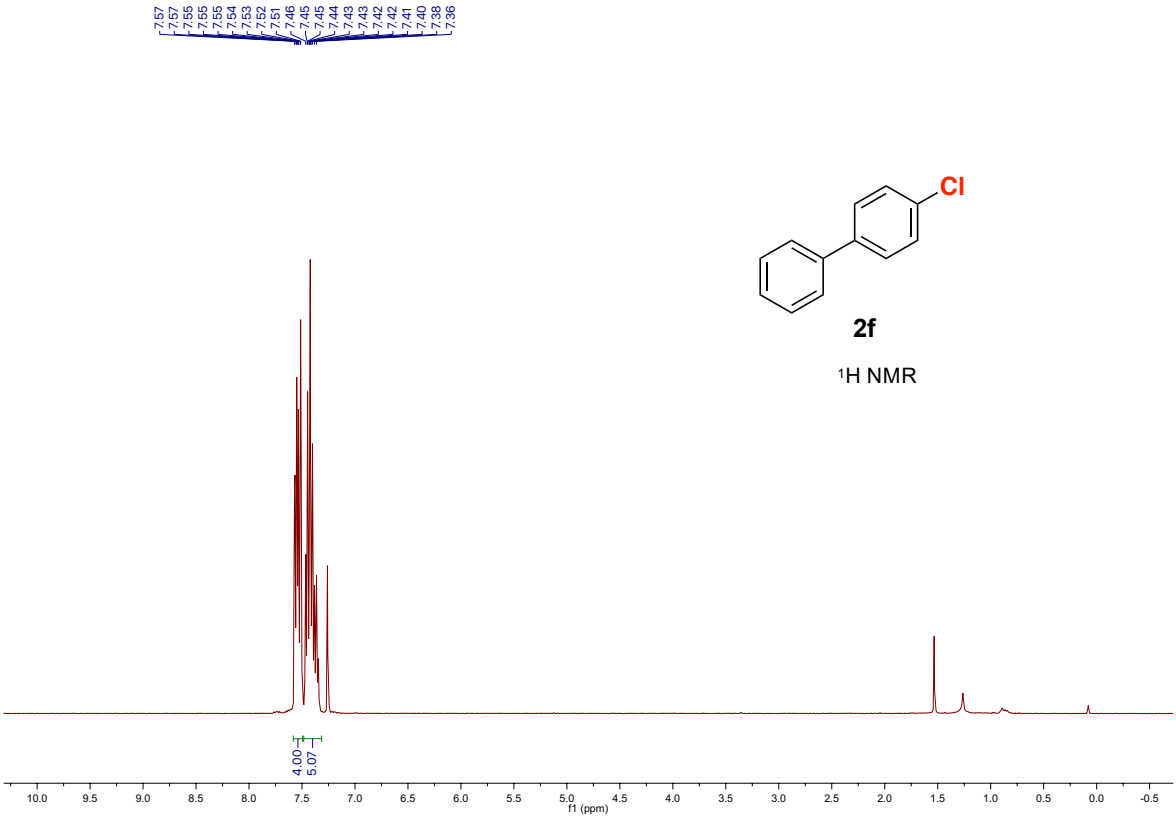

146.62
141.48
129.70
125.06
77.48
77.23
76.98
Cl
O2N
2c
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

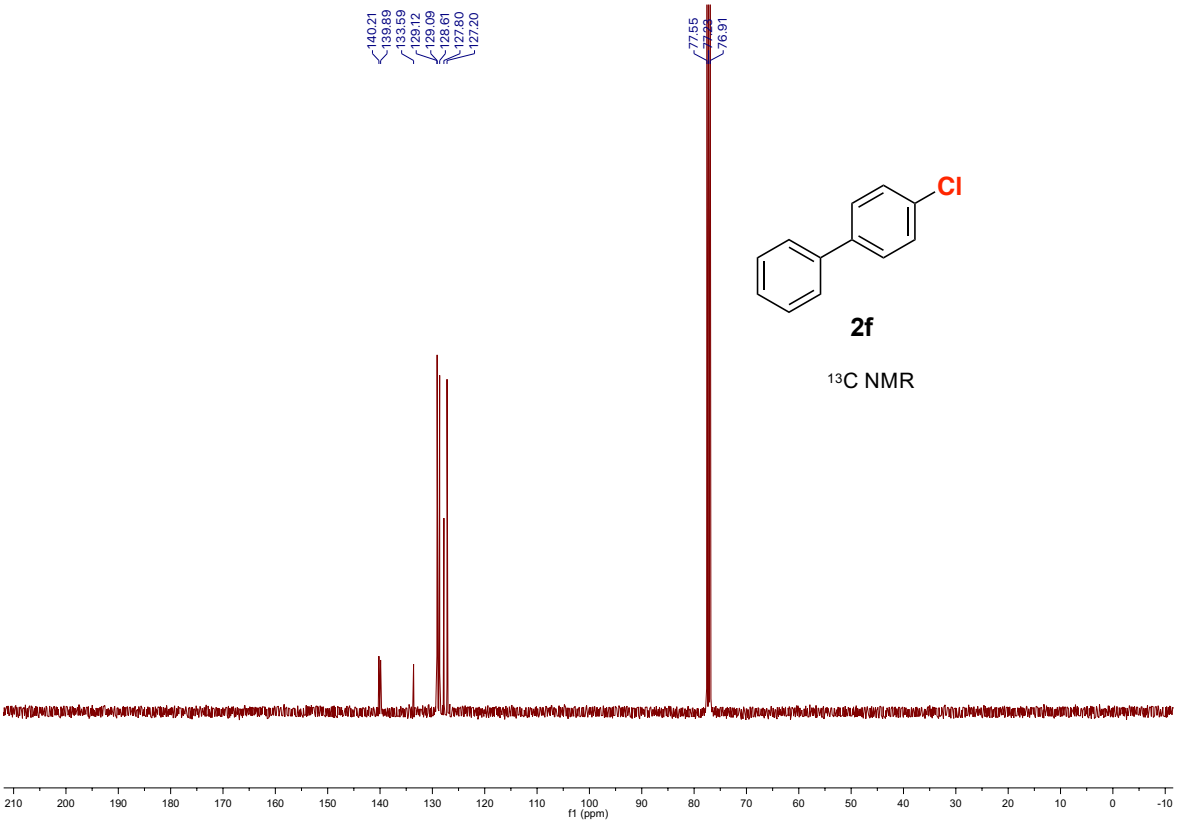

7.71
7.70
7.66
7.65
7.53
7.52
7.52
7.45
7.45
7.44
7.44
7.26 cdcl3
7.26
Cl
F3C
2d
1H NMR
2.00
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

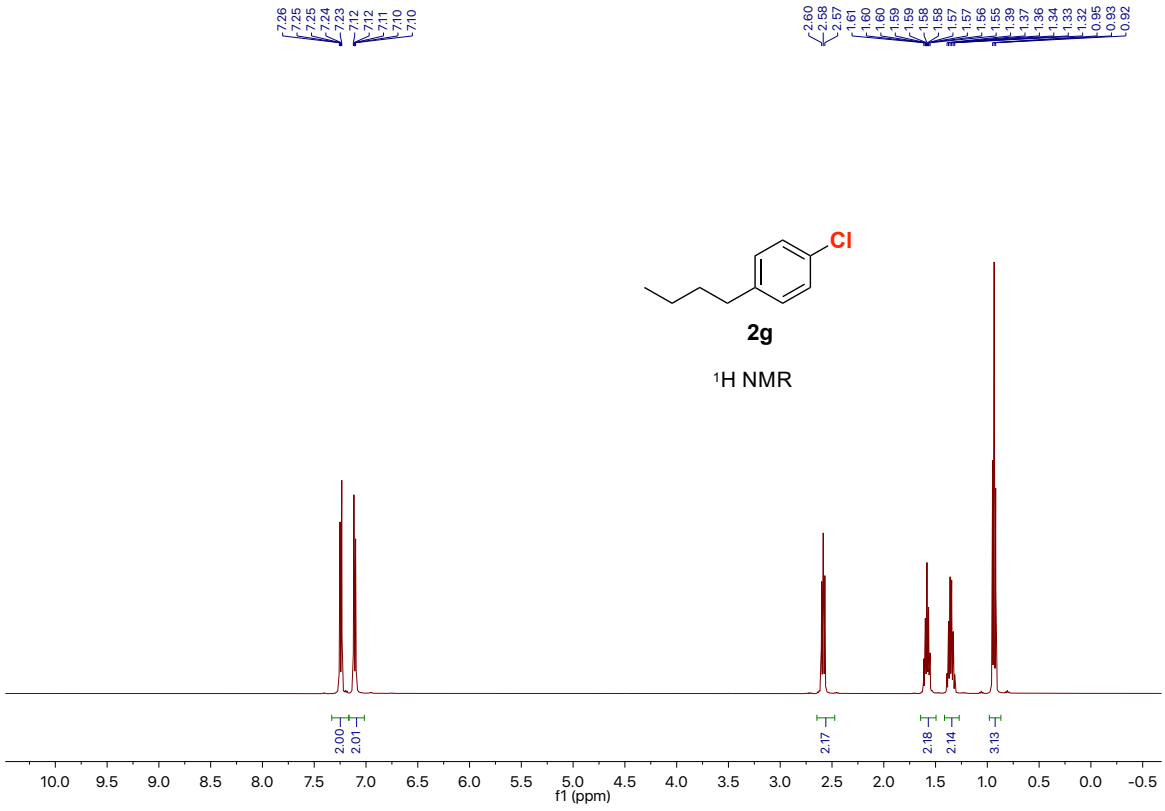

143.45
138.15
134.42
129.93
129.75
129.56
128.37
129.16
128.50
127.40
127.25
126.49
125.86
125.83
125.81
125.79
124.94
123.40
121.85
77.18 cdcl3
77.00 cdcl3
76.82 cdcl3
Cl
F3C
2d
13C NMR
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

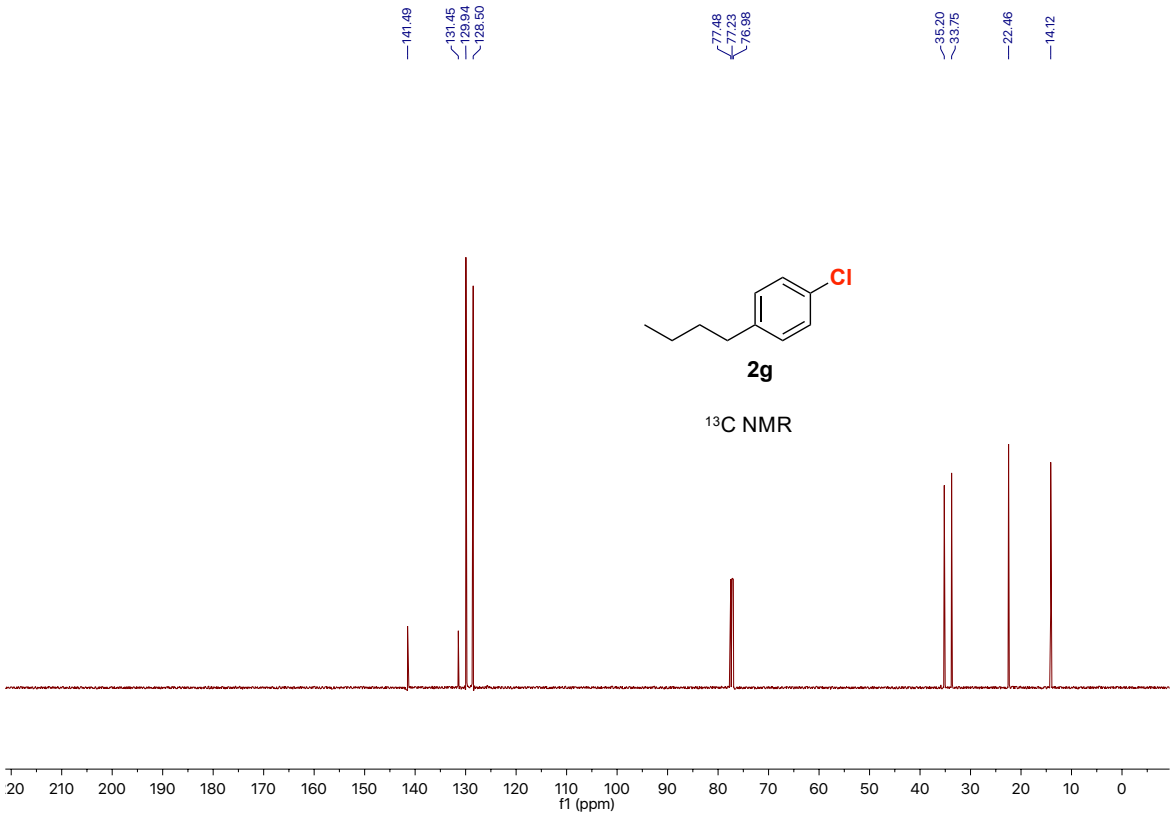

8.32
8.31
7.89
7.87
7.79
7.78
7.64
7.64
7.63
7.62
7.62
7.61
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.42
7.40
7.39
Cl
2e
1H NMR
1.00
1.09
1.07
3.00
1.02
f1 (ppm)

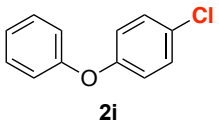

134.75
132.12
131.00
128.40
127.35
127.25
127.22
126.87
126.34
125.90
124.60
77.48
77.23
76.98
Cl
2e
13C NMR
f1 (ppm)


7.57
7.57
7.55
7.55
7.55
7.54
7.53
7.52
7.51
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.38
7.36
Cl
2f
1H NMR
4.00
5.07
f1 (ppm)


140.21
139.89
133.59
129.12
129.09
128.61
127.80
127.20
77.55
77.23
76.91
Cl
2f
13C NMR
f1 (ppm)

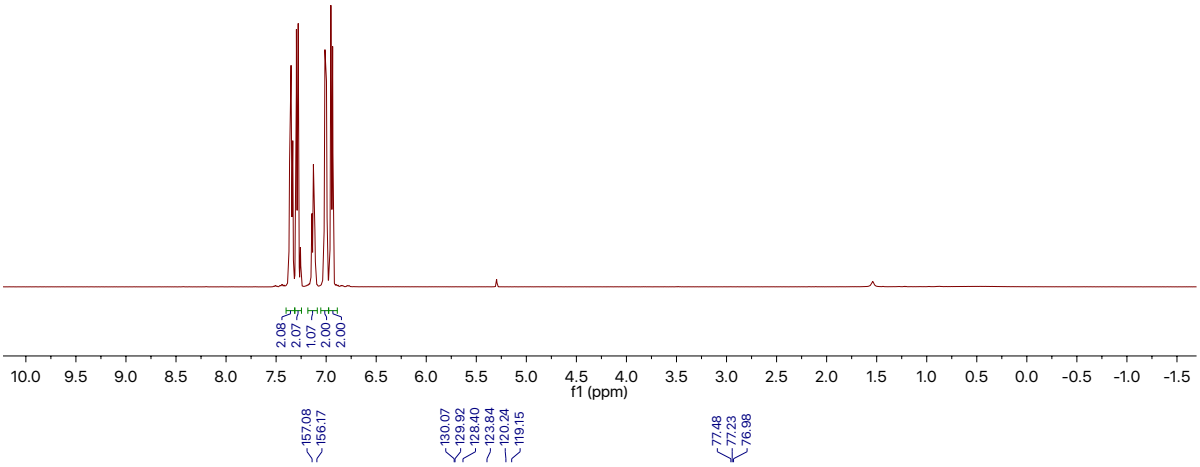

7.26
7.25
7.25
7.24
7.23
7.12
7.12
7.11
7.10
7.10
2.60
2.58
2.57
1.61
1.60
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.56
1.55
1.39
1.37
1.36
1.34
1.33
1.32
0.95
0.93
0.92
Cl
2g
1H NMR
2.00
2.01
2.17
2.18
2.14
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

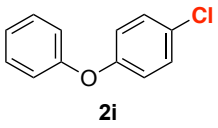

141.49
131.45
129.94
128.50
77.48
77.23
76.98
35.20
33.75
22.46
14.12
Cl
2g
13C NMR
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



2i

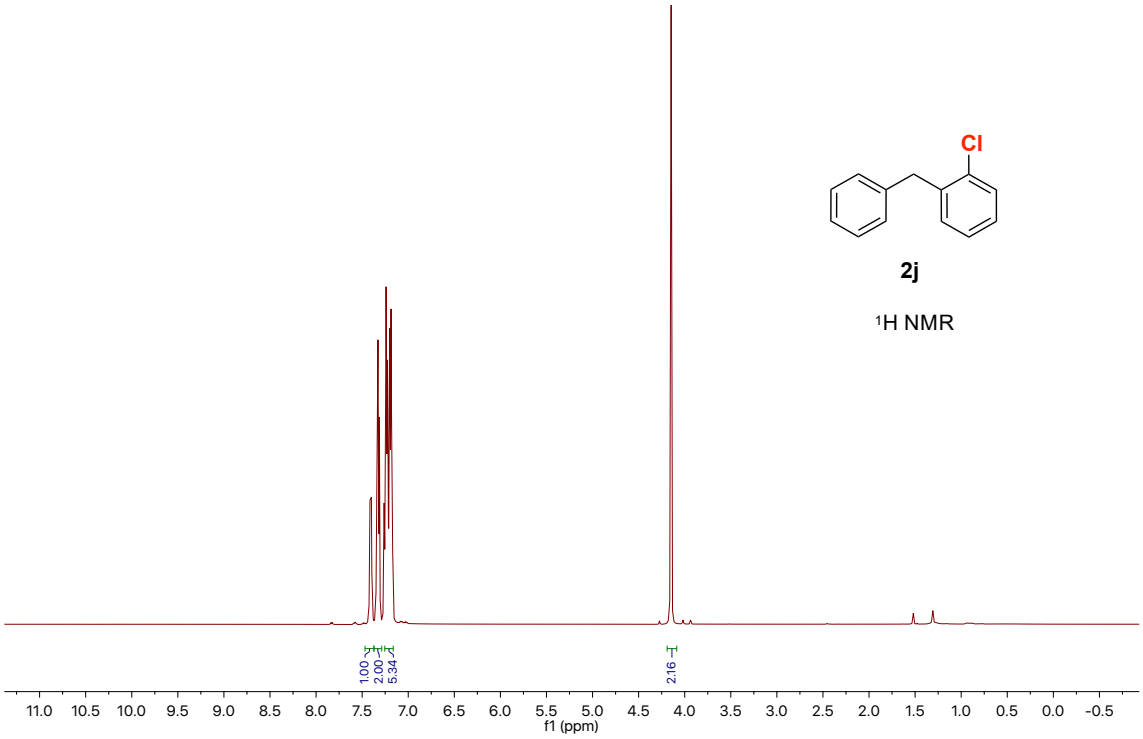
^{1}H NMR

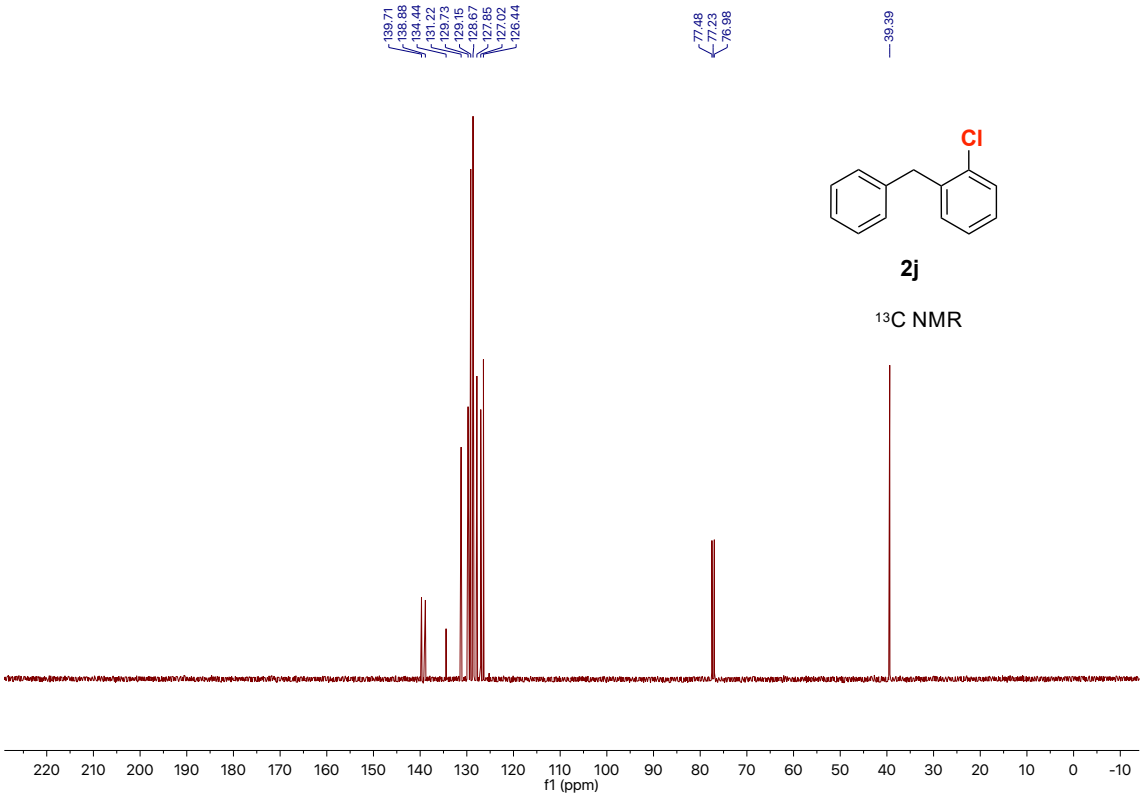


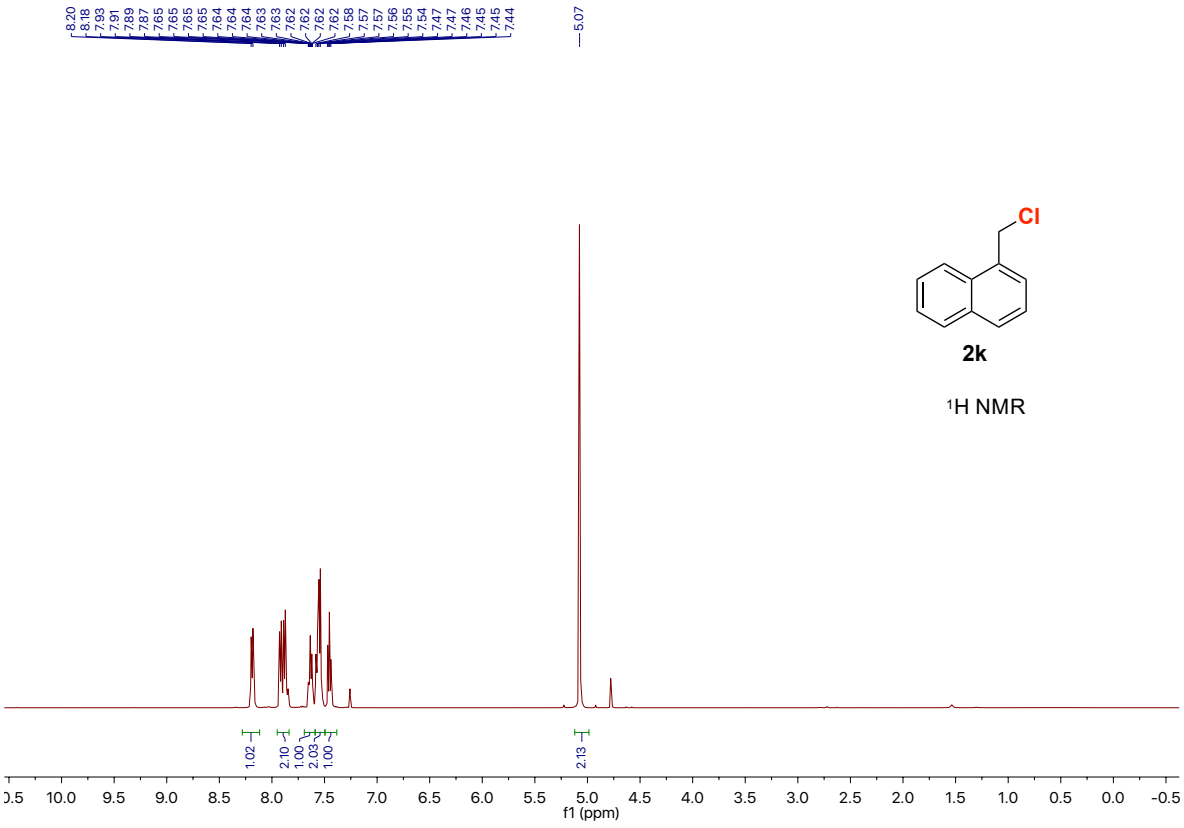


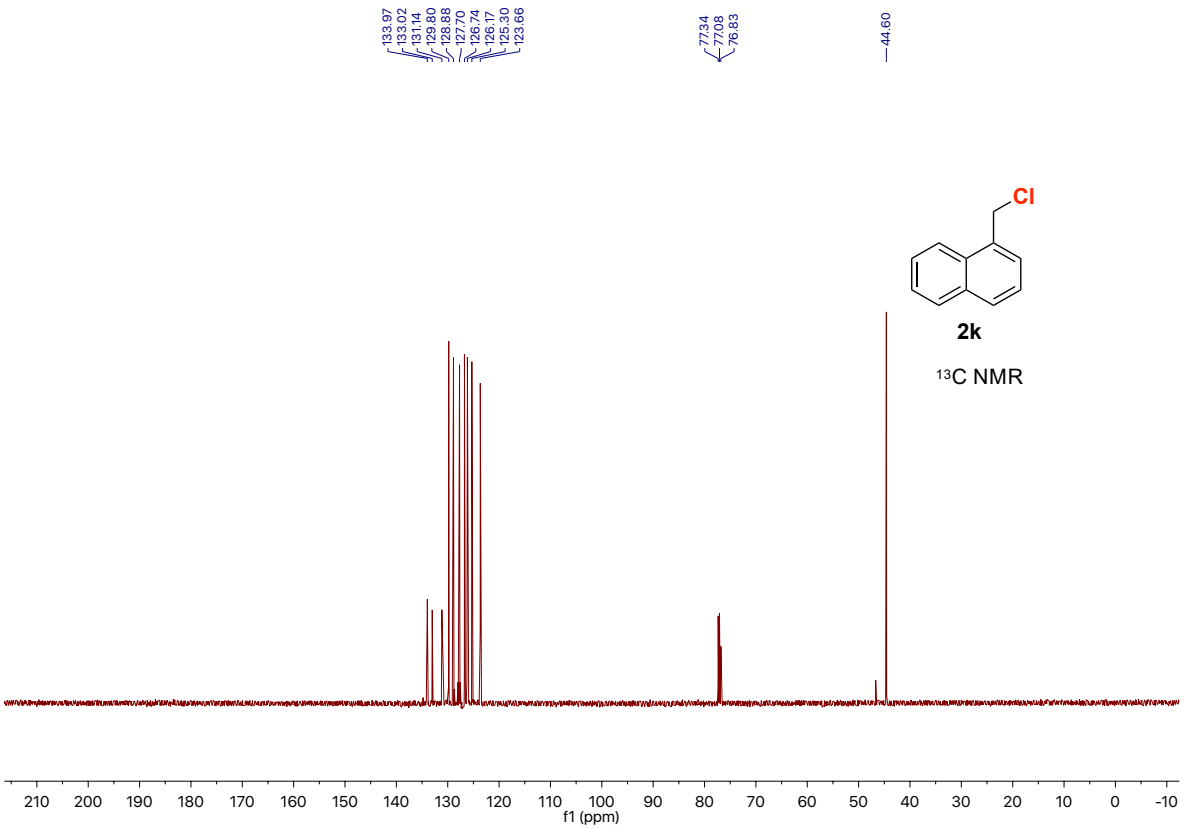
2i

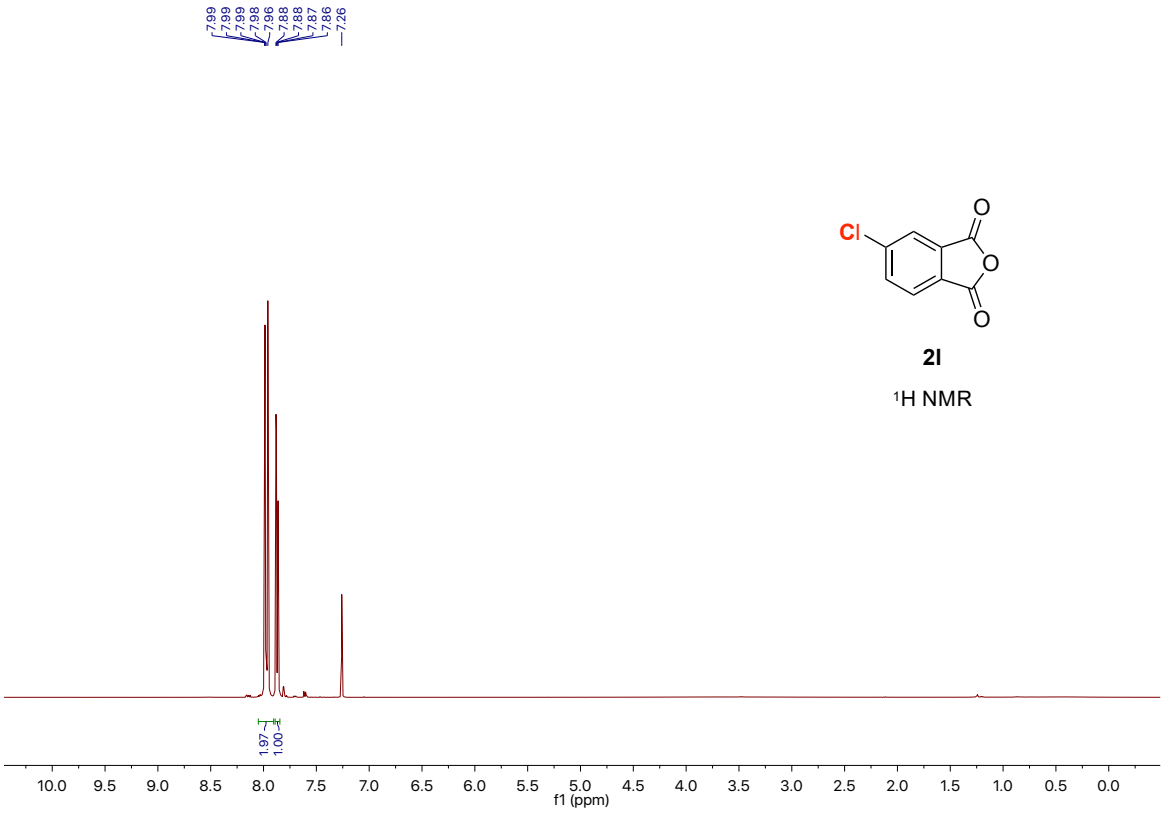
^{13}C NMR

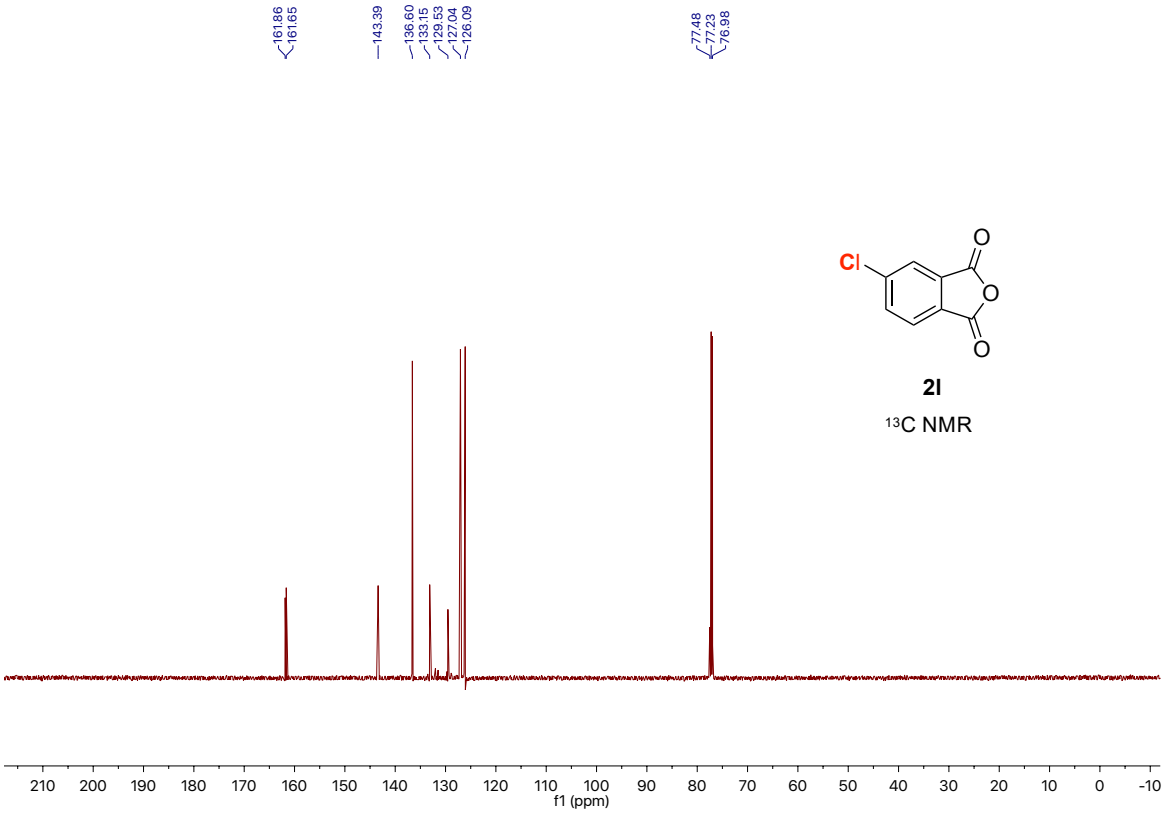

Cl
2j
1H NMR
1.00
2.00
5.34
2.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

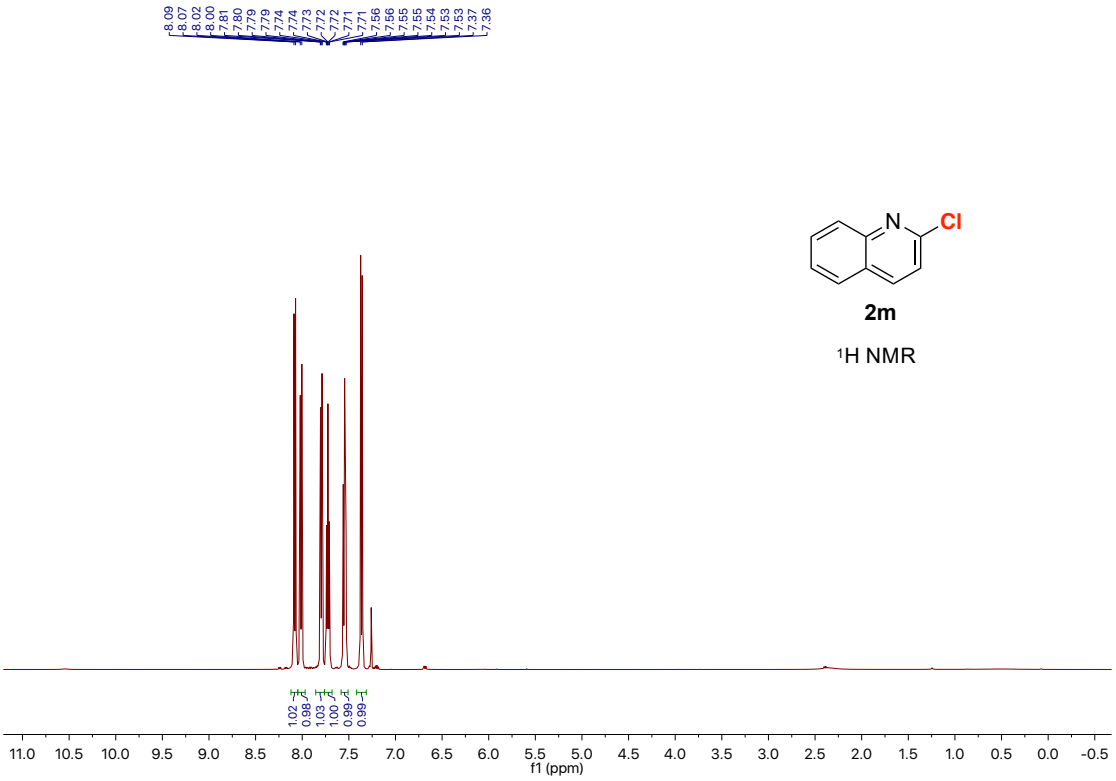

139.71
138.88
134.44
131.22
129.73
129.15
128.67
127.85
127.02
126.44
77.48
77.23
76.98
39.39
Cl
2j
13C NMR
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

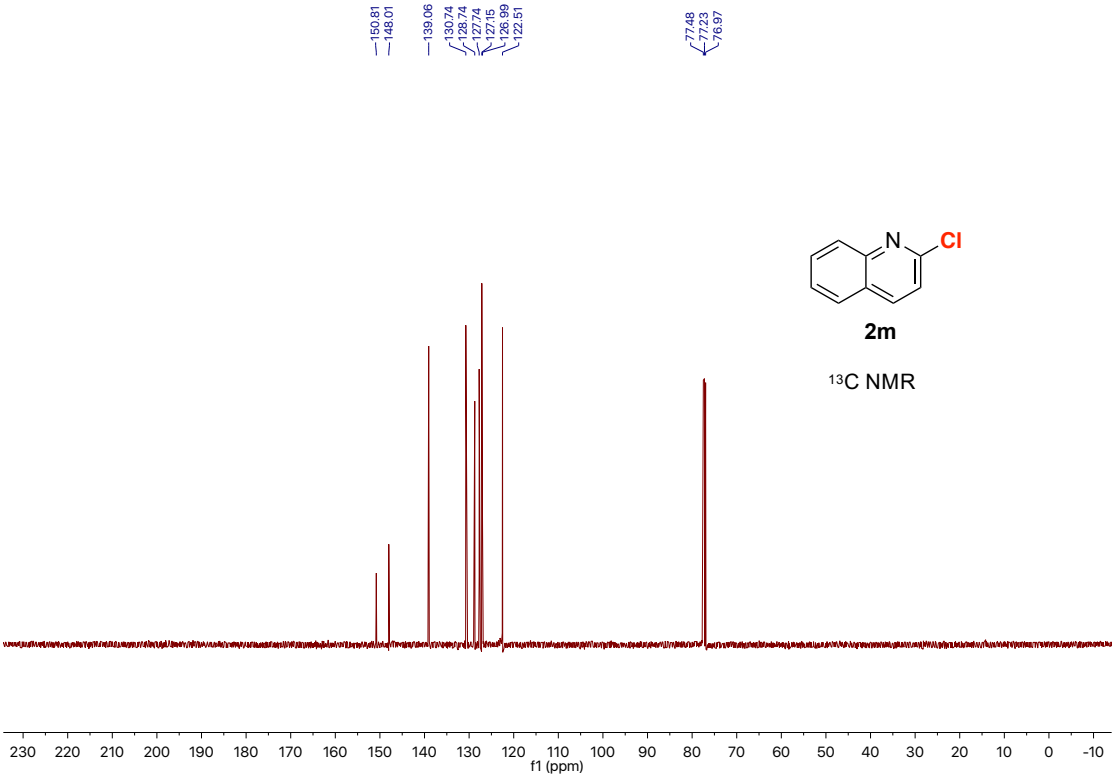

8.20
8.18
7.93
7.91
7.89
7.87
7.65
7.65
7.65
7.64
7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.62
7.62
7.58
7.57
7.57
7.56
7.55
7.54
7.47
7.47
7.46
7.45
7.45
7.44
5.07
Cl
2k
1H NMR
1.02
2.10
1.00
2.03
1.00
2.13
f1 (ppm)

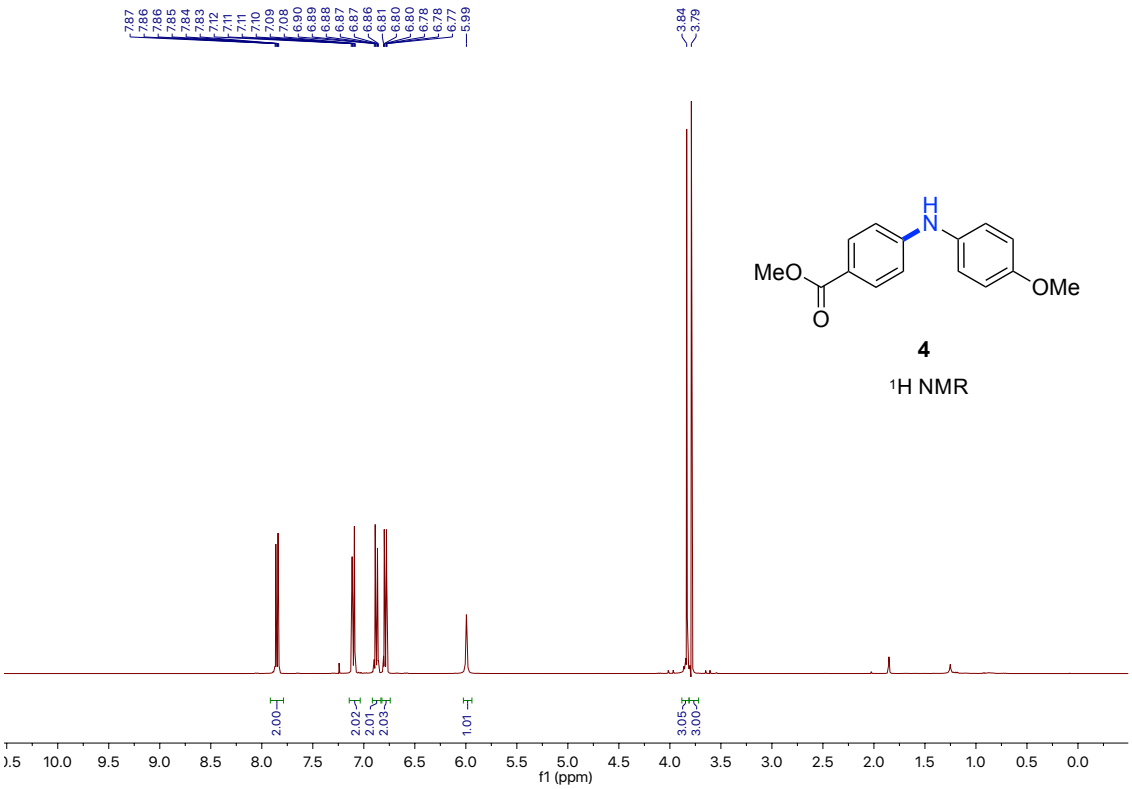

133.97
133.02
131.14
129.80
128.88
127.70
126.74
126.17
125.30
123.66
77.34
77.08
76.83
44.60
Cl
2k
13C NMR
f1 (ppm)

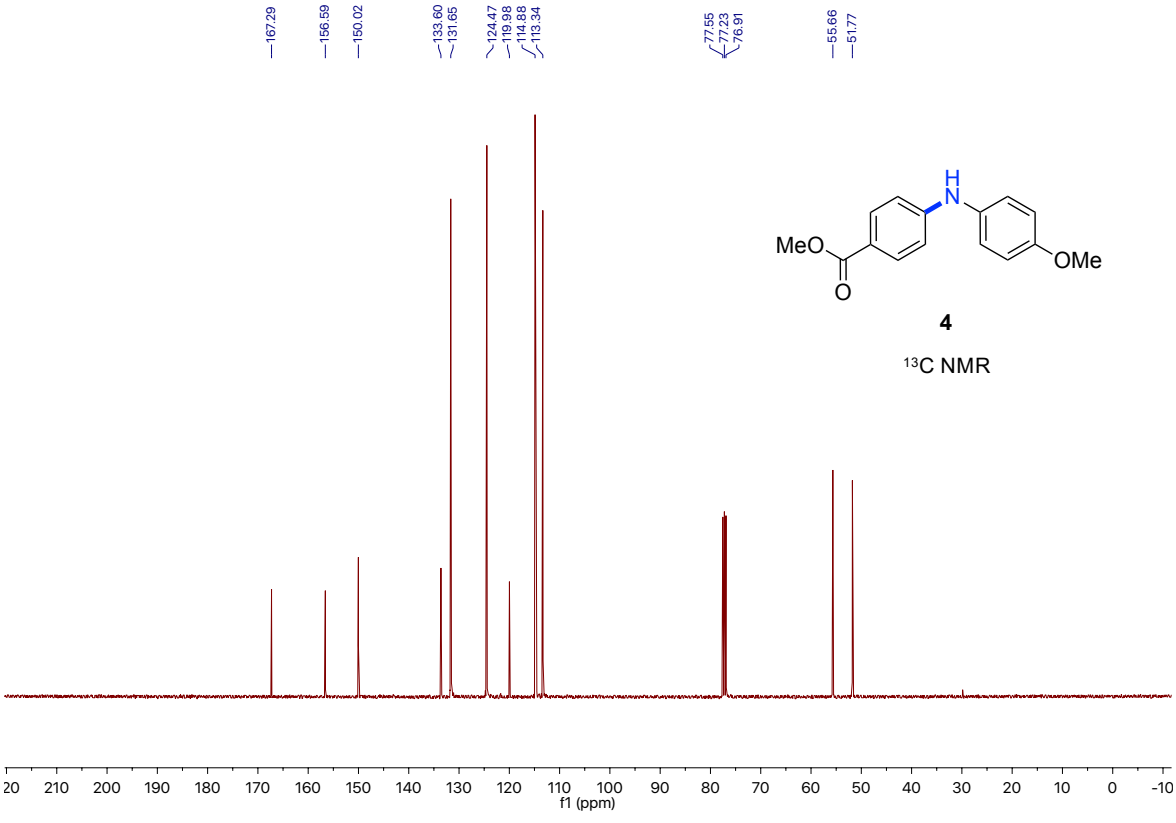

7.99
7.99
7.99
7.98
7.96
7.88
7.88
7.87
7.86
7.26
Cl
O
O
O
2I
1H NMR
1.97
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

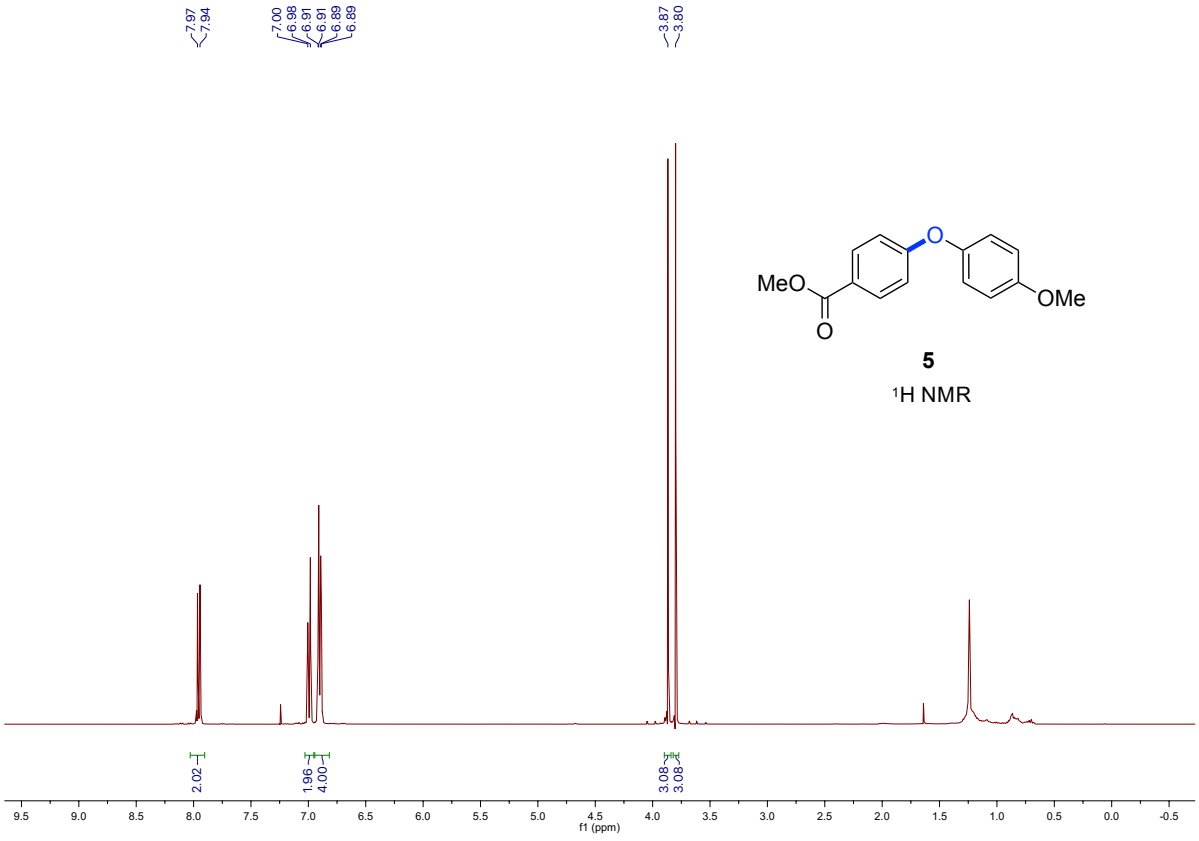

161.86
161.65
143.39
136.60
133.15
129.53
127.04
126.09
77.48
77.23
76.98
Cl
O
O
O
2I
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.09
8.07
8.02
8.00
7.81
7.80
7.79
7.79
7.74
7.74
7.73
7.72
7.72
7.71
7.71
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.37
7.36
N
Cl
2m
1H NMR
1.02
0.98
1.03
1.00
0.99
0.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


150.81
148.01
139.06
130.74
128.74
127.74
127.15
126.99
122.51
77.48
77.23
76.97
N
Cl
2m
13C NMR
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

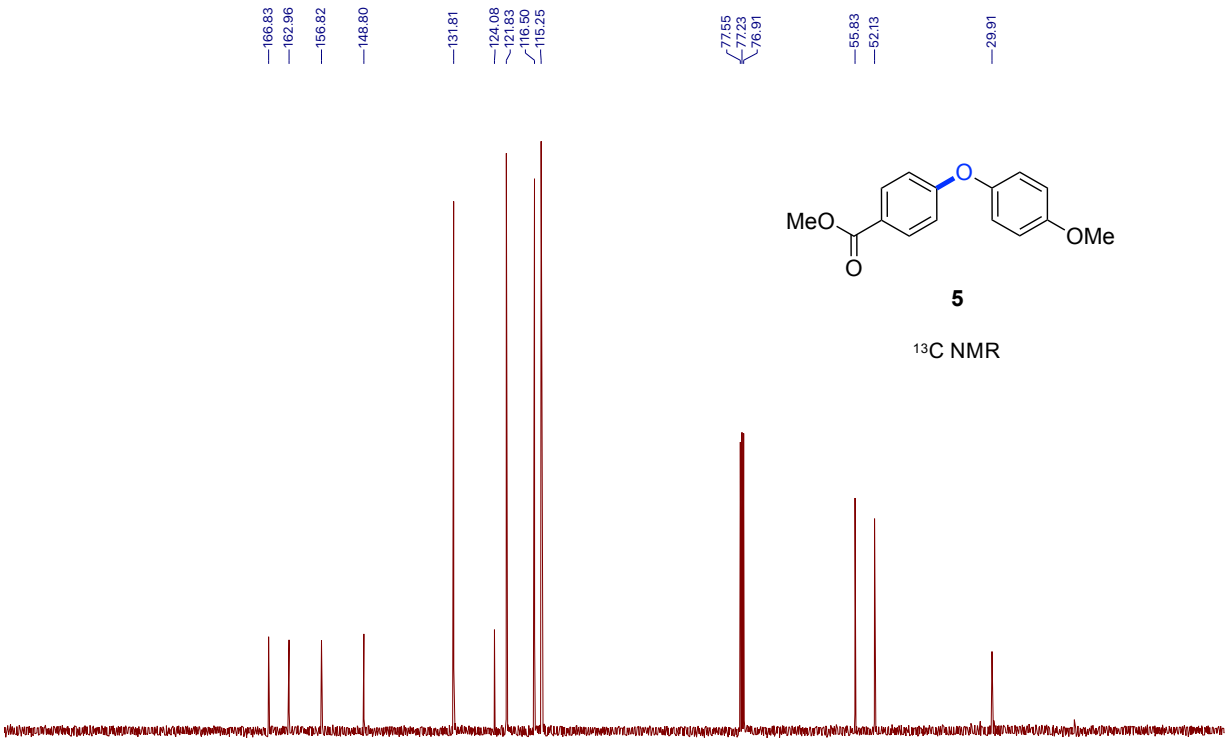

7.87
7.86
7.86
7.85
7.84
7.83
7.12
7.11
7.11
7.10
7.09
7.08
6.90
6.89
6.88
6.87
6.87
6.86
6.81
6.80
6.80
6.78
6.78
6.77
5.99
3.84
3.79
MeO
O
H
N
OMe
4
1H NMR
2.00
2.02
2.01
2.03
1.01
3.05
3.00
f1 (ppm)


167.29
156.59
150.02
133.60
131.65
124.47
119.98
114.88
113.34
77.55
77.23
76.91
55.66
51.77
MeO
O
H
N
OMe
4
13C NMR
f1 (ppm)



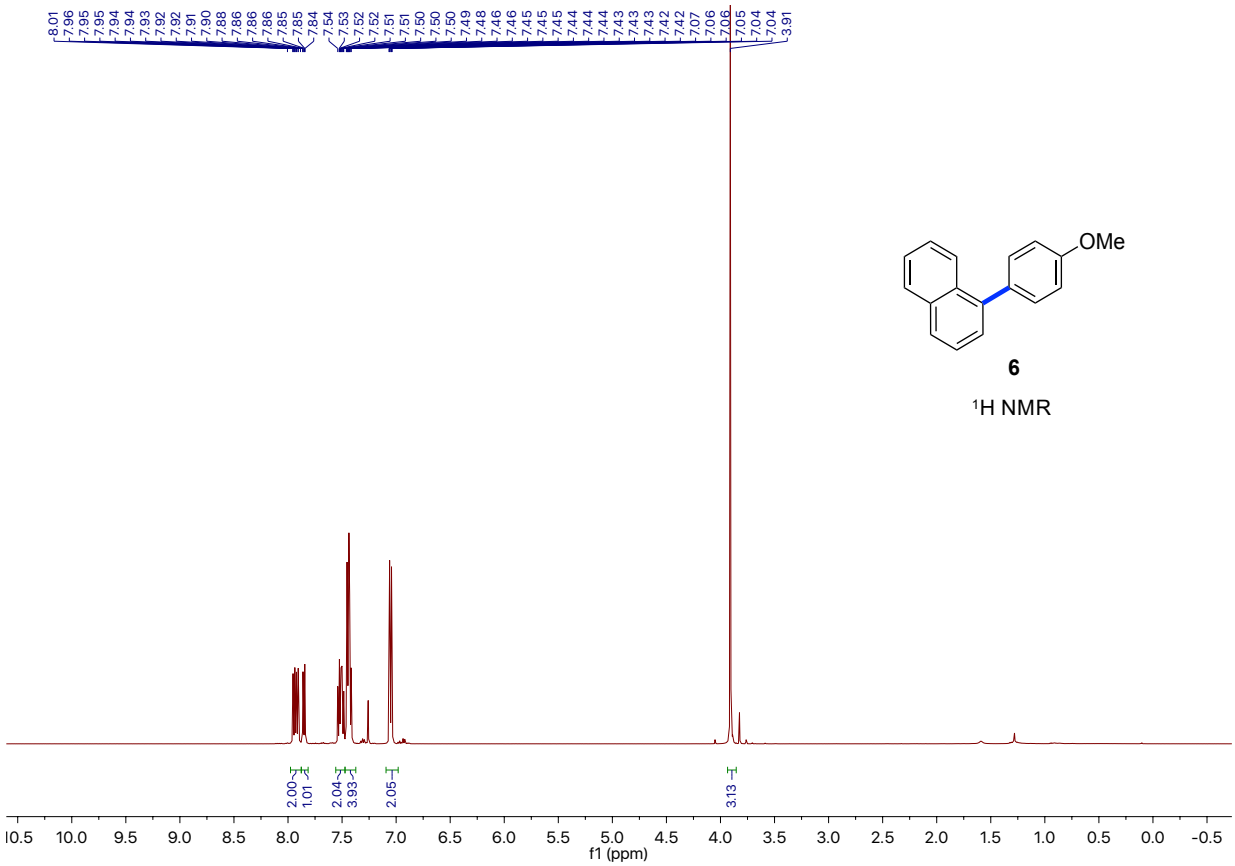
5

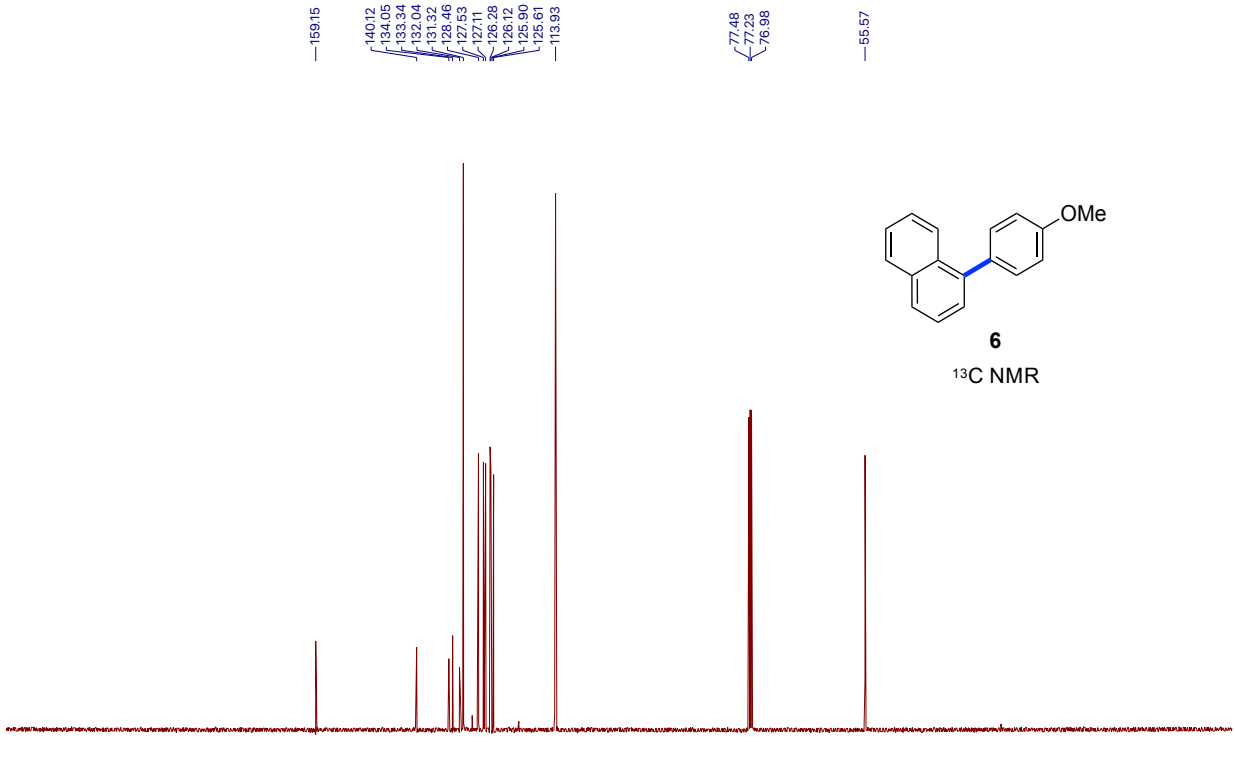
^{1}H NMR

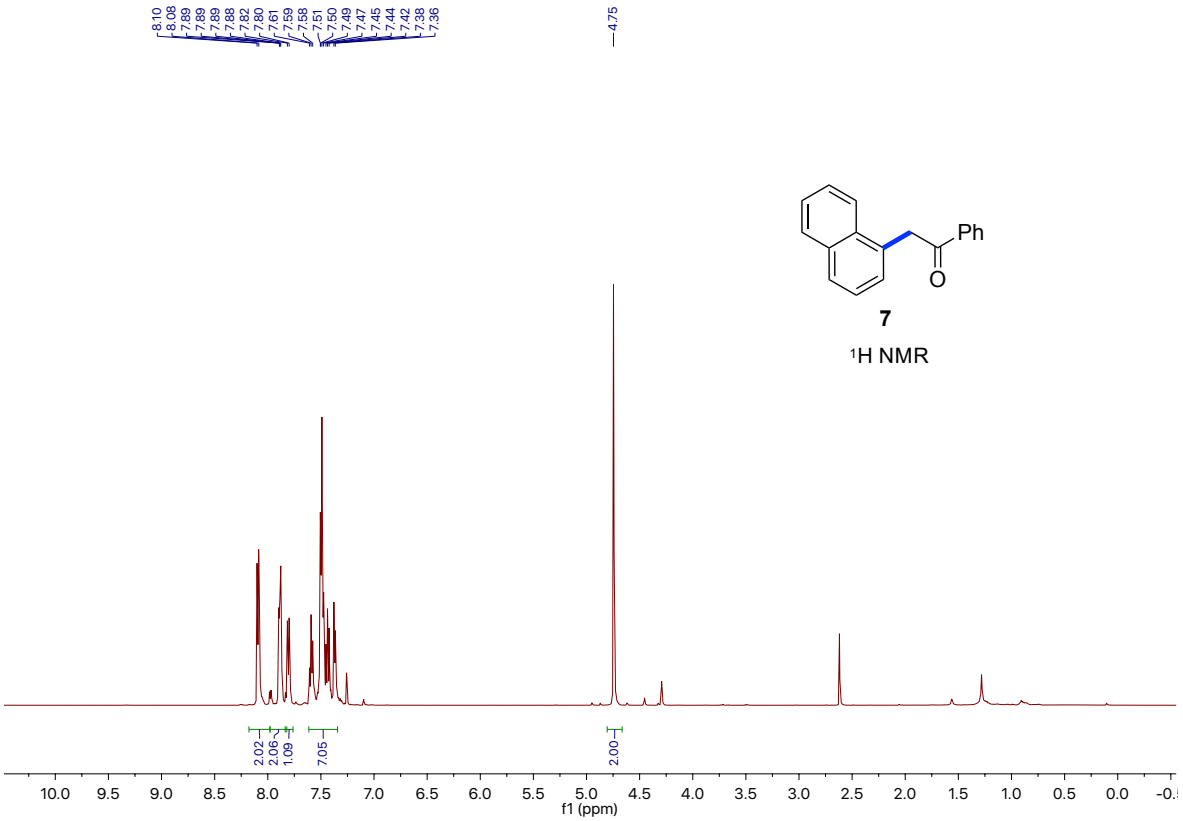


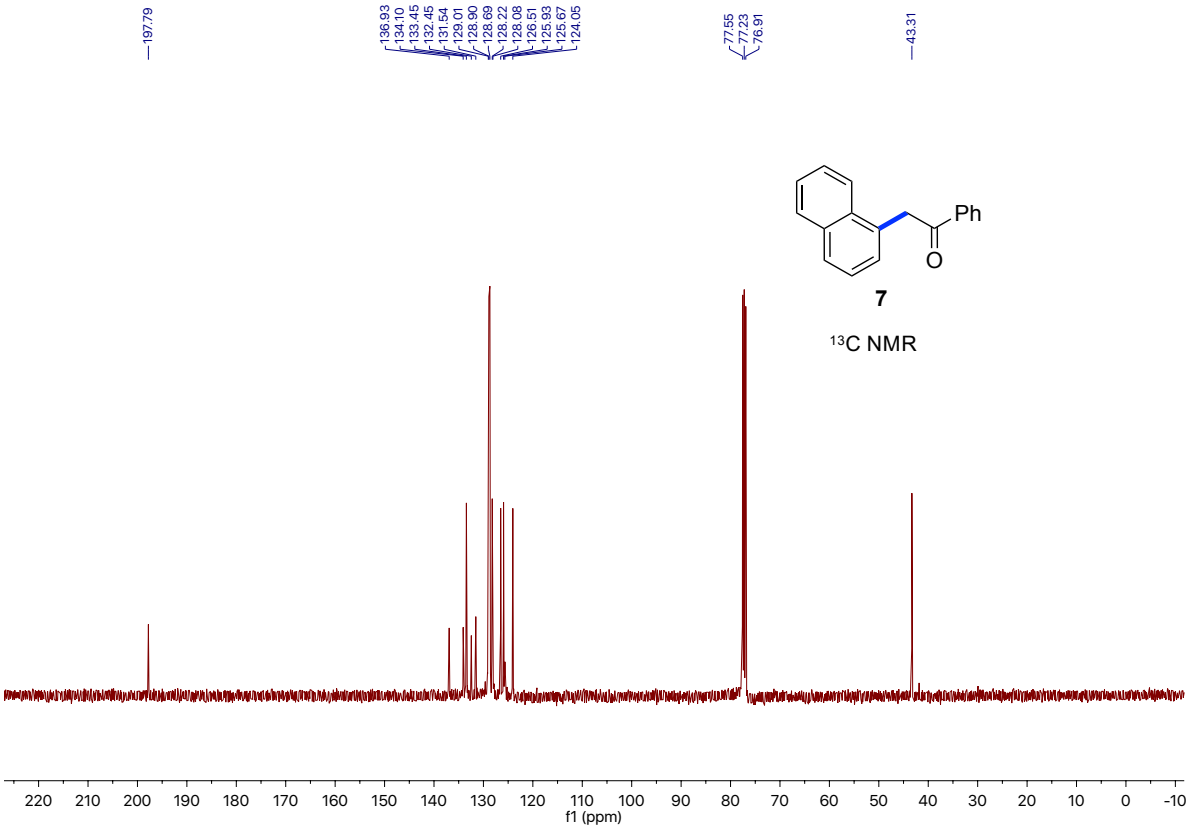
5

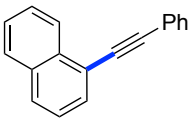
^{13}C NMR


8.01
7.96
7.95
7.95
7.94
7.94
7.93
7.92
7.92
7.91
7.90
7.88
7.86
7.86
7.86
7.85
7.85
7.84
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.48
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.07
7.06
7.06
7.05
7.04
7.04
3.91
OMe
6
1H NMR
2.00
1.01
2.04
3.93
2.05
3.13
f1 (ppm)


159.15
140.12
134.05
133.34
132.04
131.32
128.46
127.53
127.11
126.28
126.12
125.90
125.61
113.93
77.48
77.23
76.98
55.57
OMe
6
13C NMR
f1 (ppm)

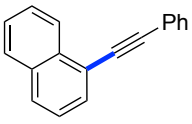

8.10
8.08
7.89
7.89
7.89
7.89
7.88
7.82
7.80
7.61
7.59
7.58
7.51
7.50
7.49
7.47
7.45
7.44
7.42
7.38
7.36
4.75
Ph
O
7
1H NMR
2.02
2.06
1.09
7.05
2.00
f1 (ppm)


197.79
136.93
134.10
133.45
132.45
131.54
129.01
128.90
128.69
128.22
128.08
126.51
125.93
125.67
124.05
77.55
77.23
76.91
43.31
Ph
O
7
13C NMR
f1 (ppm)



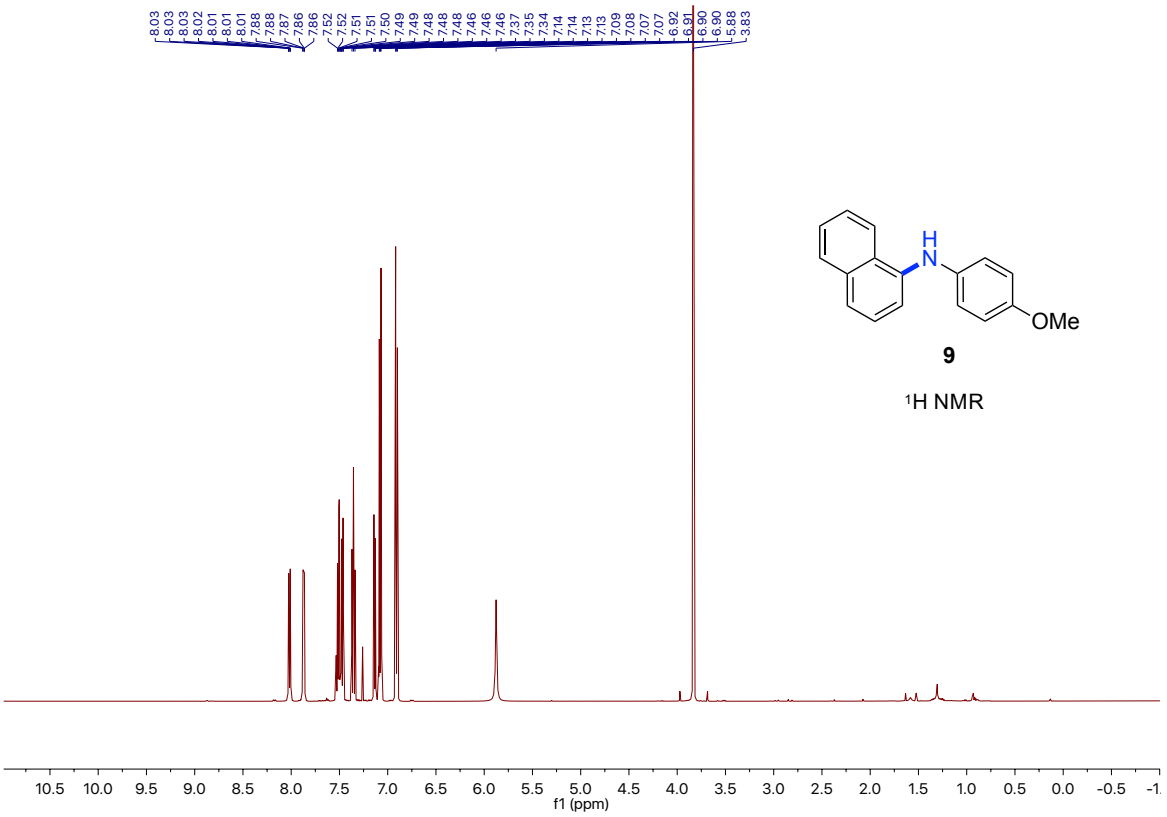
8

^{1}H NMR



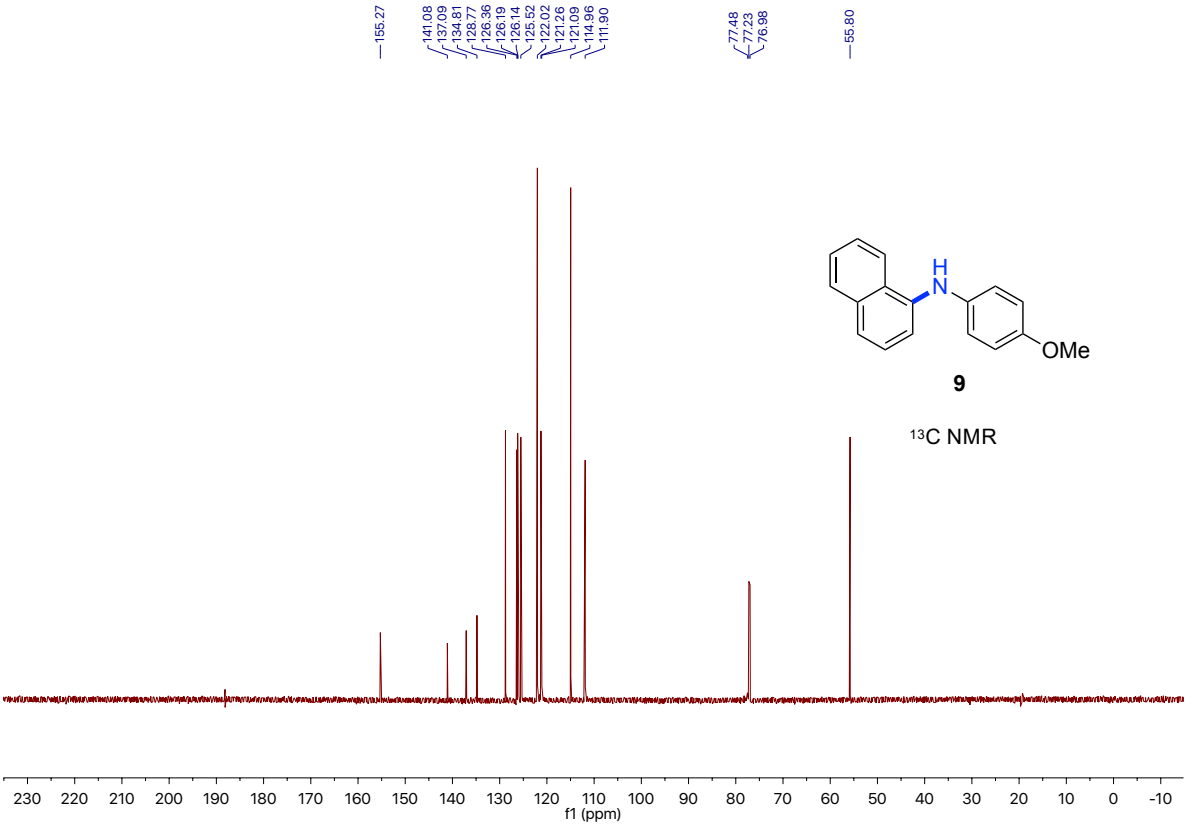
8

^{13}C NMR



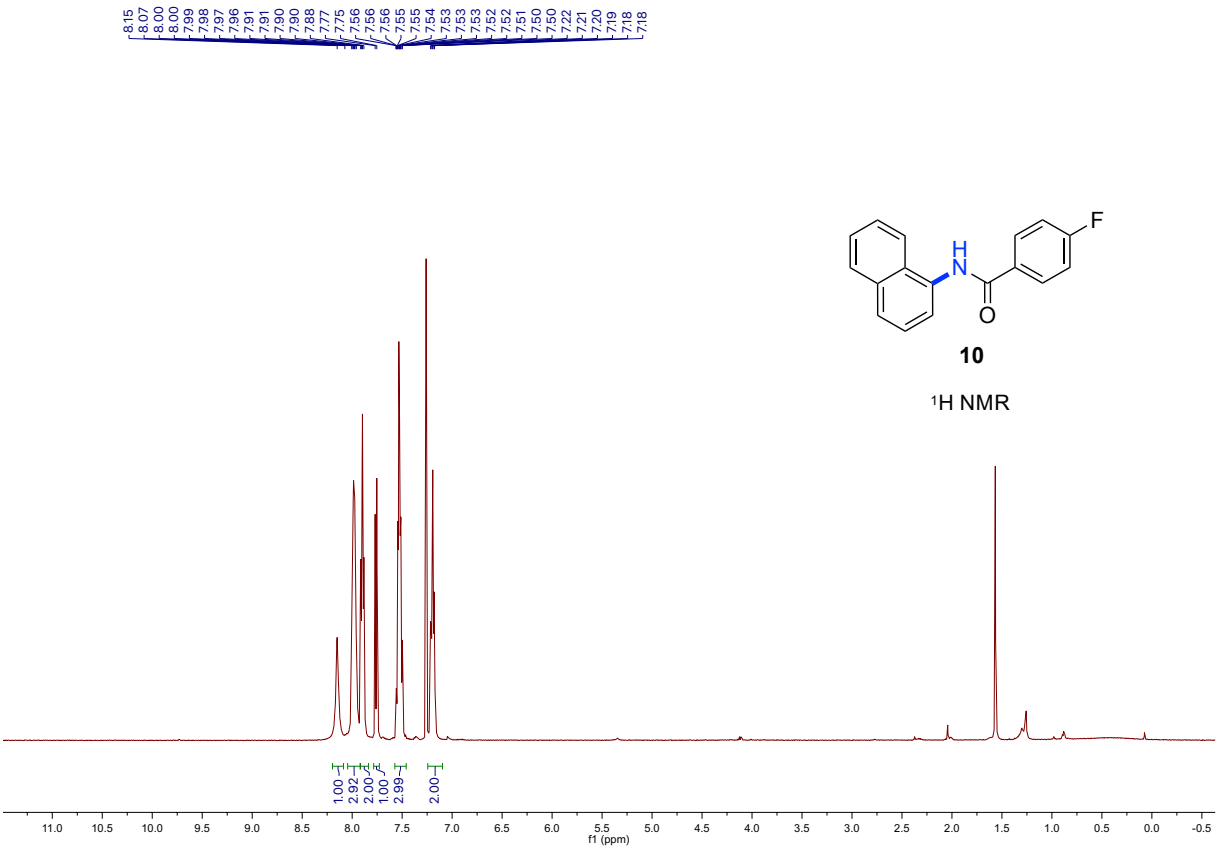
9

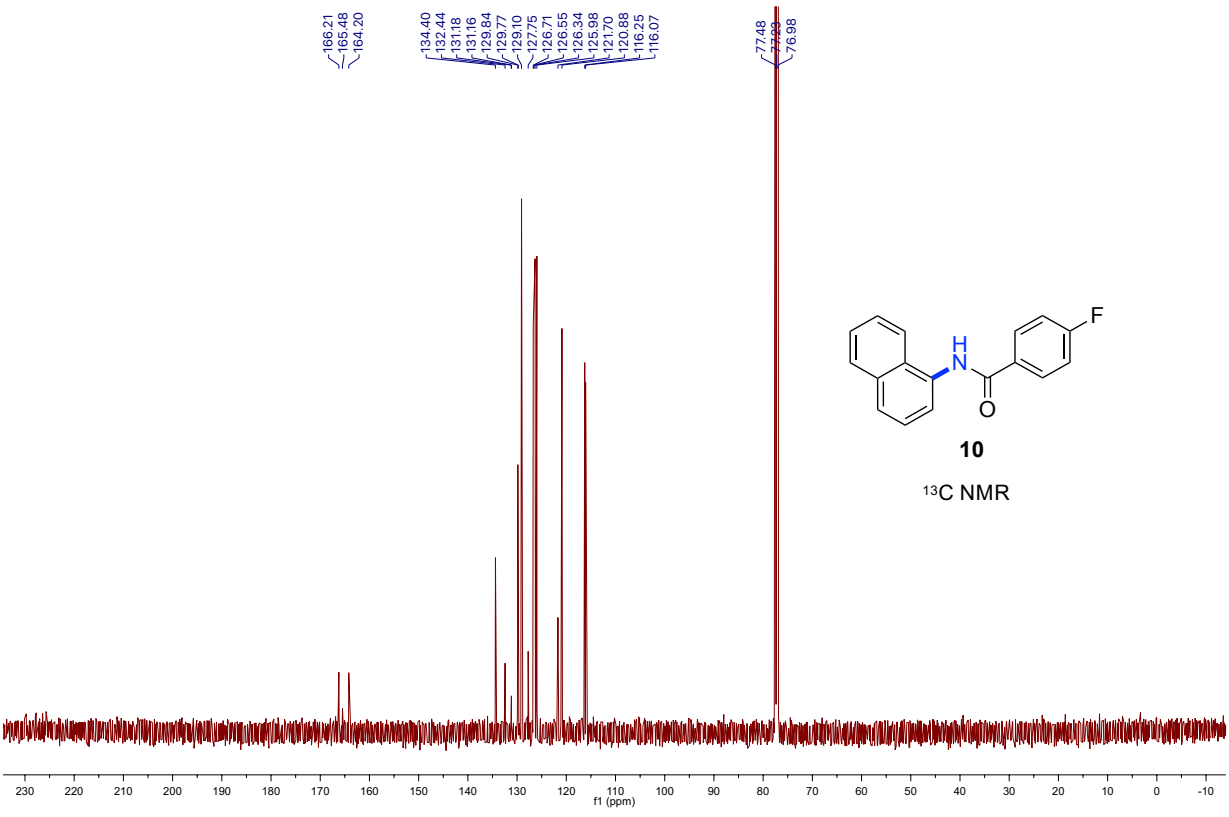
^{1}H NMR

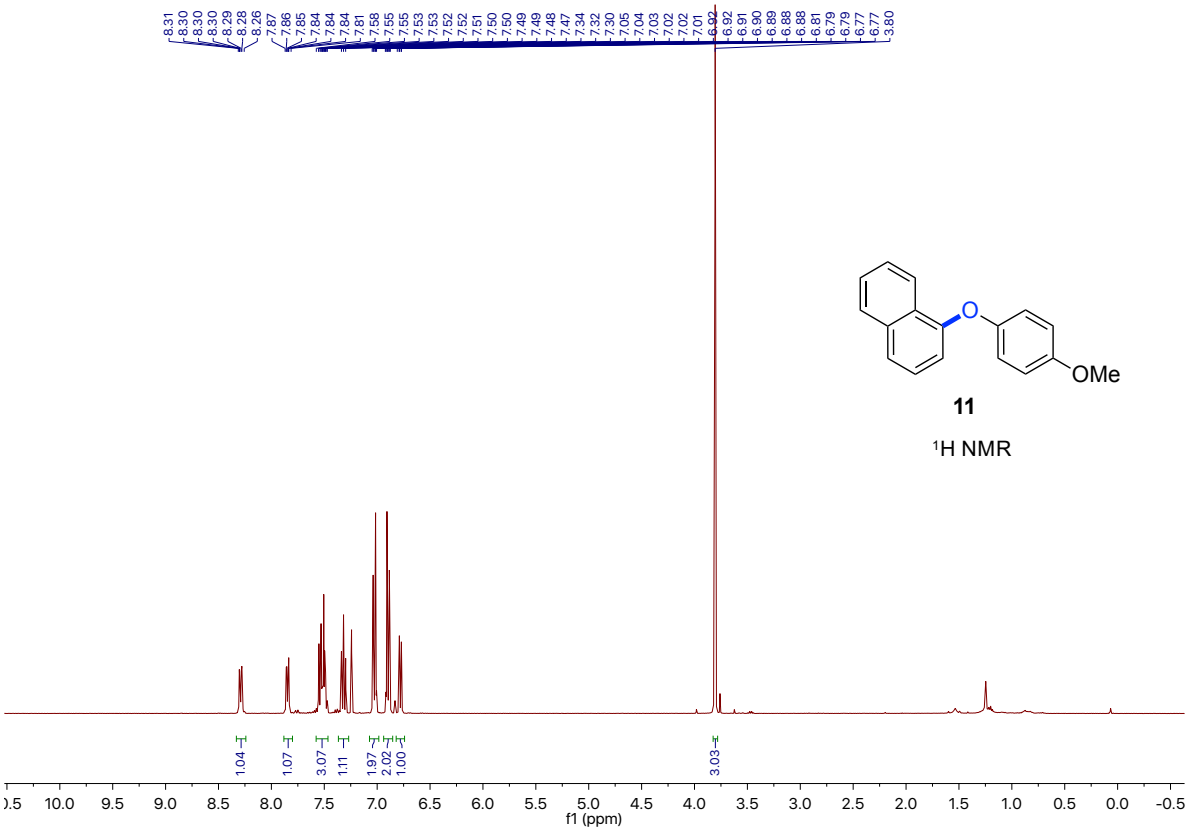


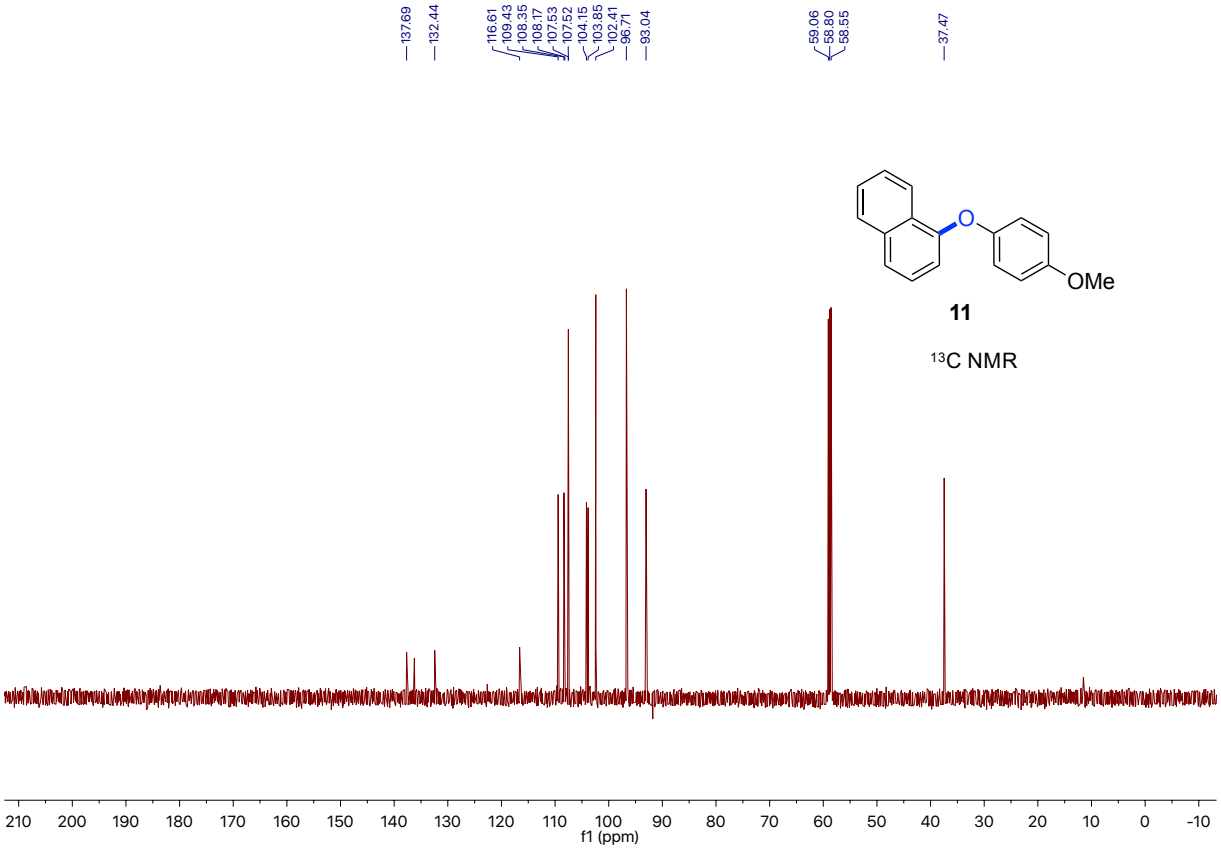
9

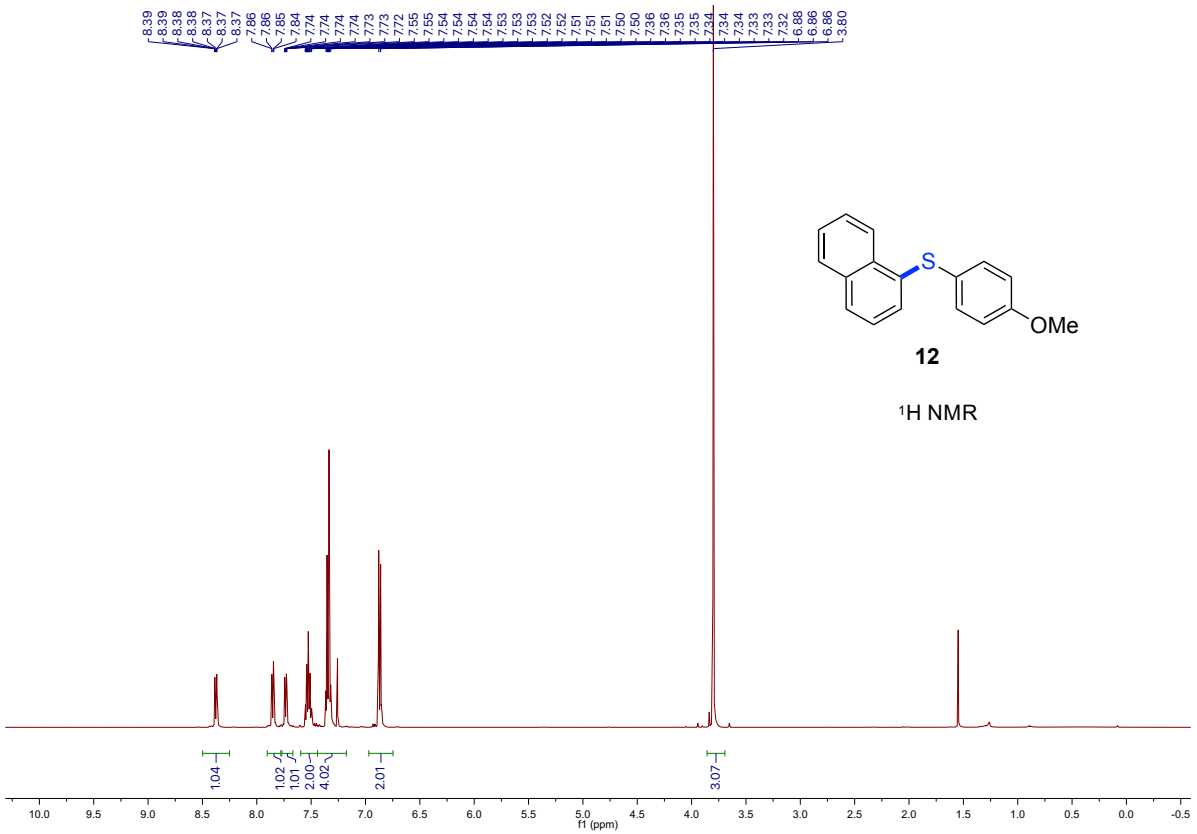
^{13}C NMR

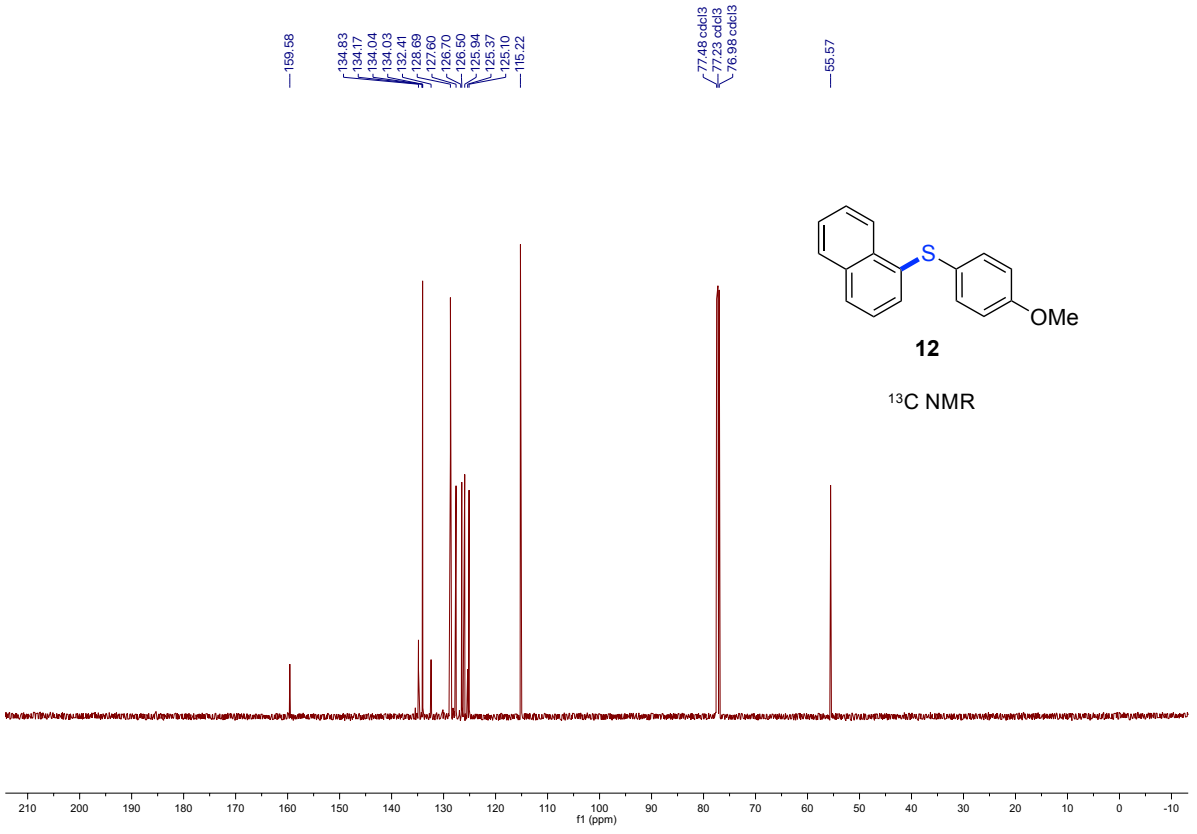

8.15
8.07
8.00
8.00
7.99
7.98
7.97
7.96
7.91
7.91
7.90
7.90
7.88
7.77
7.75
7.56
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.22
7.21
7.20
7.19
7.18
7.18
F
H
N
O
10
1H NMR
1.00
2.92
2.00
1.00
2.99
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

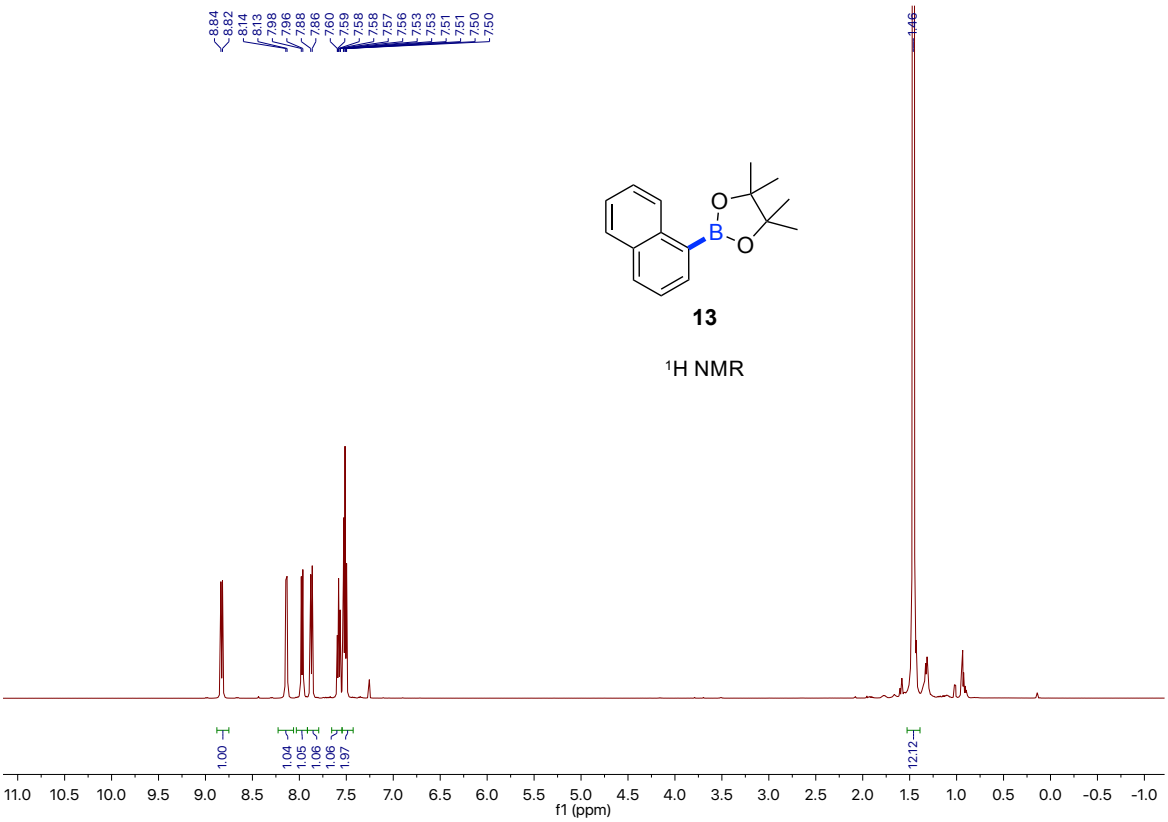

166.21
165.48
164.20
134.40
132.44
131.18
131.16
129.84
129.77
129.10
127.75
126.71
126.55
126.34
125.98
121.70
120.88
116.25
116.07
77.48
77.33
76.98
F
H
N
O
10
13C NMR
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.31 8.30 8.30 8.30 8.29 8.28 8.26 7.87 7.86 7.85 7.84 7.84 7.84 7.81 7.58 7.55 7.55 7.53 7.53 7.52 7.52 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.34 7.32 7.30 7.05 7.04 7.03 7.02 7.02 7.01 6.92 6.92 6.91 6.90 6.89 6.88 6.88 6.81 6.79 6.79 6.77 6.77 3.80
O
OMe
11
1H NMR
1.04 1.07 3.07 1.11 1.97 2.02 1.00 3.03
f1 (ppm)


137.69 132.44 116.61 109.43 108.35 108.17 107.53 107.52 104.15 103.85 102.41 96.71 93.04 59.06 58.80 58.55 37.47
O
OMe
11
13C NMR
f1 (ppm)

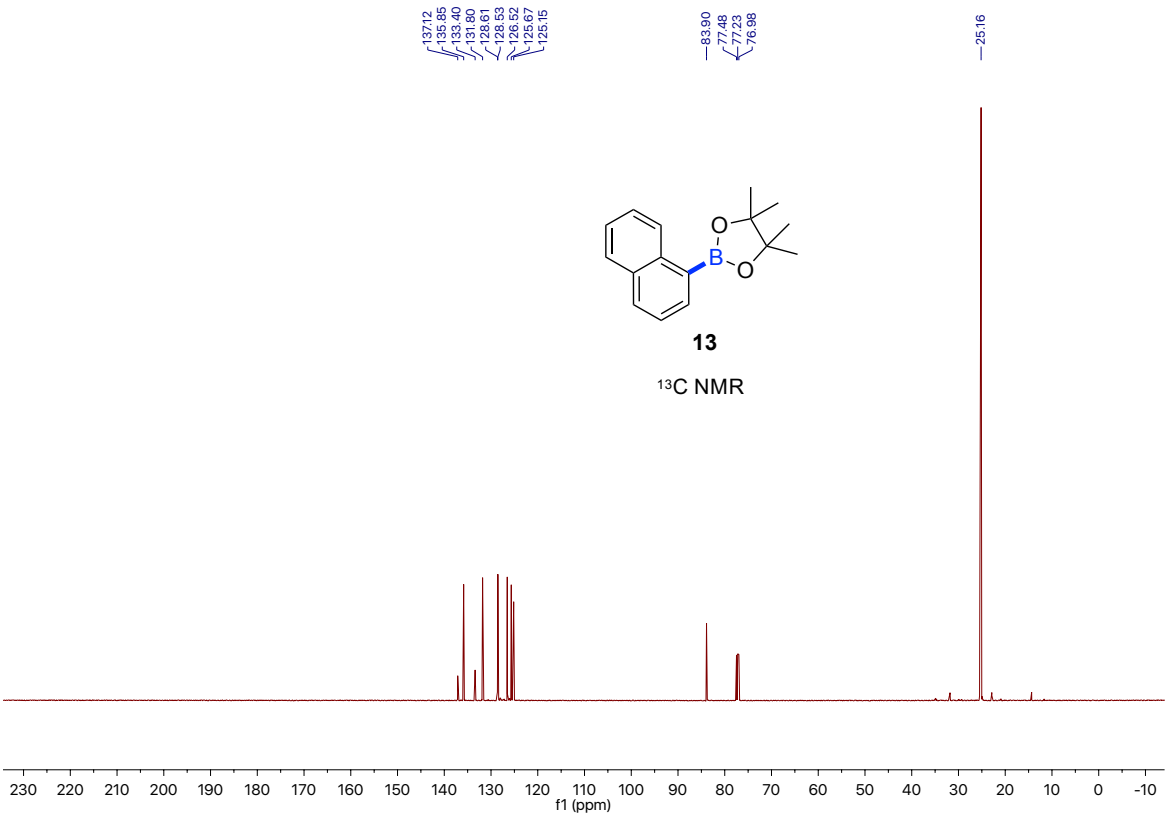

8.39
8.39
8.38
8.38
8.37
8.37
8.37
7.86
7.86
7.85
7.84
7.74
7.74
7.74
7.74
7.73
7.73
7.72
7.55
7.55
7.54
7.54
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.50
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
6.88
6.86
6.86
3.80
S
OMe
12
1H NMR
1.04
1.02
1.01
2.00
4.02
2.01
3.07
f1 (ppm)


159.58
134.83
134.17
134.04
134.03
132.41
128.69
127.60
126.70
126.50
125.94
125.37
125.10
115.22
77.48 cdcl3
77.23 cdcl3
76.98 cdcl3
55.57
S
OMe
12
13C NMR
f1 (ppm)



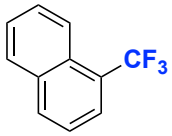
13

^{1}H NMR



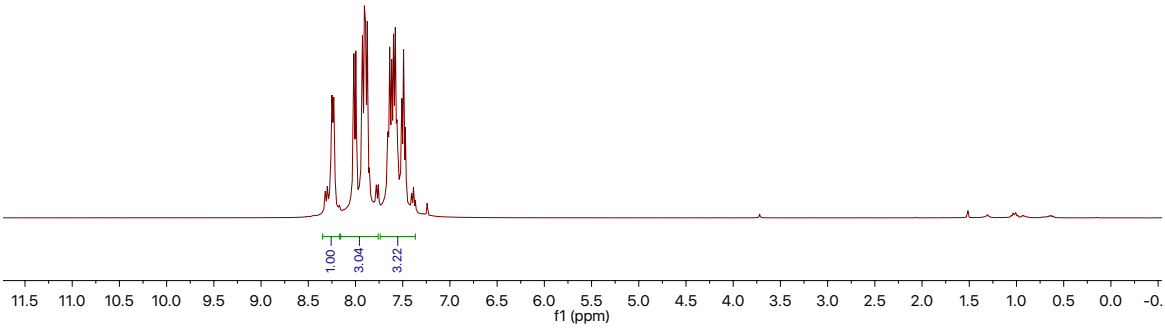
13

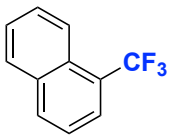
^{13}C NMR



14

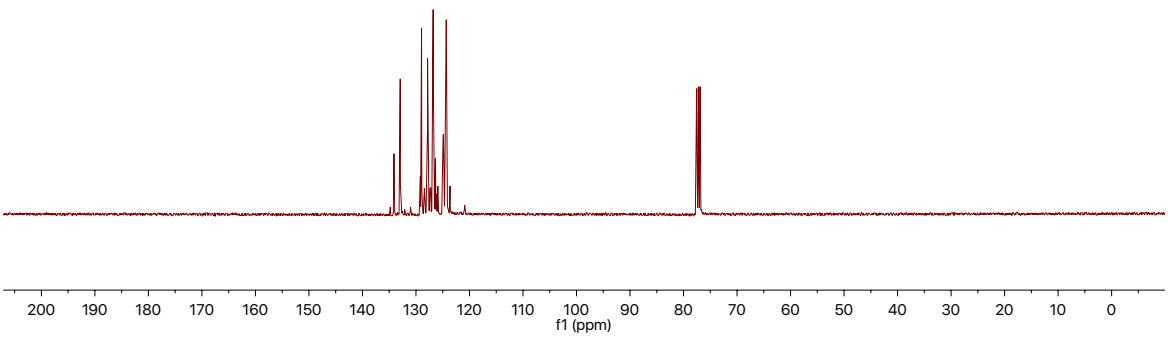
^{1}H NMR

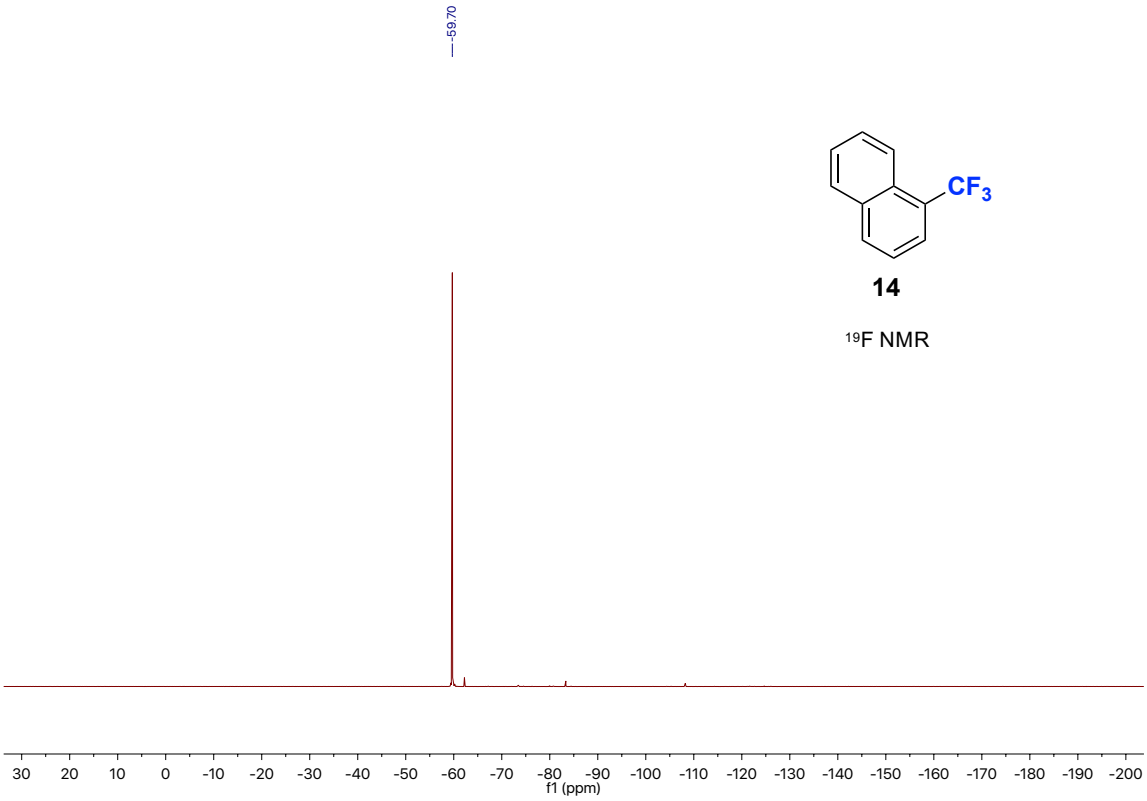


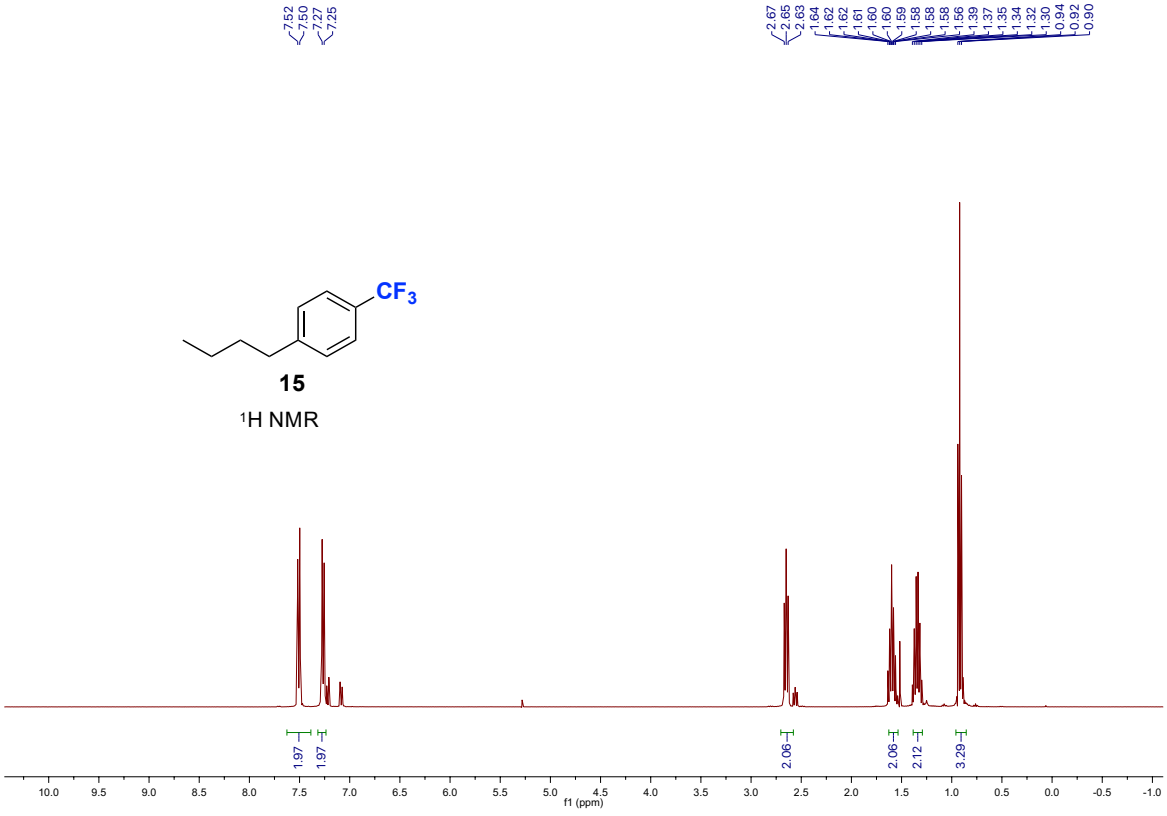


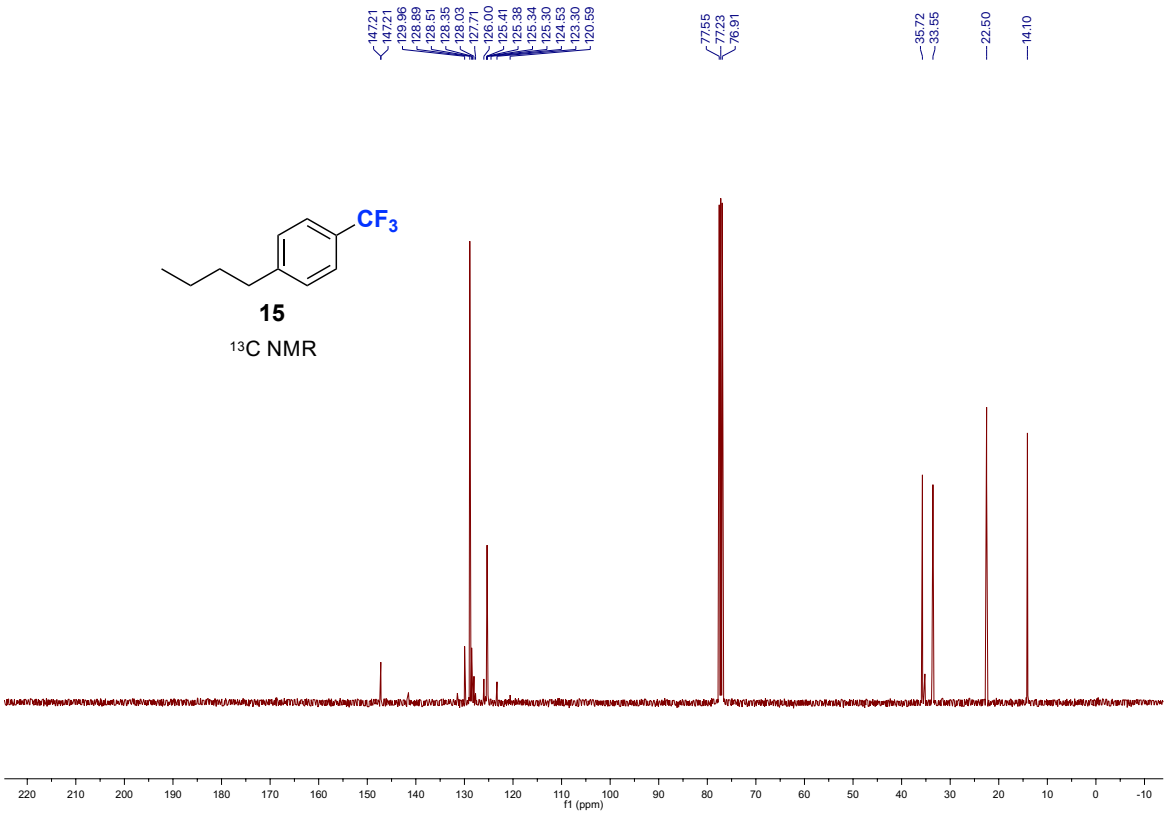
14

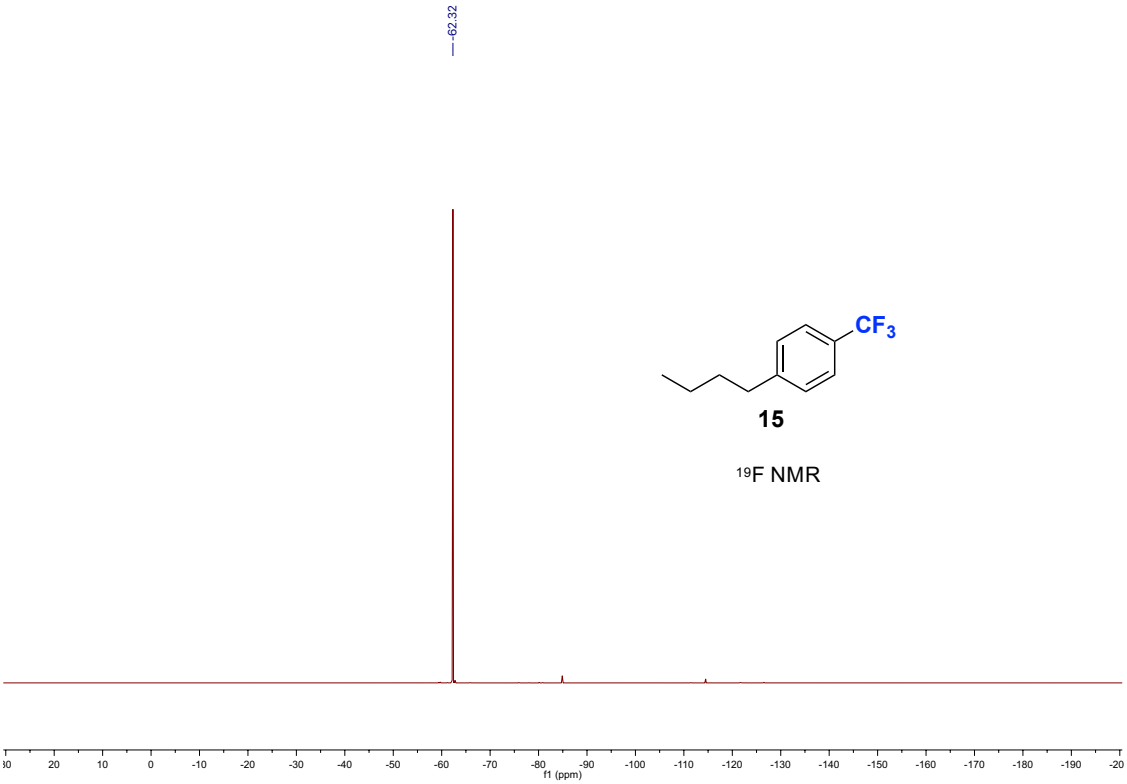
^{13}C NMR

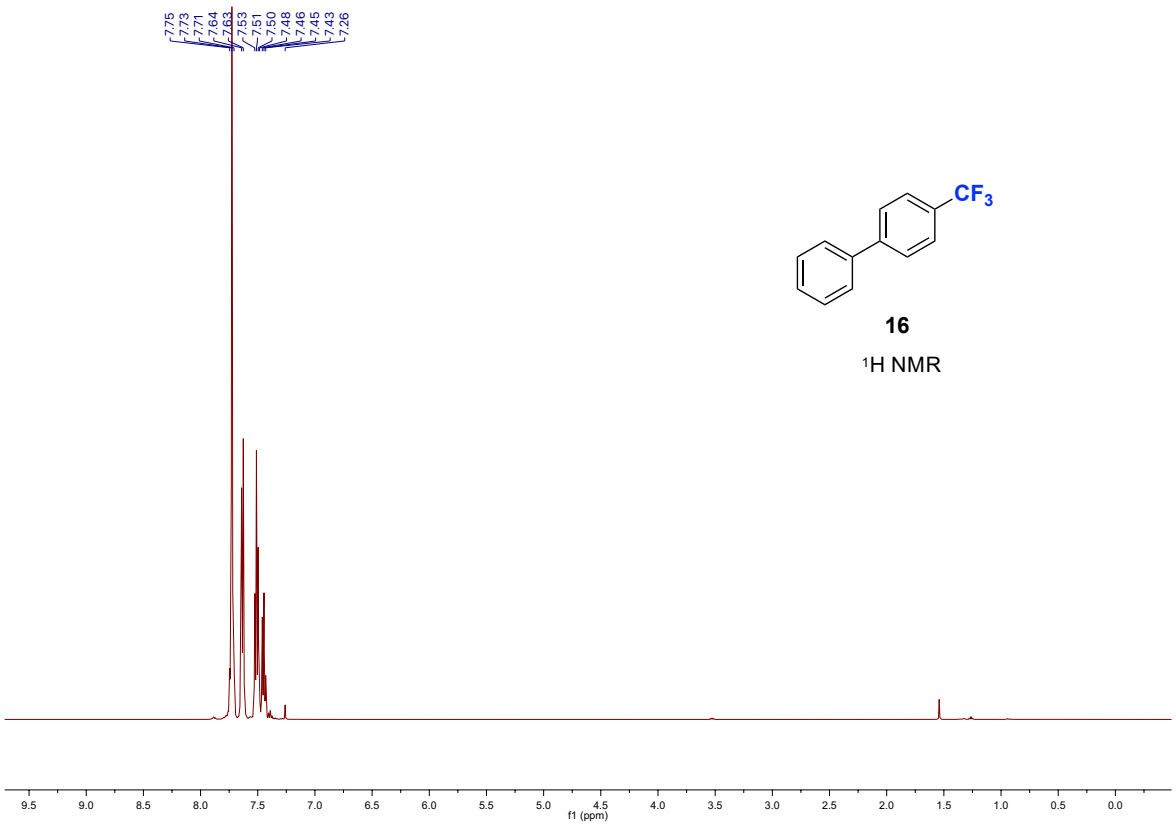



-59.70
CF3
14
19F NMR
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.52
7.50
7.27
7.25
2.67
2.65
2.63
1.64
1.62
1.62
1.61
1.60
1.60
1.59
1.58
1.58
1.58
1.56
1.39
1.37
1.35
1.34
1.32
1.30
0.94
0.92
0.90
CF3
15
1H NMR
1.97
1.97
2.06
2.06
2.12
3.29
f1 (ppm)

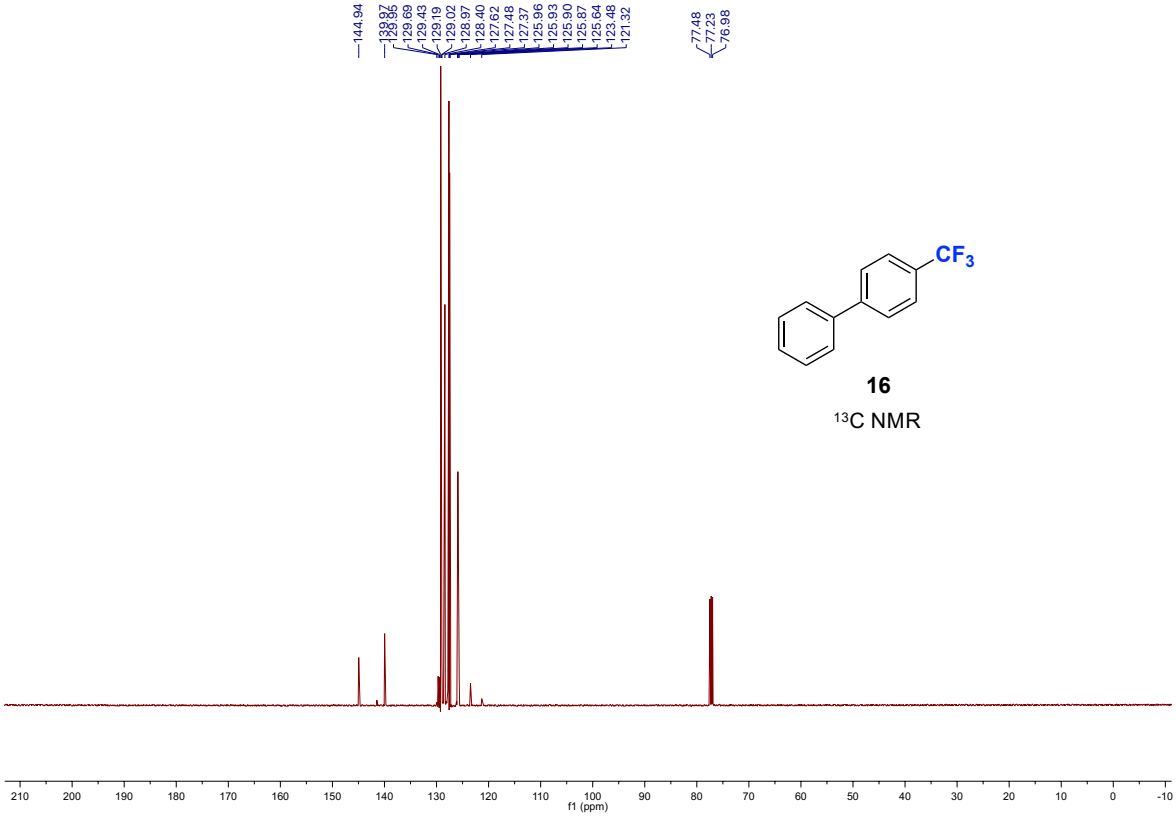

147.21
147.21
129.96
128.89
128.51
128.35
128.03
127.71
126.00
125.41
125.38
125.34
125.30
124.53
123.30
120.59
77.55
77.23
76.91
35.72
33.55
22.50
14.10
CF3
15
13C NMR
f1 (ppm)


-62.32
CF3
15
19F NMR
f1 (ppm)



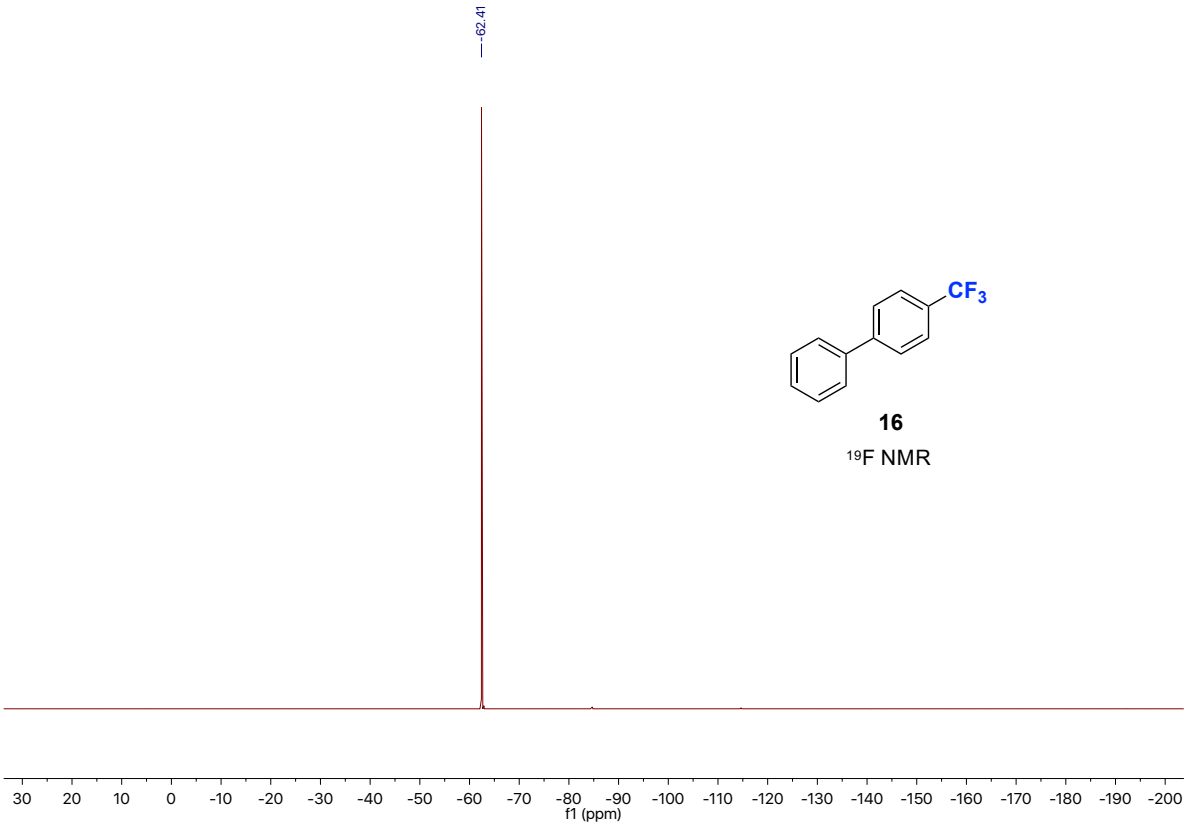
16

^{1}H NMR



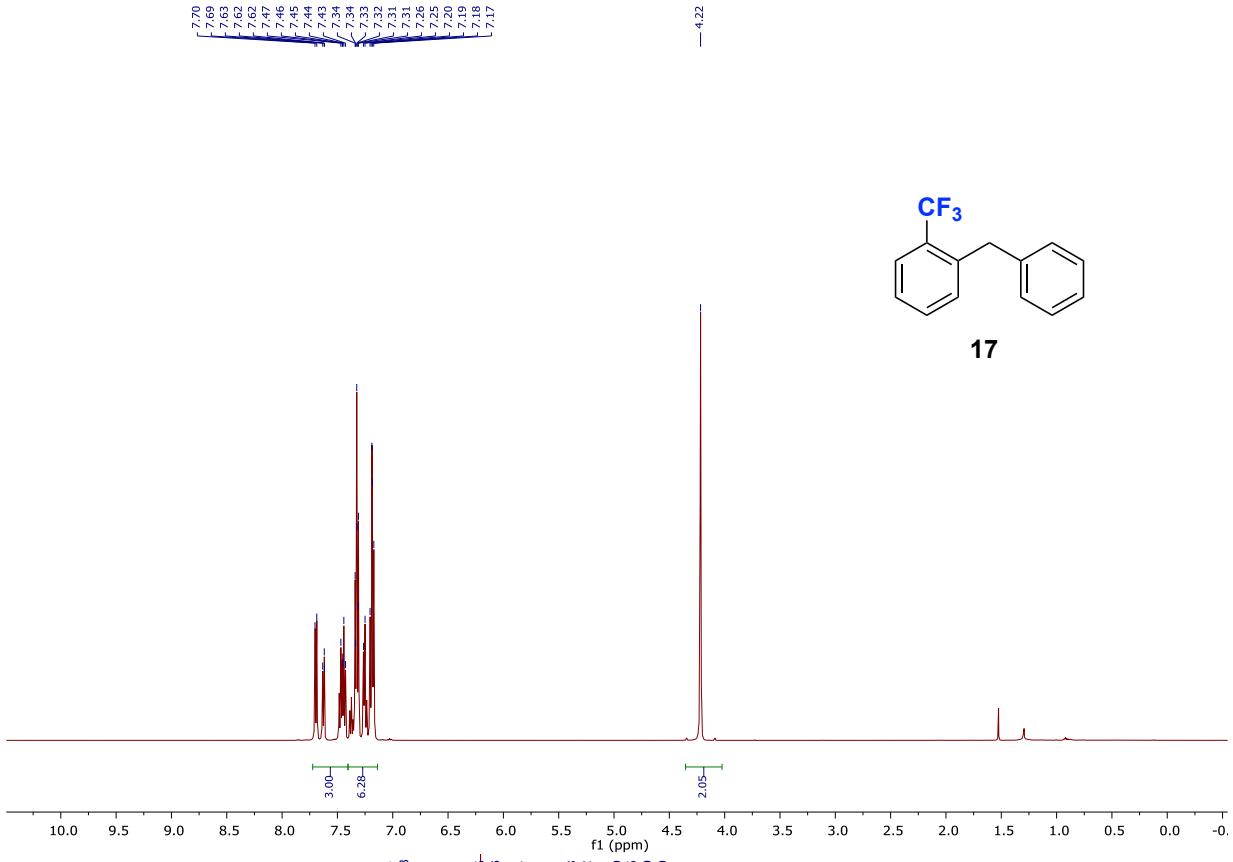
16

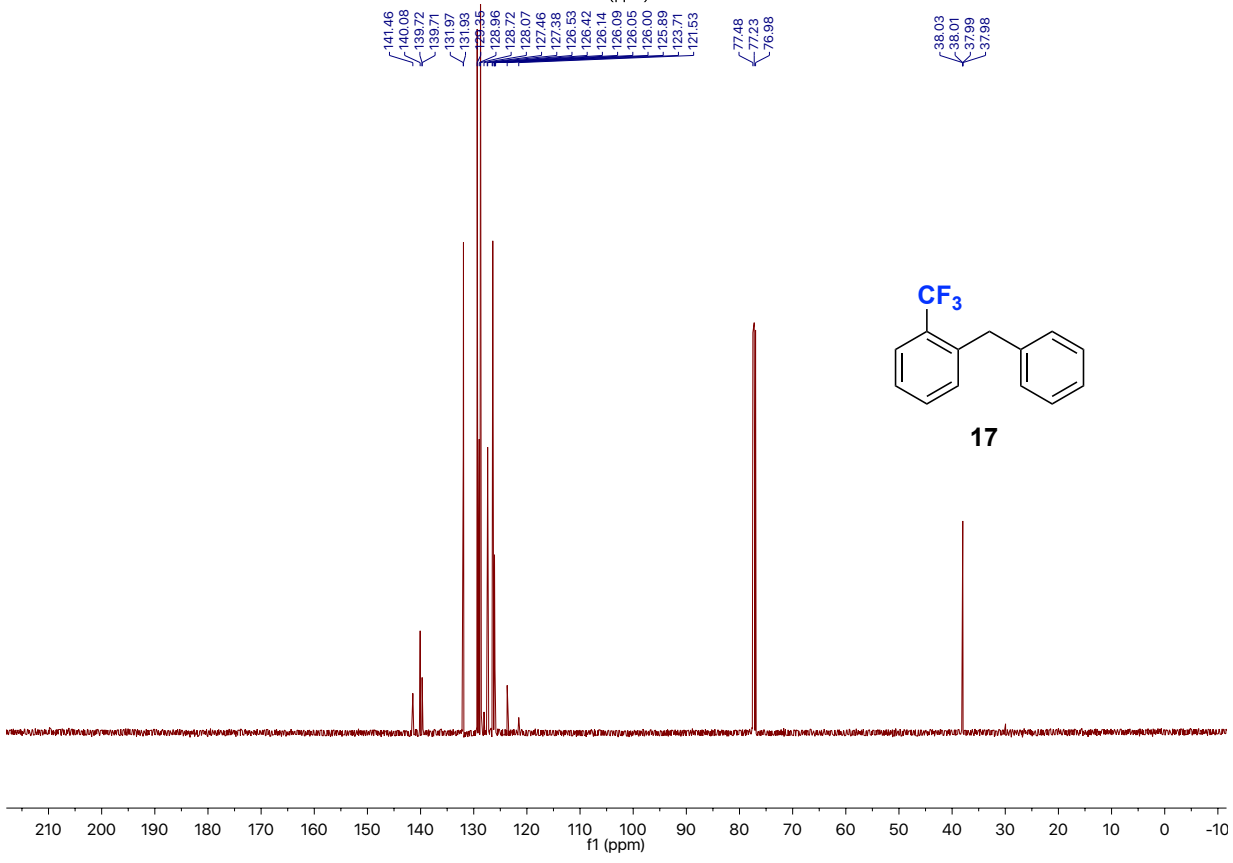
^{13}C NMR

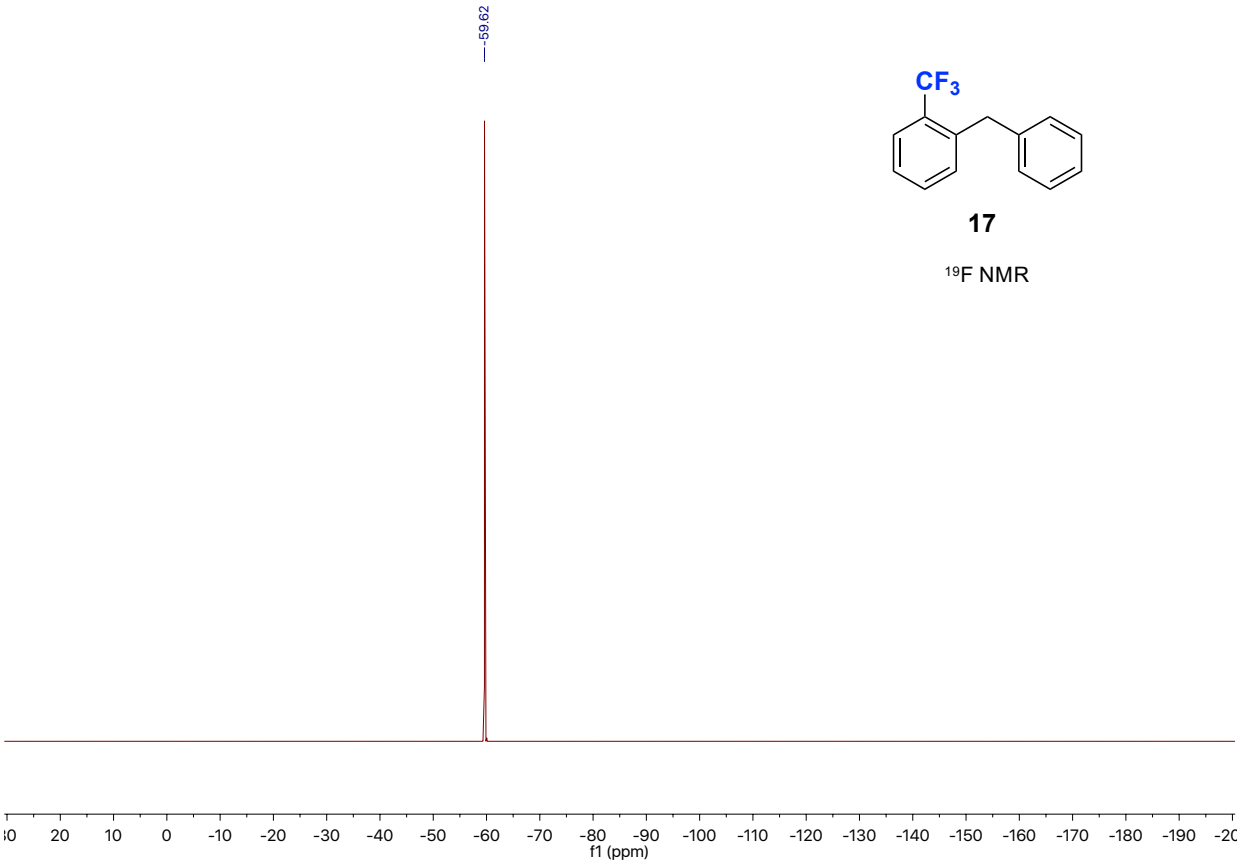

-62.41
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

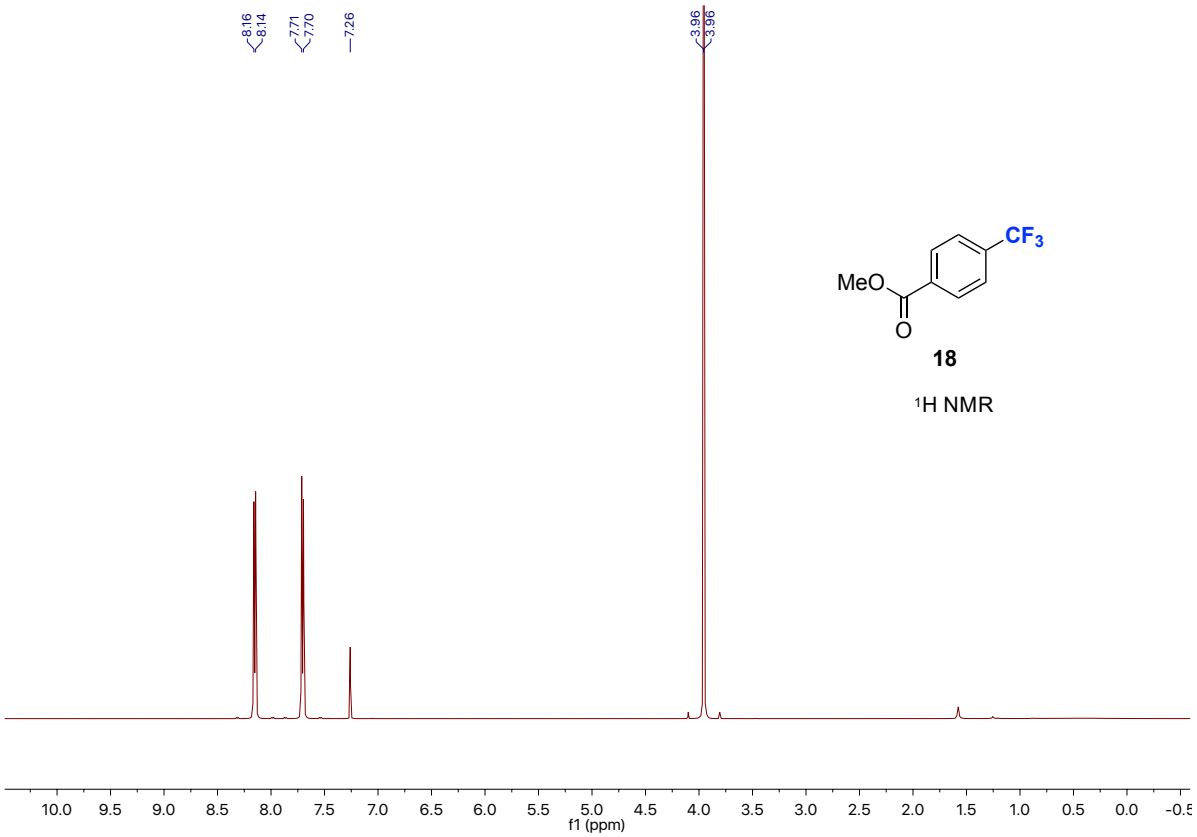
16

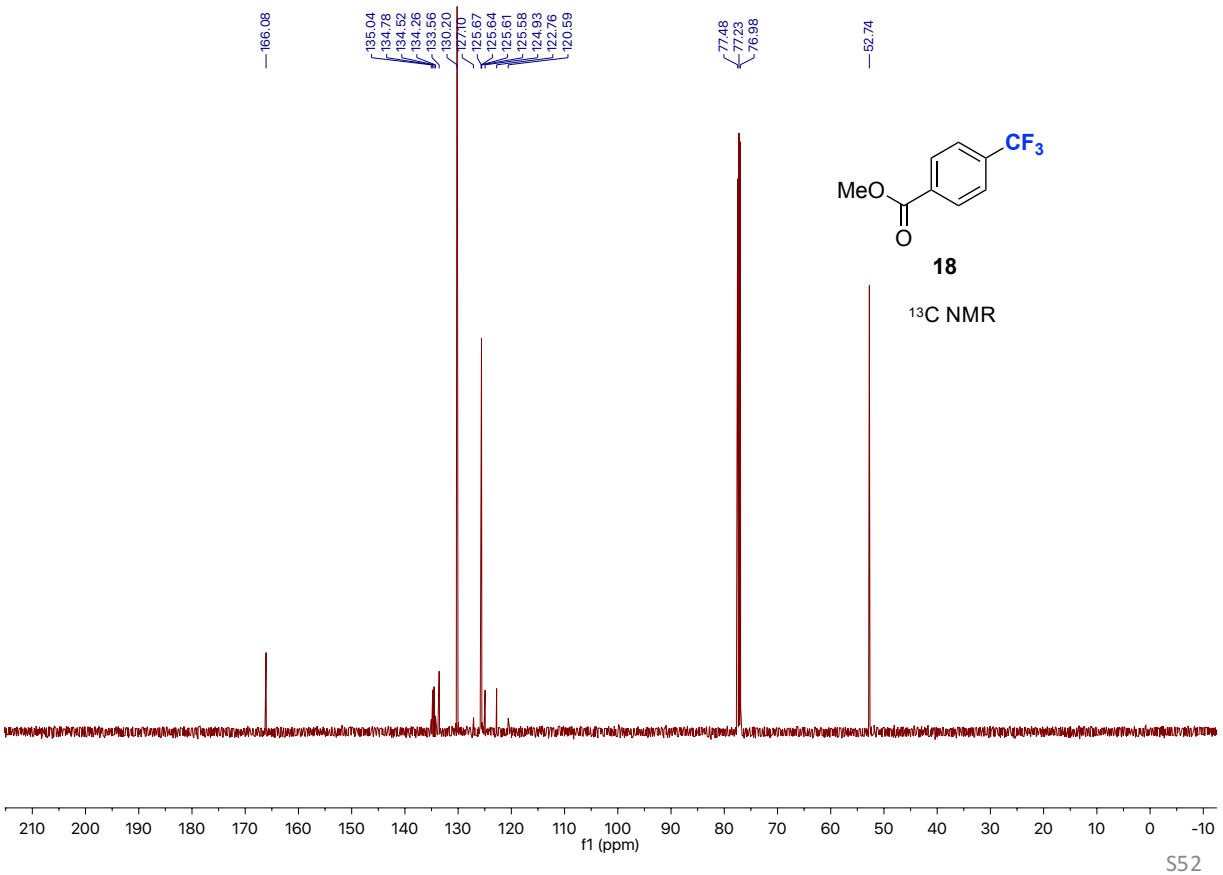
^{19}F NMR

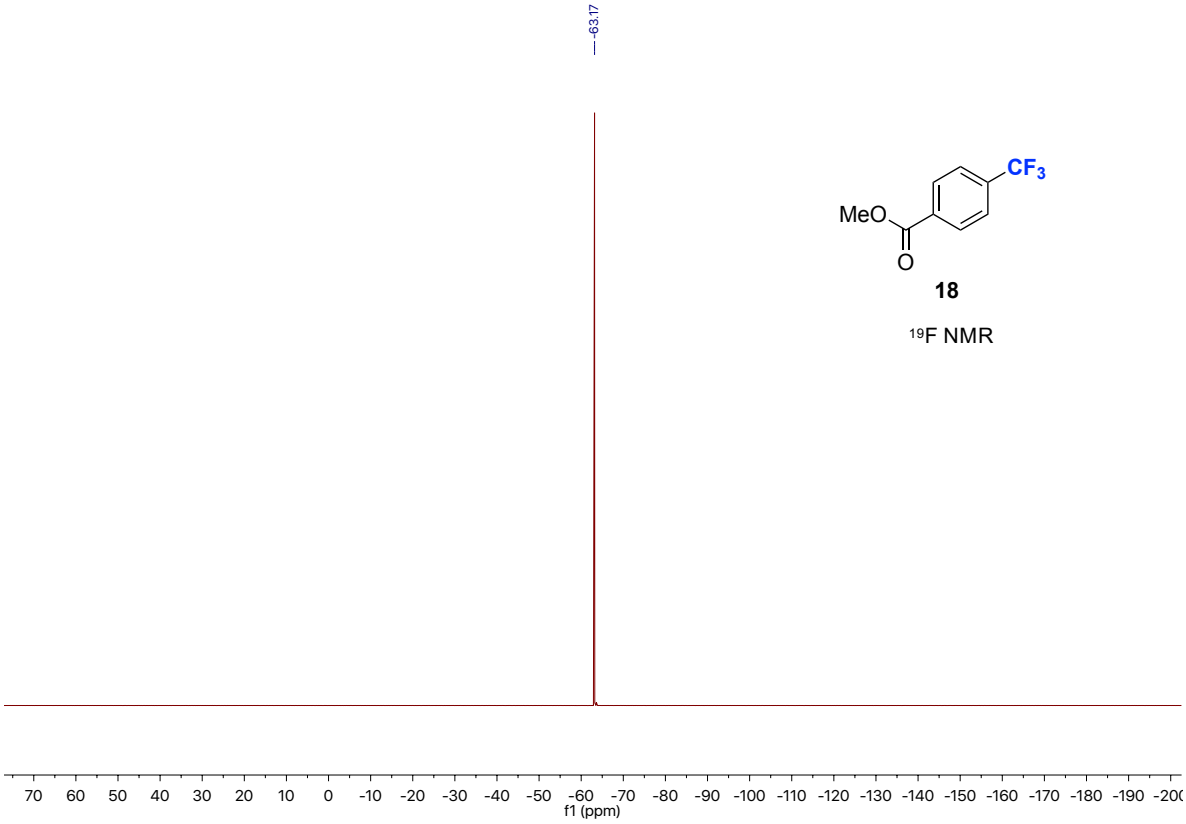

7.70
7.69
7.63
7.62
7.62
7.47
7.46
7.45
7.44
7.43
7.34
7.34
7.33
7.32
7.31
7.31
7.26
7.25
7.20
7.19
7.18
7.17
4.22
CF3
17
3.00
6.28
2.05
f1 (ppm)


141.46
140.08
139.72
139.71
131.97
131.93
129.35
128.96
128.72
128.07
127.46
127.38
126.53
126.42
126.14
126.09
126.05
126.00
125.89
123.71
121.53
77.48
77.23
76.98
38.03
38.01
37.99
37.98
CF3
17
f1 (ppm)


-59.62
CF3
17
19F NMR
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


8.16
8.14
7.71
7.70
7.26
3.96
3.96
CF3
MeO
O
18
1H NMR
f1 (ppm)


166.08
135.04
134.78
134.52
134.26
133.56
130.20
127.10
125.67
125.64
125.61
125.58
124.93
122.76
120.59
77.48
77.23
76.98
52.74
CF3
MeO
O
18
13C NMR
f1 (ppm)


-63.17
CF3
MeO
O
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

18

^{19}F NMR