

Supporting Information

Regioselective Copper-Catalyzed Boracarboxylation of Vinyl Arenes

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General Considerations

All commercially available compounds were used as received, and all were purchased from either Sigma Aldrich, ACROS Organics, Alfa Aesar, or STREM Chemicals. Solvents were purchased from Fisher and those used for reactions were dried with a Glass Contour solvent purification system. Flash chromatography was performed on silica gel 60 (particle size 0.040- 0.063mm, 230-400 mesh ASTM, purchased from Silicycle). The manipulation of air- and moisture-sensitive compounds was conducted and performed under a nitrogen atmosphere utilizing either standard Schlenk or glove box techniques. Procedures for the preparation and characterization of (NHC)CuCl complexes were followed from the literature.¹

¹H, ¹³C, ¹⁹F, and ¹¹B NMR spectra were recorded on Agilent 400 MHz and Varian INOVA 600 MHz NMR spectrometers, and all deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. The chemical shifts (δ) are given in parts per million and referenced relative to internal TMS (0 ppm for ¹H) or residual proteo solvent (7.26 or 2.50 ppm for CHCl₃ and DMSO, respectively), CDCl₃ or d⁶-DMSO (77.3 or 39.5 ppm for ¹³C), internal (capillary) CF₃CO₂H (-76.5 ppm for ¹⁹F), and internal (capillary) BF₃•OEt₂ (32.1 ppm). ¹¹B NMR spectra recorded using quartz NMR tubes. Precise coupling constants for Compounds **2k**, **2l**, **7a**, and **7v** were determined by iterative calculation and fitting to experimental data. High-resolution mass spectra were recorded on a Thermofisher Scientific Q Exactive Mass Spectrometer using MeOH (Fisher Optima grade). Infrared spectra were recorded on a salt plate or on a universal ATR assembly with a Perkin-Elmer Spectrum 100 FTIR spectrometer.

General Procedure for Reaction Screening

The diagram illustrates a catalytic cycle for the asymmetric hydrogenation of α,β -unsaturated esters. The cycle begins with a copper-Bpin complex, $[Cu]-Bpin$. This complex reacts with CO_2 to form $(Bpin)_2O$. Alternatively, it reacts with an α,β -unsaturated ester (Ar-CH=CH-CO_2R) to form a copper-alkoxide intermediate, $[Cu]-CH(Ar)-CH_2-CO_2R$, which then yields a β -alkoxy ester product, $Ar-CH_2-CH_2-CO_2R$. The cycle is closed by regenerating the $[Cu]-Bpin$ catalyst from the $[Cu]-CH(Ar)-CH_2-CO_2R$ intermediate. This regeneration can occur via two pathways: one involving CO_2 and H^+ to release $Ar-CH_2-CH_2-CO_2R$ and $[Cu]-Bpin$, and another involving $MOtBu$ to release $Ar-CH_2-CH_2-CO_2R$ and $[Cu]-OtBu$, which is then converted back to $[Cu]-Bpin$ by B_2pin_2 and $tBuO-Bpin$.

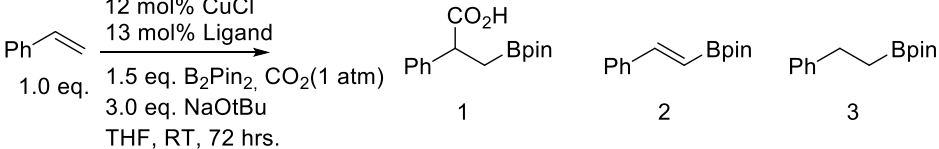
S3

Screening Tables

Table S1. Monophosphine Ligand Screening for Cu-catalyzed Boracaroxylation of Styrene

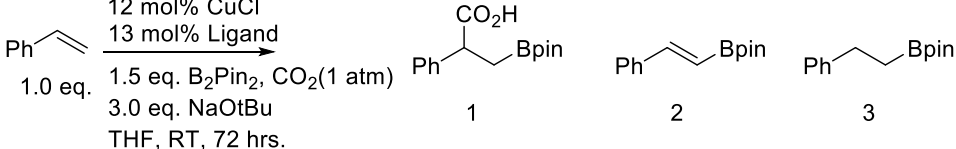
<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;"> Ph-CH=CH_2 1.0 eq. </div> <div style="text-align: center;"> $\xrightarrow[\text{THF, RT, 72 hrs.}]{\begin{array}{l} 12 \text{ mol\% CuCl} \\ 13 \text{ mol\% Ligand} \\ 1.5 \text{ eq. B}_2\text{Pin}_2, \text{ CO}_2(1 \text{ atm}) \\ 3.0 \text{ eq. NaOtBu} \end{array}}$ </div> <div style="text-align: center;"> $\text{Ph-CH(CO}_2\text{H)-CH}_2\text{-Bpin}$ 1 </div> <div style="text-align: center;"> Ph-CH=CH-Bpin 2 </div> <div style="text-align: center;"> $\text{Ph-CH}_2\text{-CH}_2\text{-Bpin}$ 3 </div> </div>					
Entry	Ligand	Yield of 1 (%)	Yield of 2 (%)	Yield of 3 (%)	Conv. (%)
1	PPh ₃	1 %	22 %	13 %	99 %
2	P(2-furyl) ₃	0 %	3 %	5 %	95 %
3	P(p-MeOPh) ₃	8 %	24 %	31 %	99 %
4	P(2,4,6-trimethoxyphenyl) ₃	9 %	0 %	5 %	78 %
5	PMePh ₂	21 %	11 %	17 %	98 %
6	P ^t Bu ₂ Me	45 %	14 %	10 %	100 %
7	PEt ₃	58 %	14 %	11 %	100 %
8	P ^t Bu ₃	72 %	6 %	9 %	100 %
9	PCy ₃	79 %	5 %	14 %	99 %
10	Cy-JohnPhos	0 %	0 %	6 %	96 %
11	Xphos	0 %	2 %	2 %	90 %
12	BrettPhos	5 %	0 %	1 %	89 %

Table S2. Bisphosphine Ligand Screening for Cu-catalyzed Boracarboxylation of Styrene



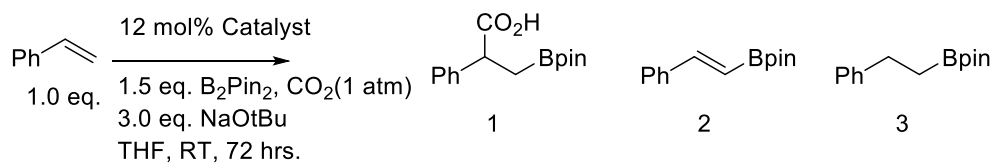
Entry	Ligand	Yield of 1 (%)	Yield of 2 (%)	Yield of 3 (%)	Conv. (%)
13	DMPM	2 %	26 %	23 %	99 %
14	DMPE	5 %	29 %	13 %	100 %
15	dppbz	3 %	31 %	8 %	99 %
16	BINAP	3 %	45 %	8 %	99 %
17	DPPF	7 %	36 %	12 %	99 %
18	Xantphos	20 %	8 %	17 %	98 %
19	Et2N-Xantphos	0 %	2 %	3 %	97 %
20	DPE Phos (R = Cy)	27 %	3 %	15 %	99 %
21	DTBM-SEGPHOS	0 %	6 %	2 %	94 %
22	Me-BPE	11 %	41 %	12 %	100 %

Table S3. Nitrogen Ligand Screening for Cu-catalyzed Boracarboxylation of Styrene



Entry	Ligand	Yield of 1 (%)	Yield of 2 (%)	Yield of 3 (%)	Conv. (%)
23	Pyridine	0 %	2 %	1 %	99 %
24	DMAP	0 %	2 %	0 %	82 %
25	Bipy	0 %	4 %	3 %	100 %
26	MeOBipy	0 %	n.d.	n.d.	100 %

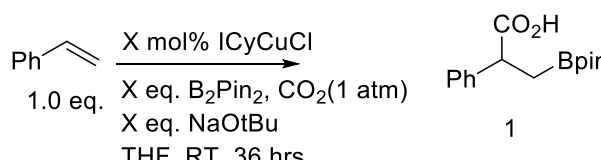
Table S4. (*N*-Heterocyclic carbene)CuCl Complex Screening for Cu-catalyzed Boracarboxylation of Styrene



Entry	Ligand	Yield of 1 (%)	Yield of 2 (%)	Yield of 3 (%)	Conv. (%)
27	CuCl (No Ligand)	0 %	< 1 %	< 1 %	92 %
28	IPrCuCl	17 %	< 1 %	< 1 %	99 %
29	SIPrCuCl	0 %	2 %	< 1 %	99 %
30	IMesCuCl	85 %	8 %	< 1 %	100 %
31	SIMesCuCl	< 70 % ^a	< 1 %	4 %	100 %
32	ICyCuCl	92 %	< 1 %	3 %	100 %

^aThe existence of paramagnetic impurities made accurate yield determination difficult in this case

Table S5. Optimization of Reagent, Base, and Catalyst Loading for Cu-catalyzed Boracarboxylation of Styrene



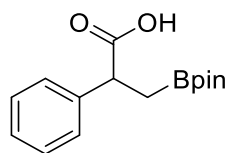
Entry	B ₂ Pin ₂ (eq.)	NaOtBu (eq.)	ICyCuCl (mol%)	Yield (%)
1	1.5	3.0	12	90 %
2	1.1	3.0	12	91 %
3	1.0	3.0	12	82 %
4	1.1	2.0	12	91 %
5	1.1	1.5	12	81 %
6	1.1	2.0	6	61 %
7	1.1	2.0	2.5	46 %

Catalytic Boracarboxylation

General Procedure for the Boracarboxylation of Vinylarenes

Working inside a nitrogen-filled glove box, a septum-capped 4-dram vial was charged with ICyCuCl (10.0 mg, 0.030 mmol, 12 mol %), sodium tert-butoxide (48.0 mg, 0.75 mmol, 2.0 eq.), and a magnetic stir bar. Anhydrous, degassed THF (0.90 mL) was added, the vial was sealed with an air-tight septum, and the resulting suspension was stirred under nitrogen for two hours at room temperature to give a clear, colorless solution. In a separate 25 mL round-bottomed flask, bis(pinacolato)diboron (70.0 mg, 0.375 mmol, 1.1 eq.) and 3.1 mL THF were added. To this solution, vinylarene (0.25 mmol, 1.0 eq.) was added. The round-bottomed flask was charged with a magnetic stir bar, sealed with a septum, and taken out of the glove box. The pre-prepared catalyst solution, under nitrogen, was transferred to this reaction vessel by gas-tight syringe. Immediately after catalyst addition, the reaction vessel was fitted with a double-walled CO₂ balloon and the reaction was stirred at ambient temperature for 36 hours. With less reactive substrates, the reaction temperature was raised to 40–50 °C. Upon reaction completion, the reaction was quenched with 20 mL of 1.0M aqueous HCl and extracted with DCM (3 x 12 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo to give the crude product. The crude product was then taken up in 8 mL of diethyl ether and extracted with saturated NaHCO₃ (3 x 6 mL). The combined aqueous layers were carefully acidified with 12 M HCl (to pH ≤ 1.0 by litmus paper) and subsequently extracted with DCM (5 x 10 mL). The combined organic layers were dried over sodium sulfate and dried in vacuo to afford the pure boracarboxylated product. In many products a small amount of bis(pinacolato)diboron (typically < 10 %) persists. The mole percentage of bis(pinacolato)diboron was determined by ¹H NMR and is reported for each compound below. Corrected yields were calculated by subtracting out the mass of this impurity from the isolated mass.

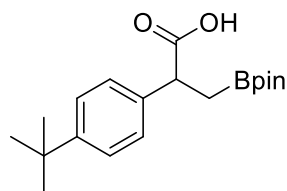
Boracarboxylation Product Characterization



2a: White, microcrystalline solid. (61.5 mg isolated). 9.2 % B₂pin₂.

Corrected Yield: 82 %

¹H NMR (400 MHz, CDCl₃): δ 11.06 (br s, 1H), 7.26 – 7.17 (m, 5H), 3.81 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.51 (dd, *J* = 16.4, 9.6 Hz, 1H), 1.24 (dd, *J* = 16.4, 7.6 Hz, 1H), 1.10 (s, 6H), 1.08 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 180.83, 140.27, 128.47, 127.80, 127.13, 83.36, 46.80, 24.60, 24.47, 15.81; ¹¹B NMR (128 MHz, CDCl₃): δ 33.17 (br s); IR (neat) 2978, 1701, 1370, 1323, 1142, 966, 884, 846, 758, 697, 673 cm⁻¹; HRMS (ESI) *m/z* 275.14603 [C₁₅H₂₀BO₄⁻ (M-H)⁻ requires 275.14601]. The ¹³C NMR resonance at 15.81 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



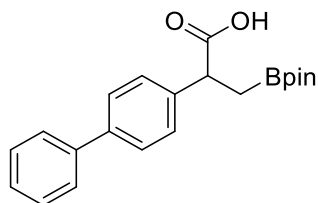
2b: Pale yellow solid. (75.8 mg isolated). 7.7 % B₂pin₂.

Corrected Yield: 85.8 %

2.5 mmol scale (10-fold scale-up): (761.0 mg isolated). 13.2 % B₂pin₂.

Corrected Yield: 82.1 %

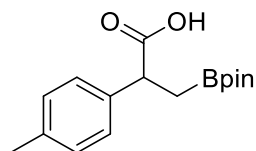
¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.83 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.54 (dd, *J* = 15.8, 9.6 Hz, 1H), 1.29 (s, 9H), 1.28 (dd, *J* = 15.8, 7.2 Hz, 1H), 1.14 (s, 6H), 1.11 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 180.65, 149.93, 137.29, 127.46, 125.37, 83.30, 46.35, 34.40, 31.31, 24.66, 24.47, 15.87; ¹¹B NMR (128 MHz, CDCl₃): δ 33.10 (br s); IR (neat) 2964, 1704, 1514, 1365, 1321, 1267, 1142, 1108, 968, 889, 847, 831, 671 cm⁻¹; HRMS (ESI) *m/z* 331.20856 [C₁₉H₂₈BO₄⁻ (M-H)⁻ requires 331.20861]. The ¹³C NMR resonance at 15.87 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2c: White Crystalline Solid. (73.1 mg isolated). 6.6 % B₂pin₂.

Corrected Yield: 79.0 %

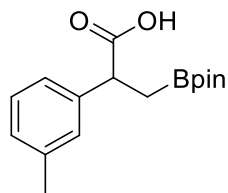
¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.52 (m, 4H), 7.46 – 7.39 (m, 4H), 7.34 (t, *J* = 7.4, 1H), 3.94 (dd, *J* = 9.4, 7.4 Hz, 1H), 1.62 (dd, *J* = 15.8, 9.4 Hz, 1H), 1.35 (dd, *J* = 15.8, 7.4 Hz, 1H), 1.17 (s, 6H), 1.16 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 180.53, 140.78, 140.06, 139.42, 128.67, 128.25, 127.20, 127.16, 126.99, 83.40, 46.51, 24.62, 24.51, 15.86; ¹¹B NMR (128 MHz, CDCl₃): δ 33.57 (br s); IR (neat) 2979, 1705, 1488, 1372, 1324, 1143, 968, 848, 759, 733, 698 cm⁻¹; HRMS (ESI) *m/z* 351.17744 [C₂₁H₂₄BO₄⁻ (M-H)⁻ requires 351.17731]. The ¹³C NMR resonance at 15.86 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2d: White Solid. (58.1 mg isolated). 1.0 % B₂pin₂.

Corrected yield: 79.4 %

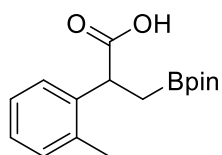
¹H NMR (400 MHz, CDCl₃): δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.83 (dd, *J* = 9.4 Hz, 7.1 Hz, 1H), 2.31 (s, 3H), 1.54 (dd, *J* = 16.0, 9.4 Hz, 1H), 1.25 (dd, *J* = 16.0, 7.1 Hz, 1H), 1.16 (s, 6H), 1.14 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 180.80, 137.42, 136.66, 129.12, 127.62, 83.31, 46.41, 24.61, 24.48, 20.99, 15.91; ¹¹B NMR (128 MHz, CDCl₃): δ 33.50 (br s); IR (neat) 2978, 1704, 1514, 1371, 1323, 1264, 1144, 1106, 968, 889, 897, 819, 676 cm⁻¹; HRMS (ESI) *m/z* 289.16160 [C₁₆H₂₂BO₄⁻ (M-H)⁻ requires 289.16166]. The ¹³C NMR resonance at 15.91 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2e: White Solid. (61.6 mg isolated). 3.5 % B₂pin₂.

Corrected Yield: 82.3 %

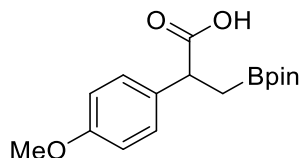
¹H NMR (600 MHz, CDCl₃): δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 3.83 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.32 (s, 3H), 1.54 (dd, *J* = 16.0, 9.3 Hz, 1H), 1.27 (dd, *J* = 7.3, 16.0 Hz, 1H), 1.15 (s, 6H), 1.14 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 180.77, 140.29, 138.01, 128.54, 128.36, 127.86, 124.81, 83.33, 46.76, 24.62, 24.50, 21.35, 15.92; ¹¹B NMR (192 MHz, CDCl₃): δ 32.88 (br s); IR (neat) 2978, 2930, 1730, 1607, 1369, 1320, 1265, 1215, 1142, 967, 847, 781 cm⁻¹; HRMS (ESI) *m/z* 289.16174 [C₁₆H₂₂BO₄⁻ (M-H)⁻ requires 289.16166]. The ¹³C NMR resonance at 15.92 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2f: White Microcrystalline Solid. (43.1 mg isolated). 2.0 % B₂pin₂.

Corrected Yield: 58.4 %

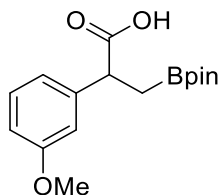
¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.10 (m, 3H), 4.10 (dd, *J* = 8.8, 7.8 Hz, 1H), 2.40 (s, 3H), 1.50 (dd, *J* = 15.9, 8.8 Hz, 1H), 1.29 (dd, *J* = 15.9, 7.8 Hz, 1H), 1.10 (s, 12H); ¹³C NMR (101 MHz, CDCl₃): δ 180.73, 138.91, 136.15, 130.30, 126.95, 126.92, 126.26, 83.27, 42.46, 24.59, 24.46, 19.79, 15.42; ¹¹B NMR (128 MHz, CDCl₃): δ 33.10 (br s); IR (neat) 2978, 1703, 1370, 1322, 1215, 1143, 968, 888, 847, 753, 729 cm⁻¹; HRMS (ESI) *m/z* 289.16180 [C₁₆H₂₂BO₄⁻ (M-H)⁻ requires 289.16166]. The ¹³C NMR resonance at 15.42 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2g: White Solid. (73.0 mg isolated). 8.8 % B₂pin₂.

Corrected Yield: 88.3 %.

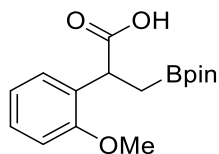
¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.80 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.77 (s, 3H), 1.51 (dd, *J* = 15.8 Hz, 9.2 Hz, 1H), 1.26 (dd, *J* = 15.8, 7.6 Hz, 1H), 1.14 (s, 6H), 1.13 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 180.74, 158.65, 132.51, 128.84, 113.84, 83.31, 55.20, 45.95, 24.61, 24.53, 15.97.; ¹¹B NMR (128 MHz, CDCl₃): δ 33.20 (br s); IR (neat) 2977, 1703, 1611, 1511, 1370, 1322, 1247, 1141, 1104, 1034, 968, 887, 847, 830, 734, 674 cm⁻¹; HRMS (ESI) *m/z* 305.15668 [C₁₆H₂₂BO₅⁻ (M-H)⁻ requires 305.15658]. The ¹³C NMR resonance at 15.97 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2h: Clear Oil. (72.0 mg isolated). 7.3 % B₂pin₂.

Corrected Yield: 88.3 %

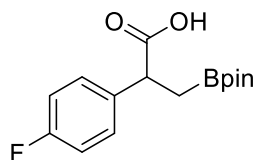
¹H NMR (600 MHz, CDCl₃): δ 7.19 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.85 (s, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 3.83 (dd, 9.4, 7.2 Hz, 1H), 3.76 (s, 3H), 1.53 (dd, *J* = 15.8, 9.4 Hz, 1H), 1.26 (dd, *J* = 15.8, 7.2 Hz, 1H), 1.15 (s, 6H), 1.13 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): 180.32, 159.53, 141.87, 129.38, 120.11, 113.33, 112.70, 83.33, 55.05, 46.82, 24.57, 24.45, 15.77; ¹¹B NMR (192 MHz, CDCl₃): δ 33.07 (br s); IR (neat) 2978, 1707, 1600, 1490, 1372, 1322, 1262, 1144, 1048, 968, 848, 698, 620 cm⁻¹; HRMS (ESI) *m/z* 305.15671 [C₁₆H₂₂BO₅⁻ (M-H)⁻ requires 305.15658]. The ¹³C NMR resonance at 15.77 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2i: White Solid. (54.9 mg isolated). 6.5 % B₂pin₂.

Corrected Yield: 67.8 %

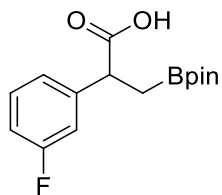
¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 7.5 Hz, 1H), 7.21 (td, *J* = 7.8, 1.6 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.17 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.80 (s, 3H), 1.56 (dd, *J* = 15.9, 9.8 Hz, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 1.16 (dd, *J* = 15.9, 6.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): 180.32, 156.69, 129.59, 128.72, 128.13, 120.68, 110.80, 83.19, 55.41, 41.38, 24.72, 24.55, 14.63. ; ¹¹B NMR (128 MHz, CDCl₃): δ 33.50 (br s); IR (neat) 2979, 1702, 1601, 1494, 1464, 1370, 1320, 1141, 1029, 967, 878, 846, 808, 752 cm⁻¹; HRMS (ESI) *m/z* 305.15668 [C₁₆H₂₂BO₅⁻ (M-H)⁻ requires 305.15658]. The ¹³C NMR resonance at 14.63 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2j: White Solid (46.5 mg isolated). < 1 % B₂pin₂.

Corrected Yield: 63.2 %

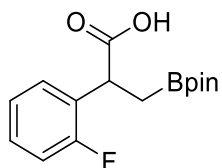
¹H NMR (400 MHz, CDCl₃): δ 7.28 (dd, ³*J*_{H-H} = 8.8 Hz, ⁴*J*_{H-F} = 5.2 Hz, 2H), 6.98 (t, ³*J*_{H-H} = ³*J*_{H-F} = 8.8 Hz, 2H), 3.85 (dd, *J* = 8.9, 8.0 Hz, 1H), 1.53 (dd, *J* = 16.0, 8.9 Hz, 1H), 1.28 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.14 (s, 6H), 1.13 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 180.31, 163.19, 160.75, 136.06, 136.03, 129.49, 129.41, 115.37, 115.16, 83.42, 46.12, 24.60, 24.55, 16.05.; ¹¹B NMR (128 MHz, CDCl₃): δ 33.06 (br s) ¹⁹F NMR (376 MHz, CDCl₃): δ -115.72 (tt, ³*J*_{H-F} = 8.8 Hz, ⁴*J*_{H-F} = 5.2 Hz); IR (neat) 2980, 1707, 1509, 1372, 1360, 1226, 1144, 968, 847, 809 cm⁻¹; HRMS (ESI) *m/z* 293.13660 [C₁₅H₁₉BFO₄⁻ (M-H)⁻ requires 293.13659]. The ¹³C NMR resonance at 16.05 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2k: Clear Oil. (17.9 mg isolated). 11.0 % B₂pin₂.

Corrected Yield: 22.0 %

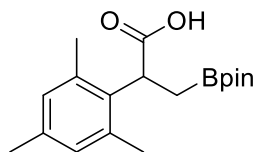
¹H NMR (600 MHz, CDCl₃): δ 7.25 (app. td, ³J_{HH} = 8.3, ³J_{HH} = 7.8, ⁴J_{HF} = 6.9 Hz, 1H), 7.09 (ddd, ³J_{HH} = 7.8, ⁴J_{HH} = 1.6, ⁴J_{HH} = 1.0, 1H), 7.03 (ddd, ³J_{HF} = 9.9 Hz, ⁴J_{HH} = 2.6 Hz, ⁴J_{HH} = 1.6 Hz, 1H), 6.93 (tdd, ³J_{HF} = ³J_{HH} = 8.3, ⁴J_{HH} = 2.6, ⁴J_{HH} = 1.0 Hz, 1H), 3.86 (dd, J = 9.1, 7.4 Hz, 1H), 1.53 (dd, J = 16.0, 9.1 Hz, 1H), 1.28 (dd, J = 16.0, 7.4 Hz, 1H), 1.15 (s, 6H), 1.14 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): 179.68, 162.77 (d, ¹J_{CF} = 246.0 Hz), 142.70 (d, ³J_{CF} = 7.5 Hz), 129.92 (d, ³J_{CF} = 8.2 Hz), 123.58 (d, ⁴J_{CF} = 2.9 Hz), 114.95 (d, ²J_{CF} = 21.9 Hz), 114.10 (d, ²J_{CF} = 21.1 Hz), 83.51, 46.52, 24.62, 24.54, 15.83; ¹¹B NMR (192 MHz, CDCl₃): δ 33.31 (br s); ¹⁹F NMR (565 MHz, CDCl₃): δ -113.03 (ddd, ³J_{H-F} = 9.9, 8.2, ⁴J_{H-F} = 6.9 Hz, 1F); IR (neat) 2981, 1710, 1615, 1591, 1489, 1449, 1325, 1373, 1325, 1216, 1143, 968, 848, 781, 692 cm⁻¹; HRMS (ESI) m/z 293.13660 [C₁₅H₁₉BFO₄⁻ (M-H)⁻ requires 293.13659]. The ¹³C NMR resonance at 15.83 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2l: Clear Oil. (14.0 mg isolated). 13.1 % B₂pin₂.

Corrected Yield: 16.8 %

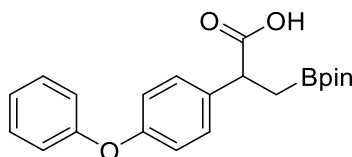
¹H NMR (600 MHz, CDCl₃): δ 7.29 (app. td, ³J_{HH} = 7.6 Hz, ⁴J_{HF} = 7.5 Hz, ⁴J_{HH} = 1.8 Hz, 1H), 7.21 (dddd, ³J_{HH} = 8.2 Hz, ³J_{HH} = 7.4 Hz, ⁴J_{HF} = 5.3 Hz, ⁴J_{HH} = 1.8 Hz, 1H), 7.08 (app. td, ³J_{HH} = 7.6 Hz, ³J_{HH} = 7.4 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 7.02 (ddd, ³J_{HF} = 10.2 Hz, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.4 Hz, 1H), 4.18 (dd, J = 9.4, 7.1 Hz, 1H), 1.57 (dd, J = 16.0, 9.4 Hz, 1H), 1.25 (dd, J = 16.0, 7.1 Hz, 1H), 1.161 (s, 6H), 1.158 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): 179.32, 160.40 (d, ¹J_{CF} = 246.8 Hz), 129.78 (d, ³J_{CF} = 3.7 Hz), 128.69 (d, ³J_{CF} = 8.1 Hz), 127.84 (d, ²J_{CF} = 15.0 Hz), 124.15 (d, ⁴J_{CF} = 3.5 Hz), 115.43 (d, ²J_{CF} = 22.4 Hz), 83.43, 40.01, 24.64, 24.55, 15.02; ¹¹B NMR (192 MHz, CDCl₃): δ 33.46 (br s); ¹⁹F NMR (565 MHz, CDCl₃): δ -117.32 (ddd, ³J_{H-F} = 10.2 Hz, ⁴J_{H-F} = 7.5, 5.3 Hz, 1F); IR (neat) 2982, 2921, 1709, 1587, 1492, 1457, 1373, 1326, 1232, 1143, 967, 847, 757 cm⁻¹; HRMS (ESI) m/z 293.13666 [C₁₅H₁₉BFO₄⁻ (M-H)⁻ requires 293.13659]. The ¹³C NMR resonance at 15.02 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2m: Clear Oil. (13.7 mg isolated). 23.8 % B₂pin₂.

Corrected Yield: 13.8 %

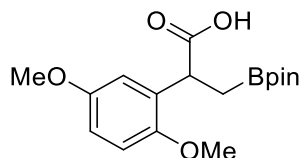
¹H NMR (600 MHz, CDCl₃): δ 6.82 (s, 2H), 4.30 (dd, *J* = 10.6, 5.5 Hz, 1H), 2.28 (br s, 6H), 2.23 (s, 3H), 1.57 (dd, *J* = 16.0, 10.6 Hz, 1H), 1.19 (s, 6H), 1.15 (s, 6H), 0.97 (dd, *J* = 16.0, 5.5 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃): 180.64, 136.12, 136.09, 135.32, 129.52, 83.22, 41.61, 24.80, 24.53, 20.76, 20.57, 13.48. ; ¹¹B NMR (192 MHz, CDCl₃): δ 33.91 (br s); IR (neat) 2978, 2927, 1700, 1461, 1369, 1321, 1144, 1108, 968, 887, 850 cm⁻¹; HRMS (ESI) *m/z* 317.19305 [C₁₈H₂₆BO₄⁻ (M-H)⁻ requires 317.19296]. The ¹³C NMR resonance at 13.48 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2n: Clear Oil. (82.6 mg isolated). 6.0 % B₂pin₂.

Corrected Yield: 86.0 %

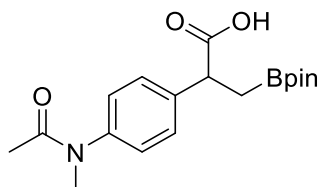
¹H NMR (600 MHz, CDCl₃): δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.86 (dd, *J* = 9.1, 7.7 Hz, 1H), 1.55 (dd, *J* = 15.9, 9.1 Hz, 1H), 1.31 (dd, *J* = 15.9, 7.7 Hz, 1H), 1.16 (s, 6H), 1.15 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): 180.66, 157.15, 156.30, 135.11, 129.65, 129.19, 123.17, 118.80, 118.78, 83.40, 46.11, 24.62, 24.53, 15.86.; ¹¹B NMR (192 MHz, CDCl₃): δ 33.32 (br s); IR (neat) 2978, 1705, 1590, 1506, 1490, 1371, 1323, 1237, 1167, 1143, 968, 875, 847, 755, 692 cm⁻¹; HRMS (ESI) *m/z* 367.17200 [C₂₁H₂₄BO₅⁻ (M-H)⁻ requires 367.17223]. The ¹³C NMR resonance at 15.86 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2o: Clear Oil. (50.1 mg isolated). 13.3 % B₂pin₂.

Corrected Yield: 53.4 %

¹H NMR (600 MHz, CDCl₃): δ 6.80 (d, *J* = 3.0 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 6.72 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.12 (dd, *J* = 9.8, 6.7 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 1.54 (dd, *J* = 15.8, 9.8 Hz, 1H), 1.18 (s, 6H), 1.16 (s, 6H), 1.14 (dd, *J* = 15.8, 6.7 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃): 179.99, 153.53, 150.91, 130.66, 114.76, 112.57, 112.00, 83.22, 56.11, 55.59, 41.52, 24.74, 24.54, 14.73.; ¹¹B NMR (192 MHz, CDCl₃): δ 33.92 (br s); IR (neat) 2979, 1705, 1501, 1466, 1371, 1322, 1225, 1144, 1048, 968, 848, 809 cm⁻¹; HRMS (ESI) *m/z* 335.16721 [C₁₇H₂₄BO₆⁻ (M-H)⁻ requires 335.16714]. The ¹³C NMR resonance at 14.73 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.

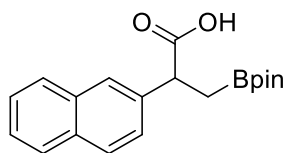


2p: White Solid. (44.0 mg isolated). 22.6 % B₂pin₂.

Corrected Yield: 41.8 %

A small amount of this product was crystallized by layering pentane onto a solution of **2o** in diethyl ether. After this operation, the B₂pin₂ impurity decreased to 4.5%.

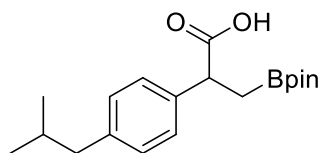
¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 3.87 (t, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 1.83 (s, 3H), 1.52 (dd, *J* = 15.4, 8.4 Hz, 1H), 1.30 (dd, *J* = 15.4, 8.4 Hz, 1H), 1.12 (s, 12H); ¹³C NMR (101 MHz, CDCl₃): δ 178.72, 170.99, 143.12, 140.55, 129.35, 126.89, 83.24, 46.52, 37.21, 24.58, 24.53, 22.20, 16.30; ¹¹B NMR (128 MHz, CDCl₃): δ 32.00 (br s); IR (neat) 2978, 2939, 1721, 1626, 1601, 1510, 1371, 1323, 1216, 1142, 969, 848, 737, 673 cm⁻¹; HRMS (ESI) *m/z* 346.18287 [C₁₈H₂₅BNO₅⁻ (M-H)⁻ requires 346.18313]. The ¹³C NMR resonance at 16.30 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2q: Clear Oil. (57.6 mg isolated). 3.8 % B₂pin₂.

Corrected Yield: 68.6 %

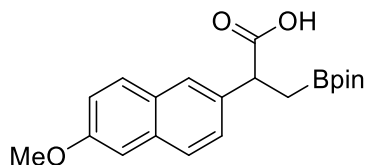
¹H NMR (400 MHz, CDCl₃): δ 7.82 – 7.76 (m, 4H), 7.48 – 7.43 (m, 3H), 4.06 (dd, *J* = 9.4, 7.2 Hz, 1H), 1.67 (dd, *J* = 16.0, 9.4 Hz, 1H), 1.39 (dd, *J* = 16.0, 7.2 Hz, 1H), 1.13 (s, 6H), 1.12 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 180.57, 137.83, 133.34, 132.57, 128.18, 127.77, 127.53, 126.56, 125.99, 125.94, 125.69, 83.40, 46.95, 24.59, 24.51, 15.90; ¹¹B NMR (128 MHz, CDCl₃): δ 33.43 (br s); IR (neat) 2978, 2936, 1704, 1371, 1324, 1143, 967, 847, 885, 747 cm⁻¹; HRMS (ESI) *m/z* 325.16156 [C₁₉H₂₂BO₄⁻ (M-H)⁻ requires 325.16166]. The ¹³C NMR resonance at 15.90 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



2s: White Solid. (75.0 mg isolated). 6.2 % B₂pin₂.

Corrected Yield: 85.9 %

¹H NMR (600 MHz, CDCl₃): δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 3.82 (dd, *J* = 9.1, 7.6 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (nonet, *J* = 6.8 Hz, 1H), 1.53 (dd, *J* = 16.0, 9.1 Hz, 1H), 1.29 (dd, *J* = 16.0, 7.6 Hz, 1H), 1.12 (s, 6H), 1.11 (s, 6H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): 180.75, 140.50, 137.53, 129.16, 127.54, 83.30, 46.42, 45.01, 30.13, 24.60, 24.49, 22.32, 22.29, 15.81; ¹¹B NMR (192 MHz, CDCl₃): δ 33.72 (br s); IR (neat) 2954, 1706, 1513, 1371, 1323, 1144, 968, 888, 848 cm⁻¹; HRMS (ESI) *m/z* 331.20850 [C₁₉H₂₈BO₄⁻ (M-H)⁻ requires 331.20861]. The ¹³C NMR resonance at 15.81 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



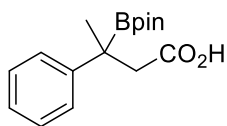
2t: Pale Yellow Solid. (66.3 mg isolated). 12.3 % B₂pin₂.

Corrected Yield: 67.7 %

1.0 mmol scale (4-fold scale-up): (218.5 mg isolated). 7.0 % B₂pin₂.

Corrected Yield: 58.2 %

¹H NMR (600 MHz, CDCl₃): δ 7.68 – 7.65 (m, 3H), 7.41 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 4.00 (dd, *J* = 9.2, 7.4 Hz, 1H), 3.89 (s, 3H), 1.64 (dd, *J* = 16.0, 9.2 Hz, 1H), 1.37 (dd, *J* = 16.0, 7.4 Hz, 1H), 1.12 (s, 6H), 1.11 (s, 6H); ¹³C NMR (151 MHz, CDCl₃): 180.41, 157.51, 135.56, 133.67, 129.25, 128.82, 127.02, 126.45, 126.36, 118.78, 105.53, 83.35, 55.21, 46.73, 24.59, 24.51, 15.97; ¹¹B NMR (192 MHz, CDCl₃): δ 33.62 (br s); IR (neat) 2979, 2936, 1704, 1634, 1606, 1506, 1484, 1371, 1325, 1265, 1143, 1032, 885, 848, 811 cm⁻¹; HRMS (ESI) *m/z* 355.17206 [C₂₀H₂₄BO₅⁻ (M-H)⁻ requires 355.17223]. The ¹³C NMR resonance at 15.97 (methylene carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.



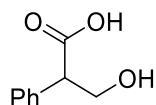
2u: White Microcrystalline Solid. (18.0 mg isolated). 2.8% B₂pin₂

Corrected Yield: 24.2 %

¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.30 (t, 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 1.70 (s, 3H), 1.62 (d, *J* = 15.4 Hz, 1H), 1.45 (d, *J* = 15.4 Hz, 1H), 1.14 (s, 6H), 1.12 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): 182.32, 144.79, 128.20, 126.62, 125.89, 83.11, 47.90, 33.33, 24.62, 24.57, 23.29; ¹¹B NMR (128 MHz, CDCl₃): δ 32.64 (br s); IR (neat) 2979, 2930, 2850, 1701, 1361, 1325, 1144, 970, 847, 698 cm⁻¹; HRMS (ESI) *m/z* 289.16171 [C₁₆H₂₂BO₄⁻ (M-H)⁻ requires 289.16166]. The ¹³C NMR resonance at 32.64 (quaternary carbon signal) has very low intensity due to ¹¹B quadrupolar broadening.

Derivatization of Boracarboxylation Product 2a

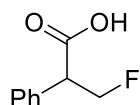
Oxidation of 2a



Compound **2a** (100 mg, 0.362 mmol) and sodium hydroxide (145 mg, 3.62 mmol) were dissolved in a mixture of THF (4 mL) and deionized water (1 mL). While stirring at room temperature, aqueous hydrogen peroxide (30% w/w, 740 μ L, 7.24 mmol) was added dropwise to this solution. This mixture was stirred at ambient temperature for 4 hours. Upon reaction completion, this mixture was neutralized with conc. HCl, diluted with water (5 mL), and extracted with ethyl acetate (5 x 15 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo to give a clear oil. Column chromatography with a gradient elution of EA/Hexanes (0% EA to 60 % EA) afforded the product **5a** as a clear crystalline solid. Yield: 34.0 mg, 0.205 mmol, 57%.

^1H NMR (400 MHz, d^6 -DMSO): δ 12.35 (br, s, 1H), 7.34 – 7.25 (m, 5H), 4.91 (br s, 1H), 3.91 (dd, J = 10.0, 8.4 Hz, 1H), 3.64 (dd, J = 8.4, 6.0 Hz, 1H), 3.56 (dd, J = 10.0, 6.0 Hz, 1H), ; ^{13}C NMR (101 MHz, d^6 -DMSO): δ 173.73, 137.06, 128.40, 128.03, 127.07, 63.40, 54.31; IR (neat) 3396 (br), 2922, 2851, 1706, 1553, 1455, 1333, 1259, 1209, 1174, 1021, 765, 728, 698 cm^{-1} ; HRMS (ESI) m/z 331.11892 [$\text{C}_{18}\text{H}_{19}\text{O}_6^-$ (2M-H) $^-$ requires 331.11871].

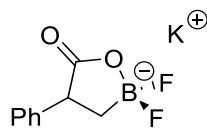
Fluorination of 2a



The fluorination of **2a** was adapted from a previously-reported method.⁴ A 50 mL Schlenk flask was charged with Compound **2a** (114.0 mg, 0.413 mmol), AgNO_3 (16.0 mg, 0.094 mmol), Selectfluor I (450.0 mg, 1.270 mmol), a magnetic stir bar, and purged with argon. DCM (6.0 mL), deionized water (7.0 mL), trifluoroacetic acid (0.80 mL), and 85% phosphoric acid (0.20 mL) were added and the reaction vessel was sealed under argon. The reaction was heated to 50 $^\circ\text{C}$ for 20 hours. Upon reaction completion, the crude, biphasic mixture was transferred to a separatory funnel and extracted with DCM (3 x 30 mL). The combined organic layers were concentrated to a 10 mL volume and extracted with saturated aqueous NaHCO_3 (4 x 15 mL). The combined aqueous layers were acidified with concentrated HCl and extracted with ethyl acetate (4 x 35 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo to provide nearly pure **6a**. Analytically pure **6a** was obtained by silica column chromatography (0% - 20 % EA/hexanes). Yield: 43.0 mg, 0.256 mmol, 62%.

^1H NMR (400 MHz, CDCl_3): δ 9.76 (br s, 1H), 7.37 – 7.31 (m, 5H), 4.96 (dt, $^2J_{\text{HF}}$ = 46.4 Hz, $^2J_{\text{HH}}$ = $^3J_{\text{HH}}$ = 9.2 Hz, 1H), 4.61 (ddd, $^2J_{\text{HF}}$ = 46.4 Hz, $^2J_{\text{HH}}$ = 9.2 Hz, $^3J_{\text{HH}}$ = 5.4 Hz, 1H), 4.05 (ddd, $^3J_{\text{HF}}$ = 14.0 Hz, $^3J_{\text{HH}}$ = 9.2 Hz, $^3J_{\text{HH}}$ = 5.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 177.12, 133.03 (d, $^3J_{\text{CF}}$ = 8.3 Hz), 129.07, 128.45, 128.27, 83.22 (d, $^1J_{\text{CF}}$ = 174.7 Hz), 52.19 (d, $^2J_{\text{CF}}$ = 19.8 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ -216.54 (td, $^2J_{\text{HF}}$ = 46.4 Hz, $^3J_{\text{HF}}$ = 14.0 Hz); IR (neat) 3035 (br), 1710, 1497, 1457, 1418, 1263, 1224, 1008, 761, 728, 698 ; HRMS (ESI) m/z 335.11020 [$\text{C}_{18}\text{H}_{17}\text{F}_2\text{O}_4^-$ (2M-H) $^-$ requires 335.11004].

Removal of Pinacol from **2a** via KHF_2

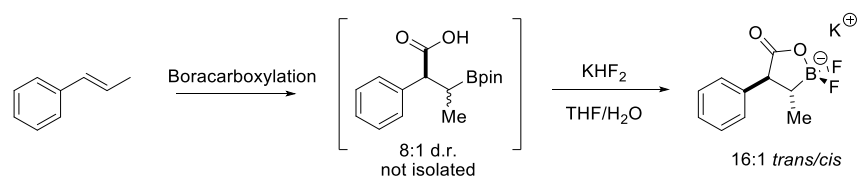


A 25 mL polyethylene bottle was charged with compound **2a** (50.0 mg, 0.1811 mmol) and KHF_2 (90.0 mg, 1.15 mmol, 6.36 eq.). A mixture of THF (2 mL) and water (2 mL) was added and the resulting suspension was stirred at ambient temperature for one hour. The solution was transferred to a round bottom flask and the volatiles were removed in vacuo to provide a crude white powder. The product was taken up in acetone (3 mL), and filtered through cotton. The insoluble material was washed with acetone (3 x 1 mL), the combined acetone filtrates were dried in vacuo, and the resulting solid was washed with ether (2 x 5 mL) to provide **7a** as a white, microcrystalline solid. Yield: 33mg, 0.139 mmol, 76.7%.

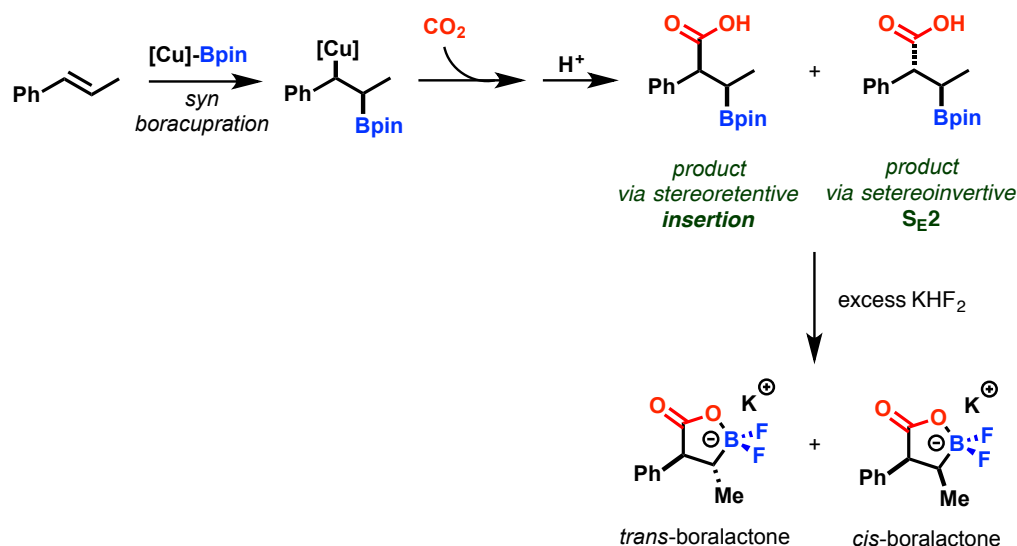
^1H NMR (600 MHz, d^6 -DMSO): δ 7.23 (t, $J = 7.7$ Hz, 2H), 7.19 (d, $J = 7.7$ Hz, 2H), 7.13 (t, $J = 7.7$ Hz, 1H), 3.49 (dd, $^3J_{\text{HH}} = 9.8$, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 0.93 (dddd, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HH}} = 9.8$ Hz, $^3J_{\text{HF}} = 5.0$ Hz, $^3J_{\text{HF}} = 4.9$ Hz, 1H), 0.51 (dddd, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HF}} = 10.8$ Hz, $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HF}} = 5.2$ Hz, 1H); ^{13}C NMR (101 MHz, d^6 DMSO): δ 179.74, 144.52, 127.88, 127.82, 125.42, 50.16, 23.79; ^{19}F NMR (376 MHz, d^6 DMSO): δ -141.65 (m, 1F), -142.50 (m, 1F); ^{11}B NMR (192 MHz, d^6 DMSO): δ 8.18 (s); IR (neat) 2952, 1699, 1605, 1495, 1431, 1312, 1269, 1237, 1217, 1122, 1060, 1035, 994, 928, 836, 791, 764, 741, 699, 690; HRMS (ESI) m/z 197.05970 [$\text{C}_9\text{H}_8\text{F}_2\text{O}_2^-$ (M-K) $^-$ requires 197.05909]. The ^{13}C NMR resonance at 23.79 (methylene carbon signal) has very low intensity due to ^{11}B quadrupolar broadening.

Stereochemical Assignment of **7v** derived from **2v**

Although *trans*-beta methyl styrene (**1v**) underwent boracarboxylation to **2v** in low yield (11% by NMR), assignment of the product's stereochemistry offers mechanistic insight into the boracarboxylation reaction (Scheme S1). In order to assign the stereochemistry of the product, the boracarboxylation of beta-methyl styrene was scaled up tenfold. After reaction completion and subsequent extraction, the crude product was treated with potassium bifluoride in a THF/water mixture. After purification, the corresponding difluoroboralactone **7v** was obtained as a pure, white solid. NOE experiments allowed for assignment of the relative stereochemistry.



Scheme S1.



*Boracarboxylation of *trans* beta-methyl styrene*

Working inside a nitrogen-filled glove box, a septum-capped 20mL vial was charged with ICyCuCl (100 mg, 0.30 mmol, 12 mol %), sodium *tert*-butoxide (480 mg, 7.5 mmol, 2.0 eq.), and a magnetic stir bar. Anhydrous, degassed THF (9.0mL) was added, the vial was sealed with an air-tight septum, and the resulting suspension was stirred under nitrogen for two hours at room temperature to give a clear, colorless solution. In a separate 100 mL round-bottomed flask, bis(pinacolato)diboron (700 mg, 3.75 mmol, 1.1 eq.) and 21 mL THF were added. To this solution,

trans-beta methyl styrene (295 mg, 2.50 mmol) was added. The round-bottomed flask was charged with a magnetic stir bar, sealed with a septum, and taken out of the glove box. The pre-prepared catalyst solution, under nitrogen, was transferred to this reaction vessel with a 10 mL gas-tight syringe. Immediately after catalyst addition, the reaction was fitted with a double-walled CO₂ balloon and the reaction was stirred at ambient temperature for 36 hours. Upon reaction completion, the reaction was quenched with 30 mL of 1.0M aqueous HCl and extracted with DCM (3 x 30 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo to give the crude product. This product was taken up in 30 mL of diethyl ether and extracted with saturated NaHCO₃ (4 x 15 mL). The combined aqueous layers were washed with dichloromethane (3 x 20 mL) to remove some of the impurities arising from catalyst decomposition. The aqueous layer was carefully acidified with 12 M HCl (to pH ≤ 1.0 by litmus paper) and subsequently extracted with DCM (5 x 10 mL). The organic layers were dried over sodium sulfate and concentrated in vacuo to give 33.6 mg of the crude boracarboxylated product with a large impurity of B₂pin₂ (>1 eq.). Broad signals dominated the ¹H NMR, suggesting the presence of paramagnetic impurities arising from catalyst decomposition as well. Regardless, the presence of a doublet at 3.56 ppm and a doublet at 3.63 with a relative integration of 8:1 suggested a mixture of diastereomeric boracarboxylation products. Additionally, a doublet at 0.70 ppm (methyl protons) and a doublet of quartets at 1.68 ppm (homobenzylic methine proton) suggested the desired product was present. Selective decoupling experiments showed that these three major signals were correlated.

Conversion to the Corresponding Difluoroboralactone

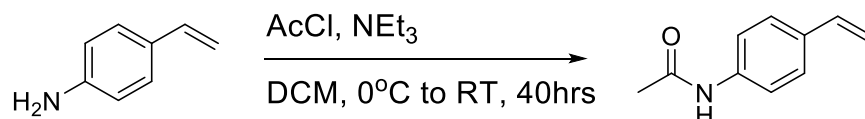
A 25 mL polyethylene bottle was charged with 20.1 mg of KHF₂ and 1.5 mL of distilled water. A solution of 16.8 mg of the crude boracarboxylated product (**2v**) in 1.5 mL of tetrahydrofuran was added, and the resulting suspension was stirred at ambient temperature for 12 hours. Upon reaction completion, the volatiles were removed in vacuo to provide a crude white powder. The product was taken up in acetone (3 mL), and filtered through cotton. The insoluble material was washed with acetone (2 x 1 mL), and the combined acetone filtrates were dried in vacuo. The resulting solid was washed with ether (2 x 3 mL) and dried in vacuo to provide a pure white powder. Yield over two-steps: 5.2 mg, 0.021 mmol, 0.8% yield).

¹H NMR (600 MHz, d⁶-acetone): δ 7.22 (m, 2H, both *cis* and *trans* meta protons), 7.17 (m, 2H, both *cis* and *trans* ortho protons), 7.11 (m, 1H, both *cis* and *trans* para protons), 3.80 (d, *J* = 8.6 Hz, 1H (minor), benzylic proton on *cis* isomer), 3.04 (d, *J* = 9.9 Hz, 1H (major), benzylic proton on *trans* isomer), 1.15 – 1.08 (m, 1H (minor), homobenzylic proton on *cis* isomer) 0.96 – 0.88 (m, 1H (major), homobenzylic proton on *trans* isomer), 0.86 (d, *J* = 6.9 Hz, 3H (major), methyl protons on *trans* isomer), 0.44 (d, *J* = 7.6 Hz, 3H (minor), methyl protons on *cis* isomer); ¹³C NMR (151 MHz, d⁶-acetone): δ 180.26, 144.39, 129.46, 128.51, 126.13, 60.44 (dd, ³*J*_{CF} = 3.7, 1.2 Hz), 14.79 (t, ³*J*_{CF} = 0.7 Hz); ¹⁹F NMR (564 MHz, d⁶-acetone): δ -150.99 (m, 1F), 156.79 (m, 1F); ¹¹B NMR (192 MHz, d⁶-acetone): δ 8.12 (br s); IR (neat) 2956, 1695, 1605, 1501, 1453, 1268, 1204, 1130, 1058, 1030, 947, 924, 893, 769, 743, 704; HRMS (ESI) *m/z* 211.07449 [C₁₀H₁₀BF₂O₂⁻ (M-H)⁻ requires 211.07474]. The homobenzylic carbon signal cannot be observed in the ¹³C NMR spectrum due to quadrupolar broadening.

Substrate Preparation

2,5-Dimethoxystyrene and 4-Isobutylstyrene were prepared by a previously-reported method.⁵ All other substrates were either commercially available or prepared as shown below:

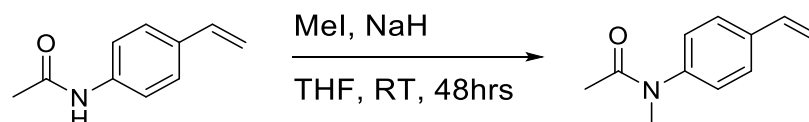
4-Vinylacetanilide



4-aminostyrene (1.058g, 8.88 mmol) was dissolved in DCM (15 mL) and cooled on ice. Triethylamine (1.4 mL, 10 mmol, 1.1 eq.) was added in one portion. With stirring, acetyl chloride (700 μ L, 9.81 mmol, 1.1 eq.) was added dropwise, and the reaction was stirred at ambient temperature for 40 hours. Upon reaction completion, the resulting DCM suspension was quenched with saturated sodium bicarbonate (20 mL). The organic layer was collected and washed with 2M HCl (2 x 20 mL) and dried over sodium sulfate. Concentrating the product in vacuo afforded pure (4-vinyl)acetanilide (1.278g, 89.3 %). NMR data is in accordance with literature data for this compound.⁶

¹H NMR (600 MHz, CDCl₃): δ 7.60 (br s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (d, J = 17.6 Hz, 1H), 5.19 (d, J = 10.9 Hz, 1H), 2.16 (s, 3H).

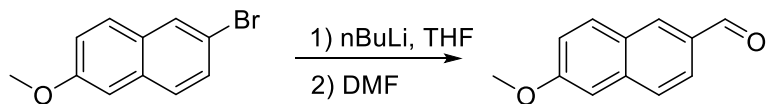
N-methyl-4-Vinylacetanilide



Under nitrogen, a 100 mL oven dried round bottom flask was charged with 4-vinylacetanilide (267 mg, 1.66 mmol) and dry THF (15 mL). In one portion, 60 wt. % sodium hydride/mineral oil suspension (786 mg, 19.7 mmol, 11.8 eq.) was added and the resulting suspension was allowed to stir at room temperature for 30 minutes. Then, methyl iodide (1.54 mL, mmmol) was added dropwise over 10 minutes. The reaction was sealed under nitrogen and allowed to stir for 48 hours. Upon reaction completion, 10 mL of water were added carefully, followed by 10 mL of 1M HCl. The resulting mixture was transferred to a separatory funnel and was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over sodium sulfate and concentrated under vacuum to leave a crude yellow oil. The product was purified by column chromatography with a gradient elution (0 % to 60 % EtOAc/Hexanes) to afford N-methyl(4-vinyl)acetanilide (220 mg, 1.26 mmol, 75.9 %).

¹H NMR (600 MHz, CDCl₃): δ 7.40 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.67 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 3.20 (s, 3H), 1.83 (s, 3H); ¹³C NMR (151 MHz, CDCl₃): 170.27, 143.78, 136.85, 135.52, 127.23, 126.97, 114.80, 36.89, 22.24. IR (neat) 3058, 3040, 3012, 2933, 1656, 1633, 1604, 1511, 1417, 1382, 1348, 1304, 1202, 1182, 1141, 1087, 1023, 985, 972, 905, 853, 760, 655 cm⁻¹; HRMS (ESI) m/z 176.10690 [C₁₁H₁₄NO⁺ (M+H)⁺ requires 176.10699].

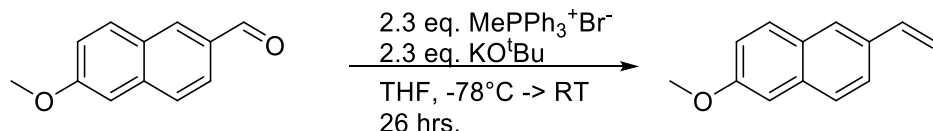
6-Methoxy-2-naphthaldehyde



Prepared via a previously reported method; NMR data is in correspondence with the previously reported literature values.⁷ Product was obtained as a yellow, crystalline solid (2.97g, 90%).

¹H NMR (400 MHz, CDCl₃): δ 10.04 (s, 1H), 8.16 (d, *J* = 1.6 Hz, 1H), 7.87 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 3.90 (s, 3H).

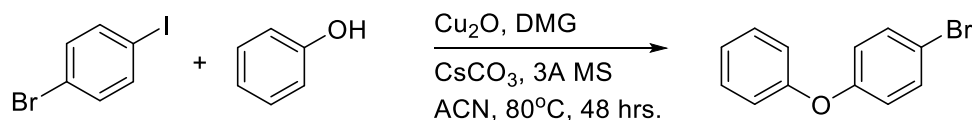
2-Methoxy-6-vinylnaphthalene



The following procedure was adapted from a previously-published method.⁸ An oven-dried, 100 mL round-bottomed flask equipped with magnetic stir bar was charged with triphenylphosphonium bromide (5.250 g, 14.70 mmol) and anhydrous, degassed THF (50 mL) under a nitrogen atmosphere. A solution of potassium tert-butoxide (1.680 g, 14.97 mmol) in THF (100 mL) was added dropwise to the stirring suspension of the triphenylphosphonium bromide at room temperature. Upon addition, the suspension turned to a bright-yellow color; this suspension was allowed to stir at RT for two hours. This mixture was cooled in a dry-ice/acetone bath (-78°C) and a solution of the aldehyde (1.150 g, 6.18 mmol) in THF (50 mL) was added dropwise to the stirring suspension. The reaction warmed slowly to room temperature and was allowed to stir for 26 hours. Upon reaction completion, the reaction was washed with 1M HCl (2 x 50 mL) and brine (50 mL). The organic layer was dried over sodium sulfate and dried in-vacuo to give an off-white solid. The product was purified by column chromatography with pure ethyl acetate to give 2-methoxy-6-vinylnaphthalene as a white solid. (544 mg, 2.95 mmol, 47.8%). NMR data is in correspondence with previously reported literature values.^{9,10}

¹H NMR (400 MHz, CDCl₃): δ 7.74 – 7.58 (m, 4H), 7.19 – 7.09 (m, 2H), 6.85 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.8 Hz, 1H), 3.92 (s, 3H).

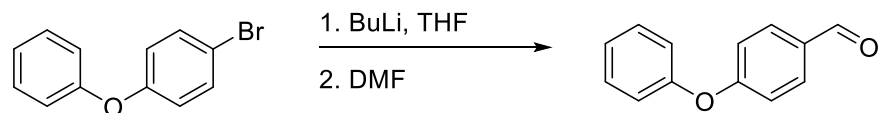
1-Bromo-4-phenoxybenzene



The following procedure was adapted from a previously-reported method.¹¹ 1-bromo-4-iodobenzene (8.504 g, 30.06 mmol, 1.5 eq.), phenol (1.888 g, 20.06 mmol, 1 eq.), cesium carbonate (13.03 g, 40.00 mmol, 2 eq.), copper(I) oxide (144 mg, 1.01 mmol, 5 mol%), dimethylglyoxime (469 mg, 4.04 mmol, 20 mol%), and activated 3 Å mol sieves (1.4 g) were all transferred to a dry, 250 mL round bottomed flask equipped with magnetic stir bar. The flask was sealed with a septum, purged with nitrogen gas, and charged with 12 mL of dry, degassed acetonitrile. The flask was heated to 80°C and stirred at this temperature for 48 hours. Upon reaction completion, the crude reaction mixture was diluted with 20 mL of ethyl acetate and filtered through silica using pure ethyl acetate. The filtrate was concentrated in vacuo and purified by silica column chromatography using a gradient elution (0% - 10% diethyl ether/hexanes) to afford the product as a clear oil (3.40 g, 13.6 mmol, 68.0 % yield). NMR data is in correspondence with previously reported literature values.¹²

^1H NMR (400 MHz, CDCl_3): δ 7.44 (d, J = 9.0 Hz, 2H), 7.36 (dd, J = 8.6, 7.5 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H).

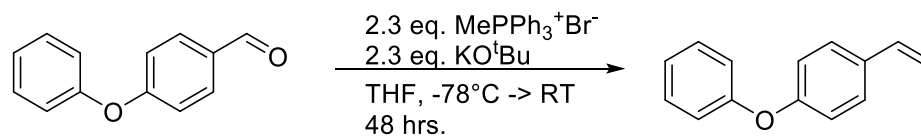
4-Phenoxybenzaldehyde



4-phenoxybenzaldehyde (2.88g, 11.56 mmol) was measured directly into a 250 mL round-bottomed flask, and the flask was purged with argon. Then, 50 mL of dry, degassed THF were added by syringe and the resulting solution was cooled to -78°C with a dry ice/acetone bath. 4.77 mL of 2.25 M *n*-butyllithium in hexanes was added dropwise to the cold solution with stirring and the mixture was allowed to stir for 30 minutes. Then, dimethylformamide (6.5 mL, 84 mmol, 7.2 eq.) was added dropwise to the cold, stirring solution. Upon complete addition, the mixture was allowed to warm to room temperature and stir for two hours. Upon reaction completion, the product was quenched with water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried in vacuo and the crude product was purified by column chromatography with a gradient elution (0% to 30% EtOAc/Hexanes) to provide the product as a clear oil. (450 mg, 2.27 mmol, 19.6%). NMR data is in correspondence with previously reported literature values.¹³

^1H NMR (400 MHz, CDCl_3): δ 9.93 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.42 (dd, J = 8.6, 7.6 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H).

4-Phenoxystyrene



The following procedure was adapted from a previously-published method.⁸ An oven-dried, 100 mL round-bottomed flask equipped with magnetic stir bar was charged with triphenylphosphonium bromide (1.447 g, 4.051 mmol) and anhydrous, degassed THF (10 mL) under a nitrogen atmosphere. A solution of potassium tert-butoxide (454.4 mg, 4.050 mmol) in THF (5 mL) was added dropwise to the stirring suspension of the triphenylphosphonium bromide at room temperature. Upon addition, the suspension turned to a bright-yellow color; this suspension was allowed to stir at RT for 1.5 hours. This mixture was cooled in a dry-ice/acetone bath (-78°C) and a solution of the aldehyde (350 mg, 1.77 mmol) in THF (5 mL) was added dropwise to the stirring suspension. The reaction warmed slowly to room temperature and was allowed to stir for 48 hours. Upon reaction completion, the reaction mixture was diluted with ethyl acetate (30 mL) and washed with 1M NH₄Cl (2 x 20 mL) and brine (20 mL). The resulting organic layer was dried over sodium sulfate and concentrated in vacuo to give a clear oil. This crude product was purified by column chromatography with a gradient elution (0% to 20% EtOAc/Hexanes) to provide 4-vinyldiphenylether as a clear oil. (140 mg, 0.713 mmol, 40.3%) NMR data is in correspondence with previously reported literature values.¹⁴

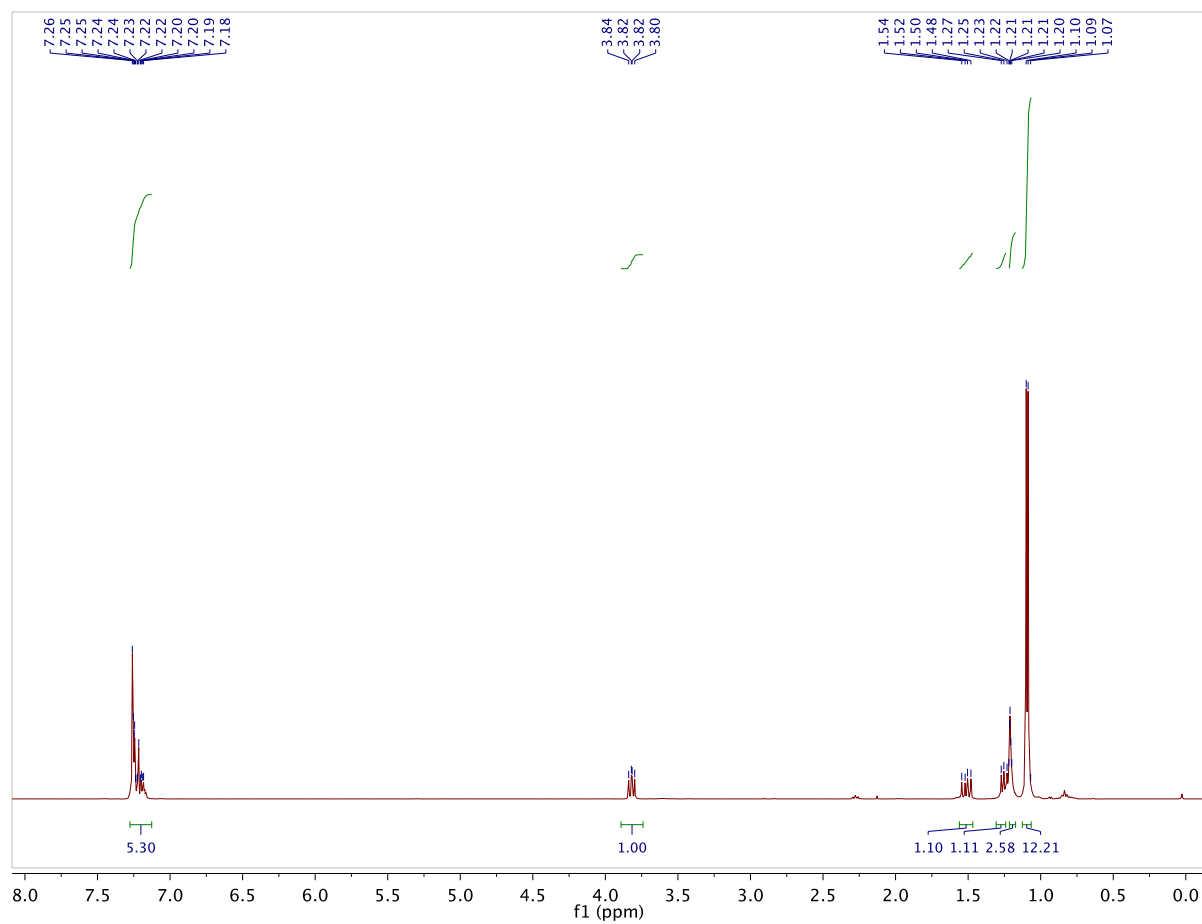
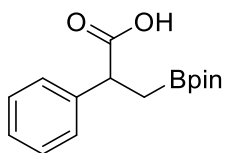
¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.11 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.02 (dd, *J* = 8.7, 1.2 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H).

REFERENCES

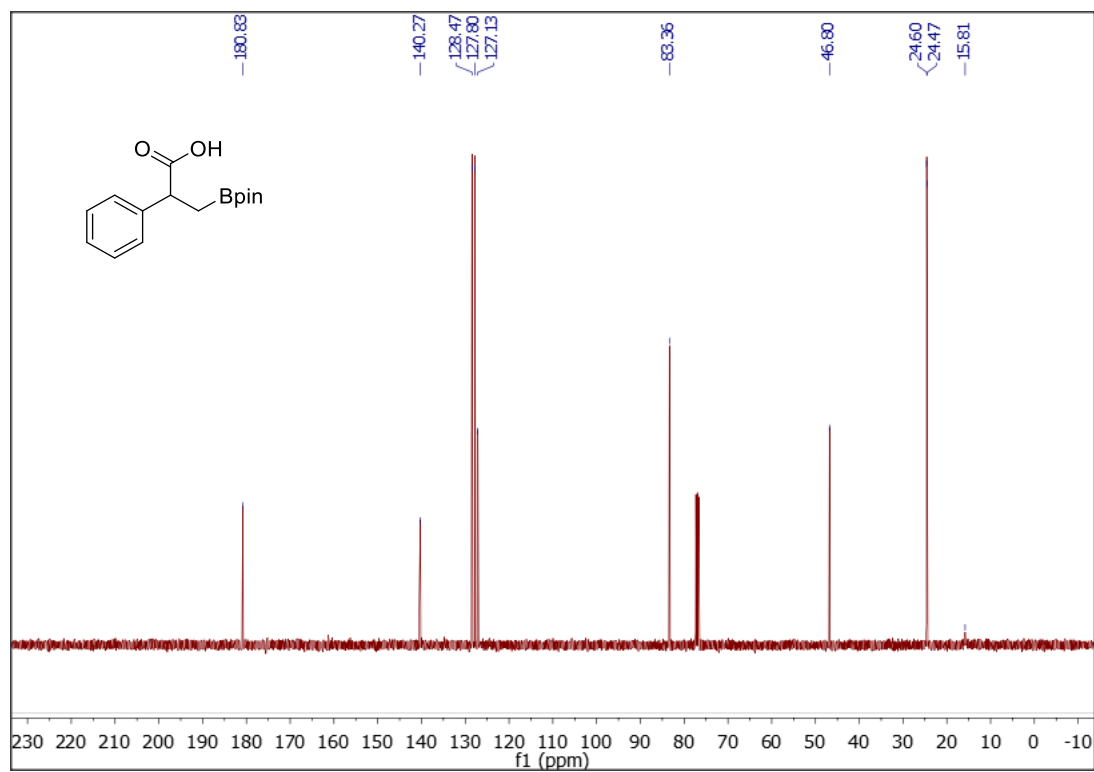
- (1) (a) Santoro, O.; Collado, A.; Slawin, A. M. Z.; Nolan, S. P.; Cazin, C. S. J. *Chem. Commun.* **2013**, 49, 10483. (b) Thomson, J. E.; Campbell, C. D.; Concellon, C.; Duguet, N.; Rix, K.; Slawin, A. M. Z.; Smith, A. D. *J. Org. Chem.* **2008**, 73, 2784. (c) Lloyd, L. S.; Asghar, A.; Burns, M. J.; Charlton, A.; Coombes, S.; Cowley, M. J.; Dear, G. J.; Duckett, S. B.; Genov, G. R.; Green, G. G. R.; Highton, L. A. R.; Hooper, A. J. J.; Khan, M.; Khazal, I. G.; Lewis, R. J.; Mewis, R. E.; Roberts, A. D.; Ruddlesden, A. J. *Catal. Sci. Technol.* **2014**, 4, 3544. (d) Opalka, S. M.; Park, J. K.; Longstreet, A. R.; McQuade, D. T. *Org. Lett.* **2013**, 15, 996.
- (2) Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, 133, 12980.
- (3) Cano, R.; Ramon, D. J.; Yus, M. *J. Org. Chem.* **2010**, 75, 3458.
- (4) Li, Z.; Wang, Z.; Zhu, L.; Tan, X.; Li, C. *J. Am. Chem. Soc.* **2014**, 136, 16439.
- (5) Greenhalgh, M. D.; Thomas, S. P. *J. Am. Chem. Soc.* **2012**, 134, 11900.
- (6) Denmark, S.; Butler, C. *Org. Lett.* **2006**, 8, 63.
- (7) Matsunaga, N.; Kaku, T.; Ojida, A.; Tanaka, T.; Hara, T.; Yamaoka, M.; Kusaka, M.; Tasaka, A. *Bioorgan. Med. Chem.* **2004**, 12, 4313.
- (8) Yang, F. Z.; Rauch, K.; Kettelhoit, K.; Ackermann, L. *Angew. Chem., Int. Edit.* **2014**, 53, 11285.
- (9) Alacid, E.; Najera, C. *J. Org. Chem.* **2008**, 73, 2315.
- (10) Gaertner, D.; Welther, A.; Rad, B. R.; Wolf, R.; Jacobi von Wangelin, A. *Angew. Chem., Int. Edit.* **2014**, 53, 3722.
- (11) Cristau, H.; Cellier, P.; Hamada, S.; Spindler, J.; Taillefer, M. *Org. Lett.* **2004**, 6, 913-916.
- (12) Hu, J.; Kolehmainen, E.; Knuutinen, J. *Magn. Reson. Chem.* **2000**, 38, 375.
- (13) Zheng, X.; Ding, J.; Chen, J.; Gao, W.; Liu, M.; Wu, H. *Org. Lett.* **2011**, 13, 1726.
- (14) Hu, W.; Li, P.; Jiang, G.; Che, C.; Chen, J. *Adv. Synth. Catal.* **2010**, 352, 3190.

^1H , ^{13}C , ^{11}B , and ^{19}F NMR Spectra

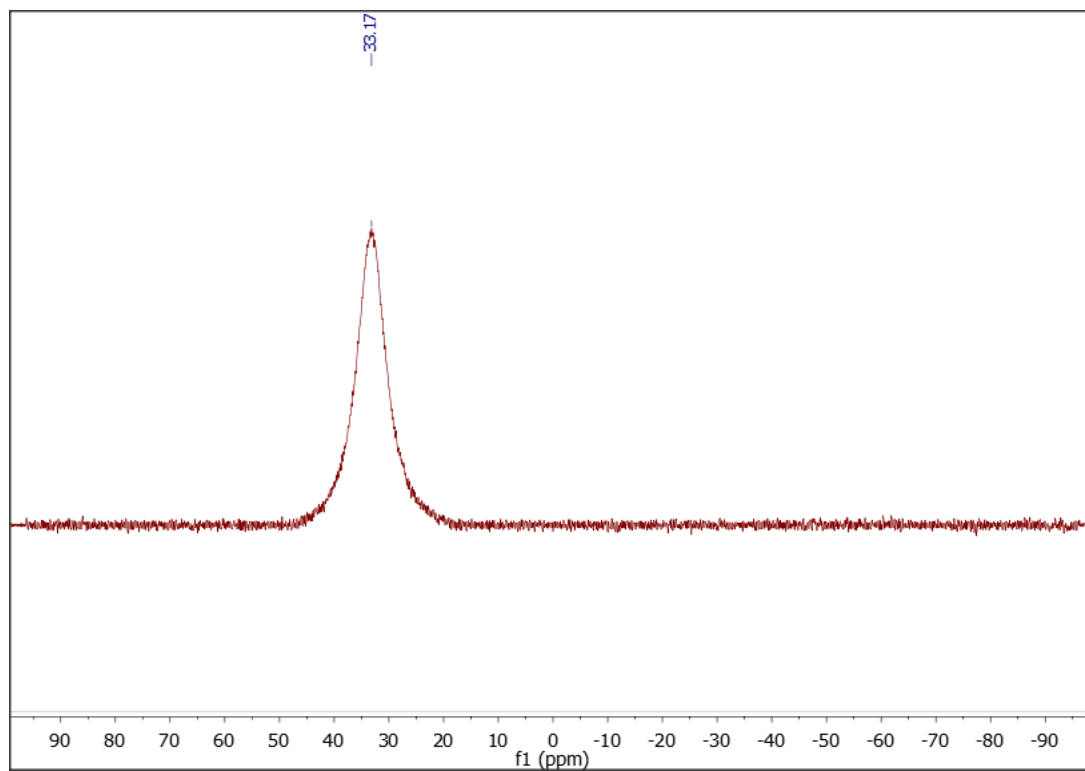
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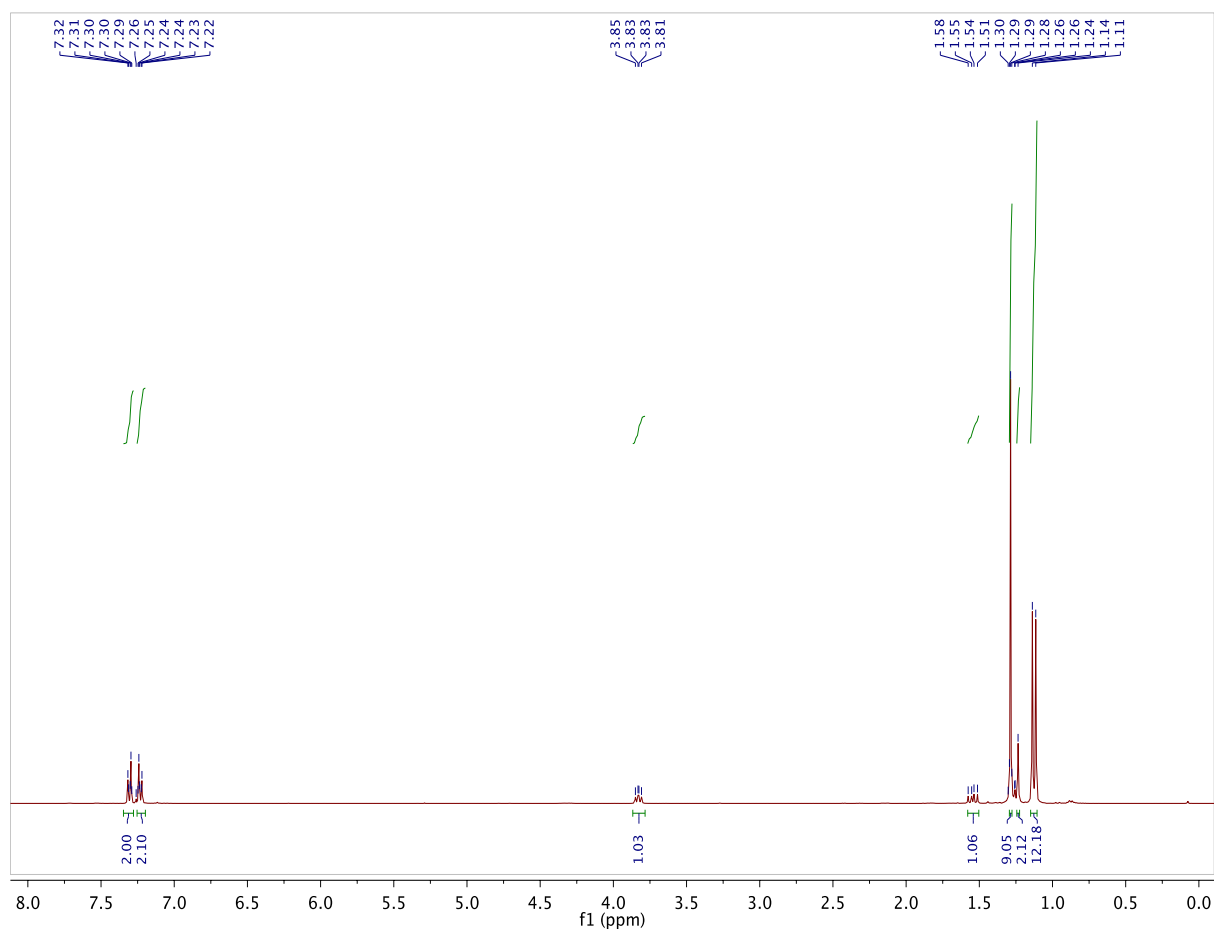
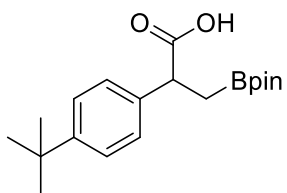
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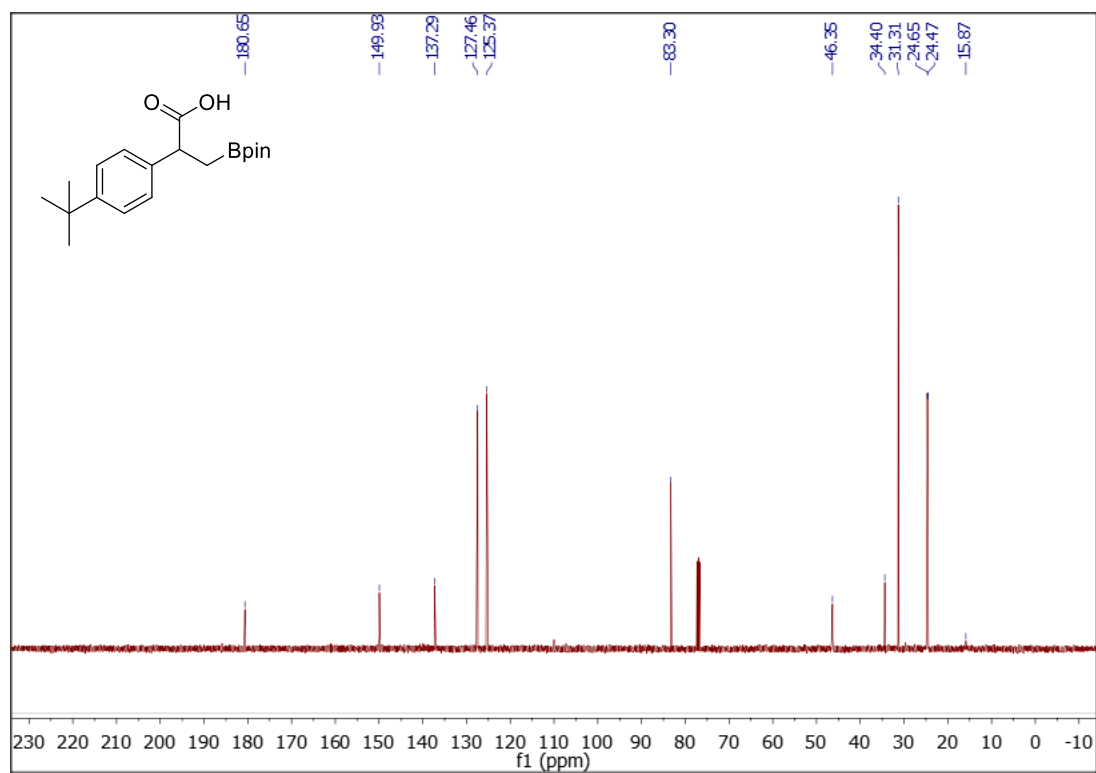
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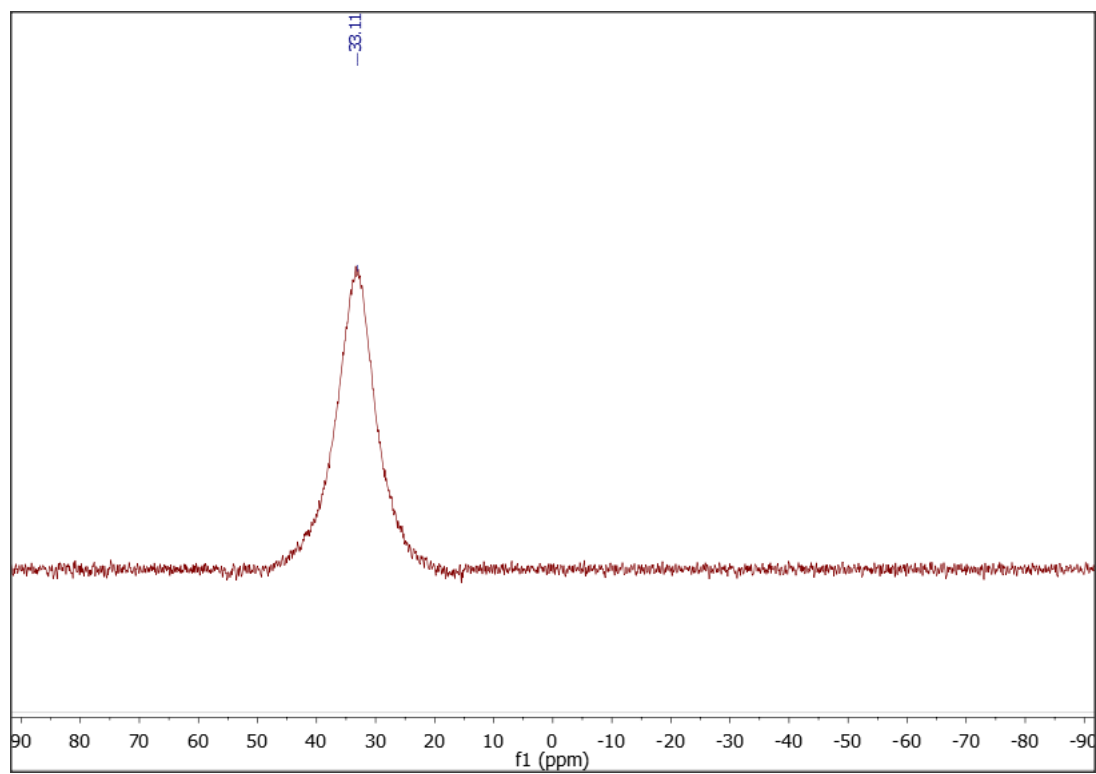
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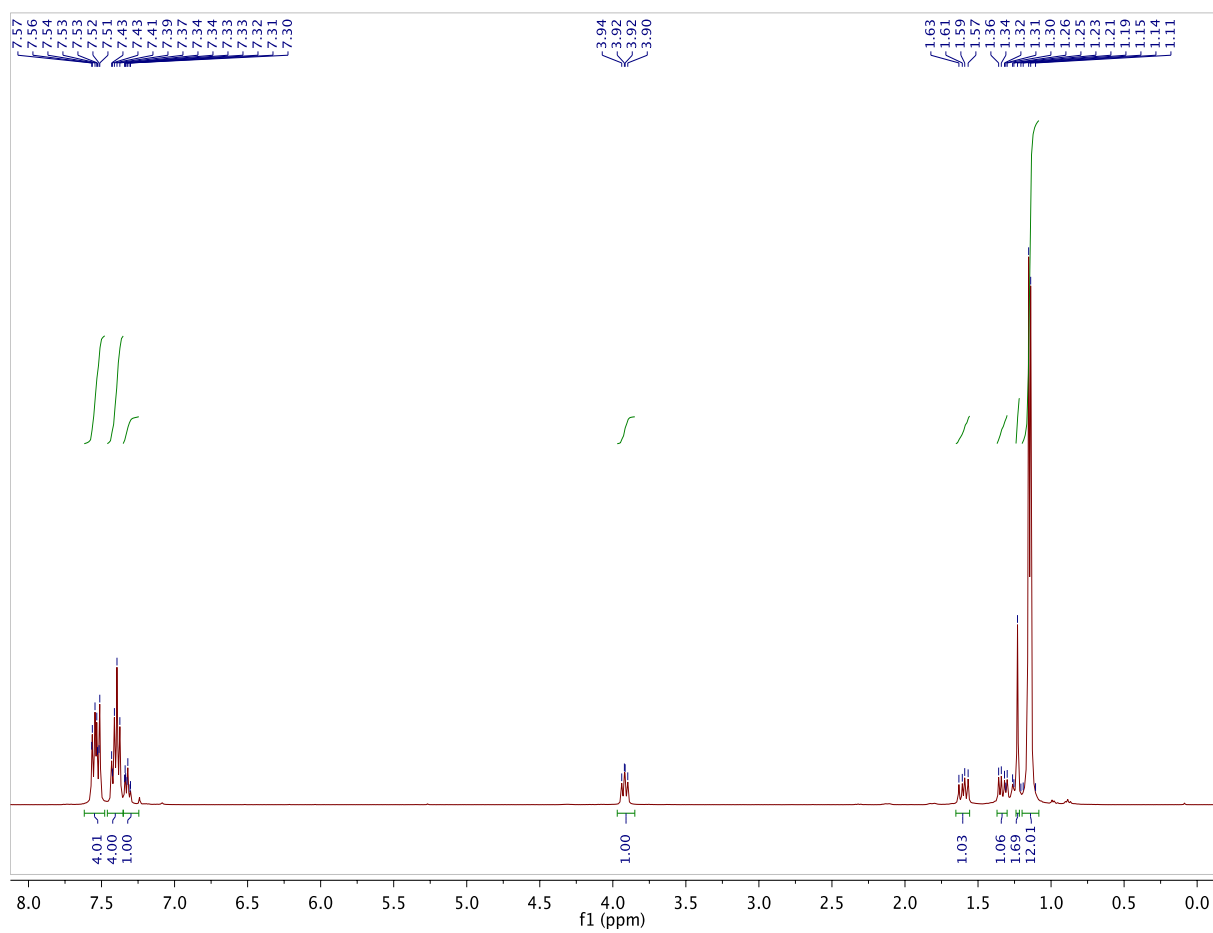
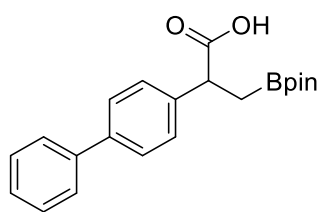
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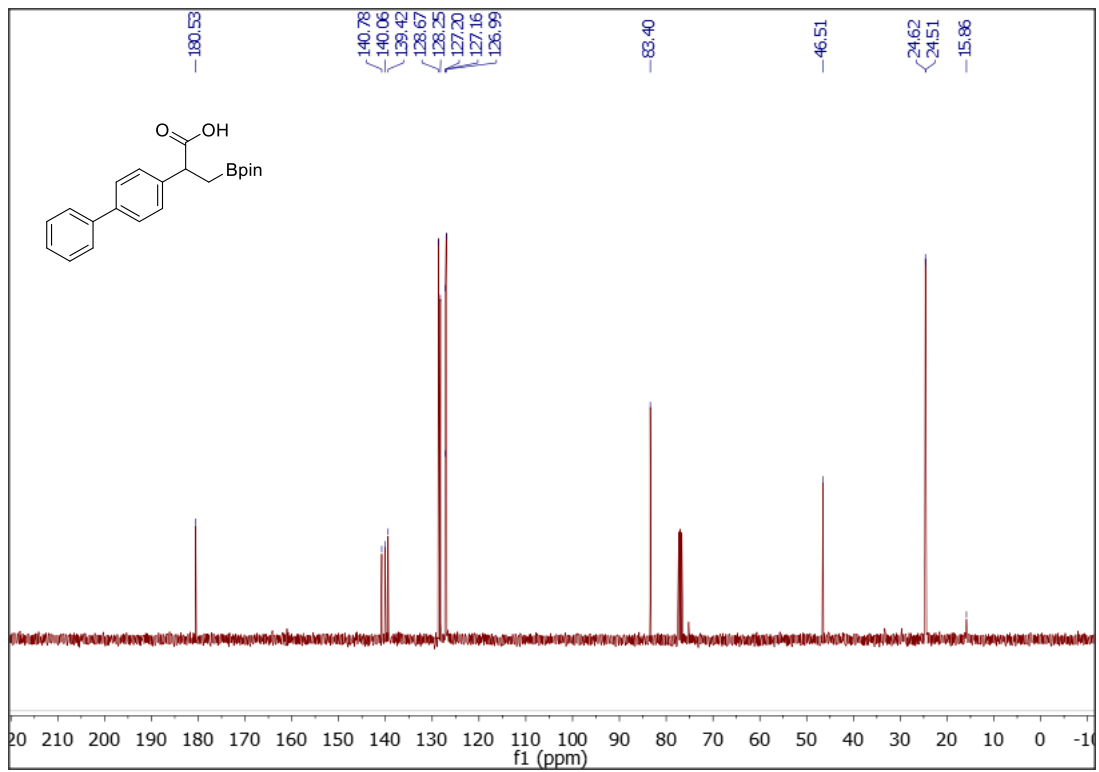
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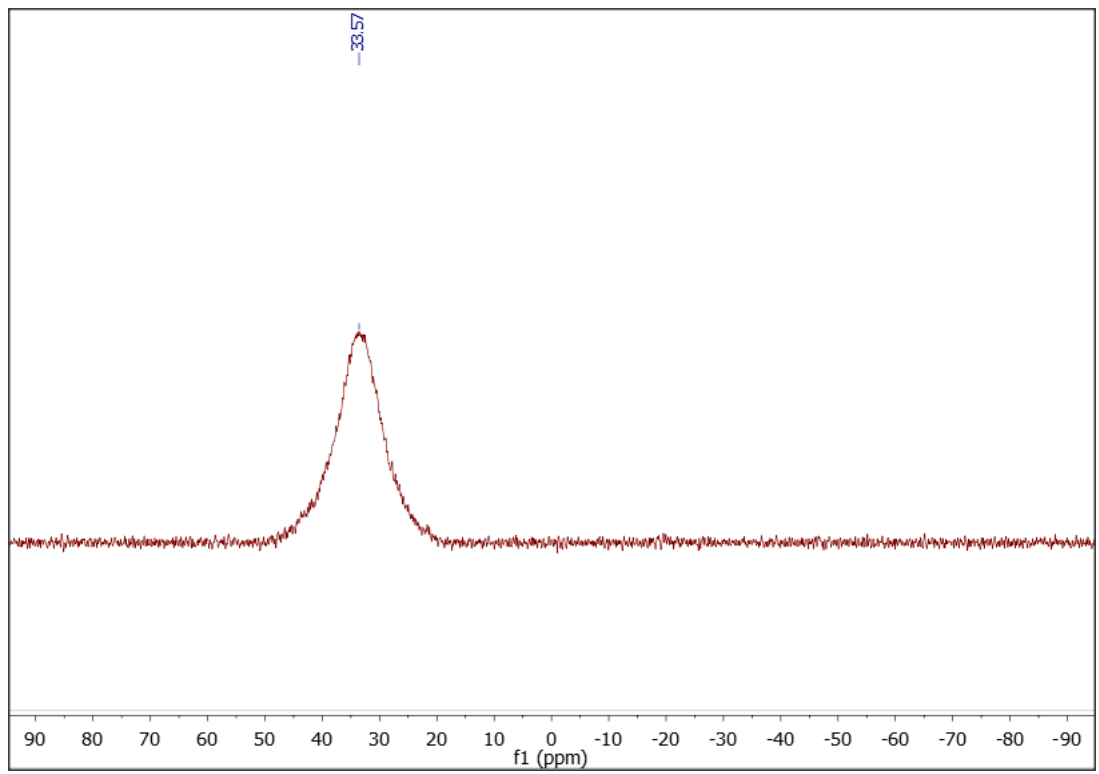
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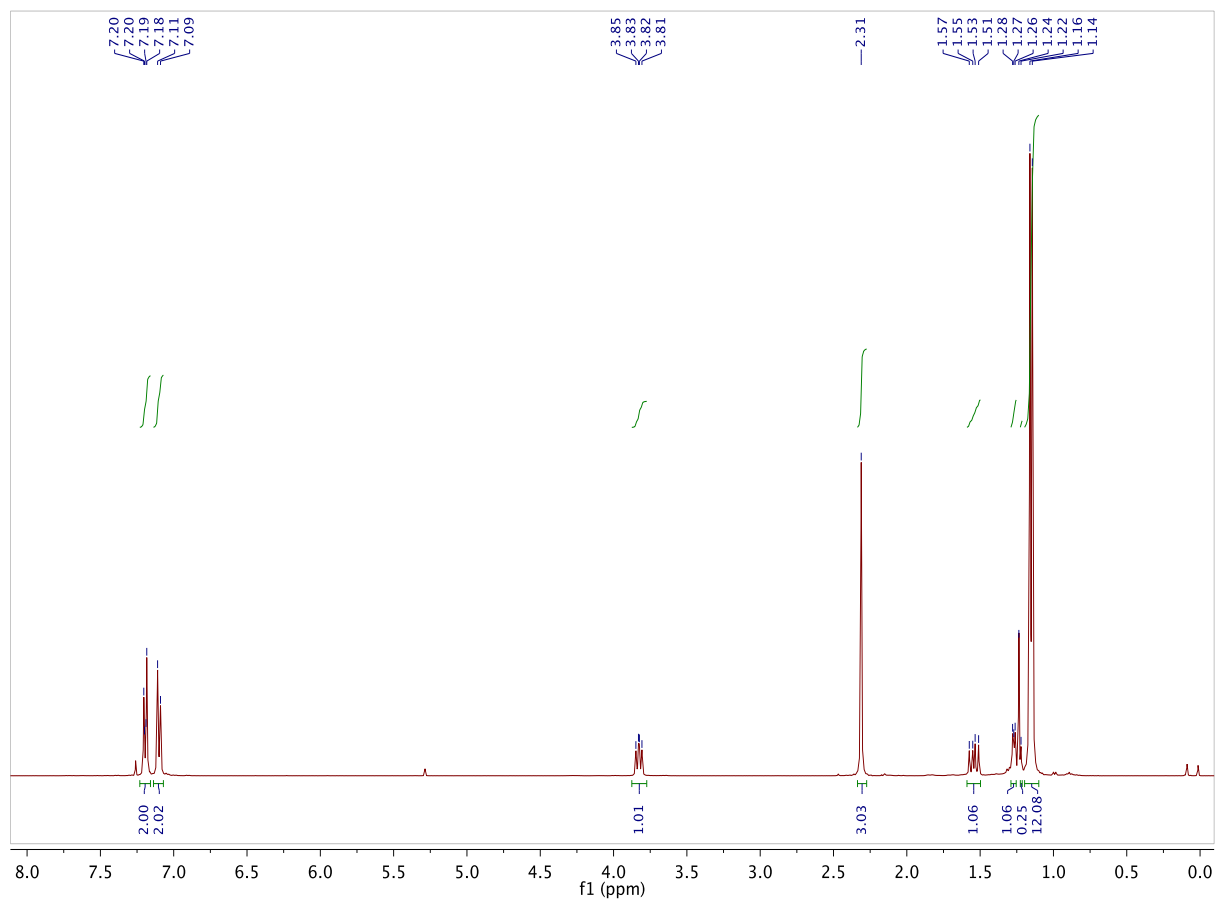
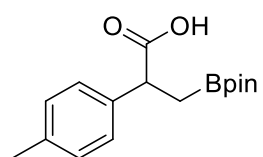
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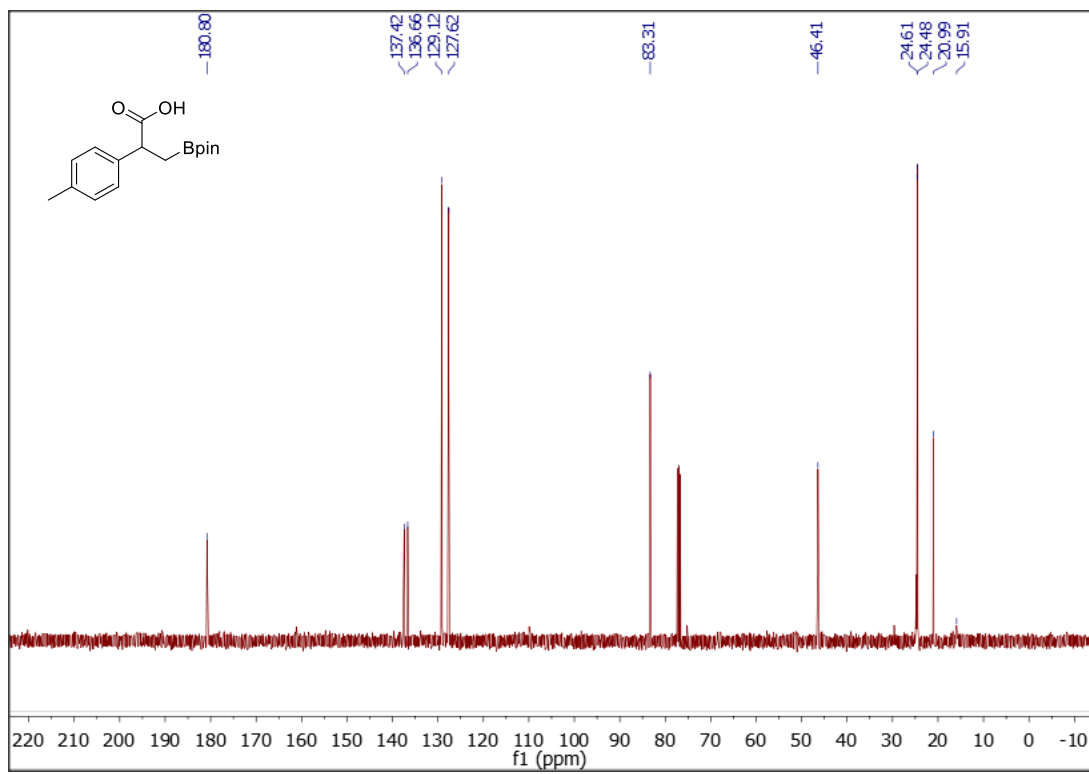
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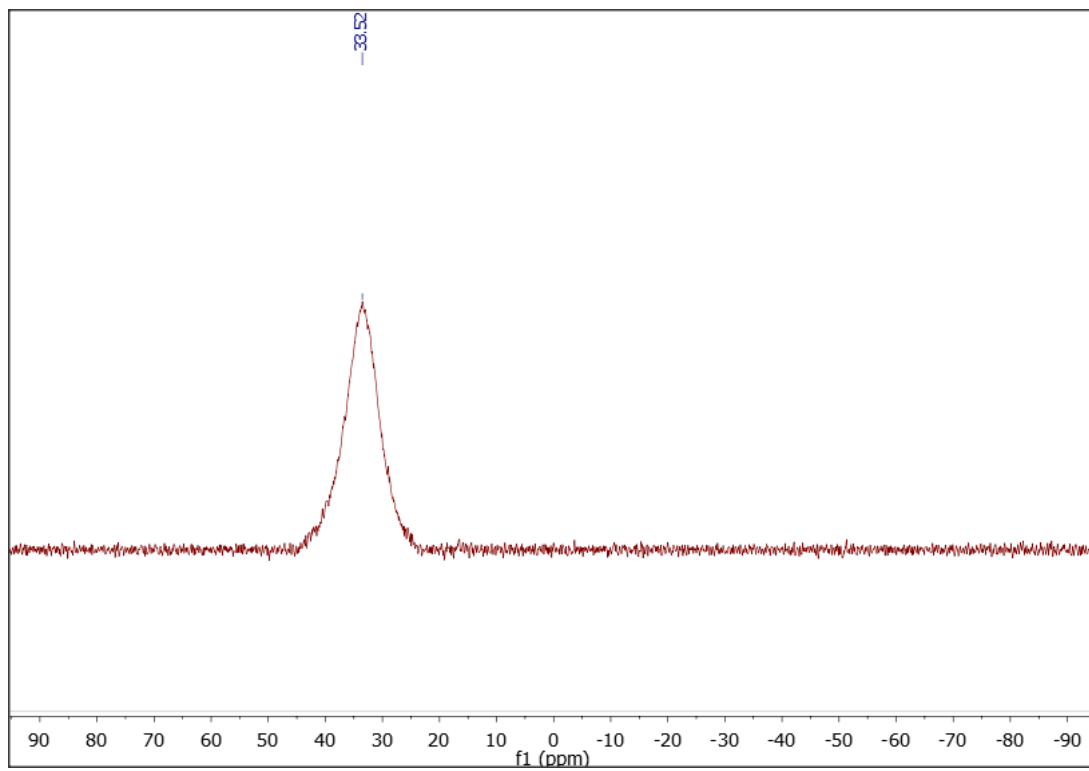
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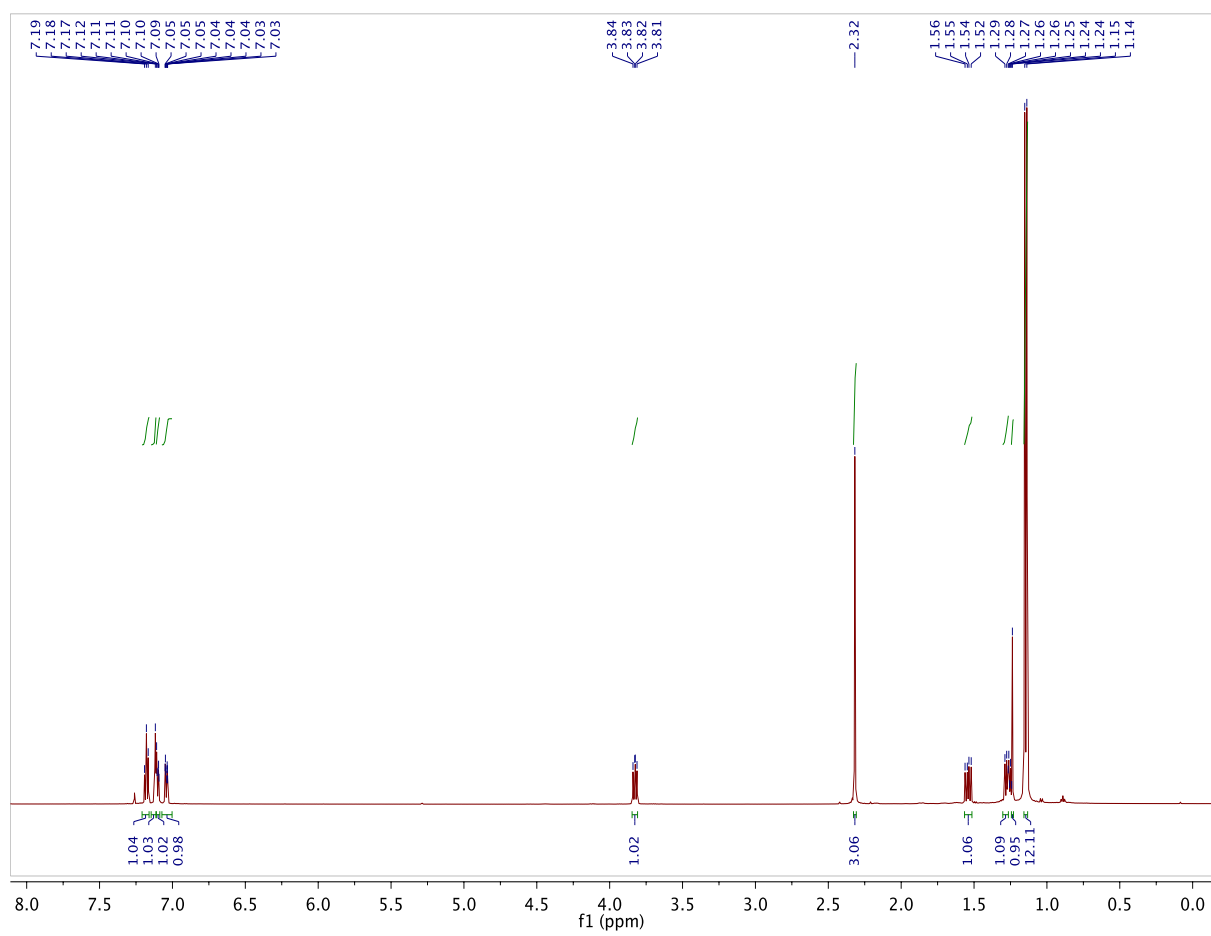
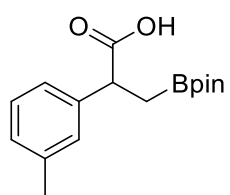
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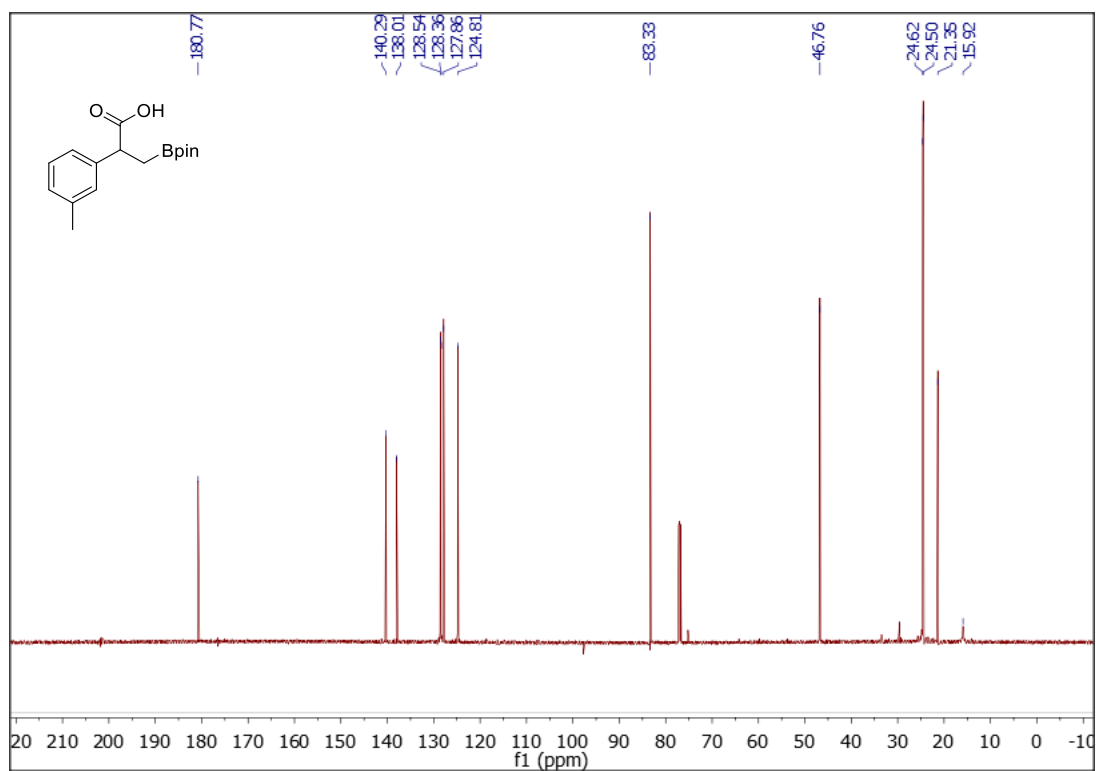
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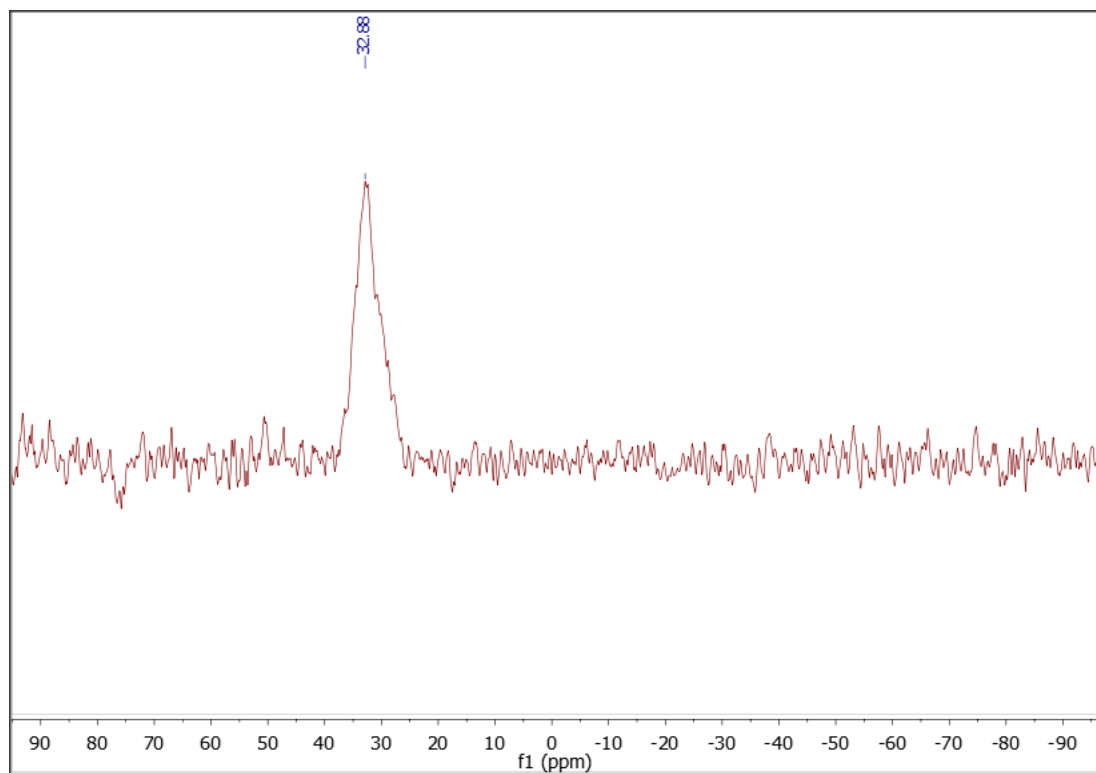
2e, ^1H NMR



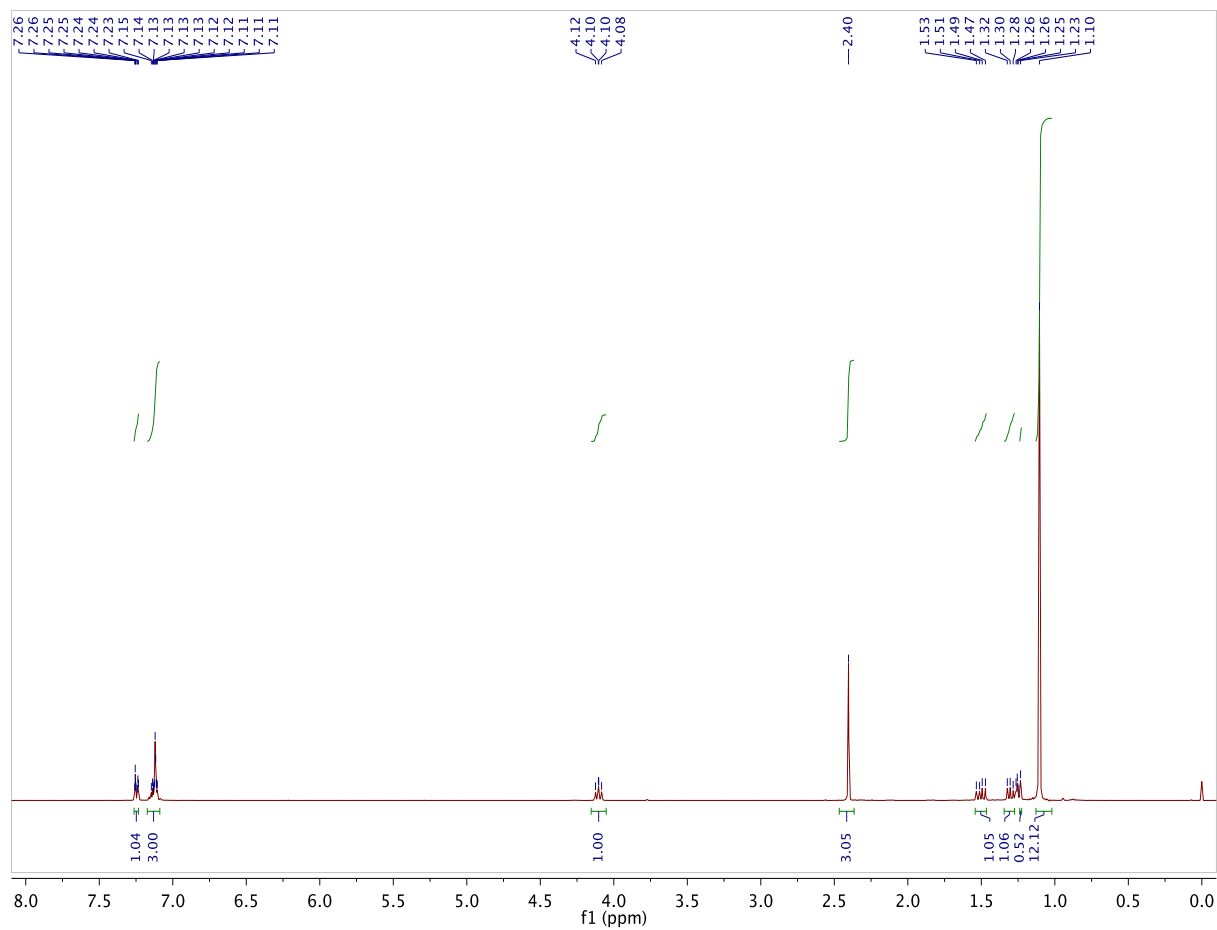
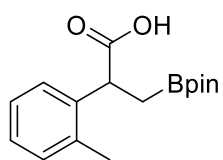
2e, $^{13}\text{C}\{^1\text{H}\}$ NMR



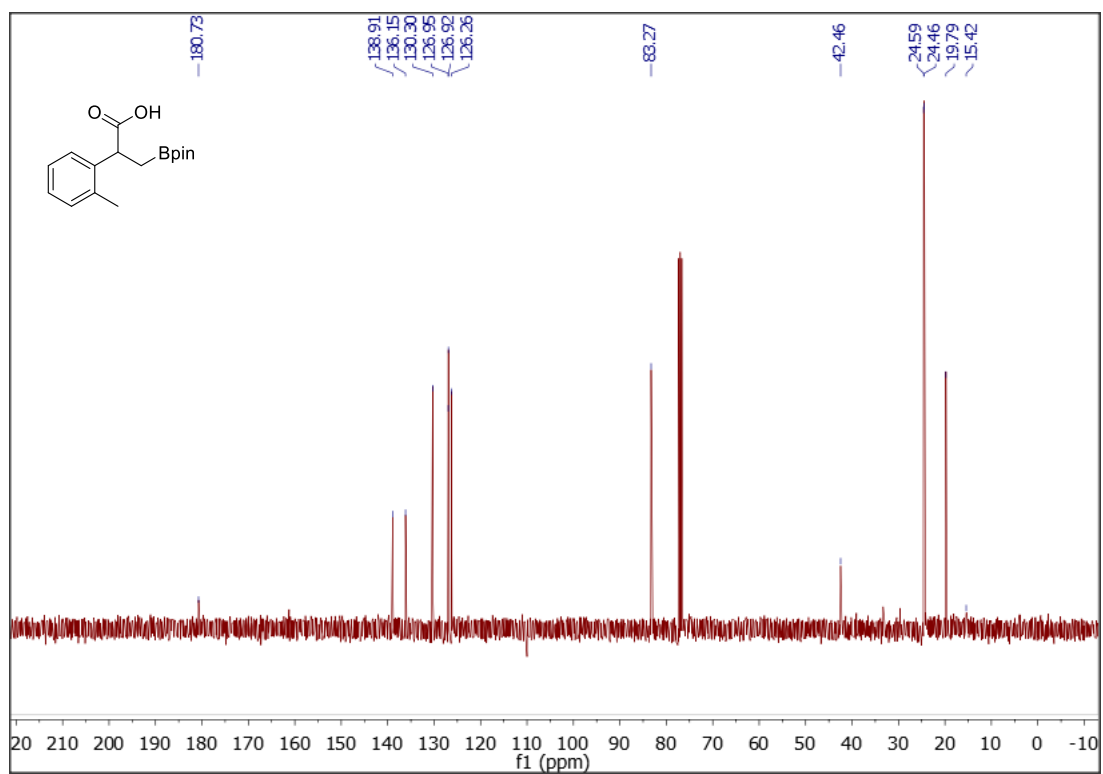
2e, ^{11}B NMR



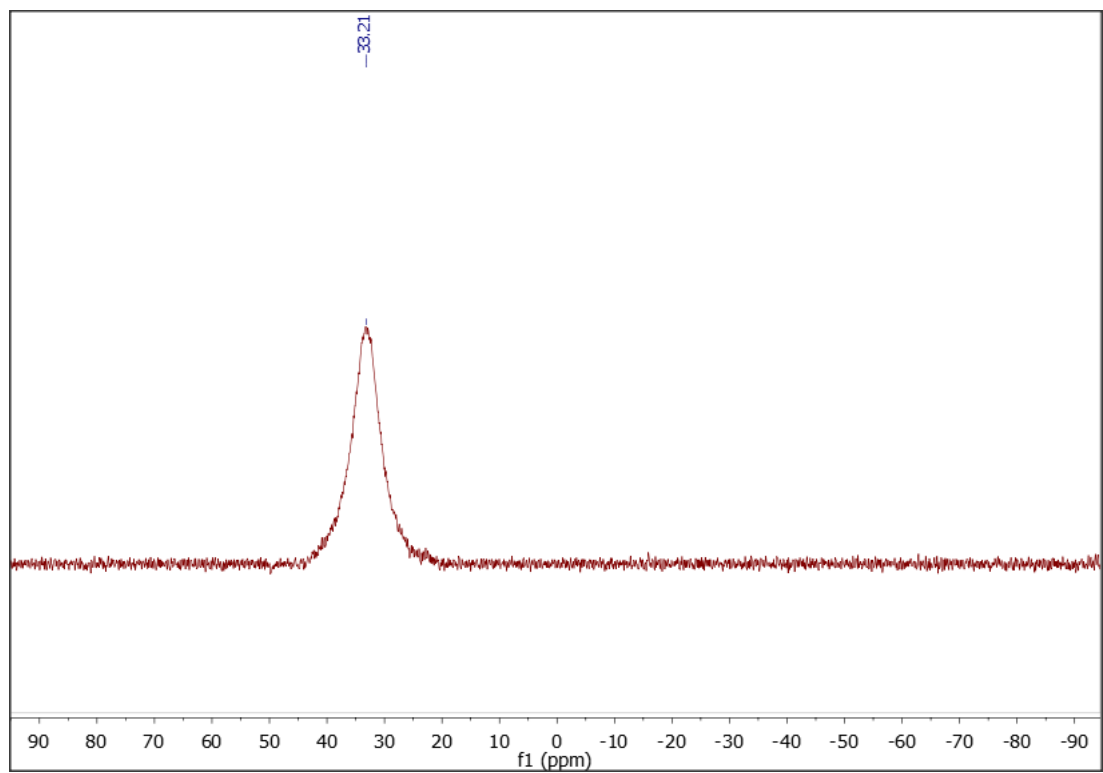
2f, ^1H NMR



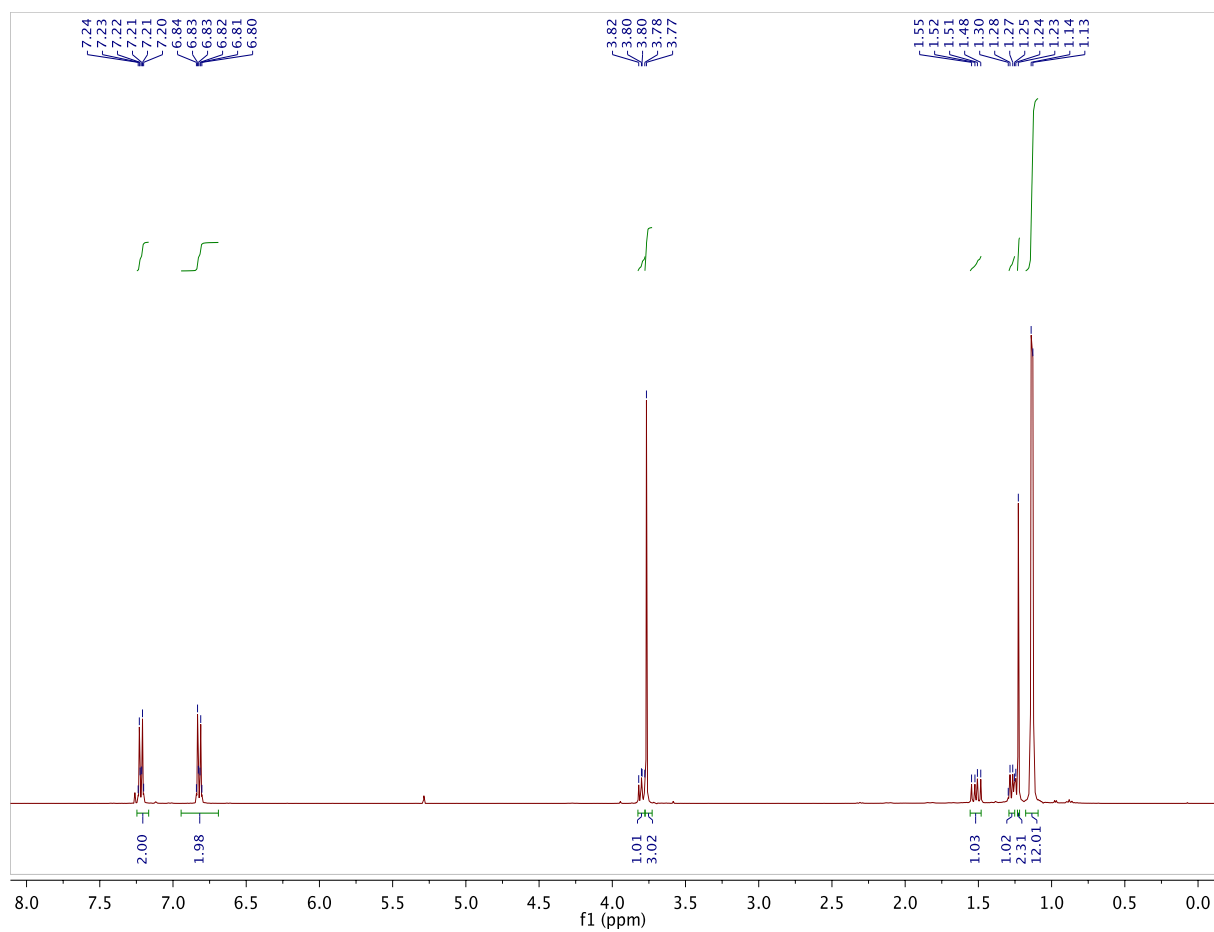
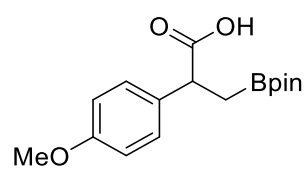
2f, $^{13}\text{C}\{^1\text{H}\}$ NMR



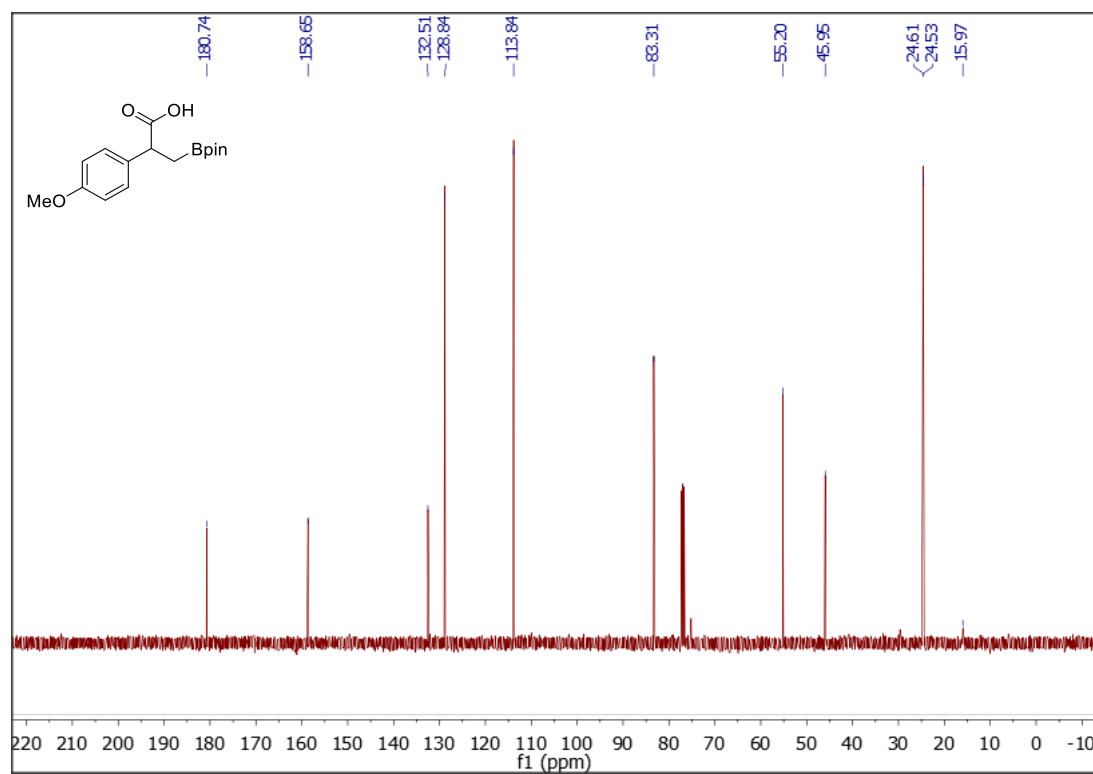
2f, ^{11}B NMR



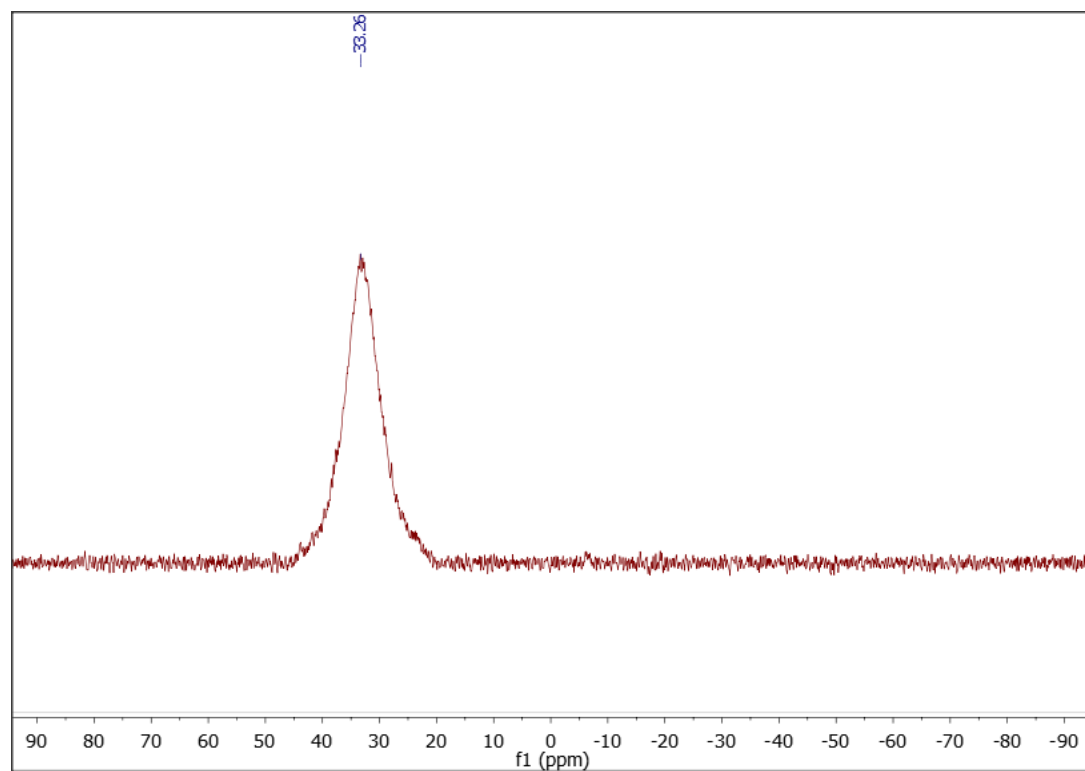
2g, ^1H NMR



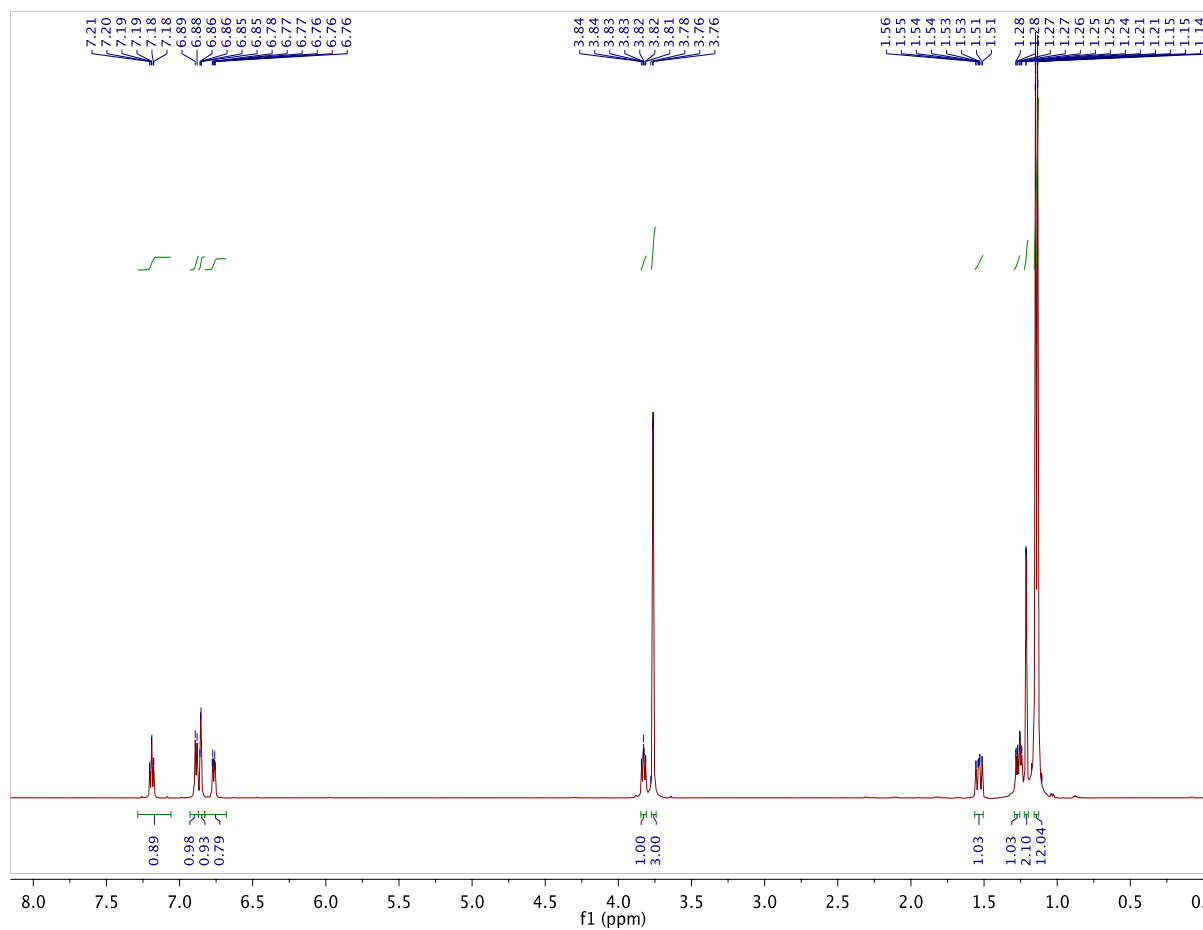
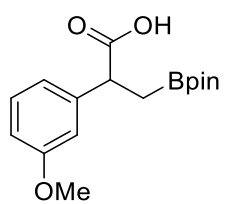
2g, $^{13}\text{C}\{^1\text{H}\}$ NMR



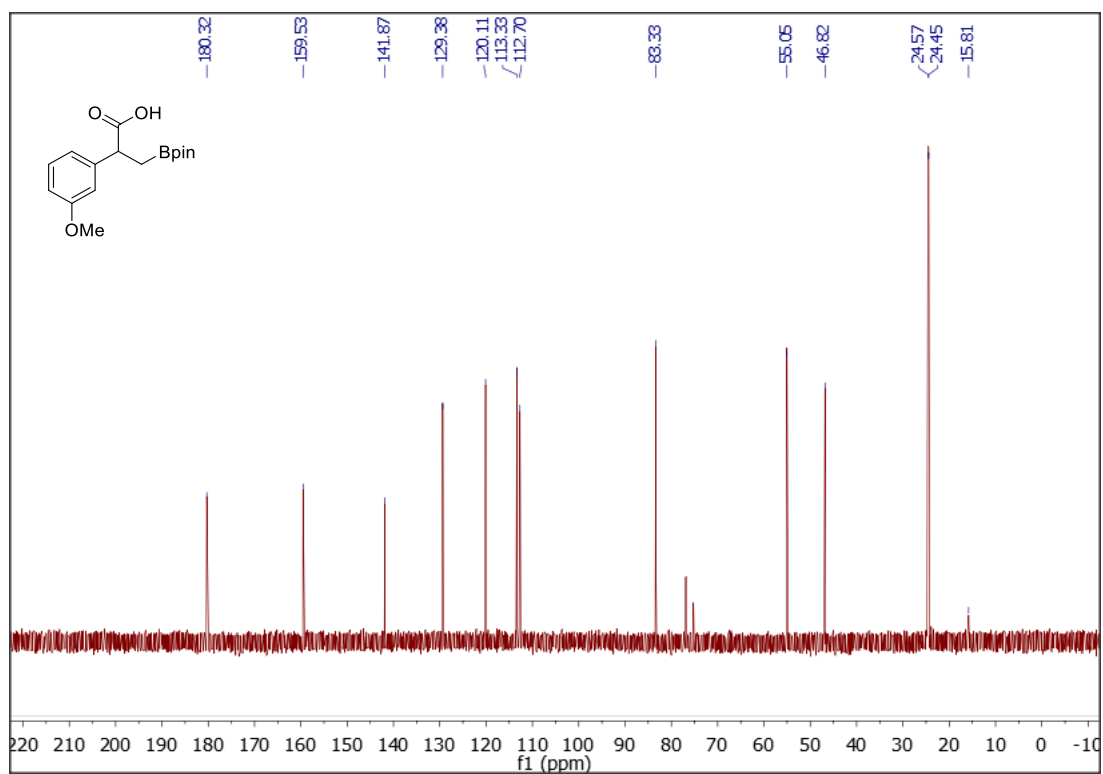
2g, ^{11}B NMR



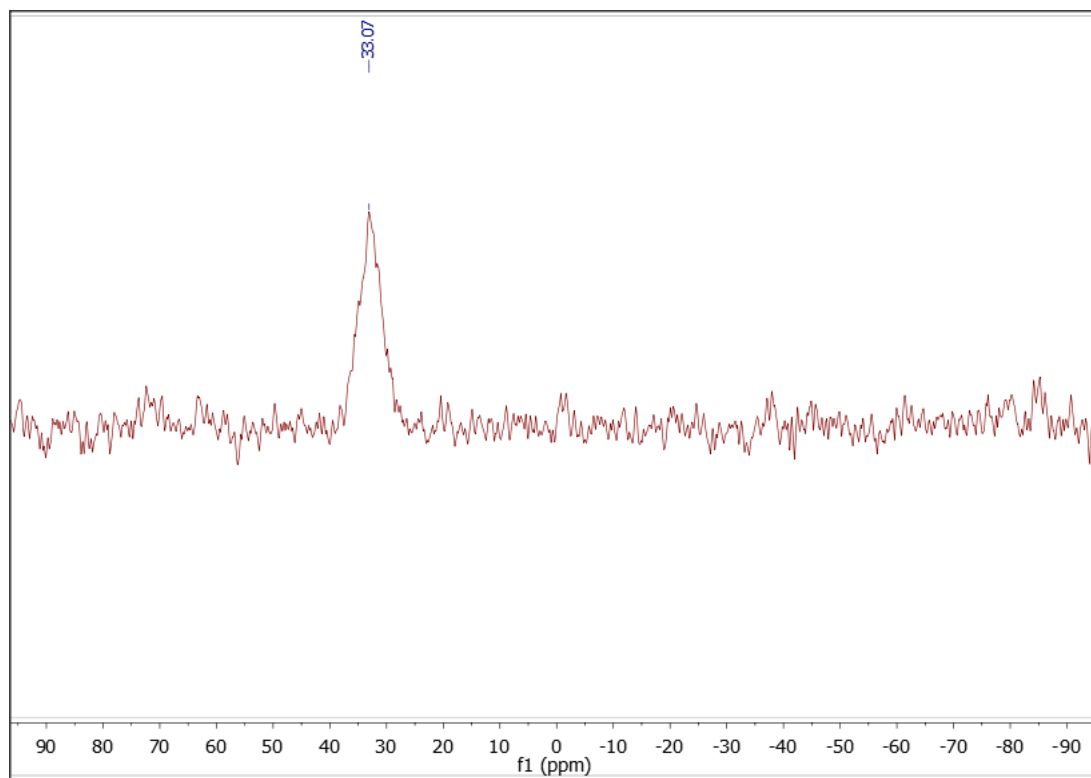
2h, ^1H NMR



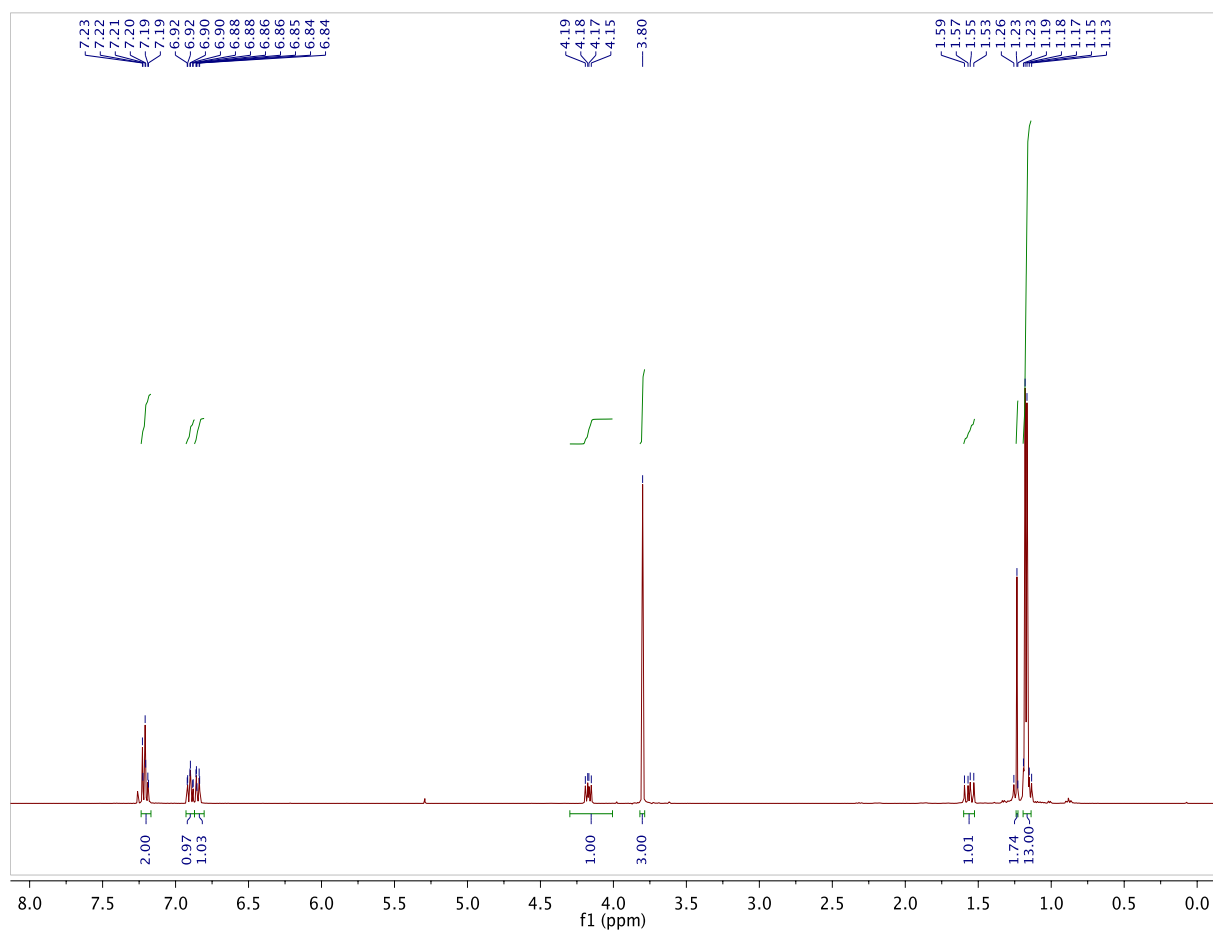
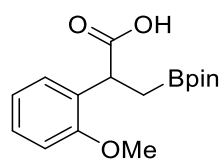
2h, $^{13}\text{C}\{^1\text{H}\}$ NMR



2h, ^{11}B NMR



2i, ^1H NMR

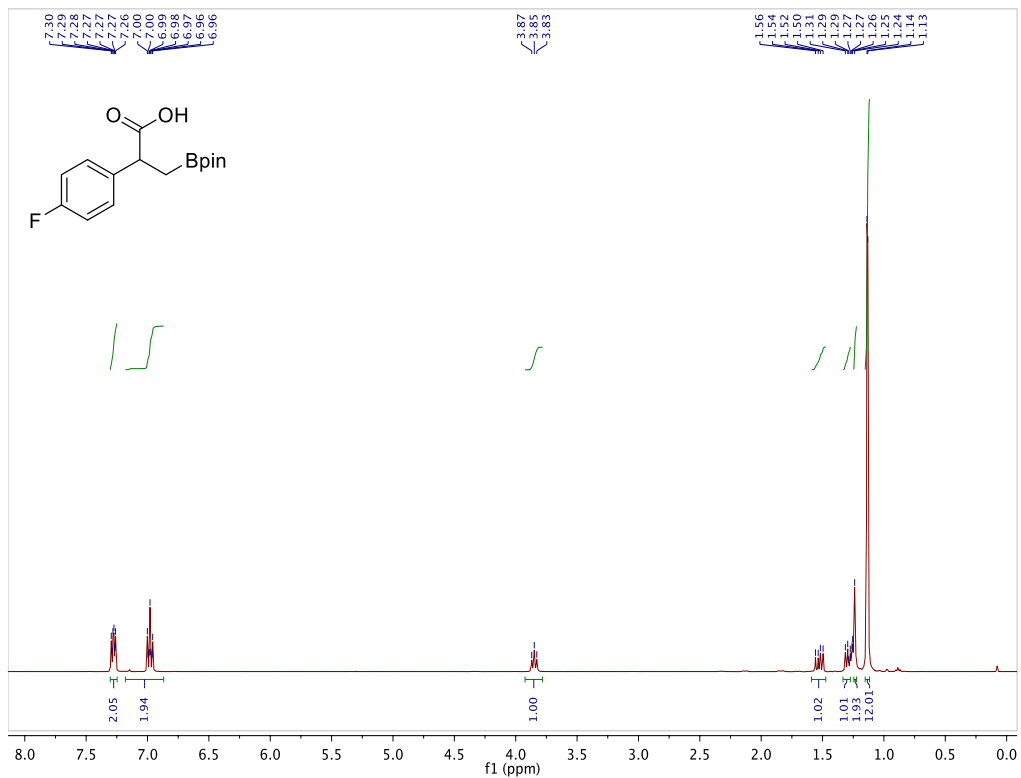


¹³C, ¹H NMR

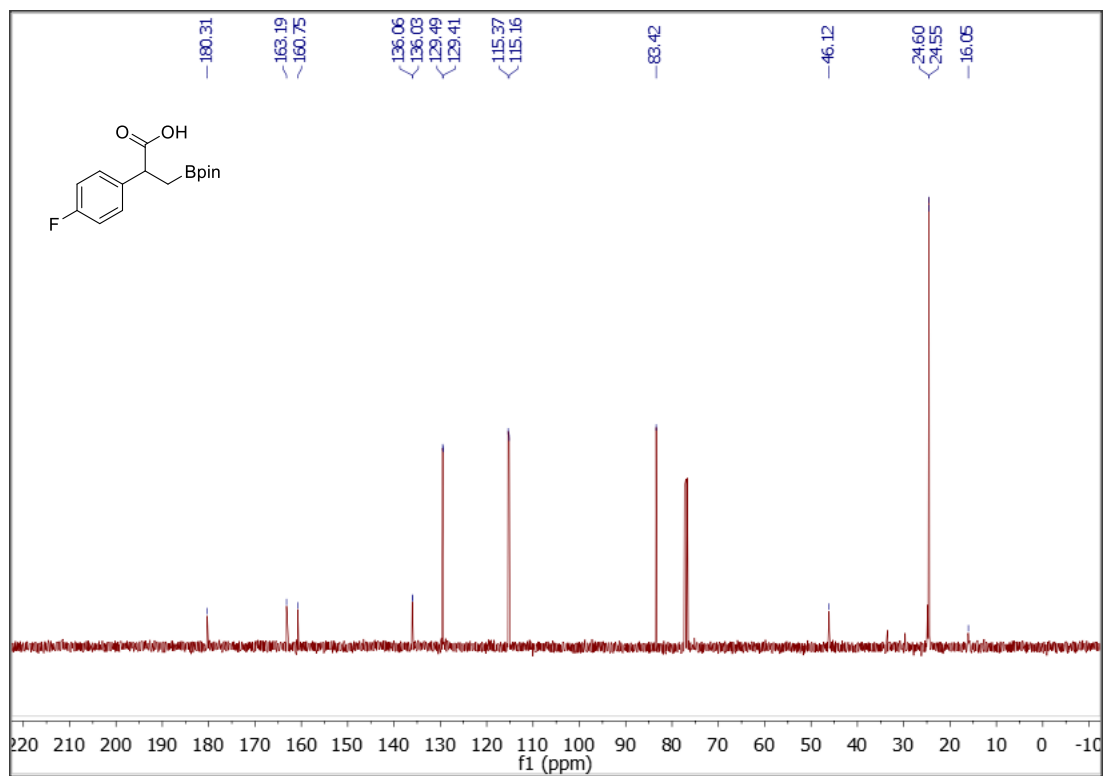
Chemical structure: COc1ccccc1C(O)(C)CC(=O)O

Chemical shift values (ppm): 180.32, 156.69, 129.59, 128.72, 128.13, 120.68, 110.80, 83.19, 55.41, 41.38, 24.72, 24.55, 14.65.

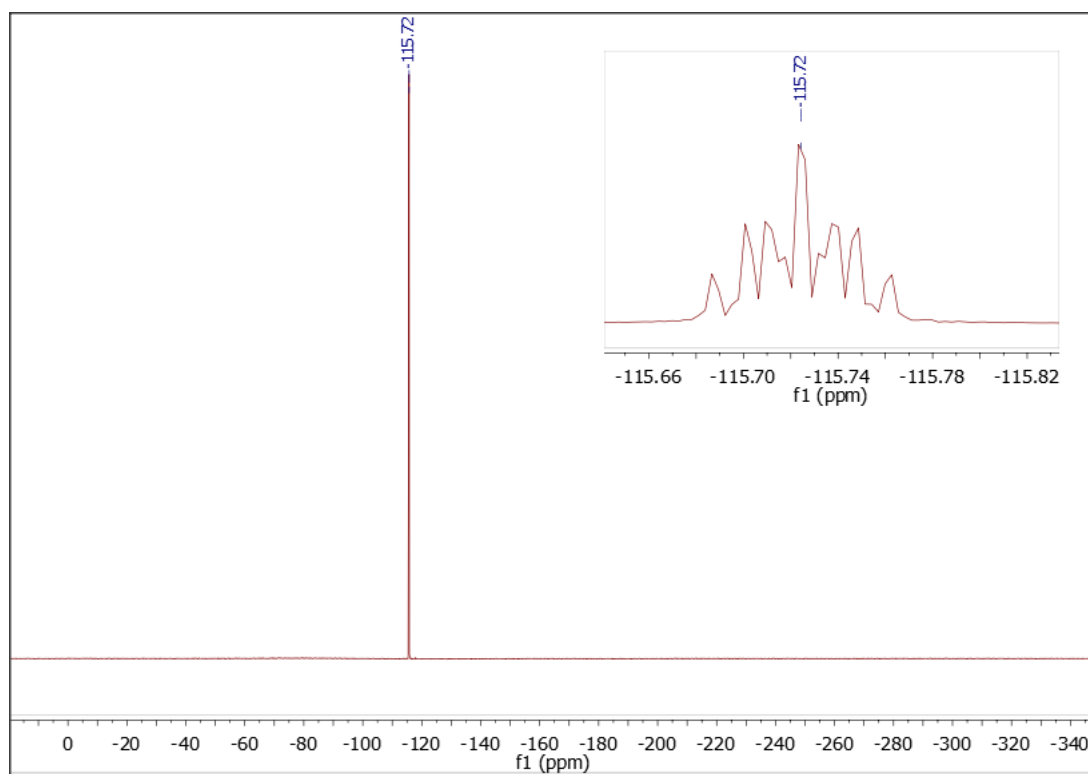
2j, ^1H NMR



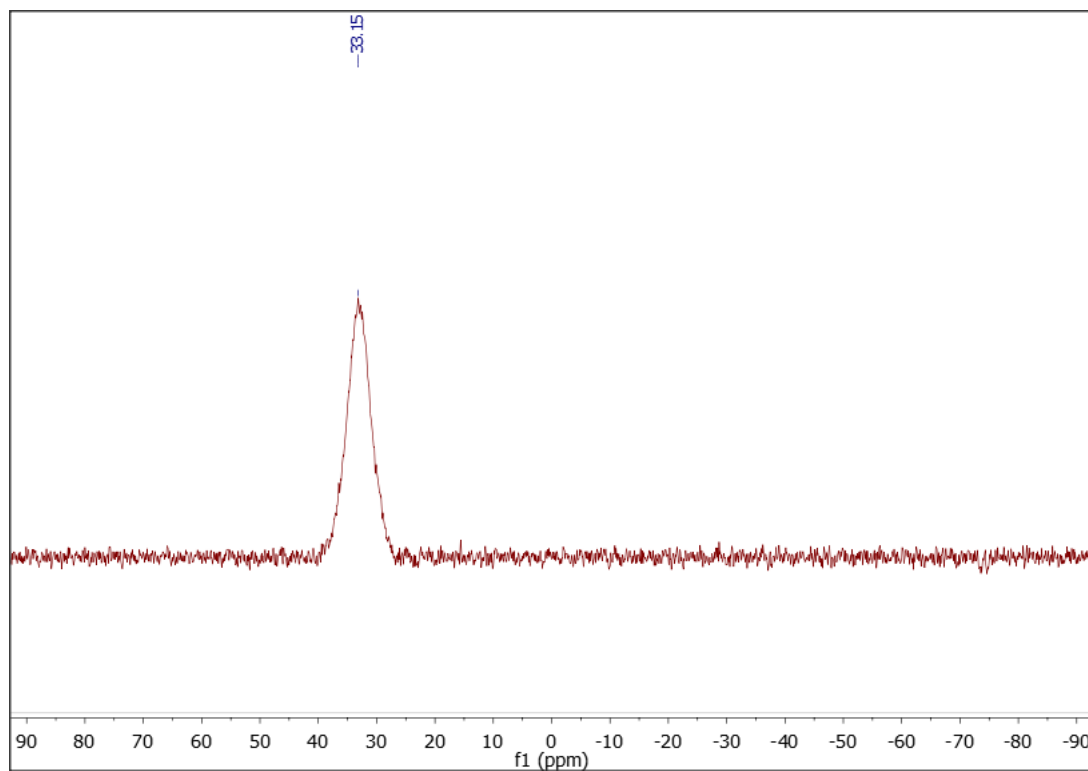
2j, $^{13}\text{C}\{^1\text{H}\}$ NMR



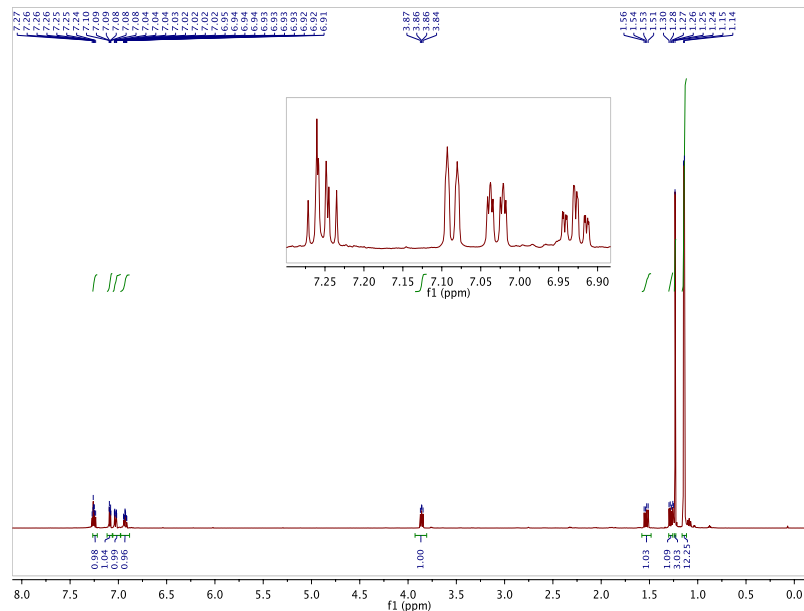
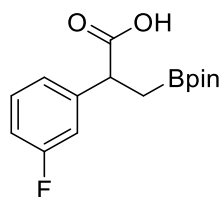
2j, ^{19}F NMR



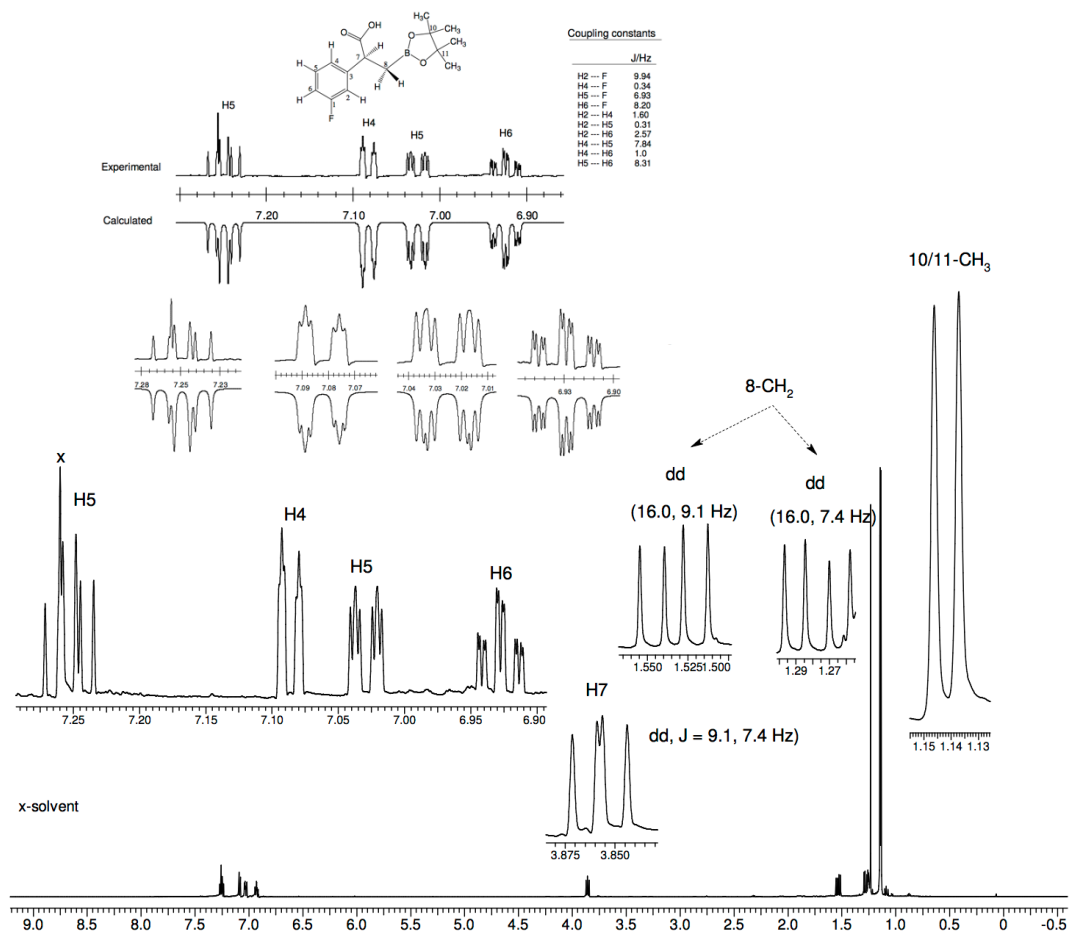
2j, ^{11}B NMR



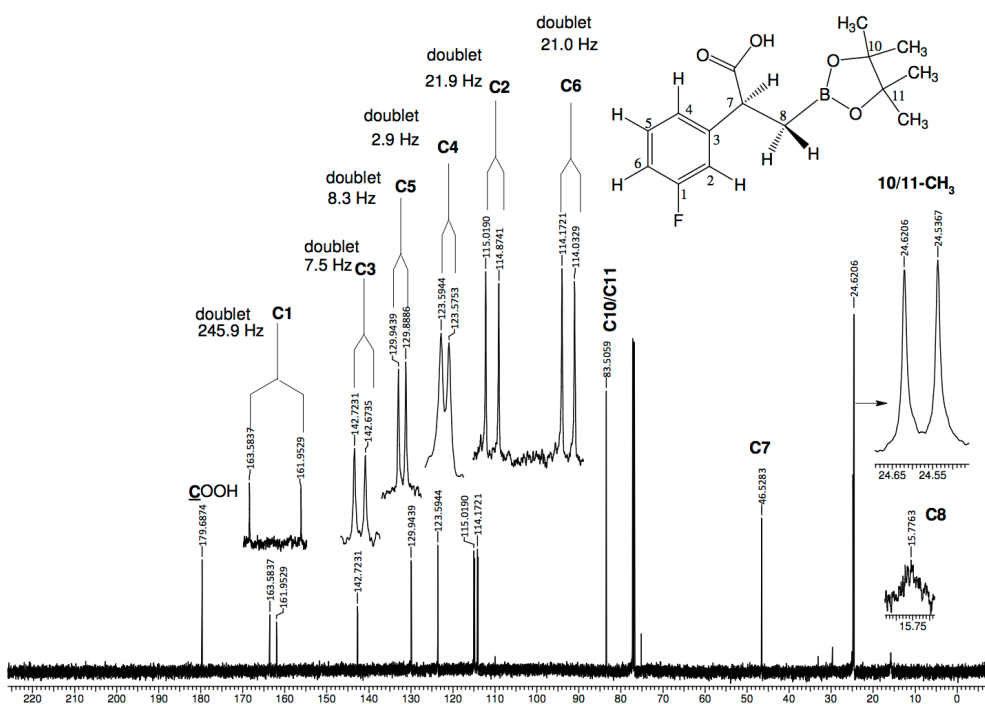
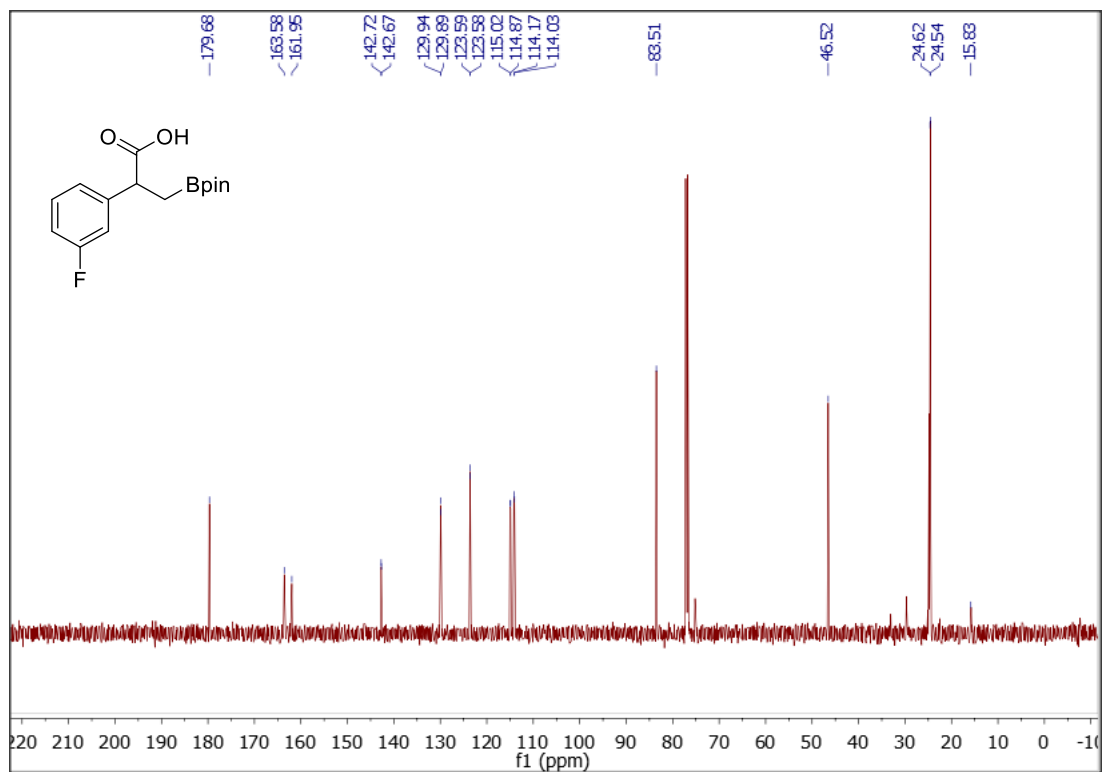
2k, ¹H NMR



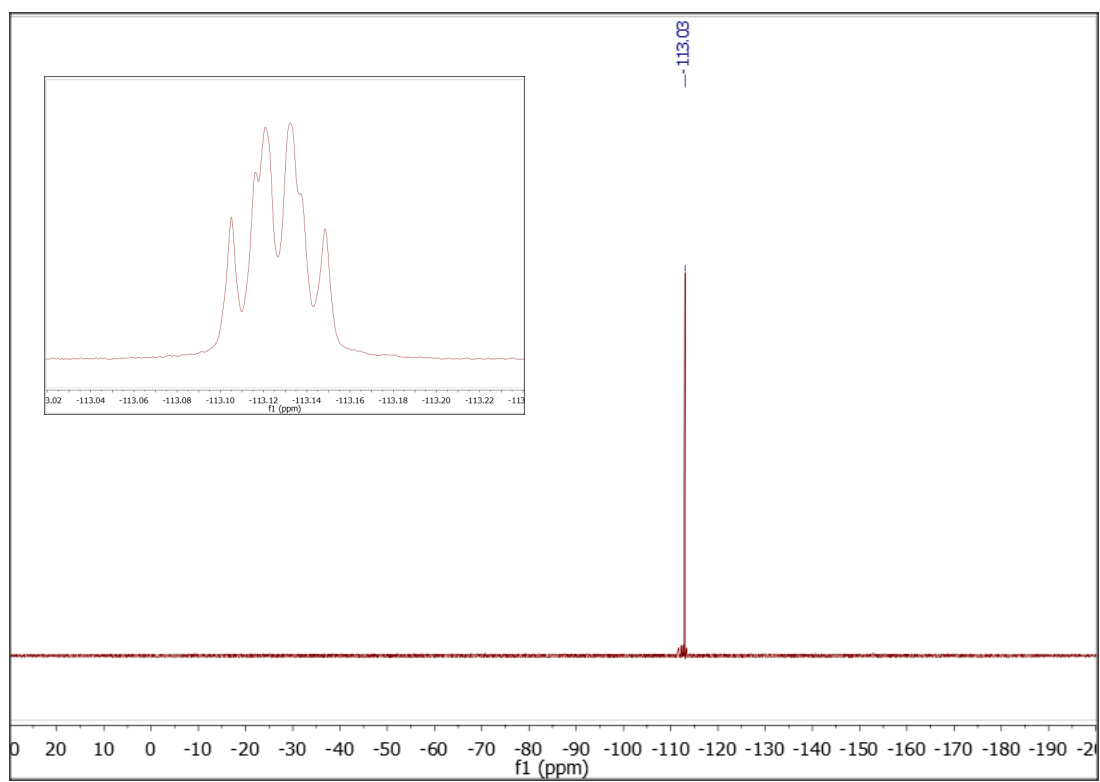
2k, ¹H NMR–J coupling analysis



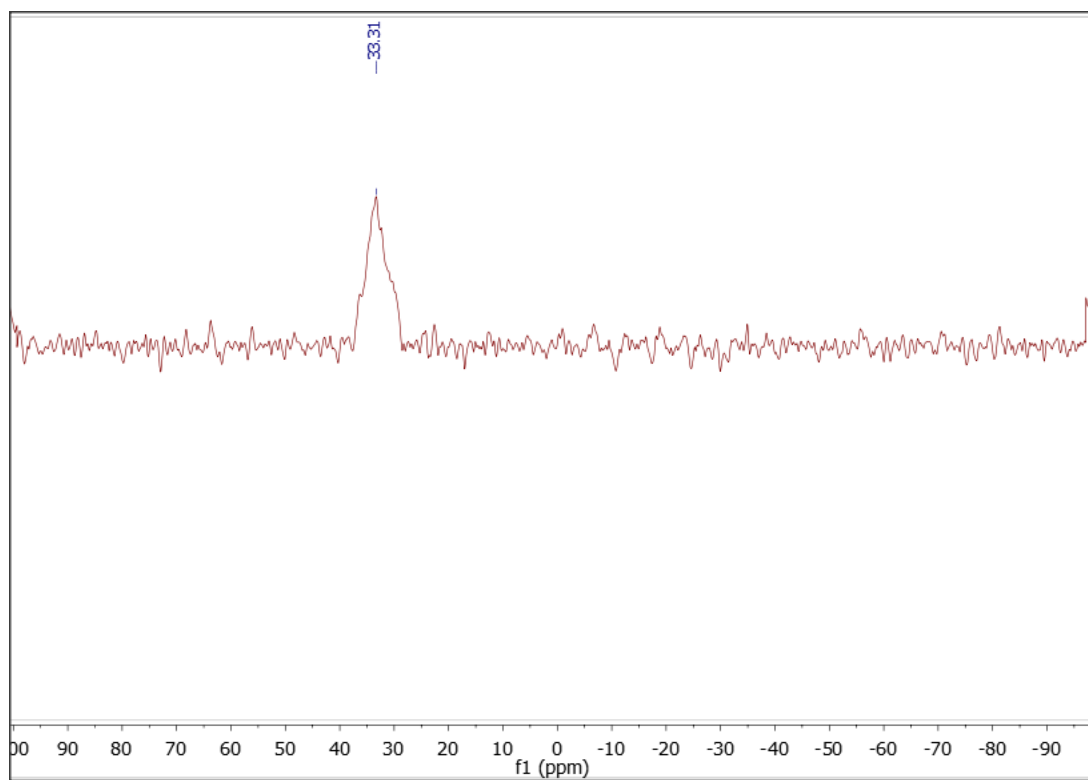
2k, $^{13}\text{C}\{^1\text{H}\}$ NMR



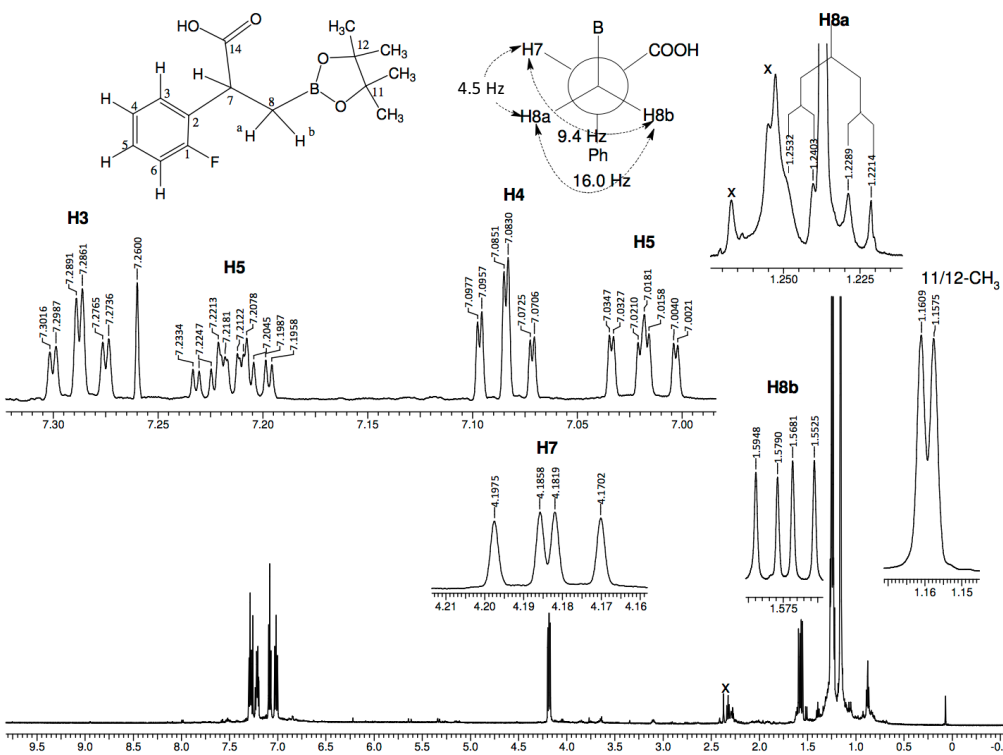
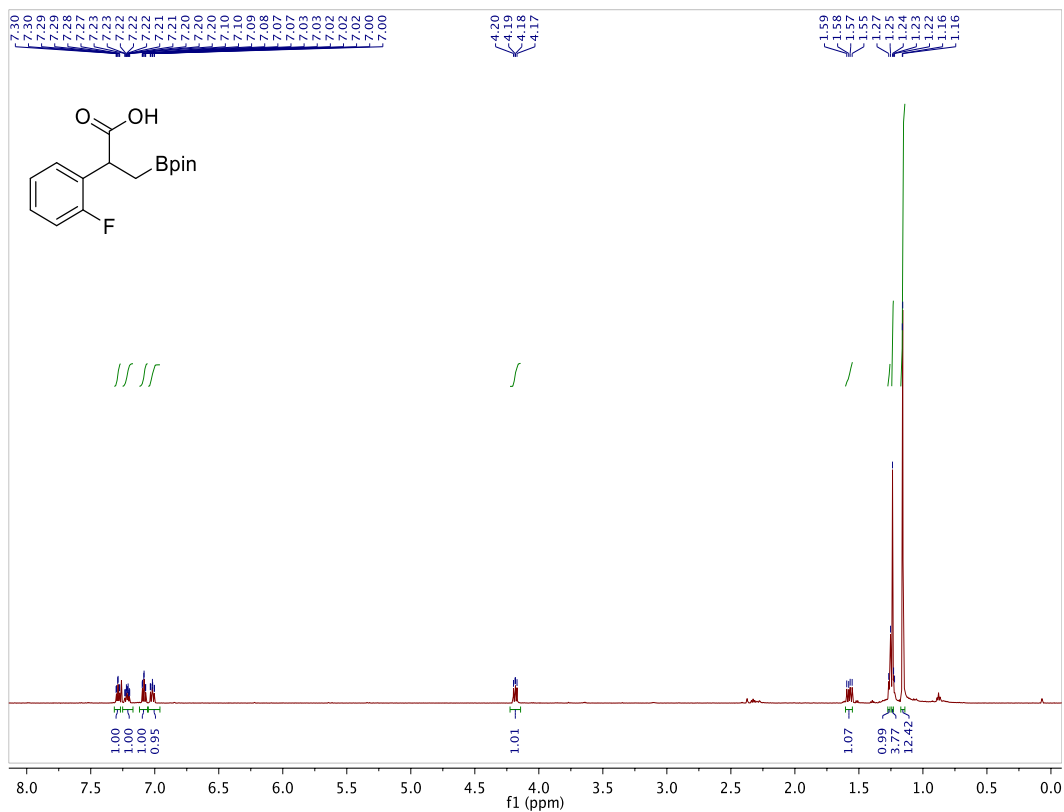
2k, ^{19}F NMR



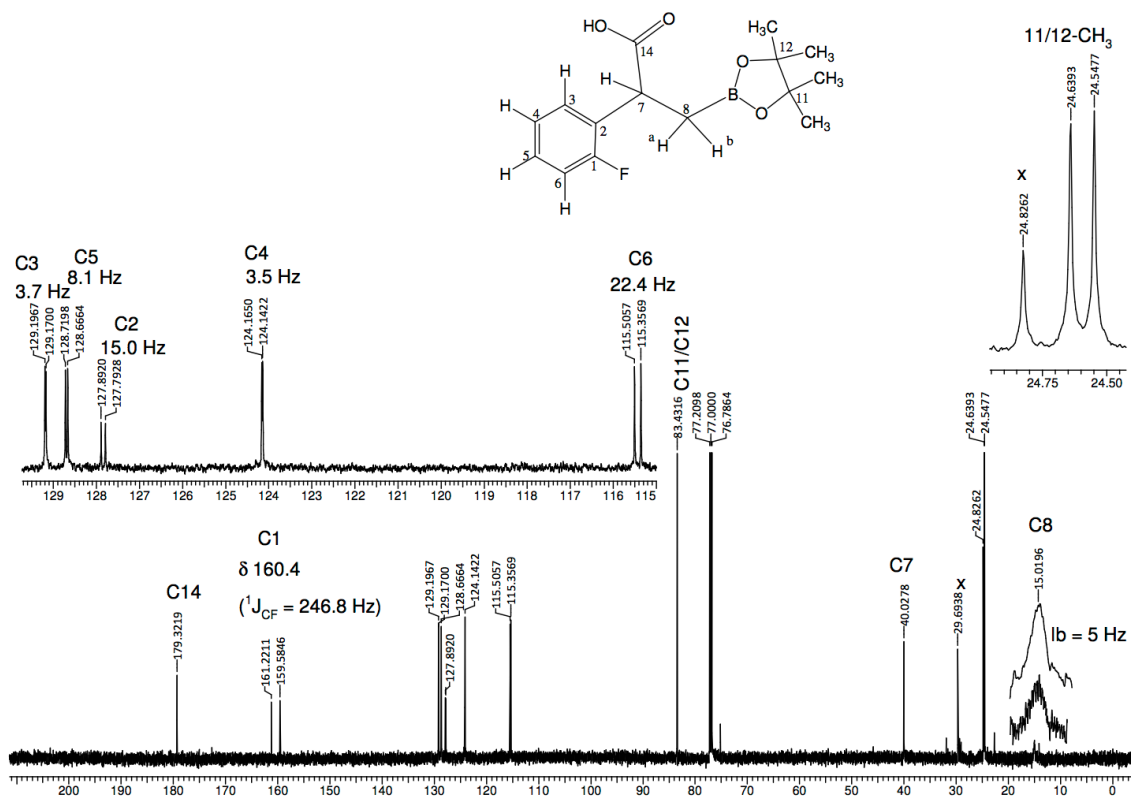
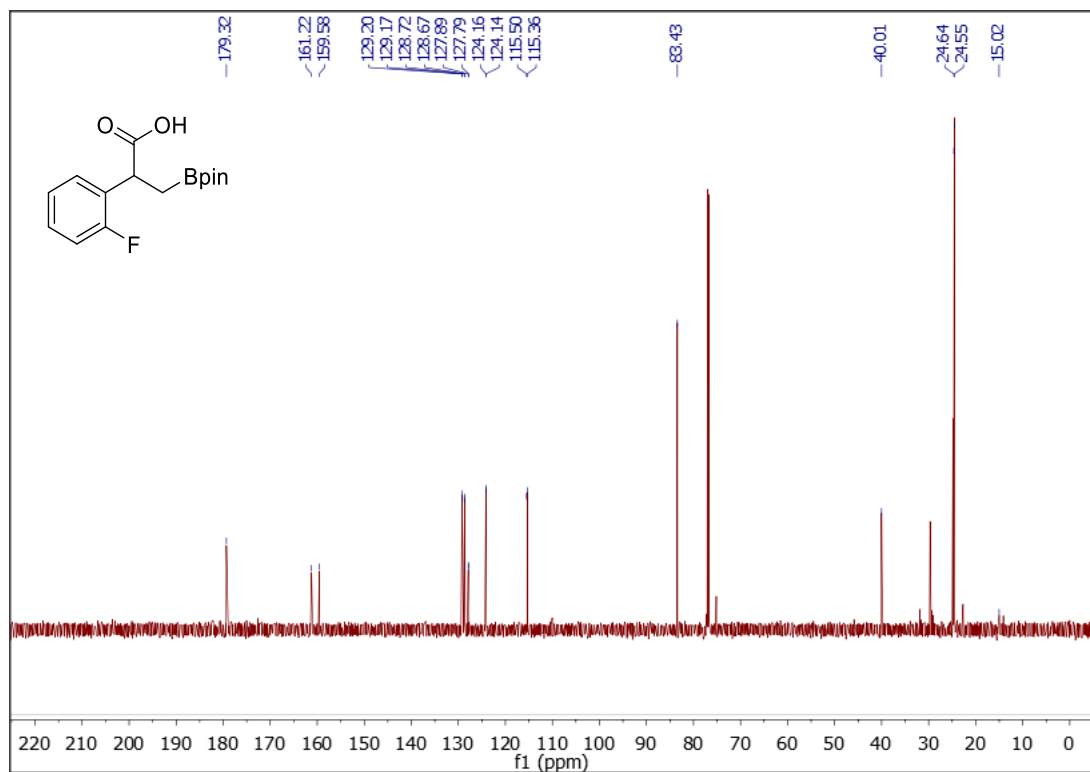
2k, ^{11}B NMR



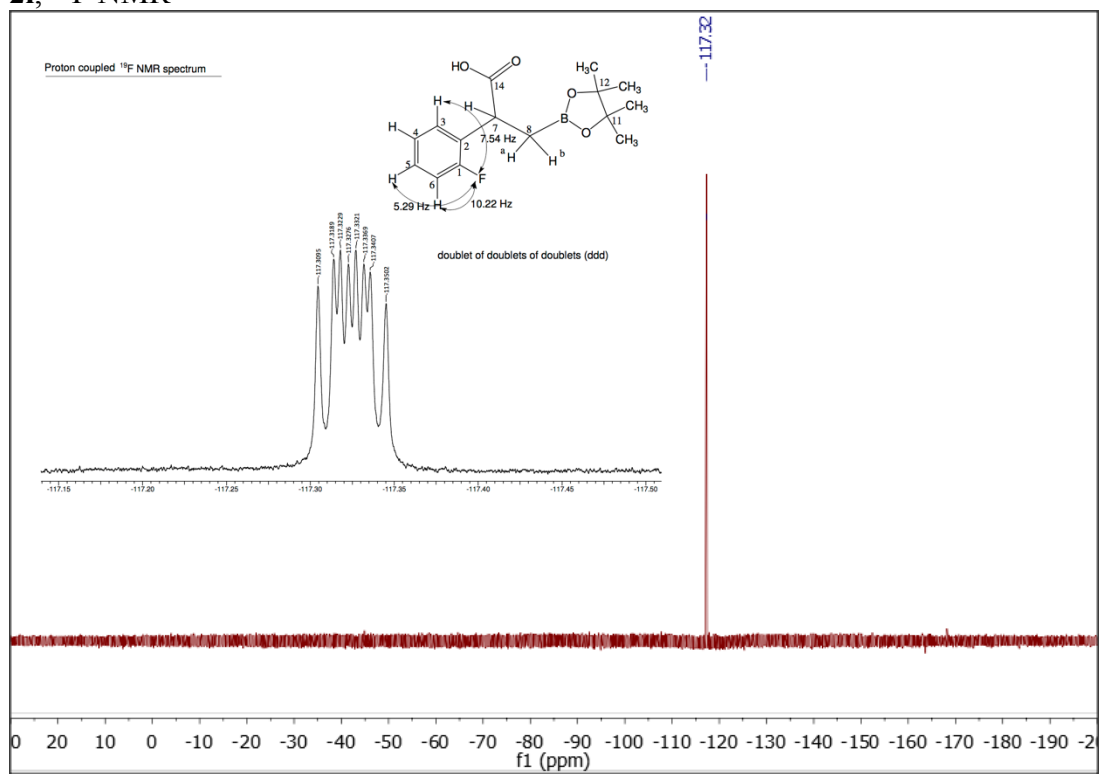
2l, ^1H NMR



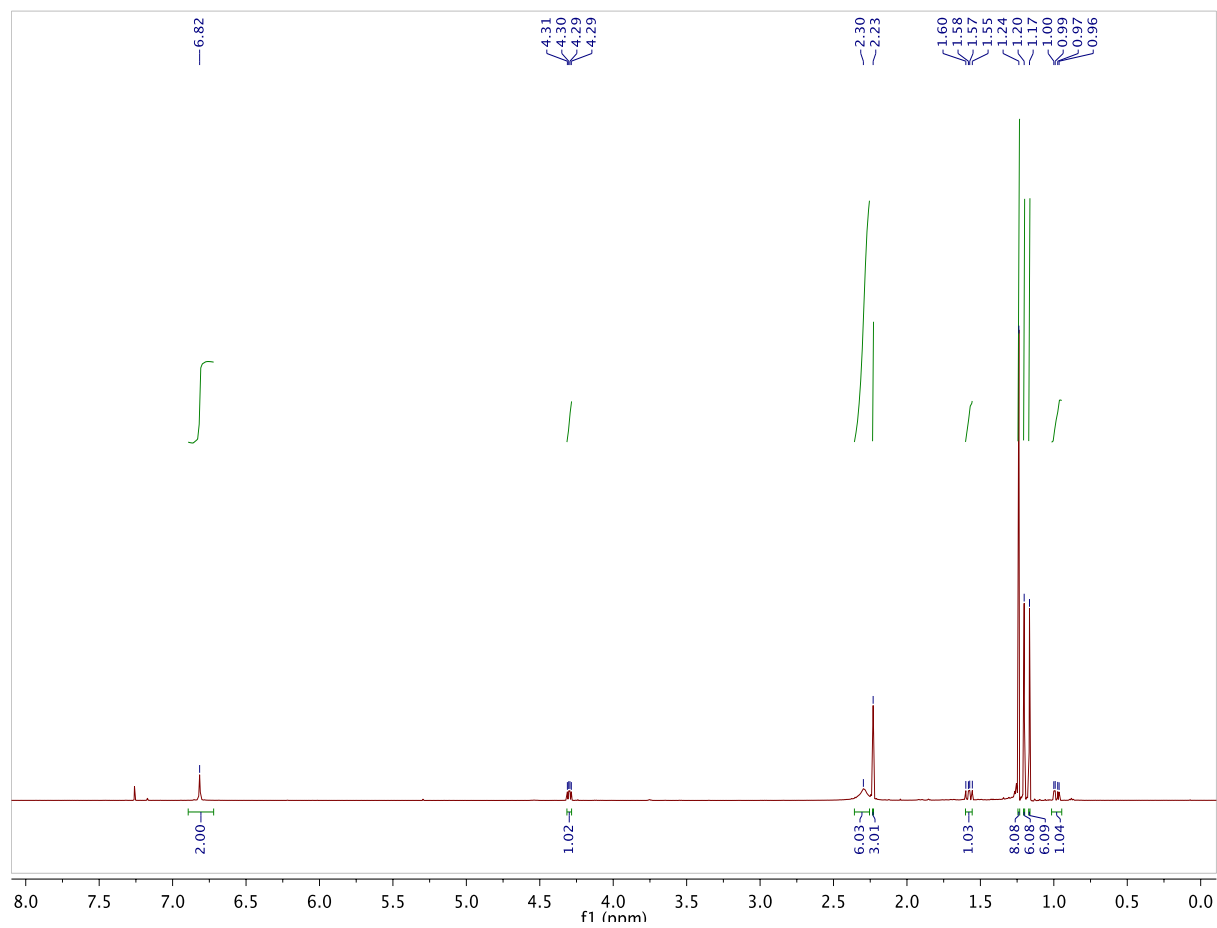
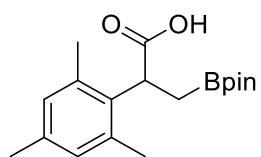
2l, $^{13}\text{C}\{^1\text{H}\}$ NMR



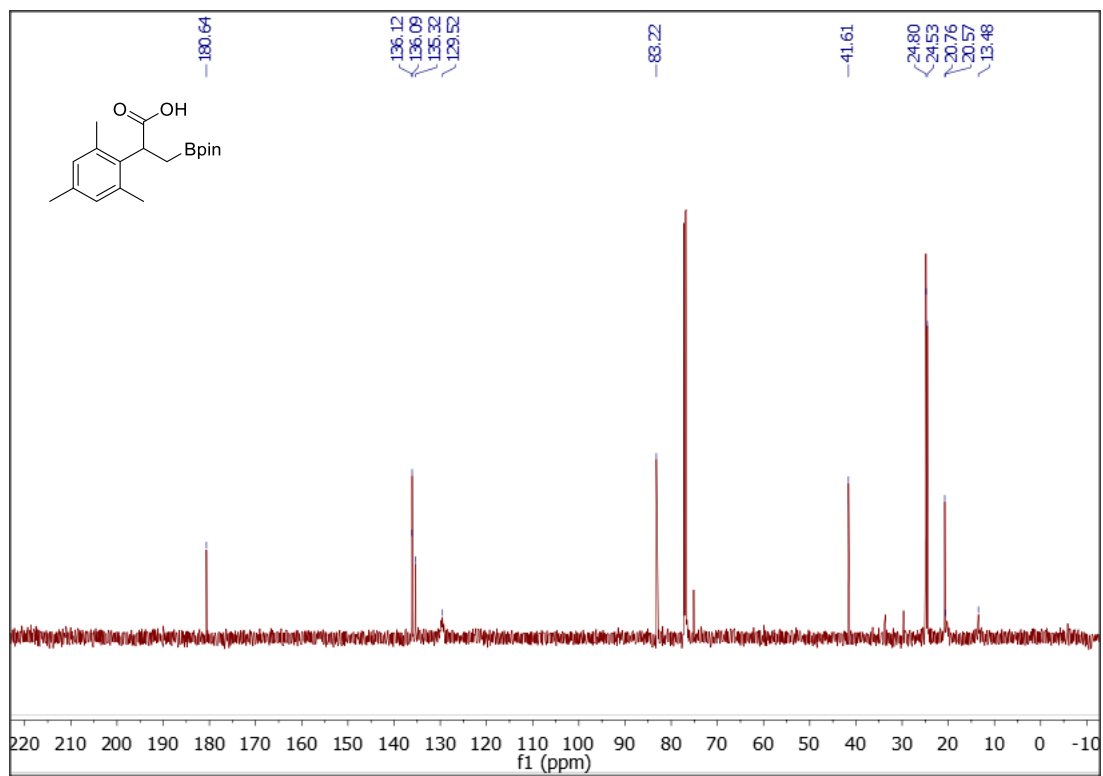
2l, ^{19}F NMR



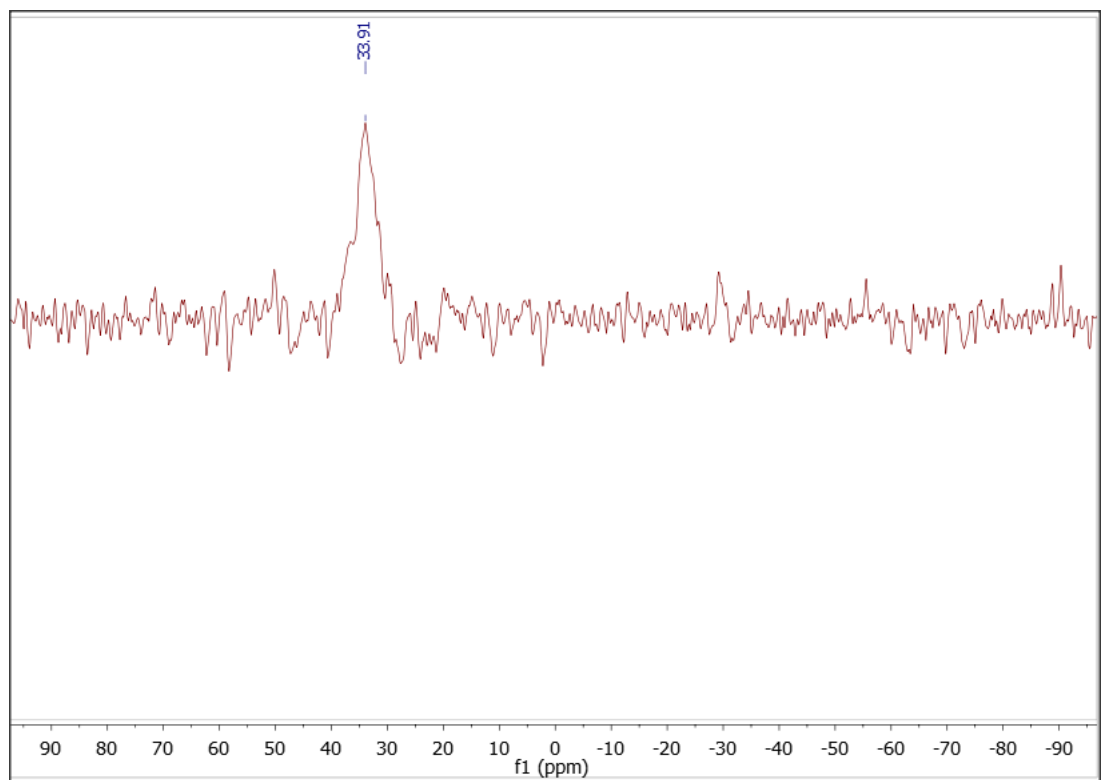
2m, ^1H NMR



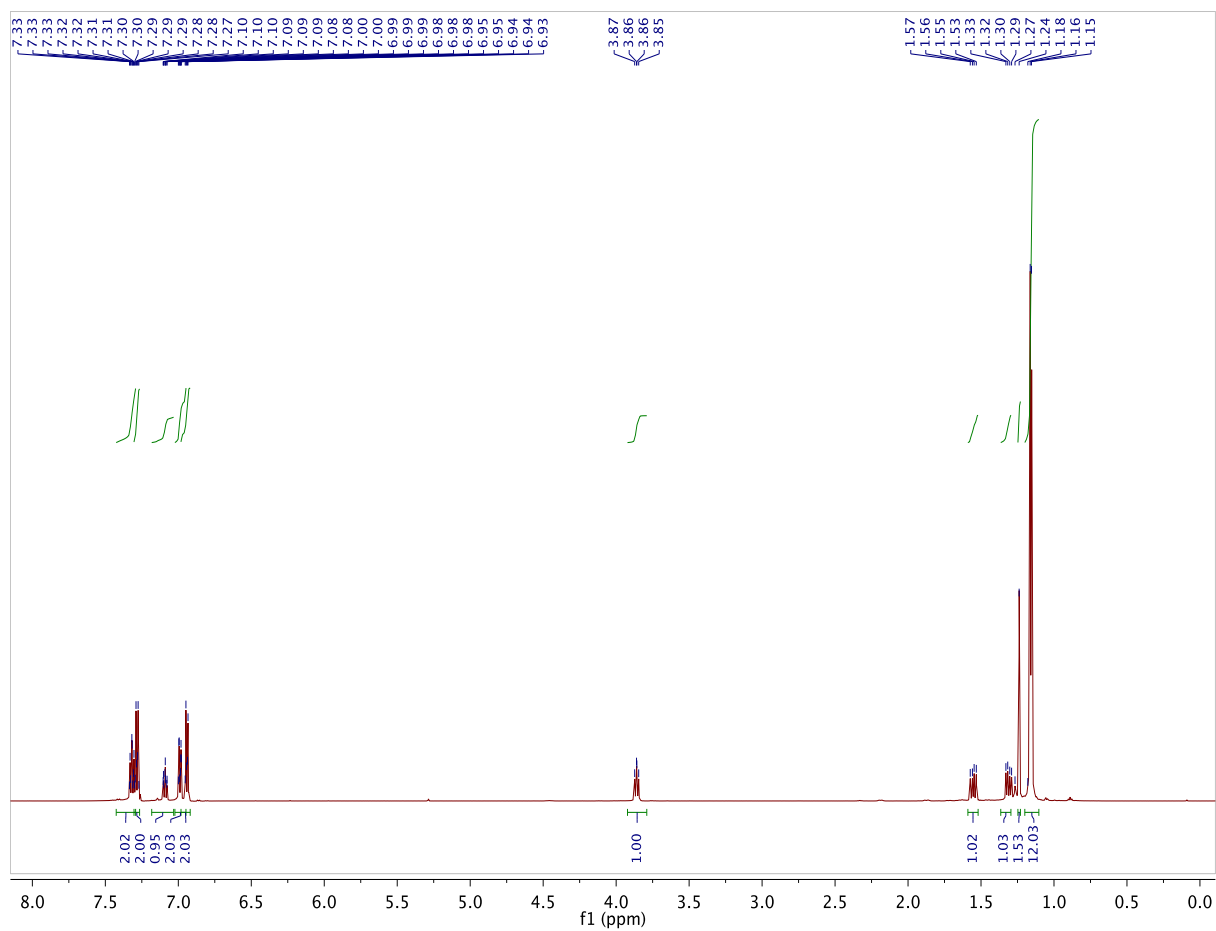
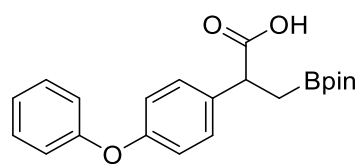
2m, $^{13}\text{C}\{^1\text{H}\}$ NMR



2m, ^{11}B NMR



2n, ^1H NMR

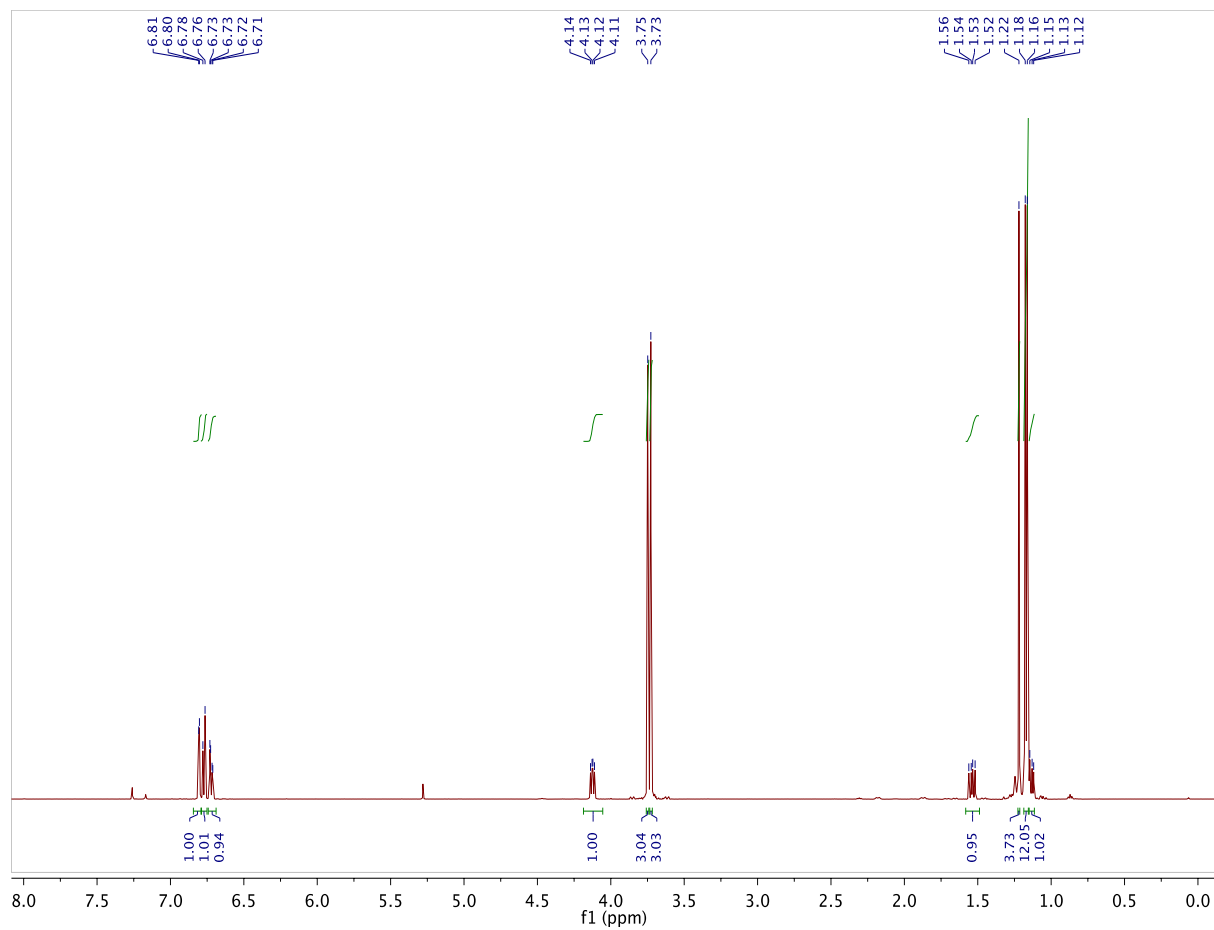
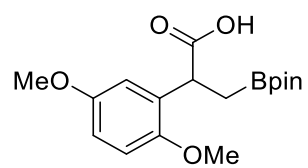


Chemical structure: O=C(O)C(c1ccc(Oc2ccccc2)cc1)C(B)(B)B

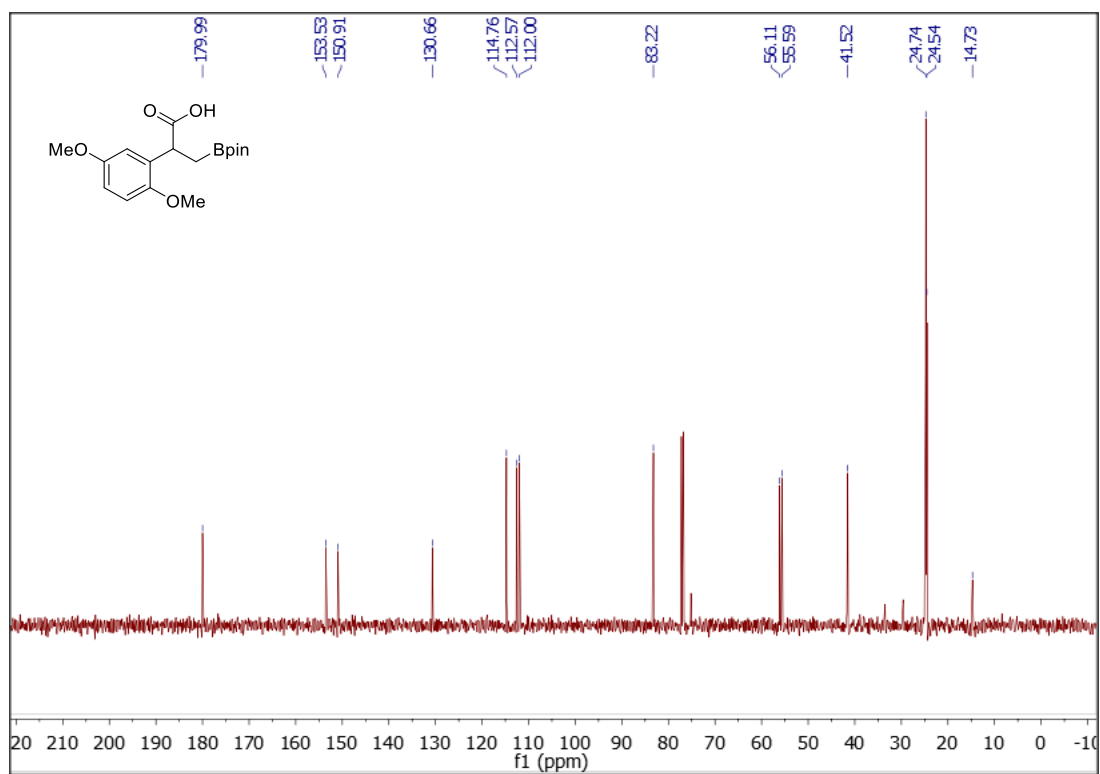
¹³C NMR peaks (ppm):

- 180.66
- 157.15
- 156.30
- 136.11
- 129.66
- 129.19
- 123.17
- 118.80
- 118.78
- 83.40
- 46.11
- 24.62
- 24.53
- 15.90

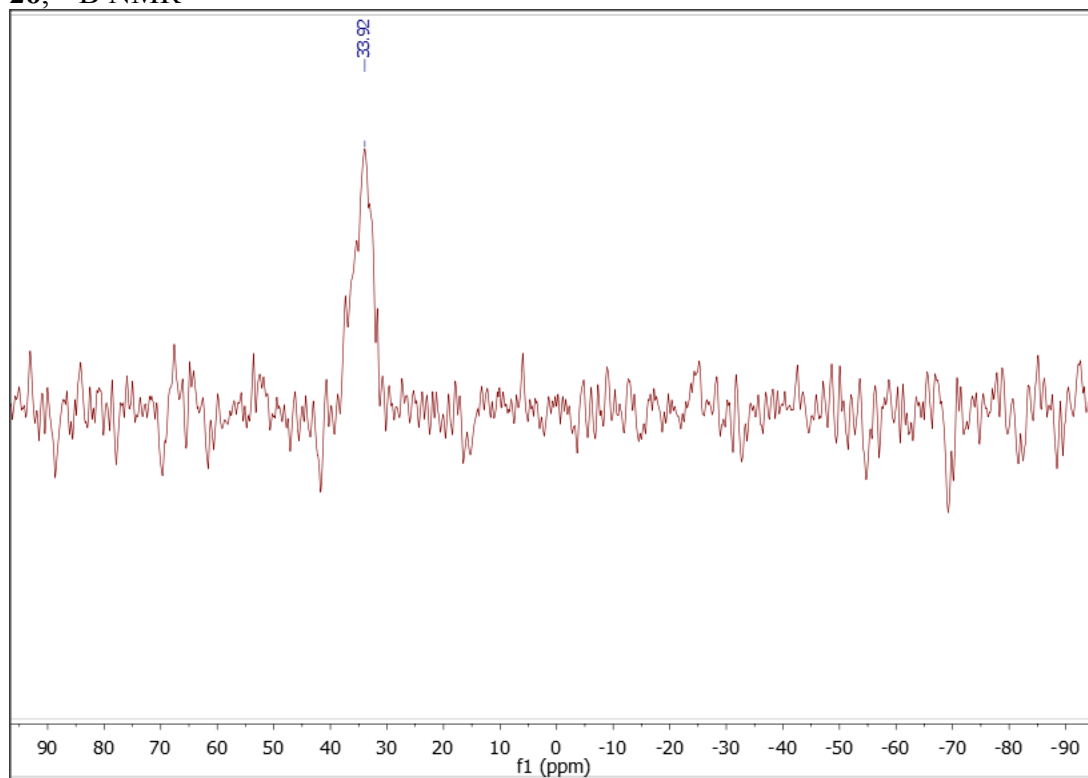
2o, ^1H NMR



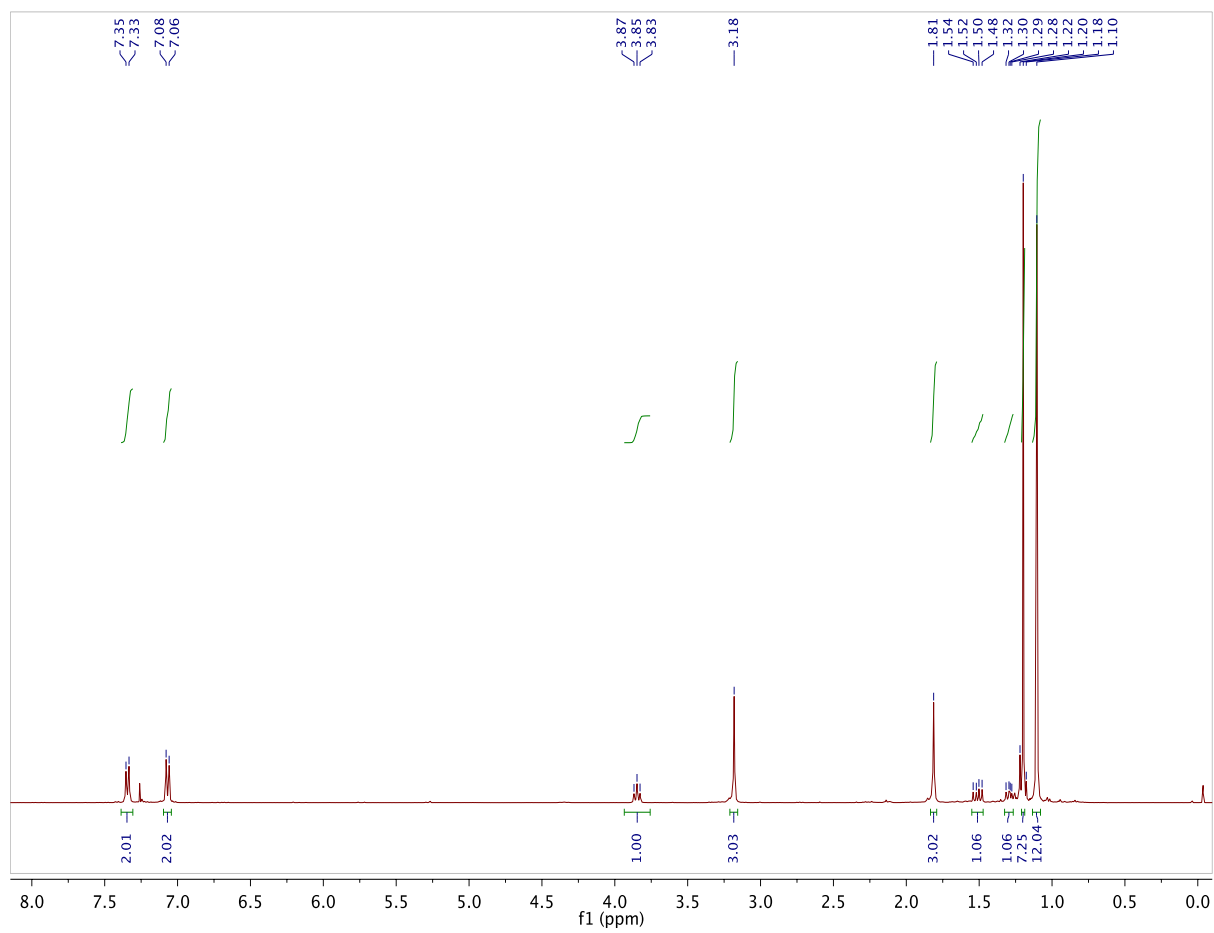
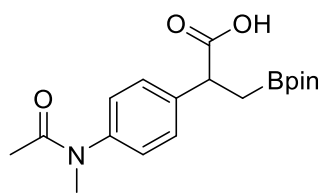
2o, $^{13}\text{C}\{^1\text{H}\}$ NMR



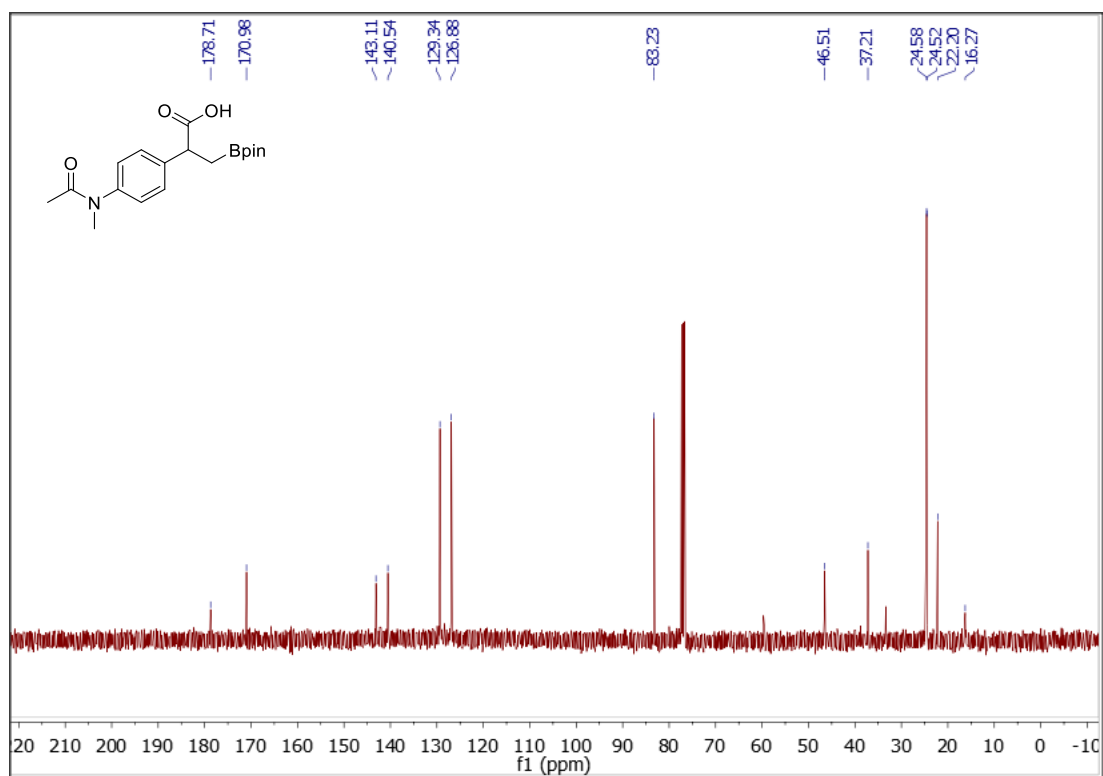
2o, ^{11}B NMR



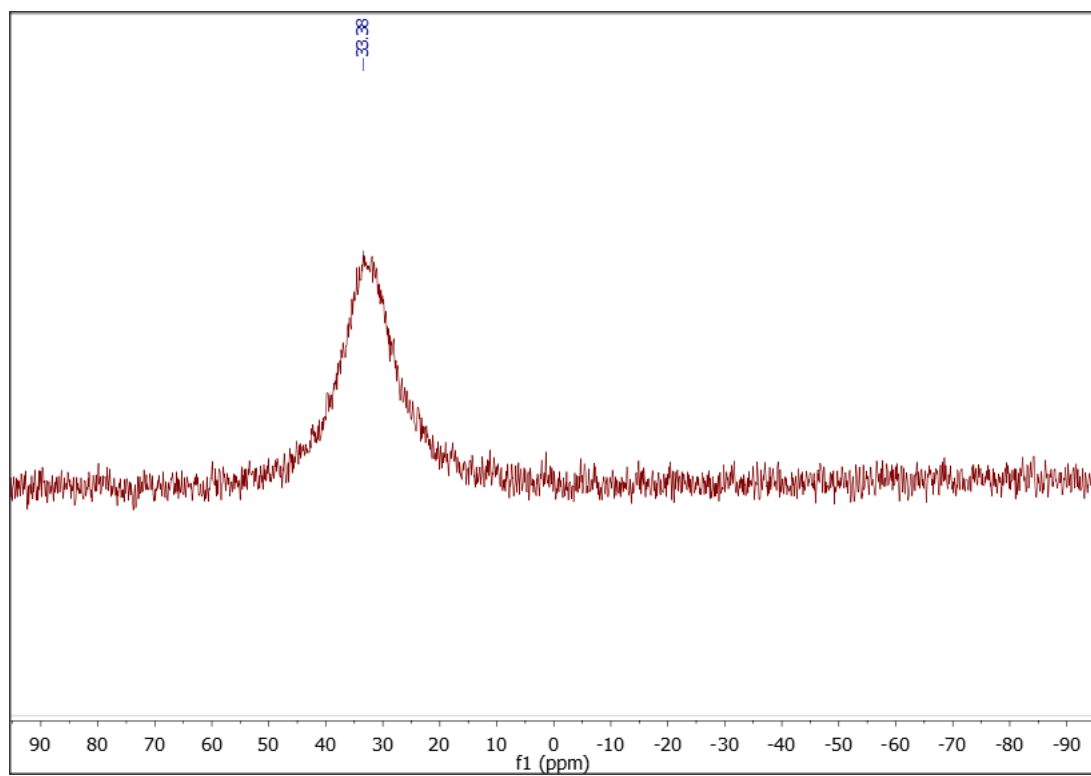
2p, ^1H NMR



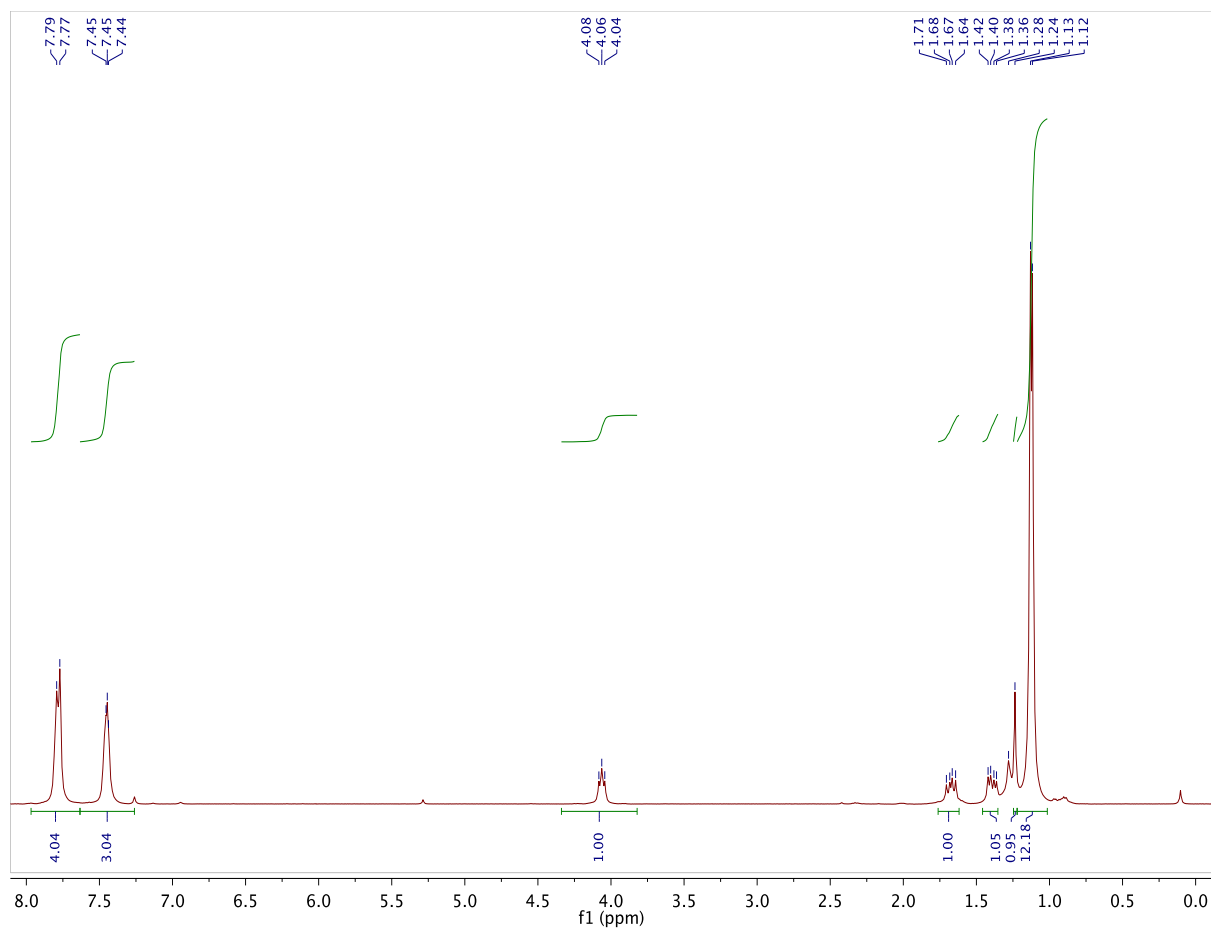
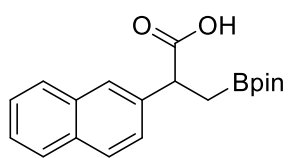
2p, $^{13}\text{C}\{^1\text{H}\}$ NMR



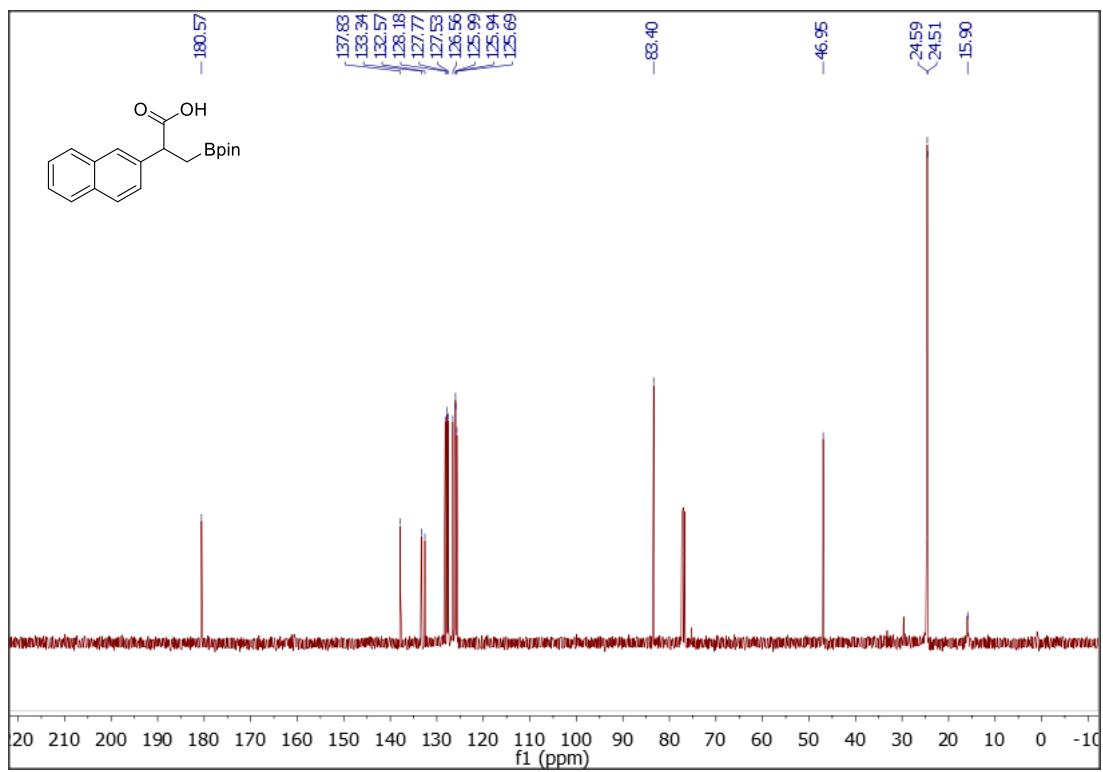
2p, ^{11}B NMR



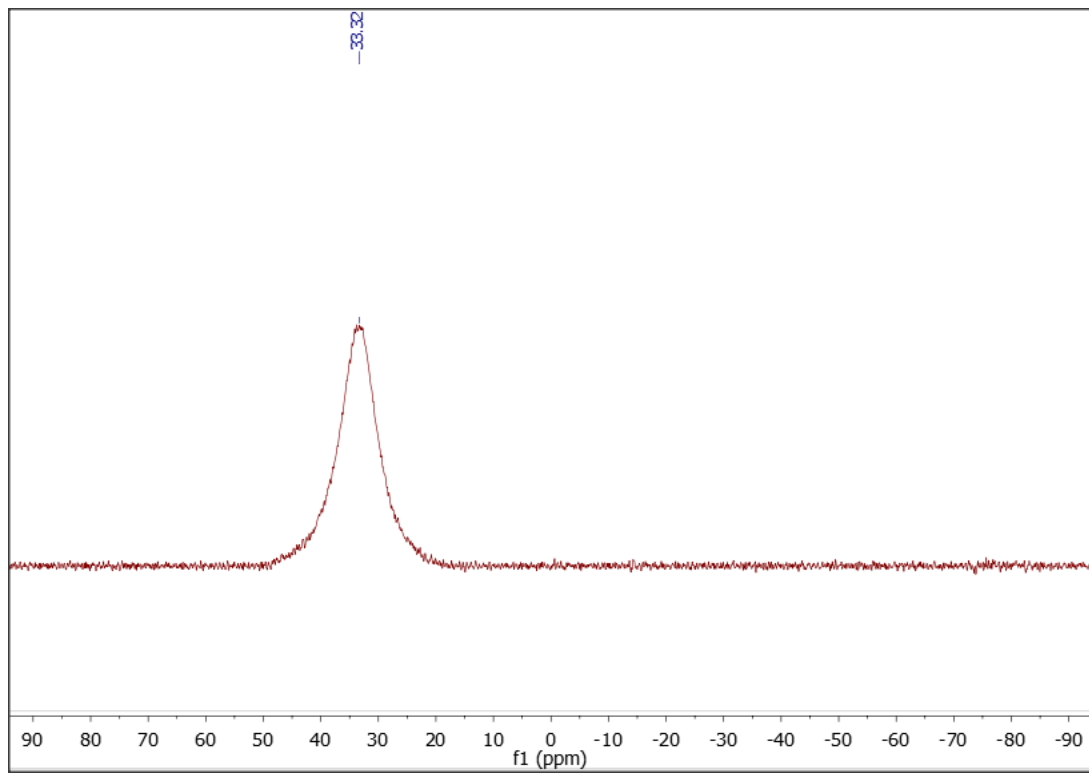
2q, ^1H NMR



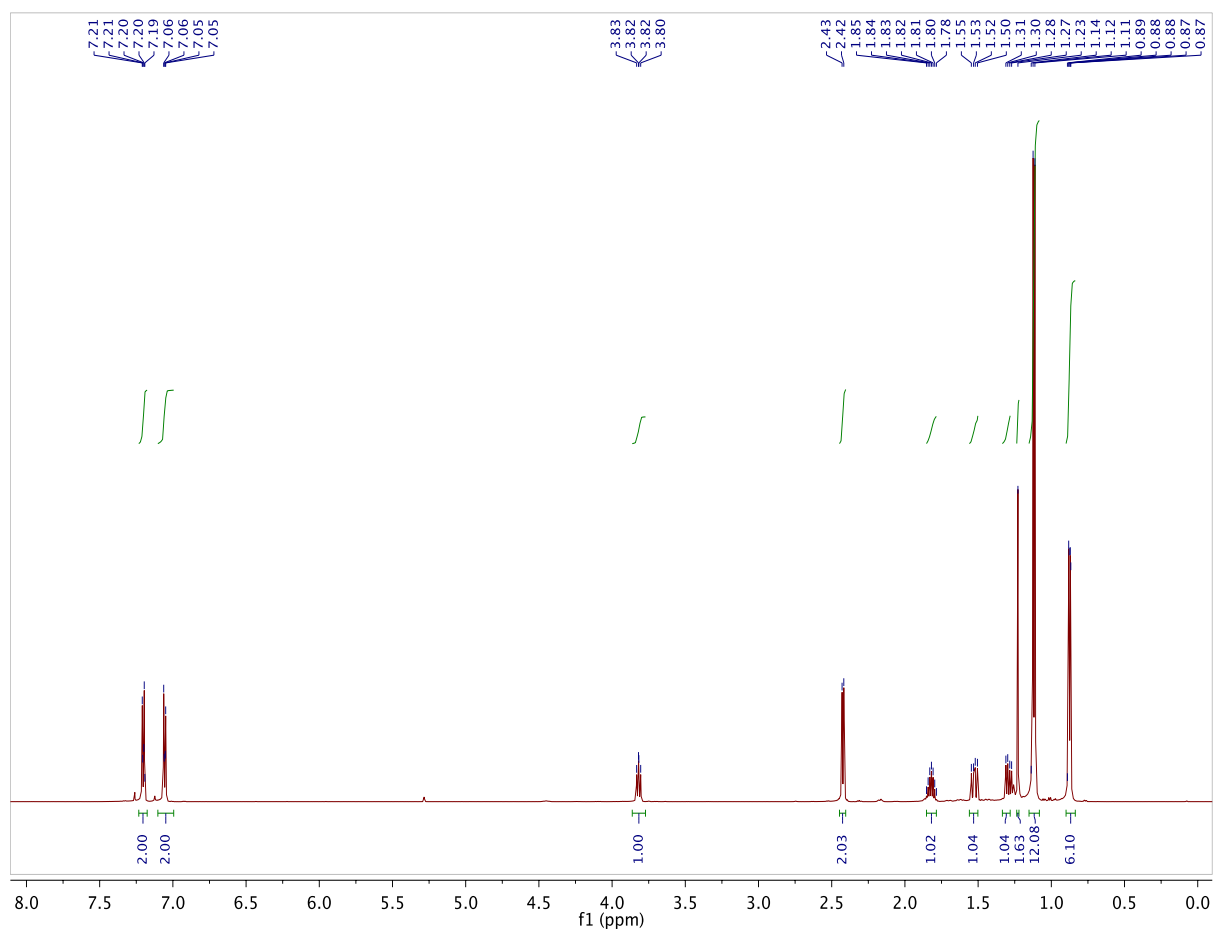
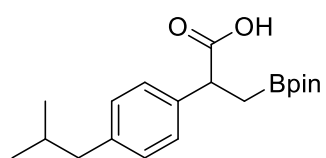
2q, $^{13}\text{C}\{^1\text{H}\}$ NMR



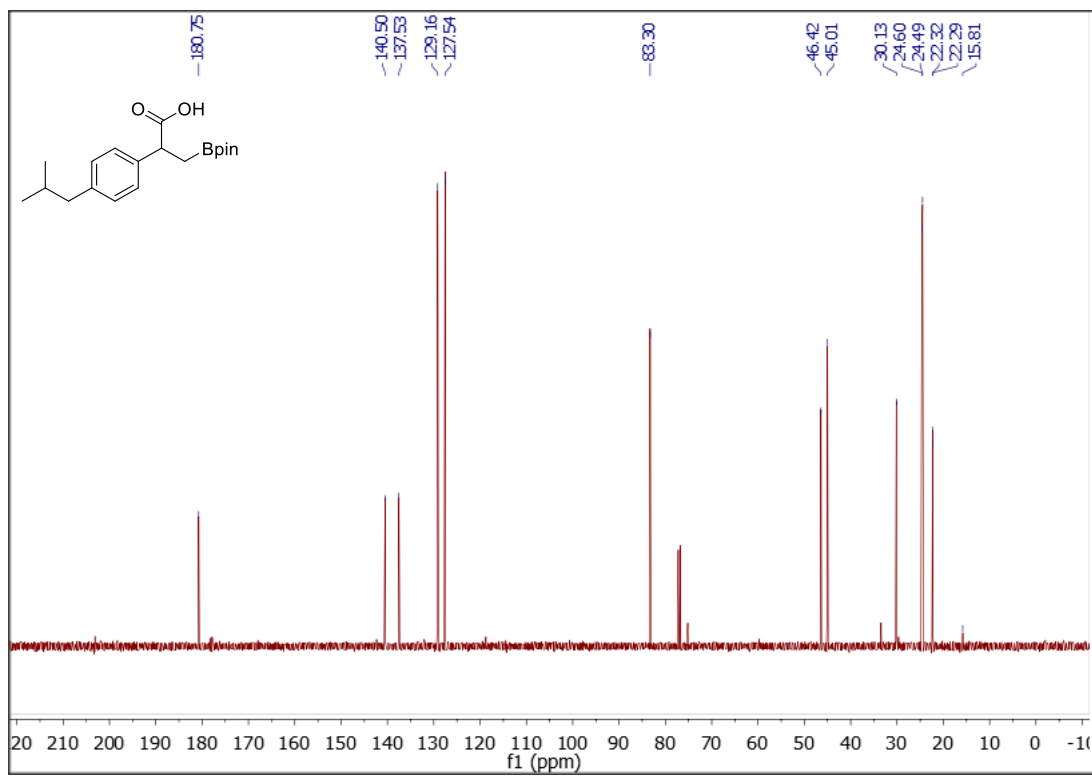
2p, ¹¹B NMR



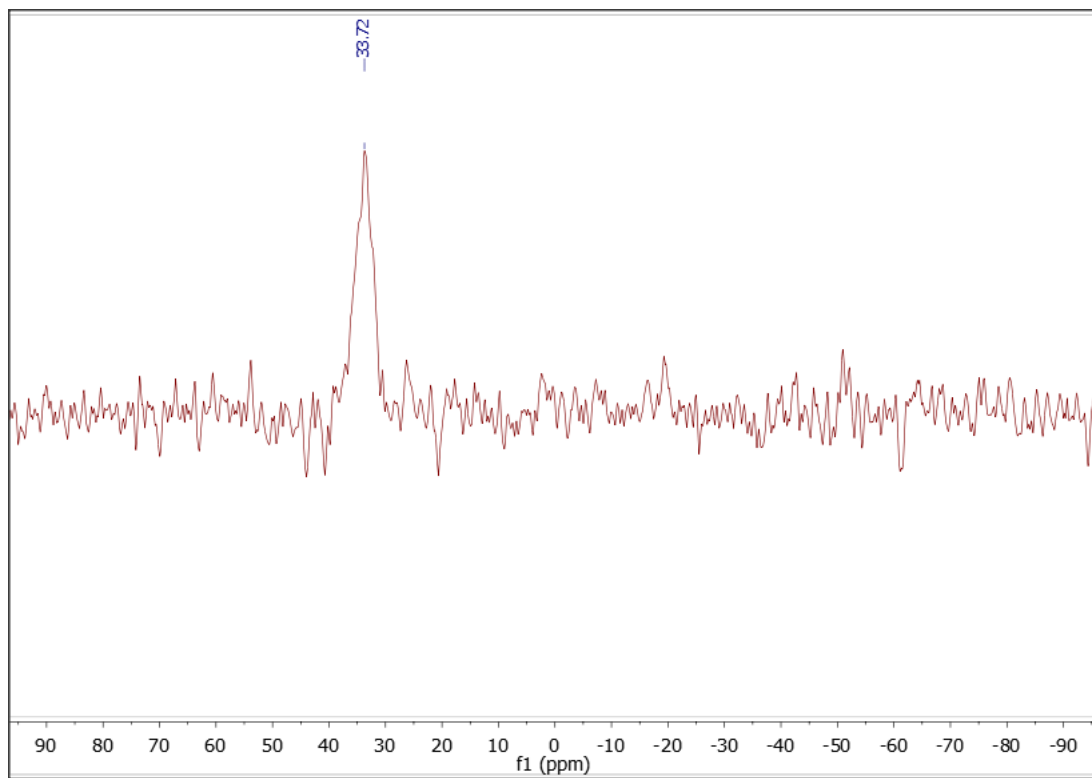
2s, ^1H NMR



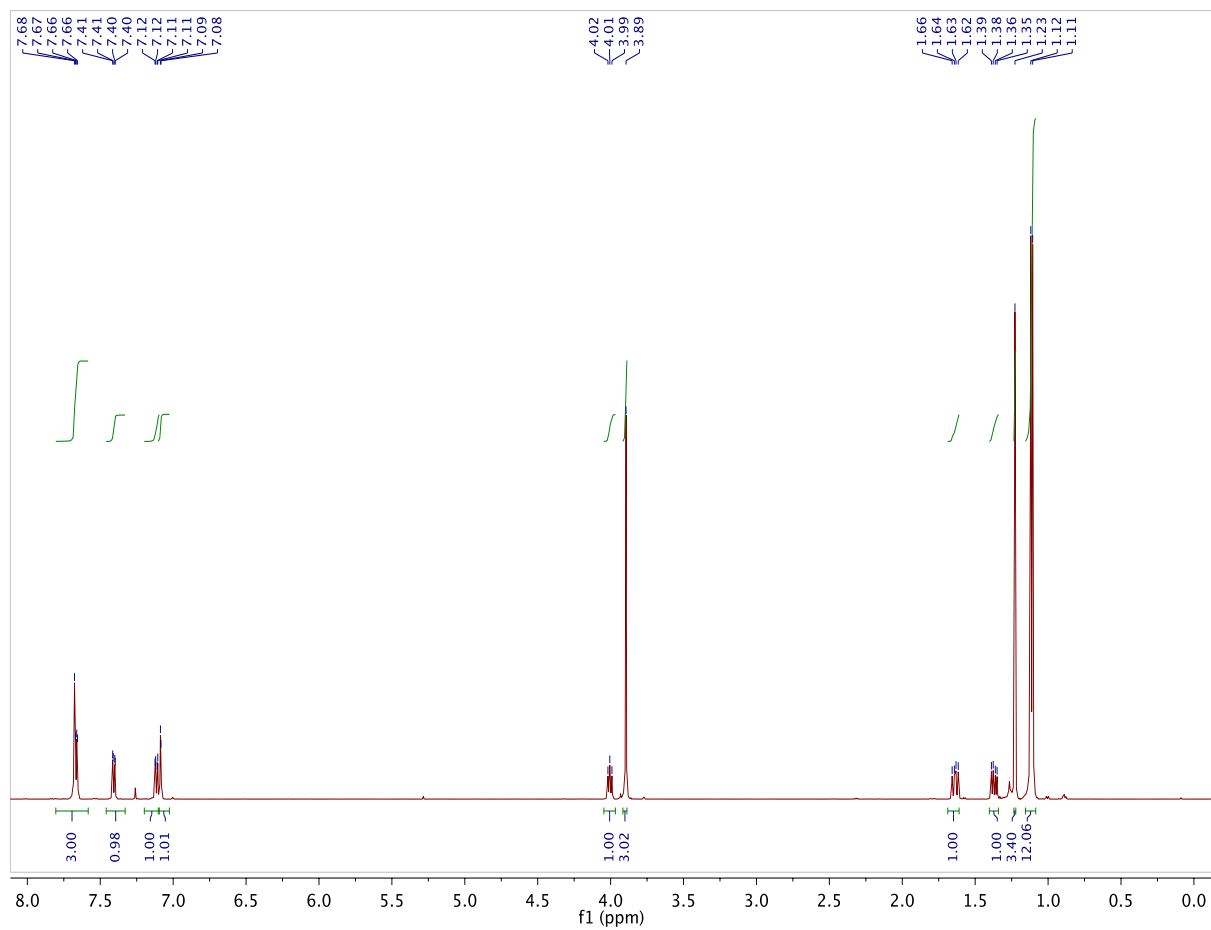
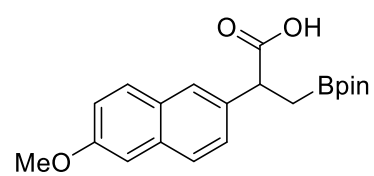
2s, $^{13}\text{C}\{^1\text{H}\}$ NMR



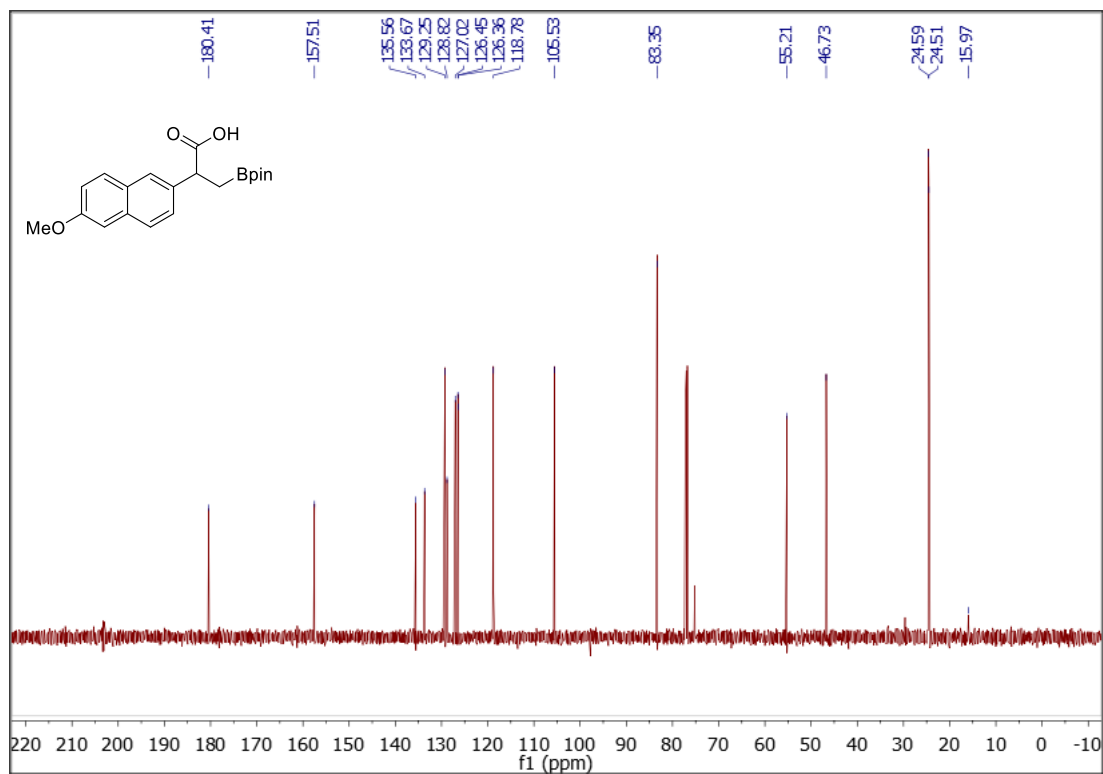
2s, ¹¹B NMR



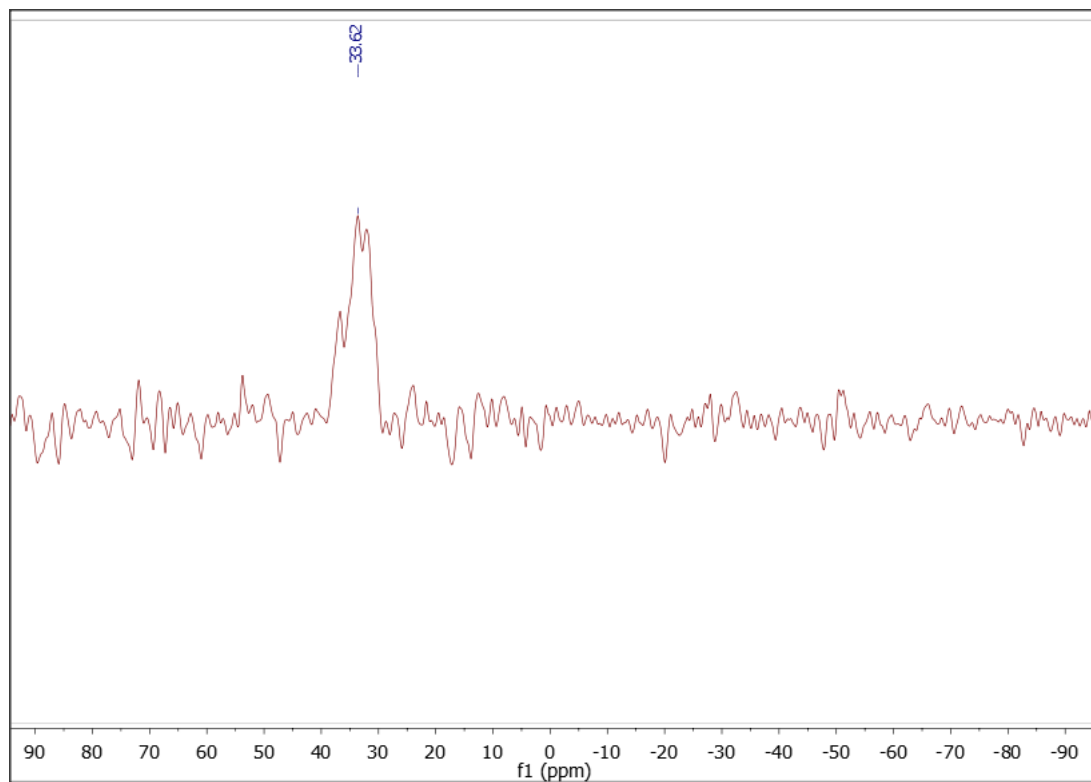
2t, ^1H NMR



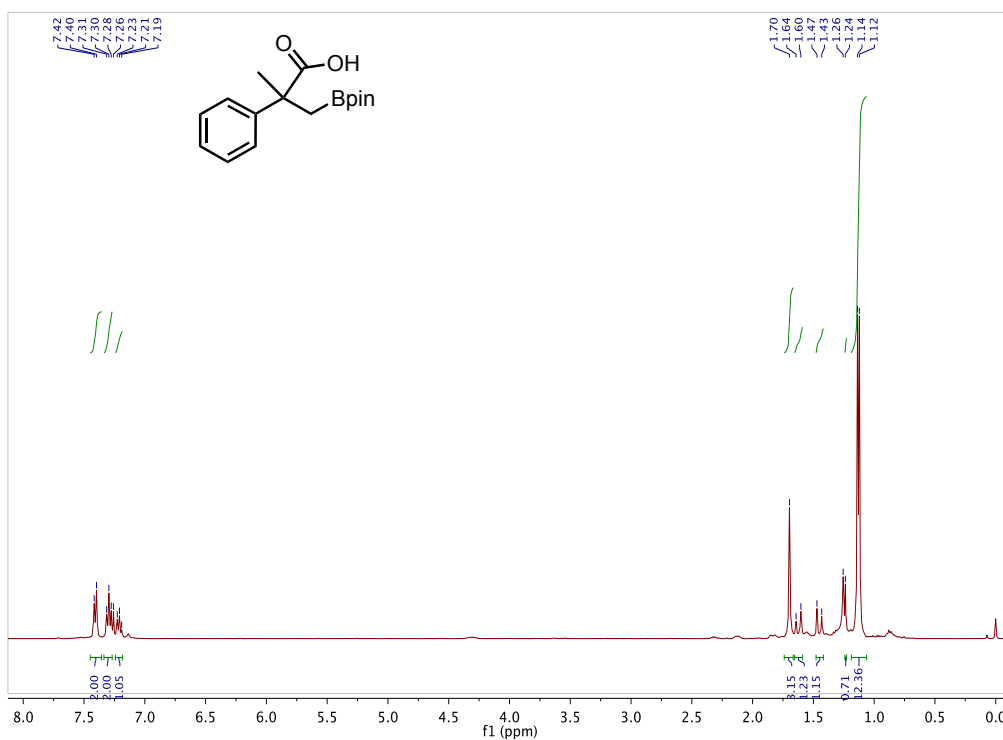
2t, $^{13}\text{C}\{^1\text{H}\}$ NMR



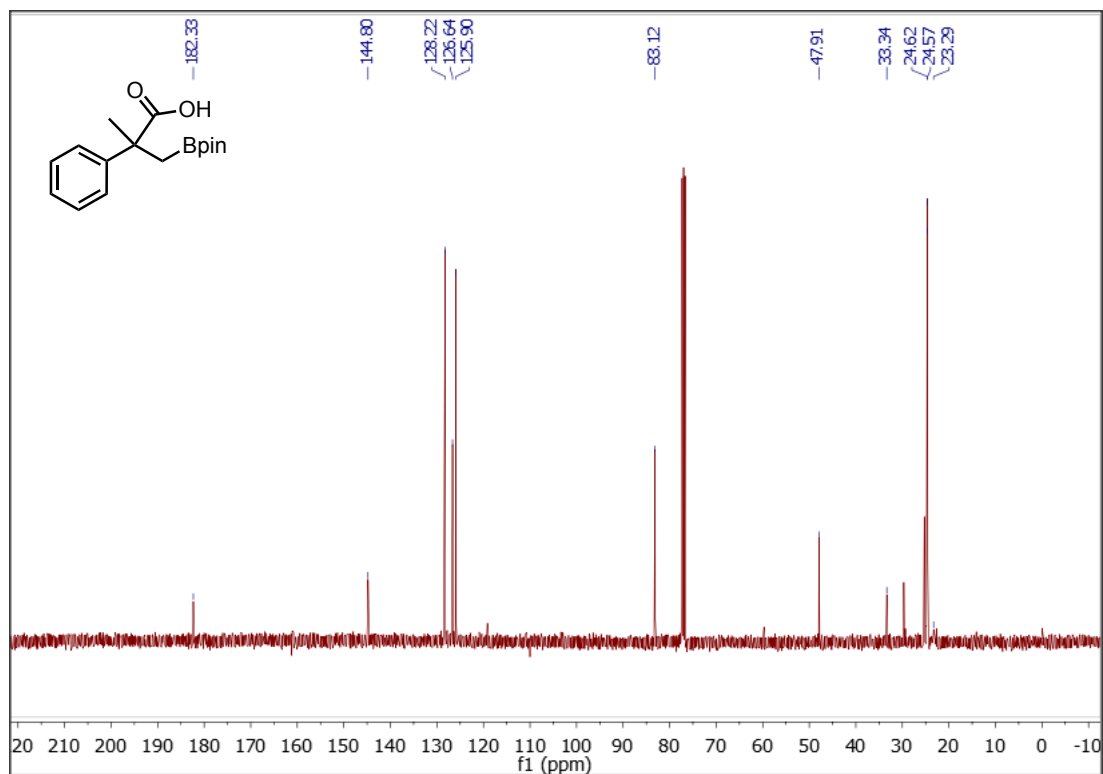
2t, ^{11}B NMR



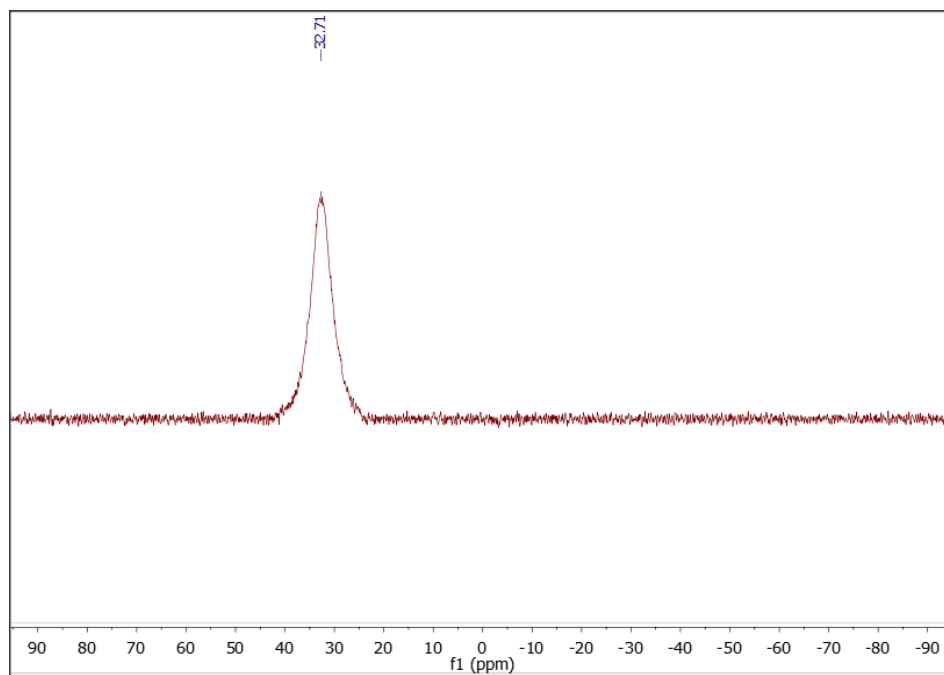
2u, ^1H NMR



2u, $^{13}\text{C}\{^1\text{H}\}$ NMR



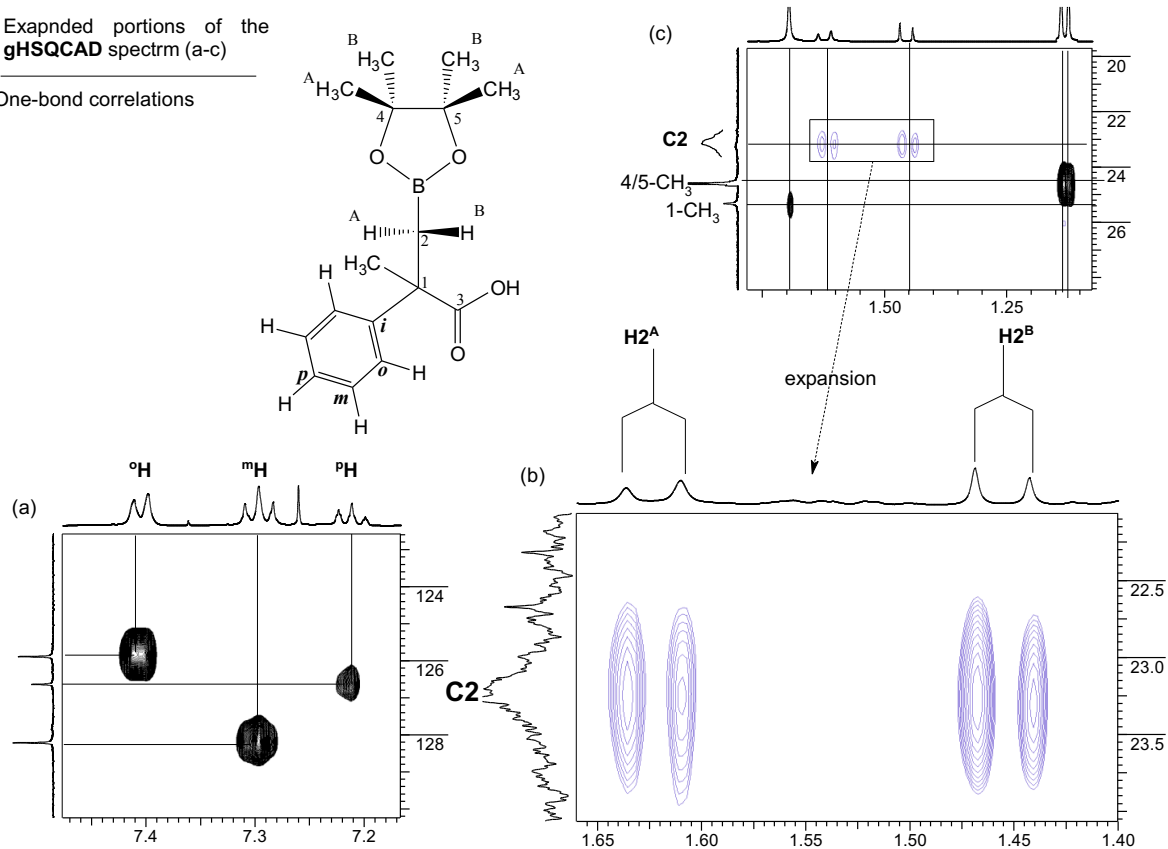
2u, ^{11}B NMR

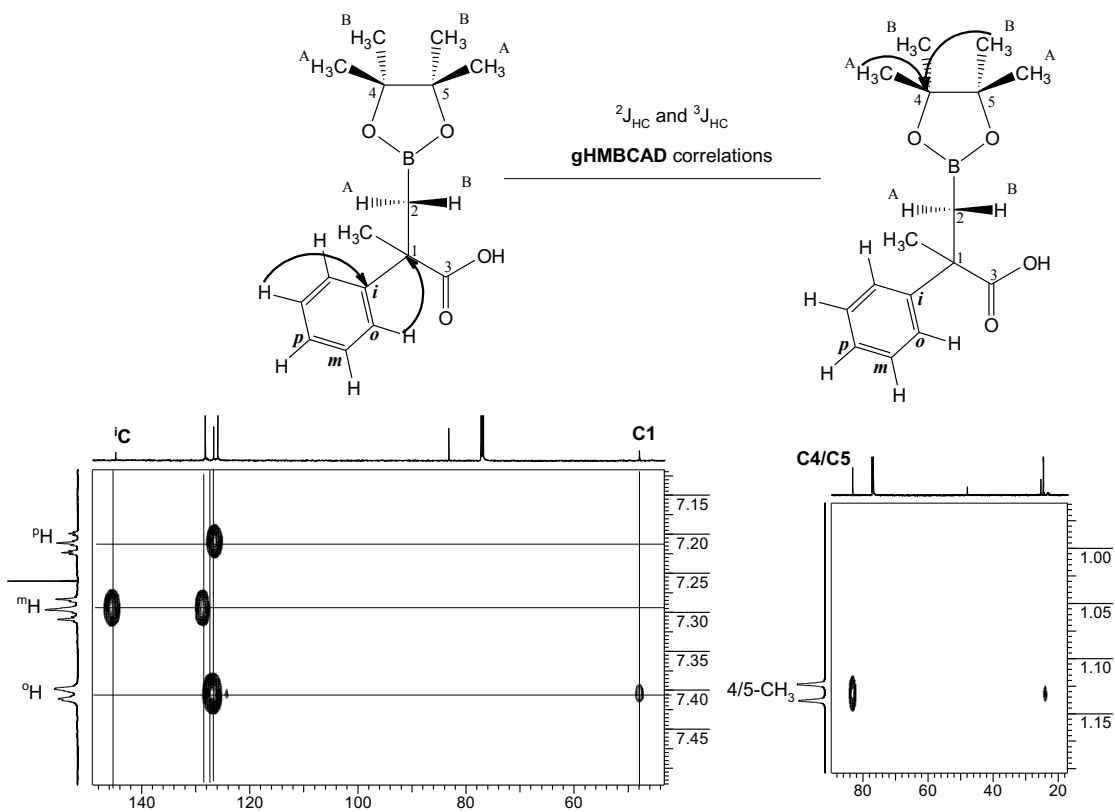
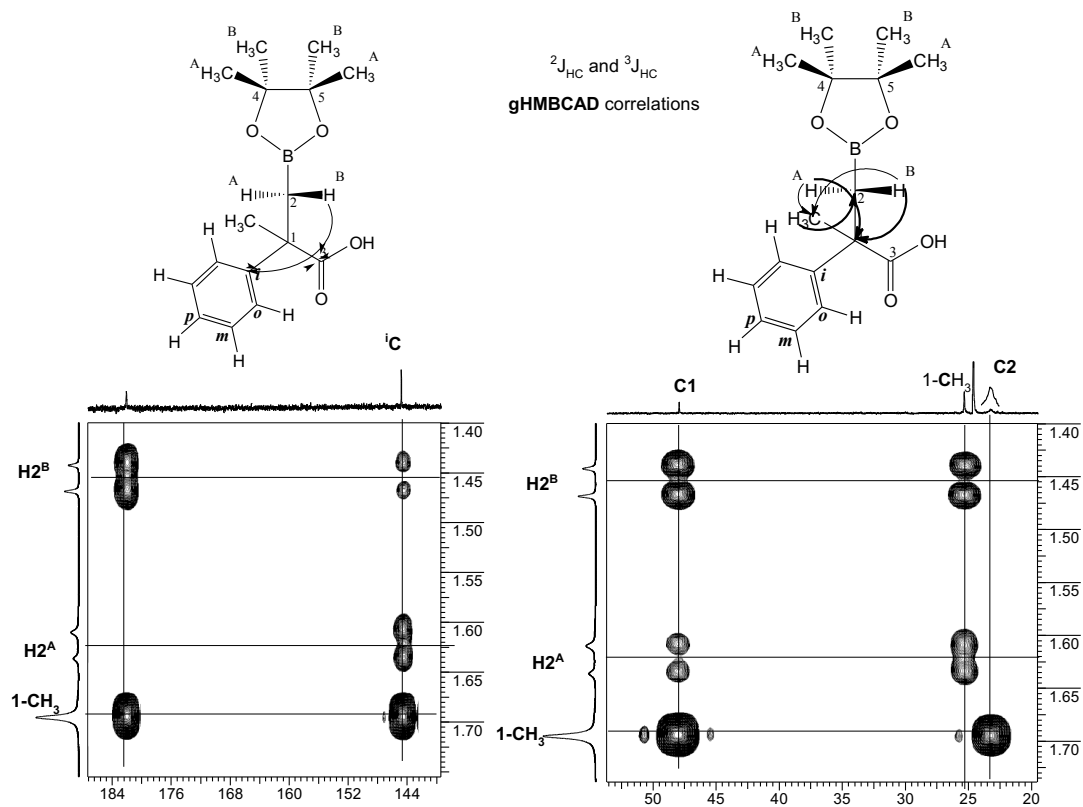


2u, Multinuclear NMR Analysis

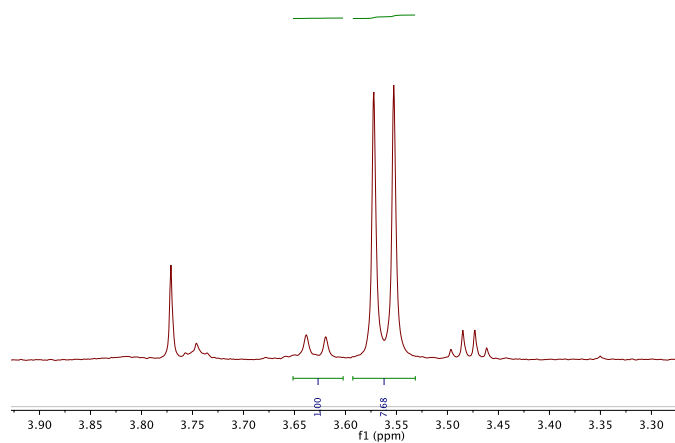
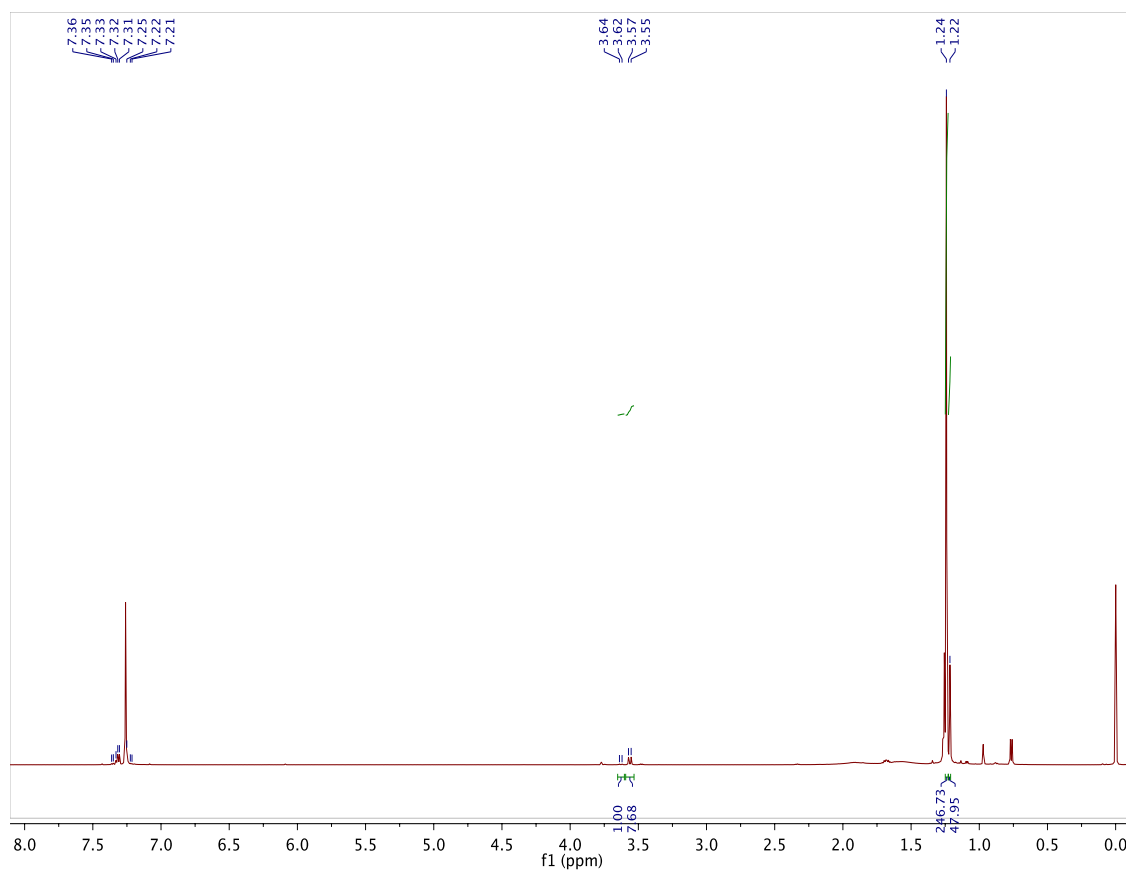
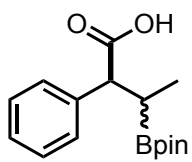
Expanded portions of the
gHSQCAD spectrum (a-c)

One-bond correlations

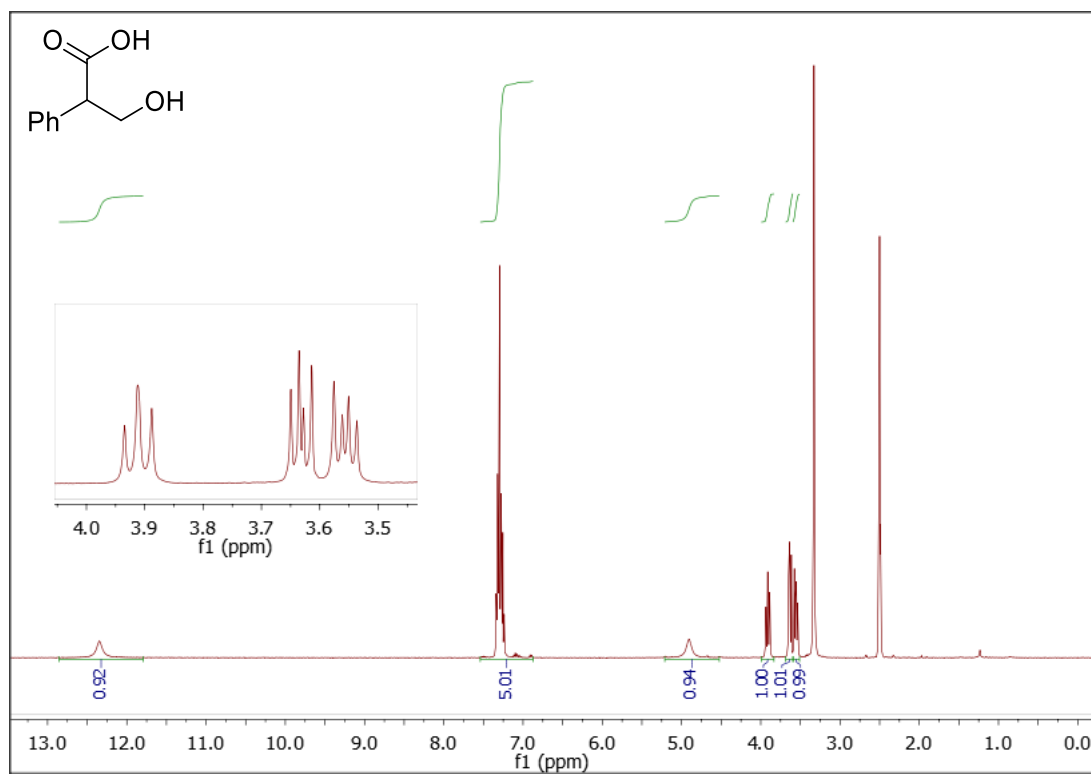




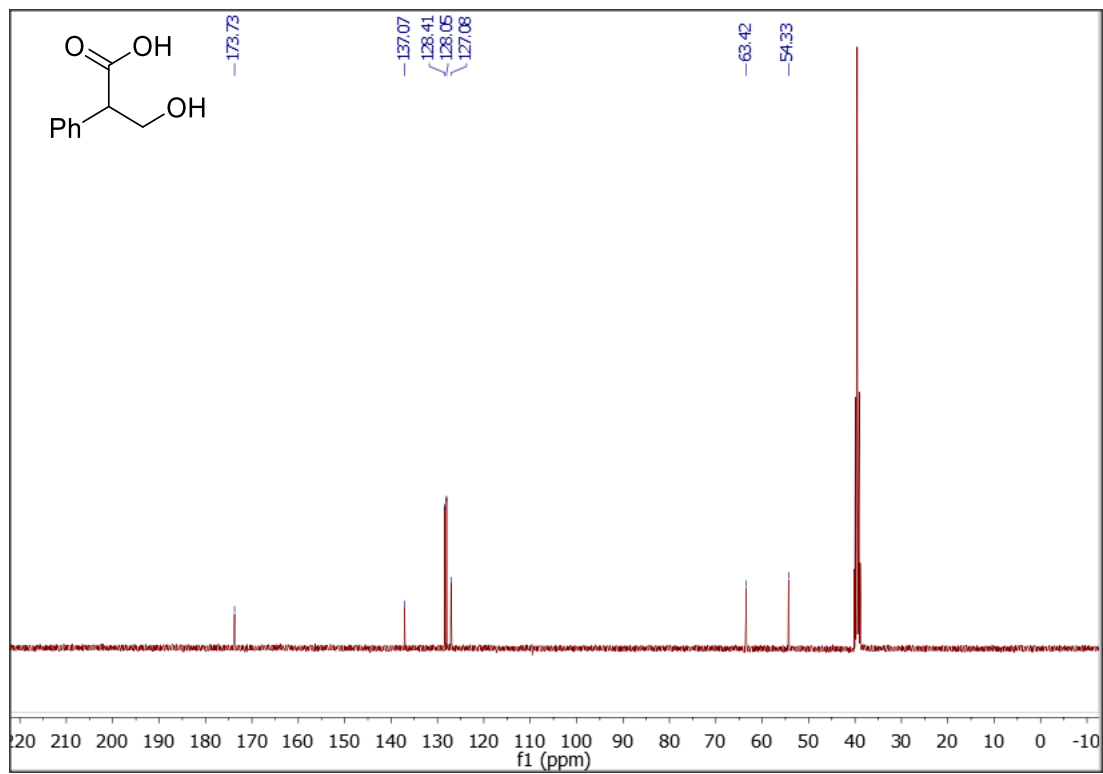
2v, ^1H NMR (crude product after extraction)



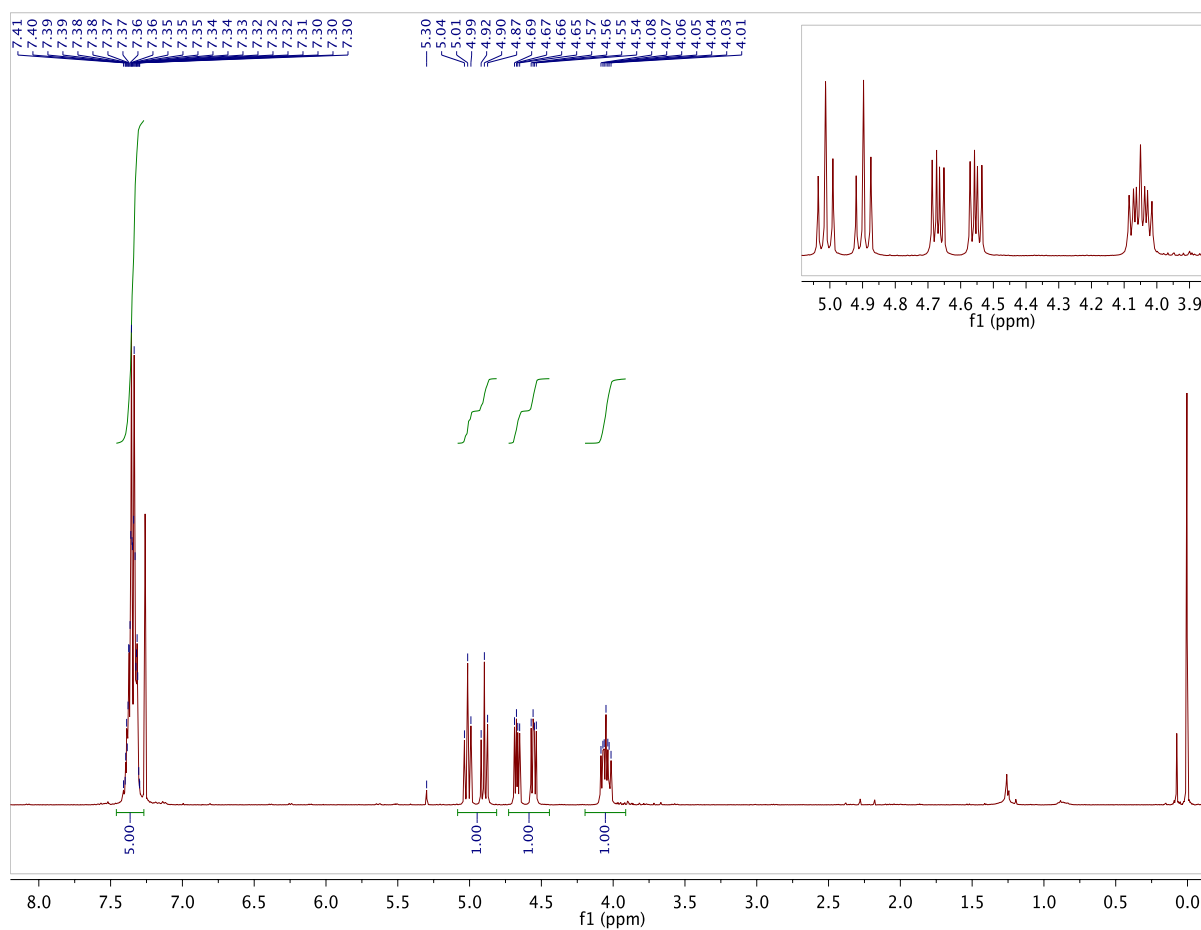
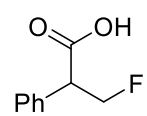
5a, ^1H NMR



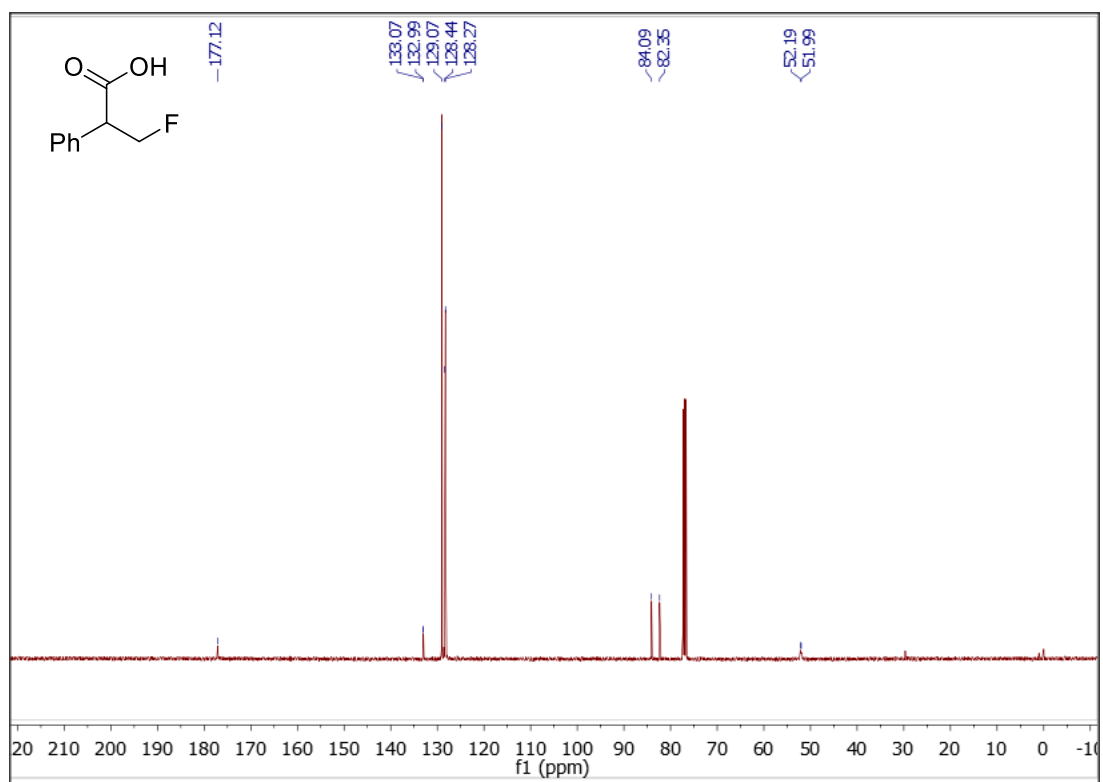
5a, $^{13}\text{C}\{^1\text{H}\}$ NMR



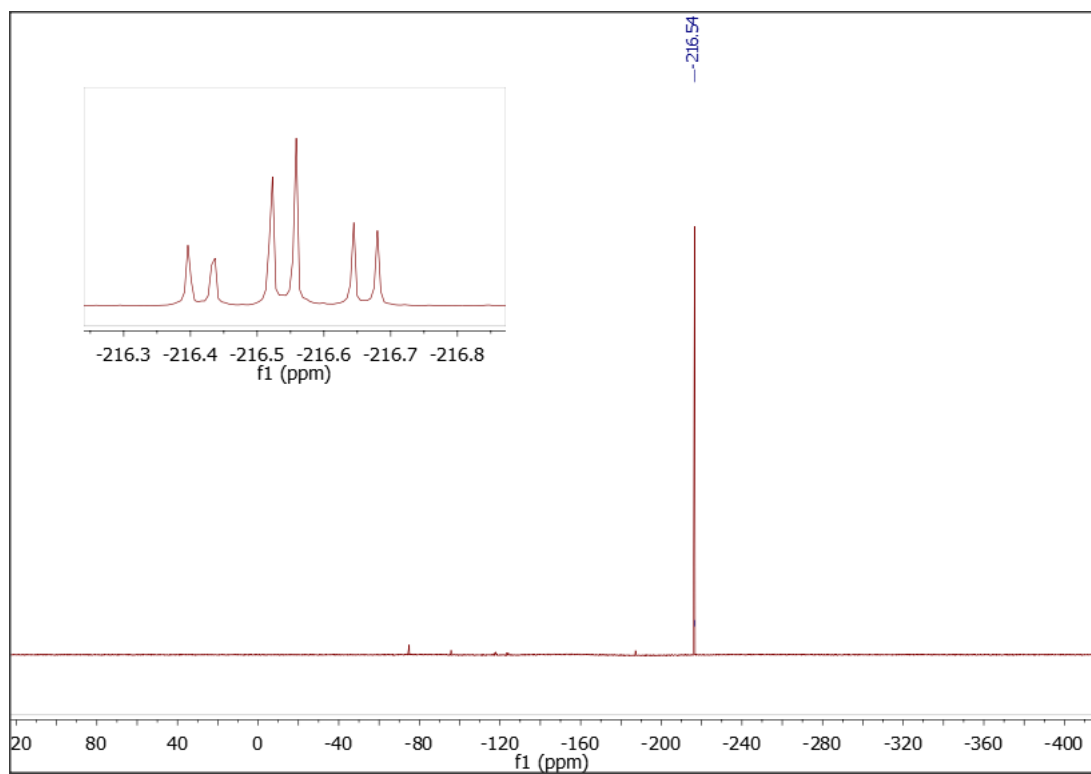
6a, ^1H NMR



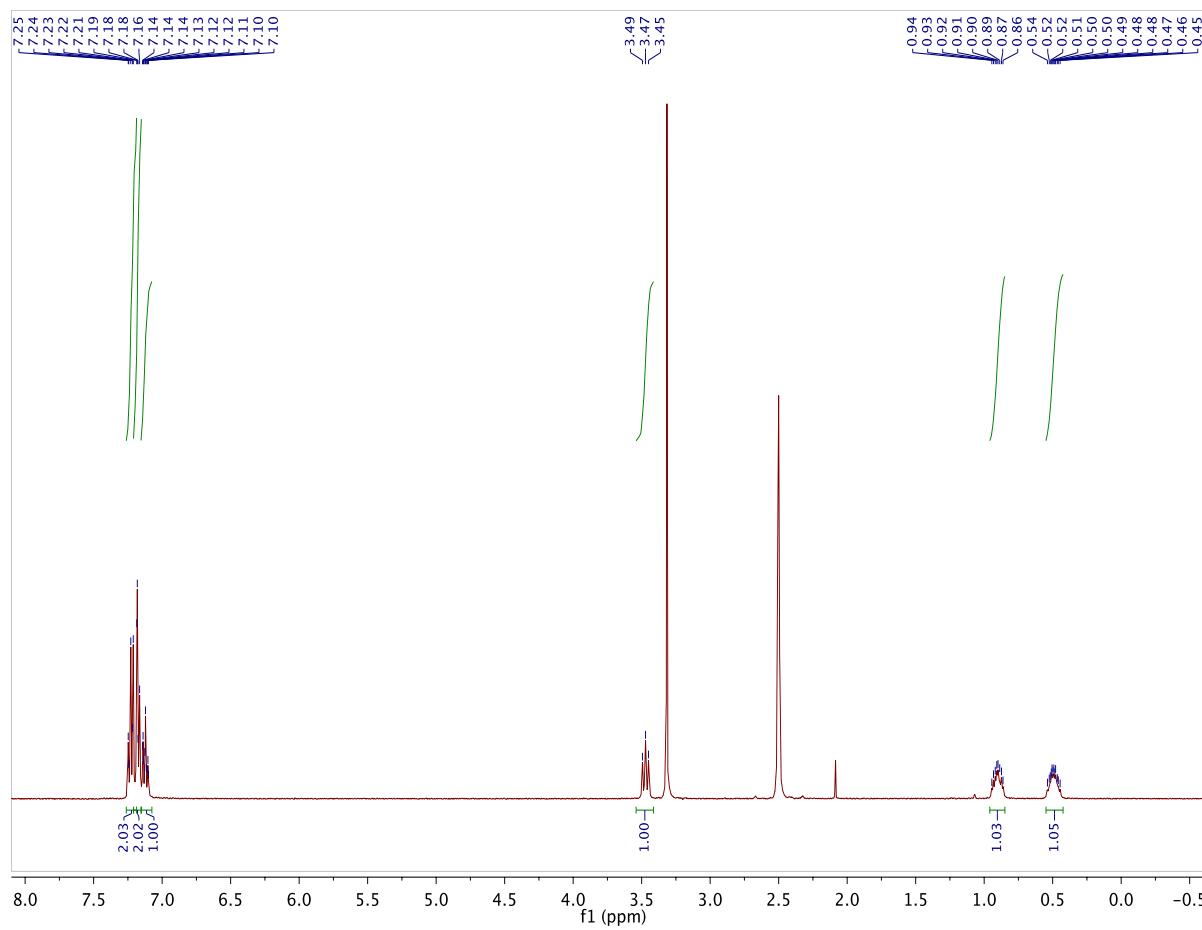
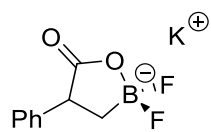
6a, $^{13}\text{C}\{^1\text{H}\}$ NMR



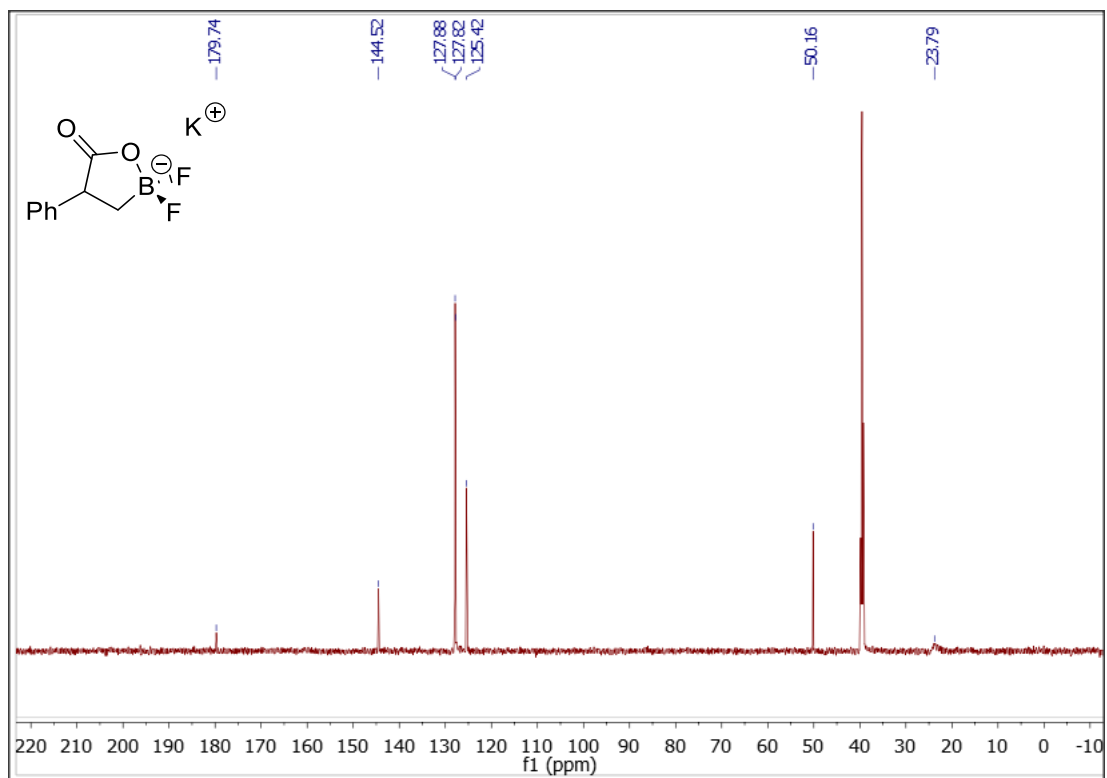
6a, ^{19}F NMR



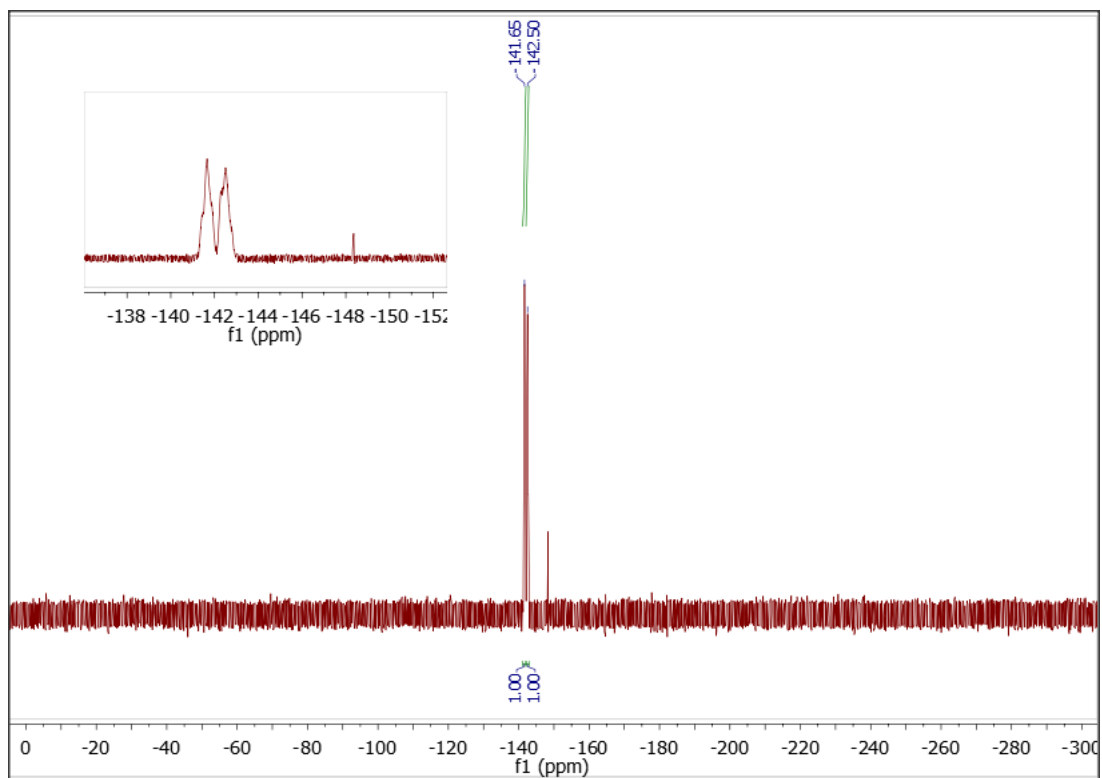
7a, ^1H NMR



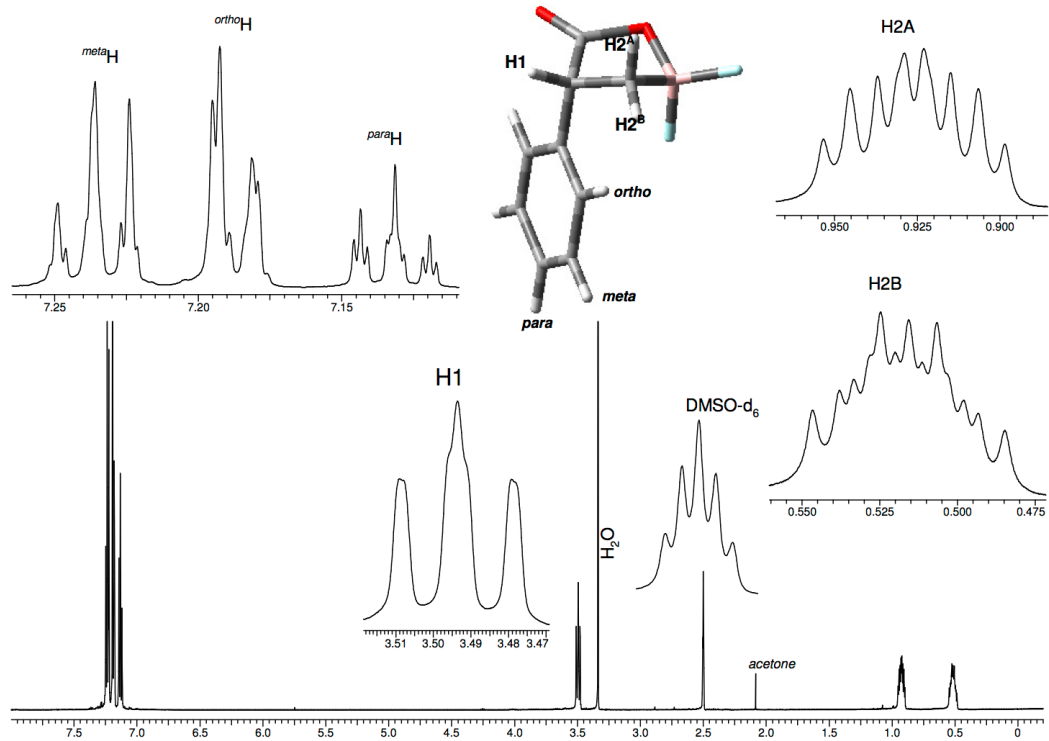
7a, ^{13}C NMR



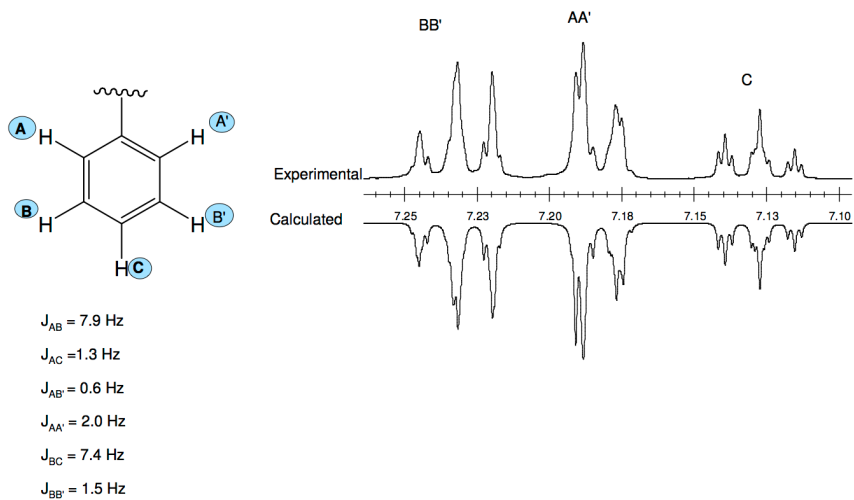
7a, ^{19}F NMR



7a, Multinuclear NMR Analysis



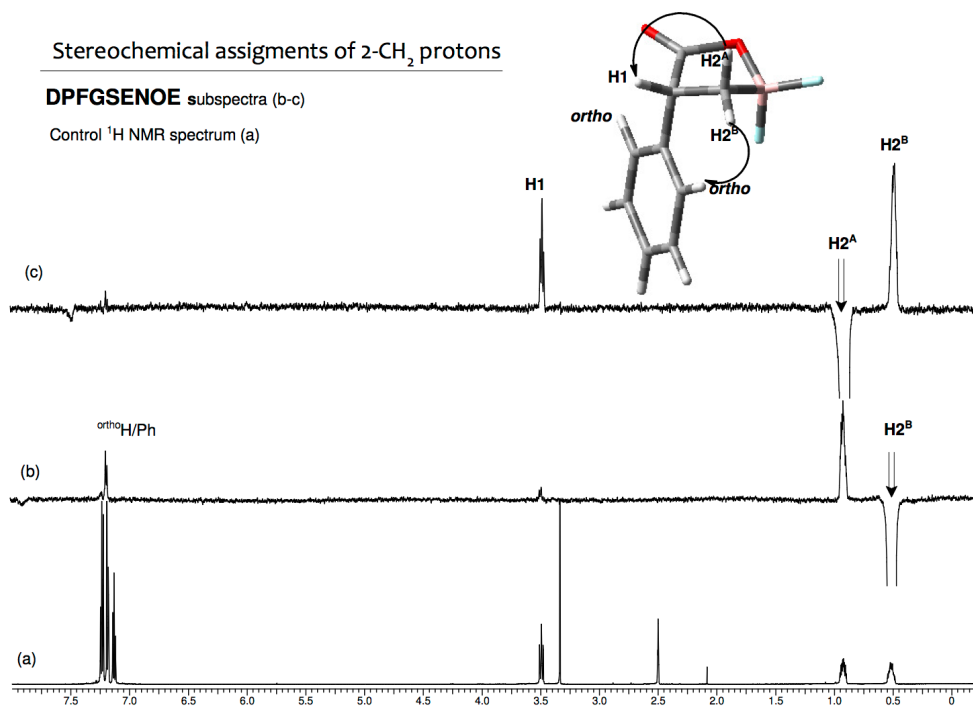
AA'BB'C spin system



Stereochemical assignments of 2-CH₂ protons

DPFGSENOE subspectra (b-c)

Control ¹H NMR spectrum (a)



¹H - {¹¹B}

¹¹B decoupled ¹H NMR spectrum (b)

Control ¹H NMR spectrum (a)

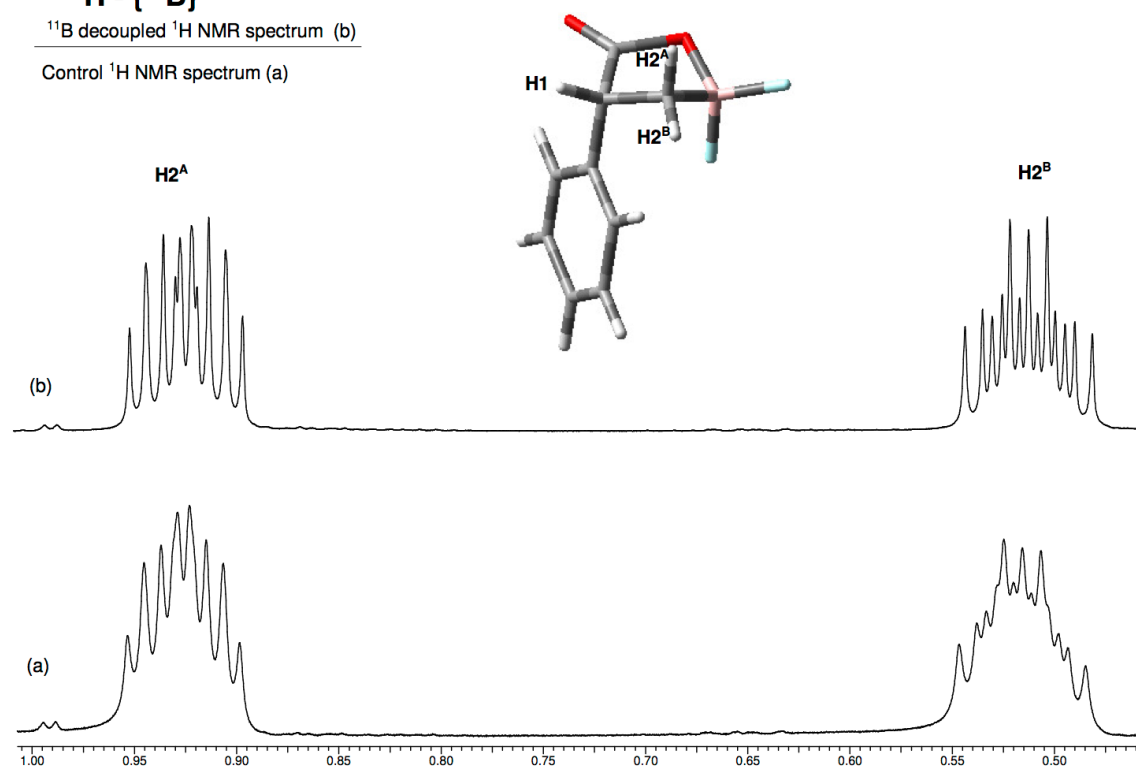
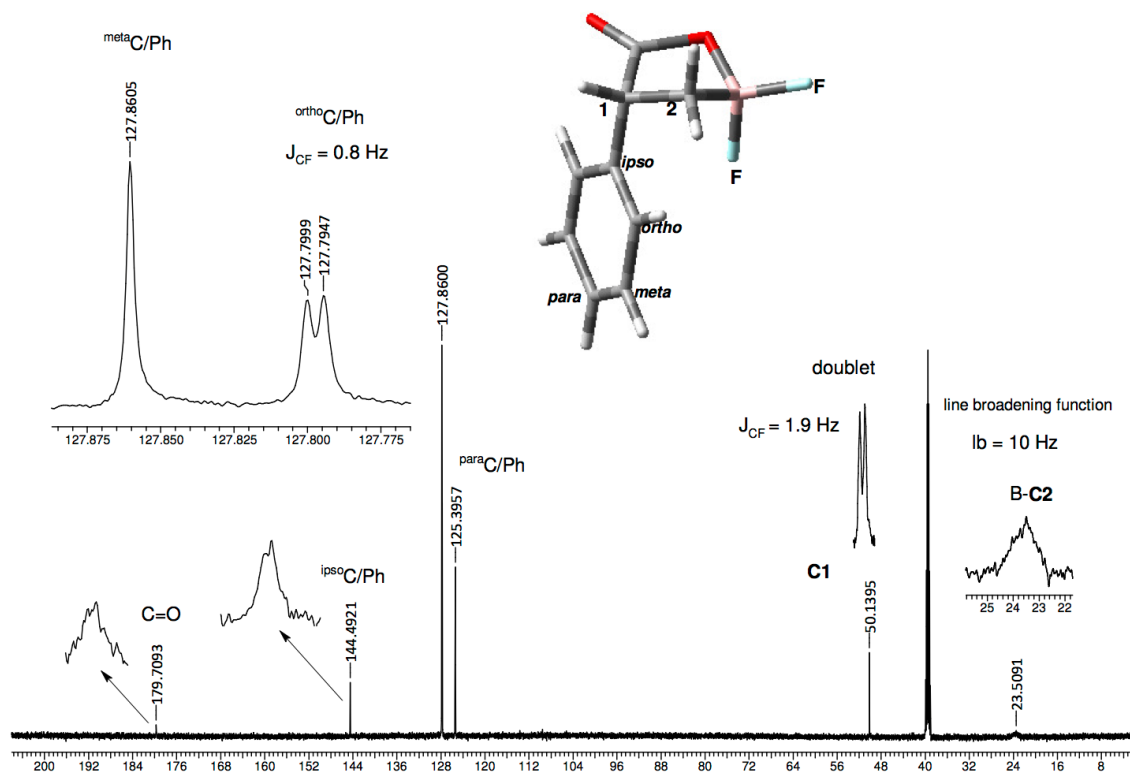
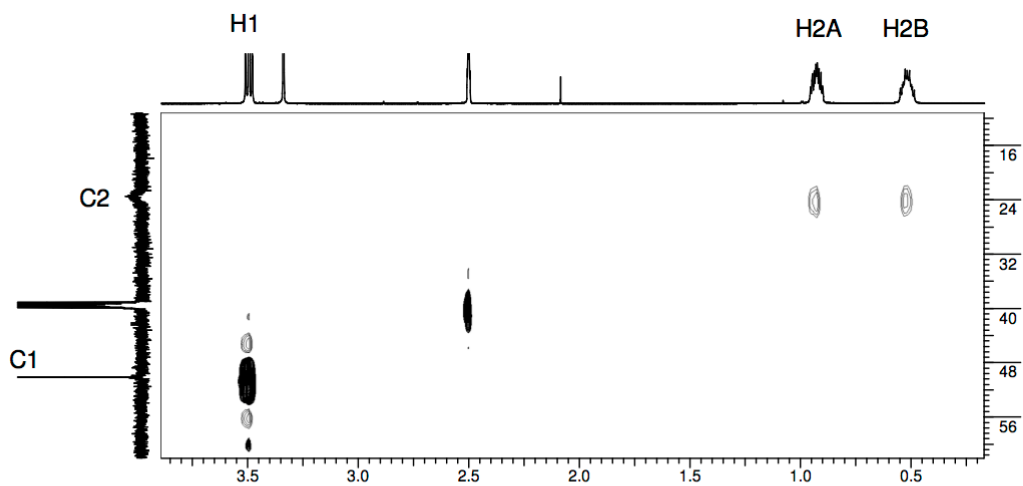


Figure 1 displays the chemical structure of ${}^1\text{H}-\{{}^{11}\text{B}\}$ and its NMR spectra. The chemical structure shows the ${}^1\text{H}$ and ${}^{11}\text{B}$ atoms, with coupling constants (in Hz) indicated: 9.77 Hz, 5.02 Hz, 4.89 Hz, 5.21 Hz, 10.8 Hz, 7.96 Hz, and -13.2 Hz. A note indicates that the ${}^4J_{(\text{ortho}, \text{H1})}$ and ${}^4J_{(\text{H1}, \text{F})}$ constants are not considered.

The NMR spectra are shown for three different positions: H1A, H2A, and H2B. The ${}^1\text{H}$ NMR spectra (a) and ${}^{11}\text{B}$ NMR spectra (b) are displayed for each position. The ${}^{19}\text{F}$ NMR spectra show the chemical shifts for B-FA and B-FB, with a coupling constant of ${}^2J_{\text{FF}} = 85 \text{ Hz}$ indicated. The ${}^{11}\text{B}$ NMR spectrum shows a peak at 8.5504 ppm.

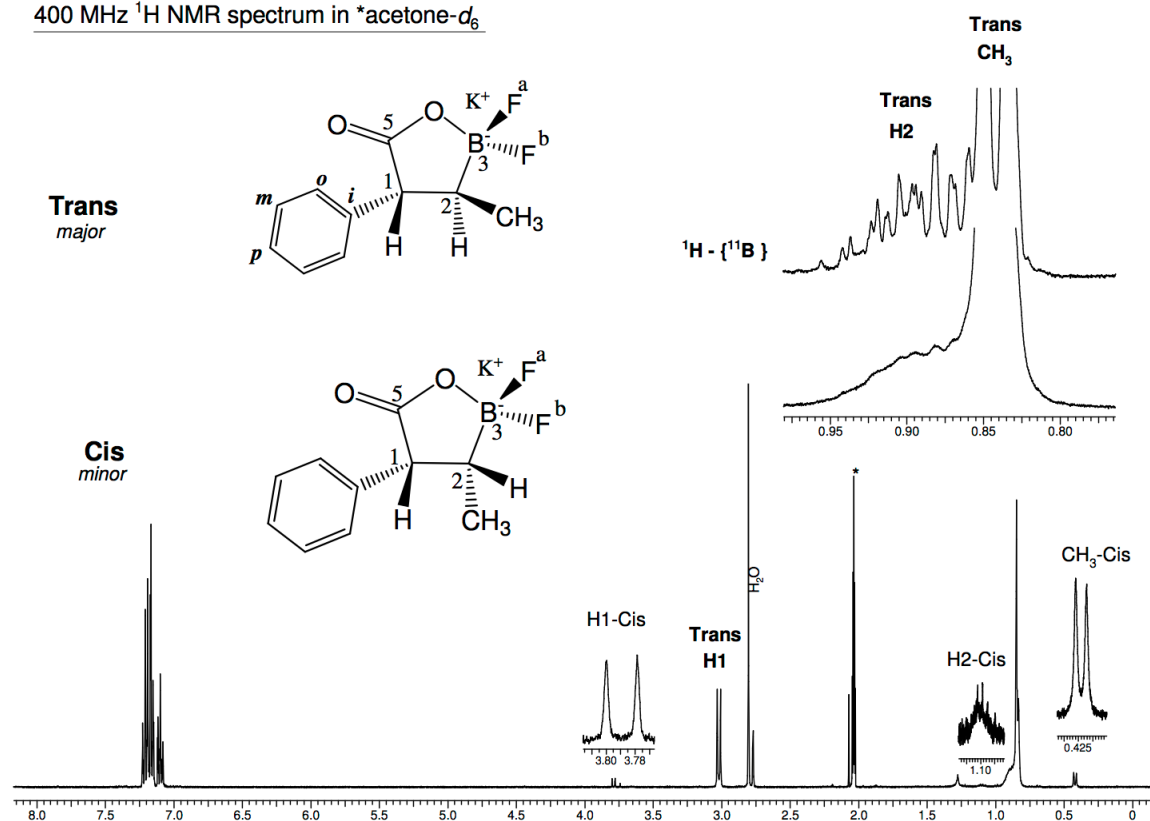


gHSQCAD

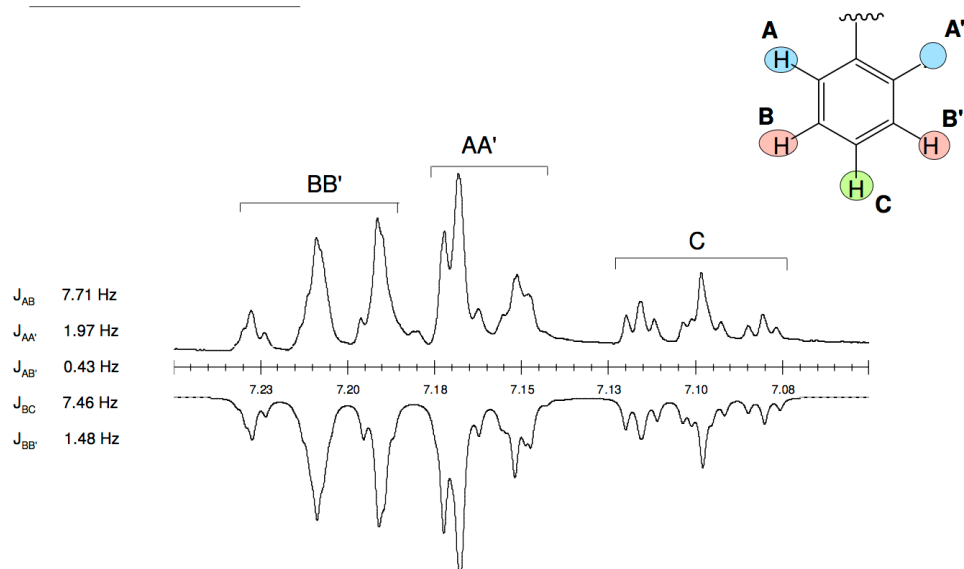


7v, Multinuclear NMR Analysis

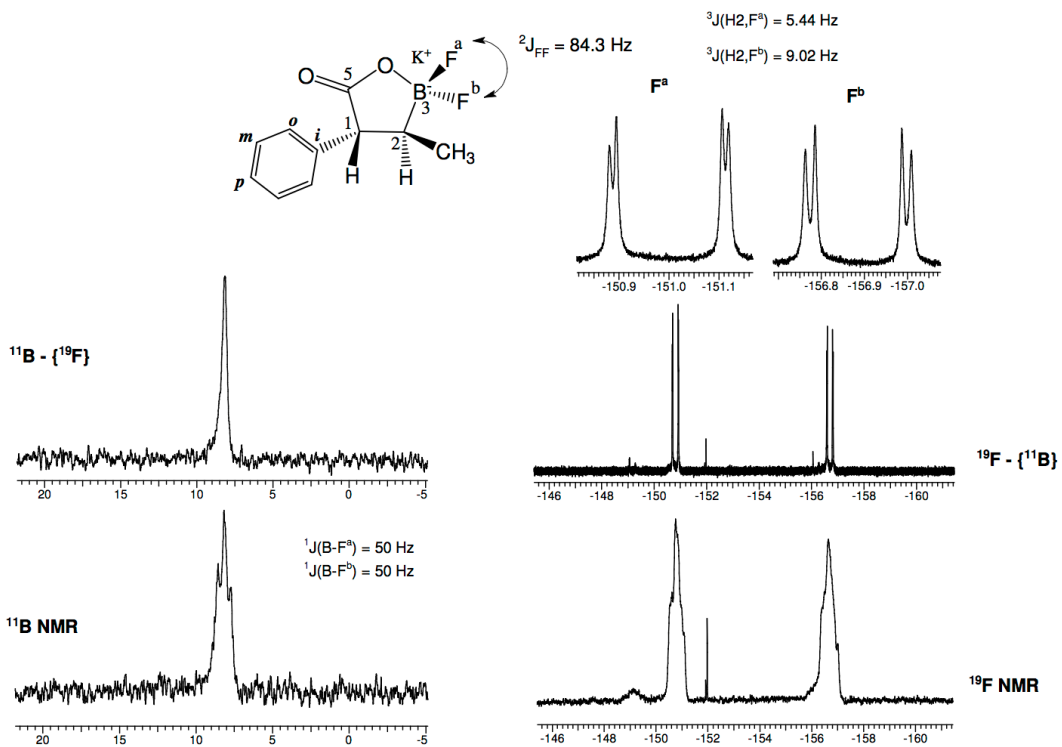
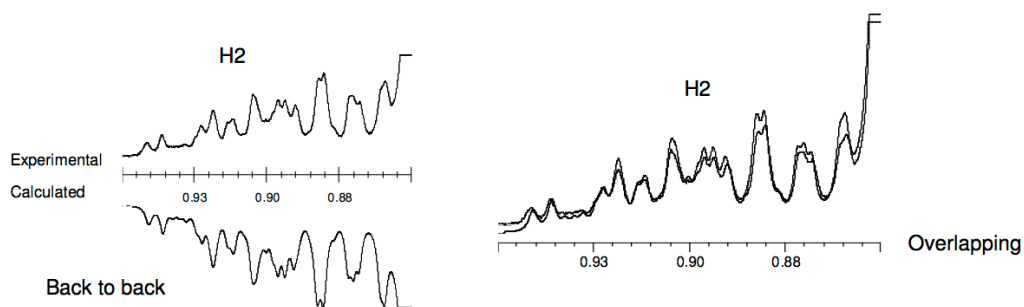
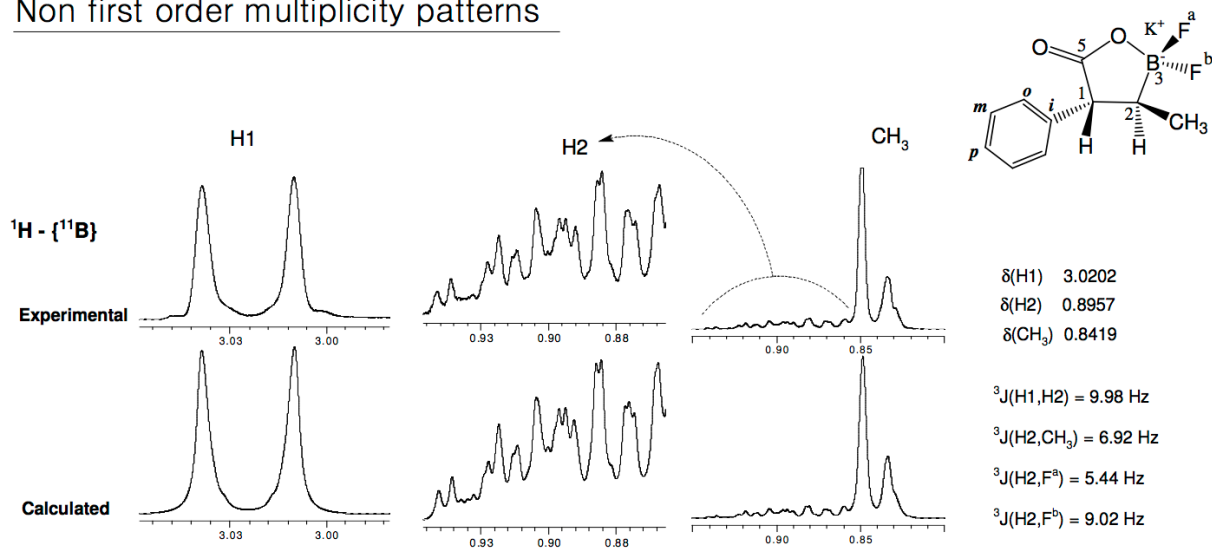
400 MHz ^1H NMR spectrum in $^*\text{acetone-}d_6$



AA'BB'C spin system



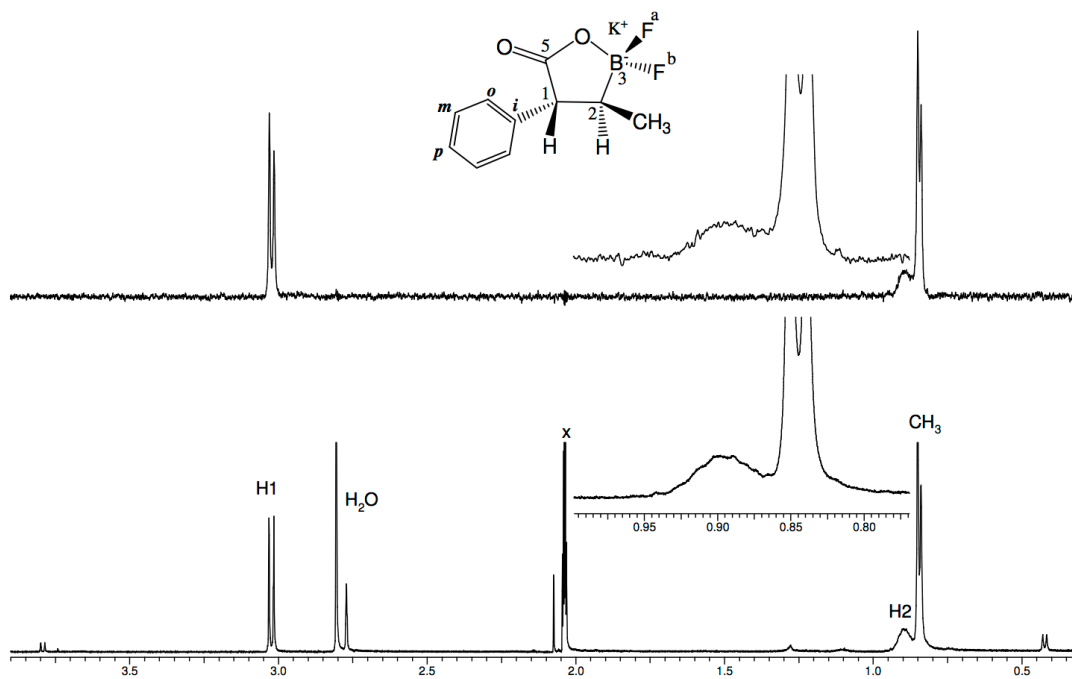
Non first order multiplicity patterns



1D TOCSY

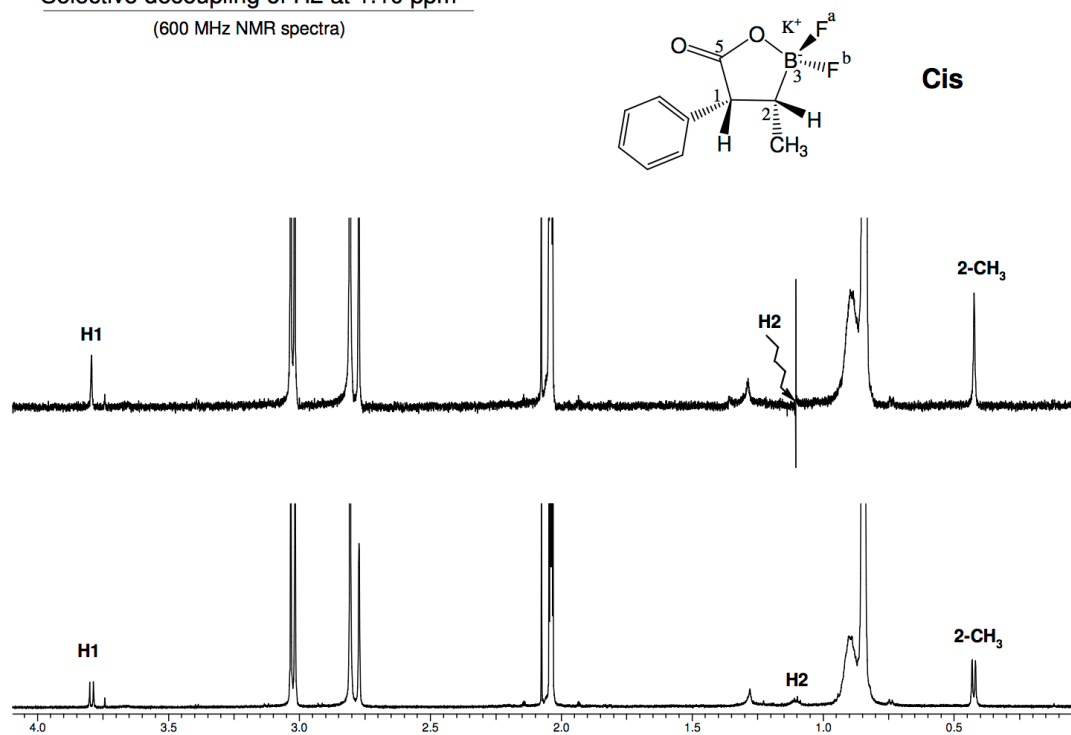
(600 MHz NMR spectra)

Selective excitation of H1 (mix = 70 ms)

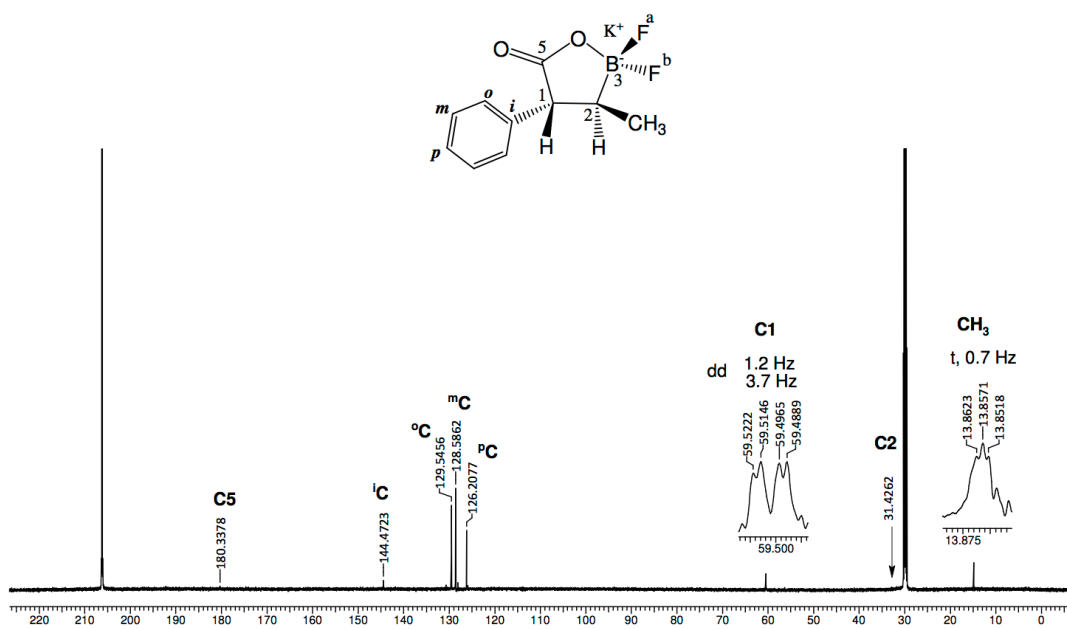
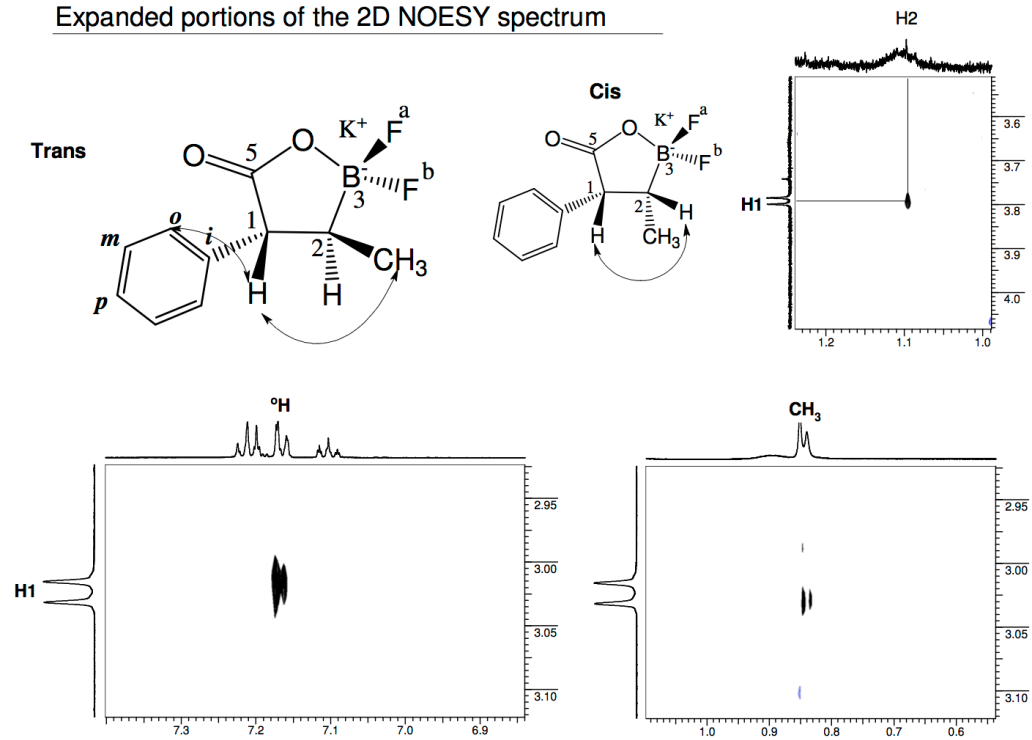


Selective decoupling of H2 at 1.10 ppm

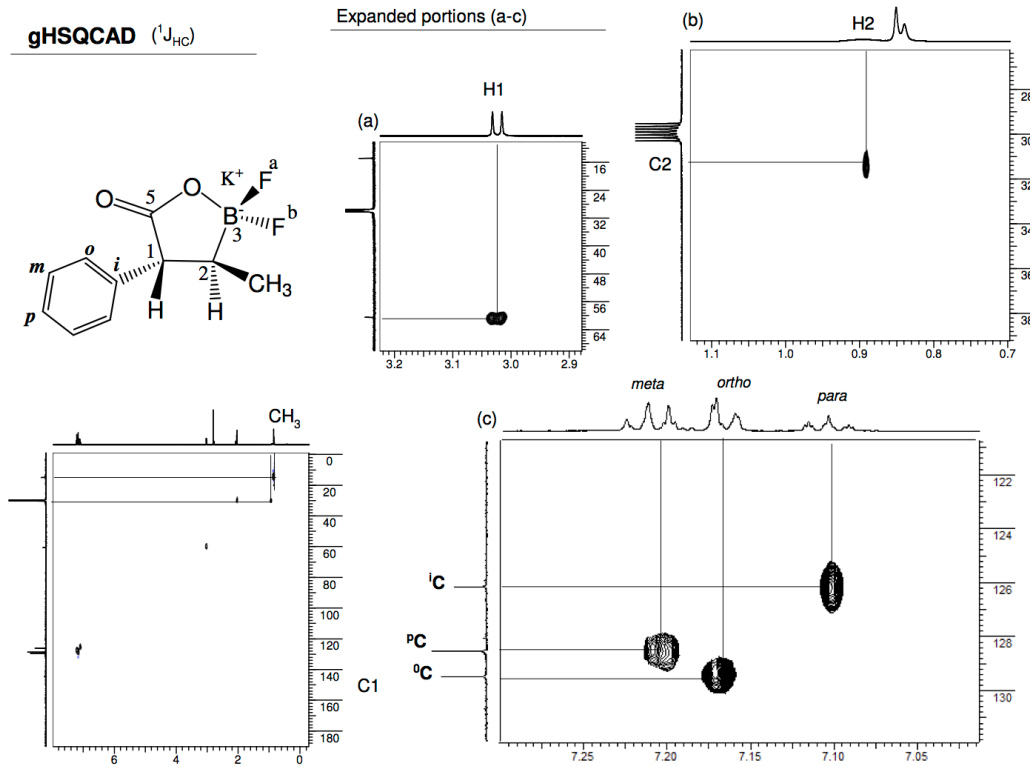
(600 MHz NMR spectra)



Expanded portions of the 2D NOESY spectrum



gHSQCAD ($^1J_{\text{HC}}$)



gHMBCAD

($^2J_{\text{HC}}$ and $^3J_{\text{HC}}$)

