Supporting Information for

Enantioselective synthesis of chiral organoborons via carbene B-H insertion catalyzed by engineered neuroglobin

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Contents

1 Experimental Section

1.1 Materials and Methods

Unless otherwise noted, all chemicals and reagents were obtained from commercial suppliers and used without further purification. Silica gel chromatography purifications were carried out using silica gel. ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded on Bruker ANANCE NEO 500 MHz, 160 MHz and 126 MHz, respectively. Chemical shifts were determined relative to internal standard TMS at 0.0 ppm. Chemical shifts are expressed in parts per million (ppm), and coupling constants are in Hertz (Hz). The following abbreviations were used to indicate the corresponding multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

High-resolution mass spectra (HRMS) were recorded on a G2-XS QTOF mass spectrometer(Waters) using ESI. The calibration curves were determined by HPLC (Shimadzu LC-16, GL1F-3P C18 5 μm, 4.6×150 mm, 25℃, UV 254 nm, flow rate = 0.6-0.8 mL/min, $MeCN/H_2O$ = 60/40). The *ee* and e.r. values of compounds were determined by chiral HPLC (Shimadzu LC-16, CHIRALCEL OD-3 and ADH, 3 μm, 4.6×250 mm, 25℃, UV 254 nm, flow rate = 1.0 mL/min, Hexane/*i*-PrOH = 95/5–80/20).

1.2 Protein Expression and Purification

1.2.1 Protein expression

Chemically competent *E. coli* BL21(DE3) cells were transformed with a pET3a expression vector carrying wild-type (WT) Ngb or its mutants. Single colonies were picked and inoculated into a starter culture in 5 mL of fresh LB medium containing 100 μg/mL ampicillin. The 3 mL overnight culture was then transferred to a 3 L fresh rich medium containing 100 μg/mL ampicillin and 10 mM 5-aminolevulinic acid hydrochloride (ALA). The culture was grown at 37℃ and shaken at 220 rpm for 12 h. Protein expression was induced by adding isopropyl β-D-1-thiogalactopyranoside (IPTG) to a final concentration of 0.4 mM for an additional 12 h. Cells were then harvested by centrifugation (6000 rpm) at 4℃ for 5 min.

1.2.2 Protein purification

The harvested cell pellets were resuspended in 80 mL KPi buffer (20 mM potassium phosphate buffer, pH 7.0) and lysed by ultrasonication (40% power, 5 sec on, 5 sec off, 60 min) on ice. The crude lysates were centrifuged (10000 rpm) at 4 ℃ for 15 min, and the pellets were discarded. The supernatant was precipitated with 30-60% $(NH_4)_2SO_4$. Pellets containing Ngb were dissolved in 20 mM KPi (pH 7.0) and concentrated to 10 mL. The Ngb was then loaded on a HiPrep™ 26/60 Sephacryl S-100 Gel filtration column (GE Healthcare) equilibrated with 100 mM KPi buffer (pH 7.0). The fraction containing Ngb was collected and oxidized by $K_3[Fe(CN)_6]$, which was further loaded on a Hiprep™ DEAE FF 16/10 column (GE Healthcare) equilibrated with 20 mM KPi buffer (pH 7.0) and eluted with 100 mM KPi (pH 7.0). Purified Ngb proteins were stored at -20℃.

1.3 B-H Insertion Reactions

1.3.1 B-H insertion reaction catalyzed by purified Ngb mutants

Initial reactions were carried out on a 1 mL scale using purified Ngb mutants (40 μM), 5 mM borane substrates, 7.5 mM diazo esters and 20 mM sodium dithionite ($Na_2S_2O_4$) in a N_2 atmosphere. $Na_2S_2O_4$ was dissolved in 50 mM KPi buffer (pH 7.0, 0.2 M stock solution).

Typical procedure: 100 μL of $Na_2S_2O_4$ (20 μmol, 4.0 equiv) stock solution was added to the 750 μL of purified Ngb solution (0.04 μmol). Reactions were initiated by adding 100 μL of borane substrates (5 μmol, 1.0 equiv), followed by adding 50 μL of diazo esters (7.5 μmol, 1.5 equiv). The mixture was stirred at room temperature for 12 h in a N_2 atmosphere, and the reaction was quenched by the addition of 10 μL of 3 M hydrochloric acid (HCl). The reaction mixture was diluted 2-fold with MeCN, and the yields of these compounds were determined by HPLC. After extraction, concentration and purification, the e.r. values of these compounds were determined by chiral HPLC.

1.3.2 Preparative-scale reactions

In a typical preparative-scale reaction procedure, a solution (100 mL) containing 0.7 g $Na_2S_2O_4$ (4 mmol, 4.0 equiv) and A15C/H64S/V68F/F28M Ngb (CSFM Ngb, 8 μmol) in 50 mM KPi buffer (pH 7.0) was stirred for 1 min. The reaction was initiated by adding 4 mL of borane substrates (1 mmol, 1.0 equiv) and 4 mL of diazo esters (1.5 mmol, 1.5 equiv), both dissolved in MeCN. The mixture was stirred at room temperature for 12 h under N_2, then extracted with dichloromethane (3×200 mL). The organic phase was evaporated under reduced pressure, and the residue was purified by flash column chromatography (Silica gel, PE/EA = 10/1–5/1) to give the corresponding products.

1.4 UV-Vis Spectroscopy

UV-Vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer. Ferrous CSFM Ngb was obtained by adding $Na_2S_2O_4$ (7 mg) to the ferric CSFM Ngb solution (10 μM, 2 mL) for 1 min. The diazo compound was dissolved in MeCN (20 mM) and added dropwise to the ferrous CSFM Ngb to a final concentration of 100 μM to produce the MDPB-CSFM Ngb complex. Spectra were recorded after the addition of diazo compounds for 3 min. The py-BH_3 was dissolved in MeCN (20 mM) and added dropwise to a final concentration of 100 μM in MDPB-CSFM Ngb complex. Spectra were recorded after the addition of py-BH_3 for 5 min.

1.5 Molecular Simulation and Docking Studies

The initial structure of A15C/H64S/V68F/F28M Ngb was generated from the X-ray structure of A15C Ngb (PDB code 7VQG)[1] using program VMD 1.9.[2] A patch of disulfide bond was applied to both Cys46-Cys55 and Cys15-Cys120. The structure of MDPB was obtained from the X-ray structure of carbene-bound *Rma* TED (PDB code 6CUN).[3] A patch of axial ligands (MDPB and His96) was then applied to the ferrous heme iron. The protein was solvated in a cubic box of TIP3 water, followed by the addition of counter ions (Na^+ and Cl^-) to obtain the physiological ionic strength of 0.15 M. The resulting complex system was minimized with NAMD 2.9 (Nanoscale Molecular Dynamics),[4] using 1000 minimization steps with the conjugate gradient method at 0 K, and equilibrated for 100,000 molecular dynamics steps (1 fs per step) at 300 K, then further minimized for 1000 steps at 0 K.

The simulated structure of carbene-bound A15C/H64S/V68F/F28M Ngb was used as the initial structure for docking with py-BH_3 using the Autodock 4 program.[5] The heme iron was set as the center, with a box size of ~80 Å × 80 Å × 90 Å, which covered most of the protein surface. Amino acid residues Met28, Ser64, and Phe68 on the protein surface near the active heme site, and the heme axial ligand MDPB were set as flexible residues. Docked conformations were automatically ranked by Autodock 4 using a binding-energy scoring function. The docking results (10 most favorable conformations) after 2000 steps were then visualized and analyzed using VMD 1.9.[2]

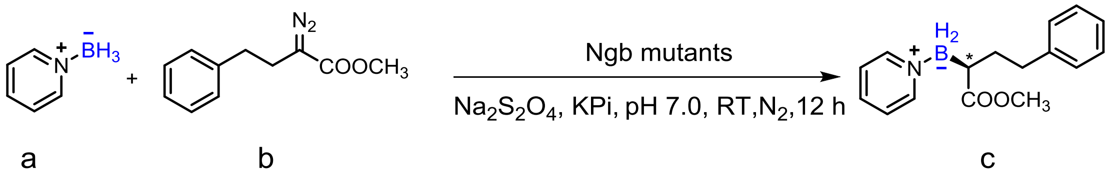
1.6 Synthesis of Racemic Organoborane Products

Racemic standard references of organoborane products were prepared *via* Rh-catalyzed B-H insertion reactions using procedures slightly modified from a previously reported method.[6] Namely, a 4 mL vial with screw cap and PTFE septum was charged with a borane substrate (0.5 mmol, 1 eq.) and $Rh_2(OAc)_4$ (11 mg, 5 mol%). The vial was evacuated and backfilled with N_2 three times, and 1 mL of anhydrous CH_2Cl_2 was added. A CH_2Cl_2 solution (1 mL) of the diazo compound (0.6 mmol) was slowly added to the reaction mixture, which was then stirred for 12 h at room temperature under N_2. The crude reaction mixture was purified by flash chromatography (dry loading) using EtOAc and petroleum ether as eluents.

1.7 HPLC Standard Curves for Organoborane Products

Product formation in enzymatic reactions was quantified by HPLC based on standard curves. To determine the standard calibration curves, stock solutions of chemically synthesized racemic products were prepared at various concentrations (0.25-10 mM in MeCN). All data points represent the average of duplicate runs. The standard curves are plots of product concentration in mM (x-axis) versus area/10^7 (y-axis).

Table S1. Catalytic activity and enantioselectivity of engineered Ngb variants in the B-H insertion reaction with pyridine borane (py-BH_3) and methyl 2-diazo-4-phenylbutanoate (MDPB).



Entry	Catalyst	*ee* (%)	Yield (%)
1	WT	25	15
2	A15C	33	18
3	A15C/H64G	22	24
4	A15C/H64V	43	49
5	A15C/H64S	50	55
6	A15C/H64D	43	39
7	A15C/H64S/V68F	64	30
8	A15C/H64S/V68F/F28M	94	60
9	A15C/H64V/V68F/F28M	83	45
10	A15C/H64G/V68F/F28M	15	33

Reaction Conditions: 5 mM py-BH_3, 7.5 mM MDPB, 20 mM $Na_2S_2O_4$, 40 μM Ngb, 50 mM KPi (15% MeCN, pH 7.0), RT, and 12 h under N_2. Yields were determined based on an HPLC calibration curve with racemic standards. The *ee* values were determined by chiral HPLC.

Table S2. Docking energies of py-BH_3 binding to the complex of MDPB-CSFM Ngb.

Model	$\mathbf{E_{binding}}$ [a]	$\mathbf{E_{inter\text{-}mol}}$ [b]	$\mathbf{E_{vdw}}$ [c]	$\mathbf{E_{total}}$ [d]	$\mathbf{E_{electr}}$ [e]	$\mathbf{E_{torsional}}$ [f]
1	-4.21	-4.49	-1.68	-10.47	0.05	0.27
2	-4.19	-4.47	-1.78	-10.28	0.03	0.27
3	-4.05	-4.32	-1.81	-10.75	-0.01	0.27
4	-4.05	-4.32	-1.60	-10.67	0.01	0.27
5	-3.90	-4.18	-1.64	-10.52	0.03	0.27
6	-3.88	-4.15	-1.68	-10.26	0.04	0.27
7	-3.87	-4.15	-1.43	-11.24	0.05	0.27
8	-3.80	-4.08	-1.41	-10.96	0.05	0.27
9	-3.79	-4.06	-1.78	-11.13	0.00	0.27
10	-3.58	-3.86	-1.20	-11.23	0.03	0.27

[a] Binding energy. [b] Intermolecular energy. [c] van der Waals energies. [d] total energy of the complex. [e] electrostatic energy. [f] torsional free energy. Unit: kcal/mol.

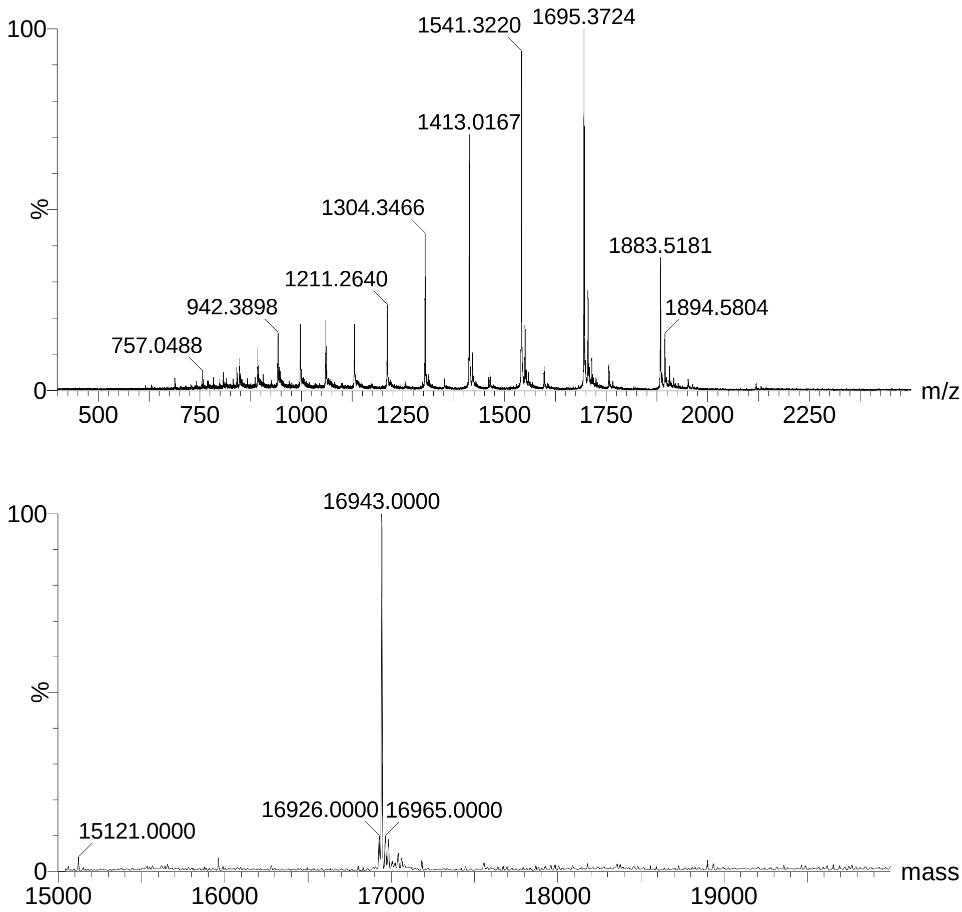


Figure S1. MS spectra of CSFM Ngb with two disulfide bonds; calculated: 16943.5 Da; observed: 16943.0 ±0.5 Da.

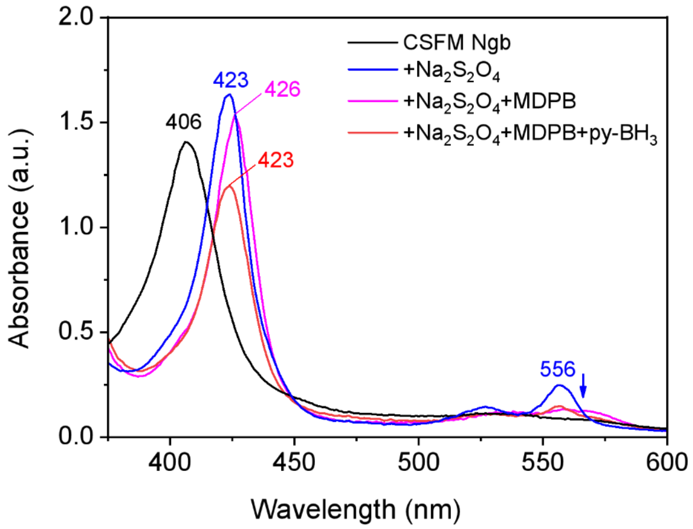
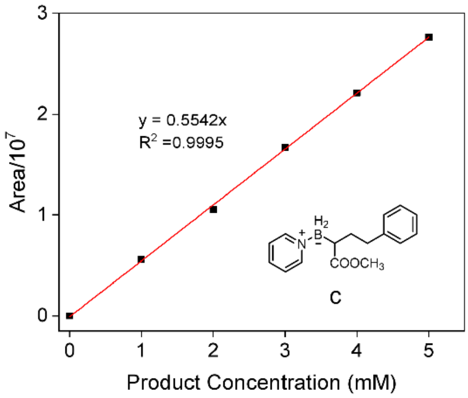
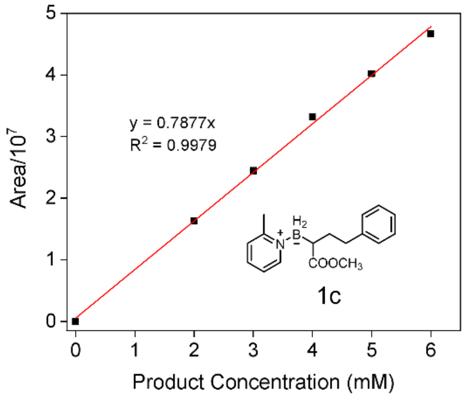


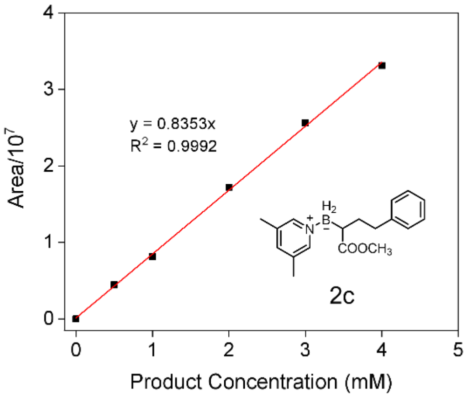
Figure S2. UV‑vis spectra of CSFM Ngb: ferric (black), ferrous (blue), MDPB‑bound form (magenta), and following py–BH_3 addition to MDPB‑CSFM Ngb (red).



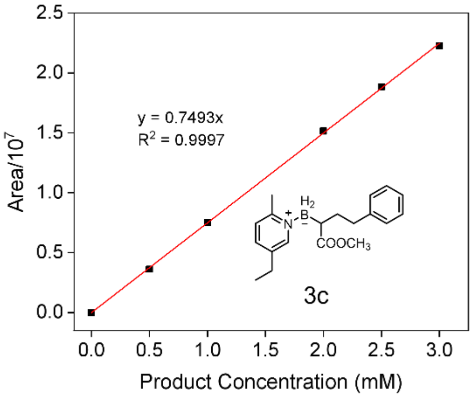
y = 0.5542x
R^2 =0.9995
COOCH3
c
Area/10^7
Product Concentration (mM)



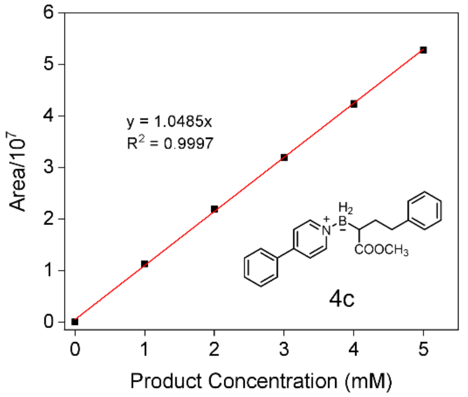
y = 0.7877x
R^2 = 0.9979
COOCH3
1c
Area/10^7
Product Concentration (mM)



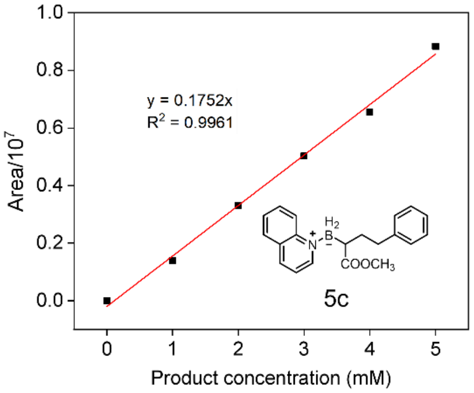
y = 0.8353x
R^2 = 0.9992
COOCH3
2c
Area/10^7
Product Concentration (mM)



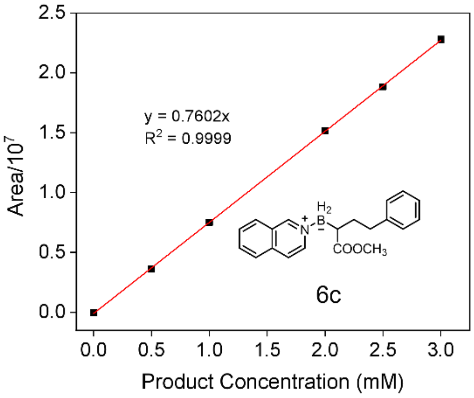
y = 0.7493x
R^2 = 0.9997
COOCH3
3c
Area/10^7
Product Concentration (mM)



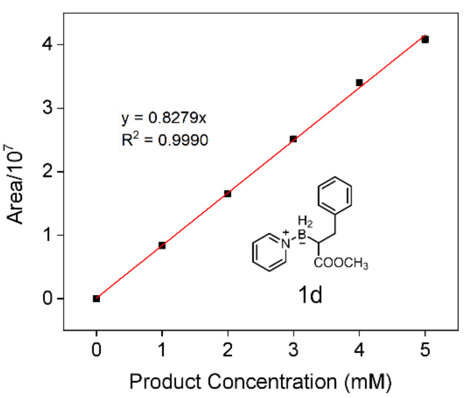
y = 1.0485x
R^2 = 0.9997
COOCH3
4c
Area/10^7
Product Concentration (mM)



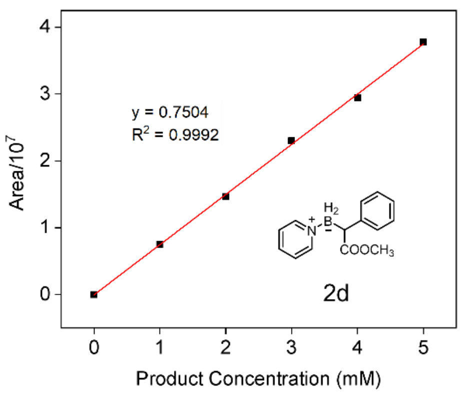
y = 0.1752x
R^2 = 0.9961
COOCH3
5c
Area/10^7
Product concentration (mM)



y = 0.7602x
R^2 = 0.9999
COOCH3
6c
Area/10^7
Product Concentration (mM)



y = 0.8279x
R^2 = 0.9990
COOCH3
1d
Area/10^7
Product Concentration (mM)


y = 0.7504
R^2 = 0.9992
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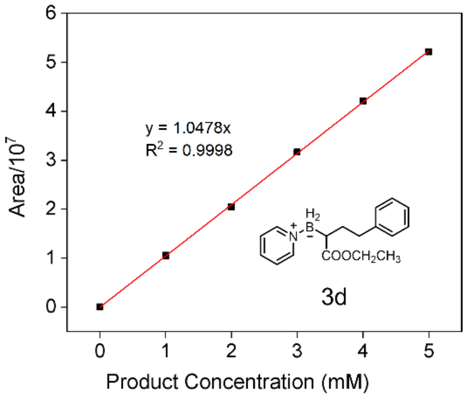
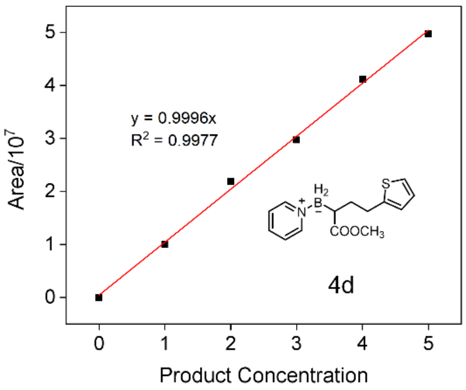
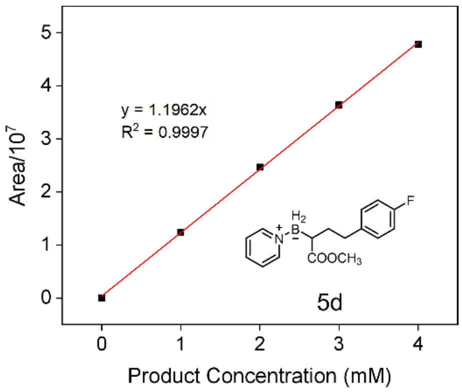
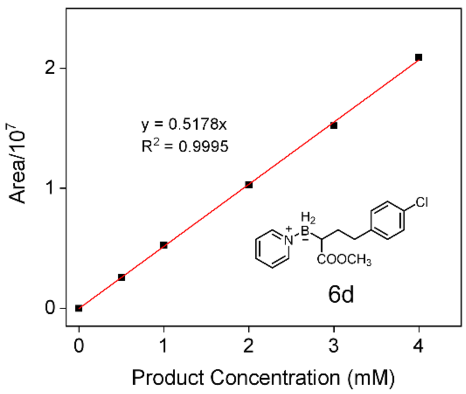
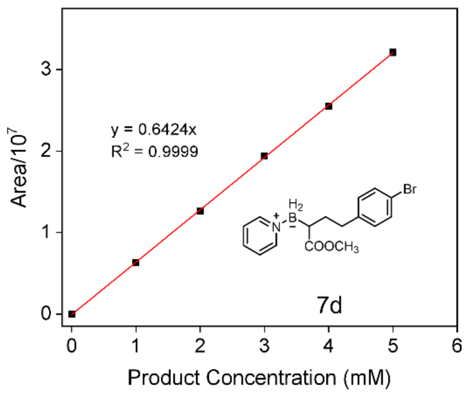
Area/10^7
Product Concentration (mM)

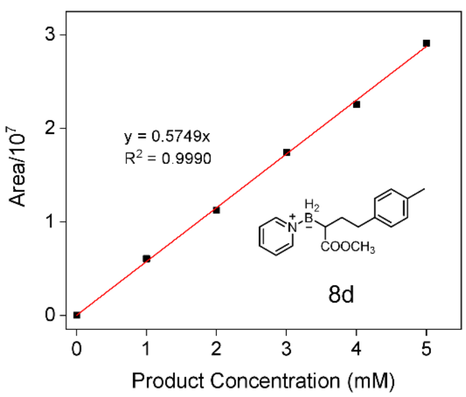

y = 1.0478x
R^2 = 0.9998
3d
Area/10^7
Product Concentration (mM)

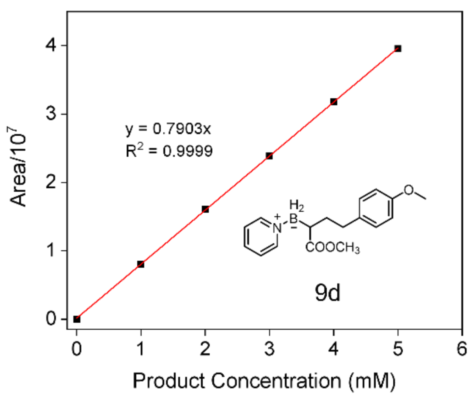

y = 0.9996x
R^2 = 0.9977
4d
Area/10^7
Product Concentration


y = 1.1962x
R^2 = 0.9997
5d
Area/10^7
Product Concentration (mM)


y = 0.5178x
R^2 = 0.9995
6d
Area/10^7
Product Concentration (mM)


y = 0.6424x
R^2 = 0.9999
7d
Area/10^7
Product Concentration (mM)


y = 0.5749x
R^2 = 0.9990
8d
Area/10^7
Product Concentration (mM)


y = 0.7903x
R^2 = 0.9999
9d
Area/10^7
Product Concentration (mM)

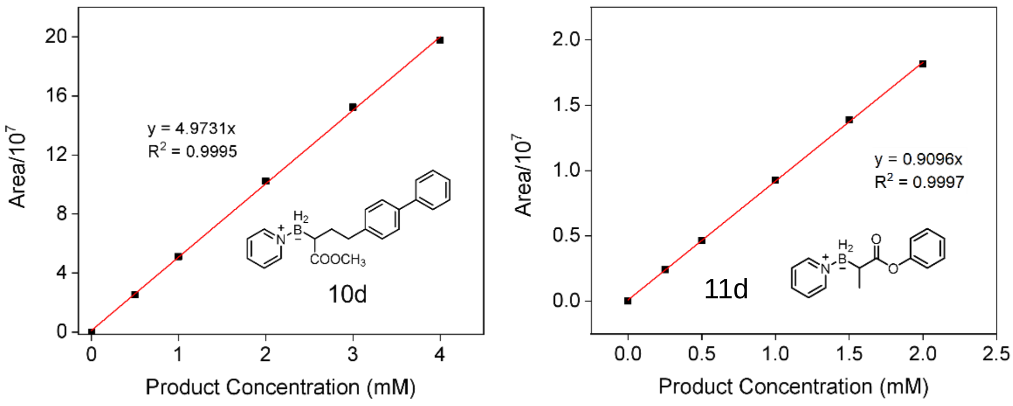
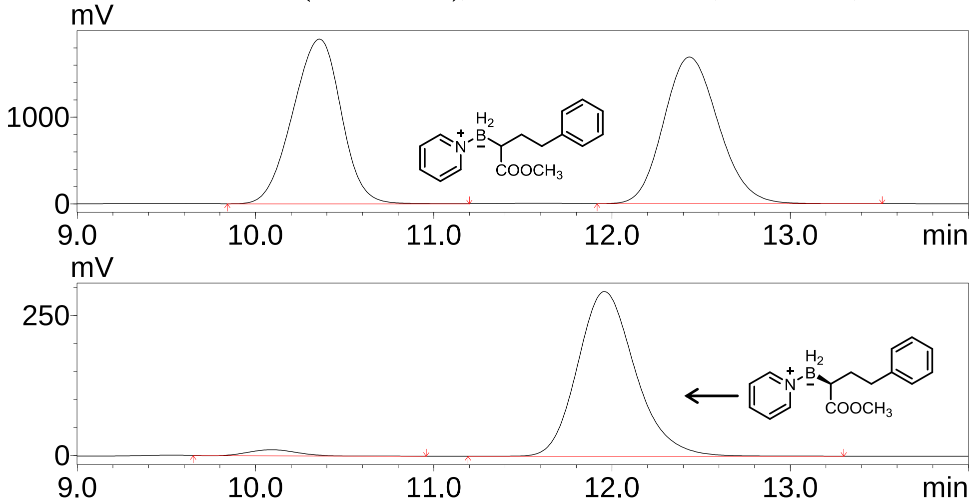


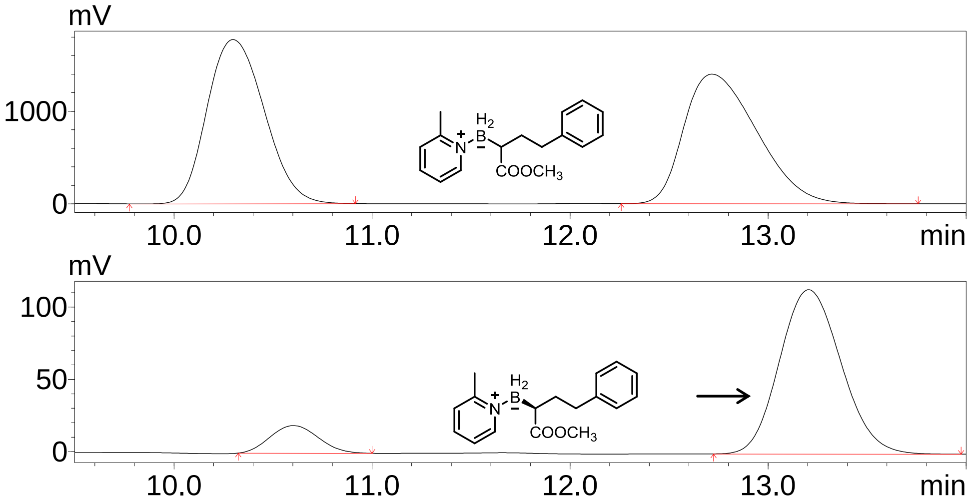
Figure S3. Calibration curves for products.

CHIRALCEL ADH (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm



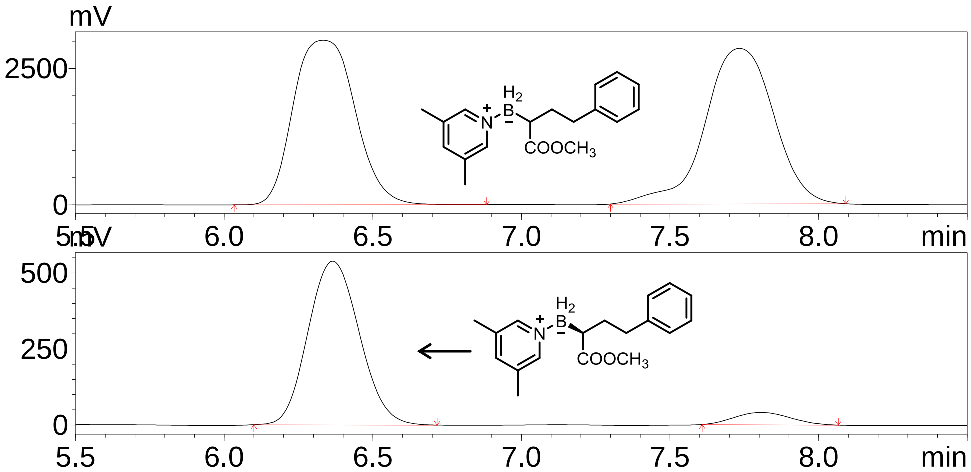
Rac-**c**			*R*-**c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
10.359	35948427	49.887	10.088	229133	3.349
12.435	36111159	50.113	11.958	6613214	96.651

CHIRALCEL ADH (4.6x250 mm), 12% i-PrOH/hexanes,1.0 mL/min, 254 nm



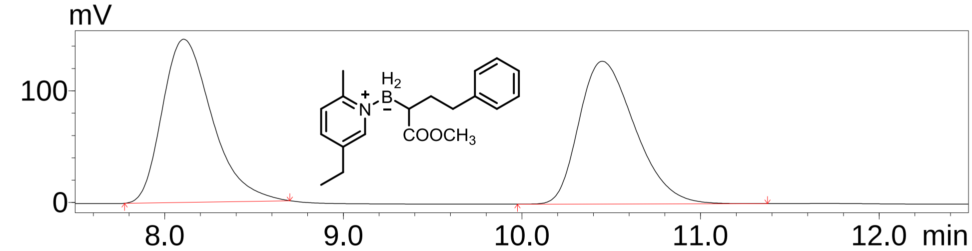
Rac-**1c**			*R*-**1c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
10.299	35620693	49.855	10.604	322919	11.610
12.717	35828360	50.145	13.205	2458485	88.390

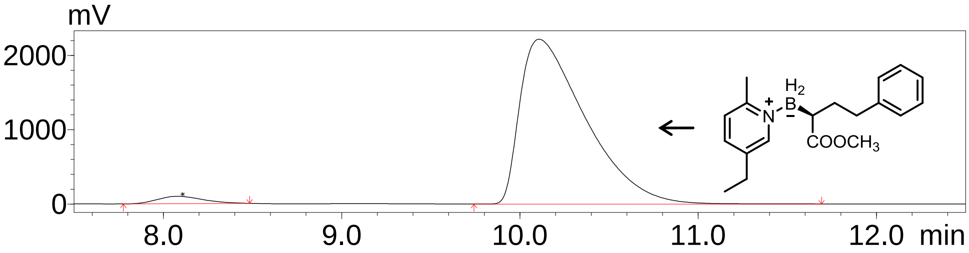
CHIRALCEL ADH (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm



Rac-**2c**			*R*-**2c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
6.334	43554111	48.696	6.365	6461076	92.443
7.734	45886301	51.304	7.806	528144	7.557

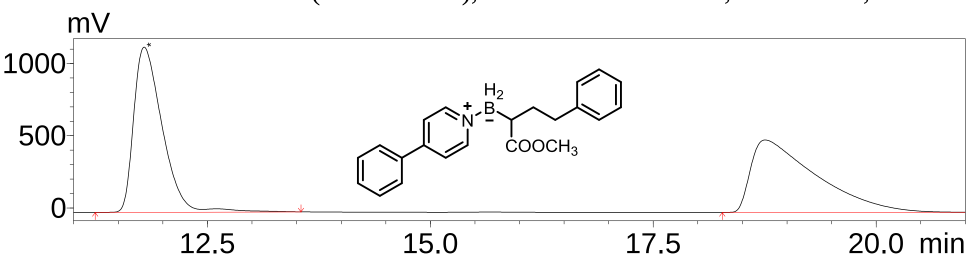
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

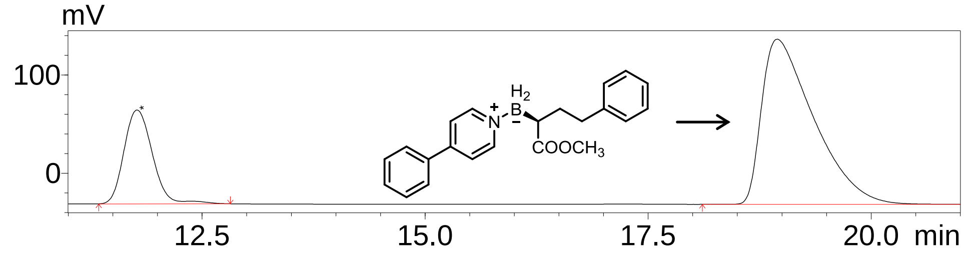




Rac-**3c**			*R*-**3c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
8.107 10.451	2834689 2780004	50.487 49.513	8.081 10.108	1750344 56464585	3.007 96.993

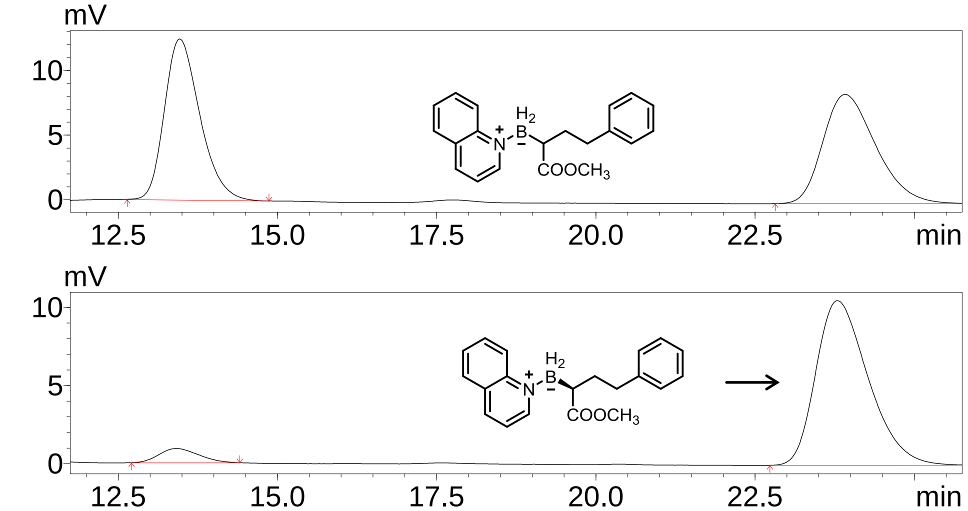
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min,





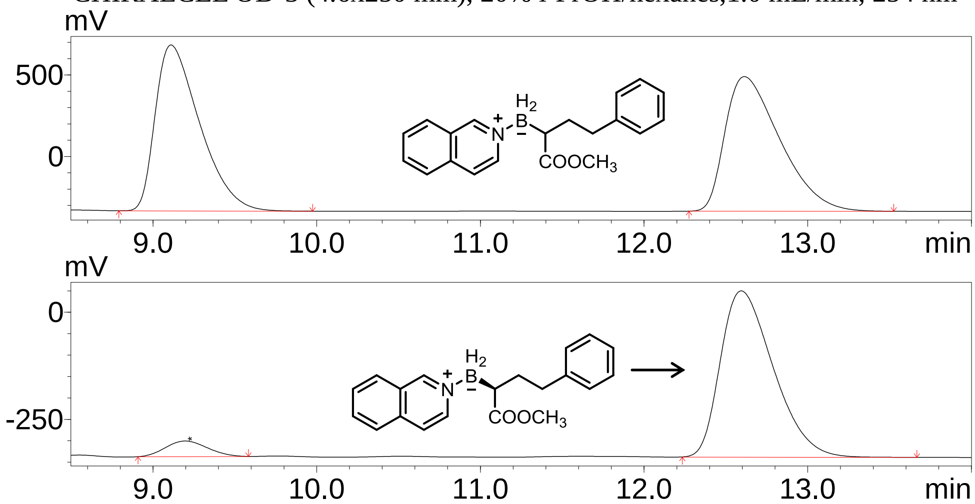
Rac-**4c**			*R*-**4c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
11.791 18.757	25517075 25551610	49.966 50.034	11.771 18.948	2114276 6820236	23.664 76.336

CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm



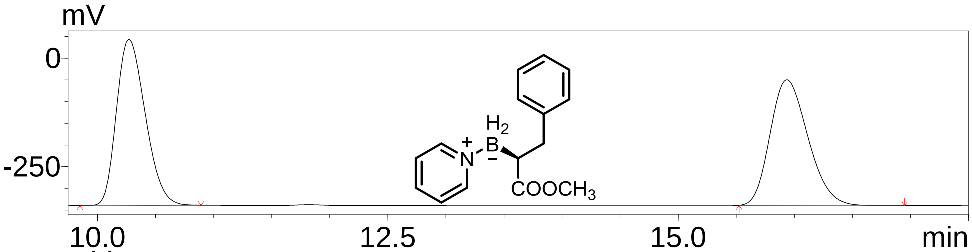
Rac-**5c**			*R*-**5c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
13.466	482827	49.863	13.415	39441	6.169
23.915	485485	50.137	23.795	599864	93.831

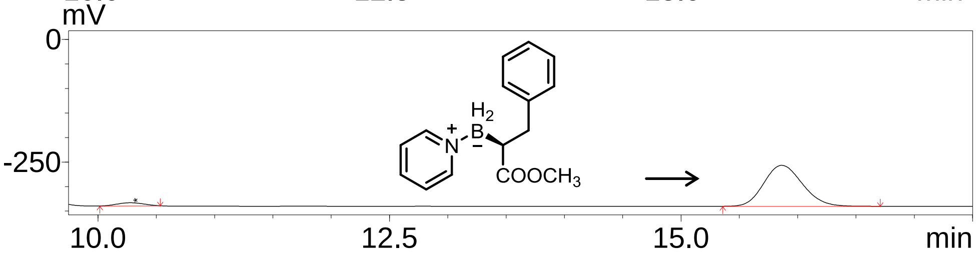
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm



Rac-**6c**			*R*-**6c**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
9.111	19208039	49.971	9.196	644114	6.884
12.613	19230333	50.029	12.594	8712221	93.116

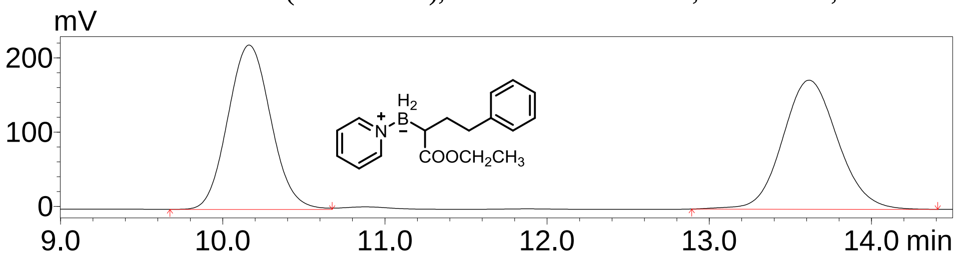
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

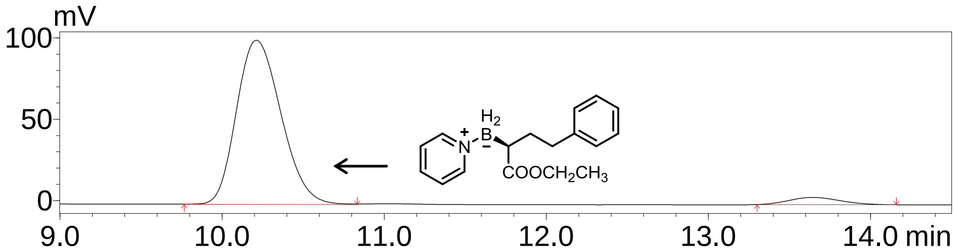




Rac-**1d**			*R*-**1d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
10.272 15.936	6595780 6566343	50.112 49.888	10.280 15.864	99839 1923220	4.935 95.065

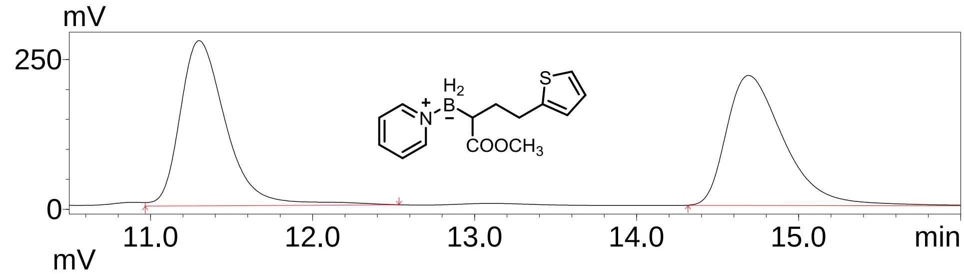
CHIRALCEL ADH (4.6x250mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

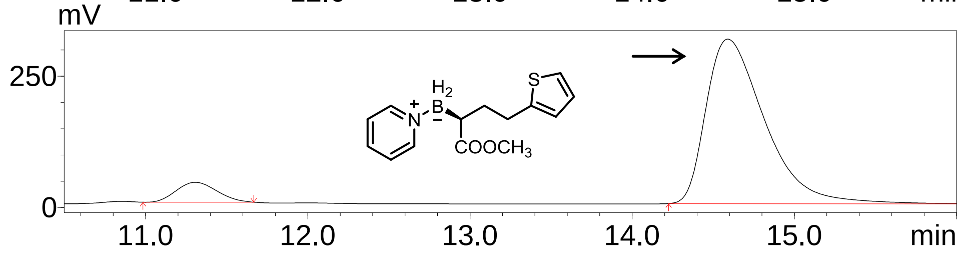




Rac-**3d**			*R*-**3d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
10.163 13.615	4075533 4125212	49.697 50.303	10.212 13.645	1923742 105112	94.819 5.181

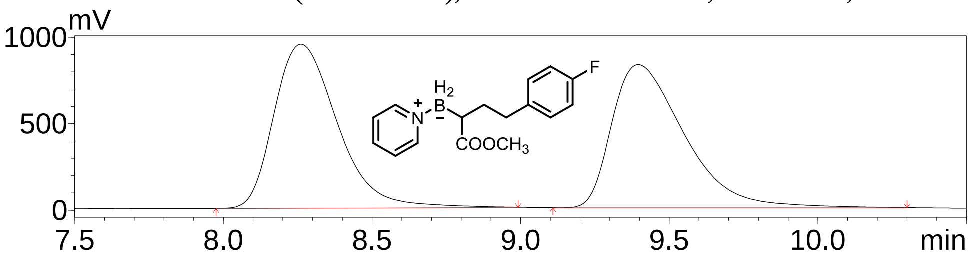
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

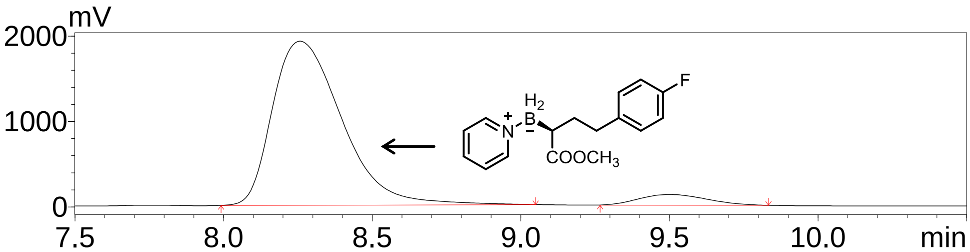




Rac-**4d**			*R*-**4d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
11.300 14.692	5442352 5328673	50.528 49.472	11.307 14.590	660079 7889828	7.720 92.280

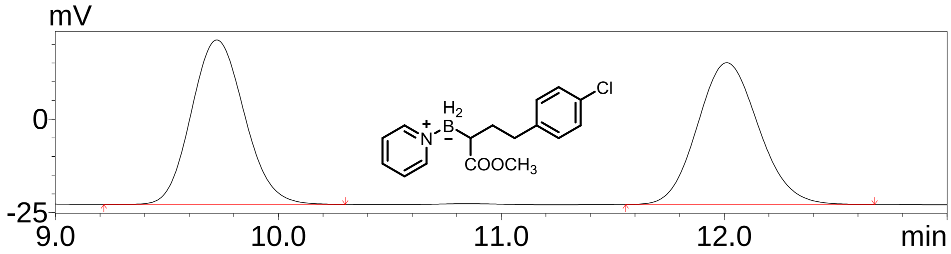
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

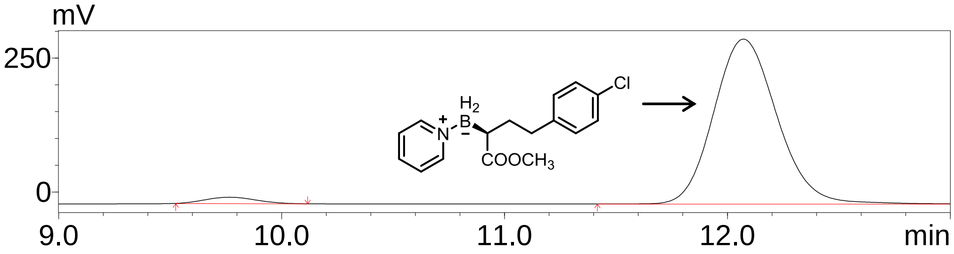




Rac-**5d**			*R*-**5d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
8.261 9.396	14051940 14026783	50.045 49.955	8.257 9.501	31143641 1961642	94.075 5.925

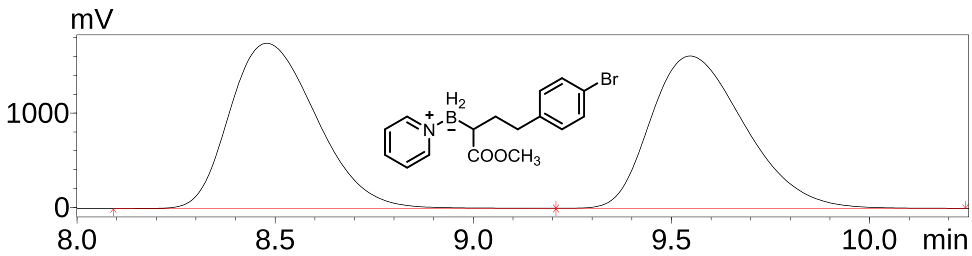
CHIRALCEL ADH (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

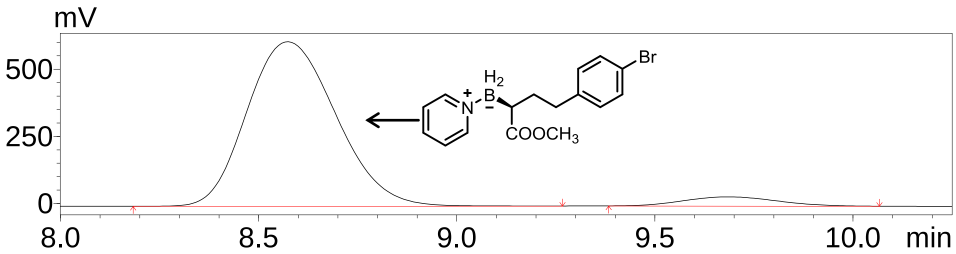




Rac-**6d**			*R*-**6d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
9.724 12.012	727796 722468	50.184 49.816	9.765 12.072	186055 6076567	2.971 97.029

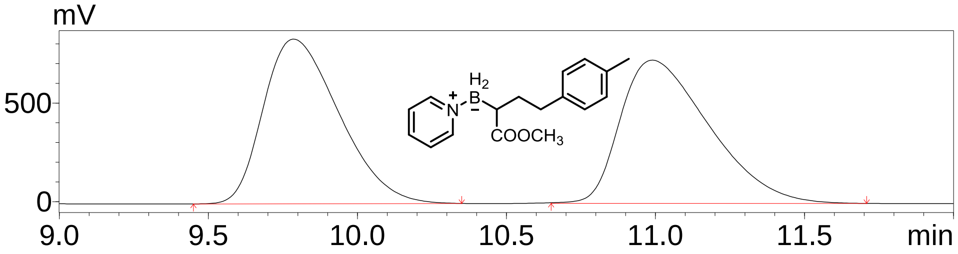
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

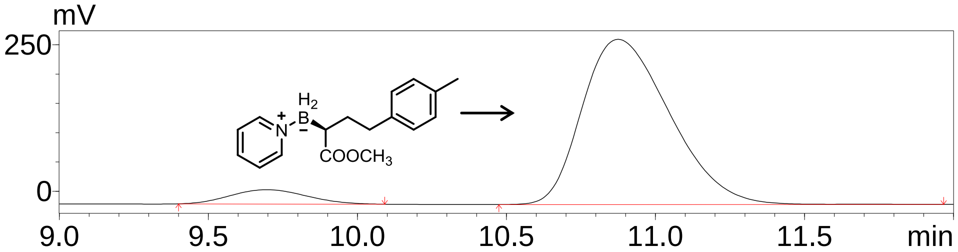




Rac-**7d**			*R*-**7d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
8.479 9.548	26750858 26799446	49.955 50.045	8.573 9.685	9549956 556155	94.497 5.503

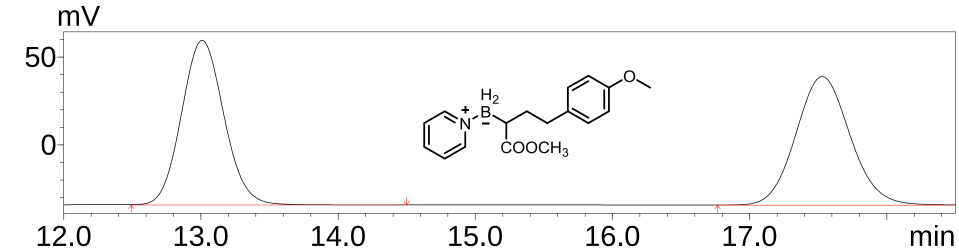
CHIRALCEL OD-3 (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm

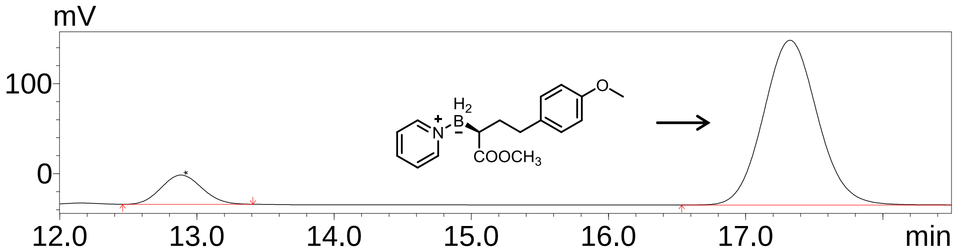




Rac-**8d**			*R*-**8d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
9.786 10.990	14783665 15084495	49.496 50.504	9.696 10.875	433446 5760416	6.998 93.002

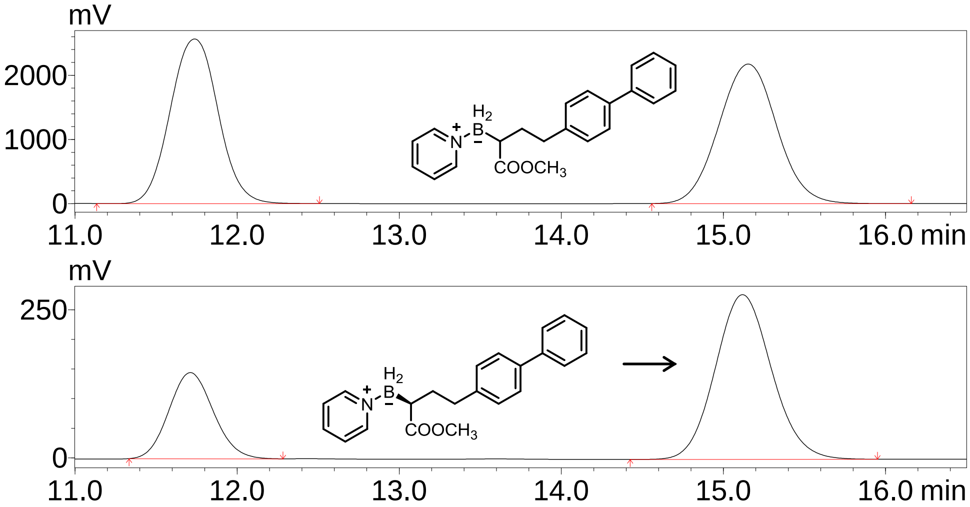
CHIRALCEL ADH (4.6x250mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm





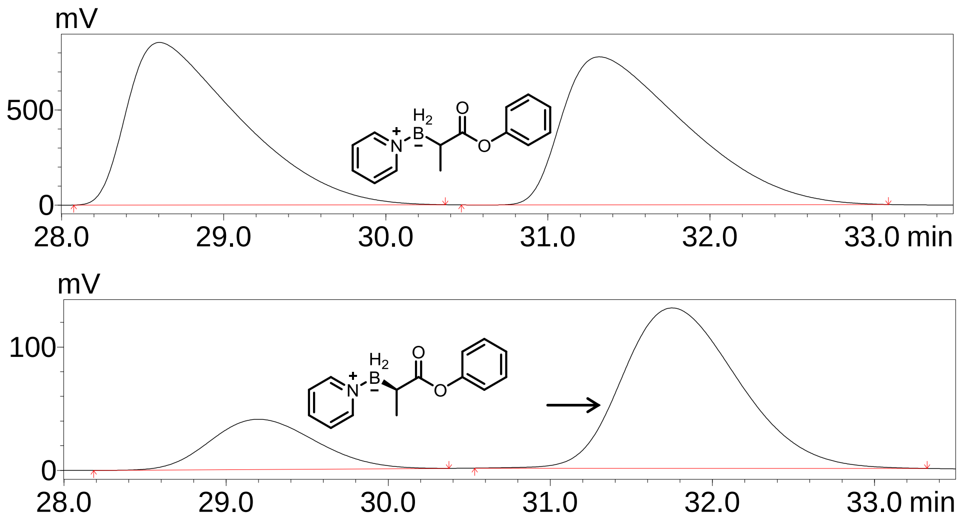
Rac-**9d**			*R*-**9d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
13.009 17.530	2012634 2010694	50.024 49.976	12.884 17.324	671097 5011191	11.810 88.190

CHIRALCEL ADH (4.6x250 mm), 20% i-PrOH/hexanes,1.0 mL/min, 254 nm



Rac-**10d**			*R*-**10d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
11.738	52708578	49.291	11.712	2772741	29.202
15.153	54225960	50.709	15.118	6722218	70.798

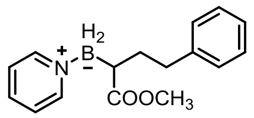
CHIRALCEL OD-3 (4.6x250 mm）5% i-PrOH/hexanes,1.0 mL/min,254 nm



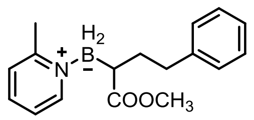
Rac-**11d**			*R*-**11d**		
Ret. Time (min)	Area (mv)	Area%	Ret. Time (min)	Area (mv)	Area%
28.604	41441055	50.090	29.200	1835500	22.090
31.317	41292652	49.910	31.752	6473769	77.91

Figure S4. Chiral HPLC traces for products.

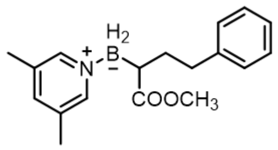
2. NMR data and spectra of the products.



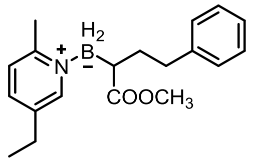
(1-methoxy-1-oxo-4-phenylbutan-2-yl)(pyridin-1-ium-1-yl)boranuide (c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.5 Hz, 2H), 7.98 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.24 (dd, *J* = 12.5, 5.0 Hz, 2H), 7.15 (dd, *J* = 16.0, 7.5 Hz, 3H), 3.48 (s, 3H), 2.69 – 2.62 (m, 1H), 2.55 (m, 1H), 2.02 (dd, *J* = 9.5, 5.0 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.68 – 1.60 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.03, 147.41, 143.27, 139.99, 128.60, 128.11, 125.38, 125.26, 50.42, 40.99, 36.48, 32.40. ^{11}B NMR (160 MHz, $CDCl_3$) δ -5.82. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{16}H_{22}BNO_2Na$: 292.1485, observed: 292.1489.



(1-methoxy-1-oxo-4-phenylbutan-2-yl)(2-methylpyridin-1-ium-1-yl)boranuide (1c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.5 Hz, 1H), 7.82 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.24 (dd, *J* = 12.0, 4.2 Hz, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 3.35 (s, 3H), 2.72 (d, *J* = 5.5 Hz, 3H), 2.70 – 2.65 (m, 1H), 2.58 – 2.53 (m, 1H), 2.14 – 2.05 (m, 1H), 2.01 (dd, *J* = 10.0, 4.5 Hz, 1H), 1.72 – 1.62 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.98, 157.67, 149.00, 143.37, 140.07, 128.59, 128.10, 127.48, 125.35, 122.38, 50.18, 39.59, 36.39, 32.56, 22.48. ^{11}B NMR (160 MHz, $CDCl_3$) δ -5.74. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{17}H_{22}BNO_2Na$: 306.1641, observed: 306.1643.

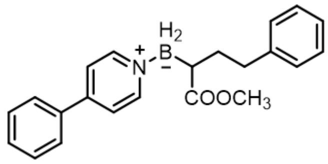


(3,5-dimethylpyridin-1-ium-1-yl)(1-methoxy-1-oxo-4-phenylbutan-2-yl)boranuide (2c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.55 (s, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.11 (m, 3H), 3.47 (s, 3H), 2.69 – 2.63 (m, 1H), 2.53 (dt, *J* = 15.0, 7.5 Hz, 1H), 2.35 (s, 6H), 2.02 – 1.93 (m, 2H), 1.62 (dt, *J* = 16.5, 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.11, 144.65, 143.35, 141.28, 135.16, 128.61, 128.09, 125.34, 50.31, 41.27, 36.48, 32.41, 18.35. ^{11}B NMR (160 MHz, $CDCl_3$) δ -101.82. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{18}H_{24}BNO_2Na$: 320.1798, observed: 320.1801.

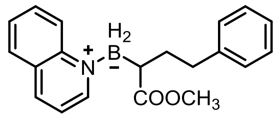


(5-ethyl-2-methylpyridin-1-ium-1-yl)(1-methoxy-1-oxo-4-phenylbutan-2-yl)boranuide (3c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 1.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.29 –

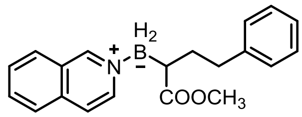
7.22 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.14 (t, *J* = 7.0 Hz, 1H), 3.36 (s, 3H), 2.74 – 2.70 (m, 1H), 2.68 (s, 3H), 2.67 – 2.63 (m, 2H), 2.59 – 2.52 (m, 1H), 2.14 – 2.05 (m, 1H), 2.03 – 1.97 (m, 1H), 1.70 – 1.63 (m, 1H), 1.25 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.03, 154.76, 148.28, 143.40, 139.61, 138.52, 128.59, 128.07, 127.08, 125.30, 50.15, 39.72, 36.38, 32.54, 25.57, 21.95, 14.89. ^{11}B NMR (160 MHz, $CDCl_3$) δ -6.46. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{19}H_{26}BNO_2Na$: 334.1954, observed: 334.1951.



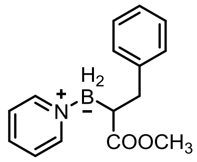
(1-methoxy-1-oxo-4-phenylbutan-2-yl)(4-phenylpyridin-1-ium-1-yl)boranuide (4c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.5 Hz, 2H), 7.70 – 7.64 (m, 4H), 7.55 – 7.51 (m, 3H), 7.24 (dd, *J* = 10.0, 4.8 Hz, 2H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 1H), 3.51 (s, 3H), 2.71 – 2.64 (m, 1H), 2.57 (m, 1H), 2.06 (dd, *J* = 9.5, 5.0 Hz, 1H), 2.01 – 1.91 (m, 1H), 1.72 – 1.64 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.17, 152.28, 147.50, 143.33, 135.52, 130.84, 129.61, 128.64, 128.15, 127.28, 125.41, 122.73, 50.48, 41.11, 36.56, 32.52. ^{11}B NMR (160 MHz, $CDCl_3$) δ -4.53. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{22}H_{24}BNO_2Na$: 368.1798, observed: 368.1800.



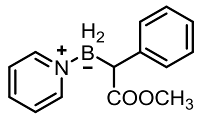
(1-methoxy-1-oxo-4-phenylbutan-2-yl)(quinolin-1-ium-1-yl)boranuide (5c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 5.0 Hz, 1H), 8.82 (d, *J* = 9.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 8.0, 5.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 3.27 (s, 3H), 2.77 – 2.67 (m, 1H), 2.60 – 2.51 (m, 1H), 2.20 – 2.10 (m, 2H), 1.77 – 1.69 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.02, 150.68, 143.39, 142.65, 141.91, 132.40, 129.29, 128.73, 128.59, 128.34, 128.09, 125.33, 124.45, 120.47, 50.20, 40.29, 36.41, 32.67. ^{11}B NMR (160 MHz, $CDCl_3$) δ -5.83. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{20}H_{22}BNO_2Na$: 342.1641, observed: 342.1645.



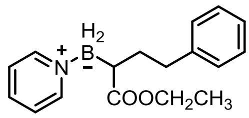
(isoquinolin-2-ium-2-yl) (1-methoxy-1-oxo-4-phenylbutan-2-yl) boranuide (6c). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.28 (d, *J* = 6.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.84 (d, *J* = 6.5 Hz, 1H), 7.77 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.15 (dd, *J* = 15.0, 7.2 Hz, 3H), 3.44 (s, 3H), 2.71 – 2.65 (m, 1H), 2.57 (m, 1H), 2.11 (dd, *J* = 9.5, 5.0 Hz, 1H), 2.07 – 1.93 (m, 1H), 1.70 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.13, 150.68, 143.33, 139.34, 136.27, 133.79, 129.41, 128.98, 128.62, 128.09, 127.88, 126.64, 125.35, 122.91, 50.37, 41.26, 36.52, 32.49. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.87. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{20}H_{22}BNO_2Na$: 342.1641, observed: 342.1645.



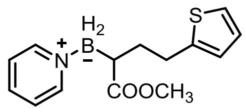
(1-methoxy-1-oxo-3-phenylpropan-2-yl)(pyridin-1-ium-1-yl)boranuide (1d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.5 Hz, 2H), 7.91 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.14 – 7.08 (m, 4H), 7.05 – 7.00 (m, 1H), 3.30 (s, 3H), 2.87 (dd, *J* = 14.5, 10.5 Hz, 1H), 2.62 (dd, *J* = 14.5, 4.0 Hz, 1H), 2.27 (dd, *J* = 10.0, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.40, 146.36, 142.85, 139.06, 127.44, 126.97, 124.29, 124.21, 49.36, 42.30, 35.26. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.57. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{15}H_{18}BNO_2Na$: 278.1328, observed: 278.1323.



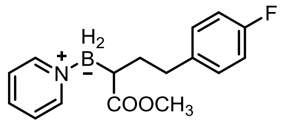
(2-methoxy-2-oxo-1-phenylethyl)(pyridin-1-ium-1-yl)boranuide (2d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 5.5 Hz, 2H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.14 (dt, *J* = 13.0, 7.5 Hz, 4H), 7.05 – 7.01 (m, 1H), 3.58 (s, 3H), 3.38 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.17, 147.34, 142.58, 140.21, 127.90, 127.75, 125.02, 124.45, 50.90, 49.06. ^{11}B NMR (160 MHz, $CDCl_3$) δ -2.83. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{14}H_{16}BNO_2Na$: 264.1172, observed: 264.1176.



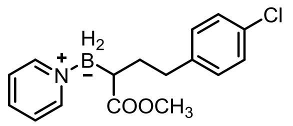
(1-ethoxy-1-oxo-4-phenylbutan-2-yl)(pyridin-1-ium-1-yl)boranuide (3d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.0 Hz, 2H), 7.98 (m, 1H), 7.53 (dd, *J* = 7.5, 6.5 Hz, 2H), 7.25 (dd, *J* = 12.5, 5.0 Hz, 2H), 7.19 – 7.12 (m, 3H), 3.95 (m, 2H), 2.70 – 2.63 (m, 1H), 2.56 (m, 1H), 2.02 – 1.96 (m, 1H), 1.96 – 1.87 (m, 1H), 1.68 – 1.61 (m, 1H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.69, 147.46, 143.38, 139.92, 128.61, 128.11, 125.36, 125.22, 58.73, 41.05, 36.46, 32.44, 14.55. ^{11}B NMR (160 MHz, $CDCl_3$) δ -4.53. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{17}H_{22}BNO_2Na$: 306.1641, observed: 306.1644.



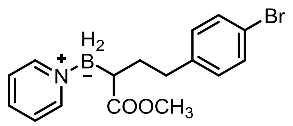
[1-methoxy-1-oxo-4-(thiophen-2-yl)butan-2-yl](pyridin-1-ium-1-yl)boranuide (4d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.0 Hz, 2H), 8.02 – 7.93 (m, 1H), 7.53 (dd, *J* = 10.0, 4.0 Hz, 2H), 7.05 (d, *J* = 5.0 Hz, 1H), 6.87 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.75 (d, *J* = 3.0 Hz, 1H), 3.45 (s, 3H), 2.87 (m, 1H), 2.81 – 2.74 (m, 1H), 2.06 – 1.94 (m, 2H), 1.74 – 1.65 (m, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ 176.86, 143.42, 142.25, 136.19, 122.67, 121.41, 120.03, 118.65, 46.48, 36.83, 28.62, 26.27. ^{11}B NMR (160 MHz, CD_3OD) δ -7.84. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{14}H_{18}BNO_2SNa$: 298.1049, observed: 298.1054.



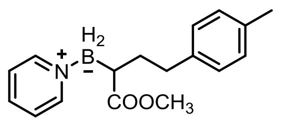
[4-(4-fluorophenyl)-1-methoxy-1-oxobutan-2-yl](pyridin-1-ium-1-yl)boranuide (5d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.5 Hz, 2H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.09 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.90 (t, *J* = 8.5 Hz, 2H), 3.44 (s, 3H), 2.64 – 2.58 (m, 1H), 2.54 – 2.47 (m, 1H), 1.97 (dd, *J* = 9.5, 5.0 Hz, 1H), 1.93 – 1.85 (m, 1H), 1.65 – 1.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.93, 161.04（d, *J* = 240.5 Hz）, 147.34, 140.09, 138.82, 129.85 (d, *J* = 7.9 Hz), 125.32, 114.75（d, *J* = 20 Hz）, 50.38, 40.90, 35.56, 32.49. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.77. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{16}H_{19}BFNO_2Na$: 310.1391, observed: 310.1392.



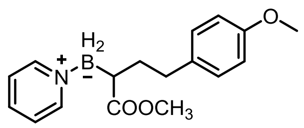
[4-(4-chlorophenyl)-1-methoxy-1-oxobutan-2-yl](pyridin-1-ium-1-yl)boranuide (6d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 2H), 7.99 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.45 (s, 3H), 2.65 – 2.58 (m, 1H), 2.54 – 2.47 (m, 1H), 2.00 – 1.94 (m, 1H), 1.93 – 1.84 (m, 1H), 1.65 – 1.57 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.91, 147.36, 141.67, 140.07, 131.00, 129.96, 128.16, 125.30, 50.42, 40.91, 35.71, 32.26. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.86. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{16}H_{19}BClNO_2Na$: 326.1095, observed: 326.1100.



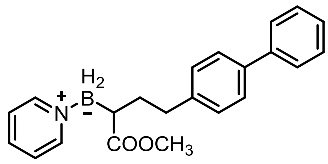
[4-(4-bromophenyl)-1-methoxy-1-oxobutan-2-yl](pyridin-1-ium-1-yl)boranuide (7d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.5 Hz, 2H), 7.98 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.45 (s, 3H), 2.64 – 2.57 (m, 1H), 2.54 – 2.46 (m, 1H), 1.97 (dd, *J* = 9.5, 5.0 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.66 – 1.55 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.87, 147.30, 142.22, 140.14, 131.11, 130.42, 125.35, 119.04, 50.40, 40.88, 35.75, 32.22. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.89. HRMS (ESI) m/z $[M+Na]^+$ calculated for $C_{16}H_{19}BBrNO_2Na$: 370.0590, observed: 370.0592.



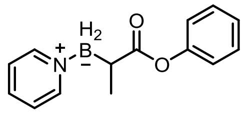
[1-methoxy-4-(methylphenyl)-1-oxobutan-2-yl](pyridin-1-ium-1-yl)boranuide (8d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 2H), 7.97 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.06 (s, 4H), 3.48 (s, 3H), 2.66 – 2.59 (m, 1H), 2.51 (m, 1H), 2.30 (s, 3H), 2.02 (dd, *J* = 9.5, 5.0 Hz, 1H), 1.90 (m, 1H), 1.67 – 1.58 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.09, 147.36, 140.18, 140.08, 134.74, 128.84, 128.48, 125.31, 50.40, 41.11, 36.04, 32.59, 21.03. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.78. HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{17}H_{22}BNO_2Na$: 306.1641, observed: 306.1643.



[1-methoxy-4-(methoxyphenyl)-1-oxobutan-2-yl](pyridin-1-ium-1-yl)boranuide (9d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 2H), 7.97 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 3.76 (s, 3H), 3.47 (s, 3H), 2.63 – 2.55 (m, 1H), 2.51 – 2.44 (m, 1H), 2.00 (dd, *J* = 9.5, 4.9 Hz, 1H), 1.88 (m, 1H), 1.64 – 1.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.09, 157.46, 147.38, 140.02, 135.38, 129.44, 125.27, 113.54, 55.25, 50.41, 41.02, 35.51, 32.62. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.89. HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{17}H_{22}BNO_3Na$: 322.1590, observed: 322.1595.

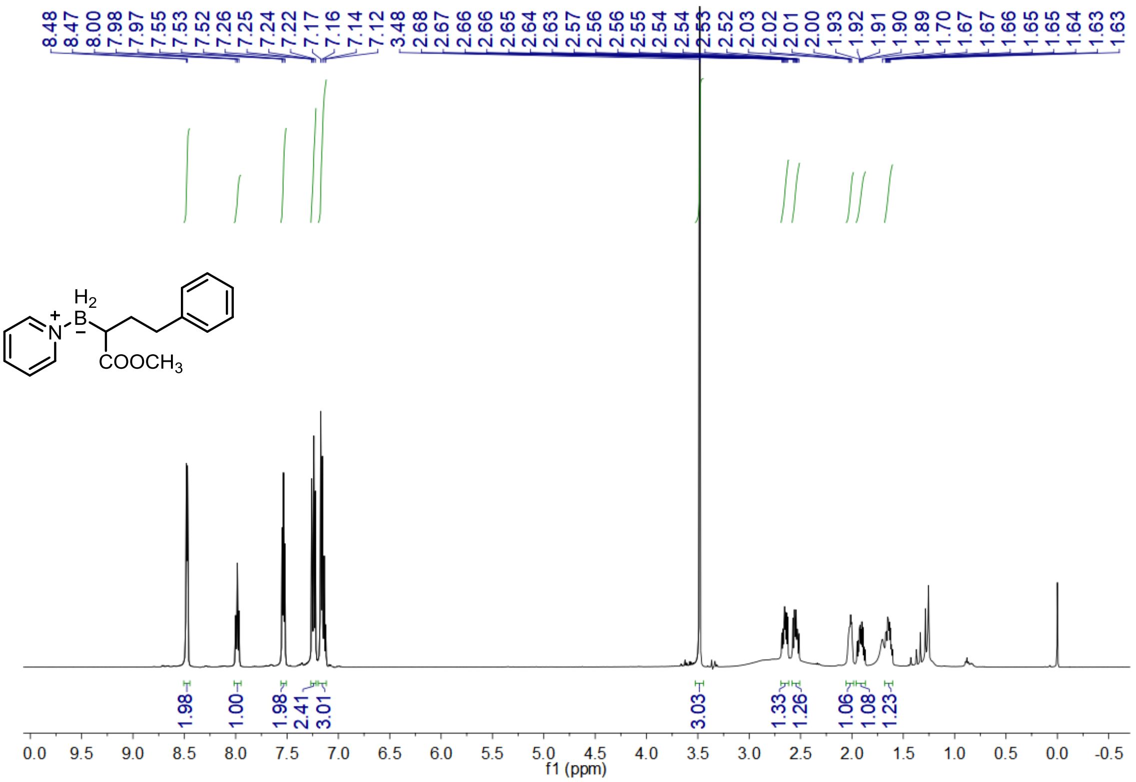


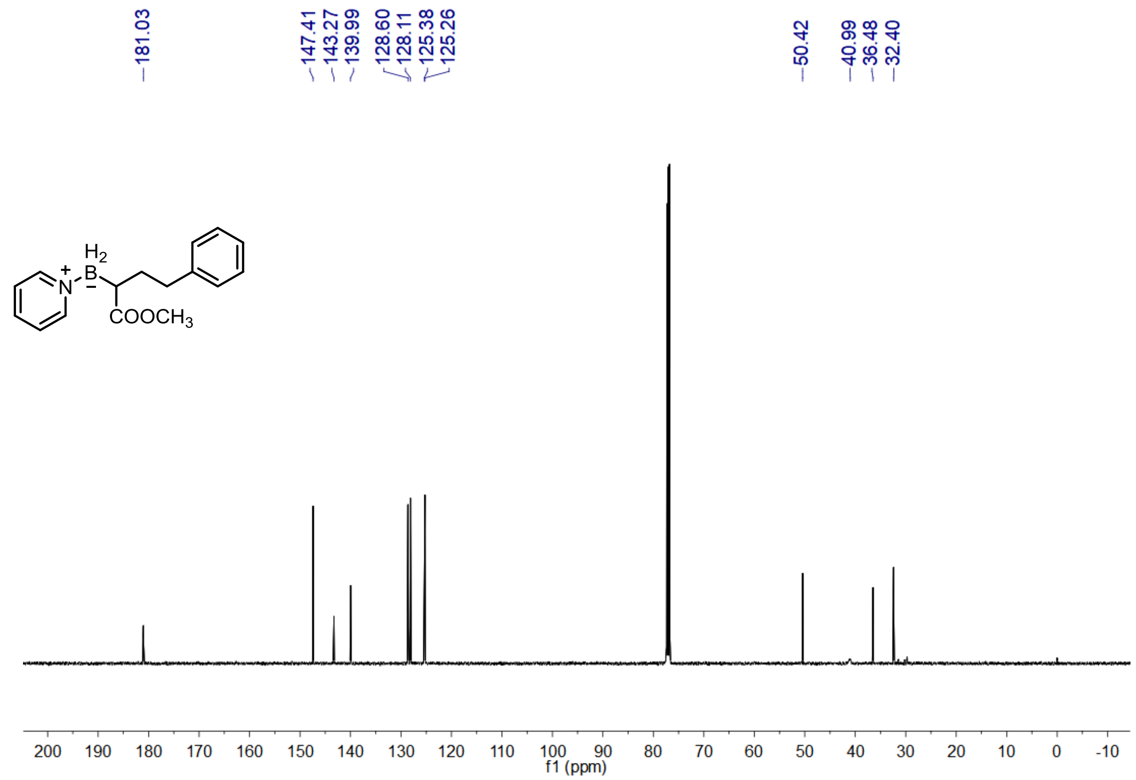
[1-methoxy-1-oxo-4-(4-phenylphenyl)-butan-2-yl](pyridin-1-ium-1-yl)boranuide (10d). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.5 Hz, 2H), 7.93 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 8.5 Hz, 4H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.47 (s, 3H), 2.74 – 2.67 (m, 1H), 2.63 – 2.56 (m, 1H), 2.04 (d, *J* = 10.0 Hz, 1H), 1.97 (m, 1H), 1.68 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.03, 147.37, 142.49, 141.27, 140.08, 138.32, 129.07, 128.74, 126.99, 126.94, 126.89, 125.32, 50.44, 41.11, 36.11, 32.43. ^{11}B NMR (160 MHz, $CDCl_3$) δ -3.86. HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{22}H_{24}BNO_2Na$: 368.1798, observed: 368.1789.

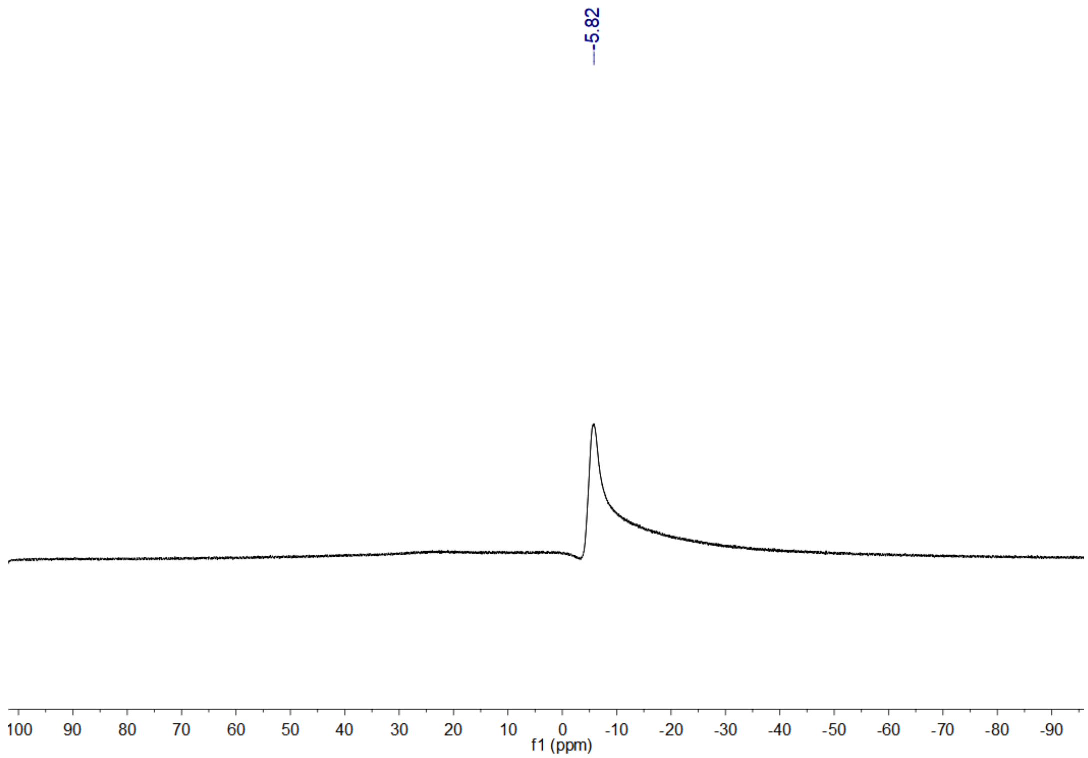


[1-(benzyloxy)-1-oxopropan-2-yl](pyridin-1-ium-1-yl)boranuide (11d). ^{1}H NMR NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 6.0 Hz, 2H), 7.84 (t, J = 7.5 Hz, 1H), 7.39 – 7.27 (m, 7H), 5.01 (d, J = 12.5 Hz, 1H), 4.89 (d, J = 12.5 Hz, 1H), 2.73 (d, J = 101.5 Hz, 2H), 2.08 (dd, J = 10.0, 6.0 Hz, 1H), 1.06 (d, J = 6.8 Hz, 3H). The H NMR data were consistent with those previously reported.[7]

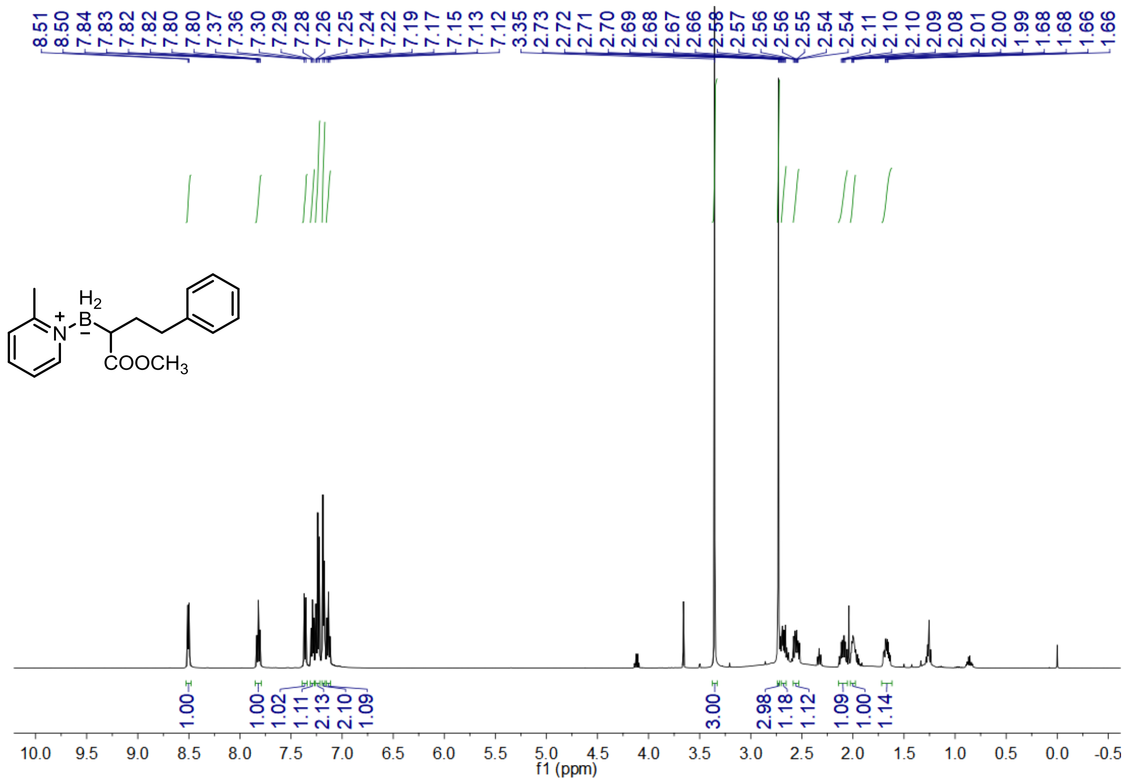
[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$) & [11]B NMR (160 MHz, $CDCl_3$) for **c.**

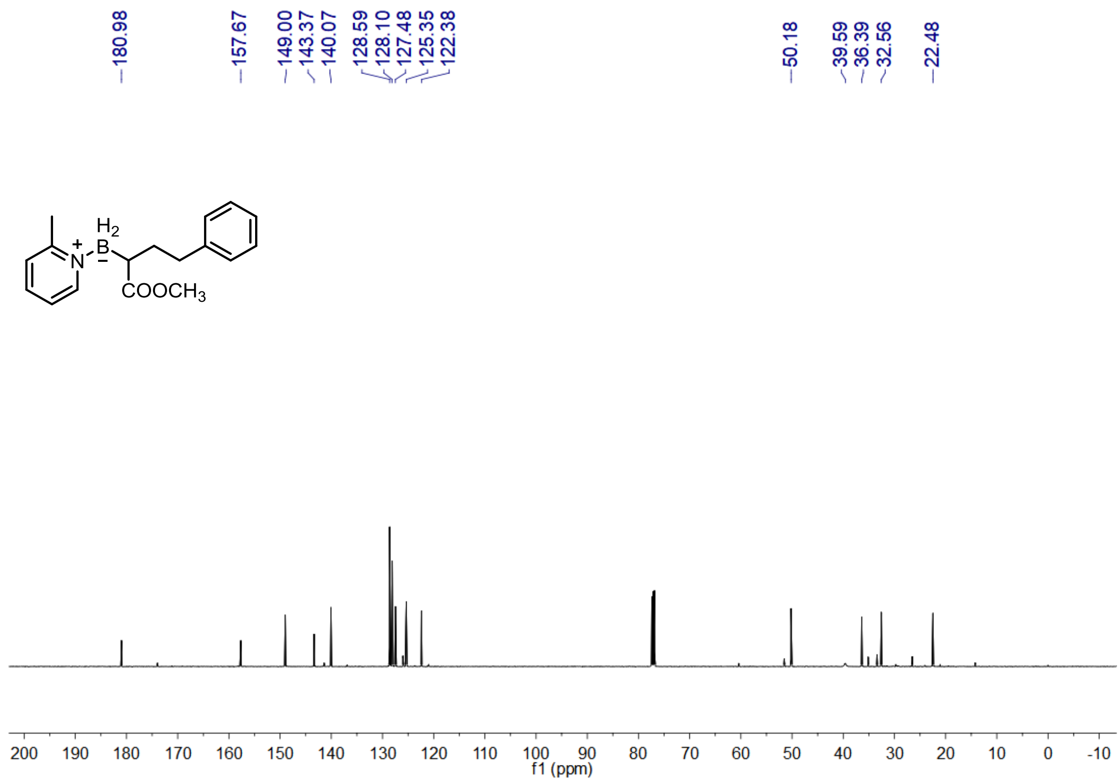


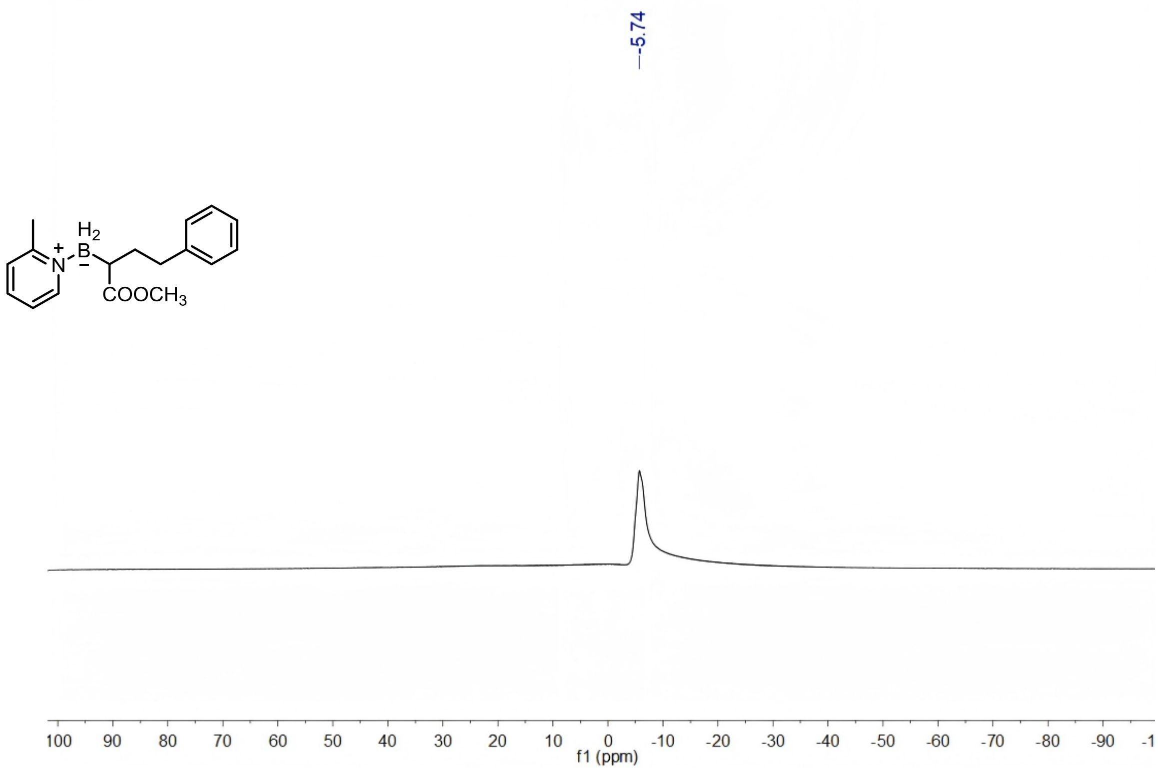




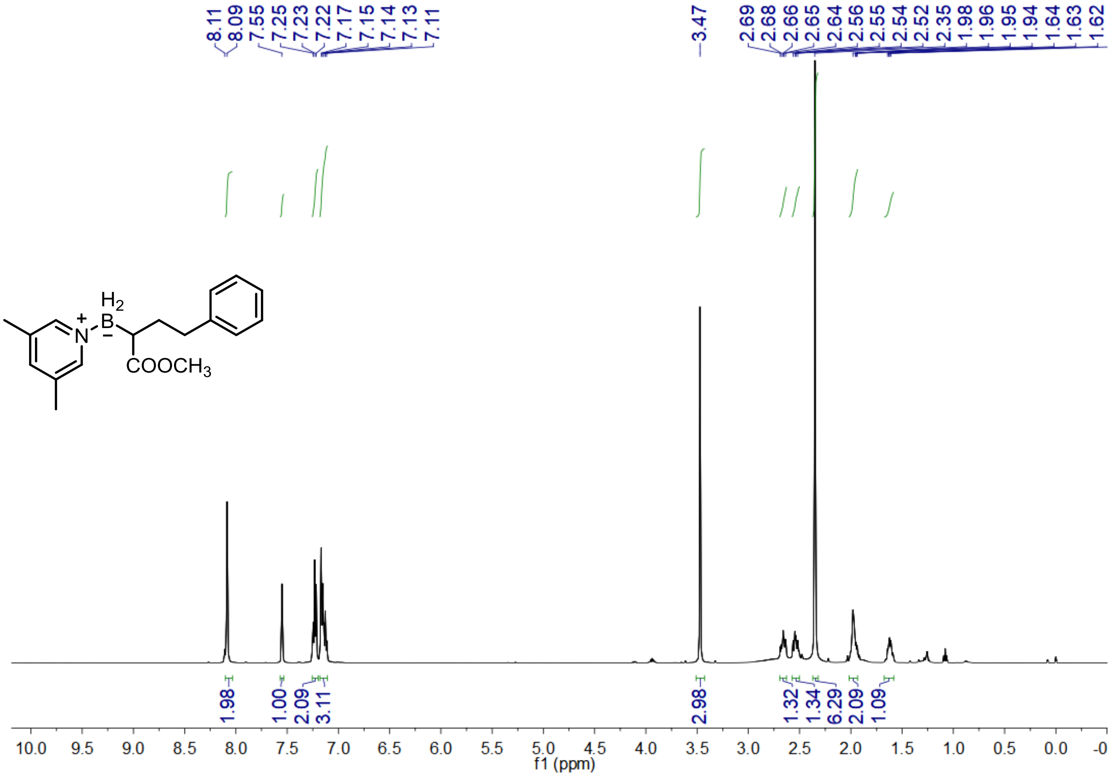
[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$) & [11]B NMR (160 MHz, $CDCl_3$) for **1c**

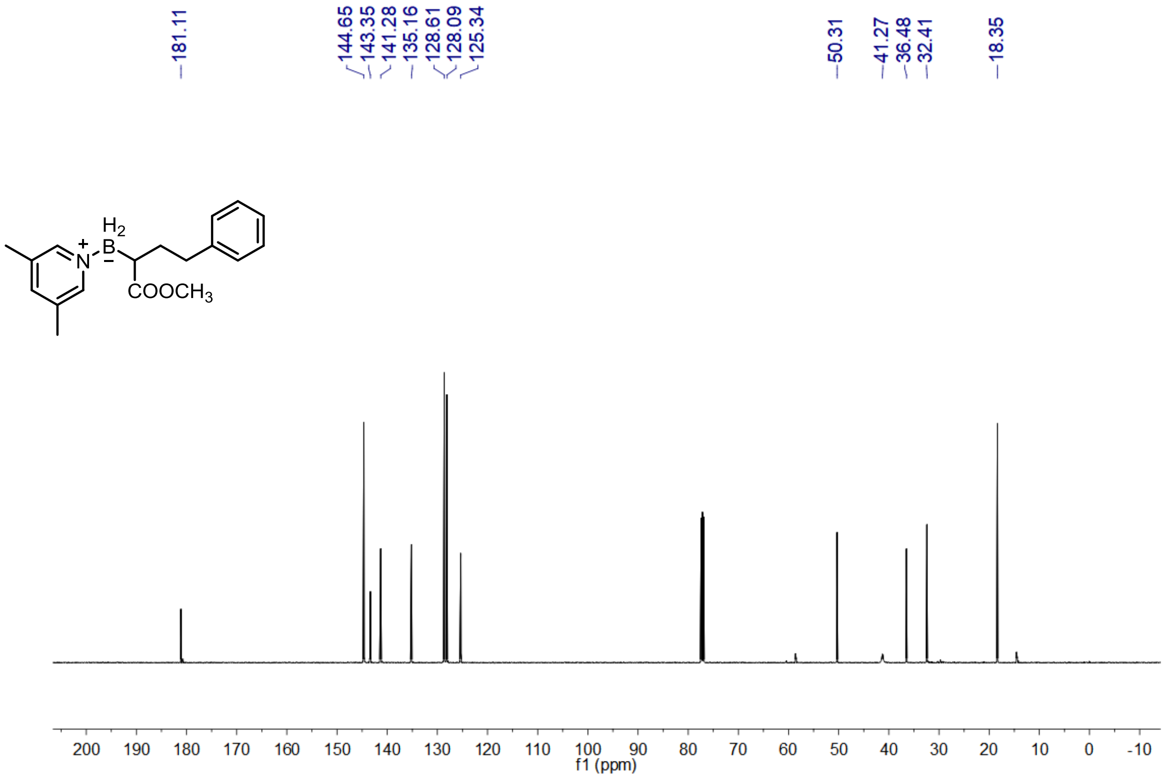


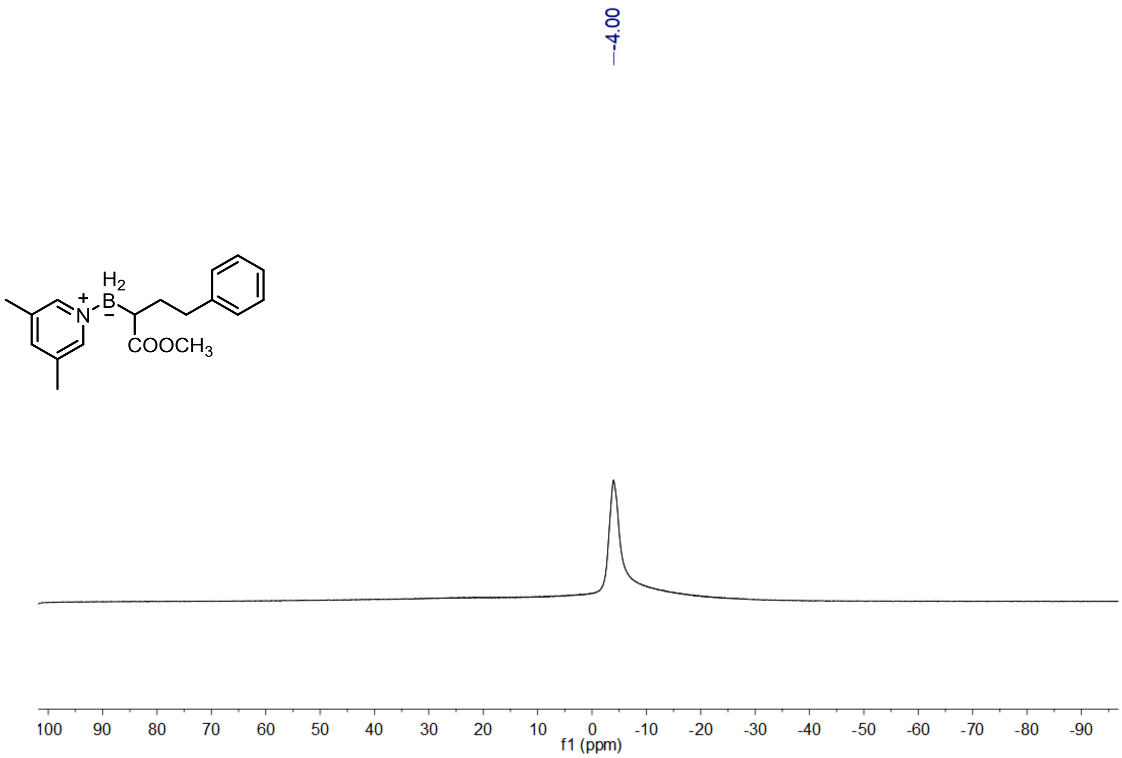

180.98
157.67
149.00
143.37
140.07
128.59
128.10
127.48
125.35
122.38
50.18
39.59
36.39
32.56
22.48
H2
B
N
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-5.74
H2
B
N
COOCH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1
f1 (ppm)

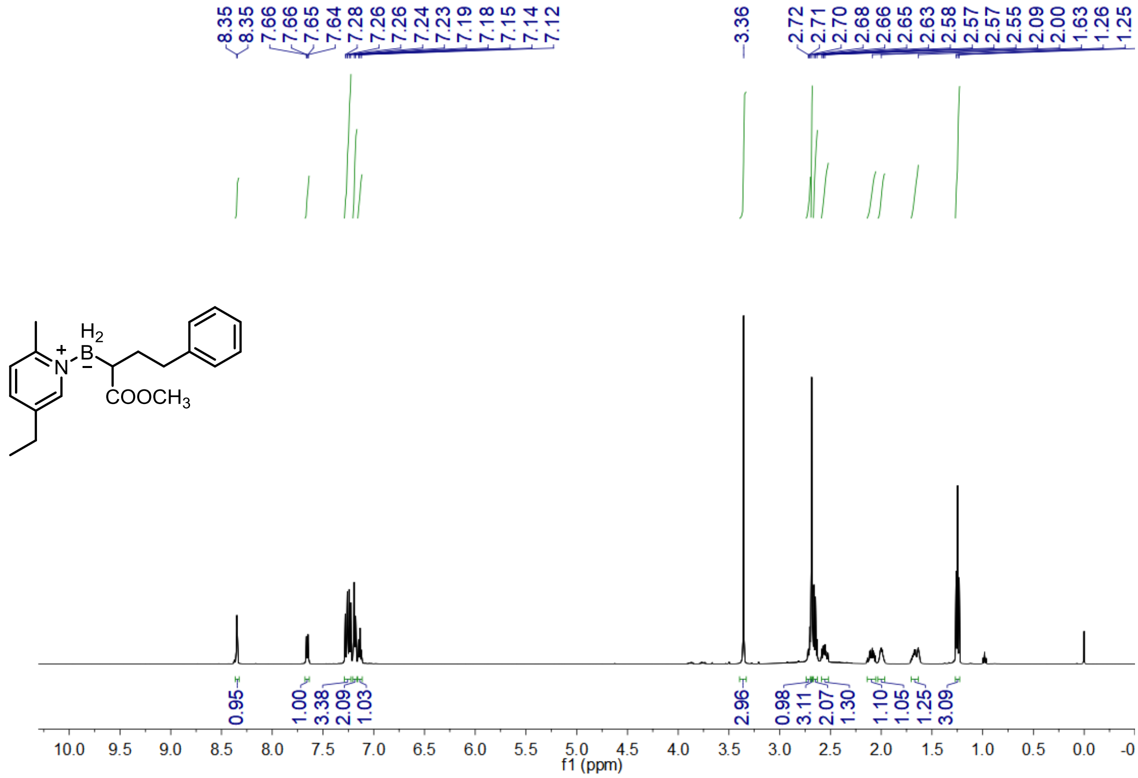
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **2c**

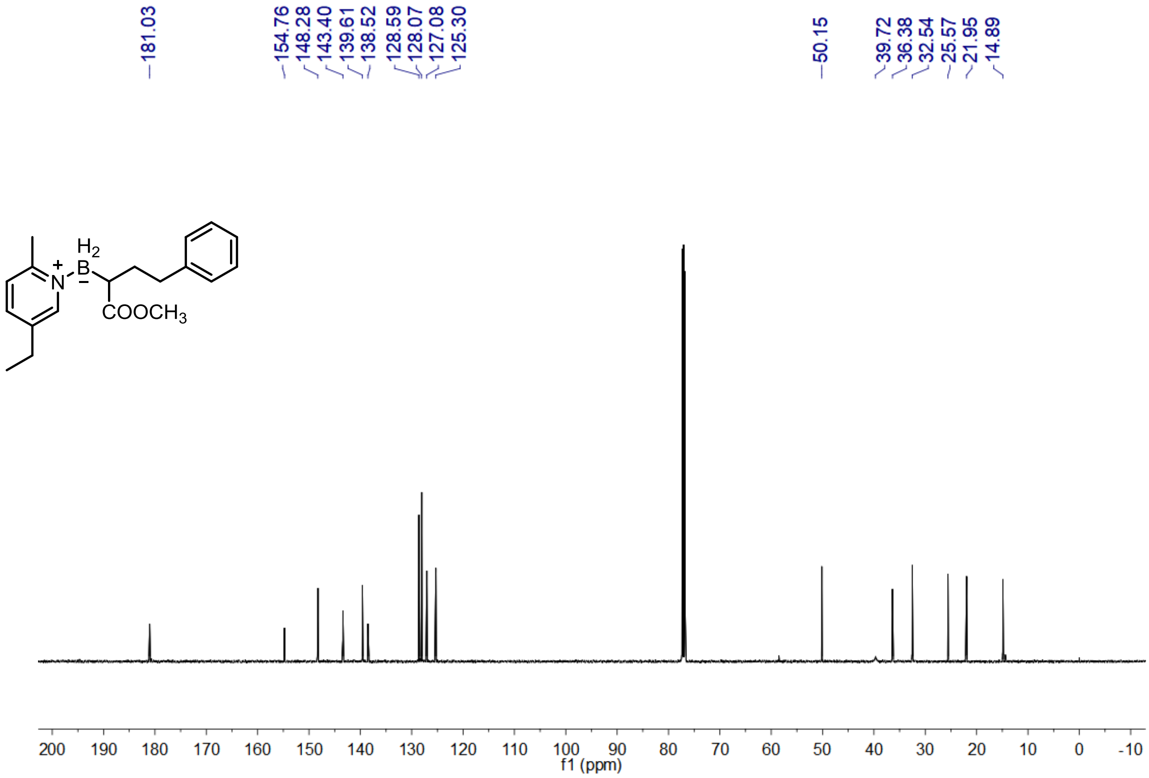


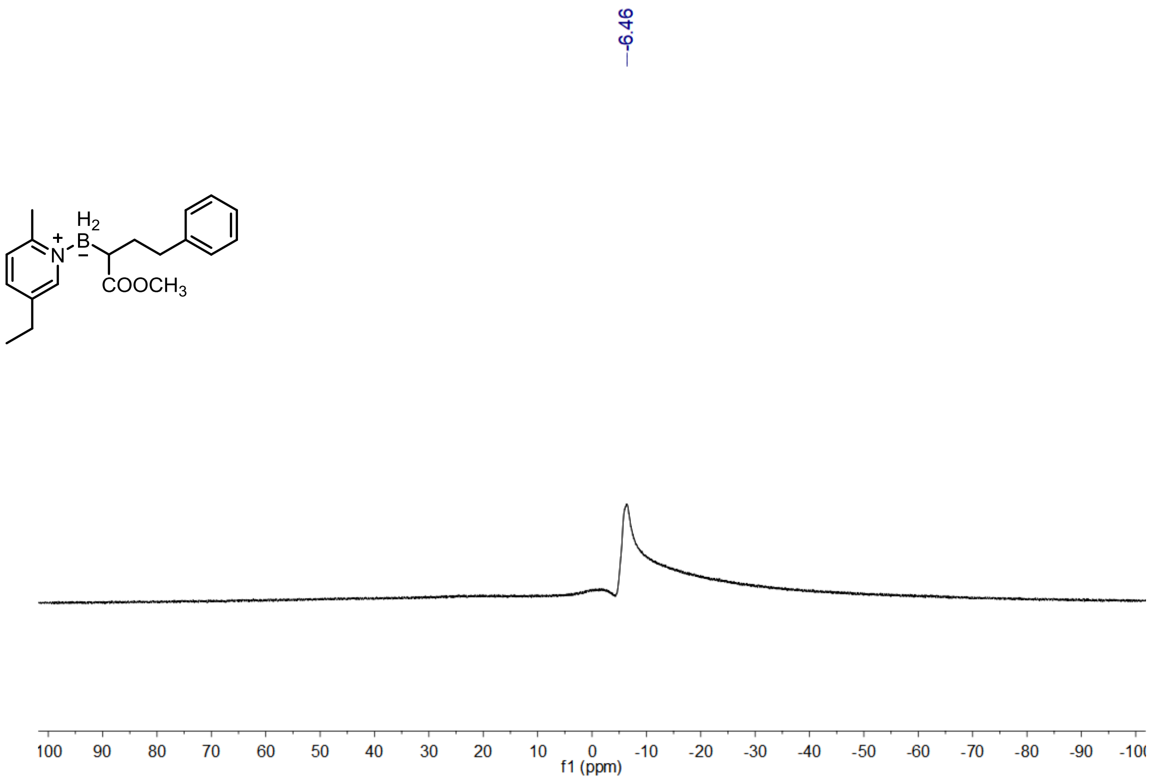




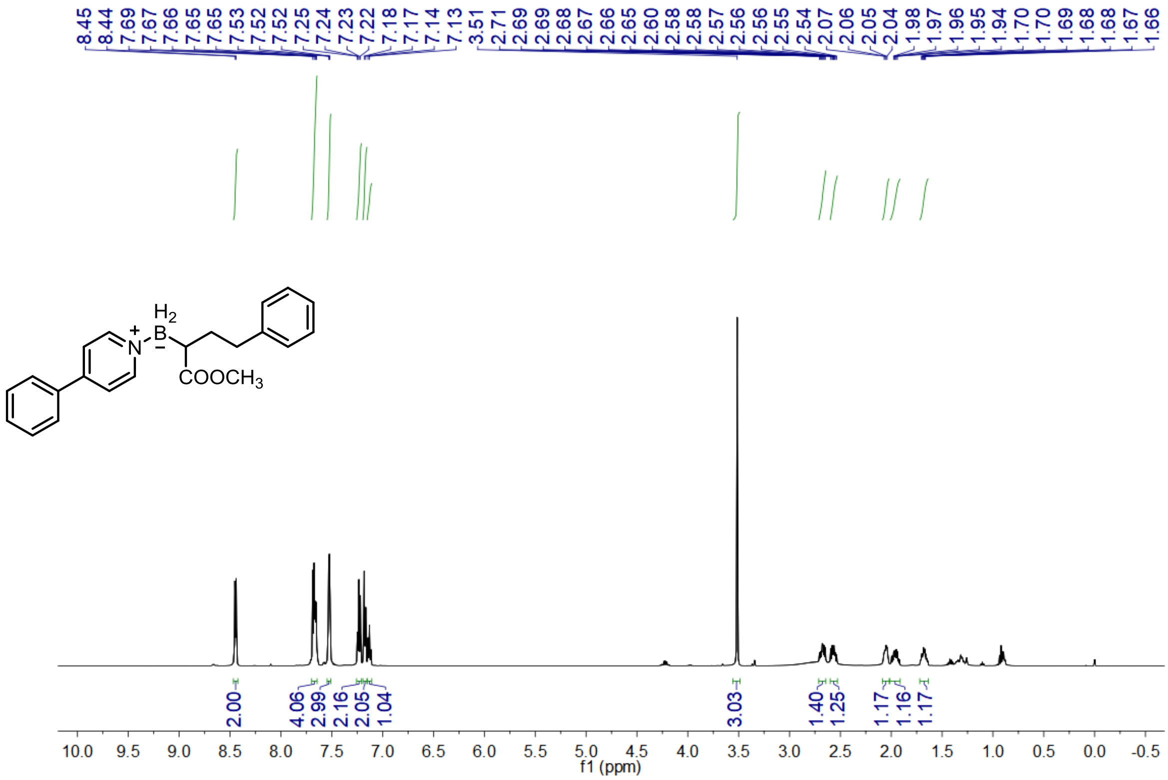
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **3c**

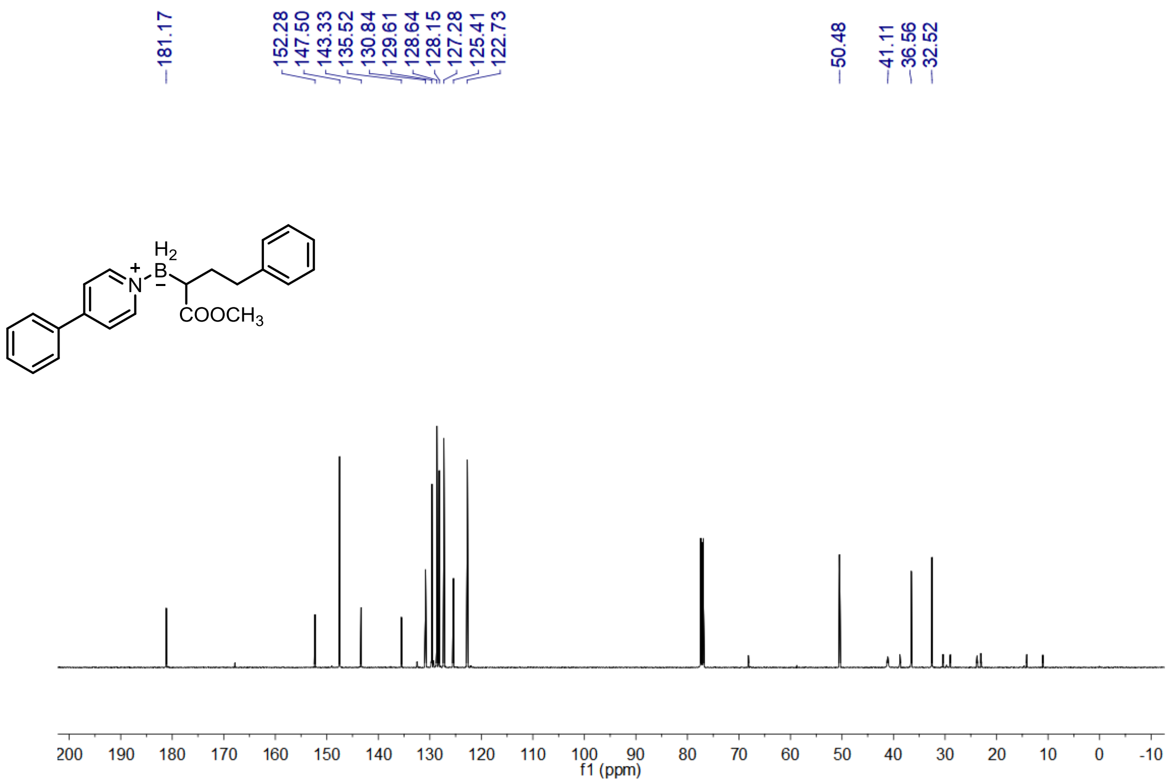


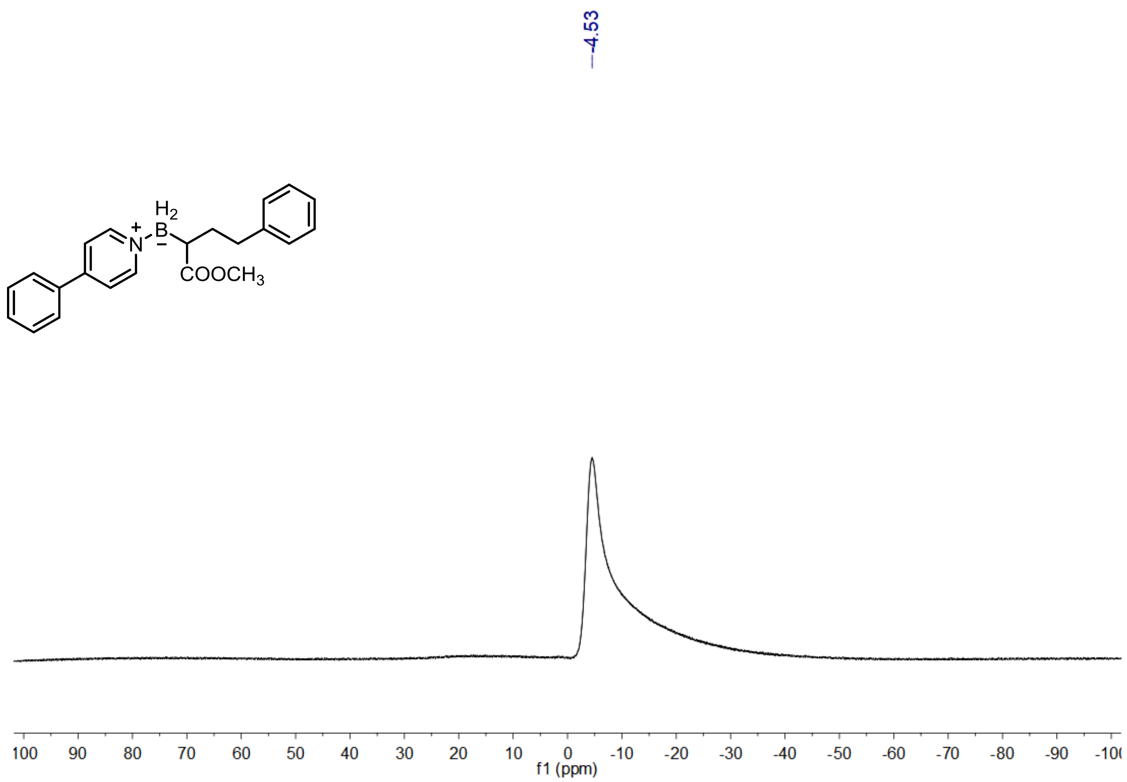

181.03
154.76
148.28
143.40
139.61
138.52
128.59
128.07
127.08
125.30
50.15
39.72
36.38
32.54
25.57
21.95
14.89
H2
B
N
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-6.46
H2
B
N
COOCH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

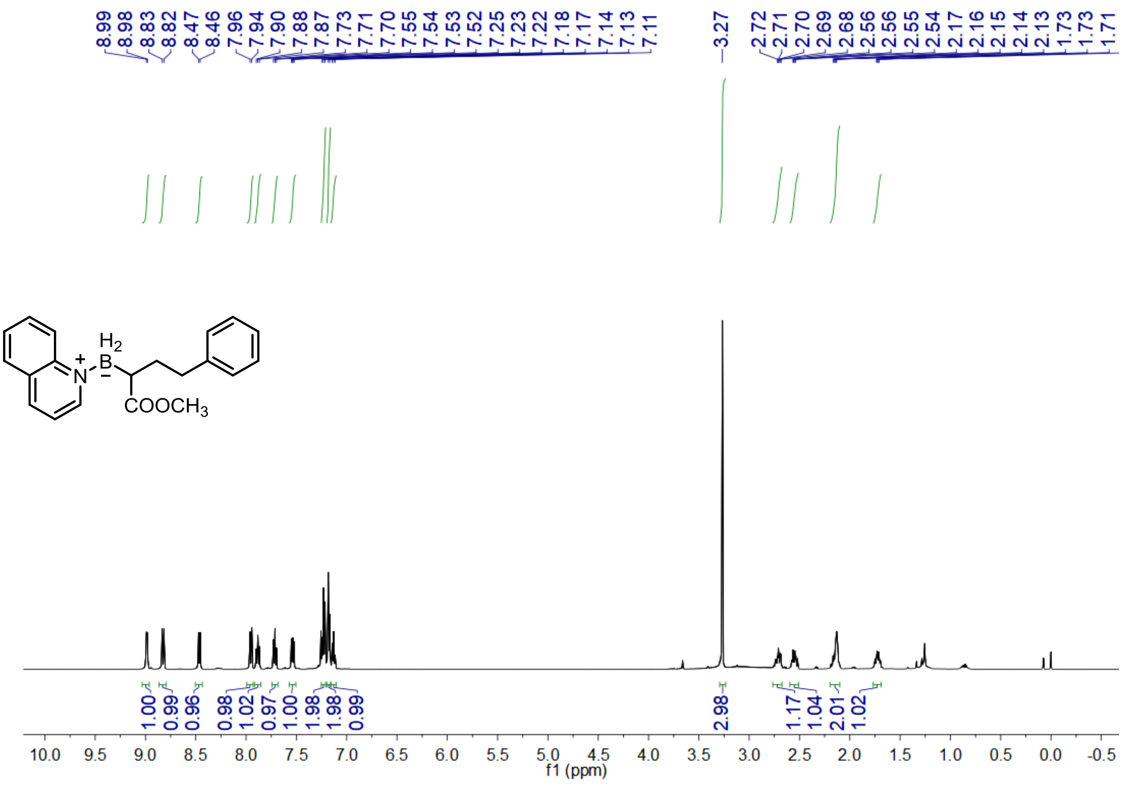
[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$) & [11]B NMR (160 MHz, $CDCl_3$) for **4c**

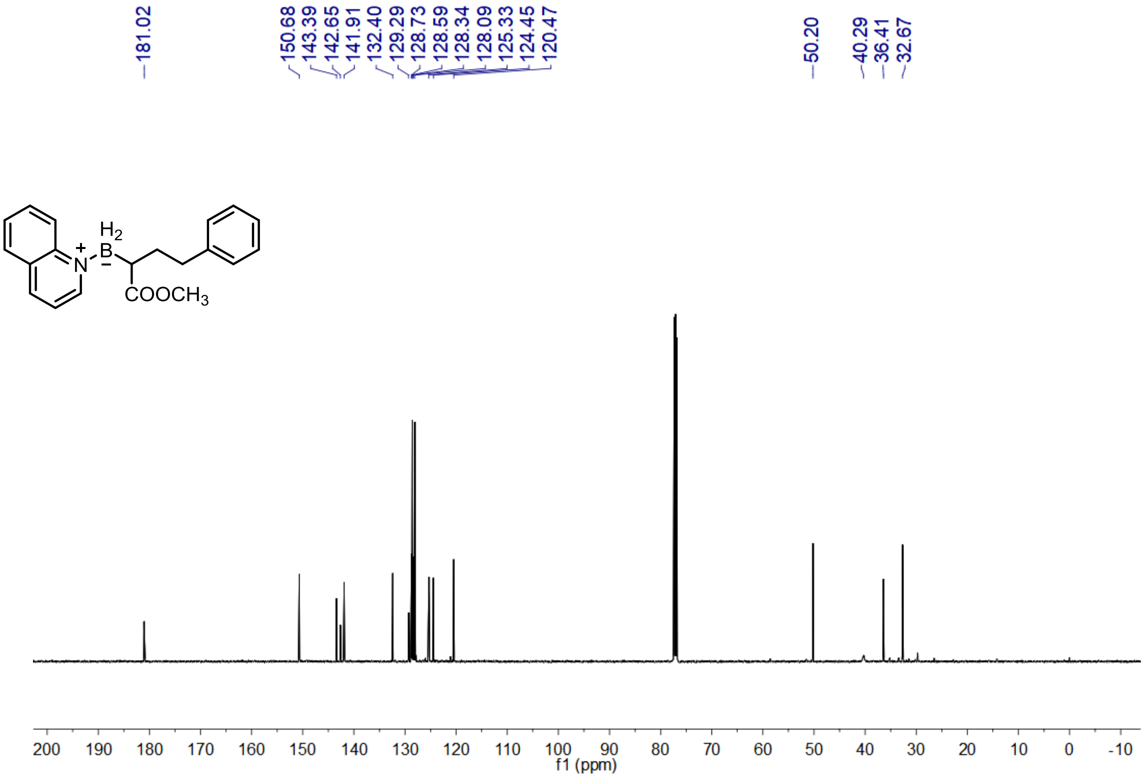


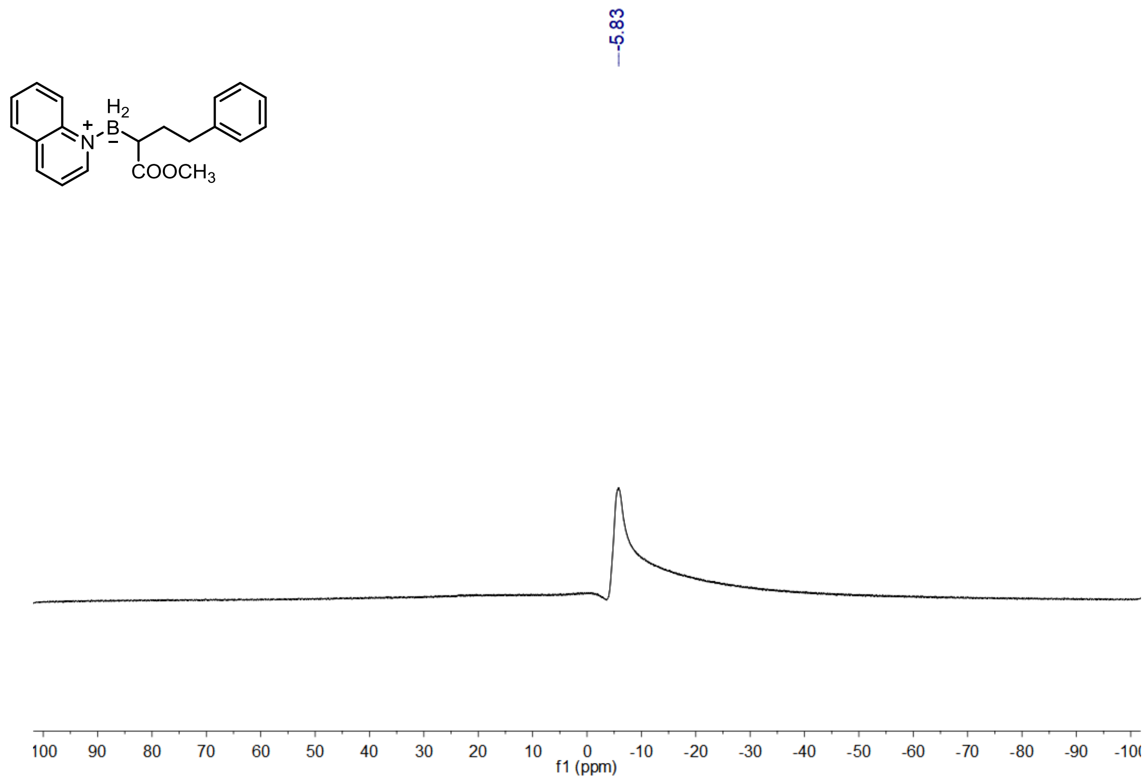




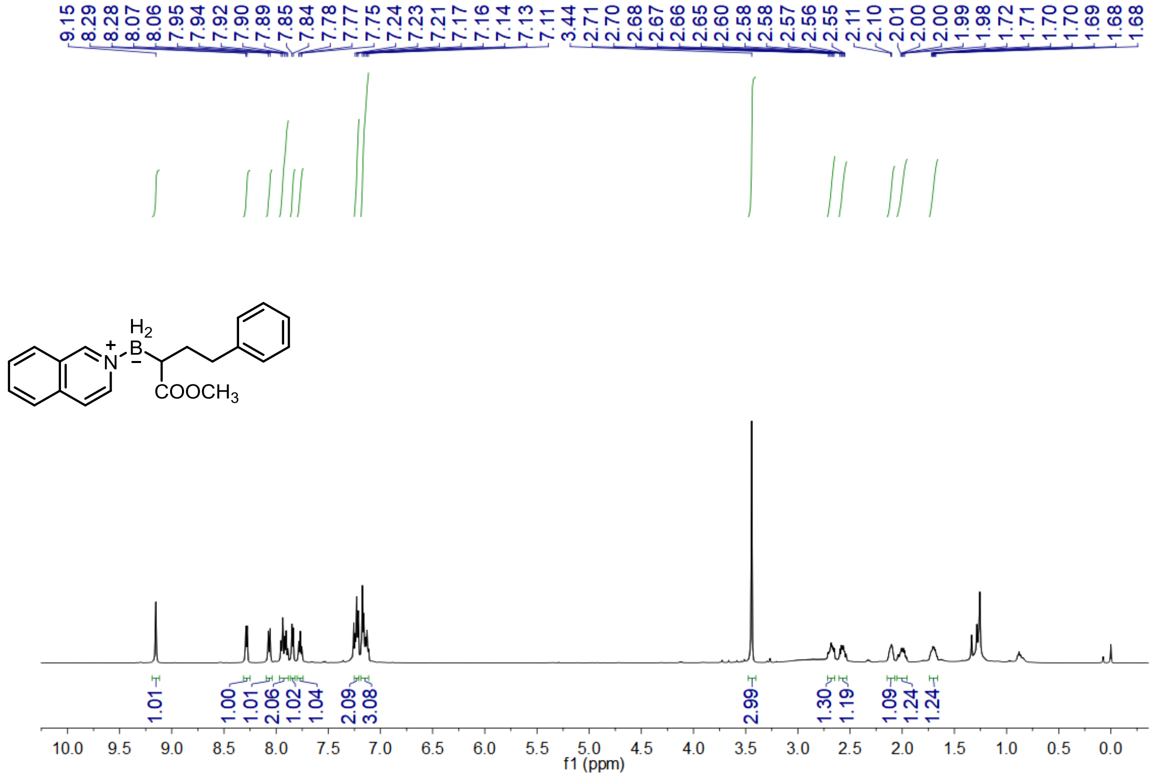
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **5c**

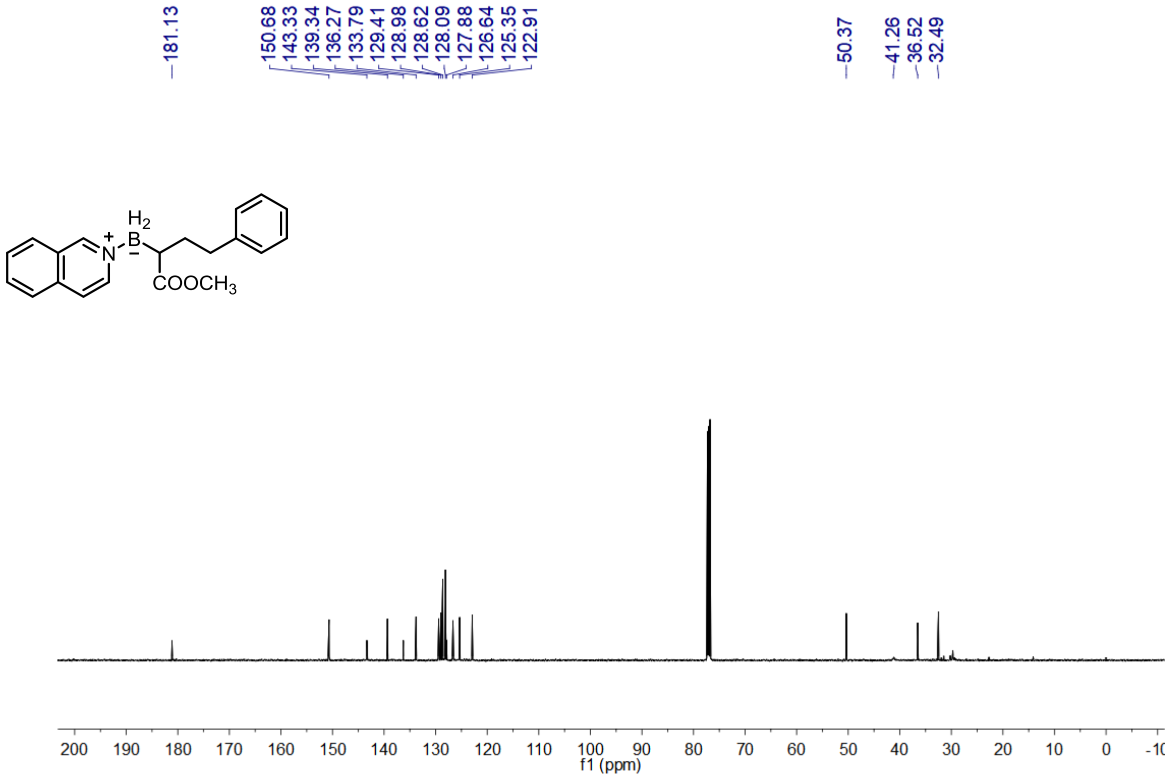


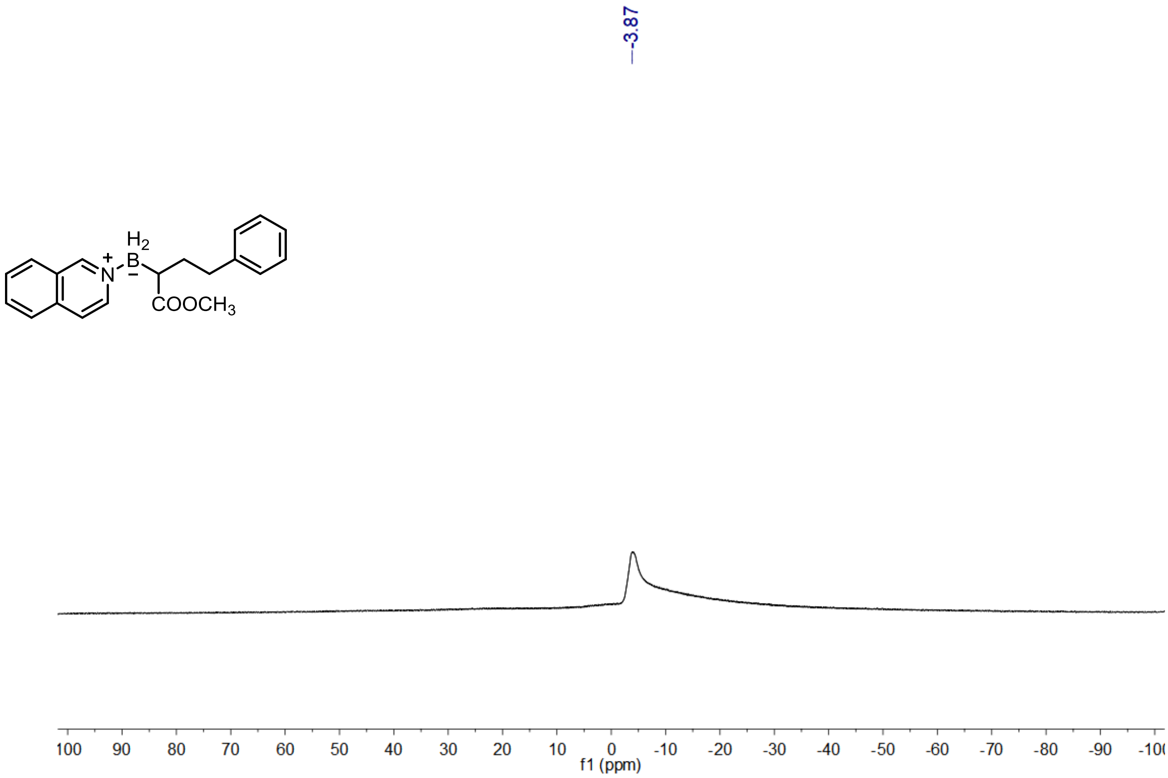

181.02
150.68
143.39
142.65
141.91
132.40
129.29
128.73
128.59
128.34
128.09
125.33
124.45
120.47
50.20
40.29
36.41
32.67
H2
B
N
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-5.83
H2
B
N
COOCH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

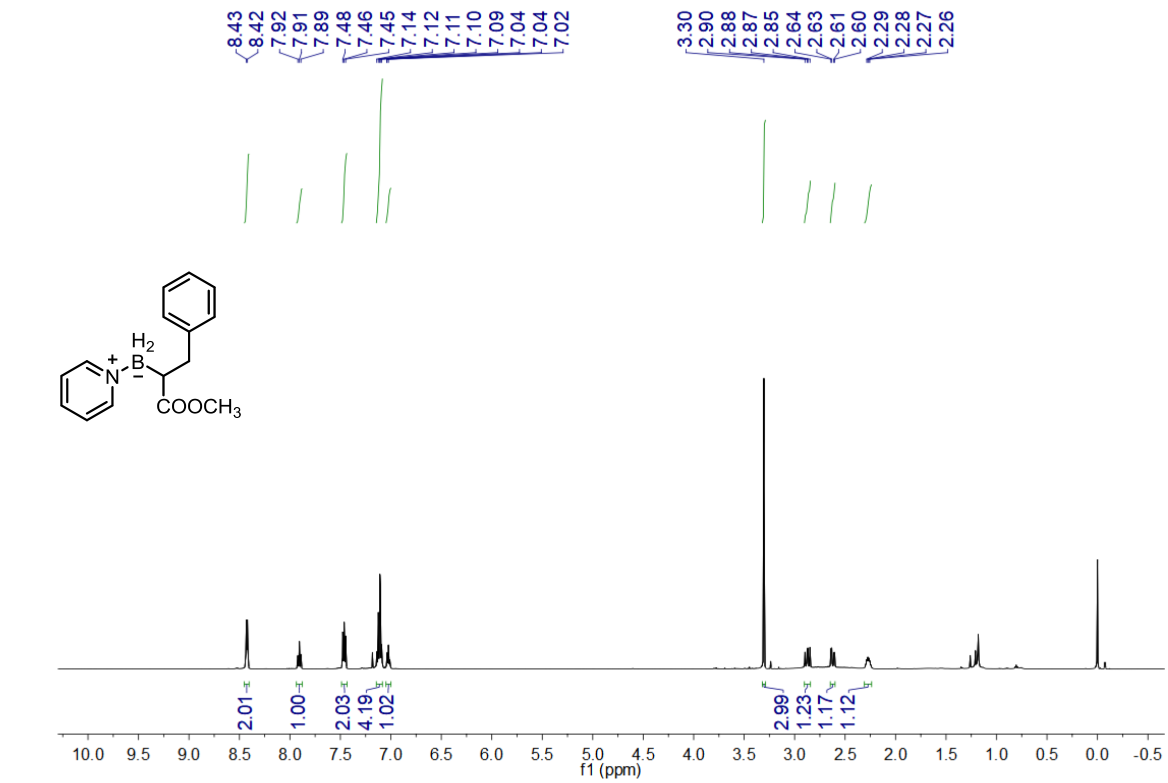
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **6c**

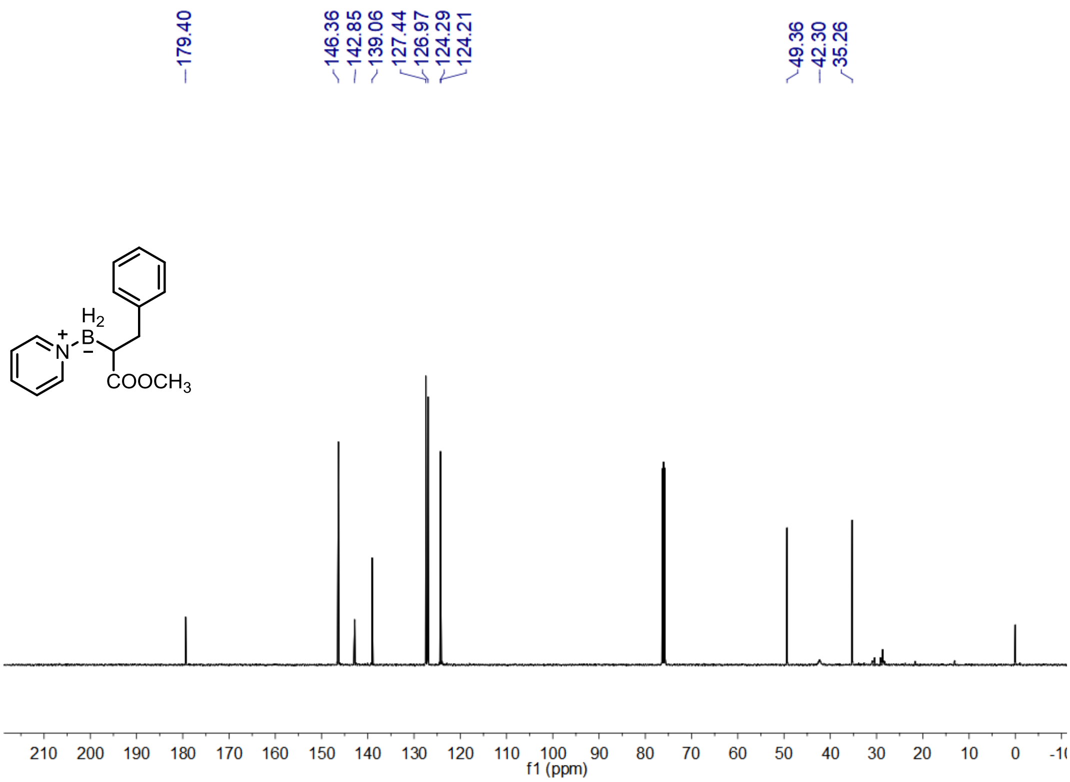


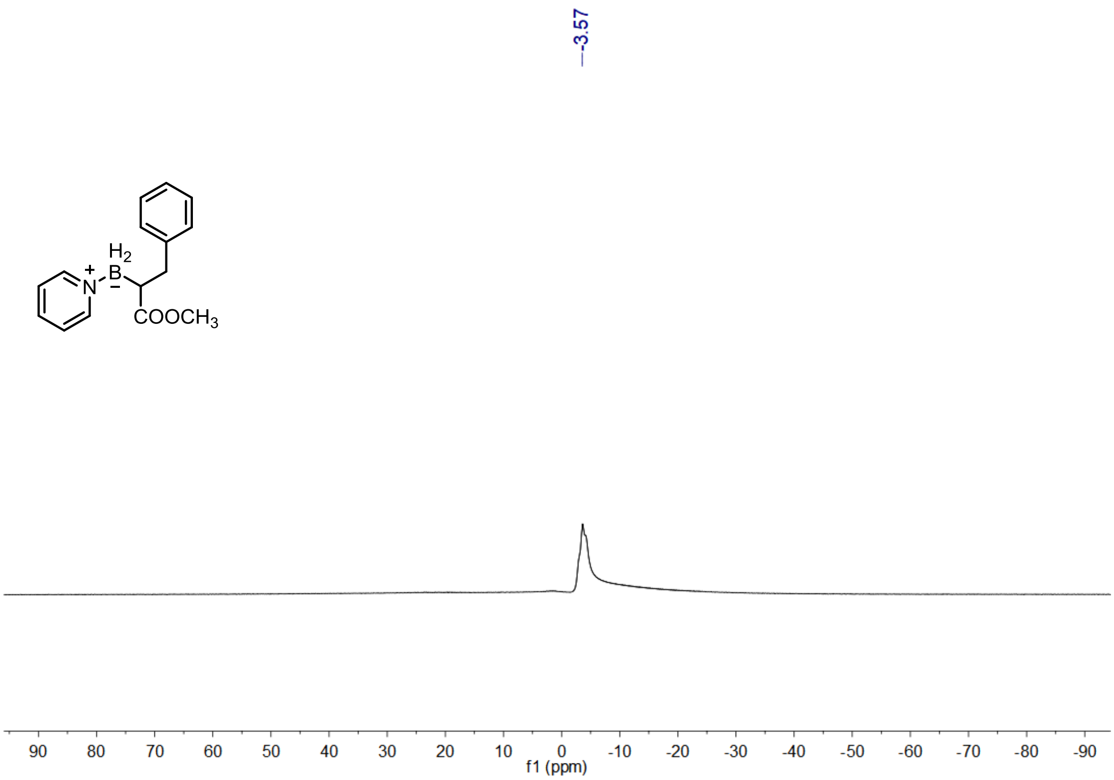




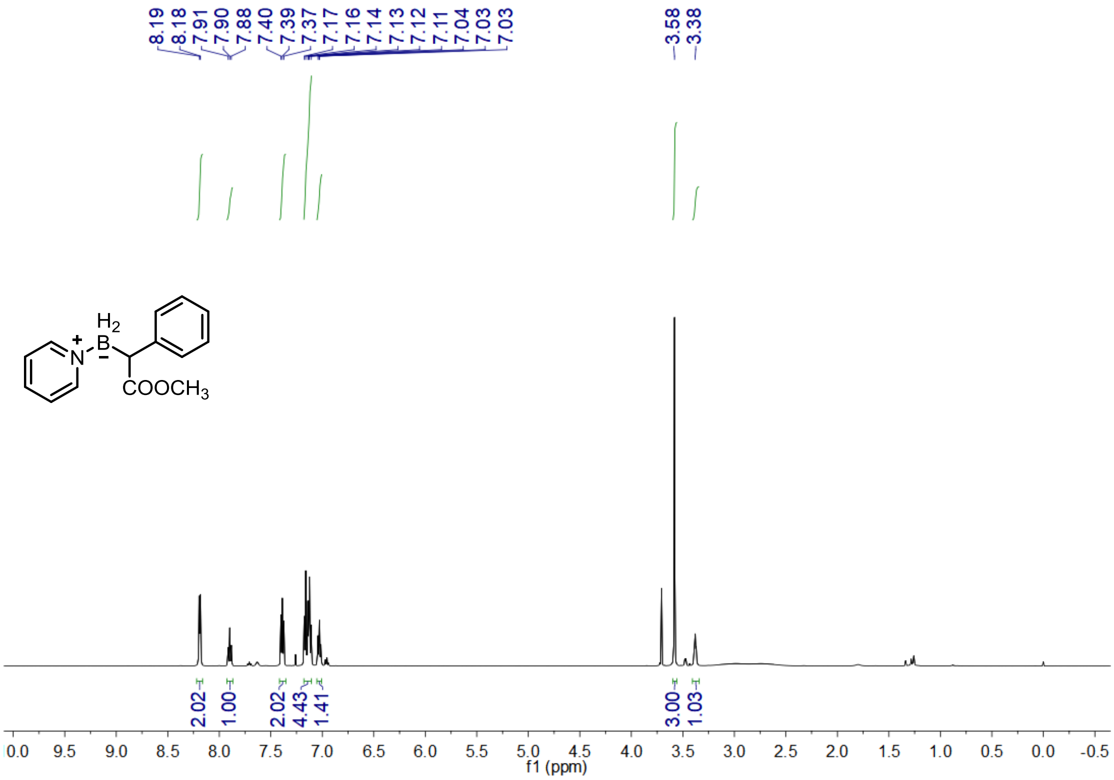
[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$) & [11]B NMR (160 MHz, $CDCl_3$) for **1d**

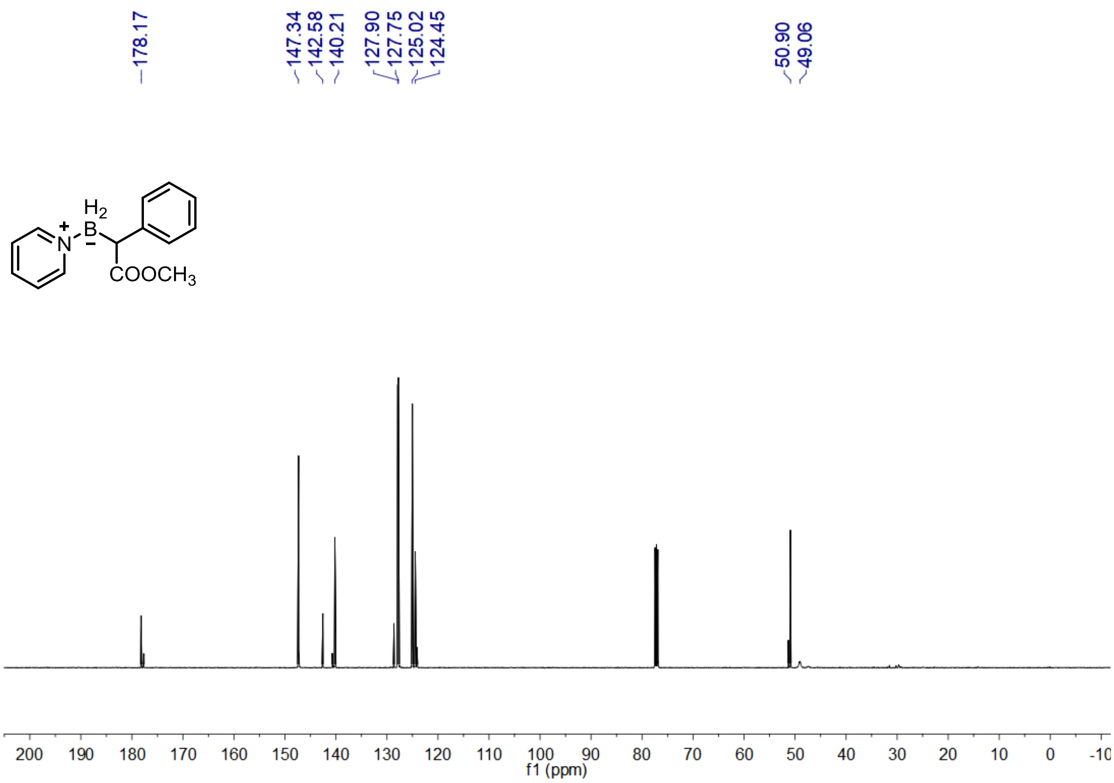


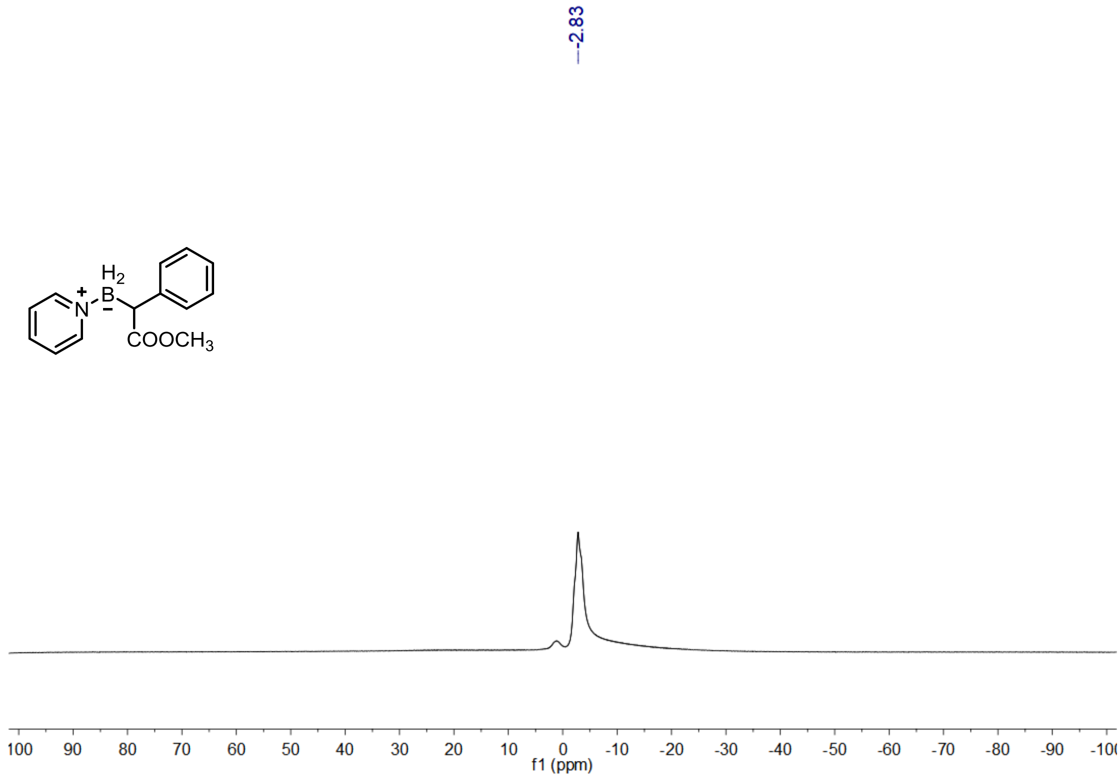

179.40
146.36
142.85
139.06
127.44
126.97
124.29
124.21
49.36
42.30
35.26
H2
B
N
COOCH3
f1 (ppm)


-3.57
H2
B
N
COOCH3
f1 (ppm)

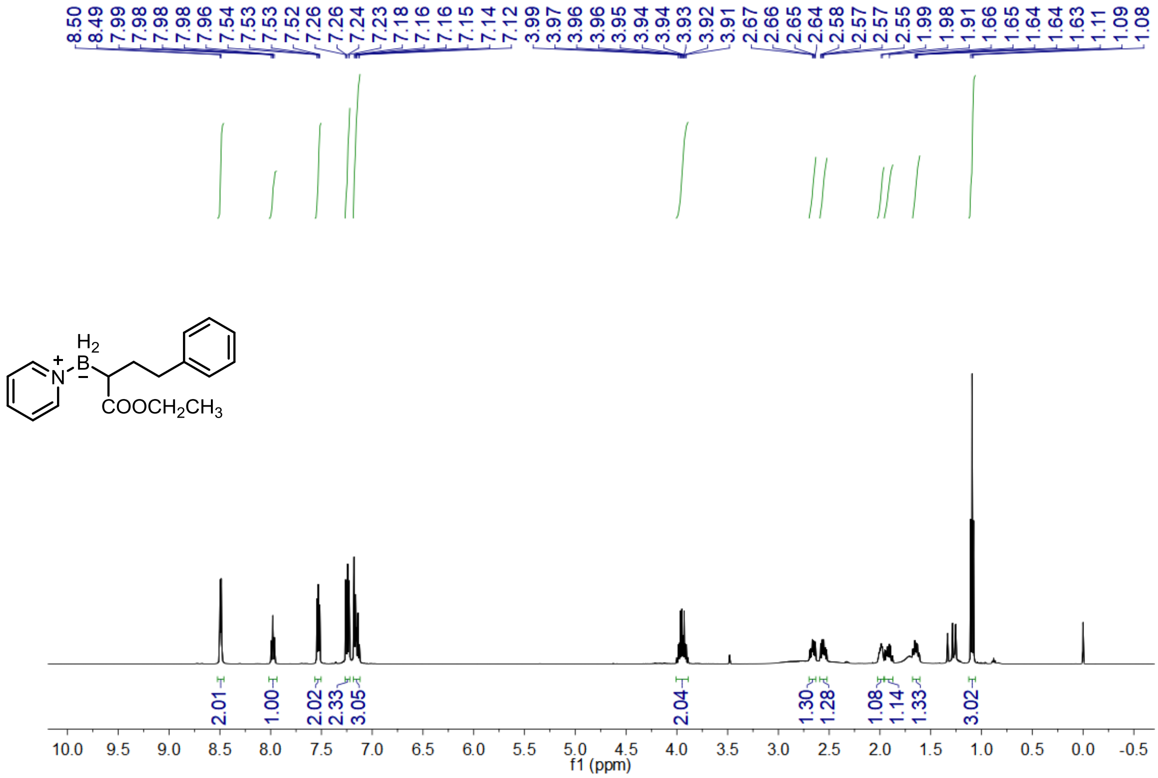
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **2d**

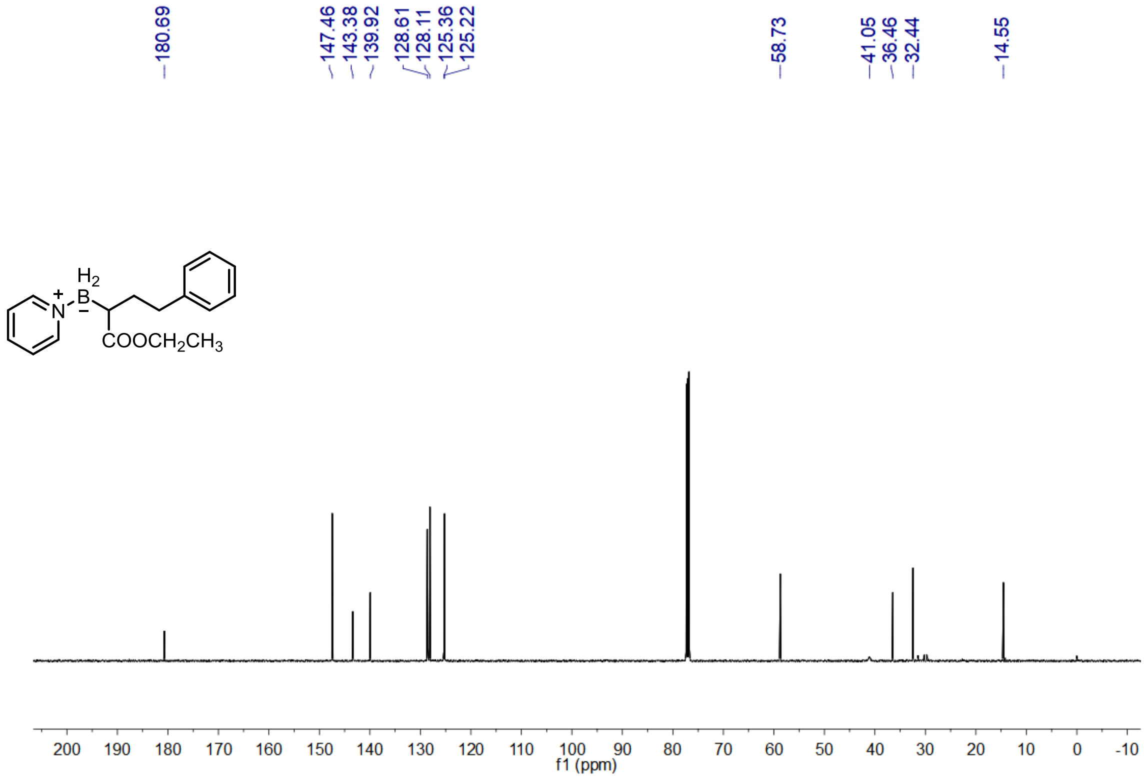


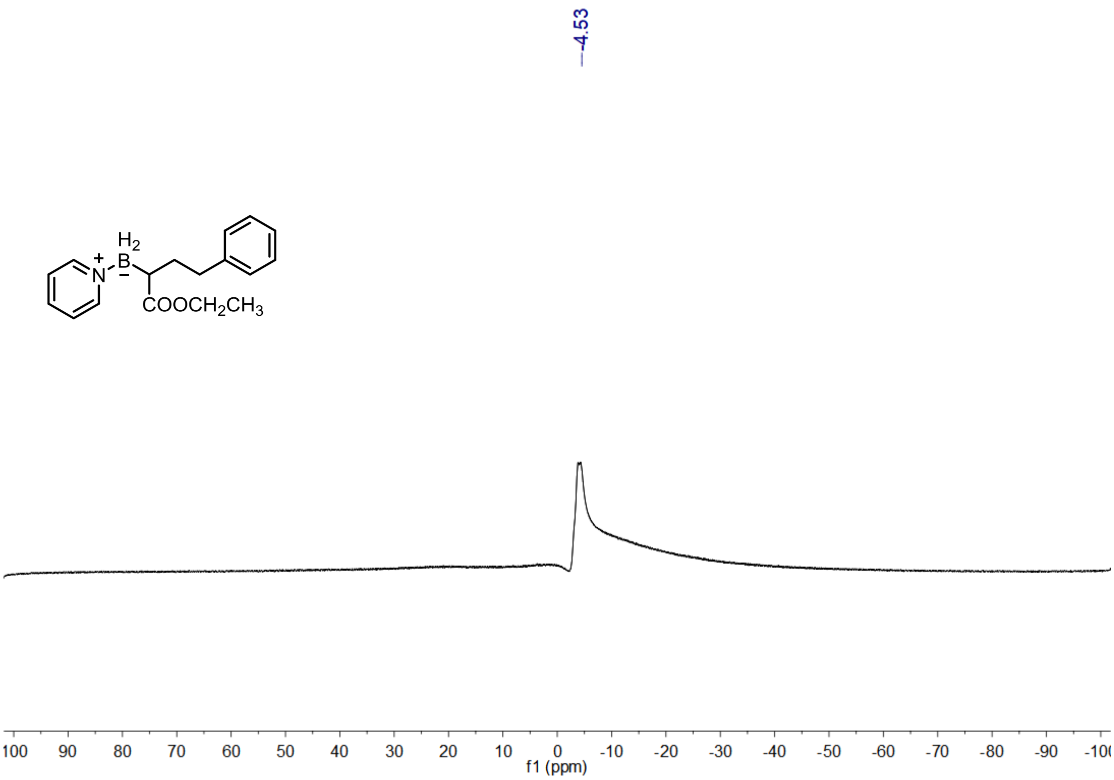




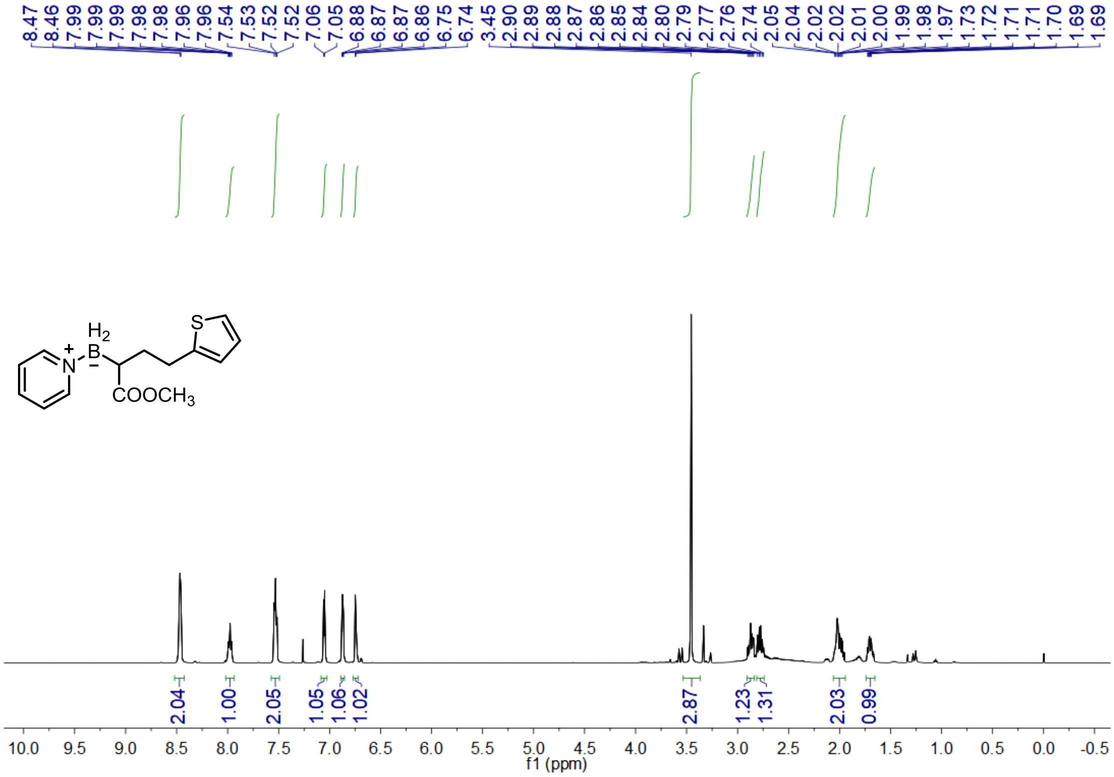
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **3d**

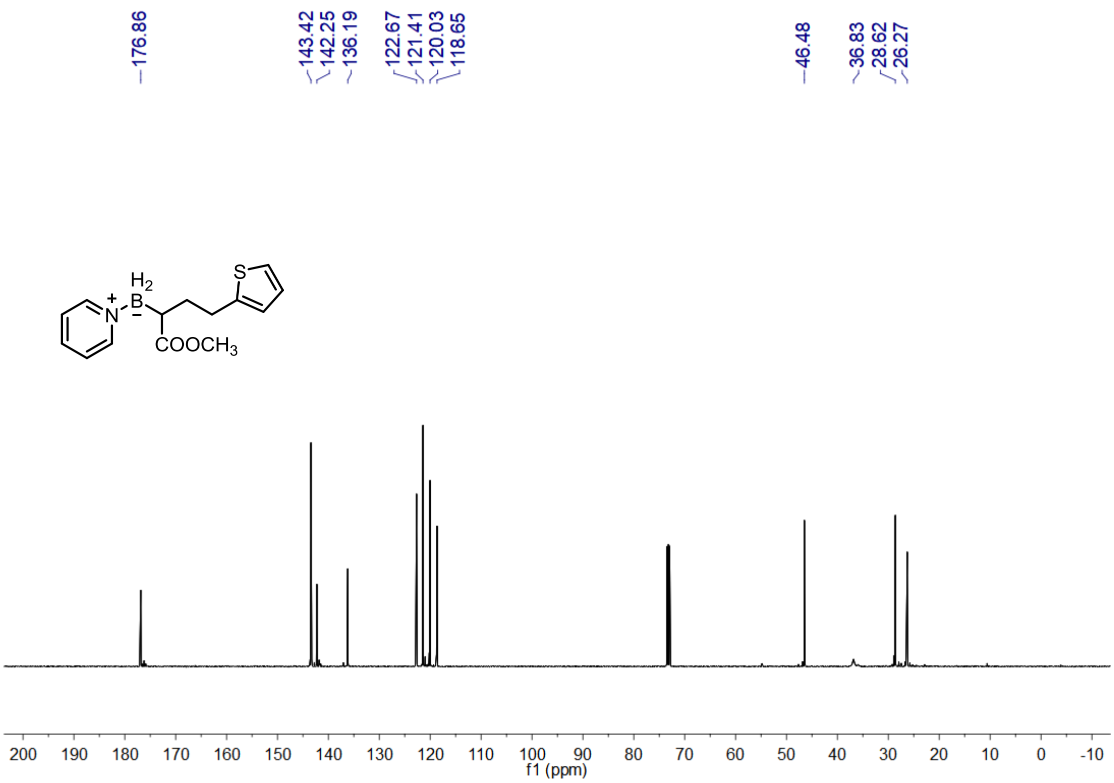


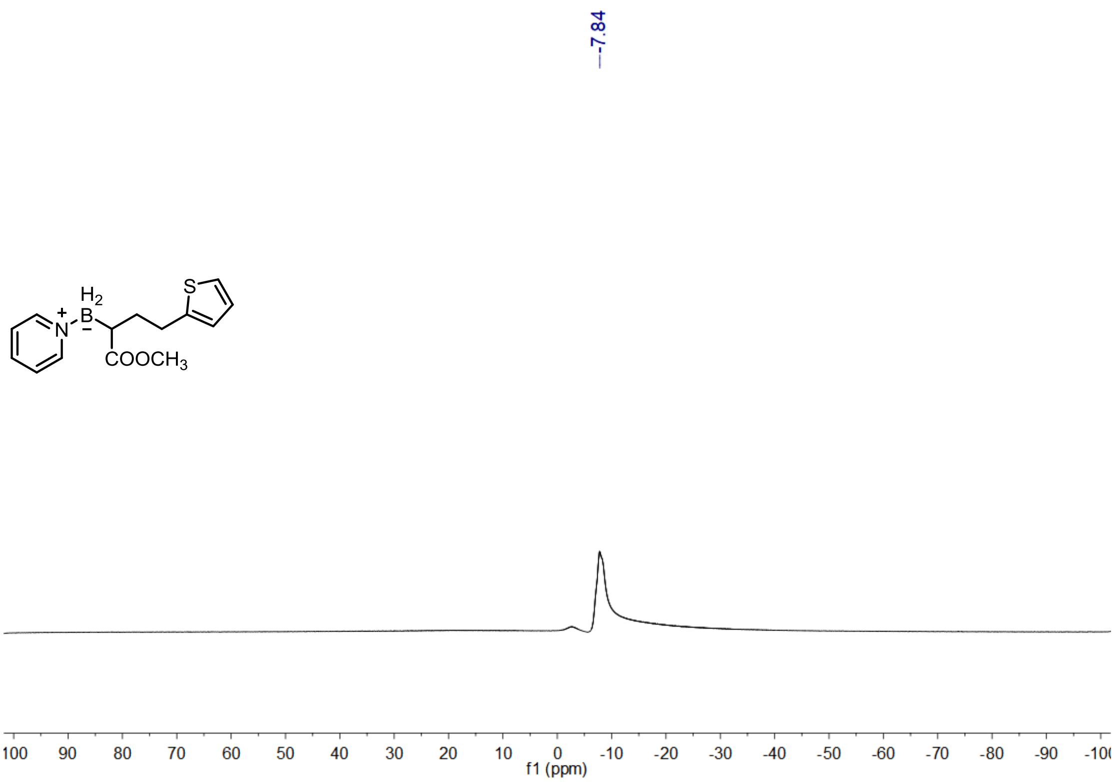

180.69
147.46
143.38
139.92
128.61
128.11
125.36
125.22
58.73
41.05
36.46
32.44
14.55
H2
B
N
COOCH2CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-4.53
H2
B
N
COOCH2CH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

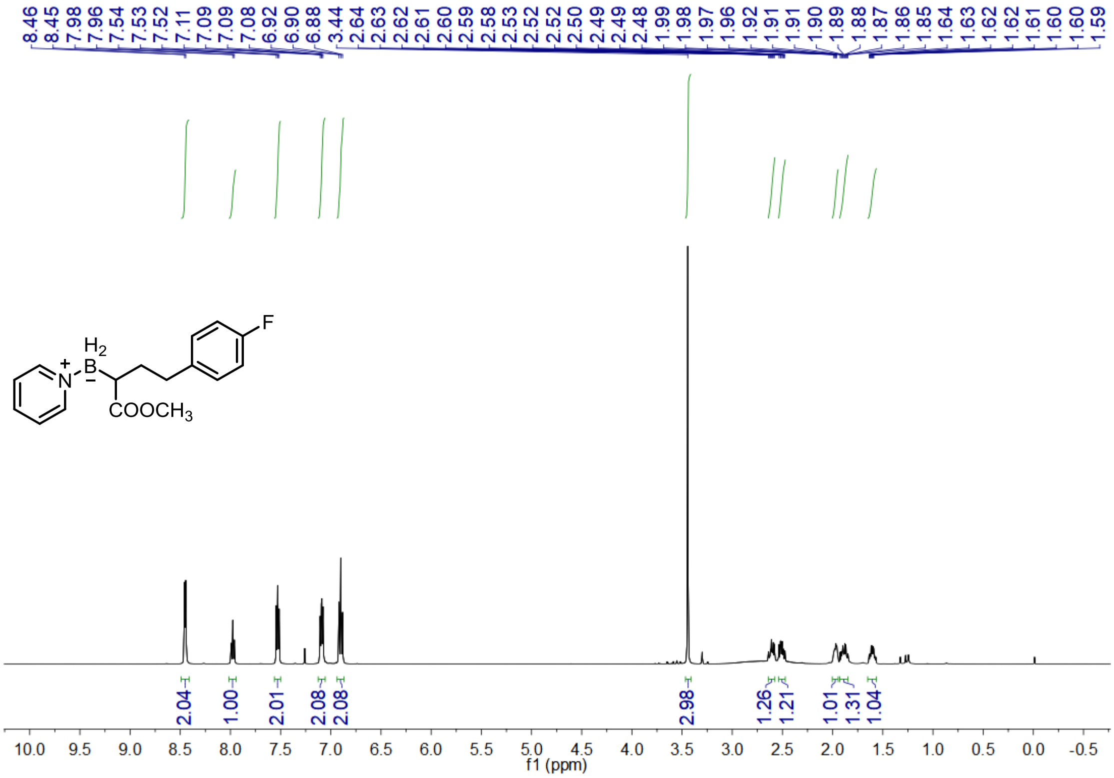
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, CD_3OD) & ^{11}B NMR (160 MHz, CD_3OD) for **4d.**

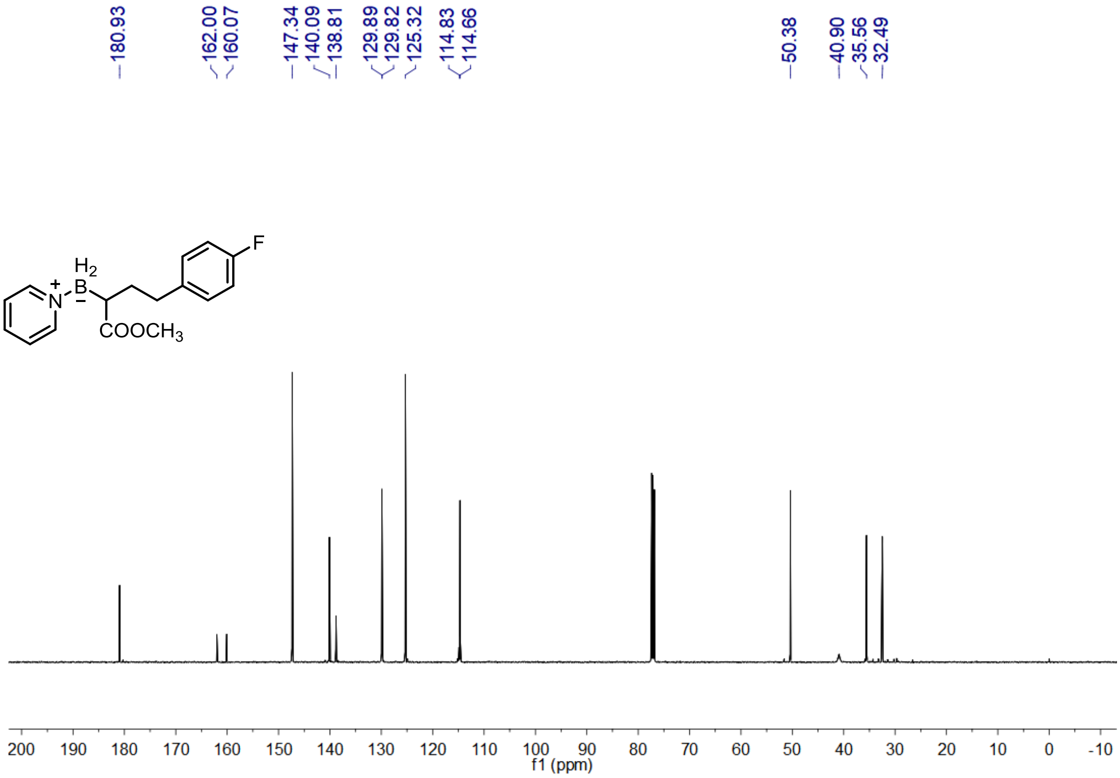




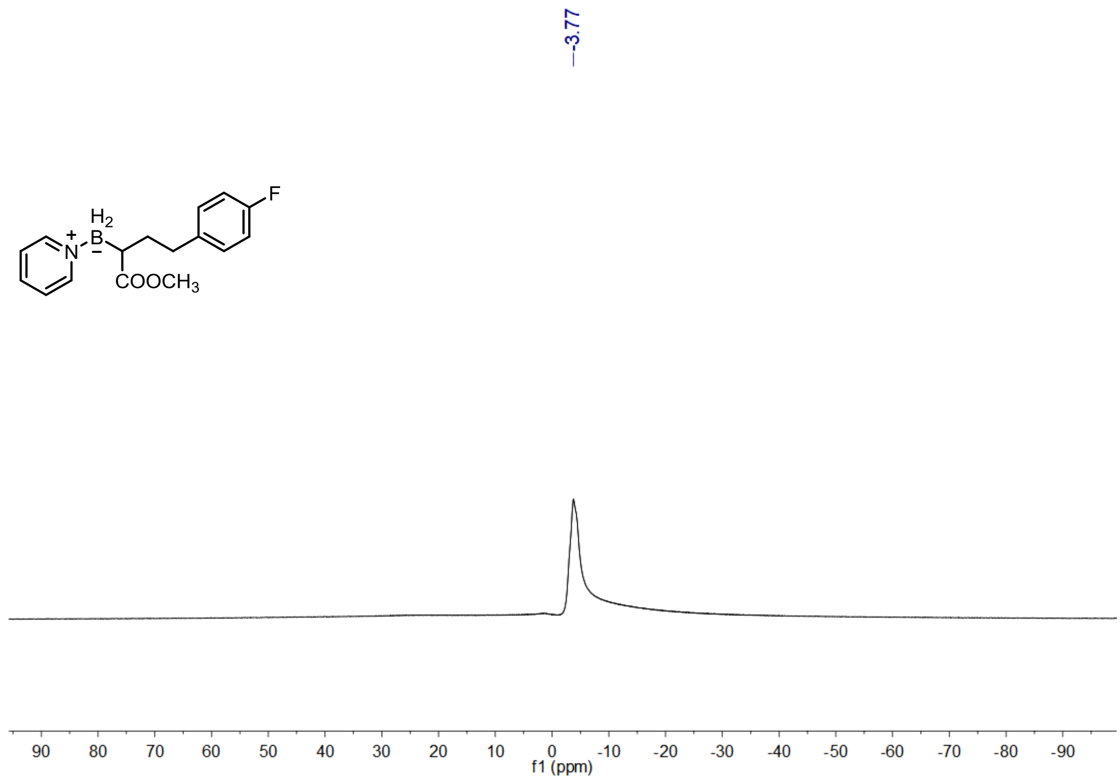


[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$), [11]B NMR (160 MHz, $CDCl_3$) for **5d.**



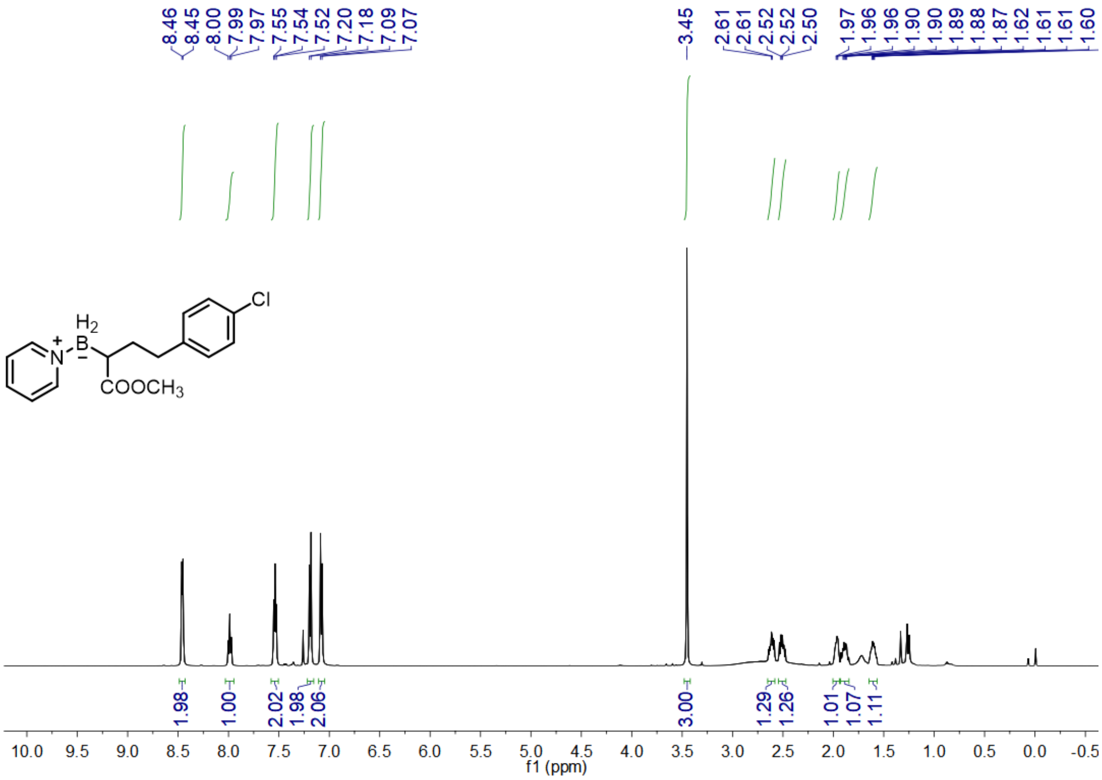


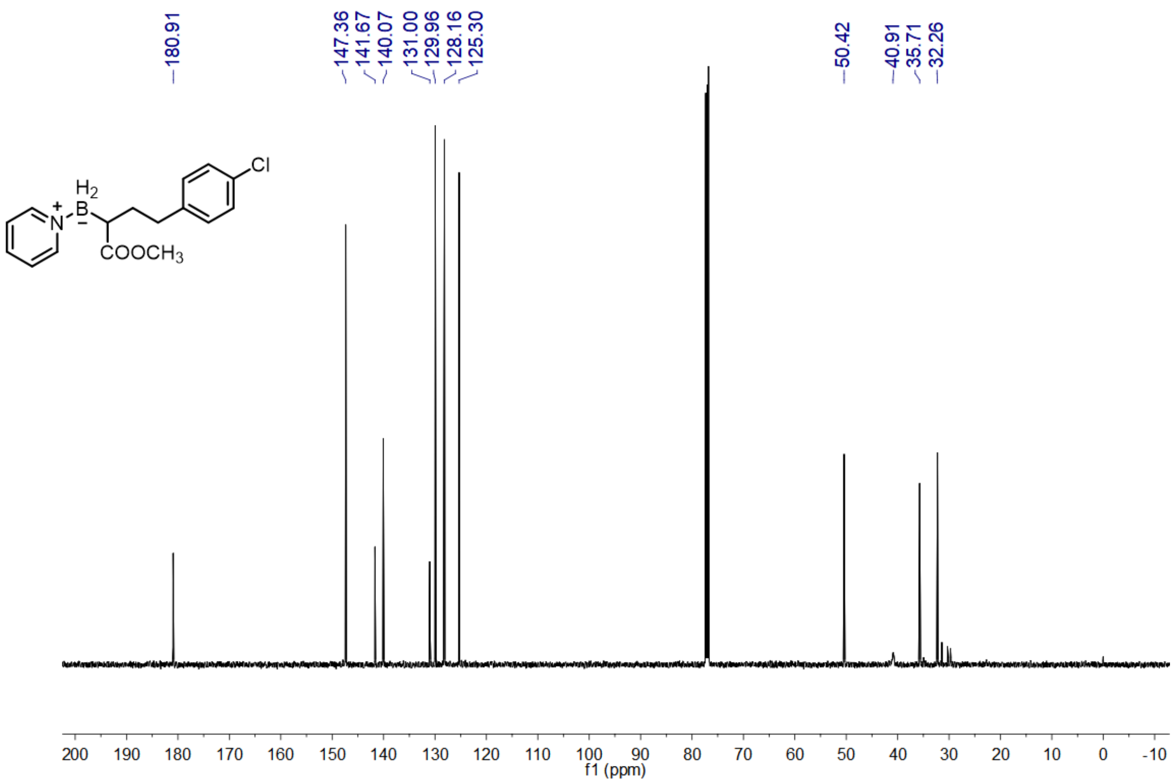
180.93
162.00
160.07
147.34
140.09
138.81
129.89
129.82
125.32
114.83
114.66
50.38
40.90
35.56
32.49
F
H2
B
N
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

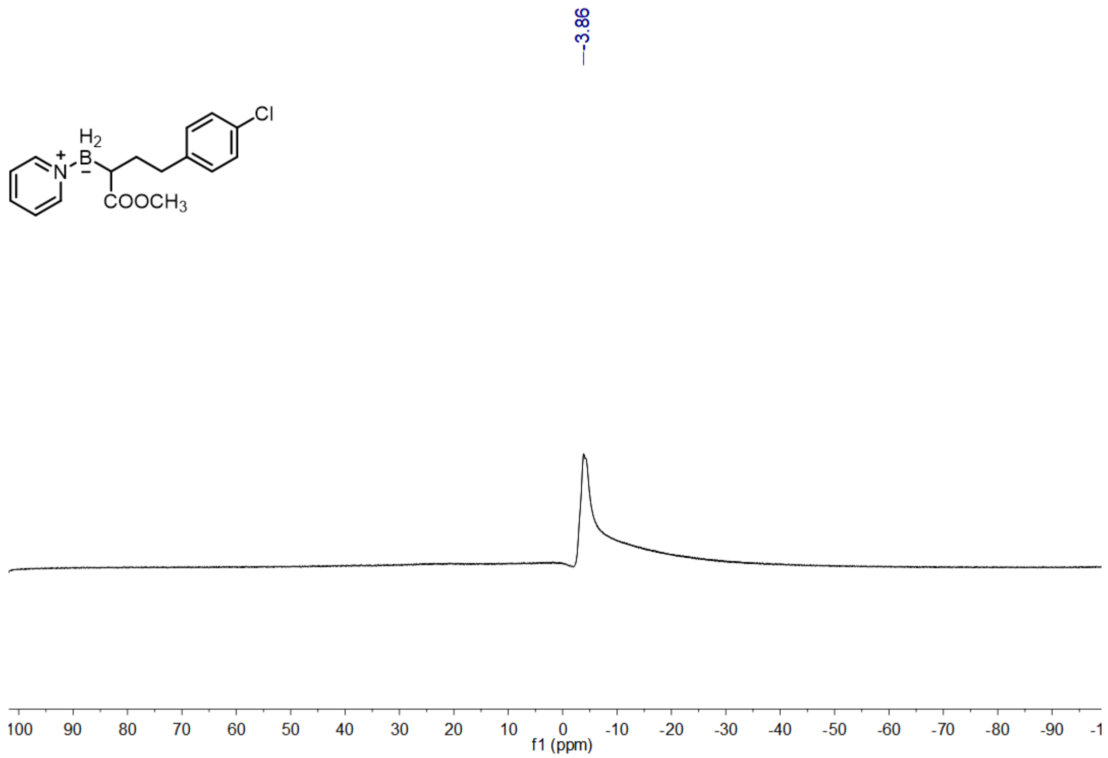


-3.77
F
H2
B
N
COOCH3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

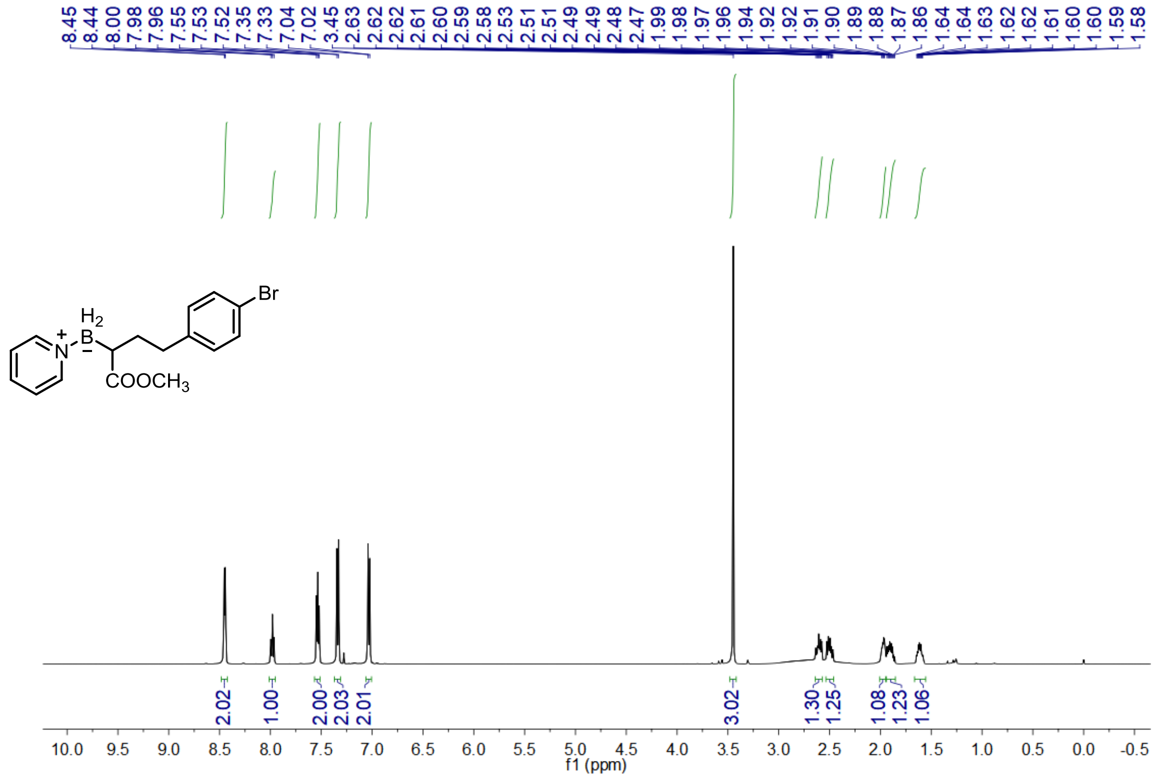
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **6d.**

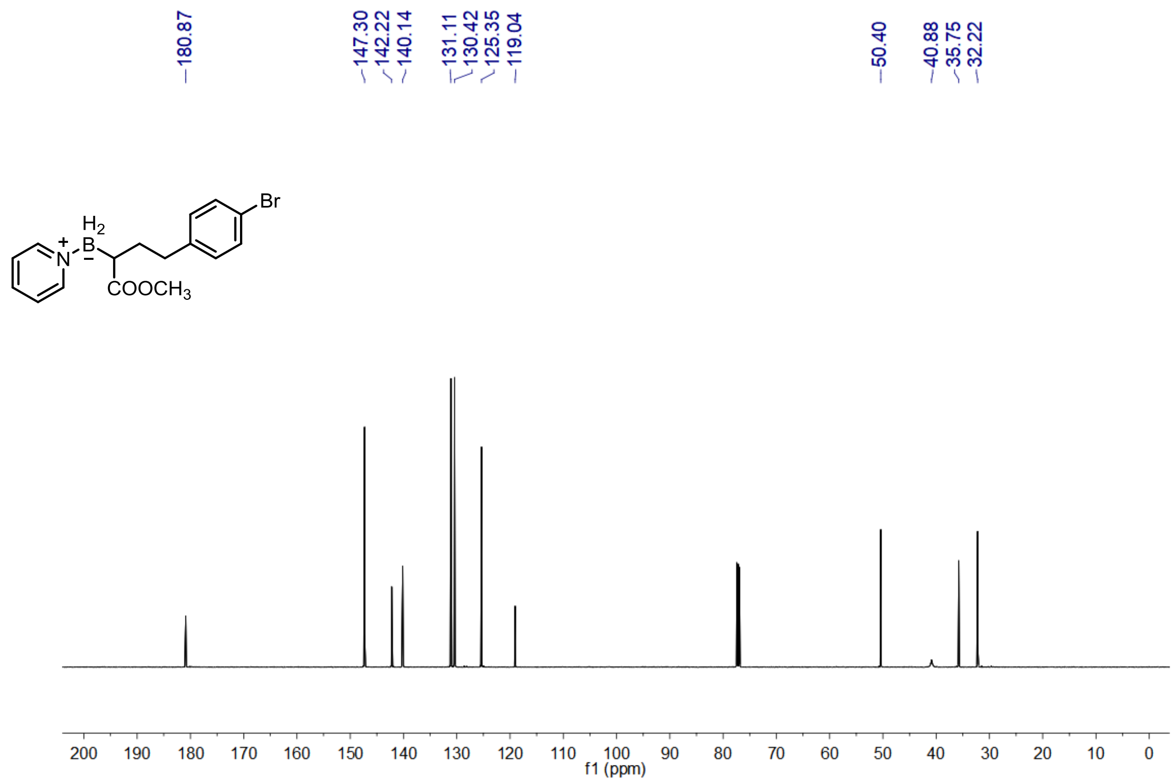


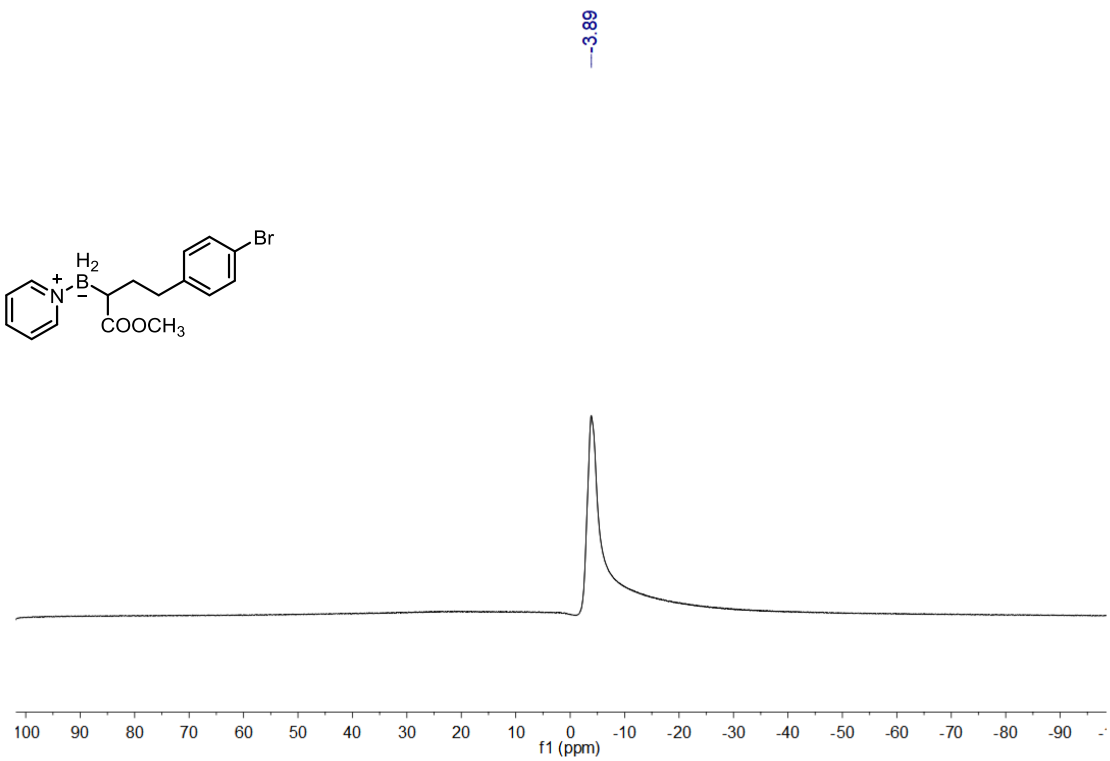




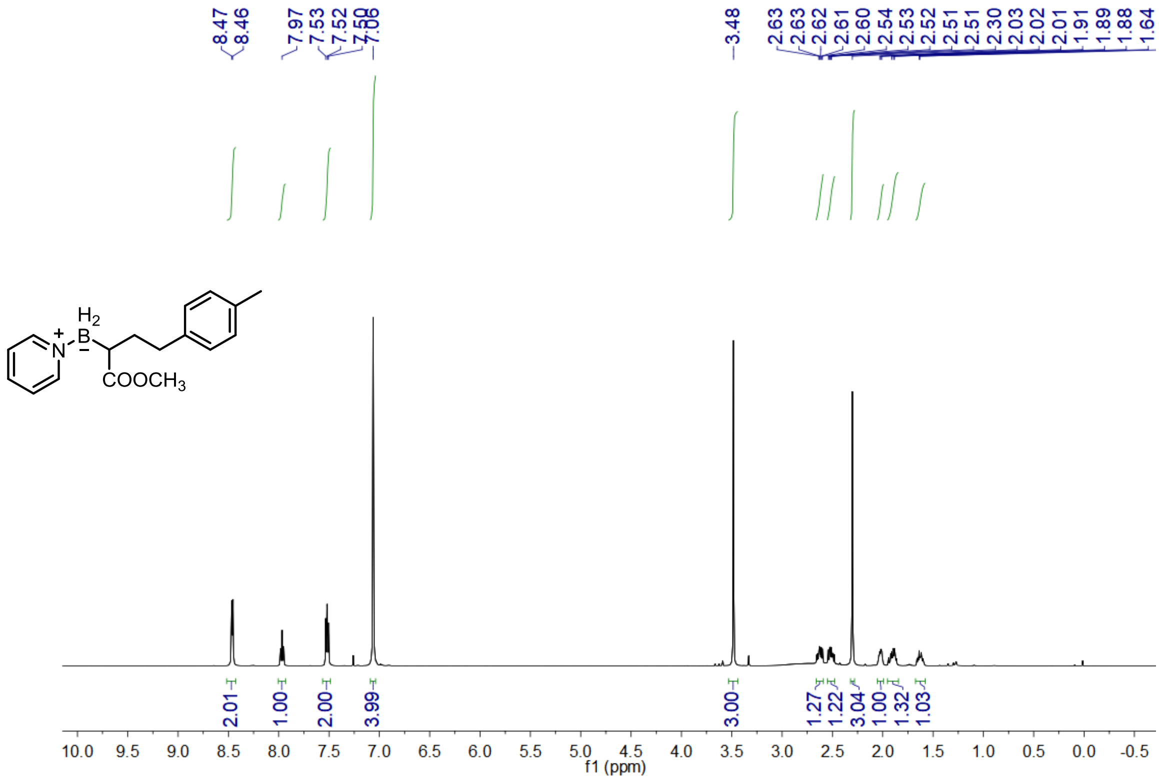
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **7d.**

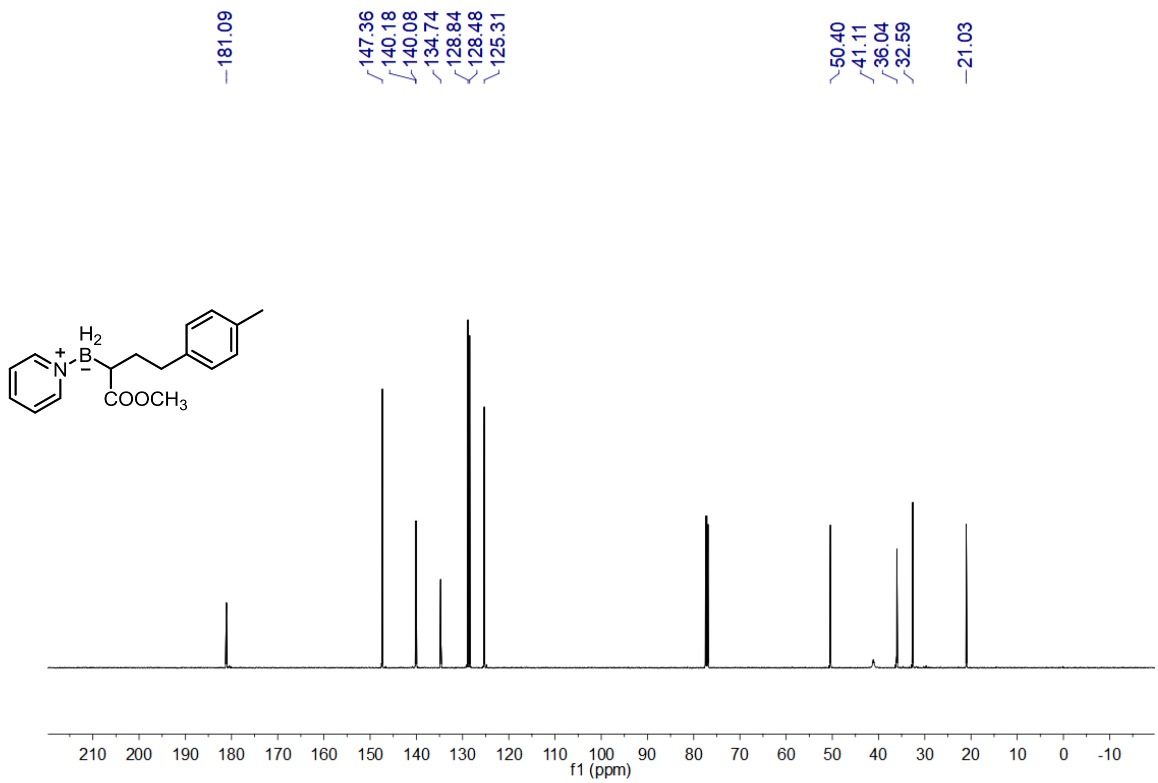


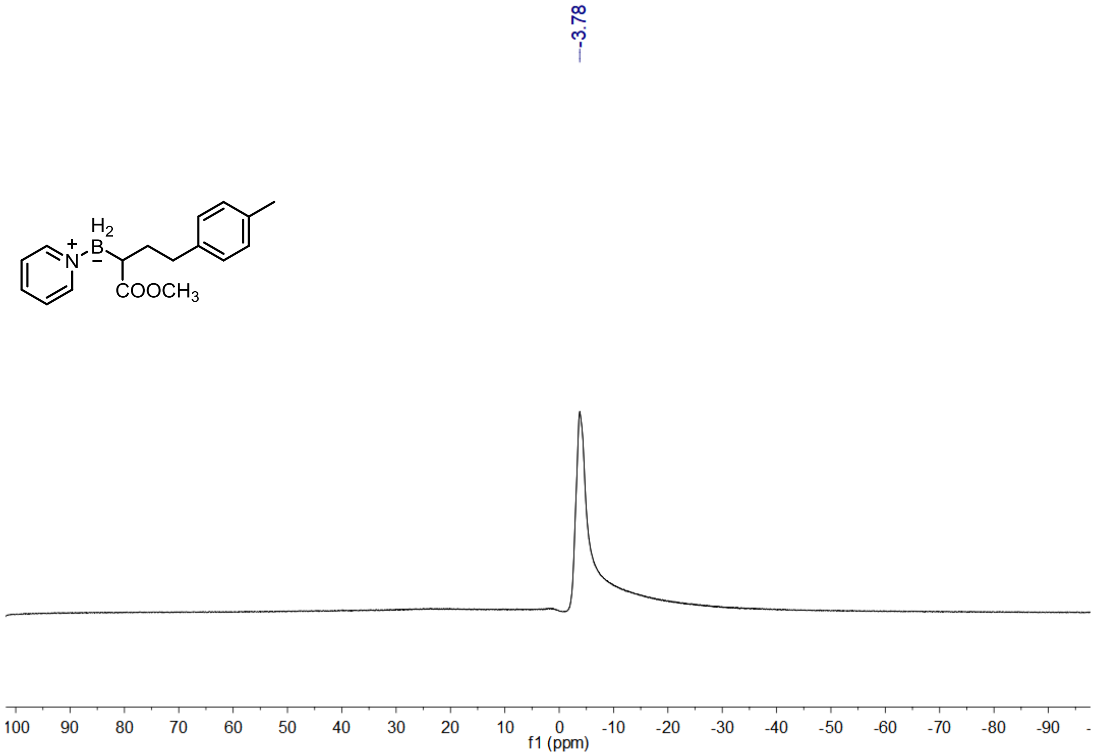

180.87
147.30
142.22
140.14
131.11
130.42
125.35
119.04
50.40
40.88
35.75
32.22
Br
H2
B
N
COOCH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-3.89
Br
H2
B
N
COOCH3
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

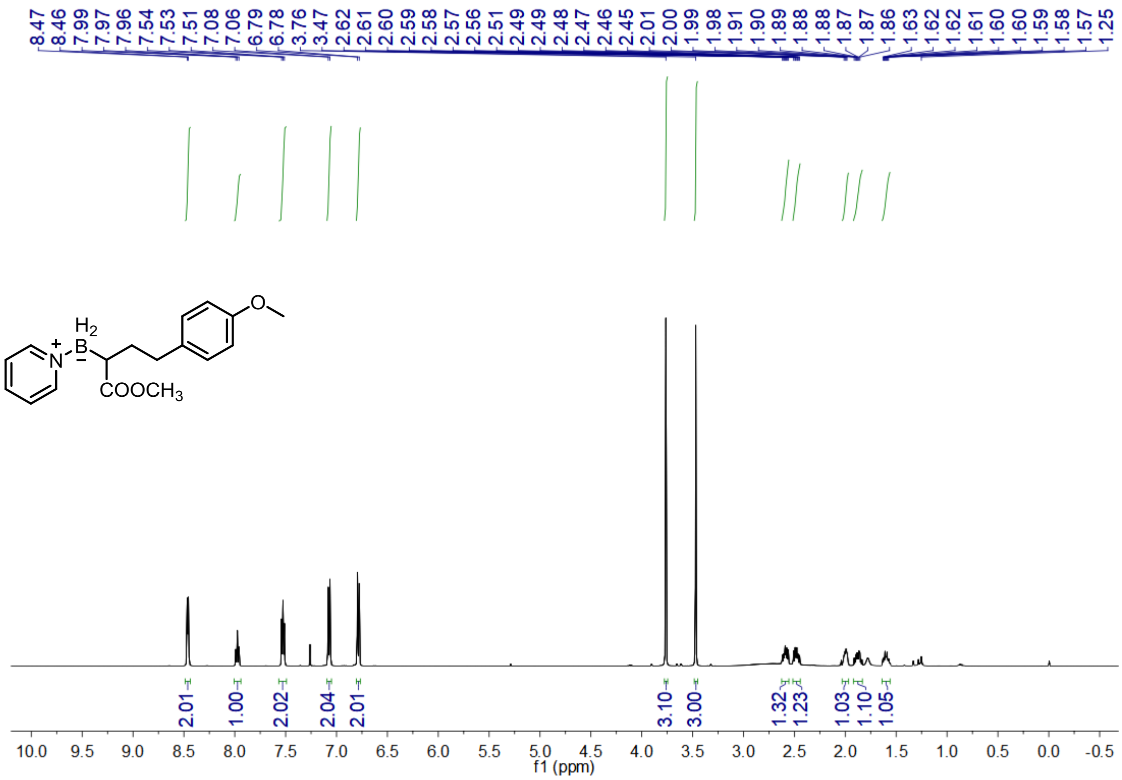
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **8d.**

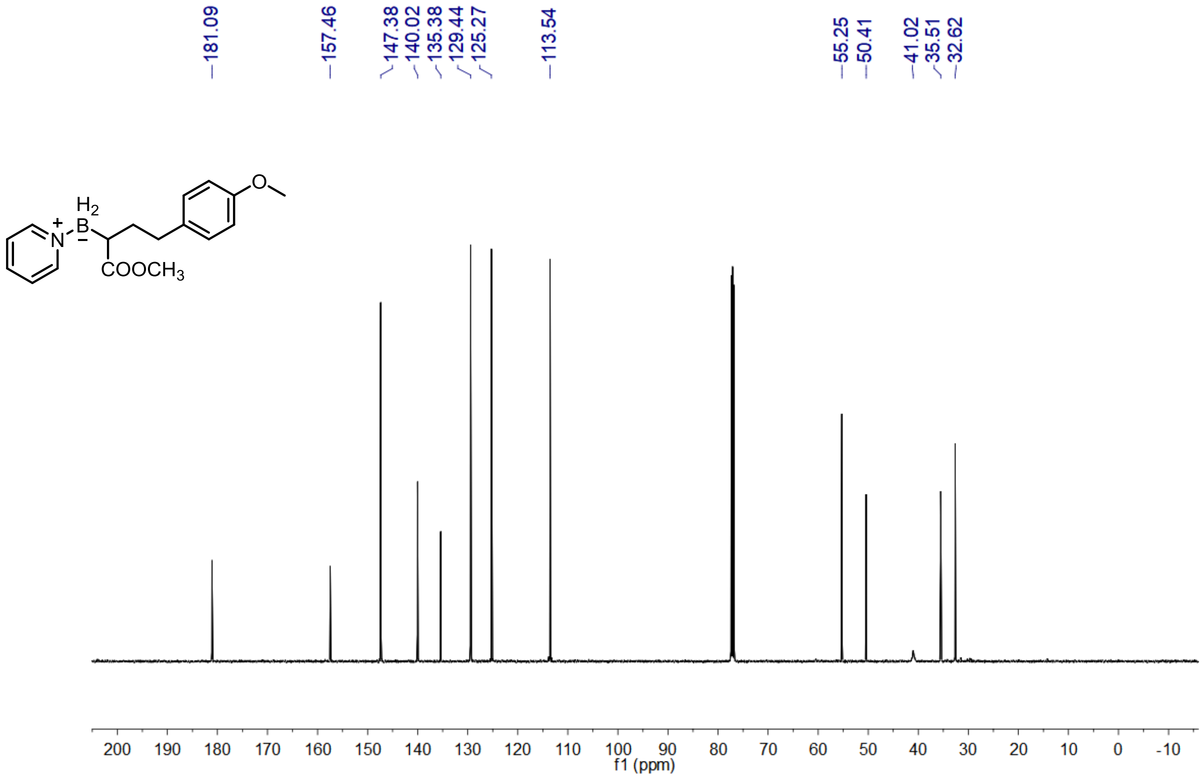


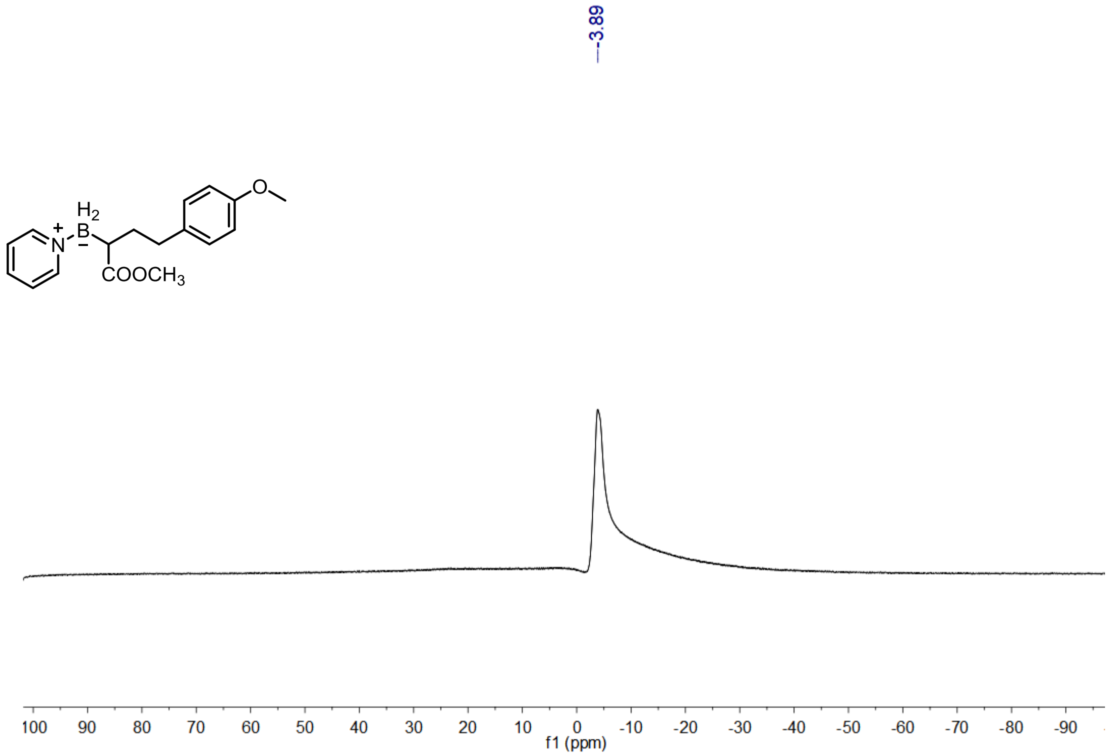




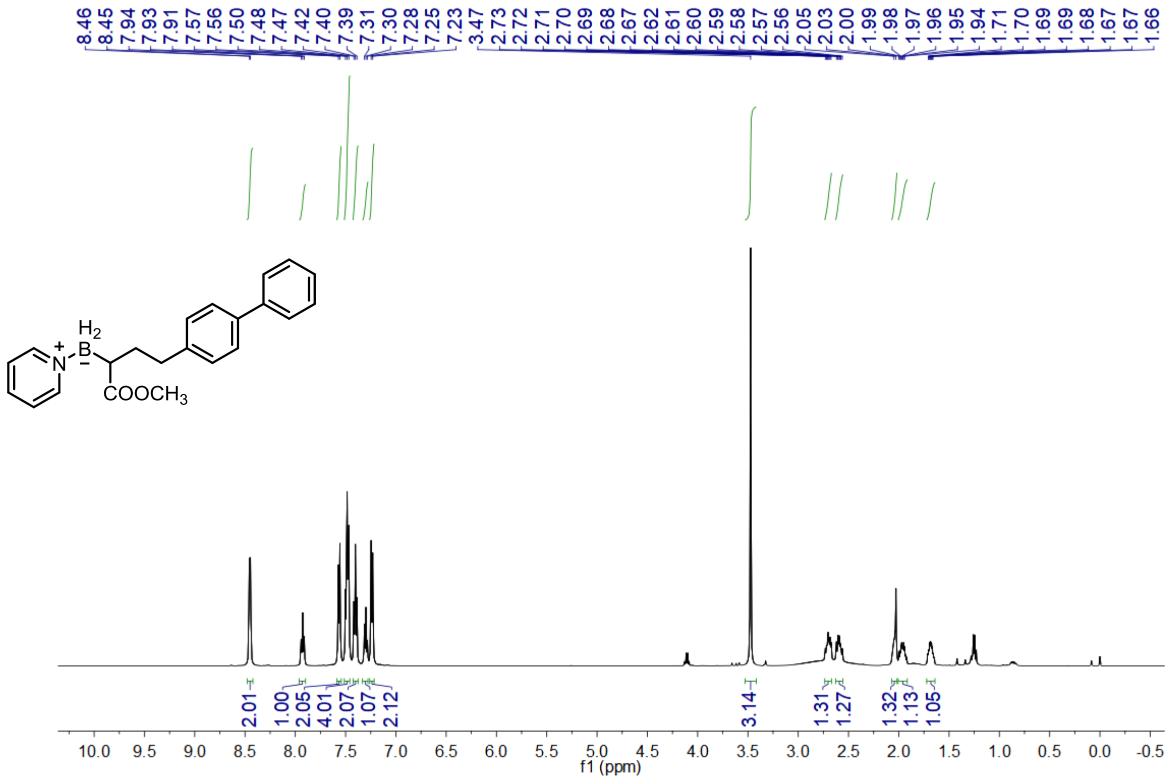
[1]H NMR (500 MHz, $CDCl_3$), [13]C NMR (126 MHz, $CDCl_3$) & [11]B NMR (160 MHz, $CDCl_3$) for **9d.**

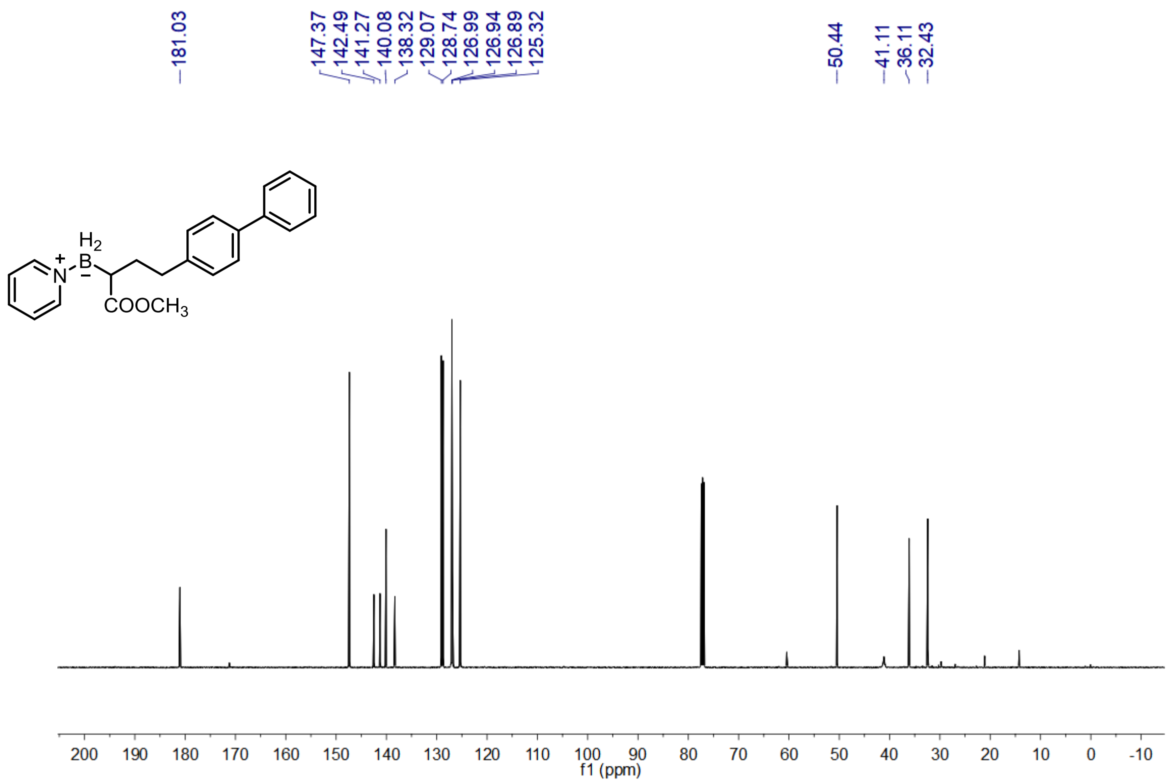


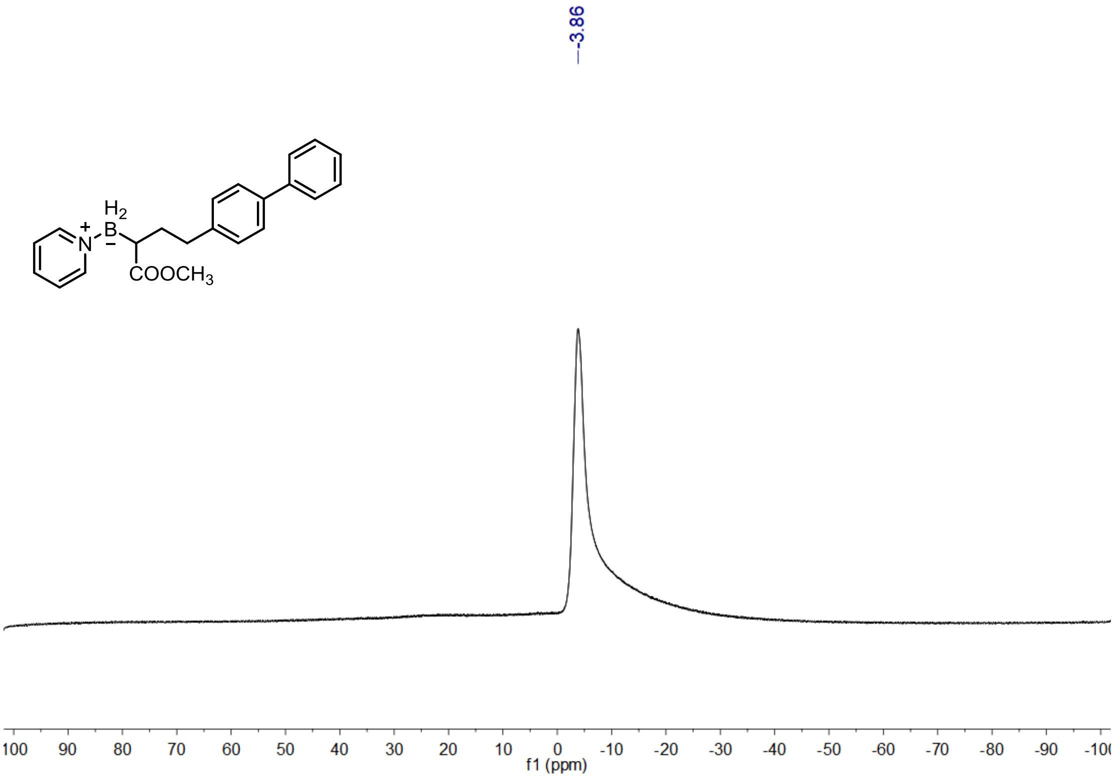

181.09
157.46
147.38
140.02
135.38
129.44
125.27
113.54
55.25
50.41
41.02
35.51
32.62
H2
B
N
O
COOCH3
f1 (ppm)


-3.89
H2
B
N
O
COOCH3
f1 (ppm)

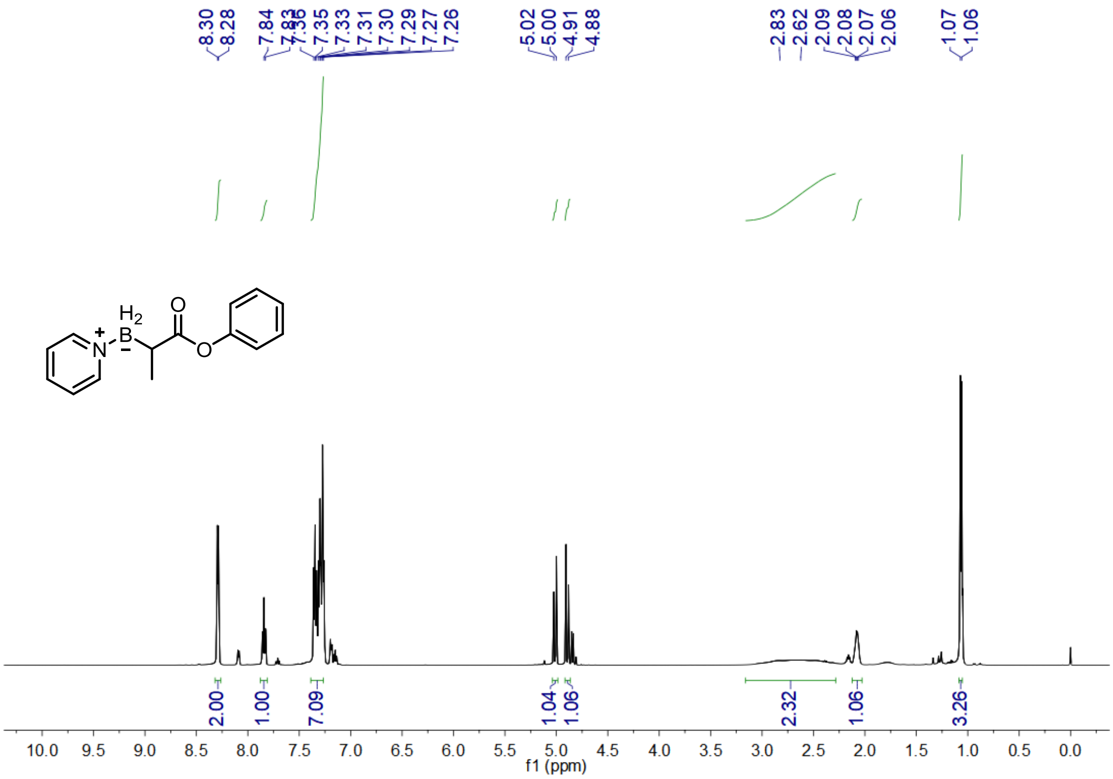
^{1}H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (126 MHz, $CDCl_3$) & ^{11}B NMR (160 MHz, $CDCl_3$) for **10d.**







^{1}H NMR (500 MHz, $CDCl_3$) for **11d.**



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