Supporting Information

for

Nickel-Catalyzed Reductive Coupling of α-Haloboronates to Access Internal Vicinal Bis(boronate) Esters

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1. Supplementary Notes

^{1}H and ^{13}C spectra were recorded on a Bruker Avance 400, 600 spectrometers, and $CDCl_3$ was purchased from J&K. Chemical shifts are given in ppm with the internal standards as TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 200-300 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. GC spectra were recorded on Agilent Technologies 7890A spectrometer; GC-MS spectra were conducted on Shimadzu GC-MS-QP2010 SE W spectrometer; High-resolution mass spectra HRMS-ESI were obtained from a Bruker micrOTOF-II instrument.

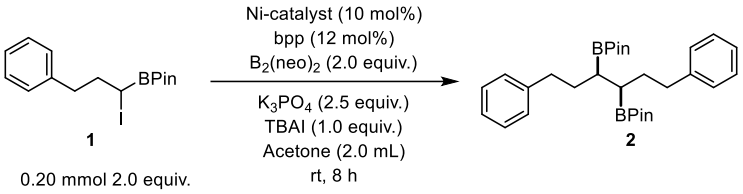
Unless otherwise noted, all reagents and starting materials were purchased from commercial sources and used without further purification. All reactions were performed under the N_2 atmosphere using dried solvents which were dried and purified according to procedures from 'Purification of Laboratory Chemicals book'.

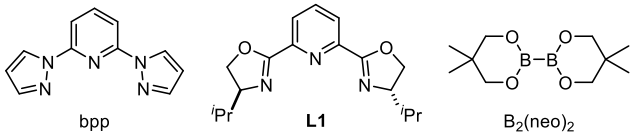
2. Procedures for Reaction Optimization

General procedure A for Reaction Optimization: In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with Ni-catalyst (0.01 mmol, 10 mol%), ligand (0.012 mmol, 12 mol%), reductant (0.20 mmol, 2.0 equiv.), base (0.25 mmol, 2.5 equiv.), additive (0.1 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, the solvent (2.0 mL) was added via syringe, and then compound **1** (0.20 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (2.0 mL) and quenched with H_2O (2.0 mL). The yields were determined by GC with pentadecane as an internal standard. The resultant solution was treated following General procedure B, then the crude product was concentrated in vacuo and analyzed by ^{1}H NMR to obtain the *dr* ratio according to the reference. The *cis* structure of the product was determined according to the reference[S1].

General procedure B for the oxidation of boronic ester to alcohol: The residue of general procedure A was concentrated in vacuo and dissolved in THF/H_2O (4.0 mL, v/v=1:1), and then $NaBO_3$•$4H_2O$ (1.0 mmol) was added at room temperature. The suspension was stirred for 4 hours and the reaction mixture was extracted with EtOAc (3*2.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to obtain the crude alcohol.

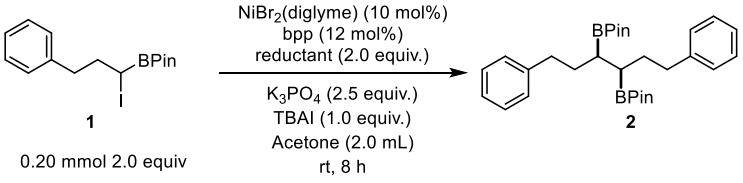
Table S1. Screening results on Ni-catalysts.

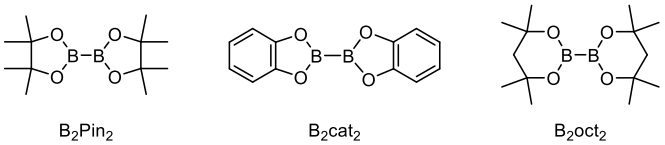




Entry	Ni-catalyst	Yield of 2 (%)	*dr*
1	$NiBr_2$(diglyme)	77	13:1
2	$NiBr_2$(DME)	64	13:1
3	$NiCl_2$(DME)	66	9:1
4	NiI_2	23	5:1
5	$Ni(cod)_2$	68	13:1
6	$Ni(acac)_2$	29	1:1
7	$Ni(OTf)_2$	67	9:1
8	$Ni(PPh_3)_2Br_2$	0	n.d.

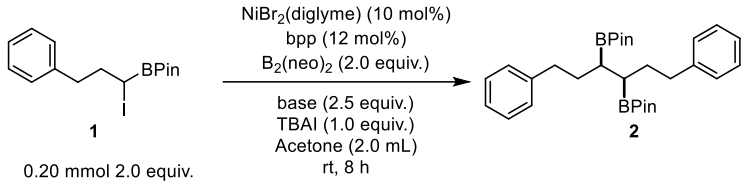
Table S2. Screening results on reductants.





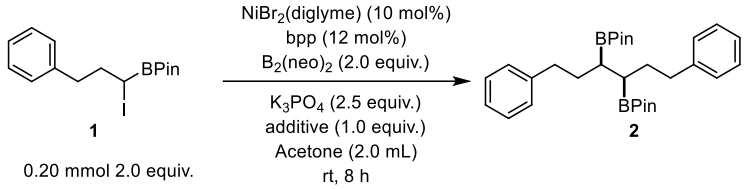
Entry	Reductant	Yield of 2 (%)	*dr*
1	Zn	38	2:1
2	Mn	0	n.d.
3	Mg	0	n.d.
4	B_2Pin_2	0	n.d.
5	B_2cat_2	54	19:1
6	$B_2(neo)_2$	77	13:1
7	B_2oct_2	0	n.d.

Table S3. Screening results on bases.



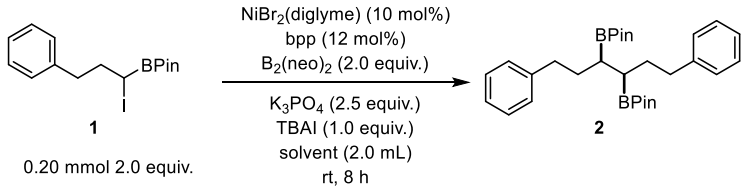
Entry	Base	Yield of 2 (%)	*dr*
1	K_3PO_4	77	13:1
2	$KHCO_3$	54	11:1
3	Na_2CO_3	44	13:1
4	K_2HPO_4	7	n.d.
5	KH_2PO_4	0	n.d.
6	CH_3COOK	0	n.d.
7	K_2CO_3	47	11:1
8	Na_3PO_4	33	13:1

Table S4 Screening results on additives.



Entry	Additive	Yield of 2 (%)	*dr*
1	TBAI	77	13:1
2	TBAC	44	6:1
3	$AlCl_3$	0	n.d.
4	$Al(OTf)_3$	11	n.d.
5	4ÅMS	57	>20:1

Table S5. Screening results on solvents.



Entry	Solvent	Yield of 2 (%)	*dr*
1	Acetone	77	13:1
2	DME	16	13:1
3	DMA	37	9:1
4	NMP	0	n.d.
5	THF	5	n.d.

6	$PhCF_3$	0	n.d.
7	EA	9	n.d.
8	CH_3CN	56	9:1

Table S6 Screening results on ligands.

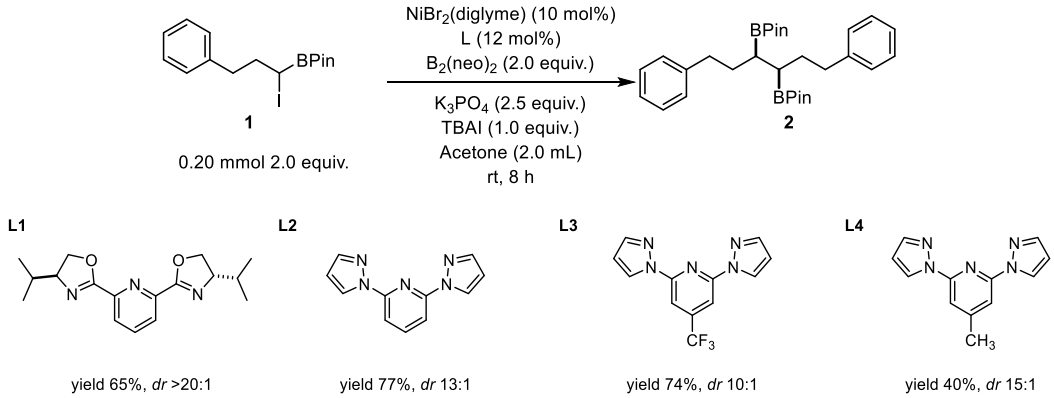
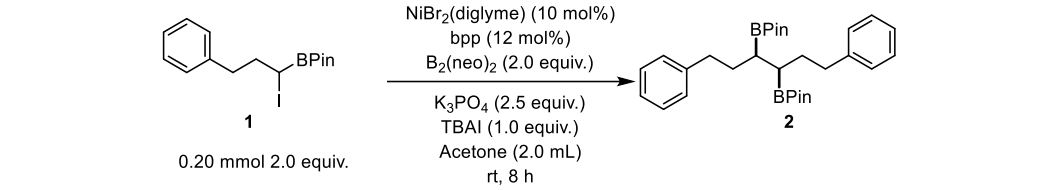


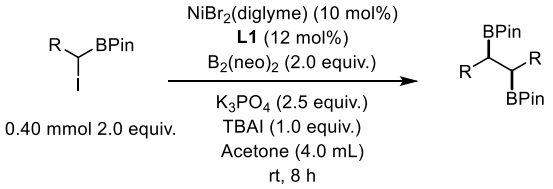
Table S7. Control reactions.



Entry	Variation from standard conditions	Yield of 2 (%)	*dr*
1	Without Ni-catalysts	0	n.d.
2	Without ligand	trace	n.d.
3	Without reductant	0	n.d.
4	Without base	0	n.d.
5	Without additive	51	13:1
6	In air	0	n.d.

3. Procedures for Scope Studies

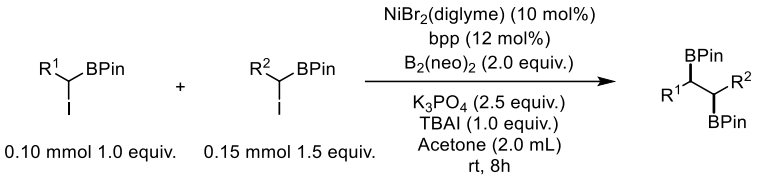
3.1 General procedure C for the homo-coupling reaction of *α*-iodoboronates



In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.020 mmol, 10 mol%), **L1** (0.024 mmol, 12 mol%), $B_2(neo)_2$ (0.40 mmol, 2.0 equiv.), K_3PO_4 (0.50 mmol, 2.5 equiv.), TBAI (0.2 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of

the glovebox. Under N_2 atmosphere, acetone (4.0 mL) was added via syringe, and then α-iodoboronate (0.40 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (4.0 mL) and quenched with H_2O (4.0 mL). The aqueous solution was extracted with EtOAc (4.0 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the product. The boronic ester product was oxidized to the corresponding alcohol following General procedure B, then the mixture was analyzed by ^1H NMR to obtain the *dr* ratio. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

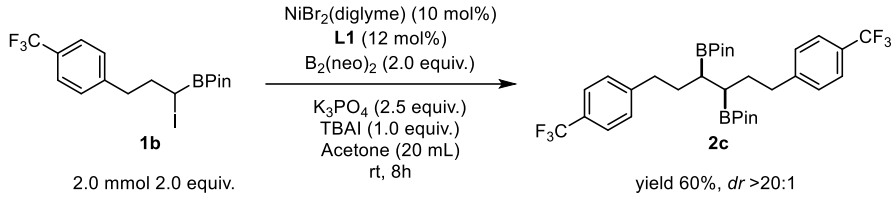
3.2 General procedure D for the cross-coupling of two distinct α-iodoboronates



In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.010 mmol, 10 mol%), bpp (0.012 mmol, 12 mol%), $B_2(neo)_2$ (0.20 mmol, 2.0 equiv.), K_3PO_4 (0.25 mmol, 2.5 equiv.), TBAI (0.1 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (2.0 mL) was added via syringe, and then the two substrates α-iodoboronate (0.15 mmol, 1.5 equiv.) and α-iodoboronate (0.10 mmol, 1.0 equiv) were added in sequence, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (2.0 mL) and quenched with H_2O (2.0 mL). The aqueous solution was extracted with EtOAc (2.0 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the product. The boronic ester product was oxidized to the corresponding alcohol following General procedure B, then the mixture was analyzed by ^1H NMR to obtain the *dr* ratio. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

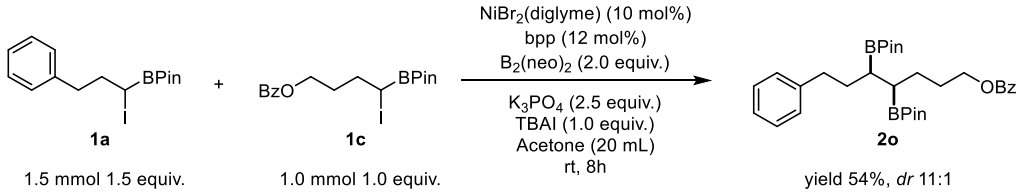
4. Procedures for applications of the products

4.1 Procedure E for scale-up reaction of homo-coupling reaction



In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.10 mmol, 10 mol%), **L1** (0.12 mmol, 12 mol%), $B_2(neo)_2$ (2.0 mmol, 2.0 equiv.), K_3PO_4 (2.5 mmol, 2.5 equiv.), TBAI (1.0 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (20.0 mL) was added via syringe, and then **1c** (2.0 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (20 mL) and quenched with H_2O (20 mL). The aqueous solution was extracted with EtOAc (20 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The residues were purified by silica gel column chromatography with an eluent of petroleum ether/ethyl acetate (20/1) affording product **2c** (0.38g, 60% yield, *dr* >20:1, white solid). The boronic ester product **2c** was oxidized to the corresponding alcohol following General procedure B, then the mixture was analyzed by ^1H NMR to obtain the *dr* ratio. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

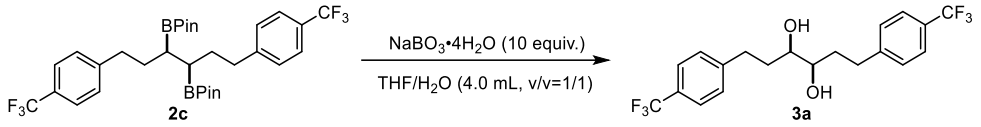
4.2 Procedure F for scale-up reaction of cross-coupling reaction



In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.10 mmol, 10 mol%), bpp (0.12 mmol, 12 mol%), $B_2(neo)_2$ (2.0 mmol, 2.0 equiv.), K_3PO_4 (2.5 mmol, 2.5 equiv.), TBAI (1.0 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (20.0 mL) was added via syringe, and then **1a** (1.5 mmol, 1.5 equiv.) and **1c** (1.0 mmol, 1.0 equiv.) were added in sequence, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (20 mL) and quenched with H_2O (20 mL). The aqueous solution was extracted with EtOAc (20 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The residues were purified by silica gel column chromatography with an eluent of petroleum ether/ethyl acetate (15/1) affording product **2o** (0.30g, 54% yield, *dr* 11:1, colorless oil). The boronic ester product **2o** was oxidized to the corresponding alcohol

following General procedure B, then the alcohol was analyzed by ^{1}H NMR to obtain the *dr* ratio. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

4.3 Procedure G for synthesis of 3a



0.20 mmol 1.0 equiv. yield 91% *dr* >20:1

The preparation of **3a** was conducted according to literature procedures [S2]. The boronic ester **2c** (0.2 mmol, 1.0 equiv.) was dissolved in THF/H_2O (4.0 mL, v/v=1:1), and then $NaBO_3$•$4H_2O$ (2.0 mmol, 10 equiv.) was added at room temperature. The suspension was stirred for 4 hours and the reaction mixture was extracted with EtOAc (3*4.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure, and the crude product was purified carefully by column chromatography on silica gel with an eluent of petroleum ether/ethyl acetate (1/1) affording product **3a** (91% yield, *dr* >20:1, white solid). The *dr* ratio was determined by ^{1}H NMR.

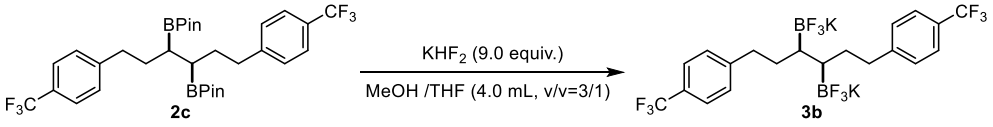
^{1}H NMR (400 MHz, MeOD) δ 7.54 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 4H), 3.44-3.40 (m, 2H), 2.91-2.84 (m, 2H), 2.76-2.68 (m, 2H), 1.88-1.71 (m, 4H).

^{13}C NMR (101 MHz, MeOD) δ 148.4, 130.1, 129.2 (q, *J* = 32.3 Hz), 126.2 (q, *J* = 4.0 Hz), 125.9 (q, *J* = 271.7 Hz), 74.3, 35.5, 33.0.

^{19}F NMR (376 MHz, MeOD) δ -63.80.

HRMS: m/z (ESI) calculated for $C_{20}H_{20}F_6NaO_2$ $[M+Na]^+$: 429.1265, found: 429.1260.

4.4 Procedure H for synthesis of 3b



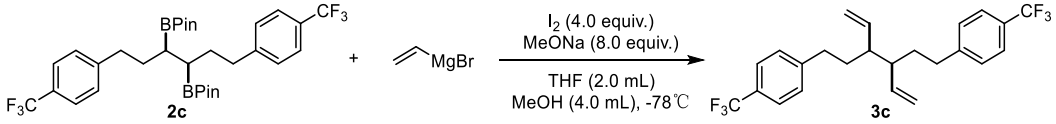
0.20 mmol 1.0 equiv.

The preparation of **3b** was conducted according to literature procedures [S3]. The boronic ester **2c** (0.2 mmol, 1.0 equiv.) was dissolved in MeOH/THF (4.0 mL, v/v=3/1). Then a solution of KHF_2 (2.0 M, 9.0 mL, 9.0 equiv.) was added dropwise at 0°C. Once added, the ice bath was removed and the reaction mixture was stirred overnight. Upon finished, the resultant solution was concentrated under reduced pressure. Pinacol and H_2O were removed by suspension in toluene (3*10 mL) followed by rotary evaporation. The remaining solid was dried under high vacuum and then suspended in hot acetone (3*10 mL) and filtered. The filtrate was concentrated to a minimal volume and hexane (50 mL) was added to yield a white precipitate. The precipitate was isolated by filtration, washing with hexanes (10 mL) and CH_2Cl_2 (10 mL) to afford the desired potassium trifluoroborate **3b** (yield 51%, *dr* >20:1, white solid).

^{1}H NMR (400 MHz, Acetone) δ 7.41 (d, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 2.74-2.56 (m, 4H), 1.90-1.77 (m, 2H), 1.75-1.66 (m, 2H), 1.24-1.21 (m, 2H).

^{13}C NMR (151 MHz, Acetone) δ 151.8, 130.1, 127.4 (q, *J* = 31.7 Hz), 125.9 (q, *J* = 270.3 Hz), 125.5 (q, *J* = 3.0 Hz), 36.2, 34.5.
^{19}F NMR (376 MHz, Acetone) δ -62.53.

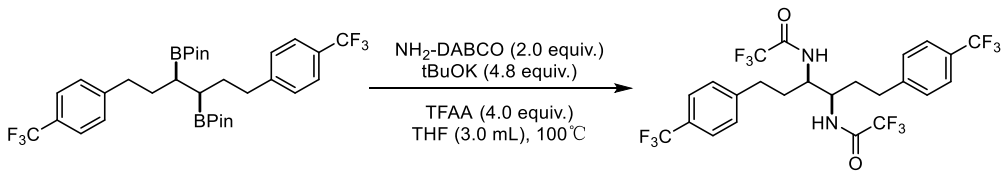
4.5 Procedure I for synthesis of 3c



0.20 mmol 1.0 equiv. 0.80 mmol 4.0 equiv. yield 86% *dr* >20:1

The preparation of **3c** was conducted according to literature procedures [S4]. The boronic ester **2c** (0.2 mmol, 1.0 equiv.) was dissolved in THF (2.0 mL) under N_2 atmosphere. Then a solution of vinylmagnesium bromide (0.80 mmol, 0.80 mL, 1.0 M in THF) was added dropwise, and the mixture was stirred for 30 min at room temperature. Then the tube was cooled to -78°C and a solution of I_2 (0.80 mmol in 2.0 mL MeOH) was added dropwise. The solution was stirred for another 30 min at this temperature, followed by addition of a solution of NaOMe (1.6 mmol in 2.0 mL MeOH). The reaction mixture was allowed to warm to room temperature and stirred for another 2 hours. Once finished, the reaction was quenched with 4 mL saturated sodium thiosulfate aqueous. The aqueous solution was extracted with EtOAc (3*4.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude material was purified by silica gel column chromatography with an eluent of petroleum ether affording **3c** (yield 86%, *dr* >20:1, colorless oil). The *dr* ratio was determined by ^{1}H NMR.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 5.65-5.56 (m, 2H), 5.13 (dd, *J* = 10.0, 2.0 Hz, 2H), 5.03 (dd, *J* = 16.8, 2.0 Hz, 2H), 2.70-2.63 (m, 2H), 2.57-2.49 (m, 2H), 2.09-2.02 (m, 2H), 1.70-1.56 (m, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 138.8, 128.7, 128.1 (q, *J* = 31.7 Hz), 125.20 (q, *J* = 3.0 Hz), 124.4 (q, *J* = 271.8 Hz), 117.02, 47.84, 34.50, 33.49.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.26.
MS: (EI) [M]$^+$ $C_{24}H_{24}F_6$: 426.20.

4.6 Procedure J for synthesis of 3d



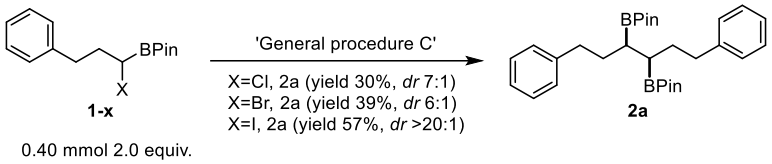
0.20 mmol 1.0 equiv. yield 57% *dr* >20:1

The preparation of **3d** was conducted according to literature procedures [S5]. In the nitrogen-filled glove box, an oven-dried 25-mL Schlenk flask containing a Teflon stir bar was charged with **2c** (0.20 mmol, 1.0 equiv.), NH_2-DABCO (0.40 mmol, 2.0 equiv.), tBuOK (0.96 mmol, 4.8 equiv.) and THF (3.0 mL). Then, the flask was heated to 100°C and stirred for 1 hour. Upon completion, TFAA (0.80 mmol, 4.0 equiv.) was added, and the reaction mixture was heated to 100°C again for 1 hour. After that, the reaction was

quenched by EtOAc (2.0 mL) and H_2O (2.0 mL). The aqueous solution was extracted with EtOAc (3*2.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (10/1) to afford **3d** (yield 57%, *dr* >20:1, white solid). The *dr* ratio was determined by ^{1}H NMR.
^{1}H NMR (400 MHz, DMSO) δ 8.25 (s, 2H), 6.63 (d, *J* = 8.0 Hz, 4H), 6.40 (d, *J* = 8.0 Hz, 4H), 3.13-2.85 (m, 2H), 1.73-1.53 (m, 4H), 0.94-0.82 (m, 4H).
^{13}C NMR (101 MHz, DMSO) δ 156.7 (q, *J* = 36.4 Hz), 146.0, 129.2, 126.9 (q, *J* = 31.3 Hz), 125.11 (q, *J* = 4.0 Hz), 124.4 (q, *J* = 272.7 Hz), 116.0 (q, *J* = 289.9 Hz), 52.6, 31.6, 31.4.
^{19}F NMR (376 MHz, DMSO) δ -60.89, -74.22.
HRMS: m/z (ESI) calculated for $C_{24}H_{20}F_{12}N_2NaO_2$ $[M+Na]^+$: 619.1231, found: 619.1225.

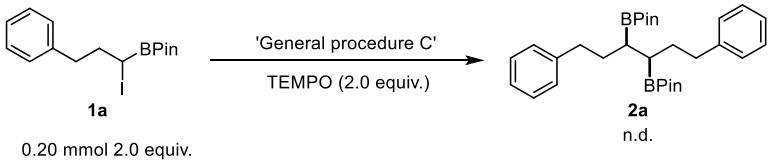
5. Mechanistic Studies

5.1 Comparison Reactions



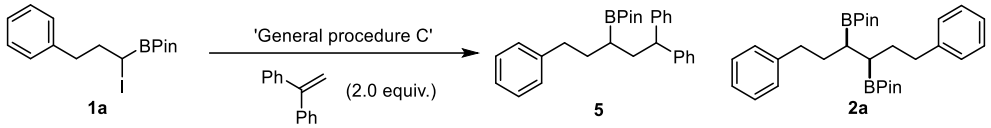
In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.020 mmol, 10 mol%), **L1** (0.024 mmol, 12 mol%), $B_2(neo)_2$ (0.40 mmol, 2.0 equiv.), K_3PO_4 (0.50 mmol, 2.5 equiv.), TBAI (0.20 mmol, 1.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (4.0 mL) was added via syringe, and then *α*-haloboronates (0.40 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (4.0 mL) and quenched with H_2O (4.0 mL). The aqueous solution was extracted with EtOAc (4.0 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography with an eluent of petroleum ether/ethyl acetate (20/1) affording product **2a**. The boronic ester product **2a** was oxidized to the corresponding alcohol following General procedure B, then the alcohol was analyzed by ^{1}H NMR to obtain the *dr* ratio. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

5.2 Reaction with the radical scavenger



In the nitrogen-filled glovebox, an oven-dried 10-mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.010 mmol, 10 mol%), **L1** (0.012 mmol, 12 mol%), $B_2(neo)_2$ (0.20 mmol, 2.0 equiv.), K_3PO_4 (0.25 mmol, 2.5 equiv.), TBAI (0.10 mmol, 1.0 equiv.), TEMPO (0.20 mmol, 2.0 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (2.0 mL) was added via syringe, and then α-iodoboronates (0.20 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (2.0 mL) and quenched with H_2O (2.0 mL). The aqueous solution was extracted with EtOAc (2.0 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The yield was determined by GC and pentadecane was the internal standard.

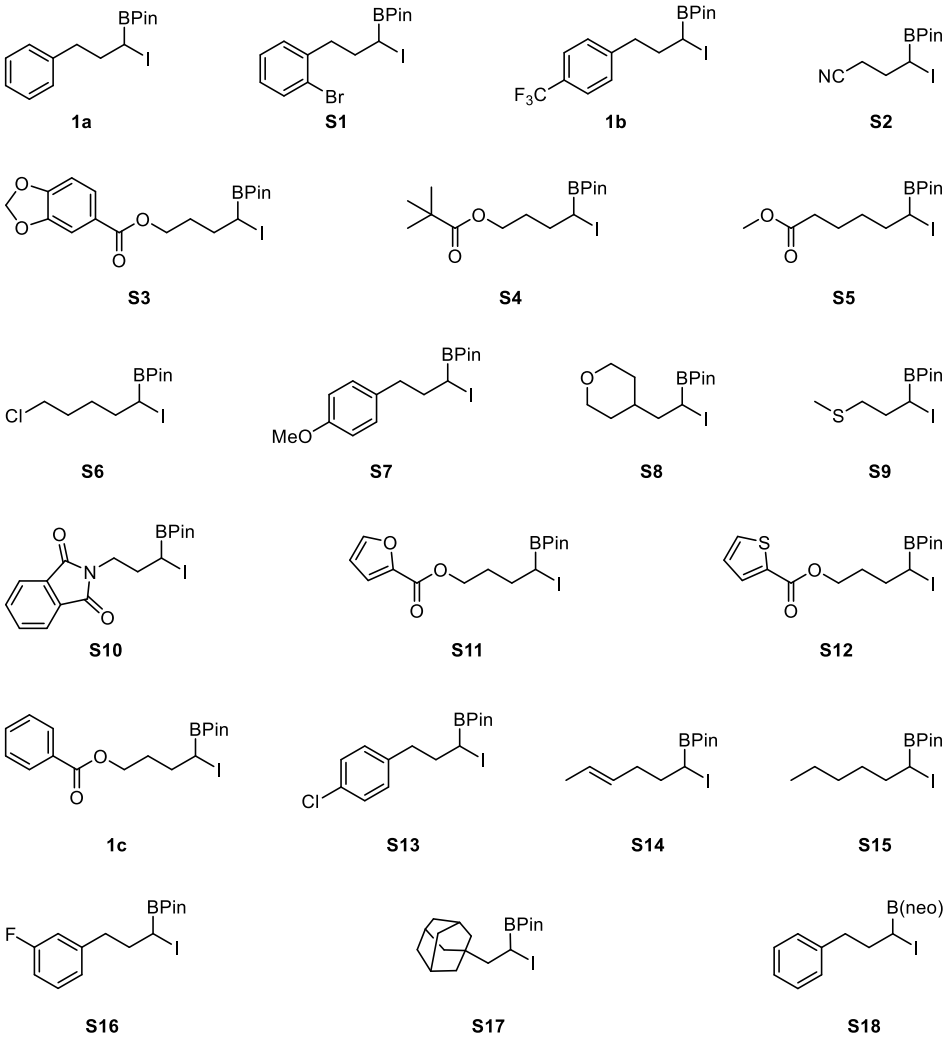
5.3 Reaction with 1,1-diphenylethylene



0.2 mmol 2.0 equiv. | yield 47% | n.d.

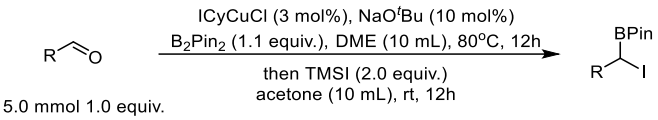
In the nitrogen-filled glovebox, an oven-dried 10 mL Schlenk tube containing a Teflon stir bar was charged with $NiBr_2$(diglyme) (0.010 mmol, 10 mol%), L1 (0.012 mmol, 12 mol%), $B_2(neo)_2$ (0.20 mmol, 2.0 equiv.), K_3PO_4 (0.25 mmol, 2.5 equiv.). Then the tube was sealed with a septum and taken out of the glovebox. Under N_2 atmosphere, acetone (2.0 mL) was added via syringe, and then α-iodoboronates (0.20 mmol, 2.0 equiv.) and 1,1-diphenylethylene (0.20 mmol, 2.0 equiv.) was added, and the reaction mixture was stirred for 8 hours at room temperature. Upon completion, the mixture was diluted with EtOAc (2.0 mL) and quenched with H_2O (2.0 mL). The aqueous solution was extracted with EtOAc (2.0 mL*3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through Celite, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether to afford **5** (yield 47%, colorless oil).

6. Synthesis and characterization of Substrates



The *α*-iodoboronates **1a, S2, S9** were synthesized according to the reference[S6], and all analytical data matched the reports.

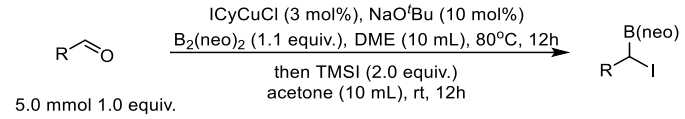
General procedure K for synthesis of S5, S6, S10, S15



According to the reference[S6], in the nitrogen-filled glovebox, an oven-dried 25 mL Schlenk flask equipped with a Teflon stir bar was charged with B_2Pin_2 (5.5 mmol, 1.1 equiv.), NaO^{t}Bu (0.50 mmol, 10 mol%), ICyCuCl (0.15 mmol, 3 mol%) and aldehyde (5.0 mmol, 1.0 equiv.), DME (10 mL). The tube was sealed and heated at 80 ºC with stirring for 12 h. The reaction solution was cooled to room temperature, and the solvent was concentrated in vacuo. The crude mixture was dissolved by acetone (10 mL). TMSI (10 mmol, 2.0 equiv.) was added to the solution. After stirring for 12 h at room temperature, the solvent was concentrated in vacuo. The crude material was purified by

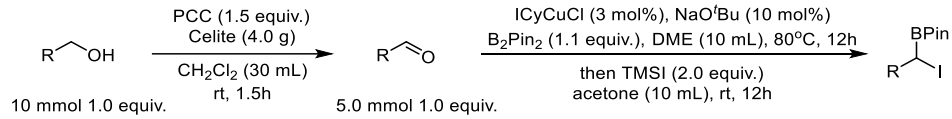
flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to give the product. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

General procedure L for synthesis of S18



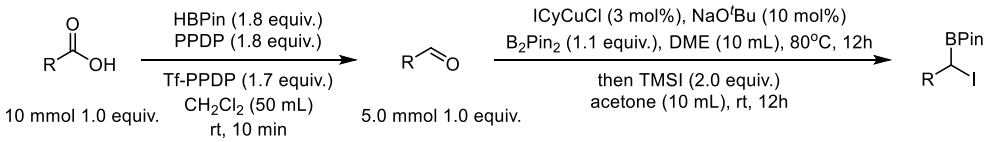
In the nitrogen-filled glovebox, an oven-dried 25 mL Schlenk flask equipped with a Teflon stir bar was charged with $B_2(neo)_2$ (5.5 mmol, 1.1 equiv.), tBuONa (0.50 mmol, 10 mol%), ICyCuCl (0.15 mmol, 3 mol%) and aldehyde (5.0 mmol, 1.0 equiv.), DME (10 mL). The tube was sealed and heated at 80 ºC with stirring for 12 h. The reaction solution was cooled to room temperature, and the solvent was concentrated in vacuo. The crude mixture was dissolved by acetone (10 mL). TMSI (10 mmol, 2.0 equiv.) was added to the solution. After stirring for 12 h at room temperature, the solvent was concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to give the product. Note: generally, the flash column chromatography should be done fast and is better to finish within 30 min; otherwise the product could be decomposed to give a lower yield.

General procedure M for synthesis of S7, S14, S17



The first step of preparation procedures was conducted according to literature procedures[S7]. An oven-dried 100 mL Schlenk flask equipped with a Teflon stir bar was charged with pyridinium chlorochromate (PCC) (15 mmol, 1.5 equiv.), Celite (4.0 g) and anhydrous CH_2Cl_2 (20 mL). Then a solution of alcohol (10 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added in one portion to the suspension. The resulting dark-brown reaction mixture was kept at room temperature for 1.5 h. Then the mixture was diluted with CH_2Cl_2 (20 mL) and filtered through Celite and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the pure aldehyde. Then the aldehyde was treated following General procedure K to give the desired α-iodoboronate.

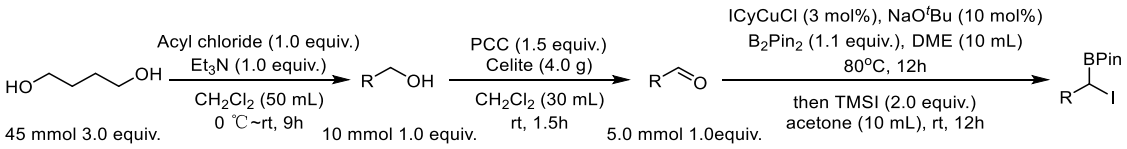
General procedure N for synthesis of S1, 1b, S8, S13, S16



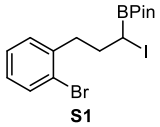
The first step of preparation procedures was conducted according to literature procedures[S8]. To a 25 mL Schlenk tube equipped with a magnetic stirring bar,

carboxylic acid (10 mmol, 1.0 equiv.), 1-Pyridin-4-ylpiperidine (PPDP, 18 mmol, 1.8 equiv.) and CH_2Cl_2 (50 mL) were added under a dry nitrogen atmosphere. Then the Tf-PPDP (17 mmol, 1.7 equiv.) and HBPin (18 mmol, 1.8 equiv.) were added to the reaction mixture. After the reaction was stirred for 10 min, the crude mixture was quenched by H_2O (20 mL) and extracted by CH_2Cl_2 (3*20 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the desired aldehyde. Then the aldehyde was treated following General procedure K to give the desired *α*-iodoboronate.

General procedure O for synthesis of S3, S4, S11, S12, 1c



The first step of preparation procedures was conducted according to literature procedures[S9]. To a 100 mL Schlenk tube equipped with a magnetic stirring bar, 1,4-butanediol (45 mmol, 3.0 equiv.) and Et_3N (15 mmol, 1.0 equiv.) and CH_2Cl_2 (50 mL) was added. Then the acyl chloride was added dropwise at 0 °C. The solution was warmed to room temperature and stirred for 9 hours. The mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3*20 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the desired aldehyde. Then the alcohol was treated following General procedure M to give the desired *α*-iodoboronate.



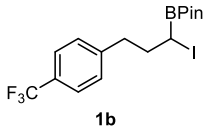
S1

Compound **S1** was synthesized according to General procedure **N**, and it was purified with silica gel chromatography (PE/EA = 30:1) (60% yield, colorless oil).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.19-7.13 (m, 2H), 6.98 (m, 1H), 3.16 (dd, *J* = 3.0, 1.8 Hz, 1H), 2.87-2.82 (m, 1H), 2.70-2.65 (m, 1H), 2.10-1.97 (m, 2H), 1.20 (d, *J* = 3.0, 12H).

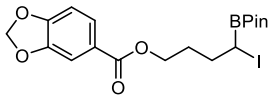
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.1, 132.8, 130.6, 127.8, 127.4, 124.4, 84.0, 37.4, 34.4, 24.4, 24.2.

MS: (EI) [M]$^+$ $C_{15}H_{21}BBrIO_2$: 449.90.



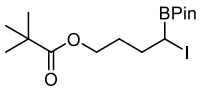
1b

Compound **1b** was synthesized according to General procedure **N**, and it was purified with silica gel chromatography (PE/EA = 30:1) (68% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.16 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.89-2.82 (m, 1H), 2.73-2.66 (m, 1H), 2.22-2.13 (m, 1H), 2.10-2.01 (m, 1H), 1.27 (s, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 128.9, 128.5 (q, *J* = 32.3 Hz), 125.4 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 272.7 Hz), 84.1, 37.0, 35.9, 24.4, 24.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3.
HRMS: m/z (ESI) calculated for $C_{16}H_{22}BF_3IO_2$ $[M+H]^+$: 441.0710, found: 441.0707.



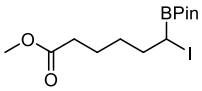
S3

Compound **S3** was synthesized according to General procedure **O**, and it was purified with silica gel chromatography (PE/EA = 10:1) (55% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H), 4.28 (t, *J* = 6.0 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 1H), 2.05-1.90 (m, 3H), 1.81-1.73 (m, 1H), 1.28 (d, *J* = 3.6 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 151.5, 147.7, 125.3, 124.3, 109.5, 107.9, 101.7, 84.1, 64.1, 31.5, 30.4, 24.4, 24.2.
HRMS: m/z (ESI) calculated for $C_{18}H_{24}BINaO_6$ $[M+Na]^+$: 497.0608, found: 497.0606.



S4

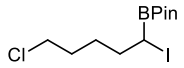
Compound **S4** was synthesized according to General procedure **O**, and it was purified with silica gel chromatography (PE/EA = 15:1) (59% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (t, *J* = 6.4 Hz, 2H), 3.16 (t, *J* = 8.0 Hz, 1H), 1.87-1.80 (m, 2H), 1.77-1.69 (m, 1H), 1.63-1.54 (m, 1H), 1.20 (d, *J* = 2.4 Hz, 12H), 1.13 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 84.0, 63.4, 38.7, 31.4, 30.3, 27.2, 24.4, 24.2.
MS: (EI) $[M]^+$ $C_{15}H_{28}BIO_4$: 410.10



S5

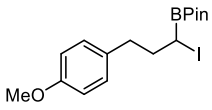
Compound **S5** was synthesized according to General procedure **K**, and it was purified with silica gel chromatography (PE/EA = 15:1) (47% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.59 (s, 3H), 3.13 (t, *J* = 8.0 Hz, 1H), 2.25 (t, *J* = 8.0 Hz, 2H), 1.86-1.69 (m, 2H), 1.64-1.51 (m, 2H), 1.46-1.34 (m, 1H), 1.31-1.23 (m, 1H), 1.20 (d, *J* = 2.8 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 83.9, 51.4, 34.3, 33.7, 30.6, 24.3, 24.14, 24.06.
MS: (EI) [M]$^+$ $C_{13}H_{24}BIO_4$: 382.00.



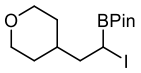
S6

Compound **S6** was synthesized according to General procedure **K**, and it was purified with silica gel chromatography (PE/EA = 30:1) (60% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.47 (t, *J* = 6.6 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 1H), 1.86-1.67 (m, 4H), 1.57-1.49 (m, 1H), 1.42-1.34 (m, 1H), 1.21 (d, *J* = 4.2 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 83.9, 44.6, 33.9, 31.7, 28.5, 24.3, 24.1.
MS: (EI) [M]$^+$ $C_{11}H_{21}BClIO_2$: 358.00.



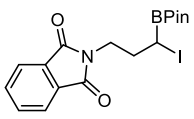
S7

Compound **S7** was synthesized according to General procedure **M**, and it was purified with silica gel chromatography (PE/EA = 15:1) (68% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.69 (s, 3H), 3.10 (dd, *J* = 8.8, 7.2 Hz, 1H), 2.66-2.58 (m, 1H), 2.53-2.45 (m, 1H), 2.10-2.01 (m, 1H), 1.98-1.89 (m, 1H), 1.18 (d, *J* = 2.0 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 132.7, 129.4, 113.8, 83.9, 55.2, 36.5, 36.1, 24.4, 24.2.
MS: (EI) [M]$^+$ $C_{16}H_{24}BIO_3$: 402.05.



S8

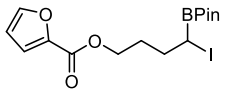
Compound **S8** was synthesized according to General procedure **N**, and it was purified with silica gel chromatography (PE/EA = 15:1) (64% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98-3.92 (m, 2H), 3.41-3.34 (m, 2H), 3.32-3.28 (m, 1H), 1.95-1.87 (m, 1H), 1.70-1.54 (m, 4H), 1.44-1.33 (m, 1H), 1.28 (s, 12H), 1.24-1.12 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 84.0, 67.9, 67.8, 41.0, 36.3, 32.7, 31.6, 24.3, 24.2.
HRMS: m/z (ESI) calculated for $C_{13}H_{24}BINaO_3$ $[M+Na]^+$: 389.0761, found: 389.0758.



S10

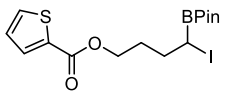
Compound **S10** was synthesized according to General procedure **K**, and it was

purified with silica gel chromatography (PE/EA = 7:1) (71% yield, white solid).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.64 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.78-3.74 (m, 1H), 3.67-3.63 (m, 1H), 3.12 (t, *J* = 8.4 Hz, 1H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.20 (d, *J* = 9.6 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 133.9, 132.0, 123.2, 84.1, 39.1, 33.7, 24.3, 24.2.
MS: (EI) [M]$^+$ $C_{17}H_{21}BINO_4$: 441.10.



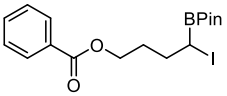
S11

Compound **S11** was synthesized according to General procedure **O**, and it was purified with silica gel chromatography (PE/EA = 10:1) (67% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.12 (d, *J* = 3.6 Hz, 1H), 6.44 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.23 (t, *J* = 6.0 Hz, 2H), 3.19 (t, *J* = 7.8 Hz, 1H), 1.95-1.82 (m, 3H), 1.75-1.66 (m, 1H), 1.19 (d, *J* = 3.0 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.5, 146.2, 144.5, 117.8, 111.7, 83.9, 64.0, 31.2, 30.3, 24.3, 24.1.
HRMS: m/z (ESI) calculated for $C_{15}H_{22}BINaO_5$ $[M+Na]^+$: 443.0503, found: 443.0500.



S12

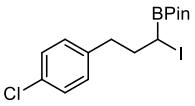
Compound **S12** was synthesized according to General procedure **O**, and it was purified with silica gel chromatography (PE/EA = 10:1) (74% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 4.2, 1.8 Hz, 1H), 7.56 (dd, *J* = 5.4, 1.8 Hz, 1H), 7.10 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.30 (t, *J* = 6.0 Hz, 2H), 3.28 (t, *J* = 7.8 Hz, 1H), 2.03-1.90 (m, 3H), 1.81-1.74 (m, 1H), 1.27 (d, *J* = 3.0 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 133.8, 133.3, 132.3, 127.6, 84.0, 64.2, 31.3, 30.3, 24.3, 24.1.
HRMS: m/z (ESI) calculated for $C_{15}H_{22}BINaO_4S$ $[M+Na]^+$: 459.0274, found: 459.0271.



1c

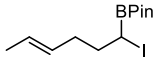
Compound **1c** was synthesized according to General procedure **O**, and it was purified with silica gel chromatography (PE/EA = 15:1) (72% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.50-7.45 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.21 (t, *J* = 6.8 Hz, 1H), 2.00-1.83 (m, 3H), 1.78-1.66 (m, 1H), 1.19 (d, *J* = 2.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 132.8, 130.2, 129.5, 128.3, 84.0, 64.1, 31.4, 30.4, 24.3, 24.2.
MS: (EI) [M]$^+$ $C_{17}H_{24}BIO_4$: 430.05.



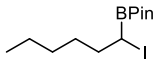
S13

Compound **S13** was synthesized according to General procedure **N**, and it was purified with silica gel chromatography (PE/EA = 30:1) (70% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.16 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.77-2.72 (m, 1H), 2.62-2.57 (m, 1H), 2.17-2.09 (m, 1H), 2.04-1.98 (m, 1H), 1.27 (d, *J* = 3.0 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.2, 131.8, 129.9, 128.5, 84.0, 36.4, 36.1, 24.4, 24.2.
MS: (EI) [M]$^+$ $C_{15}H_{21}BClIO_2$: 406.00.



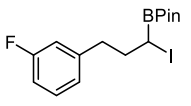
S14

Compound **S14** was synthesized according to General procedure **M**, and it was purified with silica gel chromatography (PE/EA = 50:1) (39% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45-5.37 (m, 1H), 5.32-5.24 (m, 1H), 3.16 (t, *J* = 8.0 Hz, 1H), 2.07-1.71 (m, 4H), 1.57 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.20 (d, *J* = 2.4 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 129.3, 126.3, 83.9, 34.4, 33.9, 24.4, 24.2, 17.9.
MS: (EI) [M]$^+$ $C_{12}H_{22}BIO_2$: 336.0758.



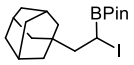
S15

Compound **S15** was synthesized according to General procedure **K**, and it was purified with silica gel chromatography (PE/EA = 30:1) (58% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (t, *J* = 8.4 Hz, 1H), 1.83-1.69 (m, 2H), 1.38-1.32 (m, 1H), 1.27-1.22 (m, 4H), 1.20 (d, *J* = 3.2 Hz, 12H), 1.18-1.17 (m, 1H), 0.81 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 83.8, 34.8, 31.0, 30.9, 24.4, 24.2, 22.4, 13.9.
MS: (EI) [M]$^+$ $C_{12}H_{24}BIO_2$: 338.05.



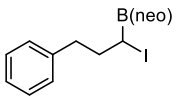
S16

Compound **S16** was synthesized according to General procedure **N**, and it was purified with silica gel chromatography (PE/EA = 30:1) (60% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.91-6.87 (m, 2H), 3.18 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.80-2.76 (m, 1H), 2.66-2.61 (m, 1H), 2.19-2.13 (m, 1H), 2.07-2.01 (m, 1H), 1.28 (d, *J* = 3.0 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.6 Hz), 143.3 (d, *J* = 7.6 Hz), 129.8 (d, *J* = 9.1 Hz), 124.2 (d, *J* = 3.0 Hz), 115.4 (d, *J* = 21.1 Hz), 112.9 (d, *J* = 19.6 Hz), 84.0, 36.8, 35.9, 24.4, 24.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.64.
HRMS: m/z (ESI) calculated for $C_{15}H_{22}BFIO_2$ $[M+H]^+$: 391.0742, found: 391.0739.



S17

Compound **S17** was synthesized according to General procedure **M**, and it was purified with silica gel chromatography (PE/EA = 30:1) (55% yield, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.04 (t, *J* = 13.2 Hz, 1H), 1.95-1.93 (m, 3H), 1.84 (dd, *J* = 13.2, 3.6 Hz, 1H), 1.69-1.66 (m, 3H), 1.63-1.59 (m, 3H), 1.57-1.54 (m, 3H), 1.43-1.40 (m, 3H), 1.27 (d, *J* = 1.8 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 83.8, 50.7, 42.0, 36.9, 35.7, 28.5, 24.22, 24.19.
HRMS: m/z (ESI) calculated for $C_{18}H_{30}BINaO_2$ $[M+Na]^+$: 439.1281, found: 439.1279.



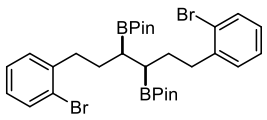
S18

Compound **S18** was synthesized according to General procedure **L**, and it was purified with silica gel chromatography (PE/EA = 25:1) (44% yield, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 2H), 7.14-7.09 (m, 3H), 3.54 (s, 4H), 3.06 (dd, *J* = 8.8, 7.2 Hz, 1H), 2.75-2.68 (m, 1H), 2.58-2.50 (m, 1H), 2.13-2.03 (m, 1H), 2.01-1.91 (m, 1H), 0.93 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 128.6, 128.3, 125.9, 72.3, 37.2, 36.3, 32.0, 22.0.
MS: (EI) $[M]^+$ $C_{14}H_{20}BIO_2$: 358.05.

7. Characterization of products

7.1 Products of homo-coupling reactions

Compound **2a** was synthesized according to General procedure **C**, and all analytical data matched the report.[S10]



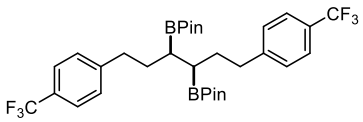
2b

Compound **2b** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 20:1). (52% yield, *dr* >20:1, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 4H), 7.00 (m, 2H), 2.82-2.72 (m, 2H), 2.70-2.60 (m, 2H), 1.87-1.77 (m, 2H), 1.75-1.65 (m, 2H), 1.33-1.26 (m, 26H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 132.6, 130.4, 127.2, 127.1, 124.4, 83.0, 36.2, 30.3, 25.2, 24.7.

HRMS: m/z (ESI) calculated for $C_{30}H_{42}B_2Br_2NaO_4$ $[M+Na]^+$: 669.1534, found: 669.1530.



2c

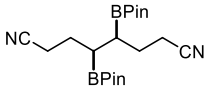
Compound **2c** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 20:1). (59% yield, *dr* >20:1, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 4H), 2.64-2.49 (m, 4H), 1.81-1.71 (m, 2H), 1.62-1.52 (m, 2H), 1.22-1.10 (m, 26H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 128.8, 127.9 (q, *J* = 32.3 Hz), 125.1 (q, *J* = 4.0 Hz), 124.5 (q, *J* = 272.7 Hz), 83.1, 35.6, 32.0, 25.1, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2.

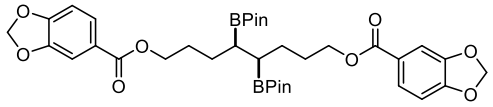
HRMS: m/z (ESI) calculated for $C_{32}H_{43}B_2F_6O_4$ $[M+H]^+$: 627.3252, found: 627.3257.



2d

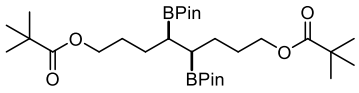
Compound **2d** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 10:1). (62% yield, *dr* >20:1, colorless

oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52-2.34 (m, 4H), 1.97-1.85 (m, 2H), 1.73-1.63 (m, 2H), 1.26-1.16 (m, 26H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 120.0, 83.5, 26.5, 24.9, 24.7, 16.8.
HRMS: m/z (ESI) calculated for $C_{20}H_{35}B_2N_2O_4$ $[M+H]^+$: 389.2783, found: 389.2784.



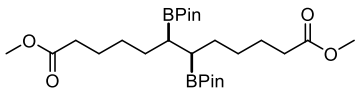
2e

Compound **2e** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 5:1). (62% yield, *dr* 10:1, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.47 (d, *J* = 1.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.02 (s, 4H), 4.25 (t, *J* = 6.4 Hz, 4H), 1.84-1.62 (m, 6H), 1.56-1.46 (m, 2H), 1.31-1.16 (m, 26H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 151.3, 147.6, 125.2, 124.7, 109.5, 107.8, 101.6, 82.9, 65.3, 28.5, 26.5, 25.1, 24.5.
HRMS: m/z (ESI) calculated for $C_{36}H_{49}B_2O_{12}$ $[M+H]^+$: 695.3410, found: 695.3416.



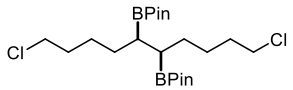
2f

Compound **2f** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 8:1). (57% yield, *dr* 7:1, white solid).
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00-3.90 (m, 4H), 1.63-1.45 (m, 7H), 1.36-1.27 (m, 3H), 1.16 (d, J = 2.8 Hz, 24H), 1.12 (s, 18H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 82.9, 64.8, 38.7, 28.5, 27.2, 26.5, 25.1, 24.6.
MS: (EI) $[M]^+$ $C_{30}H_{56}B_2O_8$: 556.40.



2g

Compound **2g** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 8:1). (47% yield, *dr* 6:1, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 6H), 2.22 (t, *J* = 8.0 Hz, 4H), 1.58-1.50 (m, 5H), 1.47-1.36 (m, 2H), 1.29-1.15 (m, 29H), 1.04-0.99 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 82.8, 51.3, 34.1, 29.6, 29.0, 25.3, 25.1, 24.6.
HRMS: m/z (ESI) calculated for $C_{26}H_{49}B_2O_8$ $[M+H]^+$: 511.3614, found: 511.3617.



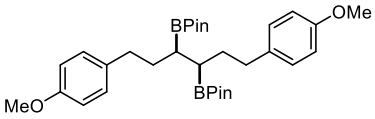
2h

Compound **2h** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 20:1). (50% yield, *dr* 17:1, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (t, *J* = 6.8 Hz, 4H), 1.75-1.63 (m, 4H), 1.47-1.25 (m, 6H), 1.20-1.13 (m, 26H), 1.07-1.00 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.9, 45.2, 32.9, 29.2, 26.7, 25.1, 24.6.

HRMS: m/z (ESI) calculated for $C_{22}H_{43}B_2Cl_2O_4$ $[M+H]^+$: 463.2725, found: 463.2728.



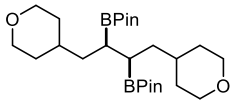
2i

Compound **2i** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 12:1). (49% yield, *dr* 9:1, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.0 Hz, 4H), 6.80 (d, *J* = 8.0 Hz, 4H), 3.77 (s, 6H), 2.61-2.53 (m, 2H), 2.50-2.40 (m, 2H), 1.84-1.71 (m, 2H), 1.68-1.55 (m, 2H), 1.29-1.18 (m, 26H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 135.5 (major), 135.4 (minor), 129.3 (major), 129.2 (minor), 113.6, 82.9 (minor), 82.8 (major), 55.2, 35.0 (minor), 34.8 (major), 32.7 (minor), 32.4 (major), 25.1 (major), 25.0 (minor), 24.9 (minor), 24.7 (major).

HRMS: m/z (ESI) calculated for $C_{32}H_{49}B_2O_6$ $[M+H]^+$: 551.3715, found: 551.3720.



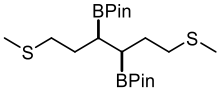
2j

Compound **2j** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 10:1). (55% yield, *dr* 12:1, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88-3.83 (m, 4H), 3.30-3.21 (m, 4H), 1.59-1.54 (m, 2H), 1.50-1.35 (m, 6H), 1.24-1.06 (m, 32H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 82.8, 68.21, 68.20, 37.0, 34.6, 33.8, 32.9, 25.0, 24.6.

HRMS: m/z (ESI) calculated for $C_{26}H_{49}B_2O_6$ $[M+H]^+$: 479.3715, found: 479.3718.



2k

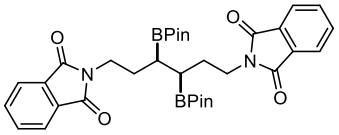
Compound **2k** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 12:1). (55% yield, *dr* 7:1, colorless

oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63-2.40 (m, 4H), 2.09 (s, 6H), 1.88-1.75 (m, 2H), 1.69-1.58 (m, 2H), 1.29-1.19 (m, 26H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 83.02 (minor), 82.98 (major), 34.0 (minor), 33.9 (major), 29.7, 25.1 (major), 25.0 (minor), 24.8 (minor), 24.6 (major), 15.4 (minor), 15.3 (major).

HRMS: m/z (ESI) calculated for $C_{20}H_{41}B_2O_4S_2$ $[M+H]^+$: 431.2632, found: 431.2634.



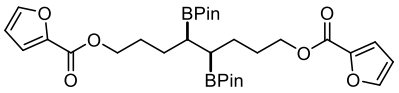
2l

Compound **2l** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 5:1). (64% yield, *dr* 10:1, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 5.4, 3.0 Hz, 4H), 7.60 (dd, *J* = 5.4, 3.0 Hz, 4H), 3.70-3.59 (m, 4H), 1.81-1.75 (m, 2H), 1.64-1.56 (m, 2H), 1.20-1.10 (m, 26H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 133.5, 132.4, 122.9, 83.2, 38.0, 29.0, 24.9, 24.6.

HRMS: m/z (ESI) calculated for $C_{34}H_{43}B_2N_2O_8$ $[M+H]^+$: 629.3206, found: 629.3211.



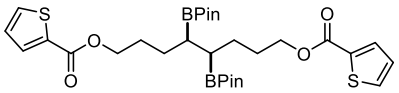
2m

Compound **2m** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 10:1). (53% yield, *dr* 17:1, white solid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.16 (d, *J* = 3.6 Hz, 2H), 6.49 (dd, *J* = 3.6, 2.0 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 4H), 1.84-1.58 (m, 6H), 1.51-1.42 (m, 2H), 1.29-1.16 (m, 26H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 146.0, 145.0, 117.5, 111.6, 82.9, 65.3, 28.4, 26.2, 25.0, 24.5.

MS: (EI) $[M]^+$ $C_{30}H_{44}B_2O_{10}$: 586.40.



2n

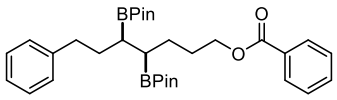
Compound **2n** was synthesized according to General procedure **C**, and it was purified with silica gel chromatography (PE/EA = 10:1). (59% yield, *dr* 8:1, white solid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 3.6, 1.2Hz, 2H), 7.52 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.08 (dd, *J* = 4.8, 3.6 Hz, 2H), 4.27 (t, *J* = 6.0 Hz, 4H), 1.83-1.75 (m, 2H), 1.74-1.61 (m, 4H), 1.52-1.46 (m, 2H), 1.29-1.17 (m, 26H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 134.2, 133.1, 132.0, 127.5, 82.9, 65.6, 28.7

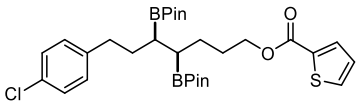
(minor), 28.4 (major), 26.5 (minor), 26.3 (major), 25.0 (major), 24.9 (minor), 24.7 (minor), 24.5 (major).
HRMS: m/z (ESI) calculated for $C_{30}H_{45}B_2O_8S_2$ $[M+H]^+$: 619.2742, found: 619.2746.

7.2 Products of cross-coupling reactions



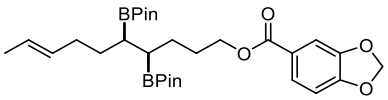
2o

Compound **2o** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 10:1). (58% yield, *dr* 10:1, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.20-7.15 (m, 2H), 7.11-7.05 (m, 3H), 4.21 (t, *J* = 6.0 Hz, 2H), 2.61-2.54 (m, 1H), 2.51-2.44 (m, 1H), 1.81-1.69 (m, 2H), 1.68-1.58 (m, 3H), 1.51-1.40 (m, 1H), 1.20-1.15 (m, 26H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.3, 132.6, 130.7, 129.6, 128.4, 128.2, 128.1, 125.4, 82.9, 65.5, 35.7, 32.2, 28.6, 26.5, 25.1, 24.64, 24.60.
HRMS: m/z (ESI) calculated for $C_{32}H_{47}B_2O_6$ $[M+H]^+$: 549.3559, found: 549,3564.



2p

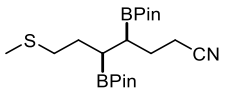
Compound **2p** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 10:1). (43% yield, *dr* 9:1, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.45 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.03-7.00 (m, 3H), 4.19 (t, *J* = 6.6 Hz, 2H), 2.56-2.51 (m, 1H), 2.47-2.42 (m, 1H), 1.75-1.66 (m, 2H), 1.65-1.53 (m, 3H), 1.45-1.35 (m, 1H), 1.21-1.10 (m, 26H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 141.7, 134.2, 133.1, 132.0, 131.1, 129.8, 128.2, 127.6, 83.0, 82.9, 65.6, 35.0, 32.0, 28.5, 26.3, 25.11, 25.08, 24.63, 24.59.
HRMS: m/z (ESI) calculated for $C_{30}H_{43}B_2ClNaO_6S$ $[M+Na]^+$: 611.2553, found: 611.2558.



2q

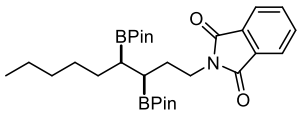
Compound **2q** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 8:1). (73% yield, *dr* 10:1, colorless oil).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.41 (d, *J* = 1.8 Hz, 1H), 6.75 (dd, *J* = 8.4, 3.0 Hz, 1H), 5.96 (s, 2H), 5.39-5.28 (m, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.98-1.91 (m, 1H), 1.87-1.78 (m, 2H), 1.74-1.66 (m, 2H), 1.48-1.38 (m, 2H), 1.35-1.29 (m, 2H), 1.33-1.21 (m, 26H), 1.10-1.07 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 151.3, 147.6, 131.8, 125.2, 124.7, 124.4, 109.5, 107.8, 101.7, 82.9, 82.8, 65.4, 32.4, 30.0, 28.6, 26.4, 25.10, 25.07, 24.6, 17.9.



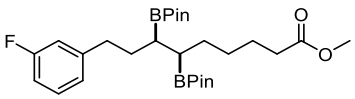
2r

Compound **2r** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 7:1). (60% yield, *dr* 7:1, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53-2.36 (m, 3H), 2.32-2.25 (m, 1H), 2.02 (s, 3H), 1.84-1.72 (m, 2H), 1.67-1.61 (m, 1H), 1.58-1.52 (m, 1H), 1.20-1.12 (m, 26H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 120.32 (minor), 120.26 (major), 83.4 (minor), 83.3 (major), 83.21 (minor), 83.19 (major), 33.91 (minor), 33.86 (major), 29.6 (major), 29.3 (minor), 26.3 (major), 25.5 (minor), 25.02 (minor), 24.98 (major), 24.8 (minor), 24.73 (minor), 24.70 (major), 24.6 (major), 16.9 (minor), 16.8 (major), 15.4 (minor), 15.3 (major).
MS: (EI) $[M]^+$ $C_{20}H_{37}B_2NO_4S$: 409.20.



2s

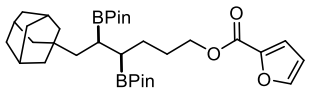
Compound **2s** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 7:1). (46% yield, *dr* 13:1, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.60 (dd, *J* = 5.6, 3.2 Hz, 2H), 3.71-3.59 (m, 2H), 1.80-1.71 (m, 1H), 1.70-1.63 (m, 1H), 1.47-1.38 (m, 1H), 1.26-1.05 (m, 33H), 0.78 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 133.6, 132.4, 123.0, 83.1, 82.8, 38.0, 32.1, 29.7, 29.2, 28.8, 25.1, 25.0, 24.6, 22.6, 14.0.
HRMS: m/z (ESI) calculated for $C_{29}H_{46}B_2NO_6$ $[M+H]^+$: 526.3511, found: 526.3515.



2t

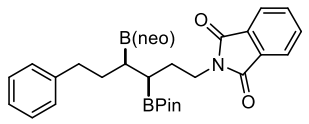
Compound **2t** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 10:1). (56% yield, *dr* 6:1, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.83-6.74 (m, 2H), 3.57 (s, 3H), 2.59-2.43 (m, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.76-1.67 (m, 1H), 1.64-1.42 (m, 5H), 1.28-1.06 (m, 28H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 162.9 (d, *J* = 246.4 Hz), 146.0 (d, *J* = 8.1 Hz), 129.4 (d, *J* = 8.1 Hz), 124.1 (d, *J* = 3.0 Hz), 115.2 (d, *J* = 20.2 Hz), 112.2 (d, *J* = 21.2 Hz), 82.9, 82.8, 51.3, 35.5 (d, *J* = 2.0 Hz), 34.1, 31.9, 29.6, 29.0, 25.2, 25.1, 25.0, 24.63, 24.60.
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4.
HRMS: m/z (ESI) calculated for $C_{28}H_{46}B_2FO_6$ $[M+H]^+$: 519.3465, found: 519.3468.



2u

Compound **2u** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 10:1). (62% yield, *dr* 10:1, colorless oil).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.8 Hz, 1H), 7.09 (d, *J* = 3.6 Hz, 1H), 6.42 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.21-4.19 (m, 2H), 1.83-1.82 (m, 3H), 1.74-1.67 (m, 1H), 1.65-1.49 (m, 9H), 1.46-1.39 (m, 5H), 1.31-1.28 (m, 3H), 1.23-1.12 (m, 26H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 146.0, 145.0, 117.5, 111.6, 82.9, 82.8, 65.5, 44.7, 42.5, 37.2, 32.8, 29.0, 28.7, 26.0, 25.2, 24.9, 24.7, 24.6.
MS: (EI) $[M]^+$ $C_{33}H_{52}B_2O_7$: 582.35.



2v

Compound **2v** was synthesized according to General procedure **D**, and it was purified with silica gel chromatography (PE/EA = 5:1). (47% yield, *dr* 2:1, colorless oil).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.73 (m, 2H), 7.64-7.60 (m, 2H), 7.28-7.04 (m, 5H), 3.80-3.58 (m, 2H), 3.54-3.43 (m, 4H), 2.74-2.43 (m, 2H), 1.79-1.56 (m, 4H), 1.21-1.14 (m, 14H), 0.92-0.86 (m, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 168.41, 168.35, 143.4, 140.9, 133.9, 133.7, 132.2, 132.0, 128.6, 128.5, 128.3, 128.0, 125.9, 125.3, 123.2, 123.0, 84.1, 82.9, 72.2, 71.6, 39.8, 39.1, 37.9, 37.1, 36.3, 35.8, 33.9, 33.7, 31.9, 31.4, 25.0, 24.7, 24.3, 24.2, 24.0, 23.1, 22.0, 21.9.
MS: (EI) $[M]^+$ $C_{31}H_{41}B_2NO_7$: 545.30.

8. Supplementary References

S1. T. Mukaiyama, N. Yoshimura, K. Igarashi and A. Kagayama, *Tetrahedron*, 2001, **57**, 2499-2506.

S2. J. Schmidt, J. Choi, A. T. Liu, M. Slusarczyk and G. C. Fu, *Science*, 2016, **354**, 1265-1269.

S3. J. C. Tellis, D. N. Primer and G. A. Molander, *Science*, 2014, **345**, 433-436.

S4. D. Wang and T. XU, *ACS Catal*. 2020, **11**, 12469-12475.

S5. X. Liu, Q. Zhu, D. Chen, L. Wang, L. Jin and C. Liu, *Angew. Chem., Int. Ed.*, 2020, **59**, 2745-2749.

S6. D. Wang, J. Zhou, Z. Hu and T. XU, *J. Am. Chem. Soc*., 2022, **144**, 22870-22876.

S7. B. J. Eckstein, F. S. Melkonyan, E. F. Manley, S. Fabiano, A. R. Mouat, L. X. Chen, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc*., 2017, **139**, 14356-14359.

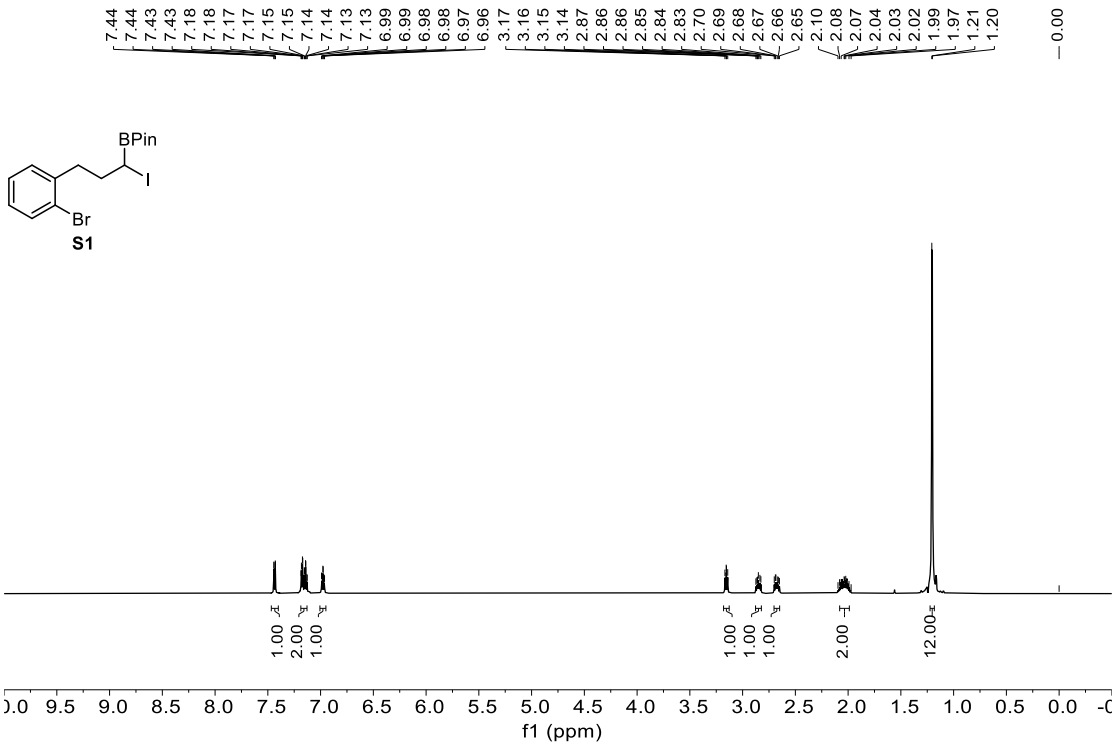
S8. D. Chen, X. Liu, Y. Yu, Q. Mo, X. Qi, C. Liu, C. *Angew. Chem., Int. Ed*. 2023, **62**, e202215168.

S9. S. Nagasawa, Y. Sasano and Y. Iwabuchi, *Angew. Chem., Int. Ed.*, 2016, **55**, 13189-13194.

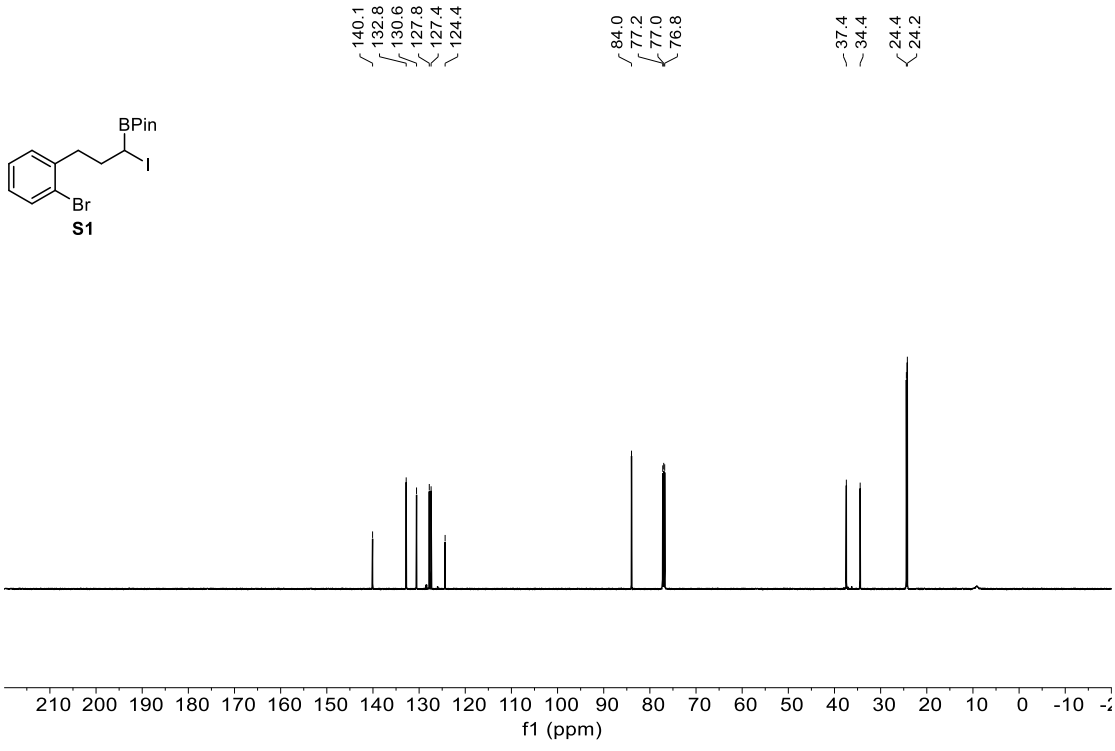
S10. Z. Bao, M. Huang, Y. Xu, X. Zhang, Y.-D. Wu, J. Wang, *Angew. Chem. Int. Ed*. 2023, **62**, e202216356.

9. NMR Spectra Data of New Compounds

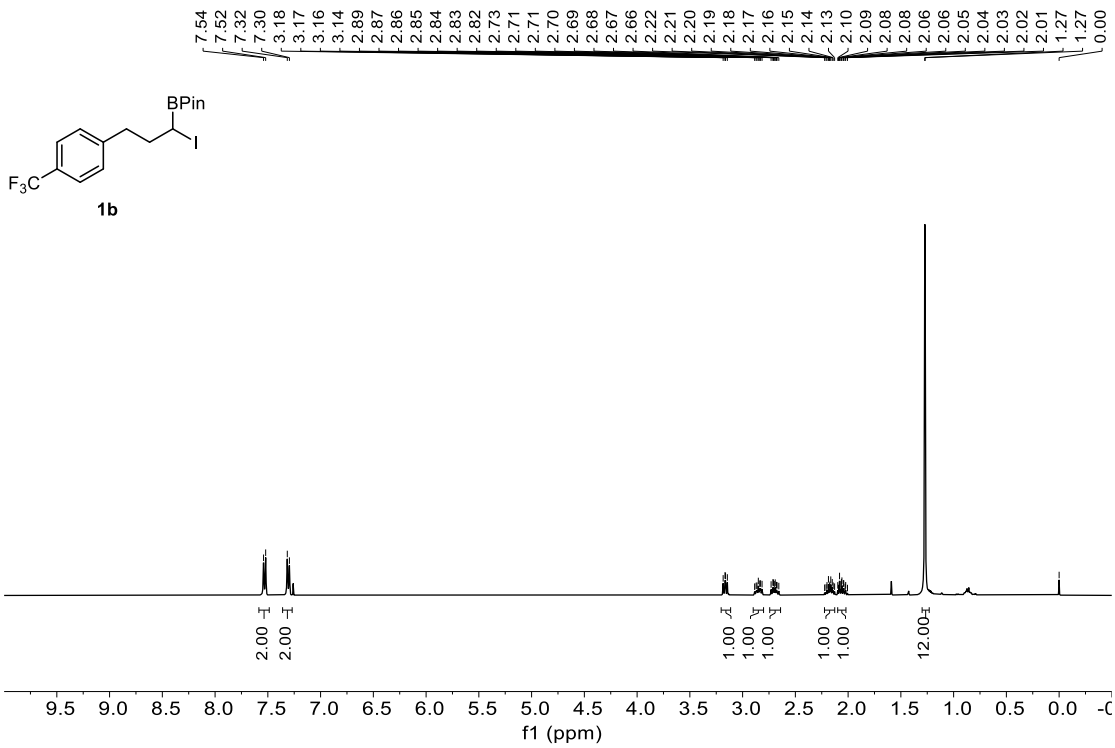
Compound **S1** ^{1}H NMR (600 MHz, $CDCl_3$)



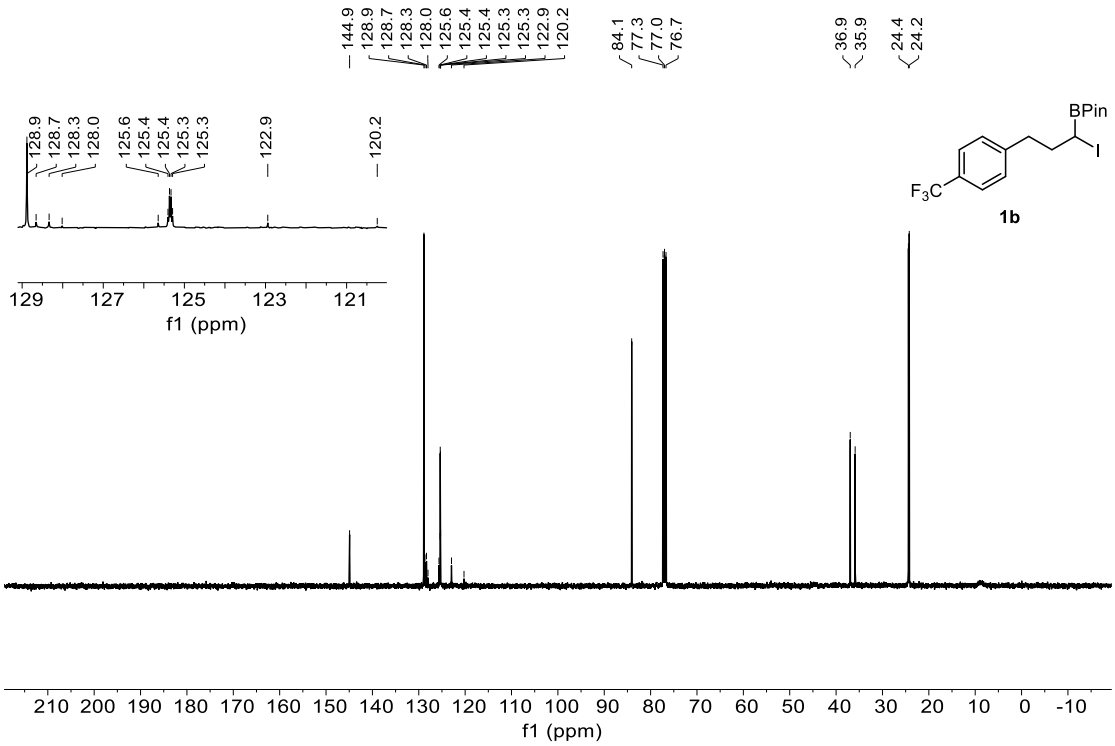
Compound **S1** ^{13}C NMR (151 MHz, $CDCl_3$)



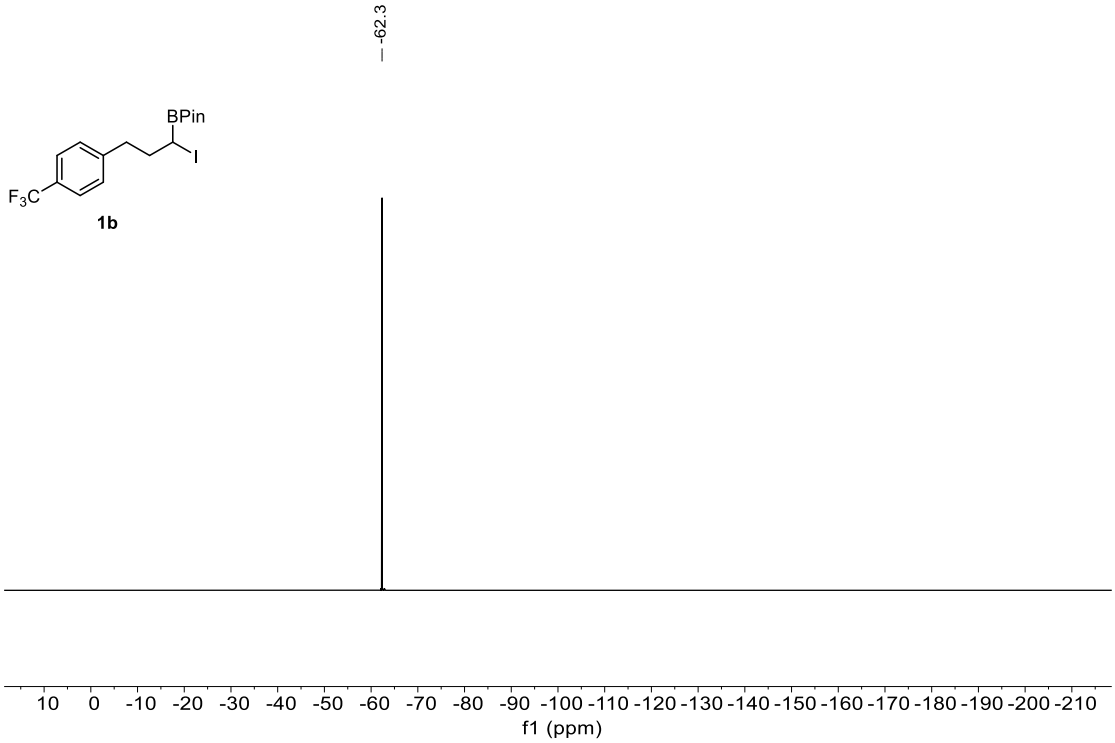
Compound **1b** ^{1}H NMR (400 MHz, $CDCl_3$)



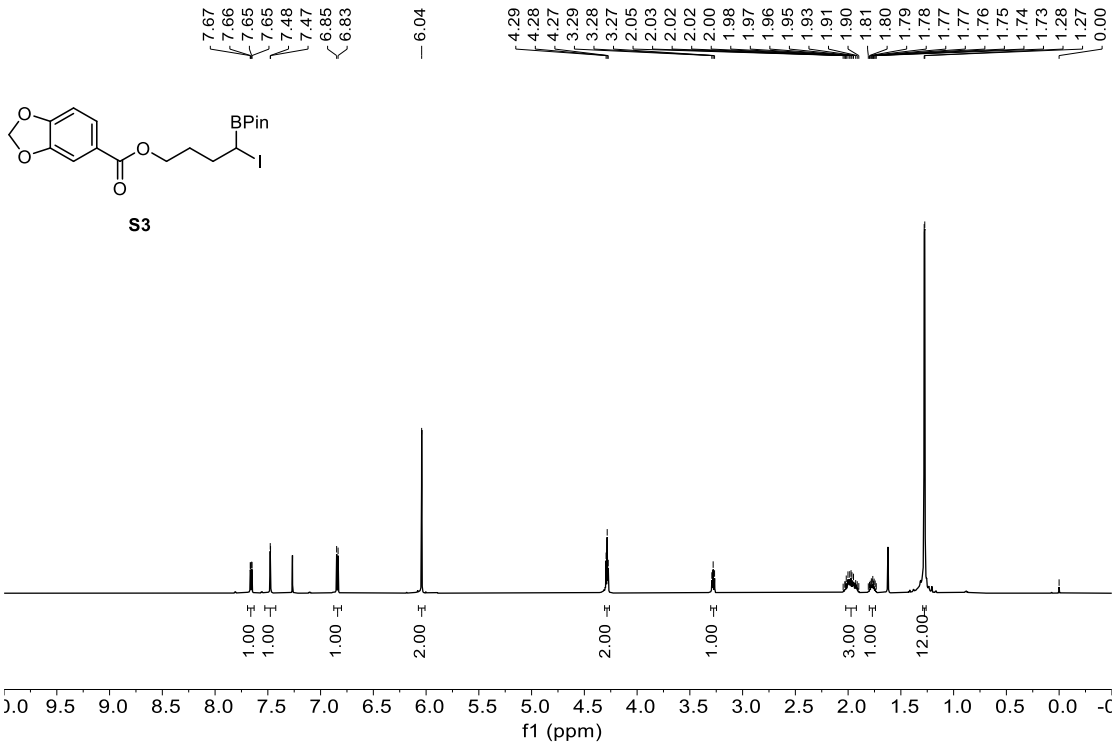
Compound **1b** ^{13}C NMR (101 MHz, $CDCl_3$)



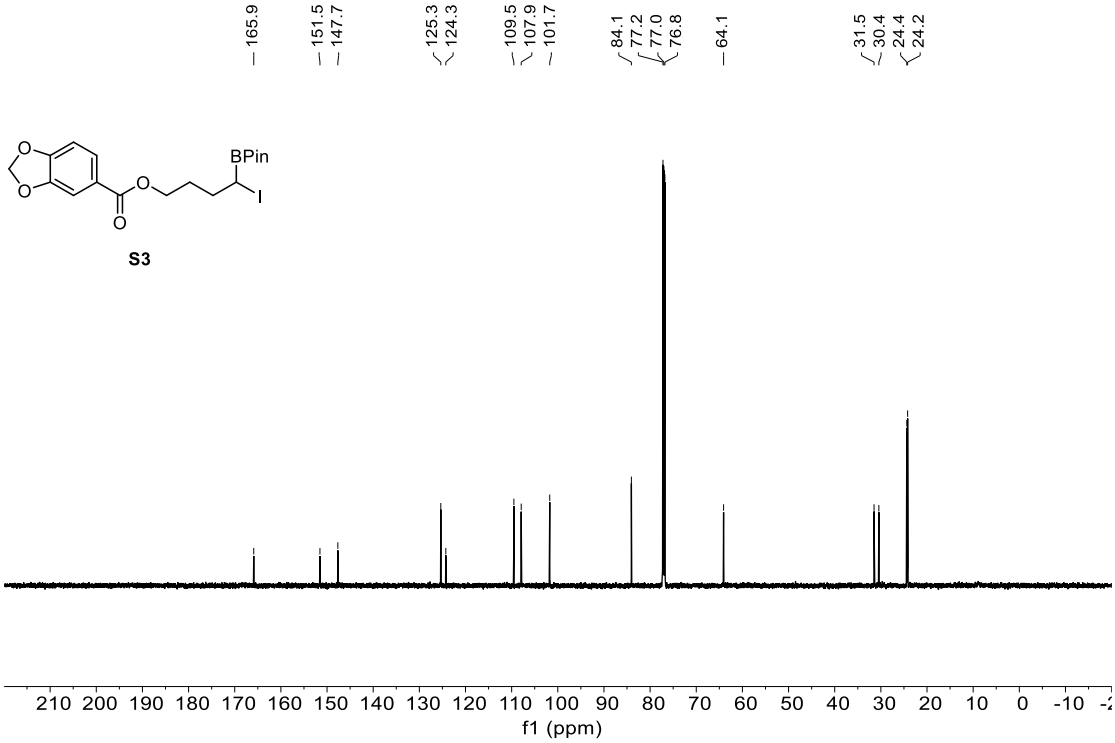
Compound **1b** ^{19}F NMR (376 MHz, $CDCl_3$)



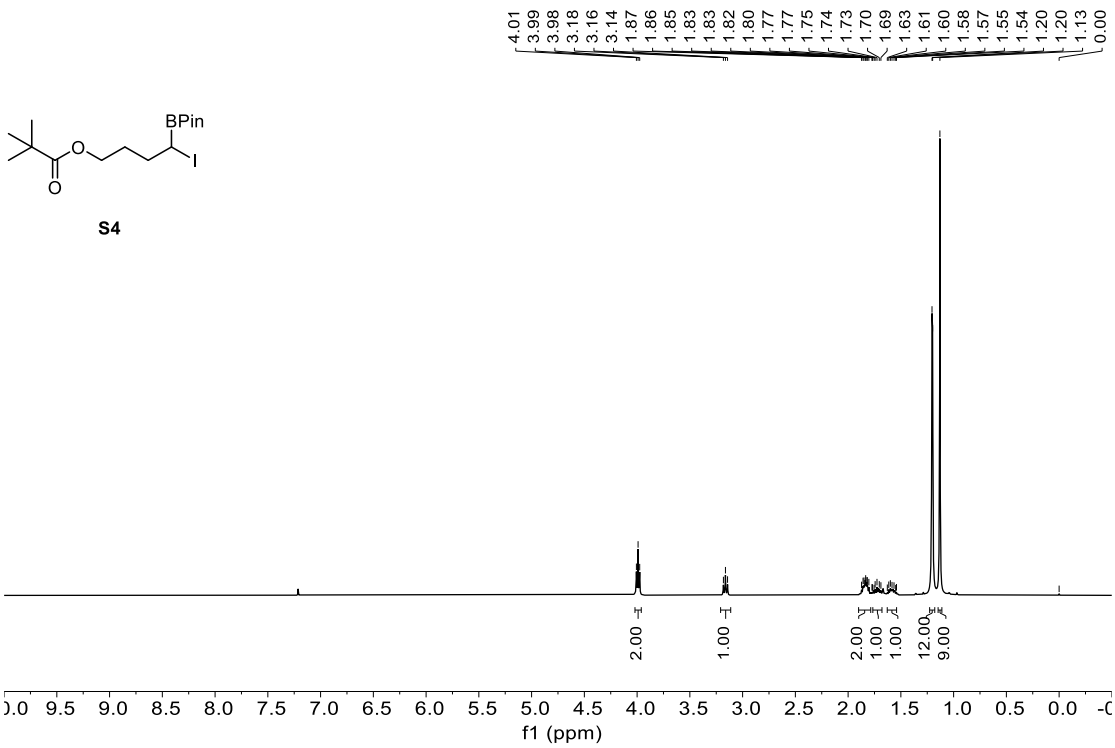
Compound **S3** ^{1}H NMR (600 MHz, $CDCl_3$)



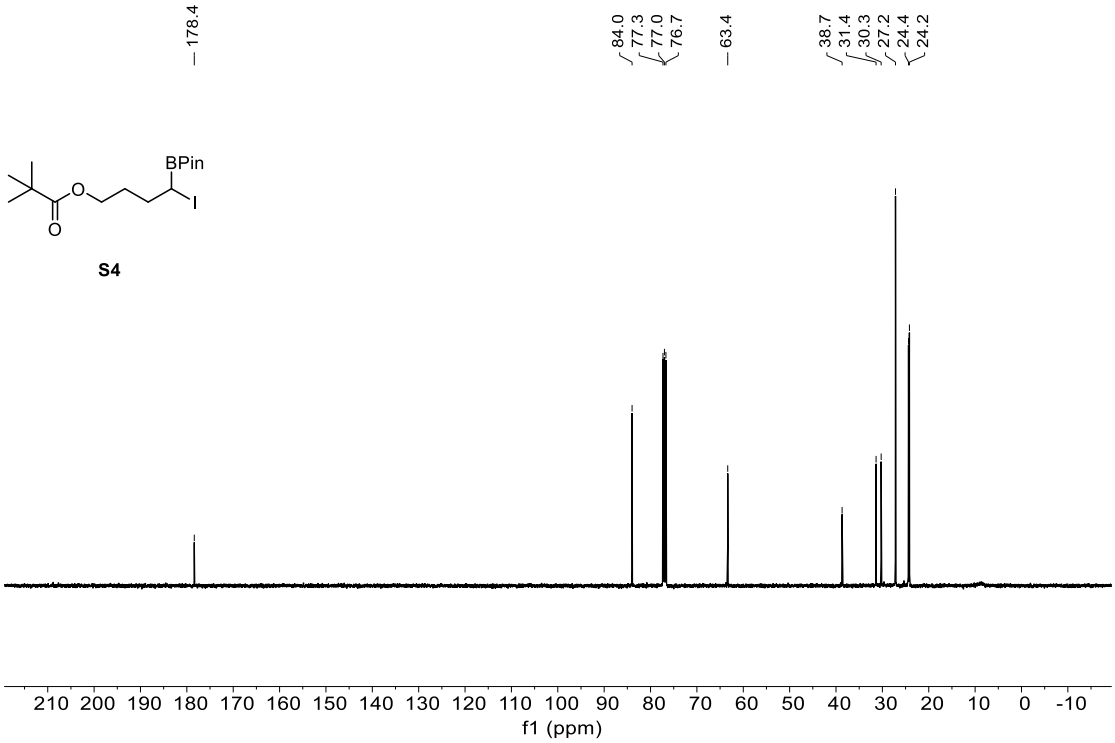
Compound **S3** ^{13}C NMR (151 MHz, $CDCl_3$)



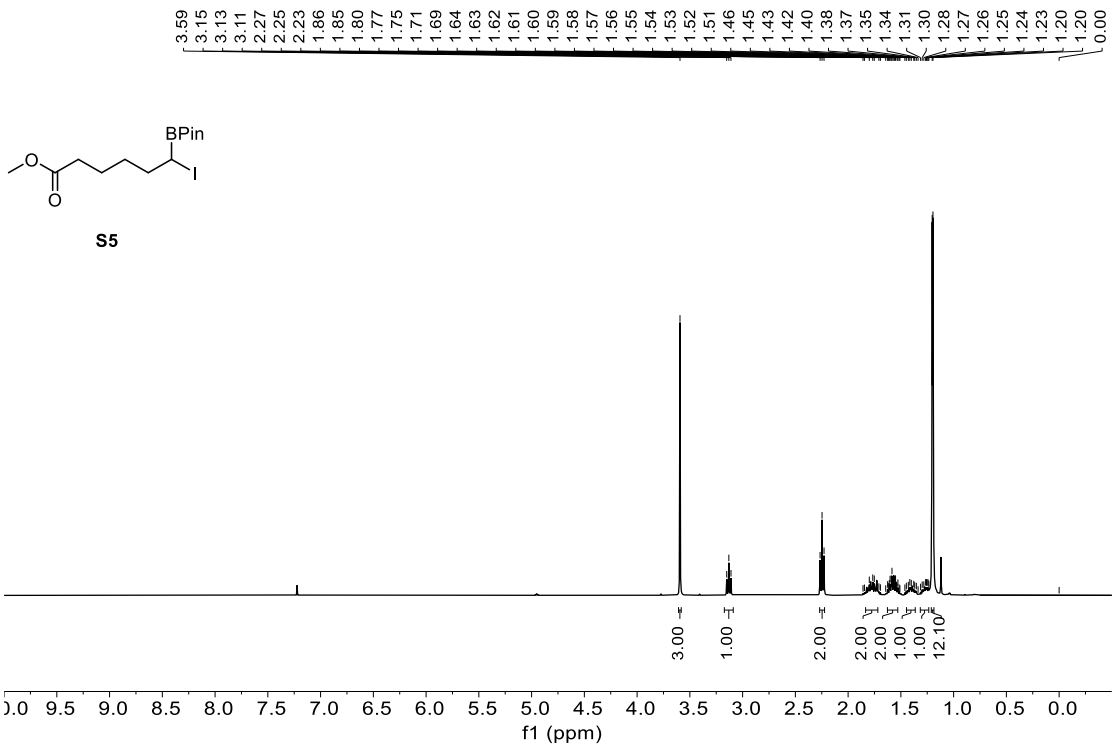
Compound **S4** ^{1}H NMR (400 MHz, $CDCl_3$)



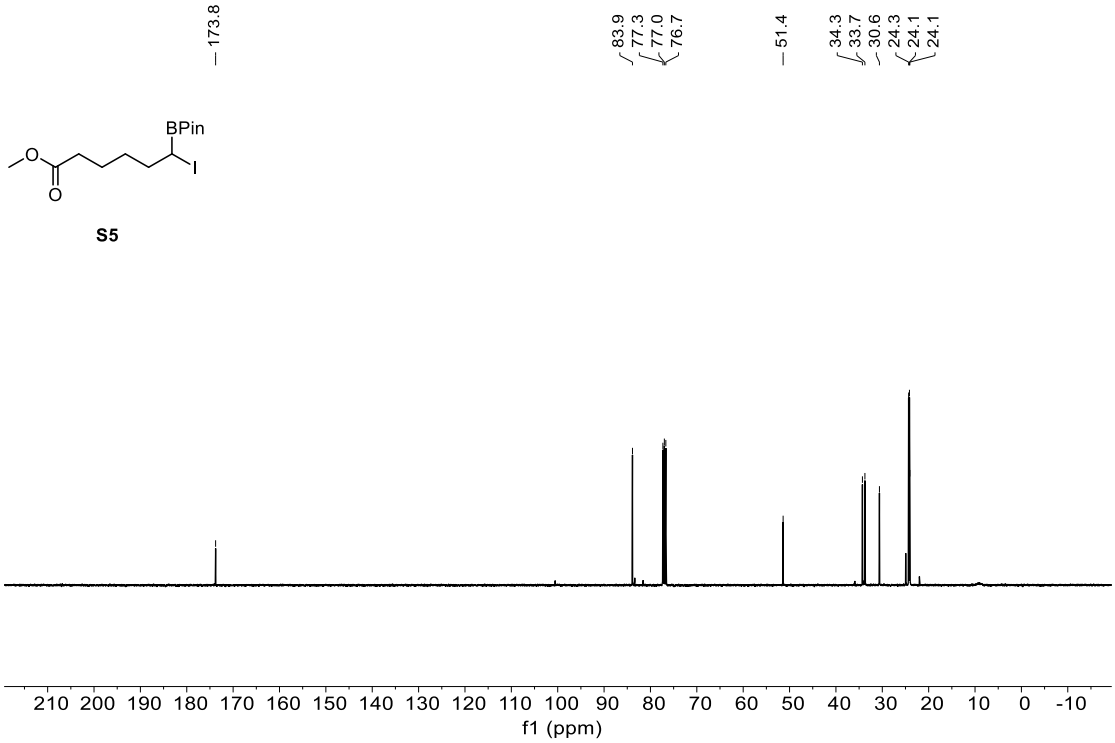
Compound **S4** ^{13}C NMR (101 MHz, $CDCl_3$)



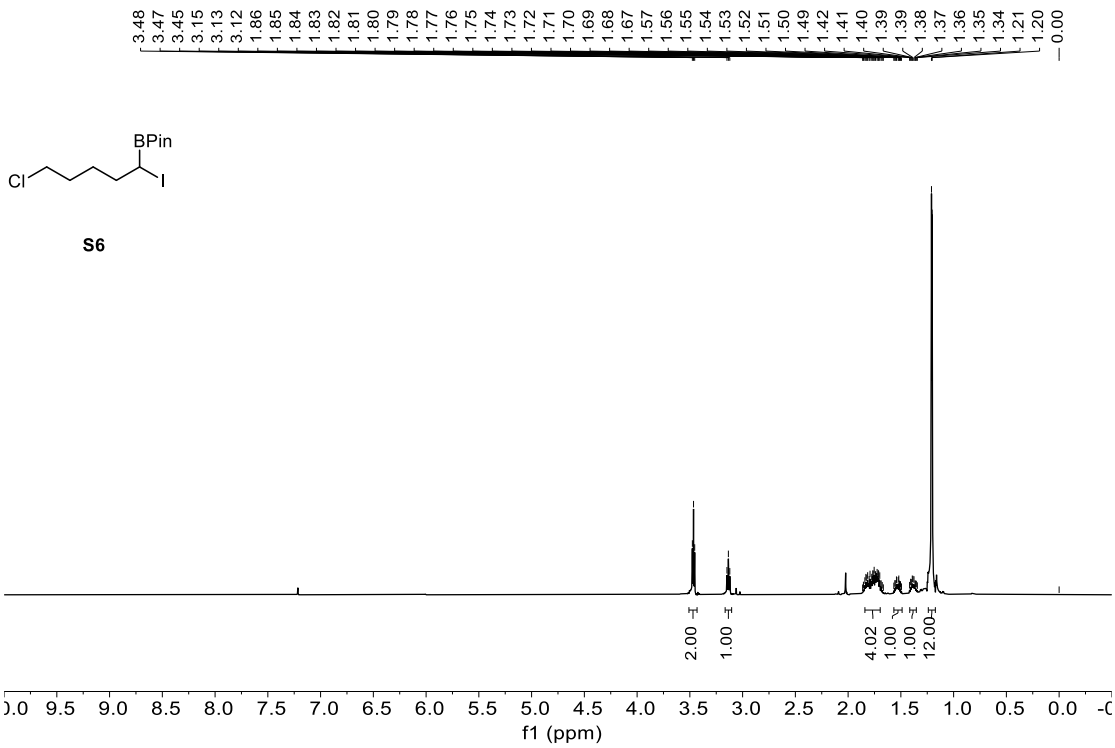
Compound **S5** ^{1}H NMR (400 MHz, $CDCl_3$)



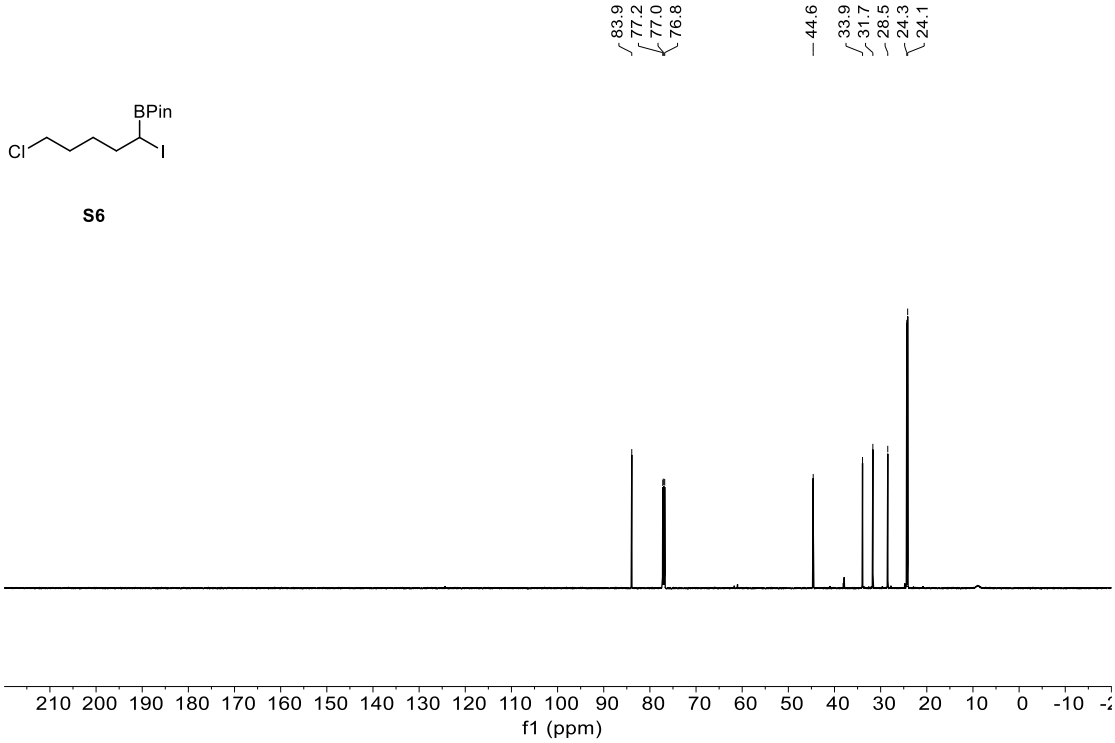
Compound **S5** ^{13}C NMR (101 MHz, $CDCl_3$)



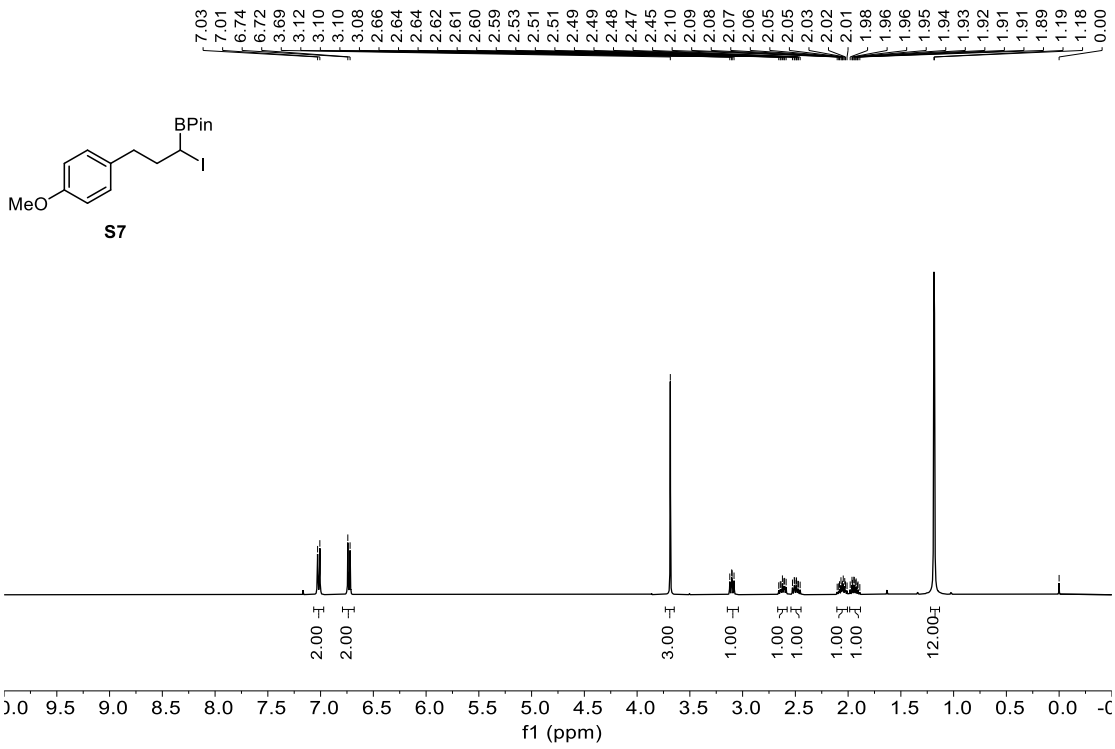
Compound **S6** ^{1}H NMR (600 MHz, $CDCl_3$)



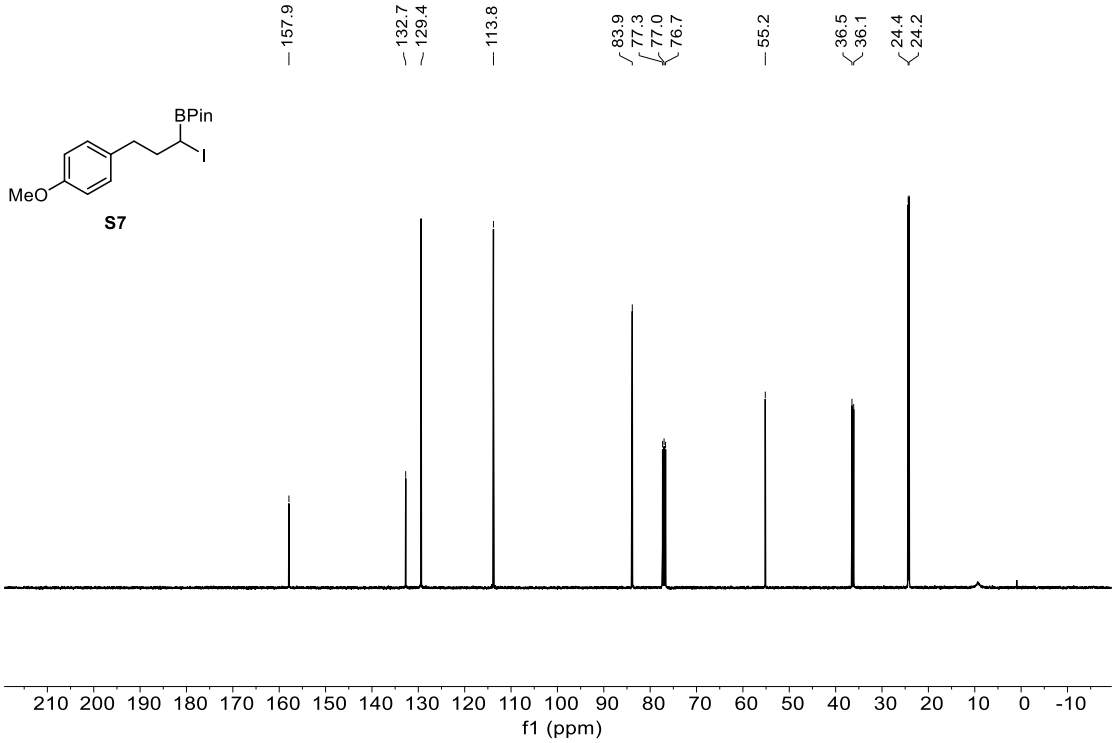
Compound **S6** ^{13}C NMR (151 MHz, $CDCl_3$)



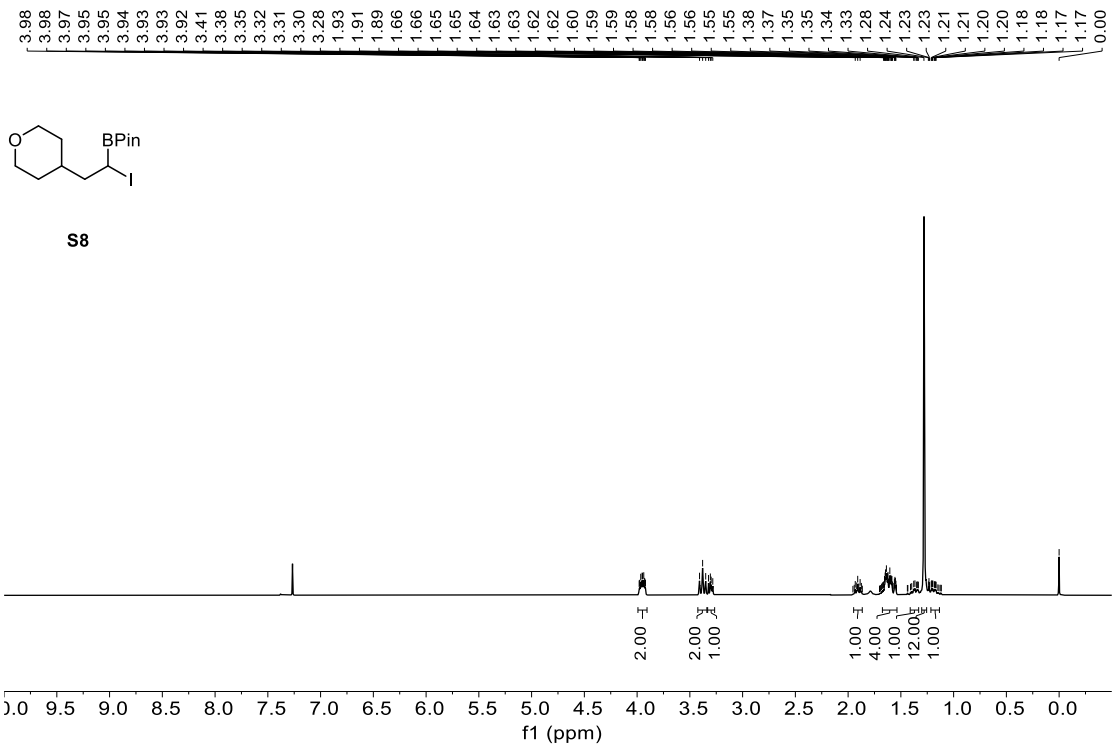
Compound **S7** ^{1}H NMR (400 MHz, $CDCl_3$)



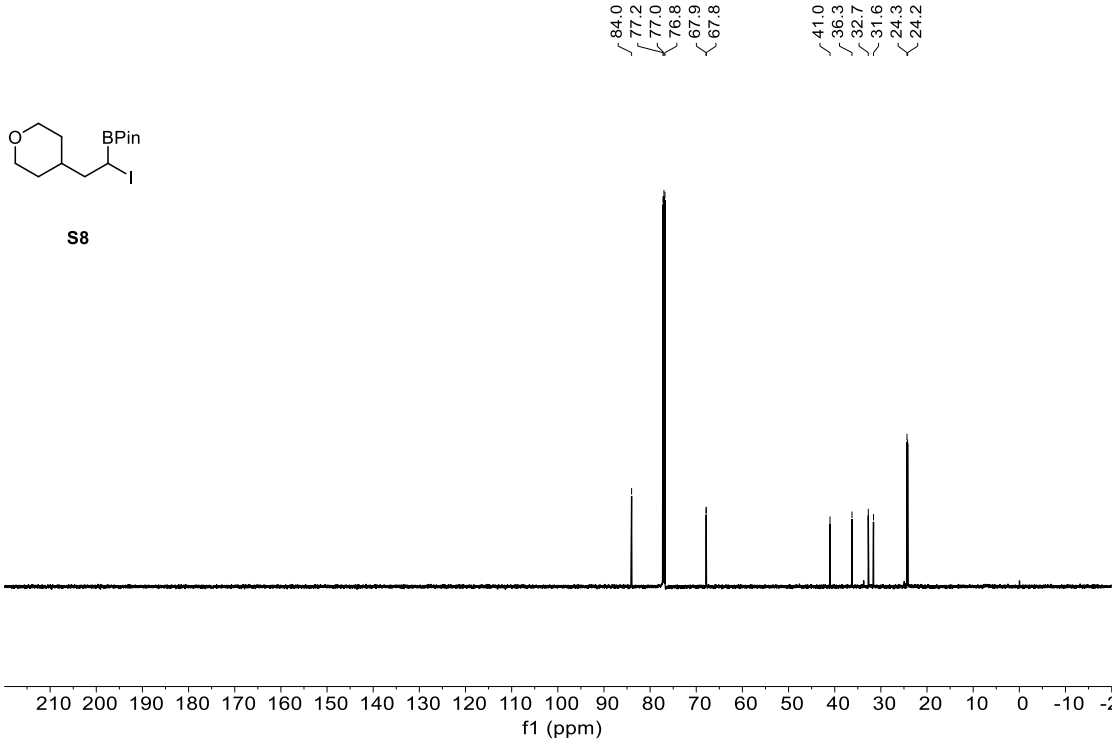
Compound **S7** ^{13}C NMR (101 MHz, $CDCl_3$)



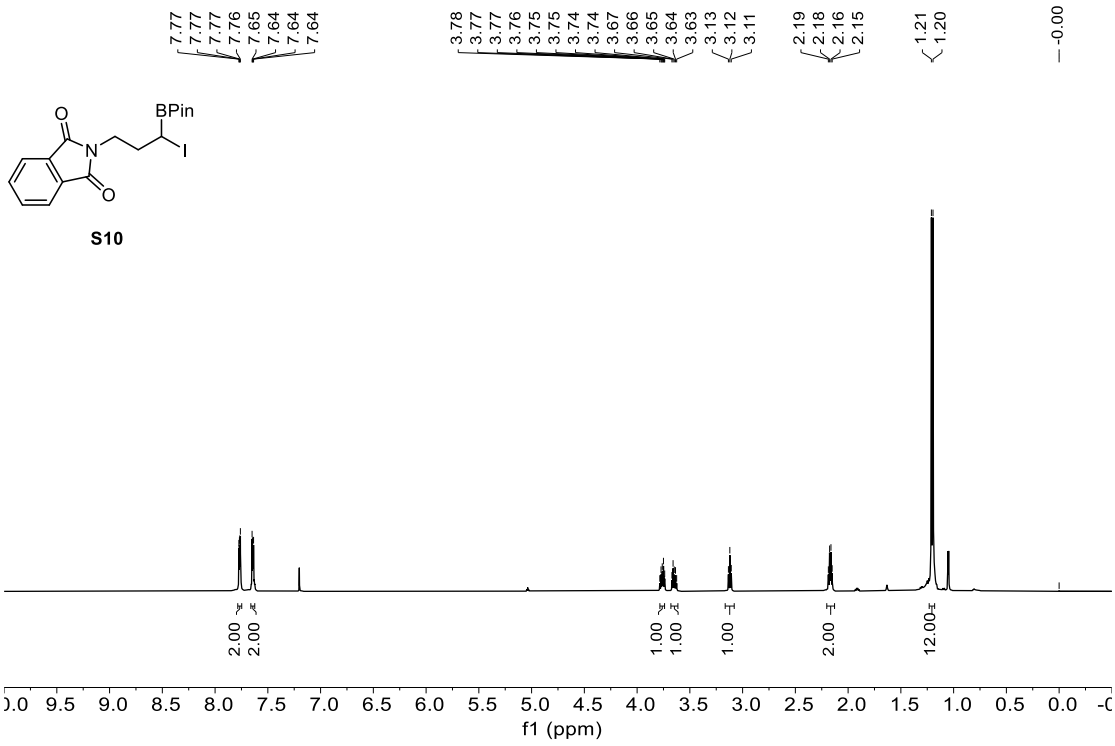
Compound **S8** ^{1}H NMR (400 MHz, $CDCl_3$)



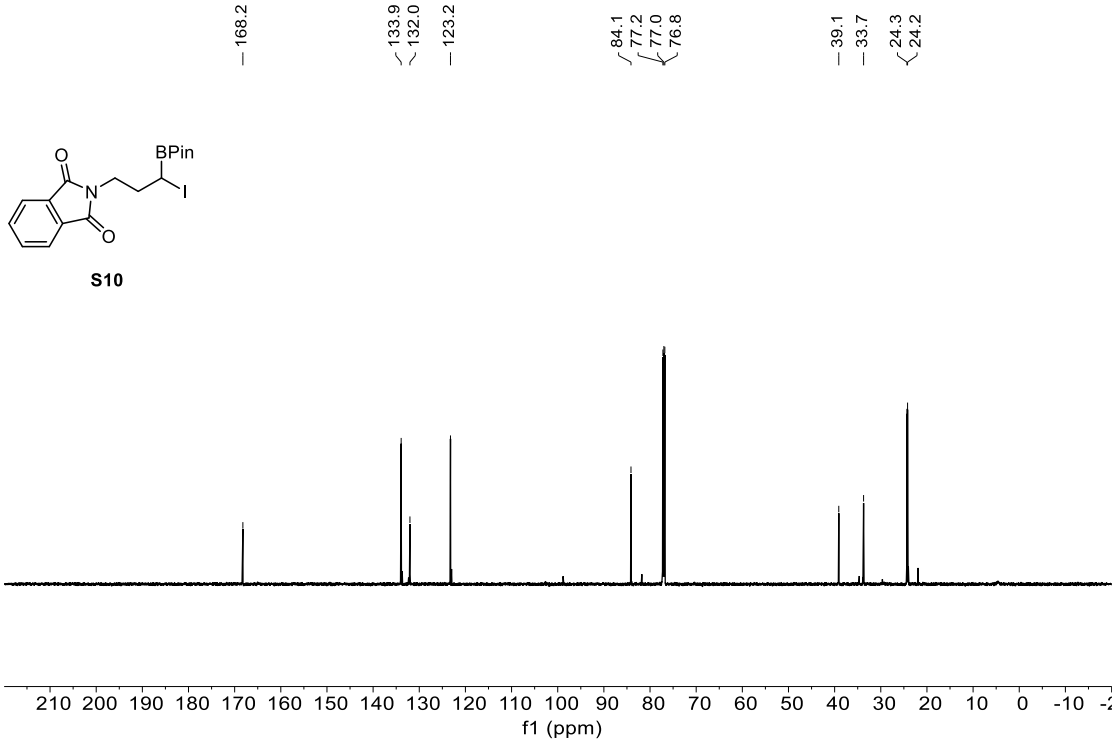
Compound **S8** ^{13}C NMR (151 MHz, $CDCl_3$)



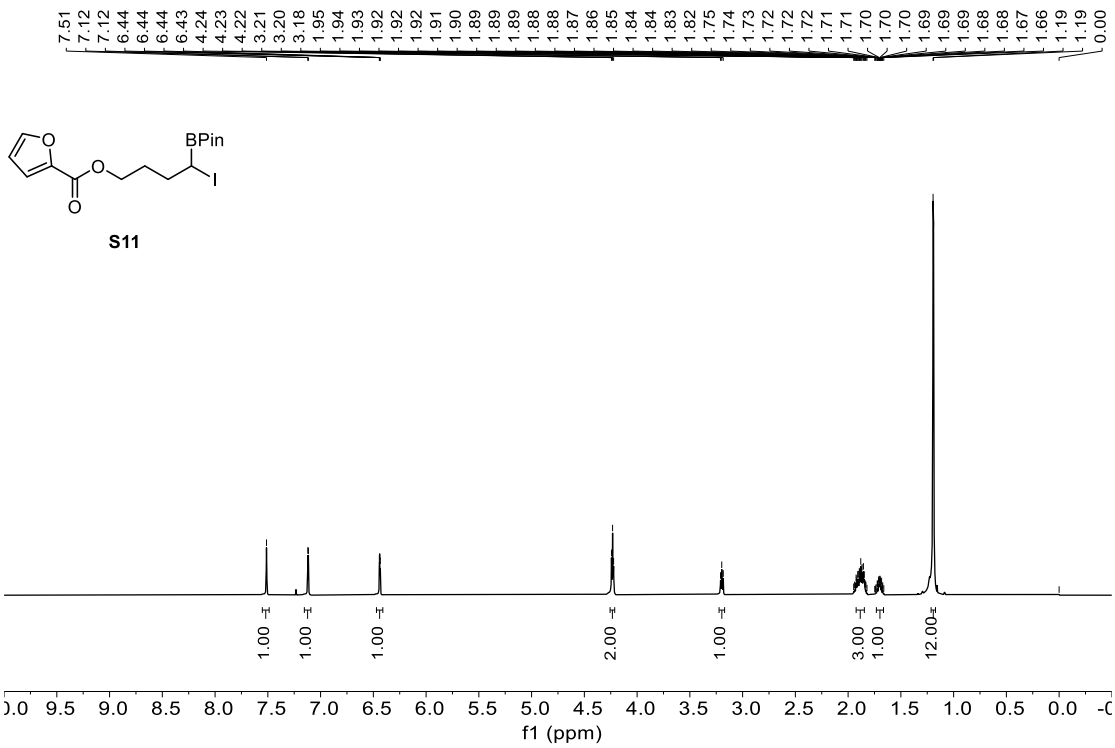
Compound **S10** ^{1}H NMR (600 MHz, $CDCl_3$)



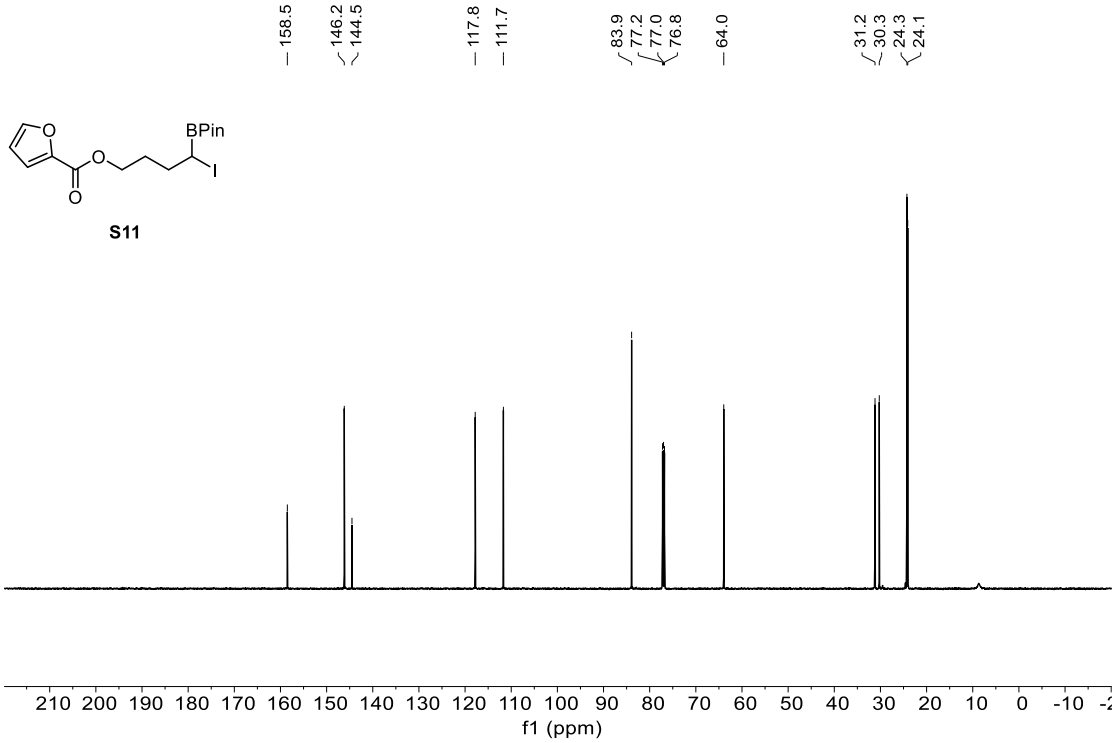
Compound **S10** ^{13}C NMR (151 MHz, $CDCl_3$)



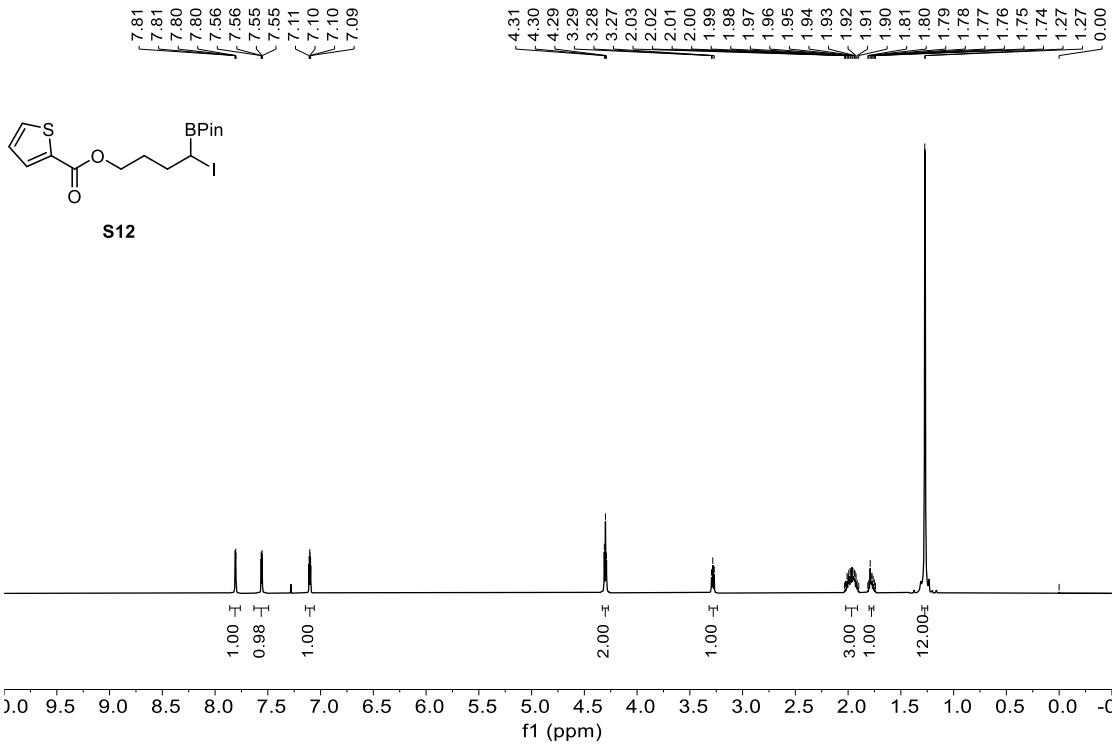
Compound **S11** ^{1}H NMR (600 MHz, $CDCl_3$)



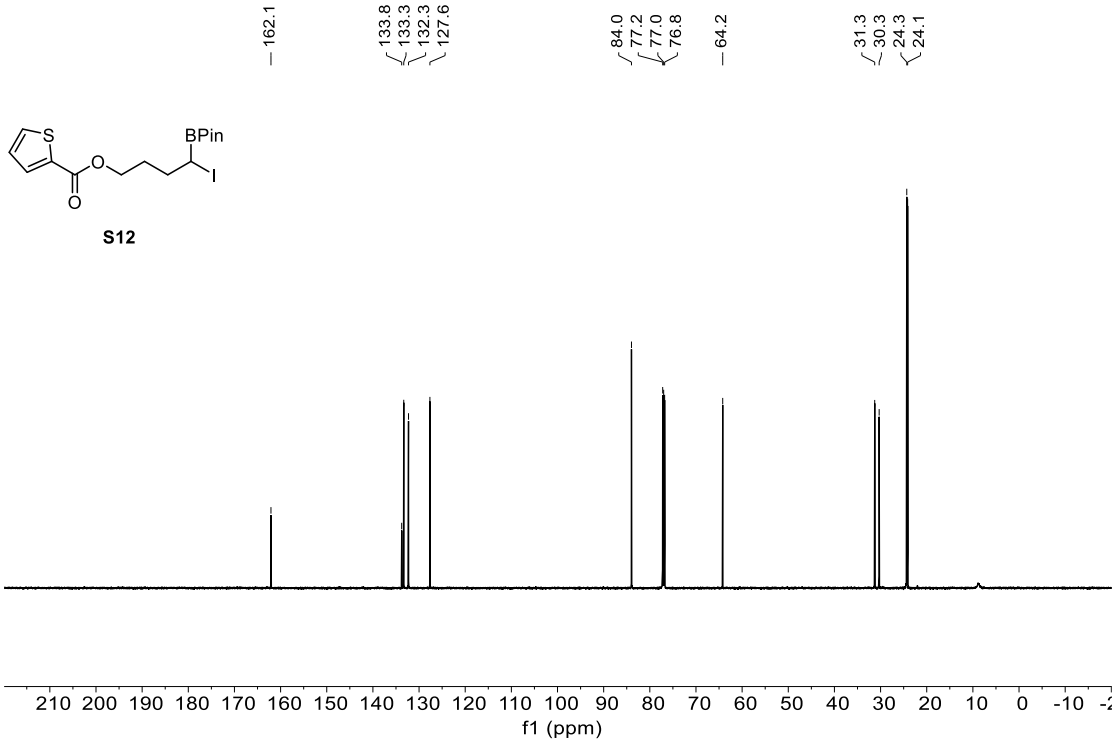
Compound **S11** ^{13}C NMR (151 MHz, $CDCl_3$)



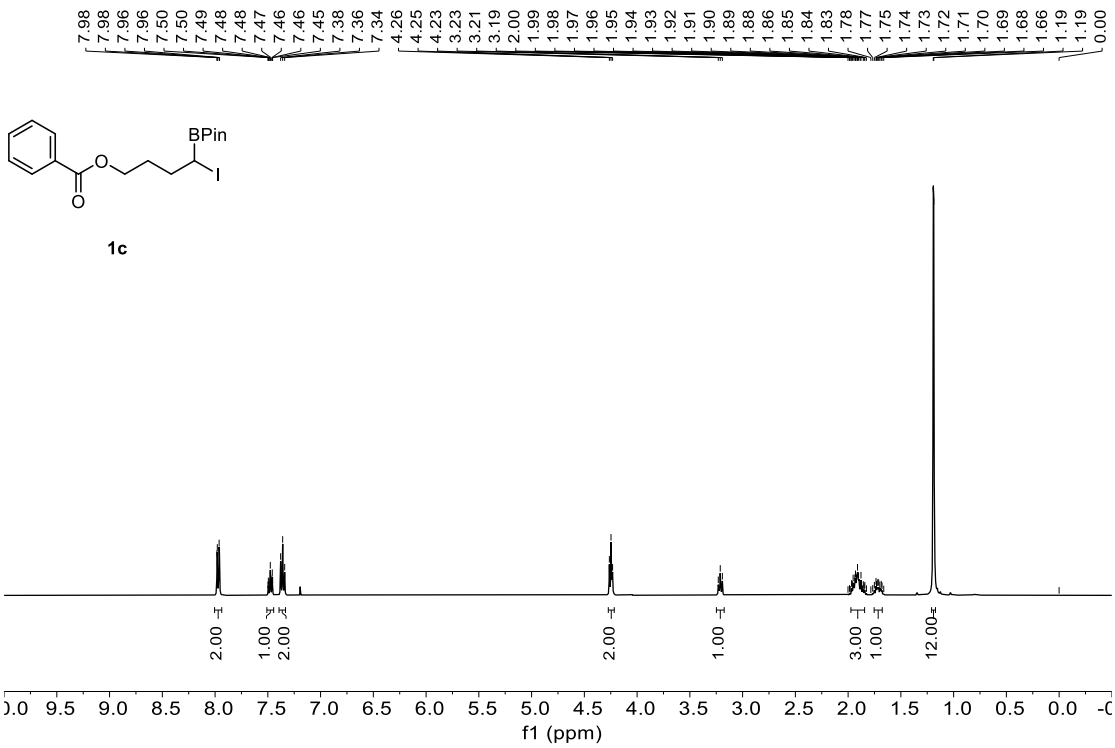
Compound **S12** ^{1}H NMR (600 MHz, $CDCl_3$)



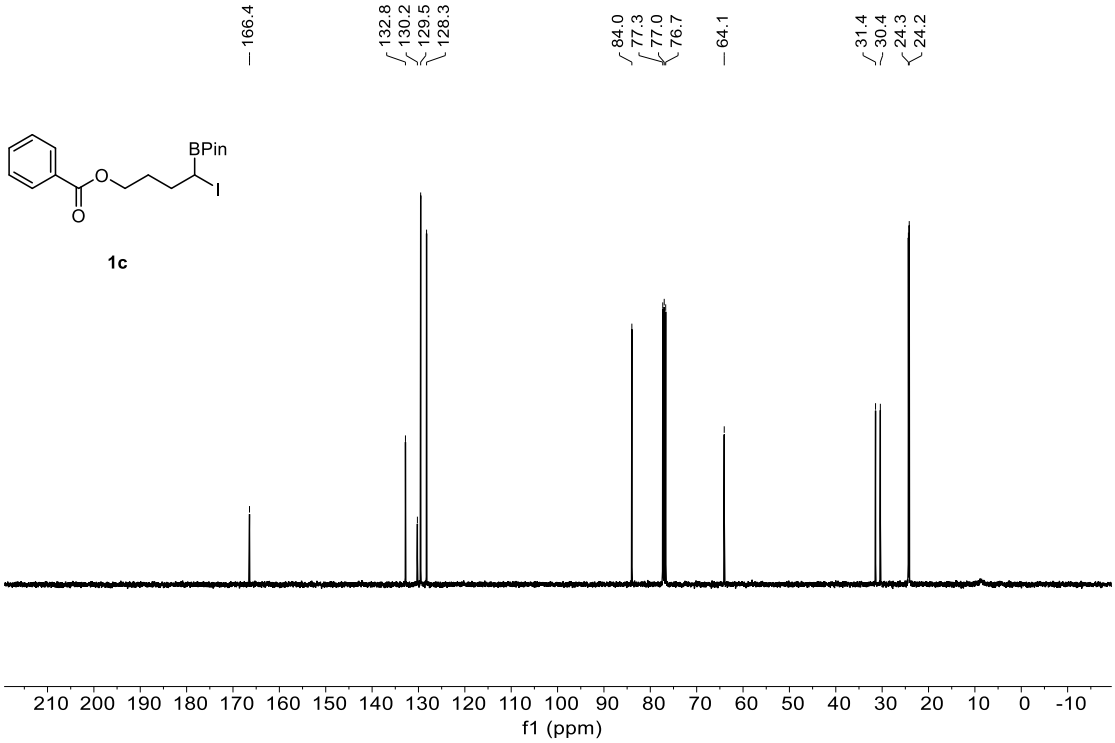
Compound **S12** ^{13}C NMR (151 MHz, $CDCl_3$)



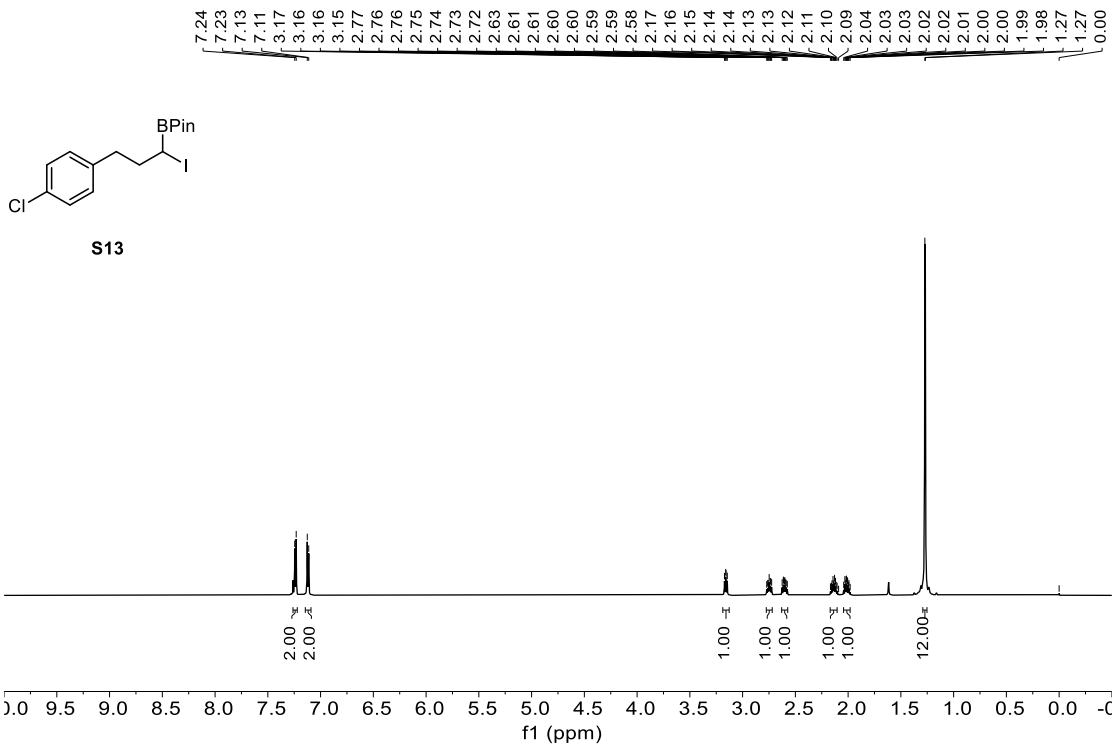
Compound **1c** ^{1}H NMR (400 MHz, $CDCl_3$)



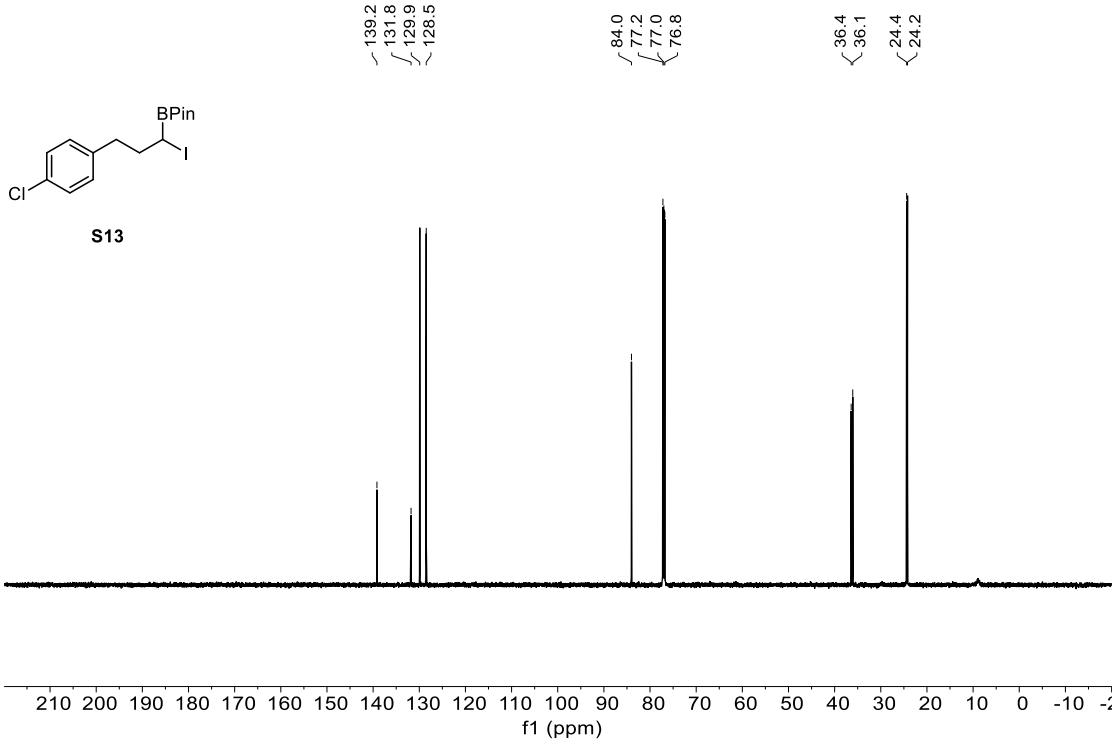
Compound **1c** ^{13}C NMR (101 MHz, $CDCl_3$)



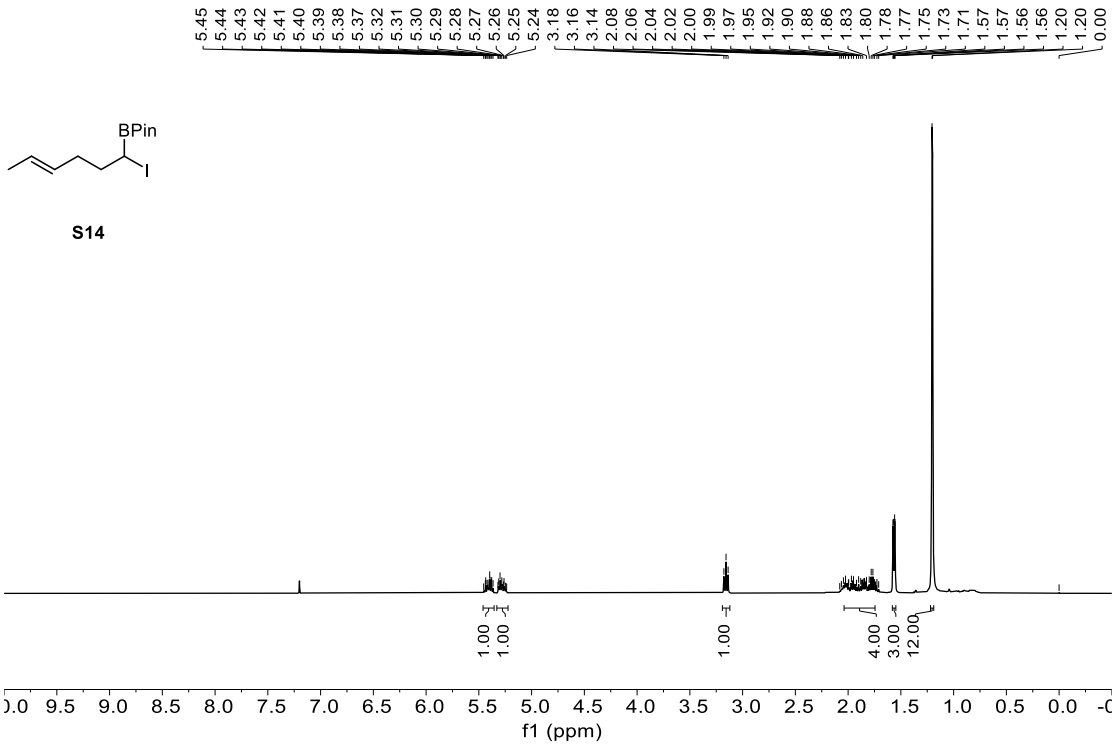
Compound **S13** ^{1}H NMR (600 MHz, $CDCl_3$)



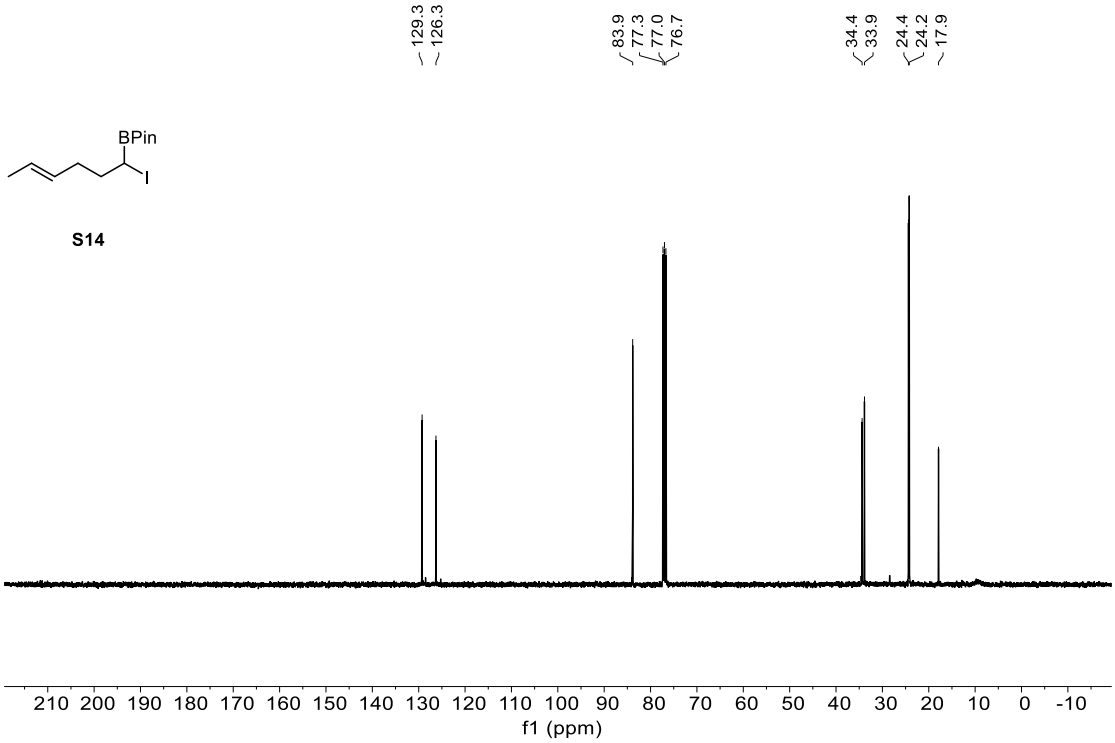
Compound **S13** ^{13}C NMR (151 MHz, $CDCl_3$)



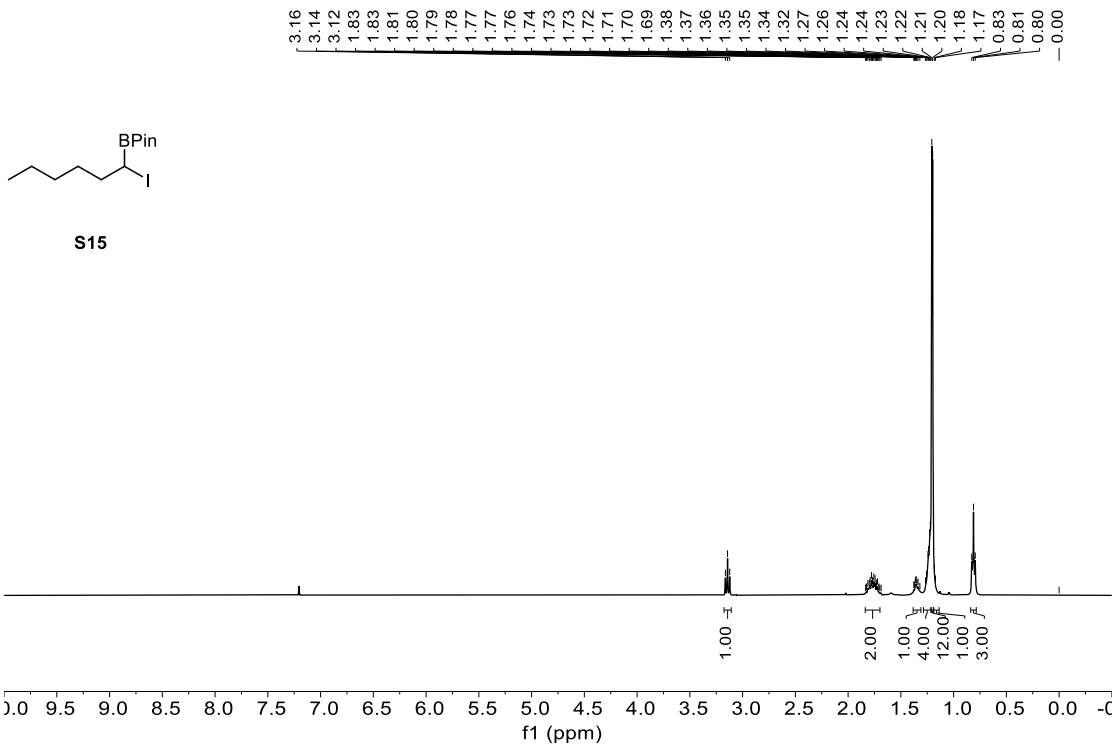
Compound **S14** ^{1}H NMR (400 MHz, $CDCl_3$)



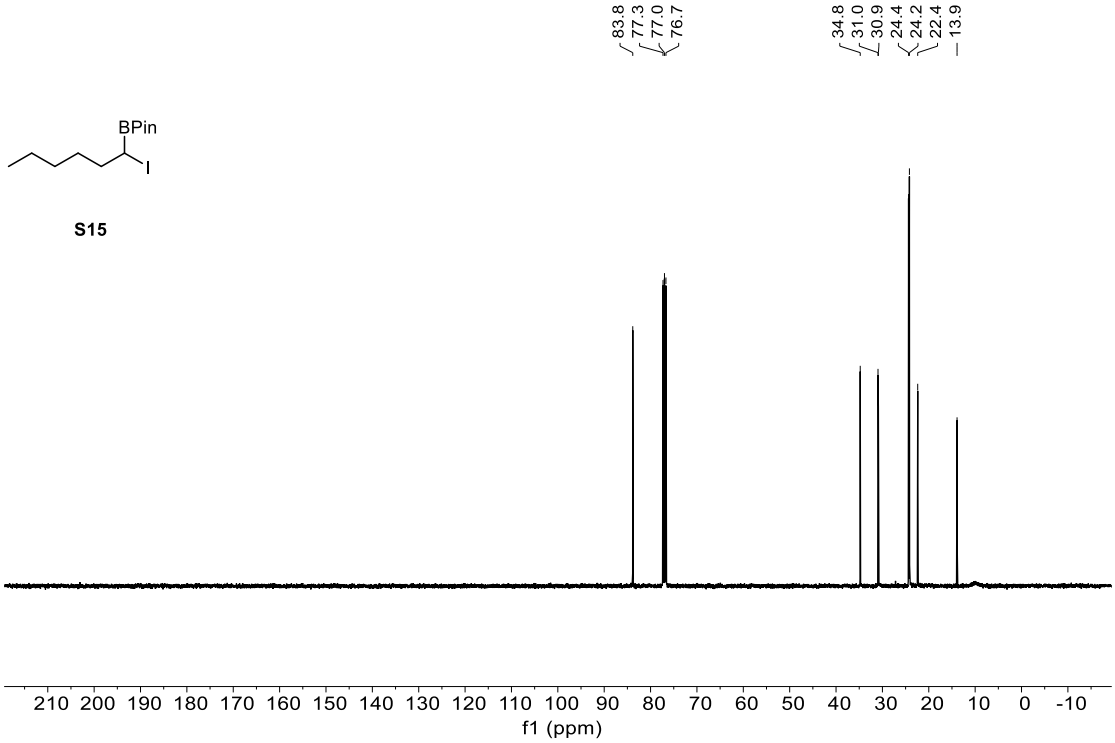
Compound **S14** ^{13}C NMR (101 MHz, $CDCl_3$)



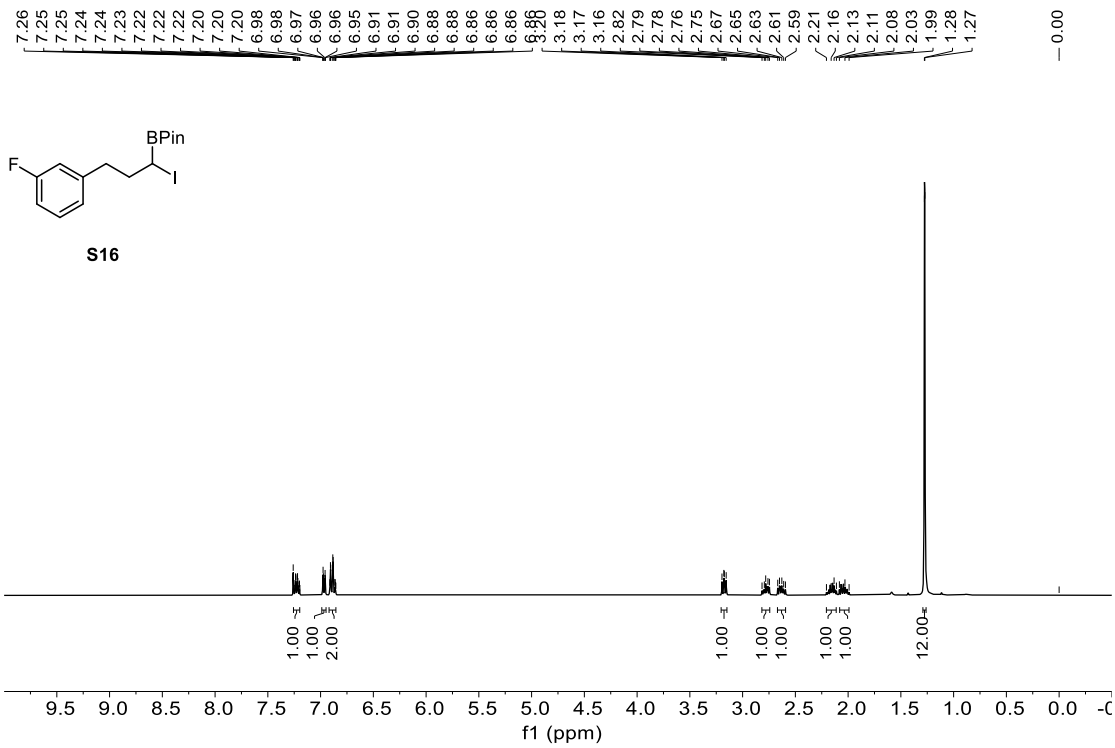
Compound **S15** ^{1}H NMR (400 MHz, $CDCl_3$)



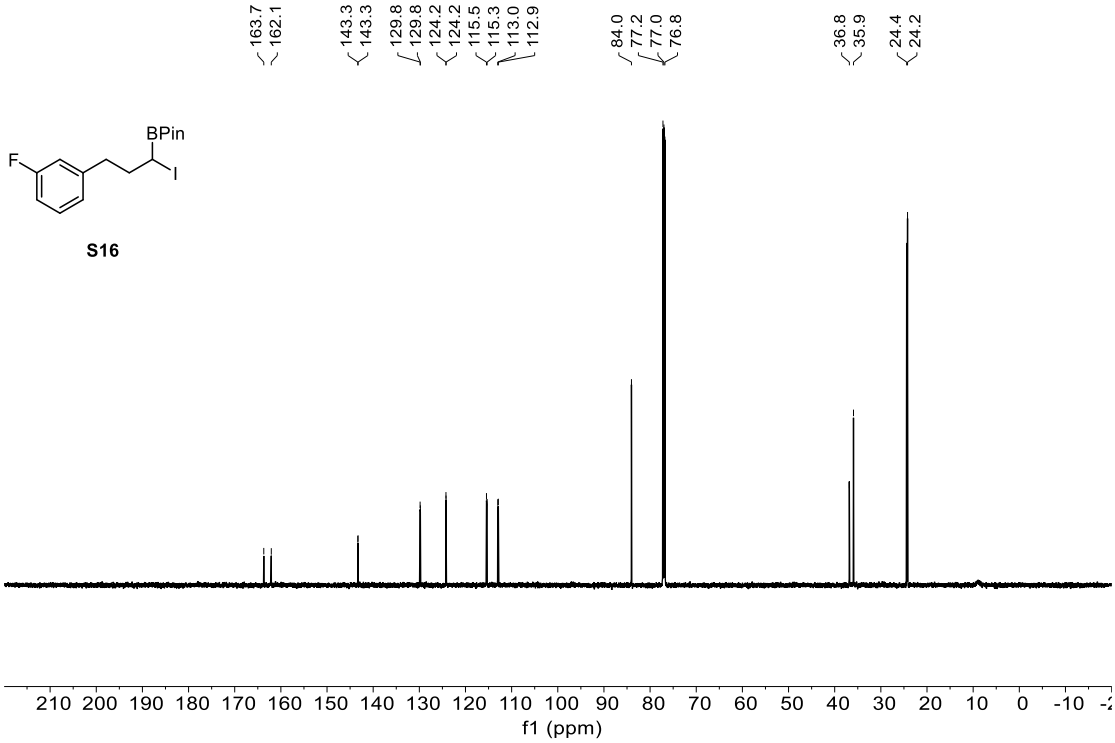
Compound **S15** ^{13}C NMR (101 MHz, $CDCl_3$)



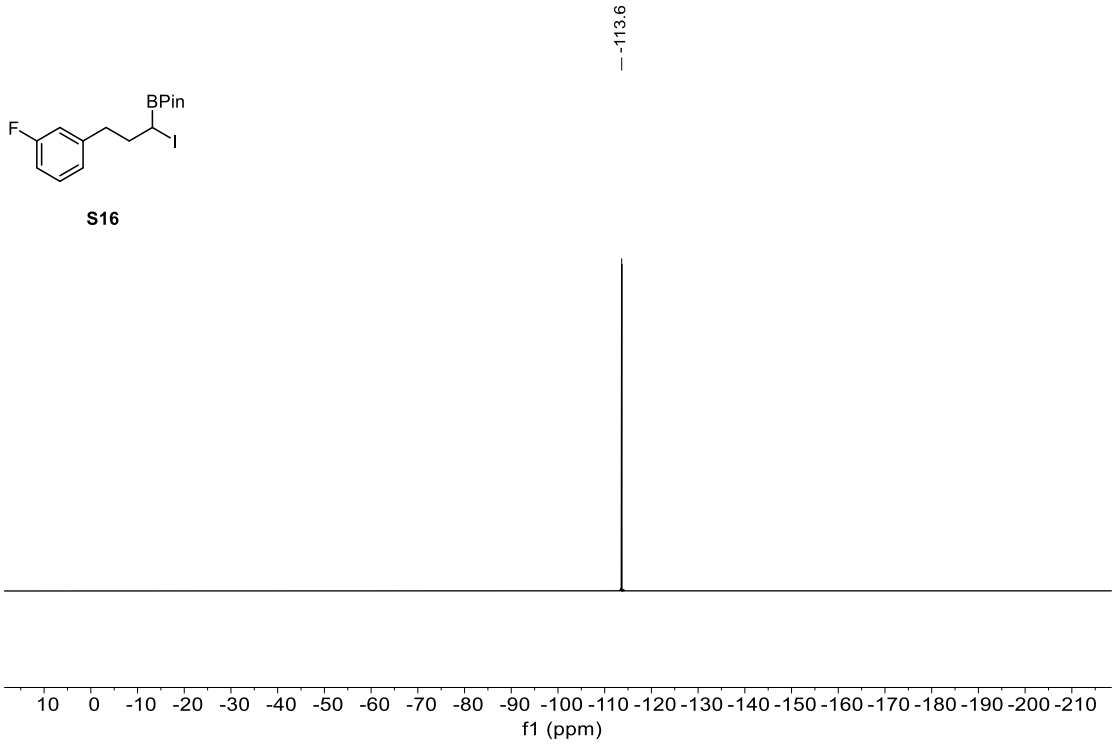
Compound **S16** ^{1}H NMR (600 MHz, $CDCl_3$)



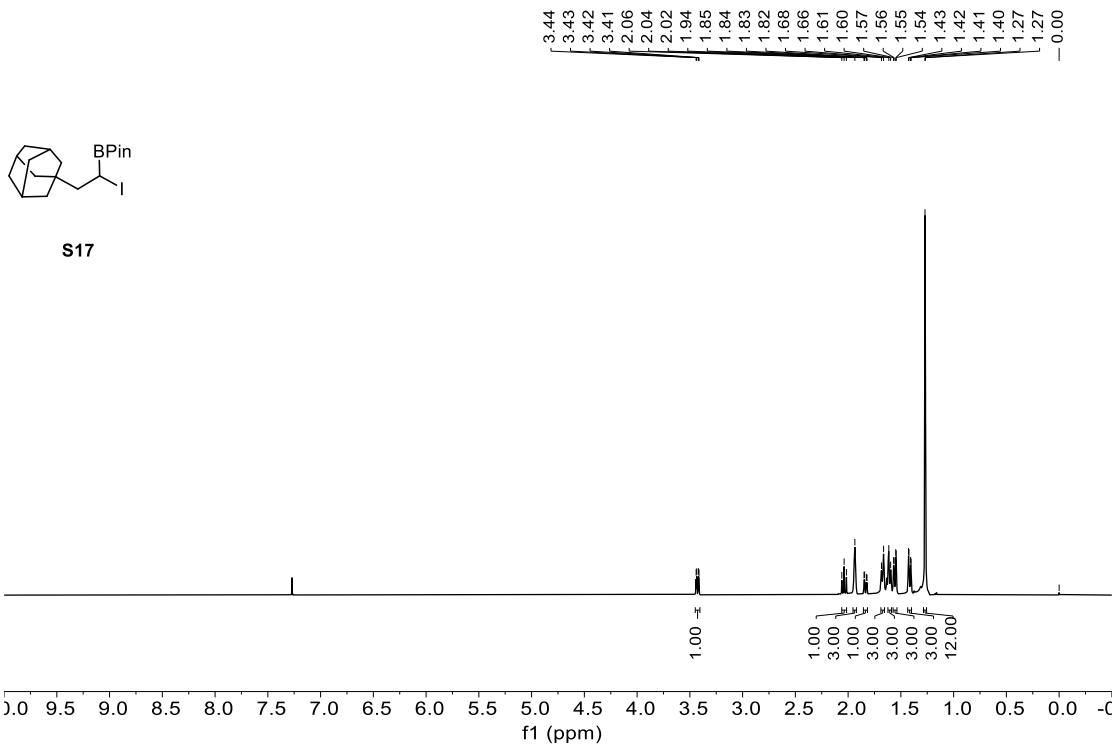
Compound **S16** ^{13}C NMR (151 MHz, $CDCl_3$)



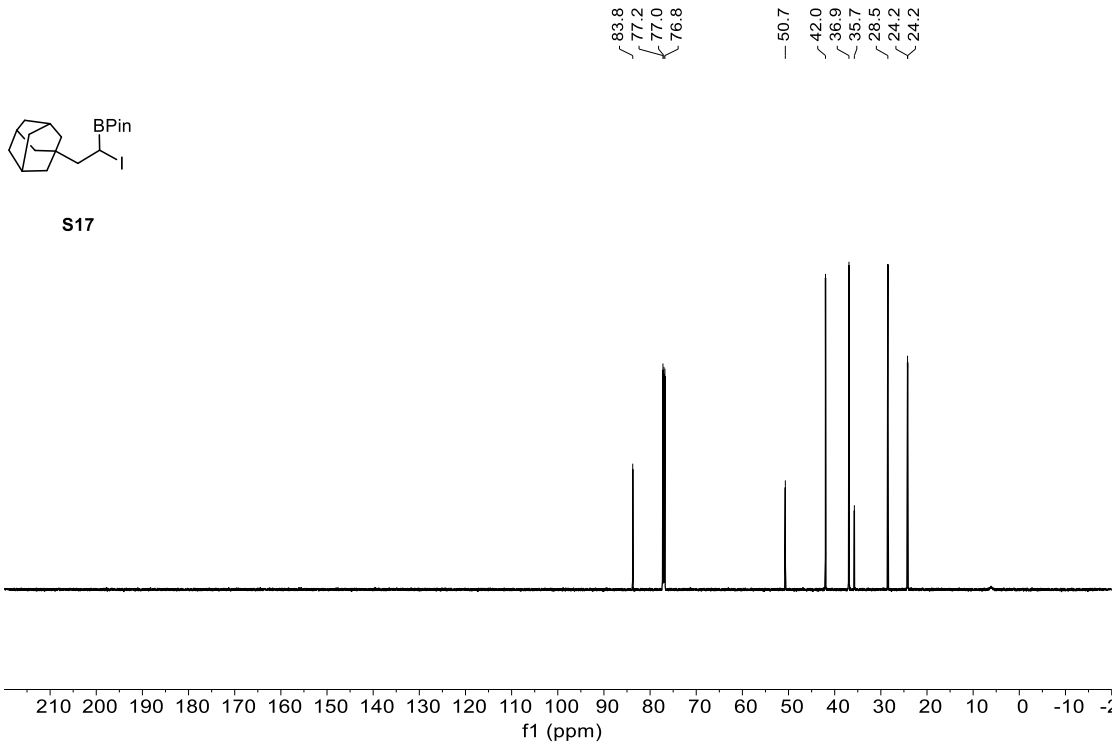
Compound **S16** ^{19}F NMR (376 MHz, $CDCl_3$)



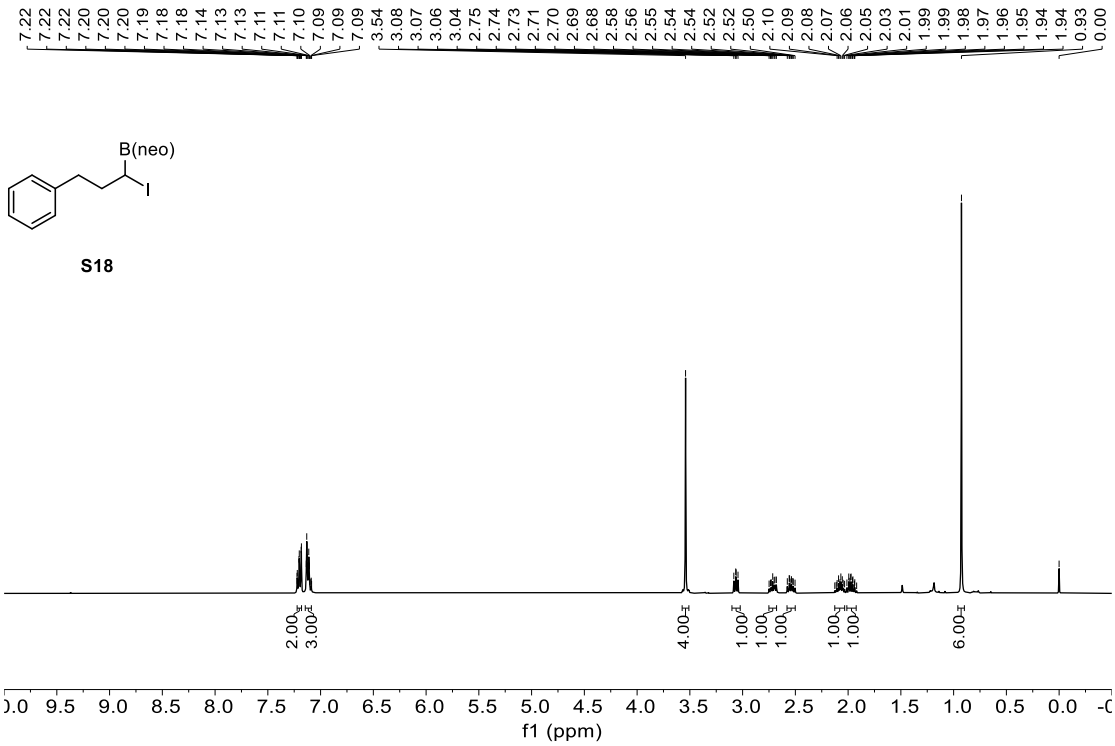
Compound **S17** ^{1}H NMR (600 MHz, $CDCl_3$)



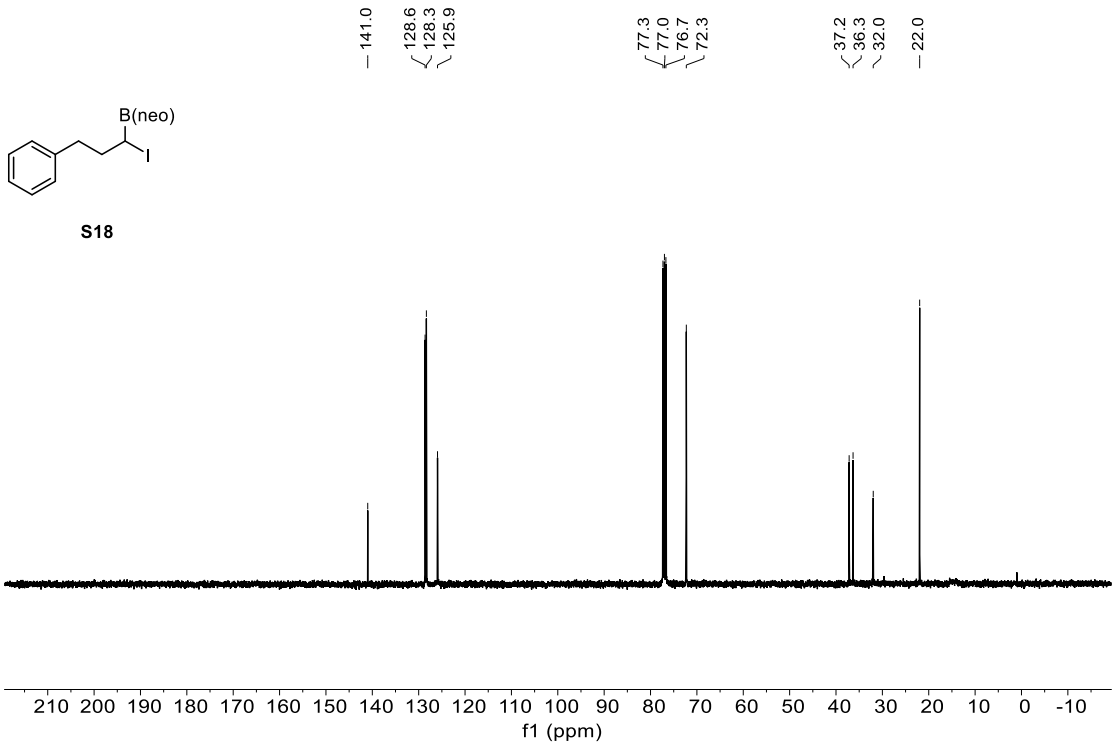
Compound **S17** ^{13}C NMR (151 MHz, $CDCl_3$)



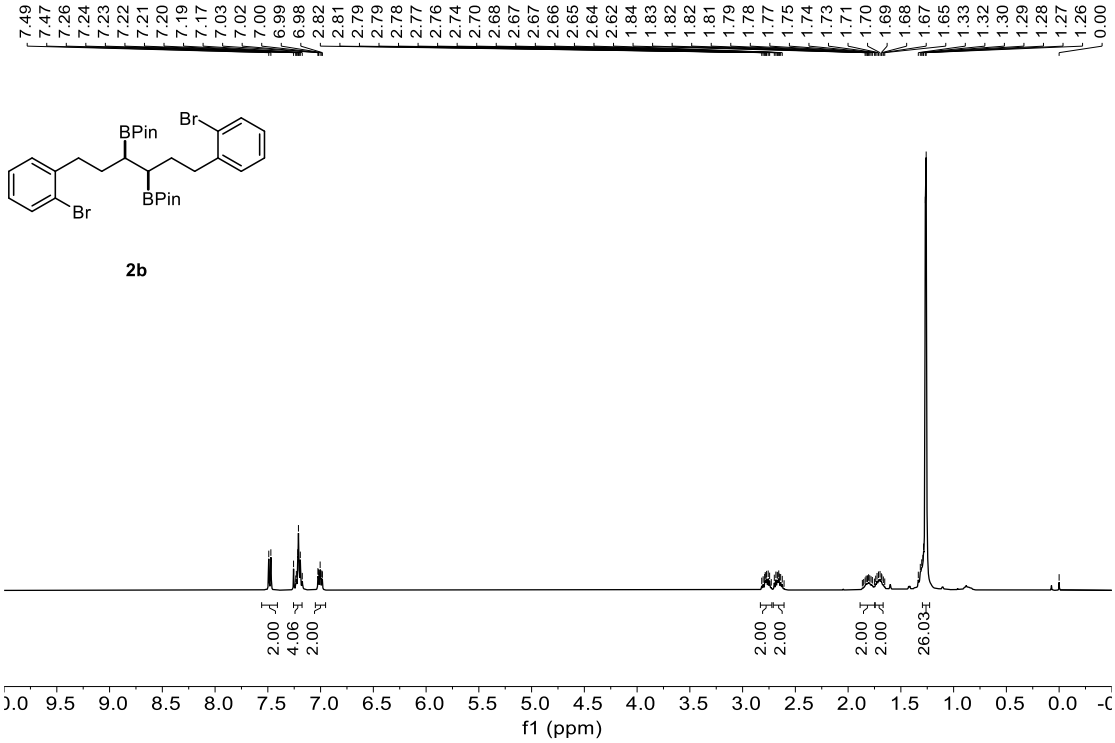
Compound **S18** ^{1}H NMR (400 MHz, $CDCl_3$)



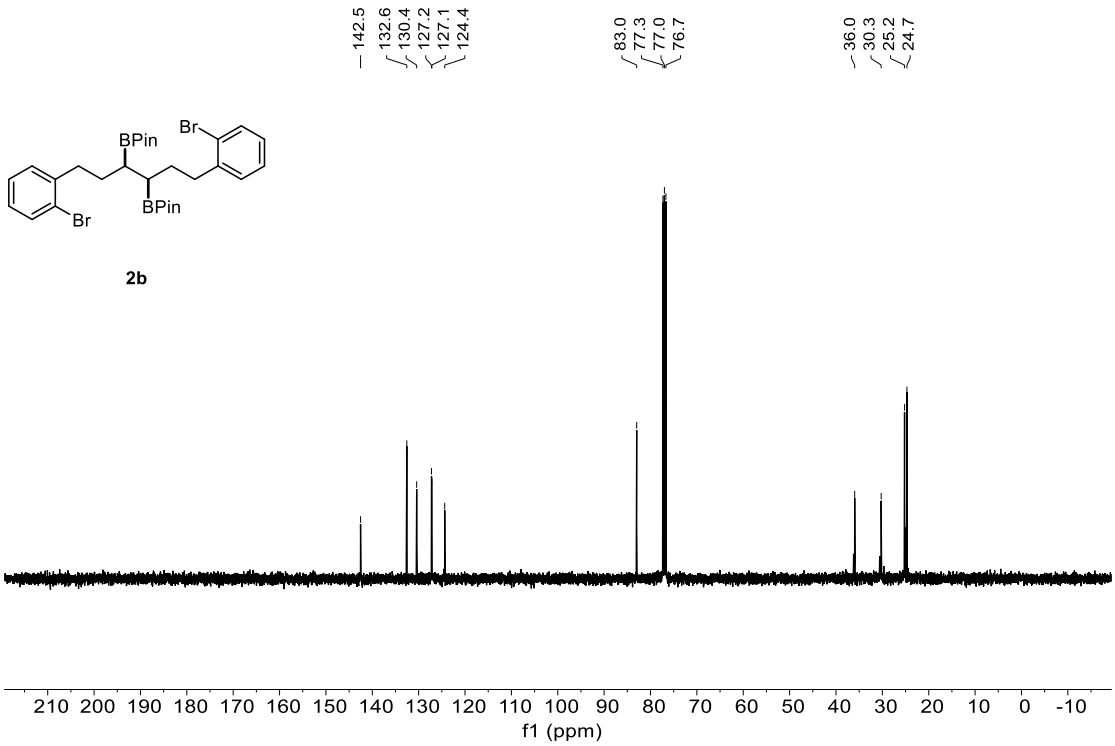
Compound **S18** ^{13}C NMR (101 MHz, $CDCl_3$)



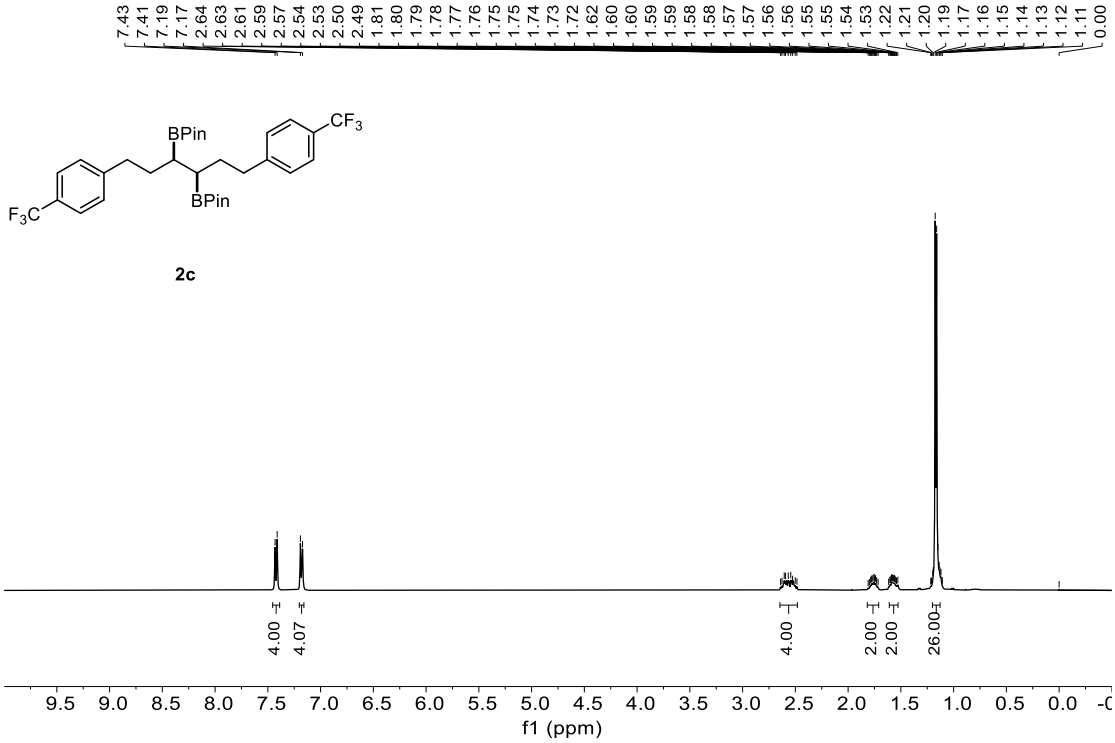
Compound **2b** ^{1}H NMR (400 MHz, $CDCl_3$)



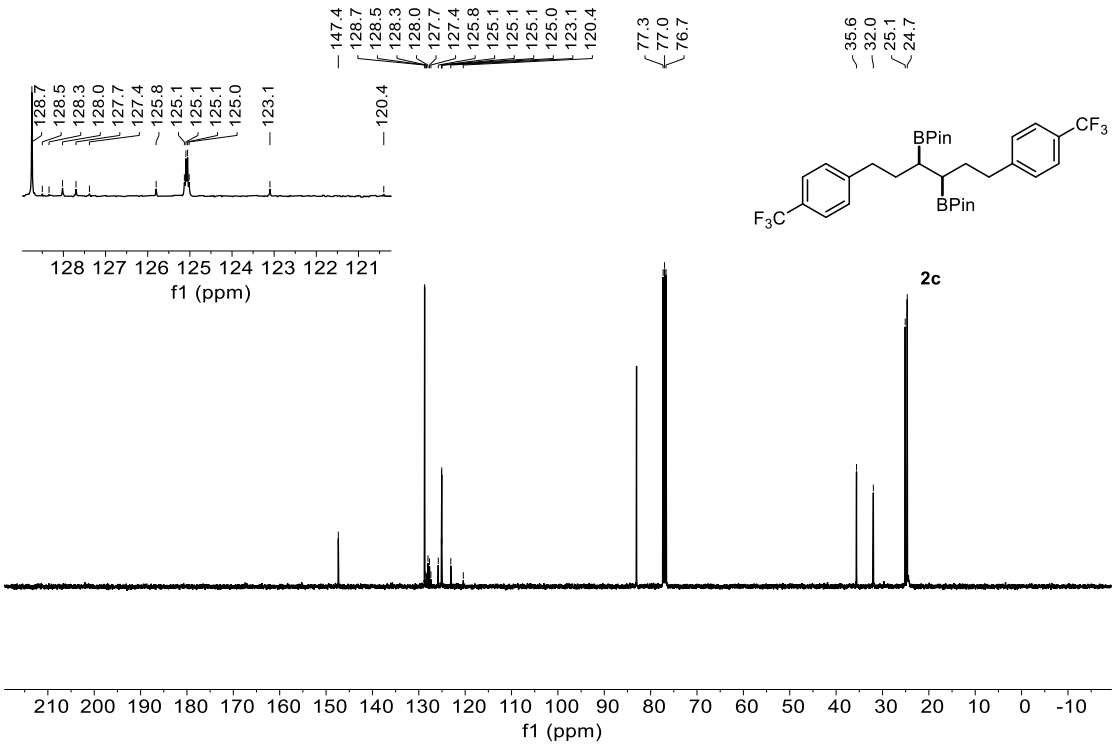
Compound **2b** ^{13}C NMR (101 MHz, $CDCl_3$)



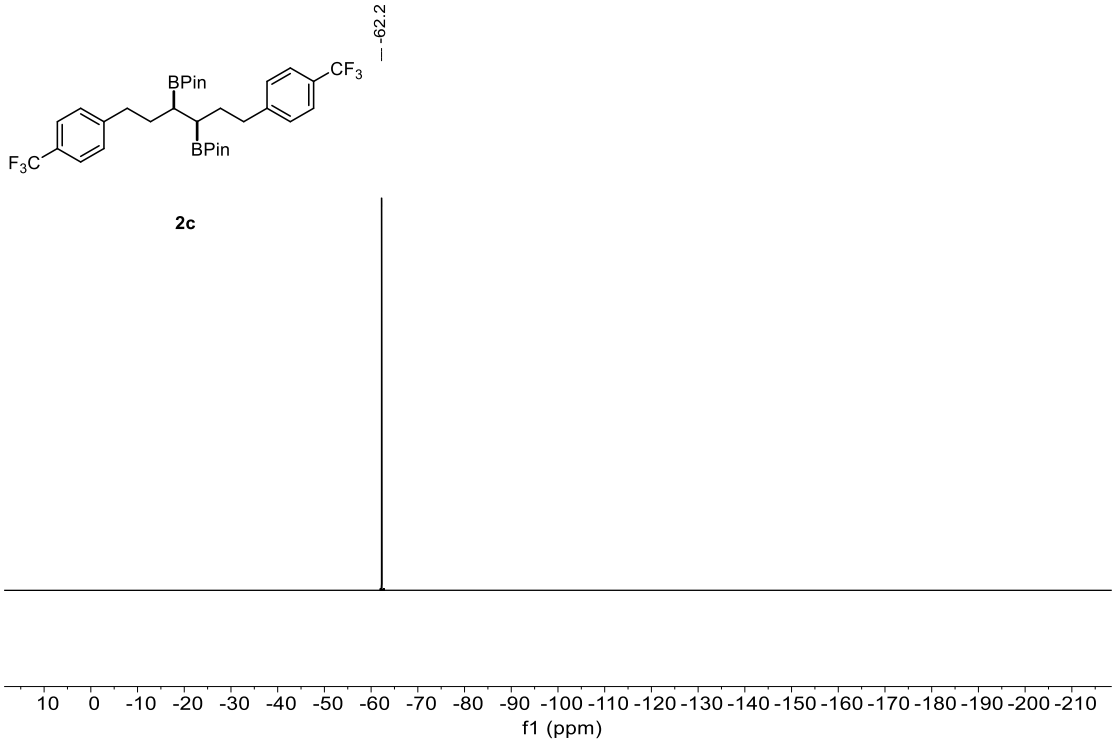
Compound **2c** ^{1}H NMR (400 MHz, $CDCl_3$)



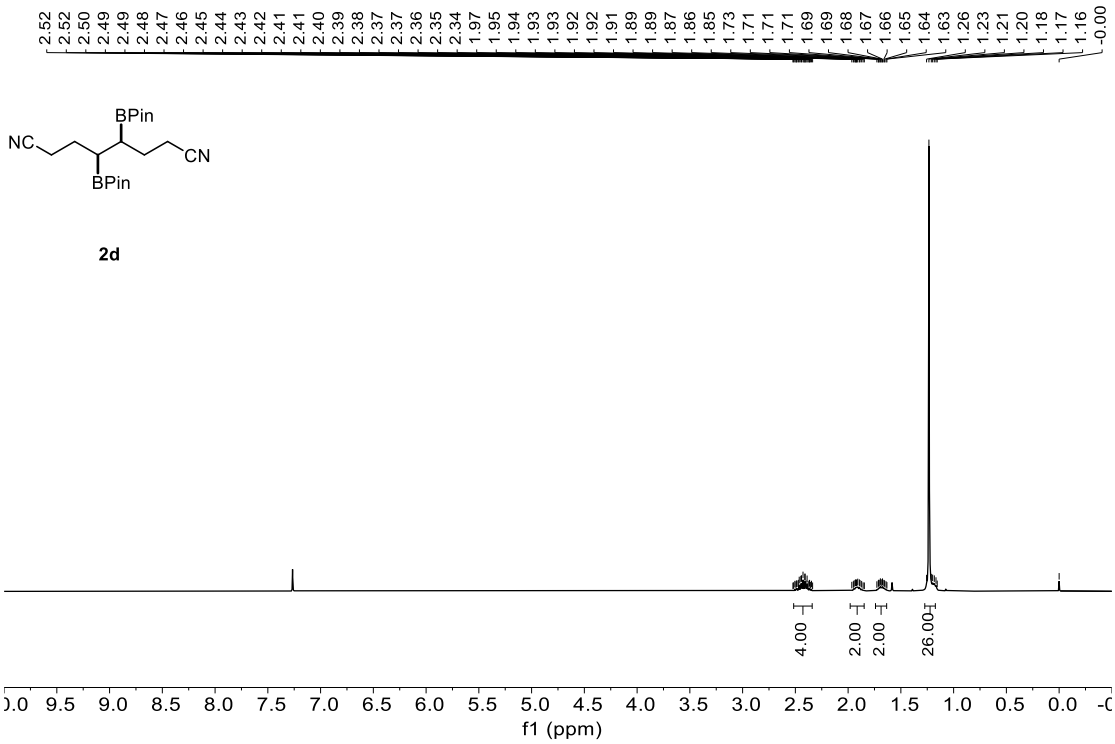
Compound **2c** ^{13}C NMR (101 MHz, $CDCl_3$)



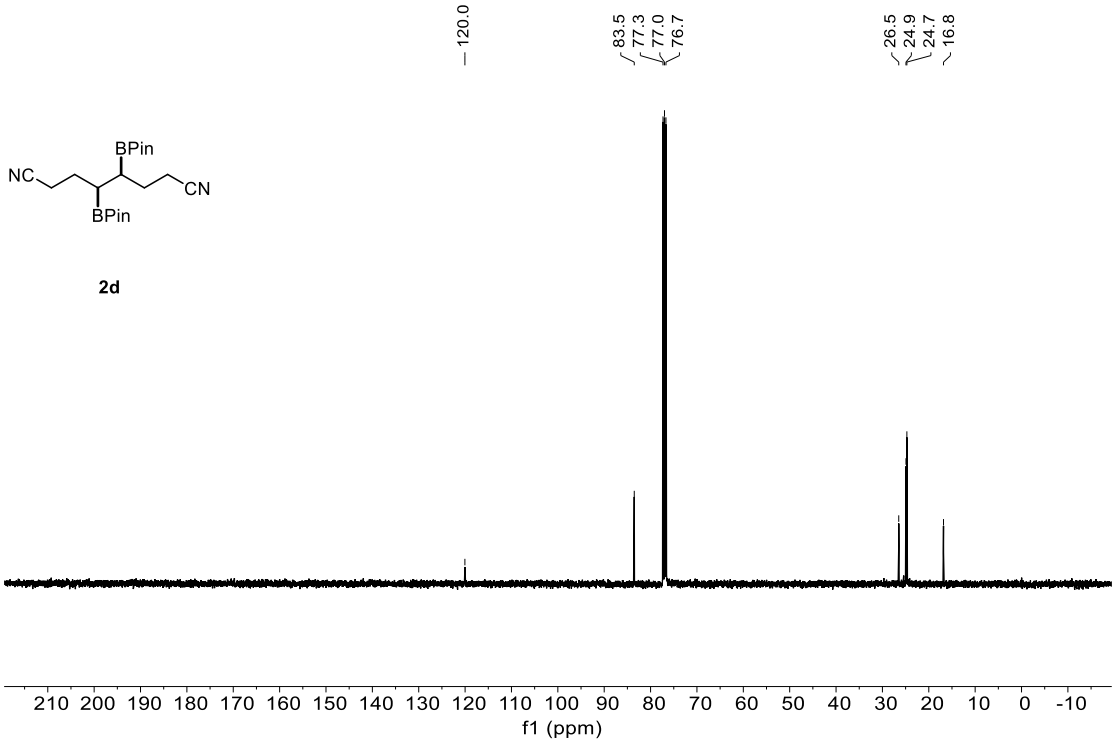
Compound **2c** ^{19}F NMR (376 MHz, $CDCl_3$)



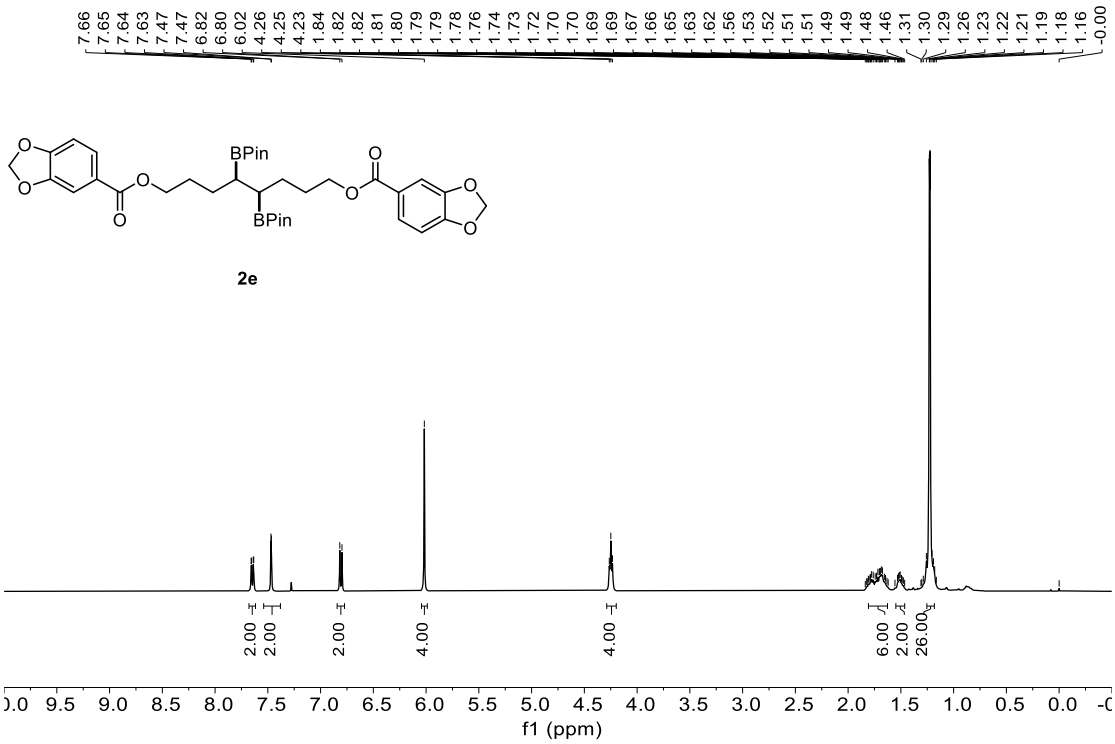
Compound **2d** ^{1}H NMR (400 MHz, $CDCl_3$)



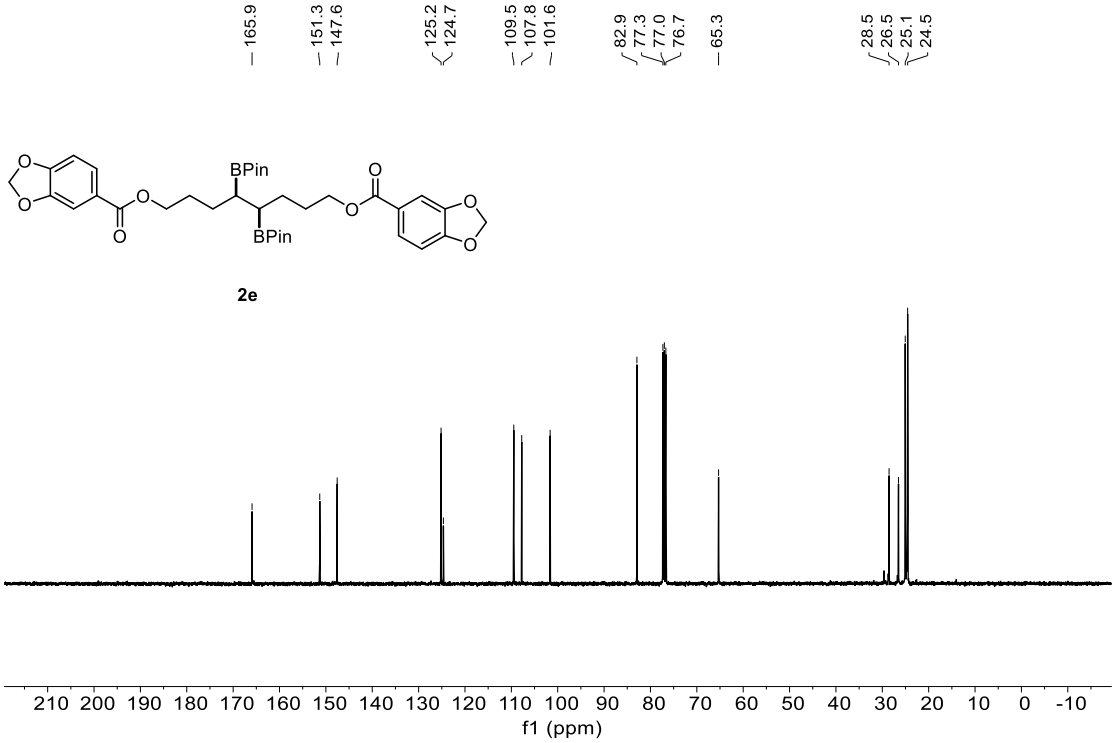
Compound **2d** ^{13}C NMR (101 MHz, $CDCl_3$)



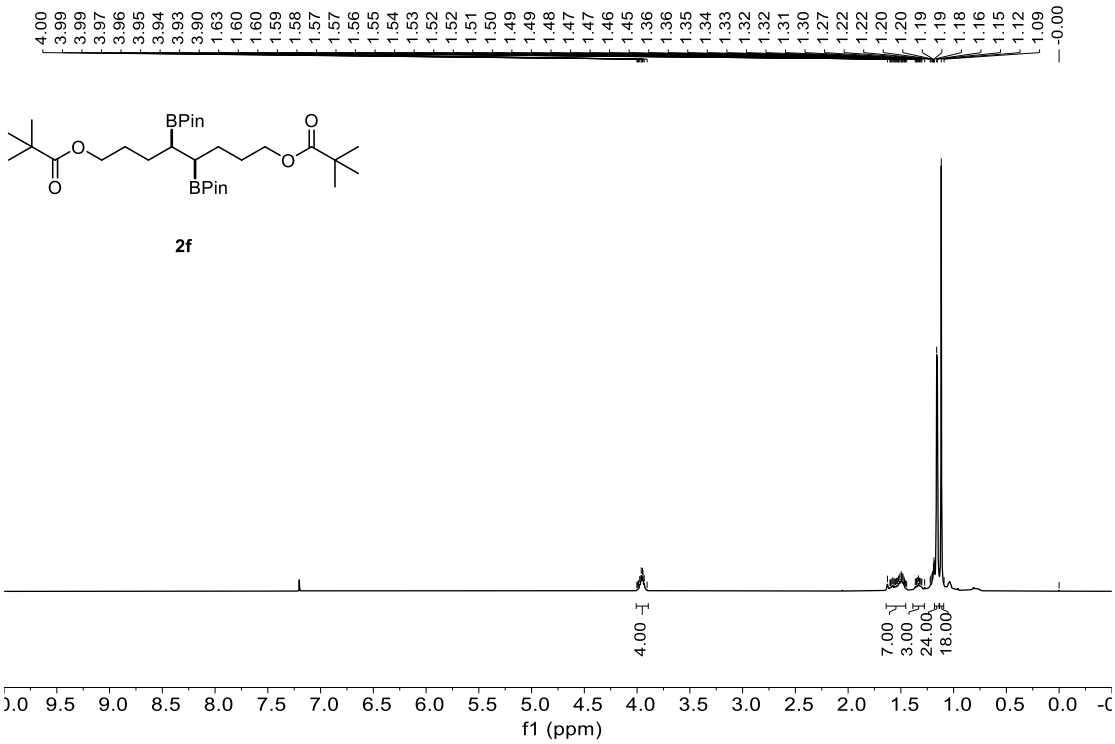
Compound **2e** ^{1}H NMR (400 MHz, $CDCl_3$)



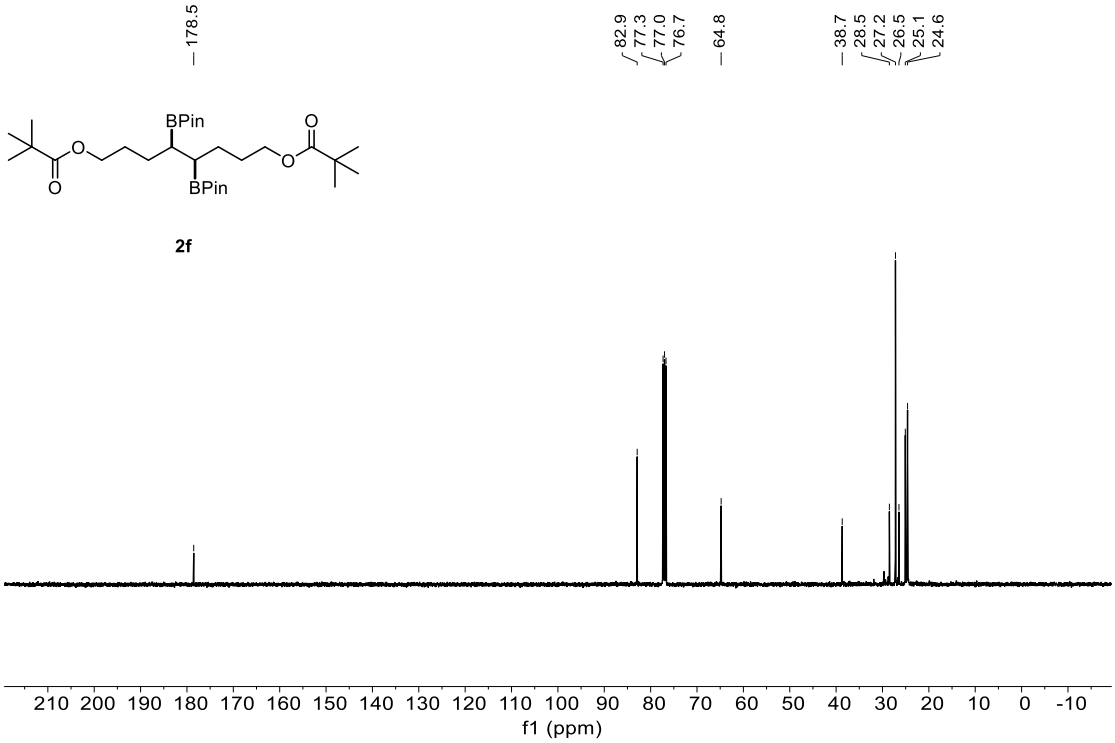
Compound **2e** ^{13}C NMR (101 MHz, $CDCl_3$)



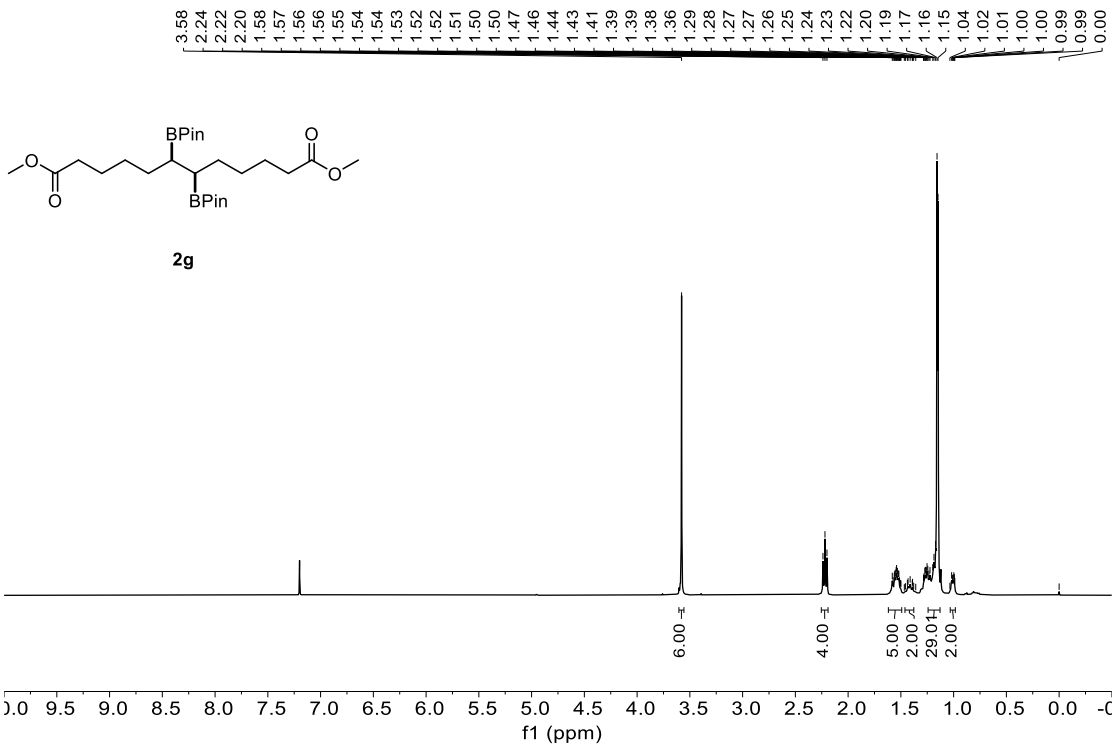
Compound **2f** ^{1}H NMR (400 MHz, $CDCl_3$)



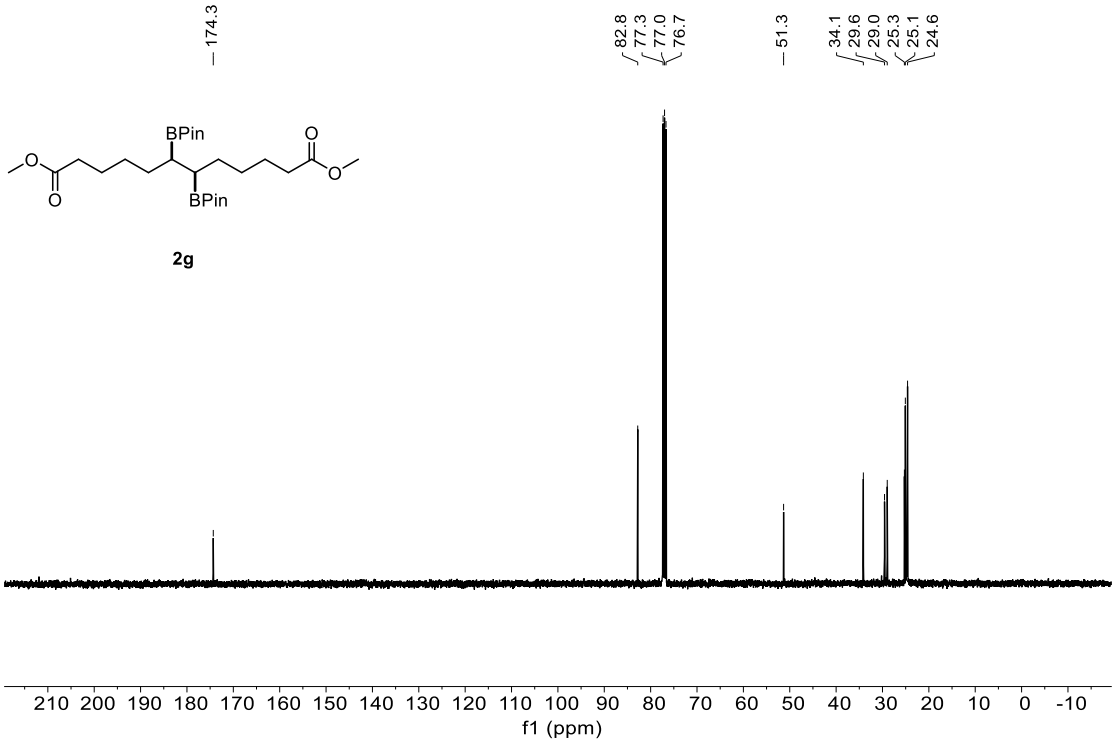
Compound **2f** ^{13}C NMR (101 MHz, $CDCl_3$)



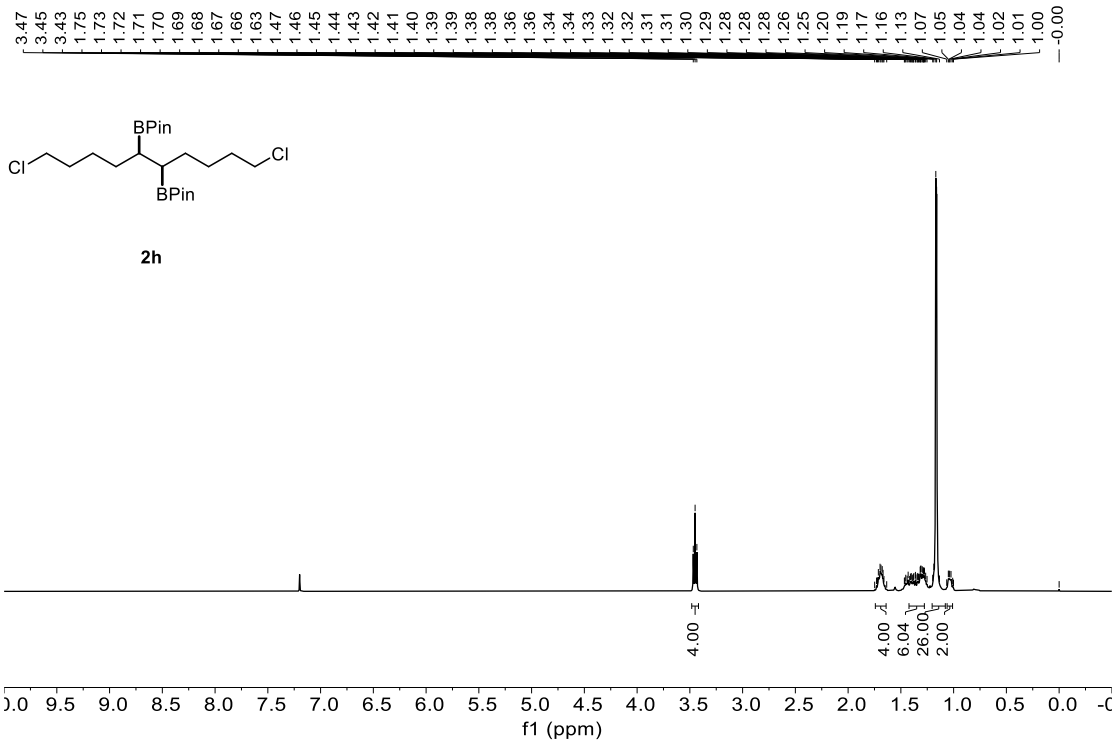
Compound **2g** ^{1}H NMR (400 MHz, $CDCl_3$)



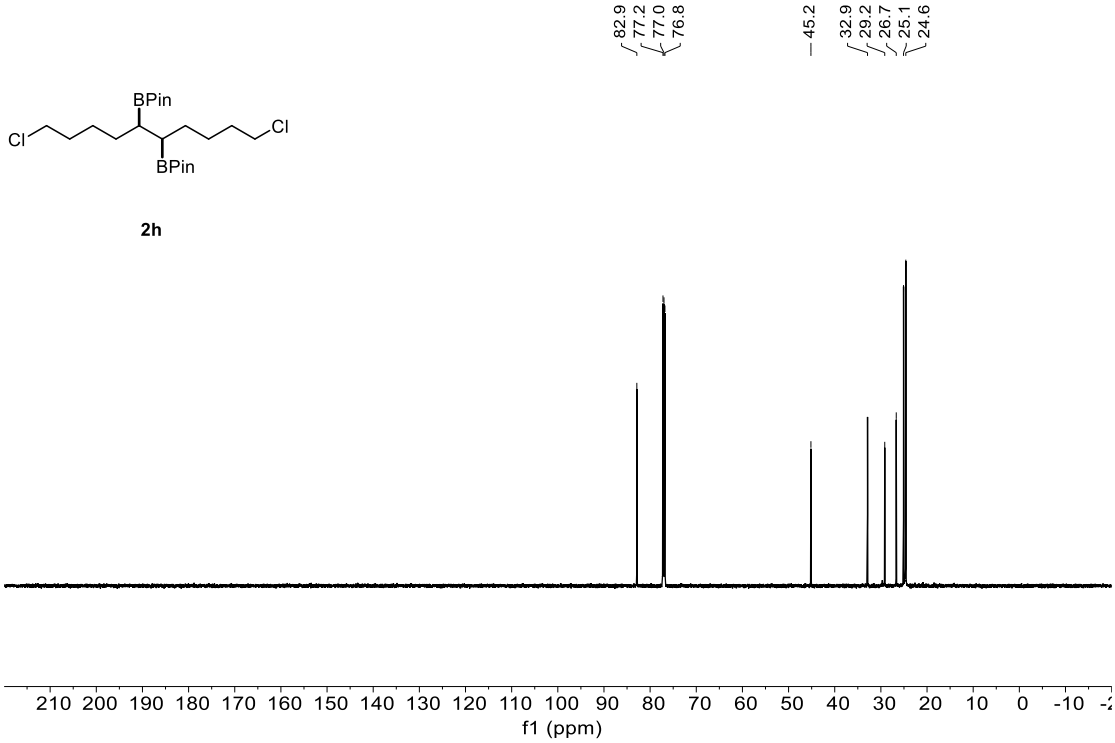
Compound **2g** ^{13}C NMR (101 MHz, $CDCl_3$)



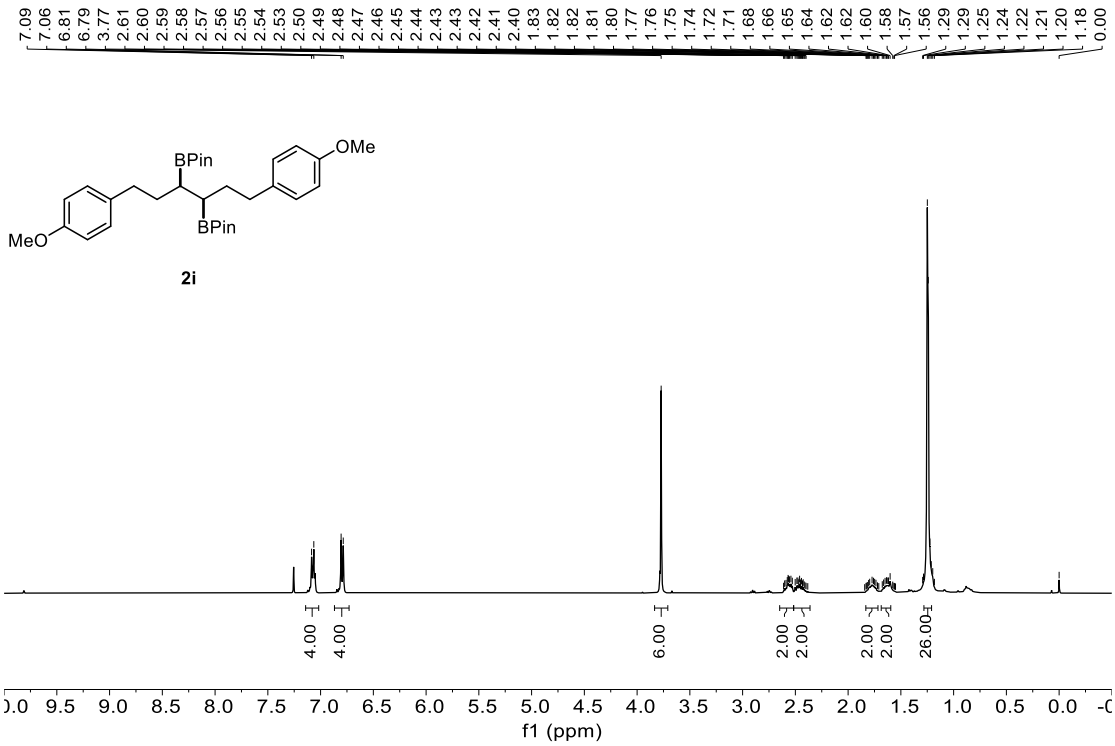
Compound **2h** ^{1}H NMR (400 MHz, $CDCl_3$)



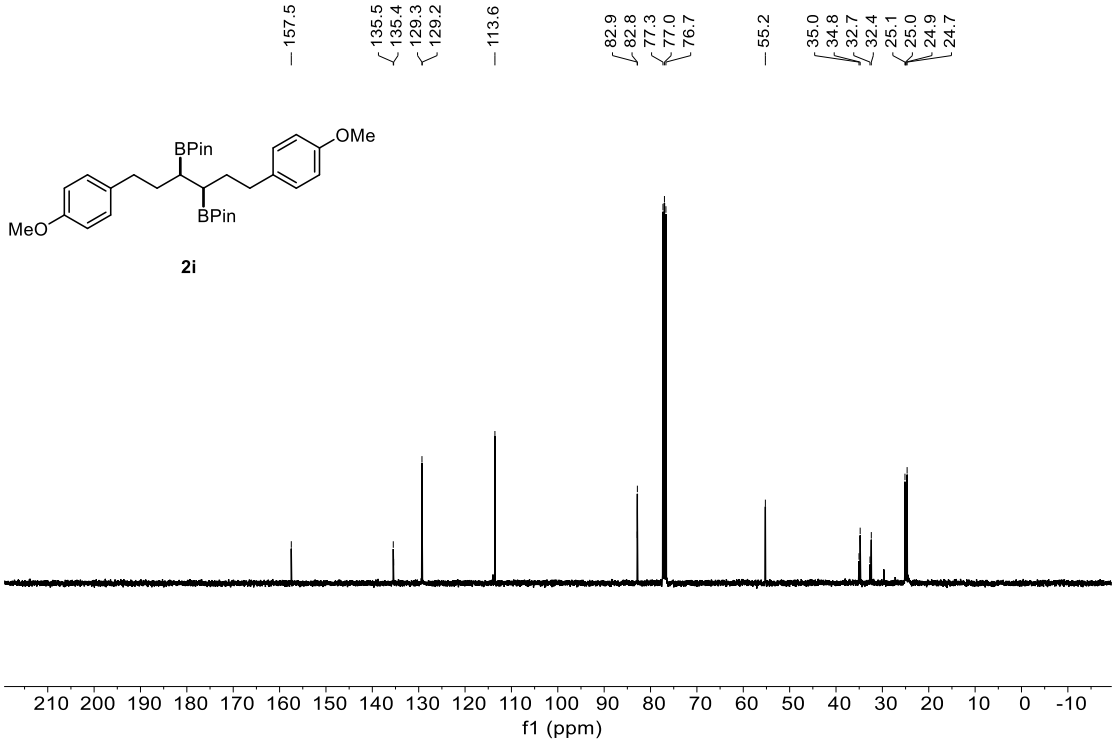
Compound **2h** ^{13}C NMR (151 MHz, $CDCl_3$)



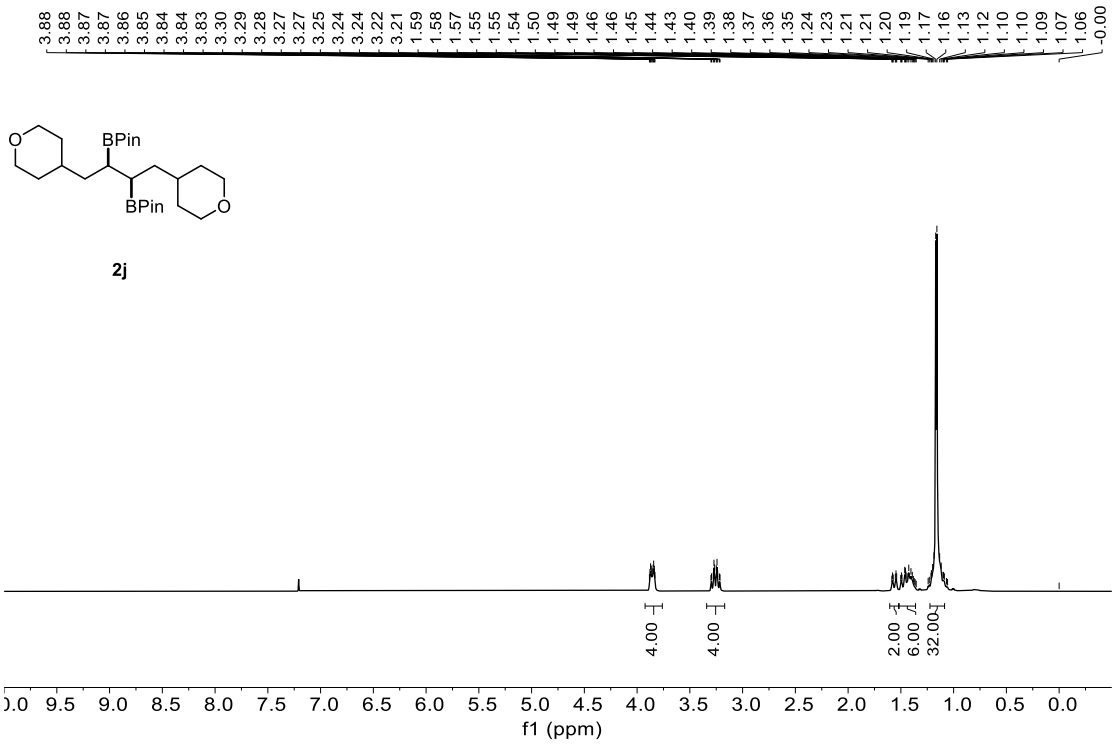
Compound **2i** ^{1}H NMR (400 MHz, $CDCl_3$)



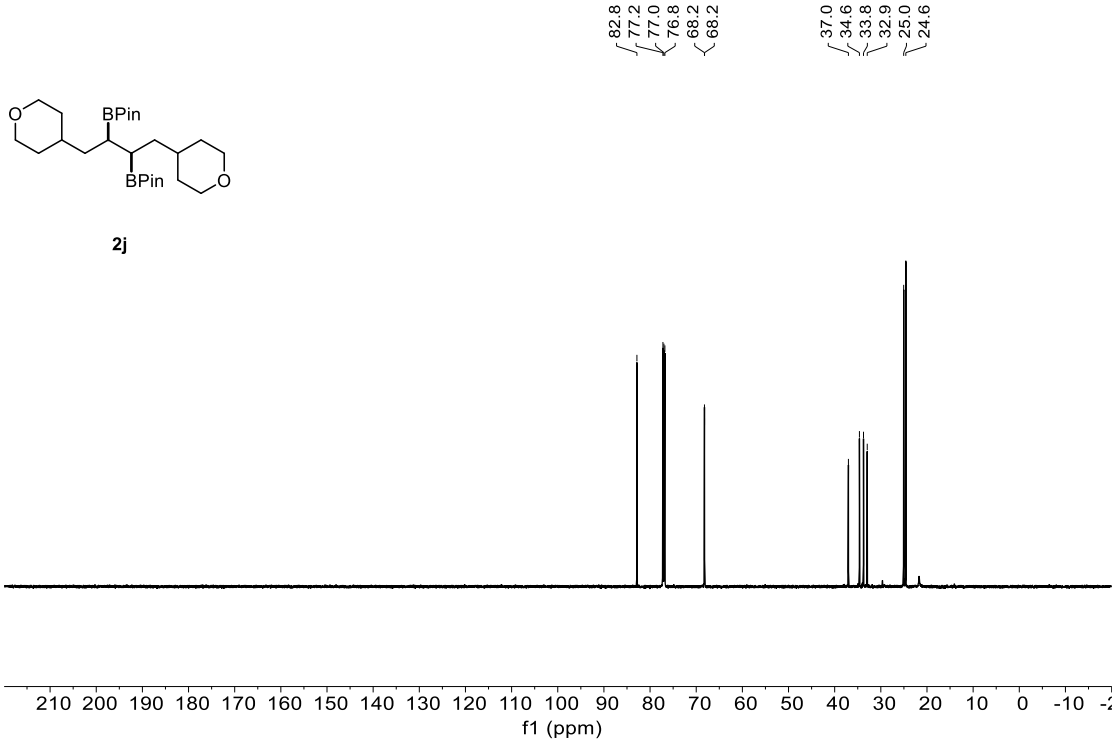
Compound **2i** ^{13}C NMR (101 MHz, $CDCl_3$)



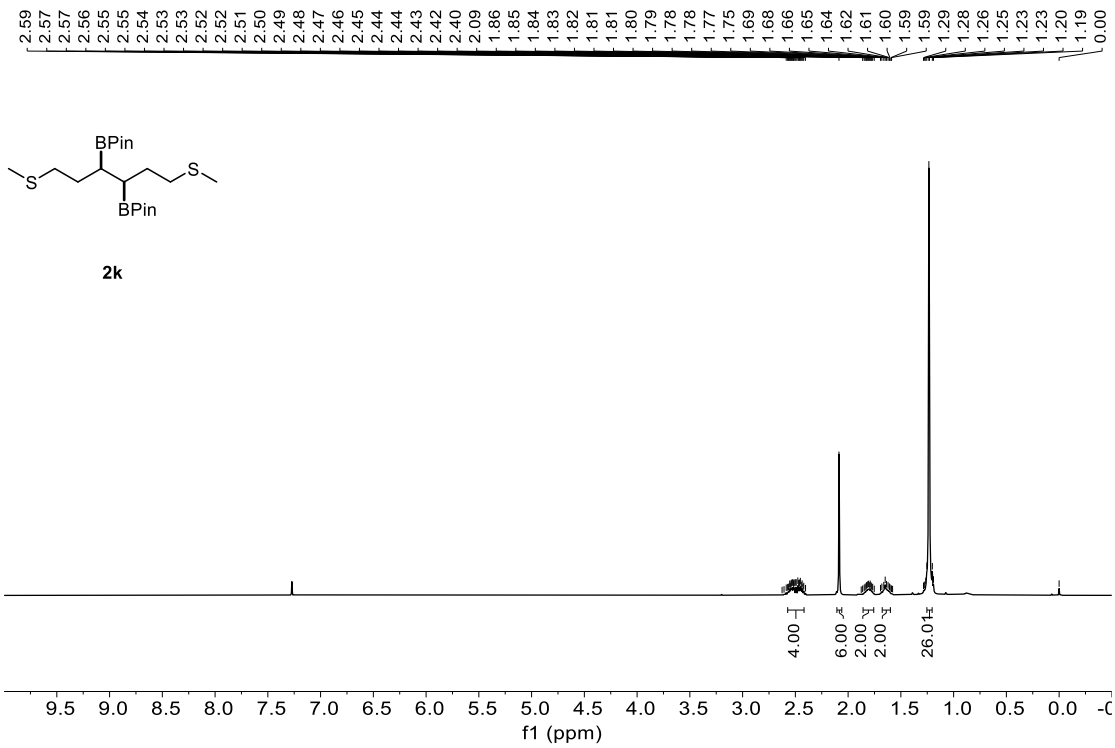
Compound **2j** ^{1}H NMR (400 MHz, $CDCl_3$)



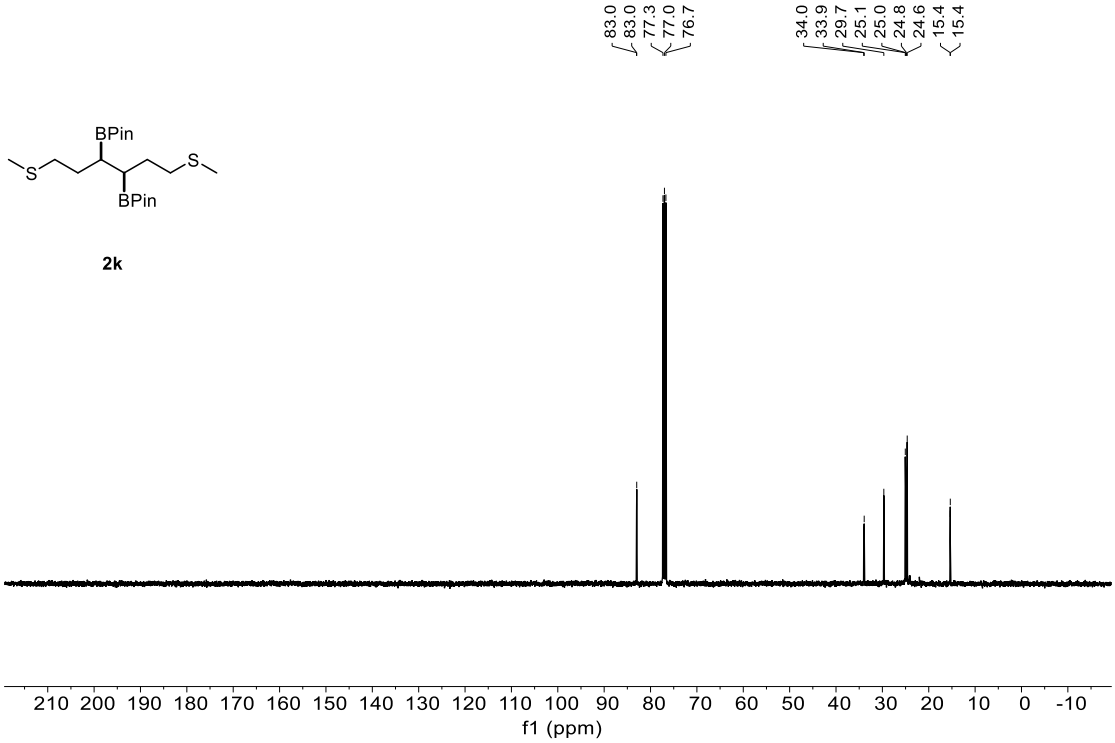
Compound **2j** ^{13}C NMR (151 MHz, $CDCl_3$)



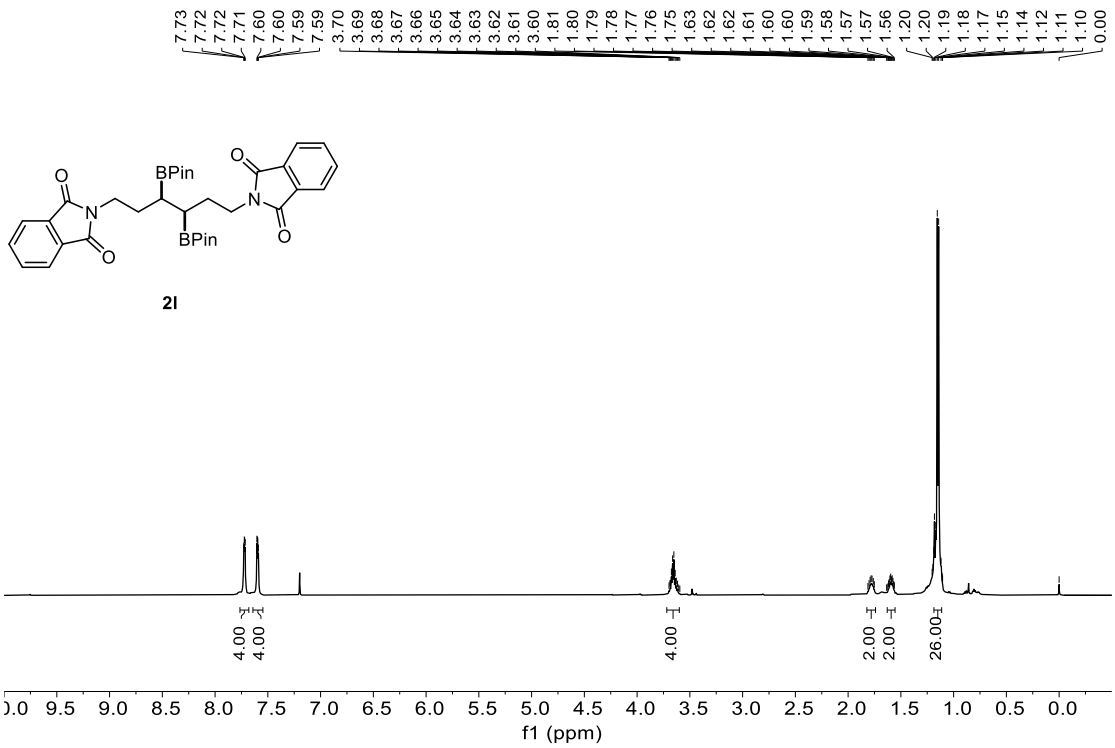
Compound **2k** ^{1}H NMR (400 MHz, $CDCl_3$)



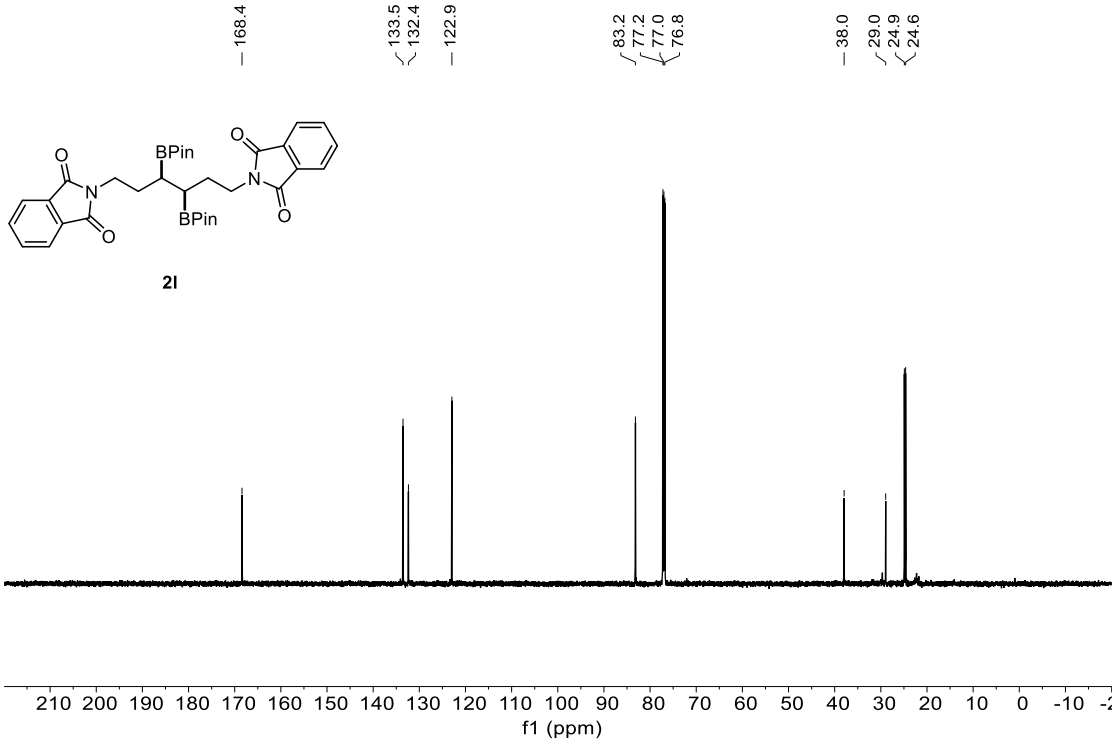
Compound **2k** ^{13}C NMR (101 MHz, $CDCl_3$)



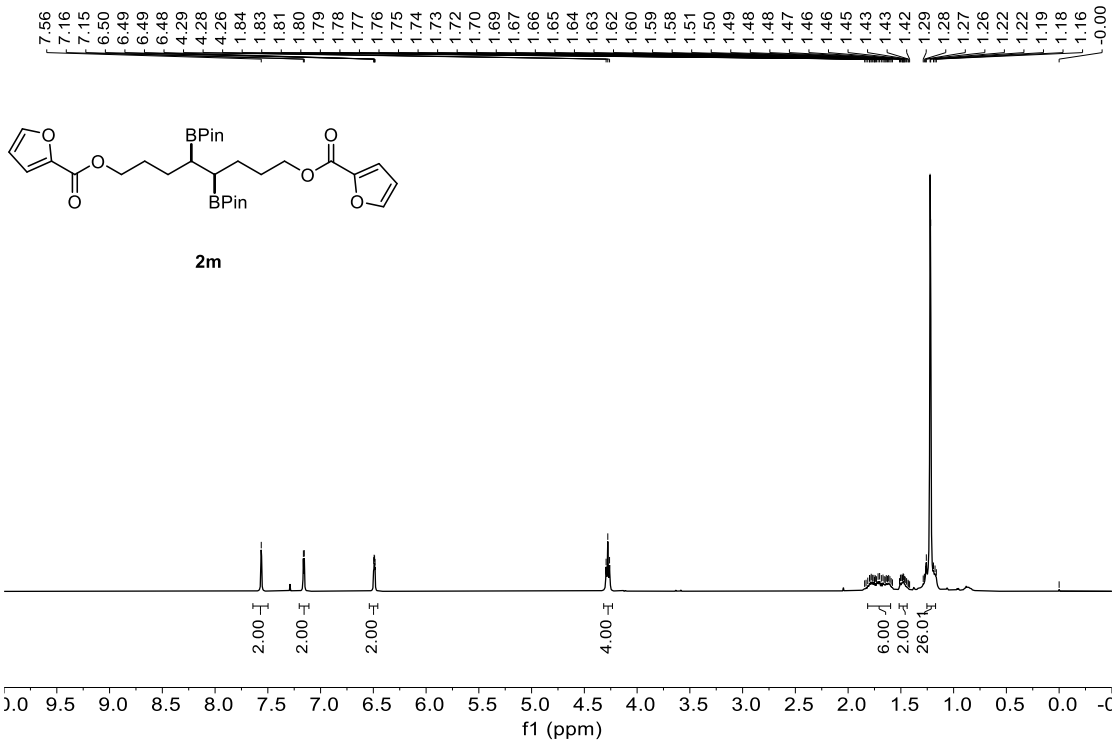
Compound **2l** ^{1}H NMR (600 MHz, $CDCl_3$)



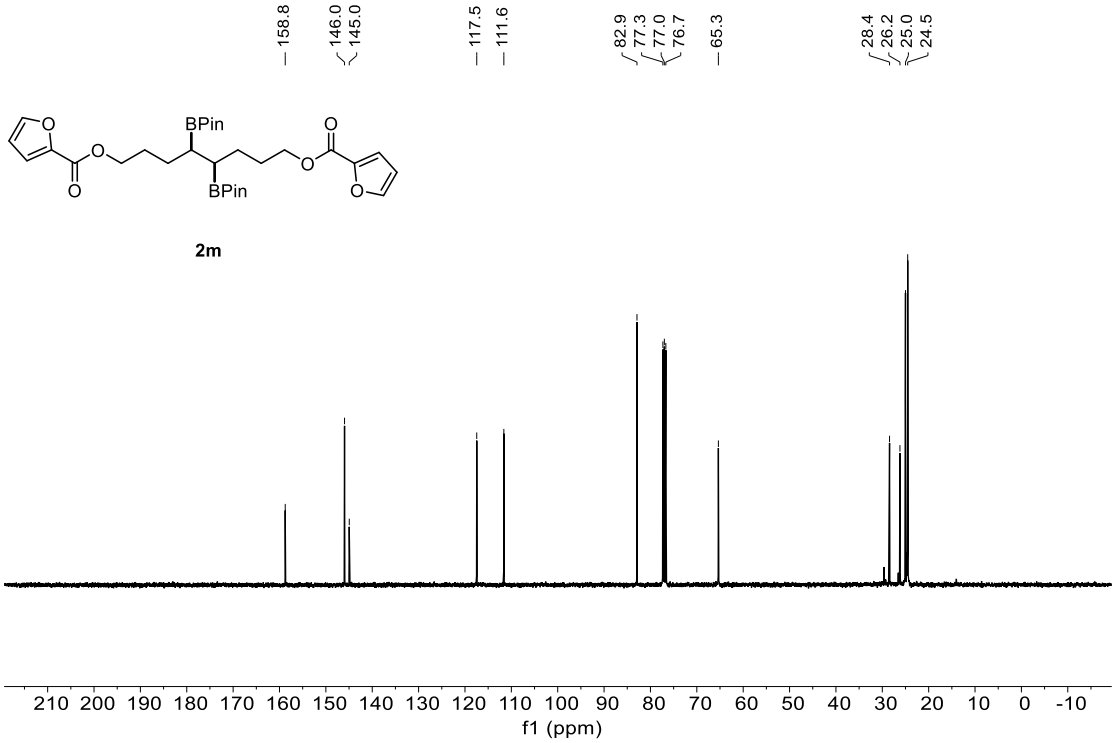
Compound **2l** ^{13}C NMR (151 MHz, $CDCl_3$)



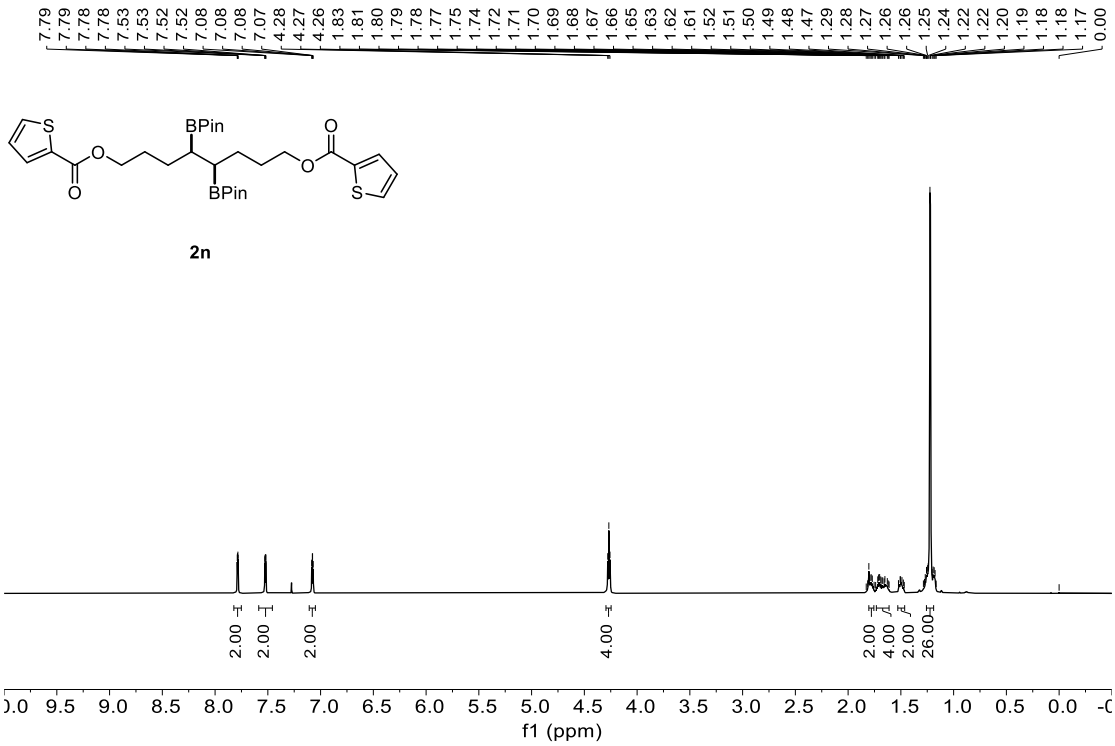
Compound **2m** ^{1}H NMR (400 MHz, $CDCl_3$)



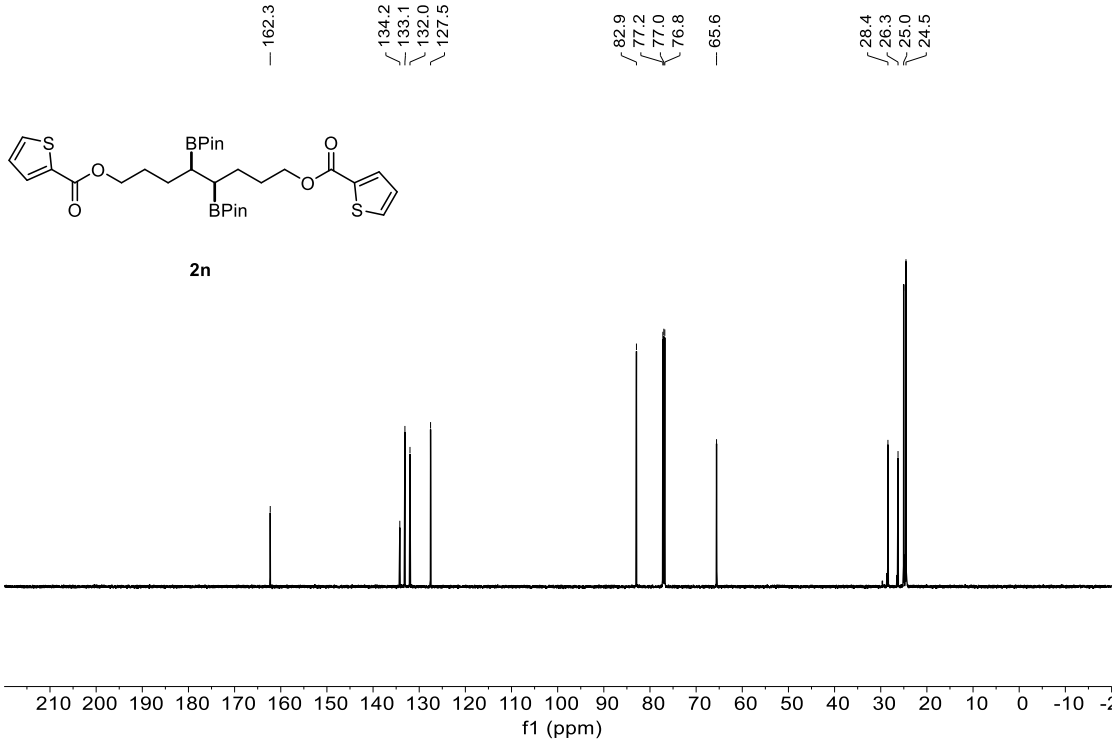
Compound **2m** ^{13}C NMR (101 MHz, $CDCl_3$)



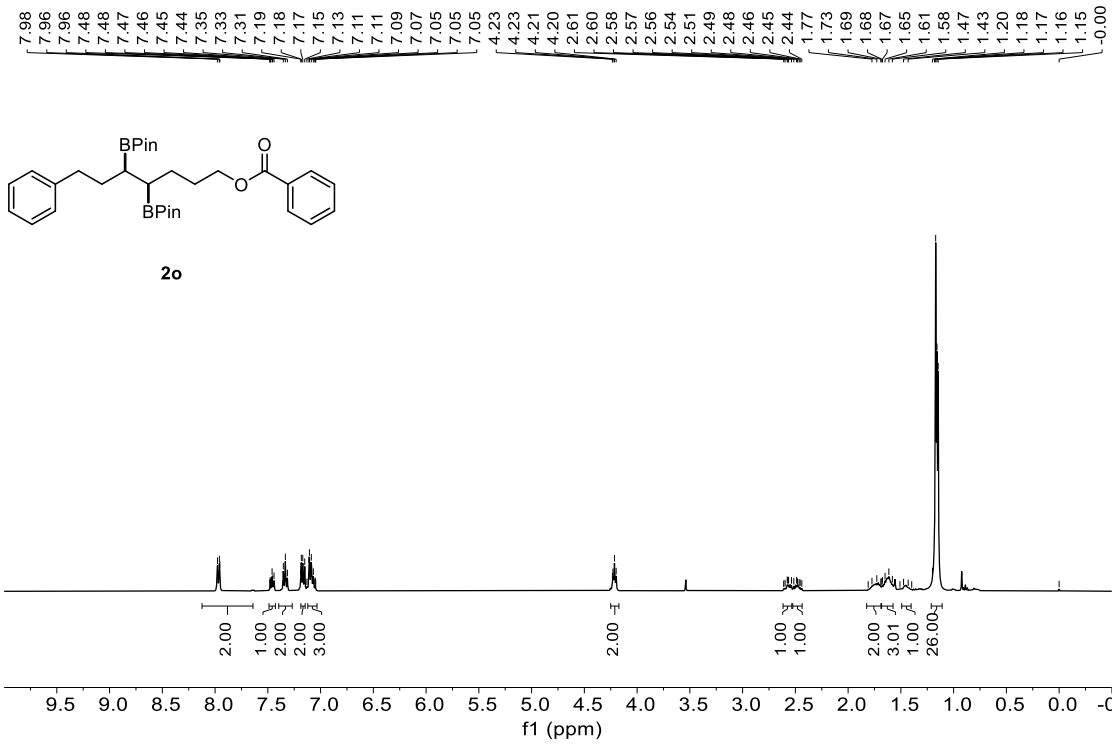
Compound **2n** ^{1}H NMR (600 MHz, $CDCl_3$)



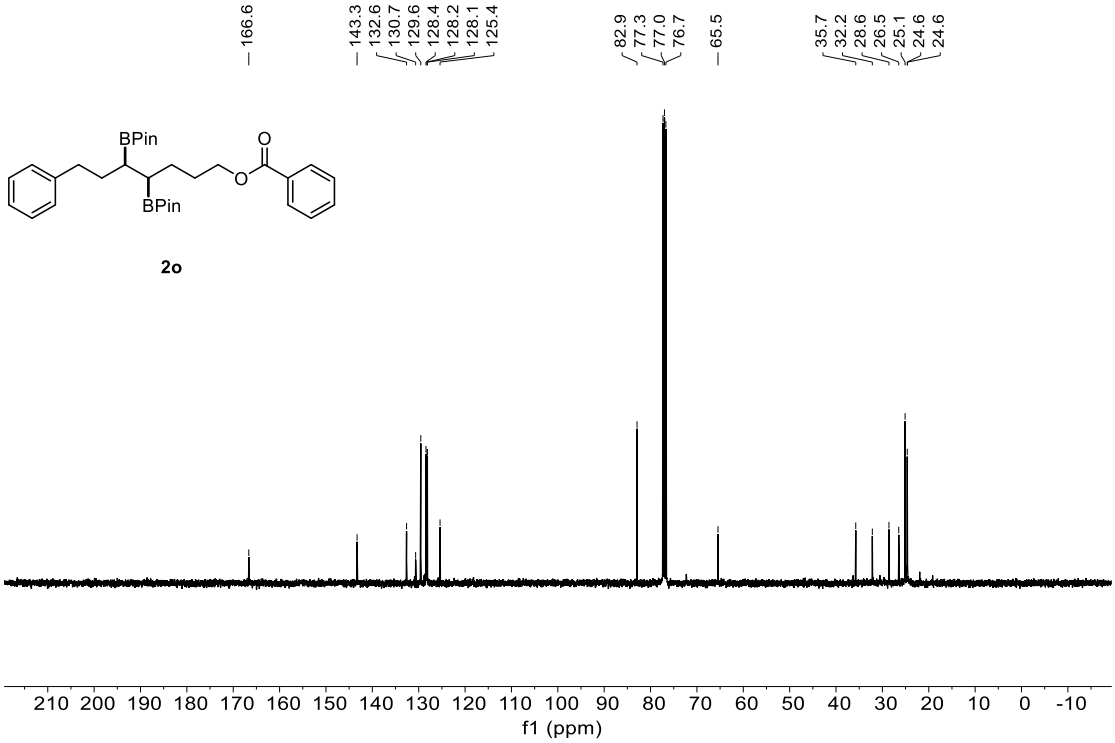
Compound **2n** ^{13}C NMR (151 MHz, $CDCl_3$)



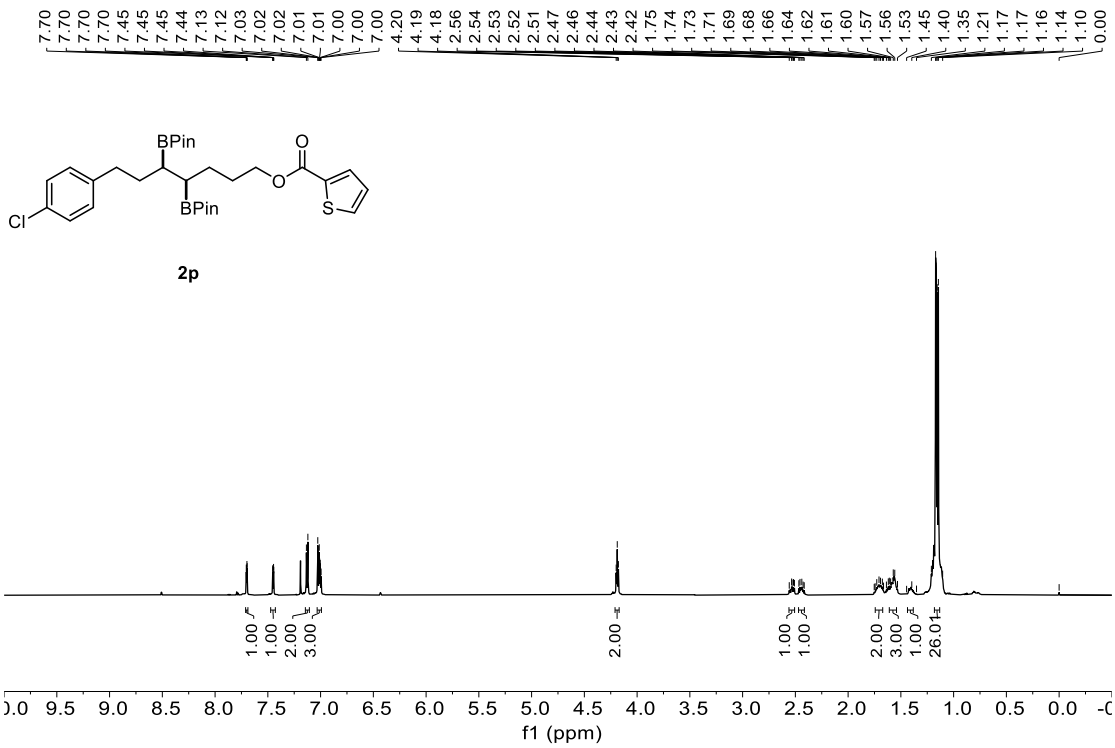
Compound **2o** ^{1}H NMR (400 MHz, $CDCl_3$)



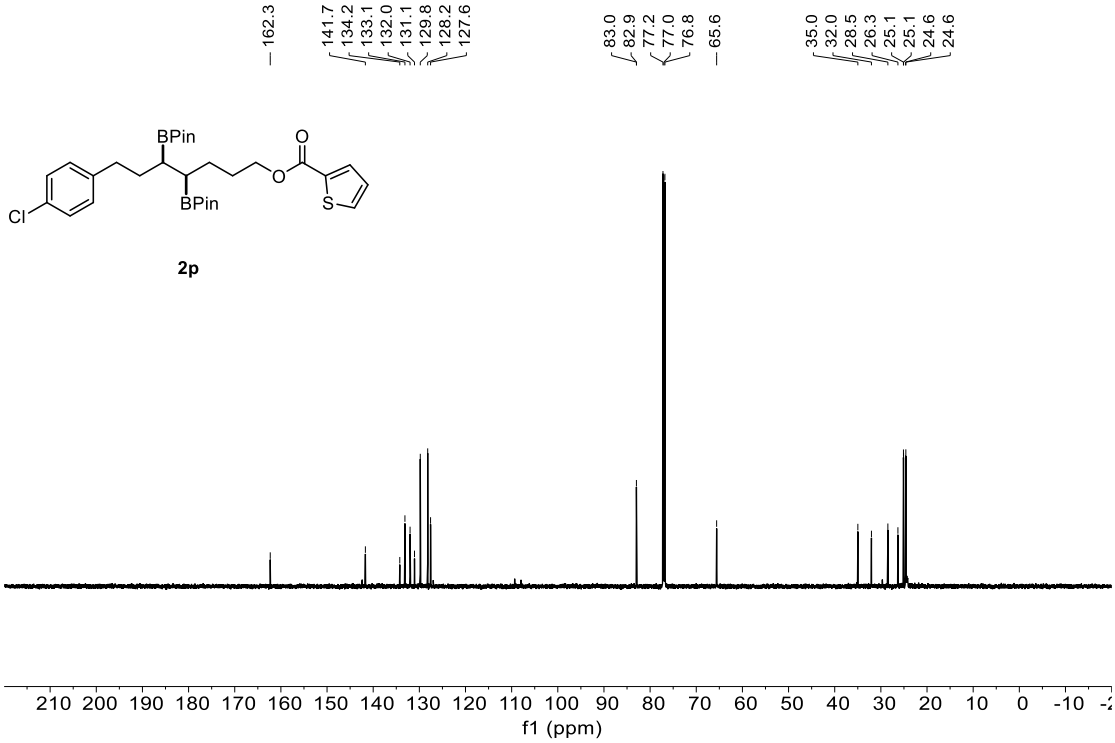
Compound **2o** ^{13}C NMR (101 MHz, $CDCl_3$)



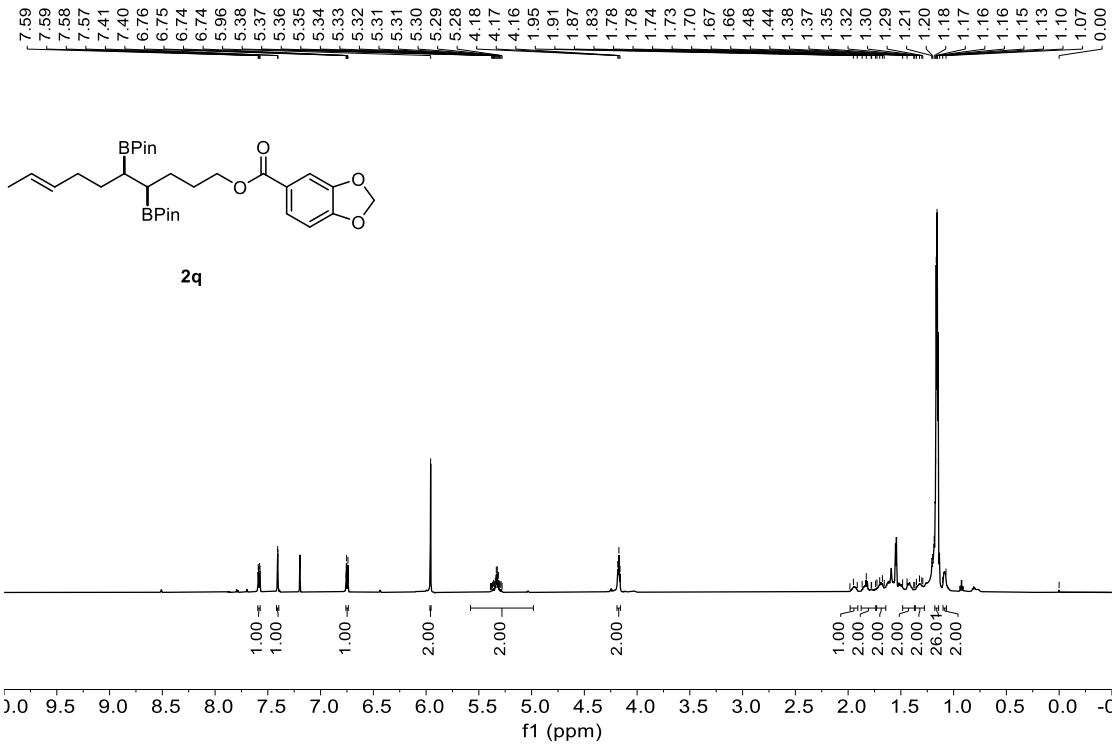
Compound **2p** ^{1}H NMR (600 MHz, $CDCl_3$)



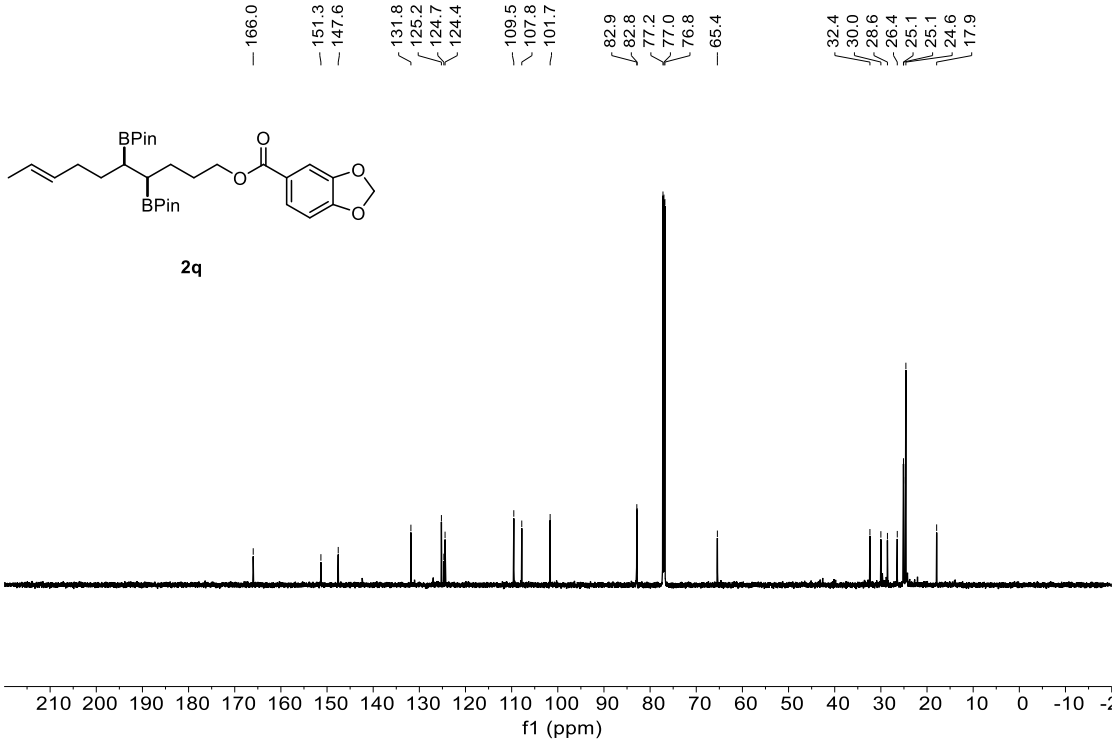
Compound **2p** ^{13}C NMR (151 MHz, $CDCl_3$)



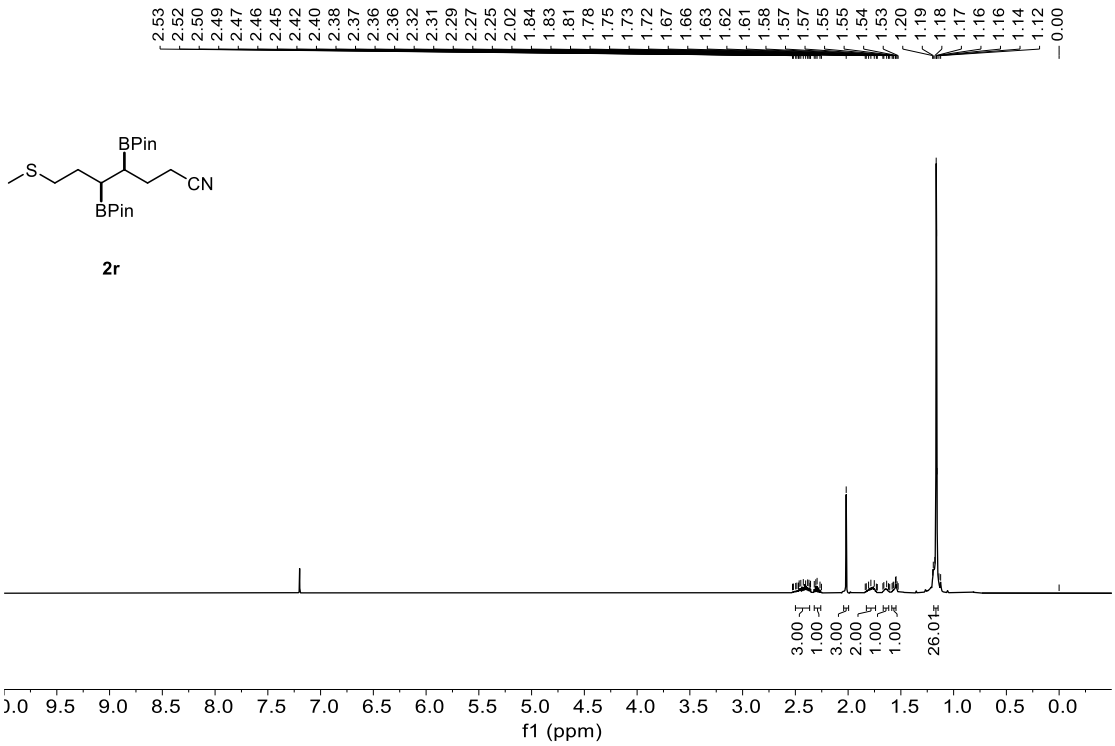
Compound **2q** ^{1}H NMR (600 MHz, $CDCl_3$)



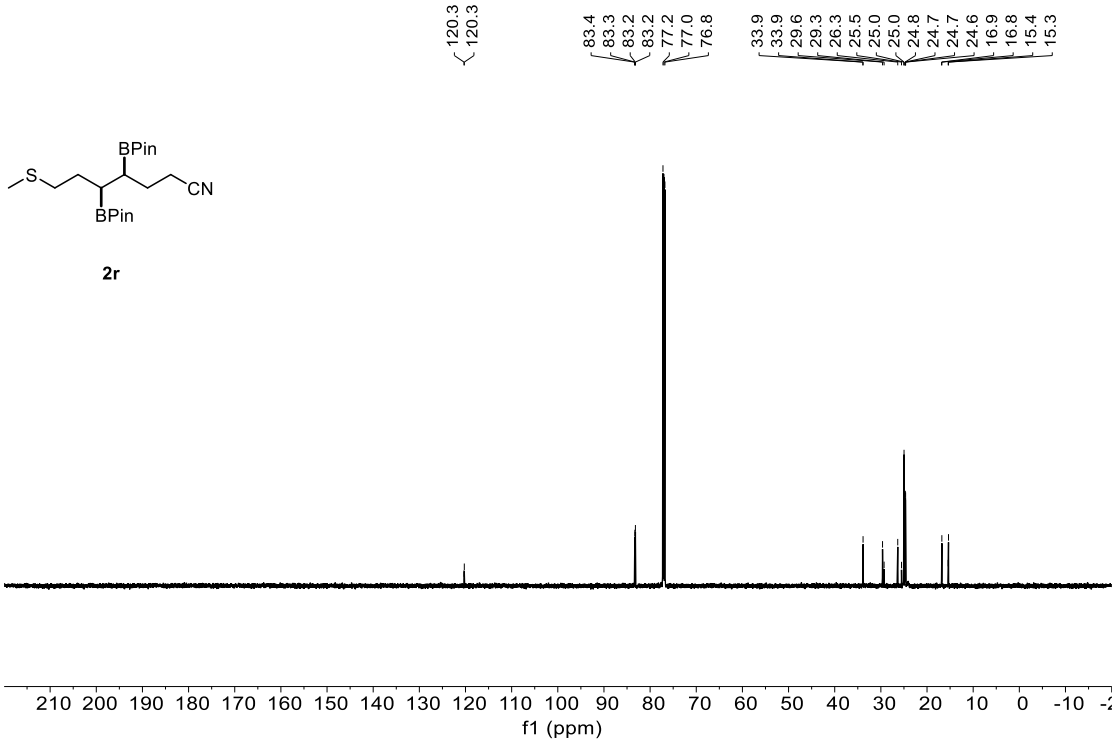
Compound **2q** ^{13}C NMR (151 MHz, $CDCl_3$)



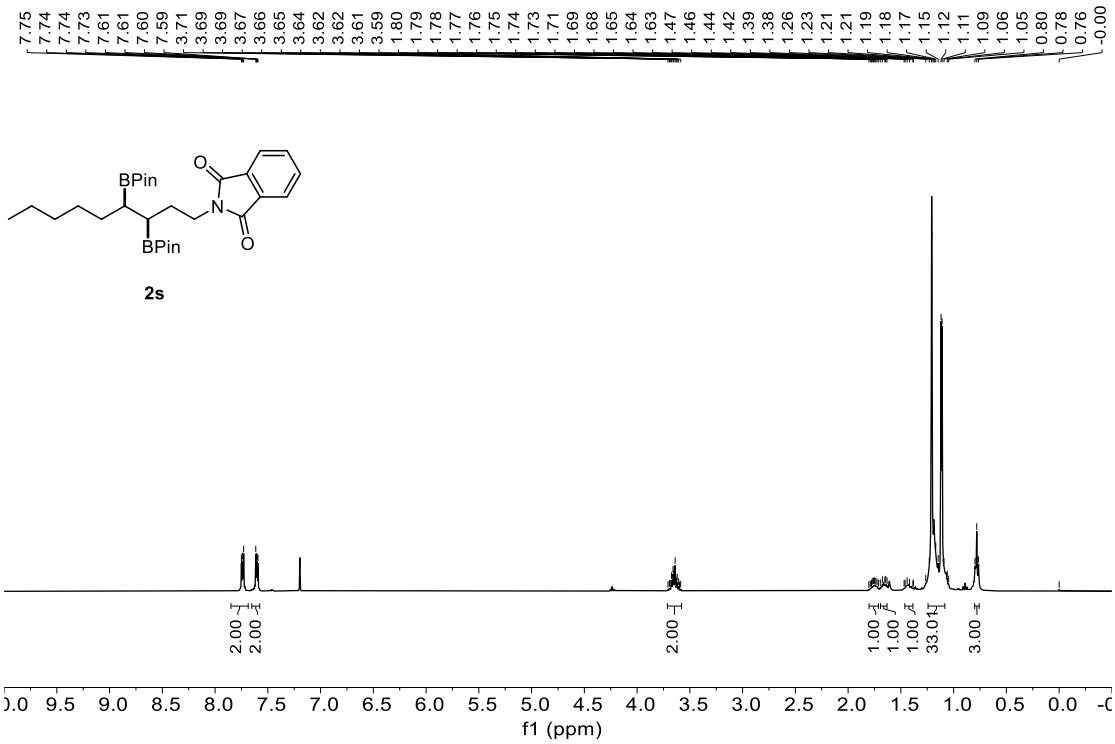
Compound **2r** ^{1}H NMR (600 MHz, $CDCl_3$)



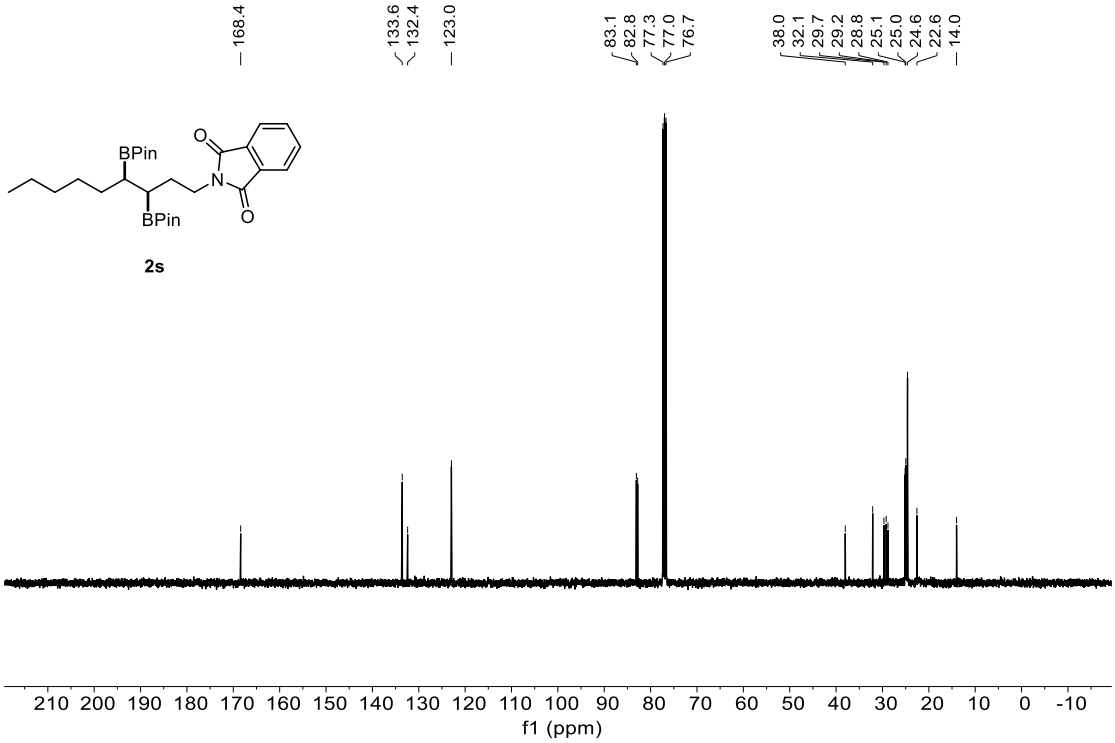
Compound **2r** ^{13}C NMR (151 MHz, $CDCl_3$)



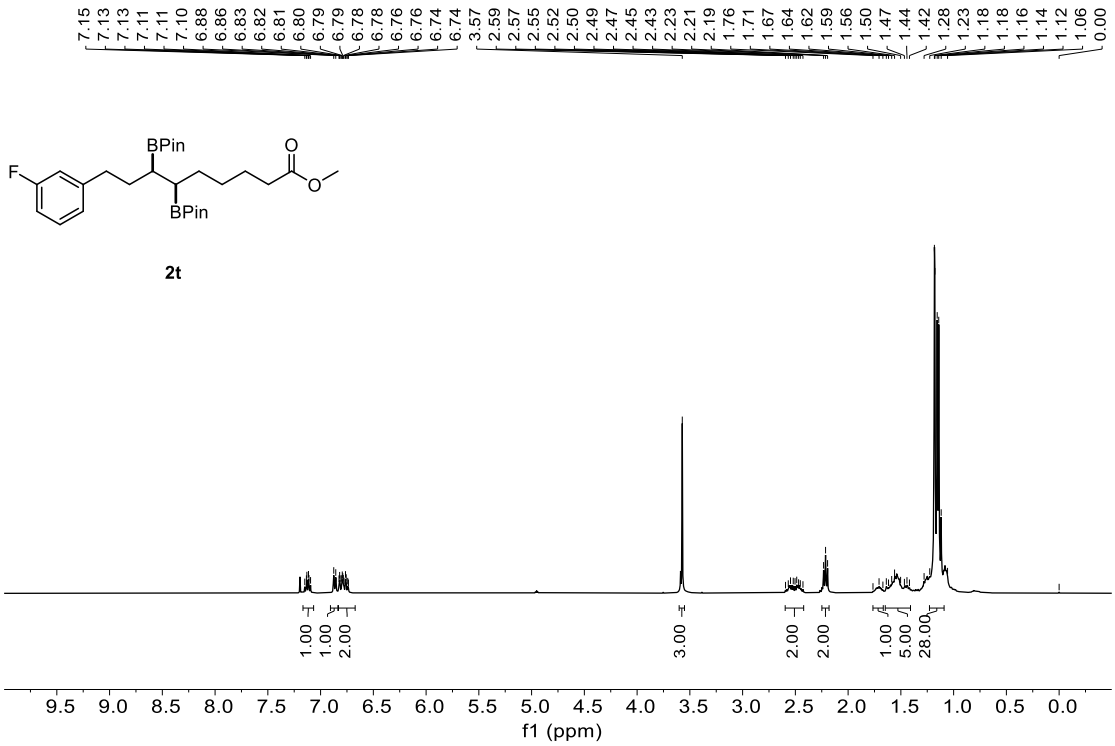
Compound **2s** ^{1}H NMR (400 MHz, $CDCl_3$)



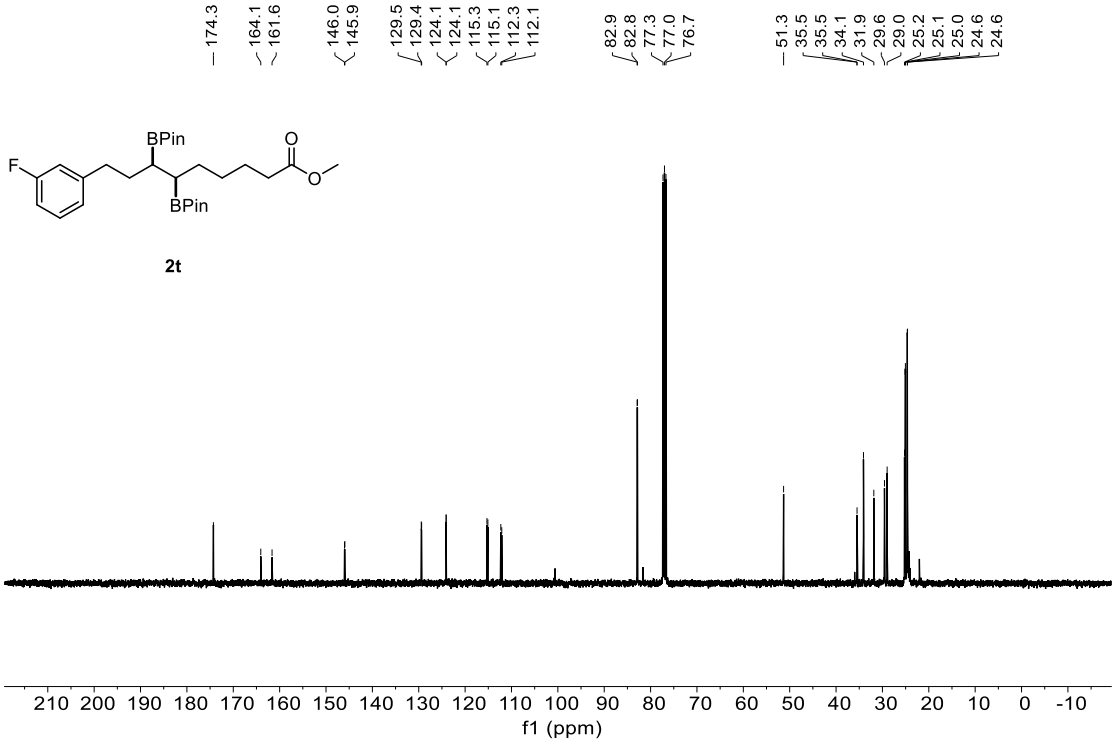
Compound **2s** ^{13}C NMR (101 MHz, $CDCl_3$)



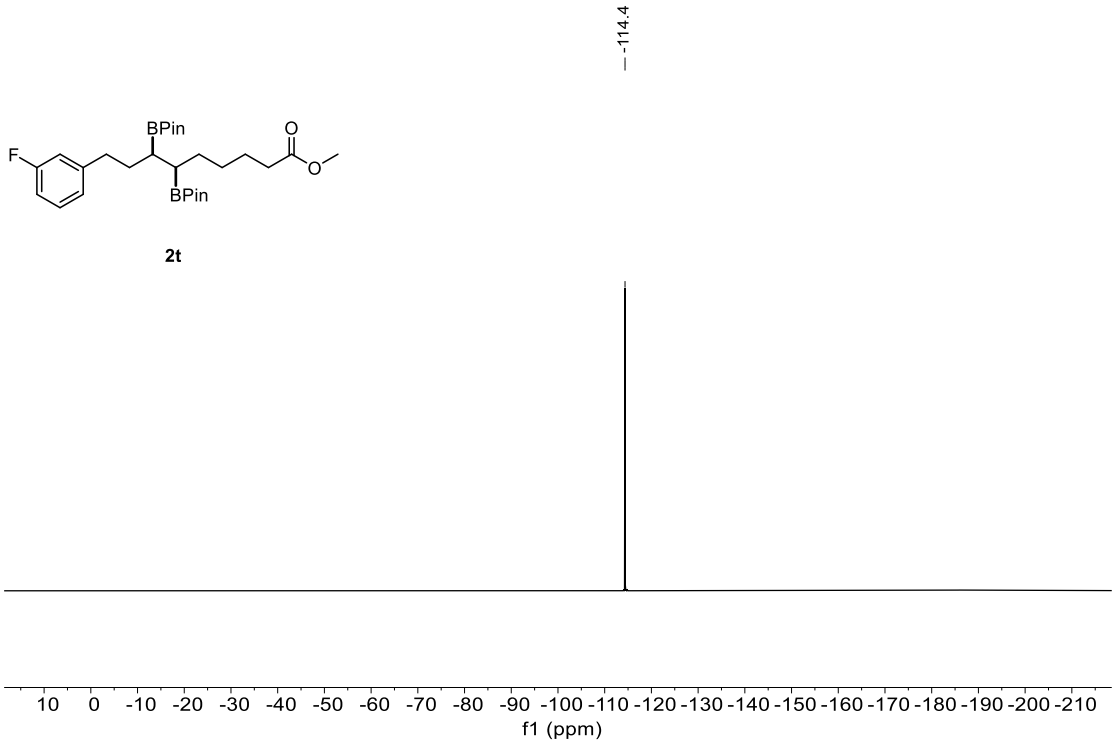
Compound **2t** ^{1}H NMR (400 MHz, $CDCl_3$)



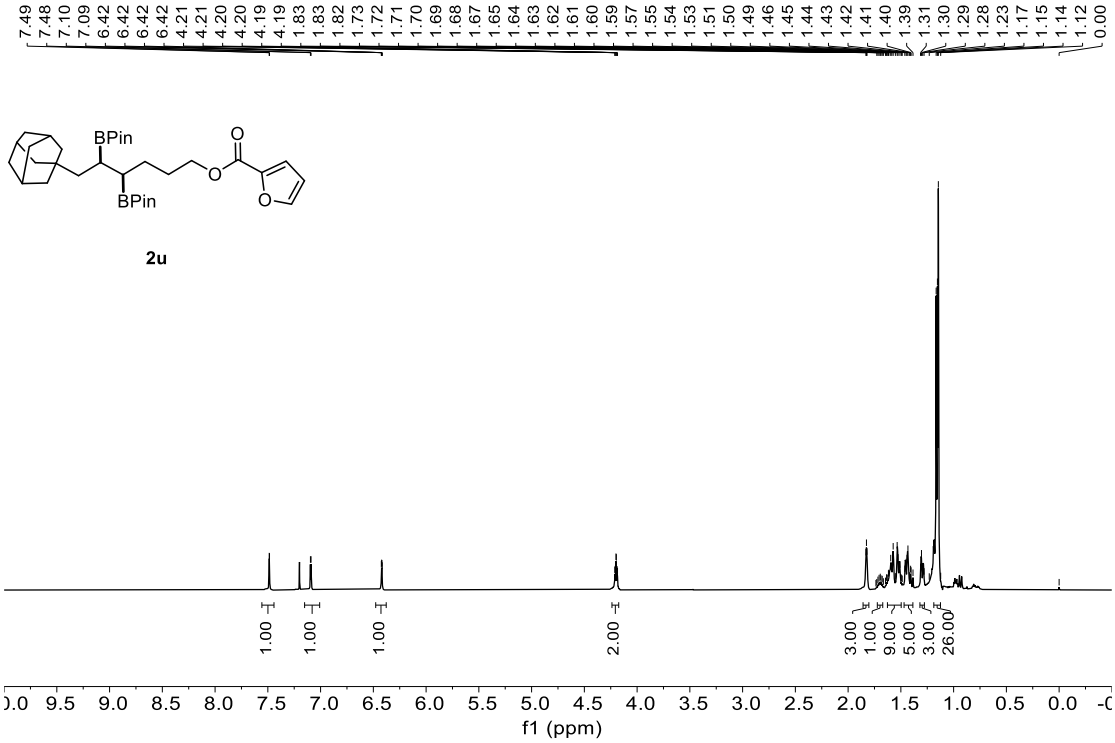
Compound **2t** ^{13}C NMR (101 MHz, $CDCl_3$)



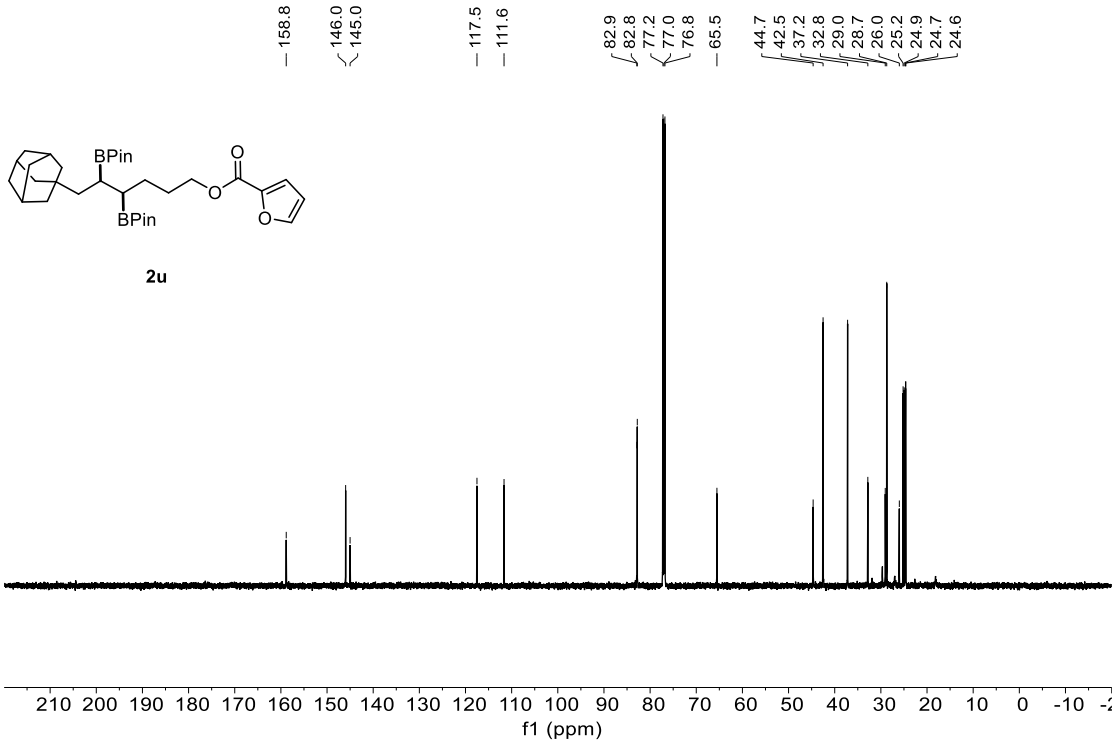
Compound **2t** ^{19}F NMR (376 MHz, $CDCl_3$)



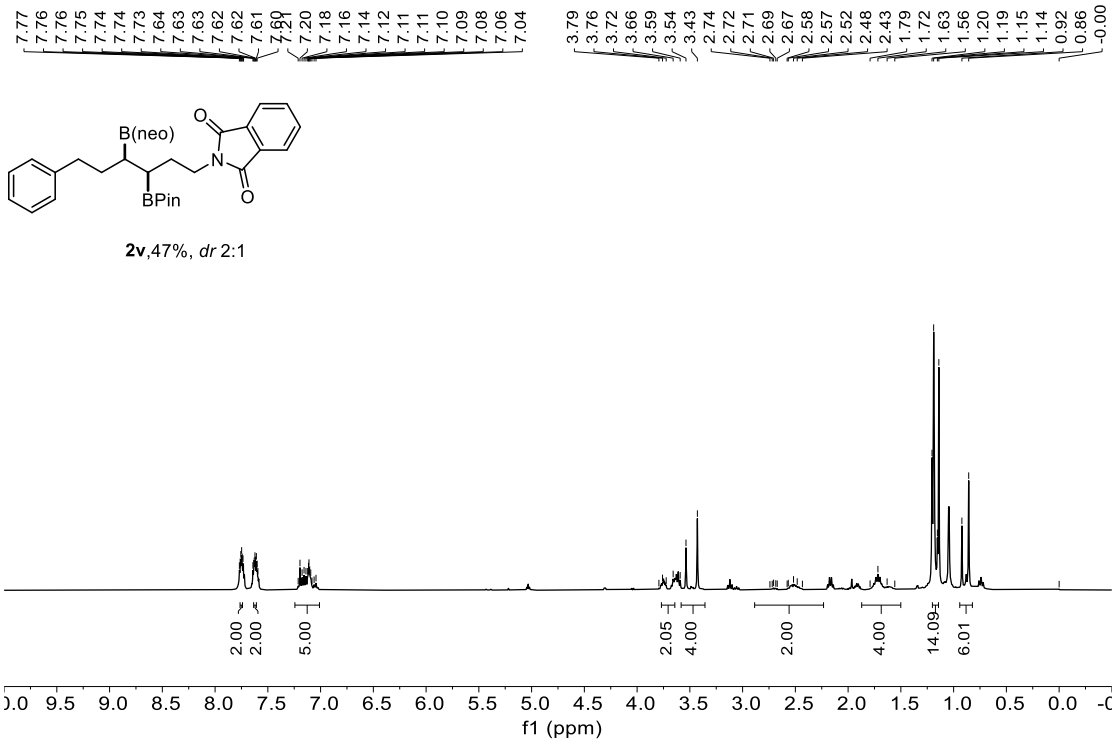
Compound **2u** ^{1}H NMR (600 MHz, $CDCl_3$)



Compound **2u** ^{13}C NMR (151 MHz, $CDCl_3$)

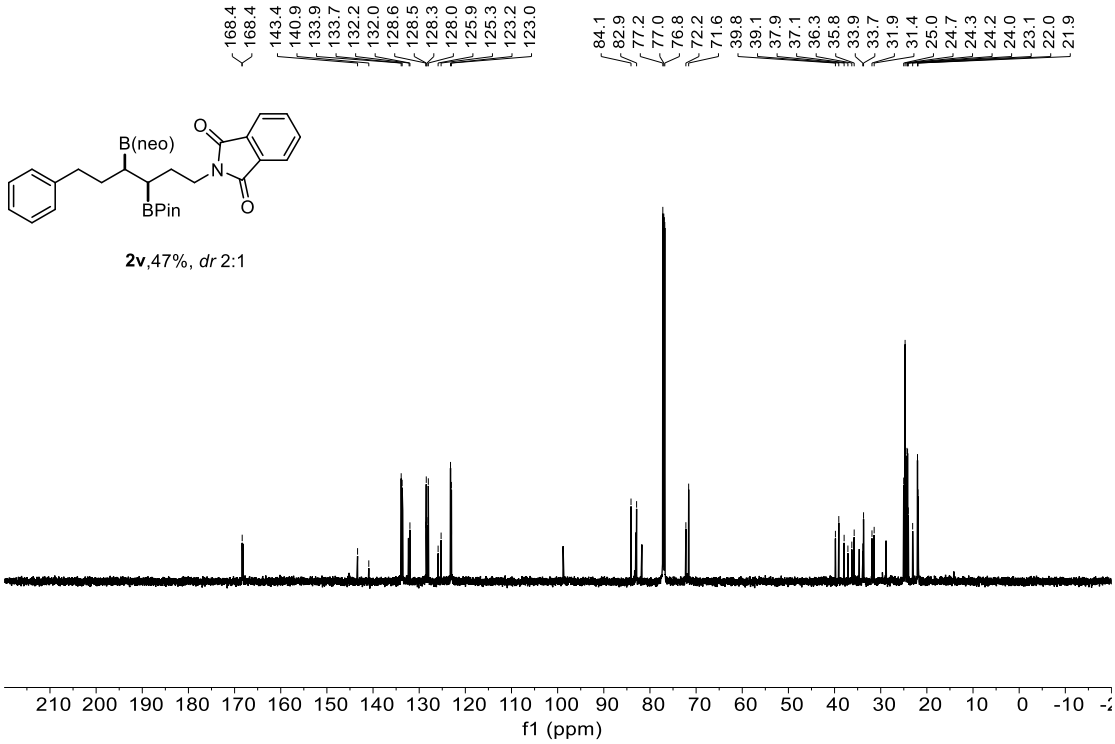


Compound **2v** ^{1}H NMR (400 MHz, $CDCl_3$)



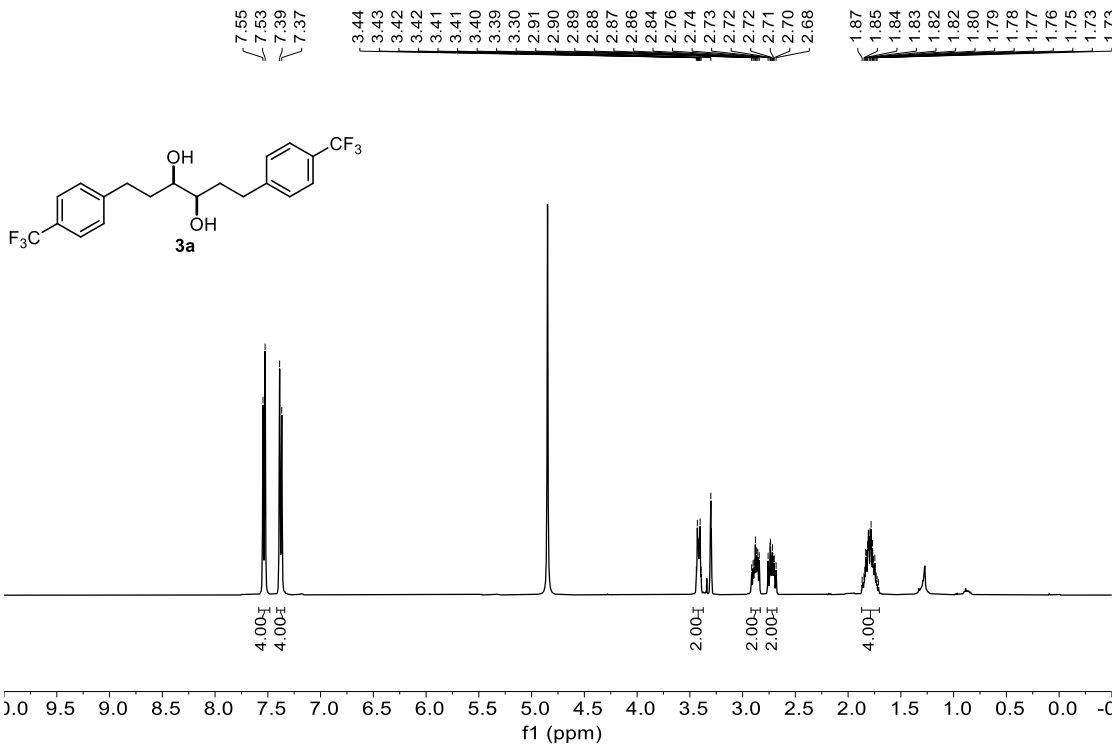
2v,47%, *dr* 2:1

Compound **2v** ^{13}C NMR (151 MHz, $CDCl_3$)

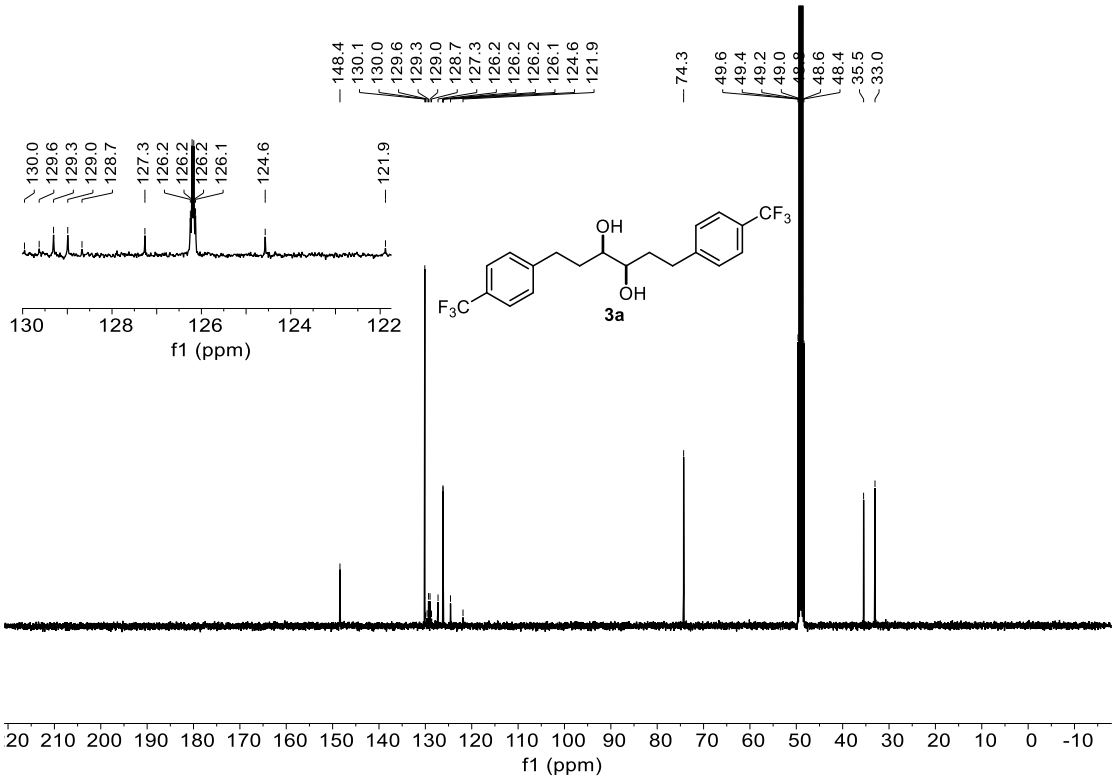


2v,47%, *dr* 2:1

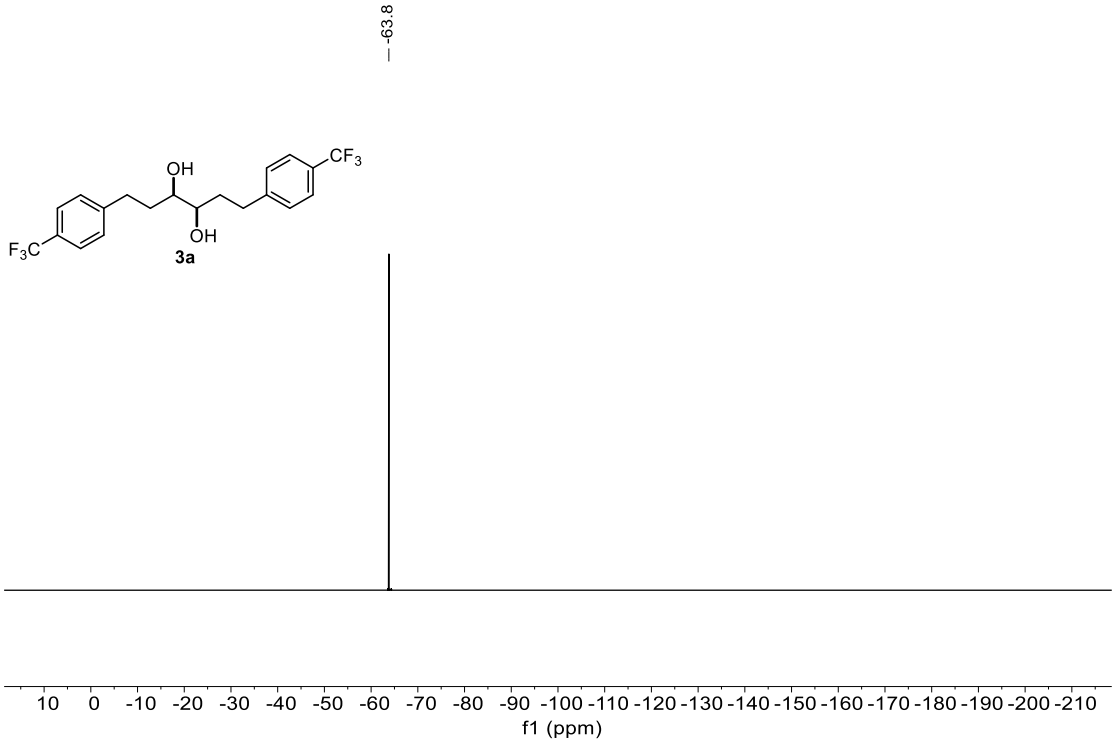
Compound **3a** ^{1}H NMR (400 MHz, CD_3OD)



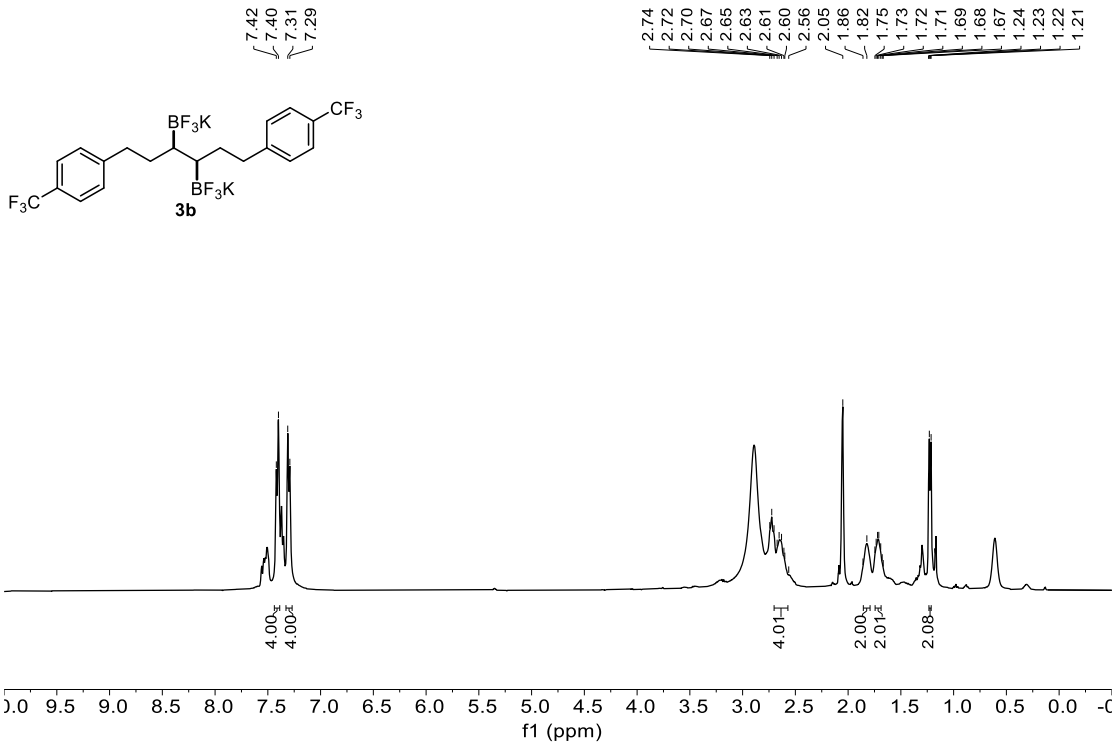
Compound **3a** ^{13}C NMR (101 MHz, CD_3OD)



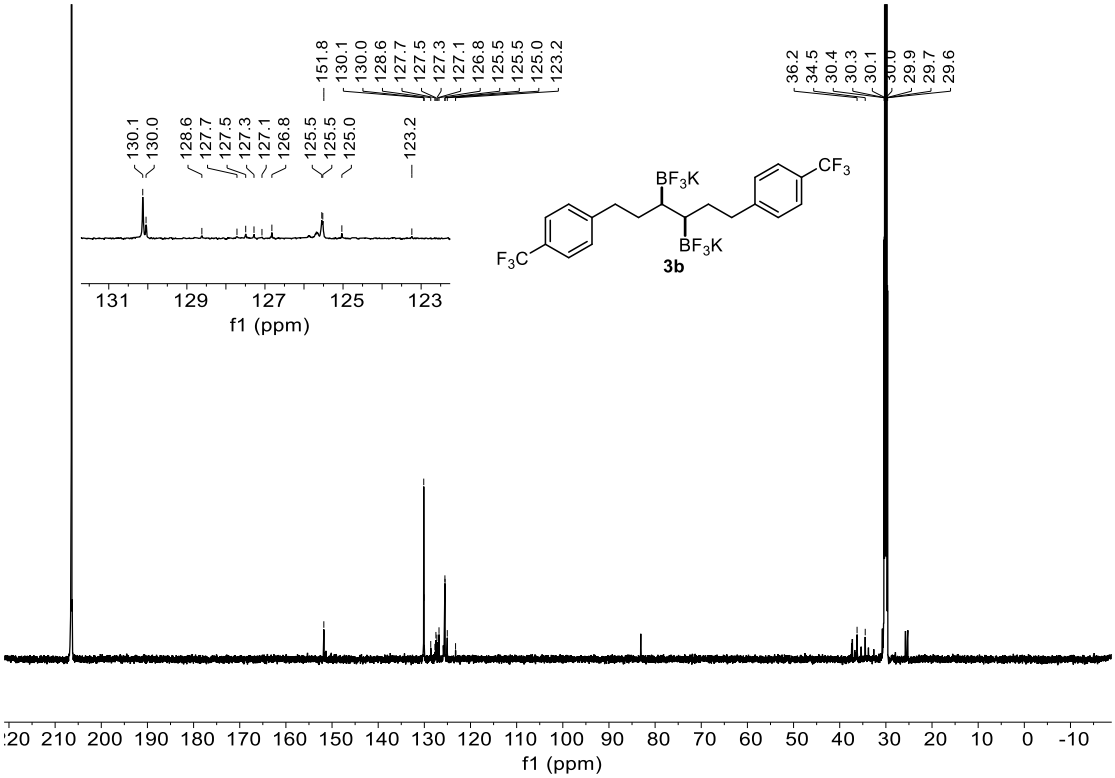
Compound **3a** ^{19}F NMR (376 MHz, CD_3OD)



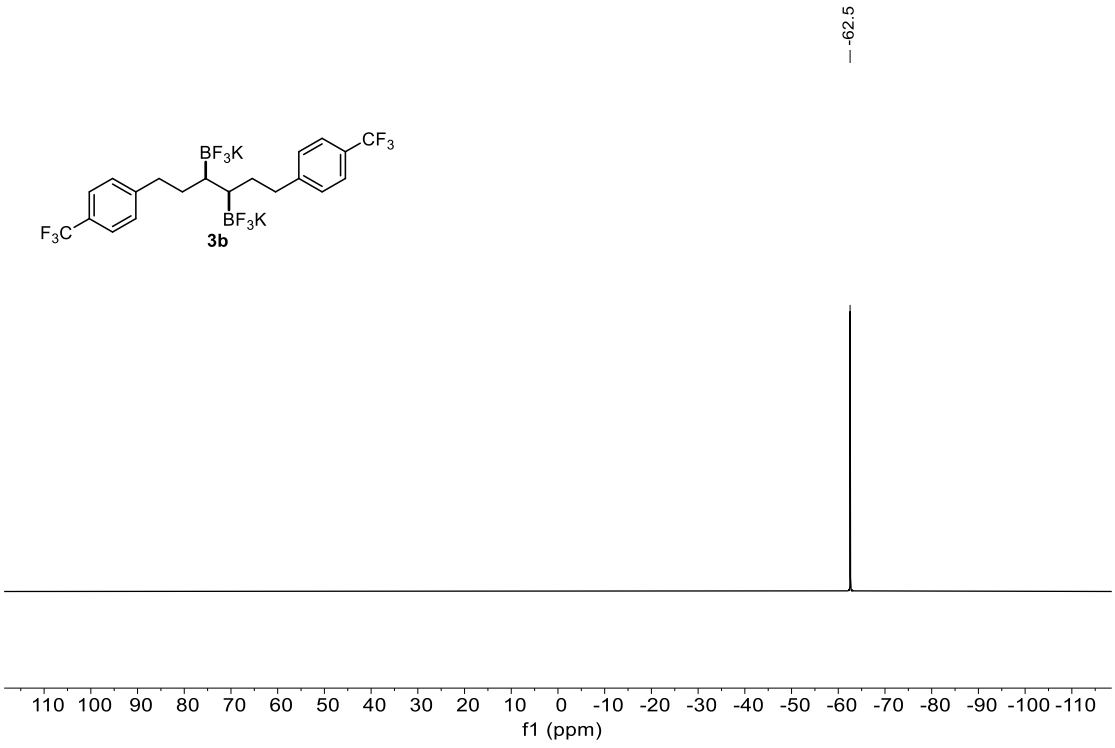
Compound **3b** ^{1}H NMR (400 MHz, Acetone)



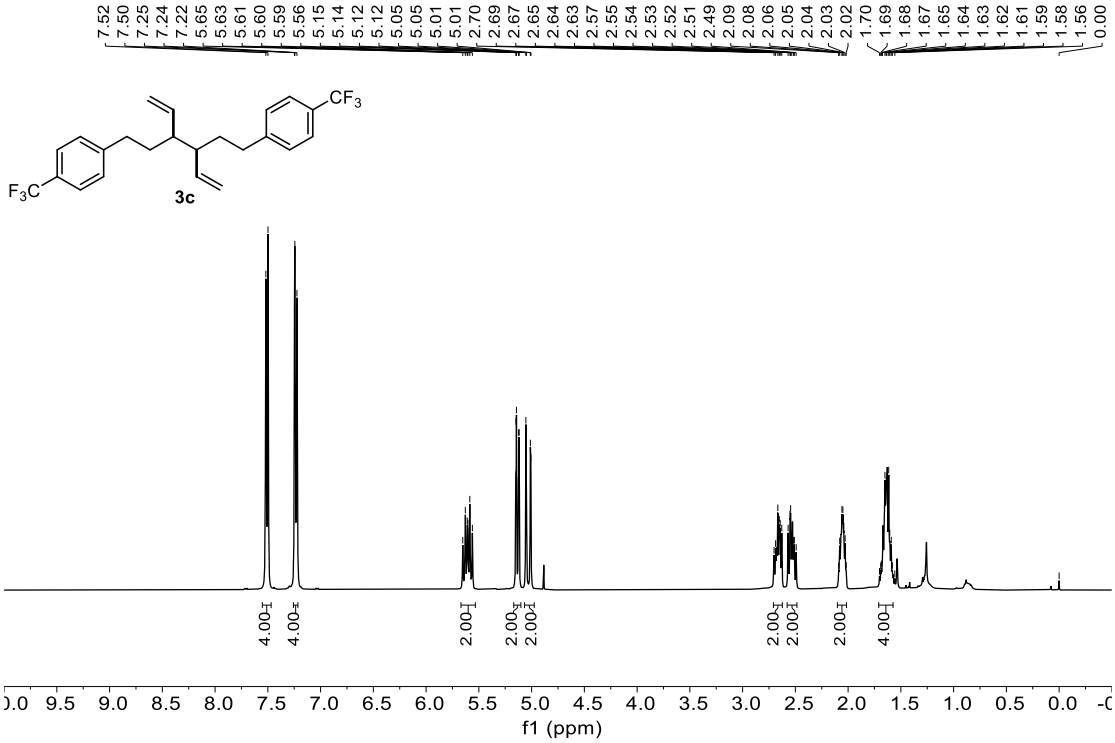
Compound **3b** ^{13}C NMR (151 MHz, Acetone)



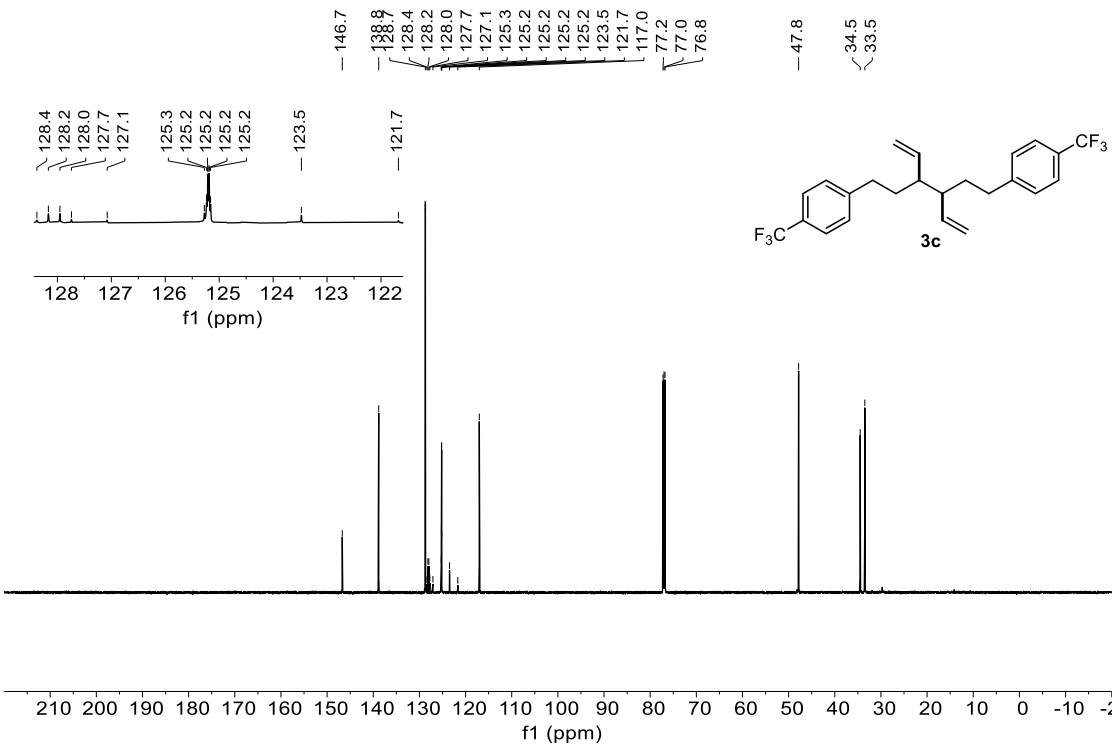
Compound **3b** ^{19}F NMR (376 MHz, Acetone)



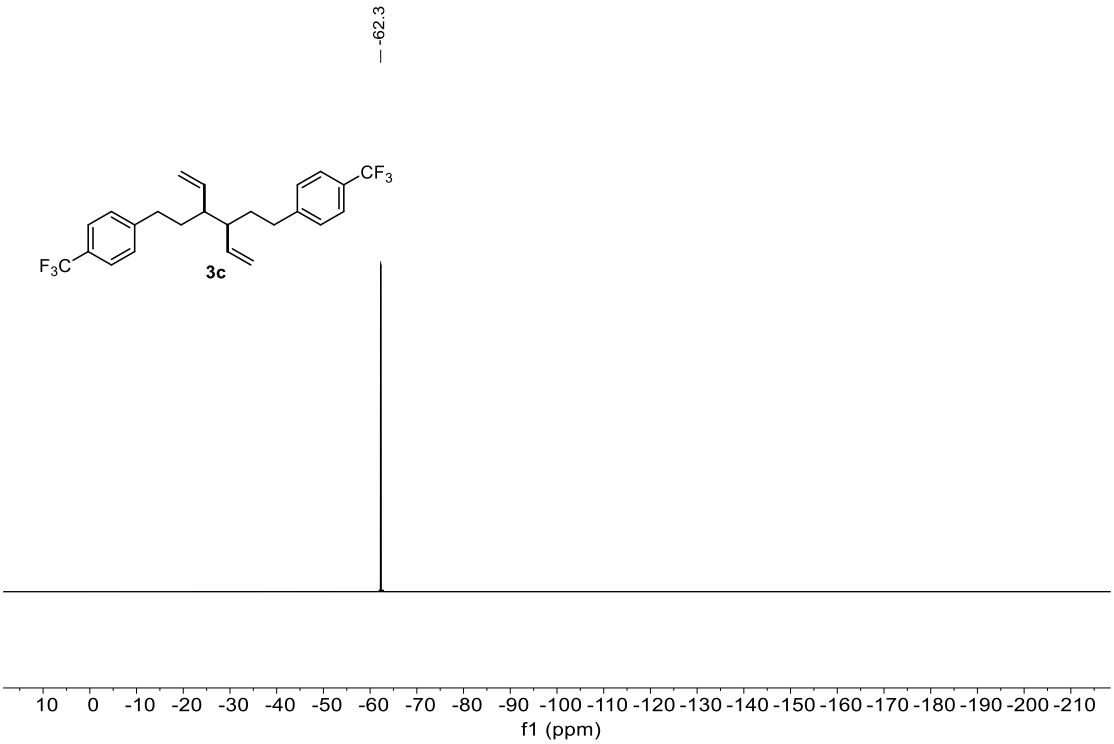
Compound **3c** ^{1}H NMR (400 MHz, $CDCl_3$)



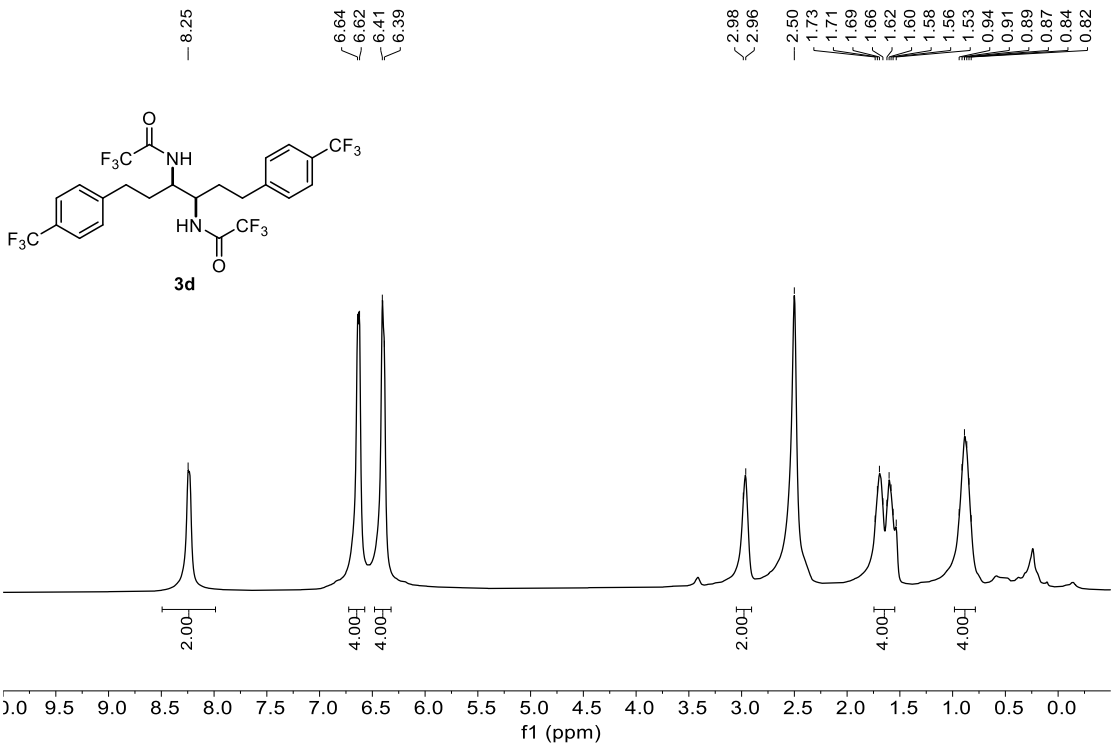
Compound **3c** ^{13}C NMR (151 MHz, $CDCl_3$)



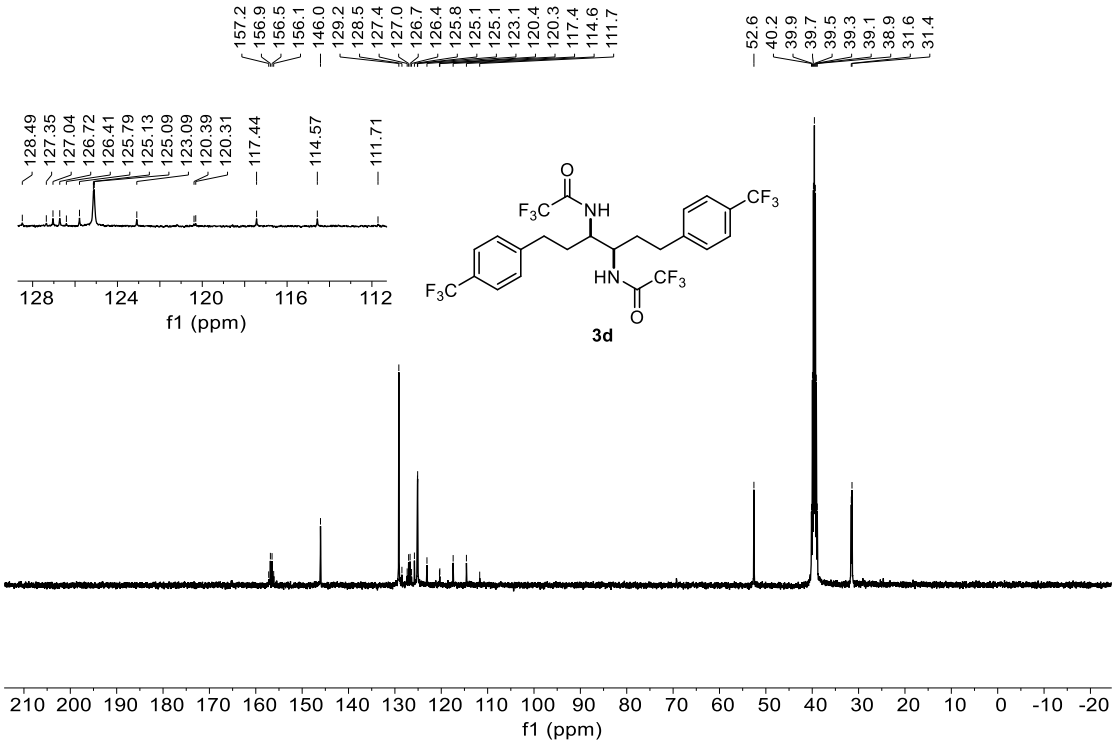
Compound **3c** ^{19}F NMR (376 MHz, $CDCl_3$)



Compound **3d** ^{1}H NMR (400 MHz, DMSO)



Compound **3d** ^{13}C NMR (101 MHz, DMSO)



Compound **3d** ^{19}F NMR (376 MHz, DMSO)