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Supporting Information

Copper-Catalyzed Triboration of Terminal Alkynes Using B_2pin_2: Efficient Synthesis of 1,1,2-Triborylalkenes

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SUPPORTING INFORMATION

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I. General Information

All reagents were purchased from Alfa-Aesar, Aldrich, ABCR or VWR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. B_2pin_2 was kindly provided by AllyChem Co. Ltd. (Dalian, China). HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Pure-Solv Solvent Purification System, and further deoxygenated by using the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. All manipulations in this paper were performed in an argon-filled glove box.

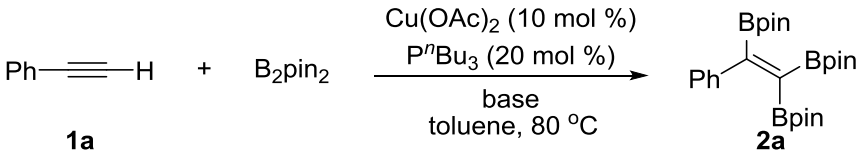
Products were purified on silica gel columns using $B(OH)_3$-impregnated SiO_2 to suppress over-adsorption on the silica gel. Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 40 °C.

GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 80 °C (2 min), 80 °C to 180 °C (20 °C min^{-1}), 180 °C to 280 °C (50 °C min^{-1}), 280 °C (5 min); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. Elemental analysis was performed on a Leco CHNS-932 Elemental Analyzer. High-resolution mass spectra were recorded using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe).

All NMR spectra were recorded at ambient temperature using Bruker DRX-300 (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz), or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz; ^{11}B, 160 MHz; ^{19}F, 471 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonance of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signal of the deuterated solvent ($CDCl_3$: 77.00 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as the external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

II. Optimization of the Reaction Conditions

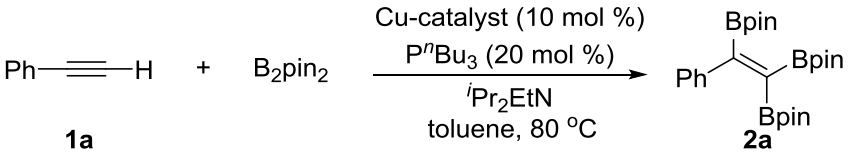
Table S1: Screening of bases for the triboration of alkynes.[a]



Entry	Base (1 equiv)	Product Yield **2a**[b]
1	4-picoline	21%
2	N,N-dimethylaniline	37%
3	DABCO	33%
4	LDA	-
5	-	28% (16%)
6	$^{i}Pr_2EtN$	45% (38%)
7	2,6-lutidine	32% (15%)
8	Et_3N	24%
9	$^{n}Pr_3N$	29%
10	$^{i}Pr_2EtN$ + N,N-dimethylaniline	36% (31%)
11	NaOAc	<10%
12	Na_2CO_3	<10%
13	Cs_2CO_3	0
14	NaOH	0
15	KOH	0
16	K_3PO_4	<10%

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), $P^{n}Bu_3$ (20 mol %), base (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. DABCO: 1,4-diazabicyclo[2.2.2]octane; LDA: lithium diisopropylamide.

Table S2: Screening of Cu-catalysts for the triboration of alkynes.[a]

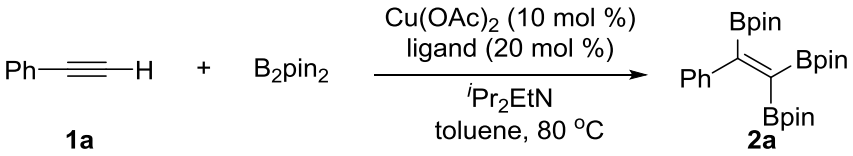


1a **2a**

Entry	Catalyst (10 mol %)	Product Yield **2a**[b]
1	$CuBr_2$	0
2	$Cu(OTf)_2$	0
3	$Cu(NO_3)_2 \cdot 3H_2O$	0
4	$CuSO_4$	0
5	$Cu(acac)_2$	0
6	$CuCl_2$	0
7[c]	$CuCl_2$	42%
8[d]	$CuCl_2$	<10%
9	CuOAc	29% (31%)
10	CuI	0
11	CuCl	0
12	Cu_2O	0

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), Cu-catalyst (10 mol %), P^{n}Bu$_3$ (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. [c] 20 mol % of KOAc added. [d] 20 mol % of KOAc and 20 mol % of 18-Crown-6 added.

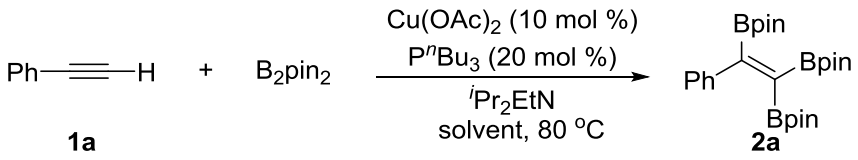
Table S3: Screening of ligands for the triboration of alkynes.[a]



Entry	Ligand (20 mol %)	Product Yield **2a**[b]
1	PPh_3	18%
2	Phen	< 10%
3	BPY	0
4	TFP	25%
5	P(p-tolyl)$_3$	14%
6	P(o-tolyl)$_3$	0
7	P(1-naphthyl)$_3$	0
8	P^{t}Bu$_3$ (1M in toluene)	< 10%
9	DPPP	13%
10	Xantphos	0
11	DPPF	17%
12	TBP	0
13	Xphos	0
14	PCy_3	33%

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), ligand (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Phen: 1,10-phenanthroline; BPY: 2,2'-bipyridine; TFP: tri(2-furyl)phosphine; DPPP: 1,3-bis(diphenylphosphino)propane; DPPF: 1,1′- bis(diphenylphosphinferrocene); TBP: tris(hydroxymethyl)propane bicyclic phosphite.

Table S4: Screening of solvents for the triboration of alkynes.[a]

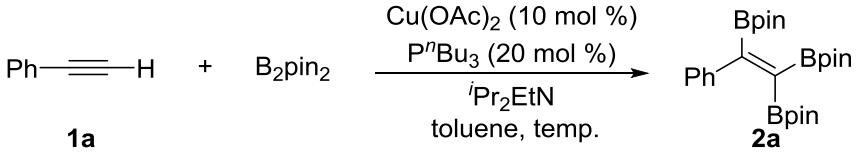


1a **2a**

Entry	Solvent (1 mL)	Product Yield **2a**[b]
1	ethyl acetate	15%
2	MeCN	< 10%
3	MTBE	35%
4	THF	10%
5	hexane	16%
6	1,2-dioxane	14%
7	diethyl ether	30%
8	acetone	0

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), solvent (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. MTBE: methyl tert-butyl ether; THF: tetrahydrofuran

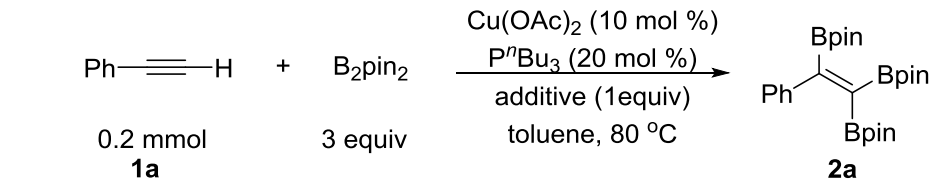
Table S5: Screening of temperatures for the triboration of alkynes.[a]

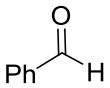
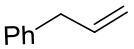
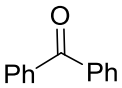


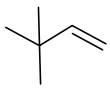
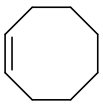
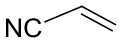
1a **2a**

Entry	T/ °C	Product Yield **2a**[b]
1	40	< 10%
2	60	14%
3	90	31%
4	100	31%
5	110	26%

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), DIPEA (1 equiv), B_2pin_2 (3 equiv), toluene (1 mL), 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard.



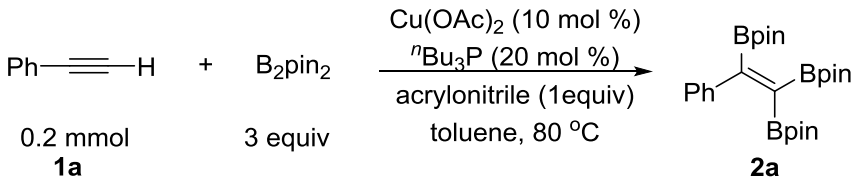
Additive		$(CHO)_n$				
Yield **2a**	17%	23%	16%	21%	38%	48%

Additive						
Yield **2a**	39%	34%	44%	59% (50%)[b]	57% (57%)[b]	69% (66%)[b]

[a] Standard conditions: In an argon-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), B_2pin_2 (3 equiv), additives (1 equiv), toluene (1 mL), at 80 °C for 24 h. [b] The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses.

Scheme S1: Screening of additives for the triboration of alkynes.

Table S6: Screening of other conditions for the triboration of alkynes.[a]



0.2 mmol **1a** | 3 equiv | **2a**

Entry	Catalyst	Ligand	Time/ h	T/ °C	Product Yield **2a**[b]
1[c]	$Cu(OAc)_2$	P^nBu_3	24	80	42% (37%)
2	$Cu(OAc)_2$	P^nBu_3	14	80	49%
3	$Cu(OAc)_2$	P^nBu_3	14	r.t	0
4	$Cu(OAc)_2$	P^nBu_3	14	60	22%
5	$Cu(OAc)_2$	P^nBu_3	12	80	47% (44%)
6	$Cu(OAc)_2$	P^nBu_3	12	90	38%
7	$Cu(OAc)_2$	P^nBu_3	12	100	42%
8	$Cu(OAc)_2$	--	12	80	0
9	--	P^nBu_3	12	80	0
10	$Cu(OAc)_2$	P^nBu_3	10	80	(60%)
11	$Cu(OAc)_2$	P^nBu_3	8	80	(51%)
12	$Cu(OAc)_2$	P^nBu_3	6	80	(52%)
13	$Cu(OAc)_2$	P^nBu_3	5	80	(52%)
14	$Cu(OAc)_2$	P^nBu_3	4	80	78% (73%)
15	$Cu(OAc)_2$	P^nBu_3	3	80	(39%)
16	$Cu(OAc)_2$	P^nBu_3	2	80	(60%)
17[d]	$Cu(OAc)_2$	P^nBu_3	4	80	(31%)
18[e]	$Cu(OAc)_2$	P^nBu_3	4	80	67% (59%)

[a] Standard conditions: In an Ar-filled glove box, **1a** (0.2 mmol, 1 equiv), $Cu(OAc)_2$ (10 mol %), P^nBu_3 (20 mol %), B_2pin_2 (3 equiv), acrylonitrile (1 equiv), toluene (1 mL). [b]The product yield was determined by GC-MS using *n*-dodecane as the internal calibration standard. Isolated yields are given in parentheses. [c] $^iPr_2EtN$ (1 equiv). [d] Without acrylonitrile. [e] P^nBu_3 (10 mol %)

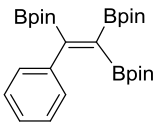
III. Substrate Scope

Experimental procedures

General procedure: In a glove box, to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, $Cu(OAc)_2$ (10 mol %, 3.6 mg, 0.02 mmol), B_2pin_2 (3 equiv, 152.4 mg, 0.6 mmol) and toluene (1 mL) were added. Then, phenylacetylene **1a** (20.4 mg, 22 µL, 0.2 mmol), acrylonitrile (10.6 mg, 13 µL, 0.2 mmol) and P^nBu_3 (8.1 mg, 9.9 µL, 0.04 mmol) were added in that order and the tube was sealed with a crimped septum cap. The reaction was heated at 80 °C under argon for the indicated amount of time. The reaction mixture was then diluted with Et_2O (4 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was purified by column chromatography on silica gel (pentane: ethyl acetate = 25:1).

Characterization data for products

2,2',2''-(2-phenylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a)



Isolated yield: 73%

White solid, m.p: 244.8 °C. Its spectroscopic data are consistent with a literature report.[1]

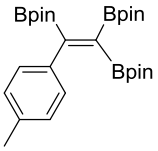
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 1.30 (s, 12H), 1.27 (s, 12H), 1.08 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.2, 127.7, 127.6, 126.6, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.9.

HRMS (ASAP): m/z for $C_{26}H_{42}B_3O_6$ [M+H$^+$] calcd: 483.3255, found: 483.3245

2,2',2''-(2-(p-tolyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b)



Isolated yield: 72%

White solid, m.p: 230.9 °C. Its spectroscopic data are consistent with a literature report.[1]

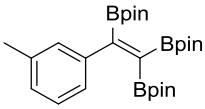
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 2.29 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.3, 136.3, 128.3, 127.6, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_6$ [M+H$^+$] calcd: 497.3412, found: 497.3402

2,2',2''-(2-(m-tolyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c)



Isolated yield: 58%

White solid, m.p: 230.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.1 – 7.1 (m, 1H), 7.1 – 7.1 (m, 2H), 7.0 – 7.0 (m, 1H), 2.28 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.09 (s, 12H).

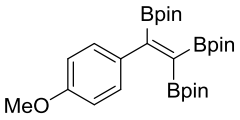
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.1, 136.8, 128.5, 127.5, 127.5, 124.7, 83.8, 83.4, 83.1, 24.9, 24.8, 24.5, 21.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_6$ [M+H$^+$] calcd: 497.3412, found: 497.3414.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 65.37; H, 8.74; Found: C, 65.28; H, 8.54.

2,2',2''-(2-(4-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2d)



Isolated yield: 70%

White solid, m.p: 137.1 °C. Its spectroscopic data are consistent with a literature report.[1]

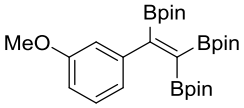
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9 Hz, 2H), 6.78 (d, *J* = 9 Hz, 2H), 3.77 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.11 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 137.9, 129.0, 113.1, 83.8, 83.3, 83.1, 55.2, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ [M+H$^+$] calcd: 513.3361, found: 513.3353.

2,2',2''-(2-(3-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2e)



Isolated yield: 58%

White solid, m.p: 217.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 1H), 6.9 (ddd, J = 8, 2, 1 Hz, 1H), 6.8 (dd, J = 3, 2 Hz, 1H), 6.7 (ddd, J = 8, 3, 1 Hz, 1H), 3.77 (s, 3H), 1.30 (s, 12H), 1.27 (s, 12H), 1.08 (s, 12H).

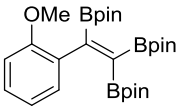
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 146.7, 128.6, 120.1, 113.0, 112.7, 83.8, 83.4, 83.2, 55.0, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ [M+H$^+$] calcd: 513.3361, found: 513.3362.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 63.33; H, 8.46; Found: C, 63.45; H, 8.71.

2,2',2''-(2-(2-methoxyphenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2f)



Isolated yield: 49%

White solid, m.p: 166.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 2H), 6.80 (apparent td, *J* = 7, 1 Hz, 1H), 6.75 (dd, *J* = 8, 1 Hz, 1H), 3.73 (s, 3H), 1.31 (s, 12H), 1.25 (s, 12H), 1.06 (s, 12H).

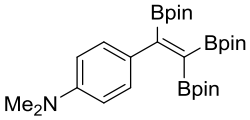
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.4, 135.2, 129.8, 128.1, 120.3, 109.8, 83.5, 83.3, 83.0, 55.1, 24.9, 24.7, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 31.0.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ [M+H$^+$] calcd: 513.3361, found: 513.3357.

Anal. Calcd for $C_{27}H_{43}B_3O_7$: C, 63.33; H, 8.46; Found: C, 63.05; H, 8.56.

N,N-dimethyl-4-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (2g)



Isolated yield: 35%

White solid, m.p: 220.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9 Hz, 2H), 6.62 (d, *J* = 9 Hz, 2H), 2.91 (s, 6H), 1.29 (s, 12H), 1.28 (s, 12H), 1.14 (s, 12H).

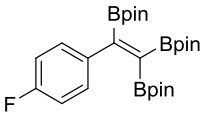
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.8, 134.0, 128.7, 112.0, 83.6, 83.1, 82.9, 40.7, 24.9 (2C), 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4.

HRMS (ASAP): m/z for $C_{28}H_{47}B_3NO_6$ [M+H$^+$] calcd: 526.3677, found: 526.3672.

Anal. Calcd for $C_{28}H_{46}B_3NO_6$: C, 64.05; H, 8.83; N, 2.67; Found: C, 63.91; H, 9.03; N, 2.63.

2,2',2''-(2-(4-fluorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2j)



Isolated yield: 72%

White solid, m.p: 235.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.95-6.88 (m, 2H), 1.30 (s, 12H), 1.26 (s, 12H), 1.09 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245 Hz), 141.2 (d, *J* = 4 Hz), 129.4 (d, *J* = 8 Hz), 114.3 (d, *J* = 21 Hz), 84.0, 83.5, 83.2, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

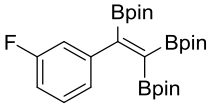
^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -116.7 (tt, *J* = 9, 6 Hz).

HRMS (ASAP): m/z for $C_{26}H_{41}B_3F_1O_6$ [M+H$^+$] calcd: 501.3161, found: 501.3156.

Anal. Calcd for $C_{26}H_{40}B_3F_1O_6$: C, 62.45; H, 8.06; Found: C, 62.96; H, 8.19.

2,2',2''-(2-(3-fluorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k)



Isolated yield: 59%

White solid, m.p: 196.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (td, *J* = 8, 6 Hz, 1H), 7.04 (ddd, *J* = 8, 2, 1 Hz, 1H), 6.99 (ddd, *J* = 10, 3, 2 Hz, 1H), 6.87 (dddd, *J* = 9, 8, 3, 1 Hz, 1H), 1.31 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.3 (d, *J* = 245 Hz), 147.4 (d, *J* = 7 Hz), 129.0 (d, *J* = 8 Hz), 123.5 (d, *J* = 3 Hz), 114.7 (d, *J* = 21 Hz), 113.4 (d, *J* = 21 Hz), 84.0, 83.5, 83.3, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

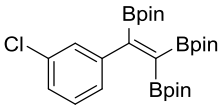
^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.6 (dddd, *J* = 10, 9, 6, 1 Hz).

HRMS (ASAP): m/z for $C_{26}H_{41}B_3FO_6$ [M+H$^+$] calcd: 501.3161, found: 501.3162.

Anal. Calcd for $C_{26}H_{40}B_3FO_6$: C, 62.45; H, 8.06; Found: C, 62.80; H, 8.37.

2,2',2''-(2-(3-chlorophenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2l)



Isolated yield: 56%

White solid, m.p: 186.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.26 (m, 1H), 7.17 – 7.14 (m, 3H), 1.31 (s, 12H), 1.27 (s, 12H), 1.10 (s, 12H).

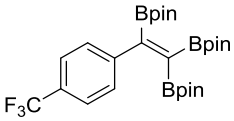
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.9, 133.4, 128.8, 127.9, 126.6, 125.9, 84.0, 83.6, 83.4, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): m/z for $C_{26}H_{41}B_3Cl_1O_6$ [M+H$^+$] calcd: 517.2865, found: 517.2870.

Anal. Calcd for $C_{26}H_{40}B_3ClO_6$: C, 60.46; H, 7.81; Found: C, 60.48; H, 7.95.

2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2m)



Isolated yield: 47%

White solid, m.p: 201.0 °C. Its spectroscopic data are consistent with a literature report.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 1.32 (s, 12H), 1.27 (s, 12H), 1.06 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.9, 128.5 (q, *J* = 32 Hz), 128.0, 124.5 (q, *J* = 272 Hz), 124.5 (q, *J* = 4 Hz), 84.1, 83.7, 83.4, 24.9, 24.7, 24.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

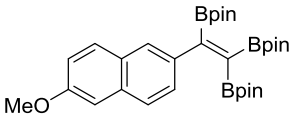
^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.3.

HRMS (ASAP): m/z for $C_{27}H_{41}B_3F_3O_6$ [M+H$^+$] calcd: 551,3129, found: 551.3124.

Anal. Calcd for $C_{27}H_{40}B_3F_3O_6$: C, 58.96; H, 7.33; Found: C, 59.31; H, 7.64.

2,2',2''-(2-(6-methoxynaphthalen-2-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2n)



Isolated yield: 49%

White solid, m.p: 190.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 3H), 7.43 (dd, *J* = 8, 2 Hz, 1H), 7.11 – 7.04 (m, 2H), 3.90 (s, 3H), 1.32 (s, 12H), 1.29 (s, 12H), 1.02 (s, 12H).

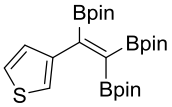
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.2, 141.0, 133.6, 129.6, 128.7, 127.0, 126.2, 125.9, 118.3, 105.6, 83.9, 83.4, 83.1, 55.2, 24.9, 24.8, 24.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): m/z for $C_{31}H_{46}B_3O_7$ [M+H$^+$] calcd: 563.3517, found: 563.3514.

Anal. Calcd for $C_{31}H_{45}B_3O_7$: C, 66.24; H, 8.07; Found: C, 66.46; H, 8.11.

2,2',2''-(2-(thiophen-3-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2o)



Isolated yield: 61%

White solid, m.p: 170.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 3, 1 Hz, 1H), 7.15 (dd, *J* = 5, 3 Hz, 1H), 7.10 (dd, *J* = 5, 1 Hz, 1H), 1.29 (s, 12H), 1.27 (s, 12H), 1.15 (s, 12H).

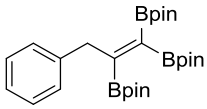
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.2, 128.2, 124.2, 122.1, 83.8, 83.4, 83.3, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): m/z for $C_{24}H_{40}B_3O_6S_1$ [M+H$^+$] calcd: 489.2819, found: 489.2811.

Anal. Calcd for $C_{24}H_{39}B_3O_6S$: C, 59.06; H, 8.05; S, 6.57; Found: C, 59.27; H, 8.36; S, 6.01.

2,2',2''-(3-phenylprop-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2p)



Isolated yield: 69%

White solid, m.p: 167.2 °C. Its spectroscopic data are consistent with a literature report.[1]

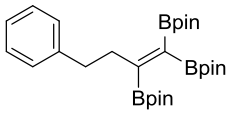
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 1H), 3.76 (s, 2H), 1.29 (s, 12H), 1.25 (s, 12H), 1.07 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.8, 129.7, 127.8, 125.4, 83.5, 83.3, 83.1, 43.6, 24.9, 24.8, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): m/z for $C_{27}H_{44}B_3O_7$ [M+H$^+$] calcd: 497.3412, found: 497.3412.

2,2',2''-(4-phenylbut-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2q)



Isolated yield: 74%

White solid, m.p: 226.8 °C. Its spectroscopic data are consistent with a literature report.[1]

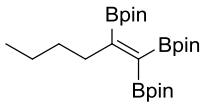
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1 Hz, 2H), 7.25 (s, 2H), 7.17 – 7.12 (m, 1H), 2.66 (s, 4H), 1.31 (s, 12H), 1.27 (s, 12H), 1.25 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.5, 128.5, 128.1, 125.3, 83.7, 83.3, 83.0, 40.2, 37.2, 24.9, 24.9, 24.8. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): m/z for $C_{28}H_{46}B_3O_6$ [M+H$^+$] calcd: 511.3568, found: 511.3571.

2,2',2''-(hex-1-ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2r)



Isolated yield: 58%

White solid, m.p: 216.2 °C. Its spectroscopic data are consistent with a literature report.[1]

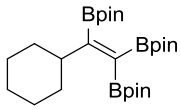
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (t, *J* = 7 Hz, 2H), 1.38 – 1.29 (m, 4H), 1.28 (s, 12H), 1.24 (s, 12H), 1.23 (s, 12H), 0.86 (t, *J* = 7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.5, 83.1, 82.8, 37.5, 32.7, 24.9, 24.8, 24.7, 22.8, 14.1. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8.

HRMS (ASAP): m/z for $C_{24}H_{46}B_3O_6$ [M+H$^+$] calcd: 463.3568, found: 463.3569.

2,2',2''-(2-cyclohexylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2s)



Isolated yield: 71%

White solid, m.p: 278.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.32 (tt, *J* = 12, 4 Hz, 1H), 1.76 – 1.58 (m, 6H), 1.48 – 1.34 (m, 2H), 1.27 (s, 12H), 1.25 (s, 12H), 1.23 (s, 12H), 1.22 – 1.06 (m, 2H).

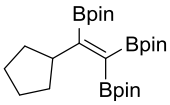
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.3, 83.0, 82.9, 49.9, 32.2, 26.6, 26.1, 25.1, 24.9, 24.7. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

HRMS (ASAP): m/z for $C_{26}H_{48}B_3O_6$ [M+H$^+$] calcd: 489.3725, found: 489.3726.

Anal. Calcd for $C_{26}H_{47}B_3O_6$: C, 63.98; H, 9.71; Found: C, 64.38; H, 9.90.

2,2',2''-(2-cyclopentylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2t)



Isolated yield: 64%

White solid, m.p: 278.6 °C. Its spectroscopic data are consistent with a literature report.[1]

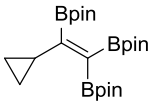
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.87 – 2.75 (apparent quintet, *J* = 9 Hz,1H), 1.77 – 1.44 (m, 8H), 1.26 (s, 12H), 1.24 (s, 12H), 1.23 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.3, 83.0, 82.9, 50.6, 32.6, 26.1, 25.1, 24.9, 24.7. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): m/z for $C_{26}H_{46}B_3O_6$ [M+H$^+$] calcd: 487.3568, found: 487.3565.

2,2',2''-(2-cyclopropylethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2u)



Isolated yield: 54%

White solid, m.p: 233.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (tt, *J* = 8, 5 Hz, 1H), 1.24 (s, 12H), 1.24 (s, 24H), 0.77 (m, 2H), 0.71 – 0.63 (m, 2H).

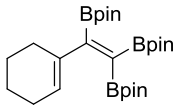
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 83.4, 82.9, 82.8, 25.0, 24.9, 24.7, 20.2, 7.5. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

HRMS (ASAP): m/z for $C_{23}H_{42}B_3O_6$ [M+H$^+$] calcd: 447.3255, found: 447.3258.

Anal. Calcd for $C_{23}H_{41}B_3O_6$: C, 61.94; H, 9.27; Found: C, 62.12; H, 9.42.

2,2',2''-(2-(cyclohex-1-en-1-yl)ethene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2v)



Isolated yield: 52%

White solid, m.p: 235 °C. Its spectroscopic data are consistent with a literature report.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.48 (tt, *J* = 4, 2 Hz, 1H), 2.10 (m, 2H), 2.05 – 1.97 (m, 2H), 1.65 – 1.56 (m, 2H), 1.53 (m, 2H), 1.25 (s, 12H), 1.25 (s, 12H), 1.20 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.4, 122.4, 83.5, 83.1, 82.8, 28.0, 25.4, 24.9, 24.8, 24.7, 22.6, 22.1. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7.

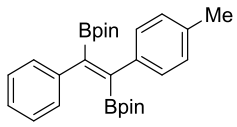
HRMS (ASAP): m/z for $C_{26}H_{46}B_3O_6$ [M+H$^+$] calcd: 487.3568, found: 487.3565.

IV. Synthetic Applications of Triborylalkenes

Selective monoarylation of 2a yielding 6

In a glove box, a tube (20 mL) containing $Pd(PPh_3)_4$ (30 mg, 0.026 mol), **2a** (129 mg, 0.26 mmol), and 4-iodoanisole (61 mg, 0.26 mmol) was capped with a septum, and the system was evacuated and purged with argon three times. Dried THF (3 mL) and degassed aqueous K_3PO_4 (520 µL, 1.5 M, 0.78 mmol) were transferred to the system via syringes, and the mixture was stirred at 70 °C for 24 h. After cooling to room temperature, the mixture was filtered through a pad of Celite and washed through with Et_2O (25 mL). The filtrate was concentrated under vacuum, the residue was purified by flash column chromatography (ethyl acetate: hexanes = 1:10) to yield a white solid.

(*E*)-2,2'-(1-phenyl-2-(p-tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6a)



Isolated yield: 78%; White solid, m.p: 137.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.19 (m, 5H), 7.12 – 7.06 (m, 2H), 2.33 (s, 3H), 1.10 (s, 12H), 1.08 (s, 12H).

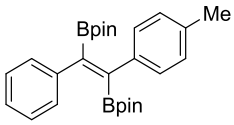
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.4, 140.2, 136.2, 128.6, 128.1, 128.0, 127.9, 126.5, 83.5, 24.6, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 30.3.

HRMS (ASAP): m/z for $C_{27}H_{37}B_2O_4$ $[M+H^+]$ calcd: 447.2872, found: 447.2866

Anal. Calcd for $C_{27}H_{37}B_2O_4$: C, 72.68; H, 8.73; Found: C, 72.52; H, 8.15.

(*E*)-2,2'-(1-(4-methoxyphenyl)-2-phenylethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6b)



Isolated yield: 68%, White solid, m.p: 179.0 °C.

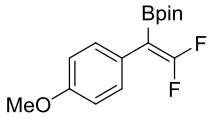
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.25 (m, 4H), 7.23 – 7.17 (m, 1H), 6.87 – 6.80 (m, 2H), 3.80 (s, 3H), 1.11 (s, 12H), 1.08 (s, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 143.4, 135.9, 129.3, 128.1, 127.9, 126.5, 113.4, 83.5, 83.5, 55.3, 24.6, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8.

HRMS (ASAP): m/z for $C_{27}H_{37}B_2O_5$ [M+H$^+$] calcd: 463.2822, found: 463.2812

Difluorination of 2d yielding 7a



To a solution of **2d** (102.4 mg, 0.2 mmol) in MeCN (2 mL), under argon, Selectfluor (212.6 mg, 3 equiv) and $NaHCO_3$ (38.2 mg, 2.2 equiv) were added and the reaction mixture was stirred at r.t. for 7 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then the solvent was removed under reduced pressure at room temperature. The residue was purified by column chromatography on silica gel (*n*-pentane: ethyl acetate = 100:1) to yield 55 mg (93%) of a colorless liquid **7a**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.87 (m, 2H), 3.80 (s, 3H), 1.31 (s, 12H).

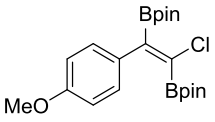
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.5 (dd, *J* = 306, 299 Hz), 158.3, 130.6 (t, *J* = 3 Hz), 124.7 (dd, *J* = 8, 1 Hz), 113.7, 83.9, 55.2, 24.7. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -70.0 (s, br), -72.0 (d, *J* = 5 Hz).

HRMS (ASAP): m/z for $C_{15}H_{20}B_1F_2O_3$ [M+H$^+$] calcd: 297.1468, found: 297.1457

Monochlorination of 2d yielding 8a



To a solution of **2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added NCS (35 mg, 1.3 equiv). The reaction mixture was stirred at 60 °C for 12 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: ethyl acetate = 50:1) to give the product **8a** as a white solid (59 mg, 70%).

White solid, m.p: 157.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 9 Hz, 2H), 6.81 (d, *J* = 9 Hz, 2H), 3.79 (s, 3H), 1.31 (s, 12H), 1.17 (s, 12H).

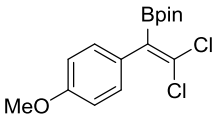
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.2, 131.8, 129.2, 113.5, 84.3, 84.3, 55.2, 24.7, 24.4. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 28.2.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Cl_1O_5$ [M+H$^+$] calcd: 421.2119, found: 421.2112

Anal. Calcd for $C_{21}H_{32}B_2Cl_1O_5$: C, 59.98; H, 7.43; Found: C, 59.67; H, 7.58.

Dibromination of 2d yielding 9a



To a solution of **2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added NCS (53.4 mg, 2 equiv). The reaction mixture was stirred at 60 °C for 48 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: diethyl ether = 100:1) to yield 34 mg (53%) of a colorless liquid **9a**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9 Hz, 2H), 6.88 (d, *J* = 9 Hz, 2H), 3.81 (s, 3H), 1.30 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.9, 129.6, 129.5, 125.2, 113.7, 84.6, 55.2, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

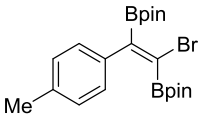
^{11}B NMR (96 MHz, $CDCl_3$) δ 29.4.

HRMS (ASAP): m/z for $C_{15}H_{20}B_1Cl_2O_3$ [M+H$^+$] calcd: 329.0877, found: 329.0867.

Monobromination of 2 yielding 10

To a solution of **2** (0.2 mmol) in MeCN (1 mL) under argon and protected from light was added N-bromosuccinimide (46.3 mg, 1.3 equiv). The reaction mixture was stirred at r.t. for 72 h, and then washed with a saturated solution of $Na_2S_2O_3$ (10 mL). The organic phase was extracted with CH_2Cl_2 (3 x 10 mL), dried over $MgSO_4$ and filtered. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (*n*-pentane: ethyl acetate = 50:1) to give the product **10a** as a white solid (67 mg, 75%).

(*E*)-2,2'-(1-bromo-2-(p-tolyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10a)



Isolated yield: 75%; White solid, m.p: 200.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 2.31 (s, 3H), 1.32 (s, 12H), 1.16 (s, 12H).

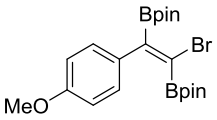
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.8, 137.2, 128.8, 127.4, 84.3, 84.3, 24.7, 24.3, 21.2. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 28.5.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Br_1O_4$ [M+H$^+$] calcd: 449.1665, found: 449.1661

Anal. Calcd for $C_{21}H_{31}B_2BrO_4$: C,56.18; H, 6.96; Found: C, 56.83; H, 7.13.

(E)-2,2'-(1-bromo-2-(4-methoxyphenyl)ethene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10b)



Reaction time: 2 h; Isolated yield: 70%; White solid, m.p: 249.0 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 9 Hz, 2H), 6.80 (d, *J* = 9 Hz, 2H), 3.78 (s, 3H), 1.32 (s, 12H), 1.17 (s, 12H).

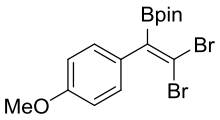
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.2, 133.3, 128.8, 113.6, 84.3, 84.3, 55.2, 24.8, 24.3. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (160 MHz, $CDCl_3$) δ 28.1.

HRMS (ASAP): m/z for $C_{21}H_{32}B_2Br_1O_5$ [M+H$^+$] calcd: 465.1614, found: 465.1613

Anal. Calcd for $C_{21}H_{31}B_2BrO_5$: C, 54.24; H, 6.72; Found: C, 54.87; H, 6.79.

Dibromination of 2d yielding 11a



To a solution of **2d** (102.4 mg, 0.2 mmol) in MeCN (1 mL) under argon and protected from light was added N-bromosuccinimide (71.2 mg, 2 equiv). The reaction mixture was stirred at r.t. for 72 h. The mixture was filtered through a pad of celite and washed through with CH_2Cl_2 (25 mL). Then the solvent was removed under reduced pressure at room temperature. The residue was purified quickly by column chromatography on silica gel (*n*-pentane: diethyl ether = 20:1) to yield 74 mg (86%) of a colorless liquid **11a**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.88 (m, 2H), 3.81 (s, 3H), 1.29 (s, 12H).

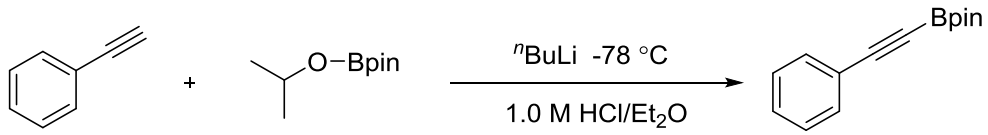
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.9, 132.1, 129.0, 113.8, 94.2, 84.7, 55.2, 24.6. The carbon atoms directly attached to boron were not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, $CDCl_3$) δ 29.6.

HRMS (ASAP): m/z for $C_{15}H_{20}B_1Br_2O_3$ [M+H$^+$] calcd: 418.9846, found: 418.9841.

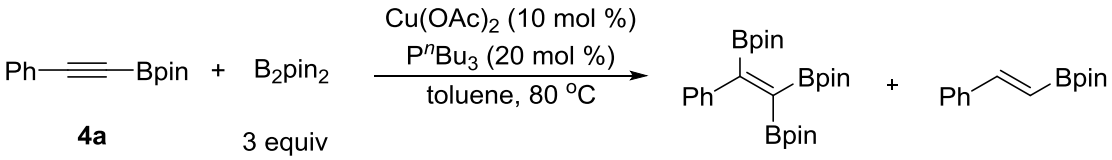
V. Investigations Concerning the Reaction Mechanism

Evidence for an alkynylboronate intermediate



Synthesis of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (4a):[2] A solution of phenylacetylene (1.32 mL, 12 mmol) in THF (30 mL) in a 50 mL of Schlenk tube was cooled to -78 °C and, under an argon atmosphere ^{n}BuLi (7.5 mL, 1.6 M hexane solution, 12 mmol) was added dropwise. The reaction mixture was stirred for 1 h at -78 °C. The resulting reaction mixture was then added to a solution of 4,4,5,5-tetramethyl-2-(isopropoxy)-1,3,2-dioxaborolane (2.04 mL, 10 mmol) in THF (30 mL) at -78 °C. After being stirred for 2 h at -78 °C, the reaction mixture was quenched with 1.0 M HCl/Et$_2$O (12.6 mL, 12.6 mmol), and the mixture was warmed to room temperature with additional stirring for 1 h. Filtration and evaporation afforded a pale yellow oil. Bulb to bulb distillation (160 °C/2 Torr) gave **4a** (1.98 g, 8.7 mmol, 87% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 1.32 (s, 12H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 132.5, 129.4, 128.3, 121.8, 84.4, 24.7.
^{11}B NMR (96 MHz, $CDCl_3$) δ 24.2.
Its spectroscopic data are consistent with a literature report.[2]



With acrylonitrile	Isolated yield 87%	0 %
Without acrylonitrile	Isolated yield 90%	0 %

Scheme S2: Diboration of alkynylboronate.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, Cu(OAc)$_2$ (10 mol %, 3.6 mg, 0.02 mmol), B$_2$pin$_2$ (3 equiv, 152.4 mg, 0.6 mmol) and toluene (1 mL) were added. Then, 1-alkynyldioxaborolane **4a** (45.6 mg, 0.2 mmol), acrylonitrile

(10.6 mg, 13 µL, 0.2 mmol) (or without acrylonitrile) and P^nBu_3 (8.1 mg, 9.9 µL, 0.04 mmol) were added in this order. The reaction was heated at 80 °C under argon for 4 h, and then diluted with Et_2O (4 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) with copious washing (Et_2O). The solvents were removed *in vacuo*, and the residue was purified by column chromatography on silica gel (pentane: ethyl acetate = 25:1).

Evidence for the formation of R-C_6H_4-C≡C-Bpin (4j, R = F) as a reaction intermediate

In a Young's tap NMR tube, $Cu(OAc)_2$ (10 mol %, 1.8 mg, 0.01 mmol), B_2pin_2 (3 equiv, 76.2 mg, 0.3 mmol) and toluene (0.7 mL) were added. Then, alkyne **1j** (12 mg, 0.1 mmol), acrylonitrile (5.3 mg, 6.5 µL, 0.1 mmol) and P^nBu_3 (4 mg, 4.5 µL, 0.02 mmol) were added in this order. The mixture was kept under argon at 80 °C. The formation of **4j** was detected by *in situ* ^{19}F NMR spectroscopy and GC/MS (Figure S1).

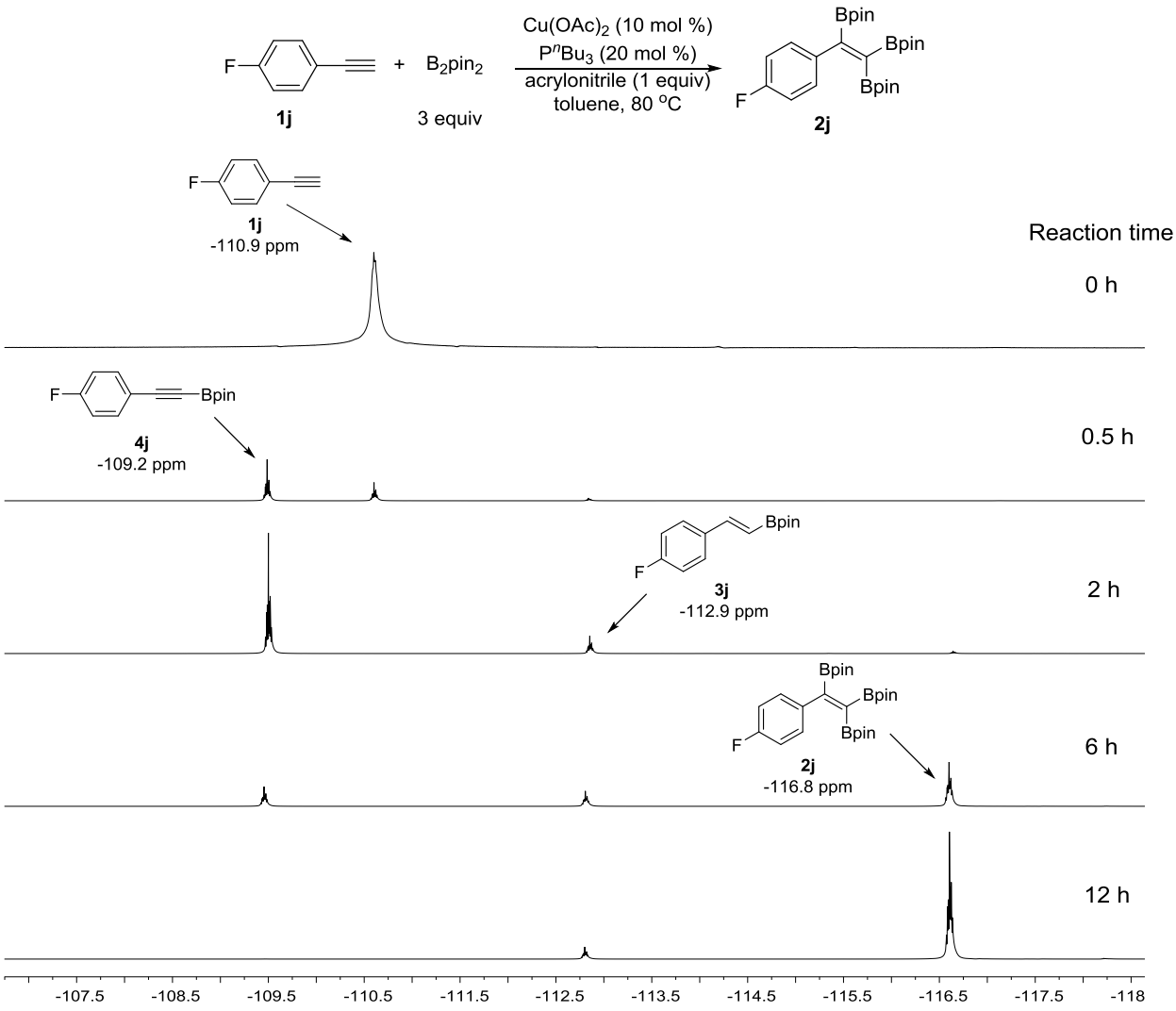


Figure S1 (a). Reaction progress monitored by *in situ* ^{19}F NMR spectroscopy (471 MHz)

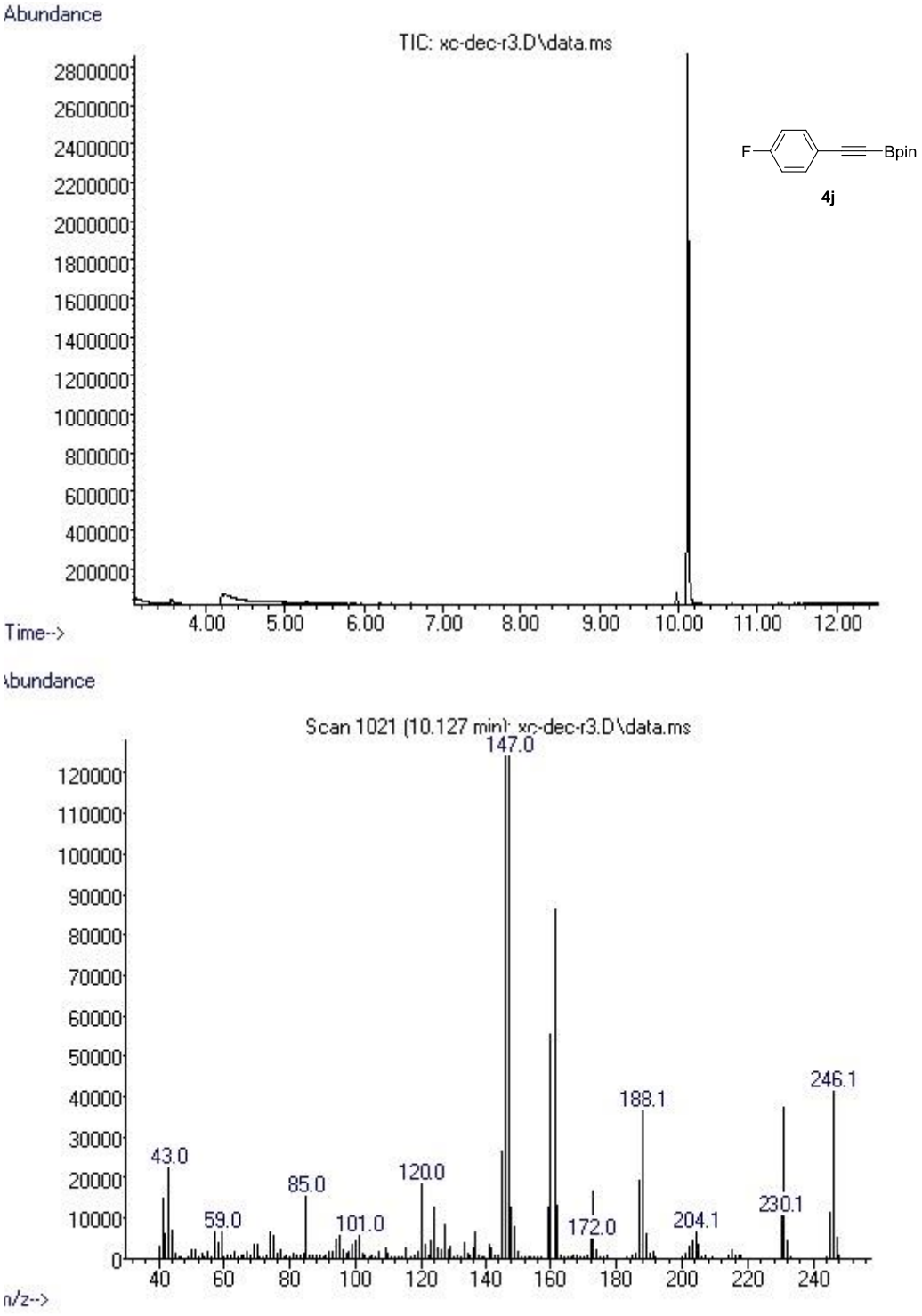


Figure S1 (b). GC/MS of an authentic sample of **4j** (m/z for $C_{14}H_{16}BFO_2$ $[M]^+$ calcd: 246, found: 246) prepared using the method described in: E. A. Romero, R. Jazzar, G. Bertrand, *Chem. Sci.* **2017**, *8*, 165-168.

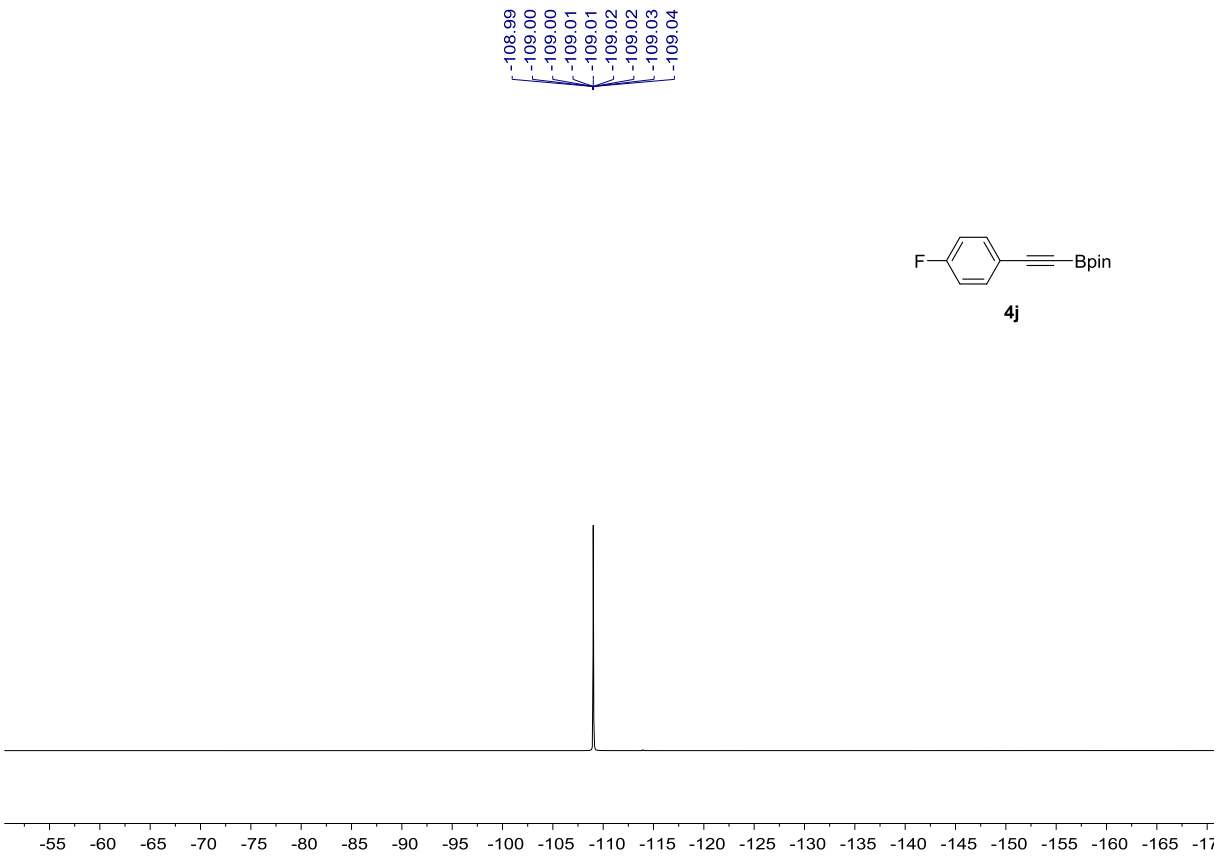
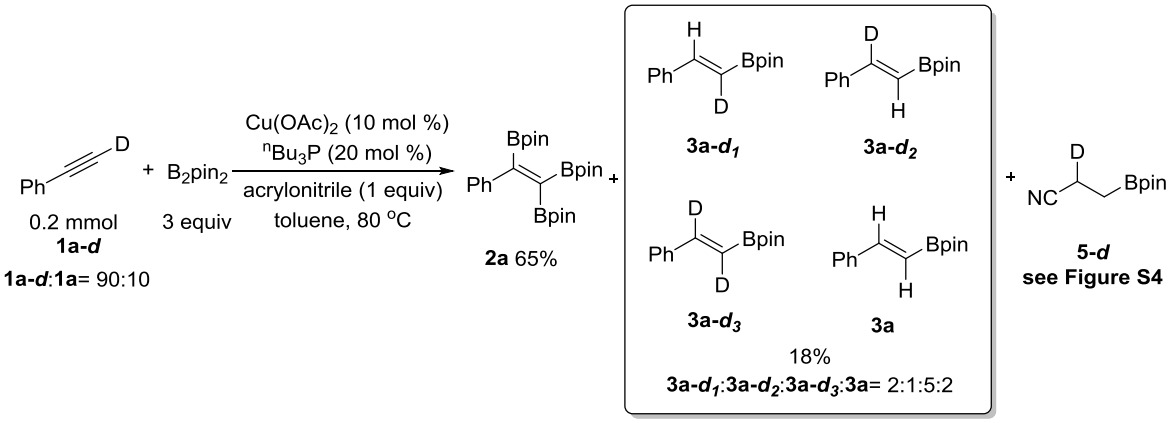


Figure S1 (c). ^{19}F NMR (471 MHz, toluene) spectrum of authentic **4j** (δ -109.0; td, *J* = 9, 5 Hz).

Deuterium labeling studies

Deuterium labeling studies were conducted using 1-deutero-2-phenylethyne **1a-*d*** as the substrate (the level of deuterium content was 90%, as shown below in **Figure S2**) under the standard reaction conditions.[3] The reaction gave **3a-*d*$_1$**, **3a-*d*$_2$**, **3a-*d*$_3$**, and **3a** in a 2:1:5:2 ratio (see NMR spectrum in **Figure S3**). HRMS analysis indicated the formation of **5-*d*** (see **Figure S4**).



Scheme S3. Deuterium labeling studies

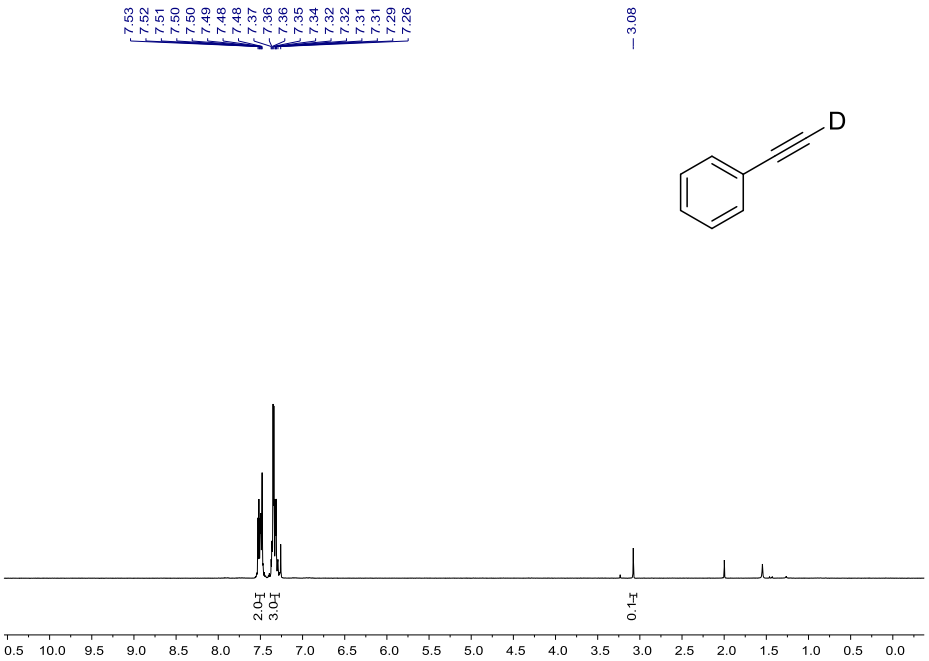


Figure S2. ^{1}H NMR spectrum of **1a-*d***. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.6 – 7.4 (m, 2H), 7.4 – 7.3 (m, 3H), 3.1 (s, 0.1H).

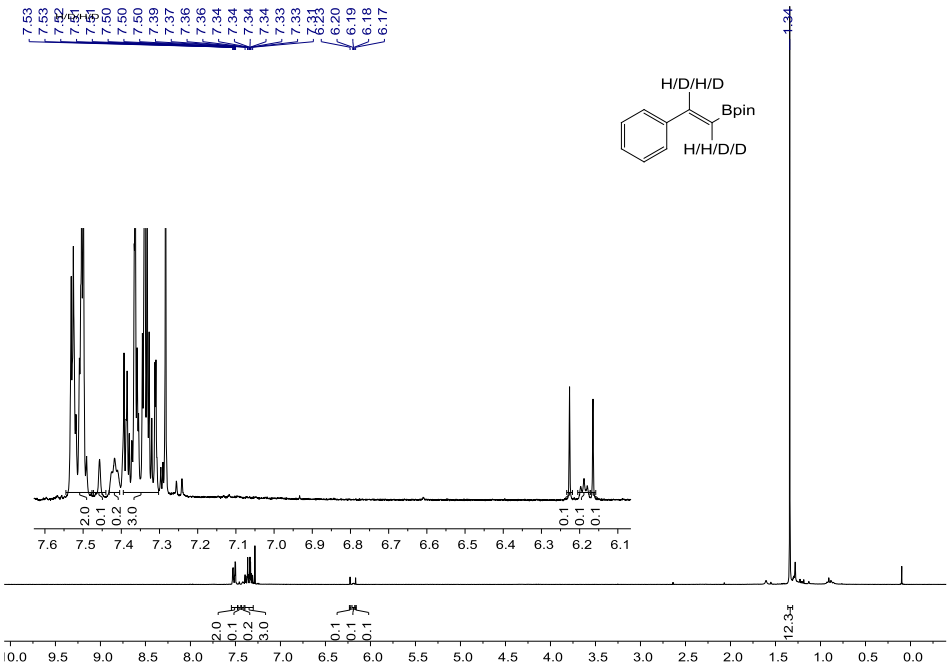


Figure S3. **^{1}H NMR** spectrum of **3a** (300 MHz, $CDCl_3$).

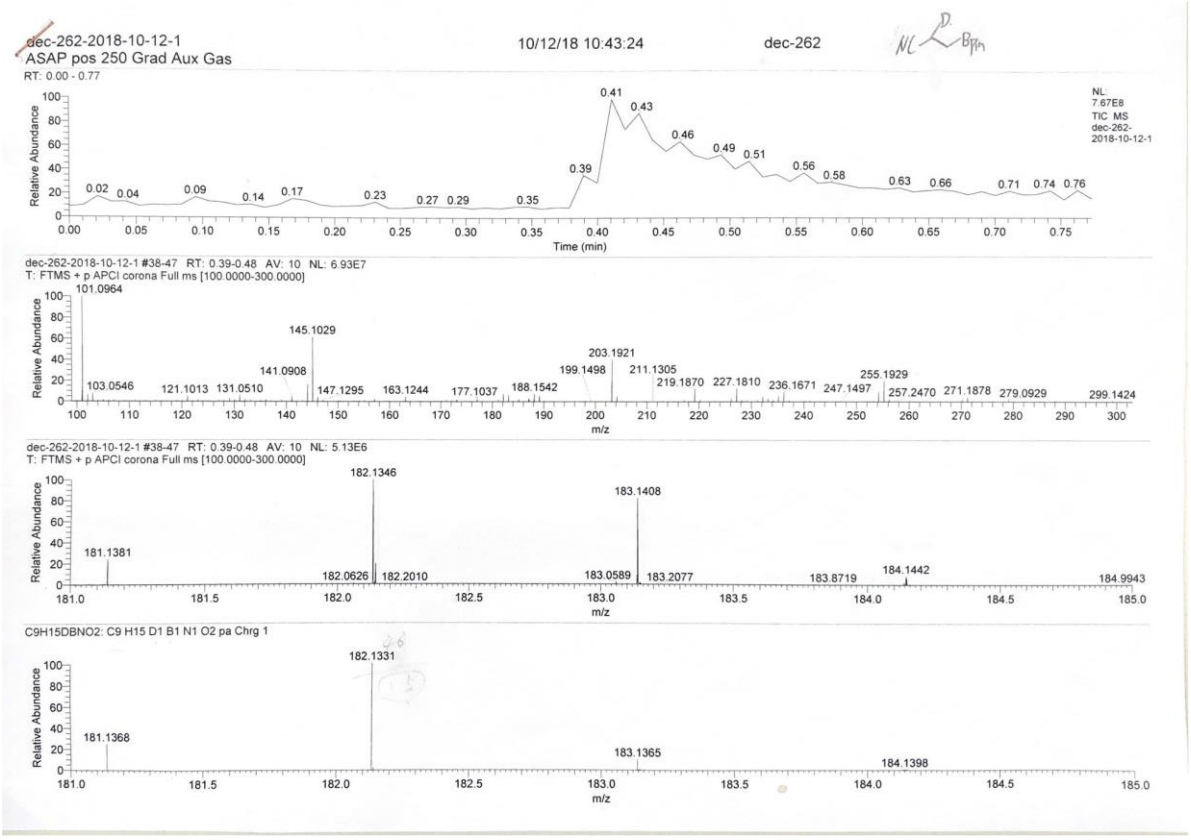
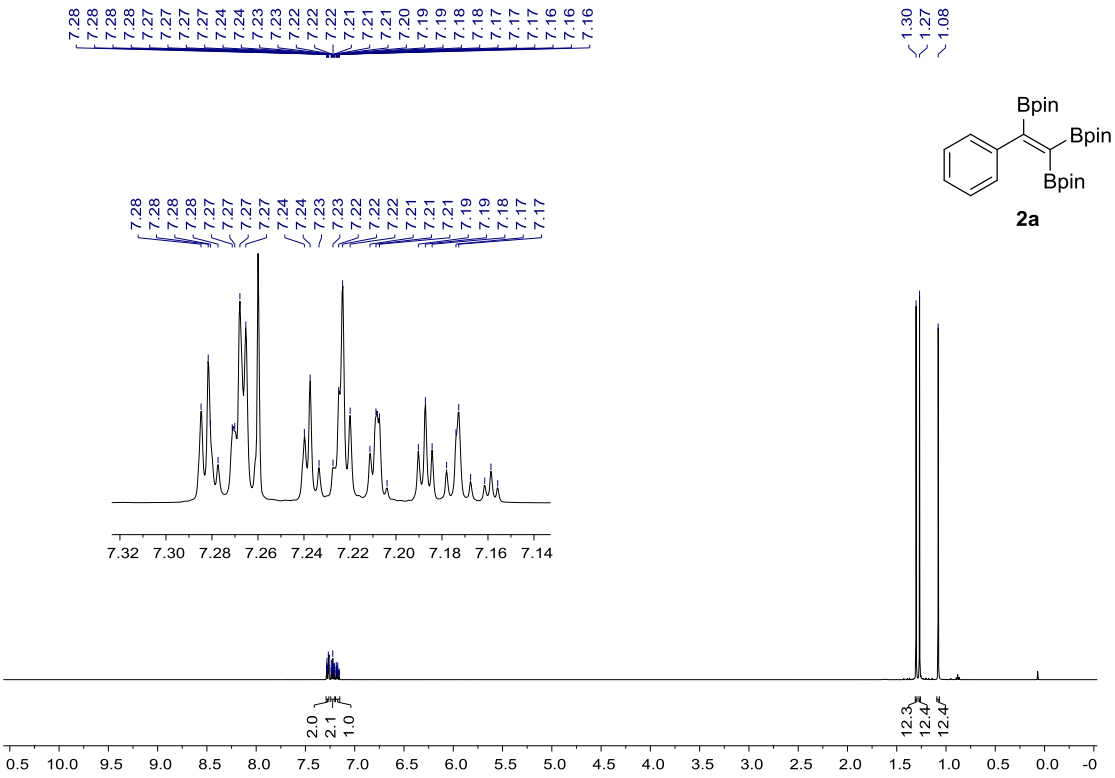


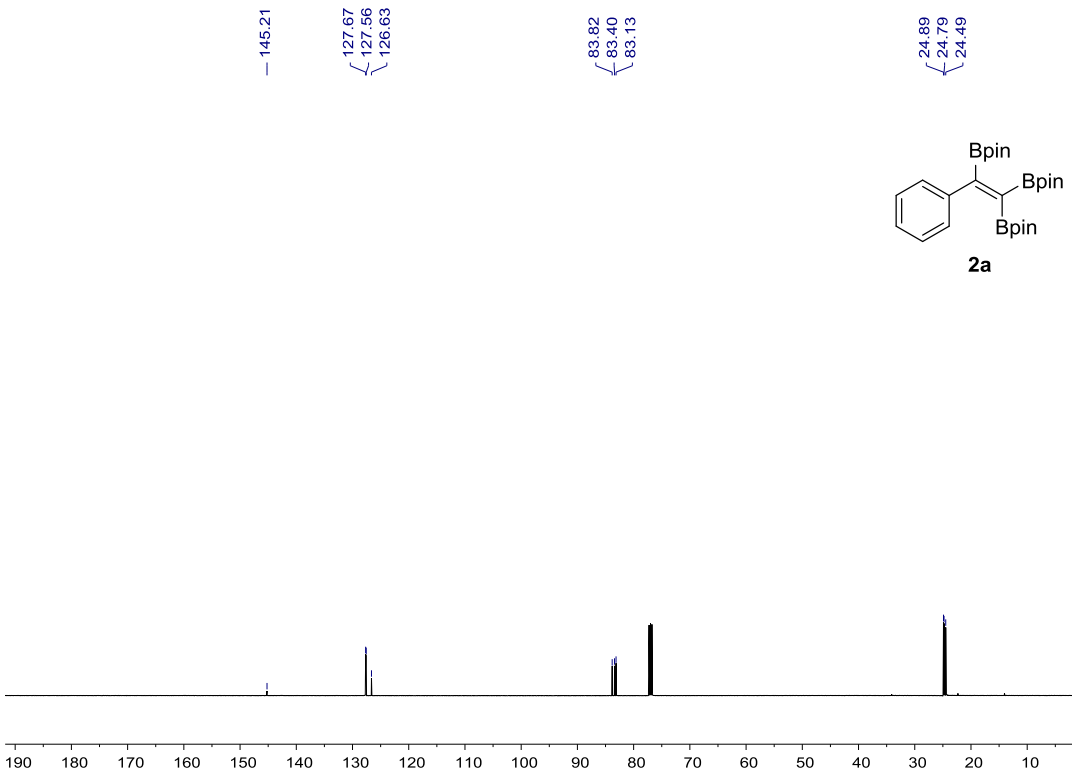
Figure S4. **HRMS** (ASAP) of **5-*d***: m/z for $C_9H_{15}DBNO_2$ [M^+] calcd: 182.1331, found: 182.1346.

VI. NMR Spectra

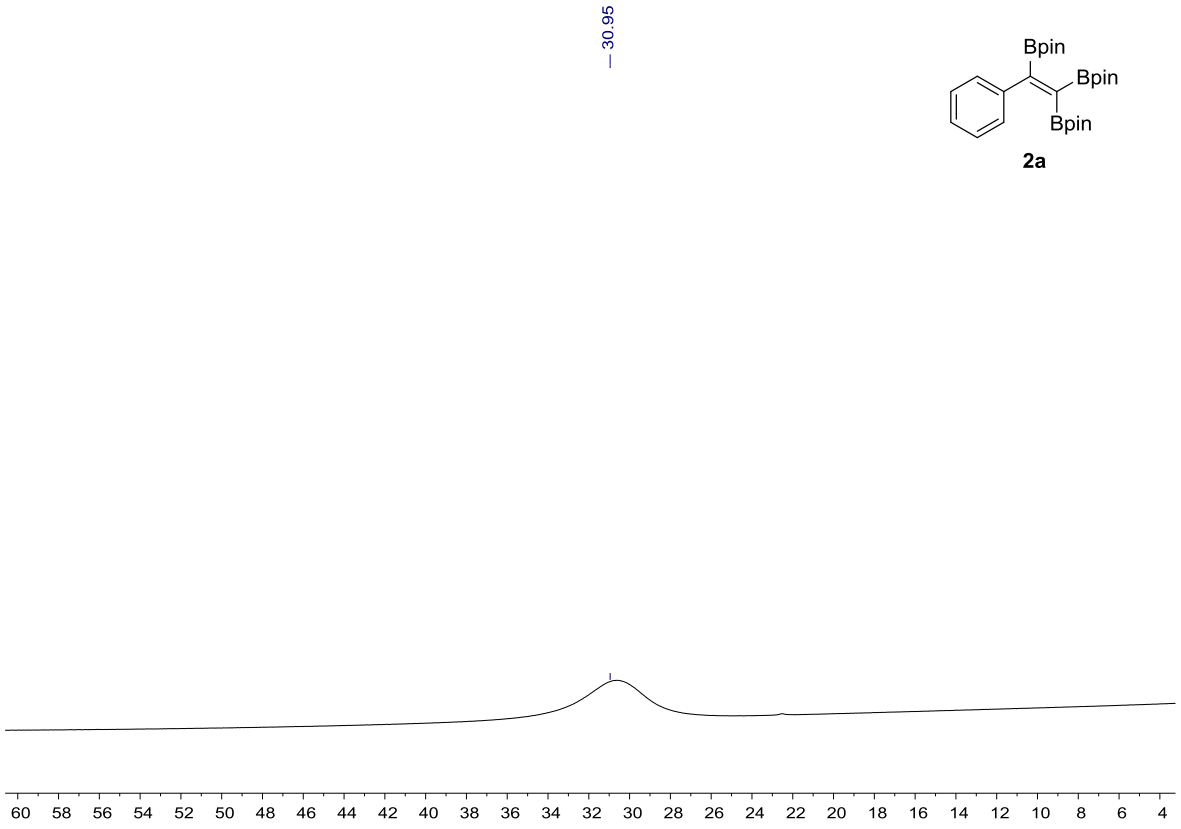
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2a**



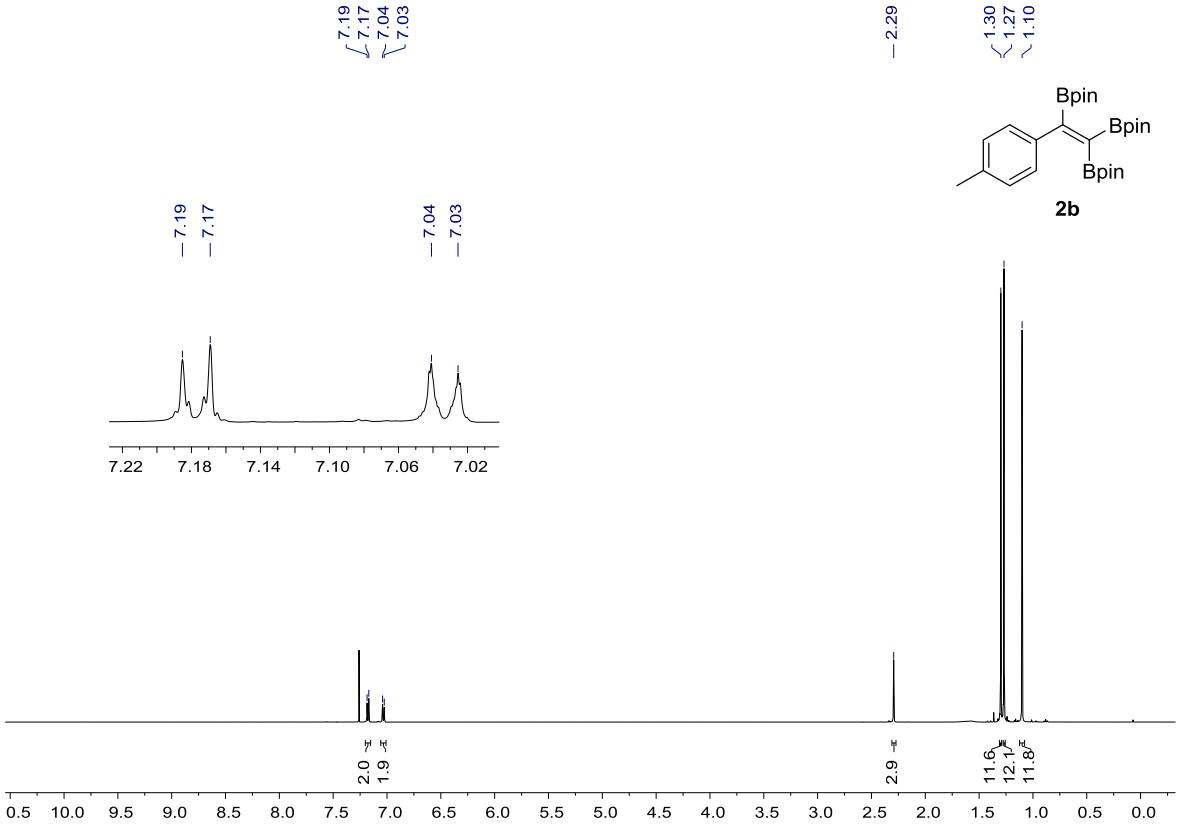
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2a**



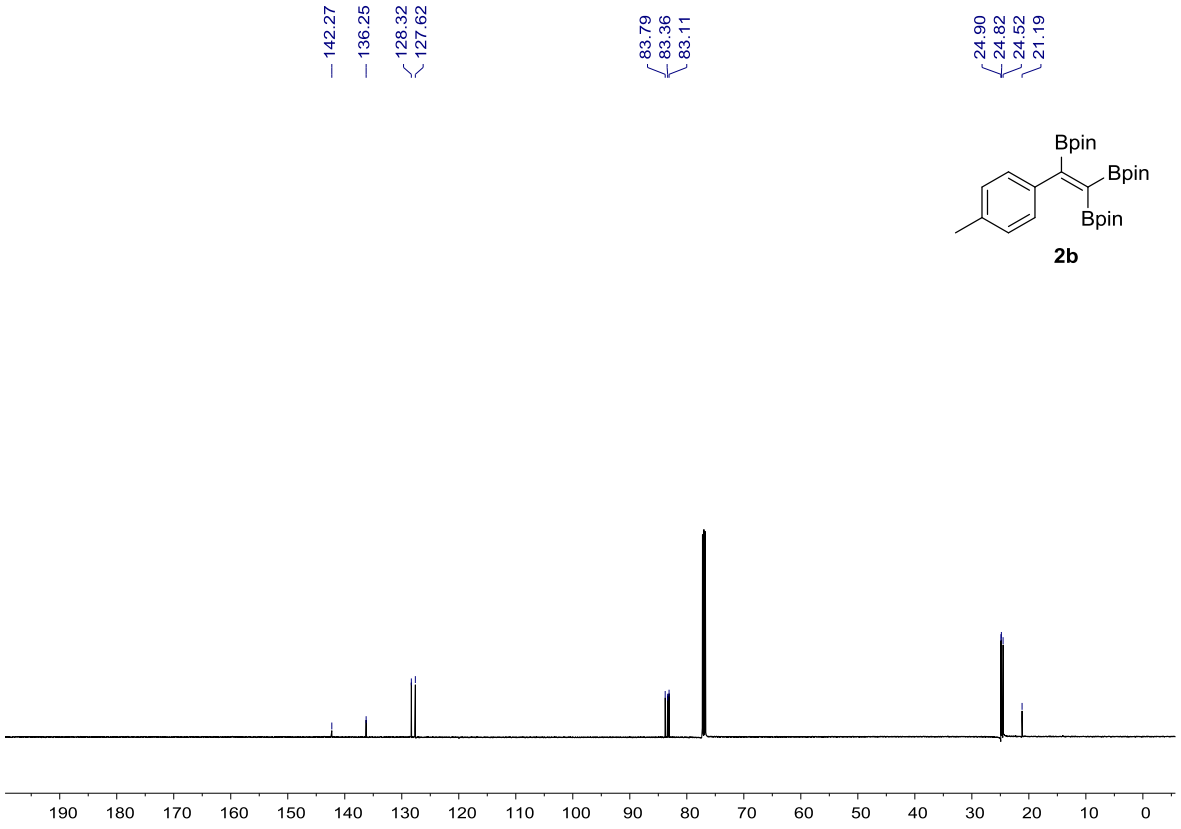
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2a**



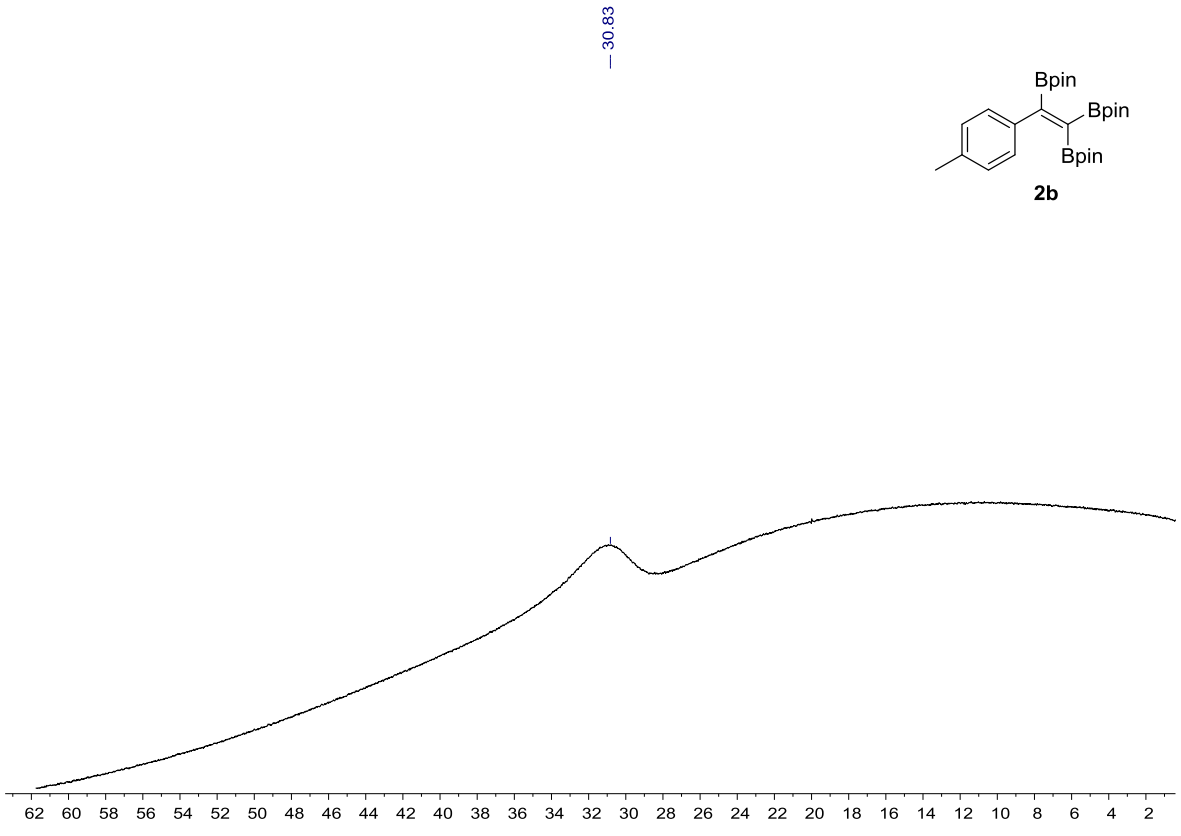
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2b**



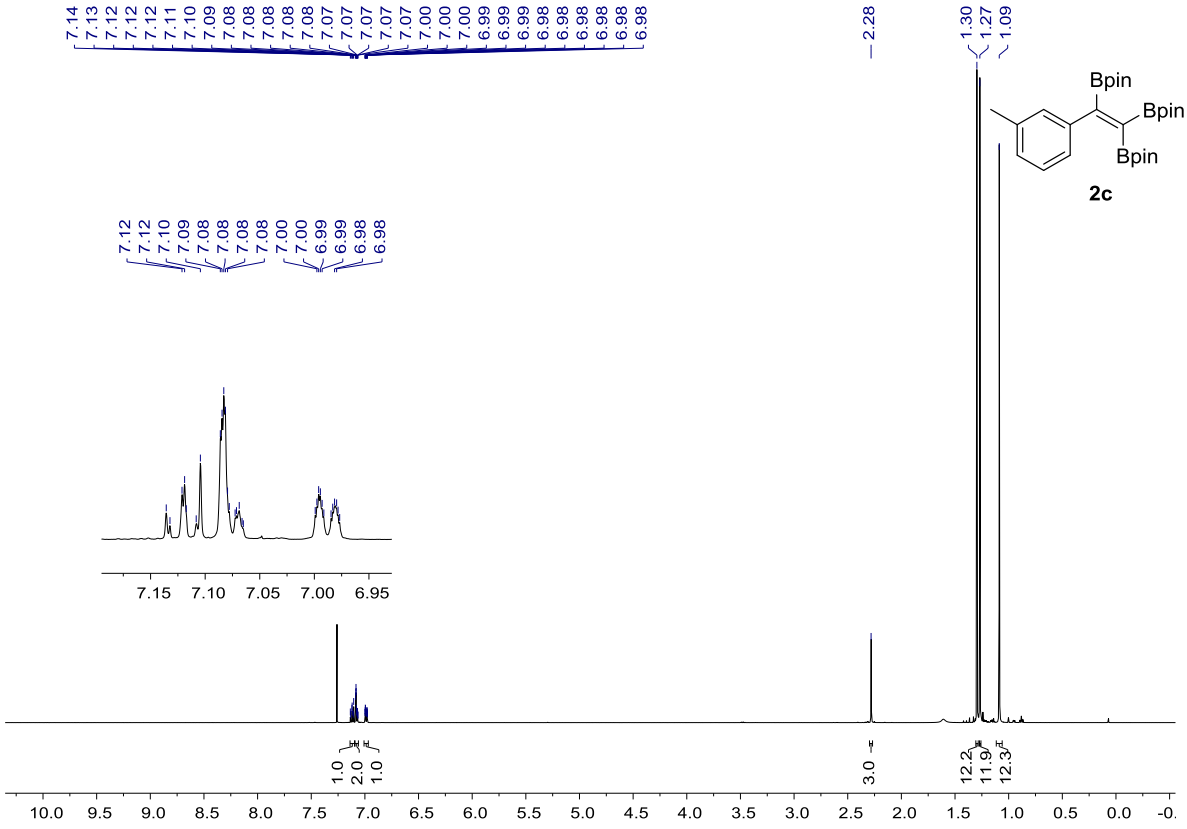
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2b**



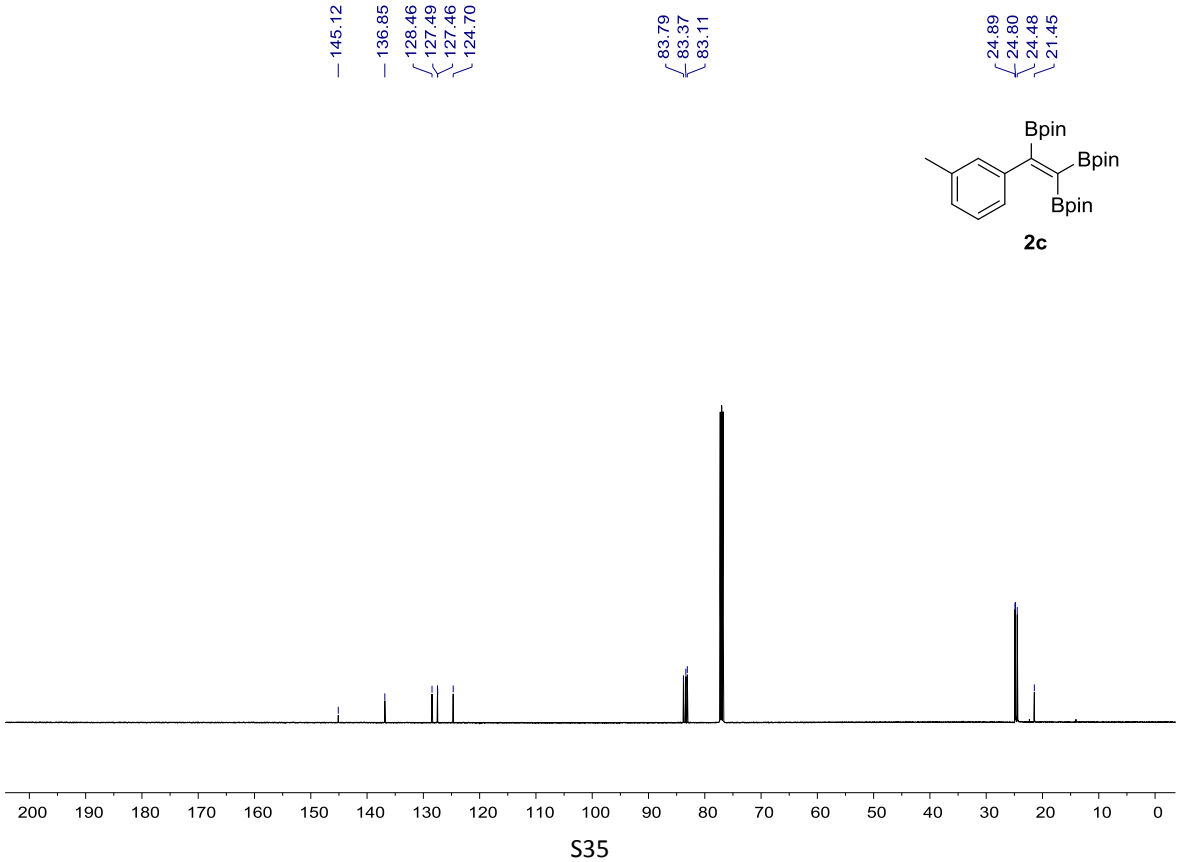
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2b**



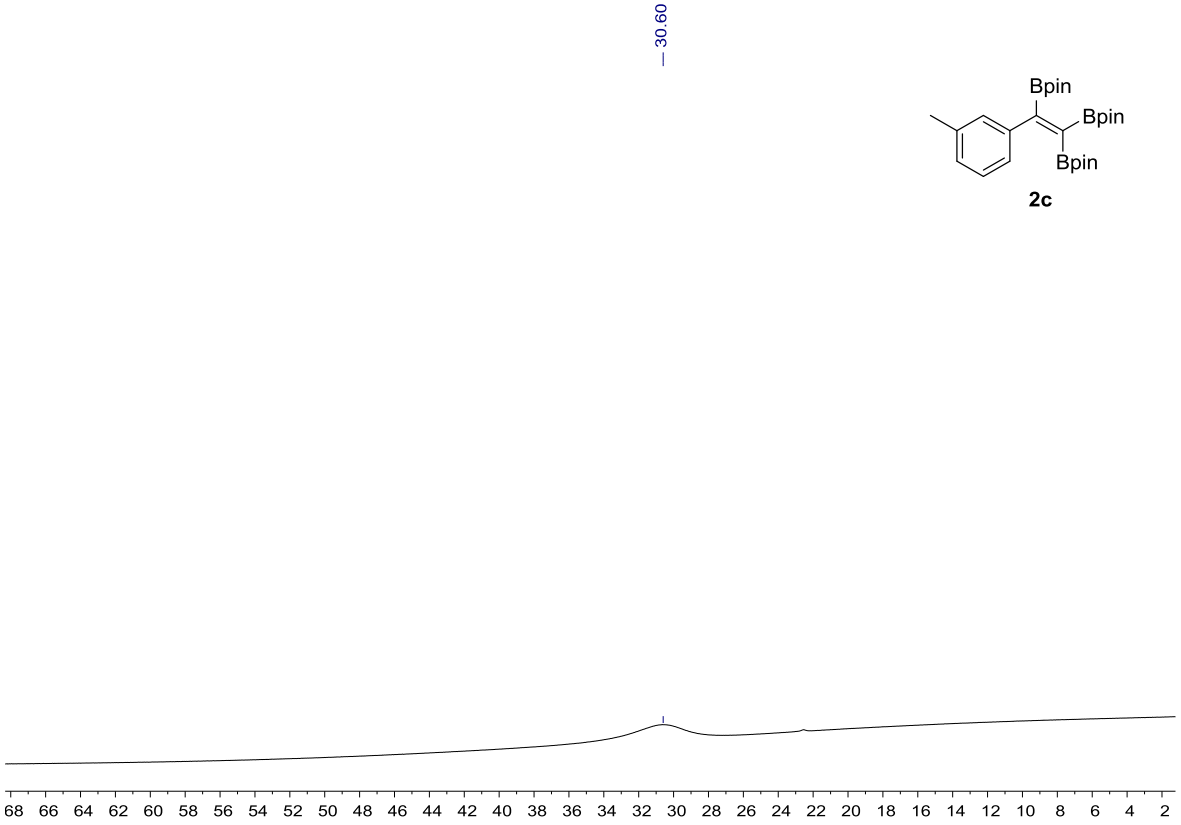
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2c**



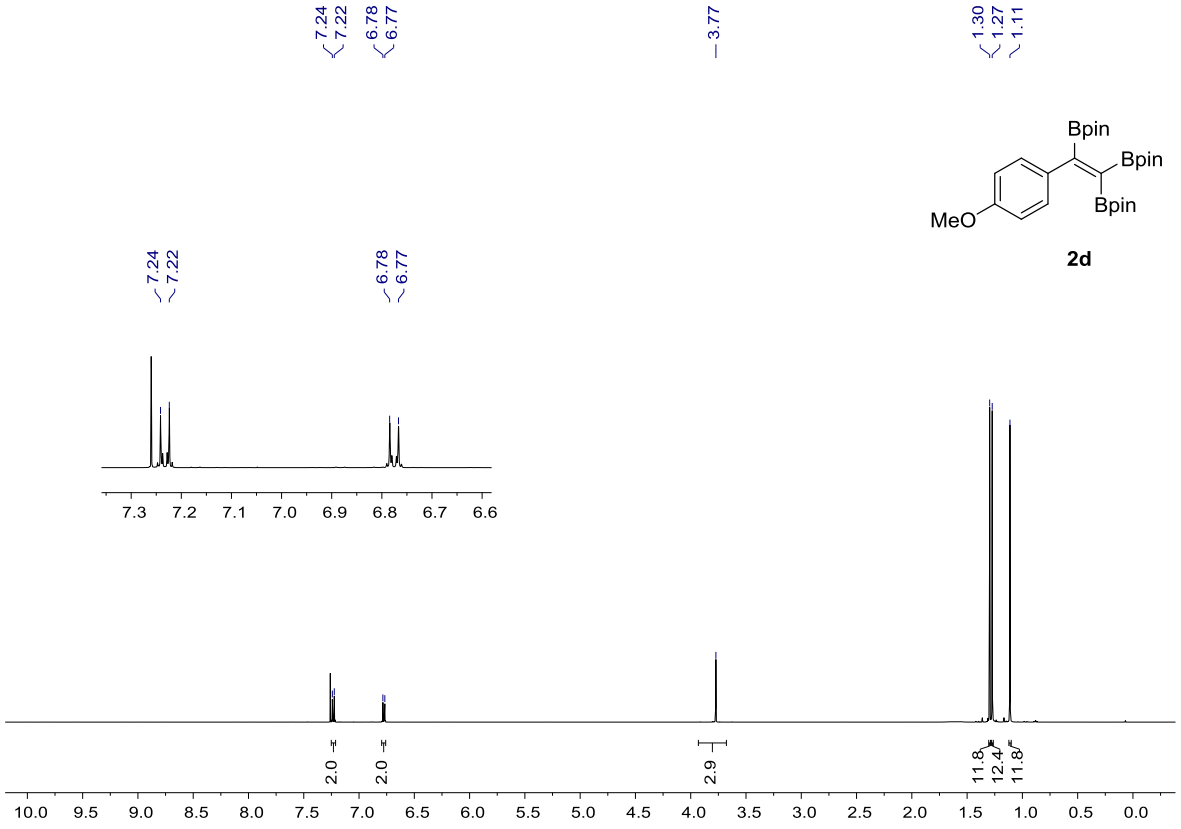
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2c**



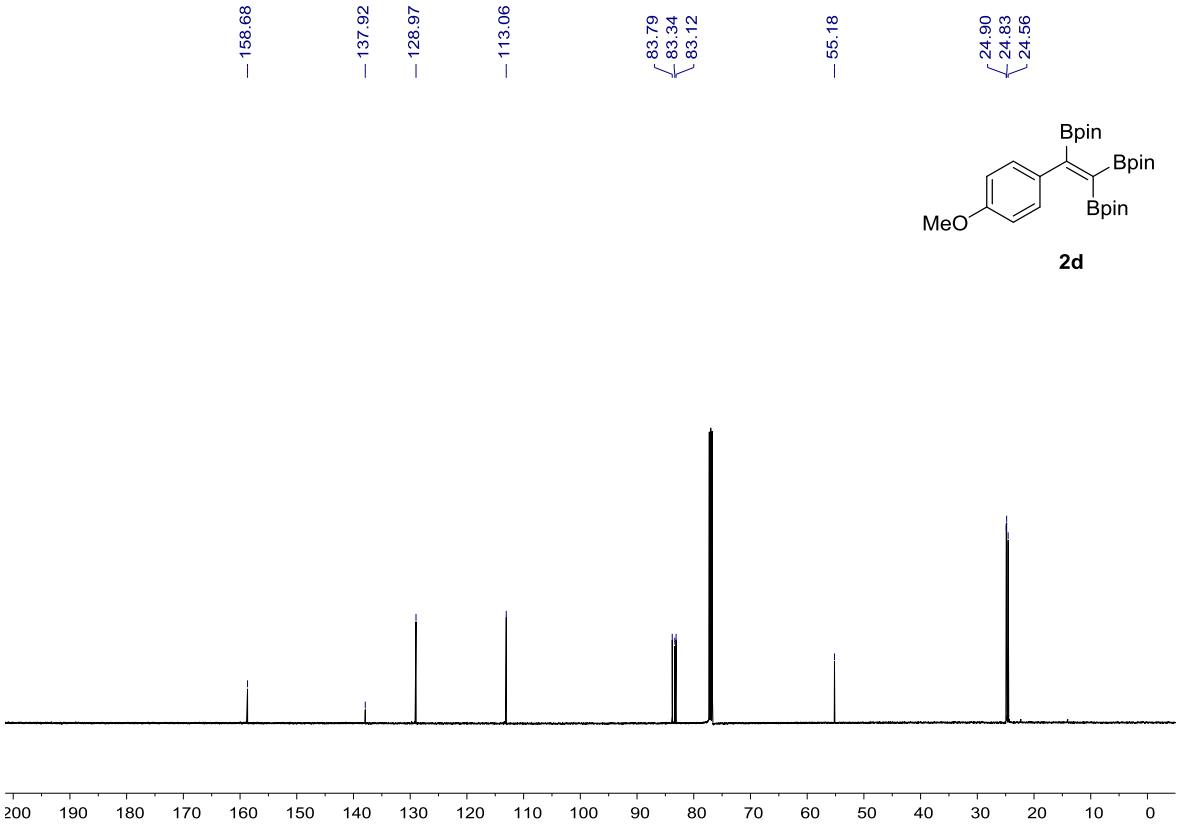
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2c**



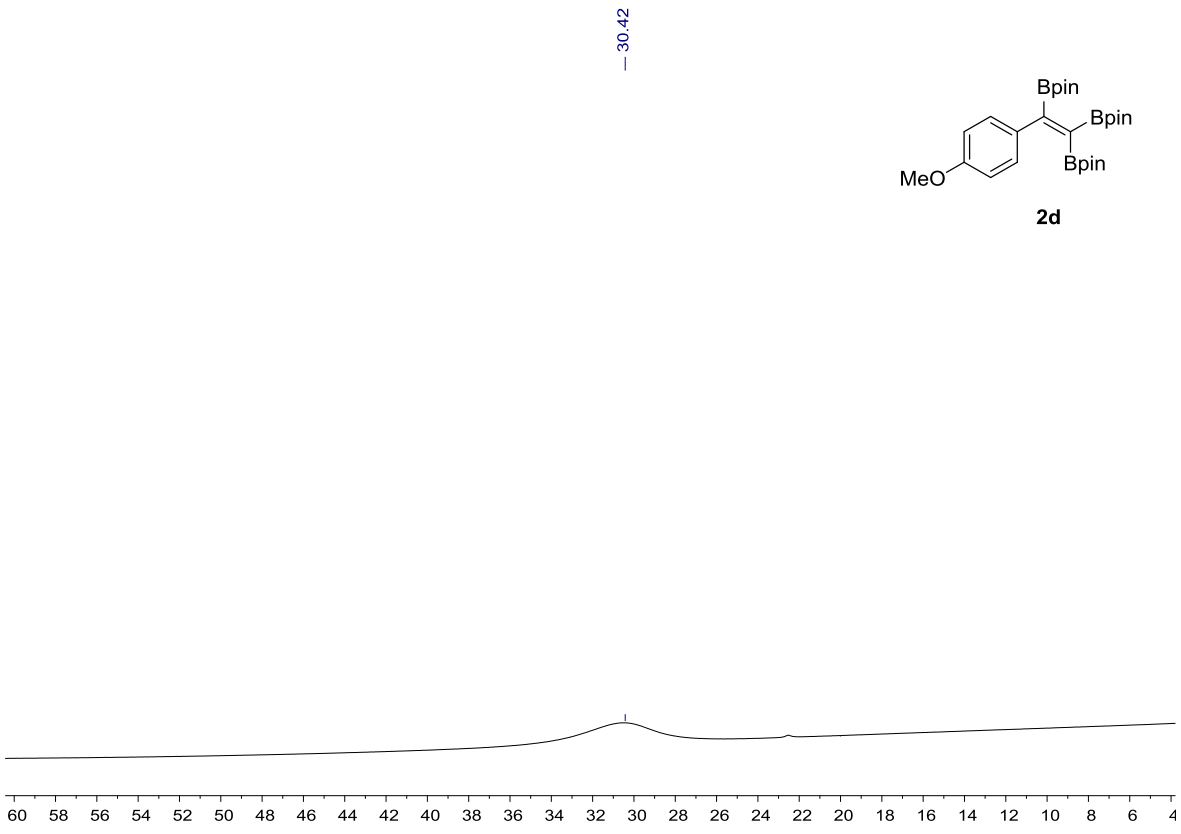
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2d**



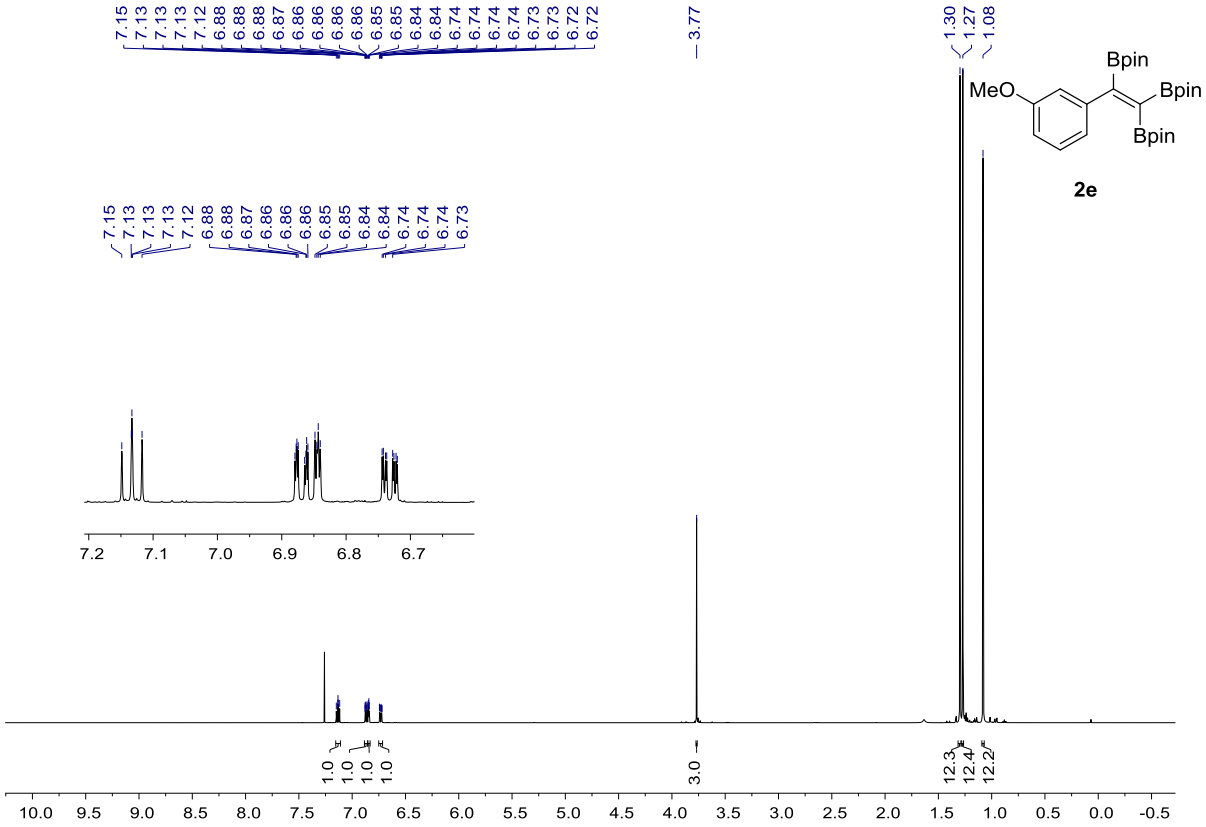
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2d**



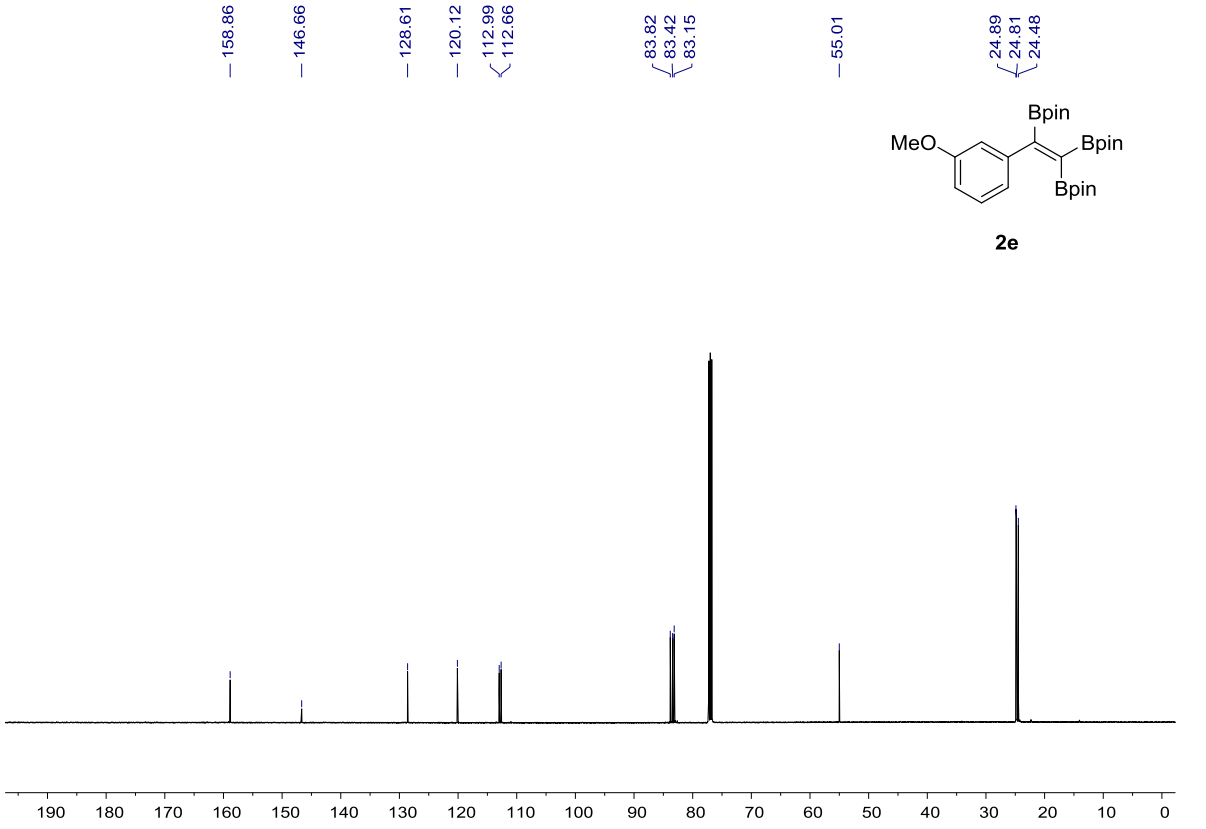
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2d**



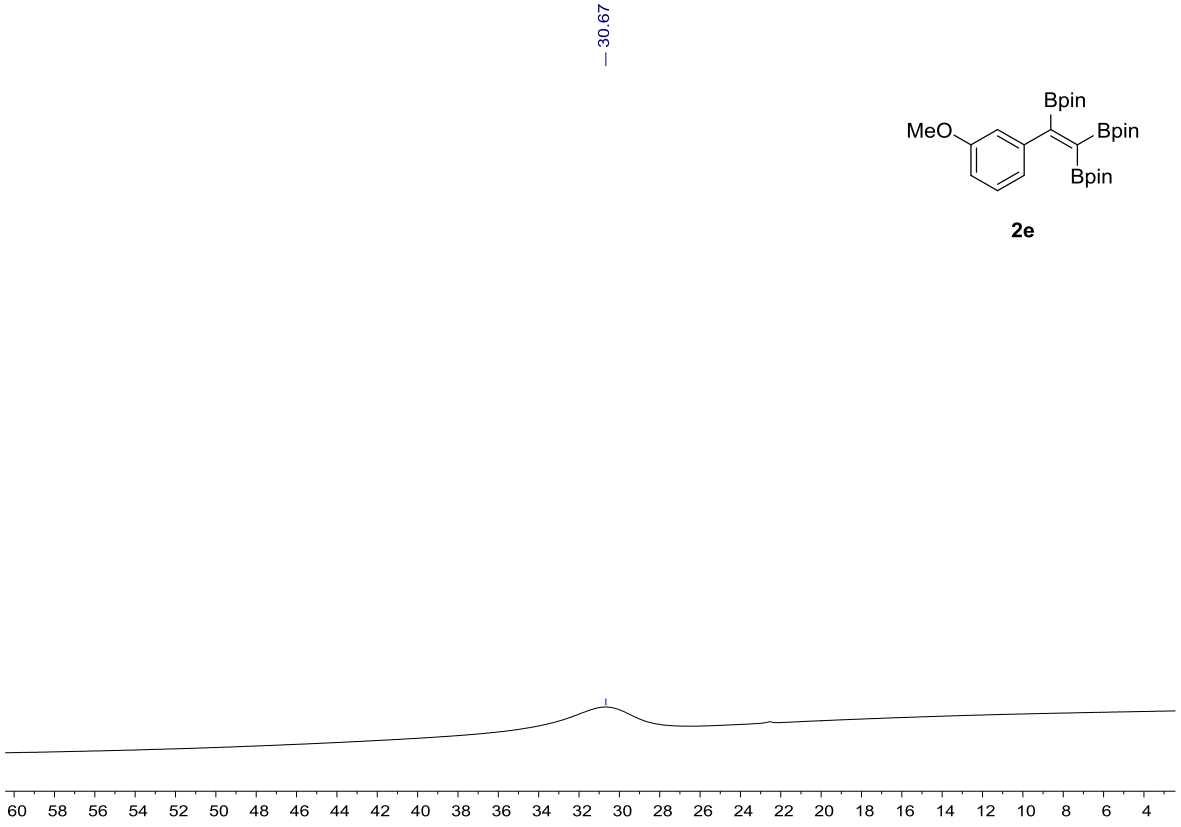
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2e**



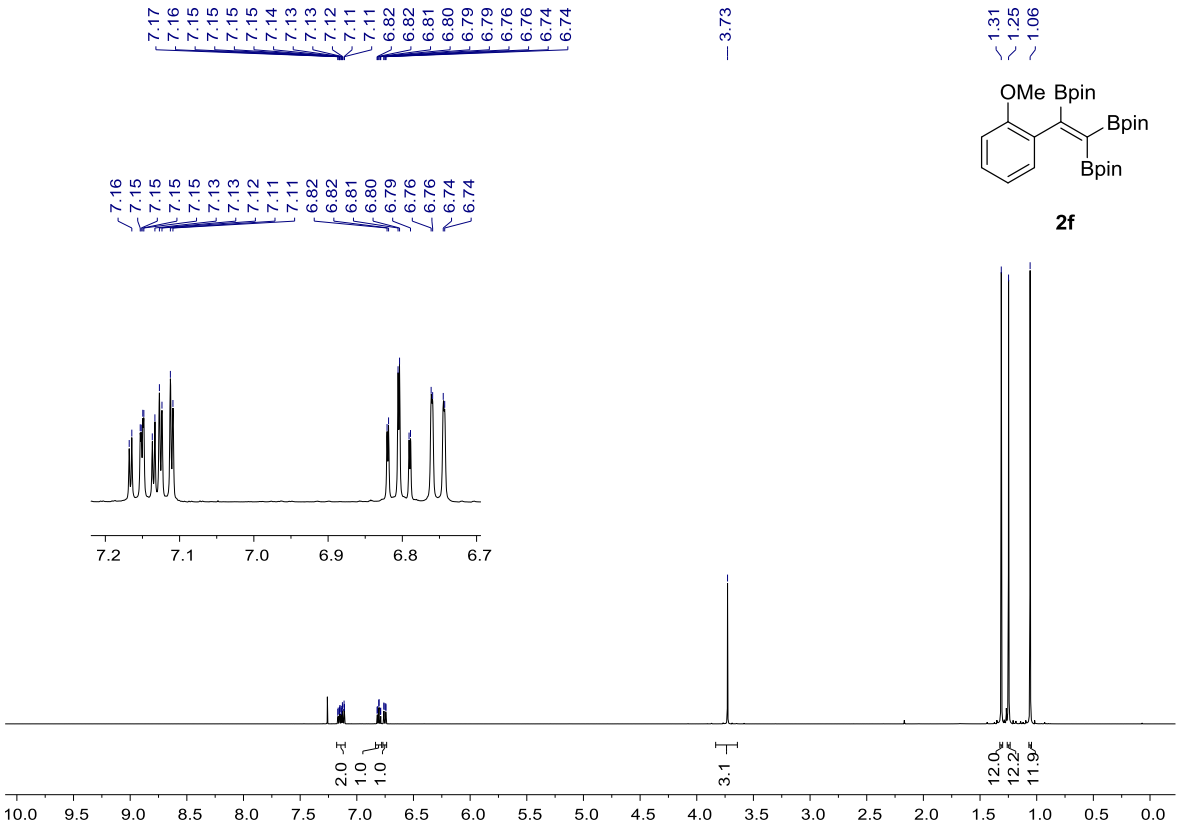
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2e**



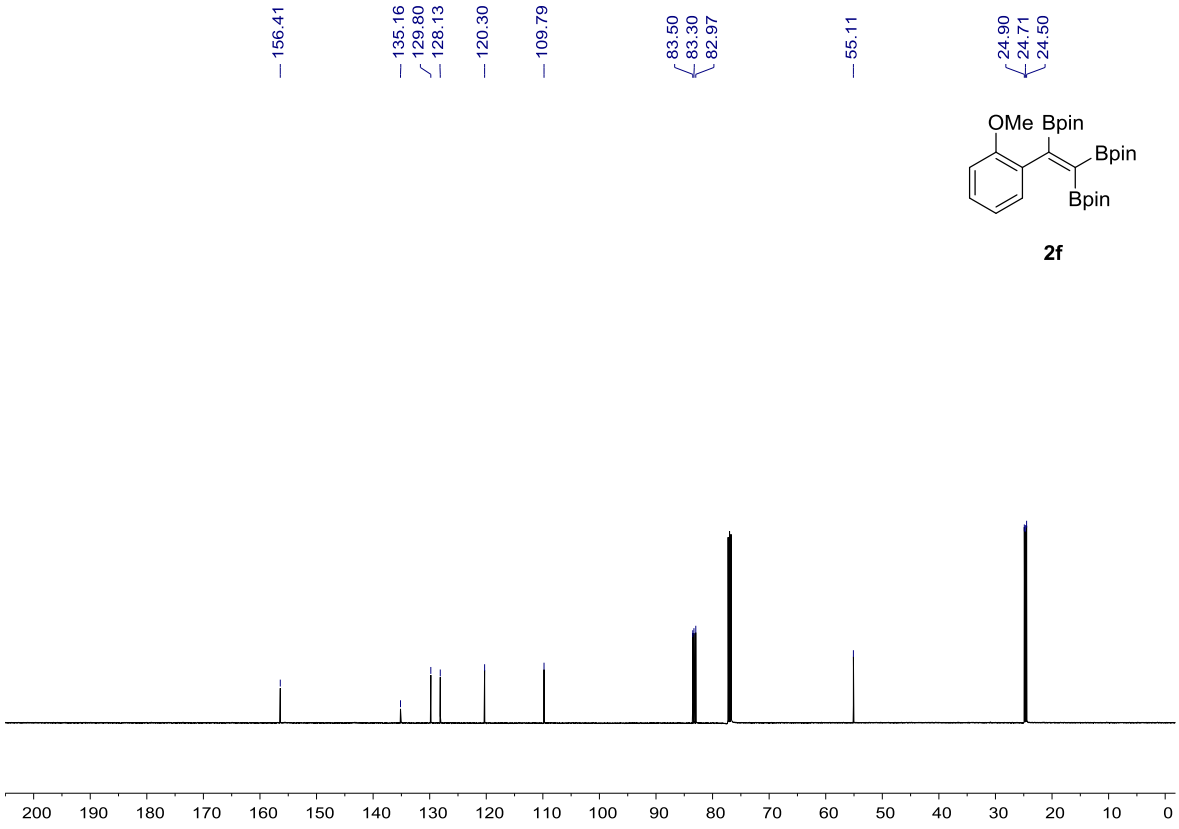
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2e**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2f**

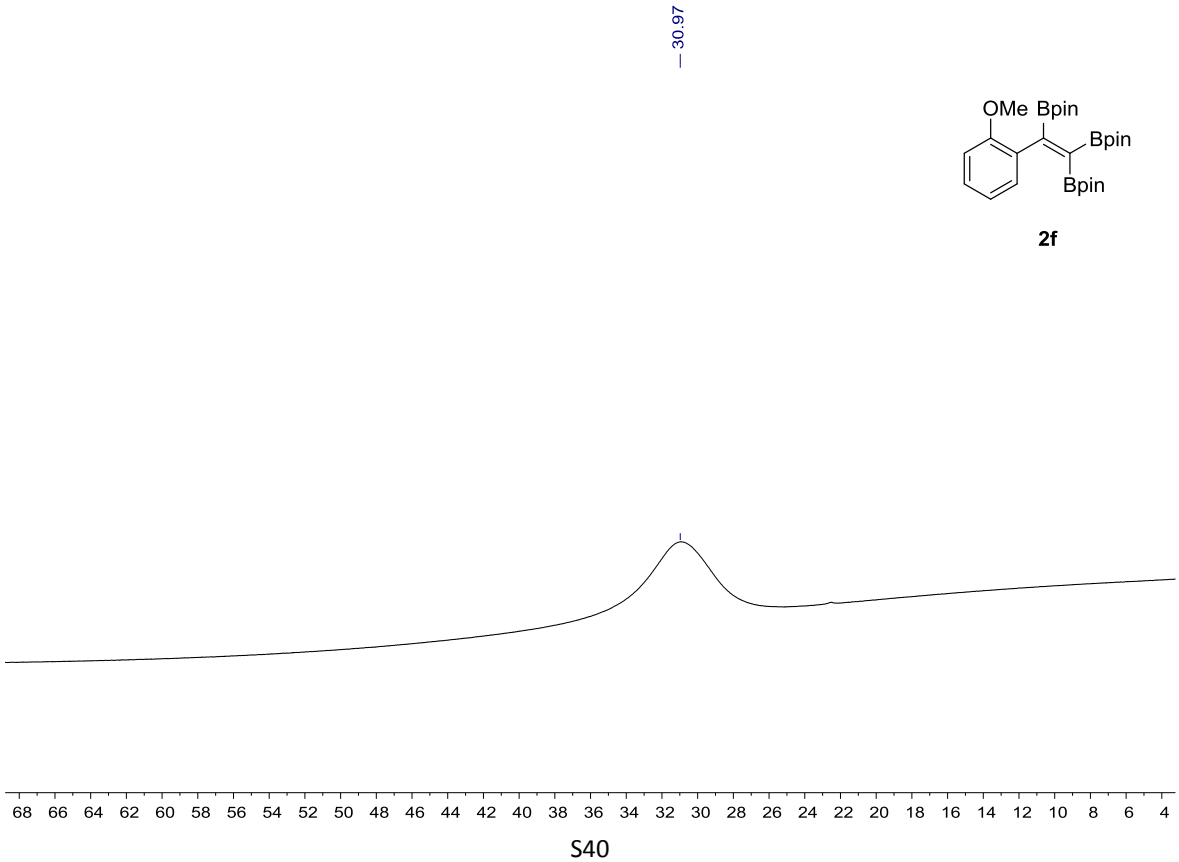


$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2f**



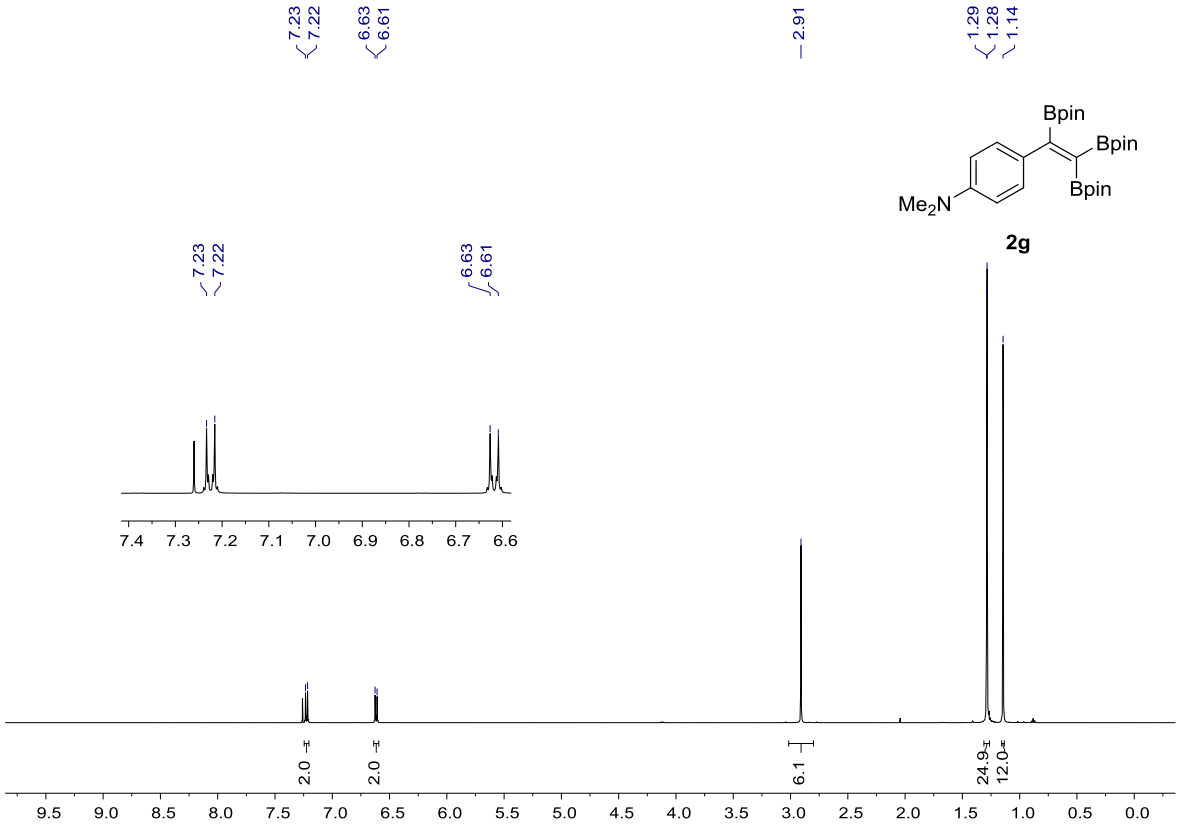
2f

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2f**

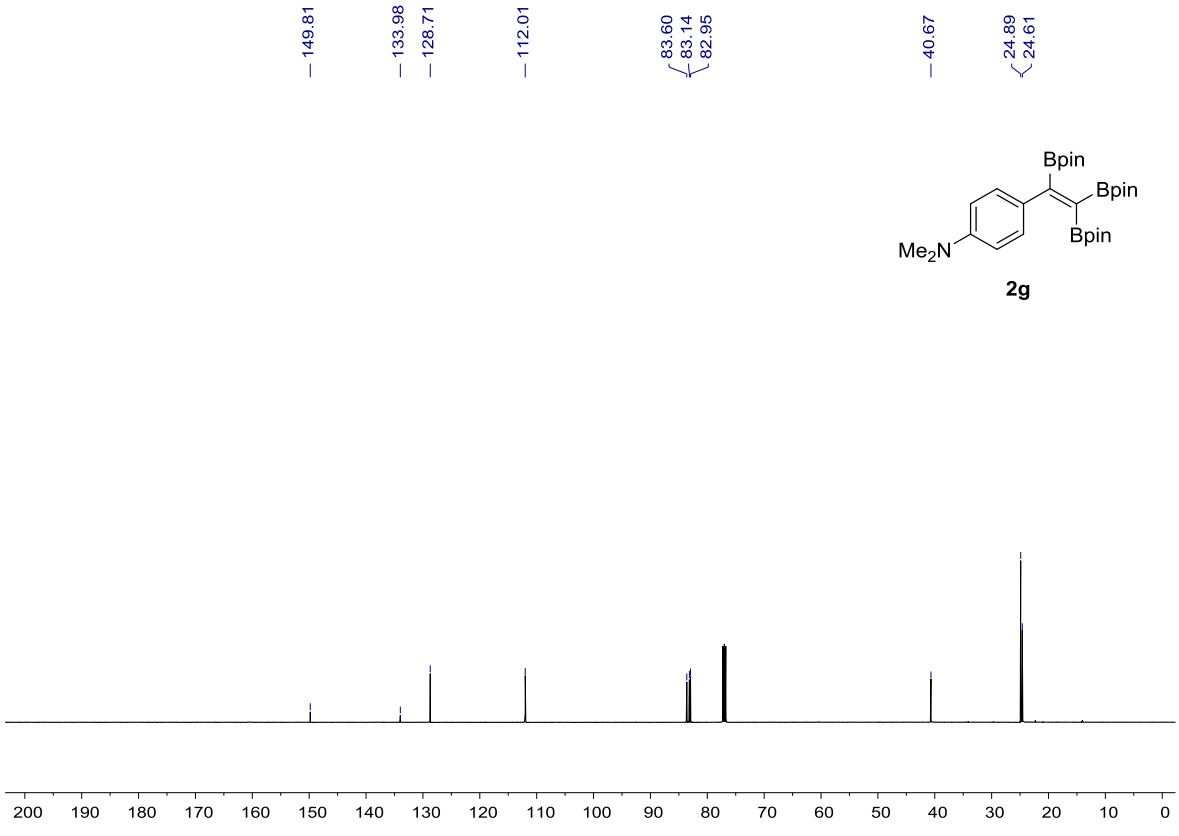


2f

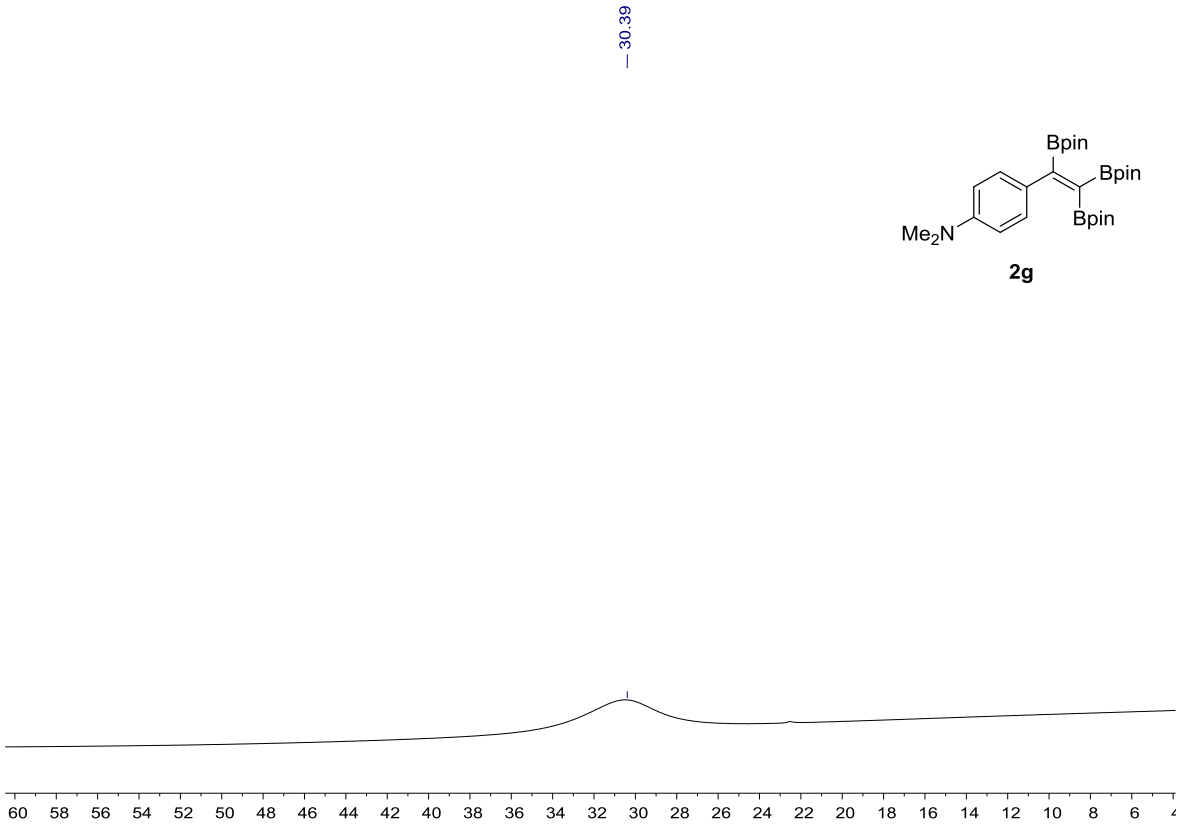
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2g**



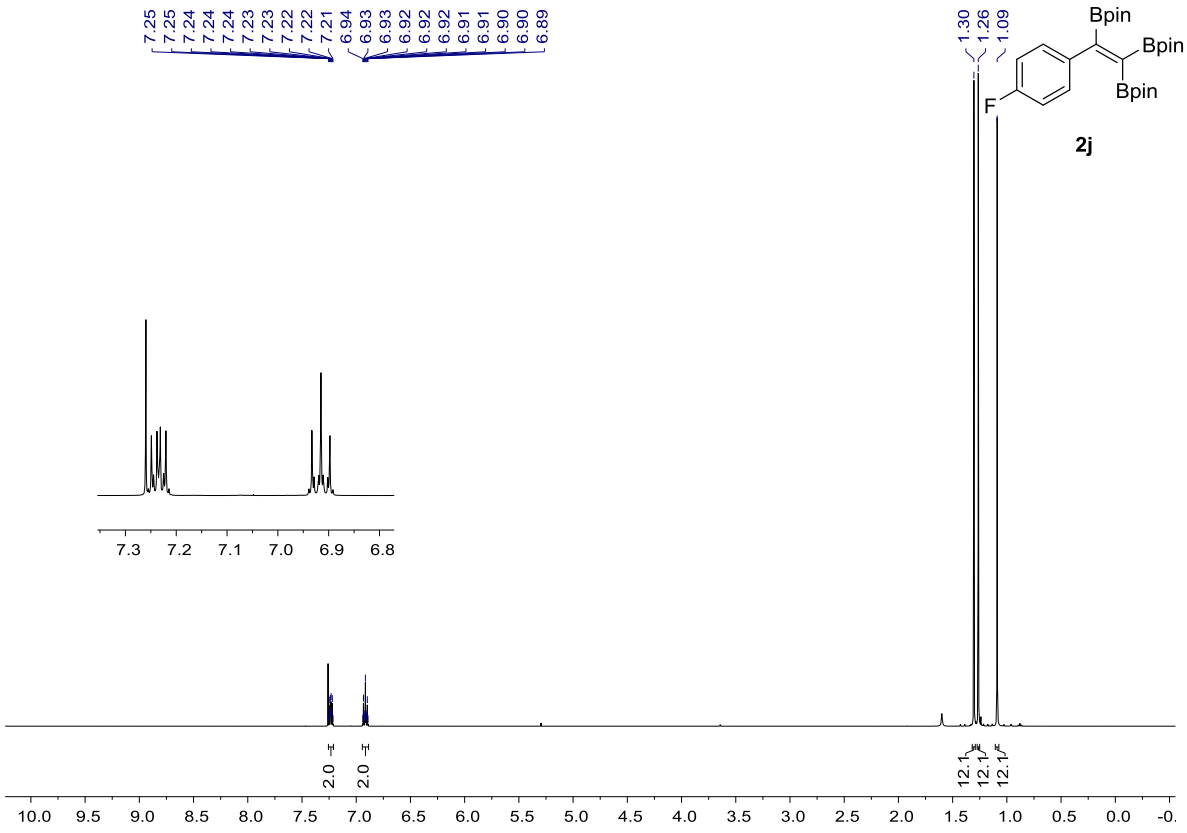
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2g**



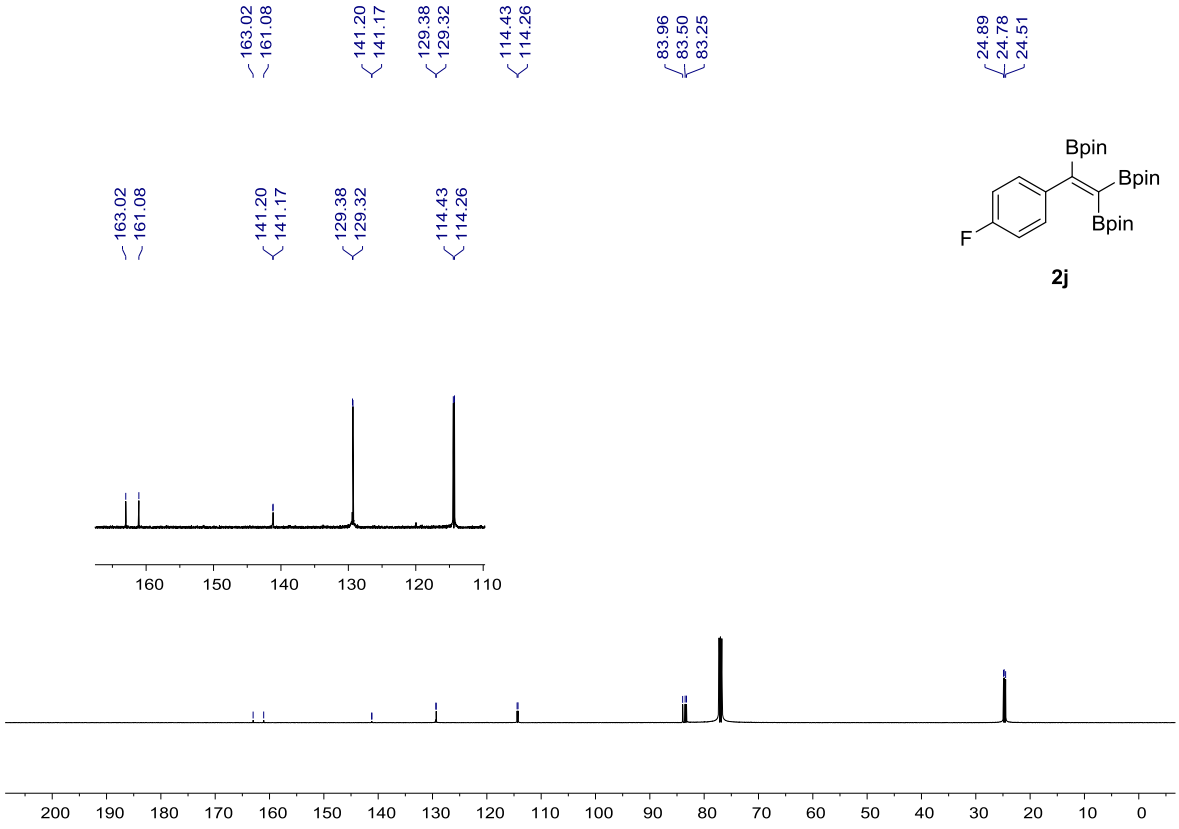
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2g**



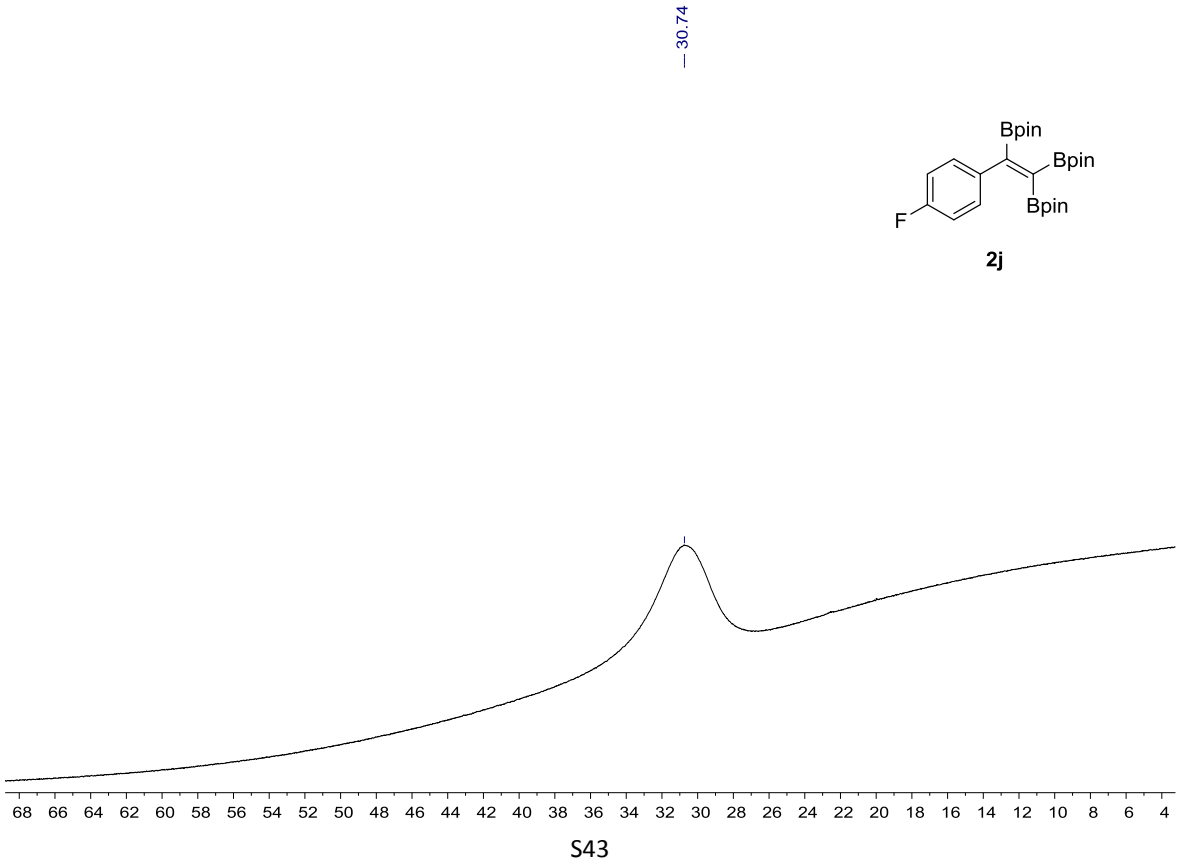
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2j**



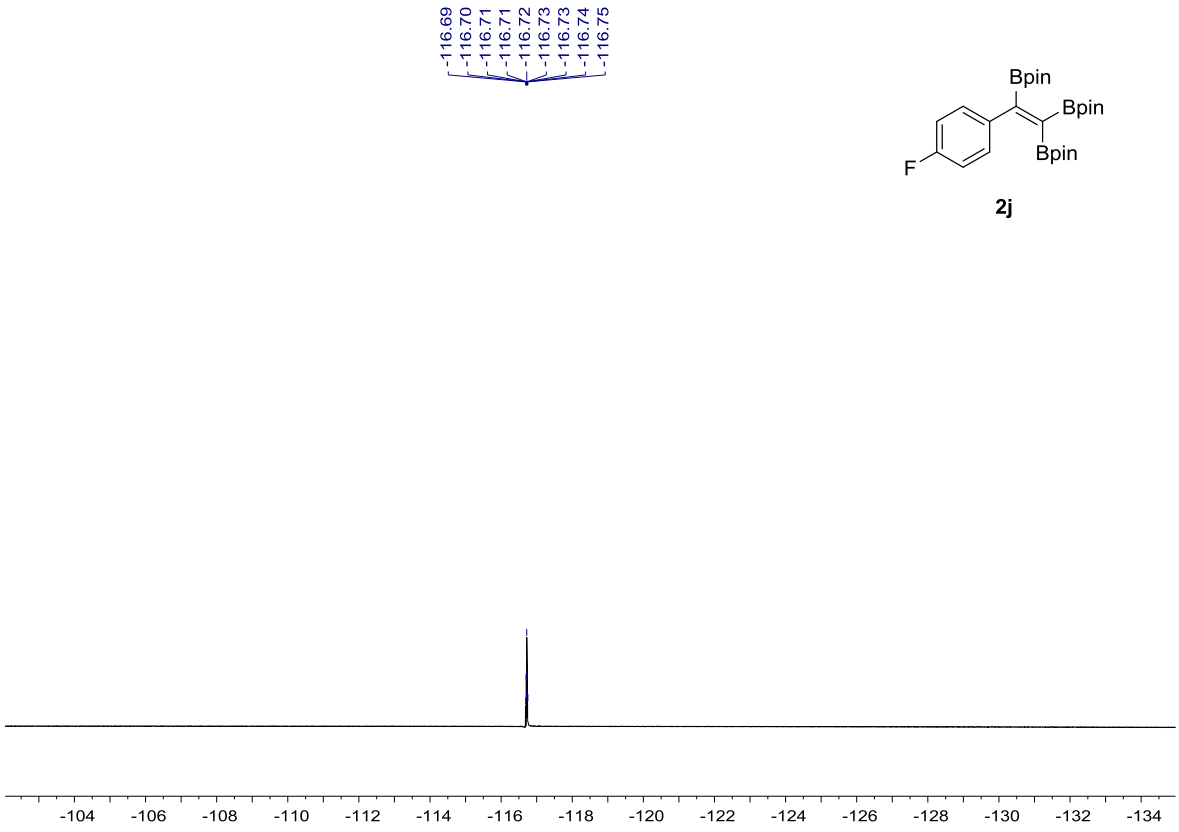
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2j**



^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2j**

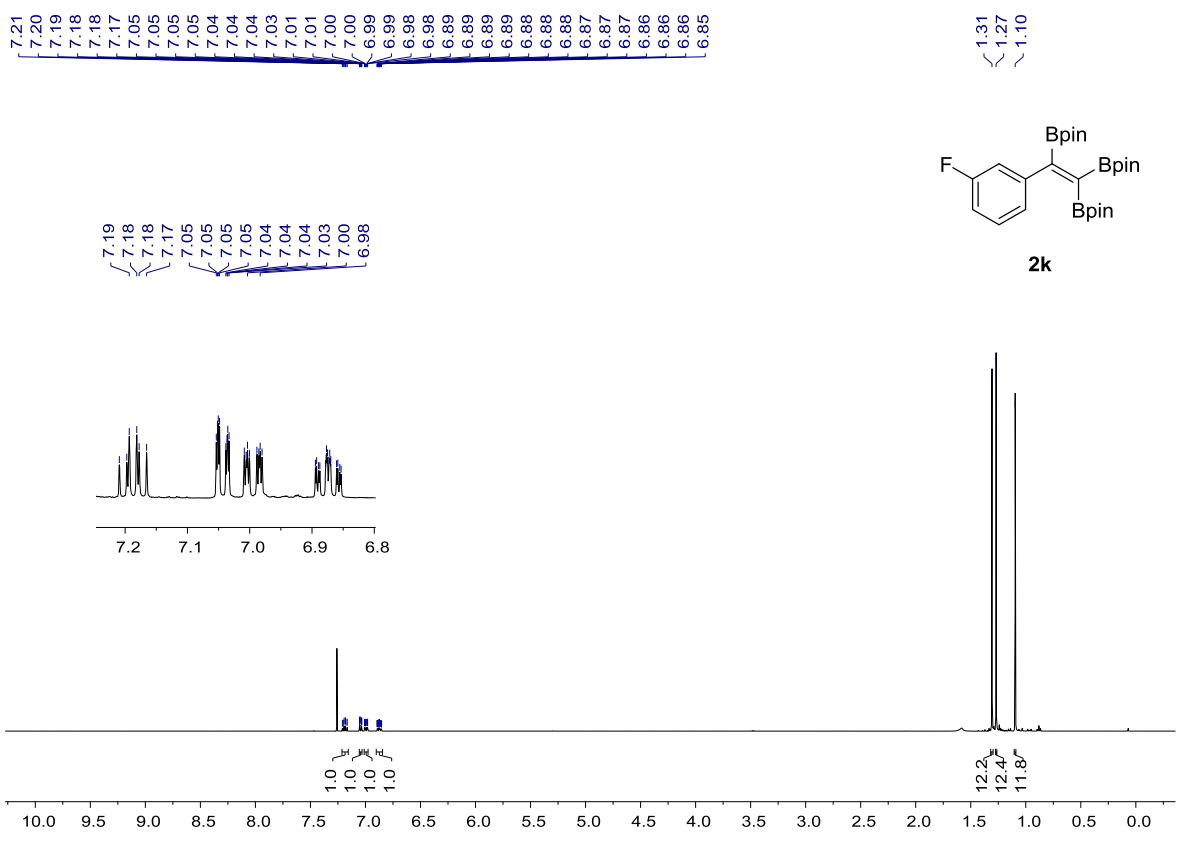


^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2j**



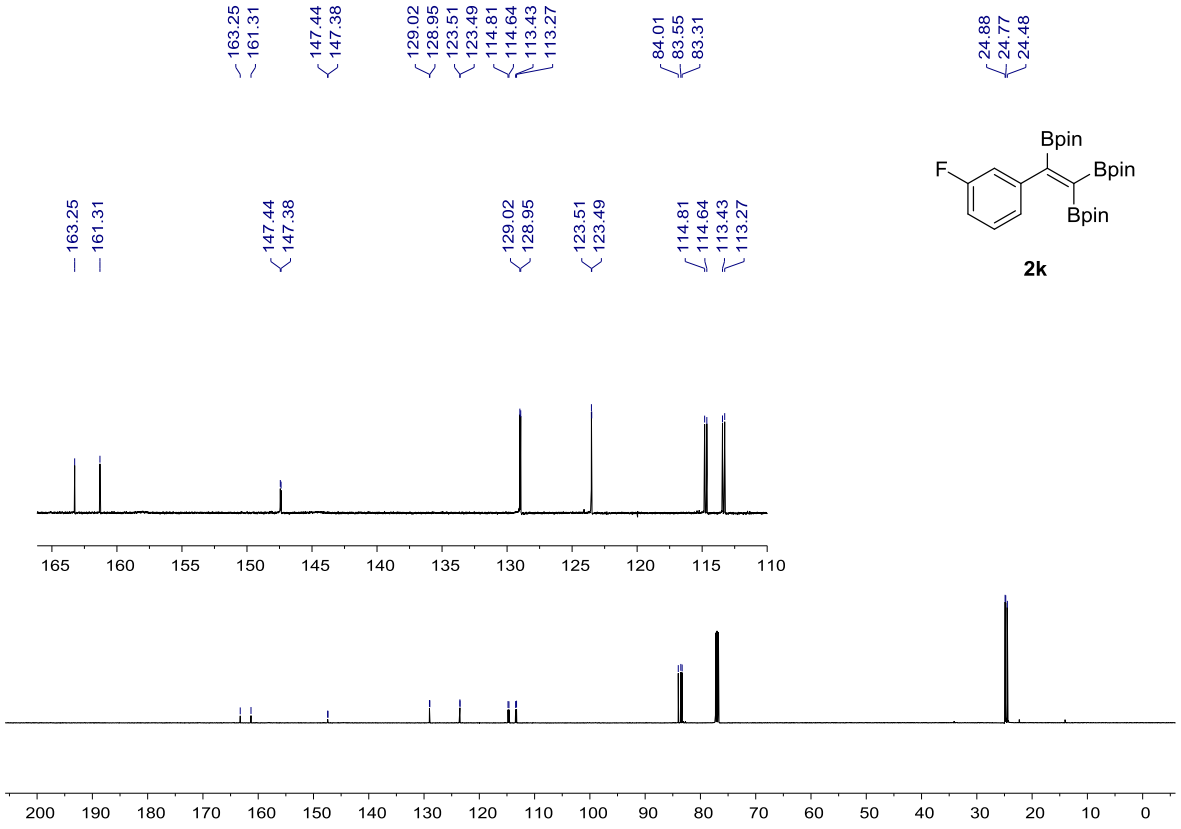
2j

^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2k**

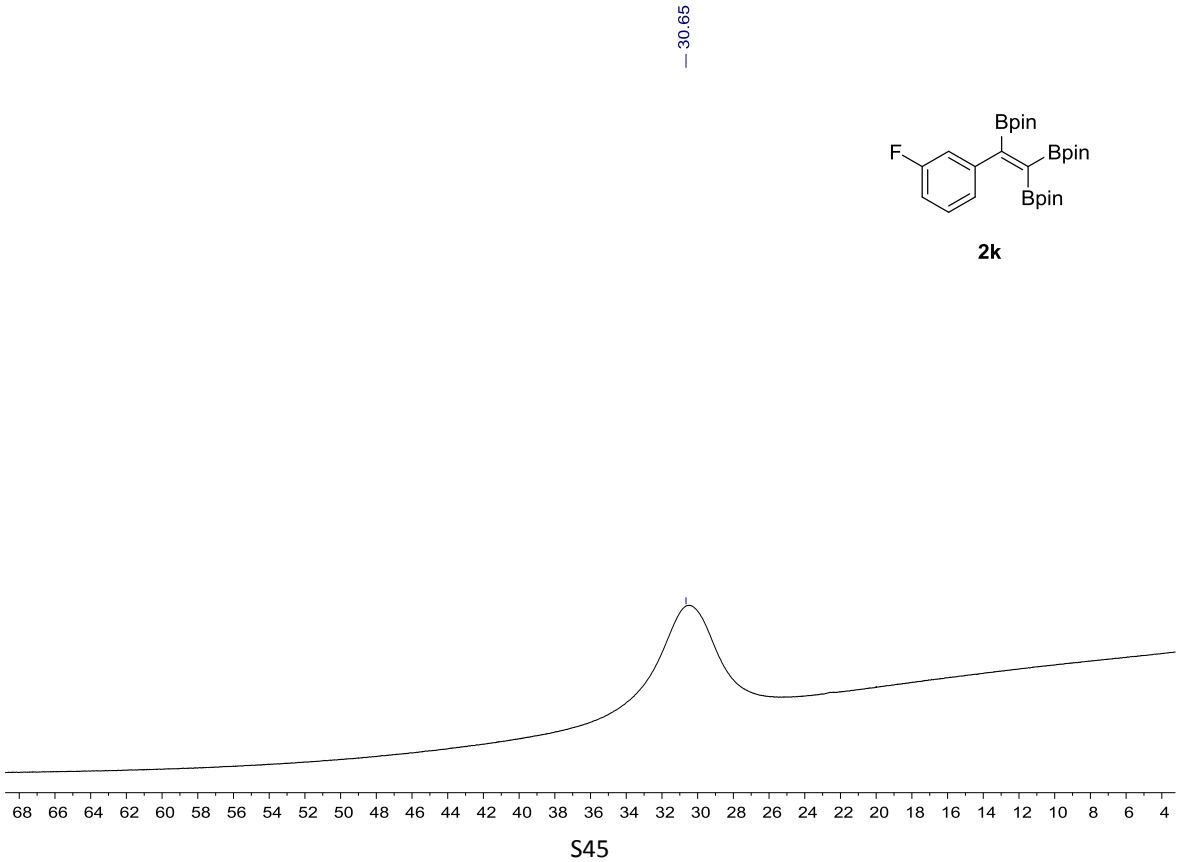


2k

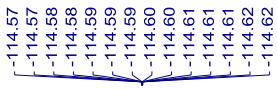
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2k**

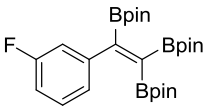


^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2k**

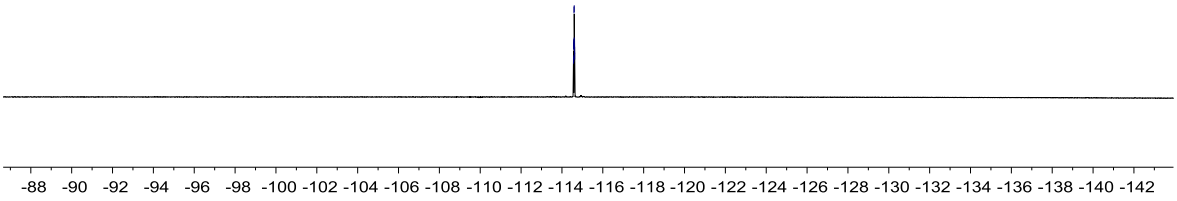


^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2k**

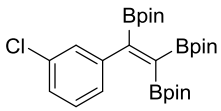




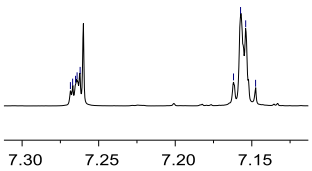
2k

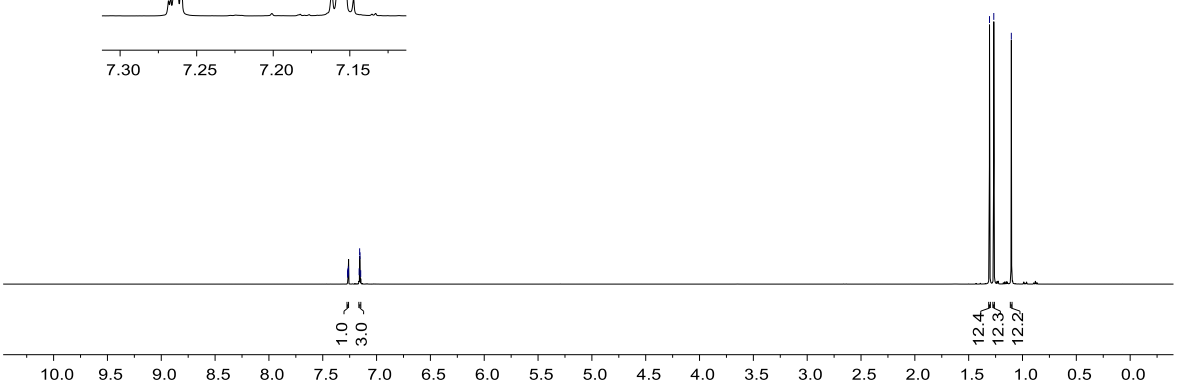


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2l**

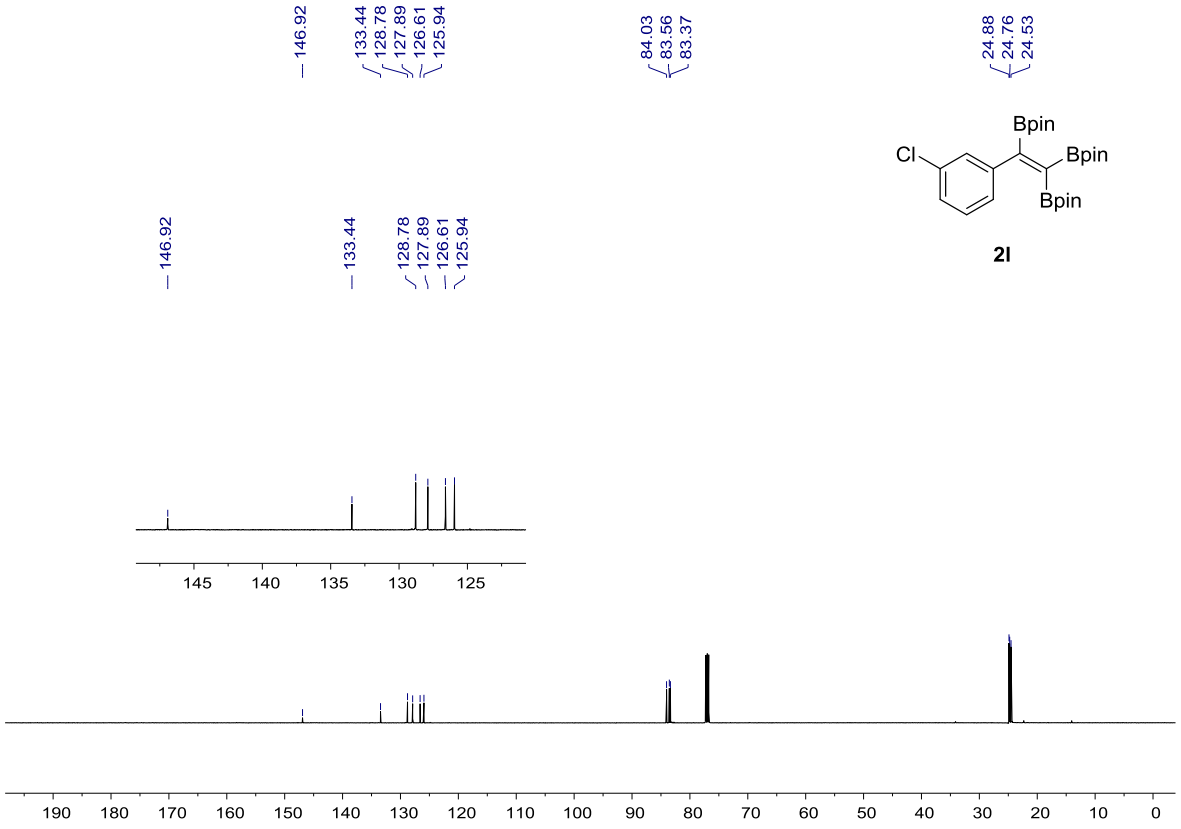


2l

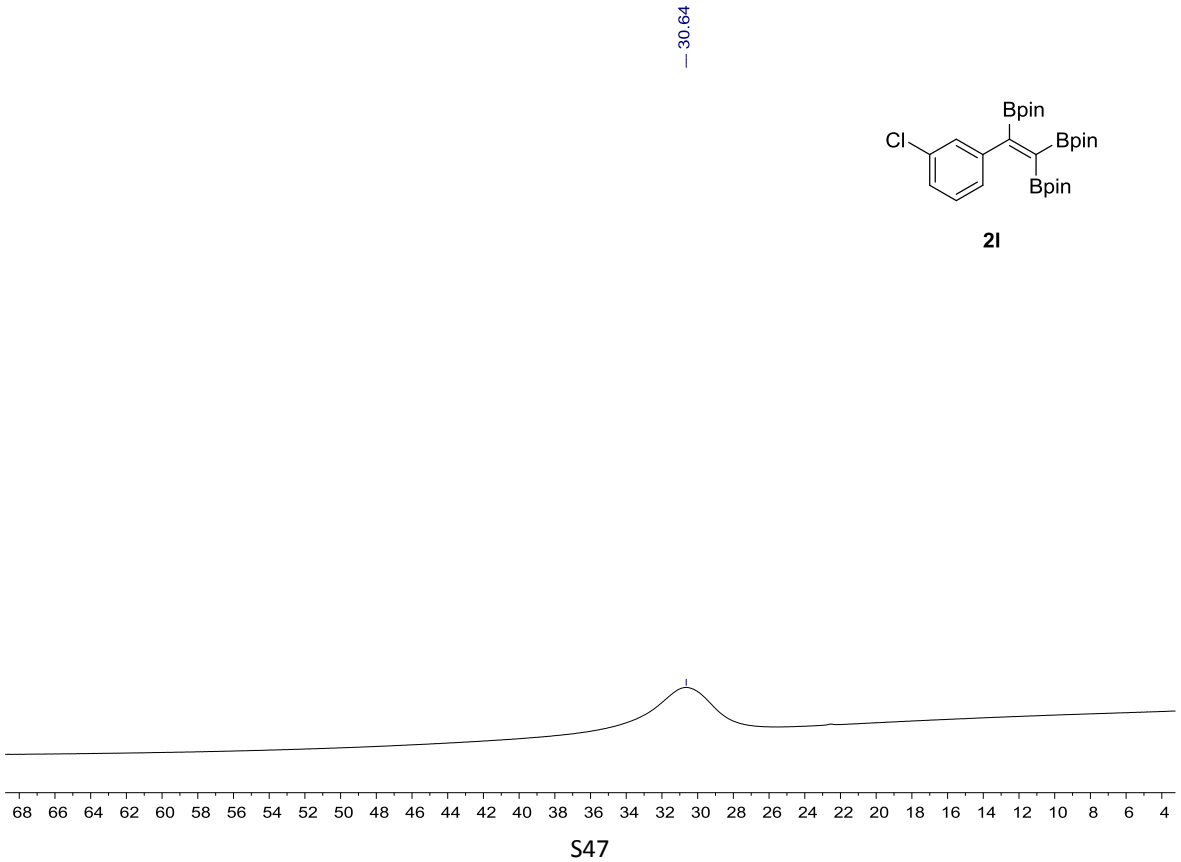




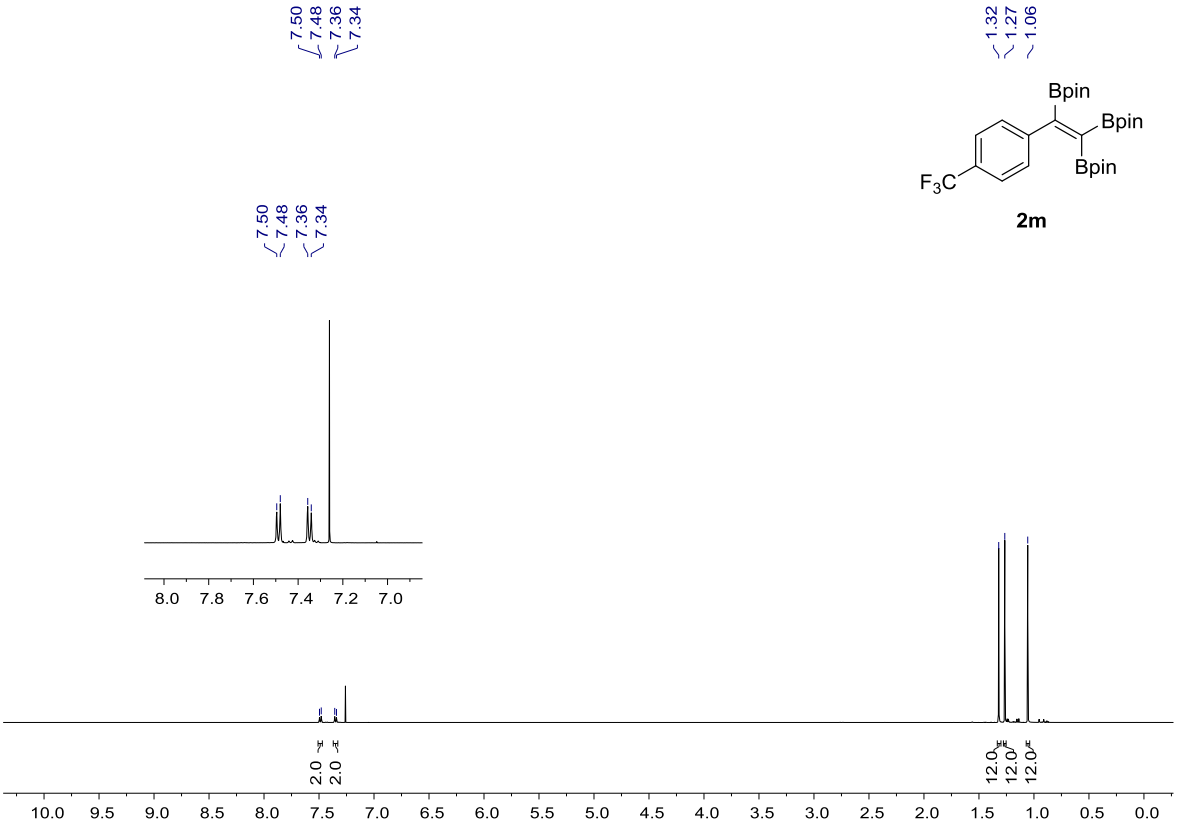
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2l**



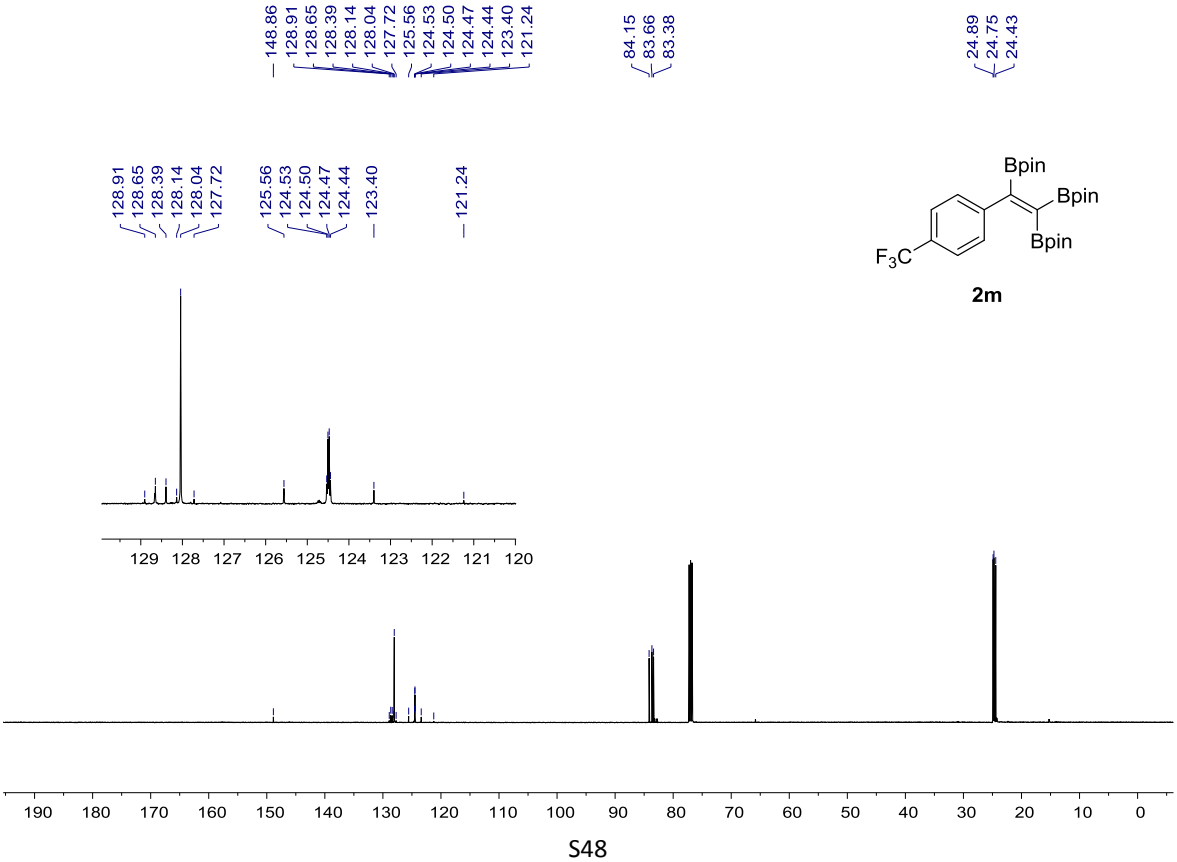
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2l**



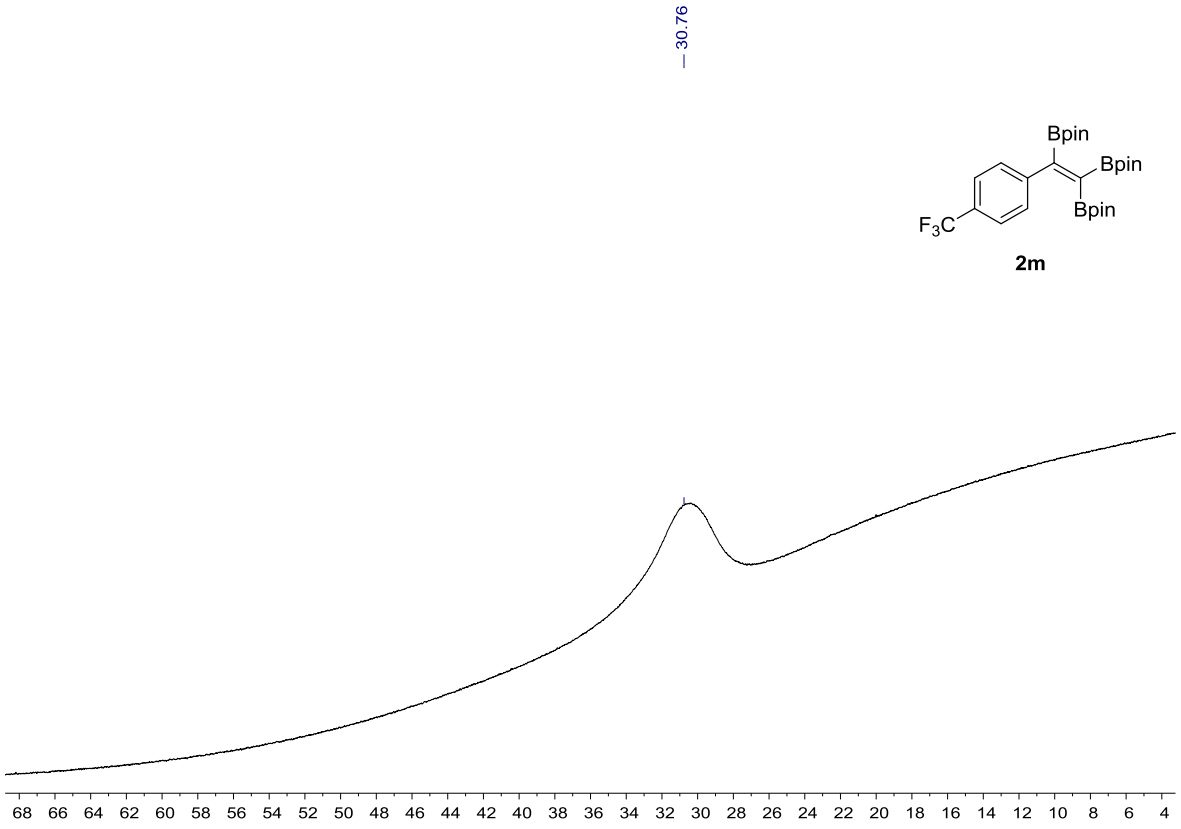
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2m**



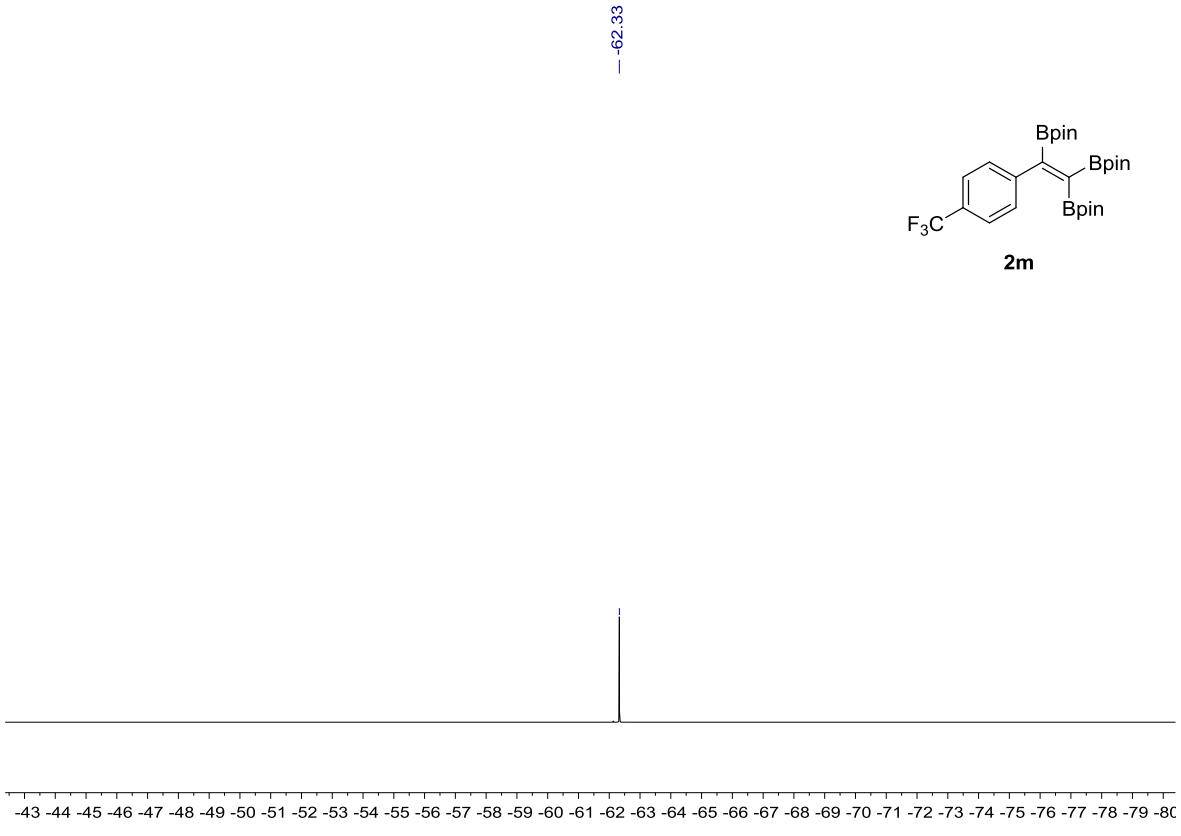
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2m**



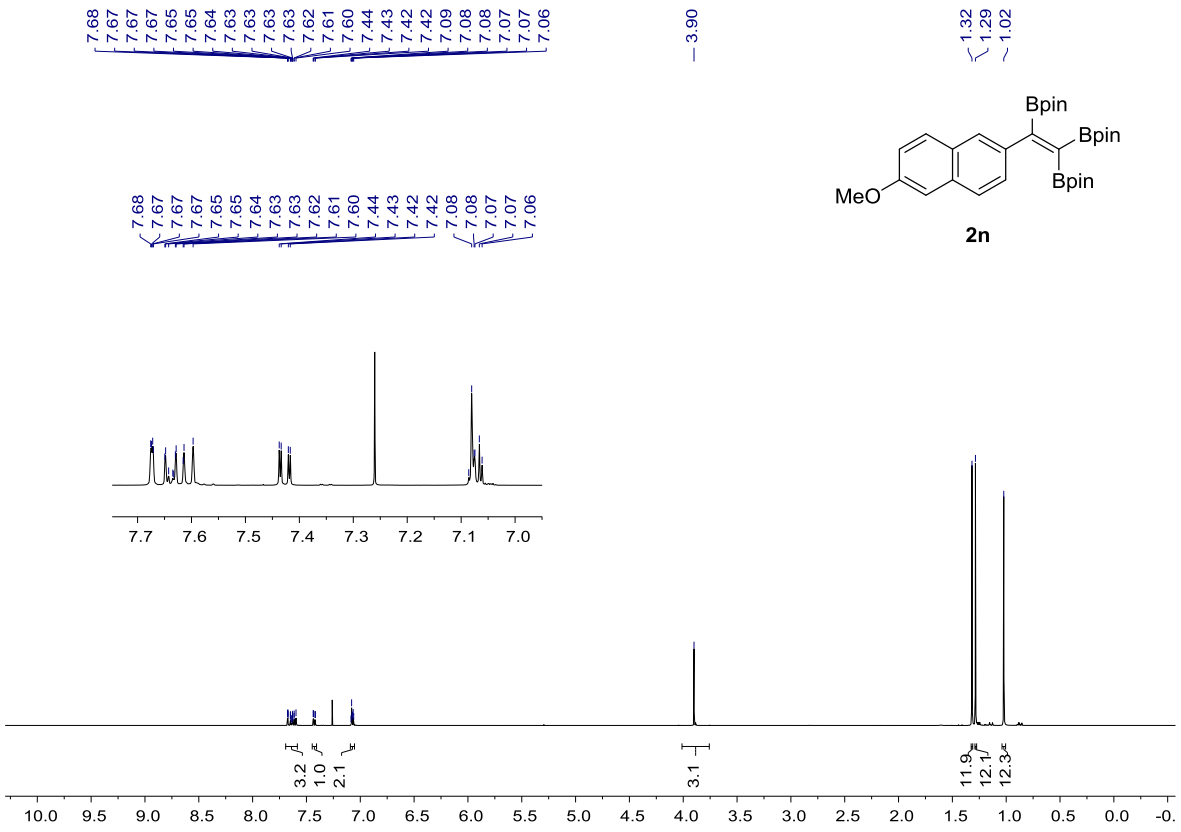
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2m**



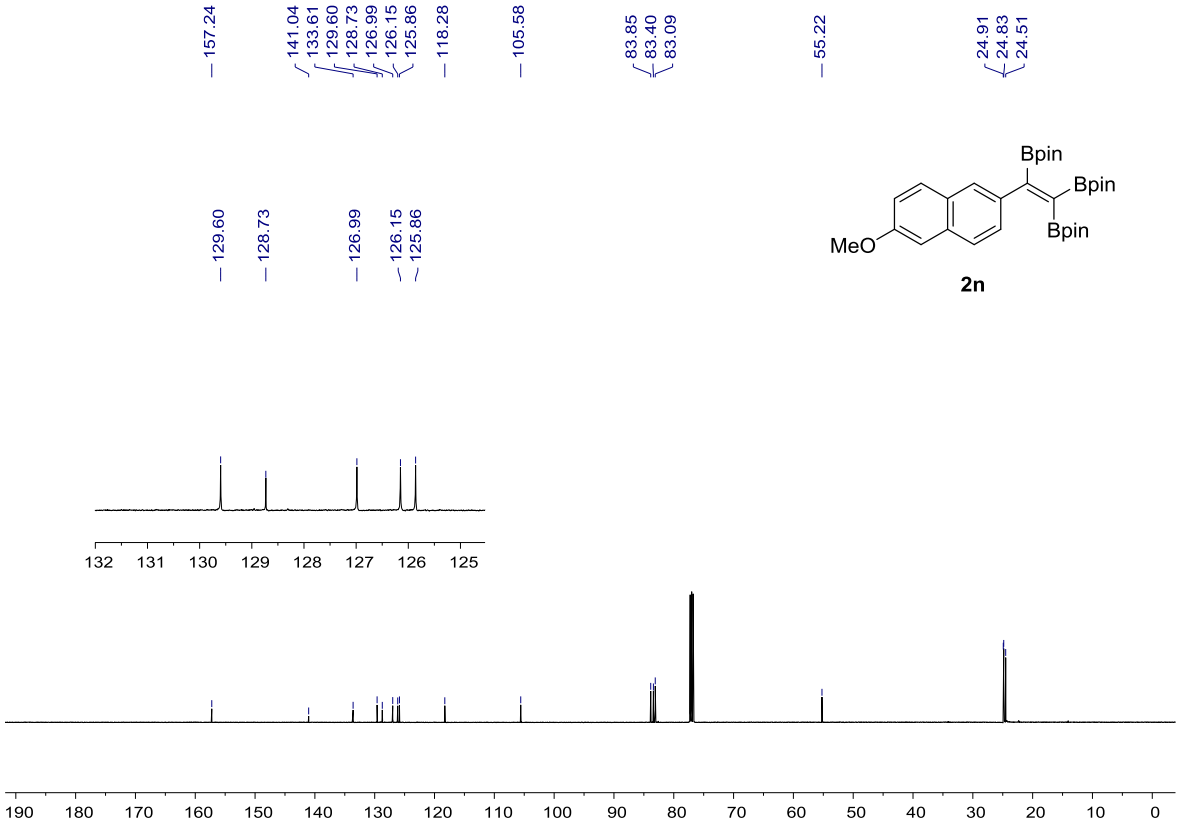
^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **2m**



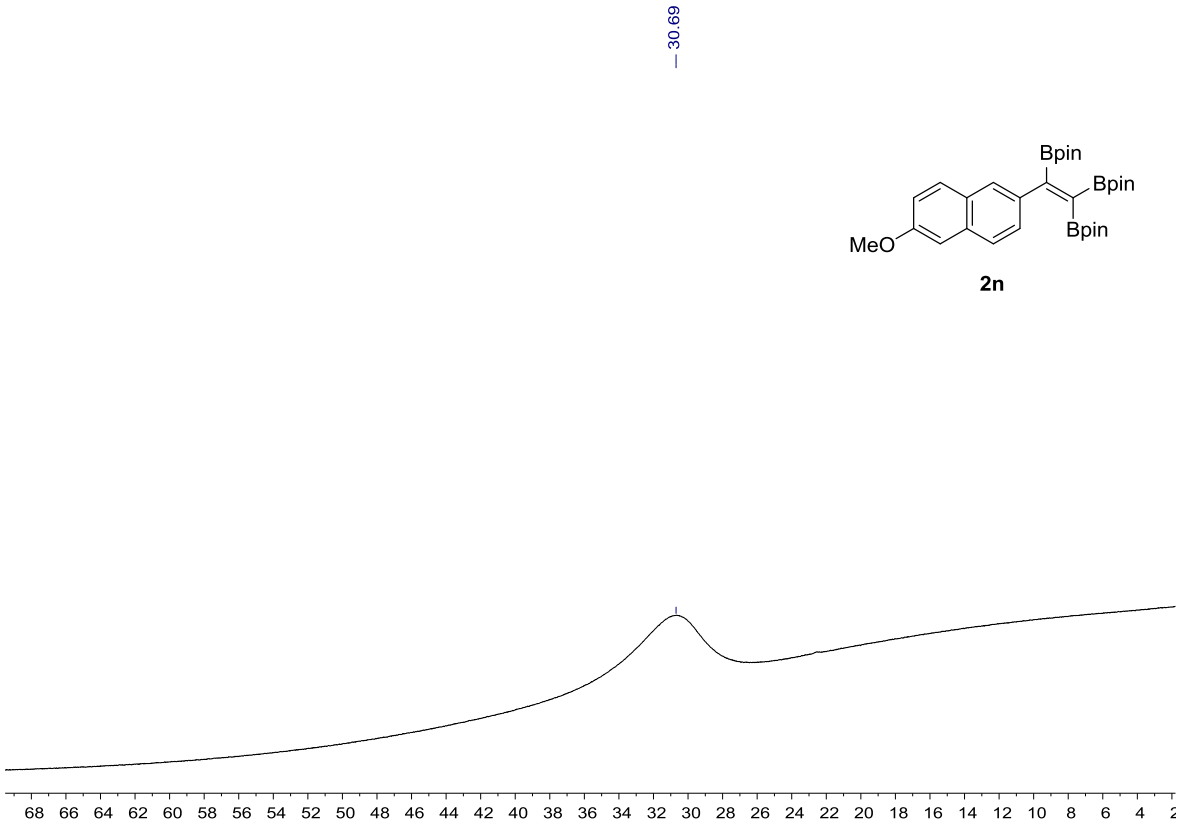
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2n**



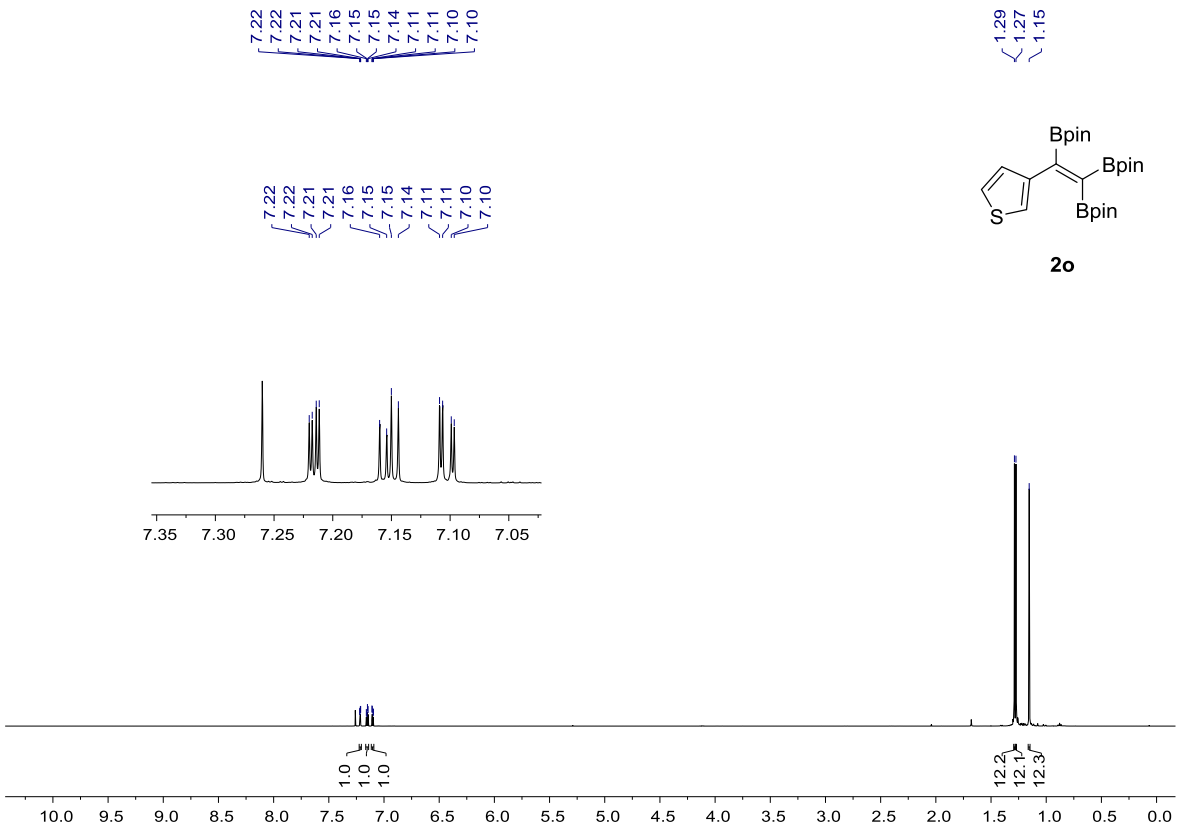
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2n**



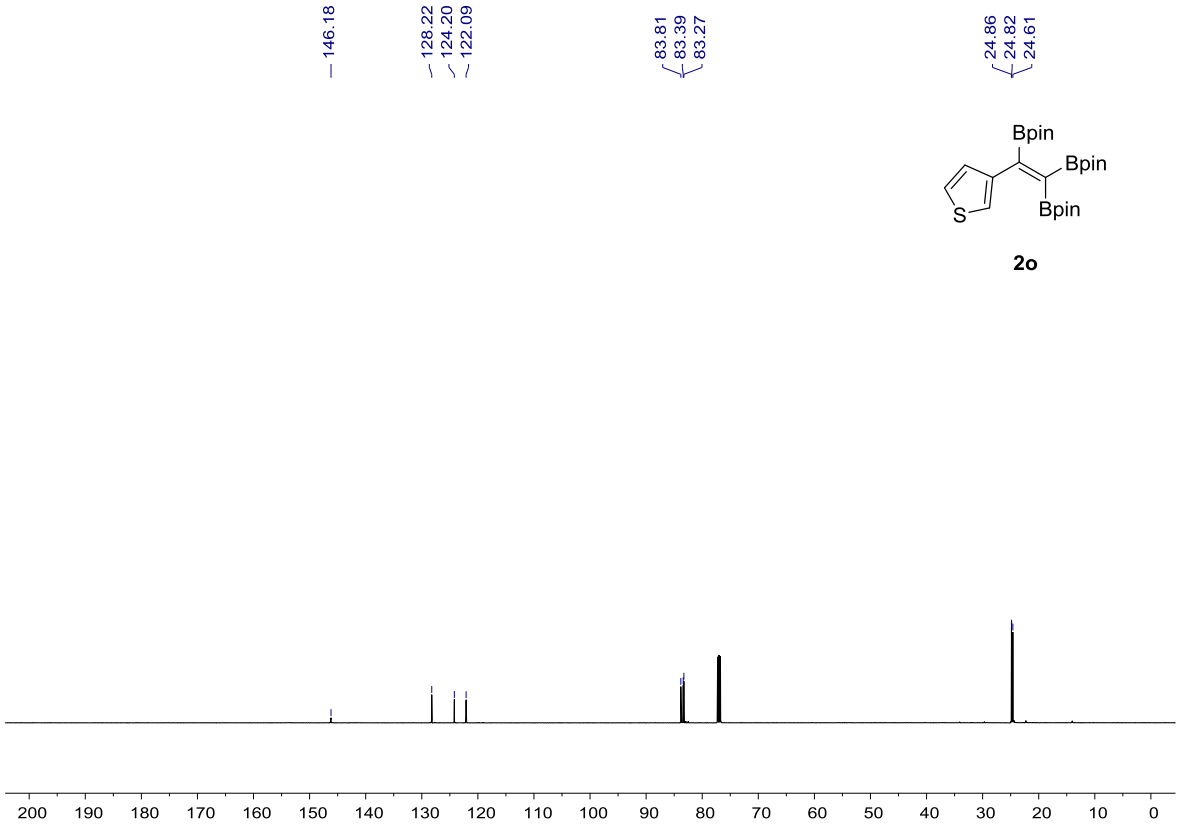
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2n**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2o**

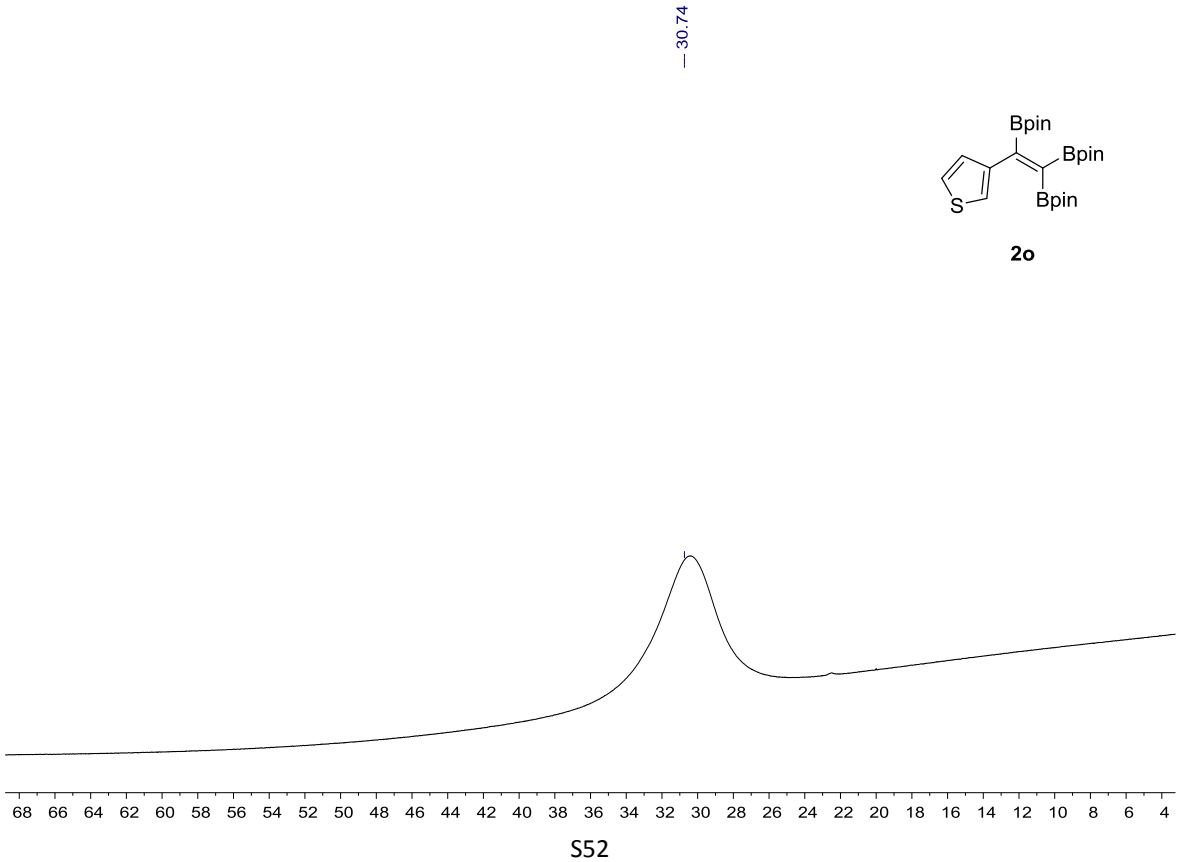


$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2o**



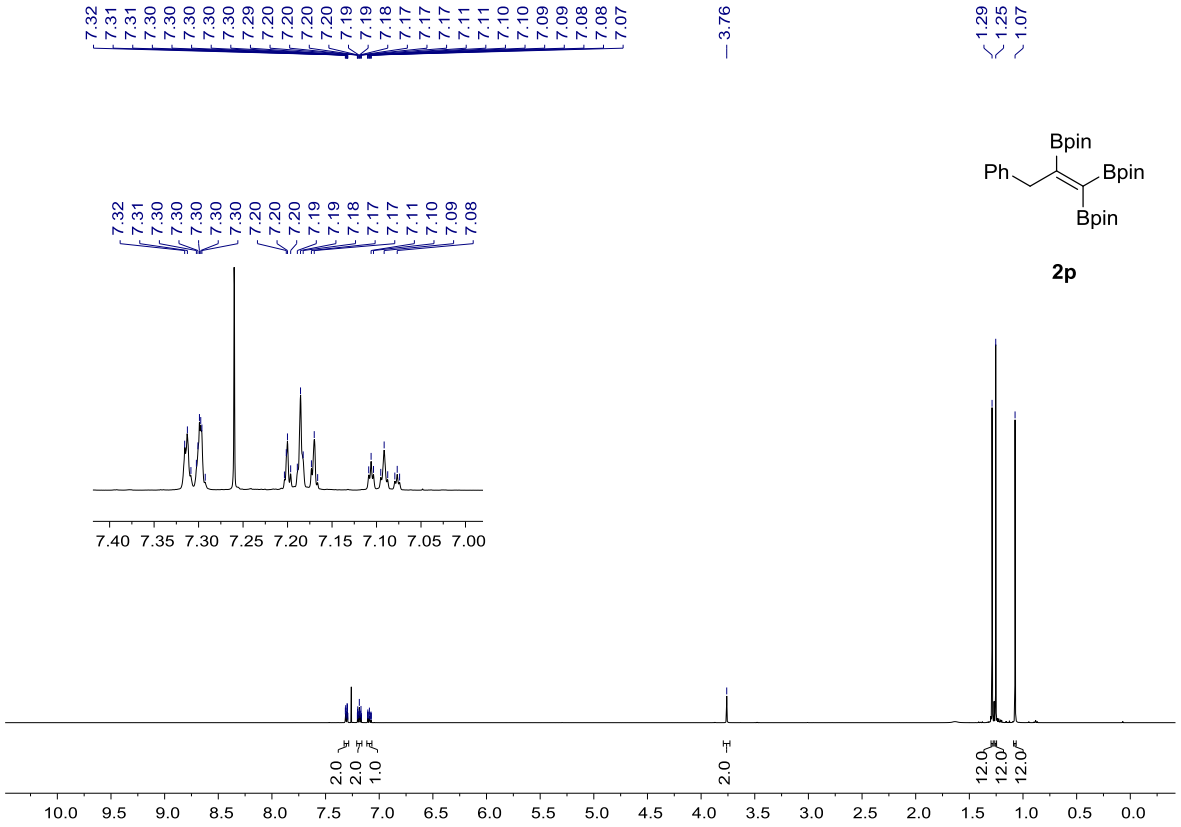
2o

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2o**

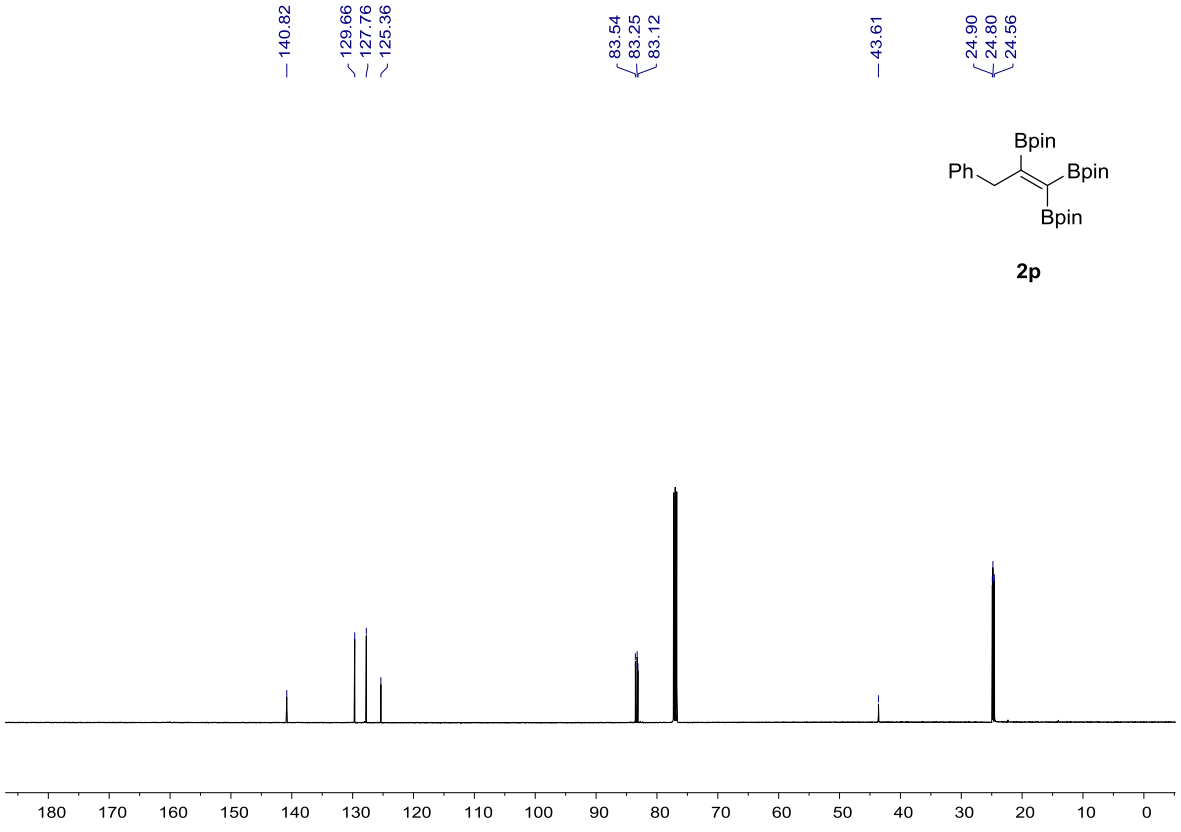


2o

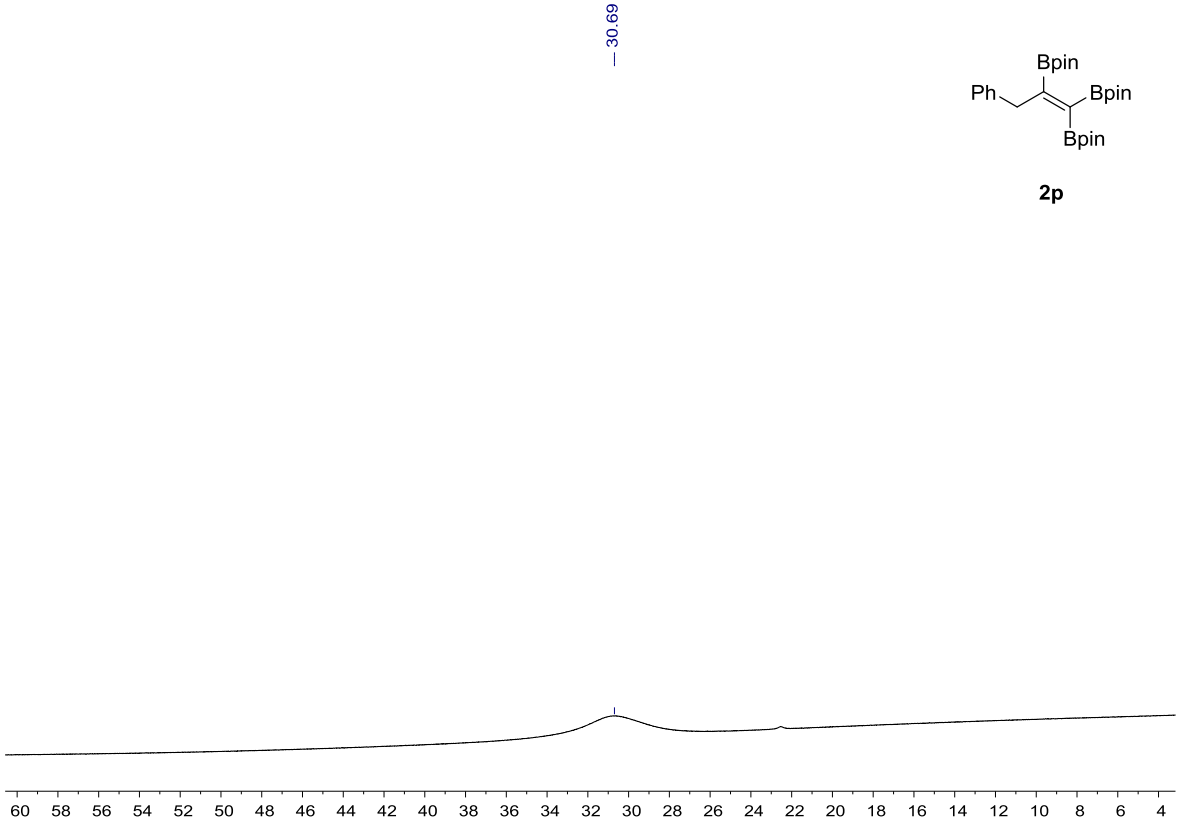
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2p**



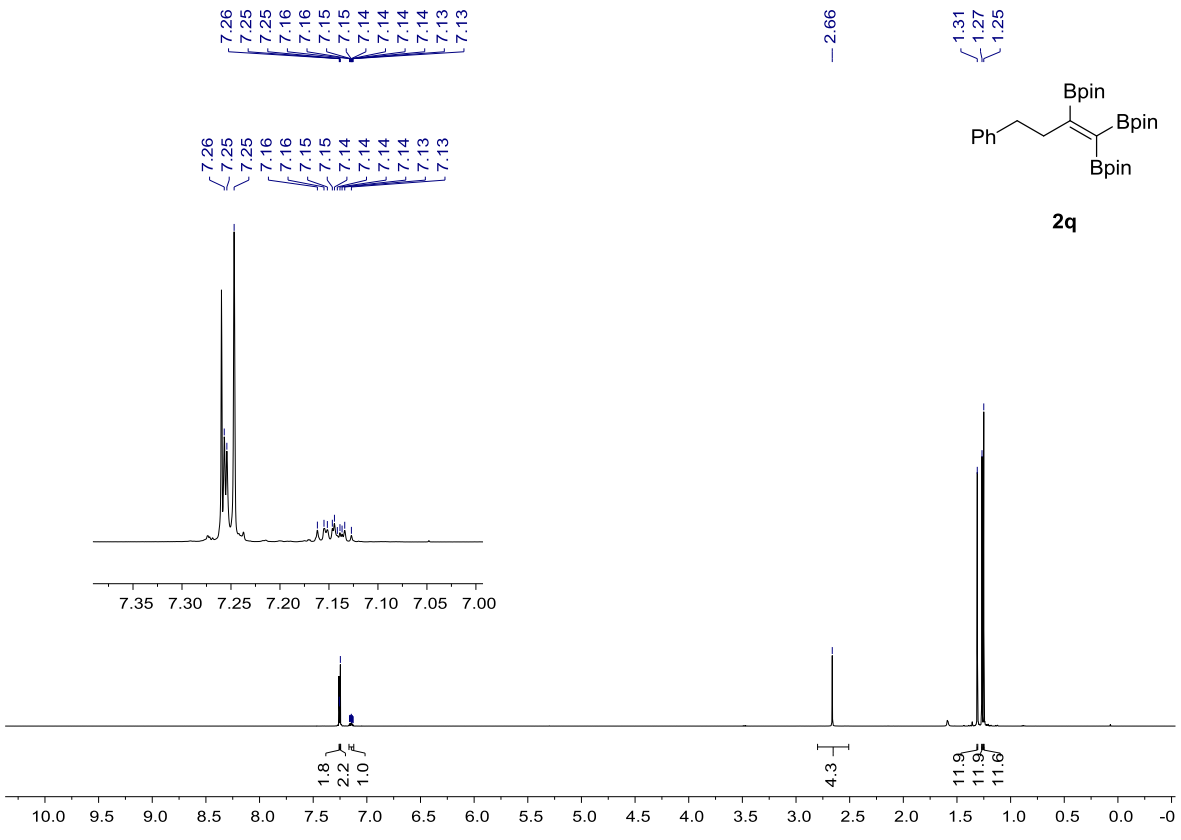
^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **2p**



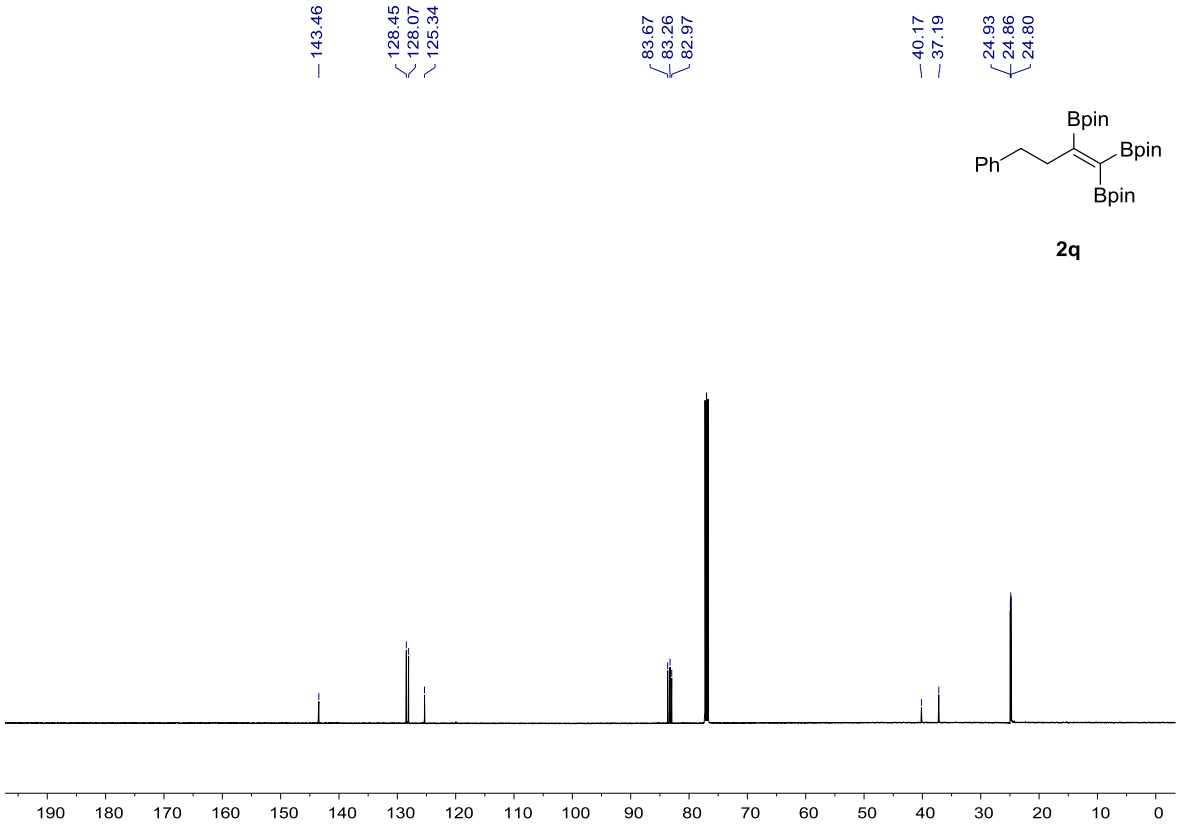
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2p**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2q**

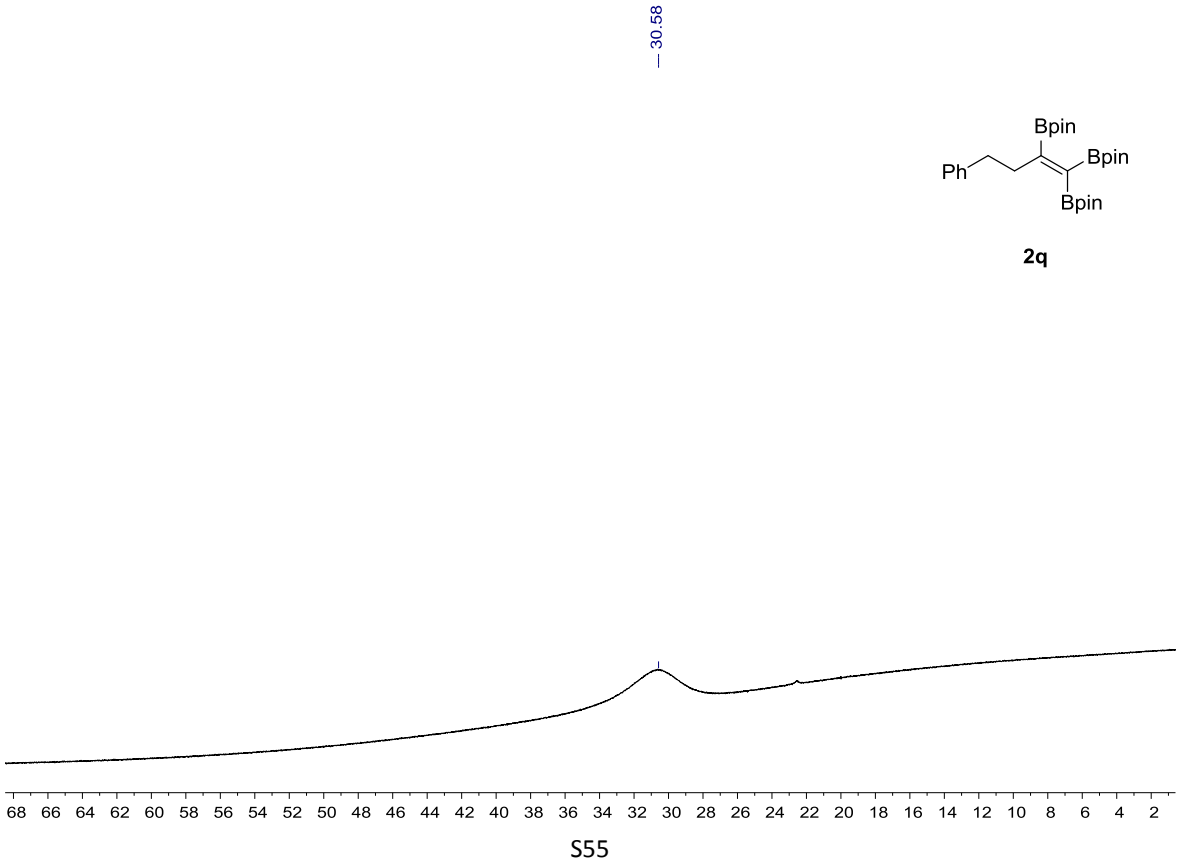


$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2q**



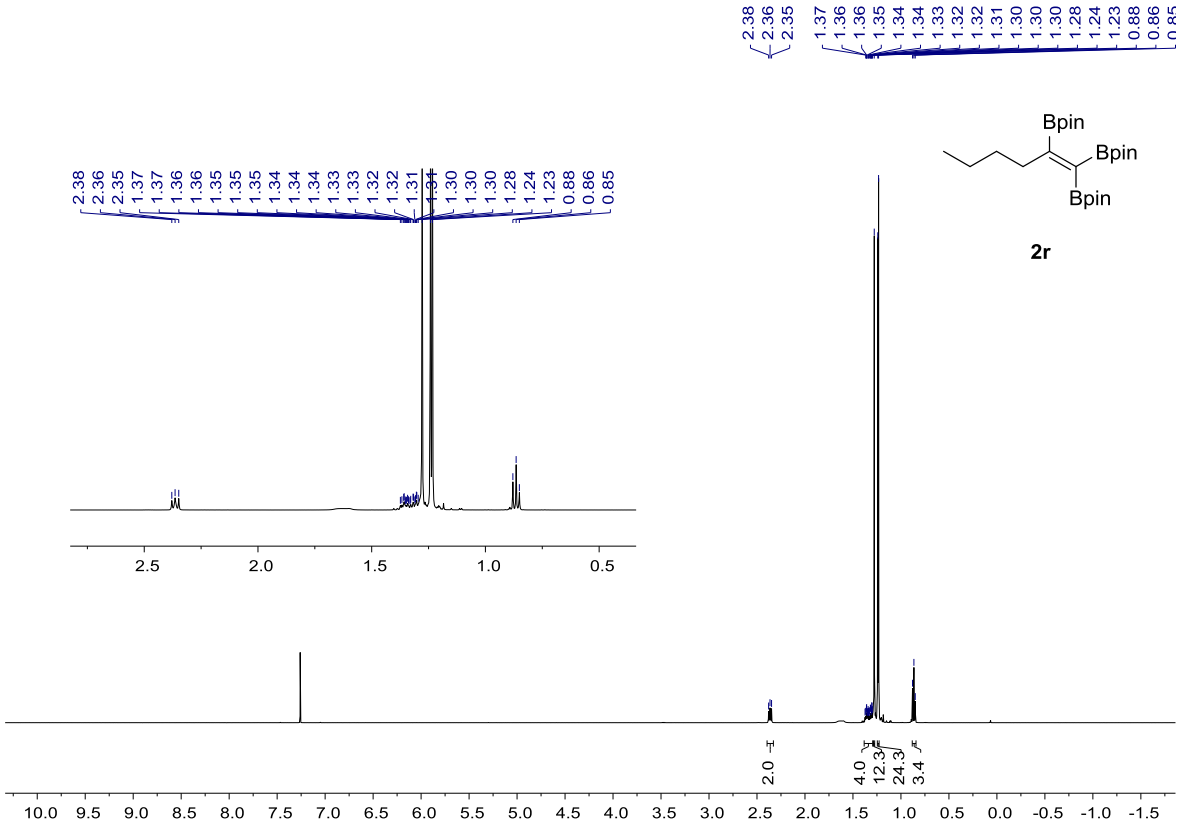
2q

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2q**

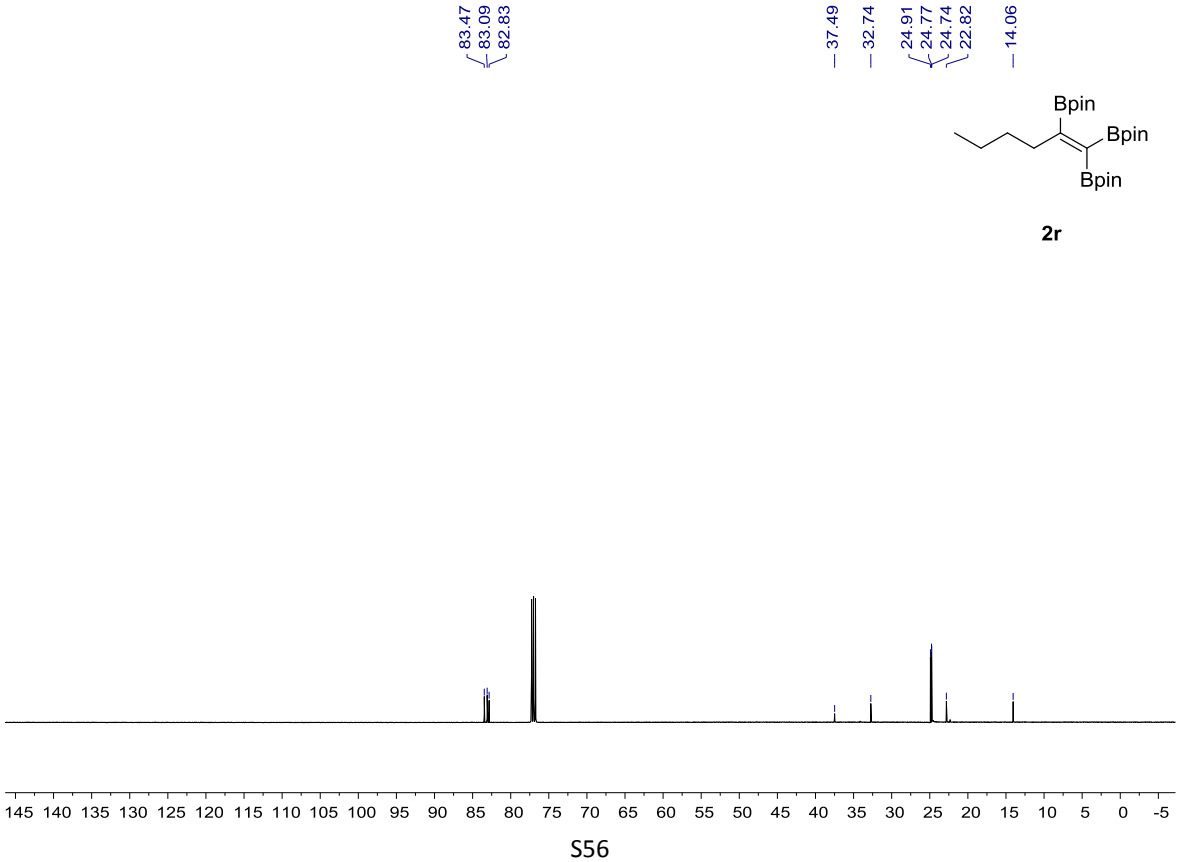


2q

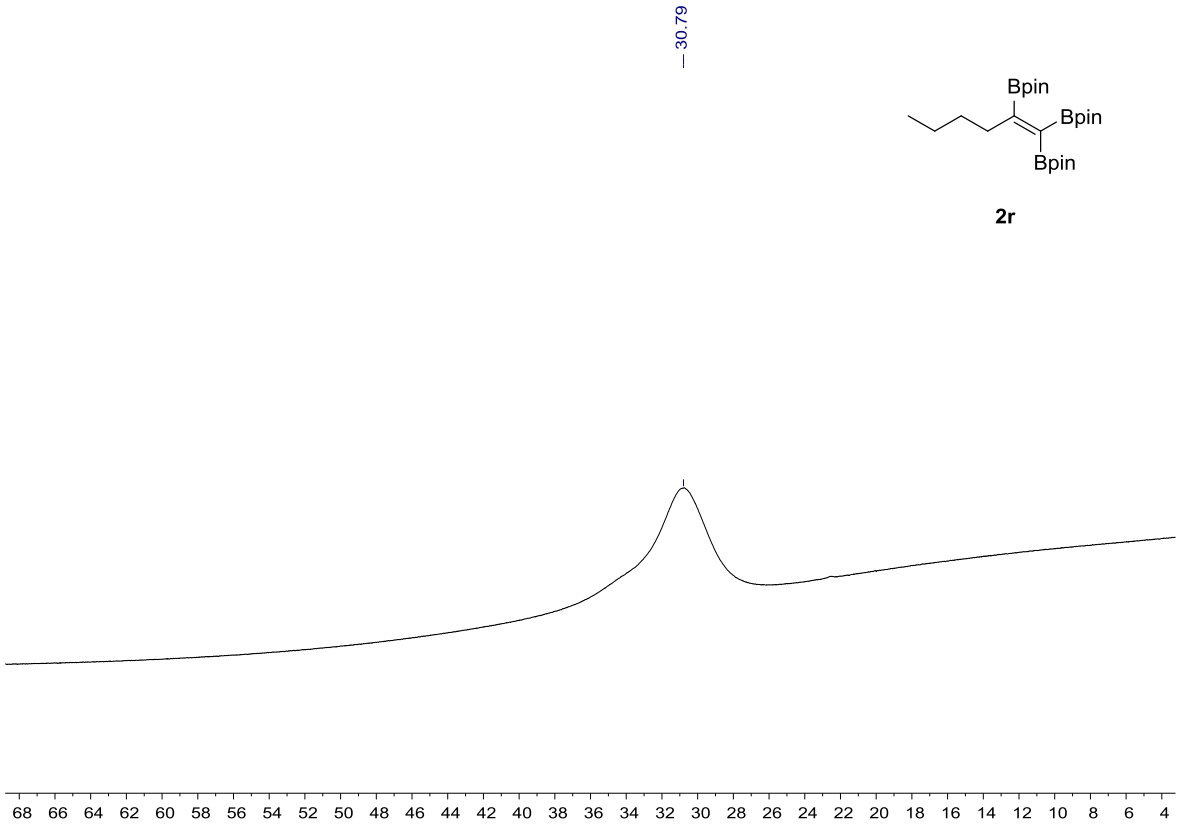
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2r**



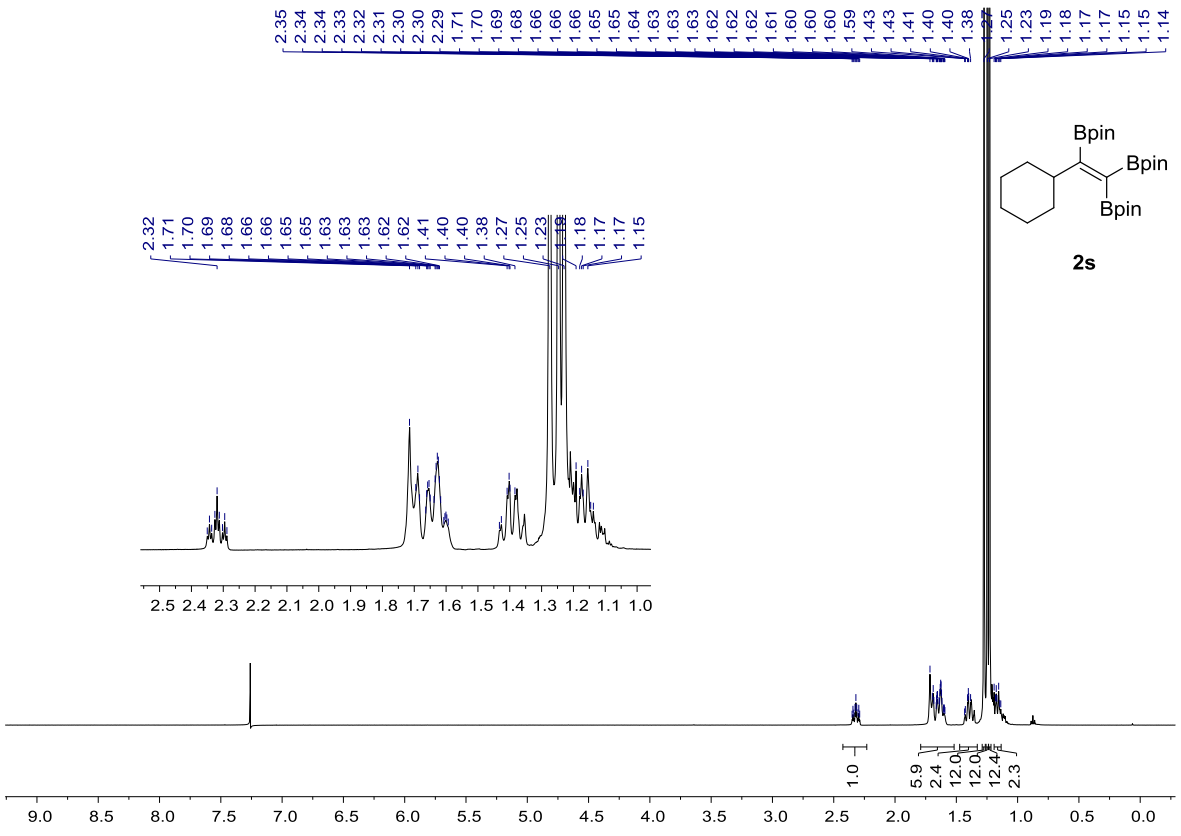
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2r**



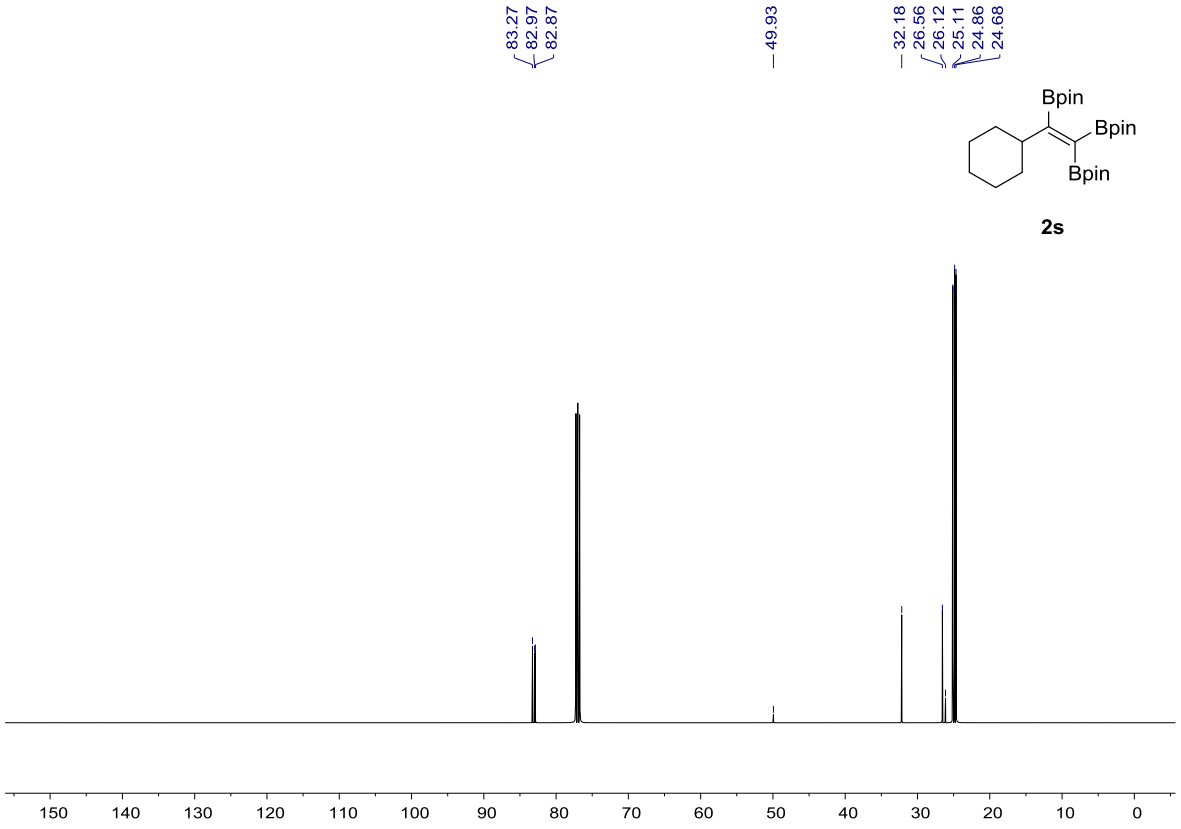
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2r**



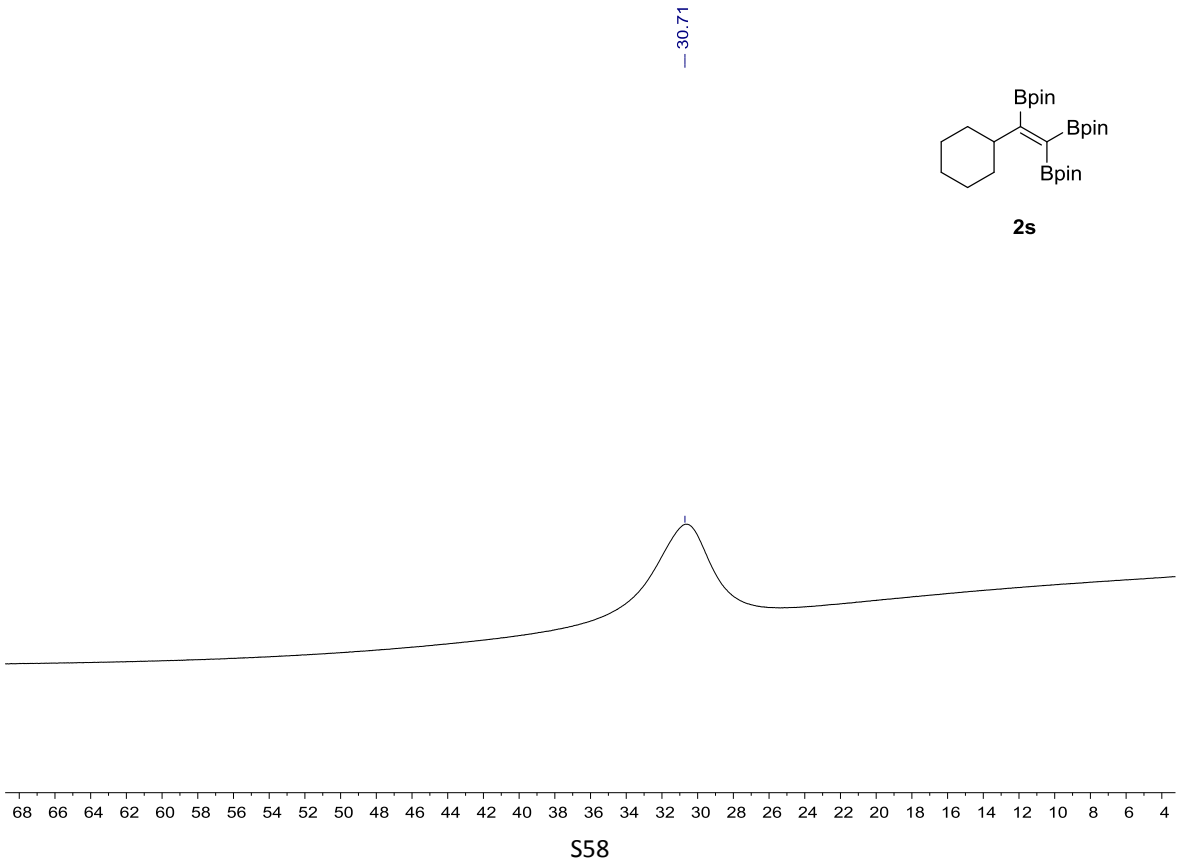
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2s**



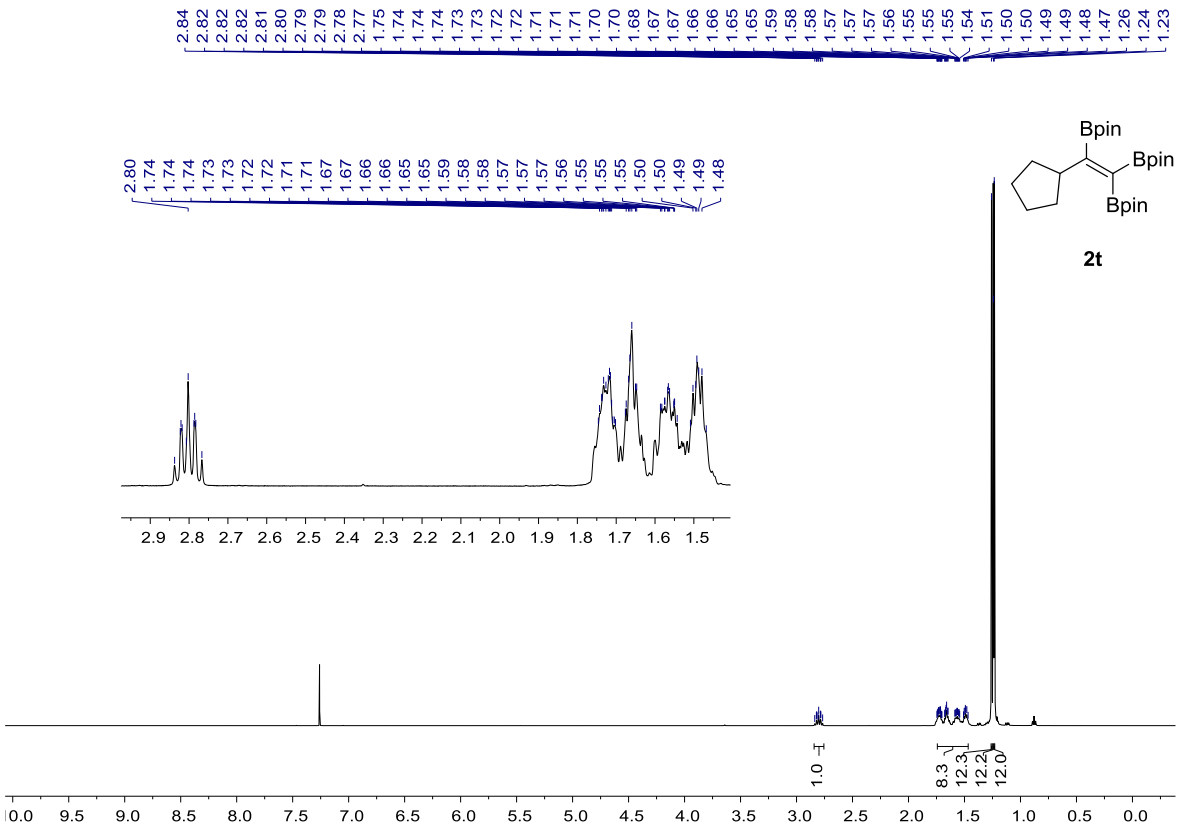
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2s**



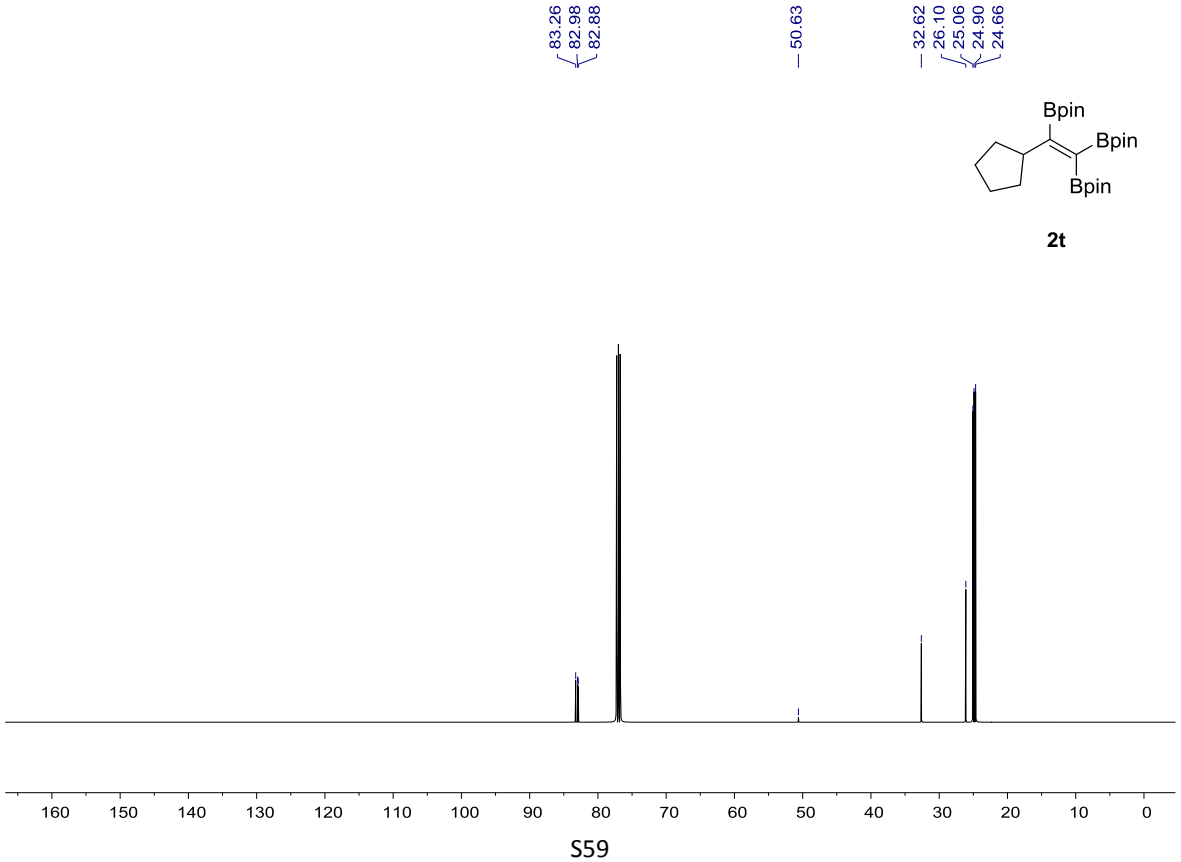
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2s**



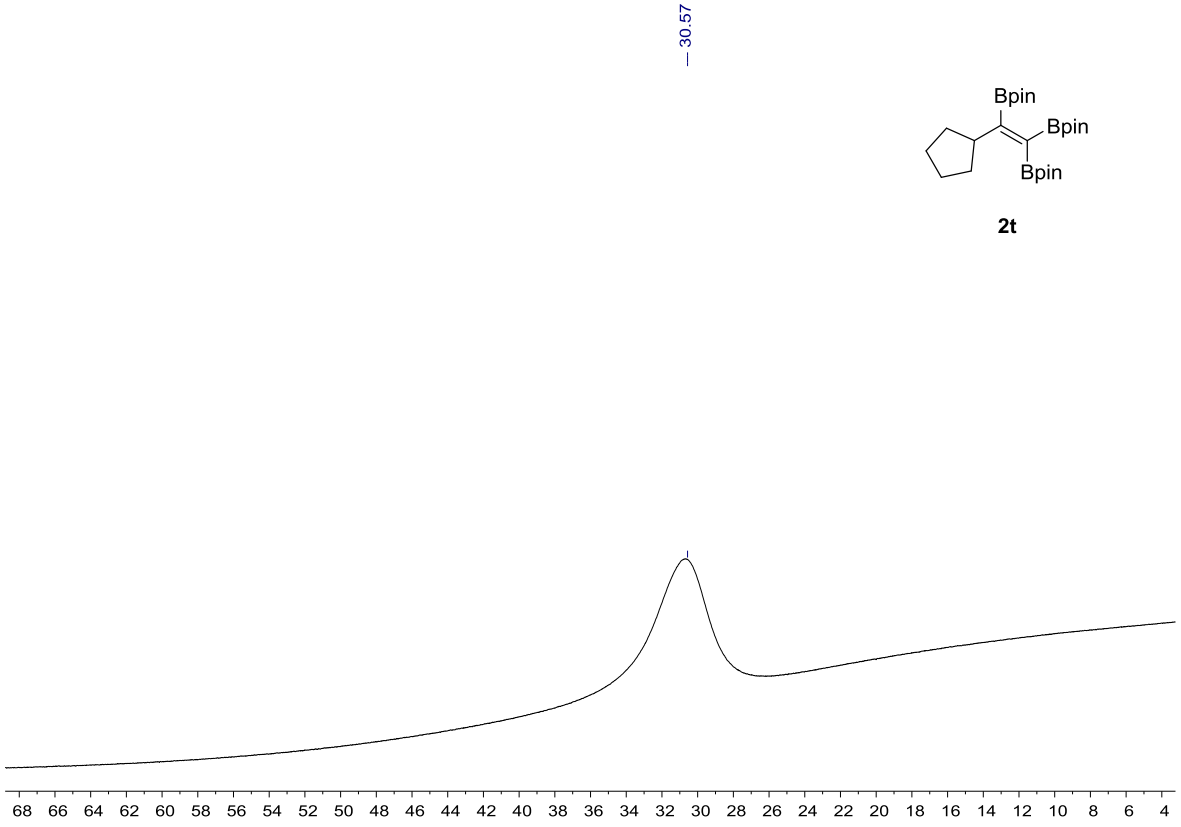
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2t**



$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2t**



^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2t**



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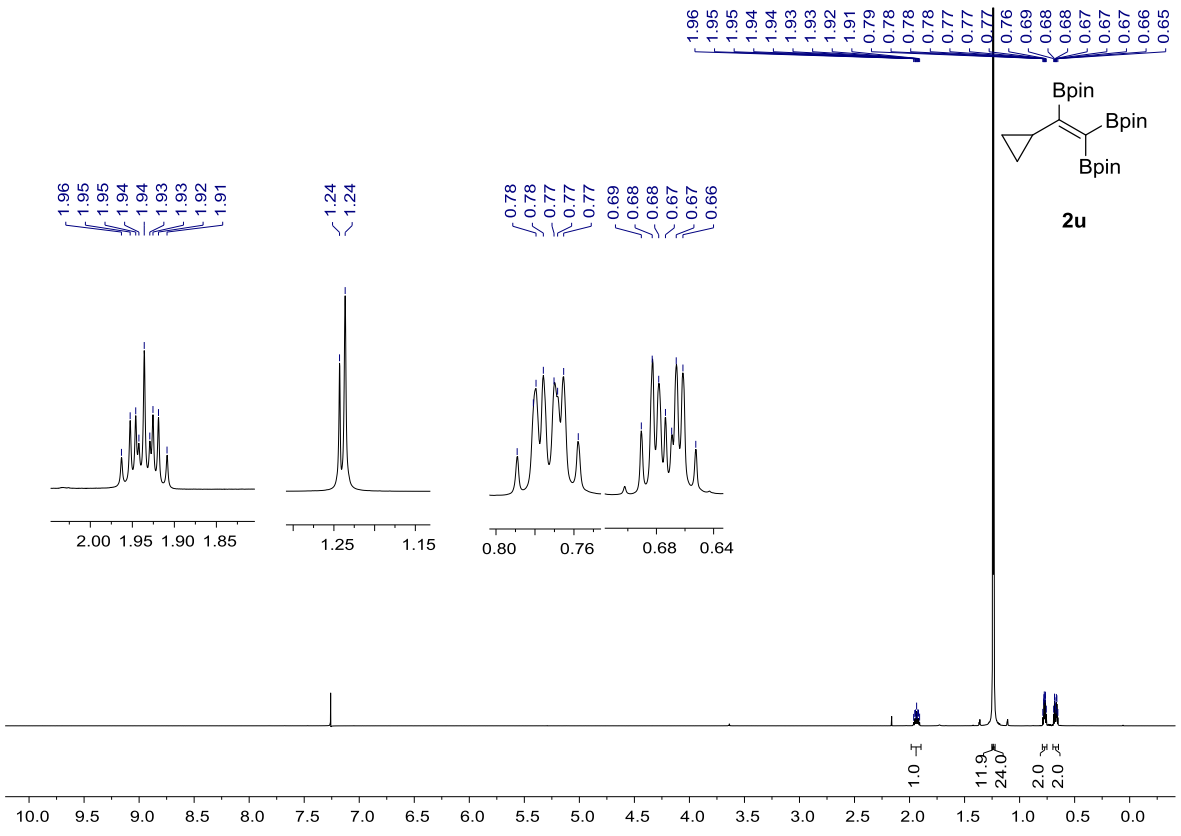
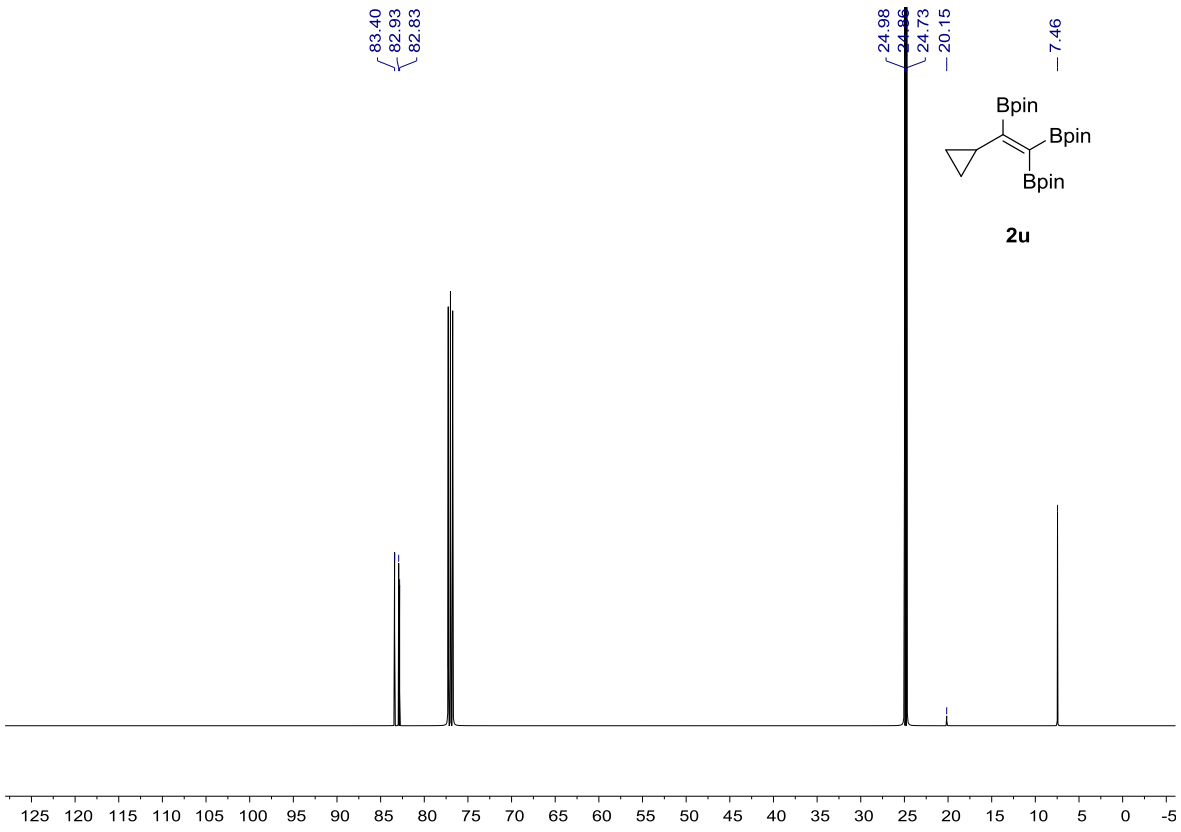
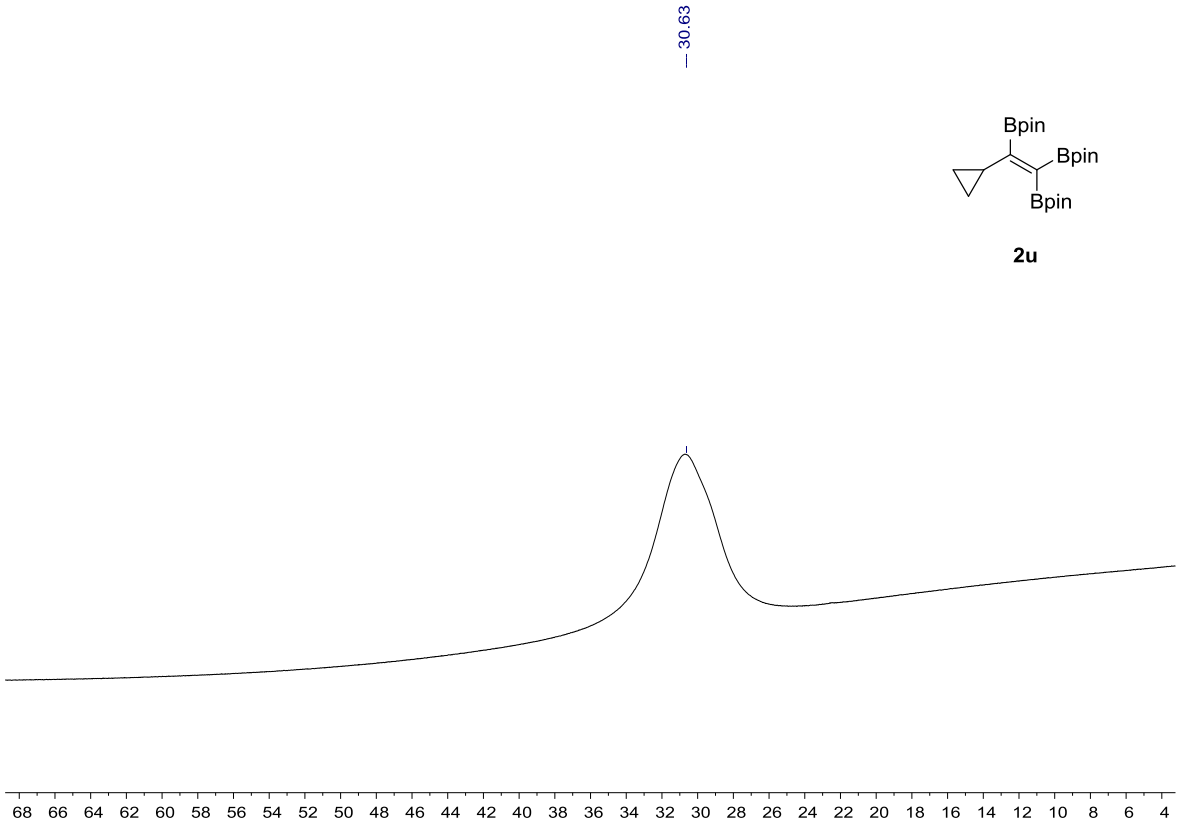


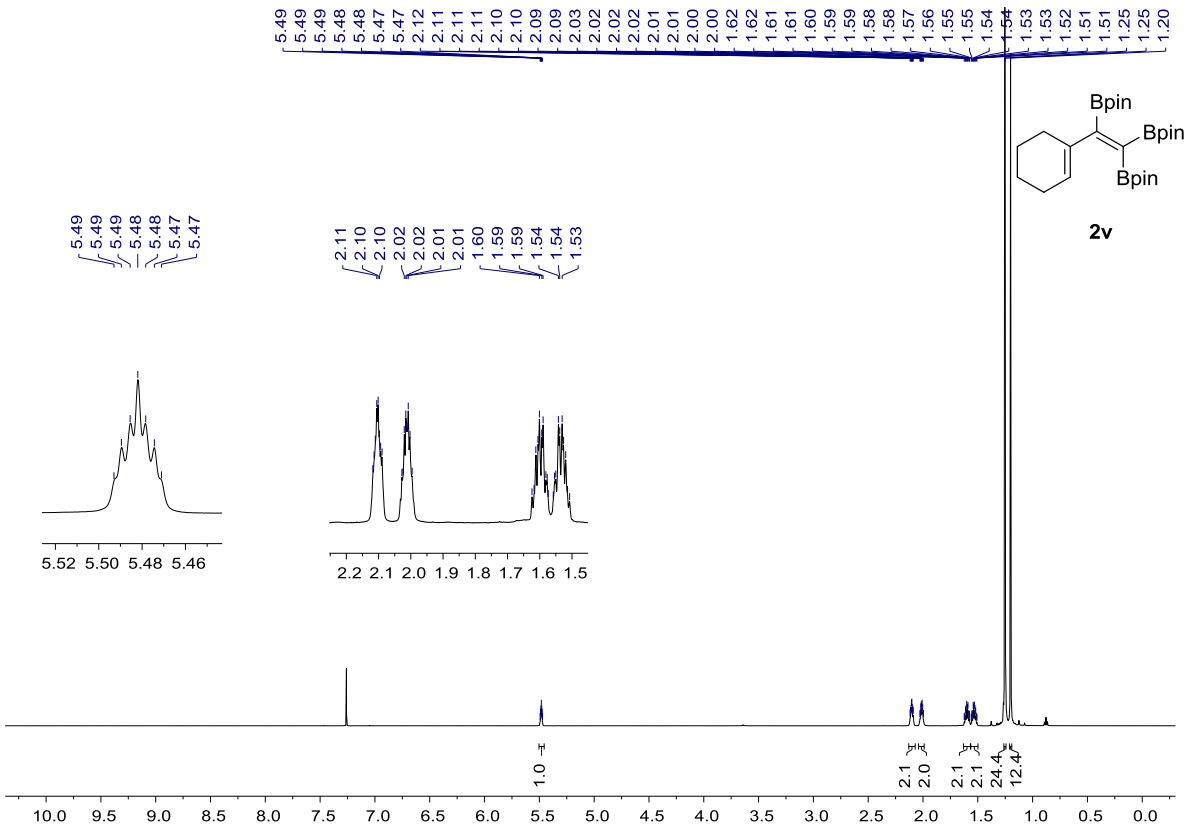
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2u**



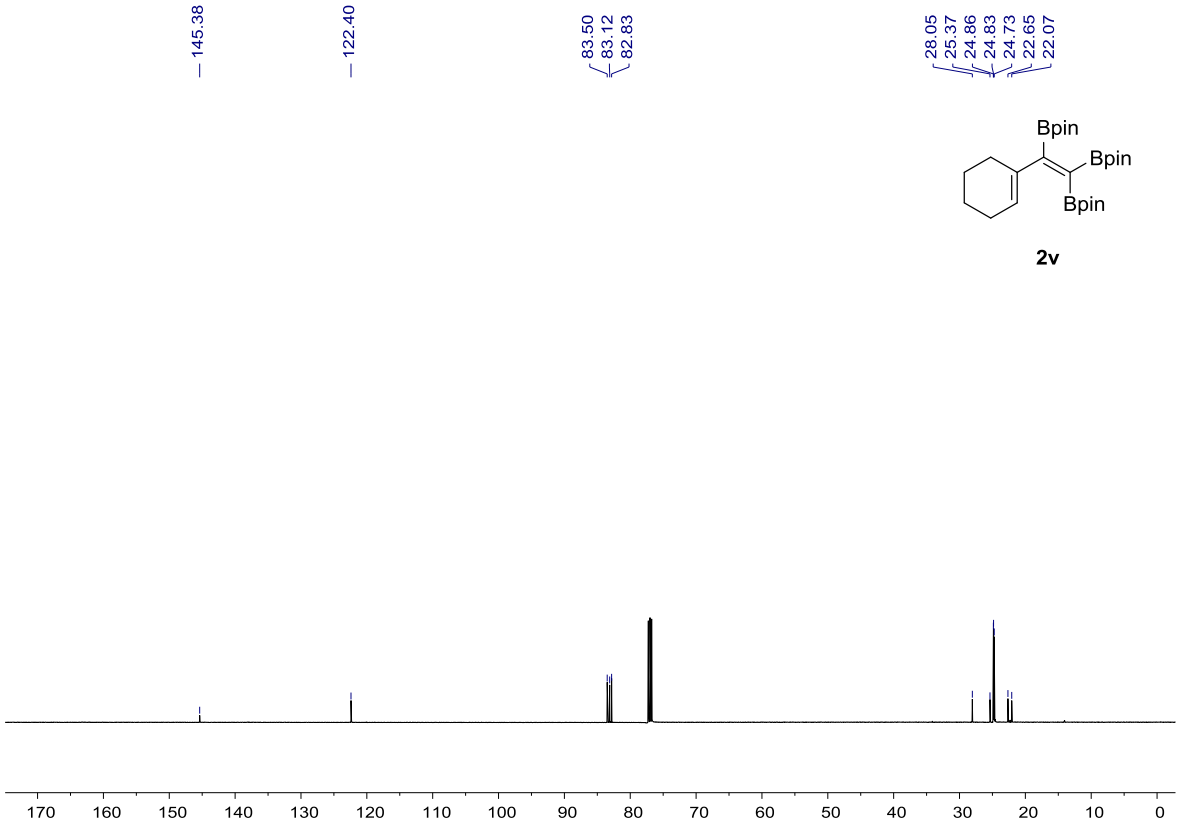
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2u**



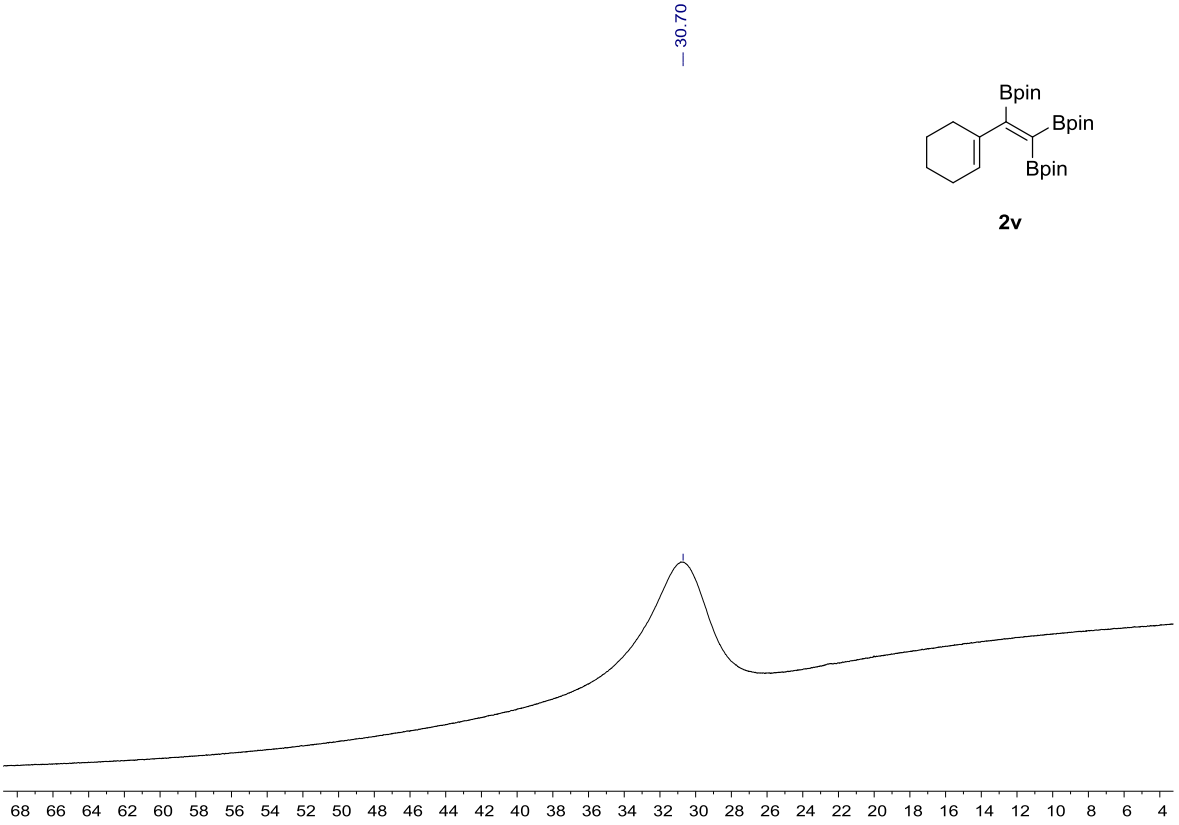
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **2v**



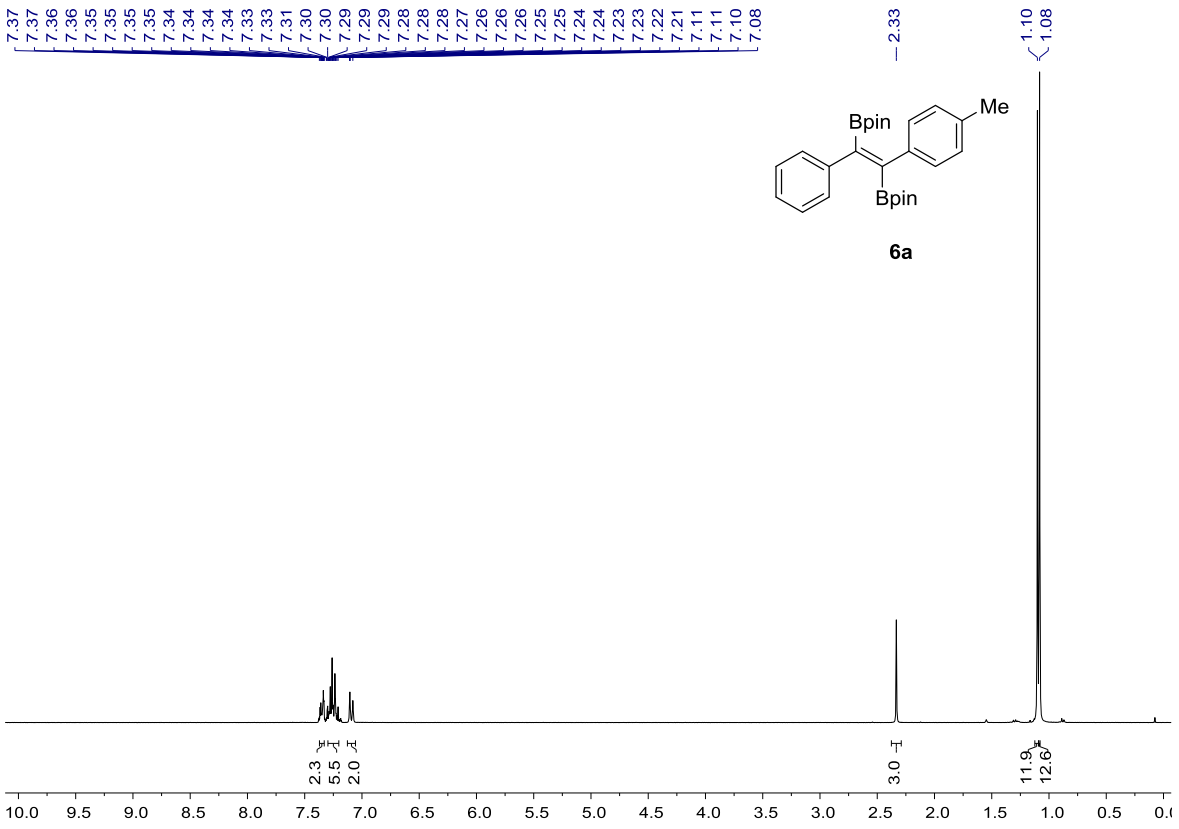
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **2v**



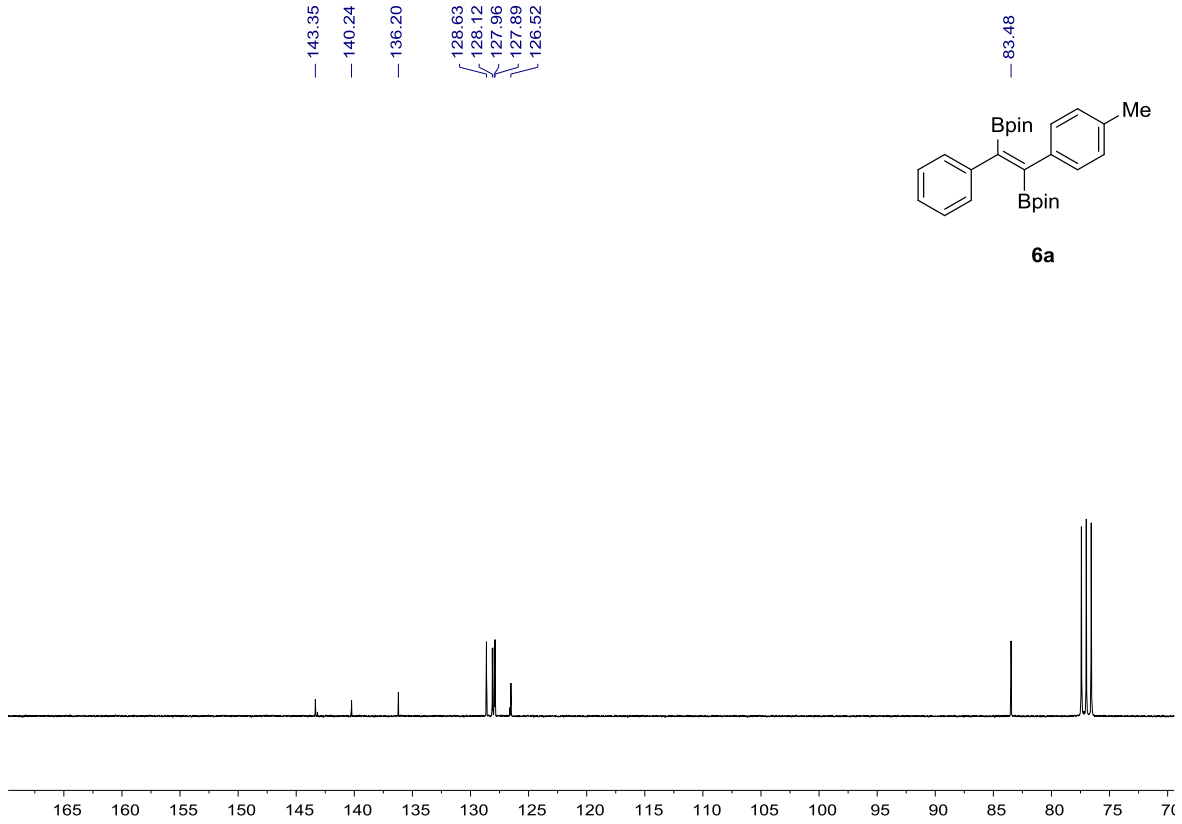
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **2v**



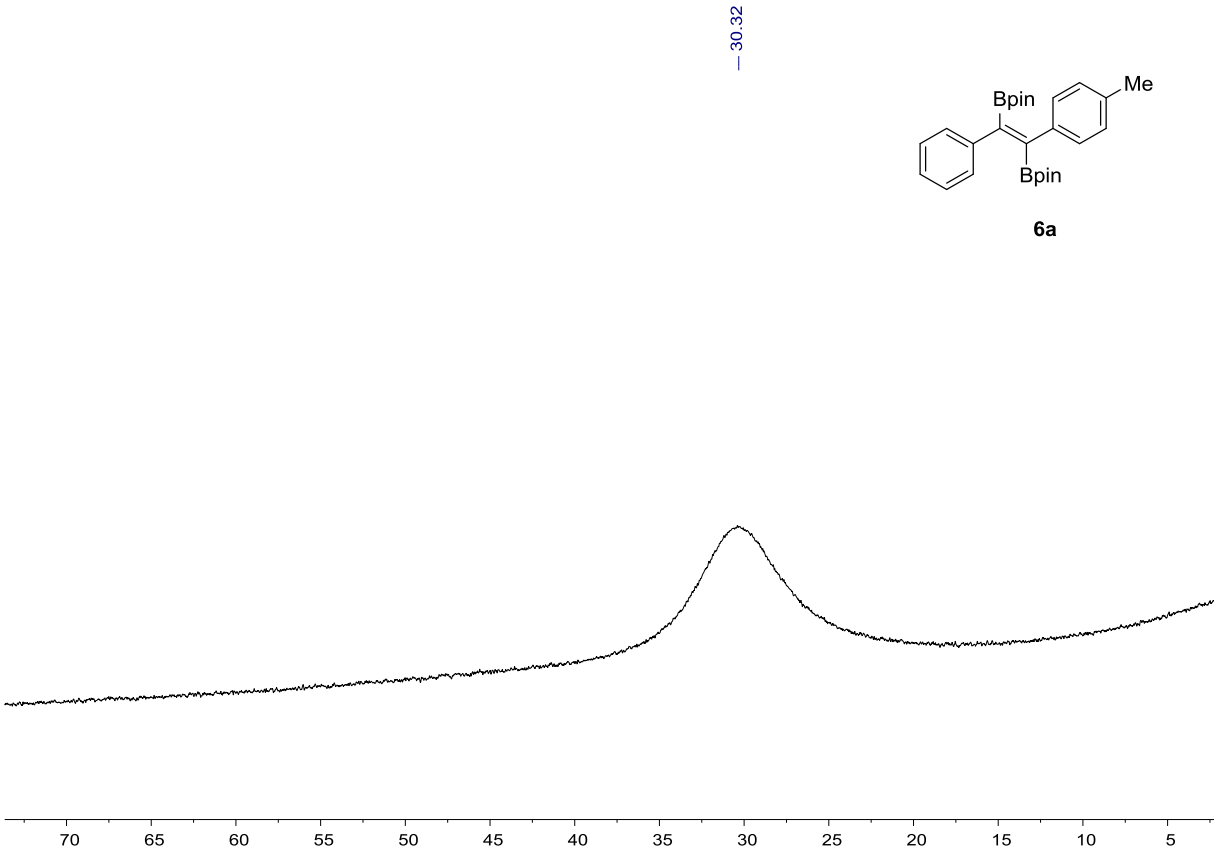
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6a**



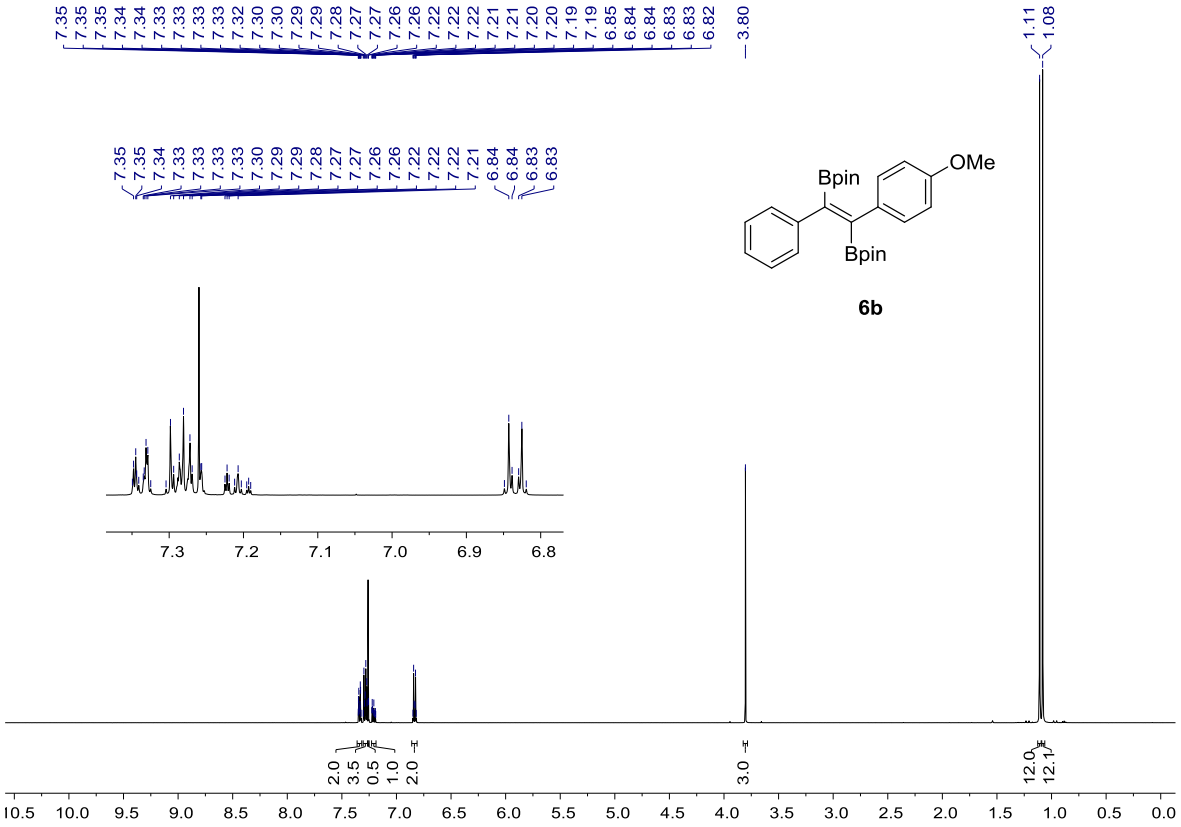
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **6a**



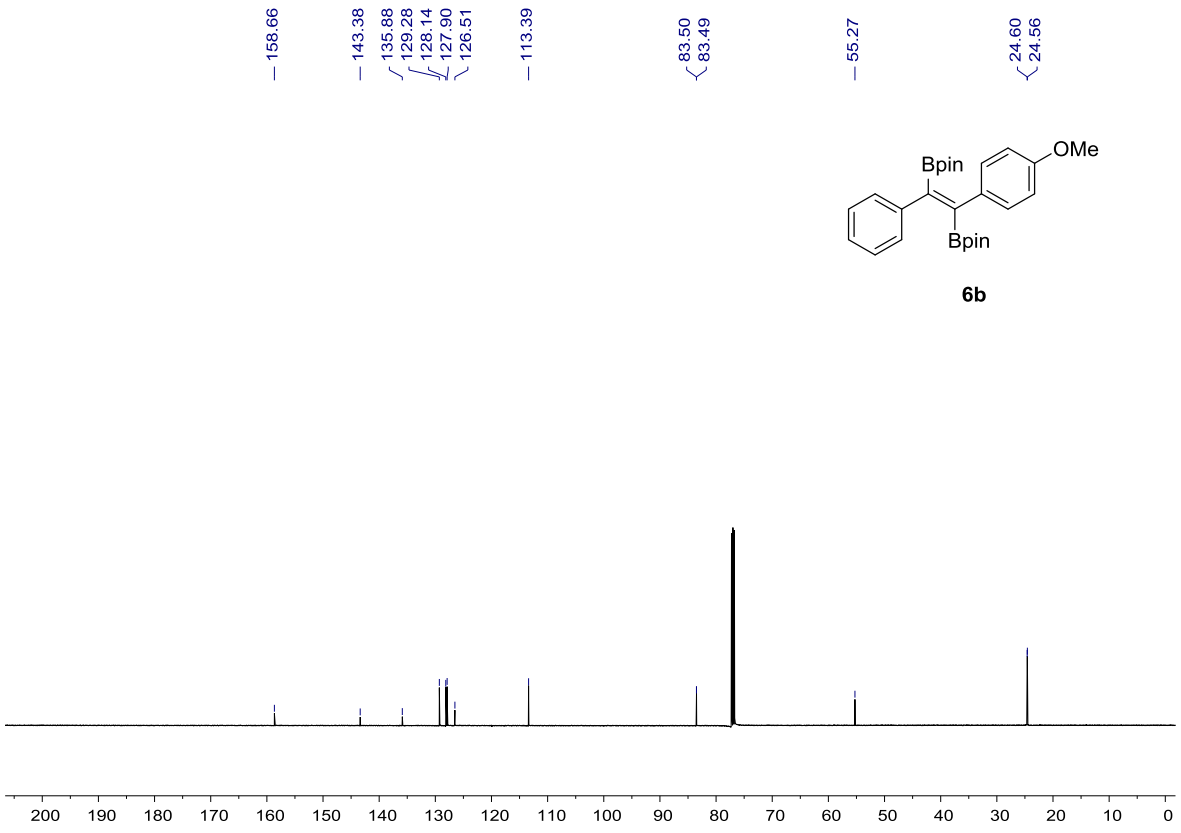
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **6a**



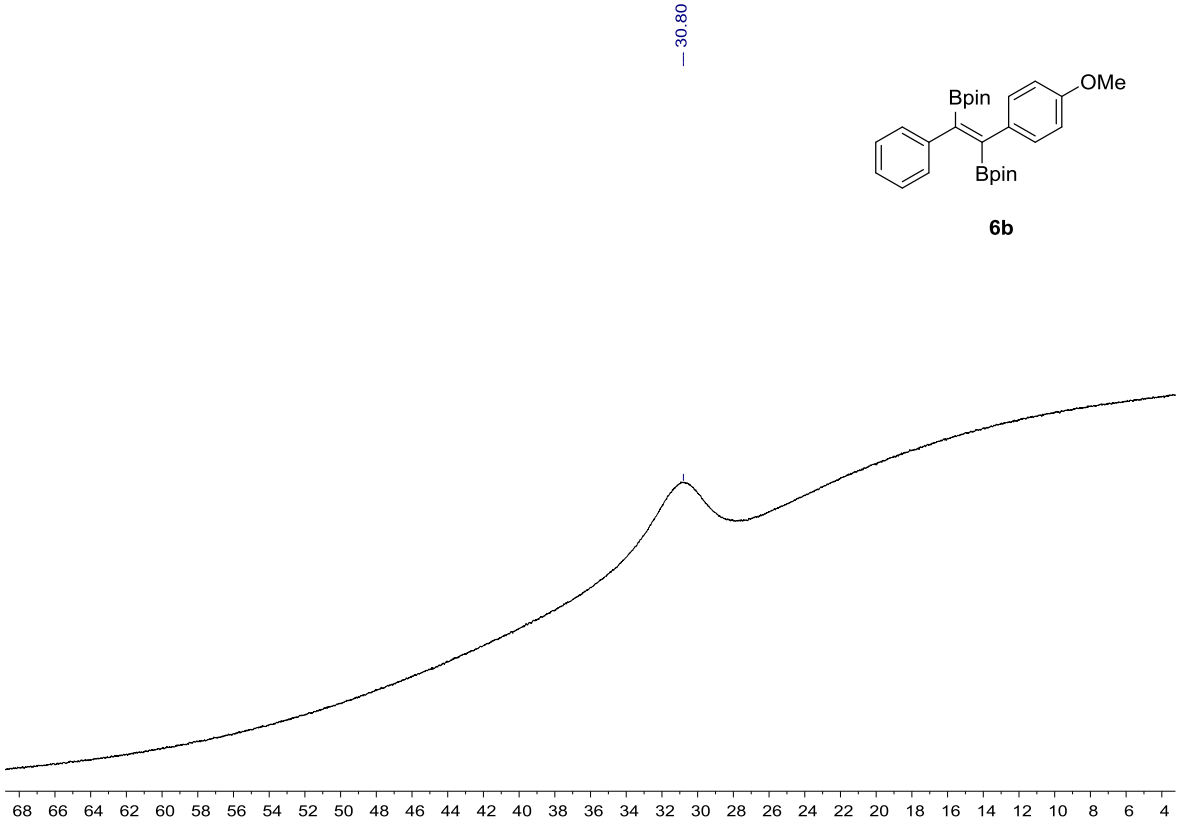
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **6b**



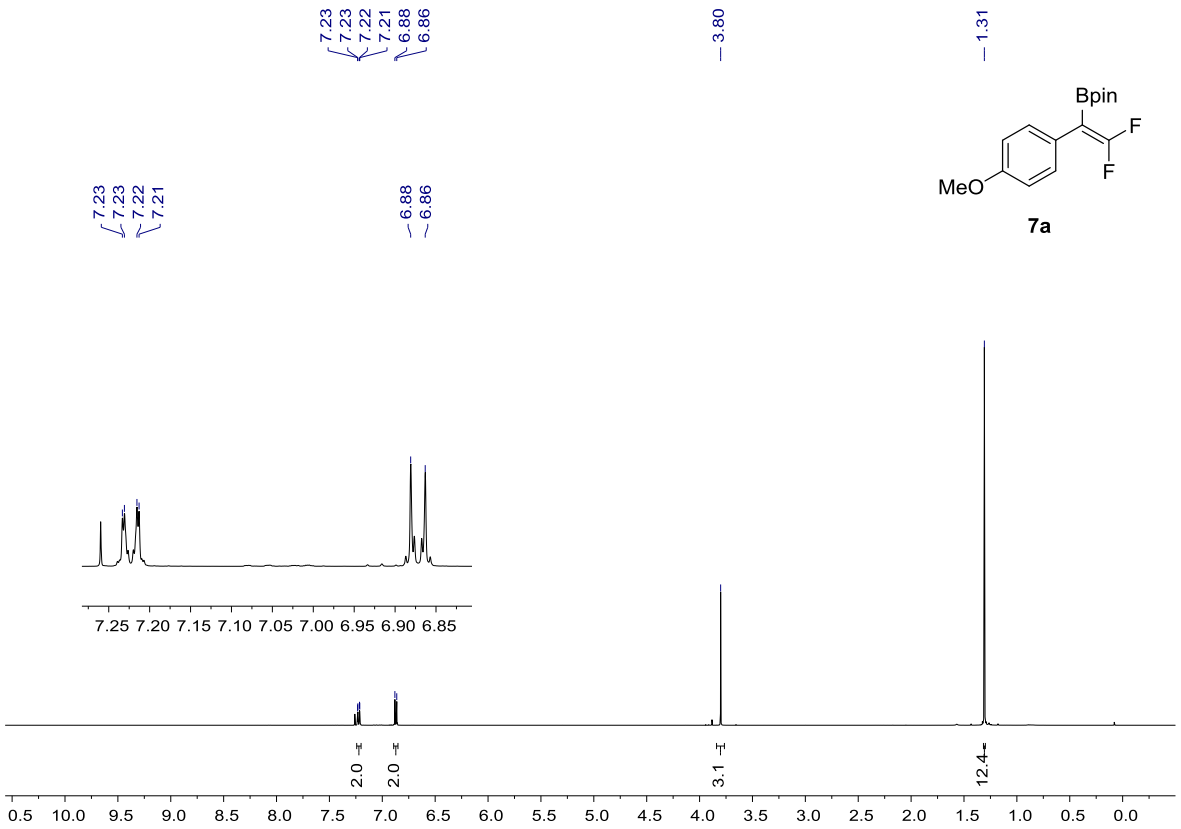
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **6b**



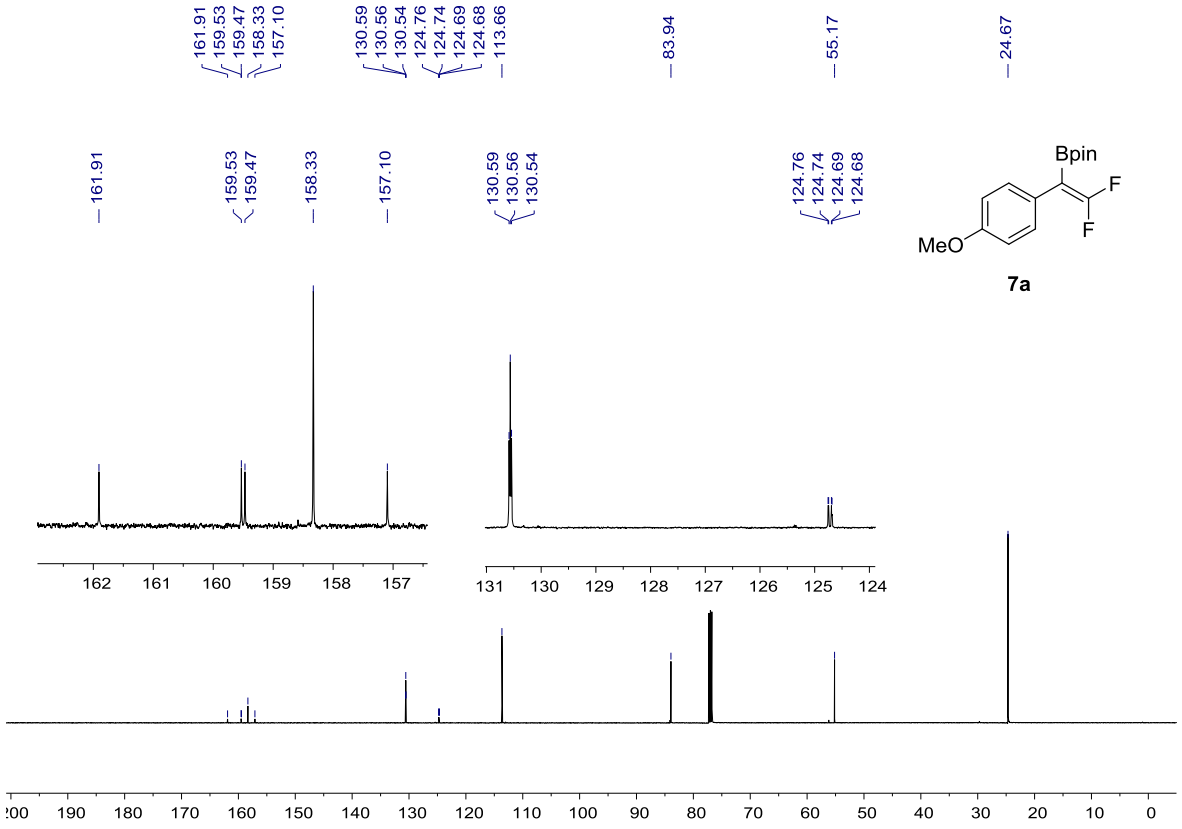
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **6b**



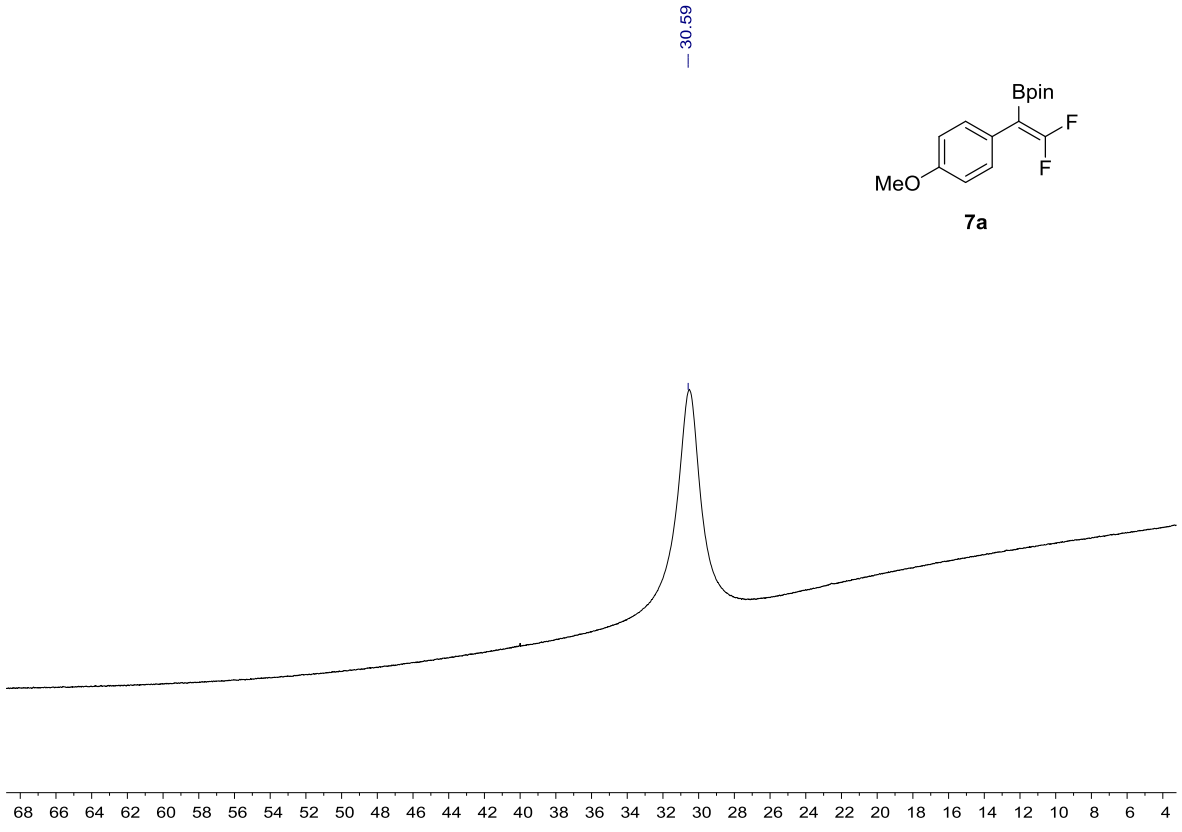
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **7a**



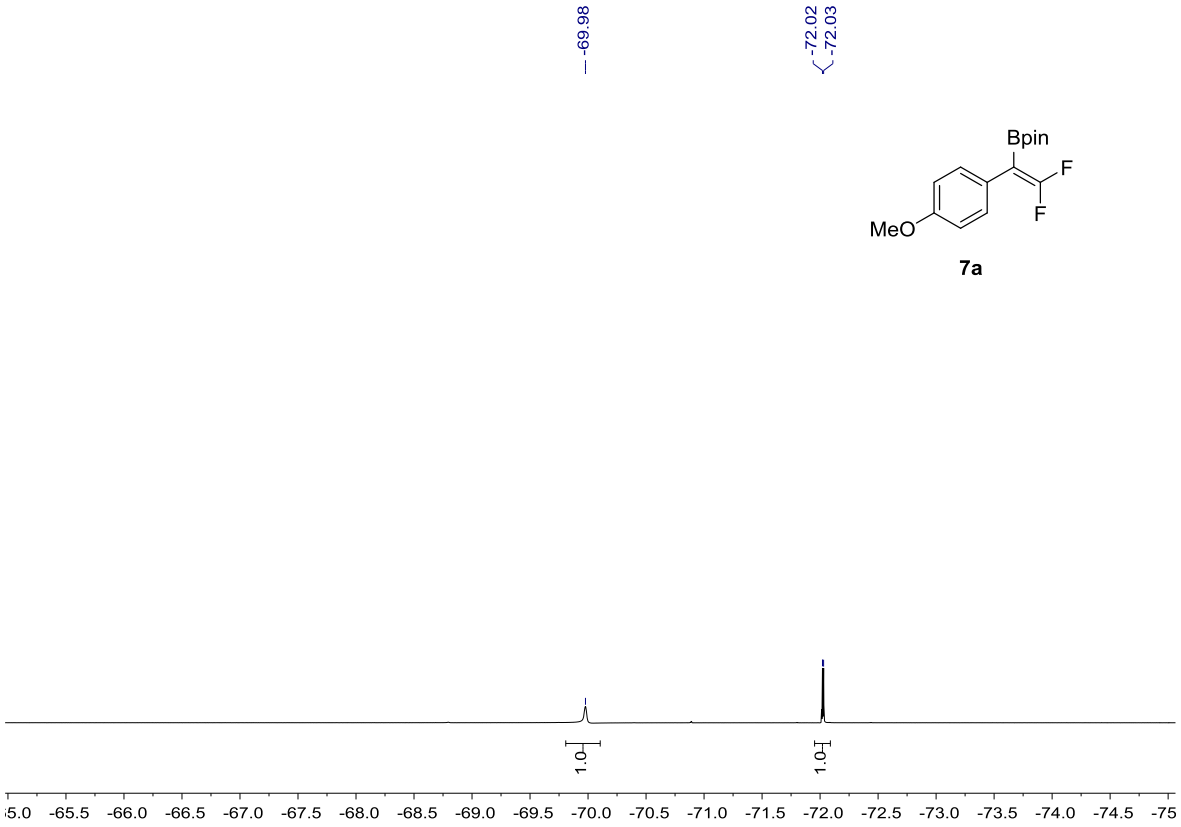
$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **7a**



^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **7a**

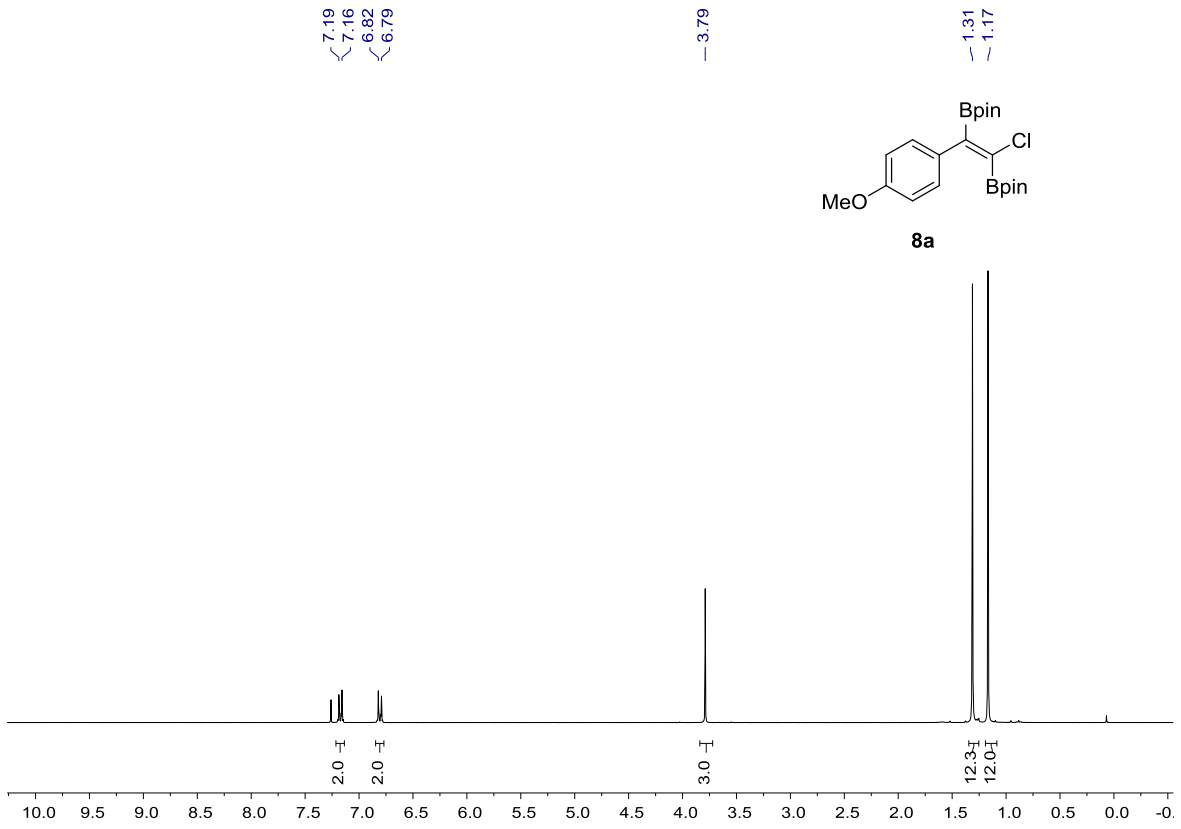


^{19}F NMR spectrum (470 MHz, $CDCl_3$) of **7a**



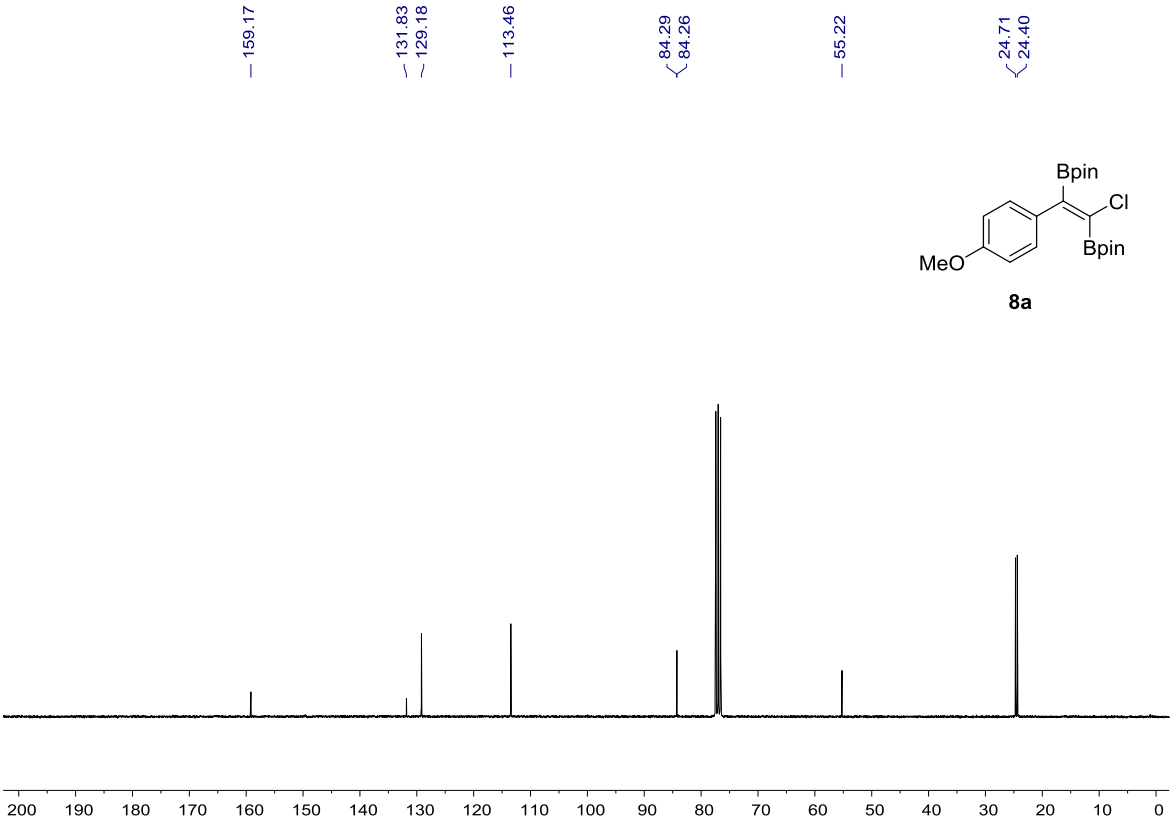
7a

^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **8a**

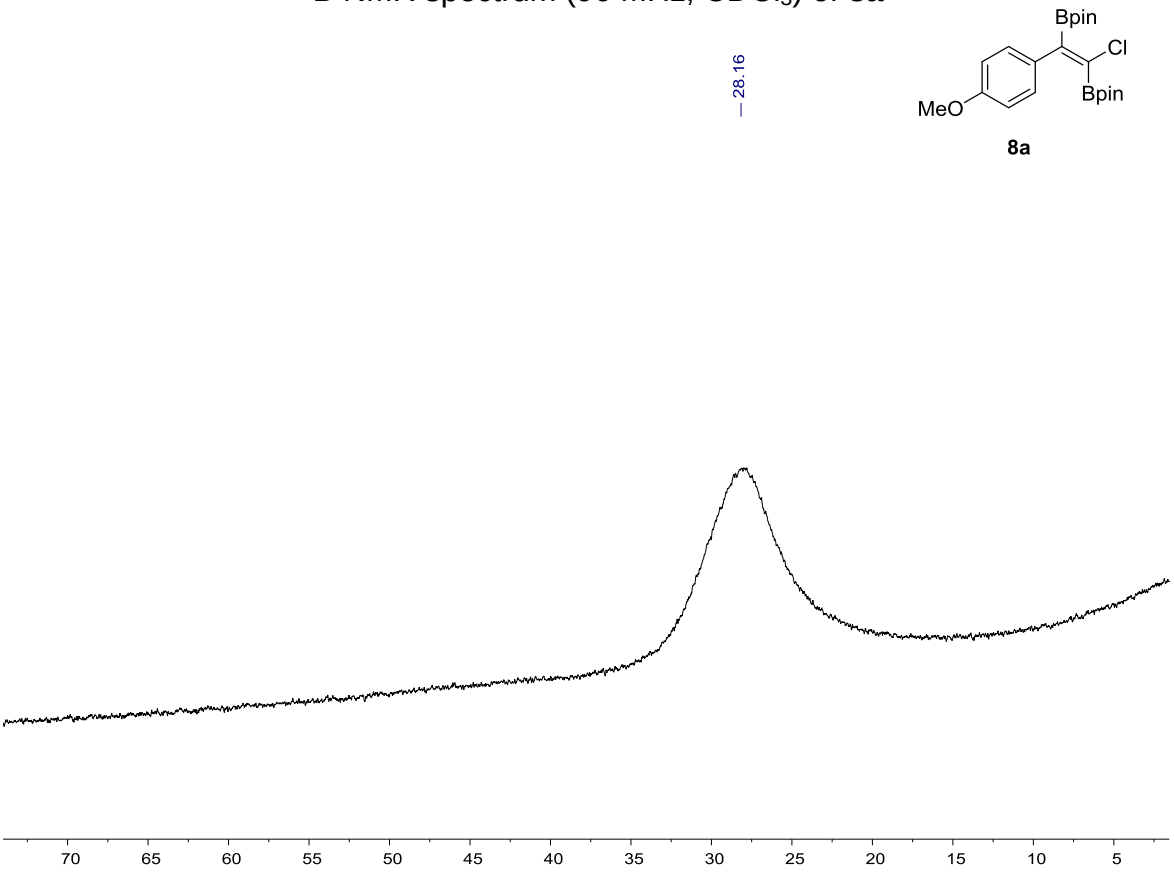


8a

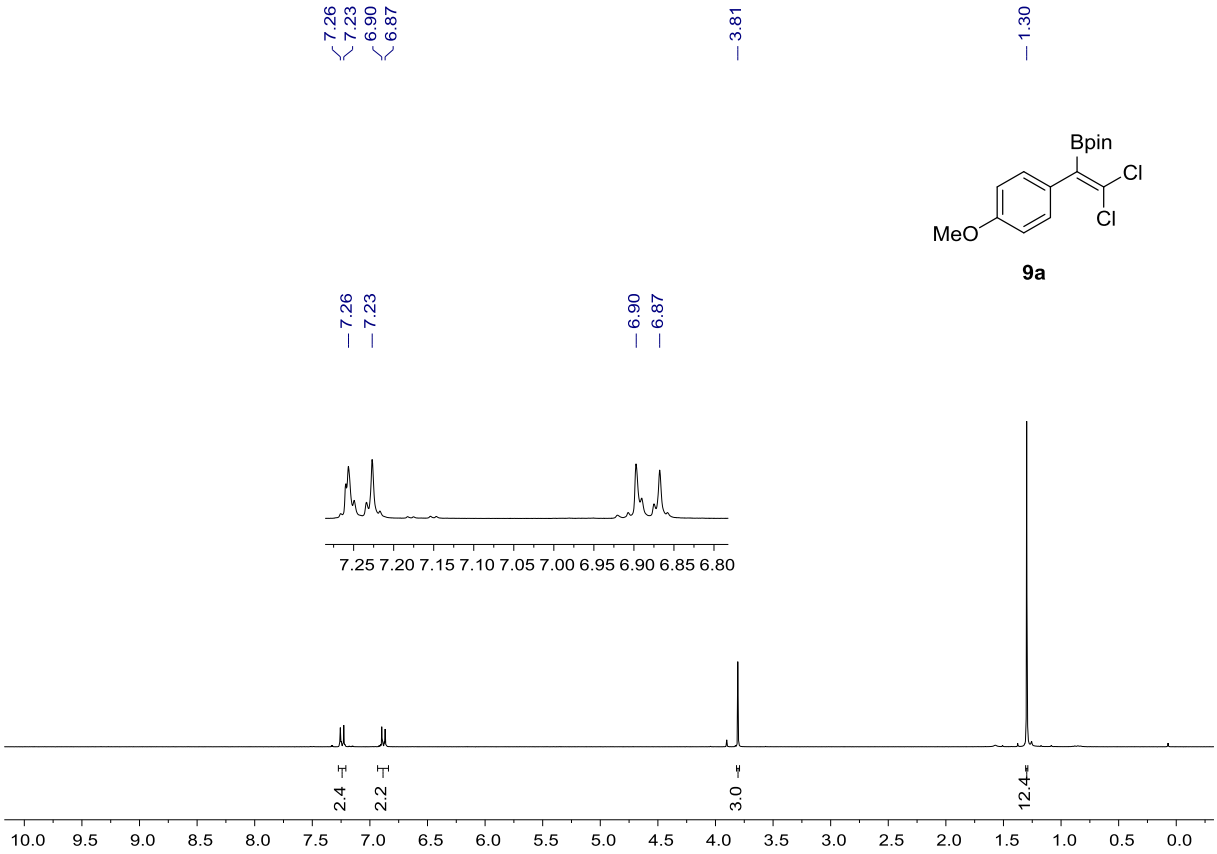
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **8a**



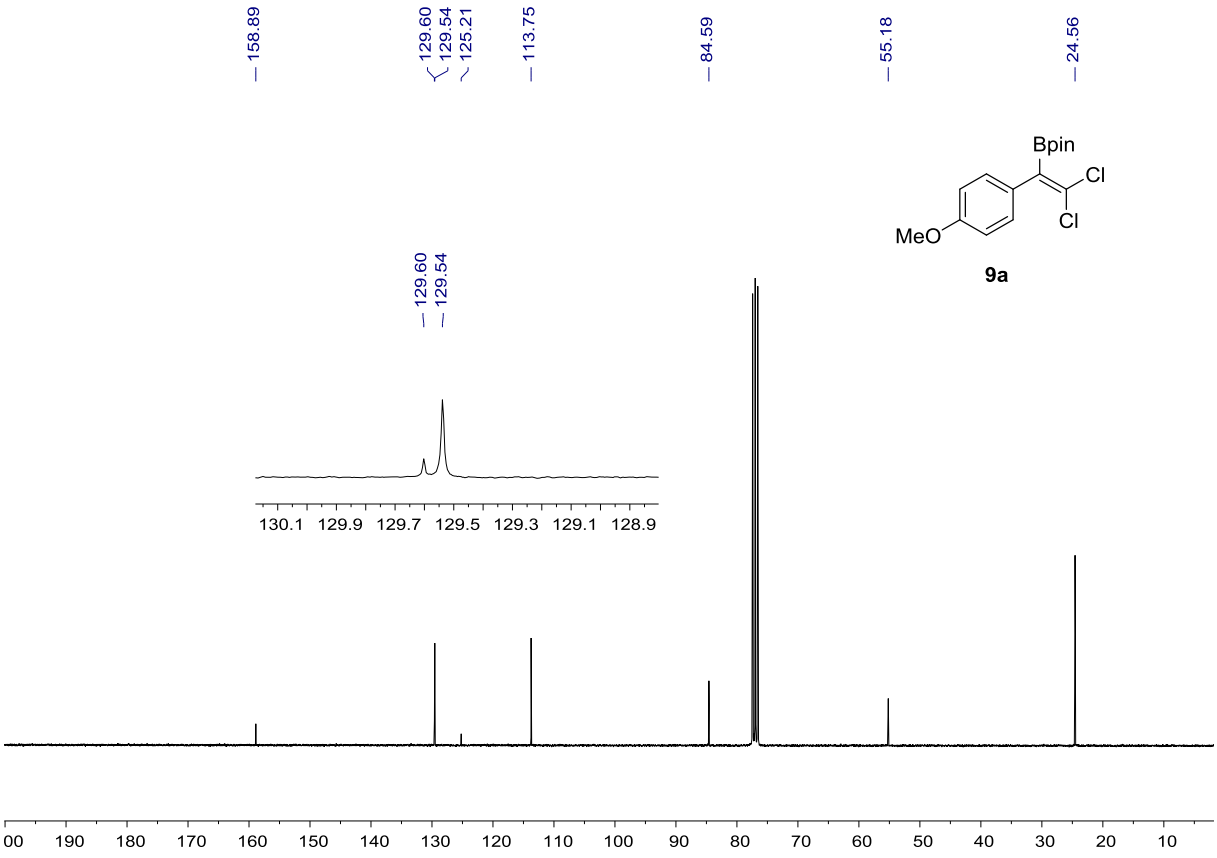
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **8a**



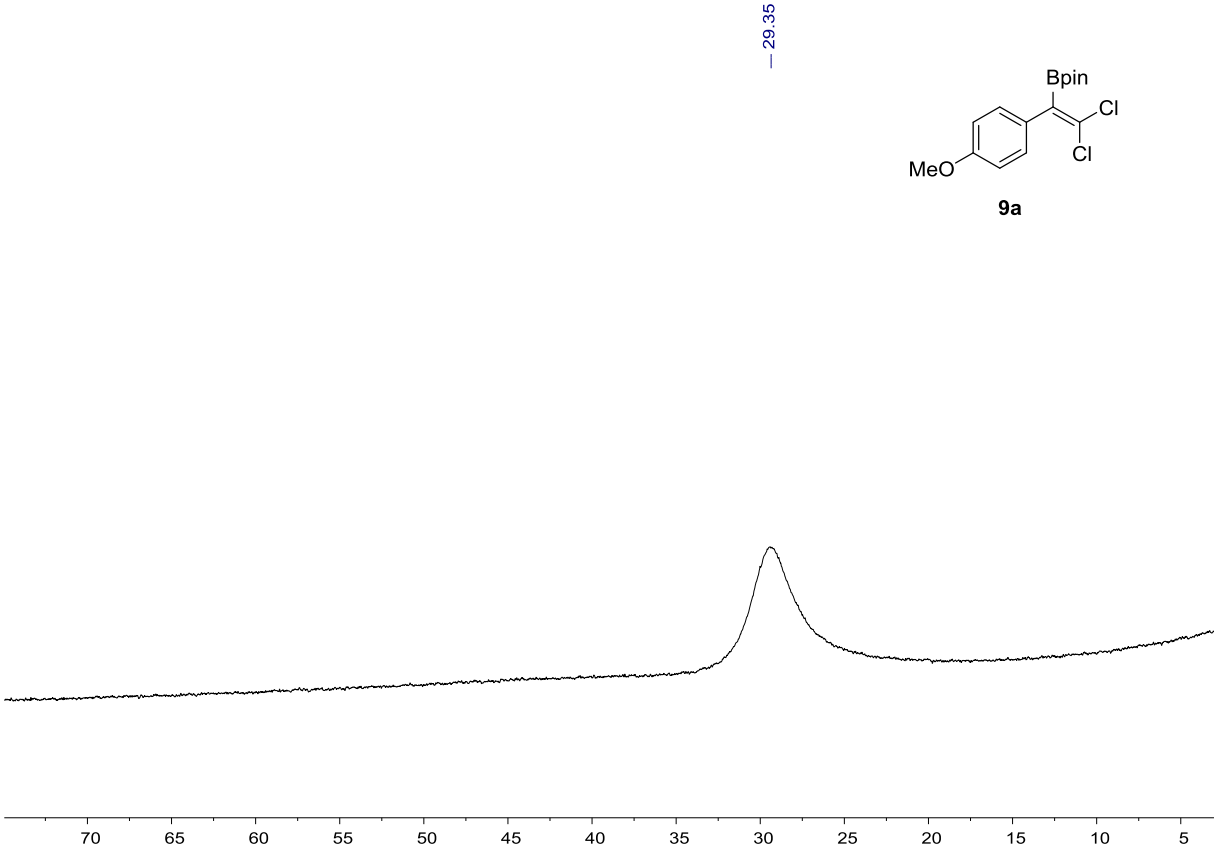
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **9a**



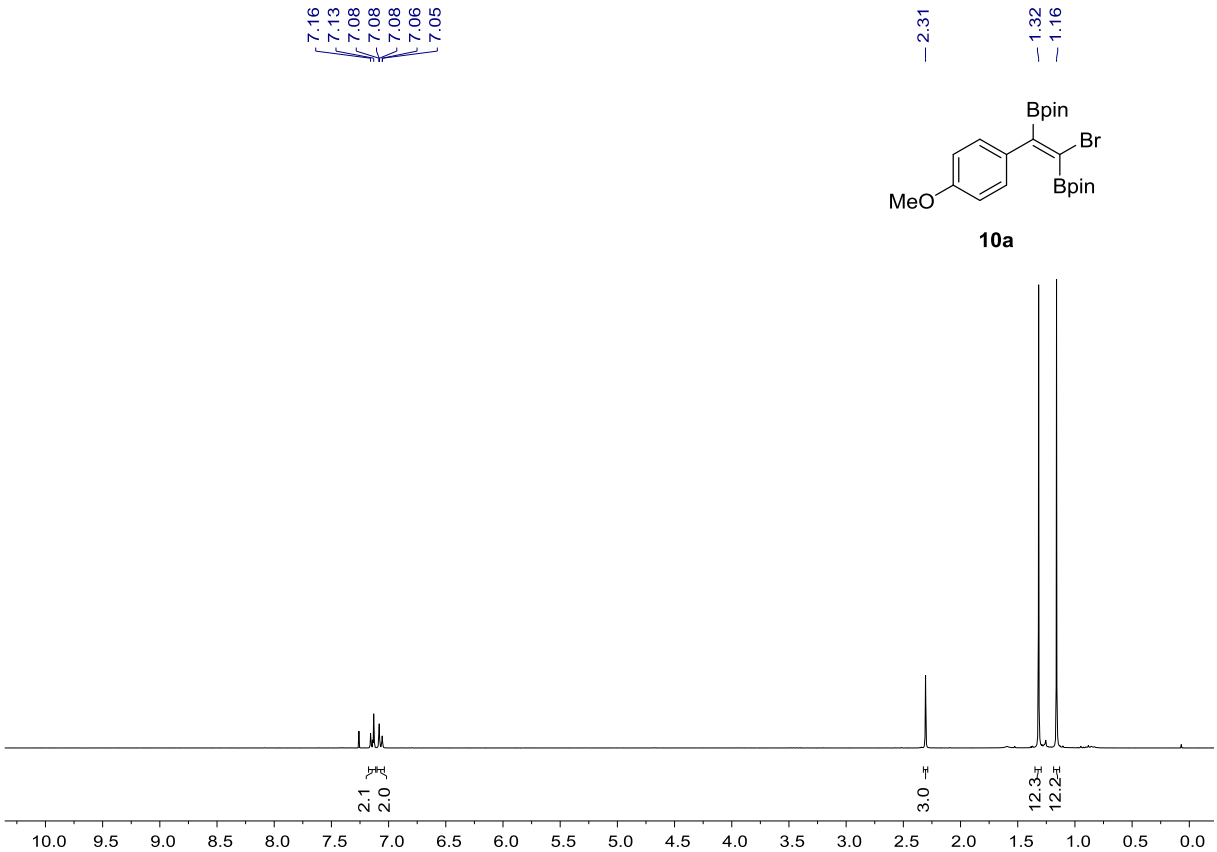
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **9a**



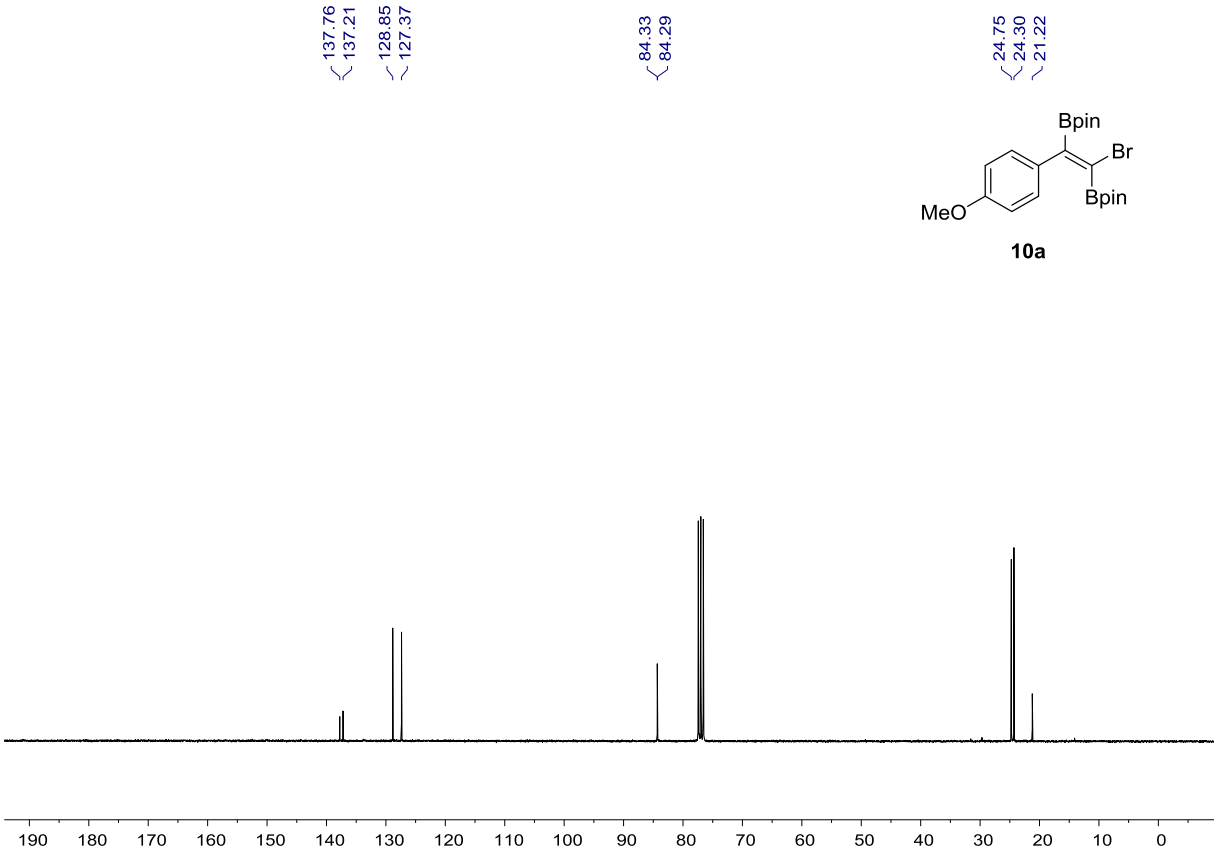
^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **9a**



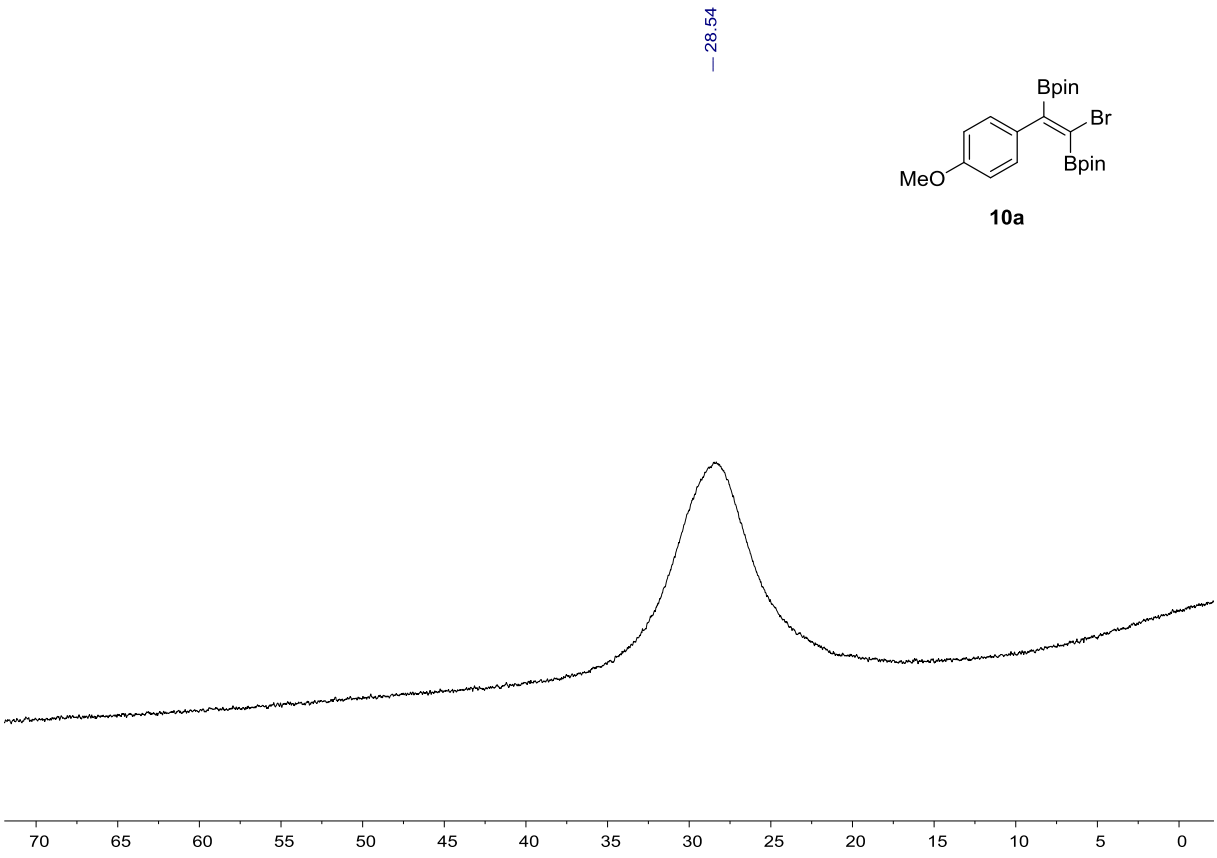
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **10a**



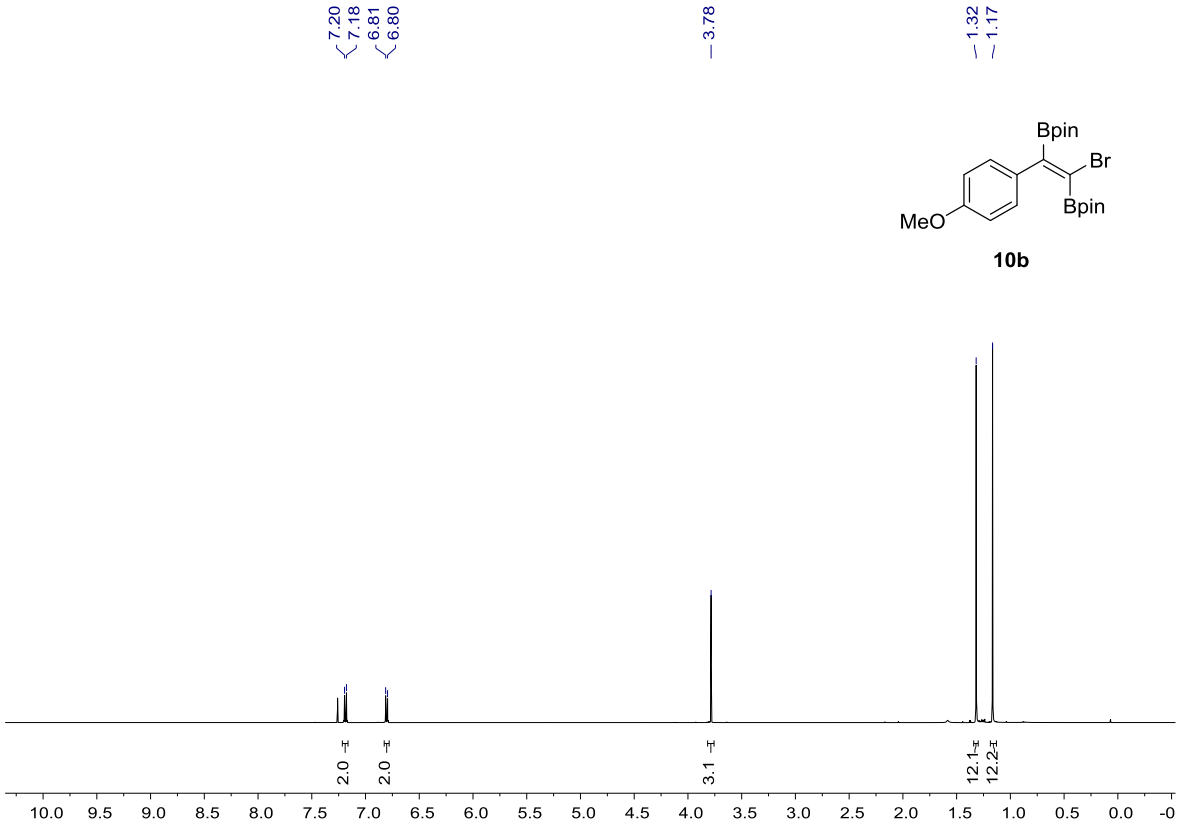
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, $CDCl_3$) of **10a**



^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **10a**

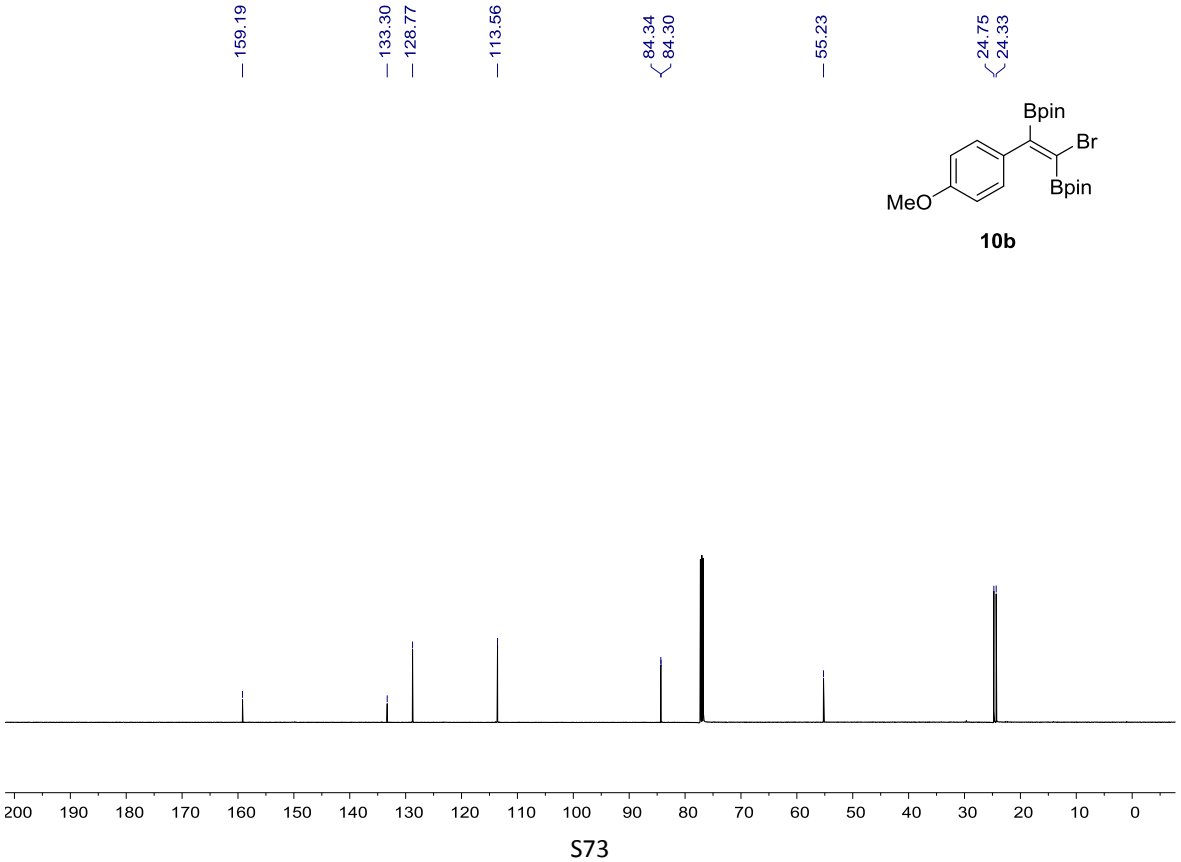


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **10b**



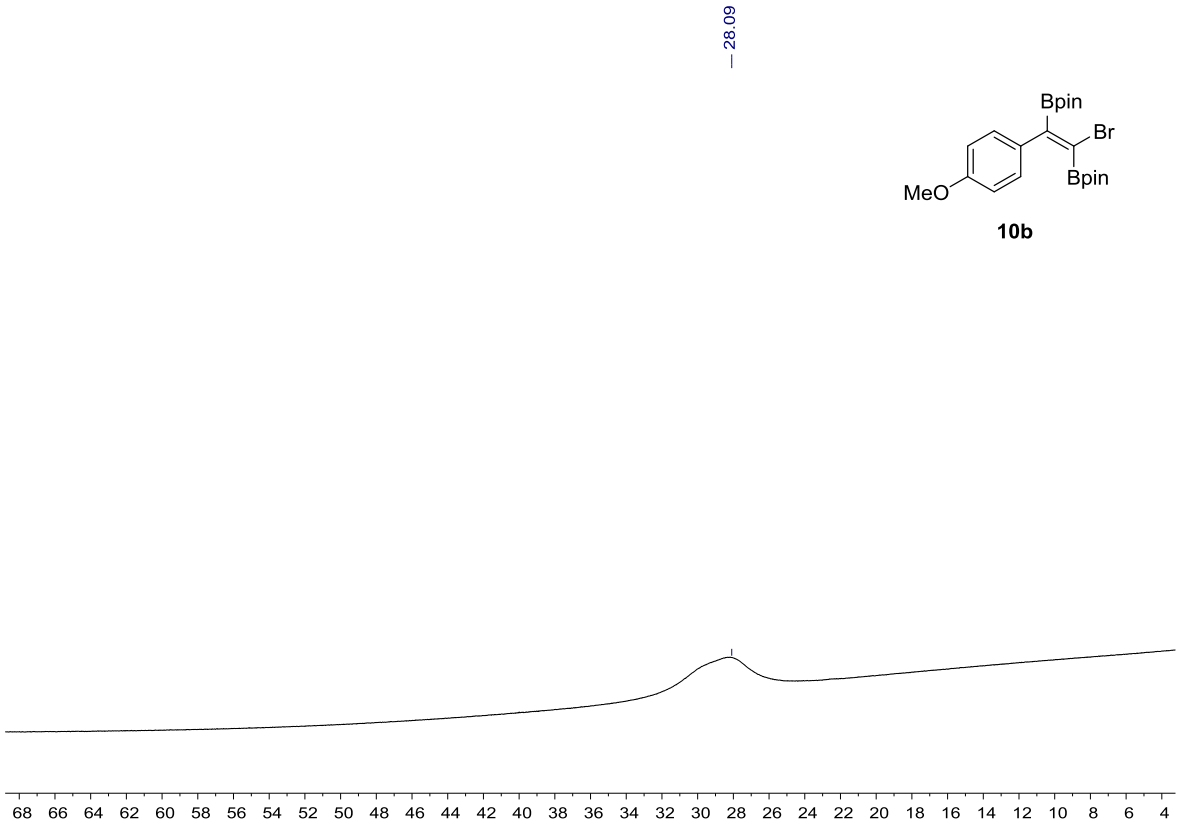
10b

^{13}C{^{1}H} NMR spectrum (125 MHz, $CDCl_3$) of **10b**

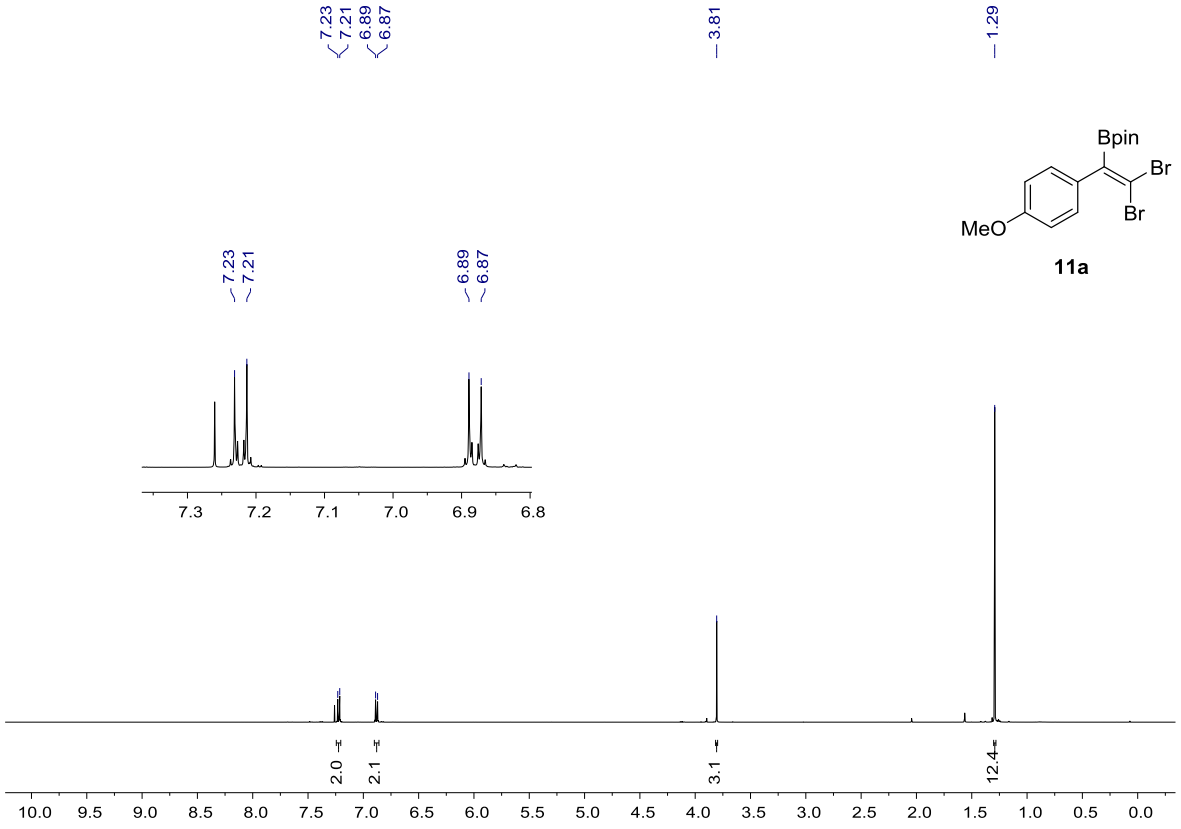


10b

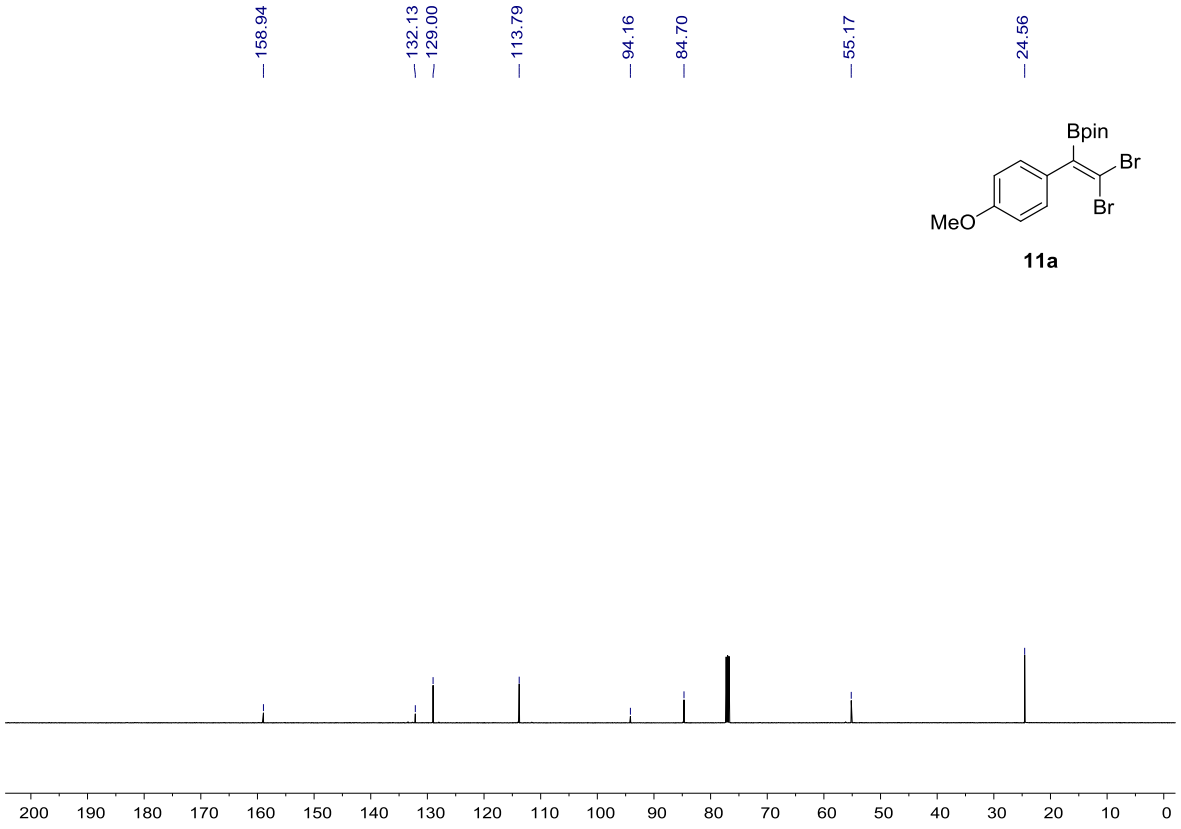
^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **10b**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **11a**

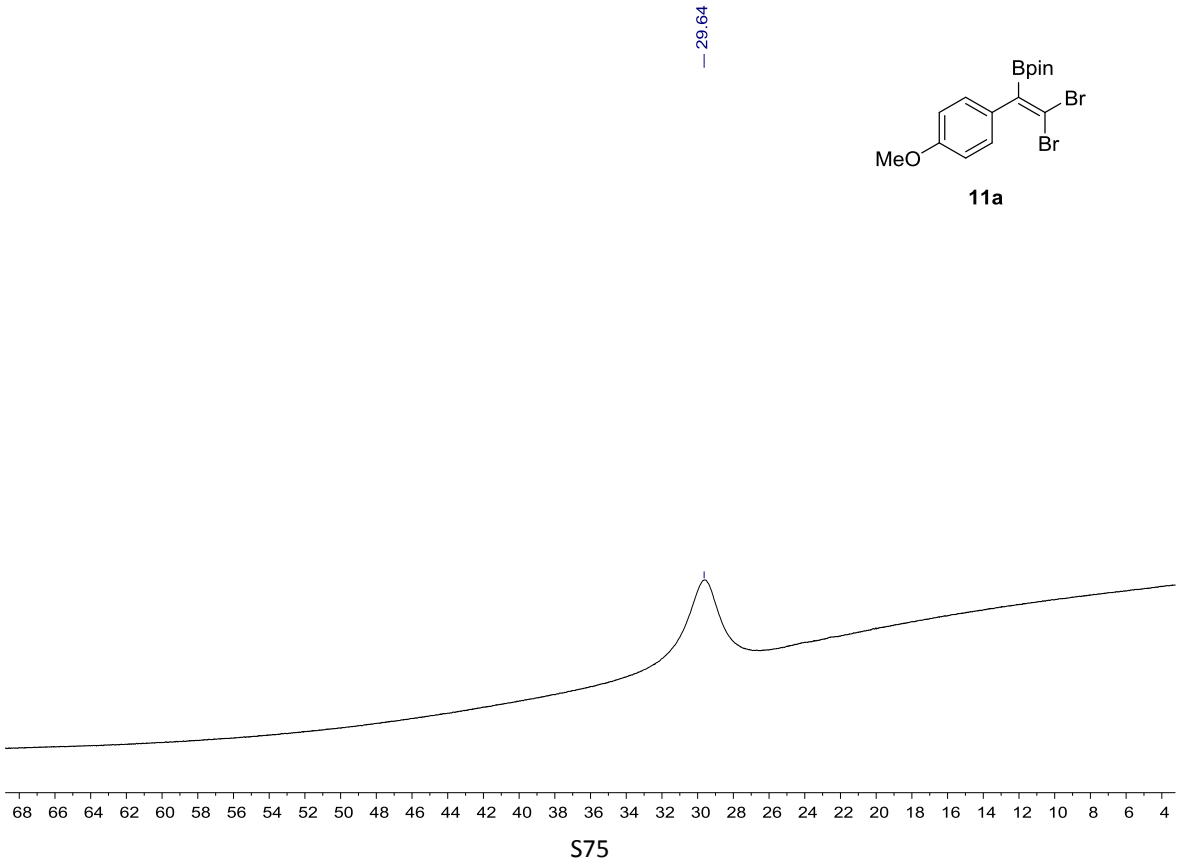


$^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$) of **11a**



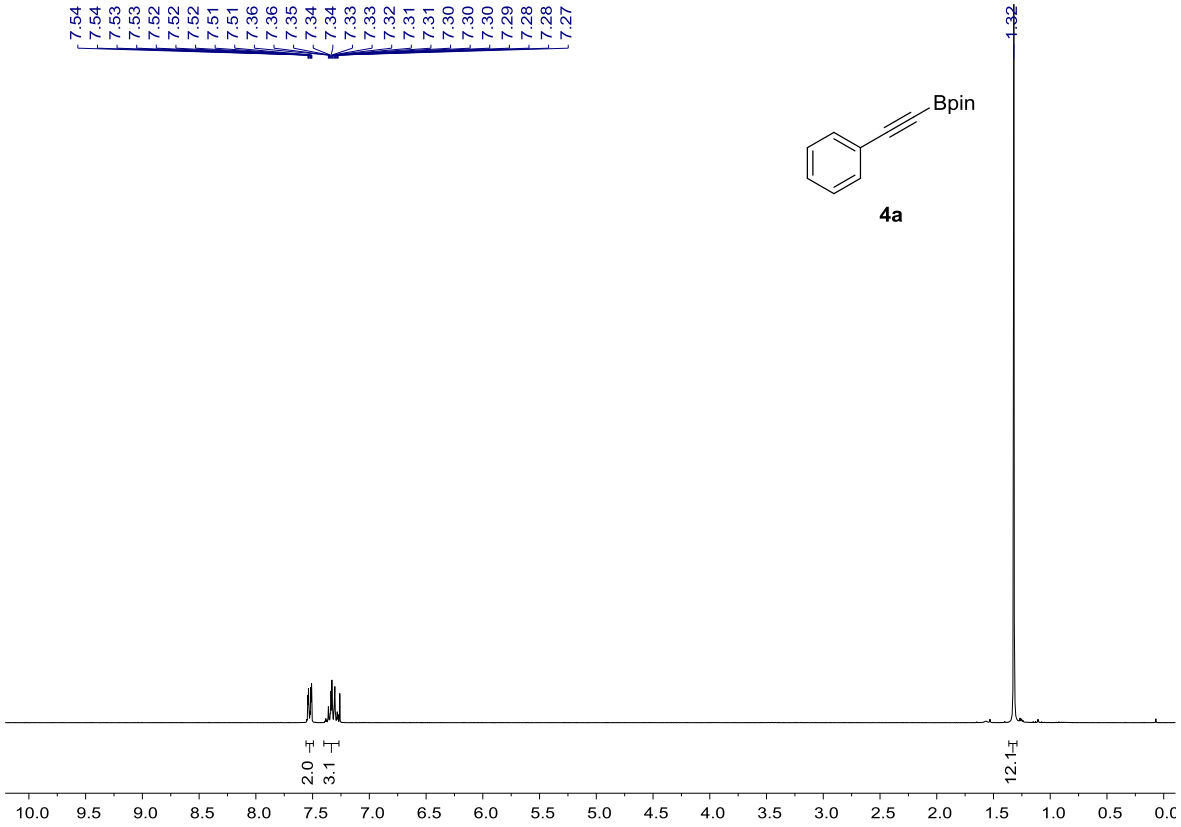
11a

^{11}B NMR spectrum (160 MHz, $CDCl_3$) of **11a**

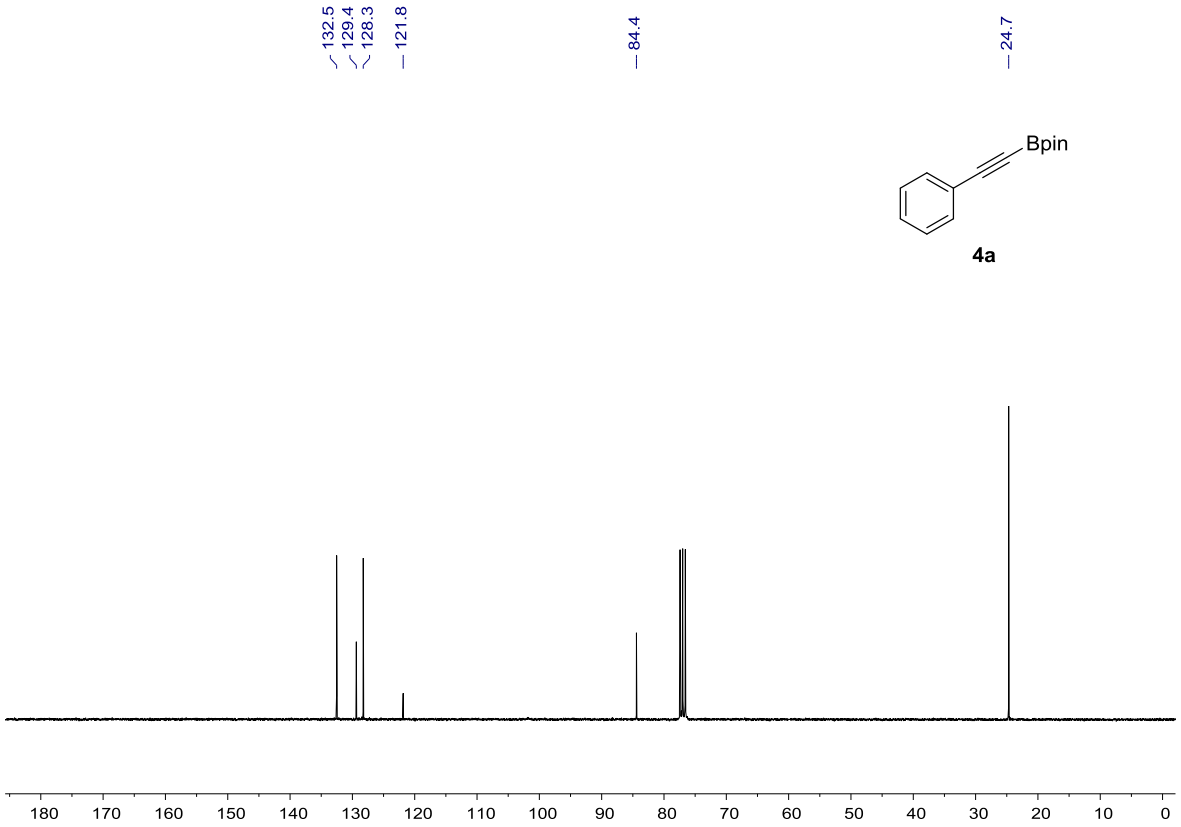


11a

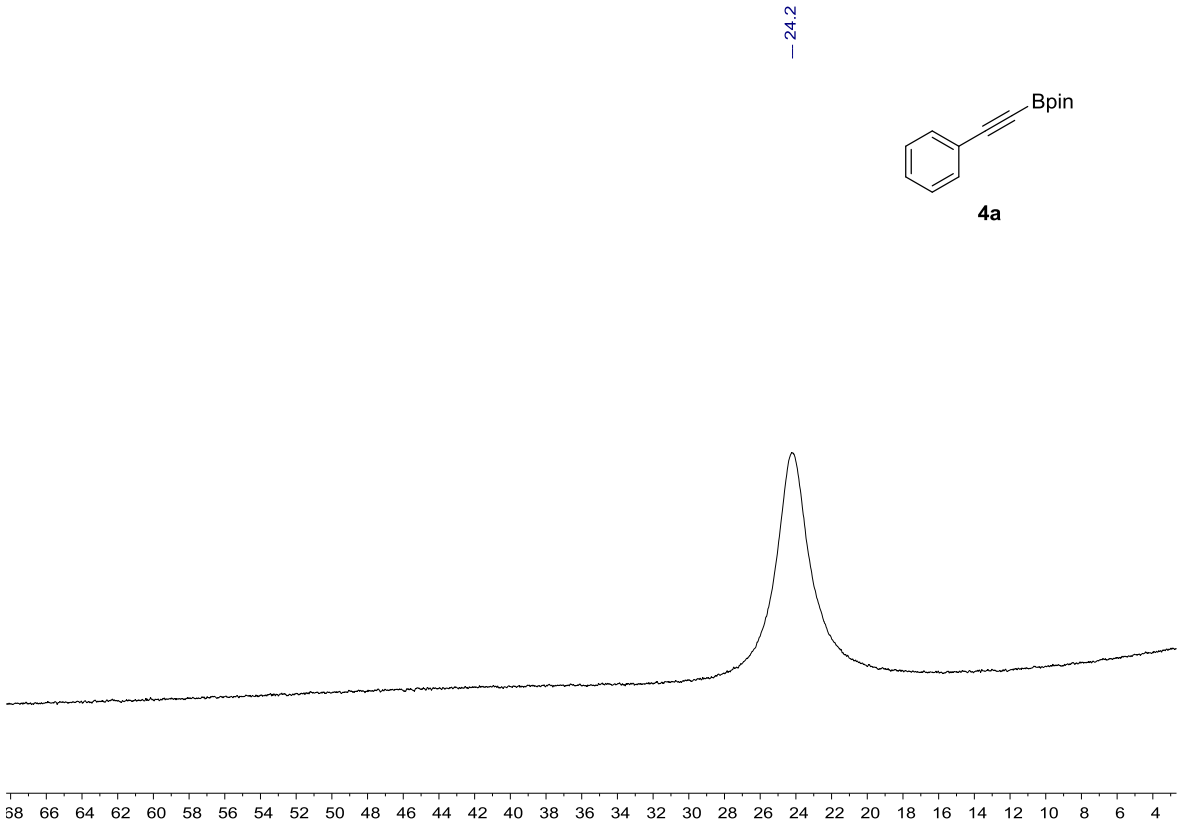
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4a**



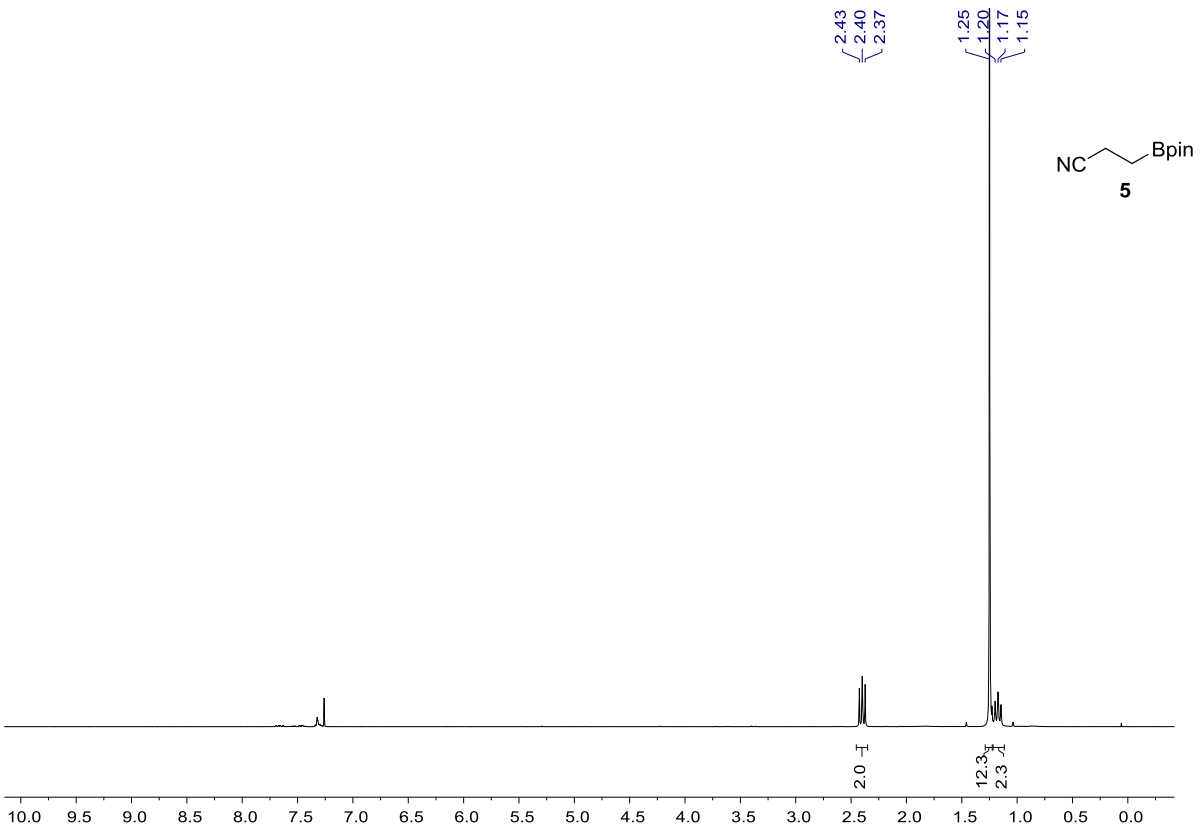
^{13}C{^{1}H} NMR spectrum (75 MHz, $CDCl_3$) of **4a**



^{11}B NMR spectrum (96 MHz, $CDCl_3$) of **4a**



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5**



VII. Single-crystal X-ray Diffraction

Crystal structure determination Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-Kα radiation monochromated by graphite (**6b, 10b**) or multi-layer focusing mirrors (**2a**). The crystals were cooled using an Oxford Cryostreams or Bruker Kryoflex II low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[4] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[5] software and the SHELXLE graphical user interface.[6] The crystal structure of **2a** was solved in space group $P2_1$ and transformed to higher symmetry (space group $P2_1/c$) using the PLATON program.[7] The PLATON program[7] was also used for the determination of the occurrence of twinning. The crystal structure of **2a** was refined as a twin applying the twin matrix (-1 0 0, 0 -1 0, 0 0 1). The twin component was refined to 47.5%. The crystal structure of **10b** was refined as a twin applying the twin matrix (0 2 0, 0.5 0 0, 0 0 -1). The twin component was refined to 1.9%. Diamond[8] software was used for graphical representation. Crystal data and experimental details are listed in Table **S7**; full structural information has been deposited with Cambridge Crystallographic Data Centre. CCDC-1918365 (**2a**), 1918366 (**6b**), and 1918367 (**10b**).

Table S7: Single-crystal X-ray diffraction data and structure refinements of **2a**, **6b**, and **10b**.

Data	**2a**	**6b**	**10b**
CCDC number	1918365	1918366	1918367
Empirical formula	$C_{26}H_{41}B_3O_6$	$C_{27}H_{36}B_2O_5$	$C_{21}H_{31}B_2BrO_5$
Formula weight / g·mol^{-1}	482.02	462.18	464.99
T / K	100(2)	100(2)	100(2)
λ / Å, radiation	MoKα 0.71073	MoKα 0.71073	MoKα 0.71073
Crystal size / mm³	0.15×0.30×0.40	0.21×0.32×0.70	0.19×0.30×0.34
Crystal color, habit	colorless block	colorless block	colorless block
μ / mm^{-1}	0.077	0.079	1.841
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a / Å	13.084(7)	9.492(3)	18.711(5)
b / Å	11.994(5)	11.493(7)	9.336(2)
c / Å	17.812(7)	13.055(3)	12.982(3)
α / °	90	72.7910(10)	90
β / °	90.124(12)	74.7050(10)	90
γ / °	90	74.3700(10)	90
Volume / Å^3	2795(2)	1283.7(9)	2267.6(9)
Z	4	2	4
ρ_{calc} / g·cm^{-3}	1.145	1.196	1.362
F(000)	1040	496	968
θ range / °	1.556 - 26.053	1.667 - 26.022	1.088 - 30.039
Reflections collected	20326	23816	76146
Unique reflections	5512	5067	6647
Parameters / restraints	329 / 0	393 / 0	458 / 625
GooF on F^2	1.027	1.023	1.246
R_1 [I>2σ(I)]	0.0465	0.0387	0.0466
wR^2 (all data)	0.1091	0.0982	0.1049
Max. / min. residual electron density / e·Å^{-3}	0.591 / –0.239	0.273 / –0.233	0.543 / –1.387

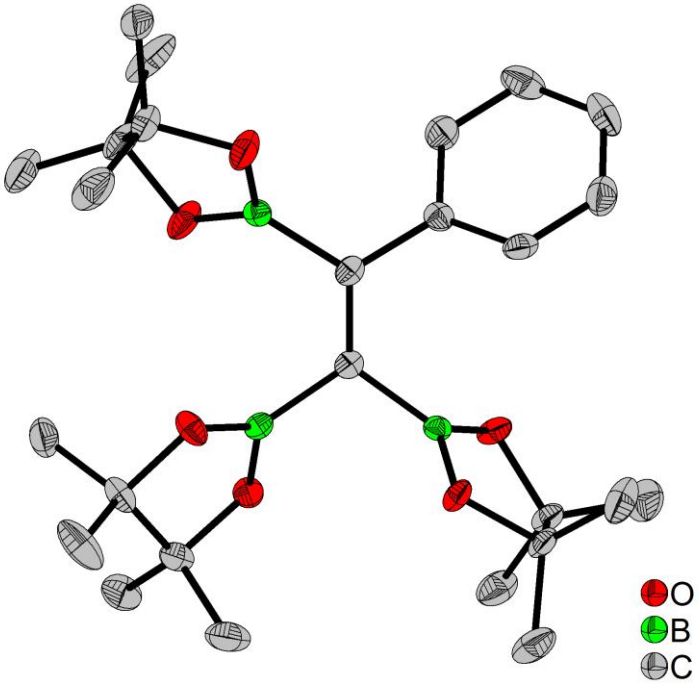


Figure S5. Molecular structure of **2a** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

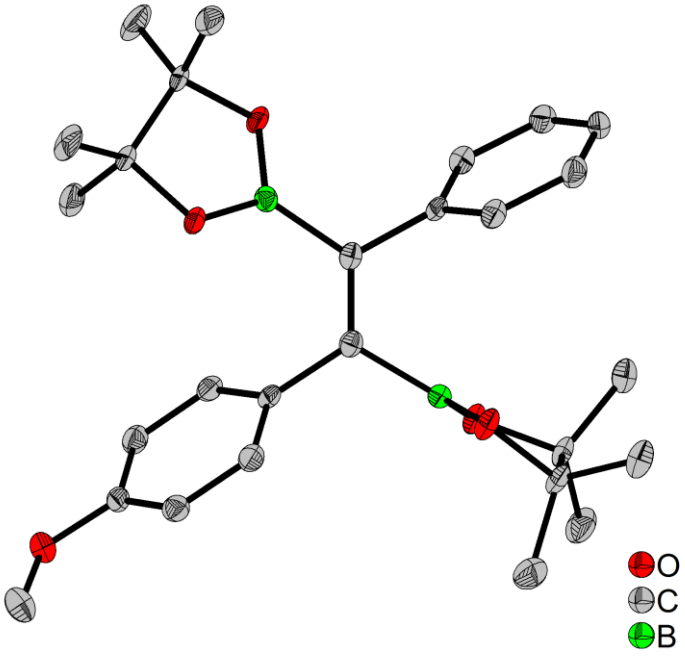


Figure S6. Molecular structure of **6b** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. One of the Bpin moieties is disordered and only the part with 88% occupancy is shown.

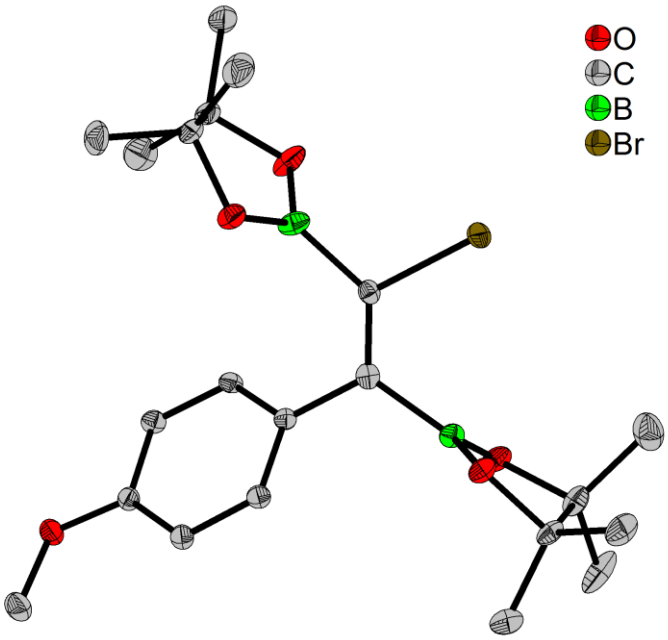


Figure S7. Molecular structure of **10b** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule is disordered except for one Bpin moiety and only the part with 85.5% occupancy is shown.

VIII. References

[1] C. I. Lee, W. C. Shih, J. Zhou, J. H. Reibenspies, O. V. Ozerov, *Angew. Chem. Int. Ed.* **2015**, *54*, 14003-14007; *Angew. Chem.* **2015**, *127*, 14209-14213.

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[7] A. Spek, *Acta Crystallogr.* **2009**, *D65*, 148-155.

[8] Brandenburg, K. Diamond (version 4.4.0), Crystal and Molecular Structure Visualization, Crystal Impact, H. Putz & K. Brandenburg GbR, Bonn (Germany), **2017**