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Supporting Information

Iron-Catalyzed Boration of Cinnamyl Carbonates: a Highly Stereoselective Approach to Cyclopropylboronates

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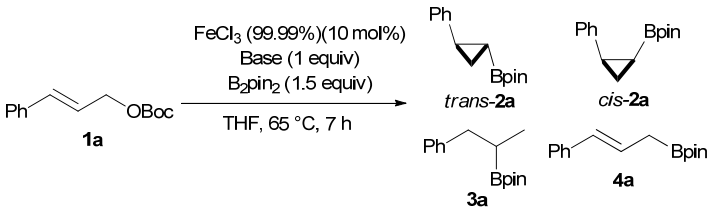
Contents

Detail information for screening of reaction conditions

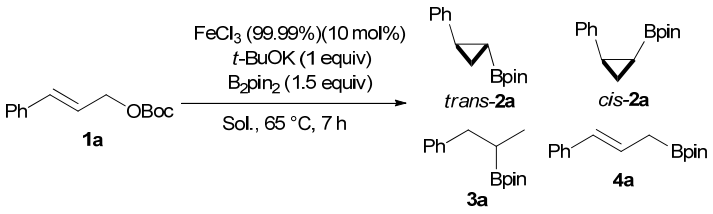
Table S1. Screening of bases[a,b,c]



Entry	Base	Covn./%	*trans*-**2a** Yiled/%	*trans*-**2a**: *cis*-**2a**: **3a**: **4a**
1	*t*-BuOK	94	73	92: 1: 2: 5
2	*t*-BuONa	96	68	97: 1: 1: 1
3	*t*-BuOLi	49	19	-
4	MeOK	95	44	86: 2: 1: 11
5	MeONa	10	0	-
6	K_2CO_3	9	0	-
7	K_3PO_4	6	0	-
8	Cs_2CO_3	13	0	-
9	-	2	0	-

[a]Reaction conditions: **1a** (0.3 mmol), B_2pin_2 (0.45 mmol, 1.5 equiv), $FeCl_3$ (10 mol%), base (0.3 mmol, 1 equiv), THF (10 mL), 65 °C, 7 h. [b]Conversion and yield were determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [c]Stereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture.

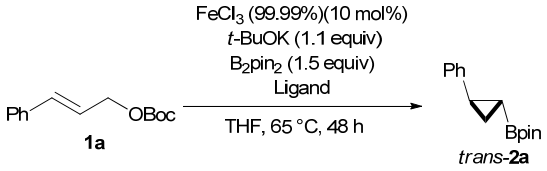
Table S2. Screening of solvents[a,b,c]



Entry	Solvent	Covn./%	*trans*-**2a** Yiled/%	*trans*-**2a**: *cis*-**2a**: **3a**: **4a**
1	THF	94	73	92: 1: 2: 5
2	MTBE	57	31	89: 1: 2: 8
3	dioxane	37	15	-
4	*n*-Bu_2O	75	62	97: 1: 1: 1
5	*i*-Pr_2O	68	36	85: 1: 3: 11
6	1,2-DME	20	4	-
7	DMSO	22	12	-
8	1,2-DCE	2	0	-
9	MeCN	19	6	-
10	toluene	42	17	-

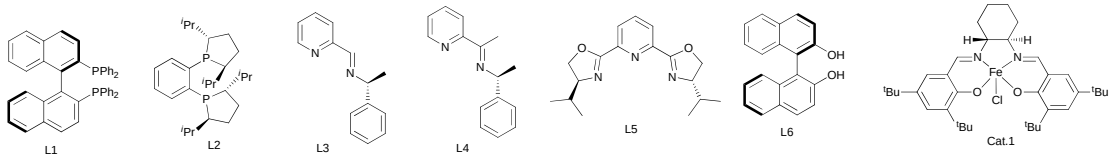
[a]Reaction conditions: **1a** (0.3 mmol), B_2pin_2 (0.45 mmol, 1.5 equiv), $FeCl_3$ (10 mol%), *t*-BuOK (0.3 mmol, 1 equiv), solvent (10 mL), 65 °C, 7 h. [b]Conversion and yield were determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [c]Stereomeric ratio was determined by ^1H NMR analysis of the crude reaction mixture. 1,2-DME (1,2-dimethoxyethane). 1,2-DCE (1,2-dichloroethane).

Table S3. Screening of chiral ligands[a,b,c]



Entry	Catalyst	Covn./%	*trans*-**2a** Yiled/%	Ee%
1	L1 : $FeCl_3$ = 1:1	100	80	0
2	L1 : $FeCl_3$ = 2:1	100	85	0
3	L2 : $FeCl_3$ = 1:1	80	50	0
4	L2 : $FeCl_3$ = 2:1	100	70	0
5	L3 : $FeCl_3$ = 1:1	70	56	0
6	L3 : $FeCl_3$ = 2:1	85	70	0
7	L4 : $FeCl_3$ = 1:1	90	85	0
8	L5 : $FeCl_3$ = 1:1	90	85	0
9	L6 : $FeCl_3$ = 2:1	40	20	0
10	Cat.1	85	70	0

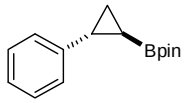
[a]Reaction conditions: **1a** (0.3 mmol), B_2pin_2 (0.45 mmol, 1.5 equiv), $FeCl_3$ (10 mol%), ligand, *t*-BuOK (0.33 mmol, 1.1 equiv), THF (10 mL), 65 °C, 48 h. [b]Conversion and yield were determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee value was determined by HPLC analysis (CHIRALCEL OD-H, hexane, 0.5 mL/min, UV detector at 254 nm, 30 °C, tR^1 = 16.1 min, tR^2 = 18.9 min.).



The spectra data of Cyclopropylboronates

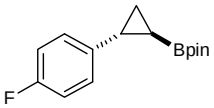
Note: The carbon attached to boron is not observed, or just a broad and low intensity signal around 10 ppm in ^{13}C NMR spectra.[1]

4,4,5,5-Tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane (2a)



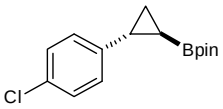
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (118 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.25 (m, 2H), 7.11-7.14 (m, 1H), 7.07-7.08 (m, 2H), 2.08-2.13 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.14-1.18 (m, 1H), 0.97-1.02 (m, 1H), 0.28-0.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 128.4, 125.8, 125.6, 83.3, 24.9, 24.8, 22.0, 15.1, 5.99. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.21. HRMS-ESI: calcd for $C_{15}H_{22}BO_2$ ($[M+H]^+$), 245.1713; found, 245.1705. These spectroscopic data correspond to reported data.[1d]

2-(2-(4-fluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



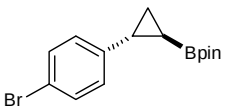
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (124 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01-7.05 (m, 2H), 6.90-6.95 (m, 2H), 2.06-2.11 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.11-1.16 (m, 1H), 0.92-0.97 (m, 1H), 0.21-0.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, J = 241.8), 139.0 (d, J = 3.2), 127.2 (d, J = 7.7), 115.1 (d, J = 21.1), 83.3, 24.83, 24.82, 21.30, 14.82, 5.75. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.06. HRMS-ESI: calcd for $C_{15}H_{21}BFO_2$ ($[M+H]^+$), 263.1619; found, 263.1609. These spectroscopic data correspond to reported data.[2]

2-(2-(4-Chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



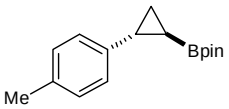
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (103 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 8.5 Hz , 2H), 7.00 (d, J = 8.5 Hz , 2H), 2.05-2.09 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.14-1.19 (m, 1H), 0.94-0.98 (m, 1H), 0.23-0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 131.2, 128.4, 127.1, 83.4, 24.83, 24.80, 21.4, 15.1, 6.11. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.06. HRMS-ESI: calcd for $C_{15}H_{21}BClO_2$ ($[M+H]^+$), 279.1323; found, 279.1322. These spectroscopic data correspond to reported data.[1d]

2-(2-(4-Bromophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (104 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.4 Hz , 2H), 6.94 (d, J = 8.4 Hz , 2H), 2.03-2.07 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.13-1.17 (m, 1H), 0.94-0.98 (m, 1H), 0.23-0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 131.3, 127.6, 119.1, 83.4, 24.9, 24.8, 21.5, 15.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.73. HRMS-ESI: calcd for $C_{15}H_{21}BBrO_2$ ($[M+H]^+$), 323.0818; found, 323.0815. These spectroscopic data correspond to reported data.[1d]

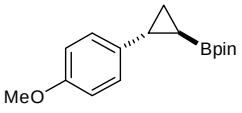
4,4,5,5-Tetramethyl-2-(2-(*p*-tolyl)cyclopropyl)-1,3,2-dioxaborolane (2e)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (120 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, J = 8.0 Hz , 2H), 6.99 (d, J = 8.0 Hz , 2H), 2,31 (s, 3H), 2.07-2.12 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.12-1.16 (m, 1H), 0.96-1.00 (m, 1H), 0.25-0.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 135.1, 129.0, 125.7, 83.2, 24.9, 24.8, 21.7, 21.0, 14.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.22. HRMS-ESI: calcd for

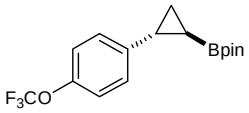
$C_{16}H_{24}BO_2$ ([M+H]$^+$), 259.1869; found, 259.1865. These spectroscopic data correspond to reported data.[3]

2-(2-(4-Methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



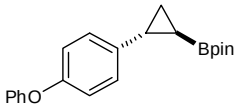
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (118 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J = 8.7 Hz , 2H), 6.79 (d, J = 8.7 Hz , 2H), 3.77 (s, 3H), 2.04-2.09 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.08-1.13 (m, 1H), 0.91-0.96 (m, 1H), 0.19-0.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 135.4, 126.9, 113.9, 83.2, 55.4, 24.9, 24.8, 21.3, 14.6, 4.53. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.02. HRMS-ESI: calcd for $C_{16}H_{24}BO_2$ ([M+H]$^+$), 275.1819; found, 275.1809. These spectroscopic data correspond to reported data.[1d]

4,4,5,5-Tetramethyl-2-(2-(4-(trifluoromethoxy)phenyl)cyclopropyl)-1,3,2-dioxaborolane (2g)



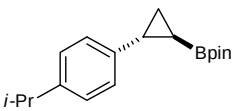
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (115 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 4H), 2.08-2.12 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15-1.19 (m, 1H), 0.96-1.00 (m, 1H), 0.24-0.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3 (q, J = 1.7 Hz), 142.4, 127.0, 121.0, 120.7 (q, J = 254.8 Hz), 83.4, 24.9, 24.8, 21.4, 15.2, 6.36. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.01. HRMS-ESI: calcd for $C_{16}H_{21}BF_3O_2$ ([M+H]$^+$), 329.1536; found, 329.1530.

4,4,5,5-Tetramethyl-2-(2-(4-phenoxyphenyl)cyclopropyl)-1,3,2-dioxaborolane (2h)



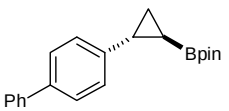
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (154 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.33 (m, 2H), 7.05-7.08 (m, 3H), 6.96-6.98 (m, 2H), 6.90-6.92 (m, 2H), 2.09-2.13 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.14-1.19 (m, 1H), 0.96-1.01 (m, 1H), 0.25-0.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 155.0, 138.6, 129.8, 127.1, 122.9, 119.3, 118.4, 83.3, 24.9, 24.8, 21.5, 15.0. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.14. HRMS-ESI: calcd for $C_{21}H_{26}BO_3$ ([M+H]$^+$), 337.1975; found, 337.1967.

2-(2-(4-Isopropylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (113 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.2 Hz , 2H), 7.02 (d, J = 8.2 Hz , 2H), 2.83-2.90 (m, 1H), 2.07-2.11 (m, 1H), 1.22-1.25 (m, 18H), 1.12-1.17 (m, 1H), 0.96-1.02 (m, 1H), 0.26-0.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 140.8, 126.4, 125.7, 83.2, 33.8, 24.9, 24.8, 24.2, 21.7, 15.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.23. HRMS-ESI: calcd for $C_{18}H_{28}BO_2$ ([M+H]$^+$), 287.2182; found, 287.2180.

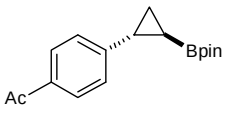
2-(2-([1,1'-Biphenyl]-4-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). White solid (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.42 (m,

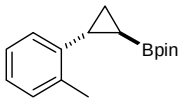
2H), 7.32 (m, 1H), 7.16 (d, J = 8.2 Hz, 2H), 2.13-2.18 (m, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 1.18-1.23 (m, 1H), 1.03-1.08 (m, 1H), 0.33-0.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 141.2, 138.7, 128.8, 127.14, 127.09, 127.07, 126.2, 83.3, 24.9, 24.8, 21.8, 15.3. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.12. HRMS-ESI: calcd for $C_{21}H_{26}BO_2$ ($[M+H]^+$), 321.2026; found, 321.2020. These spectroscopic data correspond to reported data.[1d]

1-(4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)ethanone (2k)



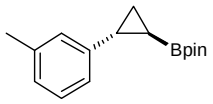
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:5). Colorless oil (126 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz , 2H), 7.13 (d, J = 8.2 Hz , 2H), 2.56 (s, 3H), 2.12-2.16 (m, 1H), 1.24-1.25 (m, 13H), 1.05-1.09 (m, 1H), 0.35-0.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 149.8, 138.5, 128.6, 125.7, 83.5, 26.7, 24.88, 24.86, 22.1, 16.0. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.58. HRMS-ESI: calcd for $C_{17}H_{24}BO_3$ ($[M+H]^+$), 287.1819; found, 287.1812. These spectroscopic data correspond to reported data.[1d]

4,4,5,5-Tetramethyl-2-(2-(*o*-tolyl)cyclopropyl)-1,3,2-dioxaborolane (2l)



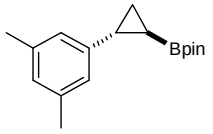
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (97 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.15 (m, 1H), 7.08-7.11 (m, 2H), 7.00-7.02 (m, 1H), 2.41 (s, 3H), 2.08-2.13 (m, 1H), 1.27 (s, 12H), 1.11-1.16 (m, 1H), 0.99-1.05 (m, 1H), 0.13-0.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 138.0, 129.6, 126.0, 125.9, 125.6, 83.3, 24.9, 24.8, 20.4, 19.7, 12.4. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.55. HRMS-ESI: calcd for $C_{16}H_{24}BO_2$ ($[M+H]^+$), 259.1869; found, 259.1861. These spectroscopic data correspond to reported data.[1d]

4,4,5,5-Tetramethyl-2-(2-(*m*-tolyl)cyclopropyl)-1,3,2-dioxaborolane (2m)



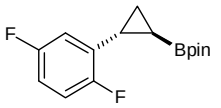
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (83 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 2.3 (s, 3H), 2.06-2.10 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.11-1.15 (m, 1H), 0.97-1.02 (m, 1H), 0.26-0.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.9, 128.3, 126.8, 126.5, 122.7, 83.3, 24.9, 24.8, 22.0, 21.5, 15.0. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.11. HRMS-ESI: calcd for $C_{16}H_{24}BO_2$ ($[M+H]^+$), 259.1869; found, 259.1862.

2-(2-(3,5-Dimethylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



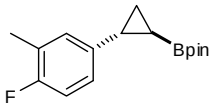
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (101 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (s, 1H), 6.71 (s, 2H), 2.26 (s, 6H), 2.02-2.07 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.10-1.14 (m, 1H), 0.96-1.01 (m, 1H), 0.25-0.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.9, 127.4, 123.7, 83.3, 24.9, 24.8, 21.9, 21.4, 14.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.83. HRMS-ESI: calcd for $C_{17}H_{26}BO_2$ ($[M+H]^+$), 273.2026; found, 273.2021. These spectroscopic data correspond to reported data.[1d]

2-(2-(2,5-Difluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)



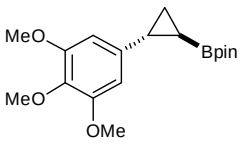
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89-6.95 (m, 1H), 6.73-6.79 (m, 1H), 6.54-6.59 (m, 1H), 2.25-2.30 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.17-1.21 (m, 1H), 0.98-1.03 (m, 1H), 0.24-0.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (dd, J = 239.3, 2.0 Hz), 157.9 (dd, J = 241.6, 2.4 Hz), 132.4 (dd, J = 16.7, 7.9 Hz), 115.9 (dd, J = 25.2, 9.2 Hz), 113.0 (dd, J = 23.8, 8.3 Hz), 112.3 (dd, J = 24.4, 4.6 Hz), 83.5, 24.9, 24.8, 22.0, 15.3 (dd, J = 5.1, 1.1 Hz), 13.8, 5.21. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.83. HRMS-ESI: calcd for $C_{15}H_{20}BF_2O_2$ ([M+H]$^+$), 281.1524; found, 281.1518.

2-(2-(4-Fluoro-3-methylphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)



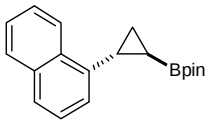
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (117 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-7.04 (m, 1H), 6.75-6.78 (m, 1H), 6.69-6.72 (m, 1H), 2.21 (s, 3H), 2.04-2.08 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.12-1.17 (m, 1H), 0.94-0.98 (m, 1H), 0.22-0.0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, J = 240.2 Hz), 143,4 (d, J = 7.6 Hz), 131.2 (d, J = 5.7 Hz), 121.8 (d, J = 17.2 Hz), 121.3 (d, J = 3.0 Hz), 112.2 (d, J = 22.5 Hz), 83.3, 24.84, 24.80, 21.5 (d, J = 1.7 Hz), 15.0, 14.2 (d, J = 3.4 Hz), 5.69. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.16. HRMS-ESI: calcd for $C_{16}H_{23}BFO_2$ ([M+H]$^+$), 277.1775; found, 277.1770.

4,4,5,5-Tetramethyl-2-(2-(3,4,5-trimethoxyphenyl)cyclopropyl)-1,3,2-dioxaborolane (2q)



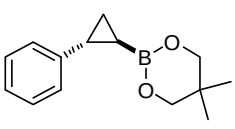
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (150 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (s, 2H), 3.82 (s, 6H), 3.79 (s, 3H), 2.04-2.08 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.10-1.15 (m, 1H), 0.92-0.97 (m, 1H), 0.25-0.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 139.2, 136.2, 102.9, 83.3, 61.0, 56.2, 24.9, 24.8, 22.3, 15.1. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.59. HRMS-ESI: calcd for $C_{18}H_{27}BO_5$ ([M+H]$^+$), 335.2030; found, 335.2029.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)cyclopropyl)-1,3,2-dioxaborolane (2r)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.2 Hz , 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.45-7.53 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 3.9 Hz, 1H), 2.55-2.60 (m, 1H), 1.29 (s, 13H), 1.06-1.10 (m, 1H), 0.32-0.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 133.6, 133.5, 128.6, 126.8, 125.9, 125.7, 125.6, 124.5, 123.6, 83.4, 24.91, 24.89, 22.0, 12.6. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.49. HRMS-ESI: calcd for $C_{14}H_{24}BO_2$ ([M+H]$^+$), 295.1869; found, 295.1863. These spectroscopic data correspond to reported data.[1d]

5,5-Dimethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborinane (2s)



Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, J = 7.7 Hz , 2H), 7.06-7.13 (m, *3*H),

3.78 (s, 4H), 2.00-2.05 (m, 1H), 1.08-1.12 (m, 1H), 0.95 (s, 7H), 0.15-0.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 128.3, 125.8, 125.4, 72.2, 31.9, 21.9, 21.7, 14.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.18. HRMS-ESI: calcd for $C_{14}H_{20}BO_2$ ($[M+H]^+$), 231.1556; found, 231.1552. These spectroscopic data correspond to reported data.[1e]

References

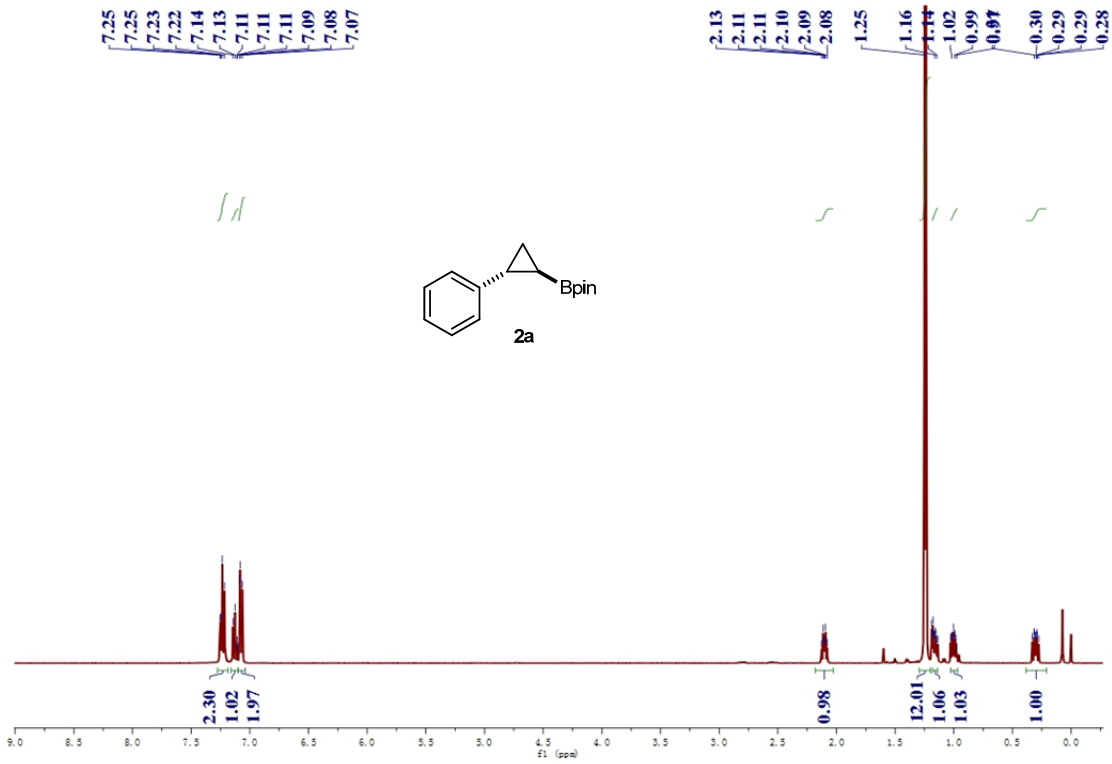
[1] a) P. J. Unsworth, D. Leonori and V. K. Aggarwal, *Angew. Chem.* **2014**, *126*, 10004-10008; *Angew. Chem. Int. Ed.* **2014**, *53*, 9846-9850; b) K. Semba and Y. Nakao, *J. Am. Chem. Soc*. **2014**, *136*, 7567-7570; c) E. Yamamoto, K. Izumi, Y. Horita and H. Ito, *J. Am. Chem. Soc*. **2012**, *134*, 19997-20000; d) C. Zhong, S. Kunii, Y. Kosaka, M. Sawamura and H. Ito, *J. Am. Chem. Soc.* **2010**, *132*, 11440-11442; e) Y. Zhao and V. Snieckus, *Adv. Synth. Catal.* **2014**, *356*, 1527-1532.

[2] G. Benoit and A. B. Charette, *J. Am. Chem. Soc.* **2017**, *139*, 1364-1367.

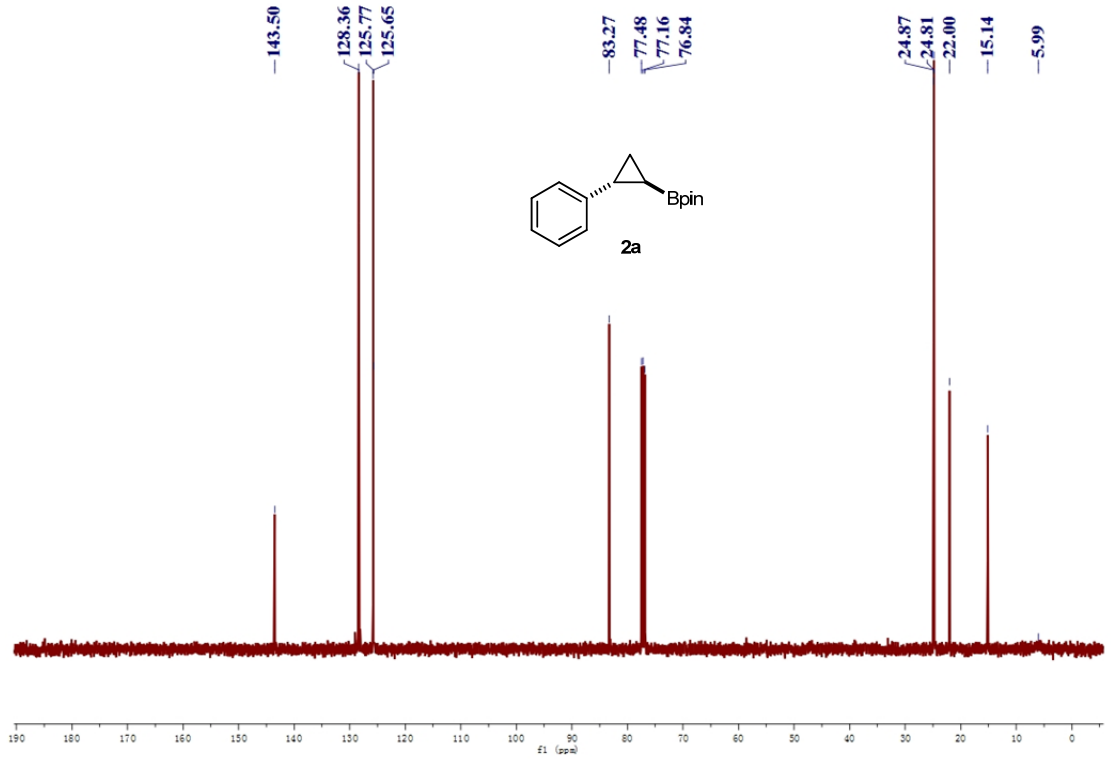
[3] H. F. Koolman, S. Kantor, A. R. Bogdan, Y. Wang, J. Y. Pan and S. W. Djuric, *Org. Biomol. Chem.* **2016**, *14*, 6591-6595.

NMR Spectra of Cyclopropylboronates

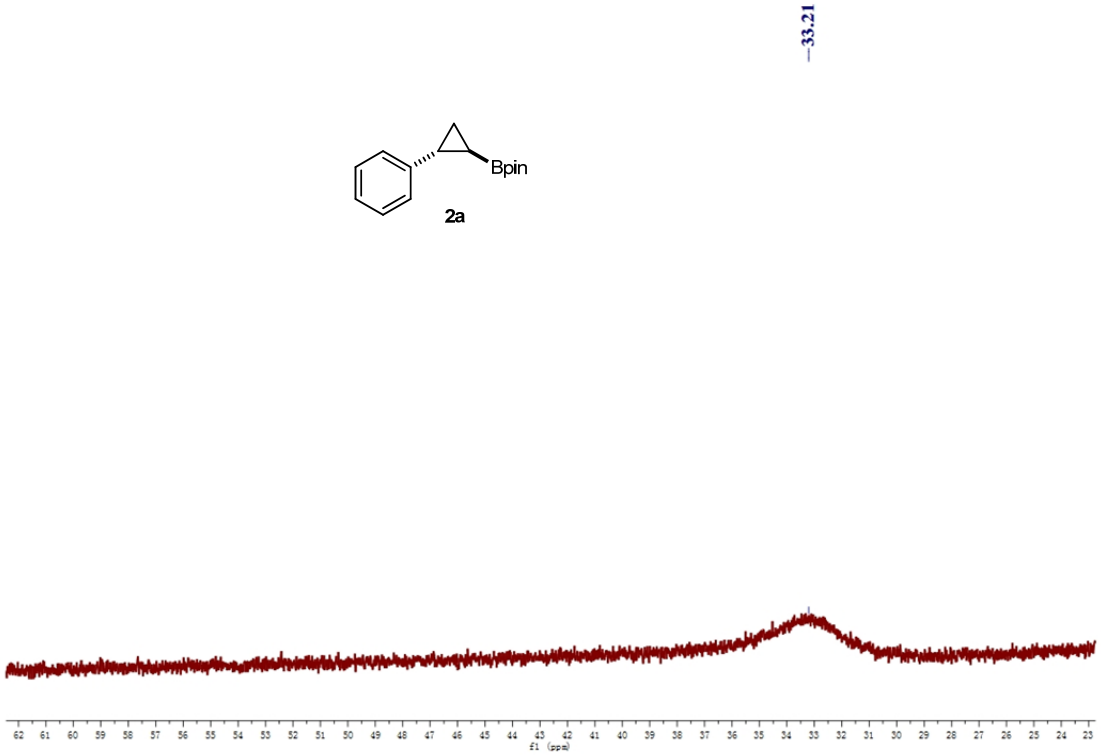
^{1}H NMR (400 MHz, $CDCl_3$) (**2a**)



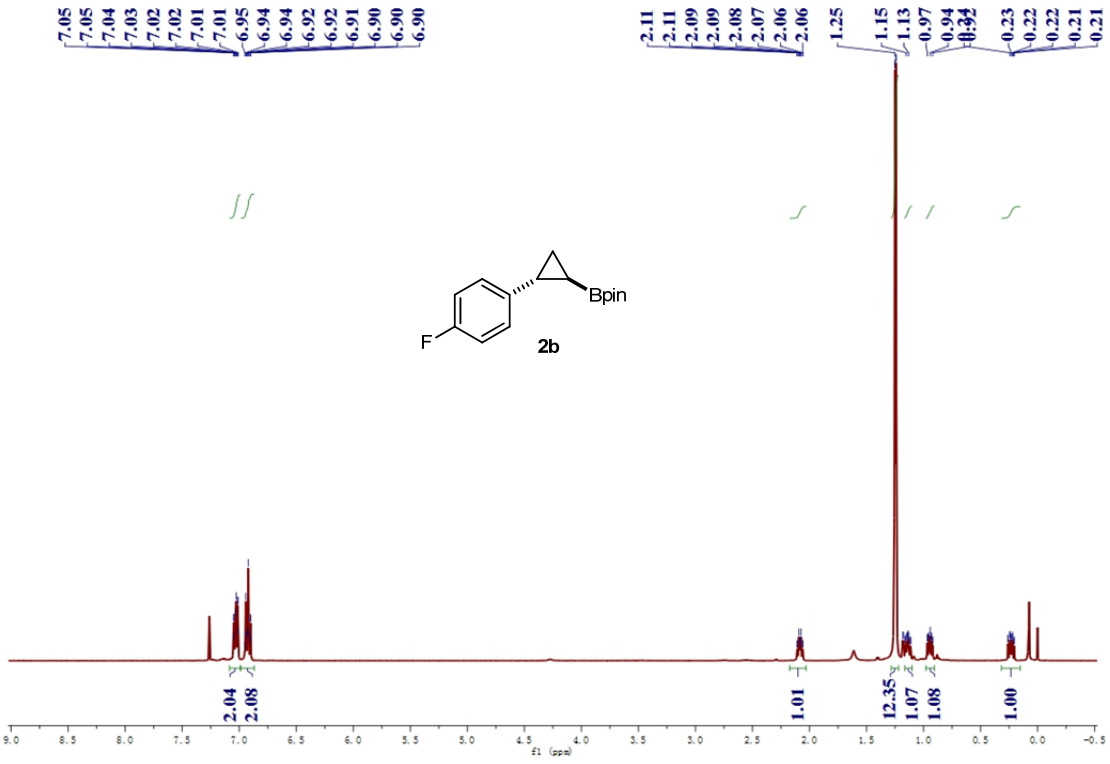
^{13}C NMR (100 MHz, $CDCl_3$) (**2a**)



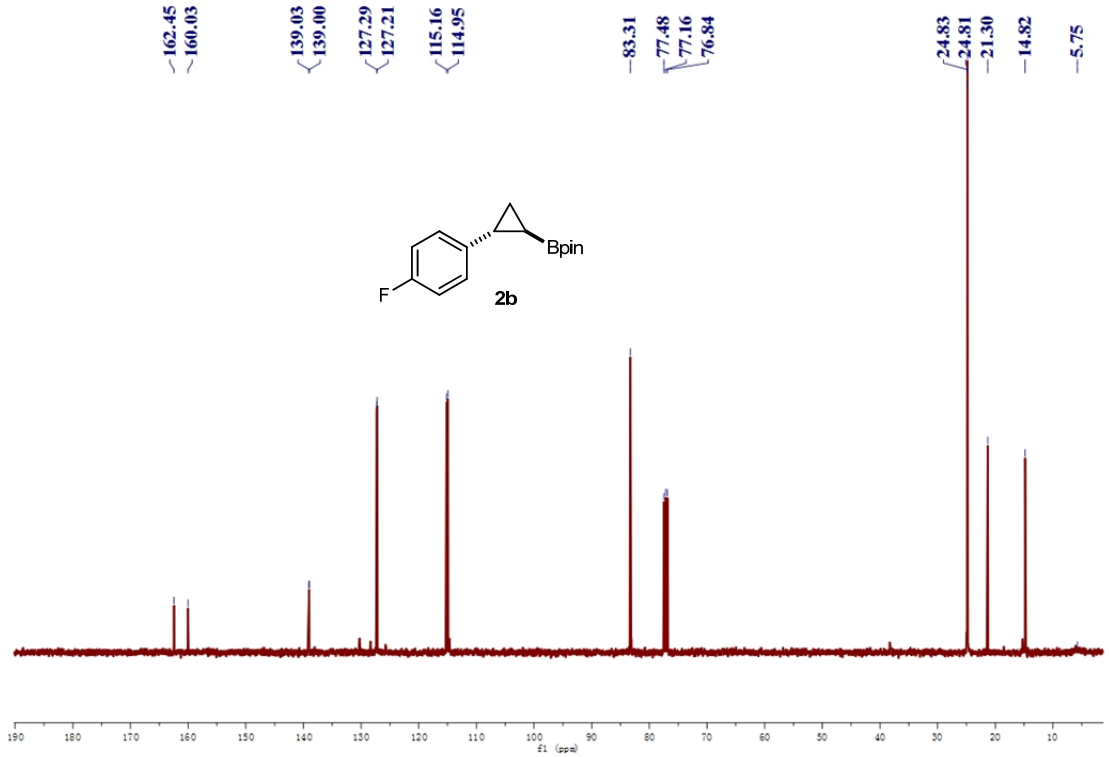
^{11}B NMR (128 MHz, $CDCl_3$) (**2a**)



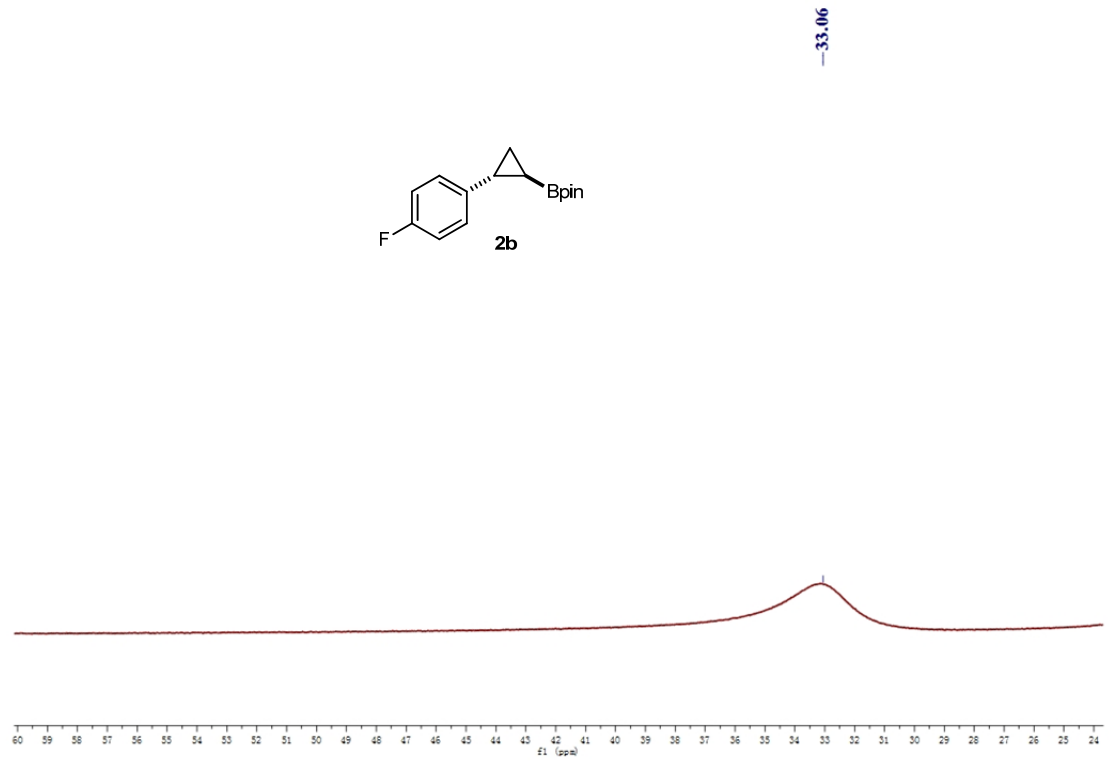
^{1}H NMR (400 MHz, $CDCl_3$) (**2b**)



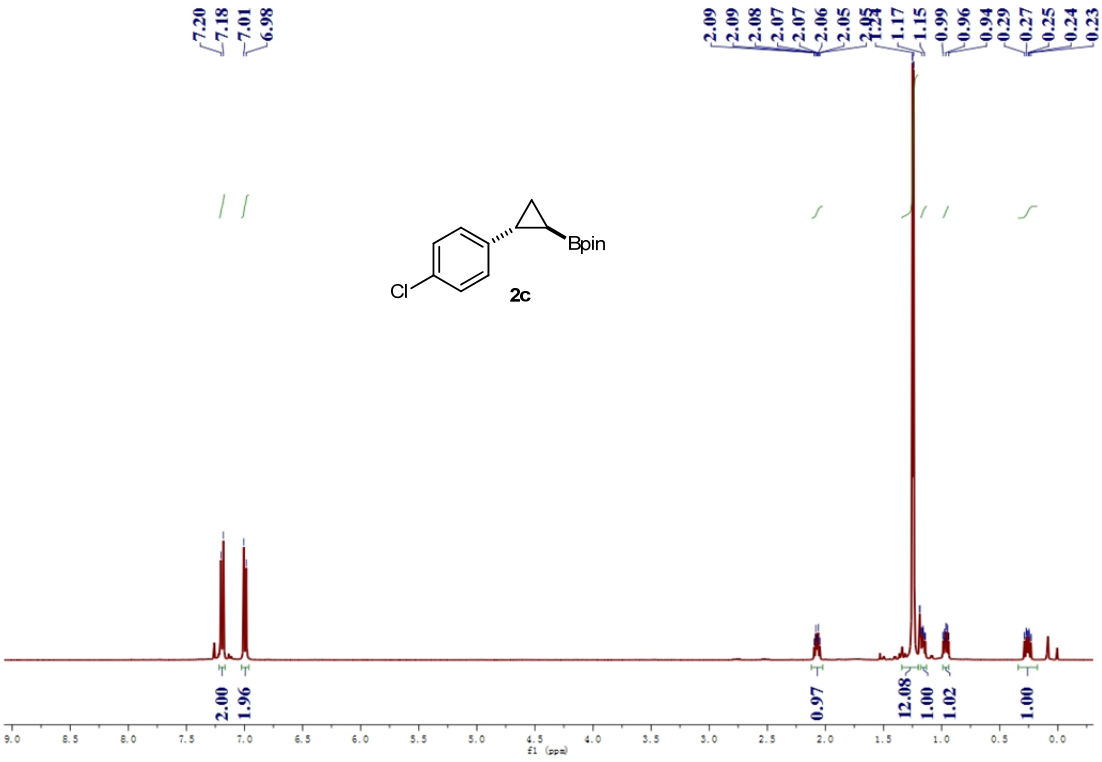
^{13}C NMR (100 MHz, $CDCl_3$) (**2b**)



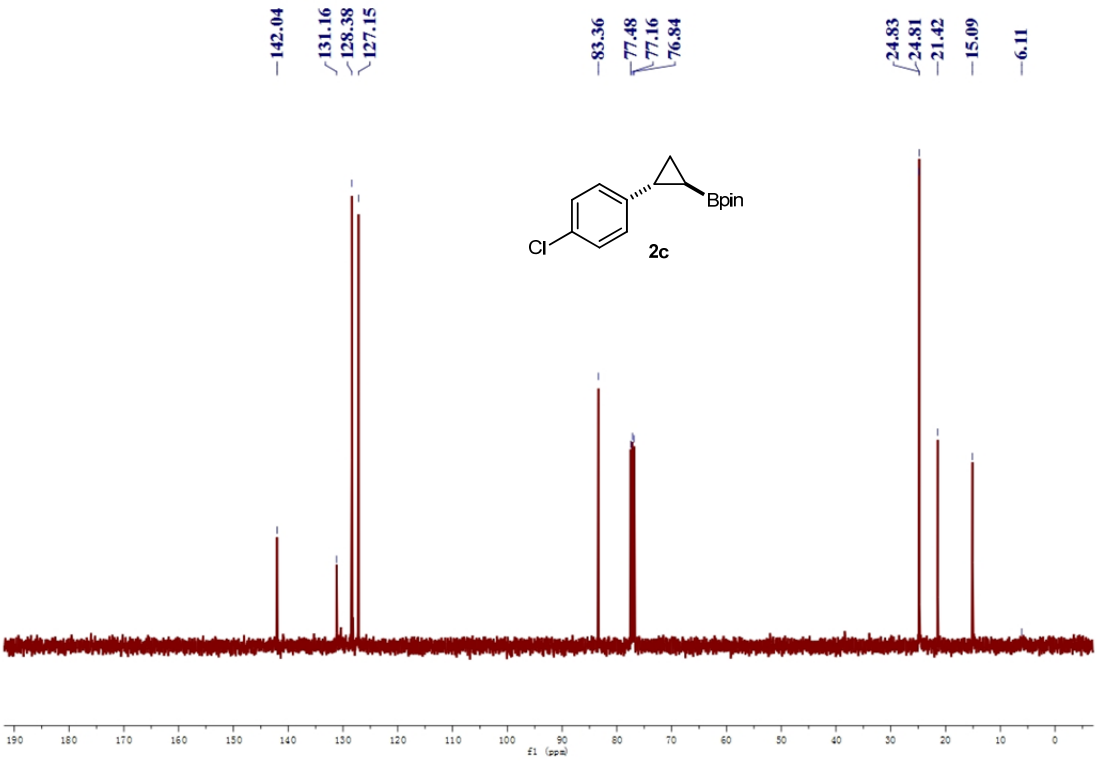
^{11}B NMR (128 MHz, $CDCl_3$) (**2b**)



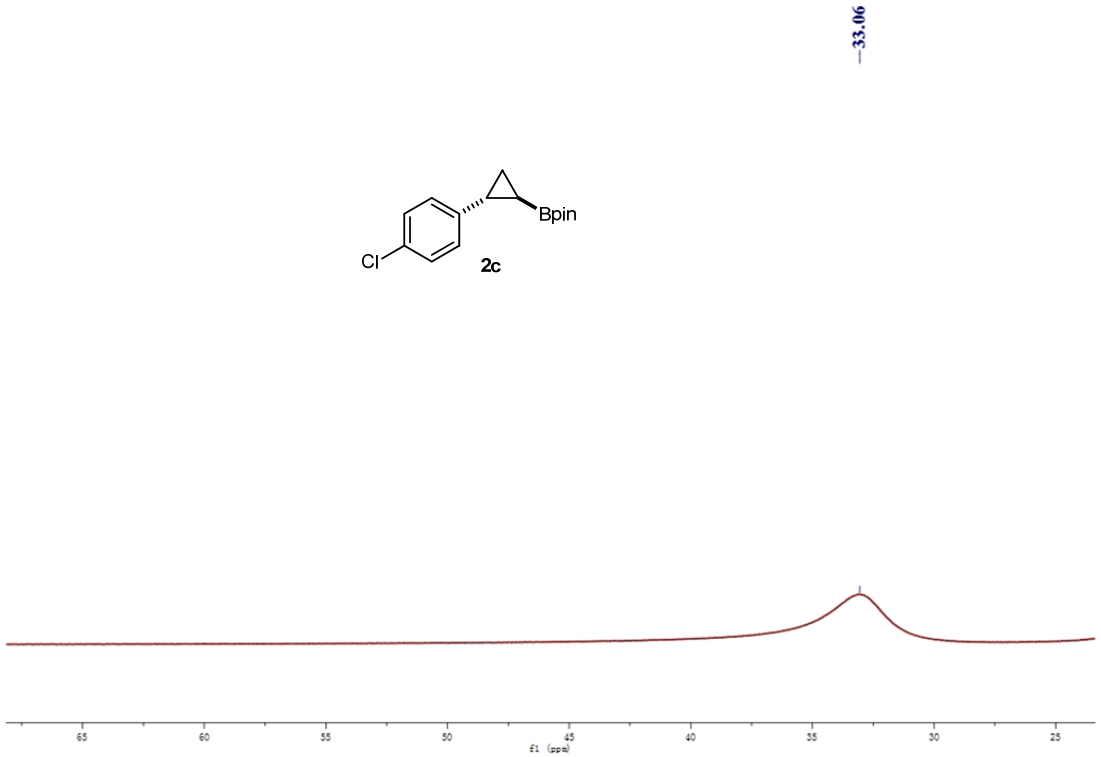
^{1}H NMR (400 MHz, $CDCl_3$) (**2c**)



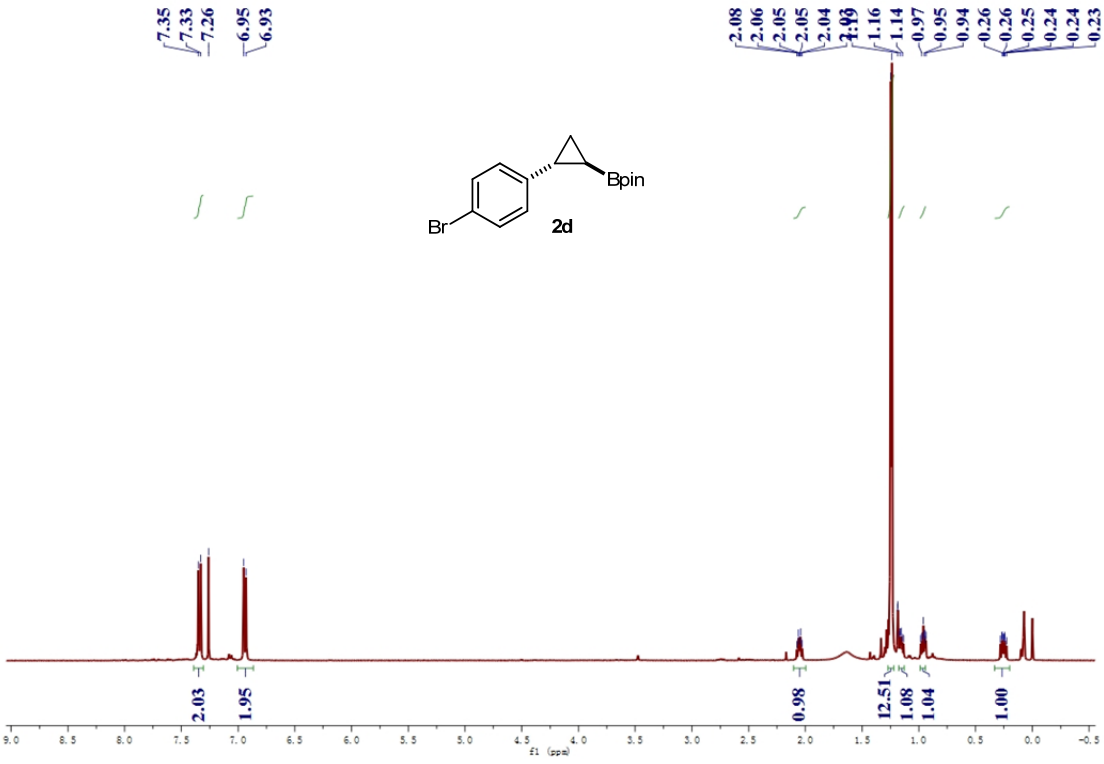
^{13}C NMR (100 MHz, $CDCl_3$) (**2c**)



^{11}B NMR (128 MHz, $CDCl_3$) (**2c**)



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



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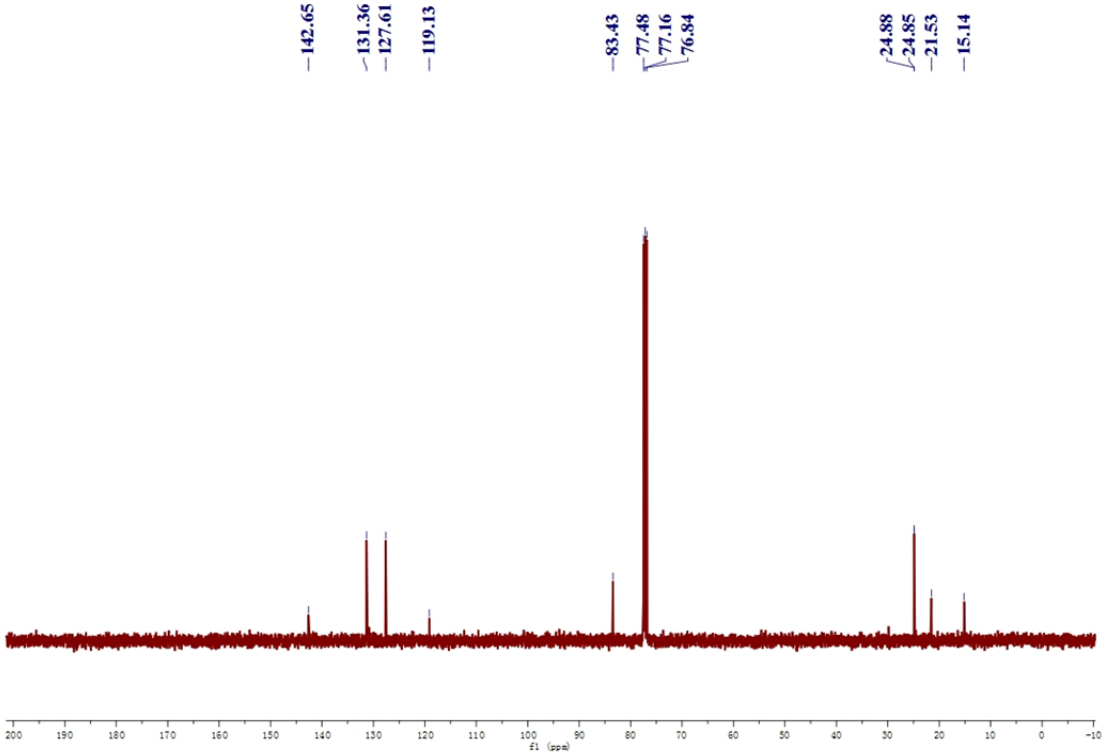
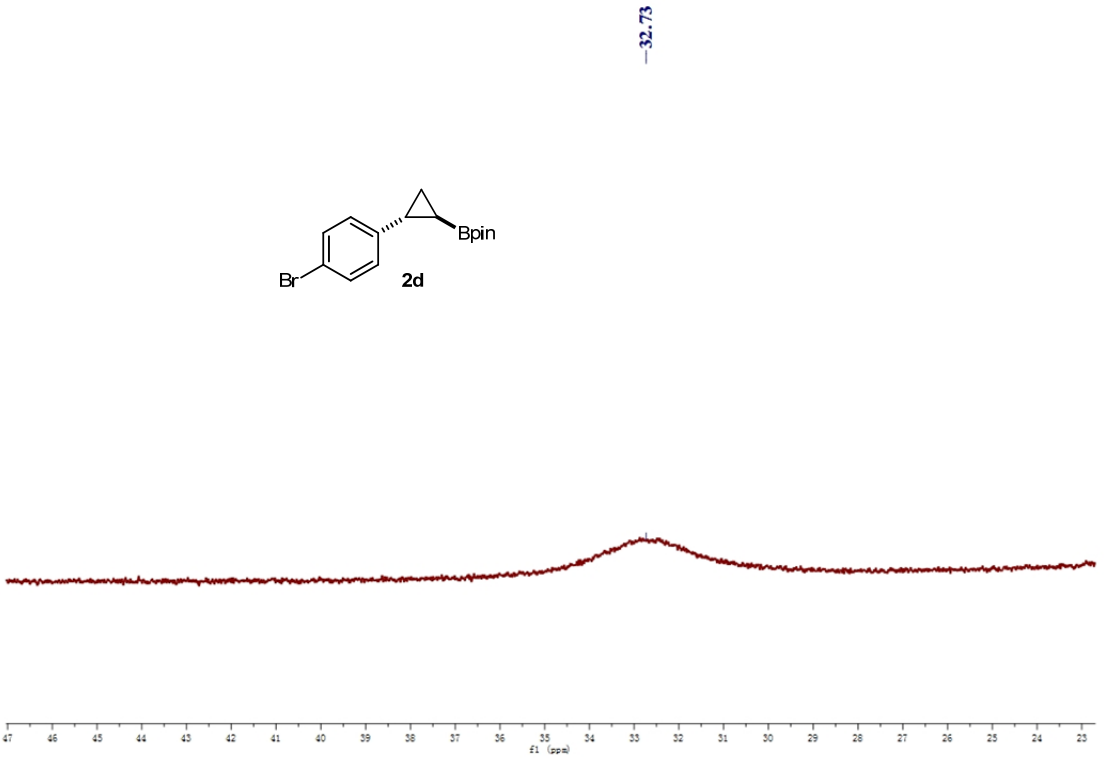
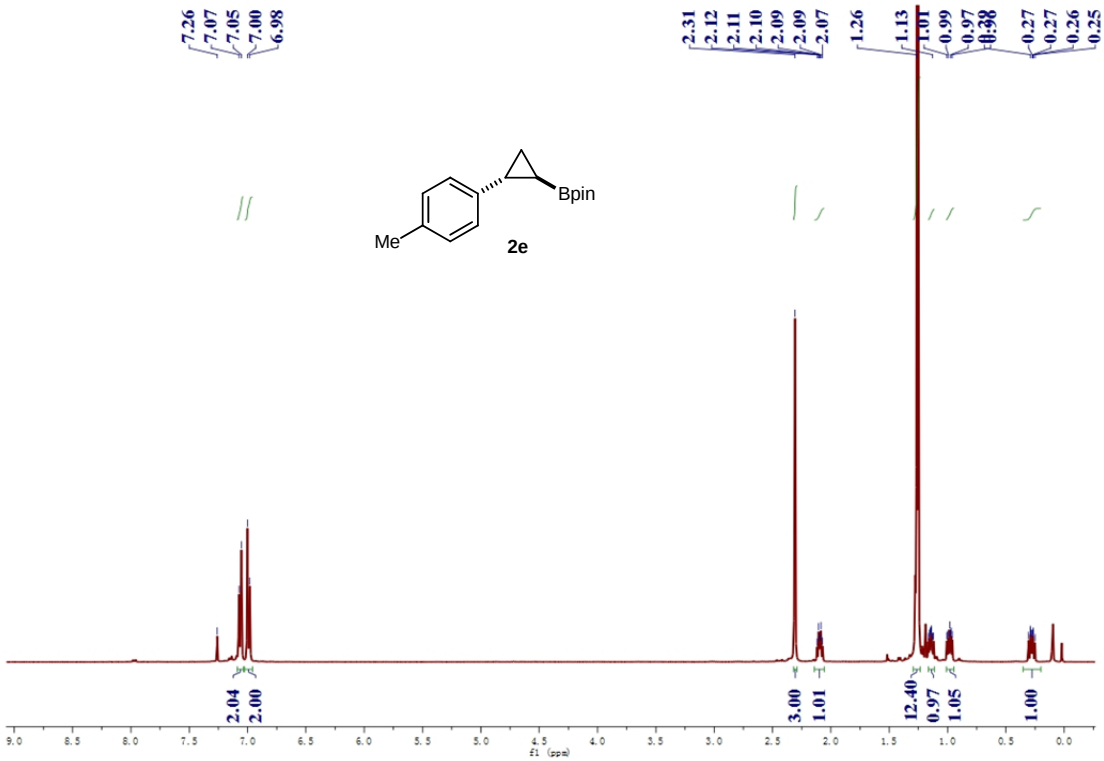


^{11}B NMR (128 MHz, $CDCl_3$) (**2d**)

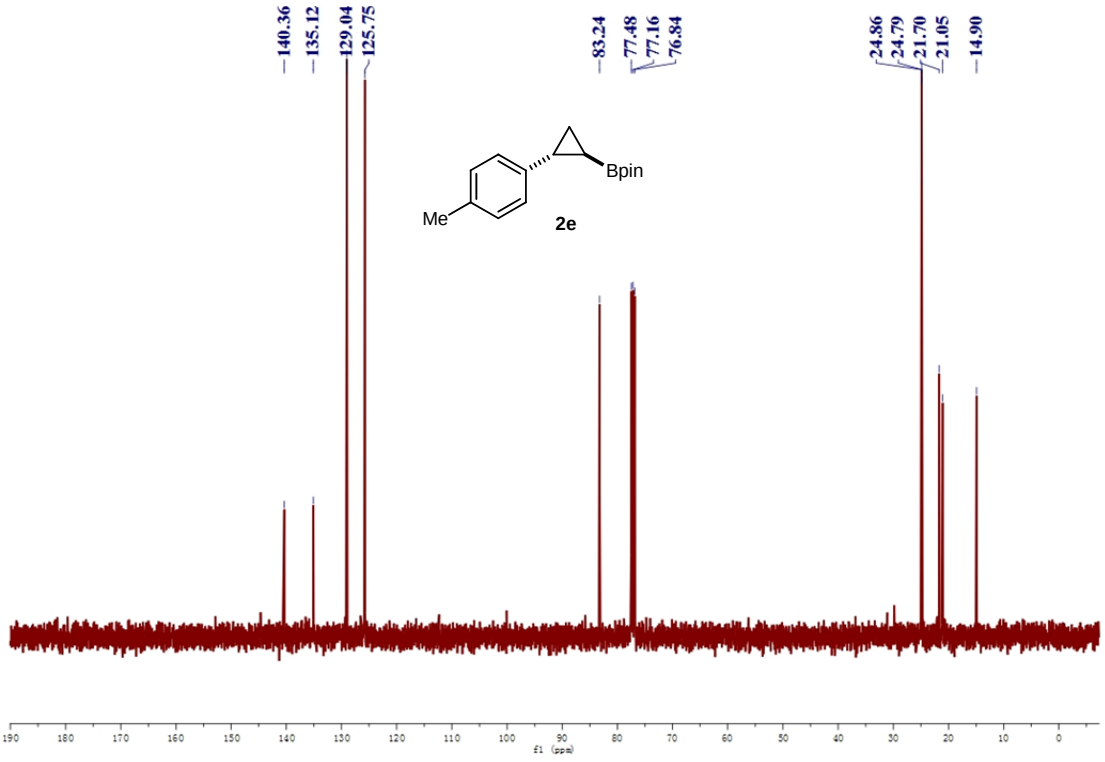


2d

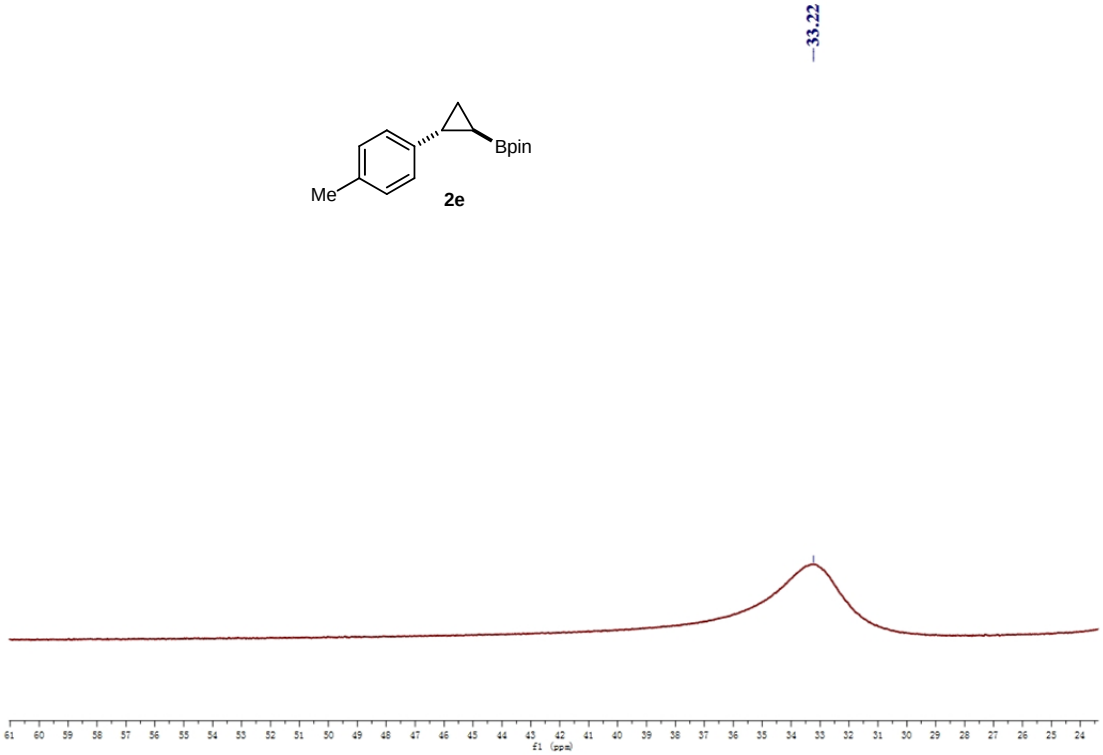
^{1}H NMR (400 MHz, $CDCl_3$) (**2e**)



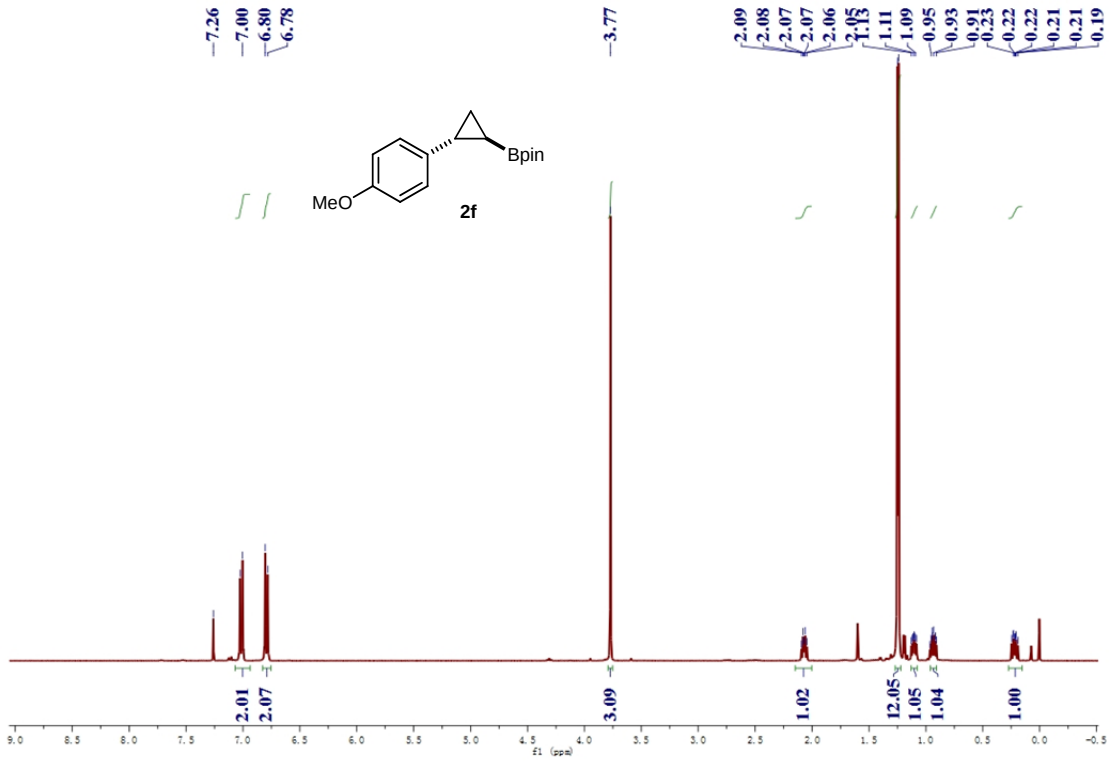
^{13}C NMR (100 MHz, $CDCl_3$) (**2e**)



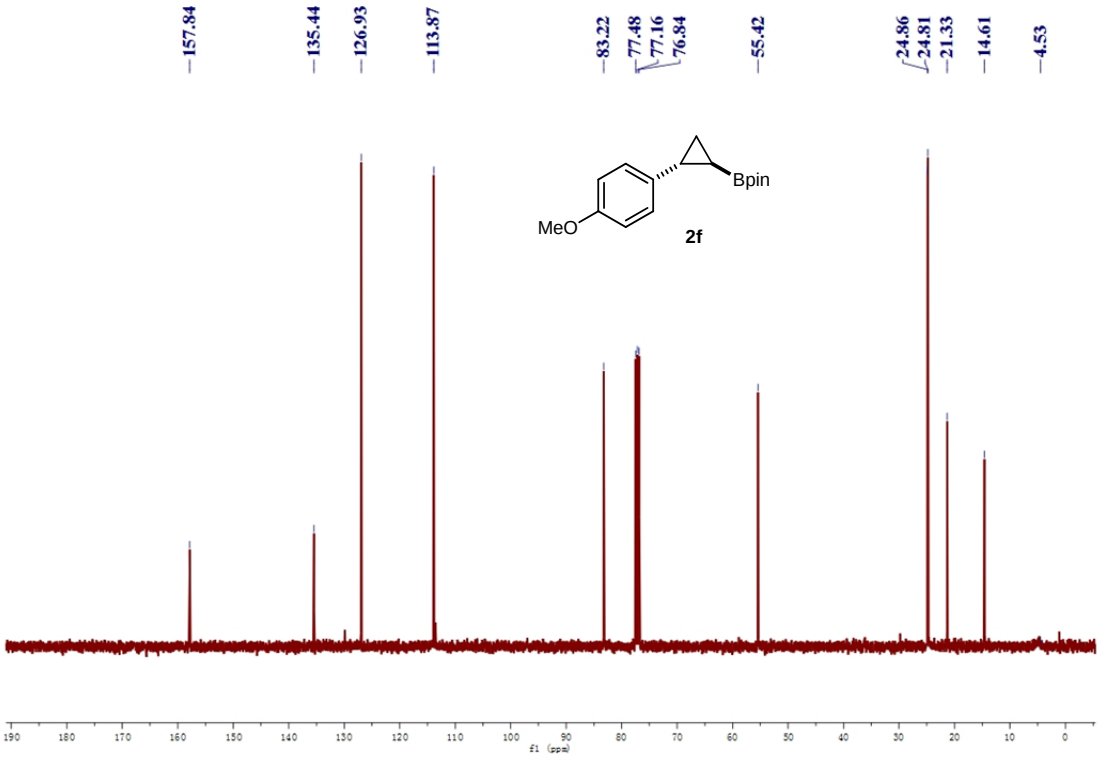
^{11}B NMR (128 MHz, $CDCl_3$) (**2e**)



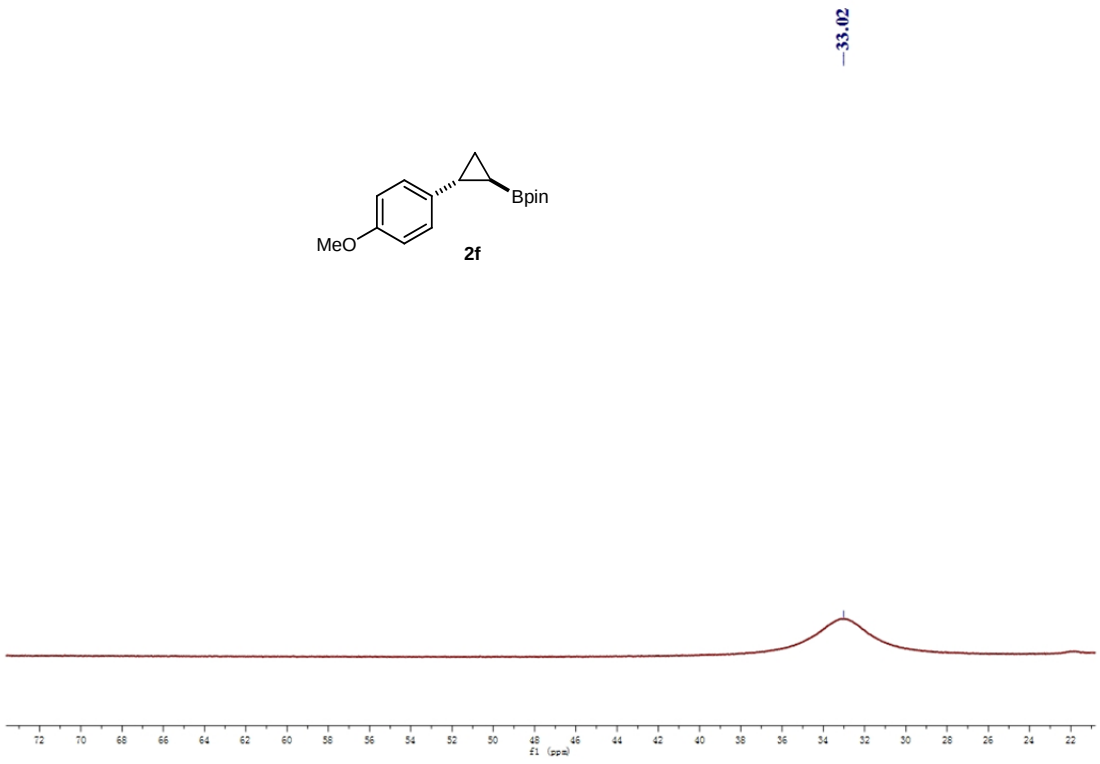
^{1}H NMR (400 MHz, $CDCl_3$) (**2f**)



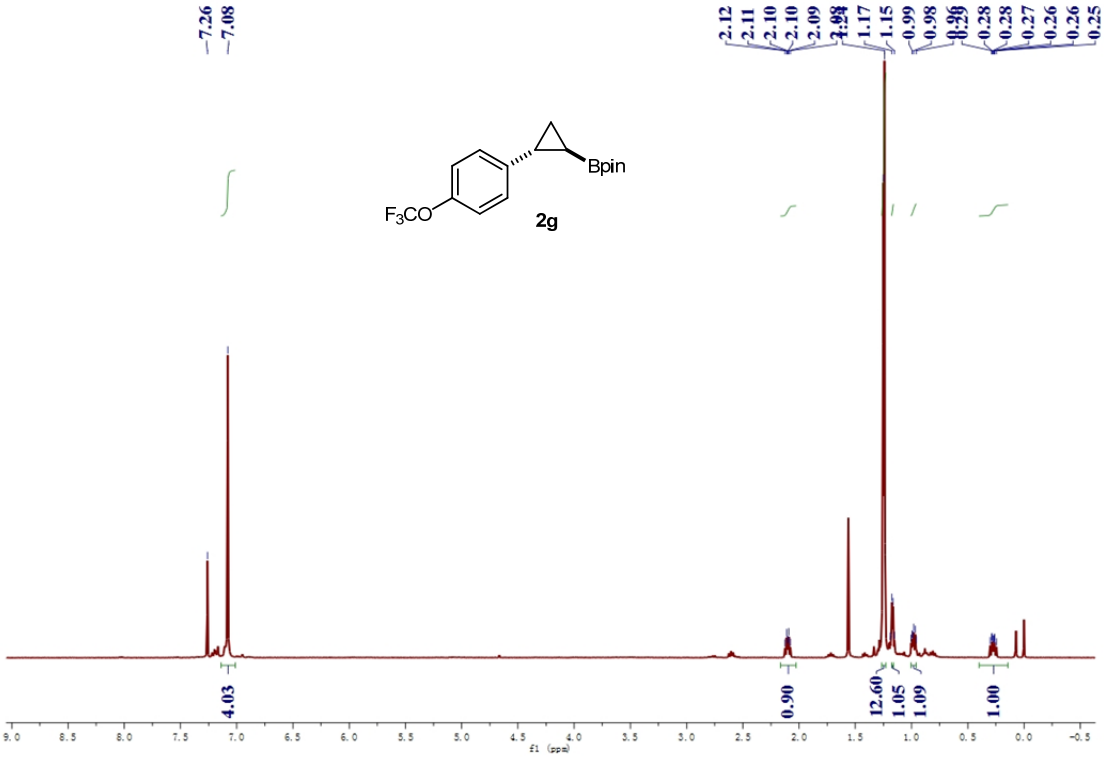
^{13}C NMR (100 MHz, $CDCl_3$) (**2f**)



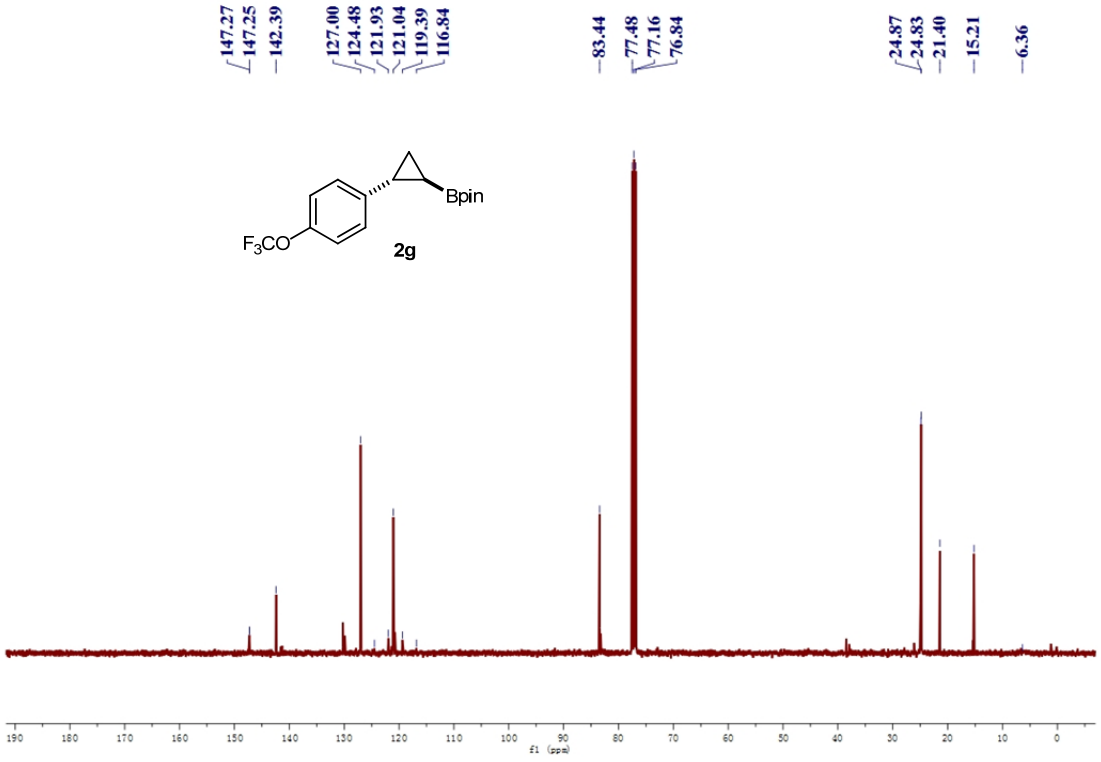
^{11}B NMR (128 MHz, $CDCl_3$) (**2f**)



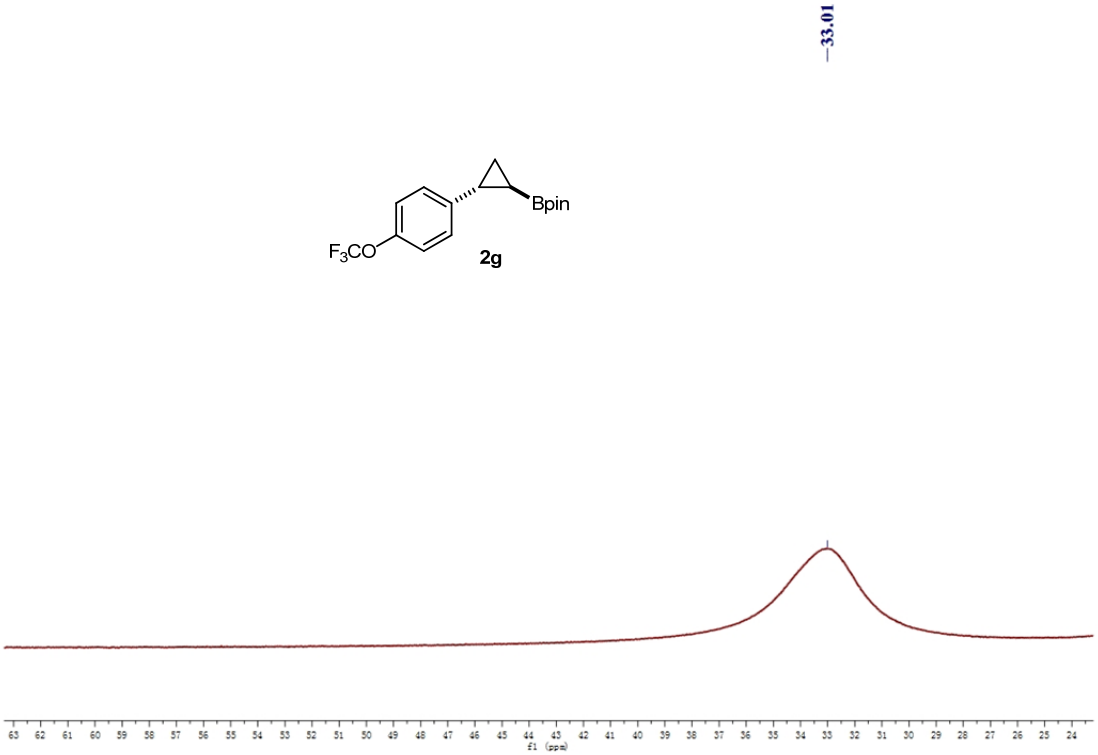
^{1}H NMR (400 MHz, $CDCl_3$) (**2g**)



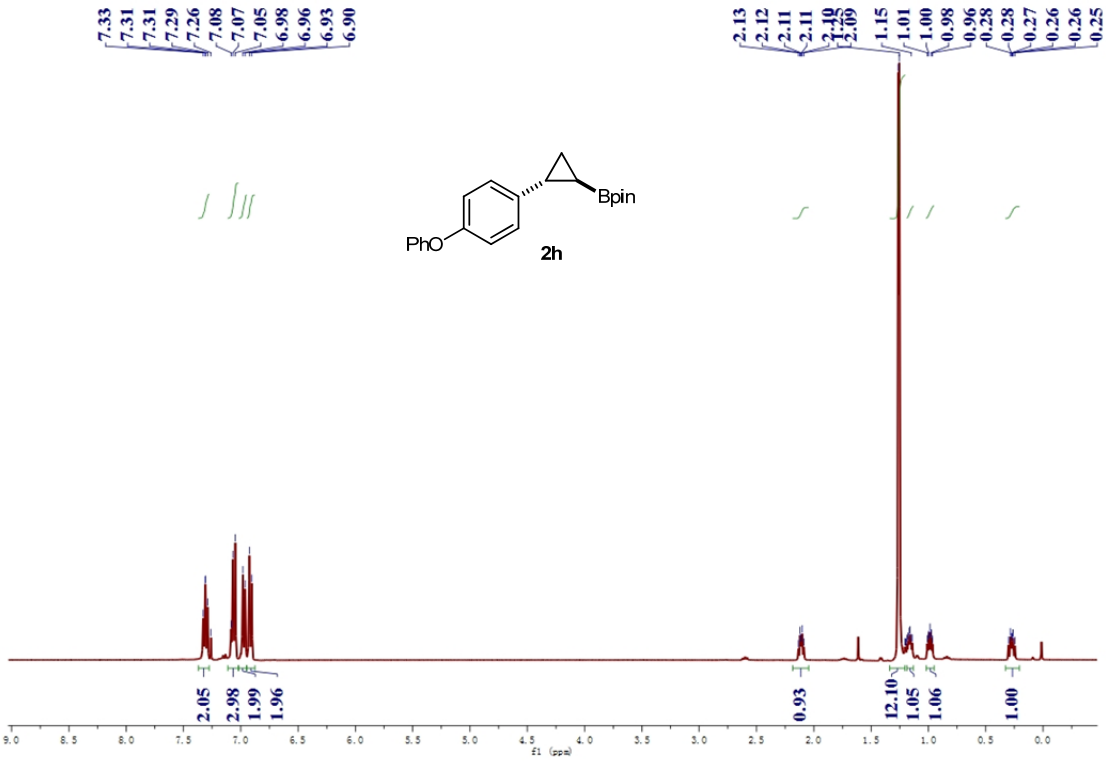
^{13}C NMR (100 MHz, $CDCl_3$) (**2g**)



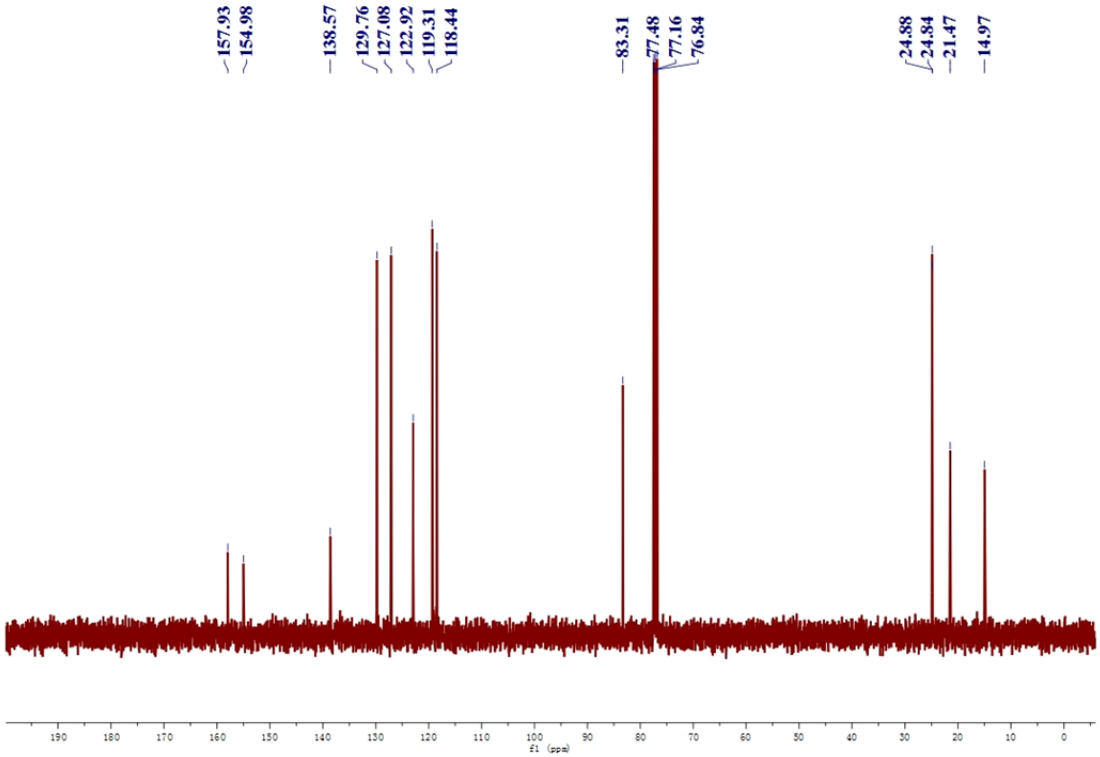
^{11}B NMR (128 MHz, $CDCl_3$) (**2g**)



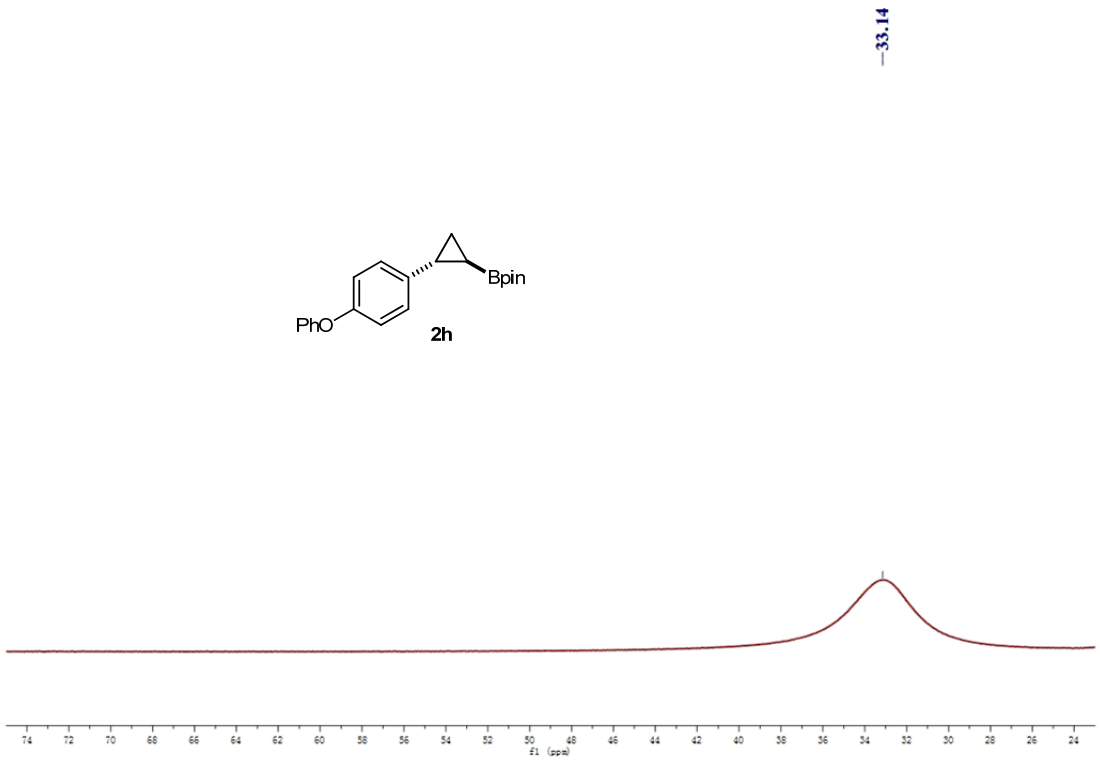
^{1}H NMR (400 MHz, $CDCl_3$) (**2h**)



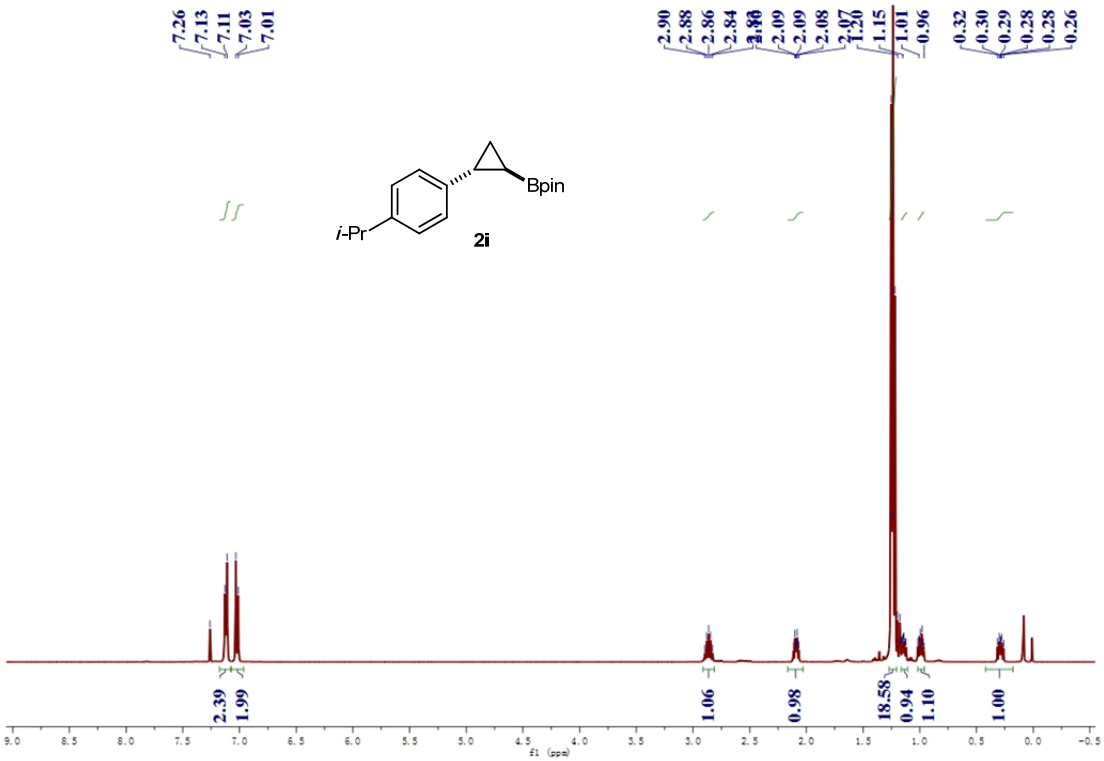
^{13}C NMR (100 MHz, $CDCl_3$) (**2h**)



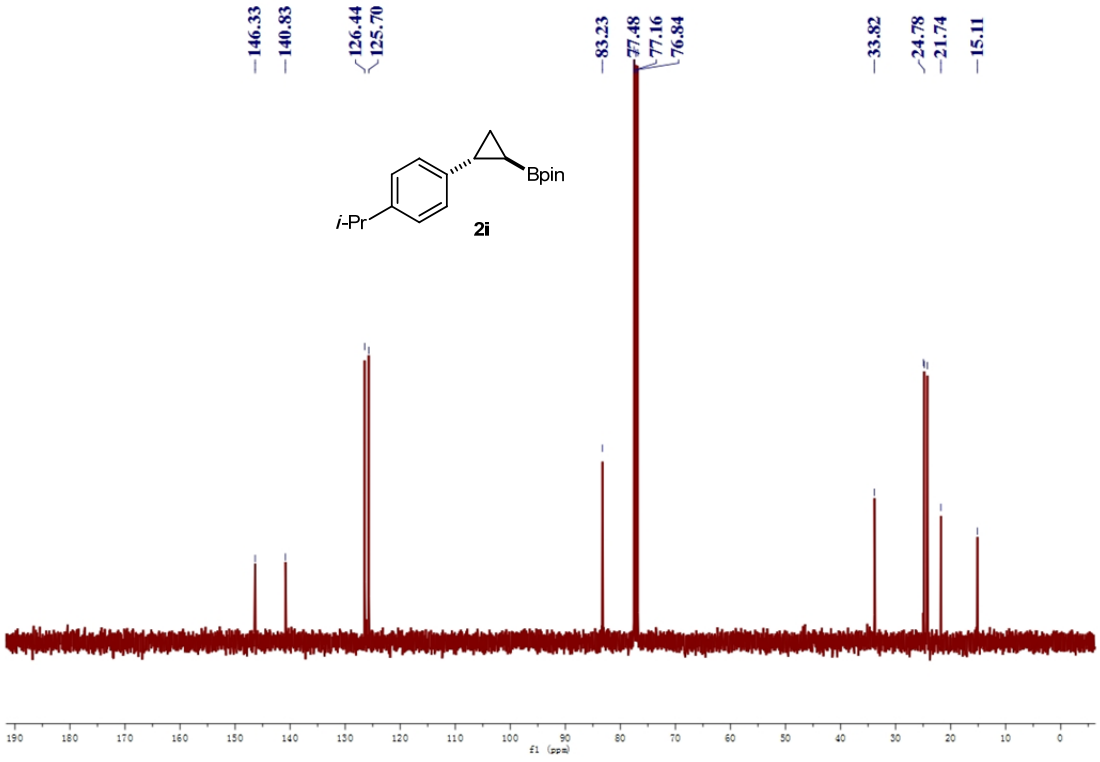
^{11}B NMR (128 MHz, $CDCl_3$) (**2h**)



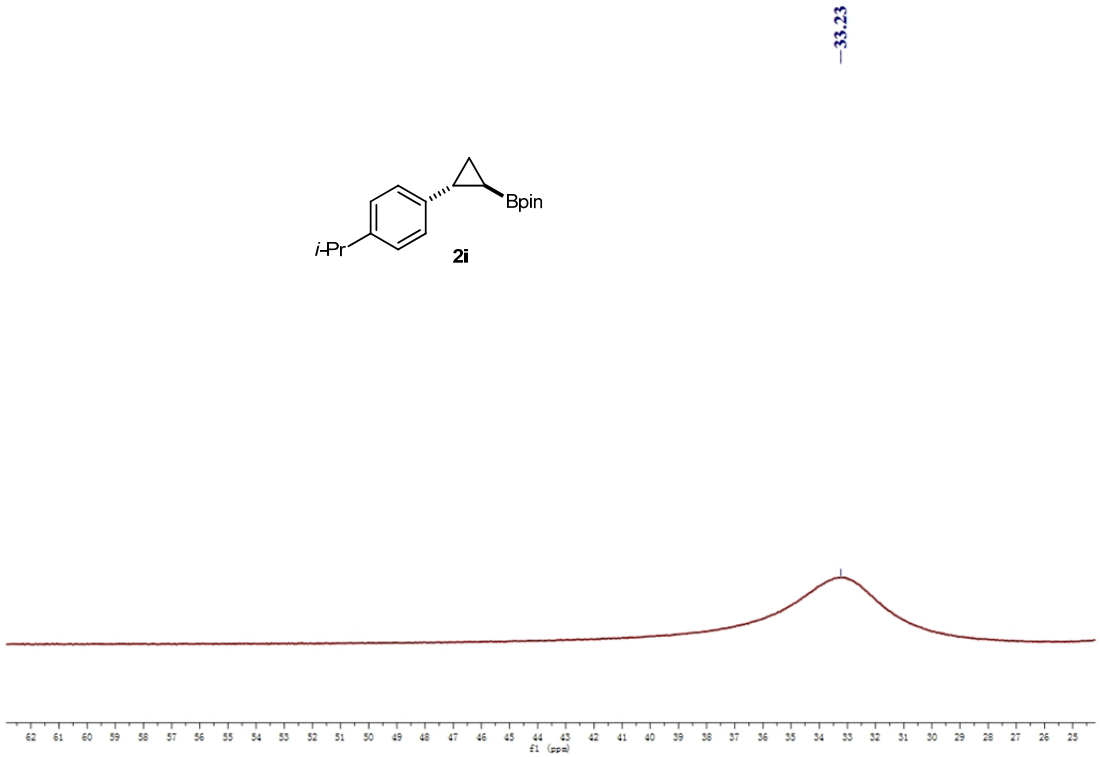
^{1}H NMR (400 MHz, $CDCl_3$) (**2i**)



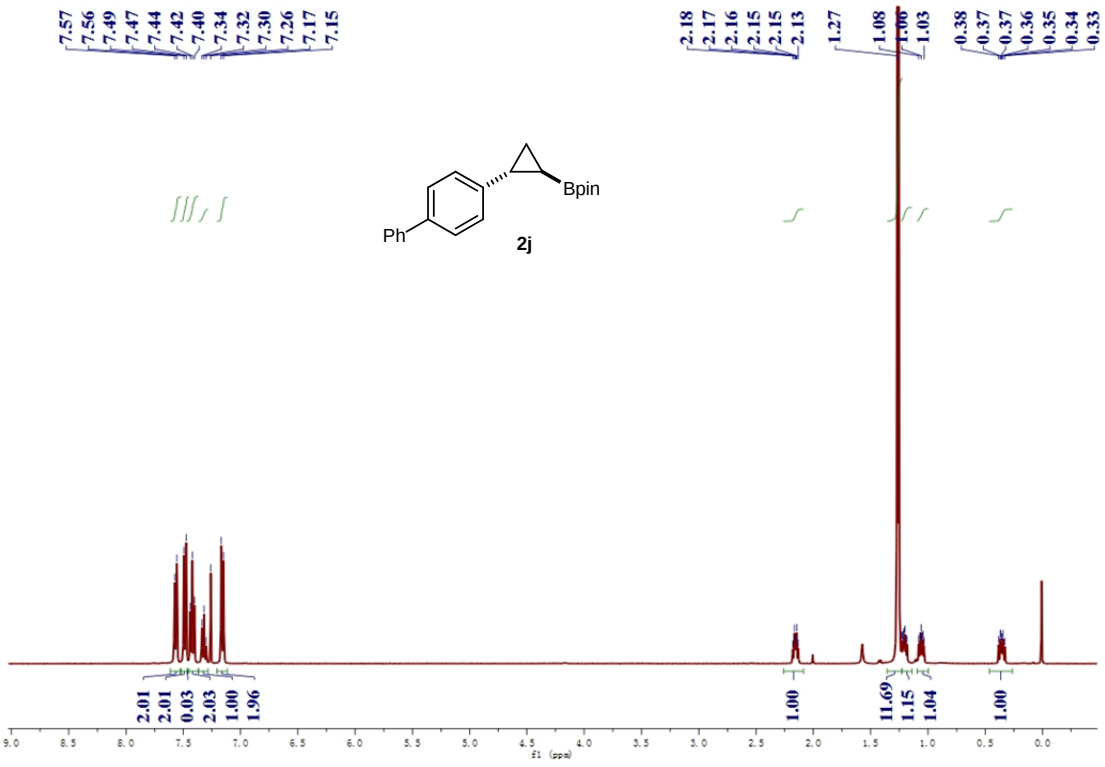
^{13}C NMR (100 MHz, $CDCl_3$) (**2i**)



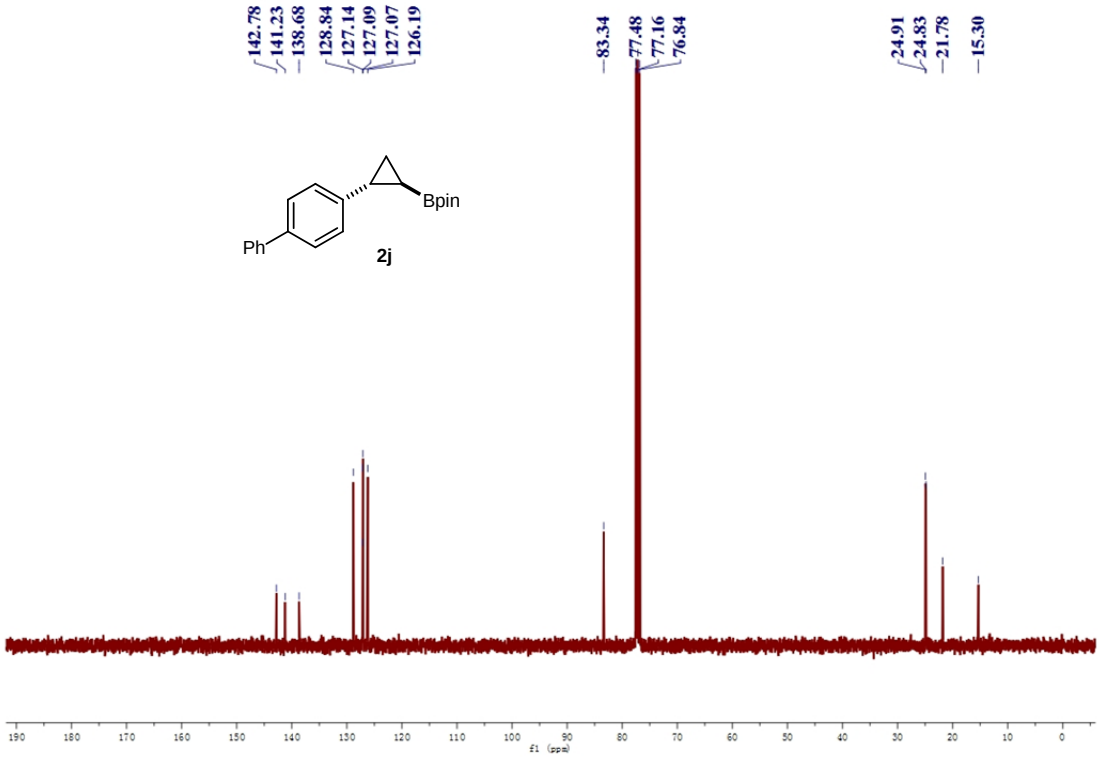
^{11}B NMR (128 MHz, $CDCl_3$) (**2i**)



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



^{13}C NMR (100 MHz, $CDCl_3$) (**2j**)



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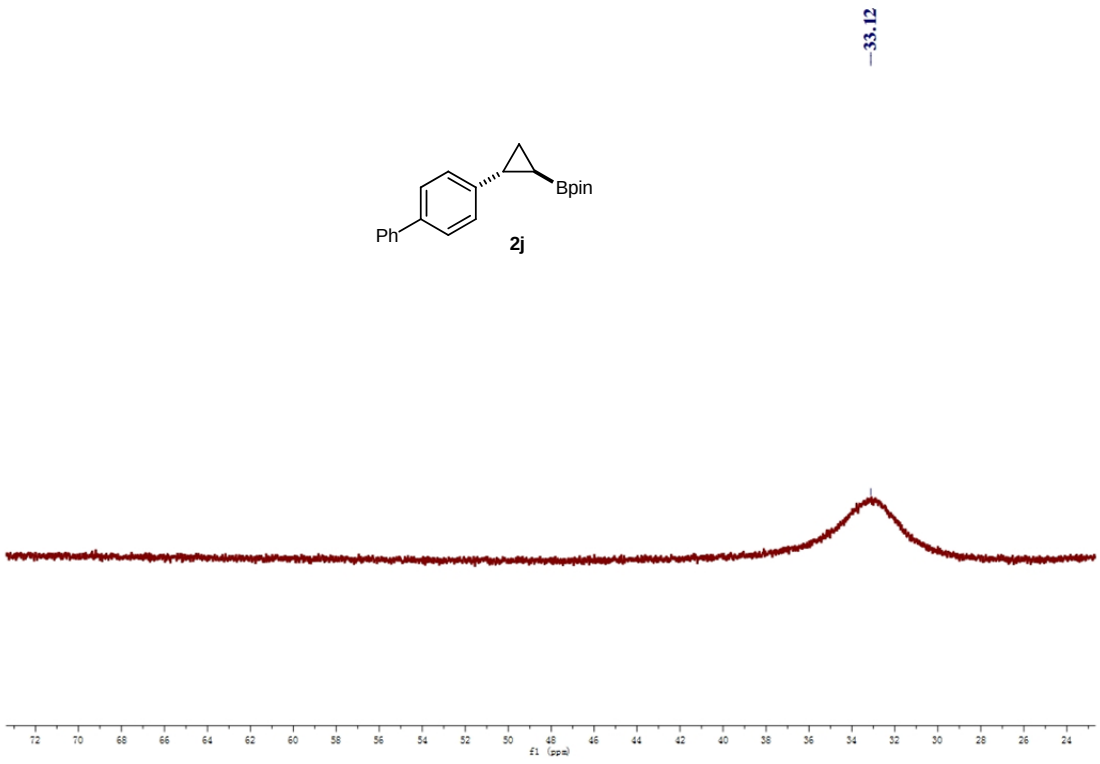

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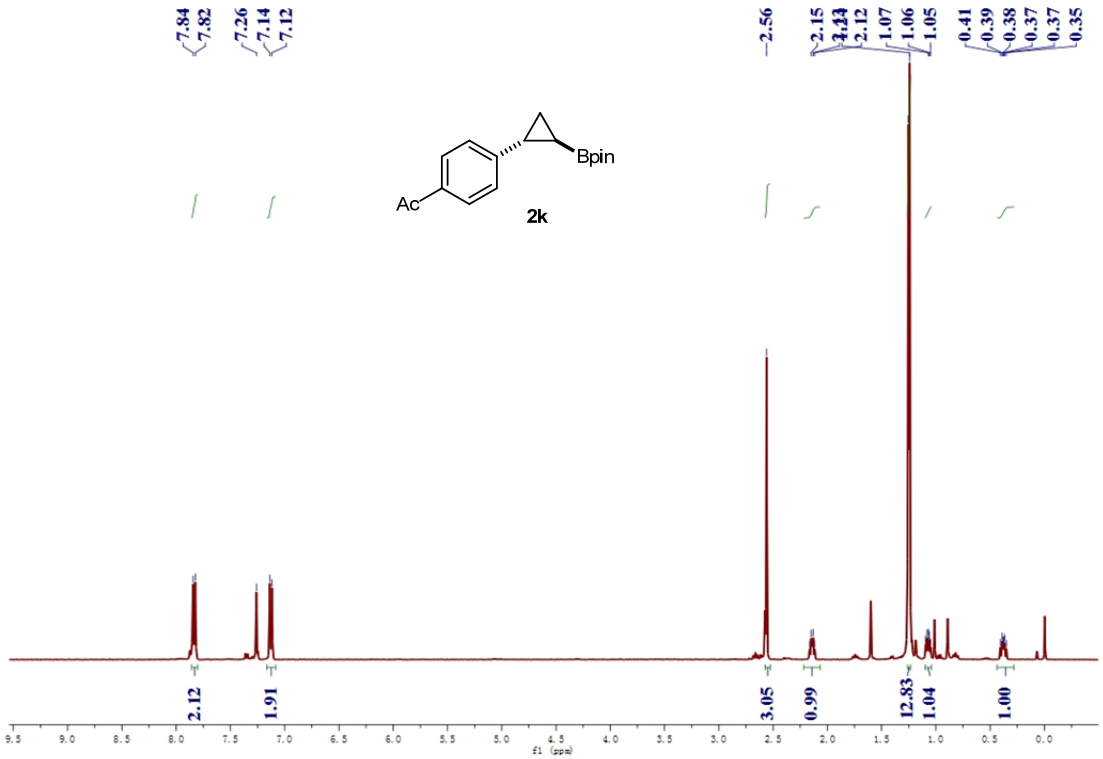
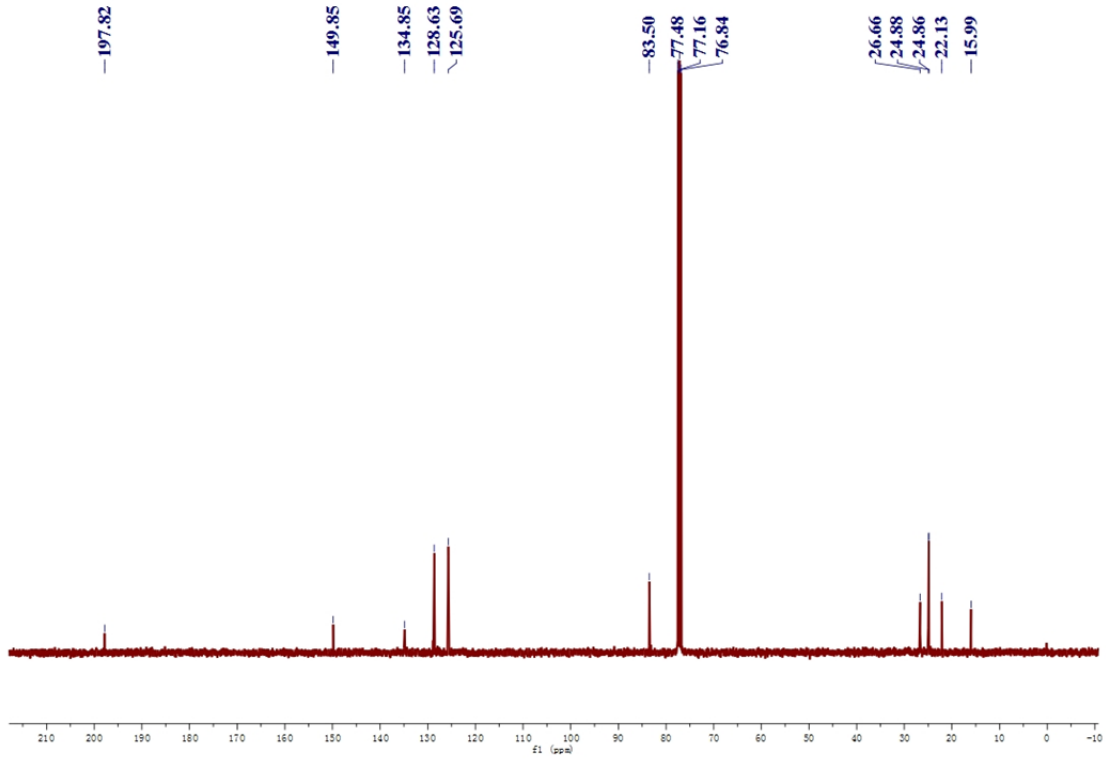
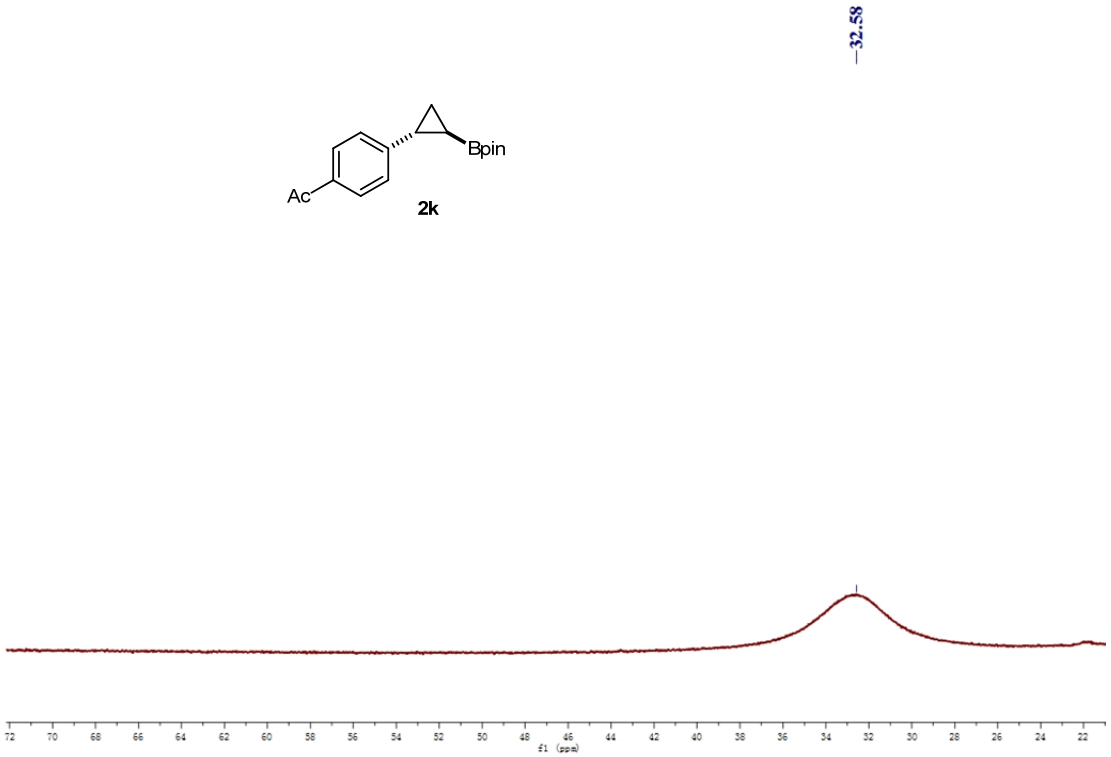


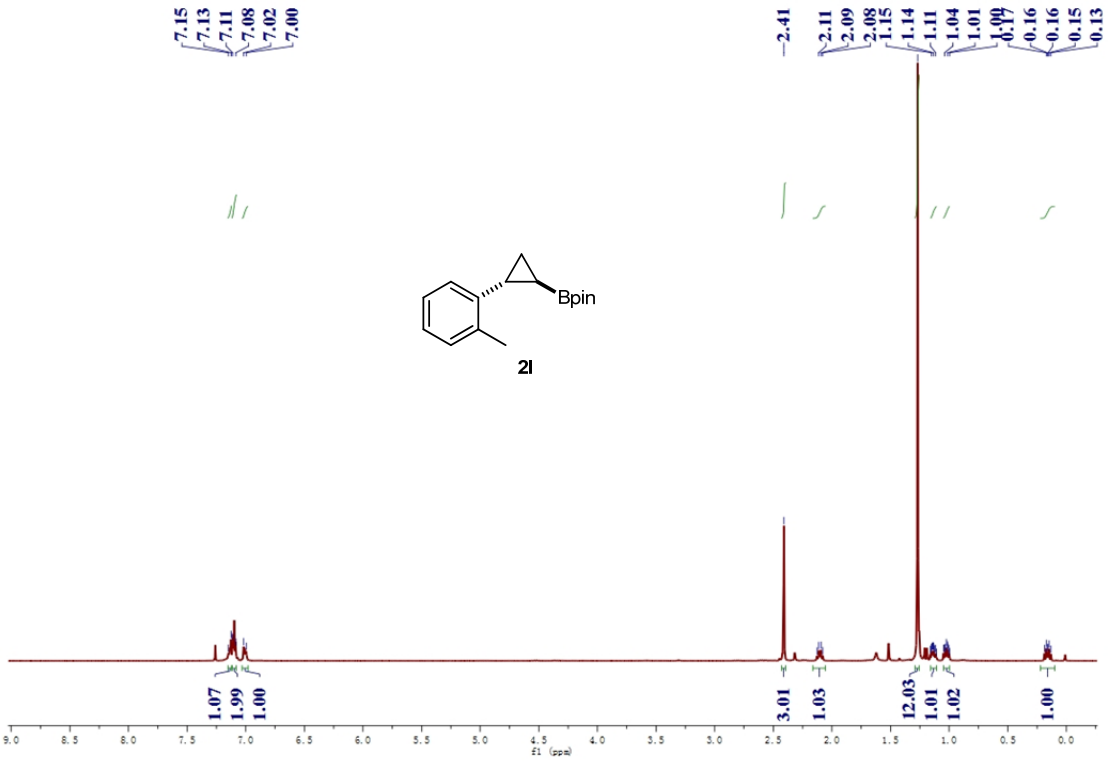
^{13}C NMR (100 MHz, $CDCl_3$) (**2k**)



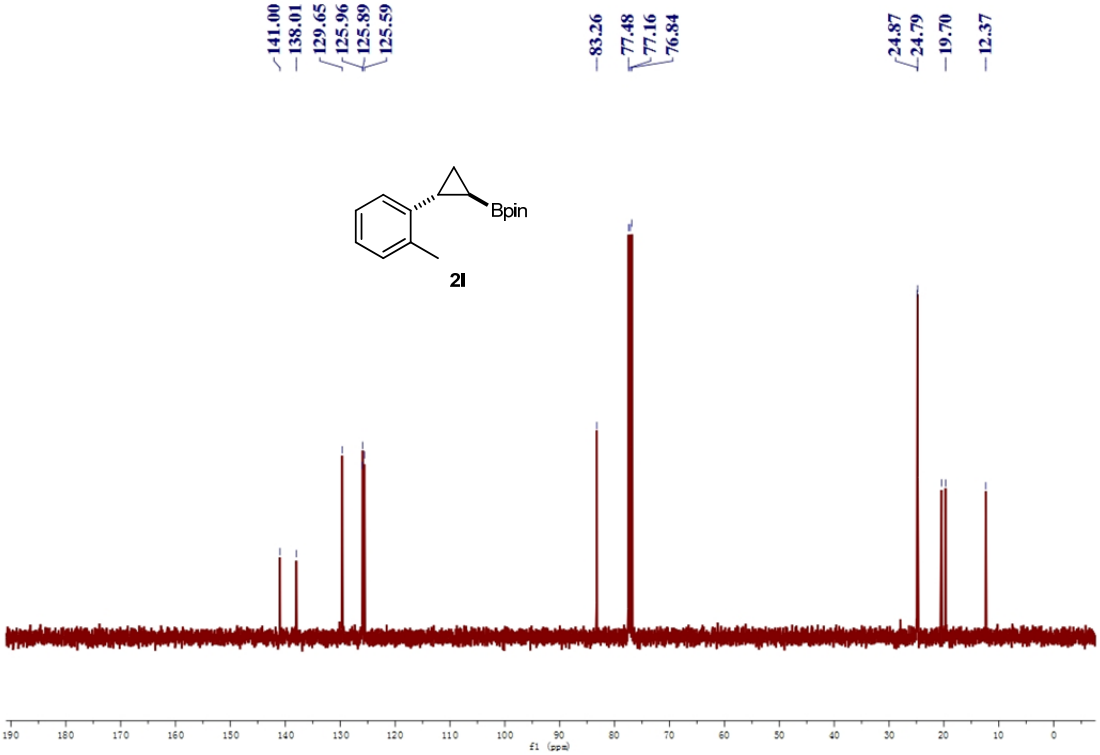
^{11}B NMR (128 MHz, $CDCl_3$) (**2k**)



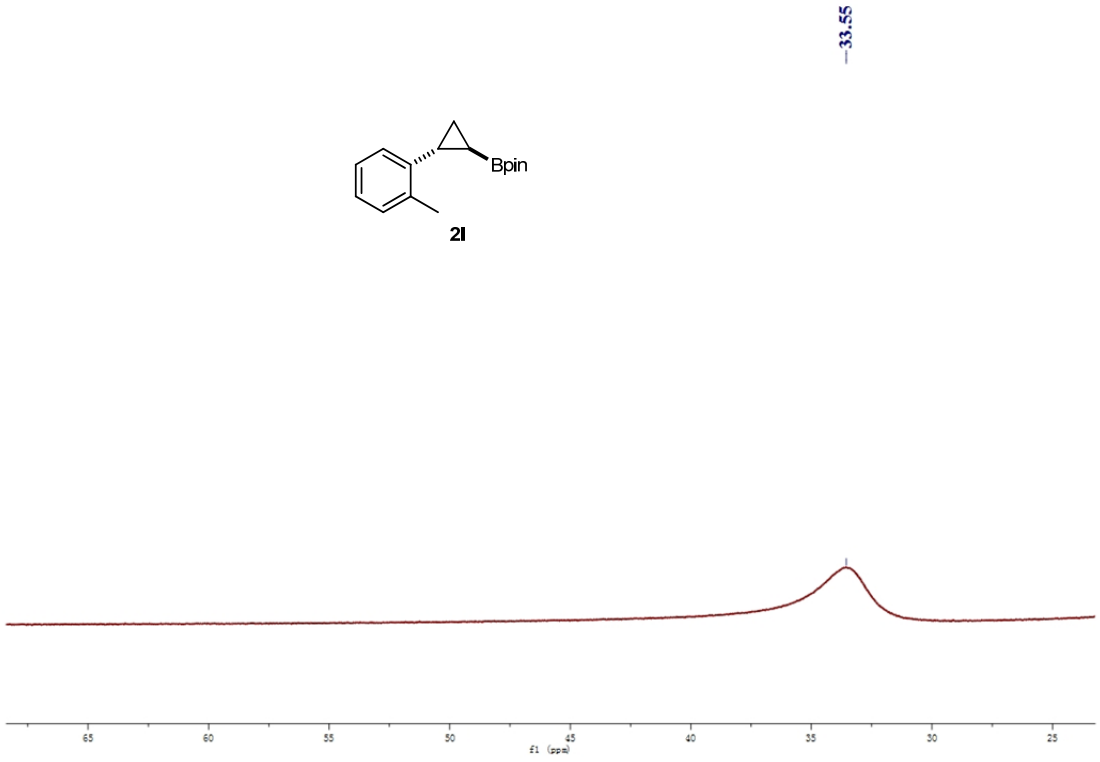
^{1}H NMR (400 MHz, $CDCl_3$) (**2l**)



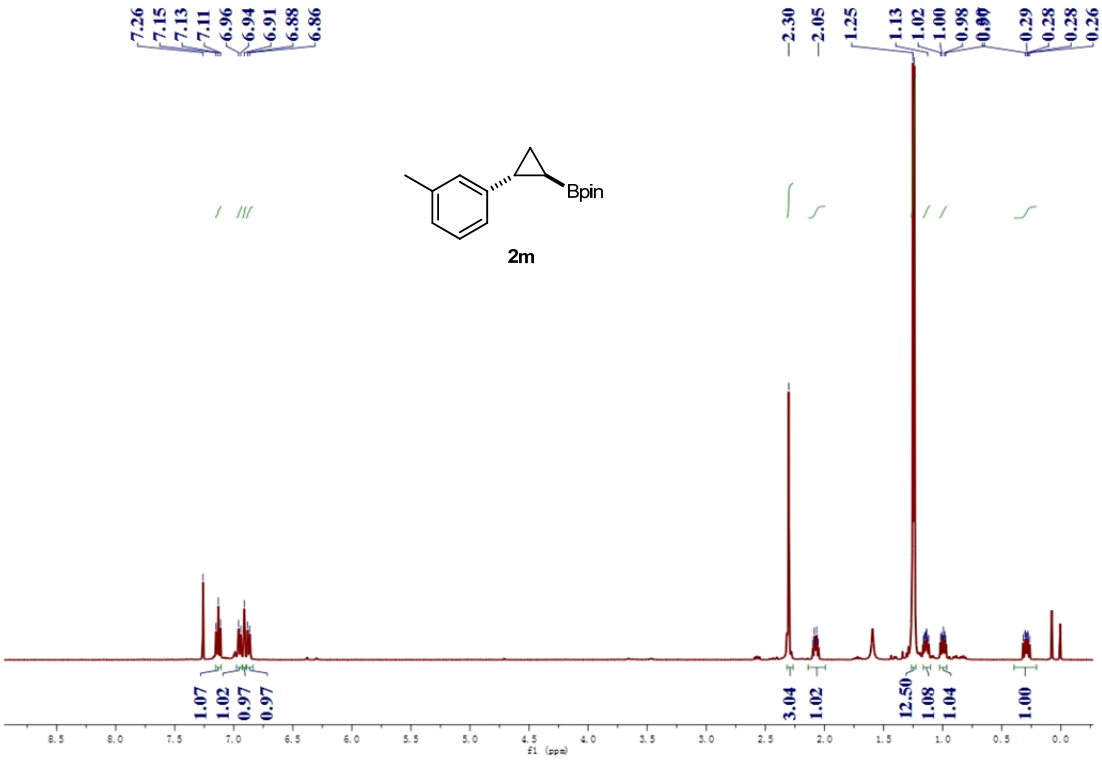
^{13}C NMR (100 MHz, $CDCl_3$) (**2l**)



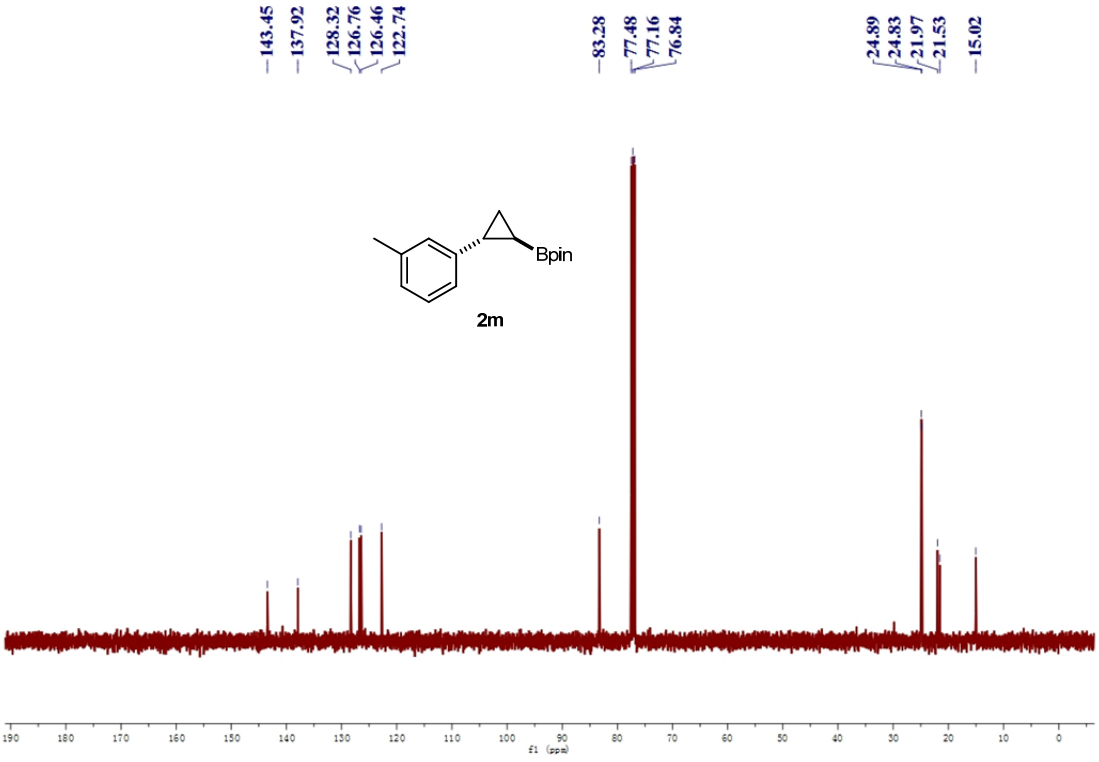
^{11}B NMR (128 MHz, $CDCl_3$) (**2l**)



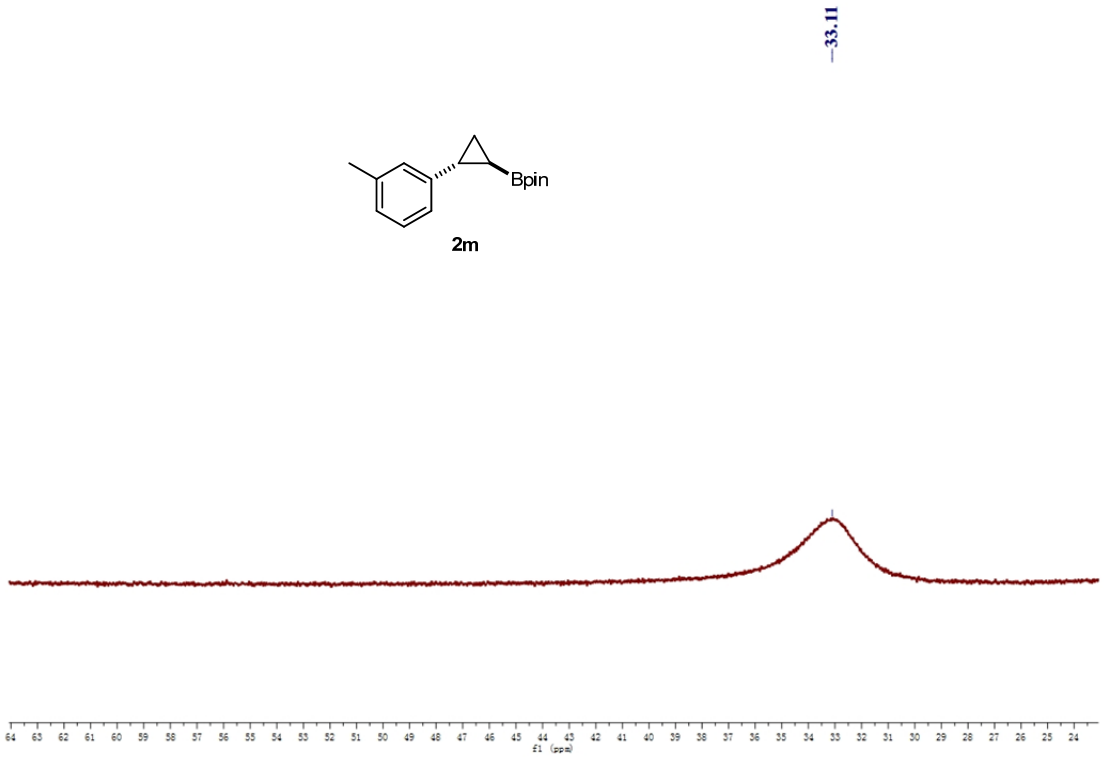
^{1}H NMR (400 MHz, $CDCl_3$) (**2m**)



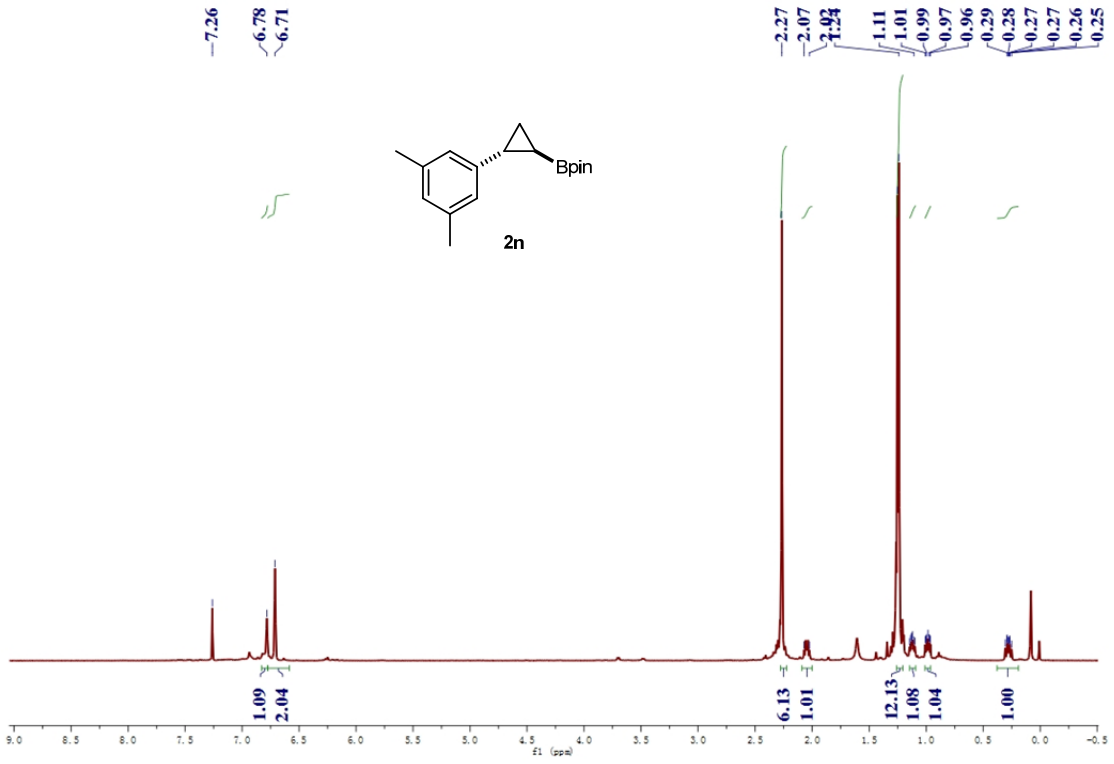
^{13}C NMR (100 MHz, $CDCl_3$) (**2m**)



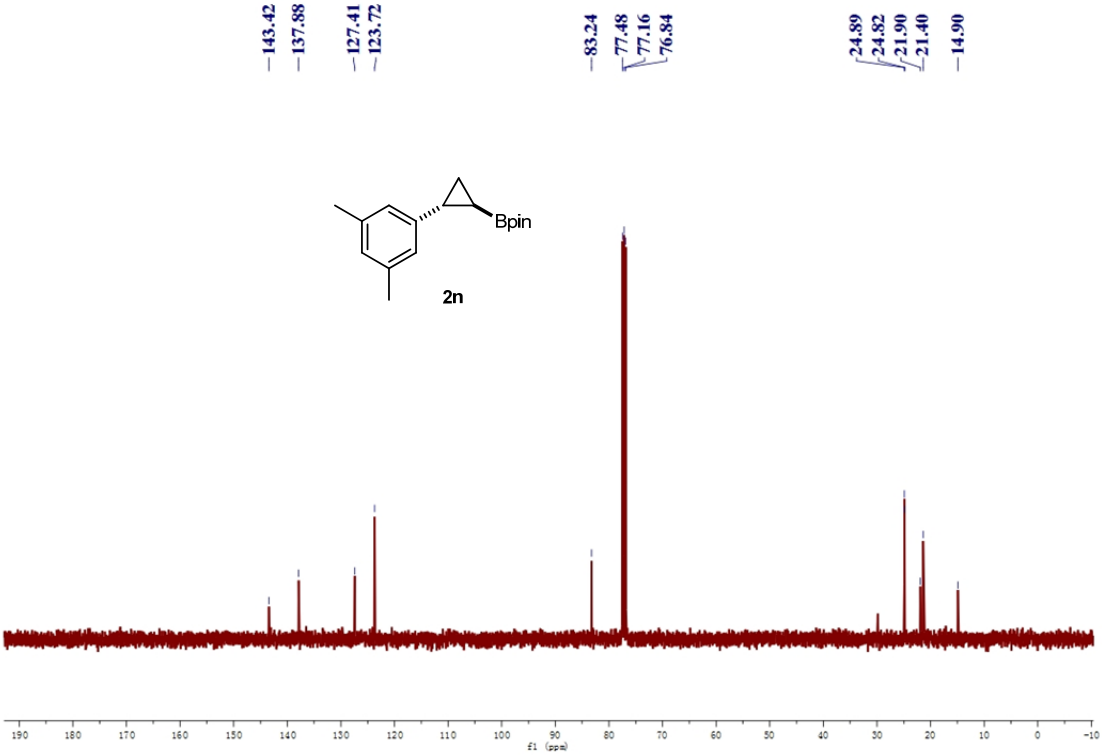
^{11}B NMR (128 MHz, $CDCl_3$) (**2m**)



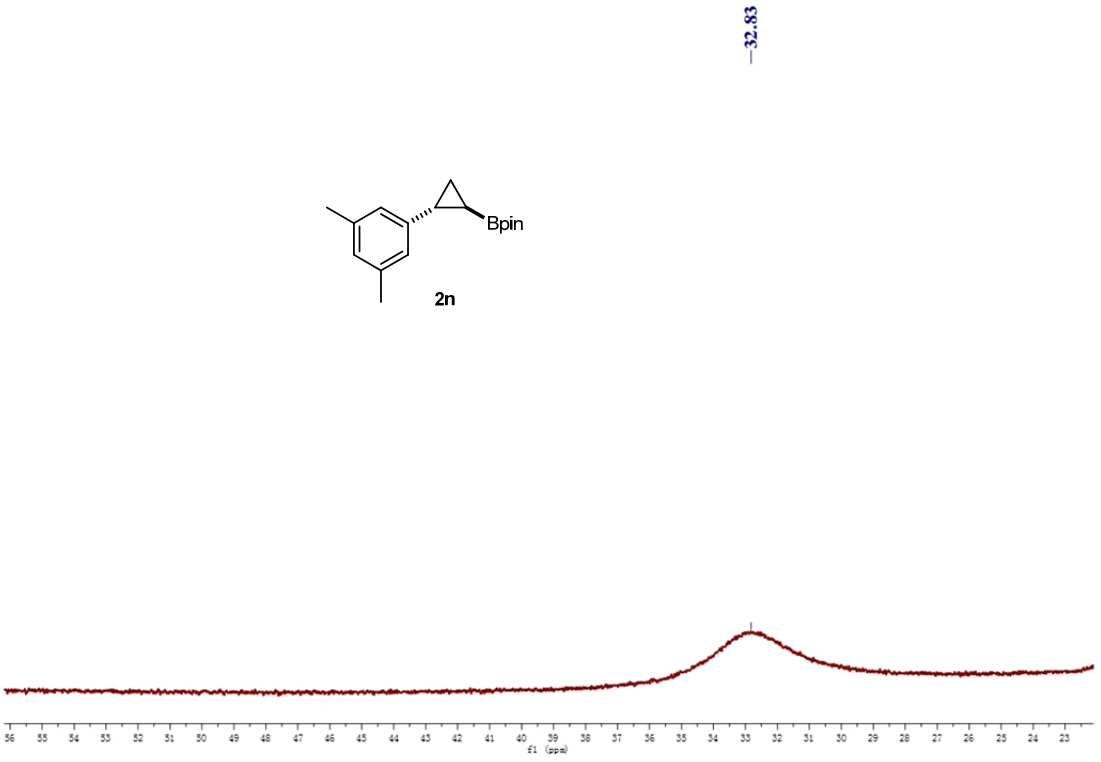
^{1}H NMR (400 MHz, $CDCl_3$) (**2n**)



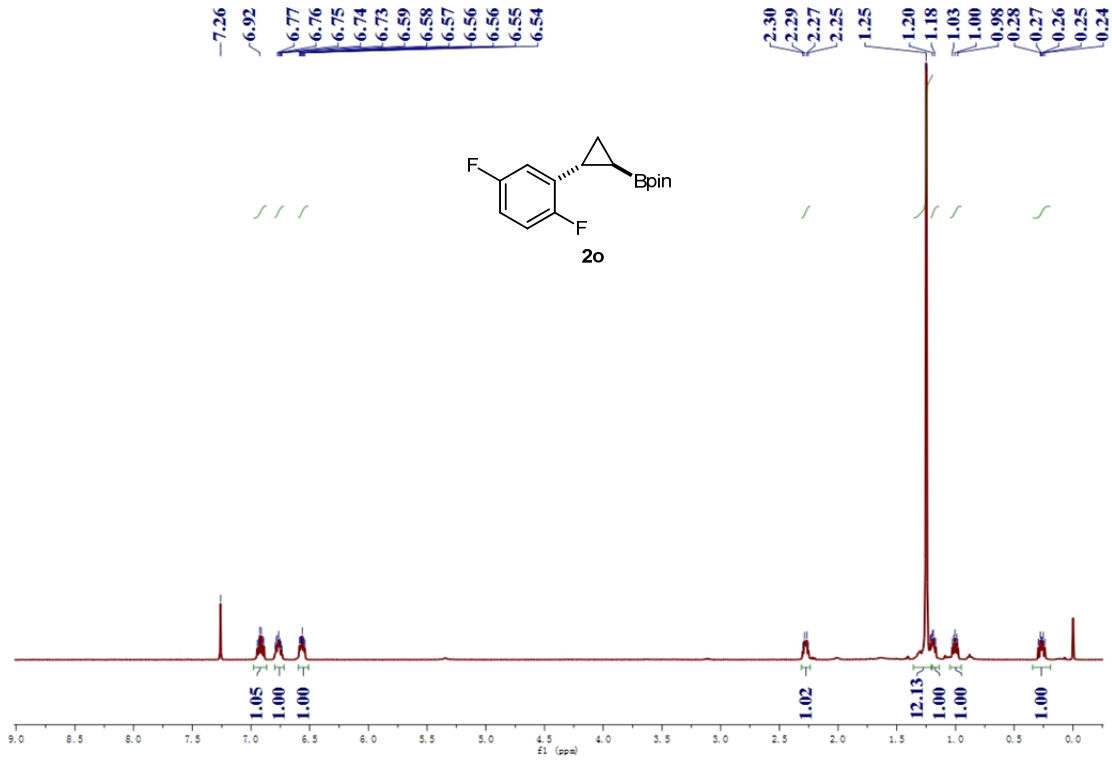
^{13}C NMR (100 MHz, $CDCl_3$) (**2n**)



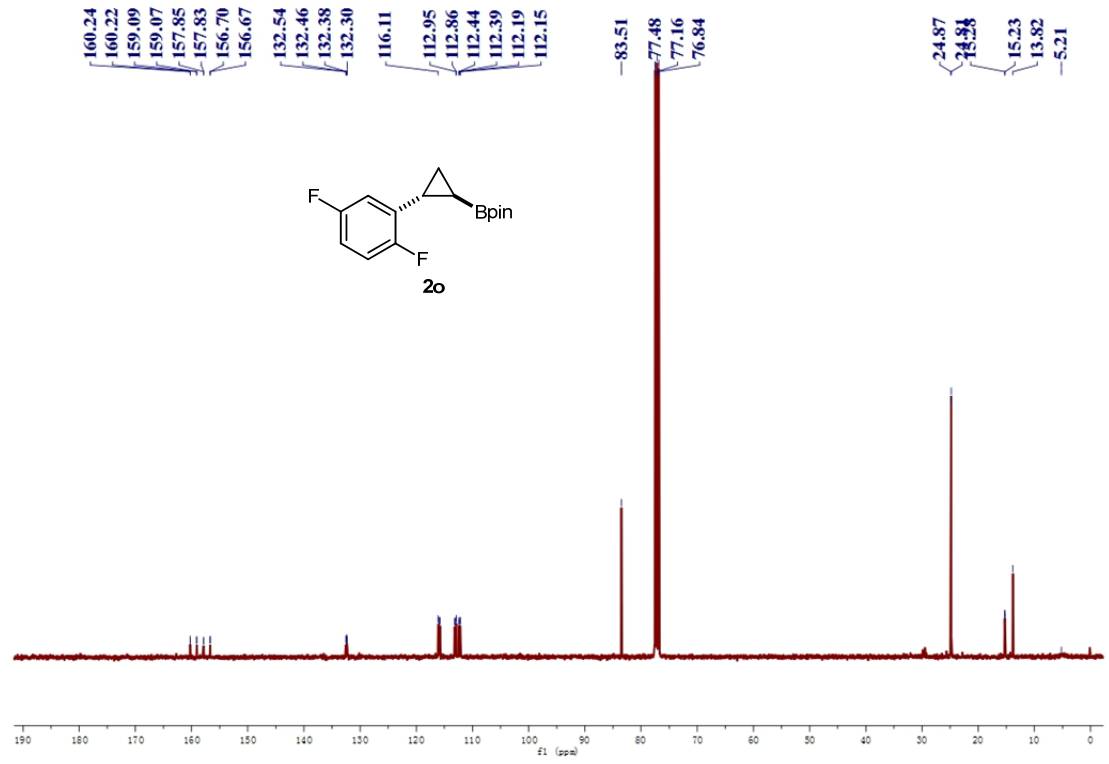
^{11}B NMR (128 MHz, $CDCl_3$) (**2n**)



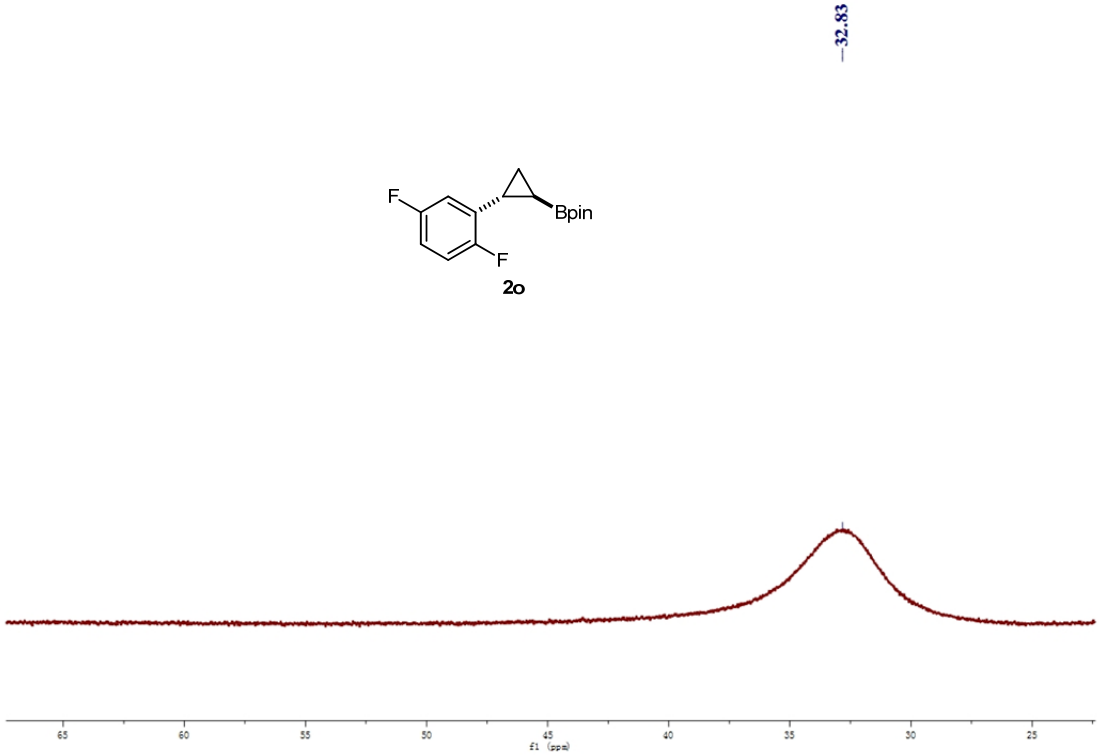
^{1}H NMR (400 MHz, $CDCl_3$) (**2o**)



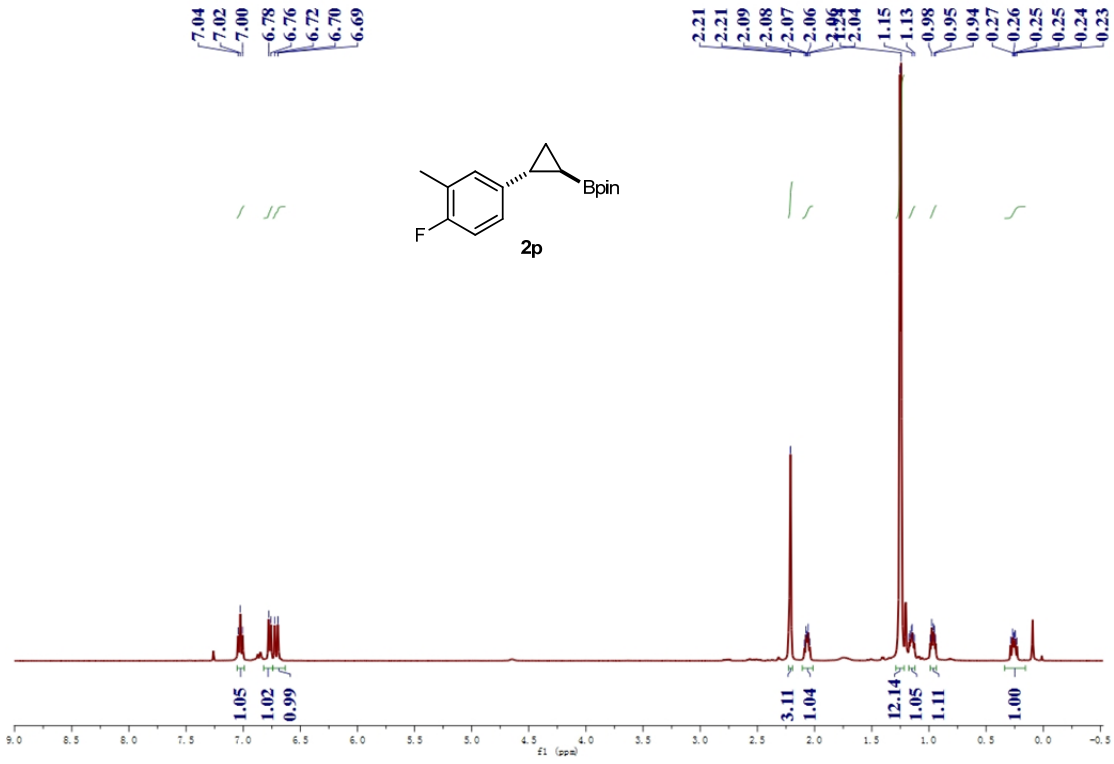
^{13}C NMR (100 MHz, $CDCl_3$) (**2o**)



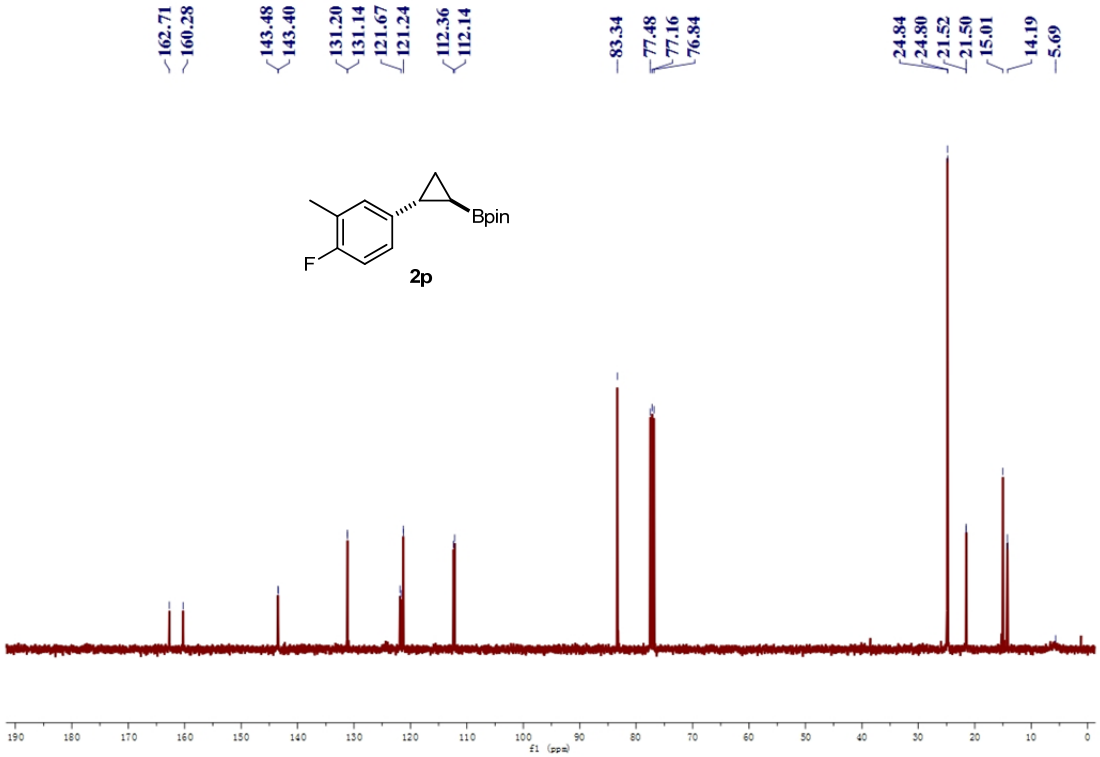
^{11}B NMR (128 MHz, $CDCl_3$) (**2o**)



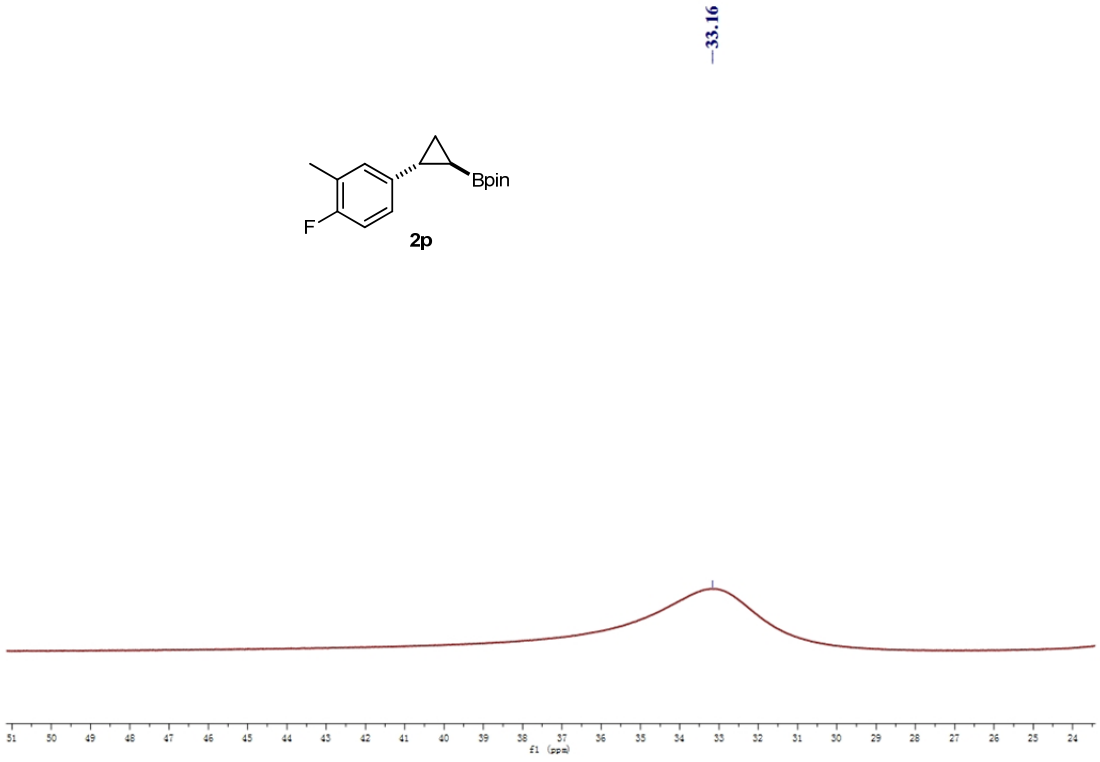
^{1}H NMR (400 MHz, $CDCl_3$) (**2p**)



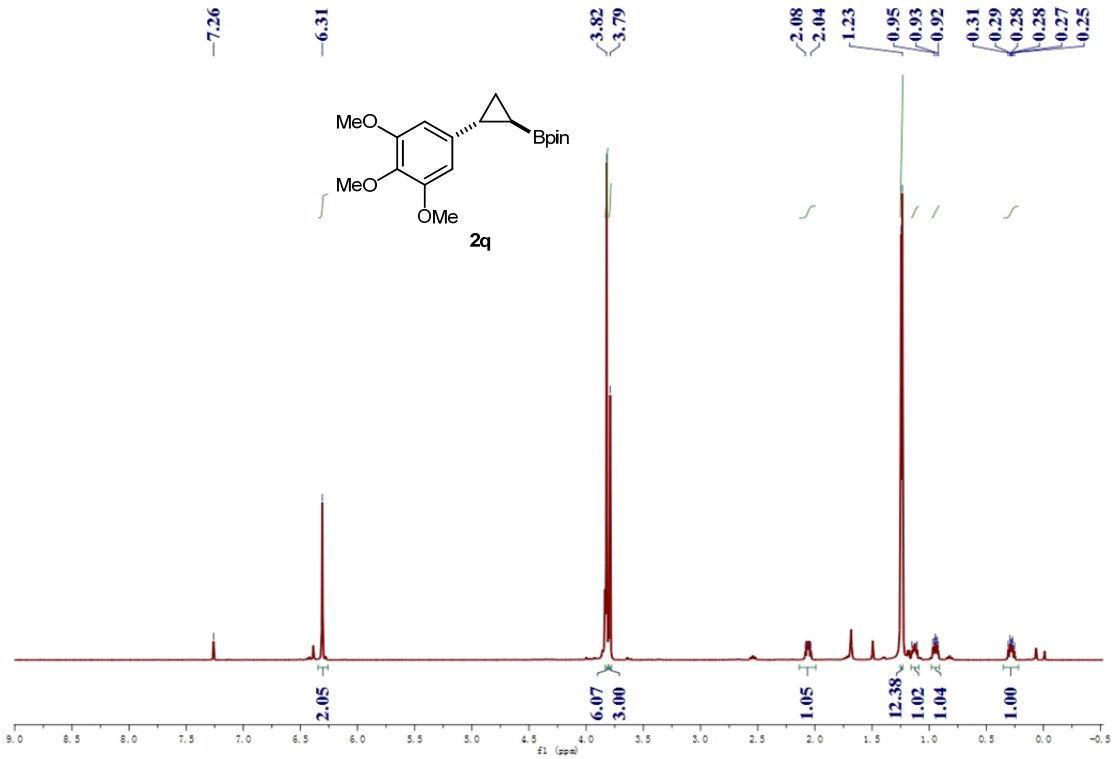
^{13}C NMR (100 MHz, $CDCl_3$) (**2p**)



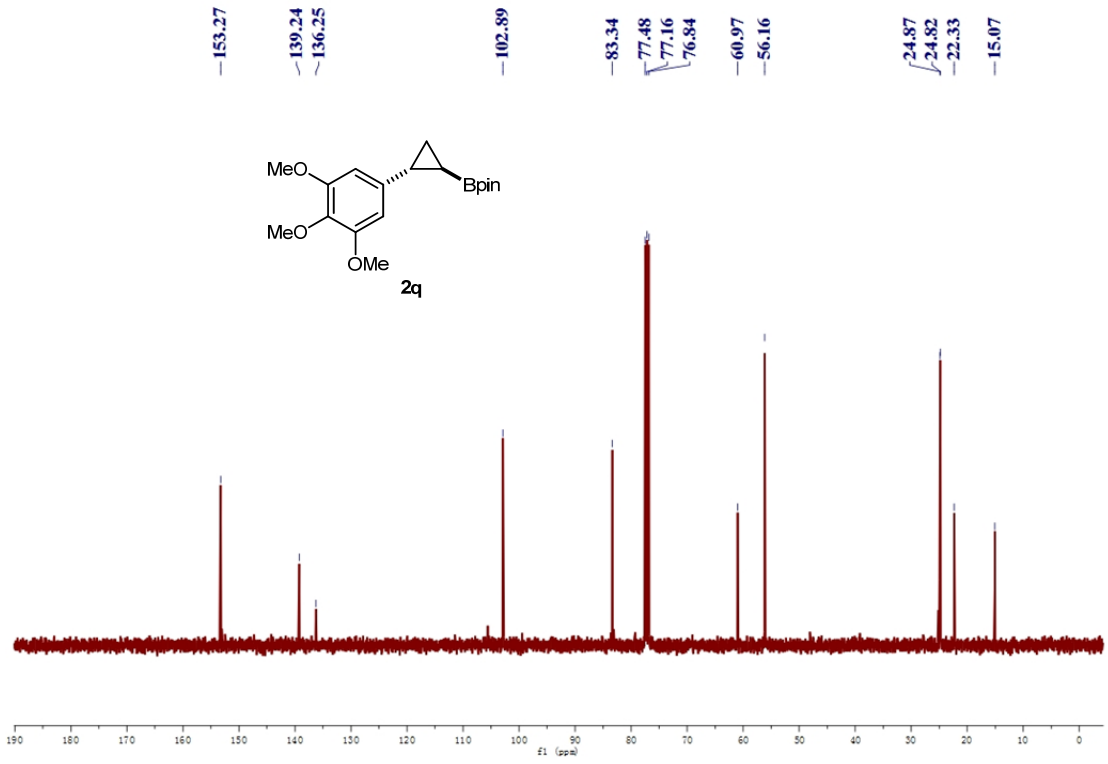
^{11}B NMR (128 MHz, $CDCl_3$) (**2p**)



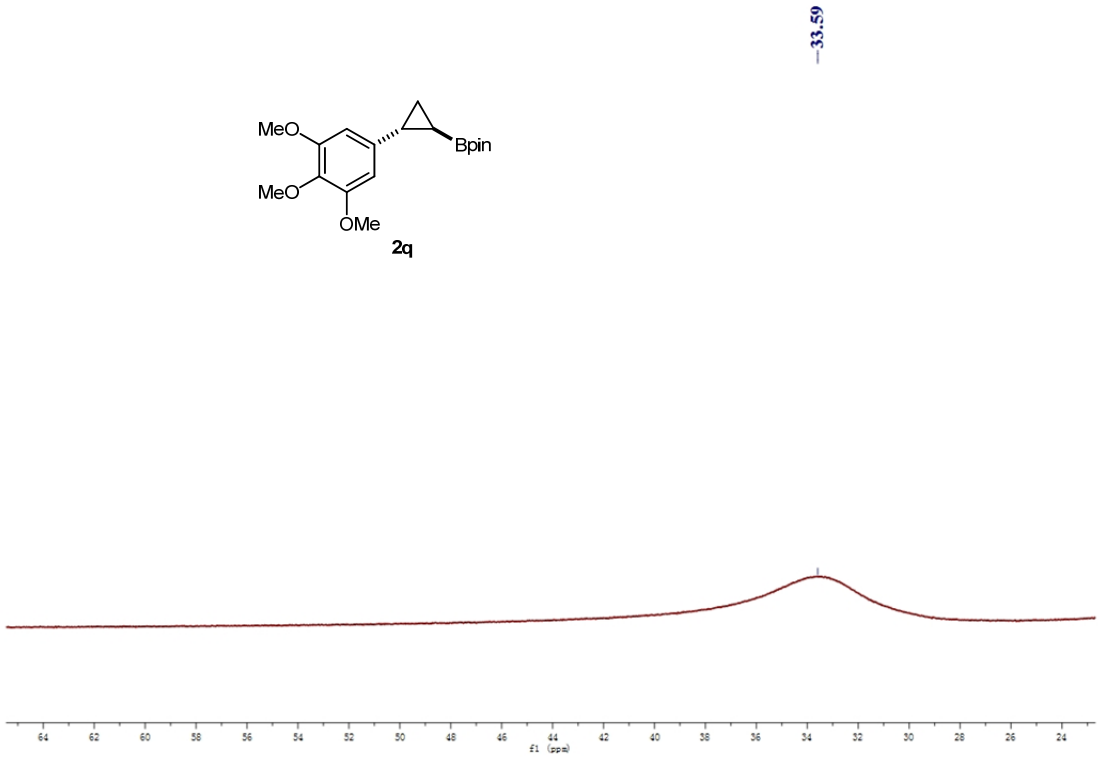
^{1}H NMR (400 MHz, $CDCl_3$) (**2q**)



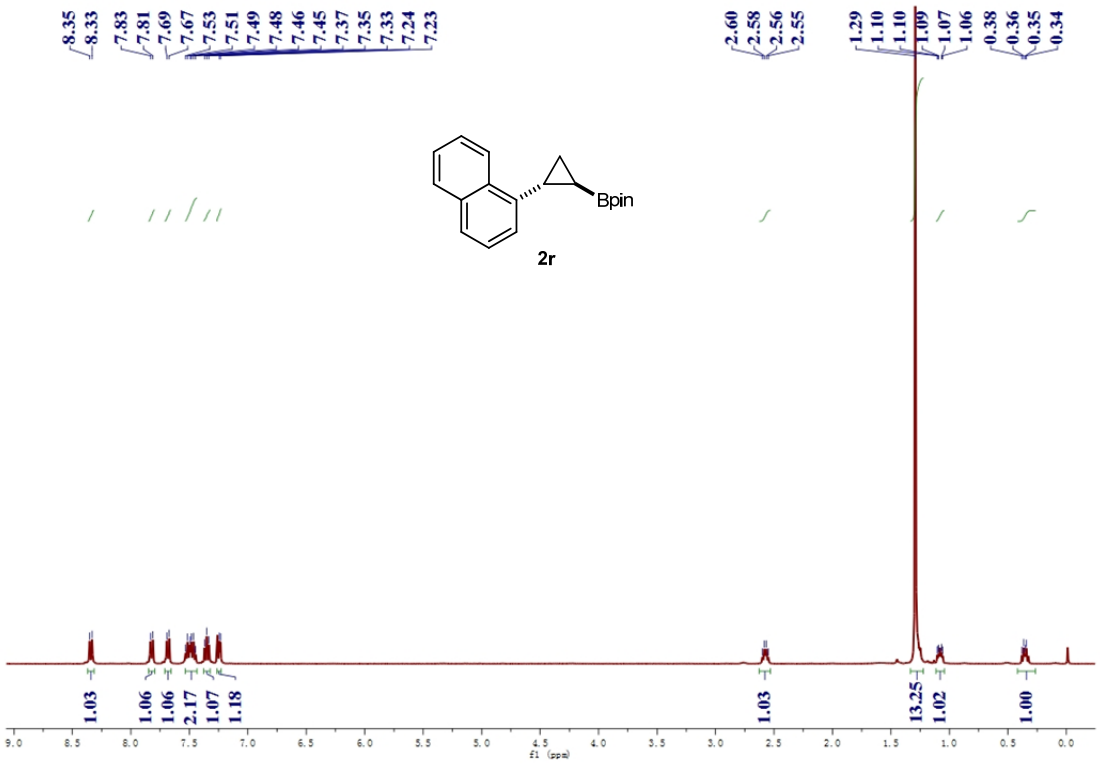
^{13}C NMR (100 MHz, $CDCl_3$) (**2q**)



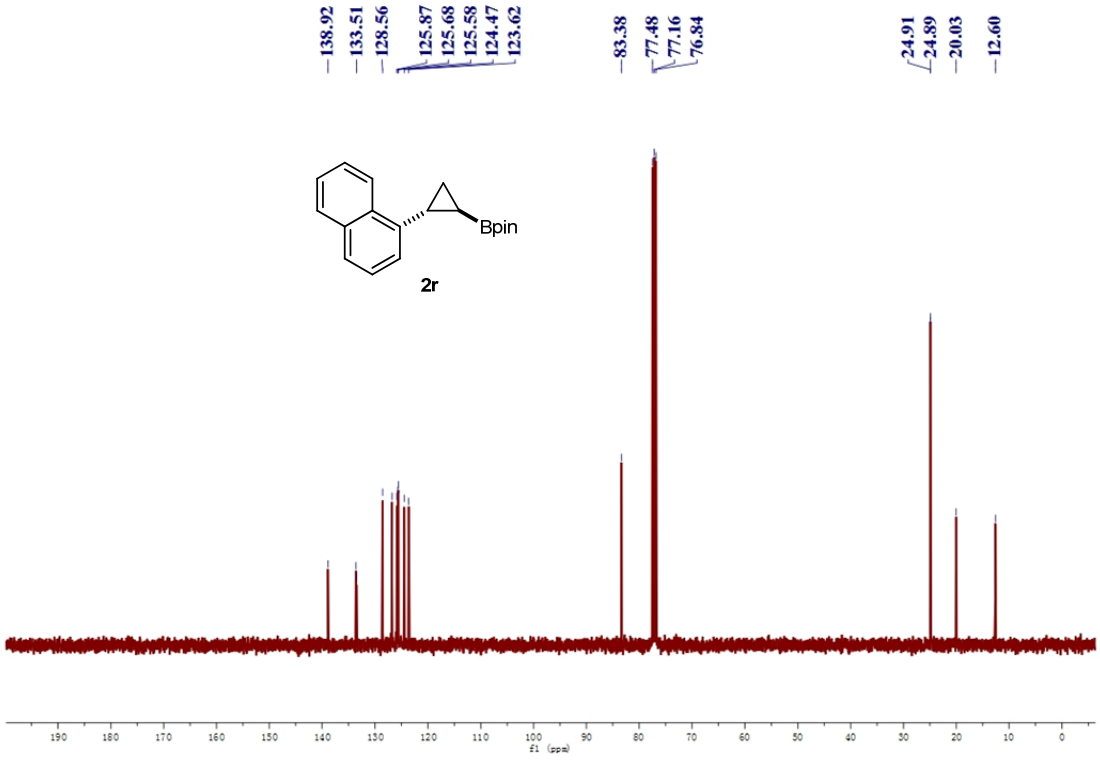
^{11}B NMR (128 MHz, $CDCl_3$) (**2q**)



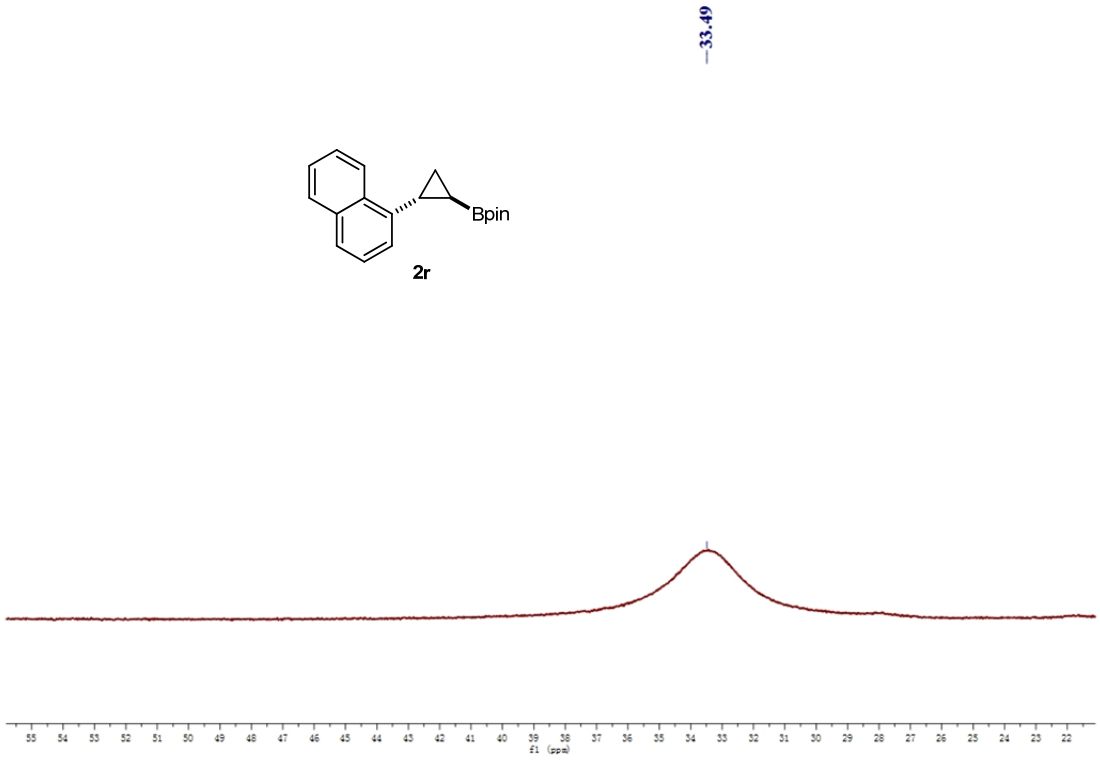
^{1}H NMR (400 MHz, $CDCl_3$) (**2r**)



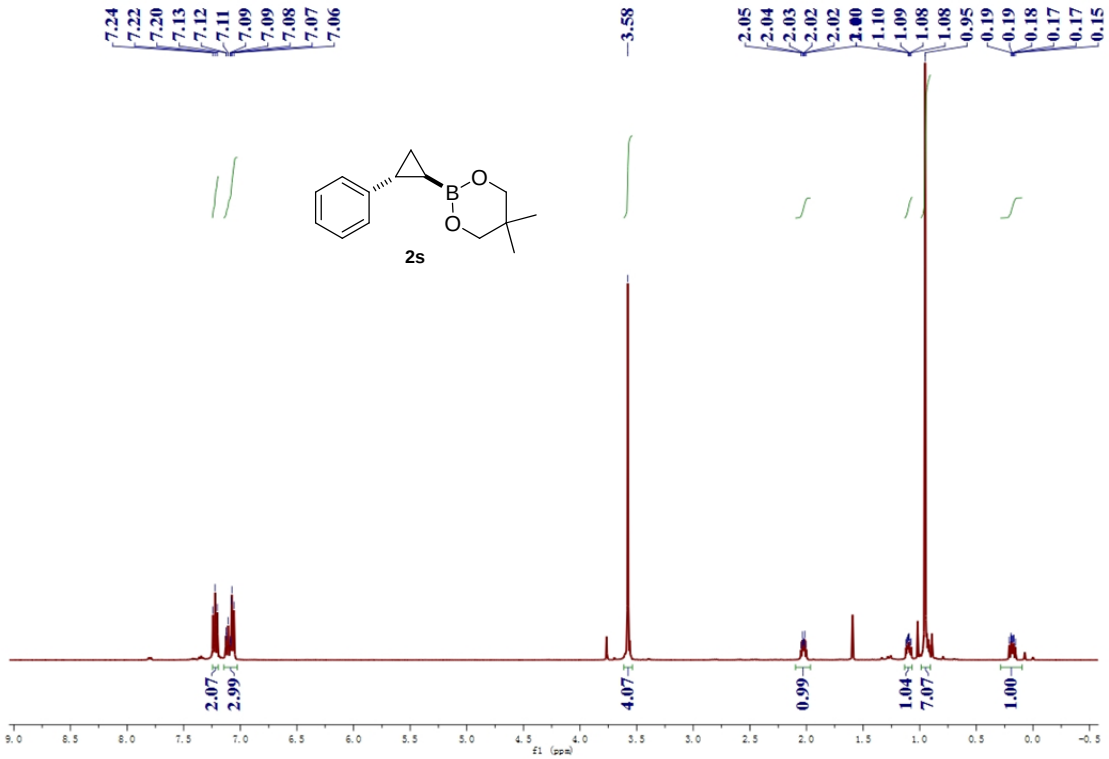
^{13}C NMR (100 MHz, $CDCl_3$) (**2r**)



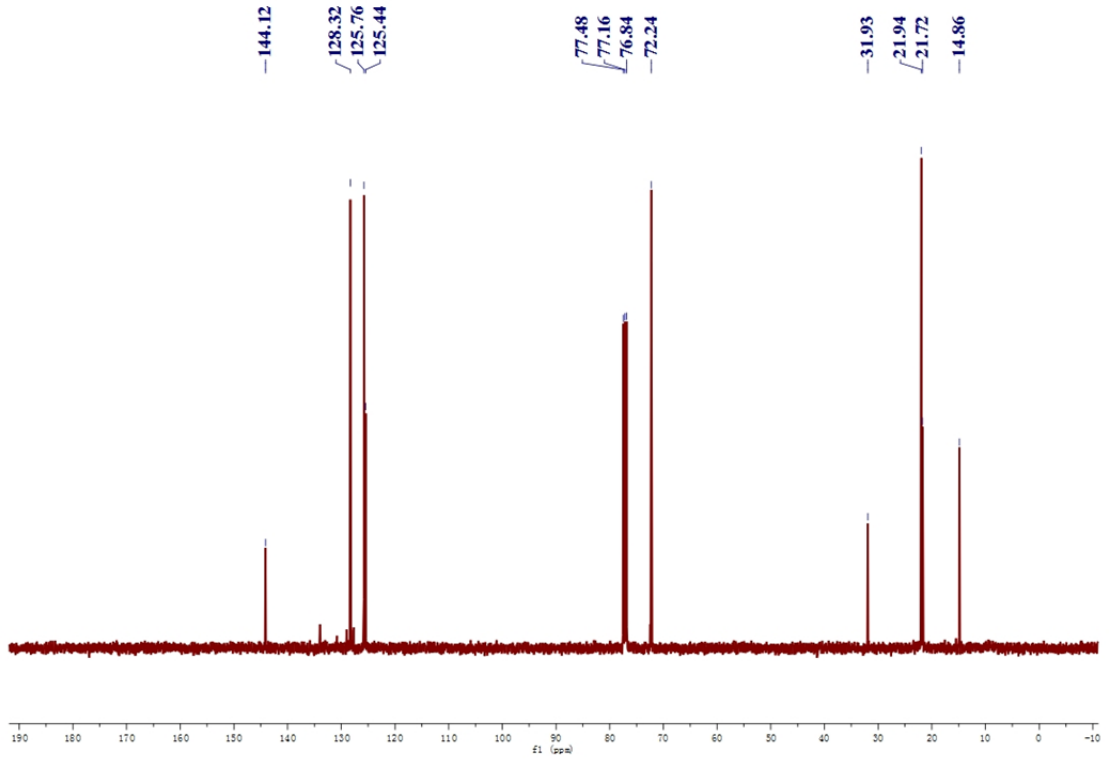
^{11}B NMR (128 MHz, $CDCl_3$) (**2r**)



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



^{13}C NMR (100 MHz, $CDCl_3$) (**2s**)



^{11}B NMR (128 MHz, $CDCl_3$) (**2s**)