

Supporting Information

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

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Detail information for screening of reaction conditions

Table S1. Screening of bases^{a,b,c}

Entry	Base	Covn./%	<i>trans</i> - 2a Yiled/%	<i>trans</i> - 2a : <i>cis</i> - 2a : 3a : 4a
1	<i>t</i> -BuOK	94	73	92: 1: 2: 5
2	<i>t</i> -BuONa	96	68	97: 1: 1: 1
3	<i>t</i> -BuOLi	49	19	-
4	MeOK	95	44	86: 2: 1: 11
5	MeONa	10	0	-
6	K ₂ CO ₃	9	0	-
7	K ₃ PO ₄	6	0	-
8	Cs ₂ CO ₃	13	0	-
9	-	2	0	-

^aReaction conditions: **1a** (0.3 mmol), B₂pin₂ (0.45 mmol, 1.5 equiv), FeCl₃ (10 mol%), base (0.3 mmol, 1 equiv), THF (10 mL), 65 °C, 7 h. ^bConversion and yield were determined by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard. ^cStereomeric ratio was determined by ¹H NMR analysis of the crude reaction mixture.

Table S2. Screening of solvents^{a,b,c}

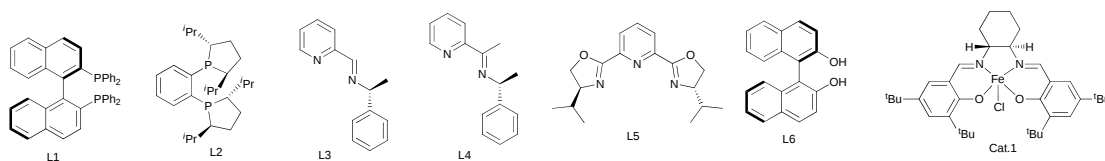
Entry	Solvent	Covn./%	<i>trans</i> - 2a Yiled/%	<i>trans</i> - 2a : <i>cis</i> - 2a : 3a : 4a
1	THF	94	73	92: 1: 2: 5
2	MTBE	57	31	89: 1: 2: 8
3	dioxane	37	15	-
4	<i>n</i> -Bu ₂ O	75	62	97: 1: 1: 1
5	<i>i</i> -Pr ₂ O	68	36	85: 1: 3: 11
6	1,2-DME	20	4	-
7	DMSO	22	12	-
8	1,2-DCE	2	0	-
9	MeCN	19	6	-
10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

^aReaction conditions: **1a** (0.3 mmol), B₂pin₂ (0.45 mmol, 1.5 equiv), FeCl₃ (10 mol%), *t*-BuOK (0.3 mmol, 1 equiv), solvent (10 mL), 65 °C, 7 h. ^bConversion and yield were determined by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard. ^cStereomeric 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./%	<i>trans</i> - 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

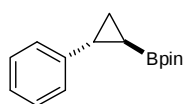
^aReaction conditions: **1a** (0.3 mmol), B₂pin₂ (0.45 mmol, 1.5 equiv), FeCl₃ (10 mol%), ligand, *t*-BuOK (0.33 mmol, 1.1 equiv), THF (10 mL), 65 °C, 48 h. ^bConversion and yield were determined by ¹H NMR with 1,1,2,2-tetrachloroethane as an internal standard. ^cThe ee value was determined by HPLC analysis (CHIRALCEL OD-H, hexane, 0.5 mL/min, UV detector at 254 nm, 30 °C, tR¹ = 16.1 min, tR² = 18.9 min.).



The spectra data of Cyclopropylboronates

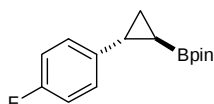
Note: The carbon attached to boron is not observed, or just a broad and low intensity signal around 10 ppm in ¹³C NMR spectra.¹

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



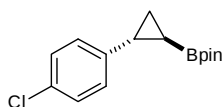
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (118 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 7.22-7.25 (m, 2H), 7.11-7.14 (m, 1H), 7.07-7.08 (m, 2H), 2.08-2.13 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.14-1.18 (m, 1H), 0.97-1.02 (m, 1H), 0.28-0.33 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 143.5, 128.4, 125.8, 125.6, 83.3, 24.9, 24.8, 22.0, 15.1, 5.99. ¹¹B NMR (128 MHz, CDCl₃): δ 33.21. HRMS-ESI: calcd for C₁₅H₂₂BO₂ ([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)



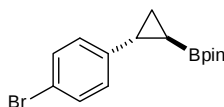
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (124 mg, 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.01-7.05 (m, 2H), 6.90-6.95 (m, 2H), 2.06-2.11 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.11-1.16 (m, 1H), 0.92-0.97 (m, 1H), 0.21-0.26 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): 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. ¹¹B NMR (128 MHz, CDCl₃): δ 33.06. HRMS-ESI: calcd for C₁₅H₂₁BFO₂ ([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)



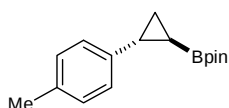
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (103 mg, 74%). ¹H NMR (400 MHz, CDCl₃): δ 7.19 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 2.05-2.09 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.14-1.19 (m, 1H), 0.94-0.98 (m, 1H), 0.23-0.28 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 142.0, 131.2, 128.4, 127.1, 83.4, 24.83, 24.80, 21.4, 15.1, 6.11. ¹¹B NMR (128 MHz, CDCl₃): δ 33.06. HRMS-ESI: calcd for C₁₅H₂₁BClO₂ ([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%). ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ 142.6, 131.3, 127.6, 119.1, 83.4, 24.9, 24.8, 21.5, 15.1. ¹¹B NMR (128 MHz, CDCl₃): δ 32.73. HRMS-ESI: calcd for C₁₅H₂₁BBrO₂ ([M+H]⁺), 323.0818; found, 323.0815. These spectroscopic data correspond to reported data.^{1d}

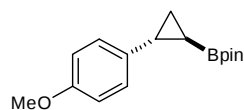
4,4,5,5-Tetramethyl-2-(2-(*p*-tolyl)cyclopropyl)-1,3,2-dioxaborolane (2e)



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%). ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ 140.4, 135.1, 129.0, 125.7, 83.2, 24.9, 24.8, 21.7, 21.0, 14.9. ¹¹B NMR (128 MHz, CDCl₃): δ 33.22. HRMS-ESI: calcd for

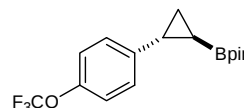
$C_{16}H_{24}BO_2$ ($[M+H]^+$), 259.1869; found, 259.1865. These spectroscopic data correspond to reported data.³

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



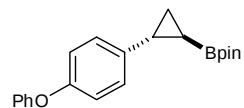
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (118 mg, 86%). 1H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.77 (s, 3H), 2.04-2.09 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.08-1.13 (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)



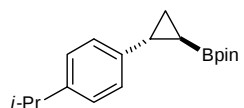
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (115 mg, 70%). 1H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 4H), 2.08-2.12 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15-1.19 (m, 1H), 0.96-1.00 (m, 1H), 0.24-0.30 (m, 1H). ^{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)



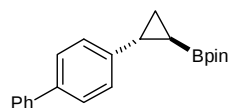
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (154 mg, 92%). 1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.33 (m, 2H), 7.05-7.08 (m, 3H), 6.96-6.98 (m, 2H), 6.90-6.92 (m, 2H), 2.09-2.13 (m, 1H), 1.26 (s, 6H), 1.25 (s, 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%). 1H 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.

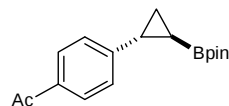
2-(2-([1,1'-Biphenyl]-4-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)



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

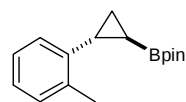
2H), 7.32 (m, 1H), 7.16 (d, $J = 8.2$ Hz, 2H), 2.13-2.18 (m, 1H), 1.27 (s, 6H), 1.25 (s, 6H), 1.18-1.23 (m, 1H), 1.03-1.08 (m, 1H), 0.33-0.38 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 142.8, 141.2, 138.7, 128.8, 127.14, 127.09, 127.07, 126.2, 83.3, 24.9, 24.8, 21.8, 15.3. ^{11}B NMR (128 MHz, CDCl_3): δ 33.12. HRMS-ESI: calcd for $\text{C}_{21}\text{H}_{26}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 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)



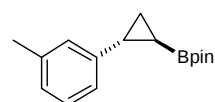
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:5). Colorless oil (126 mg, 88%). ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 2.56 (s, 3H), 2.12-2.16 (m, 1H), 1.24-1.25 (m, 13H), 1.05-1.09 (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 $\text{C}_{17}\text{H}_{24}\text{BO}_3$ ($[\text{M}+\text{H}]^+$), 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)



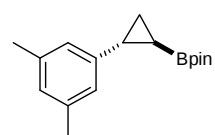
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (97 mg, 75%). ^1H NMR (400 MHz, CDCl_3): δ 7.12-7.15 (m, 1H), 7.08-7.11 (m, 2H), 7.00-7.02 (m, 1H), 2.41 (s, 3H), 2.08-2.13 (m, 1H), 1.27 (s, 12H), 1.11-1.16 (m, 1H), 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 $\text{C}_{16}\text{H}_{24}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 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)



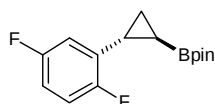
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (83 mg, 64%). ^1H NMR (400 MHz, CDCl_3): δ 7.13 (t, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.91 (s, 1H), 6.87 (d, $J = 7.6$ Hz, 1H), 2.3 (s, 3H), 2.06-2.10 (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 $\text{C}_{16}\text{H}_{24}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 259.1869; found, 259.1862.

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



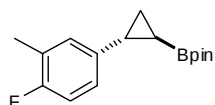
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (101 mg, 74%). ^1H NMR (400 MHz, CDCl_3): δ 6.78 (s, 1H), 6.71 (s, 2H), 2.26 (s, 6H), 2.02-2.07 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.10-1.14 (m, 1H), 0.96-1.01 (m, 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 $\text{C}_{17}\text{H}_{26}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 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)



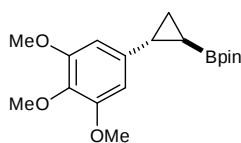
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (50%). ^1H NMR (400 MHz, CDCl_3): δ 6.89-6.95 (m, 1H), 6.73-6.79 (m, 1H), 6.54-6.59 (m, 1H), 2.25-2.30 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.17-1.21 (m, 1H), 0.98-1.03 (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 $\text{C}_{15}\text{H}_{20}\text{BF}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$), 281.1524; found, 281.1518.

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



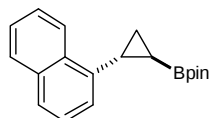
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (117 mg, 85%). ^1H NMR (400 MHz, CDCl_3): δ 7.00-7.04 (m, 1H), 6.75-6.78 (m, 1H), 6.69-6.72 (m, 1H), 2.21 (s, 3H), 2.04-2.08 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.12-1.17 (m, 1H), 0.94-0.98 (m, 1H), 0.22-0.28 (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 $\text{C}_{16}\text{H}_{23}\text{BFO}_2$ ($[\text{M}+\text{H}]^+$), 277.1775; found, 277.1770.

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



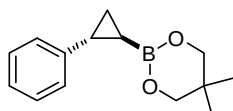
Title compound was isolated by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (100:1-100:3). Colorless oil (150 mg, 90%). ^1H NMR (400 MHz, CDCl_3): δ 6.31 (s, 2H), 3.82 (s, 6H), 3.79 (s, 3H), 2.04-2.08 (m, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.10-1.15 (m, 1H), 0.92-0.97 (m, 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 $\text{C}_{18}\text{H}_{27}\text{BO}_5$ ($[\text{M}+\text{H}]^+$), 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%). ^1H 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 $\text{C}_{14}\text{H}_{24}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 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%). ^1H NMR (400 MHz, CDCl_3): δ 7.22 (t, $J = 7.7$ Hz, 2H), 7.06-7.13 (m, 3H),

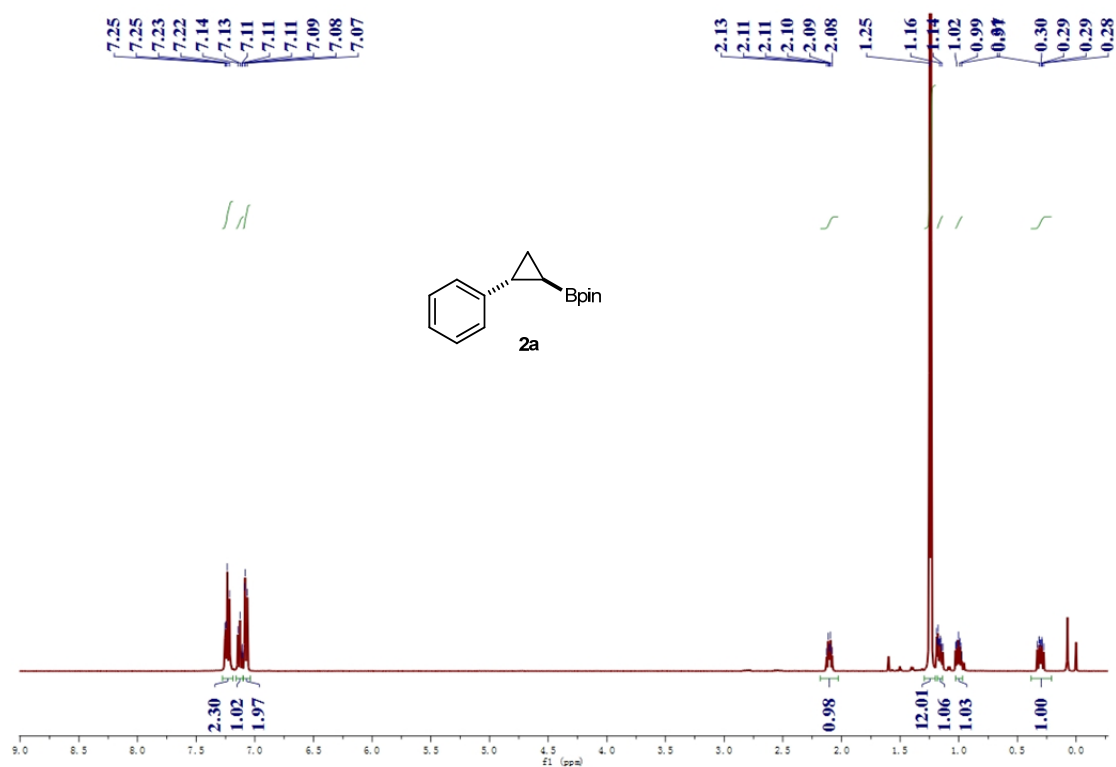
3.78 (s, 4H), 2.00-2.05 (m, 1H), 1.08-1.12 (m, 1H), 0.95 (s, 7H), 0.15-0.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.1, 128.3, 125.8, 125.4, 72.2, 31.9, 21.9, 21.7, 14.9. ^{11}B NMR (128 MHz, CDCl_3): δ 33.18. HRMS-ESI: calcd for $\text{C}_{14}\text{H}_{20}\text{BO}_2$ ($[\text{M}+\text{H}]^+$), 231.1556; found, 231.1552. These spectroscopic data correspond to reported data.^{1e}

References

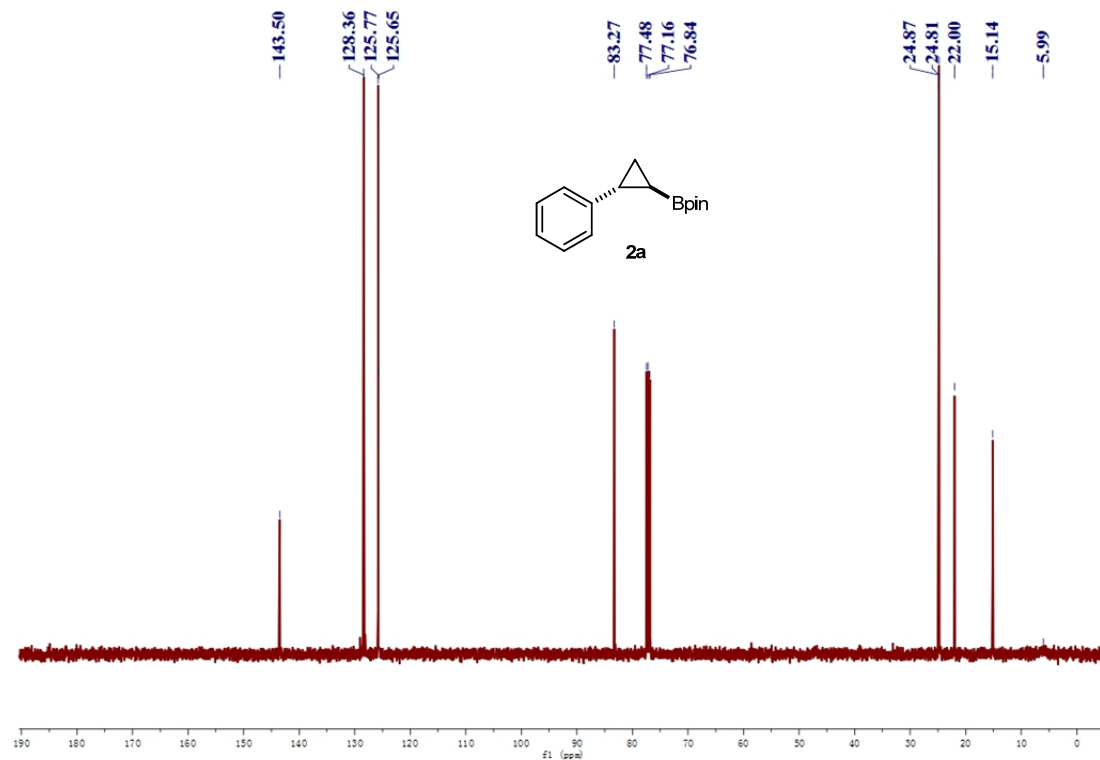
- [1] a) P. J. Unsworth, D. Leonori and V. K. Aggarwal, *Angew. Chem.* **2014**, *126*, 10004-10008; *Angew. Chem. Int. Ed.* **2014**, *53*, 9846-9850; b) K. Semba and Y. Nakao, *J. Am. Chem. Soc.* **2014**, *136*, 7567-7570; c) E. Yamamoto, K. Izumi, Y. Horita and H. Ito, *J. Am. Chem. Soc.* **2012**, *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

^1H NMR (400 MHz, CDCl_3) (2a)



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



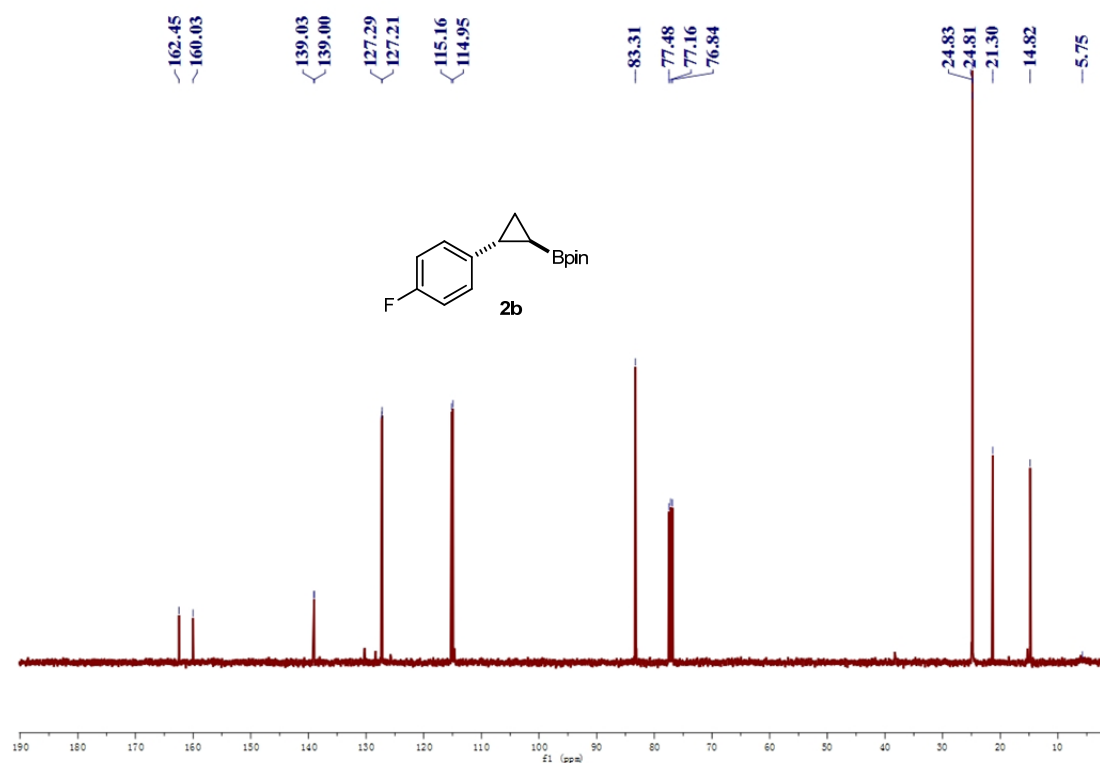
Chemical structure of **2a** is shown above the spectrum. The structure is (S)-1-phenyl-2-(pinacolat-1-yl)cyclopropane, where a phenyl group is attached to a cyclopropane ring, which is also substituted with a pinacolat-1-yl group (Bpin).

Chemical structure of **2b** is shown above the spectrum: Fc1ccc(cc1)[C@H]2CC2Bpin.

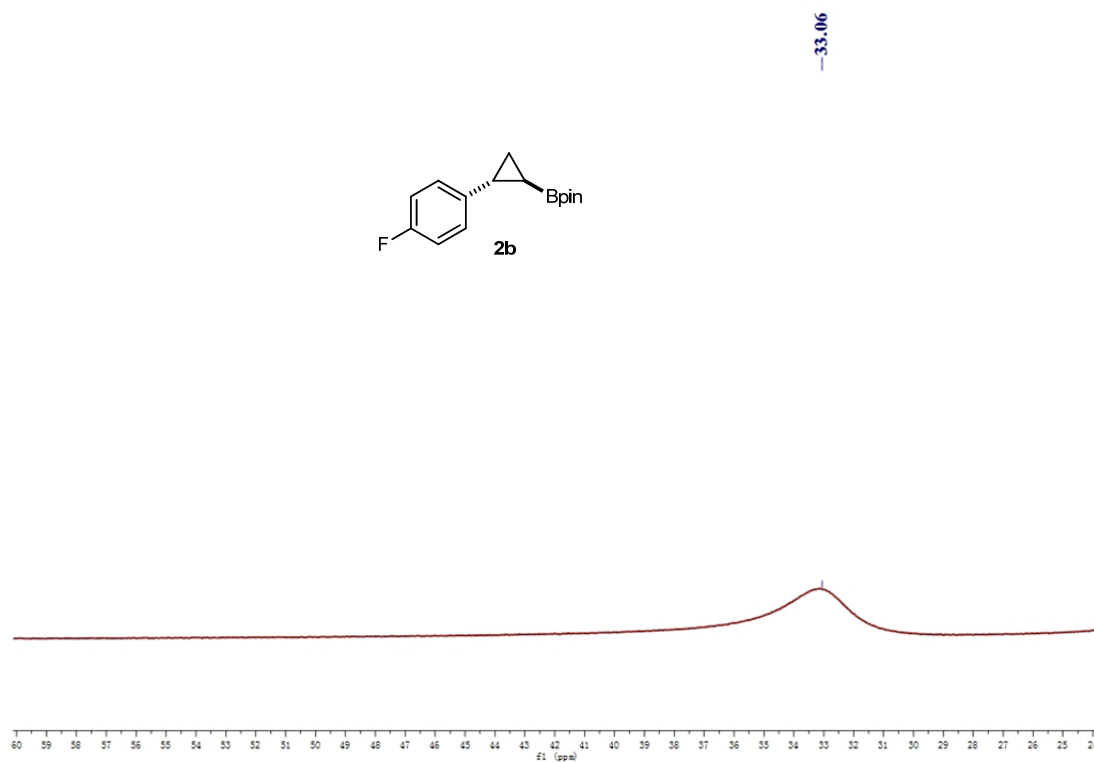
¹H NMR spectrum (CDCl₃) of compound **2b**. The spectrum displays several signals with corresponding integrations and chemical shifts (ppm):

- Aromatic region (6.90–7.05 ppm): Multiplet, integration 2.04 and 2.08.
- 2.06 ppm: Singlet, integration 1.01.
- 1.25 ppm: Large singlet, integration 12.35.
- 1.13 ppm: Doublet, integration 1.07.
- 0.94 ppm: Doublet, integration 1.08.
- 0.21 ppm: Triplet, integration 1.00.

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



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



Chemical structure of compound **2c** is shown above the spectrum: Clc1ccc([C@H]2CC2Bpin)cc1.

¹H NMR spectrum (CDCl₃) of compound **2c**. The spectrum displays aromatic signals between 6.9 and 7.2 ppm, a broad singlet for the Bpin group at 1.15 ppm, and aliphatic signals between 0.2 and 0.3 ppm. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.18	2.00
7.01	1.96
1.15	12.08
0.99	1.00
0.94	1.02
0.27	1.00
0.25	
0.24	
0.23	

Chemical structure of compound **2c** is shown as an inset: BrC1=CC=C(Cl)C=C1.

¹H NMR spectrum (CDCl₃) of compound **2c** is displayed. The spectrum shows peaks at the following chemical shifts (ppm): 7.684, 7.716, 7.748, 83.36, 127.15, 128.38, 131.16, 142.04, 21.42, 24.81, 24.83, 15.09, and 6.11.

Chemical structure of compound **2c** is shown above the spectrum. It is a cyclohexane ring substituted with a chlorine atom (Cl) and a pinacol boronate ester group (Bpin) in a trans configuration.

Chemical structure of **2d**: BrC1=CC=C(C=C1)[C@H]2CC[C@@H]2C#CC(=O)OC

¹H NMR spectrum (CDCl₃) of **2d**. The x-axis represents the chemical shift in ppm, ranging from -0.5 to 9.0. The spectrum shows several peaks with corresponding integration values.

Peak list (ppm) and integration values:

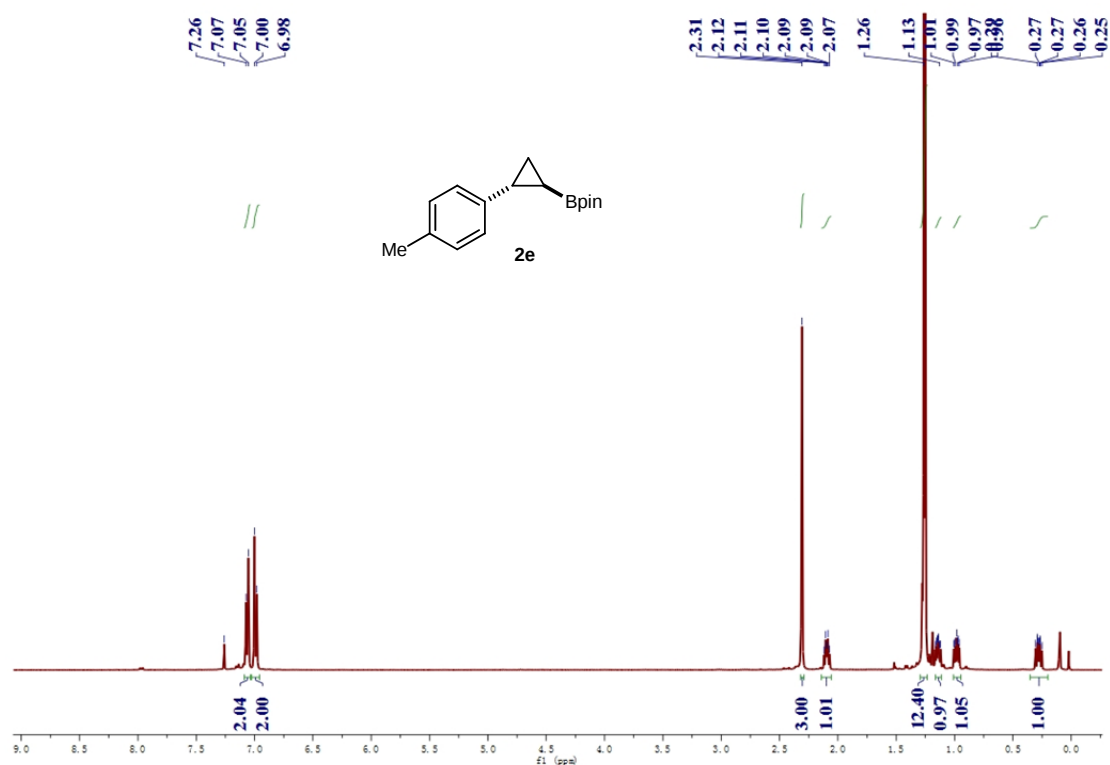
Chemical Shift (ppm)	Integration
7.35	2.03
7.26	1.95
2.05	0.98
1.16	12.51
1.14	1.08
1.04	1.04
0.93	1.00

¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift δ in ppm, ranging from -10 to 200. The spectrum shows several peaks, with the following chemical shifts labeled above the baseline:

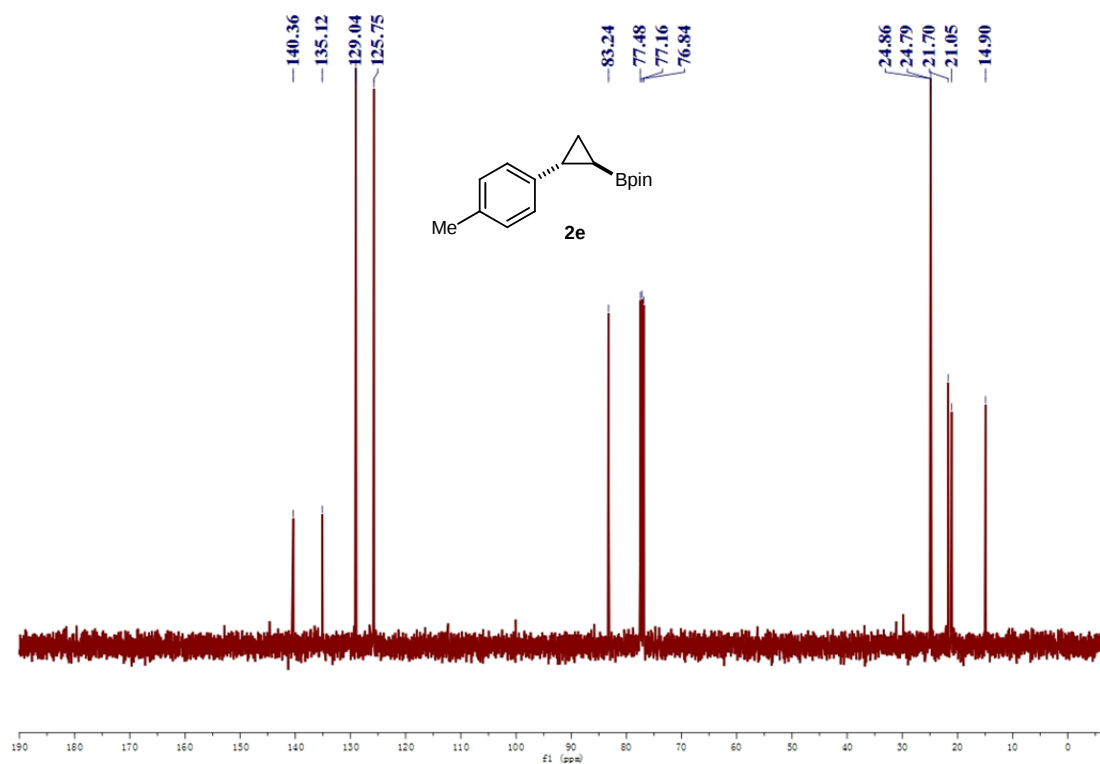
- 142.65
- 131.36
- 127.61
- 119.13
- 83.43
- 77.48 (solvent, CDCl₃)
- 77.16
- 76.84
- 24.88
- 24.85
- 21.53
- 15.14

Chemical structure of **2d** is shown above the spectrum. The structure is 1-(4-bromophenyl)-2-(pinacolatylidene)cyclopropane, featuring a cyclopropane ring substituted with a 4-bromophenyl group and a pinacolatylidene group.

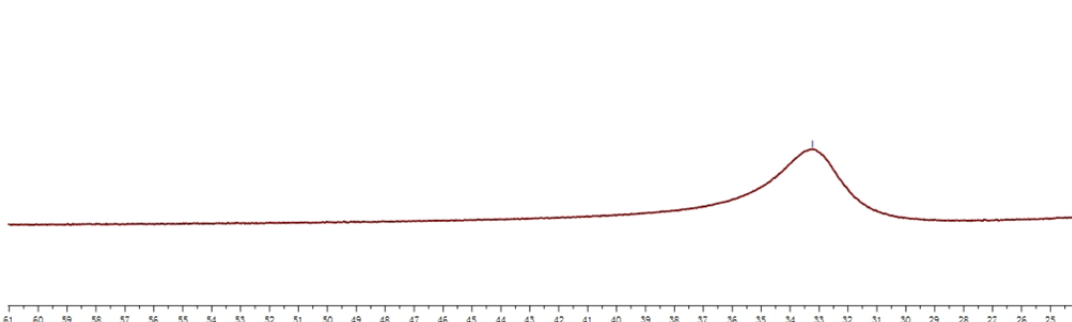
^1H NMR (400 MHz, CDCl_3) (**2e**)



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



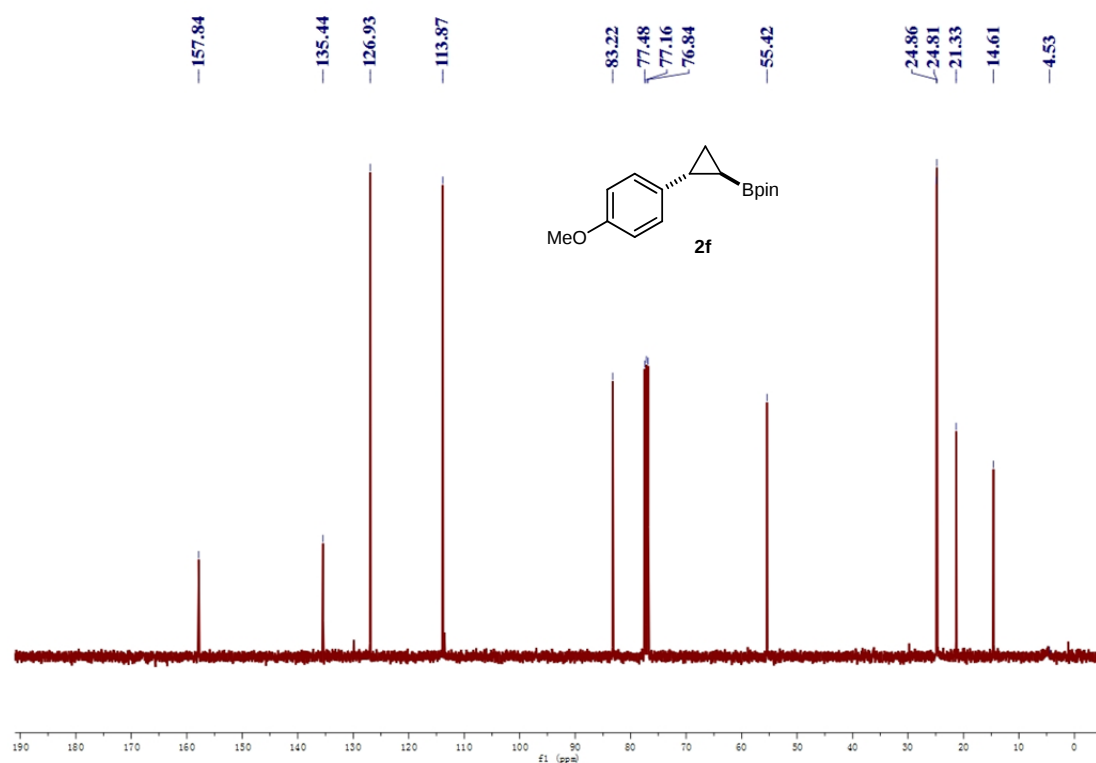
Chemical structure of **2e** is shown above the spectrum. It is a 4-methylphenyl group attached to a cyclopropyl ring, which is further substituted with a Bpin group.



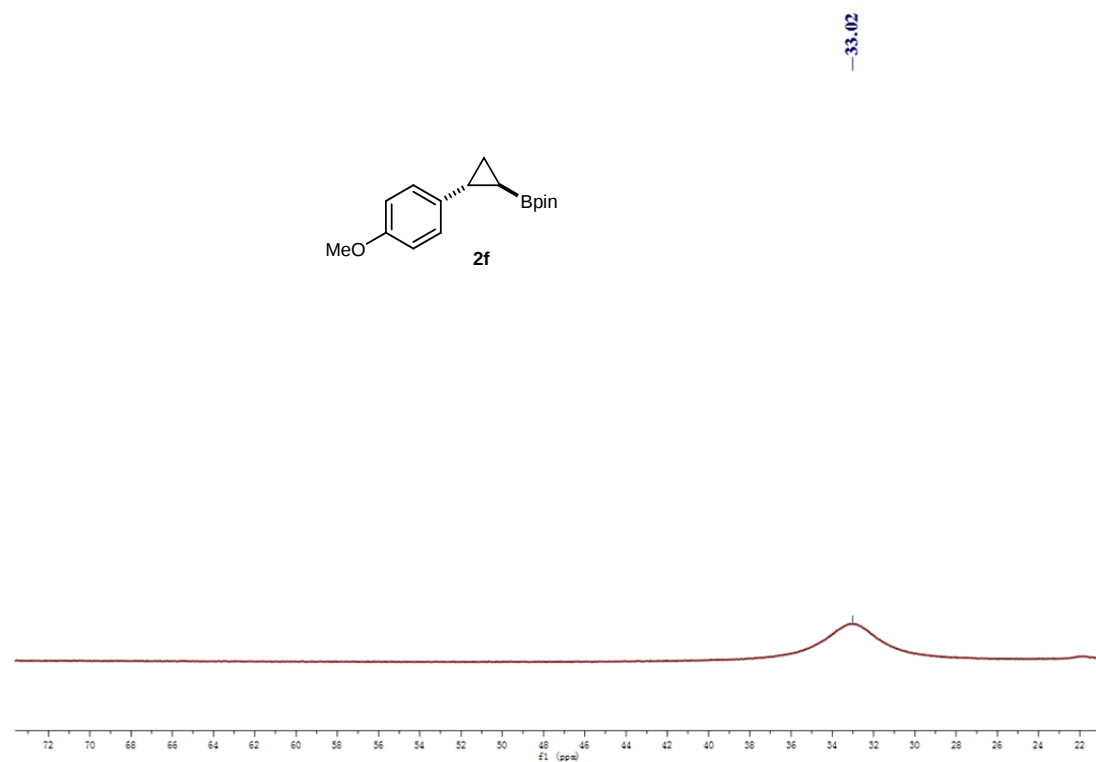
The spectrum shows a single broad peak at approximately 33.22 ppm, indicating the presence of a specific functional group or environment in the molecule.

[illegible]

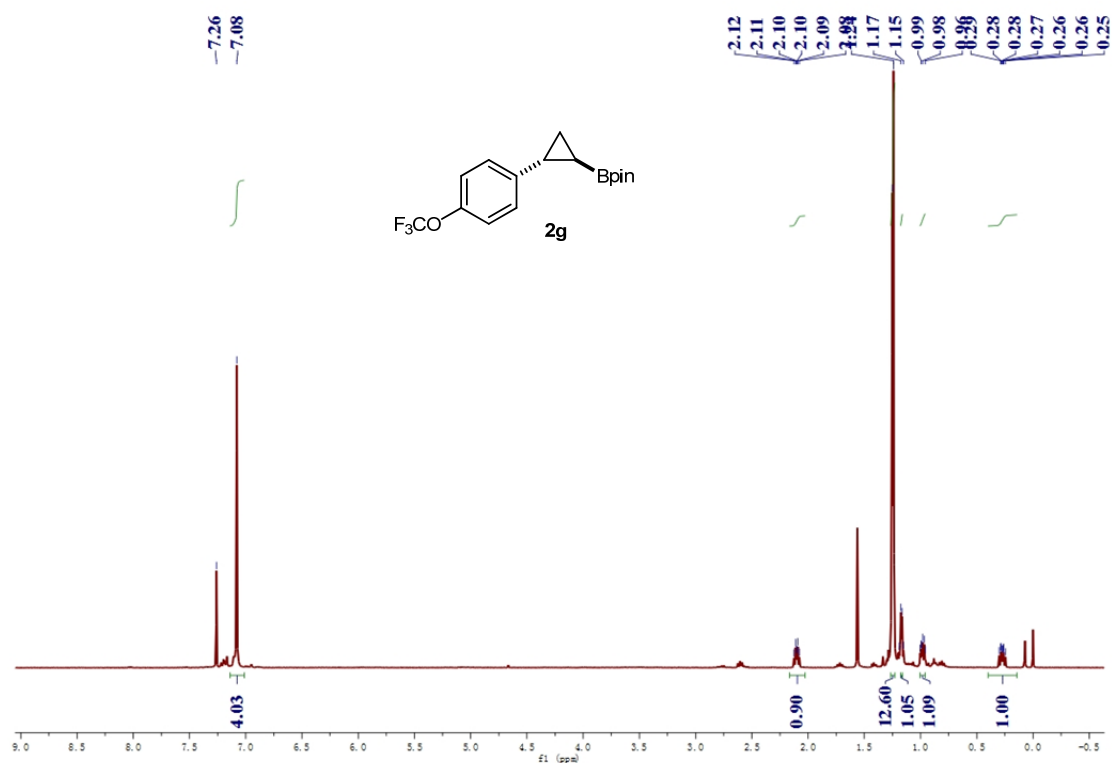
^{13}C NMR (100 MHz, CDCl_3) (**2f**)



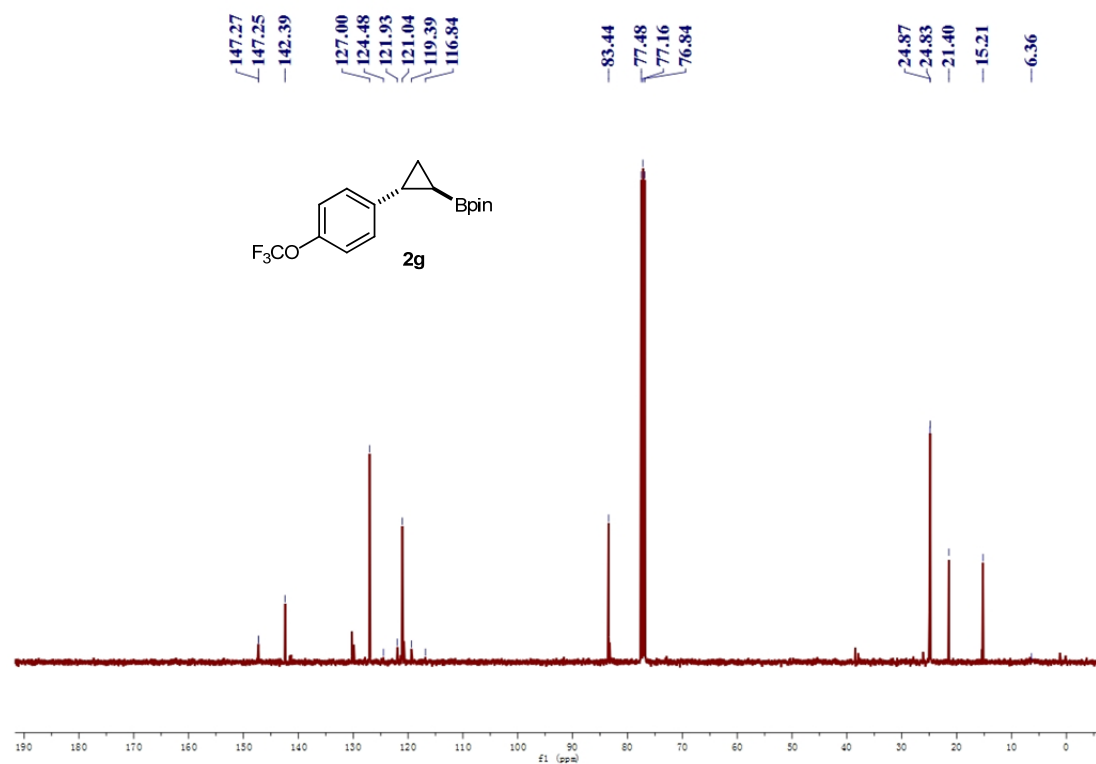
^{11}B NMR (128 MHz, CDCl_3) (**2f**)



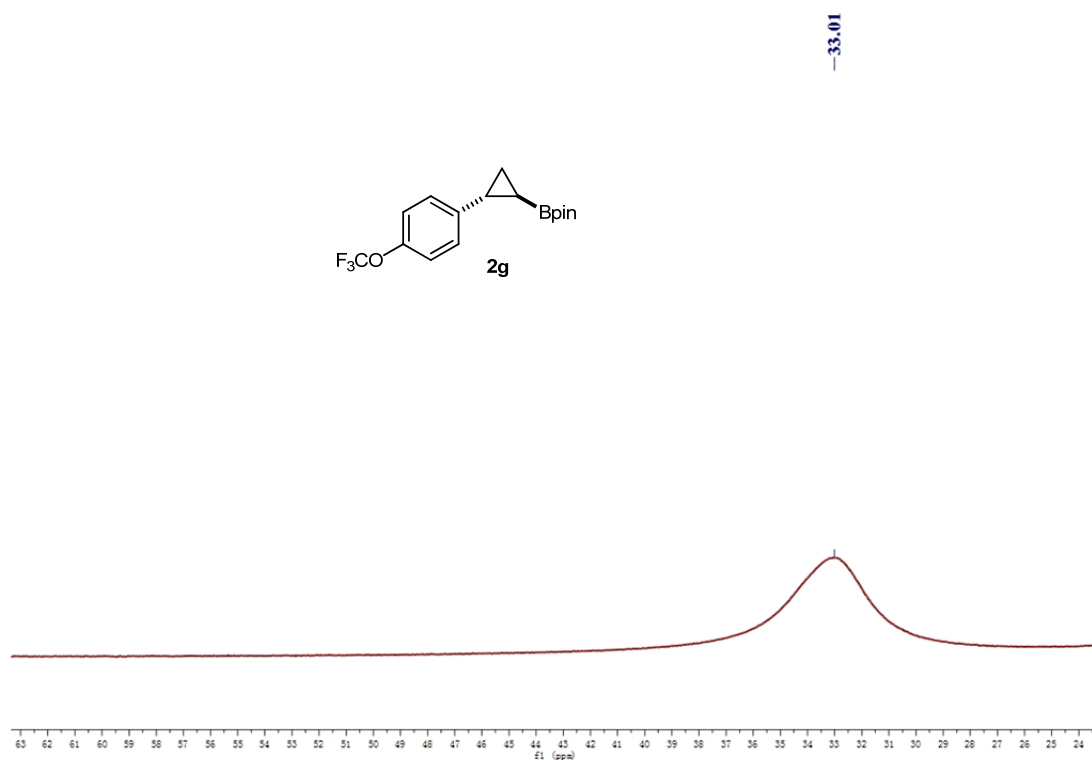
^1H NMR (400 MHz, CDCl_3) (2g)



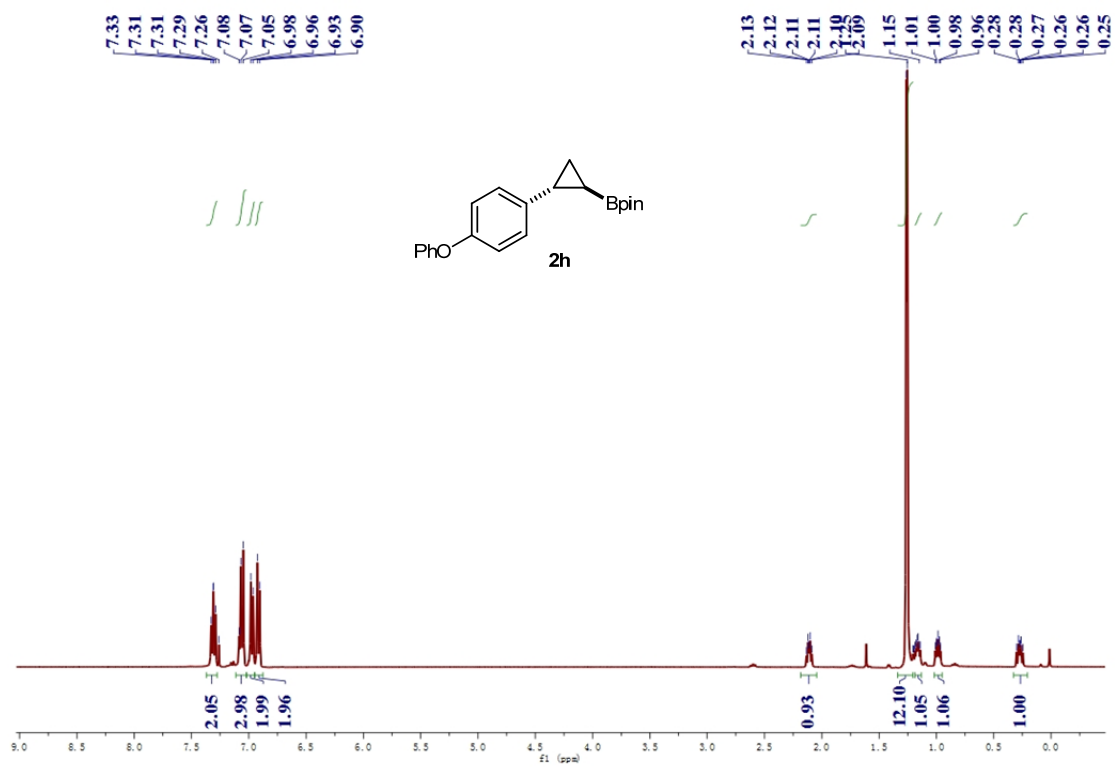
^{13}C NMR (100 MHz, CDCl_3) (2g)



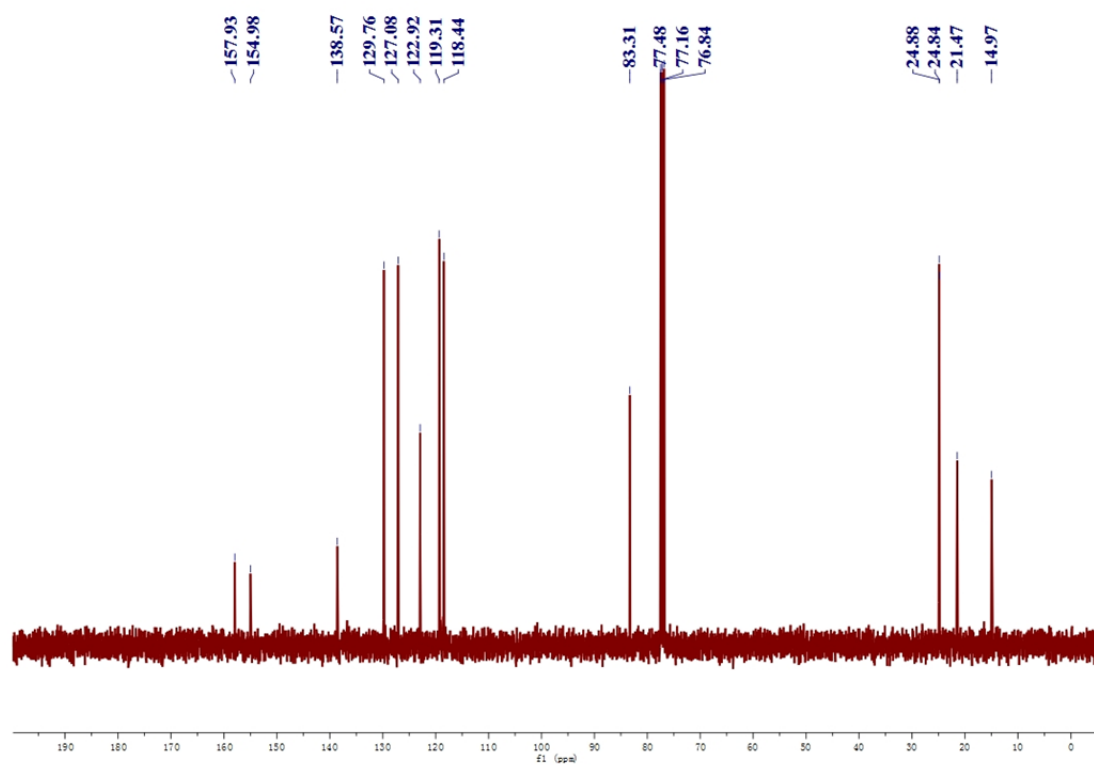
^{11}B NMR (128 MHz, CDCl_3) (**2g**)



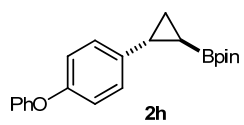
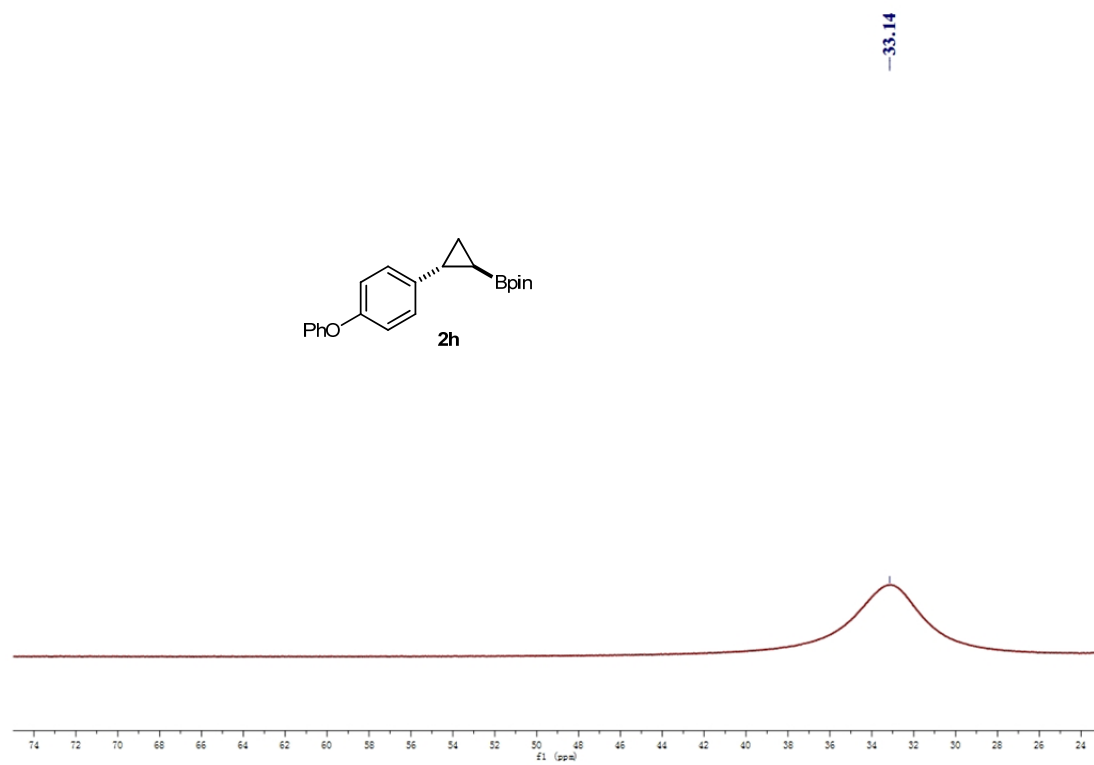
^1H NMR (400 MHz, CDCl_3) (**2h**)



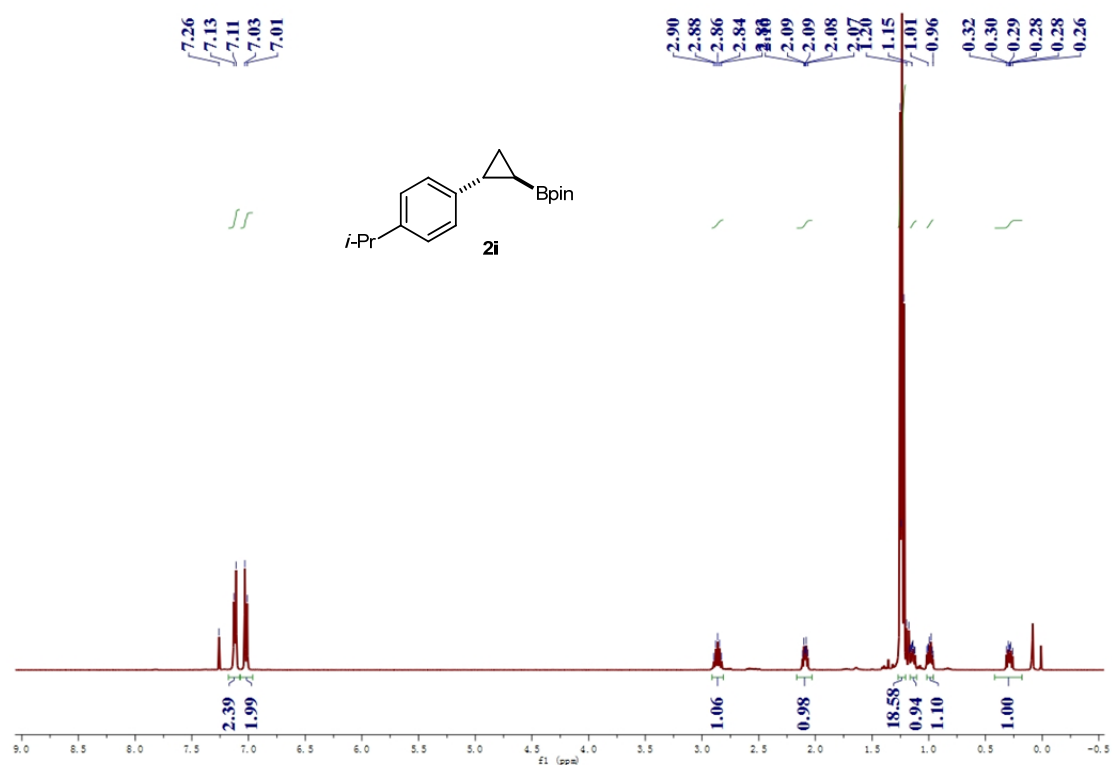
^{13}C NMR (100 MHz, CDCl_3) (**2h**)



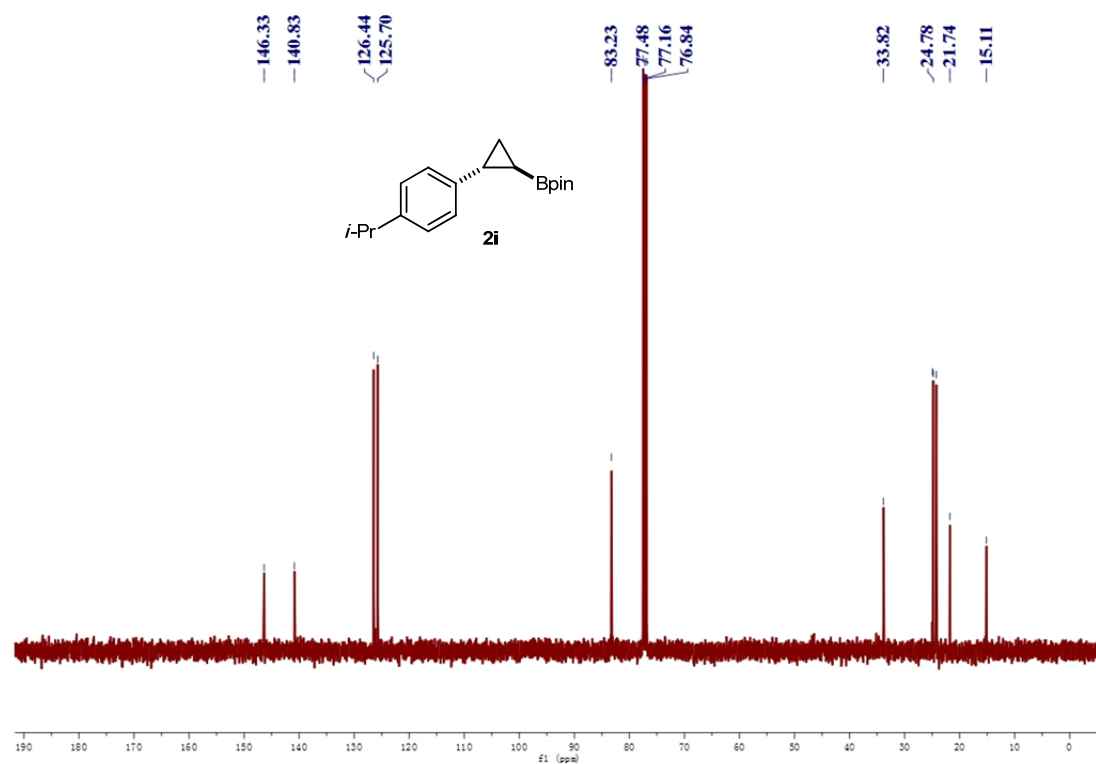
^{11}B NMR (128 MHz, CDCl_3) (**2h**)



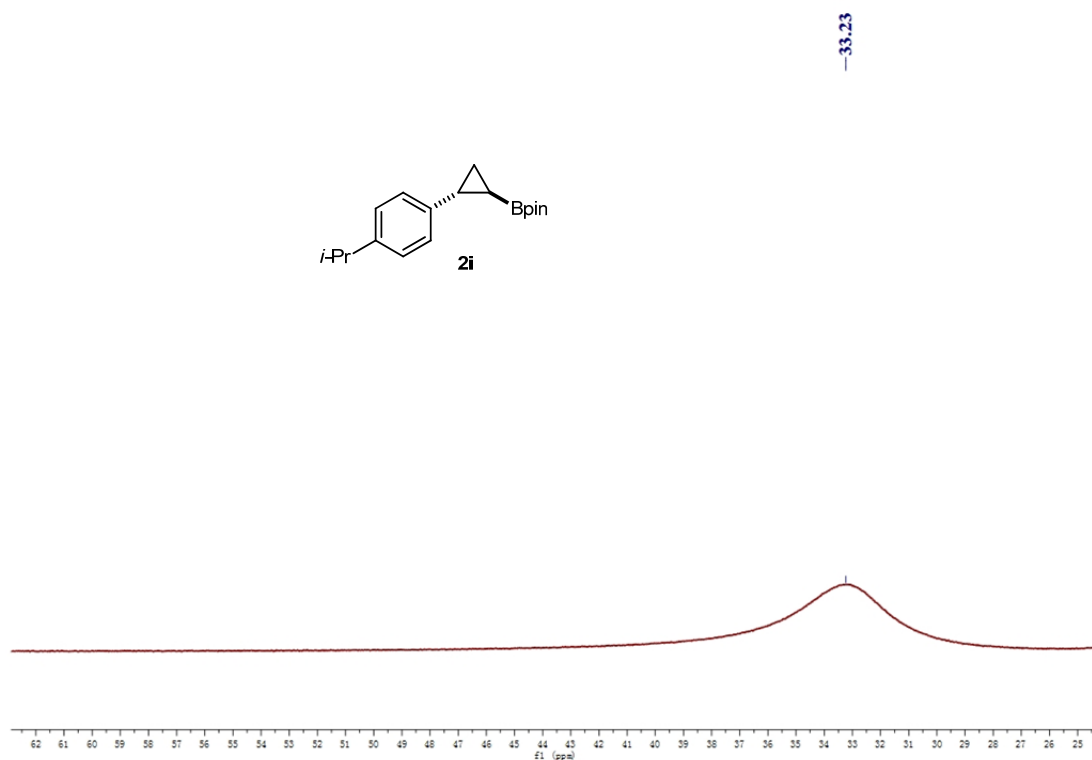
^1H NMR (400 MHz, CDCl_3) (**2i**)



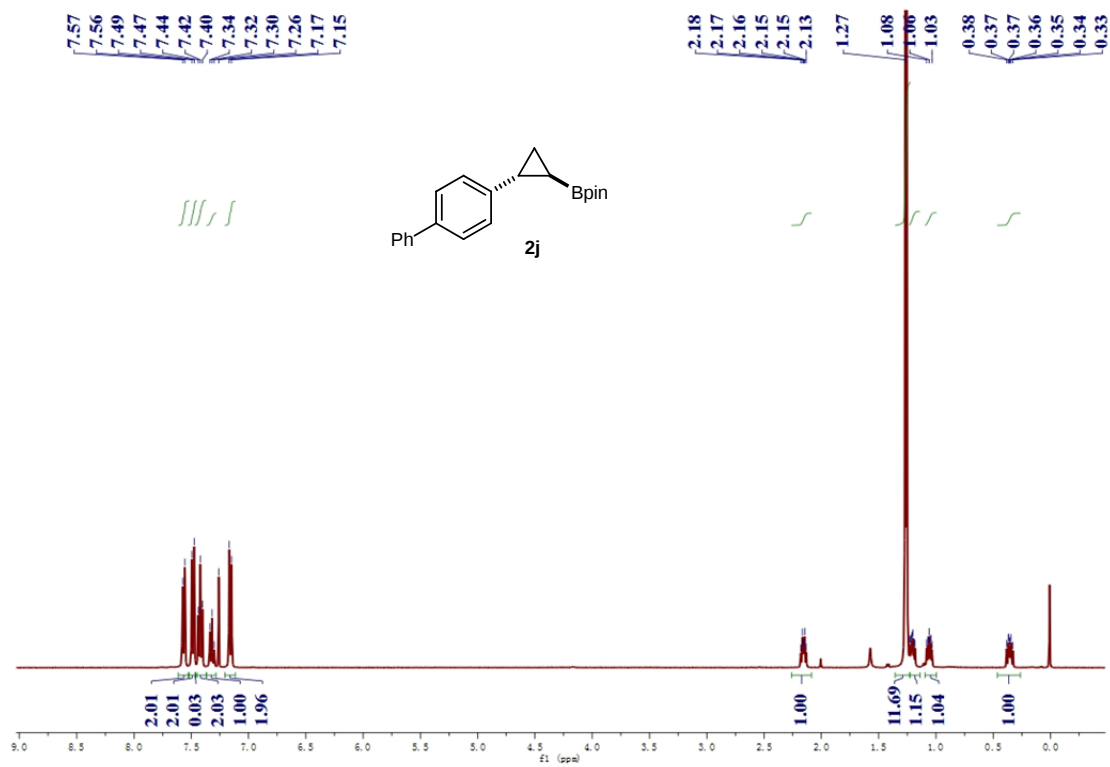
^{13}C NMR (100 MHz, CDCl_3) (**2i**)



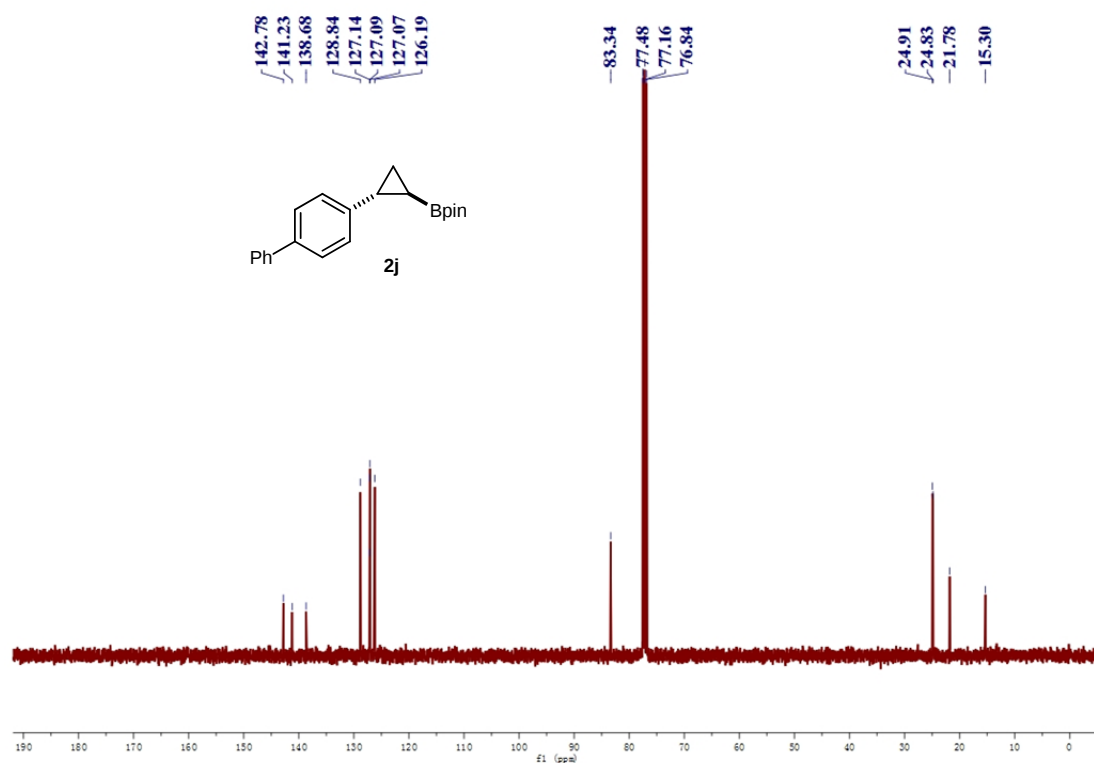
^{11}B NMR (128 MHz, CDCl_3) (**2i**)



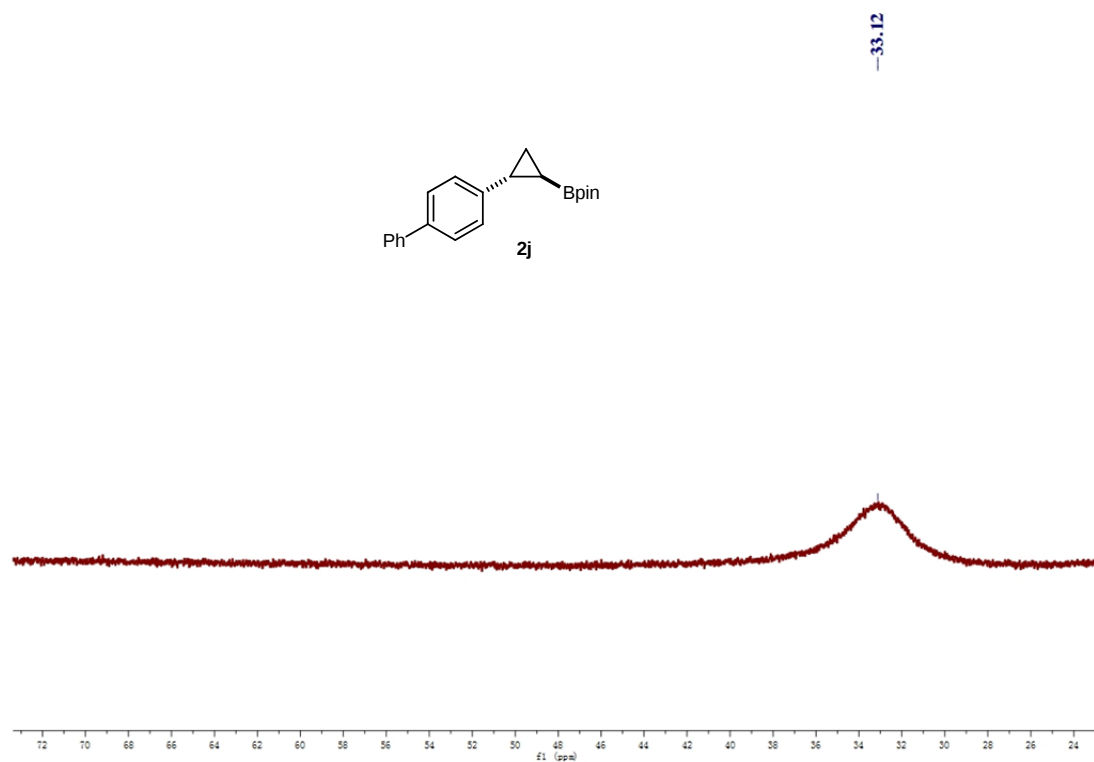
^1H NMR (400 MHz, CDCl_3) (**2j**)



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



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



Chemical structure of **2k** is shown above the spectrum. The structure is 4-(4-acetylphenyl)cyclopropylboronic pinacol ester, featuring a cyclopropyl group attached to a 4-acetylphenyl ring via a chiral center (indicated by a wedge bond).

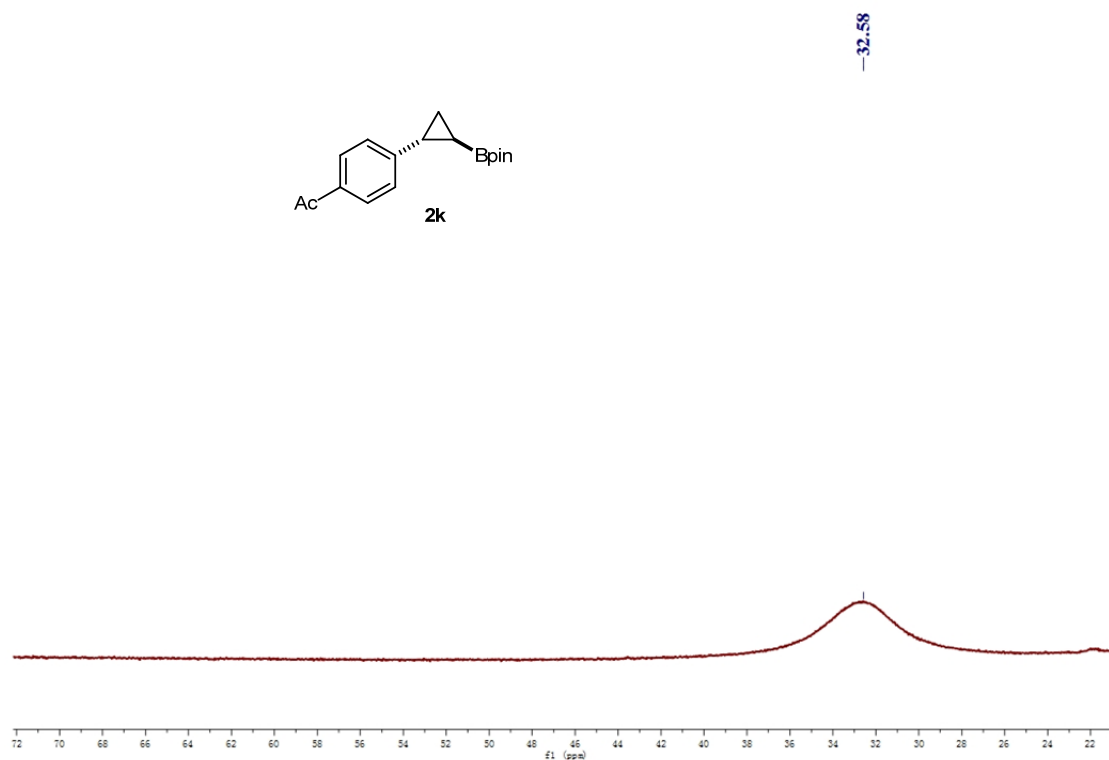
The ¹H NMR spectrum (CDCl₃) displays the following peaks and integrations:

- Aromatic protons: Multiplet at 7.84 ppm (integration 2.12) and multiplet at 7.12 ppm (integration 1.91).
- Acetyl methyl protons: Singlet at 2.56 ppm (integration 3.05).
- Cyclopropyl protons: Multiplet at 2.15 ppm (integration 0.99) and multiplet at 1.07 ppm (integration 12.83).
- Bpin group protons: Multiplet at 1.06 ppm (integration 1.04) and multiplet at 0.37 ppm (integration 1.00).

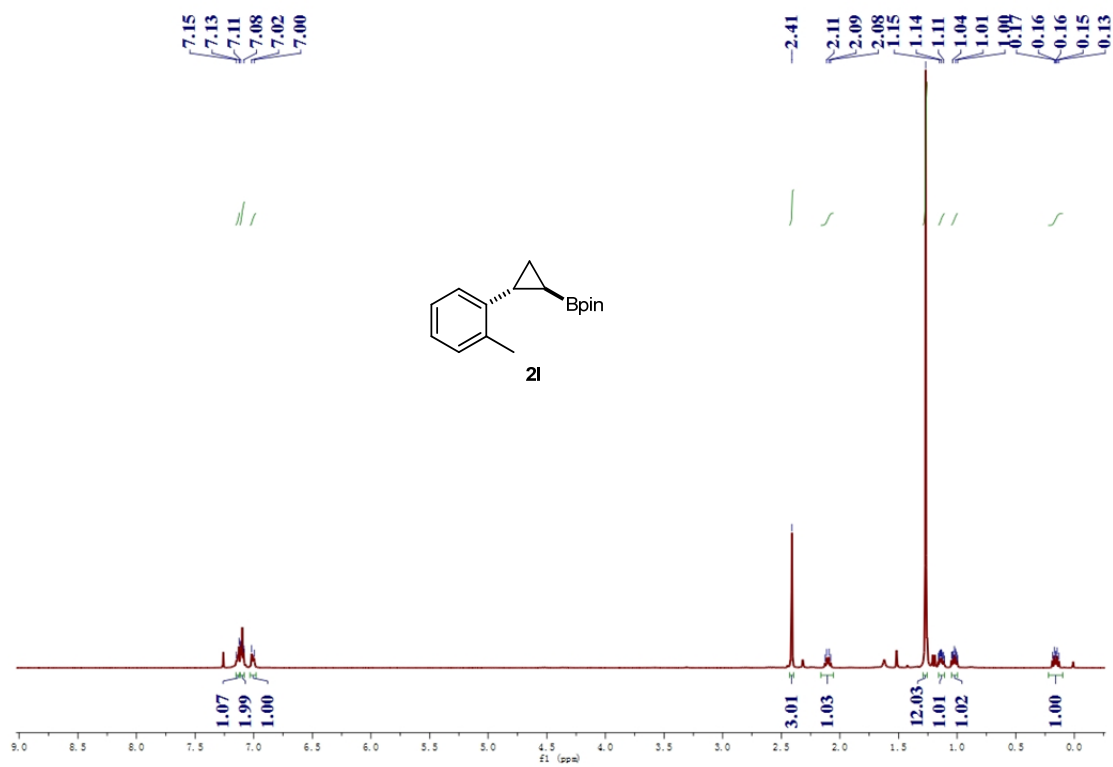
¹³C NMR spectrum (CDCl₃) of compound 10a. The x-axis represents the chemical shift in ppm, ranging from -10 to 210. The spectrum shows several peaks: a triplet for the CDCl₃ solvent at 77.16, 77.48, and 77.84 ppm; a peak at 83.50 ppm; aromatic and carbonyl peaks between 125 and 198 ppm; and aliphatic peaks between 15 and 27 ppm. The peak at 15.99 ppm is specifically labeled as the methyl group.

Chemical Shift (ppm)
197.82
149.85
134.85
128.63
125.69
83.50
77.48
77.16
76.84
26.66
24.88
24.86
22.13
15.99

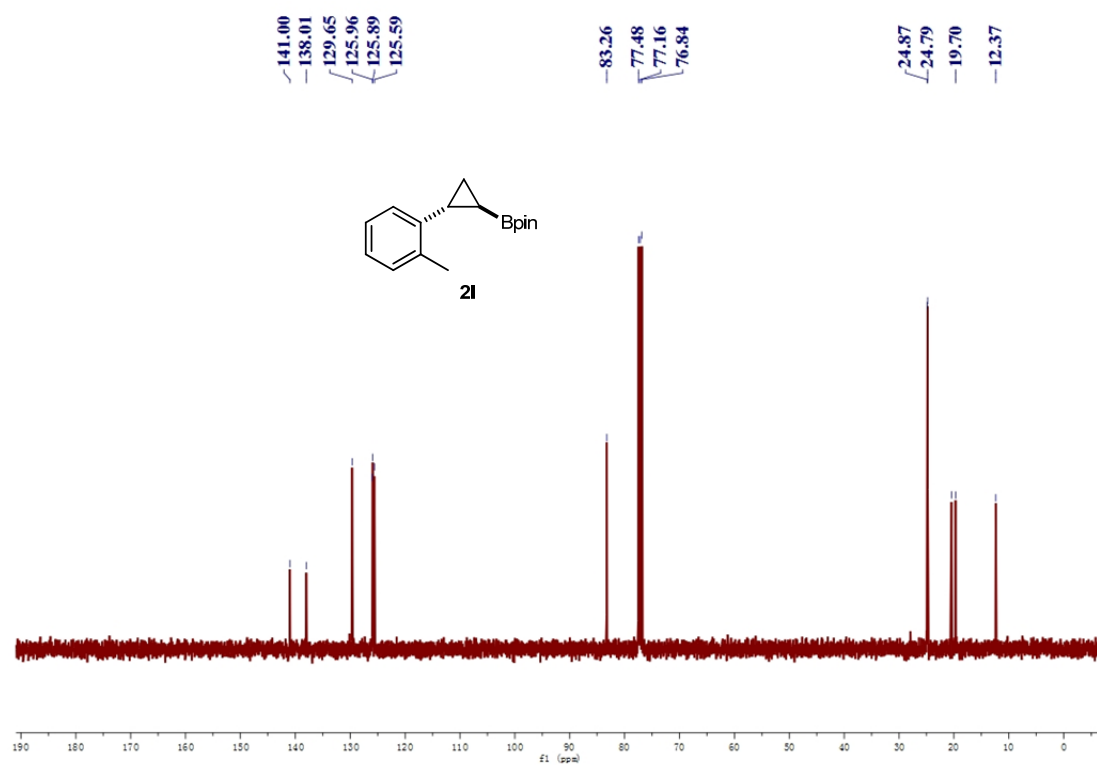
^{11}B NMR (128 MHz, CDCl_3) (**2k**)



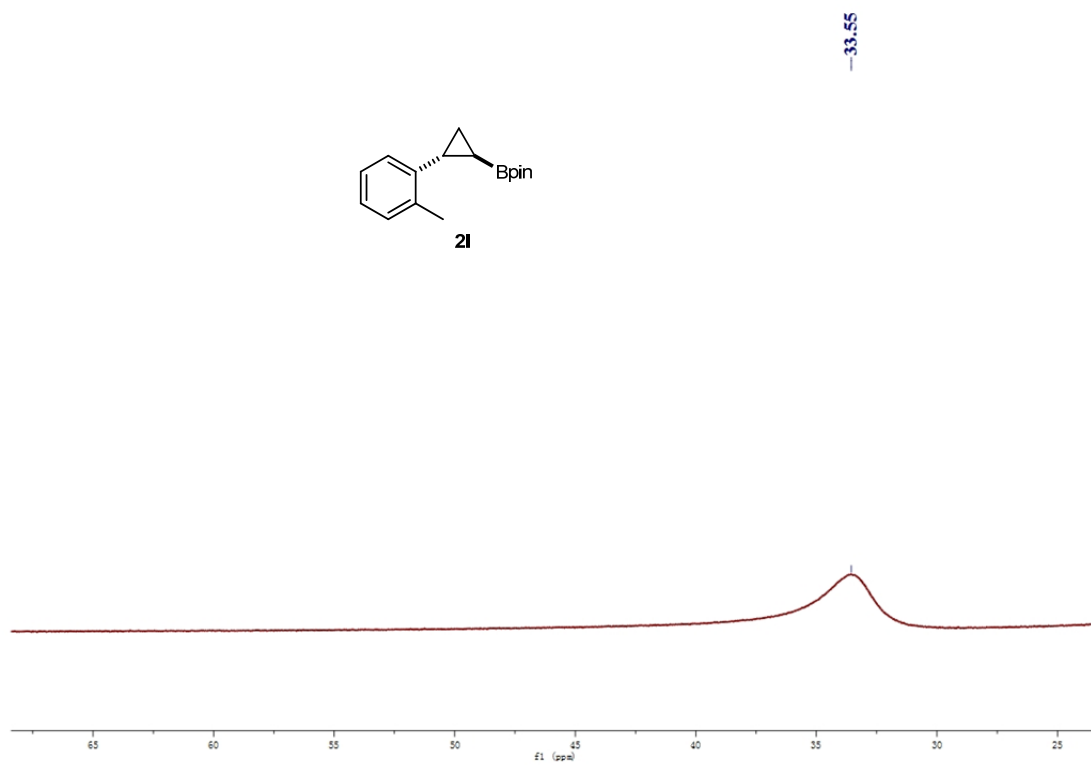
^1H NMR (400 MHz, CDCl_3) (**2l**)



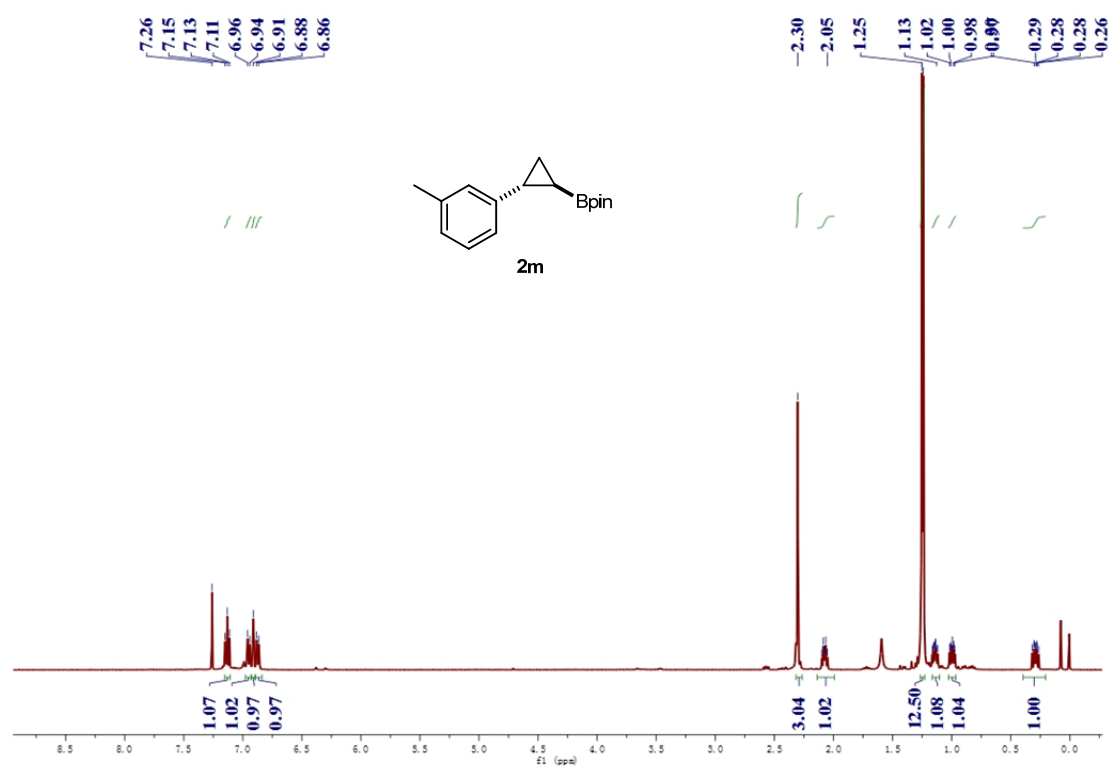
^{13}C NMR (100 MHz, CDCl_3) (**21**)



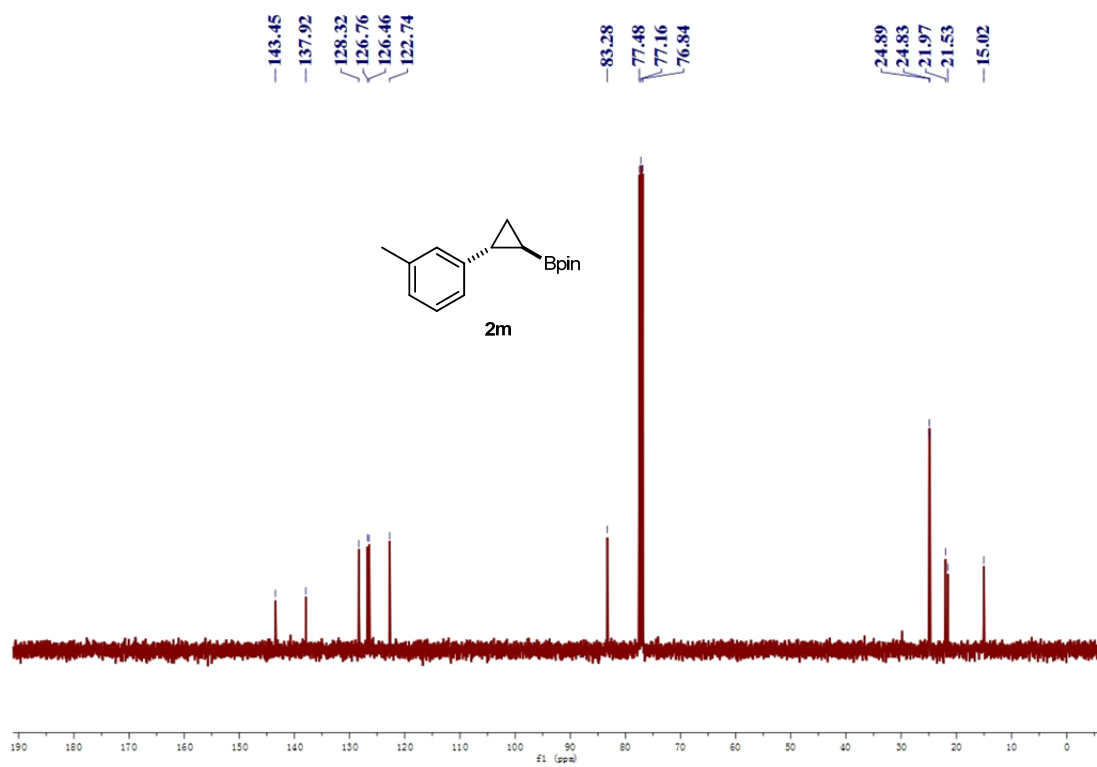
^{11}B NMR (128 MHz, CDCl_3) (**21**)



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



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



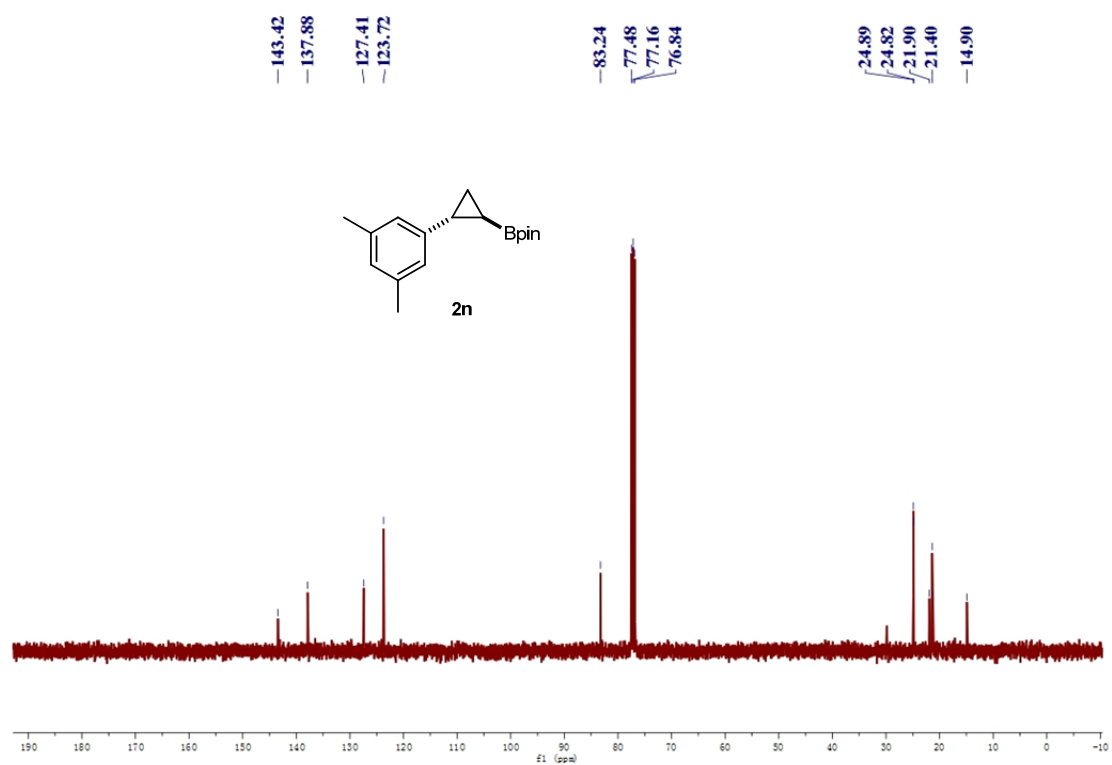
Chemical structure of **2m** is shown above the spectrum. The structure is a 4-methylphenyl group attached to a cyclopropyl ring, which is further substituted with a Bpin group. The spectrum shows a broad peak centered around 33.11 ppm, corresponding to the Bpin group.

Chemical structure of **2n**: 1-(4,6-dimethylphenyl)ethynylcyclopropanecarboxylate.

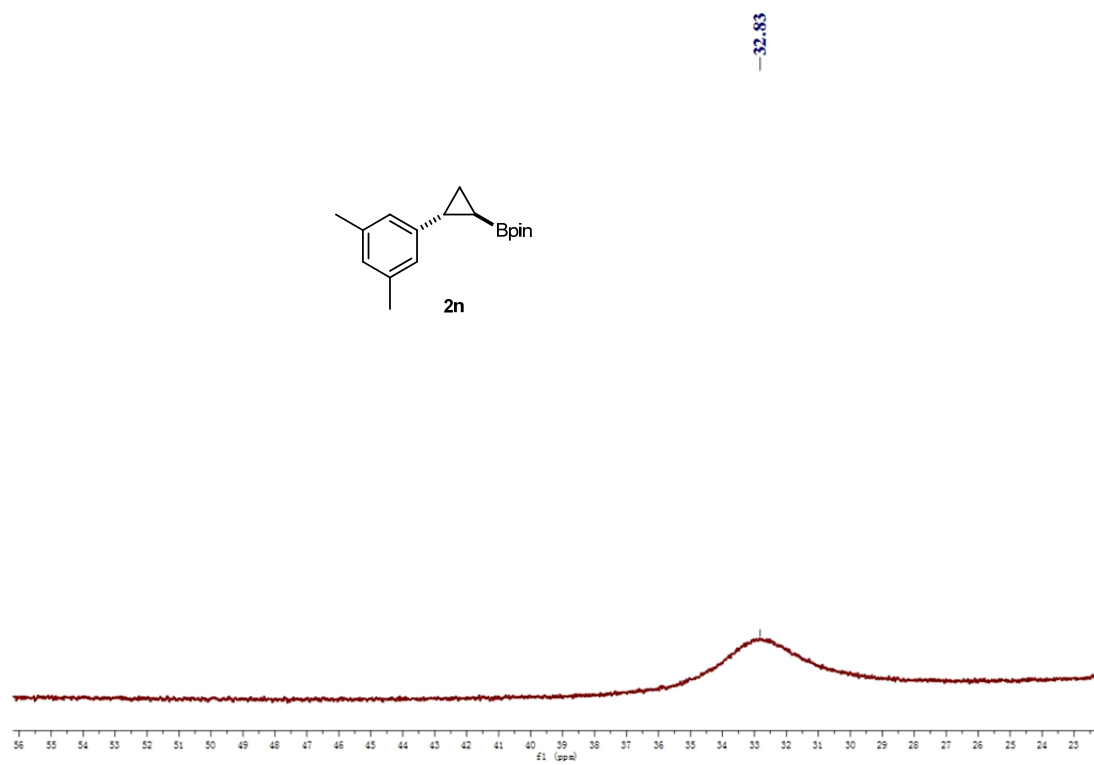
¹H NMR spectrum (CDCl₃) showing peaks and integration values:

Chemical Shift (ppm)	Integration
7.26	1.09
6.78, 6.71	2.04
2.27	6.13
2.07	1.01
1.93	12.13
1.11	1.08
1.01	1.04
0.99, 0.97, 0.96	1.00
0.29, 0.28, 0.27, 0.27, 0.26, 0.25	-

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



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



Chemical structure of **2o** is shown above the spectrum.

¹H NMR spectrum (CDCl₃) of compound **2o** is displayed below the structure. The x-axis represents the chemical shift in ppm (δ), ranging from 0.0 to 9.0. The spectrum shows several peaks, with integrations provided for the main signals.

Peak list (ppm): 7.26, 6.92, 6.77, 6.76, 6.75, 6.74, 6.73, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 2.30, 2.29, 2.27, 2.25, 1.25, 1.20, 1.18, 1.03, 0.98, 0.28, 0.27, 0.26, 0.25, 0.24.

Integration values: 1.05, 1.00, 1.00, 1.02, 12.13, 1.00, 1.00, 1.00.

Chemical structure of **2o** is shown above the spectrum. The structure is 1-(4,6-difluorophenyl)ethynylcyclopropane.

13C NMR peaks (ppm):

- 160.24, 160.22, 159.09, 159.07, 157.85, 157.83, 156.70, 156.67
- 132.54, 132.46, 132.38, 132.30
- 116.11, 112.95, 112.86, 112.44, 112.39, 112.19, 112.15
- 83.51, 77.48, 77.16, 76.84
- 24.87, 24.84, 24.28, 15.23, 13.82, -5.21

Chemical structure of compound **2o** is shown above the spectrum. The structure is 1-(2,4-difluorophenyl)ethane-1,2-diol, where the phenyl ring is substituted with fluorine atoms at the 2 and 4 positions, and the ethane-1,2-diol group is attached to the 1 position.

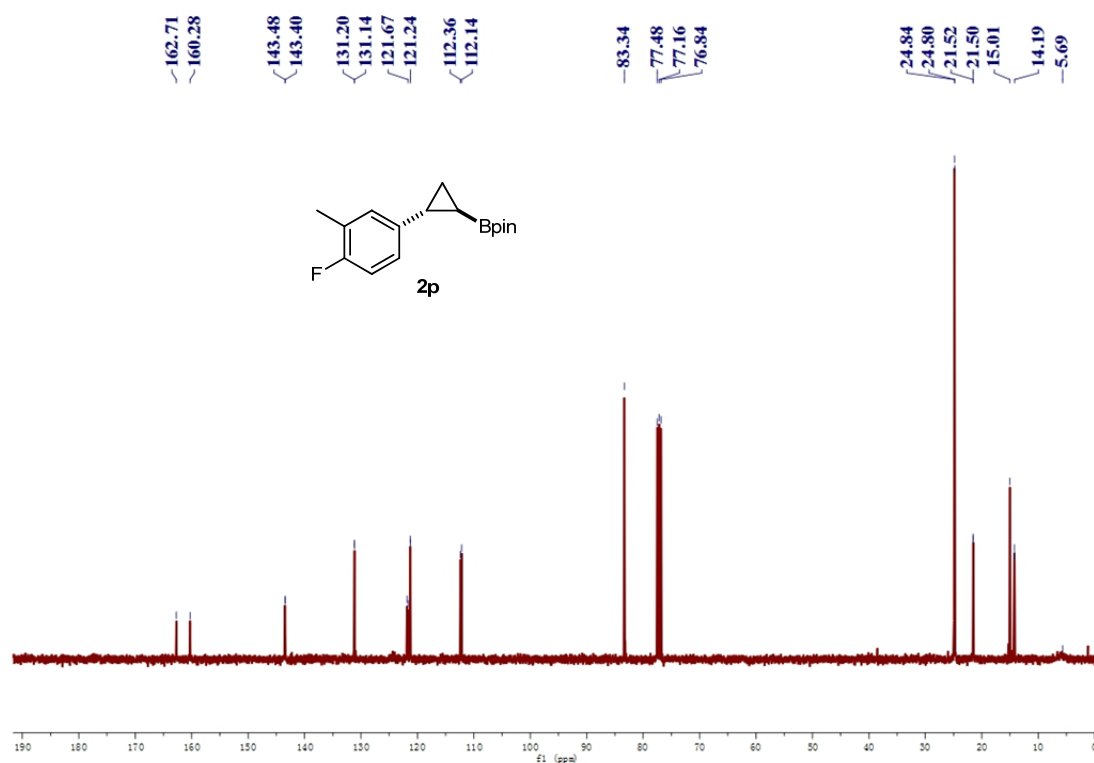
Chemical structure of compound **2p** is shown above the spectrum. The structure is 1-(4-fluorophenyl)-2-methylcyclopropylboronic pinacol ester.

¹H NMR spectrum (CDCl₃) of compound **2p** is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from -0.5 to 9.0. The spectrum shows several peaks corresponding to the protons in the molecule.

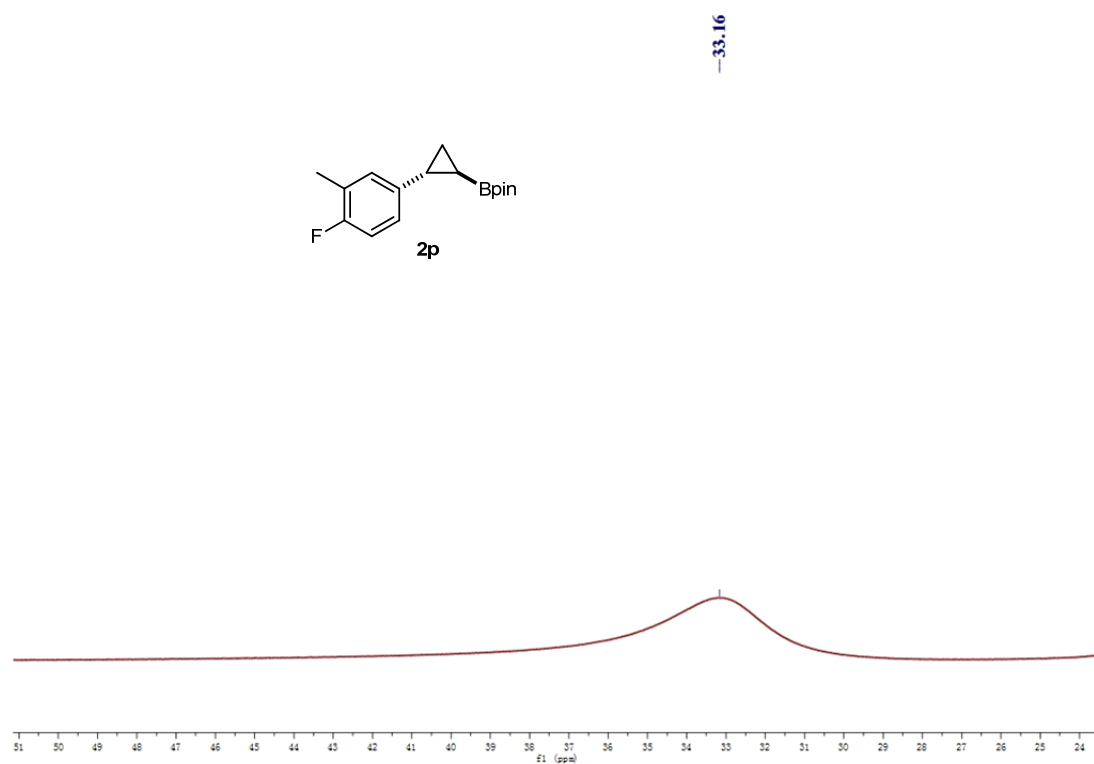
Key peaks and integrations are labeled:

- Aromatic protons (multiplet, 6.69–7.04 ppm): Integration values 1.05, 1.02, 0.99.
- Methine proton (doublet, ~2.1 ppm): Integration values 3.11, 1.04.
- Cyclopropyl methyl group (doublet, ~1.1 ppm): Integration values 12.14, 1.05, 1.11.
- Bpin group (large singlet, ~1.0 ppm): Integration value 1.00.
- Bpin group (smaller doublet, ~0.2 ppm): Integration value 1.00.

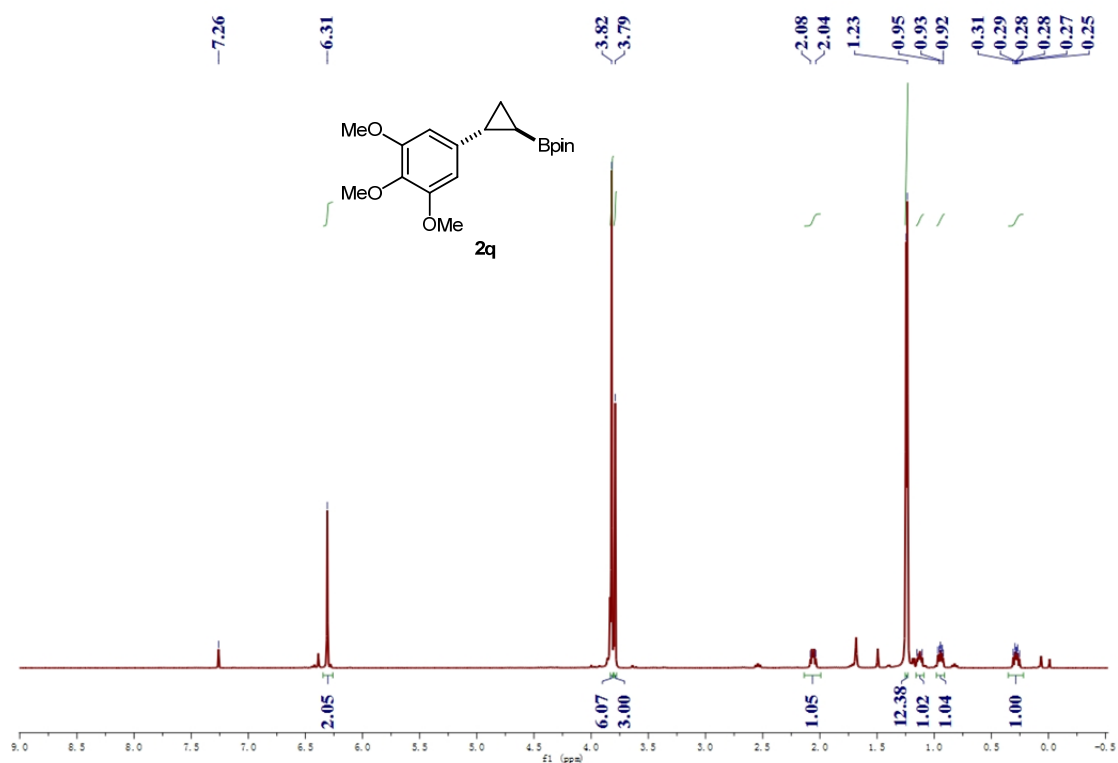
^{13}C NMR (100 MHz, CDCl_3) (**2p**)



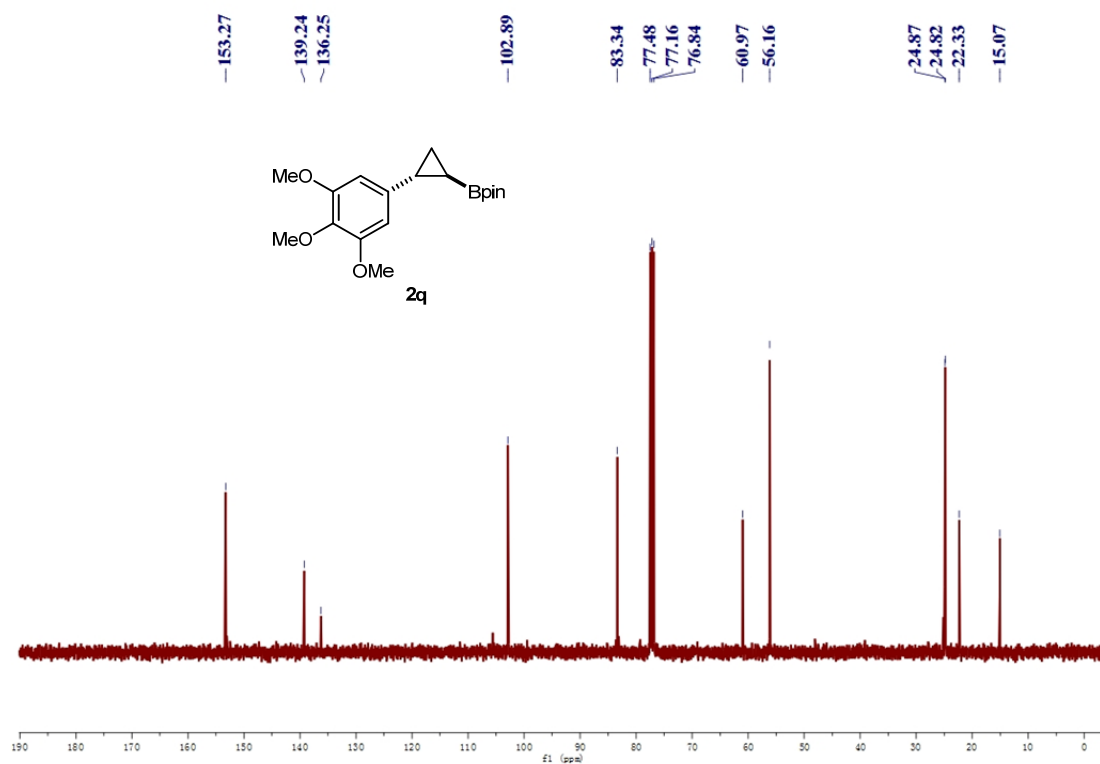
^{11}B NMR (128 MHz, CDCl_3) (**2p**)



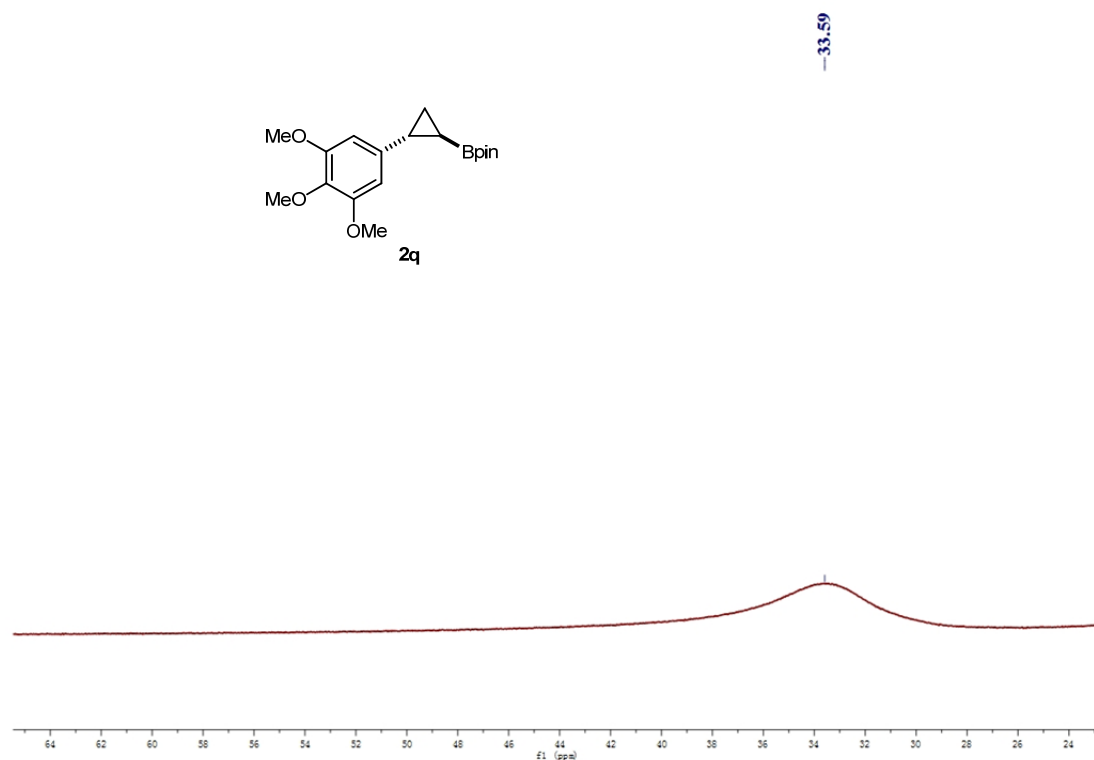
^1H NMR (400 MHz, CDCl_3) (**2q**)



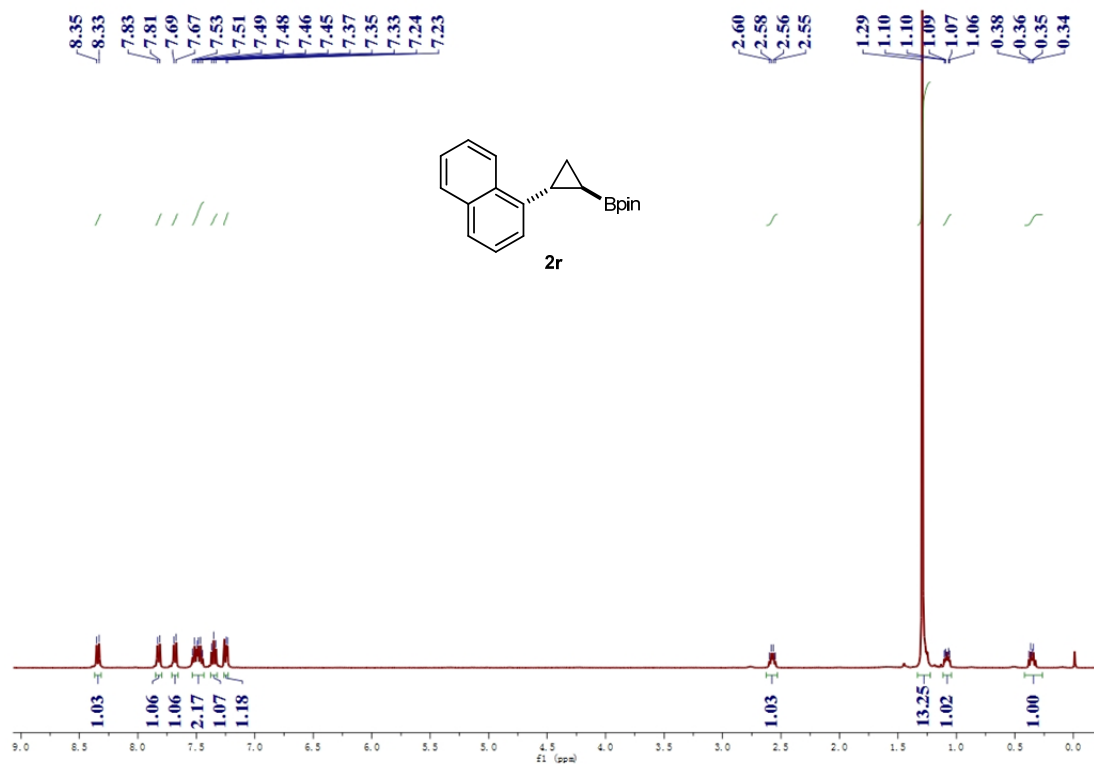
^{13}C NMR (100 MHz, CDCl_3) (**2q**)



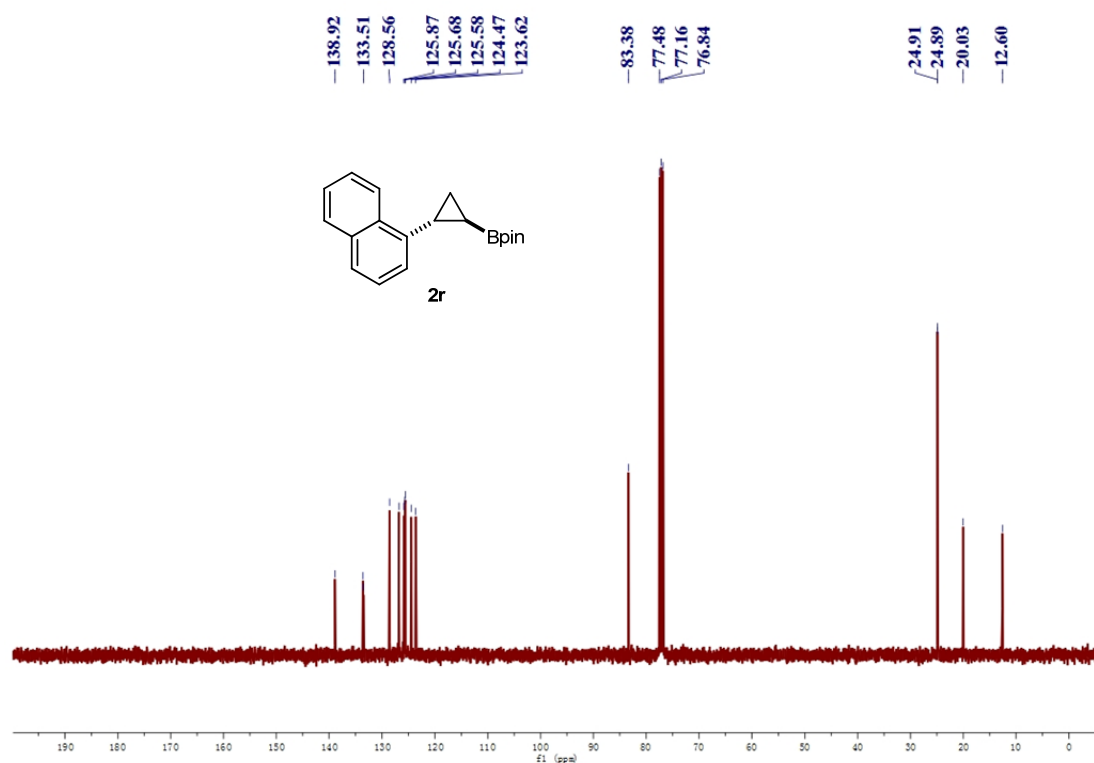
^{11}B NMR (128 MHz, CDCl_3) (**2q**)



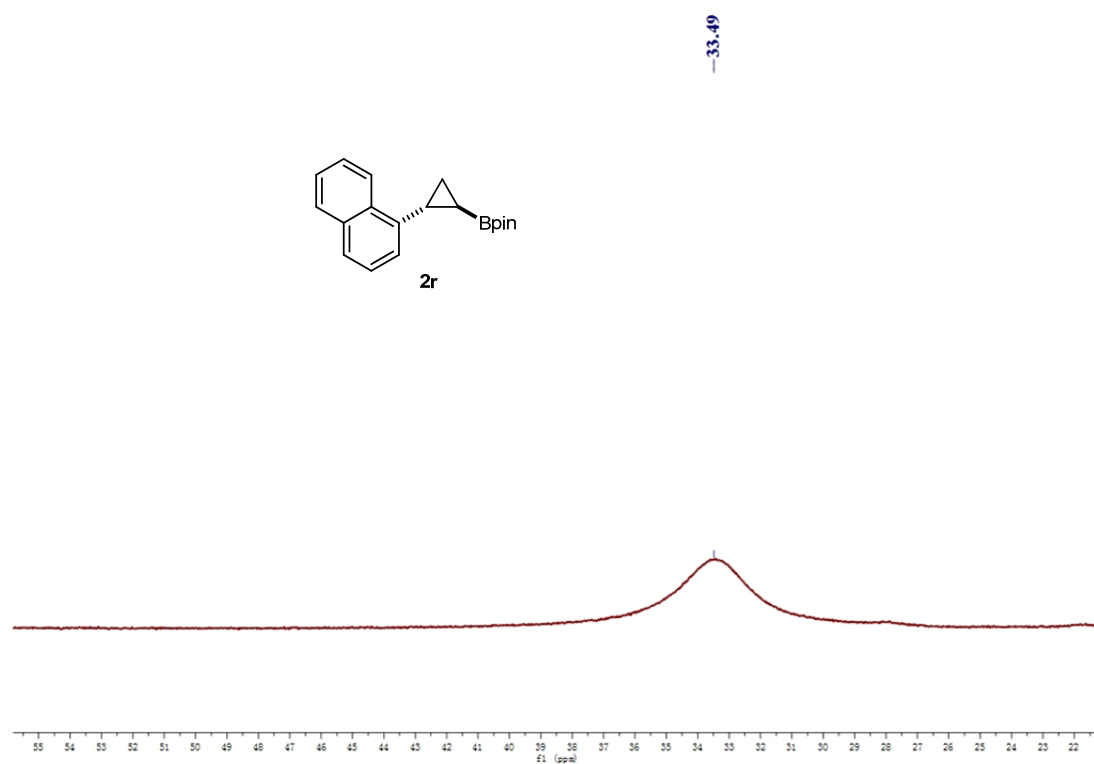
^1H NMR (400 MHz, CDCl_3) (**2r**)



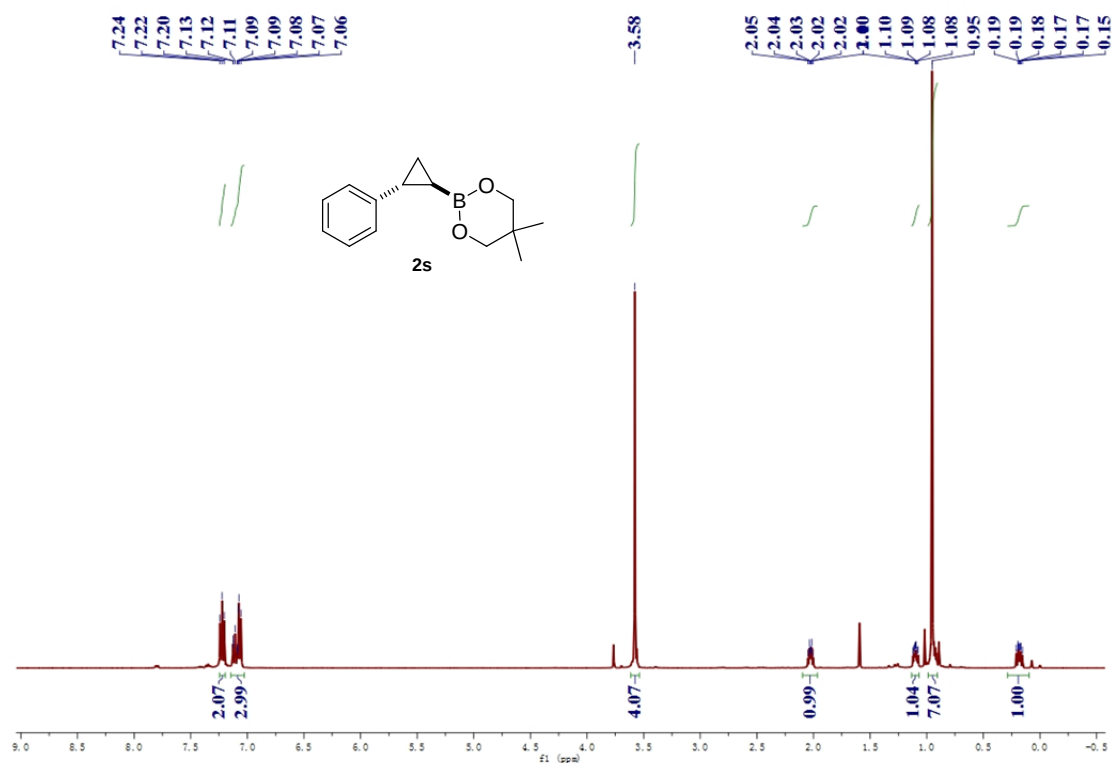
^{13}C NMR (100 MHz, CDCl_3) (**2r**)



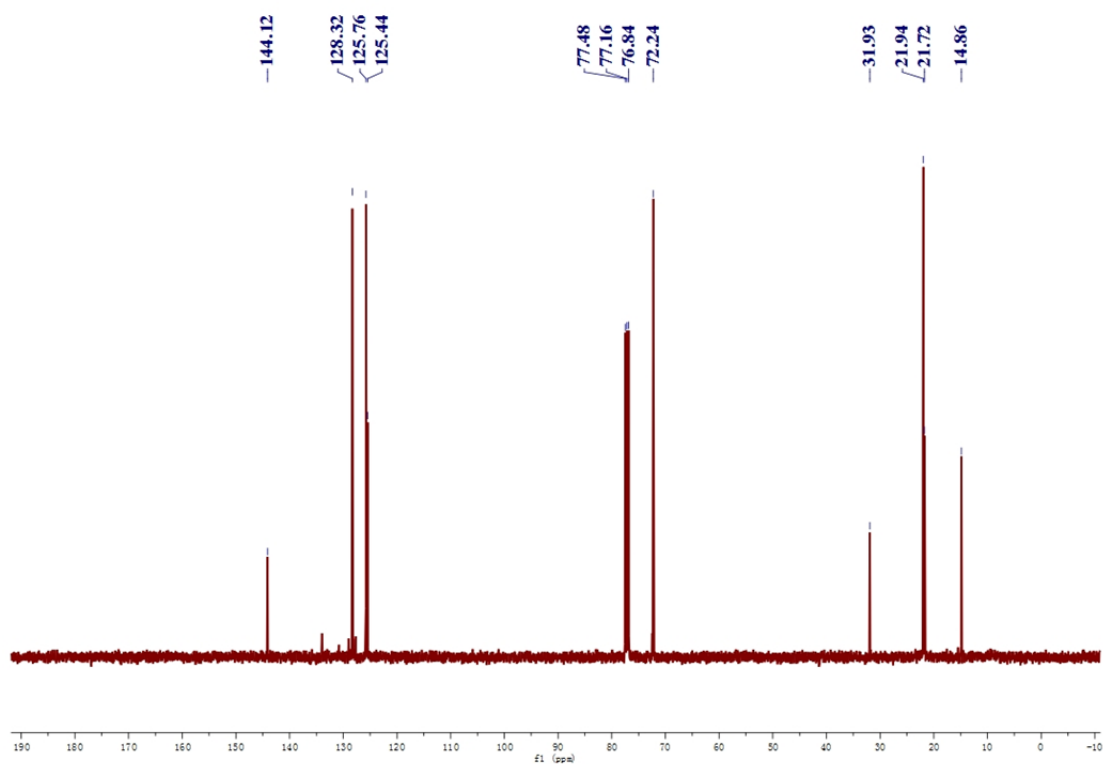
^{11}B NMR (128 MHz, CDCl_3) (**2r**)



^1H NMR (400 MHz, CDCl_3) (2s)



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



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

—33.18

