Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light Photoredox Catalysis-Enabled Borocyclo-propanation of Alkenes

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1. General information

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on Merk TLC silica gel 60 F_{254} (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating using hot air gun. Blue LED (30 W) and CFL (26 W) were used as visible light sources.

Proton, carbon and fluorine nuclear magnetic resonance spectra (^1H, ^{13}C, and ^{19}F NMR were recorded on a Bruke-400M Advance III (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, 77.0 ppm). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were obtained with Bruker impact II QTOF (ESI or APCI).

All the commercially available materials were used without further purification. $[Ru(phen)_3](PF_6)_2$ was purchased from TCI Shanghai, N,N-Diisopropylethylamine (DIPEA) and other anhydrous solvents (CH_3CN, DCM, Acetone, DMSO, DMF and DCE) were purchased from Beijing Innochem Science & Technology Company Ltd.

Unactivated olefins were purchased from Beijing Innochem Science & Technology Company Ltd. and used as received or were prepared by a Wittig reaction. 2-(diiodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized according to the literature precedents.

Flash chromatography was performed with Haiyang Chem silica gel 60 (300-400 mesh). Thin layer chromatography was carried out using CCIS TLC Silica gel 60 F_{254}.

2. Starting materials

Unactivated olefins were synthesized using Wittig olefination[1]. 2-(diiodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was synthesized according to the literature procedure[2].

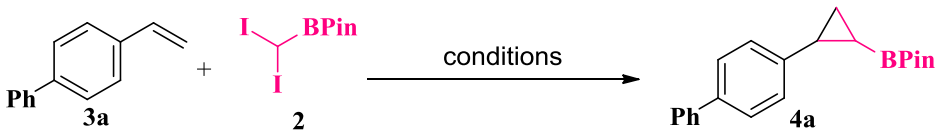
3. General procedure for visible light mediated borocyclopropanation reaction

***General Procedure*:** An oven-dried Schlenk tube containing a stirring bar was charged with unactivated olefins (0.2 mmol, 1.0 eq.), $I_2CHBPin$ (0.4 mmol, 2.0 eq.) and $[Ru(phen)_3](PF_6)_2$ (1 mol %), the tube was evacuated and back-filled with nitrogen for three times. Then DCM (2.0 ml) and DIPEA (0.6 mmol, 3.0 eq.) were added. The reaction mixture was irradiated with visible light for 15 h at room

temperature. The mixture was diluted with EtOAc (3.0 mL), concentrated under reduced pressure and purified by column chromatography on silica gel to afford the corresponding borocyclopropanated product.

4. Optimization studies

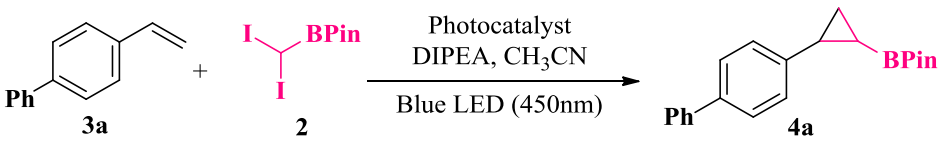
Table S1: Control experiments[a].



Entry	Photocatalyst	Base	Light	Yield/%[b]
1	$[Ru(phen)_3](PF_6)_2$	DIPEA	Blue LED (450nm)	84
2	-	DIPEA	Blue LED (450nm)	45
3	$[Ru(phen)_3](PF_6)_2$	-	Blue LED (450nm)	0
4	-	-	Blue LED (450nm)	0
5	$[Ru(phen)_3](PF_6)_2$	DIPEA	CFL	0
6	$[Ru(phen)_3](PF_6)_2$	DIPEA	-	0

[a] Reaction conditions: **3a** (0.1 mmol), **2** (0.2 mmol), $[Ru(phen)_3](PF_6)_2$ (1 mol%), DIPEA (0.5 mmol), CH_3CN (1.0 mL) for 15 h. [b] Isolated yields.

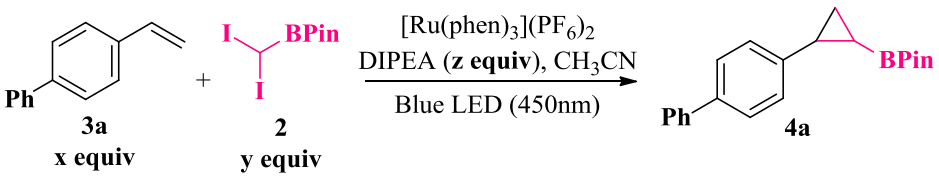
Table S2: Optimization of photocatalysts[a].



Entry	Photocatalyst	Yield/%[b]
1	$[Ru(phen)_3](PF_6)_2$	84
2	$[Ru(bpy)_3]Cl_2$	72
3	$[Ru(bpy)_3](PF_6)_2$	75
4[c]	Xanthone	50

[a] Reaction conditions: **3a** (0.1 mmol), **2** (0.2 mmol), Photocatalyst (1 mol%), DIPEA (0.5 mmol), CH_3CN (1.0 mL) for 15 h. [b] Isolated yields. [c] 5 mol%

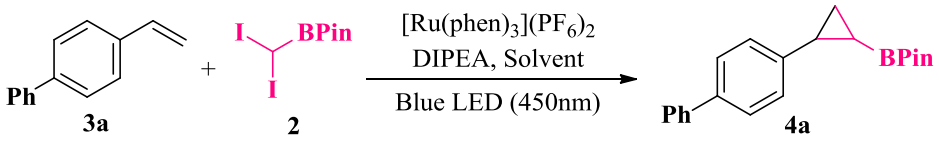
Table S3: Optimization of stoichiometry[a].



Entry	3a (x)	2 (y)	DIPEA (z)	Yield/%[b]
1	1	1	3	39
2	1	1.5	3	64
3	1	2	3	84
4	1	2.5	3	89
5	1	2	2	74
6	1	2	4	87
7	1	2	5	85

[a] Reaction conditions: **3a** (0.1 mmol), **2** (0.1-0.25 mmol), $[Ru(phen)_3](PF_6)_2$ (1 mol%), DIPEA (0.2-0.5 mmol), CH_3CN (1.0 mL) for 15 h. [b] Isolated yields.

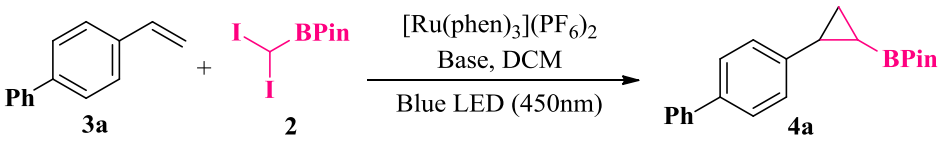
Table S4: Optimization of solvents[a].



Entry	Solvent	Yield/%[b]
1	CH_3CN	84
2	DCE	49
3	DCM	87
4	Acetone	33
5	DMF	49
6	DMSO	22

[a] Reaction conditions: **3a** (0.1 mmol), **2** (0.2 mmol), $[Ru(phen)_3](PF_6)_2$ (1 mol%), DIPEA (0.3 mmol), Solvent (1.0 mL) for 15 h. [b] Isolated yields.

Table S5: Optimization of bases[a].

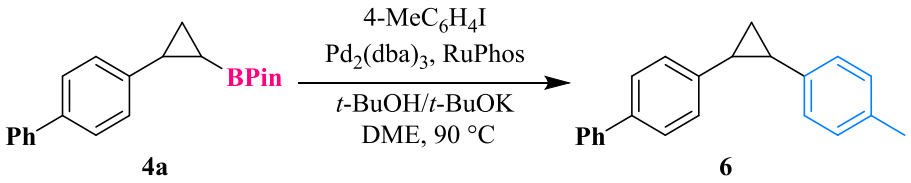


Entry	Base	Yield/%[b]
1	DIPEA	83
2	TEA	33
3	DIPA	49
4	DMAP	NR

[a] Reaction conditions: **3a** (0.1 mmol), **2** (0.2 mmol), $[Ru(phen)_3](PF_6)_2$ (1 mol%), Base (0.3 mmol), DCM (1.0 mL) for 15 h. [b] Isolated yields.

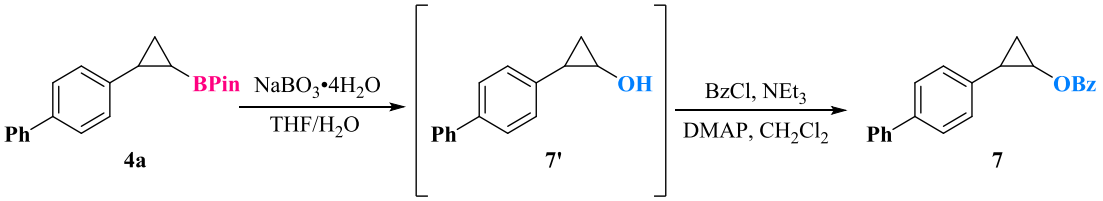
5. Functionalization of the C-B bond

Toward the synthesis of 4-(2-(p-tolyl)cyclopropyl)-1,1'-biphenyl[3].



An oven-dried Schlenk tube containing a stirring bar was charged with $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol), dicyclohexyl (2',6'-diisopropoxy-[1,1'-biphenyl]-2-yl) phosphine (RuPhos) (4.1 mg, 10 μmol), *t*-BuOK (44.9 mg, 0.40 mmol), 4-iodotoluene (65.4 mg, 0.30 mmol), *t*-BuOH (0.40 mL), and dissolved in DME (1.2 mL). The mixture was added borylcyclopropane **4a** (32 mg, 0.10 mmol) stirred at 90 ℃ overnight. The mixture was then allowed to warm to room temperature, the mixture was diluted with EtOAc (3.0 mL), concentrated under reduced pressure and purified by column chromatography on silica gel to afford the corresponding final product **6** as a colorless oil with 66% yield.

Toward the synthesis of 2- ([1,1'-biphenyl]-4-yl) cyclopropyl benzoate[4].

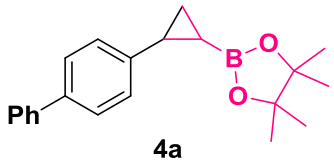


$NaBO_3$ ·$4H_2O$ (4 equiv) was added to a solution of borylcyclopropane **4a** (64 mg, 0.2 mmol) in THF/H_2O (1:1). The reaction mixture was stirred overnight at room temperature and then quenched with H_2O and extracted with Et_2O (x3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and

concentrated in vacuum to afford compound **7′**. This compound was used in the next step without further purification.

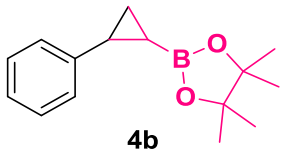
To a solution of alcohol **7′** in CH_2Cl_2, 4-dimethylaminopyridine (DMAP) (27 mol%), triethylamine (3.0 eq.) and benzyl chloride (2.0 eq.) were added. The reaction mixture was stirred for 30 min at room temperature and then quenched with H_2O. The aqueous layer was extracted with Et_2O (x3) and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure and purified by column chromatography on silica gel to afford the corresponding product **7** in 60% yield (two steps) as a colorless oil.

6. Characterization data



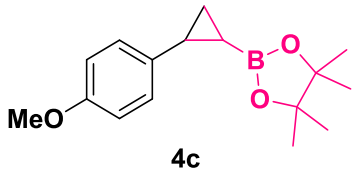
4a

2-[-2-[1,1'-Biphenyl]-4-ylcyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[5]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.7:1 *trans:cis*), colorless oil (isolated yield: 87%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.43 (m, *J* = 8.0 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.20 – 7.16 (d, 2H), 2.18 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H), 1.26 – 1.22 (m, 1H), 1.11 – 1.06 (m, 1H), 0.38 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 1.5 Hz, 2H), 7.45 (s, 2H), 7.44 (d, *J* = 1.4 Hz, 2H), 7.33 – 7.29 (m, 3H), 2.40 (ddd, *J* = 10.2, 7.8, 5.9 Hz, 1H), 1.18 (t, *J* = 3.4 Hz, 1H), 1.03 (s, 6H), 0.90 (s, 6H), 0.49 (td, *J* = 9.6, 7.2 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



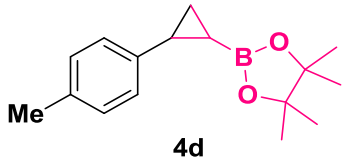
4b

(4,4,5,5-tetramethyl-2-(-2-phenylcyclopropyl)-1,3,2-dioxaborolane[6]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (3.5:1 *trans:cis*), colorless oil (isolated yield: 71%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 2H), 7.16 – 7.12 (m, 1H), 7.10 – 7.06 (m, 2H), 2.10 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.16 (ddd, *J* = 8.0, 6.8, 3.7 Hz, 1H), 0.99 (ddd, *J* = 5.4, 3.8 Hz, 1H), 0.30 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (m, 2H), 7.11 (m, 1H), 7.07 (m, 2H), 2.39 – 2.31 (m, 1H), 1.11 – 1.08 (m, 1H), 1.01 (s, 6H), 0.88 (s, 6H), 0.44 (ddd, *J* = 10.1, 9.2, 7.2 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



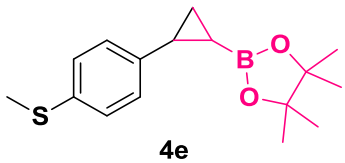
4c

2-(-2-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane[7]. Product in accordance with literature characterization data. **Rf** = 0.2 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.8:1 *trans:cis*), colorless oil (isolated yield: 68%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 – 6.99 (m, 2H), 6.81 – 6.78 (m, 2H), 3.77 (s, 3H), 2.06 (dd, *J* = 8.2, 5.5 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.13 – 1.09 (m, 1H), 0.96 – 0.91 (m, 1H), 0.22 (ddd, *J* = 9.8, 6.7, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (m, *J* = 8.6 Hz, 2H), 6.77 (m, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.29 (ddd, *J* = 10.1, 7.9, 6.0 Hz, 1H), 1.21 – 1.19 (m, 1H), 1.08 – 1.05 (m, 1H), 1.03 (s, 6H), 0.90 (s, 6H), 0.39 (td, *J* = 9.6, 7.1 Hz, 1H).



4d

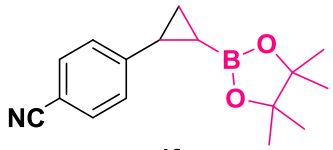
4,4,5,5-tetramethyl-2-(-2-(p-tolyl)cyclopropyl)-1,3,2-dioxaborolane[7]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (3.9:1 *trans:cis*), colorless oil (isolated yield: 66%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.04 (m, 2H), 7.01 – 6.90 (m, 2H), 2.30 (s, 3H), 2.12 – 2.04 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.17 – 1.12 (m, 1H), 1.02 – 0.95 (m, 1H), 0.34 – 0.23 (m, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.03 (m, *J* = 7.7 Hz, 2H), 6.88 (m, *J* = 7.7 Hz, 2H), 2.29 (s, 3H), 2.10 (d, *J* = 5.6 Hz, 1H), 1.08 (dd, *J* = 8.1, 4.4 Hz, 1H), 1.05 – 1.02 (m, 6H), 0.91 (d, *J* = 3.5 Hz, 6H), 0.48 – 0.37 (m, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4e

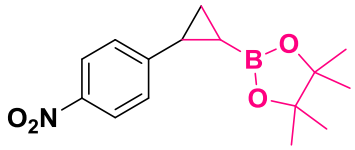
4,4,5,5-tetramethyl-2-(-2-(4-(methylthio)phenyl)cyclopropyl)-1,3,2-Dioxaborolan e[8]. Product in accordance with literature characterization data. **Rf** = 0.6 (PE/EtOAc 10:1). A mixture of diastereoisomers (3.6:1 *trans:cis*), colorless oil (isolated yield: 60%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.15 (m, 2H), 7.03 – 6.98 (m, 2H), 2.45 (s, 3H), 2.07 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.14 (ddd, *J* = 8.0, 6.8, 3.6 Hz, 1H), 0.97 (ddd, *J* = 9.4, 5.3, 3.7 Hz, 1H), 0.26 (ddd, *J* = 9.8, 6.8, 5.6 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 (m, 2H), 7.15 (m, 2H), 2.44 (s, 3H), 2.30 (ddd, *J* = 10.4, 8.0, 6.1 Hz, 1H), 1.09 (ddd, *J* = 9.2, 4.6, 3.2 Hz, 1H), 1.03 (s, 6H), 0.90 (s, 6H), 0.43 (ddd, *J* = 10.1, 9.3, 7.2 Hz, 1H), one of the H of

the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



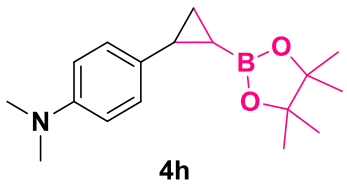
4f

4-(-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile[8]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 10:1). A mixture of diastereoisomers (2.6:1 *trans:cis*), yellow oil (isolated yield: 46%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.49 (m, 2H), 7.14 – 7.10 (m, 2H), 2.11 (dt, *J* = 8.0, 5.3 Hz, 1H), 1.31 (ddd, *J* = 7.8, 6.2, 4.5 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.08 – 1.03 (m, 1H), 0.35 (ddd, *J* = 9.8, 7.0, 5.4 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 2.35 (ddd, *J* = 10.1, 7.7, 6.0 Hz, 1H), 1.19 (m, 1H), 1.01 (s, 6H), 0.89 (s, 6H), 0.54 (td, *J* = 9.7, 7.4 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4g

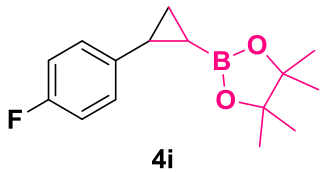
4,4,5,5-tetramethyl-2-(-2-(4-nitrophenyl)cyclopropyl)-1,3,2-dioxaborolane[8]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 10:1). A mixture of diastereoisomers (2.3:1 *cis:trans*), yellow oil (isolated yield: 55%). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 – 8.07 (m, 2H), 7.44 – 7.39 (m, 2H), 2.40 (ddd, *J* = 10.3, 7.5, 5.9 Hz, 1H), 1.37 – 1.33 (m, 1H), 1.14 – 1.06 (m, 1H), 1.03 (s, 6H), 0.91 (s, 6H), 0.59 (td, *J* = 9.8, 7.5 Hz, 1H). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (m, 2H), 7.19 – 7.14 (m, 2H), 2.18 (dt, *J* = 8.2, 5.3 Hz, 1H), 1.32 – 1.29 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.41 (ddd, *J* = 10.0, 7.1, 5.5 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4h

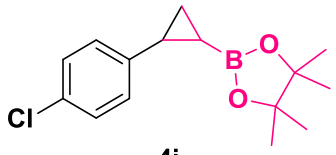
N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl) -aniline. Rf = 0.6 (PE/EtOAc 10:1). A mixture of diastereoisomers (7.5:1 *trans:cis*), yellow oil (isolated yield: 69%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.03 – 6.97 (m, 2H), 6.71 – 6.67 (m, 2H), 2.89 (s, 6H), 2.05 (dt, *J* = 8.3, 5.5 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.11 – 1.07 (m, 1H), 0.94 (dd, *J* = 5.6, 3.8 Hz, 1H), 0.21 (ddd, *J* = 9.7, 6.6, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (m, 2H), 6.66 (m, 2H), 2.88 (s, 6H), 2.31 – 2.24 (m, 1H), 1.06 (m, 1H), 1.05 (s, 6H), 0.91 (s, 6H),

0.36 (td, *J* = 9.6, 7.2 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer. **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.08, 131.50, 126.60, 113.19, 83.04, 41.06, 24.78, 24.70, 21.23, 14.34, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{17}H_{26}BNO_2$ $[M+H]^+$: 288.2129, found: 288.2129.



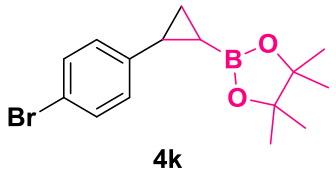
4i

2-(2-(4-fluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[9].
Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.8:1 *trans:cis*), colorless oil (isolated yield: 65%). ***Trans:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.06 – 6.99 (m, 2H), 6.93 – 6.89 (m, 2H), 2.08 (dt, *J* = 8.1, 5.5 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.17 – 1.12 (m, 1H), 0.94 (ddd, *J* = 9.4, 5.3, 3.8 Hz, 1H), 0.23 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ***Cis:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 2H), 6.94 (d, *J* = 2.3 Hz, 2H), 2.31 (ddd, *J* = 10.1, 7.6, 5.8 Hz, 1H), 1.09 (ddd, *J* = 7.9, 4.2, 2.0 Hz, 1H), 1.03 (s, 6H), 0.90 (s, 6H), 0.46 – 0.38 (m, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4j

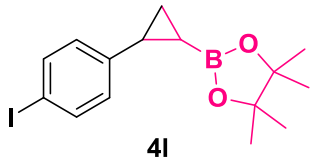
2-(2-(4-chlorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[5].
Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.7:1 *trans:cis*), colorless oil (isolated yield: 56%). ***Trans:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 2.6 Hz, 2H), 7.00 (dd, *J* = 8.2, 1.7 Hz, 2H), 2.07 (dt, *J* = 8.0, 5.3 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.16 (ddd, *J* = 8.1, 6.9, 3.7 Hz, 1H), 0.96 (ddd, *J* = 9.4, 5.3, 3.8 Hz, 1H), 0.25 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ***Cis:*^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.20 (s, 2H), 6.99 (d, *J* = 1.9 Hz, 2H), 2.29 (ddd, *J* = 10.1, 7.9, 6.0 Hz, 1H), 1.13 – 1.07 (m, 1H), 1.03 (s, 6H), 0.91 (s, 6H), 0.45 (td, *J* = 9.7, 7.2 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4k

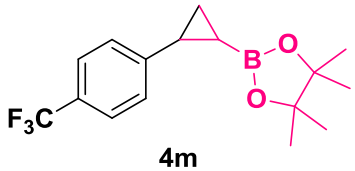
2-(2-(4-bromophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[5].
Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.0:1 *trans:cis*), colorless oil (isolated yield: 56%).

Trans: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 3.4 Hz, 2H), 6.96 – 6.92 (m, 2H), 2.08 – 2.02 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.19 – 1.13 (m, 1H), 0.96 (ddd, *J* = 9.4, 5.2, 3.8 Hz, 1H), 0.25 (ddd, *J* = 9.8, 6.9, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 3.4 Hz, 2H), 7.16 – 7.12 (m, 2H), 2.28 (ddd, *J* = 10.2, 7.8, 6.0 Hz, 1H), 1.13 – 1.07 (m, 1H), 1.04 (s, 6H), 0.91 (s, 6H), 0.45 (td, *J* = 9.7, 7.3 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



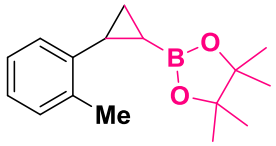
4l

2-(2-(4-iodophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (1.6:1 *trans:cis*), colorless oil (isolated yield: 45%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.5 Hz, 2H), 6.84 – 6.79 (m, 2H), 2.03 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.16 (ddd, *J* = 8.0, 6.8, 3.7 Hz, 1H), 0.96 (ddd, *J* = 9.3, 5.2, 3.8 Hz, 1H), 0.25 (ddd, *J* = 9.9, 6.9, 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.26, 137.18, 127.81, 90.08, 83.29, 24.75, 24.71, 21.50, 15.08, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 2.4 Hz, 2H), 7.04 – 7.00 (m, 2H), 2.27 (ddd, *J* = 10.2, 7.9, 6.0 Hz, 1H), 1.12 – 1.08 (m, 1H), 1.03 (s, 6H), 0.91 (s, 6H), 0.45 (td, *J* = 9.7, 7.3 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.67, 136.61, 130.98, 90.55, 83.08, 24.82, 24.37, 21.42, 9.18, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{15}H_{20}BIO_2$ $[M+Na]^+$: 393.0493, found: 393.0492.



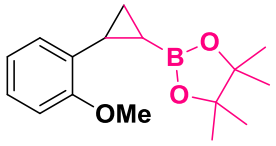
4m

4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)-1,3,2-dioxaborolane[6]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.3:1 *trans:cis*), colorless oil (isolated yield: 33%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.14 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.23 – 1.19 (m, 1H), 1.07 – 1.02 (m, 1H), 0.34 (ddd, *J* = 9.9, 6.9, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.38 (dt, *J* = 9.4, 6.9 Hz, 1H), 1.19 – 1.14 (m, 1H), 1.01 (s, 6H), 0.87 (s, 6H), 0.51 (td, *J* = 9.7, 7.3 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



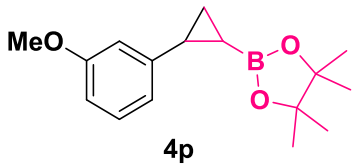
4n

4,4,5,5-tetramethyl-2-(2-(o-tolyl)cyclopropyl)-1,3,2-dioxaborolane[5]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (4.9:1 *trans:cis*), colorless oil (isolated yield: 73%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 – 7.08 (m, 3H), 7.01 (m, 1H), 2.42 (s, 3H), 2.11 (dt, *J* = 8.2, 5.8 Hz, 1H), 1.28 (s, 12H), 1.18 – 1.13 (m, 1H), 1.03 (ddd, *J* = 9.3, 5.6, 3.5 Hz, 1H), 0.17 (dt, *J* = 9.6, 6.3 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.14 (m, 3H), 7.01 (m, 1H), 2.43 (s, 3H), 2.27 – 2.18 (m, 1H), 1.12 – 1.08 (m, 1H), 1.00 (s, 6H), 0.79 (s, 6H), 0.53 (ddd, *J* = 10.1, 9.1, 6.9 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4o

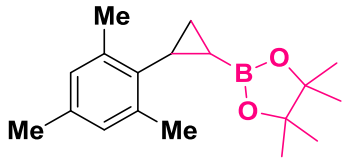
2-(2-(2-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[10]. Product in accordance with literature characterization data. **Rf** = 0.2 (PE/EtOAc 50:1). A mixture of diastereoisomers (6.0:1 *trans:cis*), colorless oil (isolated yield: 69%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 – 7.09 (m, 1H), 6.89 – 6.81 (m, 3H), 3.84 (s, 3H), 2.37 (dt, *J* = 8.2, 5.7 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.13 (ddd, *J* = 8.2, 6.6, 3.4 Hz, 1H), 0.96 (ddd, *J* = 9.3, 5.5, 3.4 Hz, 1H), 0.25 (dt, *J* = 9.6, 6.2 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 – 7.09 (m, 1H), 6.89 – 6.81 (m, 3H), 3.84 (s, 3H), 1.09 – 1.04 (m, 1H), 0.99 (s, 6H), 0.92 – 0.86 (m, 1H), 0.84 (s, 6H), 0.48 (td, *J* = 9.7, 7.1 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4p

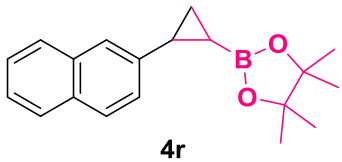
2-(2-(3-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[6]. Product in accordance with literature characterization data. **Rf** = 0.2 (PE/EtOAc 50:1). A mixture of diastereoisomers (3.4:1 *trans:cis*), colorless oil (isolated yield: 68%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (m, 1H), 6.68 (m, 2H), 6.63 (m, 1H), 3.78 (s, 3H), 2.09 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.15 (ddd, *J* = 8.0, 6.8, 3.7 Hz, 1H), 1.02 – 0.97 (m, 1H), 0.31 (ddd, *J* = 9.7, 6.8, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 – 7.10 (m, 2H), 6.88 (m, 1H), 6.83 (m, 1H), 3.79 (s, 3H), 2.33 (ddd, *J* = 10.2, 7.8, 5.9 Hz, 1H), 1.11 – 1.07 (m, 1H), 1.03 (s, 6H), 0.92 (s, 6H), 0.44 (td, *J* = 9.7, 7.3 Hz, 1H), one of the H of the cyclopropane ring

was not detected due to superposition with the methyl groups of the major diastereoisomer.



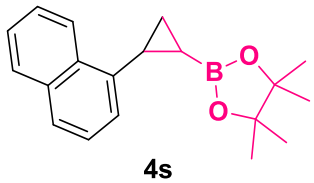
4q

2-(2-mesitylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[8]. Product in accordance with literature characterization data. **Rf** = 0.3 (PE/EtOAc 50:1). A mixture of diastereoisomers (1.1:1 *trans:cis*), colorless oil (isolated yield: 60%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.82 (s, 2H), 2.37 (s, 6H), 2.25 (s, 3H), 1.88 (q, *J* = 6.7 Hz, 1H), 1.28 (s, 12H), 1.21-1.22 (m, 1H), 0.91 – 0.88 (m, 1H), 0.06 – 0.02 (m, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.74 (s, 2H), 2.38 (s, 6H), 2.22 (s, 3H), 2.03 (q, *J* = 8.1 Hz, 1H), 1.23-1.24 (m, 1H), 1.05 (s, 6H), 0.88 – 0.86 (m, 1H), 0.83 (s, 6H), 0.49 (td, *J* = 9.4, 6.6 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer.



4r

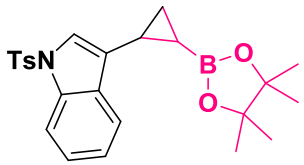
4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)cyclopropyl)-1,3,2-dioxaborolane. Rf = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (4.1:1 *trans:cis*), colorless oil (isolated yield: 59%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 3H), 7.57 (s, 1H), 7.50 – 7.34 (m, 3H), 2.29 (dt, *J* = 8.1, 5.4 Hz, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 1.24 (dd, *J* = 4.4, 3.1 Hz, 1H), 1.13 (ddd, *J* = 9.2, 5.2, 3.6 Hz, 1H), 0.44 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (m, 3H), 7.58 (s, 1H), 7.18 (m, 3H), 2.50 (ddd, *J* = 10.3, 7.6, 5.8 Hz, 1H), 1.43 (dd, *J* = 6.0, 2.4 Hz, 1H), 1.21 – 1.18 (m, 1H), 0.95 (s, 6H), 0.77 (s, 6H), 0.54 (td, *J* = 9.6, 7.2 Hz, 1H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.84, 133.52, 132.00, 127.86, 127.56, 127.26, 125.95, 124.92, 124.36, 124.15, 83.23, 82.93, 29.70, 24.76, 24.74, 24.32, 22.17, 22.03, 14.88, 9.31.the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{19}H_{23}BO_2$ $[M+H]^+$: 295.1864, found: 295.1866.



4s

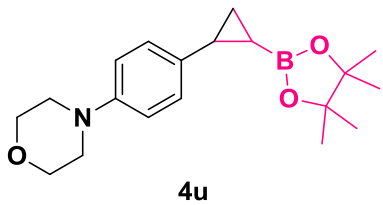
4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)cyclopropyl)-1,3,2-dioxaborolane[8]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.9:1 *trans:cis*), colorless oil (isolated yield: 63%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.86 (dd,

J = 8.0, 1.5 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.56 (dd, *J* = 6.8, 1.5 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.40 – 7.35 (m, 1H), 7.29 (dt, *J* = 7.1, 1.2 Hz, 1H), 2.62 (dt, *J* = 8.1, 5.9 Hz, 1H), 1.33 (s, 12H), 1.29 (q, *J* = 3.2 Hz, 1H), 1.12 (ddd, *J* = 9.4, 5.7, 3.4 Hz, 1H), 0.40 (dt, *J* = 9.6, 6.2 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 – 8.41 (m, 1H), 7.82 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.41 (d, *J* = 2.3 Hz, 2H), 2.75 – 2.68 (m, 1H), 1.43 (td, *J* = 6.3, 3.9 Hz, 1H), 1.28 – 1.25 (m, 1H), 0.74 (s, 6H), 0.49 (s, 6H), one of the H of the cyclopropane ring was not detected due to superposition with one of the methyl groups.



4t

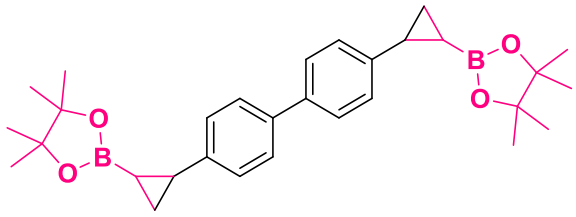
3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-1-tosyl-1H-indole. Rf = 0.4 (PE/EtOAc 10:1). A mixture of diastereoisomers (1.6:1 *trans:cis*), yellow oil (isolated yield: 60%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 1H), 7.81 – 7.77 (m, 1H), 7.74 – 7.69 (m, 2H), 7.32 (m, 1H), 7.29 – 7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 7.20 (m, 1H), 2.31 (s, 3H), 2.09 – 2.03 (m, 1H), 1.27 (s, 12H), 1.14 – 1.11 (m, 1H), 0.96 (ddd, *J* = 9.2, 5.4, 3.4 Hz, 1H), 0.25 (ddd, *J* = 9.7, 6.6, 5.6 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (m, 1H), 7.67 – 7.63 (m, 1H), 7.57 (m, 2H), 7.32 (m, 1H), 7.28 (m, 1H), 7.24 (m, 1H), 7.17 (m, 1H), 2.32 (s, 3H), 2.19 – 2.12 (m, 1H), 1.19 – 1.15 (m, 1H), 0.86 (s, 6H), 0.60 (s, 6H), 0.45 (td, *J* = 9.4, 7.1 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer. **Mixture: ^{13}C NMR** (101 MHz, Chloroform-d) δ 144.68, 144.60, 135.71, 135.37, 135.32, 135.06, 132.23, 131.43, 129.80, 129.79, 126.88, 126.74, 125.60, 124.69, 124.47, 123.64, 123.02, 122.96, 122.84, 121.45, 120.01, 119.62, 113.70, 113.38, 83.30, 82.81, 29.70, 24.77, 24.70, 24.58, 24.01, 21.53, 12.53, 12.51, 11.67, 8.97, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{24}H_{28}BNO_4S$ $[M+H]^+$: 438.1905, found: 438.1909.



4u

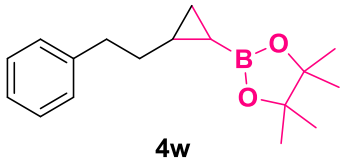
4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)phenyl)morpholine. Rf = 0.3 (PE/EtOAc 10:1). A mixture of diastereoisomers (5.1:1 *trans:cis*), yellow oil (isolated yield: 67%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.87 – 3.84 (m, 4H), 3.12 – 3.08 (m, 4H), 2.06 (dt, *J* = 8.2, 5.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.11 (td, *J* = 7.5, 3.5 Hz, 1H),

0.94 (ddd, *J* = 9.3, 5.3, 3.6 Hz, 1H), 0.23 (dt, *J* = 9.8, 6.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.45, 135.00, 126.56, 116.03, 83.11, 66.96, 49.87, 24.77, 24.71, 21.24, 14.56, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. ***Cis:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.2 Hz, 2H), 6.80 (s, 2H), 3.86 (s, 4H), 3.07 (d, *J* = 7.4 Hz, 4H), 2.28 (ddd, *J* = 10.1, 8.1, 6.0 Hz, 1H), 1.06 (s, 1H), 1.03 (s, 6H), 0.90 (s, 6H), 0.39 (td, *J* = 9.6, 7.1 Hz, 1H), one of the H of the cyclopropane ring was not detected due to superposition with the methyl groups of the major diastereoisomer. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.75, 132.78, 129.56, 115.66, 82.84, 66.93, 50.16, 24.87, 24.39, 21.01, 8.90, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{19}H_{28}BNO_3$ $[M+Na]^+$: 352.2054, found: 352.2053.



4v

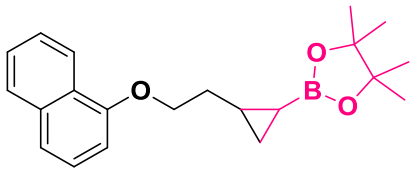
4,4'-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-1,1'-biphenyl. **Rf** = 0.5 (PE/EtOAc 10:1). A mixture of diastereoisomers (3.3:1 *trans:cis*), colorless oil (isolated yield: 52%). ***Trans:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.1 Hz, 4H), 7.15 (m, 4H), 2.16 (dt, *J* = 7.8, 5.4 Hz, 2H), 1.28 (s, 12H), 1.27 (s, 12H), 1.24 – 1.20 (m, 2H), 1.09 – 1.05 (m, 2H), 0.36 (ddd, *J* = 9.8, 6.8, 5.5 Hz, 2H). ***Cis:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 4H), 2.40 (ddd, *J* = 10.0, 7.9, 6.0 Hz, 2H), 1.51 (m, 2H), 1.16 – 1.13 (m, 2H), 1.04 (m, 12H), 0.90 (s, 12H), 0.49 (td, *J* = 9.6, 7.2 Hz, 2H). **Mixture：^{13}C NMR** (101 MHz, Chloroform-d) δ 142.31, 138.41, 138.41, 129.17, 127.23, 126.78, 126.17, 126.01, 83.20, 82.99, 24.78, 24.69, 24.37, 21.66, 21.45, 15.14, 14.22, 9.02, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{30}H_{40}B_2O_4$ $[M+Na]^+$: 509.3005, found: 509.3003.



4w

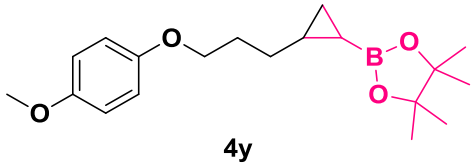
4,4,5,5-tetramethyl-2-(2-phenethylcyclopropyl)-1,3,2-dioxaborolane[6]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.7:1 *trans:cis*), colorless oil (isolated yield: 50%). ***Trans:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.26 (m, 1H), 7.24 (m, 1H), 7.17 (dd, *J* = 7.6, 1.9 Hz, 3H), 2.70 (tt, *J* = 9.0, 4.3 Hz, 2H), 1.55 (d, *J* = 7.5 Hz, 2H), 1.22 (s, 6H), 1.21 (s, 6H), 0.97 – 0.94 (m, 1H), 0.68 (ddd, *J* = 7.8, 6.1, 3.4 Hz, 1H), 0.41 (ddd, *J* = 8.9, 5.2, 3.3 Hz, 1H), -0.38 (dt, *J* = 9.4, 5.7 Hz, 1H). ***Cis:* ^{1}H NMR** (400 MHz, Chloroform-*d*) δ δ 7.29 – 7.26 (m, 1H), 7.24 (s, 1H), 7.17 (dd, *J* = 7.6, 1.9 Hz, 3H),

2.88 (m, 2H), 1.76 (m, 2H), 1.23 (s, 12H), 0.99 (d, *J* = 1.7 Hz, 1H), 0.44 (d, *J* = 4.2 Hz, 2H), -0.07 (m, 1H).



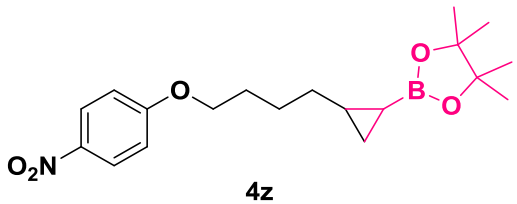
4x

4,4,5,5-tetramethyl-2-(2-(2-(naphthalen-2-yloxy)ethyl)cyclopropyl)-1,3,2-dioxaborolane. Rf = 0.3 (PE/EtOAc 50:1). Colorless oil (isolated yield: 25%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 3H), 7.45 – 7.40 (m, 1H), 7.35 – 7.29 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.15 (t, *J* = 6.7 Hz, 2H), 1.90 (dq, *J* = 13.4, 6.6 Hz, 1H), 1.71 (dd, *J* = 13.9, 7.0 Hz, 1H), 1.21 (d, *J* = 1.7 Hz, 12H), 0.92 – 0.82 (m, 1H), 0.76 (ddd, *J* = 7.8, 6.1, 3.5 Hz, 1H), 0.53 (ddd, *J* = 9.0, 5.2, 3.5 Hz, 1H), -0.27 (dt, *J* = 9.5, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.09, 134.63, 129.27, 128.90, 127.62, 126.71, 126.25, 123.44, 119.08, 106.65, 82.94, 67.98, 34.89, 24.69, 14.95, 11.07, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{21}H_{27}BO_3$ $[M+H]^+$: 339.2126, found: 339.2127.



4y

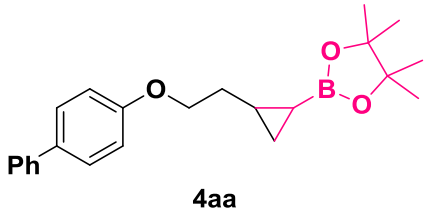
2-(2-(3-(4-methoxyphenoxy)propyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.2 (PE/EtOAc 50:1). Colorless oil (isolated yield: 23%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.82 (s, 4H), 3.93 (td, *J* = 6.7, 1.9 Hz, 2H), 3.76 (s, 3H), 1.87 (p, *J* = 7.0 Hz, 2H), 1.42 (d, *J* = 4.8 Hz, 2H), 1.21 (s, 12H), 0.97 (dd, *J* = 7.3, 3.3 Hz, 1H), 0.72 – 0.67 (m, 1H), 0.43 (ddd, *J* = 8.9, 5.2, 3.4 Hz, 1H), -0.37 (dt, *J* = 9.5, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.68, 153.31, 115.47, 114.62, 82.84, 68.29, 55.75, 31.56, 29.71, 24.69, 17.80, 14.12, 11.40, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{19}H_{29}BO_4$ $[M+H]^+$: 333.2232, found: 333.2233.



4z

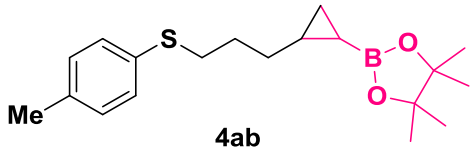
4,4,5,5-tetramethyl-2-(2-(4-(4-nitrophenoxy)butyl)cyclopropyl)-1,3,2-dioxaborolane. Rf = 0.2 (PE/EtOAc 10:1). Yellow oil (isolated yield: 36%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.16 (m, 2H), 6.97 – 6.90 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.80 (m, 2H), 1.63 – 1.57 (m, 2H), 1.45 – 1.34 (m, 2H), 1.21 (s, 12H),

0.98 – 0.91 (m, 1H), 0.69 (ddd, *J* = 7.7, 6.1, 3.3 Hz, 1H), 0.41 (ddd, *J* = 8.8, 5.2, 3.3 Hz, 1H), -0.39 (dt, *J* = 9.4, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.25, 141.34, 125.92, 114.41, 82.87, 68.90, 34.80, 28.74, 25.97, 24.74, 24.68, 17.98, 11.38, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{19}H_{28}BNO_5$ $[M+H]^+$: 362.2133, found: 362.2135.



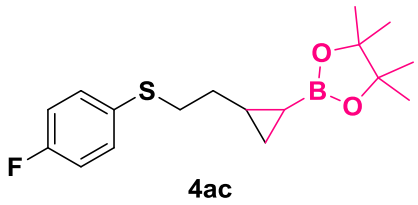
4aa

2-(2-(2-([1,1'-biphenyl]-4-yloxy)ethyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.3 (PE/EtOAc 50:1). Colorless oil (isolated yield: 43%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 4H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.01 – 6.94 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 1.86 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.67 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.22 (s, 12H), 1.15 – 1.09 (m, 1H), 0.75 (ddd, *J* = 7.7, 6.1, 3.5 Hz, 1H), 0.51 (ddd, *J* = 9.0, 5.2, 3.4 Hz, 1H), -0.29 (dt, *J* = 9.4, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.72, 140.93, 133.57, 128.69, 128.08, 126.72, 126.58, 114.87, 82.94, 68.08, 34.93, 24.69, 14.88, 11.04, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{23}H_{29}BO_3$ $[M+H]^+$: 365.2283, found: 365.2284.



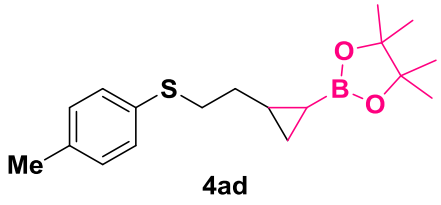
4ab

4,4,5,5-tetramethyl-2-(2-(3-(p-tolylthio)propyl)cyclopropyl)-1,3,2-dioxaborolane Rf = 0.4 (PE/EtOAc 50:1). Colorless oil (isolated yield: 35%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 2.93 – 2.86 (m, 2H), 2.31 (s, 3H), 1.73 (p, *J* = 7.4 Hz, 3H), 1.50 – 1.41 (m, 2H), 1.21 (s, 12H), 0.67 (ddd, *J* = 7.8, 6.1, 3.3 Hz, 1H), 0.39 (ddd, *J* = 8.8, 5.2, 3.3 Hz, 1H), -0.40 (dt, *J* = 9.5, 5.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.82, 133.07, 129.79, 129.61, 82.85, 34.18, 34.06, 29.27, 24.68, 20.99, 17.61, 11.34, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{19}H_{29}BO_2S$ $[M+H]^+$: 333.2054, found: 333.2052.



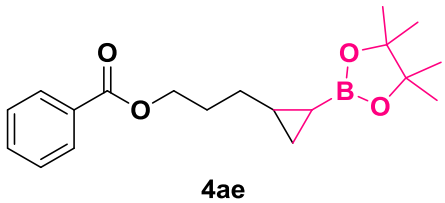
4ac

2-(2-(2-((4-fluorophenyl)thio)ethyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane Rf = 0.4 (PE/EtOAc 50:1). Colorless oil (isolated yield: 38%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.00 – 6.95 (m, 2H), 2.93 (ddd, *J* = 8.5, 6.6, 2.0 Hz, 2H), 1.62 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.49 (ddd, *J* = 13.7, 7.0, 1.5 Hz, 1H), 1.21 (s, 12H), 1.06 – 1.01 (m, 1H), 0.70 (ddd, *J* = 7.7, 6.1, 3.5 Hz, 1H), 0.42 (ddd, *J* = 9.0, 5.1, 3.4 Hz, 1H), -0.38 (dt, *J* = 9.5, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 132.08, 132.00, 116.02, 115.81, 82.94, 35.04, 34.88, 29.70, 24.68, 17.40, 11.24, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{17}H_{24}BFO_2S$ $[M+H]^+$: 323.1647, found: 323.1649.



4ad

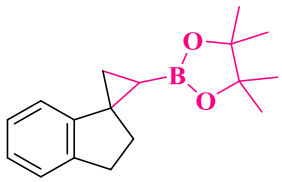
4,4,5,5-tetramethyl-2-(2-(2-(p-tolylthio)ethyl)cyclopropyl)-1,3,2-dioxaborolane Rf = 0.4 (PE/EtOAc 50:1). Colorless oil (isolated yield: 36%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 2.94 (td, *J* = 6.6, 3.2 Hz, 2H), 2.31 (s, 3H), 1.65 – 1.59 (m, 1H), 1.53 – 1.46 (m, 1H), 1.21 (d, *J* = 0.9 Hz, 12H), 1.08 – 1.01 (m, 1H), 0.70 (ddd, *J* = 7.9, 6.2, 3.4 Hz, 1H), 0.42 (ddd, *J* = 9.0, 5.2, 3.5 Hz, 1H), -0.38 (dt, *J* = 9.7, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.88, 132.99, 129.85, 129.61, 82.91, 35.11, 34.19, 29.70, 24.68, 20.99, 17.51, 11.24, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{18}H_{27}BO_2S$ $[M+H]^+$: 319.1898, found: 319.1895.



4ae

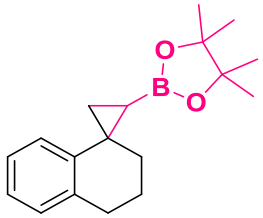
3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)propyl benzoate Rf = 0.5 (PE/EtOAc 5:1). Colorless oil (isolated yield: 40%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (dd, *J* = 8.3, 7.0 Hz, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.53 – 1.47 (m, 1H), 1.38 –

1.34 (m, 1H), 1.21 (s, 12H), 1.01 – 0.95 (m, 1H), 0.71 (ddd, *J* = 7.7, 6.0, 3.4 Hz, 1H), 0.43 (ddd, *J* = 8.9, 5.2, 3.4 Hz, 1H), -0.37 (dt, *J* = 9.5, 5.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.64, 132.78, 130.53, 129.54, 128.31, 82.88, 64.78, 31.62, 29.70, 28.81, 24.69, 17.68, 11.43, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{19}H_{27}BO_4$ $[M+H]^+$: 331.2075, found: 331.2077.



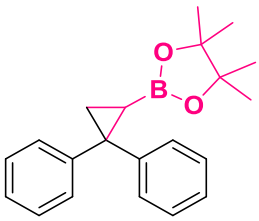
4af

2-(2-2',3'-dihydrospiro[cyclopropane-1,1'-inden]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[8]. Product in accordance with literature characterization data. **Rf** = 0.3 (PE/EtOAc 50:1). A mixture of diastereoisomers (1.7:1 *trans:cis*), colorless oil (isolated yield: 61%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 – 7.03 (m, 3H), 6.68 (m, 1H), 3.03 – 2.96 (m, 2H), 2.33 – 2.28 (m, 1H), 2.15 (ddd, *J* = 13.2, 8.6, 5.8 Hz, 1H), 1.25 (s, 12H), 1.23 (m, 1H), 1.19 – 1.16 (m, 1H), 0.49 – 0.45 (m, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 – 7.11 (m, 3H), 6.68 (m, 1H), 3.14 – 3.07 (m, 1H), 2.99 – 2.96 (m, 1H), 2.39 – 2.33 (m, 1H), 1.94 (ddd, *J* = 12.1, 8.4, 2.9 Hz, 1H), 1.41 (m, 1H), 1.22 (m, 1H), 1.13 (s, 6H), 1.11 (s, 6H), 0.50 – 0.47 (m, 1H).



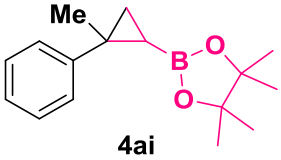
4ag

2-(3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalen]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[4]. Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (2.5:1 *trans:cis*), colorless oil (isolated yield: 69%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.05 – 7.02 (m, 3H), 6.73 (d, *J* = 7.5 Hz, 1H), 2.88 (t, *J* = 5.5 Hz, 2H), 1.91 – 1.86 (m, 4H), 1.35 (dd, *J* = 9.6, 4.0 Hz, 1H), 1.27 (s, 6H), 1.26 (s, 6H), 1.10 (dd, *J* = 7.8, 4.0 Hz, 1H), 0.42 (dd, *J* = 9.6, 7.7 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.05 – 7.02 (m, 3H), 6.73 (d, *J* = 7.5 Hz, 1H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.85 (m, 1H), 2.14 – 2.03 (m, 2H), 1.87 – 1.83 (m, 2H), 1.66 (dd, *J* = 7.5, 4.5 Hz, 1H), 1.02 (dd, *J* = 9.5, 4.5 Hz, 1H), 0.98 (s, 6H), 0.98 (s, 6H), 0.25 (dd, *J* = 9.5, 7.4 Hz, 1H).



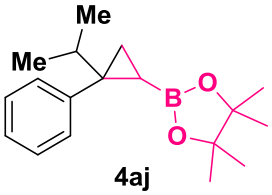
4ah

2-(2,2-diphenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.4 (PE/EtOAc 50:1), colorless oil (isolated yield: 64%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.26 – 7.19 (m, 5H), 7.18 – 7.09 (m, 2H), 1.79 (dd, *J* = 7.2, 3.8 Hz, 1H), 1.31 (dd, *J* = 9.6, 3.8 Hz, 1H), 1.09 (s, 6H), 1.04 (dd, *J* = 9.5, 7.3 Hz, 1H), 0.89 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.15, 143.41, 130.31, 128.10, 128.04, 127.78, 126.26, 125.77, 83.04, 36.41, 24.91, 24.48, 18.83, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{21}H_{25}BO_2$ $[M+Na]^+$: 343.1840, found: 343.1839.



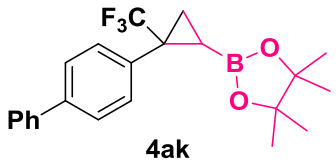
4ai

4,4,5,5-tetramethyl-2-(2-methyl-2-phenylcyclopropyl)-1,3,2-dioxaborolane[8].
Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (1.3:1 *trans:cis*), colorless oil (isolated yield: 75%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.10 (m, 5H), 1.50 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H), 1.19 (dd, *J* = 9.7, 3.6 Hz, 1H), 1.02 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.37 (dd, *J* = 9.7, 7.2 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.11 (m, 5H), 1.46 (s, 3H), 1.19 (dd, *J* = 9.7, 3.6 Hz, 1H), 1.04 (s, 6H), 0.90 (dd, *J* = 9.1, 3.8 Hz, 1H), 0.82 (s, 6H), 0.28 (dd, *J* = 9.1, 6.8 Hz, 1H).



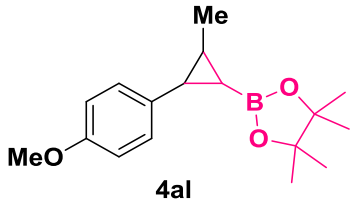
4aj

2-(2-isopropyl-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[8].
Product in accordance with literature characterization data. **Rf** = 0.4 (PE/EtOAc 50:1), colorless oil (isolated yield: 67%). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 – 7.12 (m, 5H), 1.20 (q, *J* = 6.8 Hz, 1H), 1.12 (dd, *J* = 6.6, 3.4 Hz, 1H), 1.09 (s, 6H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 6H), 0.86 – 0.84 (m, 1H), 0.80 (d, *J* = 6.8 Hz, 3H), 0.24 (dd, *J* = 9.1, 6.7 Hz, 1H).



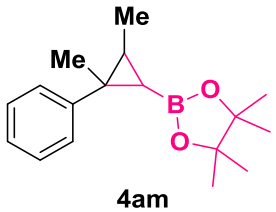
4ak

2-(2-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.4 (PE/EtOAc 50:1), colorless oil (isolated yield: 32%). A NOE NMR analysis confirmed that biphenyl and boron are in a cis-relationship. ***Cis:*** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 6H), 7.44 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.38 – 7.33 (m, 1H), 1.55 – 1.51 (m, 1H), 1.43 (q, *J* = 3.2, 1.8 Hz, 1H), 1.09 (s, 6H), 0.95 (dd, *J* = 10.2, 7.6 Hz, 1H), 0.87 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.16, 140.84, 133.62, 132.09, 128.79, 127.41, 127.14, 126.83, 83.56, 32.61, 29.72, 24.90, 24.38, 12.71, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -70.45. **HRMS (ESI):** calcd for $C_{22}H_{24}BF_3O_2$ $[M+Na]^+$: 411.1714, found: 411.1713.



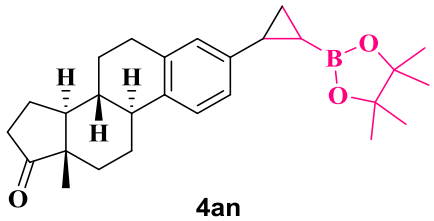
4al

2-(2-(4-methoxyphenyl)-3-methylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.2 (PE/EtOAc 50:1). A mixture of diastereoisomers(1:1 *trans:cis*), colorless oil (isolated yield: 51%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.13 (m, 2H), 7.01 – 6.96 (m, 2H), 6.81 – 6.73 (m, 4H), 3.77 (s, 3H, *trans*), 3.76 (s, 3H, *cis*), 1.98 (dd, *J* = 10.2, 5.4 Hz, 1H, *trans*), 1.89 (dd, *J* = 6.2, 4.9 Hz, 1H, *cis*), 1.61 (d, *J* = 6.3 Hz, 1H, *trans*), 1.34 – 1.30 (m, 1H, *cis*), 1.26 (s, 6H, *trans*), 1.25 (d, *J* = 1.9 Hz, 3H, *cis*), 1.24 (s, 6H, *trans*), 1.21 (d, *J* = 5.9 Hz, 3H, *trans*), 1.04 (s, 6H, *cis*), 0.91 (s, 6H, *cis*), 0.36 (dd, *J* = 9.4, 6.2 Hz, 1H, *cis*), 0.15 (dd, *J* = 10.1, 6.6 Hz, 1H, *trans*). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.71, 157.55, 135.79, 135.32, 133.23, 129.84, 129.57, 126.80, 126.53, 113.73, 113.13, 113.11, 83.16, 83.12, 82.81, 55.35, 55.33, 29.97, 29.36, 25.19, 24.91, 24.84, 24.76, 24.71, 24.56, 24.39, 23.61, 21.23, 19.71, 17.31, 15.85, 14.56, 8.95, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{17}H_{25}BO_3$ $[M+Na]^+$: 311.1789, found: 311.1788.



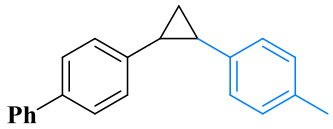
4am

2-(2,3-dimethyl-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. **Rf** = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (1.1:1 *trans:cis*), colorless oil (isolated yield: 56%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 3H), 7.16 – 7.09 (m, 2H), 1.66 (p, *J* = 6.3 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.26 (s, 12H), -0.13 (d, *J* = 6.8 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 1.66 (p, *J* = 6.3 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.06 (s, 6H), 0.83 (s, 6H), 0.45 (d, *J* = 9.9 Hz, 1H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.06, 147.09, 129.14, 128.07, 127.90, 127.04, 125.69, 125.39, 82.76, 82.63, 32.29, 30.47, 29.72, 25.55, 24.94, 24.91, 24.34, 23.55, 21.45, 17.68, 14.37, 11.55, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{17}H_{25}BO_2$ $[M+Na]^+$: 295.1840, found: 295.1839.



4an

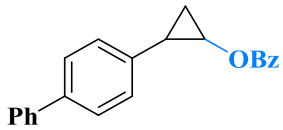
(8R,9S,13S,14S)-13-methyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one. **Rf** = 0.2 (PE/EtOAc 10:1). A mixture of diastereoisomers (6.2:1 *trans:cis*), colorless solid (isolated yield: 77%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 2.91 – 2.84 (m, 2H), 2.54 – 2.38 (m, 2H), 2.31 – 1.92 (m, 7H), 1.64 – 1.52 (m, 3H), 1.49 – 1.41 (m, 2H), 1.25 (s, 6H), 1.23 (s, 6H), 1.13 (ddd, *J* = 8.1, 6.8, 3.7 Hz, 1H), 0.98 (ddd, *J* = 9.3, 5.3, 3.6 Hz, 1H), 0.90 (s, 3H), 0.27 (dt, *J* = 9.8, 6.2 Hz, 1H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.1 Hz, 1H), 7.08 – 6.99 (m, 2H), 2.91 – 2.84 (m, 2H), 2.55 – 2.37 (m, 2H), 2.31 – 1.92 (m, 7H), 1.64 – 1.52 (m, 3H), 1.49 – 1.41 (m, 2H), 1.13 (m, 1H), 1.10 – 1.06 (m, 1H), δ 1.04 (d, *J* = 2.7 Hz, 6H), 0.91 (d, *J* = 1.7 Hz, 6H), 0.90 (s, 3H), 0.41 (td, *J* = 9.6, 7.2 Hz, 1H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 220.97, 140.86, 137.09, 136.30, 126.52, 125.35, 123.10, 83.13, 50.49, 48.02, 44.29, 38.28, 35.89, 31.61, 29.42, 26.57, 25.80, 24.79, 24.67, 21.60, 21.48, 14.78, 13.86, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (ESI):** calcd for $C_{27}H_{37}BO_3$ $[M+Na]^+$: 443.2728, found: 443.2726. **mp:** 62–63 ℃.



6

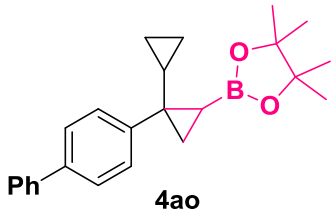
4-(2-(p-tolyl)cyclopropyl)-1,1'-biphenyl. **Rf** = 0.8 (PE/EtOAc 100:1). A mixture of diastereoisomers (2.5:1 *trans:cis*), colorless oil (isolated yield: 66%). ***Trans:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.3, 2.5 Hz, 3H), 7.44 (t, *J* = 7.6 Hz, 3H), 7.38 – 7.33 (m, 2H), 7.23 (dd, *J* = 7.3, 5.4 Hz, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.35

(s, 3H), 2.18 (td, *J* = 7.3, 6.8, 3.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 2H). ***Cis:*** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.58 (m, 4H), 7.33 – 7.28 (m, 2H), 7.19 – 7.16 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 4H), 7.01 (dt, *J* = 6.2, 1.8 Hz, 1H), 6.91 (q, *J* = 8.1 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.35 (s, 3H), 2.23 (d, *J* = 4.6 Hz, 1H), 1.54 – 1.50 (m, 1H), 1.44 – 1.32 (m, 1H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.94, 141.04, 139.40, 138.72, 135.37, 129.27, 129.14, 129.01, 128.78, 128.67, 128.54, 128.46, 127.17, 127.15, 127.09, 127.07, 126.99, 126.93, 126.85, 126.33, 126.21, 126.17, 125.83, 125.77, 29.76, 27.95, 27.66, 24.32, 23.89, 21.02, 18.12, 11.79. **HRMS (APCI):** calcd for $C_{22}H_{20}$ $[M+H]^+$: 285.1638, found: 285.1637.



7

2-([1,1'-biphenyl]-4-yl)cyclopropyl benzoate. Rf = 0.4 (PE/EtOAc 50:1). A colorless oil (isolated yield: 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.58 (dd, *J* = 16.6, 7.8 Hz, 5H), 7.46 (q, *J* = 8.0 Hz, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.50 (dt, *J* = 6.6, 3.2 Hz, 1H), 2.42 (ddd, *J* = 10.2, 6.8, 2.7 Hz, 1H), 1.53 (ddd, *J* = 10.5, 6.6, 3.7 Hz, 1H), 1.40 – 1.35 (m, 1H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.20, 140.93, 139.36, 138.75, 133.17, 129.86, 129.63, 128.76, 128.43, 127.71, 127.22, 127.15, 127.02, 56.52, 31.45, 30.22, 29.71, 22.98, 14.82. **HRMS (APCI):** calcd for $C_{22}H_{18}O_2$ $[M+H]^+$: 315.1380, found: 315.1379.



4ao

2-(1-([1,1'-biphenyl]-4-yl)-[1,1'-bi(cyclopropan)]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Rf = 0.4 (PE/EtOAc 50:1). A mixture of diastereoisomers (3.4:1 *cis: trans*), colorless oil (isolated yield: 50%). ***Cis:*** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.55 (m, 2H), 7.47 (d, *J* = 2.7 Hz, 2H), 7.45 – 7.41 (m, 4H), 7.34 – 7.31 (m, 1H), 1.34 (td, *J* = 5.3, 2.5 Hz, 1H), 1.06 (s, 6H), 0.84 (s, 6H), 0.48 – 0.31 (m, 3H), 0.29 – 0.12 (m, 4H). ***Trans:*** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.50 – 7.49 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 4H), 7.30 (p, *J* = 1.4 Hz, 1H), 1.32 (d, *J* = 2.2 Hz, 1H), 1.31 (s, 6H), 1.28 (s, 6H), 0.36 – 0.31 (m, 3H), 0.18 – 0.12 (m, 4H). **Mixture: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.84, 141.43, 139.00, 130.07, 128.68, 127.03, 126.93, 126.60, 83.13, 82.85, 32.43, 31.94, 25.13, 24.89, 24.71, 24.36, 20.06, 16.16, 13.36, 4.16, 3.46, 3.17, 2.84, 1.03, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. **HRMS (APCI):** calcd for $C_{24}H_{29}BO_2$ $[M+H]^+$: 361.2333, found: 361.2335.

7. References

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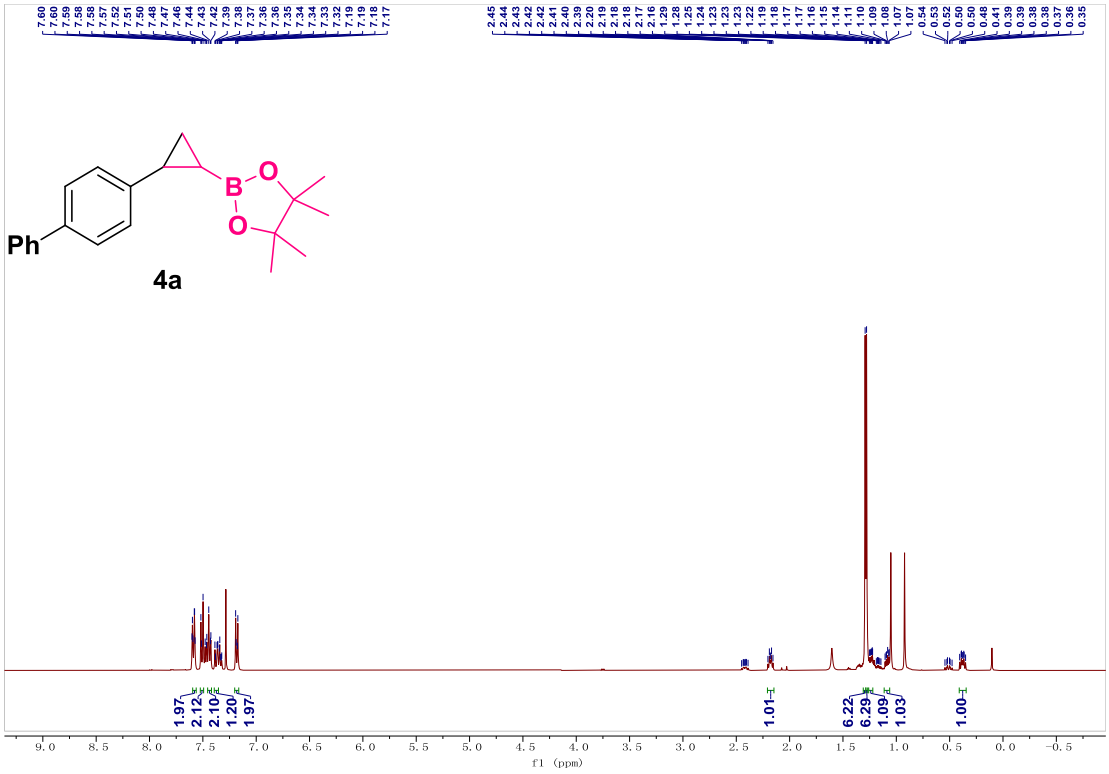
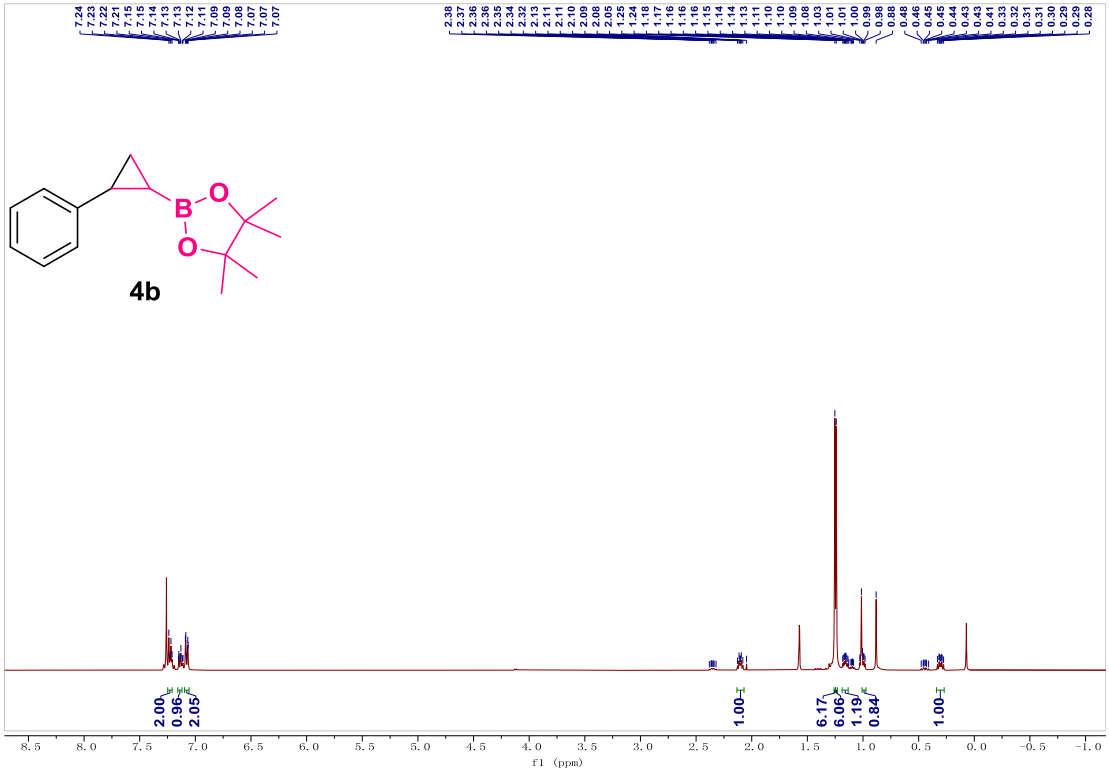
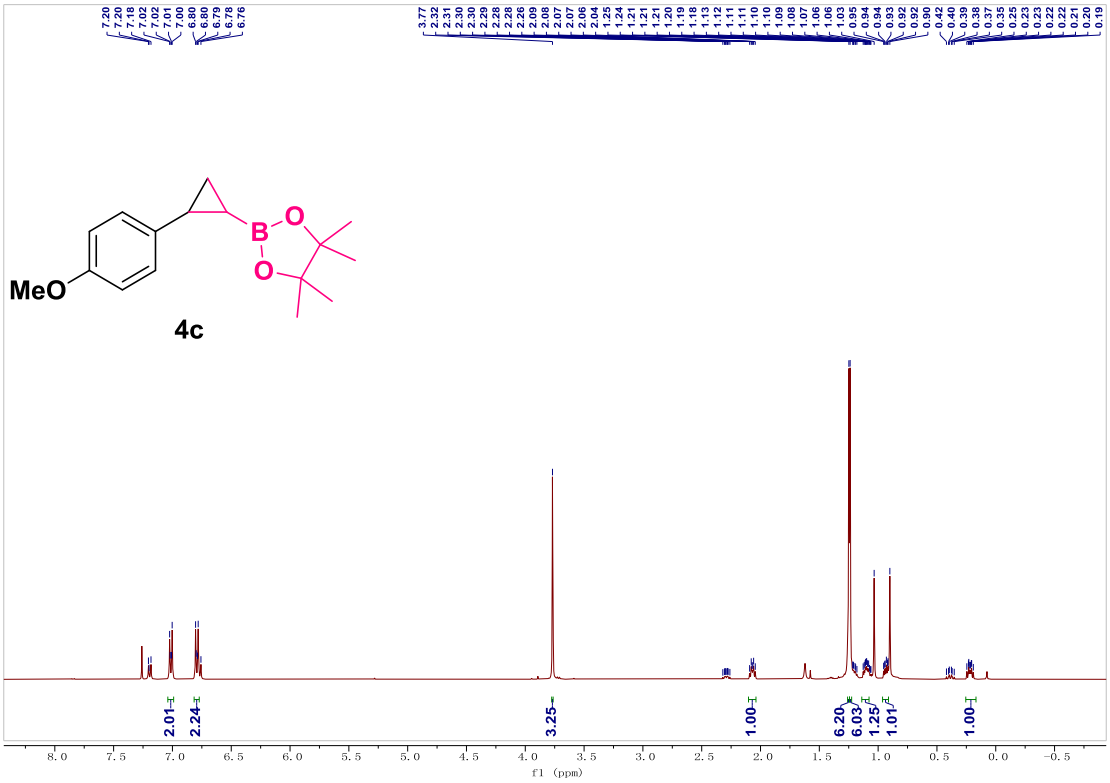
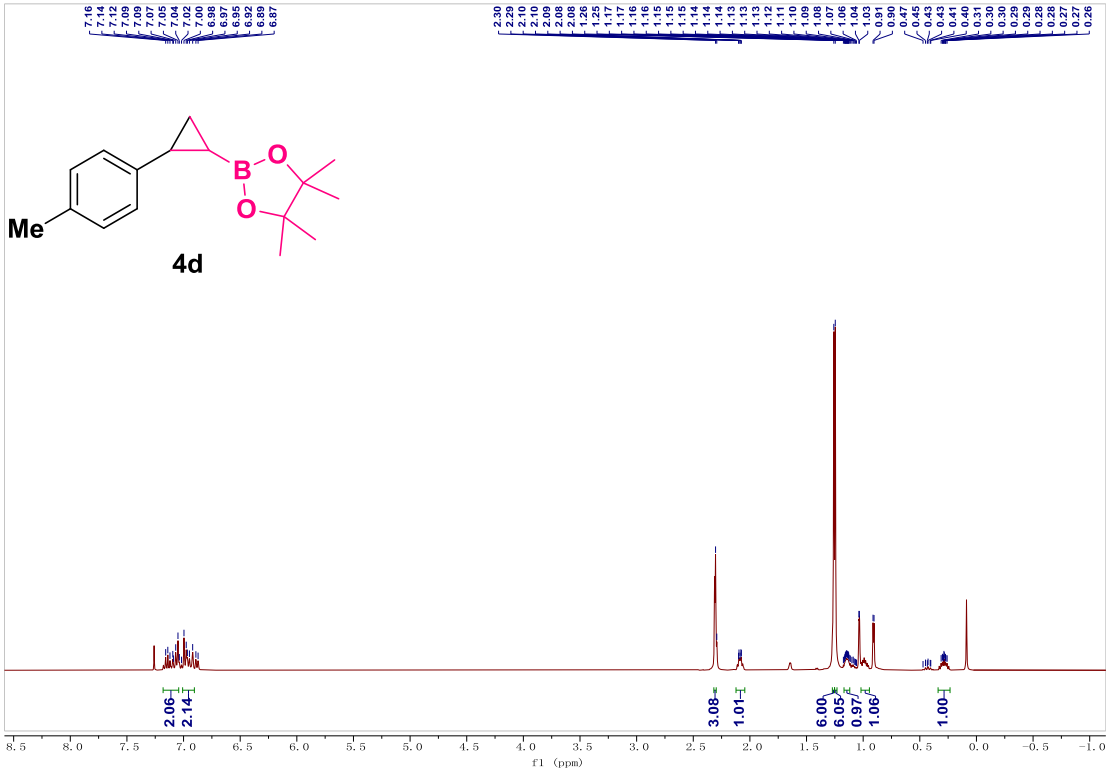
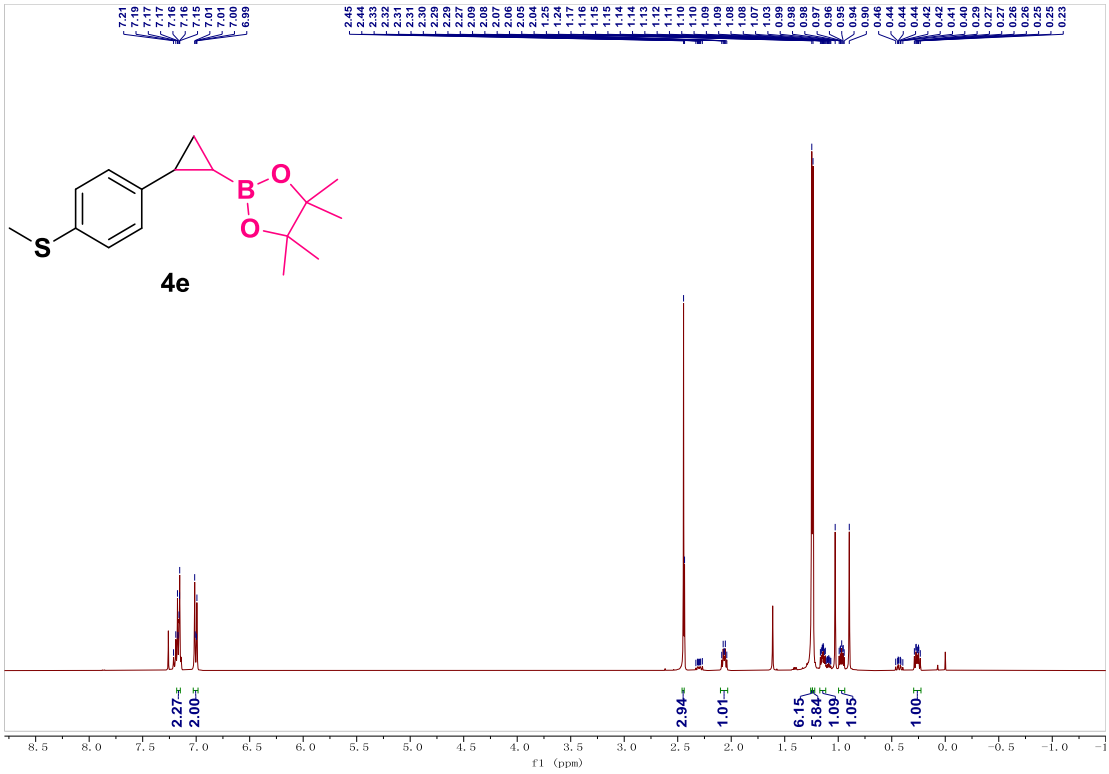
8. ^{1}H and ^{13}C NMR spectra






MeO
B
O
O
4c
f1 (ppm)


Me
B
O
O
4d
f1 (ppm)


4e
S
B
O
O
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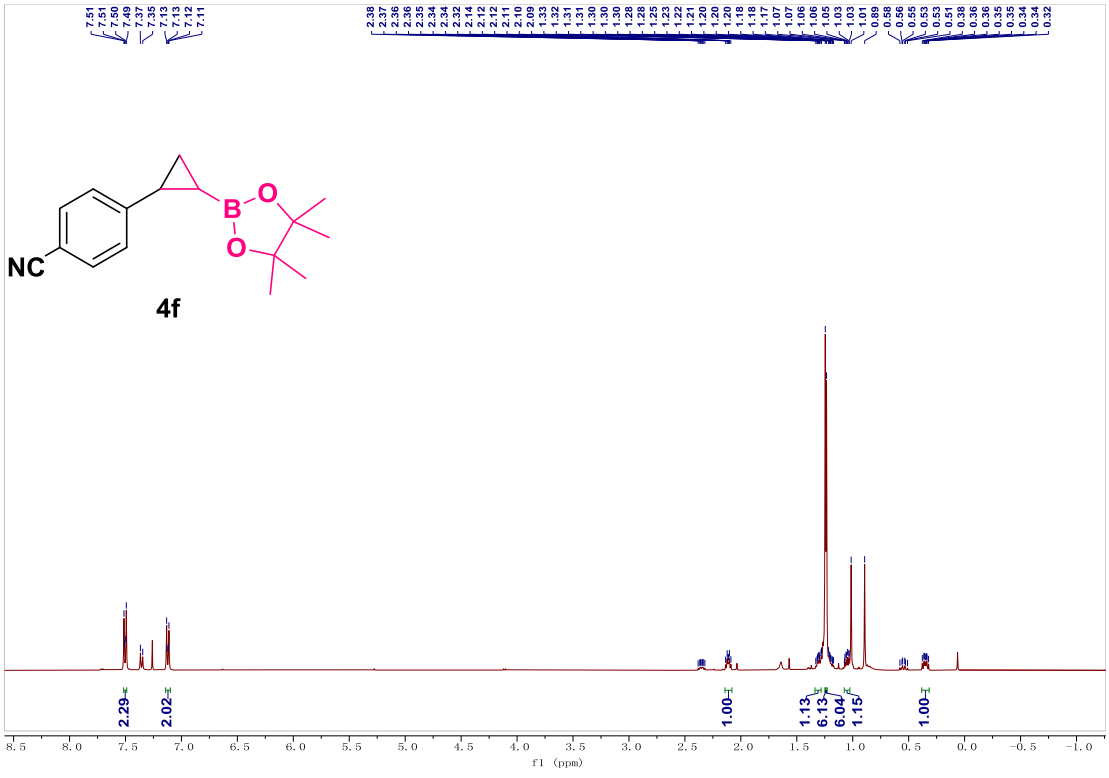
2.00
2.94
1.01
6.15
5.84
1.09
1.05
1.00
f1 (ppm)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O
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1.00
1.13
6.13
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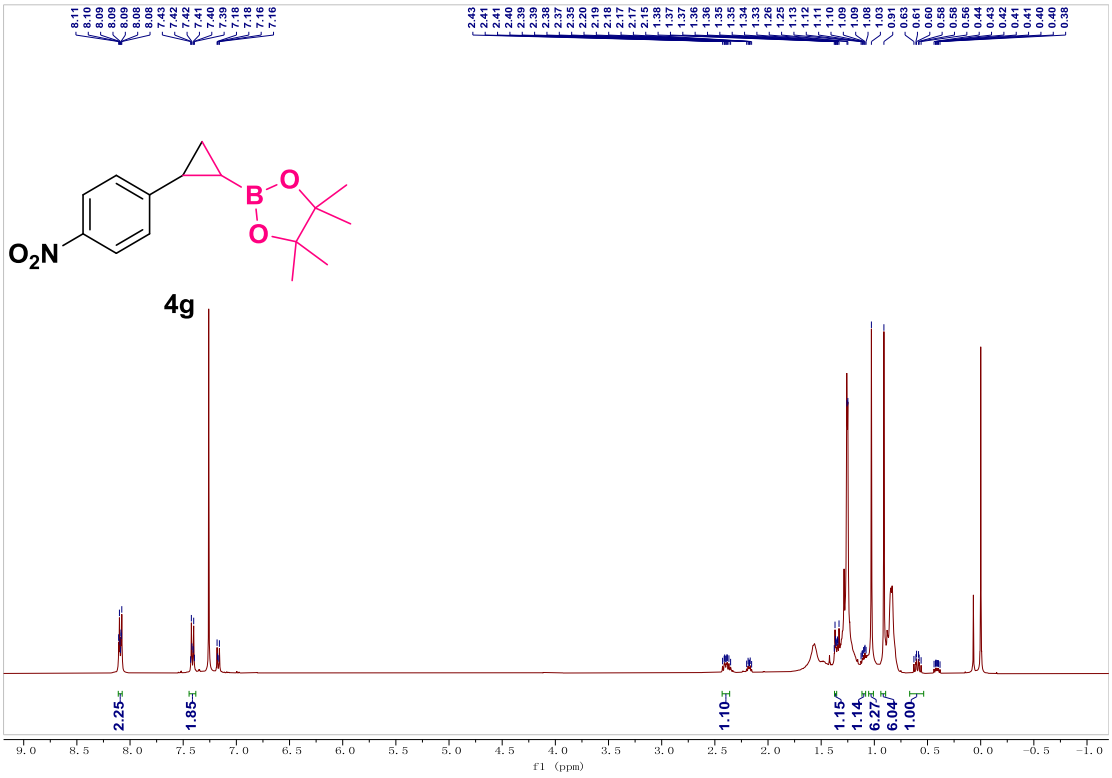
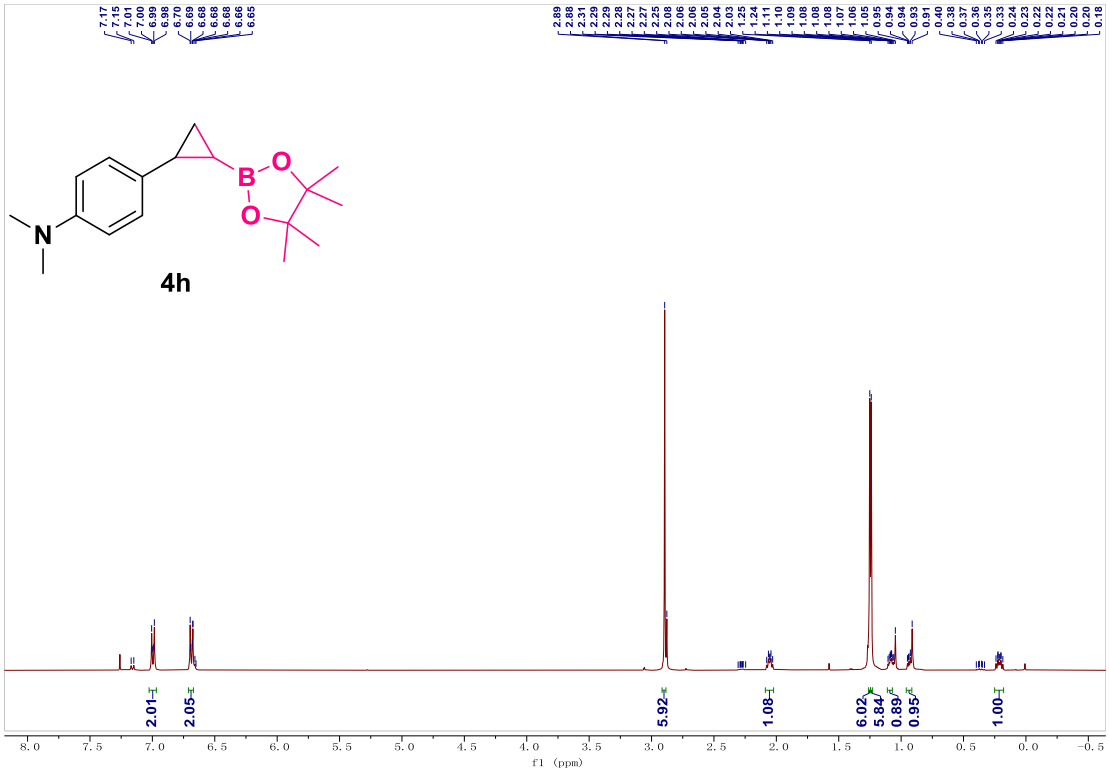
1.00
f1 (ppm)


4g
O2N
B
O
O
2.25
1.85
1.10
1.15
1.14
6.27
6.04
1.00
f1 (ppm)


4h
N
B
O
O
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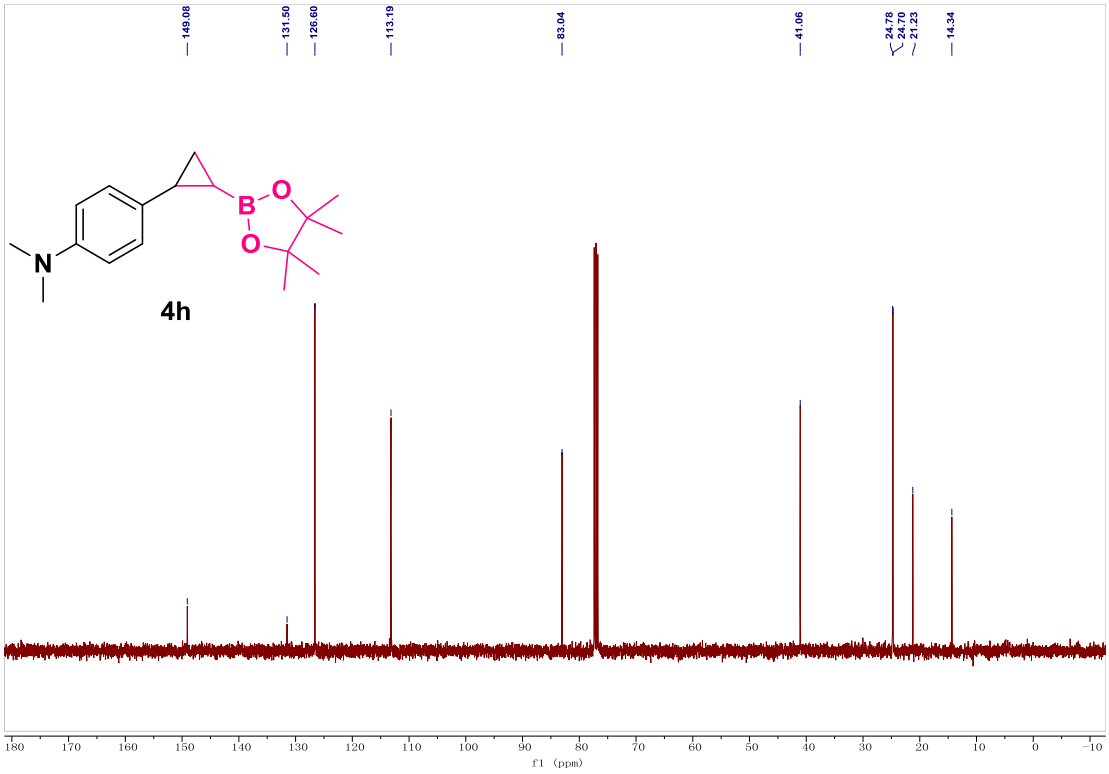
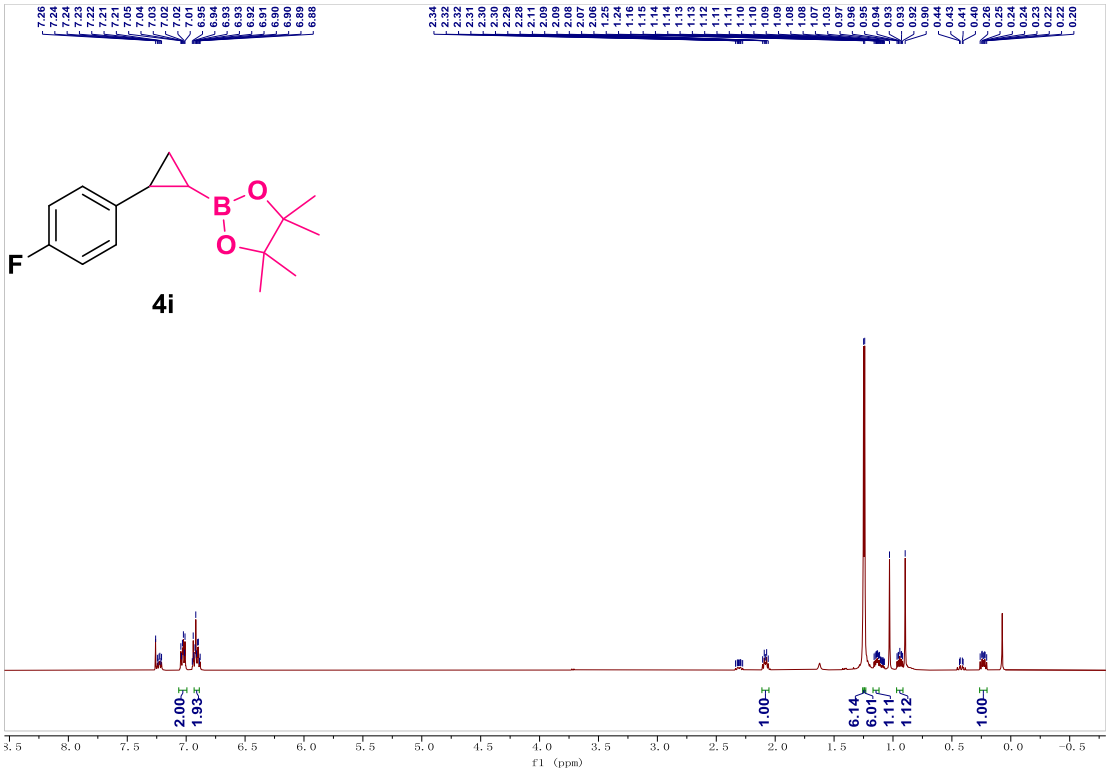
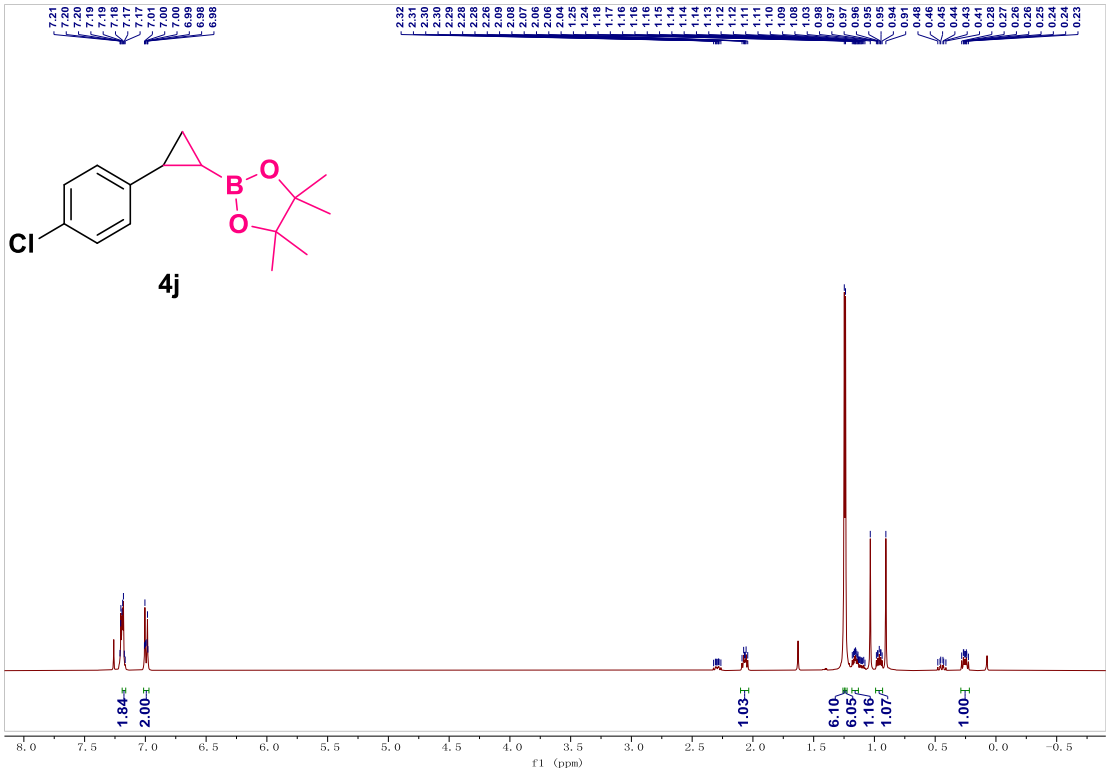
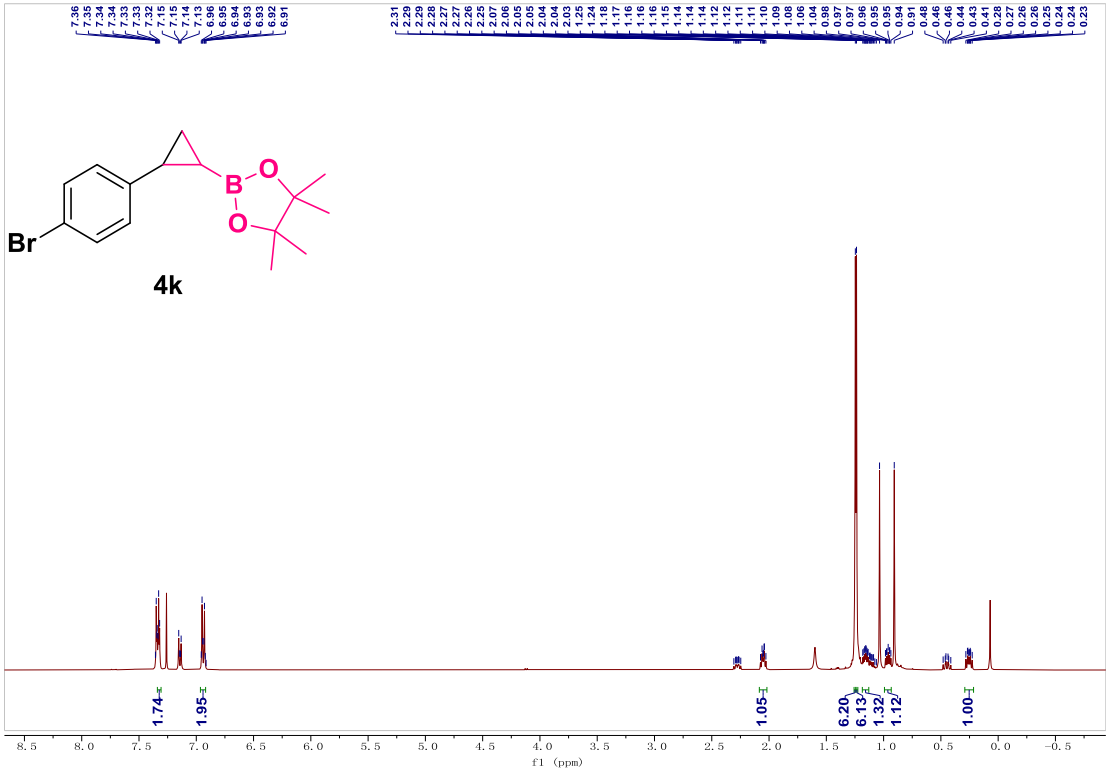
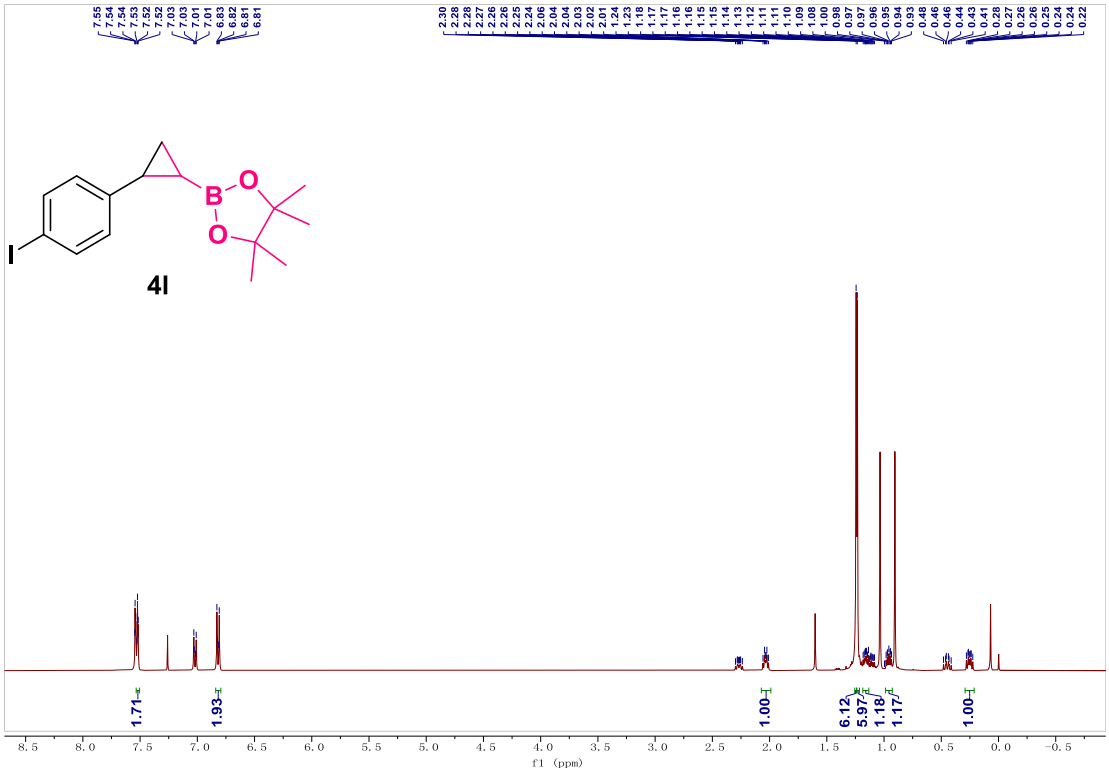
2.05
5.92
1.08
6.02
5.84
0.89
0.95
1.00
f1 (ppm)

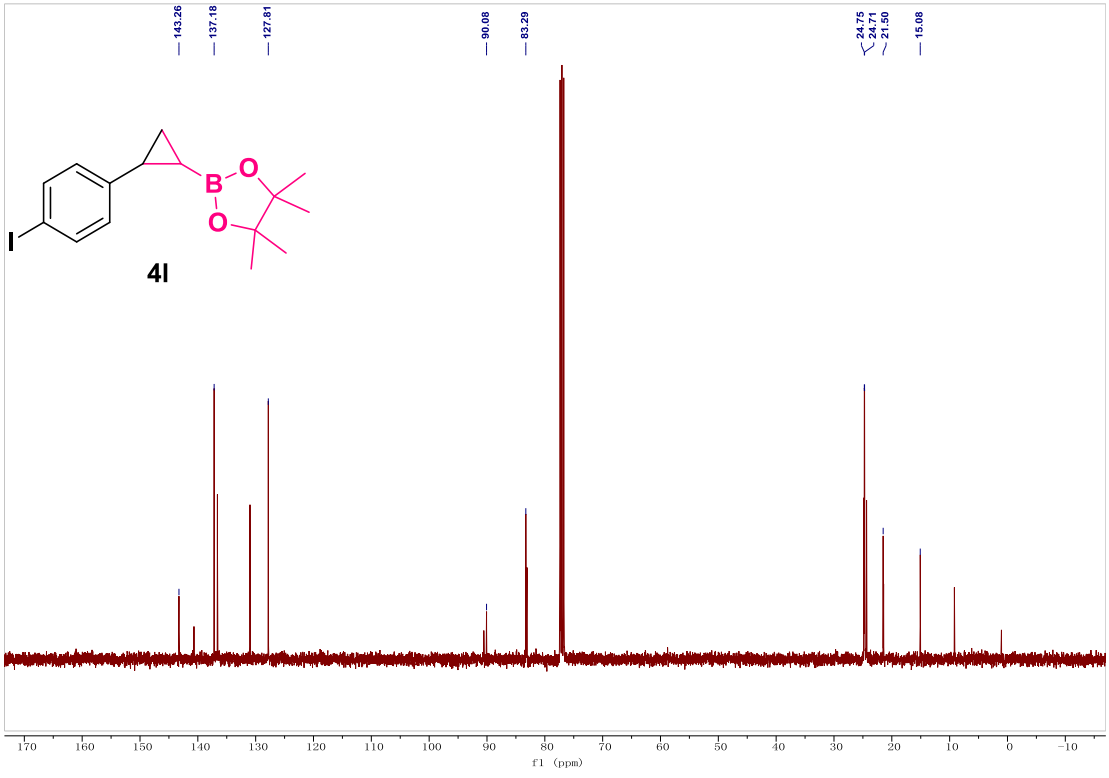

149.08
131.50
126.60
113.19
83.04
41.06
24.78
24.70
21.23
14.34
B
O
O
N
4h
f1 (ppm)

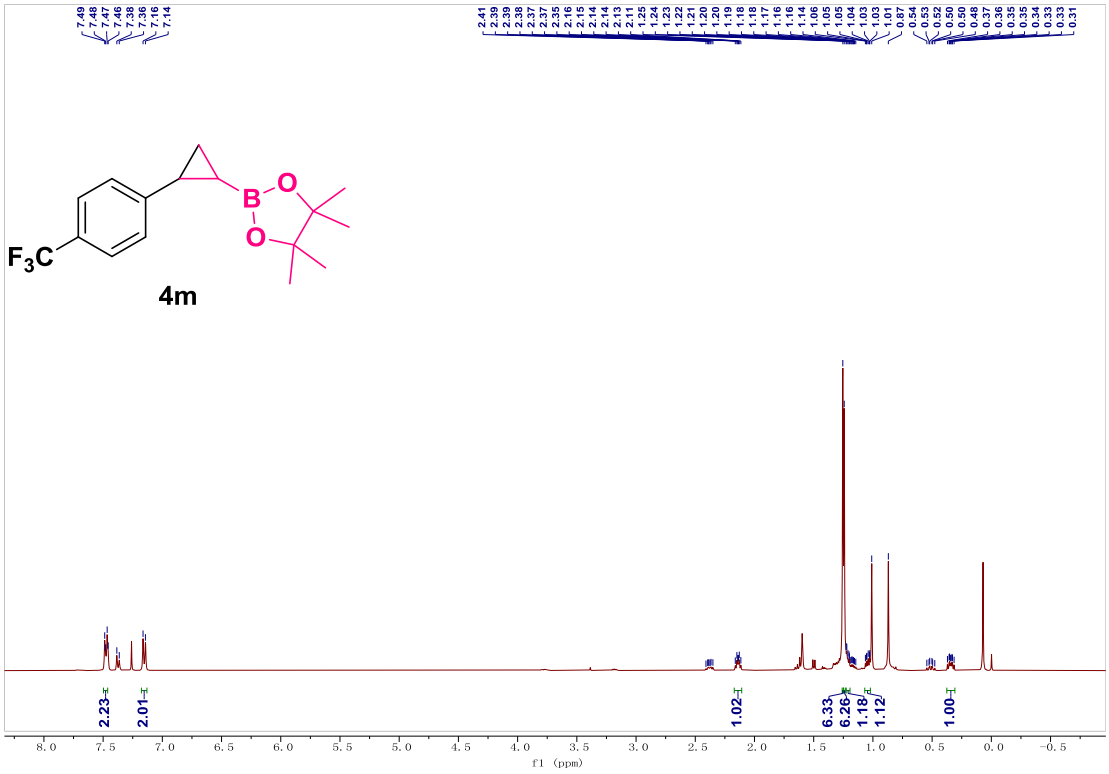

B
O
O
F
4i
2.00
1.93
1.00
6.14
6.01
1.11
1.12
1.00
f1 (ppm)

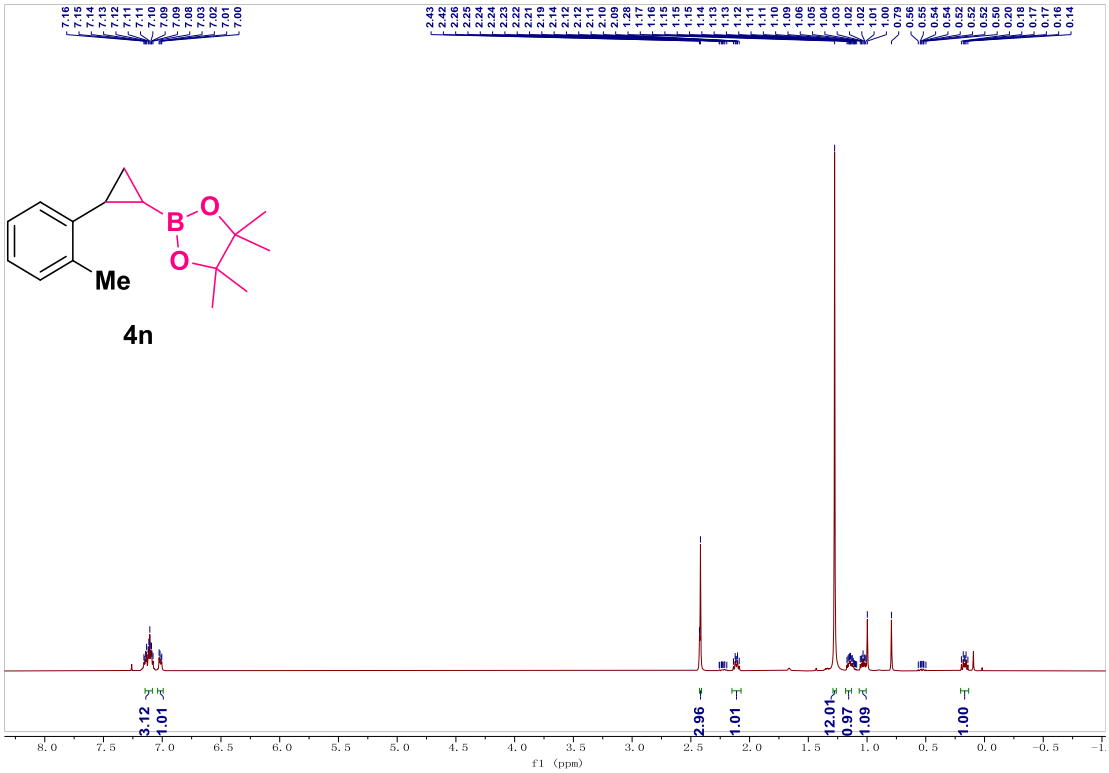

Cl
B
O
O
4j
1.84
2.00
1.03
6.10
6.05
1.16
1.07
1.00
f1 (ppm)

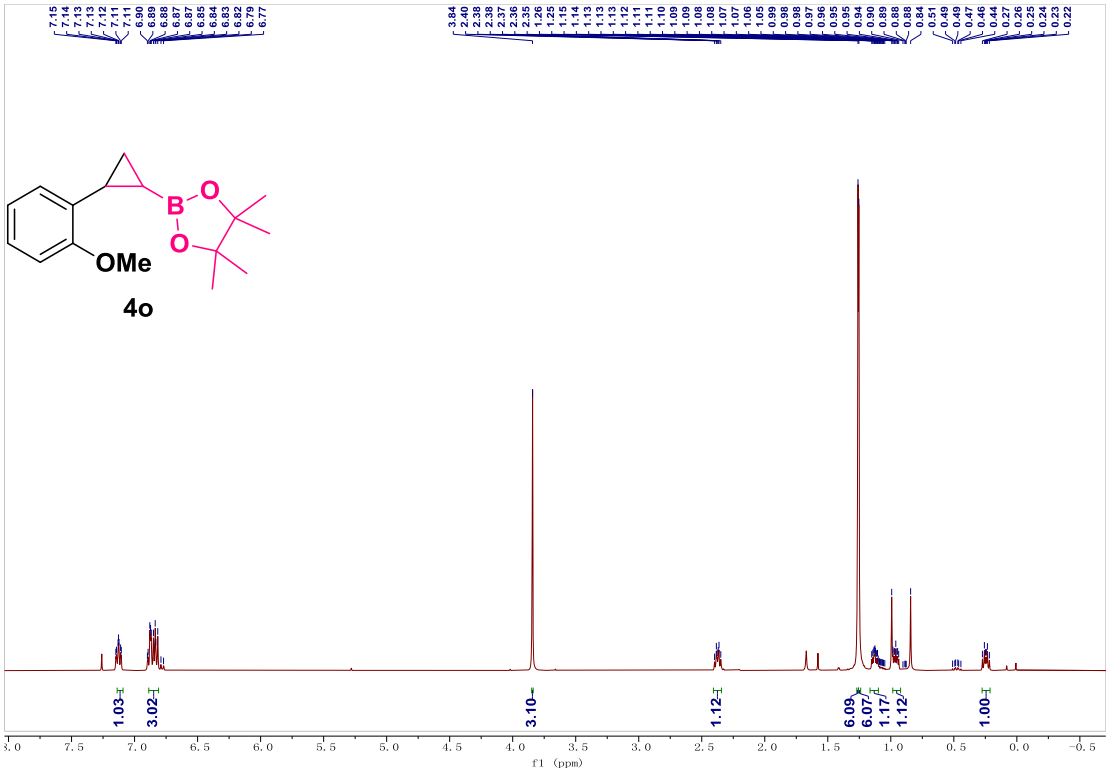

Br
B
O
O
4k
1.74
1.95
1.05
6.20
6.13
1.32
1.12
1.00
f1 (ppm)

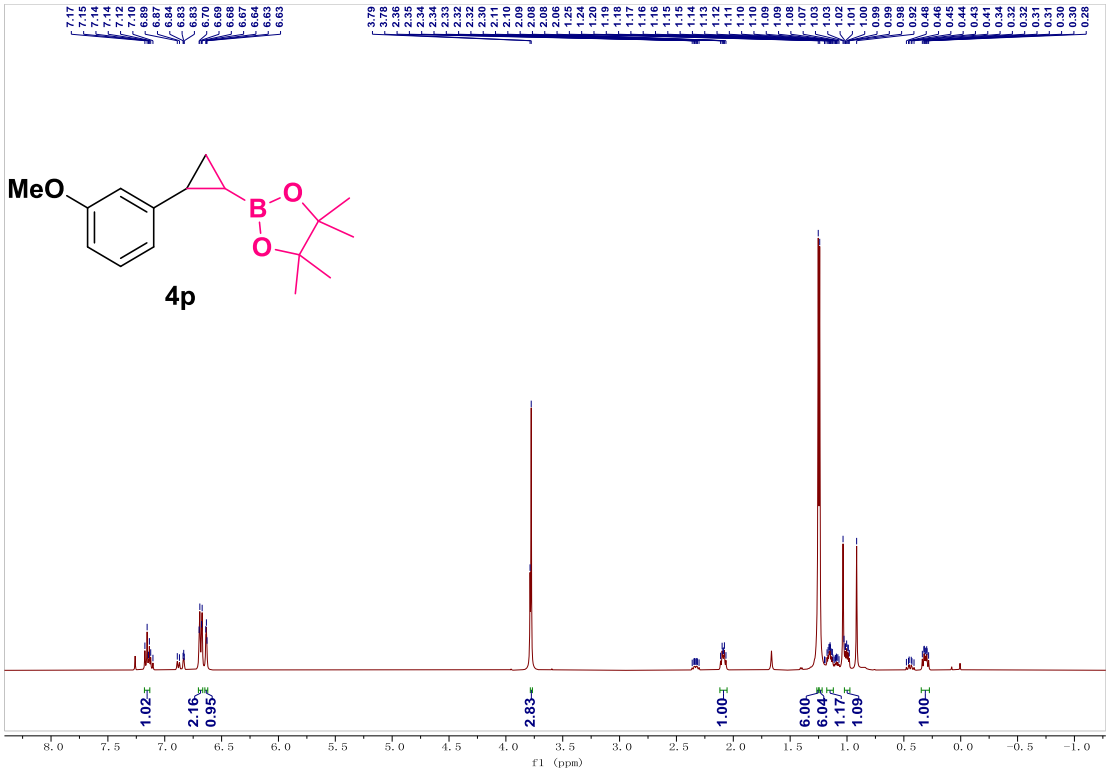

7.55
7.54
7.54
7.53
7.52
7.52
7.03
7.03
7.01
7.01
6.83
6.82
6.81
6.81
2.30
2.28
2.28
2.27
2.26
2.26
2.25
2.24
2.06
2.04
2.04
2.03
2.02
2.01
1.24
1.23
1.18
1.17
1.17
1.16
1.16
1.15
1.15
1.14
1.13
1.12
1.11
1.11
1.10
1.09
1.08
1.08
0.98
0.97
0.97
0.96
0.95
0.94
0.93
0.46
0.46
0.44
0.43
0.41
0.28
0.27
0.26
0.26
0.25
0.24
0.24
0.22
O
B
O
I
4l
1.71
1.93
1.00
6.12
5.97
1.18
1.17
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

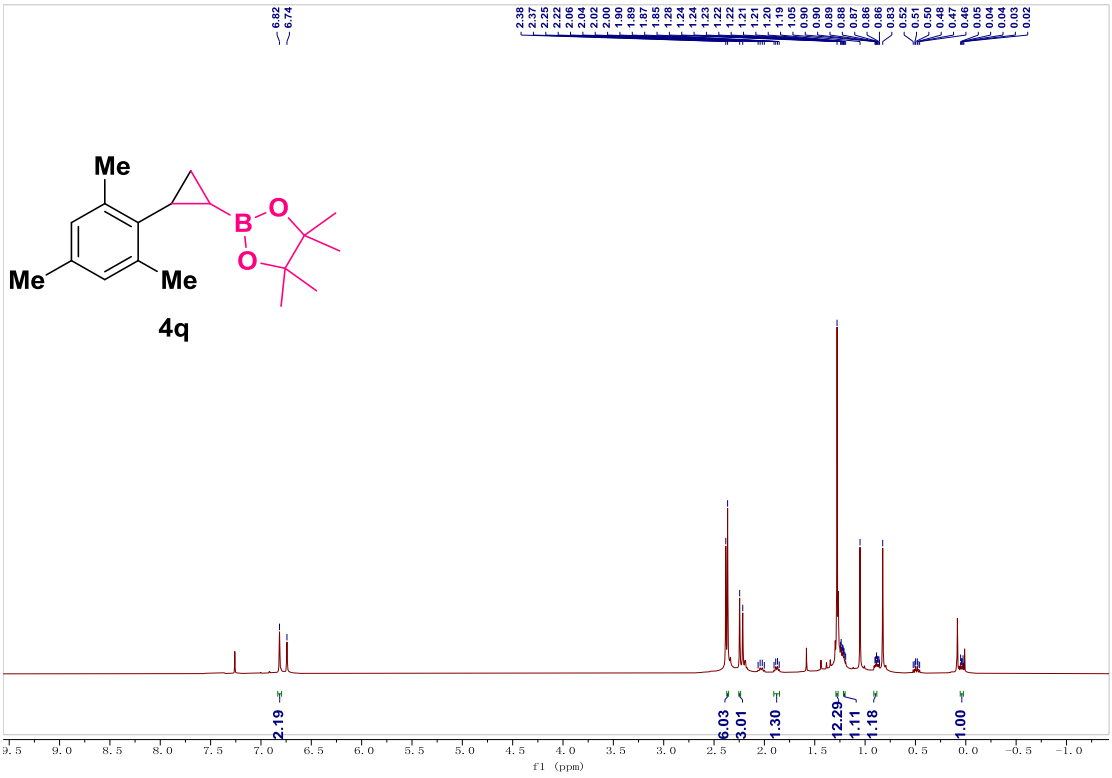

143.26
137.18
127.81
90.08
83.29
24.75
24.71
21.50
15.08
O
B
O
I
4l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

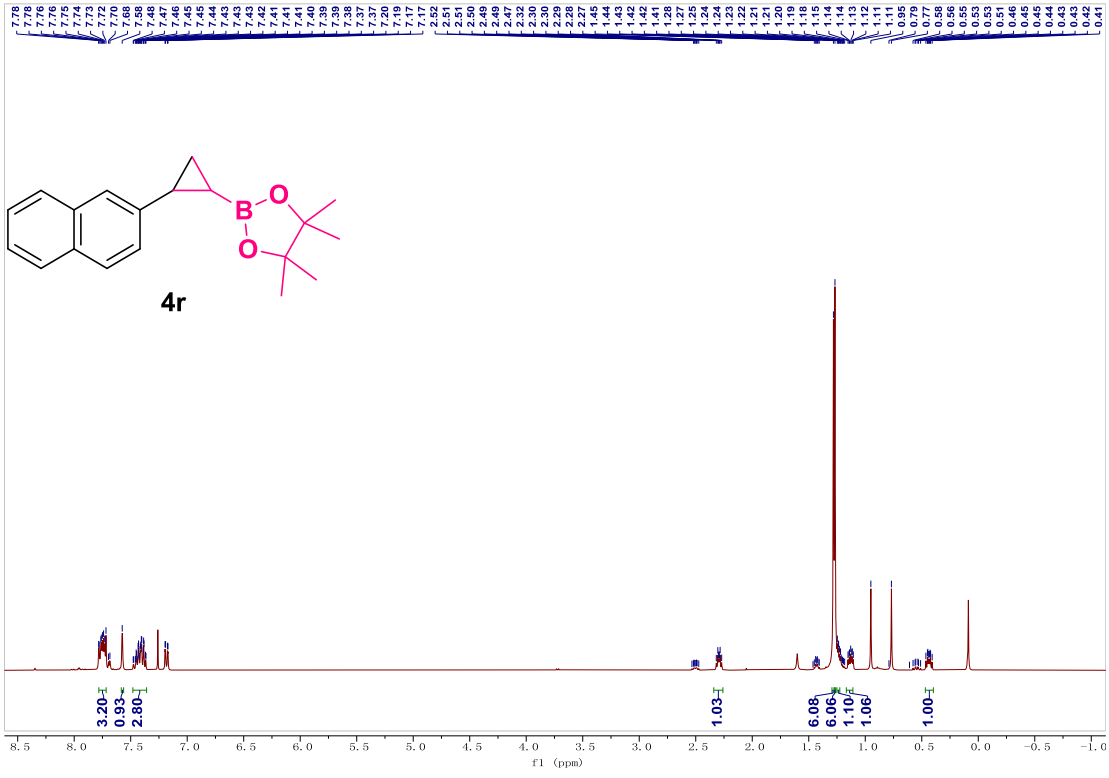

F3C
B
O
O
4m
f1 (ppm)

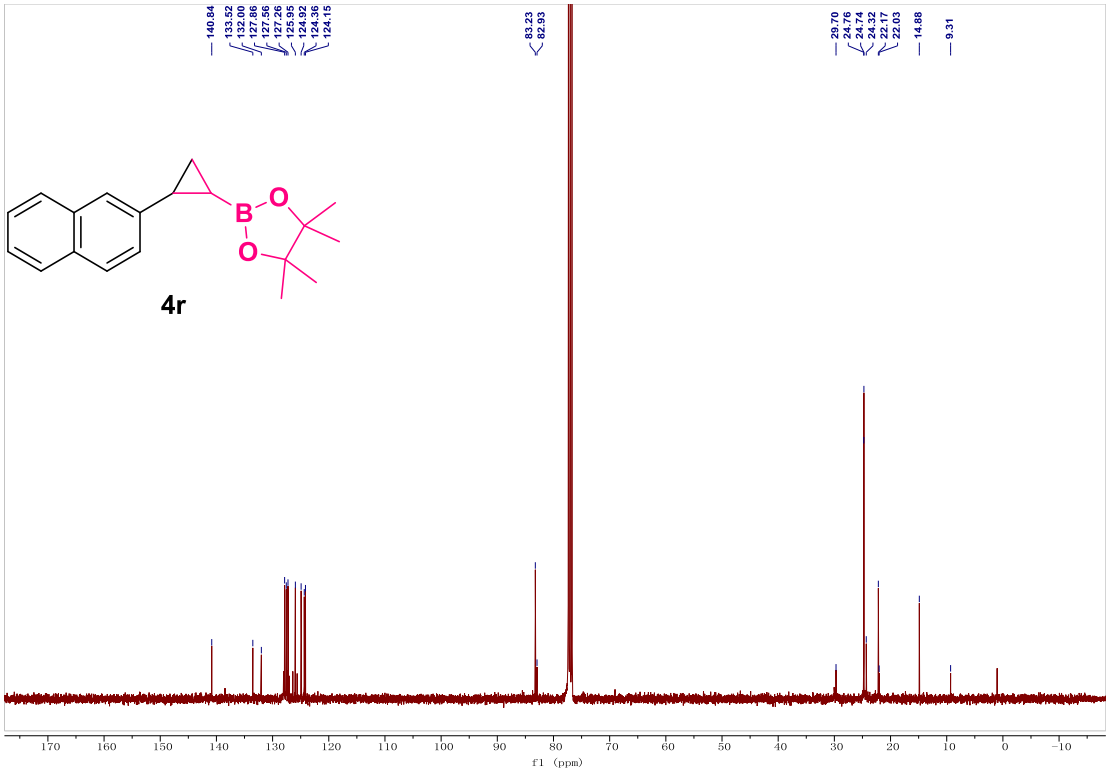

Me
B
O
O
4n
f1 (ppm)

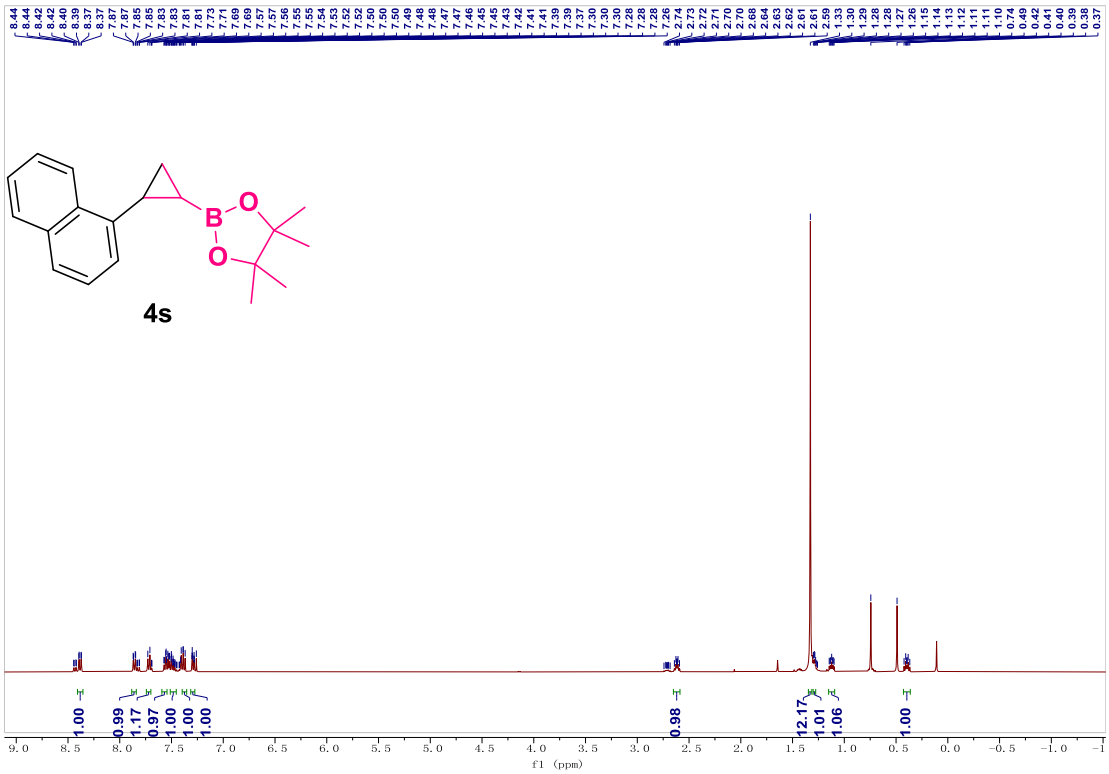

OMe
4o
1.03
3.02
3.10
1.12
6.09
6.07
1.17
1.12
1.00
f1 (ppm)

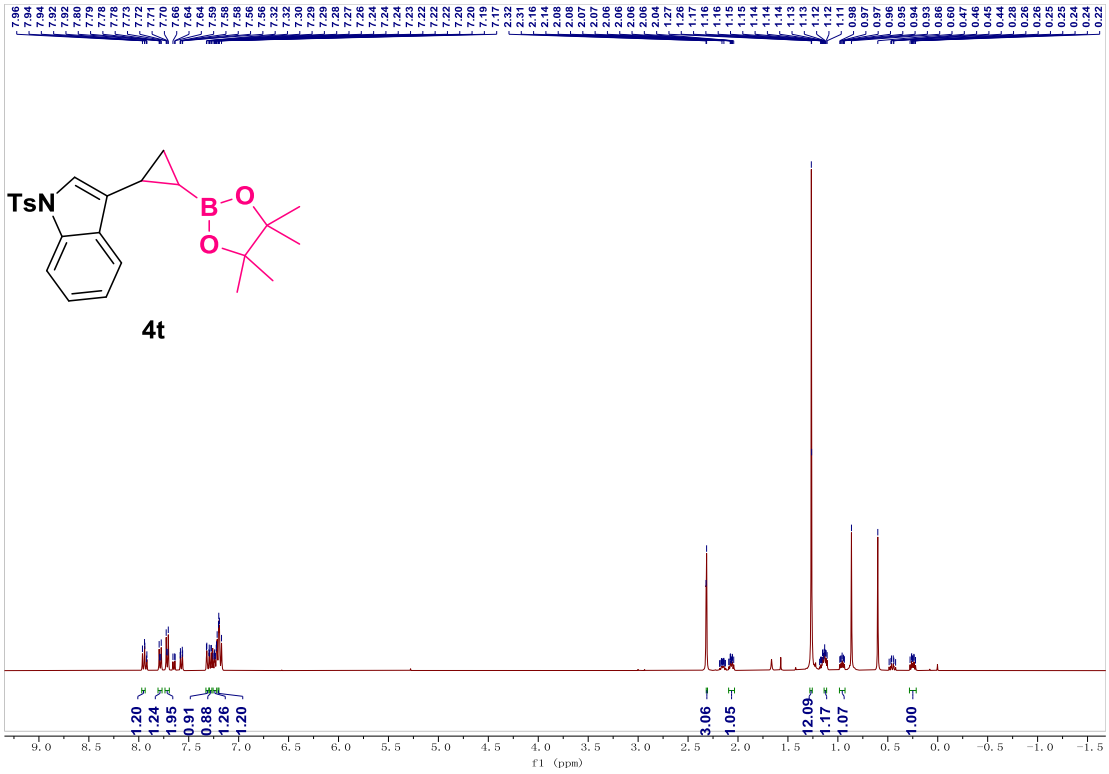

MeO
4p
1.02
2.16
0.95
2.83
1.00
6.00
6.04
1.17
1.09
1.00
f1 (ppm)

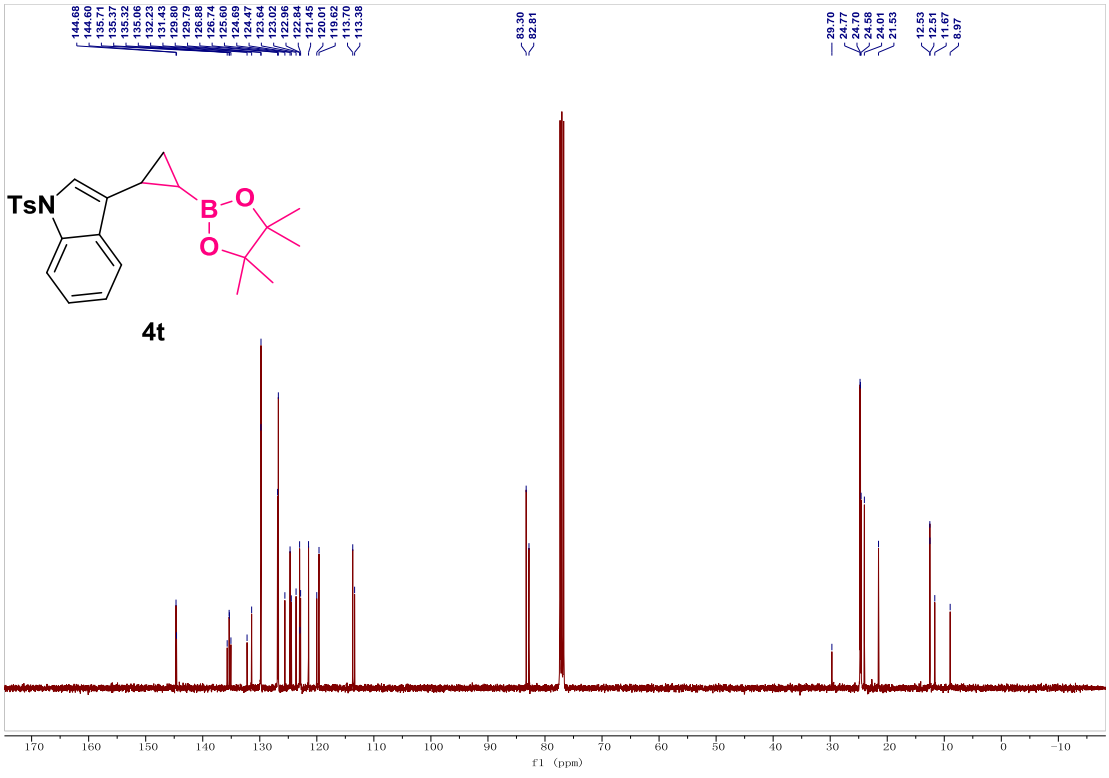

Me
Me
Me
B
O
O
4q
f1 (ppm)

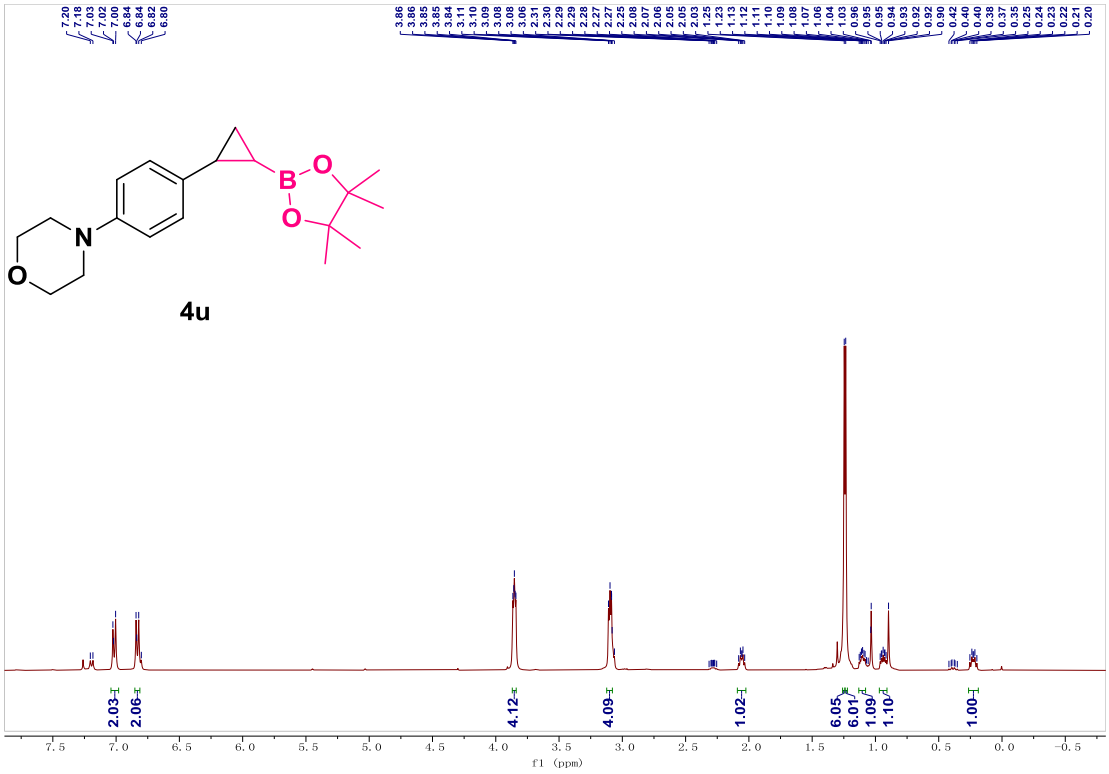

B
O
O
4r
f1 (ppm)

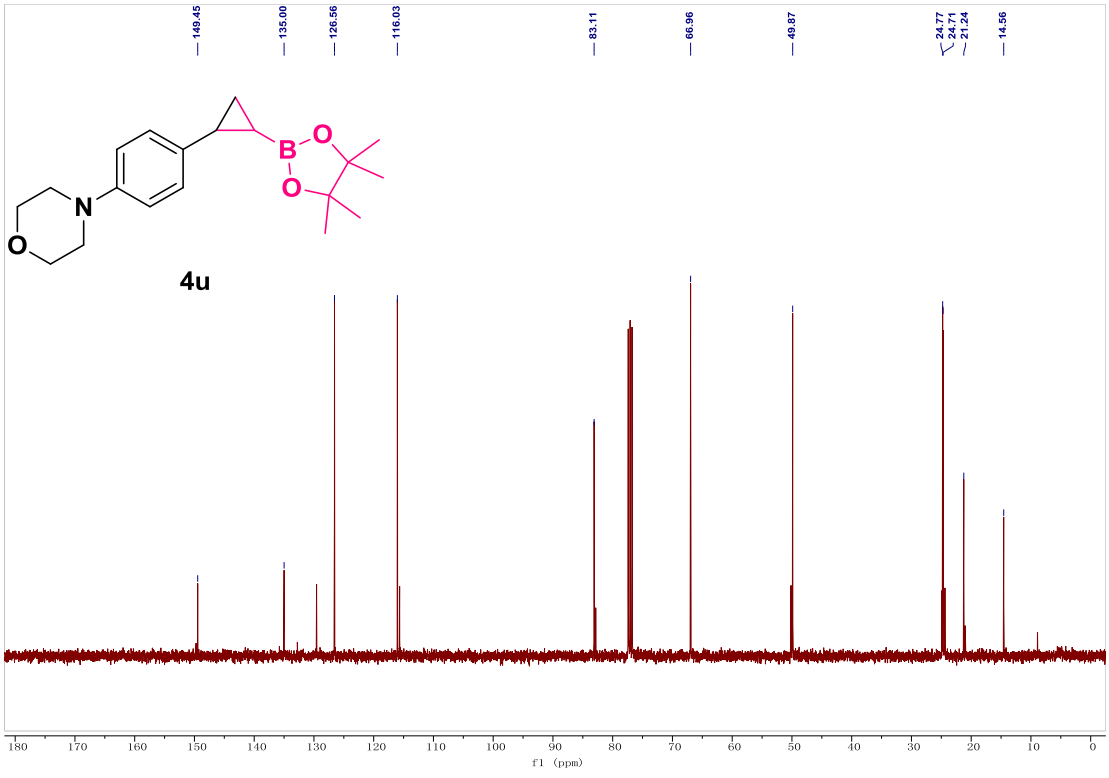

140.84
133.52
132.00
127.86
127.56
127.26
125.95
124.92
124.36
124.15
83.23
82.93
29.70
24.76
24.74
24.32
22.17
22.03
14.88
9.31
4r
f1 (ppm)

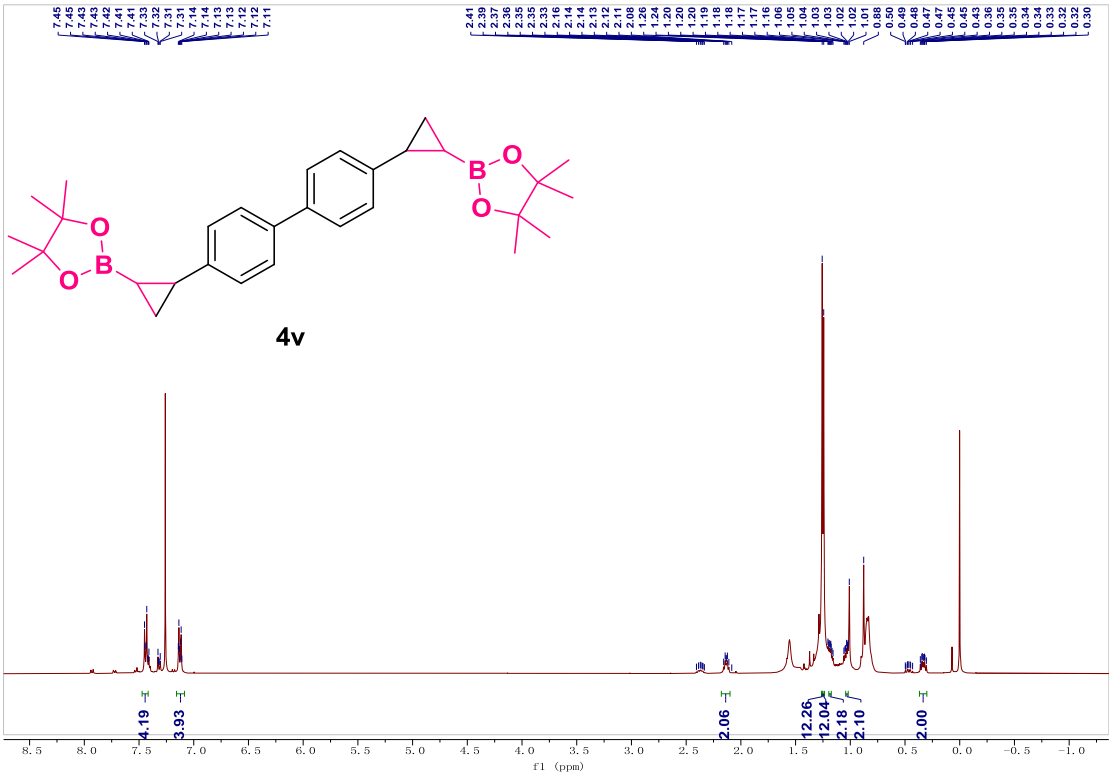

4s
1.00
0.99
1.17
0.97
1.00
1.00
1.00
0.98
12.17
1.01
1.06
1.00
f1 (ppm)

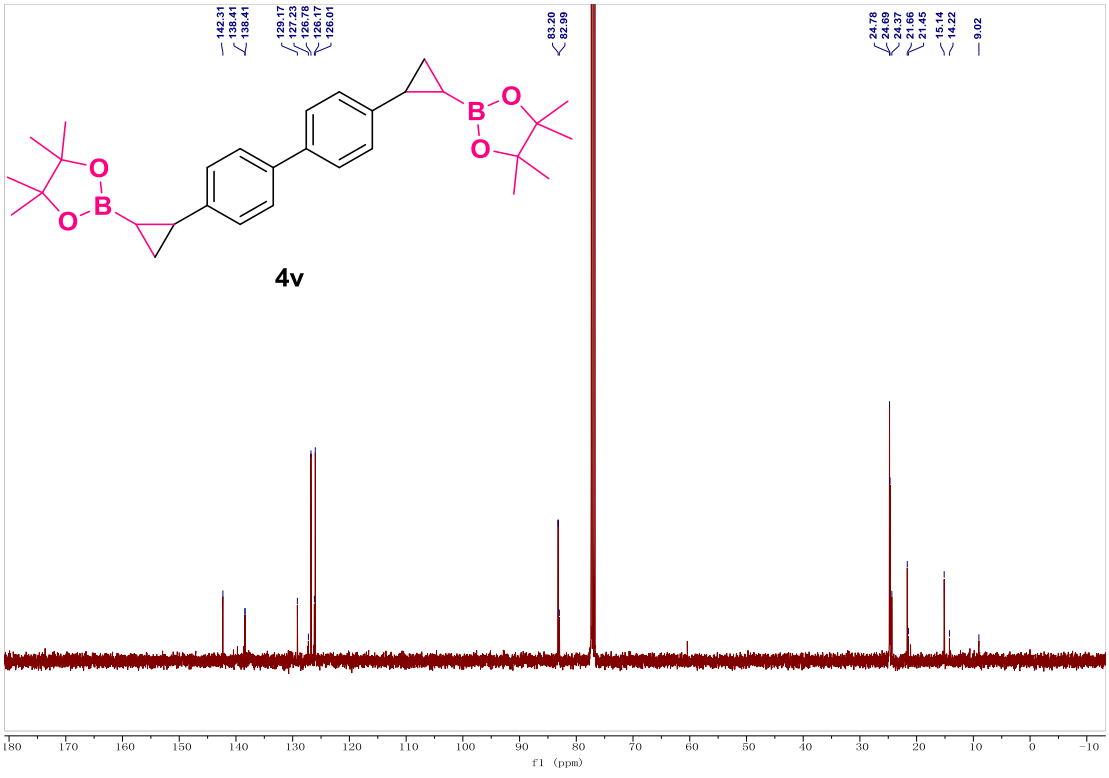

TsN
B
O
O
4t
f1 (ppm)

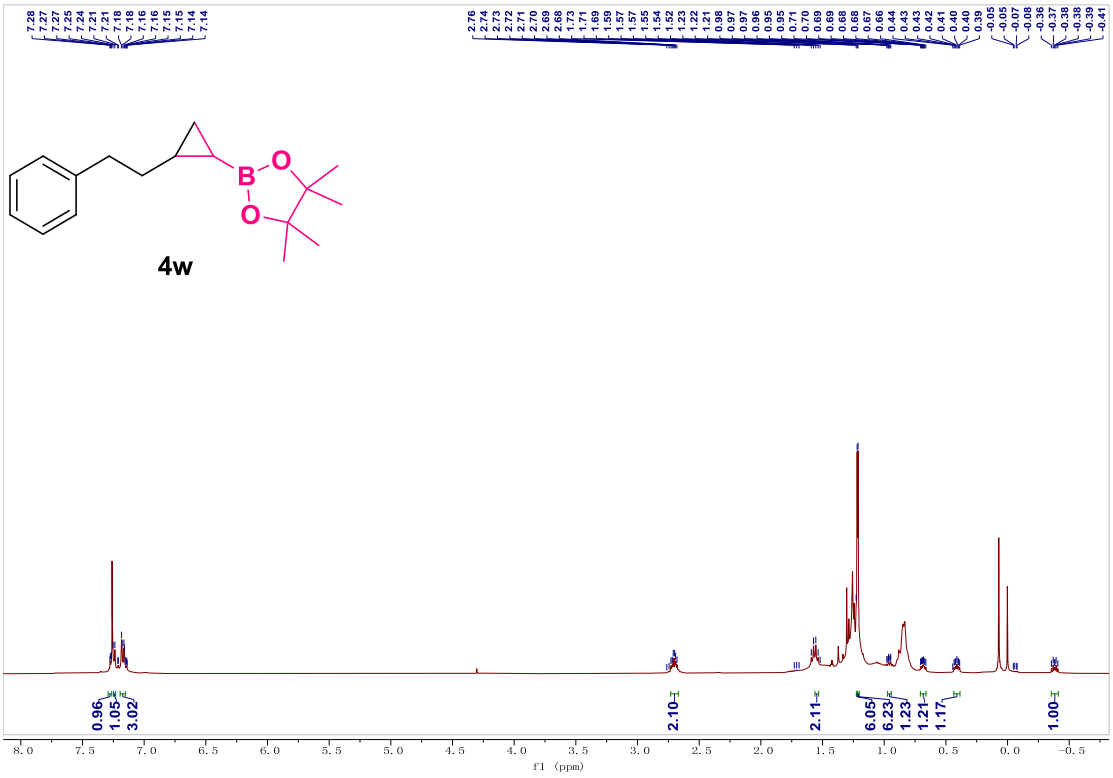

TsN
B
O
O
4t
f1 (ppm)

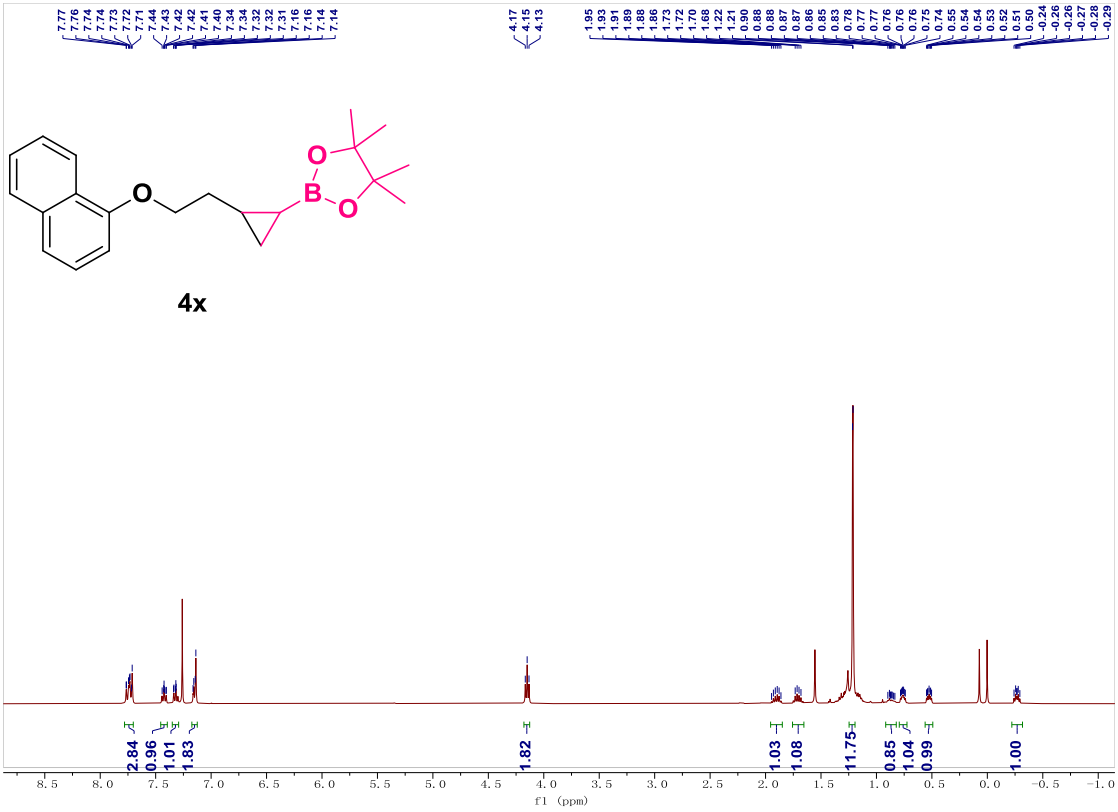

4u
f1 (ppm)

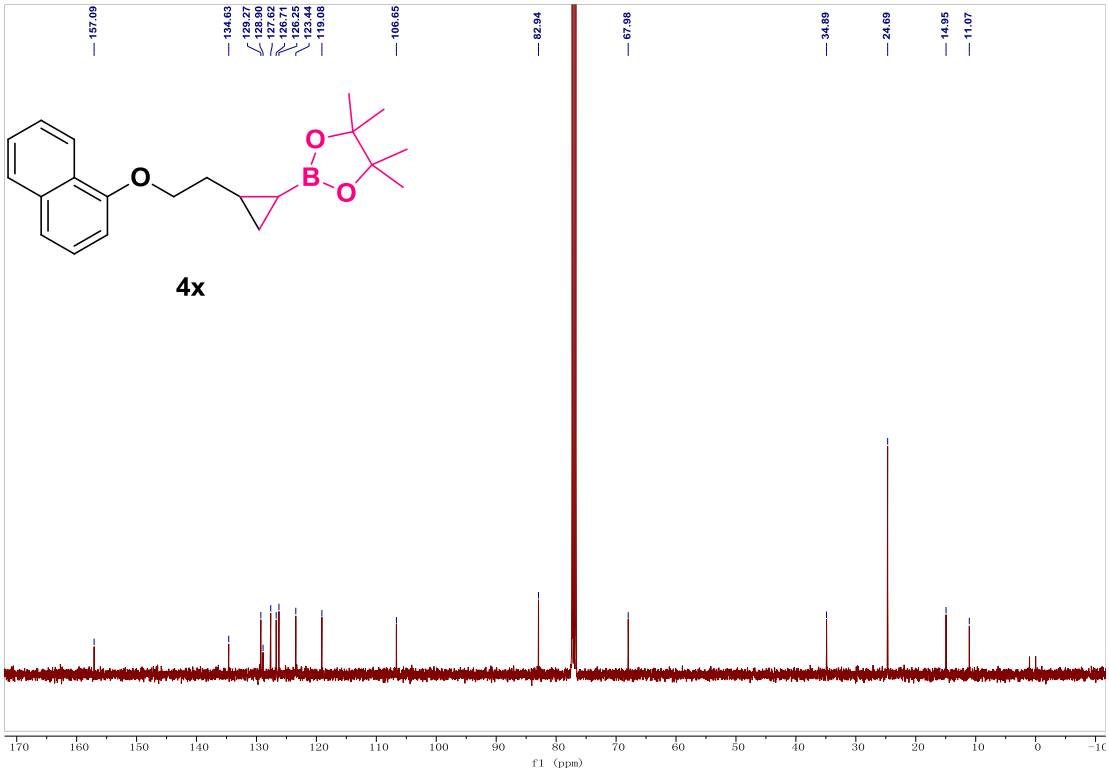

4u
f1 (ppm)

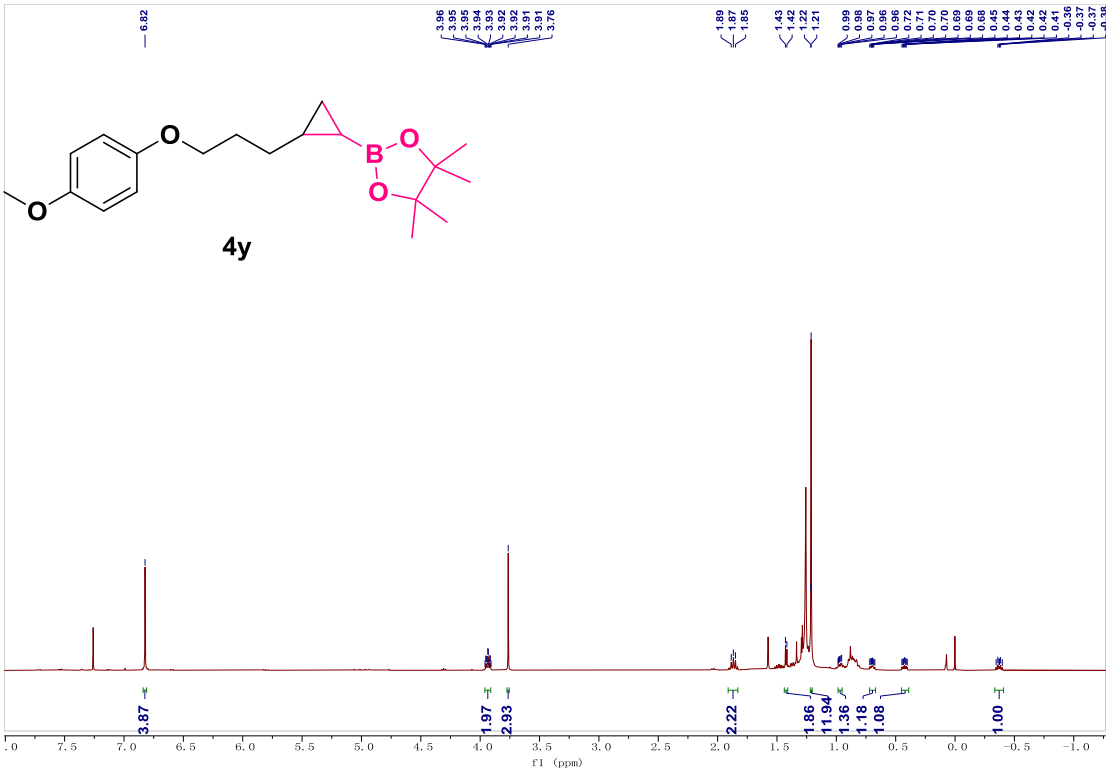

4v
4.19
3.93
2.06
12.26
12.04
2.18
2.10
2.00
f1 (ppm)

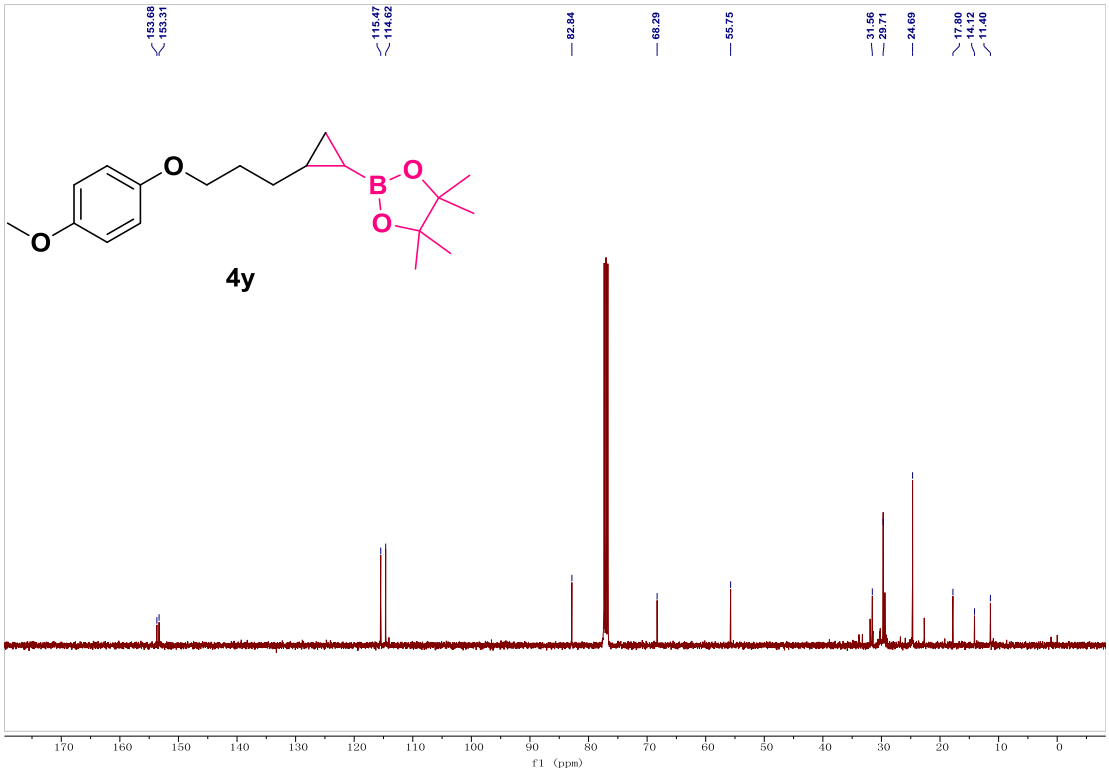

4v
f1 (ppm)

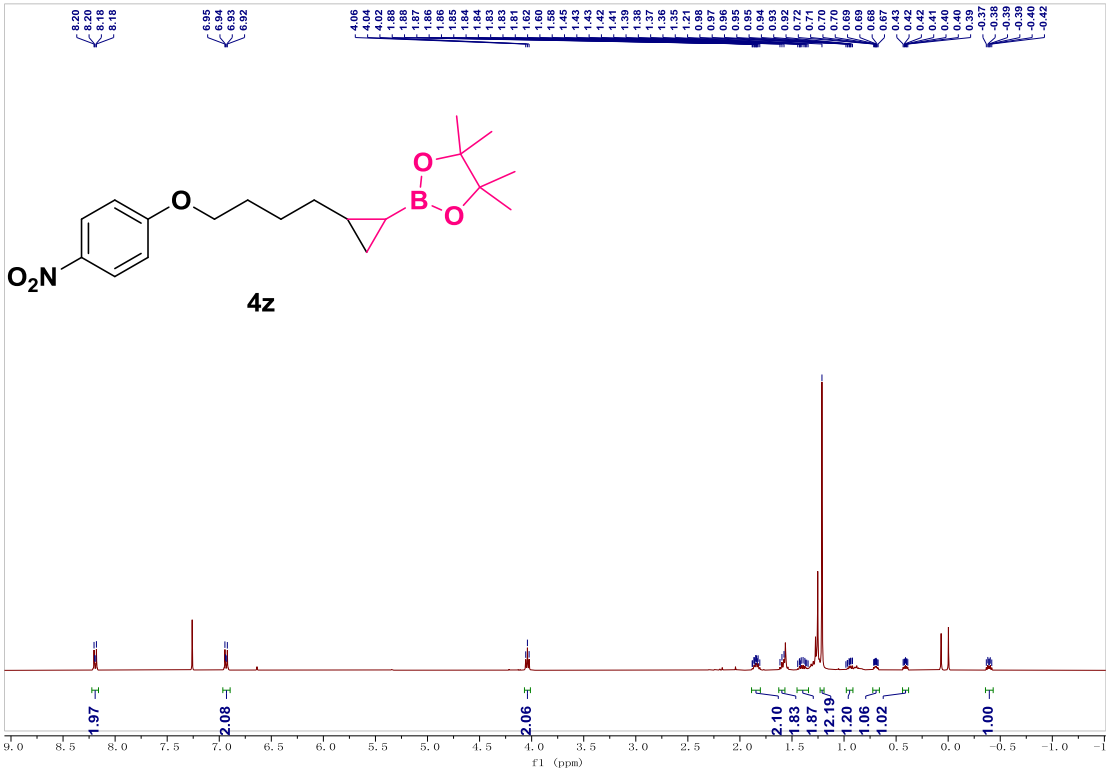

4w
f1 (ppm)

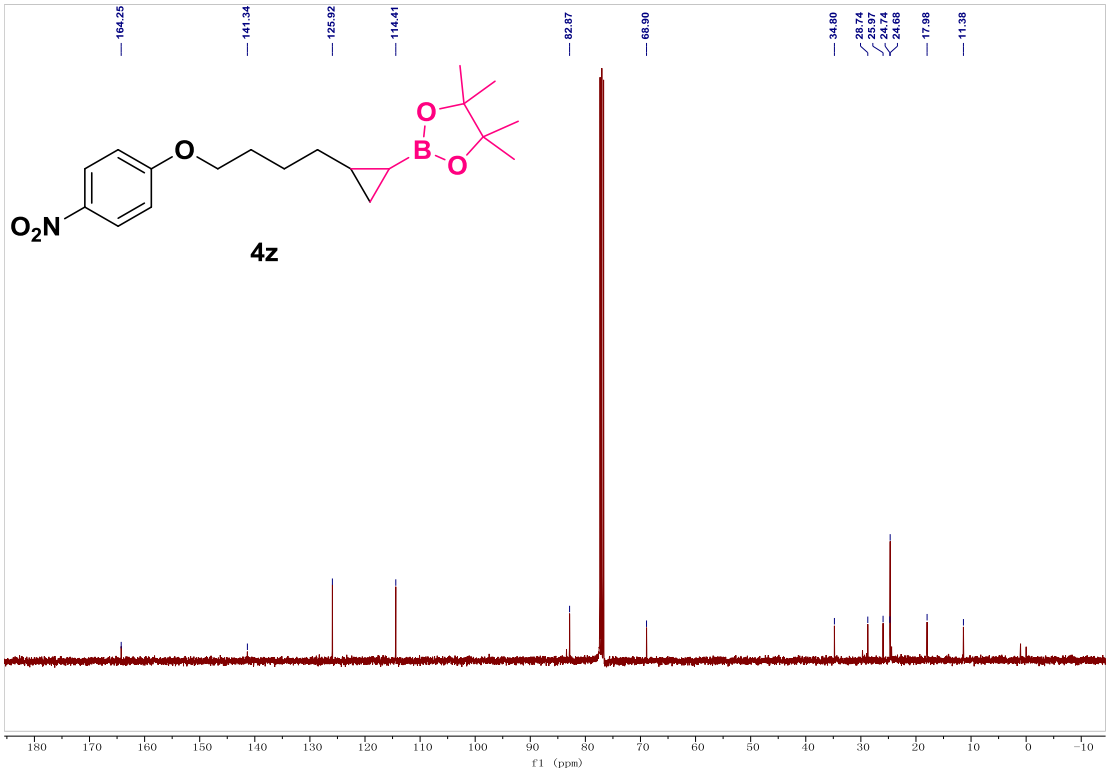

4x
f1 (ppm)

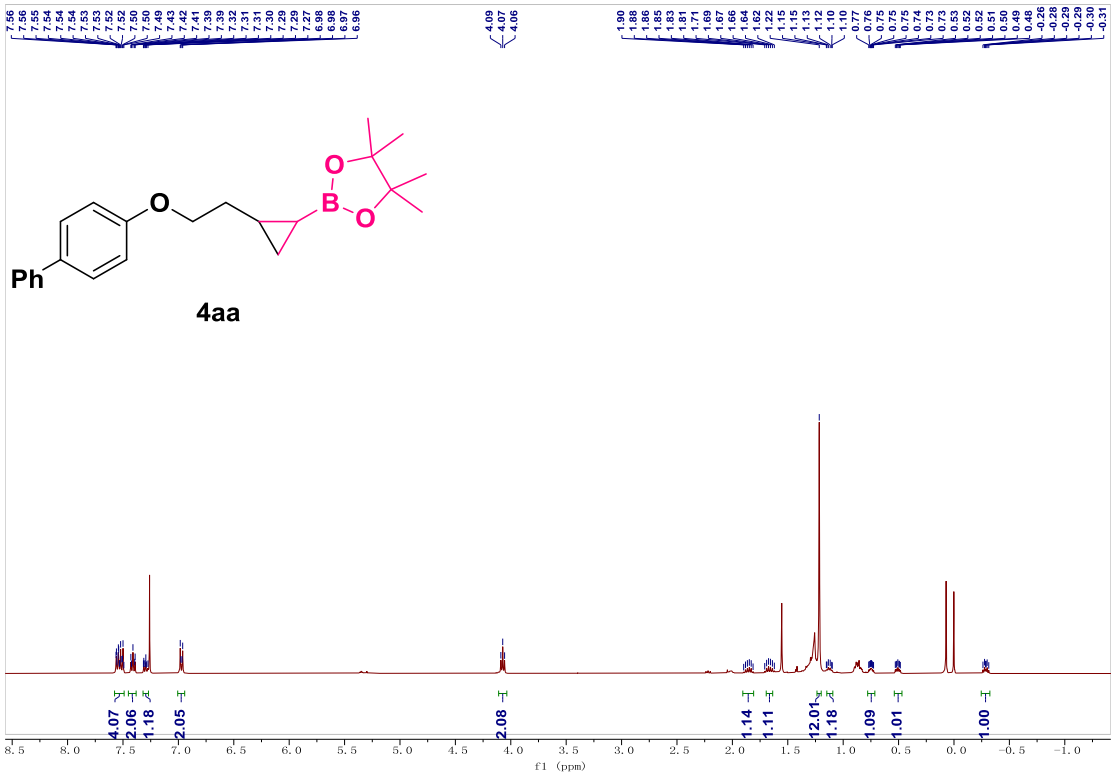

157.09
134.63
129.27
128.90
127.62
126.71
126.25
123.44
119.08
106.65
82.94
67.98
34.89
24.69
14.95
11.07
O
O
B
O
4x
f1 (ppm)

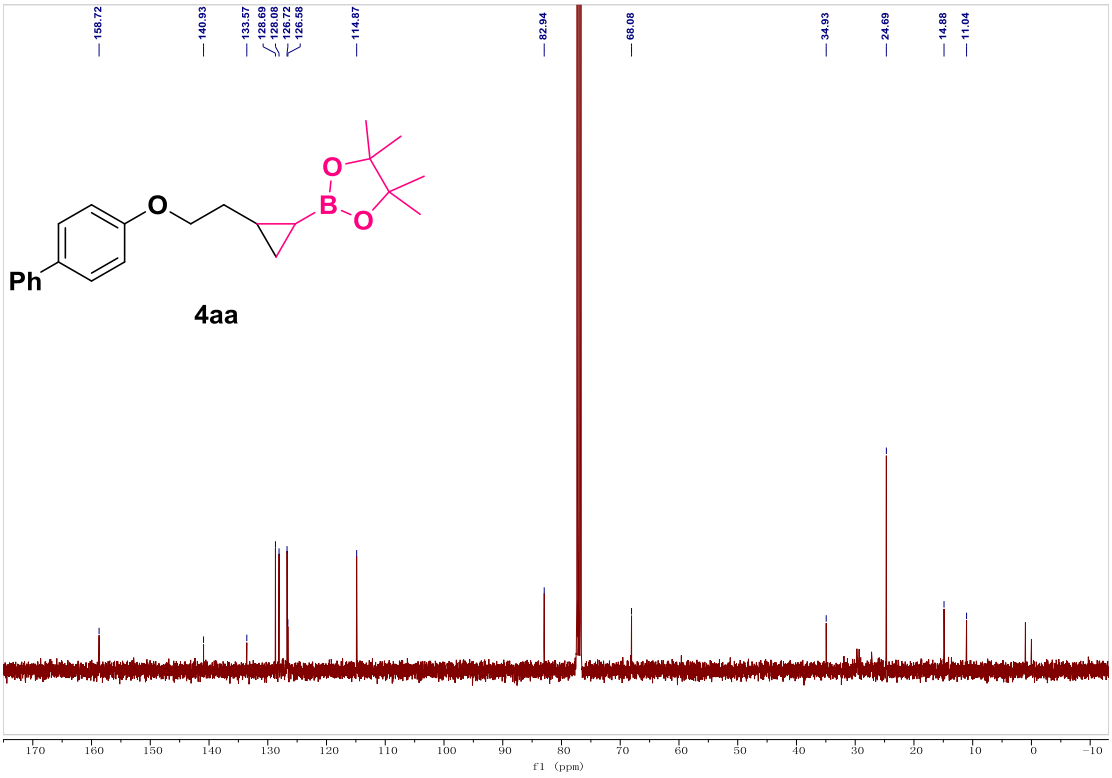

6.82
3.96
3.95
3.95
3.94
3.93
3.92
3.92
3.91
3.91
3.76
1.89
1.87
1.85
1.43
1.42
1.22
1.21
0.99
0.98
0.97
0.96
0.72
0.71
0.70
0.70
0.69
0.69
0.68
0.45
0.44
0.43
0.42
0.42
0.41
-0.36
-0.37
-0.37
O
O
B
O
O
4y
3.87
1.97
2.93
2.22
1.86
11.94
1.36
1.18
1.08
1.00
f1 (ppm)

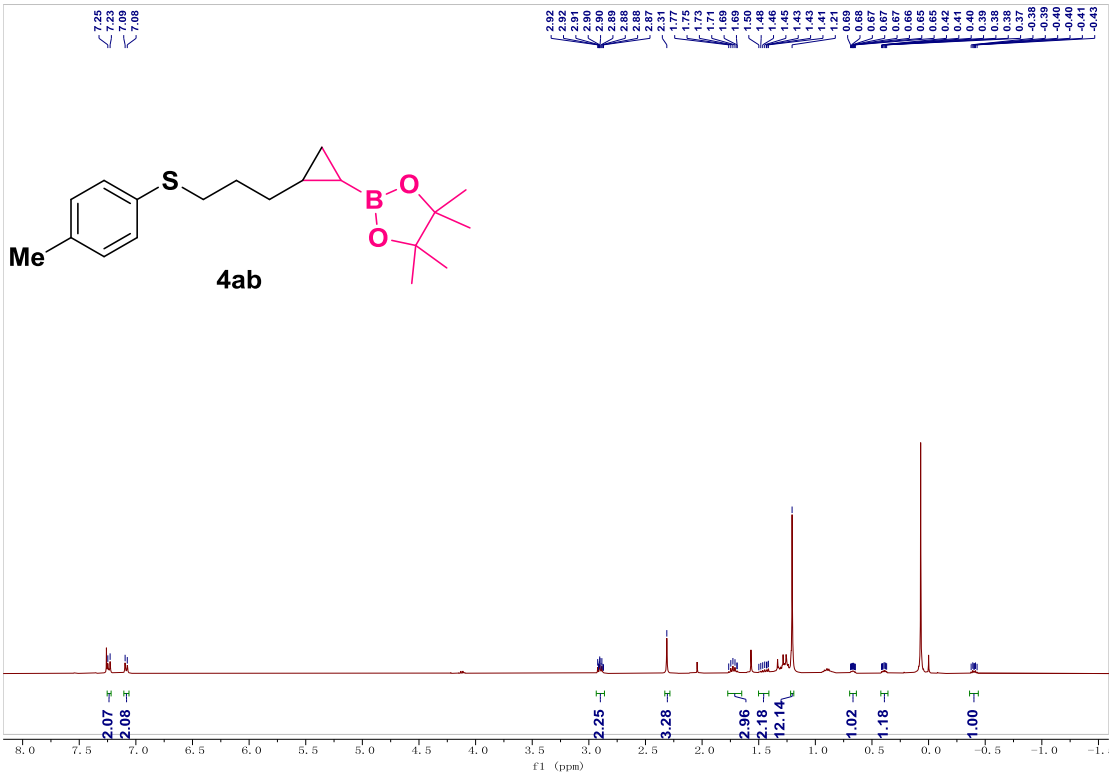

153.68
153.31
115.47
114.62
82.84
68.29
55.75
31.56
29.71
24.69
17.80
14.12
11.40
O
O
B
O
O
4y
f1 (ppm)

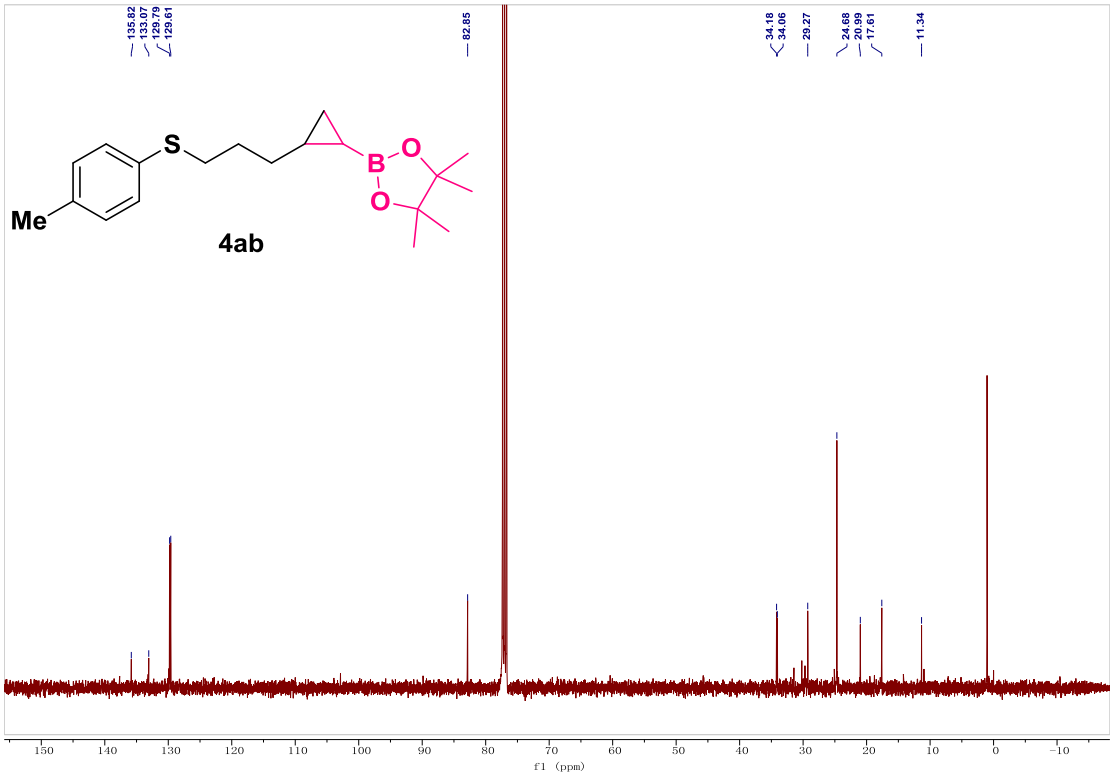

8.20
8.20
8.18
8.18
6.95
6.94
6.93
6.92
O
B
O
O
O_2N
4z
1.97
2.08
2.06
2.10
1.83
1.87
12.19
1.20
1.06
1.02
1.00
f1 (ppm)

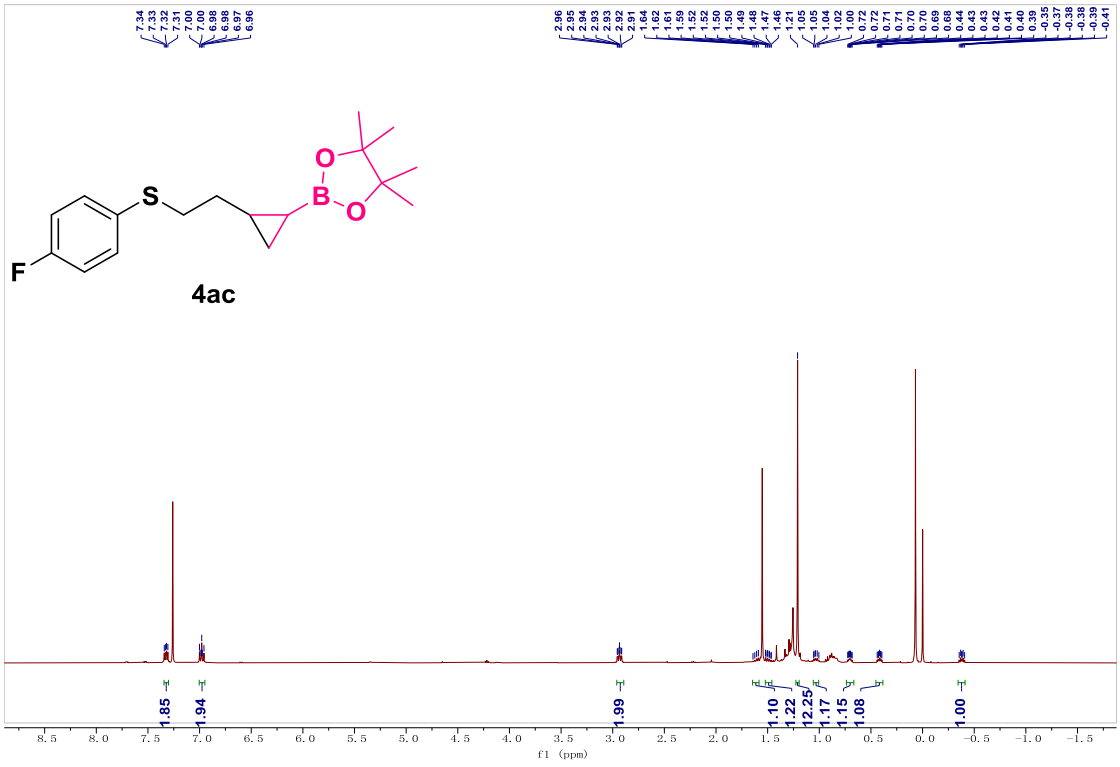

164.25
141.34
125.92
114.41
82.87
68.90
34.80
28.74
25.97
24.74
24.68
17.98
11.38
O
B
O
O
O2N
4z
f1 (ppm)

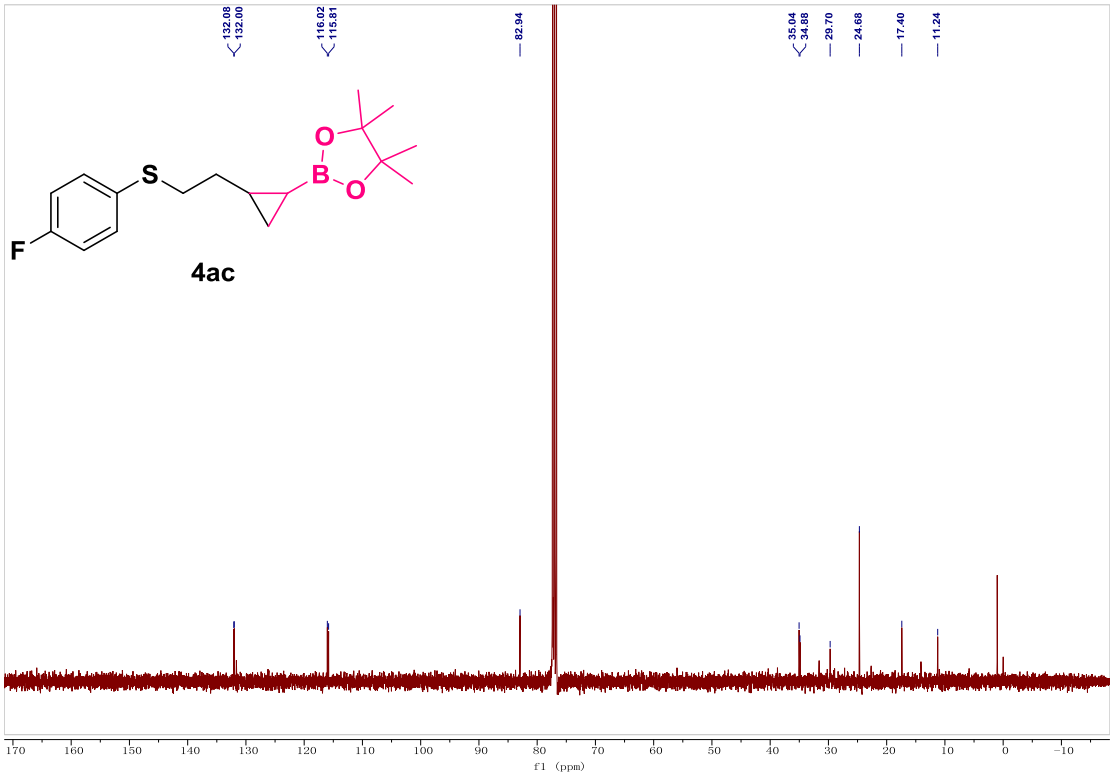

O
B
O
O
Ph
4aa
4.07
2.06
1.18
2.05
2.08
1.14
1.11
12.01
1.18
1.09
1.01
1.00
f1 (ppm)

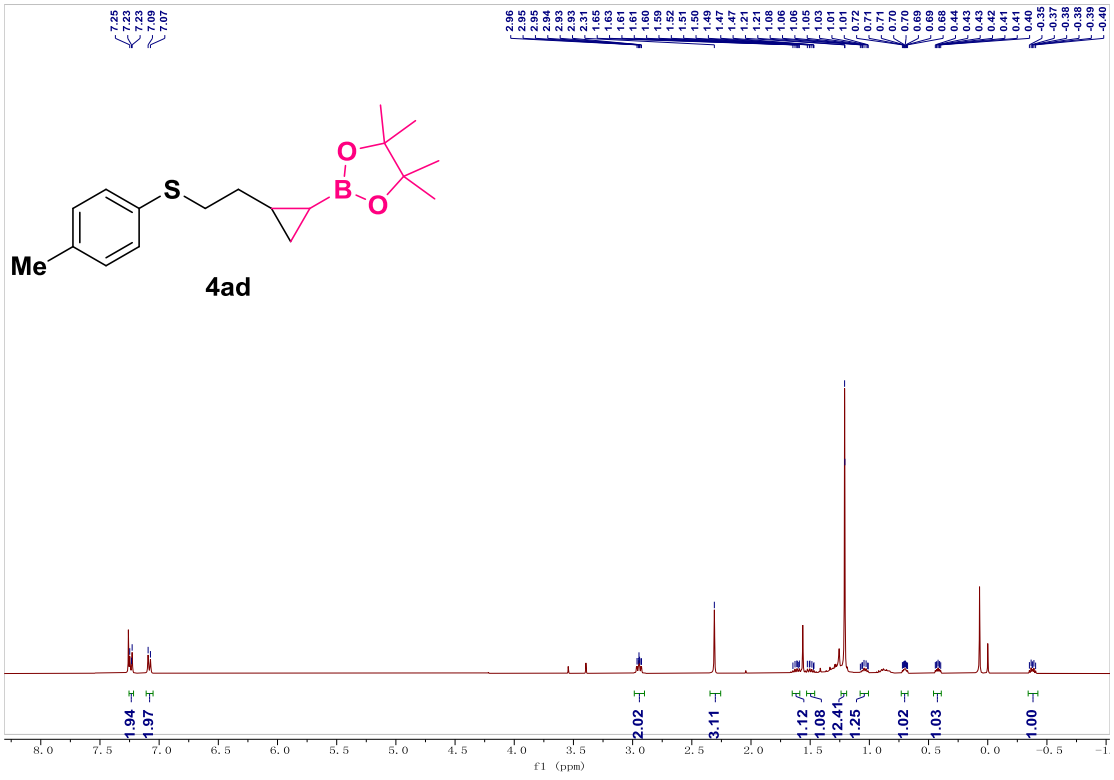

158.72
140.93
133.57
128.69
128.08
126.72
126.58
114.87
82.94
68.08
34.93
24.69
14.88
11.04
O
B
O
O
Ph
4aa
f1 (ppm)

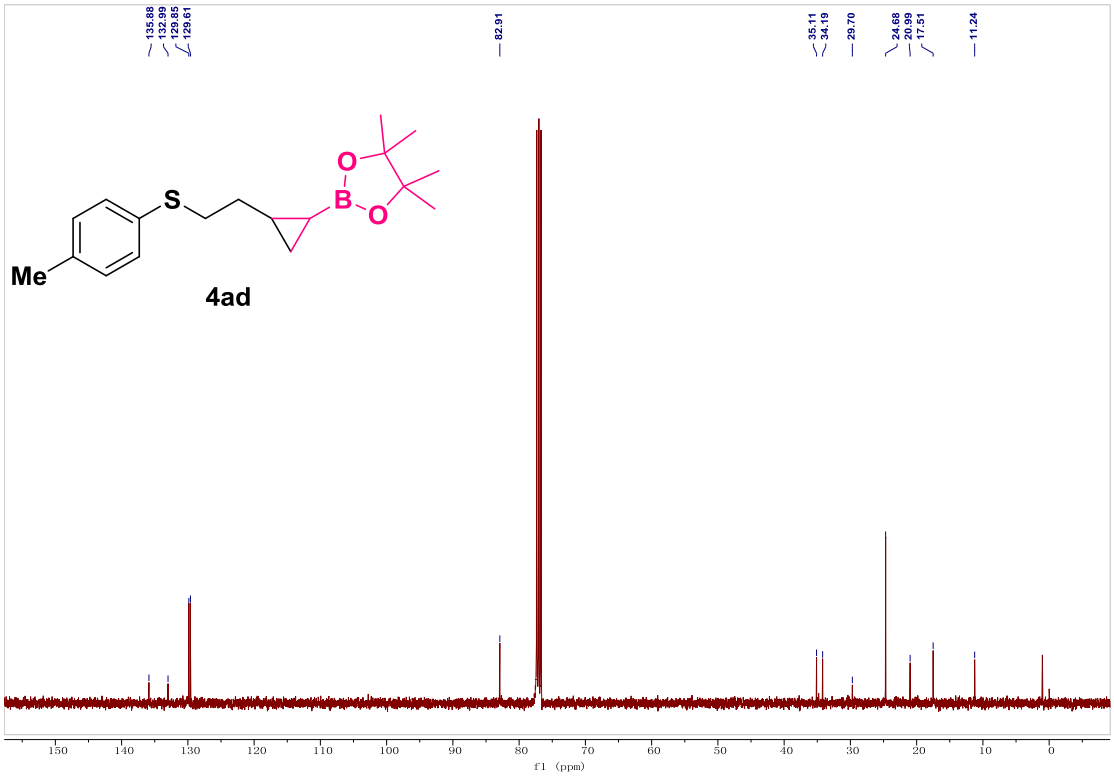

7.25
7.23
7.09
7.08
S
B
O
O
Me
4ab
2.07
2.08
2.25
3.28
2.96
2.18
12.14
1.02
1.18
1.00
f1 (ppm)

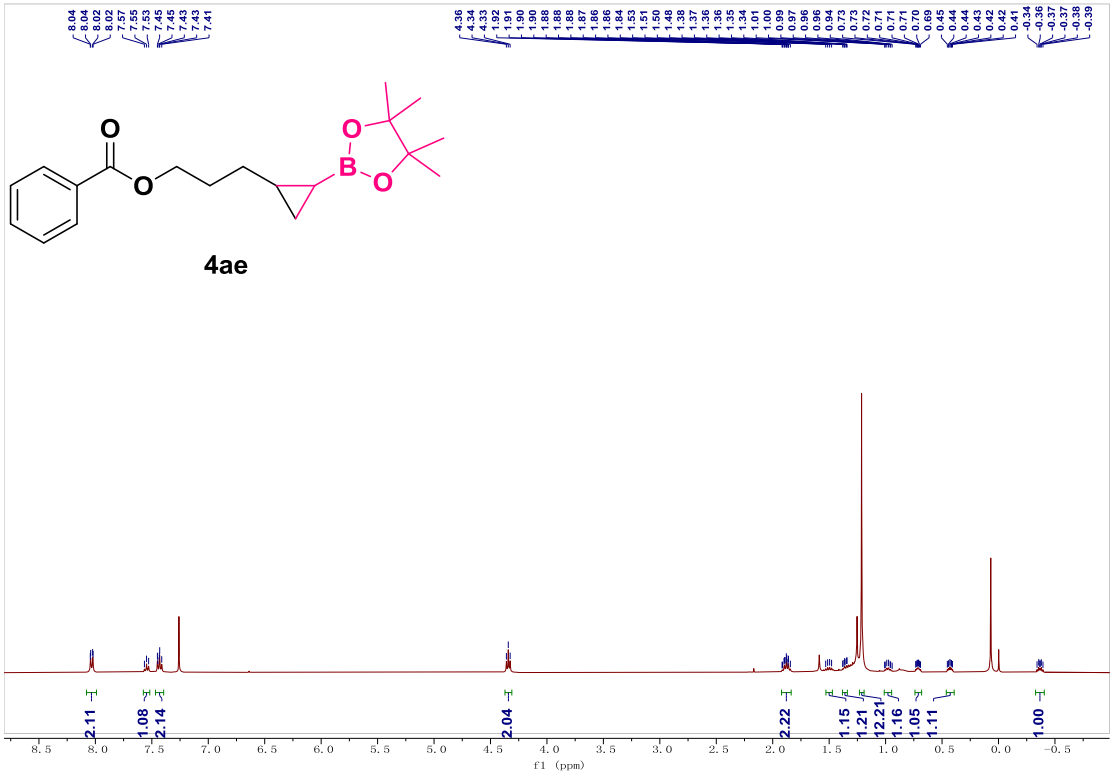

135.82
133.07
130.79
129.61
82.85
34.18
34.06
29.27
24.68
20.99
17.61
11.34
S
B
O
O
Me
4ab
f1 (ppm)

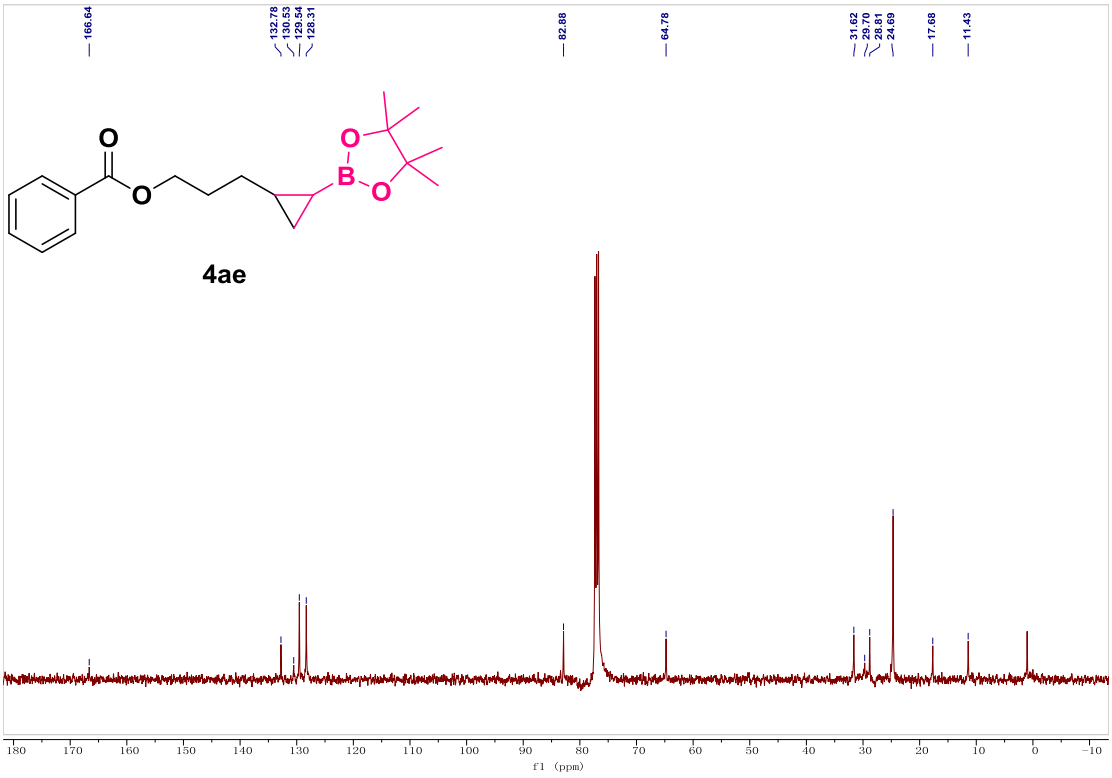

7.34
7.33
7.32
7.31
7.00
7.00
6.98
6.98
6.97
6.96
2.96
2.95
2.94
2.93
2.92
2.91
1.64
1.62
1.61
1.59
1.52
1.52
1.50
1.50
1.49
1.48
1.47
1.46
1.21
1.05
1.05
1.04
1.02
1.00
0.72
0.72
0.71
0.71
0.70
0.70
0.69
0.68
0.44
0.43
0.43
0.42
0.41
0.40
0.39
-0.35
-0.37
-0.38
-0.38
-0.39
-0.41
O
B
O
S
F
4ac
1.85
1.94
1.99
1.10
1.22
12.25
1.17
1.15
1.08
1.00
f1 (ppm)

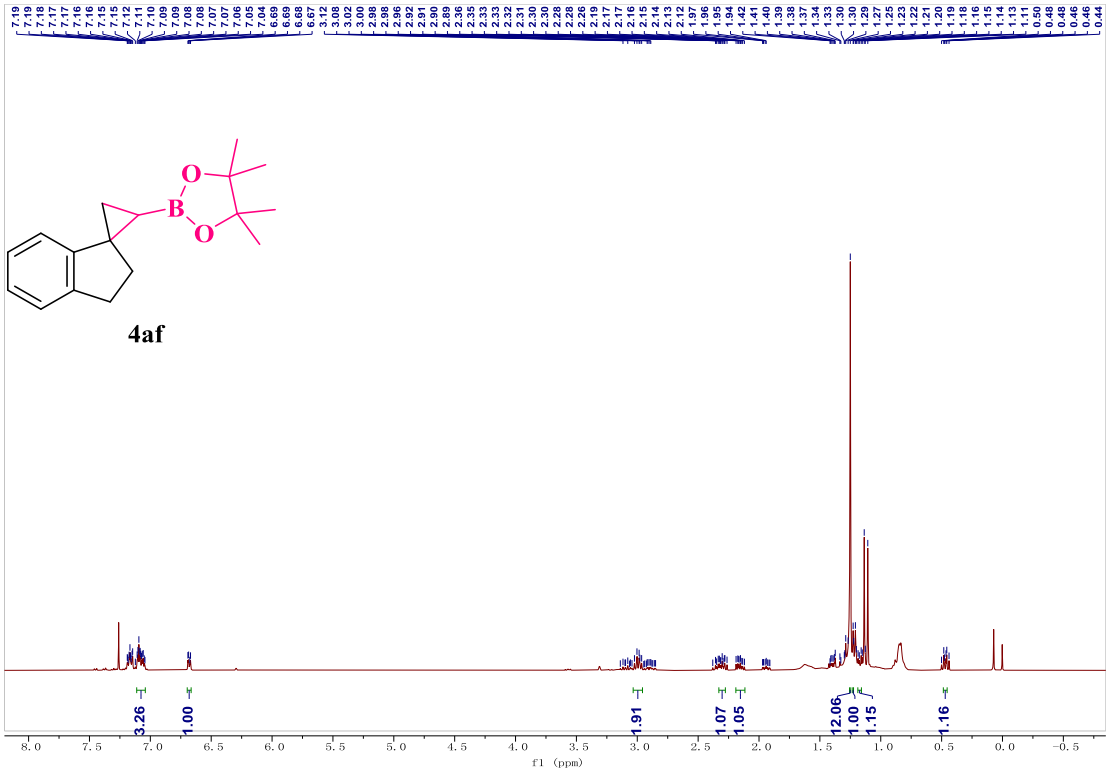

132.08
132.00
116.02
115.81
82.94
35.04
34.88
29.70
24.68
17.40
11.24
O
B
O
S
F
4ac
f1 (ppm)

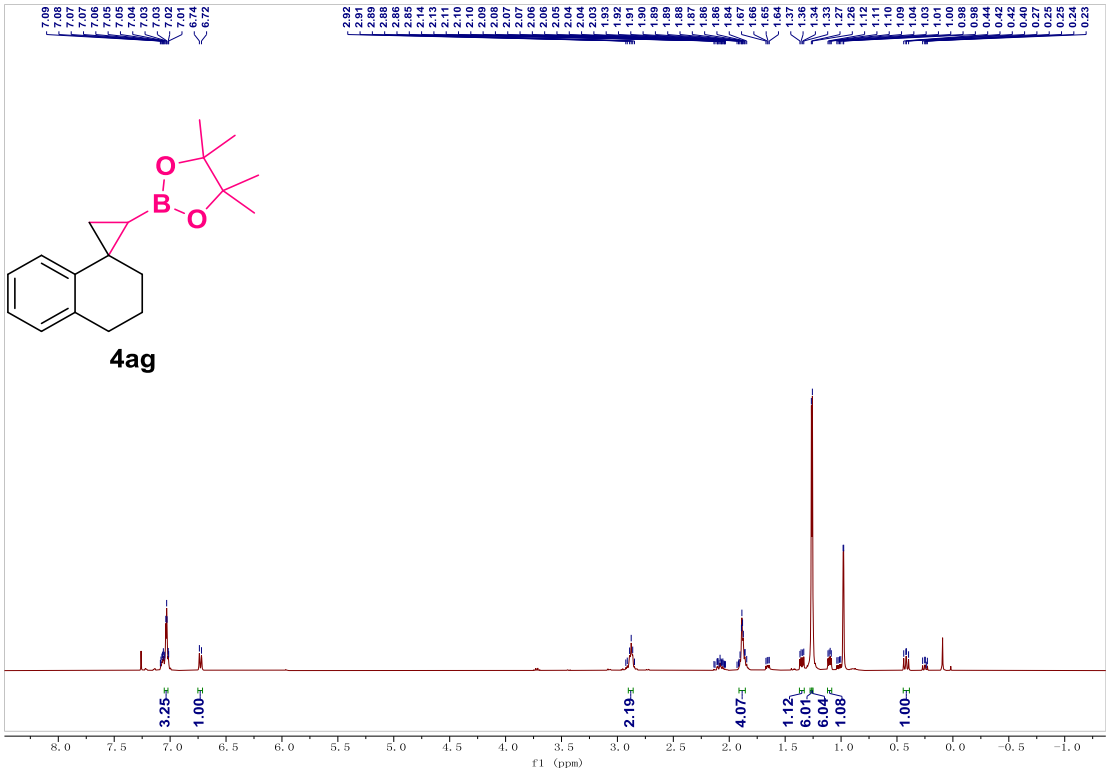

7.25
7.23
7.23
7.09
7.07
O
B
O
S
Me
4ad
1.94
1.97
2.02
3.11
1.12
1.08
12.41
1.25
1.02
1.03
1.00
f1 (ppm)

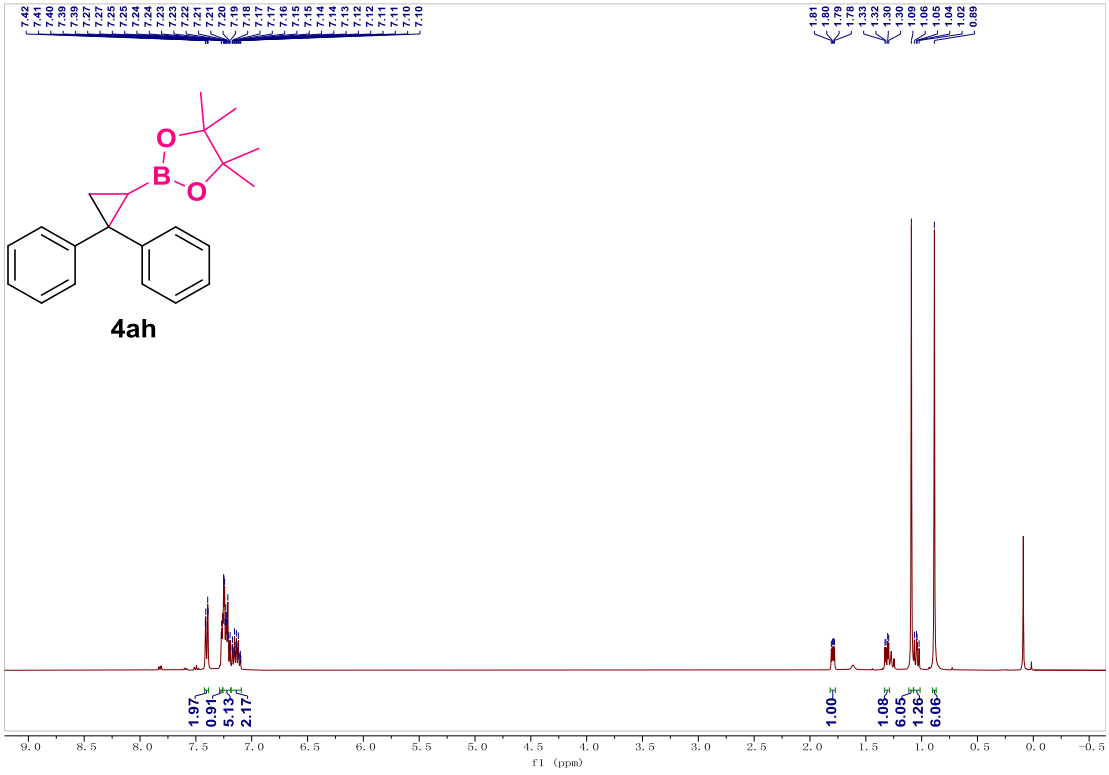

135.88
132.99
129.85
129.61
82.91
35.11
34.19
29.70
24.68
20.99
17.51
11.24
S
O
B
O
Me
4ad
f1 (ppm)

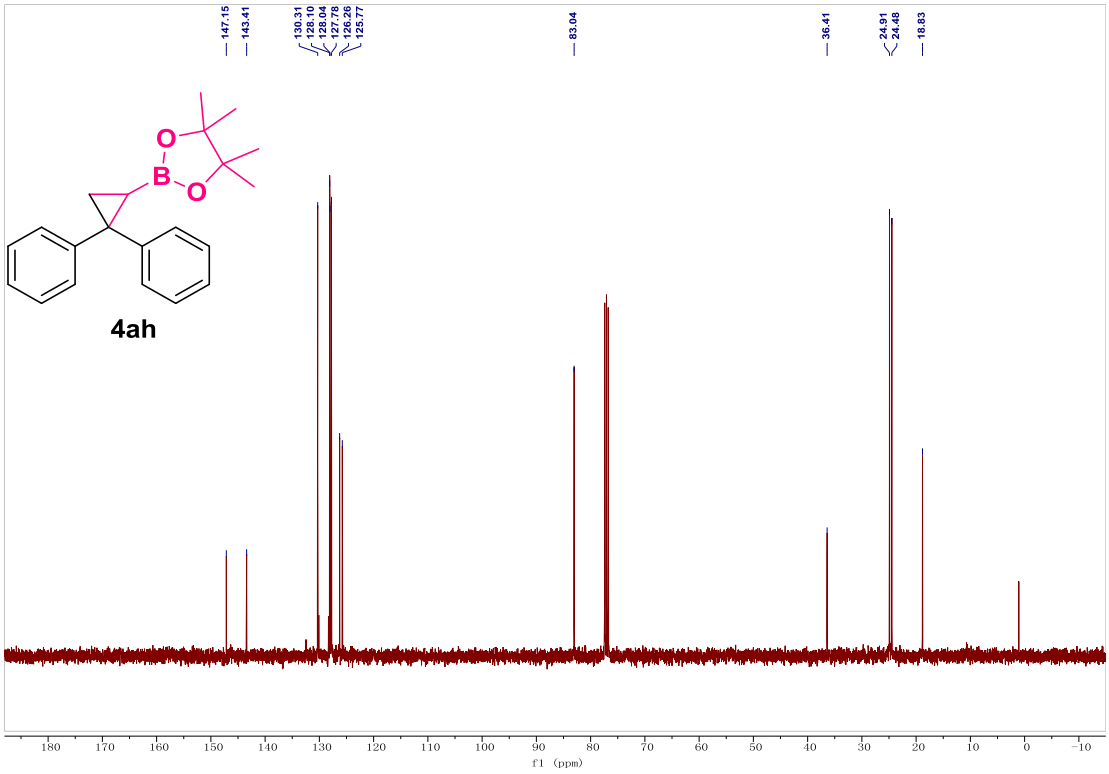

8.04
8.04
8.02
8.02
7.57
7.55
7.53
7.45
7.45
7.43
7.43
7.41
O
O
B
O
4ae
2.11
1.08
2.14
2.04
2.22
1.15
1.21
12.21
1.16
1.05
1.11
1.00
f1 (ppm)

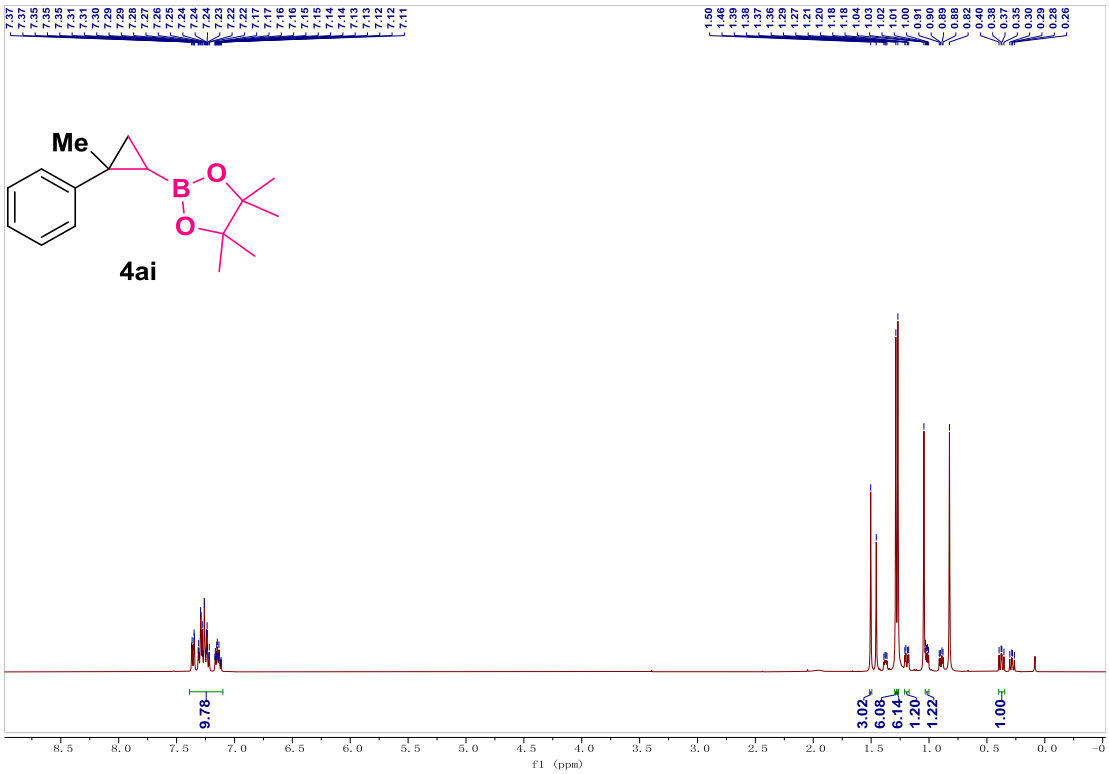

166.64
132.78
130.53
129.54
128.31
82.88
64.78
31.62
29.70
28.81
24.69
17.68
11.43
O
O
O
B
O
4ae
f1 (ppm)

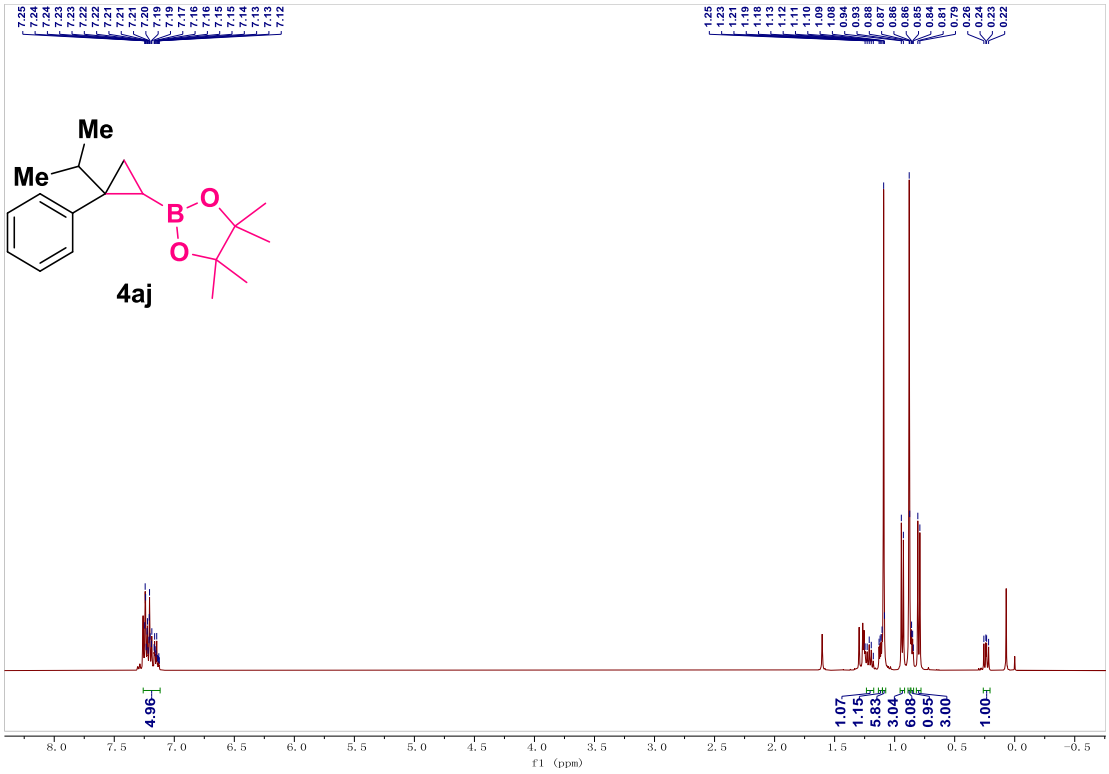

O
B
O
4af
3.26
1.00
1.91
1.07
1.05
12.06
1.00
1.15
1.16
f1 (ppm)

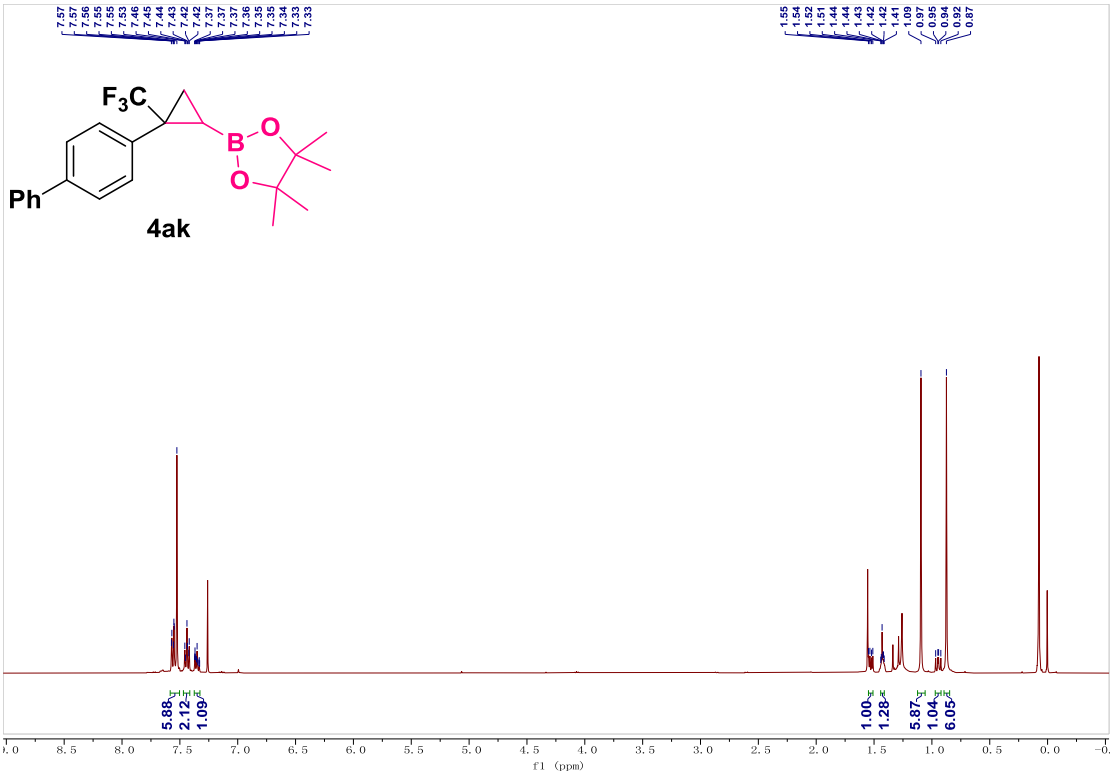

4ag
3.25
1.00
2.19
4.07
1.12
6.01
6.04
1.08
1.00
f1 (ppm)

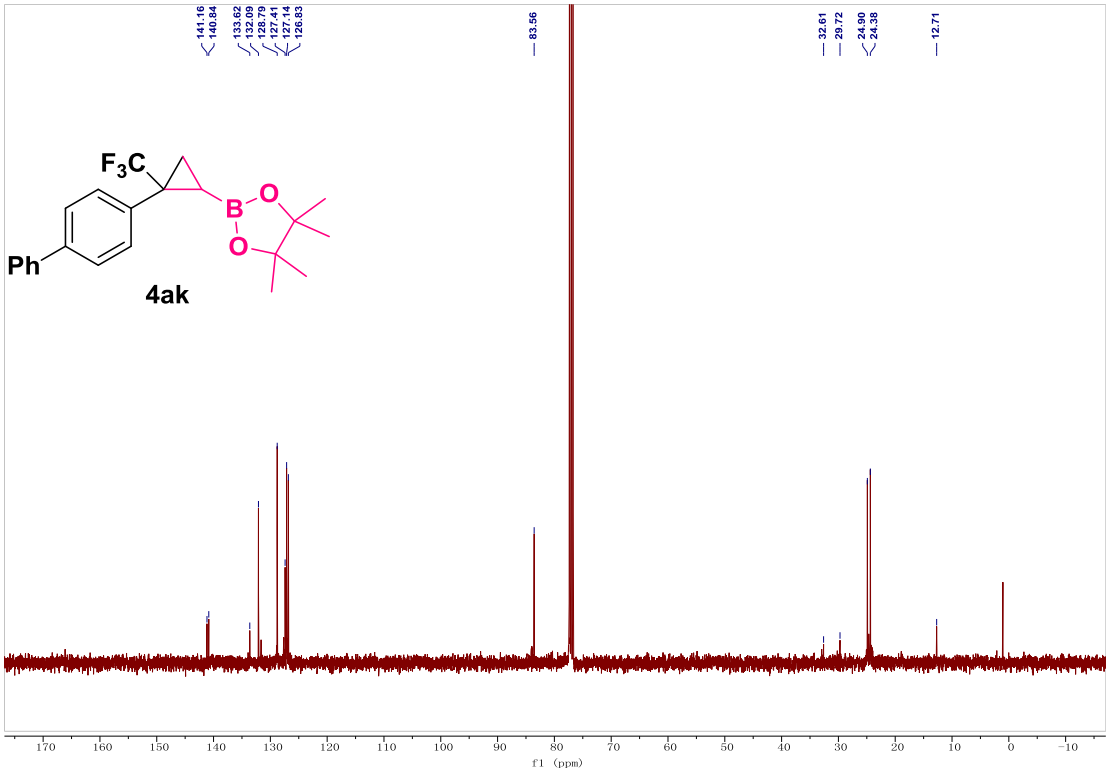

4ah
1.97
0.91
5.13
2.17
1.00
1.08
6.05
1.26
6.06
f1 (ppm)

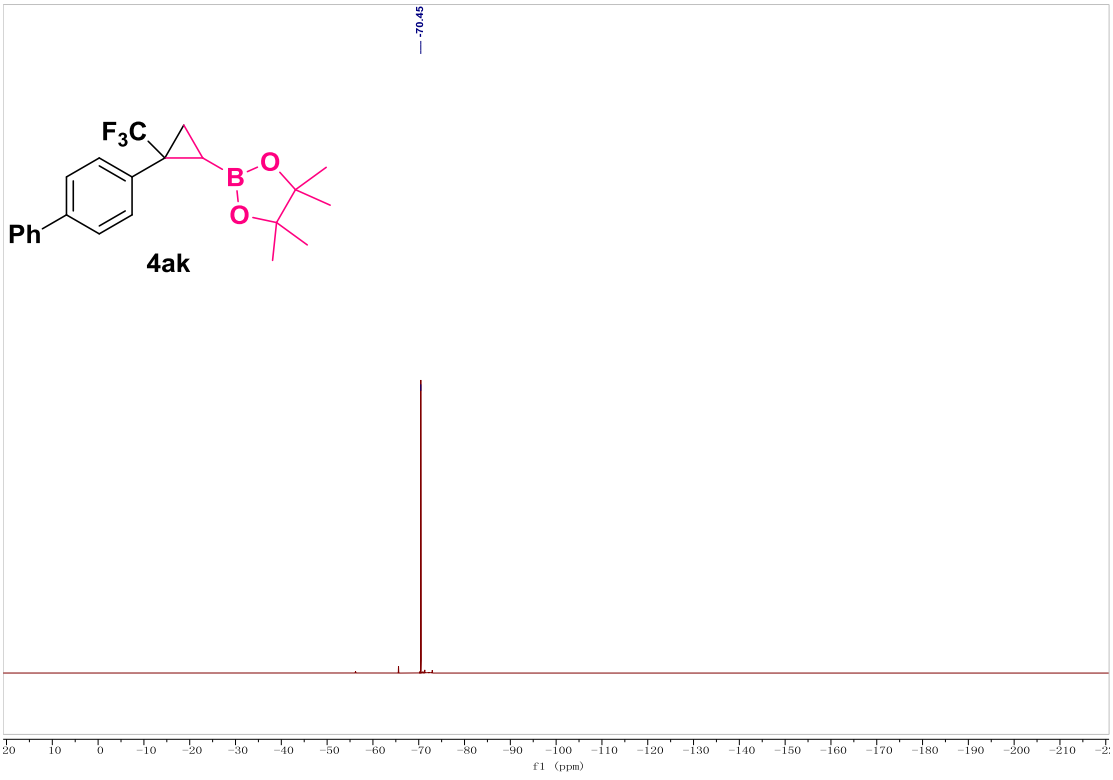

147.15
143.41
130.31
128.10
128.04
127.78
126.26
125.77
83.04
36.41
24.91
24.48
18.83
O
B
O
4ah
f1 (ppm)

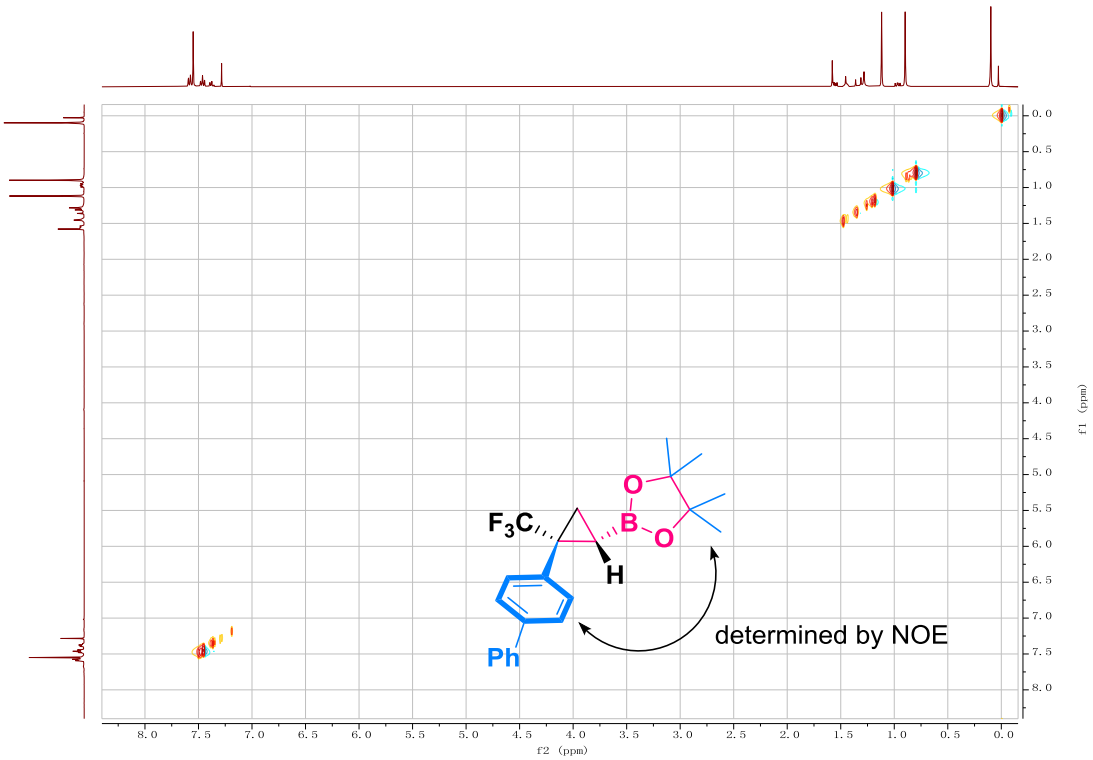

Me
B
O
O
O
4ai
9.78
3.02
6.08
6.14
1.20
1.22
1.00
f1 (ppm)

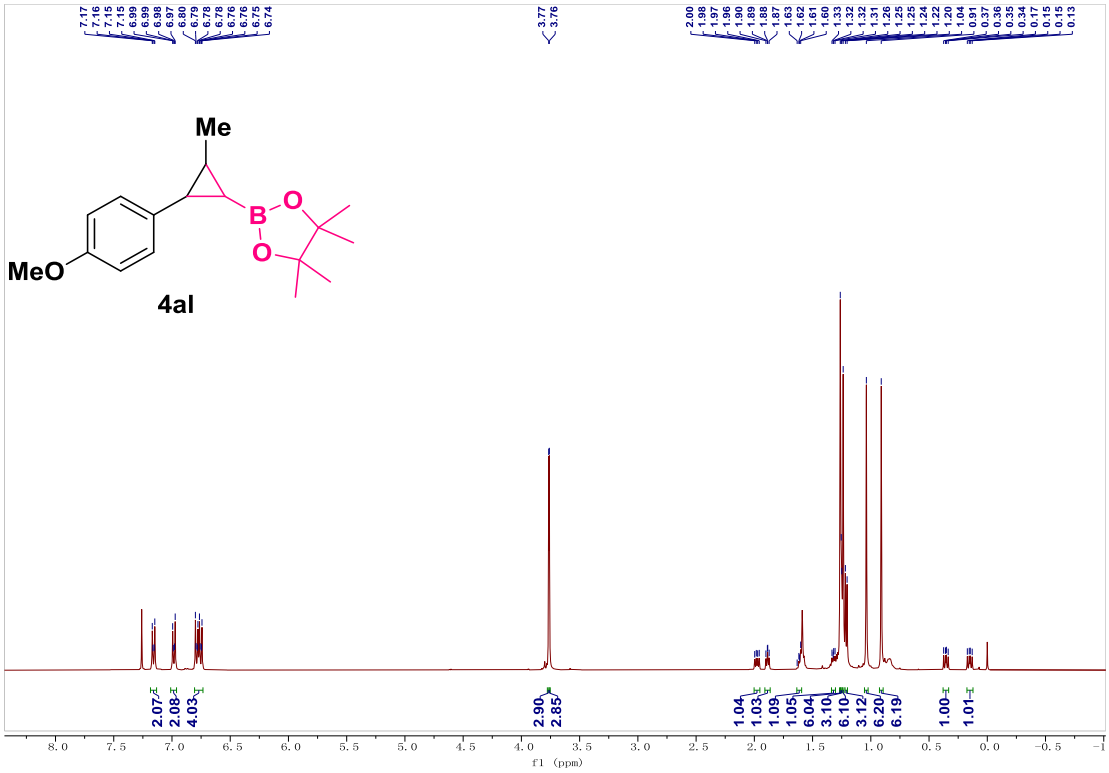

Me
Me
B
O
O
4aj
4.96
1.07
1.15
5.83
3.04
6.08
0.95
3.00
1.00
f1 (ppm)

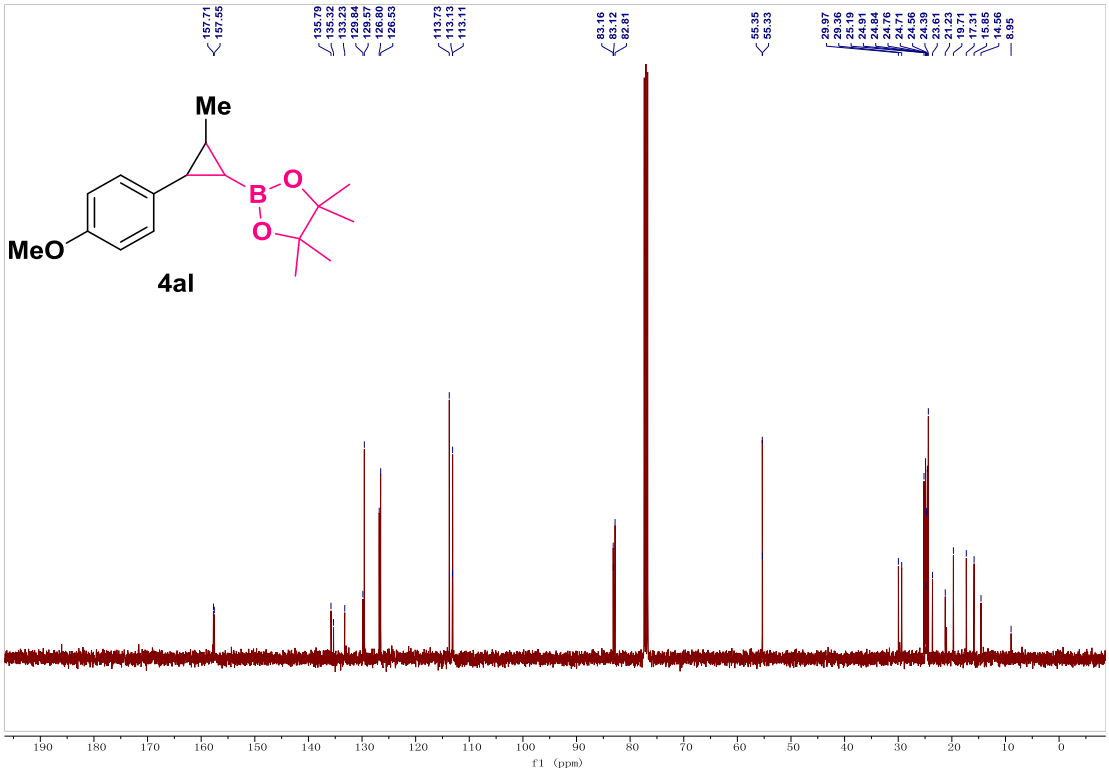

F3C
Ph
B
O
O
4ak
5.88
2.12
1.09
1.00
1.28
5.87
1.04
6.05
f1 (ppm)

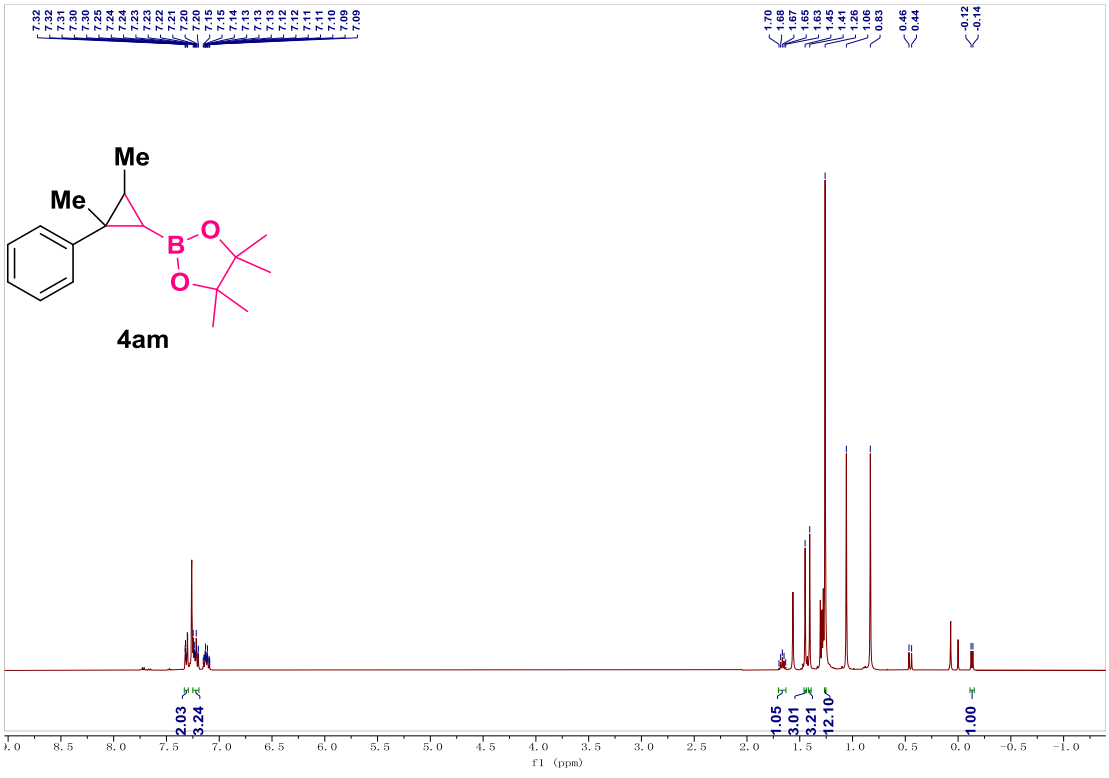

141.16
140.84
133.62
132.06
128.79
127.41
127.14
126.83
83.56
32.61
29.72
24.90
24.38
12.71
F3C
B
O
O
Ph
4ak
f1 (ppm)

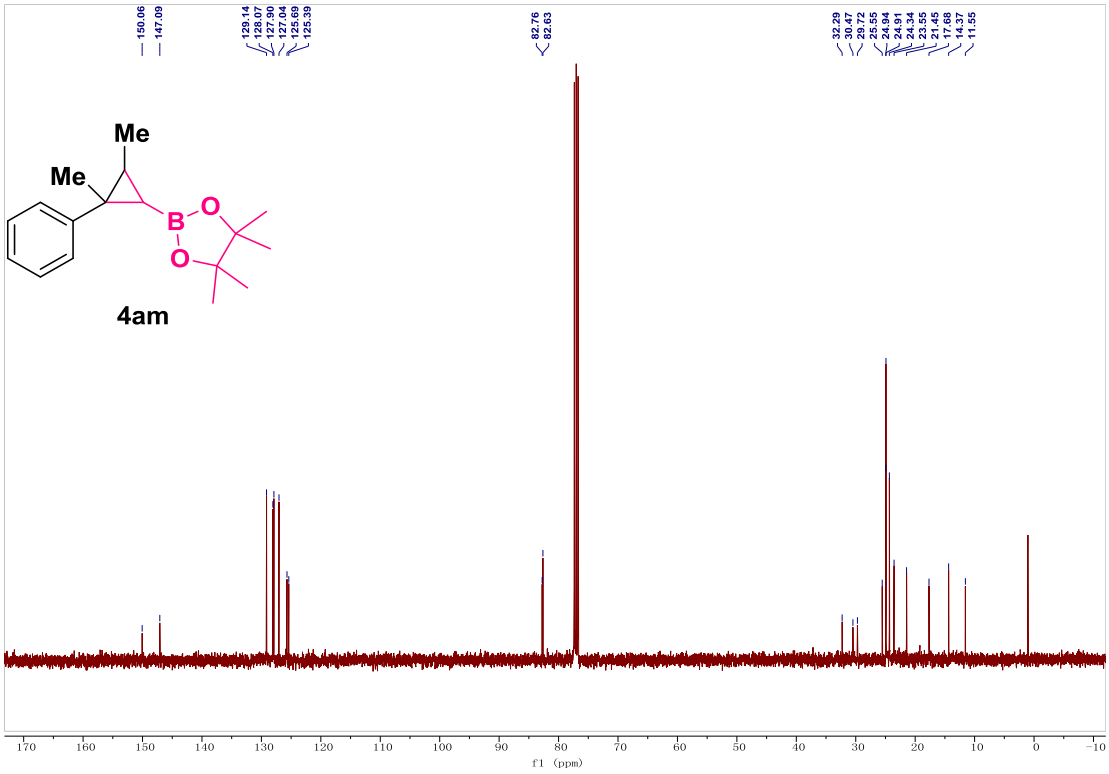

-70.45
F3C
B
O
O
Ph
4ak
f1 (ppm)

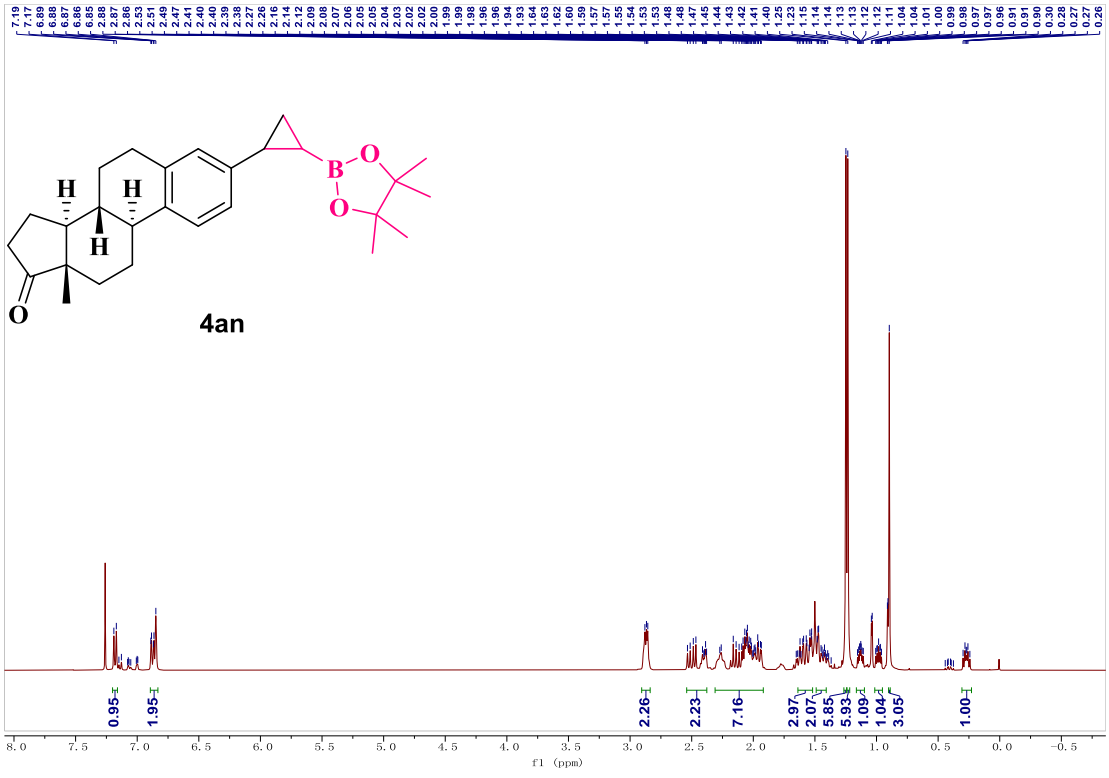

F3C
O
B
O
H
Ph
determined by NOE
f2 (ppm)
f1 (ppm)

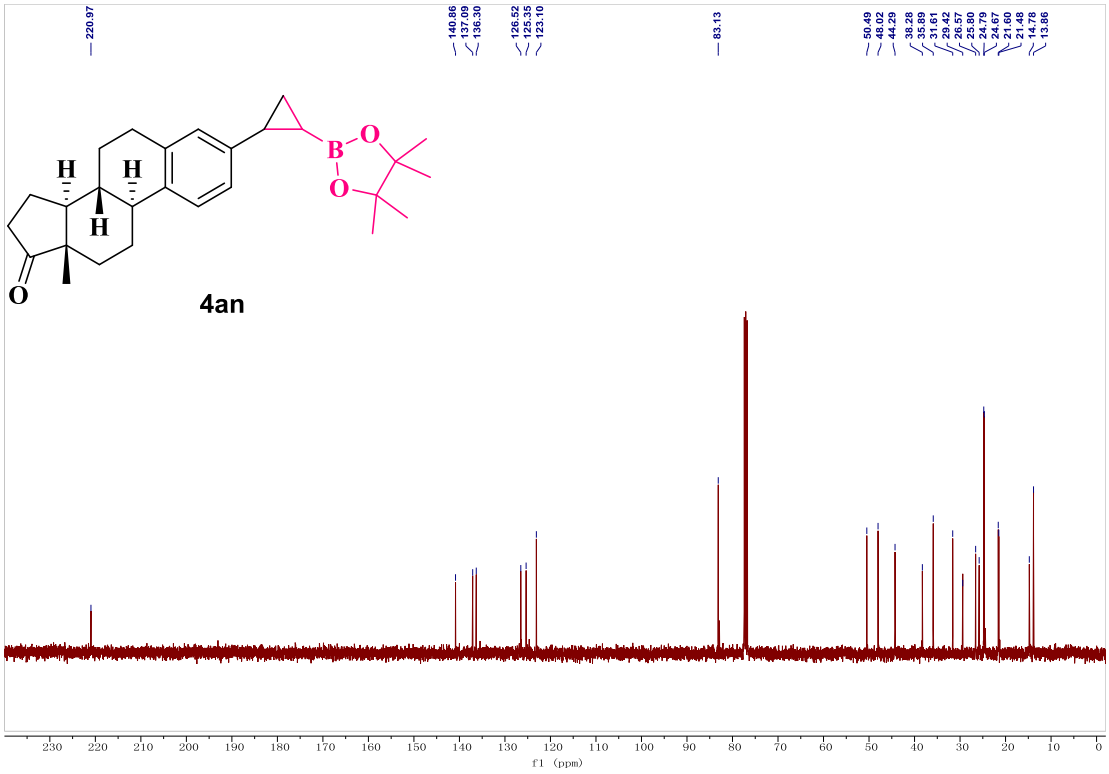

Me
MeO
B
O
O
4al
f1 (ppm)

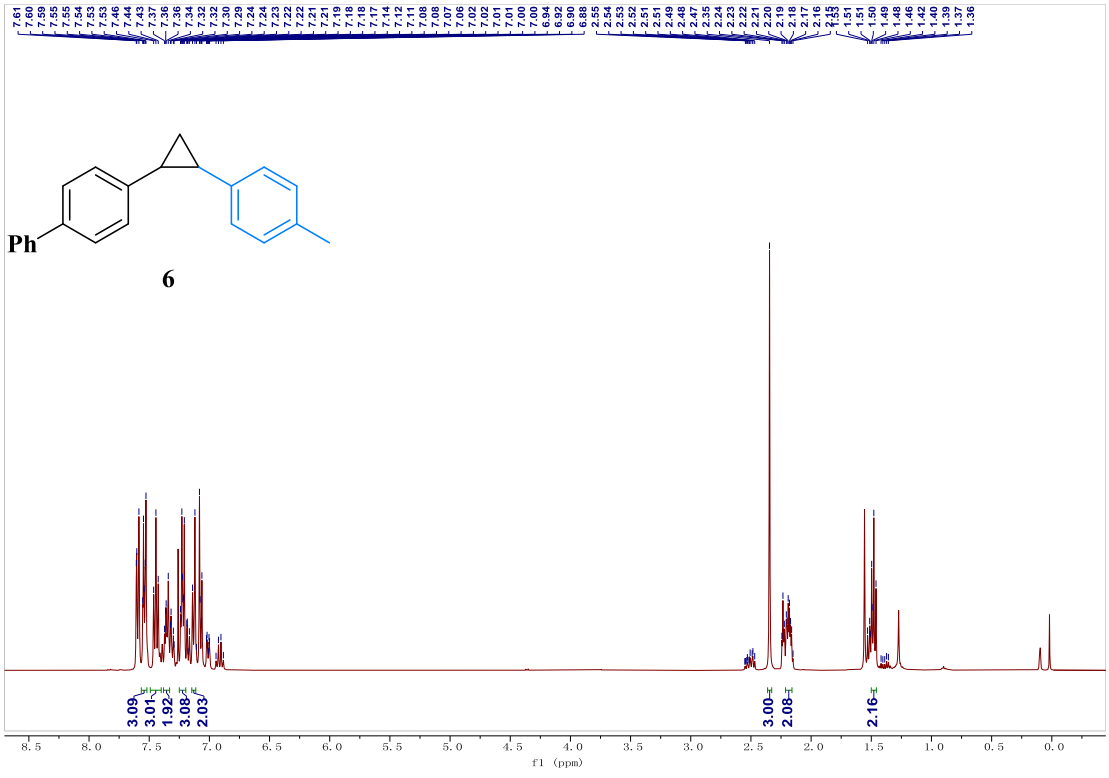

Me
MeO
B
O
O
4al
f1 (ppm)

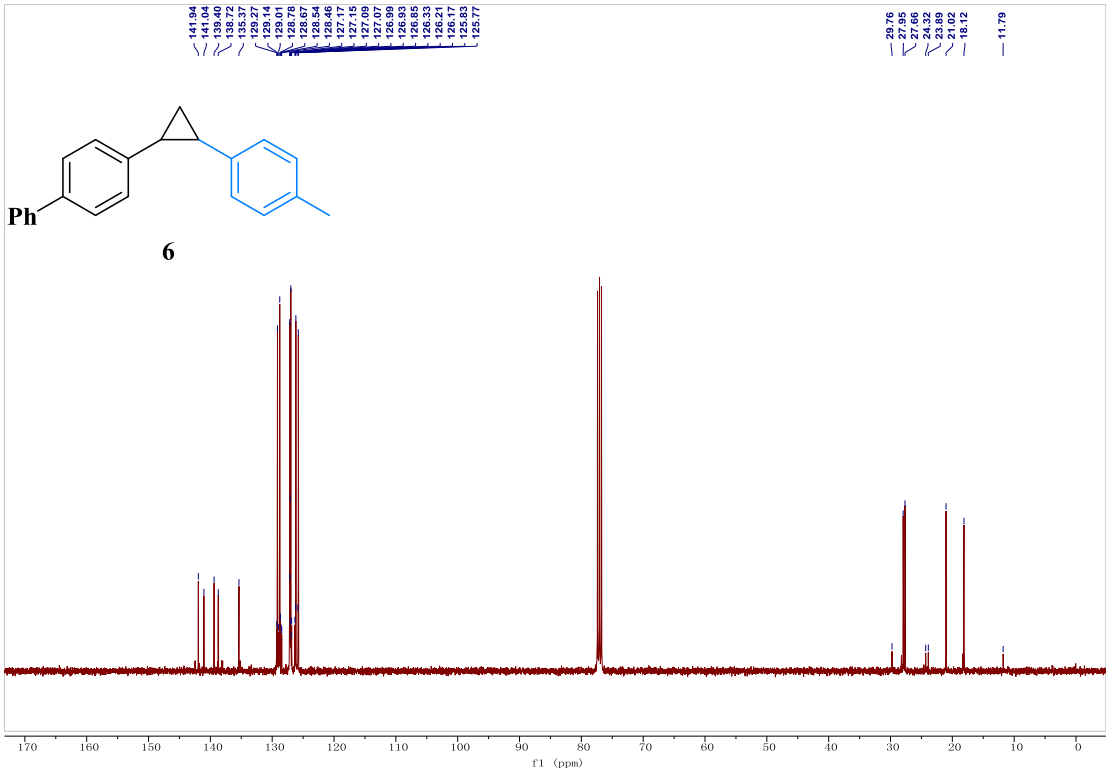

Me
Me
B
O
O
4am
f1 (ppm)

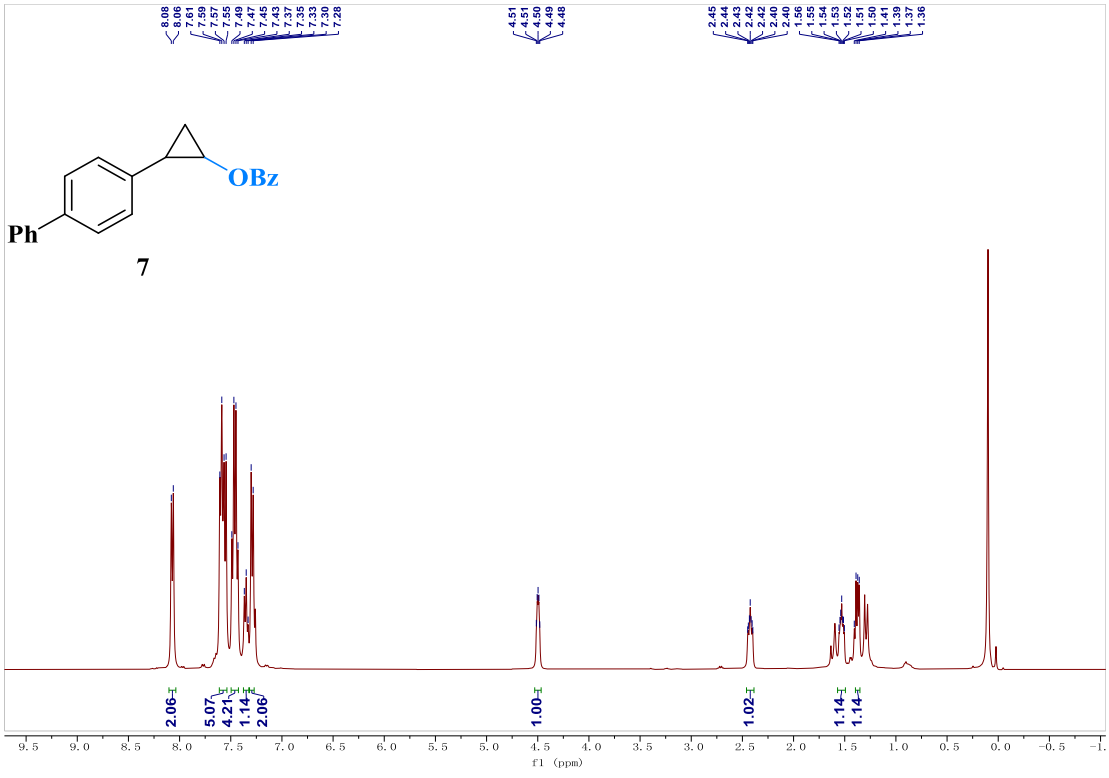

150.06
147.09
129.14
128.07
127.90
127.04
125.69
125.39
82.76
82.63
32.29
30.47
29.72
25.55
24.94
24.91
24.34
23.55
21.45
17.68
14.37
11.55
Me
Me
B
O
O
4am
f1 (ppm)

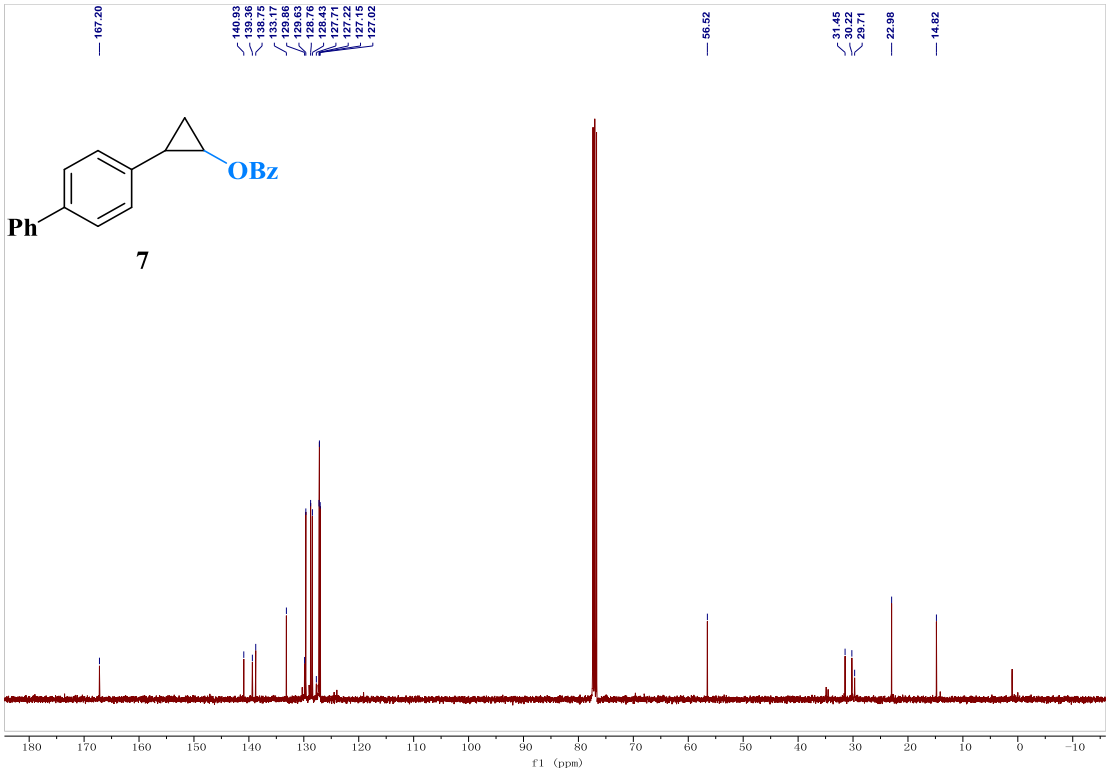

H
H
H
B
O
O
O
4an
0.95
1.95
2.26
2.23
7.16
2.97
2.07
5.85
5.93
1.09
1.04
3.05
1.00
f1 (ppm)

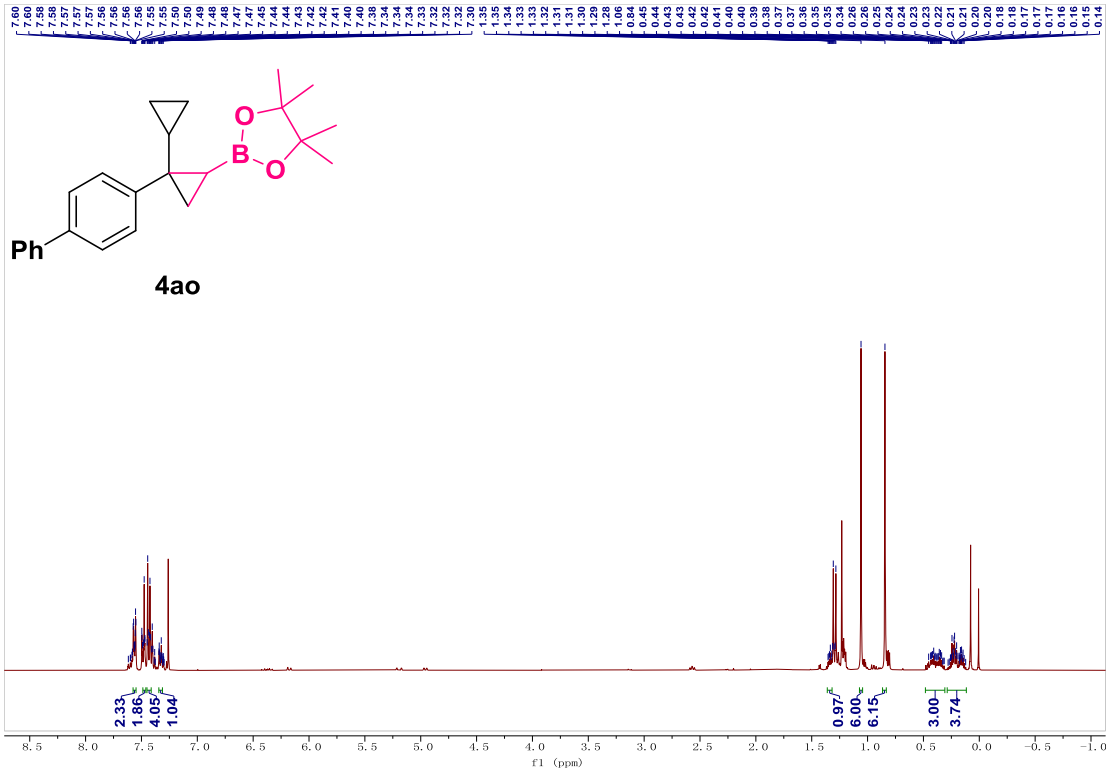

220.97
140.86
137.09
136.30
126.52
125.35
123.10
83.13
50.49
48.02
44.29
38.28
35.89
31.61
29.42
26.57
25.80
24.79
24.67
24.60
21.48
14.78
13.86
H
H
H
O
B
O
O
4an
f1 (ppm)

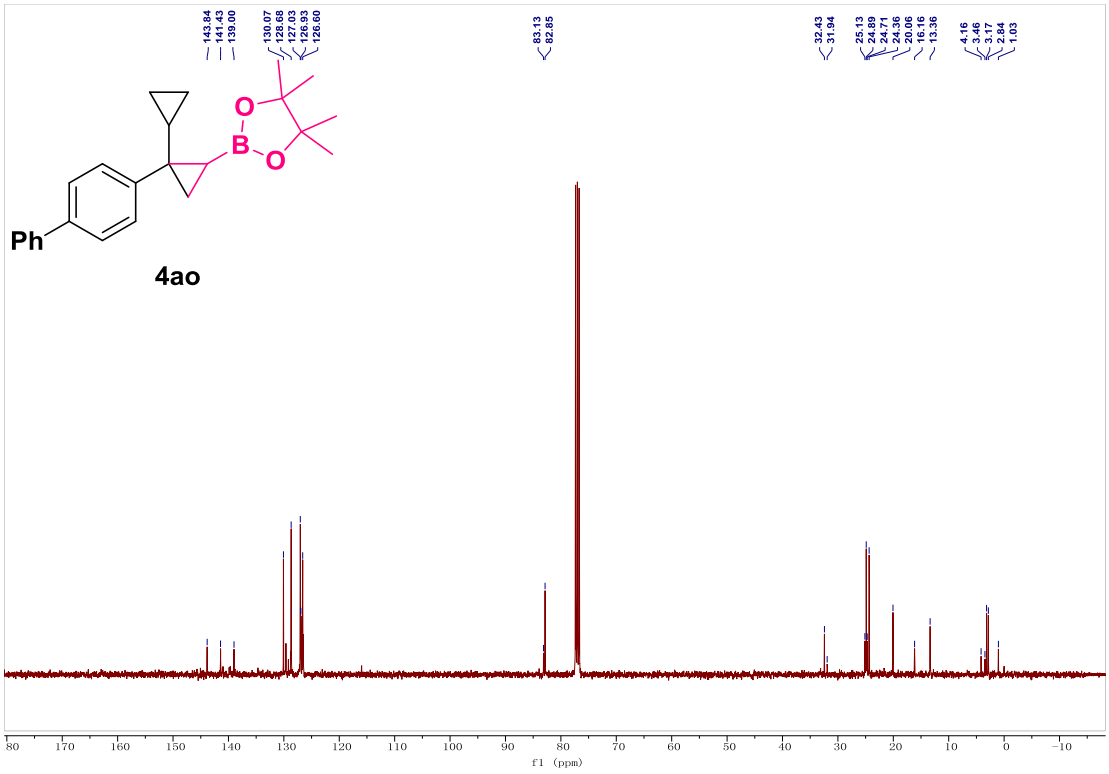

Ph
6
3.09
3.01
1.92
3.08
2.03
3.00
2.08
2.16
f1 (ppm)


Ph
6
f1 (ppm)


OBz
Ph
7
f1 (ppm)


167.20
140.93
139.36
138.75
133.17
129.86
129.63
128.76
128.43
127.71
127.22
127.15
127.02
56.52
31.45
30.22
29.71
22.98
14.82
OBz
Ph
7
f1 (ppm)


O
B
O
Ph
4ao
2.33
1.86
4.05
1.04
0.97
6.00
6.15
3.00
3.74
f1 (ppm)


143.84
141.43
139.00
130.07
128.68
127.03
126.93
126.60
83.13
82.85
32.43
31.94
25.13
24.89
24.71
24.16
20.06
16.16
13.36
4.16
3.46
3.17
2.84
1.03
O
B
O
Ph
4ao
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)