Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper nitride nanocube catalyst for the highly efficient hydroboration of alkynes

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1. Characterization of Cu_3N NCs

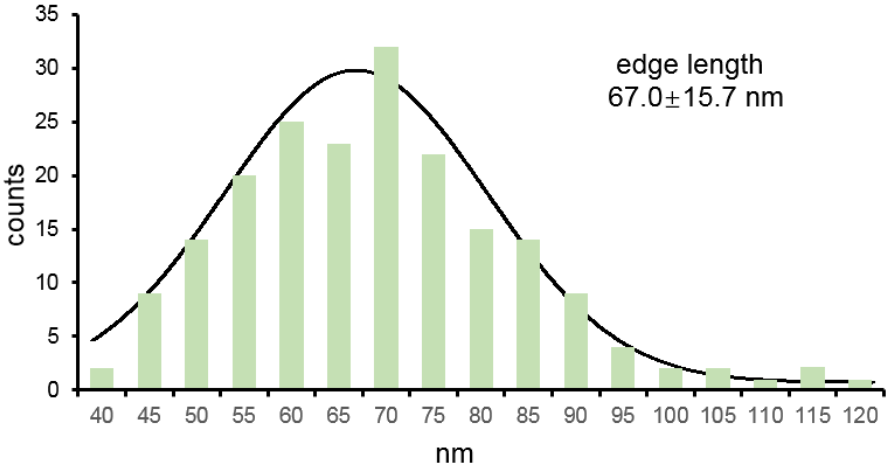
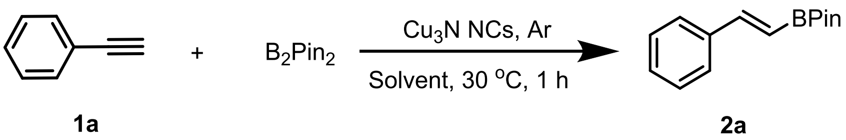


Fig. S1 Size distribution histogram of Cu_3N NCs.

2. Optimization of reaction conditions

Table S1 The screen of different solvents.[a]



Entry	Solvent	Yield of **2a** (%)[b]
1	EtOH	99
2	MeOH	90
3	IPA	25

[a] Reaction conditions: Cu_3N NCs (5 mol% of Cu), **1a** (0.5 mmol), B_2Pin_2 (0.6 mmol), solvent (2 mL), 30 °C, 1 h, Ar. [b] Yield was calculated by ^{1}H NMR analysis using 1,4-nitrobenzene as an internal standard.

3. Comparison of Cu_3N NCs catalytic system and reported Cu catalytic systems for hydroboration of 1a with B_2Pin_2

Table S2 Heterogeneous Cu catalysts for the hydroboration of **1a** with B_2Pin_2

Catalyst	**Additives**	**Solvent**	**Temp. (°C)**	**TON**	***Ref.***
Cu_3N NCs	-	EtOH	30	912	***This work***
Cu-3D-MOF	K_2CO_3	CH_3CN/H_2O	rt	41734	S1
Cu-TiC	H_2O	Toluene	80	612	S2
Cu-NPs/rGO	MeONa	MeOH/ 1,4-dioxane	50	14	S3
PCN-222(Cu)	3-methyl pyridine	EtOH/ H_2O	80	66	S4
Cu-MOF	MeONa	EtOH	25	310	S5
Cu-CeO_2	-	EtOH	90	192	S6
Cu_2O RD	PPh_3	1,4-dioxane	60	14	S7
Cu-$CuFe_2O_4$	MeONa	MeOH	rt	190	S8
Nano-Cu@Si	MeONa	EtOH	rt	10	S9
$CuFe_2O_4$	*t*-BuOK	MeOH	50	180	S10
micro copper powder	MeONa	MeOH	rt	9	S11
Basic $CuCO_3$	PPh_3	H_2O	27	16	S12
Cu/MgO	PPh_3	Toluene	45	23	S13

Note: rt = room temperature.

4. Preparation and characterization of Cu_2O NCs

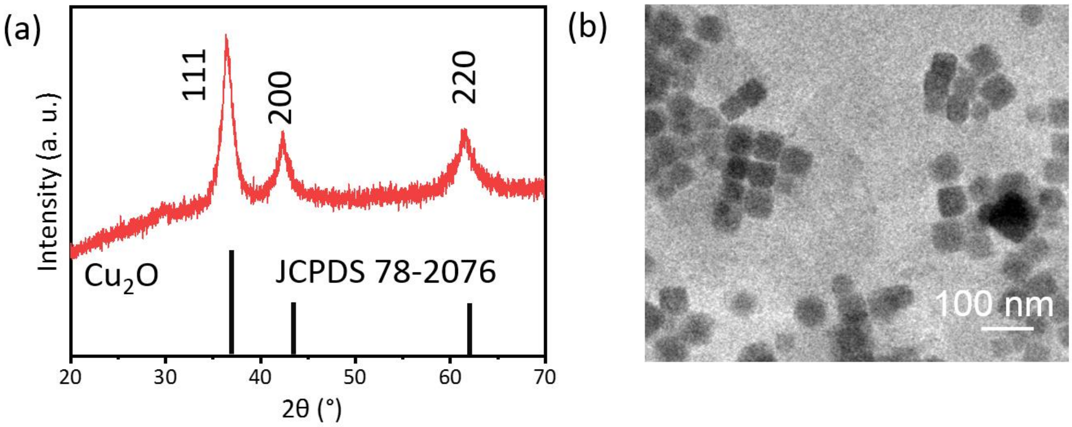


Fig. S2 (a) PXRD pattern and (b) TEM image of Cu_2O NCs.

The Cu_2O NCs was prepared by a facile wet chemical approach.[S14] In a typical reaction, 0.075 mol L^{-1} of NaOH (10 mL) was added dropwise to 0.5 mol L^{-1} of $CuSO_4$ aqueous solution (5 mL) under stirring at pH = 10.5. Subsequently, the 0.1 mol L^{-1} of ascorbic acid (13 mL) was added dropwise into the solution under continuous stirring and was reacted for 1 h at room temperature. Then, a yellow precipitate was obtained (pH = 4.0–4.5). To remove any impurities, redispersion and precipitation cycles were repeated using a water and ethanol to afford the yellow powder.

5. Reuse experiments

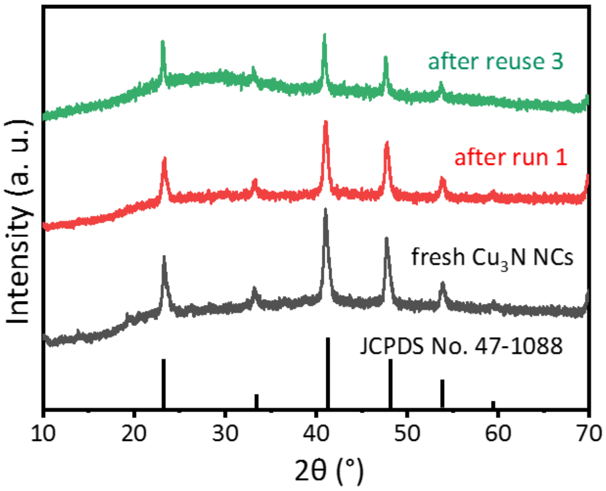


Fig. S3 PXRD patterns of fresh and reused Cu_3N NCs.

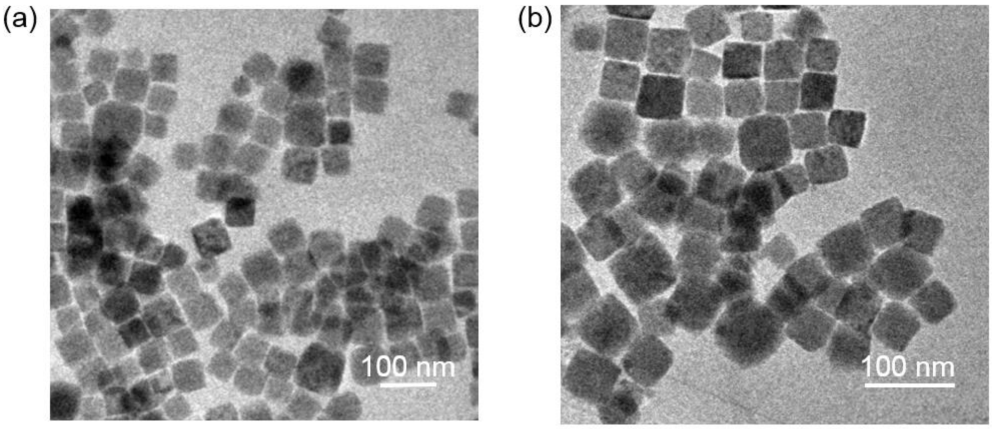


Fig. S4 TEM images of Cu_3N NCs (a) fresh and (b) after run 1.

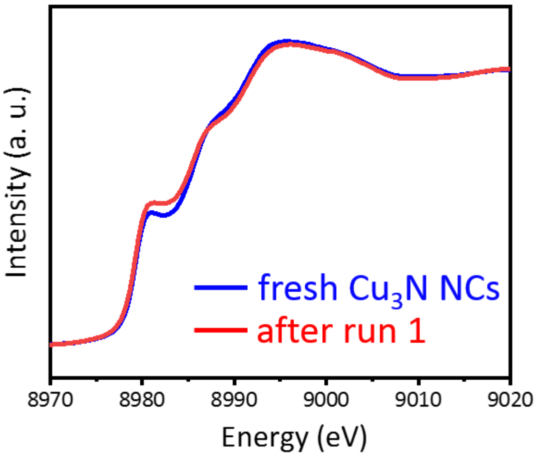
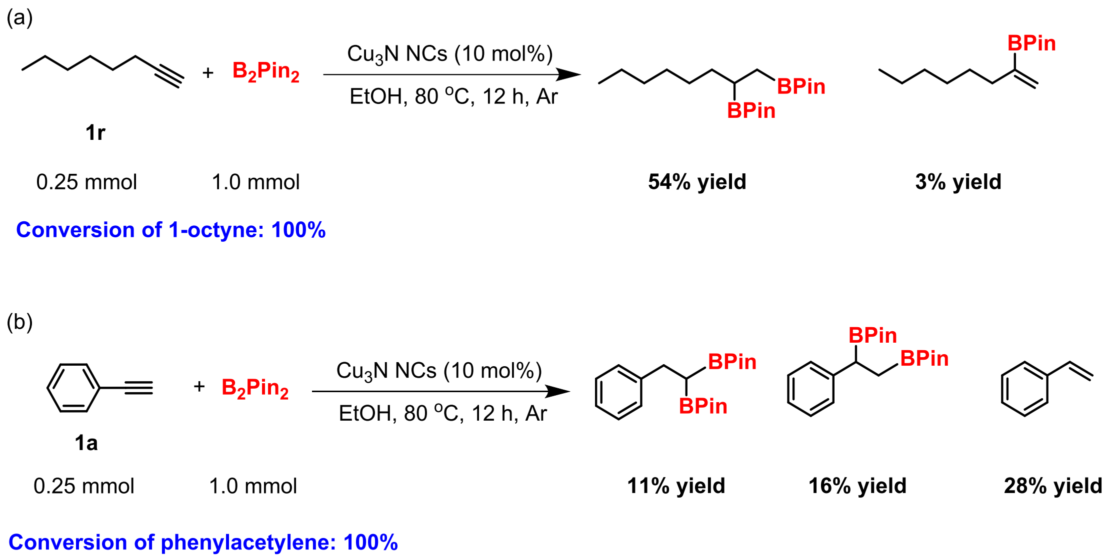


Fig. S5 Cu *K*-edge XANES spectra of fresh Cu_3N NCs (blue line) and Cu_3N NCs after run 1 (red line).

6. Limitation of substrate scope



Scheme S1 Dihydroboration of (a) **1r** and (b) **1a**. Reaction conditions: **1r** or **1a** (0.25 mmol), B_2Pin_2 (1.0 mmol), Cu_3N NCs (5.0 mg), EtOH (1.0 mL), 80 °C, Ar, 12 h. Yields were calculated by ^1H NMR analysis using 1,4-nitrobenzene as an internal standard.

7. Lewis acid-base property of Cu_3N NCs

In a typical NH_3-TPD experiment, about 30 mg of the Cu_3N NCs was loaded in U-shaped quartz cell above a small amount of quartz wool. The sample was treated under helium (He) flow at 100 °C for 60 min. After the treatment, the temperature was cooled to 30 °C. For NH_3 adsorption, thermally treated sample was saturated with 5.5% NH_3/He mixture at 100 °C. After pulse NH_3 adsorption, the sample was flushed in He flow at 100 °C for removal of physically adsorbed NH_3 on the sample. An NH_3-TPD profile of the sample was recorded by increasing the temperature from 100 to 500 °C at a heating rate of 10 °C min^{-1} under 30 mL min^{-1} of He flow. The desorbed products were analyzed by a mass spectrometer. The desorbed NH_3 and CO_2 were identified on the basis of the intensity of the mass fragments with $m/z = 16$ and 44, respectively. The peak $m/z = 16$ was used for NH_3 because the parent peak.

For CO_2 adsorption experiment, the 10% CO_2/H_2 gas was used instead of 5.5% NH_3/He gas under same procedure.

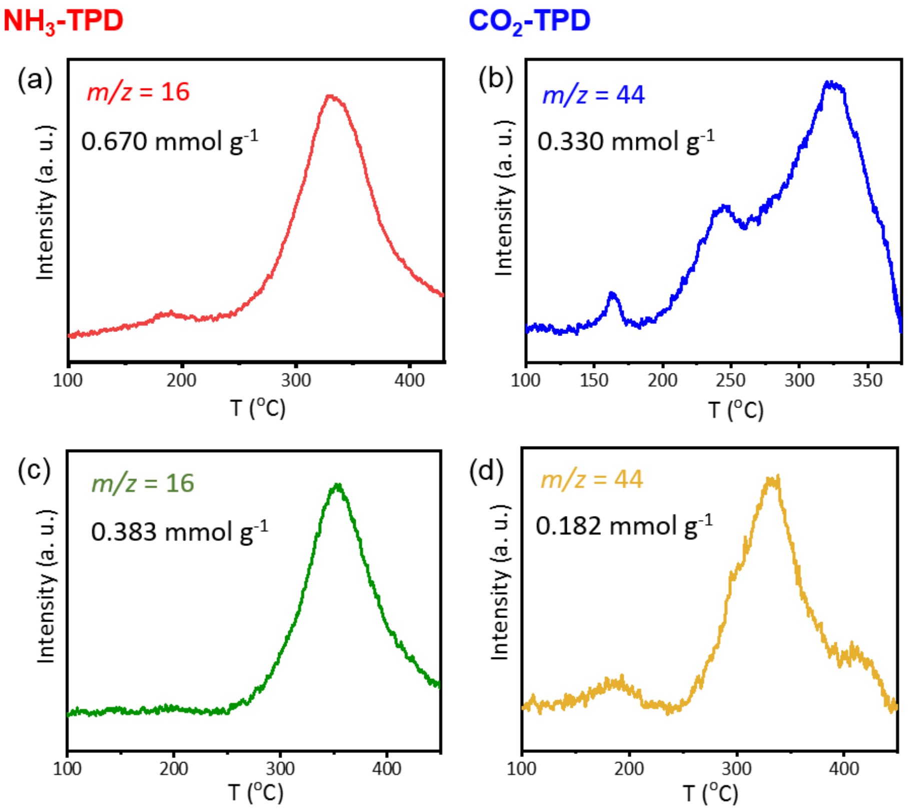


Fig. S6 (a) NH_3-TPD and (b) CO_2-TPD signals of Cu_3N NCs monitored at m/z 16 and 44. (c) NH_3-TPD and (d) CO_2-TPD signals of Cu_3N NCs (without NH_3 or CO_2 pretreatment) monitored at m/z 16 and 44.

Table S3 The amount of Lewis acid and base

	Lewis acid site amount (mmol g^{-1})	Lewis base site amount (mmol g^{-1})
Cu_3N NCs	0.287	0.148

The details for the Lewis acid-base property of Cu_3N NCs were investigated through NH_3 and CO_2-TPD analyses (Fig. S6). Firstly, the NH_3 and CO_2-TPD spectra of Cu_3N NCs show the amounts of Lewis acid-base sites of Cu_3N NCs, which are 0.670 and 0.330 mmol g^{-1}, respectively (Fig. S6a and S6b). Furthermore, the experiments using Cu_3N NCs without NH_3 or CO_2 pretreatment were performed, and the amounts of Lewis acid-base sites were calculated to be 0.383 and 0.182 mmol g^{-1}, respectively (Fig. S6c and S6d). Based on these results, the exact amount of Lewis acid-base sites of Cu_3N NCs except for the other components are estimated as shown in Table S3.

8. Proposed mechanism

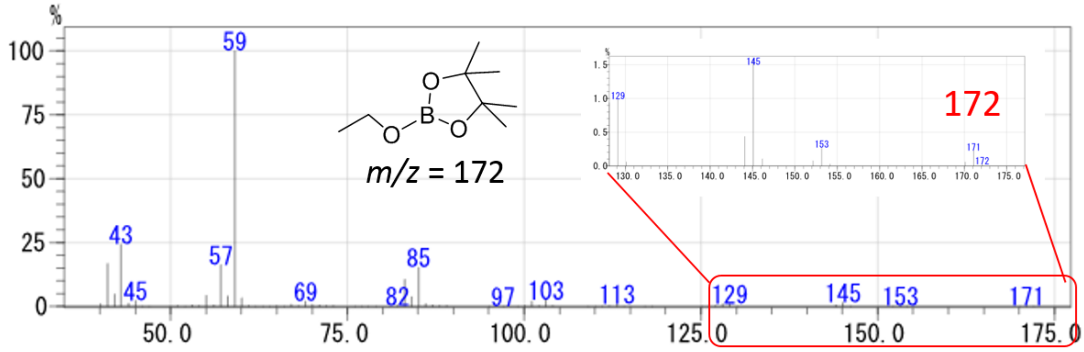
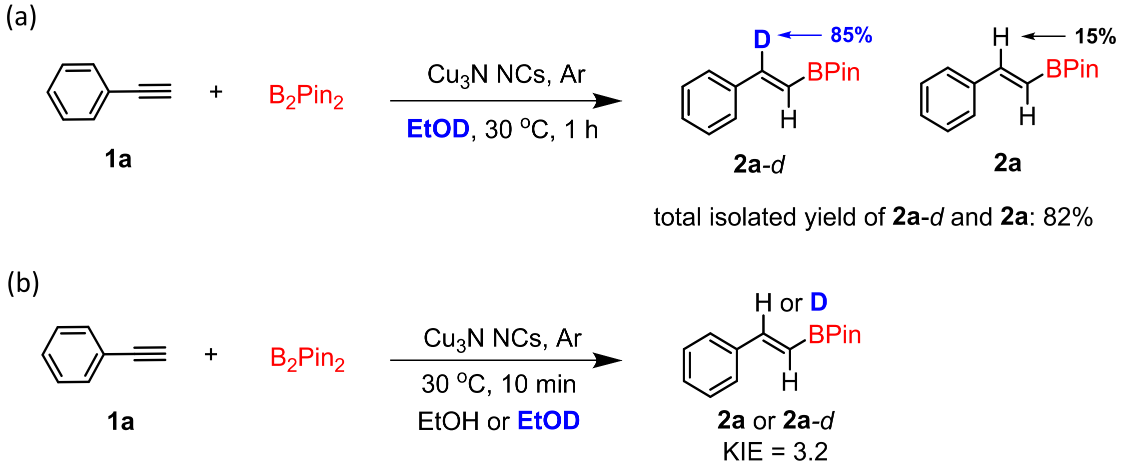


Fig. S7 EI-MS spectrum of 2-ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

9. Deuterium labelling experiments



Scheme S2 The deuterium-labelling experiments.

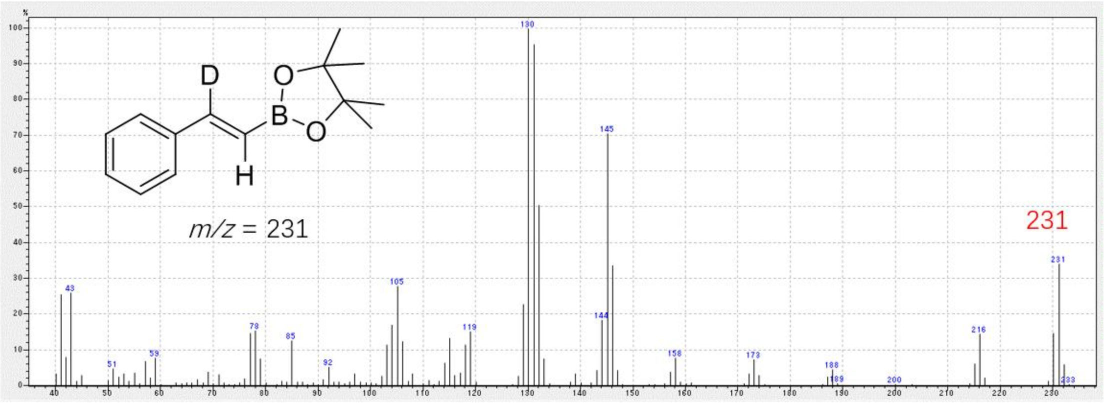


Fig. S8 EI-MS spectrum of **2a**-*d*.

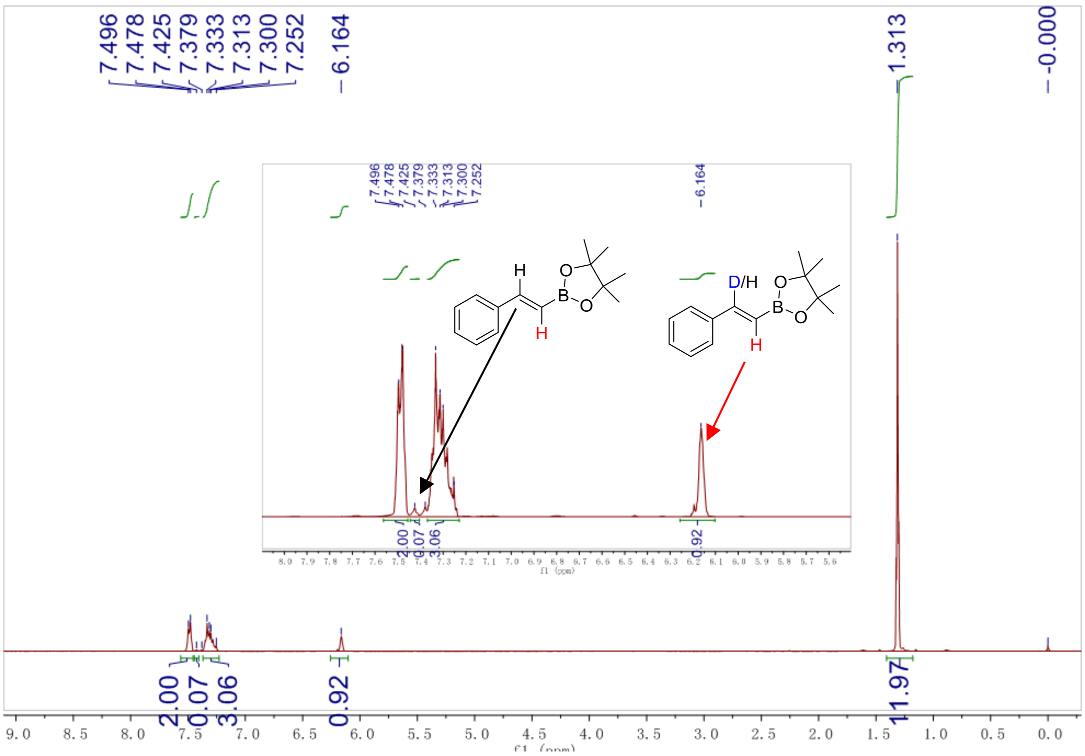
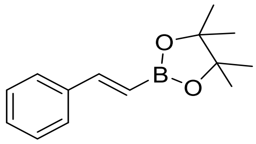


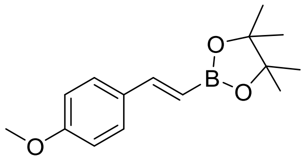
Fig. S9 ^{1}H NMR analysis of **Scheme S2a**.

10. Product identification

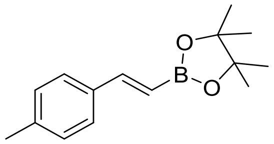
General information: chemical shifts were reported in parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane in $CDCl_3$. The ^{13}C NMR spectral data were reported using the following standard chemical shift: $CDCl_3$ (77.16 ppm). NMR multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constants in hertz.



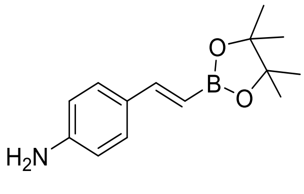
(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (2a) [S6]: CAS registry No. [83947-56-2], white solid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51–7.48 (m, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.36–7.26 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 137.7, 129.1, 128.7, 127.2, 83.5, 25.0.



(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b) [S6]: CAS registry No. [149777-83-3], colorless liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.78 (s, 3H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 149.1, 130.4, 128.5, 114.0, 83.2, 55.3, 24.9.

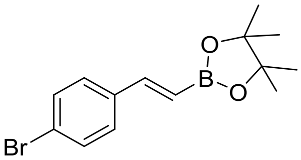


(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2c) [S6]: CAS registry No. [149777-84-4], yellow liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.32 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 18.8 Hz, 1H), 2.33 (s, 3H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 139.0, 134.9, 129.4, 127.1, 83.3, 24.9, 21.4.

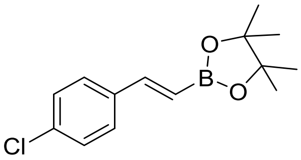


(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (**2d**) [S8]: CAS registry No. [2159091-30-0], yellow solid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–7.24 (m, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.93 (d, *J* = 18.4 Hz, 1H), 3.79 (s, 2H), 1.30 (s, 12H);

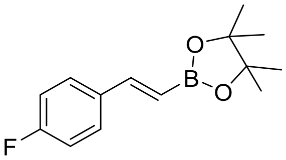
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.5, 128.6, 128.1, 114.9, 83.1, 24.8.



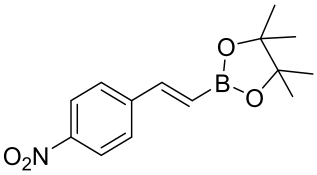
(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) ^{S1}: CAS registry No. [1242770-51-9], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.42–7.28 (m, 3H), 6.15 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 136.5, 131.9, 128.6, 123.0, 83.6, 24.9.



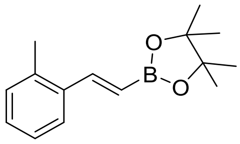
(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**) ^{S6}: CAS registry No. [223919-54-8], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.38–7.29 (m, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 136.1, 134.7, 128.9, 128.3, 83.5, 24.9.



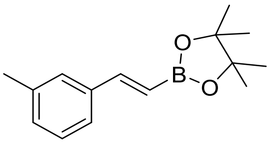
(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g) ^{S1}: CAS registry No. [504433-86-7], colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51–7.42 (m, 2H), 7.36 (d, *J* = 18.4 Hz, 1H), 7.01 (t, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.2 (d, *J* = 248.0 Hz), 148.2, 133.8 (d, *J* = 4.0 Hz), 128.7 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 22.0 Hz), 83.5, 24.9.



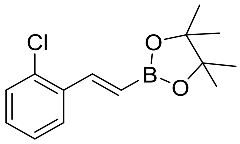
(*E*)-4,4,5,5-tetramethyl-2-(4-nitrostyryl)-1,3,2-dioxaborolane (2h) ^{S4}: CAS registry No. [149777-86-6], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 18.4 Hz, 1H), 6.33 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 146.7, 143.7, 127.7, 124.1, 83.9, 24.9.



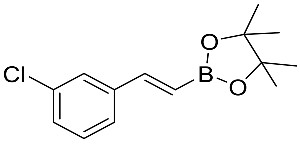
(*E*)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane (**2i**)[S6]: CAS registry No. [1294009-26-9], yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 18.4 Hz, 1H), 7.57–7.53 (m, 1H), 7.20–7.12 (m, 3H), 6.08 (d, *J* = 18.4 Hz, 1H), 2.42 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 136.8, 136.4, 130.5, 128.7, 126.2, 125.9, 83.4, 24.9, 19.9.



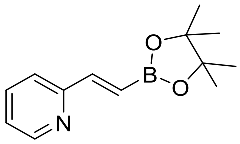
(*E*)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (2j)[S6]: CAS registry No. [1421061-31-5], yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 18.4 Hz, 1H), 7.33–7.26 (m, 2H), 7.24–7.18 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.15 (d, *J* = 18.4 Hz, 1H), 2.33 (s, 3H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 138.1, 137.5, 129.8, 128.5, 127.8, 124.3, 83.3, 24.9, 21.4.



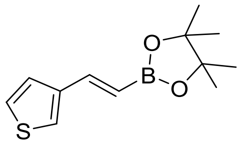
(*E*)-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)[S4]: CAS registry No. [1355094-04-0], yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 18.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.42–7.32 (m, 1H), 7.31–7.18 (m, 2H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 135.7, 133.9, 129.9, 129.8, 127.1, 126.9, 83.5, 24.9.



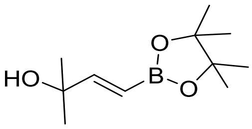
(*E*)-2-(3-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)[S4]: CAS registry No. [871125-84-7], yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.34–7.24 (m, 4H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 139.4, 134.7, 129.9, 128.8, 127.0, 125.3, 83.6, 24.9.



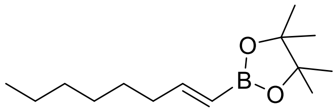
(*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine (3m)[S6]: CAS registry No. [161395-83-1], yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 4.8 Hz, 1H), 7.69–7.62 (m, 1H), 7.46 (d, *J* = 18.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.23–7.16 (m, 1H), 6.63 (d, *J* = 18.0 Hz, 1H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 149.8, 148.9, 136.6, 123.2, 122.3, 83.6, 24.9.



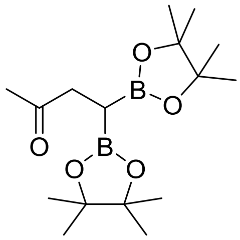
(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (2n) [S4]: CAS registry No. [736987-75-0], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.32–7.28 (m, 2H), 7.27–7.24 (m, 1H), 5.94 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.4, 126.2, 125.2, 125.0, 83.4, 24.9.



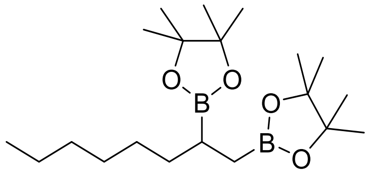
(*E*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (2o) [S5]: CAS registry No. [581802-26-8], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (d, *J* = 18.4 Hz, 1H), 5.61 (d, *J* = 18.4 Hz, 1H), 1.62 (s, 1H), 1.31 (s, 6H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.9, 83.4, 71.9, 29.2, 24.9.



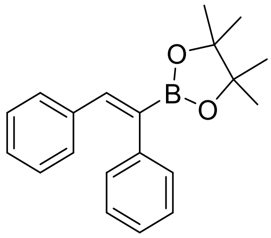
(*E*)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (2p) [S6]: CAS registry No. [83947-55-1], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.42 (d, *J* = 18.0, 1H), 2.21–2.09 (m, 2H), 1.45–1.29 (m, 2H), 1.29–1.25 (m, 18H), 0.88 (t, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 83.1, 36.0, 31.9, 29.1, 28.3, 24.9, 22.7, 14.2.



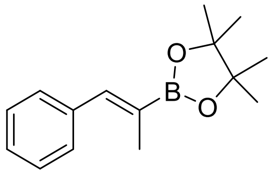
4,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (2q) [S15]: CAS registry No. [1175712-38-5], yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.74 (d, *J* = 8.0 Hz, 2H), 2.11 (s, 3H), 1.24 (s, 12H), 1.21 (s, 12H), 0.97 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 83.2, 40.7, 29.1, 24.8, 24.6.



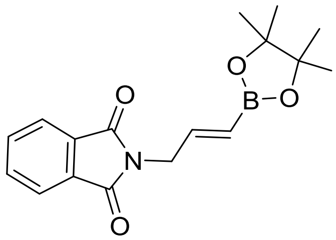
2,2'-(octane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2r) [S16]: CAS registry No. [1240790-15-1], colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52–1.43 (m, 1H), 1.39–1.19 (m, 32H), 1.17–1.05 (m, 2H), 0.96–0.77 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.9, 82.9, 34.0, 32.0, 29.7, 29.0, 25.1, 25.0, 24.9, 24.9, 22.8, 14.3.



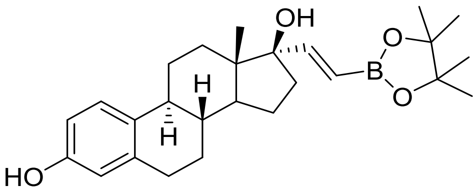
(*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2s**) [S6]: CAS registry No. [264144-59-4], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H), 7.31–7.23 (m, 2H), 7.22–7.14 (m, 3H), 7.13–7.09 (m, 3H), 7.07–7.03 (m, 2H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 140.6, 137.1, 130.1, 129.0, 128.4, 128.0, 127.7, 126.4, 83.9, 24.9.



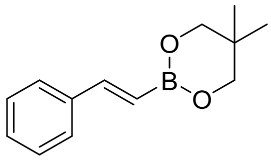
(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (**2t**) [S1]: CAS registry No. [141091-35-2], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.29 (m, 4H), 7.26–7.19 (m, 2H), 1.99 (d, *J* = 1.7 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 138.1, 129.6, 128.2, 127.2, 83.7, 25.0, 16.1.



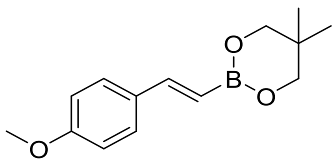
(*E*)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (**2u**) [S17]: CAS registry No. [581802-29-1], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): 7.95–7.83 (m, 2H), 7.80–7.71 (m, 2H), 6.55 (dt, *J* = 18.0, 4.4 Hz, 1H), 5.49 (d, *J* = 18.0 Hz, 1H), 4.38 (s, 2H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.8, 145.3, 134.1, 132.1, 123.4, 83.4, 41.0, 24.8.



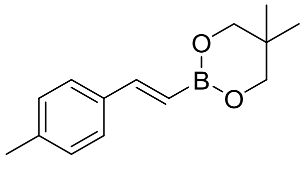
(8*R*,9*S*,13*S*,14*S*,17*R*)-13-methyl-17-((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (**2v**) [S2]: CAS registry No. [2661398-14-5], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): 7.01–6.86 (m, 3H), 6.64–6.54 (m, 2H), 5.67 (d, *J* = 18.0 Hz, 1H), 2.85–2.61 (m, 2H), 2.05–1.59 (m, 6H), 1.34 (s, 12H), 1.27–1.14 (m, 8H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):158.7, 154.2, 138.5, 132.5, 126.1, 115.6, 112.2, 85.1, 84.1, 49.3, 47.3, 42.4, 39.0, 37.3, 32.4, 29.8, 27.3., 25.9, 25.0, 24.8, 23.5, 14.3.



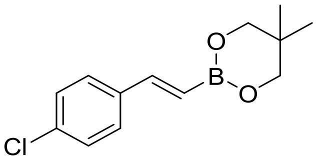
(*E*)-5,5-dimethyl-2-styryl-1,3,2-dioxaborinane (**3a**) [S18]: CAS registry No. [202864-71-9], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.39–7.20 (m, 4H), 6.11 (d, *J* = 18.4 Hz, 1H), 3.69 (s, 4H), 0.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 137.9, 128.6, 127.1, 72.3, 31.9, 22.0.



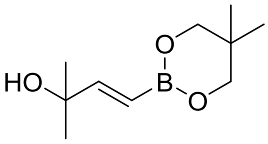
(*E*)-2-(4-methoxystyryl)-5,5-dimethyl-1,3,2-dioxaborinane (**3b**) [S19]: CAS registry No. [905966-49-6], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 18.4 Hz, 1H), 6.84 (d, *J* = 6.8 Hz, 2H), 5.95 (d, *J* = 18.4 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 4H), 0.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 146.7, 130.8, 128.4, 114.0, 72.2, 55.3, 31.9, 21.90.



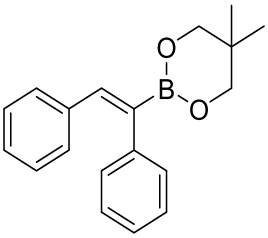
(*E*)-2-(4-methylstyryl)-5,5-dimethyl-1,3,2-dioxaborinane (**3c**) [S20]: CAS registry No. [938080-15-0], colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 18.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.04 (d, *J* = 18.0 Hz, 1H), 3.69 (s, 4H), 2.34 (s, 3H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 138.7, 135.2, 129.4, 127.1, 72.3, 32.0, 22.0, 21.4.



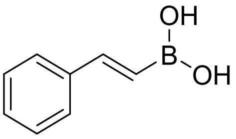
(*E*)-2-(4-chlorostyryl)-5,5-dimethyl-1,3,2-dioxaborinane (**3d**) [S21]: CAS registry No. [2493295-76-2], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.37 (m, 2H), 7.32–7.26 (m, 3H), 6.07 (d, *J* = 18.0 Hz, 1H), 3.70 (s, 4H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 136.4, 134.3, 128.9, 128.3, 72.4, 32.0, 22.0.



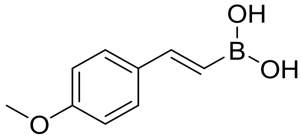
(*E*)-4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-2-methylbut-3-en-2-ol (**3e**): colorless liquid; **^{1}**H NMR (400 MHz, $CDCl_3$): δ 6.64 (d, *J* = 18.0 Hz, 1H), 5.52 (d, *J* = 18.0 Hz, 1H), 3.65 (s, 4H), 1.31 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 72.2, 71.8, 31.9, 29.3, 22.0. IR (ATR): ν_{max} = 3470, 2964, 1640, 1423, 1312, 1250, 1083, 755, 638 cm^{-1}. HRMS (ESI): *m/z* Calculated for $C_{10}H_{19}BO_3$ $[M]^+$: 198.1427, found 198.1429.



(*Z*)-2-(1,2-diphenylvinyl)-5,5-dimethyl-1,3,2-dioxaborinane (**3f**) [S22]: CAS registry No. [1942884-64-1], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.30–7.24 (m, 2H), 7.23–7.15 (m, 1H), 7.14–7.06 (m, 5H), 7.04–6.97 (m, 2H), 3.69 (s, 4H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 141.2, 137.4, 130.1, 128.9, 128.4, 127.9, 127.4, 126.1, 72.6, 31.8, 22.0.



(*E*)-2-phenylvinylboronic acid (**4a**) [S23]: CAS registry No. [4363-35-3], white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 18.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.46–7.33 (m, 3H), 6.35 (d, *J* = 18.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 137.3, 129.6, 128.8, 127.7.



(*E*)-(4-methoxystyryl)boronic acid (**4b**) [S24]: CAS registry No. [214907-25-2], white solid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, *J* = 18.0 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.18 (d, *J* = 18.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.9, 151.8, 130.3, 129.2, 127.5, 114.2, 55.5.

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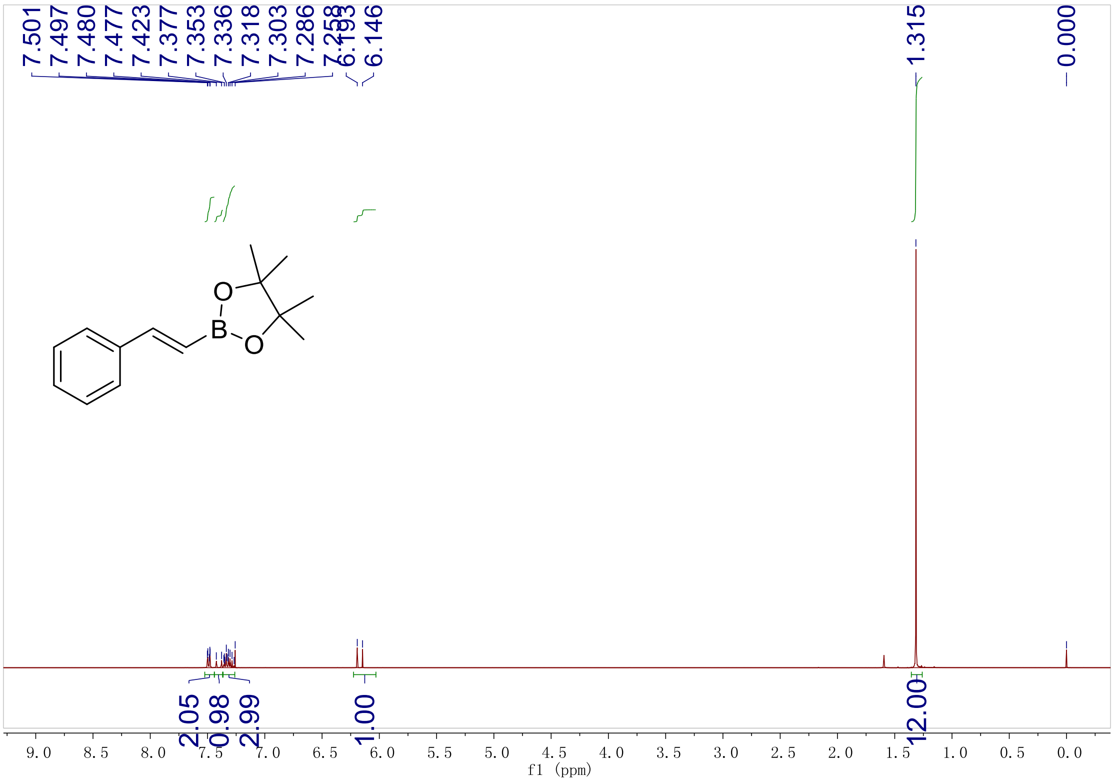
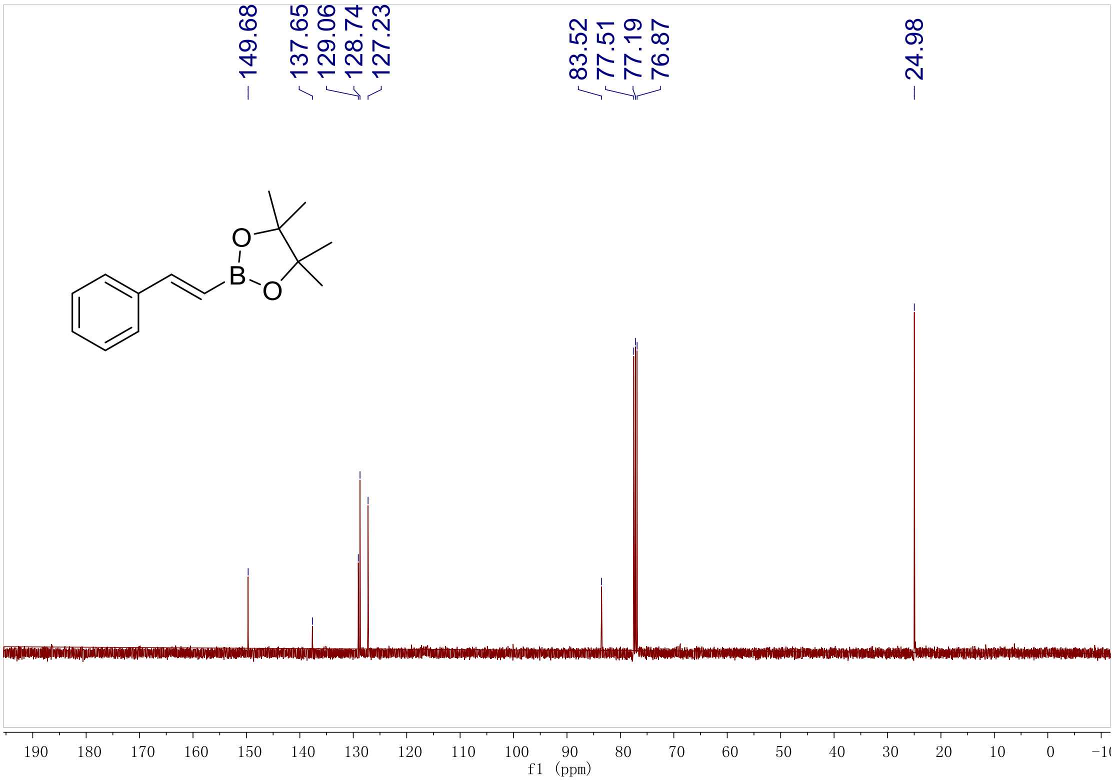
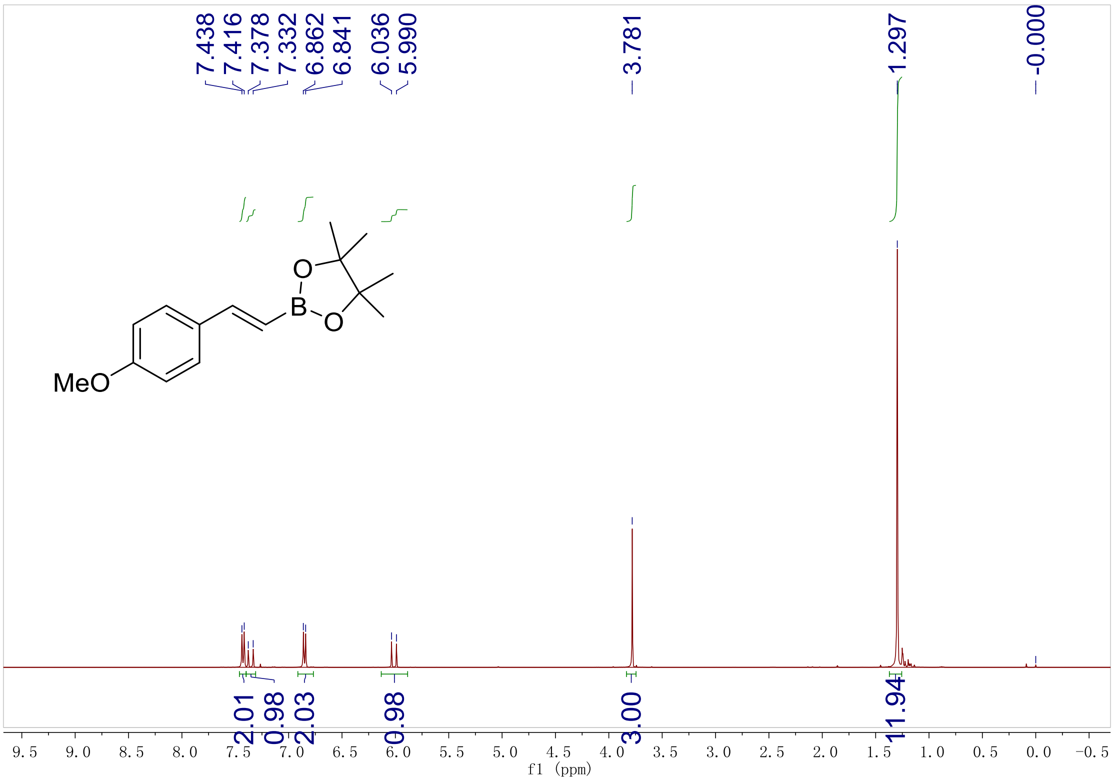
12. ^{1}H and ^{13}C NMR spectra



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O
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0.98
2.03
0.98
3.00
11.94
9.5 9.0 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
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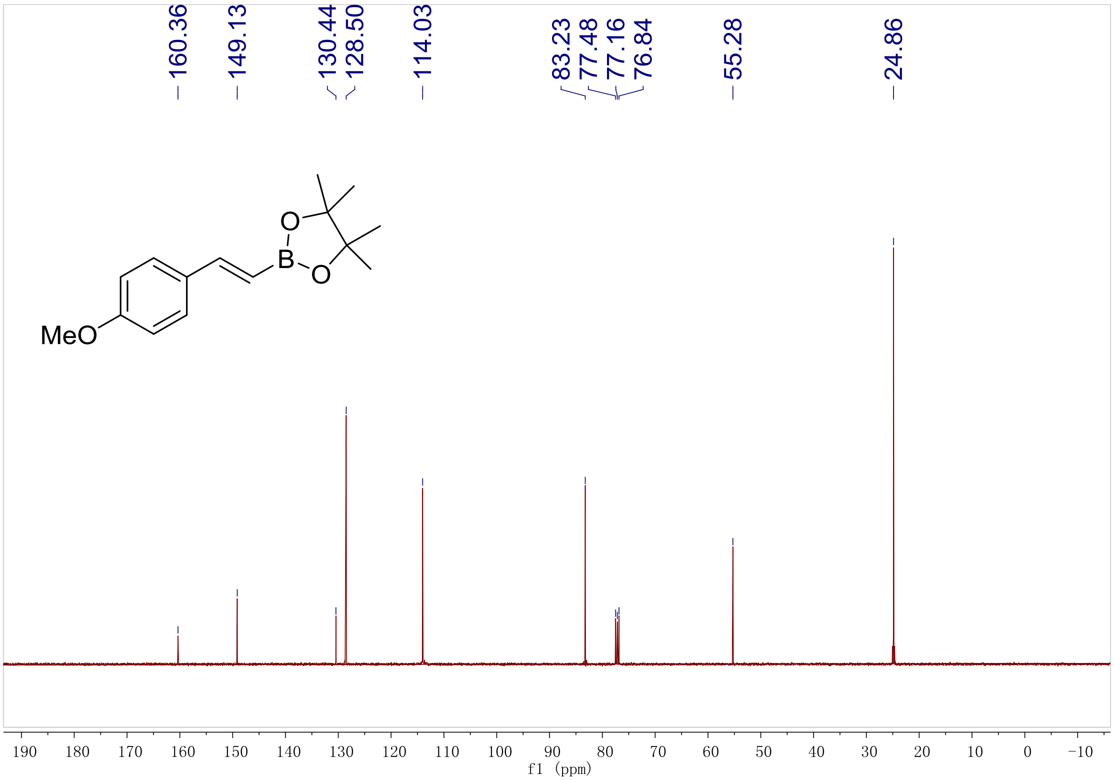
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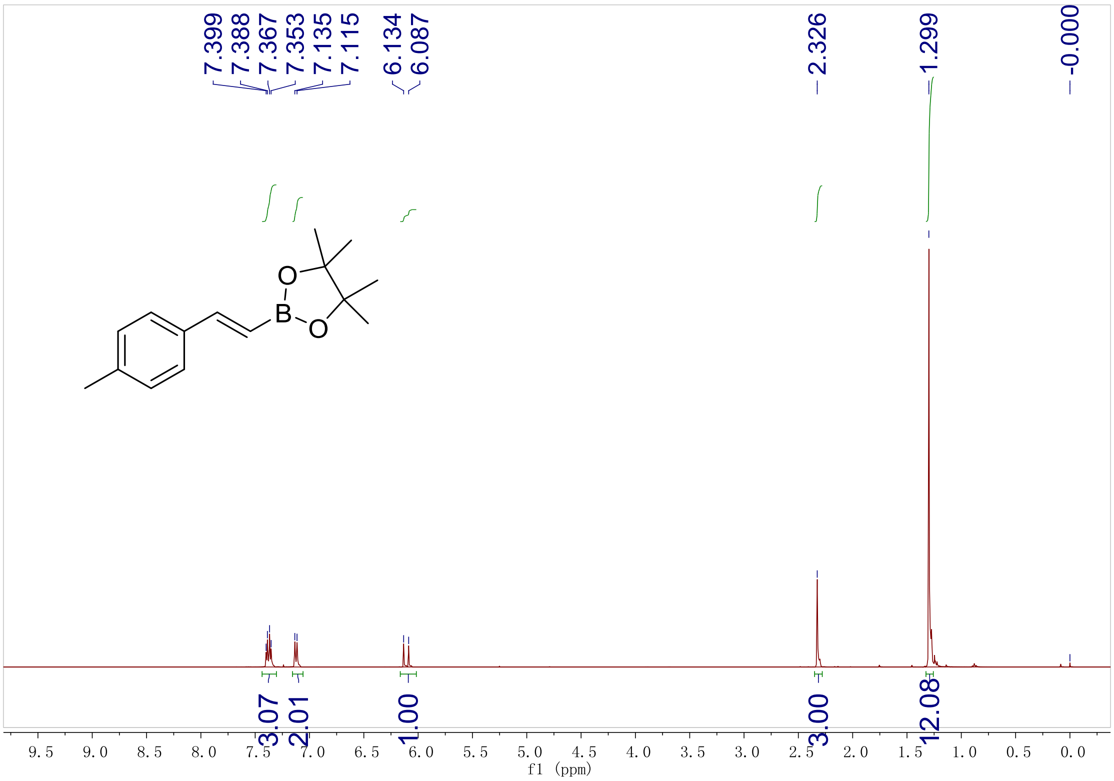
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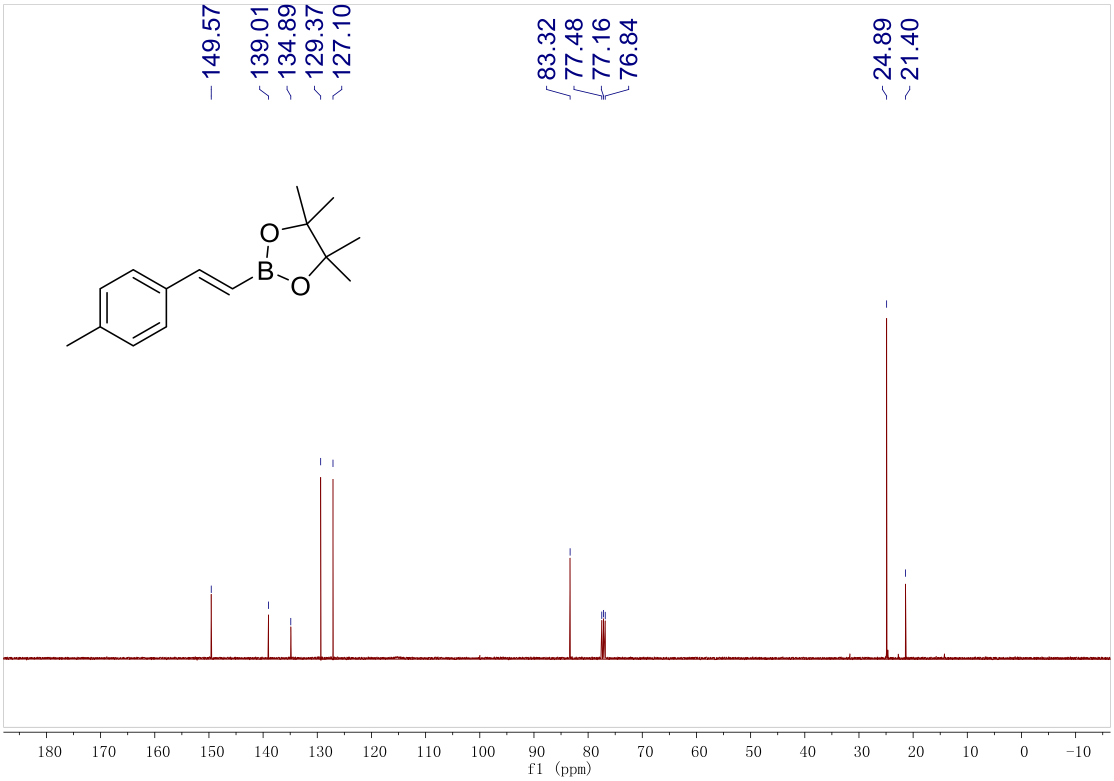
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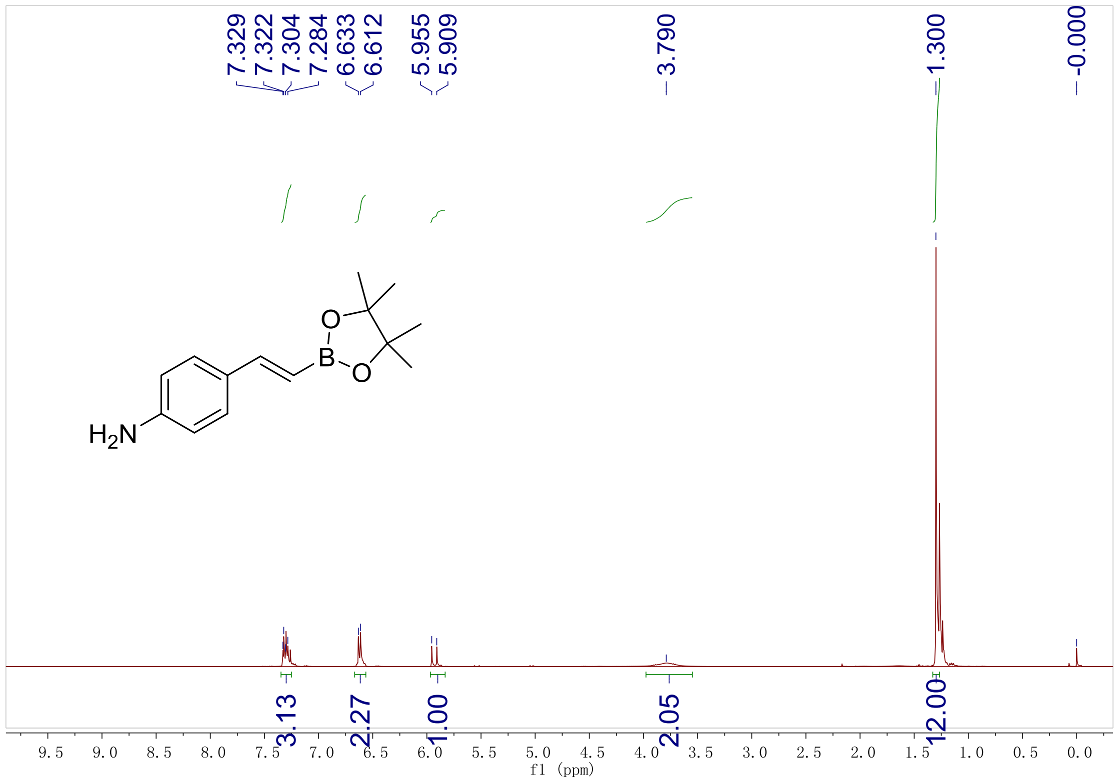
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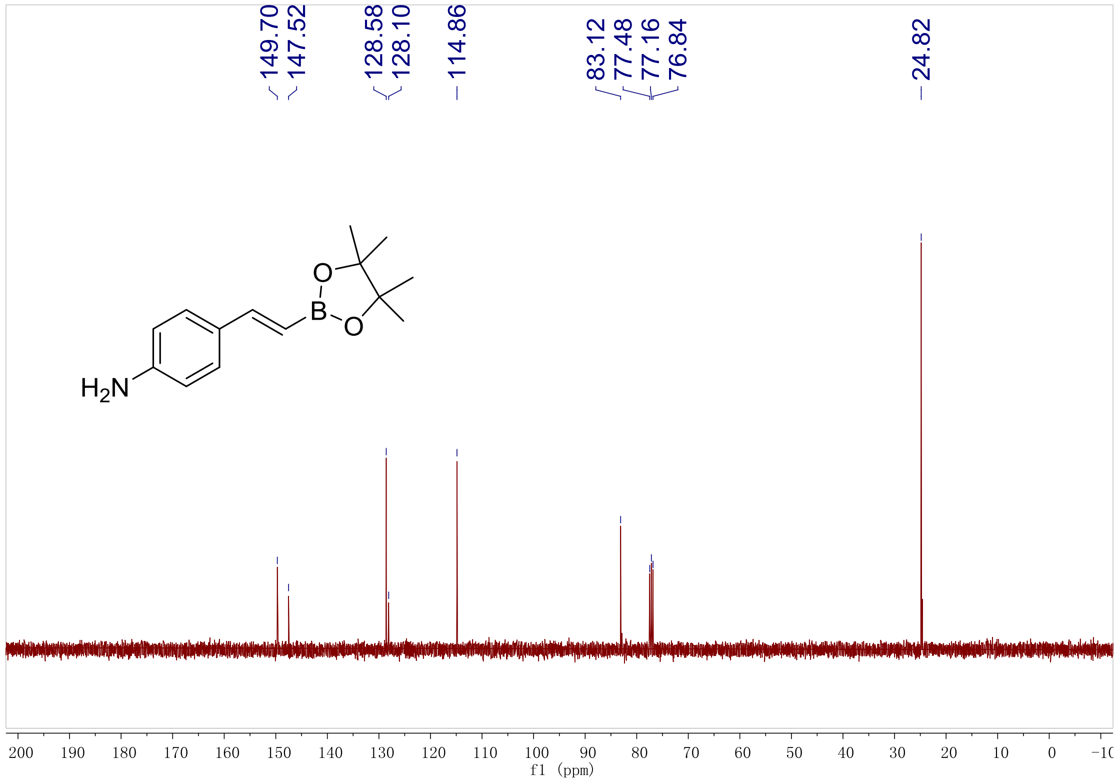
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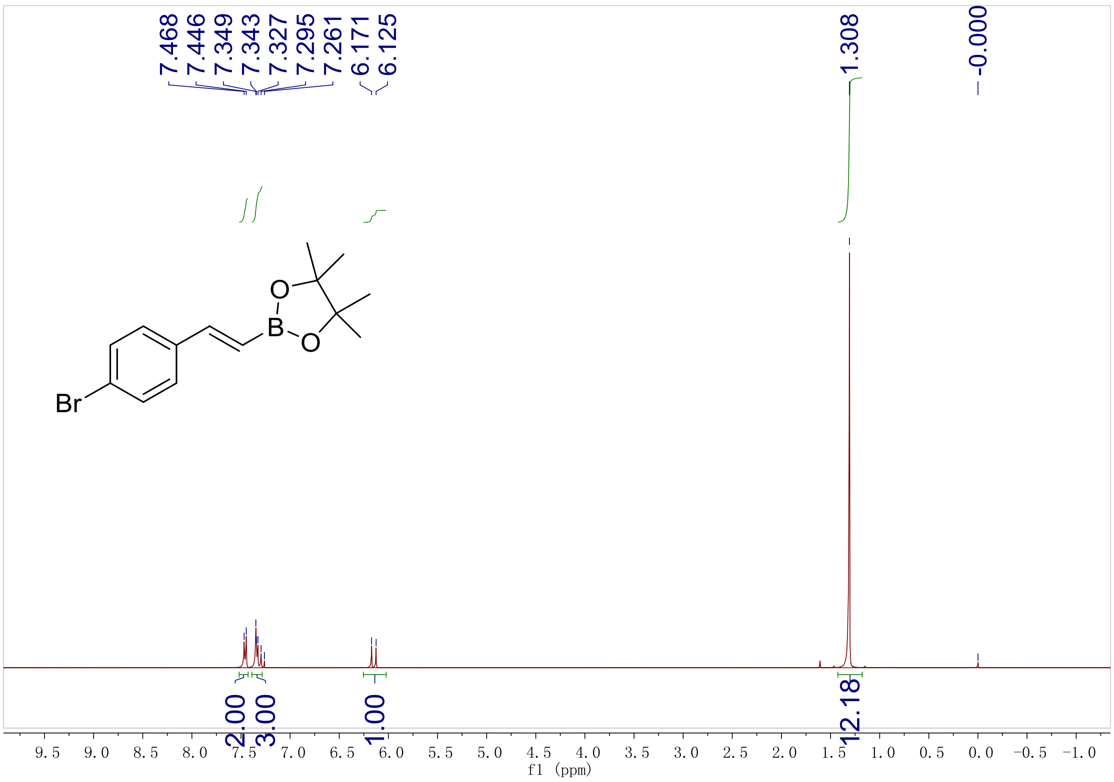
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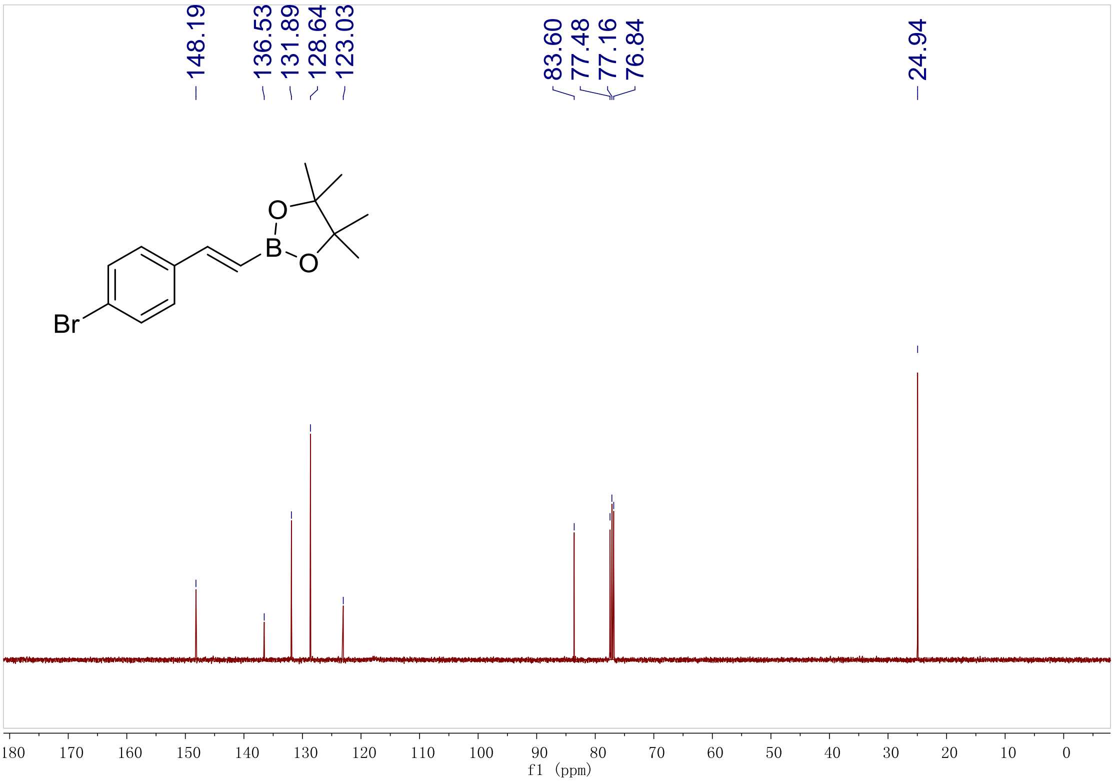
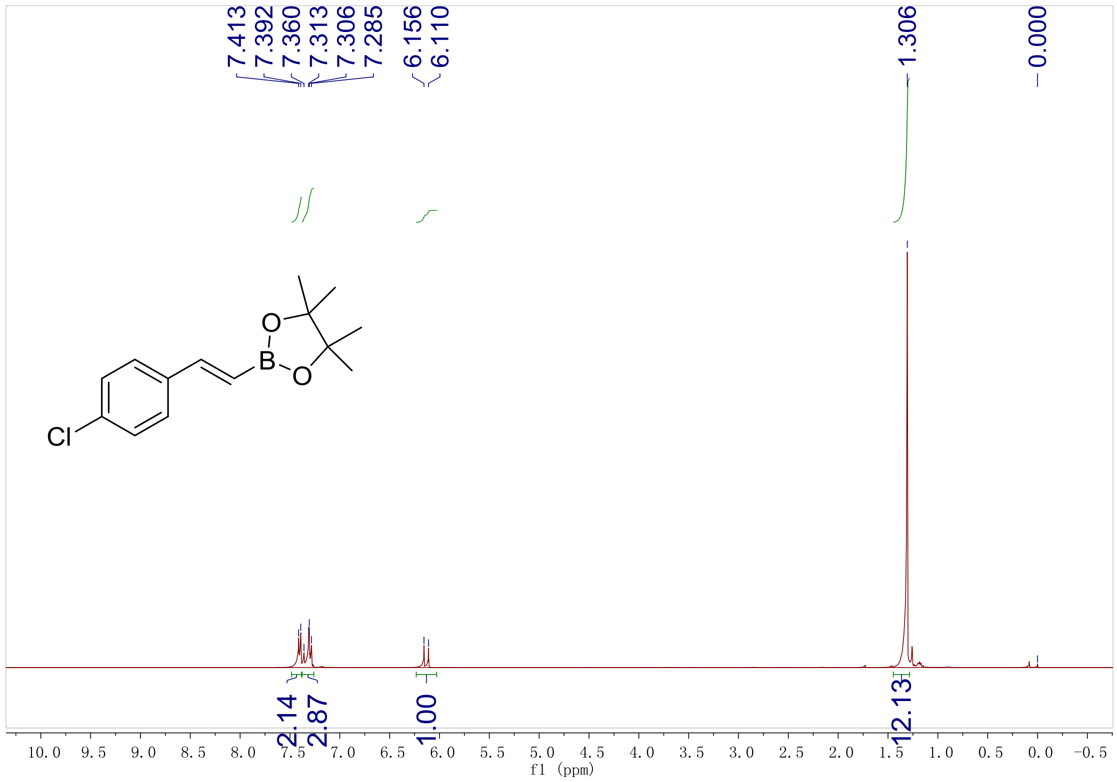
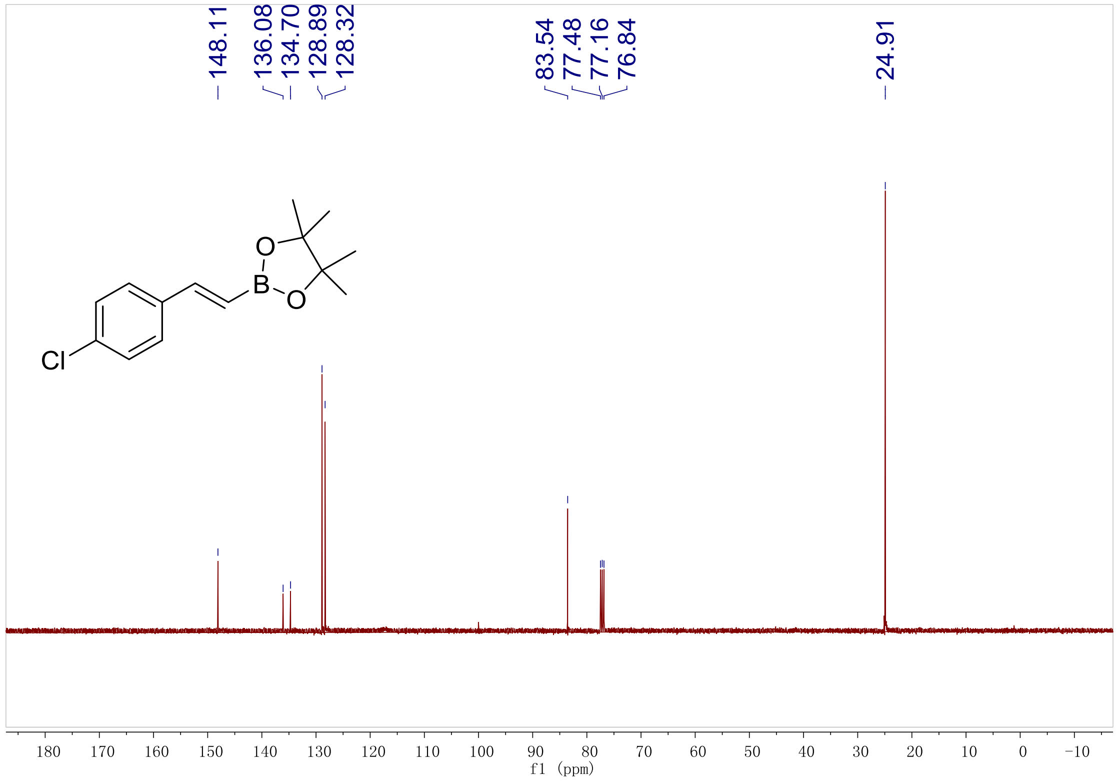
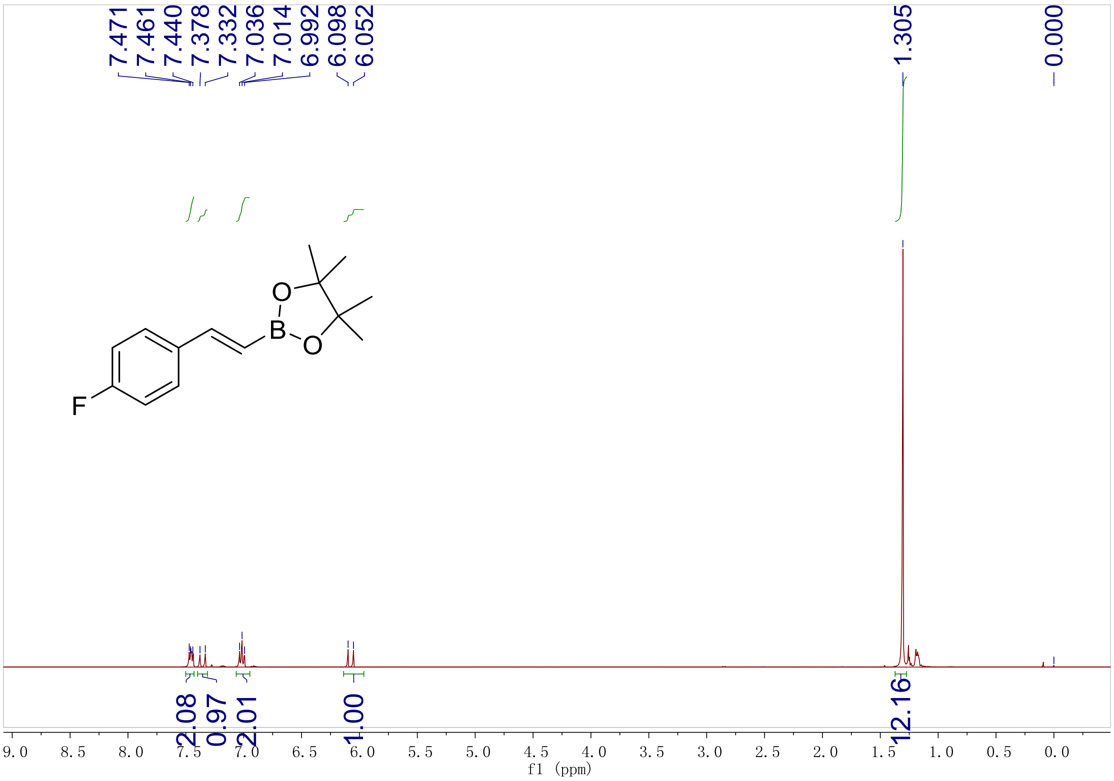
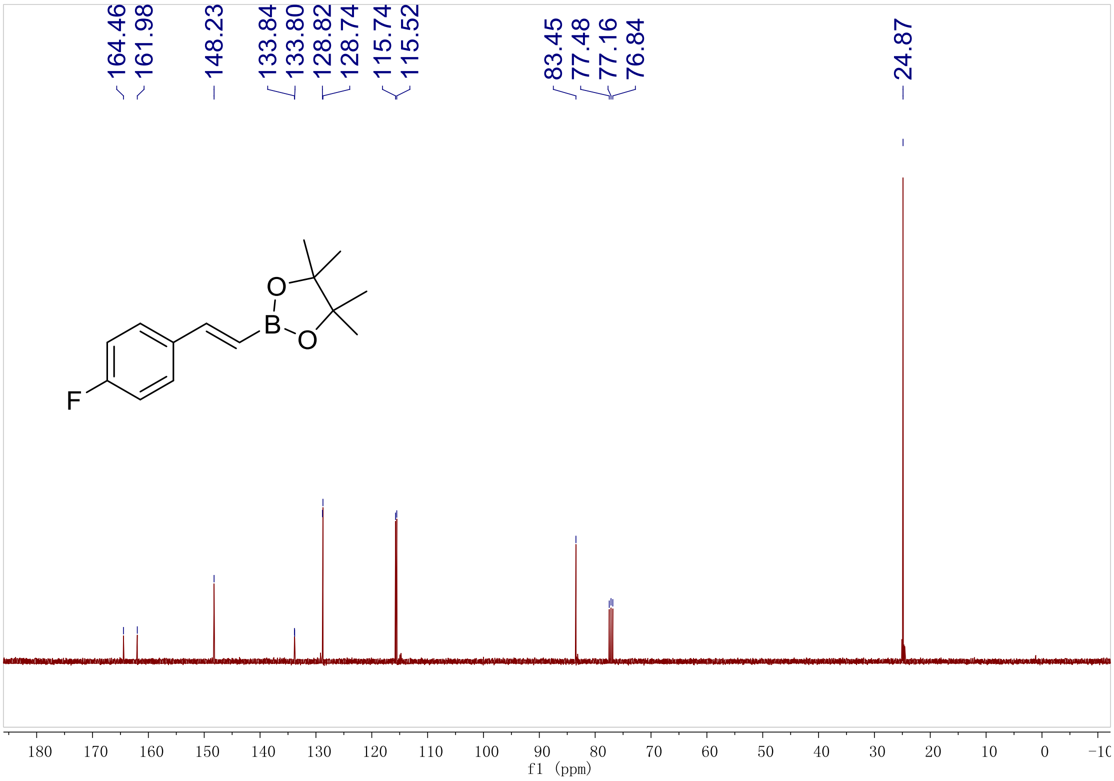
1.00
12.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

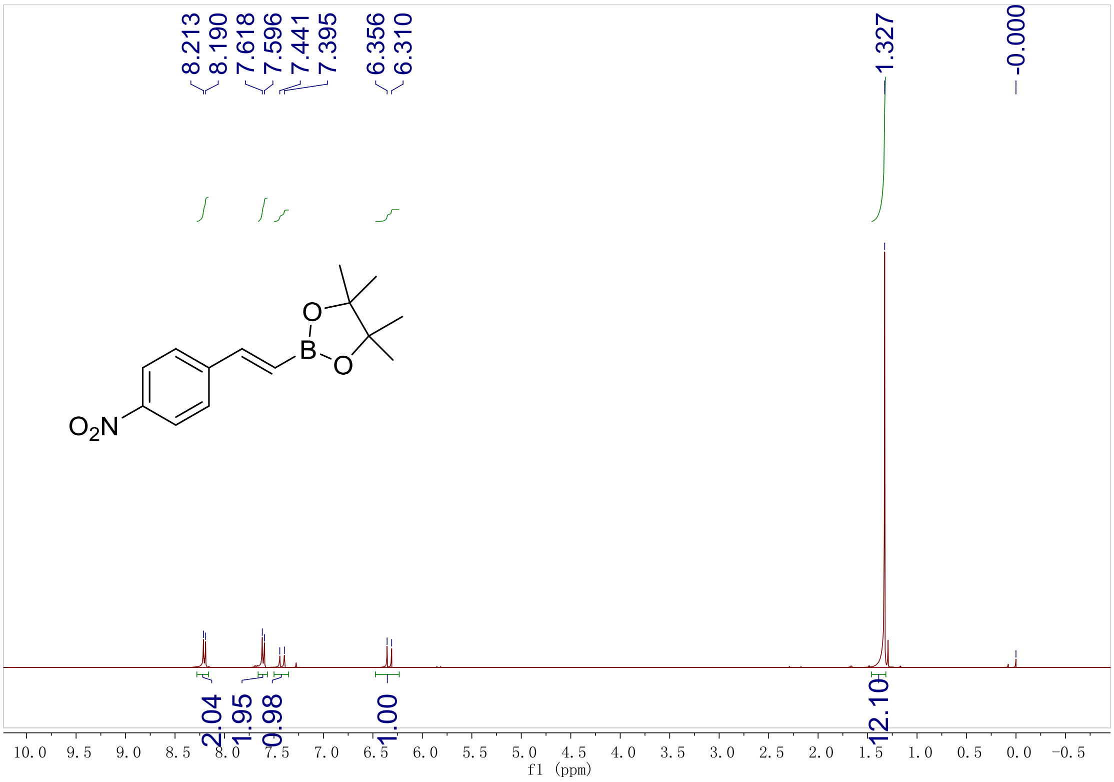

148.19
136.53
131.89
128.64
123.03
83.60
77.48
77.16
76.84
24.94
O
B
O
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

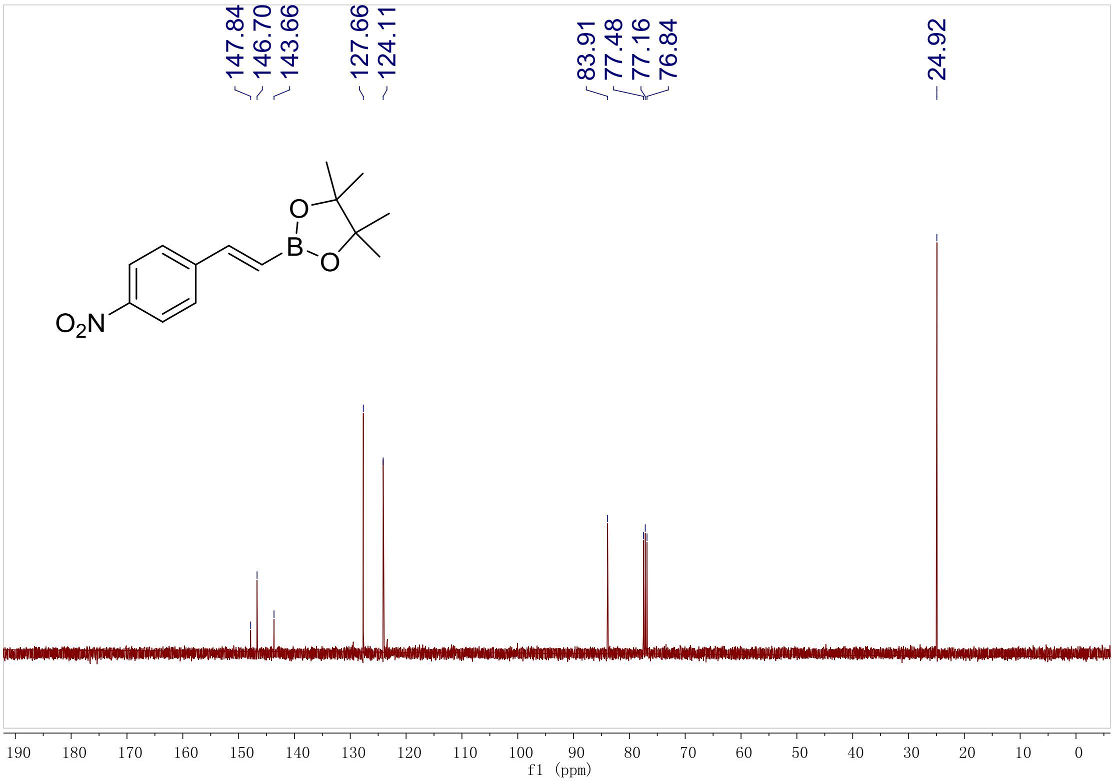

7.413
7.392
7.360
7.313
7.306
7.285
6.156
6.110
1.306
0.000
Cl
B
O
O
2.14
2.87
1.00
12.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

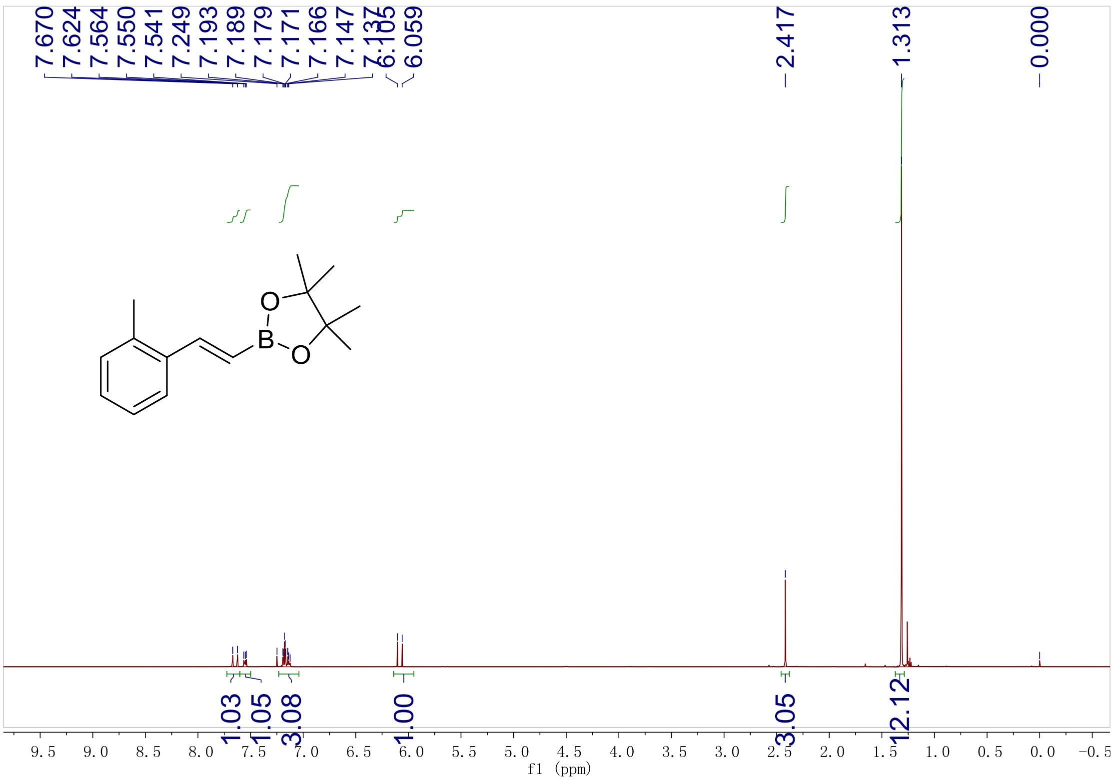

148.11
136.08
134.70
128.89
128.32
83.54
77.48
77.16
76.84
24.91
Cl
B
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

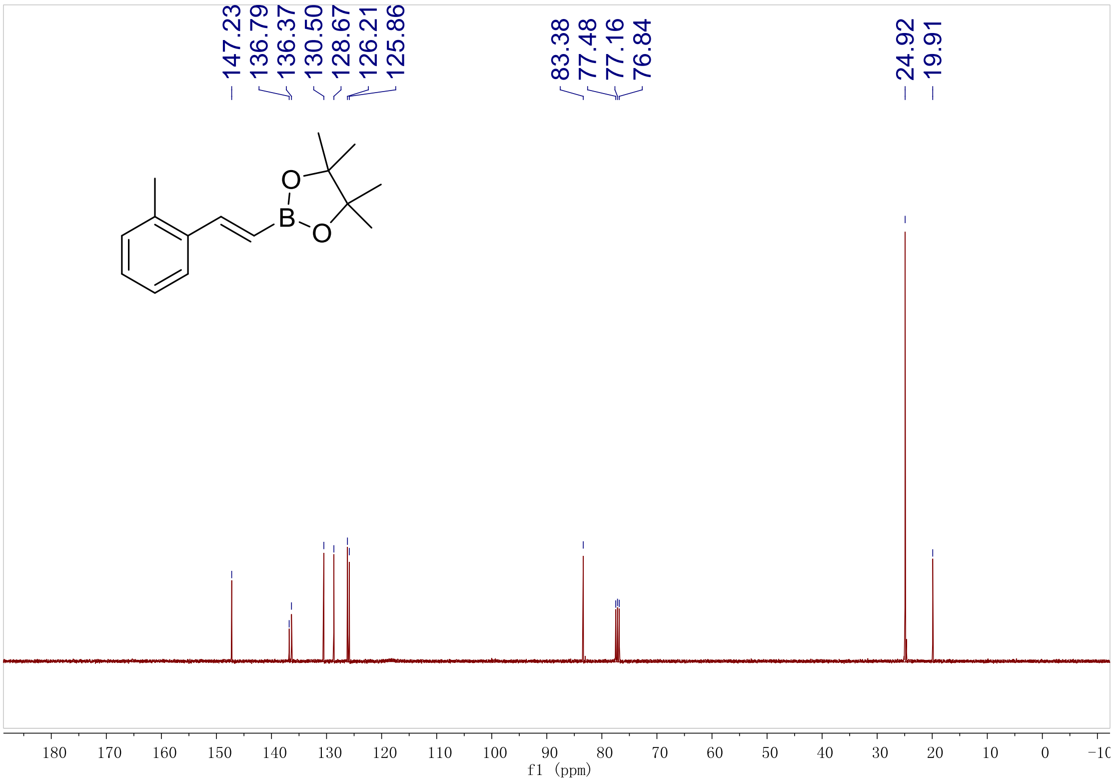

7.471
7.461
7.440
7.378
7.332
7.036
7.014
6.992
6.098
6.052
1.305
0.000
F
B
O
O
2.08
0.97
2.01
1.00
12.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

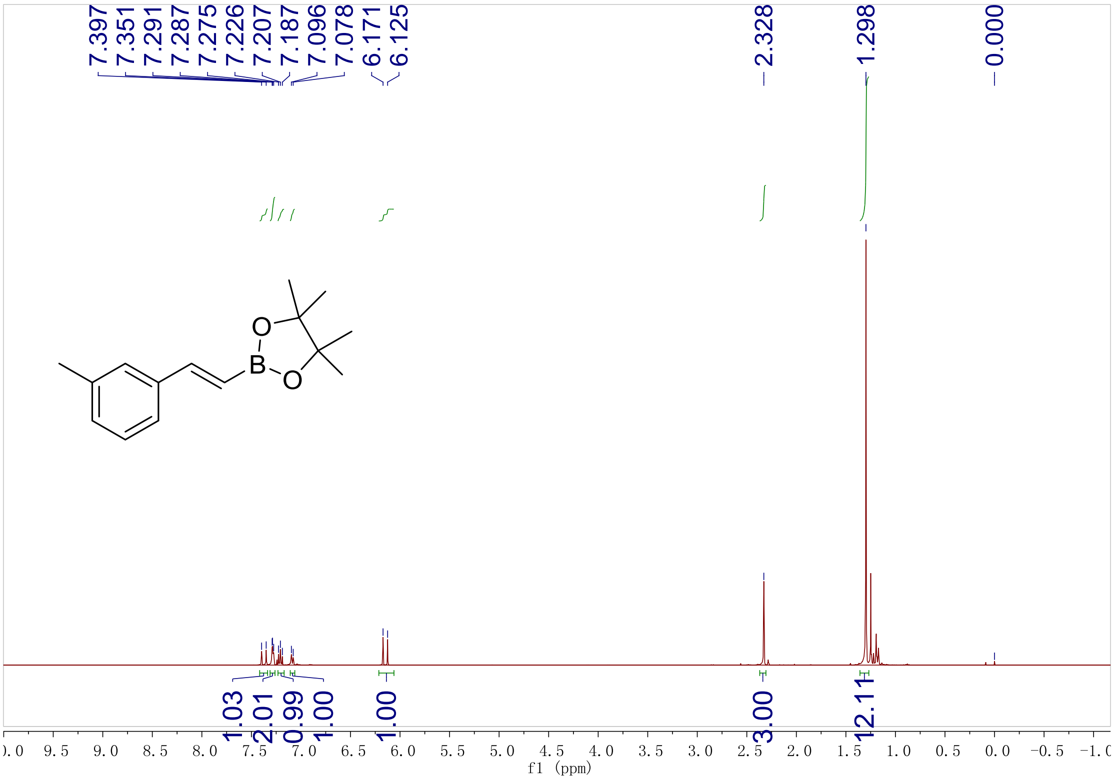

164.46
161.98
148.23
133.84
133.80
128.82
128.74
115.74
115.52
83.45
77.48
77.16
76.84
24.87
F
B
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

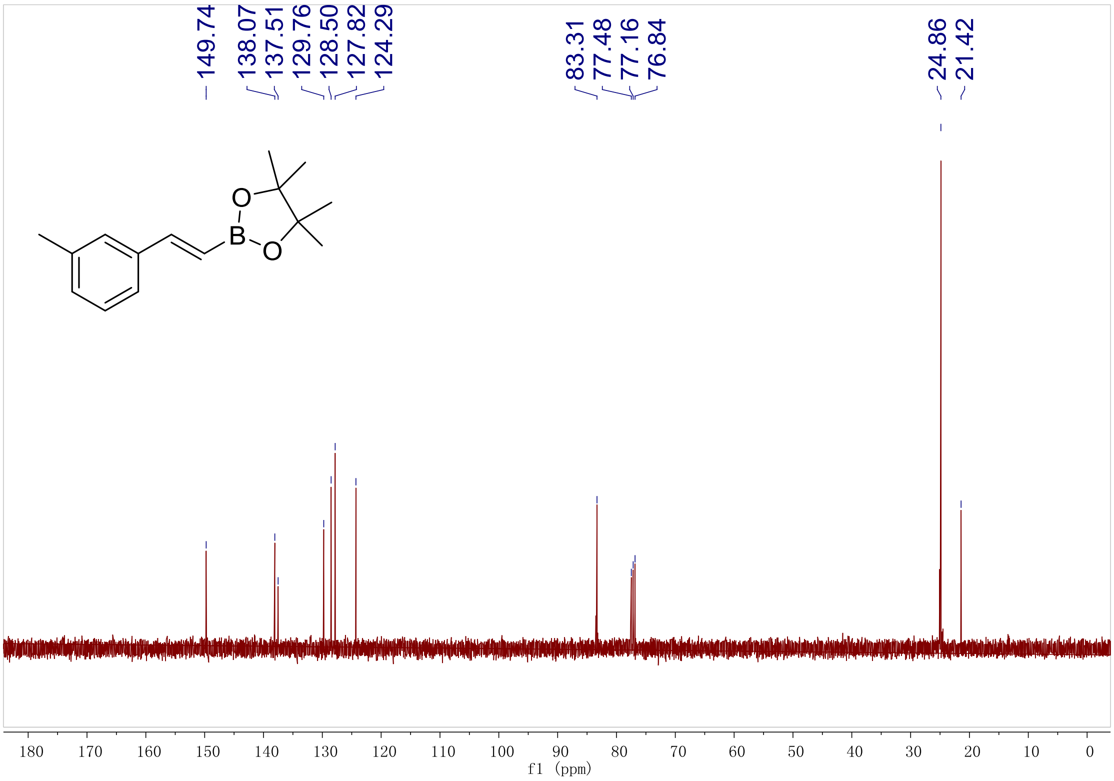

8.213
8.190
7.618
7.596
7.441
7.395
6.356
6.310
1.327
-0.000
O
B
O
O_2N
2.04
1.95
0.98
1.00
12.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

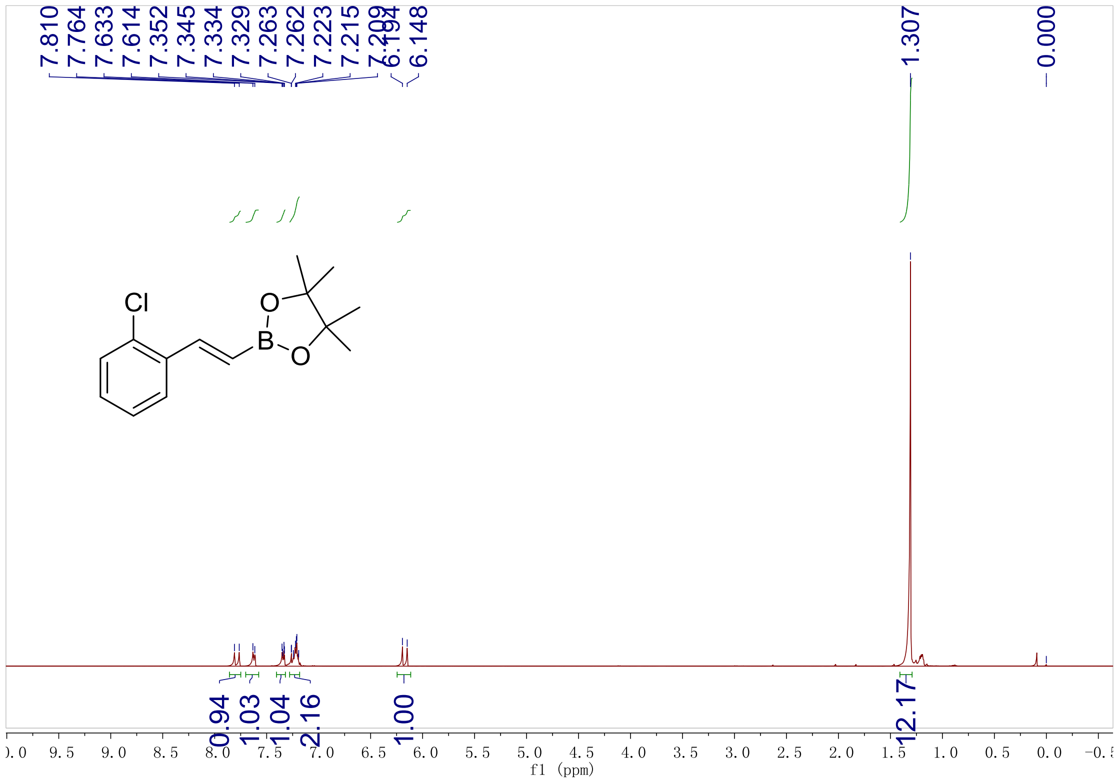

147.84
146.70
143.66
127.66
124.11
83.91
77.48
77.16
76.84
24.92
O
B
O
O_2N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

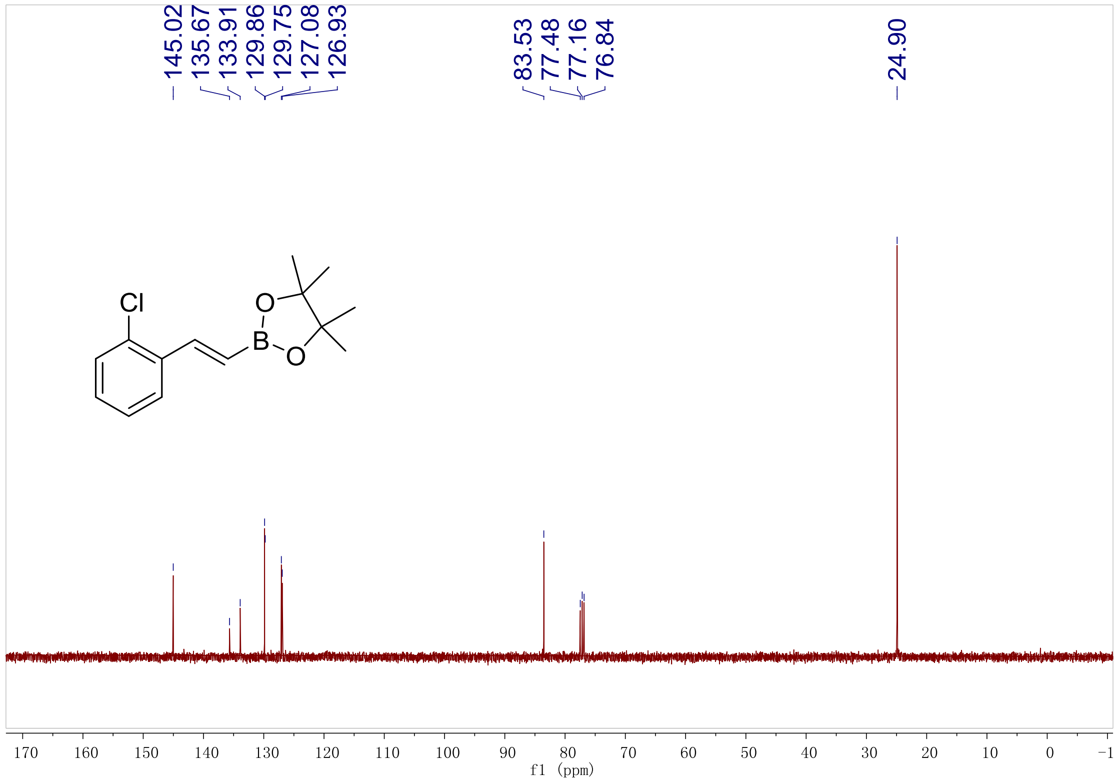

7.670
7.624
7.564
7.550
7.541
7.249
7.193
7.189
7.179
7.171
7.166
7.147
7.137
6.105
6.059
2.417
1.313
0.000
O
B
O
1.03
1.05
3.08
1.00
3.05
12.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

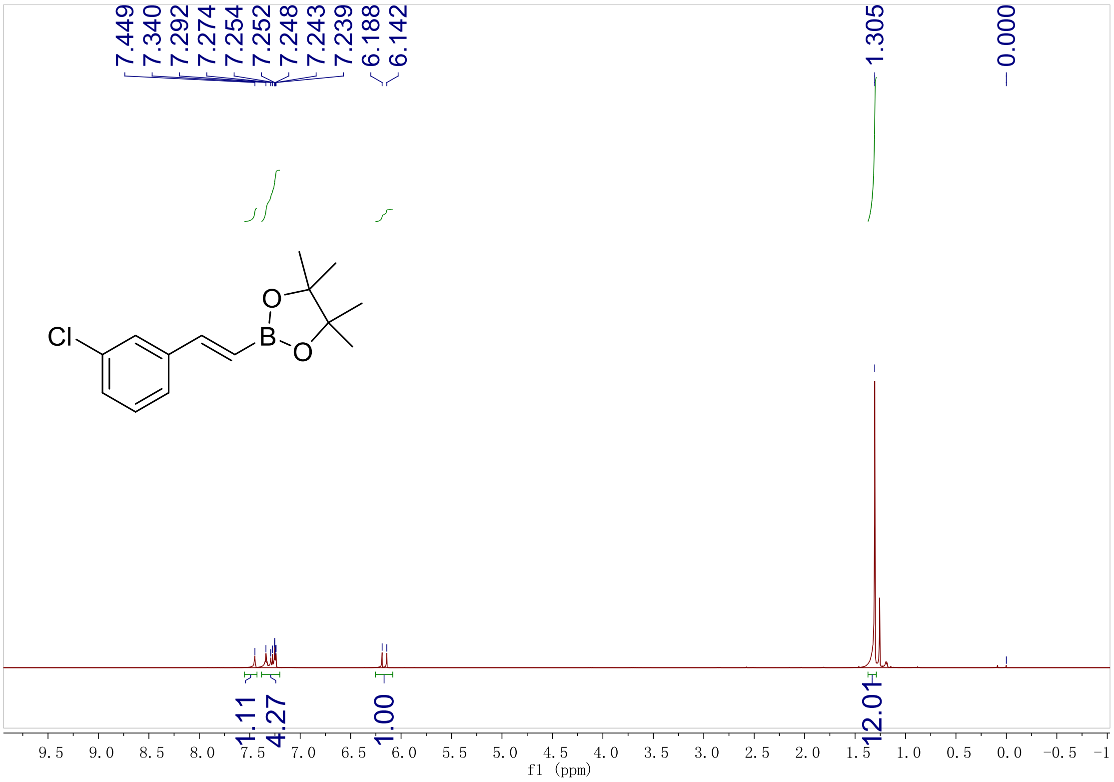

147.23
136.79
136.37
130.50
128.67
126.21
125.86
83.38
77.48
77.16
76.84
24.92
19.91
O
B
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

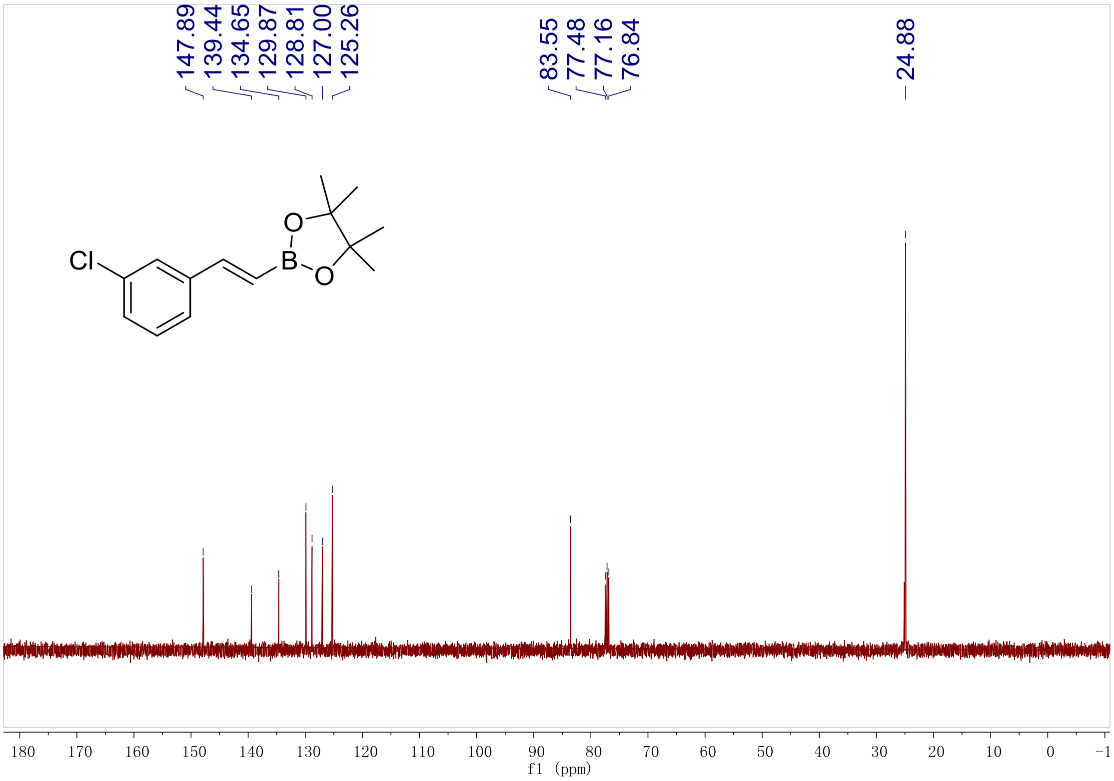

7.397
7.351
7.291
7.287
7.275
7.226
7.207
7.187
7.096
7.078
6.171
6.125
2.328
1.298
0.000
O
B
O
1.03
2.01
0.99
1.00
1.00
3.00
12.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

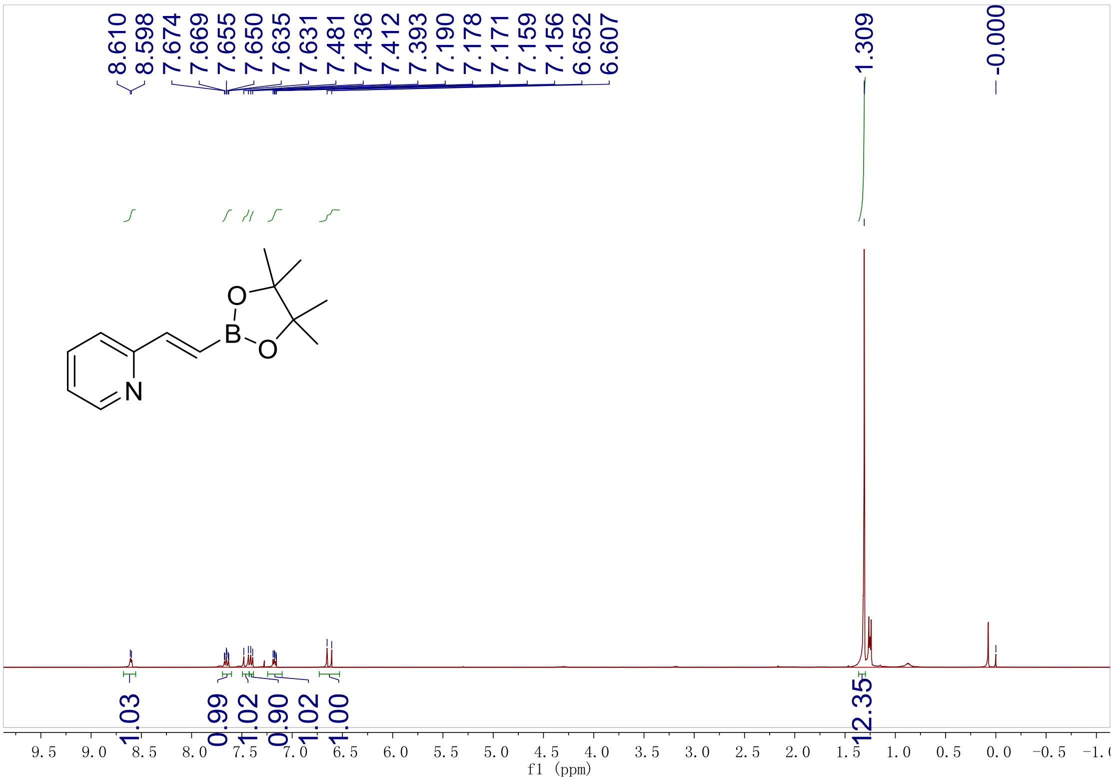

149.74
138.07
137.51
129.76
128.50
127.82
124.29
83.31
77.48
77.16
76.84
24.86
21.42
O
B
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

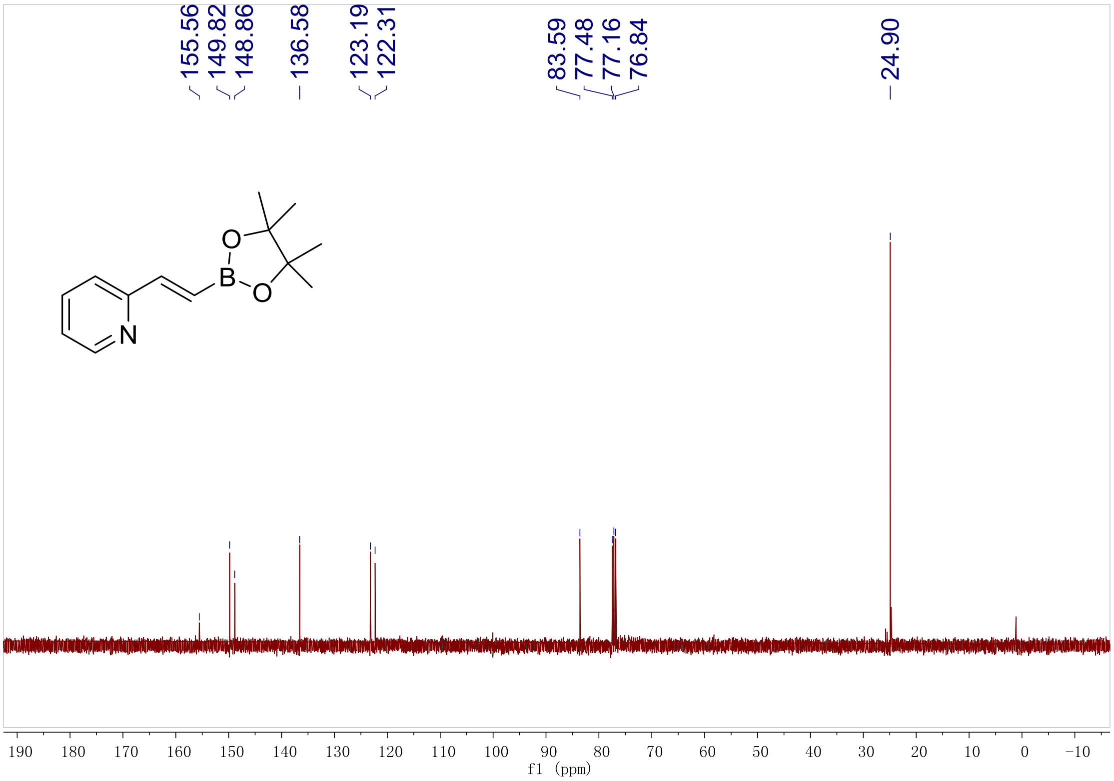

7.810
7.764
7.633
7.614
7.352
7.345
7.334
7.329
7.263
7.262
7.223
7.215
7.209
6.194
6.148
1.307
0.000
Cl
O
B
O
0.94
1.03
1.04
2.16
1.00
12.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

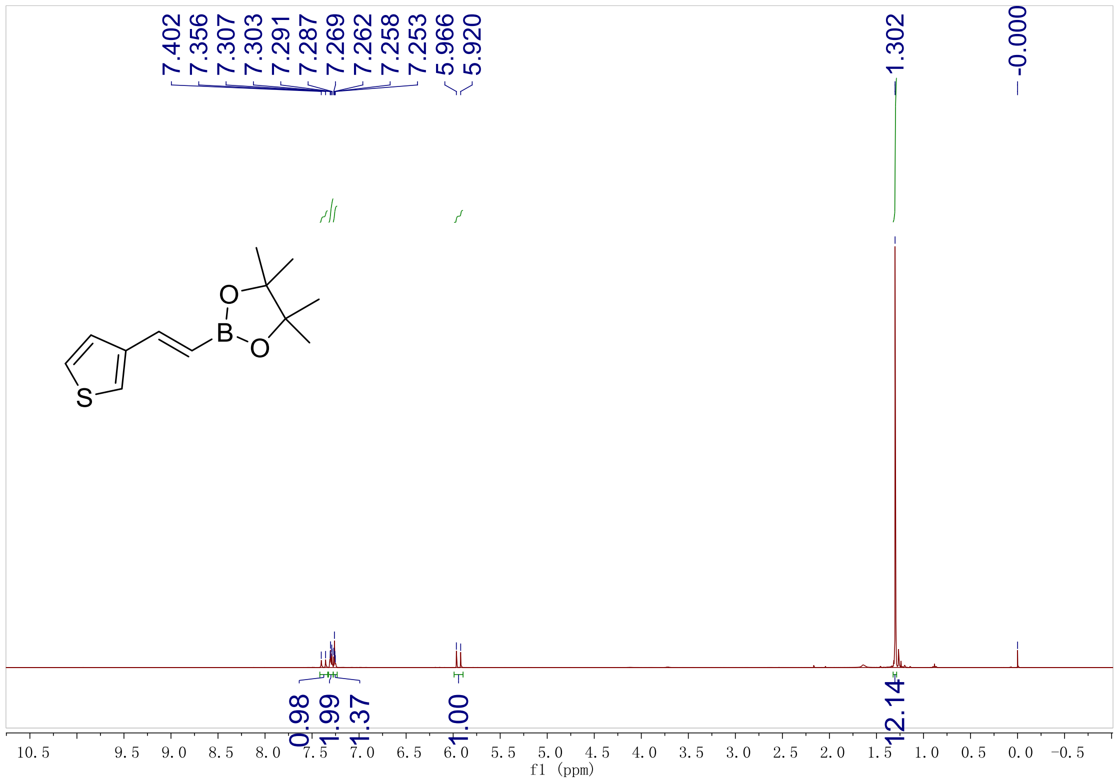

145.02
135.67
133.91
129.86
129.75
127.08
126.93
83.53
77.48
77.16
76.84
24.90
Cl
O
B
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

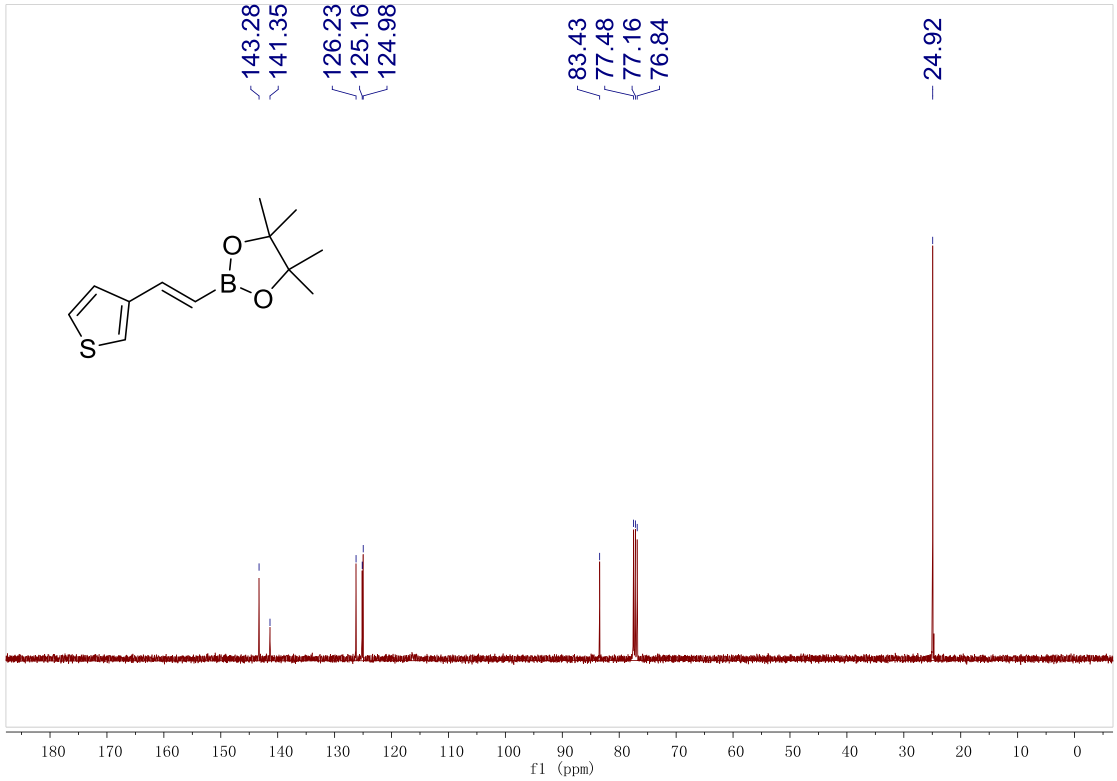

7.449
7.340
7.292
7.274
7.254
7.252
7.248
7.243
7.239
6.188
6.142
1.305
0.000
Cl
B
O
O
1.11
4.27
1.00
12.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

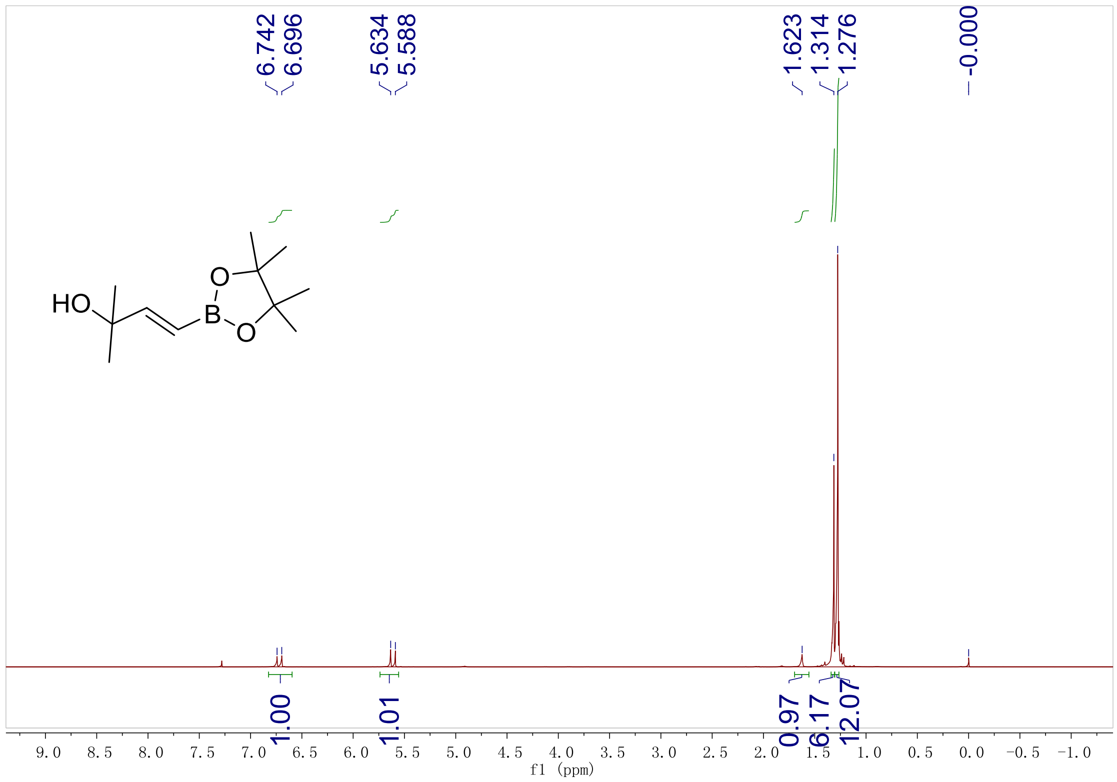

147.89
139.44
134.65
129.87
128.81
127.00
125.26
83.55
77.48
77.16
76.84
24.88
Cl
B
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

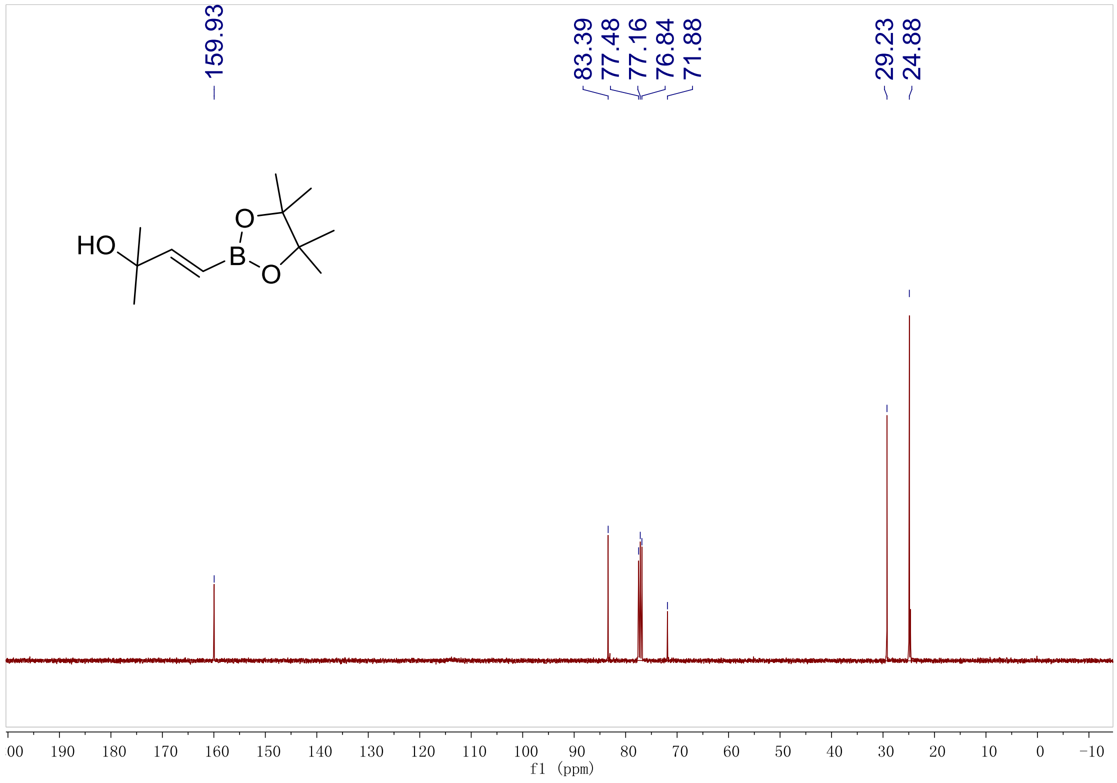

8.610
8.598
7.674
7.669
7.655
7.650
7.635
7.631
7.481
7.436
7.412
7.393
7.190
7.178
7.171
7.159
7.156
6.652
6.607
1.309
-0.000
O
B
O
N
1.03
0.99
1.02
0.90
1.02
1.00
12.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

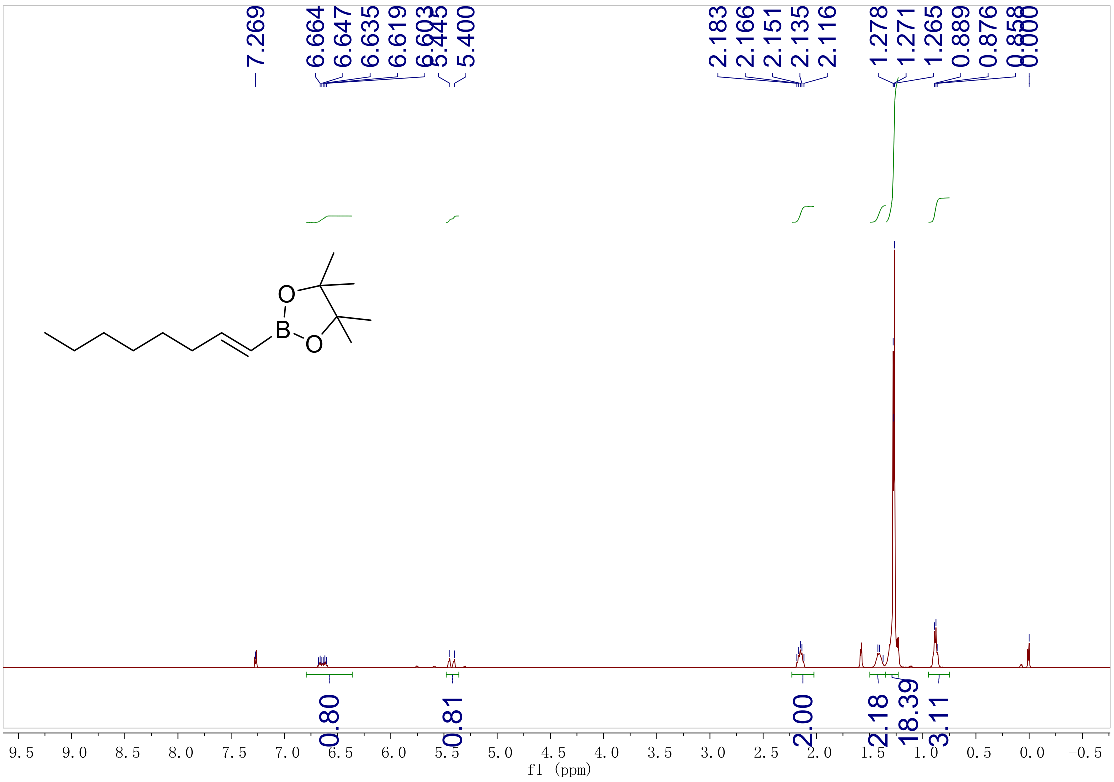

155.56
149.82
148.86
136.58
123.19
122.31
83.59
77.48
77.16
76.84
24.90
O
B
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

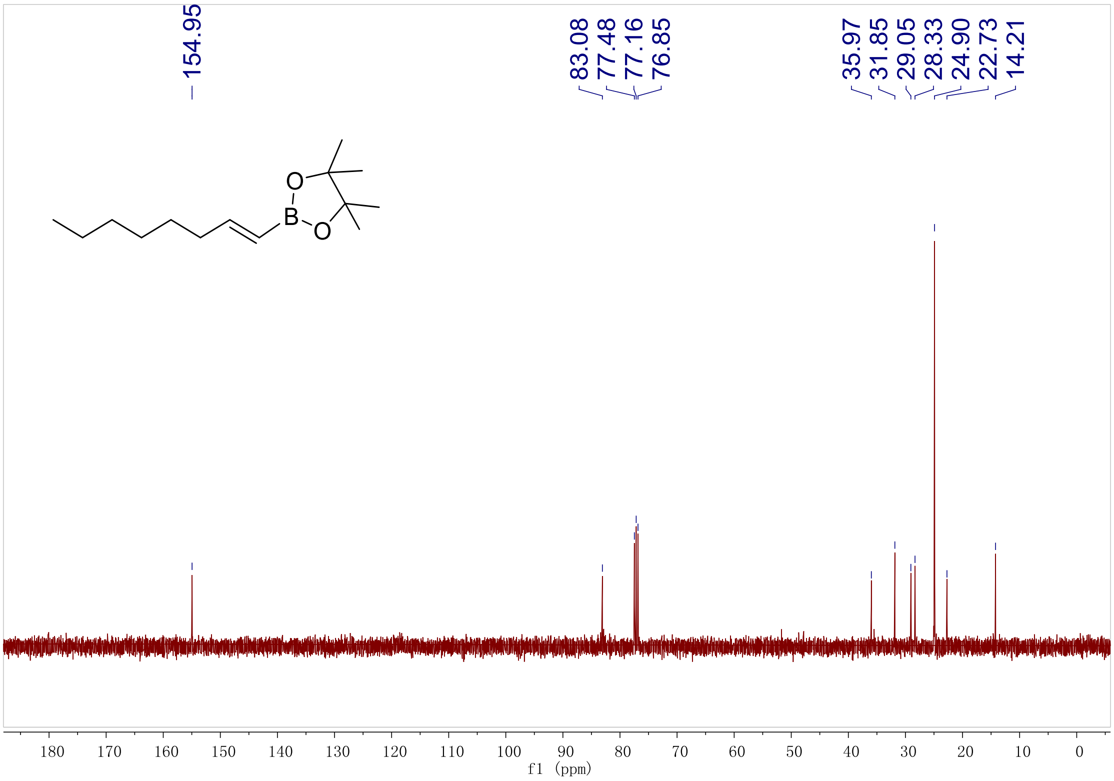

7.402
7.356
7.307
7.303
7.291
7.287
7.269
7.262
7.258
7.253
5.966
5.920
1.302
-0.000
0.98
1.99
1.37
1.00
12.14
O
B
O
S
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

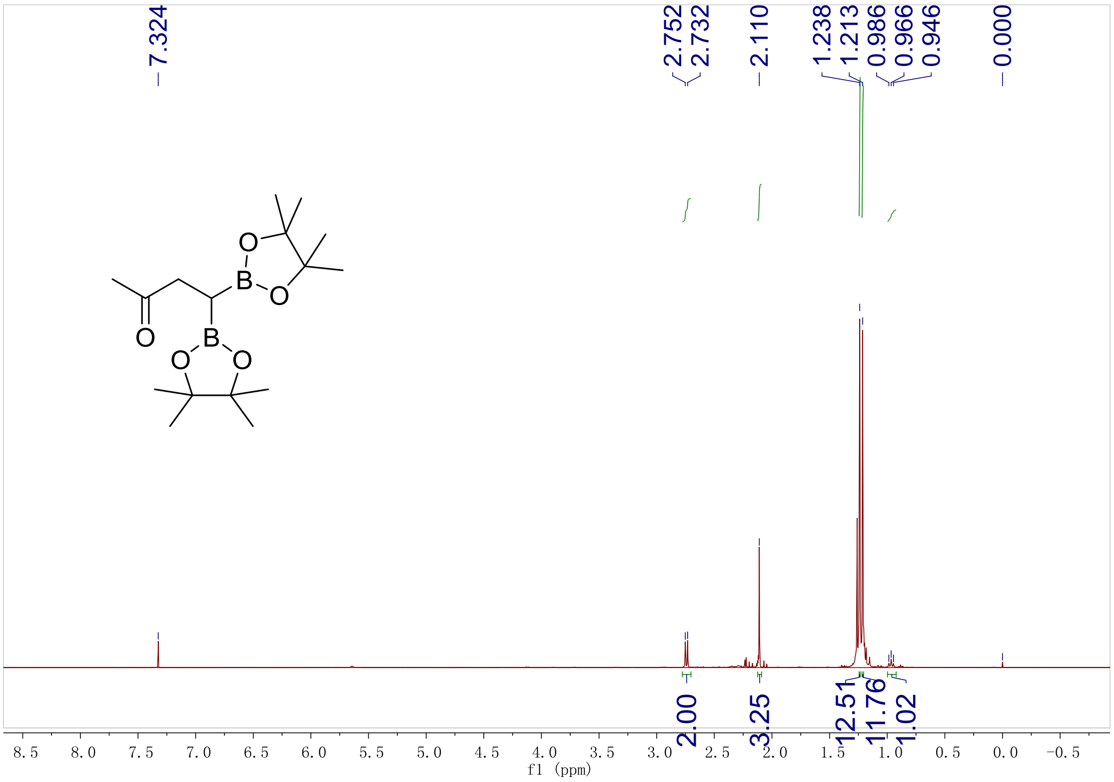

143.28
141.35
126.23
125.16
124.98
83.43
77.48
77.16
76.84
24.92
O
B
O
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

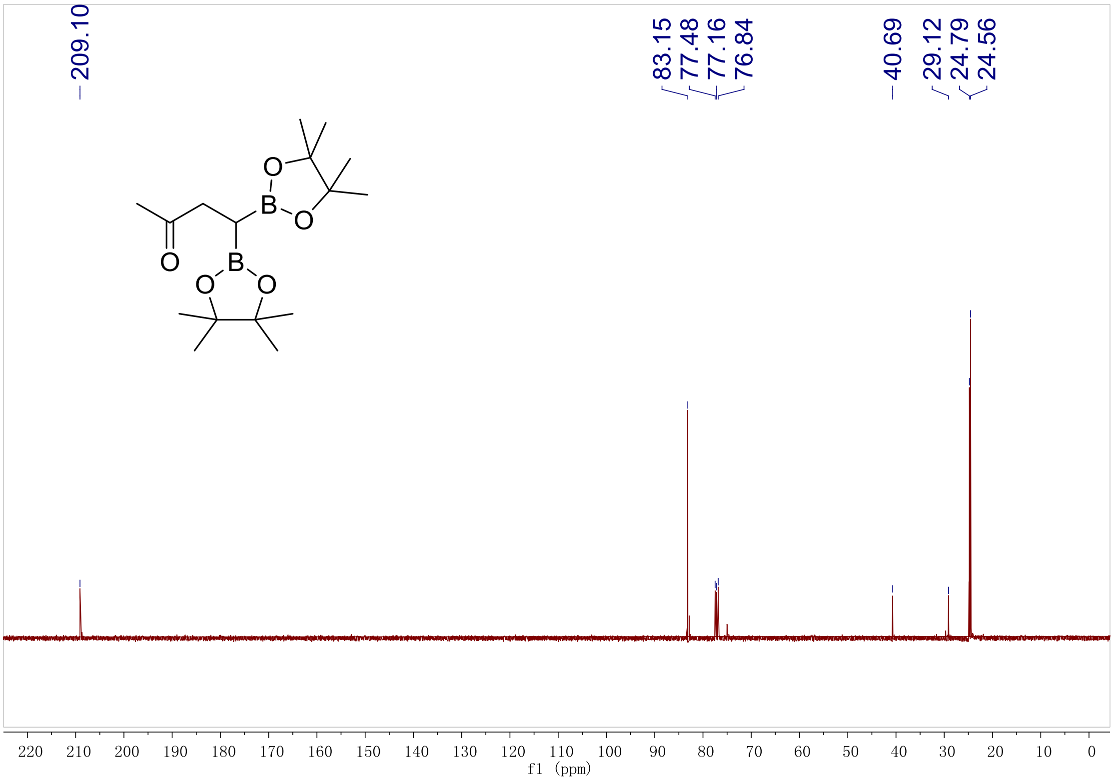

6.742
6.696
5.634
5.588
1.623
1.314
1.276
-0.000
HO
B
O
O
1.00
1.01
0.97
6.17
12.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

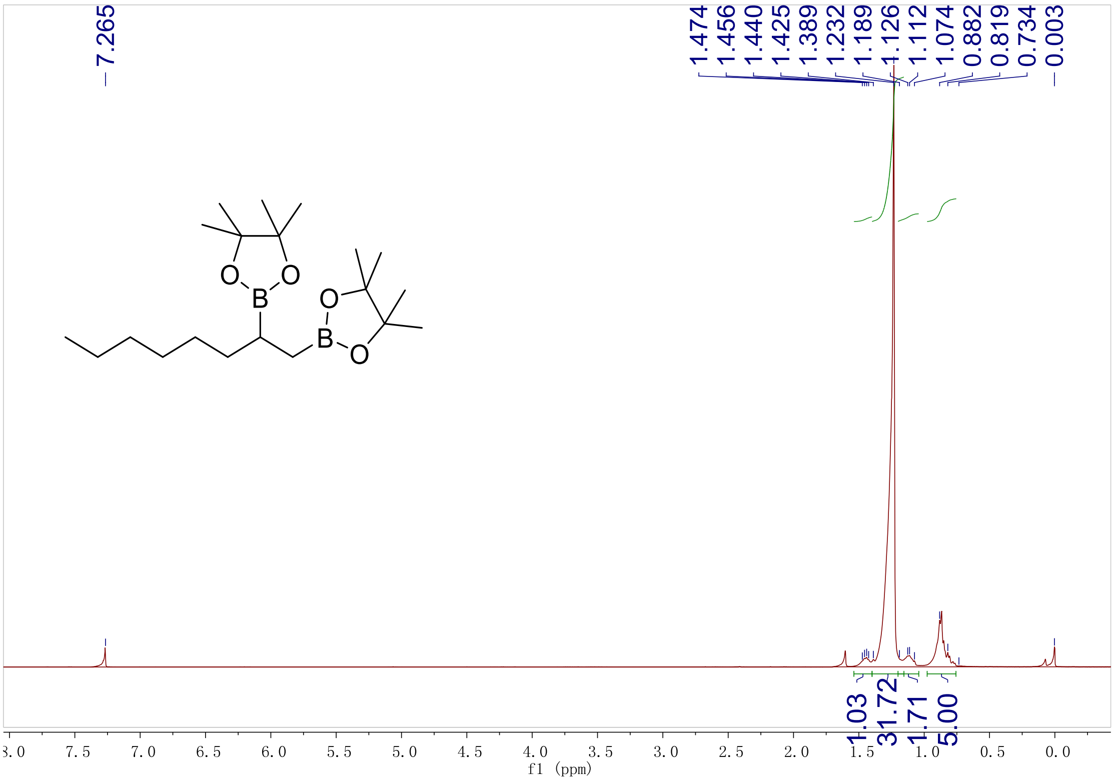

159.93
83.39
77.48
77.16
76.84
71.88
29.23
24.88
HO
B
O
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

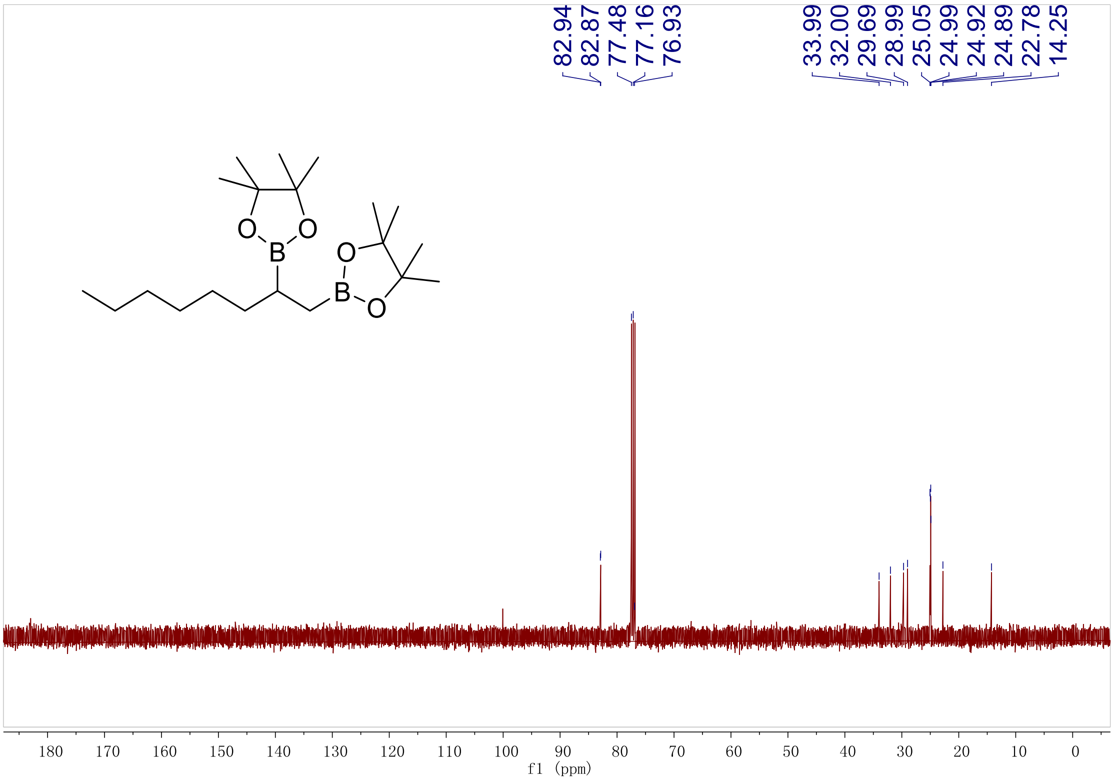

7.269
6.664
6.647
6.635
6.619
6.603
5.445
5.400
2.183
2.166
2.151
2.135
2.116
1.278
1.271
1.265
0.889
0.876
0.858
0.000
O
B
O
0.80
0.81
2.00
2.18
18.39
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

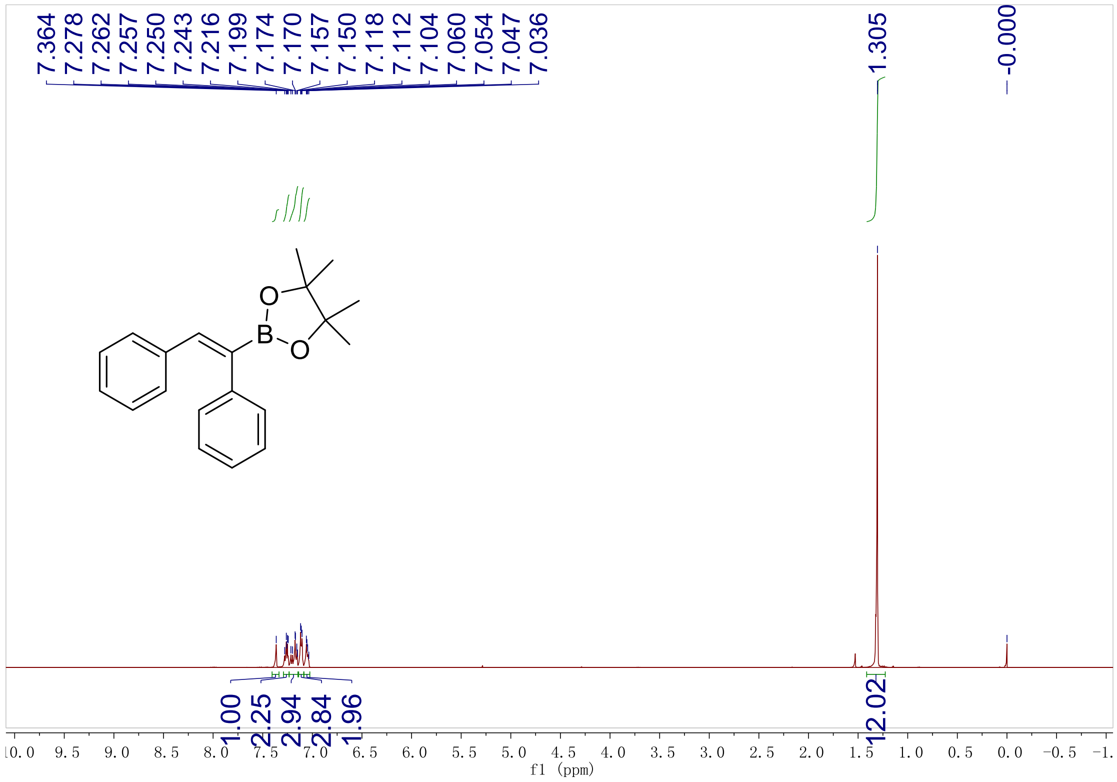

154.95
83.08
77.48
77.16
76.85
35.97
31.85
29.05
28.33
24.90
22.73
14.21
O
B
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.324
2.752
2.732
2.110
1.238
1.213
0.986
0.966
0.946
0.000
O
B
O
O
B
O
O
2.00
3.25
12.51
11.76
1.02
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)


209.10
83.15
77.48
77.16
76.84
40.69
29.12
24.79
24.56
O
B
O
O
B
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.265
1.474
1.456
1.440
1.425
1.389
1.232
1.189
1.126
1.112
1.074
0.882
0.819
0.734
0.003
1.03
31.72
1.71
5.00
O
B
O
O
B
O
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
f1 (ppm)


82.94
82.87
77.48
77.16
76.93
33.99
32.00
29.69
28.99
25.05
24.99
24.92
24.89
22.78
14.25
O
B
O
O
B
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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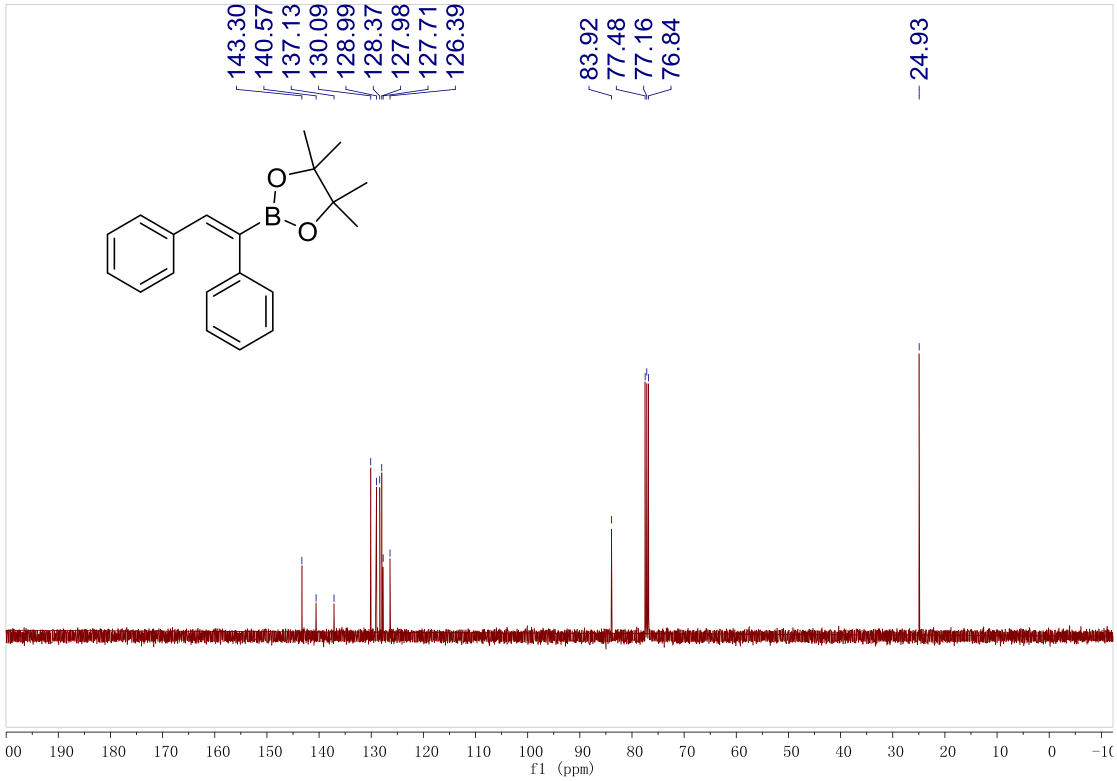
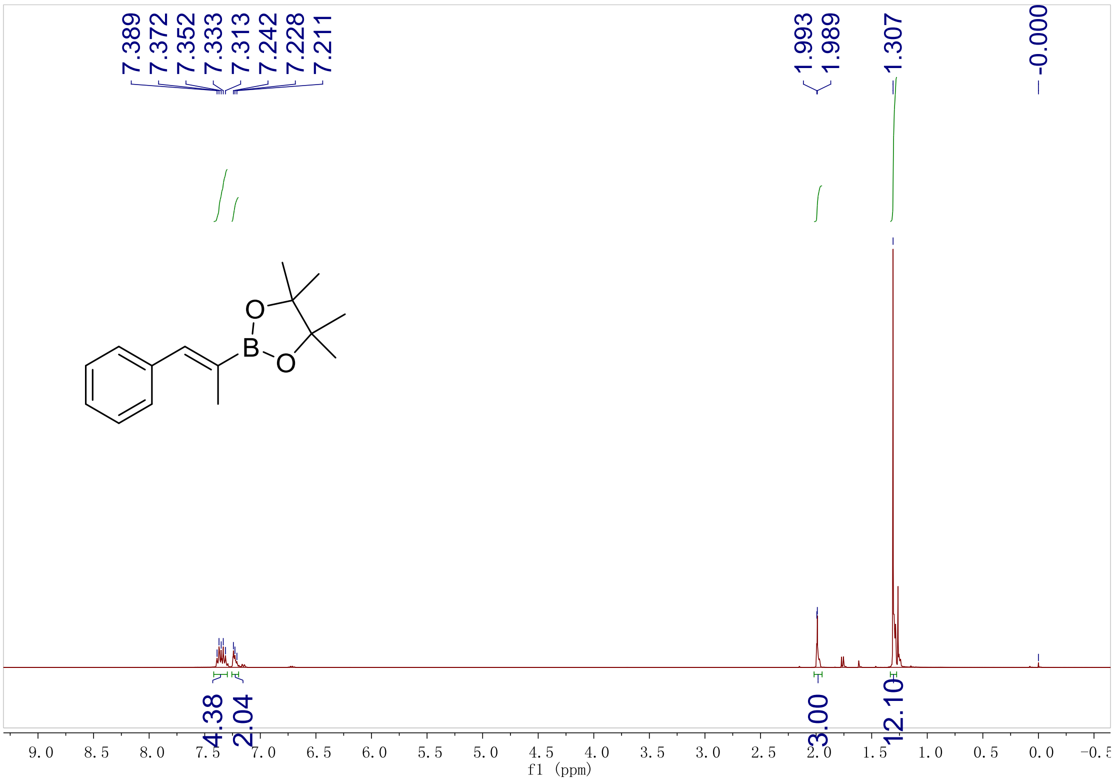
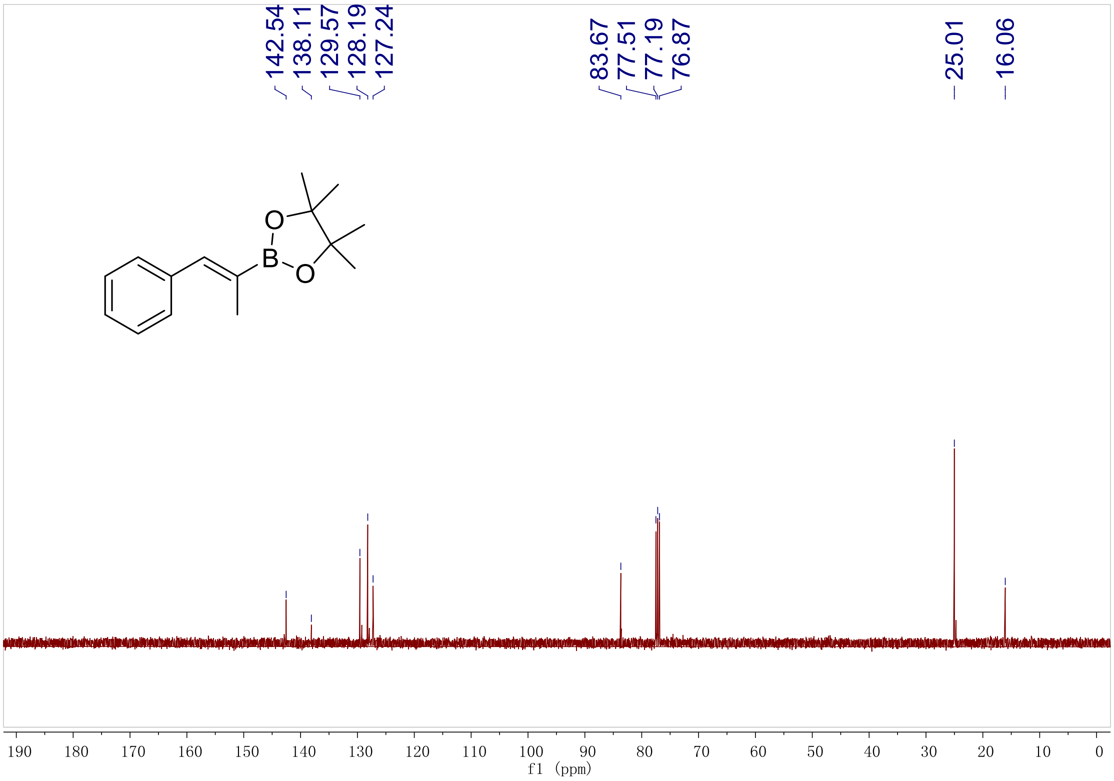
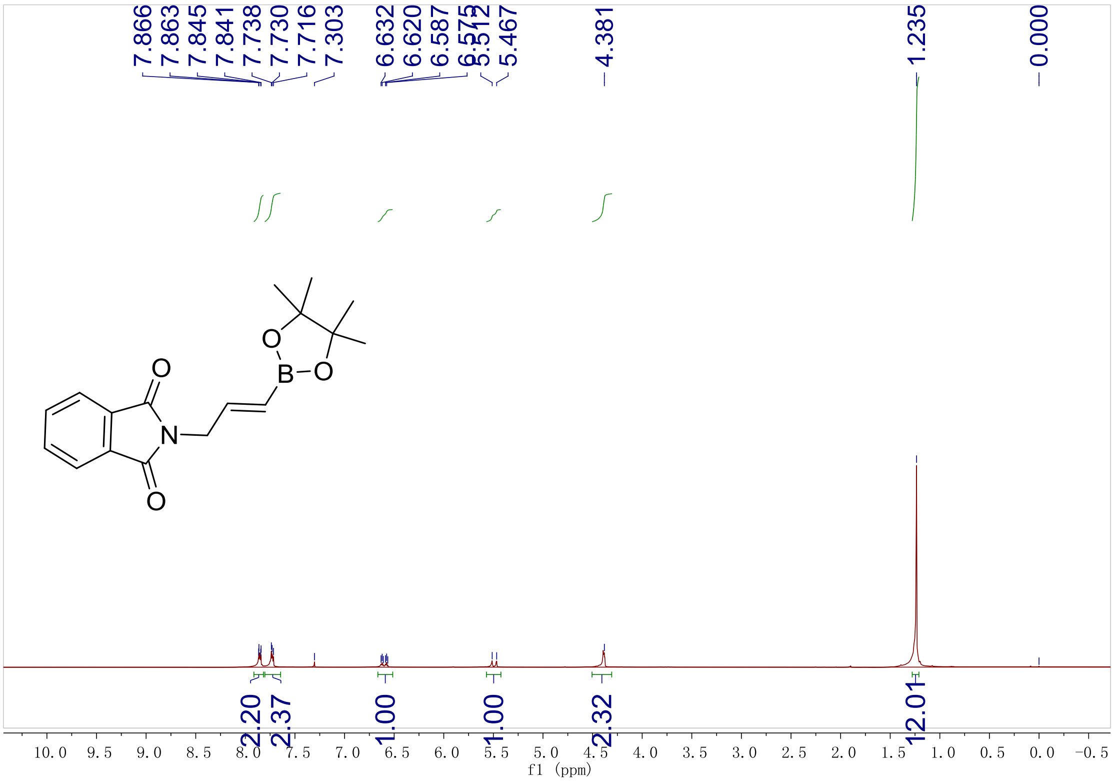
7.262
7.257
7.250
7.243
7.216
7.199
7.174
7.170
7.157
7.150
7.118
7.112
7.104
7.060
7.054
7.047
7.036
1.305
-0.000
O
B
O
1.00
2.25
2.94
2.84
1.96
12.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


143.30
140.57
137.13
130.09
128.99
128.37
127.98
127.71
126.39
83.92
77.48
77.16
76.84
24.93
O
B
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.389
7.372
7.352
7.333
7.313
7.242
7.228
7.211
1.993
1.989
1.307
-0.000
O
B
O
4.38
2.04
3.00
12.10
9.0 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)


142.54
138.11
129.57
128.19
127.24
83.67
77.51
77.19
76.87
25.01
16.06
O
B
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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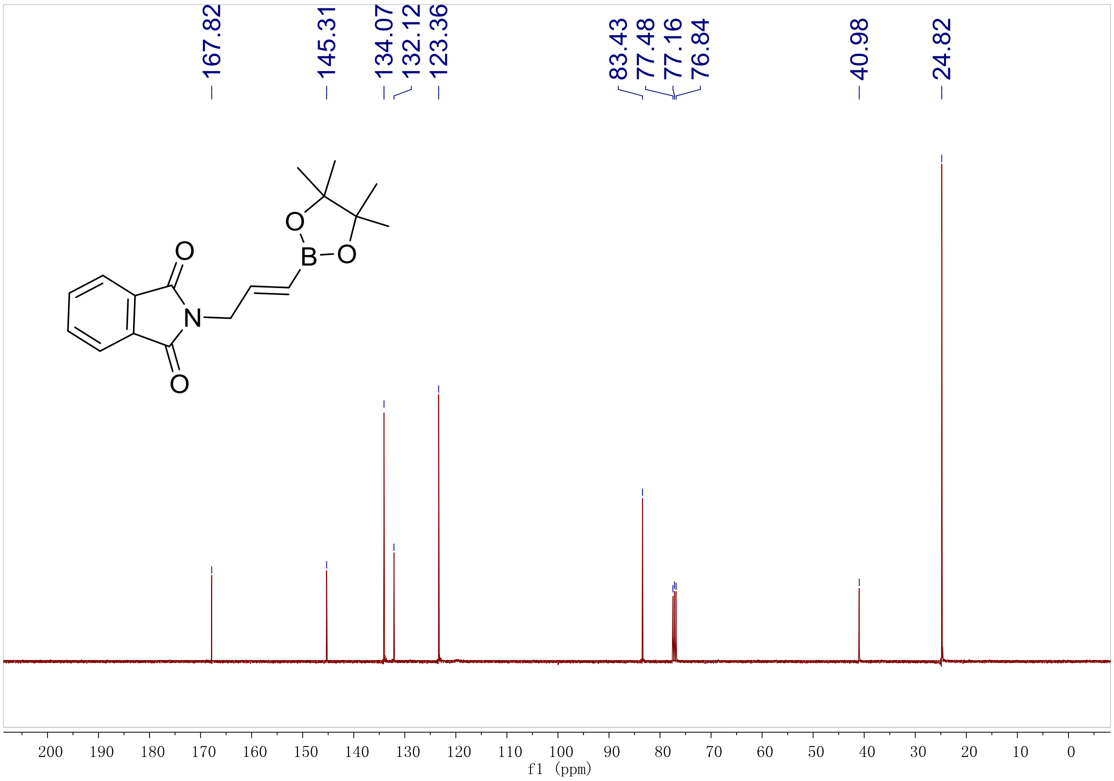
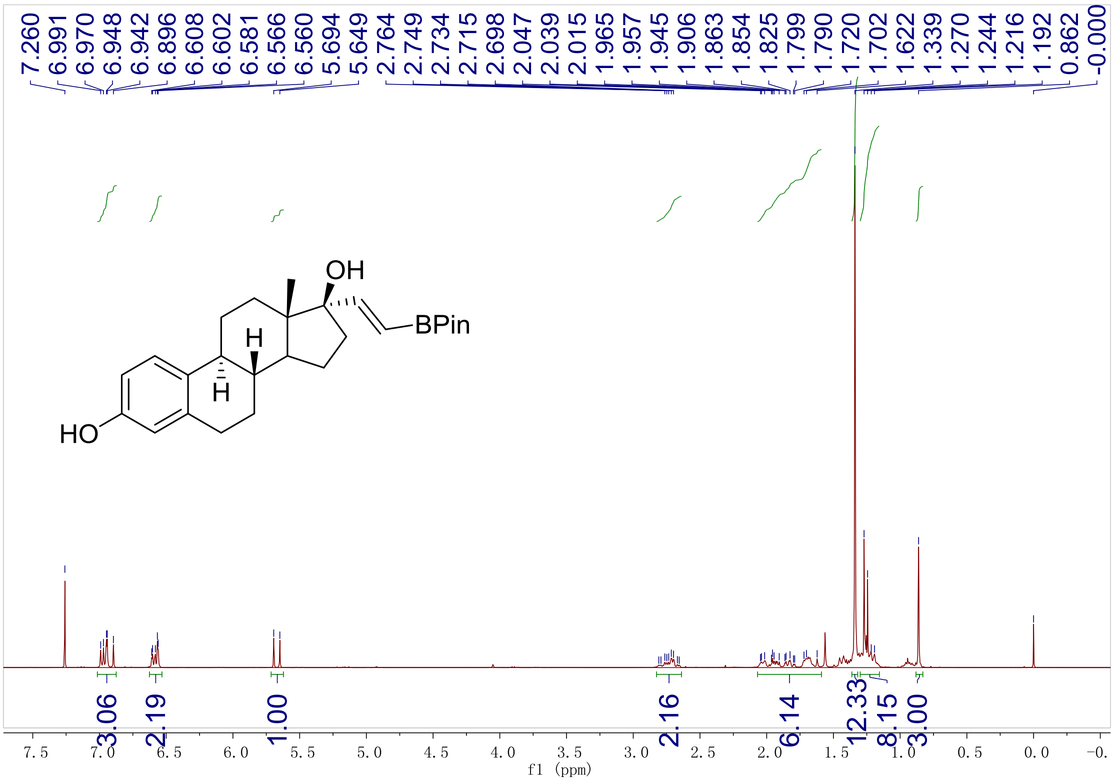
7.863
7.845
7.841
7.738
7.730
7.716
7.303
6.632
6.620
6.587
6.575
5.512
5.467
4.381
1.235
0.000
O
N
O
B
O
O
2.20
2.37
1.00
1.00
2.32
12.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


167.82
145.31
134.07
132.12
123.36
83.43
77.48
77.16
76.84
40.98
24.82
O
N
O
B
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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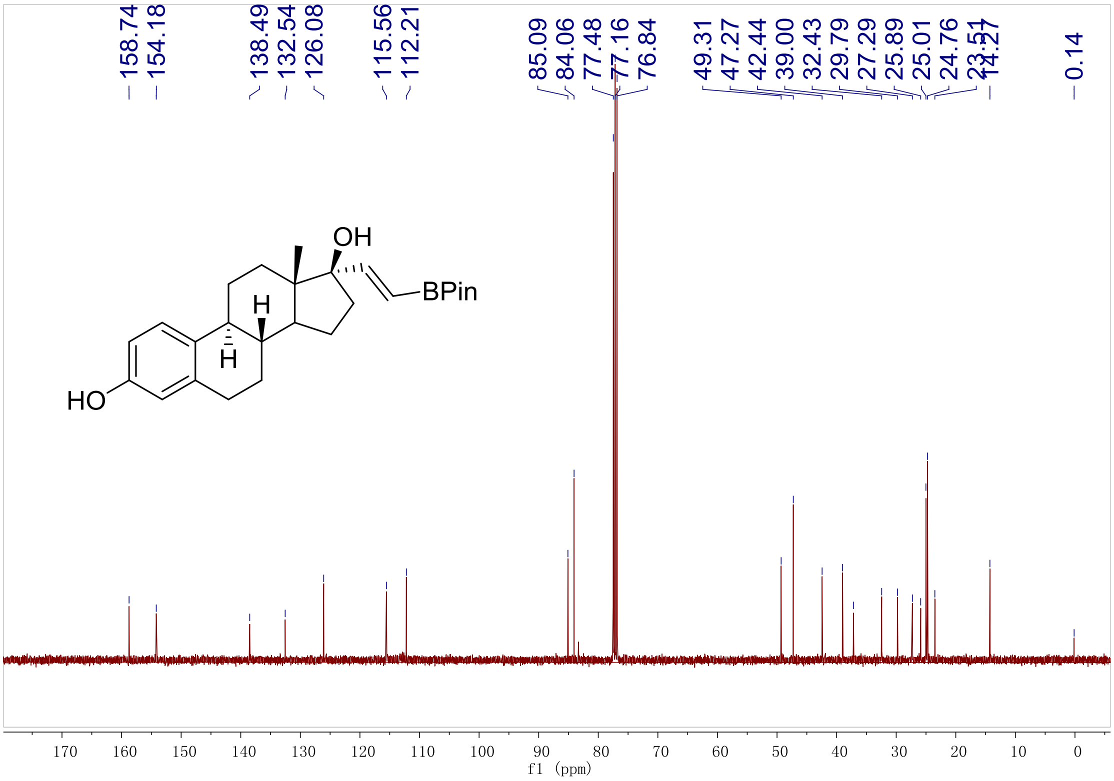
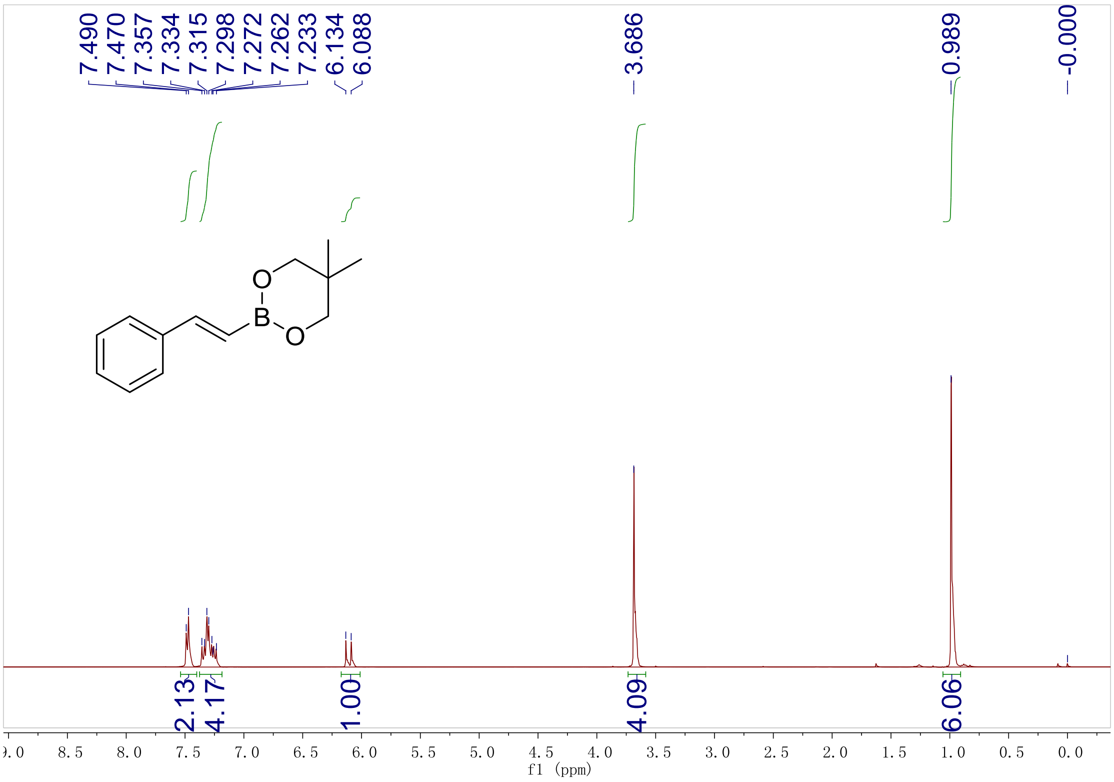
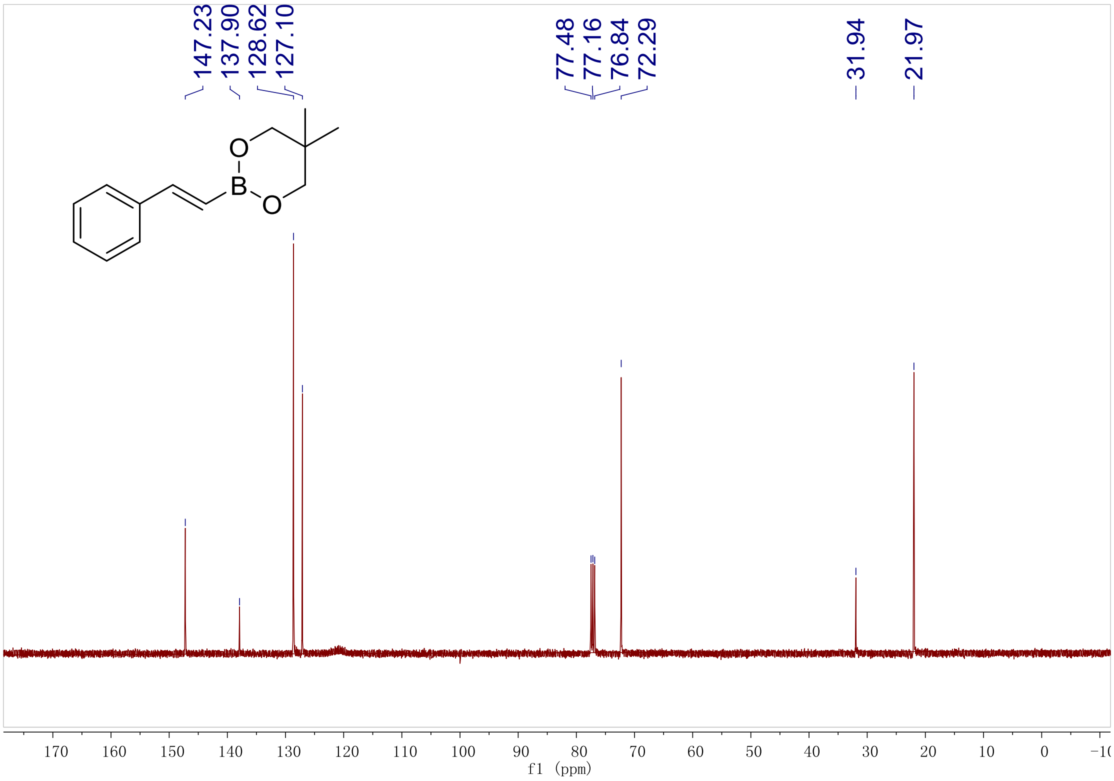
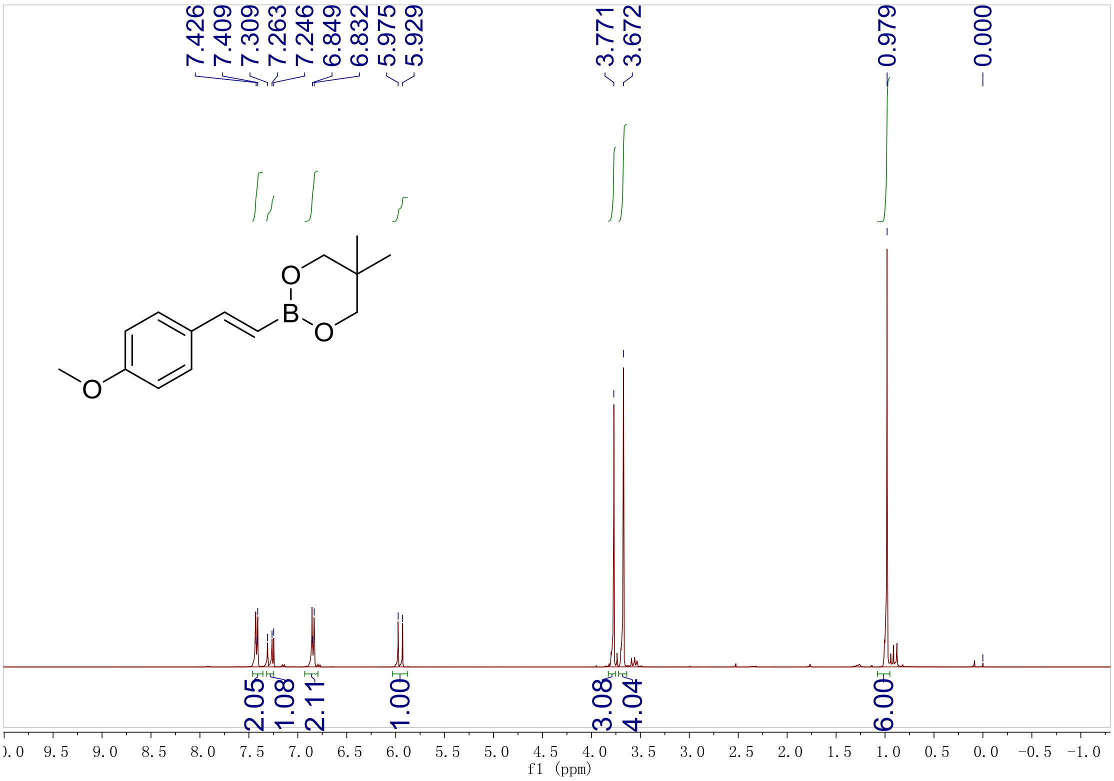
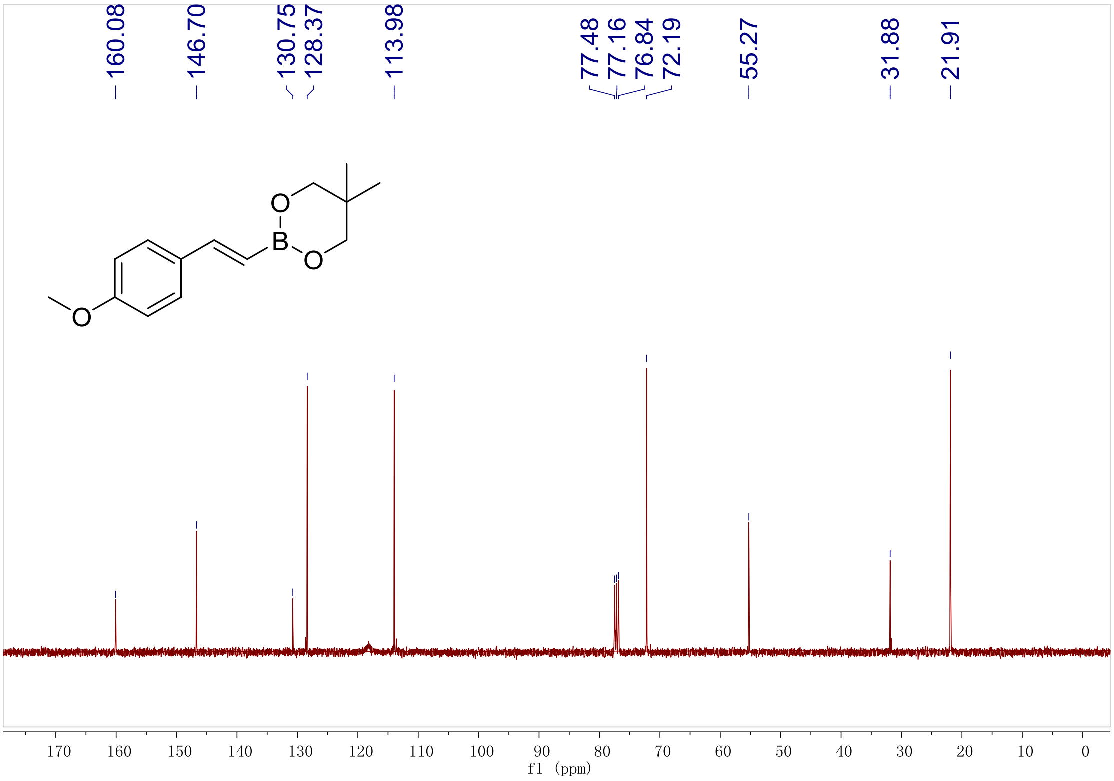
6.991
6.970
6.948
6.942
6.896
6.608
6.602
6.581
6.566
6.560
5.694
5.649
2.764
2.749
2.734
2.715
2.698
2.047
2.039
2.015
1.965
1.957
1.945
1.906
1.863
1.854
1.825
1.799
1.790
1.720
1.702
1.622
1.339
1.270
1.244
1.216
1.192
0.862
-0.000
OH
BPin
H
H
HO
3.06
2.19
1.00
2.16
6.14
12.33
8.15
3.00
7.5
7.0
6.5
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.
f1 (ppm)

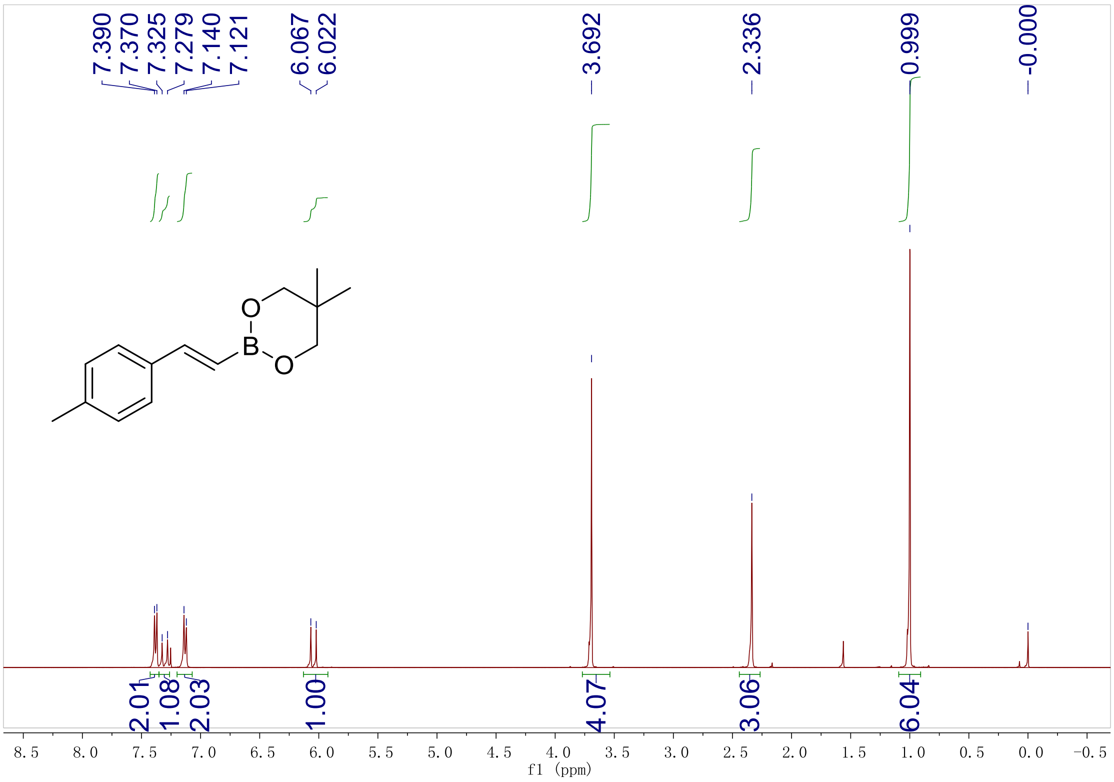

158.74
154.18
138.49
132.54
126.08
115.56
112.21
85.09
84.06
77.48
77.16
76.84
49.31
47.27
42.44
39.00
32.43
29.79
27.29
25.89
25.01
24.76
23.51
14.27
0.14
OH
BPin
H
H
HO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

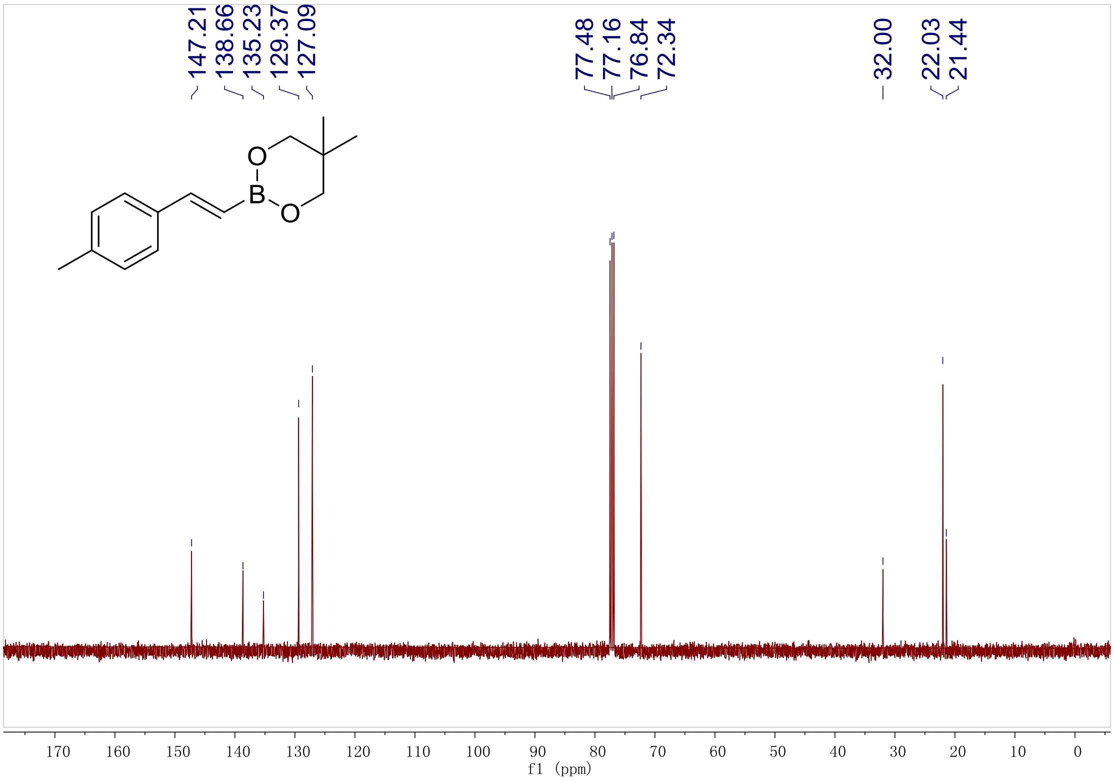

7.490
7.470
7.357
7.334
7.315
7.298
7.272
7.262
7.233
6.134
6.088
3.686
0.989
-0.000
O
B
O
2.13
4.17
1.00
4.09
6.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

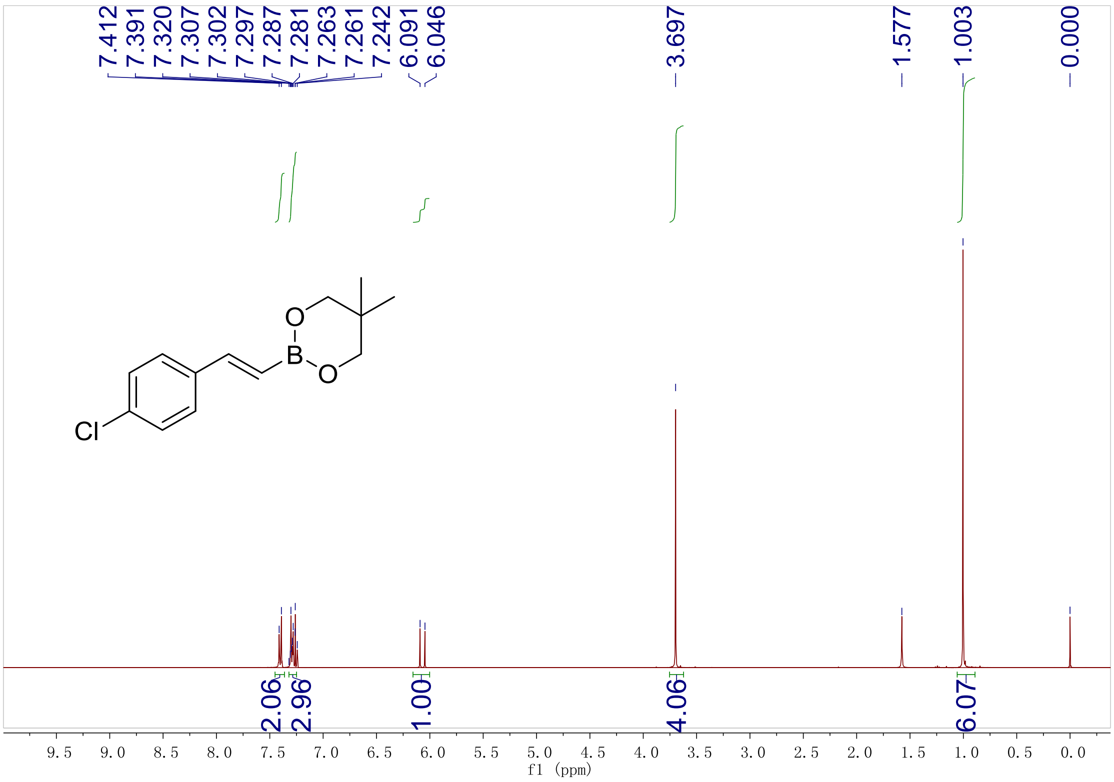

147.23
137.90
128.62
127.10
77.48
77.16
76.84
72.29
31.94
21.97
O
B
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

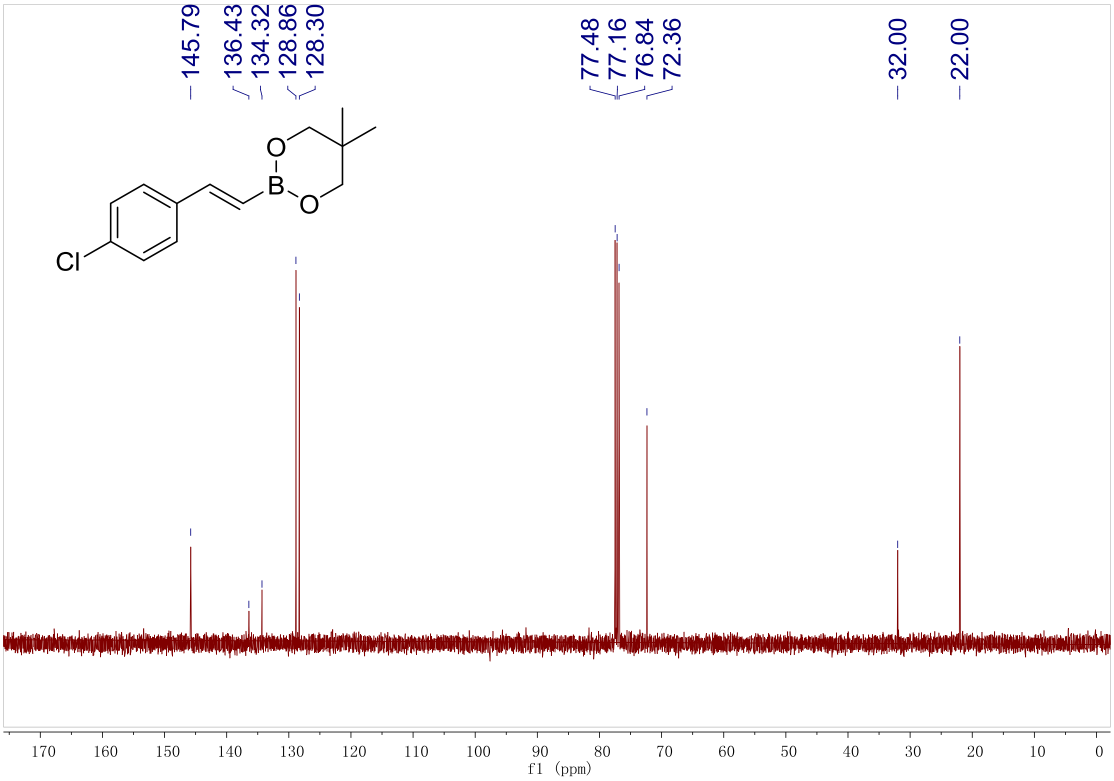

7.426
7.409
7.309
7.263
7.246
6.849
6.832
5.975
5.929
3.771
3.672
0.979
0.000
O
B
O
O
2.05
1.08
2.11
1.00
3.08
4.04
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

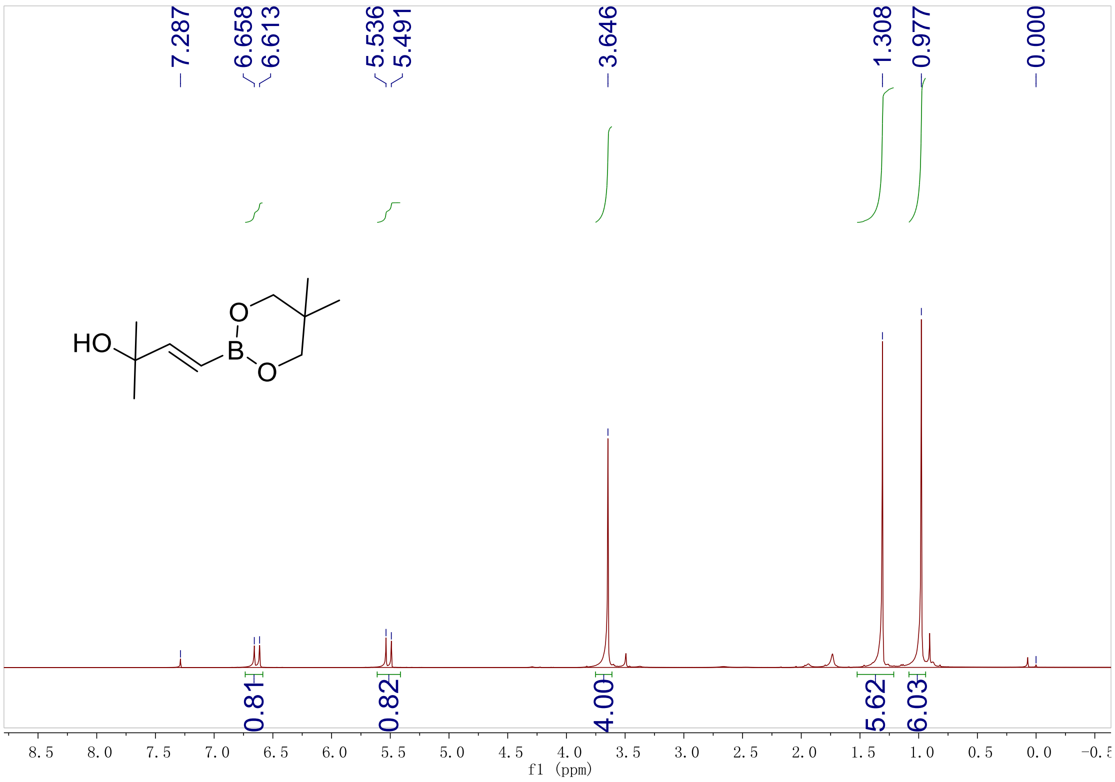

160.08
146.70
130.75
128.37
113.98
77.48
77.16
76.84
72.19
55.27
31.88
21.91
O
B
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

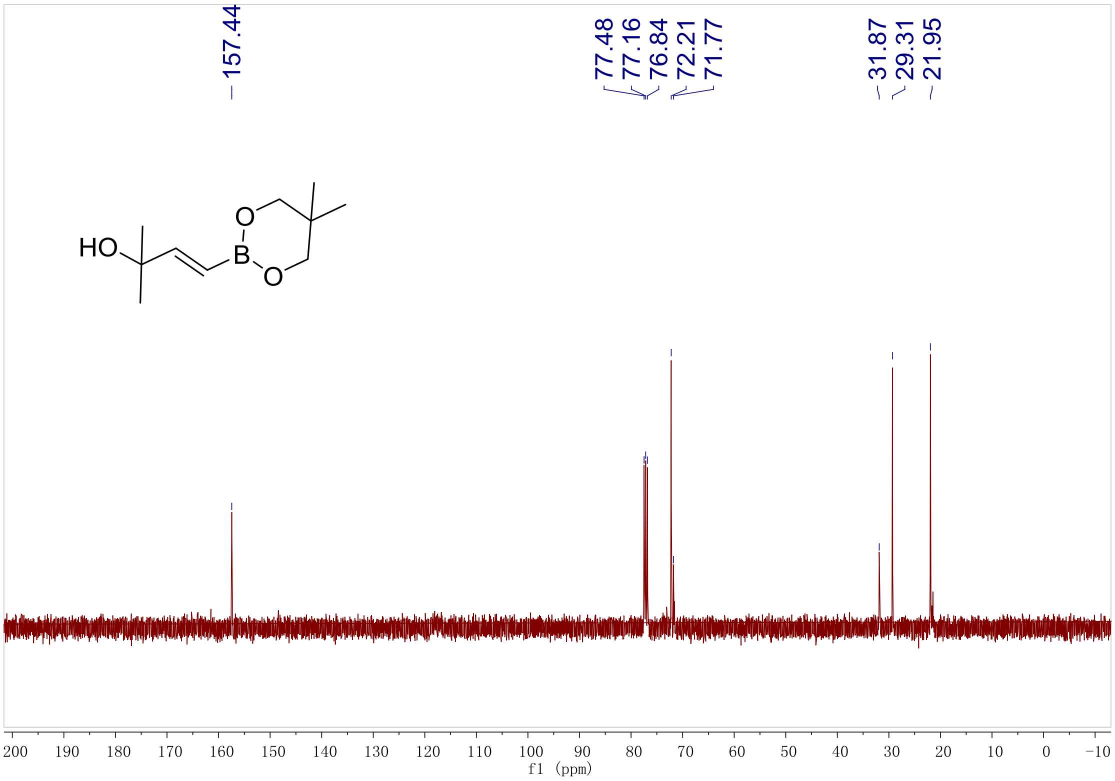

7.390
7.370
7.325
7.279
7.140
7.121
6.067
6.022
3.692
2.336
0.999
-0.000
O
B
O
2.01
1.08
2.03
1.00
4.07
3.06
6.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

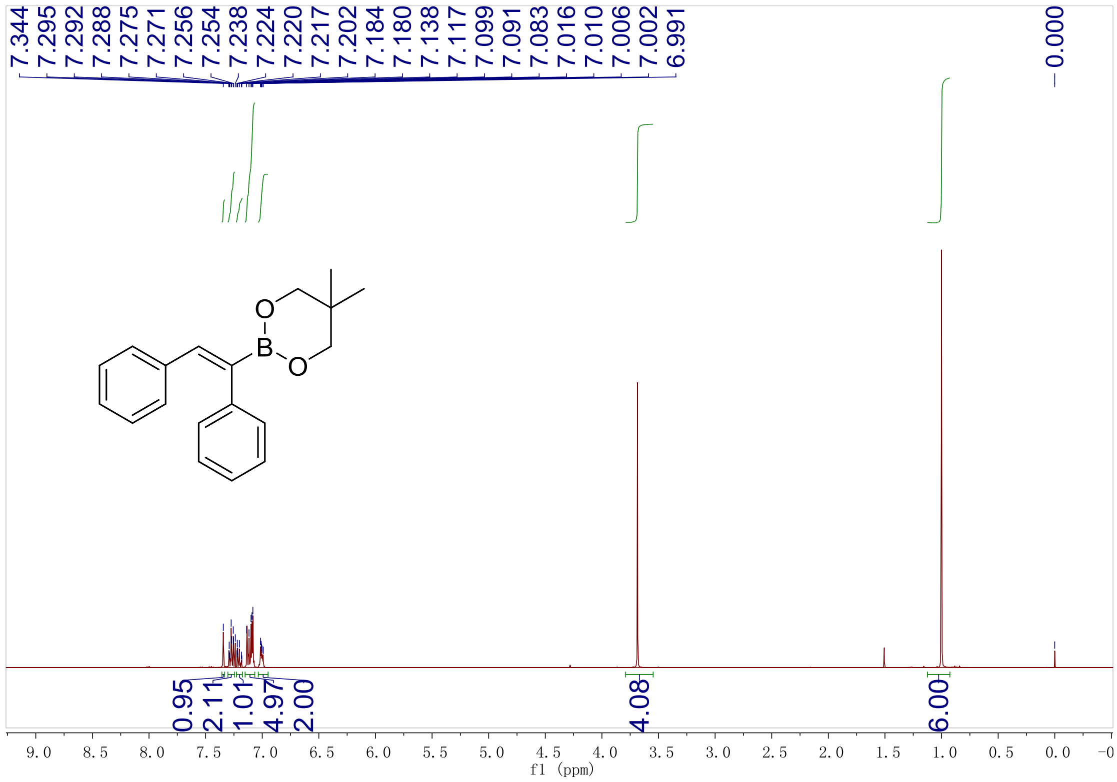

147.21
138.66
135.23
129.37
127.09
77.48
77.16
76.84
72.34
32.00
22.03
21.44
O
B
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

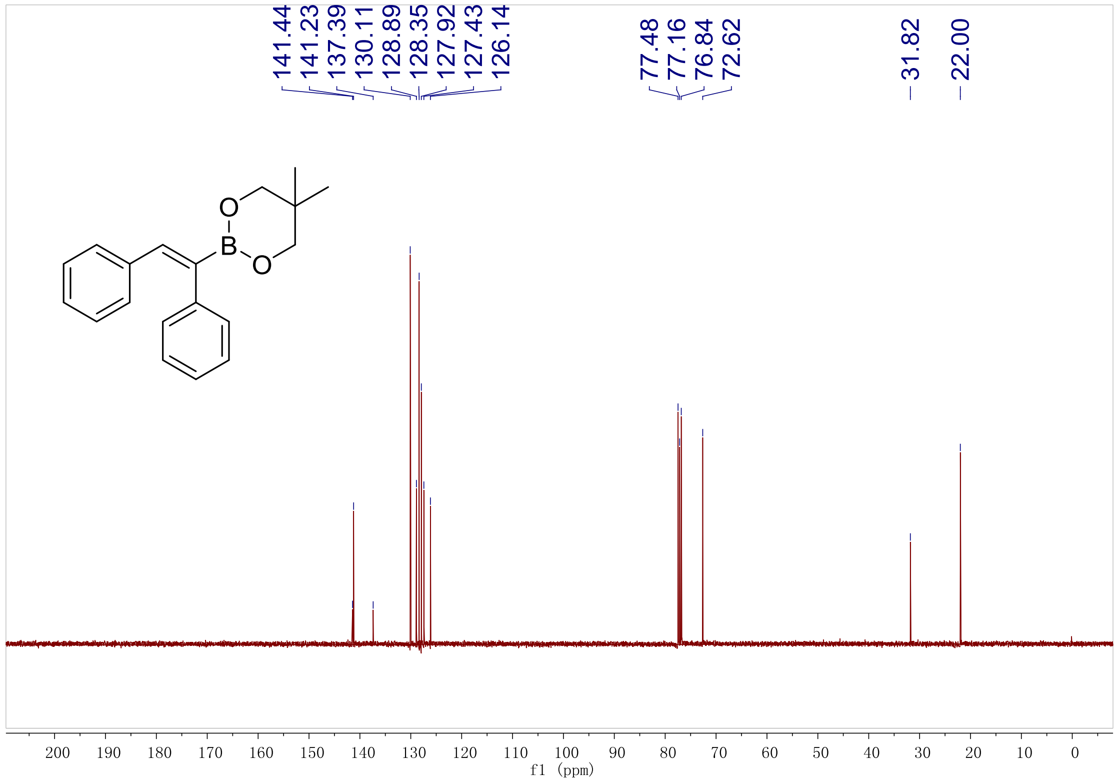

7.412
7.391
7.320
7.307
7.302
7.297
7.287
7.281
7.263
7.261
7.242
6.091
6.046
3.697
1.577
1.003
0.000
O
B
O
Cl
2.06
2.96
1.00
4.06
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

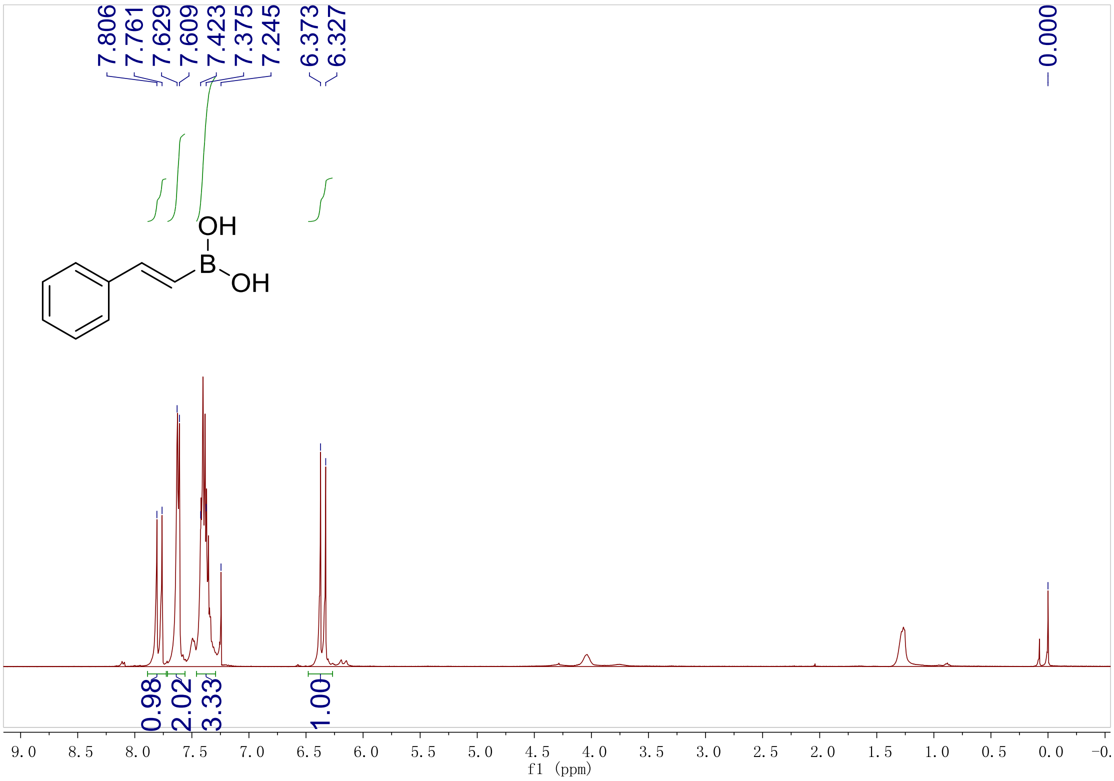

145.79
136.43
134.32
128.86
128.30
77.48
77.16
76.84
72.36
32.00
22.00
O
B
O
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

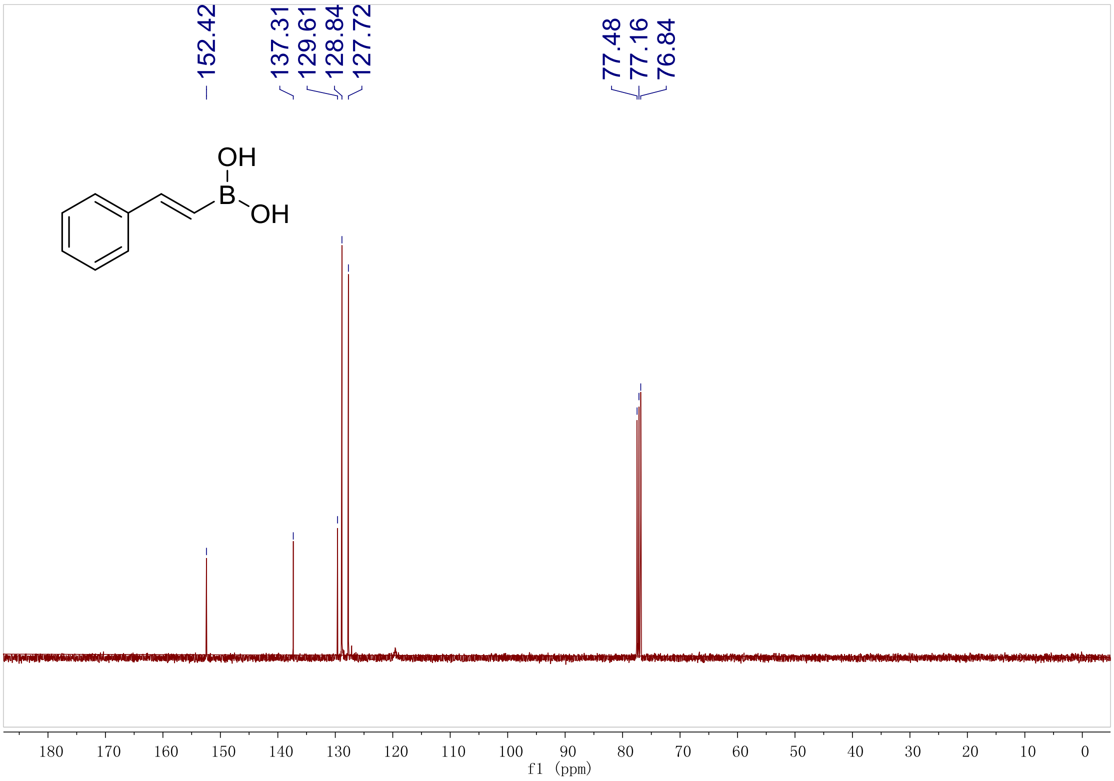

7.287
6.658
6.613
5.536
5.491
3.646
1.308
0.977
0.000
HO
O
B
O
0.81
0.82
4.00
5.62
6.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

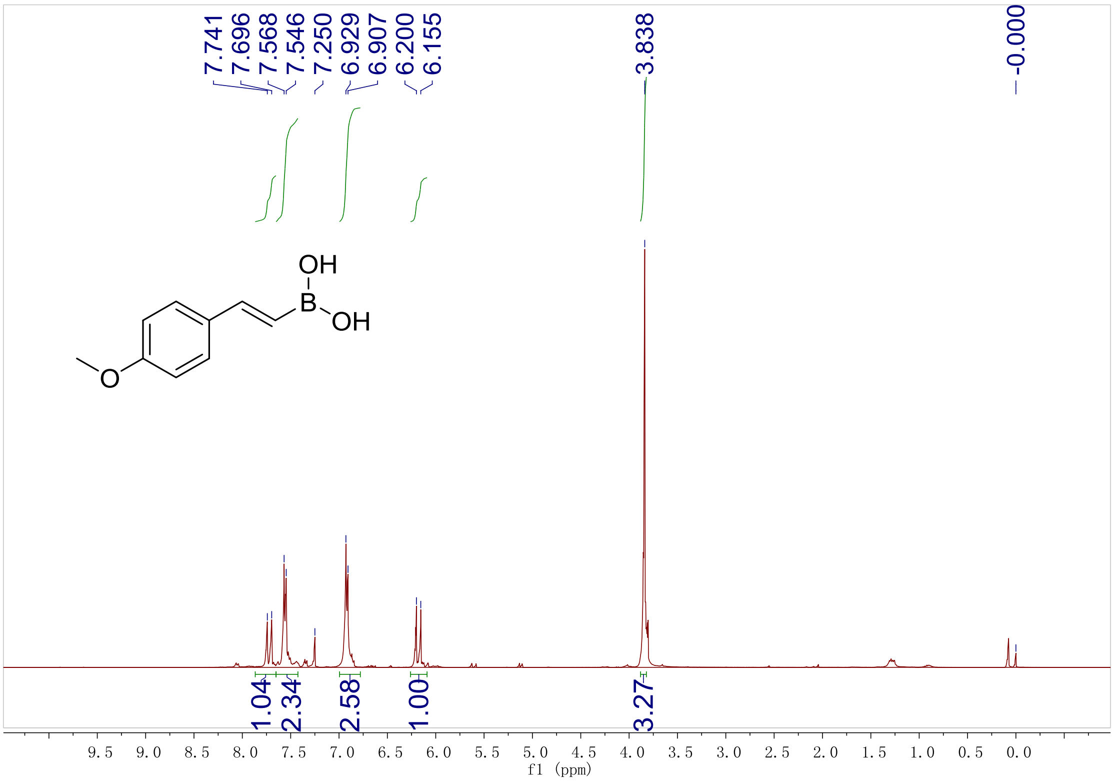

157.44
77.48
77.16
76.84
72.21
71.77
31.87
29.31
21.95
HO
O
B
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

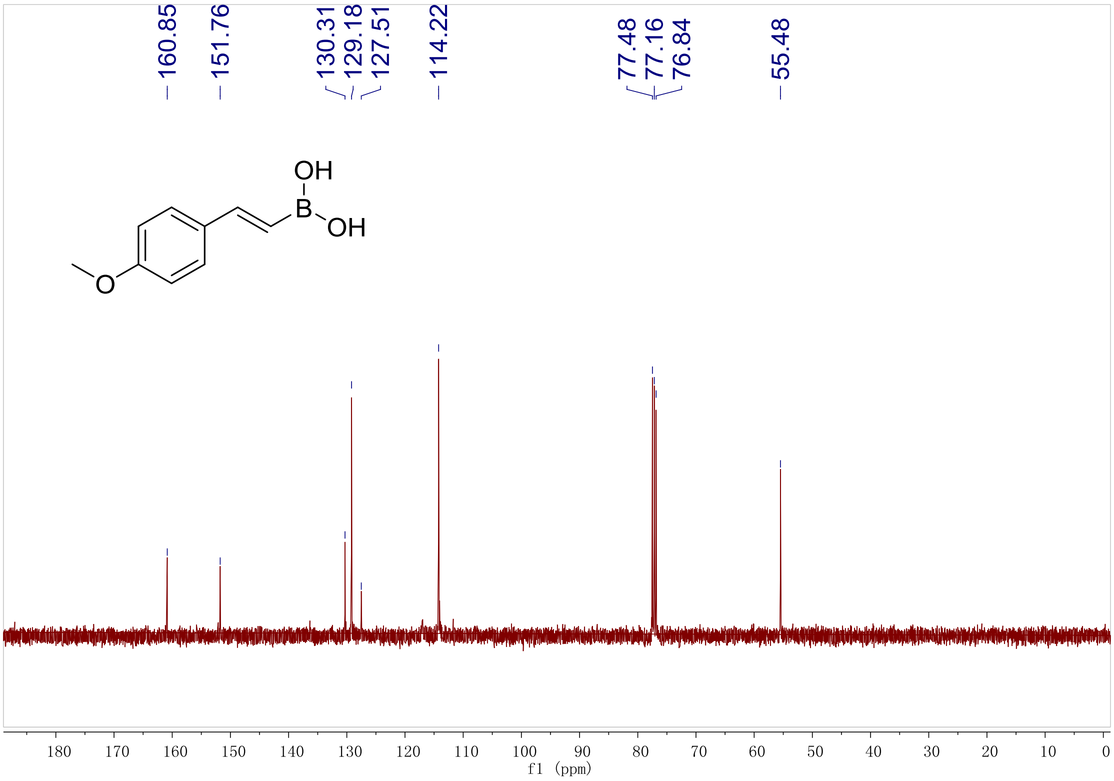

7.344
7.295
7.292
7.288
7.275
7.271
7.256
7.254
7.238
7.224
7.220
7.217
7.202
7.184
7.180
7.138
7.117
7.099
7.091
7.083
7.016
7.010
7.006
7.002
6.991
0.000
O
B
O
0.95
2.11
1.01
4.97
2.00
4.08
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


141.44
141.23
137.39
130.11
128.89
128.35
127.92
127.43
126.14
77.48
77.16
76.84
72.62
31.82
22.00
O
B
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.806
7.761
7.629
7.609
7.423
7.375
7.245
6.373
6.327
0.000
OH
B
OH
0.98
2.02
3.33
1.00
9.0
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.
f1 (ppm)


152.42
137.31
129.61
128.84
127.72
77.48
77.16
76.84
OH
B
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.741
7.696
7.568
7.546
7.250
6.929
6.907
6.200
6.155
3.838
-0.000
OH
B
OH
O
1.04
2.34
2.58
1.00
3.27
9.5
9.0
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
f1 (ppm)


160.85
151.76
130.31
129.18
127.51
114.22
77.48
77.16
76.84
55.48
OH
B
OH
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)