Supporting Information

Carboxylic Acid-Catalyzed Highly Efficient and Selective Hydroboration of Alkynes with Pinacolborane

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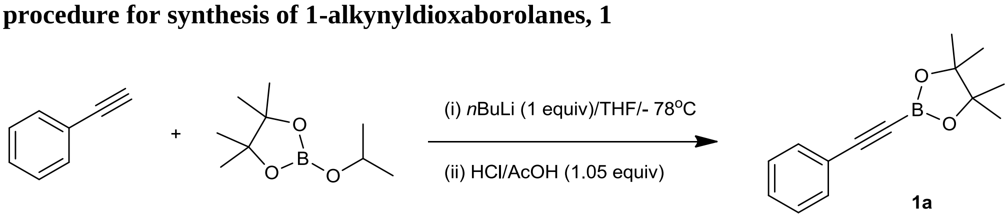
Content

General Information. GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m x 0.25 mm capillary column, HP-5MS). ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) spectrometer. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet, and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. ^{11}B NMR spectra were recorded on JEOL JNM AL 700 (225MHz) spectrometers. High-resolution mass spectra were obtained on a Bruker Daltonics Solarix 9.4T spectrometer and JEOL JMS-T100GCV. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~63 μm, Merck Chemicals). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). Kugelrohr distillation was performed under vacuum by using Sibata Glass Tube Oven (GTO-250RS).

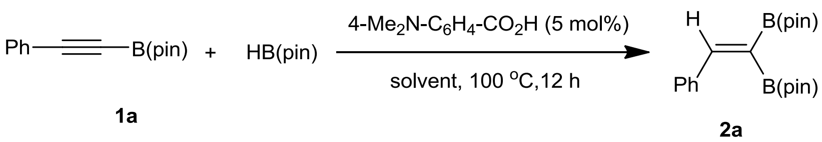
Materials. Pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (Aldrich), carboxylic acids (Tokyo Chemical Industry), alkynes were purchased and used as received. The structures of new compounds are determined by using ^{1}H, ^{13}C, ^{13}B NMR, and HRMS. The corresponding products, **2a**, **2e**, **3i**, and **3k** of the internal alkynes were determined unambiguously by the reported authentic compounds and the references are shown. Alkynes **1** were prepared following the reported literature from the terminal alkynes precursors.[1] Internal alkynes **3i** and **3l** were prepared by Sonogashira coupling reaction.

General procedure for synthesis of 1-alkynyldioxaborolanes, 1



Synthesis of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (1a). To a solution of phenylacetylene (0.62 mL, 6 mmol) in THF (0.4 M, 15 mL) in a 50 mL of Schlenk tube -78 °C under an Ar atmosphere was added *n*-BuLi (3.75 mL, 1.6 M hexane solution, 6 mmol). The reaction mixture was stirred for 1 h at -78 °C. A THF solution (0.4 M, 13 mL) of 4,4,5,5-tetramethyl-2-(1-methylethoxy)-1,3,2-dioxaborolane [(*i*-PrO)B(pin), 5 mmol] was added to the lithiated reaction mixture at -78 °C. After being stirred for 2 h at -78 °C, the reaction mixture was quenched with 1.0 M HCl/Et_2O solution (5.25 mL, 5.25 mmol), and the mixture was warmed to room temperature with additional 1 h stirring. Filtration and evaporation afforded pale yellow oil. Bulb to bulb distillation gave **1a** in 98% yield (1.12 g) as a white solid.

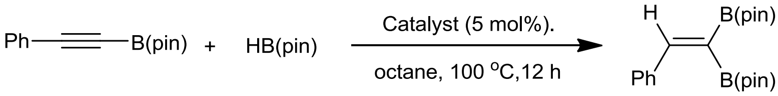
Representative procedure for carboxylic acid-catalyzed hydroboration of alkynes



To an octane solution (0.4 mL, 1 M) were added 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**1a**, 91.2 mg, 0.4 mmol), and 4-(dimethylamino)benzoic acid (3.3 mg, 5 mol%), and pinacol borane (0.29 mL, 2.0 mmol) under an Ar atmosphere. The reaction was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum. The low-boiling point impurities were removed by Kugelrohr distillation and the residue was further purified by passing through a short silica column chromatography using hexane/ethyl acetate (10/1) as eluents to afford **2a** in 94% (134 mg) as pale yellow oil.

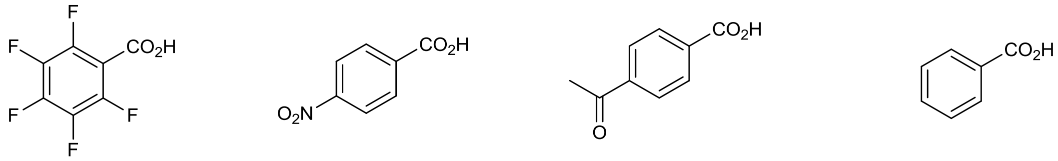
[1] Brown, H. C.; Bhat, N. G.; Srebnik, M.; *Tetrahedron Lett.* **1998**, *29,* 2631.

Table S1. Optimization of various organocatalysts[a]

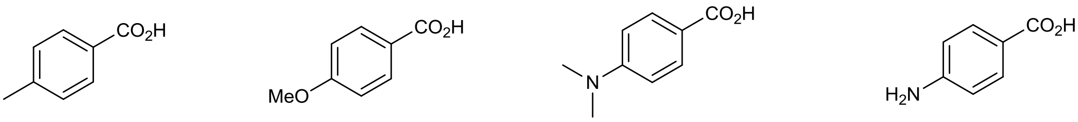


1a **2a**

entry	catalyst (5 mol%)	yield of **2a** (%)[b]
1	HCOOH	85
2	AcOH	94
3	CF_3COOH	83
4	Pivalic acid	79
5	Adamantane carboxylic acid	72
6	$(Ph)_3CCO_2H$	79
7	$PhCO_2H$	99 (94)
8	TfOH	0
9	H_3PO_4	50
10	PPh_3	0
11	NaO*t*Bu	0
12	-	0

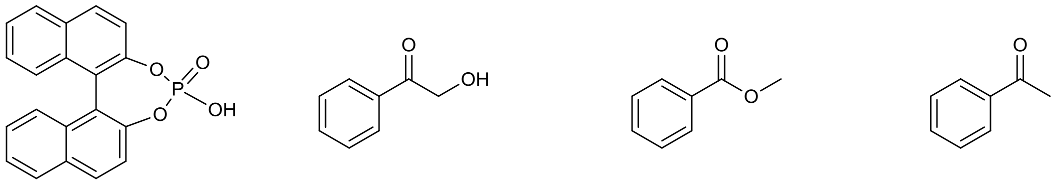


48% 72% 85% 99%

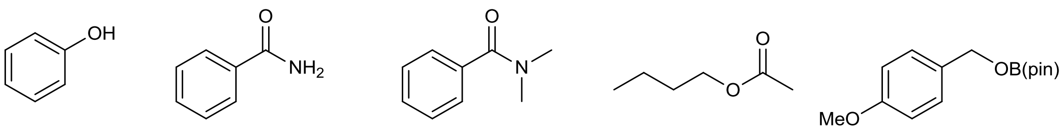


99% 99% 99 (94),[c] 72[d] 82%

33% 0% 0% 80%



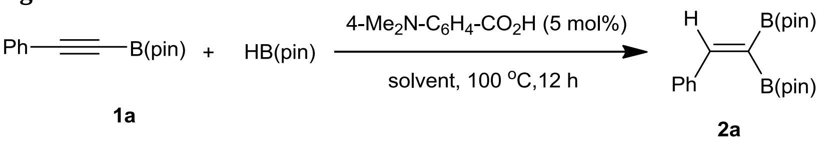
55% 14% 0% 0%



10% 14% 0% 0% 0%

[a] Reaction condition: **1a** (0.4 mmol), HB(pin) (2 mmol), octane (1 M), 100 °C, 12 h. [b] Yield determined by using CH_2Br_2 as internal standard. Isolated yield is shown in parenthesis. [c] 8 h. [d] 3 mol% of catalyst loading.

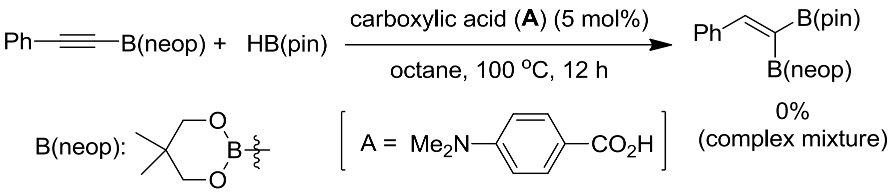
Table S2. Screening of solvents.[a]



entry	solvent	yield of **2a** (%)[b]
1	octane	99 (94)
2	decane	85
3	cyclooctane	80
4	toluene	37
5	1,4-dioxane	38
6	DCE	33
7	ethyl acetate	40
8	acetonitrile	20
9	THF	40

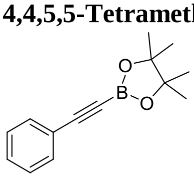
[a] Reaction condition: **1a** (0.4 mmol), HBPin (5 equiv), 4-(dimethylamino)benzoic acid (5 mol %), solvent (1 M), 100 °C, 12 h. [b] Yield determined by using CH_2Br_2 as internal standard. Isolated yield is shown in parenthesis.

Scheme S1. Reaction of 5,5-dimethyl-2-(phenylethynyl)-1,3,2-dioxaborinane with HB(pin) under the standard conditions.



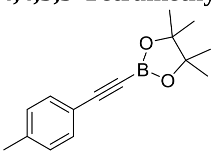
Analytical data of alkynes 1.

4,4,5,5-Tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (1a)[2]



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.38-7.28 (m, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4, 129.3, 128.1, 121.7, 84.4, 24.7. The carbon signals of triple bond were not observed due to low intensity.

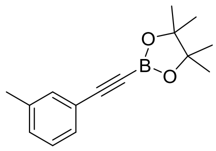
4,4,5,5-Tetramethyl-2-(*p*-tolylethynyl)-1,3,2-dioxaborolane (1b)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H), 1.32(s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 132.4, 128.9, 118.7, 84.3, 24.7, 21.6 (The carbon signals of triple bond were not observed due to low intensity); HRMS (ESI): calcd for $C_{15}H_{19}BO_2$ [M+Na]: 265.1370; found 265.1369.

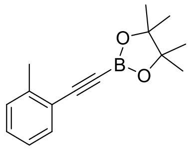
4,4,5,5-Tetramethyl-2-(*m*-tolylethynyl)-1,3,2-dioxaborolane (1c)

[2] Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 12980.



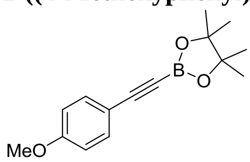
Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.20-7.15 (m, 2H), 2.30 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 132.9, 130.1, 129.5, 128.0, 121.5, 101.9, 84.3, 24.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{15}H_{19}BO_2$ [M+H]: 243.1550; found, 243.1550.

4,4,5,5-Tetramethyl-2-(*o*-tolylethynyl)-1,3,2-dioxaborolane (1d)



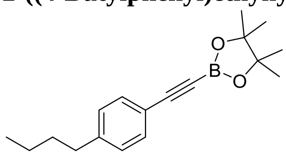
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 1H), 7.27-7.23 (m, 1H), 7.19-7.10 (m, 2H), 2.48 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 132.9, 129.3, 129.2, 125.3, 121.6, 100.5, 84.2, 24.7, 20.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{15}H_{19}BO_2$ [M+H]: 243.1550; found, 243.1550.

2-((4-Methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e)[3]



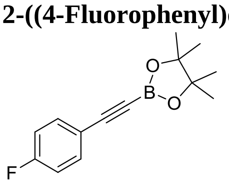
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 134.1, 113.8(8), 113.8(1), 102.1, 84.2, 55.2, 24.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{15}H_{19}BO_3$ [M+H]: 259.1500; found, 259.1499.

2-((4-Butylphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 2.59 (t, J =7.6 Hz, 2H), 1.61-1.53 (m, 2H), 1.38-1.27 (m, 14H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 132.4, 131.9, 128.3, 118.8,102.1, 84.3, 35.6, 33.2, 24.7, 24.6, 22.3, 13.9 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{18}H_{25}BO_2$ [M+H]: 285.2020, found: 285.2020.

2-((4-Fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 6.99-6.94 (m, 2H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J^1 = 249.1 Hz), 134.3 (d, J^3 = 9.1 Hz), 117.8 (d, J^4 = 3.3), 115.5 (d, J^2 = 22.3), 100.4, 84.3, 24.6 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{14}H_{16}BFO_2$ [M+H]: 247.1300, found: 247.1299.

4,4,5,5-Tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-1,3,2-dioxaborolane (1h)[4]

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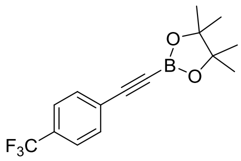
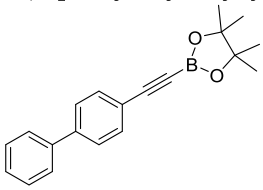
[3] Coapes, R. B.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Marder, T. B. *Chem. Commun.* **2003**, 614.

[4] Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 12634.



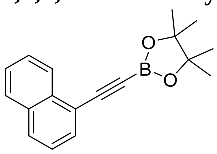
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 130.9 (q, J^2 = 32.2 Hz), 125.7, 125.1 (q, J^3 = 4.1 Hz), 123.7 (q, J^1 = 270.6 Hz), 99.7, 84.6, 24.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{15}H_{16}BFO_3$ [M+H]: 297.1268, found: 297.1267.

2-(Biphenyl-4-ylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1i)



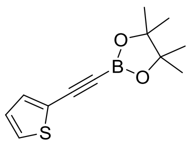
Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.53 (m, 6H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0. 140.0, 132.9, 132.4, 128.7, 127.7, 126.9(8), 126.9(0), 120.5, 101.68, 84.4, 24.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{20}H_{21}BO_2$ [M+H]: 305.1707, found: 305.1707.

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylethynyl)-1,3,2-dioxaborolane (1j)



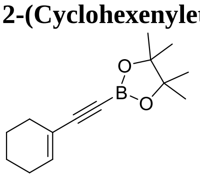
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.0 Hz, 1H), 7.85 (t, J = 9.2 Hz, 2H), 7.79 (dd, J = 7.2, 1.2 Hz, 1H), 7.59-7.49 (m, 2H), 7.41 (dd, J = 8.0, 7.2 Hz, 1H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 132.8, 132.0, 129.8, 128.1. 126.9, 126.4, 126.2, 124.9, 119.4, 99.6, 84.4, 24.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{18}H_{19}BO_2$ [M+H]: 279.1550, found: 279.1550.

4,4,5,5-Tetramethyl-2-(thiophen-2-ylethynyl)-1,3,2-dioxaborolane (1k)



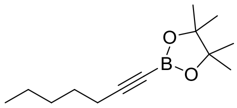
Brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 3.6 Hz, 1H), 7.30 (d, J = 5.2 Hz, 1H), 6.97 (dd, J = 5.2, 3.6 Hz, 1H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 128.8, 126.9, 121.7, 84.5, 24.7 (The carbon signals of triple bond were not observed due to low intensity); HRMS (APCI): calcd for $C_{12}H_{15}BO_2S$ [M+H]: 235.0958, found: 235.0957.

2-(Cyclohexenylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1l)



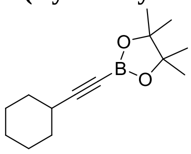
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29-6.27 (m, 1H), 2.13-2.05 (m, 4H), 1.61-1.53 (m, 4H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 119.9, 104.0, 84.0, 28.5, 25.7, 24.6, 22.0, 21.3 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{14}H_{21}BO_2$ [M+H]: 233.1707, found: 233.1706.

2-(Hept-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1m)



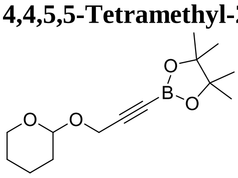
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (t, J = 7.2 Hz, 2H), 1.58-1.49 (m, 2H), 1.38-1.28 (m, 4H), 1.26 (s, 12H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.2, 83.9, 31.0, 27.8, 24.7, 22.2, 19.5, 13.9 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{13}H_{23}BO_2$ [M+H]: 223.1863, found: 223.1863.

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



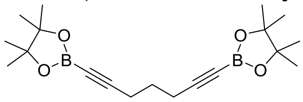
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44-2.39 (m, 1H), 1.83-1.79 (m, 2H), 1.74-1.67 (m, 2H), 1.56-1.39 (m, 3H), 1.28-1.26 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.9, 32.0, 29.7, 25.7, 24.8, 24.7 (The carbon signals of triple bond were not observed due to low intensity); HRMS (APCI): calcd for $C_{14}H_{21}BO_2$ [M+H]: 235.1863, found: 235.1863.

4,4,5,5-Tetramethyl-2-(3-(tetrahydro-2*H*-pyran-2-yloxy)prop-1-ynyl)-1,3,2-dioxaborolane (1o)



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (t, J = 3.2 Hz, 1H), 4.28 (d, J = 3.2 Hz, 2H), 3.83-3.77 (m 1H), 3.54-3.48 (m, 1H), 1.84-1.70 (m, 2H), 1.69-1.48 (m, 2H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.9, 96.5, 84.3, 61.8, 54.1, 30.1, 25.3, 24.6, 18.9 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{14}H_{23}BO_4$ [M+Na]: 289.1581, found: 289.1581.

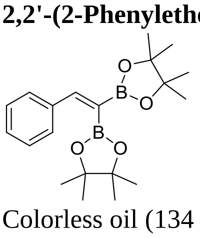
1,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-diyne (1p)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (t, J = 6.8 Hz, 4H), 1.76 (m, 2H), 1.26 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.4, 84.0, 26.6, 24.7, 18.7 (The carbon signal attached to B was not observed due to low intensity); HRMS (APCI): calcd for $C_{22}H_{28}B_2O_4$ [M+H]: 345.2403, found: 345.2402.

Analytical data of products 2 and 3

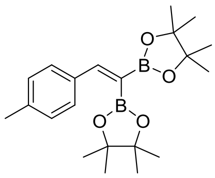
2,2'-(2-Phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a)[5]



Colorless oil (134 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.48-7.46 (m, 2H), 7.30-7.23 (m, 3H), 1.30 (s, 12H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 139.4, 128.3, 128.0, 127.9, 83.5, 83.1, 24.9, 24.6 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.17, 30.62; HRMS (ESI): calcd for $C_{20}H_{30}B_2O_4$ [M+Na]: 379.2222, found: 379.2221.

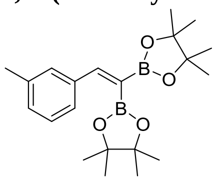
2,2'-(2-*p*-Tolylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b)

[5] Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 12980.



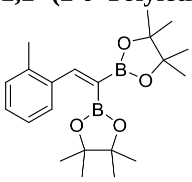
Colorless oil (130.3 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.32 (s, 12H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 138.3, 136.7, 128.7, 128.1, 83.5, 83.0, 24.9, 24.7, 21.3 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.35, 30.79; HRMS (ESI) calcd for $C_{21}H_{32}B_2O_4$ [M+Na]: 393.2378, found: 393.2378.

2,2'-(2-*m*-Tolylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c)



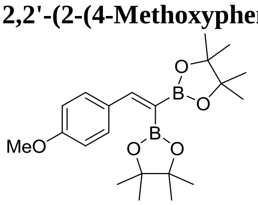
Colorless oil (124.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.33 (s, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 2.32 (s, 3H), 1.32 (s, 12H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 139.4, 137.4, 129.1, 128.3, 127.9, 125.4, 83.4, 83.0, 24.8, 24.6, 21.3 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.67, 30.64; HRMS (ESI): calcd for $C_{21}H_{32}B_2O_4$ [M+Na]: 393.2378, found: 393.2378.

2,2'-(2-*o*-Tolylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2d)



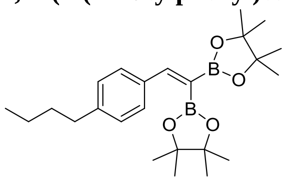
Colorless oil (125.9 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.18-7.08 (m 3H), 2.35 (s, 3H), 1.28 (s, 12H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 139.0, 136.1, 129.6, 128.1, 127.5, 125.3, 83.3, 83.0, 24.8, 24.5, 19.7 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR 32.09, 30.53; ($CDCl_3$, 225 MHz, rt) δ HRMS (ESI): calcd for $C_{21}H_{32}B_2O_4$ [M+Na]:393. 2378, found: 393.2378.

2,2'-(2-(4-Methoxyphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2e)[6]



Pale yellow oil (128.2 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 1.32 (s, 12H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 154.6, 132.3, 129.6, 113.4, 83.4, 82.9, 55.2, 24.8, 24.7 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.48, 30.89; HRMS (ESI): calcd for $C_{21}H_{32}B_2O_5$ [M+Na]: 409.2328, found: 409.2327.

2,2'-(2-(4-Butylphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2f)

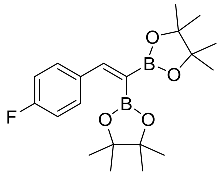


Pale yellow oil (135.2 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz. 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.62-1.54 (m, 2H), 1.33-1.31 (s, 14H), 1.27 (s, 12H), 0.91 (t, *J* = 7.6

[6] Coapes, R. B.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Marder, T. B. *Chem. Commun.* **2003**, 614.

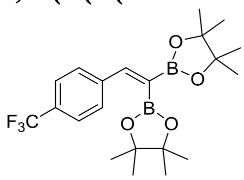
Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.3, 136.8, 128.0, 127.8, 83.4, 83.0, 35.4, 33.4, 24.8, 24.6, 22.3, 13.9 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.59, 31.11; HRMS (ESI): calcd for $C_{24}H_{38}B_2O_4$ [M+Na]: 435.2848, found: 435.2847.

2,2'-(2-(4-Fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2g)



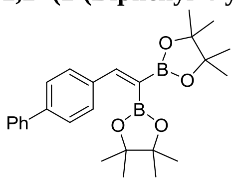
Pale yellow oil (136.2 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.49-7.44 (m, 2H), 6.99-6.95 (m, 2H), 1.30 (s, 12H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J^1 = 246.7 Hz), 153.6, 135.7 (d, J^4 = 3.3 Hz), 129.7 (d, J^3 = 8.3 Hz), 114.9 (d, J^2 = 21.5 Hz), 83.6, 83.2, 24.8, 24.6 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 30.84; HRMS (ESI): calcd for $C_{20}H_{29}B_2FO_4$ [M+Na]: 397.2128, found: 397.2128.

2,2'-(2-(4-(Trifluoromethyl)phenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2h)



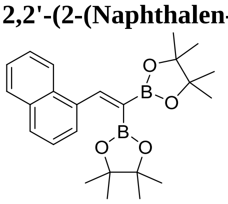
Pale yellow oil (140.8 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.59-7.53 (m, 4H), 1.31 (s, 12H), 1.28 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 142.8, 129.9 (q, J^2 = 32.2 Hz), 128.5, 125.0 (q, J^3 = 4.0 Hz), 124.0 (q, J^1 = 276 Hz), 83.8, 83.4, 24.9, 24.6 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 31.54; HRMS (ESI): calcd for $C_{20}H_{29}B_2FO_4$ [M+Na]:447.2096, found: 447.2096.

2,2'-(2-(Biphenyl-4-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2i)



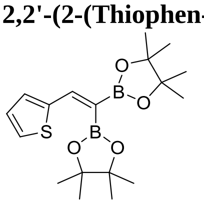
Yellow oil (155.6 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.62-7.54 (m, 6H), 7.43 (t, J = 7.2 Hz, 2H), 7.36-7.32 (m, 1H), 1.35 (s, 12H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 141.0, 138.4, 132.4, 128.6, 128.5, 127.2, 126.9, 126.7, 83.6, 83.1, 24.9, 24.7. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 30.71; HRMS (ESI): calcd for $C_{26}H_{34}B_2O_4$ [M+Na]: 307.1863, found: 307.1863.

2,2'-(2-(Naphthalen-1-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2j)



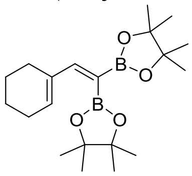
White solid. (123.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.12 (d, J = 7.2 Hz, 1H), 7.83-7.76 (m, 2H), 7.62 (d, J = 7.2 Hz, 1H), 7.50-7.40 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H), 1.32 (s, 12H), 1.17 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 137.7, 133.2, 131.2, 128.5, 128.0, 125.8, 125.7, 125.4, 125.0, 124.8, 83.4, 83.2, 25.0, 24.5 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.09; HRMS (ESI): calcd for $C_{24}H_{32}B_2O_4$ [M+Na]: 429.2378, found: 429.2378.

2,2'-(2-(Thiophen-2-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k)



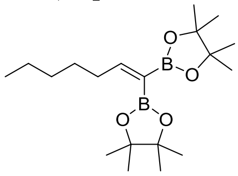
Pale yellow oil (76.8 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.27-7.26 (m, 1H), 7.19-7.18 (m, 1H), 6.96 (dd, *J* = 5.2, 3.6 Hz, 1H), 1.37 (s, 12H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.2, 129.2, 127.1, 127.0, 83.6, 83.1, 24.8, 24.5. The carbon signal attached to B was not observed due to low intensity; ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 31.22; HRMS (ESI): calcd for $C_{18}H_{28}B_2O_4S$ [M+Na]: 385.1786, found: 385.1786.

2,2'-(2-Cyclohexenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2l)



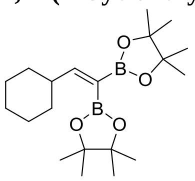
Colorless oil (89.3 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.00-5.98 (m, 1H), 2.20-2.12 (m, 4H), 1.66-1.53 (m, 4H), 1.30 (s, 12H), 1.22 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 138.6, 134.9, 83.3, 82.7, 26.2, 25.8, 24.8, 24.7, 22.3, 22.0 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 32.49; HRMS (ESI): calcd for $C_{20}H_{34}B_2O_4$ [M+Na]: 383.2535, found: 383.2535.

2,2'-(Hept-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2m)



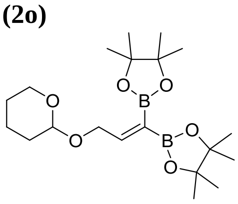
Yellow oil. (99.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (t, *J* = 7.2 Hz, 1H), 2.24 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.44-1.36 (m, 2H), 1.28-1.22 (m, 28H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 83.0, 82.7, 35.4, 31.5, 28.7, 24.8, 24.7, 22.5, 14.0 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR 34.08, 31.47; ($CDCl_3$, 225 MHz, rt) δ HRMS (ESI): calcd for $C_{19}H_{36}B_2O_4$ [M+Na]: 373.2691, found: 373.2691.

2,2'-(2-Cyclohexylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2n)



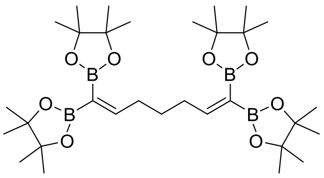
Colorless oil (128.9 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 8.8 Hz, 1H), 2.30-2.21 (m, 1H), 1.73-1.70 (m, 4H), 1.29 (s, 12H), 1.22-1.08 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 83.0, 82.7, 44.1, 32.6, 25.9, 25.8, 24.8, 24.6 (The carbon signal attached to B was not observed due to low intensity); ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 31.56; HRMS (ESI): calcd for $C_{20}H_{36}B_2O_4$ [M+Na]: 385.2691, found: 385.2691.

2,2'-(3-(Tetrahydro-2*H*-pyran-2-yloxy)prop-1-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2o)



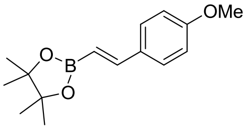
Colorless oil (118.3 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 6.0, 5.2 Hz, 1H), 4.63 (t, *J* = 3.6 Hz, 1H), 4.38 (dd, *J* = 14.0, 5.2 Hz, 1H), 4.21, (dd, *J* = 14.0, 6.0 Hz, 1H), 3.87-3.82 (m 1H), 3.51-3.45 (m, 1H), 1.88-1.77 (m, 1H), 1.74-1.65 (m, 1H), 1.63-1.48 (m, 4H), 1.28 (s, 12H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 97.7, 83.2, 83.0, 68.2, 61.9, 30.5, 25.5, 24.8, 24.7, 19.3; ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 30.87; HRMS (ESI): calcd for $C_{20}H_{36}B_2O_6$ [M+Na]: 417.2590, found: 417.2589.

1,1,7,7-Tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,6-diene (2p)



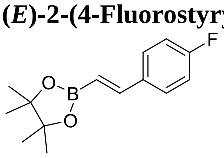
Colorless oil (156.1 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (t, *J* = 7.2 Hz, 2H), 2.28-2.23 (m, 4H), 1.56-1.49 (m, 2H), 1.25 (s, 24H), 1.20 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 82.9, 82.6, 35.0, 31.5, 28.5, 24.8, 24.7; ^{11}B NMR ($CDCl_3$, 225 MHz, rt) δ 31.16; HRMS (ESI): calcd for $C_{31}H_{56}B_4O_8$ [M+Na]:623.4239, found: 623.4239.

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)[7]



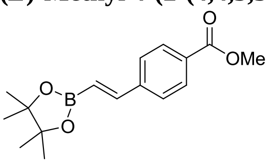
White solid (93.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.01 (d, *J* = 18.4 Hz, 1H), 3.79 (s, 3H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 148.9, 130.2, 128.3, 113.8, 83.1, 55.2, 24.8. The carbon signal attached to B was not observed due to low intensity.

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[8]



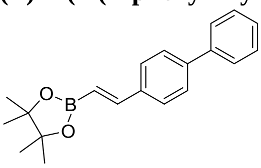
Colorless oil (69.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.04-6.98 (m, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.0 Hz), 148.2, 133.5 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 8.2 Hz), 115.4 (d, *J* = 21.4 Hz), 83.1, 24.8. The carbon signal attached to B was not observed due to low intensity.

(*E*)-Methyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (3c)[9]



White solid (86.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.27 (s, *J* = 18.4, 1H), 3.90 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 147.9, 141.5, 130.0, 129.8, 126.8, 83.5, 52.1, 24.8. The carbon signal attached to B was not observed due to low intensity; HRMS (APCI): calcd for $C_{16}H_{21}BO_4$ [M+H]: 289.1605, found: 289.1605.

(*E*)-2-(2-(Biphenyl-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)



Yellow solid (96.8 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 6H), 7.46-7.41 (m, 3H), 7.36-7.34 (m, 1H), 6.21 (d, *J* = 18.4 Hz, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 141.5, 140.4, 136.4, 128.7, 127.4, 127.3, 127.1, 126.9, 83.6, 24.8. The carbon signal attached to B was not observed due to low intensity; HRMS (APCI): calcd for $C_{20}H_{23}BO_2$ [M+H]: 307.1863, found: 307.1863.

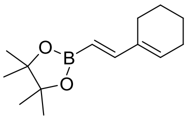
(*E*)-2-(2-Cyclohexenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)[10]

[7] Stewart, S. K.; Whiting, A. *J. Organomet. Chem.* **1994**, *482*, 293.

[8] Wen, K.; Chen, J.; Gao, F.; Bhadury, P. S.; Fan, E.; Sun, Z. *Org. Biomol. Chem.* **2013**, *11*, 6350.

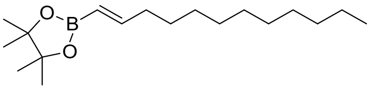
[9] Haberberger, M. and Enthaler, S. *Chem. Asian J.* **2013**, *8*, 50

[10] Shade, R. E.; Hyde, A. M.; Olsen, J.-C.; Merlic, C. *J. Am. Chem. Soc.* **2010**, *132*, 1202.



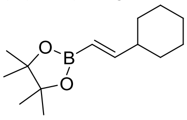
Colorless oil (46.8 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 18.4 Hz, 1H), 5.97-5.95 (m, 1H), 5.42 (d, J = 18.4 Hz, 1H), 2.14 (br, 4H), 1.69-1.55 (m, 4H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 137.0, 134.1, 82.9, 26.2, 24.8, 23.7, 22.4, 22.3. The carbon signal attached to B was not observed due to low intensity.

(*E*)-2-(Dodec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)[11]



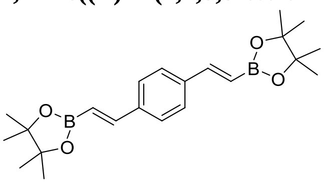
Colorless oil (100 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (dt, J = 18.0, 6.4 Hz, 1H), 5.41 (d, J = 18.0, 1.6 Hz, 1H), 2.16-2.11 (m, 2H), 1.42-1.26 (m, 28H), 0.87 (t, J = 6.8 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 82.9, 35.8, 31.9, 29.6(6), 29.6(2), 29.5, 29.3, 29.2(7), 29.2(6), 24.8, 22.7, 14.1. The carbon signal attached to B was not observed due to low intensity.

(*E*)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)[12]



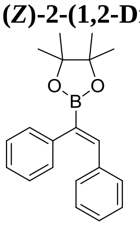
Colorless oil (51.0 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, J = 18.4, 6.0 Hz, 1H), 5.37 (d, J = 18.4 Hz, 1H), 2.06-1.99 (m, 1H), 1.75-1.62 (m, 6H), 1.27 (s, 12H), 1.19-1.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 82.9, 43.2, 31.9, 26.1, 25.9, 24.8. The carbon signal attached to B was not observed due to low intensity. HRMS (ESI): calcd for [M+H]: 237.1913, found: 237.1913.

1,4-Bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (3h)[13]



White solid (122.3 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H), 7.36 (d, J = 18.4 Hz, 2H), 6.16 (d, J = 18.4 Hz, 2H), 1.31 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.8, 127.2, 119.6, 83.8, 24.8. The carbon signal attached to B was not observed due to low intensity.

(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)[14]



Pale yellow solid (118.8 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.28-7.03 (m, 10H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.2, 136.8, 129.8, 128.7, 128.1, 127.7, 127.4, 126.1, 83.7, 24.8. The carbon signal attached to B was not observed due to low intensity.

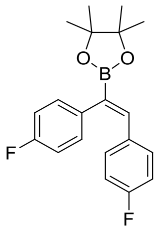
(*Z*)-2-(1,2-Bis(4-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

[11] Quigley, B. L.; Grubbs, R. H. *Chem. Sci*. **2014**, *5*, 501.

[12] Haberberger, M. and Enthaler, S. *Chem. Asian J*. **2013**, *8*, 50

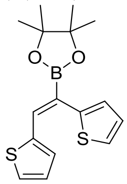
[13] Lee, T.; Baik, C.; Jung, I.; Song, K. H.; Kim, S.; Kim, D.; Kang, S. O.; Ko, J. *Organometallics*. **2004**, *23*, 4569.

[14] Grirrane, A.; Corma, A.; Garcia, H. *Chem. Eur. J*. **2011**, *17*, 2467.



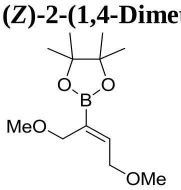
White solid (110.9 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.13-6.95 (m, 6H), 6.83 (t, *J* = 8.4 Hz, 2H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 246.7 Hz), 161.5 (d, *J* = 243.4 Hz), 142.1, 135.7 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 3.3 Hz), 131.4 (d, *J* = 8.3 Hz), 130.2 (d, *J* = 8.2 Hz), 115.2 (d, *J* = 20.7 Hz), 114.8 (d, *J* = 20.7 Hz), 83.8, 24.8; HRMS (APCI): calcd for $C_{20}H_{21}BF_2O_2$ [M+H]: 343.1675, found: 343.1675.

(*Z*)-2-(1,2-Di(thiophen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)[15]



Yellow oil (99.2 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.38 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.21-7.19 (m, 1H), 7.12-7.11 (m, 1H), 7.08 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.93-6.90 (m, 2H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.8, 139.1, 131.4, 128.7, 127.3, 126.0, 125.7, 83.8, 24.7; HRMS (APCI): calcd for $C_{14}H_{16}BO_2S_2$ [M+H]: 319.0992, found: 319.0991.

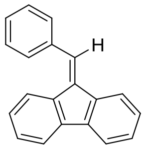
(*Z*)-2-(1,4-Dimethoxybut-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



Colorless oil (58.1 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (t, *J* = 5.6 Hz, 1H), 4.14 (d, *J* = 5.6 Hz, 2H), 4.02 (s, 2H), 3.34 (s, 3H), 3.28 (s, 3H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 83.4, 69.6, 68.9, 58.3, 57.8, 24.7. The carbon signal attached to B was not observed due to low intensity; HRMS (ESI): calcd for $C_{12}H_{23}BO_4$ [M+Na]: 265.1581, found: 265.1580.

Analytical data of compounds 4 and 5

9-Benzylidene-9*H*-fluorene (4)[16]

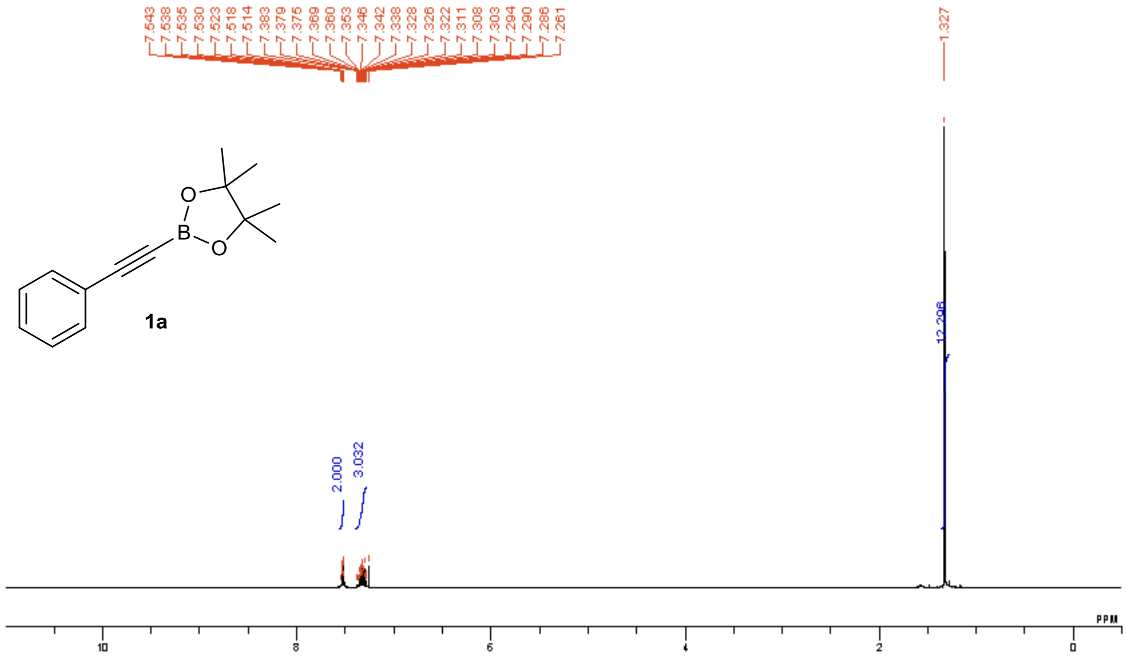


White solid (74 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.73-7.70 (m, 3H), 7.60-7.54 (m, 3H), 7.48-7.44 (m, 2H), 7.48-7.45 (m, 2H), 7.41-7.29 (m, 4H), 7.07-7.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.3, 139.0, 136.8, 136.4, 136.3, 129.1, 128.4, 128.1, 127.9, 127.1, 126.9, 126.5, 124.3, 120.1, 119.6, 119.5.

[15] Sundararaju, B. and Fürstner, A. *Angew. Chem. Int. Ed.* **2013**. *52,* 14050

[16] Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc*. **2008**, *130*, 5636.

NMR Spectra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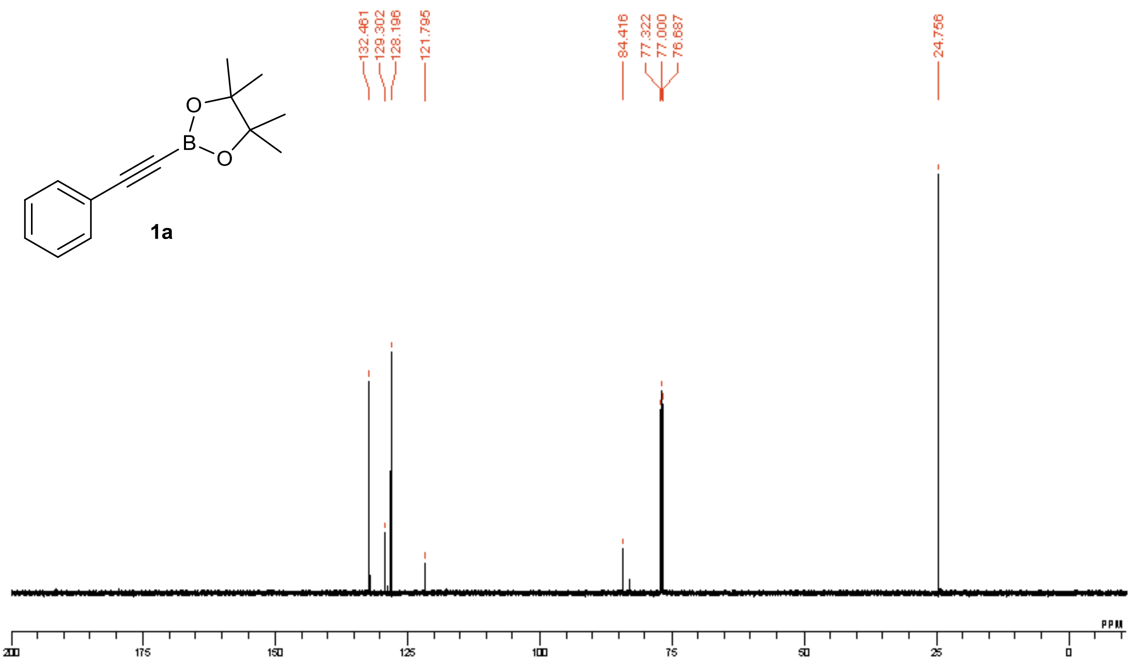
7.514
7.383
7.379
7.375
7.369
7.360
7.353
7.346
7.342
7.338
7.328
7.326
7.322
7.311
7.308
7.303
7.294
7.290
7.286
7.261
1.327
1a
2.000
3.032
12.298
PPM
10
8
6
4
2
0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128.196
121.795
84.416
77.322
77.000
76.687
24.756
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PPM
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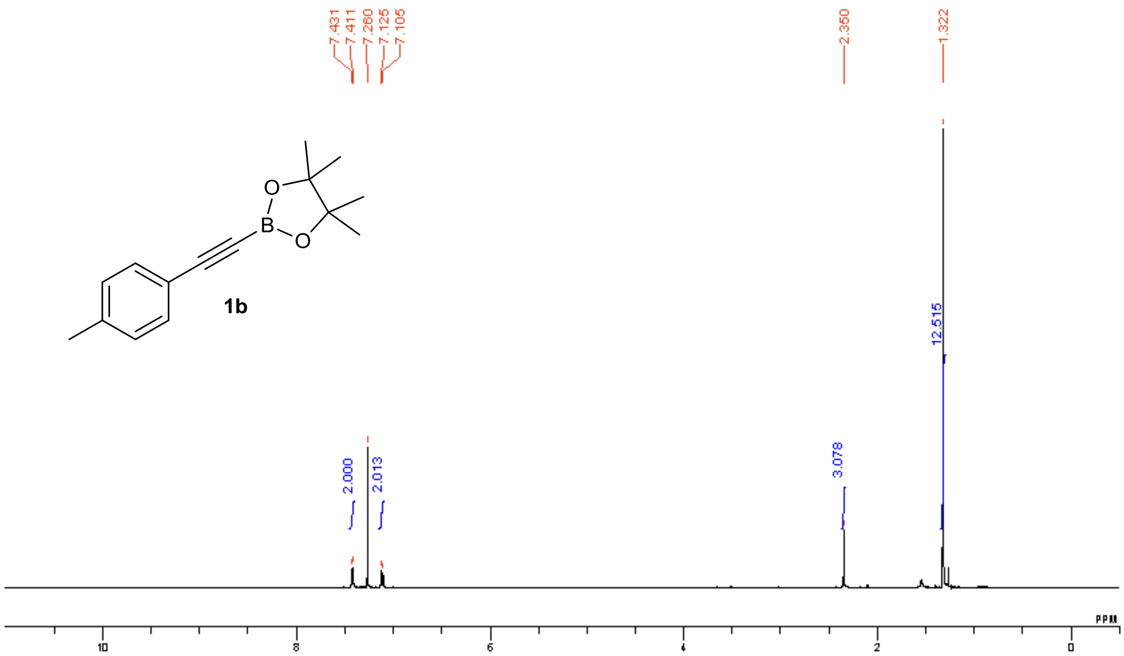
175
150
125
100
75
50
25
0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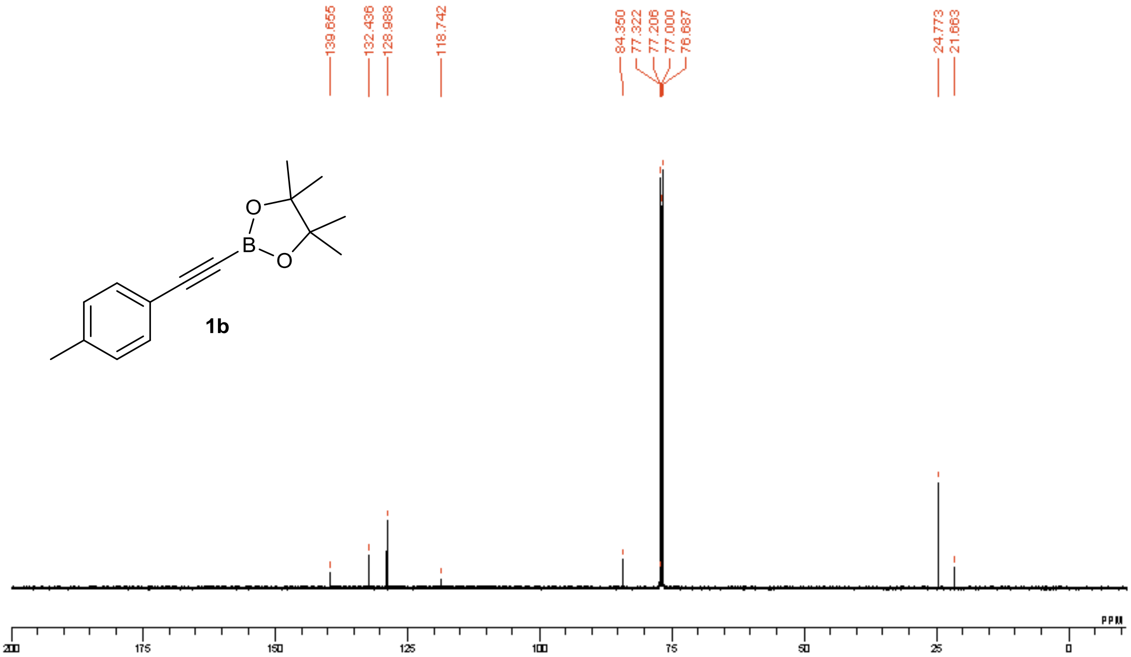
7.411
7.260
7.125
7.105
2.350
1.322
1b
2.000
2.013
3.078
12.515
PPM
10
8
6
4
2
0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128.988
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77.322
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77.000
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24.773
21.663
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175
150
125
100
75
50
25
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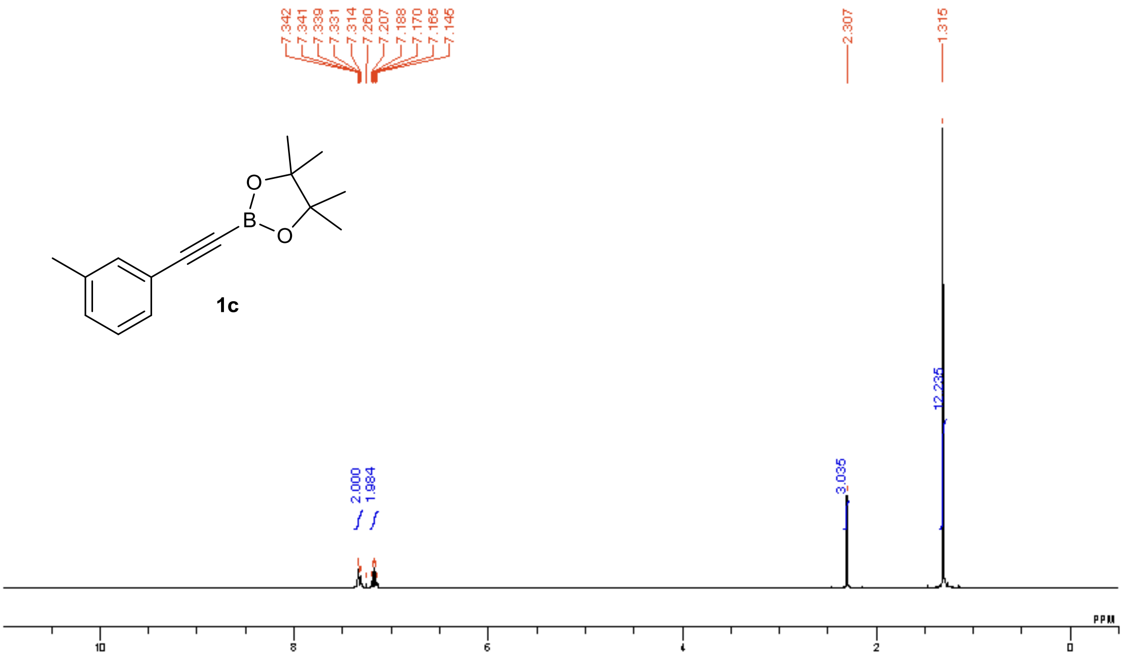
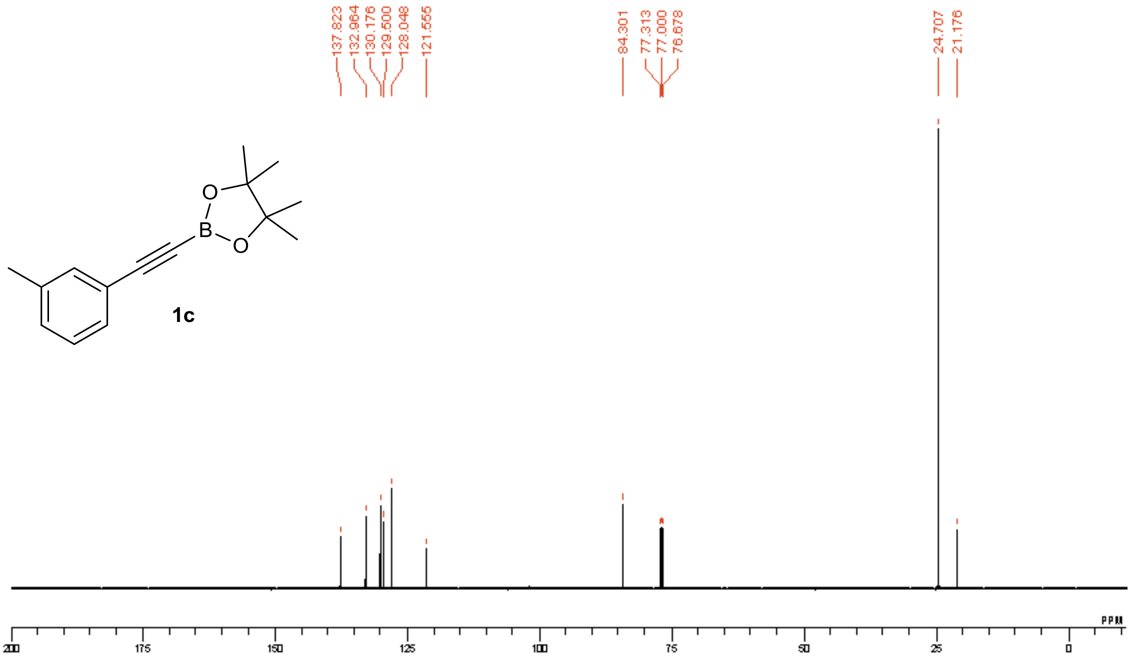


7.342
7.341
7.339
7.331
7.314
7.260
7.207
7.188
7.170
7.165
7.145
2.307
1.315
1c
2.000
1.984
3.035
12.235
PPM
10
8
6
4
2
0



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130.176
129.500
128.048
121.555
84.301
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77.000
76.678
24.707
21.176
1c
PPM
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175
150
125
100
75
50
25
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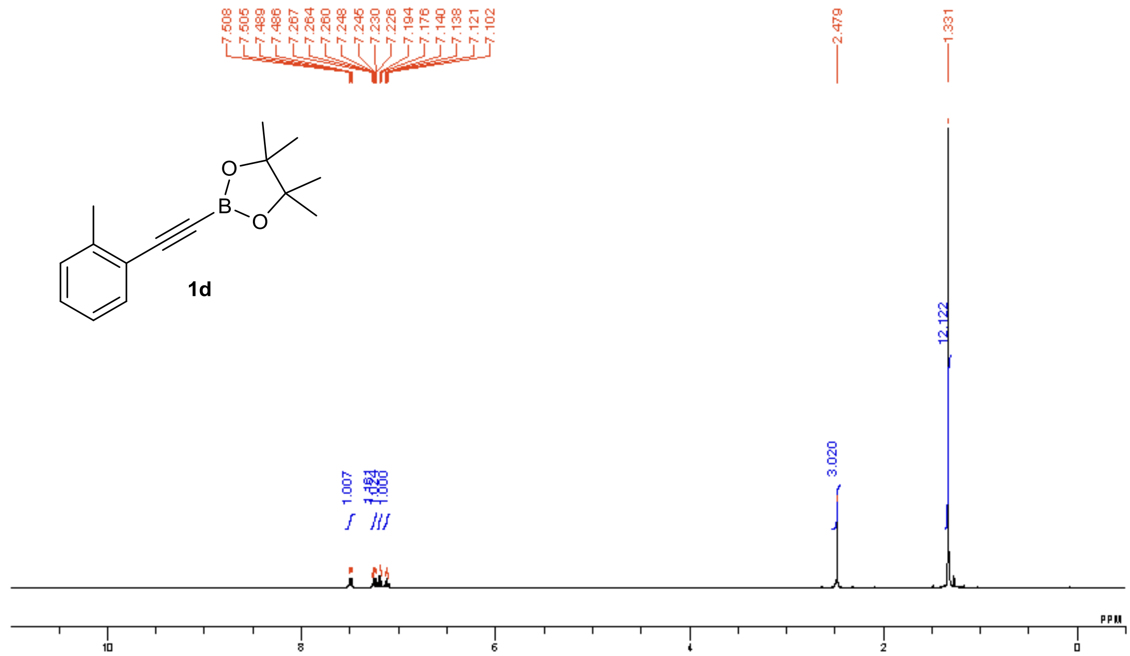
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7.267
7.264
7.260
7.248
7.245
7.230
7.226
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7.176
7.140
7.138
7.121
7.102
2.479
1.331
O
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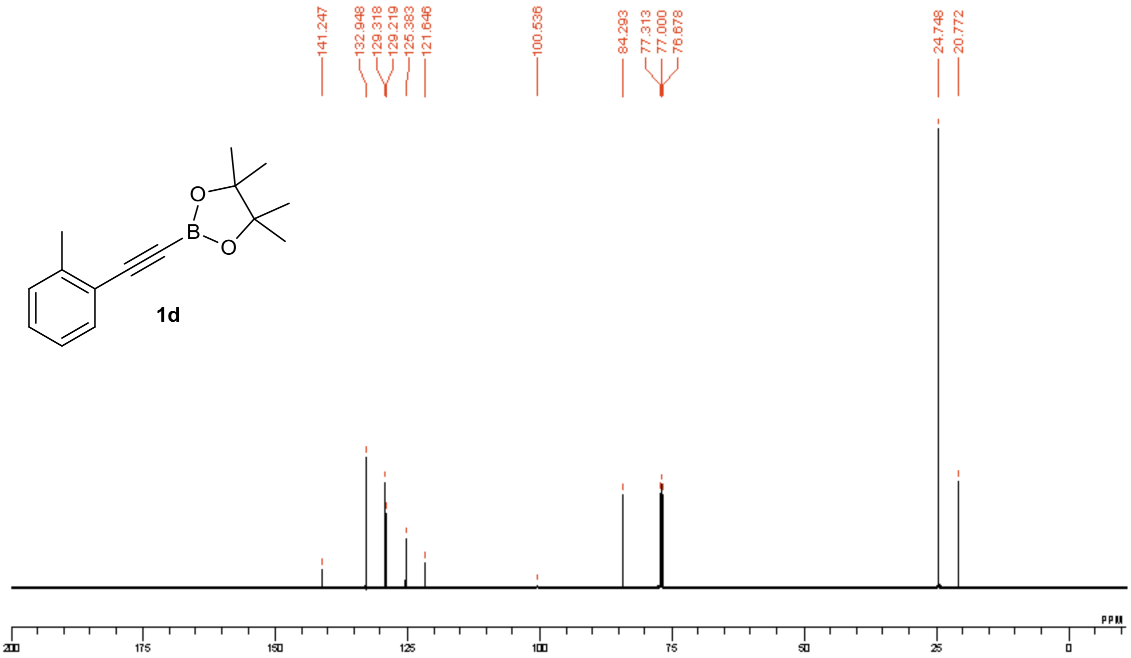
O
1d
12.122
3.020
1.007
1.000
PPM
10
8
6
4
2
0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77.000
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20.772
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B
O
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PPM
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175
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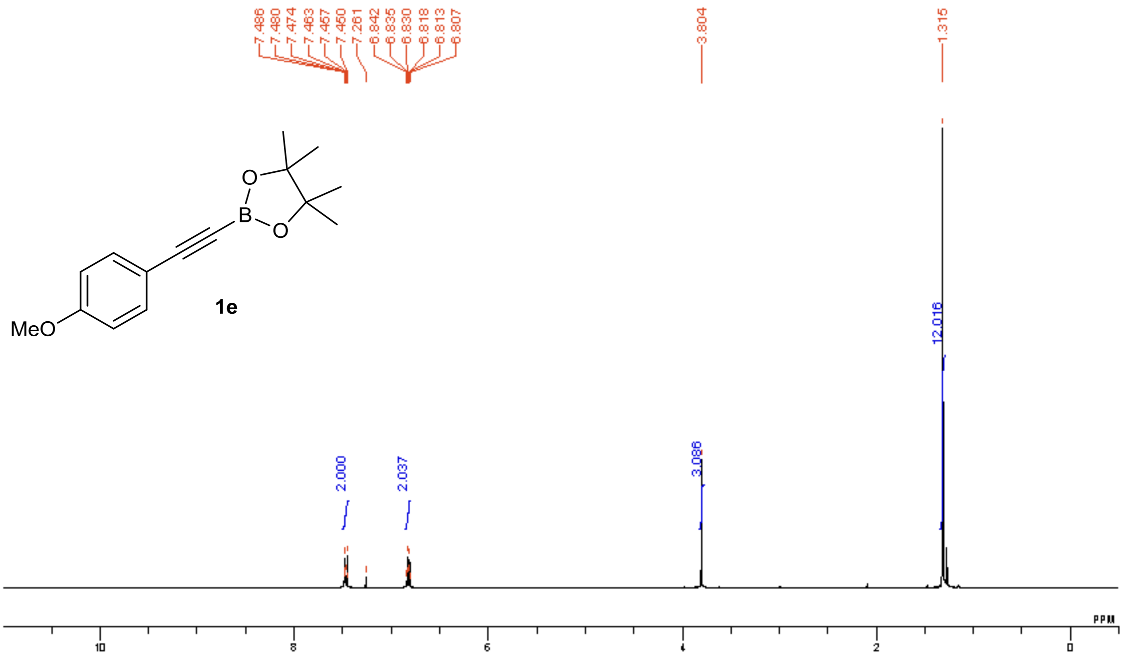
125
100
75
50
25
0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7.474
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7.450
7.261
6.842
6.835
6.830
6.818
6.813
6.807
3.804
1.315
MeO
O
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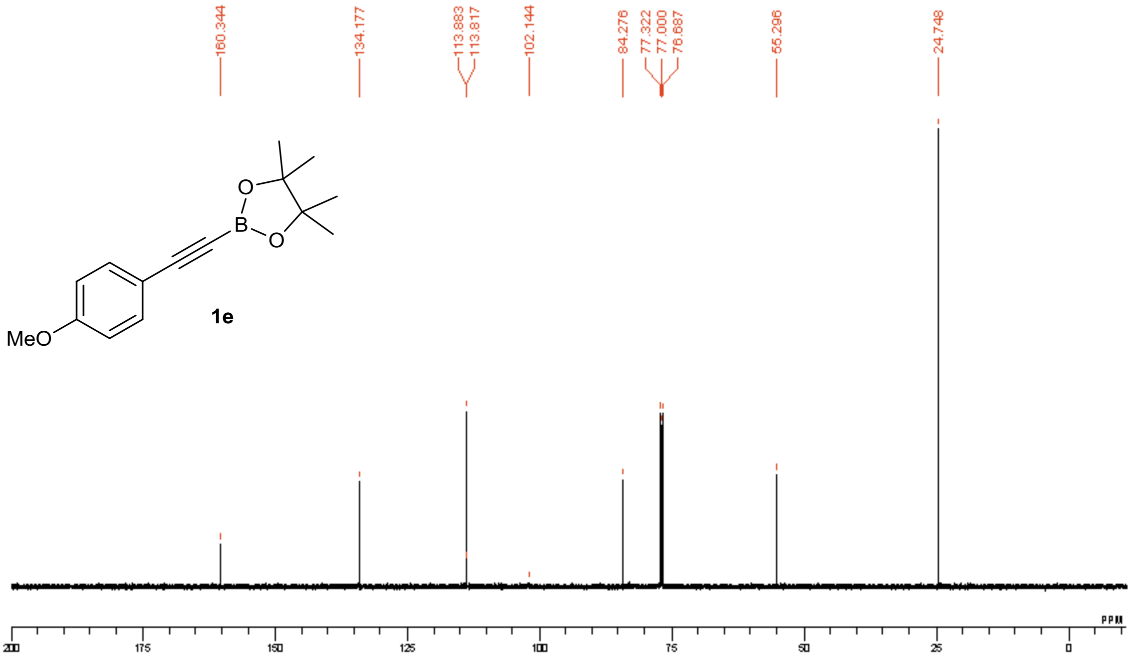
2.000
2.037
3.086
12.016
PPM
10
8
6
4
2
0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134.177
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113.817
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84.276
77.322
77.000
76.687
55.296
24.748
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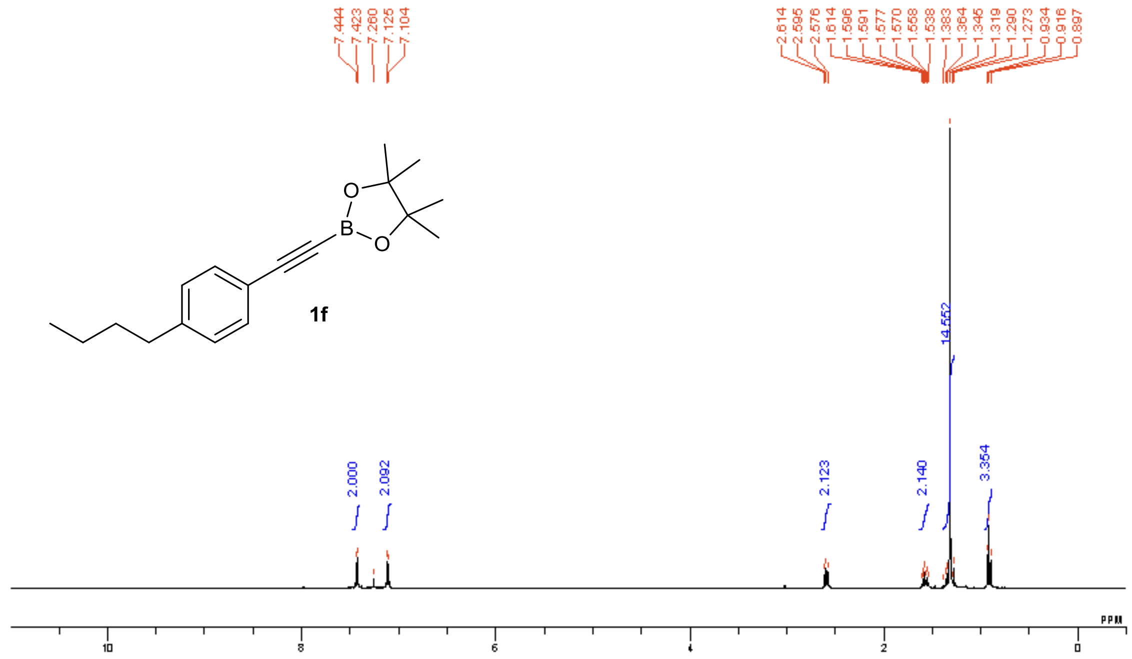
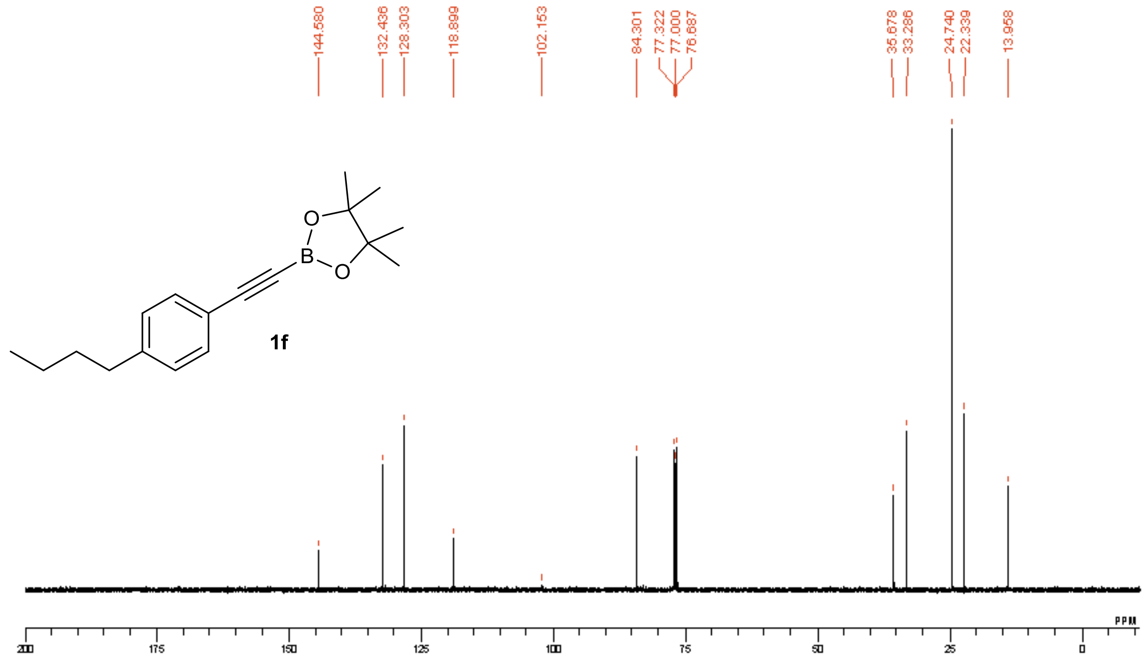
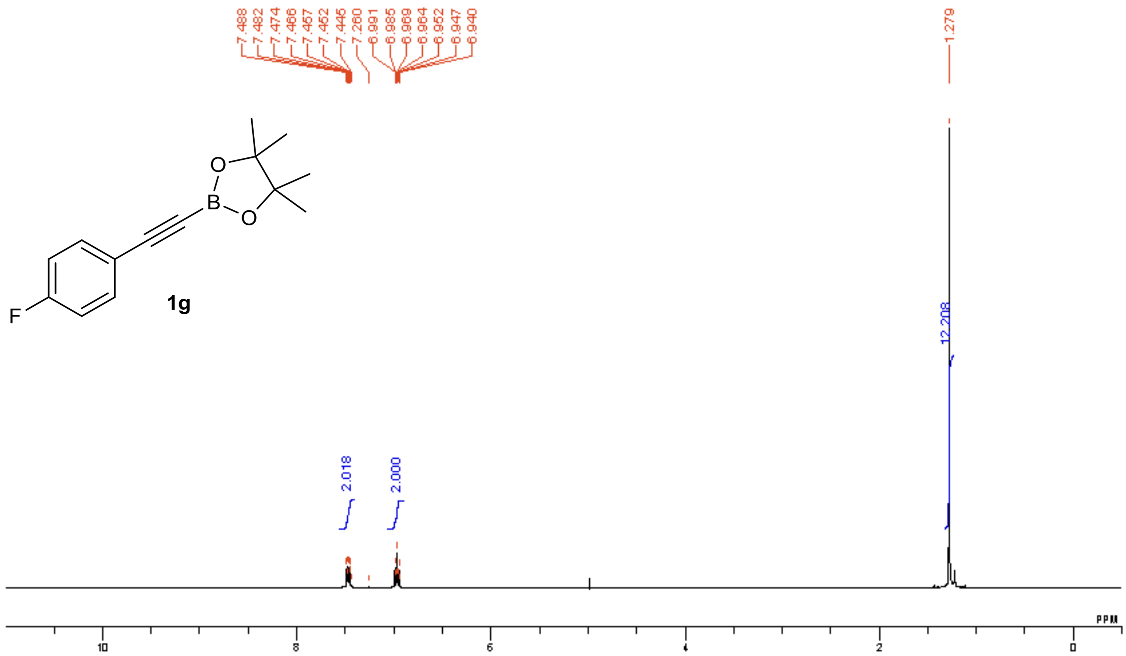
100
75
50
25
0



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7.452
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7.260
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6.985
6.969
6.964
6.952
6.947
6.940
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O
F
1g
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PPM
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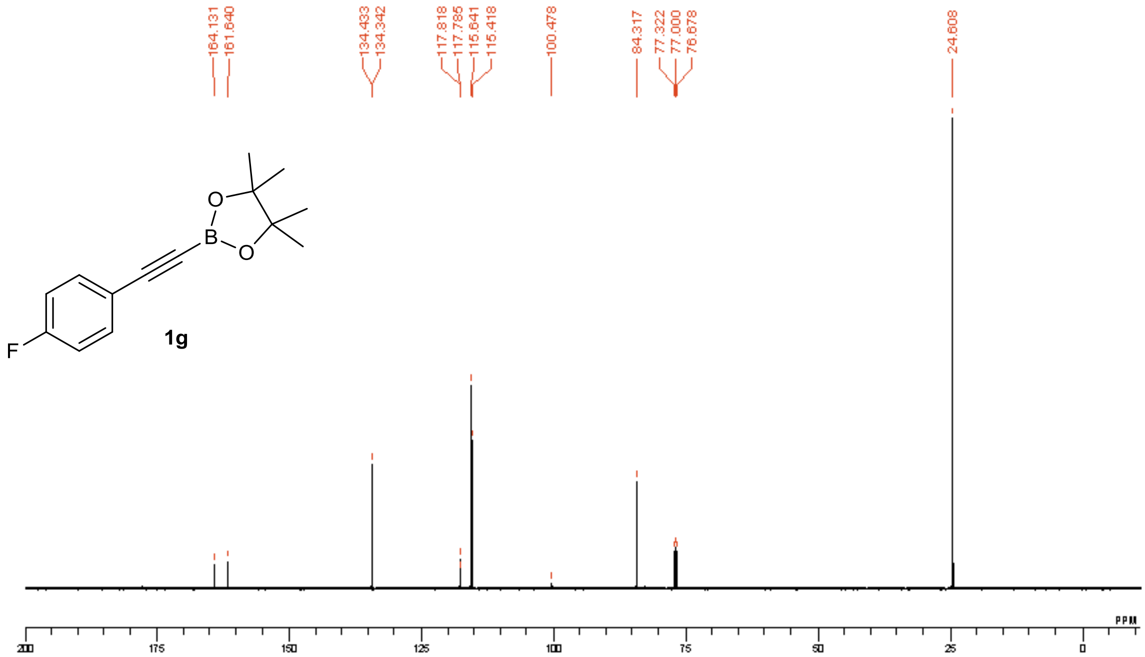
6
4
2
0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117.785
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115.418
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77.322
77.000
76.678
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B
O
F
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PPM
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175
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125
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75
50
25
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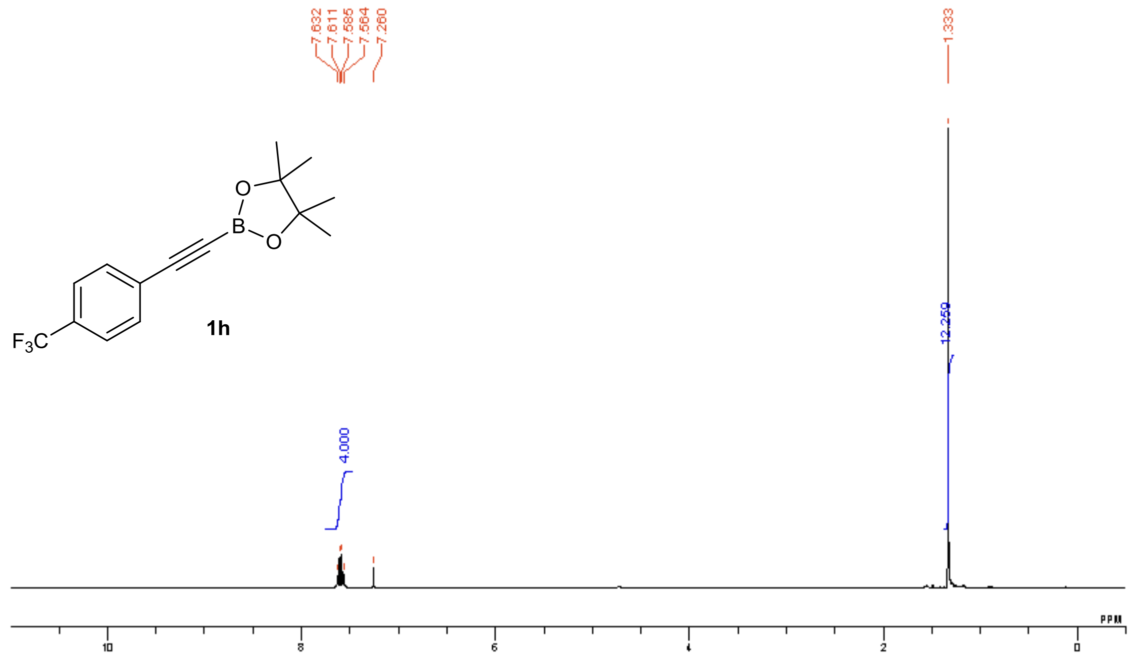

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2
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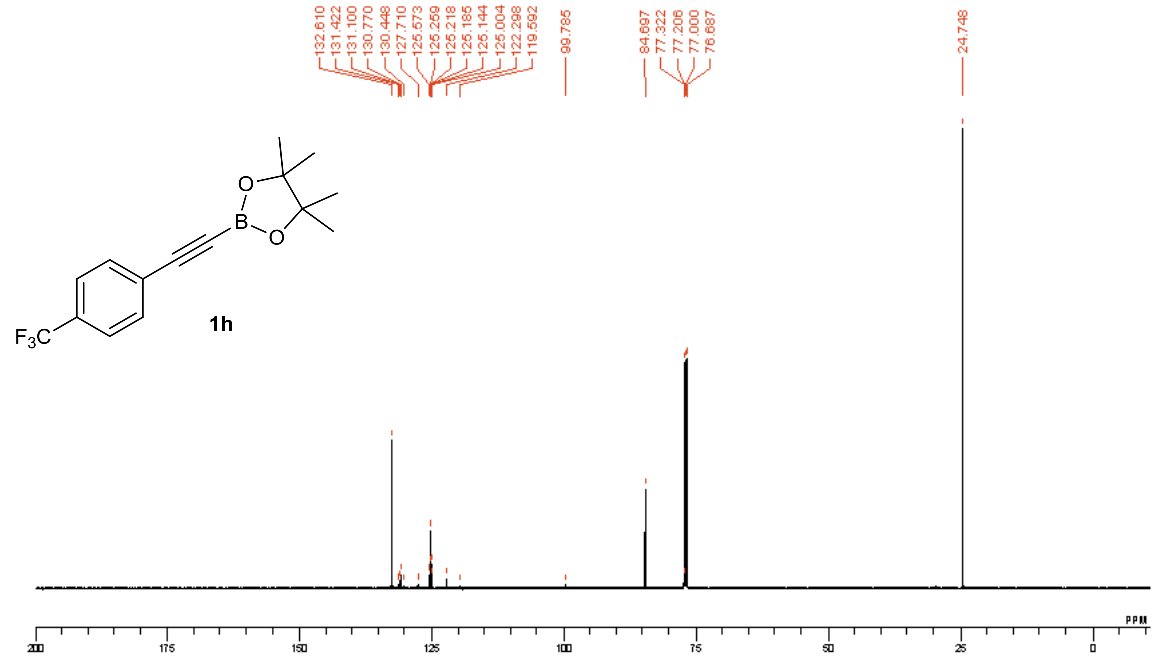

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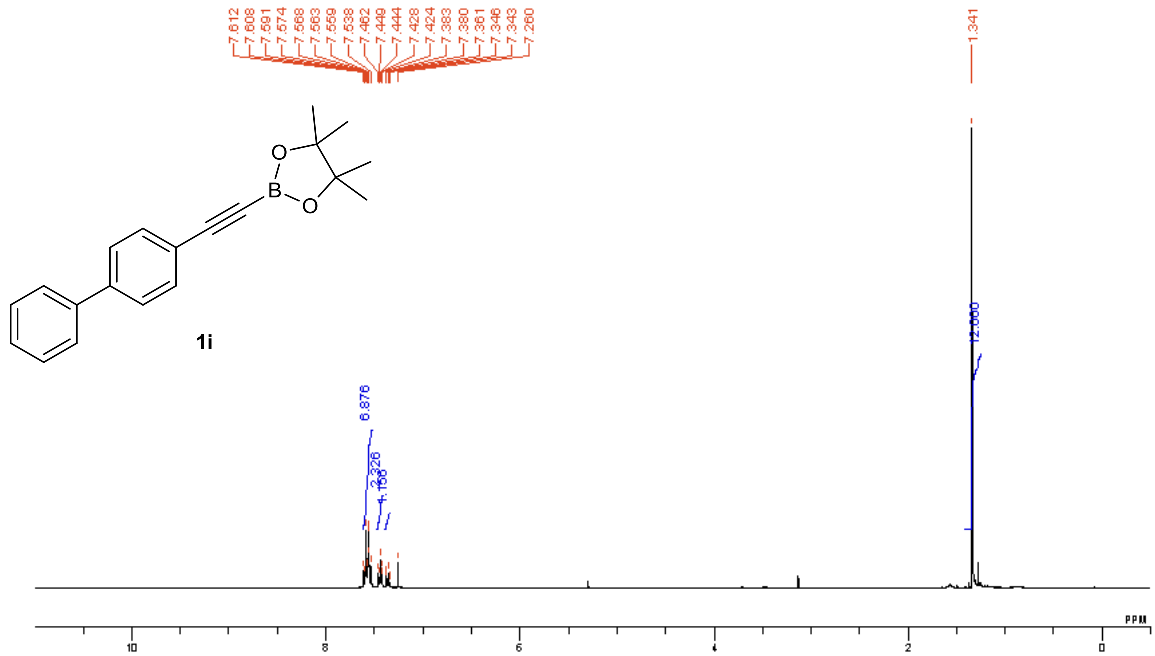
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7.444
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7.380
7.361
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6
4
2
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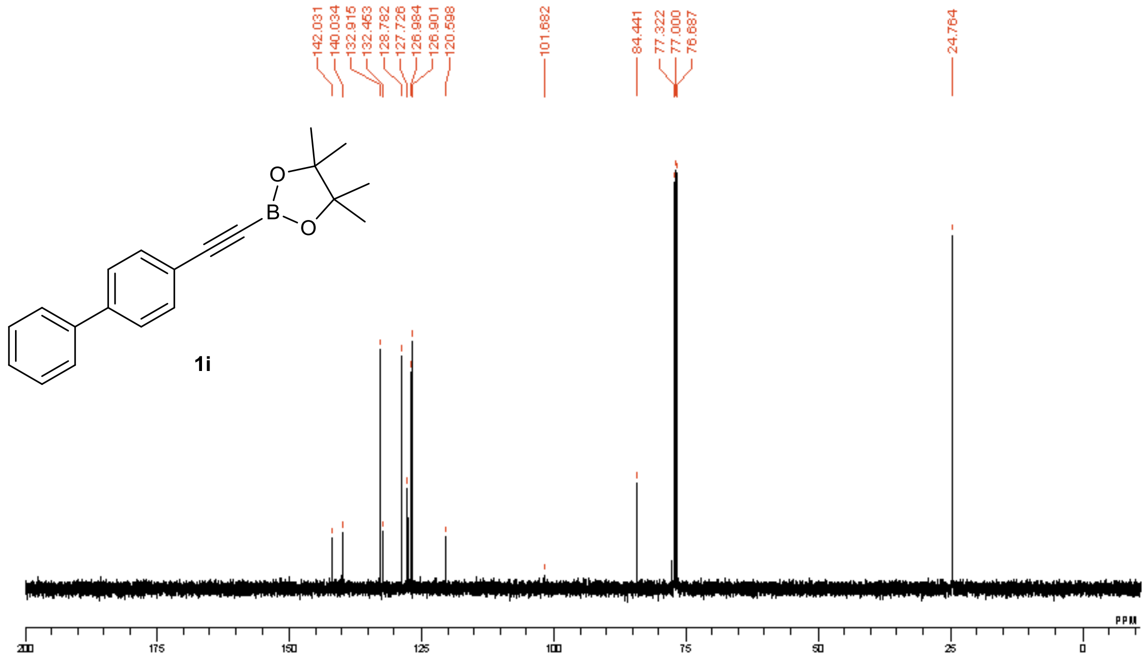
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126.901
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76.687
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175
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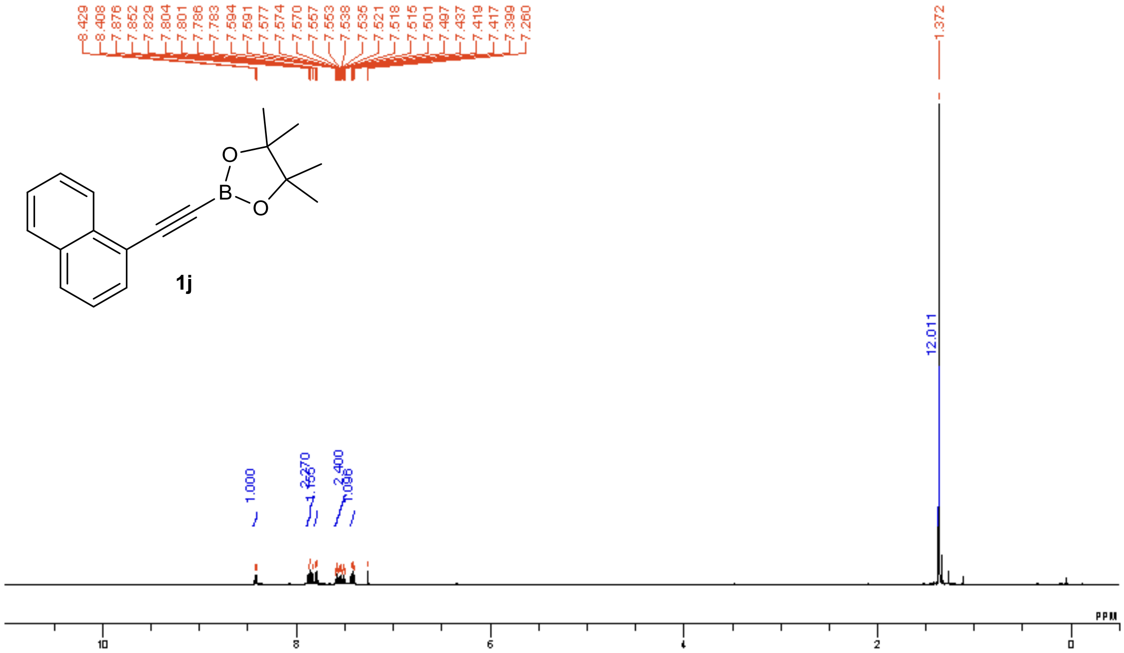
125
100
75
50
25
0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7.535
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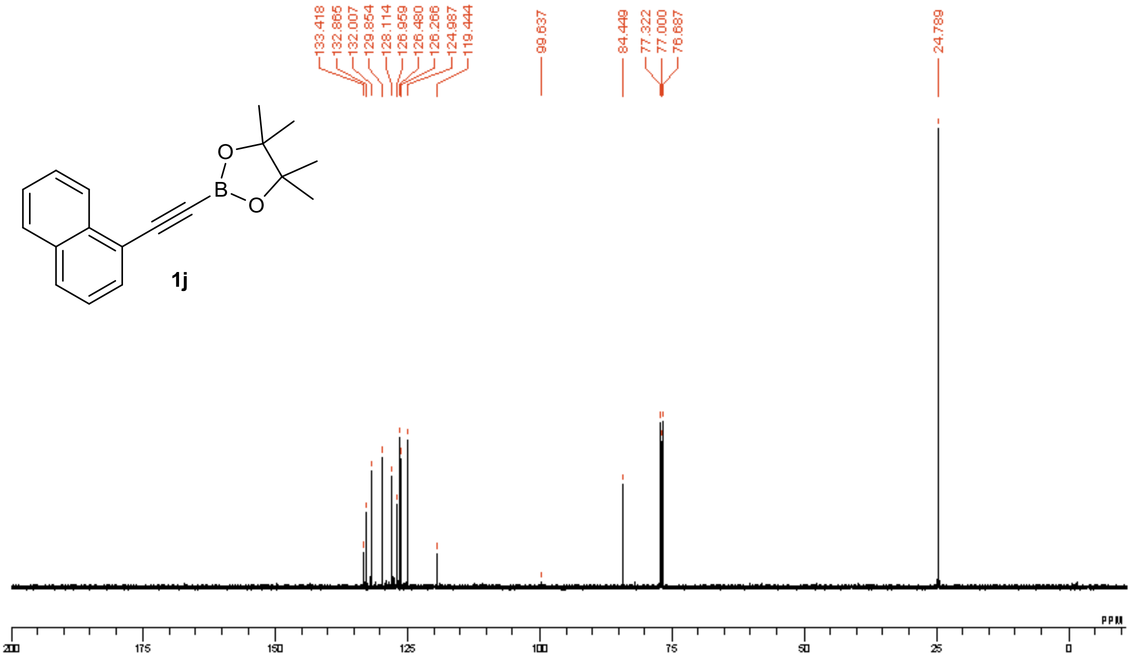
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1j
PPM
200
175
150
125
100
75
50
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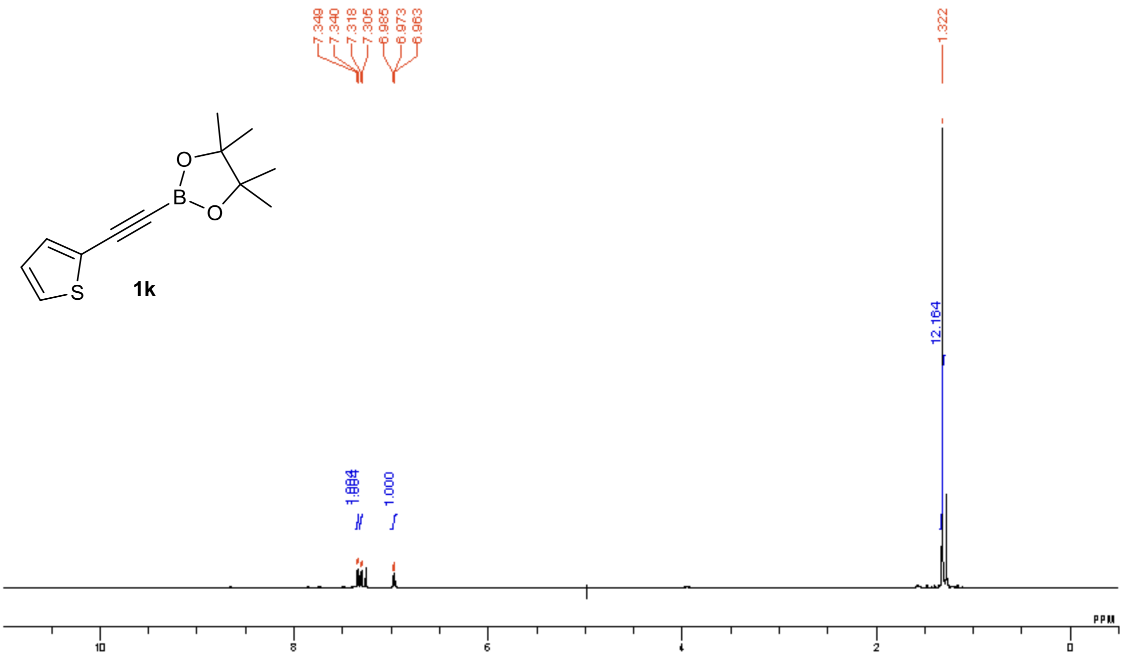
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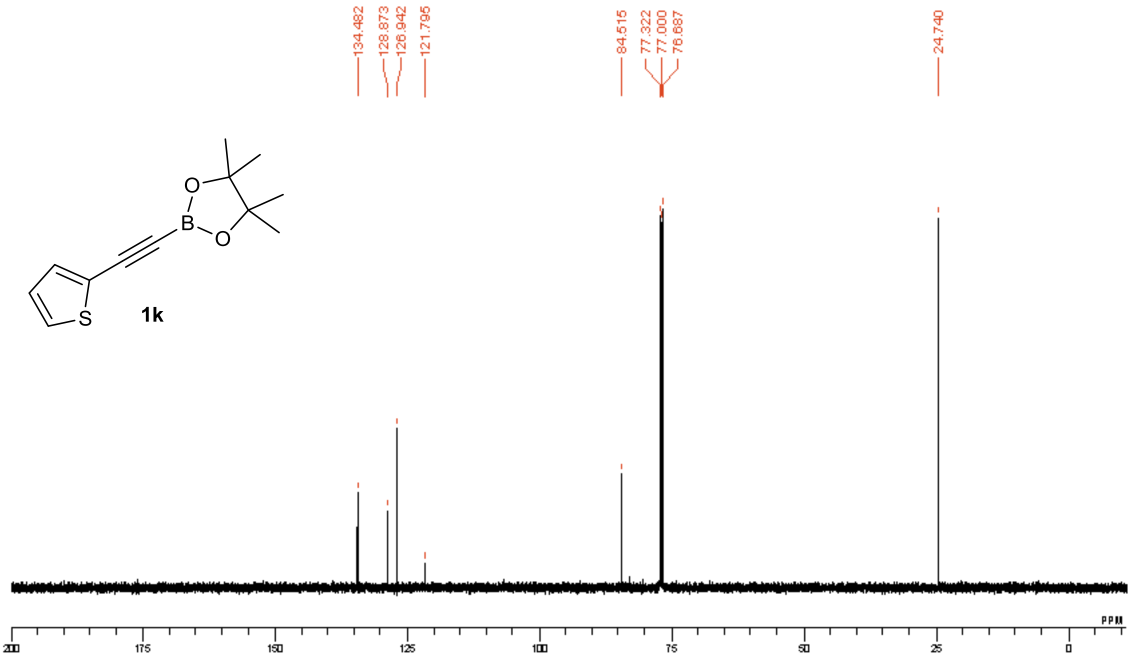
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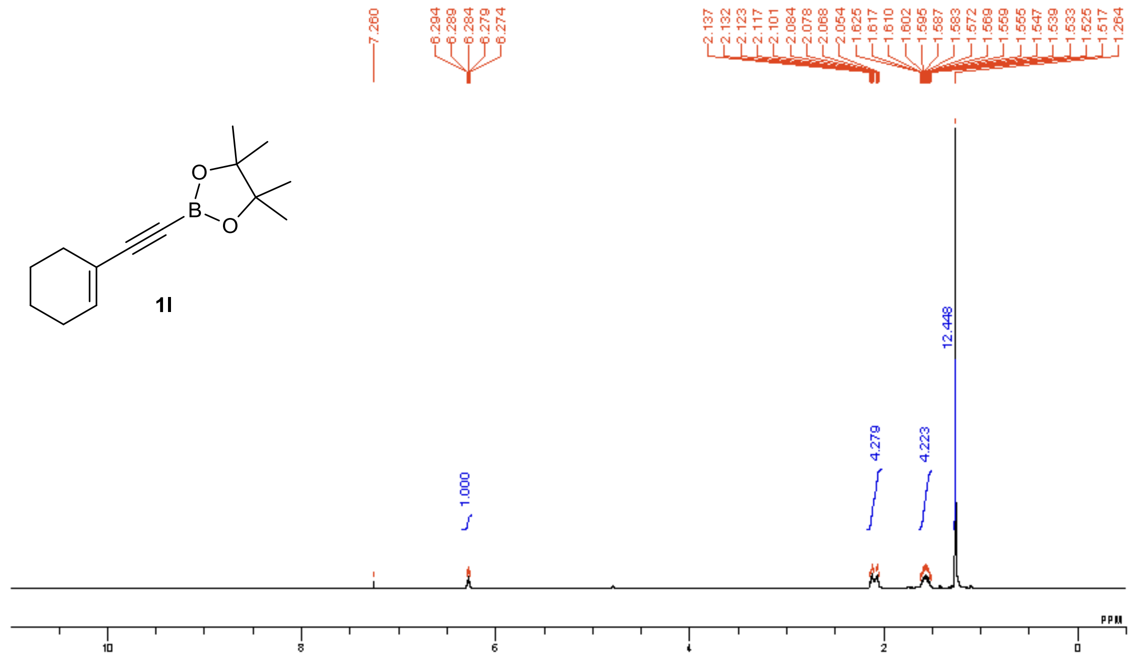

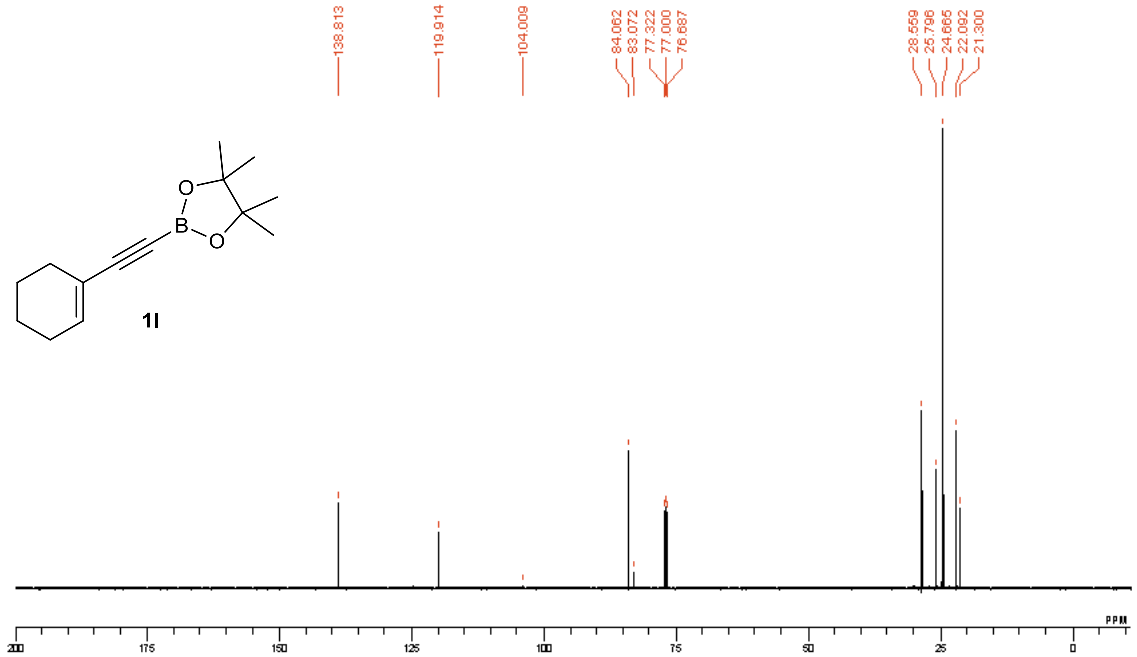

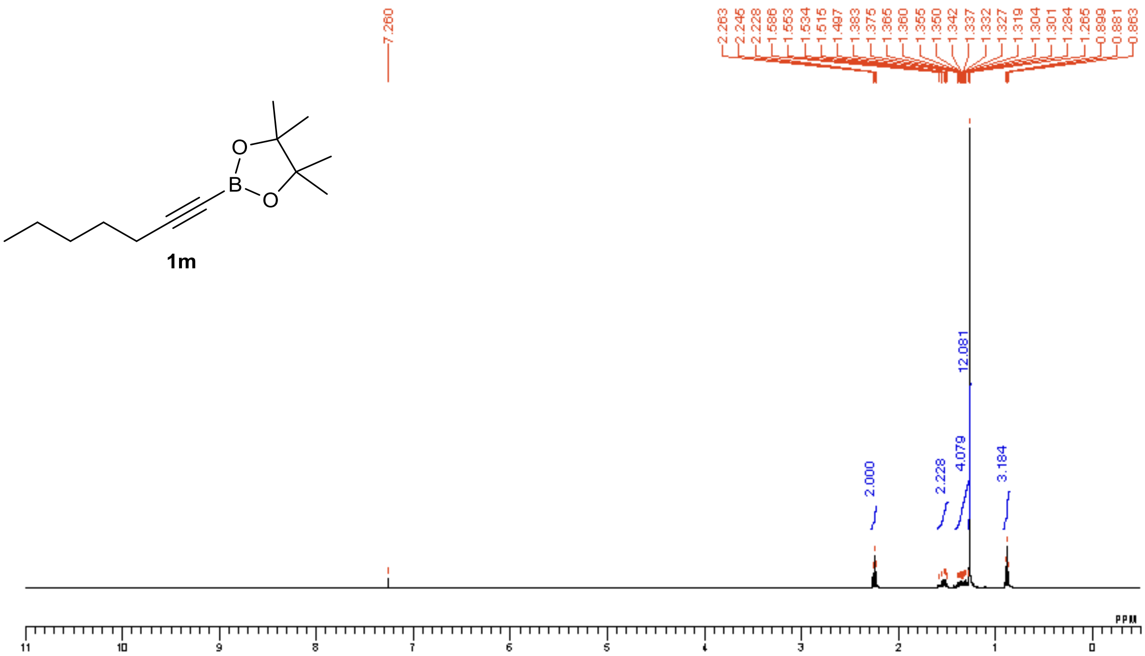

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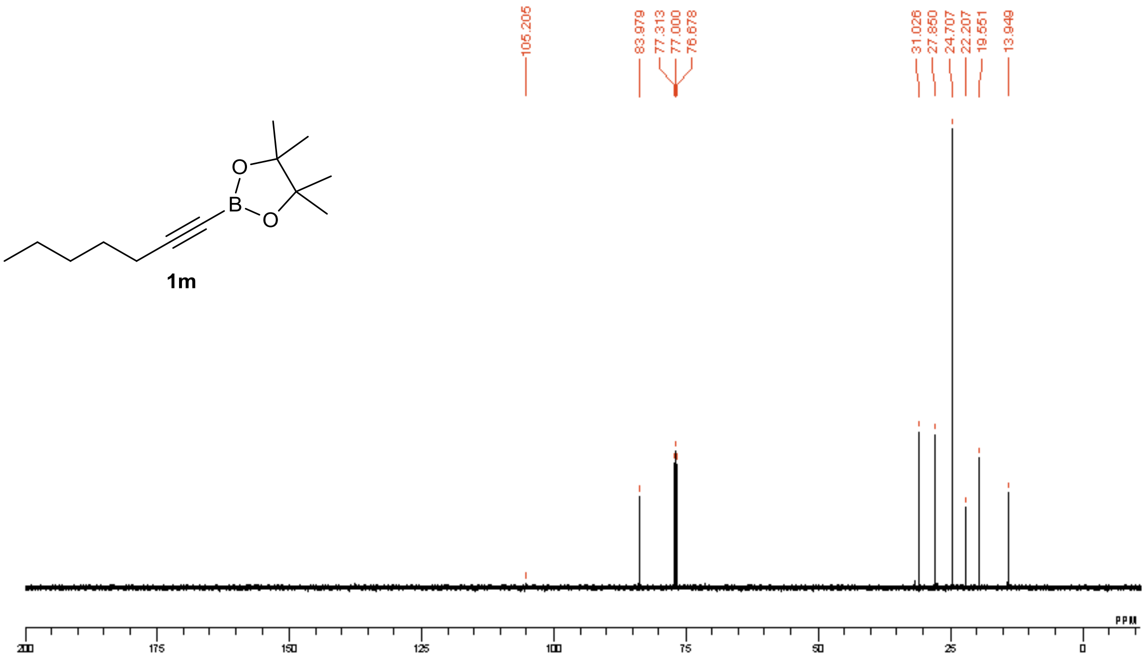

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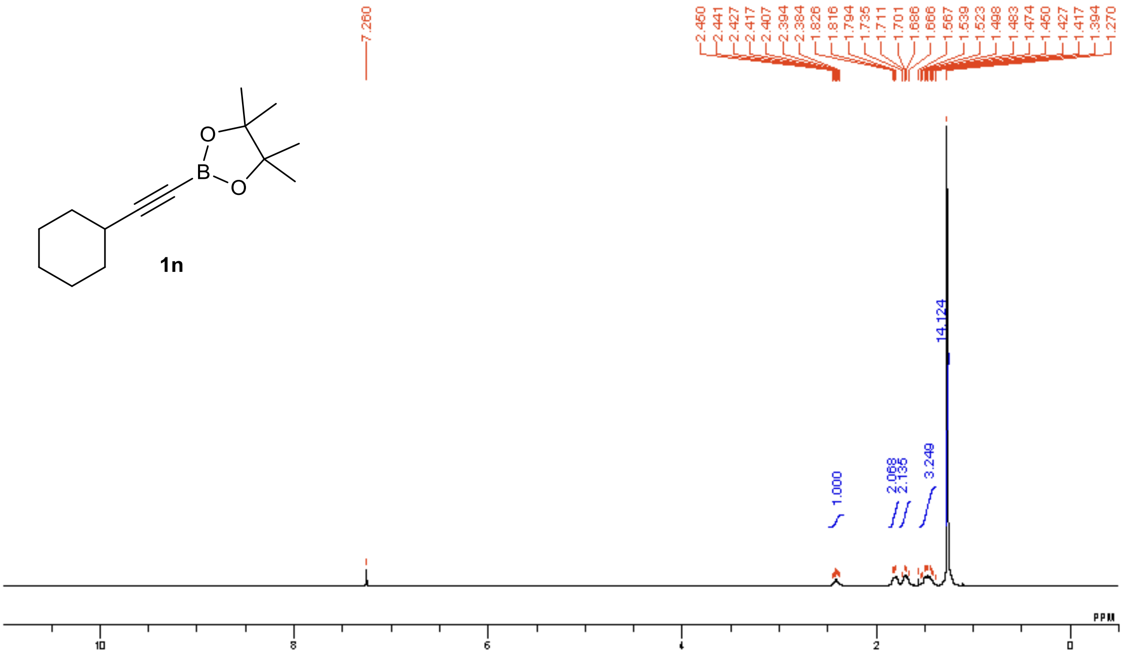
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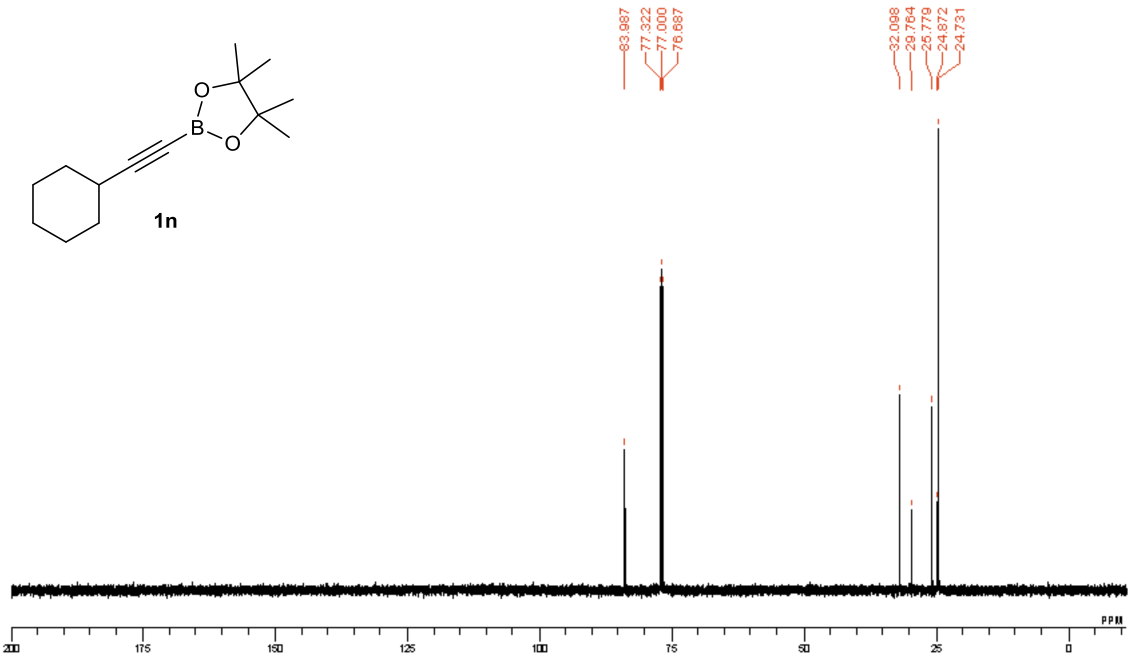
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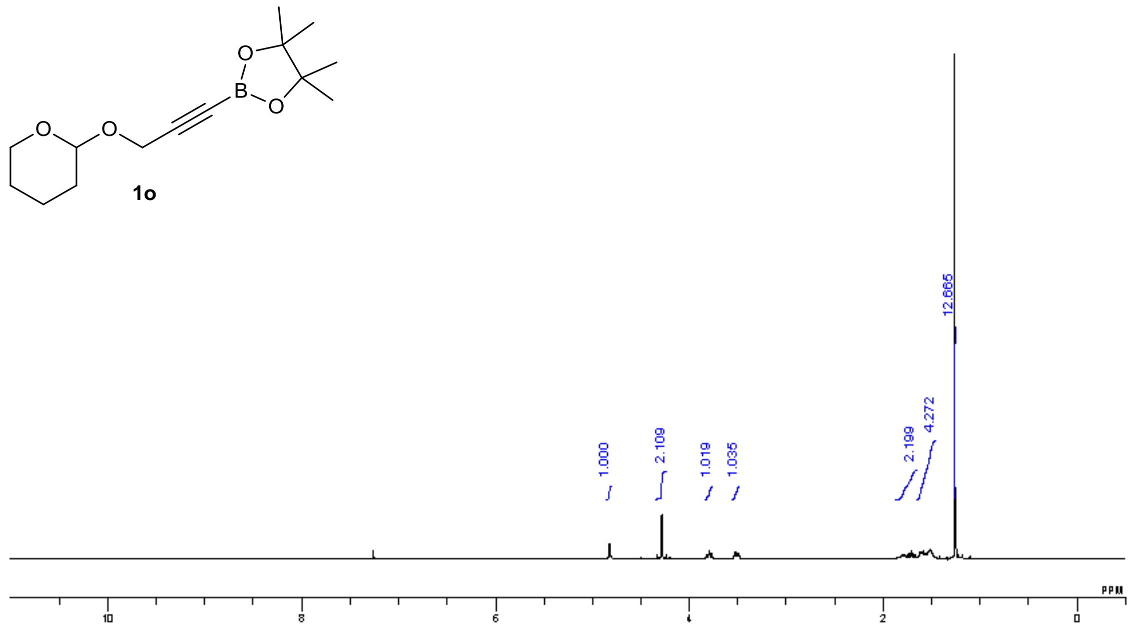

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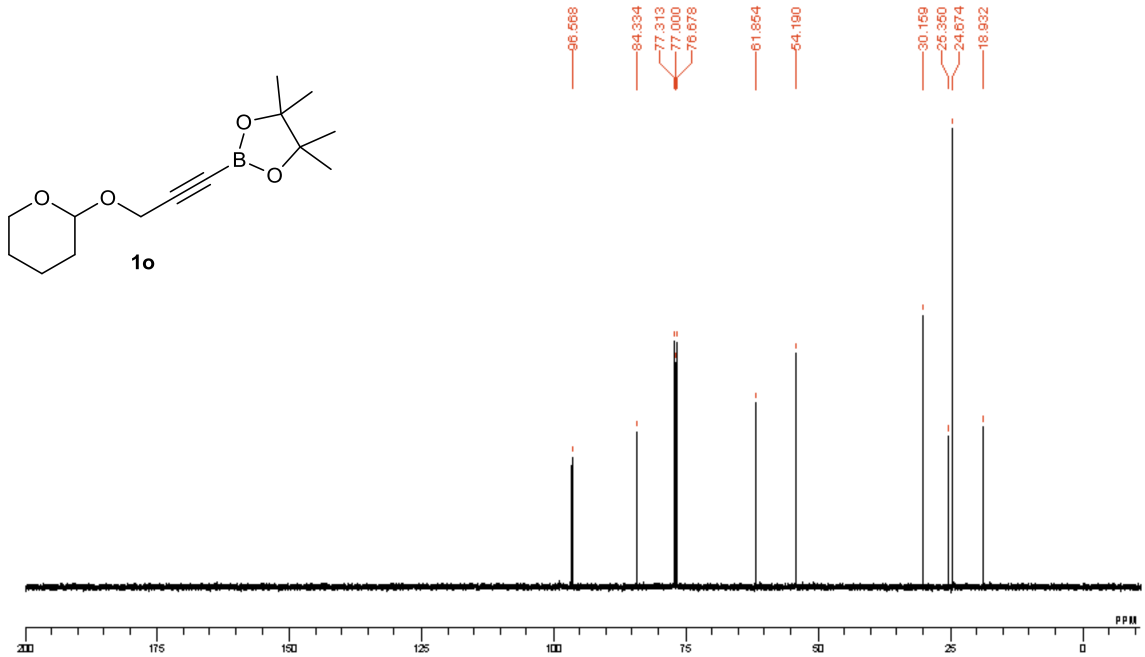

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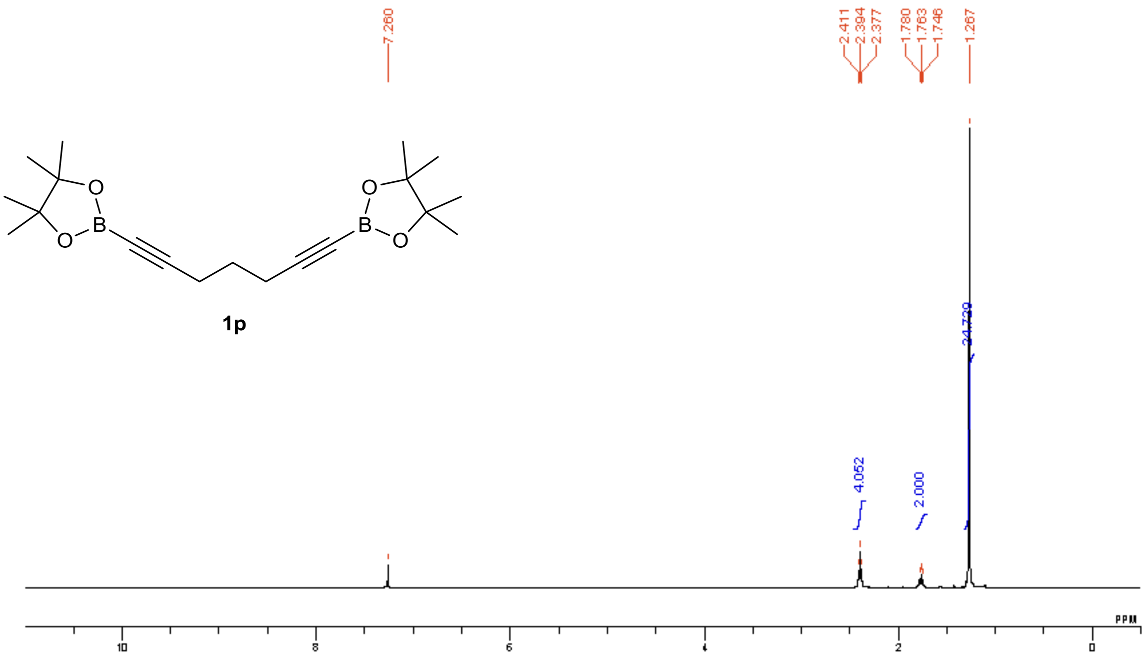
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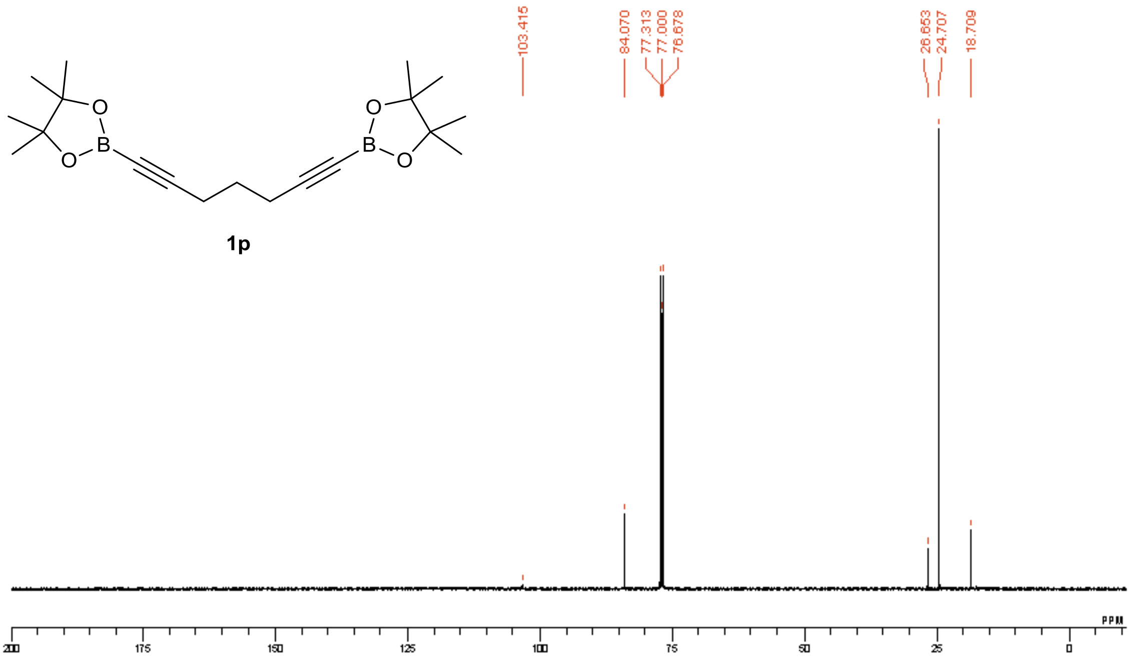
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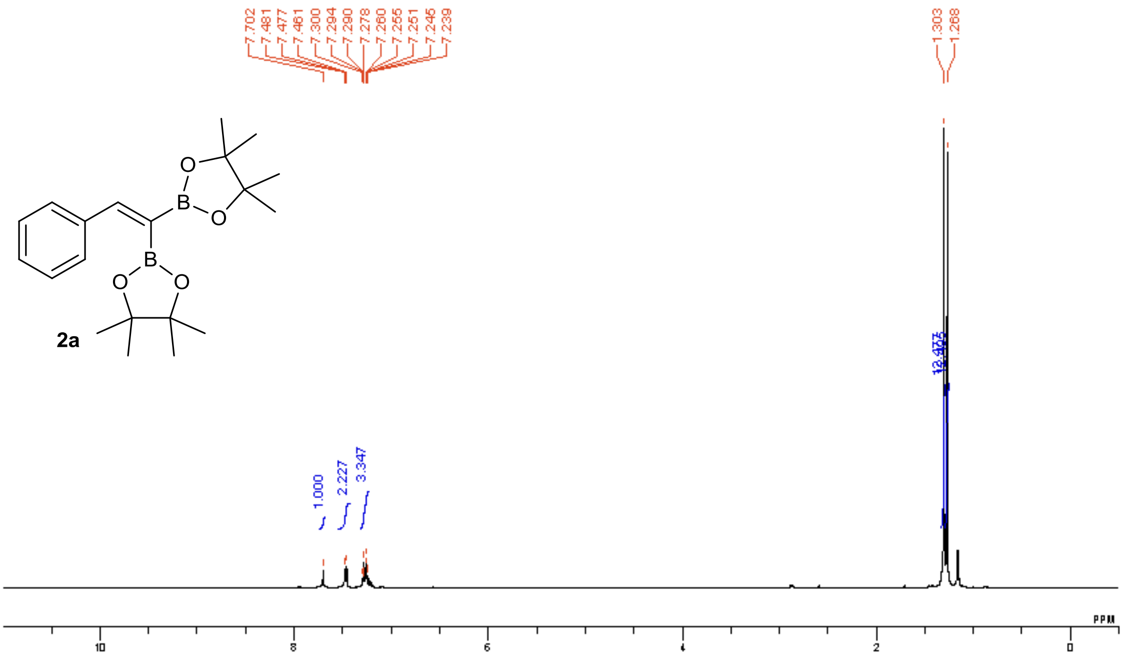
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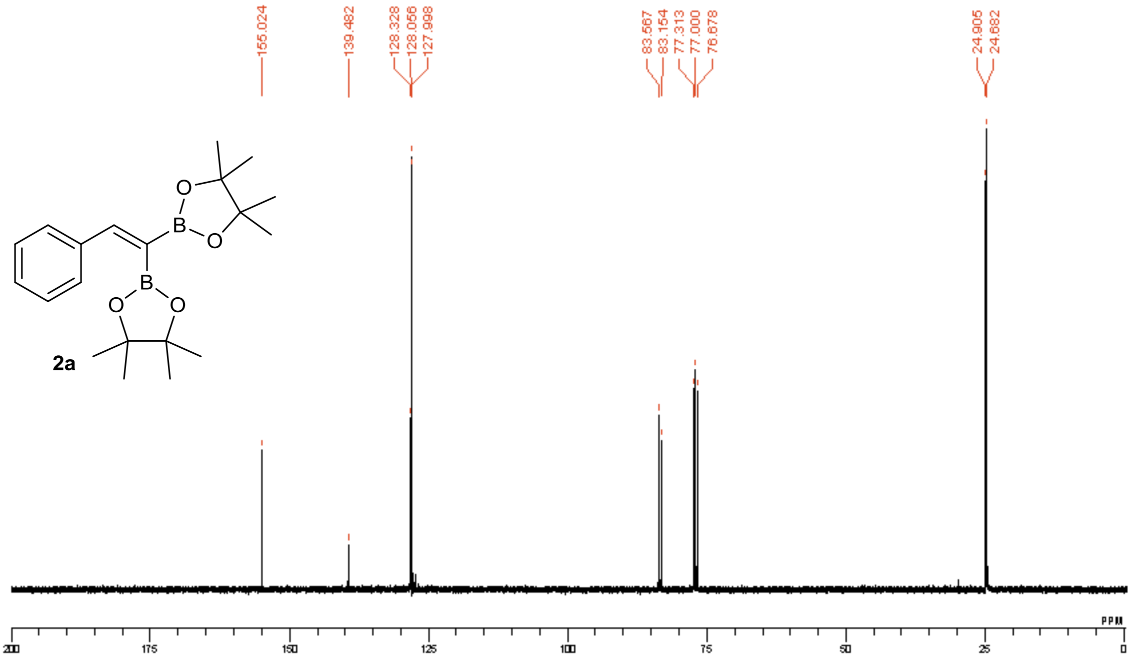
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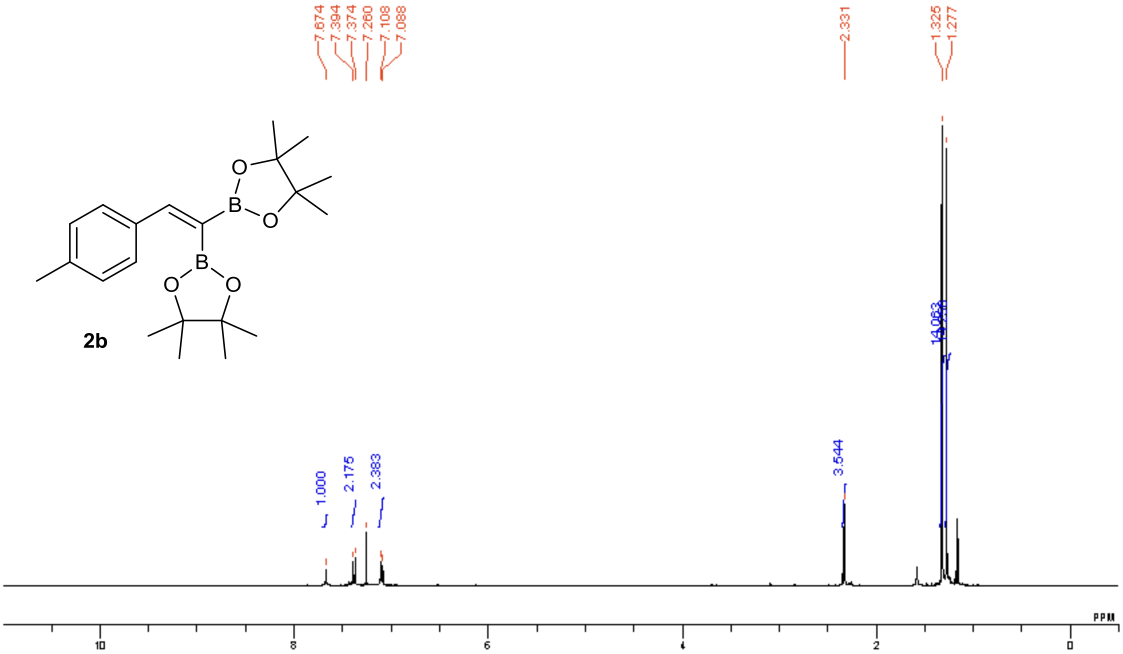
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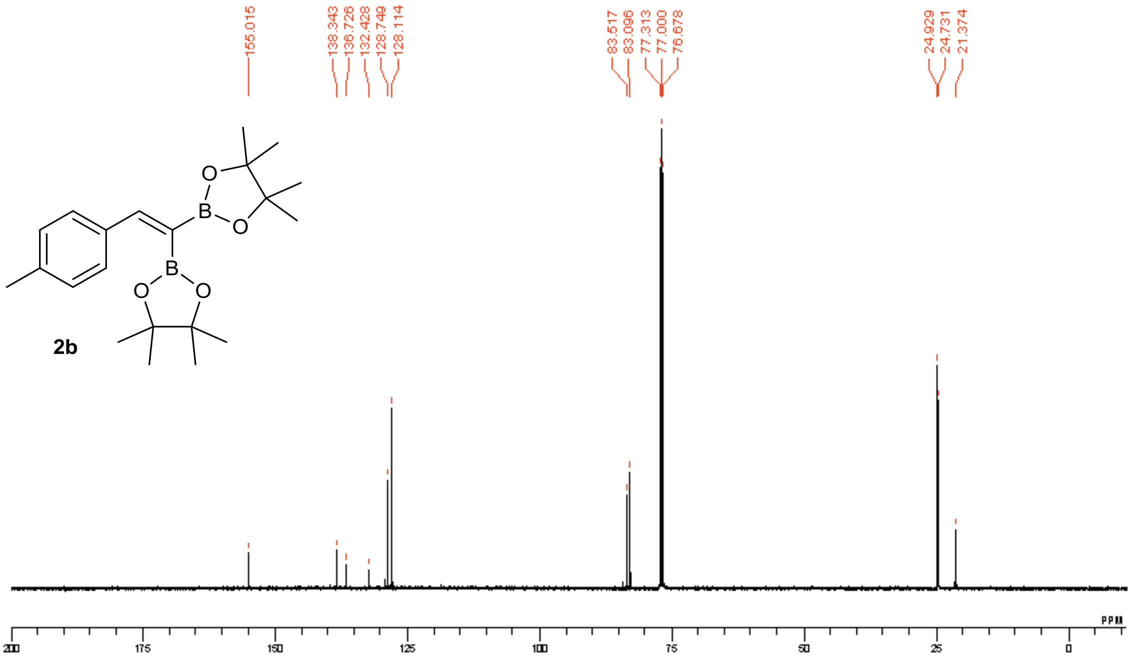
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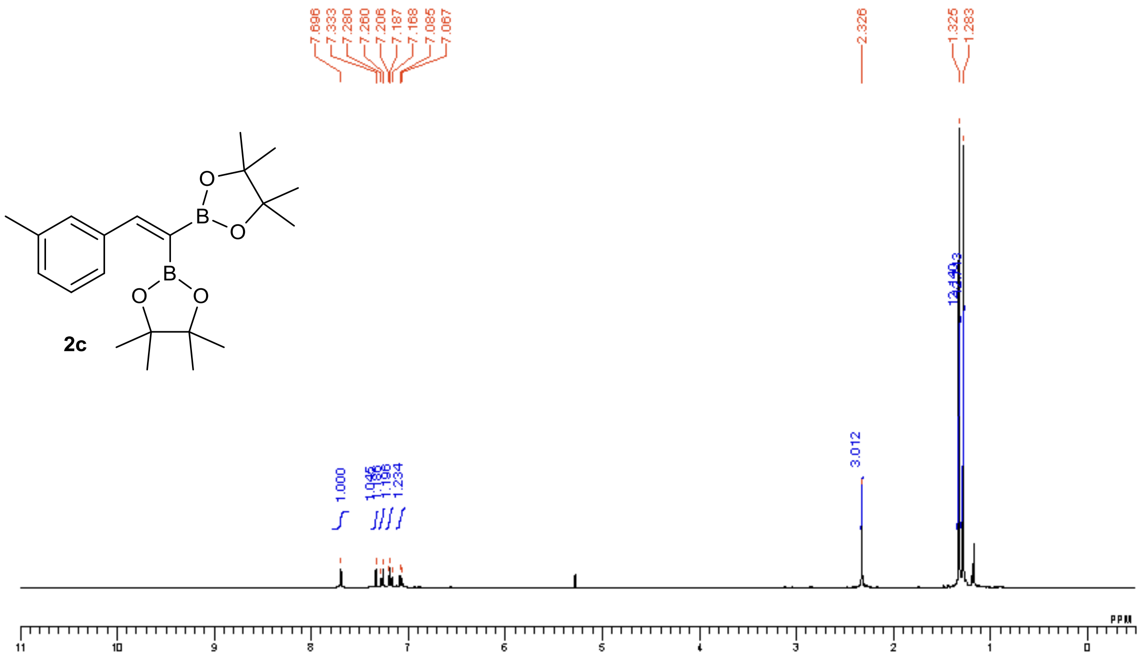
2b



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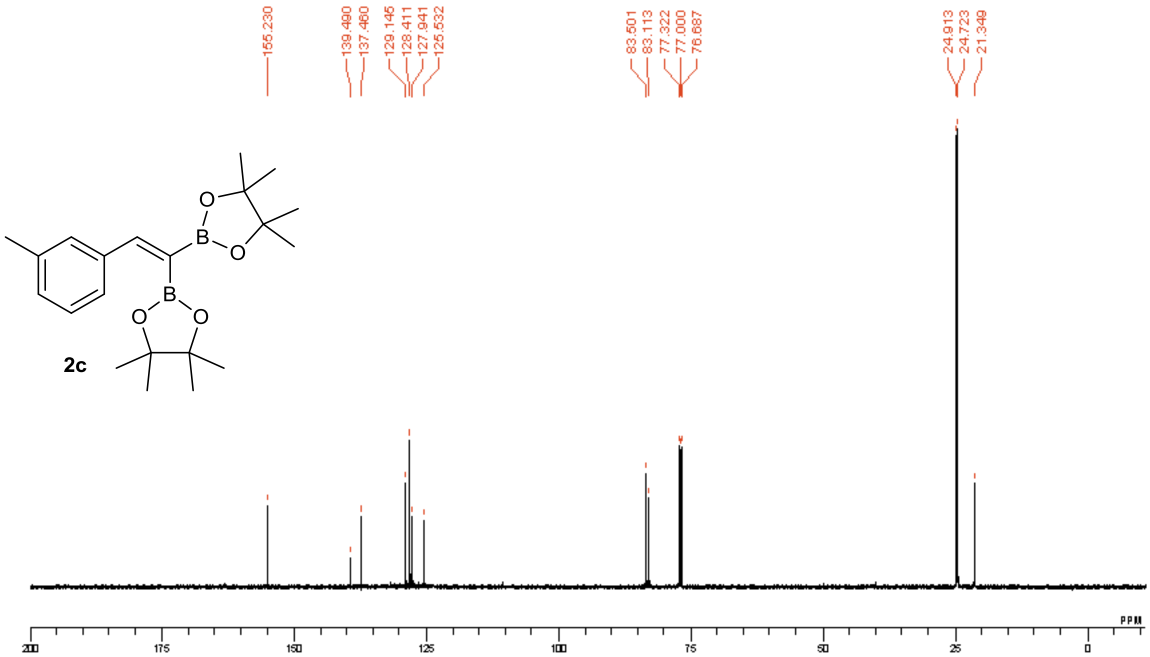

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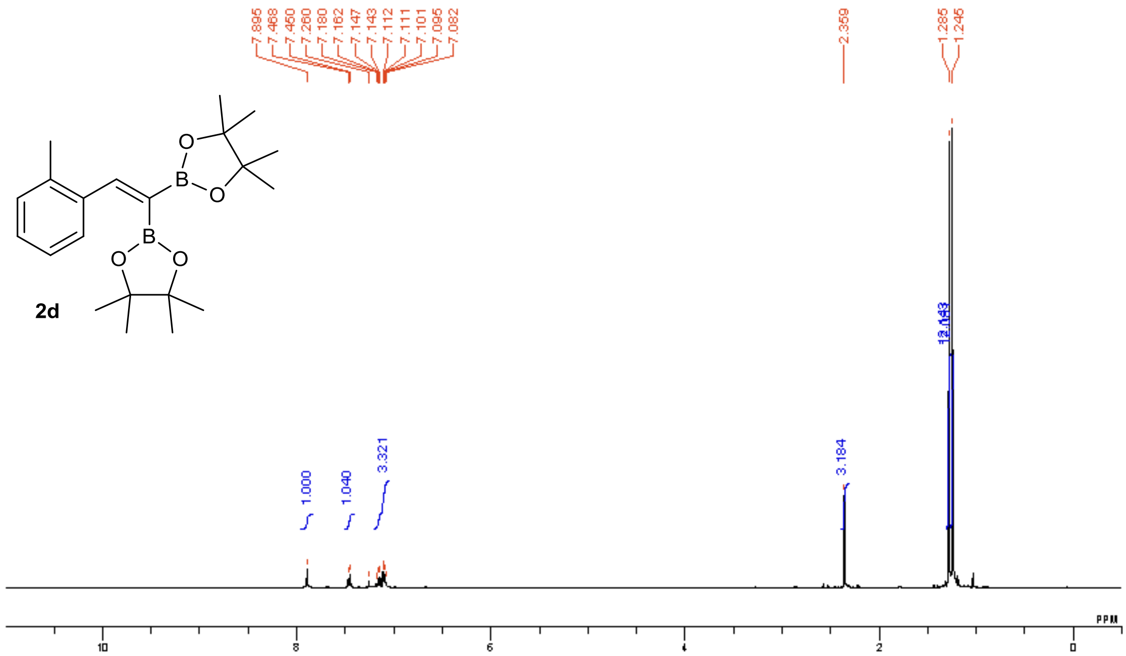
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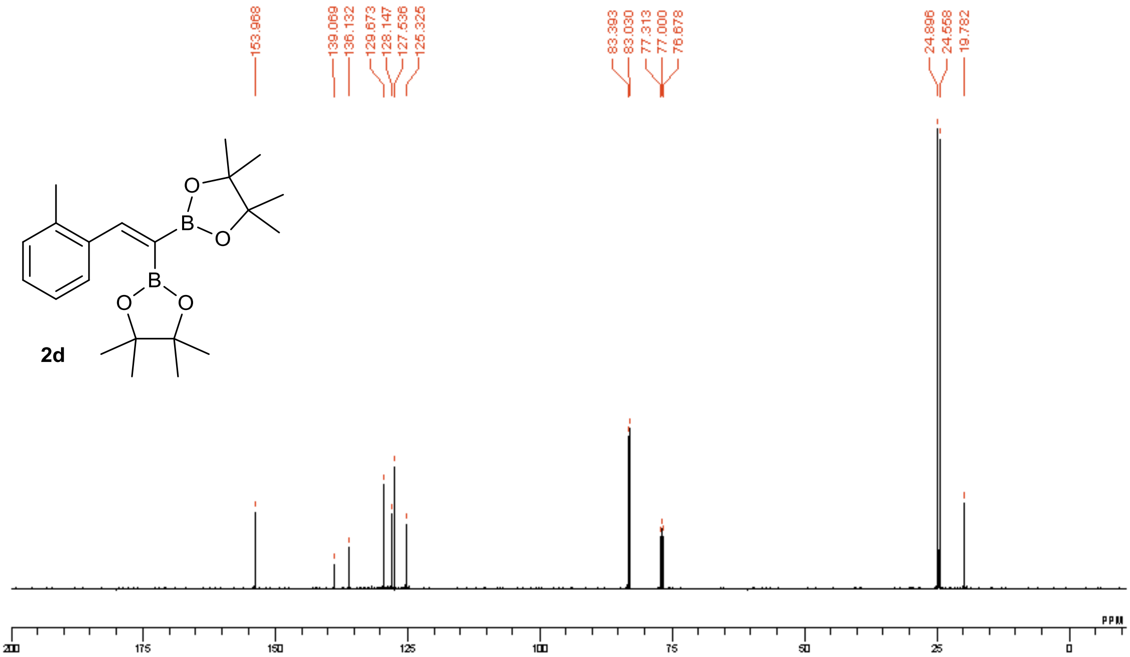
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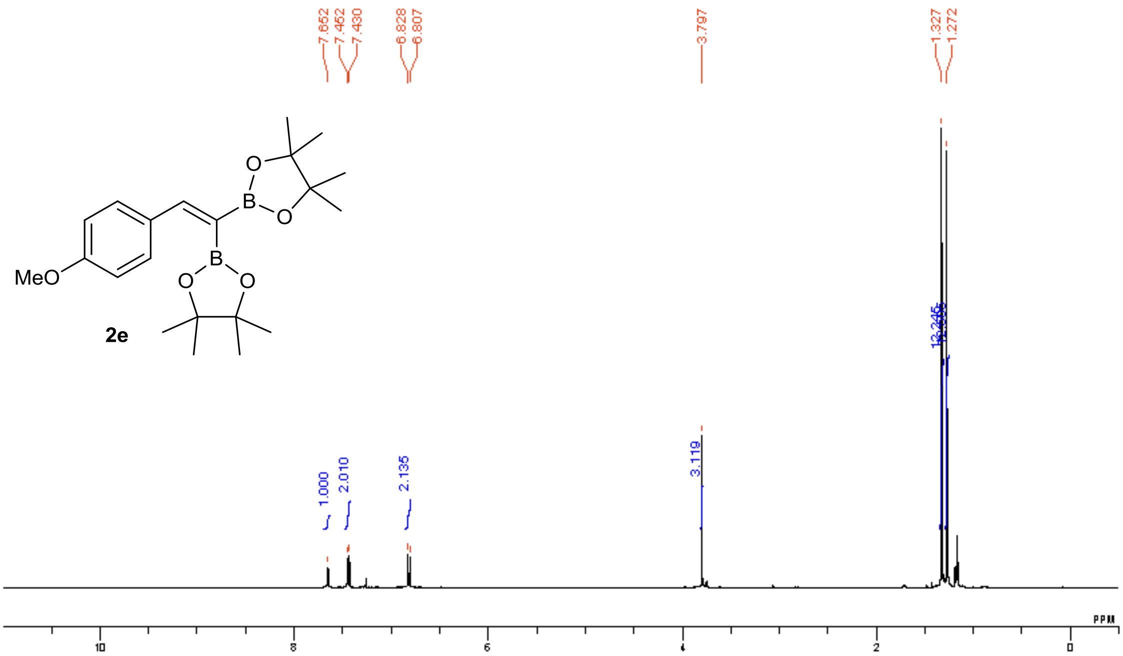

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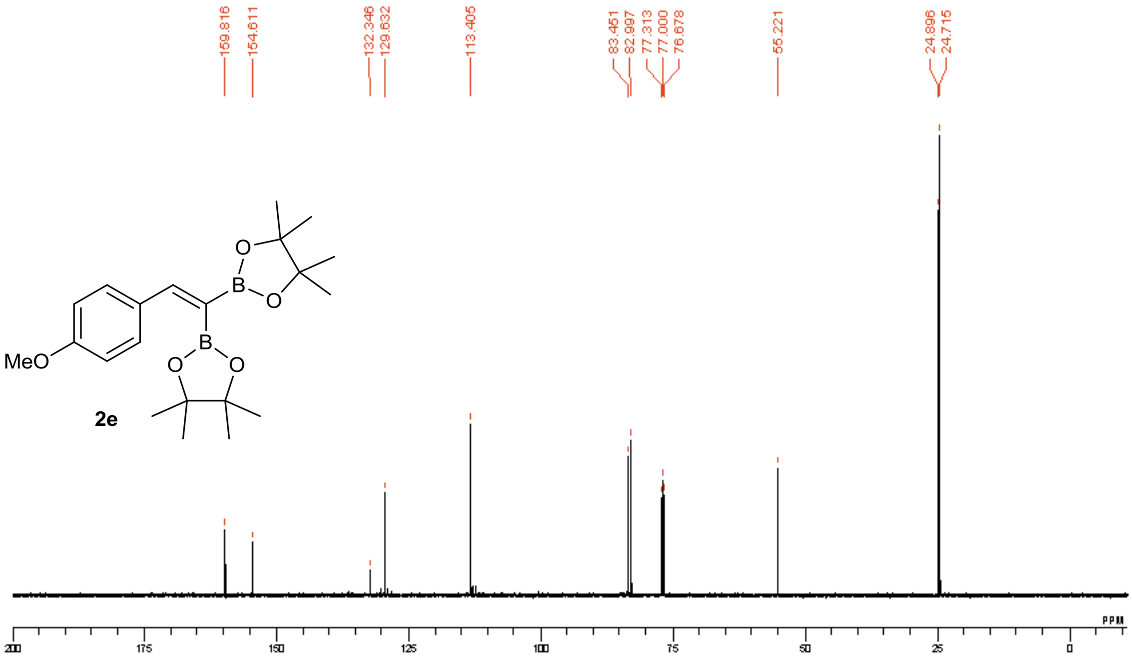

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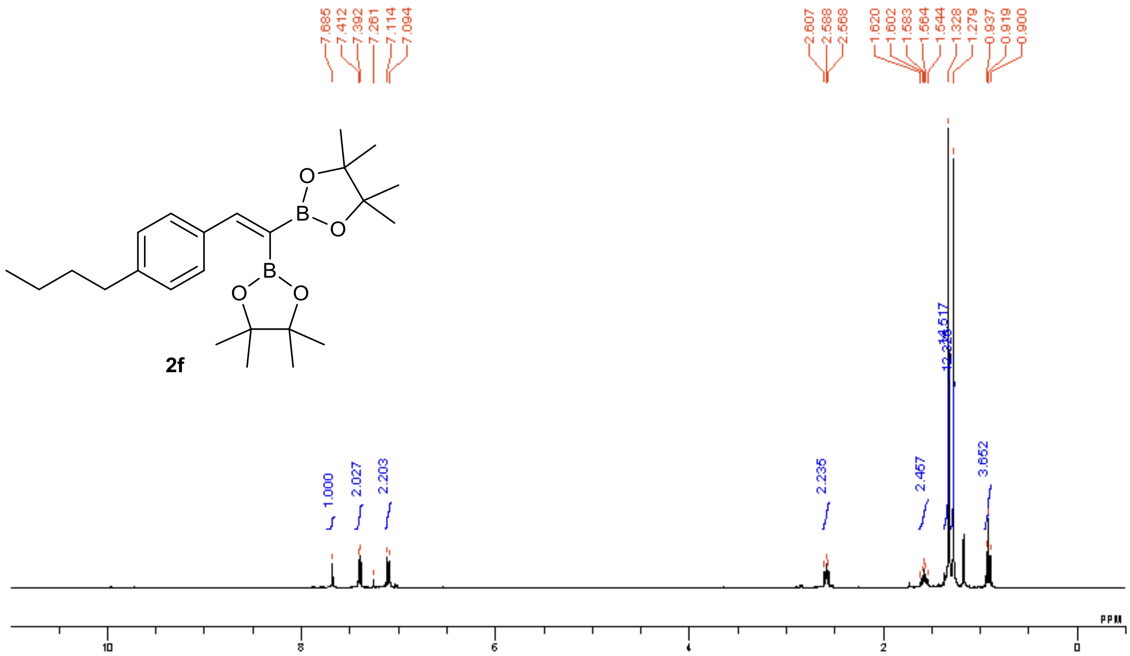

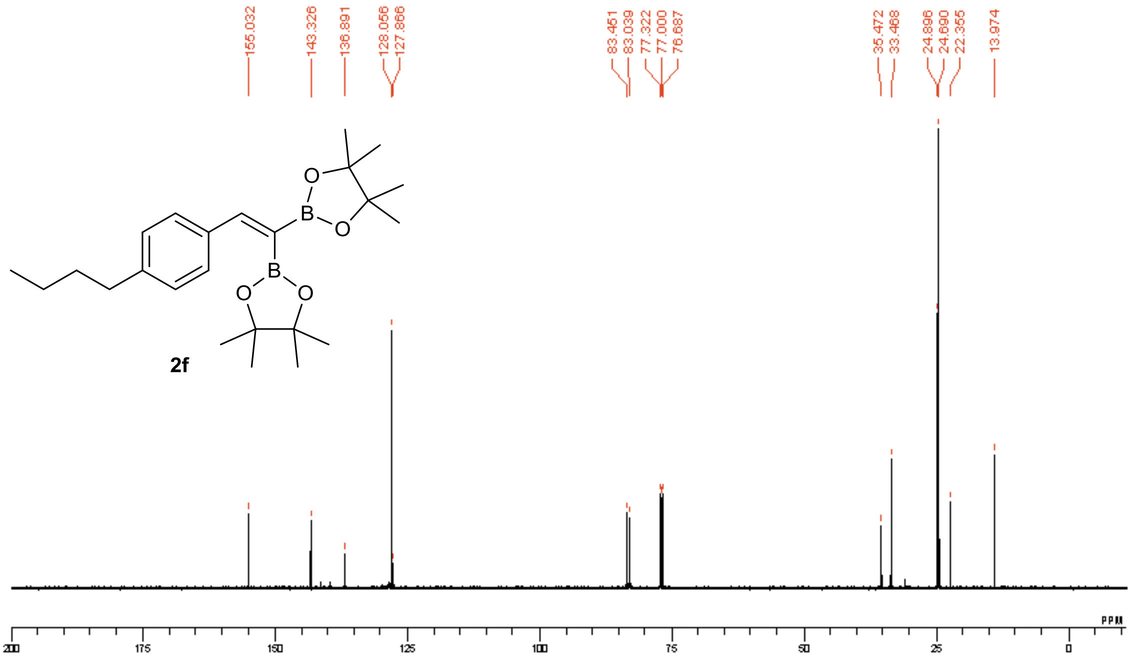

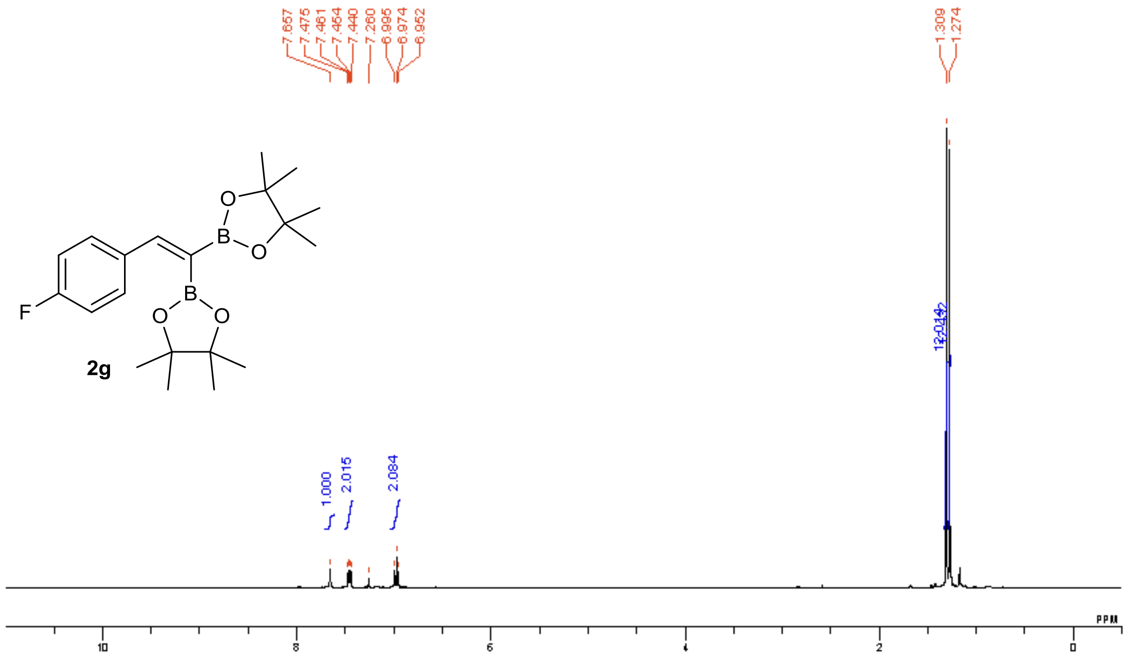
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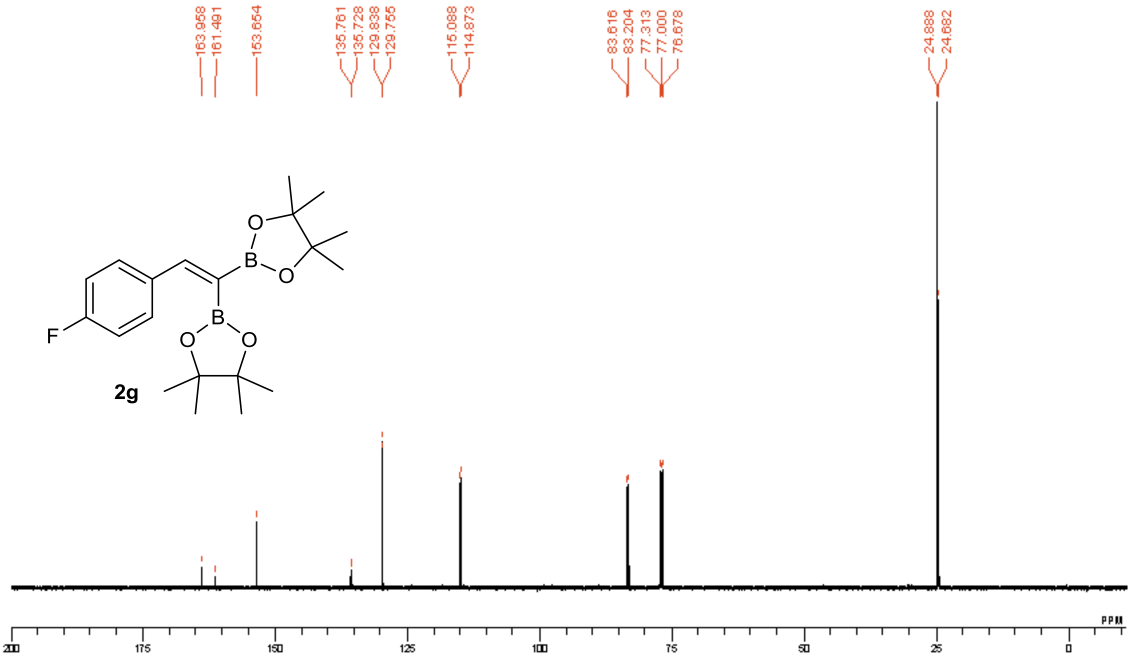
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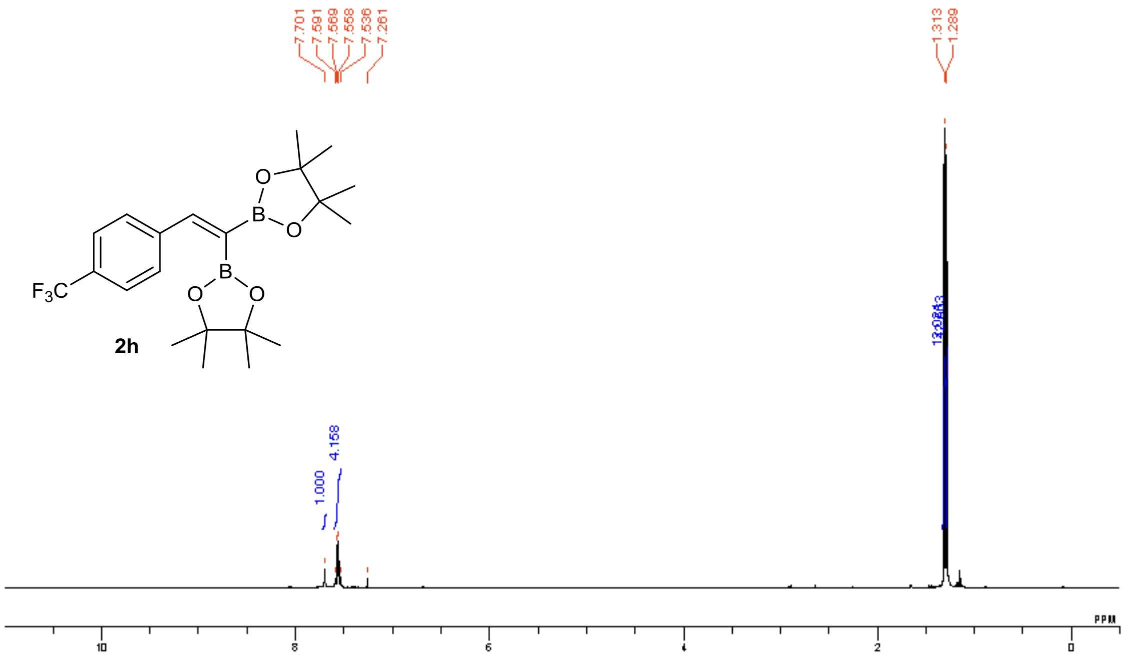

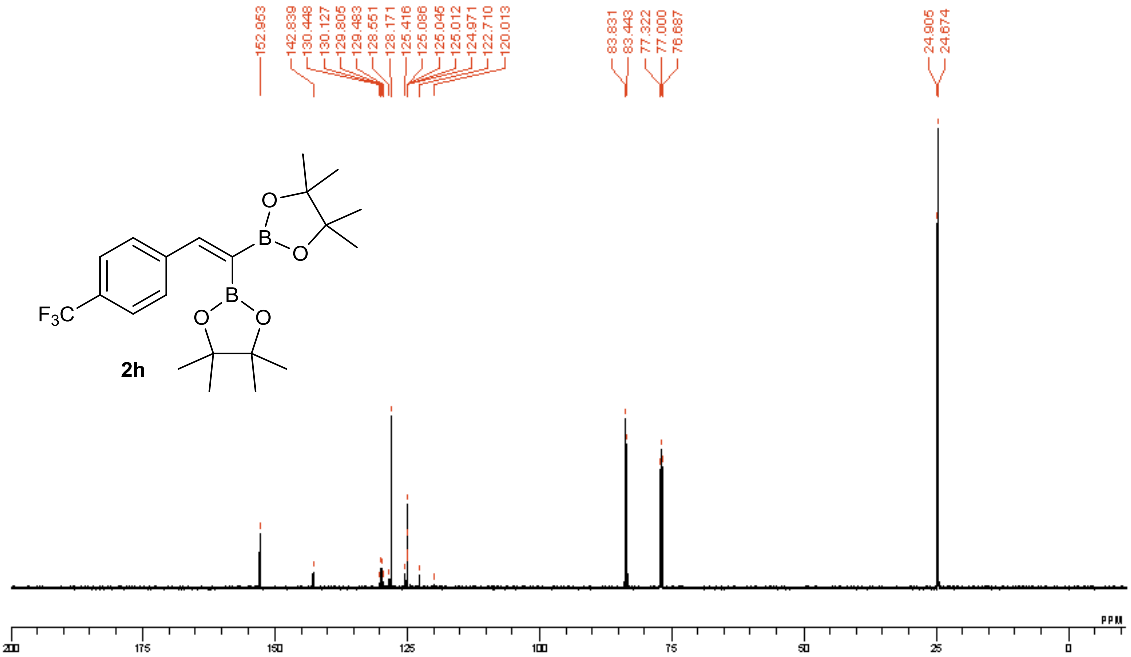

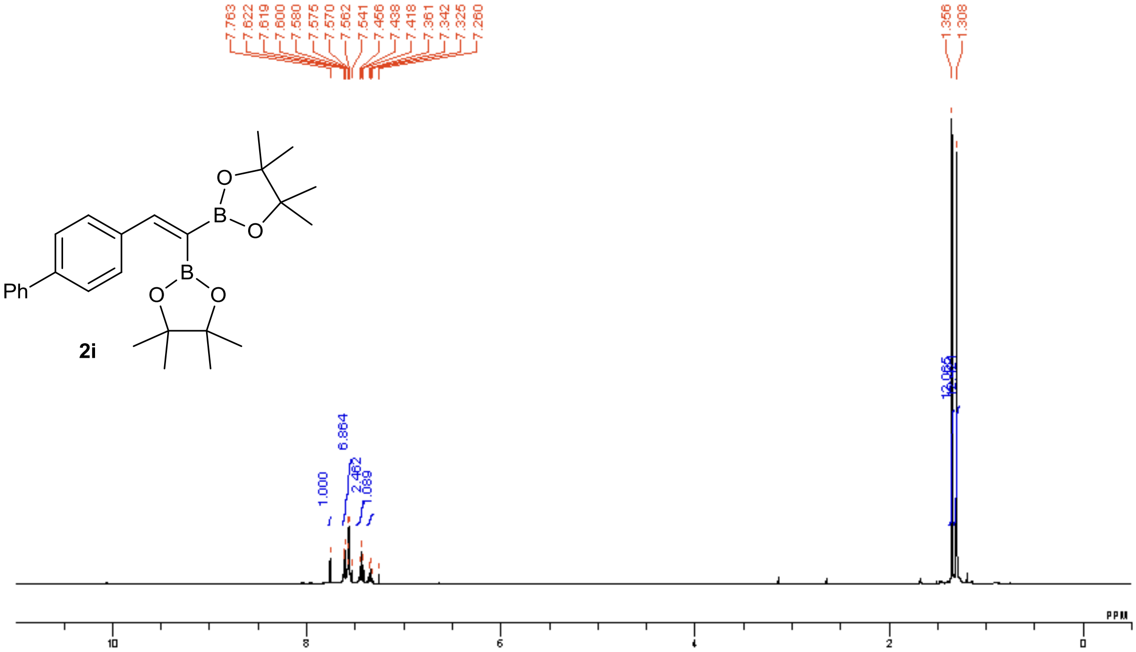
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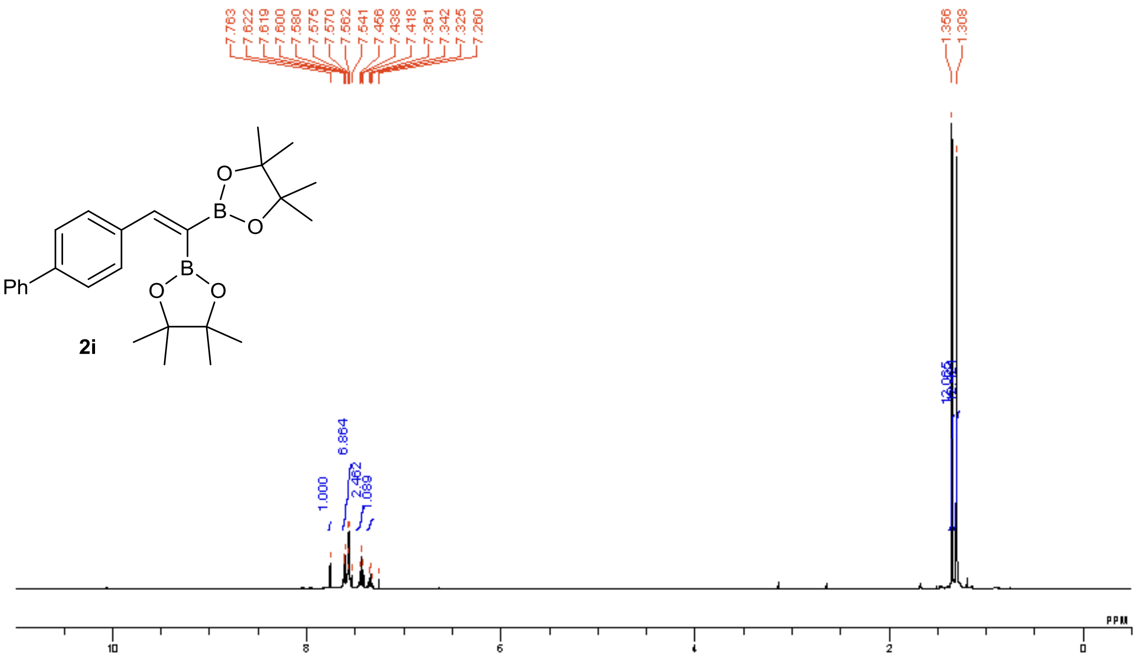
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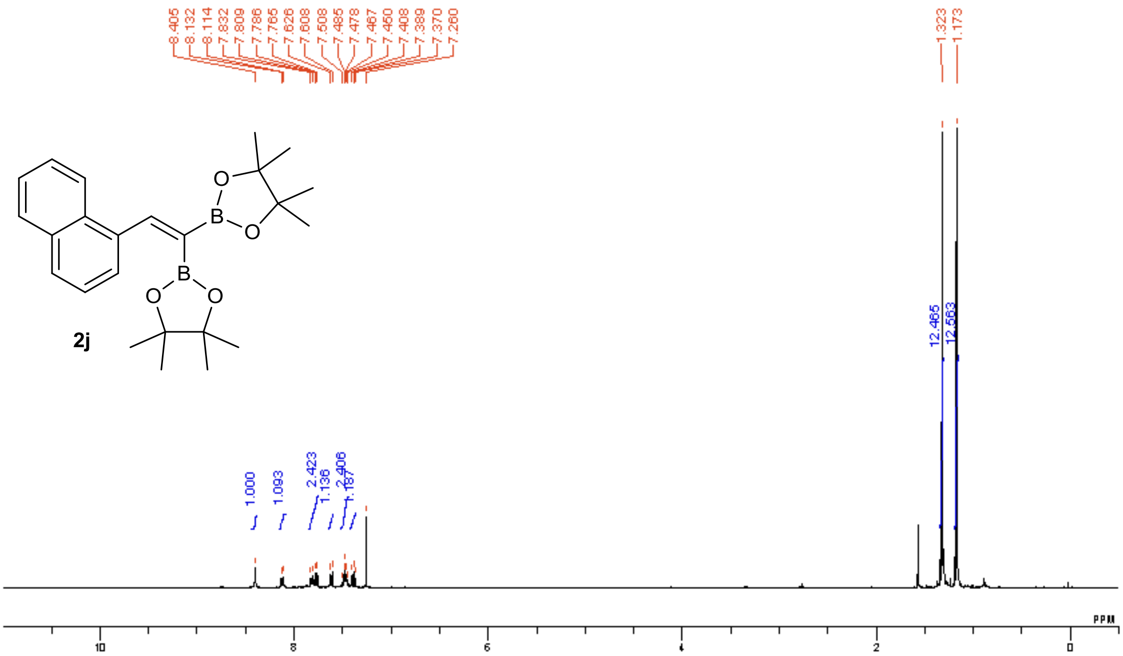

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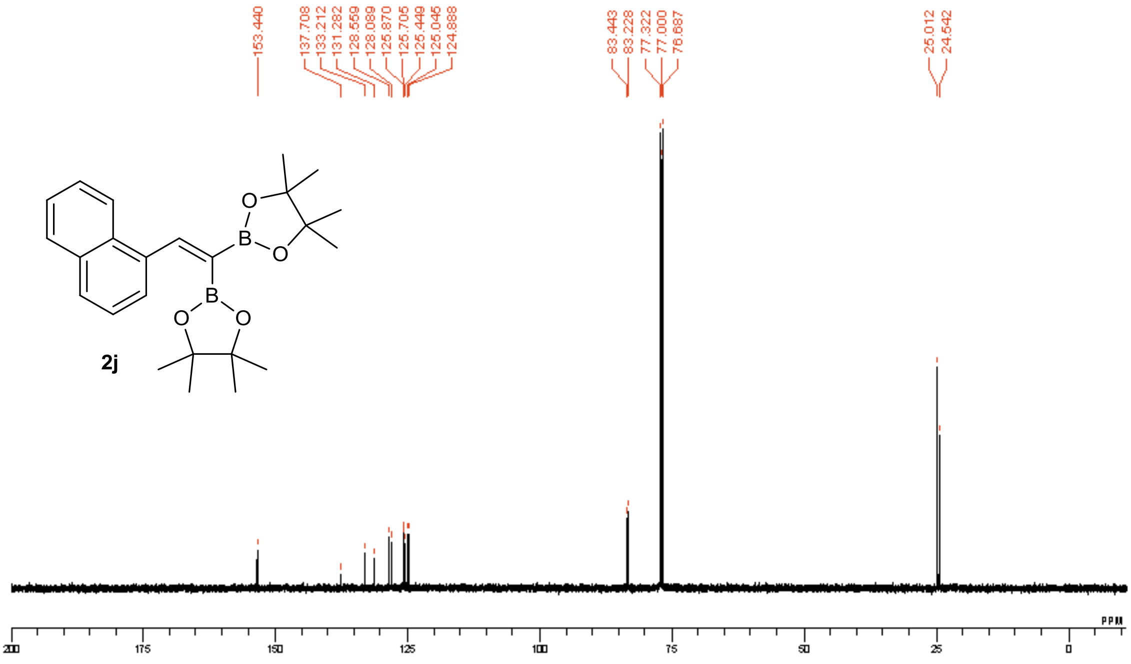

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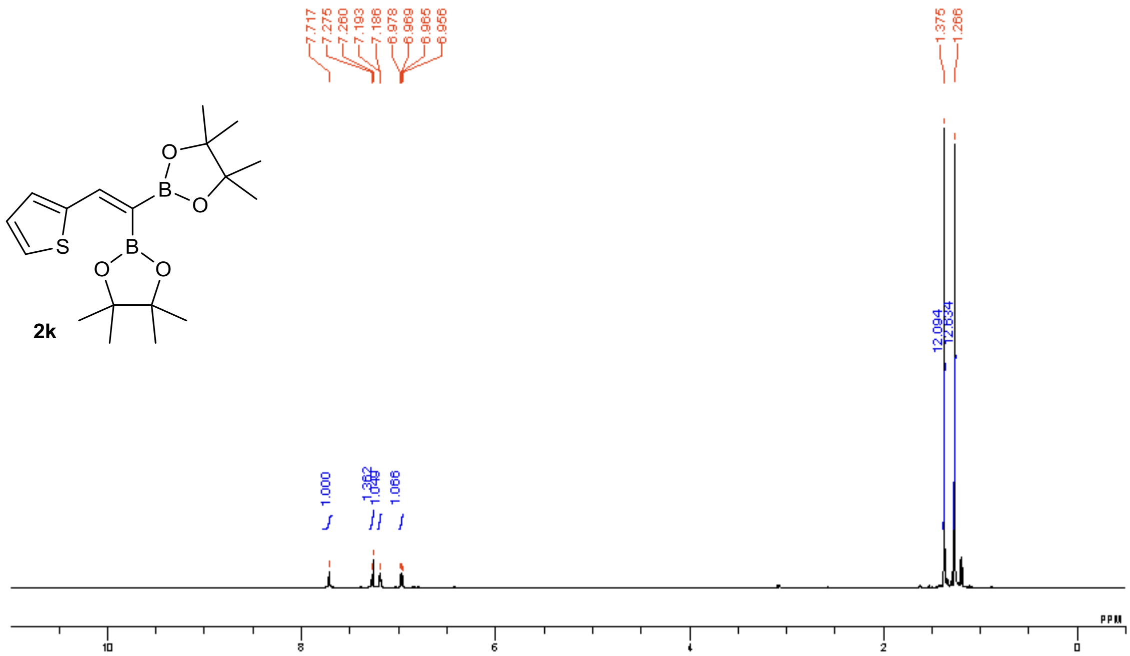
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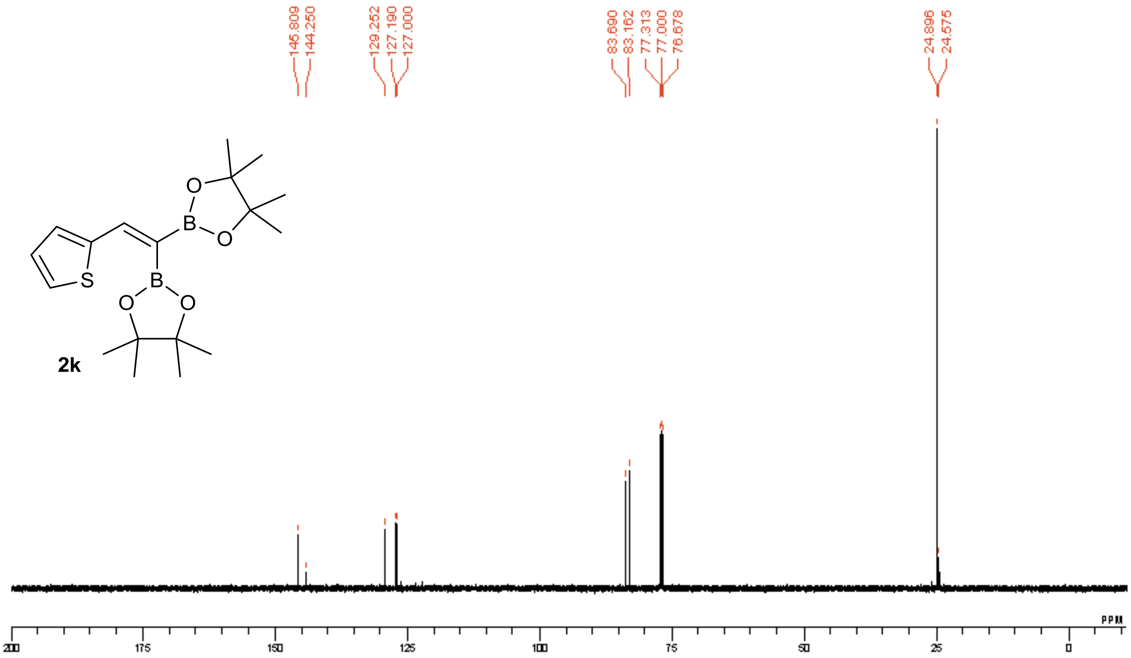
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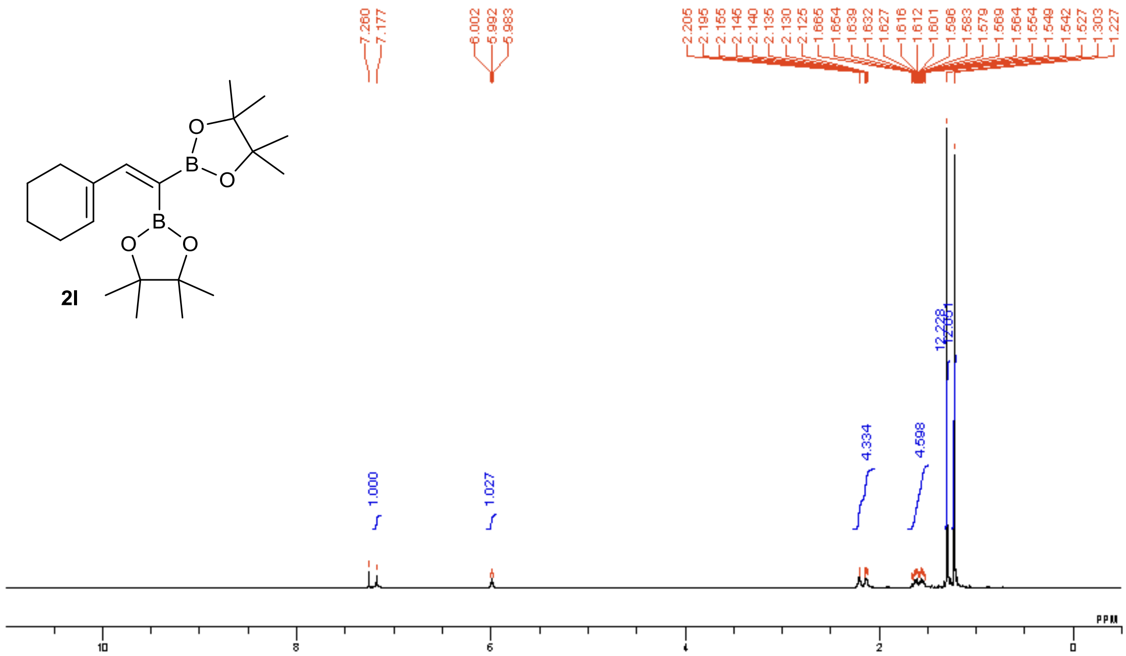
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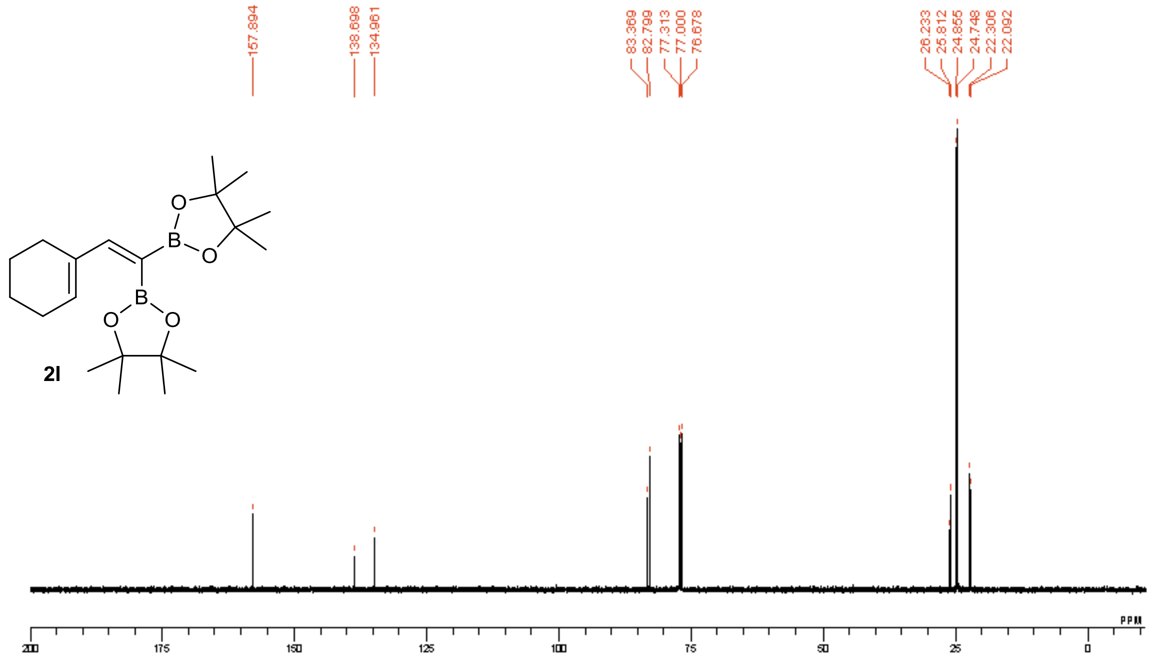
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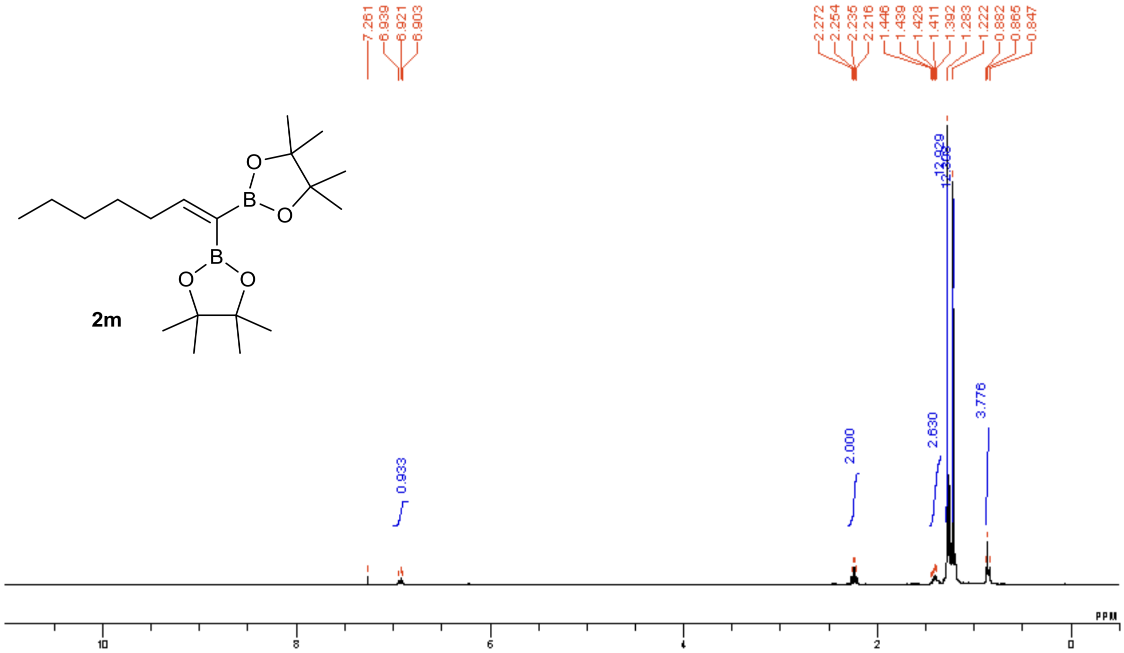

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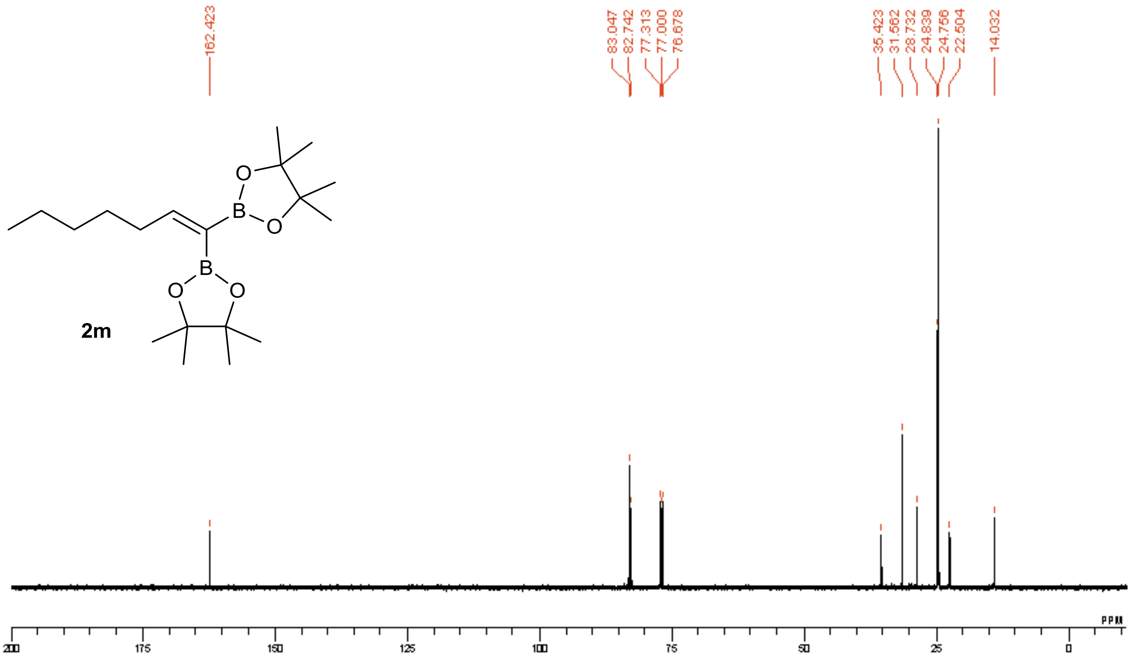

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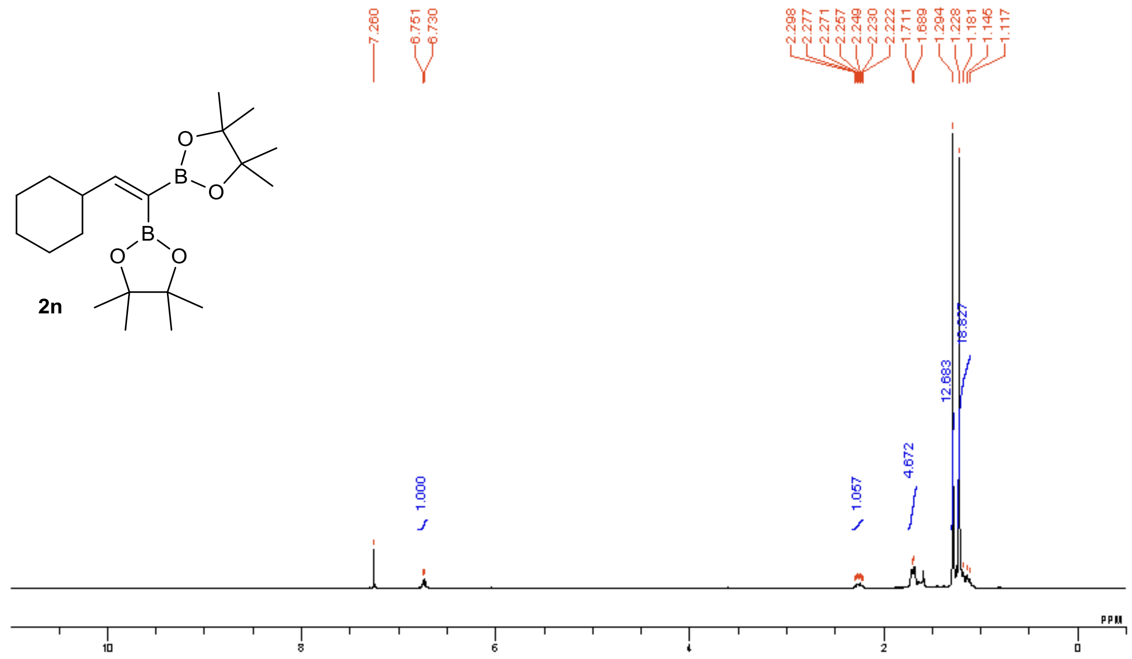

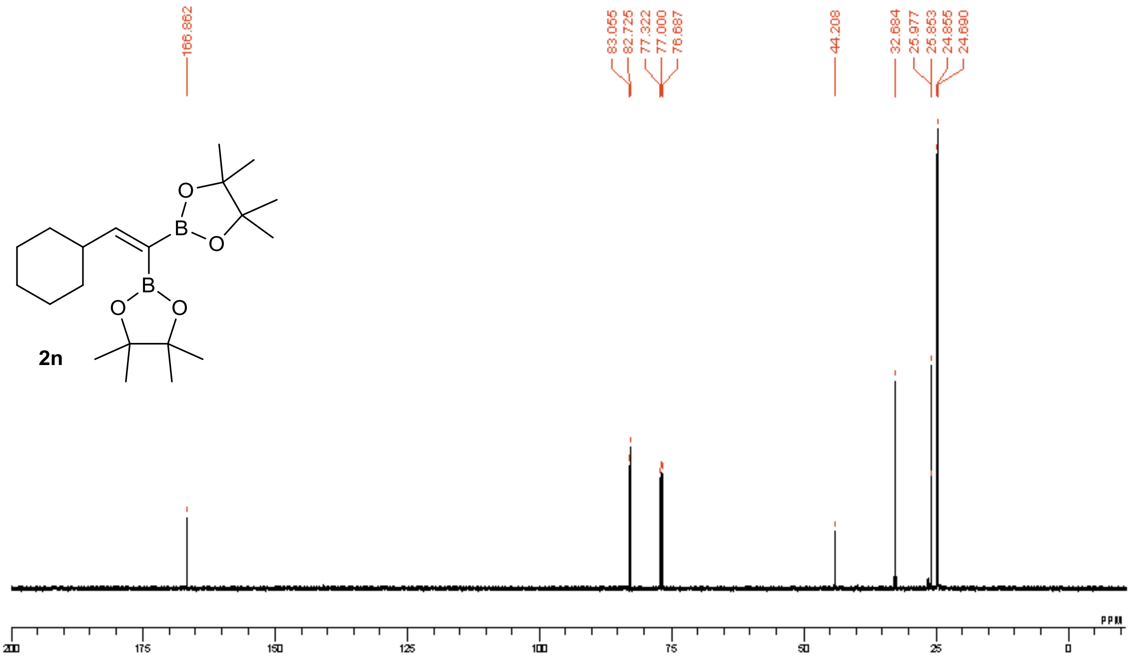

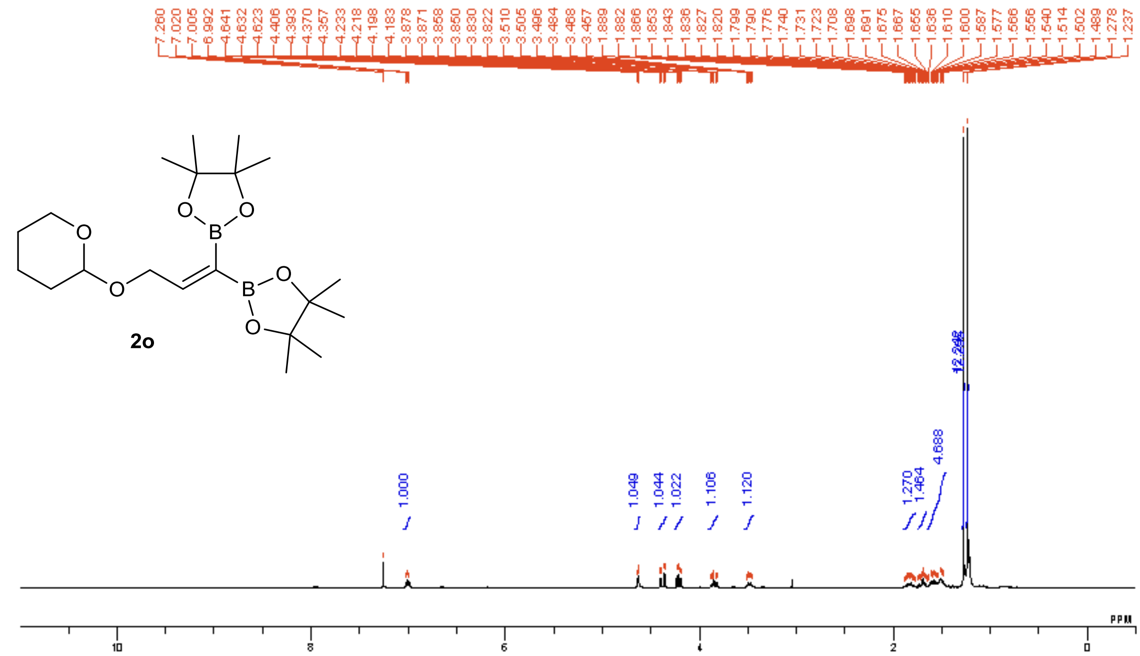
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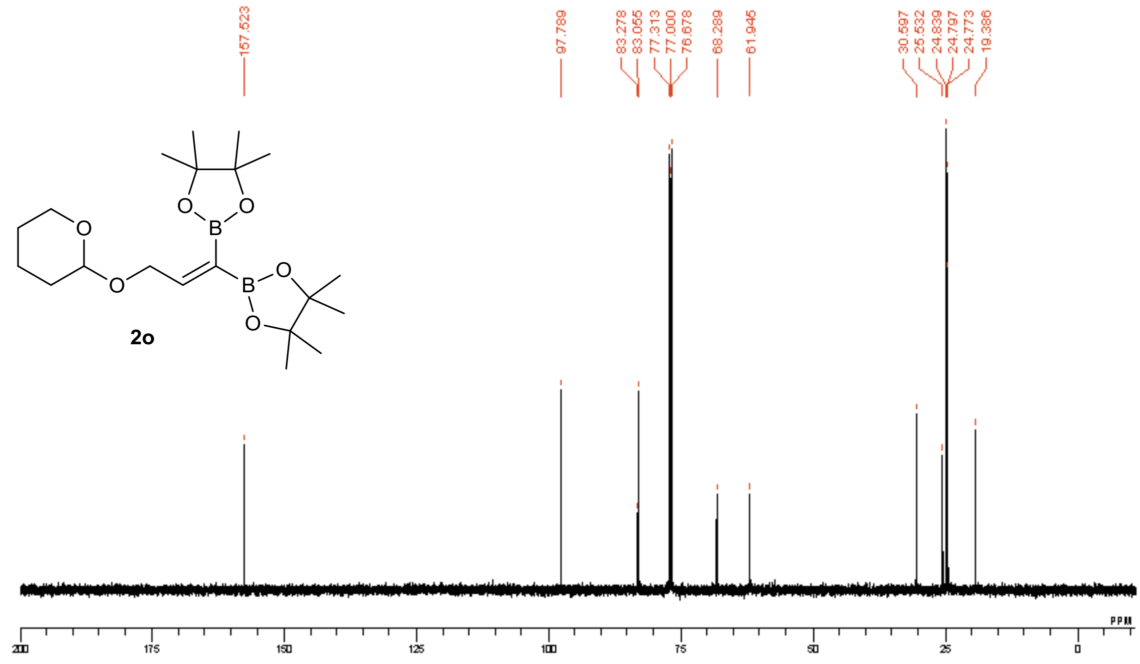
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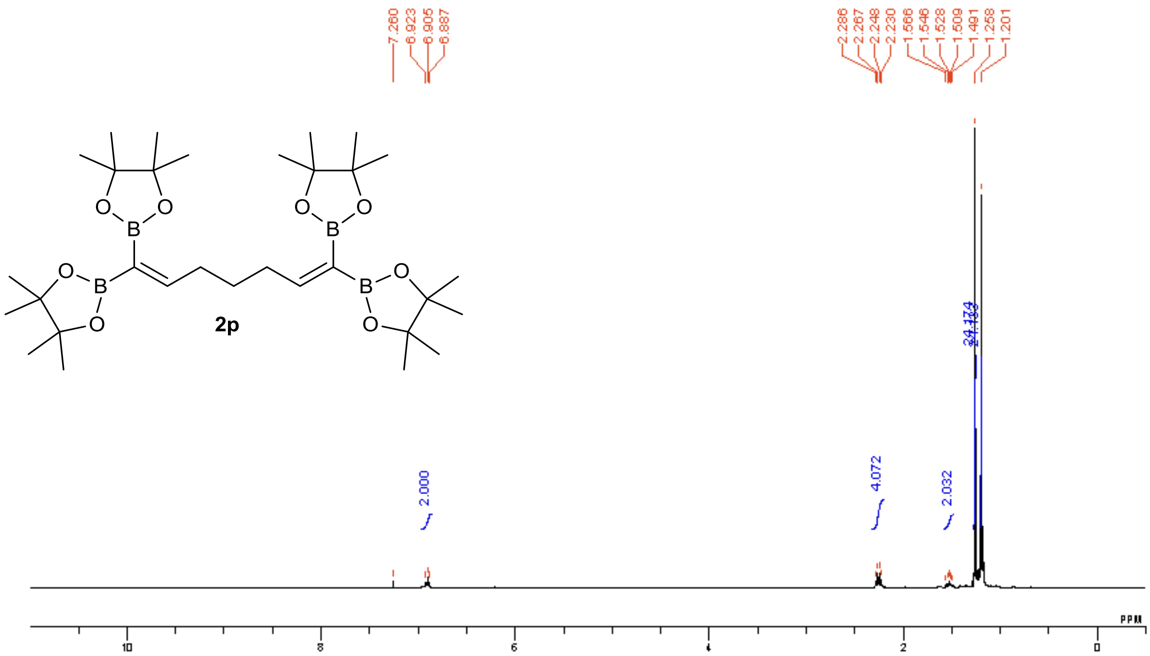

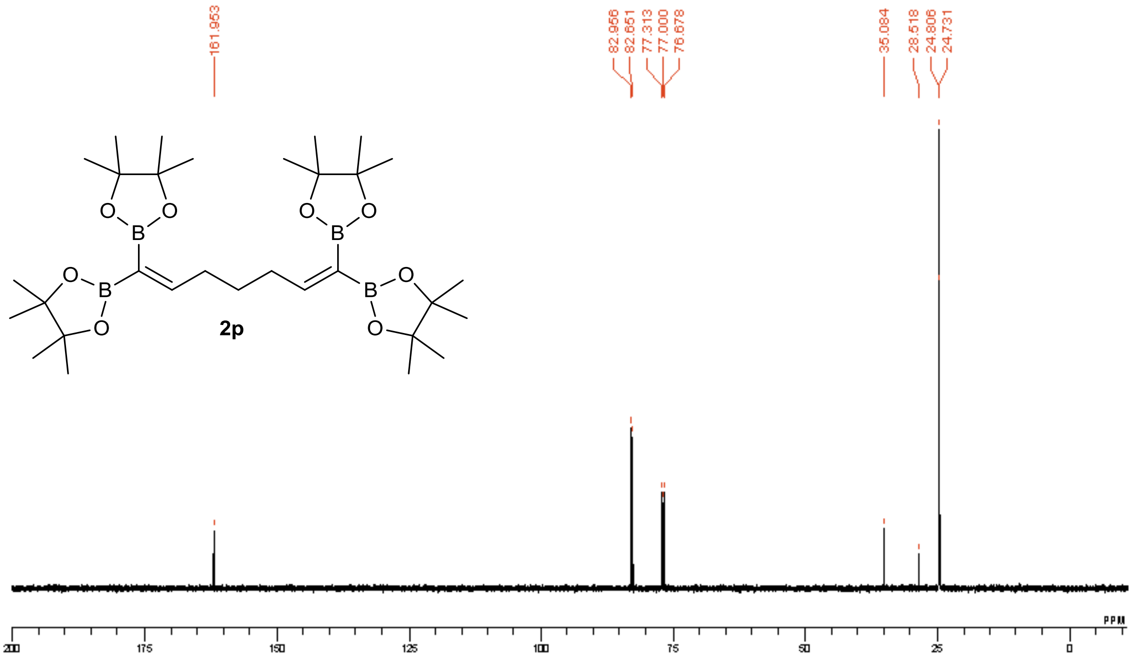

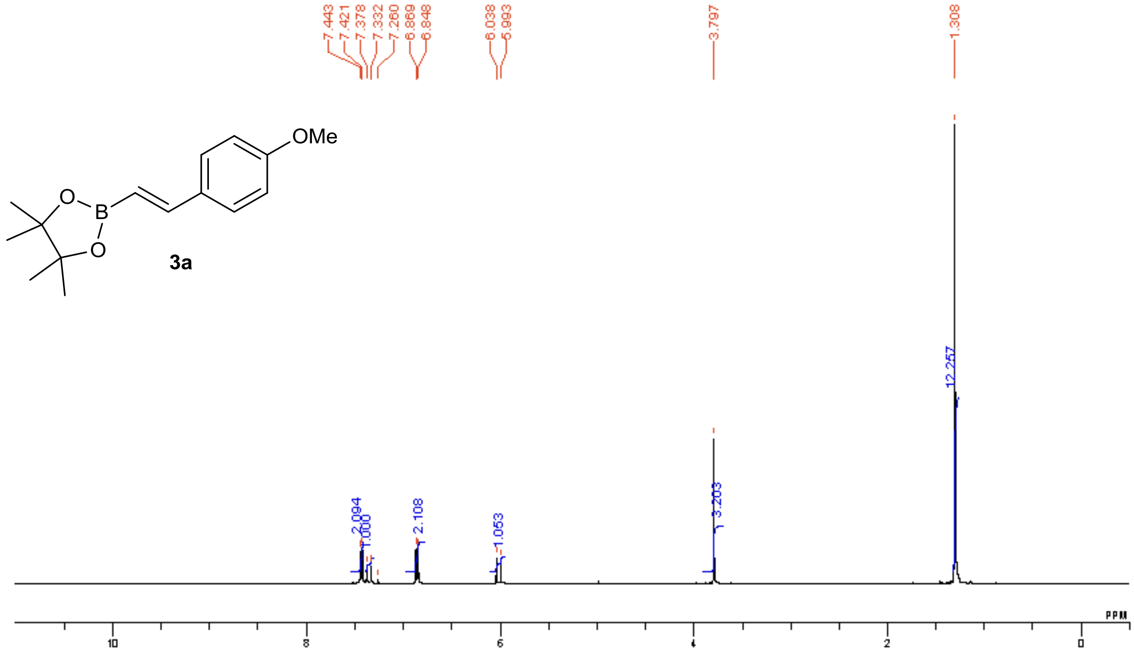

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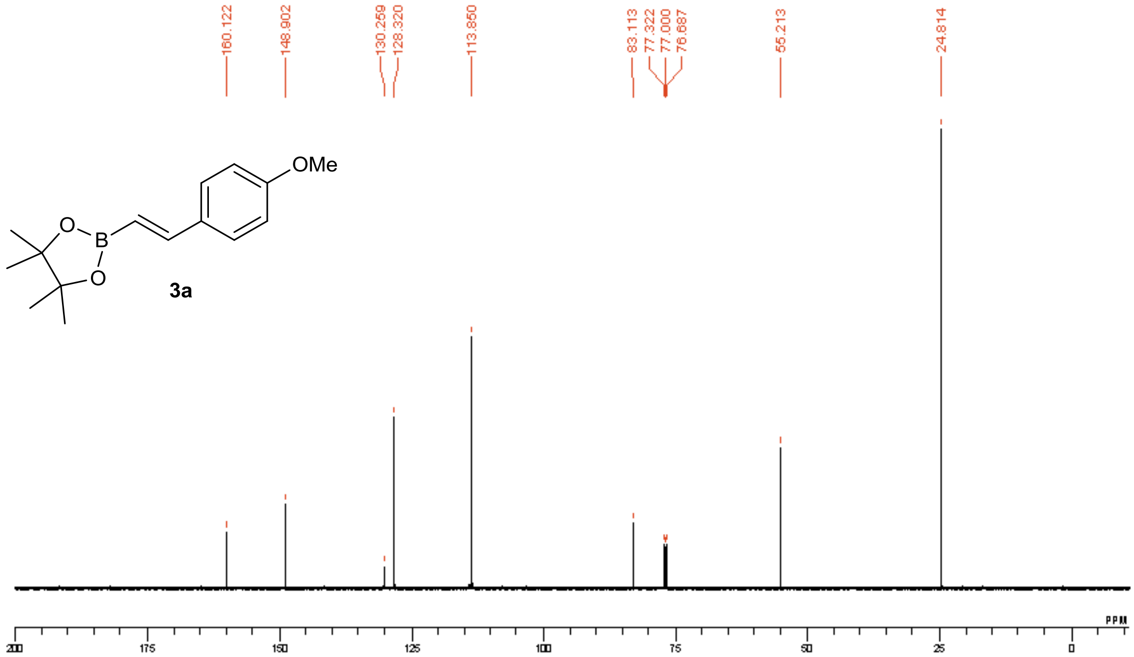

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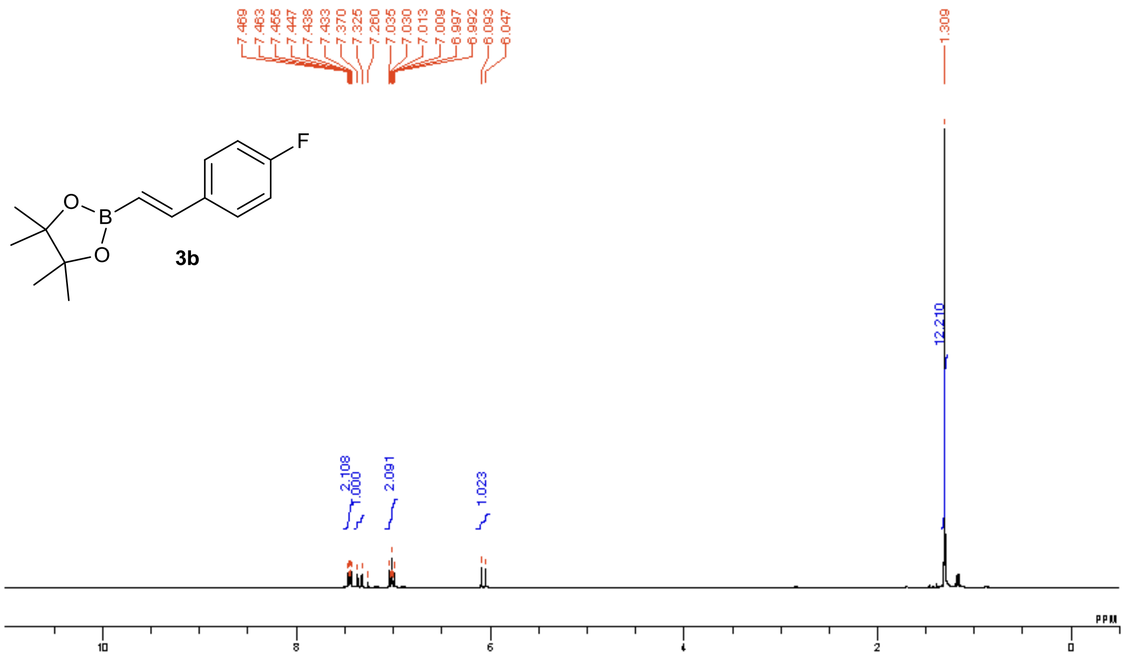
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7.013
7.009
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6.047
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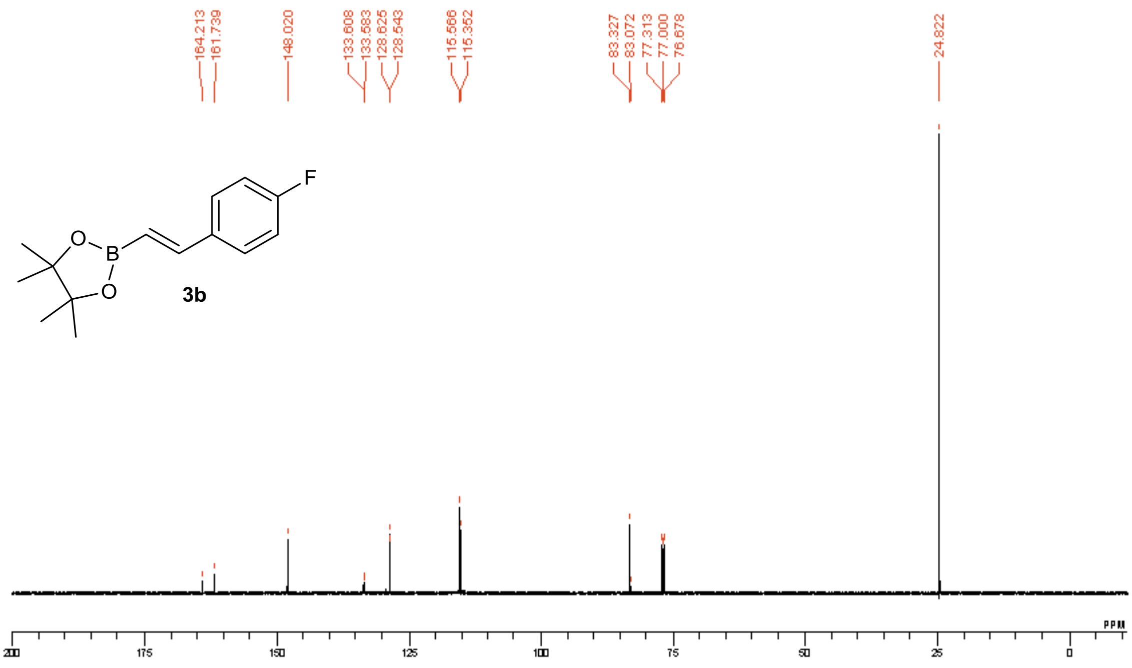
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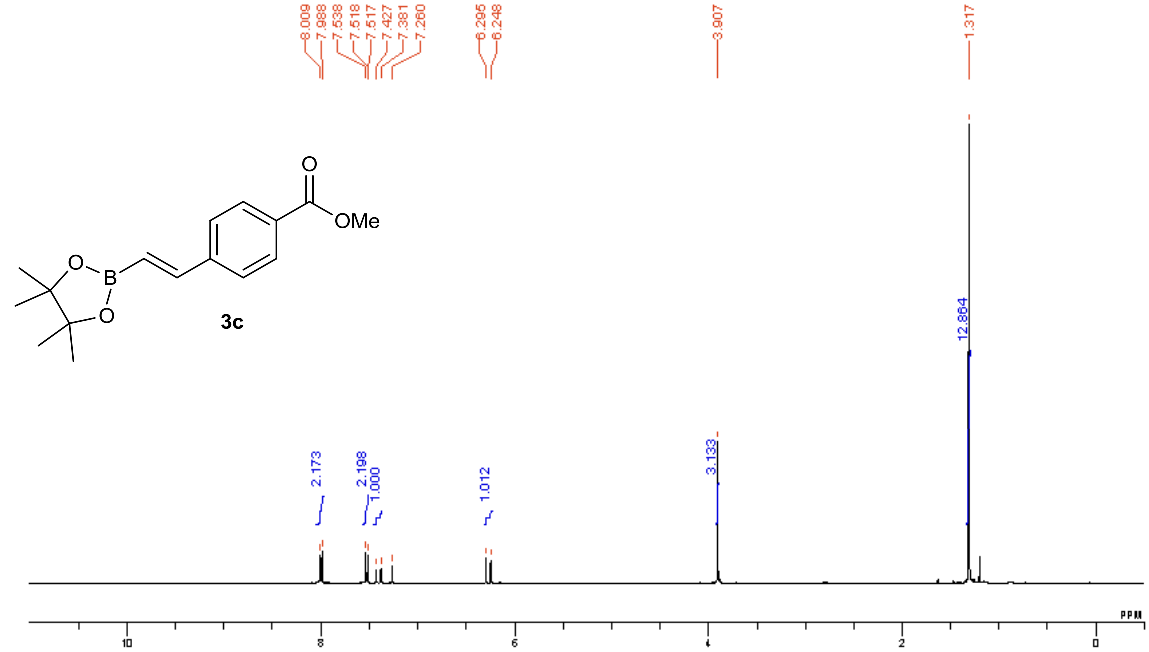
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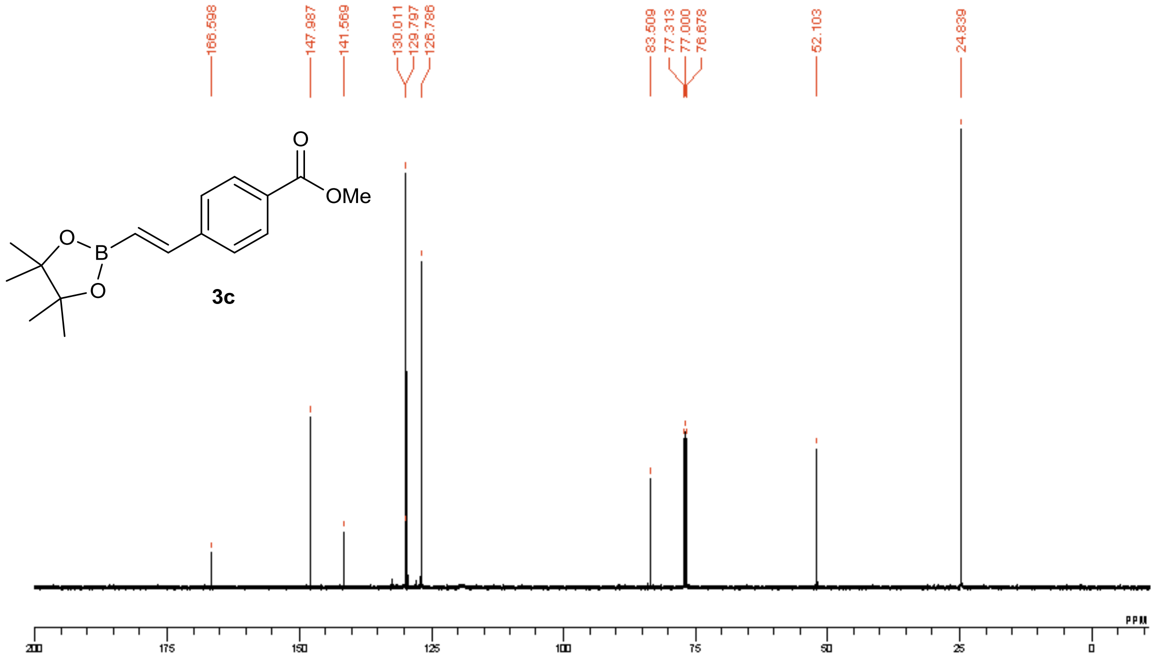
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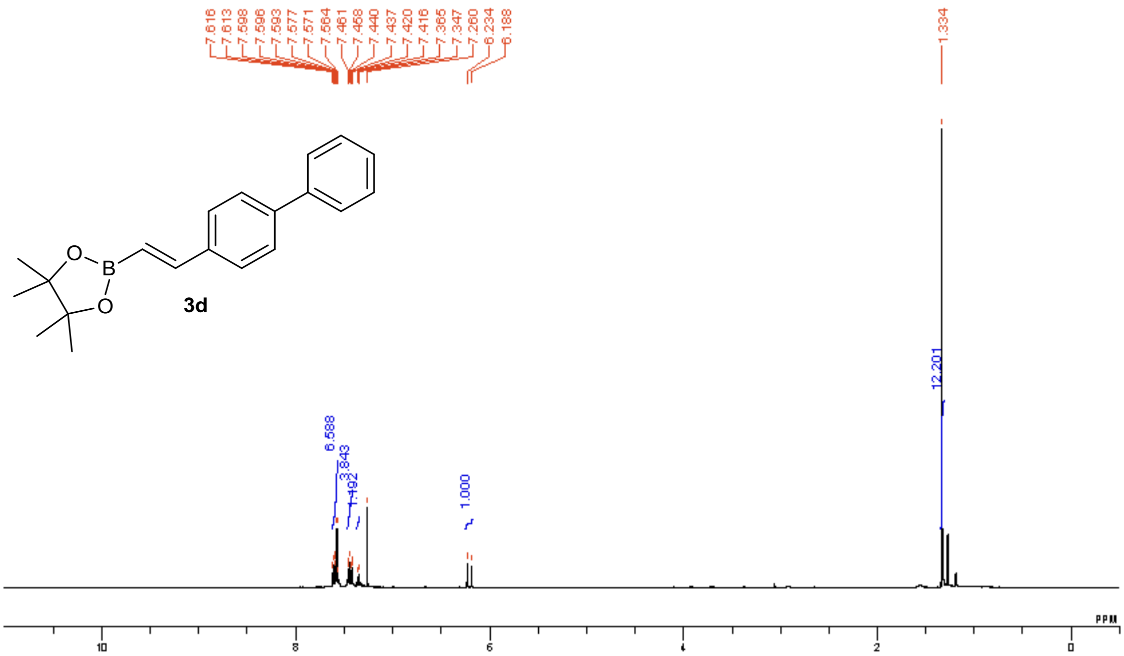
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7.420
7.416
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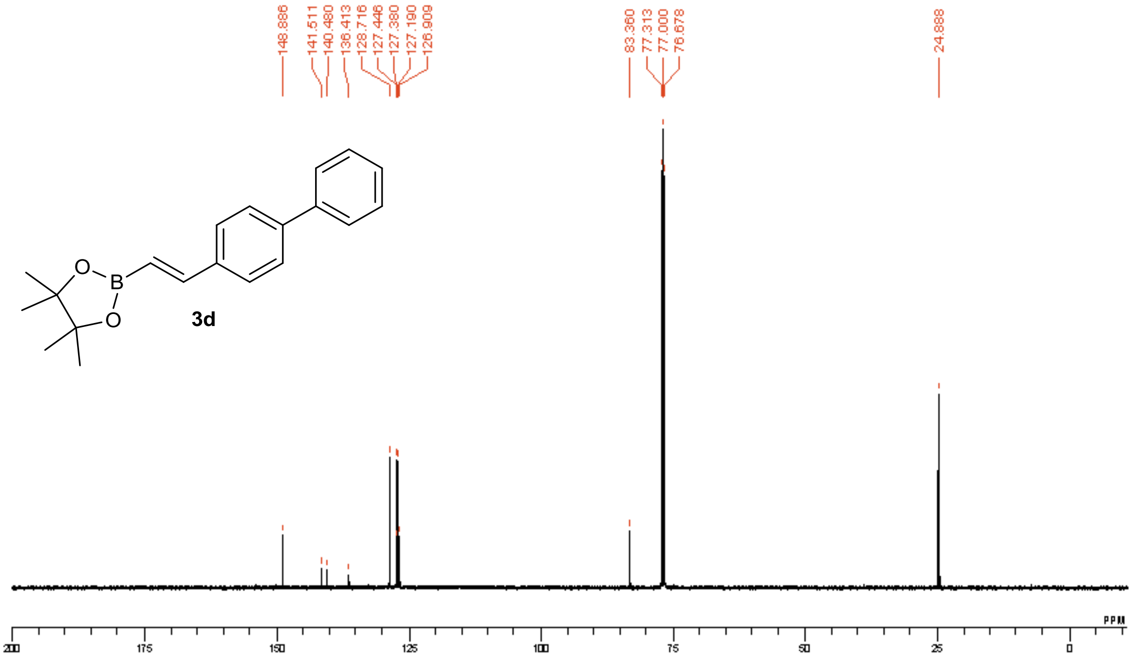
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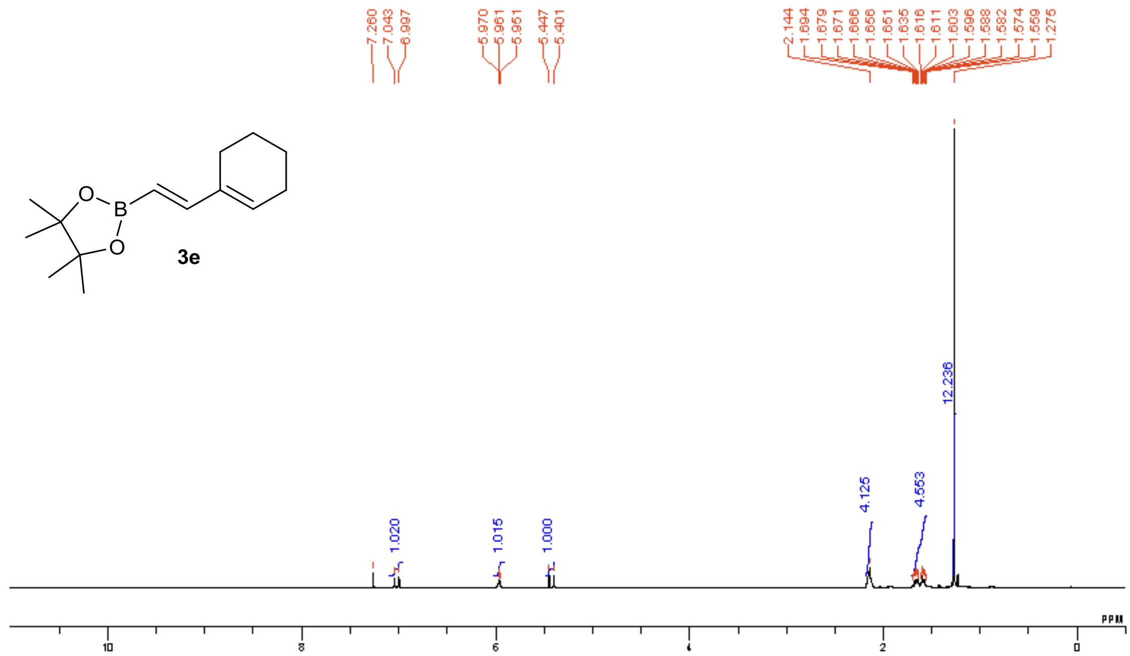

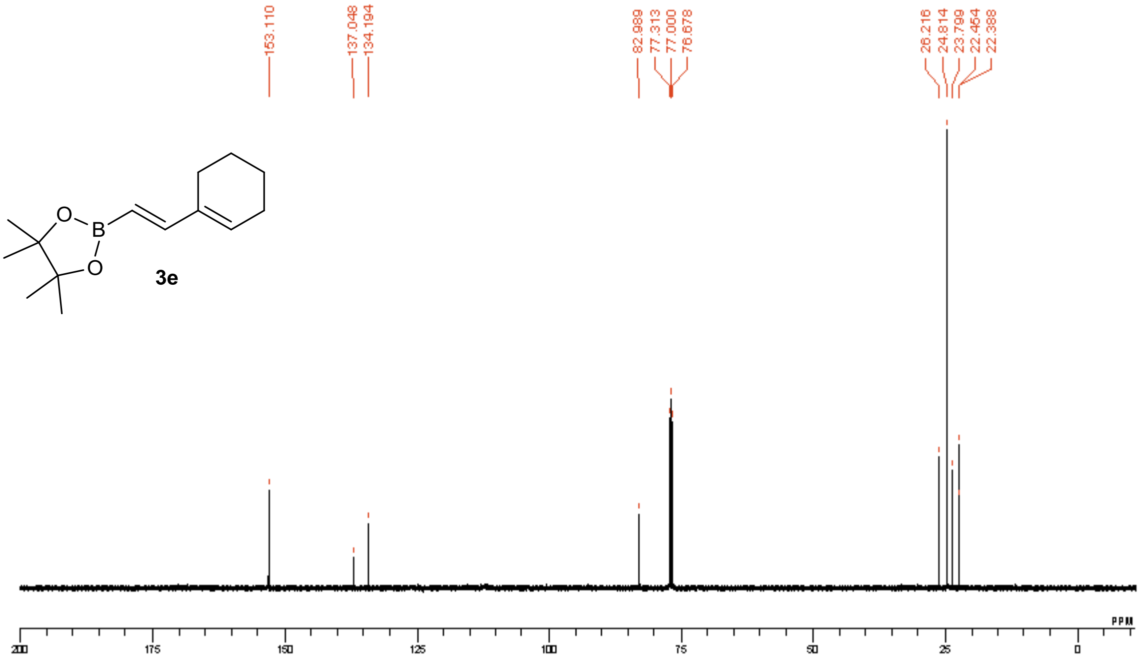

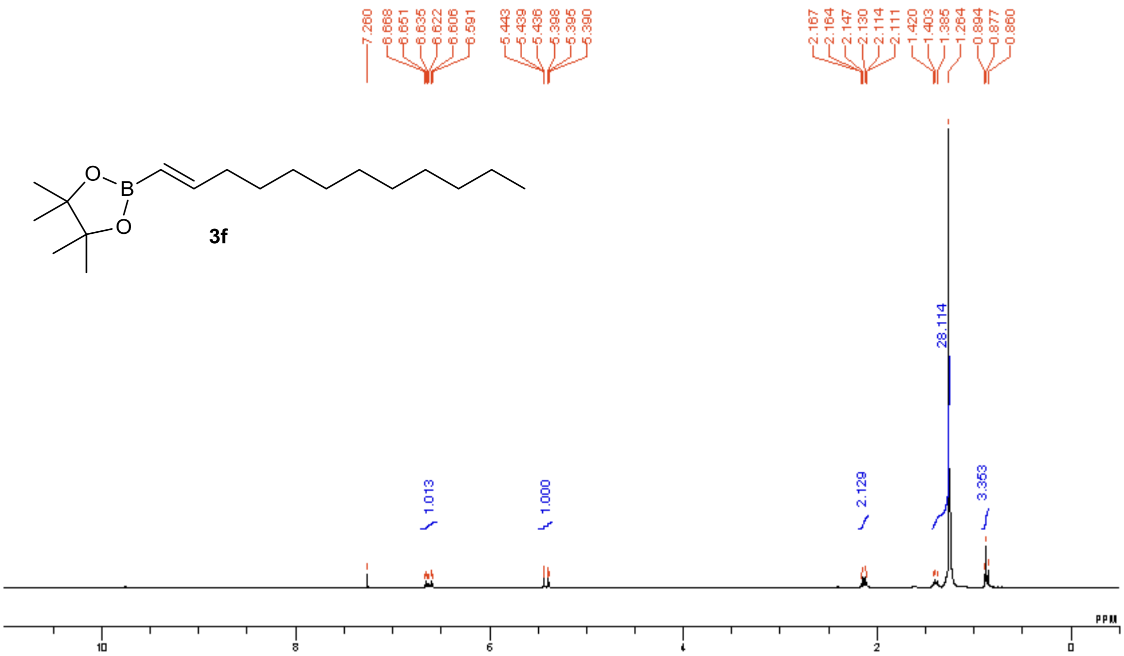
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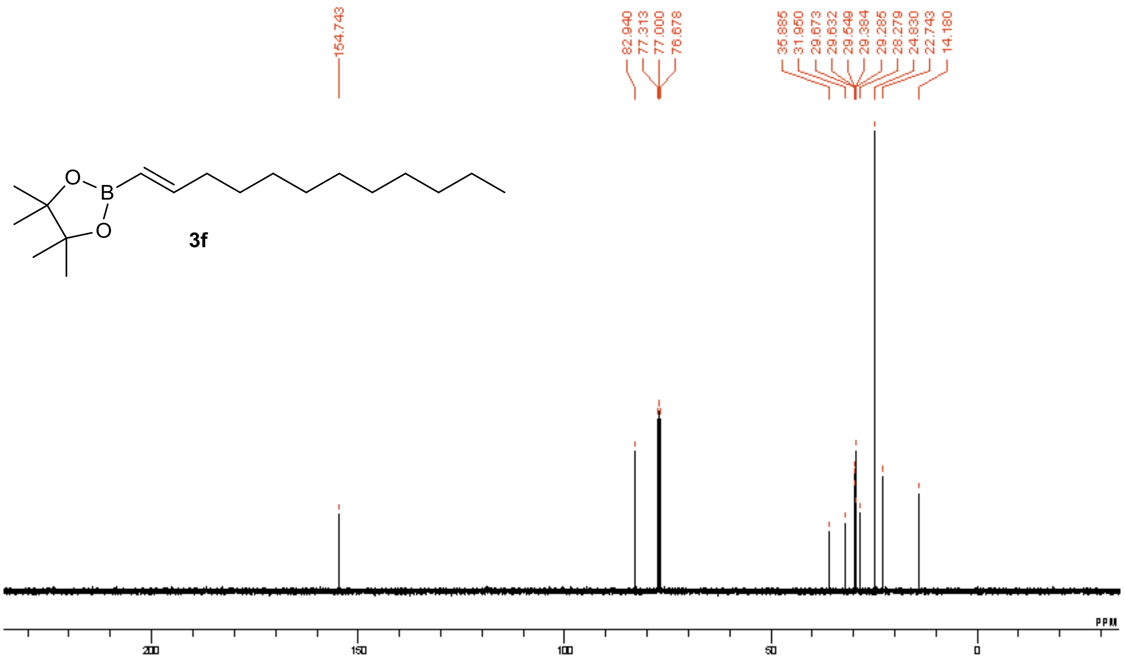
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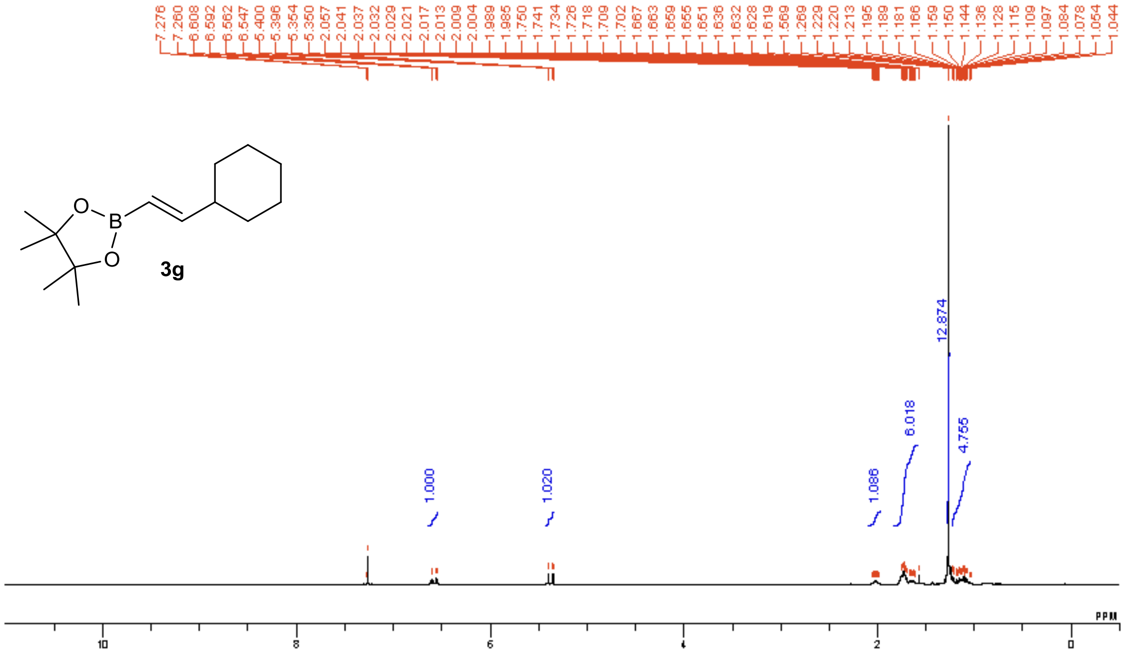
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2.037
2.032
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2.021
2.017
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1.734
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1.632
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1.220
1.213
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1.166
1.159
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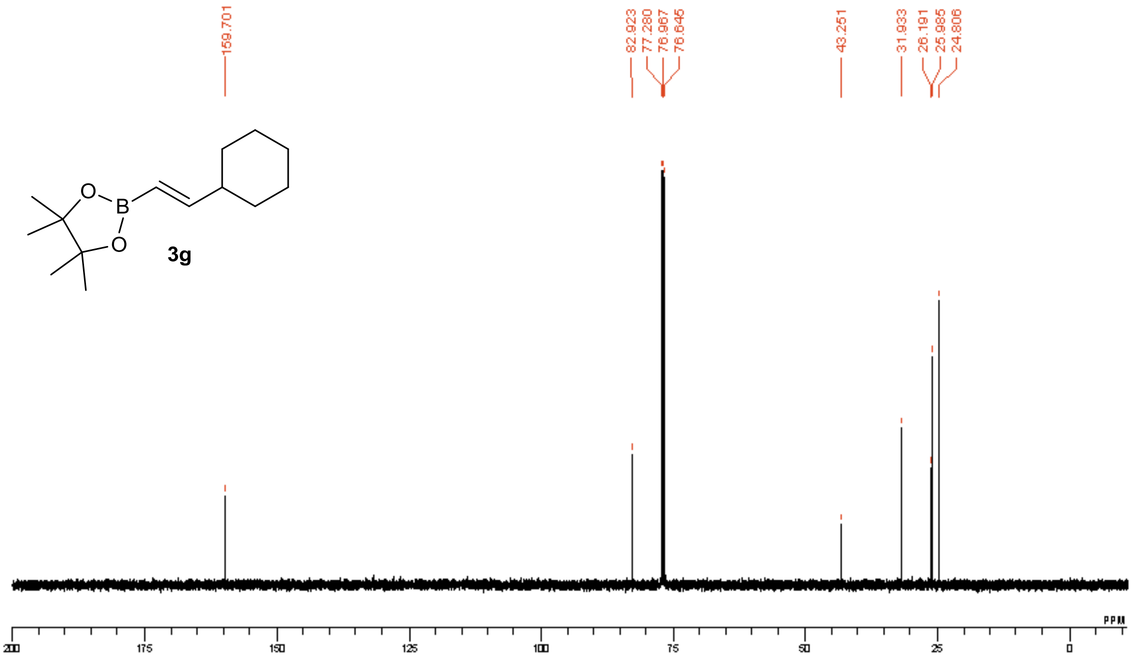
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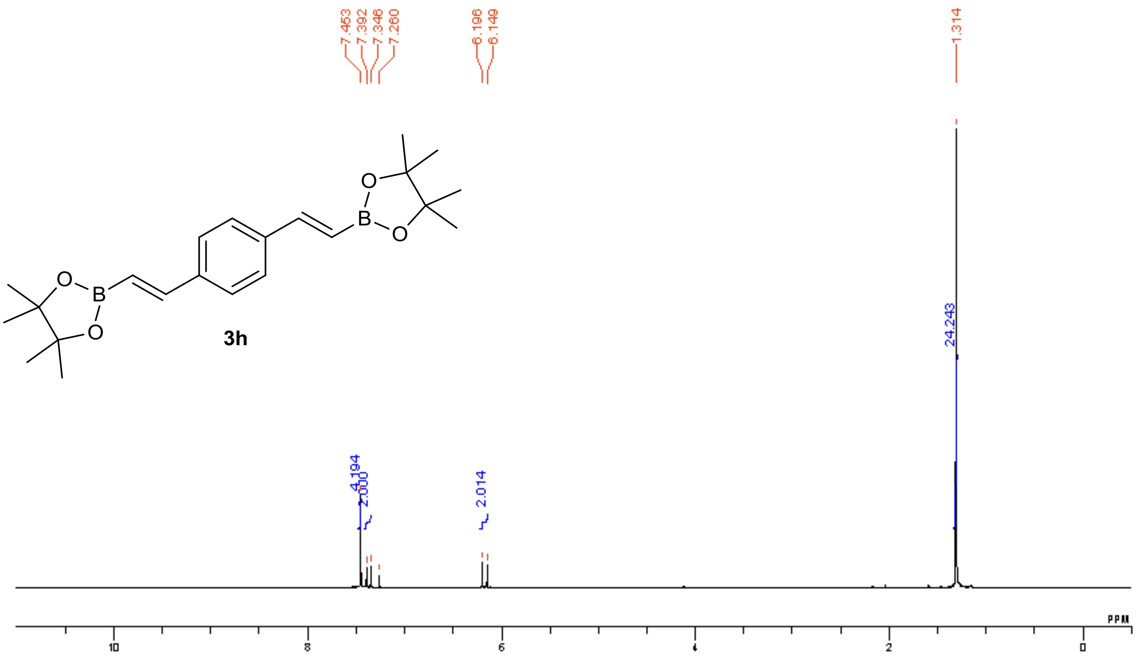
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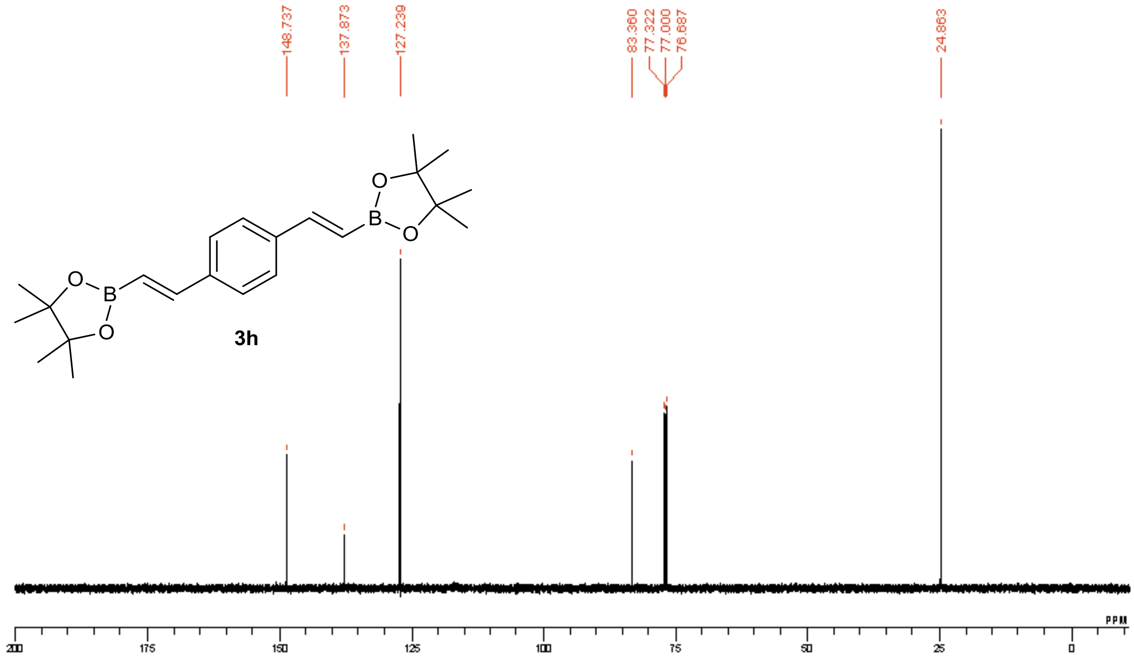
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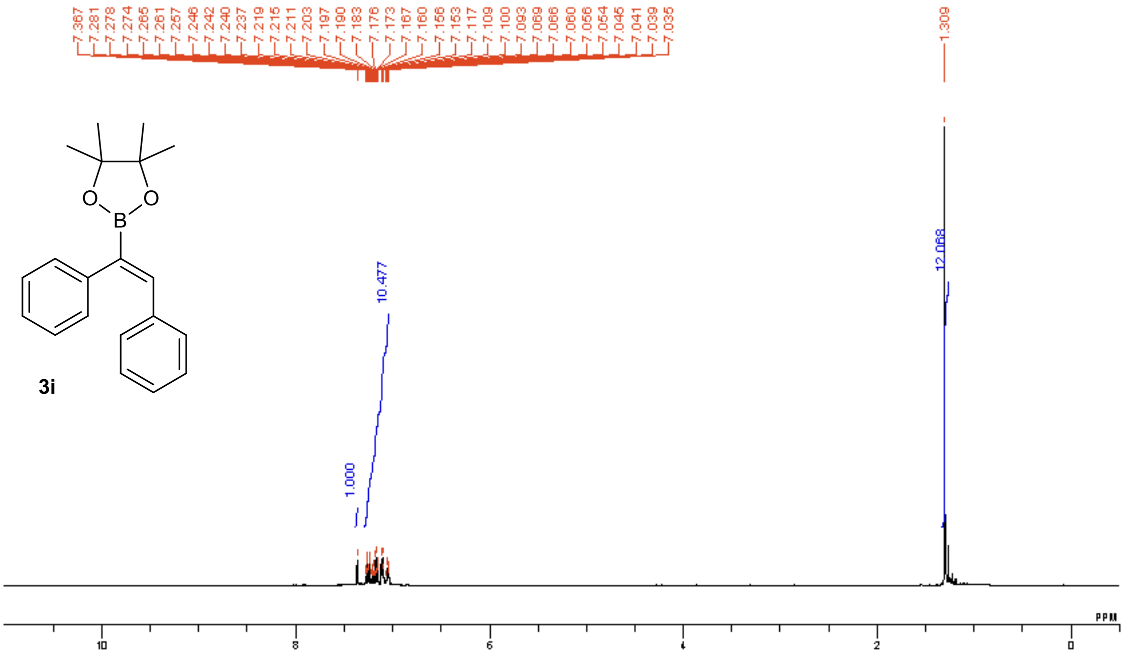
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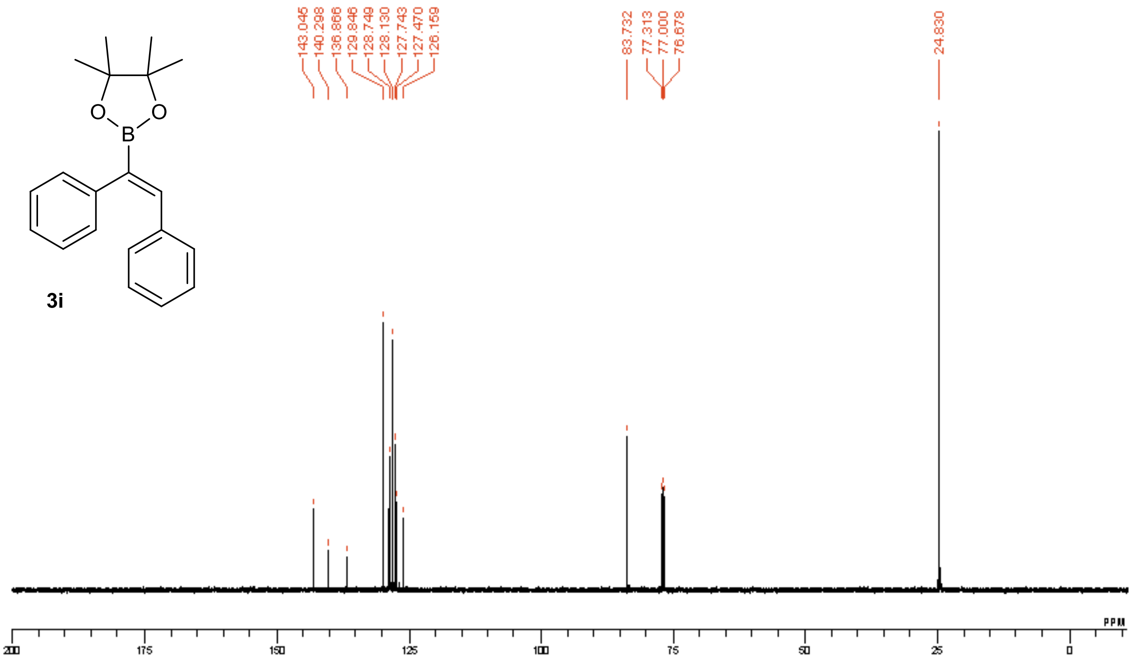
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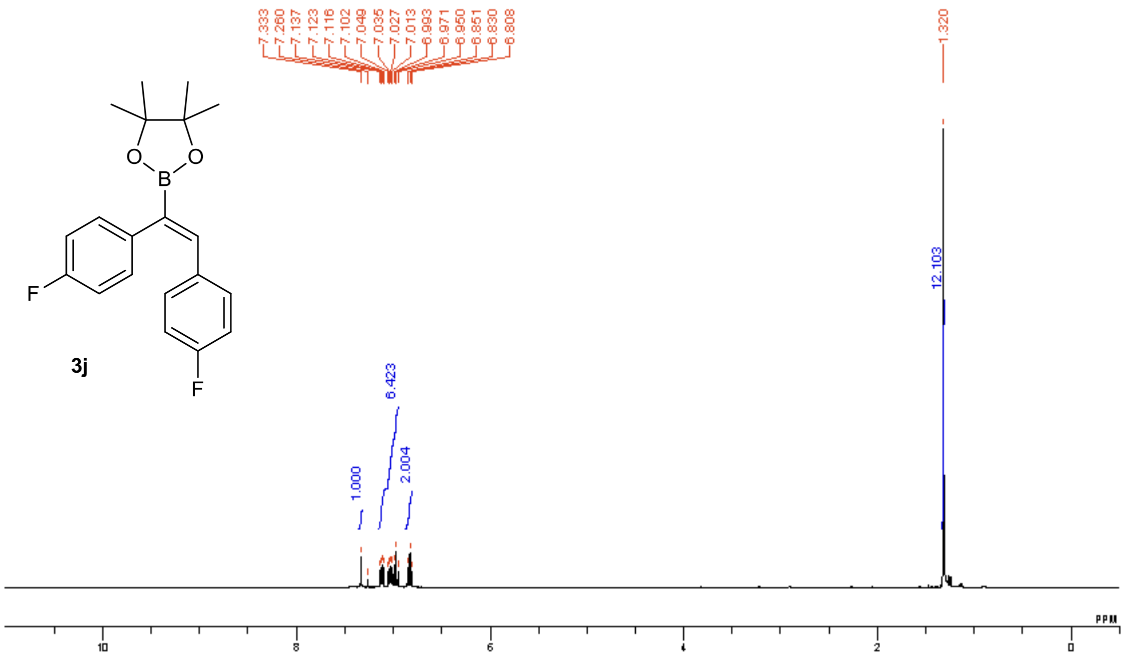
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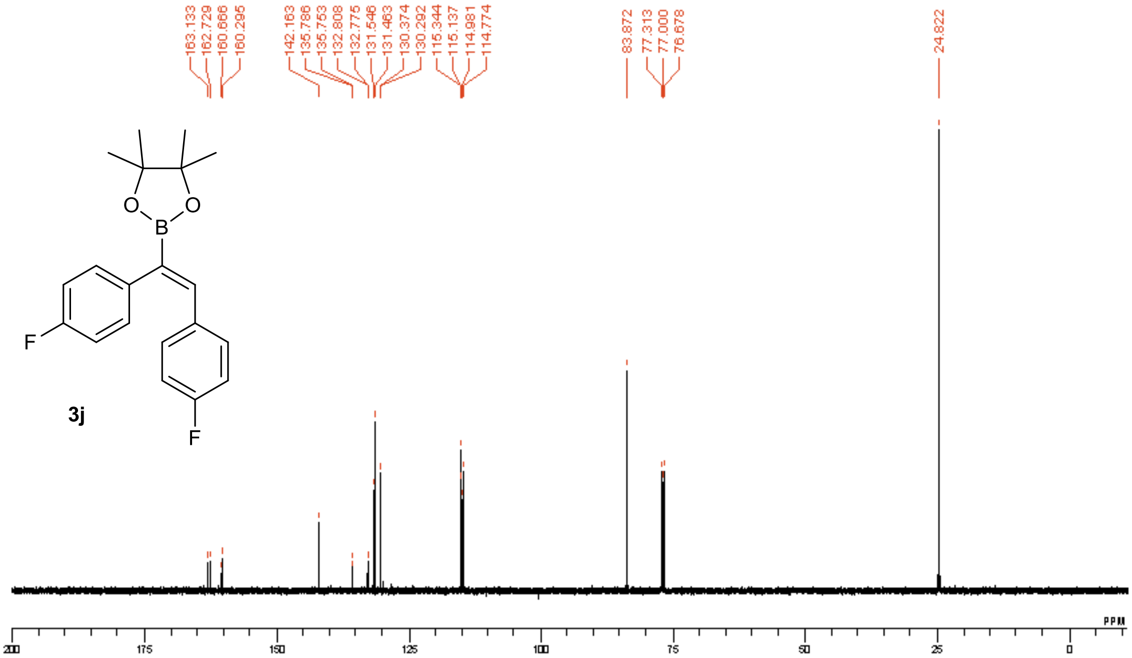
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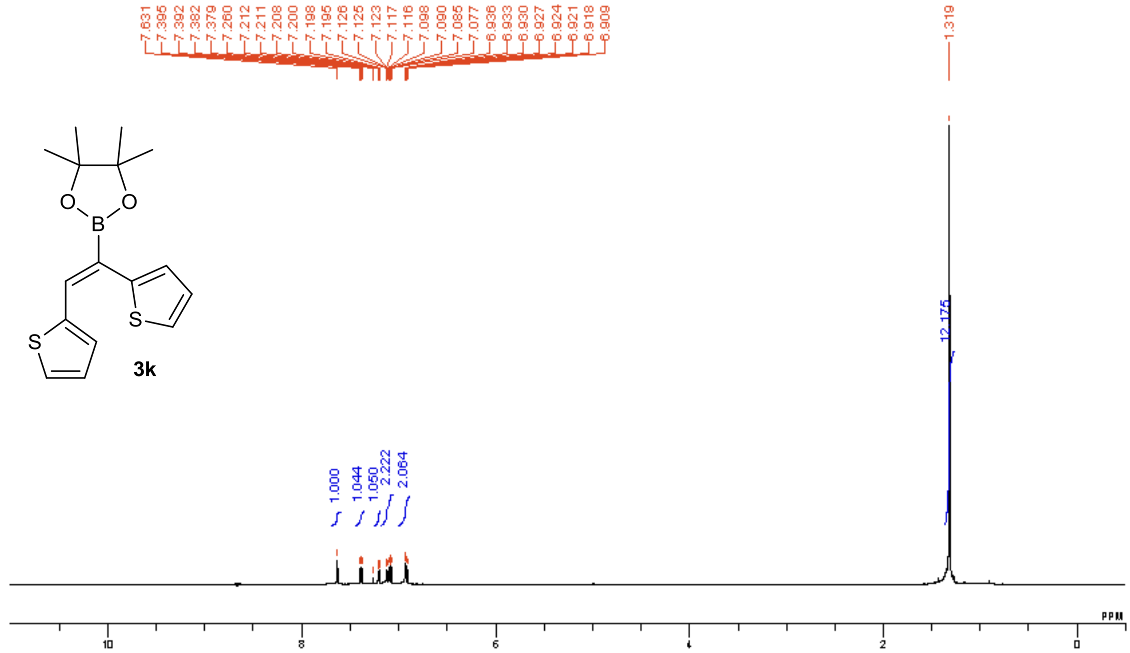
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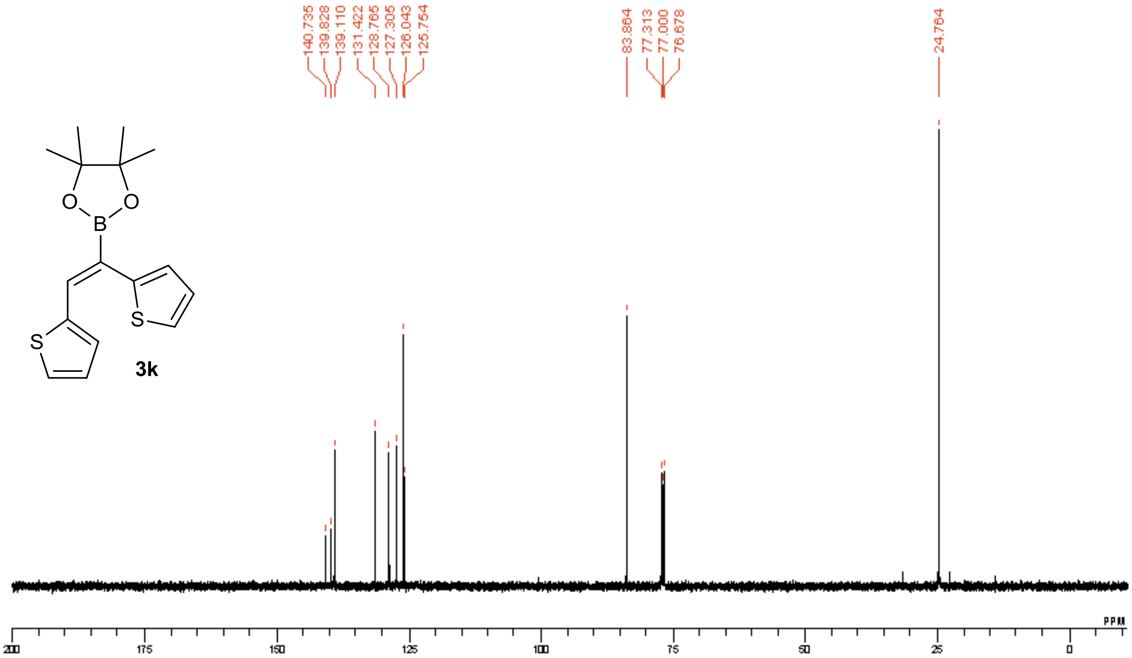
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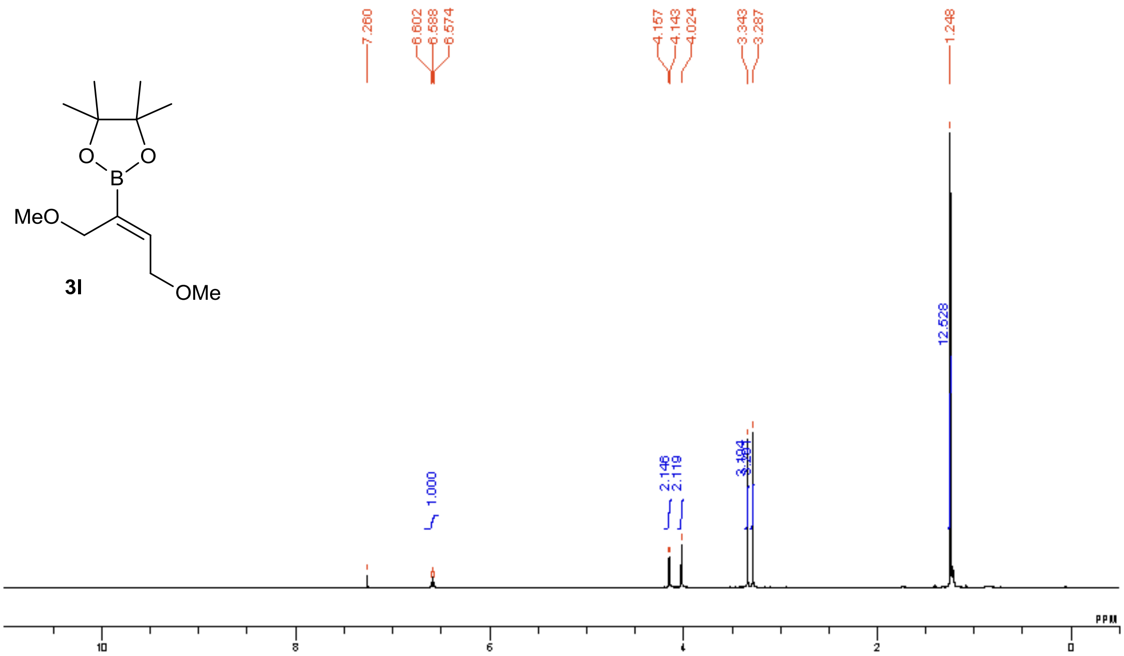

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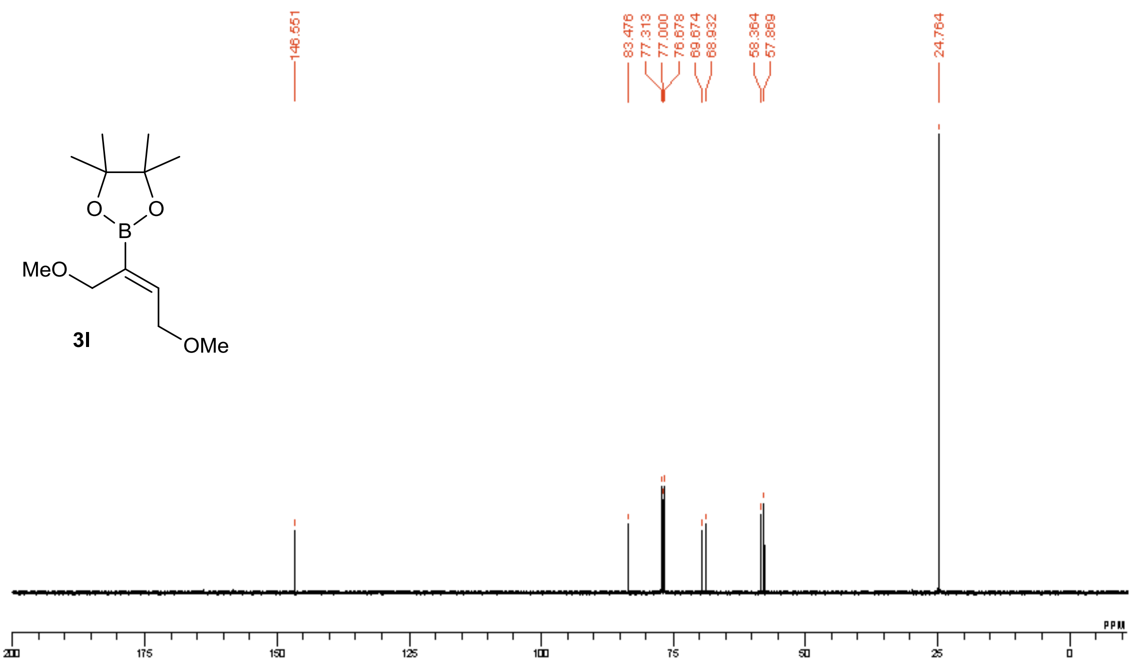

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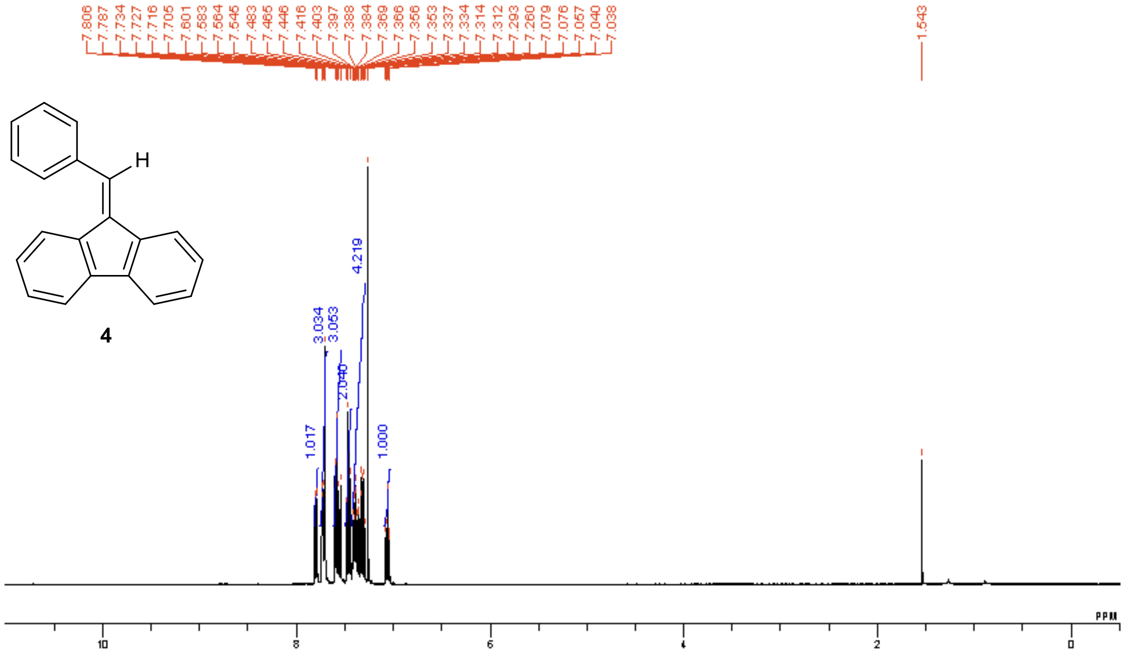
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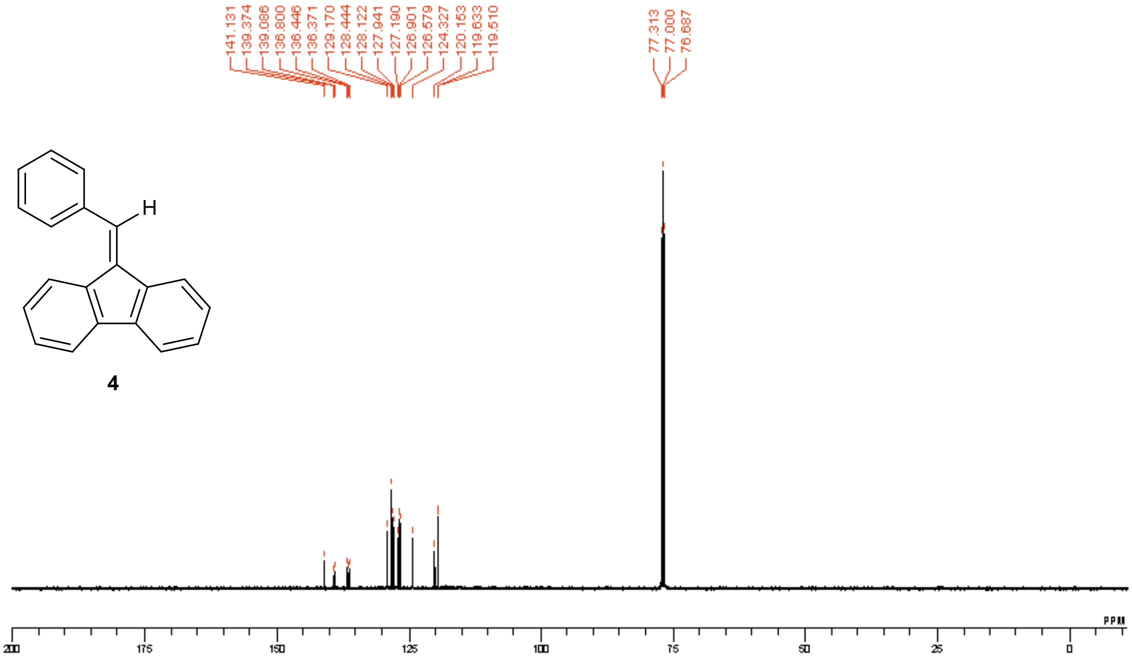
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