Supporting Information for

Copper-catalysed Asymmetric Hydroboration of 1,3-Enynes with Pinacolborane to Access Chiral Allenylboronates

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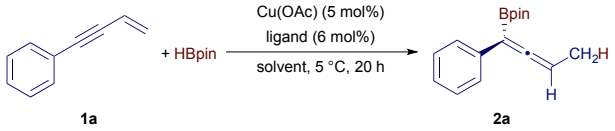
General Remarks

All the manipulations were performed in an argon-filled glovebox, unless mentioned otherwise. THF, toluene, and hexane were purified by passing the degassed solvents (N_2) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). The following chemicals were purchased and used as received: CuOAc (93%, TCI Chemicals), HBpin (Oakwood Chemicals) and chiral ligands (Strem). All 1,3-enynes were prepared according to previously reported procedures.[1] All other reagents and solvents were purchased from commercial sources and used without purification.

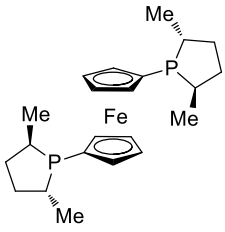
^{1}H and {^{1}H}^{13}C spectra were recorded using Bruker 300 MHz, 400 MHz, or 500 MHz NMR spectrometers. ^{1}H NMR and {^{1}H}^{13}C NMR spectra were referenced to resonances of the residual signals of the deuterated solvents. As such, the ^{1}H and {^{1}H}^{13}C signals of $CDCl_3$ were calibrated to 7.26 ppm (singlet) and 77.16 ppm (triplet) respectively. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet. GC analysis was acquired on Agilent 6850 gas chromatograph equipped with a flame-ionization detector. HR-MS analyses were performed using Thermo Scientific Exactive (APCI).

Reaction screening of ligands for Asymmetric hydroboration of but-3-en-1-yn-1-ylbenzene[a]



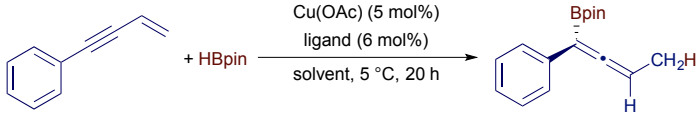
Entry	Ligand	a:b[c]	Yield (%)	ee (%)
1	(R,R)-IPr-DUPHOS	10:90	77	68[d]
2	(R,R)-Me-BPE	30:70	-	-
3	(R,R)-Me-DUPHOS	-	-	-
4	R-DTBM-SEGPHOS	0:100	81	64
5	R-DM-SEGPHOS	0:100	74	21
6	R-(+)-SEGPHOS	5:95	67	45
7	(R)-BINAP	8:92	70	45
8	(R)-DIFLUOROPHOS	5:95	80	40
9	**1**	9:10	60	7
10	(S,S)-Ph-BPE	1:99	85	97

[a]Conditions: but-3-en-1-yn-1-ylbenzene (0.200 mmol), HBpin (0.250 mmol), CuOAc (10.0 μmol), ligand (12.0 μmol), hexane (1.0 mL), 20 h 5 °C; [b]Enantiomeric ratio was determined by chiral HPLC. [c] ratio of a:b = Hydrogenated side product: Desired allenyl boronate product. [d] Opposite (S)-configuration with respect to the rest was obtained.



Ligand 1

Reaction screening of solvent for Asymmetric hydroboration of but-3-en-1-yn-1-ylbenzene[a]



1a 2a

Entry	Ligand	a:b[a]	Yield (%)	ee (%)
1	Cyclohexane	3:97	60	96
2	THF	9:91	20	96
3	Toluene	6:94	68	97
4	Hexane	0:100	85	97
5	Hexane[d]	2:98	62	95
6	Hexane[e]	3:97	86	88
7	THF[e]	3:97	57	94

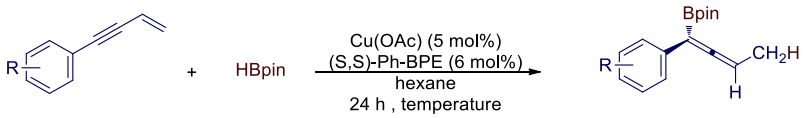
[a]Conditions: but-3-en-1-yn-1-ylbenzene (0.200 mmol), HBpin (0.250 mmol), CuOAc (10.0 μmol), (S,S)-Ph-BPE (12.0 μmol), solvent (1.0 mL), 20 h at 5ºC; [b]Enantiomeric ratio was determined by chiral HPLC. [c]ratio of a:b = Hydrogenated side product: Desired allenyl boronate product. [d]1.5 equiv of HBpin was used instead. [e]Reaction was conducted under room temperature for 20 h.

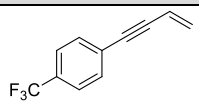
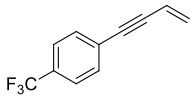
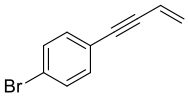
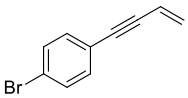
Discussion:

As illustrated in **Table 2** (of main text), when 1,3-enynes containing electron-deficient aryl groups were employed in this Cu-catalysed hydroboration protocol at 5 ºC, there are noticeable decrement of the enantioselectivity as compared to those electron-neutral and electron-rich aryl counterparts.

To investigate whether by lowering the temperature will be beneficial to the presented protocol, several reactions (as shown below) with the use of 1,3-enynes containing electron-deficient aryl groups were conducted at -10 ºC. Although the reactions afforded the respective allenylboronates with a slight improvement in terms of the enantioselectivity, it has deleterious effects on the activity of the catalytic system which lowered the yield significantly.

Effect of temperature on hydroboration of 1,3-enynes containing electron-deficient aryl groups

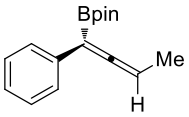


Entry	Enyne	Temperature (ºC)	Yield (%)	ee (%)
1	 (Not in maintext)	-10	69	55
2	 (Not in maintext)	5	75	50
3		-10	47	92
4		5	65	80

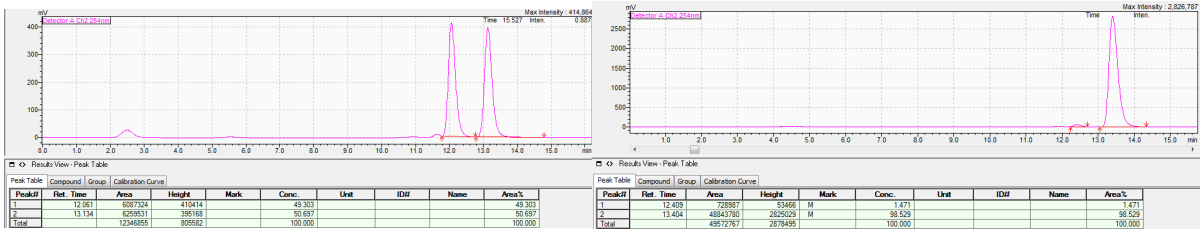
General procedure for Cu-catalysed hydroboration of 1,3-enynes

In an Ar-filled glovebox, a mixture of Cu(OAc) (1.1 mg, 10.0 μmol) and (S,S)-Ph-BPE (6.1 mg, 12.0 μmol) in hexane (1 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding HBpin (36.3 μL, 0.250 mmol) and 1,3-enynes (0.200 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature or under 5ºC for 12 or 24 hours respectively. Subsequently, the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent. The details and characterization data of the products are stated below.

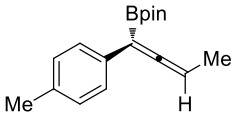
(R)-4,4,5,5-tetramethyl-2-(1-phenylbuta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2a)



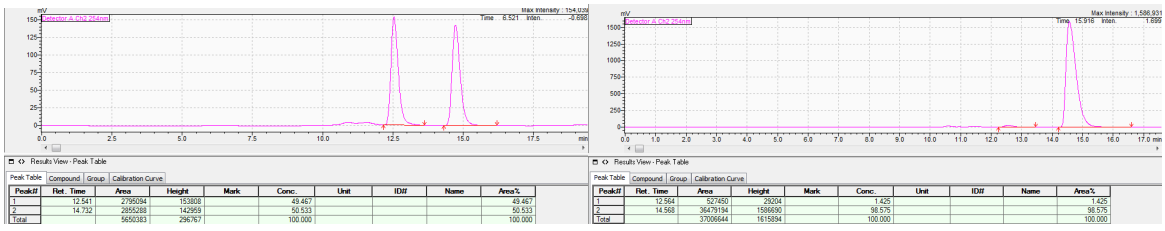
The titled compound was isolated (44.0 mg, 85%, 97% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 5.42 (q, J = 7.2 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (126 MHz, $CDCl_3$) δ 214.96, 136.79, 128.40, 128.06, 126.38, 84.52, 83.89, 24.99, 24.82, 13.22. HRMS (APCI $^+$) m/z calcd for $C_{16}H_{21}BO_2$, $[M+H]^+$ 257.1713, Found:257.1628. Optical rotation: $[\alpha]^{20}_D$ = -28.56 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u**. HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 12.4 min for minor isomer, t_R = 13.4 min for major isomer.



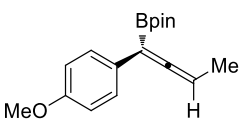
(R)-4,4,5,5-tetramethyl-2-(1-(p-tolyl)buta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2b)



The titled compound was isolated (42.1 mg, 78%, 97% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 5.40 (q, J = 7.1 Hz, 1H), 2.32 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.63, 135.98, 133.77, 129.13, 127.94, 84.34, 83.83, 24.97, 24.81, 21.21, 13.27. HRMS (APCI $^+$) m/z calcd for $C_{17}H_{23}BO_2$, $[M+H]^+$ 271.1869, Found:271.1871. Optical rotation: $[\alpha]^{20}_D$ = -9.71 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u**. HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.5:0.5, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 12.6 min for minor isomer, t_R = 14.6 min for major isomer.

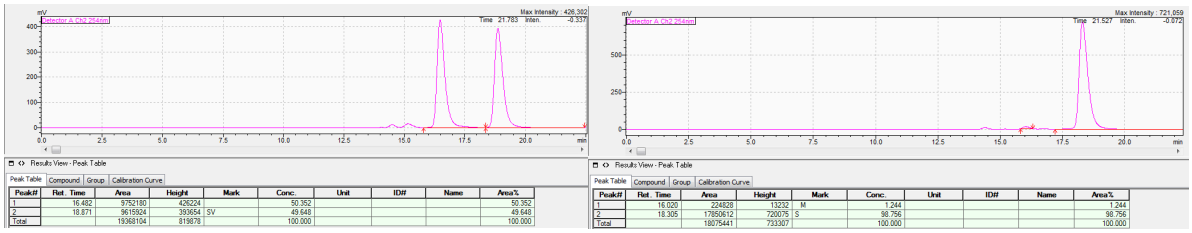


(R)-2-(1-(4-methoxyphenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)

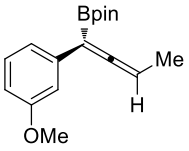


The titled compound was isolated (34.3 mg, 60%, 98% ee) as colorless oil after chromatography on silica gel (50:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 6.85 – 6.82 (m, 2H), 5.40 (q, J = 7.1 Hz, 1H), 3.79 (s, 3H), 1.78

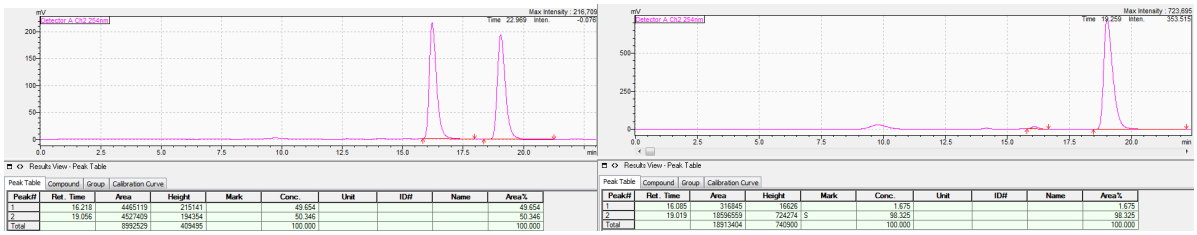
(d, J = 7.1 Hz, 3H), 1.32 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.33, 158.40, 129.09, 128.99, 113.94, 84.49, 83.85, 55.42, 24.99, 24.81, 13.35. HRMS (APCI $^+$) m/z calcd for $C_{17}H_{24}BO_3$, $[M+H]^+$ 287.1817, Found:287.1817. Optical rotation: $[\alpha]^{20}_D$ = -21.59 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u**. HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength =254 nm, t_R = 16.0 min for minor isomer, t_R = 18.3 min for major isomer.



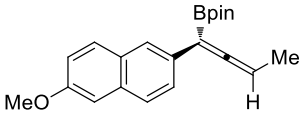
(R)-2-(1-(3-methoxyphenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



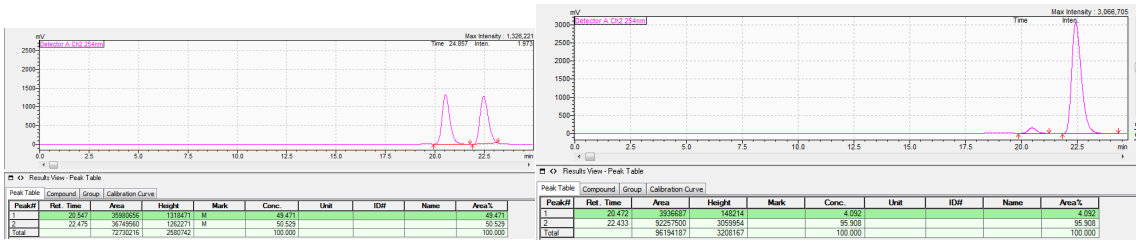
The titled compound was isolated (39.0 mg, 69%, 97% ee) as colorless oil after chromatography on silica gel (50:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.9 Hz, 1H), 7.13 (m, 2H), 6.73 (ddd, J = 8.1, 2.5, 1.0 Hz, 1H), 5.42 (q, J = 7.2 Hz, 1H), 3.80 (s, 3H), 1.79 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.92, 159.69, 138.25, 129.25, 120.68, 113.79, 111.87, 84.64, 83.89, 55.25, 24.98, 24.81, 13.18. HRMS (APCI $^+$) m/z calcd for $C_{17}H_{24}BO_3$, $[M+H]^+$ 287.1817, Found:287.1827. Optical rotation: $[\alpha]^{20}_D$ = -20.24 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 16.1 min for minor isomer, t_R = 19.0 min for major isomer.



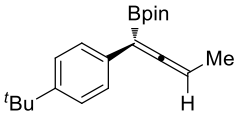
(R)-2-(1-(6-methoxynaphthalen-2-yl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



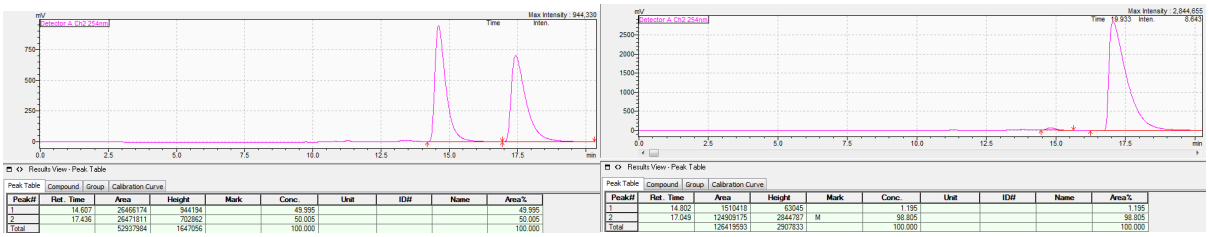
The titled compound was isolated (40.1 mg, 60%, 92% ee) as colorless oil after chromatography on silica gel (50:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.61 (dd, J = 8.6, 1.7 Hz, 1H), 7.13 – 7.08 (m, 2H), 5.49 (q, J = 7.2 Hz, 1H), 3.91 (s, 3H), 1.84 (d, J = 7.2 Hz, 3H), 1.37 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.97, 157.50, 133.47, 131.83, 129.72, 129.36, 127.00, 126.73, 126.54, 118.55, 105.83, 84.78, 83.94, 55.40, 25.02, 24.85, 24.73, 13.34. HRMS (APCI $^+$) m/z calcd for $C_{21}H_{25}BO_3$, $[M+H]^+$ 337.1975, Found:337.1974. Optical rotation: $[\alpha]^{20}_D$ = -29.95 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 97.0:3.0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 20.5 min for minor isomer, t_R = 22.4 min for major isomer.



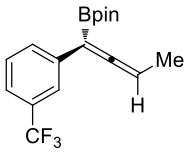
(R)-2-(1-(4-(tert-butyl)phenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)



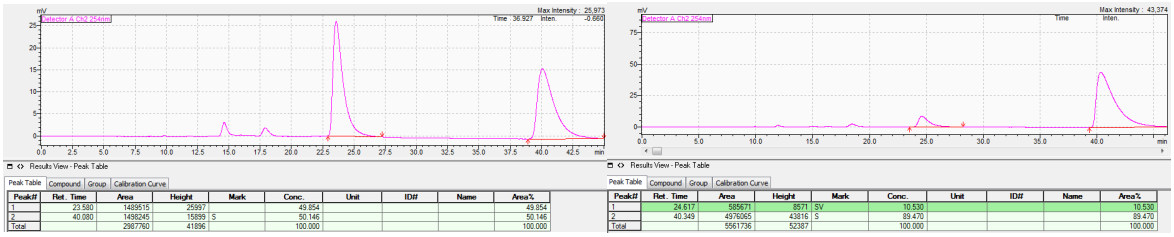
The titled compound was isolated (43.0 mg, 70%, 98% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.34 – 7.31 (m, 2H), 5.41 (q, J = 7.1 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H), 1.31 (s, 9H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.84, 149.22, 133.73, 127.68, 125.39, 84.37, 83.83, 34.54, 31.49, 24.97, 24.81, 13.29. HRMS (APCI $^+$) *m/z* calcd for $C_{20}H_{29}BO_2$, $[M+H]^+$ 313.2339, Found:313.2329. Optical rotation: $[\alpha]^{20}_D$ = -16.13 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u**. HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 14.8 min for minor isomer, t_R = 17.1 min for major isomer.



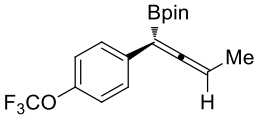
(R)-4,4,5,5-tetramethyl-2-(1-(3-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2g)



The titled compound was isolated (48.0 mg, 74%, 79% ee) as colorless oil after chromatography on silica gel (30:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.73 – 7.69 (m, 1H), 7.42 – 7.37 (m, 2H), 5.49 (q, J = 7.2 Hz, 1H), 1.81 (d, J = 7.2 Hz, 3H), 1.34 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.35 , 137.82 , 131.29 , 130.67 (q, $J_{C\text{-}F}$ = 31.8 Hz), 128.70 , 124.76 (q, $J_{C\text{-}F}$ = 3.9 Hz), 124.50 (q, $J_{C\text{-}F}$ = 272.3 Hz), 122.98 (q, $J_{C\text{-}F}$ = 3.8 Hz), 85.37 , 84.15 , 83.33 , 24.92 ,24.78, 13.00.^{19}F NMR (377 MHz, $CDCl_3$) δ -62.70. HRMS (APCI $^+$) *m/z* calcd for $C_{17}H_{21}BF_3O_2$, $[M+H]^+$ 325.1587, Found:325.1588. Optical rotation: $[\alpha]^{20}_D$ = -21.20 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 100:0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 24.6 min for minor isomer, t_R = 40.3 min for major isomer.

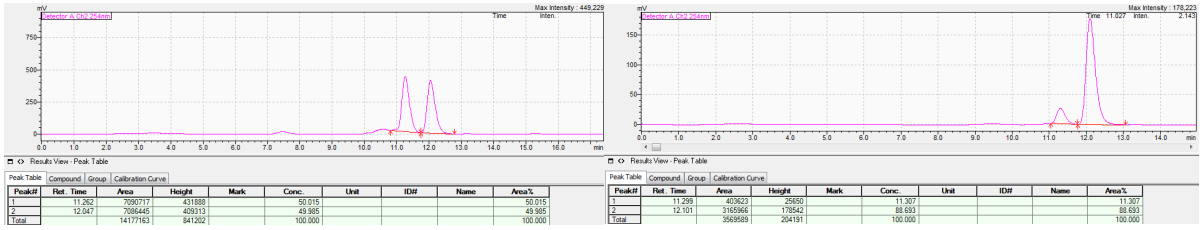


(R)-4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethoxy)phenyl)buta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2h)

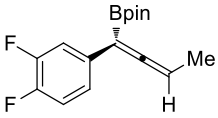


The titled compound was isolated (47.6 mg, 70%, 77% ee) as colorless oil after chromatography on silica gel (50:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.13 (dd, J = 8.9, 0.9 Hz, 2H), 5.45 (q, J = 7.2 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.29, 147.80, 135.62, 129.27, 120.91, 120.69 ($J_{C\text{-}F}$ = 256.6 Hz), 85.01, 84.06, 24.97, 24.82, 13.09. ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.84. HRMS (APCI $^+$) *m/z* calcd for $C_{17}H_{21}BF_3O_3$, $[M+H]^+$ 341.1536, Found:341.1515. Optical rotation: $[\alpha]^{20}_D$ = -14.60 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of

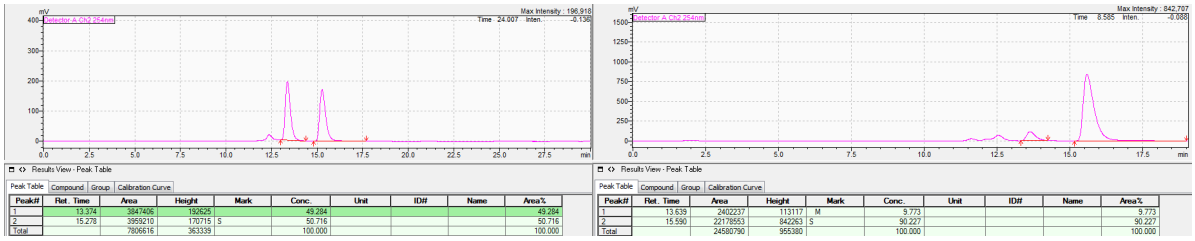
2u. HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 11.3 min for minor isomer, t_R = 12.1 min for major isomer.



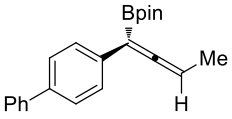
(R)-2-(1-(3,4-difluorophenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)



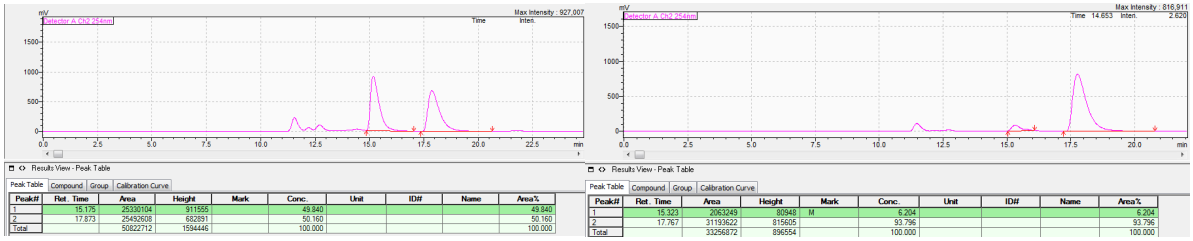
The titled compound was isolated (38.0 mg, 70%, 80% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.26 – 7.24 (m, 1H), 7.05 (m, 1H), 5.46 (q, J = 7.2 Hz, 1H), 1.79 (d, J = 7.2 Hz, 3H), 1.32 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.13, 149.72 (ddd, $J_{C\text{-}F}$ = 128.7, 115.4, 12.8 Hz), 133.84 (dd, $J_{C\text{-}F}$ = 5.8, 3.9 Hz), 123.88, 116.89 (d, $J_{C\text{-}F}$ = 13.6 Hz), 116.72 (d, $J_{C\text{-}F}$ = 14.7 Hz), 100.15, 85.39, 84.13, 24.89, 13.04. ^{19}F NMR (377 MHz, $CDCl_3$) δ -138.65, -138.71, -141.65, -141.71. HRMS (APCI $^+$) *m/z* calcd for $C_{16}H_{20}BF_3O_3$, $[M+H]^+$ 293.1524 Found: 293.1522. Optical rotation: $[\alpha]^{20}_D$ = -30.08 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 13.6 min for minor isomer, t_R = 15.6 min for major isomer.



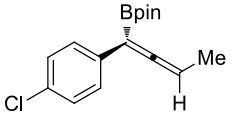
(R)-2-(1-([1,1'-biphenyl]-4-yl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j)



The titled compound was isolated (46.5 mg, 70%, 88% ee) as colorless oil after chromatography on silica gel (50:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 4H), 7.47 – 7.44 (m, 2H), 7.37 – 7.32 (m, 2H), 7.27 – 7.22 (m, 1H), 5.39 (q, J = 7.2 Hz, 1H), 1.74 (d, J = 7.2 Hz, 3H), 1.27 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.12, 141.33, 139.21, 136.22, 135.91, 128.84, 128.44, 127.19, 127.11, 84.68, 83.97, 25.01, 24.85, 13.23. HRMS (APCI $^+$) *m/z* calcd for $C_{22}H_{26}BO_2$, $[M+H]^+$ 333.2026. Found: 333.2023. Optical rotation: $[\alpha]^{20}_D$ = -3.29 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.0:1.0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 15.2 min for minor isomer, t_R = 17.8 min for major isomer.

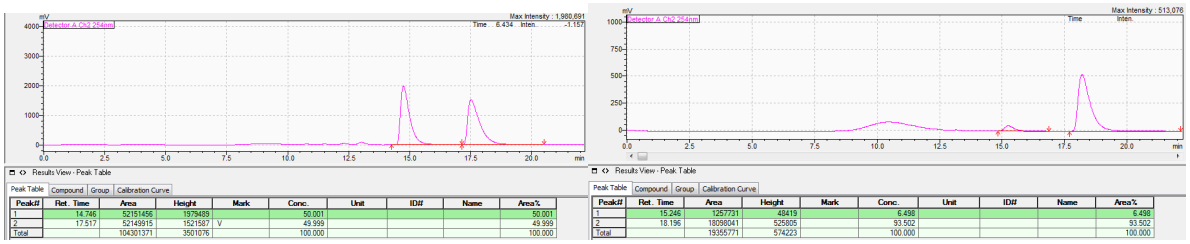


(R)-2-(1-(4-chlorophenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)

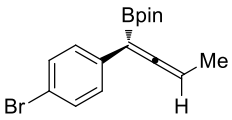


The titled compound was isolated (31.0 mg, 53%, 88% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ

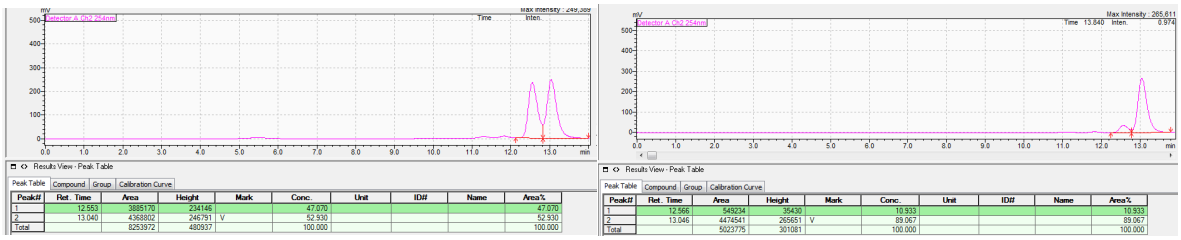
7.45 – 7.40 (m, 2H), 7.22 – 7.19 (m, 2H), 5.40 (q, J = 7.2 Hz, 1H), 1.75 (d, J = 7.2 Hz, 3H), 1.29 (s, 12H). $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 215.05, 135.32, 132.08, 129.33, 128.47, 84.96, 84.02, 24.97, 24.82, 13.09. HRMS (APCI $^+$) m/z calcd for $C_{16}H_{21}BClO_2$, $[M+H]^+$ 291.1323. Found: 291.1321. Optical rotation: $[\alpha]^{20}_D$ = -56.75 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 15.2 min for minor isomer, t_R = 18.2 min for major isomer.



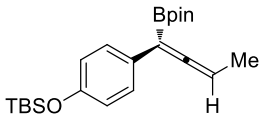
(R)-2-(1-(4-bromophenyl)buta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)



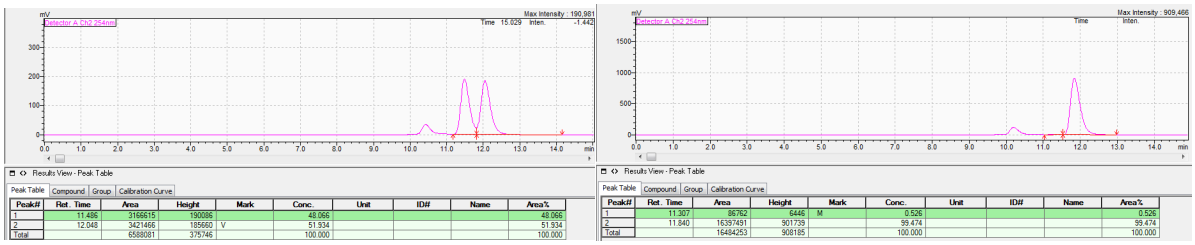
The titled compound was isolated (43.4 mg, 65%, 80% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 4H), 5.42 (q, J = 7.2 Hz, 1H), 1.78 (d, J = 7.2 Hz, 3H), 1.32 (s, 12H). $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 215.05, 135.84, 131.42, 129.72, 120.24, 85.01, 84.04, 24.97, 24.82, 13.06. HRMS (APCI $^+$) m/z calcd for $C_{16}H_{21}BBrO_2$, $[M+H]^+$ 335.0818. Found: 335.0512. Optical rotation: $[\alpha]^{20}_D$ = -12.68 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 12.6 min for minor isomer, t_R = 13.0 min for major isomer.



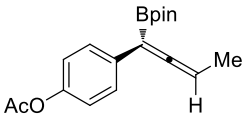
(R)-tert-butyldimethyl(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-dien-1-yl)phenoxy)silane (2m)



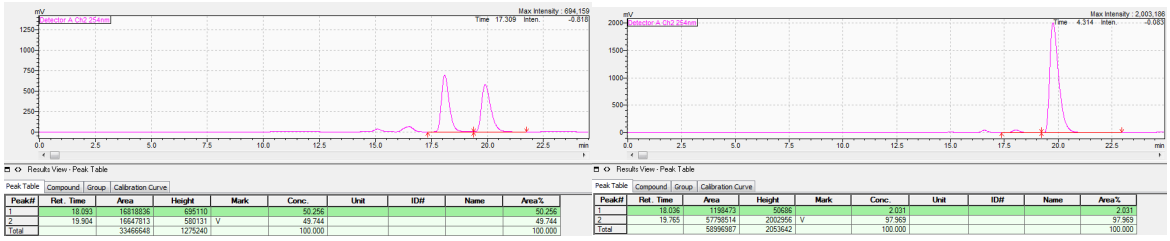
The titled compound was isolated (43.0 mg, 56%, 99% ee) as colorless oil after chromatography on silica gel (200:1 hexane/EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 5.40 (q, J = 7.1 Hz, 1H), 1.78 (d, J = 7.1 Hz, 3H), 1.32 (s, 12H), 0.98 (s, 9H), 0.18 (s, 6H). $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 214.27, 154.41, 129.36, 128.99, 120.05, 84.55, 83.82, 25.87, 25.00, 24.81, 18.38, 13.33, -4.24. HRMS (APCI $^+$) m/z calcd for $C_{22}H_{36}BO_2Si$, $[M+H]^+$ 387.2527. Found: 387.2518. Optical rotation: $[\alpha]^{20}_D$ = -13.91 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.5:0.5, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 11.3 min for minor isomer, t_R = 11.8 min for major isomer.



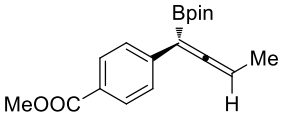
(R)-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-dien-1-yl)phenyl acetate (2n)



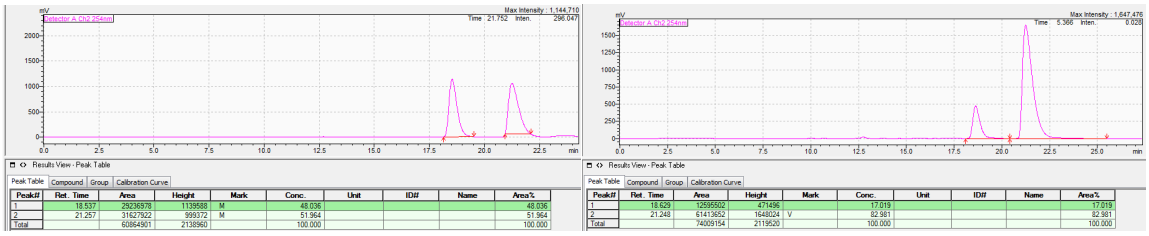
The titled compound was isolated (44.1 mg, 70%, 96% ee) as white solid after chromatography on silica gel (30:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.01 – 6.98 (m, 2H), 5.42 (q, *J* = 7.2 Hz, 1H), 2.28 (s, 3H), 1.78 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.12, 169.71, 149.26, 134.46, 129.02, 121.36, 84.73, 83.94, 24.97, 24.81, 21.29, 13.17. HRMS (APCI $^+$) *m/z* calcd for $C_{18}H_{23}BO_2$, $[M+H]^+$ 315.1768. Found: 315.1764. Optical rotation: $[\alpha]^{20}_D$ = -17.28 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 97.0:3.0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 18.0 min for minor isomer, t_R = 19.8 min for major isomer.



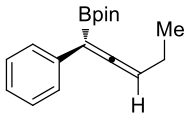
(R)-methyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-dien-1-yl)benzoate (2o)



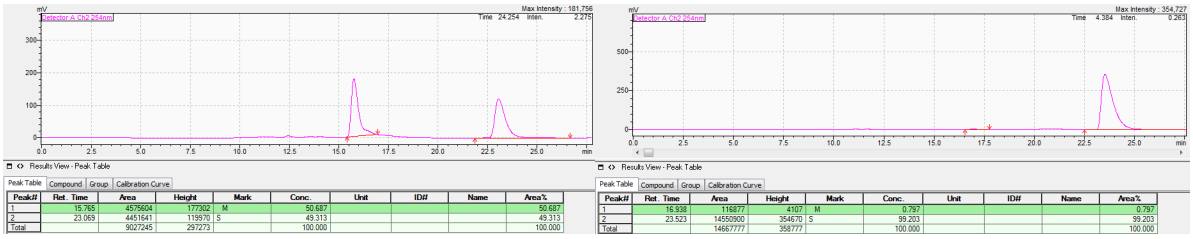
The titled compound was isolated (42.6 mg, 68%, 65% ee) as colorless oil after chromatography on silica gel (40:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 5.48 (q, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 215.89, 167.33, 142.02, 129.72, 127.90, 85.07, 84.07, 52.06, 24.96, 24.81, 12.96. HRMS (APCI $^+$) *m/z* calcd for $C_{18}H_{23}BO_2$, $[M+H]^+$ 315.1768. Found: 315.1775. Optical rotation: $[\alpha]^{20}_D$ = -28.72 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 97.0:3.0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 18.6 min for minor isomer, t_R = 21.2 min for major isomer.



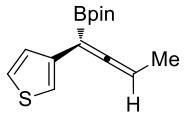
(R)-4,4,5,5-tetramethyl-2-(1-phenylpenta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2p)



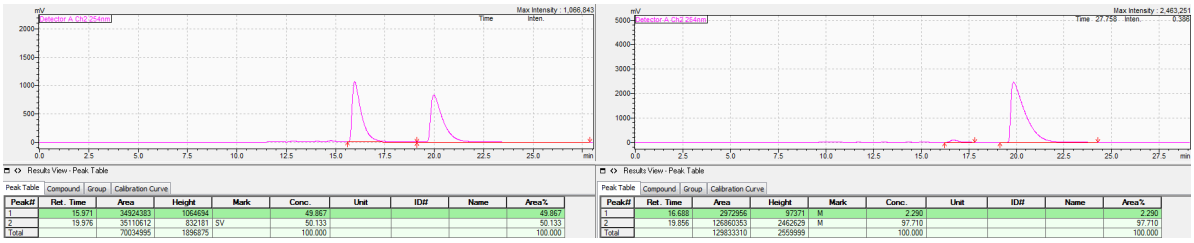
The titled compound was isolated (26.7 mg, 50%, 98% ee) as colorless oil after chromatography on silica gel (200:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.31 – 7.26 (m, 2H), 7.19 – 7.14 (m, 1H), 5.53 (t, J = 6.3 Hz, 1H), 2.25 – 2.06 (m, 3H), 1.33 (d, J = 2.2 Hz, 12H), 1.08 (t, J = 7.4 Hz, 3H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 213.93, 136.78, 128.41, 127.91, 126.37, 91.74, 83.87, 25.09, 24.66, 21.19, 13.75. HRMS (APCI $^+$) m/z calcd for $C_{17}H_{24}BO_2$, $[M+H]^+$ 271.1869. Found: 271.1856. Optical rotation: $[\alpha]^{20}_D$ = -11.92 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 16.9 min for minor isomer, t_R = 23.5 min for major isomer.



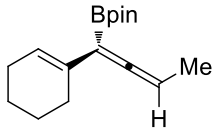
(R)-4,4,5,5-tetramethyl-2-(1-(thiophen-3-yl)buta-1,2-dien-1-yl)-1,3,2-dioxaborolane (2q)



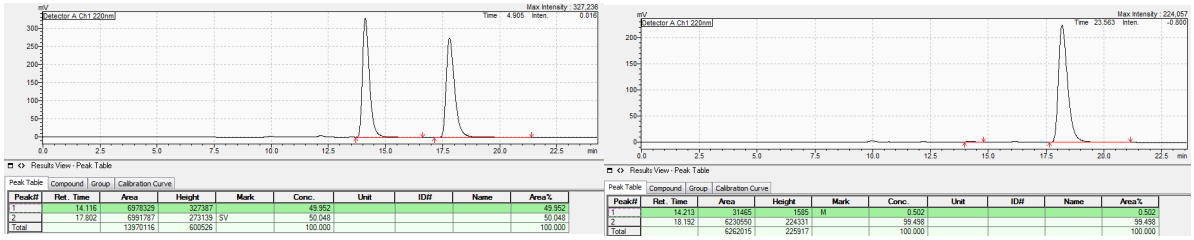
The titled compound was isolated (36.4 mg, 69%, 95% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.21 (dd, J = 5.0, 2.9 Hz, 1H), 7.18 (dd, J = 5.0, 1.3 Hz, 1H), 5.40 (q, J = 7.2 Hz, 1H), 1.78 (d, J = 7.1 Hz, 3H), 1.33 (s, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 214.84, 137.14, 127.66, 124.77, 121.66, 84.42, 83.94, 25.01, 24.87, 13.30. HRMS (APCI $^+$) m/z calcd for $C_{14}H_{20}BO_2S$, $[M+H]^+$ 263.1277. Found: 263.1284. Optical rotation: $[\alpha]^{20}_D$ = -34.05 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 16.7 min for minor isomer, t_R = 19.9 min for major isomer.



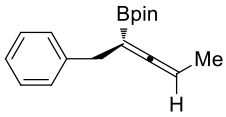
(R)-methyl 4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-dien-1-yl)benzoate (2r)



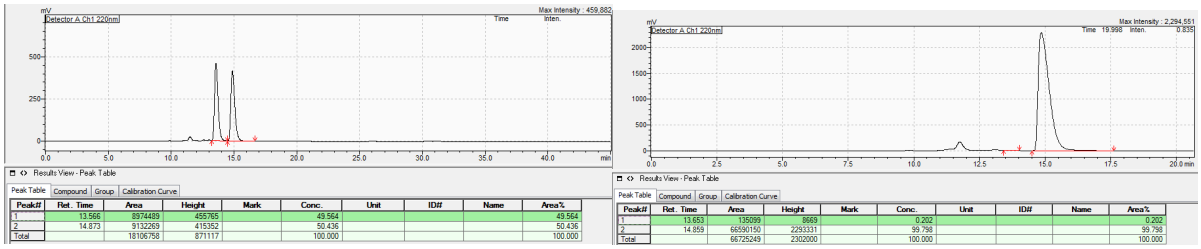
The titled compound was isolated (35.8 mg, 69%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (m, 1H), 5.27 – 5.18 (m, 1H), 2.10 (m, 4H), 1.69 – 1.67 (m, 3H), 1.66 – 1.60 (m, 2H), 1.60 – 1.52 (m, 2H), 1.28 (d, J = 1.9 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.30, 132.83, 126.12, 84.53, 83.57, 27.39, 26.28, 24.93, 24.72, 23.10, 22.48, 13.82. GC-MS (EI) m/z calcd for $C_{16}H_{25}BO_2$, $[M]^+$ 2660.19. Found: 260.20. Optical rotation: $[\alpha]^{20}_D$ = 0.98 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 14.2 min for minor isomer, t_R = 18.2 min for major isomer.



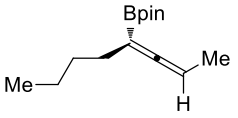
(R)-4,4,5,5-tetramethyl-2-(1-phenylpenta-2,3-dien-2-yl)-1,3,2-dioxaborolane (2t)



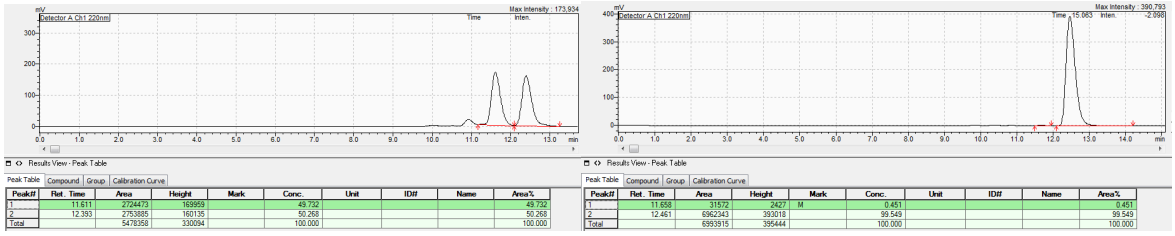
The titled compound was isolated (41.0 mg, 76%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 4H), 7.10 – 7.04 (m, 1H), 4.91 (m, 1H), 3.28 (dd, *J* = 4.4, 2.4 Hz, 2H), 1.52 (d, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 2.7 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 213.54, 141.62, 129.00, 128.06, 125.77, 83.72, 82.49, 36.85, 24.85, 24.77, 13.33. HRMS (APCI $^+$) *m/z* calcd for $C_{17}H_{24}BO_2$, $[M+H]^+$ 271.1869. Found: 271.1872. Optical rotation: $[\alpha]^{20}_D$ = 1.09 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 13.7 min for minor isomer, t_R = 14.9 min for major isomer.



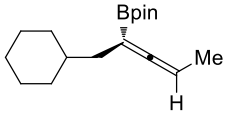
(R)-4,4,5,5-tetramethyl-2-(octa-2,3-dien-4-yl)-1,3,2-dioxaborolane (2u)



The titled compound was isolated (27.0 mg, 61%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 – 4.97 (m, 1H), 2.04 – 1.99 (m, 2H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.40 – 1.31 (m, 4H), 1.26 (d, *J* = 2.5 Hz, 12H), 0.89 (t, *J* = 7.2 Hz, 3H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.73, 83.51, 81.83, 31.58, 29.68, 24.92, 24.80, 22.37, 14.16, 13.67. GC-MS (EI) *m/z* calcd for $C_{14}H_{25}BO_2$, $[M]^+$ 236.19. Found: 236.25. Optical rotation: $[\alpha]^{20}_D$ = 17.9 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by comparing with the optical rotation reported in the literature[2]. HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 11.7 min for minor isomer, t_R = 12.5 min for major isomer.

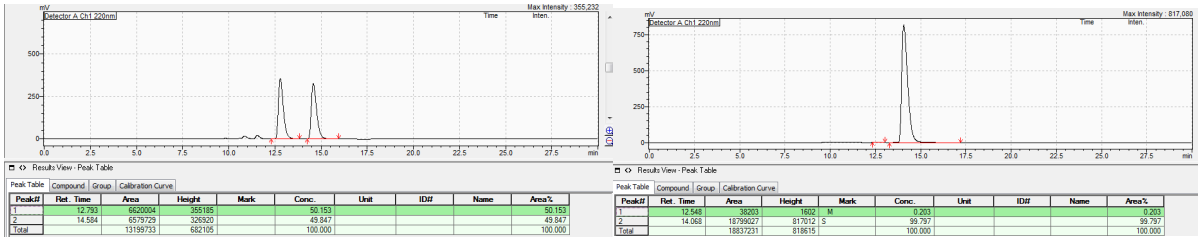


(R)-2-(1-cyclohexylpenta-2,3-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v)

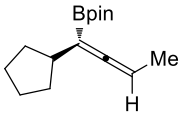


The titled compound was isolated (39.9 mg, 72%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (qt, *J* = 7.0, 2.3 Hz, 1H), 1.90 (m, 2H), 1.74 – 1.60 (m, 9H), 1.41 – 1.32 (m, 1H), 1.25 (d, *J* = 2.2 Hz, 12H), 1.18 – 1.11 (m, 2H), 0.87 (m, 2H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 213.15, 83.49, 81.06, 38.05, 37.85, 33.24, 26.85, 26.53, 26.51, 24.86, 24.76, 13.53. HRMS (APCI $^+$) *m/z* calcd for $C_{17}H_{30}BO_2$, $[M+H]^+$ 277.2339. Found: 277.2355. Optical rotation: $[\alpha]^{20}_D$ = 9.44 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-

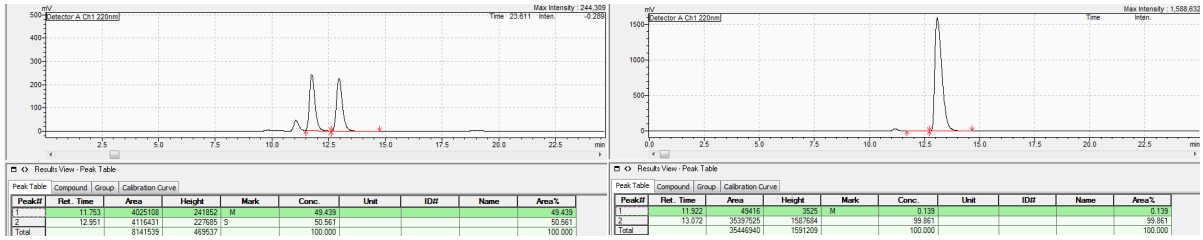
PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 12.5 min for minor isomer, t_R = 14.1 min for major isomer.



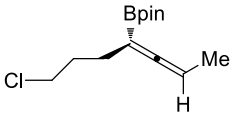
(R)-2-(1-cyclopentylbuta-1,2-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2w)



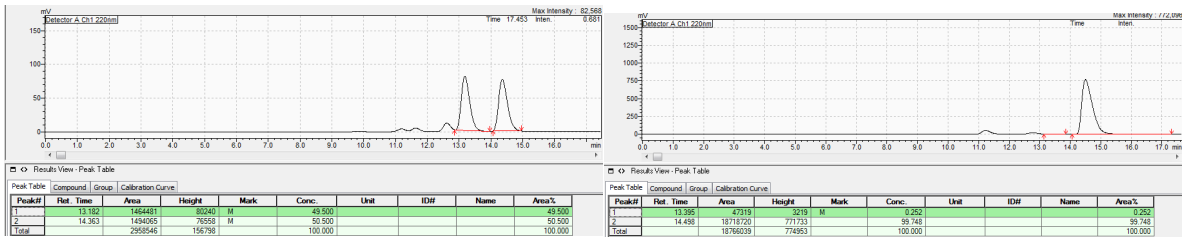
The titled compound was isolated (34.4 mg, 69%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (qd, *J* = 7.0, 2.5 Hz, 1H), 2.53 – 2.44 (m, 1H), 1.82 – 1.74 (m, 2H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.58 (m, 2H), 1.56 – 1.48 (m, 2H), 1.38 (m, 2H), 1.26 (d, *J* = 2.5 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 211.04, 83.43, 82.96, 40.00, 32.90, 32.84, 24.99, 24.94, 24.91, 24.77, 13.73. HRMS (APCI $^+$) *m/z* calcd for $C_{15}H_{26}BO_2$, $[M+H]^+$ 249.2026. Found: 249.2021. Optical rotation: $[\alpha]^{20}_D$ = 11.14 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 11.9 min for minor isomer, t_R = 13.1 min for major isomer.



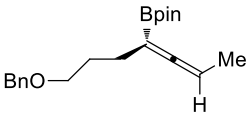
(R)-2-(8-chloroocta-2,3-dien-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2x)



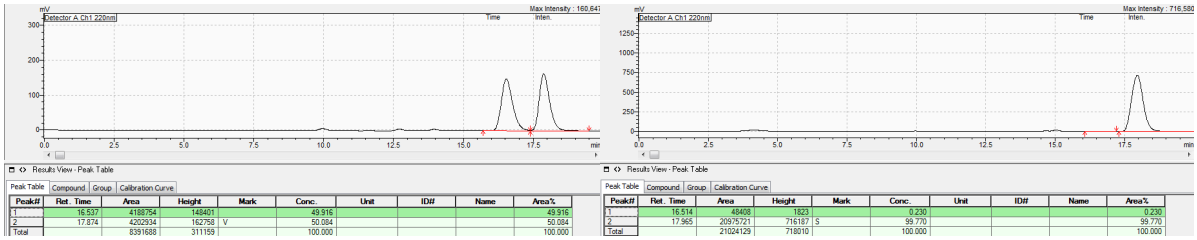
The titled compound was isolated (30.4 mg, 63%, 99% ee) as colorless oil after chromatography on silica gel (100:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (qt, *J* = 7.0, 2.7 Hz, 1H), 3.55 (t, *J* = 6.9 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.92 (m, 2H), 1.67 (d, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 2.1 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.80, 83.71, 82.67, 44.72, 32.26, 27.30, 24.91, 24.81, 13.56. HRMS (APCI $^+$) *m/z* calcd for $C_{13}H_{23}BClO_2$, $[M+H]^+$ 257.1480. Found: 256.2637. Optical rotation: $[\alpha]^{20}_D$ = 9.58 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 13.4 min for minor isomer, t_R = 14.5 min for major isomer.



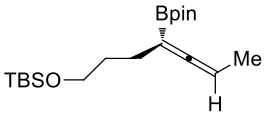
(R)-2-(7-(benzyloxy)hepta-2,3-dien-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2y)



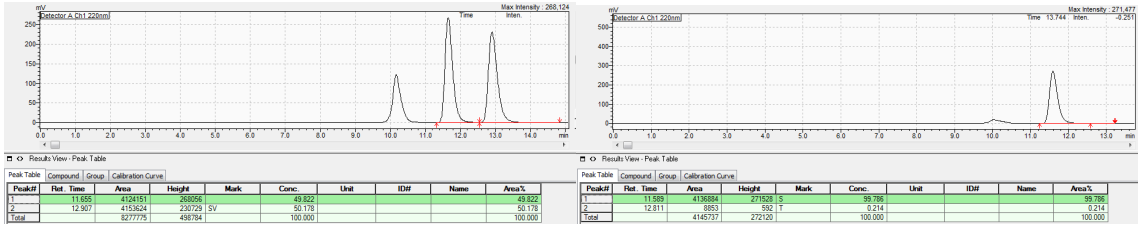
The titled compound was isolated (42.4 mg, 65%, 99% ee) as colorless oil after chromatography on silica gel (40:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 5.07 – 4.98 (m, 1H), 4.50 (s, 2H), 3.50 (t, *J* = 6.8 Hz, 2H), 2.11 (m, 2H), 1.81 – 1.73 (m, 2H), 1.65 (d, *J* = 7.0 Hz, 3H), 1.26 (d, *J* = 2.3 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.72, 138.88, 128.44, 127.80, 127.56, 83.58, 82.32, 73.00, 70.21, 29.34, 26.49, 24.90, 24.80, 13.61. HRMS (APCI $^+$) *m/z* calcd for $C_{20}H_{30}BO_2$, $[M+H]^+$ 329.2288. Found: 329.2284. Optical rotation: $[\alpha]^{20}_D$ = 12.25 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.5:0.5, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 16.5 min for minor isomer, t_R = 18.0 min for major isomer.



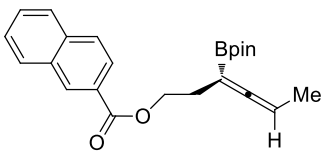
(R)-tert-butyldimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-4,5-dien-1-yl)oxy)silane (2z)



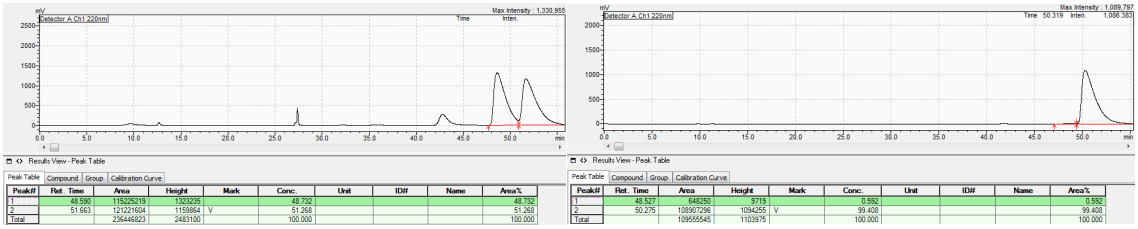
The titled compound was isolated (54.6 mg, 77%, 99% ee) as colorless oil after chromatography on silica gel (40:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (qt, *J* = 7.0, 2.7 Hz, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.68 – 1.62 (m, 5H), 1.25 (d, *J* = 2.3 Hz, 12H), 0.89 (s, 9H), 0.04 (s, 6H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.65, 83.54, 82.18, 63.05, 32.56, 26.15, 24.91, 24.80, 18.52, 13.62, -5.07. HRMS (APCI $^+$) *m/z* calcd for $C_{19}H_{38}BO_3Si$, $[M+H]^+$ 353.2683. Found: 353.2680. Optical rotation: $[\alpha]^{20}_D$ = 10.55 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IC, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 11.6 min for minor isomer, t_R = 12.8 min for major isomer.



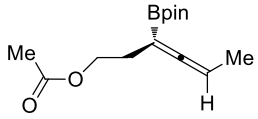
(R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,4-dien-1-yl 2-naphthoate (2aa)



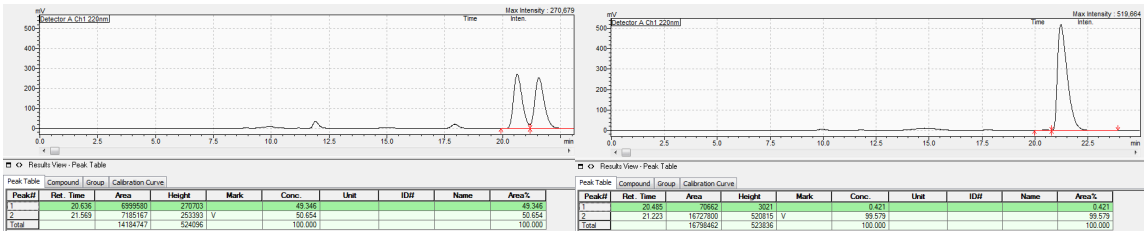
The titled compound was isolated (52.9 mg, 70%, 99% ee) as colorless oil after chromatography on silica gel (20:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 0.5 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.87 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.60 – 7.50 (m, 2H), 5.10 (qd, *J* = 7.1, 4.5 Hz, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 2.56 (m, 2H), 1.64 (d, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 2.1 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 213.66, 166.91, 135.61, 132.64, 131.11, 129.45, 128.22, 128.13, 127.98, 127.88, 126.68, 125.51, 83.84, 82.70, 64.78, 29.52, 24.91, 24.84, 13.52. GC-MS (EI) *m/z* calcd for $C_{23}H_{27}BO_{24}$, $[M]^+$ 378.20. Found: 378.20. Optical rotation: $[\alpha]^{20}_D$ = 3.42 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.0:1.0, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 48.5 min for minor isomer, t_R = 50.3 min for major isomer.



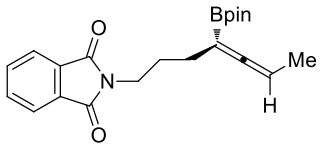
(R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-3,4-dien-1-yl acetate (2ab)



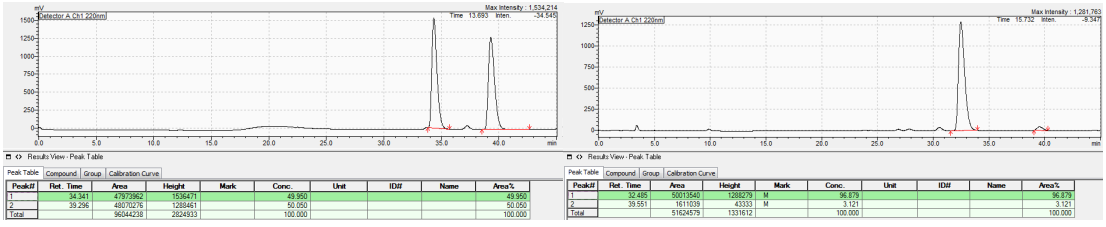
The titled compound was isolated (33.2 mg, 62%, 99% ee) as colorless oil after chromatography on silica gel (20:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 – 5.04 (m, 1H), 3.65 (s, 3H), 2.44 (m, 2H), 2.37 – 2.29 (m, 2H), 1.64 (d, J = 7.1 Hz, 3H), 1.25 (d, J = 2.0 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.41, 173.96, 83.72, 83.47, 51.52, 33.63, 25.06, 24.90, 24.82, 13.55. HRMS (APCI $^+$) m/z calcd for $C_{14}H_{24}BO_4$, $[M+H]^+$ 267.1768. Found: 267.1774. Optical rotation: $[\alpha]^{20}_D$ = 16.10 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 99.0:1.0, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 20.5 min for minor isomer, t_R = 21.2min for major isomer.



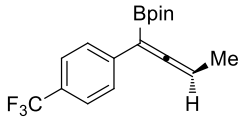
(R)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-4,5-dien-1-yl)isoindoline-1,3-dione (2ac)



The titled compound was isolated (58.4 mg, 80%, 94% ee) as white solid after chromatography on silica gel (3:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.71 – 7.66 (m, 2H), 5.09 – 5.01 (m, 1H), 3.71 – 3.65 (m, 2H), 2.12 – 2.06 (m, 2H), 1.81 (m, 2H), 1.66 (d, J = 7.1 Hz, 3H), 1.24 (d, J = 1.4 Hz, 12H). {^{1}H}^{13}C NMR (101 MHz, $CDCl_3$) δ 212.65, 168.50, 133.88, 132.42, 123.22, 83.64, 82.80, 37.98, 28.04, 27.25, 24.87, 24.78, 13.58. HRMS (APCI $^+$) m/z calcd for $C_{21}H_{27}BNO_4$, $[M+H]^+$ 368.2033. Found: 368.2032. Optical rotation: $[\alpha]^{20}_D$ = 9.58 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IE, n-hexane/i-PrOH = 93.0:7.0, flow rate = 0.35 mL/min, wavelength = 220 nm, t_R = 39.6 min for minor isomer, t_R = 32.5 min for major isomer.

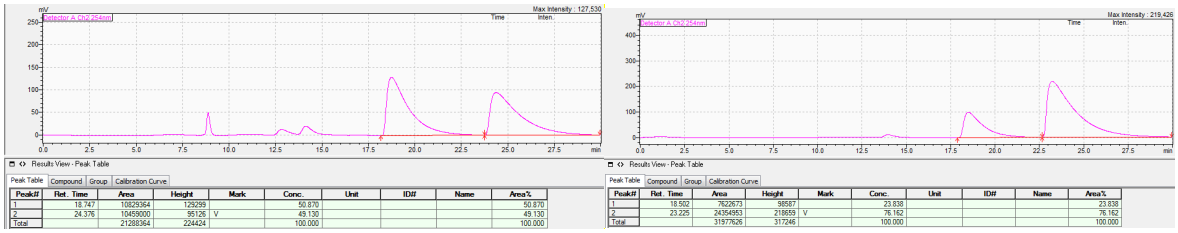


(R)-4,4,5,5-tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)buta-1,2-dien-1-yl)-1,3,2-dioxaborolane (Not in maintext)



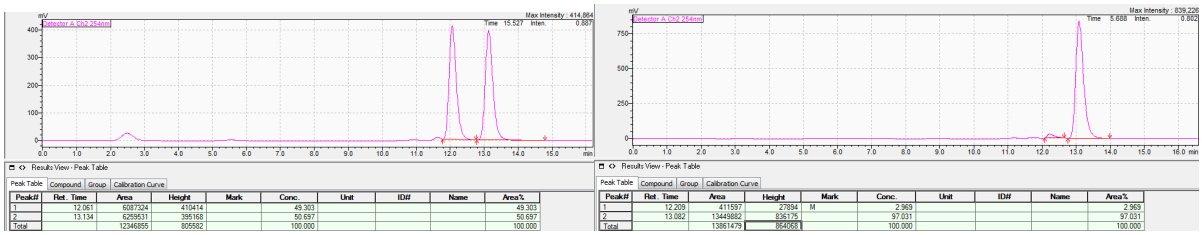
The titled compound was isolated (48.7 mg, 75%, 50% ee) as colorless oil after chromatography on silica gel (30:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 5.49 (q, J = 7.2 Hz, 1H), 1.81 (d, J = 7.2 Hz, 3H), 1.33 (s, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 215.86, 140.87 ($J_{C\text{-}F}$ = 1.4 Hz), 128.29 ($J_{C\text{-}F}$ = 32.2 Hz), 128.22, 125.27 ($J_{C\text{-}F}$ = 3.7 Hz), 124.59 ($J_{C\text{-}F}$ = 271.7 Hz), 85.15, 84.14, 24.90, 12.98.

HRMS (APCI $^{+}$) *m/z* calcd for $C_{17}H_{21}BF_3O_2$, $[M+H]^+$ 325.1587, Found:325.1588. Optical rotation: $[\alpha]^{20}_D$ = -12.10 (c = 1.0 g/cm^3, $CHCl_3$). HPLC condition: Chiral column IE, n-hexane/i-PrOH = 100:0, flow rate = 0.5 mL/min, wavelength = 254 nm, t_R = 18.5 min for minor isomer, t_R = 23.2 min for major isomer.



General procedure for gram scale for Cu-catalysed hydroboration of 1,3-enynes

CuOAc (19.6 mg, 0.160 mmol) and (S,S)-Ph-BPE (122.0 mg, 0.240 mmol) were weighted and added into a 100 mL Schlenk flask inside the glovebox. The resulting mixture was stirred for 15 mins prior adding HBpin (1.28 g, 10.0 mmol) and but-3-en-1-yn-1-ylbenzene (1.00 g, 8.0 mmol) successively. The Schlenk flask was removed from the glove box, and the mixture was stirred at 5°C for 24 hours. The residue was then purified by flash column chromatography using a mixture of hexane and ethyl acetate (100:1) as eluent yielding (R)-4,4,5,5-tetramethyl-2-(1-phenylbuta-1,2-dien-1-yl)-1,3,2-dioxaborolane**, 2a** (1.76 g, 85 %, 94% ee) as a pale yellow oil. Optical rotation: $[\alpha]^{20}_D$ = -15.06 (c = 1.0 g/cm^3, $CHCl_3$). The absolute configuration was assigned by analog to that of **2u.** HPLC condition: Chiral column IA, n-hexane/i-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 12.2 min for minor isomer, t_R = 13.1 min for major isomer.

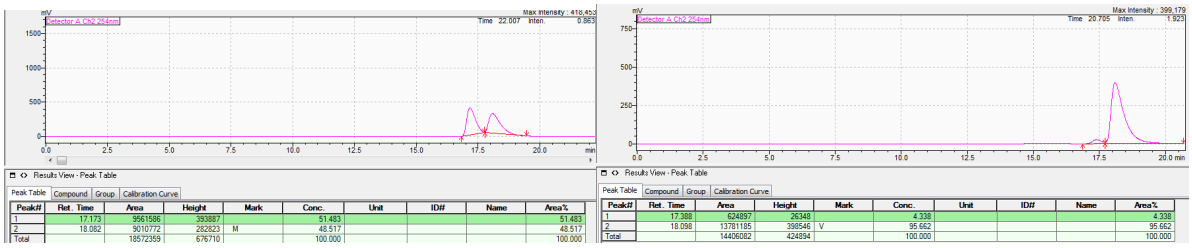


General procedure for Suzuki-Miyaura cross-coupling of bromoarene and allenylboronate

A mixture of 1-iodo-4-methylbenzene (65.4 mg, 0.300 mmol), Na_2CO_3 (43.4 mg, 0.400 mmol) and $PdCl_2(PPh_3)_2$ (7 mg, 10 μmol) was added into a mixture of methanol (0.8 mL) and toluene (0.2 mL) in a 4-mL screw-capped vial containing a magnetic stirring bar inside the glovebox. Subsequently, (R)-4,4,5,5-tetramethyl-2-(1-phenylbuta-1,2-dien-1-yl)-1,3,2-dioxaborolane (51.2 mg, 0.200 mmol) was added into the reaction mixture and then stirred at room temperature for 12 hours. After the completion of the reaction, waster was added into the reaction mixture. It was then extracted with diethyl ether, dried over sodium sulfate, filtered and concentrated under vacuum. The residue was then purified by flash column chromatography using hexane and ethyl acetate as eluents yielding (S)-1-methyl-4-(1-phenylbuta-1,2-dien-1-yl)benzene, **3** (23.3 mg, 53%, 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.29 – 7.25 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.67 (q, *J* = 7.1 Hz, 1H), 2.39 (s, 3H), 1.86 (d, *J* = 7.1 Hz, 3H). $\{^1H\}^{13}C$ NMR (101 MHz, $CDCl_3$) δ 206.32, 137.62, 136.91, 134.46, 129.18, 128.57, 128.51, 128.41, 127.07, 109.19, 88.84, 21.29, 14.53. HRMS (APCI $^{+}$) *m/z* calcd for

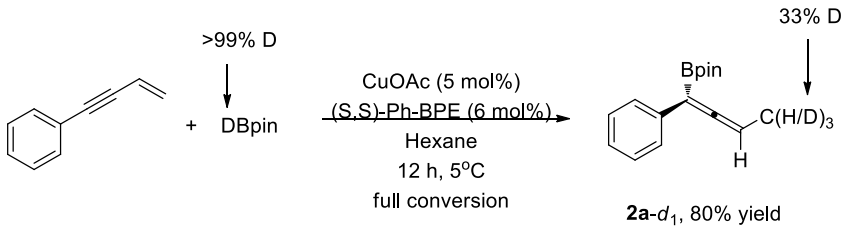
$C_{17}H_{17}$, $[M+H]^+$ 221.1330. Found: 221.1322. Optical rotation: $[\alpha]^{20}_D$ = 7.90 (c = 1.0 g/cm^3, $CHCl_3$).HPLC condition: Chiral column IC, n-hexane/i-PrOH = 100:0, flow rate = 0.35 mL/min, wavelength = 254 nm, t_R = 17.4 min for minor isomer, t_R = 18.1 min for major isomer.



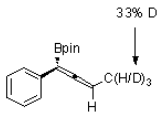
Mechanistic studies

Procedure for Deuterium-labeling Experiments

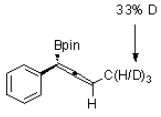
In an Ar-filled glovebox, a mixture of Cu(OAc) (1.1 mg, 10.0 μmol) and (S,S)-Ph-BPE (6.1 mg, 12.0 μmol) in hexane (1 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding DBpin (32.3 mg, 0.250 mmol) and but-3-en-1-yn-1-ylbenzene (26.0 mg, 0.200 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at under 5ºC for 24 hours respectively. Subsequently, the residue was purified by flash column chromatography using a mixture of hexane and ethyl acetate (100:1) as eluent. The details and characterization data of the products are stated below. Equimolar of chloroform-*d* was added as the internal standard for ^{2}H NMR analysis.



2a-d_1, 80% yield



2a-d_1, 80% yield

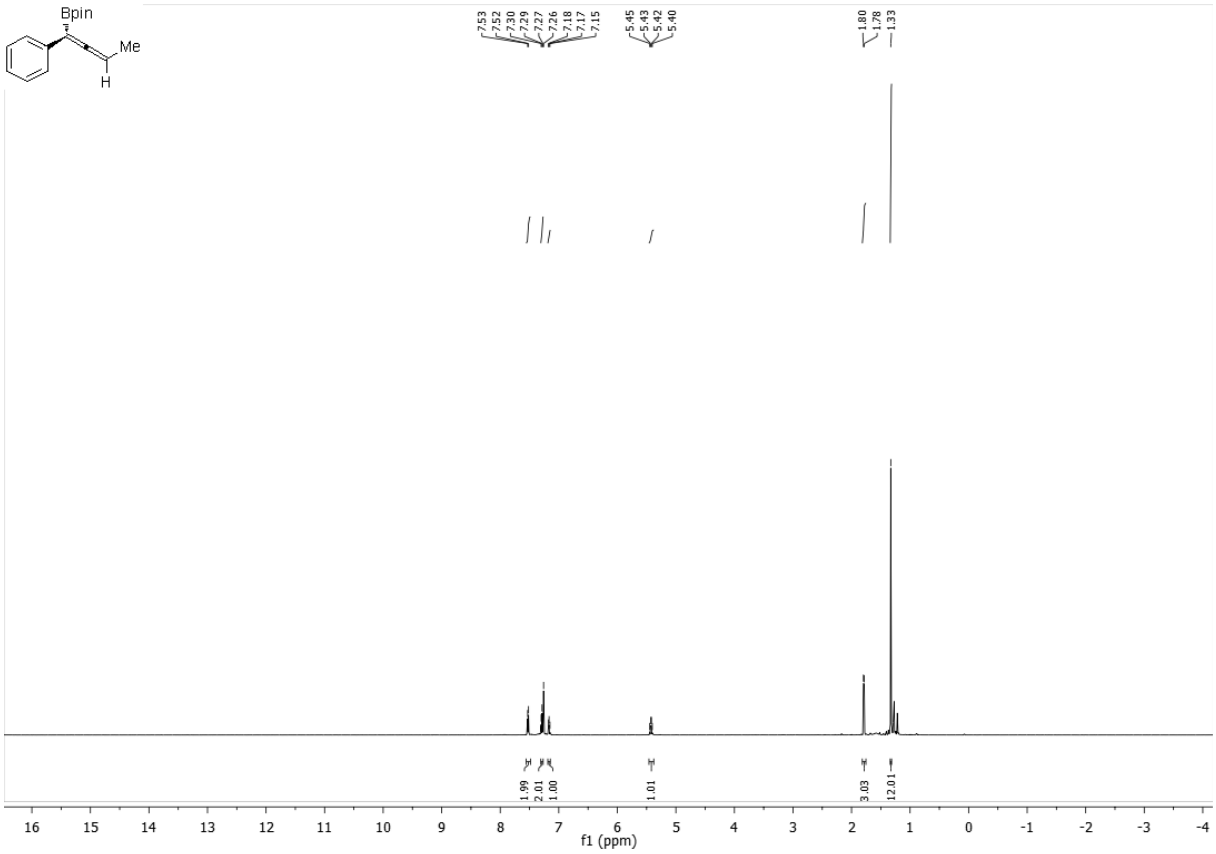


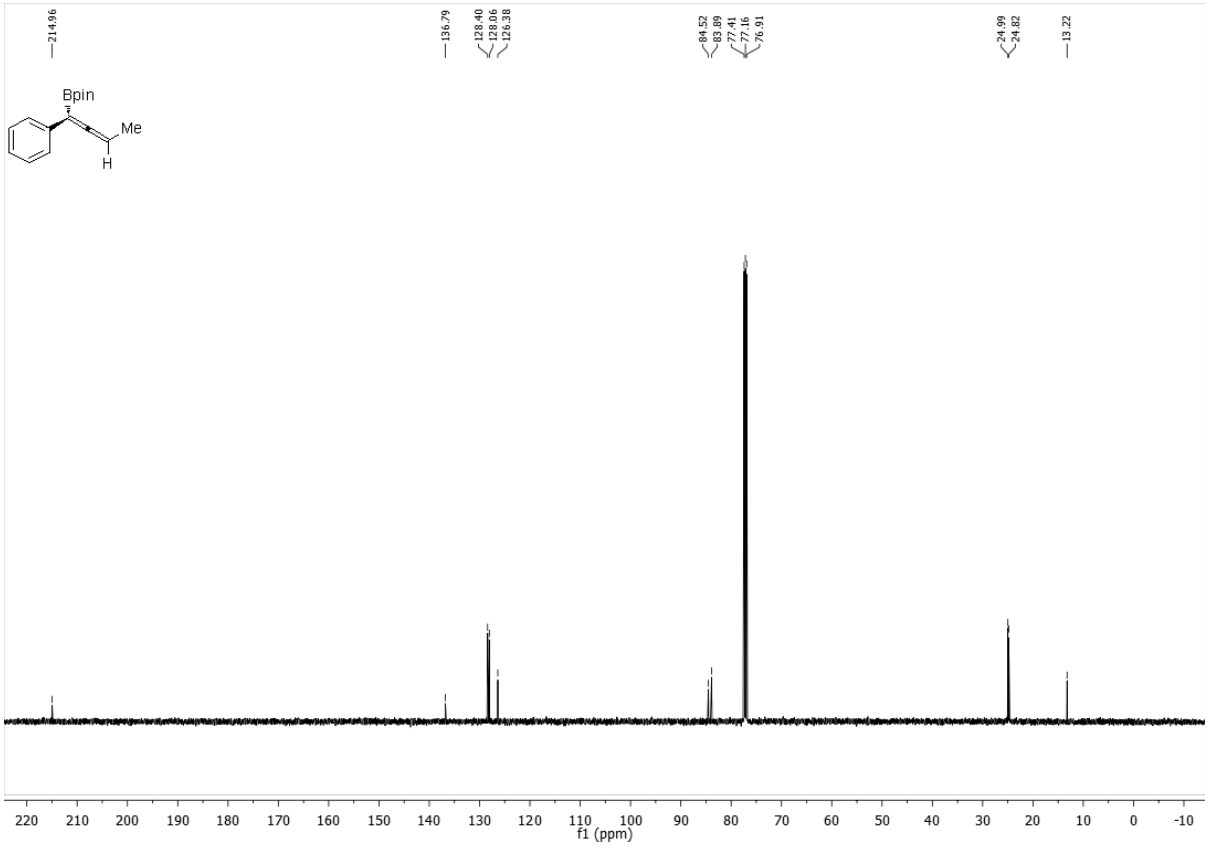
2a-d_1, 80% yield

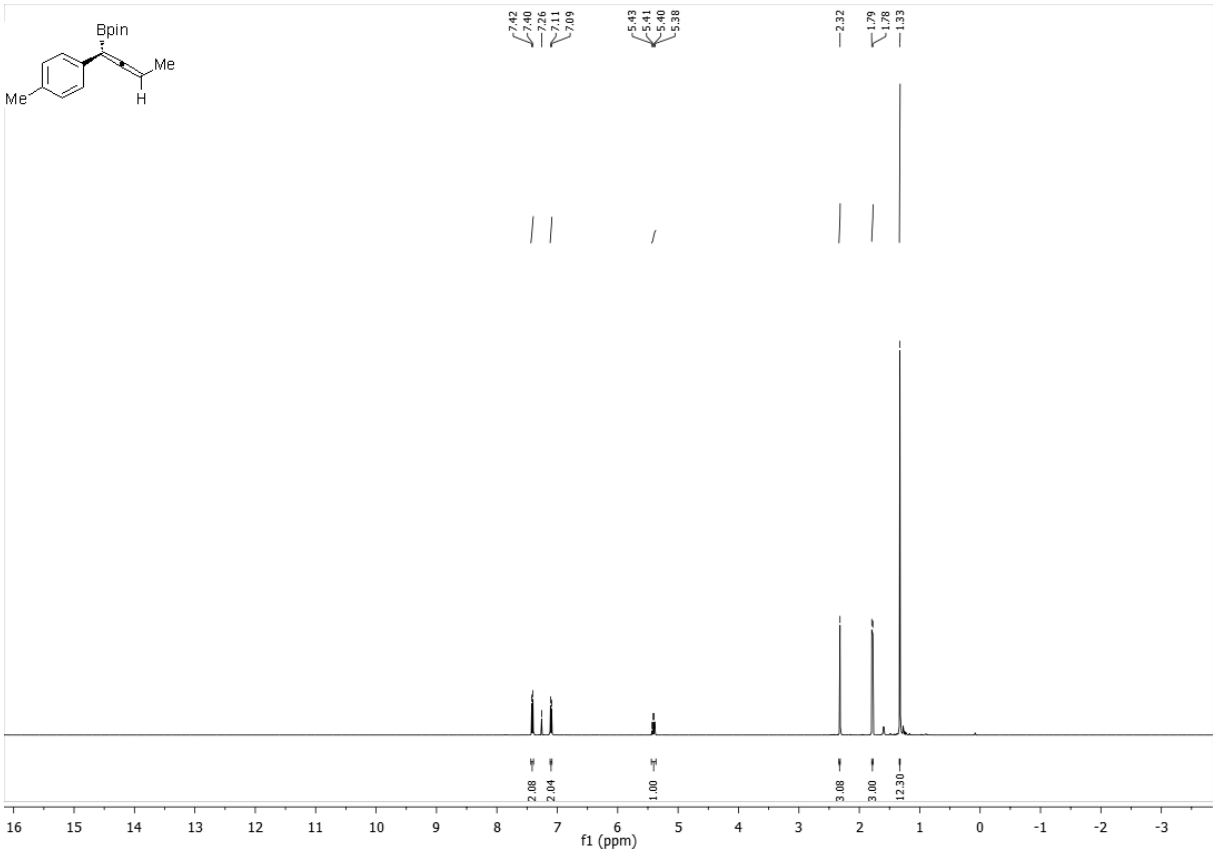
References

1. J.-K. Cheng and T.-P. Loh, *Journal of the American Chemical Society*, 2015, **137**, 42-45.
2. H. Ito, Y. Sasaki and M. Sawamura, *Journal of the American Chemical Society*, 2008, **130**, 15774-15775.

NMR Spectra (^{1}H, {^{1}H}^{13}C and ^{19}F)



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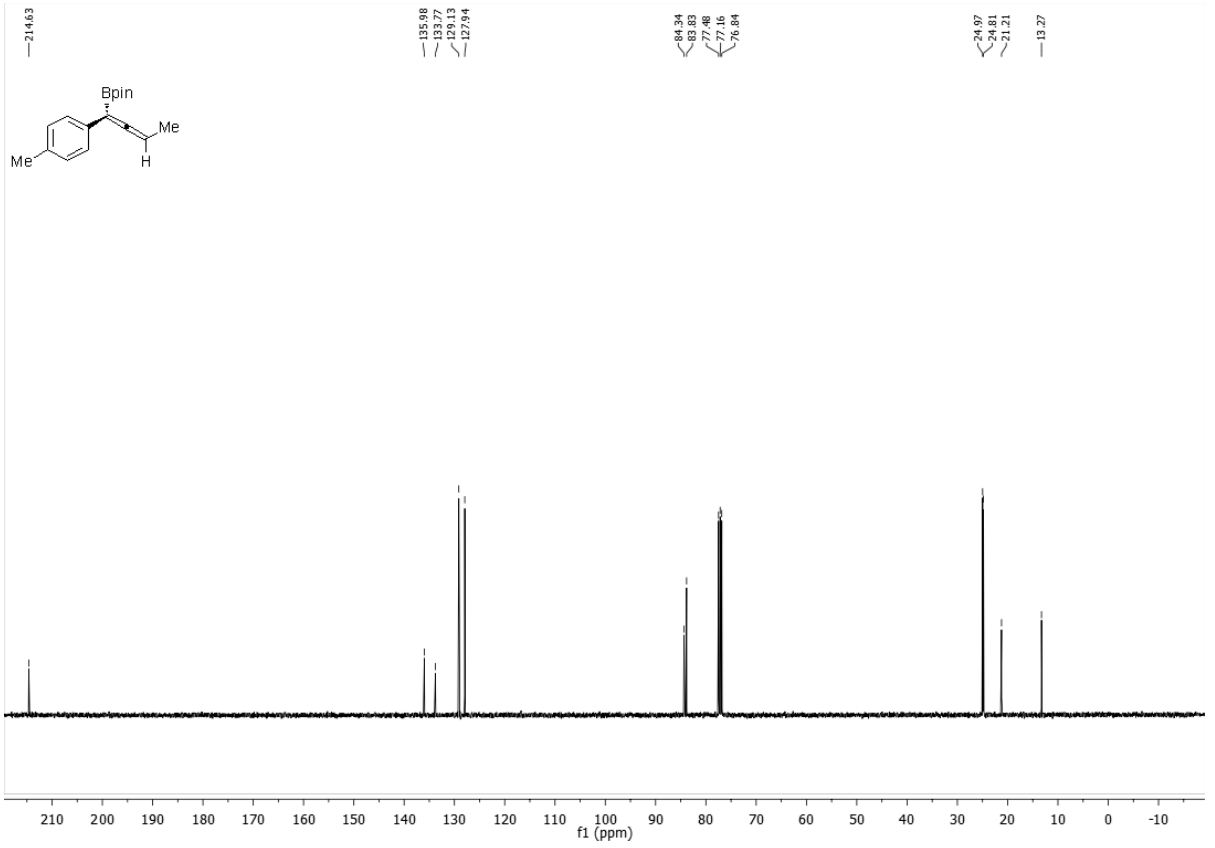
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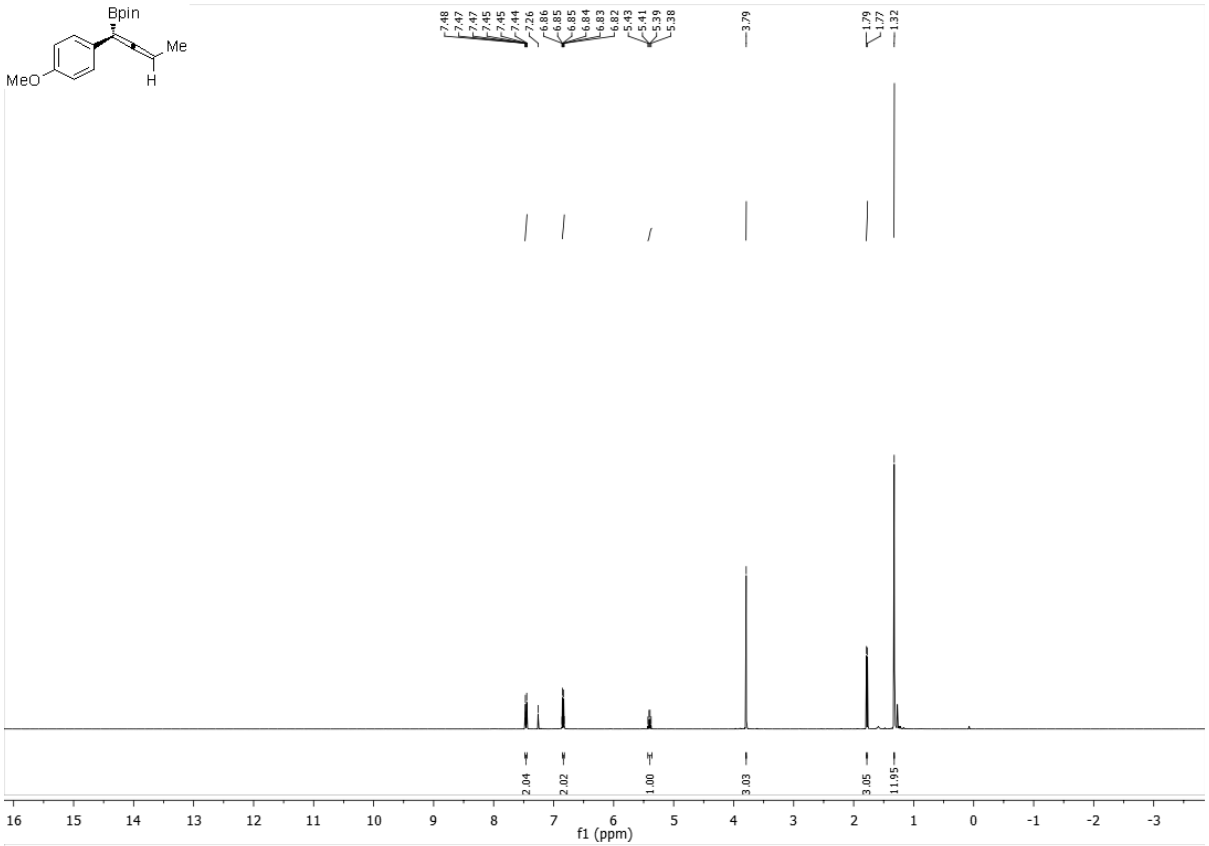
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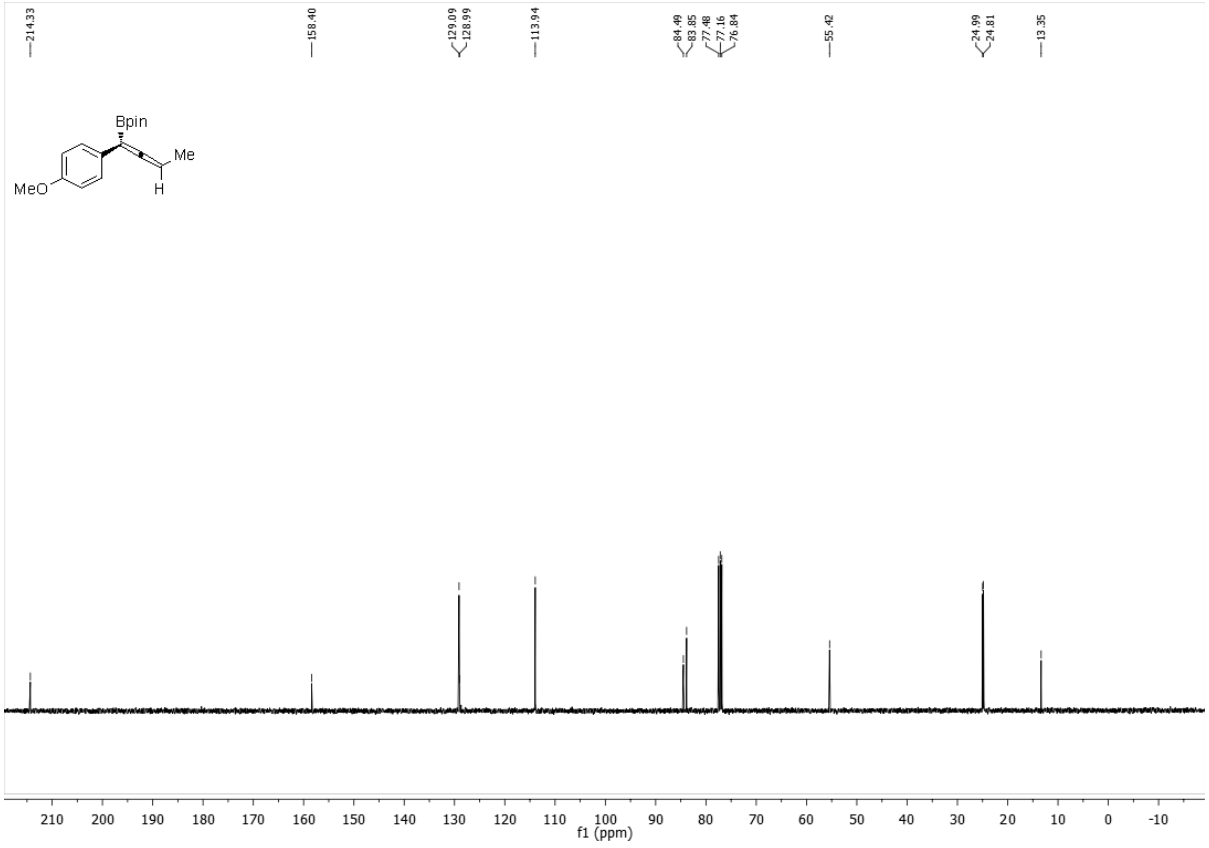
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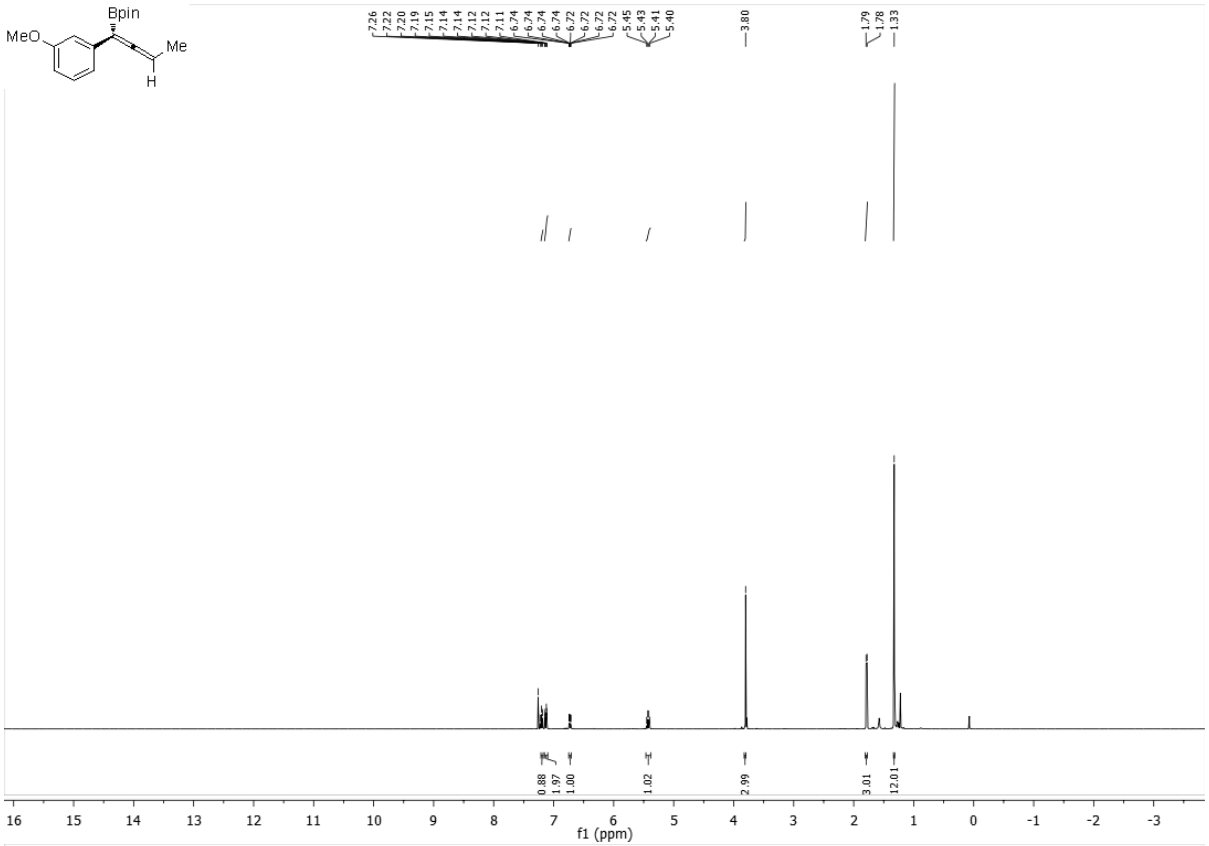
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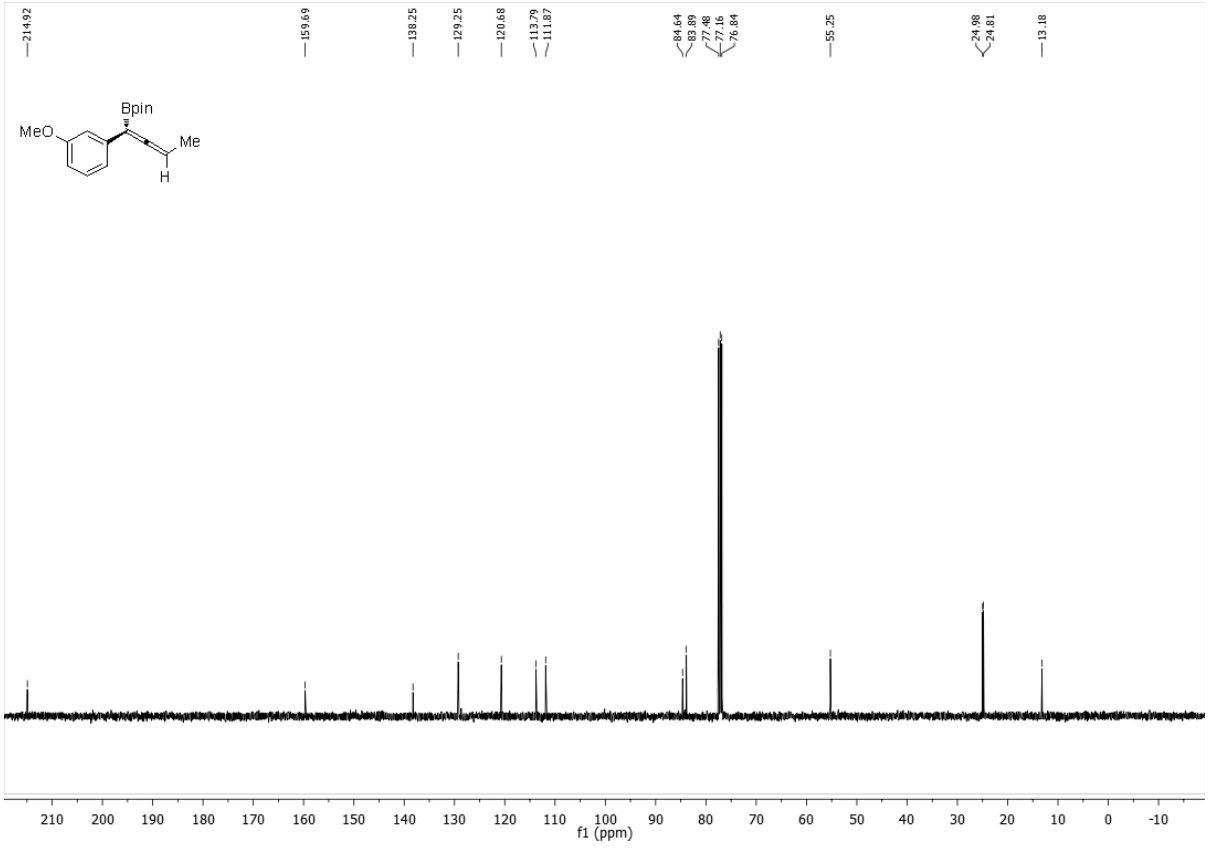
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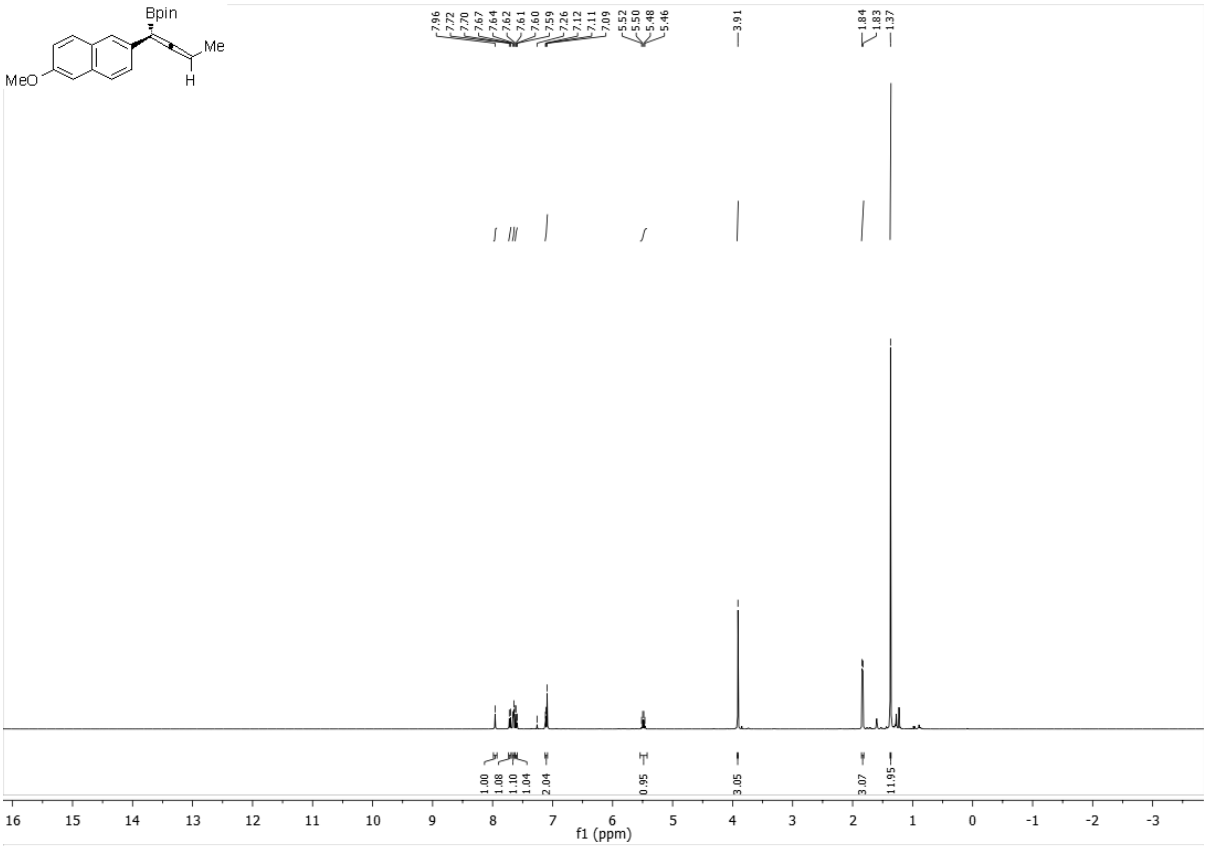
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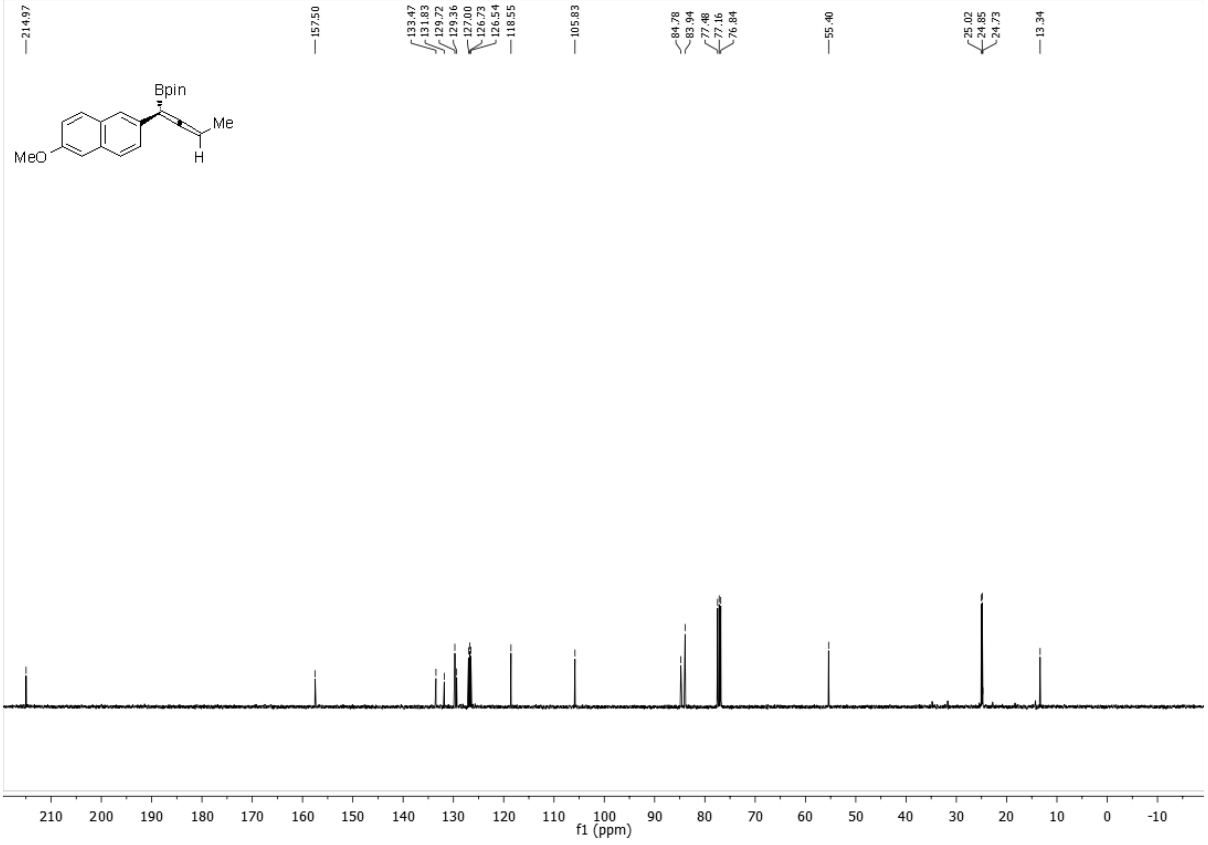
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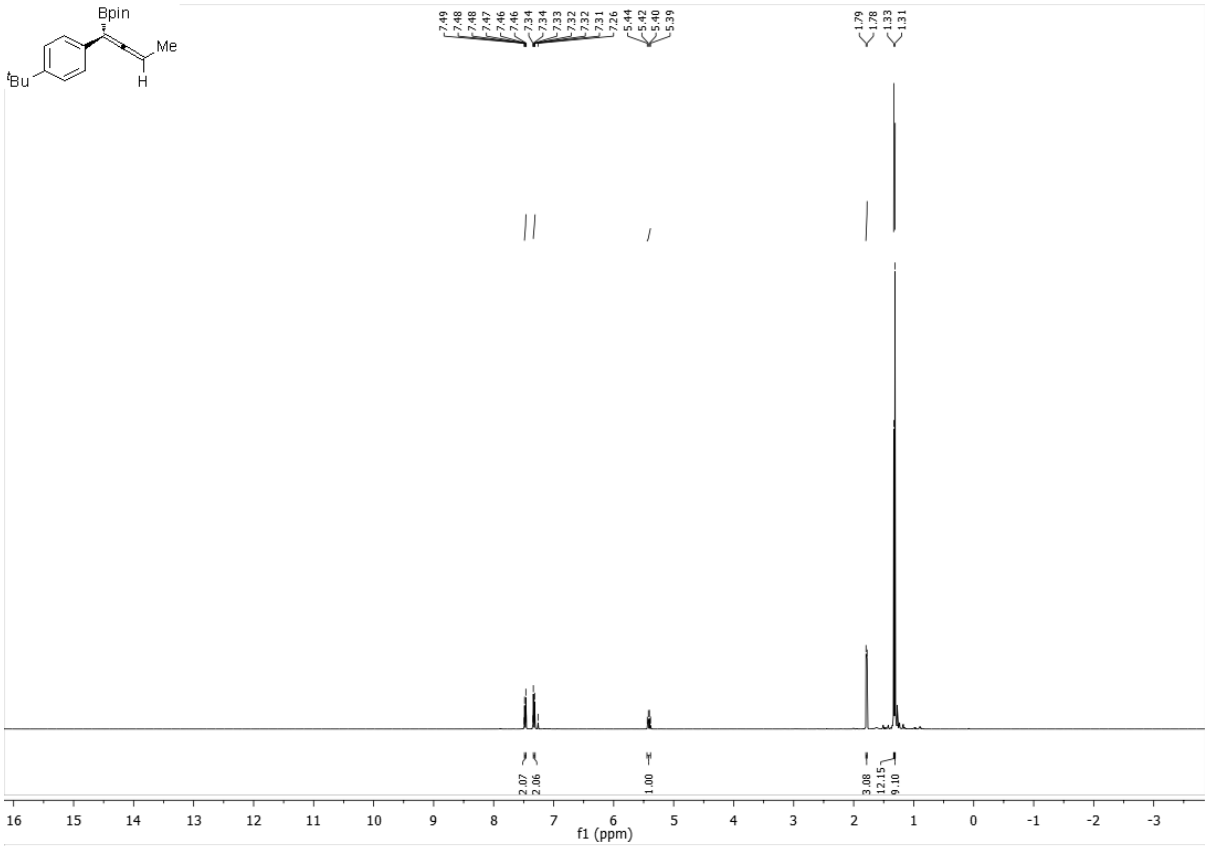
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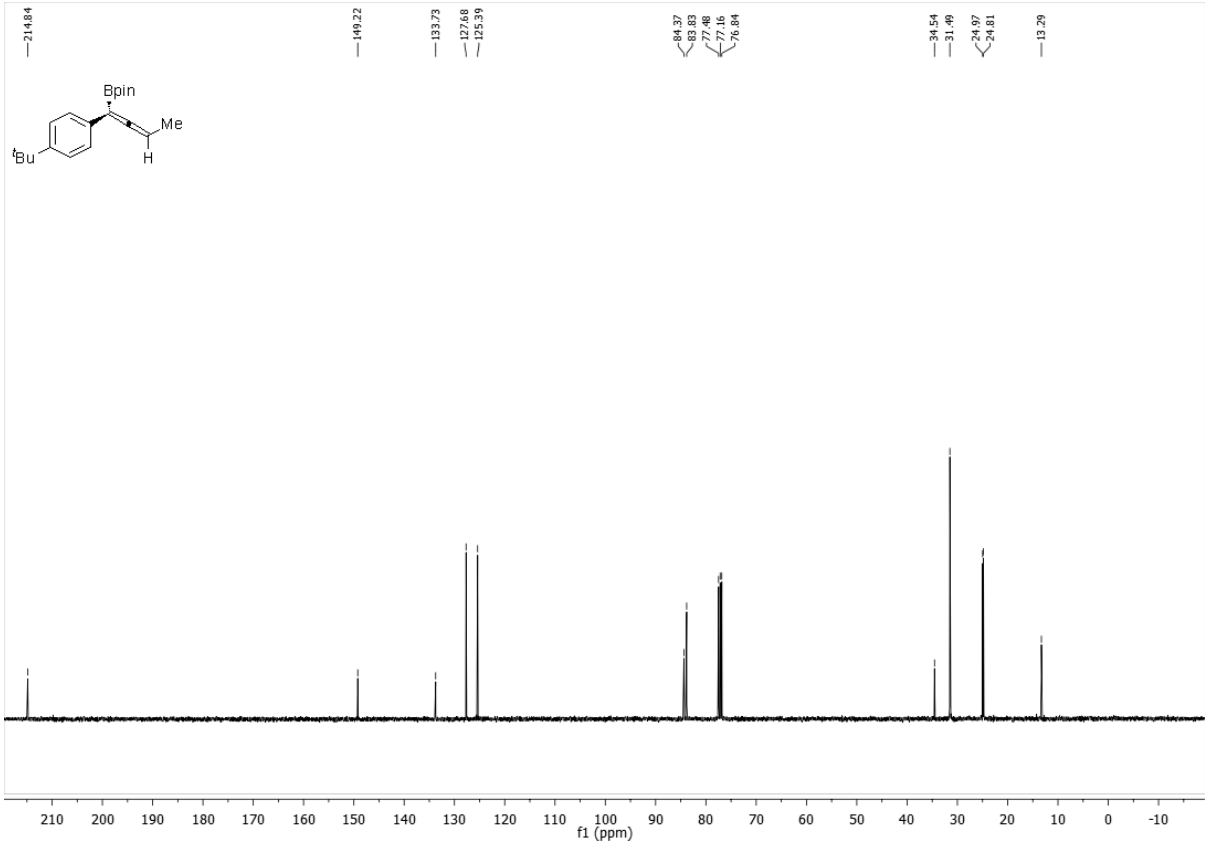
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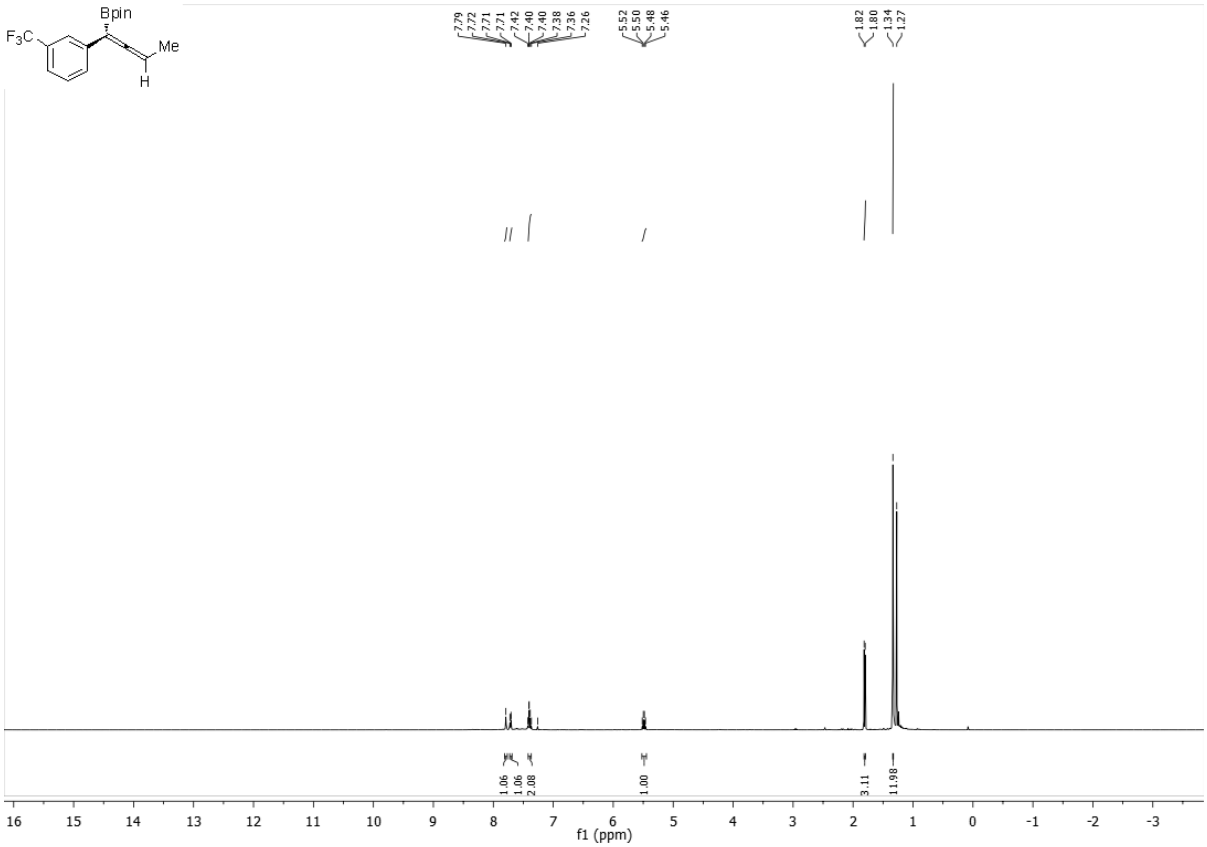
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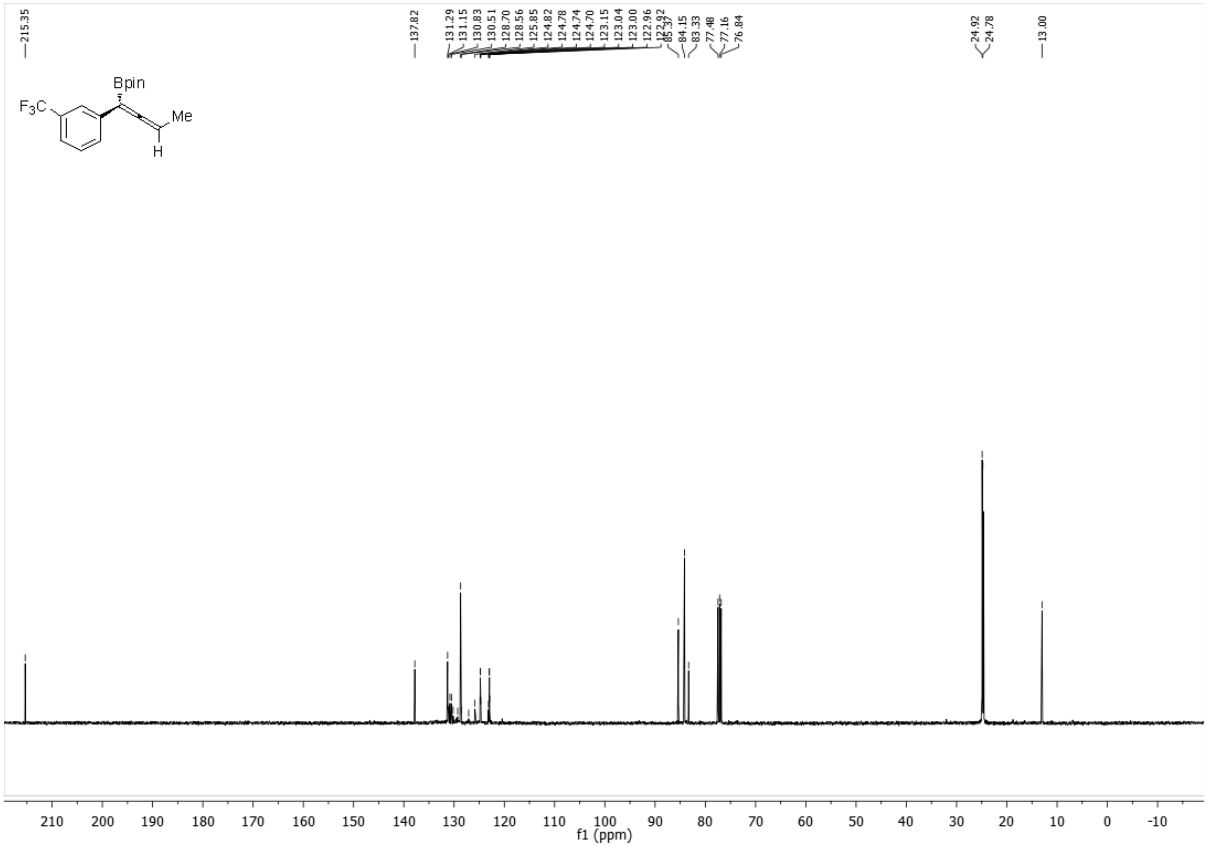
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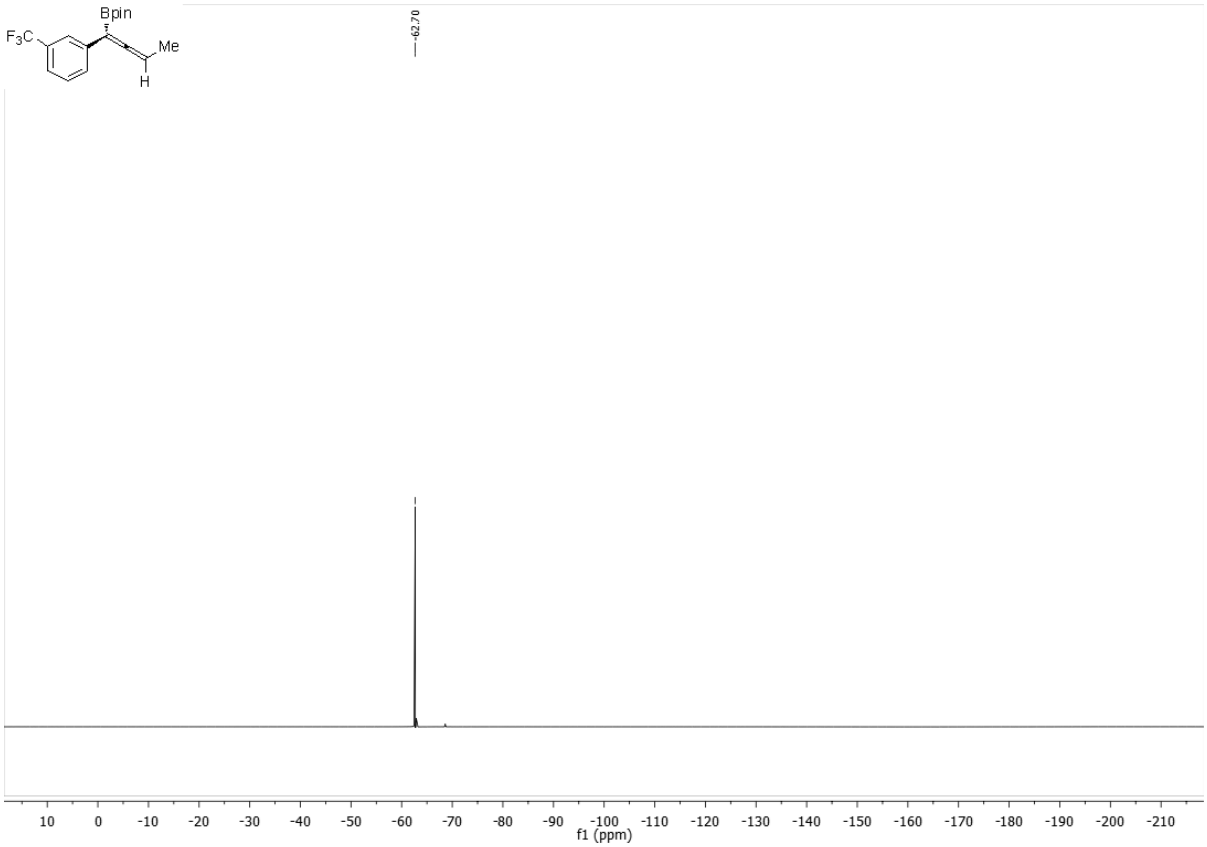
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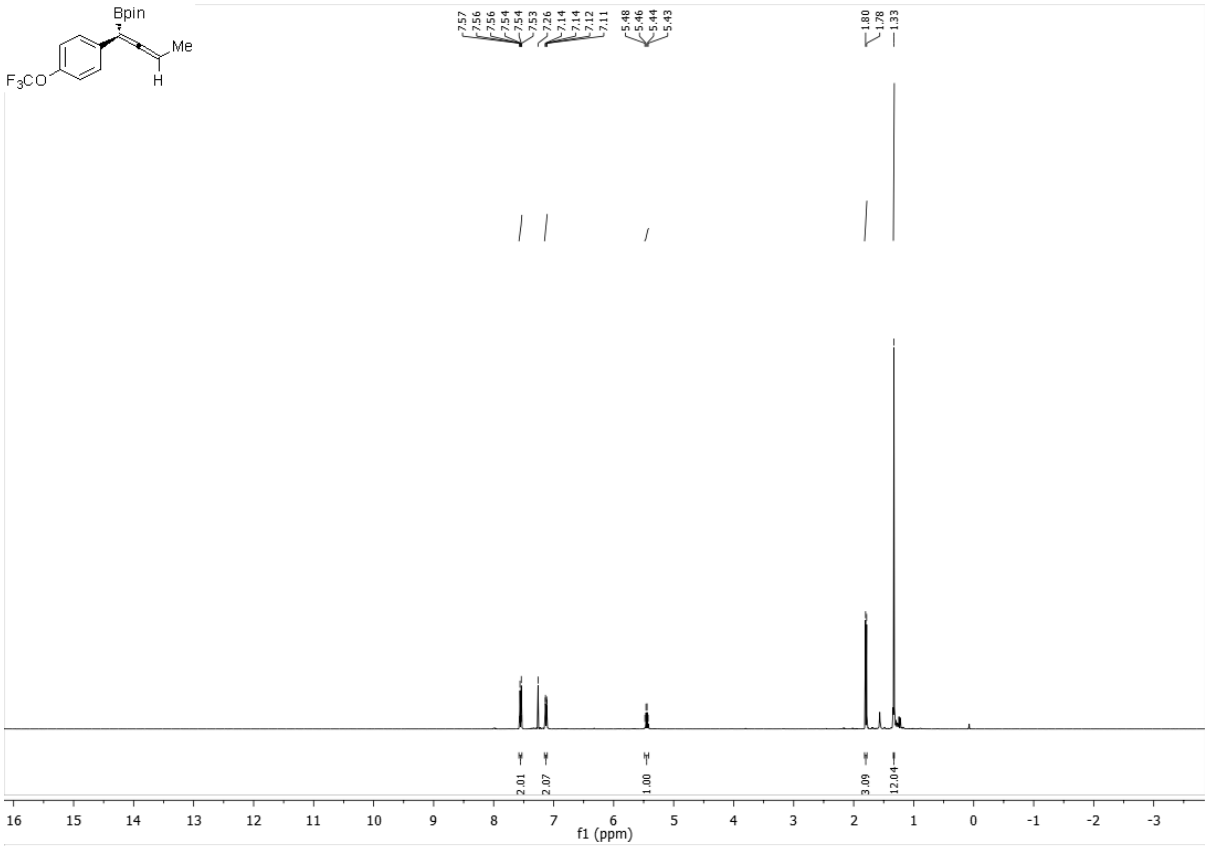
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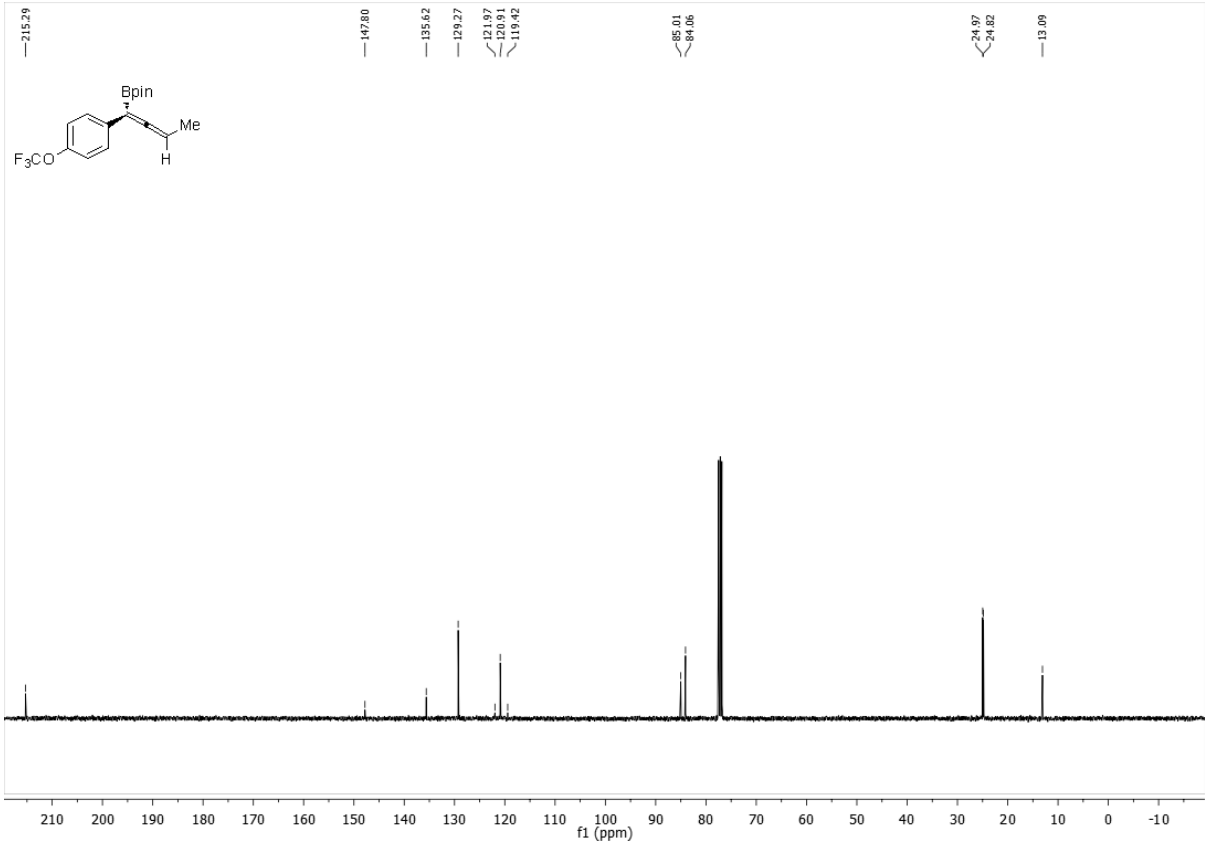
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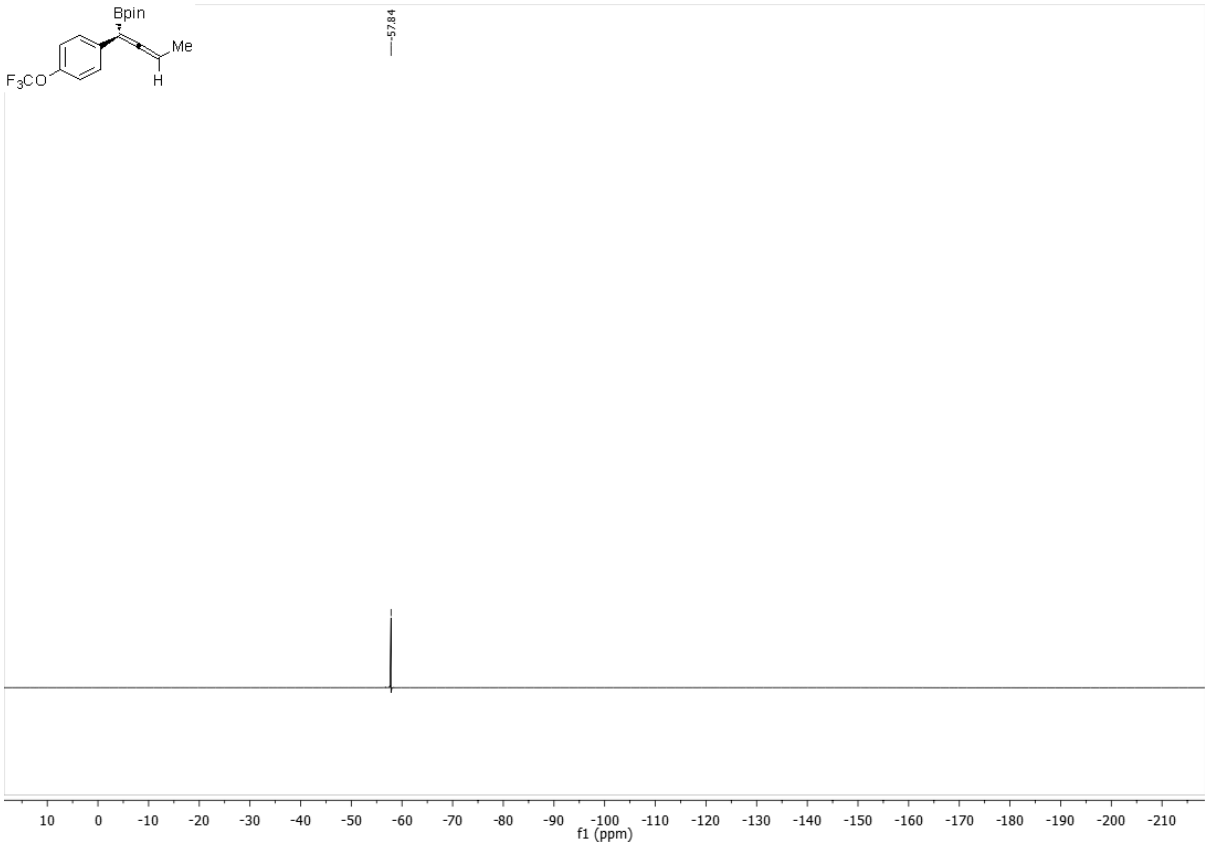
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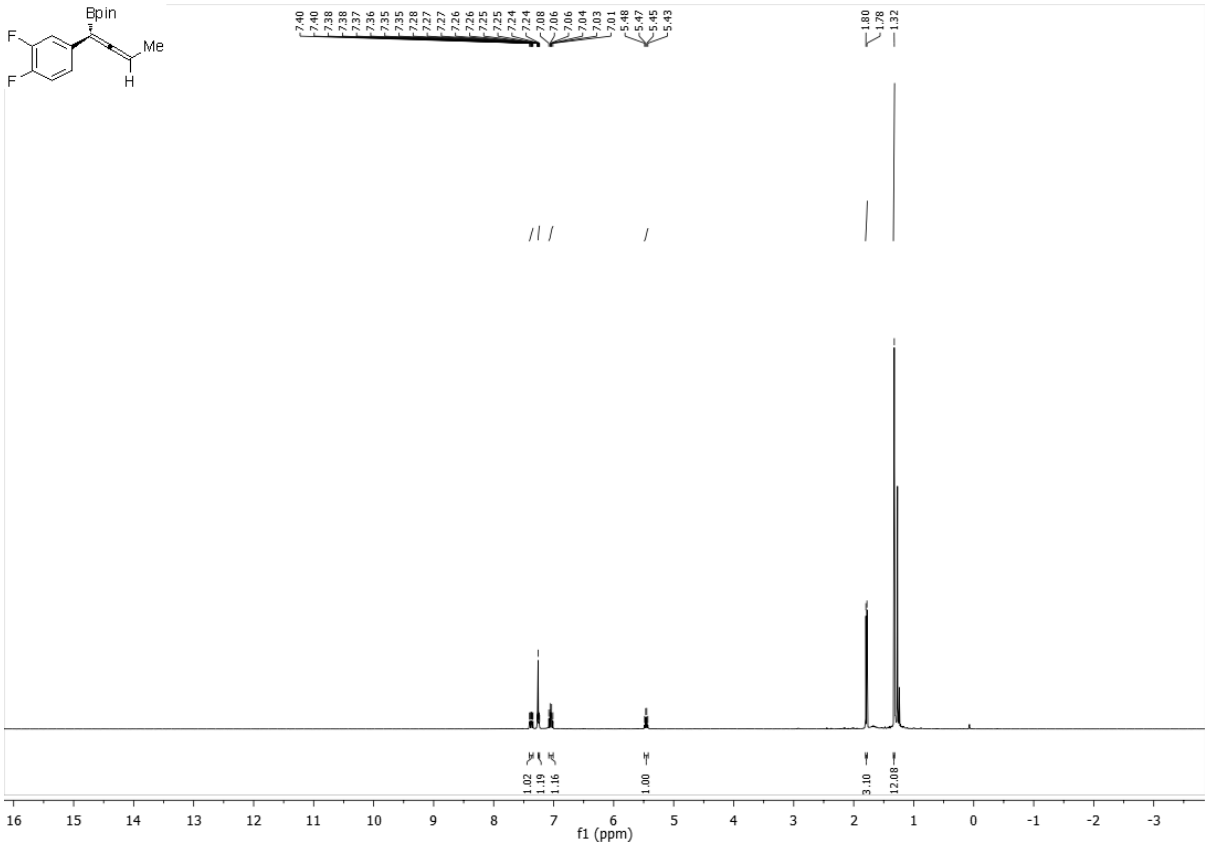
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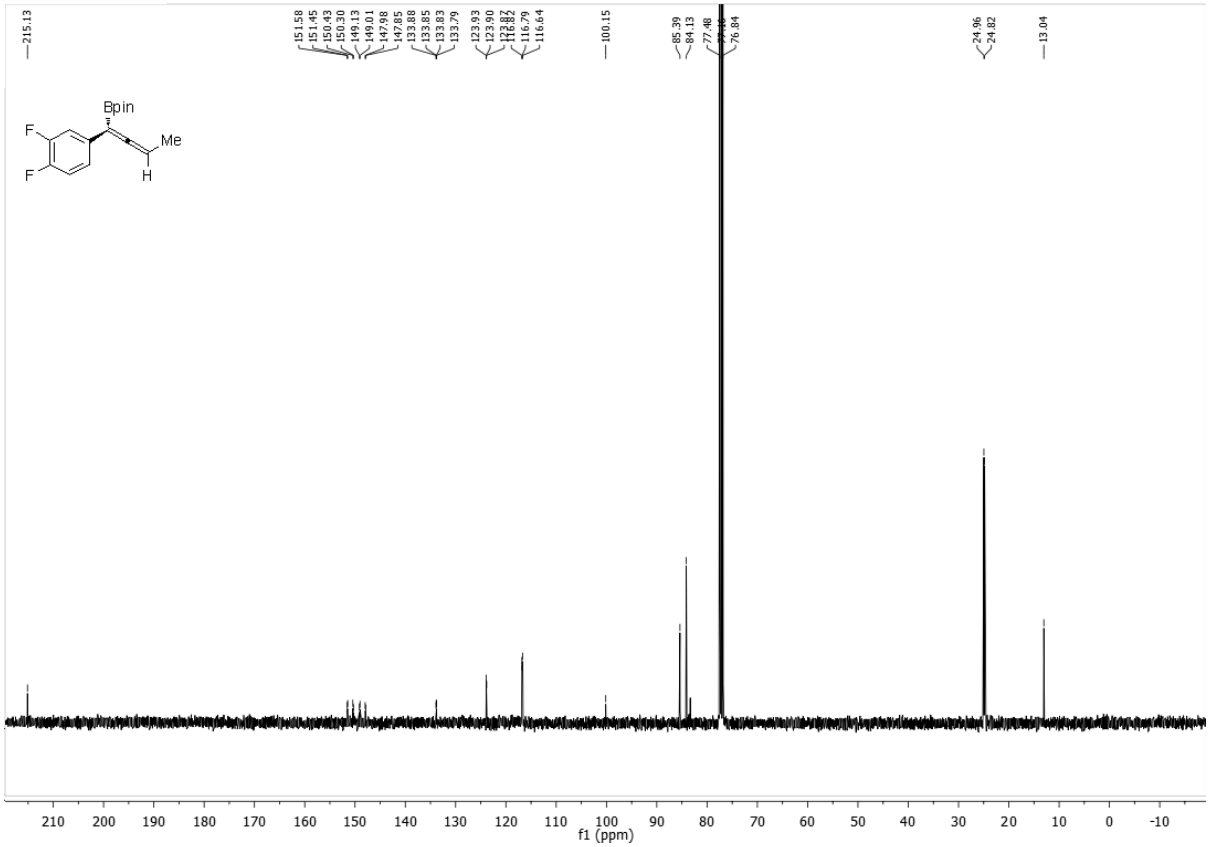
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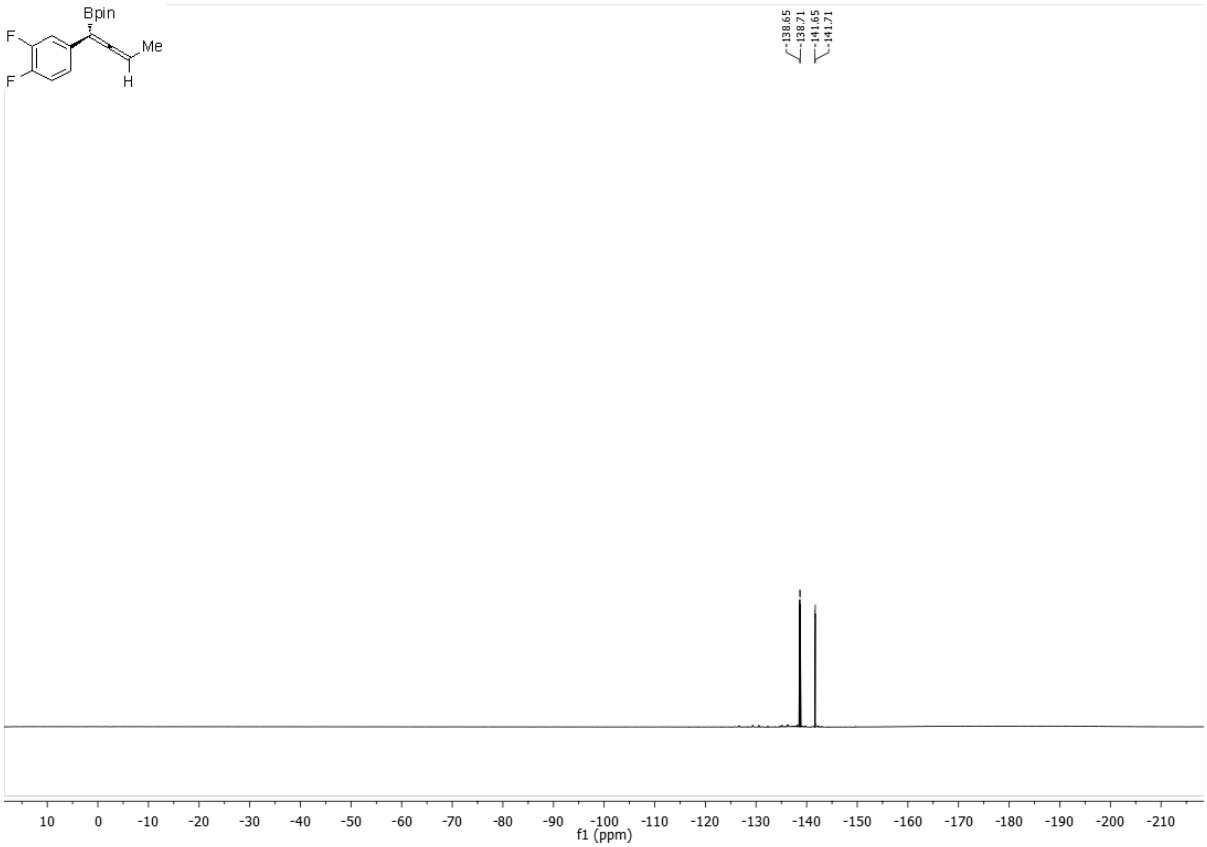
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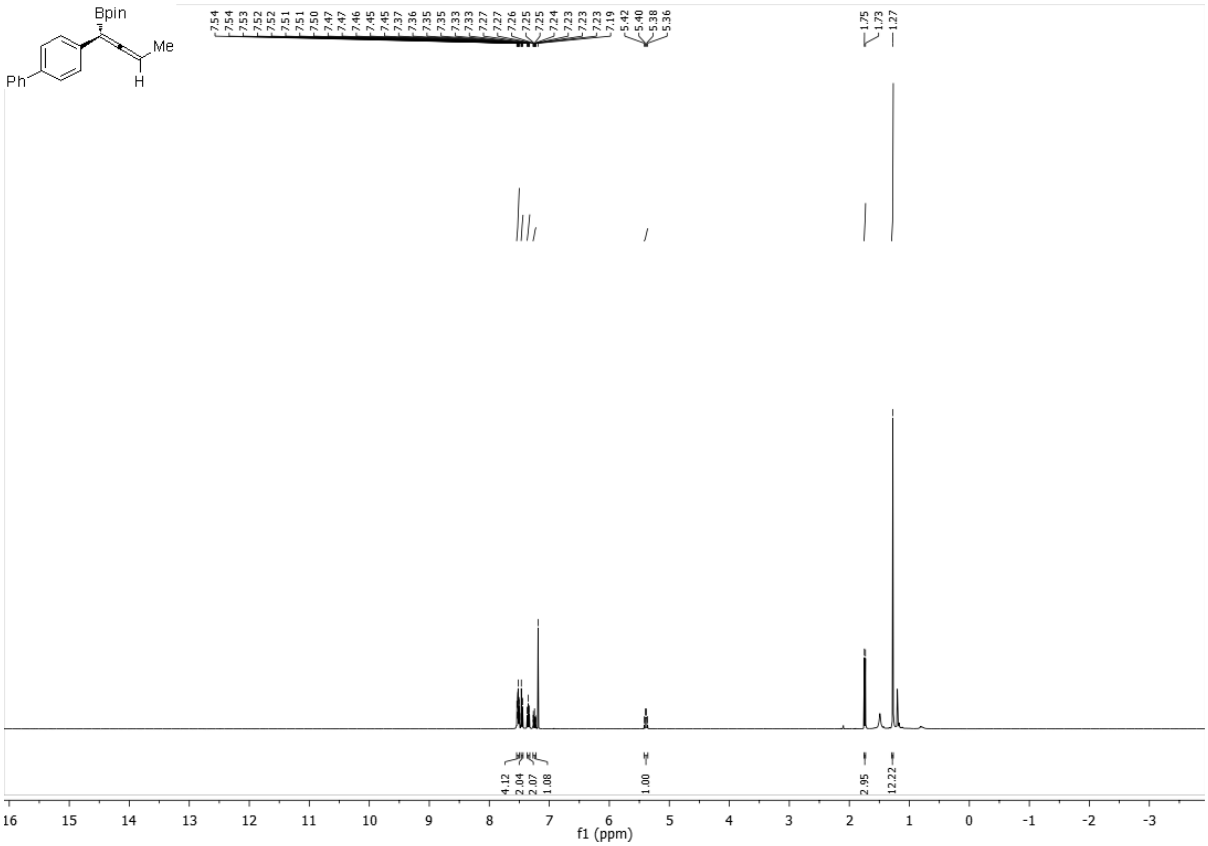
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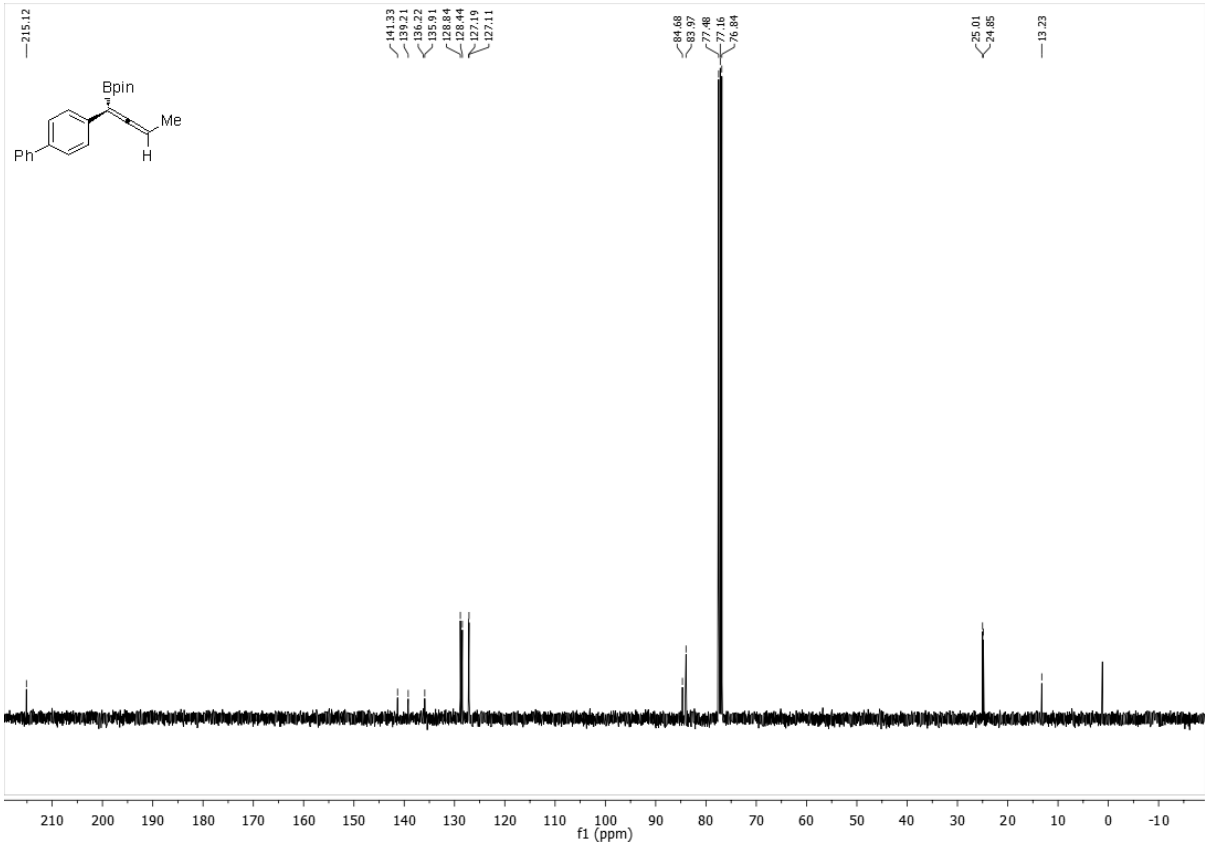
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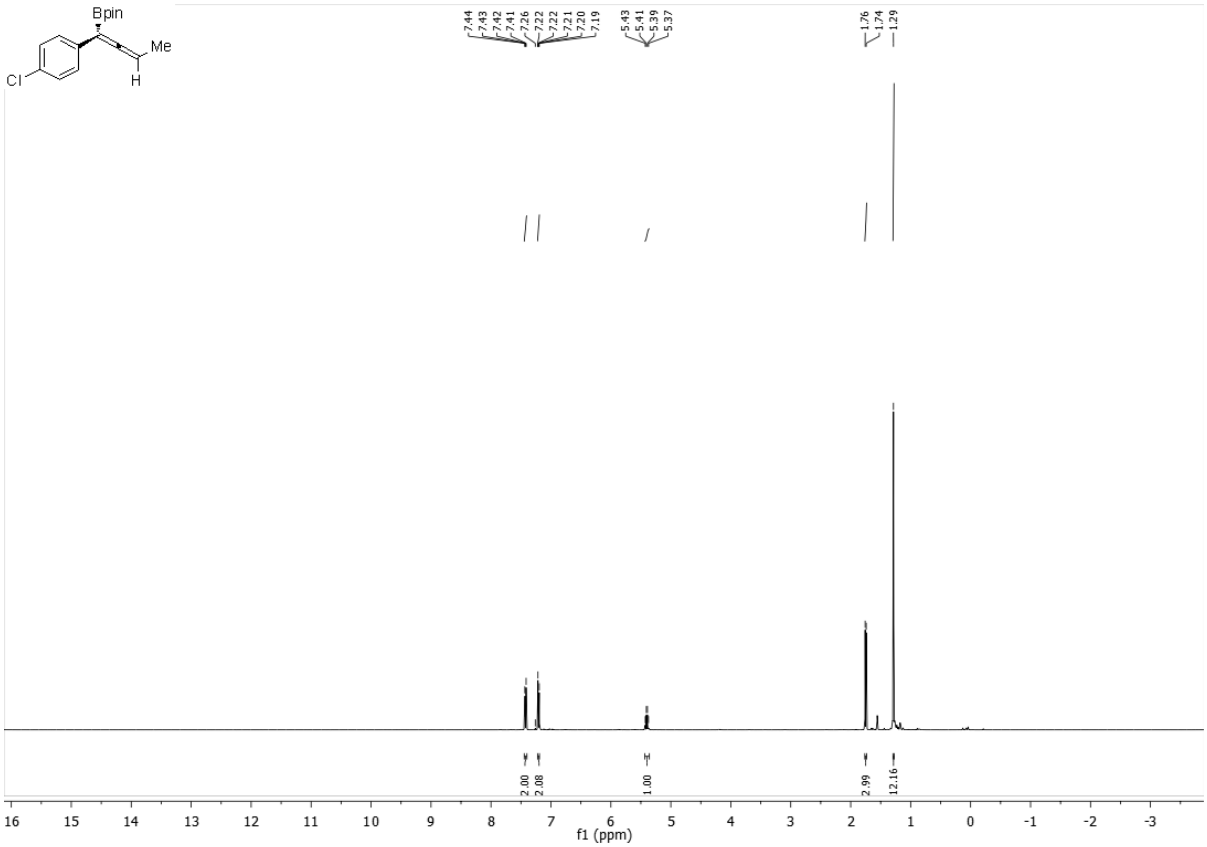
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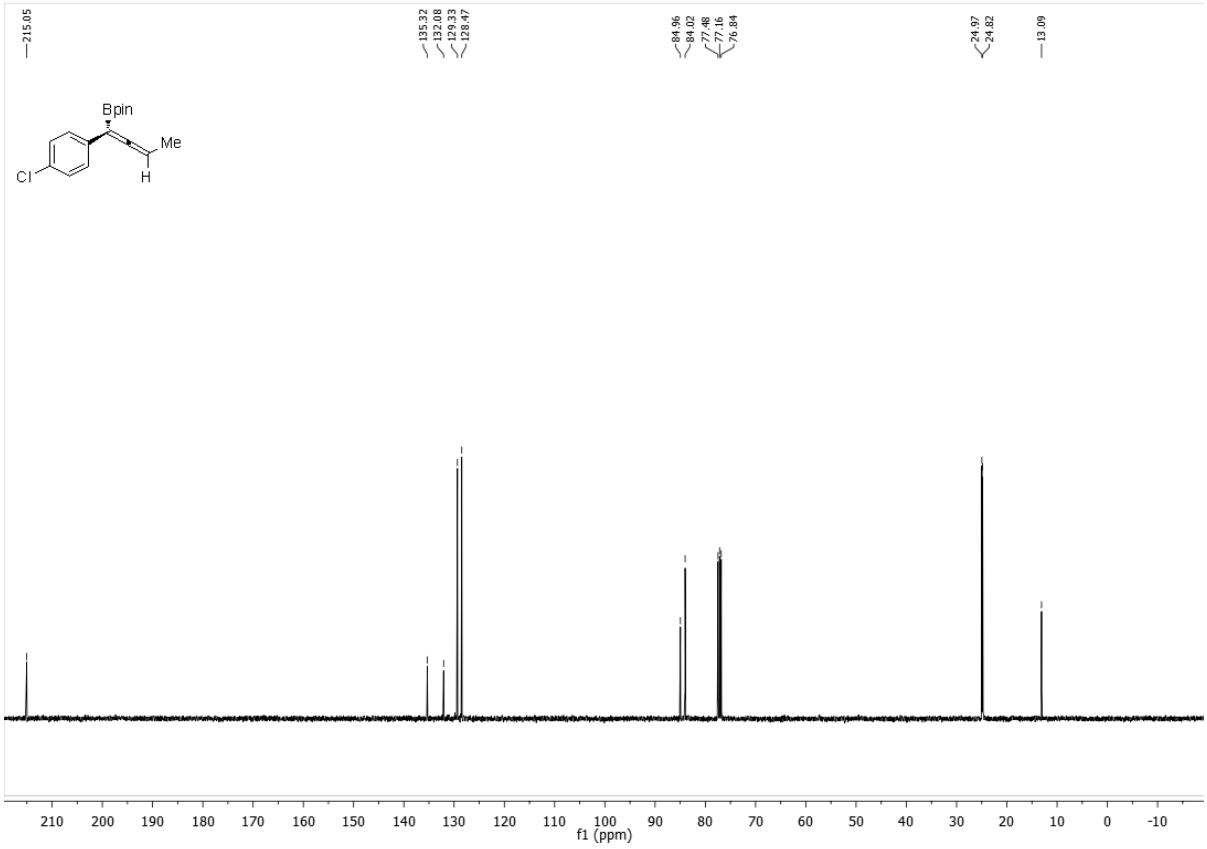
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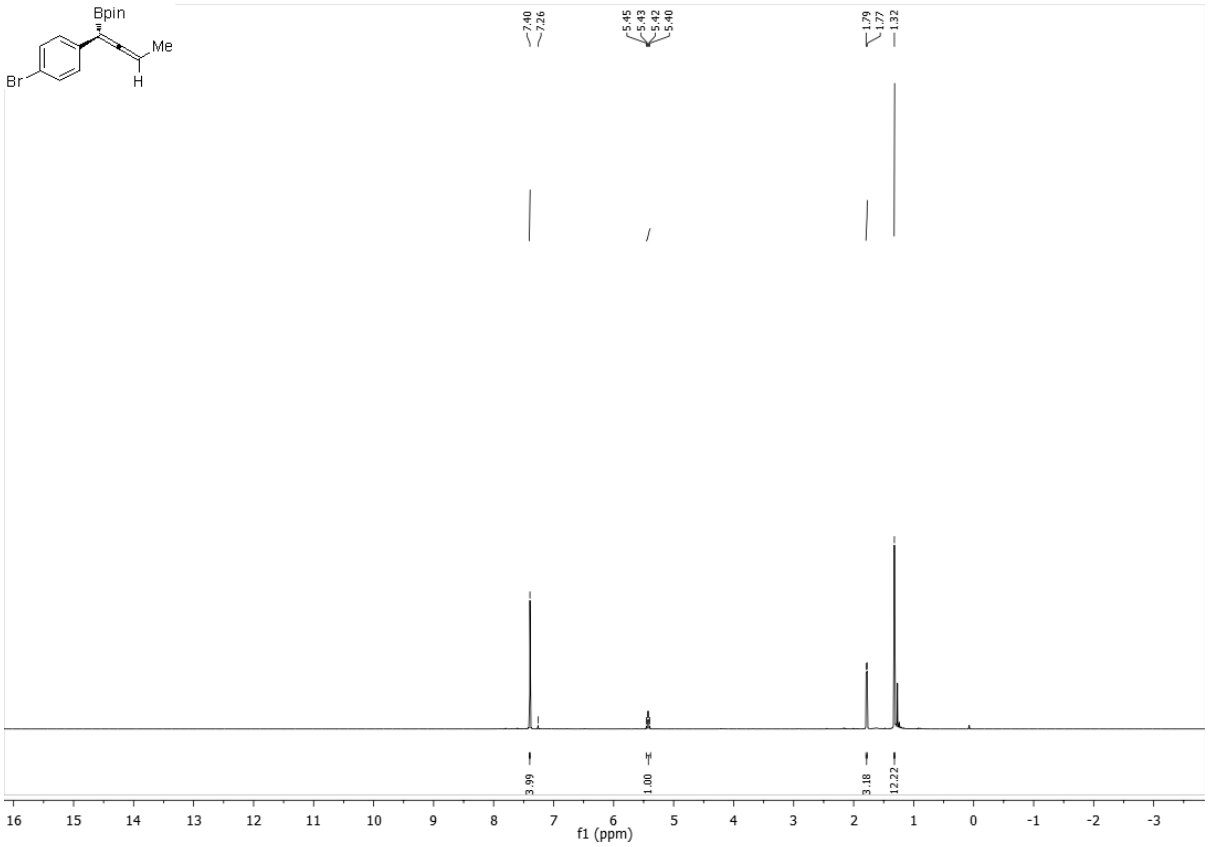
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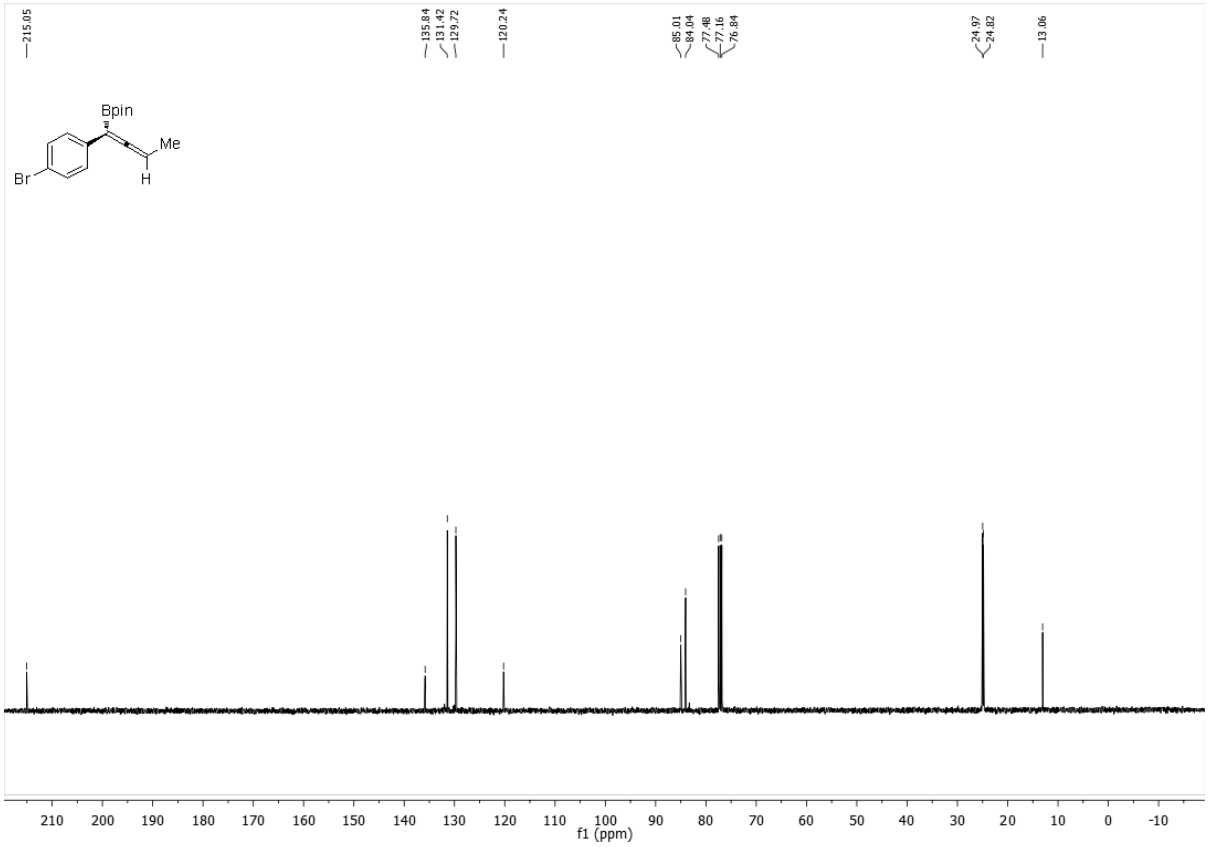
f1 (ppm)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129.72
120.24
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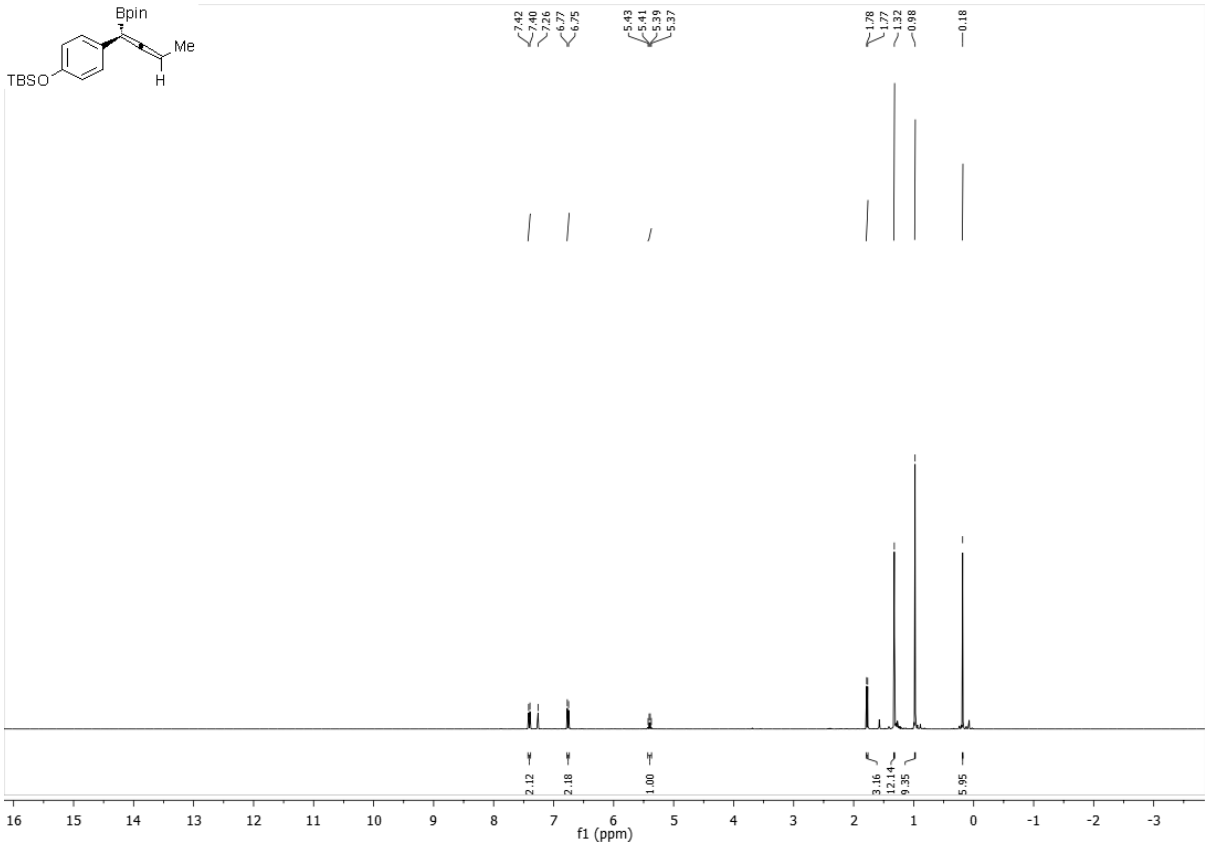
77.48
77.16
76.84
24.97
24.82
13.06
Bpin
Me
Br
H
f1 (ppm)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6.75
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5.41
5.39
5.37
1.78
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1.32
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2.18
1.00
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12.14
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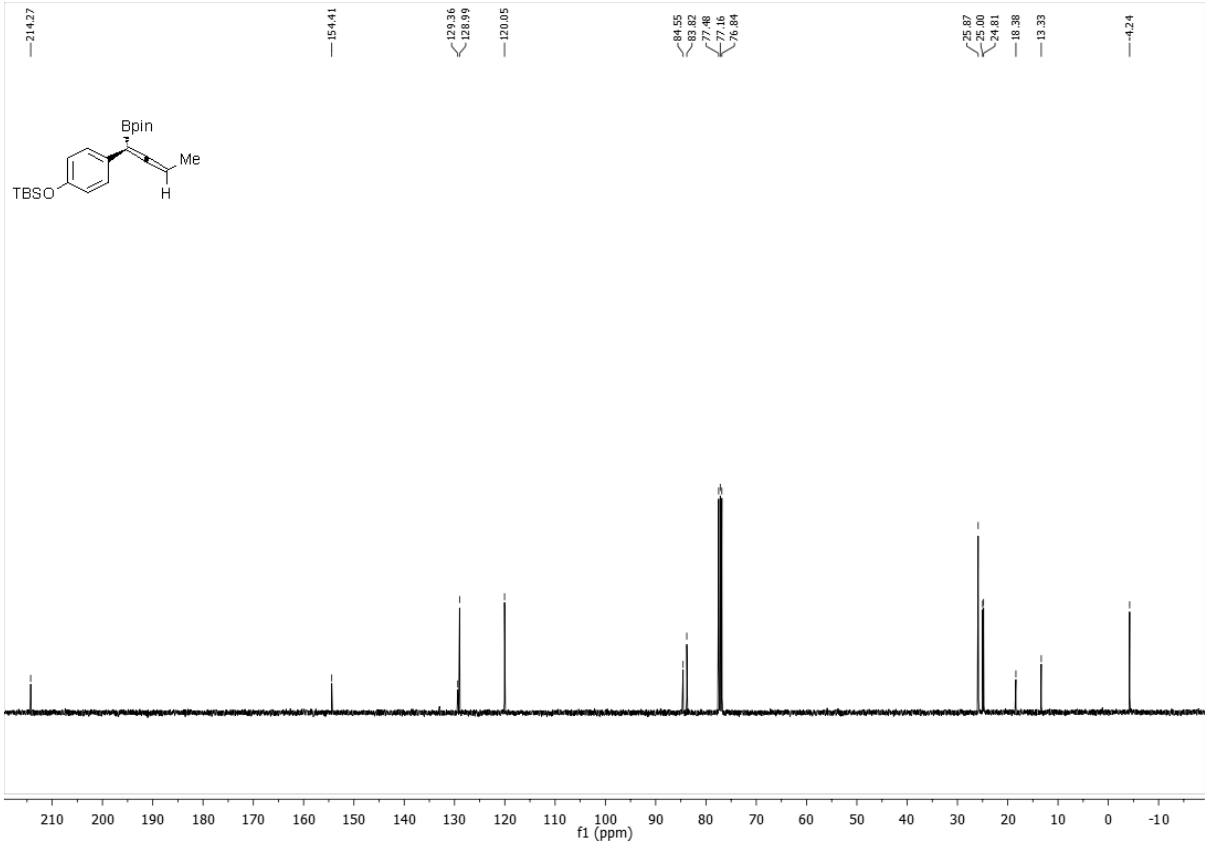
5.95
f1 (ppm)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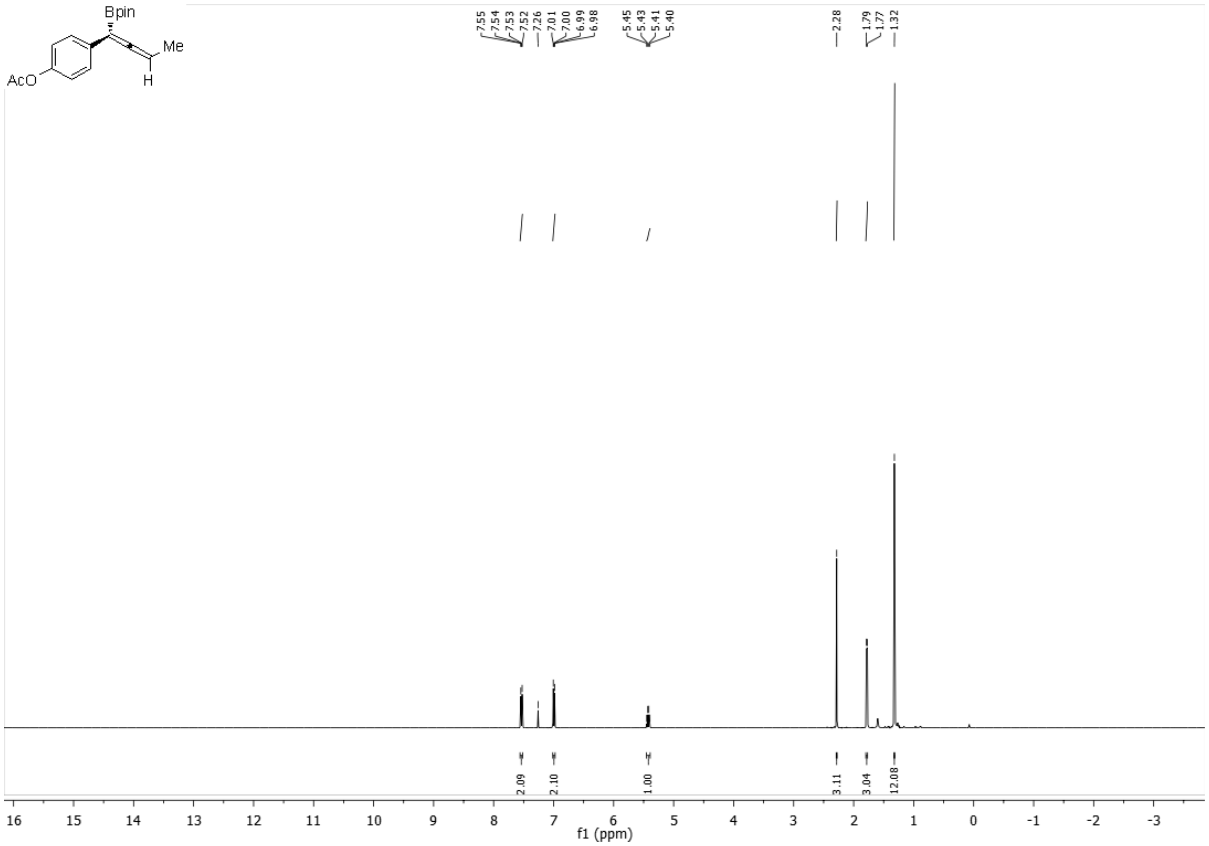
18.38
13.33
4.24
Bpin
Me
H
TBSO
f1 (ppm)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AcO
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5.43
5.41
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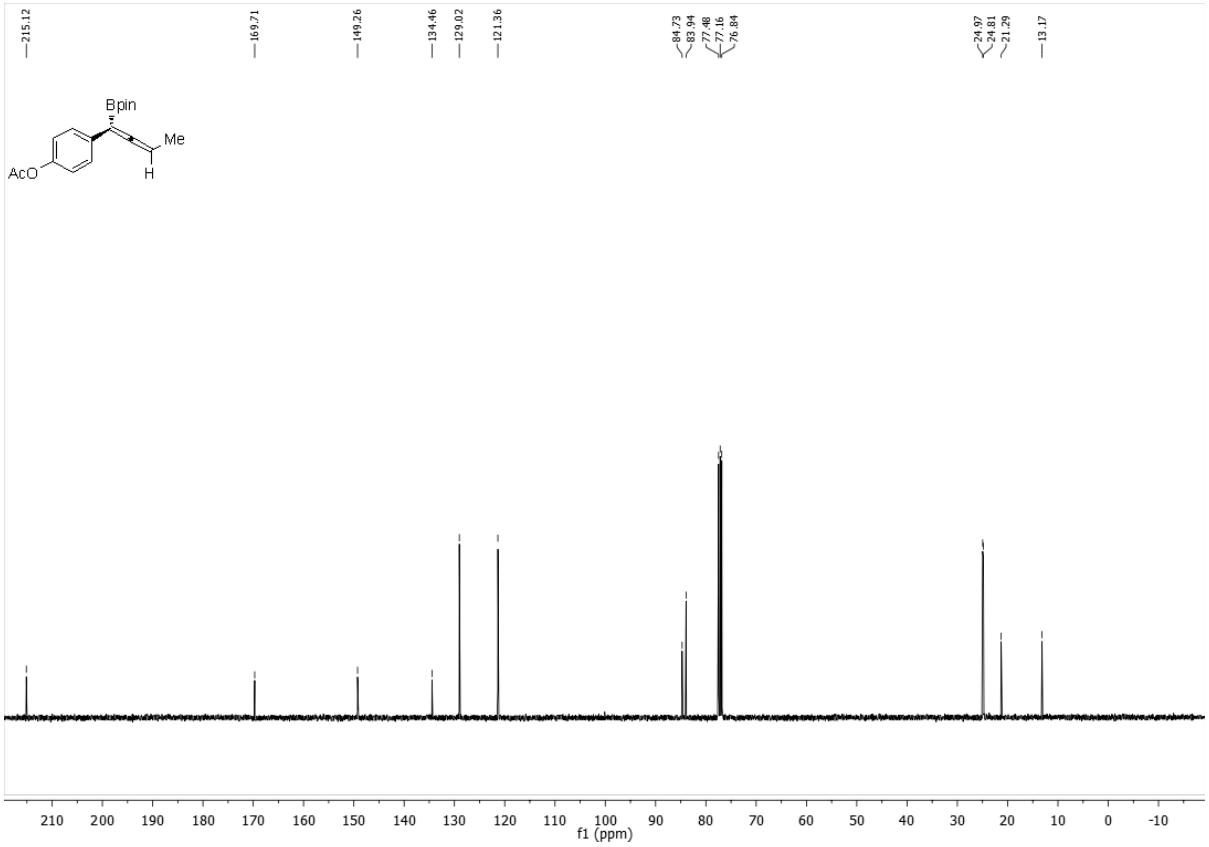
3.04
12.08
f1 (ppm)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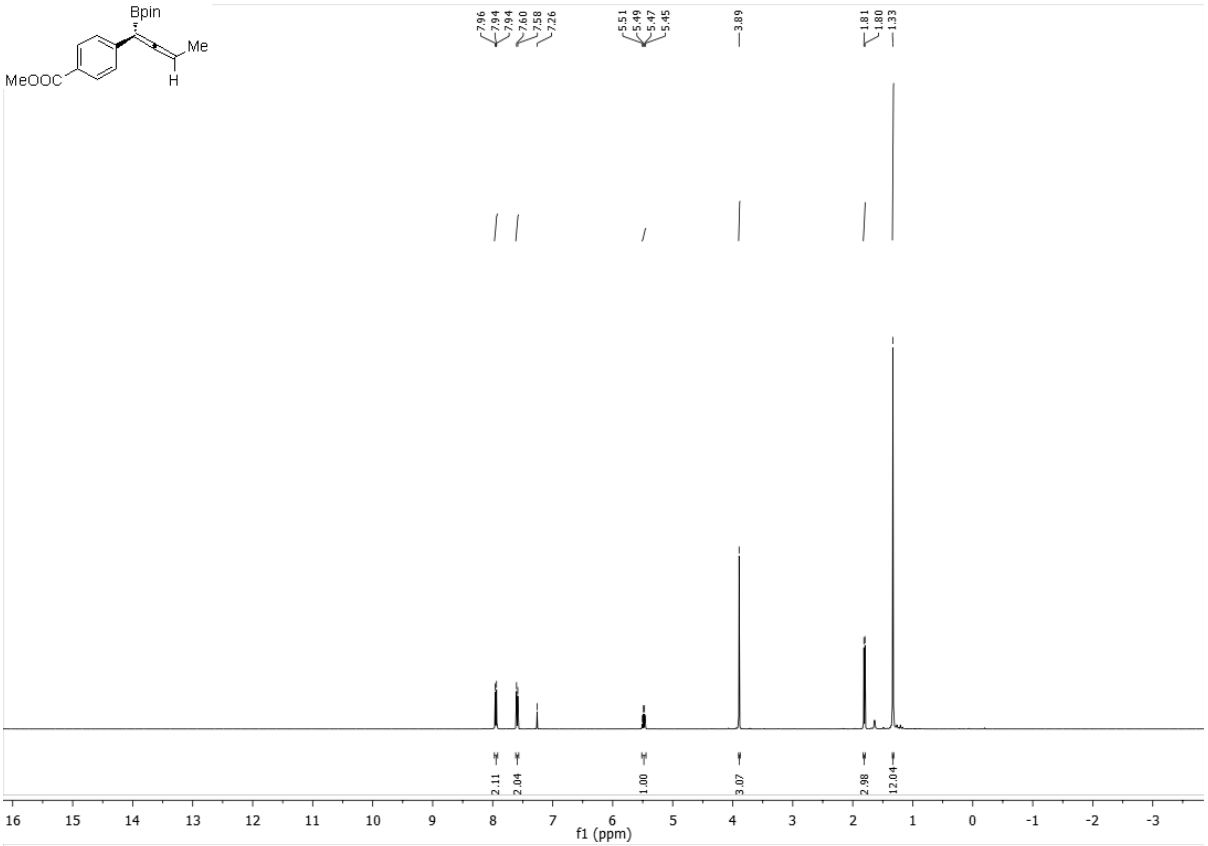
24.97
24.81
21.29
13.17
Bpin
Me
AcO
H
f1 (ppm)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MeOOC
H
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7.94
7.94
7.60
7.58
7.26
5.51
5.49
5.47
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3.89
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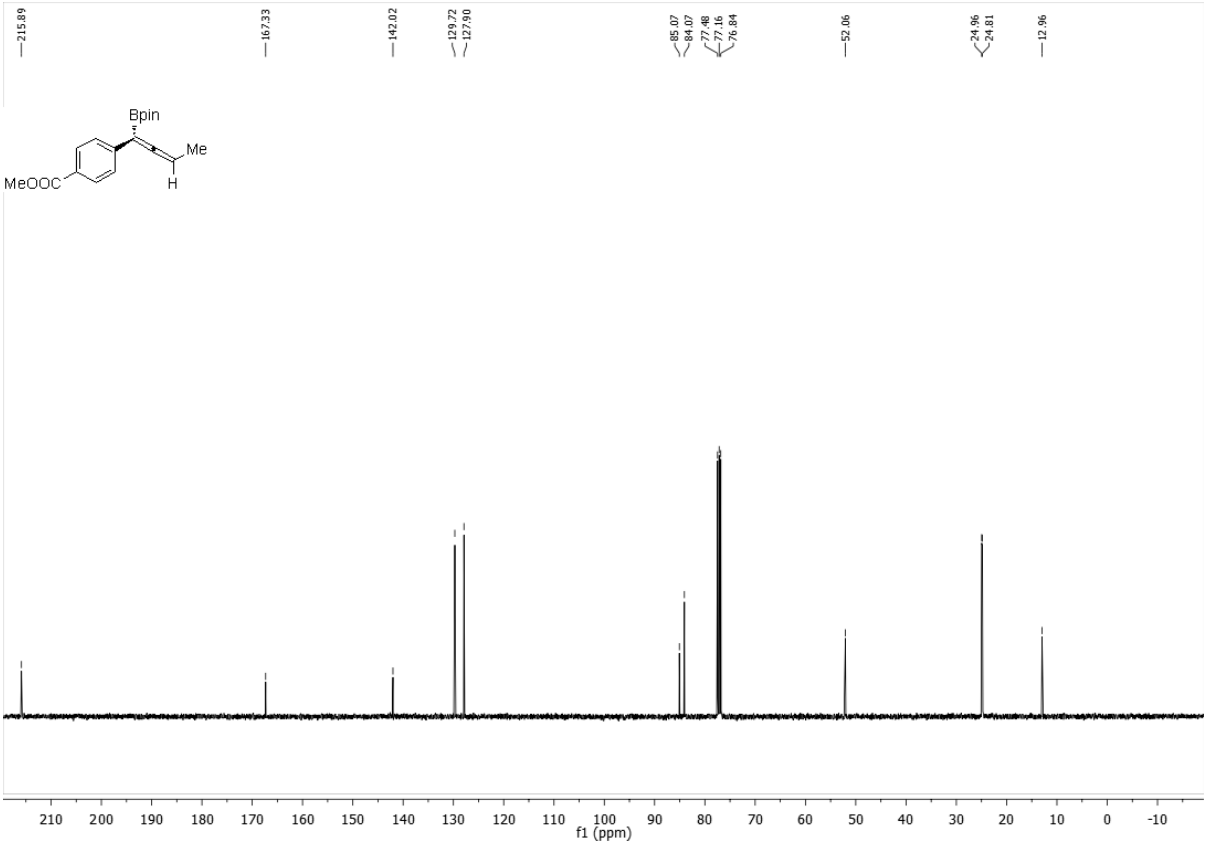
1.80
1.33
2.11
2.04
1.00
3.07
2.98
12.04
f1 (ppm)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85.07
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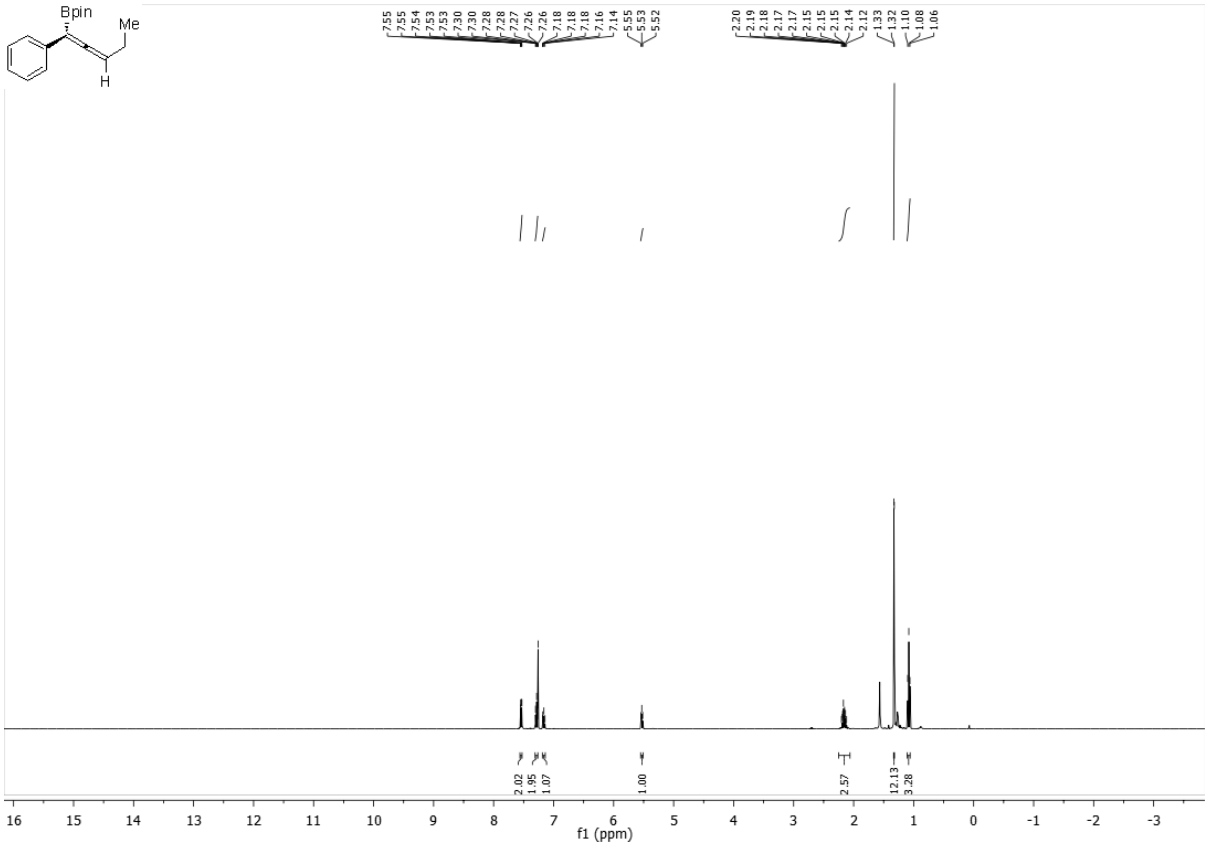
24.96
24.81
12.96
Bpin
Me
MeOOC
H
f1 (ppm)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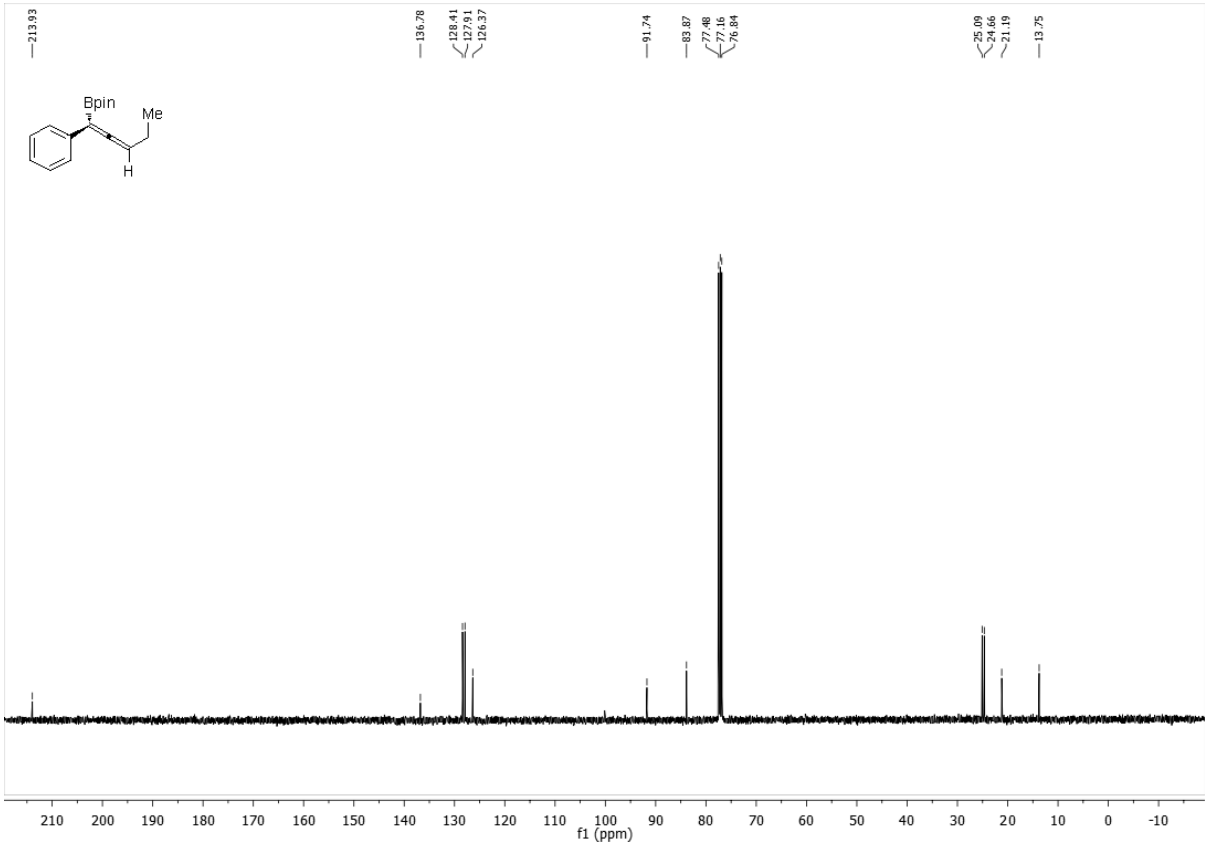
Me
H
f1 (ppm)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Me
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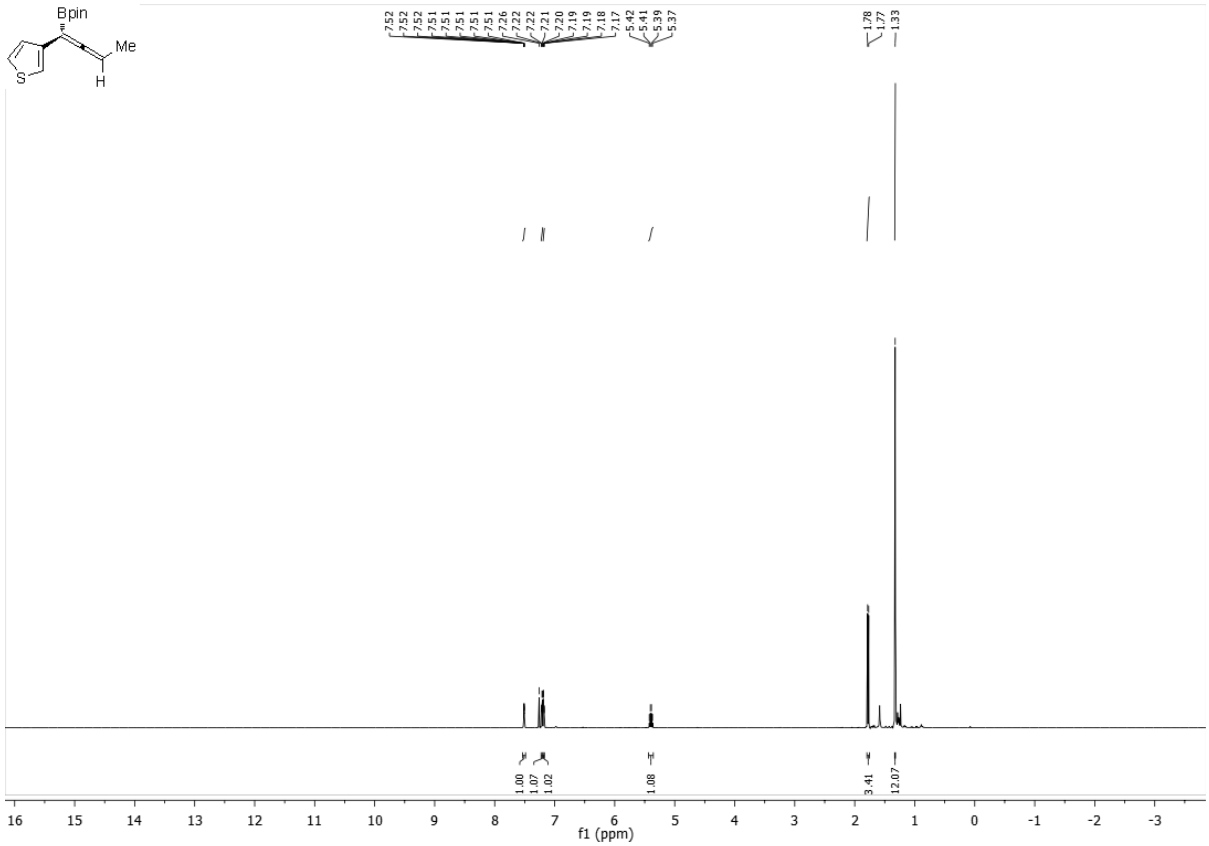
f1 (ppm)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Me
S
H
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7.52
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7.51
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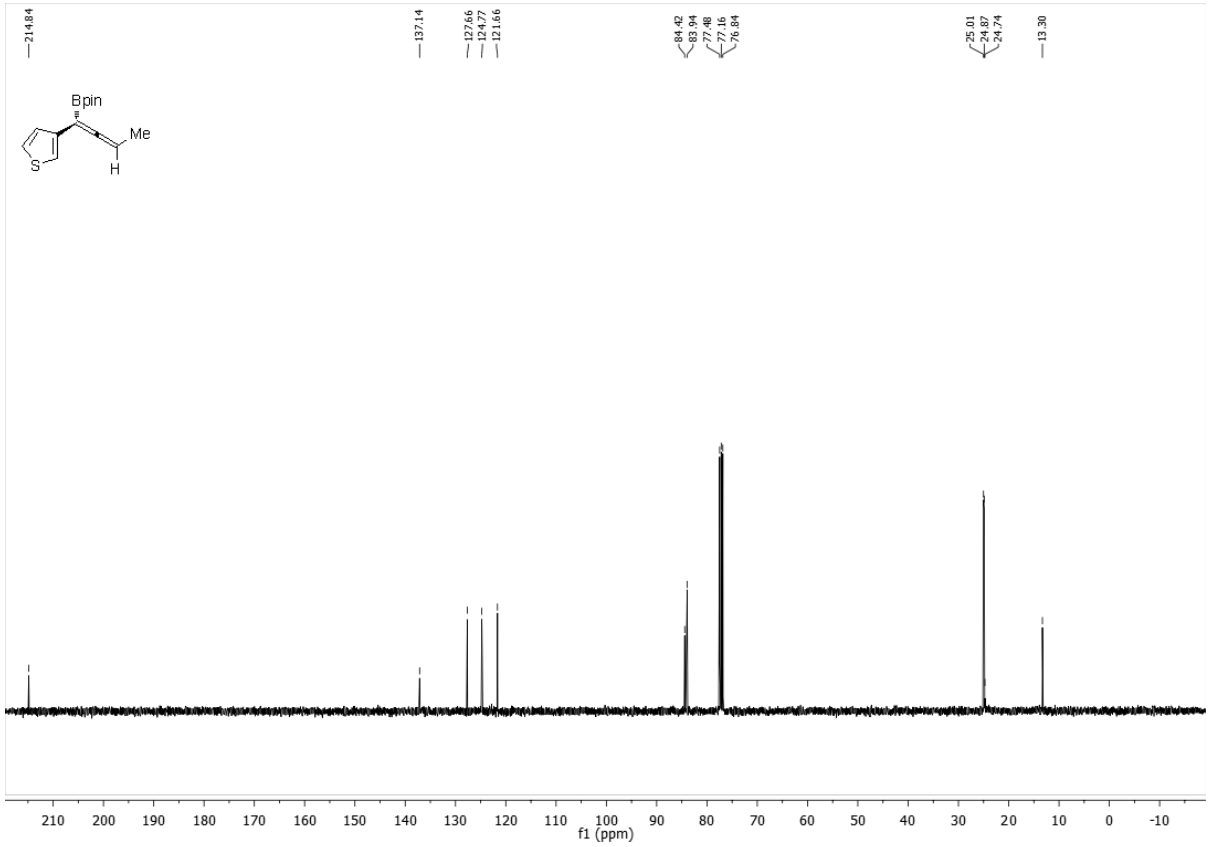
7.51
7.51
7.26
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.17
5.42
5.41
5.39
5.37
1.78
1.77
1.33
1.00
1.07
1.02
1.08
3.41
12.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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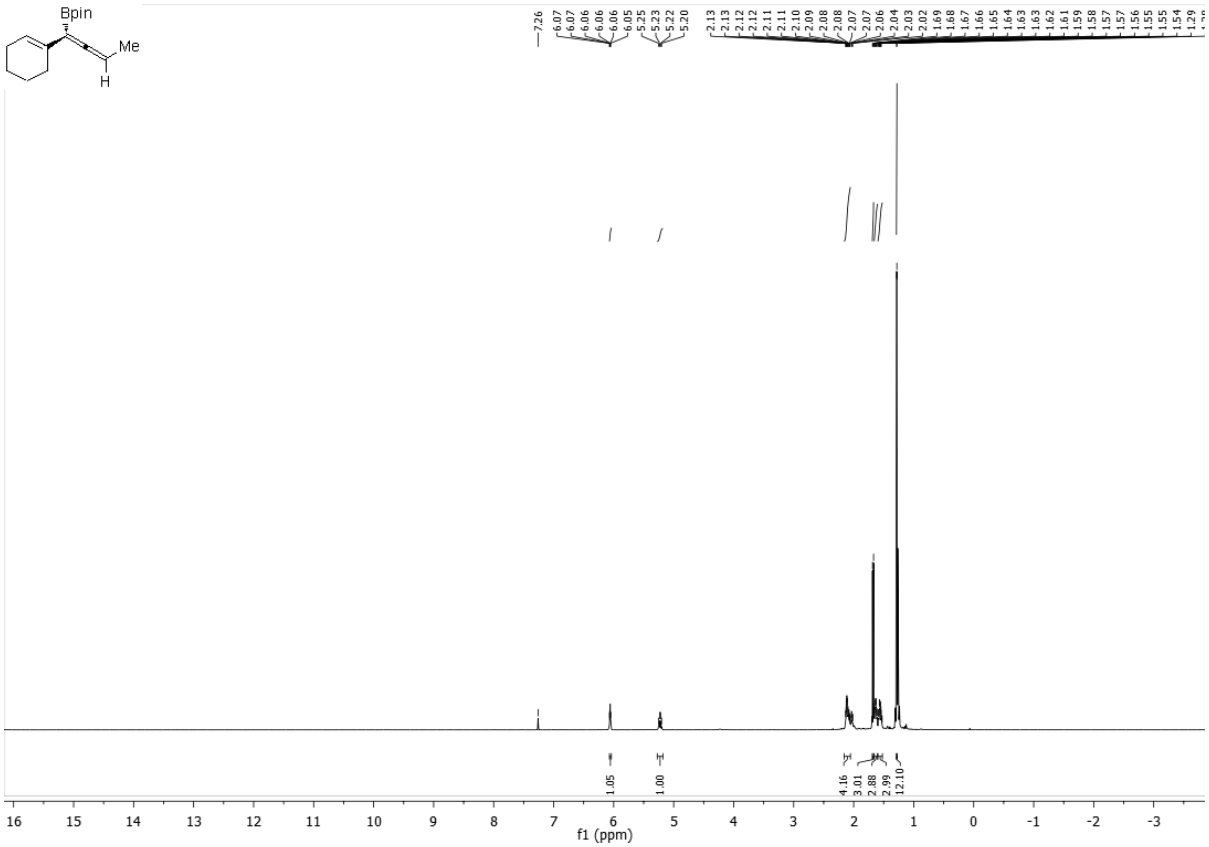
121.66
84.42
83.94
77.48
77.16
76.84
25.01
24.87
24.74
13.30
Bpin
Me
S
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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Me
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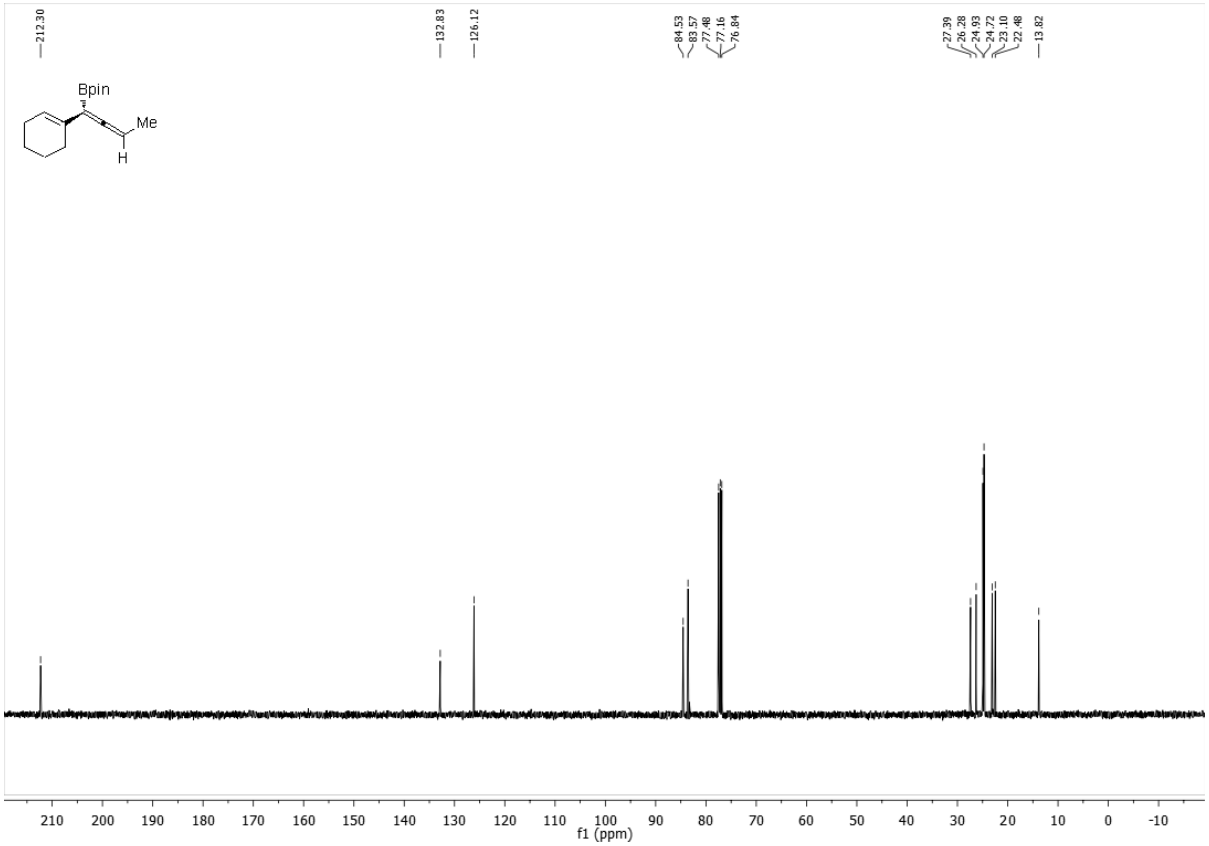
f1 (ppm)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Me
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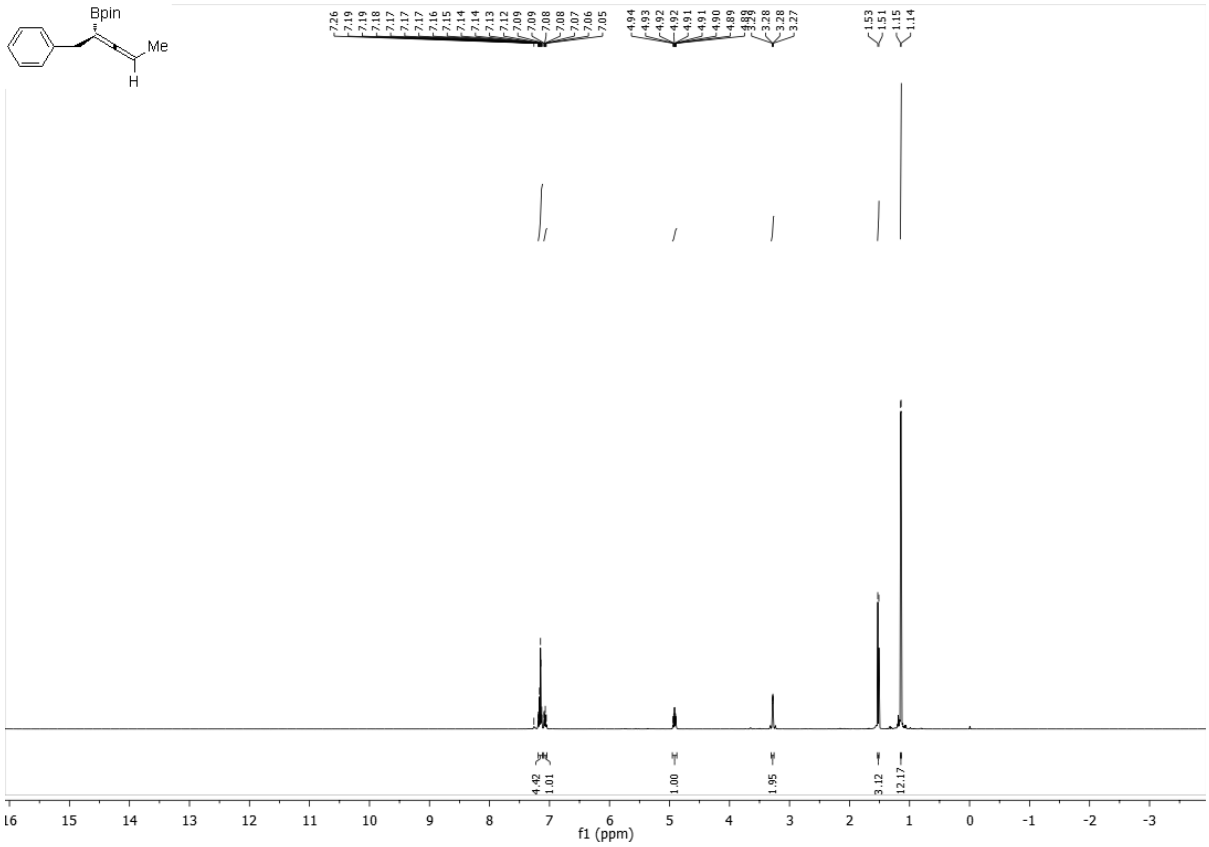
f1 (ppm)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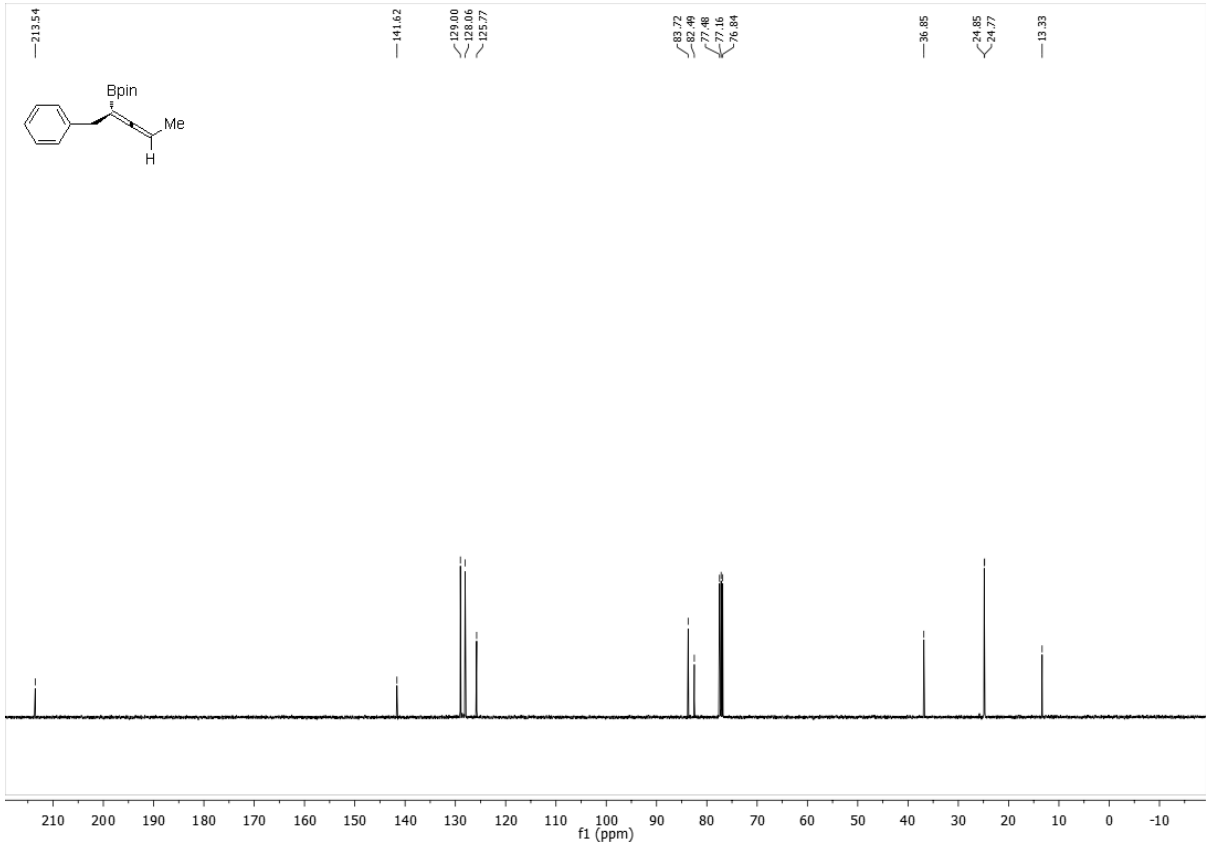
Me
H
f1 (ppm)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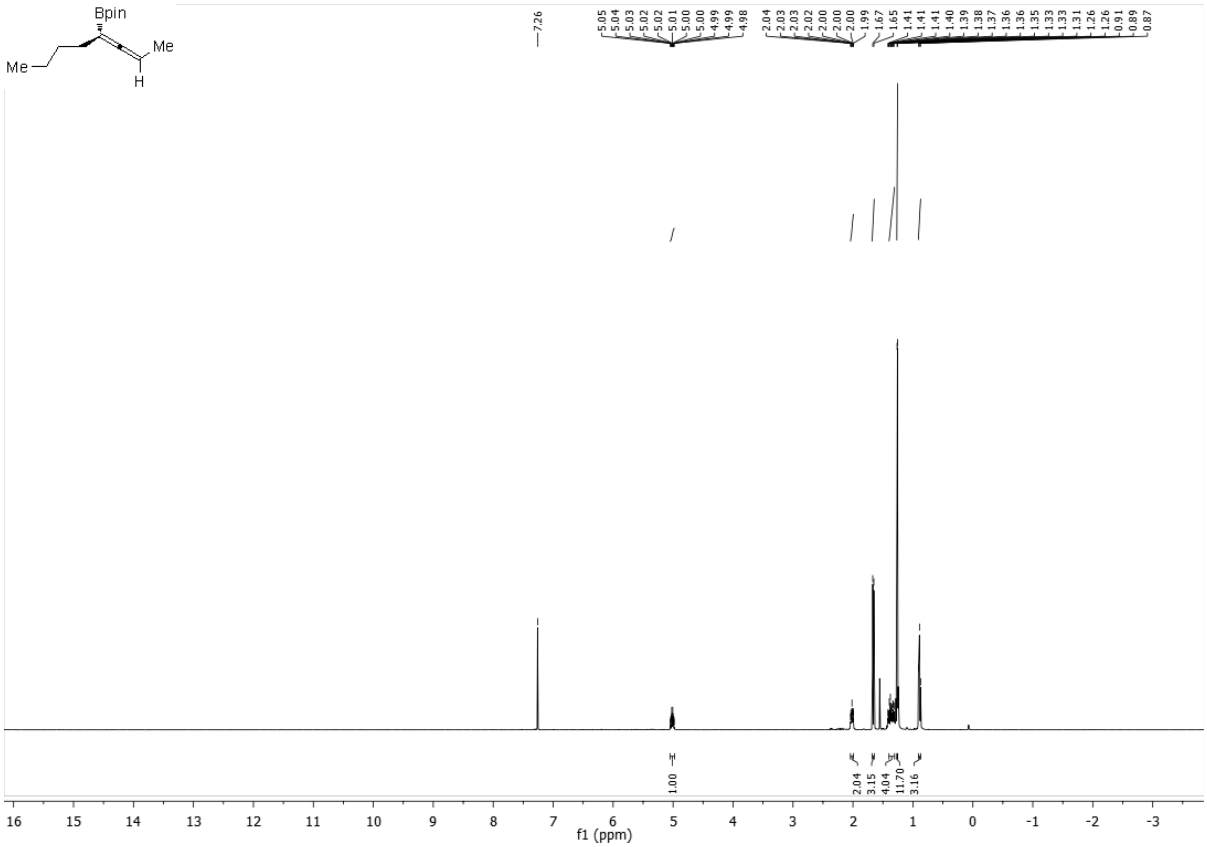
Me
H
f1 (ppm)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Me
Me
H
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5.04
5.03
5.02
5.02
5.01
5.00
5.00
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1.38
1.37
1.36
1.36
1.35
1.33
1.33
1.31
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1.00
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4.04
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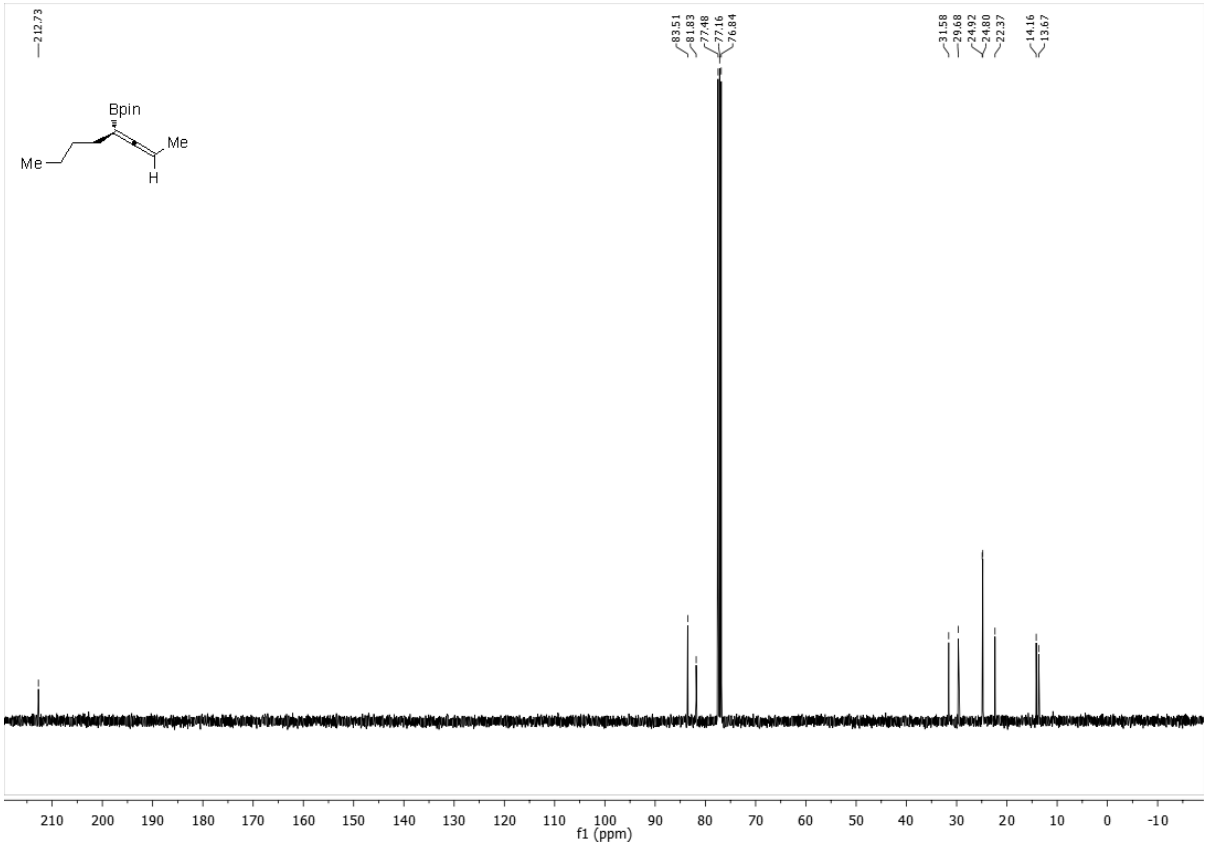
3.16
f1 (ppm)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Me
H
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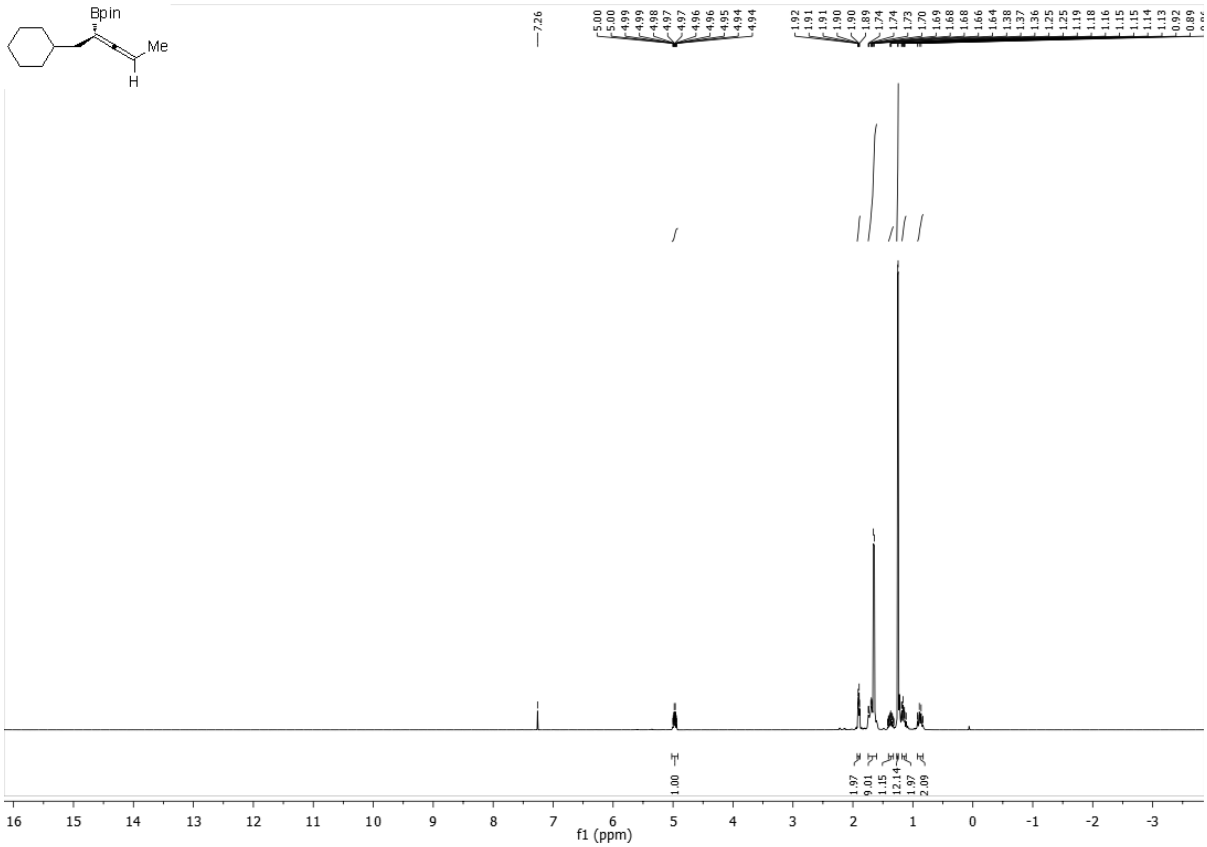
24.80
22.37
14.16
13.67
f1 (ppm)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Me
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4.99
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4.97
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4.96
4.95
4.94
4.94
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1.91
1.91
1.90
1.90
1.89
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1.74
1.73
1.70
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1.68
1.68
1.66
1.64
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1.37
1.36
1.25
1.25
1.19
1.18
1.16
1.15
1.15
1.14
1.13
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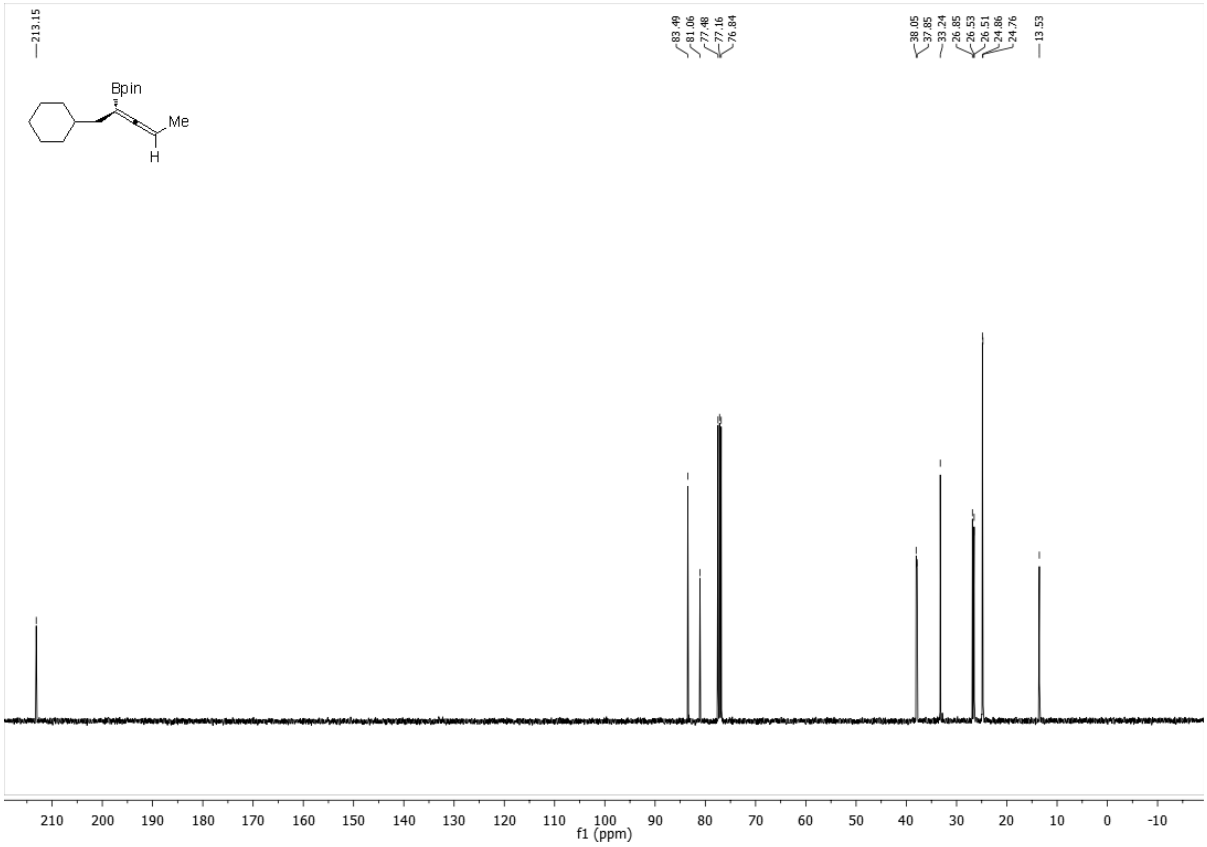
0.89
1.00
1.97
9.01
1.15
12.14
1.97
2.09
f1 (ppm)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76.84
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26.51
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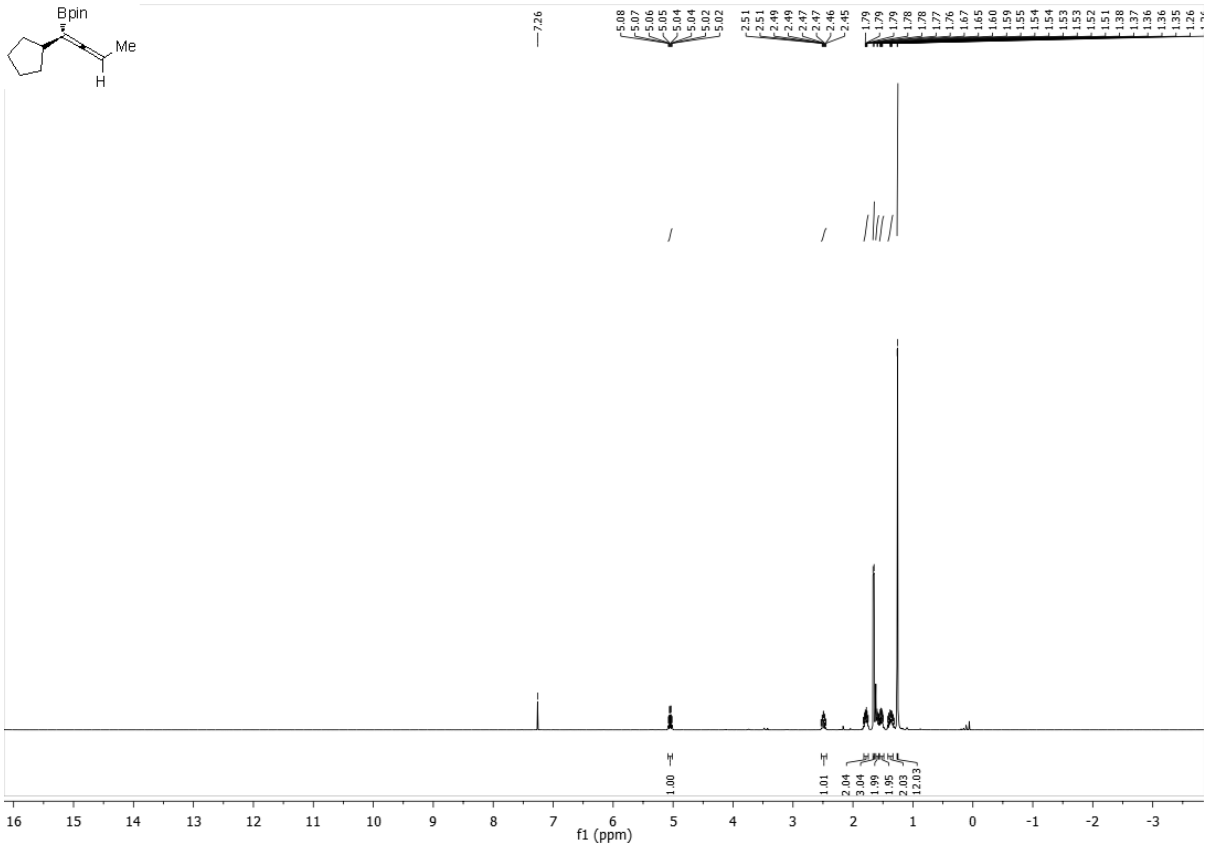
24.76
13.53
Bpin
Me
H
f1 (ppm)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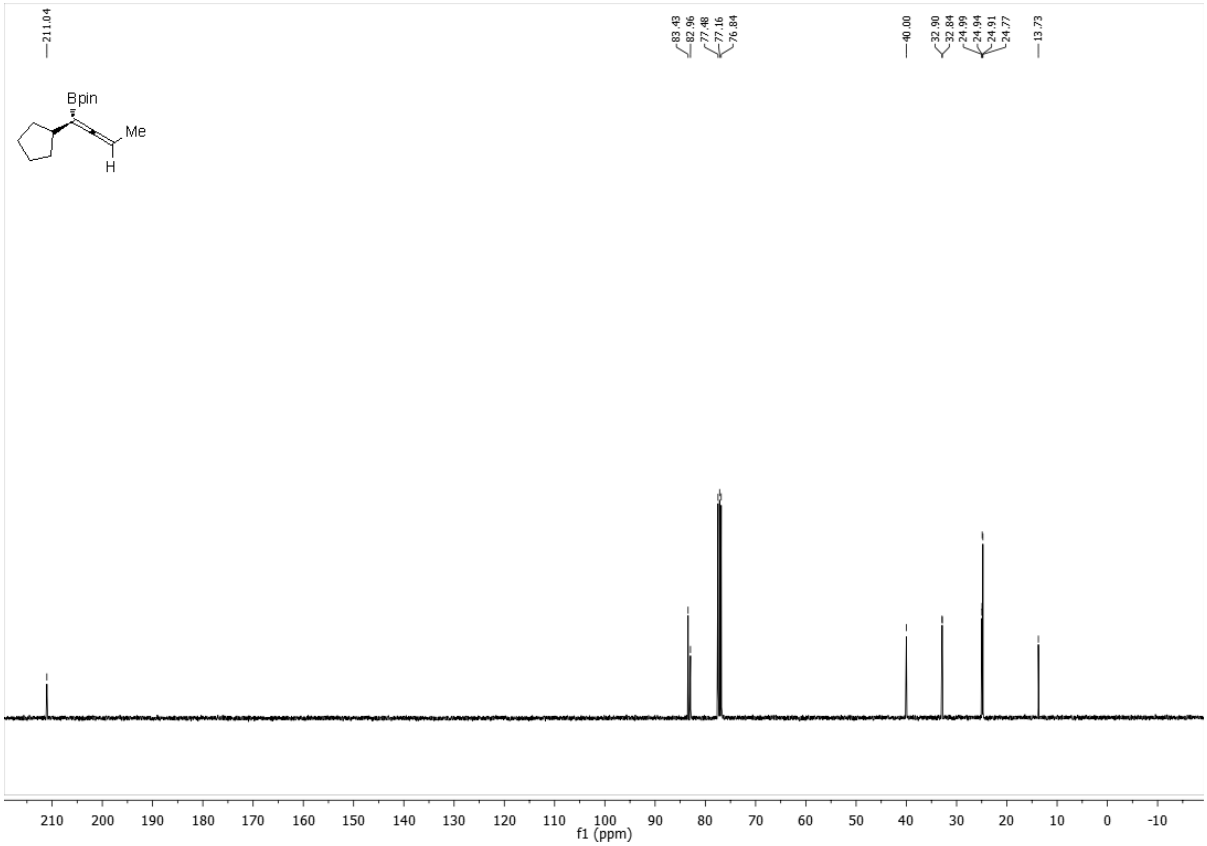
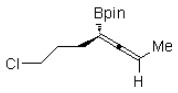
Me
H
f1 (ppm)


Bpin
Me
H
f1 (ppm)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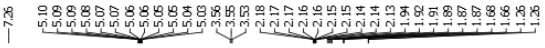
Me
Cl
H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5.09
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5.04
5.03
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3.55
3.53
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.14
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1.87
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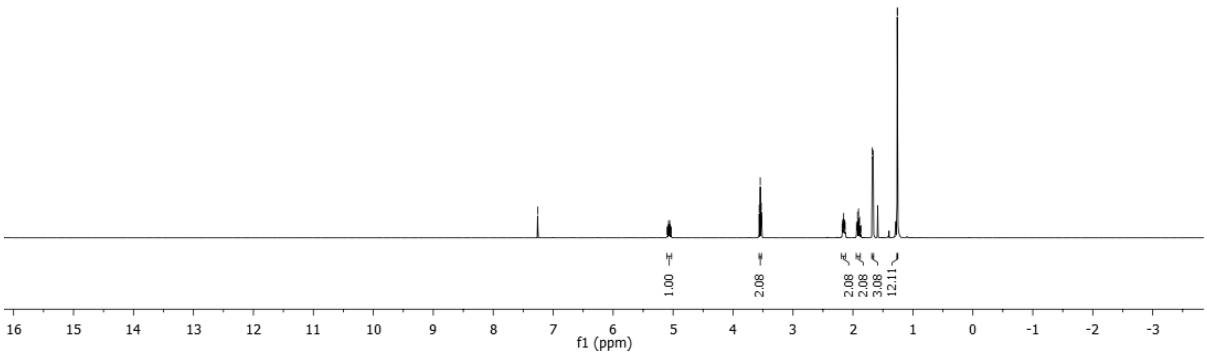
1.26
1.26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2.08
2.08
2.08
3.08
12.11
f1 (ppm)


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32.263
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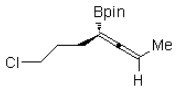
13.563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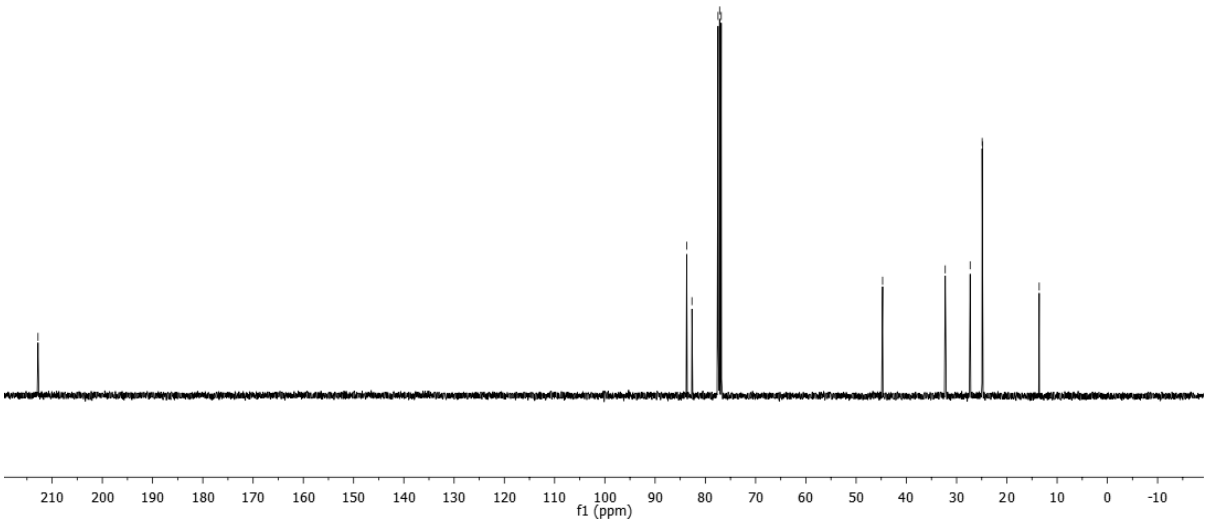
Cl
H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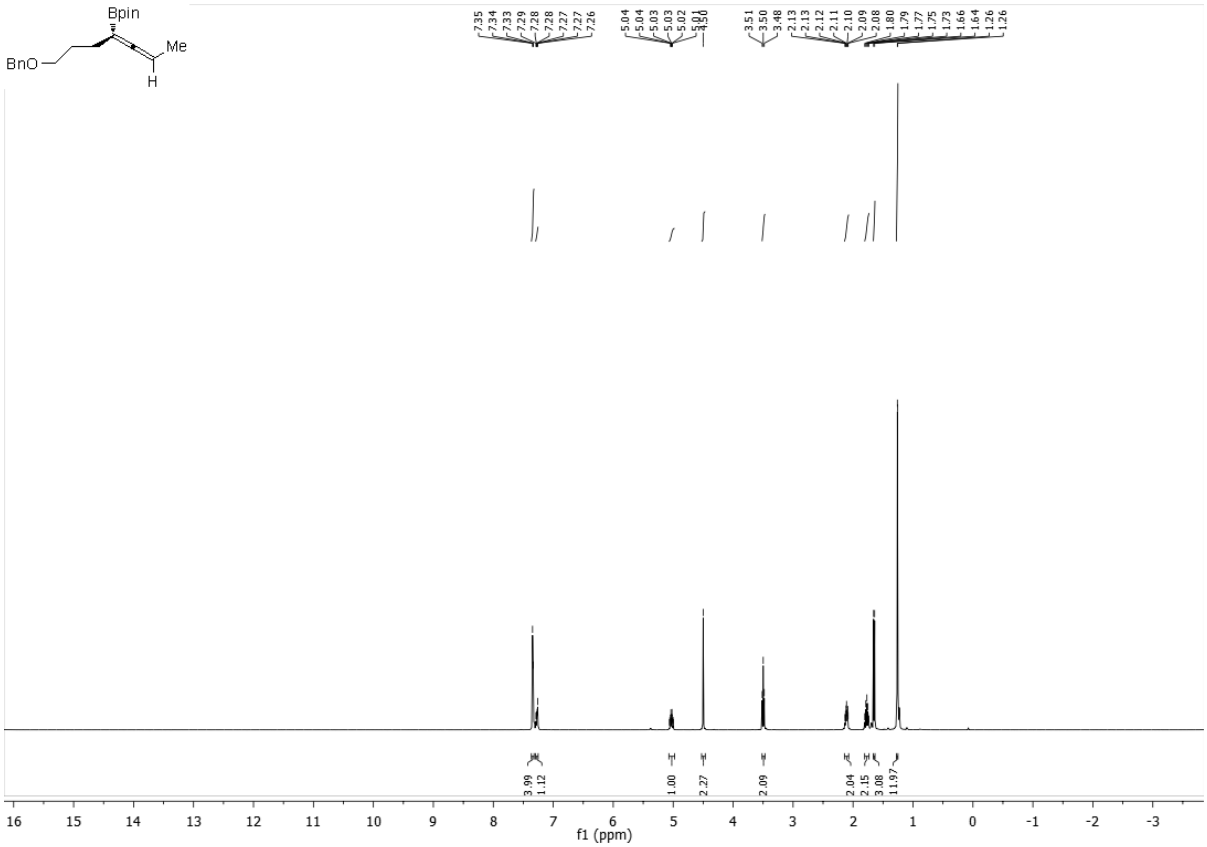
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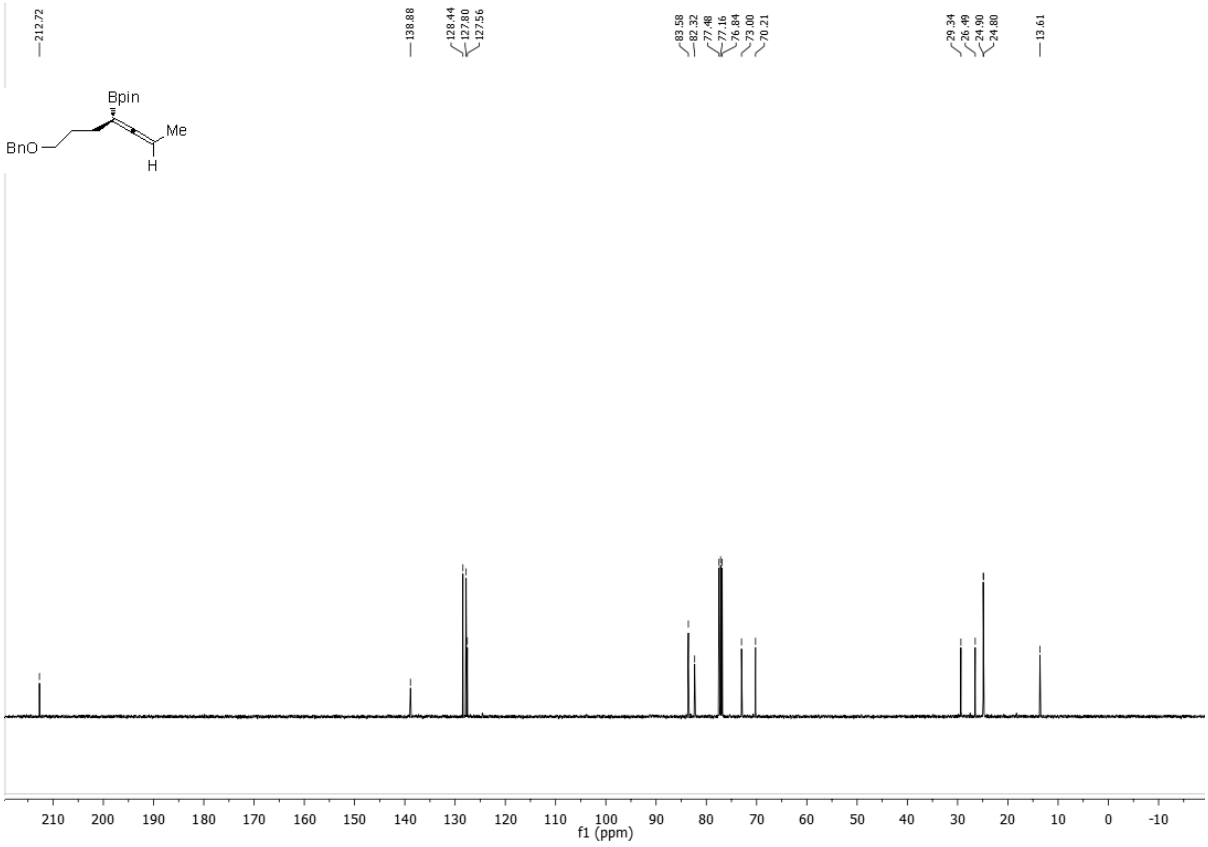
BnO
H
f1 (ppm)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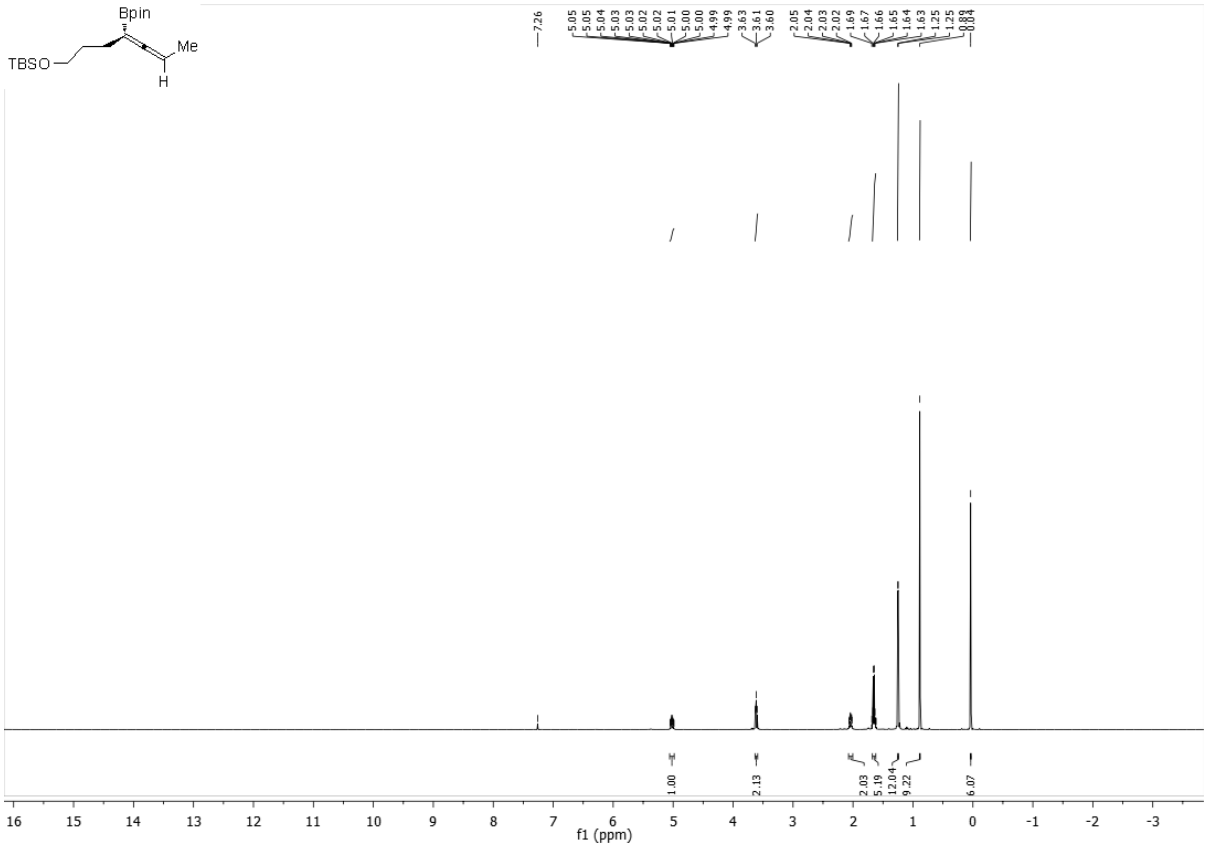
H
f1 (ppm)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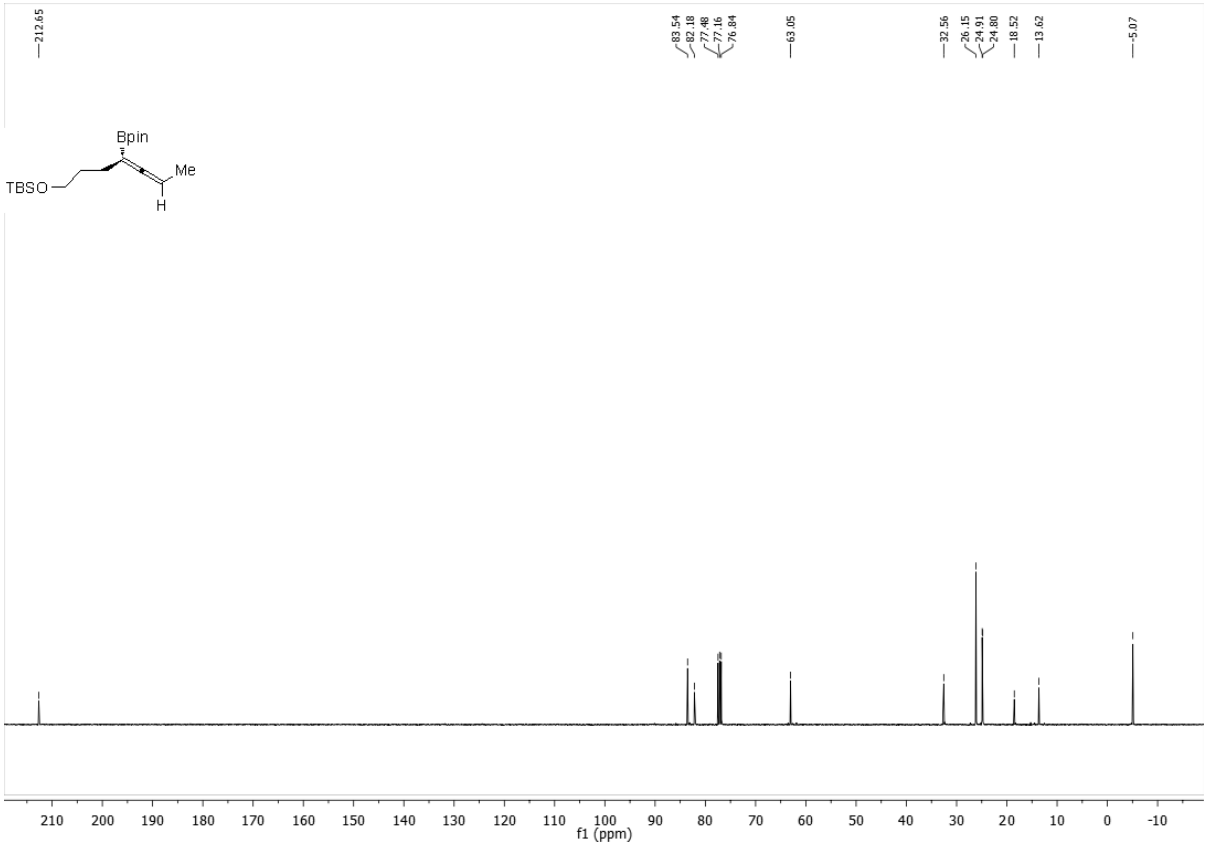
TBSO
H
f1 (ppm)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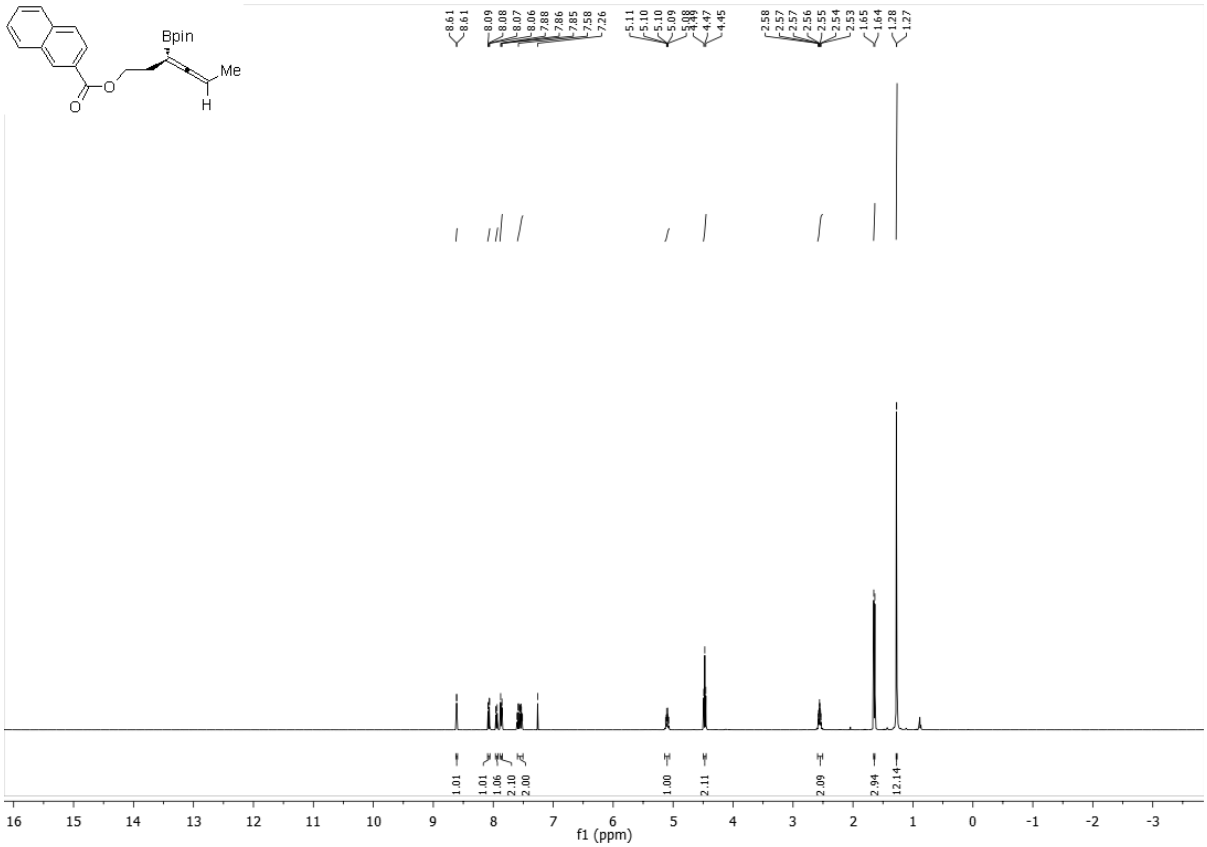
f1 (ppm)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O
O
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7.26
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5.10
5.09
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4.45
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2.56
2.55
2.54
2.53
1.65
1.64
1.28
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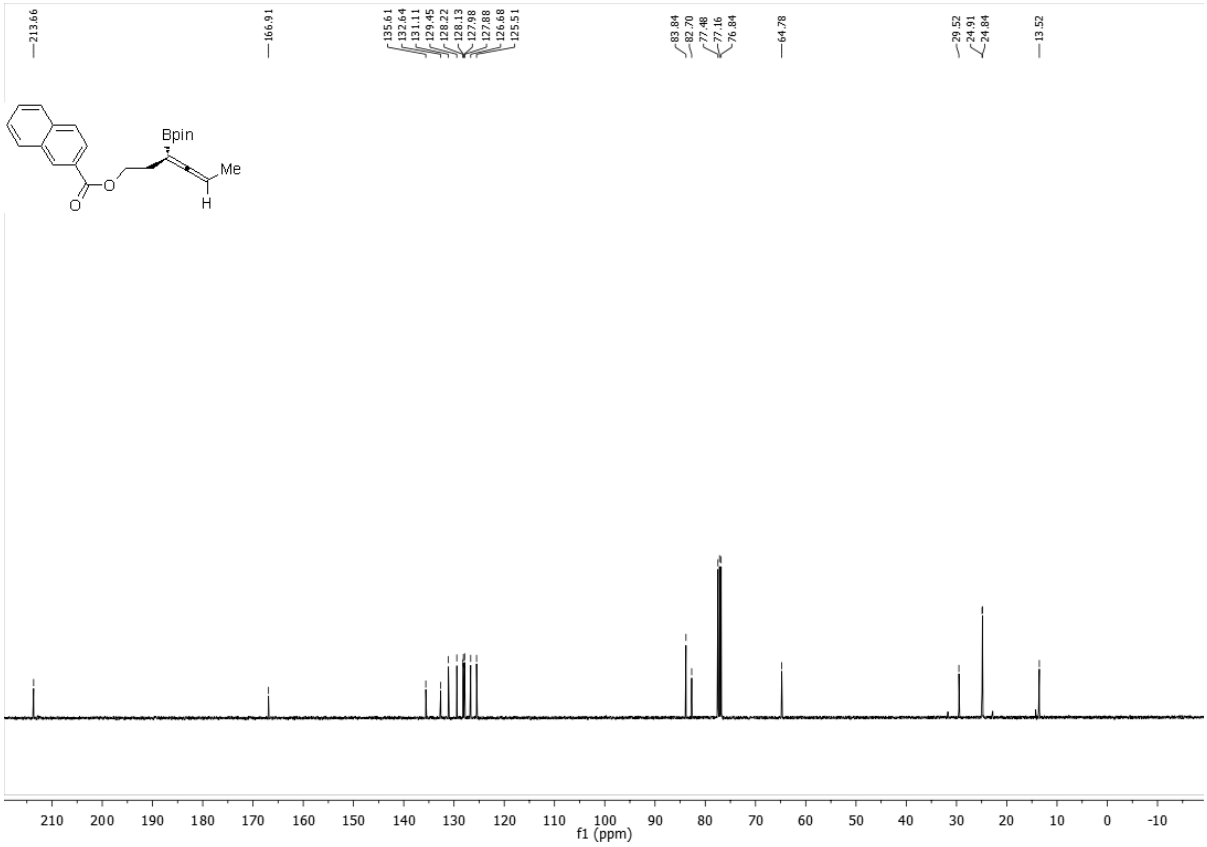
12.14
f1 (ppm)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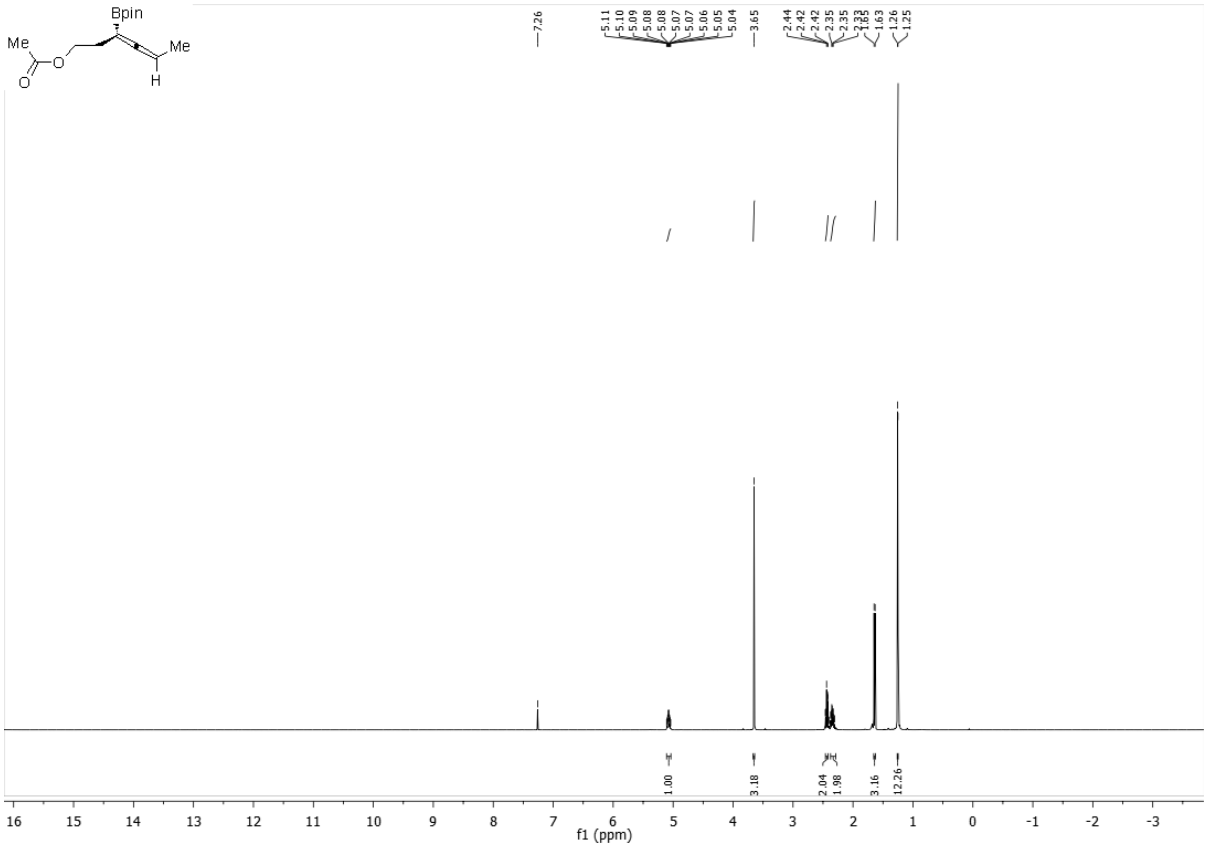
13.52
Bpin
Me
H
O
O
f1 (ppm)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Me
Me
O
O
H
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5.08
5.08
5.07
5.07
5.06
5.05
5.04
3.65
2.44
2.42
2.42
2.35
2.35
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1.26
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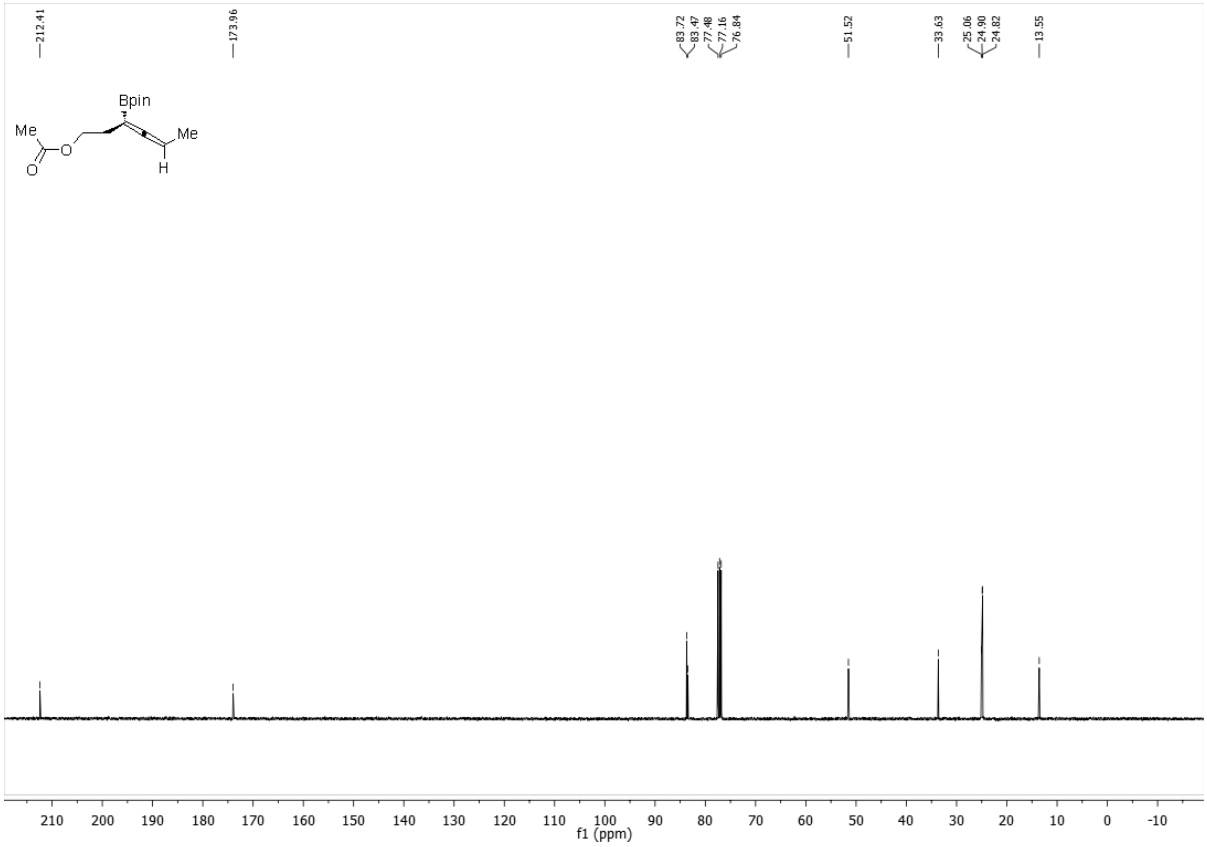
1.00
3.18
2.04
1.98
3.16
12.26
f1 (ppm)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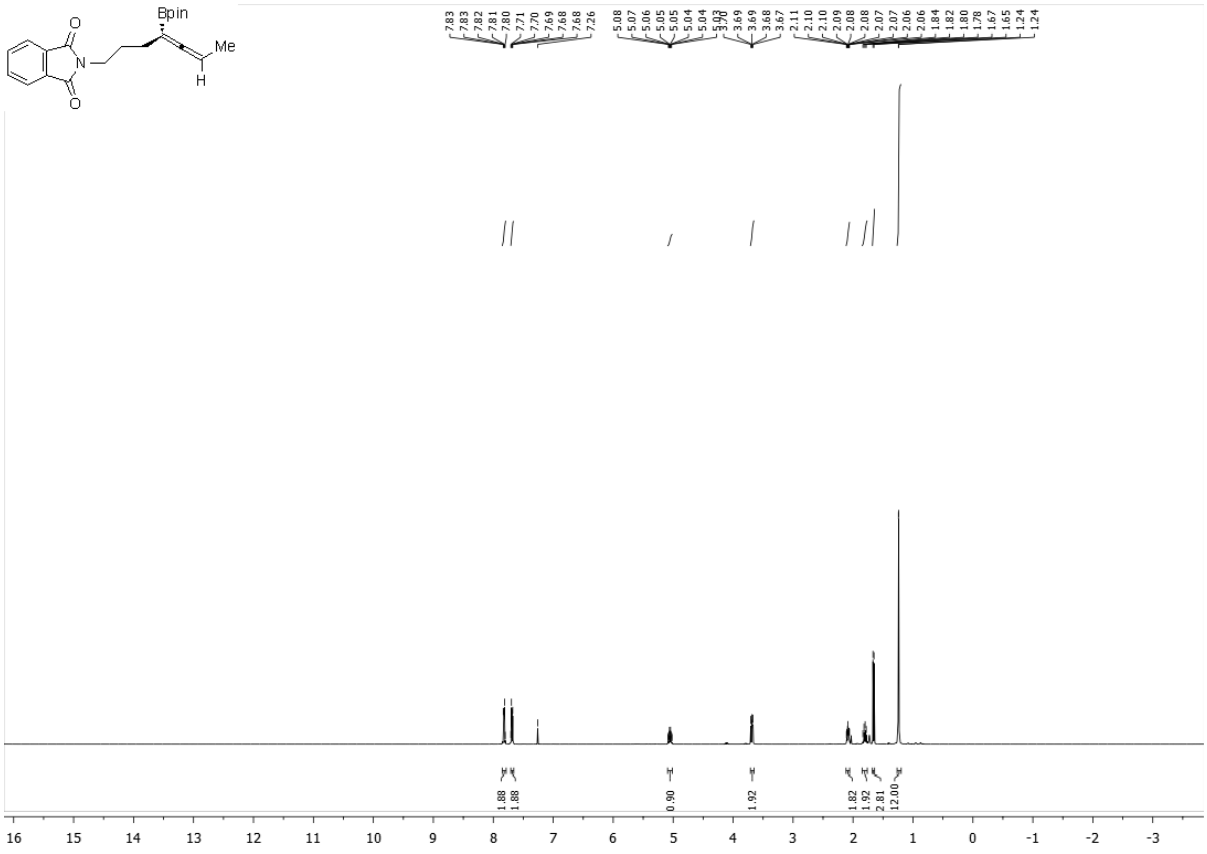
24.90
24.82
13.55
Bpin
Me
Me
O
O
H
f1 (ppm)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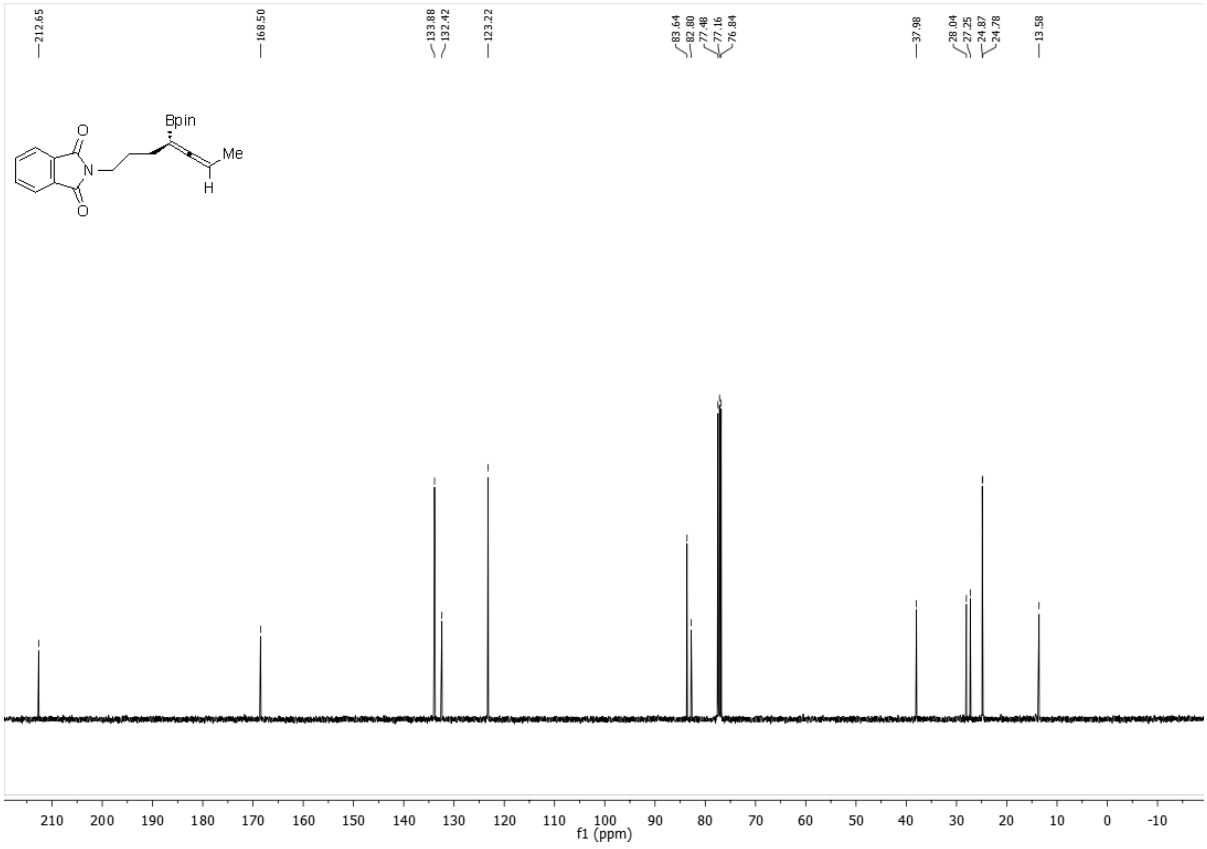
H
O
N
O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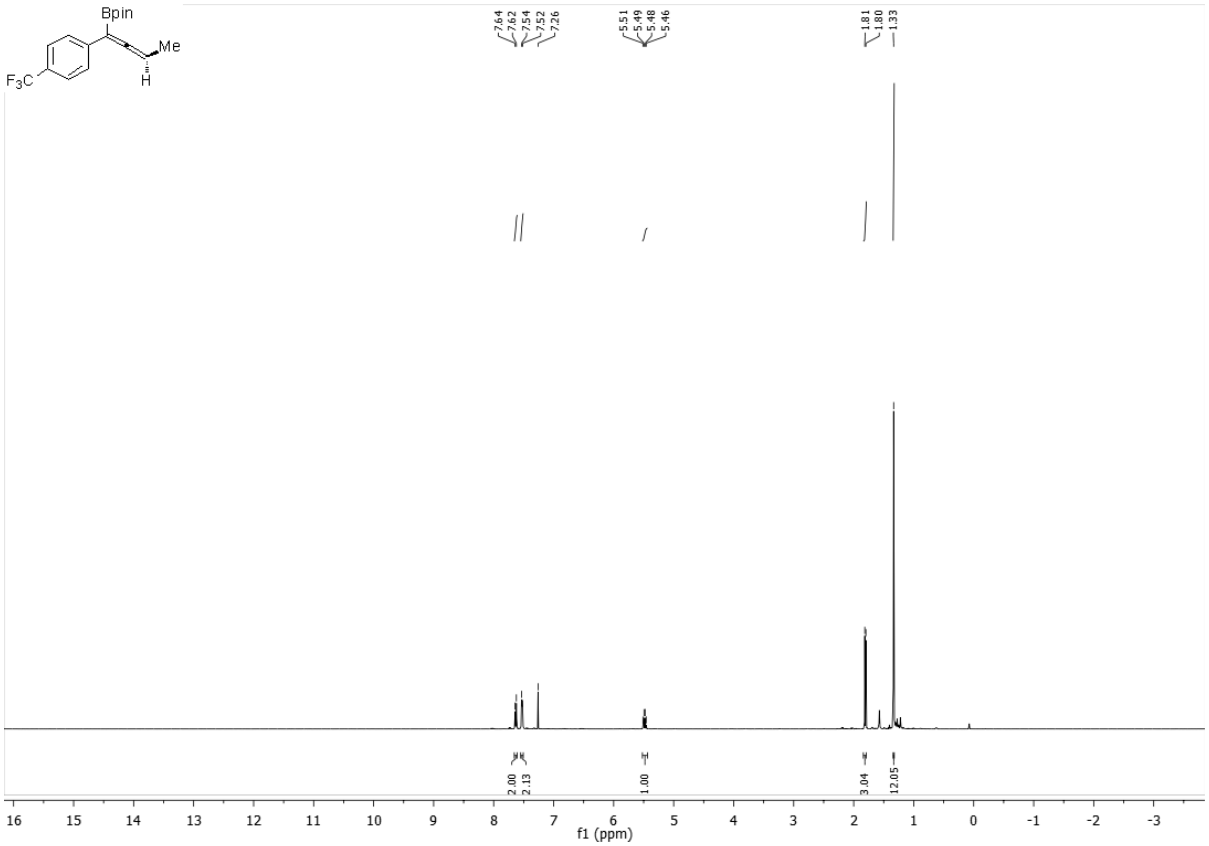
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Me
F3C
H
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1.00
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12.05
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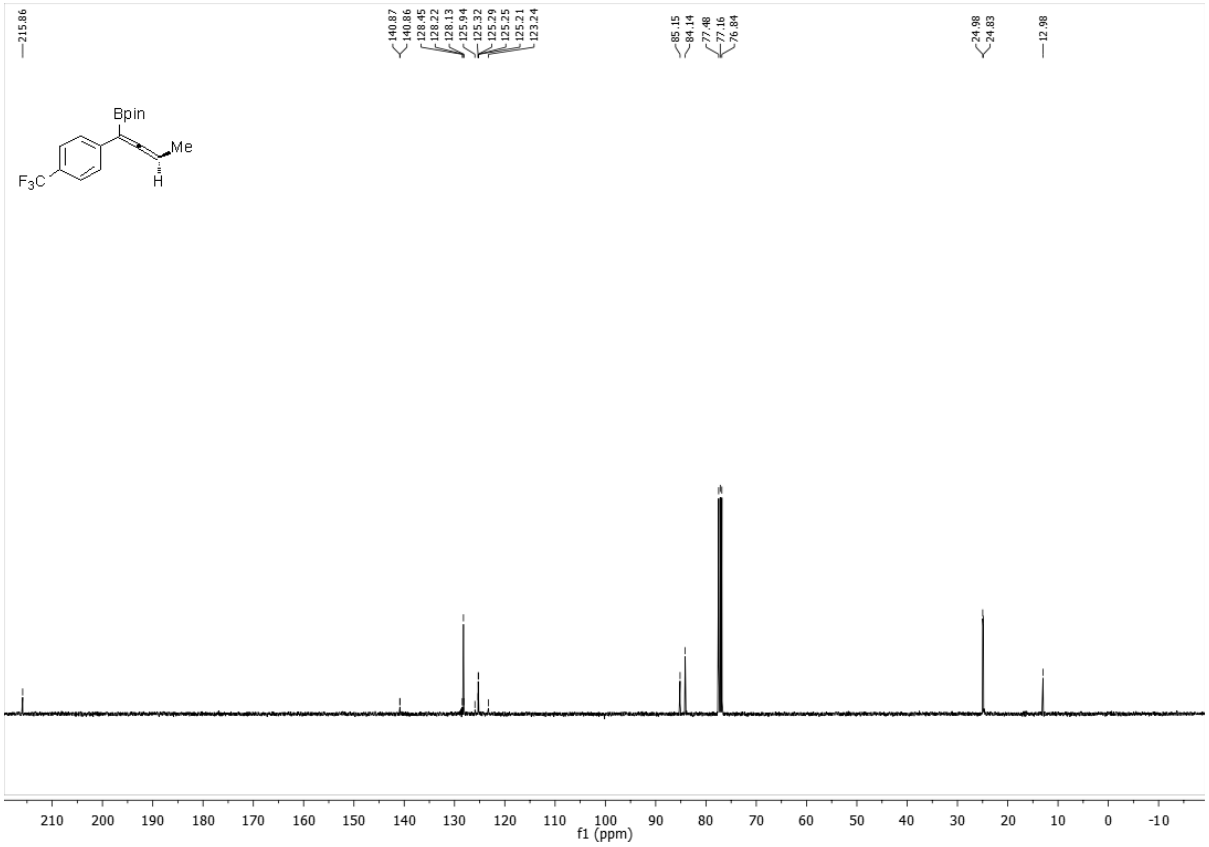
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125.21
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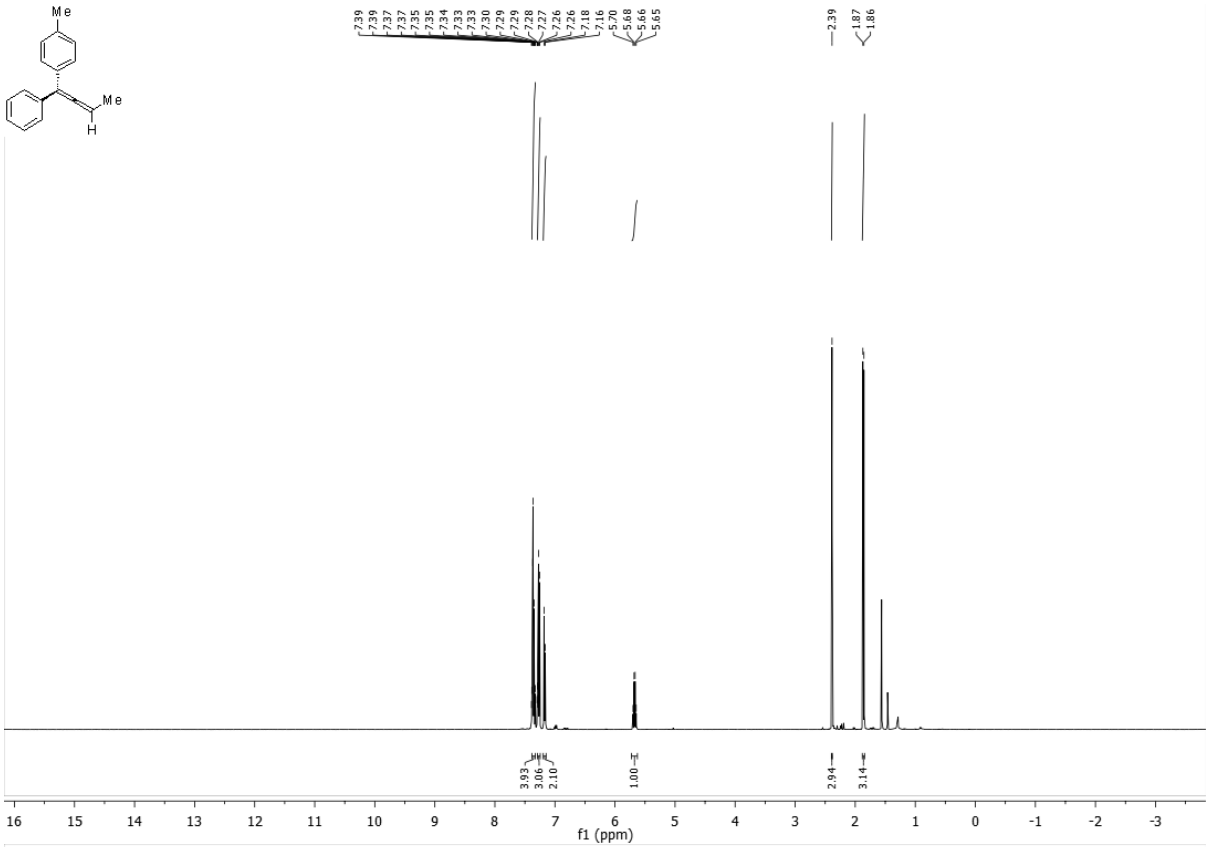
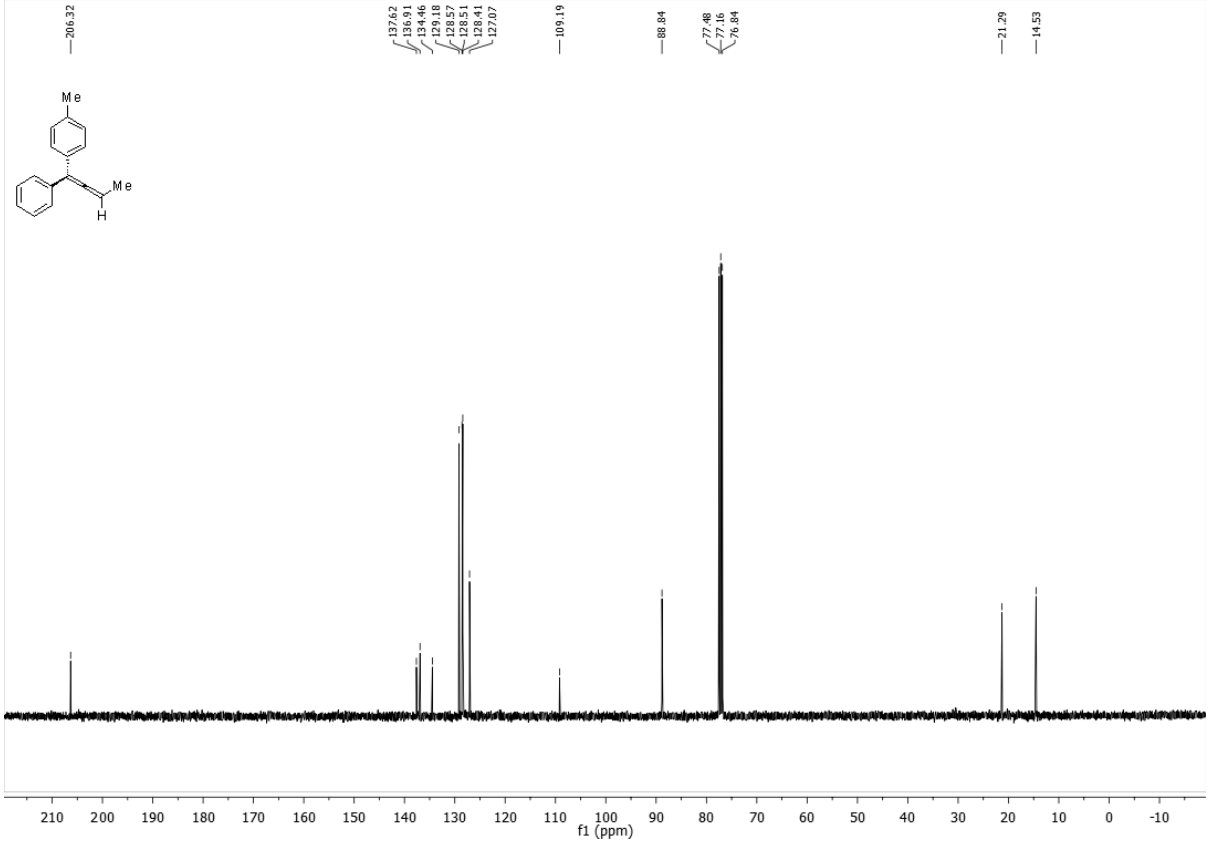
77.48
77.16
76.84
24.98
24.83
12.98
Bpin
Me
F3C
H
f1 (ppm)


Me
Me
H
7.39
7.39
7.37
7.37
7.35
7.35
7.34
7.33
7.33
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.18
7.16
5.70
5.68
5.66
5.65
2.39
1.87
1.86
3.93
3.06
2.10
1.00
2.84
3.14
f1 (ppm)


Me
Me
H
206.32
137.62
136.91
134.46
129.18
128.57
128.51
128.41
127.07
109.19
88.84
77.48
77.16
76.84
21.29
14.53
f1 (ppm)