A modular olefination reaction between aldehydes and diborylsilylmethide lithium salts

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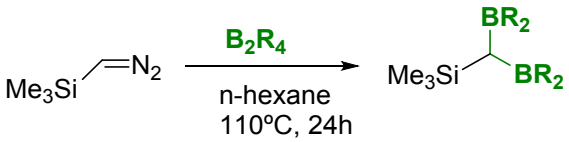
1. General Information

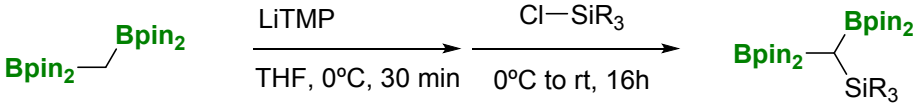
Solvents and reagents: Solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl. (Trimethylsilyl)diazomethane solution 2.0 M in hexanes was purchased from Acros Organics, and lithium 2,2,6,6-tetramethylpiperidide was purchased from Sigma Aldrich, and were used without further purification. Bis(pinacolato)diboron and Bis(hexylene glycolato)diboron was purchased from Ally Chem and used without further purification. All aldehydes were purchased from commercial sources and were used without further purification except for benzaldehyde which was distilled before used. All reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon, using Schlenk-type techniques. *Flash chromatography* was performed on standard silica gel (Merck Kieselgel 60 F254 400-630 mesh). *Thin layer chromatography* was performed on Merck Kieselgel 60 F254 which was developed using standard visualizing agents: UV fluorescence (254 and 366 nm) or potassium permanganate/Δ. *NMR spectr*a were recorded at a Varian Goku 400 or a Varian Mercury 400 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm (1 H)) and ($CDCl_3$: 77.16 ppm (^{13}C). ^{11}B{^{1}H} NMR chemical shifts (δ) are reported in ppm relative to $(CH_3)_2O\cdots BF_3$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptuplet, br = broad, m = multiplet), coupling constants (Hz) and integration. *High resolution mass spectra (HRMS)* were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface and it was performed at the Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona) or using a BIOTOF II Time of Flight (TOF) mass spectrometer from Bruker with an APCI interface or EI interface and it was performed at the Unidade de Espectrometría de Masas e Proteómica (Universidade de Santiago de Compostela, Santiago de Compostela). GC-MS analyses were performed on a HP6890 gas chromatograph and an Agilent Technologies 5973 Mass selective detector (Waldbronn, Germany) equipped with an achiral capillary column HP-5 (30m, 0.25mm i. d., 0.25µm thickness) using He as the carrier gas.

2. Experimental procedures and spectral data

2.1. General procedure A and B for the preparation of gem-diborylsilanes



An oven-dried Teflon screw-cap Schlenk flask, equipped with a magnetic stir bar, was charged with 4 mmol (1 equiv) of diboron reagent, in the glove-box. Then, 8 mmol (2 equiv) of a 2.0 M solution in hexane of (trimethylsilyl)diazomethane was added dropwise. After stirring the mixture in the glove-box for 5 min the Schlenk flask was sealed and heated at 110 °C for 24 h under constant stirring. The reaction was cooled at room temperature, the solvent was gently concentrated on a rotary evaporator and the resulting crude purified by silica gel flash chromatography to afford the product.

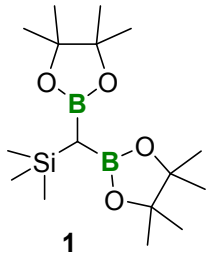


For this synthesis we followed the previous reported procedure by Cho et al.[1] with some modifications. An oven-dried Teflon screw-cap Schlenk flask, equipped with a magnetic stir bar, was charged with LiTMP (2 mmol, 1 equiv) and bis[(pinacolato)boryl]methane (2mmol, 1 equiv) in dry THF (3mL). The mixture was stirred for 30 minutes at 0ºC. Then, the corresponding chlorosilane (2.4 mmol, 1.2 equiv) in dry THF (1 mL) was added and the reaction was stirred at 0ºC for 10 minutes, followed by 16h at room temperature. The solvents were removed under vacuum and reaction crude was purified by silica gel chromatography to afford the desired product.

[1] J. Kim, S. H. Cho, ACS Catal. **2019**, *9*, 230.

2.2 Spectral data for diborylmethylsilanes HC(Bin)$_2$[Si]

(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane (1)



1

Synthesized using B_2pin_2 as diboron reagent and purified by flash column chromatography (hexane:ethyl acetate = 15:1) yielded **1** (83%, 1.17g) as a white solid.

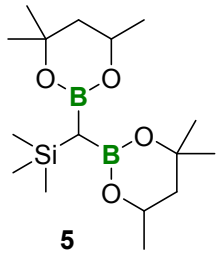
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (s, 12H), 1.20 (s, 12H), 0.28 (s, 1H), 0.09 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 82.7, 25.1, 24.6, 0.6

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.94.

HRMS (ESI) for **$C_{16}H_{34}B_2O_4SiNa$ [M+Na$^+$]$^+$:** calculated: 363.2310; found: 363.2309.

(bis(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)methyl)trimethylsilane (5)



5

Synthesized using B_2hex_2 as diboron reagent and purified by flash column chromatography (hexane:ethyl acetate = 15:1) yielded **5** (56%, 789 mg) as a colourless oil.

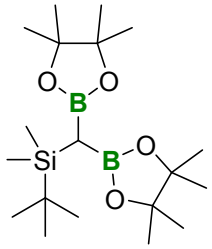
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.11 (m, J = 11.6, 6.2, 3.0 Hz, 2H), 1.68 (d, 13.9 Hz, 2H), 1.40 dd, 13.9, 2.9 Hz, 2H), 1.28 (s, 12H), 1.23 (d, 5 Hz, 6H), 0.01 (s, 9H), -0.13 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.0, 64.3, 46.2, 31.5, 28.1, 23.5, 0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.08.

HRMS (ESI) for **$C_{16}H_{34}B_2O_4SiNa$ [M+Na$^+$]$^+$:** calculated: 363.2310; found: 363.2314.

(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)(tert-butyl)dimethylsilane (35)

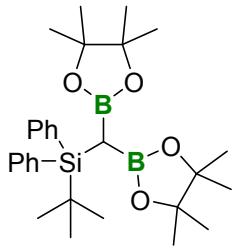


35

Synthesized by General procedure B using *tert*-butylchlorodimethylsilane and and purified by flash column chromatography (hexane:ethyl acetate = 15:1) yielded **35** (46%, 355 mg) as a white solid. Spectral data are in agreement with the reported.[1]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 9H), 1.21 (s, 12H), 0.87 (s, 12H), 0.39 (s, 1H), 0.07 (s, 6H).

(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)(tert-butyl)diphenylsilane (36)



36

Synthesized by General procedure B using *tert*-butylchlorodiphenylsilane and and purified by flash column chromatography (hexane:ethyl acetate = 15:1) yielded **36** (27%, 276 mg) as a pale yellowish solid.

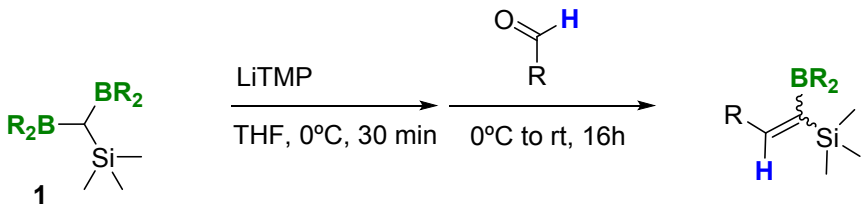
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 – 7.68 (m, 4H), 7.36 – 7.23 (m, 6H), 1.06 (s, 9H), 1.02 (s, 12H), 1.00 (s, 12H), 0.92 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.6, 128.5, 126.9, 82.8, 28.5, 24.8, 24.6, 19.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.47.

HRMS (ESI) for **$C_{29}H_{48}NB_2O_4Si$ [M+HH_4^+]$^+$:** calculated: 524.3539; found: 524.3551

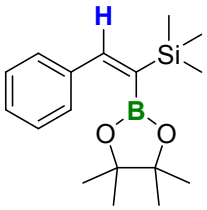
2.3 General procedure for gem-silylborylation of aldehydes



A Schlenk-tube, equipped with a magnetic stir bar, was charged with the *gem*-diborylsilane (0.3 mmol, 1 equiv) and LiTMP (0.36 mmol, 1.2 equiv) in dry THF (2 mL). The mixture was stirred for 30 minutes at 0ºC. Then the corresponding aldehyde (0.24 mmol, 0.8 equiv) was added and the reaction was stirred at 0ºC for 10 minutes, followed by 16 h at room temperature. The reaction crude was analysed by NMR, using naphthalene as internal standard, and the crude residue was purified by silica gel chromatography to afford the desired product.

2.4 Spectral data of gem-silylborylated alkenes

(E)-trimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (2-*E*)



2-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **2-*E*** (51%, 77 mg) as a pale yellowish oil.

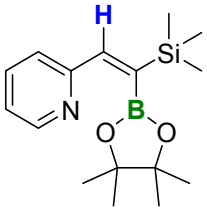
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.38 (m, 2H), 7.32 – 7.20 (m, 4H), 1.29 (s, 12H), 0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.1, 140.6, 128.1, 127.9, 127.8, 83.6, 25.2, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.36.

HRMS (ESI) for **$C_{17}H_{31}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 320.2217; found: 320.2212.

(E)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3-*E*)



3-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 10:1) (basifyed the silica gel column with 1% of NEt_3) and yielded **3-*E*** (71%, 108 mg) as a pale yellowish oil.

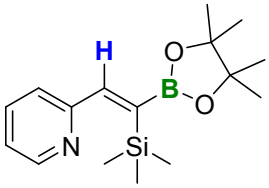
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, J = 5.0 Hz, 1H), 7.66 (dd, J = 7.6, 1.7 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.02 (s, 1H), 1.38 (s, 12H), 0.22 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 146.6, 143.6, 138.3, 122.2, 122.1, 82.5, 76.8, 26.2, -0.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 27.63.

HRMS (ESI) for **$C_{16}H_{27}BNO_2Si$ [M+H^+]$^+$:** calculated 304.1904; found: 304.1909.

(Z)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3-*Z*)



3-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **3-*Z*** (21%, 32 mg) as a pale yellowish oil.

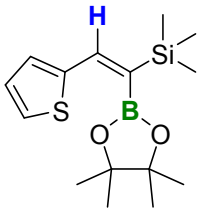
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (d, J = 4.8 Hz, 1H), 7.73 (s, 1H), 7.62 (td, J = 7.7, 1.8 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.12 (ddd, J = 7.6, 4.7, 1.1 Hz, 1H), 1.31 (s, 12H), 0.14 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7, 152.6, 148.4, 136.1, 124.3, 122.3, 83.5, 24.9, 1.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.51.

HRMS (ESI) for **$C_{16}H_{27}BNO_2Si$ [M+H$^+$]$^+$:** calculated 304.1904; found: 304.1913.

(E)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)vinyl)silane (4-*E*)



4-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **4-*E*** (71%, 176 mg) as a pale yellowish oil.

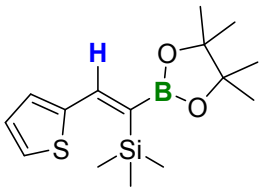
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (s, 1H), 7.22 (ddd, J = 5.0, 1.2, 0.6 Hz, 1H), 7.12 (ddd, J = 3.6, 1.2, 0.7 Hz, 1H), 6.95 (dd, J = 5.1, 3.6 Hz, 1H), 1.36 (s, 12H), 0.18 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 140.9, 128.0, 127.1, 126.0, 83.7, 25.4, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.01.

HRMS (ESI) for **$C_{15}H_{29}BNO_2SSi$ [M+NH_4^+]$^+$:** calculated 326.1781; found: 326.1784.

(Z)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)vinyl)silane (4-*Z*)



4-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **4-*Z*** (16%, 39 mg) as a pale yellowish oil.

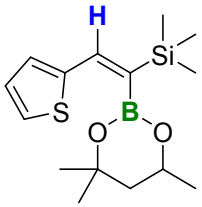
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (s, 1H), 7.28 (dd, J = 5.0, 1.2 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.97 (dd, J = 5.0, 3.5 Hz, 1H), 1.29 (s, 12H), 0.14 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.7, 143.8, 128.0, 127.0, 126.5, 83.4, 24.9, 0.8

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.97.

HRMS (ESI) for **$C_{15}H_{29}BNO_2SSi$ [M+NH_4^+]$^+$:** calculated 326.1781; found: 326.1731

(E)-trimethyl(2-(thiophen-2-yl)-1-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)silane (6-*E*)



6-*E*

Synthesized using **5** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **6-*E*** (65%, 158 mg) as a pale yellowish oil.

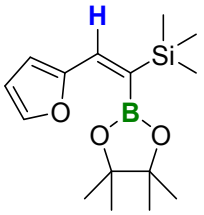
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 – 7.15 (m, 1H), 7.13 (s, 1H), 7.01 (ddd, J = 3.7, 1.3, 0.6 Hz, 1H), 6.94 (dd, J = 5.1, 3.6 Hz, 1H), 4.33 (m, J = 15.3, 6.2, 3.1 Hz, 1H), 1.86 (dd, J = 13.9, 2.9 Hz, 1H), 1.68 (ddd, J = 14.0, 11.6, 0.8 Hz, 1H), 1.41 (s, 3H), 1.34 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H), 0.15 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 137.8, 127.5, 127.0, 125.2, 71.6, 65.4, 46.1, 31.3, 28.0, 23.2, -0.9.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 28.94.

HRMS (ESI) for **$C_{15}H_{29}BNO_2SSi$ [M+NH_4^+]$^+$:** calculated 326.1781; found: 326.1787.

(E)-(2-(furan-2-yl)-1-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)vinyl)trimethylsilane (7-*E*)



7-*E*

Synthesized using **5** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded 7-***E*** (71%, 167 mg) as a pale yellowish oil.

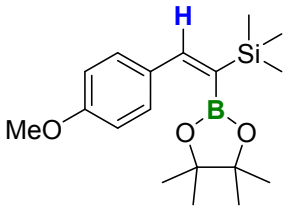
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (dd, J = 1.6, 0.8 Hz, 1H), 6.86 (s, 1H), 6.36 (dd, J = 3.3, 1.8 Hz, 1H), 6.29 (dd, J = 3.4, 0.8 Hz, 1H), 1.36 (s, 12H), 0.17 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 142.0, 134.6, 111.7, 109.9, 83.7, 25.2, -0.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.71.

HRMS (ESI) for **$C_{15}H_{29}BNO_2SSi$ [M+NH_4^+]$^+$:** calculated 310.2010; found: 310.2001

(E)-(2-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (8-*E*)



8-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **8-*E*** (63%, 105 mg) as a pale yellowish oil.

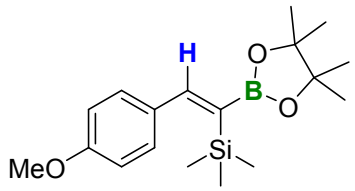
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41 – 7.32 (m, 2H), 7.20 (s, 1H), 6.84 – 6.79 (m, 2H), 3.80 (s, 3H), 1.30 (s, 12H), 0.18 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 149.8, 133.5, 129.3, 113.4, 83.5, 55.4, 25.2, -0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.85.

HRMS (ESI) for **$C_{18}H_{29}BO_3Si$ [M+H^+]$^+$:** calculated: 333.2063; found: 333.2057

(Z)-(2-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (8-*Z*)



8-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **8-Z** (29%, 49 mg) as a white solid.

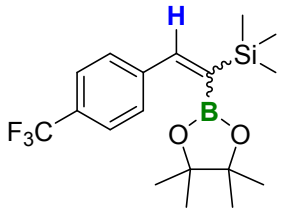
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (s, 1H), 7.24 – 7.19 (m, 2H), 6.86 – 6.81 (m, 2H), 3.81 (s, 3H), 1.29 (s, 12H), 0.04 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 156.9, 133.9, 129.9, 113.2, 83.2, 55.3, 24.9, 1.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.51.

HRMS (ESI) for **$C_{18}H_{29}BO_3Si$ [M+H^+]$^+$:** calculated: 333.2063; found: 333.2050

(E)- and (Z)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)vinyl)silane (9-*E*) and (9-*Z*)



9 *E:Z* = *2:1*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **9-*E*** and **9-Z** as mixture 2:1 (52%, 78 mg) as a pale yellowish oil.

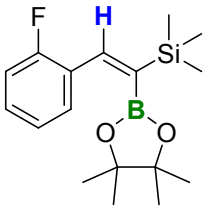
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (d, J = 4.7 Hz, 1H), 7.97 (s, 1H), 7.58 – 7.47 (m, 10H), 7.34 (ddt, J = 8.3, 1.7, 0.9 Hz, 2H), 7.32 – 7.25 (m, 1H), 1.31 (s, 12H), 1.28 (s, 24H), 0.21 (s, 18H), -0.01 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.0, 150.0, 148.3, 145.1, 144.0, 136.0, 129.7, 129.4, 128.5, 128.1, 125.1 (q, J = 3.8 Hz), 124.8 (q, J = 3.8 Hz), 123.8, 123.0, 83.8, 83.6, 25.2, 24.9, 0.9, -0.8.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.08.

HRMS (ESI) for **$C_{18}H_{30}BNF_3O_2Si$ [M+NH_4^+]$^+$:** calculated: 388.2091; found: 388.2087

(E)-(2-(2-fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (10-*E*)



10-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **10-*E*** (49%, 63 mg) as a pale yellowish oil.

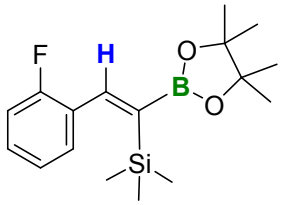
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (td, J = 7.8, 1.8 Hz, 1H), 7.38 (s, 1H), 7.26 – 7.16 (m, 1H), 7.03 (td, J = 7.6, 1.3 Hz, 1H), 6.98 (ddd, J = 10.5, 8.2, 1.2 Hz, 1H), 1.26 (s, 12H), 0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.6, 159.1, 142.4, 129.5, 129.3, 128.5 (d, J = 12.9 Hz), 123.5, 115.4 (d, J = 22.1 Hz), 83.6, 25.2, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.28.

HRMS (ESI) for **$C_{17}H_{30}BNFO_2Si$ [M+NH_4^+]$^+$:** calculated: 338.2123; found: 338.2134

(Z)-(2-(2-fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (10-Z)



10-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **10-*Z*** (36%, 47 mg) as a pale yellowish oil.

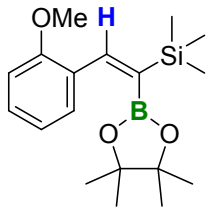
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (s, 1H), 7.26 – 7.16 (m, 2H), 7.06 (td, J = 7.5, 1.1 Hz, 1H), 7.00 (ddd, J = 9.6, 8.2, 1.2 Hz, 1H), 1.30 (s, 12H), -0.02 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.1, 158.7, 149.7, 130.7, 129.4, 129.2 (d, *J* = 16.1 Hz), 115.2 (d, J = 21.8 Hz), 83.4, 24.9, 0.5.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.53

HRMS (ESI) for **$C_{17}H_{30}BNFO_2Si$ [M+NH_4^+]$^+$:** calculated: 338.2123; found: 338.2131

(E)-(2-(2-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (11-*E*)



11-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **11-*E*** (67%, 89 mg) as a pale yellowish oil.

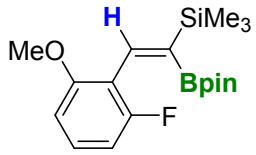
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (s, 1H), 7.42 (dd, J = 7.5, 1.7 Hz, 1H), 7.25 – 7.17 (m, 1H), 6.84 (tt, J = 7.5, 0.8 Hz, 1H), 6.80 (dd, J = 8.2, 1.0 Hz, 1H), 3.80 (S. 3H), 1.24 (s, 12H), 0.19 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.1, 146.2, 130.1, 129.2, 128.8, 119.9, 110.3, 83.4, 55.4, 25.1, -0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.75.

HRMS (ESI) for **$C_{18}H_{33}BNO_3Si$ [M+NH_4^+]$^+$:** calculated: 350.2323; found: 350.2317

(E)-(2-(2-fluoro-6-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (12-*E*)



12-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **12-*E*** (92%, 129 mg) as a pale yellowish oil.

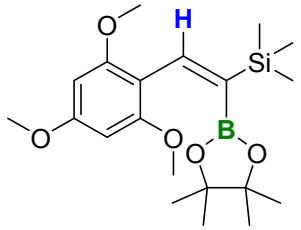
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (s, 1H), 7.13 (td, J = 8.3, 6.4 Hz, 1H), 6.66 – 6.59 (m, 2H), 3.80 (s, 3H), 1.19 (s, 12H), 0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 159.1, 158.4 (d, J = 7.7 Hz), 140.2, 128.5 (d, J = 10.9 Hz), 118.1 (d, J = 16.1 Hz), 108.0 (d, J = 23.6 Hz), 106.3, 83.0, 56.1, 25.1, -0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.24.

HRMS (ESI) for **$C_{18}H_{33}BNO_3Si$ [M+NH_4^+]$^+$:** calculated: 350.2323; found: 350.2325

(E)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)pyridine (13-*E*)



13-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **13-*E*** (67%, 132 mg) as a white solid.

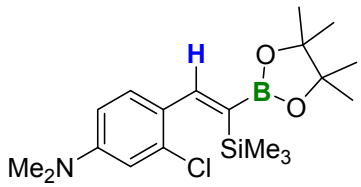
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16 (s, 1H), 6.09 (s, 2H), 3.80 (s, 3H), 3.73 (s, 6H), 1.18 (s, 12H), 0.18 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4, 158.8, 141.8, 112.9, 91.7, 82.4, 56.1, 55.4, 25.4, -0.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.00.

HRMS (ESI) for **$C_{20}H_{34}BO_5Si$ [M+H$^+$]$^+$:** calculated: 393.2269; found: 393.2279

(Z)-3-chloro-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)aniline (14-*Z*)



14-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **14-*Z*** (45%, 69 mg) as a white solid.

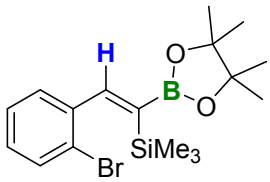
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.11 (d, J = 8.6 Hz, 1H), 6.66 (d, J = 2.6 Hz, 1H), 6.52 (dd, J = 8.6, 2.6 Hz, 1H), 2.95 (s, 6H), 1.29 (s, 12H), 0.02 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.8, 151.0, 134.3, 131.2, 127.4, 112.2, 109.7, 83.1, 40.4, 24.9, 1.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.12.

HRMS (ESI) for **$C_{19}H_{32}BNO_2SiCl$ [M+H$^+$]$^+$:** calculated: 380.1995; found: 380.1984

(Z)-(2-(2-bromophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (15-*Z*)



15-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **15-*Z*** (73%, 88 mg) as a pale yellowish oil.

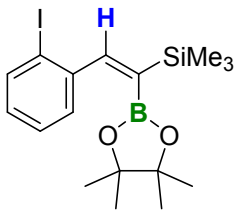
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 1H), 7.52 (dd, J = 7.9, 1.2 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.12 (m, 1H), 1.30 (s, 12H), -0.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1, 142.1, 132.1, 130.4, 129.0, 126.7, 122.8, 83.3, 24.9, 0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.86

HRMS (ESI) for **$C_{17}H_{30}BNBrO_2Si$ [M+NH_4^+]$^+$:** calculated: 398.1322; found: 398.1329

(Z)-(2-(2-iodophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (16-E)



16-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **16-E** (7%, 15 mg) as a pale yellowish oil.

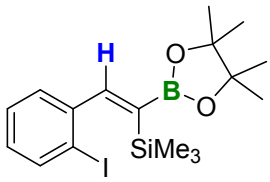
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (dd, J = 7.9, 1.2 Hz, 1H), 7.49 (dd, J = 7.7, 1.7 Hz, 1H), 7.25 – 7.19 (m, 2H), 6.91 (td, J = 7.6, 1.7 Hz, 1H), 1.22 (s, 12H), 0.22 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 143.3, 139.0, 129.2, 128.6, 127.8, 99.7, 83.6, 25.0, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.55.

HRMS (ESI) for **$C_{17}H_{30}BNIO_2Si$ [M+NH_4^+]$^+$:** calculated: 446.1184; found: 446.1174.

(Z)-(2-(2-iodophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (16-*Z*)



16-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **16-*Z*** (45%, 97 mg) as a pale yellowish oil.

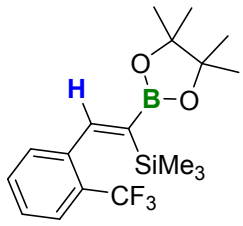
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (dd, J = 7.9, 1.2 Hz, 1H), 7.72 (s, 1H), 7.32 – 7.26 (m, 1H), 7.19 (dd, J = 7.7, 1.8 Hz, 1H), 6.95 (td, J = 7.4, 1.0 Hz, 1H), 1.30 (s, 12H), -0.08 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 145.8, 138.3, 129.5, 128.9, 127.5, 98.2, 83.3, 24.9, 0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.81

HRMS (ESI) for **$C_{17}H_{30}BNIO_2Si$ [M+NH_4^+]$^+$:** calculated: 446.1184; found: 446.1186.

(Z)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(2-(trifluoromethyl)phenyl)vinyl)silane (17-Z)



17-Z

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 300:1) yielded **17-Z** (78%, 116 mg) as a pale yellowish oil.

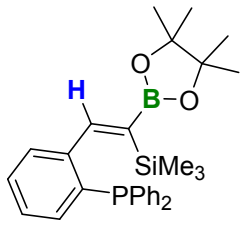
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (s, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 1.29 (s, 12H), -0.13 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 141.0, 131.1, 130.7, 128.0, 127.7, 127.4, 125.6, 125.4 (q, J = 5.3 Hz), 83.3, 24.9, 0.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.83.

HRMS (ESI) for $C_{18}H_{30}BF_3NO_2Si$ **[M+NH_4^+]$^+$:** calculated: 388.2101; found: 388.2091

(Z)-diphenyl(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl)phenyl)phosphane (18-*Z*)



18-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 300:1) yielded **18-*Z*** (28%, 36 mg) as a pale yellowish scum.

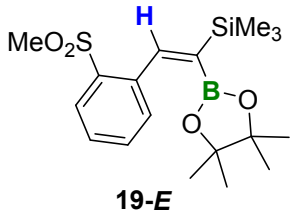
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (s, 1H), 7.38 – 7.28 (m, 10H), 7.24 (dd, J = 7.0, 1.5 Hz, 1H), 7.20 – 7.13 (m, 2H), 6.96 – 6.88 (m, 1H), 1.23 (s, 12H), -0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.0, 156.9, 136.4, 136.3, 136.2, 134.6, 134.4, 131.9, 129.3, 129.2, 128.7, 128.5, 128.4, 127.9, 127.7, 83.0, 24.9, 0.8

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.63.

HRMS (ESI) for **$C_{29}H_{40}BNO_2PSi$ [M+NH_4^+]$^+$:** calculated: 504.2659; found: 504.2654

(E)-trimethyl(2-(2-(methylsulfonyl)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (19-*E*)



19-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 10:1) yielded **19-*E*** (17%, 26 mg) as a colourless oil.

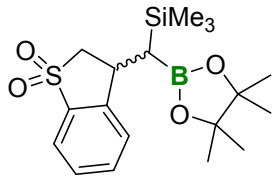
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 – 7.97 (m, 1H), 7.92 (s, 1H), 7.57 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 3.03 (s, 3H), 1.06 (s, 12H), 0.21 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.6, 142.2, 137.7, 133.3, 130.9, 128.2, 127.8, 83.5, 43.9, 24.9, -1.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.69.

HRMS (ESI) for **$C_{18}H_{33}BNO_4SSi$ [M+NH_4^+]$^+$:** calculated: 398.1993; found: 398.2012

3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(trimethylsilyl)methyl)-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (20)



20

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 10:1) yielded **20** (21%, 32 mg) as a pale yellowish oil.

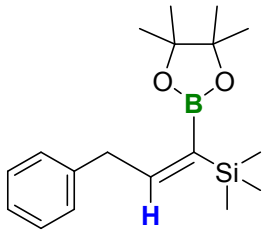
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 – 7.66 (m, 1H), 7.60 – 7.52 (m, 1H), 7.47 – 7.39 (m, 2H), 3.96 (dd, J = 12.5, 9.5 Hz, 1H), 3.82 – 3.71 (m, 1H), 3.48 (dd, J = 12.5, 7.3 Hz, 1H), 1.44 (d, J = 4.0 Hz, 1H), 1.04 (s, 6H), 0.82 (s, 6H), 0.17 (s, 9H).

^{13}C NMR has been done as a mixture of diastereoisomers (70:30). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.3, 143.8, 138.9, 133.3, 133.2, 128.5, 128.3, 125.7, 125.6, 125.2, 121.4, 121.0, 83.7, 83.2, 57.7, 56.0, 36.5, 35.5, 31.0, 30.4, 29.8, 25.3, 25.2, 25.0, 24.0, 15.4, 0.7, -0.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.05.

HRMS (ESI) for **$C_{18}H_{33}BNO_4SSi$ [M+NH_4^+]$^+$:** calculated: 398.1993; found: 398.2008

(E)-trimethyl(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (21-*E*)



21-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **21-*E*** (63%, 59 mg) as a pale yellowish oil.

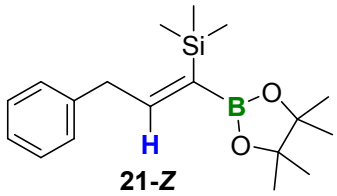
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 6.53 (t, J = 6.9 Hz, 1H), 3.63 (d, J = 7.0 Hz, 2H), 1.31 (s, 12H), 0.08 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.3, 141.3, 129.6, 129.3, 126.7, 83.9, 43.0, 25.8, -0.01.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.44.

HRMS (ESI) for **$C_{18}H_{33}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 334.2374; found: 334.2351

(Z)-trimethyl(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (21-*Z*)



21-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **21-*Z*** (21%, 19 mg) as a pale yellowish oil.

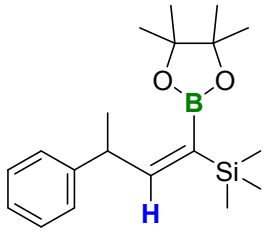
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 7.02 (t, J = 7.0 Hz, 1H), 3.58 (d, J = 7.0 Hz, 2H), 1.23 (s, 12H), 0.23 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.6, 140.1, 128.8, 128.6, 126.2, 83.1, 41.3, 24.9, 1.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.94.

HRMS (ESI) for **$C_{18}H_{33}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 334.2374; found: 334.2362

(E)-trimethyl(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)silane (22-*E*)



22-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **22-*E*** (39%, 39 mg) as a pale yellowish oil.

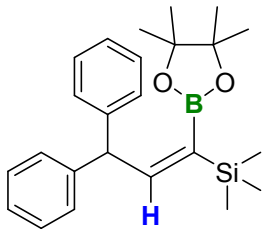
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.11 (m, 1H), 6.41 (d, J = 9.2 Hz, 1H), 3.91 (dq, J = 9.3, 6.9 Hz, 1H), 1.36 (d, J = 6.9 Hz, 3H), 1.30 (s, 6H), 1.30 (s, 6H), 0.07 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.2, 146.5, 129.1, 127.9, 126.6, 83.8, 45.7, 25.8, 25.7, 22.0, 0.00.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.32.

HRMS (ESI) for **$C_{19}H_{35}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 348.2530; found: 348.2519

(E)-(3,3-diphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)trimethylsilane (23-*E*)



23-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **23-*E*** (70%, 82 mg) as a white solid.

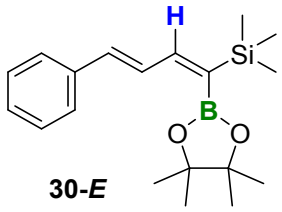
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 – 7.24 (m, 6H), 7.25 – 7.13 (m, 4H), 6.84 (d, J = 9.5 Hz, 1H), 5.28 (d, J = 10.0 Hz, 1H), 1.27 (s, 12H), 0.11 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 145.0, 129.2, 129.2, 126.8, 83.8, 56.2, 25.7, 0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.73.

HRMS (ESI) for **$C_{24}H_{37}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 410.2713; found: 410.2687

trimethyl((1E,3E)-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)silane (30-*E*)



30-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **30-*E*** (55%, 146 mg) as a pale yellowish oil.

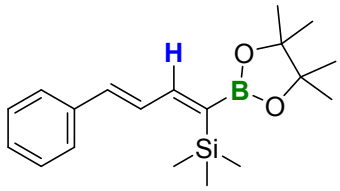
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, J = 11.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 7.18 (ddd, J = 15.3, 11.2, 0.7 Hz, 1H), 6.72 (d, J = 15.3 Hz, 1H), 1.28 (s, 12H), 0.27 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1, 137.8, 137.2, 129.6, 128.8, 128.3, 127.0, 83.1, 24.9, 1.4.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.66.

HRMS (ESI) for **$C_{19}H_{33}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 346.2374; found: 346.2387

trimethyl((1Z,3E)-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)silane (30-*Z*)



30-*Z*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **30-*Z*** (23%, 61 mg) as a pale yellowish oil.

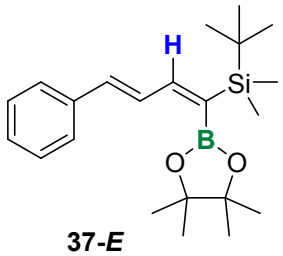
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 7.12 (d, J = 10.6 Hz, 1H), 6.66 (dd, J = 15.5, 0.7 Hz, 1H), 1.34 (s, 12H), 0.15 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 137.5, 136.0, 130.9, 128.7, 127.9, 126.9, 83.2, 25.1, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.55.

HRMS (ESI) for **$C_{19}H_{33}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 346.2374; found: 346.2367

tert-butyldimethyl((1E,3E)-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)silane (37-*E*)



37-*E*

Purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **37-*E*** (81%, 91 mg) as a white solid.

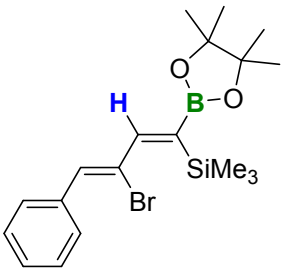
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.19 (m, 4H), 7.09 (d, J = 10.8 Hz, 1H), 6.65 (d, J = 15.4 Hz, 1H), 1.35 (s, 12H), 0.90 (s, 9H), 0.14 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 137.5, 135.9, 130.7, 128.7, 127.9, 126.8, 83.3, 27.0, 25.2, 17.7, -5.2.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.99.

HRMS (ESI) for **$C_{22}H_{36}BO_2Si$ [M+H^+]$^+$:** calculated: 371.2578; found: 371.2586

((1Z,3Z)-3-bromo-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-dien-1-yl)trimethylsilane (31-*E*)



31-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 300:1) yielded **31-*E*** (74%, 121 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 – 7.62 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H

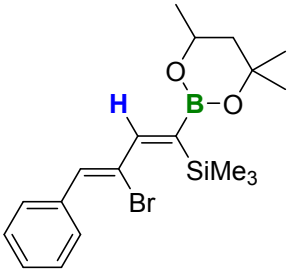
), 7.08 (s, 1H), 6.83 (s, 1H), 1.30 (s, 12H), 0.20 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 135.8, 132.3, 129.5, 128.3, 128.2, 126.1, 83.8, 25.5, -0.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 30.99.

HRMS (ESI) for **$C_{19}H_{32}BNBrO_2Si$ [M+NH_4^+]$^+$:** calculated: 424.1479; found: 424.1467

((1Z,3Z)-3-bromo-4-phenyl-1-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)buta-1,3-dien-1-yl)trimethylsilane (32-*E*)



32-*E*

Synthesized using **5** and purified by flash column chromatography (pentane:ethyl ether = 300:1) yielded **32-*E*** (73%, 119 mg) as a pale yellowish oil.

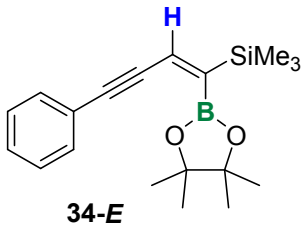
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 – 7.61 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.05 (s, 1H), 6.73 (s, 1H), 4.27 (m, 1H), 1.80 (dd, J = 13.9, 2.9 Hz, 1H), 1.64 – 1.56 (m, 1H), 1.35 (s, 3H), 1.32 (s, 3H), 1.29 (d, J = 6.1 Hz, 3H), 0.17 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 136.2, 132.8, 129.5, 128.2, 128.1, 127.3, 71.5, 65.1, 45.9, 31.5, 27.7, 23.3, -0.7.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 28.69.

HRMS (ESI) for **$C_{19}H_{32}BNBrO_2Si$ [M+NH_4^+]$^+$:** calculated: 424.1479; found: 424.1471

(E)-trimethyl(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yn-1-yl)silane (34-*E*)



34-*E*

Synthesized using **1** and purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **34-*E*** (71%, 93 mg) as a pale yellowish oil.

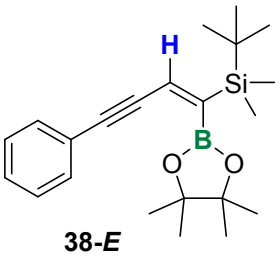
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.39 (m, 2H), 7.32 – 7.27 (m, 3H), 6.53 (s, 1H), 1.32 (s, 12H), 0.14 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 129.7, 128.3, 128.3, 123.7, 92.3, 90.1, 83.6, 25.1, -1.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.73.

HRMS (ESI) for **$C_{19}H_{31}BNO_2Si$ $[M+NH_4^+]^+$:** calculated: 344.2215; found: 344.2217

(E)-tert-butyldimethyl(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yn-1-yl)silane (38-*E*)



38-*E*

Purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **38-*E*** (85%, 94 mg) as a pale yellowish oil.

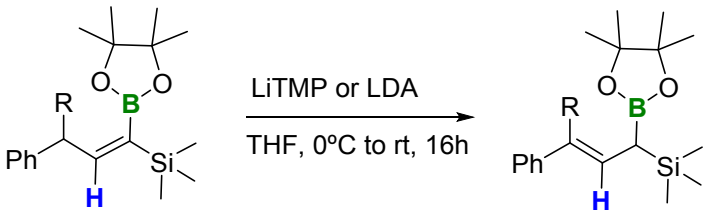
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.39 (m, 2H), 7.33 – 7.25 (m, 3H), 6.53 (s, 1H), 1.31 (s, 12H), 0.91 (s, 9H), 0.12 (s, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 130.8, 128.3, 128.3, 123.6, 92.1, 90.0, 83.7, 26.8, 25.1, -5.6.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 31.75.

HRMS (ESI) for **$C_{22}H_{37}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 386.2687; found: 386.2690

2.5 General procedure for the isomerization of gem-silylborylated alkenes

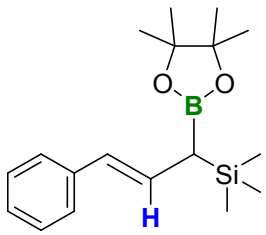


(R= H, Me, Ph)

A Schlenk-tube equipped with a magnetic stir bar was charged with the LiTMP or LDA (0.36 mmol, 1.2 equiv) and was cooled down to 0ºC. Then the gem-silylborylted alkene (0.3 mmol, 1 equiv) and dry THF (2 mL) were added. The mixture was stirred for 30 minutes at 0ºC and left at room temperature 16h. The reaction crude was analysed by NMR using naphthalene as internal standard and the crude residue was purified by silica gel chromatography to afford the desired product.

2.6 Spectral data of allylic gem-silylborylated compounds

(E)-trimethyl(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)silane (24)



24

Purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **24** (65%, 61 mg) as a white solid.

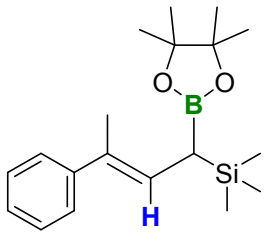
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.15 – 7.09 (m, 1H), 6.35 (dd, J = 15.7, 10.8 Hz, 1H), 6.15 (d, J = 15.4 Hz, 1H), 1.68 (d, J = 10.8 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.09 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 130.6, 129.9, 128.5, 127.4, 127.0, 84.5, 26.5, 0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 33.43.

HRMS (ESI) for **$C_{18}H_{33}BNO2Si$ $[M+NH_4^+]^+$:** calculated: 334.2374; found: 334.2344

(E)-trimethyl(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)silane (25)



25

Purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **25** (15%, 25 mg) as a white solid.

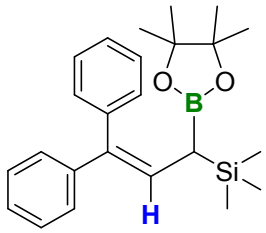
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.36 (m, 2H), 7.29 (dd, J = 8.5, 6.9 Hz, 2H), 7.21 – 7.13 (m, 1H), 6.01 (dq, J = 11.9, 1.4 Hz, 1H), 1.95 (d, J = 1.4 Hz, 3H), 1.91 (d, J = 11.9 Hz, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.7, 130.3, 128.1, 126.4, 125.9, 125.6, 83.1, 25.1, 25.1, 15.9, -1.1.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.58.

HRMS (ESI) for **$C_{19}H_{35}NBO_2Si$ $[M+NH_4^+]^+$:** calculated: 348.2530; found: 348.2546

(3,3-diphenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)trimethylsilane (26)



26

Purified by flash column chromatography (pentane:ethyl ether = 100:1) yielded **26** (33%, 39 mg) as a white solid.

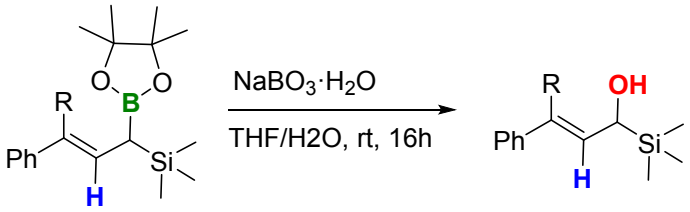
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.30 (m, 2H), 7.29 – 7.11 (m, 8H), 6.27 (d, J = 12.5 Hz, 1H), 1.90 (d, J = 12.5 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.03 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.0, 141.9, 139.2, 131.7, 129.5, 129.2, 129.1, 128.3, 127.7, 127.3, 84.2, 26.2, 26.1, 0.0.

^{11}B NMR ($CDCl_3$, 128.3 MHz) δ 32.60.

HRMS (ESI) for **$C_{24}H_{37}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 410.2713; found: 410.2694

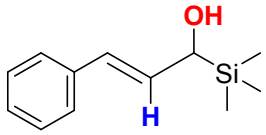
2.7 General procedure for the oxidation of the allylic gem-silylborylated compounds



An oven dried Schlenk-tube flask, was charged with the allylic gem-silylborylated compound (0.2mmol, 1 equiv), $NaBO_3{\cdot}H_2O$ (0.4mmol, 2 equiv), 1 mL of THF and 1 mL of H_2O and the mixture was stirred for 16h. The reaction was quenched with $Na_2S_2O_3$, extracted 3 times with 15 mL of Et_2O and the organic layer was dried with $MgSO_4$ anhydride, filtered and the solvent evaporated. The reaction crude was analysed by NMR using naphthalene as internal standard and the crude residue was purified by silica gel chromatography to afford the desired product.

2.8 Spectral data of allylic alcohols

(E)-3-phenyl-1-(trimethylsilyl)prop-2-en-1-ol (27)



27

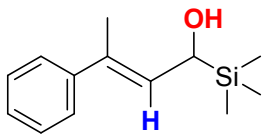
Purified by flash column chromatography (pentane:ethyl ether = 10:2) yielded **27** (92%, 37 mg) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 6.51 – 6.37 (m, 2H), 4.20 (dd, J = 4.9, 0.8 Hz, 1H), 1.26 (s, 1H), 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.5, 131.9, 128.5, 126.8, 126.0, 125.5, 68.9, -4.0.

HRMS (ESI) for **$C_{12}H_{16}Si$ [M-H_2O^+]$^+$:** calculated: 188.1021; found: 188.1027

(E)-3-phenyl-1-(trimethylsilyl)but-2-en-1-ol (28)



28

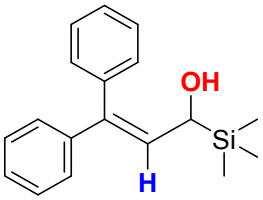
Purified by flash column chromatography (pentane:ethyl ether = 10:2) yielded **28** (78%, 32 mg) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 5.91 (dq, J = 10.1, 1.3 Hz, 1H), 4.42 (d, J = 10.1 Hz, 1H), 2.03 (d, J = 1.3 Hz, 3H), 1.37 (s, 1H), 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 133.6, 129.7, 128.4, 127.0, 125.8, 65.8, 16.7, -3.7.

HRMS (ESI) for **$C_{13}H_{19}Si$ [M-H_2O^+]$^+$:** calculated: 202.1178; found: 202.1186

3,3-diphenyl-1-(trimethylsilyl)prop-2-en-1-ol (29)



29

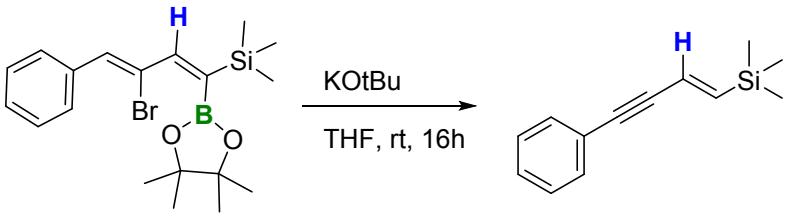
Purified by flash column chromatography (pentane:ethyl ether = 10:2) yielded 2**9** (95%, 54 mg) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 – 7.09 (m, 10H), 6.14 (d, J = 11.0 Hz, 1H), 4.06 (d, J = 11.0 Hz, 1H), 1.34 (s, 1H), 0.00 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.4, 141.7, 139.7, 129.8, 129.7, 128.3, 128.1, 127.3, 127.3, 127.2, 66.0, -3.7.

HRMS (ESI) for **$C_{18}H_{20}Si$ [M-H_2O^+]$^+$:** calculated: 264.1334; found: 264.1344

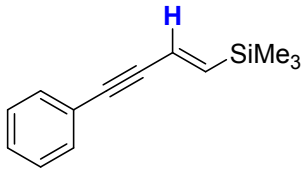
2.9 General procedure for the synthesis of compound 33-E



An oven-dried Schlenk flas was charged with KOtBu (1.6 mmol, 4 equiv). Then, the gem-borylsilane **31** (0.4 mmol, 1 equiv) was added with 2 mL of THF. The reaction was stirred for 16h at room temperature. The solvent was removed on the rotatory evaporator and the resulting crude was purified by silica gel chromatography colum to afford the desired product.

2.10.Spectral data of compound 33-E

(E)-trimethyl(4-phenylbut-1-en-3-yn-1-yl)silane (33-*E*)



33-*E*

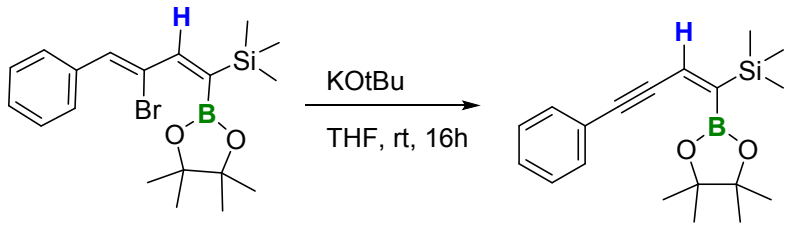
Purified by flash column chromatography (pentane) yielded **33-*E*** (20%, 20 mg) as a pale yellowish oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.41 (m, 2H), 7.36 – 7.29 (m, 3H), 6.55 (d, J = 19.3 Hz, 1H), 6.18 (d, J = 19.2 Hz, 1H), 0.13 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 131.7, 128.4, 128.3, 123.4, 89.9, 89.7, -1.4.

HRMS (ESI) for **$C_{13}H_{17}Si$ [M+H^+]$^+$:** calculated: 201,1100; found: 201,1099

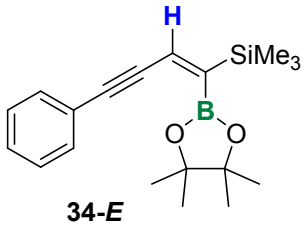
2.11.General procedure for the synthesis of compound 34-E



An oven-dried Schlenk flask was charged with KOtBu (0.6 mmol, 1.5 equiv). Then, the gem-borylsilane **31** (0.4 mmol, 1 equiv) was added with 2 mL of THF. The reaction was stirred for 16h at room temperature. The solvent was removed on the rotatory evaporator and the resulting crude was purified by silica gel chromatography colum to afford the desired product.

2.12.Spectral data of compound 34-E

(E)-trimethyl(4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-3-yn-1-yl)silane (34-*E*)



34-*E*

Purified by flash column chromatography (pentane:ethyl ether = 200:1) yielded **34-*E*** (69%, 90 mg) as a pale yellowish oil.

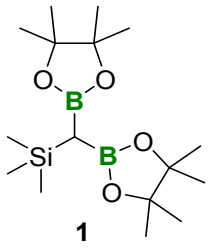
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 – 7.39 (m, 2H), 7.32 – 7.27 (m, 3H), 6.53 (s, 1H), 1.32 (s, 12H), 0.14 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.6, 129.7, 128.3, 128.3, 123.7, 92.3, 90.1, 83.6, 25.1, -1.1.

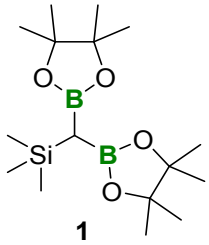
HRMS (ESI) for **$C_{19}H_{31}BNO_2Si$ [M+NH_4^+]$^+$:** calculated: 344.2215; found: 344.2217

3. ^{1}H, ^{13}C and ^{11}B spectra

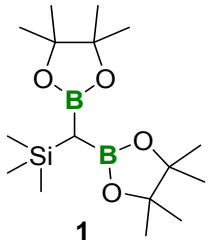
3.1 gem-Diborylsilanes



1

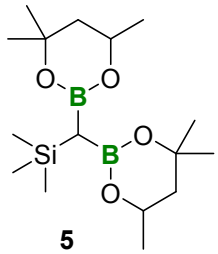


1


O
O
B
Si
B
O
O

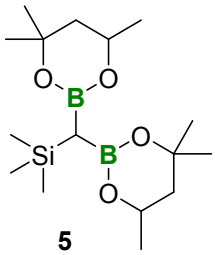
1

32.94
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15
f1 (ppm


O
O
B
Si
B
O
O

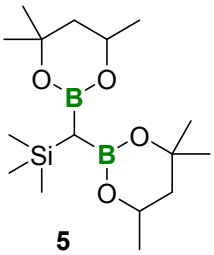
5

4.15 4.14 4.13 4.13 4.12 4.11 4.11 4.11 4.10 4.10 4.09 4.08 4.08 4.07 4.06
1.71 1.71 1.71 1.70 1.70 1.70 1.68 1.67 1.67 1.67 1.66 1.41 1.41 1.40 1.40 1.38 1.38 1.37 1.37 1.35 1.34 1.34 1.25 1.25 1.23 1.23 1.22 1.22 1.20 1.20 1.19 1.18 1.18 0.01 -0.12 -0.13 -0.14
2.00
2.07
2.27
11.53
5.85
8.93
0.94
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm


O
B
O
Si
B
O
O

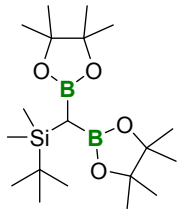
5

70.03
64.38
46.22
31.57
28.16
23.53
0.62
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


O
B
O
Si
B
O
O

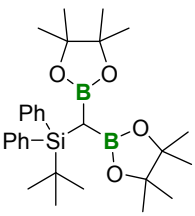
5

30.08
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13
ppm



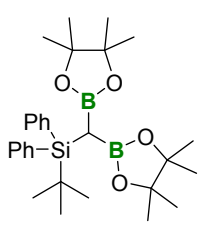
35

1.22
1.21
0.87
0.39
0.07
11.72
11.83
9.22
1.00
6.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



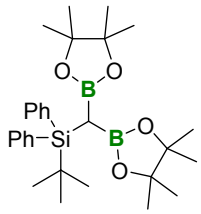
36

7.73
7.73
7.73
7.72
7.72
7.71
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.26
1.07
1.07
1.06
1.06
1.02
1.00
0.92
4.15
6.24
9.43
12.22
12.24
0.93
3.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ph
Ph–Si
B
O
O
B
O
O

36

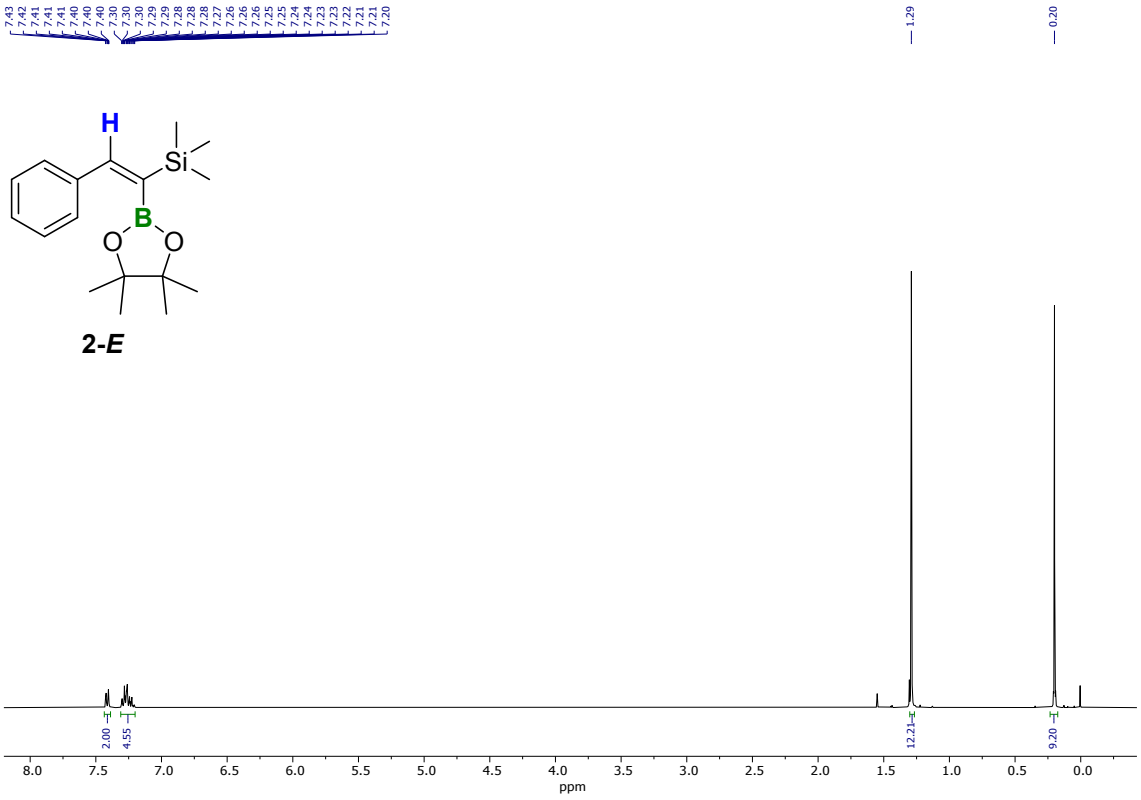
136.66
128.57
126.96
82.80
28.59
24.88
24.69
19.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm


Ph
Ph–Si
B
O
O
B
O
O

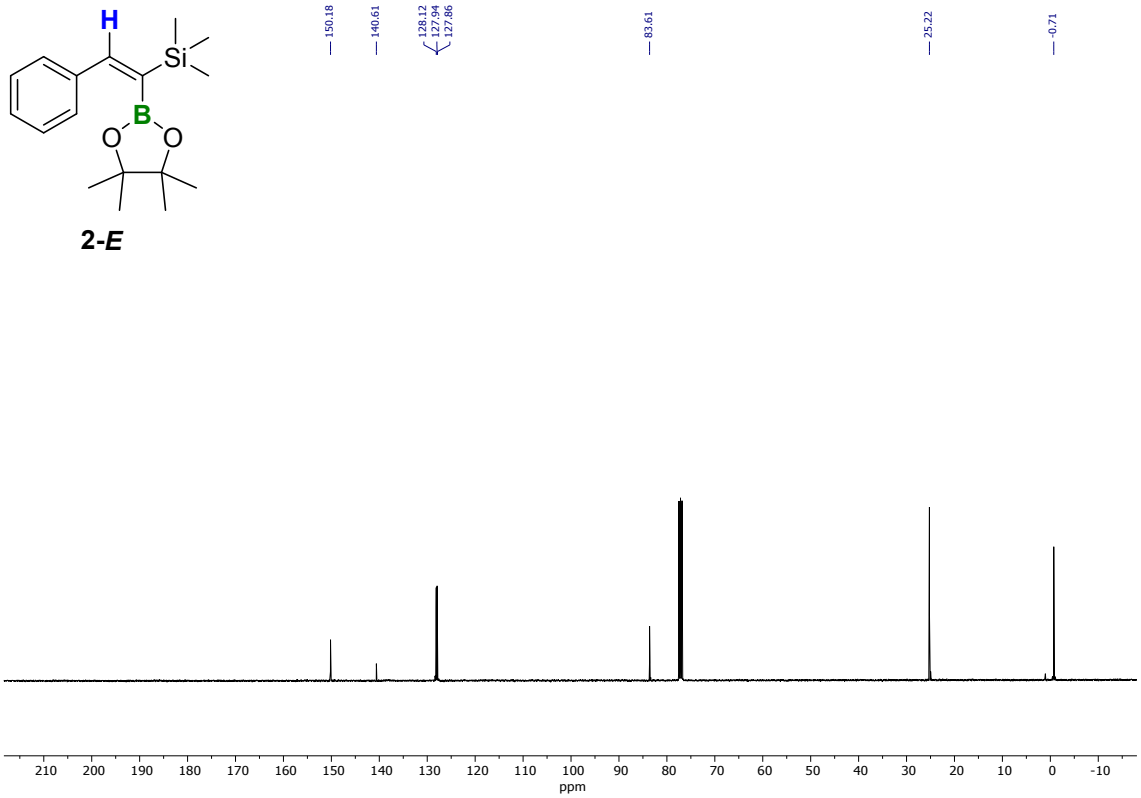
36

32.47
51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11
f1 (ppm

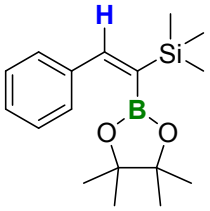
3.2 gem-Silylborylated alkene



2-*E*

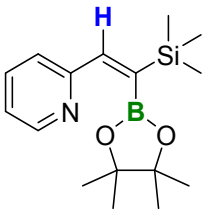


2-*E*


H
Si
B
O
O

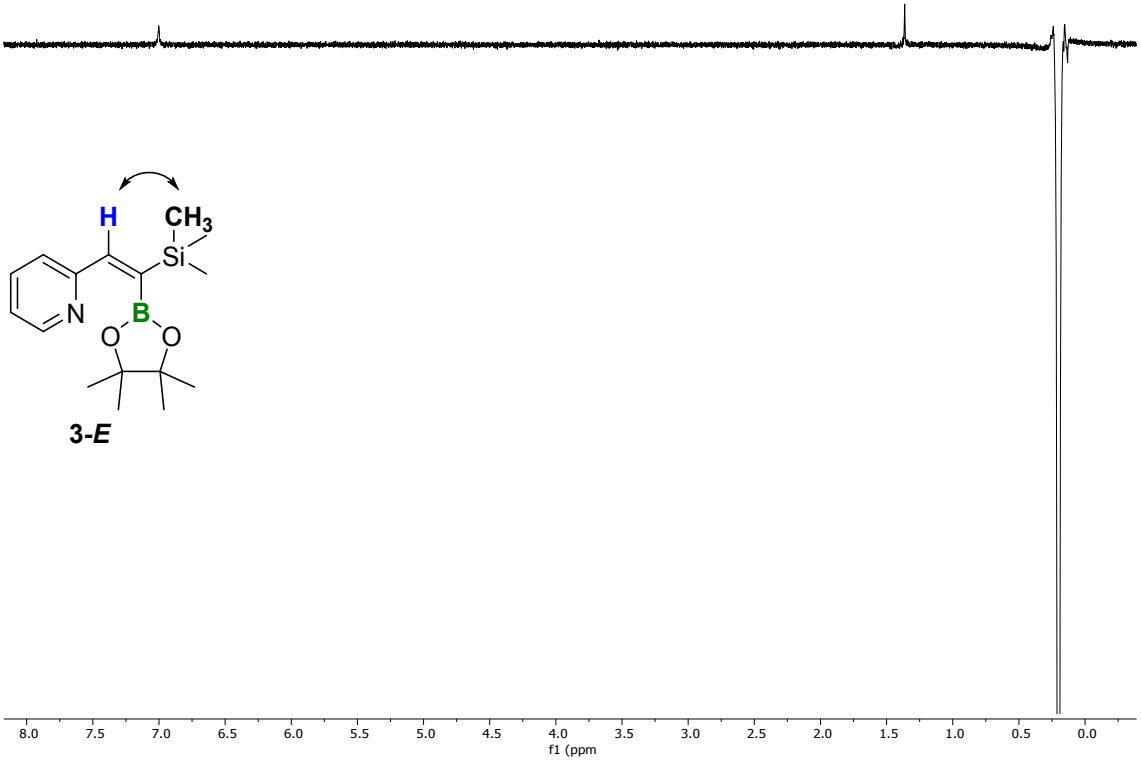
2-*E*

32.36
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
f1 (ppm)

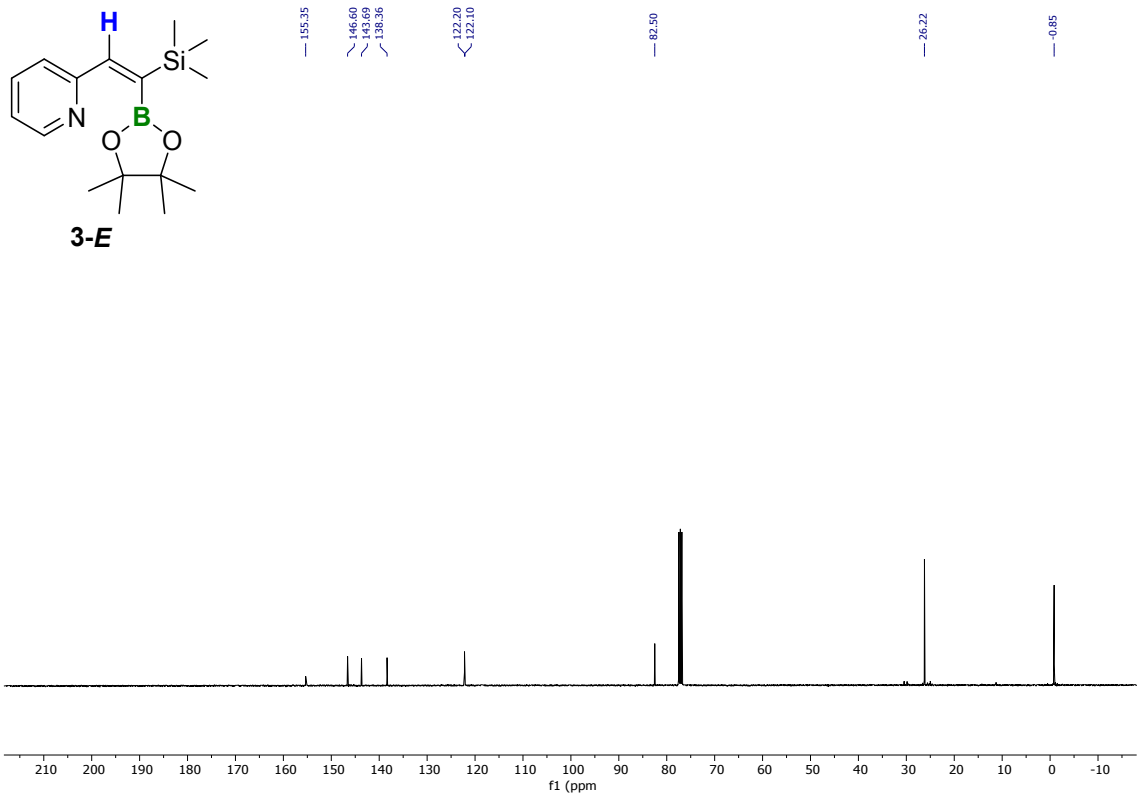

H
Si
N
B
O
O

3-*E*

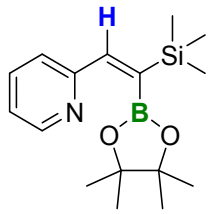
8.50 8.50 8.50 8.49 8.49 8.49 8.48 8.48 8.48 8.48 8.48 8.48
7.68 7.68 7.66 7.66 7.64 7.64
7.16 7.16 7.15 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.11 7.11 7.02
1.38
0.22
1.05
1.03
2.18
1.00
12.27
9.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
CH3
Si
N
B
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

3-*E*

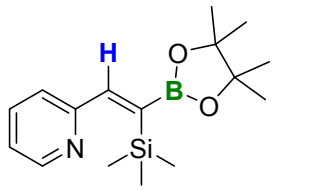

155.35
146.60
143.69
138.36
122.20
122.10
82.50
26.22
-0.85
H
Si
N
B
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3-*E*


H
Si
N
B
O
O

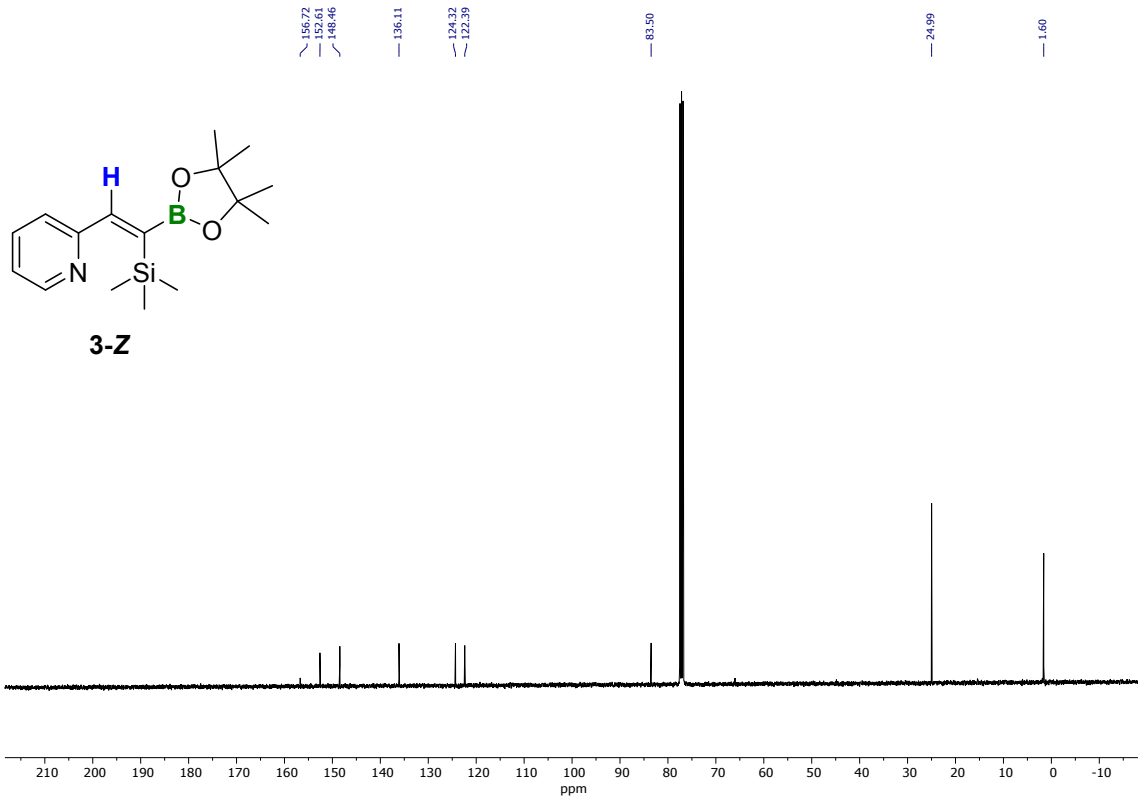
3-*E*

27.63
41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
f1 (ppm

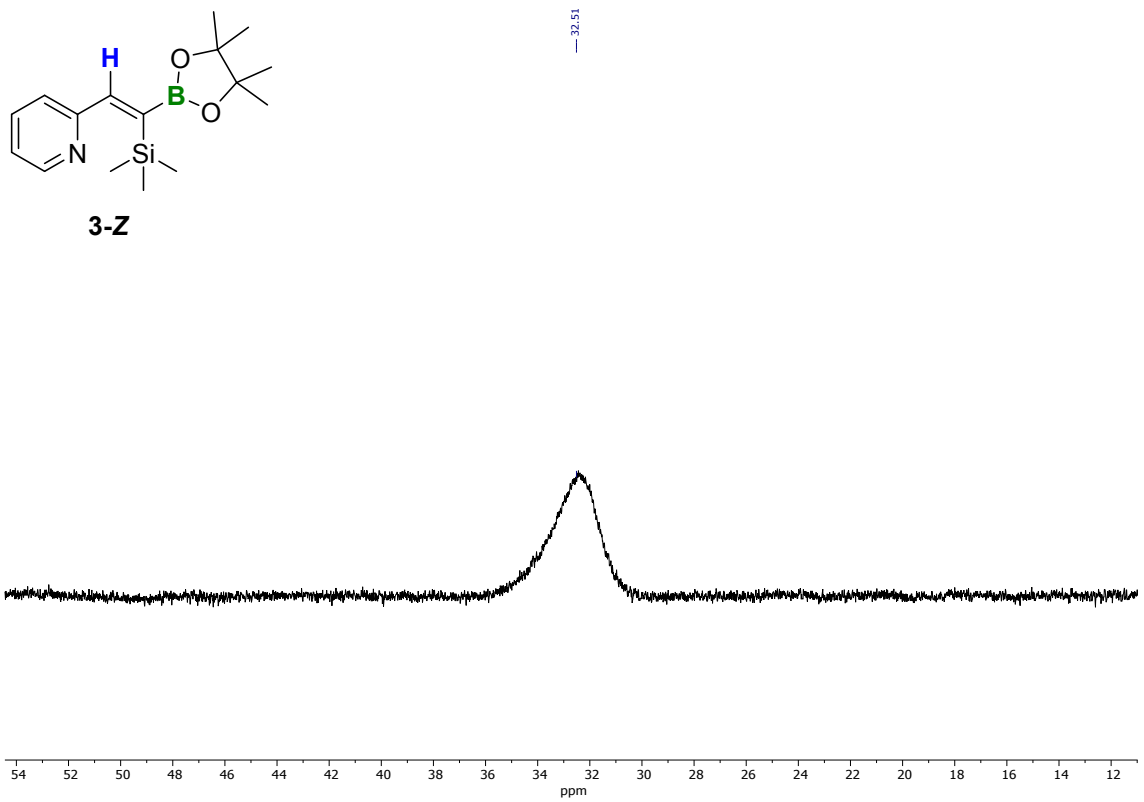

H
O
B
O
N
Si

3-*Z*

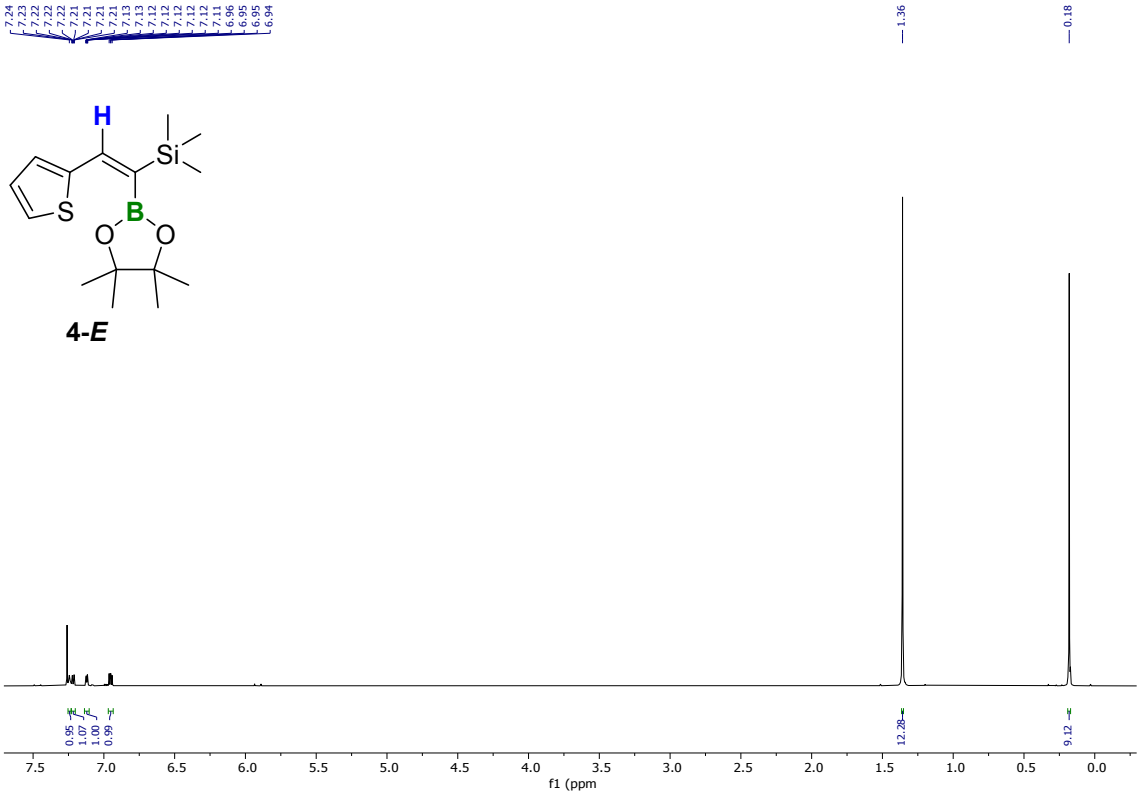
8.55
8.55
8.55
8.55
8.54
8.54
8.54
8.53
7.73
7.62
7.61
7.60
7.25
7.24
7.14
7.13
7.12
7.12
7.11
7.11
1.31
0.14
1.00
0.97
1.00
1.03
1.04
12.62
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

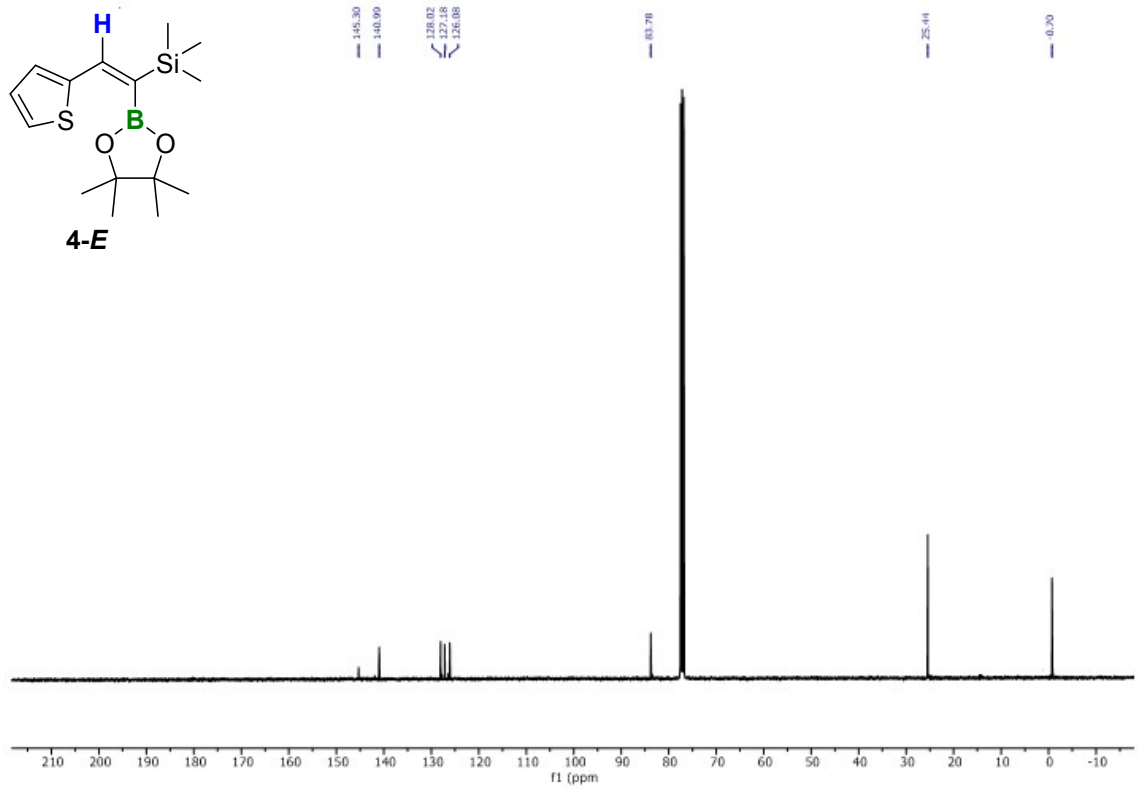

156.72
152.61
148.46
136.11
124.32
122.39
83.50
24.99
1.60
H
O
B
O
N
Si
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

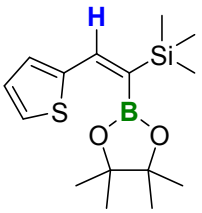
3-*Z*


32.51
H
O
B
O
N
Si
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
ppm

3-*Z*

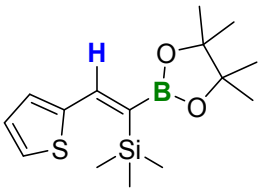

H
Si
S
B
O
O
4-E
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.21
7.21
7.13
7.12
7.12
7.12
7.12
7.11
6.96
6.95
6.95
6.94
1.36
0.18
0.95
1.07
1.00
0.99
12.28
9.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
Si
S
B
O
O
4-E
145.30
140.99
128.02
127.18
126.08
83.78
25.44
0.30
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)


H
Si
S
B
O
O

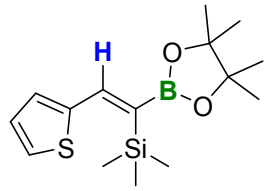
4-*E*

32.01
47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
f1 (ppm


H
O
B
O
S
Si

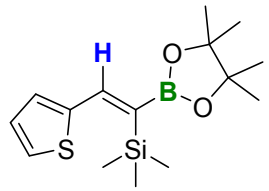
4-*Z*

7.88
7.29
7.29
7.28
7.27
7.26
7.03
7.02
7.02
7.02
7.02
6.98
6.97
6.97
6.96
1.29
0.14
1.00
1.02
1.06
1.11
12.33
9.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm


H
O
B
O
S
Si

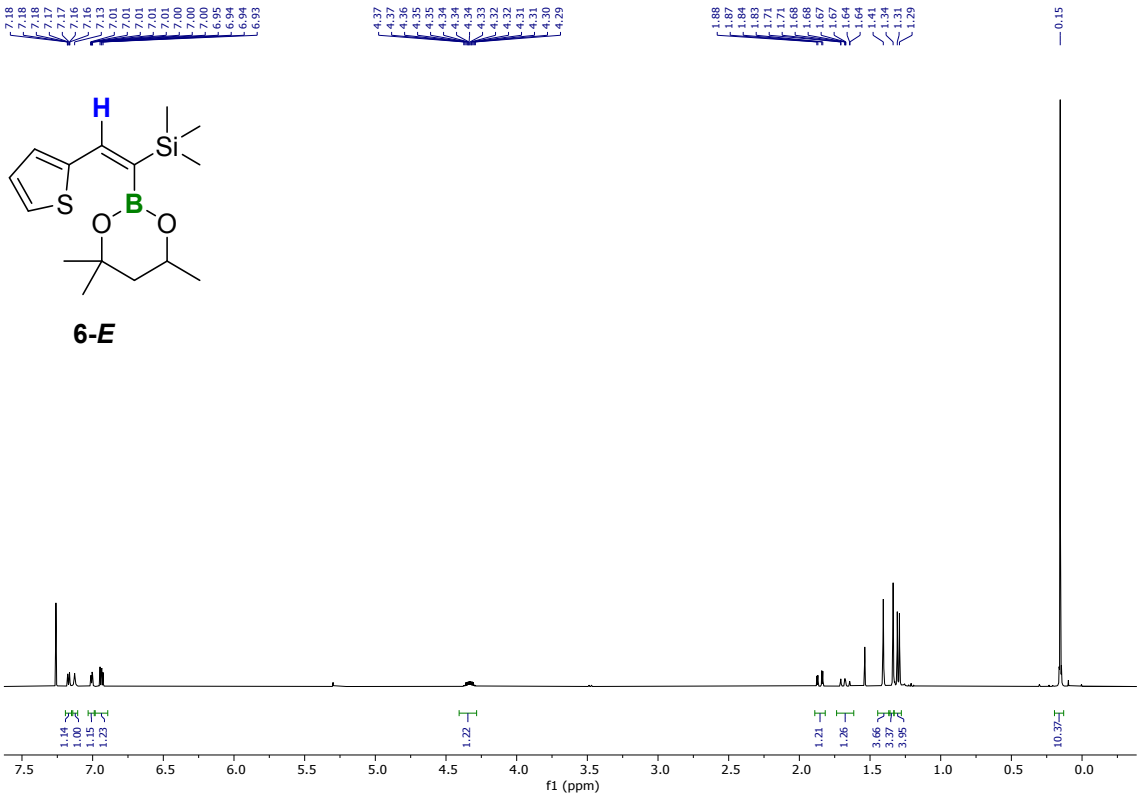
4-*Z*

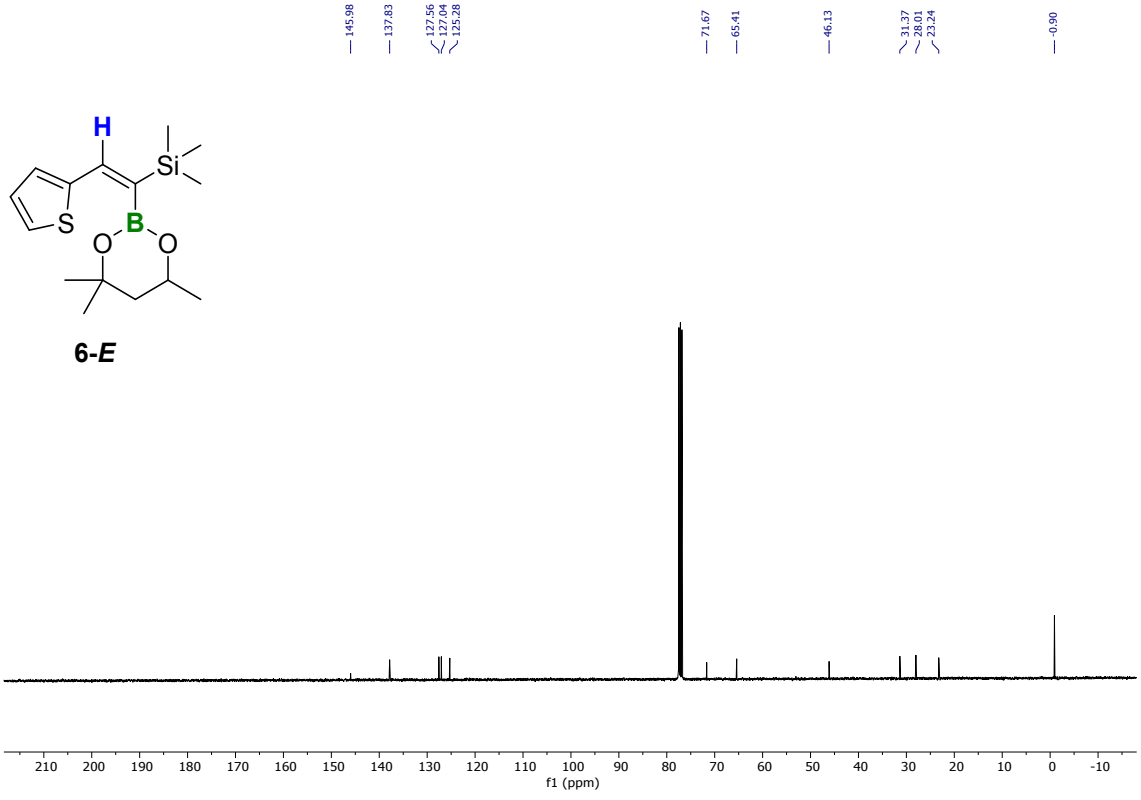
147.78
143.88
128.05
127.03
126.57
83.45
24.96
0.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

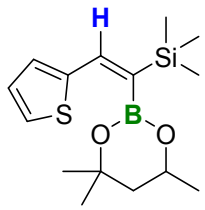

H
O
B
O
S
Si

4-*Z*

31.97
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
f1 (ppm

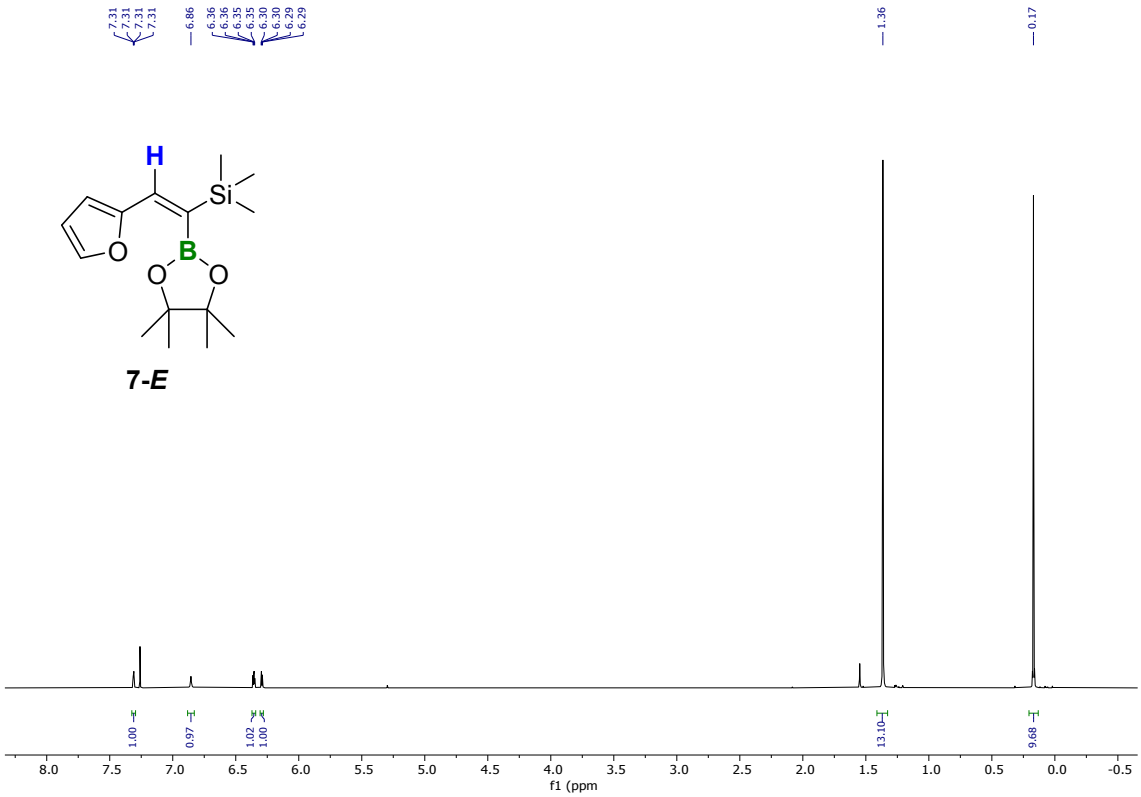

H
Si
S
B
O
O
6-E
7.18
7.18
7.18
7.17
7.17
7.16
7.16
7.13
7.01
7.01
7.01
7.01
7.00
7.00
7.00
6.95
6.94
6.94
6.93
4.37
4.37
4.36
4.35
4.35
4.34
4.34
4.34
4.33
4.32
4.31
4.31
4.30
4.29
1.88
1.87
1.84
1.83
1.71
1.71
1.68
1.68
1.67
1.67
1.64
1.64
1.41
1.34
1.31
1.29
0.15
1.14
1.00
1.15
1.23
1.22
1.21
1.26
3.66
3.37
3.95
10.37
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.98
137.83
127.56
127.04
125.28
71.67
65.41
46.13
31.37
28.01
23.24
0.90
H
Si
S
B
O
O
6-E
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)


H
Si
S
B
O
O

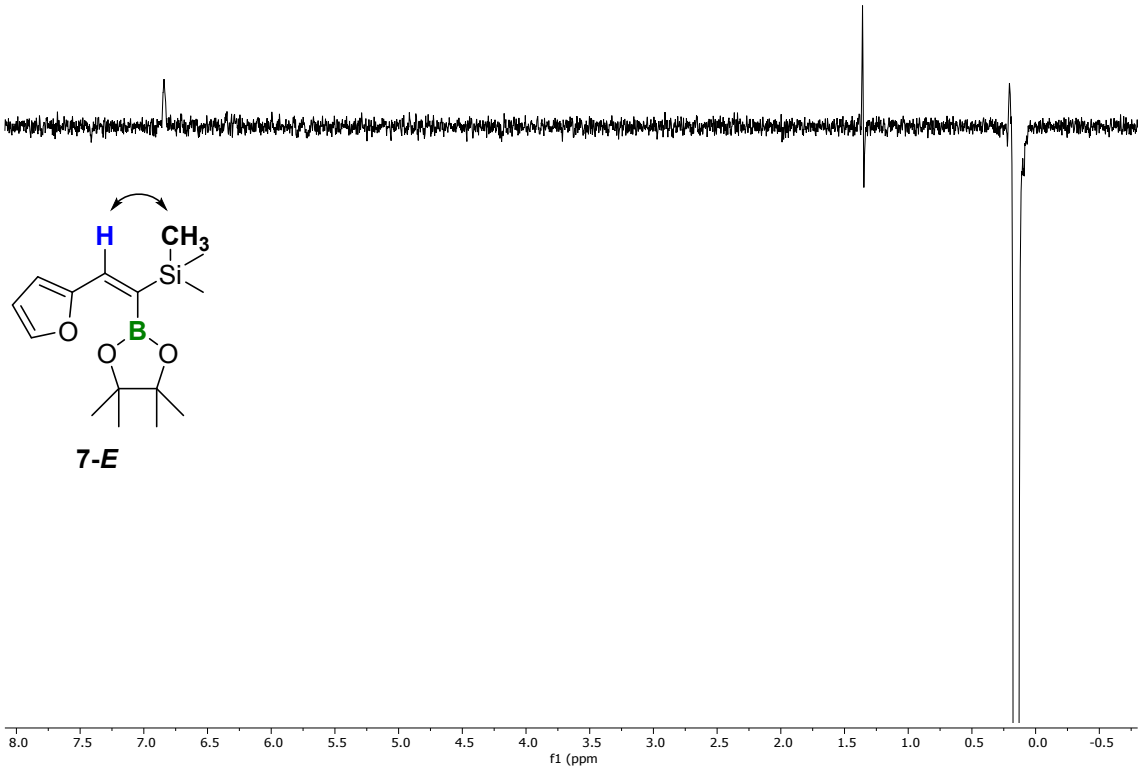
6-*E*

28.94
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm)

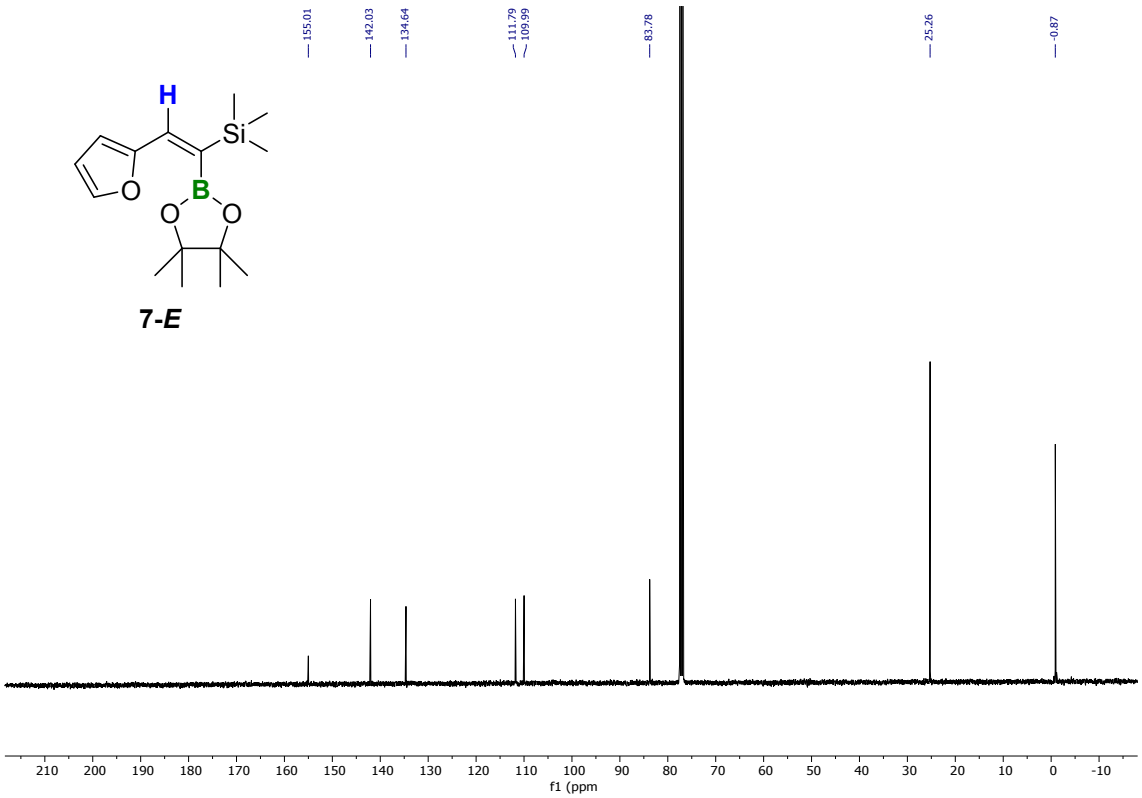

7.31
7.31
7.31
7.31
6.86
6.36
6.36
6.35
6.35
6.30
6.30
6.29
6.29
1.36
0.17
1.00
0.97
1.02
1.00
13.10
9.68
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm

H
Si
O
B
O
O

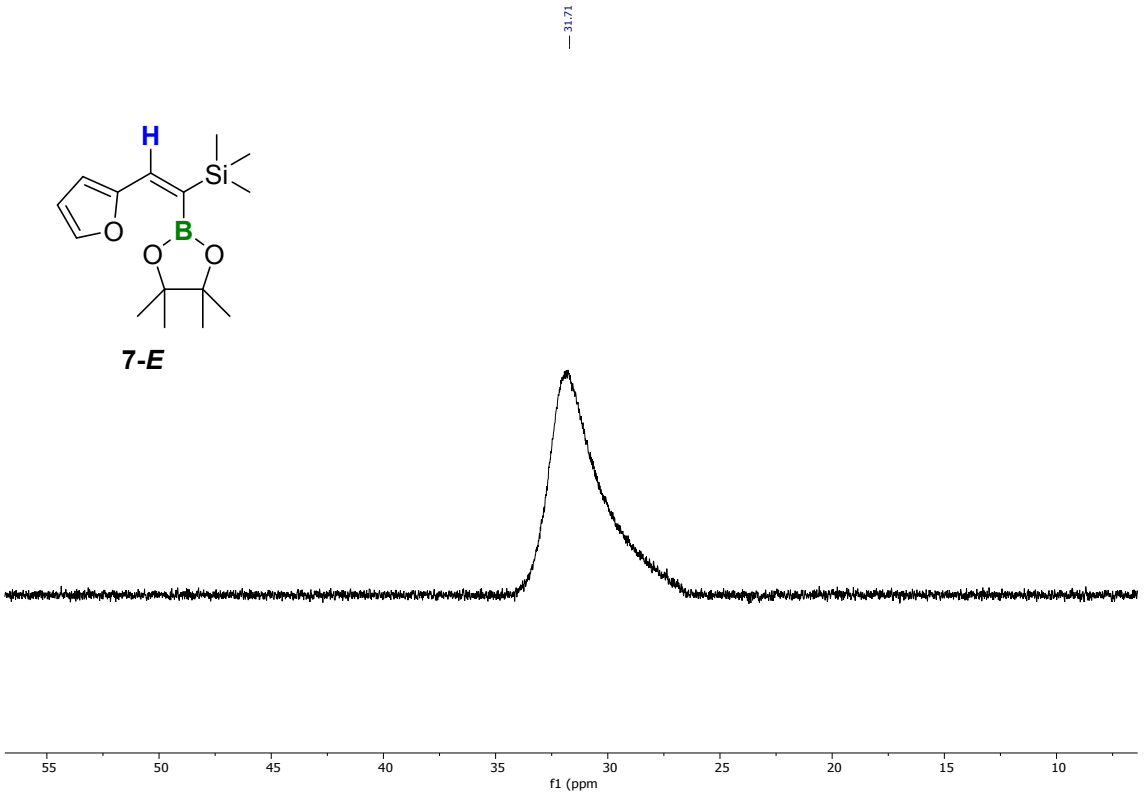
7-*E*


H
CH3
Si
O
B
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

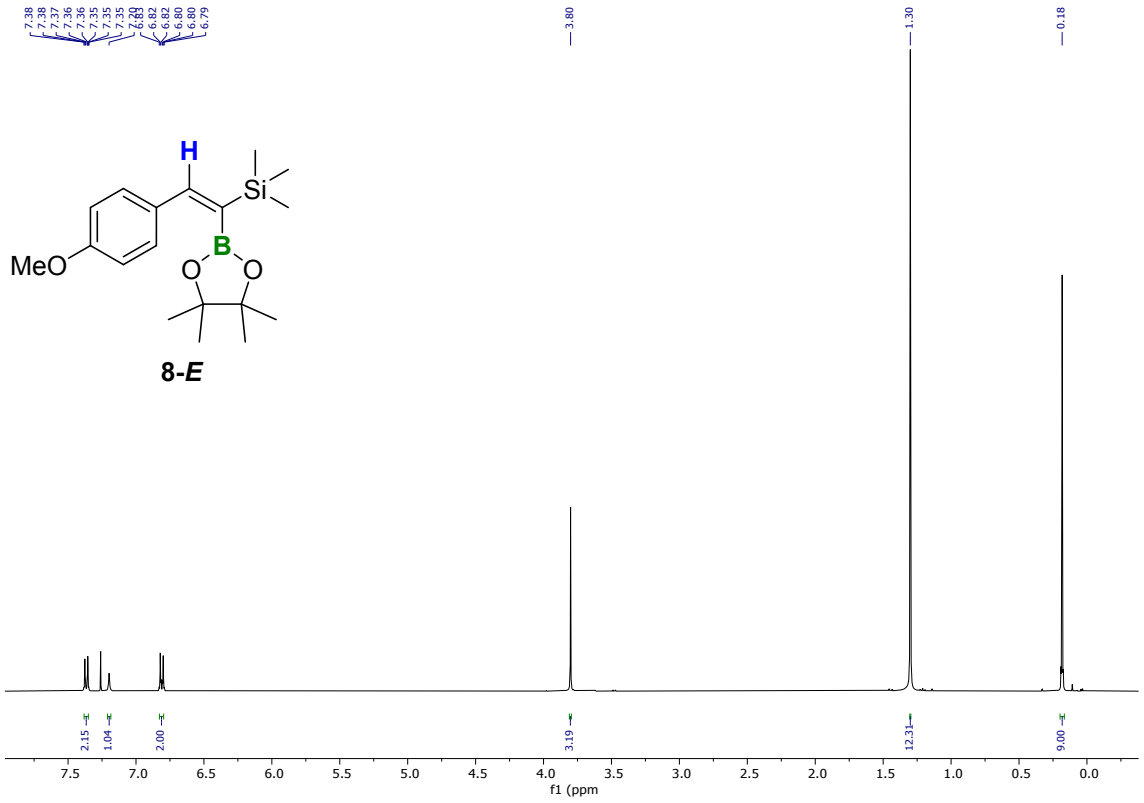
7-*E*


155.01
142.03
134.64
111.79
109.99
83.78
25.26
-0.87
H
Si
O
B
O
O
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

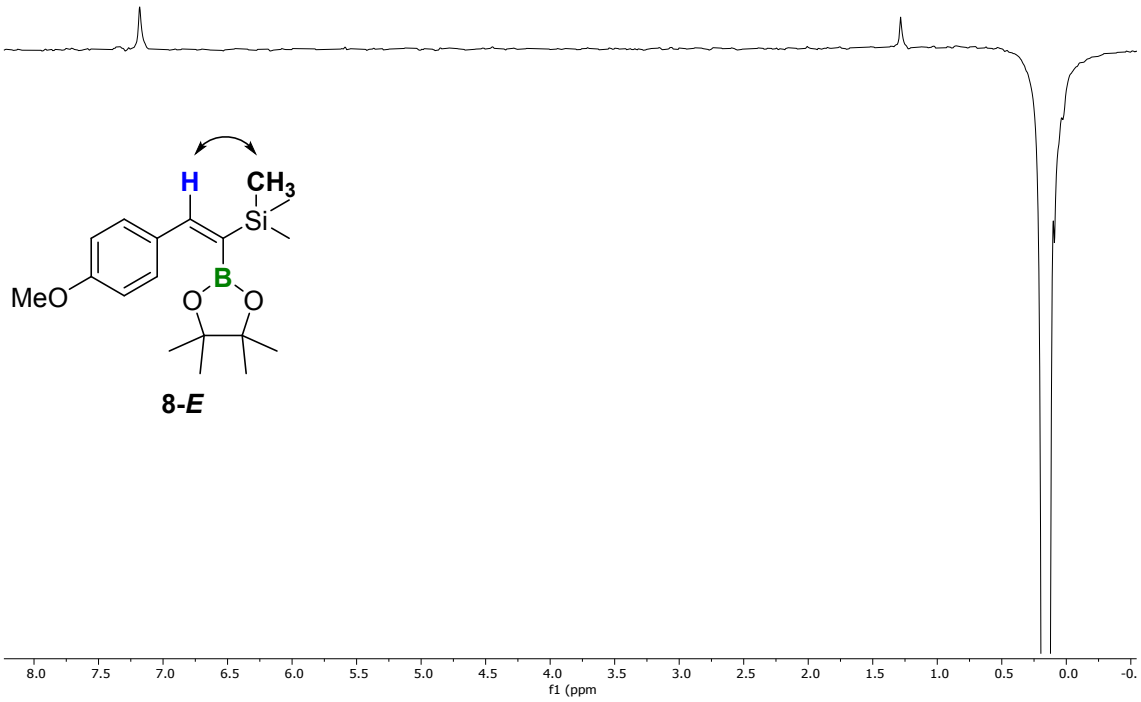
7-*E*


31.71
H
Si
O
B
O
O
55
50
45
40
35
30
25
20
15
10
f1 (ppm)

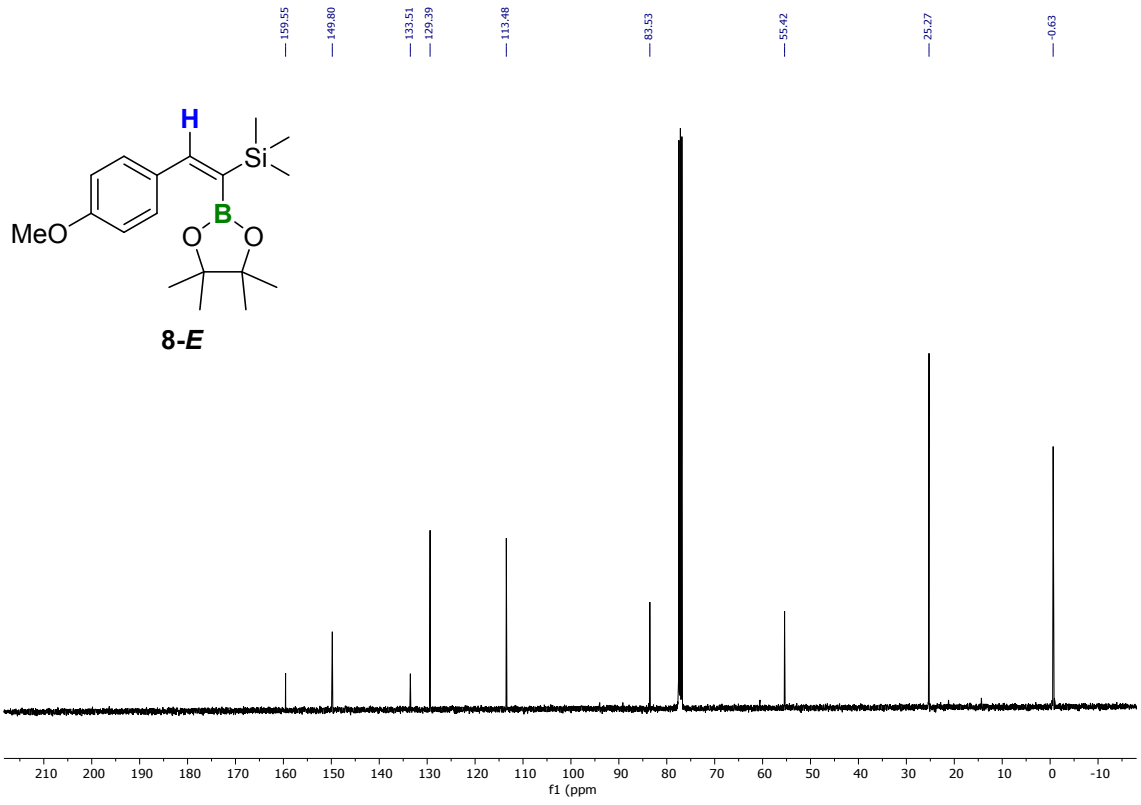
7-*E*


7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.35
6.82
6.82
6.80
6.80
6.79
3.80
1.30
0.18
H
Si
B
MeO
O
O
2.15
1.04
2.00
3.19
12.31
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

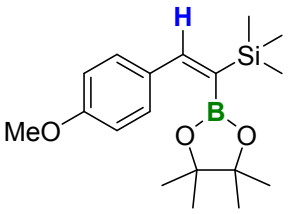
8-*E*


H
CH3
Si
B
O
O
MeO
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

8-*E*


159.55
149.80
133.51
129.39
113.48
83.53
55.42
25.27
0.63
H
Si
B
O
O
MeO
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)

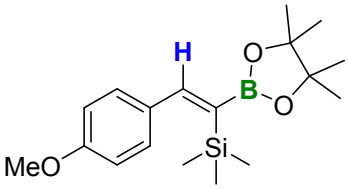
8-*E*


H
Si
B
MeO
O
O

8-*E*

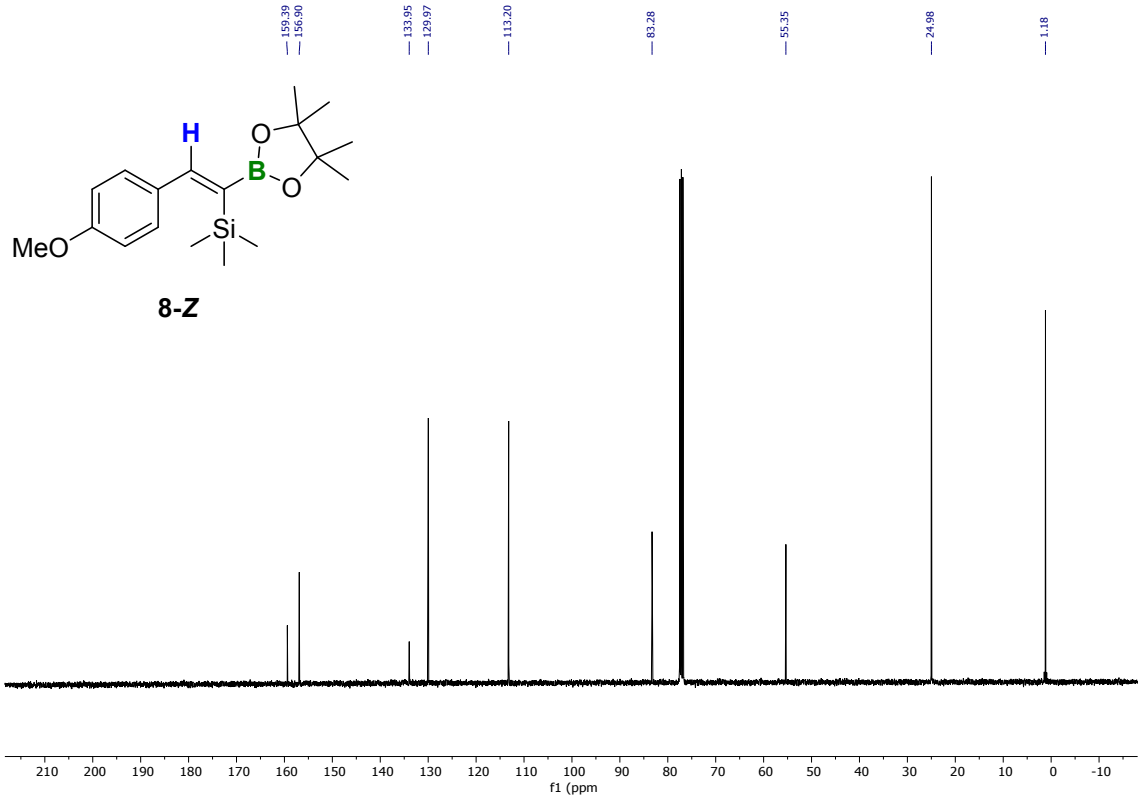
32.85
53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm


7.95
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.20
7.20
6.85
6.84
6.83
6.82
6.82
6.81
3.81
1.29
0.04

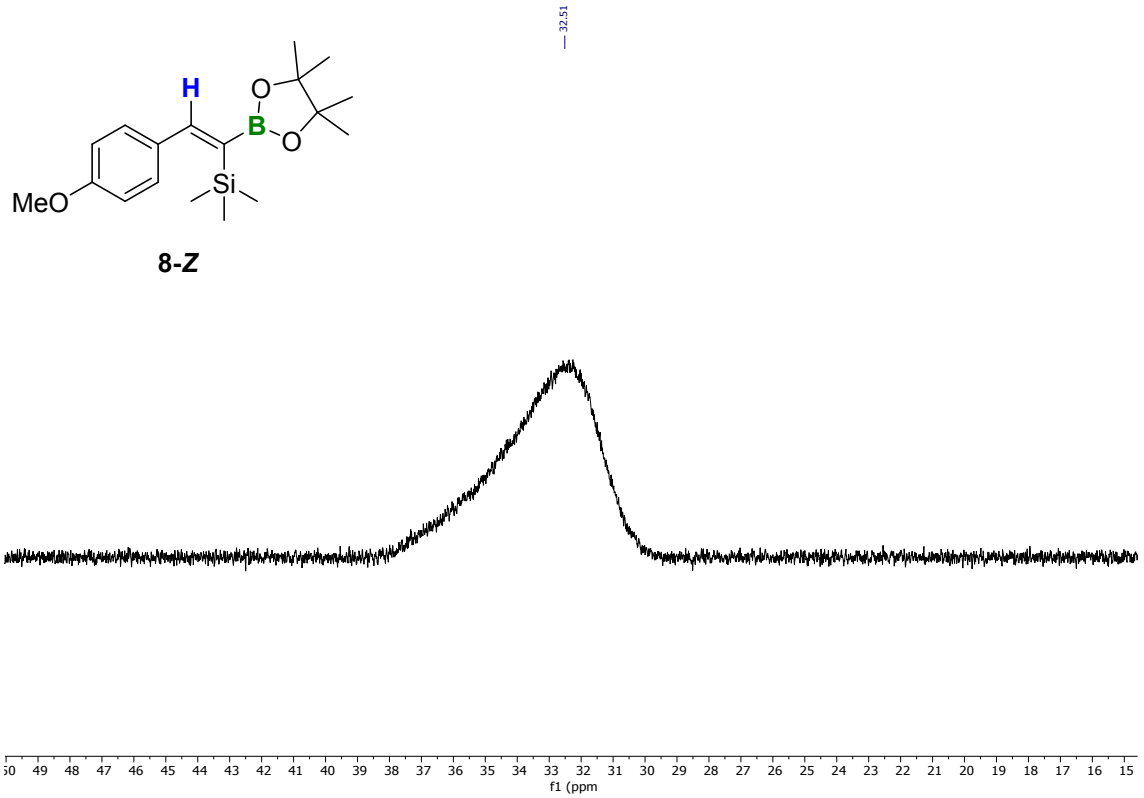

H
O
B
O
Si
MeO

8-*Z*

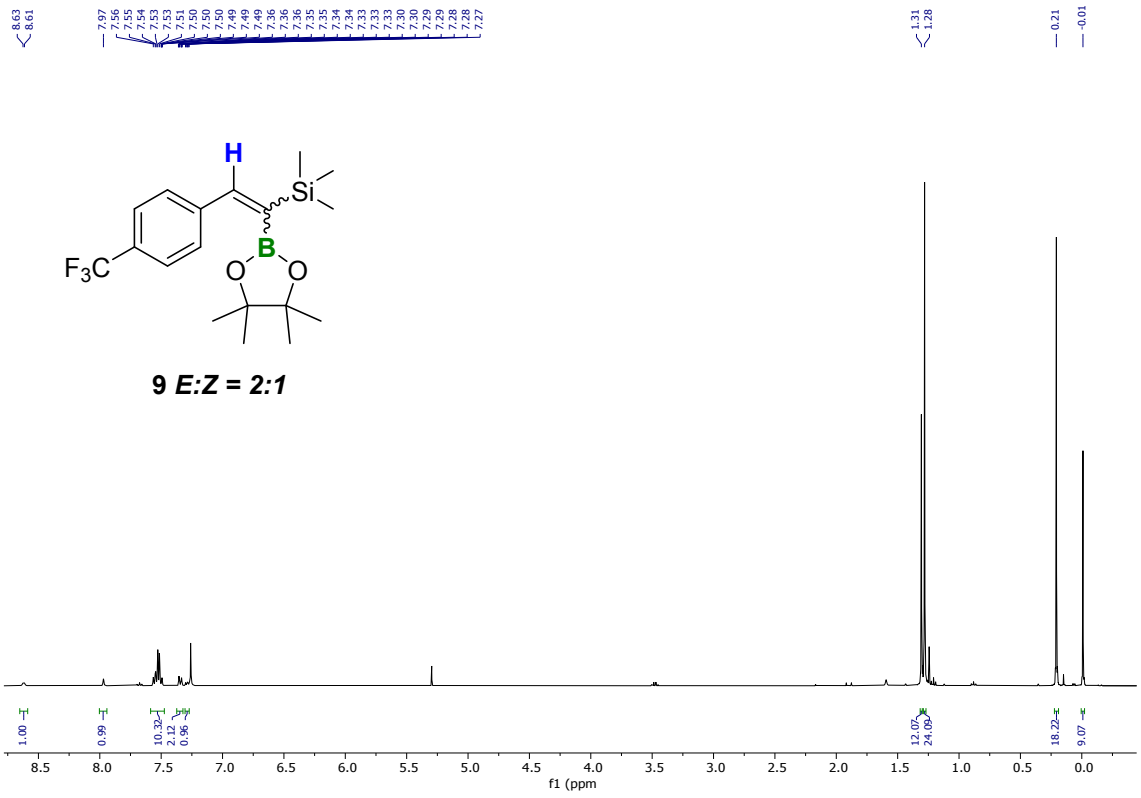
1.00
2.06
2.01
3.18
12.94
9.61
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

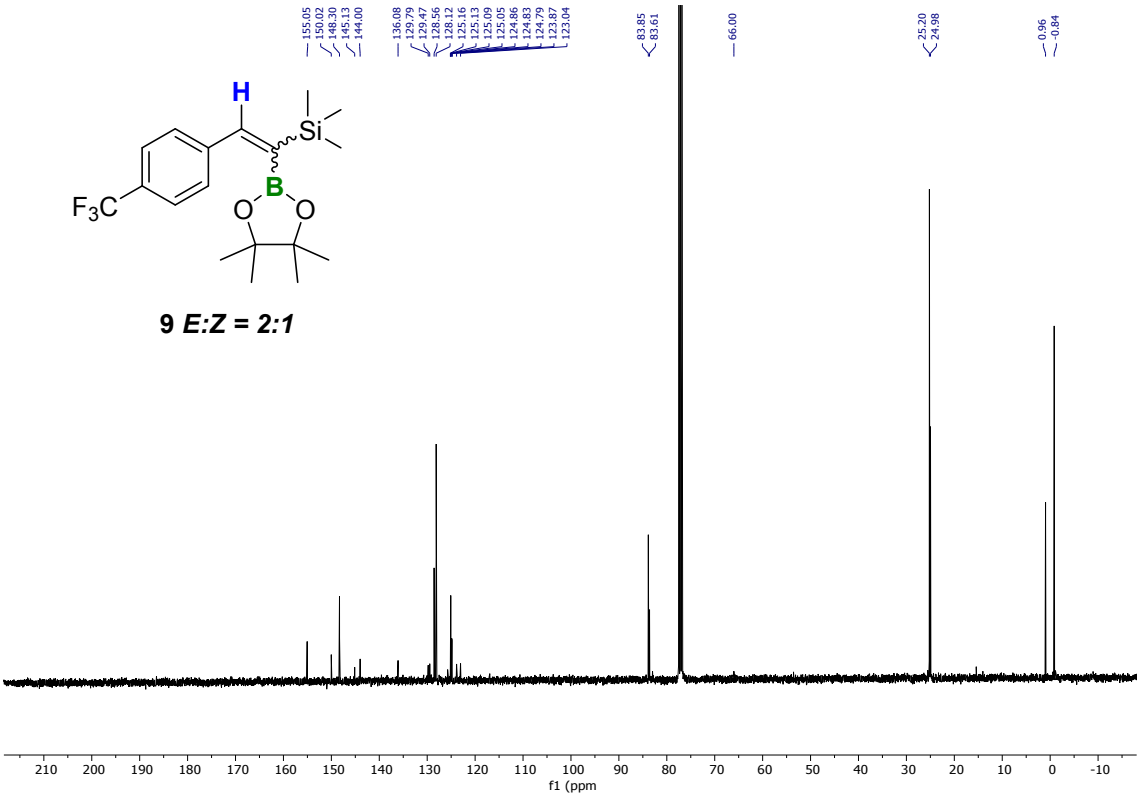

159.39
156.90
133.95
129.97
113.20
83.28
55.35
24.98
1.18
H
O
B
O
MeO
Si
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

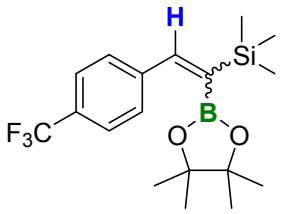
8-*Z*


32.51
H
O
B
O
MeO
Si
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15
f1 (ppm

8-*Z*


H
Si
B
O
O
F3C
9 E:Z = 2:1
f1 (ppm)

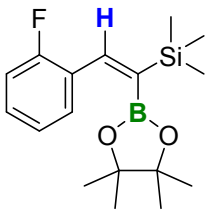

H
Si
B
O
O
F3C
9 E:Z = 2:1
f1 (ppm)


H
Si
B
O
O
F3C

9 *E:Z = 2:1*

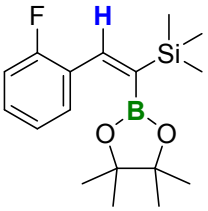
32.08
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8
f1 (ppm


7.51 7.51 7.49 7.49 7.48 7.47 7.38 7.24 7.23 7.22 7.22 7.22 7.21 7.20 7.20 7.20 7.19 7.18 7.05 7.05 7.04 7.03 7.02 7.01 7.01 7.01 6.99 6.98 6.98 6.98 6.96 6.96


F
H
Si
B
O
O

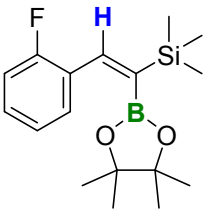
10-*E*

1.26
0.20
1.00
0.98
1.05
1.01
0.99
12.15
9.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm


F
H
Si
B
O
O

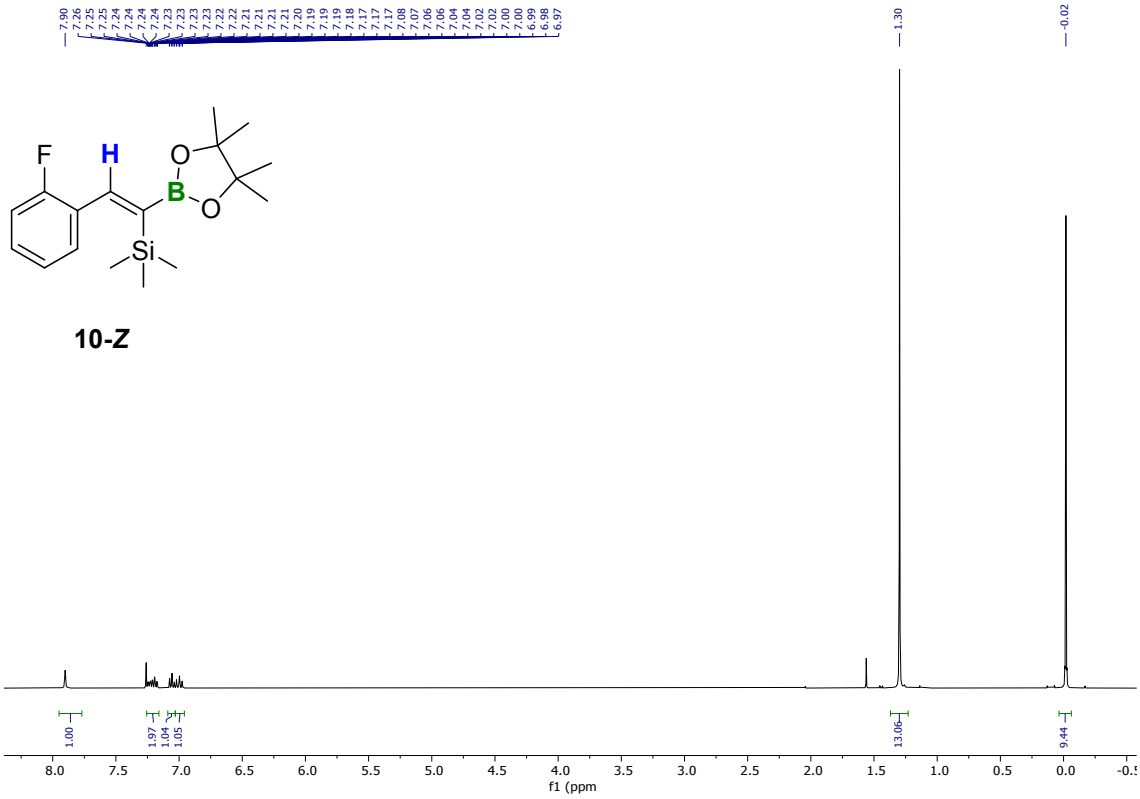
10-*E*

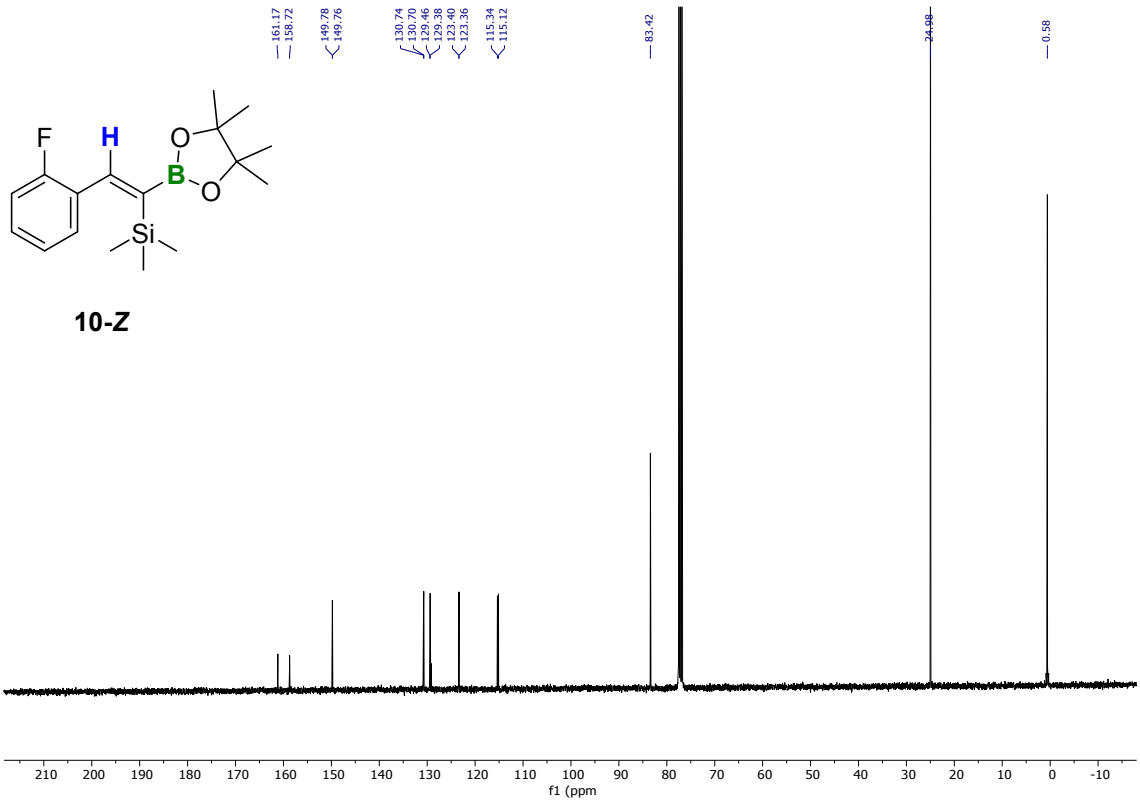
161.64
159.17
142.48
142.43
129.54
129.46
129.35
129.32
128.60
128.47
123.54
123.51
115.52
115.30
83.66
77.48
77.36
77.16
76.84
25.20
-0.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

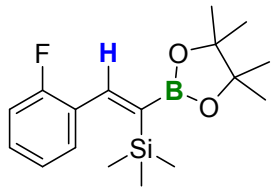

F
H
Si
B
O
O

10-*E*

32.28
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
f1 (ppm)


F
H
O
B
O
Si
10-Z
f1 (ppm)

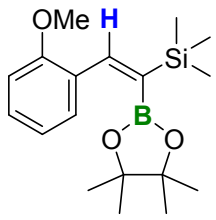

F
H
O
B
O
Si
10-Z
f1 (ppm)


F
H
O
B
O
Si

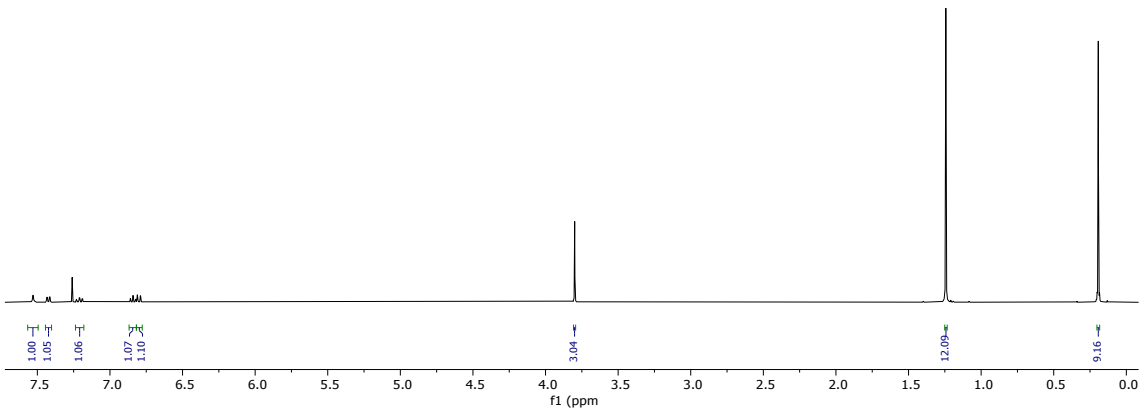
10-*Z*

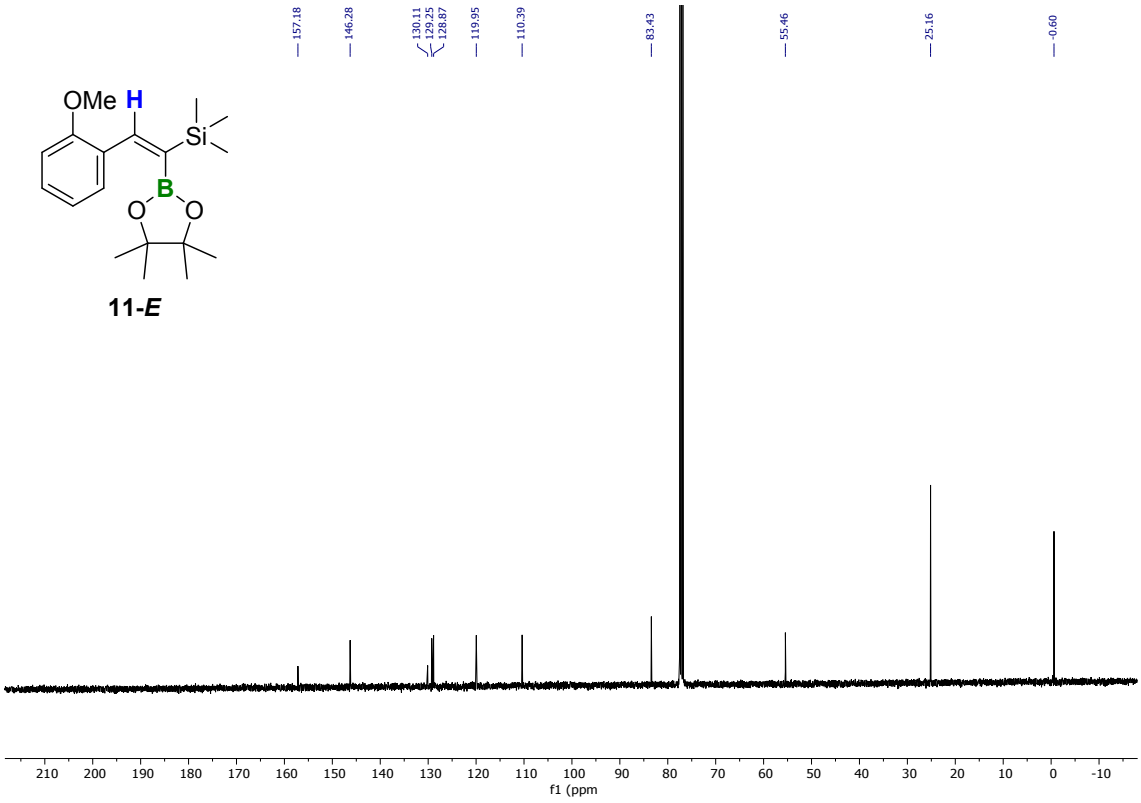
31.53
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14
f1 (ppm)


7.53
7.52
7.44
7.43
7.43
7.43
7.42
7.41
7.23
7.23
7.21
7.21
7.21
7.21
7.19
7.19
6.86
6.86
6.84
6.84
6.84
6.84
6.82
6.82
6.82
6.81
6.81
6.79
6.79
6.79
3.80
1.24
0.19

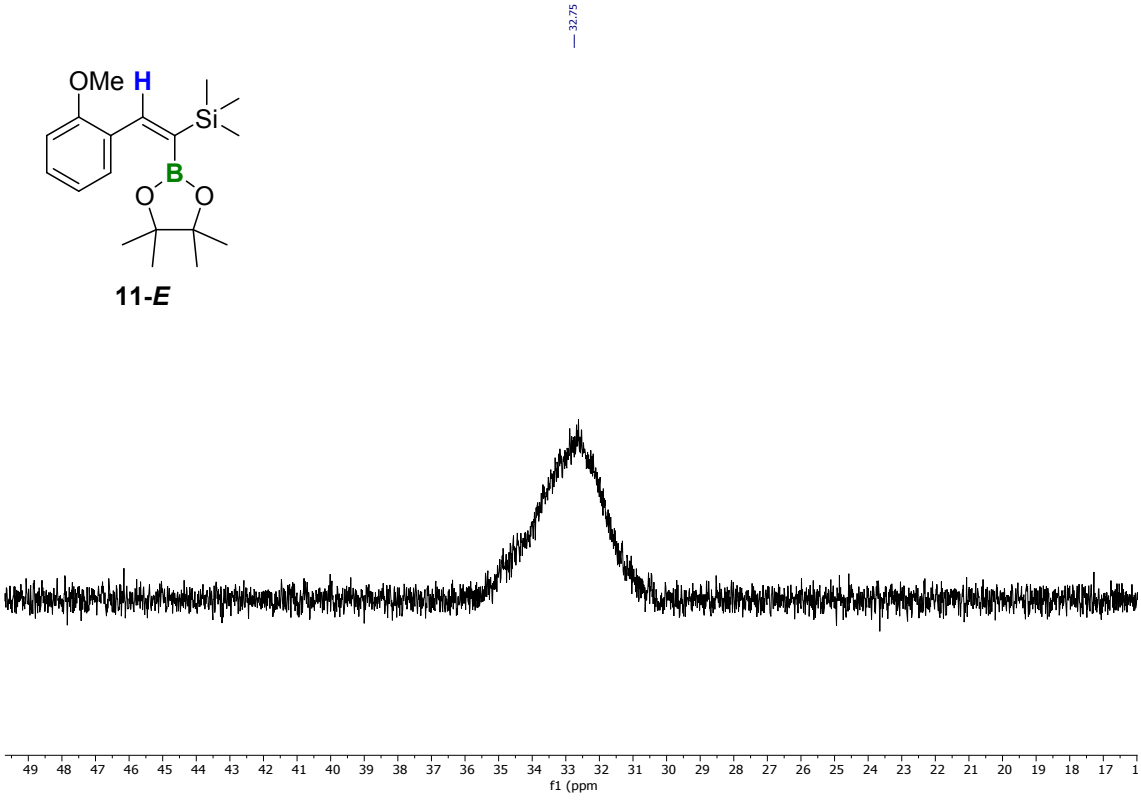

OMe
H
Si
B
O
O

11-*E*

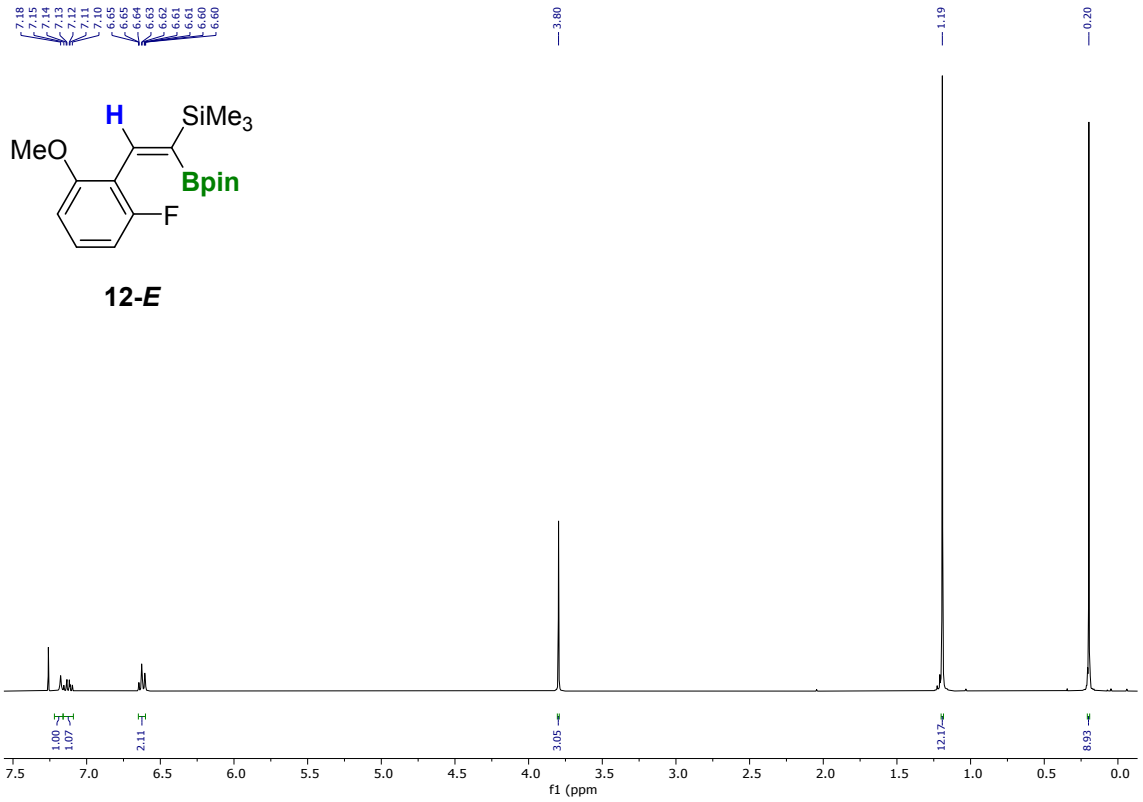

1.00
1.05
1.06
1.07
1.10
3.04
12.09
9.16
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.18
146.28
130.11
129.25
128.87
119.95
110.39
83.43
55.46
25.16
0.60
OMe H
Si
B
O
O
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

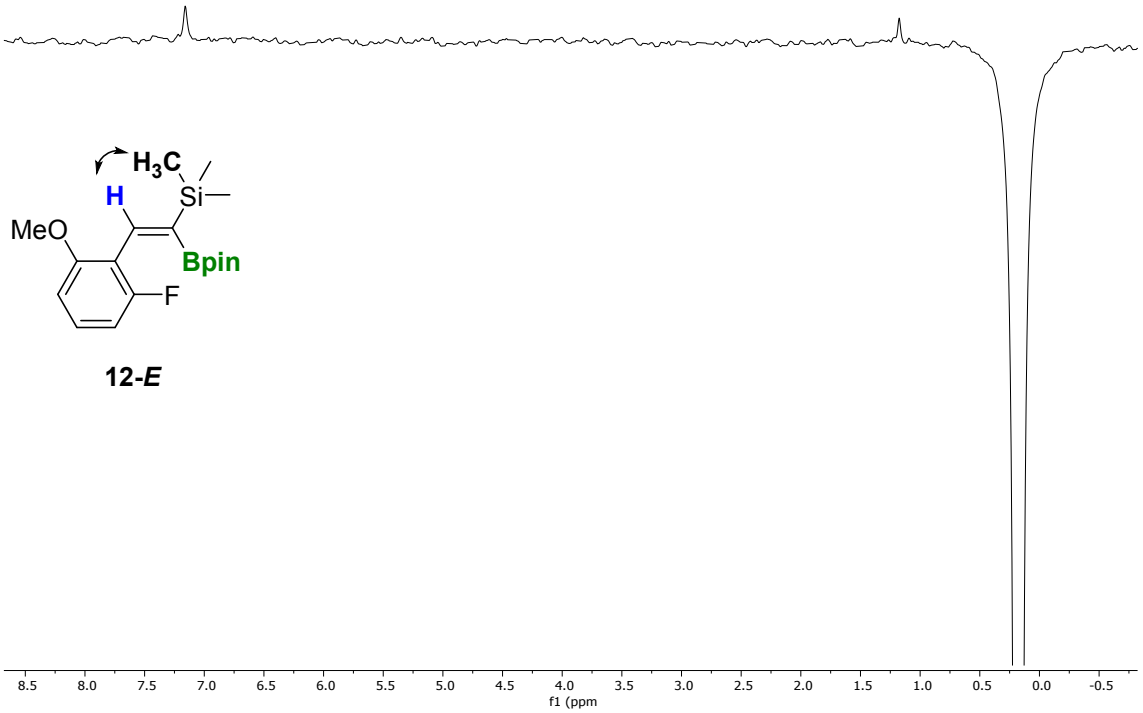
11-*E*


32.75
OMe H
Si
B
O
O
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 1
f1 (ppm

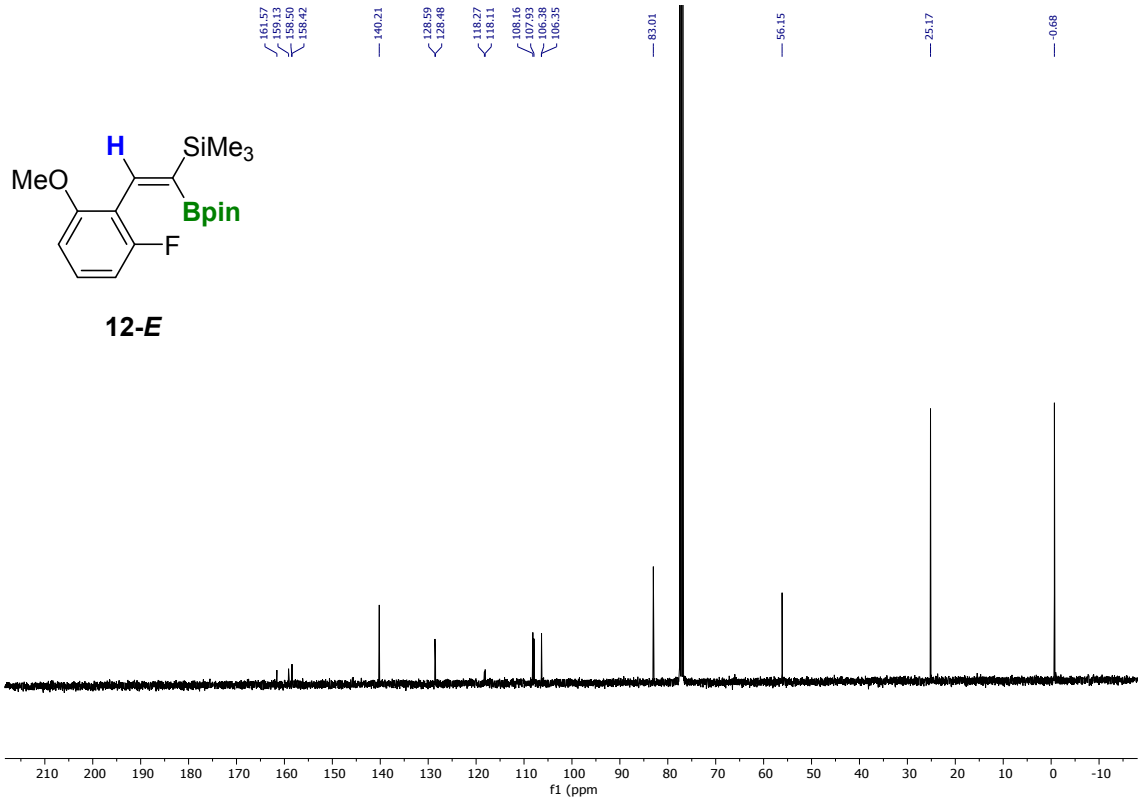
11-*E*


7.18
7.15
7.14
7.13
7.12
7.11
7.10
6.65
6.65
6.64
6.63
6.62
6.61
6.61
6.60
6.60
3.80
1.19
0.20
H
SiMe3
MeO
Bpin
F
1.00
1.07
2.11
3.05
12.17
8.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

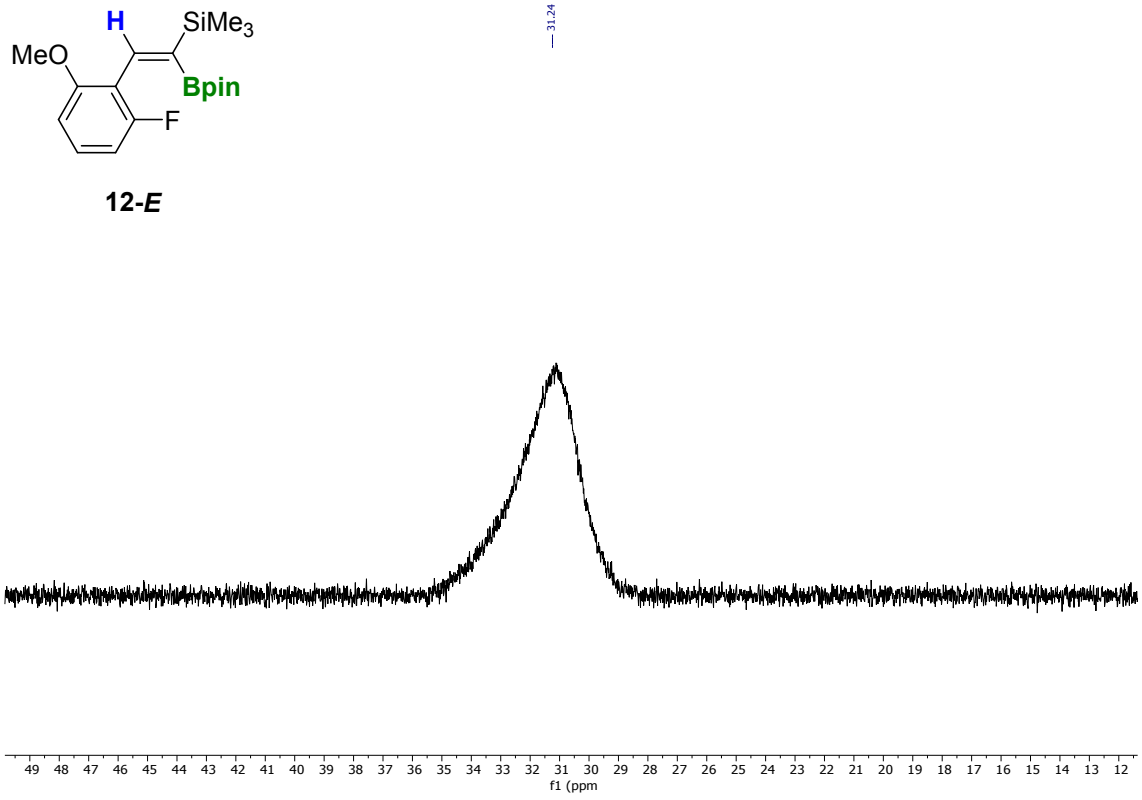
12-*E*


H3C
H
Si
MeO
Bpin
F
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

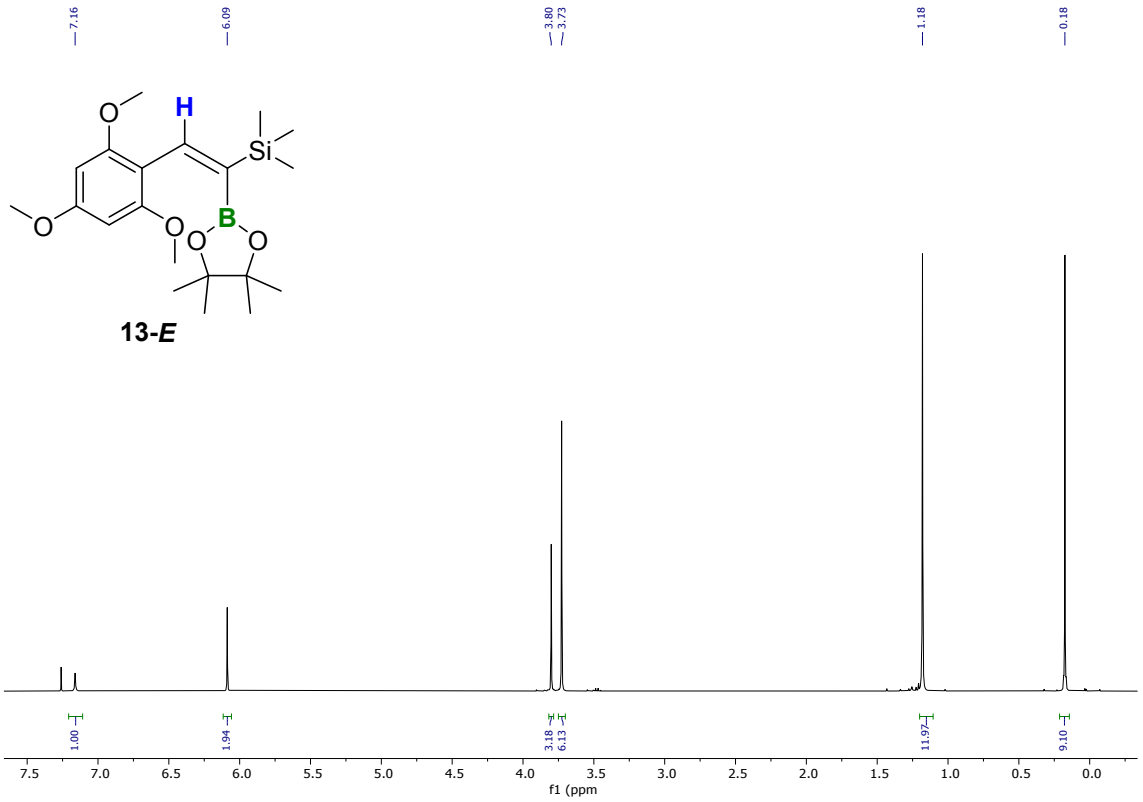
12-*E*


161.57
159.13
158.50
158.42
140.21
128.59
128.48
118.27
118.11
108.16
107.93
106.38
106.35
83.01
56.15
25.17
-0.68
H
SiMe3
MeO
Bpin
F
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

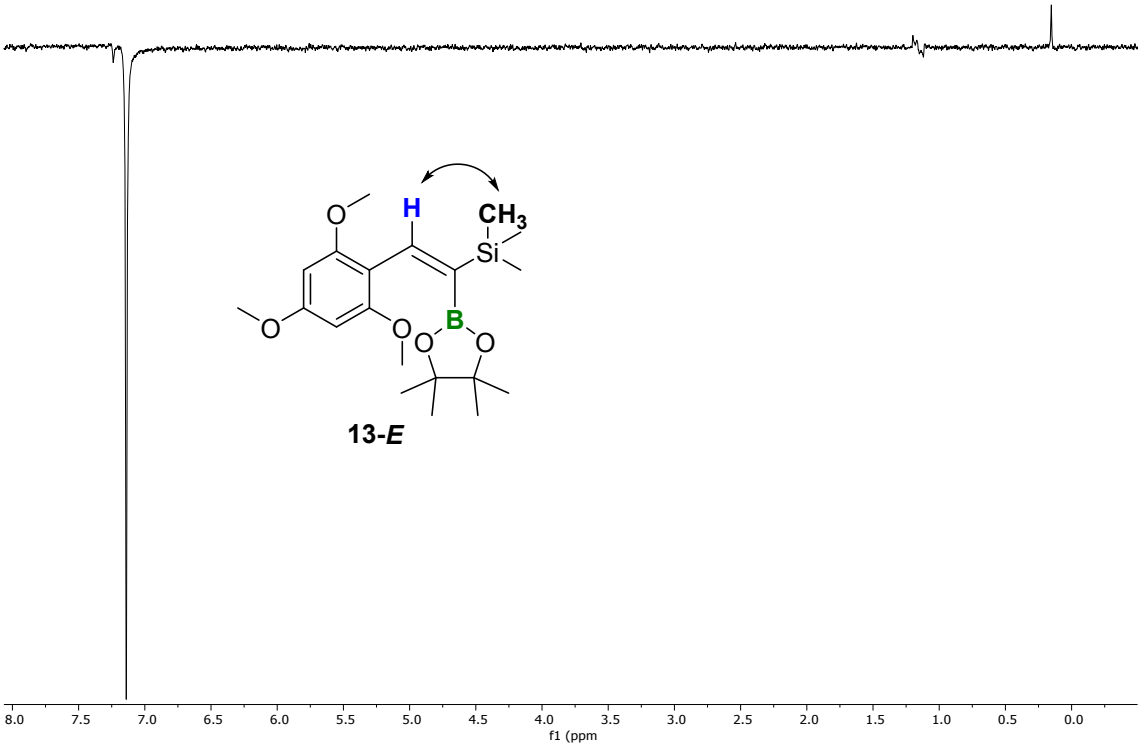
12-*E*


31.24
H
SiMe3
MeO
Bpin
F
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm

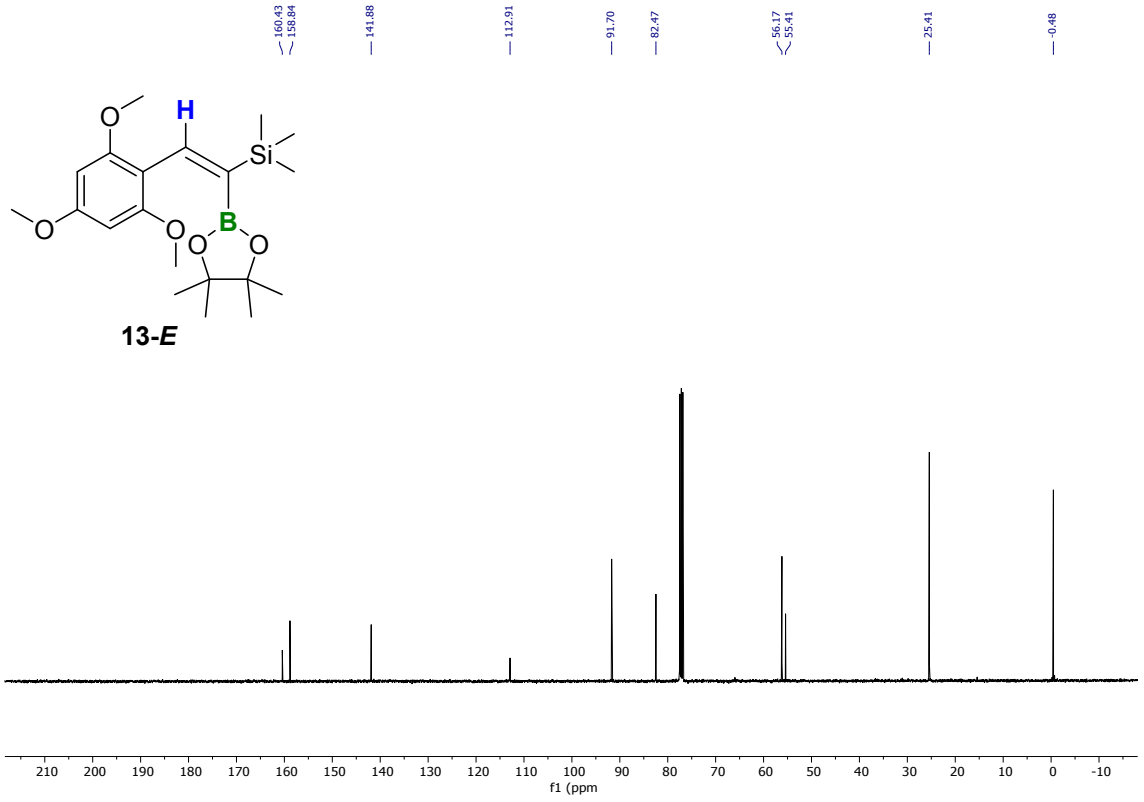
12-*E*

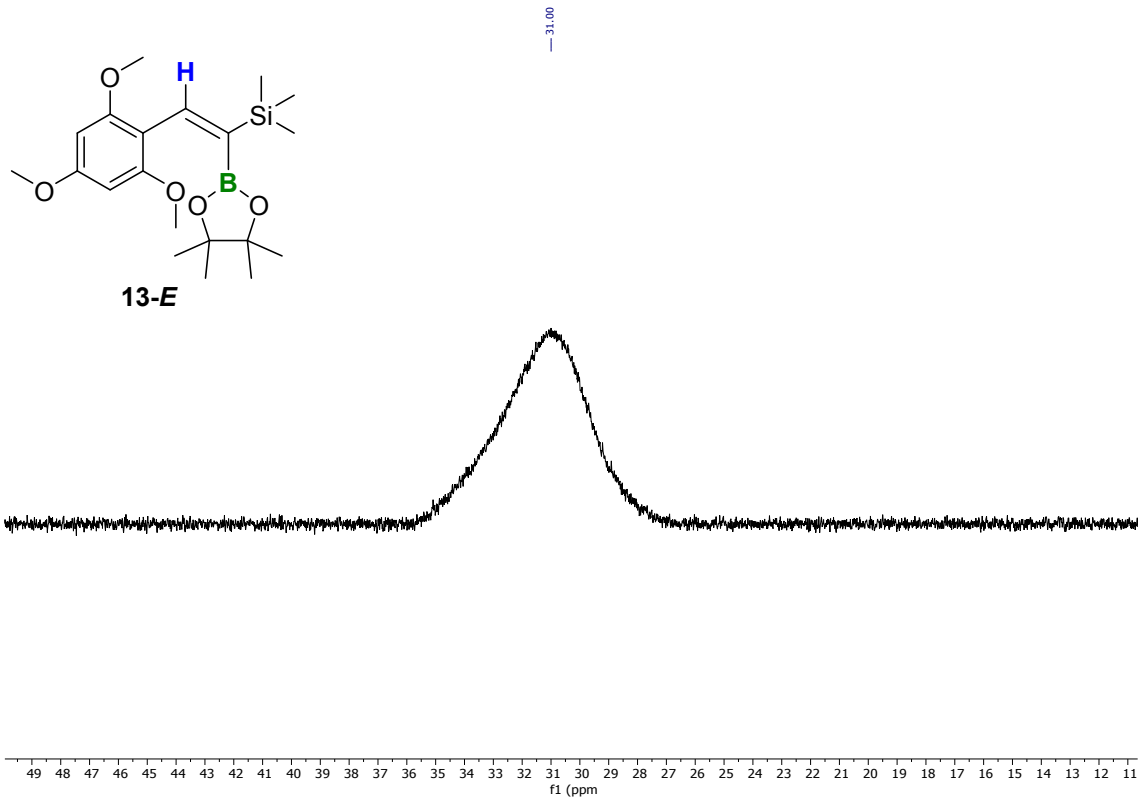

7.16
6.09
3.80
3.73
1.18
0.18
H
O
Si
O
B
O
O
O
1.00
1.94
3.18
6.13
11.97
9.10
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

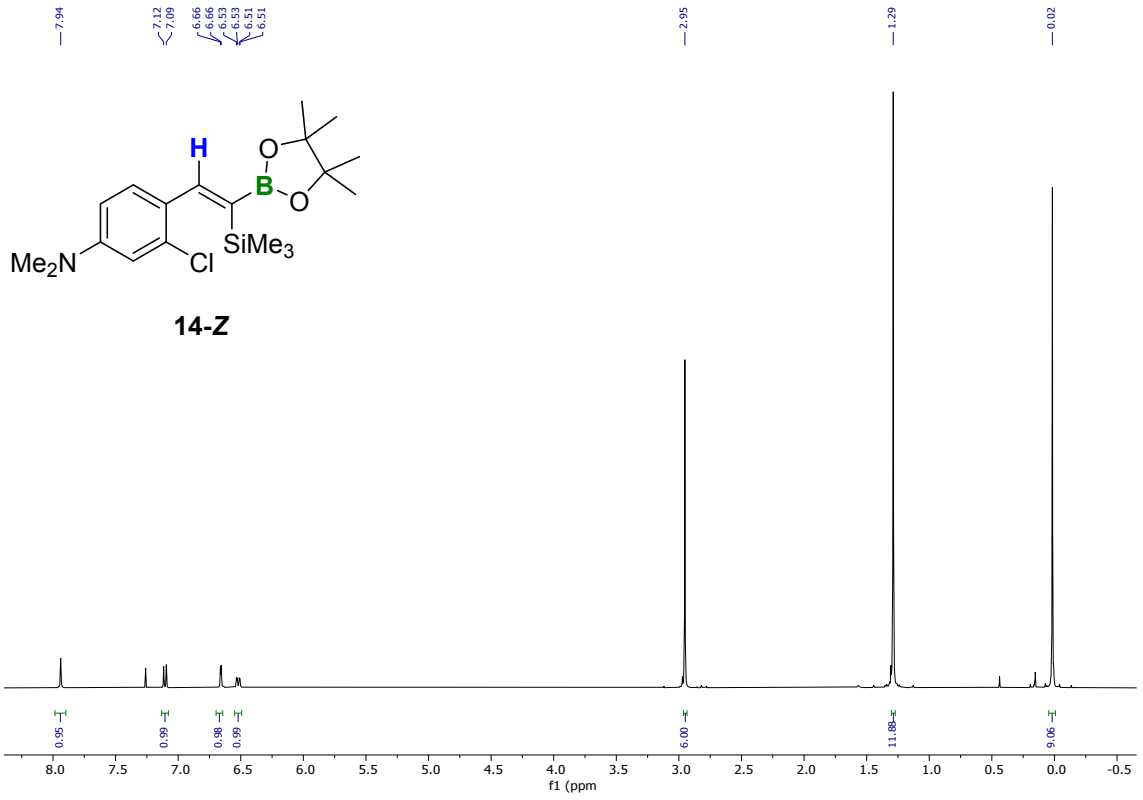
13-*E*


H
CH3
O
Si
O
B
O
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

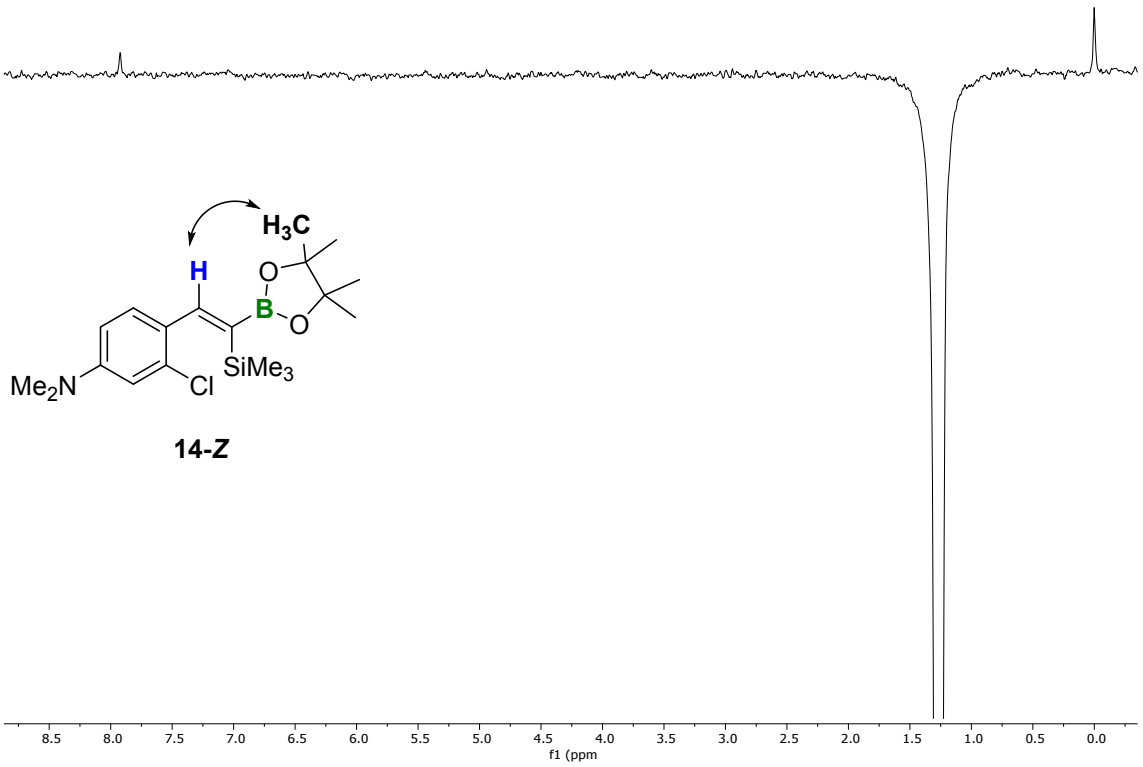
13-*E*


160.43
158.84
141.88
112.91
91.70
82.47
56.17
55.41
25.41
-0.48
O
H
Si
O
B
O
O
O
13-*E*
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

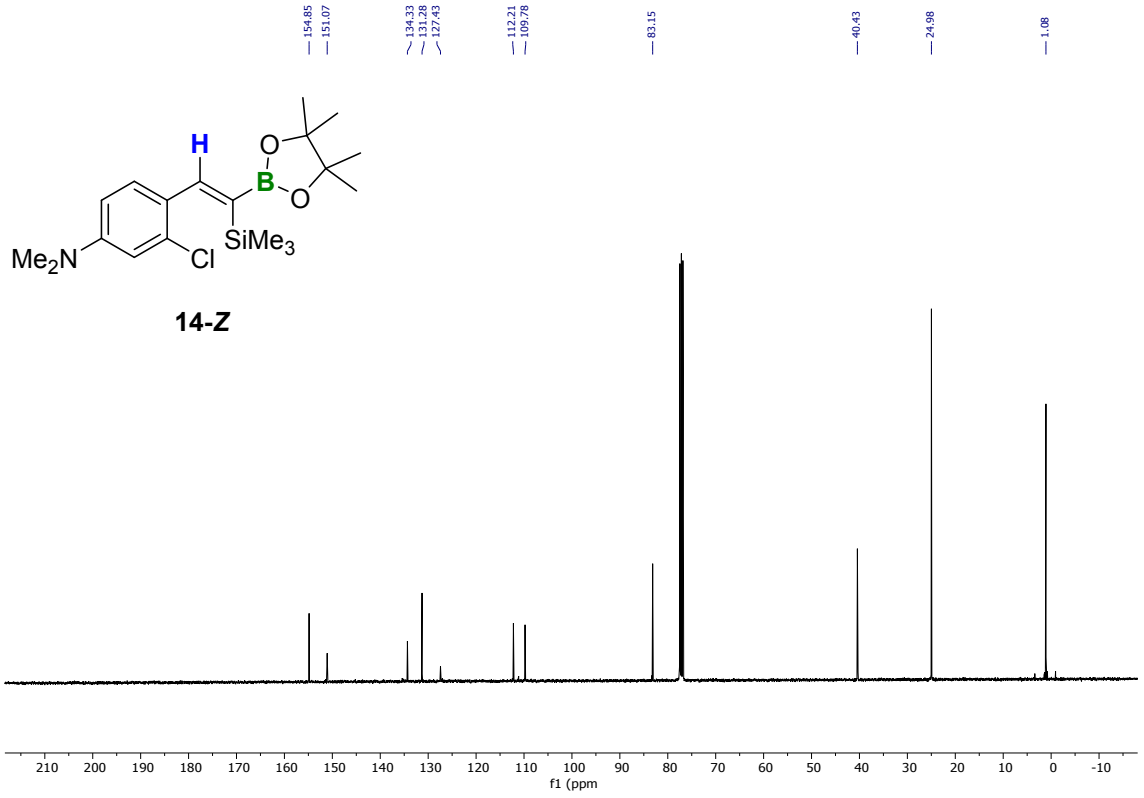

31.00
O
H
Si
O
B
O
O
O
13-*E*
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11
f1 (ppm


7.94
7.12
7.09
6.66
6.66
6.53
6.53
6.51
6.51
2.95
1.29
0.02
H
O
B
O
Me2N
Cl
SiMe3
0.95
0.99
0.98
0.99
6.00
11.88
9.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

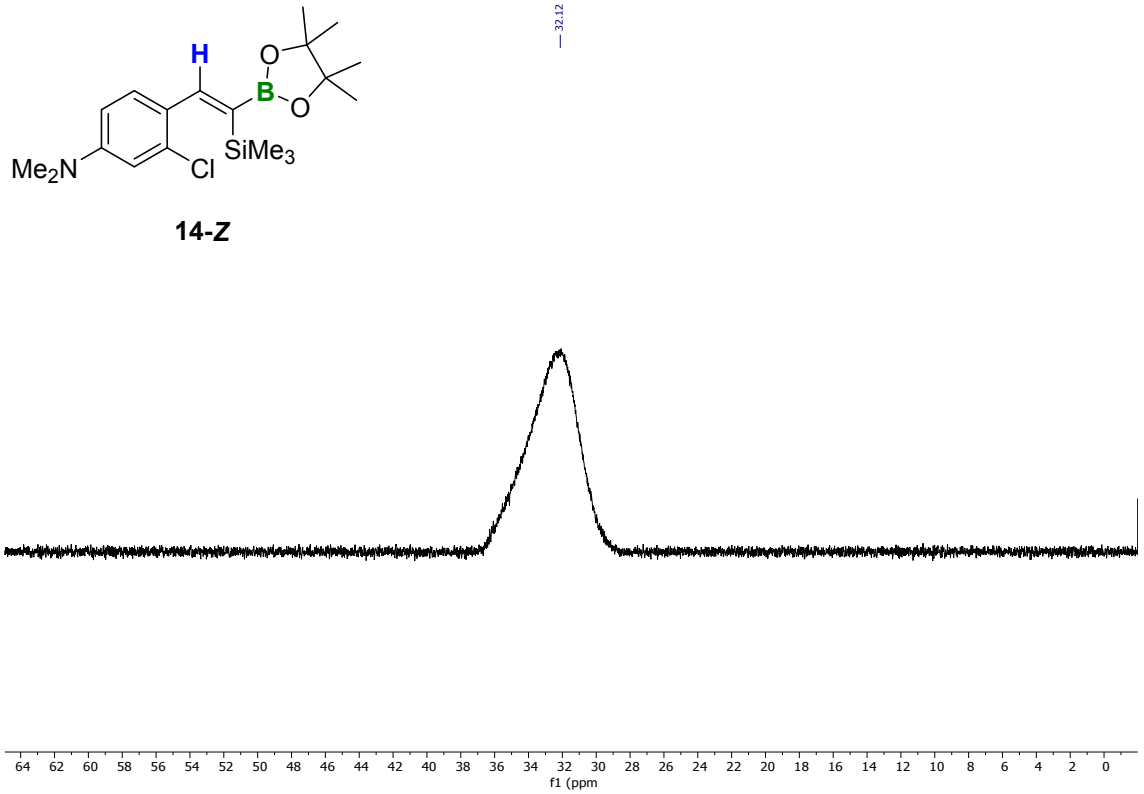
14-*Z*


H3C
H
O
B
O
Me2N
Cl
SiMe3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

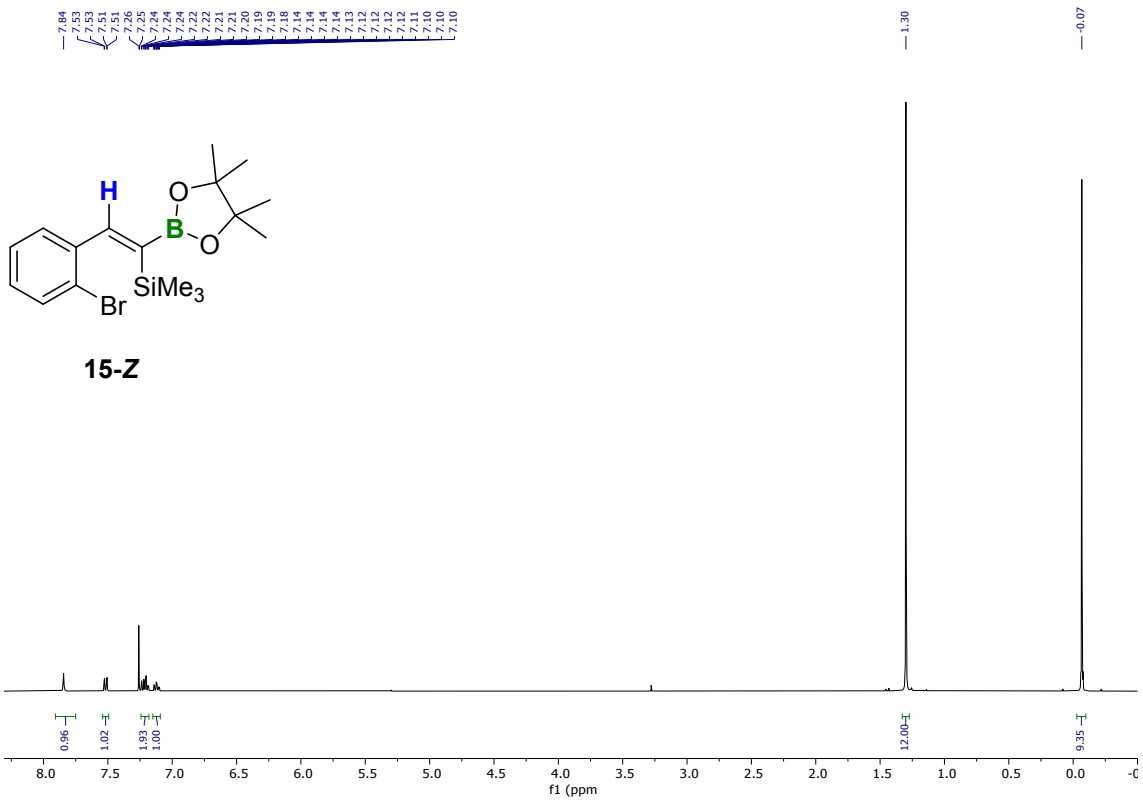
14-*Z*

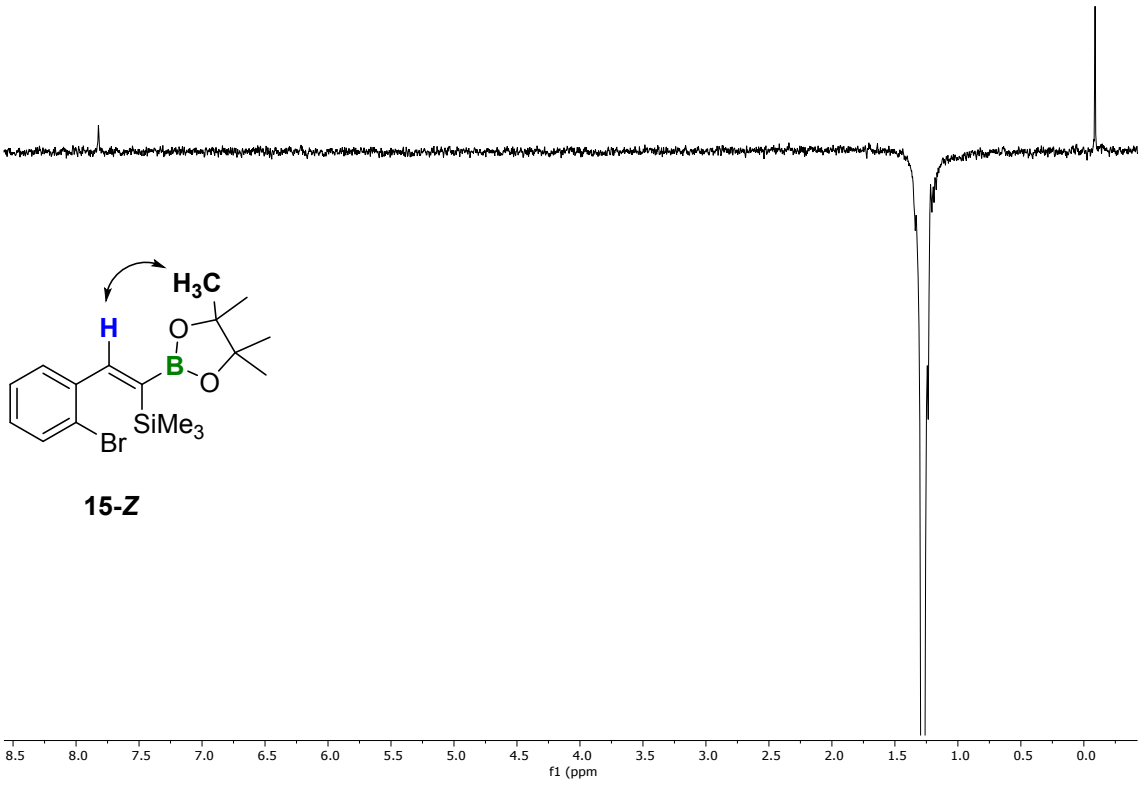

154.85
151.07
134.33
131.28
127.43
112.21
109.78
83.15
40.43
24.98
1.08
H
O
B
O
Me2N
Cl
SiMe3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

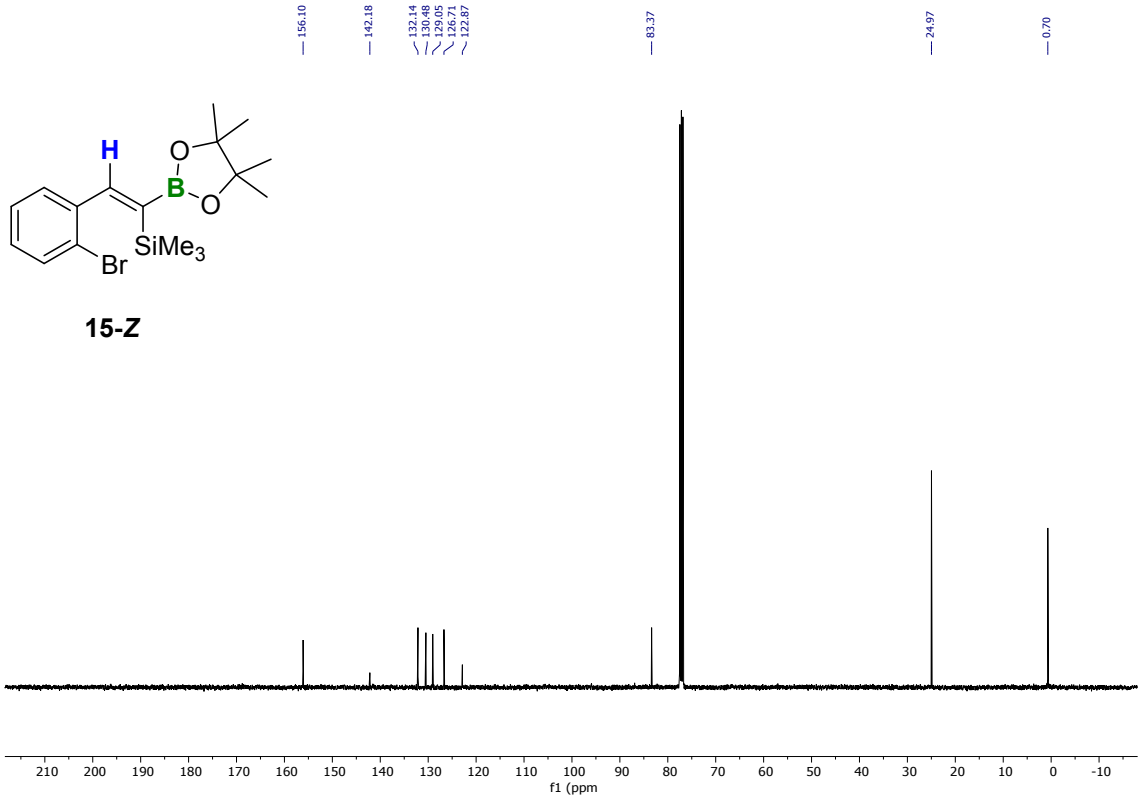
14-*Z*


32.12
H
O
B
O
Me2N
Cl
SiMe3
64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm

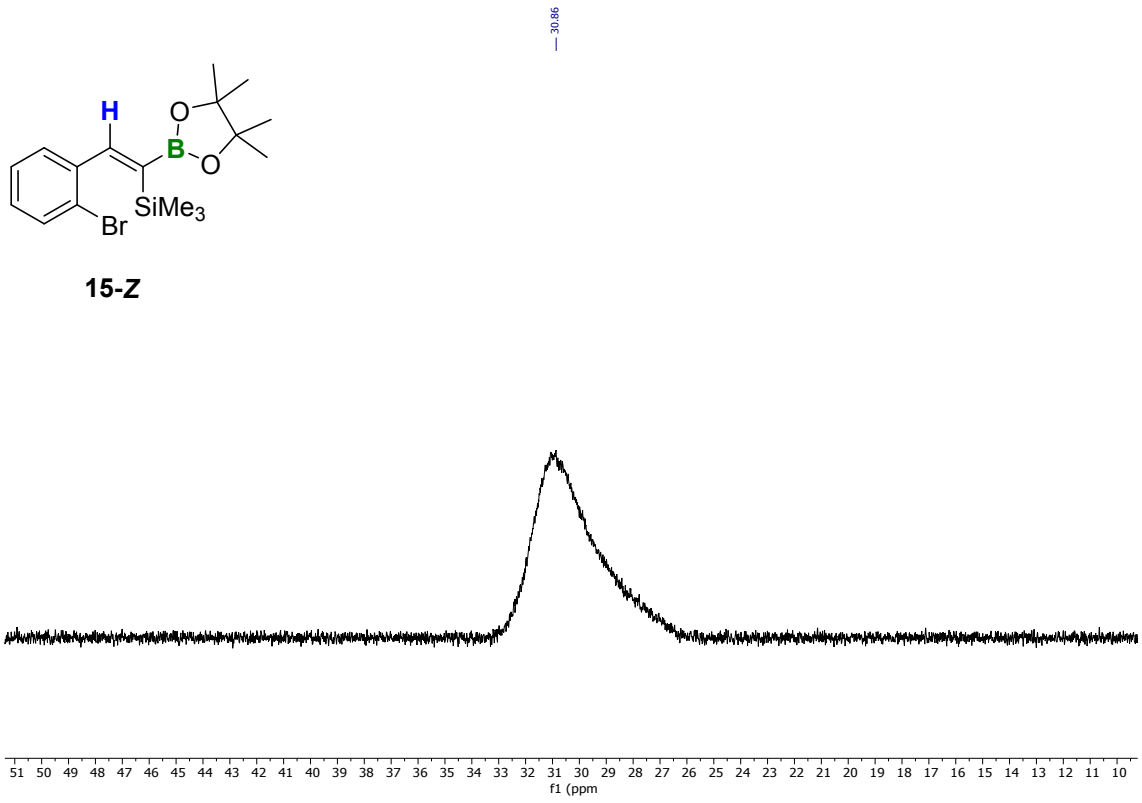
14-*Z*


H
O
B
O
SiMe3
Br
15-Z
f1 (ppm)

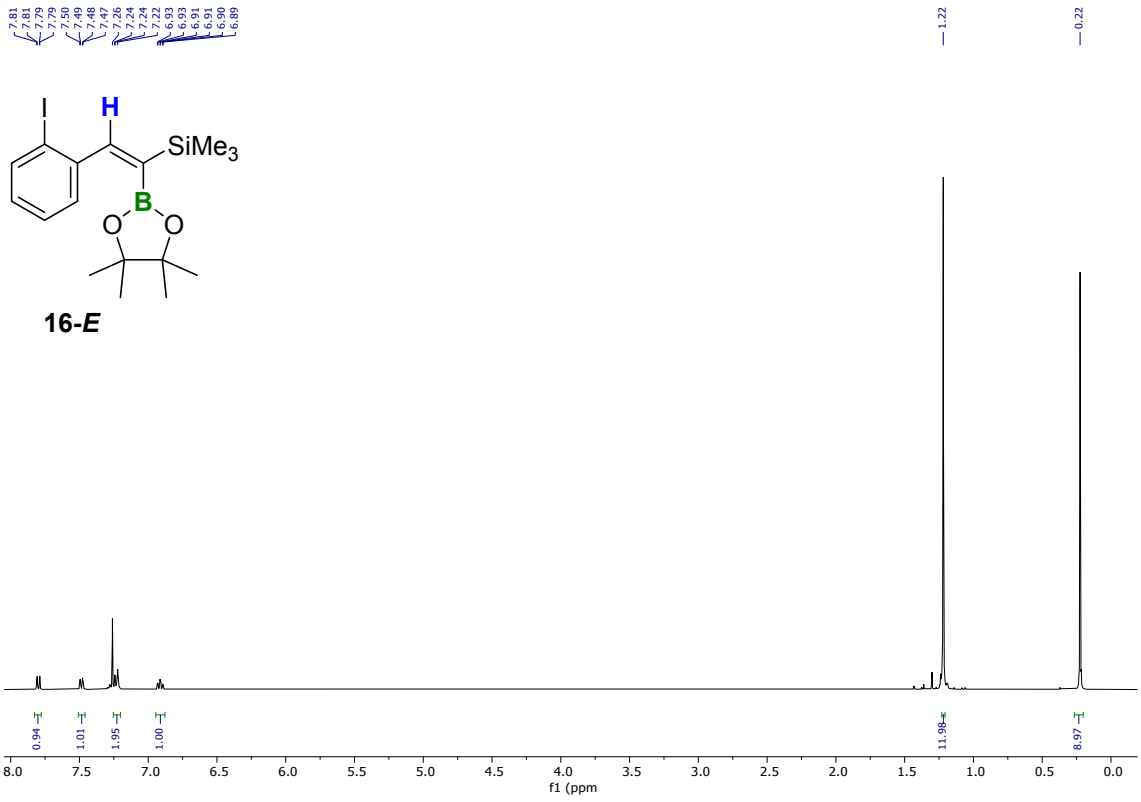

H3C
H
O
B
O
SiMe3
Br
15-Z
f1 (ppm)


156.10
142.18
132.14
130.48
129.05
126.71
122.87
83.37
24.97
0.70
H
O
B
O
SiMe3
Br
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

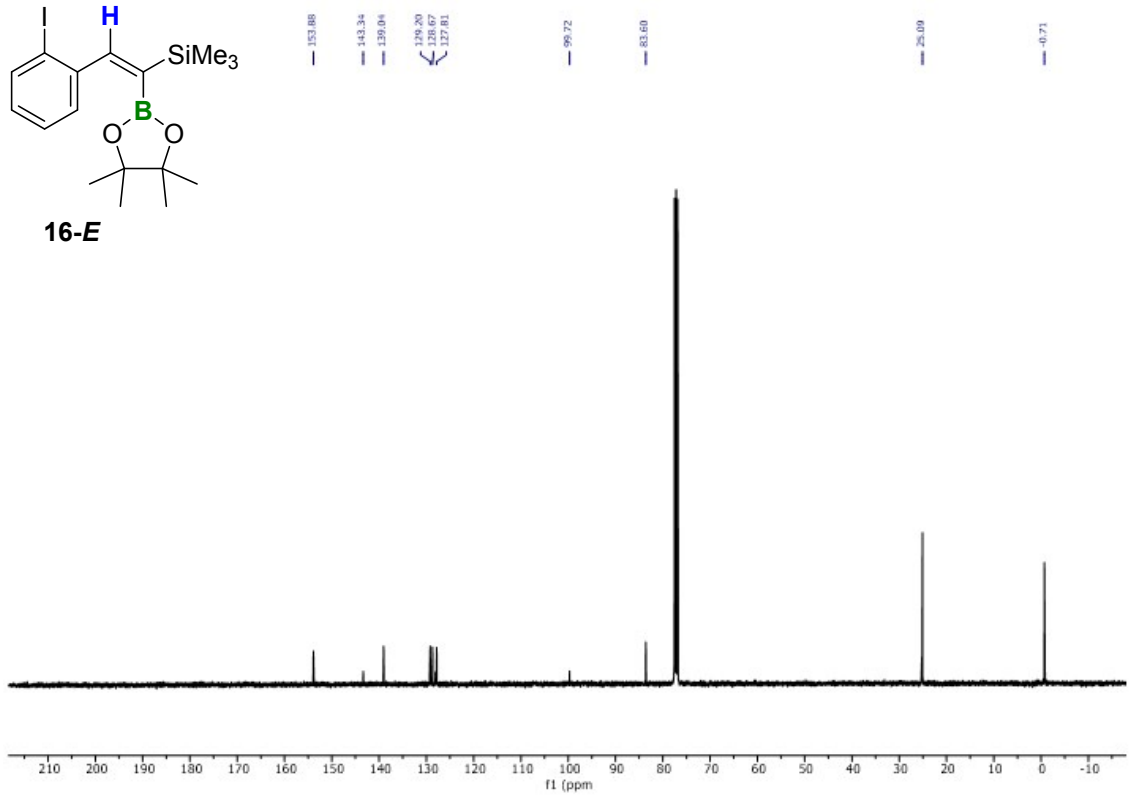
15-*Z*


30.86
H
O
B
O
SiMe3
Br
51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10
f1 (ppm

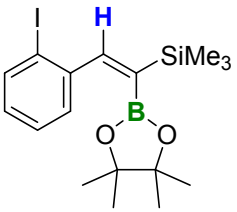
15-*Z*


7.81
7.81
7.79
7.79
7.50
7.49
7.48
7.47
7.26
7.24
7.24
7.22
6.93
6.93
6.91
6.91
6.90
6.89
1.22
0.22
I
H
SiMe3
B
O
O
0.94
1.01
1.95
1.00
11.98
8.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

16-*E*

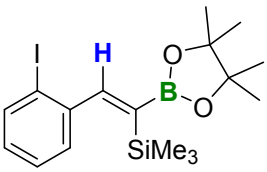

I
H
SiMe3
B
O
O
153.88
143.34
139.04
129.20
128.67
127.81
99.72
83.60
25.09
-0.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm

16-*E*


I
H
SiMe3
B
O
O

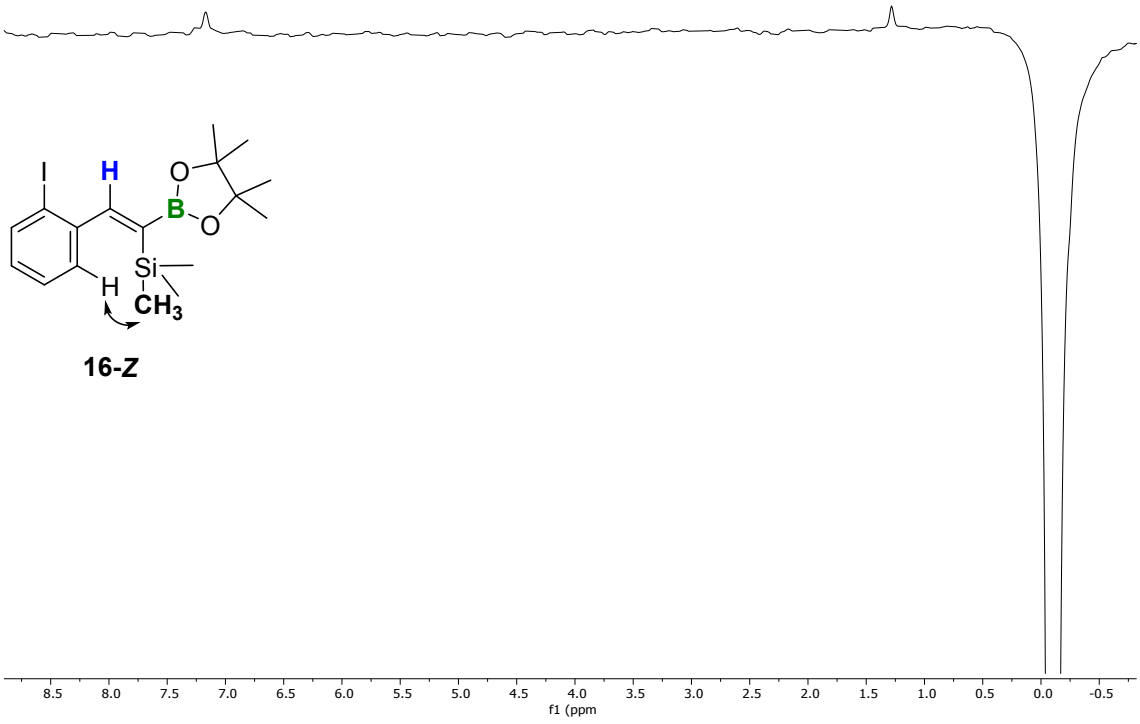
16-*E*

31.55
47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13
f1 (ppm

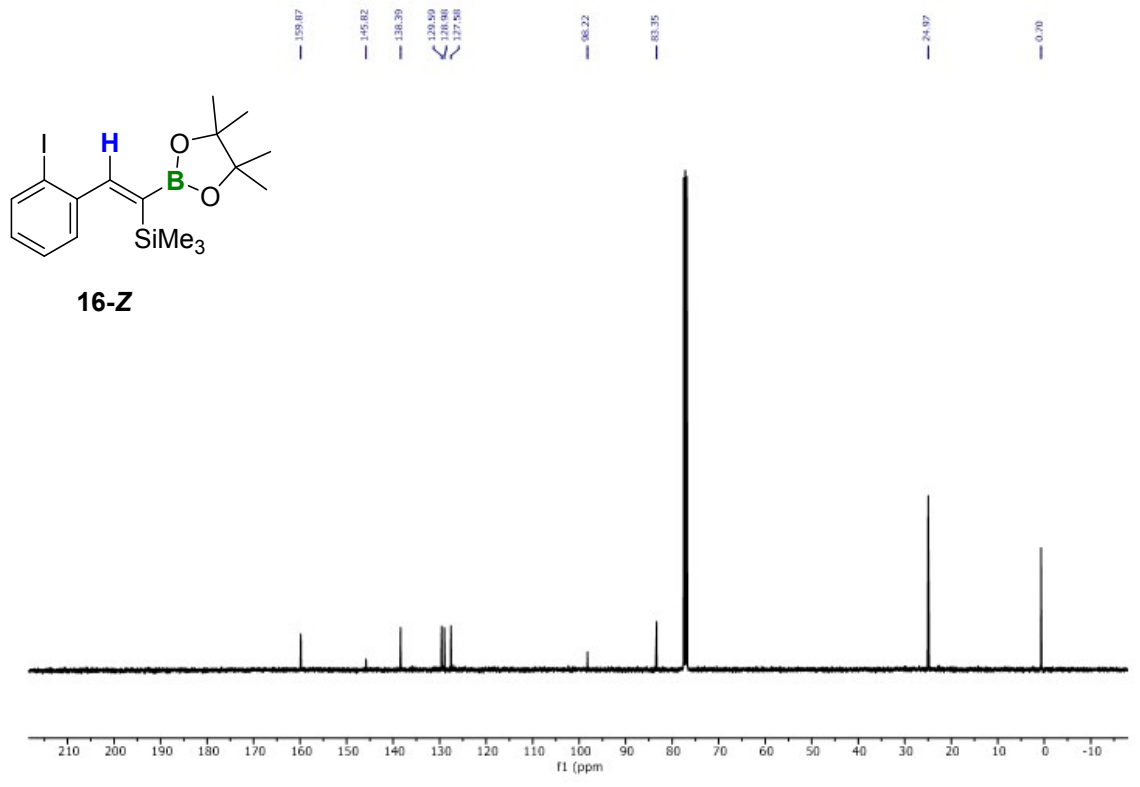

I
H
O
B
O
SiMe3

16-*Z*

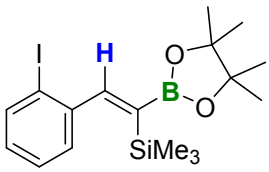
7.81
7.81
7.79
7.79
7.72
7.30
7.30
7.28
7.28
7.26
7.20
7.20
7.19
7.18
7.18
7.17
6.97
6.97
6.96
6.95
6.95
6.94
6.93
6.93
6.93
6.93
1.30
-0.08
1.12
1.00
0.97
1.05
1.10
11.92
8.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm


I
H
O
B
O
Si
H
CH3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

16-*Z*

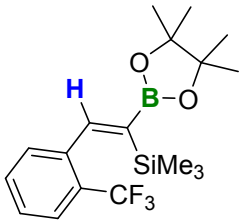

159.87
145.82
138.39
129.59
128.98
127.58
98.22
83.35
24.97
0.70
I
H
O
B
O
SiMe3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm

16-*Z*


I
H
O
B
O
SiMe3

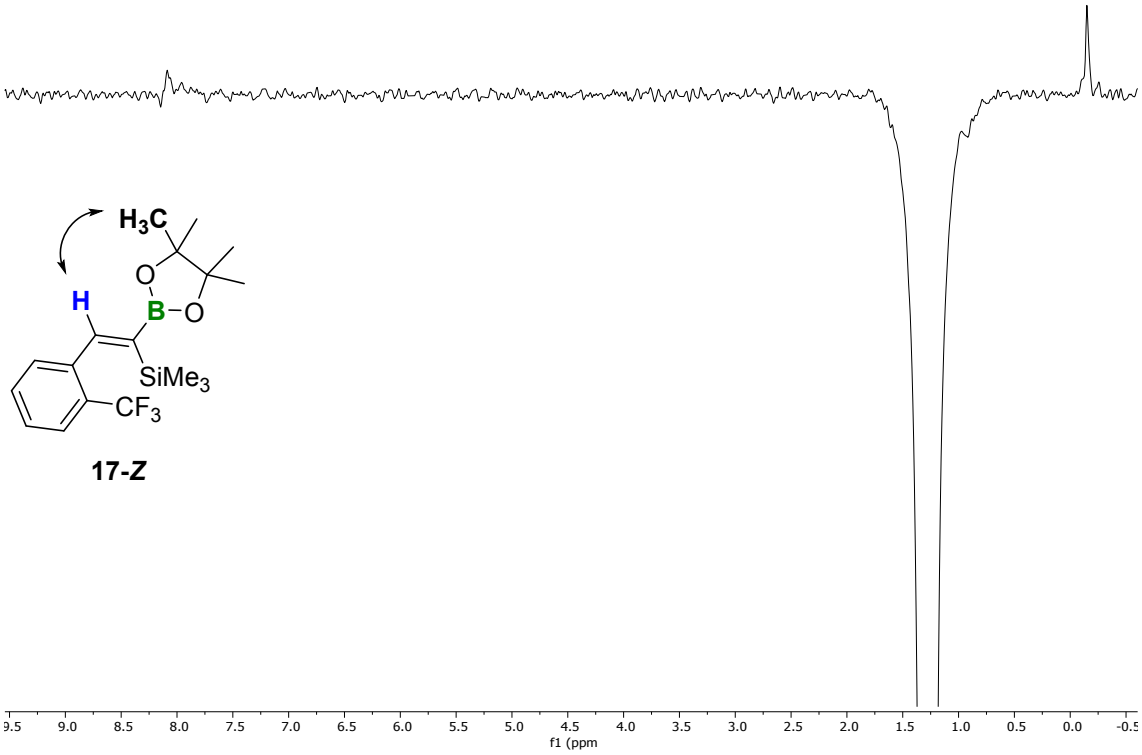
16-*Z*

30.81
46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14
f1 (ppm

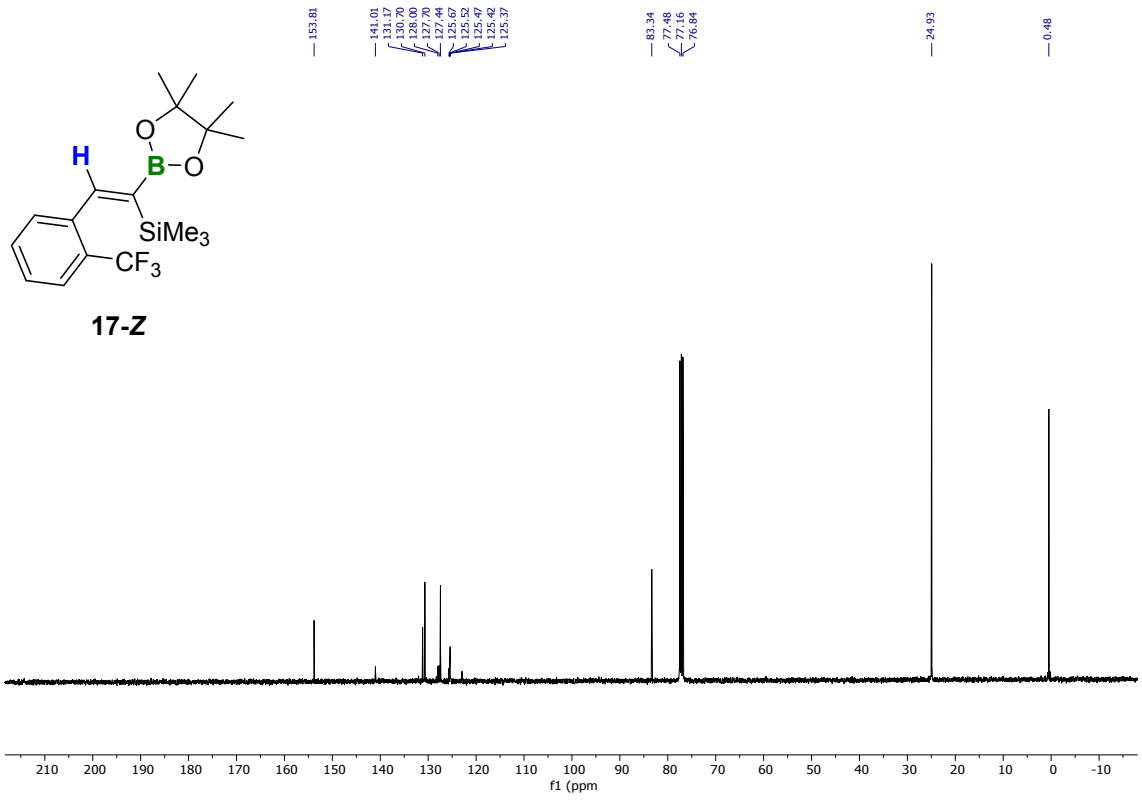

H
O
B
O
SiMe3
CF3

17-*Z*

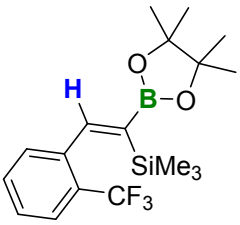
8.10
8.09
8.09
7.61
7.61
7.61
7.59
7.59
7.59
7.59
7.47
7.47
7.47
7.47
7.47
7.45
7.45
7.45
7.45
7.45
7.43
7.43
7.43
7.43
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.34
7.34
7.34
7.34
7.33
7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.22
1.29
-0.13
1.00
1.04
1.17
1.03
0.97
12.85
8.66
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm


H3C
O
H
B
O
SiMe3
CF3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm

17-*Z*

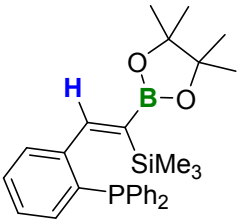

153.81
141.01
131.17
130.70
128.00
127.70
127.44
125.67
125.52
125.47
125.42
125.37
83.34
77.48
77.16
76.84
24.93
0.48
O
H
B
O
SiMe3
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

17-*Z*


H
O
B
O
SiMe3
CF3

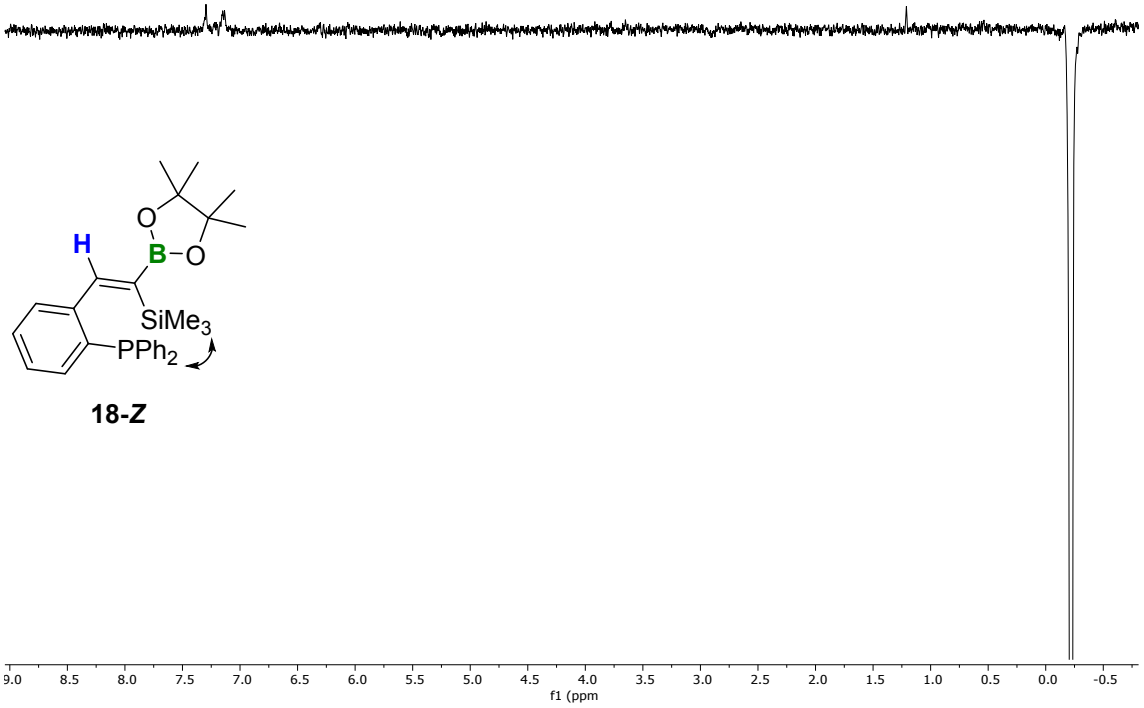
17-*Z*

30.83
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm)

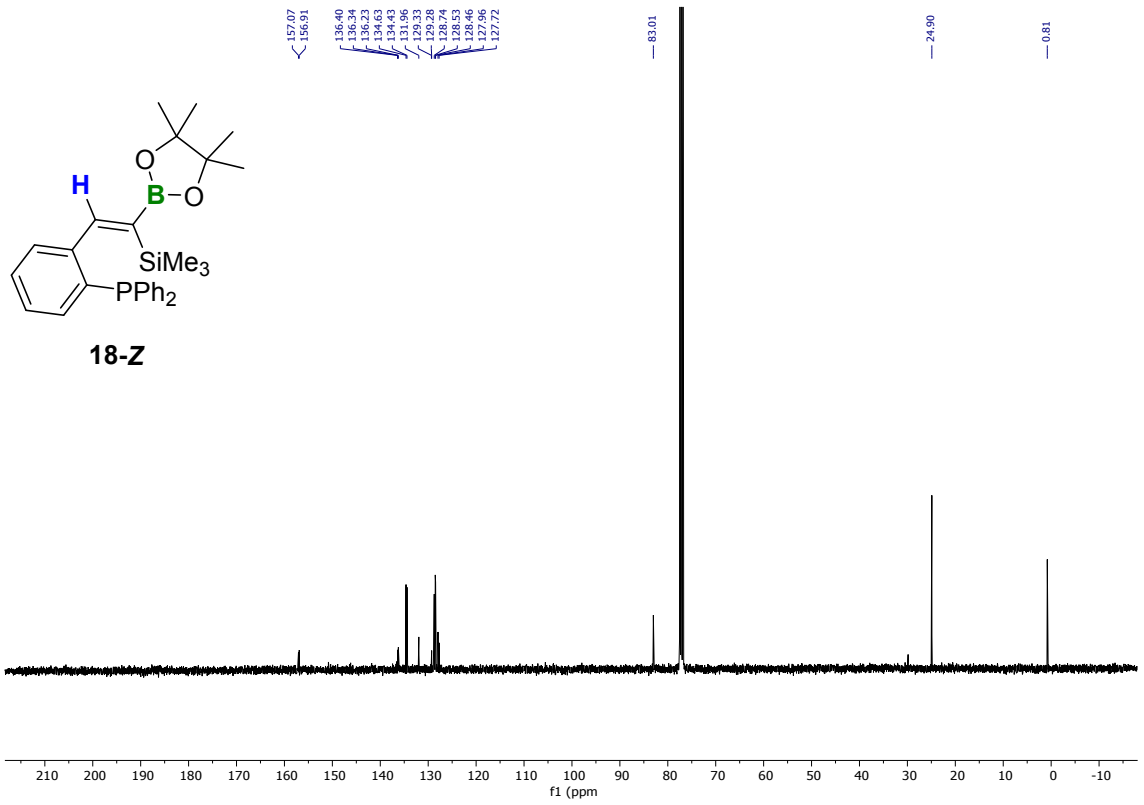

H
O
B
O
SiMe3
PPh2

18-*Z*

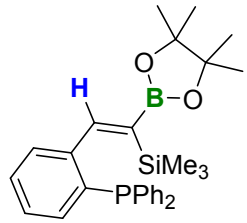
8.18 8.18 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.25 7.25 7.24 7.23 7.23 7.19 7.19 7.19 7.19 7.18 7.18 7.18 7.18 7.17 7.17 7.17 7.17 7.16 7.16 7.16 7.16 7.15 7.15 6.94 6.94 6.93 6.93 6.92 6.92 6.91 6.91 6.91
1.23
-0.20
1.00
10.00
0.95
2.14
1.01
12.67
9.39
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
O
B–O
SiMe3
PPh2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm

18-*Z*

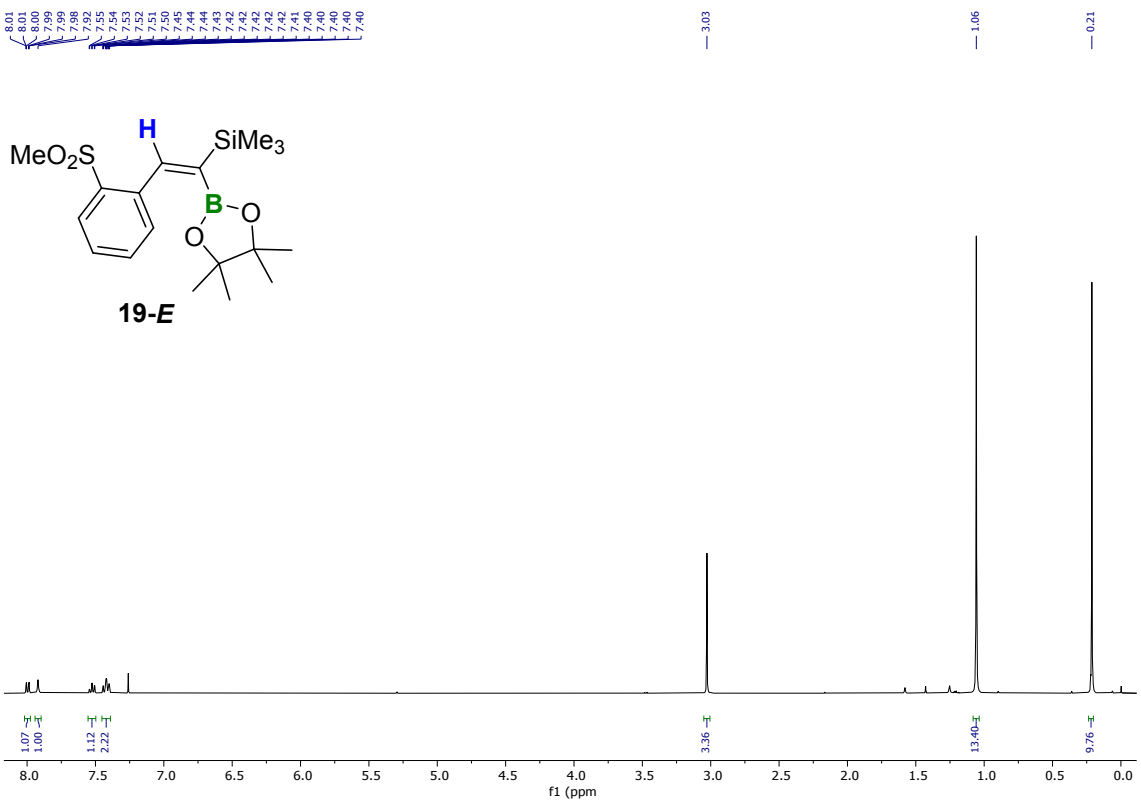

157.07
156.91
136.40
136.34
136.23
134.63
134.43
131.96
129.33
129.28
128.74
128.53
128.46
127.96
127.72
83.01
24.90
0.81
H
O
B–O
SiMe3
PPh2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

18-*Z*


H
O
B
O
SiMe3
PPh2

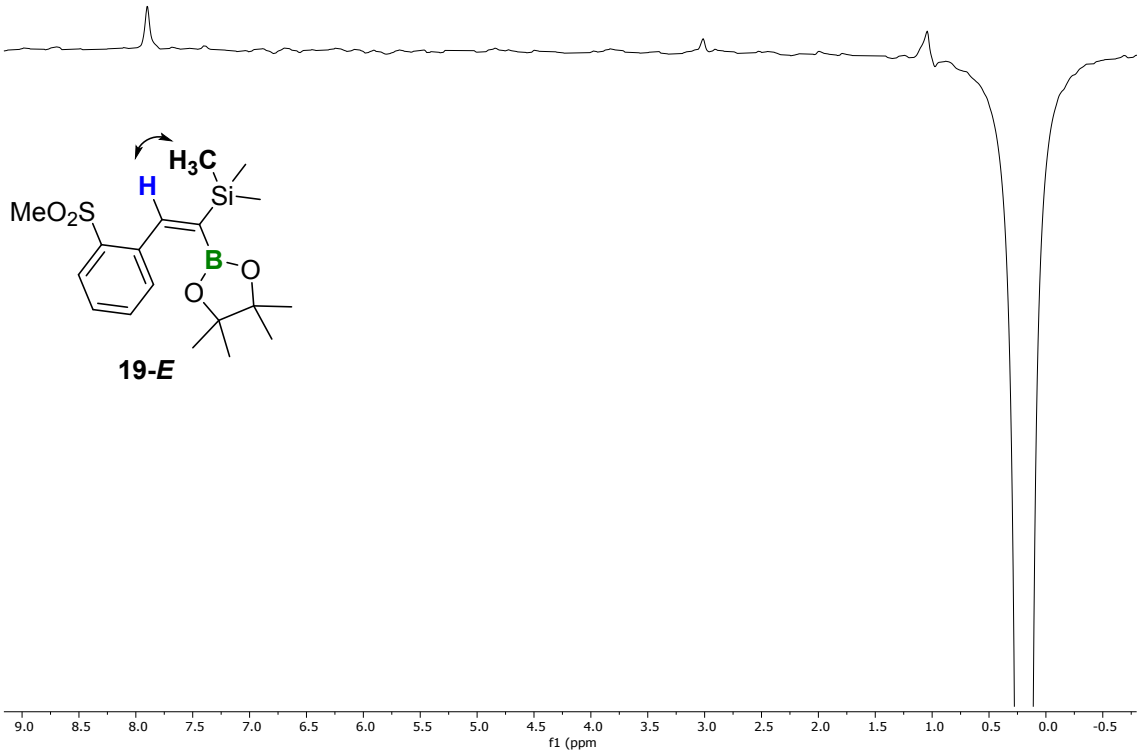
18-*Z*

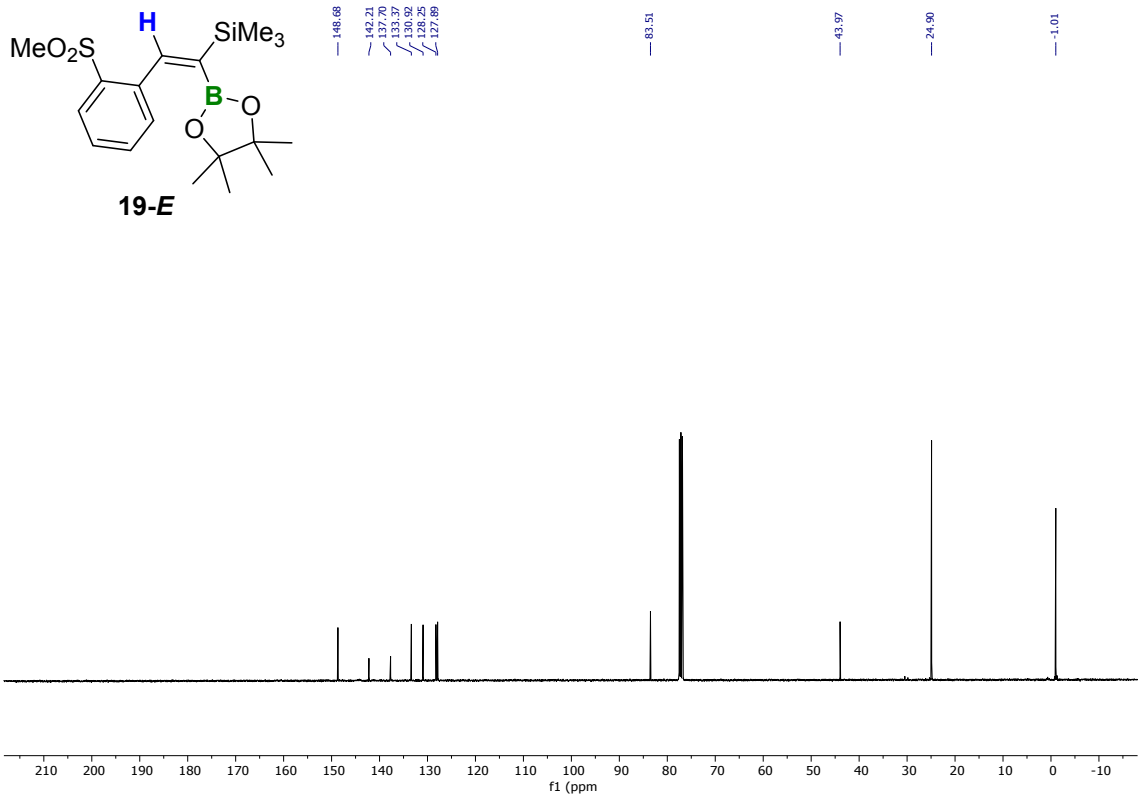
30.63
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10
f1 (ppm)

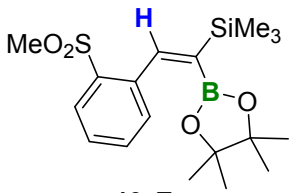

8.01 8.01 8.00 7.99 7.99 7.98 7.92 7.55 7.54 7.53 7.52 7.51 7.50 7.45 7.44 7.44 7.43 7.42 7.42 7.42 7.42 7.41 7.40 7.40 7.40 7.40 7.40
3.03
1.06
0.21
1.07 1.00 1.12 2.22 3.36 13.40 9.76
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

H
MeO2S
SiMe3
B
O
O

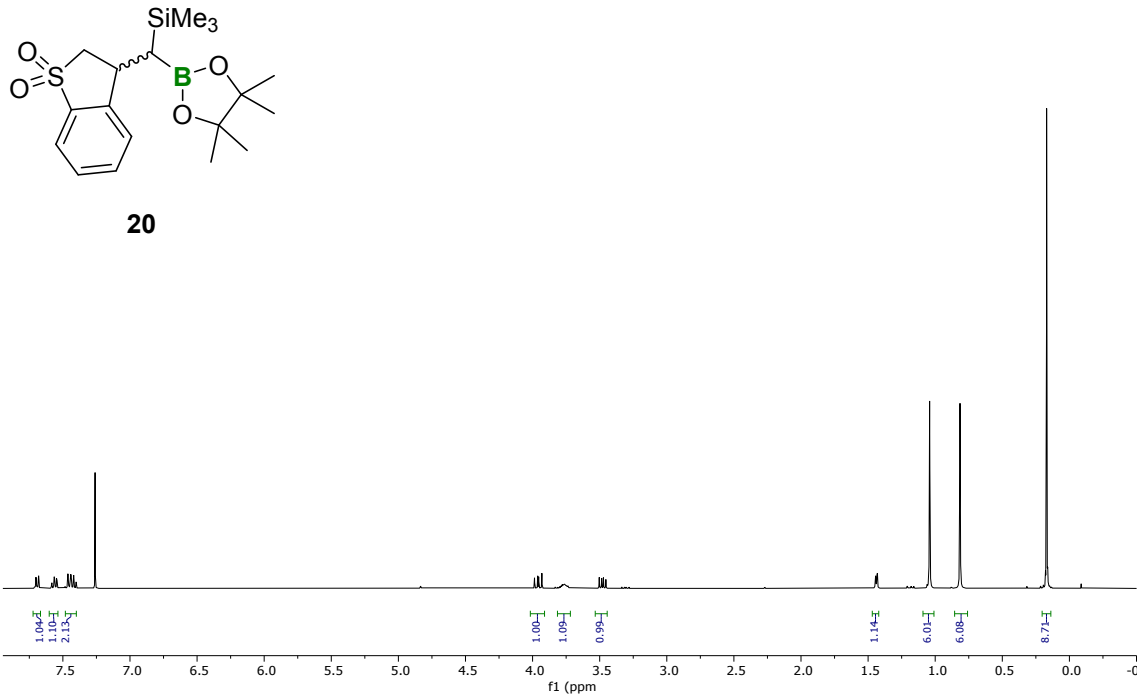
19-*E*


H3C
H
Si
MeO2S
B
O
O
19-E
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm

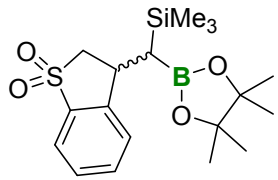

H
SiMe3
MeO2S
B
O
O
19-E
148.68
142.21
137.70
133.37
130.92
128.25
127.89
83.51
43.97
24.90
-1.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm



19-*E*

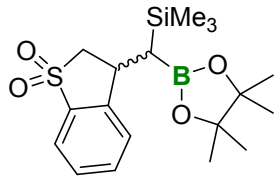


20


SiMe3
O
O
S
B
O
O

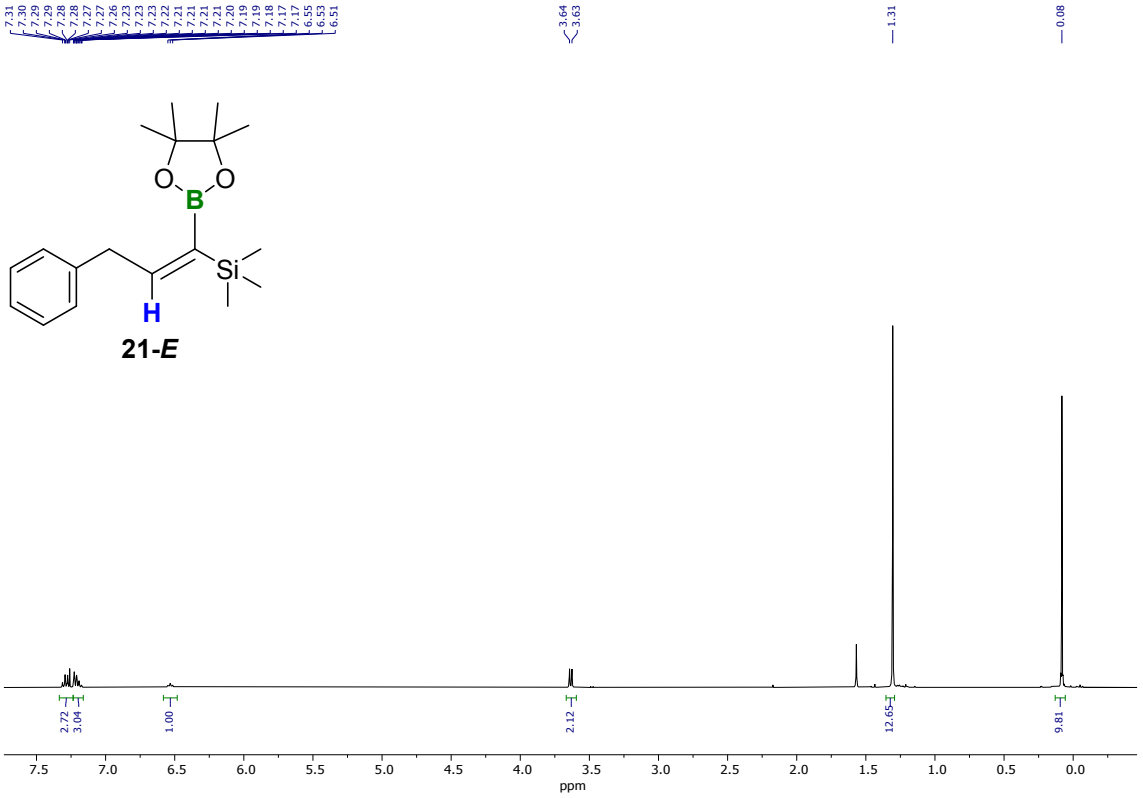
20

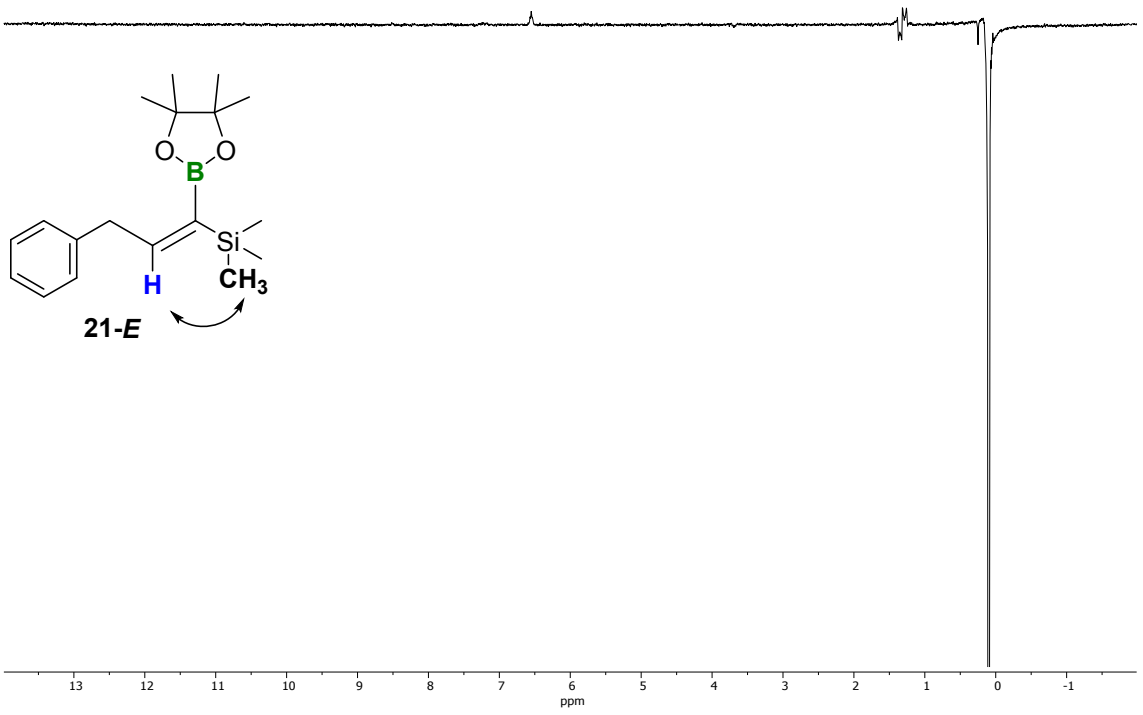
144.30
143.88
138.99
133.37
133.21
128.59
128.35
125.79
125.67
125.21
121.45
121.03
83.73
83.23
57.74
56.07
36.54
35.52
31.07
30.47
29.85
25.35
25.28
25.06
24.01
15.42
0.70
-0.41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

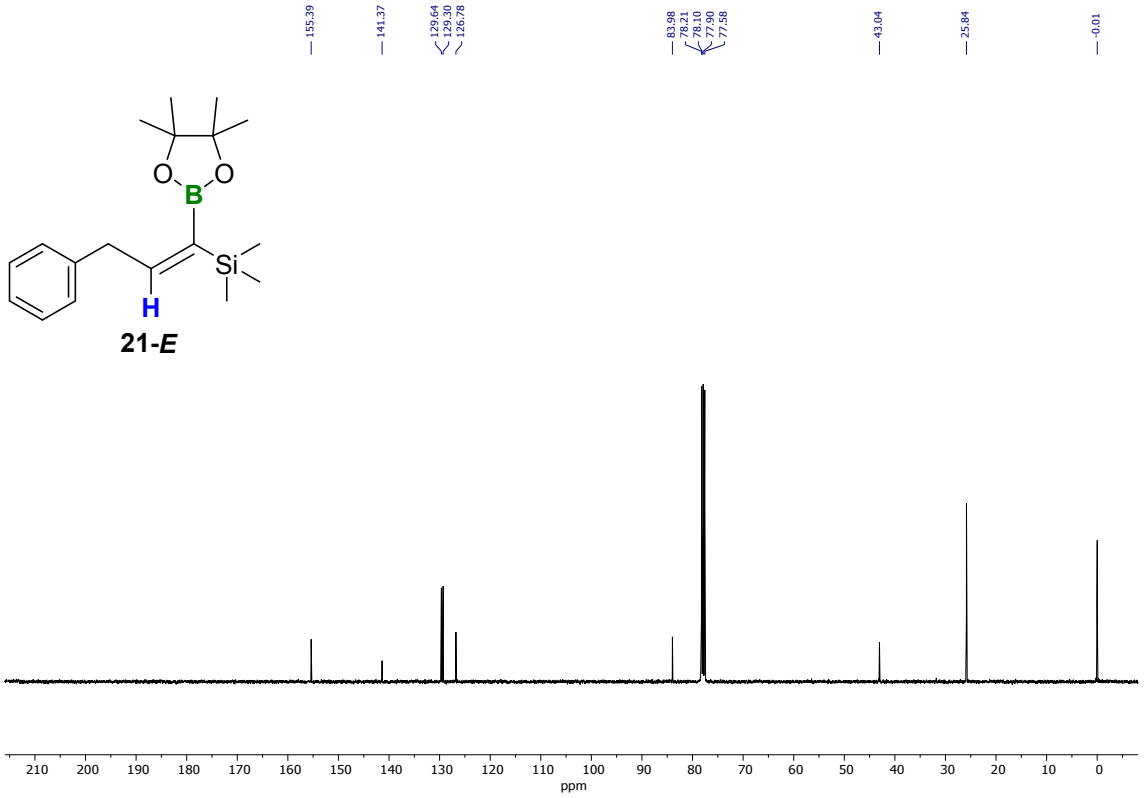

SiMe3
O
O
S
B
O
O

20

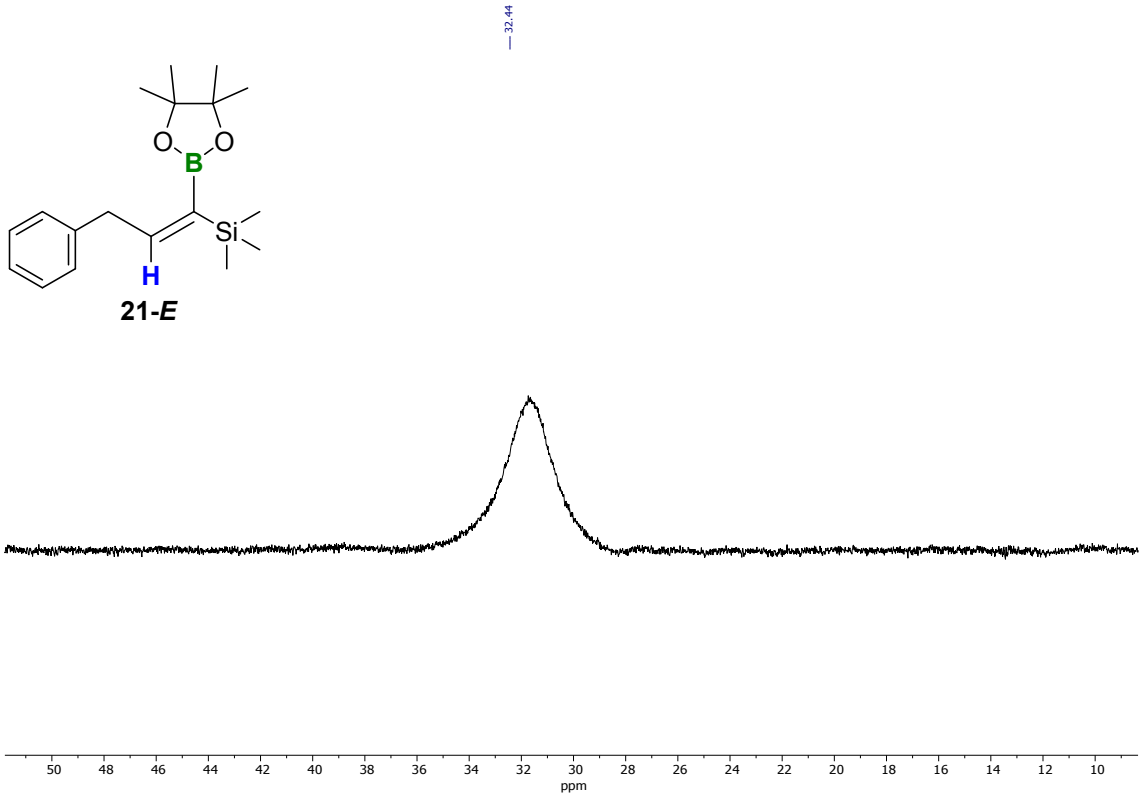
33.05
47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
f1 (ppm


7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.23
7.23
7.22
7.21
7.21
7.21
7.21
7.20
7.19
7.18
7.17
7.17
6.55
6.53
6.51
3.64
3.63
1.31
0.08
O
B
O
Si
H
21-E
2.72
3.04
1.00
2.12
12.65
9.81
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

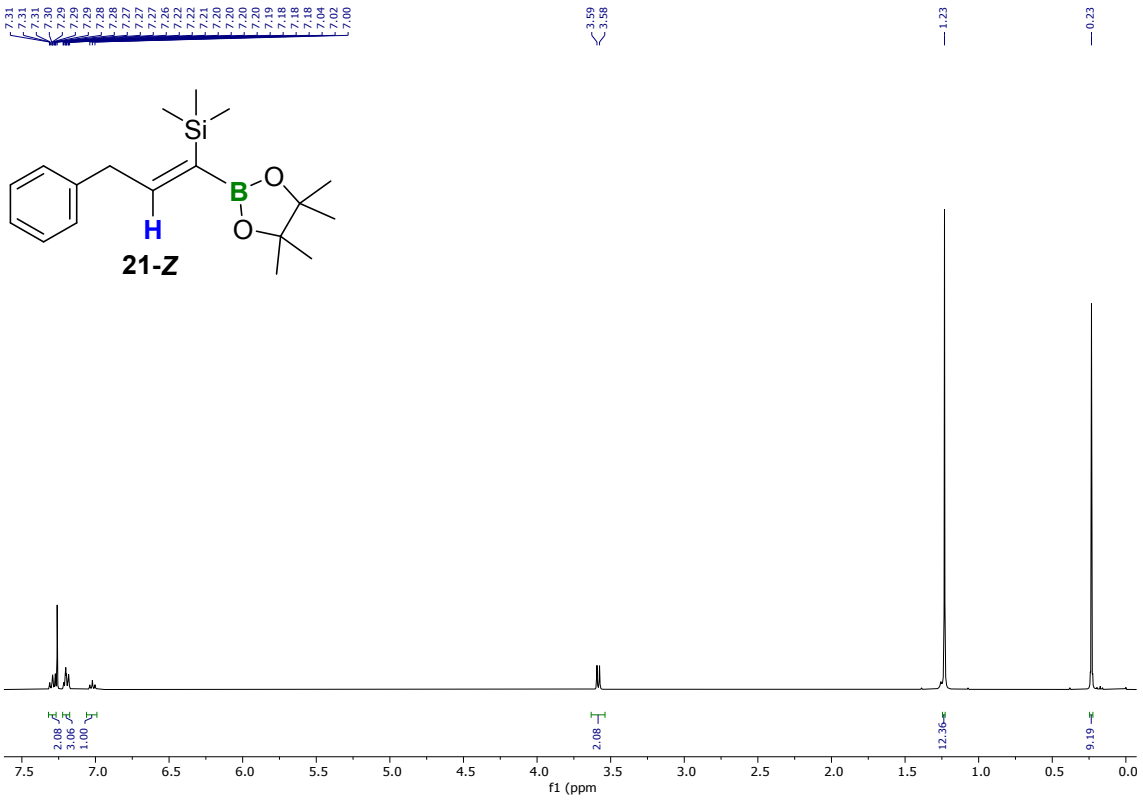

O
B
O
Si
H
CH3
21-E
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

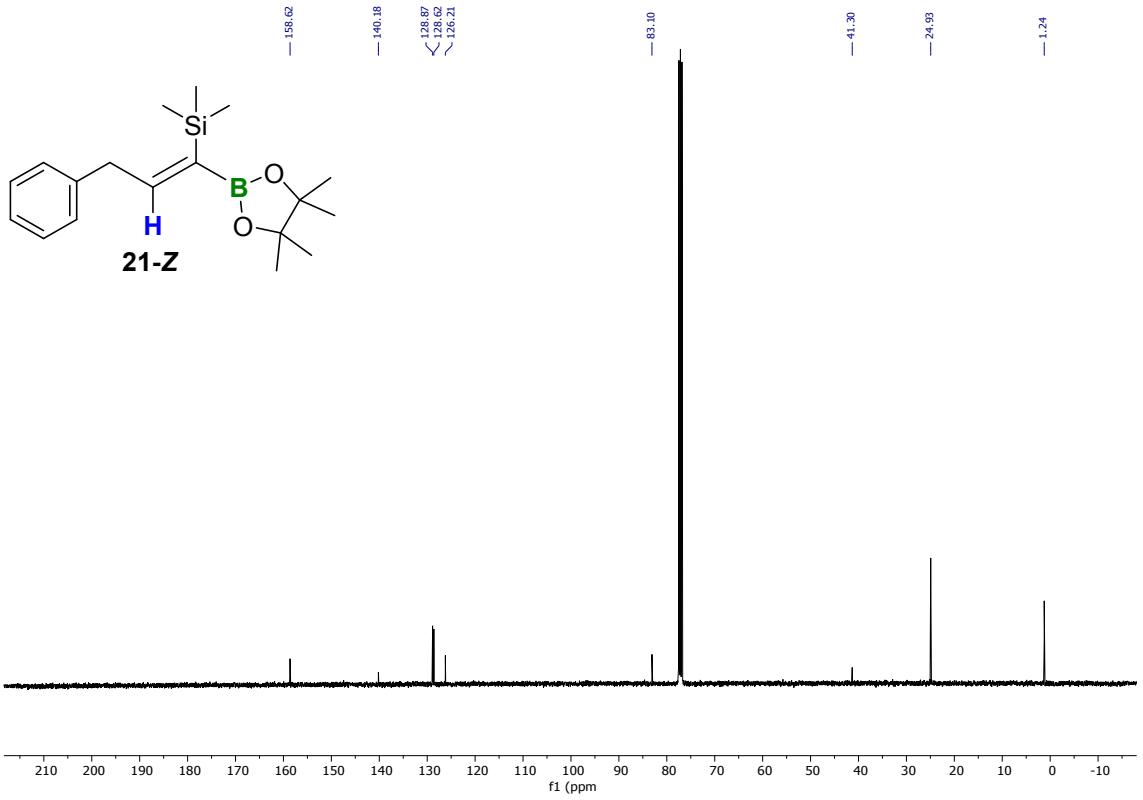

155.39
141.37
129.64
129.30
126.78
83.98
78.21
78.10
77.90
77.58
43.04
25.84
-0.01
O
O
B
Si
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

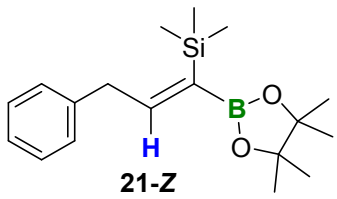
21-*E*


32.44
O
O
B
Si
H
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
ppm

21-*E*

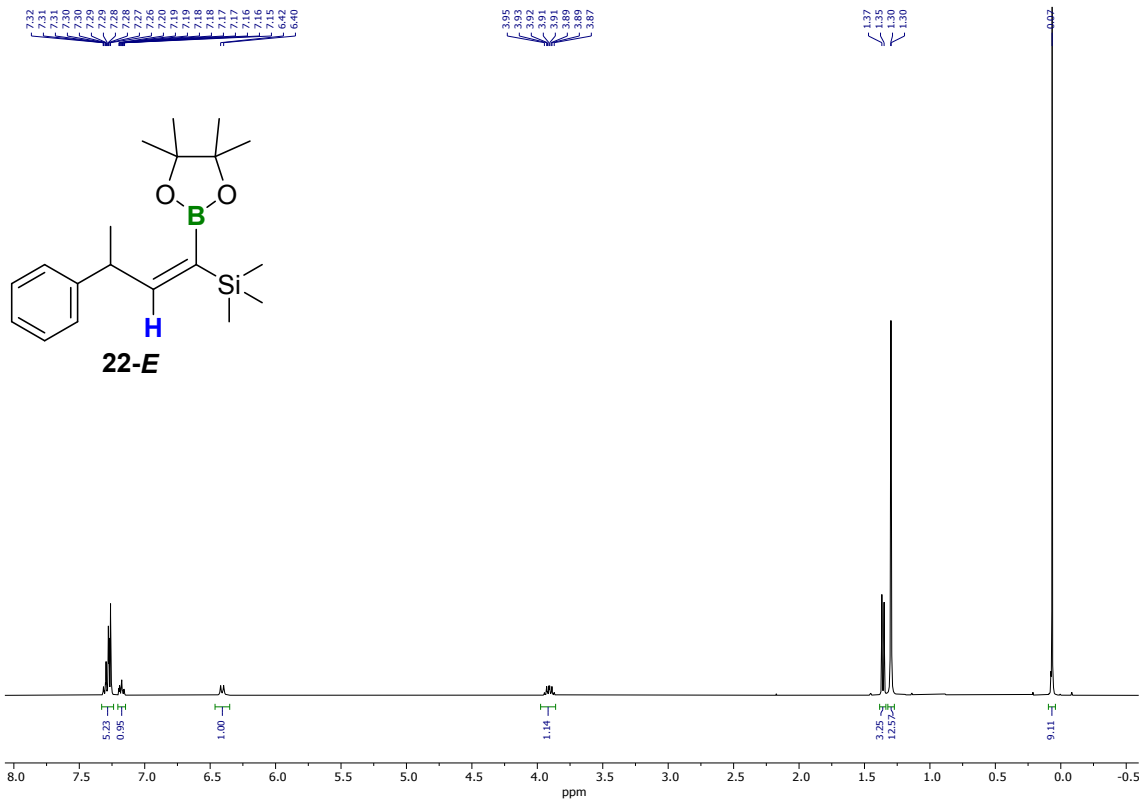

7.31
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.22
7.22
7.21
7.20
7.20
7.20
7.19
7.18
7.18
7.18
7.04
7.02
7.00
3.59
3.58
1.23
0.23
Si
B
O
O
H
21-Z
2.08
3.06
1.00
2.08
12.36
9.19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm


158.62
140.18
128.87
128.62
126.21
83.10
41.30
24.93
1.24
Si
B
O
O
H
21-Z
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


Si
B
O
O
H

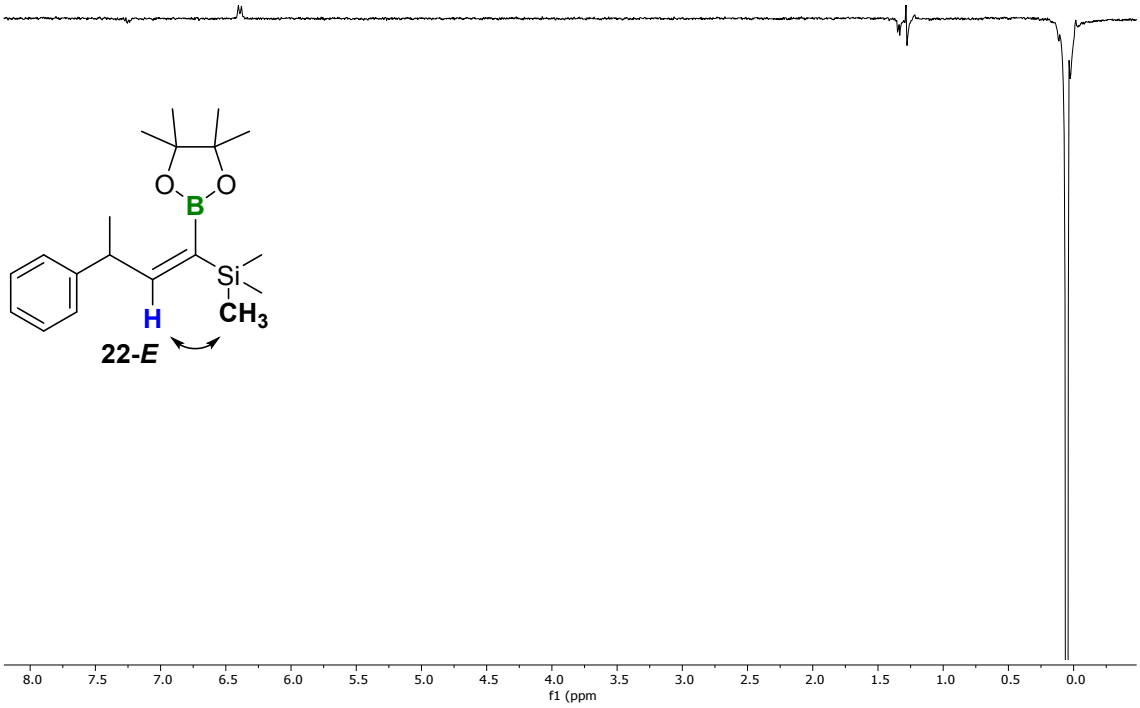
21-*Z*

30.94
47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 1
f1 (ppm

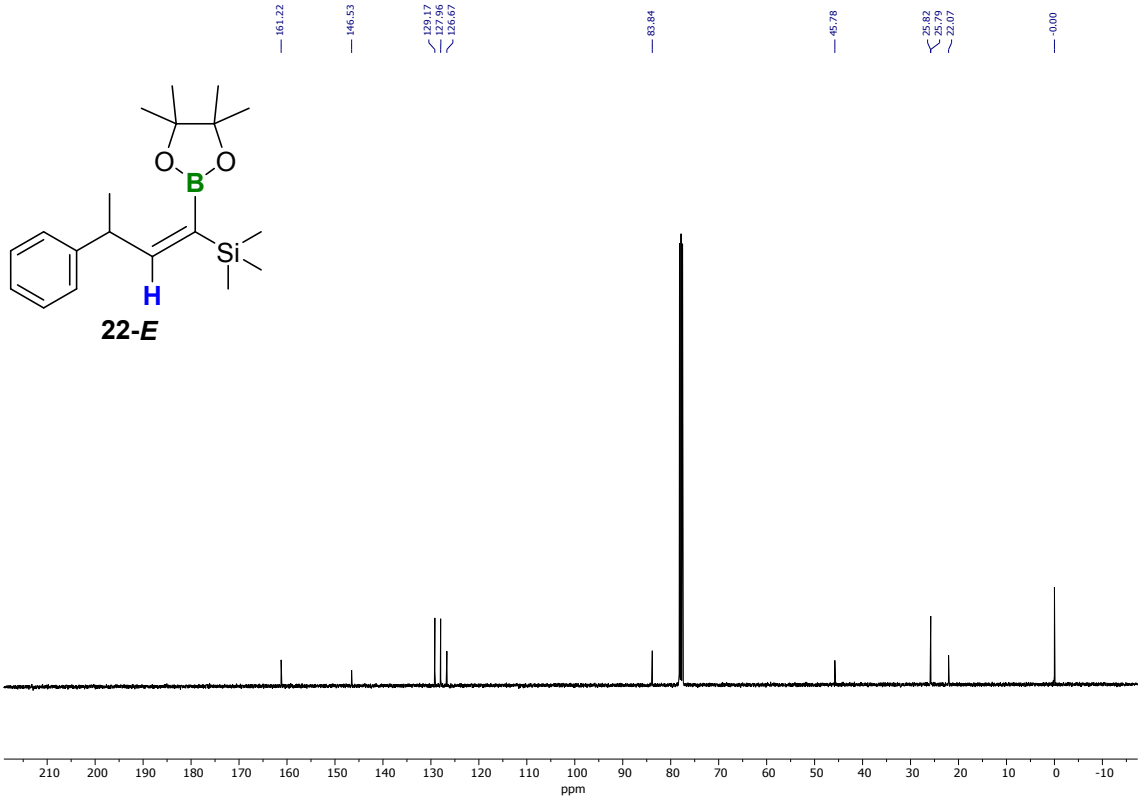

7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.15 6.42 6.40
3.95 3.93 3.92 3.91 3.91 3.89 3.89 3.87
1.37 1.35 1.30 1.30
0.02
5.23 0.95 1.00 1.14 3.25 12.57 9.11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

O
O
B
Si
H

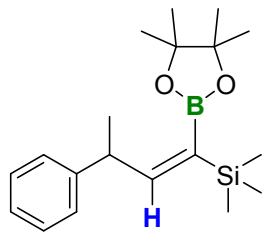
22-*E*


O
O
B
Si
CH3
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

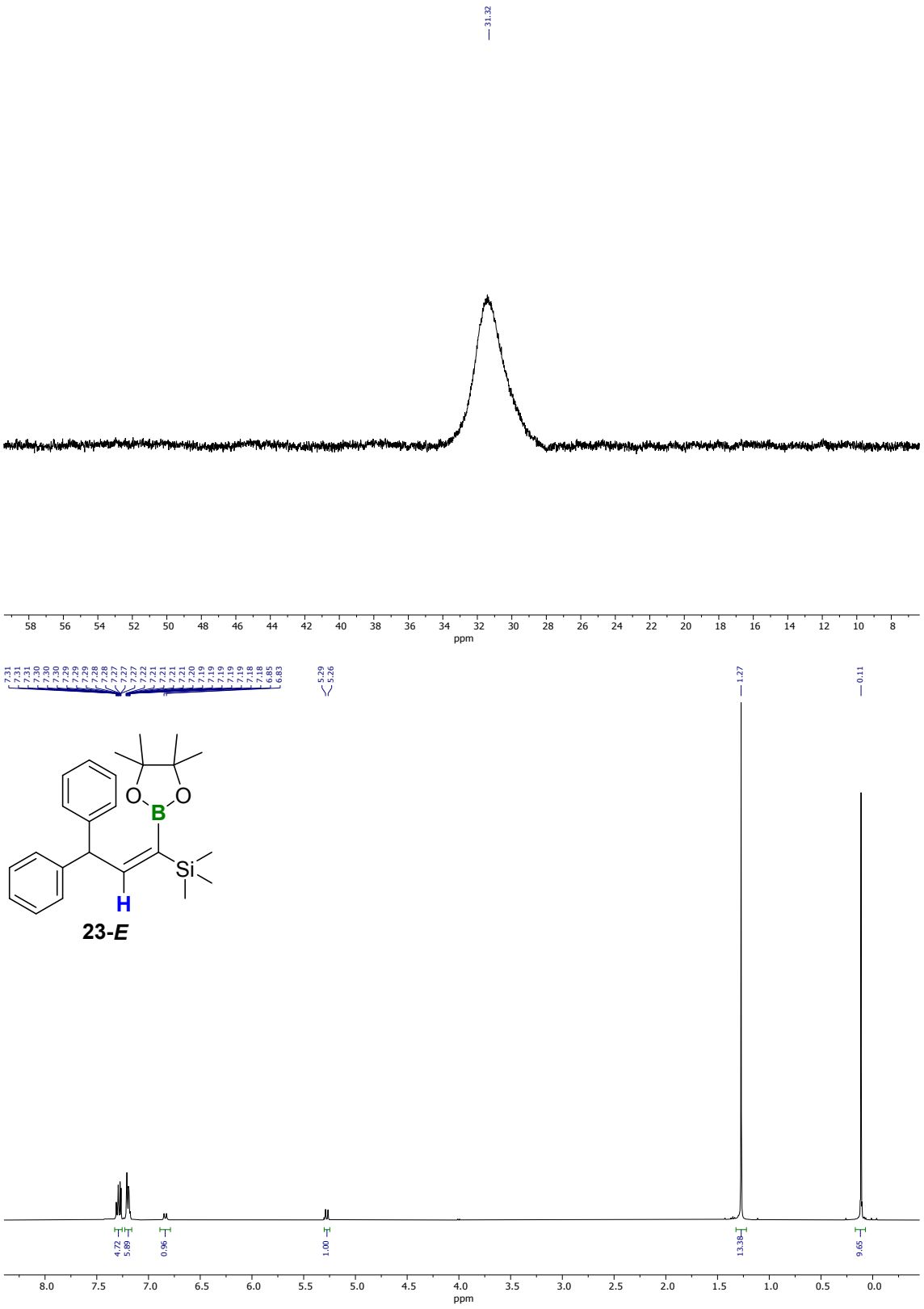
22-*E*


161.22
146.53
129.17
127.96
126.67
83.84
45.78
25.82
25.79
22.07
-0.00
O
O
B
Si
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

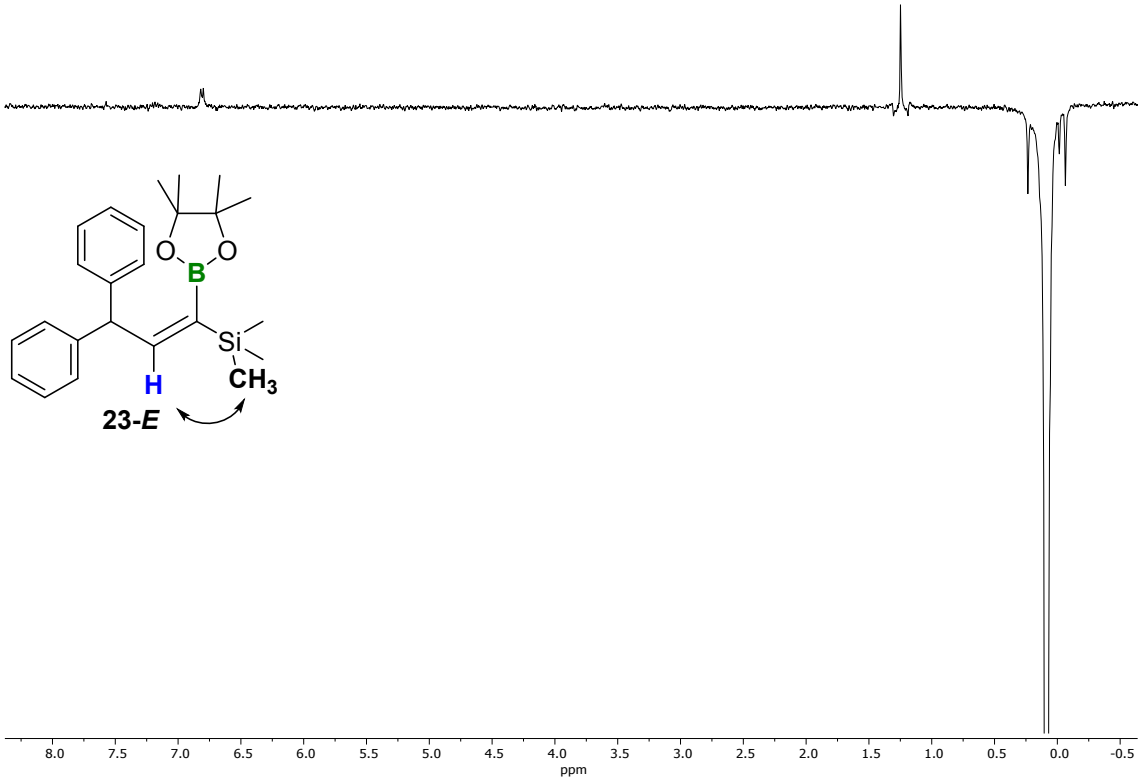
22-*E*


O
O
B
Si
H

22-*E*

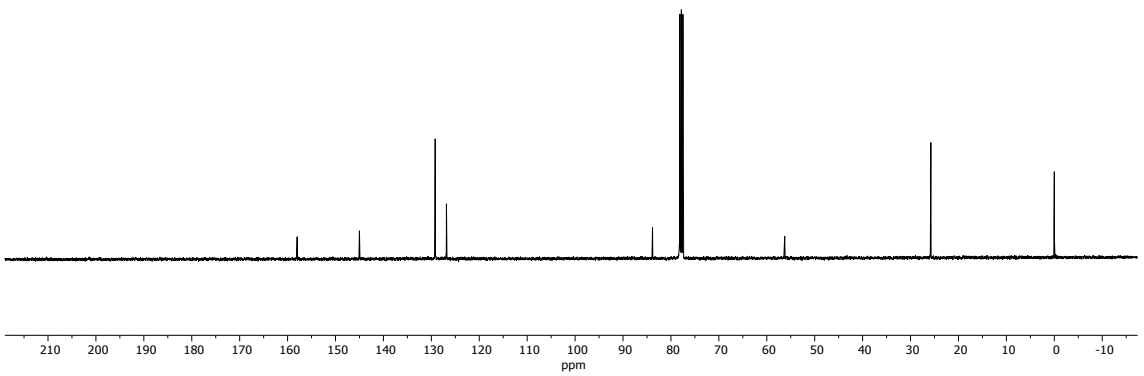

31.32
ppm
7.31
7.31
7.31
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.19
7.19
7.18
7.18
6.85
6.83
5.29
5.26
1.27
0.11
O
O
B
Si
H
4.72
5.89
0.96
1.00
13.38
9.65
ppm

23-*E*

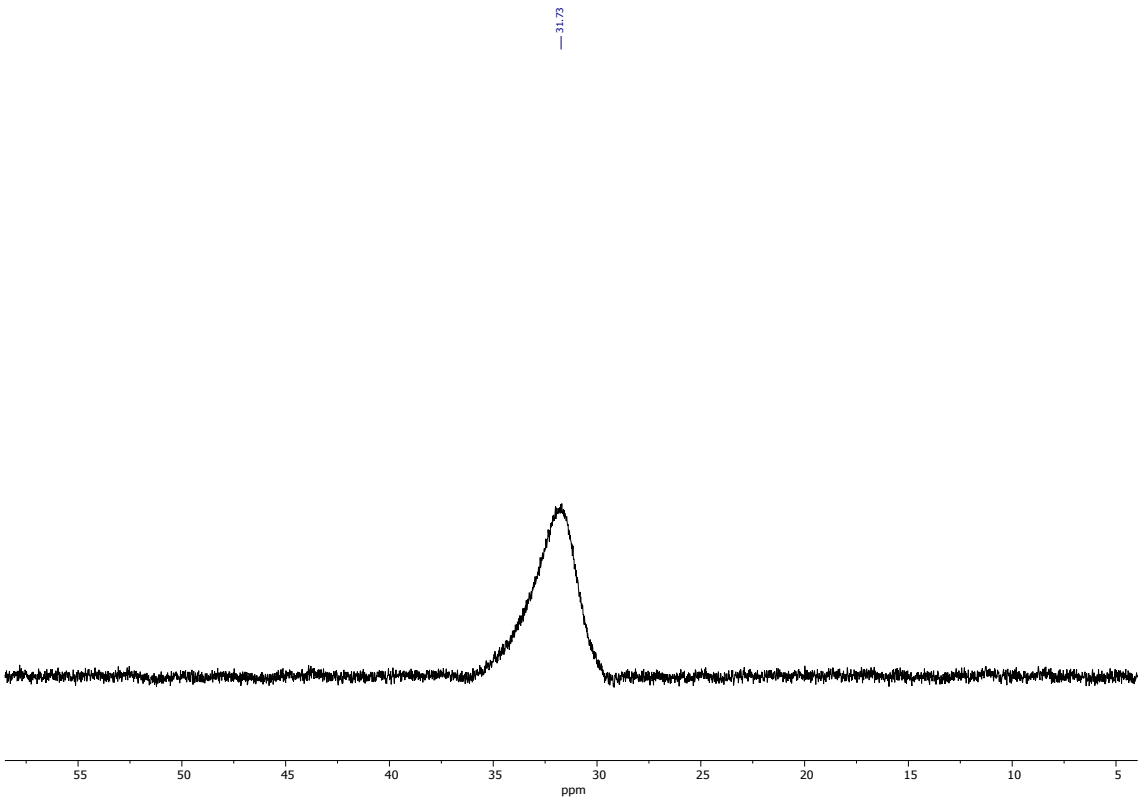


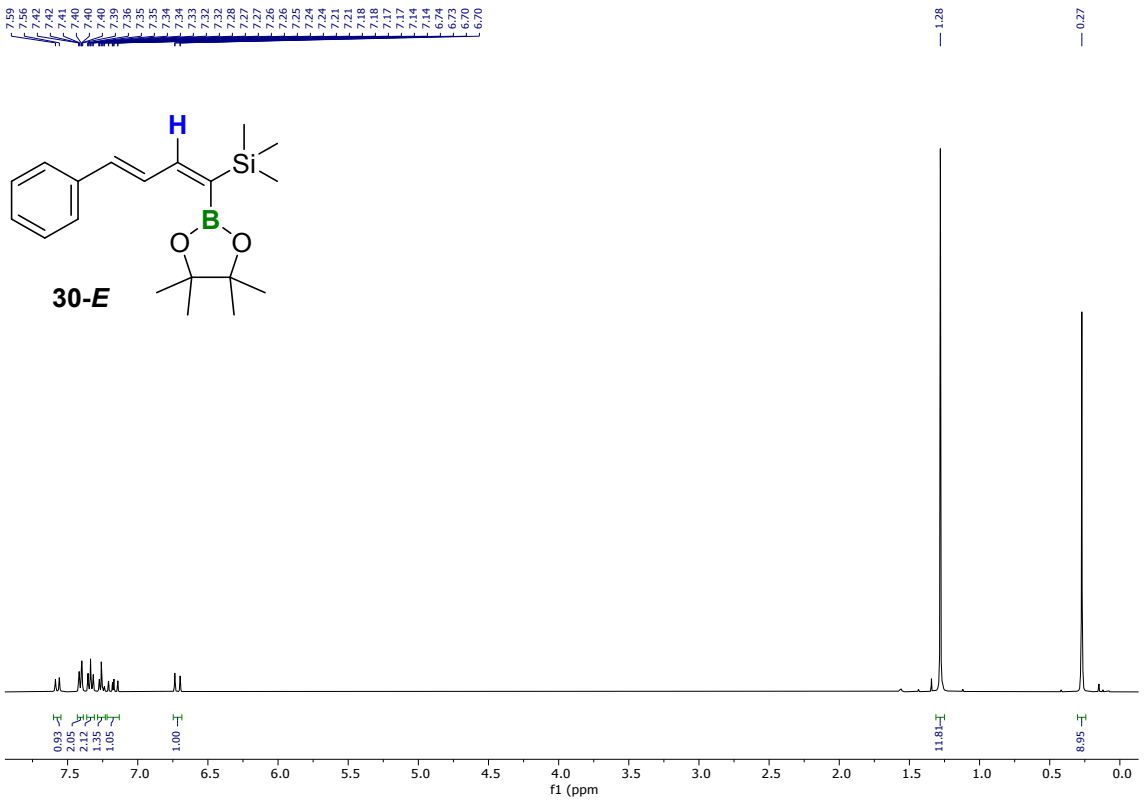
23-*E*

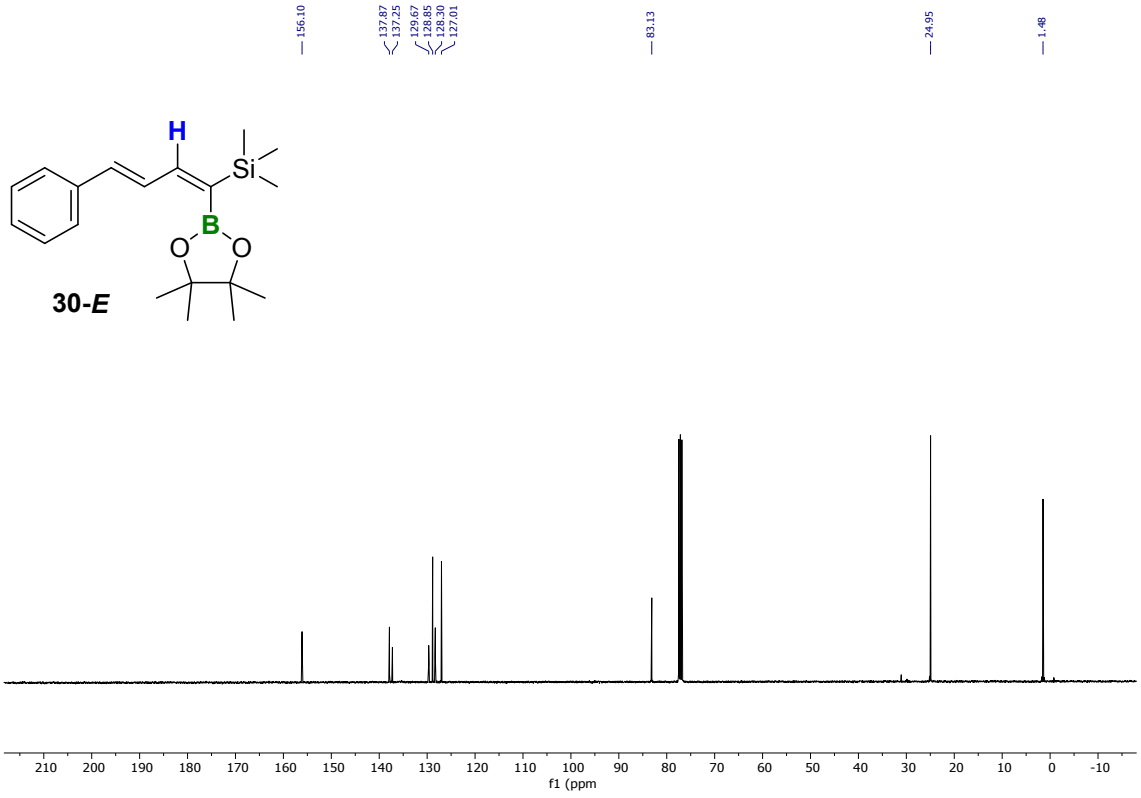
158.00
145.01
129.26
129.20
126.85
83.85
56.26
25.77
-0.00

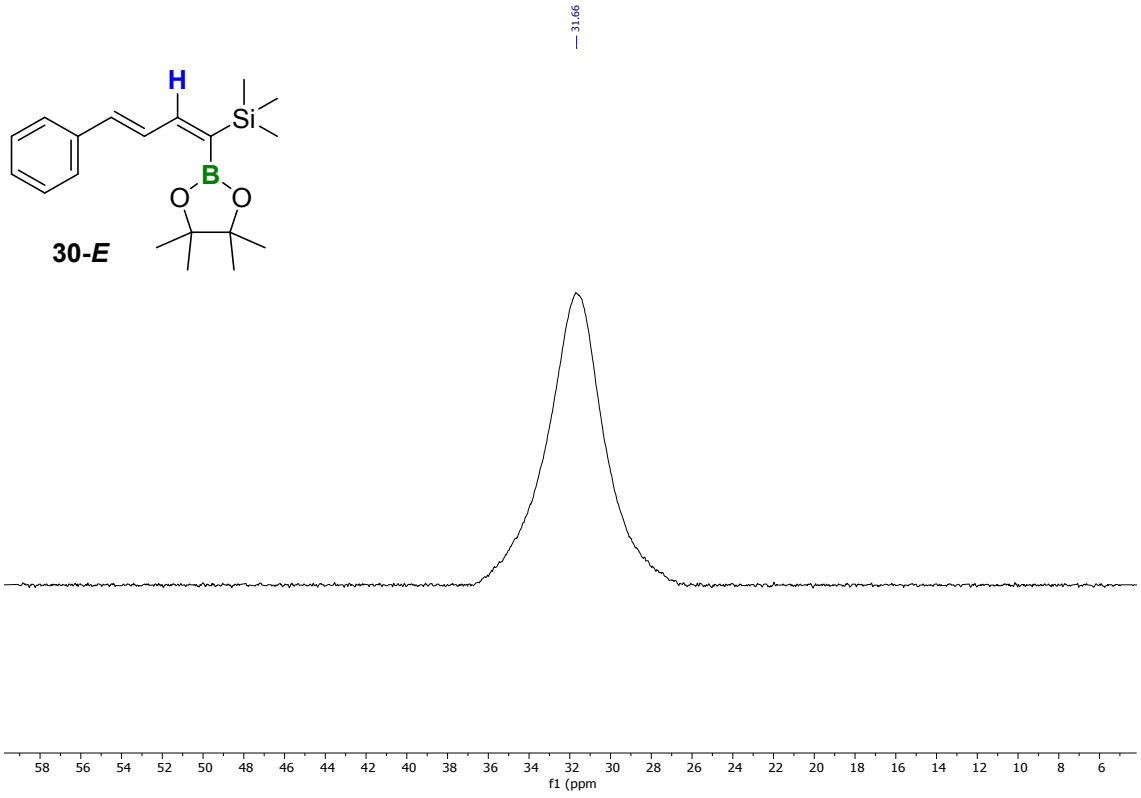


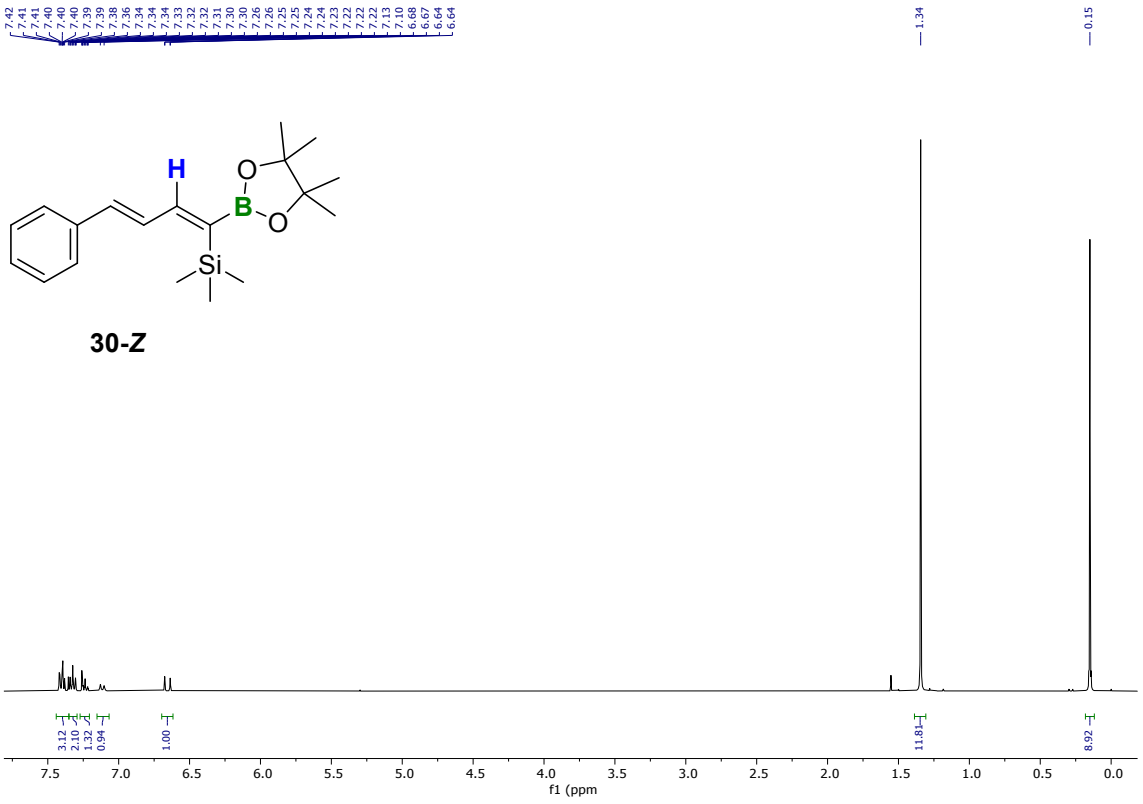
23-*E*


31.73
55
50
45
40
35
30
25
20
15
10
5
ppm

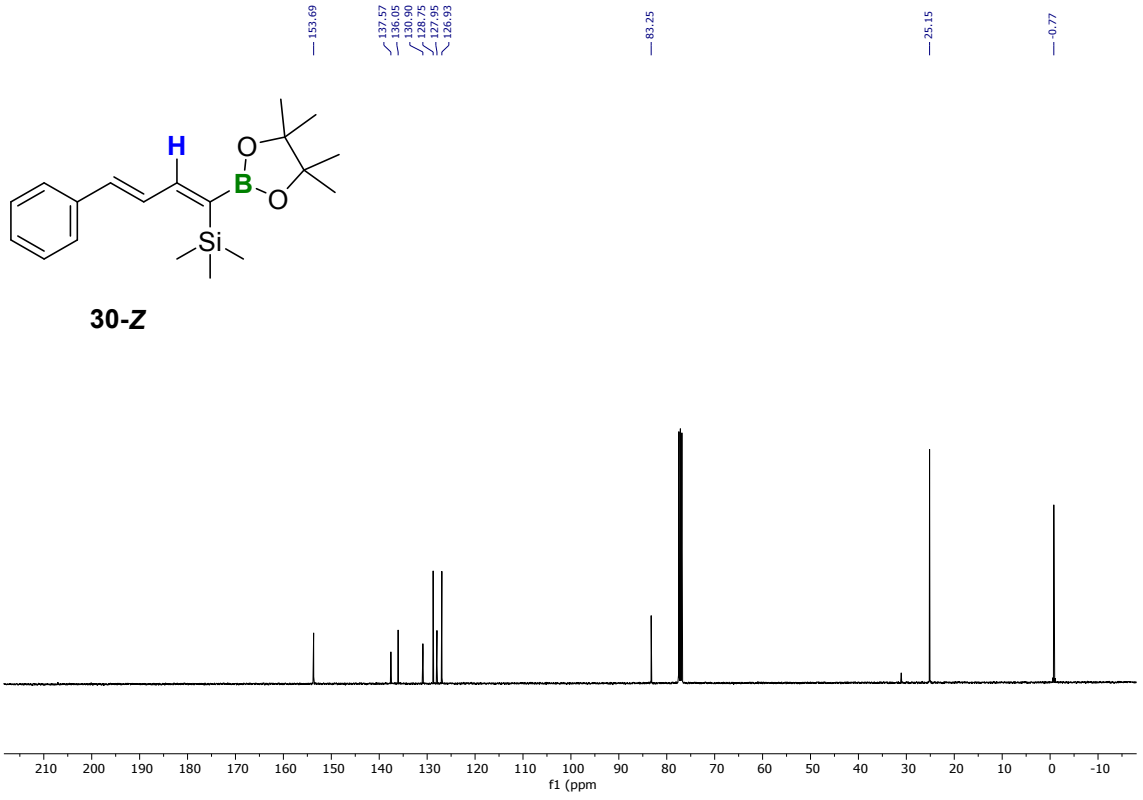

7.59
7.56
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.21
7.21
7.18
7.18
7.17
7.17
7.14
7.14
6.74
6.73
6.70
6.70
1.28
0.27
H
Si
B
O
O
30-E
0.93
2.05
2.12
1.35
1.05
1.00
11.81
8.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm


156.10
137.87
137.25
129.67
128.85
128.30
127.01
83.13
24.95
1.48
H
Si
B
O
O
30-E
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

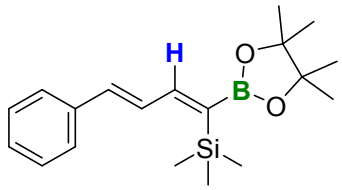

31.66
H
Si
B
O
O
30-E
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm


7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.36
7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.22
7.13
7.10
6.68
6.67
6.64
6.64
1.34
0.15
H
O
B
O
Si
3.12
2.10
1.32
0.94
1.00
11.81
8.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm

30-*Z*

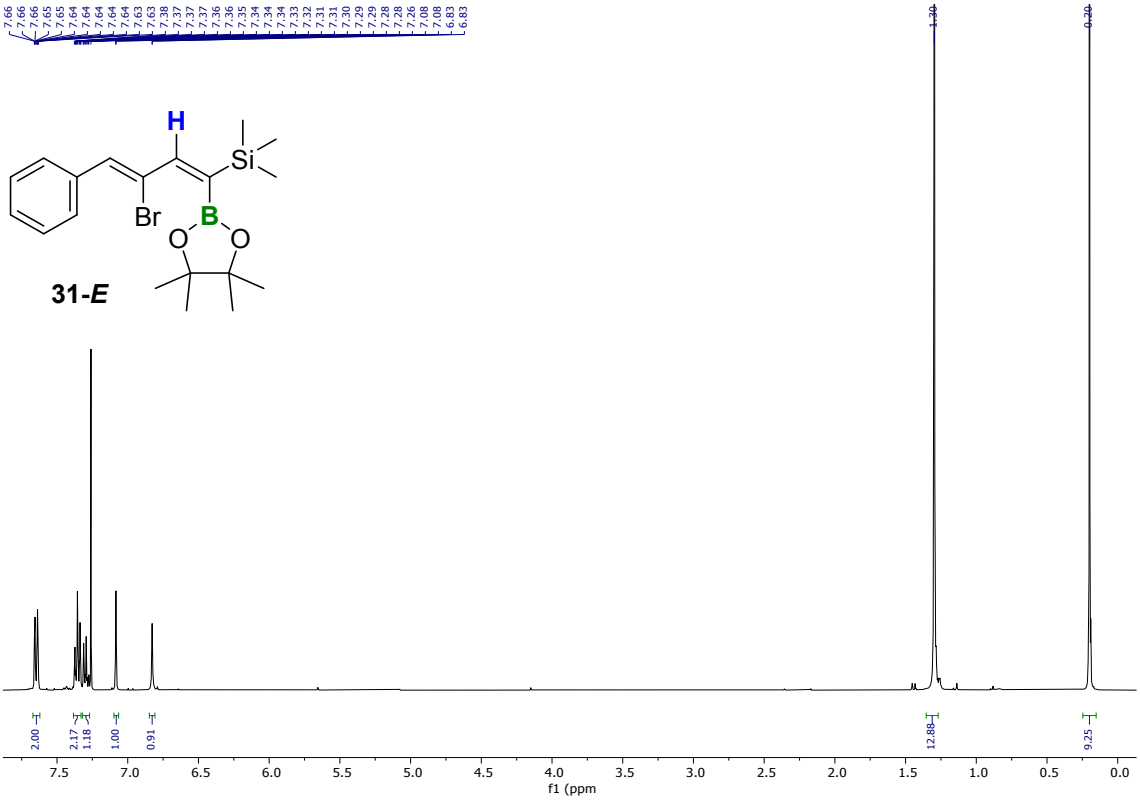

153.69
137.57
136.05
130.90
128.75
127.95
126.93
83.25
25.15
-0.77
H
O
B
O
Si
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm

30-*Z*


H
O
B
O
Si

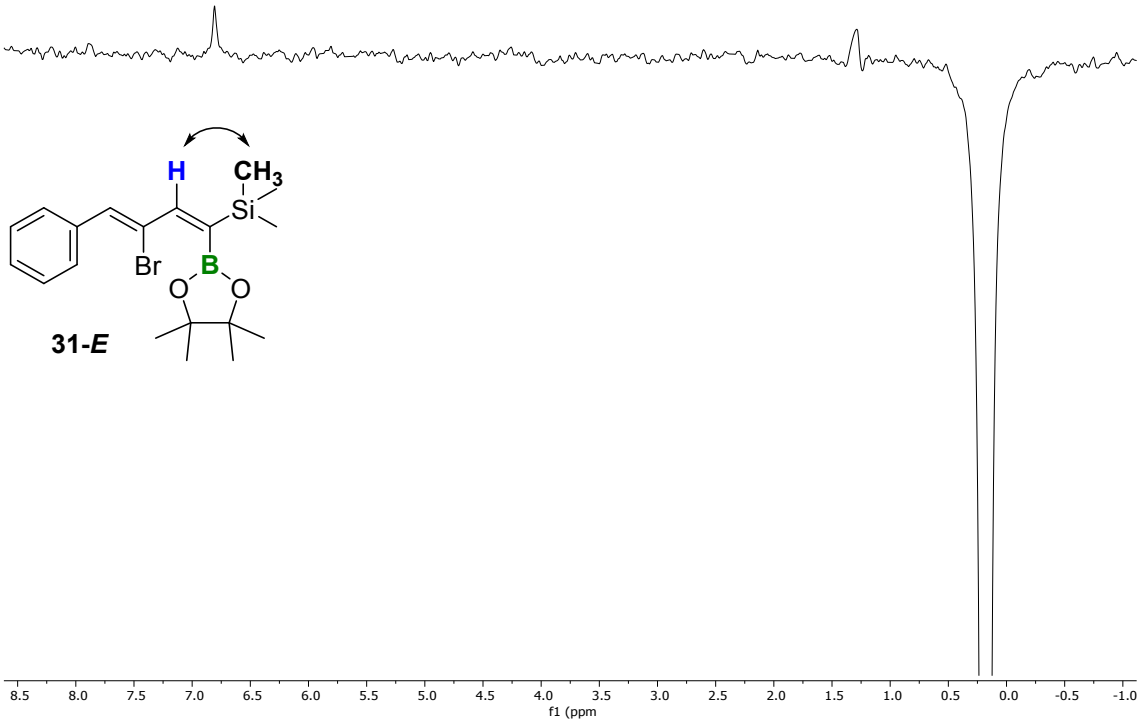
30-*Z*

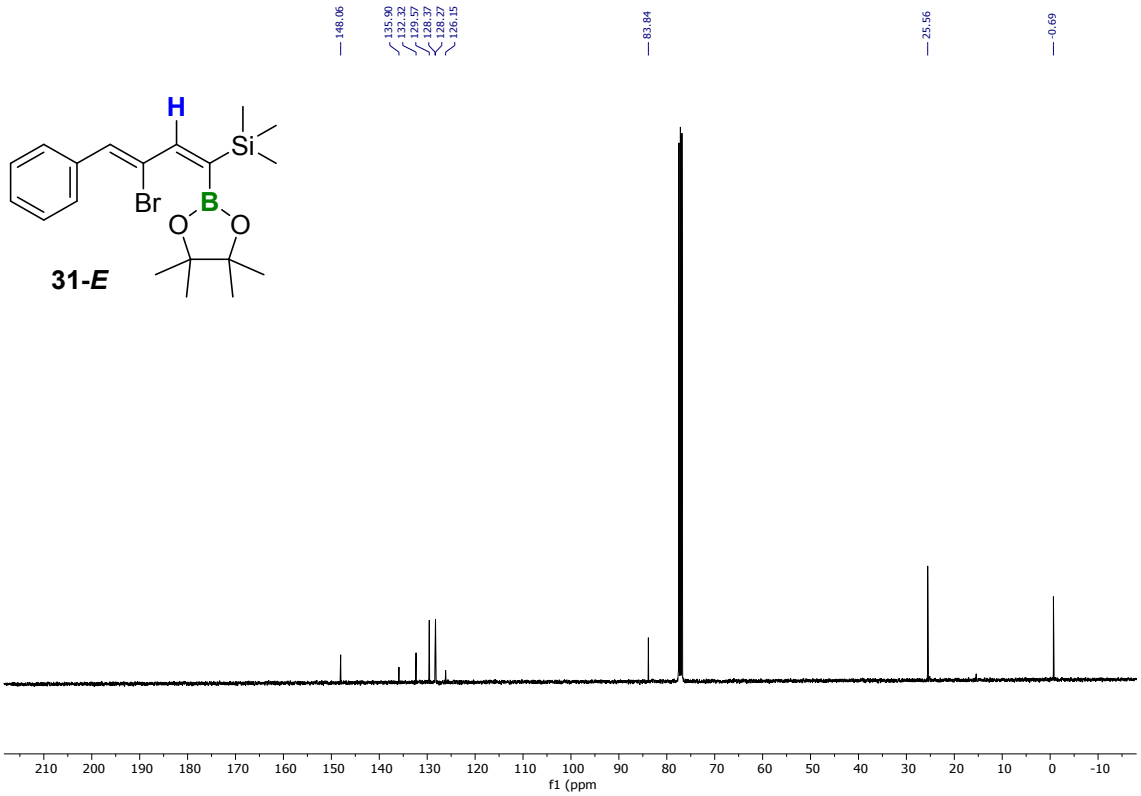
31.55
45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20
f1 (ppm

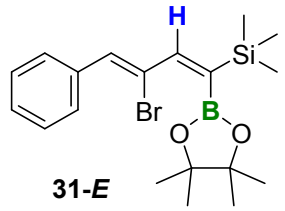

7.66 7.66 7.65 7.65 7.64 7.64 7.64 7.64 7.63 7.63 7.38 7.37 7.37 7.37 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.26 7.08 7.08 6.83 6.83
1.30
0.29
2.00
2.17
1.18
1.00
0.91
12.88
9.25
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

H
Si
Br
B
O
O

31-*E*

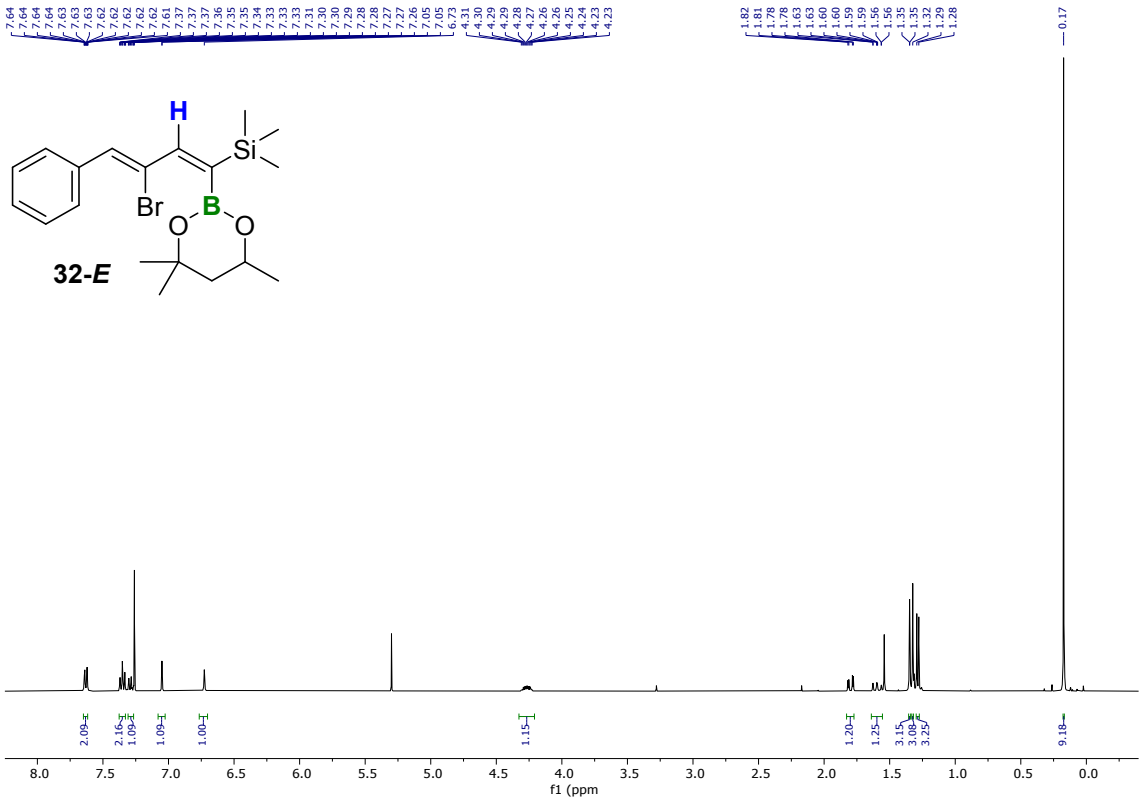

H
CH3
Si
Br
B
O
O
31-E
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm


148.06
135.90
132.32
129.57
128.37
128.27
126.15
83.84
25.56
-0.69
H
Si
Br
B
O
O
31-E
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


H
Si
Br
B
O
O

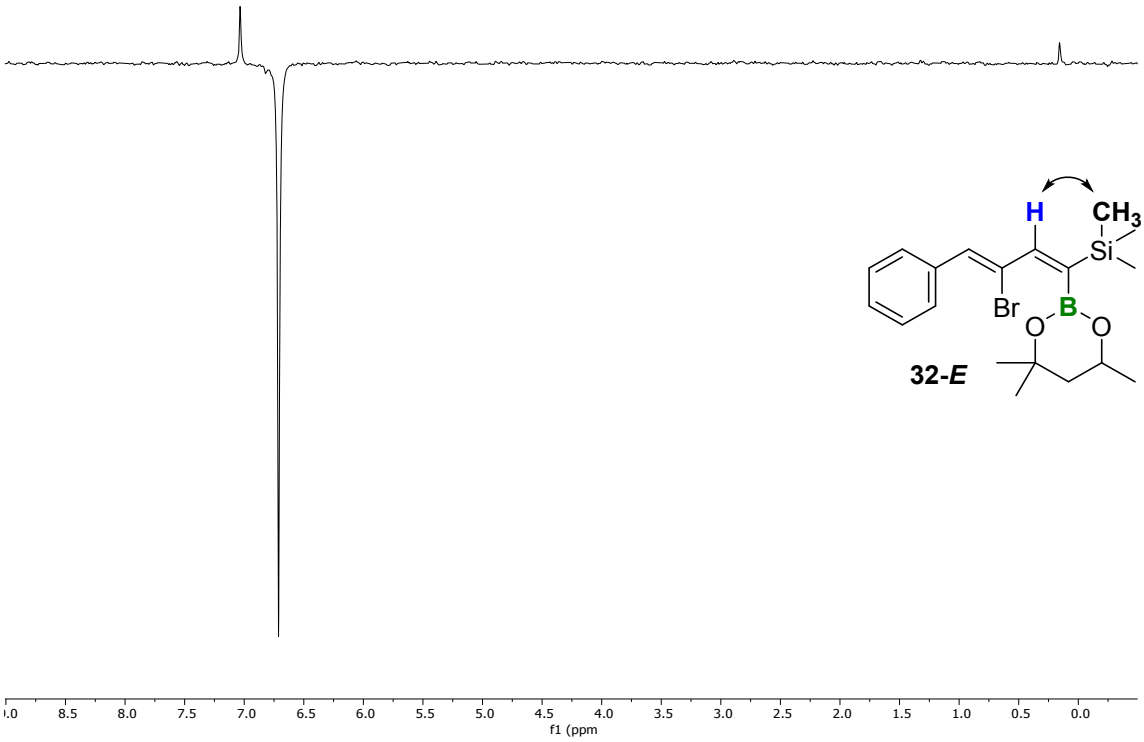
31-*E*

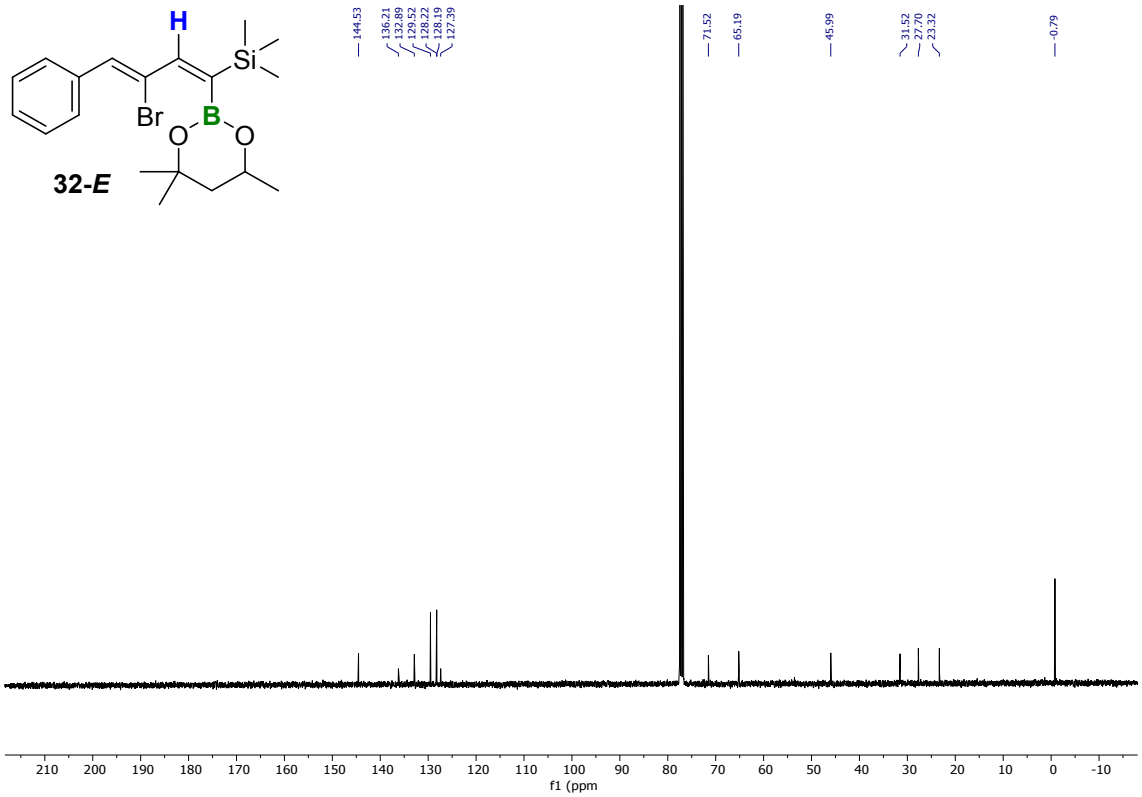
30.99
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10
f1 (ppm

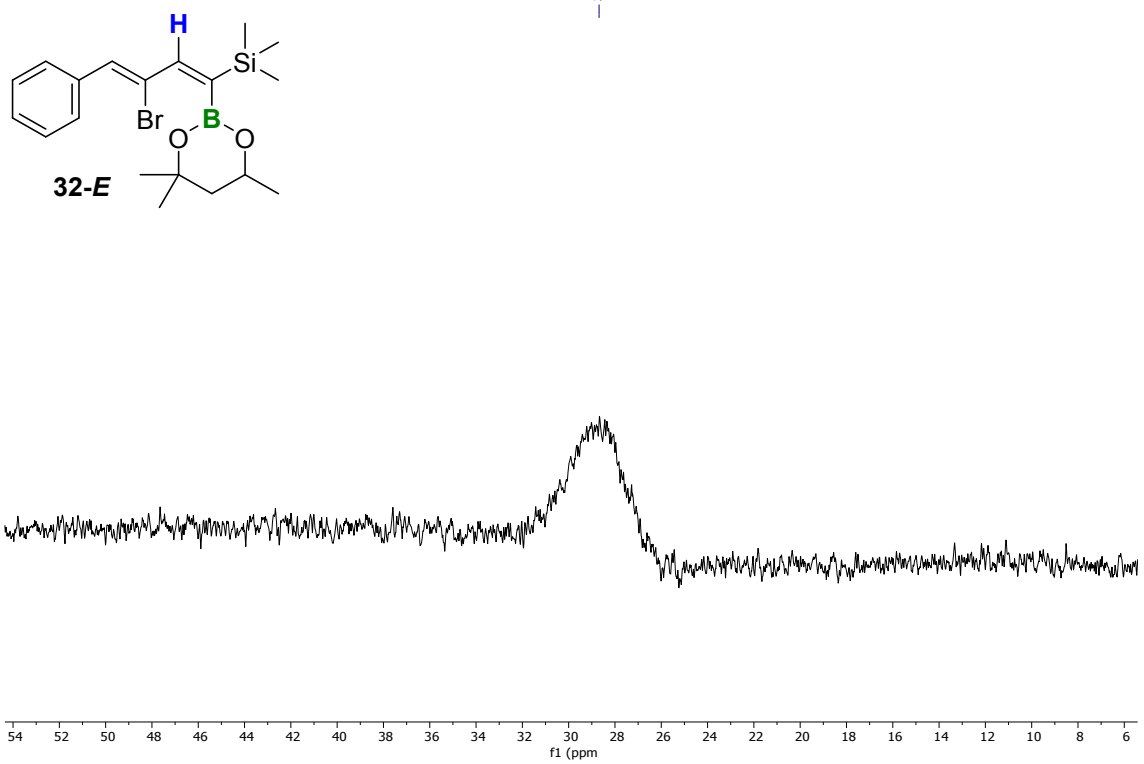

7.64 7.64 7.64 7.64 7.63 7.63 7.63 7.62 7.62 7.62 7.62 7.62 7.61 7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 7.05 7.05 6.73 4.31 4.30 4.29 4.29 4.28 4.27 4.26 4.26 4.25 4.24 4.23 4.23
1.82 1.81 1.78 1.78 1.63 1.63 1.60 1.60 1.59 1.59 1.56 1.56 1.35 1.35 1.32 1.29 1.28
0.17
2.09 2.16 1.09 1.09 1.00 1.15 1.20 1.25 3.15 3.08 3.29 9.18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

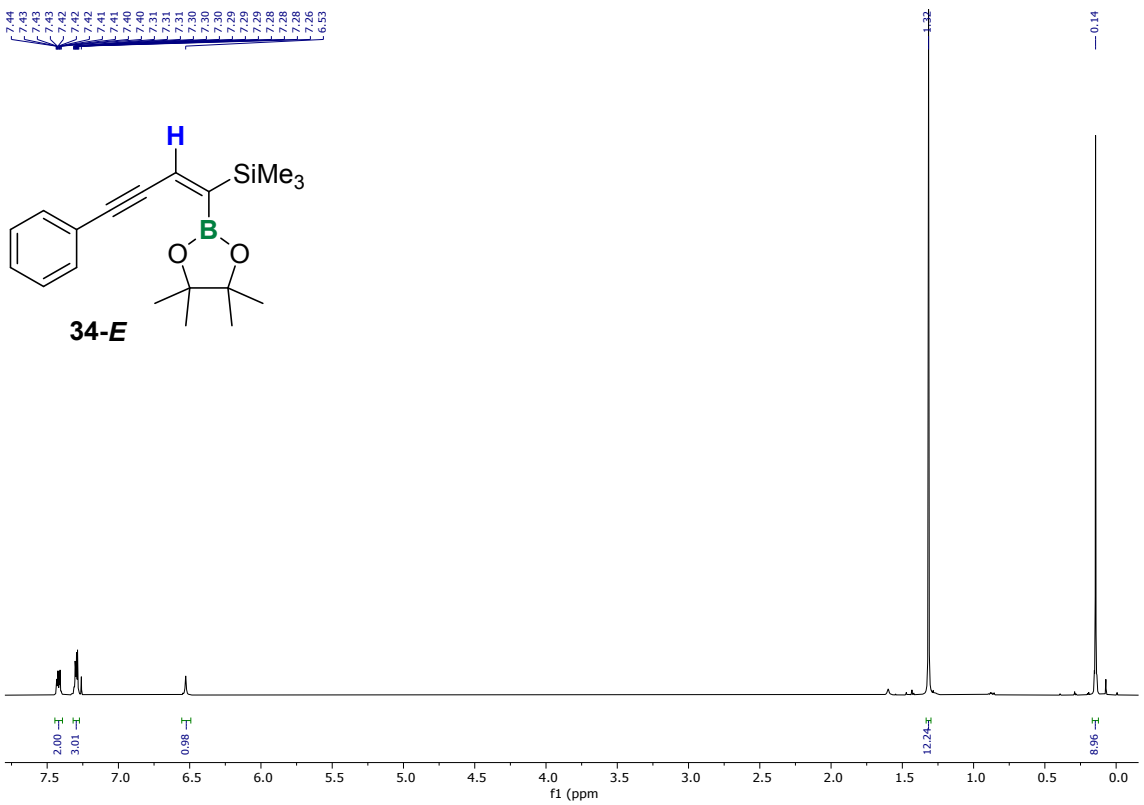
H
Si
Br
B
O
O

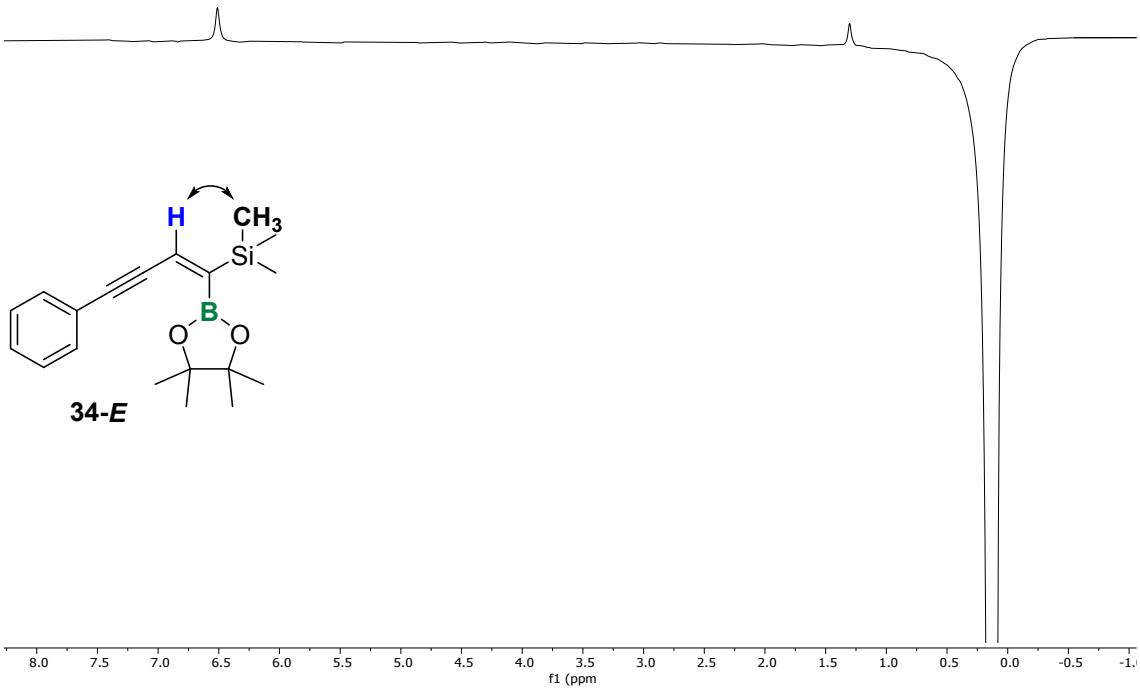
32-*E*


H
CH3
Si
Br
B
O
O
32-E
f1 (ppm

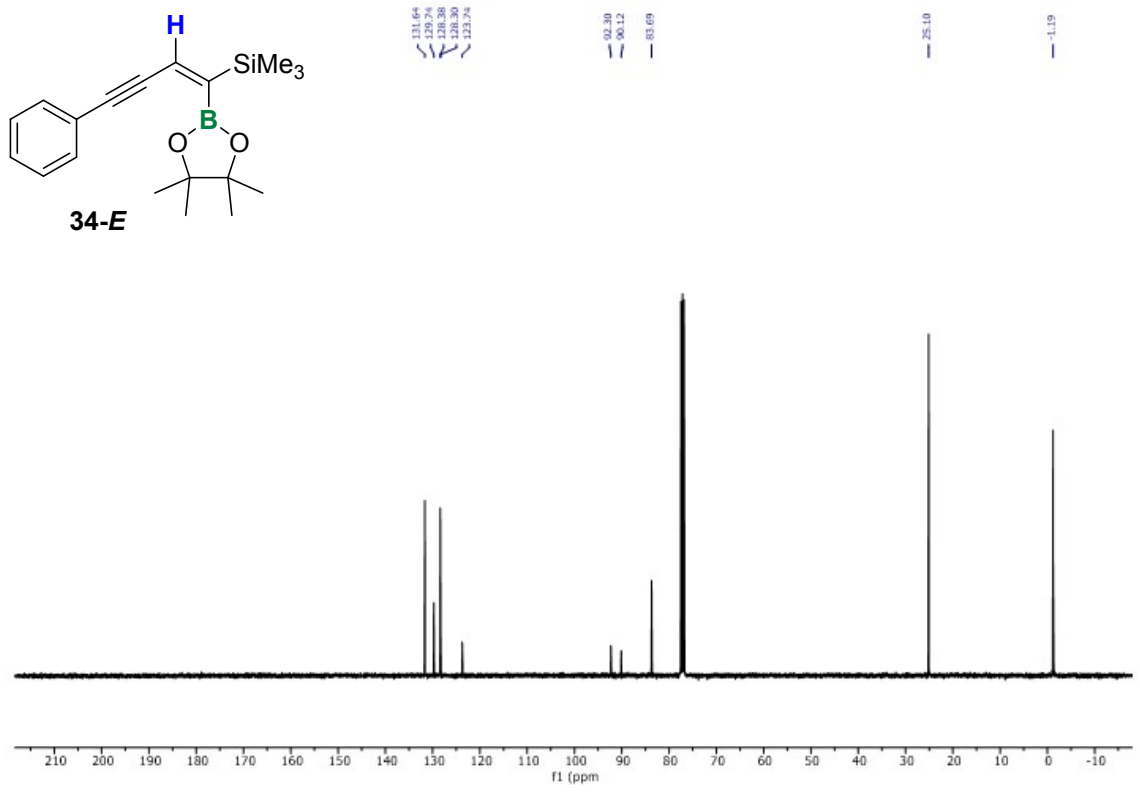

H
Si
Br
B
O
O
32-E
144.53
136.21
132.89
129.52
128.22
128.19
127.39
71.52
65.19
45.99
31.52
27.70
23.32
0.79
f1 (ppm


28.69
H
Si
Br
B
O
O
32-E
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm

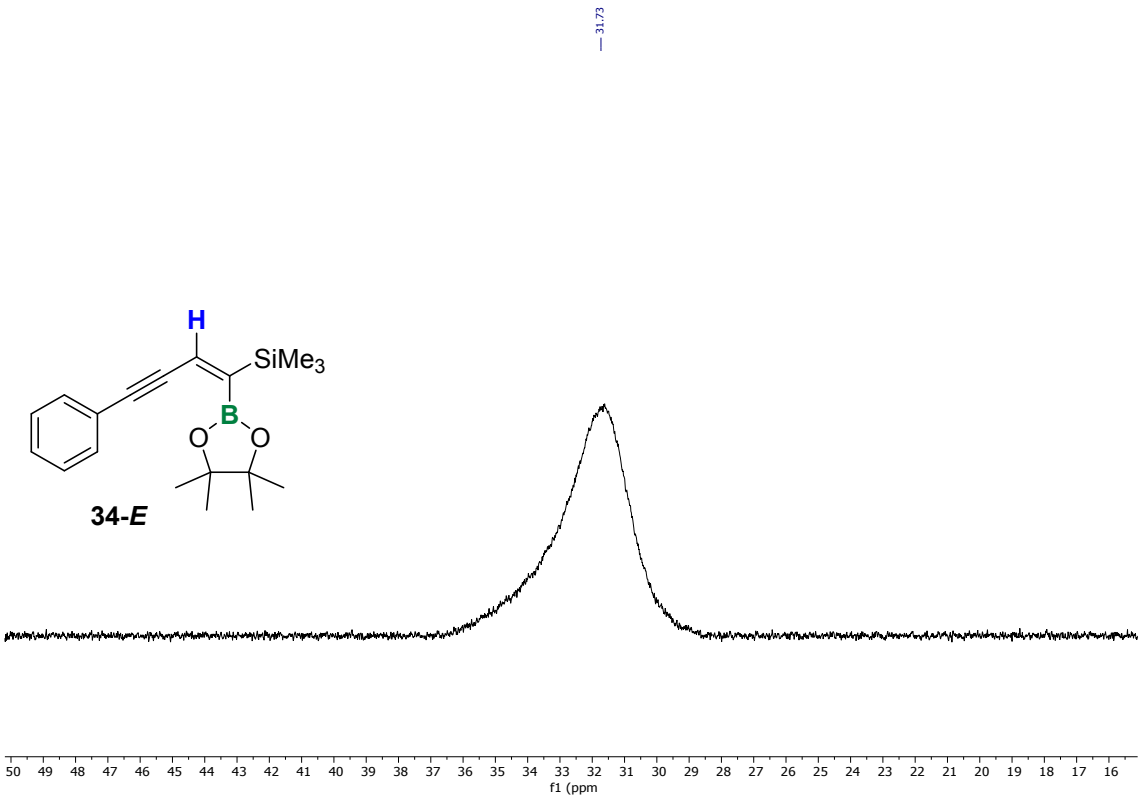

7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.26 6.53
1.32
0.14
H
SiMe3
B
O
O
34-E
2.00
3.01
0.98
12.24
8.96
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm

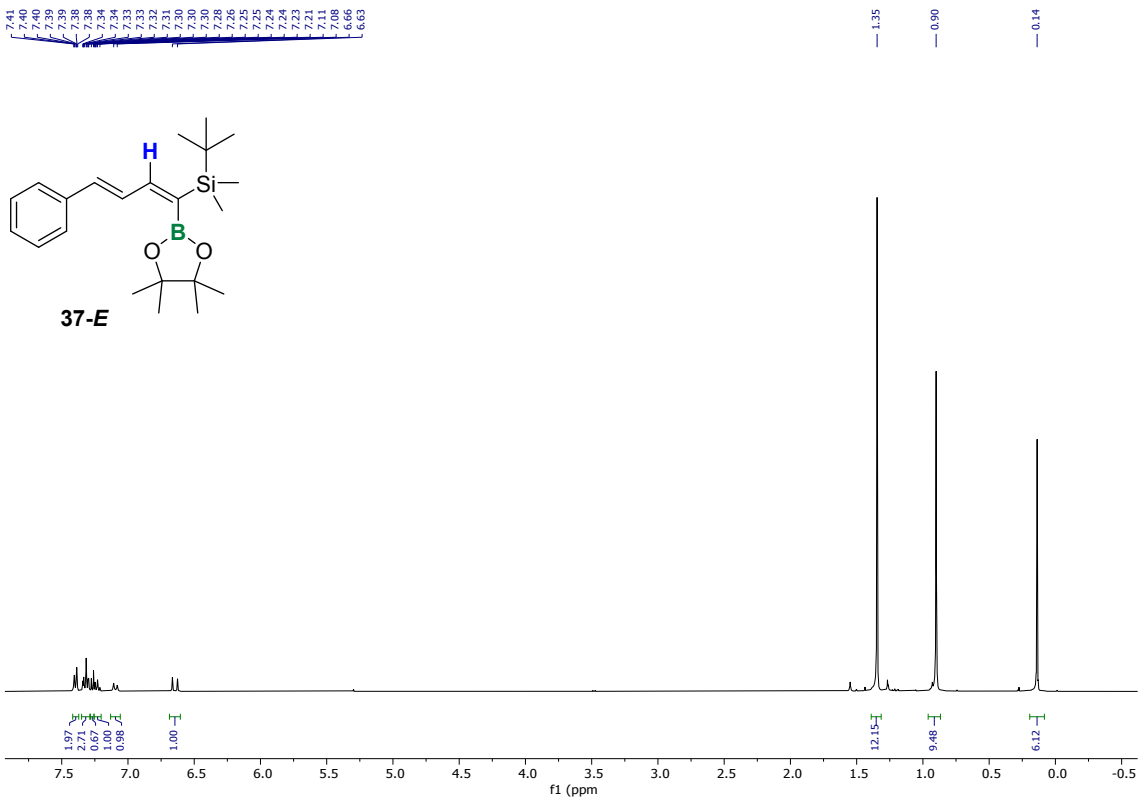

H
CH3
Si
B
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

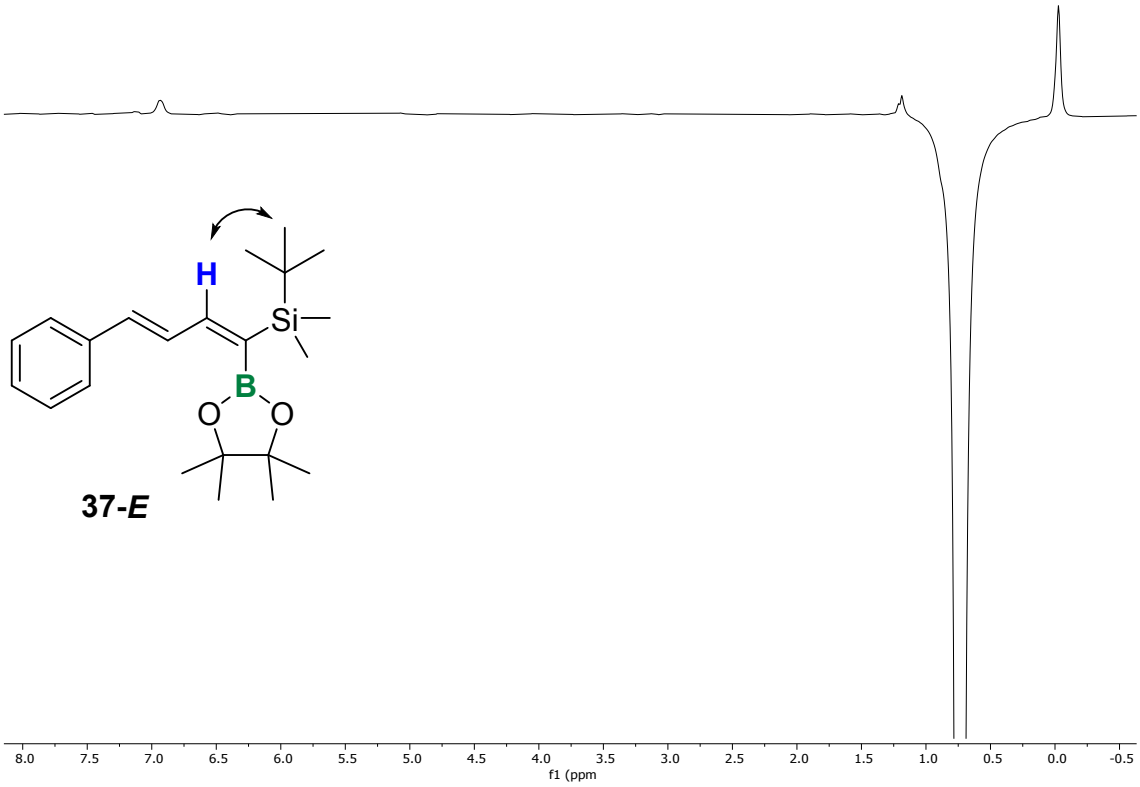
34-*E*


H
SiMe3
B
O
O
131.64
129.74
128.38
128.30
123.74
92.30
90.12
83.69
25.10
-1.19
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

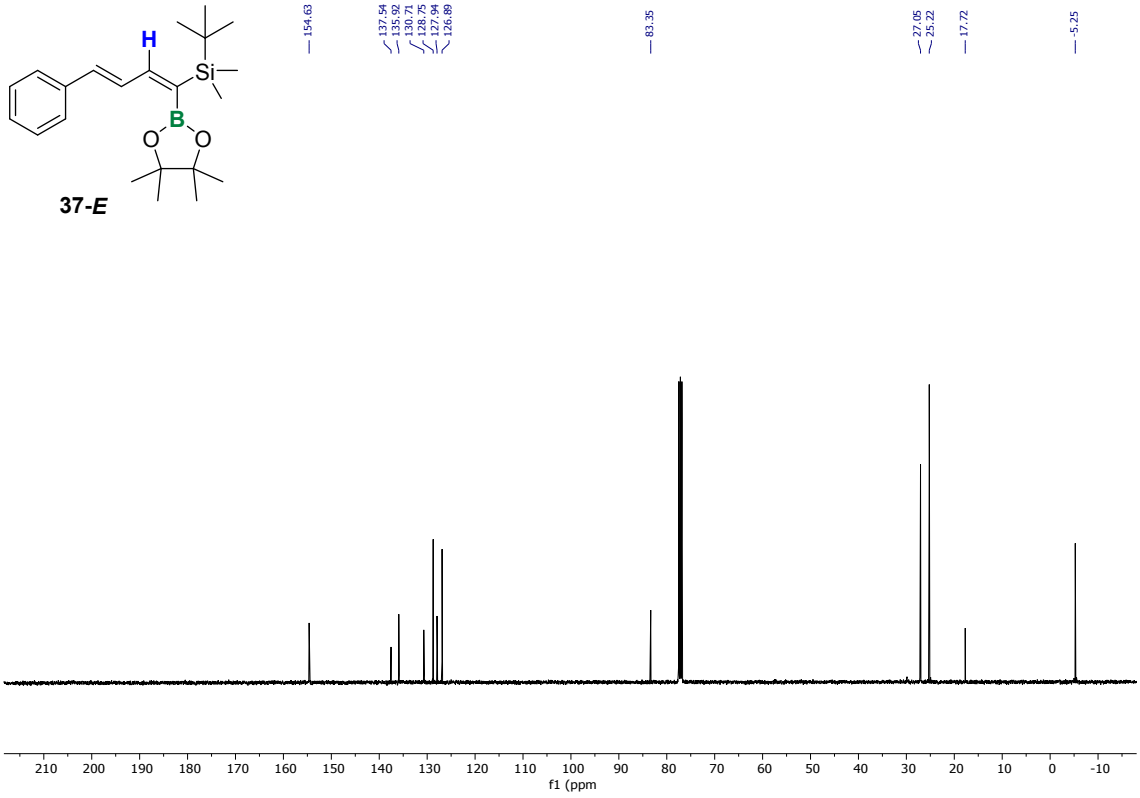
34-*E*

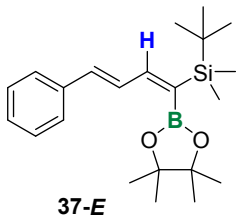

31.73
H
SiMe3
B
O
O
34-E
50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16
f1 (ppm


7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.30 7.28 7.26 7.25 7.24 7.24 7.23 7.21 7.11 7.08 6.66 6.63
1.35
0.90
0.14
H
Si
B
O
O
37-E
1.97 2.71 0.67 1.00 0.98
1.00
12.15
9.48
6.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm


H
Si
B
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm

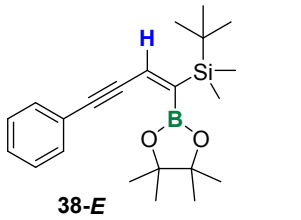
37-*E*


154.63
137.54
135.92
130.71
128.75
127.84
126.89
83.35
27.05
25.22
17.72
-5.25
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)


H
Si
B
O
O

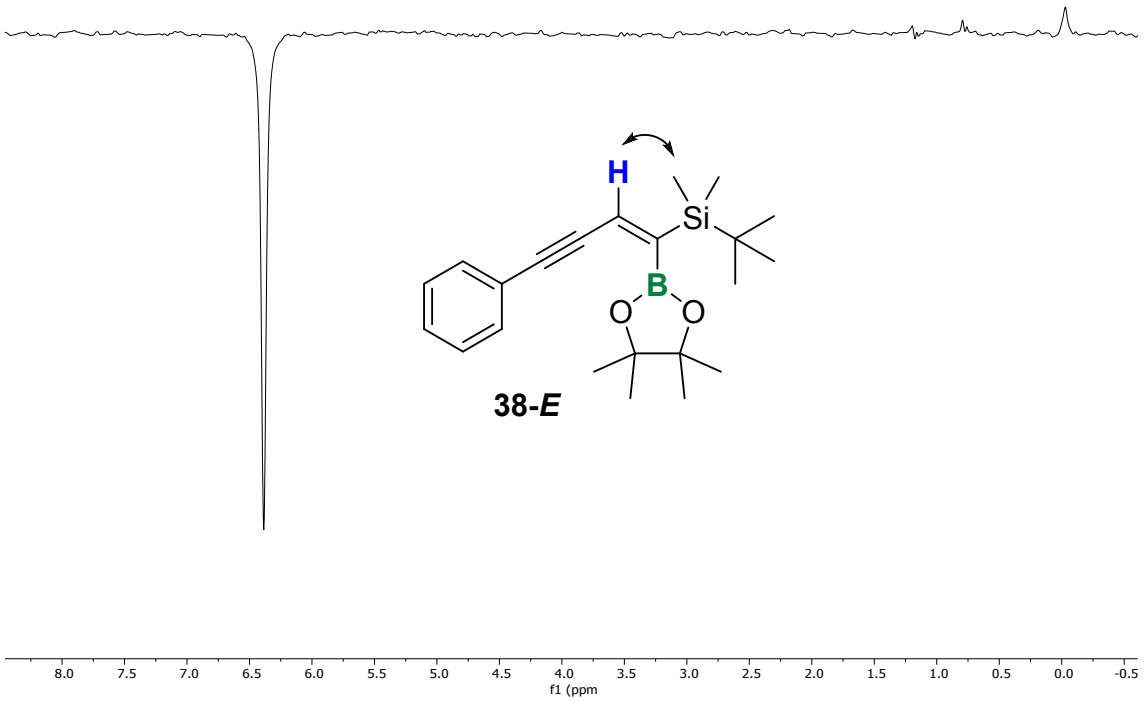
37-*E*

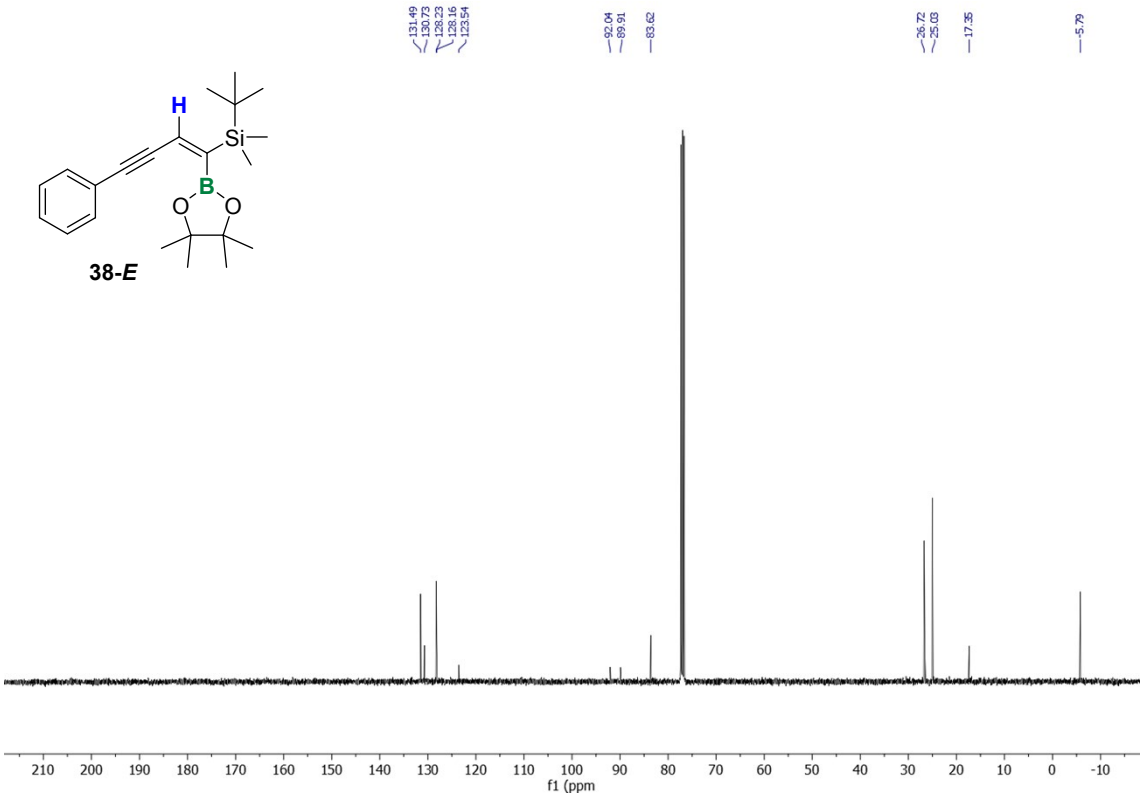
31.99
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
f1 (ppm)

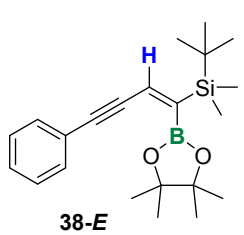

H
Si
B
O
O

38-*E*

7.63
7.62
7.61
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.31
7.31
7.30
7.29
7.29
7.28
7.27
6.53
1.31
0.91
0.12
2.05
3.04
1.00
13.28
9.18
5.85
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
Si
B
O
O
38-*E*
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm

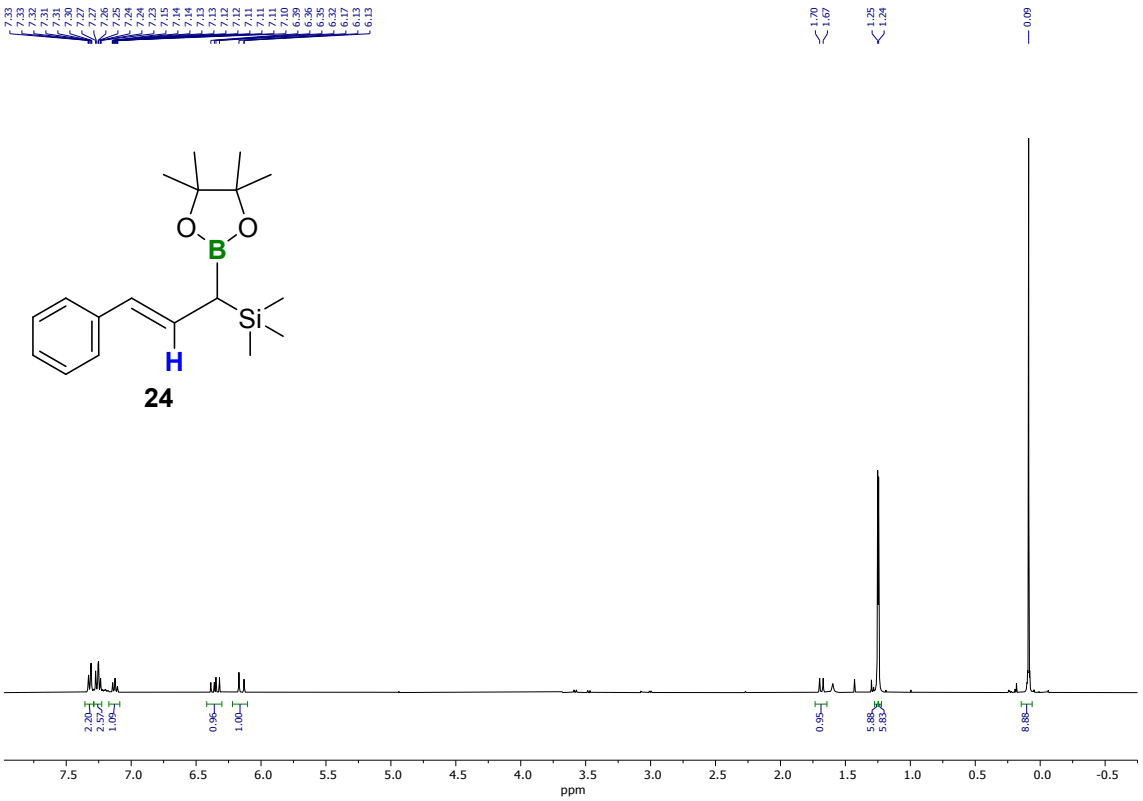

131.49
130.73
128.23
128.16
123.54
92.04
89.91
83.62
26.72
25.03
17.35
5.79
H
Si
B
O
O
38-*E*
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm

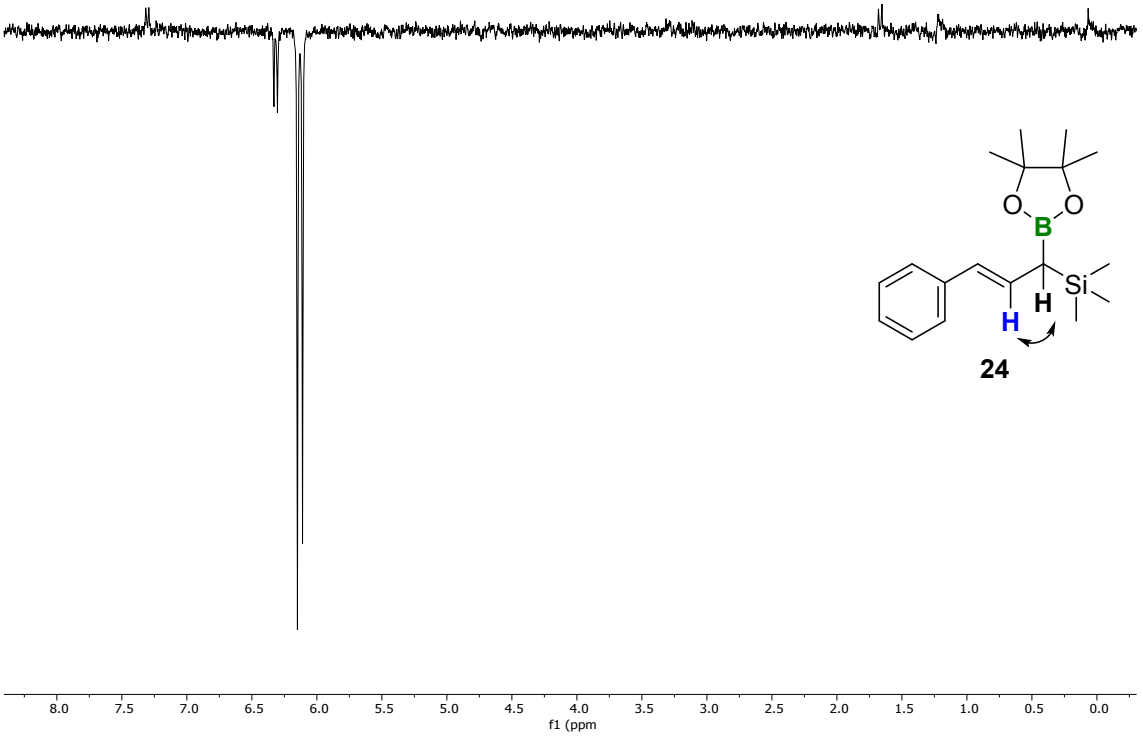

H
Si
B
O
O

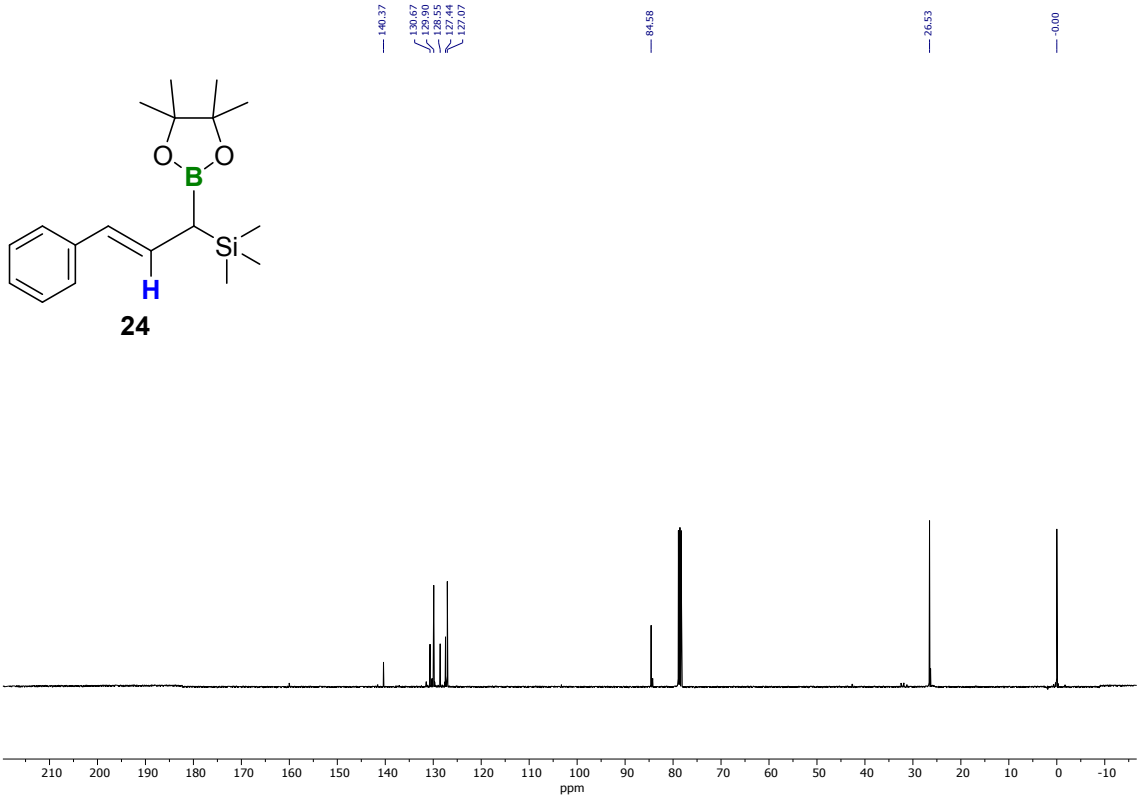
38-*E*

31.75
53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12
f1 (ppm

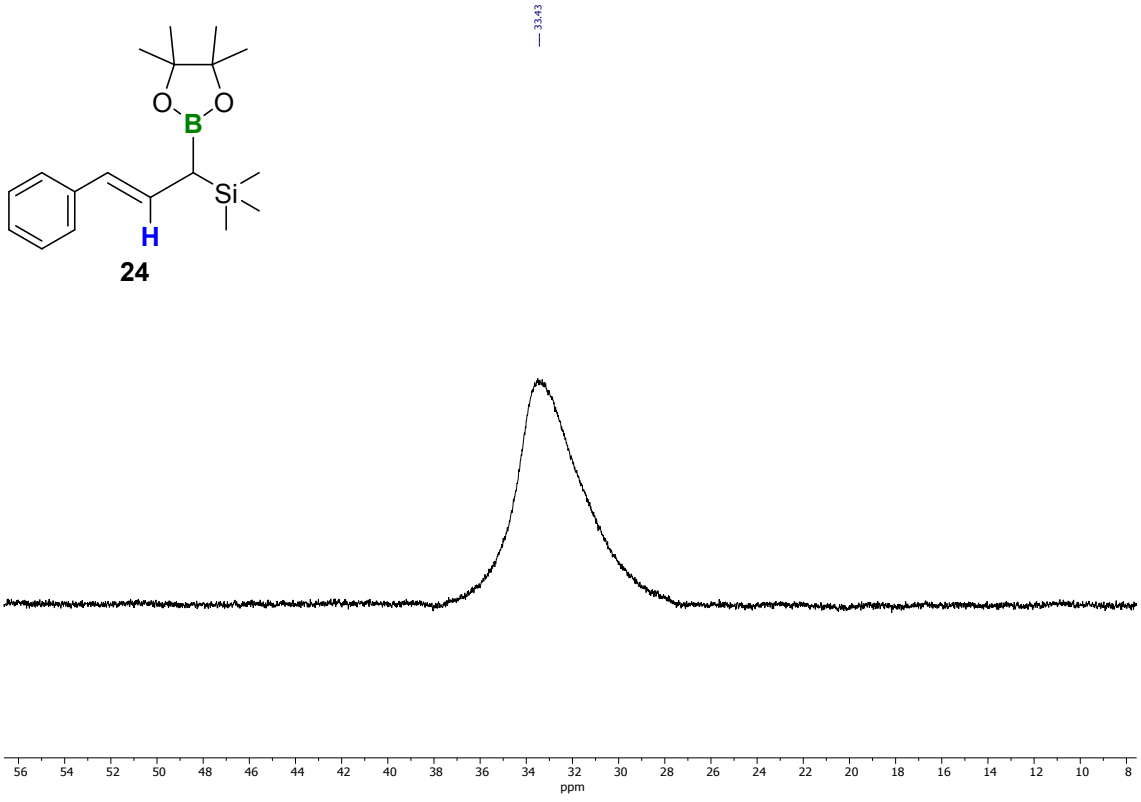
3.3. Allylic gem-Silylborylated alkene



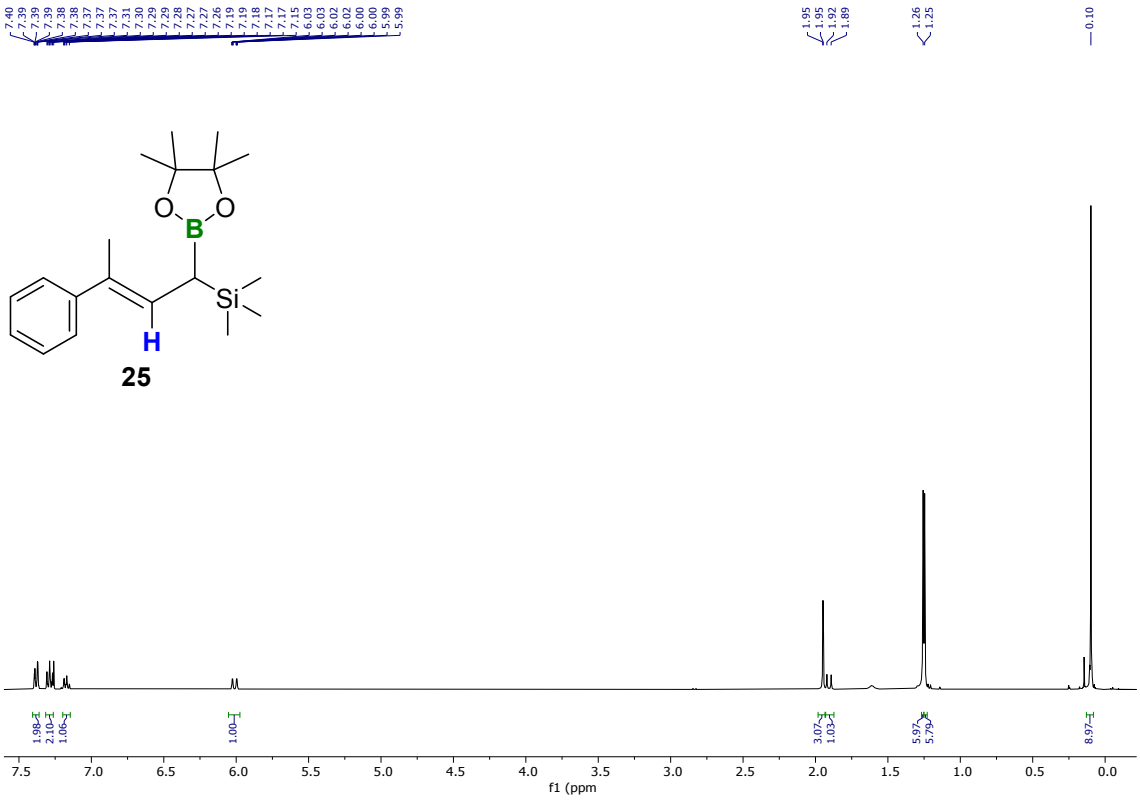


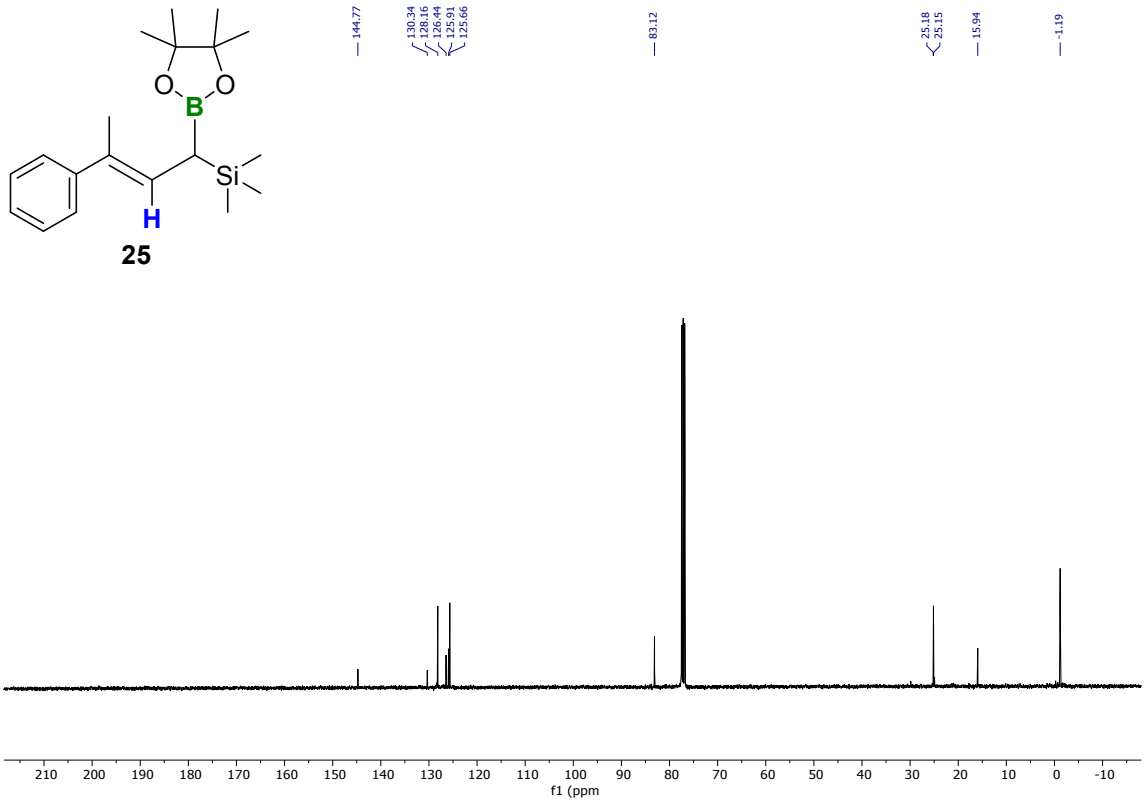

140.37
130.67
129.90
128.55
127.44
127.07
84.58
26.53
0.00
O
O
B
Si
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

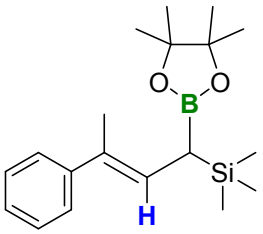
24


33.43
O
O
B
Si
H
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8
ppm

24

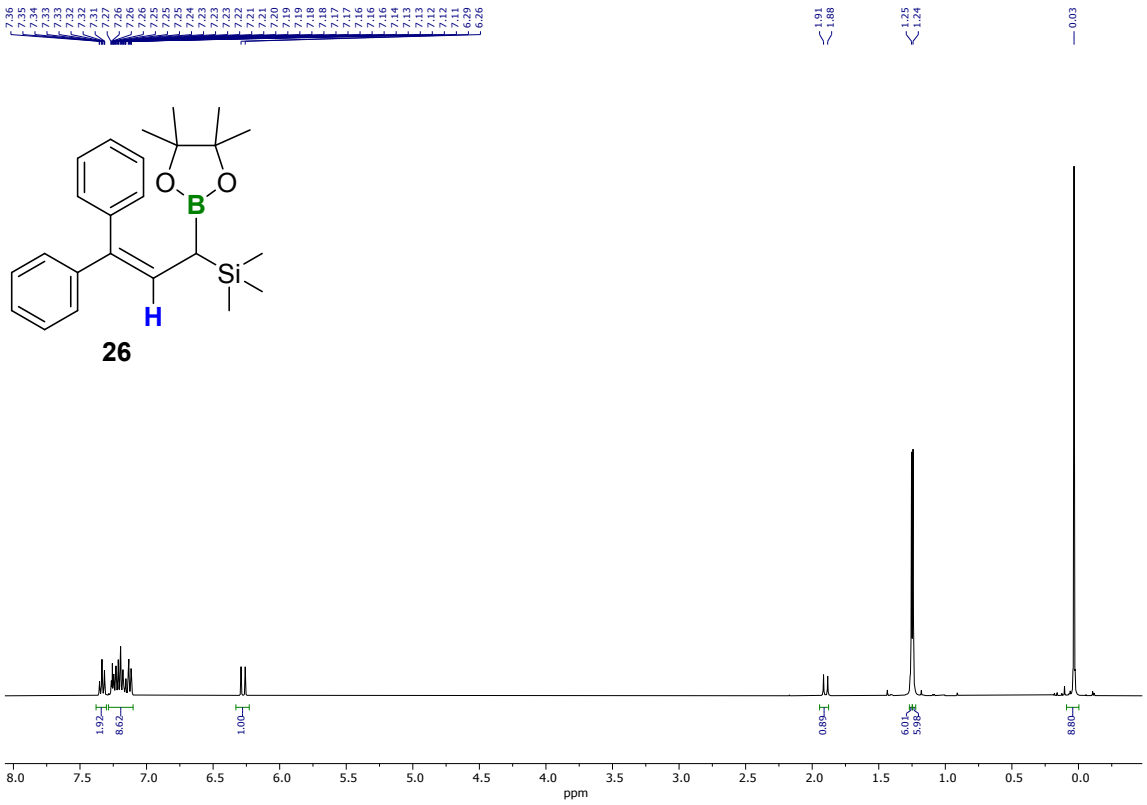

O
B
O
Si
H
25
f1 (ppm)


O
B
O
Si
H
25
f1 (ppm)


O
O
B
Si
H

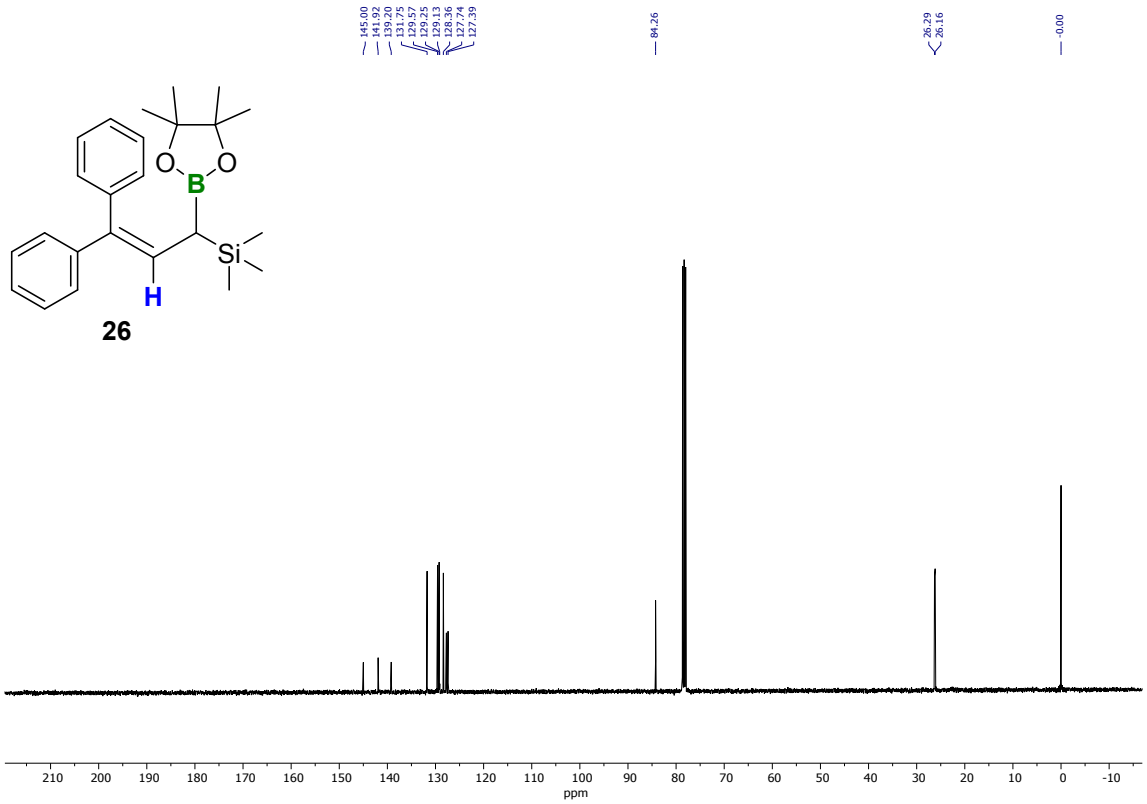
25

32.58
49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17
f1 (ppm

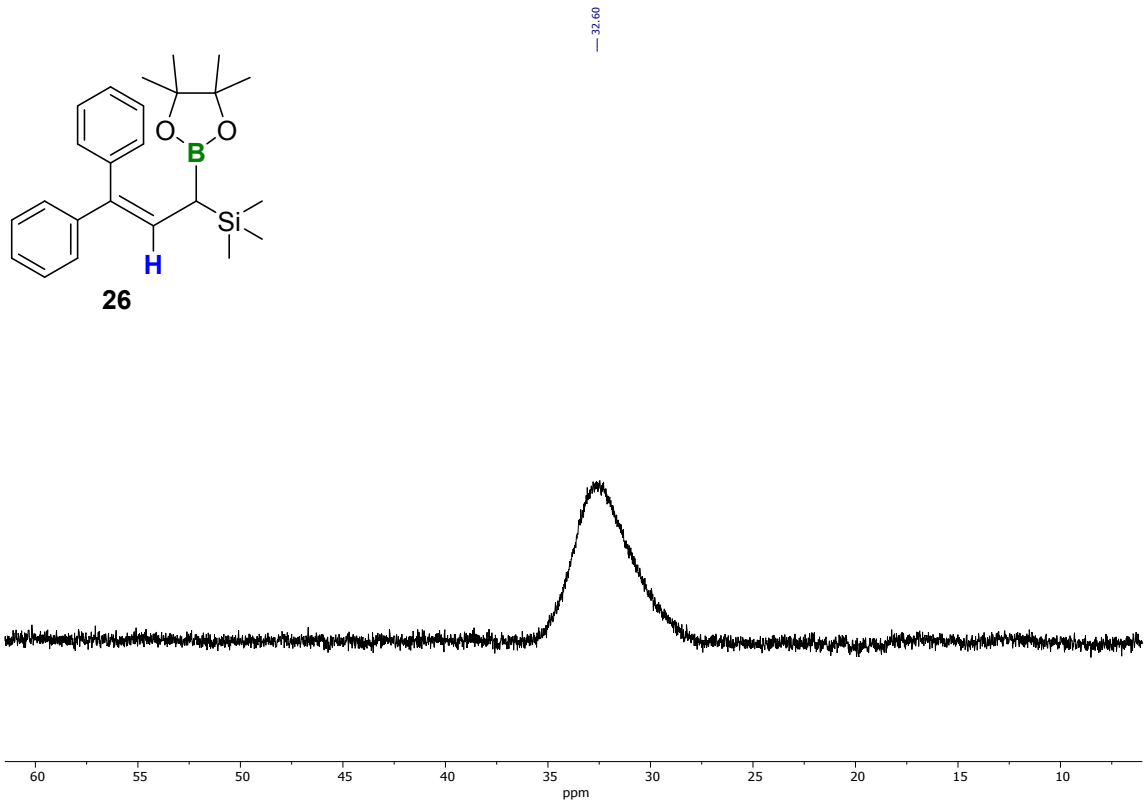

7.36 7.35 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.16 7.14 7.13 7.13 7.12 7.12 7.11 6.29 6.26
1.91
1.88
1.25
1.24
0.03
1.92
8.62
1.00
0.89
6.01
5.98
8.80
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

O
O
B
Si
H

26

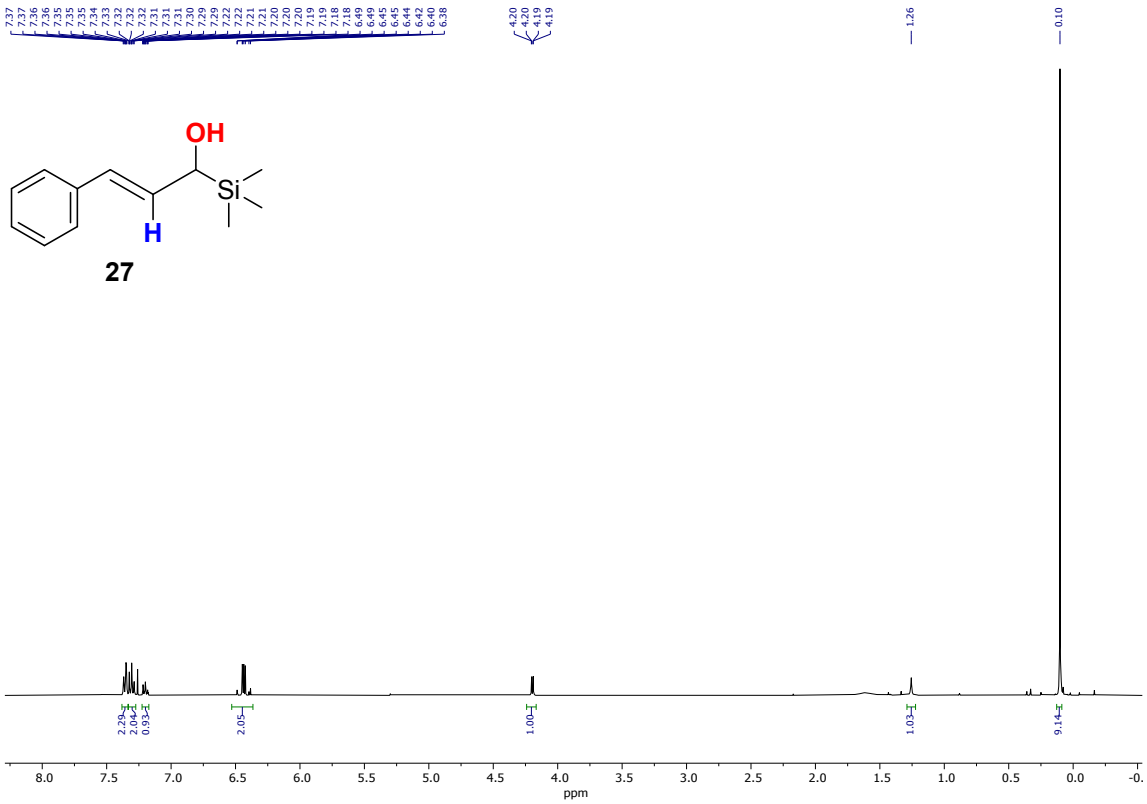


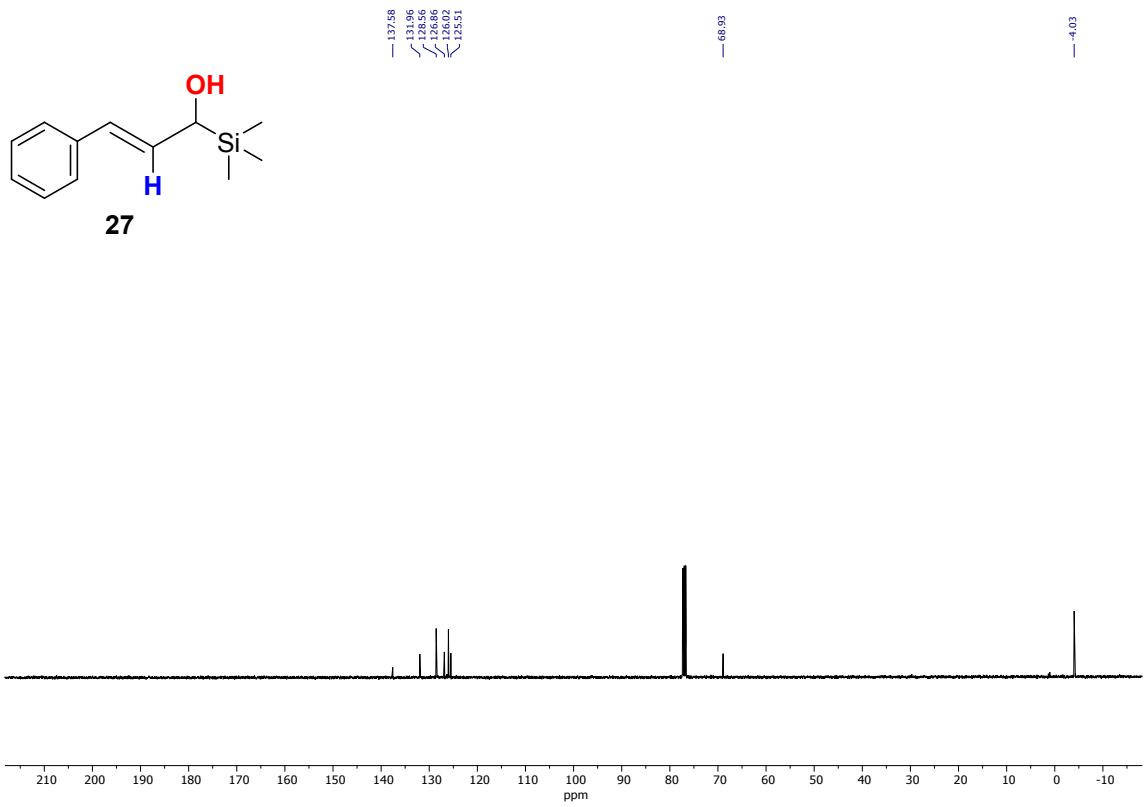
26

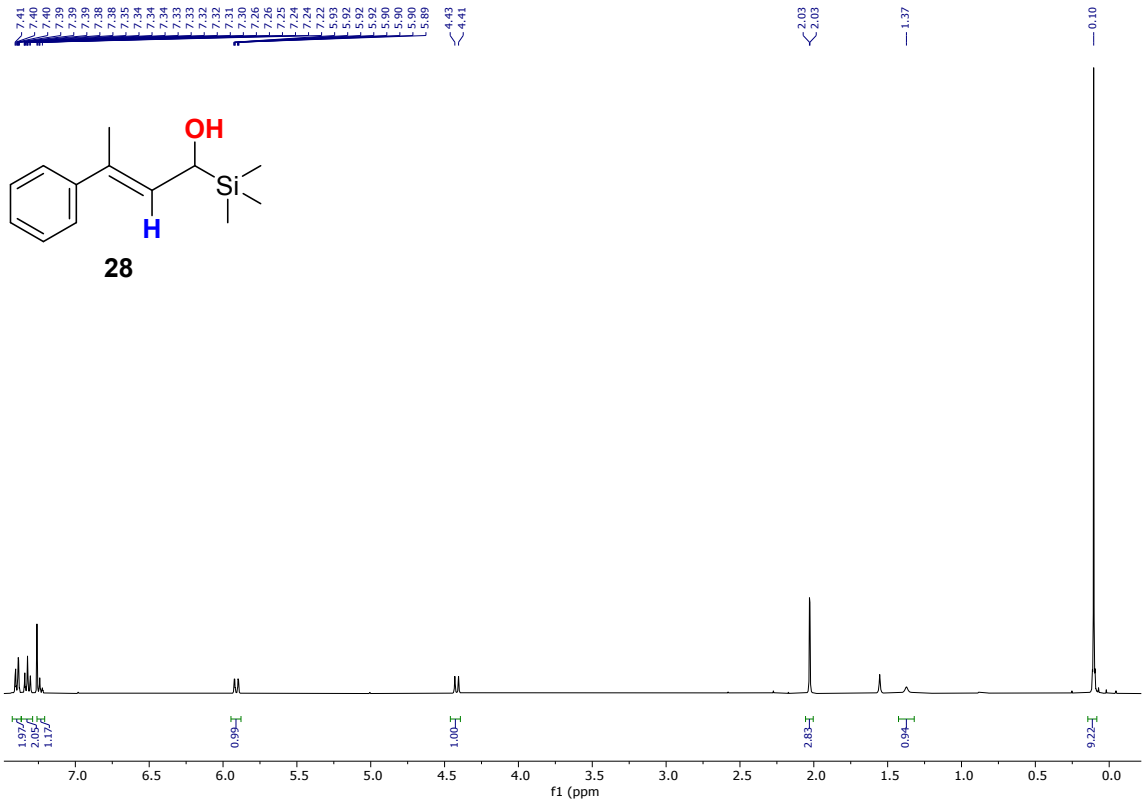


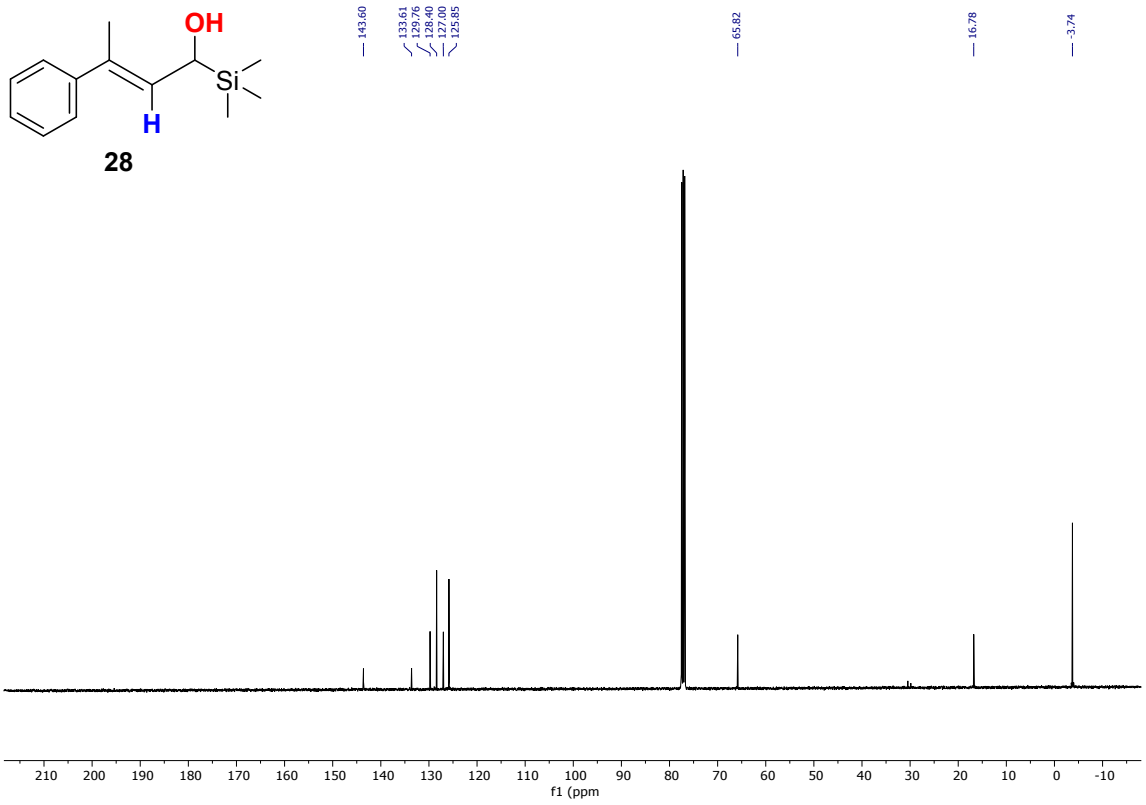
26

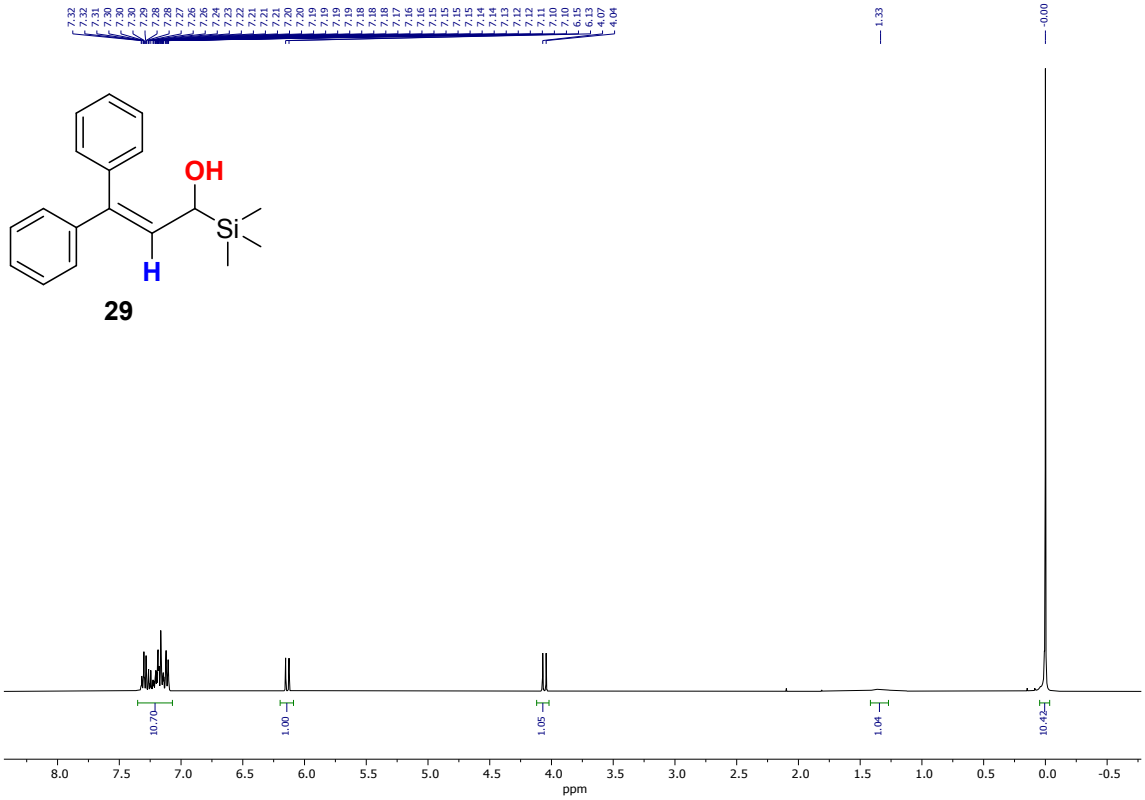
3.5 Allylic alcohols

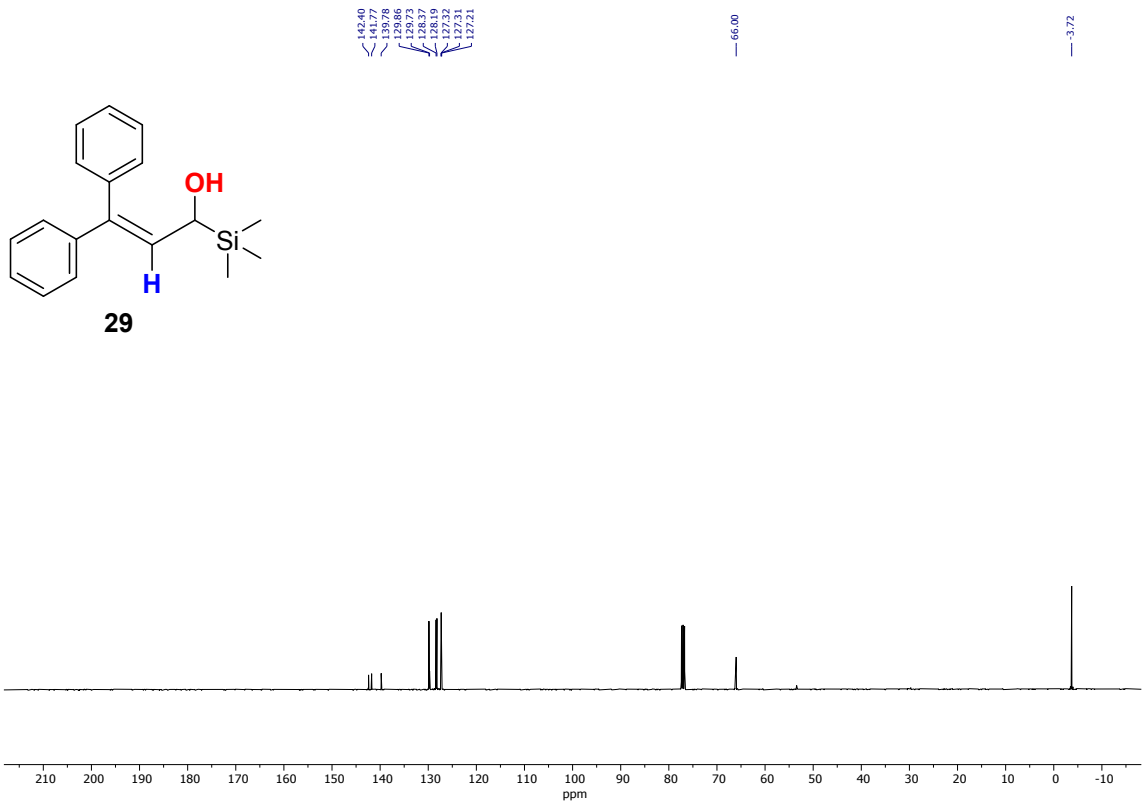

OH
Si
H
27
ppm


OH
Si
H
27
ppm

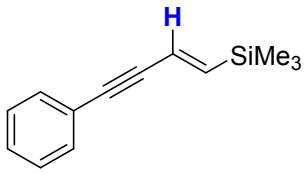

OH
Si
H
28
f1 (ppm)


OH
Si
H
28
f1 (ppm)

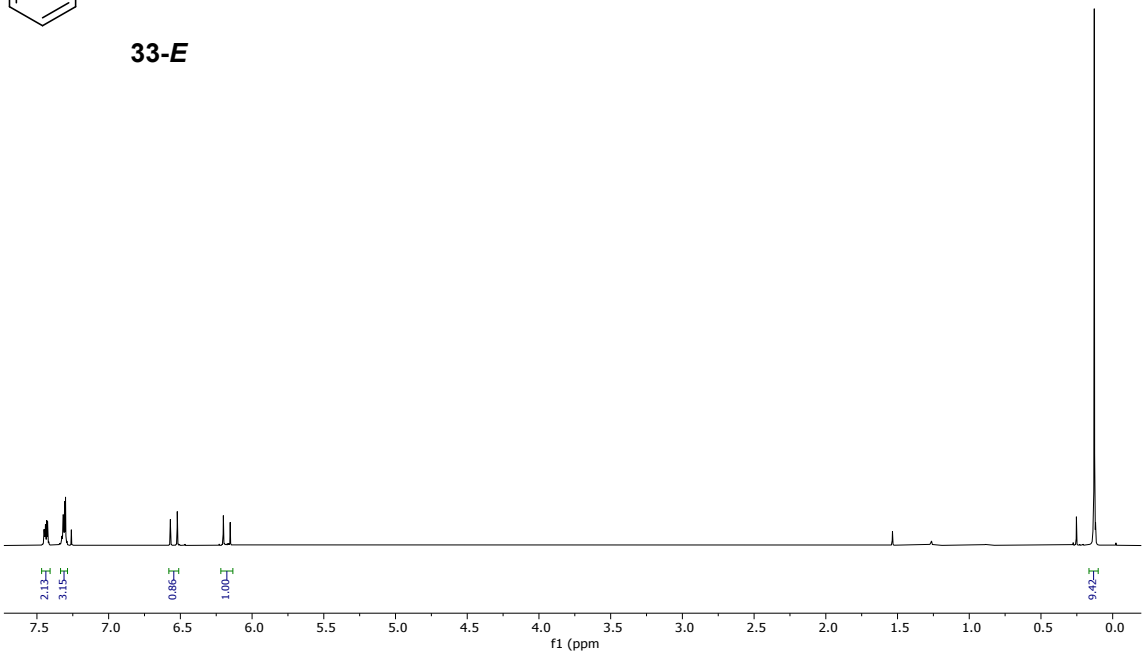

OH
Si
H
29
ppm

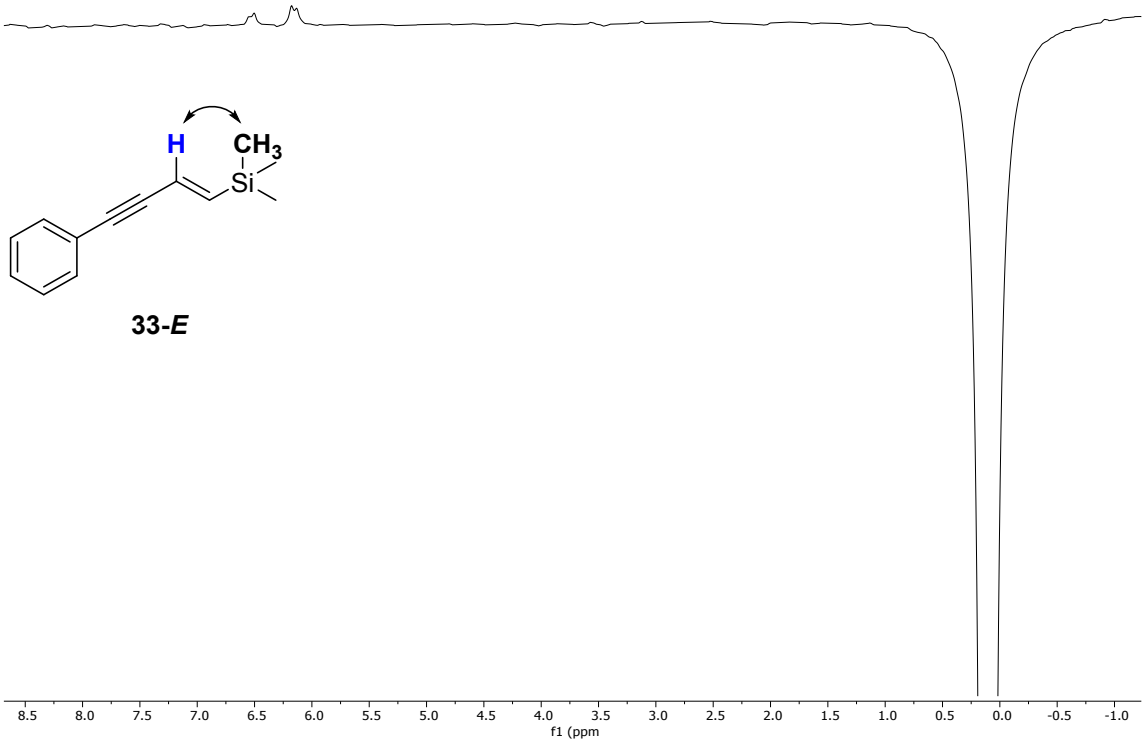

OH
Si
H
29
ppm

3.5 (E)-trimethyl(4-phenylbut-1-en-3-yn-1-yl)silane (33-E)

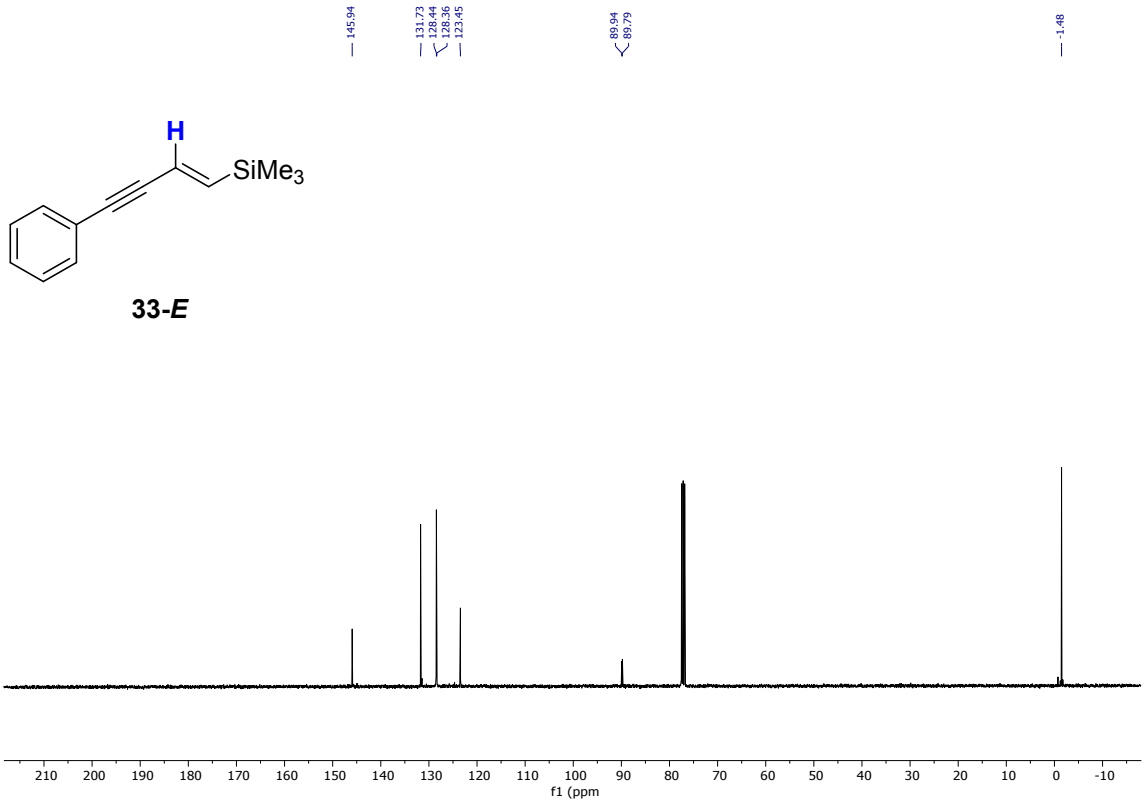


33-*E*




H
CH3
Si
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm

33-*E*


145.94
131.73
128.44
128.36
123.45
89.94
89.79
-1.48
H
SiMe3
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

33-*E*

4.X-Ray Diffraction of 13-E

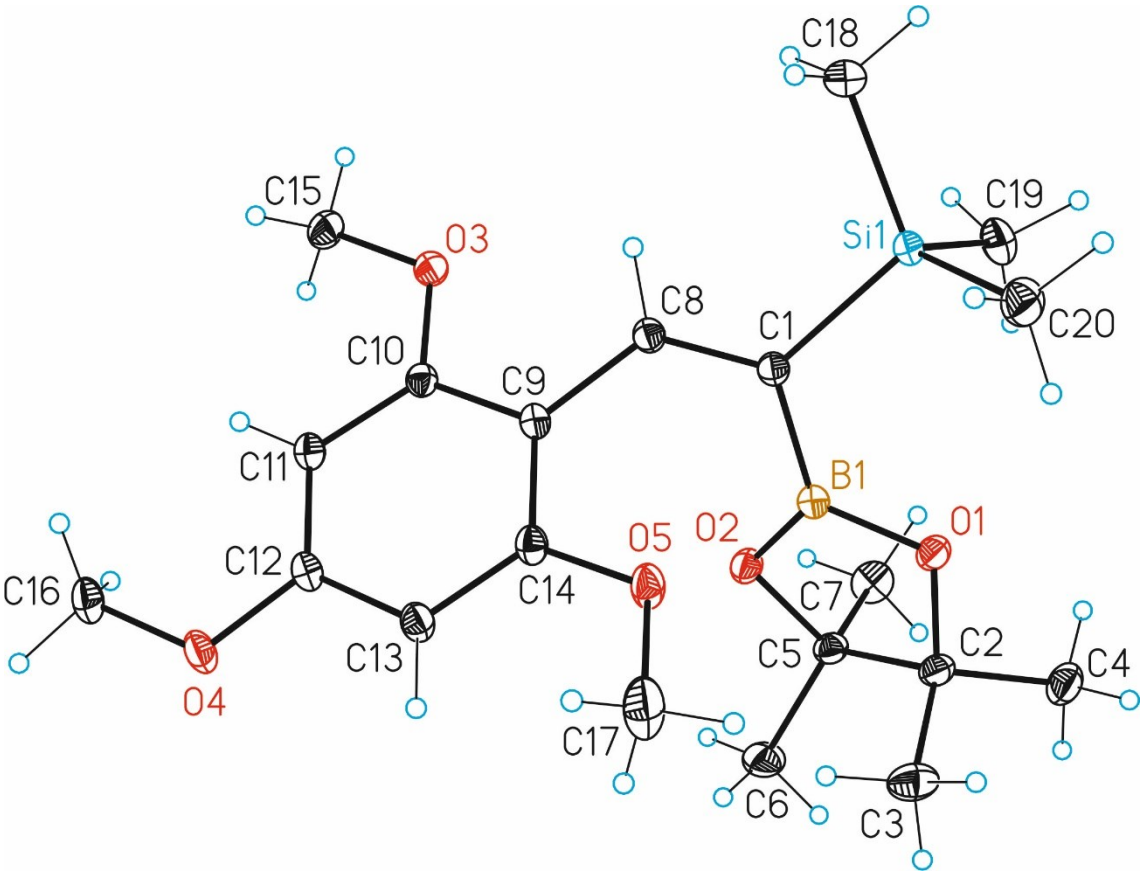


Figure S1. ORTEP drawing with thermal ellipsoids drawn to the 50 % level

Data collection: The measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Crystal structure determination for compound 13-E was carried out using a Rigaku diffractometer equipped with a Pilatus 200K area detector, a Rigaku MicroMax-007HF microfocus rotating anode with MoK_α radiation, Confocal Max Flux optics and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 ˚C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection data reduction with CrysAlisPro[1] and absorption correction with Scale3 Abspack scaling algorithm[2].

[1] Data reduction with CrysAlisPro 1.171.40.35 (Rigaku OD, 2018).
[2] Empirical absorption correction using spherical harmonics implemented in Scale3 Abspack scaling algorithm, CrysAlisPro 1.171.40.35 (Rigaku OD, 2018).

Structure Solution and Refinement: Crystal structure solution was achieved using the computer program SHELXT[3] . Visualization was performed with the program SHELXle[4]. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015[5]. All non hydrogen atoms were refined including anisotropic displacement parameters.

Table 1. Crystal data and structure refinement for 13-E.

Identification code	OSTriOMeSiB	
Empirical formula	C20 H33 B O5 Si	
Formula weight	392.36	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.32916(12)Å	α= 90°.
	b = 16.4248(2)Å	β = 100.2007(16)°.
	c = 18.8570(3)Å	γ = 90°.
Volume	2234.12(6) $Å^3$	
Z	4	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	848	
Crystal size	0.300 x 0.300 x 0.300 mm^3	
Theta range for data collection	2.480 to 34.428°.	
Index ranges	-11<=h<=10,-25<=k<=25,-30<=l<=28	
Reflections collected	27323	
Independent reflections	8944[R(int) = 0.0147]	
Completeness to theta =34.428°	94.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	1.00 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8944/ 0/ 254	

[3] SHELXT; V2018/2. Sheldrick, G.M. *Acta Cryst*. **2015** A71, 3-8.
[4] SHELXle; C.B. Huebschle, G.M. Sheldrick & B. Dittrich; J.Appl.Cryst. (2011) 44, 1281-1284.
[5] SHELXL; SHELXL-2018/3. Sheldrick, G.M. *Acta Cryst*. **2015** C71, 3-8.

Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0884
R indices (all data)	R1 = 0.0330, wR2 = 0.0903
Largest diff. peak and hole	0.584 and -0.190 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [°] for 13-E.

Bond lengths----

Si1	C20	1.8760(7)
Si1	C18	1.8769(7)
Si1	C19	1.8770(7)
Si1	C1	1.8791(6)
O1	B1	1.3796(8)
O1	C2	1.4610(7)
O2	B1	1.3794(8)
O2	C5	1.4603(7)
O3	C10	1.3701(7)
O3	C15	1.4333(8)
O4	C12	1.3667(7)
O4	C16	1.4342(8)
O5	C14	1.3668(7)
O5	C17	1.4267(8)
C1	C8	1.3559(8)
C1	B1	1.5613(9)
C2	C4	1.5215(9)
C2	C3	1.5267(9)
C2	C5	1.5666(8)
C5	C6	1.5208(9)
C5	C7	1.5291(9)
C8	C9	1.4785(8)
C9	C10	1.4067(8)
C9	C14	1.4146(8)
C10	C11	1.4010(8)
C11	C12	1.3932(8)
C12	C13	1.3987(8)
C13	C14	1.3960(8)

Angles----------

C20 Si1 C18 108.58(4)
C20 Si1 C19 110.88(3)
C18 Si1 C19 107.92(4)
C20 Si1 C1 107.72(3)
C18 Si1 C1 111.53(3)
C19 Si1 C1 110.22(3)
B1 O1 C2 107.69(5)
B1 O2 C5 107.12(5)
C10 O3 C15 117.22(5)
C12 O4 C16 116.85(5)
C14 O5 C17 117.22(5)
C8 C1 B1 123.53(5)
C8 C1 Si1 120.42(4)
B1 C1 Si1 116.04(4)
O1 C2 C4 108.79(5)
O1 C2 C3 107.07(5)
C4 C2 C3 109.76(5)
O1 C2 C5 102.09(4)
C4 C2 C5 114.96(5)
C3 C2 C5 113.52(5)
O2 C5 C6 109.05(5)
O2 C5 C7 106.25(5)
C6 C5 C7 110.18(5)
O2 C5 C2 102.60(4)
C6 C5 C2 115.01(5)
C7 C5 C2 113.05(5)
C1 C8 C9 127.66(5)
C10 C9 C14 116.73(5)
C10 C9 C8 120.09(5)
C14 C9 C8 122.97(5)
O3 C10 C11 122.08(5)
O3 C10 C9 115.17(5)
C11 C10 C9 122.75(5)
C12 C11 C10 118.25(5)
O4 C12 C11 123.49(5)
O4 C12 C13 115.14(5)
C11 C12 C13 121.38(5)
C14 C13 C12 119.05(5)

O5	C14	C13	122.15(5)
O5	C14	C9	115.98(5)
C13	C14	C9	121.85(5)
O2	B1	O1	112.55(5)
O2	B1	C1	124.66(5)
O1	B1	C1	121.95(5)

Table 3. Torsion angles [°] for 13-E.

C20	Si1	C1	C8	112.14(5)
C18	Si1	C1	C8	-6.91(6)
C19	Si1	C1	C8	-126.77(5)
C20	Si1	C1	B1	-68.83(5)
C18	Si1	C1	B1	172.12(5)
C19	Si1	C1	B1	52.27(5)
B1	O1	C2	C4	144.07(5)
B1	O1	C2	C3	-97.37(6)
B1	O1	C2	C5	22.14(6)
B1	O2	C5	C6	146.19(5)
B1	O2	C5	C7	-95.07(6)
B1	O2	C5	C2	23.81(6)
O1	C2	C5	O2	-27.64(5)
C4	C2	C5	O2	-145.23(5)
C3	C2	C5	O2	87.24(6)
O1	C2	C5	C6	-145.89(5)
C4	C2	C5	C6	96.52(7)
C3	C2	C5	C6	-31.02(8)
O1	C2	C5	C7	86.36(6)
C4	C2	C5	C7	-31.23(7)
C3	C2	C5	C7	-158.77(6)
B1	C1	C8	C9	12.02(10)
Si1	C1	C8	C9	-169.02(5)
C1	C8	C9	C10	-142.01(6)
C1	C8	C9	C14	43.41(9)
C15	O3	C10	C11	-1.23(8)
C15	O3	C10	C9	177.70(5)
C14	C9	C10	O3	-178.94(5)

C8 C9 C10 O3 6.15(8)
C14 C9 C10 C11 -0.03(8)
C8 C9 C10 C11 -174.94(5)
O3 C10 C11 C12 178.54(5)
C9 C10 C11 C12 -0.30(9)
C16 O4 C12 C11 -3.87(9)
C16 O4 C12 C13 176.05(5)
C10 C11 C12 O4 179.89(5)
C10 C11 C12 C13 -0.02(9)
O4 C12 C13 C14 -179.25(5)
C11 C12 C13 C14 0.66(9)
C17 O5 C14 C13 -9.89(10)
C17 O5 C14 C9 168.44(7)
C12 C13 C14 O5 177.22(6)
C12 C13 C14 C9 -1.02(9)
C10 C9 C14 O5 -177.64(5)
C8 C9 C14 O5 -2.89(8)
C10 C9 C14 C13 0.70(9)
C8 C9 C14 C13 175.45(6)
C5 O2 B1 O1 -10.99(7)
C5 O2 B1 C1 158.68(5)
C2 O1 B1 O2 -8.22(7)
C2 O1 B1 C1 -178.21(5)
C8 C1 B1 O2 37.72(9)
Si1 C1 B1 O2 -141.28(5)
C8 C1 B1 O1 -153.53(6)
Si1 C1 B1 O1 27.47(7)

Symetry operations

---

1 'x, y, z'

2 '-x+1/2, y+1/2, -z+1/2'

3 '-x, -y, -z'

4 'x-1/2, -y-1/2, z-1/2'