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Supporting Information for

Ruthenium-catalysed multicomponent synthesis of borasiloxanes

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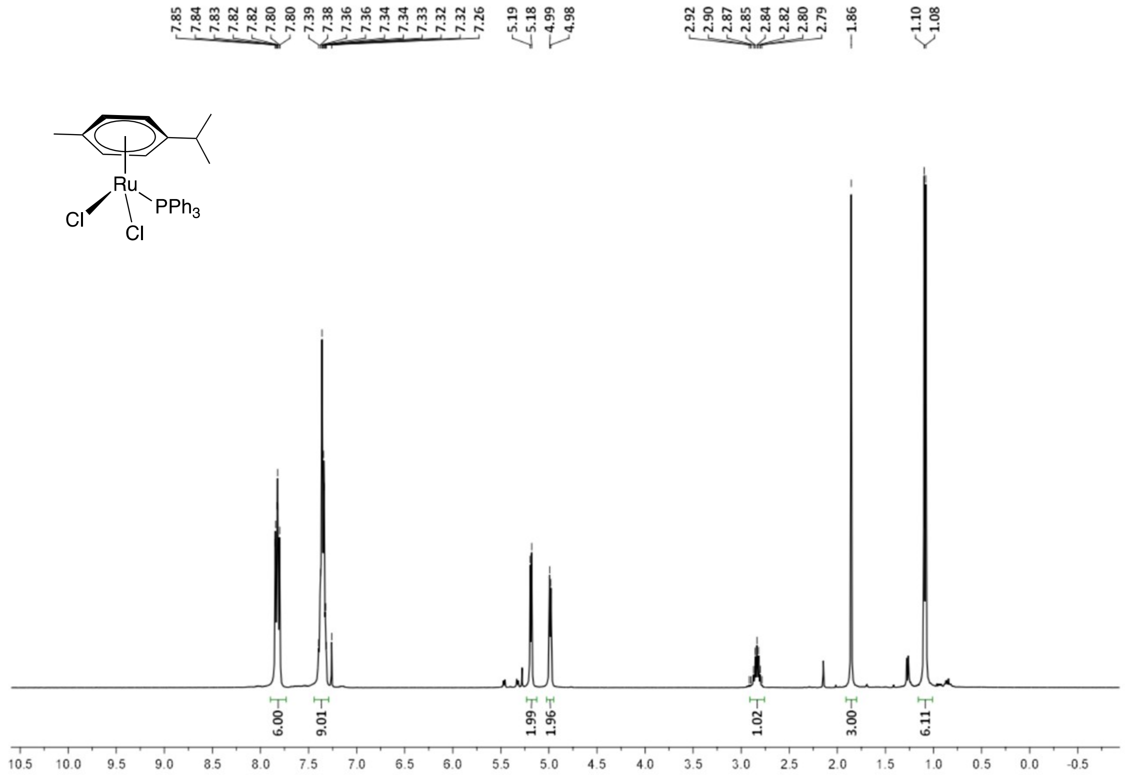
General experimental procedure: All manipulations were carried out using standard Schlenk line and glovebox techniques under nitrogen atmosphere. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Himedia Chemicals and were used without further purification. Dry solvents were prepared according to standard procedures. ^{1}H, ^{13}C, ^{11}B spectra were recorded at Bruker AV-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128 MHz). ^{1}H, ^{13}C{^{1}H} NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. Assignment of spectra was done based on one dimensional (dept-135) NMR technique. IR spectra were recorded on Bruker FTIR spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer.

Synthesis of Ruthenium Complexes: The ruthenium complex **1** was bought from Sigma-Aldrich and the complexes **2**[1], **4**[2], **5**[2] and **7**[2] were prepared by following the literature.

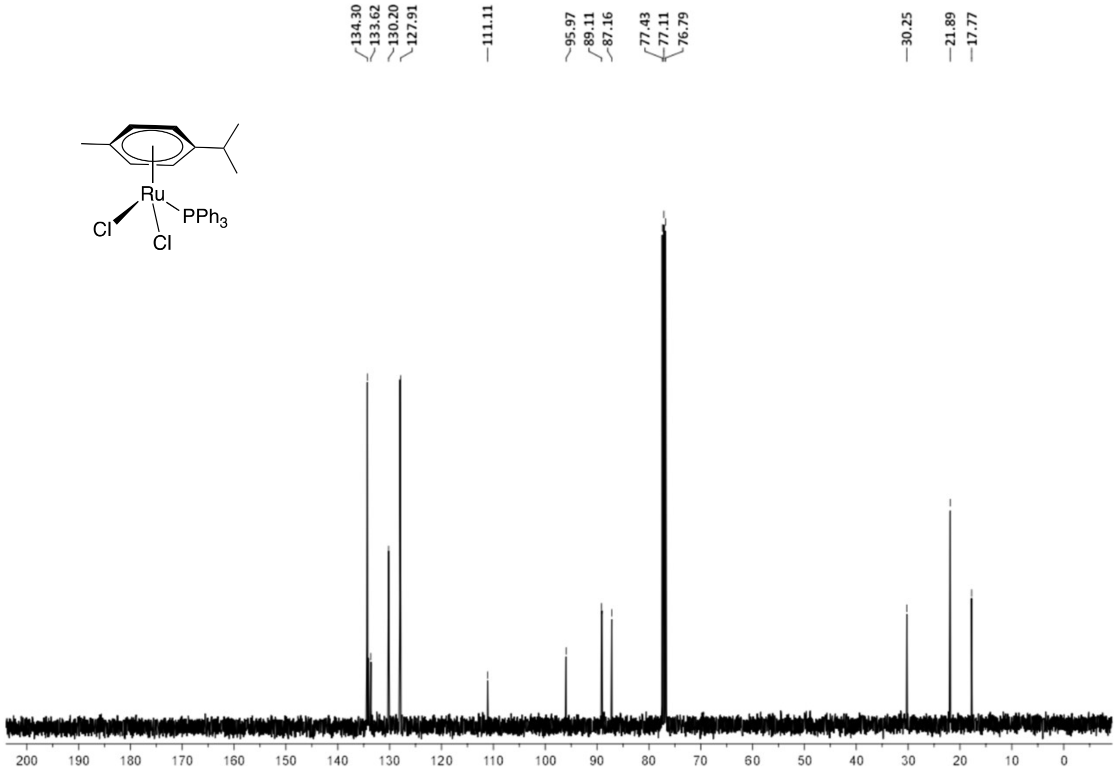
Synthesis of [Ru(η^{6}-*p*-cymene)Cl$_2$(PPh$_3$)] (3): To a dichloromethane (2 ml) solution of [Ru(p-cymene)Cl$_2$]$_2$ (0.08 mmol, 50 mg) taken in a vial, triphenylphosphine (0.16 mmol, 42 mg) was added and the resulting mixture was allowed to stir at room temperature for 24 h. The volume of dark red solution was reduced to one third. Upon slow addition of hexane (2 ml), orange precipitate was formed. The solution was decanted and the precipitate washed with hexane (1 ml) for three times. The resulted orange complex **3** was dried under vacuum (85 mg, yield 92%). ^{1}H NMR ($CDCl_3$): δ 7.85-7.80 (m, 6H, Ar*CH*), 7.39-7.32 (m, 9H, Ar*CH*), 5.19 (d, *J* = 4 Hz, 2H, Ar*CH*), 4.99 (d, *J* = 4Hz, 2H, Ar*CH*), 2.84 (m, *J* = 4 Hz, ^{1}H, ^{i}PrCH), 1.86 (s, 3H, CH_3), 1.09 (d, *J* = 8Hz, 6H, ^{i}PrCH$_3$). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 134.30 (Ar*C*H), 133.62 (quat-*C*), 130.20 (Ar*C*H), 127.91 (Ar*C*H), 111.11 (quat-*C*), 95.97 (quat-*C*), 89.11 (Ar*C*H), 87.16 (Ar*C*H), 30.25 (iPr*C*H), 21.89 (^{i}Pr*C*H$_3$), 17.77 (*C*H$_3$). HRMS (EI) m/z calcd for $C_{28}H_{30}Cl_2PRu$: 569.0506 $(M+H)^+$, found: 569.0523.

Synthesis of [Ru(η^6-*p*-cymene)Cl$_2$(*N*,*N*-dimethylpyridin-4-amine)] (6): To a dichloromethane (2 ml) solution of [Ru(*p*-cymene)Cl$_2$]$_2$ (0.08 mmol, 50 mg) taken in a vial, *N*,*N*-dimethylpyridin-4-amine (0.16 mmol, 19.5 mg) was added and the resulting mixture was allowed to stir at room temperature for 24 h. The volume of dark red solution was reduced to one third. Upon slow addition of hexane (2 ml), the product was precipitated as yellow solid. The solution was decanted and the precipitate washed with hexane (1 ml) for three times. The resulted complex was dried under vacuum (63 mg, yield 90%). ^{1}H NMR ($CDCl_3$): δ 8.38 (t, *J* = 4 Hz, 2H, Ar*CH*), 6.38 (d, *J* = 8 Hz, 2H, Ar*CH*), 5.37 (d, *J* = 4 Hz, 2H, Ar*CH*), 5.15 (d, *J* = 4 Hz, 2H, Ar*CH*), 2.95 (s, 6H, NC*H*$_3$), 2.91 (m, *J* = 4 Hz, 1H, ^{i}PrC*H*), 2.05 (s, 3H, C*H*$_3$), 1.26 (d, *J* = 8Hz, 6H, ^{i}PrC*H*$_3$). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 154.33 (quat-*C*), 153.18 (Ar*C*H), 107.35 (Ar*C*H), 102.69 (quat-*C*), 96.85 (quat-*C*), 82.76 (Ar*C*H), 81.76 (Ar*C*H), 39.25 (N*C*H$_3$), 30.59 (^{i}Pr*C*H), 22.33 (^{i}Pr*C*H$_3$), 18.33 (*C*H$_3$). HRMS (EI) m/z calcd for $C_{17}H_{25}Cl_2N_2Ru$: 429.0438 $(M+H)^+$, found: 429.0460.

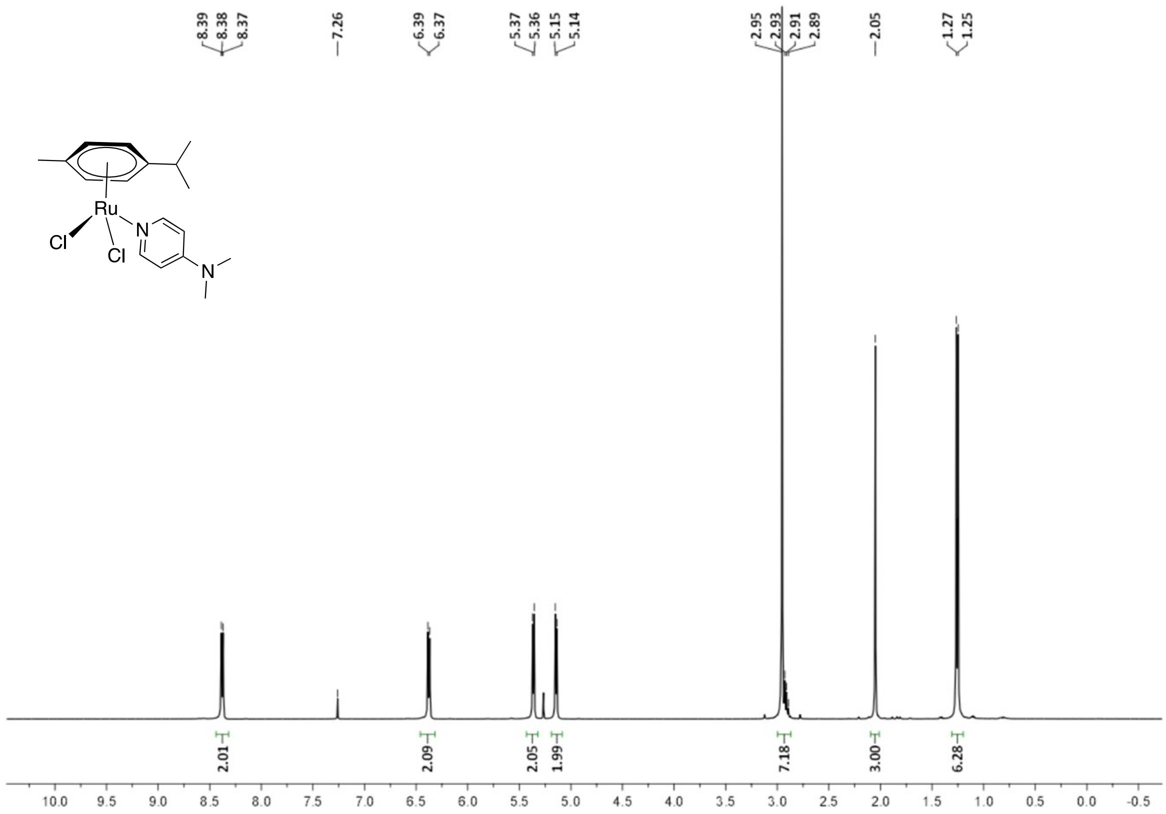
^{1}H NMR spectrum of [Ru(η^6-*p*-cymene)Cl$_2$(PPh$_3$)] (**3**):



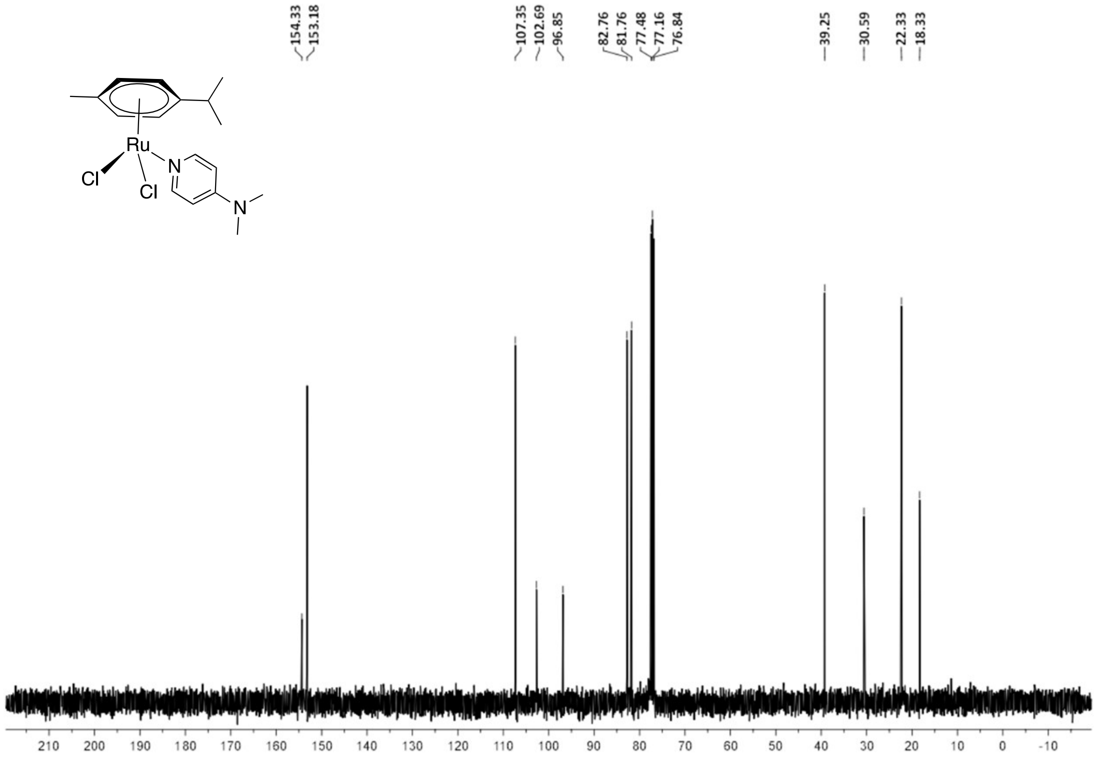
^{13}C NMR spectrum of [Ru(η^6-*p*-cymene)Cl$_2$(PPh$_3$)] (**3**):



^{1}H NMR spectrum of [Ru(η^6-*p*-cymene)Cl$_2$(4-dimethylaminopyridine)] (**6**):



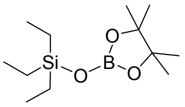
^{13}C NMR spectrum of [Ru(η^6-p-cymene)Cl$_2$(4-dimethylaminopyridine)] (**6**):



General procedure for the synthesis of mono-borasiloxanes: To an oven dried Schlenk-tube, silane (1mmol), borane (1 mmol), [Ru(*p*-cymene)Cl_2(pyridine)] **5** (0.002 mmol) and toluene (2 ml) were added under nitrogen atmosphere. Degassed water (3 mmol, 54µl) was added to the reaction mixture. The reaction mixture was allowed to stir for 2 h at room temperature (for the formation of silanol and hydroxyborane). Then the Schlenk-tube was immersed into a pre-heated oil bath of 125 °C and stirred for 24 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml x 3). Combined hexane solution was filtered through a short plug of Celite and the filtrate was evaporated under reduced pressure to obtain mono-borasiloxanes products.

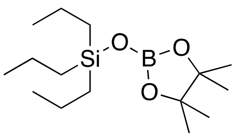
Spectral data of mono-borasiloxanes:

Triethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[3] Colorless liquid. Yield:

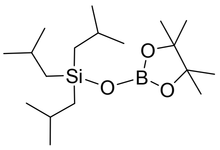


247 mg (96 %). IR (DCM): 2978, 2934, 1475, 1451, 1327, 1142, 981, 850, 672 cm^{-1} ^1H NMR ($CDCl_3$): δ 1.22 (s, 12H, PinB-CH_3), 0.94 (t, J = 8 Hz, 9H, ($SiCH_2CH_3)_3$), 0.62 (q, J = 6 Hz, 6H, ($SiCH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 82.10 (quat-*C*), 24.67 (PinB-CH_3), 6.58 ($SiCH_2CH_3$), 5.53 ($SiCH_2CH_3$). $^{11}B\{^1H\}$ NMR($CDCl_3$): δ 20.38 (br. s). ^{29}Si $\{^1H\}$ NMR ($CDCl_3$): δ 17.19.

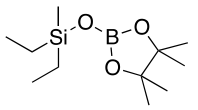
Tripropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[3] Colorless liquid.



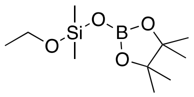
Yield: 273 mg (91 %). IR (DCM): 2975, 2891, 1457, 1389, 1291, 1039, 971, 854, 650 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.37 (m, J = 8 Hz, 6H, ($SiCH_2CH_2CH_3)_3$), 1.21 (s, 12H, PinB-CH_3), 0.94 (t, J = 8 Hz, 9H, ($SiCH_2CH_3)_3$), 0.62 (t, J = 8 Hz, 6H, ($SiCH_2CH_3)_3$). $^{13}C\{^1H\}$ NMR($CDCl_3$): δ 82.08 (quat-*C*), 24.68 (PinB-CH_3), 18.34 ($(SiCH_2CH_2CH_3)_3$), 17.44 ($SiCH_2CH_3$), 16.62 ($SiCH_2CH_3$). $^{11}B\{^1H\}$ NMR($CDCl_3$): δ 20.20 (br. s). ^{29}Si $\{^1H\}$ NMR ($CDCl_3$): δ 17.55.



Triisobutyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane: Colorless liquid. Yield: 304 mg (89 %). IR (DCM): 2954, 2911, 1443, 1359, 1270, 1009, 946, 891, 751 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.74 (m, *J* = 6 Hz, 3H, $(\mathrm{SiCH_2C}\mathit{H}\mathrm{(CH_3)_2})_3$), 1.24 (s, 12H, PinB-C*H*$_3$), 0.92 (d, *J* = 4 Hz, 18H, $(\mathrm{SiCH_2CH(C}\mathit{H}_3\mathrm{)_2})_3$), 0.56 (m, *J* = 4 Hz, 6H, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH(CH_3)_2})_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 83.17 (quat-*C*), 26.00 ($(\mathrm{(SiCH_2CH(}\mathit{C}\mathrm{H_3)_2})_3$), 25.45 ($(\mathrm{(SiCH_2}\mathit{C}\mathrm{H(CH_3)_2})_3$, 24.52 ($(\mathrm{(Si}\mathit{C}\mathrm{H_2CH(CH_3)_2})_3$), 23.09 (PinB-*C*H$_3$). ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 20.44 (br. s). ^{29}Si {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 15.71. ^{29}Si {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 16.69. HRMS (EI) m/z calcd for $\mathrm{C_{18}H_{39}BO_3Si}$: 342.2762 (M)$^{+}$, found: 342.2765.

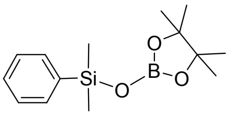


Diethyl(methyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane: Colorless liquid. Yield: 214 mg (88 %). IR (DCM): 2941, 2917, 1419, 1345, 1259, 1039, 951, 857, 681 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.23 (s, 12H, PinB-C*H*$_3$), 0.95 (t, *J* = 8 Hz, 6H, $(\mathrm{SiCH_2C}\mathit{H}_3)_3$), 0.60 (q, *J* = 6 Hz, 4H, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_3})_3$), 0.11 (s, 3H, SiC*H*$_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 81.94 (quat-*C*), 24.49 (PinB-*C*H$_3$), 7.14 (*C*H$_3$), 6.39 (*C*H$_2$), -3.59 (*C*H$_3$). ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 20.45 (br. s). ^{29}Si {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 17.55. HRMS (EI) m/z calcd for $\mathrm{C_{11}H_{25}BO_3Si}$: 244.1666 (M)$^{+}$, found: 244.1670.



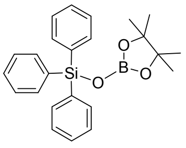
Ethoxydimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane: Colorless liquid. Yield: 226 mg (92 %). IR (DCM): 2972, 2920, 1446, 1344, 1309, 1262, 1057, 956, 806, 678 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.22 (s, 12H, PinB-C*H*$_3$), 0.16-0.08 (m, 11H, SiOC*H*$_2$, SiOCH$_2$C*H*$_3$ and 2SiC*H*$_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 82.26 (quat-*C*) , 24.73 (PinB-*C*H$_3$), 1.07 (OCH$_2$*C*H$_3$), 0.98 (2Si*C*H$_3$), 0.30 (SiO*C*H$_2$). ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 20.27 (br. s). ^{29}Si {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 15.11. HRMS (EI) m/z calcd for $\mathrm{C_{10}H_{23}BO_4Si}$: 246.1459 (M)$^{+}$, found: 246.1465.

Dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[3] Colorless



liquid. Yield: 264 mg (95 %). IR (DCM): 3010, 2959, 1434, 1357, 1278, 1047, 956, 875, 751, 679 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.63 (m, 2H, ArC*H*), 7.37 (m, 3H, ArC*H*), 1.24 (s, 12H, PinB-C*H*$_3$), 0.45 (s, 6H, (Si(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR($CDCl_3$): δ 133.28 (Ar*C*H), 129.63 (Ar*C*H), 129.24 (quat-*C*), 127.80 (Ar*C*H), 82.38 (quat-*C*), 24.68 (PinB-*C*H$_3$), -0.11 (Si*C*H$_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 20.94 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 5.05.

Triphenyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[3] White solid. Yield:

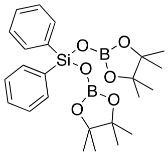


329 mg (82 %), mp 194-195 °C. IR (DCM): 3041, 2954, 1444, 1378, 1261, 1021, 843, 625 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.61 (d, *J* = 8 Hz, 6H, ArC*H*), 7.42 (m, 9H, ArC*H*), 1.31 (s, 12H, PinB-C*H*$_3$). ^{13}C{^{1}H} NMR($CDCl_3$): δ 135.93 (Ar*C*H), 133.45 (quat-*C*), 129.93 (Ar*C*H), 128.17 (Ar*C*H), 83.30 (quat-*C*), 24.61 (PinB-*C*H$_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 21.09 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ -16.09.

General procedure for the synthesis of (diboryl)siloxanes: To an oven dried Schlenk-tube silane (1mmol), borane (2 mmol), [(η^6-*p*-cymene)Ru(Cl)$_2$(pyridine)] **5** (0.004 mmol) and toluene (2 ml) were added under nitrogen atmosphere. Degassed water (10 mmol, 180 μl) was added to the reaction mixture and stirred for 5 h at room temperature (for the formation of silanol and hydroxyborane). Then the Schlenk-tube was immersed into a pre-heated oil bath of 125 °C and stirred for 24 h. After cooling of the reaction mixtrure to room temperature, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml x 3, if the product is not soluble in hexane then hexane/ether solution is used for extraction). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain (diboryl)siloxanes.

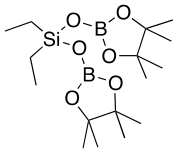
Spectral data of (diboryl)siloxanes:

Diphenylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[4] Colorless liquid.



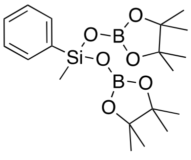
Yield: 421 mg (90 %). IR (DCM): 3011, 2975, 1401, 1354, 1031, 971, 754, 672 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.67-7.65 (m, 4H, ArC*H*), 7.44-7.35 (m, 6H, ArC*H*), 1.27 (s, 12H, PinB-C*H*$_3$), 1.24 (s, 12H, PinB-C*H*$_3$). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 134.68 (Ar*C*H), 134.56 (Ar*C*H), 130.49 (Ar*C*H), 128.04 (quat-*C*), 83.29 (quat-*C*), 82.91 (quat-*C*), 24.68 (PinB-*C*H$_3$), 24.66 (PinB-*C*H$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 20.60 (br. s). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ -24.22 (s).

Diethylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:[3] Colorless liquid.



Yield: 301 mg (81 %). IR (DCM): 2944, 2879, 1415, 1371, 1263, 1051, 1005, 951, 873, 625 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.19 (s, 24H, PinB-C*H*$_3$), 0.93 (t, 6H, *J* = 8 Hz, (SiCH$_2$C*H*$_3$)$_3$), 0.64 (q, 4H, *J* = 8 Hz, (SiC*H*$_2$CH$_3$)$_3$). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 82.29 (quat-*C*), 24.62 (PinB-*C*H$_3$), 6.01 (SiCH$_2$*C*H$_3$)$_3$), 5.95 (Si*C*H$_2$CH$_3$)$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 20.43 (br. s). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ -10.61.

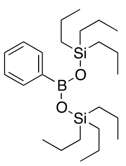
Methyl(phenyl)bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane: Colorless



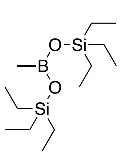
liquid. Yield: 373 mg (92 %). IR (DCM): 3021, 2977, 2891, 1432, 1387, 1046, 978, 891, 734, 669 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.71-7.61 (m, 2H, ArC*H*), 7.42-7.28 (m, 3H, ArC*H*), 1.27 (s, 12H, PinB-C*H*$_3$), 1.23 (s, 12H, PinB-C*H*$_3$), 0.50 (s, 3H, SiC*H*$_3$). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 134.98 (quat-*C*), 133.73 (Ar*C*H), 130.23 (Ar*C*H), 127.70 (Ar*C*H), 83.26 (quat-*C*), 82.60 (quat-*C*), 24.70 (PinB-*C*H$_3$), 24.63 (PinB-*C*H$_3$), -1.67 (Si*C*H$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 20.17 (br. s). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ -19.11. HRMS (EI) m/z calcd for $C_{19}H_{32}B_2O_6Si$: 406.2154 (M)$^+$, found: 406.2156.

General procedure for the synthesis of (disilyl)boroxanes: To an oven dried Schlenk-tube silane (2 mmol), boronic acid (1 mmol), [{(η6-p-cymene)RuCl}2(μ-H-μ-Cl)] 2 (0.004 mmol) and toluene (2 ml) were added under nitrogen atmosphere. Degassed water (10 mmol, 180 μl) was added under nitrogen atmosphere and the reaction mixture was allowed to stir for 5 h for the complete formation of silanol and hydroxyborane. The Schlenk-tube was then immersed into a pre-heated oil bath at 125 °C and stirred for 24 h. After the reaction mixture was cooled to rt, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml x 3, if the product is not soluble in hexane then hexane/ether solution is used for extraction). Organic layers were combined, filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain (disilyl)boroxanes in good yield.

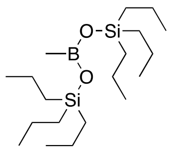
Spectral data of (disilyl)boroxanes:



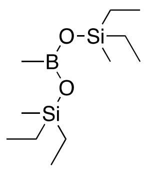
Bis(tripropylsilyl) phenylboronate:[5] Colorless liquid. Yield: 316 mg (73 %). IR (DCM): 3011, 2972, 2897, 1447, 1359, 1041, 1019, 954, 751, 658 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.87 (d, 2H, *J* = 8 Hz, ArC*H*), 7.50-7.44 (m, 3H, ArC*H*), 1.55 (m, 12H, $(\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_3})_3$), 1.11 (t, 18H, *J* = 8 Hz $(\mathrm{SiCH_2CH_2C}\mathit{H}_3)_3$), 0.85 (m, 12H, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_3})_3$). ^{13}C{^{1}H} NMR($CDCl_3$): δ 135.81 (Ar*C*H), 132.85 (Ar*C*H), 128.14 (Ar*C*H), 18.36 ($(\mathrm{SiCH_2}\mathit{C}\mathrm{H_2CH_3})_3$), 18.18 ($(\mathrm{SiCH_2CH_2}\mathit{C}\mathrm{H_3})_3$), 14.15 ($(\mathrm{Si}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_3})_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 29.75 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 5.11.



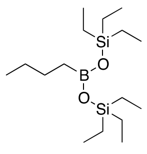
Bis(triethylsilyl) methylboronate: Colorless liquid. Yield: 259 mg (90 %). IR (DCM): 2956, 2889, 1411, 1368, 1016, 967, 773, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, *J* = 8 Hz, 18H, $(\mathrm{SiCH_2C}\mathit{H}_3)_3$), 0.61 (q, *J* = 6 Hz, 12H, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_3})_3$), 0.21 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR($CDCl_3$): δ 6.81 ($(\mathrm{SiCH_2}\mathit{C}\mathrm{H_3})_3$), 5.81 ($(\mathrm{Si}\mathit{C}\mathrm{H_2CH_3})_3$), 5.62 (B*C*H$_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 29.34 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 11.20. HRMS (EI) m/z calcd for $C_{13}H_{33}BO_2Si_2$: 288.2112 (M)$^+$, found: 288.2117.



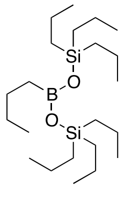
Bis(tripropylsilyl) methylboronate: Colorless liquid. Yield: 327 mg (88 %). IR (DCM): 2951, 2893, 1441, 1375, 1044, 971, 852, 769, 671 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.35 (m, 12H, $(\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_3})_3$), 0.98 (t, 18H, *J* = 8 Hz, $(\mathrm{SiCH_2CH_2C}\mathit{H}_3)_3$), 0.60 (t, 12H, *J* = 8 Hz, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_3})_3$), 0.19 (s, 3H, $\mathrm{BC}\mathit{H}_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 18.48 ($(\mathrm{SiCH_2}\mathit{C}\mathrm{H_2CH_3})_3$), 17.87 $(\mathrm{SiCH_2CH_2}\mathit{C}\mathrm{H_3})_3$, 17.70 ($\mathrm{B}\mathit{C}\mathrm{H_3}$), 16.87 ($(\mathrm{Si}\mathit{C}\mathrm{H_2CH_2CH_3})_{3)}$. ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 29.45 (br. s). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 11.52 (s). HRMS (EI) m/z calcd for $\mathrm{C_{19}H_{45}BO_2Si_2}$: 372.3051 (M)$^+$, found: 372.3054.



Bis(diethyl(methyl)silyl) methylboronate: Colorless liquid. Yield: 215 mg (83 %). IR (DCM): 2944, 2895, 1417, 1372, 1101, 1032, 975, 851, 749, 678 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.94 (t, 12H, *J* = 8Hz, $(\mathrm{SiCH_2C}\mathit{H}_3)_3$), 0.58 (q, 8H, *J* = 6Hz, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_3})_3$), 0.10 (s, 3H, $\mathrm{BC}\mathit{H}_3$), 0.07 (s, 6H, $\mathrm{SiC}\mathit{H}_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 29.86 ($\mathrm{B}\mathit{C}\mathrm{H_3}$), 7.43 ($(\mathrm{SiCH_2}\mathit{C}\mathrm{H_3})_3$), 6.78 ($(\mathrm{Si}\mathit{C}\mathrm{H_2CH_3})_3$), -3.38 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$). ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 29.57 (br. s). ^{29}Si {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 10.11. HRMS (EI) m/z calcd for $\mathrm{C_{11}H_{29}BO_2Si_2}$: 260.1799 (M)$^+$, found: 260.1805.



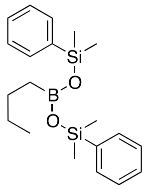
Bis(triethylsilyl) butylboronate: Colorless liquid. Yield: 270 mg (82 %). IR (DCM): 2954, 2876, 1459, 1317, 1237, 1004, 972, 844, 726 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.37-1.25 (m, 6H, $\mathrm{C}\mathit{H}_2$), 0.95 (t, *J* = 8 Hz, 18H, $(\mathrm{SiCH_2C}\mathit{H}_3)_3$), 0.88 (q, *J* = 8 Hz, 3H, $\mathrm{C}\mathit{H}_3$), 0.60 (q, *J* = 6 Hz, 12H, $(\mathrm{SiC}\mathit{H}_2\mathrm{CH_3})_3$). ^{13}C{^{1}H} NMR($\mathrm{CDCl_3}$): δ 27.37 ($\mathit{C}\mathrm{H_3}$), 25.63 ($\mathit{C}\mathrm{H_2}$), 14.22 ($\mathit{C}\mathrm{H_2}$), 6.84 ($\mathit{C}\mathrm{H_2}$), 6.78 ($\mathit{C}\mathrm{H_2}$), 5.91 ($\mathit{C}\mathrm{H_3}$). ^{11}B{^{1}H} NMR($\mathrm{CDCl_3}$): δ 30.12 (br. s). ^{29}Si{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 14.79 (s). HRMS (EI) m/z calcd for $\mathrm{C_{16}H_{39}BO_2Si_2}$: 330.2582 (M)$^+$, found: 330.2585.



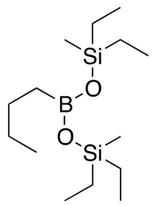
Bis(tripropylsilyl) butylboronate: Colorless liquid. Yield: 331 mg (80 %). IR (DCM): 2951, 2885, 1448, 1367, 1033, 876, 744, 681 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.41-1.32 ((m, 16H, $(\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_3})_3$ and $\mathrm{BCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$)), 0.96 (t, *J* = 8 Hz, 18H,

$(\mathrm{SiCH_2CH_2C}\mathit{H}_3)_3$), 0.87 (t, *J* = 6 Hz, 3H, $\mathrm{BCH_2CH_2CH_2C}\mathit{H}_3$), 0.67-0.58 (m, 14H, $\mathrm{Si}\mathit{CH}_2\mathrm{CH_2CH_3})_3$ and $\mathrm{B}\mathit{CH}_2\mathrm{CH_2CH_2CH_3}$)). ^{13}C{^{1}H} NMR($CDCl_3$): δ 27.34 (B*C*$H_2$), 25.62 (B*C*$H_2$), 18.51 (Si*C*$H_2$), 18.44 (B*C*$H_3$), 17.97 (Si*C*$H_3$), 16.88 (Si*C*$H_2$), 14.21 (B*C*$H_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 30.25 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 14.31. HRMS (EI) m/z calcd for $C_{22}H_{51}BO_2Si_2$: 414.3521 $(M)^+$, found: 414.3523.

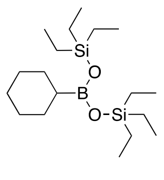
Bis(dimethyl(phenyl)silyl) butylboronate: Colorless liquid. Yield: 299 mg (81 %). IR (DCM): 3110, 2967, 2877, 1445, 1397, 1276, 1042, 1019, 978, 762, 681 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.66-7.57 (m, 4H, ArC*H*), 7.44-7.39 (m, 6H, ArC*H*), 1.42-1.27 (m, 4H, BCH_2), 0.49-0.39 (m, 14H, BCH_2 and SiCH_3), 0.15 (m, 3H, BCH_3). ^{13}C{^{1}H} NMR($CDCl_3$): δ 138.99 (quat-*C*), 133.13 (Ar*C*H), 129.38 (Ar*C*H), 127.74 (Ar*C*H), 26.93 (B*C*H_2), 25.43 (B*C*H_2), 14.02 (B*C*H_2), 0.89 (B*C*H_3), 0.20 (Si*C*H_3). ^{11}B{^{1}H} NMR($CDCl_3$): δ 30.42 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ -5.61. HRMS (EI) m/z calcd for $C_{20}H_{31}BO_2Si_2$: 370.1956 $(M)^+$, found: 370.1959.



Bis(diethyl(methyl)silyl)butylboronate: Colorless liquid. Yield: 238 mg (79 %). IR (DCM): 2951, 2896, 1452, 1381, 1039, 1011, 865, 731, 689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.35-1.25 (m, 6H, BCH_2), 0.94 (t, 12H, *J* = 8 Hz, $\mathrm{SiCH_2C}\mathit{H}_3$), 0.86 (t, 3H, *J* = 8 Hz, $\mathrm{BCH_2CH_2CH_2C}\mathit{H}_3$)0.58 (q, 8H, *J* = 6 Hz, $\mathrm{Si}\mathit{CH}_2\mathrm{CH_3}$), 0.08 (s, 6H, Si$\mathit{CH}_3$). ^{13}C{^{1}H} NMR($CDCl_3$): δ 27.26 (B*C*$H_2$), 27.01(B*C*$H_2$), 25.60 (B*C*$H_2$), 14.16 (B*C*$H_3$), 7.70 (Si*C*$H_2$), 6.78 (Si*C*$H_3$), -3.00 (Si*C*$H_3$). ^{11}B{^{1}H} NMR($CDCl_3$): δ 30. 19 (br. s). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 13.59. HRMS (EI) m/z calcd for $C_{14}H_{35}BO_2Si_2$: 302.2269 $(M)^+$, found: 302.2273.



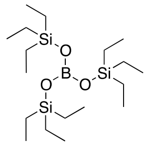
Bis(triethylsilyl) cyclohexylboronate: Colorless liquid. Yield: 267 mg (75 %). IR (DCM): 2947, 2891, 1437, 1378, 1041, 1020, 976, 861, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.33-1.22 (m, 11H, CyCH_2), 0.94 (t, 18H, *J* = 8 Hz, $\mathrm{SiCH_2C}\mathit{H}_3$), 0.59 (q, 12H,



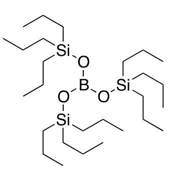
J = 8 Hz, SiCH_2CH$_3$). $^{13}C\{^1H\}$ NMR(CDCl$_3$): δ 34.35 (CyCH$_2$), 30.84 (CyCH), 25.93 (CyCH$_2$), 24.24 (CyCH$_2$), 6.78 (SiCH$_3$), 5.71 (SiCH$_3$). $^{11}B\{^1H\}$ NMR(CDCl$_3$): δ 29.79 (br. s). $^{29}Si\{^1H\}$ NMR (CDCl$_3$): δ 14.19 (s). HRMS (EI) m/z calcd for $C_{18}H_{41}BO_2Si_2$: 356.2738 (M)$^+$, found: 356.2742.

General procedure for the synthesis of tris(trisilyl) borate from boric acid: To an oven dried schlenk-tube silane (3mmol), boric acid (1 mmol, 60 mg), [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] **2** (0.006 mmol) and toluene (2 ml) were added under nitrogen atmosphere. Degassed water (10 mmol, 180 µl) was added and the reaction mixture was allowed to stir for 5 h at room temperature for the complete formation of silanol. Then the schlenk-tube was immersed into a pre-heated oil bath at 125 °C and stirred for 24h. After the reaction mixture was cooled to rt, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml x 3, if the product is not soluble in hexane then hexane/ether solution is used for the extraction). Organic layers were combined, filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain tris(trisilyl) borate.

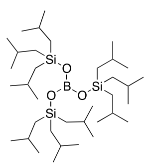
Spectral data of tris(trisilyl) borates:



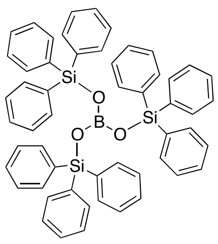
Tris(triethylsilyl) borate:[6] Colorless liquid. Yield: 335 mg (83 %). IR (DCM): 2949, 2895, 1441, 1376, 1036, 978, 871, 756, 679 cm^{-1}. ^1H NMR (CDCl$_3$): δ 0.95 (t, 27H, J = 8 Hz, SiCH$_2$CH_3), 0.60 (q, 18H, J = 8 Hz, SiCH_2CH$_3$). $^{13}C\{^1H\}$ NMR(CDCl$_3$): δ 6.80 (SiCH$_2$$CH_3$), 5.63 (SiCH$_2$$CH_3$). $^{11}B\{^1H\}$ NMR(CDCl$_3$): δ 21.21 (br. s). ^{29}Si {^1H} NMR (CDCl$_3$): δ 10.08. HRMS (EI) m/z calcd for $C_{18}H_{45}BO_3Si_3$: 404.2770 (M)$^+$, found: 407.2772.



Tris(tripropylsilyl) borate: Colorless liquid. Yield: 413 mg (78 %). IR (DCM): 2948, 2891, 1437, 1391, 1044, 971, 876, 683 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.41-1.32 (m, 18H, SiCH$_2$C*H*$_2$CH$_3$), 0.96 (t, 27H, *J* = 8 Hz, SiCH$_2$CH$_2$C*H*$_3$), 0.59 (t, 18H, *J* = 8 Hz, SiC*H*$_2$CH$_2$CH$_3$). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 18.53 (Si*C*H$_2$CH$_2$CH$_3$), 17,70 (SiCH$_2$CH$_2$*C*H$_3$), 16.85 (Si*C*H$_2$CH$_2$CH$_3$). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 21.43 (br. s). ^{29}Si{^{1}H} NMR (CDCl$_3$): δ 10.12 (s). HRMS (EI) m/z calcd for $C_{27}H_{63}BO_3Si_3$: 530.4178 (M)$^+$, found: 530.4180.



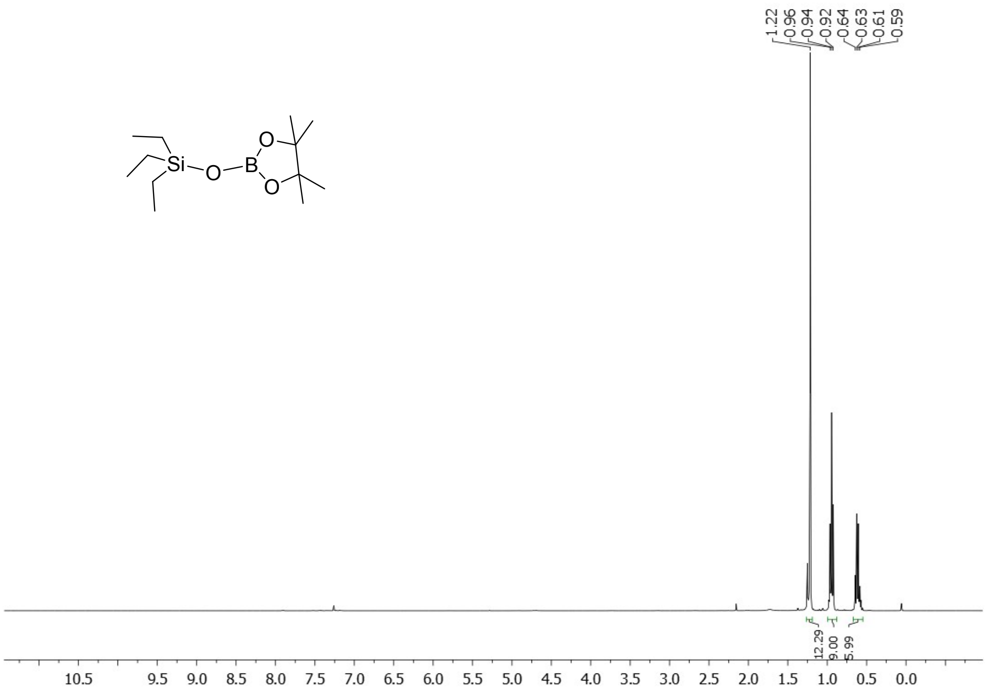
Tris(triisobutyl) borate: Colorless liquid. Yield: 473 mg (72 %). IR (DCM): 2948, 2899, 1437, 1378, 1260, 1041, 981, 765, 673 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.82-1.72 (m, 9H, ^{i}PrC*H*), 0.95 (d, *J* = 4 Hz, 54H, ^{i}PrC*H*$_3$), 0.59 (d, *J* = 4 Hz, 18H). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 26.11 (^{i}Pr*C*H$_3$), 25.56 (^{i}Pr*C*H), 23.19 (Si*C*H$_2$). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 21.38 (br. s). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ 11.29. HRMS (EI) m/z calcd for $C_{36}H_{81}BO_3Si_3$: 656.5587 (M)$^+$, found: 656.5587.



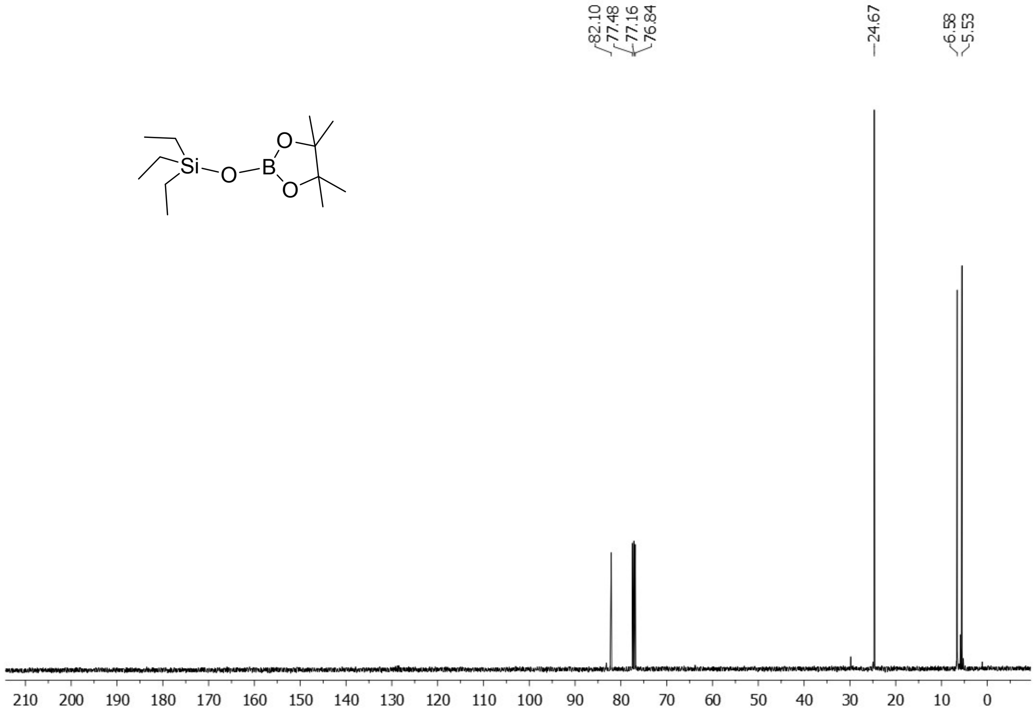
Tris(triphenylsilyl) borate: Colorless liquid. Yield: 585 mg (70 %), mp 210-211 °C. IR (DCM): 3015, 2956, 2894, 1444, 1271, 1039, 975, 861, 774, 669 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.68 (t, 18H, *J* = 4 Hz, ArC*H*), 7.52-7.44 (m, 27H, ArC*H*). ^{13}C{^{1}H} NMR(CDCl$_3$): δ 136.00 (Ar*C*H), 133.51 (quat-*C*), 130.00 (Ar*C*H), 128.21 (Ar*C*H). ^{11}B{^{1}H} NMR(CDCl$_3$): δ 21.68 (br. s). ^{29}Si {^{1}H} NMR (CDCl$_3$): δ -21.45. HRMS (EI) m/z calcd for $C_{54}H_{45}BO_3Si_3$: 836.2770 (M)$^+$, found: 836.2771.

NMR Spectra of borasiloxanes, silylboroxanes and trisilylborates:

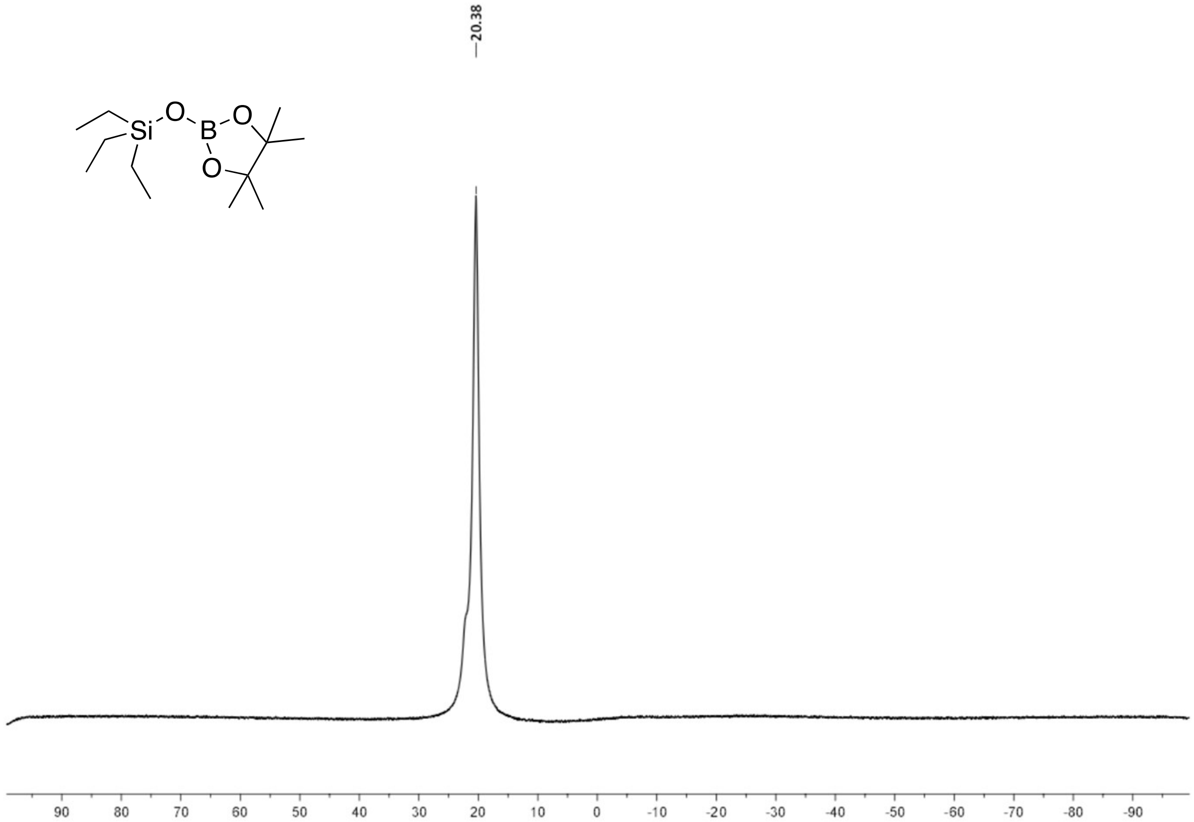
^{1}H NMR spectrum of triethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



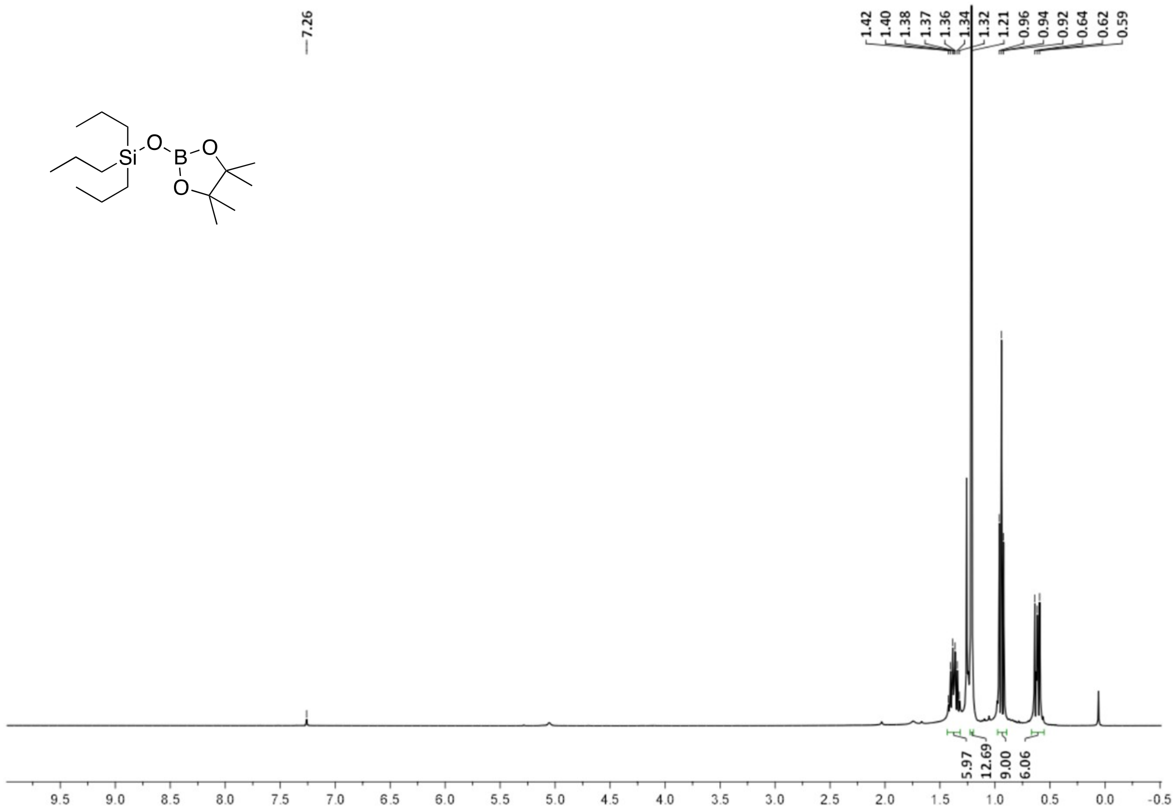
^{13}CNMR spectrum of triethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



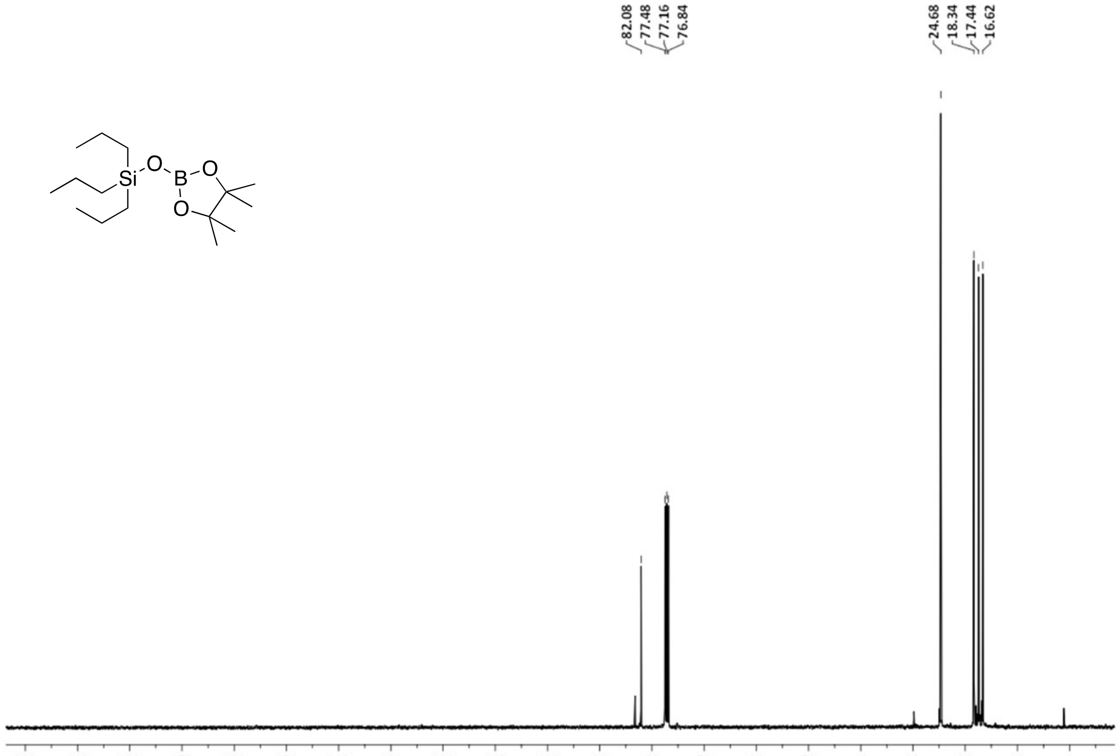
^{11}B NMR spectrum of triethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



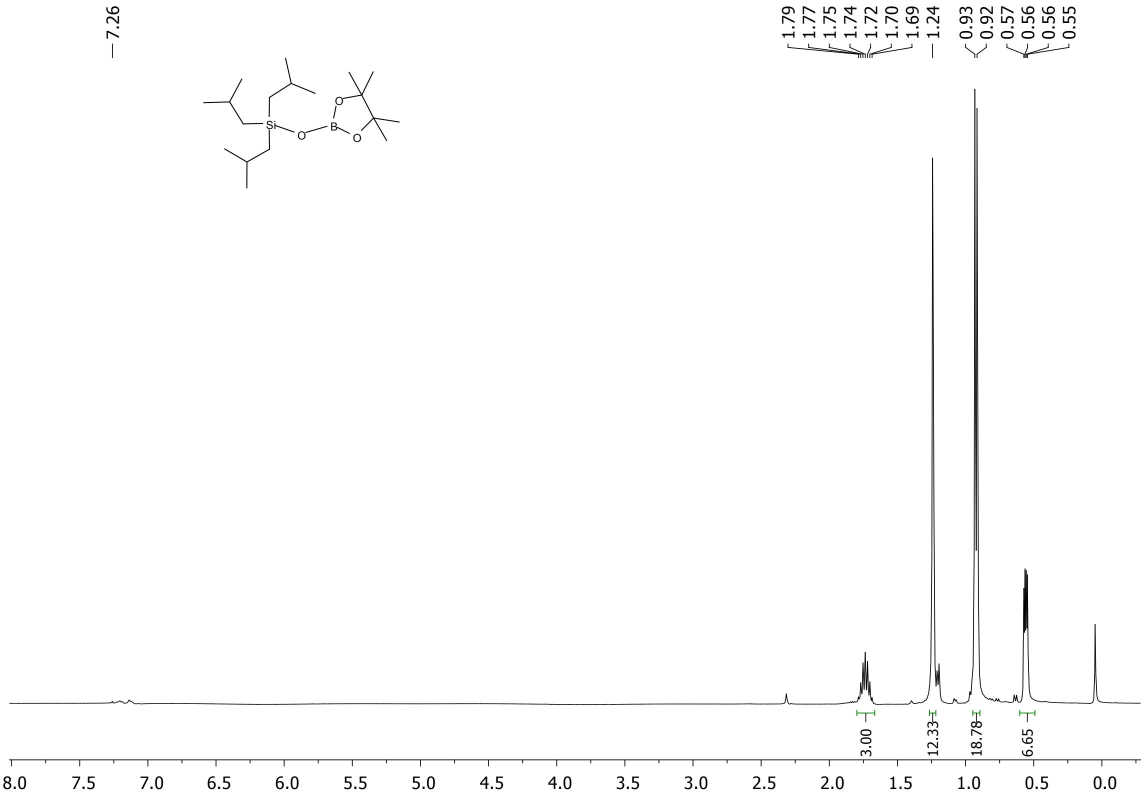
^{1}H NMR spectrum of tripropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



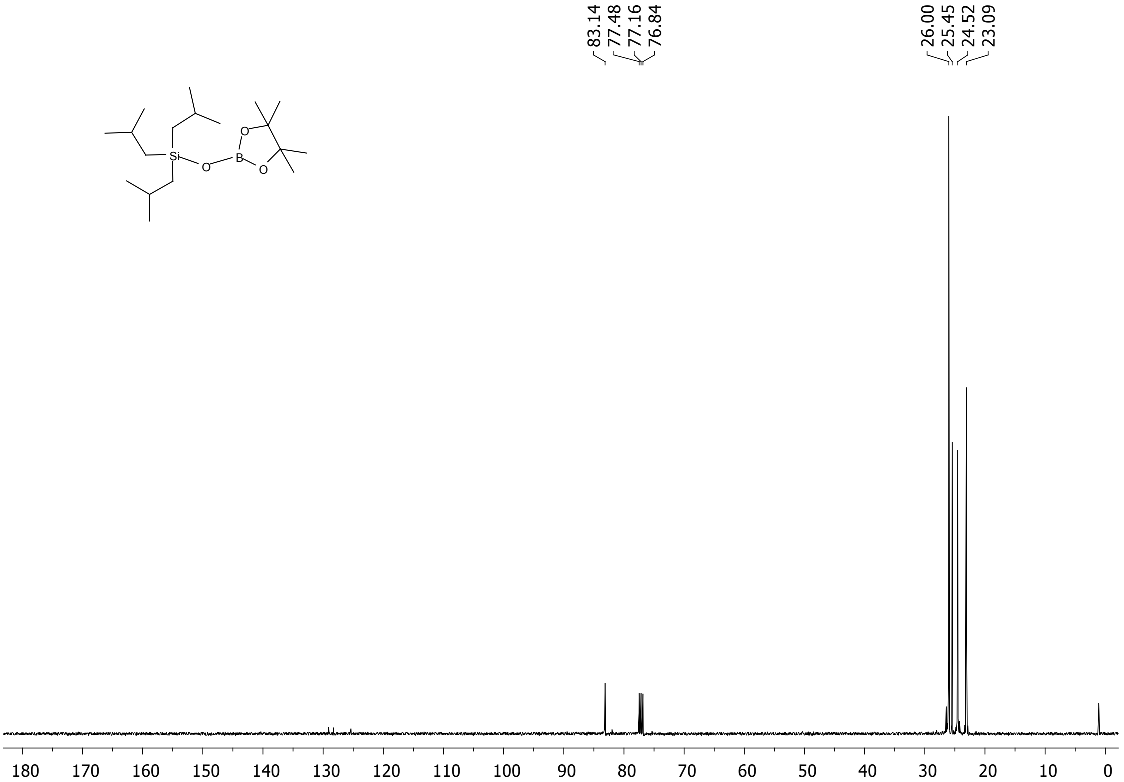
^{13}C NMR spectrum of tripropyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



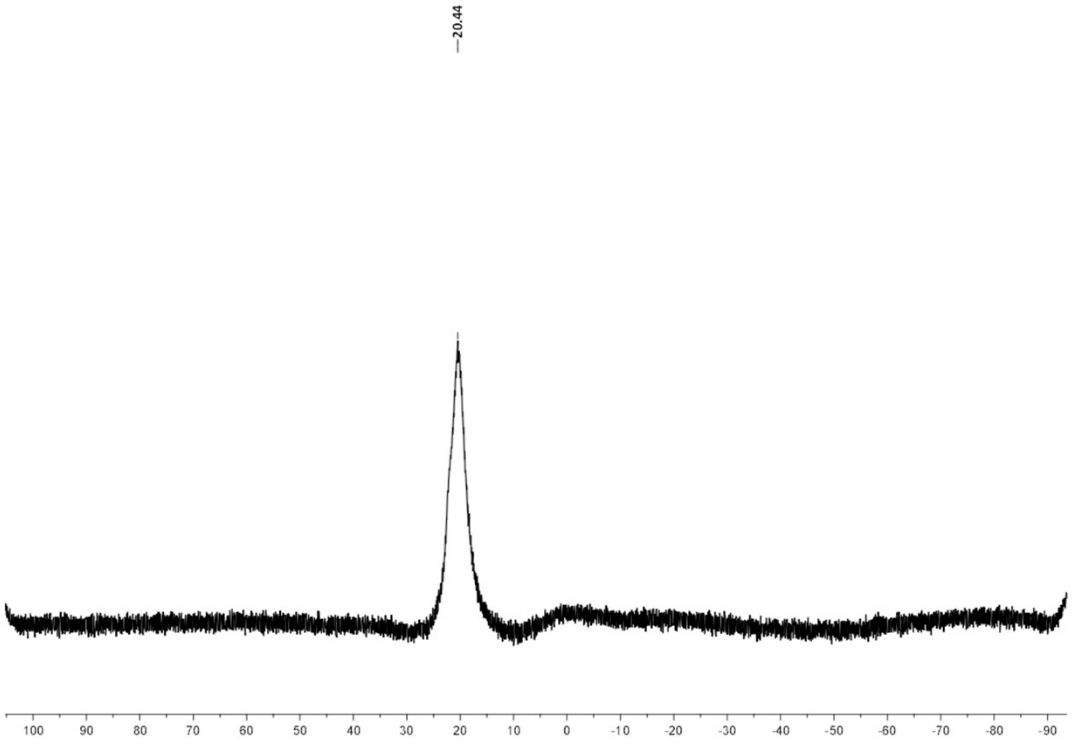
^{1}H NMR spectrum of triisobutyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



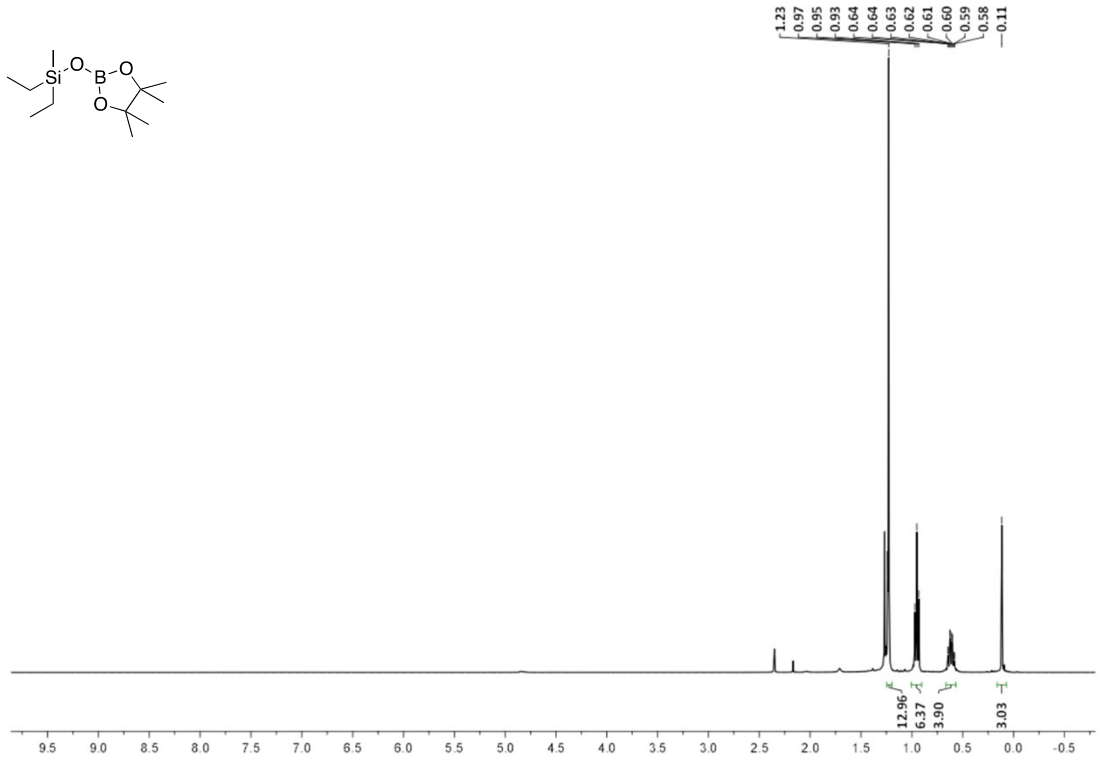
^{13}C NMR spectrum of triisobutyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



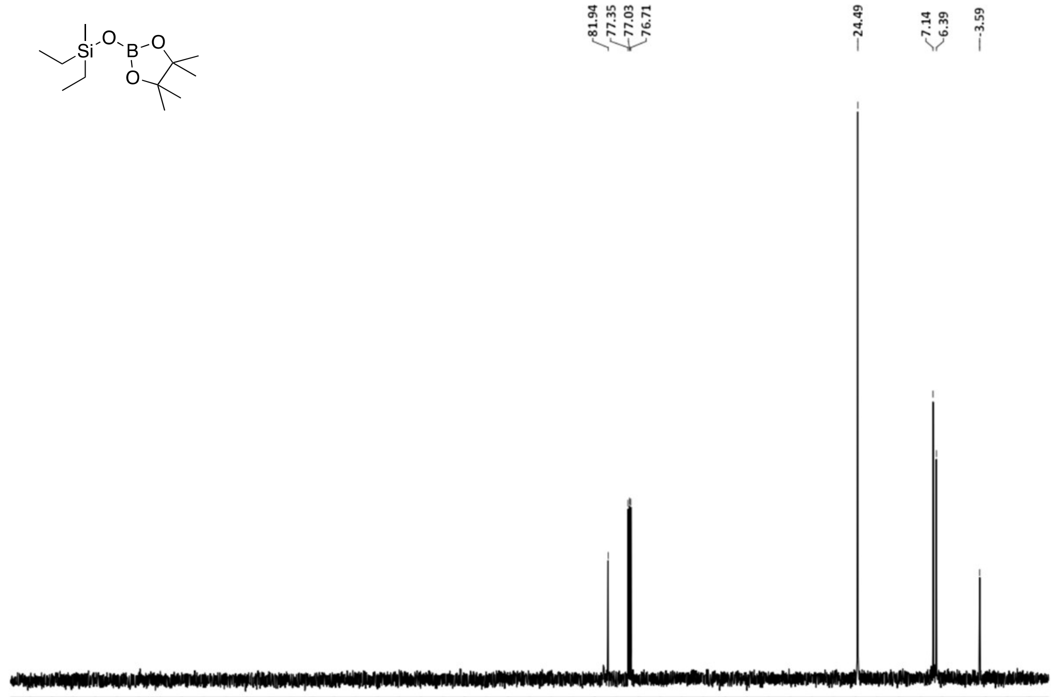
^{11}B NMR spectrum of triisobutyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



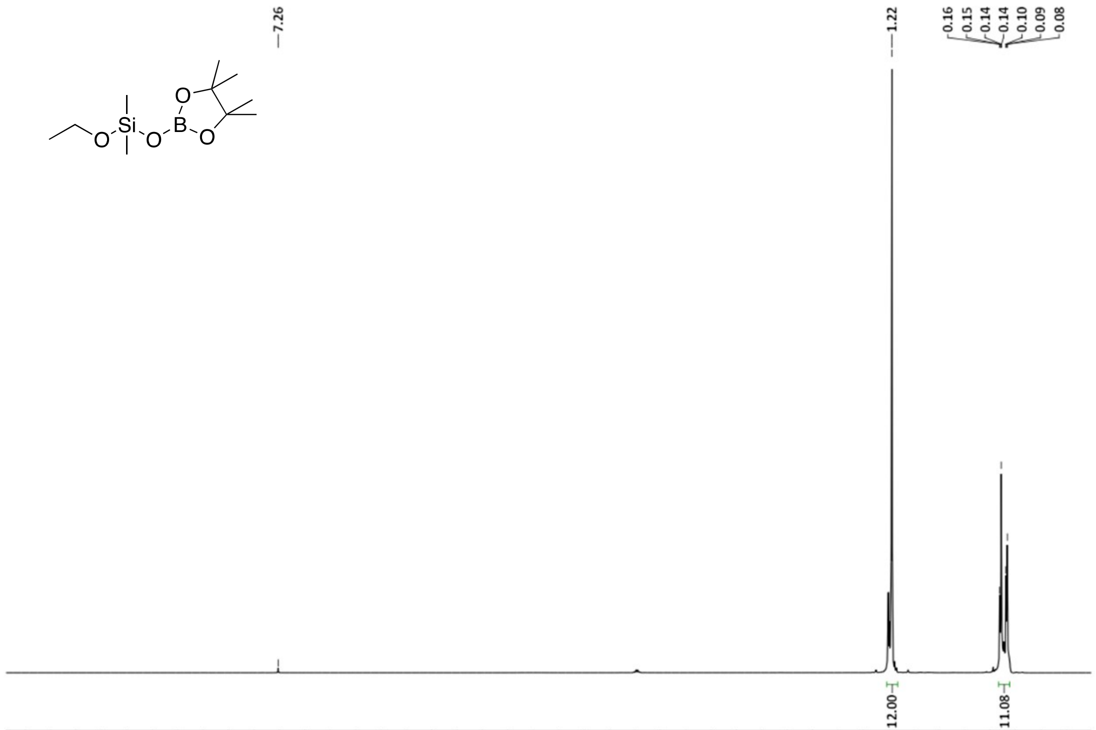
^{1}H NMR spectrum of diethyl(methyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



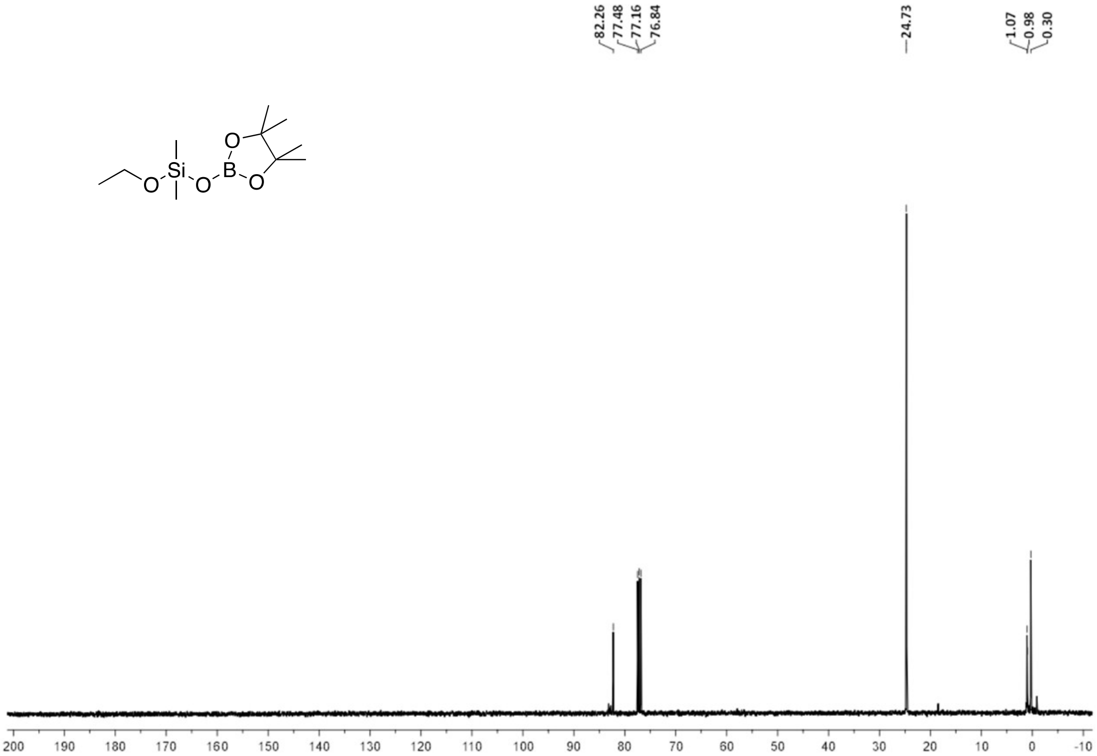
^{13}C NMR spectrum of diethyl(methyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



^{1}H NMR spectrum of ethoxydimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:

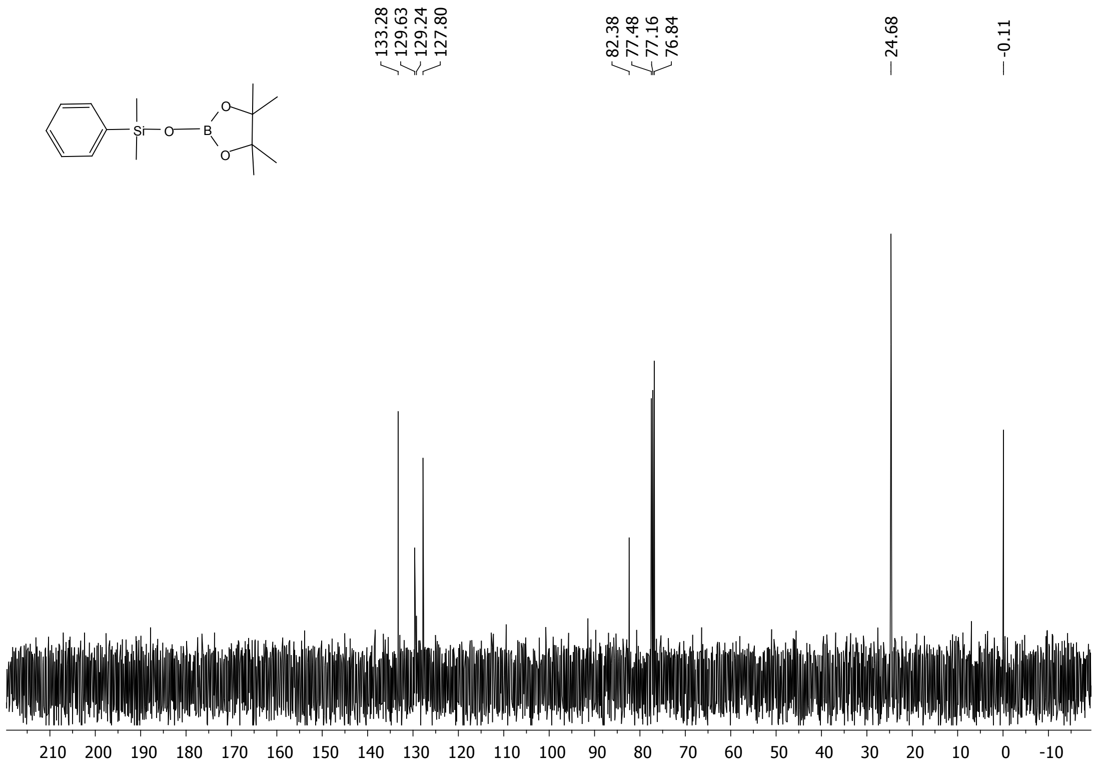


^{13}C NMR spectrum of ethoxydimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:

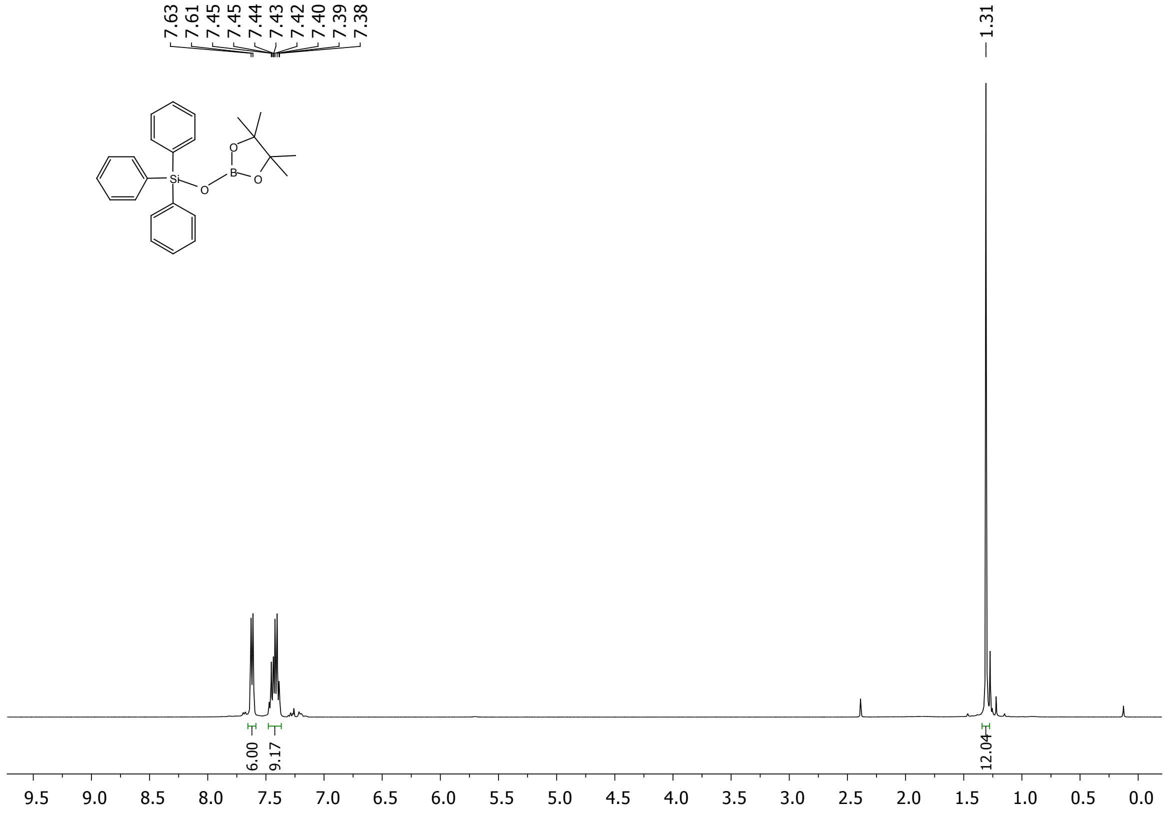


^1H NMR spectrum of dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:

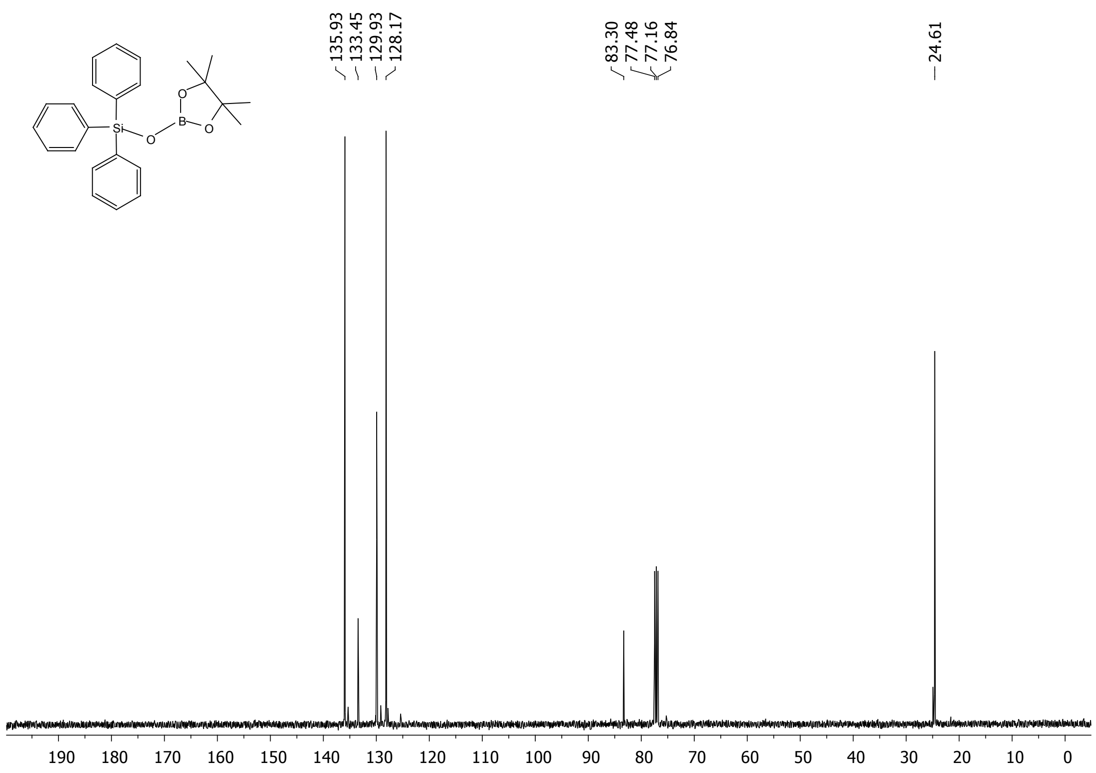
^{13}C NMR spectrum of dimethyl(phenyl)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



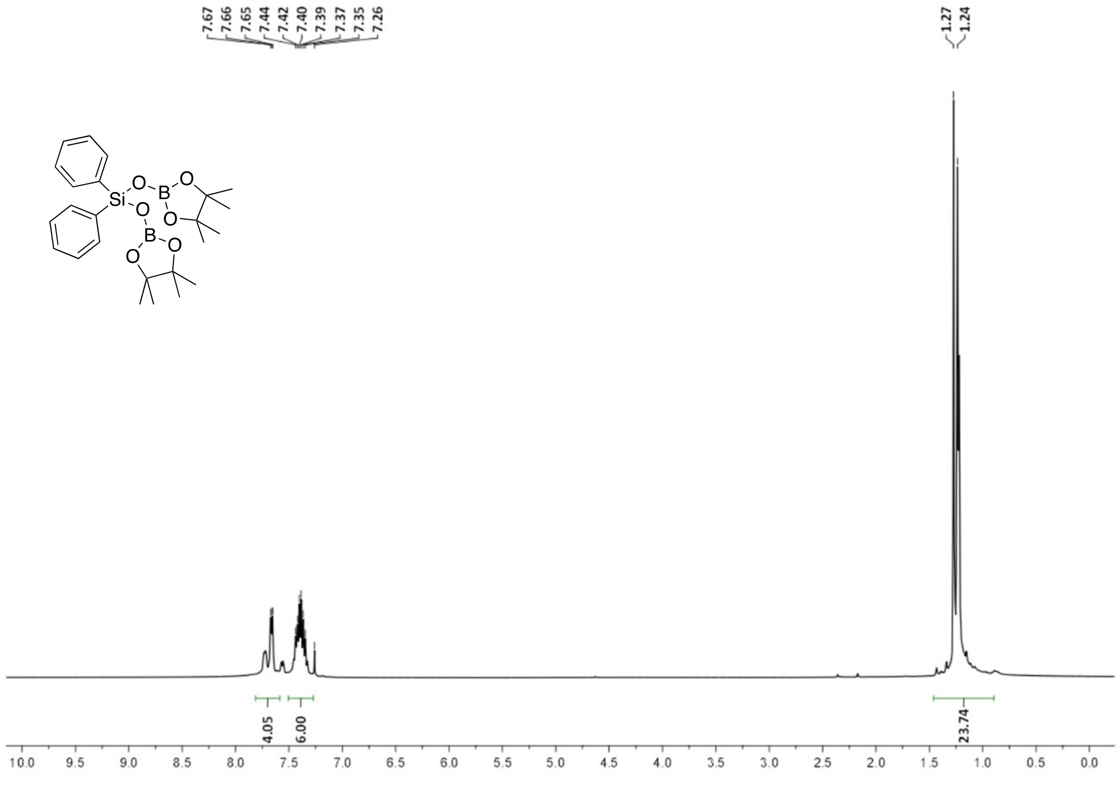
^{1}H NMR spectrum of triphenyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



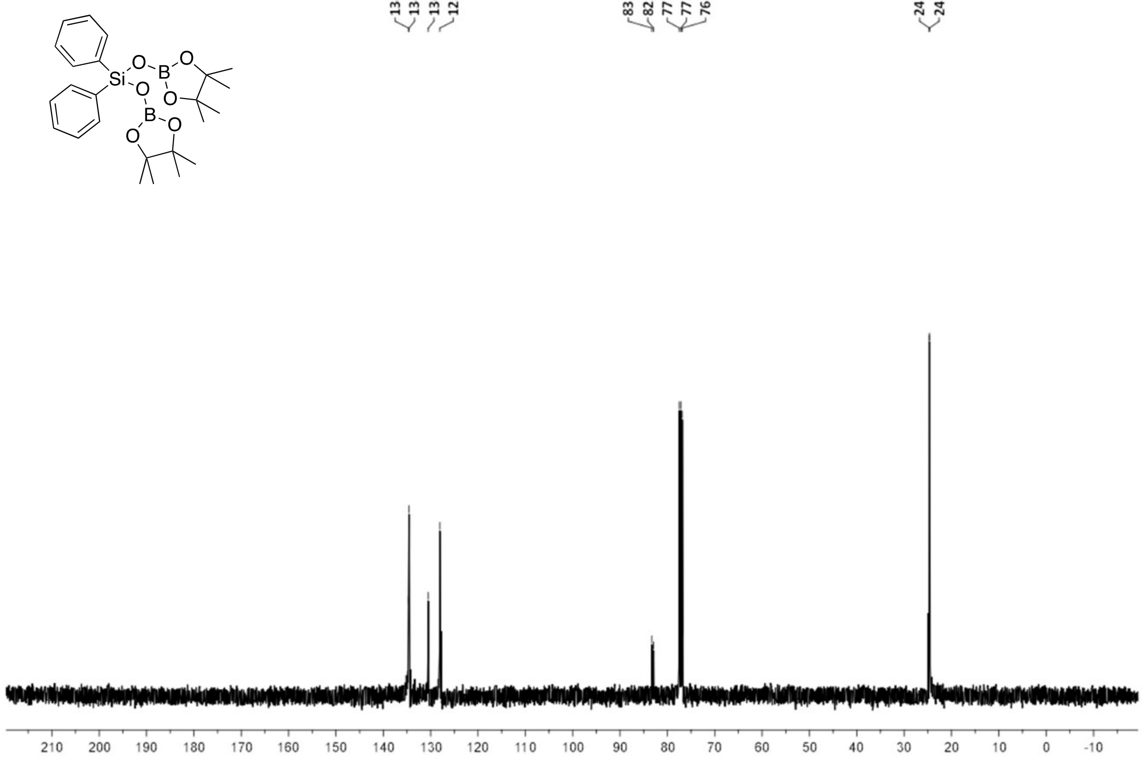
^{13}C NMR spectrum of triphenyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



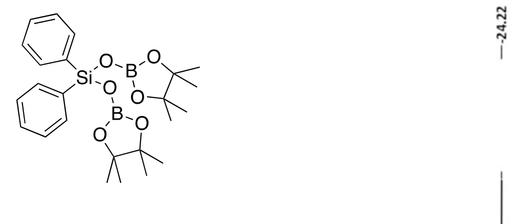
^{1}H NMR spectrum of diphenylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



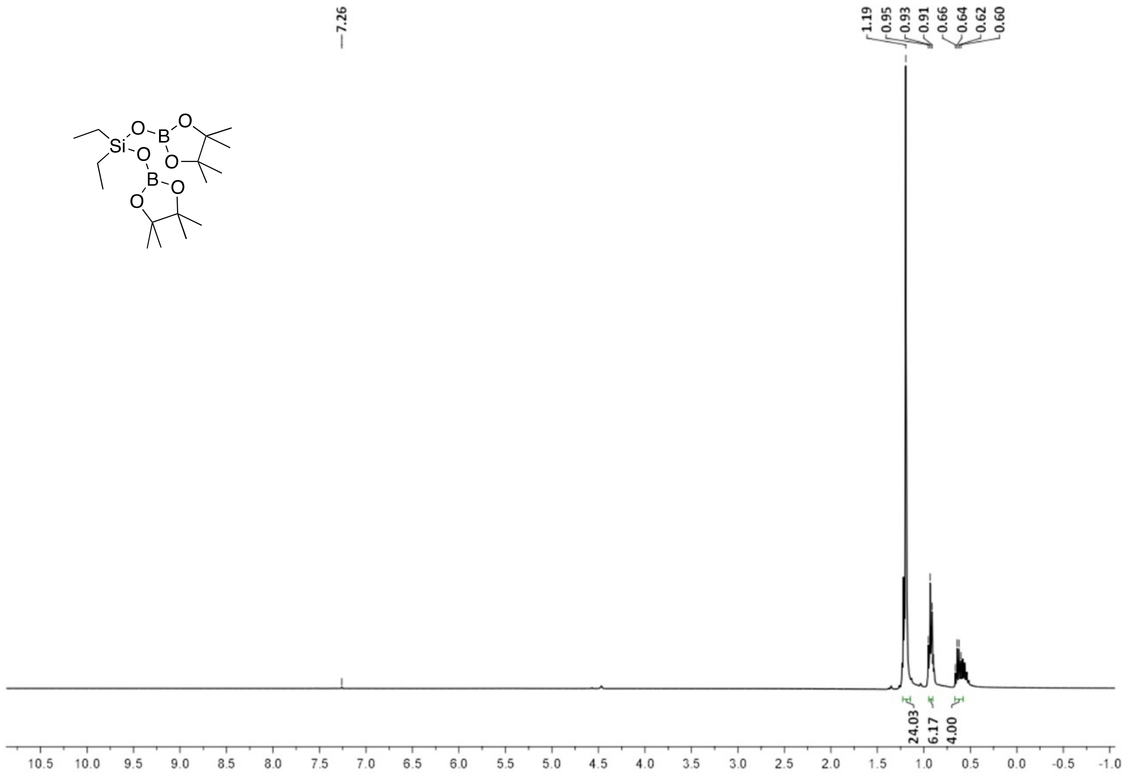
^{13}C NMR spectrum of diphenylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



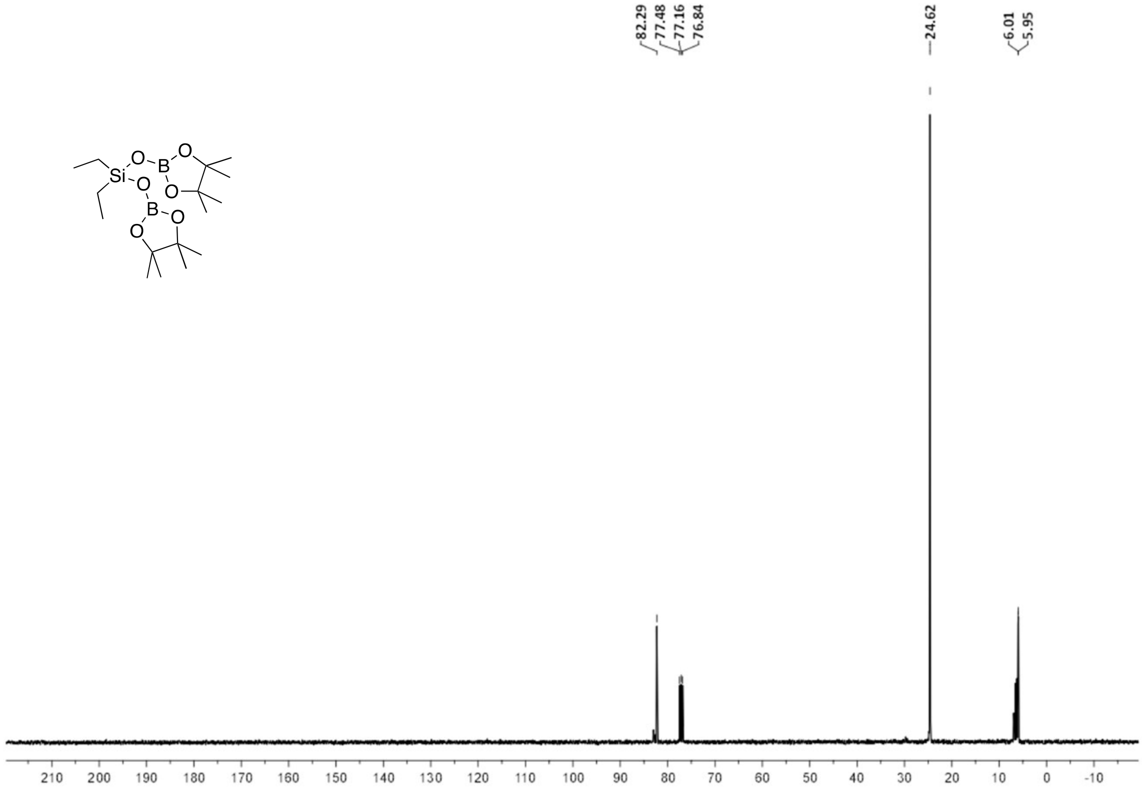
^{29}Si NMR spectrum of diphenylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



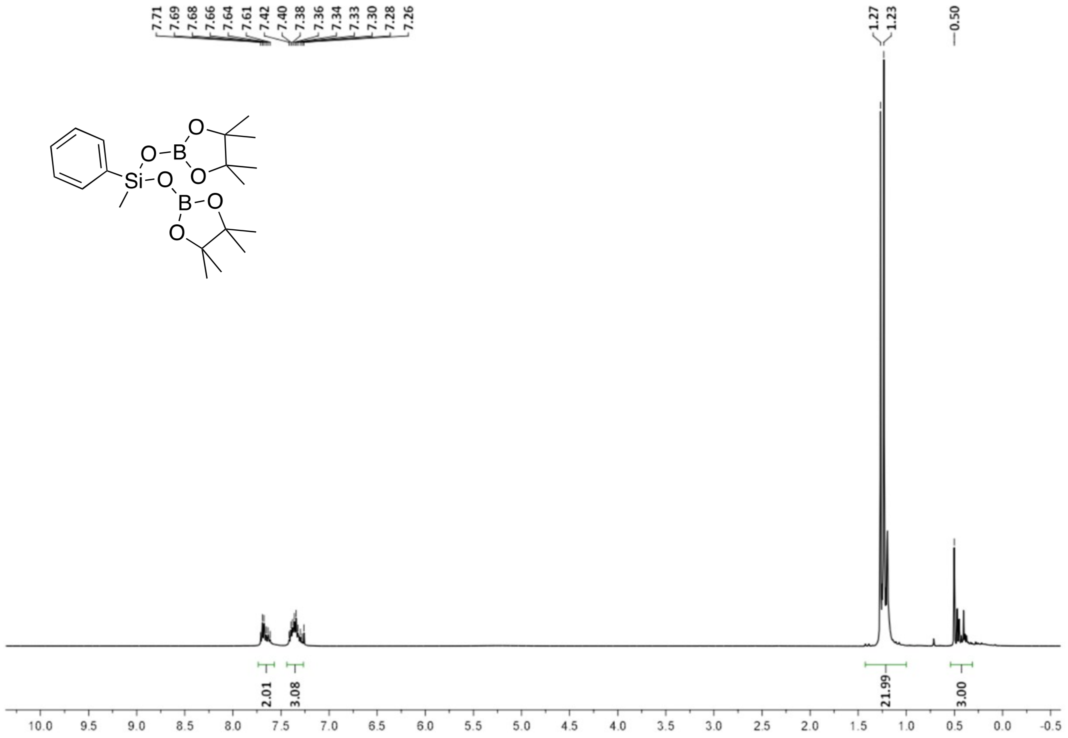
^{1}H NMR spectrum of diethylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



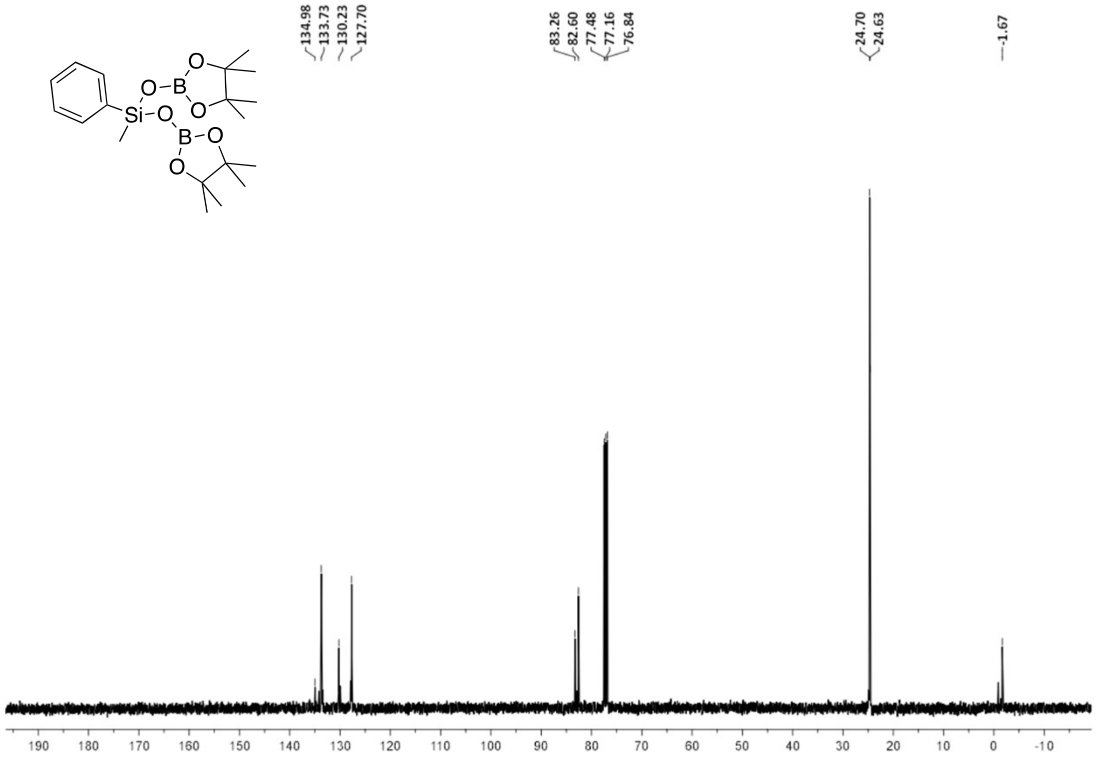
^{13}C NMR spectrum of diethylbis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



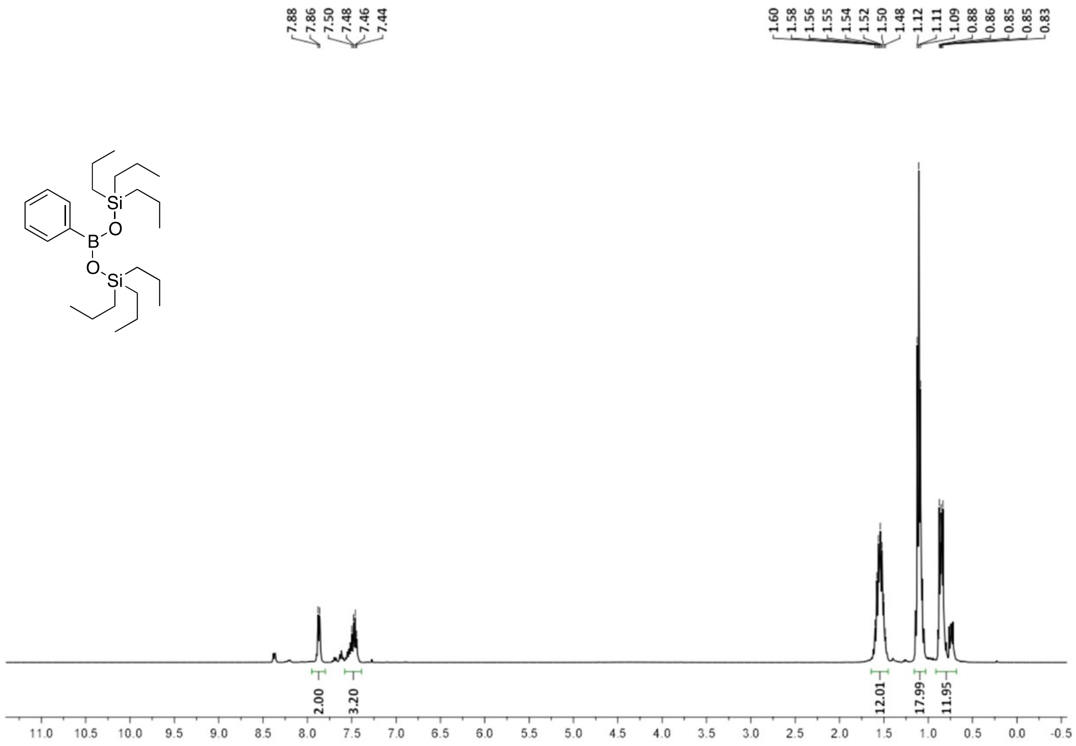
^1H NMR spectrum of methyl(phenyl)bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



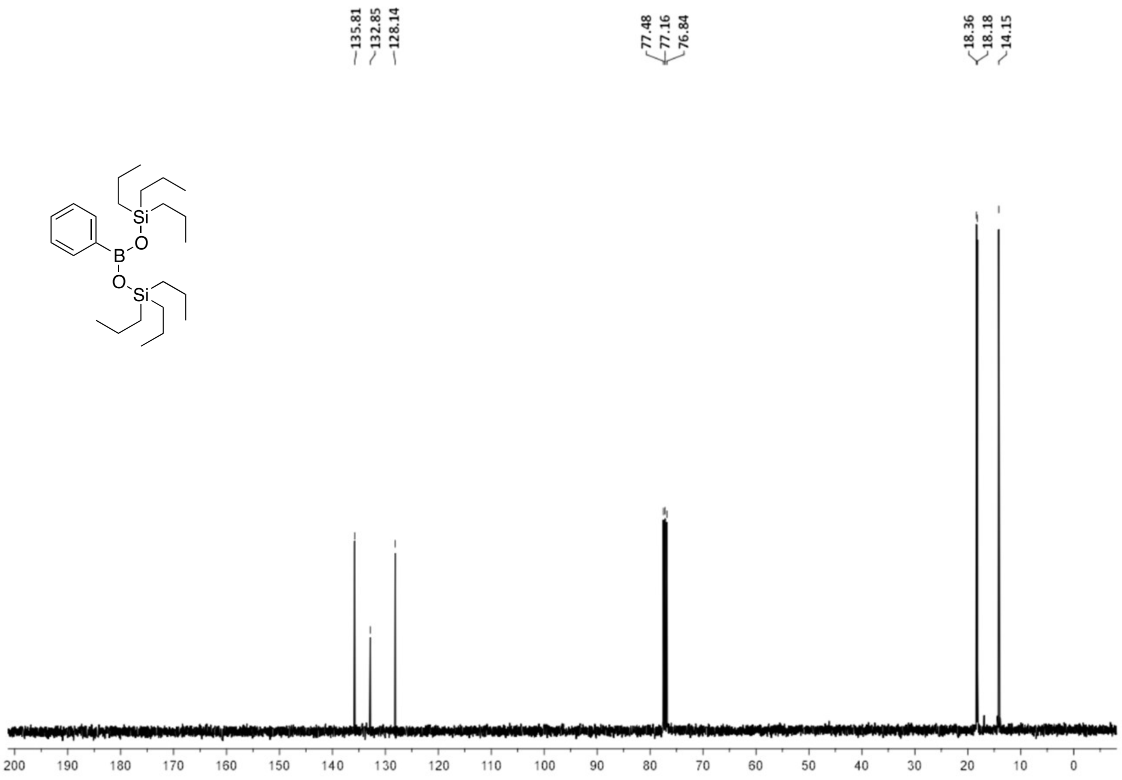
^{13}C NMR spectrum of methyl(phenyl)bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)silane:



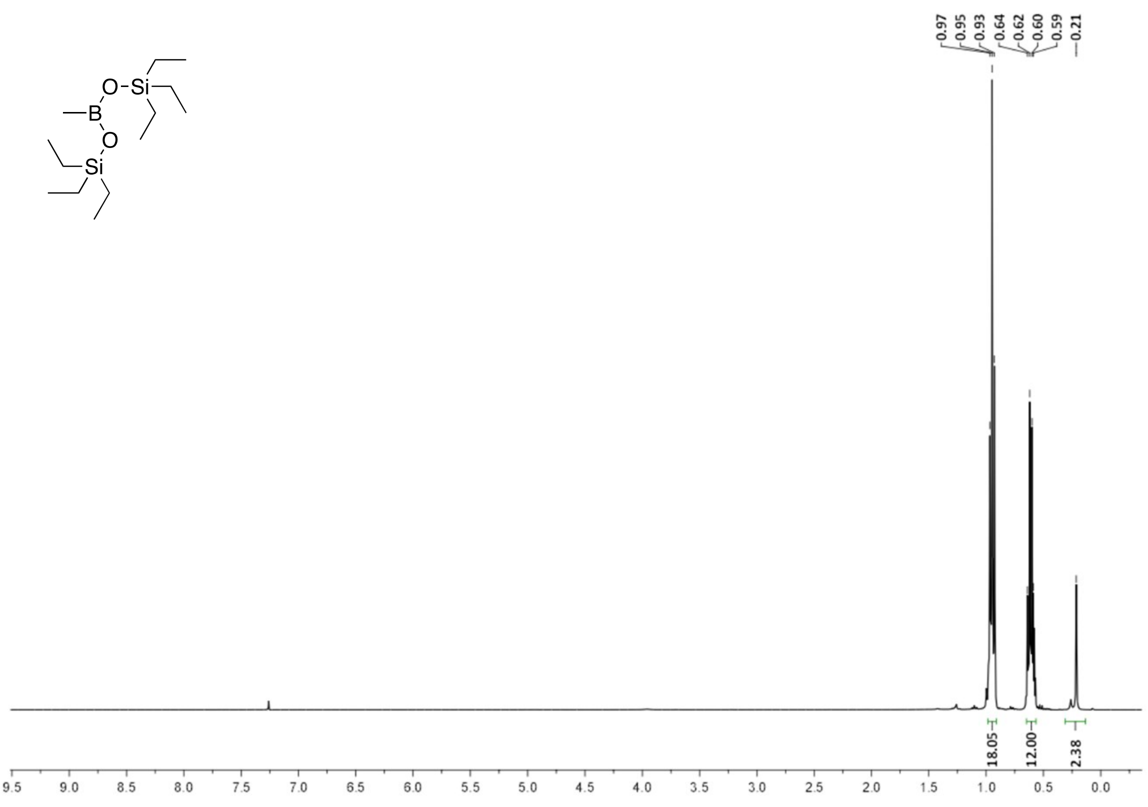
^{1}H NMR spectrum of bis(tripropylsilyl) phenylboronate:



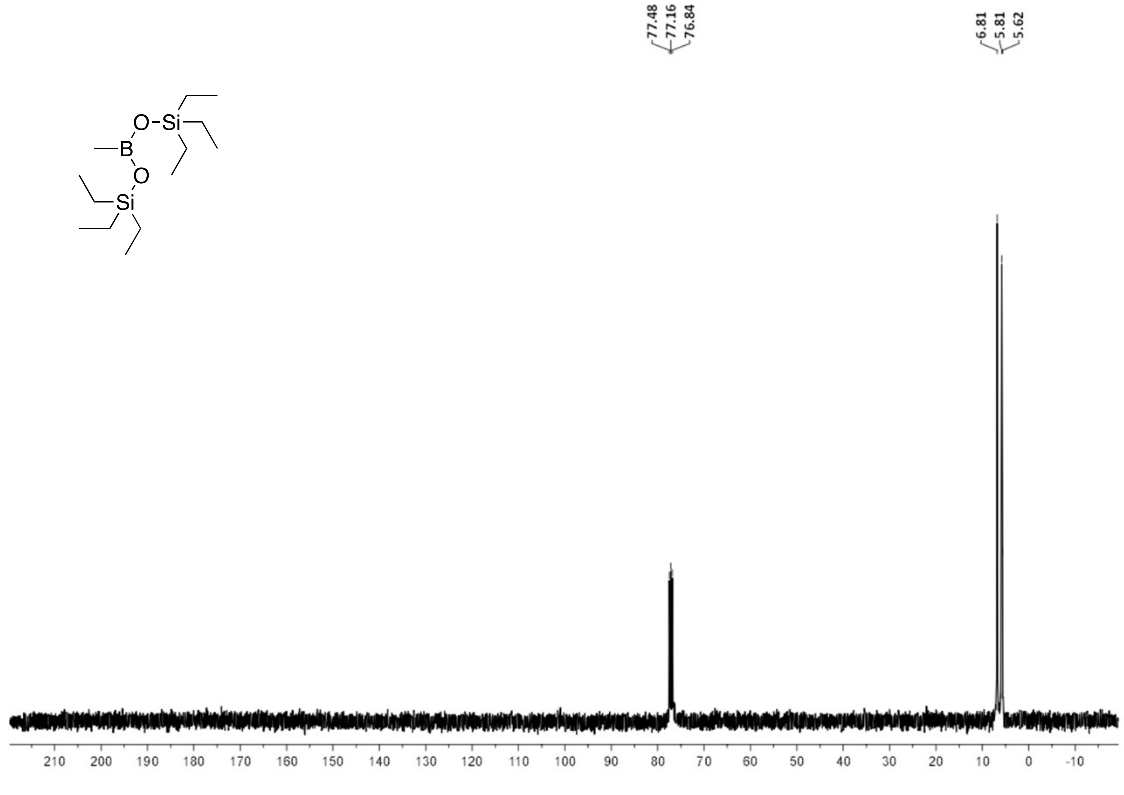
^{13}C NMR spectrum of bis(tripropylsilyl) phenylboronate:



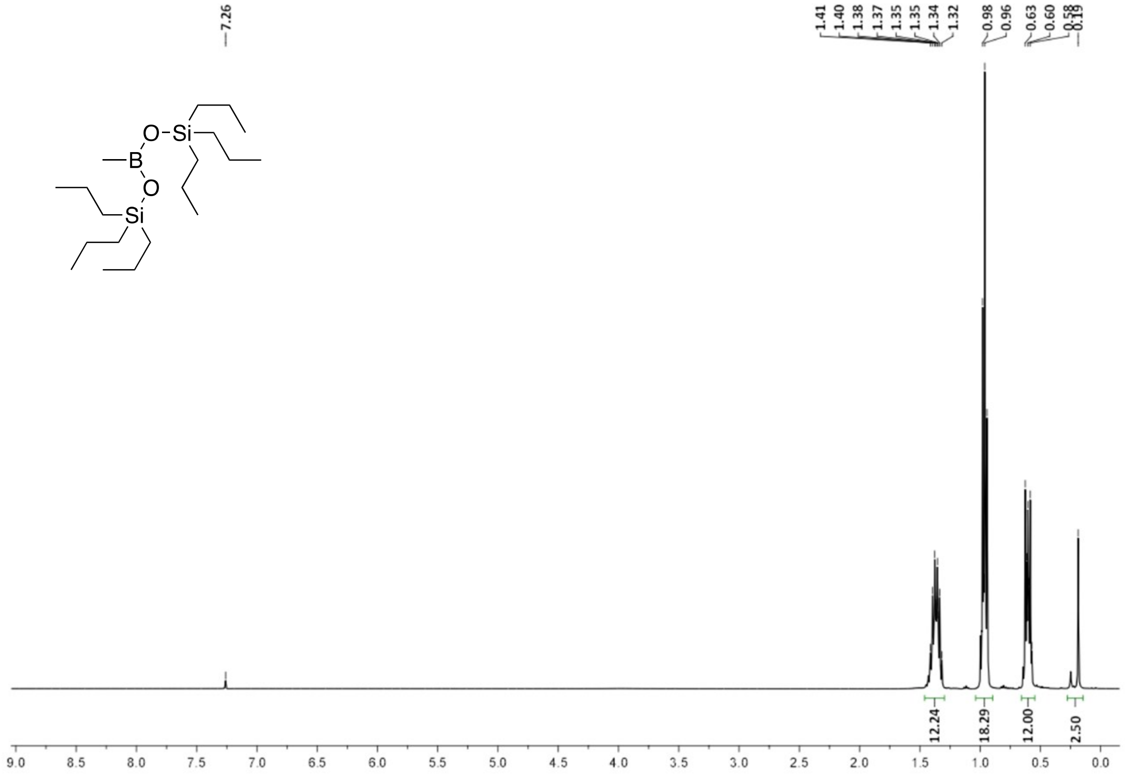
^{1}H NMR spectrum of bis(triethylsilyl) methylboronate:



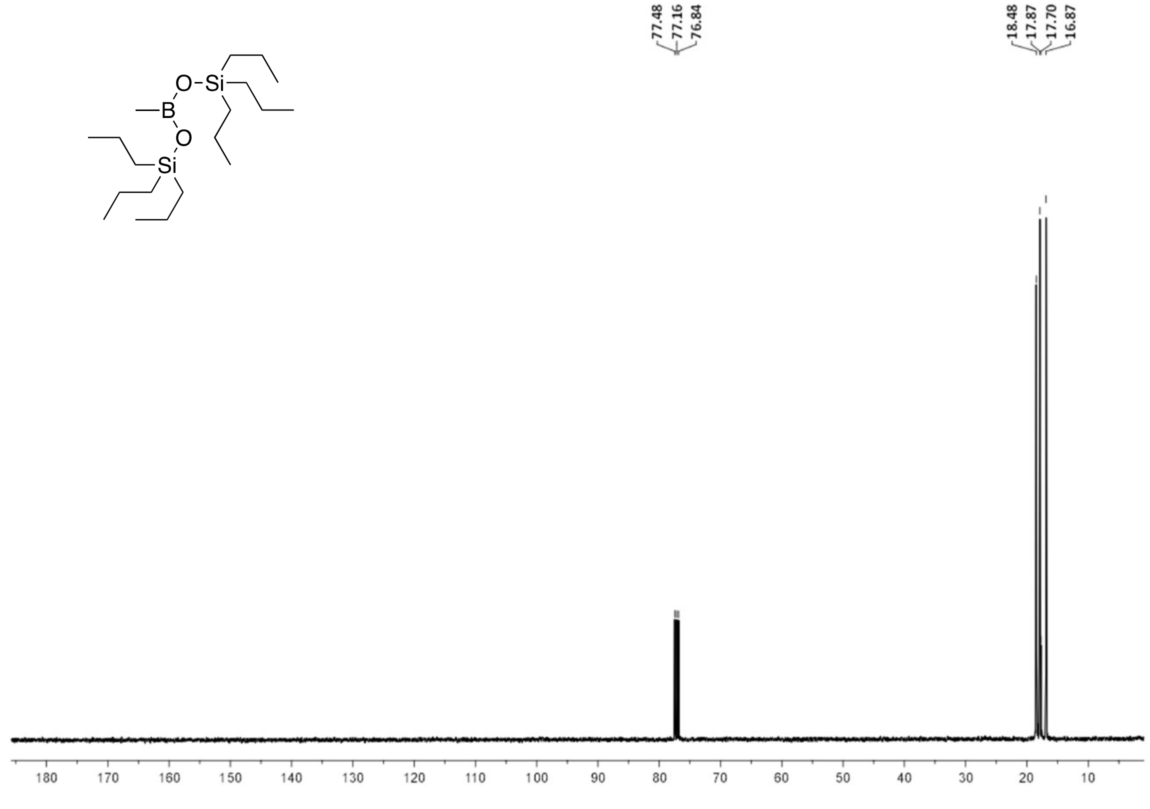
^{13}C NMR spectrum of bis(triethylsilyl) methylboronate:



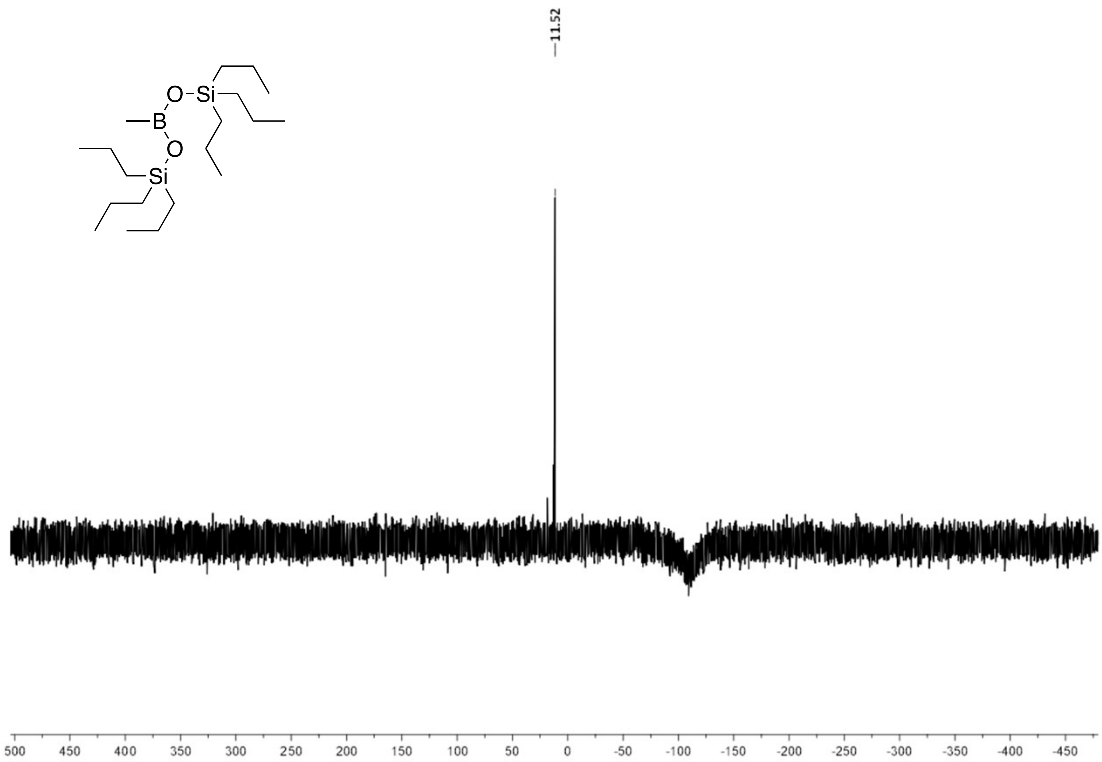
^{1}H NMR spectrum of bis(tripropylsilyl)methylboronate:



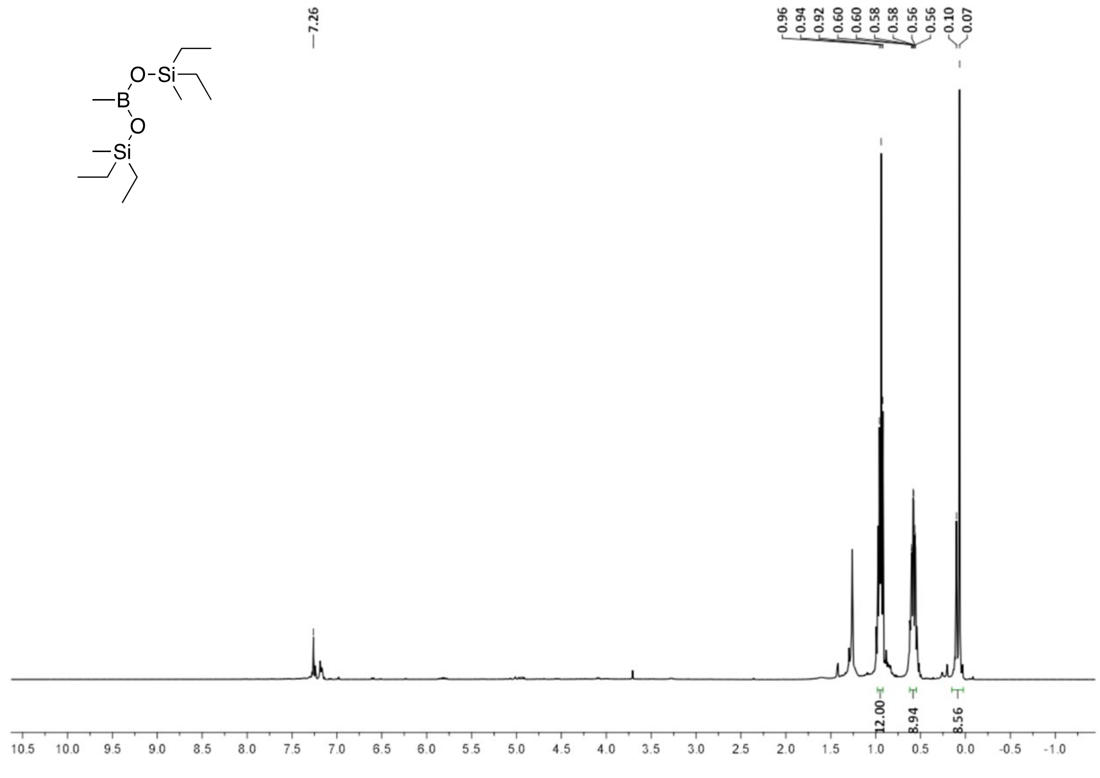
^{13}C NMR spectrum of bis(tripropylsilyl) methylboronate:



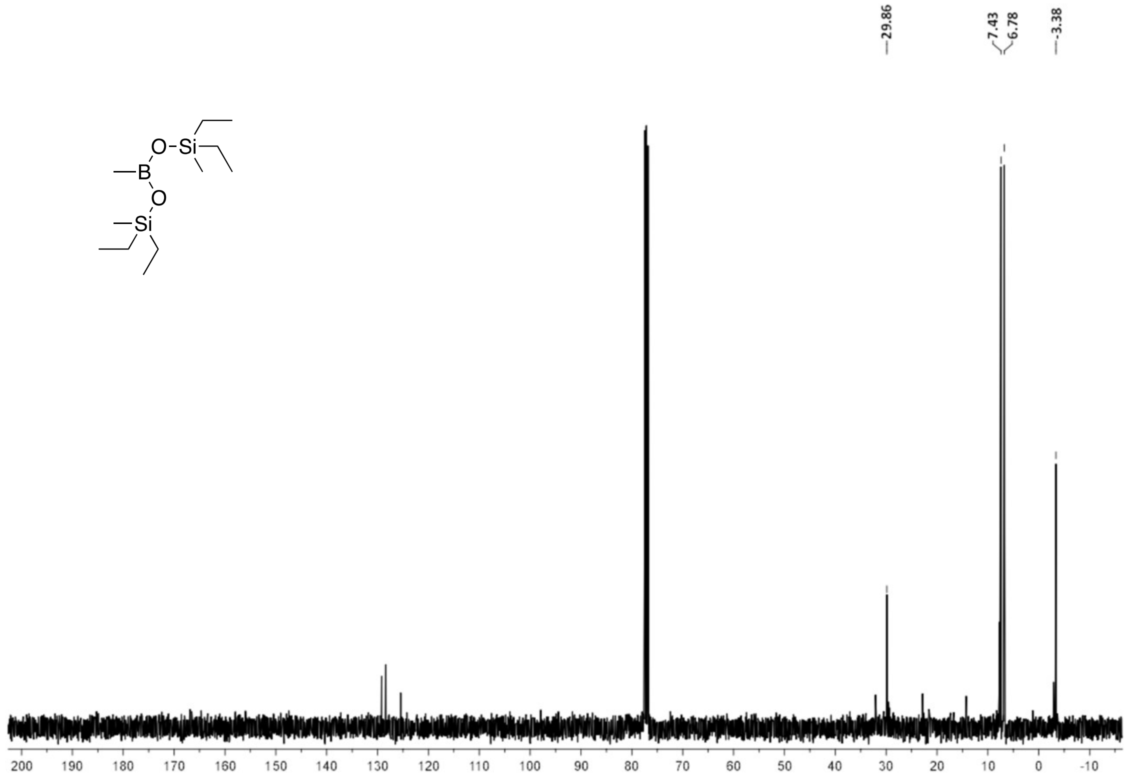
^{29}Si NMR spectrum of bis(tripropylsilyl) methylboronate:



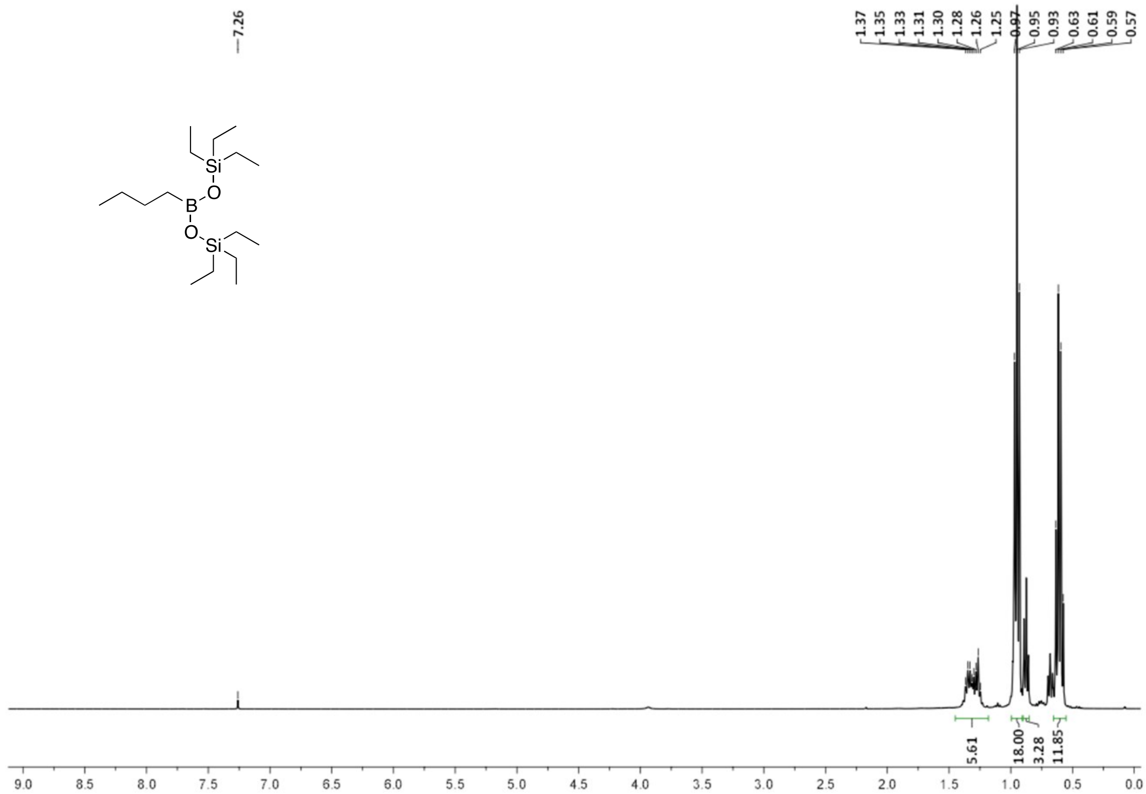
^{1}H NMR spectrum of bis(diethyl(methyl)silyl) methylboronate:



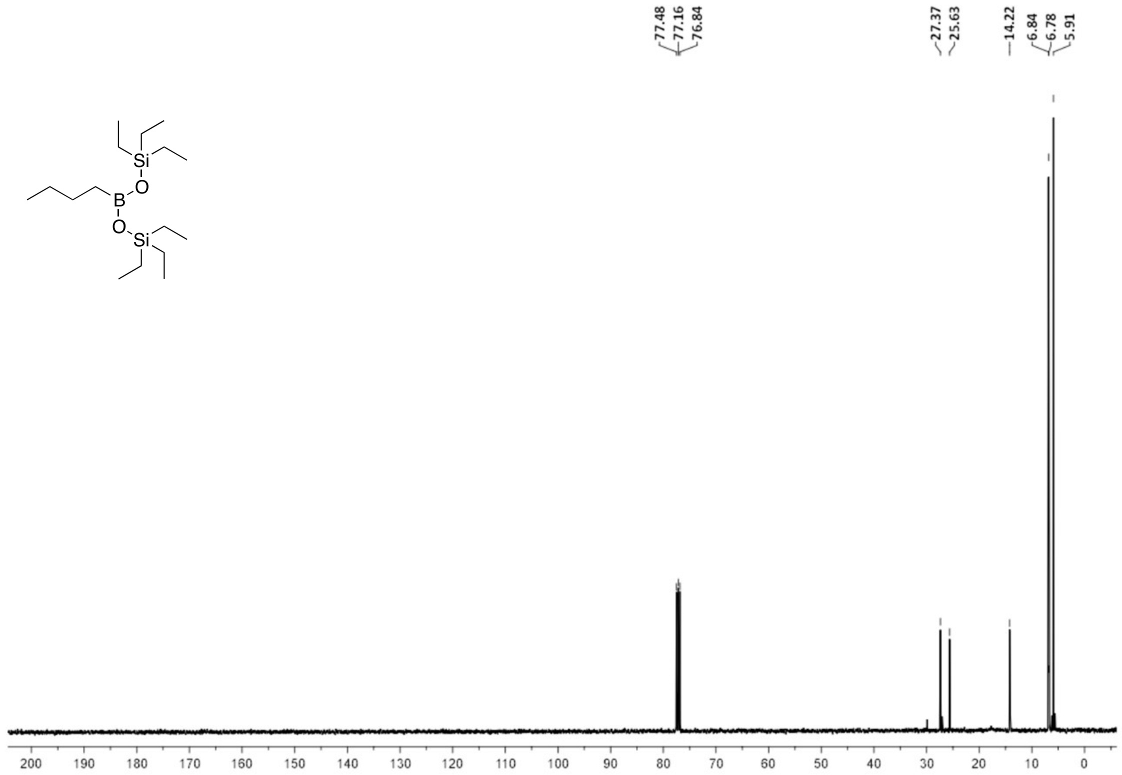
^{13}C NMR spectrum of bis(diethyl(methyl)silyl) methylboronate:



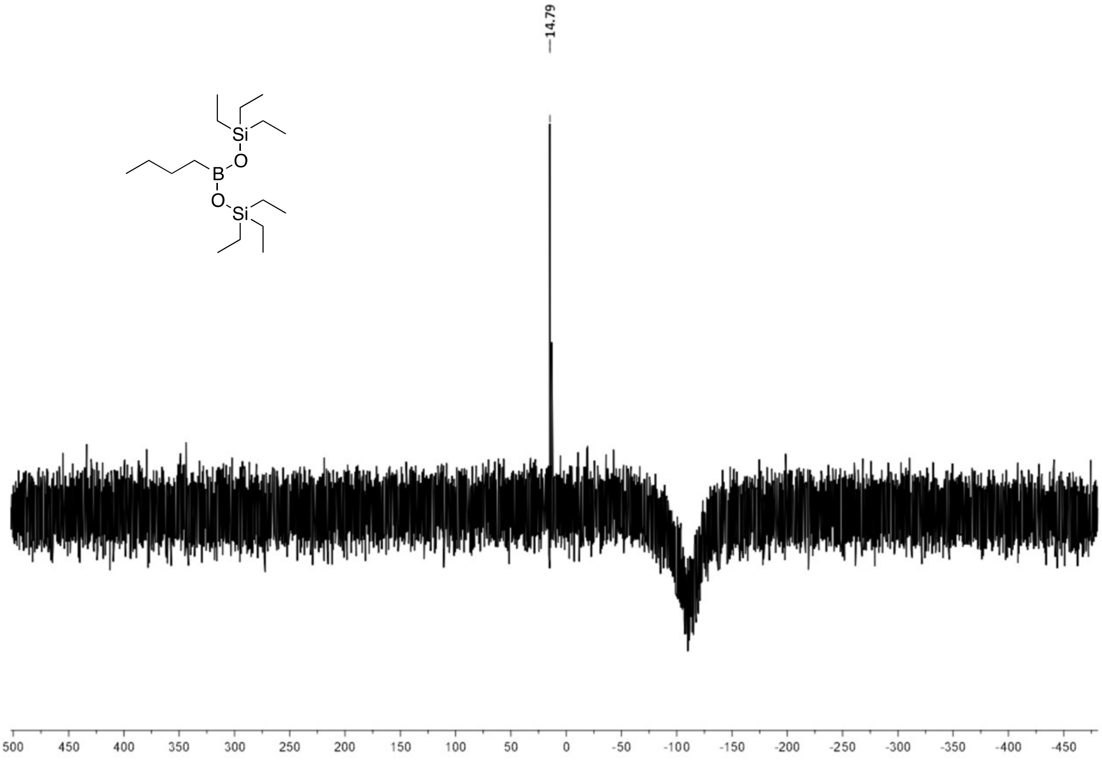
^{1}H NMR spectrum of bis(triethylsilyl) butylboronate:



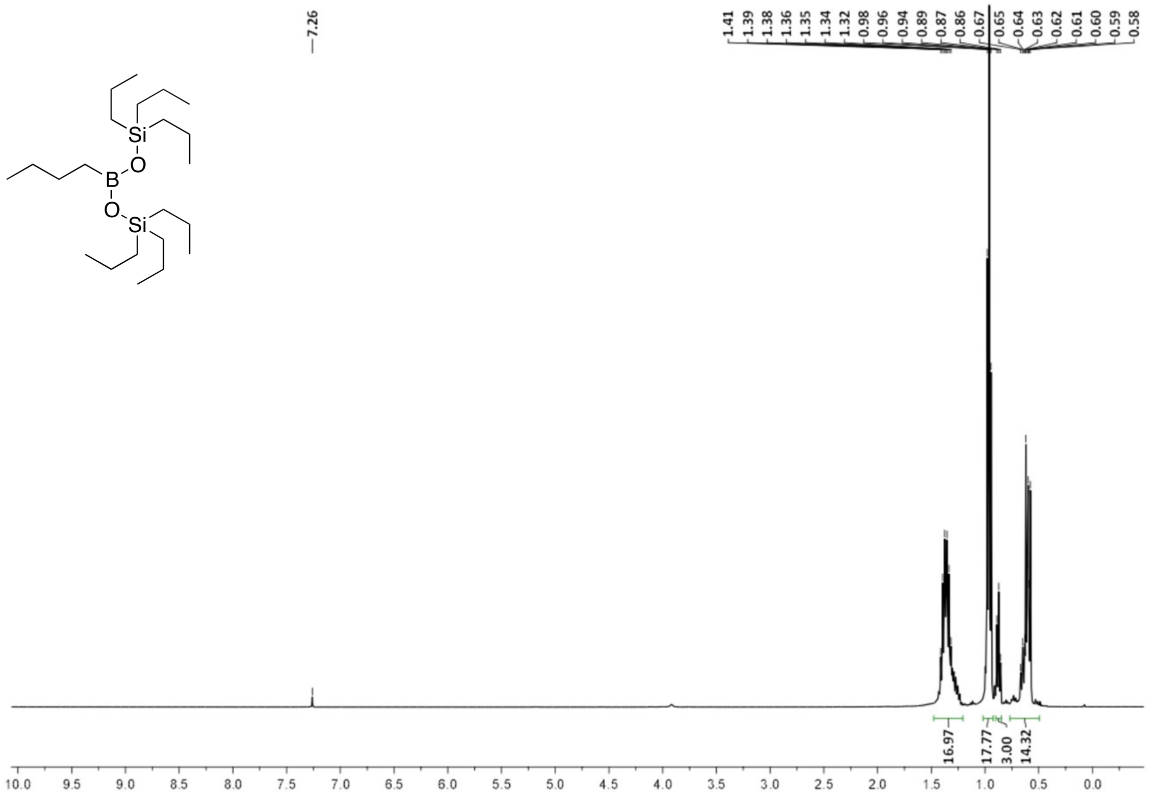
^{13}C NMR spectrum of bis(triethylsilyl) butylboronate:



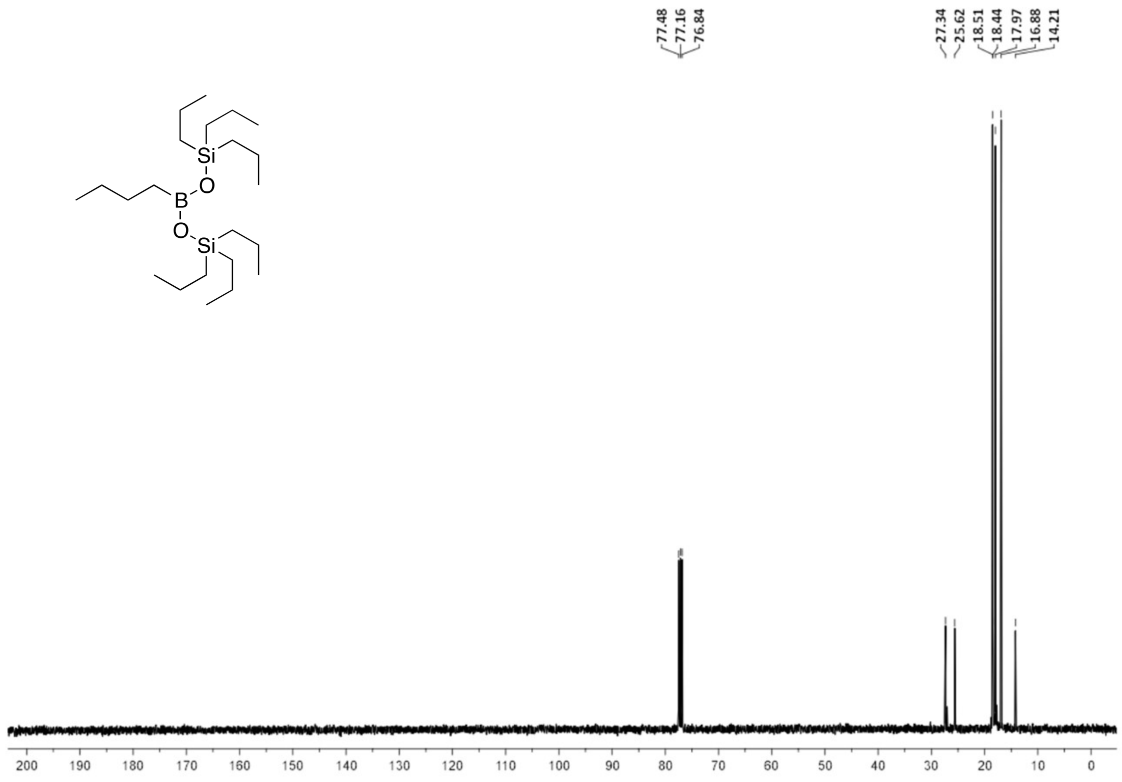
^{29}Si NMR spectrum of bis(triethylsilyl) butylboronate:



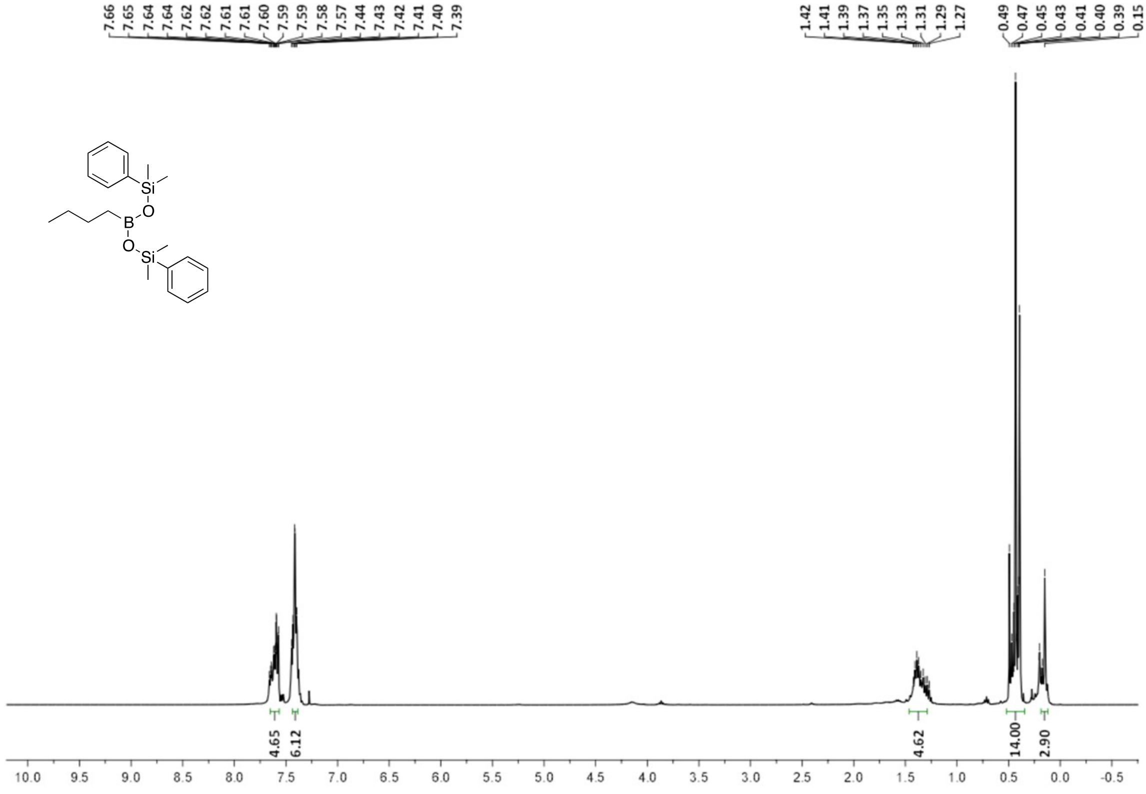
^{1}H NMR spectrum of bis(tripropylsilyl) butylboronate:



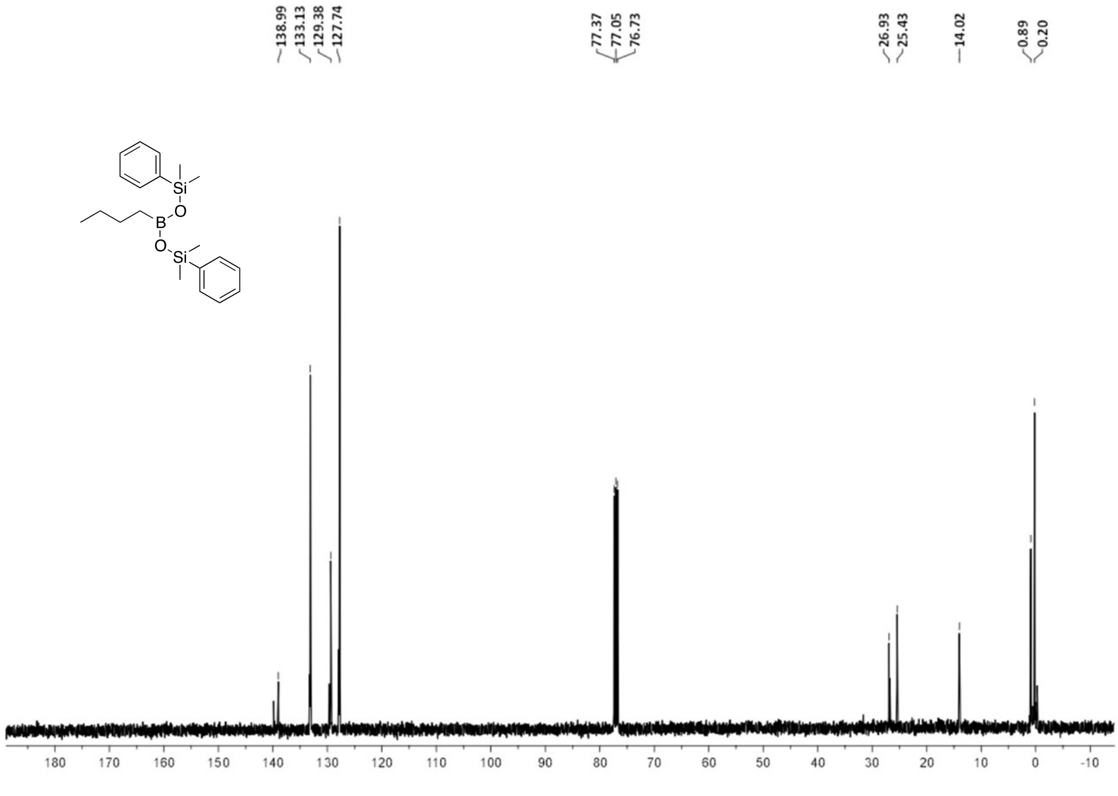
^{13}C NMR spectrum of bis(tripropylsilyl) butylboronate:



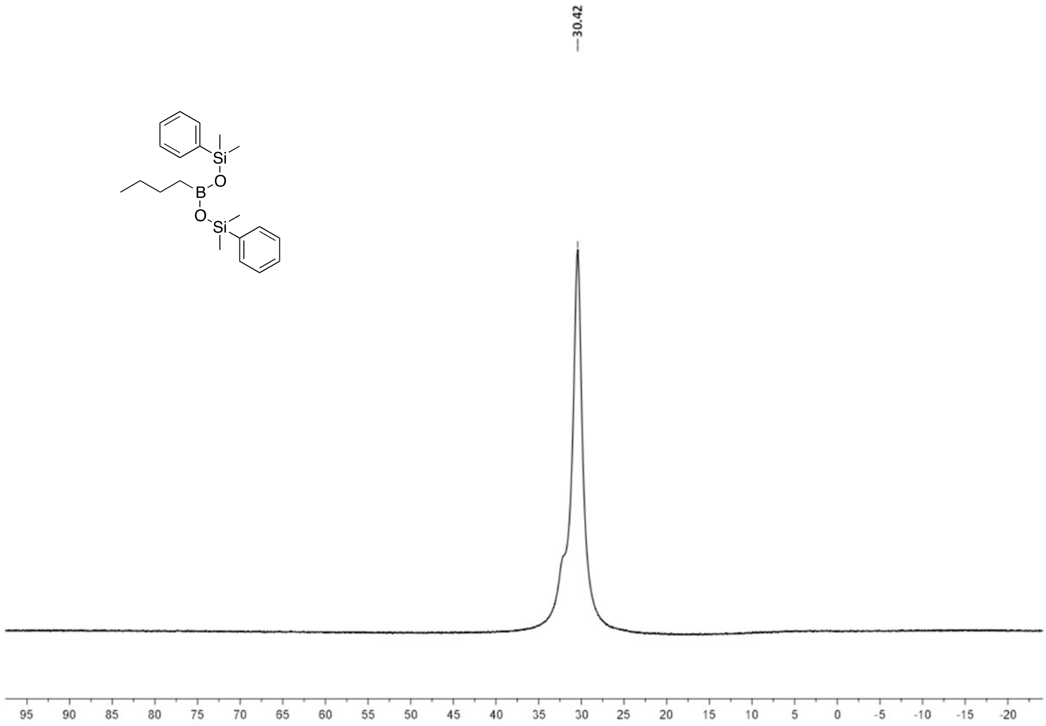
^{1}H NMR spectrum of bis(dimethyl(phenyl)silyl) butylboronate:



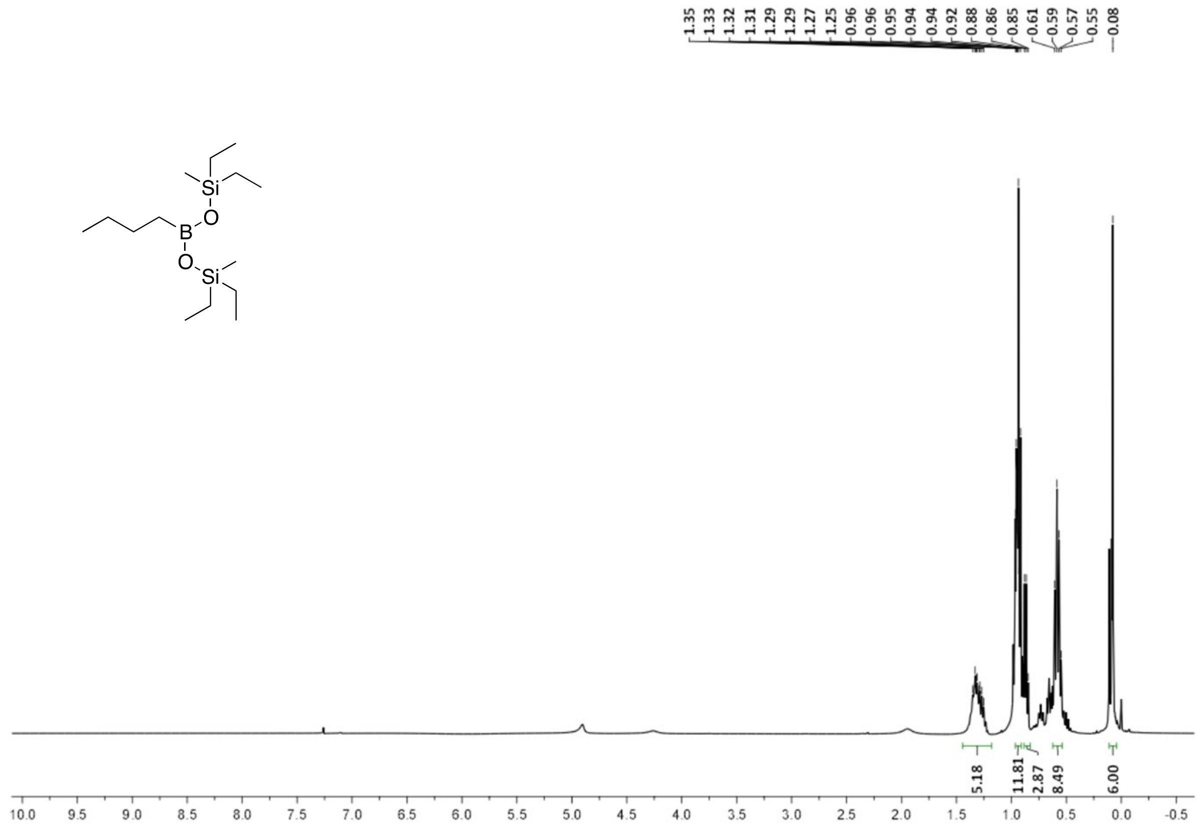
^{13}C NMR spectrum of bis(dimethyl(phenyl)silyl) butylboronate:



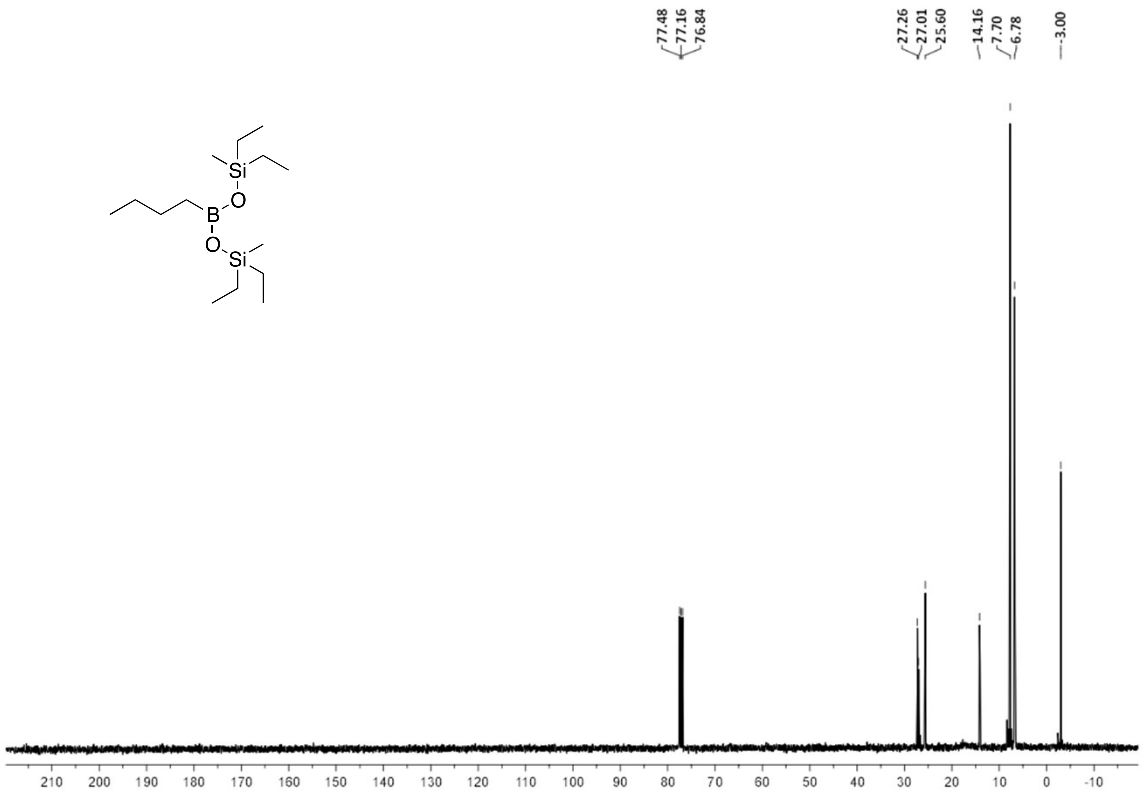
^{11}B NMR spectrum of bis(dimethyl(phenyl)silyl) butylboronate:



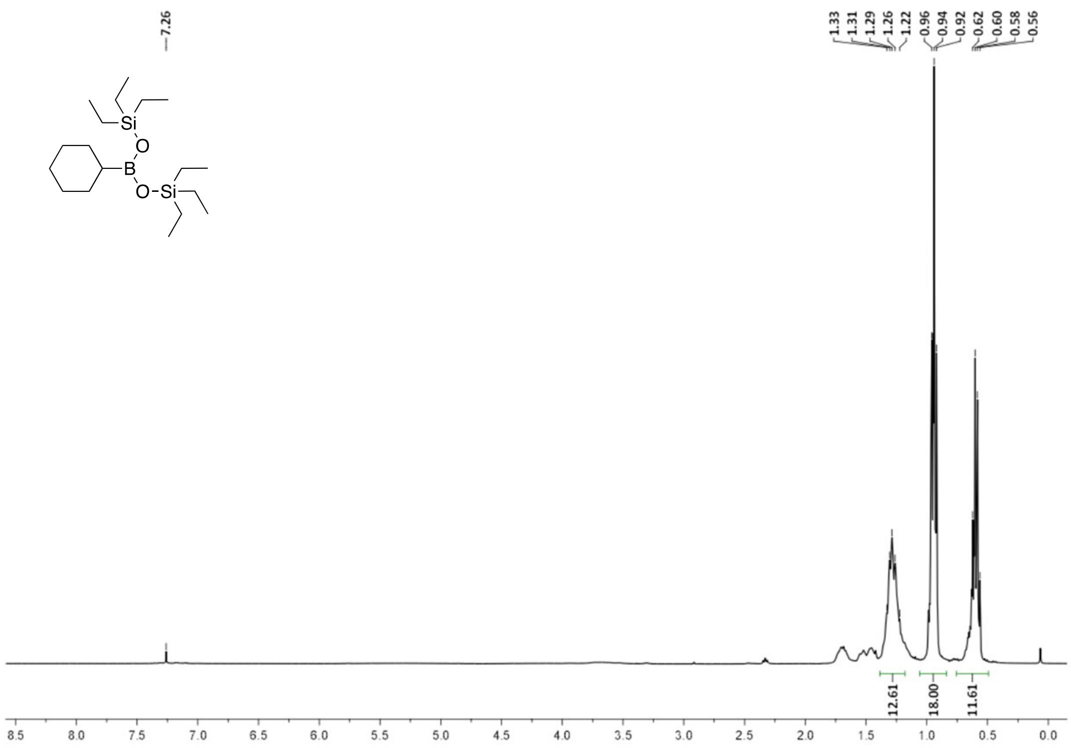
^{1}H NMR spectrum of bis(diethyl(methyl)silyl) butylboronate:



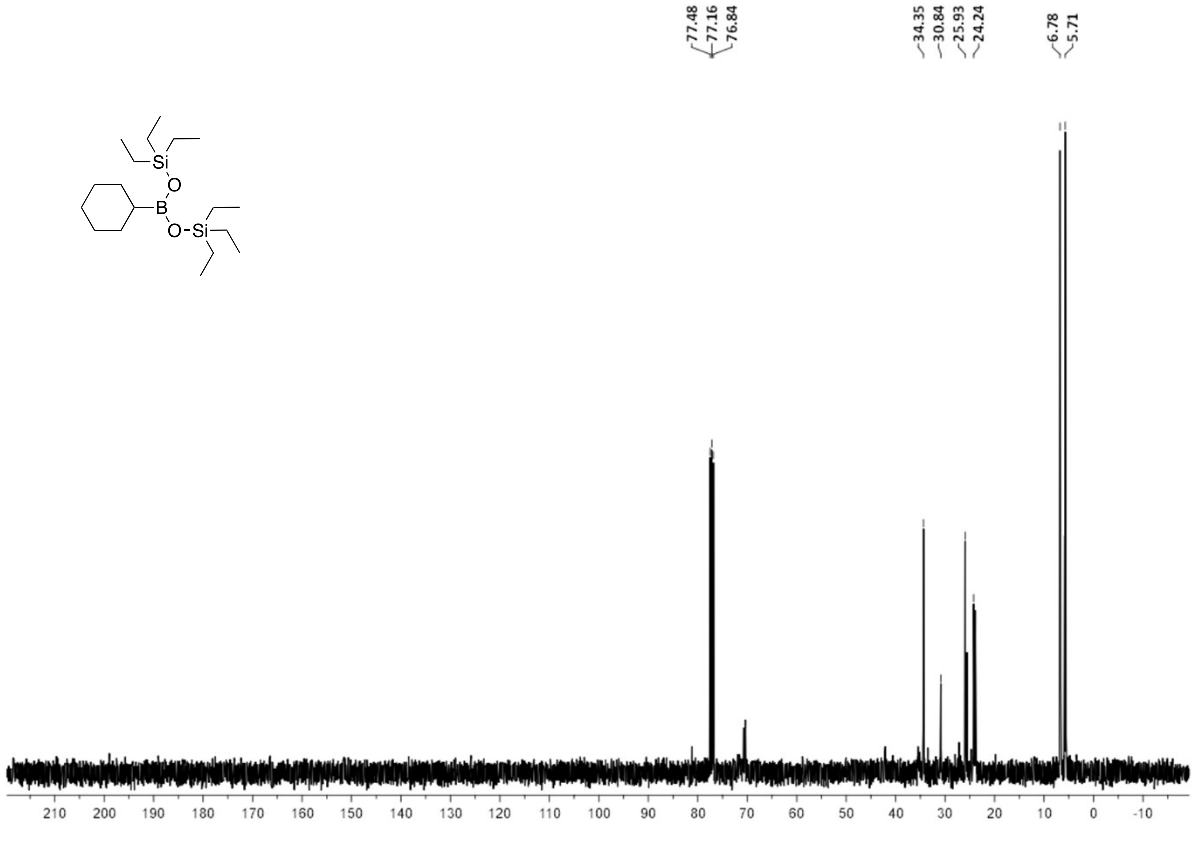
^{13}C NMR spectrum of bis(diethyl(methyl)silyl) butylboronate:



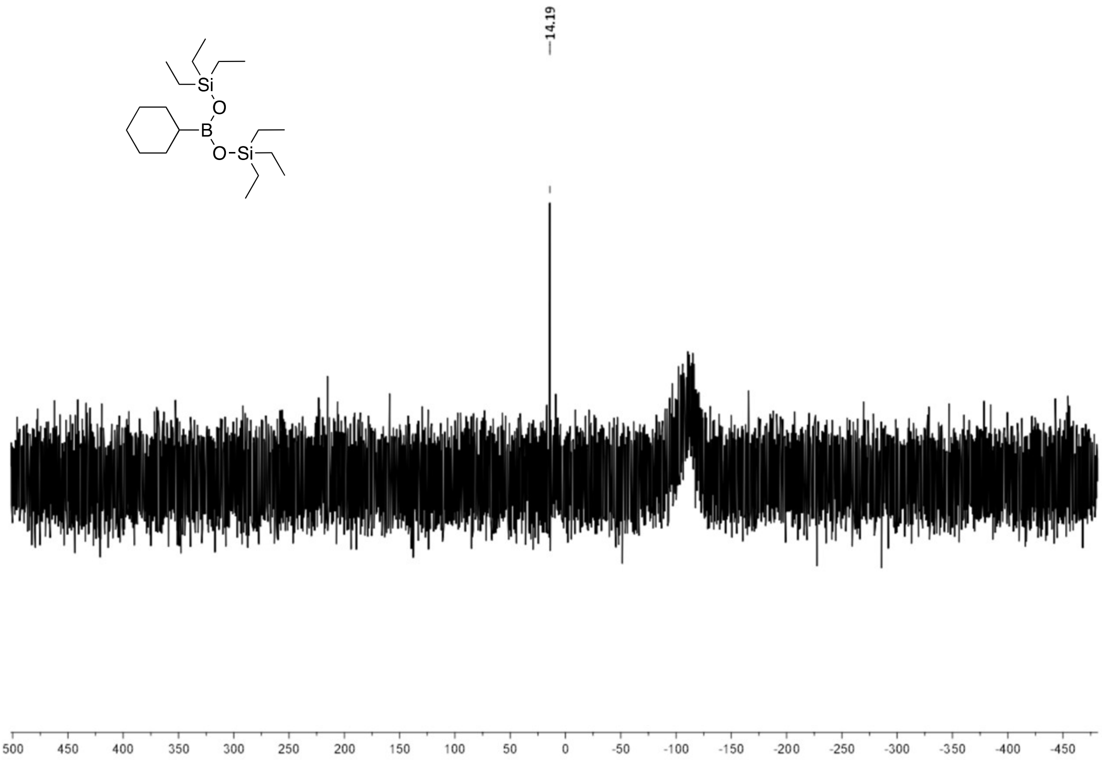
^{1}H NMR spectrum of bis(triethylsilyl) cyclohexylboronate:



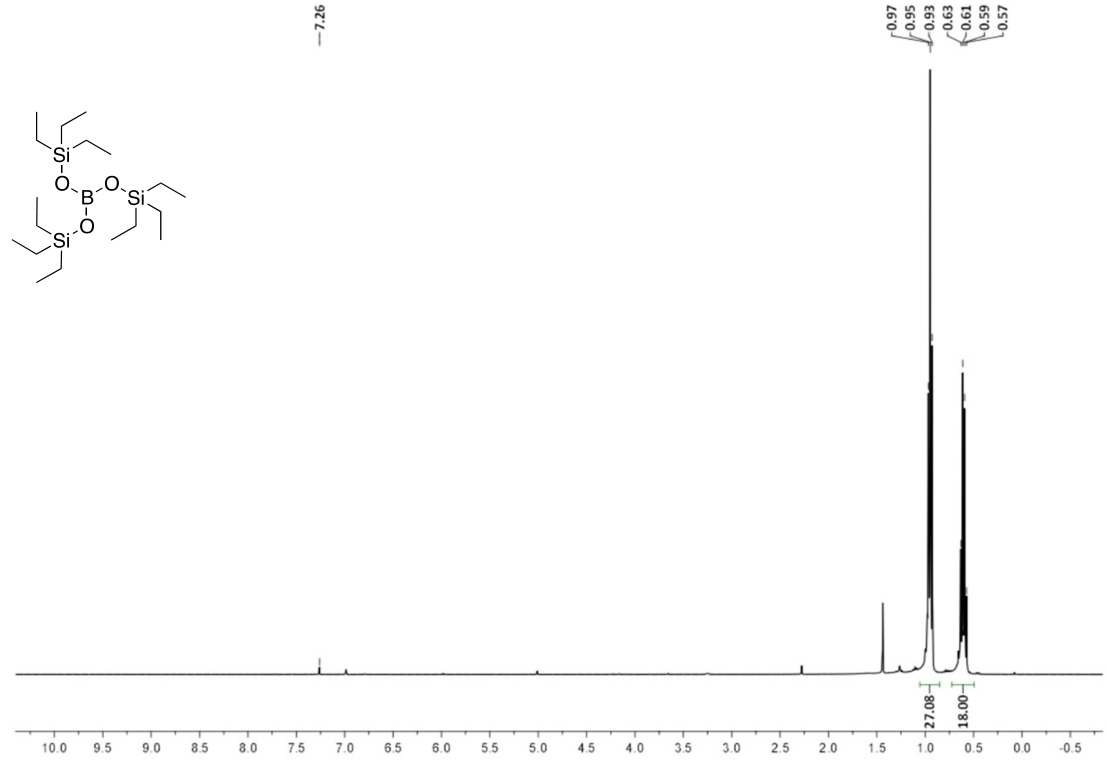
^{13}C NMR spectrum of bis(triethylsilyl) cyclohexylboronate:



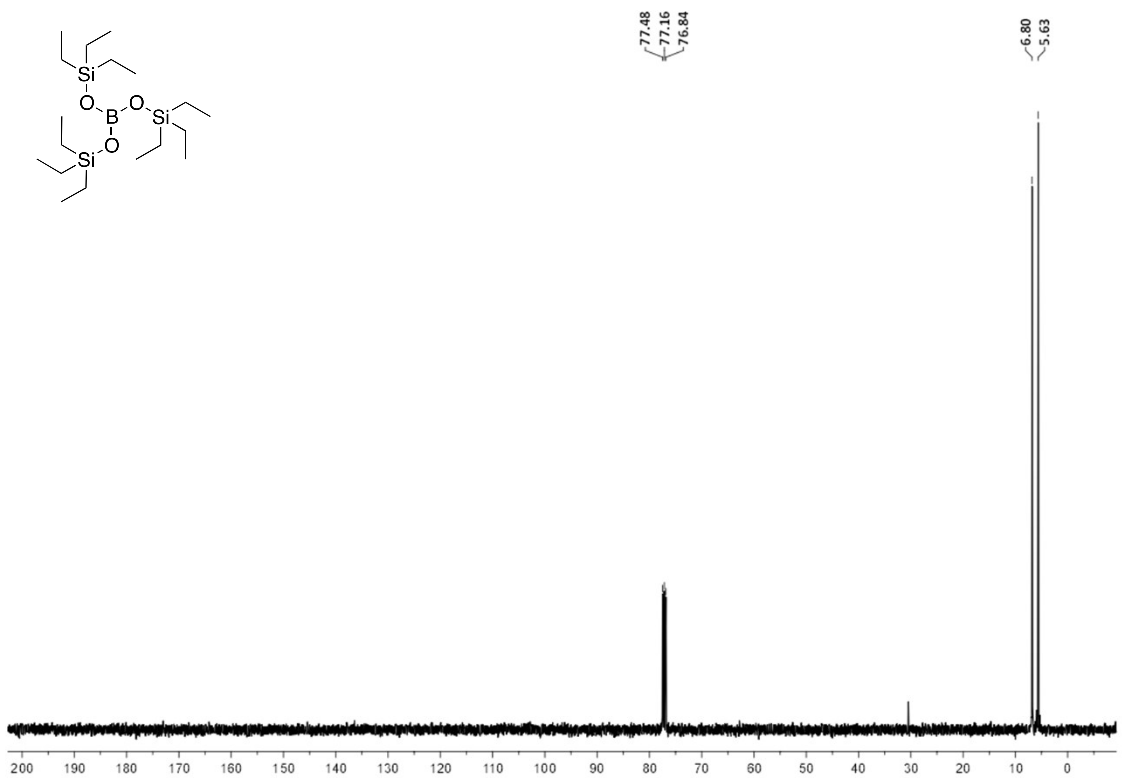
^{29}Si NMR spectrum of bis(triethylsilyl) cyclohexylboronate:



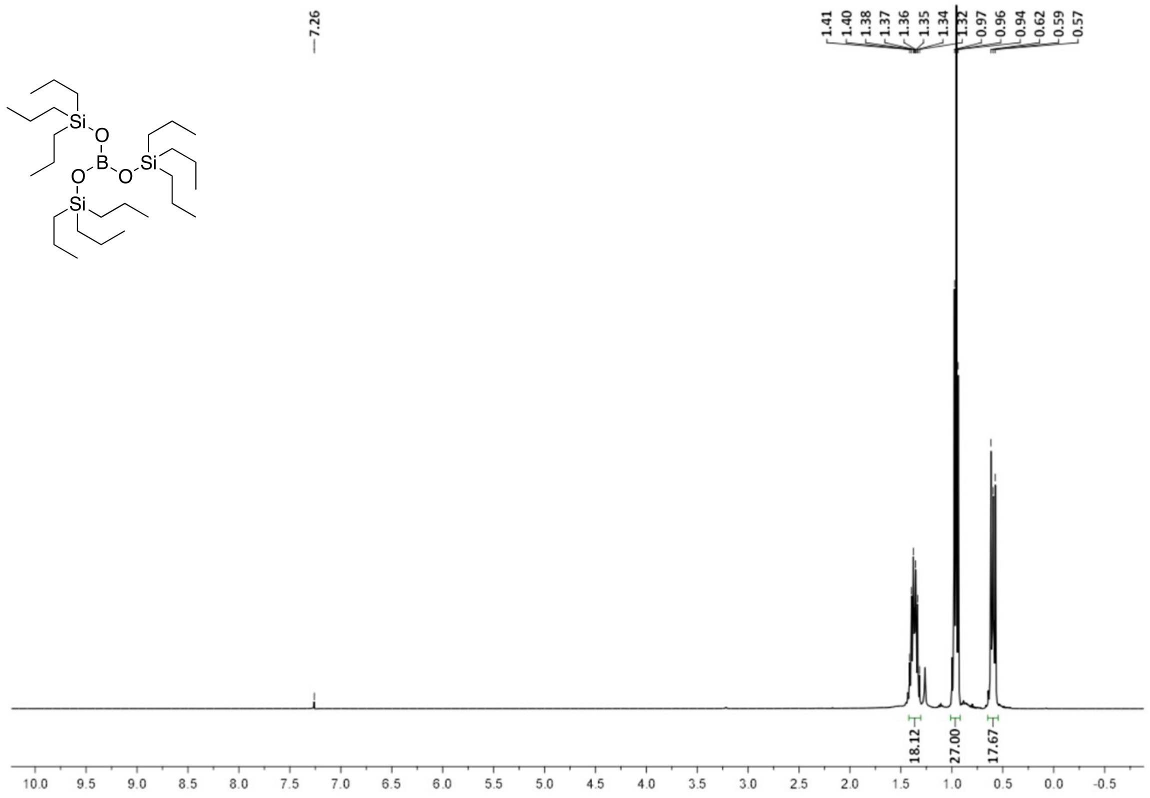
^1H NMR spectrum of tris(triethylsilyl) borate:



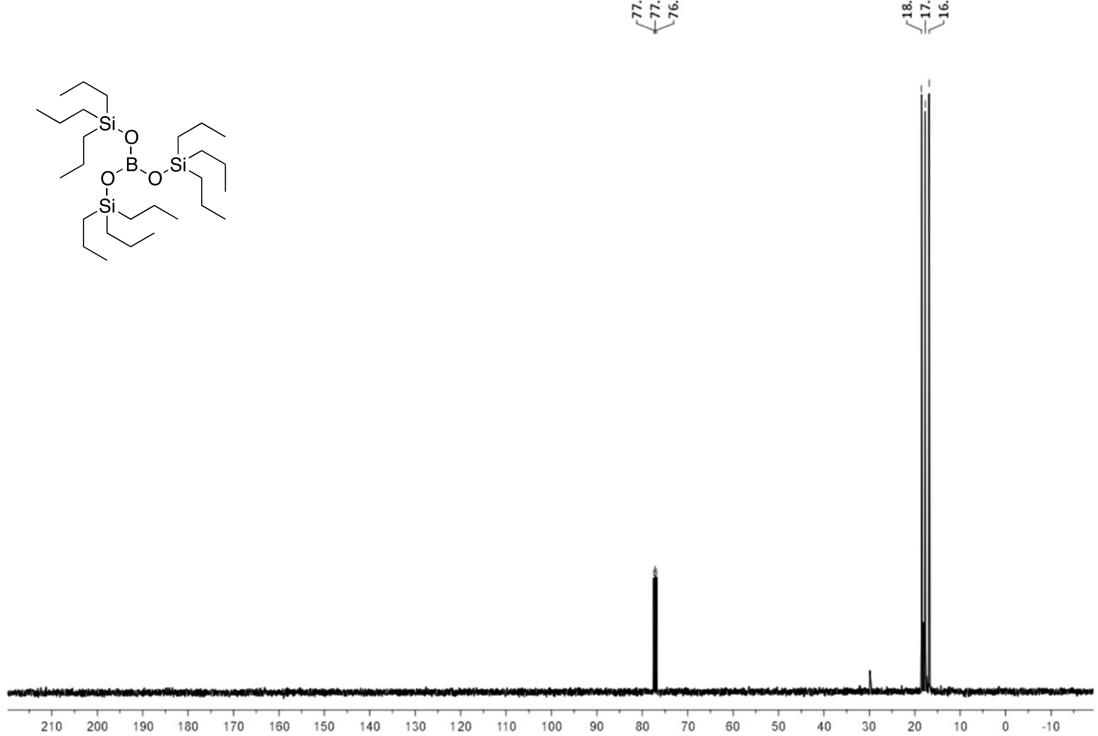
^{13}C NMR spectrum of tris(triethylsilyl) borate:



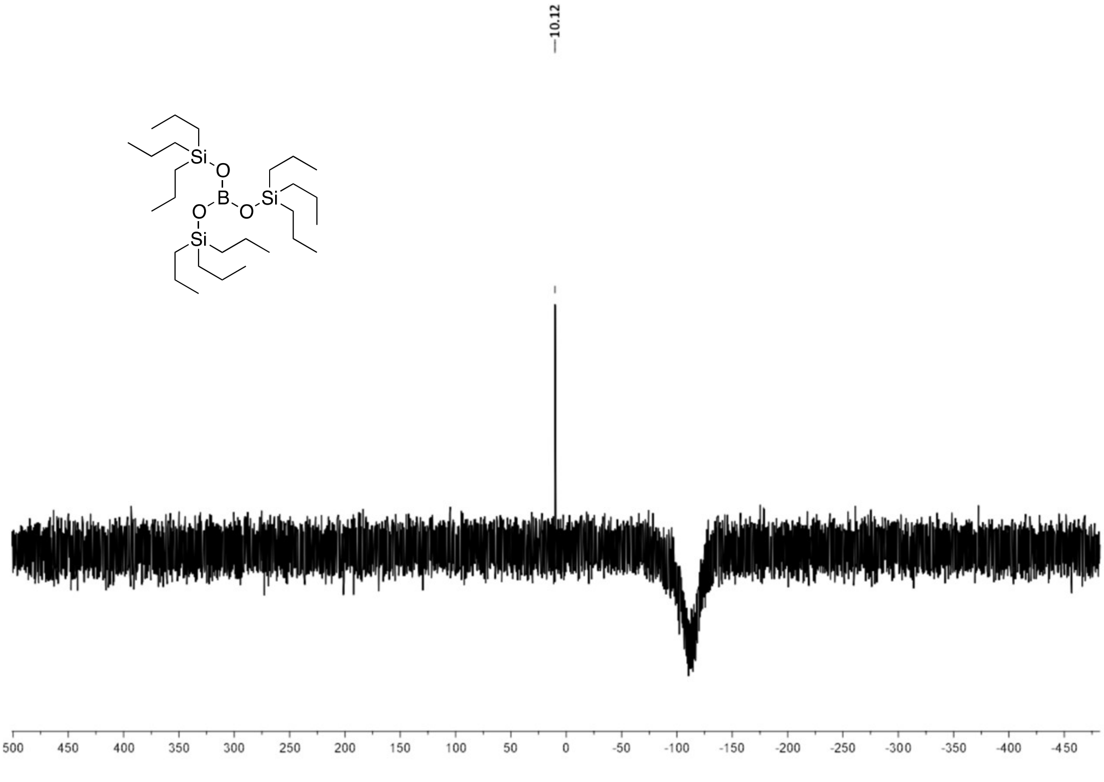
^{1}H NMR spectrum of tris(tripropylsilyl) borate:



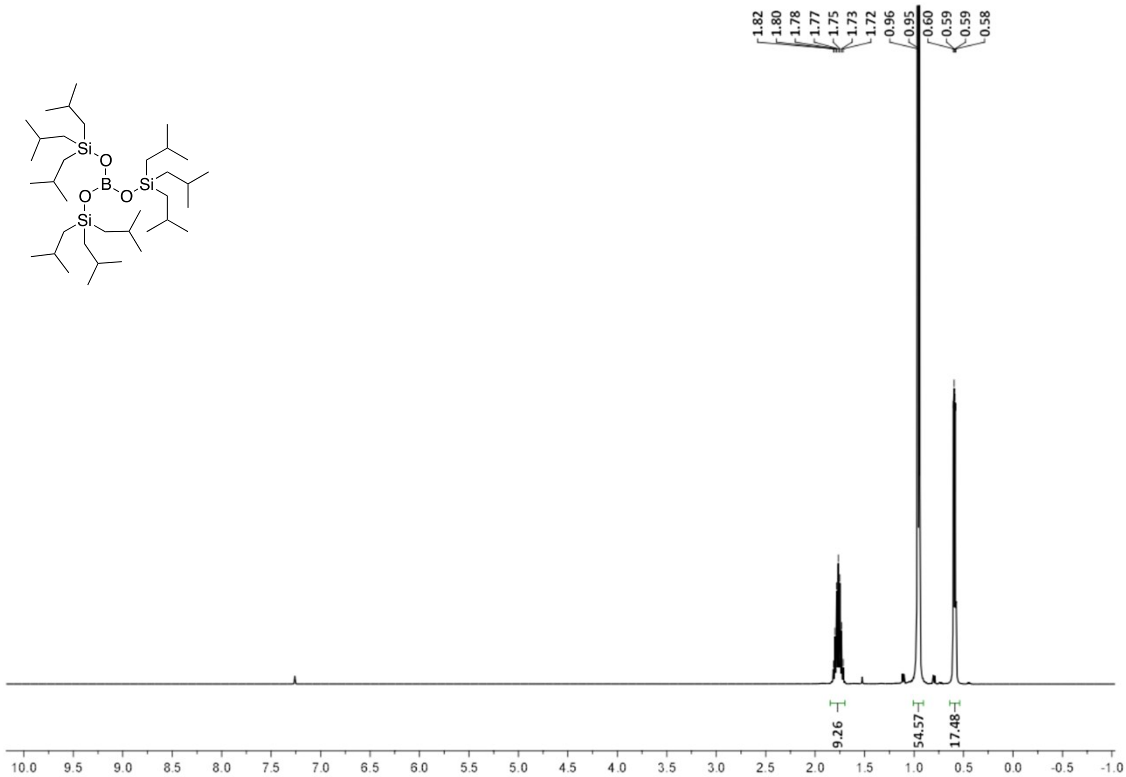
^{13}C NMR spectrum of tris(tripropylsilyl) borate:



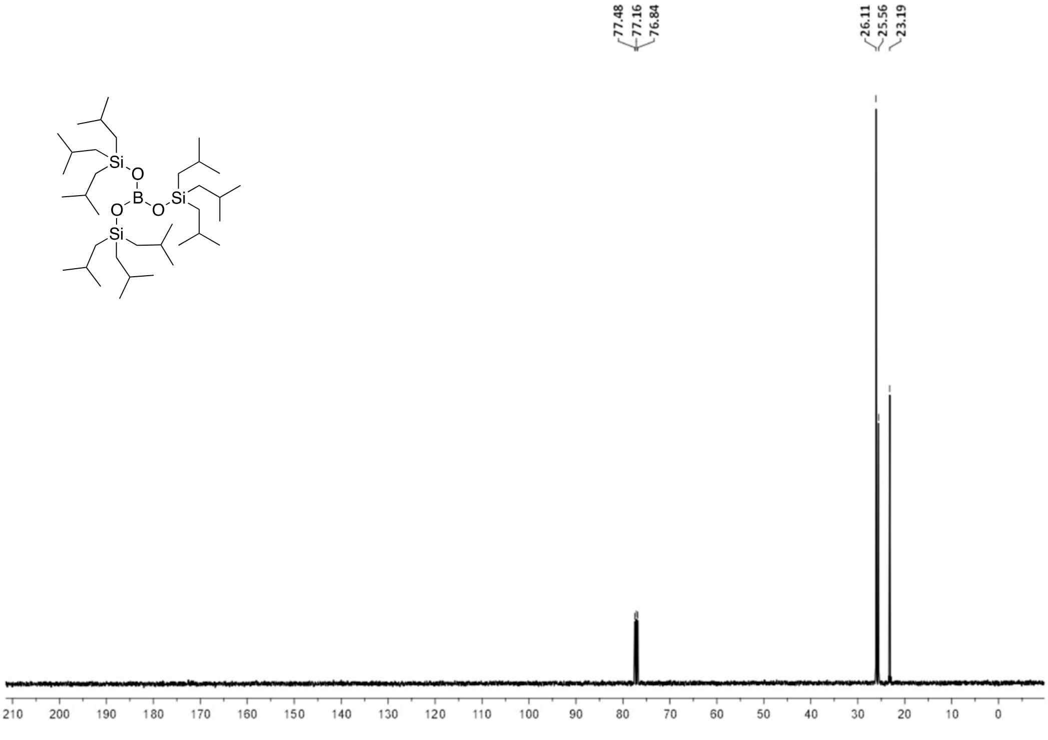
^{29}Si NMR spectrum of tris(tripropylsilyl) borate:



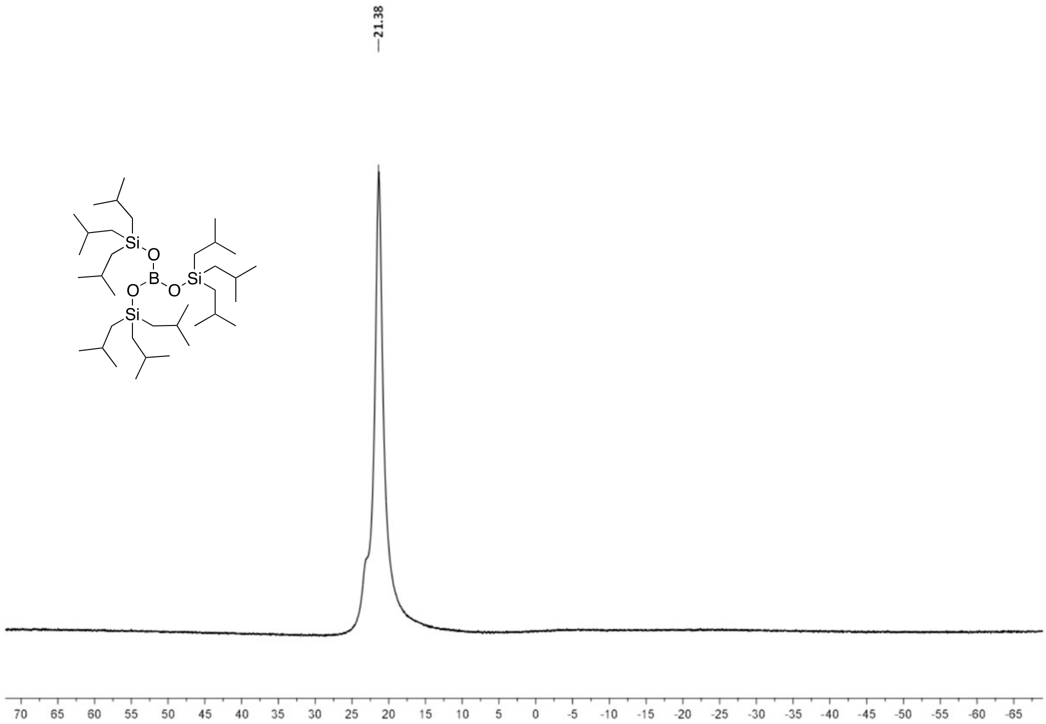
^{1}H NMR spectrum of tris(triisobutylsilyl) borate:



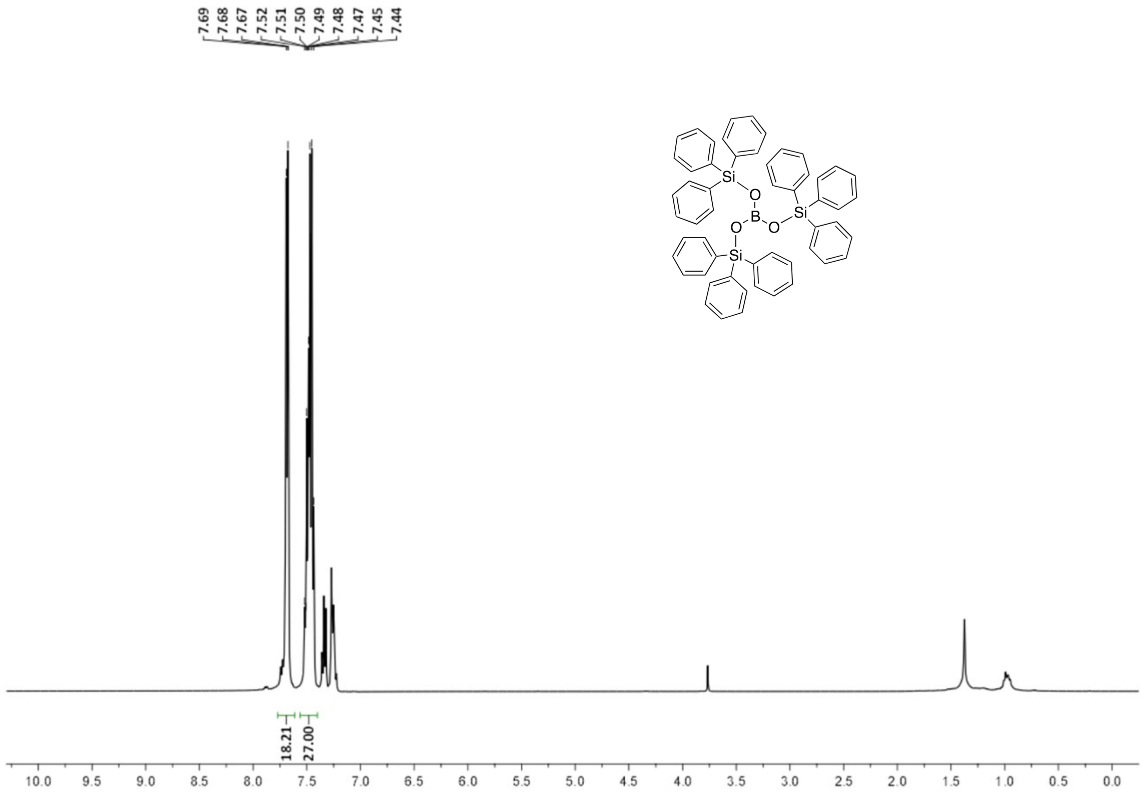
^{13}C NMR spectrum of tris(triisobutylsilyl) borate:



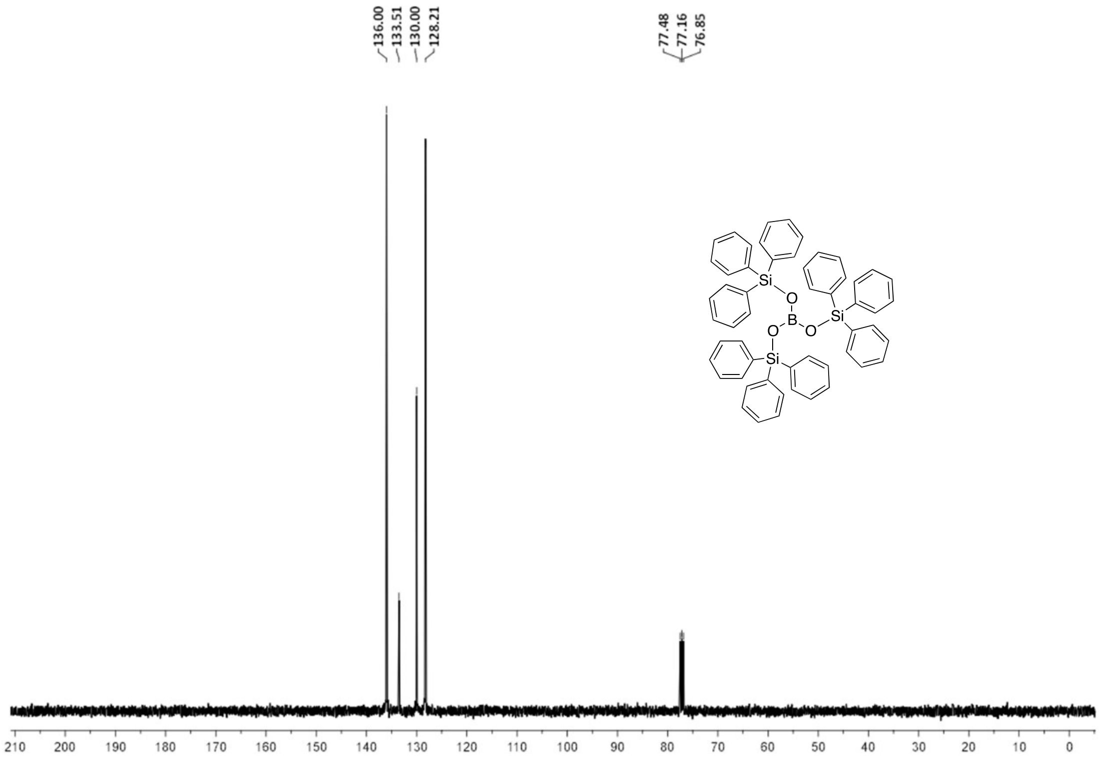
^{11}B NMR spectrum of tris(triisobutylsilyl) borate:



^{1}H NMR spectrum of tris(triphenylsilyl) borate **8**:



^{13}C NMR spectrum of tris(triphenylsilyl) borate **8**:



Determination of the molecular structure of 8 in the solid state by X-ray single crystal diffraction: Single crystals of compound **8** suitable for X-ray analysis was obtained from the solution of hexane and ether. A suitable crystal was mounted on a glass fibre. The geometry and intensity data were collected using Bruker SMART D8 goniometer equipped with an APEX CCD detector and an Incoatec microsource (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+[2] and corrected for absorption with SADABS.[3] The structure was solved by direct methods and refined on F2 with SHELXL-97.[4]

Crystal data: 2($C_{54}H_{45}BO_3Si_3$), $C_{36}H_{30}OSi_2$, crystal dimensions: 0.25 × 0.21 × 0.19, monoclinic with space group P121/c, a = 18.8982 (9) (7) Å, b = 18.8982 (9) Å, c = 28.7167 (14) Å, α = 90°, β = 90°, γ = 120°, V = 8881.9 (10) Å$_3$, Z = 3, T = 100 K, 2θmax = 30.22, ρcalcd = 1.239 g/cm^3, μ (MoKα) = 0.150 mm-1. min/max transmission factors = 0.4100/0.7461, 3662 Reflections collected, 3203 unique (R_1 = 0.0475), WR_2 = 0.1197 (all data). The structure has been deposited at the CCDC data center and can be retrieved by using the number CCDC 1483484.

Detection of hydrogen evolution during silanol formation by labeling experiment with D_2O:

In a screw cap NMR tube triethylsilane (0.25 mmol, 40 µl), catalyst **2** (0.0005 mmol, 0.3 mg), D_2O (0.25 mmol, 5 µl) and C_6D_6 (0.4 ml) were taken under nitrogen atmosphere and monitored by ^1H NMR spectroscopy at room temperature for 2 h.

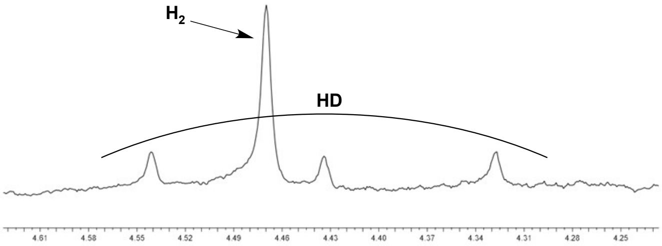
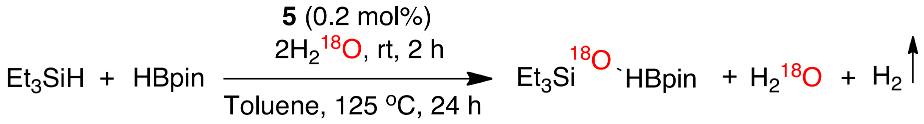


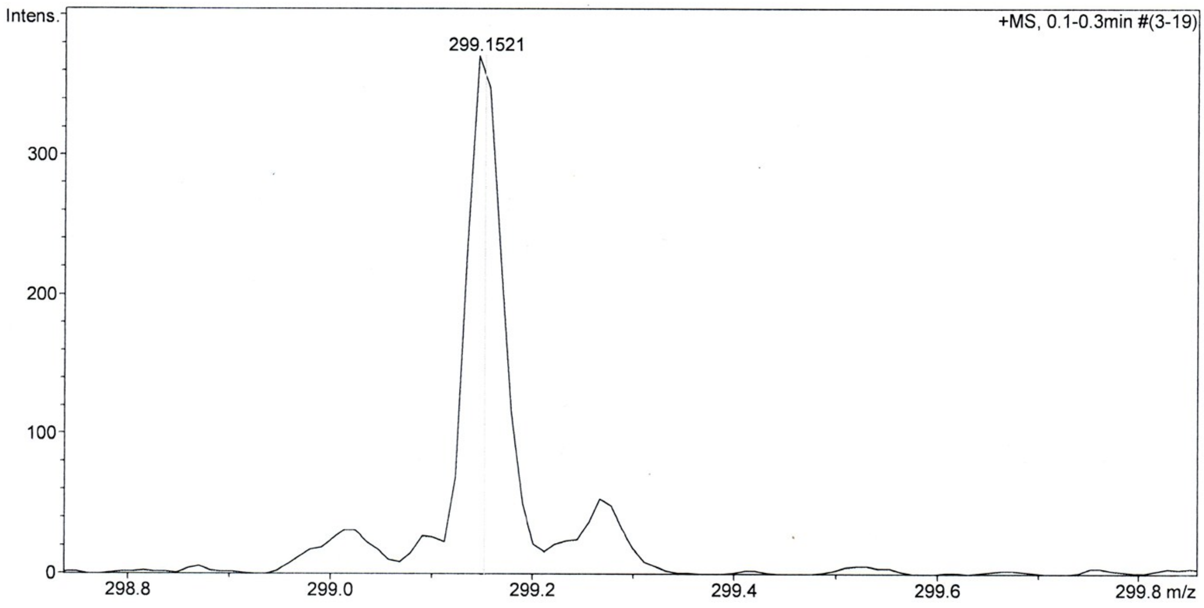
Fig S1: ^1H NMR spectrum of labeling experiment with D_2O (H_2 and DH region).

ESI-MS analysis by using labeled water ($H_2{}^{18}O$) to verify oxygen source in borasiloxane:

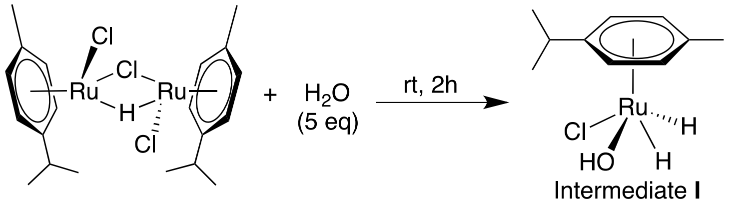


$$Et_3SiH + HBpin \xrightarrow[\text{Toluene, 125 °C, 24 h}]{\textbf{5}\text{ (0.2 mol\%)},\ 2H_2{}^{18}O\text{, rt, 2 h}} Et_3Si{}^{18}O\text{HBpin} + H_2{}^{18}O + H_2\uparrow$$

To an oven dried Schlenk-tube, triethylsilane (1mmol, 159 µl), pinacolborane (1 mmol, 145 µl), [Ru(p-cymene)Cl_2(pyridine)] **5** (0.002 mmol) and toluene (2 ml) were added under nitrogen atmosphere. Degassed labeled water $H_2{}^{18}O$ (3 mmol, 60 µl) was added and the reaction mixture was stirred for 2 h for the complete formation of $Et_3Si^{18}OH$ and $PinB^{18}OH$. The Schlenk-tube was then immersed into a pre-heated oil bath at 125 °C and heated for 24 h. After the completion of the reaction, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml X 3 times). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to produce borasiloxane. Mass spectrum was recorded on Bruker micrOTOF-Q II Spectrometer by positive tune low mode method. (EI) m/z 299.15 $(M+K)^+$. HRMS: Calcd $[C_{12}H_{27}SiB(^{16}O)_2{}^{18}OK]$: 299.1501, found 299.1521.

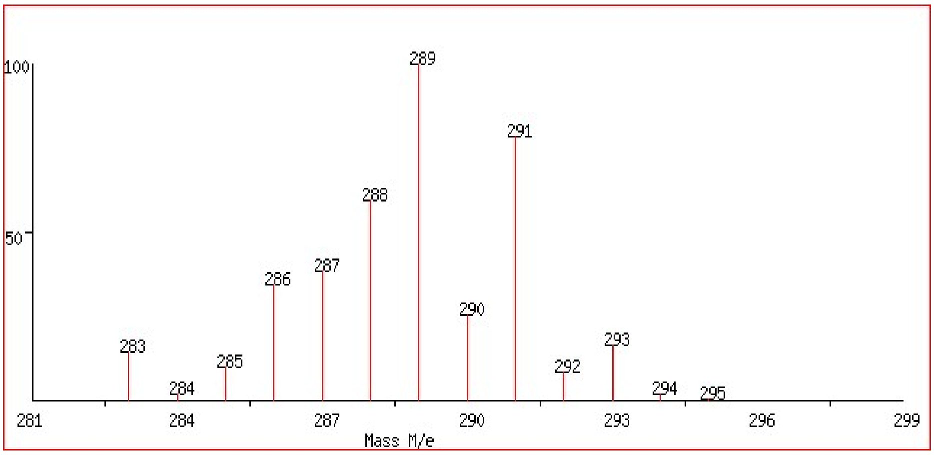


ESI-MS Analysis to Observe Intermediate I:

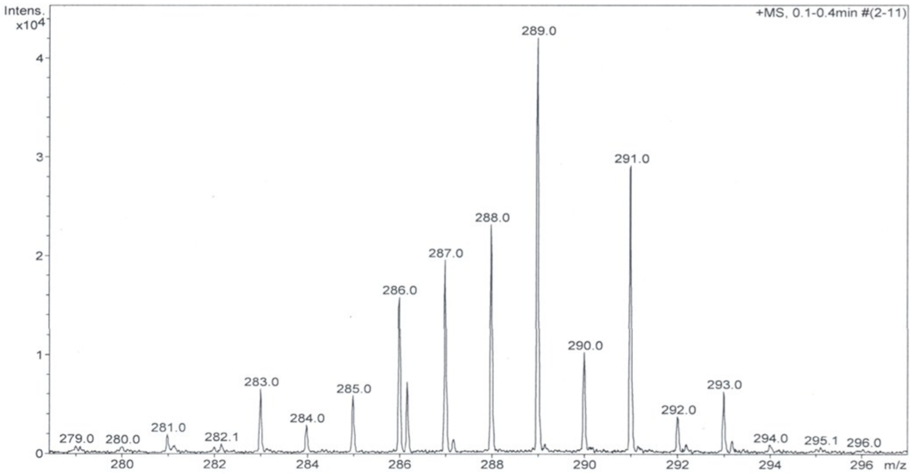


To a scintillation reaction vial, monohidrido bridged ruthenium intermediate **2** (10 mg, 0.017 mmol), degassed water (1.5 µl, 0.085 mmol) and 1,4-dioxane (50 µl) as solvent were added and stirred for 2h. The resulting reaction mixture then passed through small plug of celite under nitrogen atmosphere. Mass spectrum was recorded on Bruker micrOTOF-Q II Spectrometer.

Mass spectrum (Intermediate **I**): $C_{36}H_{60}B_3NO_7Ru$: $(M-H)^+$ 289.0 (theoretical)



Mass spectrum (Intermediate **I**): $C_{36}H_{60}B_3NO_7Ru$: $(M-H)^+$ 289.0 (obtained)



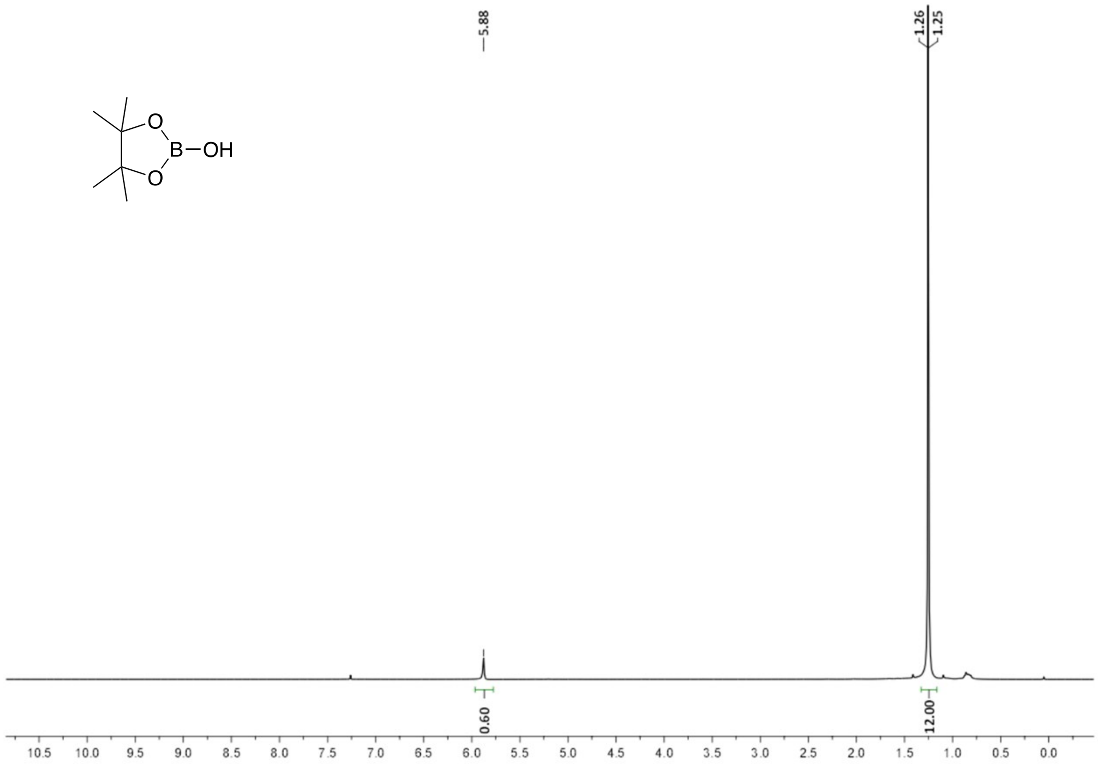
Experiments to comprehend condensation mechanism:

Verification of the formation of B-O-B bond (homocondensation product)

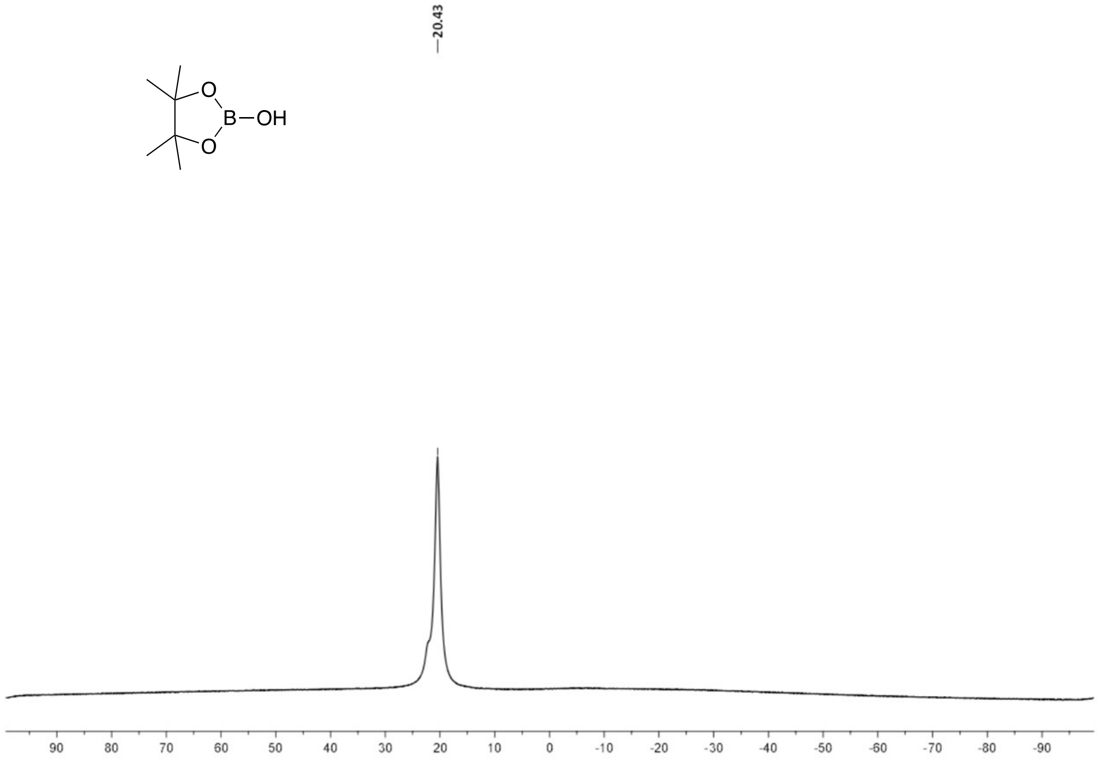
$$\text{PinBOH} \xrightarrow{\text{Toluene, 125 °C, 24 h}} \text{No formation of nipBOBPin}$$

To an oven dried Schlenk-tube, hydroxypinacolborane (1 mmol) and toluene (2 ml) were added under nitrogen atmosphere then the Schlenk-tube was immersed into a pre-heated oil bath of 125 °C and stirred for 24 h. After completion of the reaction, the solvent was evaporated under vacuumand the product was washed with hexane (2ml X 3). The white solid obtained was dried under vacuum , which provided the hydroxypinacolborane quantitatively.

^{1}H NMR reaction mixture spectrum for condensation reaction of hydroxypinacolborane:



^{11}B NMR reaction mixture spectrum for condensation reaction of hydroxypinacolborane:

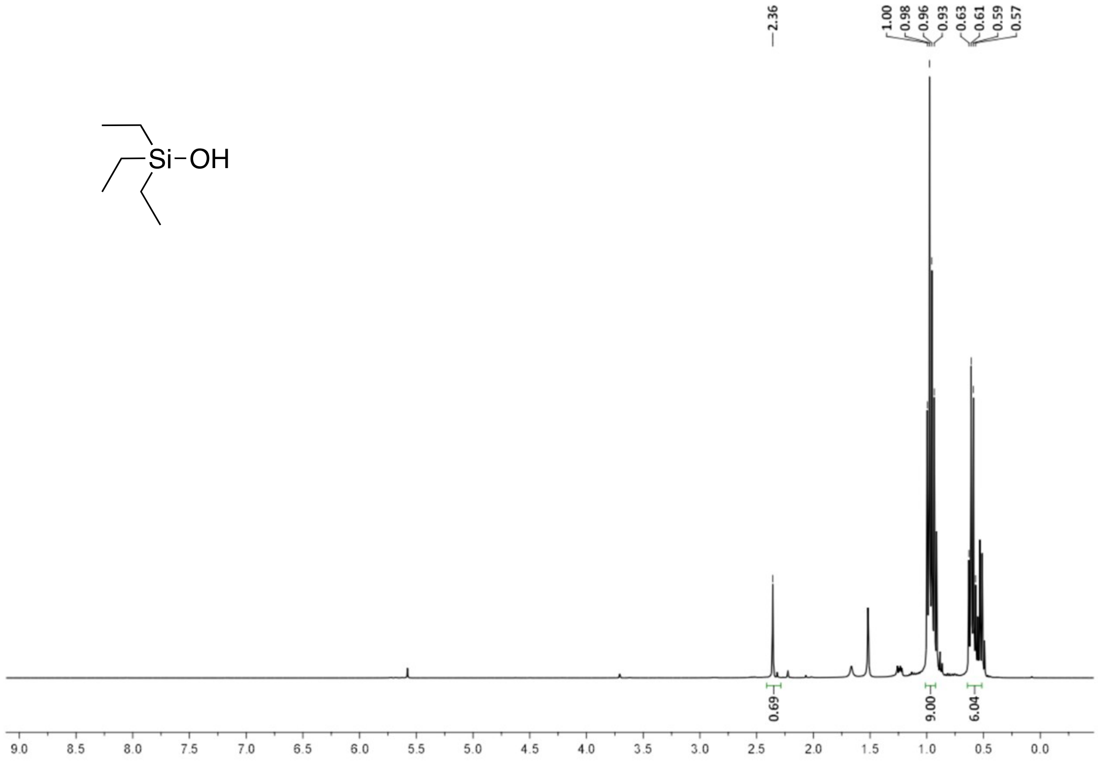


Verification of the formation of Si-O-Si bond (homocondensation product):

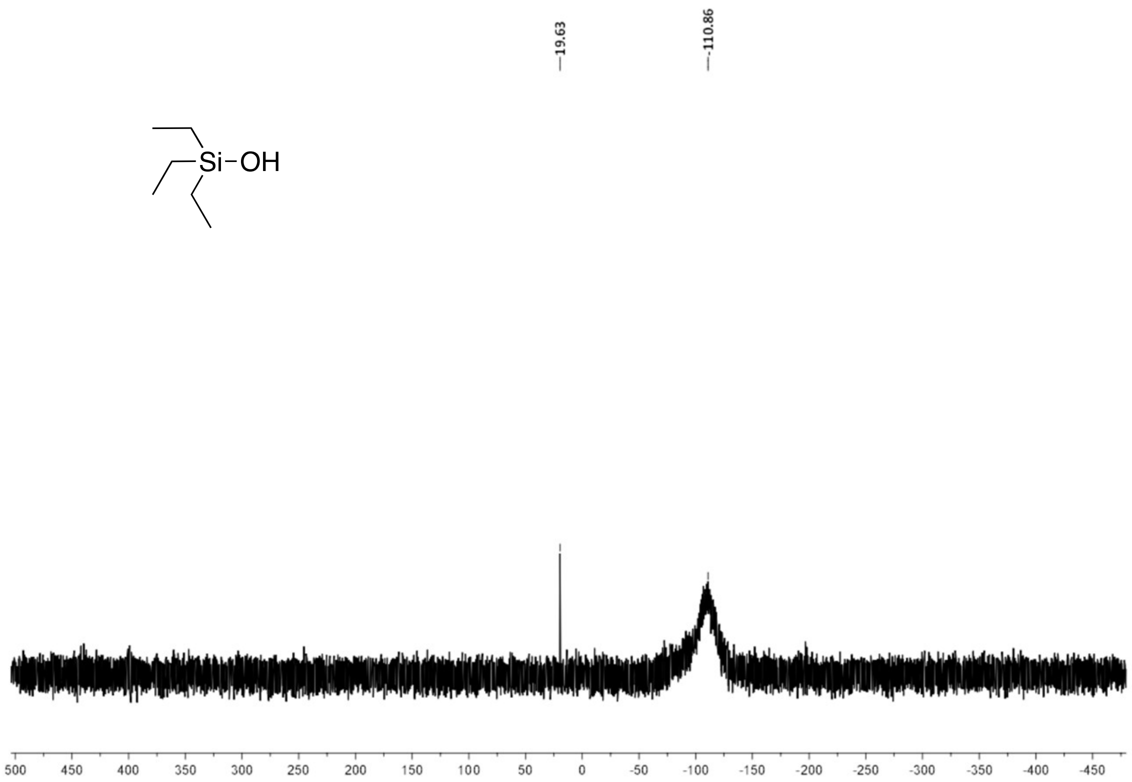
$$Et_3SiOH \xrightarrow{\text{Toluene, 125 °C, 24 h}} \text{No formation of } Et_3SiOSiEt_3$$

To an oven dried Schlenk-tube, triethylsilanol (1 mmol) and toluene (2 ml) were added under nitrogen atmosphere then the Schlenk-tube was immersed into a pre-heated oil bath of 125 °C and stirred for 24 h. After completion of the reaction, the solvent was evaporated under vacuumand the product was extracted with hexane (2ml X 3). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure, which provided the triethylsilanol quatitatively.

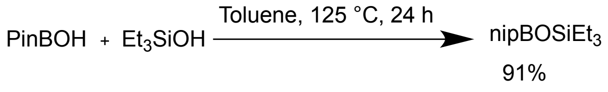
^{1}H NMR reaction mixture spectrum for condensation reaction of triethylsilanol:



^{29}Si NMR reaction mixture spectrum for condensation reaction of triethylsilanol:



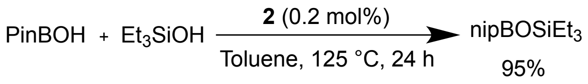
Condensation reaction of hydroxypinacolborane and triethylsilanol:



$$\text{PinBOH} + \text{Et}_3\text{SiOH} \xrightarrow{\text{Toluene, 125 °C, 24 h}} \underset{91\%}{\text{nipBOSiEt}_3}$$

To an oven dried Schlenk-tube, hydroxypinacolborane (1 mmol), triethylsilanol (1 mmol) and toluene (2 ml) were added under nitrogen atmosphere then the Schlenk-tube was immersed into a pre-heated oil bath at 125 °C and stirred for 24 h. After completion of the reaction, the solvent was evaporated under vacuumand the product was extracted with hexane (2ml X 4). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain borasiloxane.

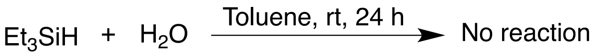
Interpretation of catalyst’s role on condensation reaction:



$$\text{PinBOH} + \text{Et}_3\text{SiOH} \xrightarrow[\text{Toluene, 125 °C, 24 h}]{\textbf{2}\text{ (0.2 mol\%)}} \underset{95\%}{\text{nipBOSiEt}_3}$$

To an oven dried Schlenk-tube, hydroxypinacolborane (1 mmol), triethylsilanol (1 mmol), [{(η^6-*p*-cymene)RuCl}$_2$(μ-H-μ-Cl)] **2** (0.002 mmol) and toluene (2 ml) were added under nitrogen atmosphere then the Schlenk-tube was immersed into a pre-heated oil bath at 125 °C and stirred for 24 h. Upon heating the reaction mixture turned black in 15 minutes and Ru-black particles appeared in solution. After completion of the reaction, the solvent was evaporated under vacuum and the product was extracted with hexane (2ml X 4). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain borasiloxane.

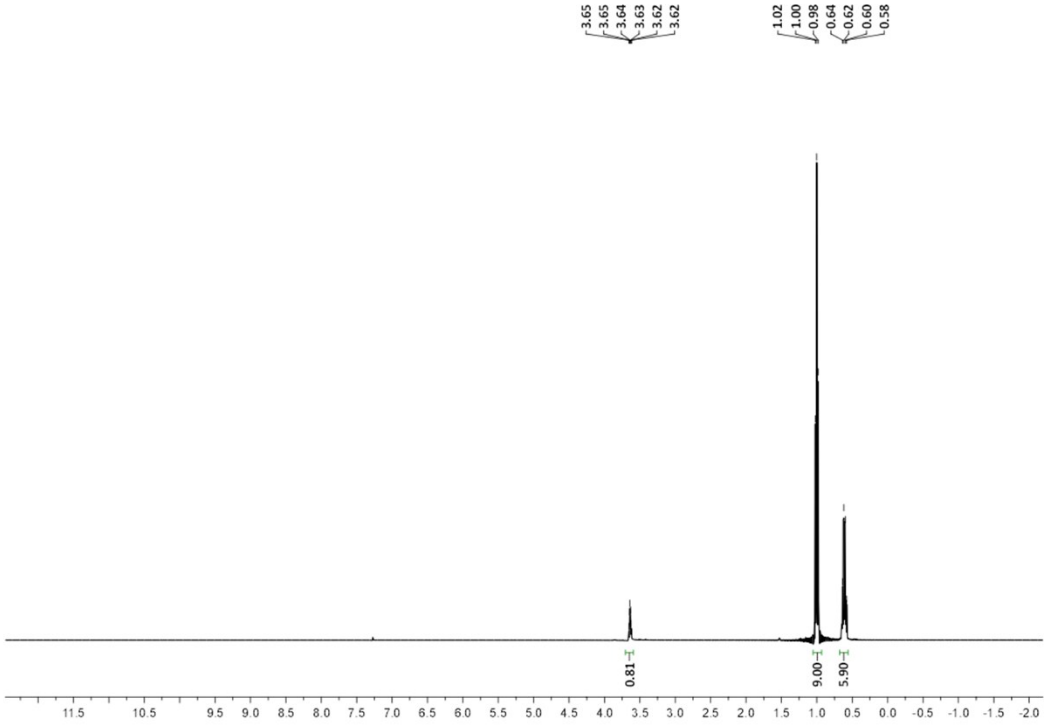
Experiments to verify the necessity of catalyst in silanol formatiom:



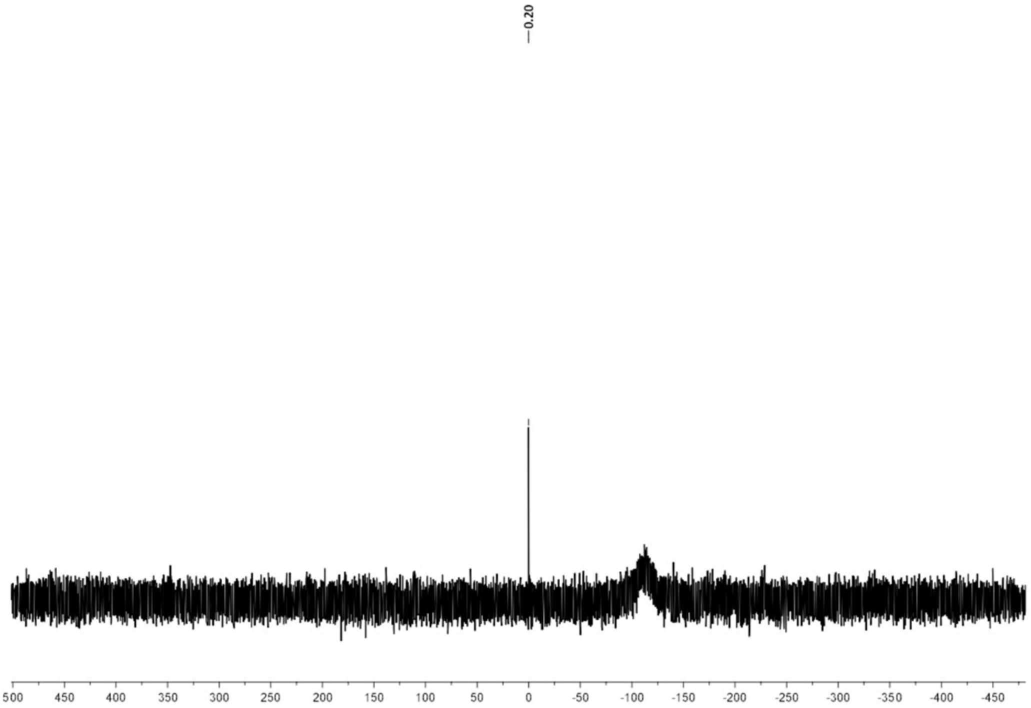
$$\text{Et}_3\text{SiH} + \text{H}_2\text{O} \xrightarrow{\text{Toluene, rt, 24 h}} \text{No reaction}$$

To an oven dried Schlenk-tube, triethylsilane (1 mmol), H_2O (3 mmol) and toluene (2 ml) were added under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 24 h. After 24 h the solvent was evaporated under vacuum and the product was extracted with hexane (2ml X 4). Combined hexane solution was filtered through a short plug of celite and the filtrate was evaporated under reduced pressure to obtain unreacted triethylsilane.

^{1}H NMR Spectrum of the unreacted triethylsilane obtained from the controlled reaction:



^{29}Si NMR Spectrum of the unreacted triethylsilane obtained from the controlled reaction:

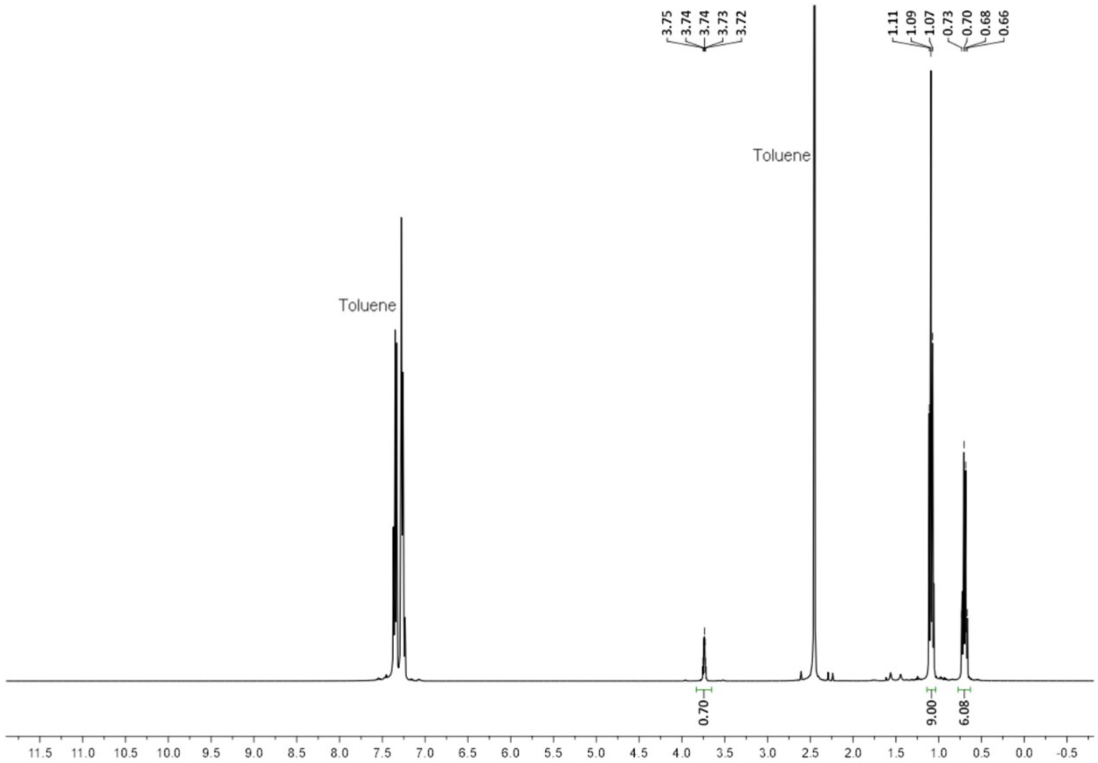


Verification of silanol formation using $RuCl_3$ as catalyst:

$$Et_3SiH + H_2O \xrightarrow[\text{Toluene, rt, 6 h}]{RuCl_3\text{ (0.2 mol\%)}} \text{No reaction}$$

To an oven dried Schlenk-tube, triethylsilane (1 mmol), H_2O (3 mmol), $RuCl_3$ (0.2 mol%, 0.002 mmol, 0.42 mg) and toluene (2 ml) were added under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 6 h. After 6 h the reaction mixture was analysed by NMR spectroscopy.

Reaction mixture ^1H NMR spectrum of the unreacted triethylsilane obtained from the reaction using $RuCl_3$ as catalyst:

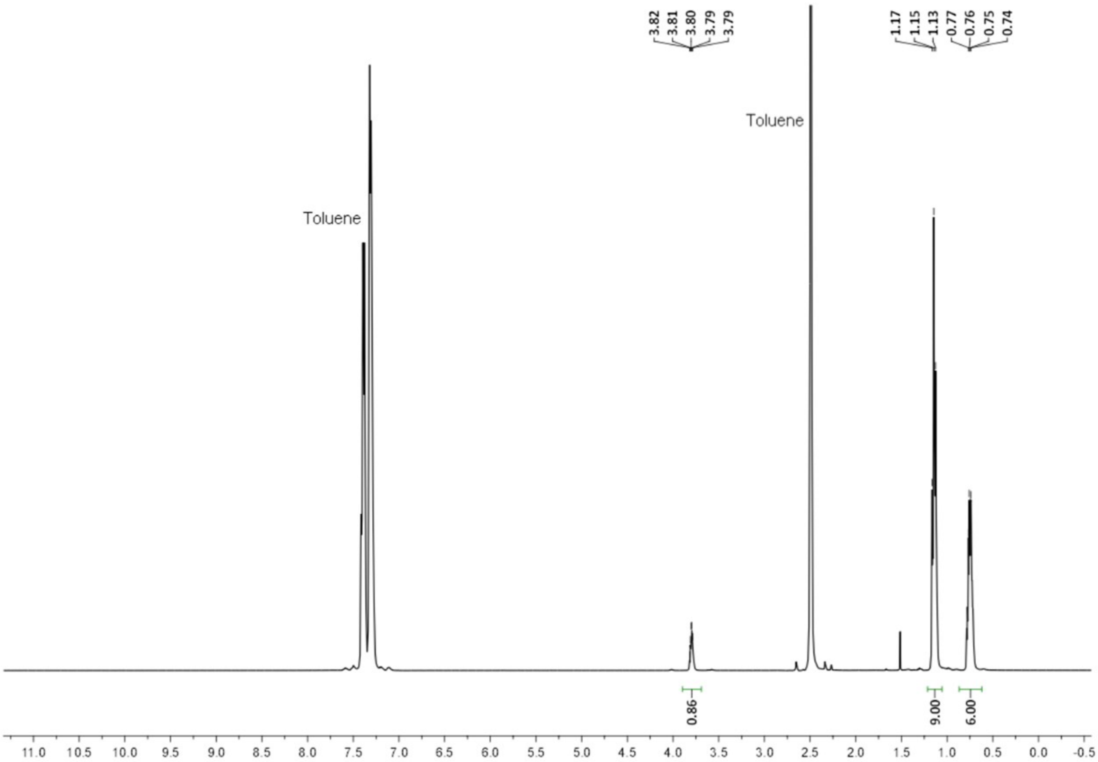


Verification of silanol formation using TBACl as catalyst:

$$Et_3SiH + H_2O \xrightarrow[\text{Toluene, rt, 24 h}]{\text{TBACl (1 mol\%)}} \text{No reaction}$$

To an oven dried Schlenk-tube, triethylsilane (1 mmol), H_2O (3 mmol), tetrabutylammonium chloride (1 mol%, 0.01 mmol, 2.8 mg) and toluene (2 ml) were added under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 24 h. After 24 h the reaction mixture was analysed by NMR spectroscopy.

Reaction mixture ^{1}H NMR spectrum of the unreacted triethylsilane obtained from the reaction using TBACl as catalyst:



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