Supplementary Information for

Stable silylborane with diminished boron-Lewis acidity

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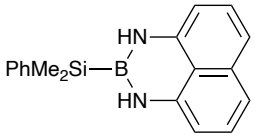
General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{11}B, 186 MHz; ^{31}P, 202 MHz) or a Varian 400MR (^{1}H, 400 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.16), or tetramethylsilane (^{1}H and ^{13}C, δ = 0) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0.00) or 85% H_3PO_4 (^{31}P, δ = 0.00) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. GC analysis was performed on a Shimadzu GC-2014 (GC conditions: Column: TC-1 (GL Science), 30 m × 0.25 mm, film 0.25 μm; Flow rate: 1.89 mL/min; Injector temperature: 250 °C; Oven temperature: 100 °C to 250 °C at 20 °C/min, hold at 250 °C for 10 min; FID temperature: 250 °C). High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL or JEOL JMS–T100GCV spectrometer. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merck Kieselgel 60 or Florisil. Unless otherwise noted, commercially available reagents were used without purification. All solvents were dried over activated molecular sieve 4Å.

Synthesis of silylborane

PhMe$_2$Si–B(dan) (1)



To a toluene (10 mL) solution of 1,8-diaminonaphthalene (0.633 g, 4.00 mmol) was added PhMe$_2$Si–B(N*i*-Pr$_2$)$_2$[1] (1.43 g, 4.12 mmol) at room temperature, and the mixture was stirred at 125 °C for 6 h. Evaporation of volatile components followed by silica gel column chromatography (hexane as an eluent) gave **1** (0.967 g, 80% yield) as a pale yellow powder.

^{1}H NMR (500 MHz, Benzene-d_6) δ 0.24 (s, 6H), 5.53 (s, 2H), 5.80 (dd, *J* = 7.2, 1.0 Hz, 2H), 6.98 – 7.02 (m, 2H), 7.05 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.20 – 7.27 (m, 3H), 7.47 – 7.51 (m, 2H),
^{13}C NMR (126 MHz, Benzene-d_6) δ -0.04, 106.26, 118.57, 121.45, 128.35, 128.46, 129.23, 134.55, 137.00, 139.08, 140.31.
^{11}B NMR (160 MHz, Benzene-d_6) δ 33.08.
HRMS Calcd for $C_{18}H_{20}BN_2Si$: $[M+H]^+$, 303.1483. Found: m/z 303.1491.

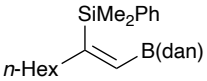
Stability test of silylboranes under dried air conditions

A flame dried Schlenk tube were charged with **1** (9.07 mg, 0.0300 mmol) and $PhMe_2Si$–B(pin) (7.87 mg, 0.0300 mmol), anisole (an internal standard, 9.73 mg, 0.0900 mmol) and benzene-d_6 (7 mL) under an argon atmosphere. A part of this solution (0.7 mL) was transferred to an NMR tube filled with dried air, and recovery of silylboranes was determined by ^{1}H NMR.

Pt-catalyzed silylboration of alkynes: a general procedure

A flame dried Schlenk tube were charged with $Pt(PPh_3)_4$ (2.49 mg, 2.00 μmol), an alkyne (0.150 mmol), 1,2-diethoxyethane (0.12 mL) and a silylborane (0.100 mmol, **1**: 30.2 mg; $PhMe_2Si$–B(pin): 26.2 mg), and the mixture was stirred at 110 °C for 22 h. After the solvent was evaporated, the residue was purified by preparative recycling gel permeation chromatography (toluene as an eluent) to afford the product.

(*Z*)-2-(2-(dimethyl(phenyl)silyl)oct-1-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3a)



Isolated in 73% yield as a pale yellow oil.

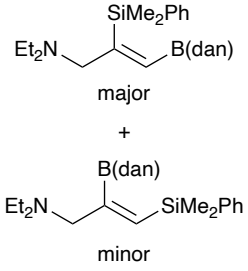
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.41 (s, 6H), 0.91 (t, *J* = 6.8 Hz, 3H), 1.26 – 1.41 (m, 6H), 1.49 (dt, *J* = 15.4, 7.2 Hz, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 5.33 (s, 2H), 5.89 (d, *J* = 7.2 Hz, 2H), 6.39 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 7.01 (t, *J* = 8.1 Hz, 2H), 7.38 – 7.42 (m,3H), 7.54 – 7.61 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 14.03, 22.57, 29.17, 29.86, 31.69, 41.93, 105.39, 117.13, 119.40, 127.31, 128.17, 129.13, 133.75, 136.06, 140.46, 140.78, 158.81.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.26.

HRMS Calcd for $C_{26}H_{34}N_2BSi$: $[M+H]^+$, 413.2579. Found: m/z 413.2588.

A mixture of (*Z*)-2-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)prop-2-en-1-amine (3b) and (*E*)-3-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-2-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)prop-2-en-1-amine (3'b)



Isolated in 86% yield as a pale yellow oil.

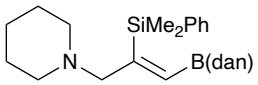
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.42 (s, 6H, minor), 0.45 (s, 6H, major), 1.04 (t, *J* = 7.1 Hz, 6H, major), 1.10 (t, *J* = 7.1 Hz, 6H, minor), 2.56 (q, *J* = 7.0 Hz, 4H), 3.26 (s, 2H), 5.37 (s, 2H, major), 5.85 (d, *J* = 7.3 Hz, 2H, minor), 5.98 (d, *J* = 7.3 Hz, 2H, major), 6.42 (s, 1H, minor), 6.54 (s, 2H, minor), 6.59 (s, 2H, minor), 6.92 (d, *J* = 8.2 Hz, 2H, minor), 6.97 (d, *J* = 8.1 Hz, 2H, major), 7.05 (t, *J* = 8.1 Hz, 2H), 7.36 – 7.38 (m, 3H, major),7.45 – 7.47 (m, 3H, minor), 7.62– 7.64 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ -0.80, 0.14, 1.00, 11.10, 12.17, 45.91, 46.70, 65.53, 105.59, 105.71, 117.09, 117.45, 119.72, 120.35, 127.57, 128.16, 128.58, 129.21, 129.56, 133.13, 134.06, 134.23, 136.35, 136.49, 140.54, 140.99, 141.35.

^{11}B NMR (127 MHz, Chloroform-*d*) δ 28.50.

HRMS Calcd for $C_{25}H_{33}N_3BSi$: $[M+H]^+$, 414.2531. Found: m/z 414.2543.

(*Z*)-2-(2-(dimethyl(phenyl)silyl)-3-(piperidin-1-yl)prop-1-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3c)



Isolated in 59% yield as a pale yellow oil.

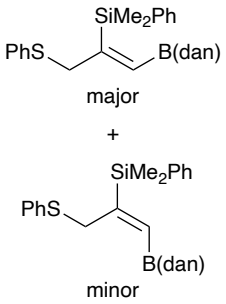
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.44 (s, 6H), 1.48 (m, 2H), 1.57 – 1.64 (m, 4H), 2.37 (s, 4H), 3.08 (d, *J* = 1.2 Hz, 2H), 5.35 (s, 2H), 5.97 (dd, *J* = 7.3, 0.8 Hz, 2H), 6.39 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 8.2 Hz, 2H), 7.36 – 7.39 (m, 3H), 7.64 – 7.69 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 0.57, 24.78, 26.24, 54.62, 71.46, 105.72, 117.46, 119.72, 127.57, 128.09, 129.17, 134.33, 136.34, 140.65, 140.98, 155.98.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.20.

HRMS Calcd for $C_{26}H_{32}N_3BSi$: $[M+H]^+$, 426.2531. Found: m/z 426.2541.

A mixture of (*Z*)-2-(2-(dimethyl(phenyl)silyl)-3-(phenylthio)prop-1-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3d) and (*E*)-2-(2-(dimethyl(phenyl)silyl)-3-(phenylthio)prop-1-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (3"d)



Isolated in 83% yield as a pale yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.51 (s, 6H, major), 0.54 (s, 6H, minor), 3.84 (s, 2H, major), 3.85 (s, 2H, minor), 5.14 (s, 2H, major), 5.88 (dd, *J* = 7.2, 1.1 Hz, 2H, major), 6.00 (s,

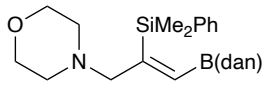
2H, minor), 6.19 (dd, *J* = 7.2, 1.0 Hz, 2H, minor), 6.24 (s, 2H, minor), 6.31 (s, *J* = 1.2 Hz, 2H, major), 6.96 (d, *J* = 8.3 Hz, 4H), 7.11 – 6.98 (m, 27H, major + minor), 7.45 – 7.20 (m, 2H), 7.62 (ddd, *J* = 10.8, 7.5, 2.5 Hz, 7H, major + minor).

^{13}C NMR (126 MHz, Chloroform-*d*) δ -2.24, -0.97, 39.74, 46.06, 105.76, 105.98, 117.57, 117.67, 117.67, 119.68, 119.99, 126.63, 127.01, 127.54, 127.67, 128.01, 128.43, 128.92, 129.18, 129.39, 129.57, 130.65, 131.03, 134.20, 134.32, 136.12, 136.19, 136.28, 136.40, 137.72, 139.87, 140.73, 141.17, 150.98, 154.39.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 27.27.

HRMS Calcd for $C_{27}H_{28}N_2BSSi$: $[M+H]^+$, 451.1830. Found: m/z 451.1840.

(*Z*)-4-(2-(dimethyl(phenyl)silyl)-3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)allyl)morpholine (3e)



Isolated in 77% yield as a white powder.

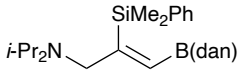
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.45 (s, 6H), 1.03 (d, *J* = 6.6 Hz, 12H), 3.08 (hept, *J* = 6.5 Hz, 2H), 3.34 (d, *J* = 1.6 Hz, 2H), 5.35 (s, 2H), 5.97 (d, *J* = 7.3 Hz, 2H), 6.92 – 6.99 (m, 3H), 7.04 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.41 (m, 3H), 7.56 – 7.59 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 0.56, 20.88, 48.11, 54.05, 105.58, 117.30, 119.63, 127.57, 128.30, 129.26, 133.91, 136.34, 140.63, 141.14, 156.92.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.12.

HRMS Calcd for $C_{25}H_{31}N_3OBSi$: $[M+H]^+$, 428.2324. Found: m/z 428.2328.

(*Z*)-2-(dimethyl(phenyl)silyl)-*N*,*N*-diisopropyl-3-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)prop-2-en-1-amine (3f)



Isolated in 66% yield as a colorless oil.

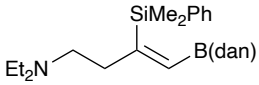
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.45 (s, 6H), 1.03 (d, *J* = 6.6 Hz, 12H), 3.08 (hept, *J* = 6.5 Hz, 2H), 3.34 (d, *J* = 1.6 Hz, 2H), 5.35 (s, 2H), 5.97 (d, *J* = 7.3 Hz, 2H), 6.93 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.37 (m, 3H), 7.60 – 7.56 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 0.56, 20.88, 48.11, 54.05, 105.58, 117.30, 119.63, 127.57, 128.30, 129.26, 133.91, 136.34, 140.63, 141.14, 156.92.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.12.

HRMS Calcd for $C_{27}H_{37}BN_3Si$: $[M+H]^+$, 442.2844. Found: m/z 442.2844.

(*Z*)-3-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)but-3-en-1-amine (3g)



Isolated in 68% yield as a pale yellow oil.

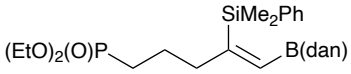
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.44 (s, 6H), 1.06 (t, *J* = 7.2 Hz, 6H), 2.47 – 2.52 (m, 4H), 2.55 – 2.63 (m, 4H), 5.34 (s, 2H), 5.91 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.45 (s, 1H), 6.95 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.02 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.38 – 7.41 (m, 2H), 7.56 – 7.59 (m, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 12.06, 38.69, 47.04, 53.94, 105.71, 117.47, 119.67, 127.56, 128.44, 129.45, 134.01, 136.31, 140.32, 140.93, 156.79.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.38.

HRMS Calcd for $C_{26}H_{35}N_3BSi$: $[M+H]^+$, 428.2688. Found: m/z 428.2702.

diethyl (*Z*)-(4-(dimethyl(phenyl)silyl)-5-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pent-4-en-1-yl)phosphonate (3h)



Isolated in 62% yield as a pale yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.42 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.75 – 1.85 (m, 4H), 2.42 (t, *J* = 6.7 Hz, 2H), 4.06 – 4.17 (m, 4H), 5.34 (s, 2H), 5.92 (d, *J* = 7.2 Hz, 2H), 6.41 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.99 – 7.04 (t, 2H), 7.38 – 7.42 (m, 3H), 7.53 – 7.58 (m, 2H).

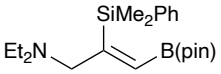
^{13}C NMR (126 MHz, Chloroform-*d*) δ 16.66 (d, *J* = 6.0 Hz), 22.49 (d, *J* = 4.9 Hz), 24.95, 26.07, 42.26 (d, *J* = 16.6 Hz), 61.62 (d, *J* = 6.5 Hz), 105.72, 117.48, 119.66, 127.54, 128.43, 129.45, 133.91, 136.28, 140.15, 140.88, 157.07.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.27.

^{31}P NMR (202 MHz, Chloroform-*d*) δ 32.54.

HRMS Calcd for $C_{27}H_{37}N_2BO_3SiP$: $[M+H]^+$, 507.2399. Found: m/z 507.2410.

(*Z*)-2-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-amine



Isolated in 36% yield as a pale yellow oil.

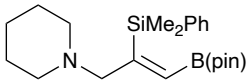
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.44 (s, 6H), 0.87 (t, *J* = 7.1 Hz, 6H), 1.09 (s, 12H), 2.37 (q, *J* = 7.1 Hz, 4H), 3.11 (d, *J* = 1.5 Hz, 2H), 6.31 (t, *J* = 1.3 Hz, 1H), 7.26 – 7.29 (m, 3H), 7.52 – 7.56 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 11.03, 24.90, 45.65, 66.09, 83.27, 127.35, 128.25, 134.28, 140.93, 163.24.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.35.

HRMS Calcd for $C_{21}H_{37}NO_2BSi$: $[M+H]^+$, 374.2681. Found: m/z 374.2689.

(*Z*)-1-(2-(dimethyl(phenyl)silyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)piperidine



Isolated in 47% yield as a colorless oil.

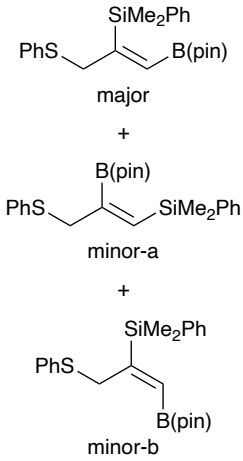
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.45 (s, 6H), 1.10 (s, 12H), 1.32 – 1.40 (m, 2H), 1.41 – 1.47 (m, 4H), 2.16 (s, 4H), 2.94 (d, *J* = 1.4 Hz, 2H), 6.17 (t, *J* = 1.3 Hz, 1H), 7.26 – 7.29 (m, *3*H), 7.55 – 7.59 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 24.74, 24.90, 26.17, 54.31, 71.75, 83.29, 127.23, 128.21, 134.37, 140.94, 162.86.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.15.

HRMS Calcd for $C_{22}H_{37}NBSi$: $[M+H]^+$, 386.2681. Found: m/z 386.2690.

A mixture of (*Z*)-dimethyl(phenyl)(3-(phenylthio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)silane, (*E*)-dimethyl(phenyl)(3-(phenylthio)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane and (*E*)-dimethyl(phenyl)(3-(phenylthio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-2-yl)silane



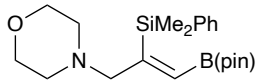
Isolated in 48% yield as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.33 (s, 6H, minor-a), 0.45 (s, 6H, minor-b), 0.54 (s, 6H, major), 1.06 (s, 12H, major), 1.15 (s, 12H, minor-a), 1.23 (s, 12H, minor-b), 3.68 (s, 2H, major), 3.71 (s, 2H, minor-a), 4.06 (s, 2H, minor-b), 6.00 (s, 1H, minor-b), 6.17 (s, 1H, major), 6.28 (s, 1H, minor-a), 7.36 – 7.11 (m, 24H, major + minor-a + minor-b), 7.40 (dd, *J* = 7.5, 2.0 Hz, 2H, minor), 7.53 (d, *J* = 8.2 Hz, 2H, minor), 7.62 – 7.56 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ -2.27, -1.12, -1.05, 24.60, 24.74, 24.84, 37.79, 44.78, 46.57, 83.20, 83.26, 83.75, 125.81, 126.14, 126.33, 127.46, 127.68, 127.91, 128.45, 128.57, 128.62, 128.79, 128.98, 129.94, 130.03, 130.24, 130.81, 131.01, 131.65, 133.77, 134.20, 136.33, 136.77, 137.70, 139.59, 146.99, 158.23, 162.91.

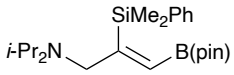
^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.29.
HRMS Calcd for $C_{23}H_{31}O_2BSSiNa$: $[M+Na]^+$, 433.1805. Found: m/z 433.1799.

(*Z*)-4-(2-(dimethyl(phenyl)silyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)morpholine



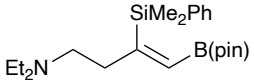
Isolated in 72% yield as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.46 (s, 6H), 1.13 (s, 12H), 2.21 (s, 4H), 2.99 (d, *J* = 1.3 Hz, 2H), 3.57 (t, *J* = 4.4 Hz, 4H), 6.20 (t, *J* = 1.4 Hz, 1H), 7.27 – 7.30 (m, 3H), 7.56 – 7.60 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 0.57, 24.92, 53.31, 67.18, 71.26, 83.45, 127.30, 128.39, 134.35, 140.46, 161.58.
^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.29.
HRMS Calcd for $C_{21}H_{35}O_3NBSi$: $[M+H]^+$, 388.2474. Found: m/z 388.2483.

(*Z*)-2-(dimethyl(phenyl)silyl)-*N*,*N*-diisopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-amine



Isolated in 71% yield as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.44 (s, 6H), 0.90 (d, *J* = 6.6 Hz, 12H), 1.08 (s, 12H), 2.95 (hept, *J* = 6.6 Hz, 2H), 3.18 (d, *J* = 1.9 Hz, 2H), 6.73 (t, *J* = 1.9 Hz, 1H), 7.29 (dp, *J* = 5.1, 1.9 Hz, 4H), 7.53 – 7.50 (m, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ -0.81, 20.75, 24.91, 48.09, 54.73, 83.08, 127.52, 128.41, 134.06, 140.74, 163.72.
^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.91.
HRMS Calcd for $C_{23}H_{41}O_2NBSi$: $[M+H]^+$, 402.2994. Found: m/z 402.3004.

(*Z*)-3-(dimethyl(phenyl)silyl)-*N*,*N*-diethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-amine

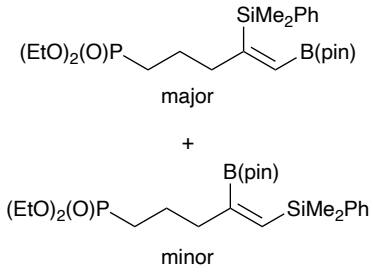


Isolated in 61% yield as a pale yellow oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.46 (s, 6H), 0.94 (t, *J* = 7.2 Hz, 6H), 1.09 (s, 12H), 2.34 – 2.47 (m, 8H), 6.23 (s, 1H), 7.28 – 7.31 (m, 3H), 7.51– 7.55 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 12.05, 24.84, 29.84, 39.12, 46.90, 53.47, 83.32, 127.63, 128.64, 134.21, 140.16, 164.61.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.49.

HRMS Calcd for $C_{22}H_{39}NBSi$: $[M+H]^+$, 388.2838. Found: m/z 388.2854.

A mixture of diethyl (*Z*)-(4-(dimethyl(phenyl)silyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)phosphonate and diethyl (*E*)-(5-(dimethyl(phenyl)silyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)phosphonate



Isolated in 84% yield as a pale yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.38 (s, 6H, minor), 0.44 (s, 6H, major), 1.07 (s, 12H, major), 1.10 (s, 12H, minor), 1.29 (t, *J* = 7.1 Hz, 6H, major + minor), 1.58 – 1.67 (m, 4H, major + minor), 2.28 (t, *J* = 6.6 Hz, 2H, major + minor), 3.99 – 4.09 (m, 4H, major + minor), 6.17 (t, *J* = 1.2 Hz, 1H, major), 6.44 (s, 1H, minor), 7.27 – 7.31 (m, 3H, major + minor), 7.48 – 7.53 (m, 2H, major + minor).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 16.60 (d, *J* = 6.1 Hz), 22.15 (d, *J* = 4.9 Hz), 24.81, 25.90, 43.14 (d, *J* = 17.1 Hz), 61.47 (d, *J* = 6.5 Hz), 83.31, 127.59, 128.61, 134.08, 140.08, 146.47, 164.69.

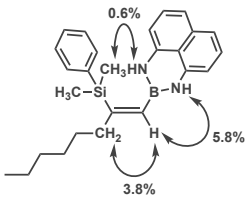
^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.15.

^{31}P NMR (202 MHz, Chloroform-*d*) δ 32.58, 33.05.

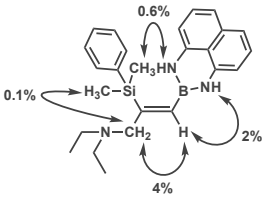
HRMS Calcd for $C_{46}H_{80}B_2O_{10}Si_2P_2Na$: $[2M+Na]^+$, 955.4849. Found: m/z 955.4852.

NOE experiments for determining stereochemistry

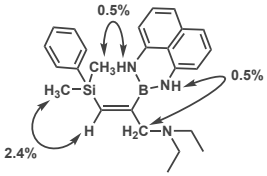
From $PhMe_2Si$–B(dan)



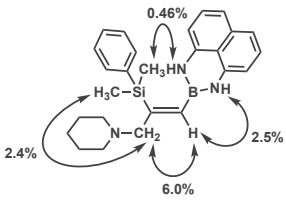
3a



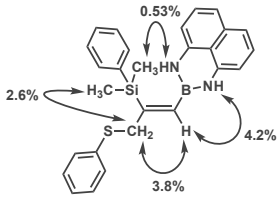
3b



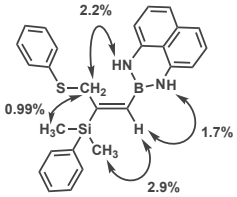
3'b



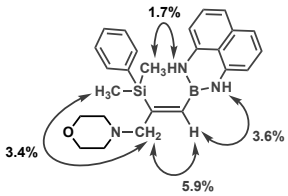
3c



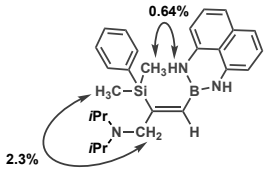
3d



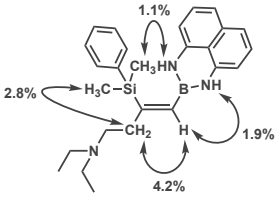
3"d



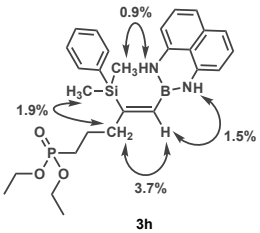
3e



3f

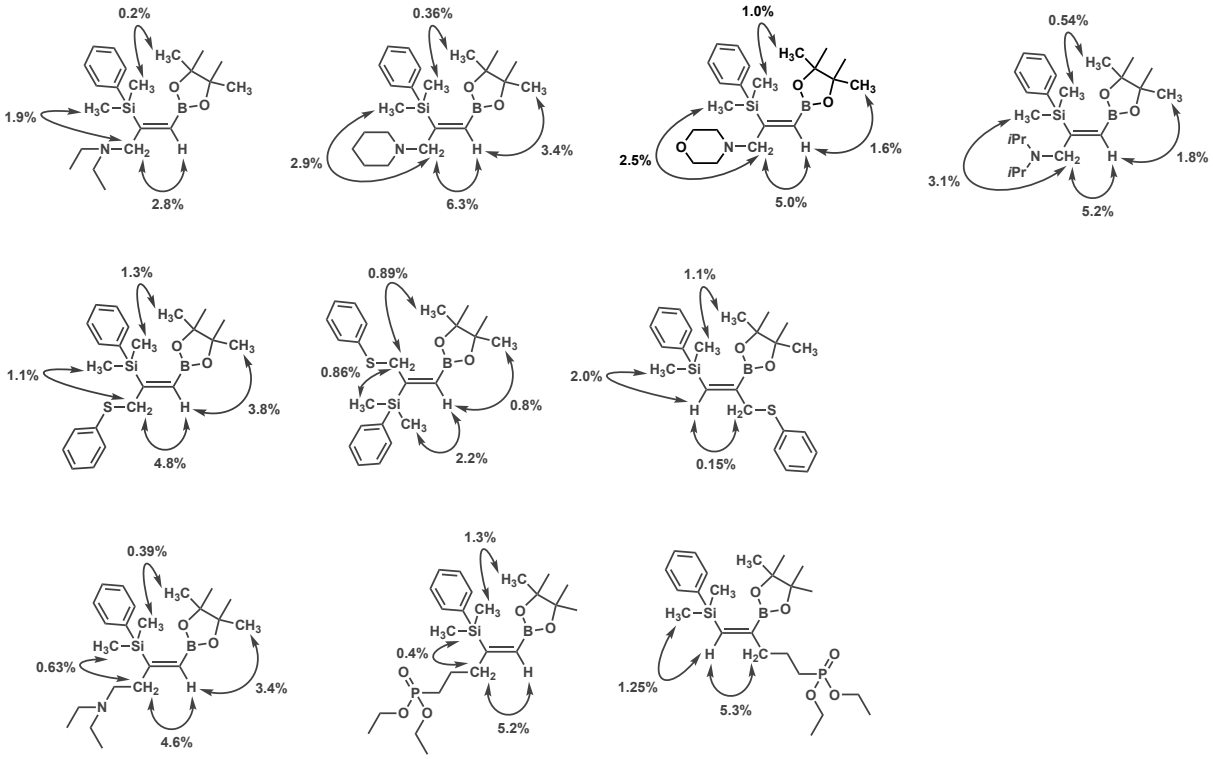


3g



3h

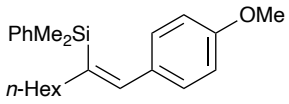
From $PhMe_2Si–B(pin)$



Direct cross-coupling of 3a

A flame-dried Schlenk tube equipped with a magnetic stirring bar were charged with $Pd(PPh_3)_4$ (15.0 mg, 0.013 mmol), **3a** (108.2 mg, 0.26 mmol), 4-bromoanisole (48.6 mg, 0.26 mmol), and 1,4-dioxane (1.73 mL). The mixture was stirred at 100 °C for 5 min before addition of *t*-BuOK (1 M in THF, 0.40 mL, 0.40 mmol). The resulting mixture was stirred at 100 °C for 1 h. After quenching the mixture with brine (20 mL), the resulting mixture was extracted with EtOAc (15 mL × 3). The organic solution was dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc as an eluent) to give a cross-coupling product.

(*Z*)-(1-(4-methoxyphenyl)oct-1-en-2-yl)dimethyl(phenyl)silane (4)



Isolated in 52% yield as a dark brown oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.33 (s, 6H), 1.03 (t, *J* = 7.0 Hz, 3H), 1.44 (m, 6H), 1.54 – 1.65 (m, 2H), 2.36 – 2.45 (m, 2H), 3.91 (s, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.37 (s, 1H), 7.42 – 7.52 (m, 3H), 7.58 – 7.69 (m, 2H).

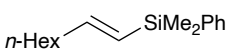
^{13}C NMR (126 MHz, Chloroform-*d*) δ 14.19, 22.75, 28.08, 29.29, 30.67, 31.82, 39.35, 55.28, 113.09, 127.70, 128.63, 129.92, 132.86, 133.95, 140.33, 141.28, 142.99, 158.56.

HRMS Calcd for $C_{23}H_{32}OSi$: $[M]^+$, 352.2222. Found: m/z 352.2226.

Copper-catalyzed reaction of 1 with 1-octyne

A flame dried Schlenk tube were charged with SIMesCuCl (2.0 mg, 5.0 μmol), *t*-BuONa (2.0 mg, 0.02 mmol) and THF (0.56 mL). The solution was allowed to stir at 22 °C for 2 h. Then **1** (158.7 mg, 0.525 mmol) was added to the solution, and the mixture was allowed to stir at 22 °C for 30 min. 1-Octyne (55.1 mg, 0.50 mmol) and MeOH (30 μL, 0.75 mmol) were added. The resulting mixture was allowed to stir at 22 °C for 12 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with ether (3 × 2 mL). The filtrate was concentrated in vacuo to provide a crude product, which was purified by silica gel chromatography (Hexane/EtOAc as an eluent) to afford the product.

(E)-dimethyl(oct-1-en-1-yl)(phenyl)silane (5)[2]



Isolated in 55% yield as a colorless oil.

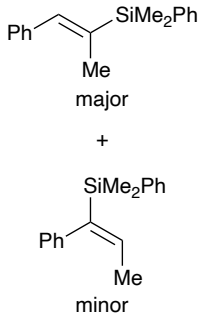
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.32 (s, 6H), 0.89 (d, *J* = 7.0 Hz, 3H), 1.25 – 1.33 (m, 6H), 1.37 – 1.44 (m, 2H), 2.14 (dtd, *J* = 7.7, 6.3, 1.6 Hz, 2H), 5.75 (dt, *J* = 18.5, 1.6 Hz, 1H),

6.12 (dt, *J* = 18.5, 6.3 Hz, 1H), 7.33 – 7.36 (m, 3H), 7.48 – 7.56 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ -2.44, 14.10, 22.63, 28.60, 28.89, 31.73, 36.84, 127.11, 127.70, 128.79, 133.80, 139.41, 149.58.

Copper-catalyzed reaction of 1 with 1-phenyl-1-propyne

1-Phenyl-1-propyne (23.2 mg, 0.2 mmol) and **1** (72.5 mg, 0.24 mmol) were added with the aid of THF (0.2 mL) to a mixture of CuI (3.8 mg, 0.02 mmol) and *t*-BuONa (7.7 mg, 0.08 mmol) in THF (0.8 mL), and the resulting mixture was stirred at 40 °C for 20 h. This was passed through a pad of silica gel with EtOAc and the solvent was removed unde vacuum. The residue was purified by preparative recycling gel permeation chromatography (chloroform as an eluent) to afford the product.

A mixture of (*E*)-dimethyl(phenyl)(1-phenylprop-1-en-2-yl)silane (6) and (*E*)-dimethyl(phenyl)(1-phenylprop-1-en-1-yl)silane (6')[3]



Isolated in 10% yield as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 0.31 (s, 6H, minor), 0.44 (s, 6H, major), 1.58 (d, *J* = 6.5 Hz, 3H, minor), 1.95 (d, *J* = 1.8 Hz, 3H, major), 6.12 (q, *J* = 6.6 Hz, 1H, minor), 6.81 (q, *J* = 1.9 Hz, 1H, major), 7.12 – 7.40 (m, 16H, major+minor), 7.47 – 7.54 (m, 2H, minor), 7.54 – 7.60 (m, 2H, major).
^{13}C NMR (126 MHz, Chloroform-*d*) δ -3.27, -2.81, 1.01, 16.85, 29.86, 76.91, 77.16, 77.41, 125.47, 126.75, 127.77, 127.85, 127.93, 128.06, 128.18, 128.24, 129.01, 129.14, 129.19, 129.39, 133.14, 134.00, 134.22, 134.31, 138.28, 138.38, 138.99, 139.96.

X-ray crystallographic analyses

Crystals suitable for the X-ray structural determination were mounted on a Bruker SMART APEXII CCD diffractometer and irradiated with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) for data collection. The data were processed using the APEX3 program suite and summarized in a table shown in next page. All structures were solved by an intrinsic phasing method using the SHELXT program (ver. 2014/4–2014/5).[4] Refinement on F^2 was carried out using full-matrix least-squares with the SHELXL[5] and expanded using Fourier techniques. All nonhydrogen atoms, except those of disordered solvents, were refined using anisotropic thermal parameters. Hydrogen atoms were assigned to idealized geometric positions and included in structure factor calculations. The SHELX was interfaced with SHELXLE GUI for most of the refinement steps.[6] The pictures of the molecules were prepared using Pov-Ray 3.6.[7]

Crystal data and structure refinement for **1**

Identification code	**1**
CCDC No.	2120998
Empirical formula	C18 H19 B N2 Si
Formula weight	302.25
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.0647(16) Å α = 90°.
	b = 11.425(3) Å β = 90°.
	c = 20.803(5) Å γ = 90°.
Volume	1679.1(7) $Å^3$
Z	4
Density (calculated)	1.196 Mg/m^3
Absorption coefficient	0.137 mm^{-1}
F(000)	640
Crystal size	0.200 x 0.050 x 0.010 mm^3
Theta range for data collection	1.958 to 26.394°.
	-8<=h<=8,
Index ranges	-13<=k<=14,
	-26<=l<=18
Reflections collected	8946
Independent reflections	3420 [R(int) = 0.0267]
Completeness to theta = 25.242°	99.90%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3420 / 0 / 201
Goodness-of-fit on F2	1.039
Final R indices [I>2sigma(I)]	R_1 = 0.0332, wR_2 = 0.0731
R indices (all data)	R_1 = 0.0397, wR_2 = 0.0760
Absolute structure parameter	0.05(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.214 and -0.181 e.$Å^{-3}$

References

(1) M. Suginome, T. Fukuda, H. Nakamura and Y. Ito, *Organometallics*, 2000, **19**, 719.

(2) F. Meng, H. Jang and A. H. Hoveyda, *Chem. Eur. J.*, 2013, **19**, 3204.

(3) J. C. Gee, B. A. Fuller, H.-M. Lockett, G. Sedghi, C. M. Robertson and K. V. Luzyanin, *Chem. Commun.*, 2018, **54**, 9450.

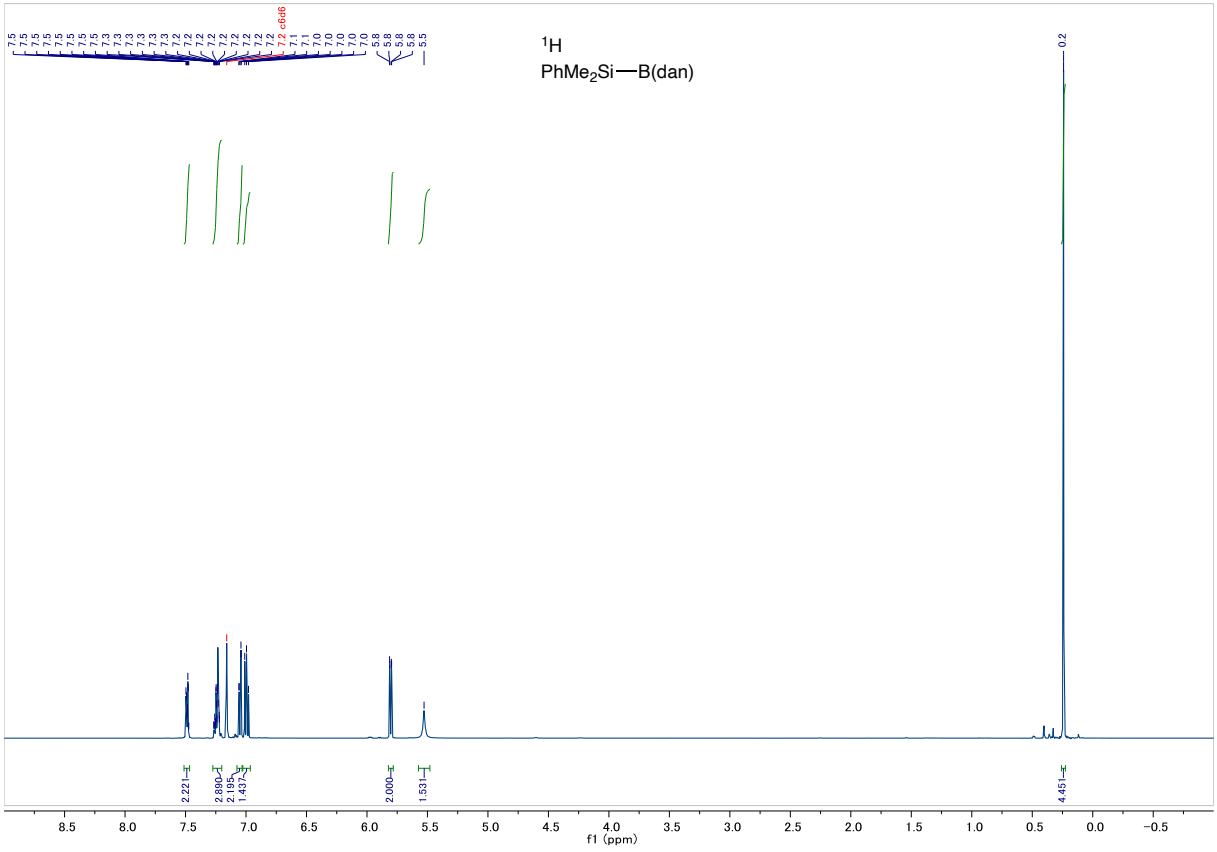
(4) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv*., 2015, **71**, 3.

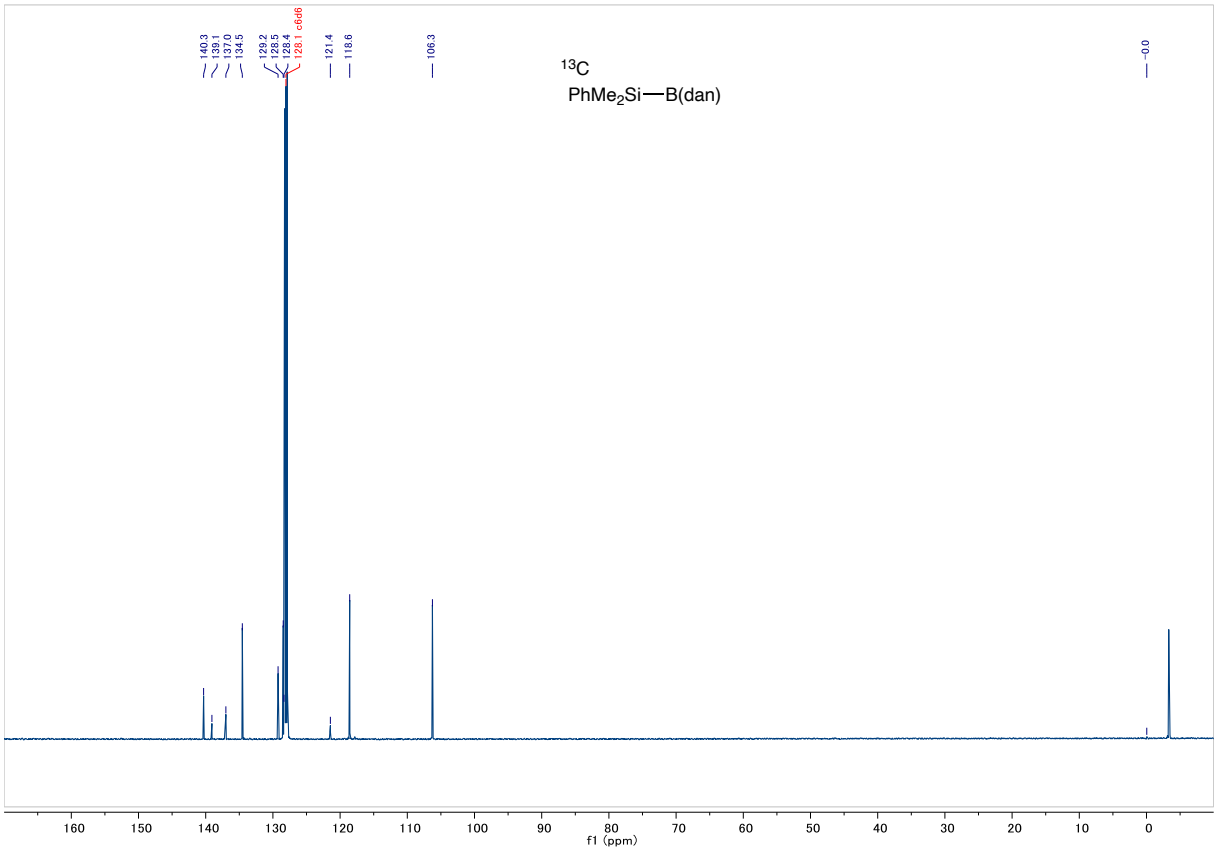
(5) G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A: Found. Crystallogr*., 2008, **A64**, 112.

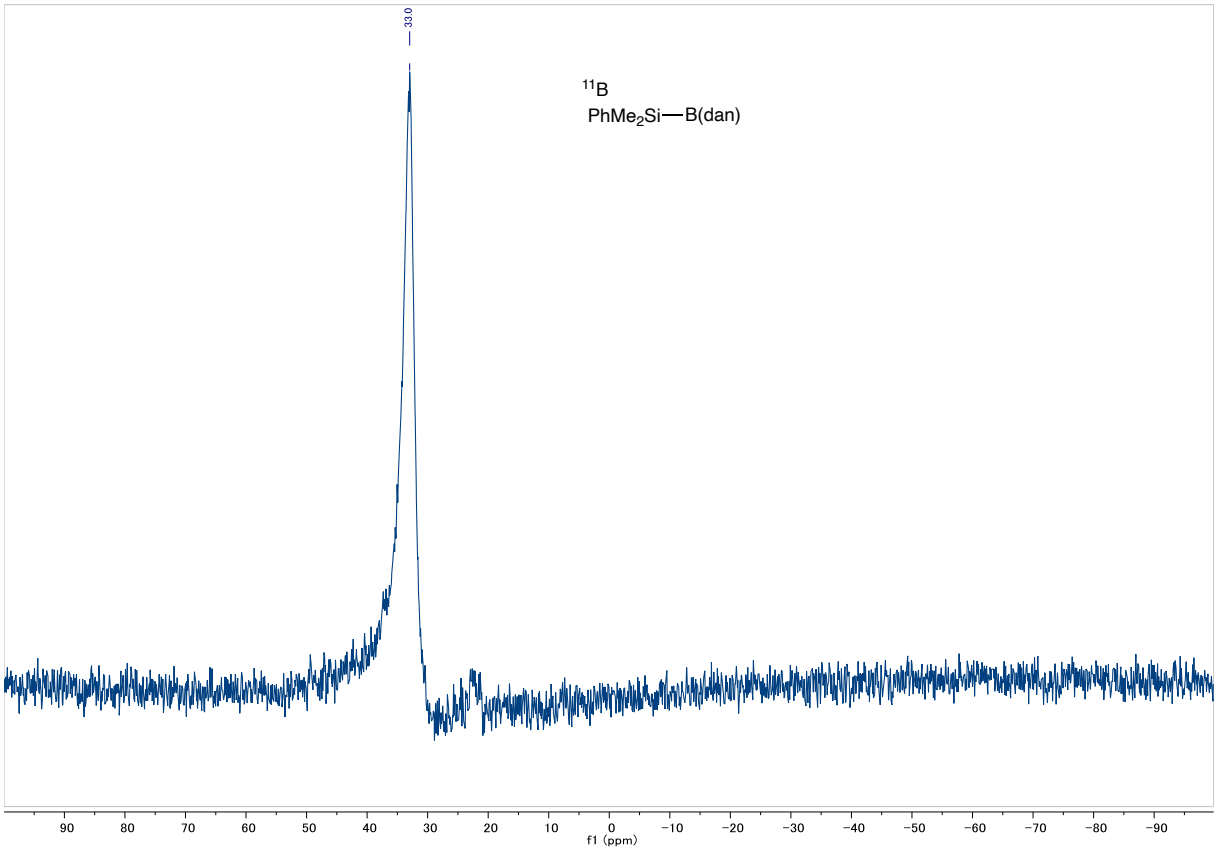
(6) C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallog*r., 2011, **44**, 1281.

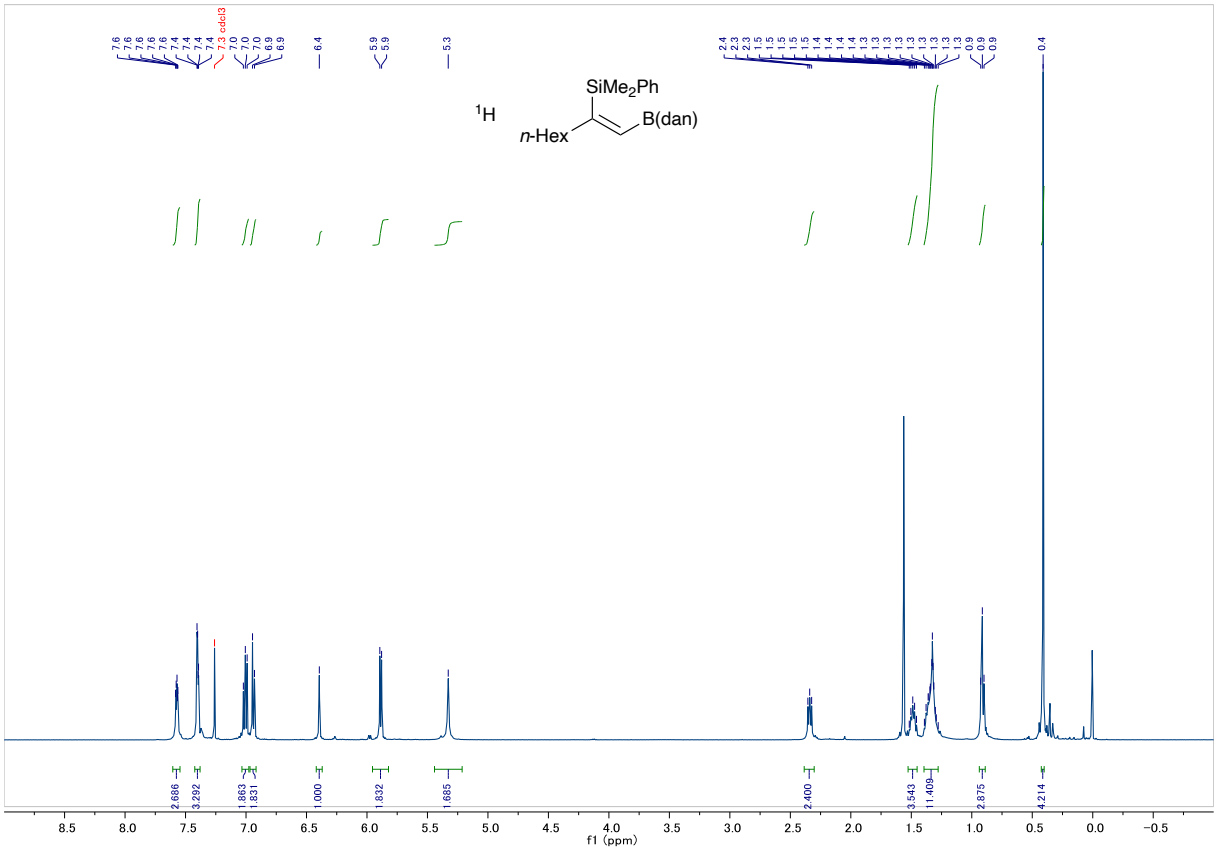
(7) C. Cason, Pov-Ray 3.6.2 Persistence of Vision, Raytracer, 2009.

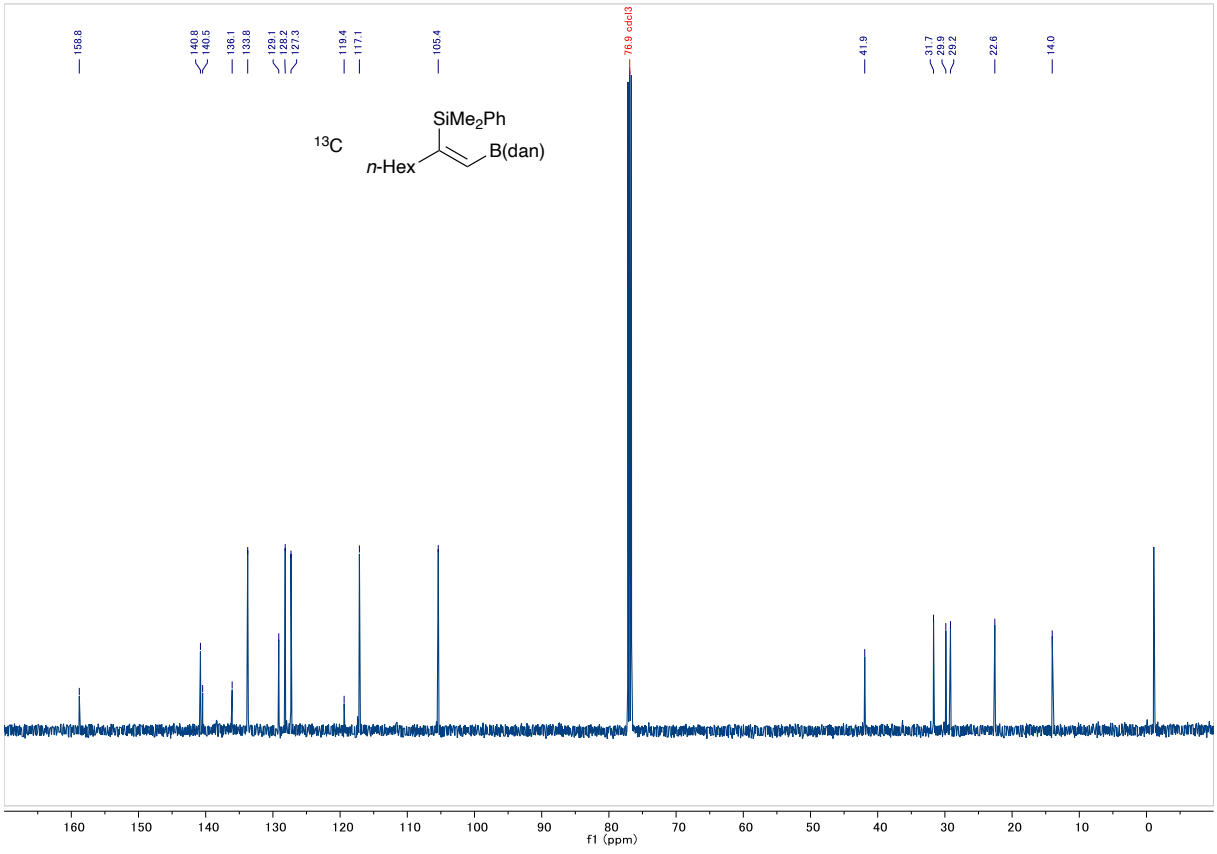
NMR spectra

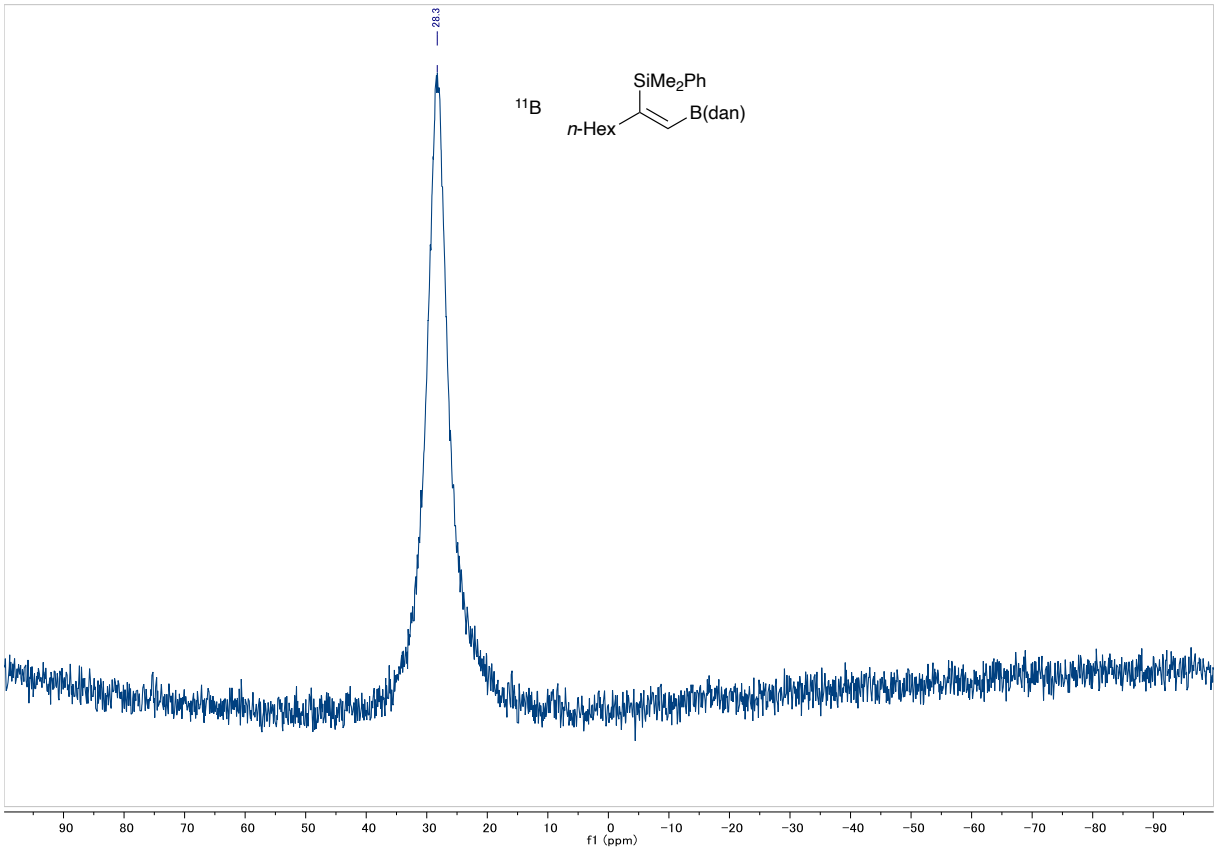


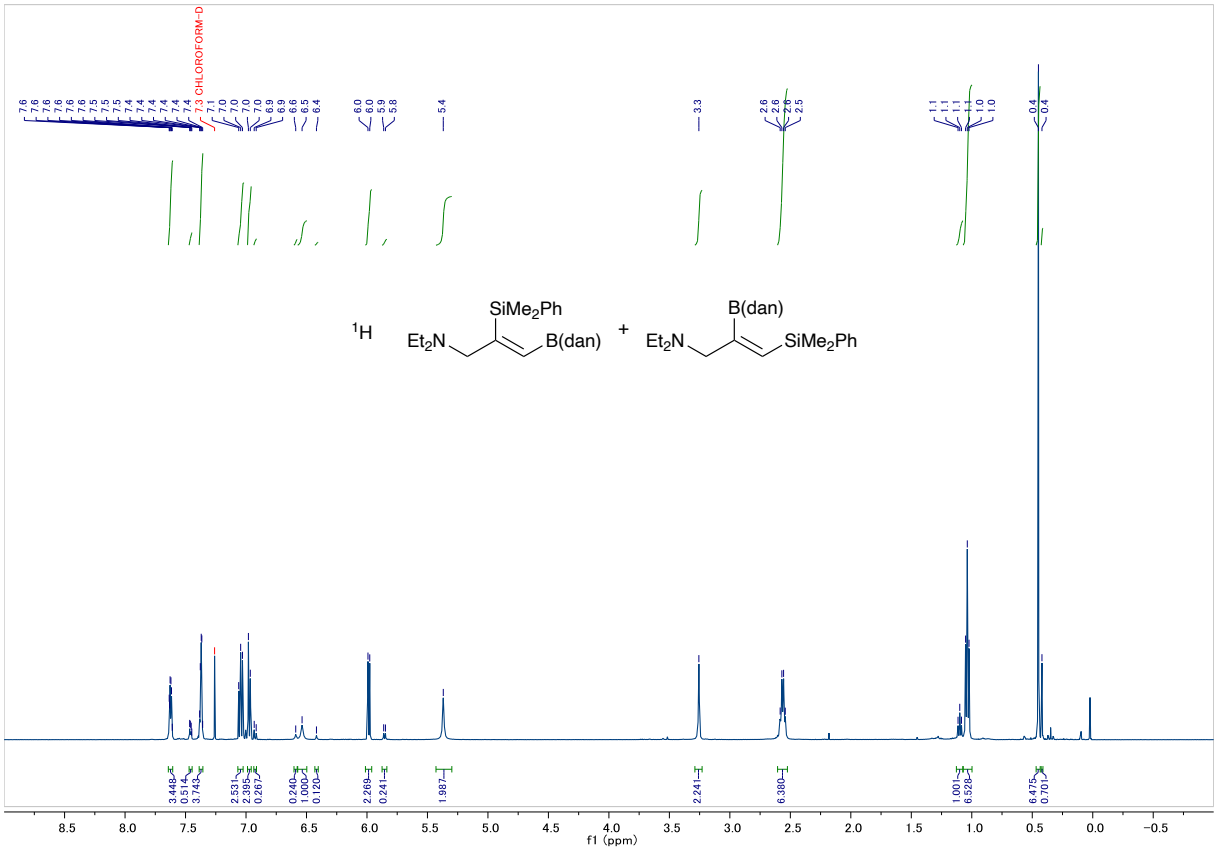


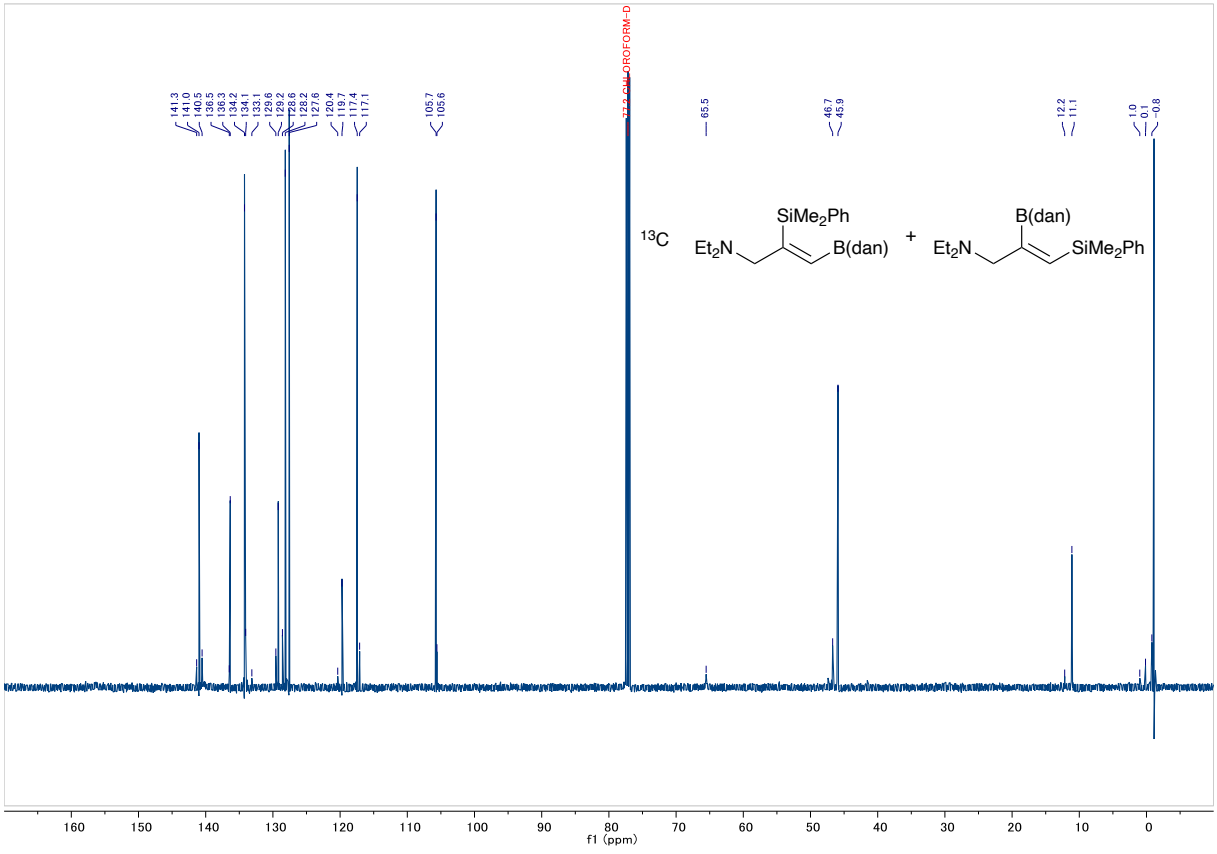

33.0
^{11}B
PhMe$_2$Si—B(dan)
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

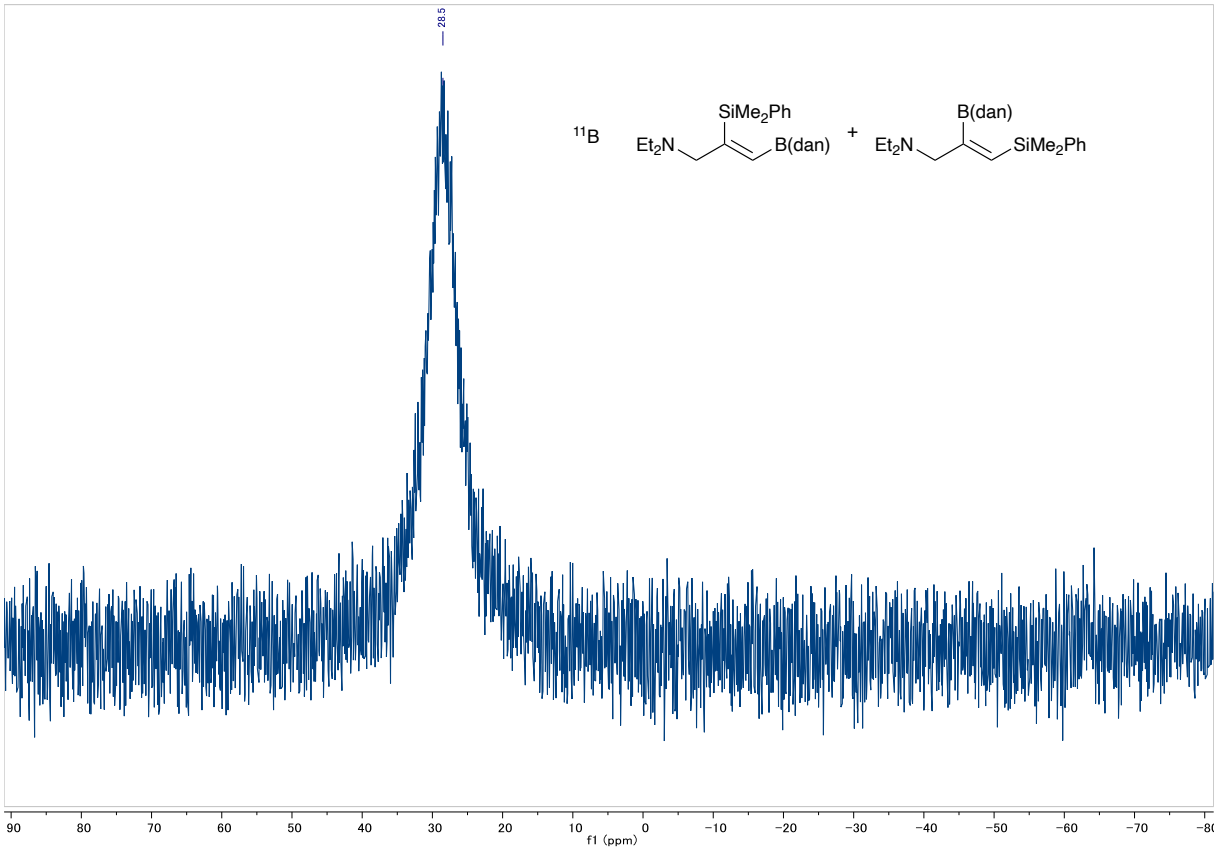

^{1}H
SiMe$_2$Ph
B(dan)
n-Hex
f1 (ppm)

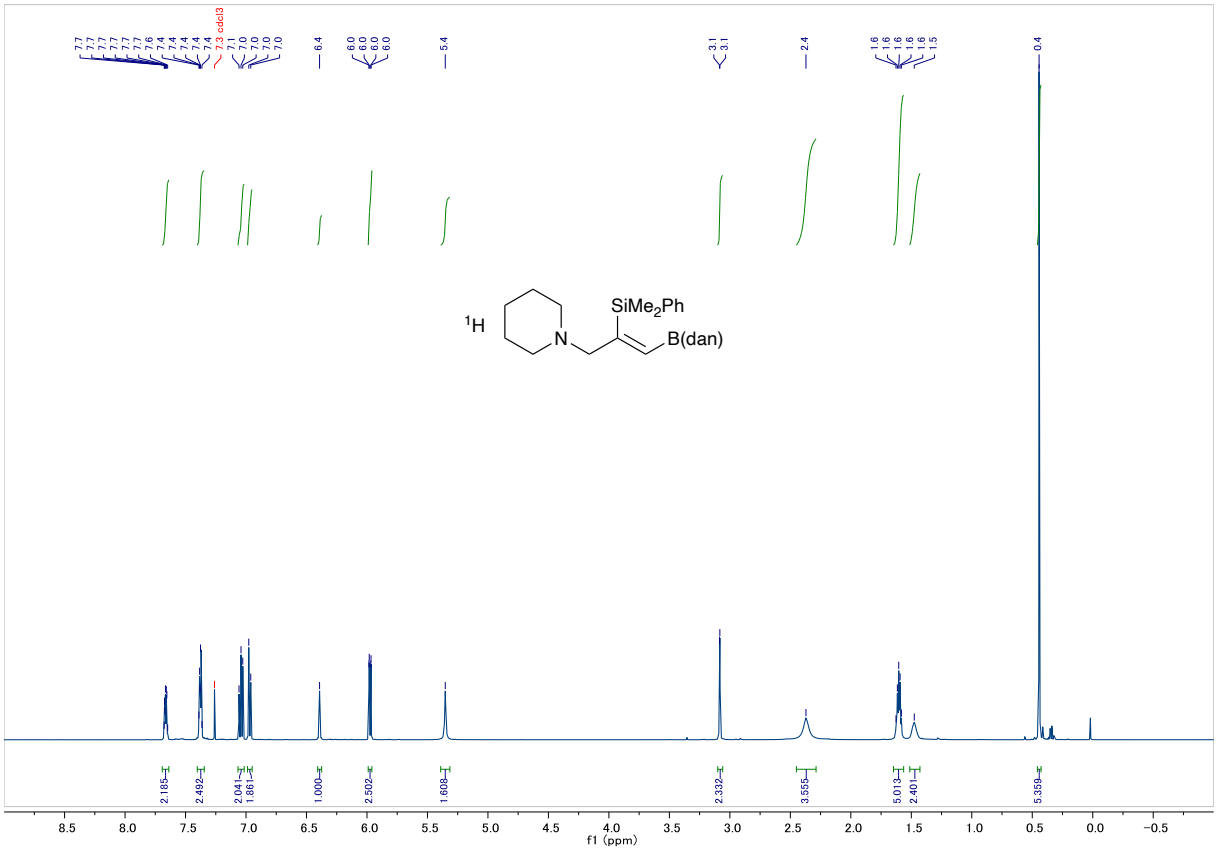

^{13}C
SiMe$_2$Ph
B(dan)
n-Hex
f1 (ppm)

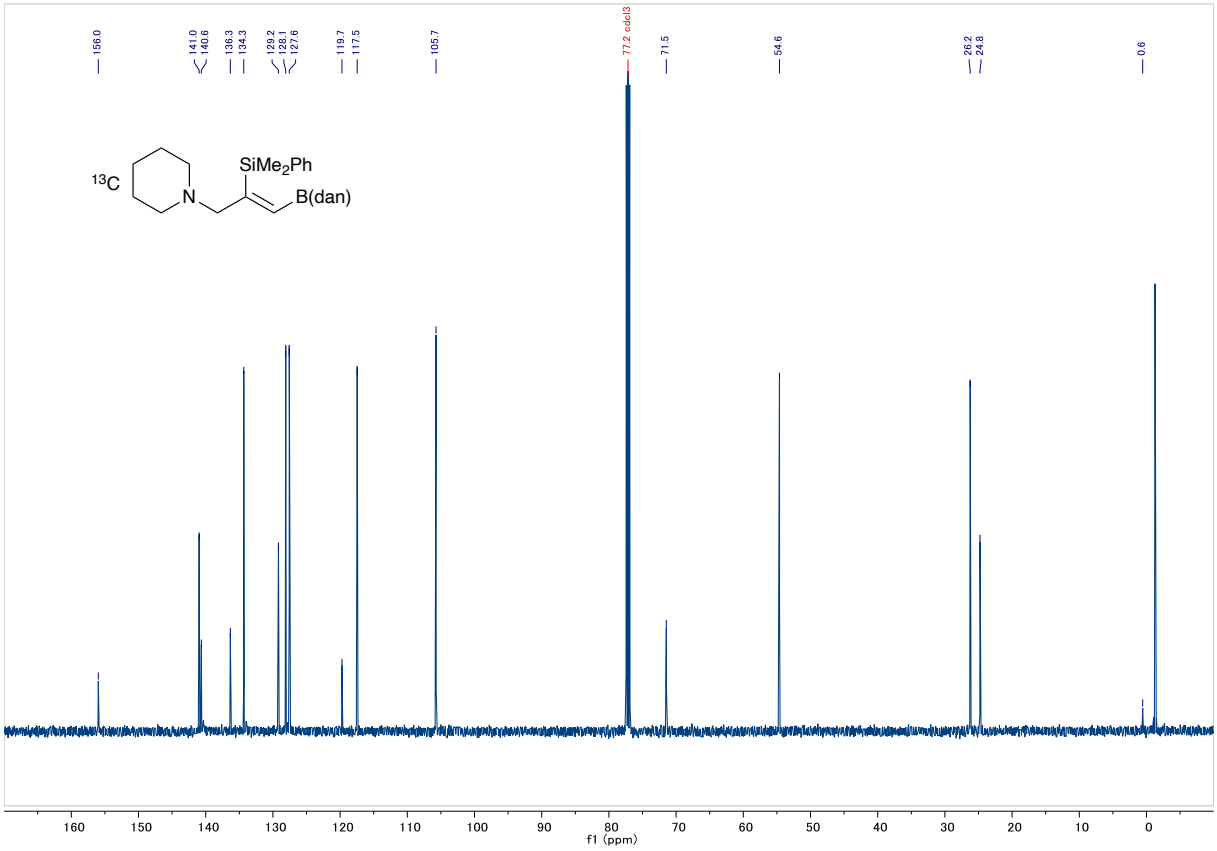

28.3
^{11}B
SiMe$_2$Ph
B(dan)
n-Hex
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

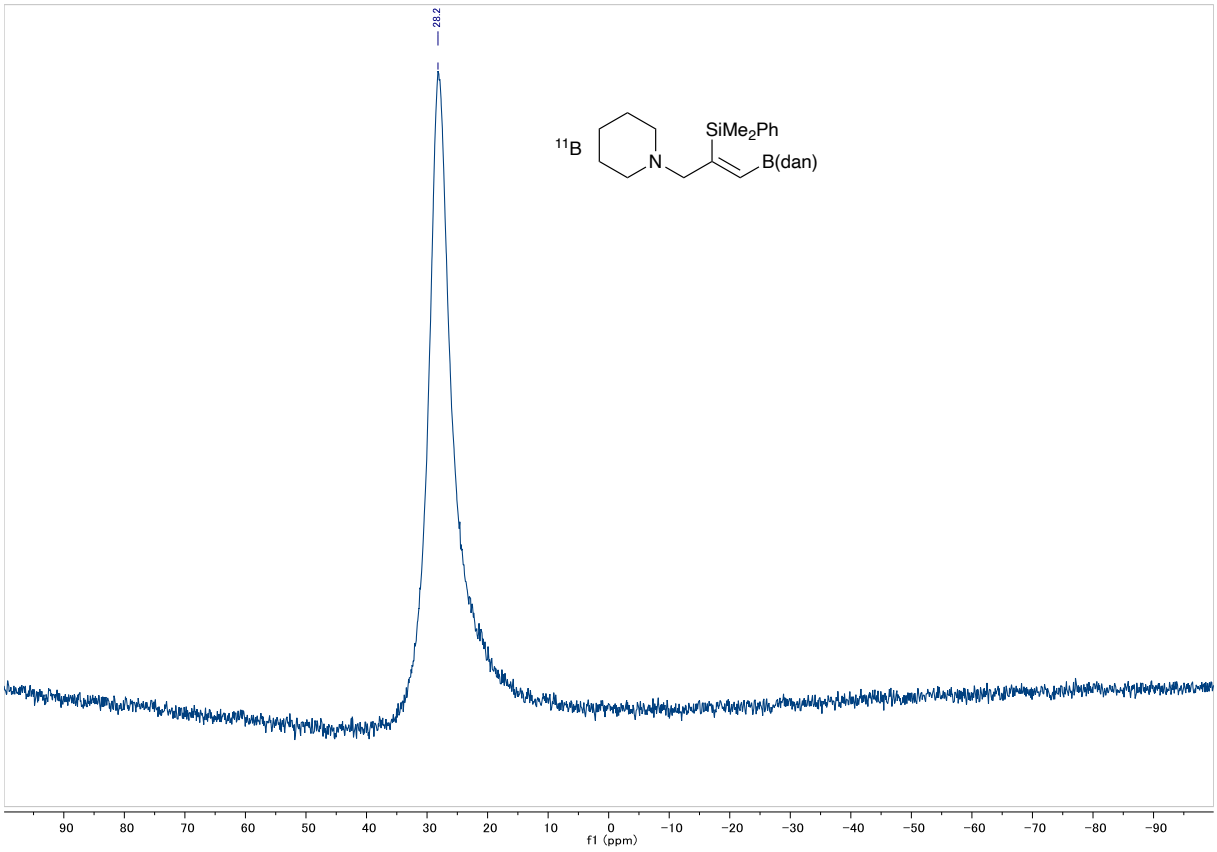

CHLOROFORM-D
^{1}H
SiMe$_2$Ph
Et$_2$N
B(dan)
+
B(dan)
Et$_2$N
SiMe$_2$Ph
f1 (ppm)

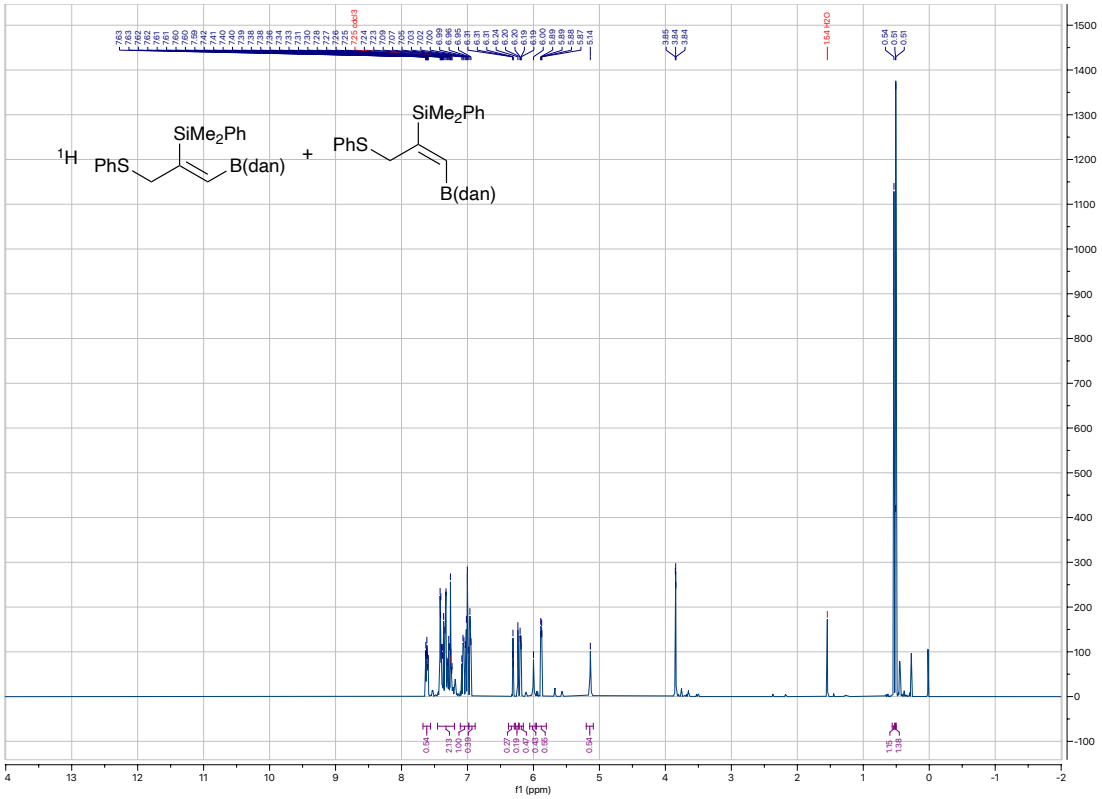

CHLOROFORM-D
^{13}C
SiMe$_2$Ph
Et$_2$N
B(dan)
+
B(dan)
Et$_2$N
SiMe$_2$Ph
f1 (ppm)

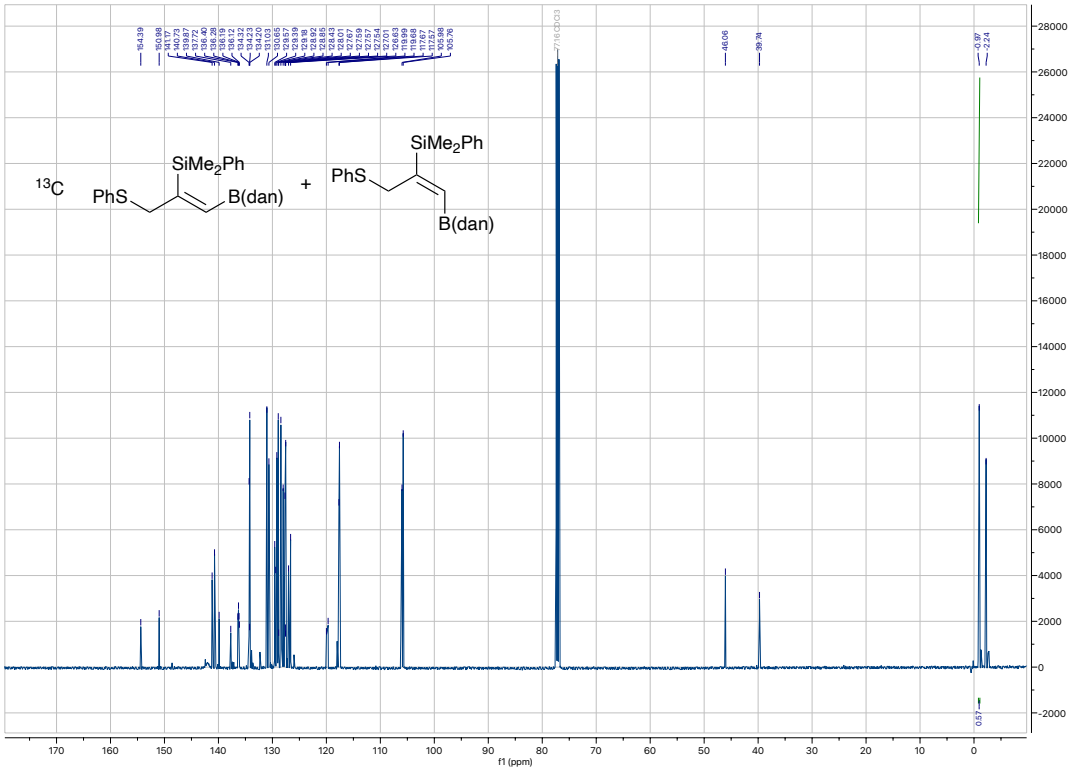

28.5
^{11}B
SiMe$_2$Ph
Et$_2$N
B(dan)
+
B(dan)
Et$_2$N
SiMe$_2$Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70
f1 (ppm)

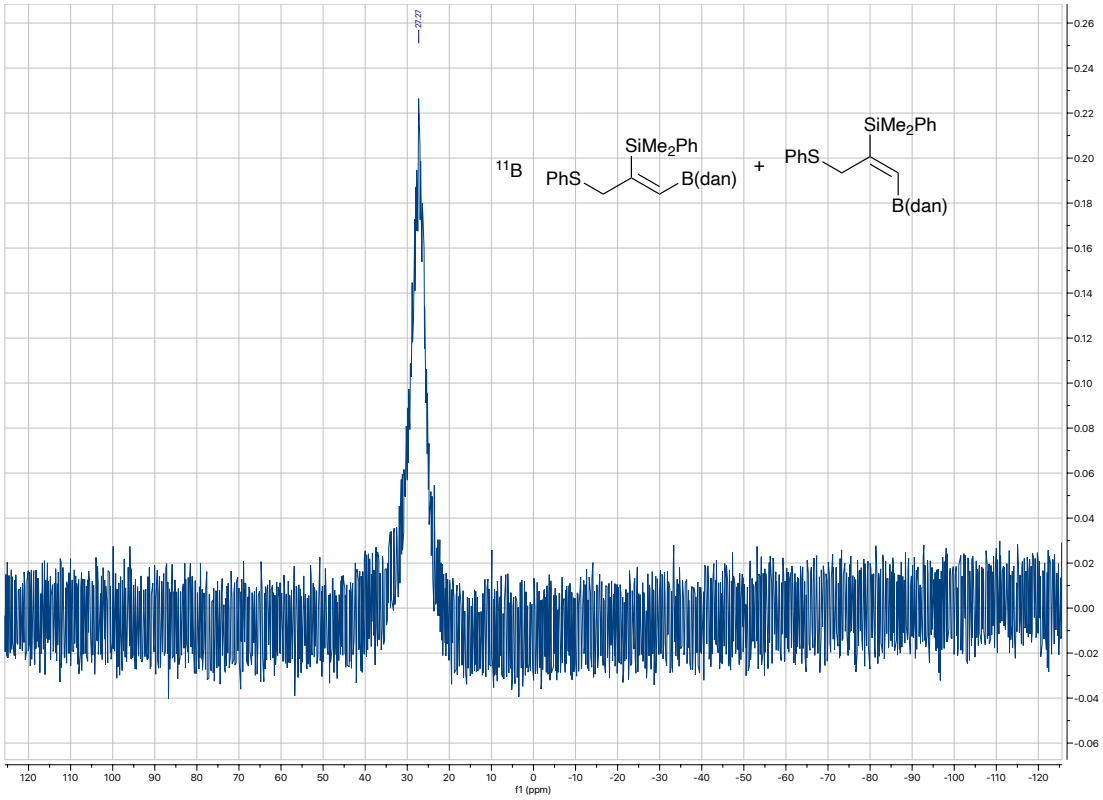

7.3 cdcl3
6.4
6.0
5.4
3.1
2.4
1.6
0.4
2.185
2.492
2.041
1.861
1.000
2.502
1.608
2.332
3.555
5.013
2.401
5.359
f1 (ppm)
^{1}H
SiMe$_2$Ph
N
B(dan)

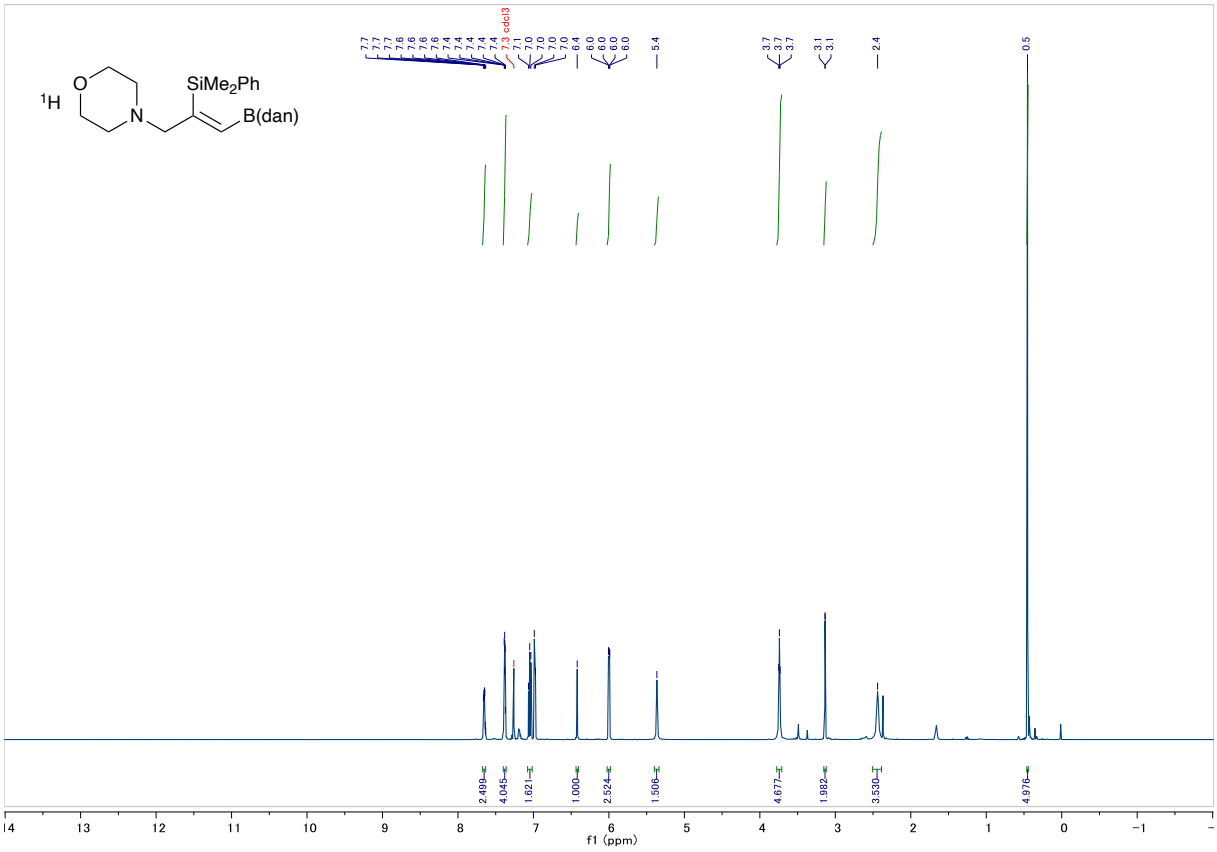

156.0
141.0
140.6
136.3
134.3
129.2
128.1
127.6
119.7
117.5
105.7
77.2 cdcl3
71.5
54.6
26.2
24.8
0.6
f1 (ppm)
^{13}C
SiMe$_2$Ph
N
B(dan)

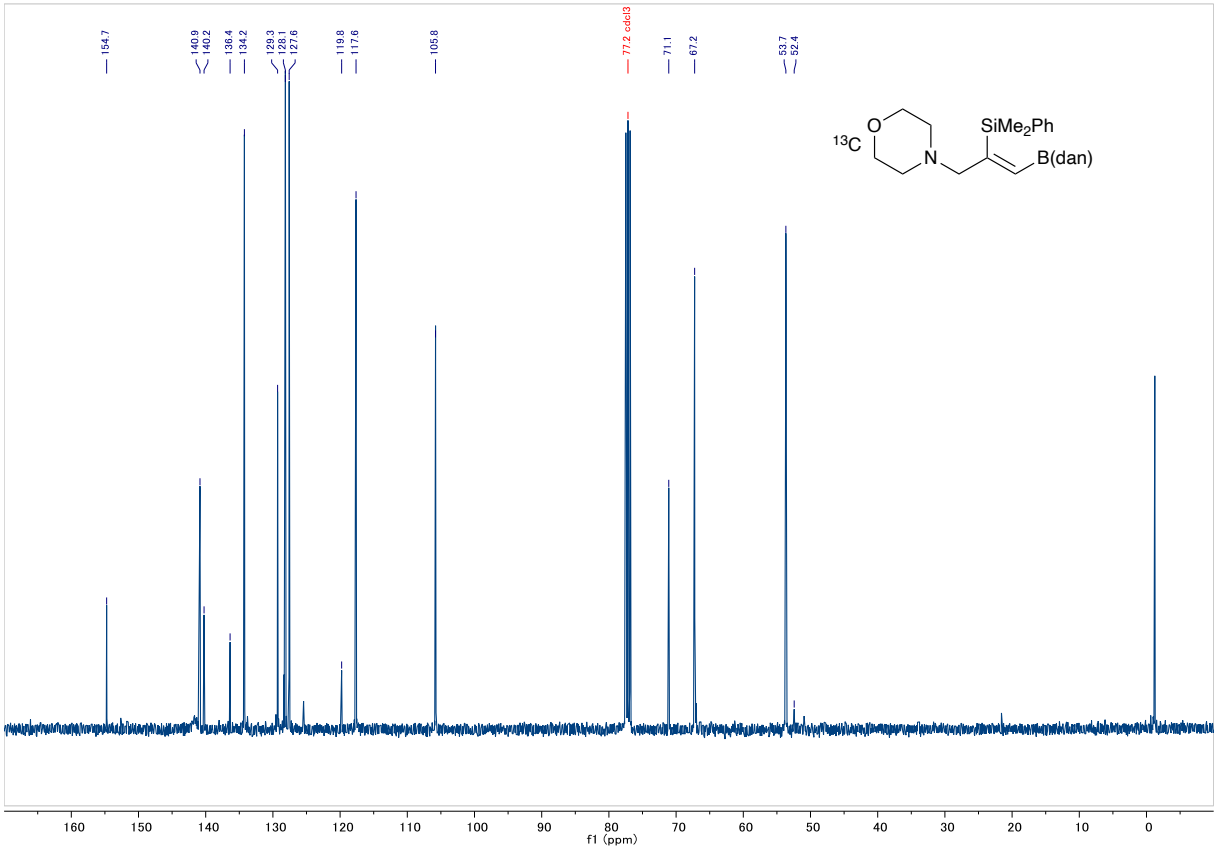

28.2
^{11}B
N
SiMe$_2$Ph
B(dan)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

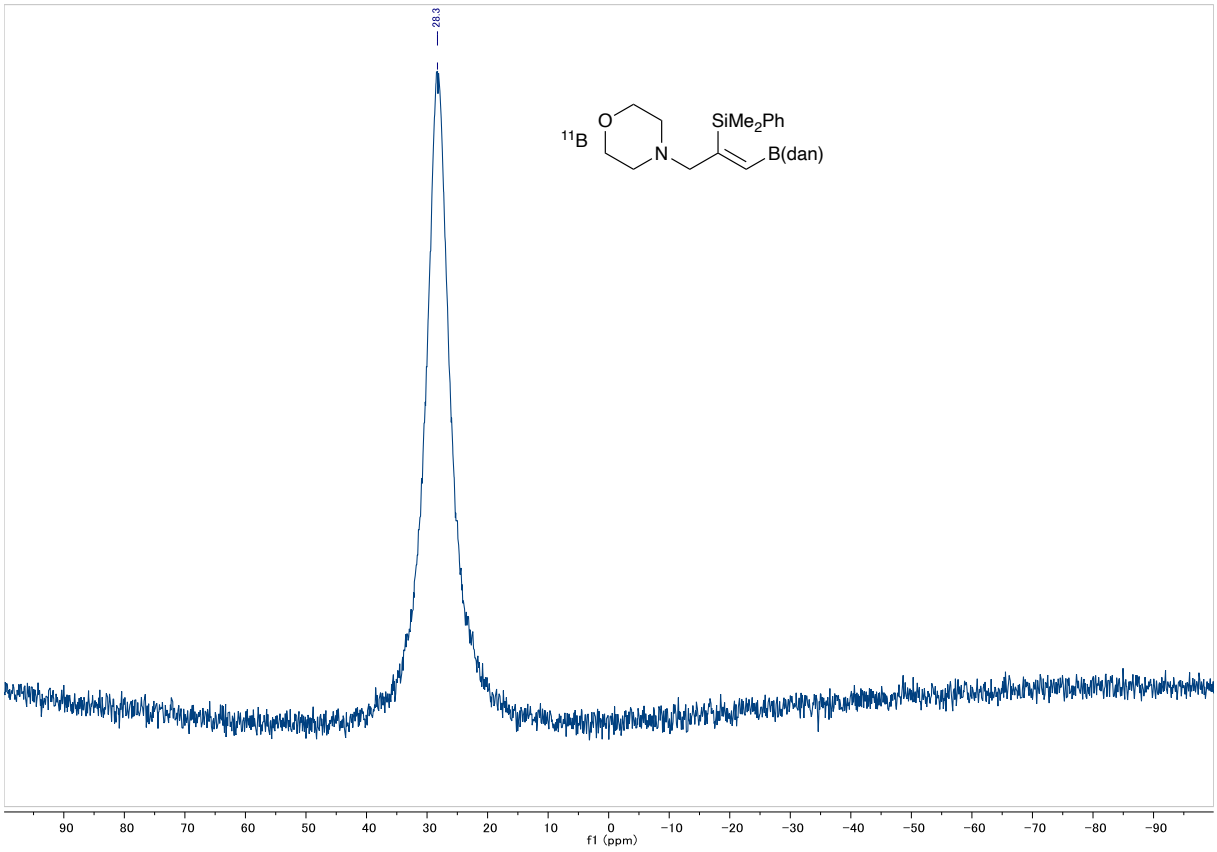

^{1}H
SiMe$_2$Ph
PhS
B(dan)
+
SiMe$_2$Ph
PhS
B(dan)
f1 (ppm)

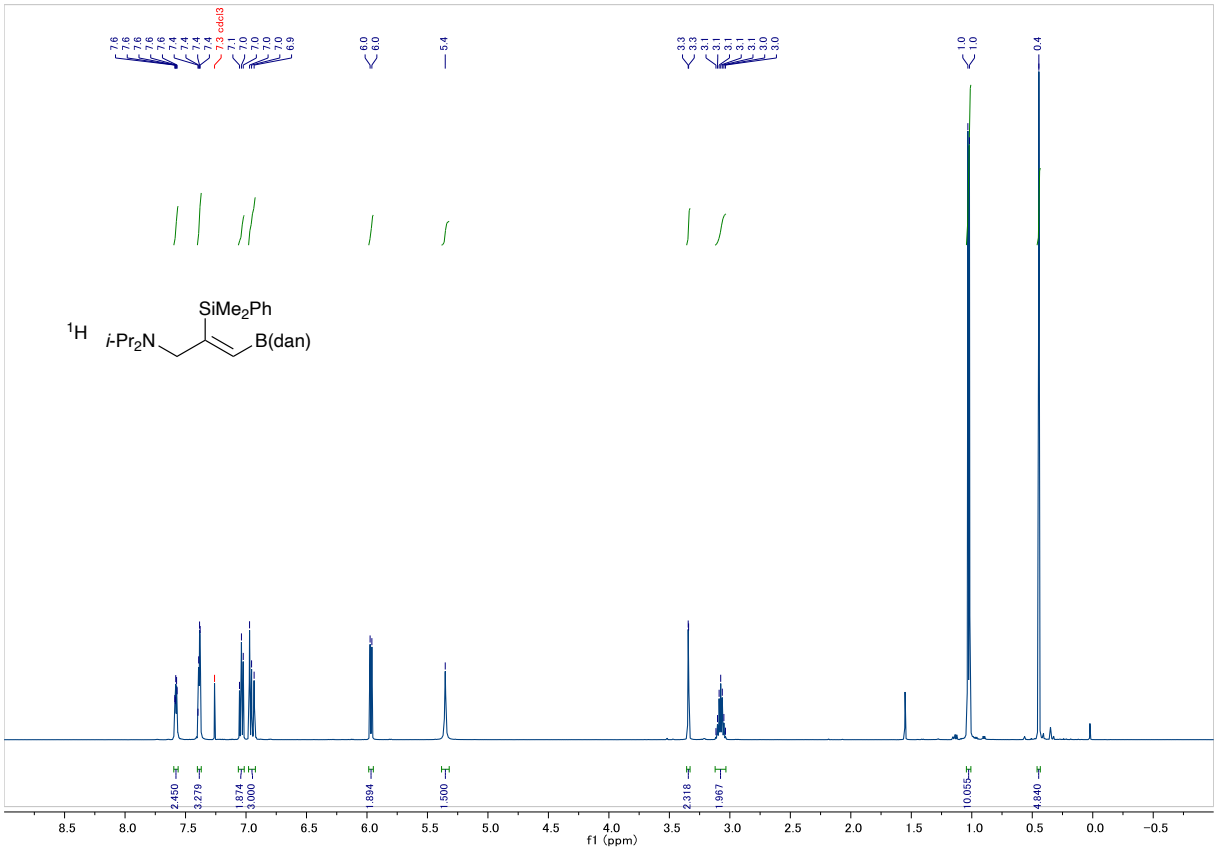

^{13}C
SiMe$_2$Ph
PhS
B(dan)
+
SiMe$_2$Ph
PhS
B(dan)
f1 (ppm)

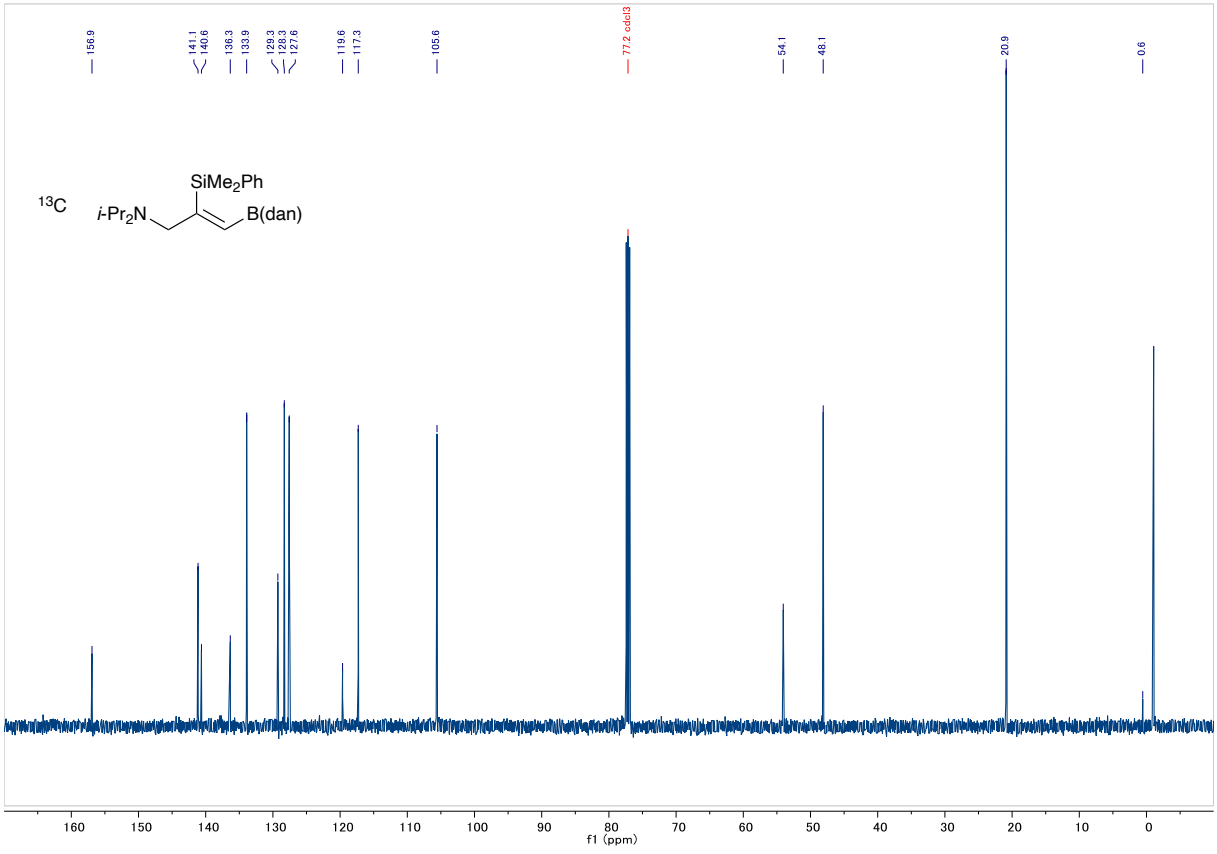

27.27
^{11}B
SiMe$_2$Ph
PhS
B(dan)
+
SiMe$_2$Ph
PhS
B(dan)
f1 (ppm)

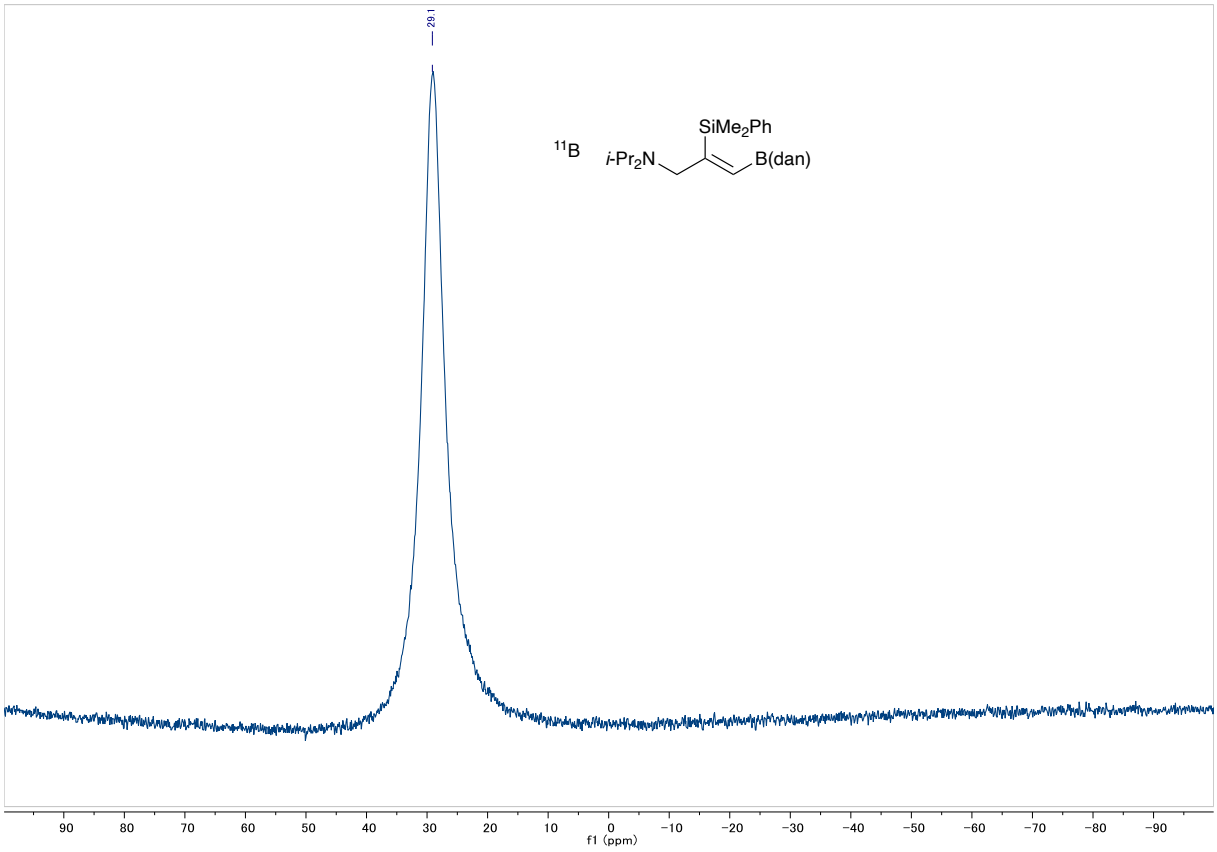

^{1}H
O
N
SiMe$_2$Ph
B(dan)
7.7
7.7
7.7
7.6
7.6
7.6
7.6
7.4
7.4
7.4
7.4
7.3 cdcl3
7.1
7.0
7.0
7.0
7.0
6.4
6.0
6.0
6.0
6.0
5.4
3.7
3.7
3.7
3.1
3.1
2.4
0.5
2.499
4.045
1.621
1.000
2.524
1.506
4.677
1.982
3.530
4.976
f1 (ppm)

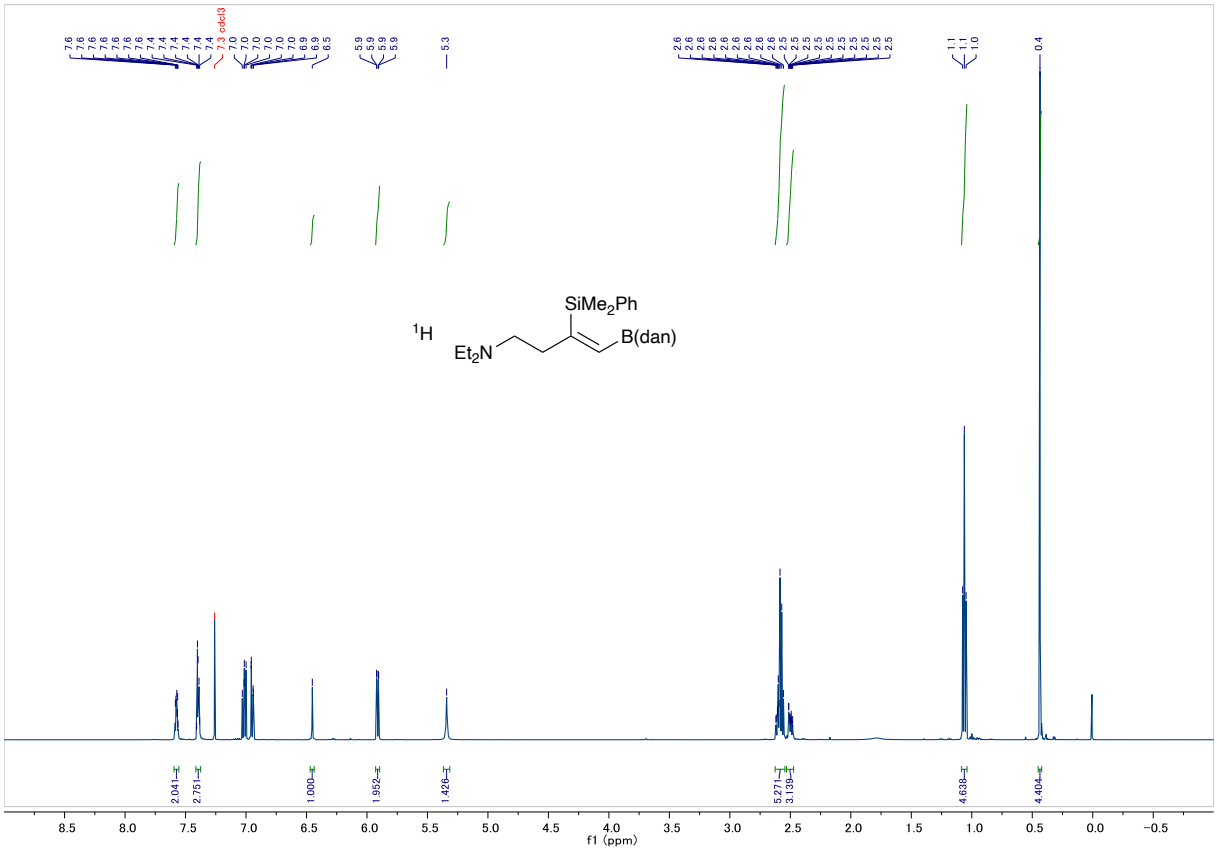

154.7
140.9
140.2
136.4
134.2
129.3
128.1
127.6
119.8
117.6
105.8
77.2 cdcl3
71.1
67.2
53.7
52.4
^{13}C
O
N
SiMe$_2$Ph
B(dan)
f1 (ppm)

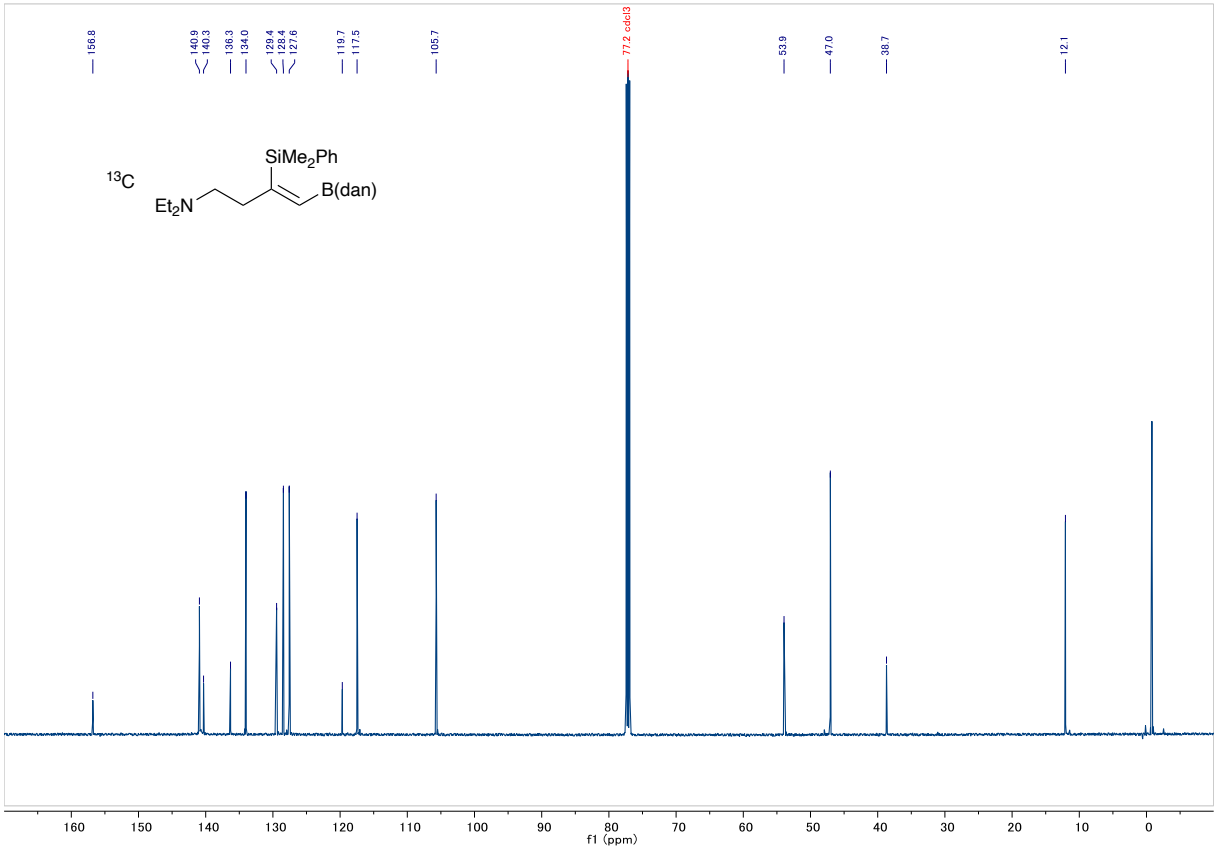

28.3
^{11}B
O
N
SiMe$_2$Ph
B(dan)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

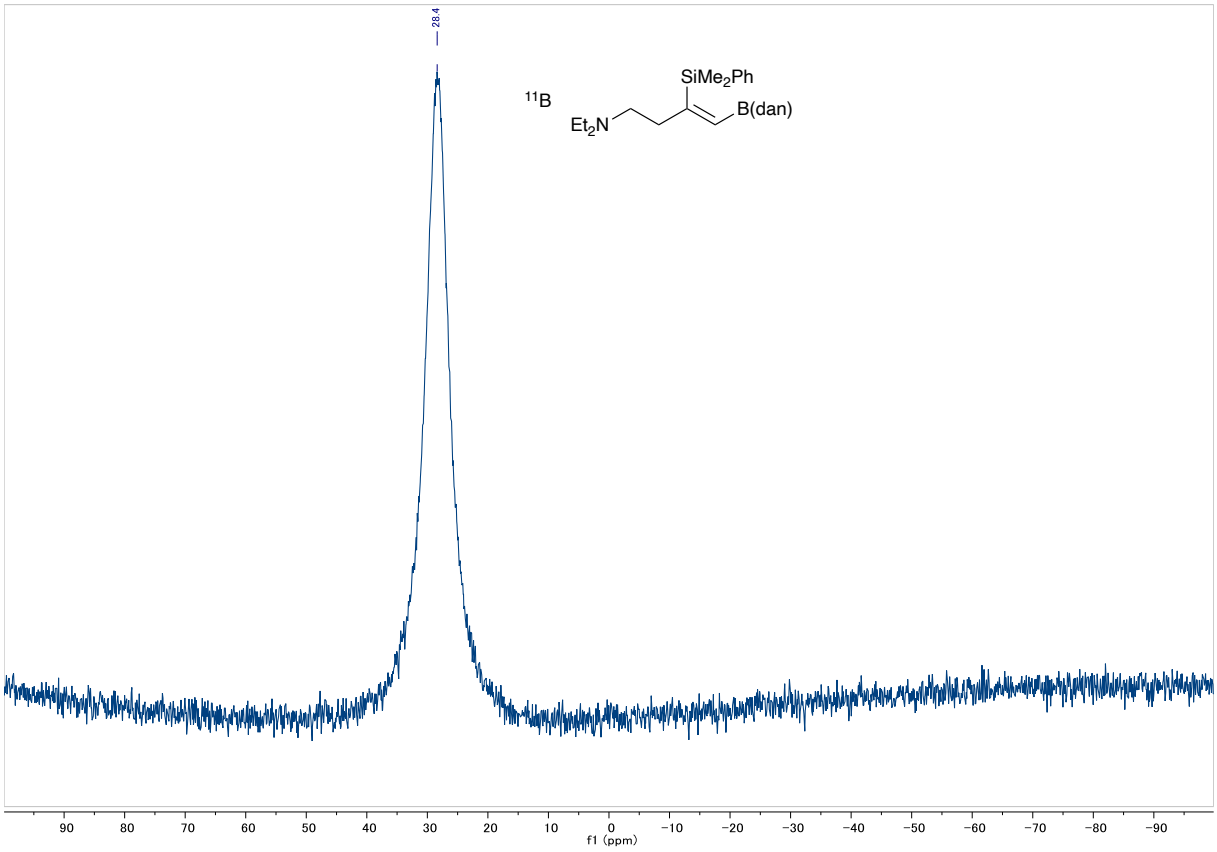

^{1}H
SiMe$_2$Ph
i-Pr$_2$N
B(dan)
f1 (ppm)

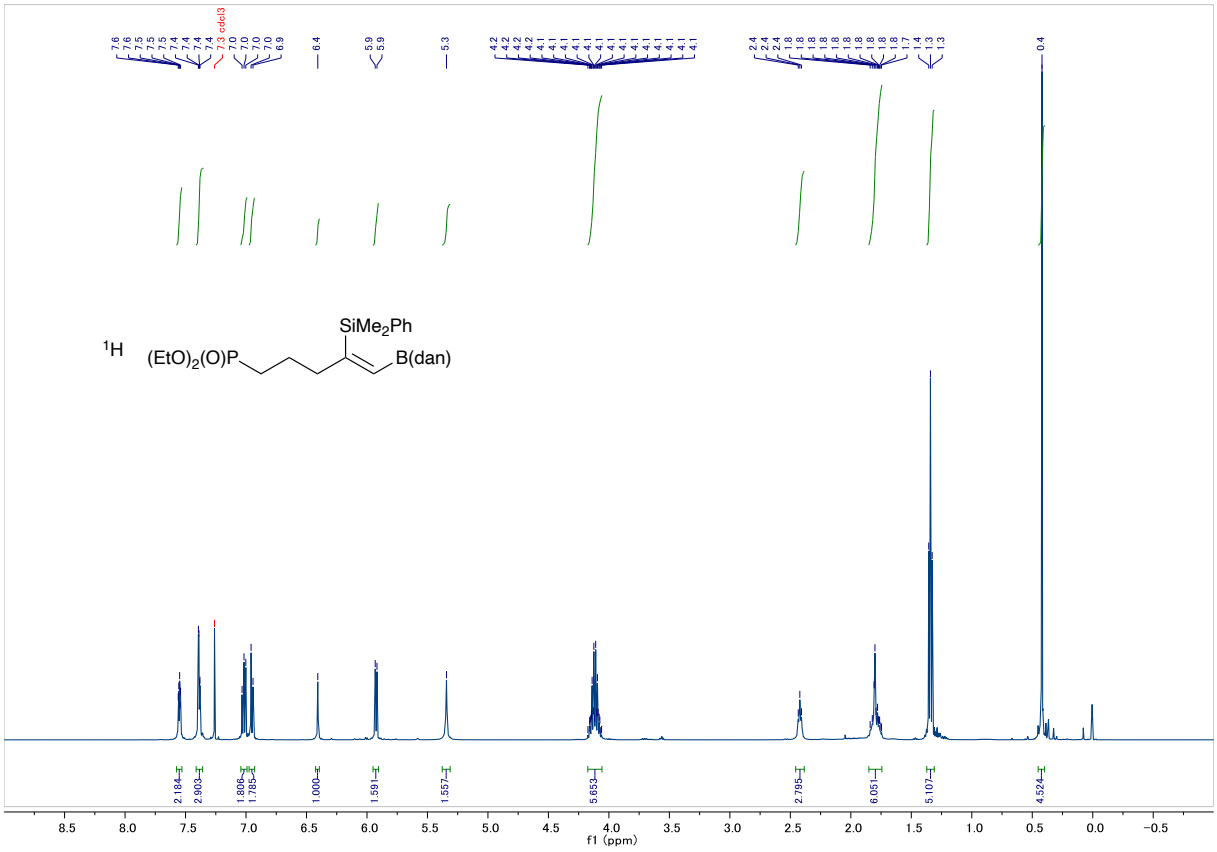

^{13}C
SiMe$_2$Ph
i-Pr$_2$N
B(dan)
f1 (ppm)

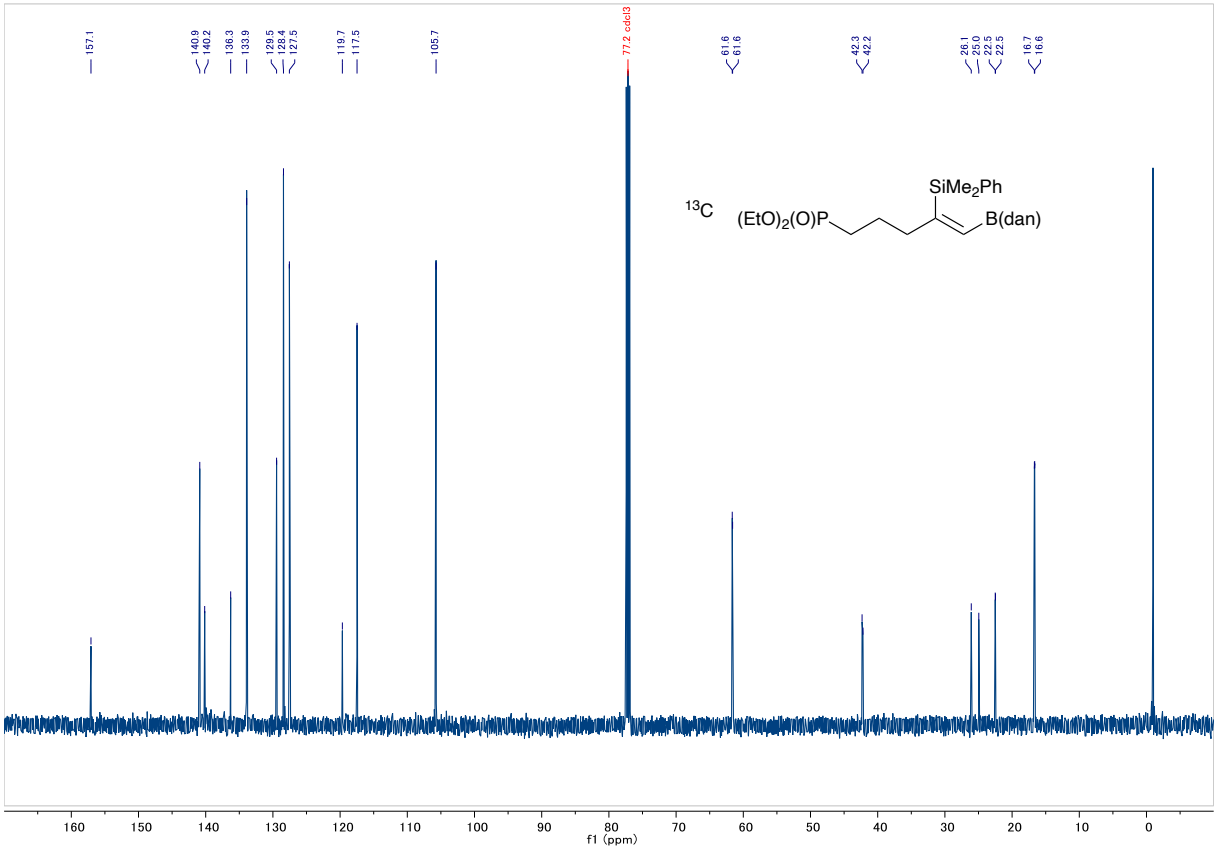

29.1
^{11}B
SiMe$_2$Ph
i-Pr$_2$N
B(dan)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

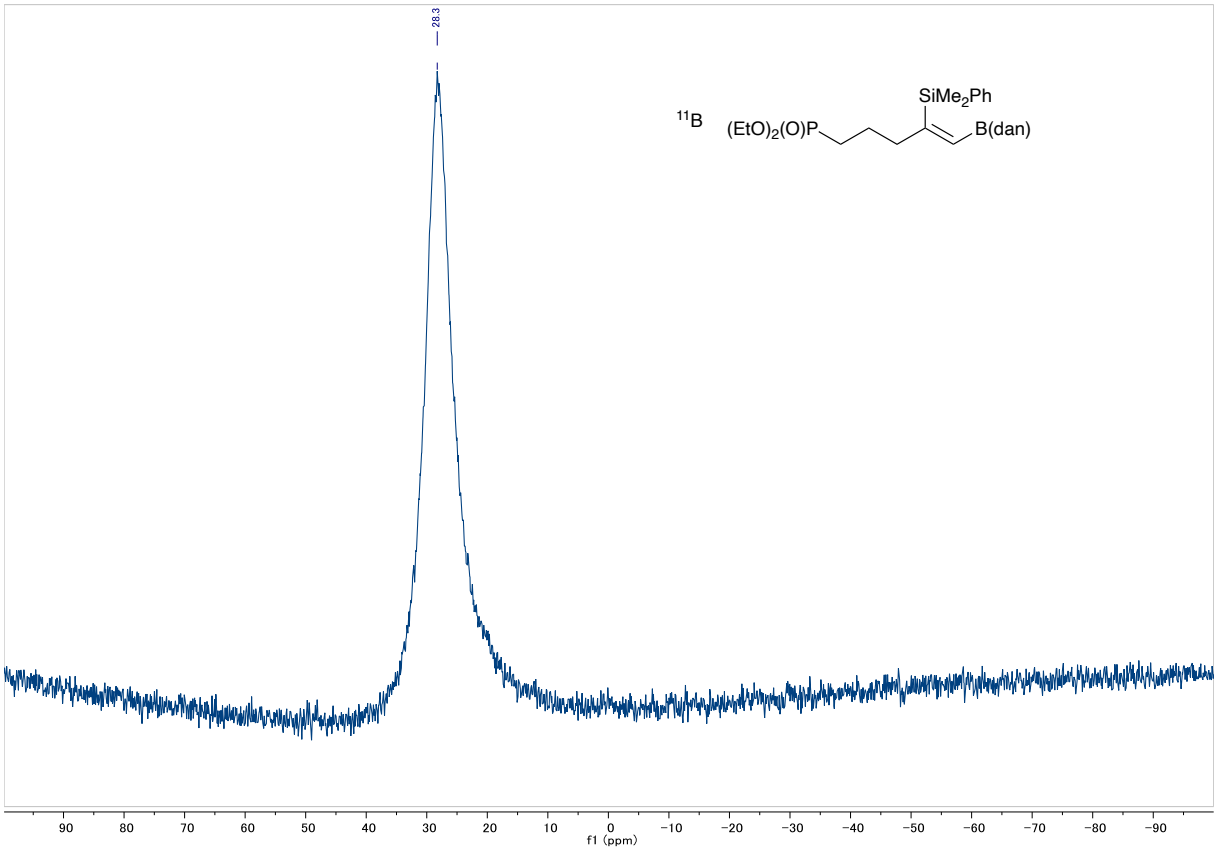

SiMe2Ph
1H
Et2N
B(dan)
f1 (ppm)

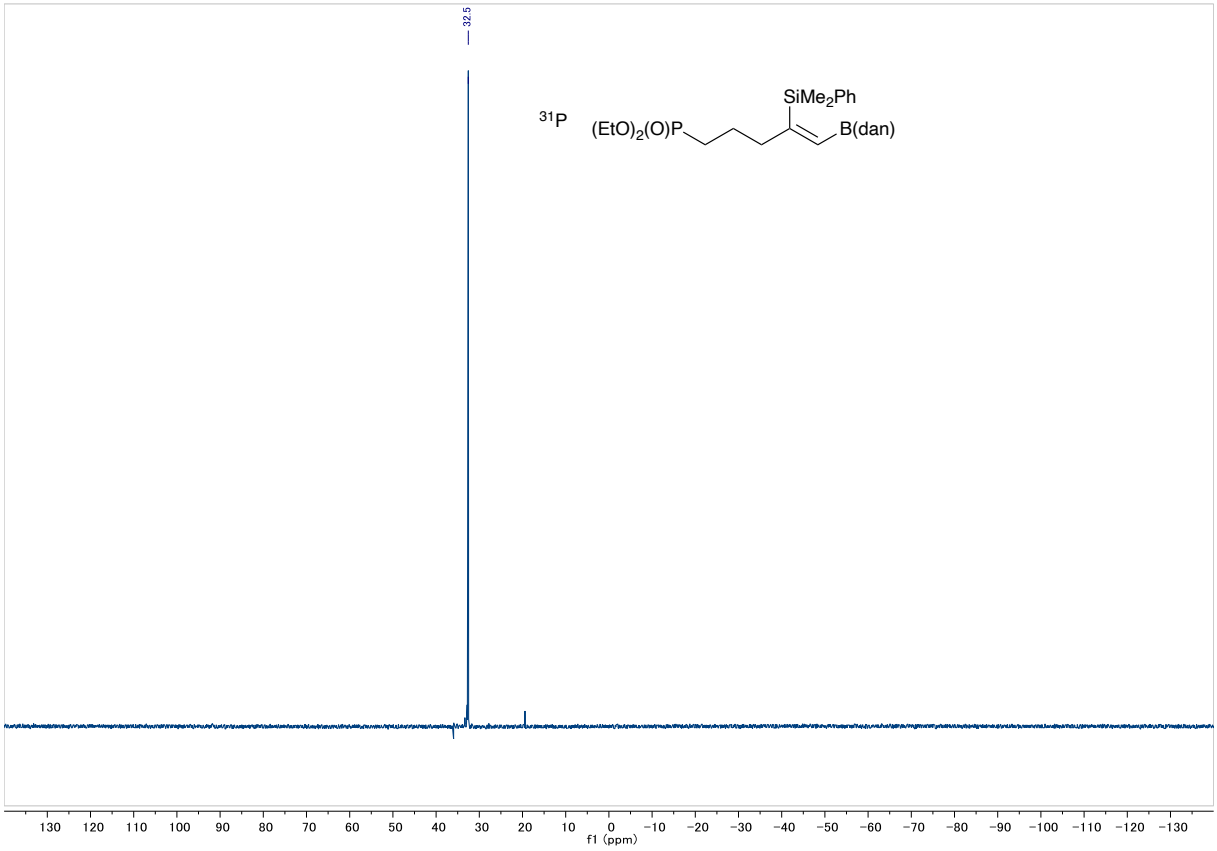

SiMe2Ph
13C
Et2N
B(dan)
f1 (ppm)

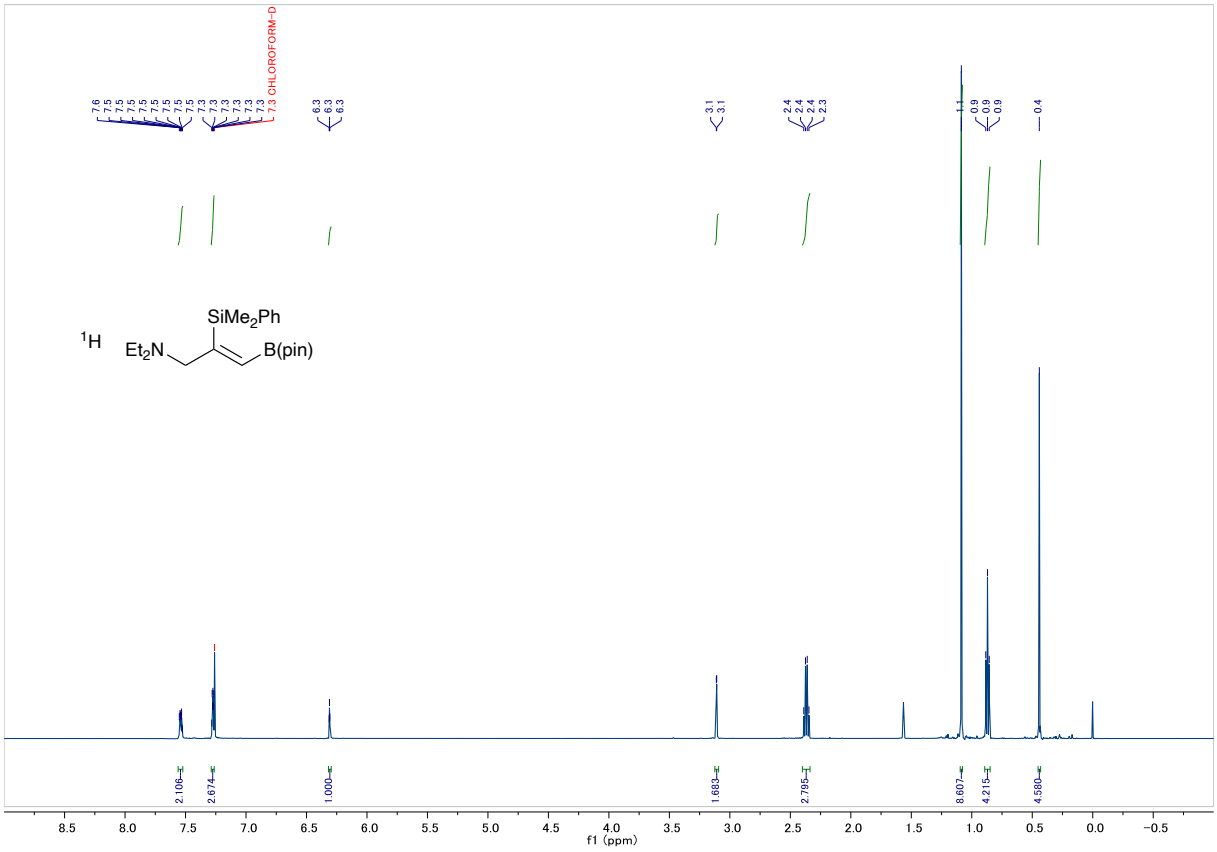

28.4
^{11}B
SiMe$_2$Ph
B(dan)
Et$_2$N
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

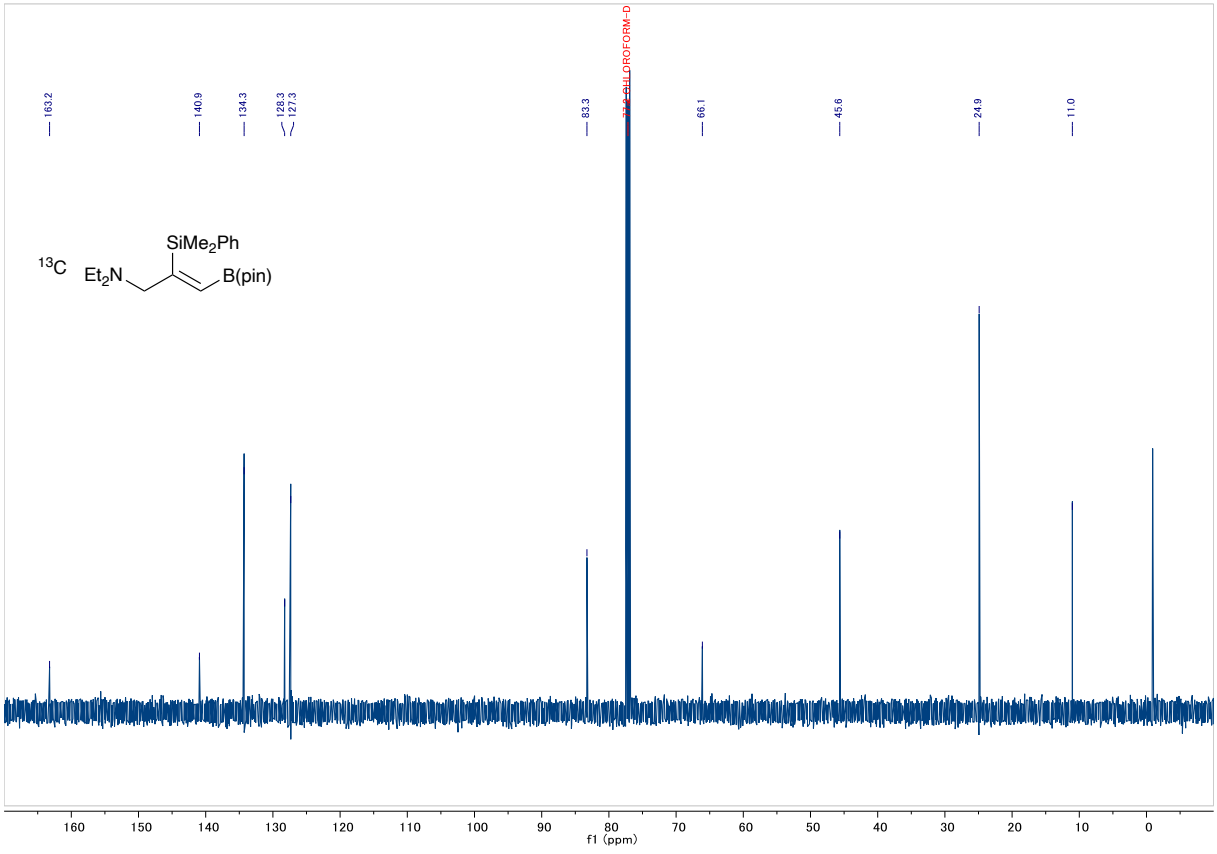

^{1}H
SiMe$_2$Ph
(EtO)$_2$(O)P
B(dan)
f1 (ppm)

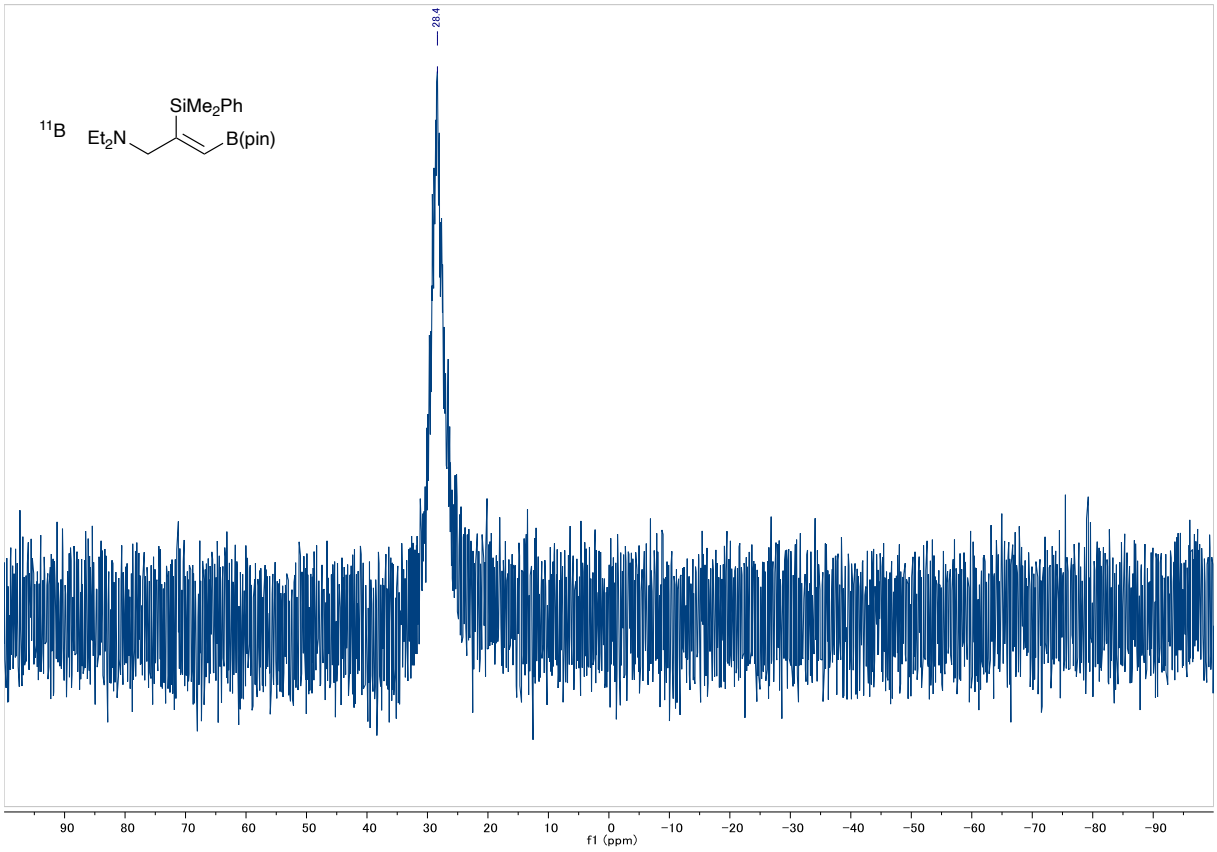

^{13}C
SiMe$_2$Ph
(EtO)$_2$(O)P
B(dan)
f1 (ppm)

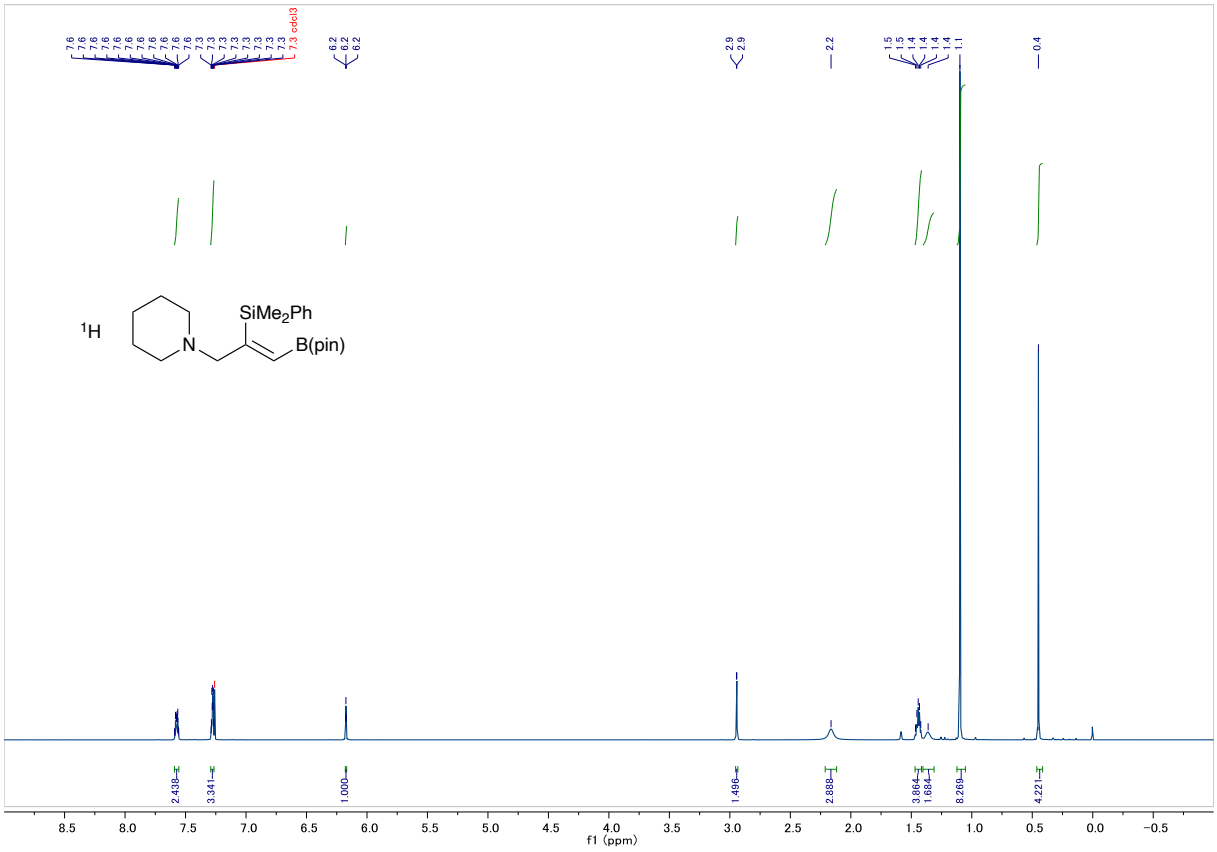

28.3
^{11}B
SiMe$_2$Ph
(EtO)$_2$(O)P
B(dan)
f1 (ppm)

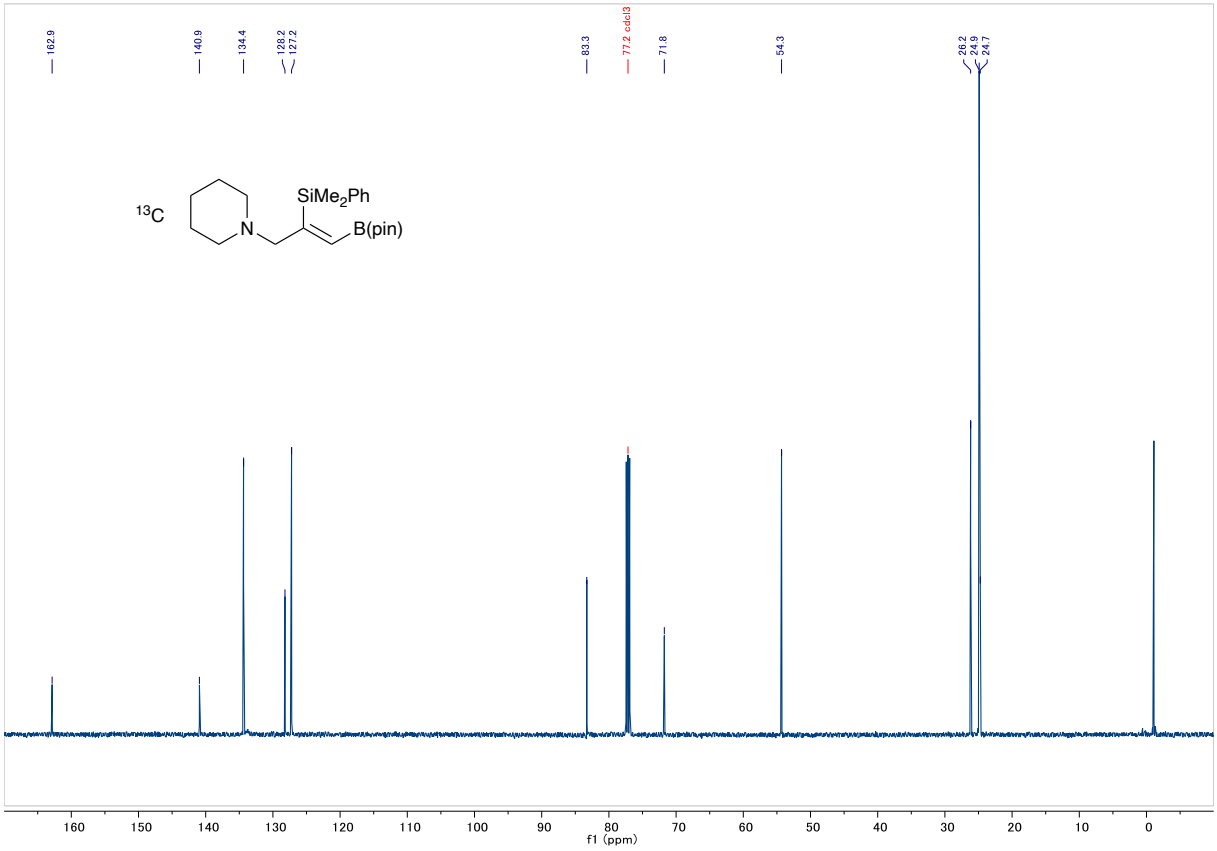

32.5
^{31}P
SiMe$_2$Ph
(EtO)$_2$(O)P
B(dan)
f1 (ppm)

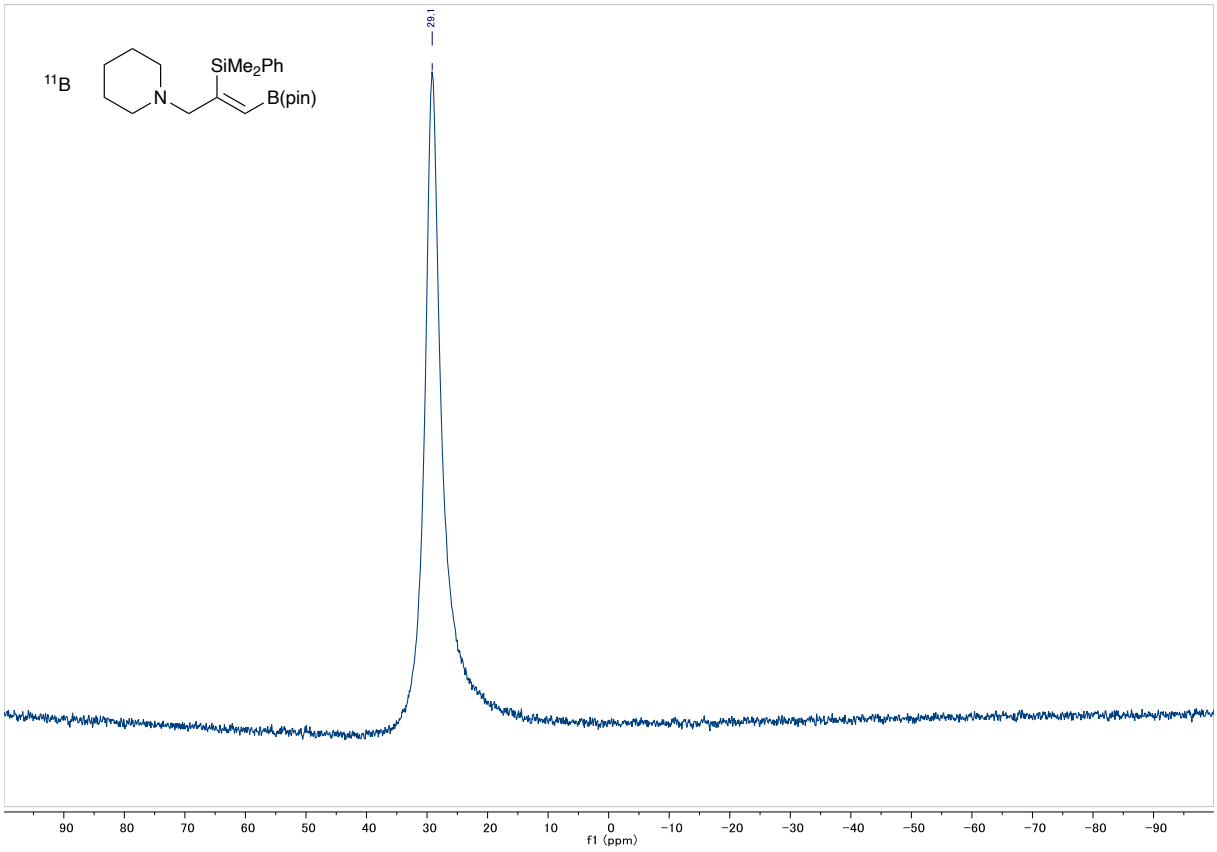

7.3 CHLOROFORM-D
SiMe2Ph
1H
Et2N
B(pin)
f1 (ppm)

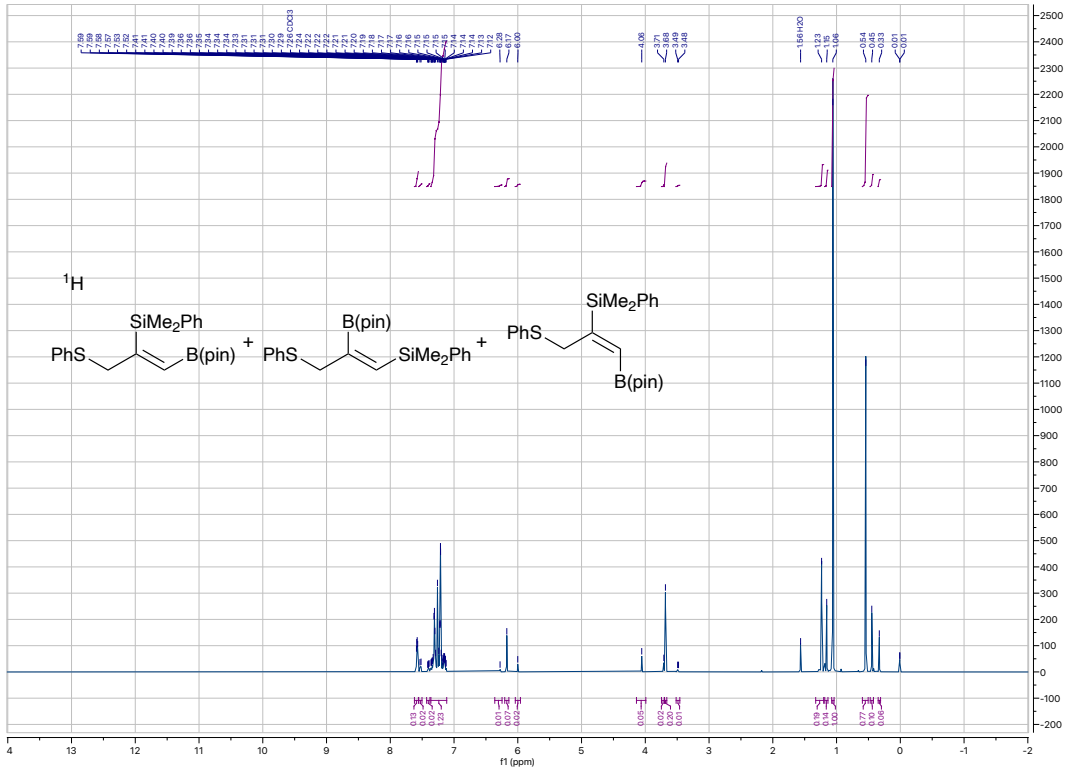

163.2
140.9
134.3
128.3
127.3
83.3
77.0 CHLOROFORM-D
66.1
45.6
24.9
11.0
SiMe2Ph
13C
Et2N
B(pin)
f1 (ppm)

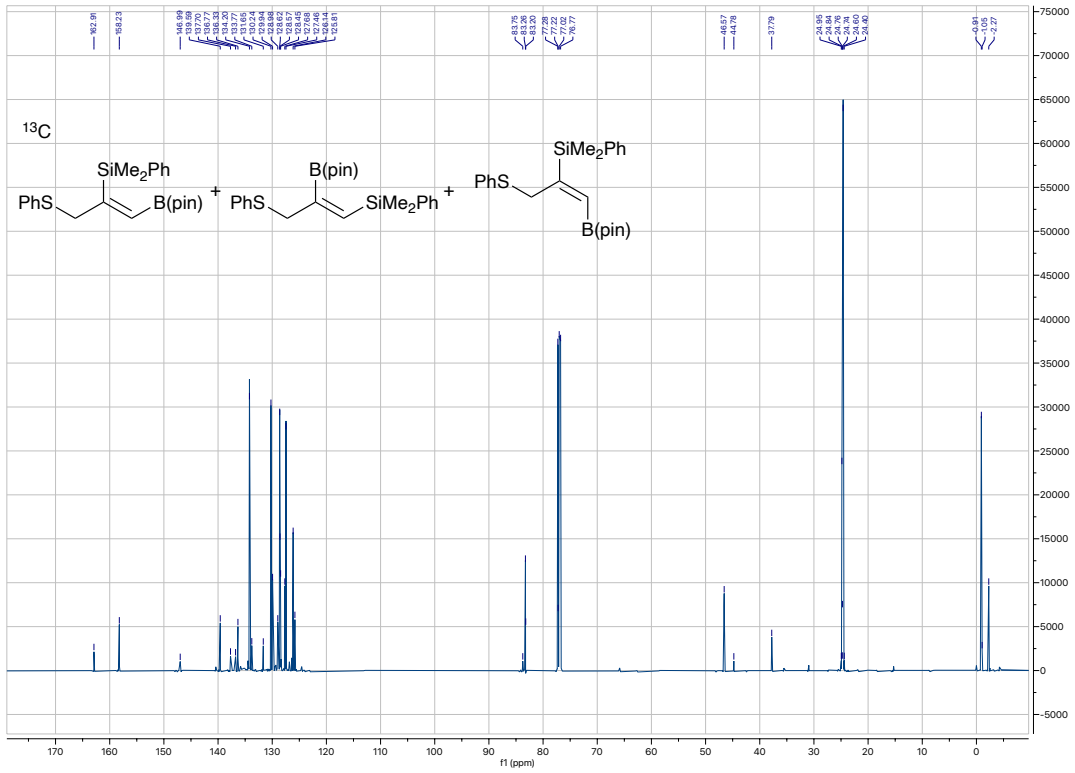

28.4
^{11}B
SiMe$_2$Ph
Et$_2$N
B(pin)
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

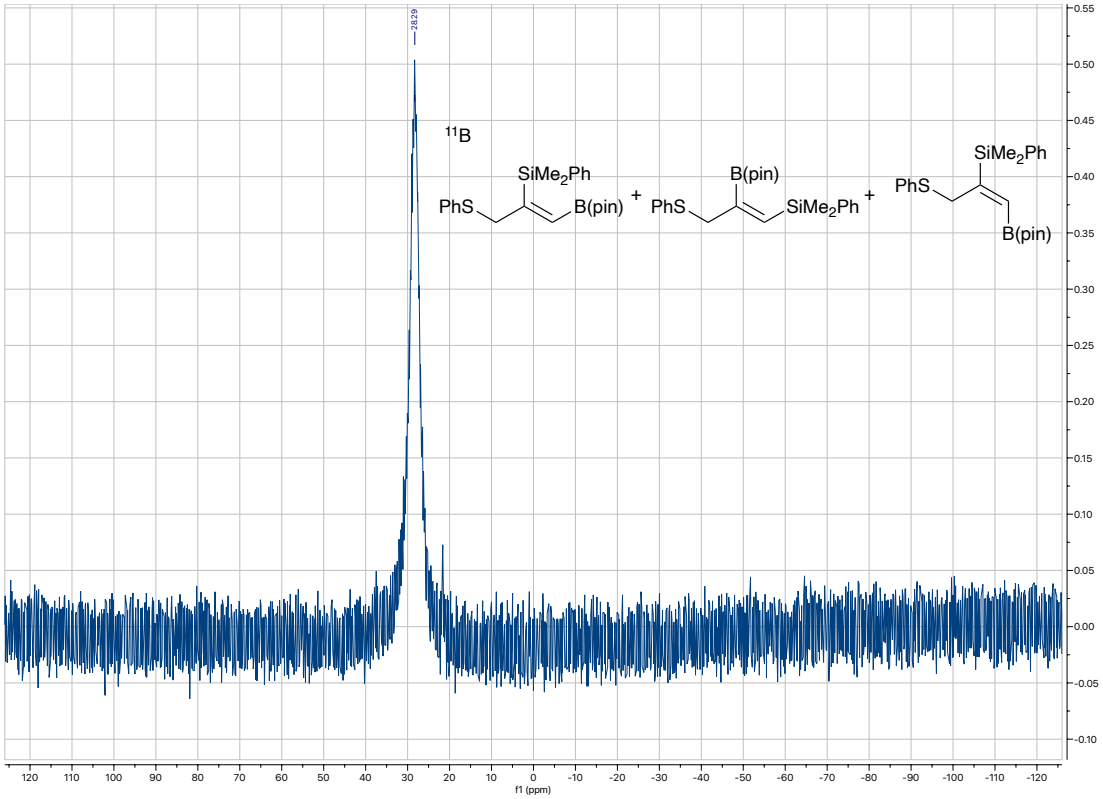

^{1}H
SiMe$_2$Ph
B(pin)
N
f1 (ppm)

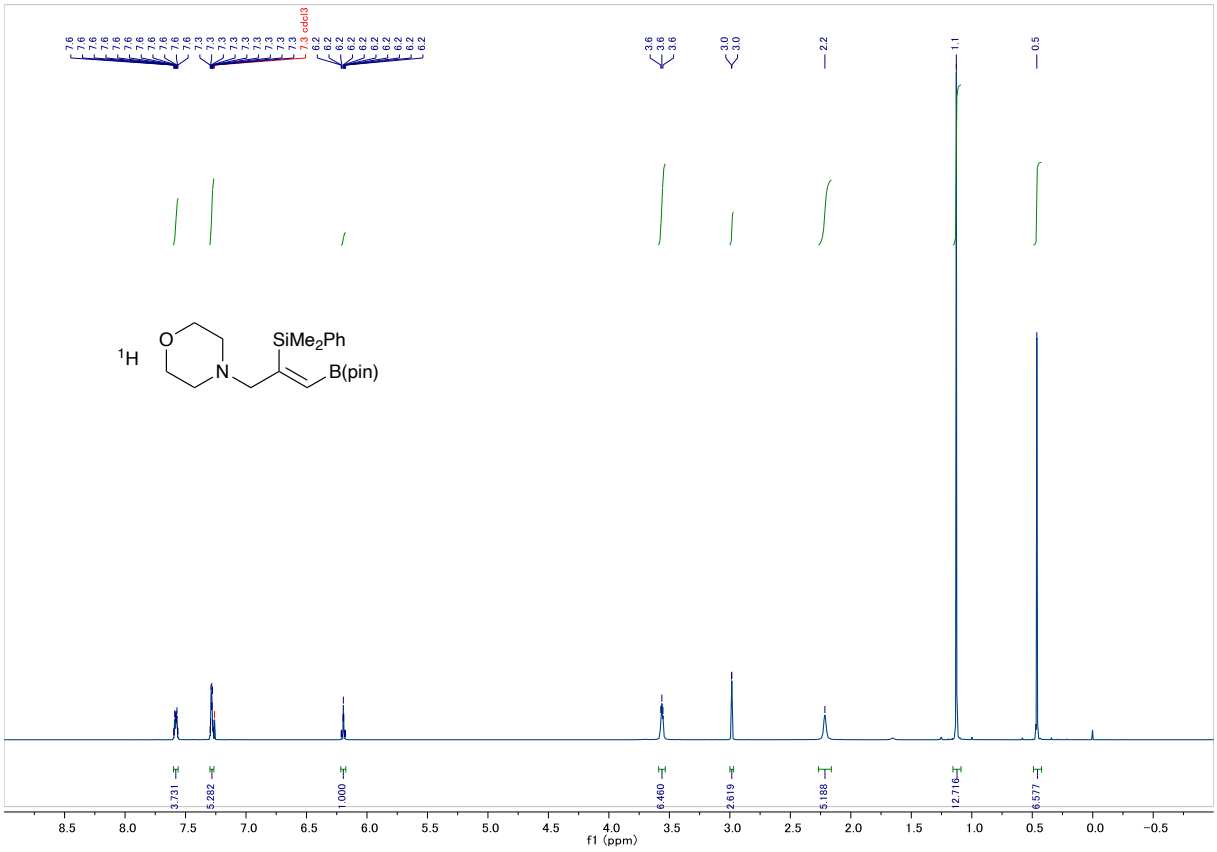

^{13}C
SiMe$_2$Ph
B(pin)
N
f1 (ppm)

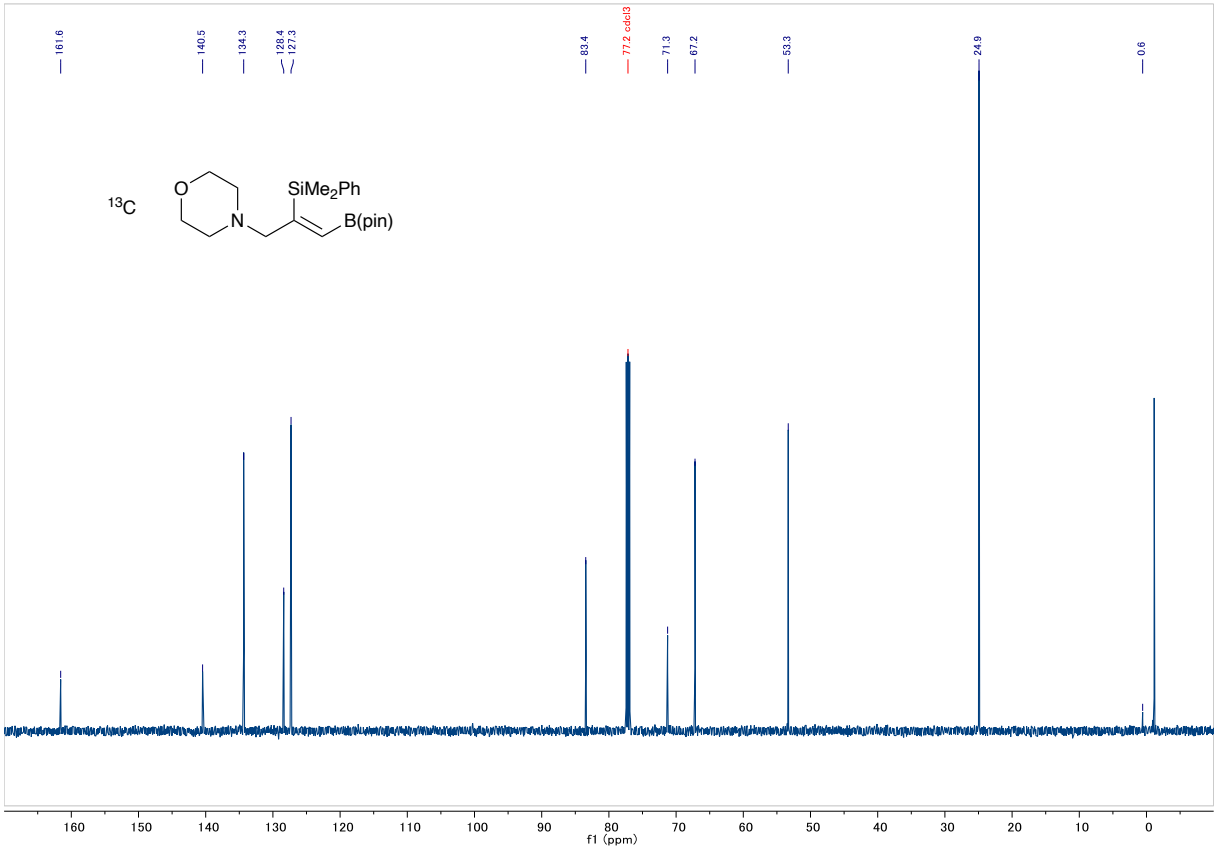

29.1
^{11}B
SiMe$_2$Ph
N
B(pin)
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

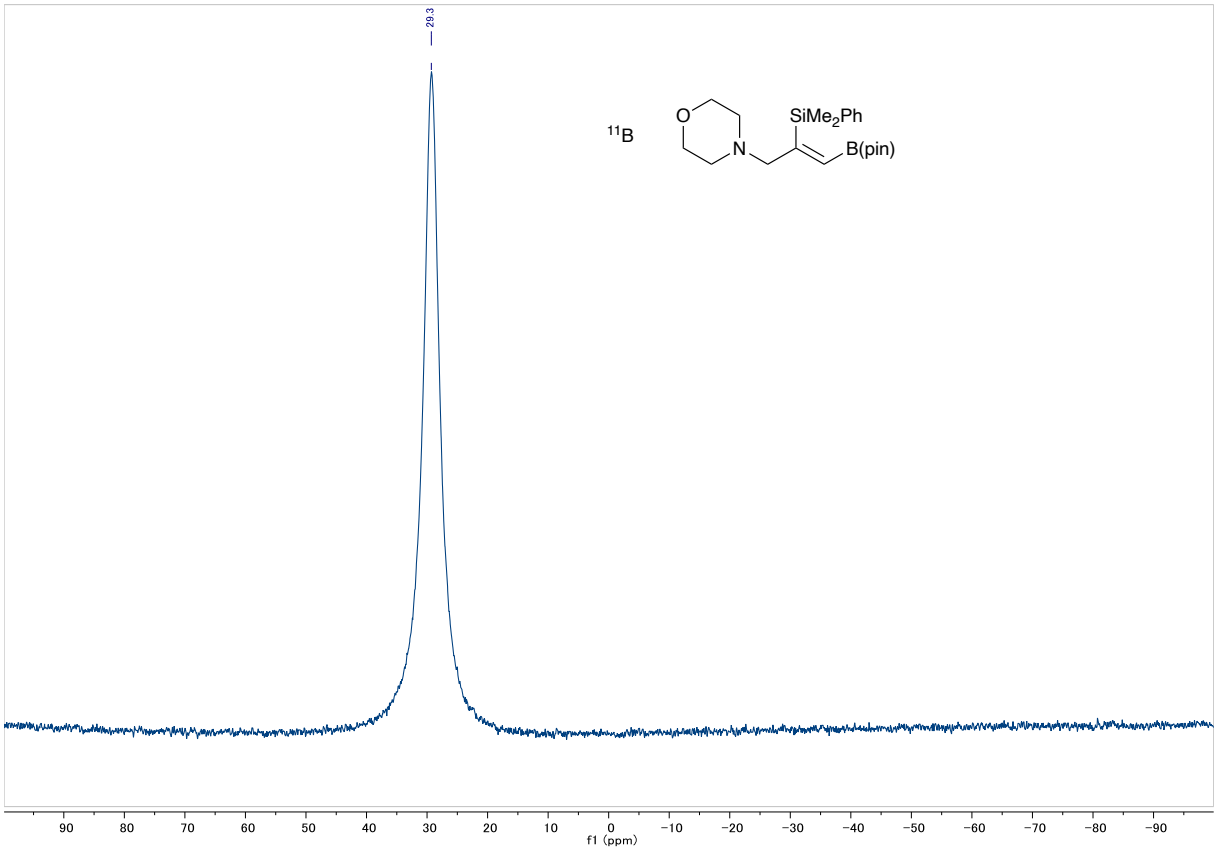

^{1}H
SiMe$_2$Ph
PhS
B(pin)
+
B(pin)
PhS
SiMe$_2$Ph
+
SiMe$_2$Ph
PhS
B(pin)
f1 (ppm)

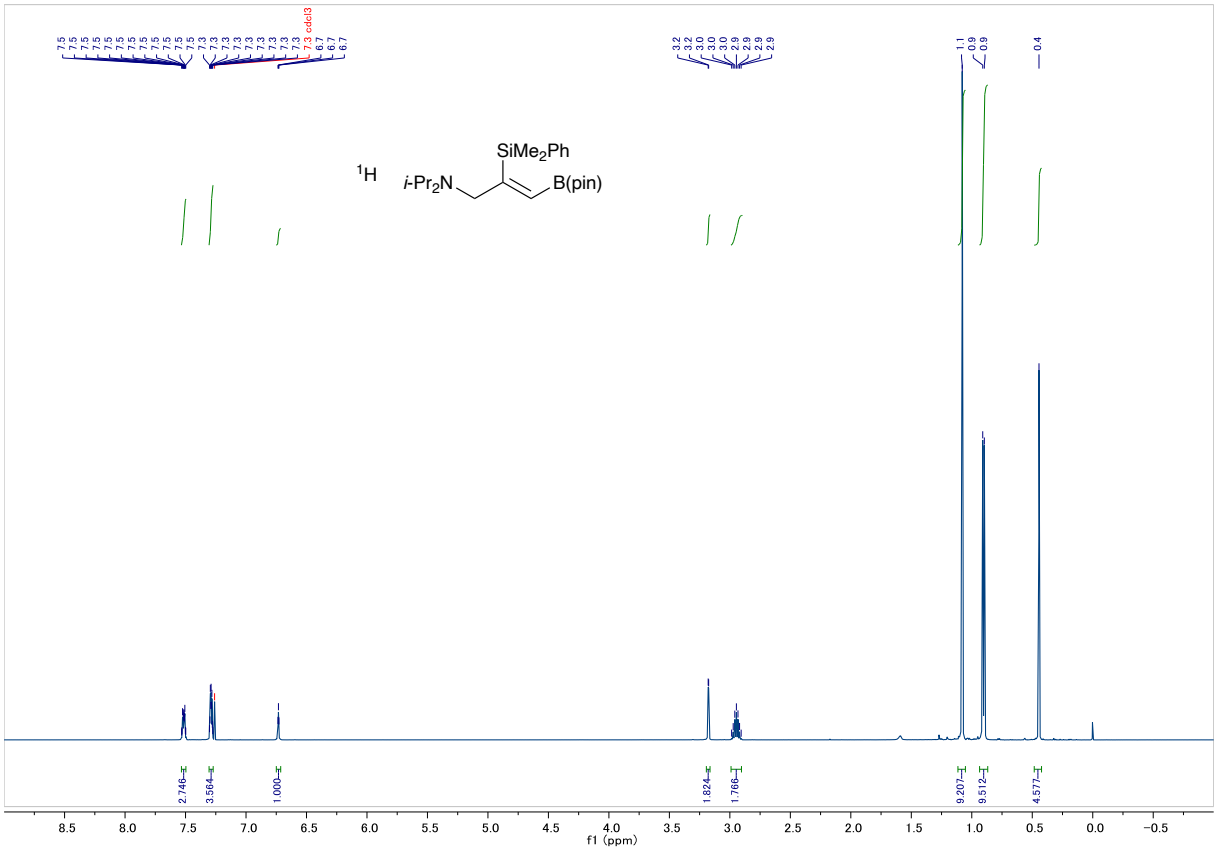

^{13}C
SiMe$_2$Ph
PhS
B(pin)
+
B(pin)
PhS
SiMe$_2$Ph
+
SiMe$_2$Ph
PhS
B(pin)
f1 (ppm)

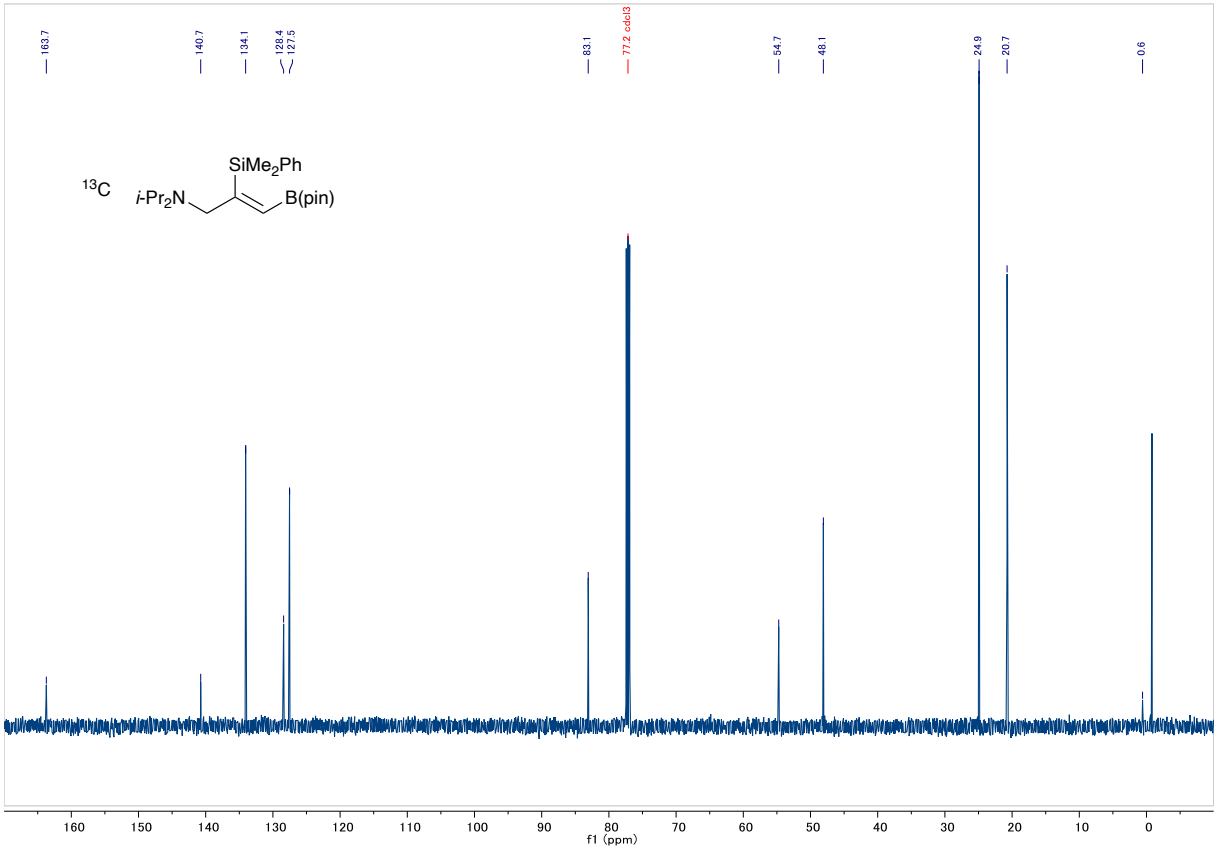

28.29
^{11}B
SiMe$_2$Ph
PhS
B(pin)
+
B(pin)
PhS
SiMe$_2$Ph
+
SiMe$_2$Ph
PhS
B(pin)
f1 (ppm)

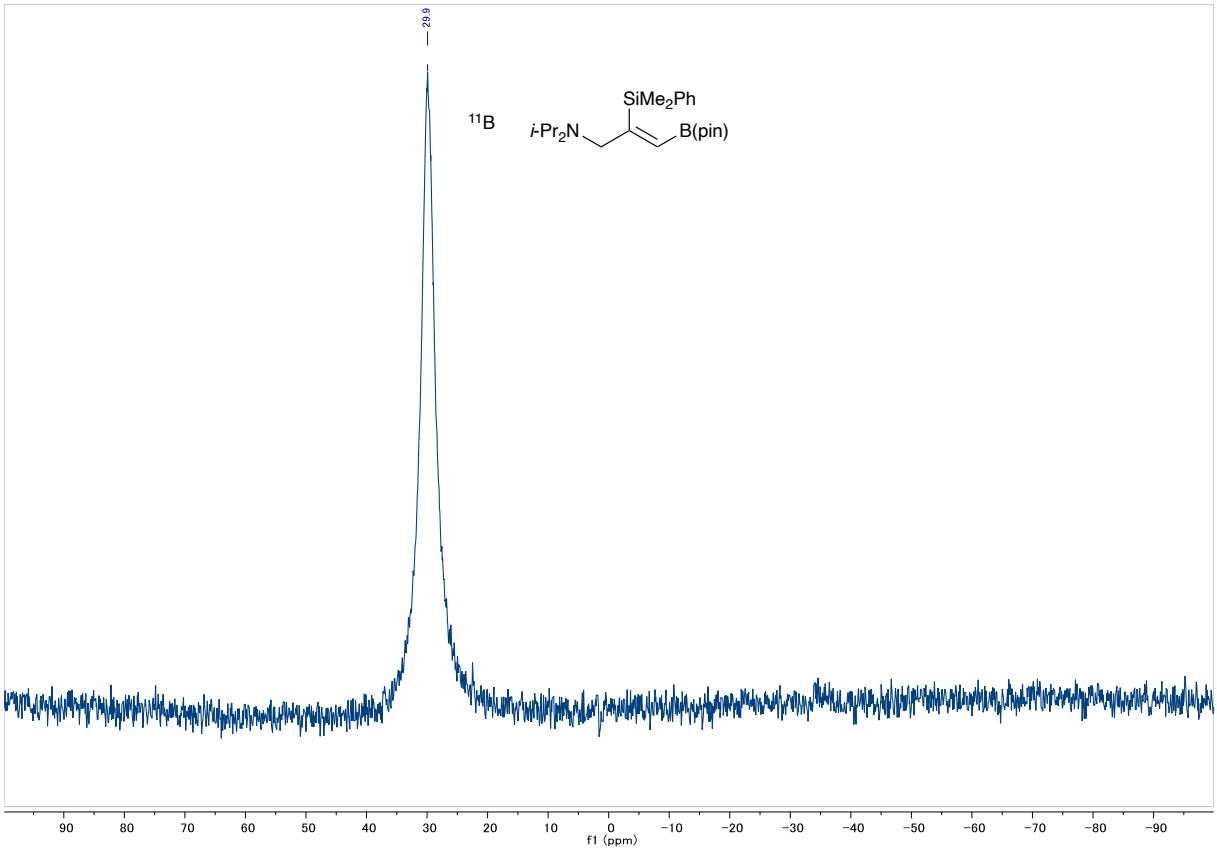

^{1}H
O
N
SiMe$_2$Ph
B(pin)
f1 (ppm)

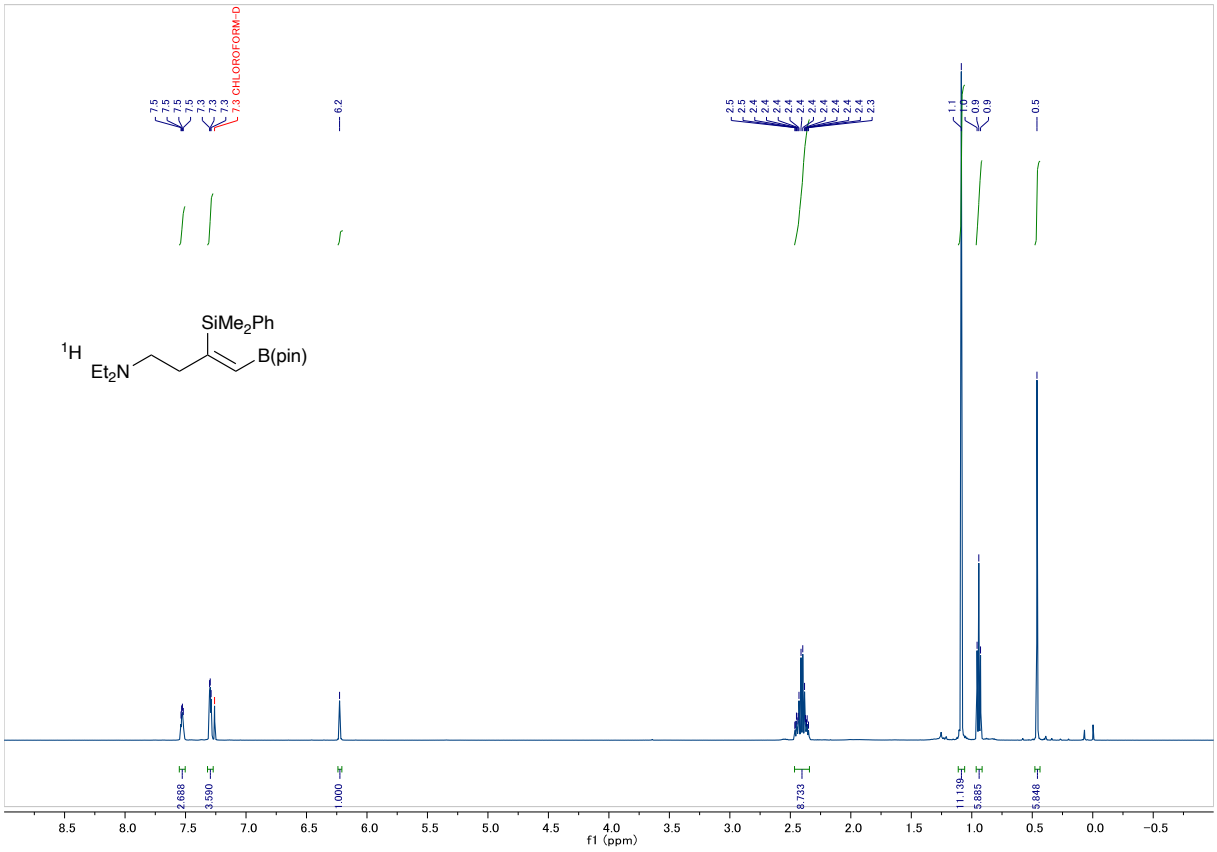

^{13}C
O
N
SiMe$_2$Ph
B(pin)
f1 (ppm)

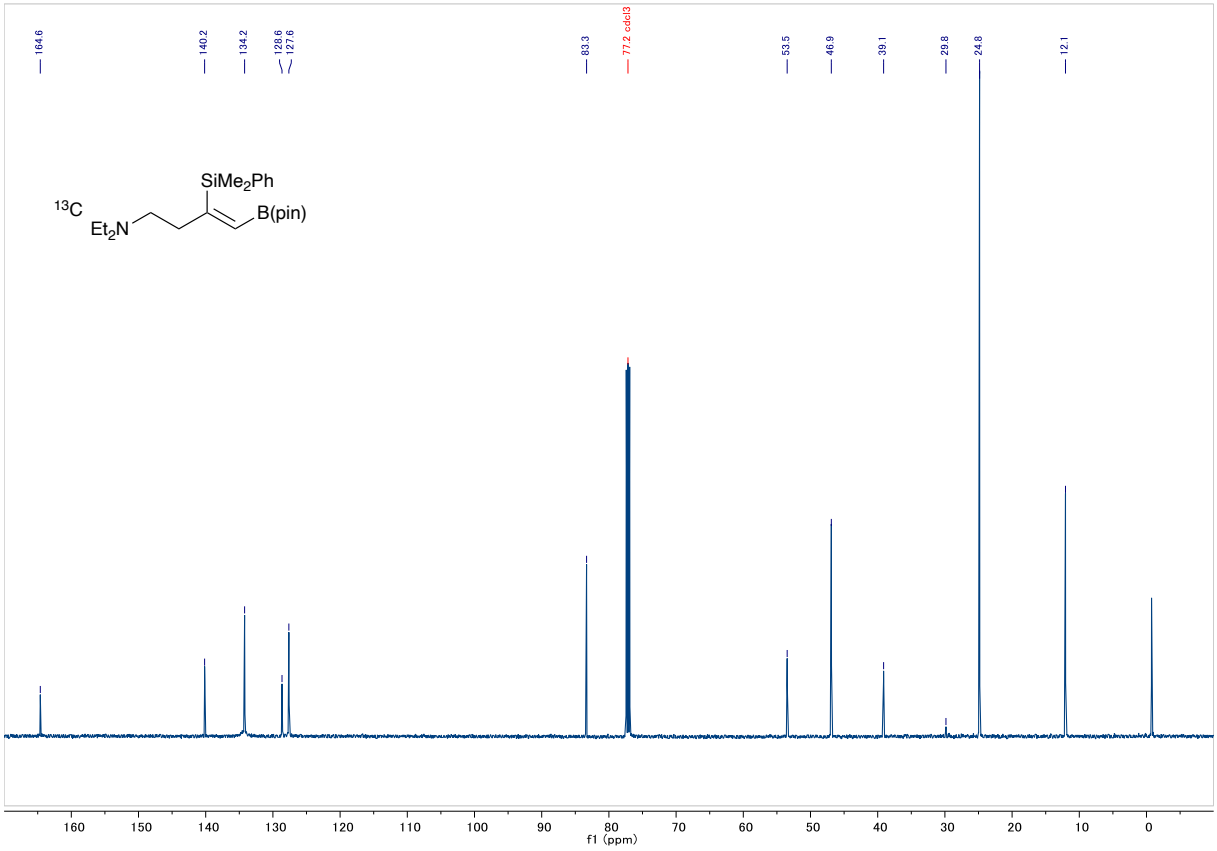

29.3
^{11}B
O
N
SiMe$_2$Ph
B(pin)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

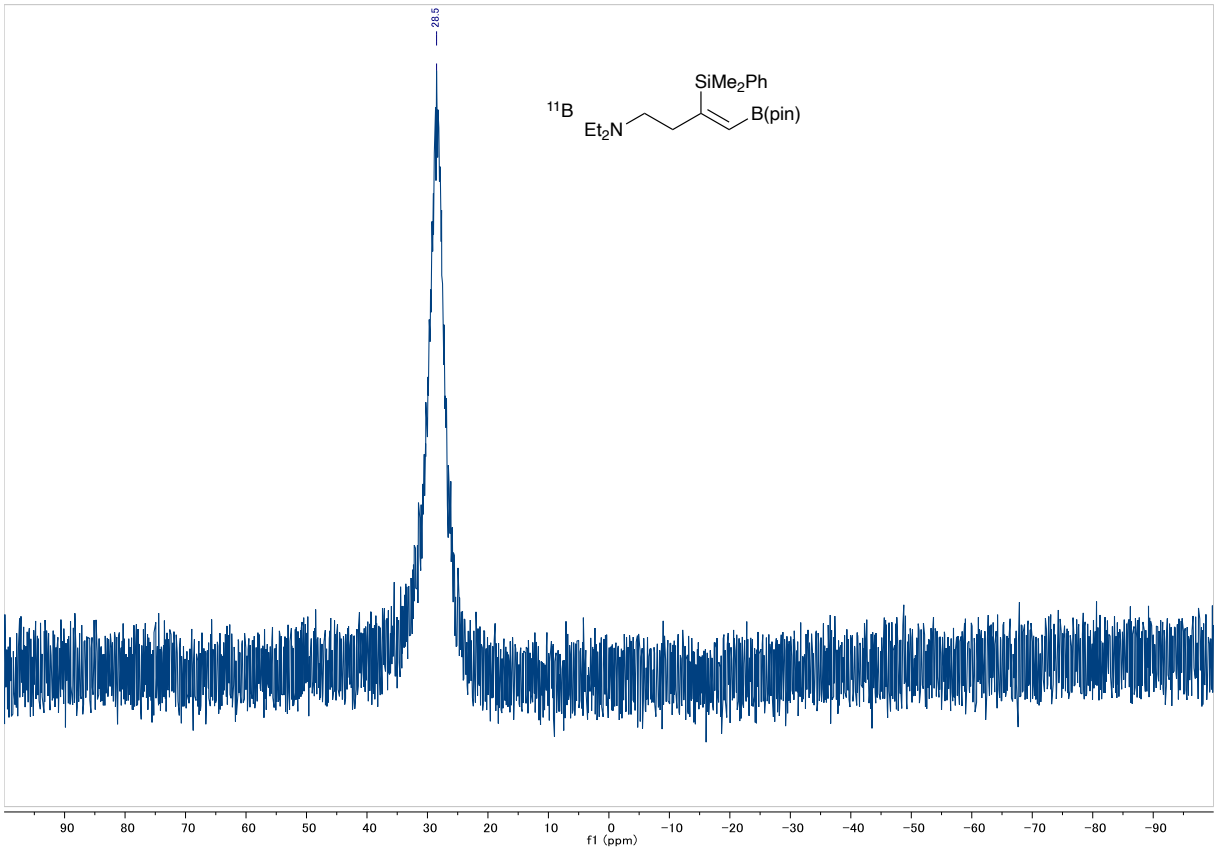

^{1}H
SiMe$_2$Ph
i-Pr$_2$N
B(pin)
f1 (ppm)

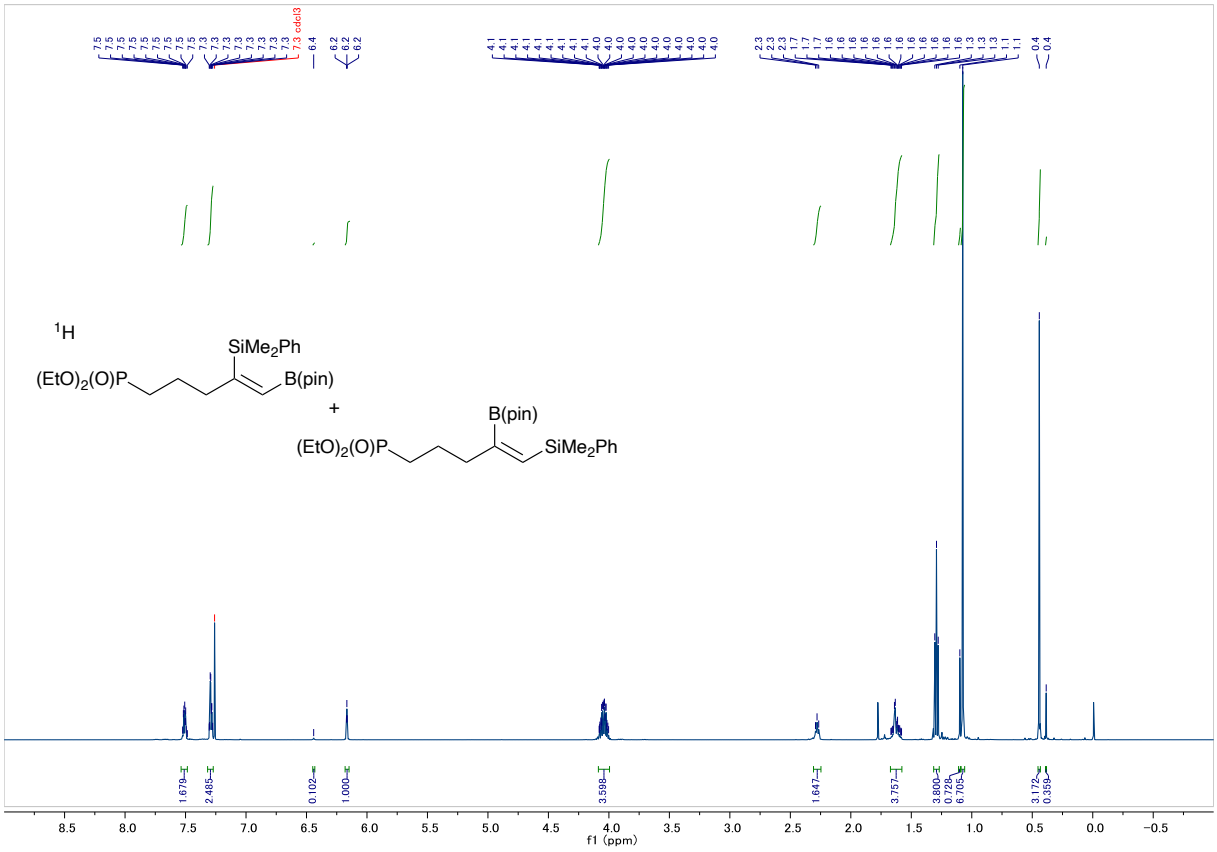

^{13}C
SiMe$_2$Ph
i-Pr$_2$N
B(pin)
f1 (ppm)

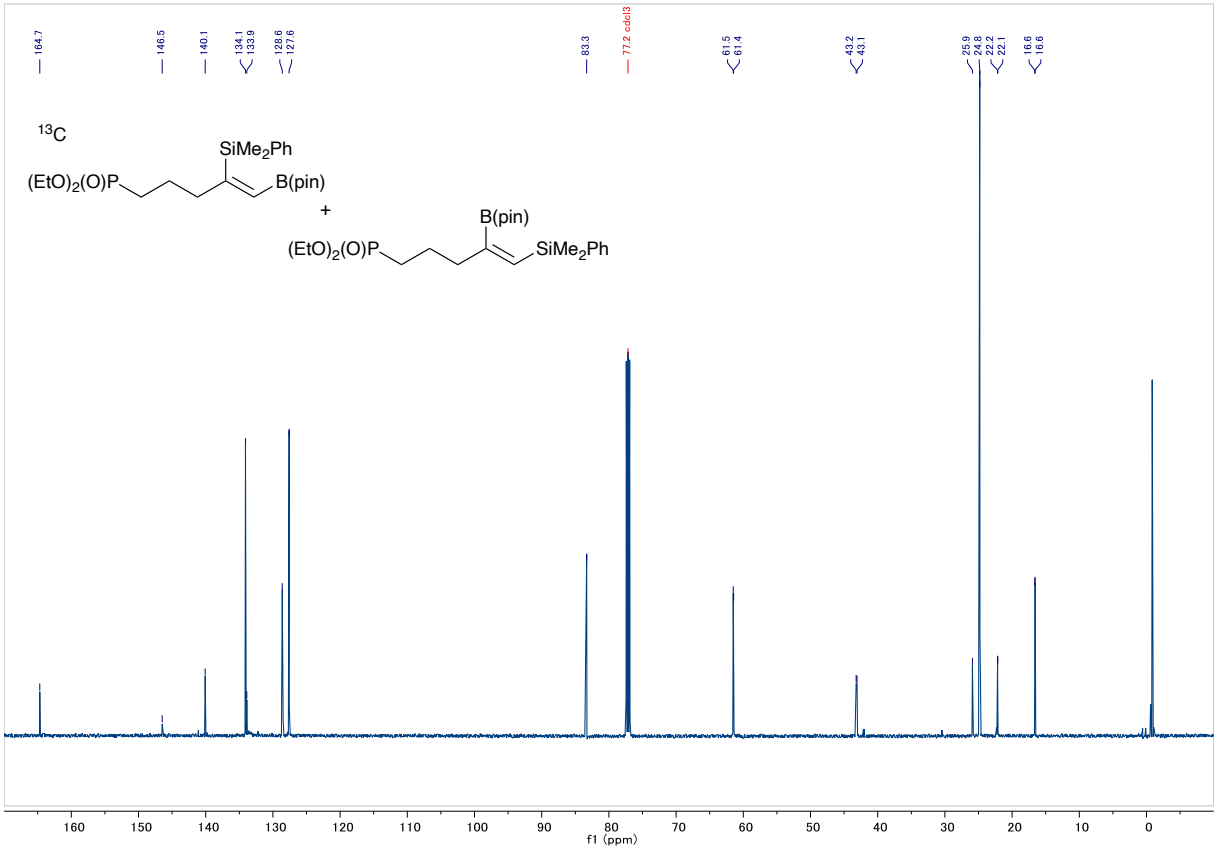

29.9
^{11}B
SiMe$_2$Ph
i-Pr$_2$N
B(pin)
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)

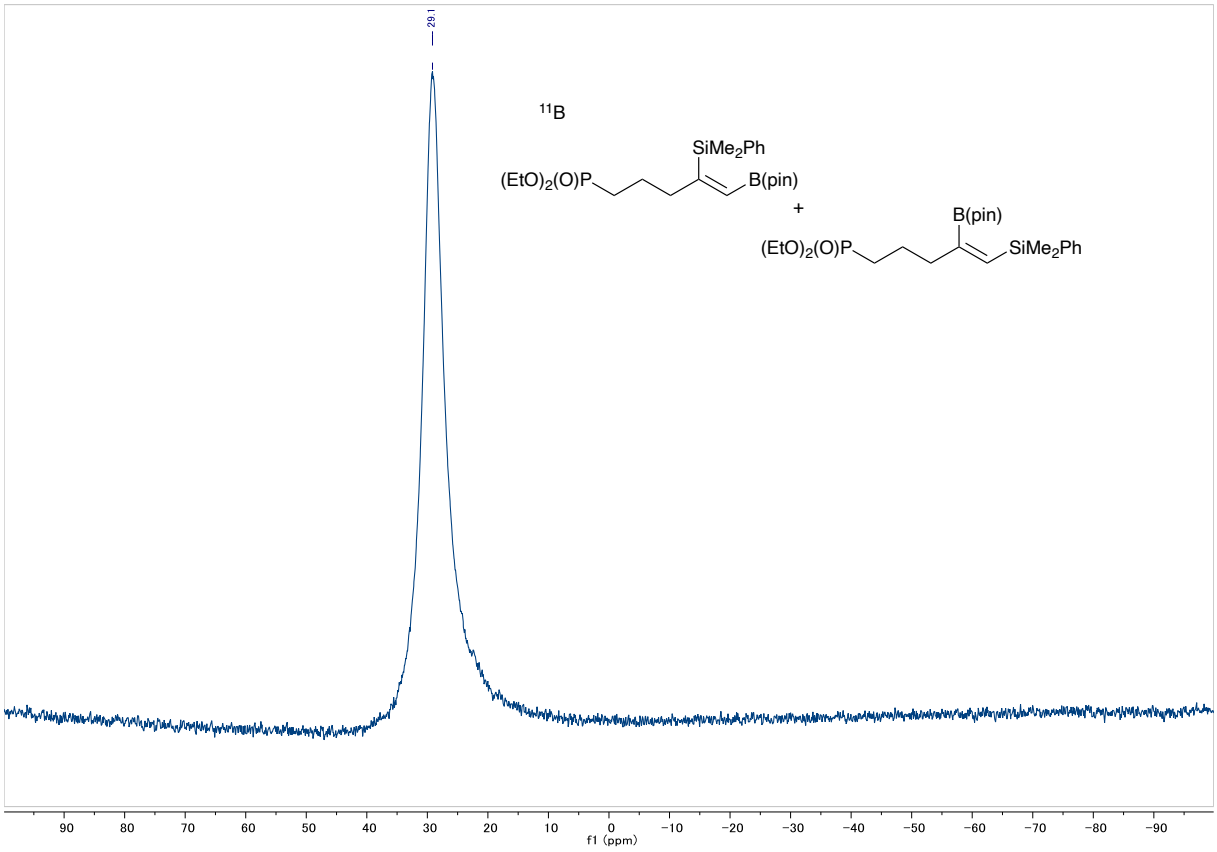

SiMe2Ph
1H
Et2N
B(pin)
f1 (ppm)

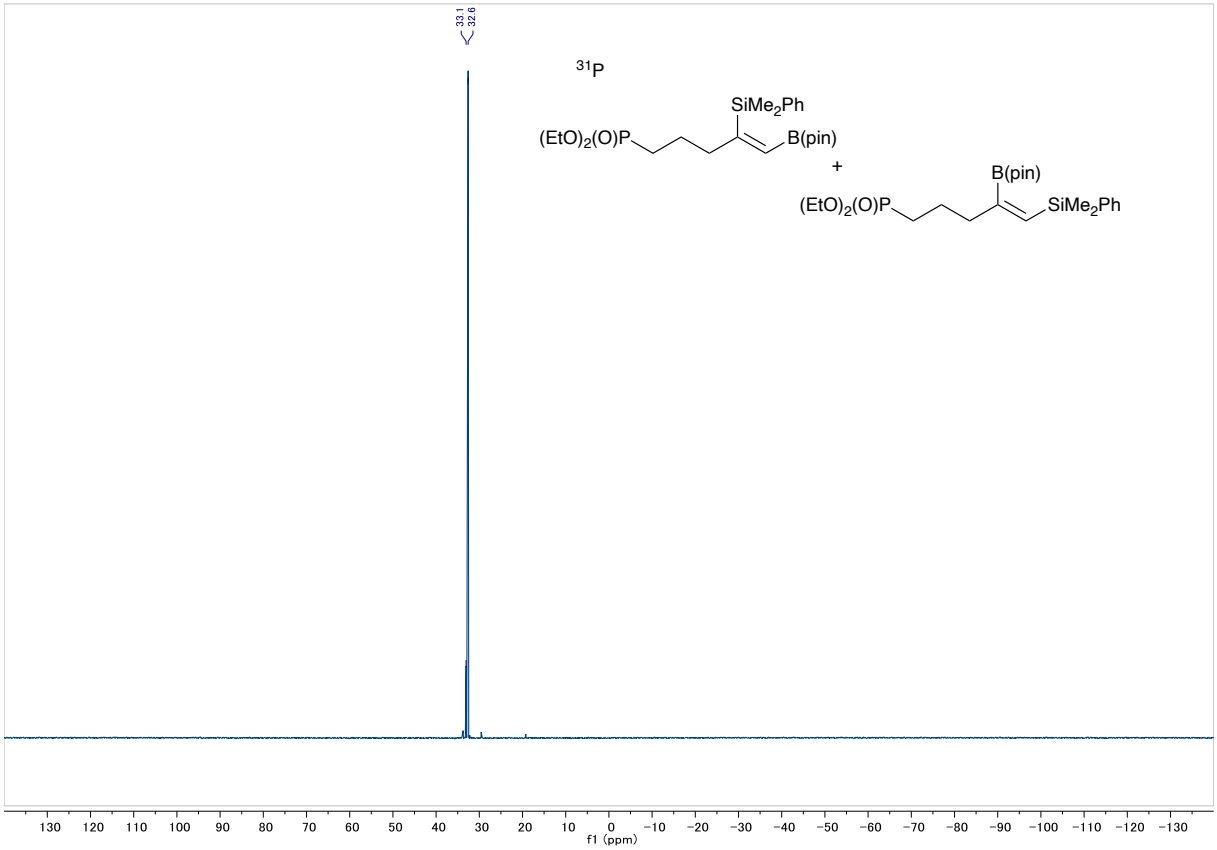

SiMe2Ph
13C
Et2N
B(pin)
f1 (ppm)

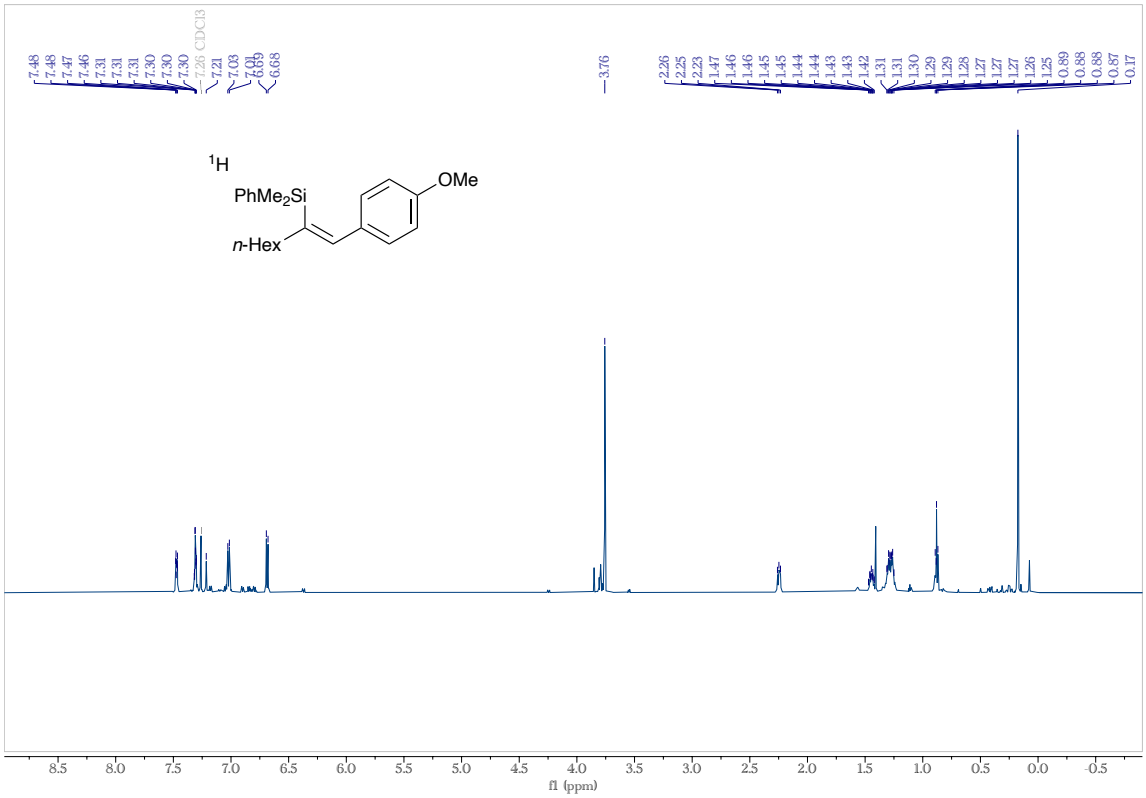

28.5
SiMe2Ph
11B
Et2N
B(pin)
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

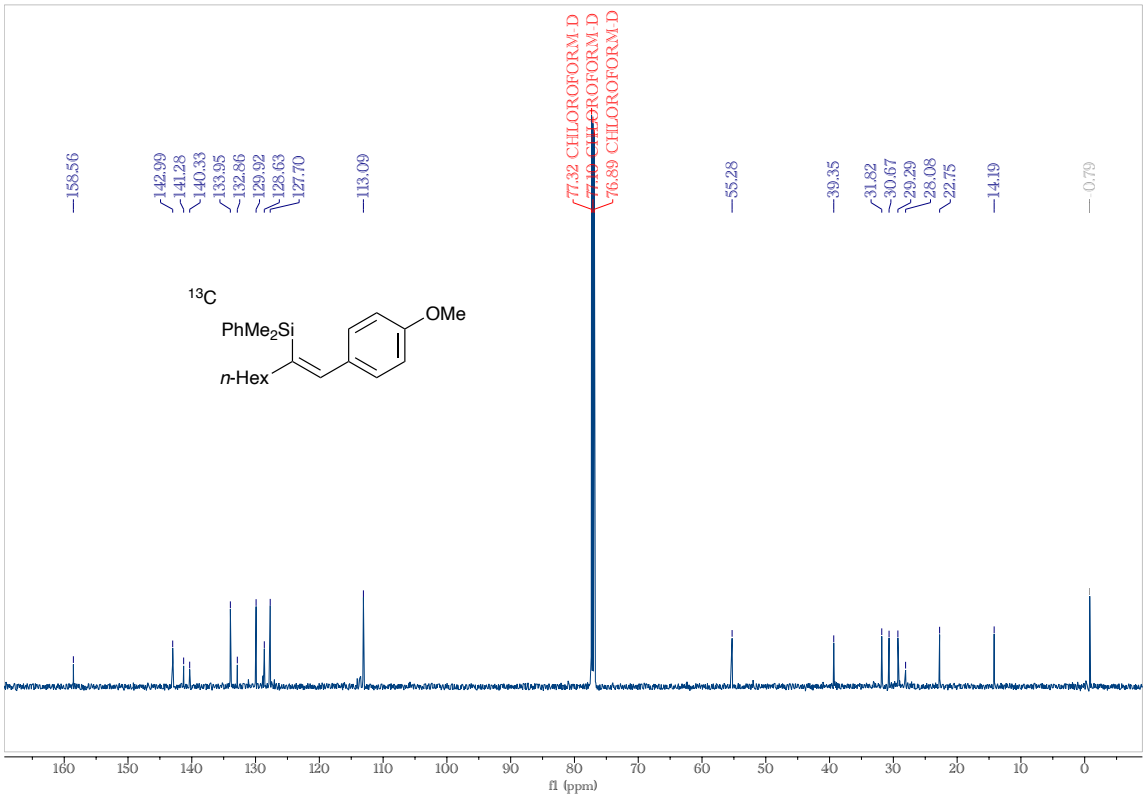

^{1}H
SiMe$_2$Ph
(EtO)$_2$(O)P
B(pin)
+
B(pin)
(EtO)$_2$(O)P
SiMe$_2$Ph
f1 (ppm)


^{13}C
SiMe$_2$Ph
(EtO)$_2$(O)P
B(pin)
+
B(pin)
(EtO)$_2$(O)P
SiMe$_2$Ph
f1 (ppm)


29.1
^{11}B
SiMe$_2$Ph
(EtO)$_2$(O)P
B(pin)
+
B(pin)
(EtO)$_2$(O)P
SiMe$_2$Ph
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90
f1 (ppm)


33.1
32.6
^{31}P
SiMe$_2$Ph
(EtO)$_2$(O)P
B(pin)
+
B(pin)
(EtO)$_2$(O)P
SiMe$_2$Ph
130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130
f1 (ppm)


7.48
7.48
7.47
7.46
7.31
7.31
7.30
7.30
7.30
7.25 CDCl3
7.21
7.03
7.01
6.69
6.68
3.76
2.26
2.25
2.23
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.42
1.31
1.31
1.30
1.29
1.29
1.28
1.27
1.27
1.27
1.26
1.25
0.89
0.88
0.88
0.87
0.17
1H
PhMe2Si
n-Hex
OMe
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)


158.56
142.99
141.28
140.33
133.95
132.86
129.92
128.63
127.70
113.09
77.32 CHLOROFORM-D
77.16 CHLOROFORM-D
76.89 CHLOROFORM-D
55.28
39.35
31.82
30.67
29.29
28.08
22.75
14.19
0.79
13C
PhMe2Si
n-Hex
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)