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Supporting Information

Bonding in Barium Boryloxides, Siloxides, Phenoxides and Silazides: A Comparison with the Lighter Alkaline Earths

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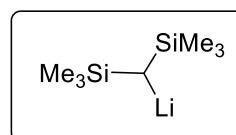
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Experimental Procedures

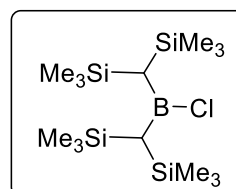
General procedures

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm). BaI_2 beads (99.999%, Aldrich) were used as purchased. THF was distilled under argon from Na/benzophenone prior to use. Petroleum ether (b.p. 40–60 °C), toluene and Et_2O were collected from MBraun SPS-800 purification alumina columns. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and degassed by several freeze–thaw cycles. $[Ae\{N(SiMe_3)_2\}_2 \cdot (thf)_2]^{[1]}$ and $[Ae\{N(SiMe_3)_2\}_2]_2^{[2]}$ ($Ae = Mg, Ca, Sr, Ba$), as well as $[SnMe_2(C_6F_5)_2]^{[3]}$ were prepared by following literature procedure. Compounds **1**, **2**, **3** and **4** were synthesised as published earlier.^[4–6] Optimised protocols based on existing procedures are reported for all borinic acids.^[7–13] All NMR spectra were recorded with Bruker AM-400 or AM-500 spectrometers; assignment of the resonances was assisted by 1D (1H , $^{13}C \{^1H\}$) and 2D (COSY, HMBC, and HMQC) NMR experiments. Reproducible elemental analysis for the new complexes could not be obtained despite repeated attempts performed on crystalline material, presumably reflecting the extreme air- and moisture-sensitivity of these complexes.

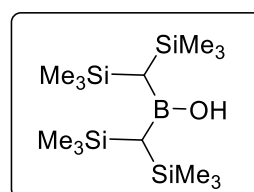
Synthesis of $[LiCH(SiMe_3)_2]$. In a three-neck round-bottom flask equipped with a condenser were added lithium powder (3.65 g, 526 mmol), sodium (0.10 g, 4.2 mmol) and Et_2O (270 mL). The mixture was refluxed under stirring for 90 min and then $ClCH(SiMe_3)_2$ (23 mL, 20.5 g, 105 mmol) was added dropwise to the lithium suspension. The mixture was reflux for 4 days and then cooled down to room temperature. The solution was filtered to eliminate insoluble materials, and all the volatiles were removed under vacuum to give the title compound as a white solid (15.3 g, 87.4%). 1H NMR (benzene- d_6 , 400.13 MHz, 298 K): $\delta = 0.16$ (s, 18H; CH_3), -2.48 (s, 1H; CH) ppm.



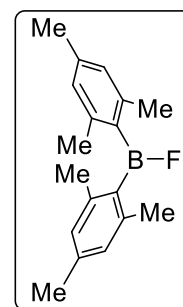
Synthesis of $ClB\{CH(SiMe_3)_2\}_2$. A solution of $[LiCH(SiMe_3)_2]$ (10.0 g, 60 mmol) in toluene (160 mL) was cooled down to -60 °C under stirring and a 1 M solution of BCl_3 in hexane (27.65 mL, 28 mmol) was added dropwise to the mixture. After complete addition, the mixture was stirred for 1 h at room temperature and then refluxed for 12 h. The mixture was then cooled down to room temperature, filtered and all the volatiles were removed under vacuum. The title compound was isolated as a white solid (8.12 g, 80%). 1H NMR (benzene- d_6 , 400.13 MHz, 298 K): $\delta = 1.17$ (s, 2H; BCH), 0.23 (s, 36H; CH_3) ppm.



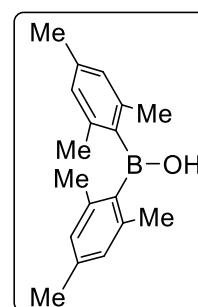
Synthesis of $HOB\{CH(SiMe_3)_2\}_2$. Water (20 mL) was added to a solution of $ClB\{CH(SiMe_3)_2\}_2$ (8.0 g, 22 mmol) in dioxane (22 mL). The mixture was stirred at room temperature for 12 h. After the stirring was stopped, the mixture separated in two layers. The upper layer was collected and transferred in another flask and dried under vacuum to give the title compound as a white solid (7.21 g, 95%). 1H NMR (benzene- d_6 , 500.13 MHz, 298 K): $\delta = 4.37$ (s, 1H; OH), 0.33 (s, 2H; BCH), 0.18 (s, 36H; CH_3) ppm. $^{13}C\{^1H\}$ NMR (benzene- d_6 , 125.77 MHz, 298 K): $\delta = 22.41$ (BCH), 2.79 (CH_3) ppm. $^{11}B \{^1H\}$ NMR (benzene- d_6 , 128.40 MHz, 298 K): $\delta = 53.76$ (br, s) ppm.



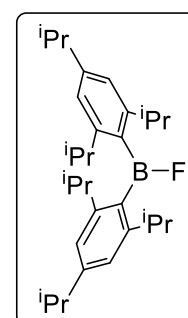
Synthesis of (mes)₂BF. In a three-neck flask equipped with a condenser were added magnesium turnings (1.0 g, 44 mmol) and dry and degassed thf (20 mL). Five drops of dibromoethane were added and the mixture was refluxed for 20 min. Then a mixture of mesityl bromide (8.0 g, 40 mmol) in thf (20 mL) was added dropwise to the activated magnesium suspension in order to maintain a small reflux. After complete addition of mesityl bromide solution the mixture was refluxed for 3 h. The mixture was cooled down to -20 °C and BF₃·OEt₂ (2.3 mL, 20 mmol) was added dropwise. After complete addition, the mixture was stirred 90 min at room temperature and refluxed for 3 h. Then the reaction was cooled down to room temperature and filtered, and the volatiles were removed in vacuo. The resulting white solid was then sublimed at 110 °C/ 0.02 Torr to give the title compound as a white crystalline solid (4.4 g, 81%). ¹H NMR (CDCl₃, 400.13 MHz, 298 K): δ = 6.83 (s, 4H; meta-CH), 2.30 (s, 12H; o-CH₃), 2.25 (s, 6H; p-CH₃) ppm. ¹¹B{¹H} NMR (CDCl₃, 128.40 MHz, 298 K): δ = 55.04 (br s) ppm.



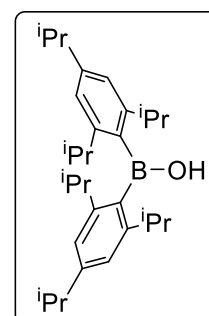
Synthesis of (2,4,6-Me₃-C₆H₂)₂BOH ≡ (mes)₂BOH. Water (6 mL) was added to a solution of (mes)₂BF (1.0 g, 4 mmol) in Et₂O (6 mL). The mixture was stirred at room temperature for 6 h. After the stirring was stopped, the mixture separated in two layers. The upper layer was collected and the volatiles were pumped off. The resulting white solid obtained was extracted with boiling petroleum ether (4x15 mL), the combined fractions were concentrated to half and the solution was stored at -43 °C to afford a large crop of colourless crystals (0.92 g, 93%). ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ = 6.74 (s, 4H; meta-CH), 5.26 (s, 1H; OH), 2.27 (s, 12H; o-CH₃), 2.15 (s, 6H; p-CH₃) ppm. ¹³C{¹H} NMR (benzene-d₆, 125.77 MHz, 298 K): δ = 141.25 (o-CCH₃), 138.77 (p-CCH₃), 137.68 (CBOH), 128.81 (m-CH), 22.66 (CH₃), 21.29 (CH₃) ppm. ¹¹B{¹H} NMR (benzene-d₆, 128.40 MHz, 298 K): δ = 50.82 (br s) ppm.



Synthesis of (2,4,6-ⁱPr₃-C₆H₂)₂BF. In a three-neck flask equipped with a condenser were added magnesium turnings (1.13 g, 47 mmol) and thf (25 mL). Five drops of dibromoethane were added and the mixture was refluxed for 20 min. Then a mixture of 2,4,6-triisopropylphenyl bromide (12.0 g, 42 mmol) in thf (25 mL) was added dropwise to the activated magnesium suspension in order to maintain a small reflux. After complete addition, the reaction mixture was refluxed for 3 h. It was then cooled down to -78 °C and BF₃·OEt₂ (2.16 mL, 19 mmol) was added dropwise. After full addition, the mixture was stirred 30 min at room temperature and refluxed for 3 h. Then the reaction was cooled down to room temperature and filtered to eliminate solid impurities. The solution was taken to dryness, and the resulting white solid was then sublimed at 150 °C/ 0.02 Torr to give the title compound as a white crystalline solid (7.10 g, 85%). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ = 7.15 (s, 4H; m-CH), 3.33 (hept, 4H; o-CH(CH₃)₂), 2.78 (hept, 2H; p-CH(CH₃)₂), 1.26-1.24 (d, 24H; o-CH(CH₃)₂), 1.21-1.19 (d, 12H; p-CH(CH₃)₂) ppm.

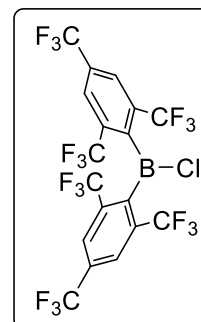


Synthesis of (2,4,6-ⁱPr₃-C₆H₂)₂BOH ≡ (Tripp)₂BOH. Water (9 mL) was added to a solution of (2,4,6-ⁱPr₃-C₆H₂)₂BF (2.5 g, 6 mmol) in Et₂O (9 mL). The mixture was stirred at room temperature for 6 h. After the stirring was stopped, the mixture separated in two layers. The upper layer was collected, and the volatiles were pumped off. The resulting white solid was dissolved in a small quantity of petroleum ether and stored at -43 °C to afford a large crop of colourless crystals (1.9 g). The mother liquor was filtered off and concentrated, and another batch of crystals (0.45 g) was grown upon its storage in the freezer. Total yield 2.35 g, 94%. ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ = 7.14 (s, 4H; m-CH), 5.58 (s, 1H; OH), 3.33 (hept, 4H; ³J_{1H-1H} = 6.8 Hz; o-CH(CH₃)₂), 2.81 (hept, 2H; ³J_{1H-1H} = 6.9 Hz; p-CH(CH₃)₂), 1.24-1.22 (d, 12H, ³J_{1H-1H} = 6.9 Hz; p-CH(CH₃)₂), 1.23-1.22 (d, 24H, ³J_{1H-1H} = 6.8 Hz; o-CH(CH₃)₂) ppm. ¹³C{¹H} NMR (benzene-d₆, 125.77 MHz, 298 K): δ = 152.35 (o-

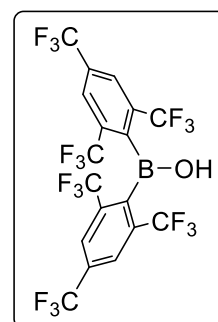


C(CH₃)₂), 150.27 (*p*-C(CH₃)₂), 137.77 (CBOH), 121.16 (*m*-CH), 34.83 (CH(CH₃)₂), 33.85 (CH(CH₃)₂), 25.08 (CH(CH₃)₂), 24.22 (CH(CH₃)₂) ppm. ¹¹B{¹H} NMR (benzene-d₆, 128.40 MHz, 298 K): δ = 52.21 (br s) ppm.

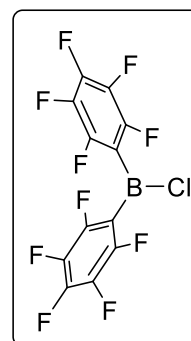
Synthesis of (2,4,6-(CF₃)₃-C₆H₂)₂BCl. ⁿBuLi (7.7 ml, 1.6 M, 12 mmol) was added dropwise to a solution of 1,3,5-tris(trifluoromethyl)benzene (3.5 g, 12 mmol) in Et₂O (35 mL) at -78 °C, and the mixture was stirred for 3 h at this temperature. After 3 h, a hexane solution of BCl₃ (6.2 ml, 1.0 M, 6 mmol) was added dropwise at -78 °C and stirred for 1 h. Then the mixture was stirred for another 3 h at room temperature to afford a colourless solution with a white precipitate. The solution was separated from the white precipitate which was washed with Et₂O (15 mL). The solutions were combined and concentrated to 10 ml. Storage at -43 °C afforded a large crop of colourless crystals (1.56 g). The mother liquor was then concentrated and stored at -43 °C to obtain a second batch of crystals. Total yield 2.28 g, 66%. ¹H NMR (CDCl₃, 400.13 MHz, 298 K): δ = 8.22 (s, 4H; *m*-CH) ppm. ¹⁹F NMR (benzene-d₆, 373.47 MHz, 298 K): δ = -56.99 (s, 12F; *o*-C(CF₃)₂), -63.69 (s, 6F; *p*-C(CF₃)₂) ppm. ¹¹B{¹H} NMR (benzene-d₆, 128.40 MHz, 298 K): δ = 48.12 (br s) ppm.



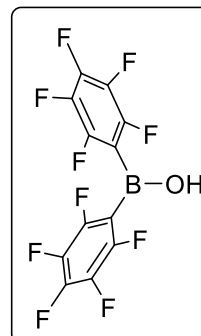
Synthesis of (2,4,6-(CF₃)₃-C₆H₂)₂BOH ≡ (Fmes)₂BOH. Water (8 mL) was added to a solution of (2,4,6-(CF₃)₃-C₆H₂)₂BCl (1.56 g, 3 mmol) in Et₂O (8 mL). The mixture was stirred at room temperature for 6 h. After the stirring was stopped, the mixture separated in two layers. The upper layer collected and the solution was then taken to dryness to give the title compound as a white solid (1.47 g, 97%). ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ = 7.87 (s, 4H; *m*-CH), 6.26 (s, 1H; *OH*) ppm. ¹⁹F NMR (benzene-d₆, 470.52 MHz, 298 K): δ = -56.05 (s, 12F; *o*-C(CF₃)₂), -63.55 (s, 6F; *p*-C(CF₃)₂) ppm. ¹³C{¹H} NMR (benzene-d₆, 125.77 MHz, 298 K): δ = 138.13 (*m*-CH), 137.02 (q, ²J_{19F-13C} = 34.2 Hz, *p*-CCF₃), 133.43 (q, ²J_{19F-13C} = 34.5 Hz, *o*-CCF₃), 126.71 (CBOH), 123.41 (q, ¹J_{19F-13C} = 275.9 Hz, CF₃), 122.80 (q, ¹J_{19F-13C} = 273.2 Hz, CF₃) ppm. ¹¹B{¹H} NMR (benzene-d₆, 128.40 MHz, 298 K): δ = 43.48 (br s) ppm.



Synthesis of (C₆F₅)₂BCl. A suspension of [SnMe₂(C₆F₅)₂] (2.0 g, 4.1 mmol) in toluene (30 mL) was cooled down at -78 °C under stirring, and a 1.0 M solution of BCl₃ in hexane (4.1 ml, 4.1 mmol) was added dropwise. After complete addition, the reaction mixture was stirred for 3 h at room temperature and then refluxed for 24 h. The mixture was then cooled down to room temperature. The solution was isolated by filtration and then taken to dryness. The unreacted Me₂SnCl₂ was removed by sublimation under atmospheric pressure at 50 °C. The title compound was then isolated as a white solid upon sublimation at 65 °C under vacuum (1.27 g, 81%). ¹⁹F NMR (benzene-d₆, 400.13 MHz, 298 K): δ = -129.6 (dtt, *J* = 4.9 Hz, *J* = 6.6 Hz, and *J* = 20.9 Hz, *o*-F), -143.9 (tt, *J* = 6.6 Hz and *J* = 21.2 Hz, *p*-F), -160.4 (m, *m*-F) ppm.

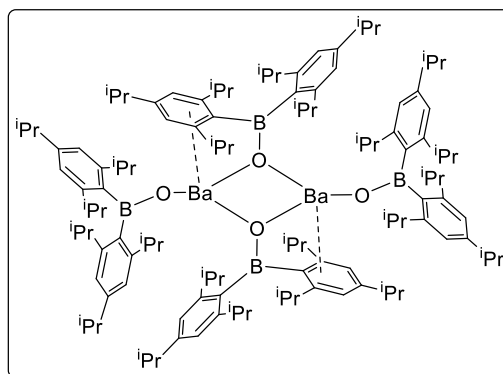


Synthesis of (C₆F₅)₂BOH. Water (10 mL) was added to a solution of (C₆F₅)₂BCl (1.2 g, 3.2 mmol) in Et₂O (10 ml). The mixture was stirred at room temperature for 4 h. After the stirring was stopped, the mixture separated in two layers. The upper layer was collected dried under vacuum to give the title compound as a white solid (1.05 g, 93%). ¹H NMR (benzene-d₆, 400.16 MHz, 298 K): δ = 6.21 (br, 1H; *OH*) ppm. ¹⁹F NMR (benzene-d₆, 376.147 MHz, 298 K): δ = -133.04 (m, *o*-F), -147.94 (tt, *J* = 6.6 Hz and *J* = 21.2 Hz, *p*-F), -161.13 (m, *m*-F) ppm. ¹¹B{¹H} NMR (benzene-d₆, 128.40 MHz, 298 K): δ = 40.48 (br s) ppm.

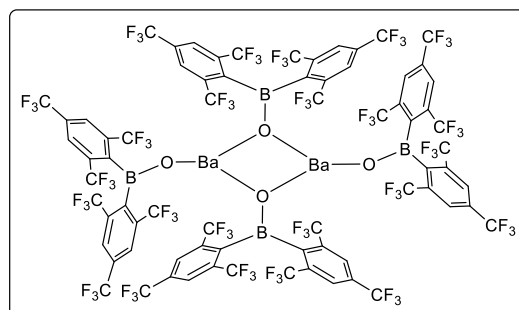


Synthesis of $[\text{Ba}\{\mu_2\text{-OB}(\text{Tripp})_2\}\{\text{OB}(\text{Tripp})_2\}]_2$ (5**₂).**

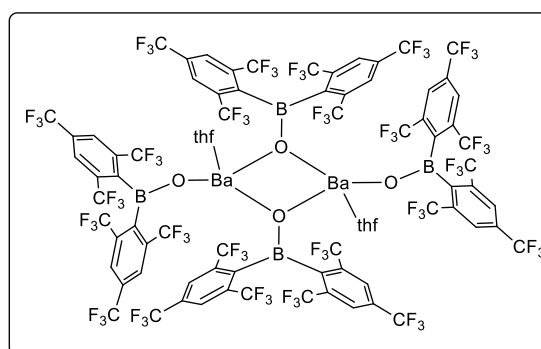
To a solution of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (250 mg, 0.41 mmol) in toluene (7 mL) was added dropwise a solution of $(\text{Tripp})_2\text{BOH}$ (358 mg, 0.82 mmol) in toluene (7 mL) at room temperature. The mixture was stirred for 2 h, and the solvent was then concentrated until the formation of a precipitate was observed. The solution was then isolated by filtration and stored at -43°C . Compound **5**₂ was obtained as colourless crystals (310 mg, 74%). Colourless monocrystals suitable for XRD were grown in toluene at -43°C . ^1H NMR (thf-d_8 , 500.13 MHz, 298 K): δ = 6.78 (s, 16H; *m*-CH), 3.49 (hept, 16H, $^3J_{\text{H-H}} = 6.8$ Hz; *o*- $\text{CH}(\text{CH}_3)_2$), 2.74 (hept, 8H, $^3J_{\text{H-H}} = 6.9$ Hz; *p*- $\text{CH}(\text{CH}_3)_2$), 1.17 (d, 48H, $^3J_{\text{H-H}} = 6.9$ Hz; *p*- $\text{CH}(\text{CH}_3)_2$), 0.99 (d, 96H, $^3J_{\text{H-H}} = 6.8$ Hz; *o*- $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf-d_8 , 125.77 MHz, 298 K): δ = 150.90 (*o*- $\text{C}(\text{CH}(\text{CH}_3)_2)$), 147.68 (CBO), 146.23 (*p*- $\text{C}(\text{CH}(\text{CH}_3)_2)$), 119.94 (*m*-CH), 35.08 (*p*- $\text{CH}(\text{CH}_3)_2$), 33.14 (*o*- $\text{CH}(\text{CH}_3)_2$), 25.07 (*p*- $\text{CH}(\text{CH}_3)_2$), 24.51 (*o*- $\text{CH}(\text{CH}_3)_2$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (thf-d_8 , 128.40 MHz, 298 K): δ = 47.1 (br s) ppm.

**Synthesis of $[\text{Ba}\{\mu_2\text{-OB}(\text{Fmes})_2\}\{\text{OB}(\text{Fmes})_2\}]_2$ (**6**₂).**

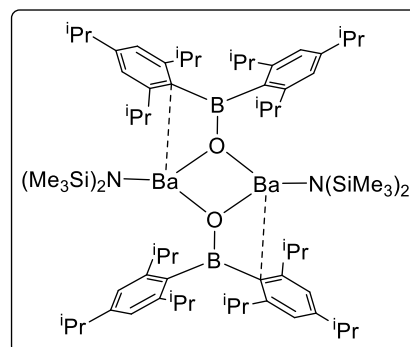
A solution of $(\text{Fmes})_2\text{BOH}$ (167 mg, 0.28 mmol) in toluene (3 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (65 mg, 0.07 mmol) in toluene (3 mL). The formation of a white precipitate was rapidly observed. The mixture was stirred at room temperature for 2 h. The supernatant was removed by filtration. The resulting white solid that was isolated was dried under vacuum to afford **6**₂ as a white solid (169 mg, 91%). Colourless monocrystals suitable for XRD were obtained by diffusion of toluene in a solution of **6**₂ in difluorobenzene. ^1H NMR (thf-d_8 , 500.13 MHz, 298 K): δ = 8.13 (s, 16H; *m*-CH) ppm. ^{19}F NMR (thf-d_8 , 470.52 MHz, 298 K): δ = -56.58 (s, 48F; *o*- $\text{C}(\text{CF}_3)_2$), -63.98 (s, 24F; *p*- $\text{C}(\text{CF}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf-d_8 , 125.77 MHz, 298 K): δ = 150.73 (*m*-CH), 136.25 (q, $^2J_{19\text{F}-13\text{C}} = 33.8$ Hz, *p*- CCF_3), 130.38 (q, $^2J_{19\text{F}-13\text{C}} = 33.8$ Hz, *o*- CCF_3), 126.67 (CBO), 125.19 (q, $^1J_{19\text{F}-13\text{C}} = 275.4$ Hz, CF_3), 124.29 (q, $^1J_{19\text{F}-13\text{C}} = 272.0$ Hz, CF_3) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (thf-d_8 , 128.40 MHz, 298 K): δ = 34.1 (br s) ppm.

**Synthesis of $[\text{Ba}\{\mu_2\text{-OB}(\text{fmes})_2\}\{\text{OB}(\text{fmes})_2\}\cdot\text{thf}]_2$ (**6**₂.(thf)₂).**

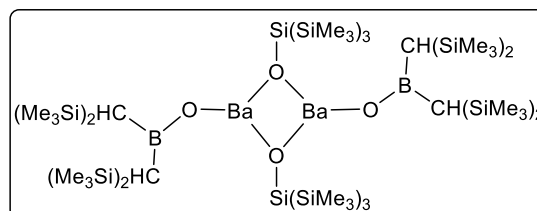
A solution of $(\text{Fmes})_2\text{BOH}$ (167 mg, 0.28 mmol) in toluene (3 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (85 mg, 0.14 mmol) in toluene (3 mL). The formation of a white precipitate was rapidly observed. The mixture was stirred at room temperature for 2 h. The solid was isolated by filtration and dried in vacuo to constant weight, affording the title compound as a white solid (174 mg, 89%). Colourless monocrystals suitable for XRD were obtained by storage of a concentrated solution of **6**₂.(thf)₂ in difluorobenzene at -43°C . ^1H NMR (thf-d_8 , 500.13 MHz, 298 K): δ = 8.13 (s, 16H; *m*-CH), 3.61 (m, 8H; $\text{CH}_2\text{CH}_2\text{O}$), 1.77 (m, 8H; $\text{CH}_2\text{CH}_2\text{O}$) ppm. ^{19}F NMR (thf-d_8 , 470.52 MHz, 298 K): δ = -56.57 (s, 48F; *o*- $\text{C}(\text{CF}_3)_2$), -63.98 (s, 24F; *p*- $\text{C}(\text{CF}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf-d_8 , 125.77 MHz, 298 K): δ = 150.73 (*m*-CH), 136.25 (q, $^2J_{19\text{F}-13\text{C}} = 33.8$, *p*- CCF_3), 130.38 (q, $^2J_{19\text{F}-13\text{C}} = 33.8$, *o*- CCF_3), 126.67 (CBOH), 125.19 (q, $^1J_{19\text{F}-13\text{C}} = 275.4$, CF_3), 124.29 (q, $^1J_{19\text{F}-13\text{C}} = 272.0$, CF_3), 68.21 ($\text{CH}_2\text{CH}_2\text{O}$), 26.37 ($\text{CH}_2\text{CH}_2\text{O}$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (thf-d_8 , 128.40 MHz, 298 K): δ = 34.1 (br, s) ppm.



Synthesis of $[\text{Ba}\{\mu_2\text{-OB(Tripp)}_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (7₂**).** A solution of $(\text{Tripp})_2\text{BOH}$ (179 mg, 0.82 mmol) in toluene (7 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$ (250 mg, 0.41 mmol) in toluene (7 mL). The mixture was stirred at room temperature for 2 h and the solvent was concentrated until a solid precipitated. The solution was isolated by filtration and stored at -43°C . Compound **7₂** crystallised as colourless crystals from this solution (201 mg, 67%). Colourless monocrystals suitable for XRD were grown in toluene at -43°C . ^1H NMR (benzene- d_6 , 500.13 MHz, 298 K): δ 7.14 (s, 8H; *m*-CH), 3.43 (br, 8H; *o*-CH(CH₃)₂), 2.83 (hept, 4H, $^3J_{\text{H-H}} = 6.9$ Hz; *p*-CH(CH₃)₂), 1.30 (br m, 48H; CH(CH₃)₂), 1.25 (d, 24H, $^3J_{\text{H-H}} = 6.9$ Hz; CH(CH₃)₂) 0.07 (s, 36H; SiCH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.77 MHz, 298 K): δ = 151.22 (CBO), 150.29 (*o*-C(CH(CH₃)₂)), 142.38 (*p*-C(CH(CH₃)₂)), 122.55 (*m*-CH), 34.41 (*p*-CH(CH₃)₂), 33.12 (*o*-CH(CH₃)₂), 25.50 (*p*-CH(CH₃)₂), 24.10 (*o*-CH(CH₃)₂), 5.78 (SiCH₃) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (benzene- d_6 , 128.40 MHz, 298 K): δ = 47.5 (br s) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 79.49 MHz, 298 K): δ = -18.57 (s) ppm.

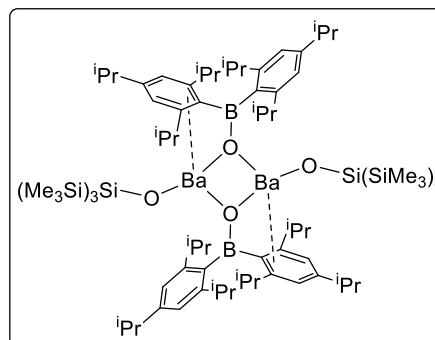


Synthesis of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{OB}(\text{CH}(\text{SiMe}_3)_2)_2)]_2$ (8₂**).** A solution of $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$ (136 mg, 0.40 mmol) in toluene (4 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{N}(\text{SiMe}_3)_2)]_2$ (220 mg, 0.20 mmol) in toluene (3.5 mL). The mixture was stirred at room temperature for 2 h and the solution was dried under vacuum. The resulting

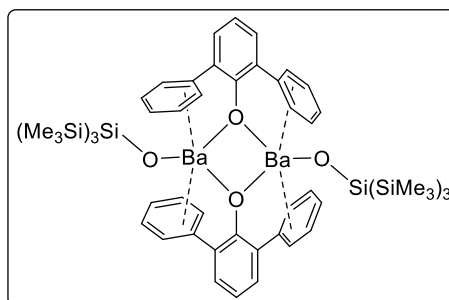


colourless oil obtained was then stripped with petroleum ether to afford **8₂** as a white solid (278 mg, 95%). Colourless monocrystals suitable for XRD were grown by slow evaporation of petroleum ether solution. ^1H NMR (benzene- d_6 , 500.13 MHz, 298 K): δ = 0.35 (s, 54H; OSi(CH₃)₃), 0.28 (s, 72H; CHSi(CH₃)₃), 0.22 (s, 4H; CHSi(CH₃)₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.77 MHz, 298 K): δ = 22.24 (CHSi(CH₃)₃), 4.10 (Si(CH₃)₃), 1.85 (Si(CH₃)₃) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (benzene- d_6 , 128.37 MHz, 298 K): δ = 43.7 ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 79.49 MHz, 298 K): δ = -3.38 (s), -19.86 (s), -27.84 (s) ppm.

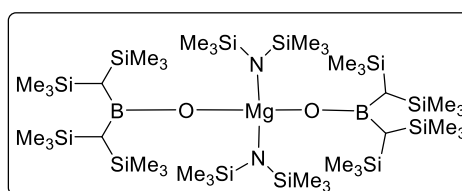
Synthesis of $[\text{Ba}\{\mu_2\text{-OB(Tripp)}_2\}\{\text{OSi}(\text{SiMe}_3)_3\}]_2$ (9₂**).** A solution of $(\text{Tripp})_2\text{BOH}$ (116 mg, 0.28 mmol) in toluene (4 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{N}(\text{SiMe}_3)_2)]_2$ (150 mg, 0.14 mmol) in toluene (3.5 mL). The formation of a white precipitate was observed. The mixture was stirred at room temperature for 2 h and the solution was filtered off. The solid was then washed with cold petroleum ether and dried under vacuum. Compound **9₂** was isolated as a white solid (178 mg, 75%). Colourless monocrystals suitable for XRD were grown by slow diffusion of toluene in a saturated Et₂O solution. ^1H NMR (thf- d_8 , 400.13 MHz, 298 K): δ = 6.78 (s, 8H; *m*-CH), 3.48 (hept, 8H, $^3J_{\text{H-H}} = 6.9$ Hz; *o*-CH(CH₃)₂), 2.74 (hept, 4H, $^3J_{\text{H-H}} = 6.9$ Hz; *p*-CH(CH₃)₂), 1.16 (d, 24H, $^3J_{\text{H-H}} = 6.9$ Hz; *p*-CH(CH₃)₂), 0.98 (d, 48H, $^3J_{\text{H-H}} = 6.9$ Hz; *o*-CH(CH₃)₂), 0.06 (s, 54H; Si(CH₃)₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_8 , 125.77 MHz, 298 K): δ = 151.05 (*o*-C(CH(CH₃)₂)), 148.13 (CBO), 146.39 (*p*-C(CH(CH₃)₂)), 120.12-120.04 (*m*-CH), 35.27 (*p*-CH(CH₃)₂), 33.37 (*o*-CH(CH₃)₂), 25.25 (*p*-CH(CH₃)₂), 24.69 (*o*-CH(CH₃)₂), 1.19 (Si(CH₃)₃) ppm. $^{29}\text{Si}\{^1\text{H}\}$ NMR (thf- d_8 , 79.49 MHz, 298 K): δ = -20.67 (s), -36.67 (s) ppm.



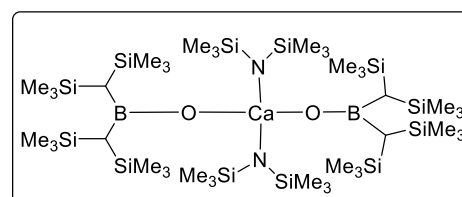
Synthesis of $[\text{Ba}\{\mu_2\text{-O}(2,6\text{-Ph}_2\text{-C}_6\text{H}_3)\}\{\text{OSi}(\text{SiMe}_3)_3\}]_2$ (10₂**).** A solution of $(2,6\text{-Ph}_2\text{-C}_6\text{H}_3)\text{OH}$ (66 mg, 0.28 mmol) in toluene (4 mL) was added dropwise at room temperature to a solution of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{N}(\text{SiMe}_3)_2)_2]$ (150 mg, 0.14 mmol) in toluene (3.5 mL). The mixture was stirred at room temperature for 2 h and concentrated until the formation of a white solid occurred. The solution was then isolated by filtration and stored at -43°C . Colourless monocystals suitable for XRD were obtained after 5 days (121 mg, 70%). ^1H NMR (thf- d_8 , 400.13 MHz, 298 K): δ = 7.67 (m, 8H; *o*-CH), 7.29-7.23 (m, 8H; *m*-CH), 7.08 (m, 4H; *p*-CH), 6.97 (m, 4H; *m*-CH), 6.23 (m, 2H; *p*-CH), 0.10 (s, 54H; $\text{Si}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_8 , 125.77 MHz, 298 K): δ = 166.12-165.81 (*i*-CO), 145.81 (*m*-C), 131.40-131.16 (*o*-CPh), 130.40-130.33 (*p*-CH), 129.99 (*m*-CH), 128.37 (*o*-CH), 125.26 (*m*-CH), 111.67-111.22 (*p*-CH), 0.87 ($\text{Si}(\text{CH}_3)_3$) ppm. The resonances for the silicon atoms could not be detected by ^{29}Si NMR spectroscopy.



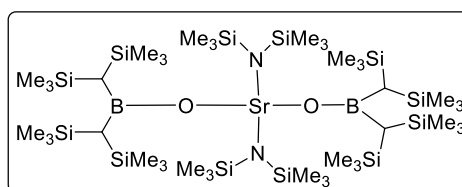
Synthesis of $[\text{Mg}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (11₂**).** A solution of $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$ (0.10 g, 0.29 mmol) in toluene (10 ml) was added to a solution of $[\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.09 g, 0.29 mmol) in toluene (10 ml). The reaction mixture was stirred for 3 h and the volatiles were removed under vacuum. The resulting white powder was washed with pentane (3 x 5 ml) and the product was dried to constant weight under vacuum. X-ray quality crystals were obtained upon cooling of a hot toluene solution. Yield: 0.12 g, 78%. ^1H NMR (thf- d_8 , 400.13 MHz, 298 K): δ = 0.14 (s, 2H, BCH), 0.13 (s, 36H, $\text{CHSi}(\text{CH}_3)_3$), 0.05 (s, 18H, $\text{NSi}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (thf- d_8 , 125.77 MHz, 298 K): δ = 21.91 (BCH), 6.79 ($\text{NSi}(\text{CH}_3)_3$), 4.78 ($\text{CHSi}(\text{CH}_3)_3$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (thf- d_8 , 128.37 MHz, 298 K): δ = 43.57 (br s) ppm.



Synthesis of $[\text{Ca}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (12₂**).** Following the same protocol described above for **11₂**, **12₂** was obtained by reacting $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$ (0.40 g, 1.15 mmol) in pentane (10 ml) with a solution of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.42 g, 1.15 mmol) in pentane (10 ml). X-ray quality crystals were obtained from a saturated solution in petroleum ether stored at -30°C . Yield: 0.53 g, 84%. ^1H NMR (benzene- d_6 , 400.13 MHz, 298 K): δ = 0.34 (s, 36H, $\text{CHSi}(\text{CH}_3)_3$), 0.32 (s, 2H, BCH), 0.29 (s, 18H, $\text{NSi}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.77 MHz, 298 K): δ = 30.08 (BCH), 6.76 ($\text{NSi}(\text{CH}_3)_3$), 4.45 ($\text{CHSi}(\text{CH}_3)_3$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (benzene- d_6 , 128.40 MHz, 298 K): δ = 46.81 (br s) ppm.



Synthesis of $[\text{Sr}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (13₂**).** Following the same protocol described for **11₂**, **13₂** was obtained by reacting $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$ (0.10 g, 0.29 mmol) in toluene (10 ml) with a solution of $[\text{Sr}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.12 g, 0.29 mmol) in toluene (10 ml). X-ray quality crystals were obtained upon cooling of a hot toluene solution. Yield: 0.09 g, 53%. ^1H NMR (benzene- d_6 , 400.13 MHz, 298 K): δ = 0.33 (s, 36H, $\text{CHSi}(\text{CH}_3)_3$), 0.29 (s, 2H, BCH), 0.27 (s, 18H, $\text{NSi}(\text{CH}_3)_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.77 MHz, 298 K): δ = 6.47 ($\text{NSi}(\text{CH}_3)_3$), 21.85 (BCH), 3.74 ($\text{CHSi}(\text{CH}_3)_3$) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (benzene- d_6 , 128.40 MHz, 298 K): δ = 43.55 (br s) ppm.



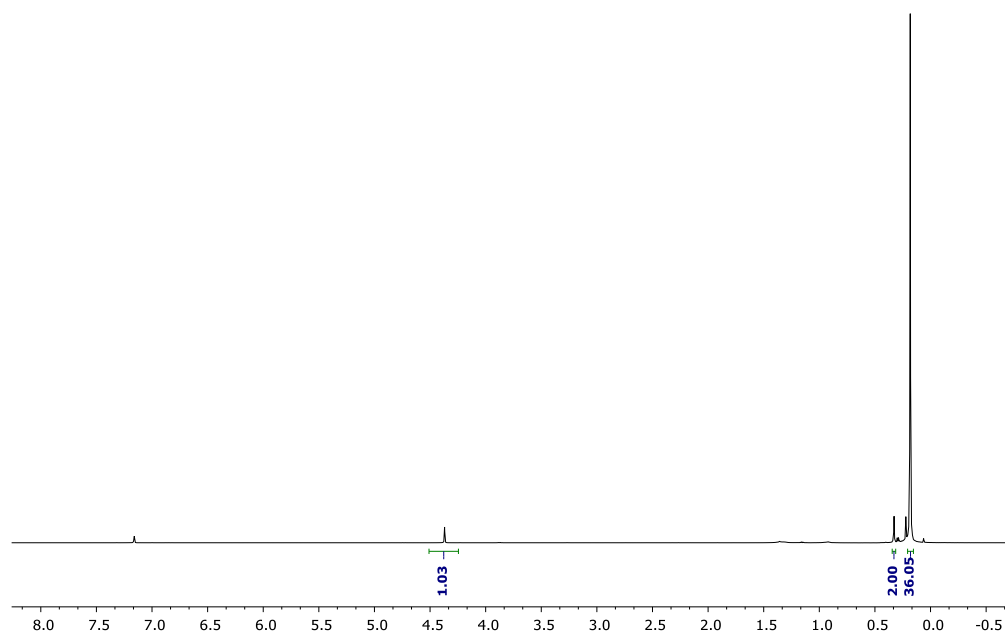


Figure S1. ^1H NMR spectrum (298 K, benzene- d_6 , 500.13 MHz) of $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$.

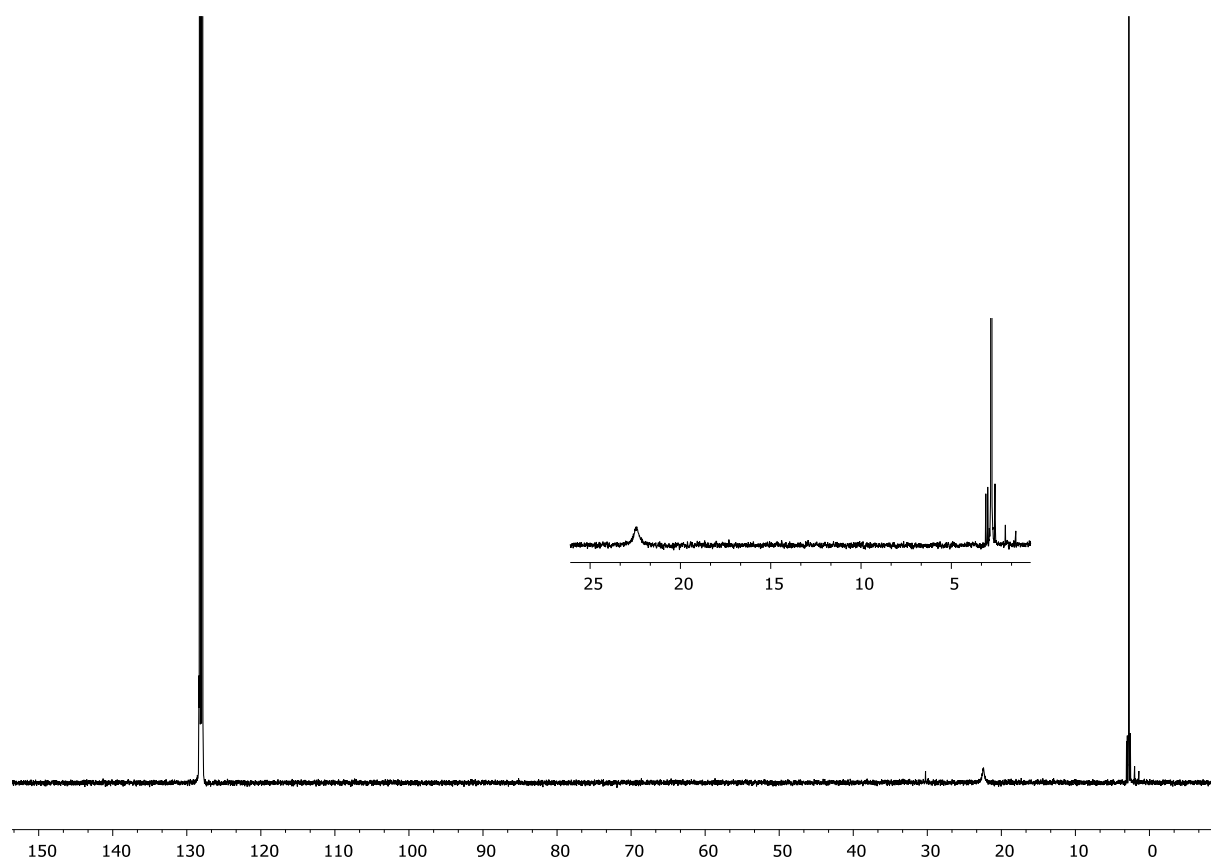


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 125.77 MHz) of $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$.

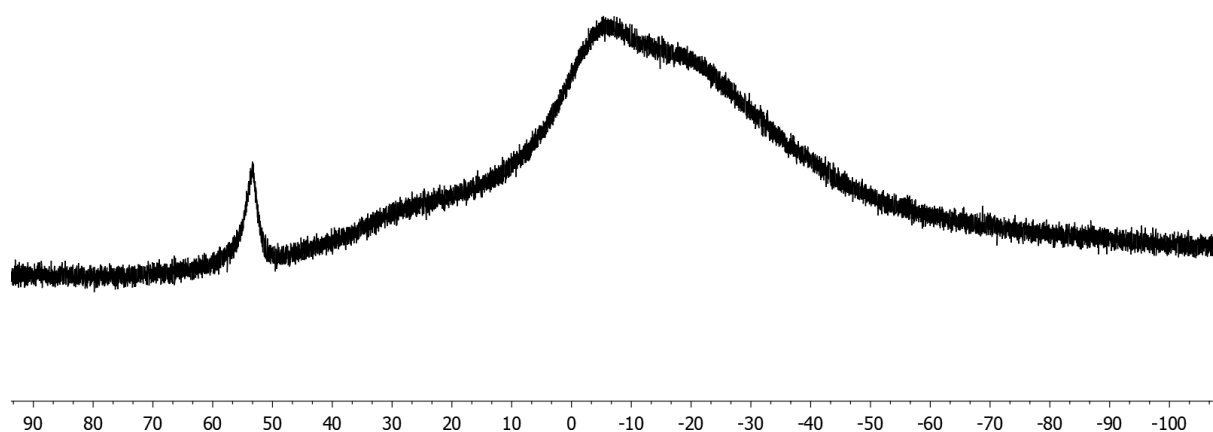


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $\{\text{CH}(\text{SiMe}_3)_2\}_2\text{BOH}$.

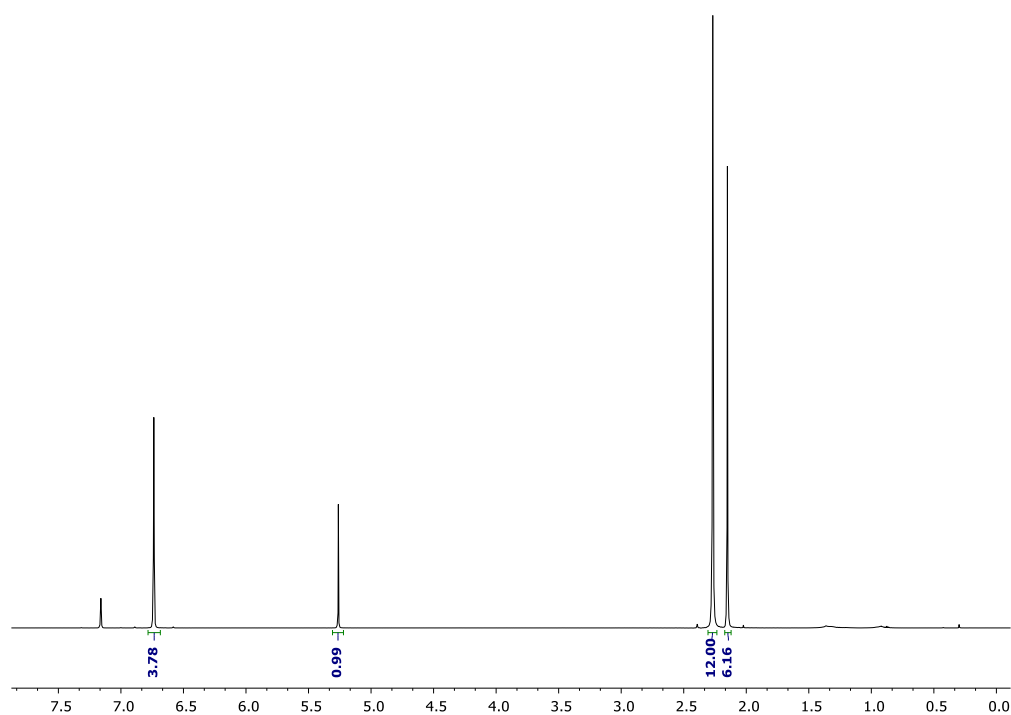


Figure S4. ^1H NMR spectrum (298 K, benzene- d_6 , 500.13 MHz) of $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)_2\text{BOH}$ (= $(\text{mes})_2\text{BOH}$).

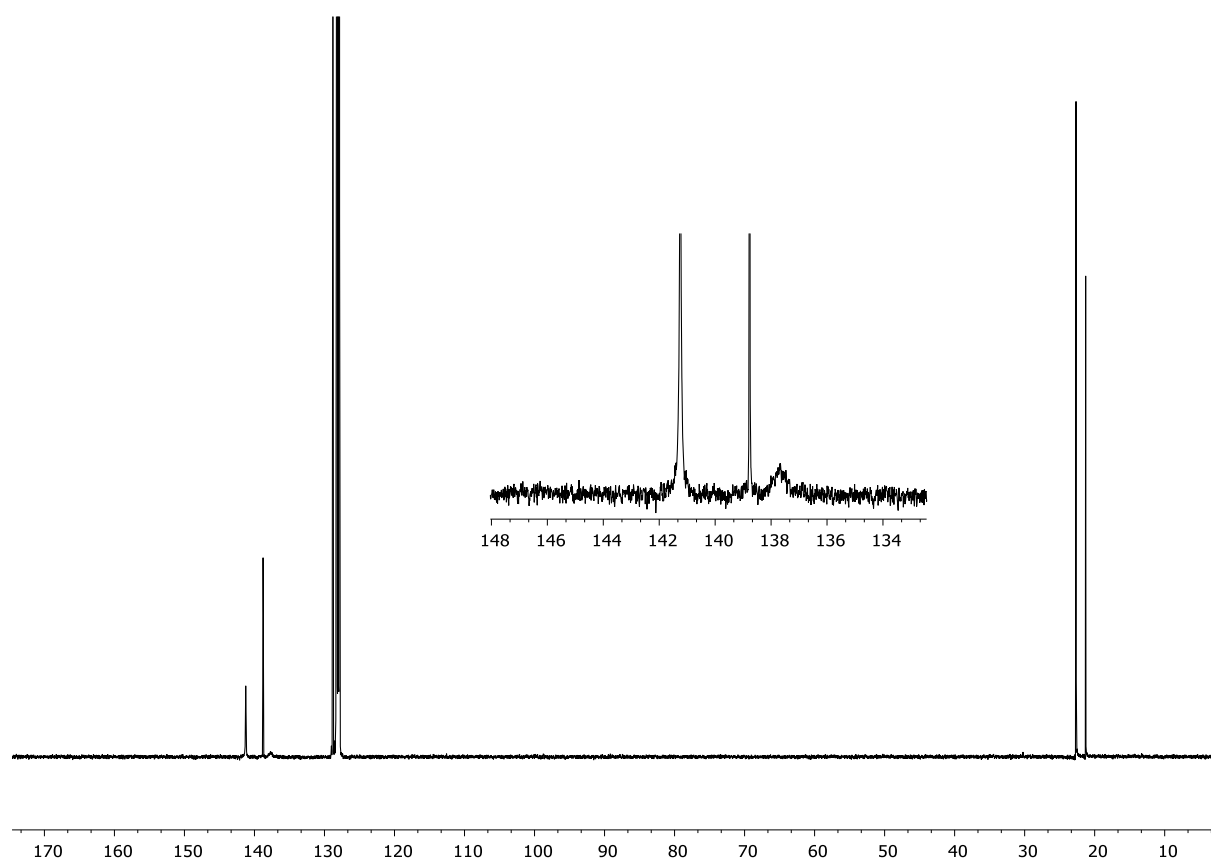


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 125.77 MHz) of $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)_2\text{BOH}$ (= (mes) $_2\text{BOH}$).

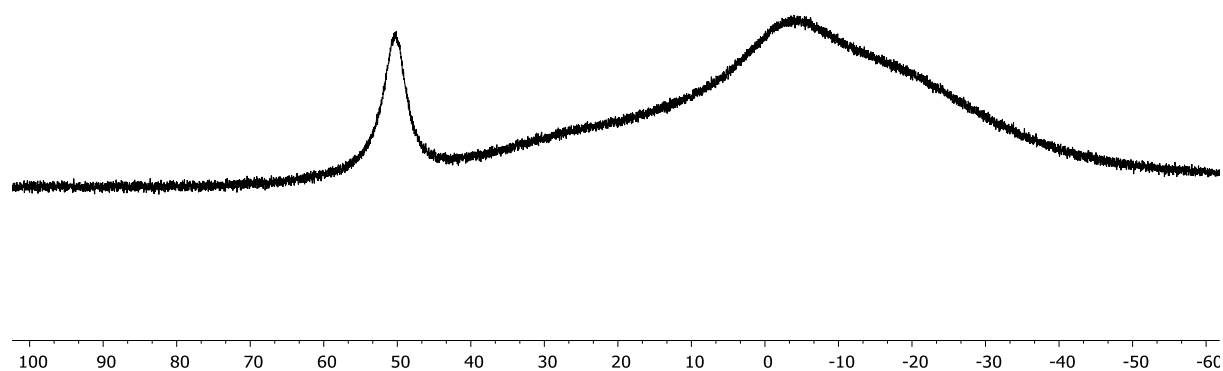


Figure S6. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)_2\text{BOH}$ (= (mes) $_2\text{BOH}$).

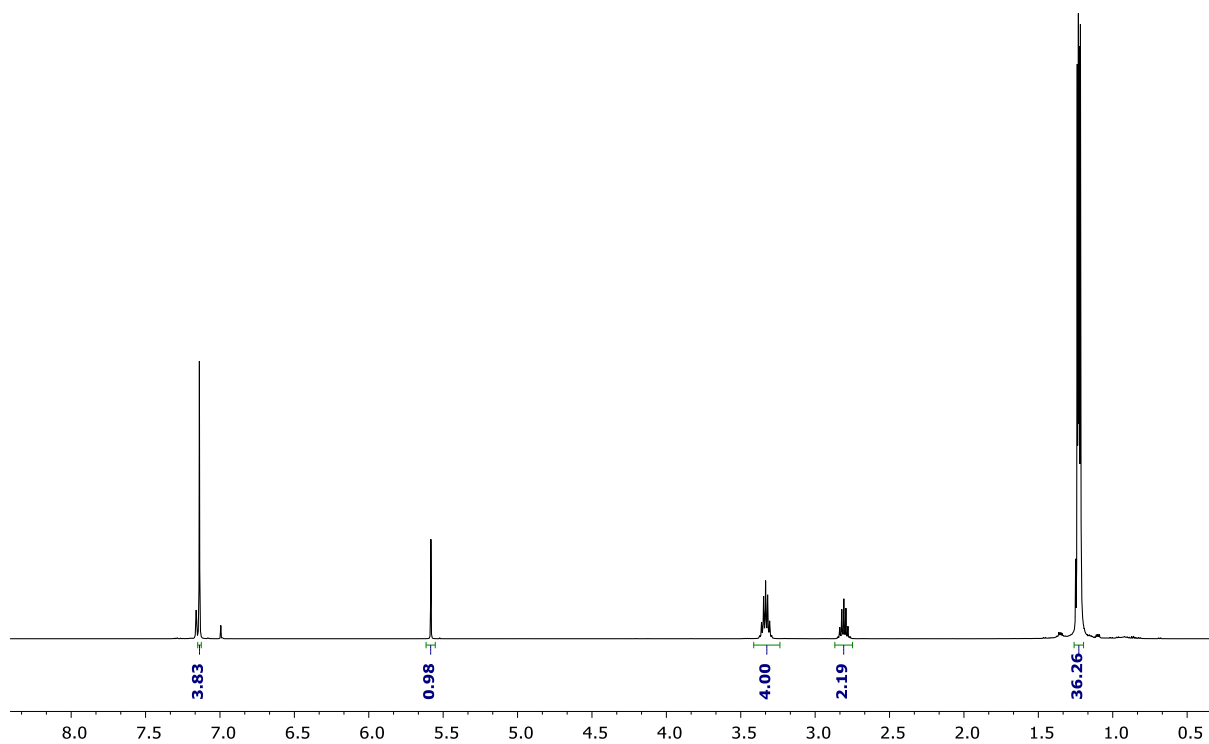


Figure S7. ¹H NMR spectrum (298 K, benzene-d₆, 500.13 MHz) of (2,4,6-ⁱPr₃-C₆H₂)₂BOH (= (Tripp)₂BOH).

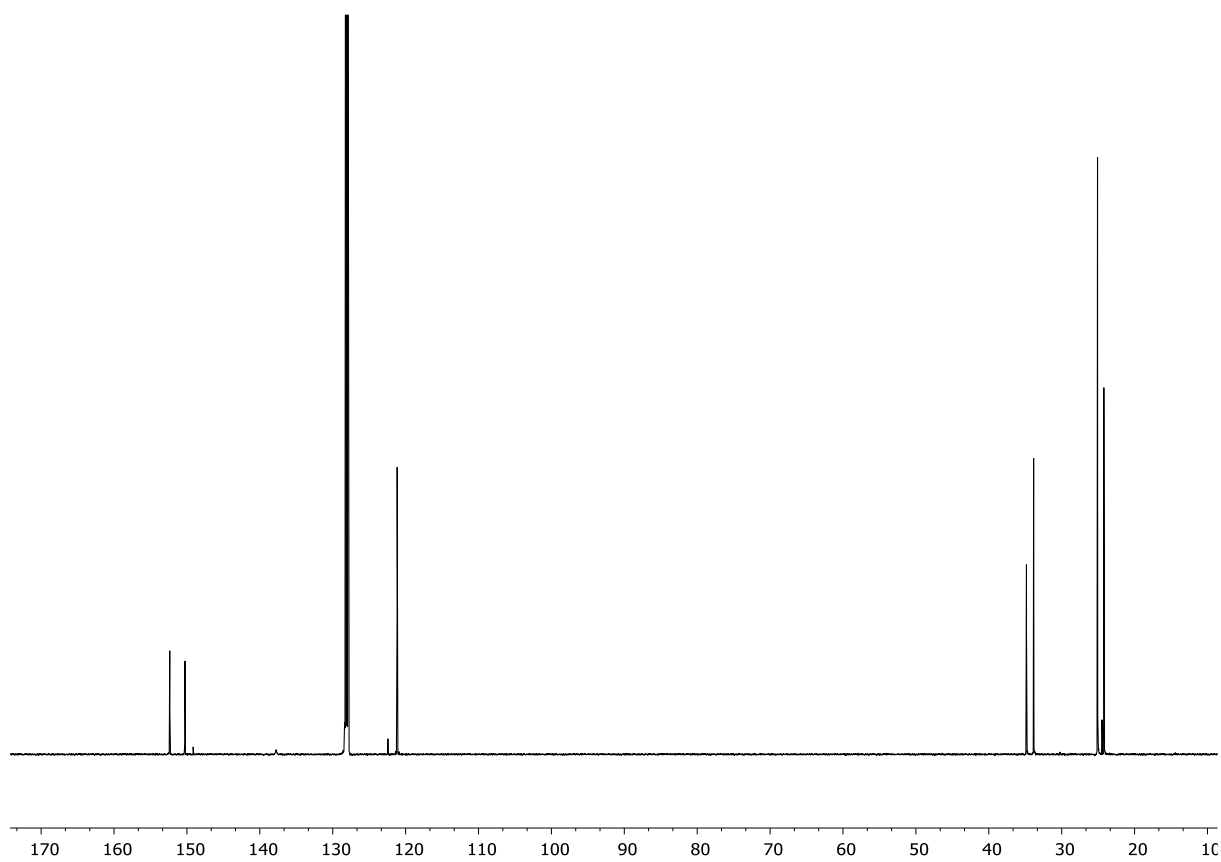


Figure S8. ¹³C{¹H} NMR spectrum (298 K, benzene-d₆, 125.77 MHz) of (2,4,6-ⁱPr₃-C₆H₂)₂BOH (= (Tripp)₂BOH).

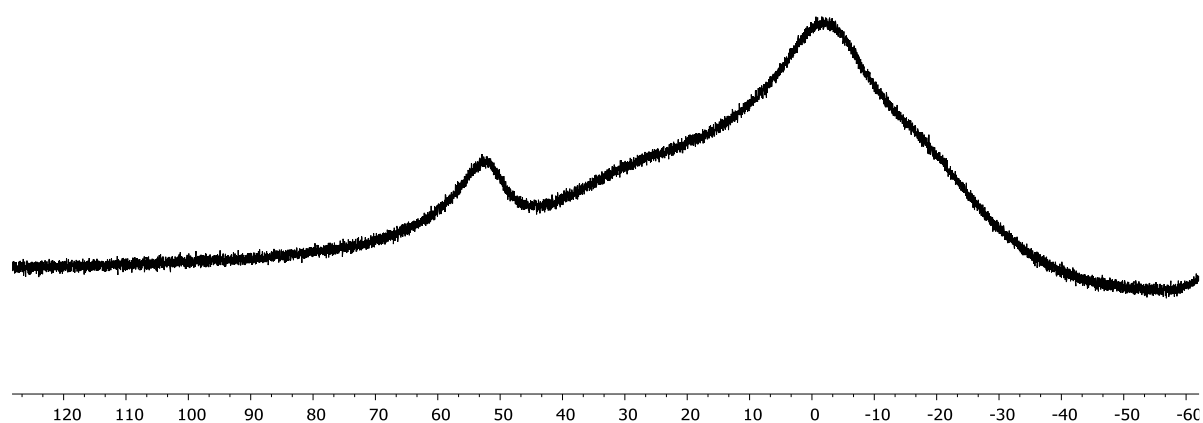


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $(2,4,6\text{-Pr}_3\text{-C}_6\text{H}_2)_2\text{BOH}$ (= (Tripp) $_2\text{BOH}$).

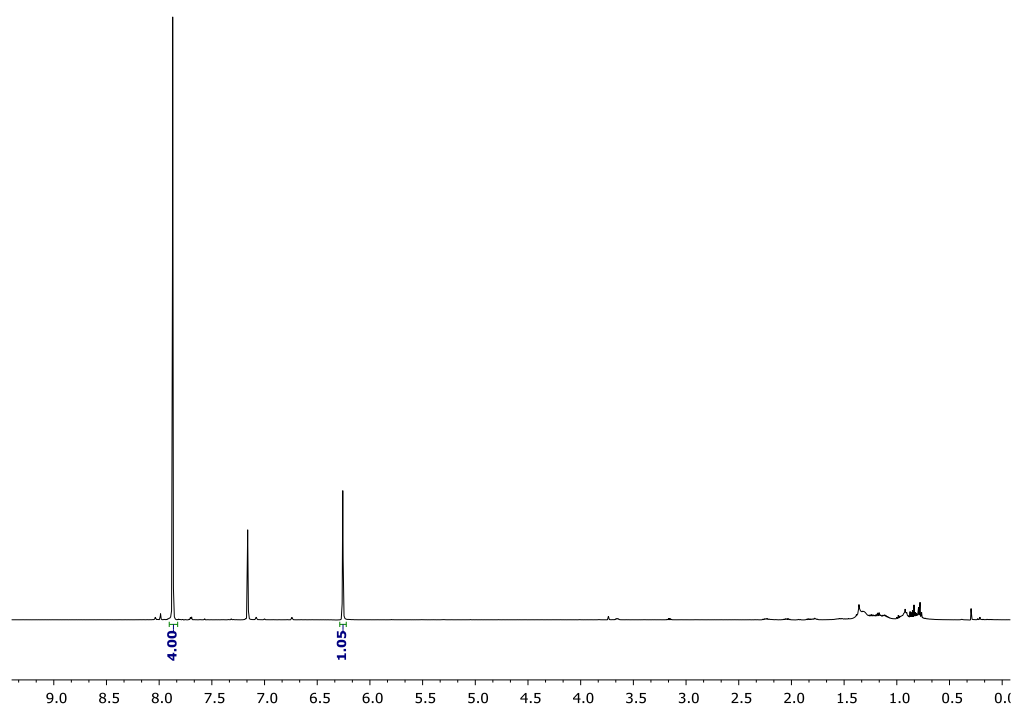
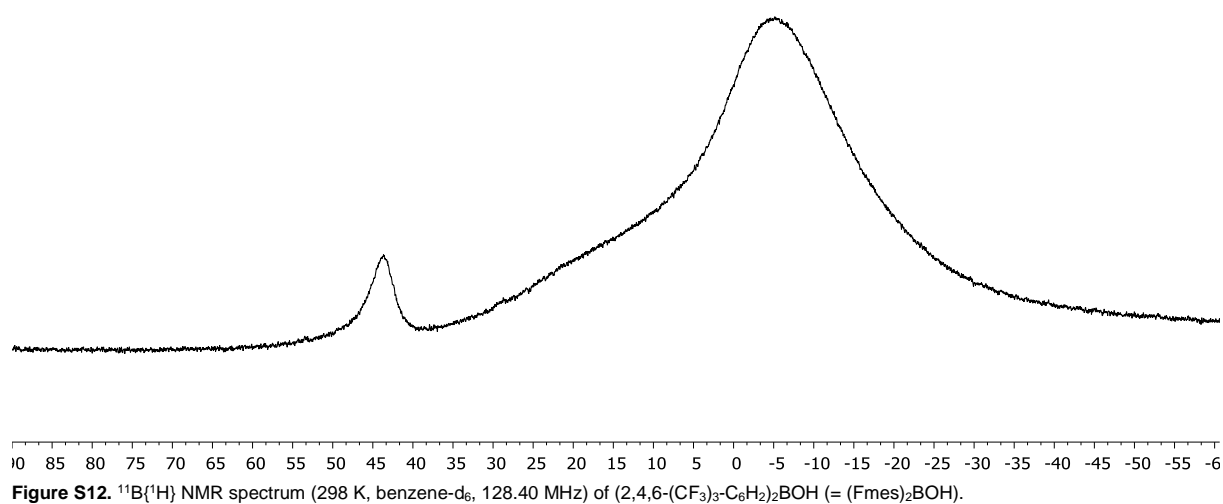
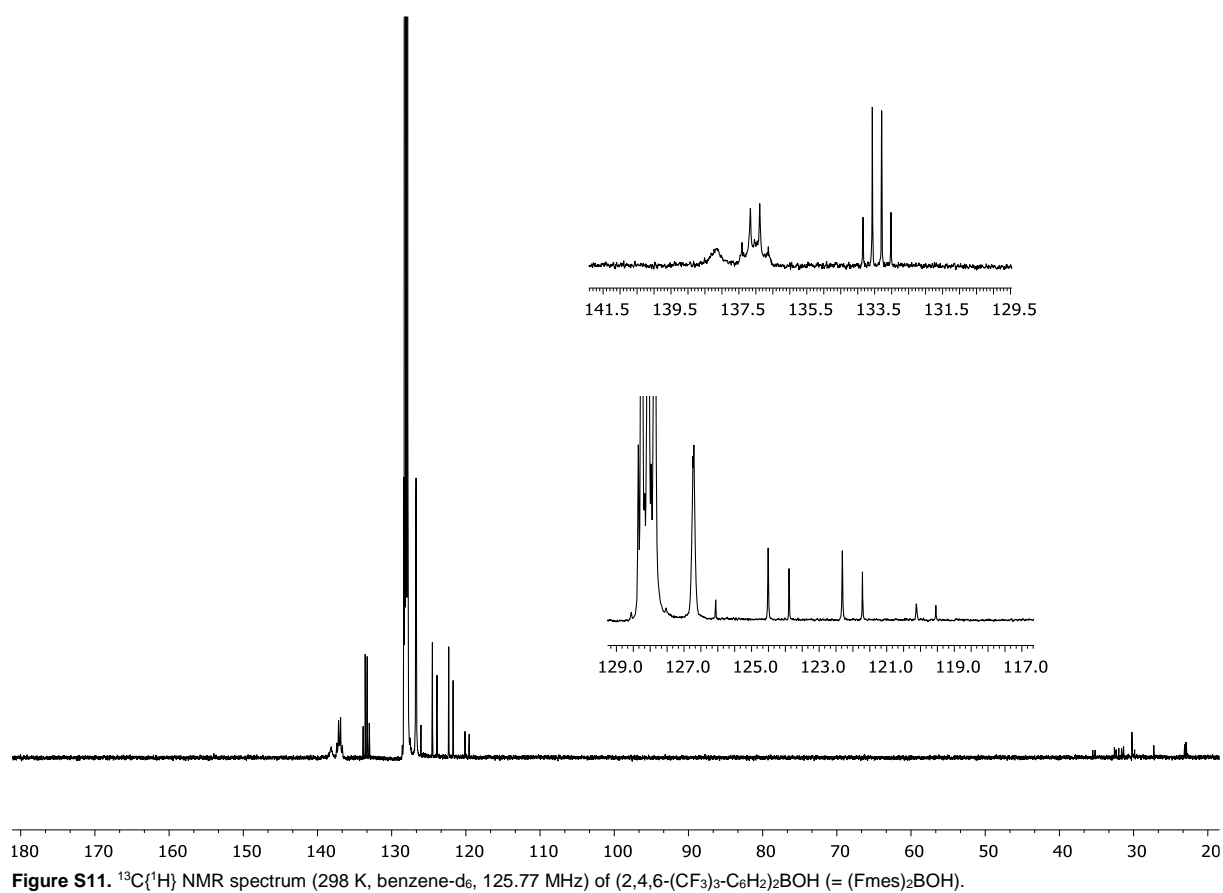


Figure S10. ^1H NMR spectrum (298 K, benzene- d_6 , 500.13 MHz) of $(2,4,6\text{-(CF}_3)_3\text{-C}_6\text{H}_2)_2\text{BOH}$ (= (Fmes) $_2\text{BOH}$).



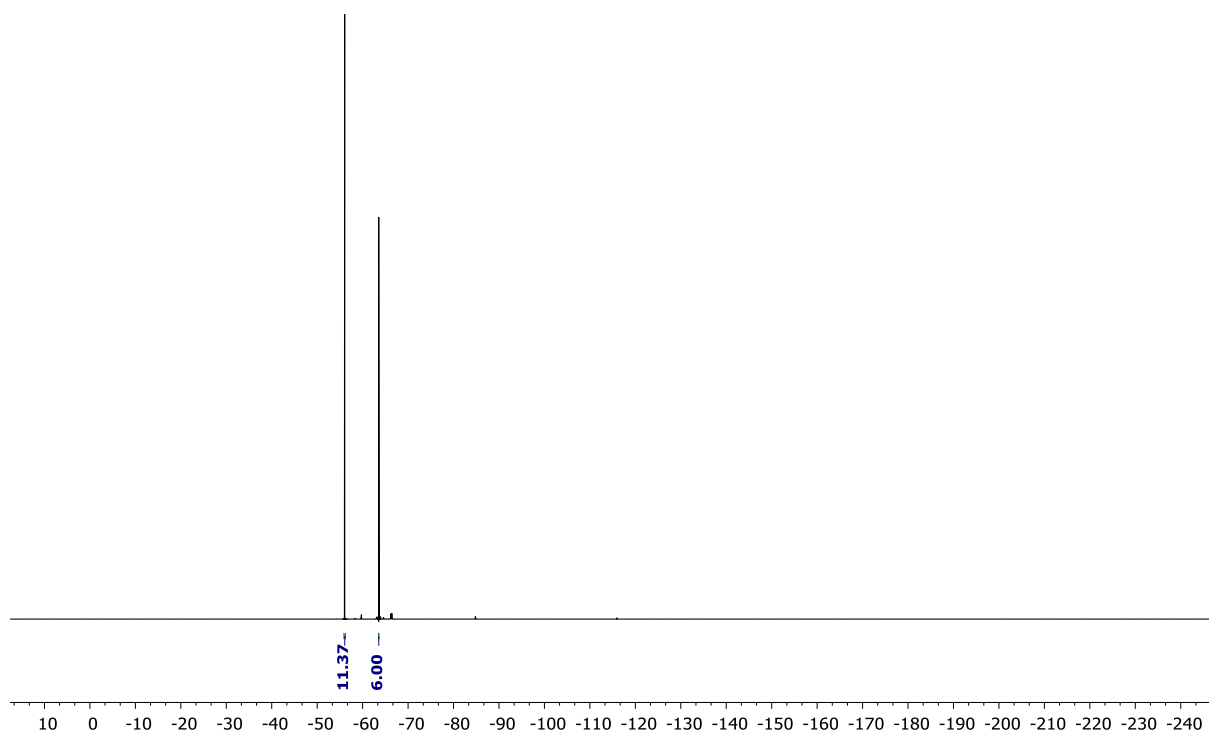


Figure S13. ¹⁹F NMR spectrum (298 K, benzene-d₆, 376.47 MHz) of (2,4,6-(CF₃)₃-C₆H₂)₂BOH (= (Fmes)₂BOH).

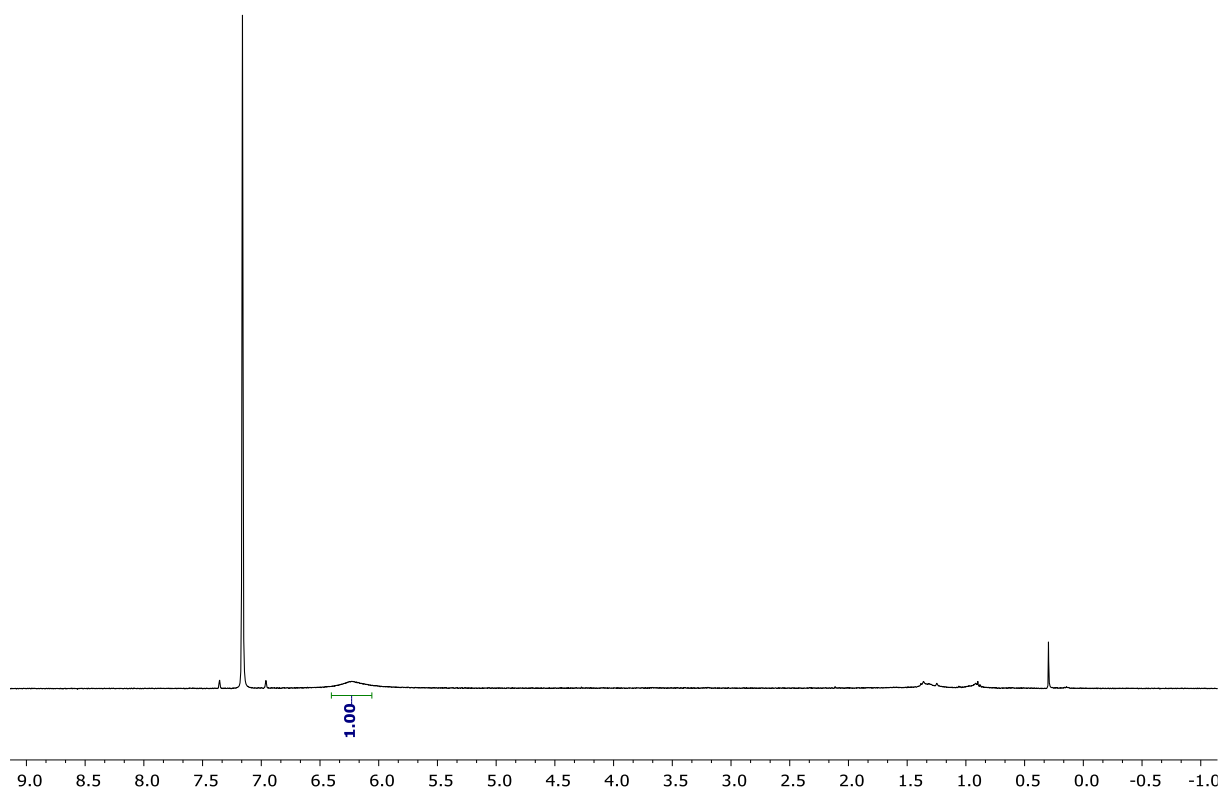


Figure S14. ¹H NMR spectrum (298 K, benzene-d₆, 400.16 MHz) of (C₆F₅)₂BOH.

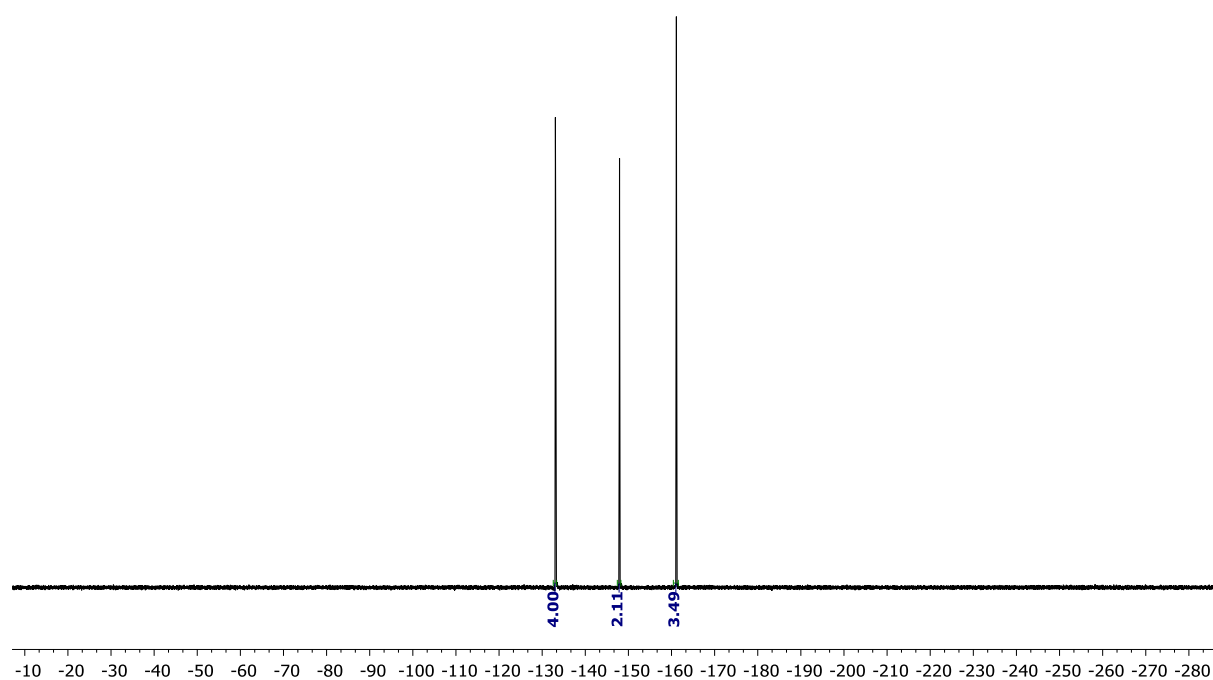


Figure S15. ^{19}F NMR spectrum (298 K, benzene- d_6 , 376.47 MHz) of $(\text{C}_6\text{F}_5)_2\text{BOH}$.

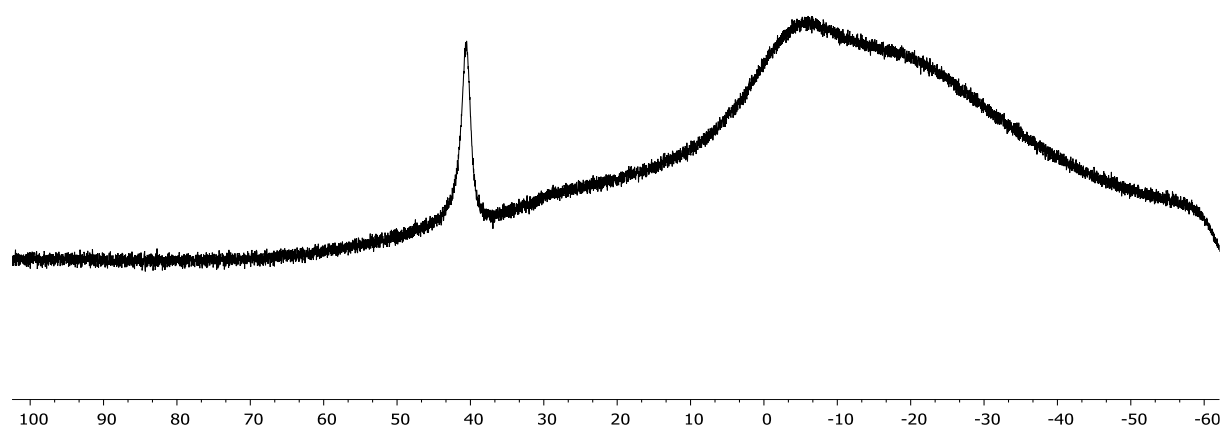


Figure S16. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $(\text{C}_6\text{F}_5)_2\text{BOH}$.

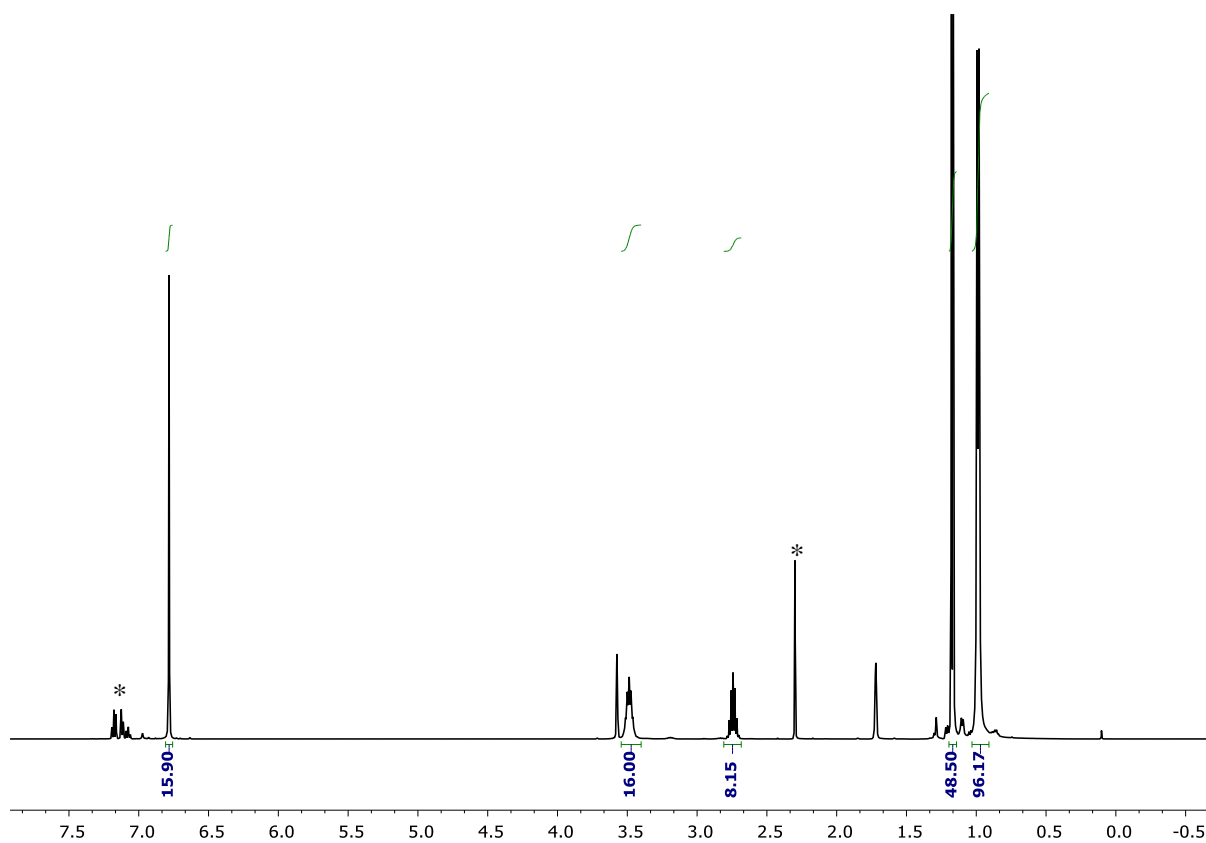


Figure S17. ^1H NMR spectrum (298 K, thf-d_8 , 500.13 MHz) of $[\text{Ba}\{\mu_2\text{-OB(Tripp)}_2\}\{\text{OB(Tripp)}_2\}]_2$ (**52**). Contains residual toluene (*).

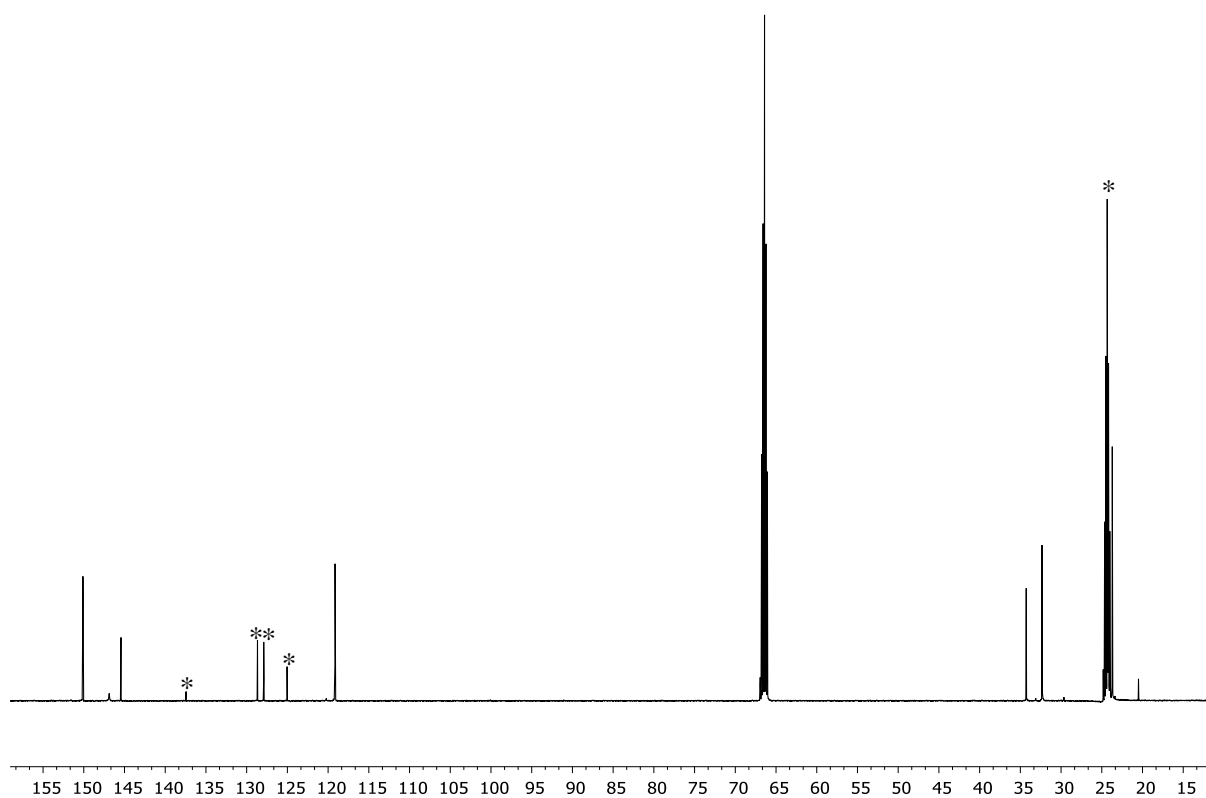


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, thf-d_8 , 125.77 MHz) of $[\text{Ba}\{\mu_2\text{-OB(Tripp)}_2\}\{\text{OB(Tripp)}_2\}]_2$ (**52**). Contains residual toluene (*).

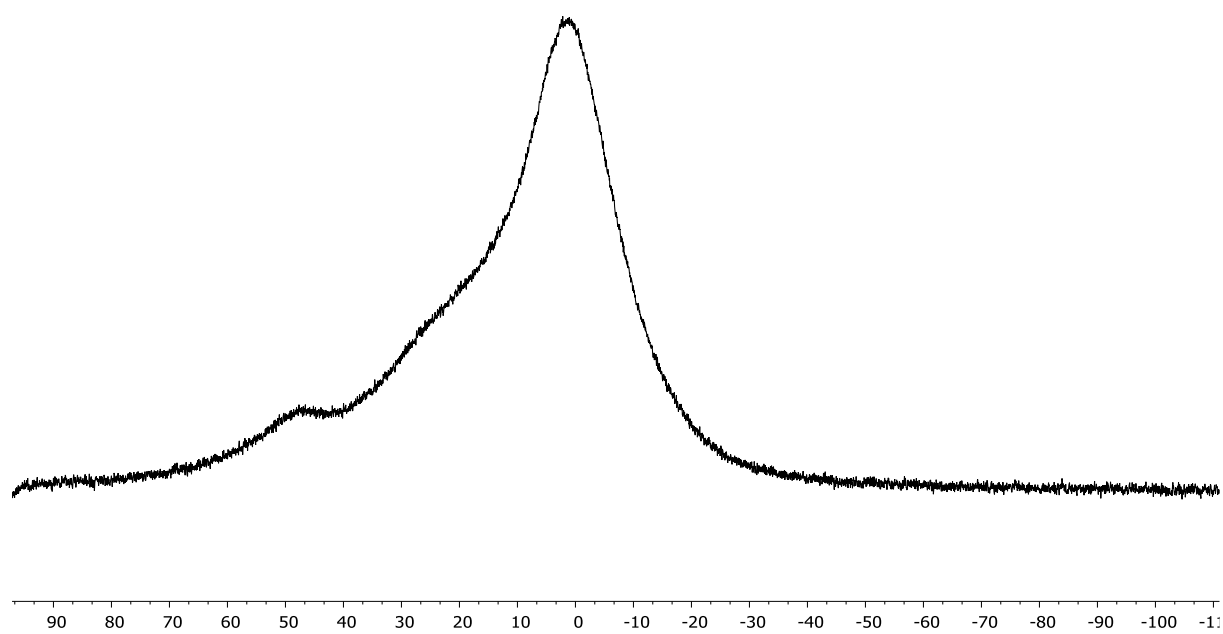


Figure S19. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, thf- d_8 , 128.40 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Tripp})_2\}\{\text{OB}(\text{Tripp})_2\}]_2$ (**52**).

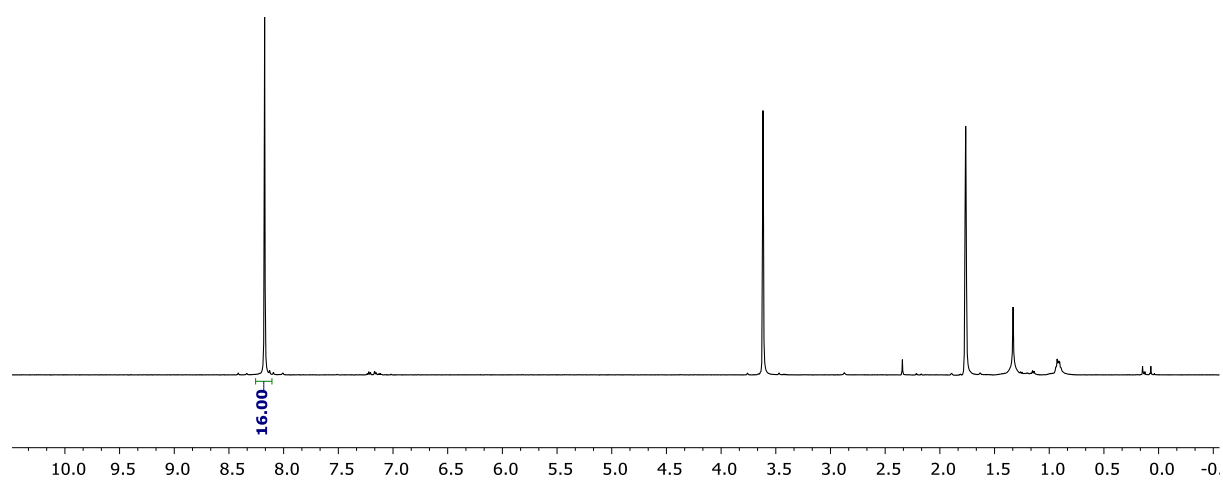


Figure S20. ^1H NMR spectrum (298 K, thf- d_8 , 500.13 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Fmes})_2\}\{\text{OB}(\text{Fmes})_2\}]_2$ (**62**).

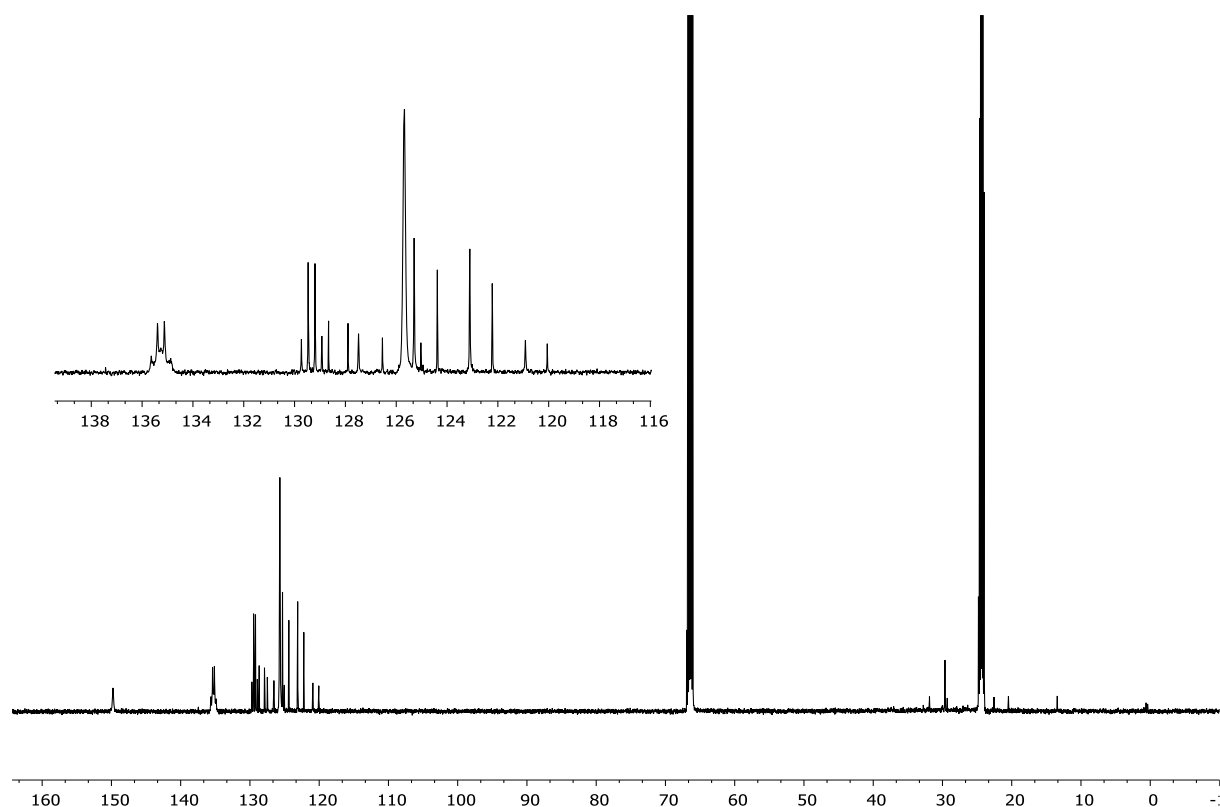


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, thf- d_8 , 125.77 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Fmes})_2\}\{\text{OB}(\text{Fmes})_2\}_2]$ (**62**).

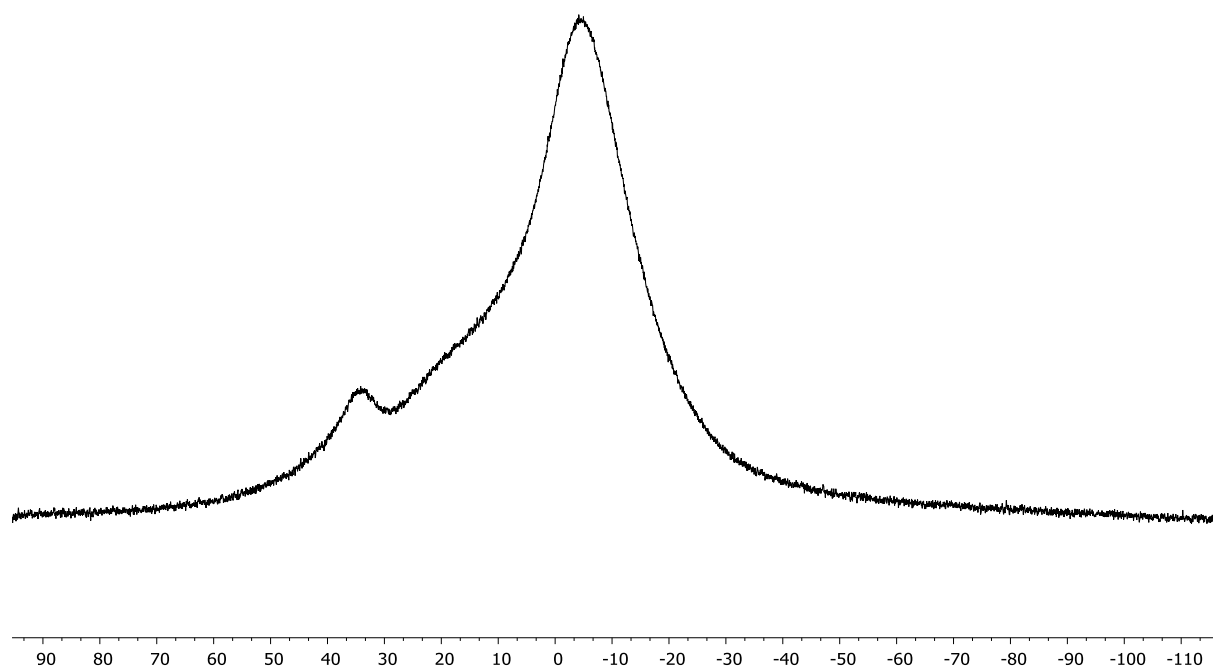


Figure S22. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, thf- d_8 , 128.40 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Fmes})_2\}\{\text{OB}(\text{Fmes})_2\}_2]$ (**62**).

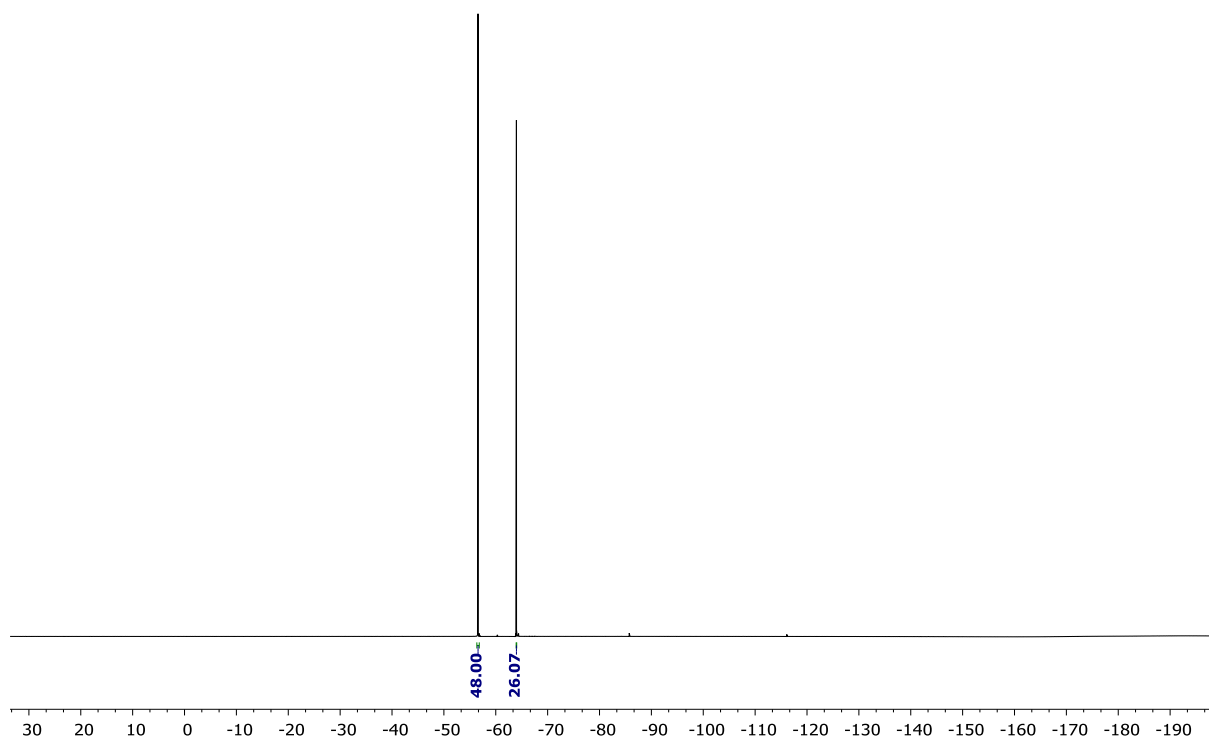


Figure S23. ^{19}F NMR spectrum (298 K, thf-d_8 , 470.52 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Fmes})_2\}\{\text{OB}(\text{Fmes})_2\}_2]$ (**62**).

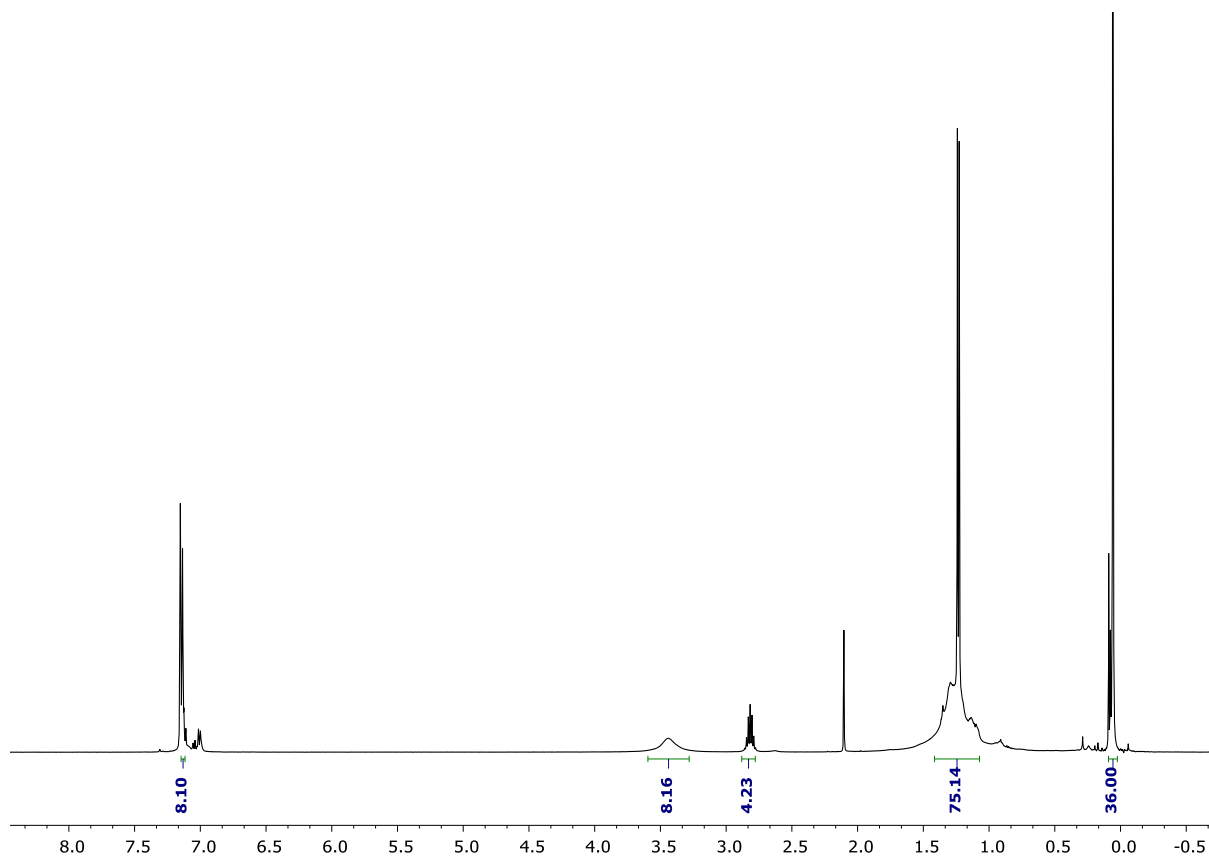


Figure S24. ^1H NMR spectrum (298 K, benzene-d_6 , 500.13 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Tripp})_2\}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**72**).

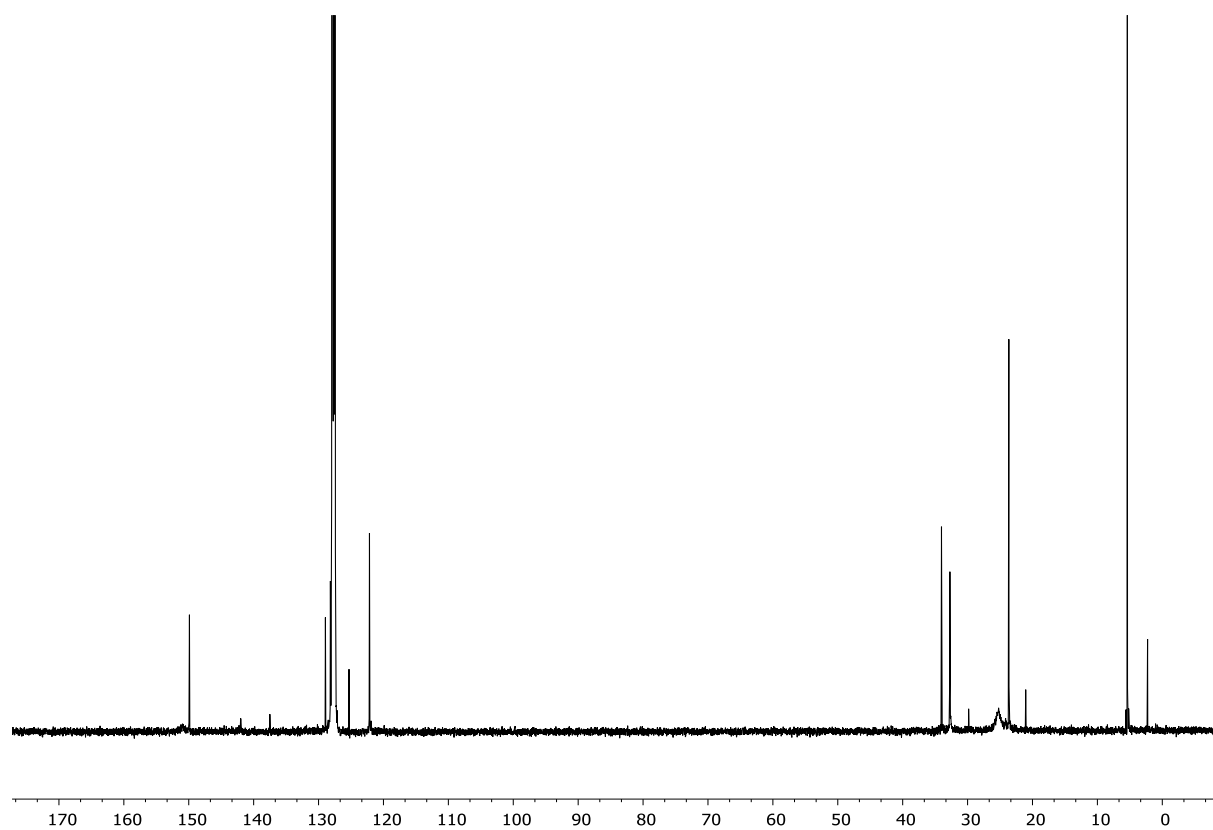


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 125.77 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Tripp})_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (**72**).

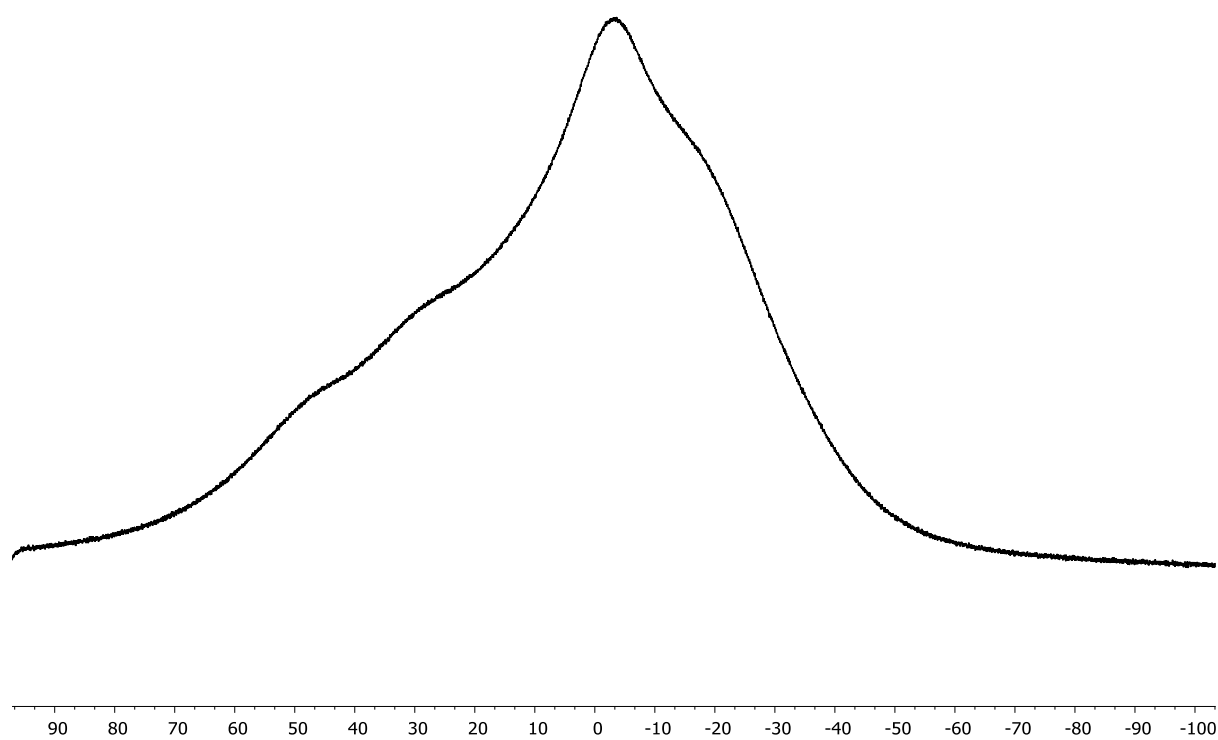


Figure S26. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $[\text{Ba}\{\mu_2\text{-OB}(\text{Tripp})_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (**72**).

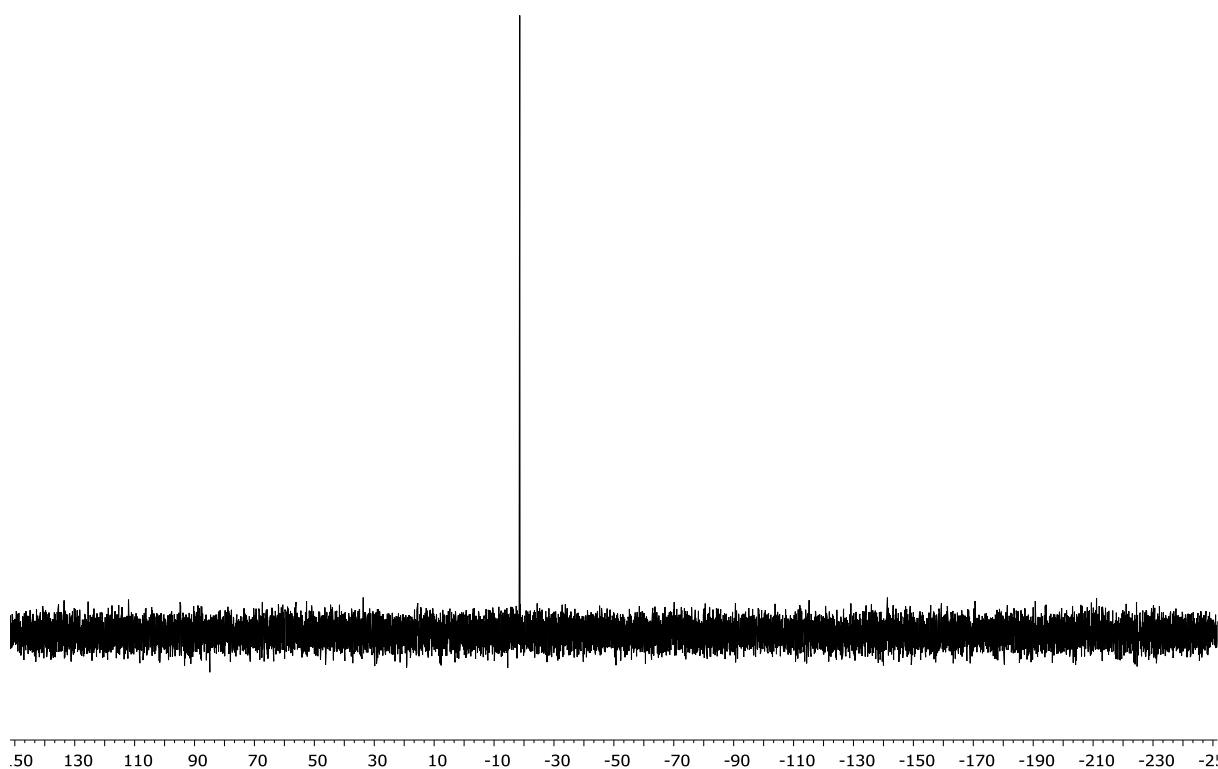


Figure S27. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 79.49 MHz) of $[\text{Ba}\{\mu_2\text{-OB(Tripp)}_2\}\{\text{N(SiMe}_3)_2\}]_2$ (**72**).

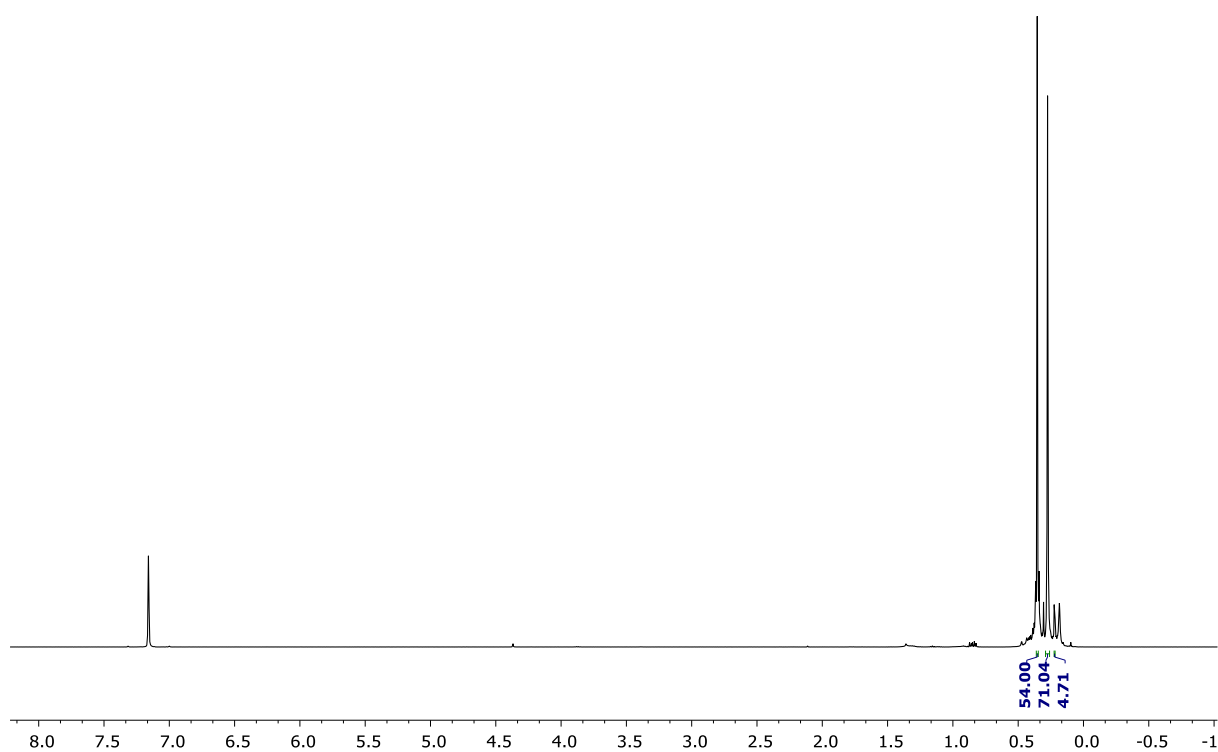


Figure S28. ^1H NMR spectrum (298 K, benzene- d_6 , 500.13 MHz) of $[\text{Ba}\{\mu_2\text{-OSi(SiMe}_3)_3\}(\text{OB}\{\text{CH(SiMe}_3)_2\}_2)]_2$ (**82**).

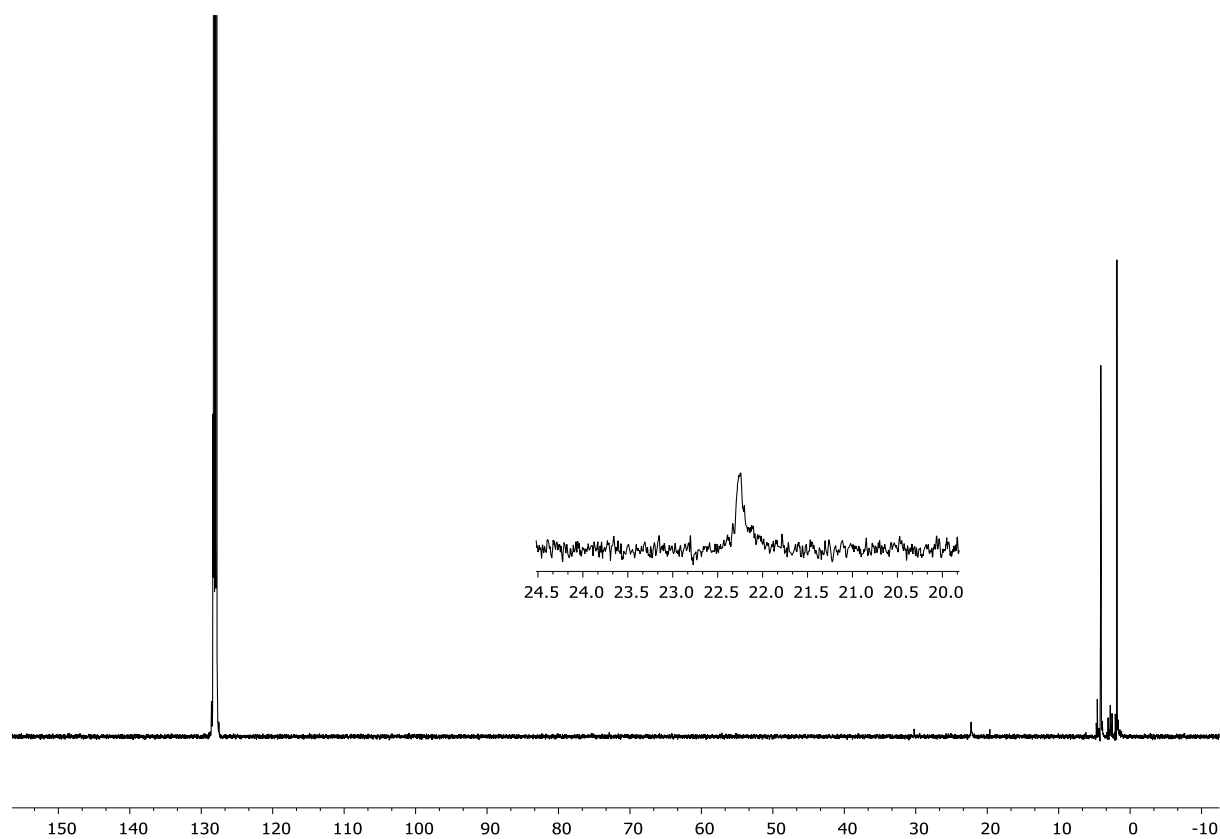


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 125.77 MHz) of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (**82**).

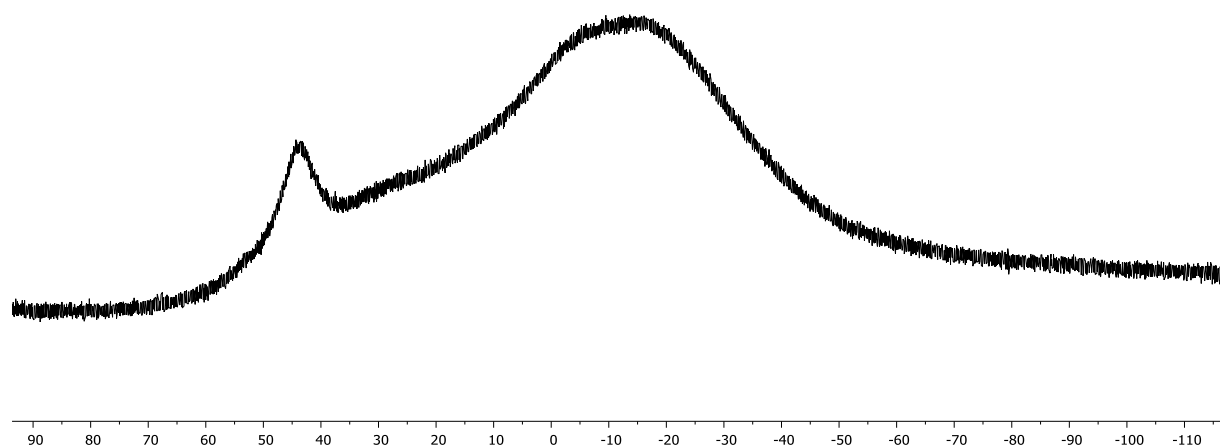
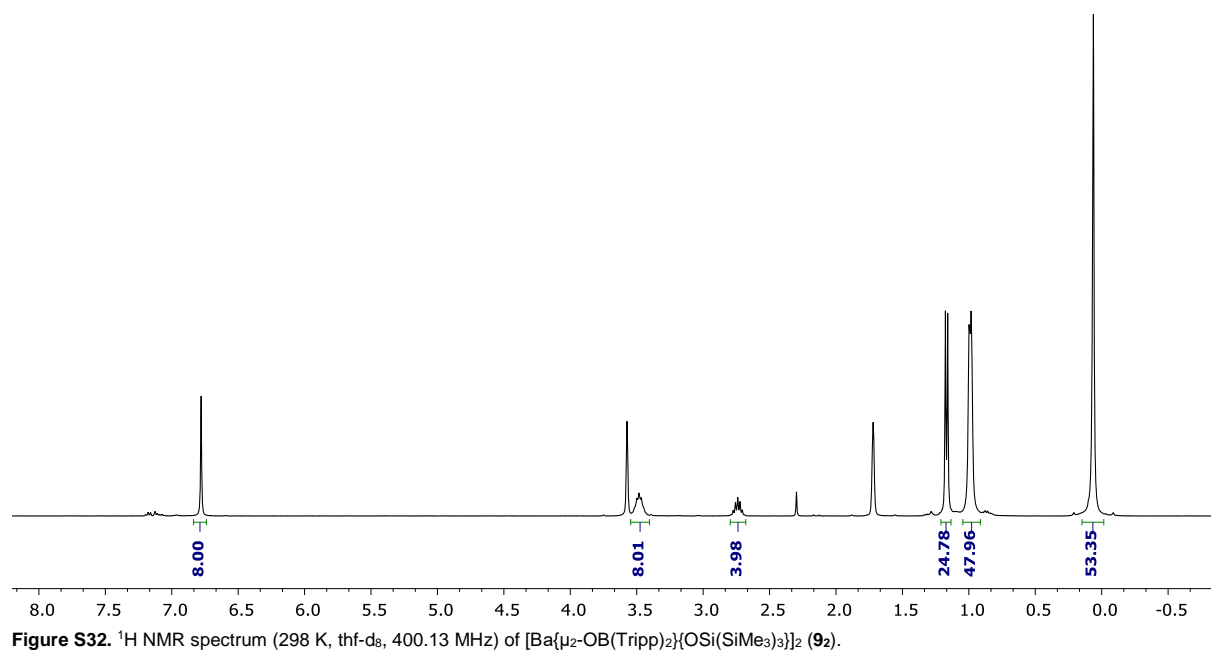
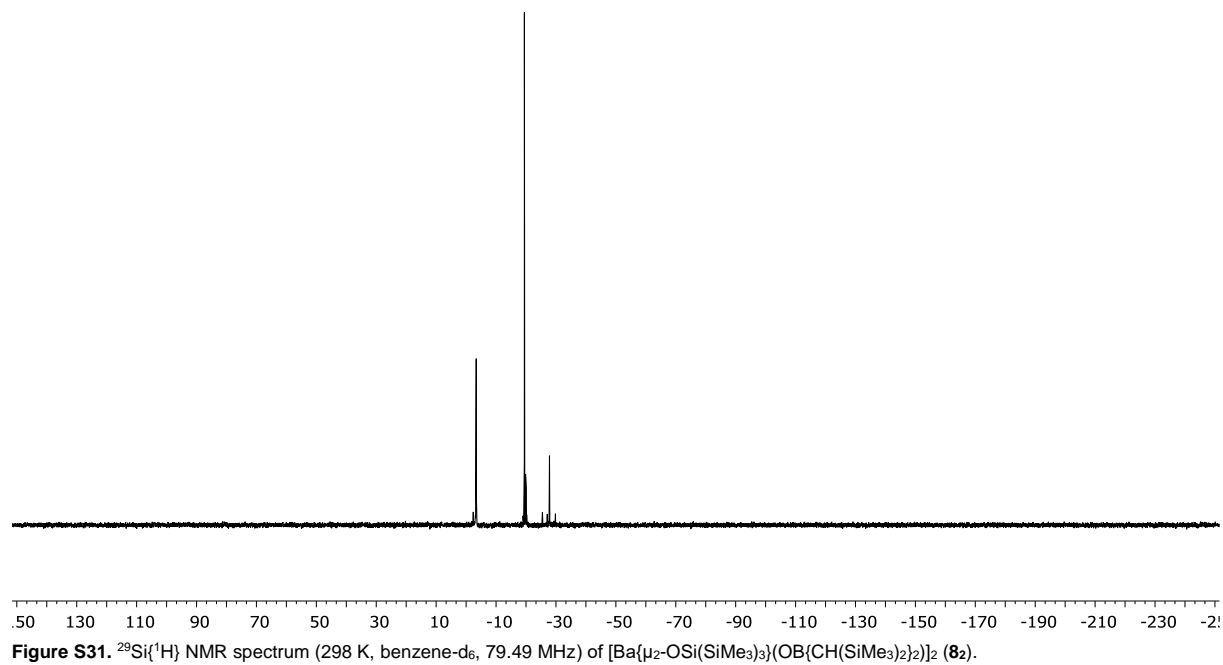
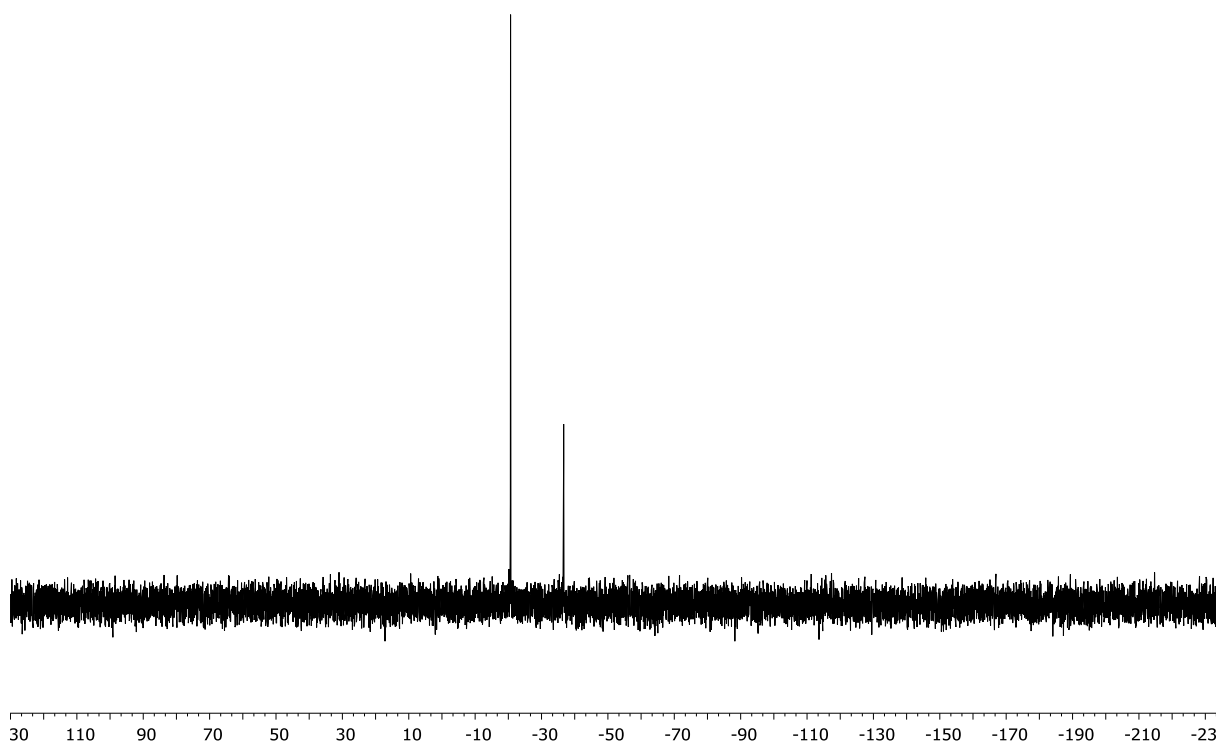
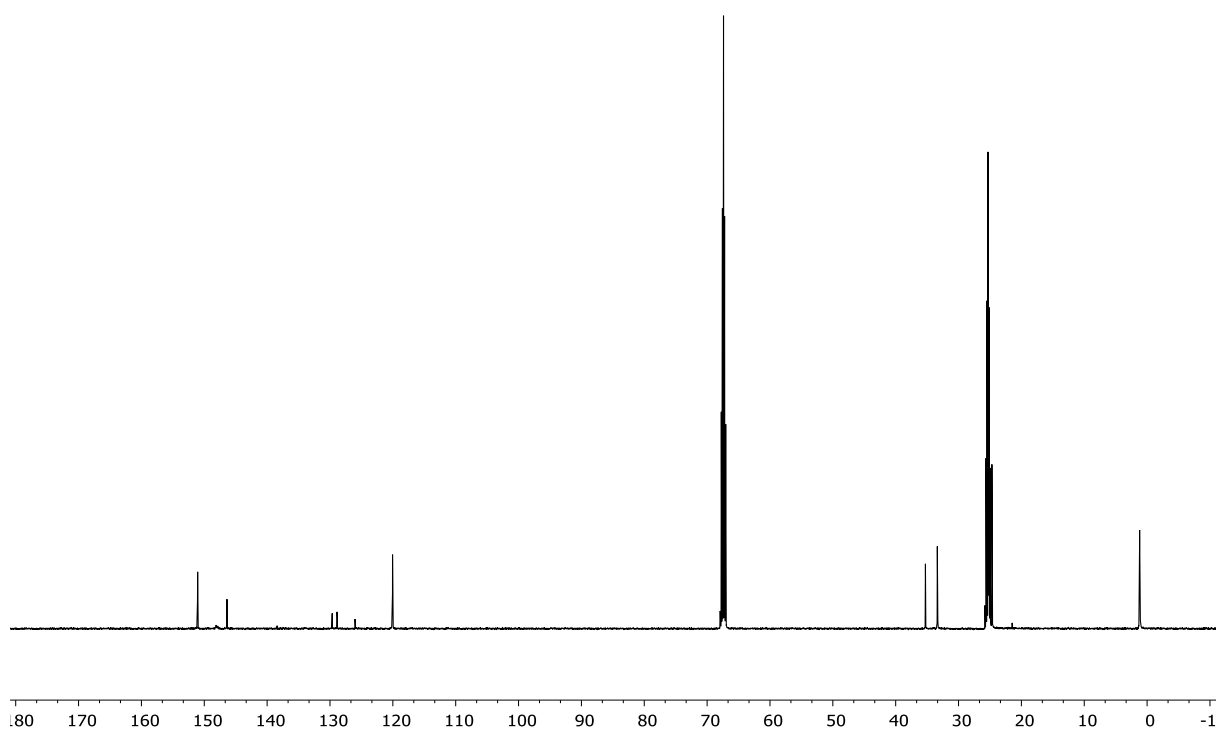


Figure S30. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.37 MHz) of $[\text{Ba}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (**82**).





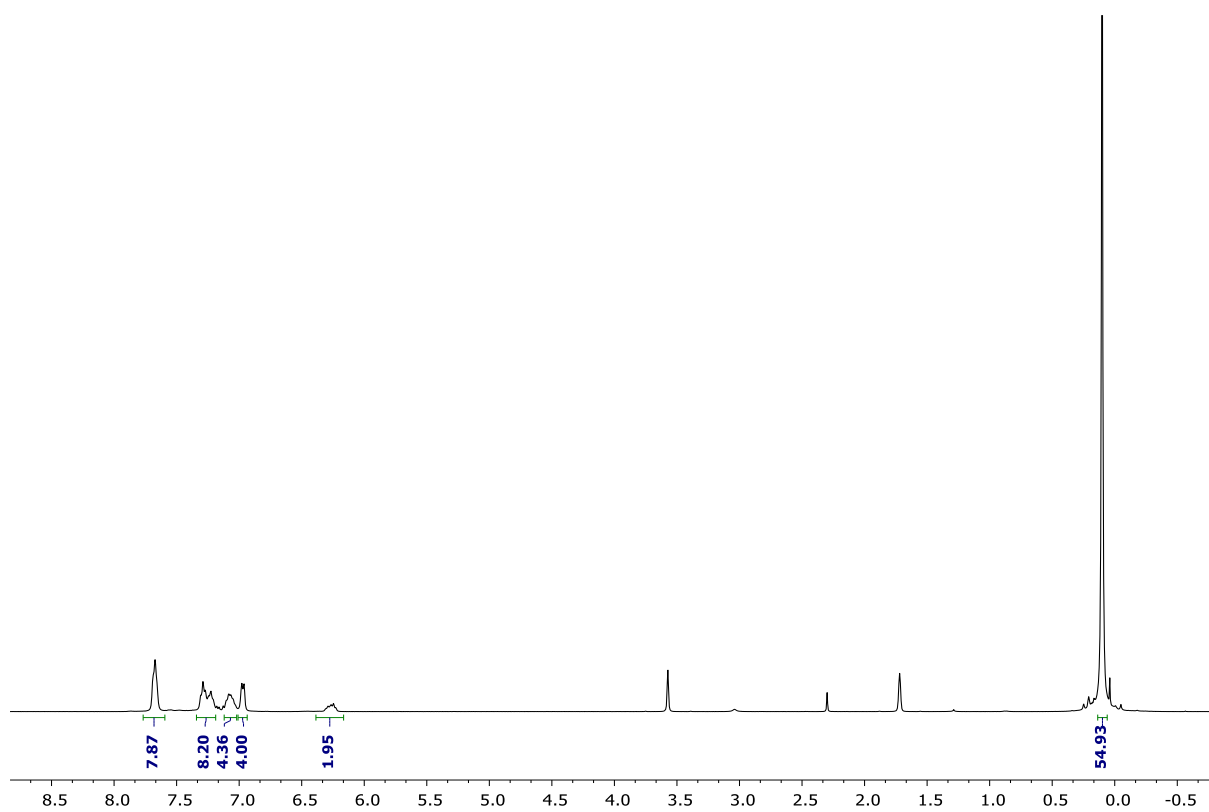


Figure S35. ¹H NMR spectrum (298 K, thf-d₈, 400.13 MHz) of [Ba{μ₂-O(2,6-Ph₂-C₆H₃)}{OSi(SiMe₃)₃}]₂ (**102**).

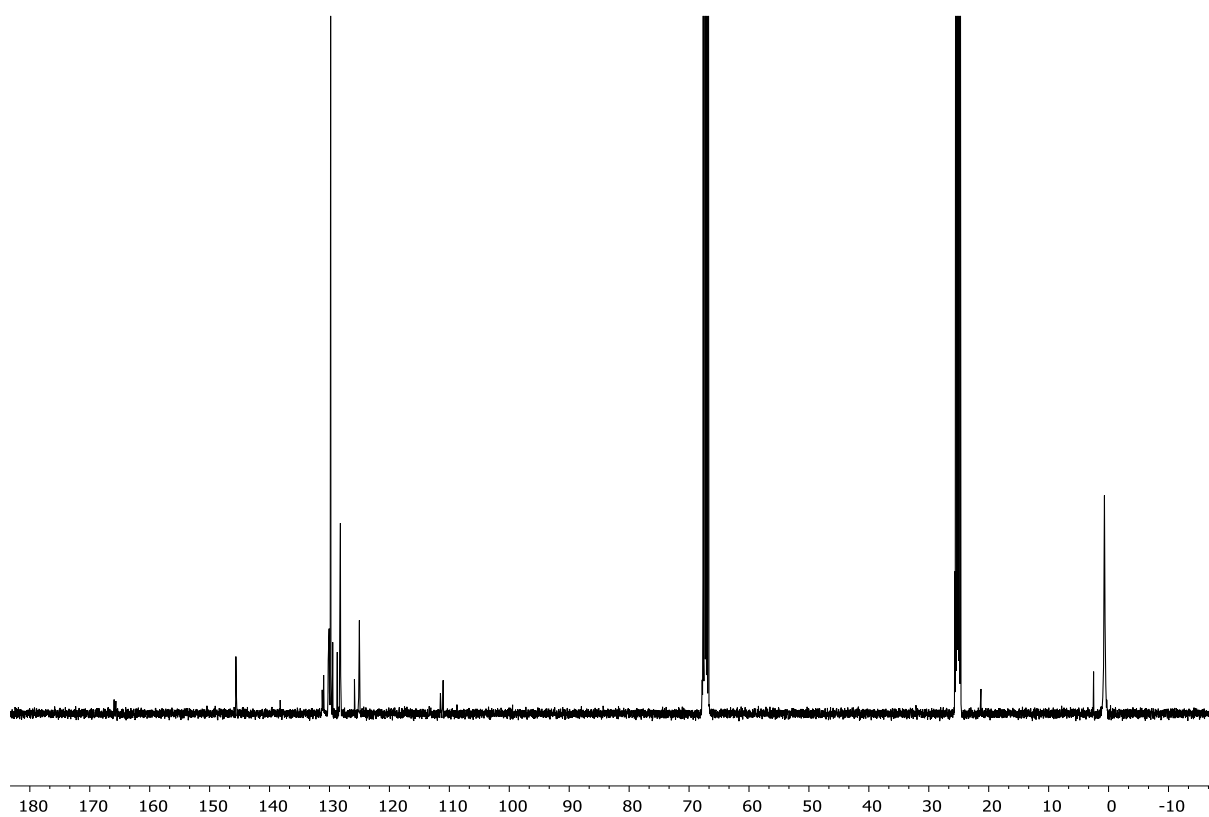


Figure S36. ¹³C{¹H} NMR spectrum (298 K, thf-d₈, 100.62 MHz) of [Ba{μ₂-O(2,6-Ph₂-C₆H₃)}{OSi(SiMe₃)₃}]₂ (**102**).

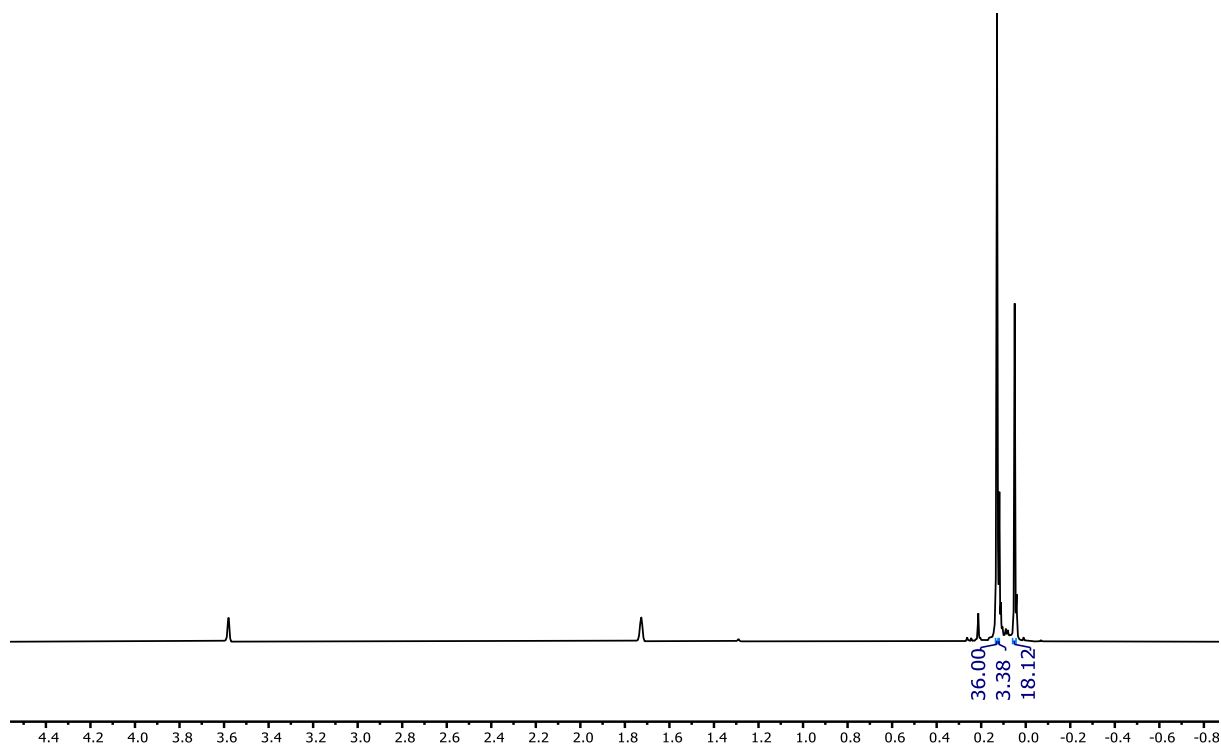


Figure S37. ^1H NMR spectrum (298 K, thf- d_8 , 500.13 MHz) of $[\text{Mg}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2]$ (**112**).

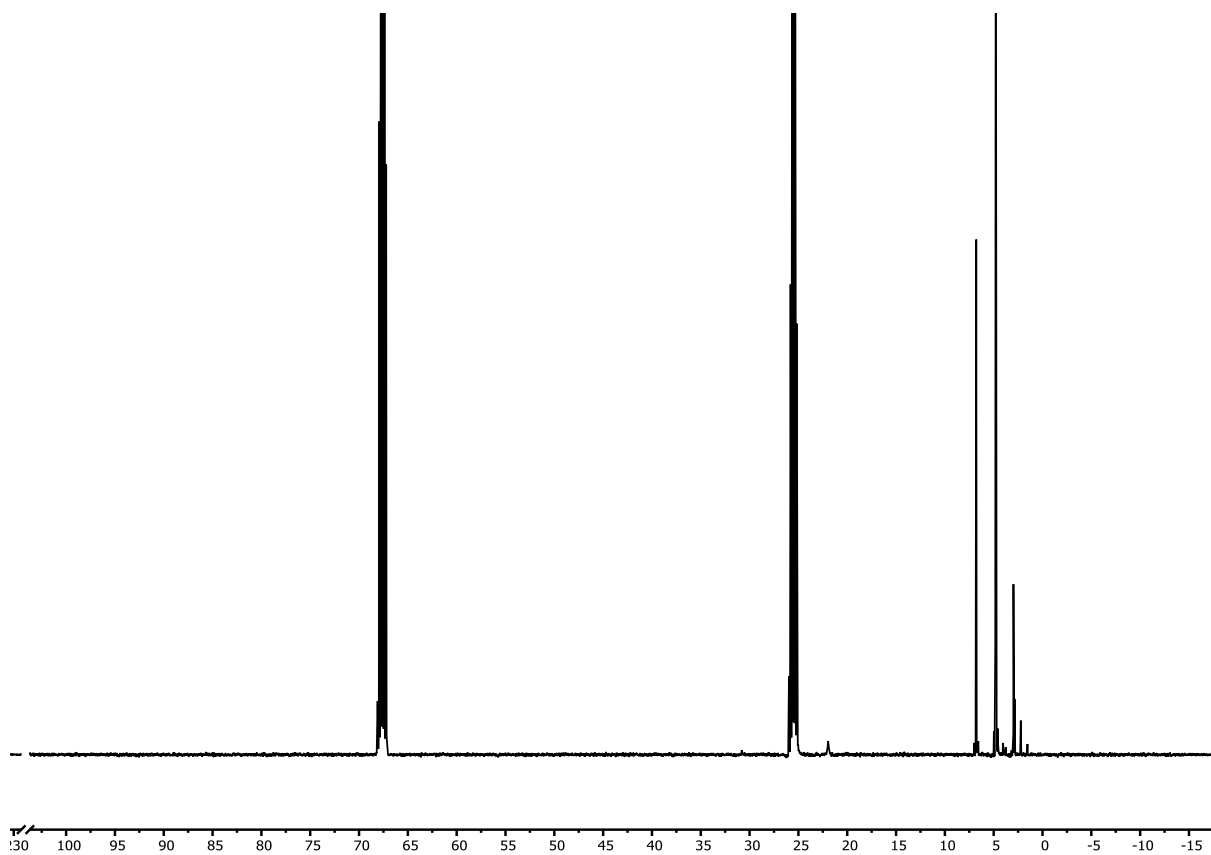


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, thf- d_8 , 125.77 MHz) of $[\text{Mg}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2]$ (**112**).

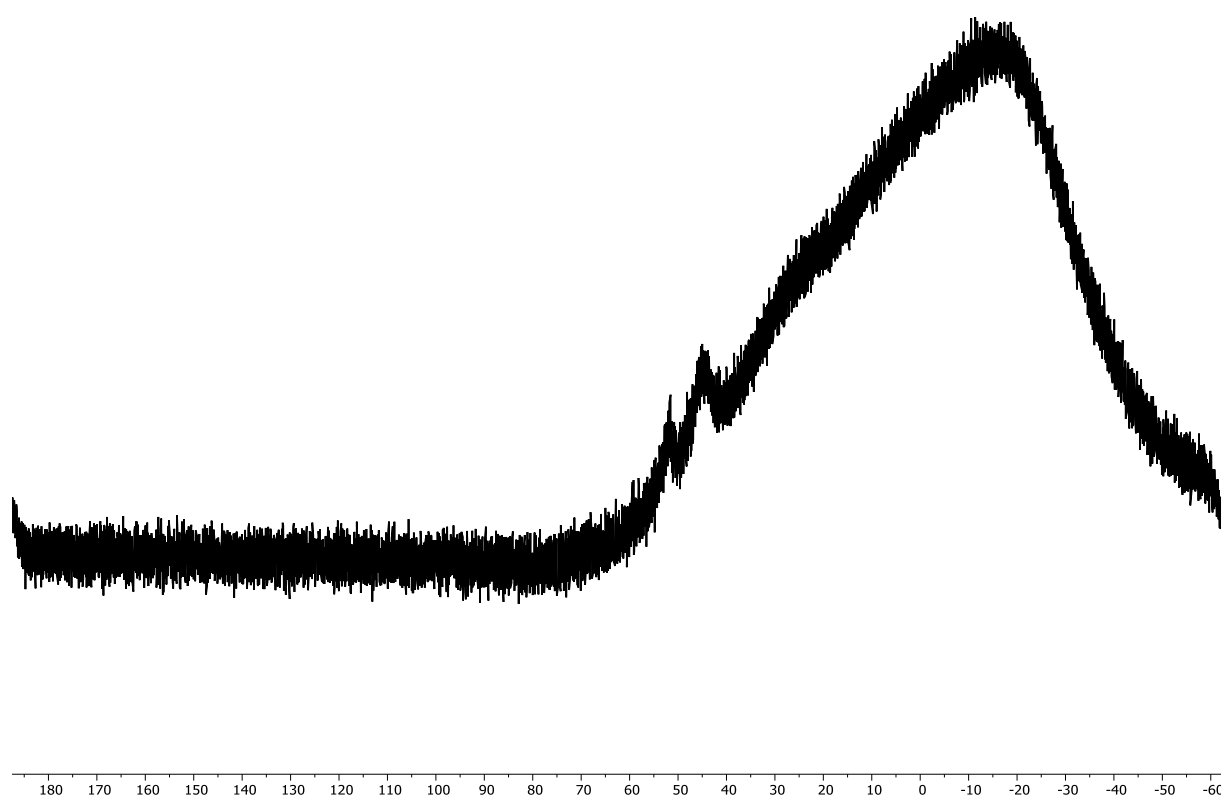


Figure S39. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, thf- d_8 , 128.40 MHz) of $[\text{Mg}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (**11z**).

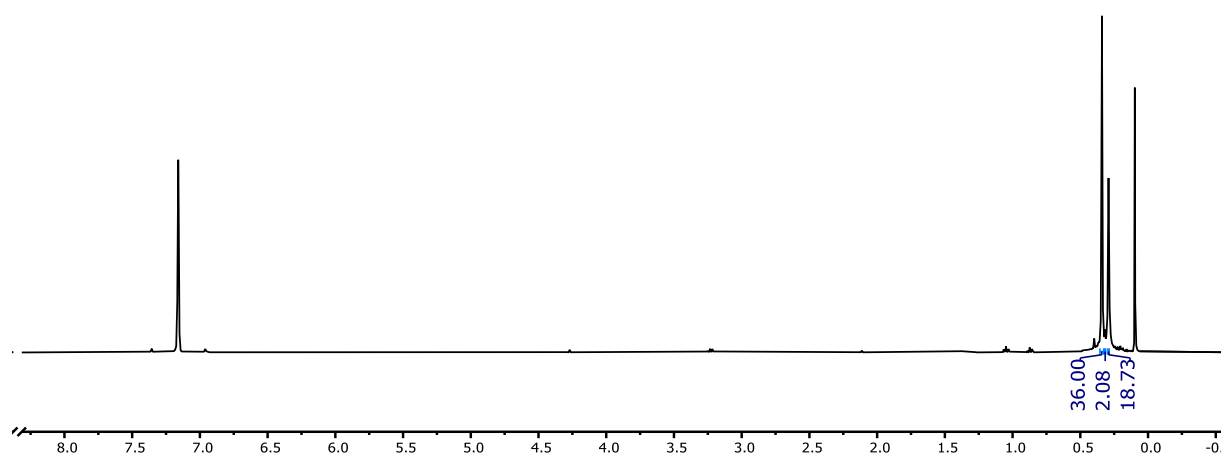


Figure S40. ^1H NMR spectrum (298 K, benzene- d_6 , 400.16 MHz) of $[\text{Ca}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (**12z**).

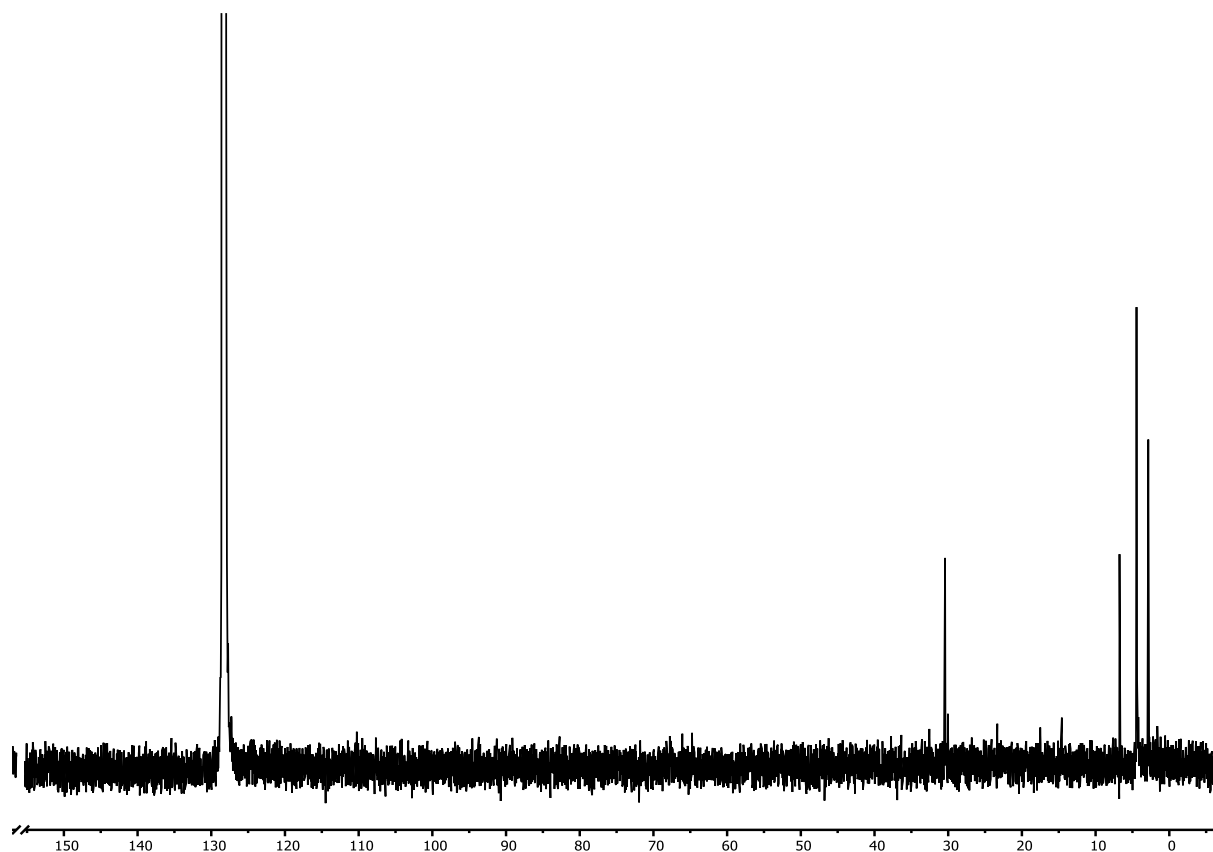


Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 125.77 MHz) of $[\text{Ca}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2$ (**12**).

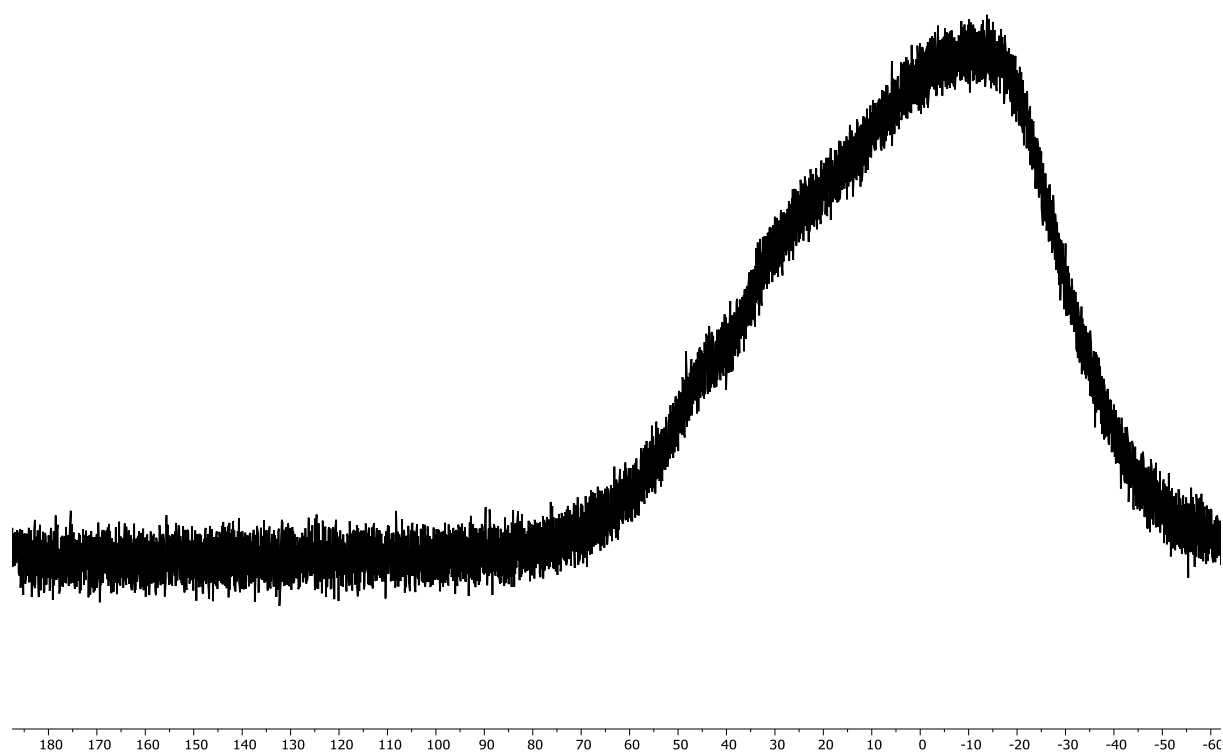


Figure S42. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $[\text{Ca}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2$ (**12**). Repeated attempts to improve the signal-to-noise ratio were unsuccessful, despite reasonable solubility in the selected solvent.

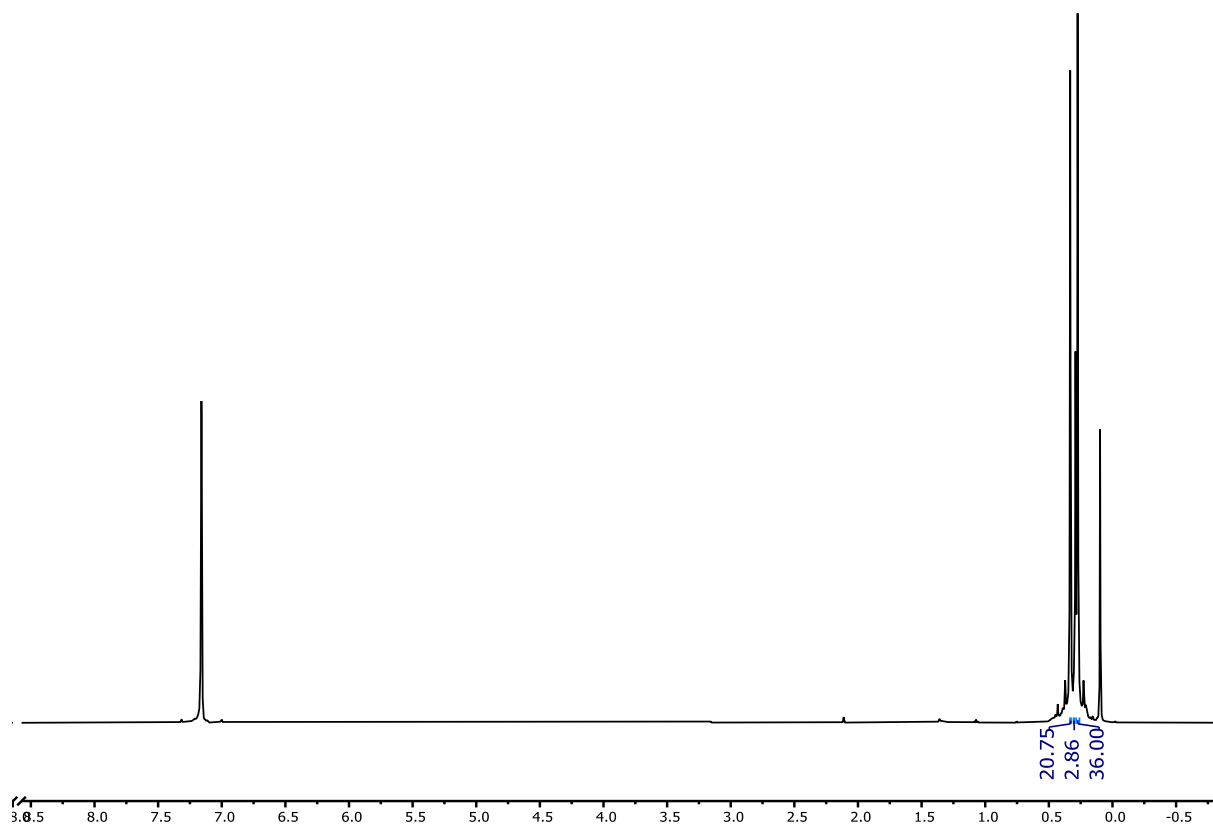


Figure S43. ¹H NMR spectrum (298 K, benzene-d₆, 500.13 MHz) of [Sr{μ₂-N(SiMe₃)₂}(OB{CH(SiMe₃)₂})₂] (13₂).

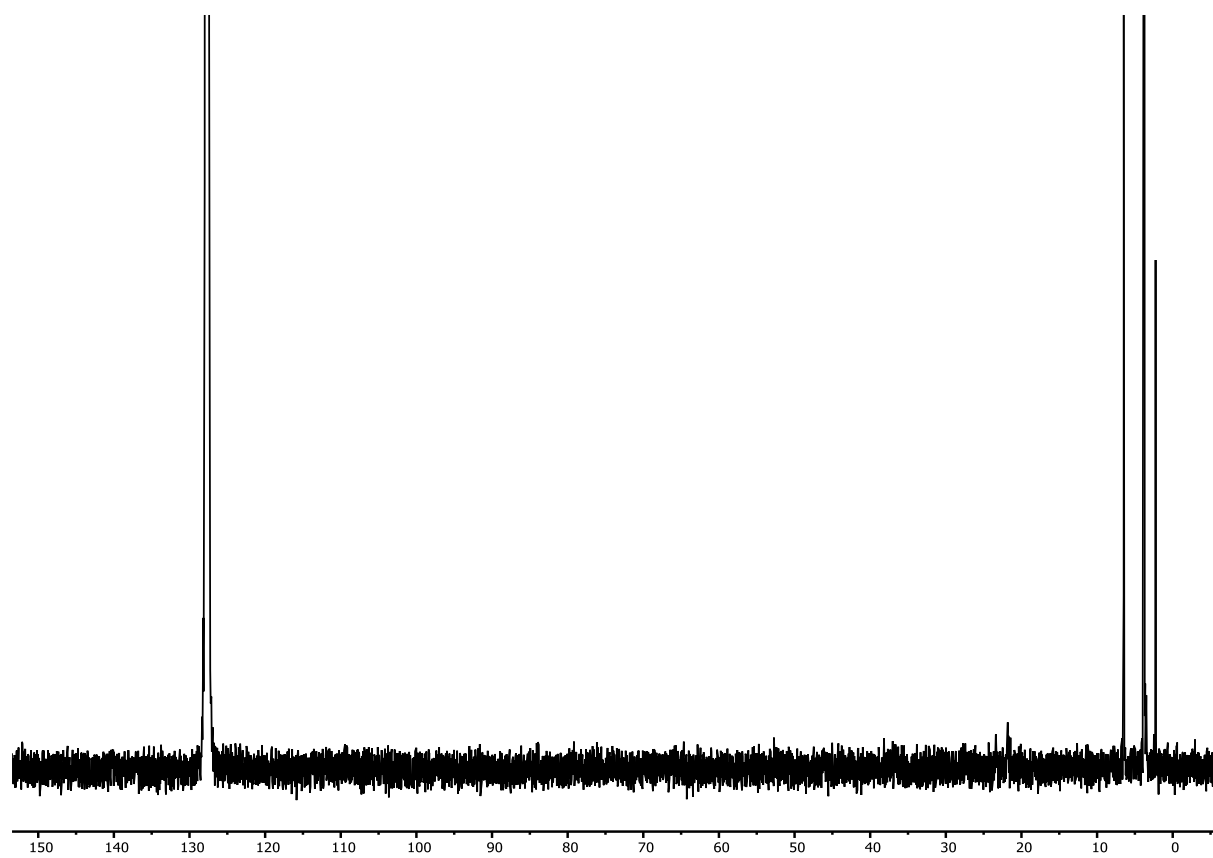


Figure S44. ¹³C{¹H} NMR spectrum (298 K, benzene-d₆, 125.77 MHz) of [Sr{μ₂-N(SiMe₃)₂}(OB{CH(SiMe₃)₂})₂] (13₂).

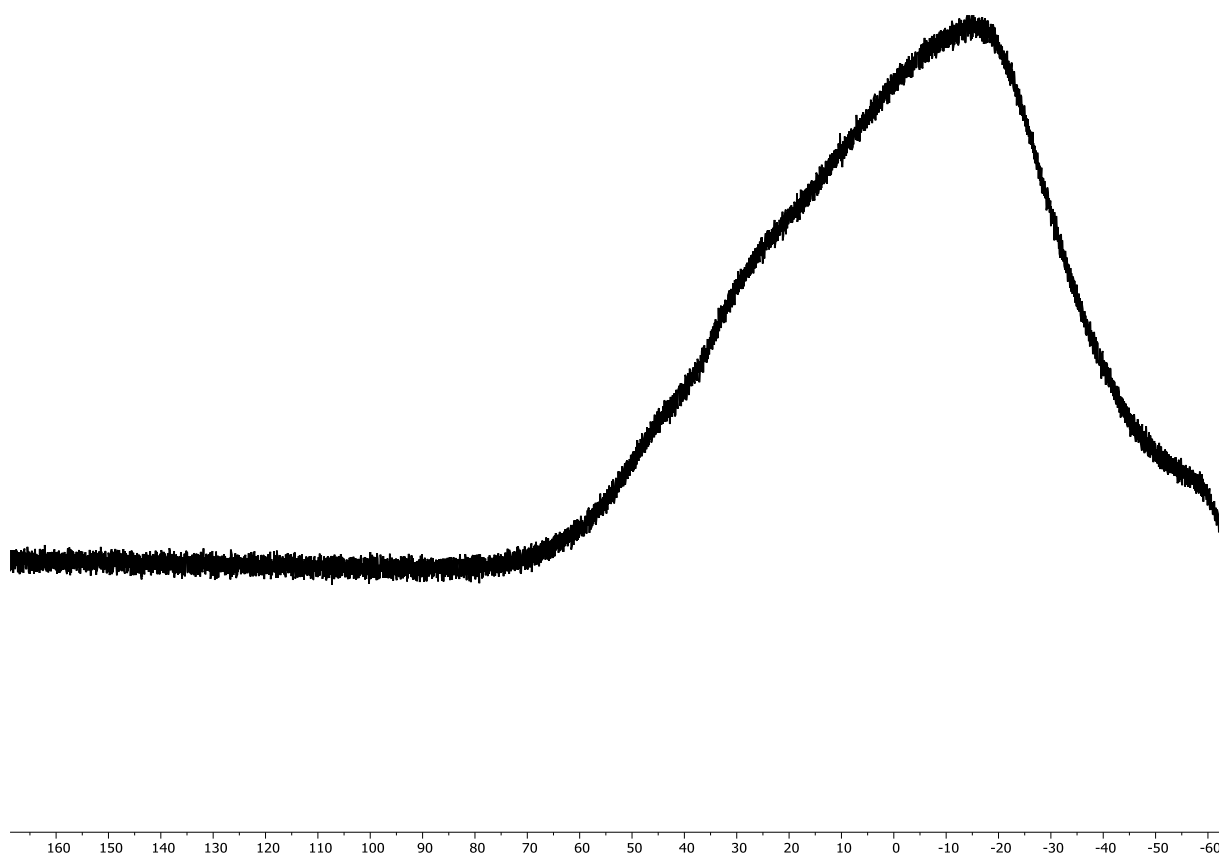


Figure S45. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (298 K, benzene- d_6 , 128.40 MHz) of $[\text{Sr}\{\mu_2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2]$ (**132**). Repeated attempts to improve the signal-to-noise ratio were unsuccessful, despite good solubility in the selected solvent.

Summary of crystallographic data

Compound	Label	Experiment code	CCDC number
[Ba{ μ_2 -OB(Tripp) ₂ }{OB(Tripp) ₂ }] ₂	5₂	ELC325	2032704
[Ba{ μ_2 -OB(Fmes) ₂ }{OB(Fmes) ₂ }] ₂	6₂	ELC438	2032705
[Ba{ μ_2 -OB(Fmes) ₂ }{OB(Fmes) ₂ }.thf] ₂	6₂.(thf)₂	ELC392	2033287
[Ba{ μ_2 -OB(Tripp) ₂ }{N(SiMe ₃) ₂ }] ₂	7₂	ELC326	2032706
[Ba{ μ_2 -OSi(SiMe ₃) ₃ }{OB{CH(SiMe ₃) ₂ }}] ₂	8₂	ELC530	2032707
[Ba{ μ_2 -OB(Tripp) ₂ }{OSi(SiMe ₃) ₃ }] ₂	9₂	ELC542	2032708
[Ba{ μ_2 -O(2,6-Ph ₂ -C ₆ H ₃)}{OSi(SiMe ₃) ₃ }] ₂	10₂	ELC543	2032709
[Mg{ μ_2 -N(SiMe ₃) ₂ }{OB{CH(SiMe ₃) ₂ }}] ₂	11₂	ELC71	2032710
[Ca{ μ_2 -N(SiMe ₃) ₂ }{OB{CH(SiMe ₃) ₂ }}] ₂	12₂	JH230	2032711
[Sr{ μ_2 -N(SiMe ₃) ₂ }{OB{CH(SiMe ₃) ₂ }}] ₂	13₂	JH235	2033281
{(Me ₃ Si) ₂ CH} ₂ BOH	n/a	ELC01	2032967
(Tripp) ₂ BOH	n/a	ELCBA4	2032712
[Ba ₄ (O){OB(mes) ₂ }] ₆	n/a	ELC238	2033317

[Ba{ μ_2 -OB(Tripp)₂}{OB(Tripp)₂}]₂ (5₂): CCDC 2032704. (C₁₂₀ H₁₈₄ B₄ Ba₂ O₄, 2(C₇ H₈)); *M* = 2192.85. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; triclinic *P*-1 (I.T. #2), *a* = 13.6956(10), *b* = 14.2334(11), *c* = 18.4299(14) Å, α = 110.145(2), β = 93.967(3), γ = 109.441(3)°, *V* = 3111.2(4) Å³. *Z* = 1, *d* = 1.170 g.cm⁻³, μ = 0.679 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 14243 unique intensities and 674 parameters converged at $\omega R(F^2)$ = 0.0660 (*R*(*F*) = 0.0266) for 13215 observed reflections with *I* > 2 σ (*I*).

[Ba{ μ_2 -OB(Fmes)₂}{OB(Fmes)₂}]₂ (6₂): CCDC 2032705. (C₃₆ H₈ B₂ Ba F₃₆ O₂); *M* = 1315.38. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; triclinic *P*-1 (I.T. #2), *a* = 12.2726(11), *b* = 14.1399(13), *c* = 14.4862(13) Å, α = 110.717(3), β = 105.629(3), γ = 100.315(3)°, *V* = 2156.8(3) Å³. *Z* = 2, *d* = 2.025 g.cm⁻³, μ = 1.113 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 9859 unique intensities and 694 parameters converged at $\omega R(F^2)$ = 0.1191 (*R*(*F*) = 0.0498) for 8671 observed reflections with *I* > 2 σ (*I*).

[Ba{ μ_2 -OB(Tripp)₂}{N(SiMe₃)₂}]₂ (7₂): CCDC 2032706. (C₇₂ H₁₂₈ B₂ Ba₂ N₂ O₂ Si₄); *M* = 1462.42. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; triclinic *P*-1 (I.T. #2), *a* = 11.2269(11), *b* = 13.8992(12), *c* = 15.0075(14) Å, α = 97.719(3), β = 106.189(3), γ = 104.324(3)°, *V* = 2126.4(3) Å³. *Z* = 1, *d* = 1.142 g.cm⁻³, μ = 1.014 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based

on F^2 (SHELXL).^[15] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,^[16] implemented as the *SQUEEZE* option in *PLATON*.^[17] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 9680 unique intensities and 397 parameters converged at $\omega R(F^2) = 0.0563$ ($R(F) = 0.0264$) for 8490 observed reflections with $I > 2\sigma(I)$.

[Ba{ μ_2 -OSi(SiMe₃)₃}{OB{CH(SiMe₃)₂}₂}]₂ (8₂): CCDC 2032707. (C₄₆H₁₃₀B₂Ba₂O₄Si₁₆); $M = 1493.23$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/n$ (I.T. #14), $a = 19.7976(18)$, $b = 28.577(3)$, $c = 44.682(4)$ Å, $\beta = 92.225(3)^\circ$, $V = 25260(4)$ Å³, $Z = 12$, $d = 1.178$ g.cm⁻³, $\mu = 1.188$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on F^2 (SHELXL).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 57323 unique intensities and 1826 parameters converged at $\omega R(F^2) = 0.1151$ ($R(F) = 0.0582$) for 43841 observed reflections with $I > 2\sigma(I)$.

[Ba{ μ_2 -OB(Tripp)₂}{OSi(SiMe₃)₃}]₂ (9₂): CCDC 2032708. (C₇₈H₁₄₆B₂Ba₂O₄Si₈); $M = 1668.96$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; triclinic $P-1$ (I.T. #2), $a = 12.613(2)$, $b = 14.978(3)$, $c = 15.260(3)$ Å, $\alpha = 114.853(6)$, $\beta = 113.720(6)$, $\gamma = 90.932(7)^\circ$, $V = 2334.5(7)$ Å³, $Z = 1$, $d = 1.187$ g.cm⁻³, $\mu = 0.981$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on F^2 (SHELXL).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 15035 unique intensities and 211 parameters converged at $\omega R(F^2) = 0.3057$ ($R(F) = 0.1271$) for 12822 observed reflections with $I > 2\sigma(I)$.

[Ba{ μ_2 -O(2,6-Ph₂-C₆H₃)}{OSi(SiMe₃)₃}]₂ (10₂): CCDC 2032709. (C₅₄H₈₀Ba₂O₄Si₈); $M = 1292.58$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/c$ (I.T. #14), $a = 12.5058(14)$, $b = 13.4796(16)$, $c = 18.995(2)$ Å, $\beta = 99.327(5)^\circ$, $V = 3159.8(6)$ Å³, $Z = 2$, $d = 1.359$ g.cm⁻³, $\mu = 1.429$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on F^2 (SHELXL).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 7237 unique intensities and 316 parameters converged at $\omega R(F^2) = 0.0672$ ($R(F) = 0.0241$) for 6209 observed reflections with $I > 2\sigma(I)$.

[Sr{ μ_2 -N(SiMe₃)₂}{OB{CH(SiMe₃)₂}₂}]₂ (13₂): CCDC 2033281. (C₄₀H₁₁₂B₂N₂O₂Si₁₂Sr₂); $M = 1187.25$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/c$ (I.T. #14), $a = 18.665(6)$, $b = 17.075(5)$, $c = 23.410(5)$ Å, $\beta = 109.580(11)^\circ$, $V = 7029(3)$ Å³, $Z = 4$, $d = 1.122$ g.cm⁻³, $\mu = 1.751$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on F^2 (SHELXL).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 15885 unique intensities and 585 parameters converged at $\omega R(F^2) = 0.0729$ ($R(F) = 0.0392$) for 10718 observed reflections with $I > 2\sigma(I)$.

[Ba{ μ_2 -OB(Fmes) $_2$ }{OB(Fmes) $_2$ }] $_2$ (6 $_2$.(thf) $_2$): CCDC 2033287. (C $_{80}$ H $_{32}$ B $_4$ Ba $_2$ F $_{72}$ O $_6$, 2(C $_6$ H $_4$ F $_2$)); $M = 3003.16$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150(2)$ K; monoclinic $P2_1/n$ (I.T. #14), $a = 16.9060(12)$, $b = 16.5122(11)$, $c = 18.7667(11)$ Å, $\beta = 93.944(2)^\circ$, $V = 5226.4(6)$ Å 3 . $Z = 2$, $d = 1.908$ g.cm $^{-3}$, $\mu = 0.938$ mm $^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 11863 unique intensities and 790 parameters converged at $\omega R(F^2) = 0.1337$ ($R(F) = 0.0548$) for 9854 observed reflections with $I > 2\sigma(I)$.

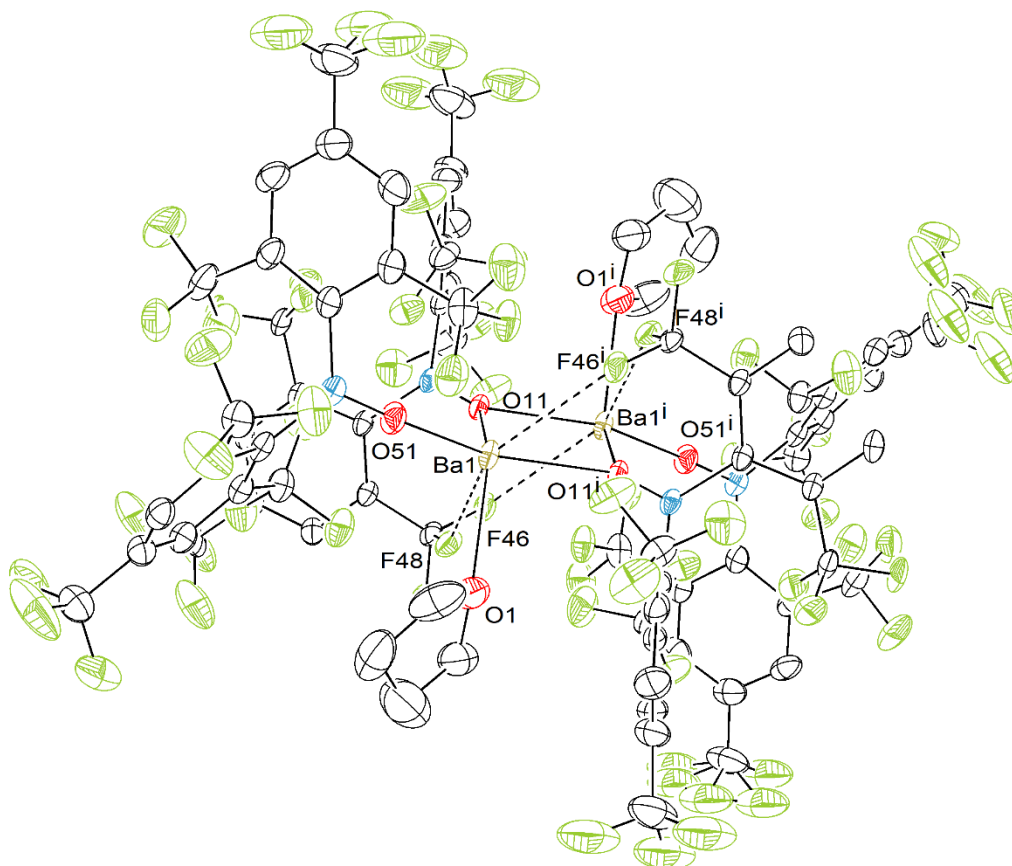


Figure S46. ORTEP representation of the molecular structure of [Ba{ μ_2 -OB(Fmes) $_2$ }{OB(Fmes) $_2$ }.thf] $_2$ (**6 $_2$** .(thf) $_2$). Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Only the most representative Ba \cdots F interactions are depicted. Selected interatomic distances (Å): Ba1-O1 = 2.735(4), Ba1-O11 = 2.598(3), Ba1-O11 i = 2.735(3), Ba1-O51 = 2.460(3), Ba1-F46 = 2.948(3), Ba1-F48 = 3.002(3).

[Mg{ μ_2 -N(SiMe₃)₂}(OB{CH(SiMe₃)₂)₂}]₂ (11₂): CCDC 2032710. (C₄₀ H₁₁₂ B₂ Mg₂ N₂ O₂ Si₁₂); *M* = 1060.63. D8 VENTURE Bruker AXS diffractometer, Mo-K α radiation (λ = 0.71073 Å), *T* = 150 K; triclinic *P*-1 (I.T. #2), *a* = 9.6510(9), *b* = 17.1927(14), *c* = 21.6649(16) Å, α = 110.468(3), β = 96.356(3), γ = 98.758(3)°, *V* = 3276.0(5) Å³. *Z* = 2, *d* = 1.075 g.cm⁻³, μ = 0.287 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on *F*² with 14872 unique intensities and 571 parameters converged at $\omega R(F^2)$ = 0.2791 (*R*(*F*) = 0.1081) for 12537 observed reflections with *I* > 2 σ (*I*).

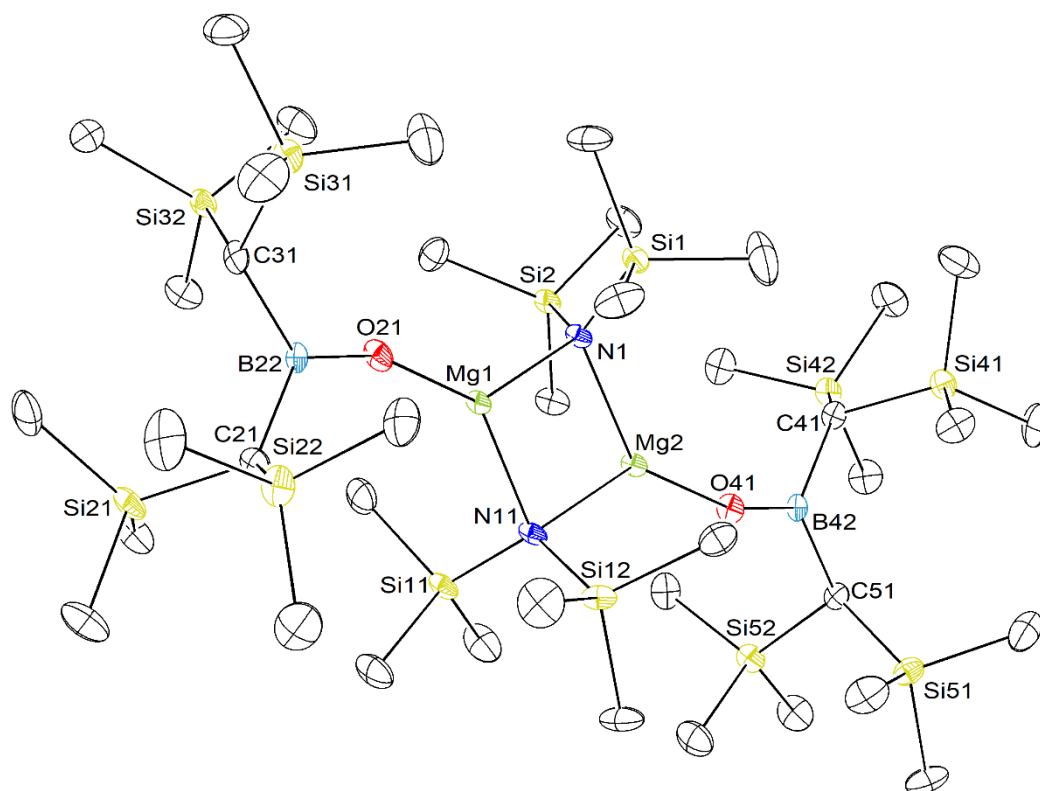


Figure S47. ORTEP representation of the molecular structure of [Mg{ μ_2 -N(SiMe₃)₂}(OB{CH(SiMe₃)₂)₂}]₂ (11₂). Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Selected interatomic distances (Å): Mg1-N1 = 2.107(4), Mg1-N11 = 2.117(4), Mg1-O21 = 1.857(3), Mg2-N1 = 2.132(4), Mg2-N11 = 2.122(4), Mg2-O41 = 1.863(3), O21-B22 = 1.341(5), O41-B42 = 1.351(5). Selected angles (°): B22-O21-Mg1 = 157.4(3), B42-O41-Mg2 = 158.3(3), N1-Mg1-N11 = 91.87(15), N1-Mg1-O21 = 131.46(16), N11-Mg1-O21 = 136.67(15), N1-Mg2-N11 = 91.05(15), N1-Mg2-O41 = 137.88(15), N11-Mg2-O41 = 130.92(16), O21-B22-C21 = 119.5(4), O21-B22-C31 = 120.9(4), C21-B22-C31 = 119.6(3), O41-B42-C41 = 118.2(4), O41-B42-C51 = 121.0(4), C41-B42-C51 = 120.8(3), Mg1-N1-Mg2 = 88.52(14), Mg1-N11-Mg2 = 88.52(14).

[Ca{ μ_2 -N(SiMe₃)₂}(OB{CH(SiMe₃)₂)₂}]₂ (12₂): CCDC 2032711. (C₄₀H₁₁₂B₂Ca₂N₂O₂Si₁₂); *M* = 1092.17. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.460 x 0.240 x 0.130 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-*K* α radiation (λ = 0.71073 Å, multilayer monochromator) at *T* = 150 K. The crystal structure has been described in triclinic symmetry and *P*-1 (I.T. #2) space group. Cell parameters have been refined as follows: *a* = 13.2241(8), *b* = 13.8604(10), *c* = 18.8414(14) Å, α = 96.745(3), β = 91.942(2), γ = 92.818(2)°, *V* = 3422.7(4) Å³. Number of formula unit *Z* is equal to 2 and calculated density *d* and absorption coefficient μ values are 1.060 g.cm⁻³ and 0.406 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 15653 unique intensities and 577 parameters converged at ωR_F^2 = 0.0714 (*R*_F = 0.0289) for 13161 observed reflections with *I* > 2 σ (*I*).

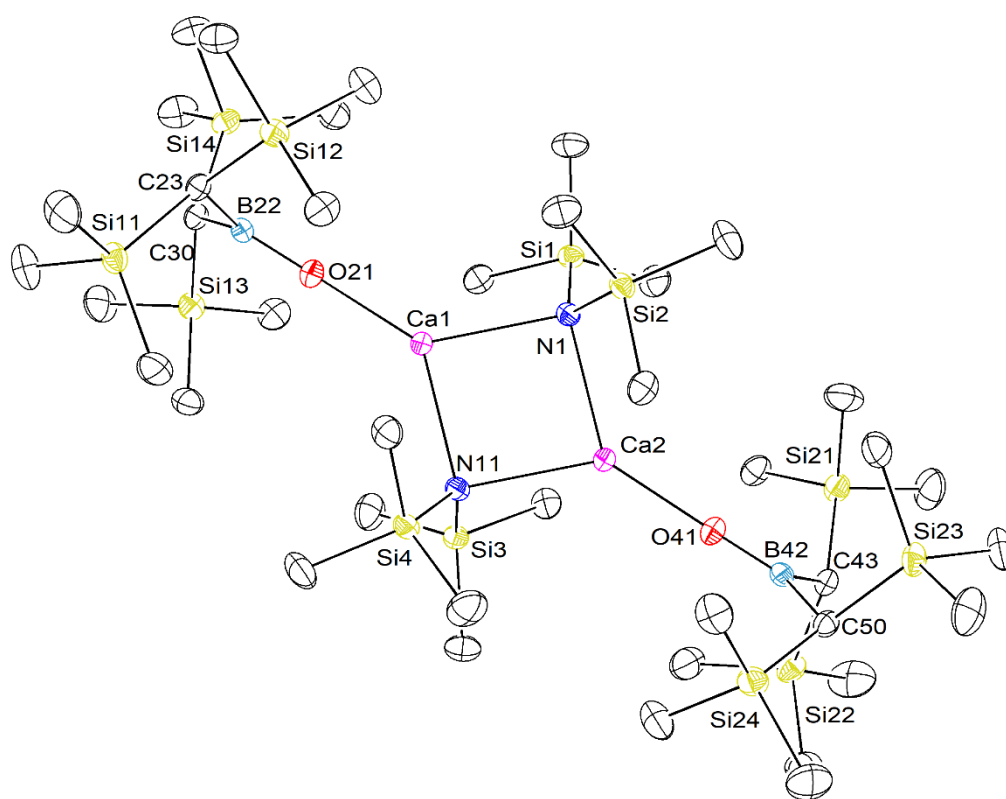


Figure S48. ORTEP representation of the molecular structure of [Ca{ μ_2 -N(SiMe₃)₂}(OB{CH(SiMe₃)₂)₂}]₂ (**12₂**). Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Selected interatomic distances (Å): Ca1-N1 = 2.4399(11), Ca1-N11 = 2.4467(11), Ca1-O21 = 2.1209(9), Ca2-N1 = 2.4471(11), Ca2-N11 = 2.4499(11), Ca2-O41 = 2.1228(10), O21-B22 = 1.3353(17), O41-B42 = 1.3376(18). Selected angles (°): B22-O21-Ca1 = 178.65(9), B42-O41-Ca2 = 178.92(10), N1-Ca1-N11 = 87.44(4), N1-Ca1-O21 = 136.30(4), N11-Ca1-O21 = 136.22(4), N1-Ca2-N11 = 87.21(4), N1-Ca2-O41 = 137.32(4), N11-Ca2-O41 = 135.47(4), O21-B22-C23 = 121.90(12), O21-B22-C30 = 122.17(12), C23-B22-C30 = 115.93(11), O41-B42-C43 = 122.15(12), O41-B42-C50 = 122.14(12), C43-B42-C50 = 115.71(11), Ca1-N1-Ca2 = 92.79(4), Ca1-N11-Ca2 = 92.56(4).

{{(Me₃Si)₂CH}₂BOH: CCDC 2032967. (C₁₄ H₃₉ B O Si₄); *M* = 346.62. D8 VENTURE Bruker AXS diffractometer, Mo-K α radiation (λ = 0.71073 Å), *T* = 150(2) K; monoclinic *P* 2₁/c (I.T. #14), *a* = 15.3175(6), *b* = 10.7879(4), *c* = 14.5323(5) Å, β = 110.8340(10) °, *V* = 2244.36(14) Å³. *Z* = 4, *d* = 1.026 g.cm⁻³, μ = 0.261 mm⁻¹. The structure was solved by dual-space algorithm using the SHELXT program,^[14] and then refined with full-matrix least-square methods based on *F*² (SHELXL-2014).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except 1 linked hydrogen atoms (H2) that was introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on *F*² with 5134 unique intensities and 190 parameters converged at $\omega R(F^2)$ = 0.0726 (*R*(*F*) = 0.0297) for 4285 observed reflections with *I* > 2 σ (*I*).

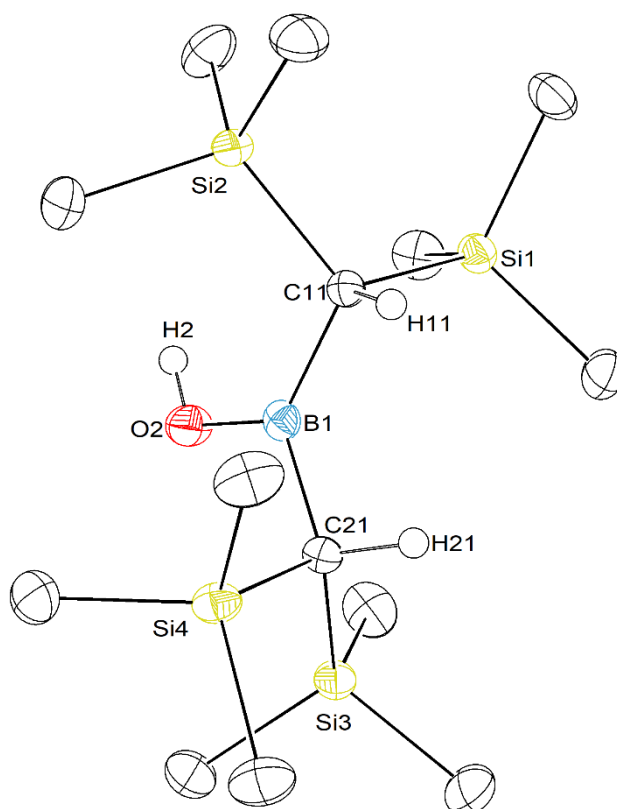


Figure S49. ORTEP representation of the molecular structure of {(Me₃Si)₂CH}₂BOH. Ellipsoids drawn at the 50% probability level. Most H atoms omitted for clarity. Selected interatomic distances (Å): B1-C11 = 1.5757(18), B1-C21 = 1.5727(18), B1-O2 = 1.3805(17). Selected angles (°): C11-B1-C21 = 123.38(11), C11-B1-O2 = 121.44(11), C21-B1-O2 = 115.17(11).

(mes)₂BOH: C₁₈ H₂₃ B O; *M* = 266.17. D8 VENTURE Bruker AXS diffractometer. Mo-K α radiation (λ = 0.71073 Å), *T* = 150 K; monoclinic *C* 2/*c* (I.T. #15), *a* = 22.910(3), *b* = 15.2485(19), *c* = 20.597(3) Å, β = 119.520(5) °, *V* = 6261.1(15) Å³. *Z* = 16, *d* = 1.129 g.cm⁻³, μ = 0.067 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except oxygen linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 7169 unique intensities and 385 parameters converged at $\omega R(F^2)$ = 0.1225 (*R*(*F*) = 0.0504) for 5207 observed reflections with *I* > 2 σ (*I*).

This compound is already referenced as FIBYIY in the CCDC database.^[18]

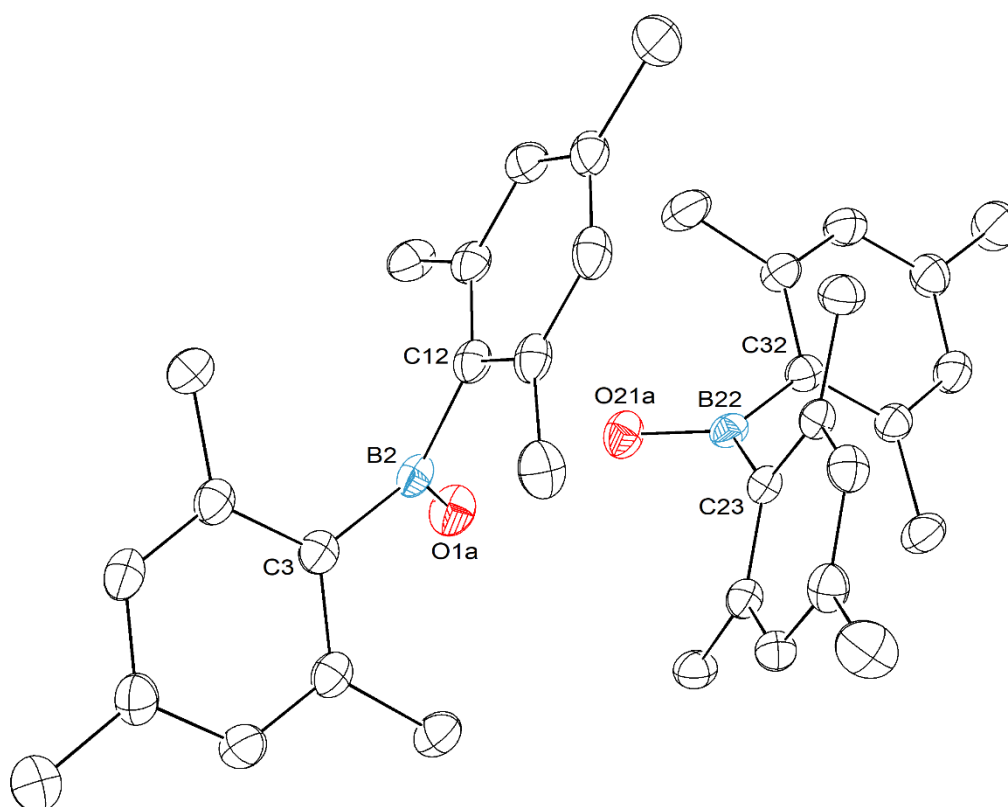


Figure S50. ORTEP representation of the molecular structure of (mes)₂BOH. Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Selected interatomic distances (Å): B2-C3 = 1.582(2), B2-C12 = 1.583(2), B2-O1 = 1.359(2), B22-C23 = 1.586(2), B22-C32 = 1.577(2), B22-O21 = 1.361(2). Selected angles (°): C3-B2-C12 = 126.26(13), C3-B2-O1 = 117.56(14), C12-B2-O1 = 116.17(14), C23-B22-C32 = 125.74(13), C23-B22-O21 = 116.66(14), C32-B22-O21 = 117.58(14).

(Tripp)₂BOH: CCDC 2032712. (C₃₀ H₄₇ B O); *M* = 434.48. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; monoclinic *P* 2₁/c (I.T. #14), *a* = 10.6814(10), *b* = 22.201(2), *c* = 12.5447(10) Å, β = 105.368(3) °, *V* = 2868.4(4) Å³. *Z* = 4, *d* = 1.006 g.cm⁻³, μ = 0.058 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 6333 unique intensities and 291 parameters converged at $\omega R(F^2)$ = 0.2321 (*R*(*F*) = 0.0939) for 4329 observed reflections with *I* > 2 σ (*I*).

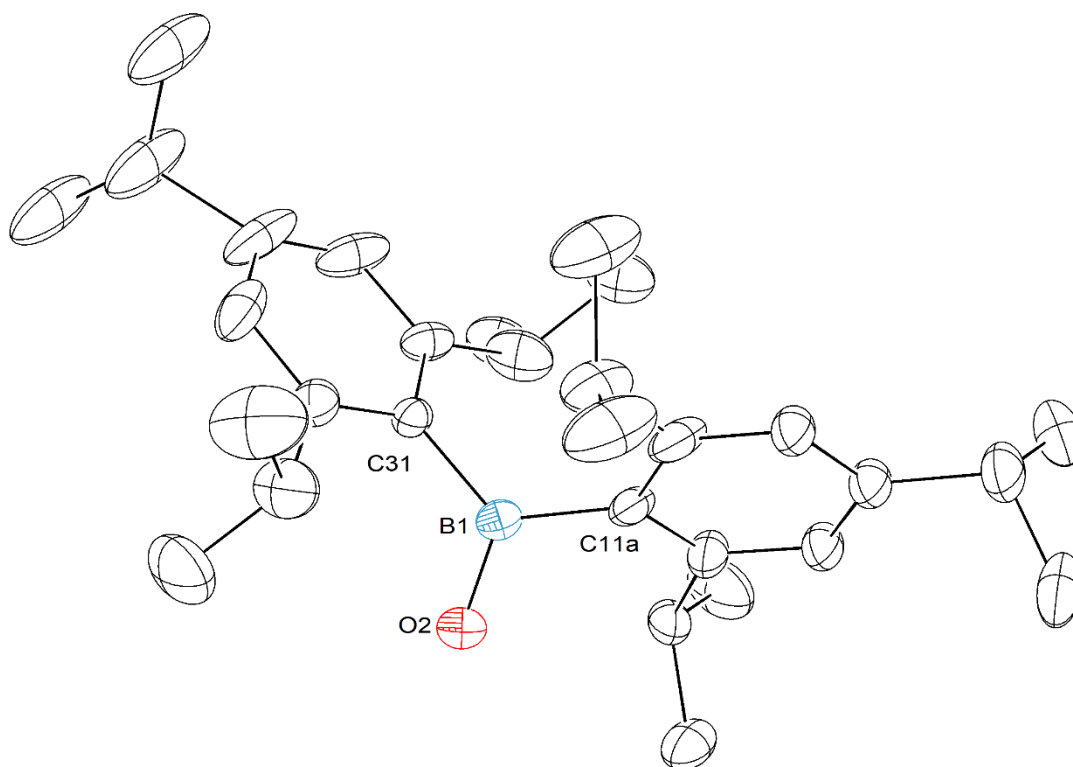


Figure S51. ORTEP representation of the molecular structure of (Tripp)₂BOH. Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Only the most components of disordered aromatic and ¹Pr groups are depicted. Selected interatomic distances (Å): B1-C11A = 1.581(4), B1-C31 = 1.591(3), B1-O2 = 1.360(3). Selected angles (°): C11A-B1-C31 = 124.6(2), C11A-B1-O2 = 115.8(2), C31-B1-O2 = 119.6(2).

(Fmes)₂BOH: C₁₈ H₅ B F₁₈ O; *M* = 590.03. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation (λ = 0.71073 Å, multilayer monochromator), *T* = 150(2) K; triclinic *P*-1 (I.T. #2), *a* = 9.1210(10), *b* = 10.1290(10), *c* = 12.5076(13) Å, α = 112.521(4), β = 99.951(4), γ = 102.629(4)°, *V* = 998.51(18) Å³. *Z* = 2, *d* = 1.962 g.cm⁻³, μ = 0.236 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 4585 unique intensities and 354 parameters converged at $\omega R(F^2)$ = 0.1138 (*R*(*F*) = 0.0437) for 4068 observed reflections with *I* > 2 σ (*I*).

This compound is already referenced as UMUHAL (deposition CCDC 217588) in the CCDC database.^[19]

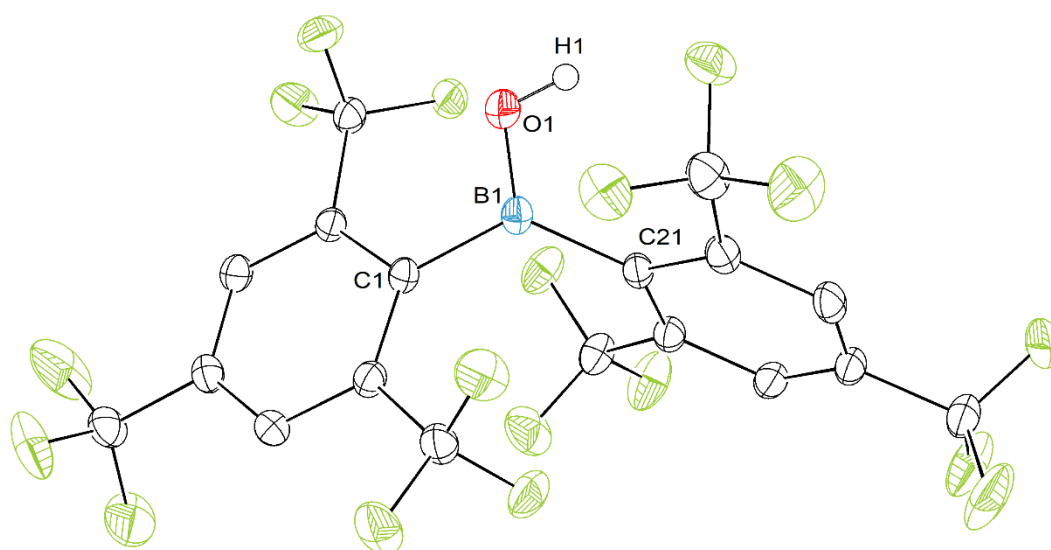


Figure S52. ORTEP representation of the molecular structure of (Fmes)₂BOH. Ellipsoids drawn at the 50% probability level. Most H atoms omitted for clarity. Only the most components of the *p*-CF₃ group is depicted. Selected interatomic distances (Å): B1-C1 = 1.600(2), B1-C21 = 1.612(2), B1-O1 = 1.334(2). Selected angles (°): C1-B1-C21 = 125.76(14), C1-B1-O1 = 112.75(14), C21-B1-O1 = 121.49(15).

$\{(\text{C}_6\text{F}_5)_2\text{BOH}\}_3$: $\text{C}_{36}\text{H}_3\text{B}_3\text{F}_{30}\text{O}_3$; $M = 1085.81$. D8 VENTURE Bruker AXS diffractometer, Mo-K α radiation ($\lambda = 0.71073$ Å), $T = 150(2)$ K; monoclinic $P 2_1/c$ (I.T. #14), $a = 19.528(2)$, $b = 12.9576(16)$, $c = 14.6765(16)$ Å, $\beta = 98.514(5)^\circ$, $V = 3672.8(8)$ Å³. $Z = 4$, $d = 1.964$ g.cm⁻³, $\mu = 0.226$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).^[15] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The 3 linked hydrogen atoms were introduced in the structural model through Fourier difference maps analysis. A final refinement on F^2 with 8398 unique intensities and 658 parameters converged at $\omega R(F) = 0.1635$ ($R(F) = 0.0681$) for 5563 observed reflections with $I > 2\sigma(I)$.

This compound is already referenced as BAVJIS in the CCDC database.^[20]

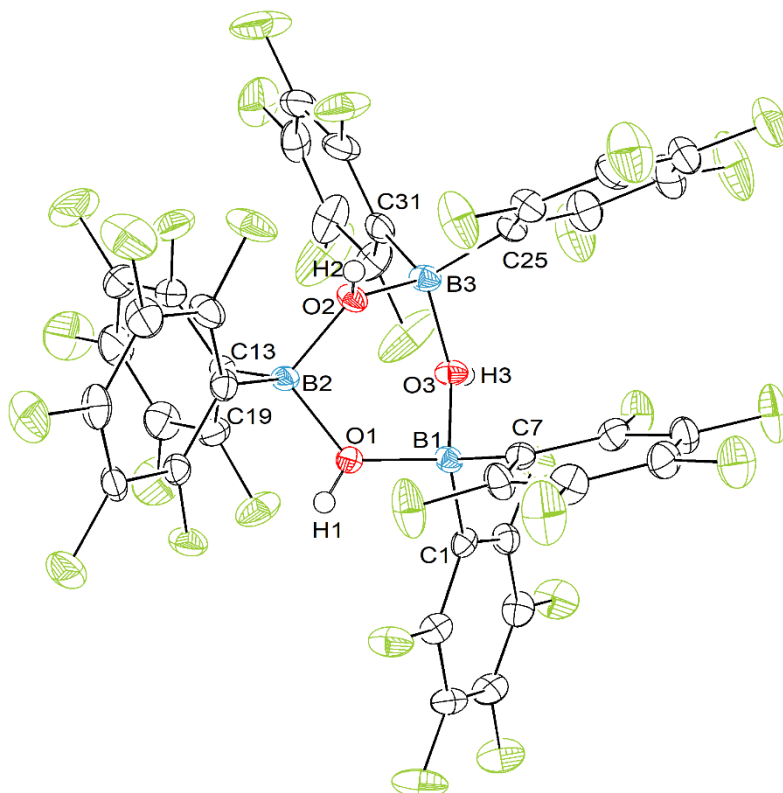


Figure S53. ORTEP representation of the molecular structure of $\{(\text{C}_6\text{F}_5)_2\text{BOH}\}_3$. Ellipsoids drawn at the 50% probability level. Selected interatomic distances (Å): B1-C1 = 1.608(4), B1-C7 = 1.619(4), B1-O1 = 1.524(4), B1-O3 = 1.524(4), B2-C13 = 1.617(5), B2-C19 = 1.616(4), B2-O1 = 1.517(4), B2-O2 = 1.521(4), B3-C25 = 1.616(5), B3-C31 = 1.630(5), B3-O2 = 1.520(4), B3-O3 = 1.524(4). Selected angles ($^\circ$): O1-B1-O3 = 101.30(2), O1-B1-C1 = 109.10(2), O3-B1-C1 = 109.50(2), O1-B1-C7 = 110.90(2), O3-B1-C7 = 111.30(2), C1-B1-C7 = 114.00(2), O1-B2-O2 = 102.00(2), O1-B2-C19 = 110.30(2), O2-B2-C19 = 109.70(2), O1-B2-C13 = 111.10(2), O2-B2-C13 = 110.50(2), C19-B2-C13 = 112.80(2), O2-B3-O3 = 101.10(2), O2-B3-C25 = 110.00(2), O3-B3-C25 = 109.60(3), O2-B3-C31 = 109.50(3), O3-B3-C31 = 109.30(3), C25-B3-C31 = 116.20(3).

[Ba₄(O)(OB(mes)₂)₆]: CCDC 2033317. (C₁₀₈ H₁₃₂ B₆ Ba₄ O₇); *M* = 2156.35. D8 VENTURE Bruker AXS diffractometer Mo-K α radiation (λ = 0.71073 Å), *T* = 150 K; trigonal *R*-3 (I.T. #148), *a* = 21.6204(14), *c* = 43.636(5) Å, *V* = 17665(3) Å³. *Z* = 6, *d* = 1.216 g.cm⁻³, μ = 1.365 mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,^[14] and then refined with full-matrix least-squares methods based on *F*² (*SHELXL*).^[15] The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,^[16] implemented as the *SQUEEZE* option in *PLATON*.^[17] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on *F*² with 8982 unique intensities and 388 parameters converged at $\omega R(F^2)$ = 0.1152 (*R*(*F*) = 0.0471) for 7039 observed reflections with *I* > 2 σ (*I*).

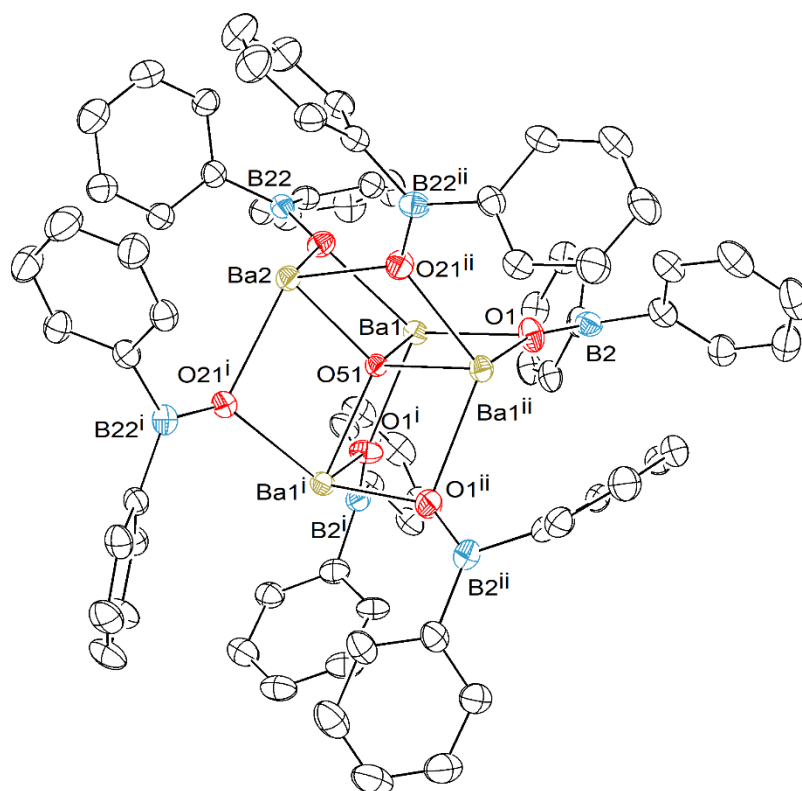


Figure S54. ORTEP representation of the molecular structure of [Ba₄(O)(OB(mes)₂)₆]. H atoms and Me groups omitted for clarity. Ellipsoids drawn at the 50% probability level. Selected interatomic distances (Å): Ba1-O1 = 2.687(3), Ba1-O1ⁱ = 2.575(3), Ba1-O21 = 2.596(3), Ba1-O51 = 2.4768(17), Ba2-O21 = 2.653(3), Ba2-O21ⁱ = 2.653(3), Ba2-O21ⁱⁱ = 2.653(3), Ba2-O51 = 2.461(5).

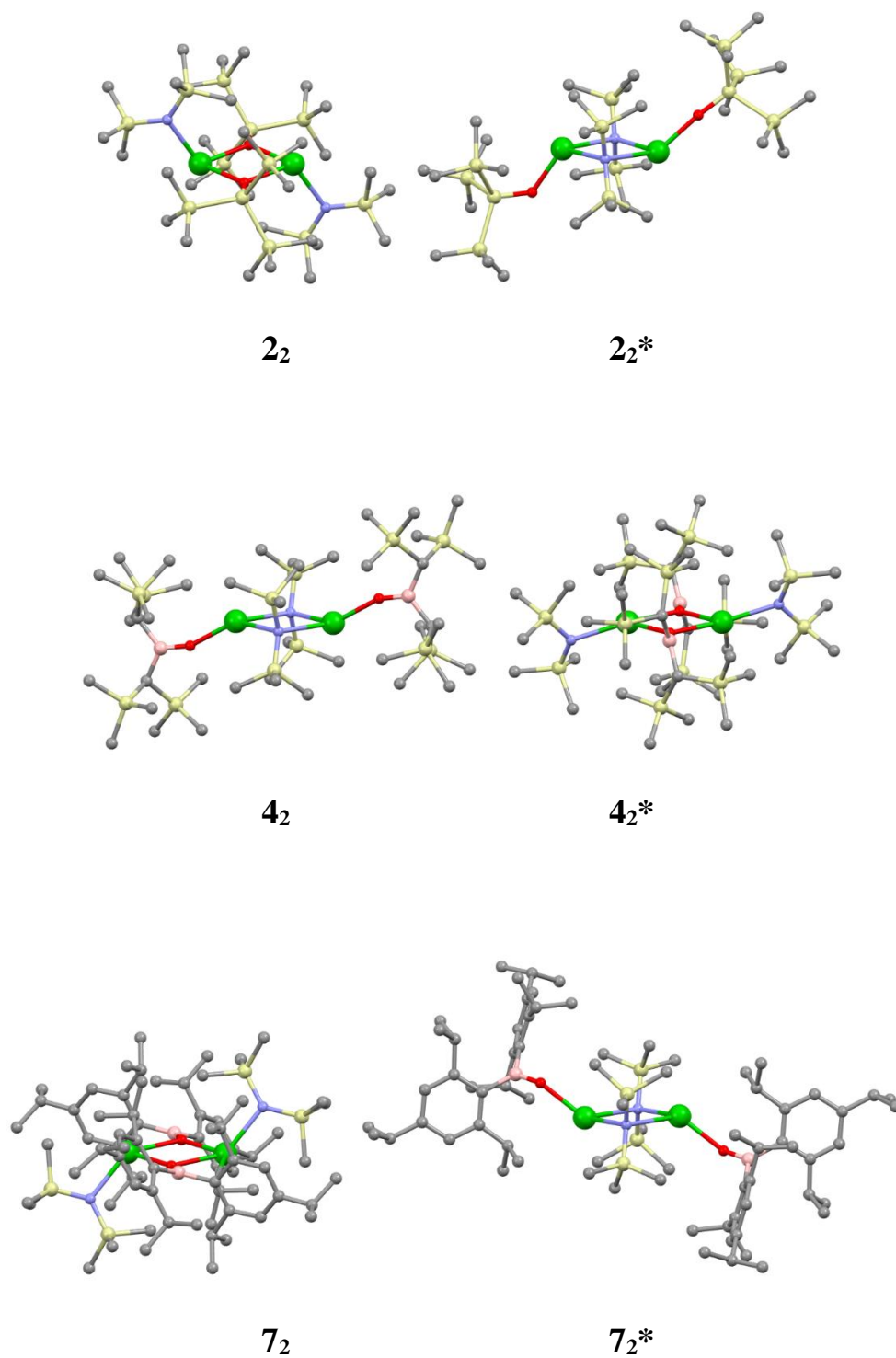


Figure S55. DFT-optimised structures of the $[\text{Ba}(\mu_2\text{-X}_1)(\text{X}_2)]_2$ complexes 2_2 , 4_2 , 7_2 and of their $[\text{Ba}(\mu_2\text{-X}_2)(\text{X}_1)]_2$ isomers 2_2^* , 4_2^* , 7_2^* .

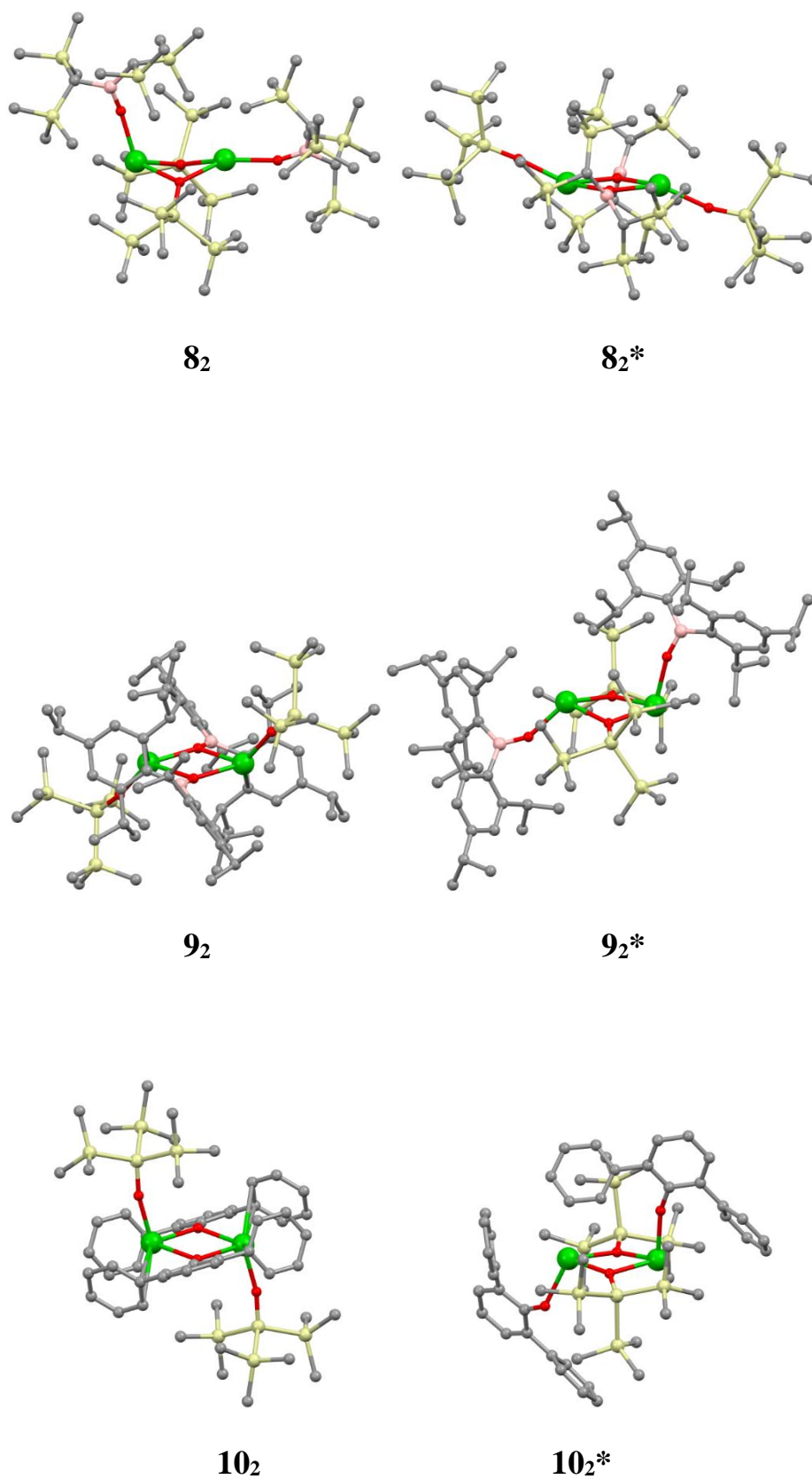


Figure S56. DFT-optimised structures of the $[\text{Ba}(\mu_2\text{-X}_1)(\text{X}_2)]_2$ complexes 8_2 , 9_2 , 10_2 and of their $[\text{Ba}(\mu_2\text{-X}_2)(\text{X}_1)]_2$ isomers 8_2^* , 9_2^* , 10_2^* .

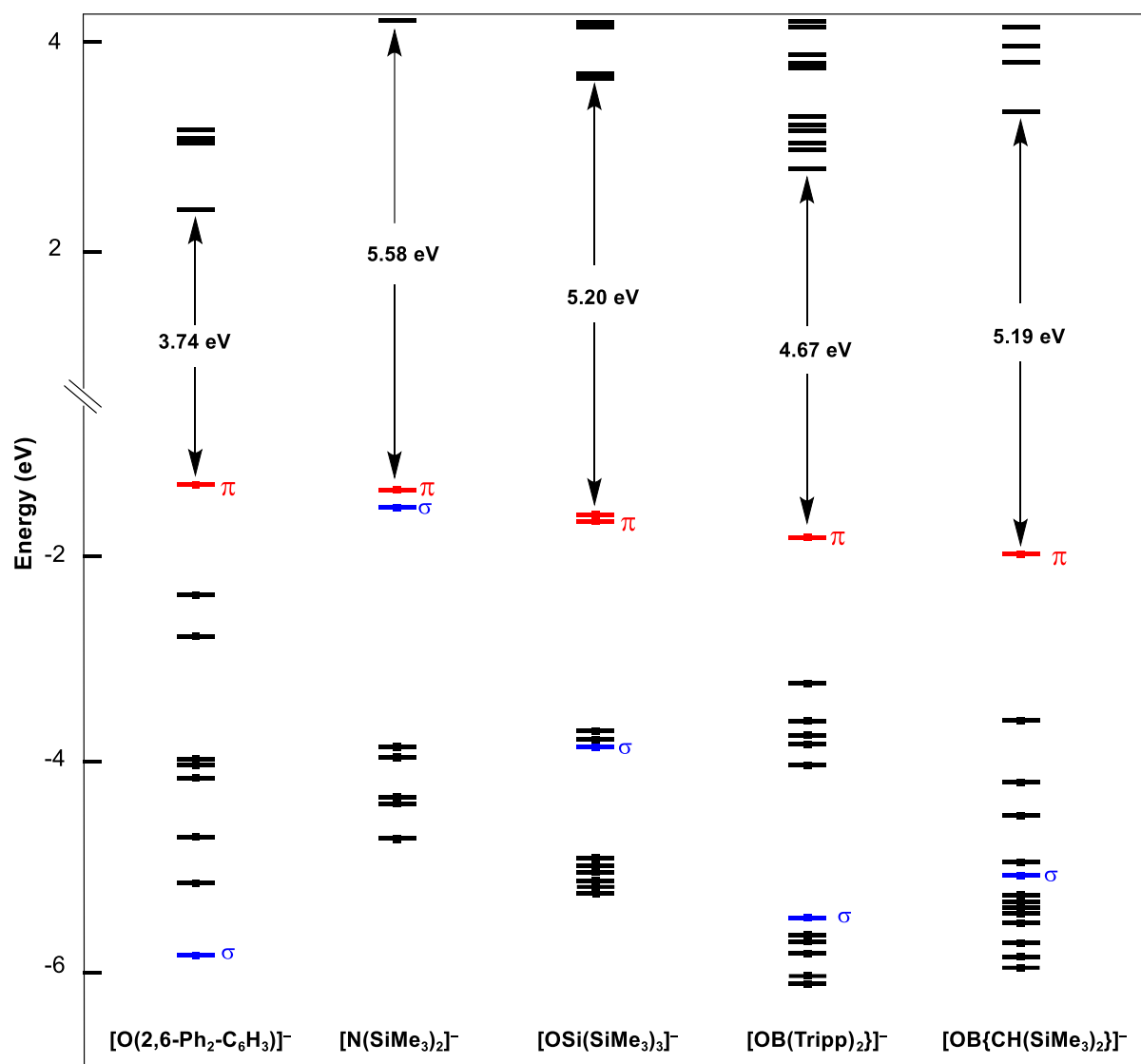


Figure S57. Kohn-Sham MO diagrams of the free ligands.

Detail of DFT calculations

Geometry optimisations at the density functional theory (DFT) level were performed with the Gaussian16 package.^[21] The PBE0 functional^[22] was used together with the general triple- ξ polarised Def2-TZVP basis set from EMSL basis set exchange library.^[23] Grimme's 3-parameter empirical dispersion correction (DFT-D3)^[24] were also applied. Analytical calculations of the vibrational frequencies were performed on all the optimised geometries to verify that these structures are local minima on the potential energy surface. Natural orbital atomic (NAO) populations were computed with the NBO6.0 program.^[25]

References

- [1] J. M. Boncella, C. J. Coston, J. K. Cammack, *Polyhedron* **1991**, *10*, 769.
- [2] M. Westerhausen, *Inorg. Chem.* **1991**, *30*, 96.
- [3] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492.
- [4] E. Le Coz, V. Dorcet, T. Roisnel, S. Tobisch, J.-F. Carpentier, Y. Sarazin, *Angew. Chem. Int. Ed.* **2018**, *57*, 11747.
- [5] E. Le Coz, Z. Zhang, T. Roisnel, L. Cavallo, L. Falivene, J.-F. Carpentier, Y. Sarazin, *Chem. Eur. J.* **2020**, *26*, 3535.
- [6] E. Le Coz, S. Kahlal, J.-Y. Saillard, T. Roisnel, V. Dorcet, J.-F. Carpentier, Y. Sarazin, *Chem. Eur. J.* **2019**, *25*, 13509.
- [7] S. Al-Hashimi, J. D. Smith, *J. Organomet. Chem.* **1978**, *153*, 253.
- [8] H. C. Brown, V. H. Dodson, *J. Am. Chem. Soc.* **1957**, *79*, 2302.
- [9] H. Chen, P. P. Power, S. C. Shoner, *Inorg. Chem.* **1991**, *30*, 2884.
- [10] V. C. Gibson, C. Redshaw, W. Clegg, M. R. J. Elsegood, *Polyhedron* **1997**, *16*, 2637.
- [11] R. D. Chambers, T. J. Chivers, *Chem. Soc.* **1964**, 4782.
- [12] R. D. Chambers, T. J. Chivers, *Chem. Soc.* **1965**, 3933.
- [13] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492.
- [14] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.
- [15] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.
- [16] P. van der Sluis, A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194.
- [17] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7.
- [18] K. J. Weese, R. A. Bartlett, B. D. Murray, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1987**, *26*, 2409.
- [19] S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder, A. L. Thompson, *Dalton Trans.* **2003**, 4395.
- [20] T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli, A. Sironi, *Organometallics* **2003**, *22*, 1588.
- [21] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
- [22] (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; (b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396; (c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
- [23] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [24] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456.
- [25] NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); <http://nbo6.chem.wisc.edu/>

Author Contributions

E. Le Coz and J. Hammoud performed synthetic experimental work and data analysis. T. Roisnel, M. Cordier and V. Dorcet performed the XRD analyses. JY. Saillard and S. Kahlal carried out all computational work and took part to the writing of the draft. JF. Carpentier participated to the design of experiments and analysis of experimental data. Y. Sarazin was the lead investigator; he participated to the design of experiments, analysis of experimental data and writing of the draft.