

Electronic Supporting Information for:

A versatile nitrogen ligand for alkaline-earth chemistry

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Experimental Procedures

General Considerations:

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O₂<1 ppm, H₂O<3 ppm). THF was distilled under argon from Na/benzophenone prior to use. Hexanes, toluene, and Et₂O were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 4 Å molecular sieves and degassed by a minimum of three freeze–thaw cycles. NMR spectra were recorded with Bruker AM-300, AM-400 or AM-500 spectrometers at 25 °C unless otherwise noted. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent or to an external standard in [D₆]benzene or [D₈]toluene: Si(SiMe₃)₄ for ²⁹Si{¹H} NMR, [Sn{N(SiMe₃)₂]₂ for ¹¹⁹Sn{¹H} NMR. Assignment of the signals was assisted by 1D (¹H, ¹³C) and 2D (COSY, HMBC, and HMQC) NMR experiments. [Ae{N(SiMe₃)₂]₂·(thf)_x] (Ae = Ca, Sr, Ba, x = 0, 2),¹ {Carb^{DiPP}}H,² [Ba{CH(SiMe₃)₂]₂·(thf)₂,³ [Ba{N(SiMe₂H)₂]₂·(thf)₄,⁴ [K{Carb^{DiPP}}·(thf)₂],² [Ca{CH(SiMe₃)₂]₂·(thf)₂,³ and [Sn(SiMe₃)₄],⁴ were prepared via adaptations to the literature procedures. Phenylsilane was purchased from Fluorochem and purified by distillation. All other chemicals were provided by commercial suppliers and used as received. Combustion analysis of the complexes could not be carried out reliably and reproducibly due to their extreme air- and moisture-sensitivity.

[{Carb^{DiPP}}BaN(SiMe₃)₂·thf] (6)

To a stirred solution of [Ba{N(SiMe₃)₂]₂·(thf)₂] (0.62 g, 1.03 mmol) in toluene (10 mL) at room temperature, a solution of {Carb^{DiPP}}H (0.65 g, 1.00 mmol) in toluene (10 mL) was added dropwise. The resulting bright yellow suspension was stirred at room temperature overnight. The resulting suspension was dried under reduced pressure and washed with hexanes (2 × 5 mL) to give a bright yellow powder. Recrystallisation of the washings room temperature gave crystals suitable for an X-ray diffraction study. Yield: (powder + crystals) 952 mg (93%).

¹H NMR (400.16 MHz, [D₈]toluene): δ 8.63 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, CH-Carb); 8.49 (s, 2H, CH=N); 7.63 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, CH-Carb); 7.11–7.06 (m, 6H, Ar-H); 3.19 (hept, $J_{\text{HH}} = 6.7$ Hz, 4H, CH(CH₃)₂); 2.88 (m, 4H, 2,5-CH₂, thf); 1.46 (s, 18H, C(CH₃)₃); 1.27 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, CH(CH₃)₂); 1.19 (m, 4H, 3,4-CH₂, thf); 1.11 (d, $J_{\text{HH}} = 6.6$ Hz, 12H, CH(CH₃)₂); –0.13 (s, 18H, Si(CH₃)₃) ppm.

¹³C{¹H} NMR (100.63 MHz, [D₈]toluene): δ 172.5 (CH=N); 149.8 (Ar-C); 149.2 (Ar-C); 140.8 (C4-H Carb); 139.0 (Ar-C); 132.3 (C2-H Carb); 129.5 (Ar-C); 126.3 (Ar-C); 124.6 (Ar-C); 123.0 (Ar-C); 120.3 (Ar-C); 67.8 (2,5-CH₂, thf); 34.9 (C(CH₃)₃); 32.5 (C(CH₃)₃); 29.3 (CH(CH₃)₂); 25.8 (CH(CH₃)₂); 25.7 (3,4-CH₂, thf); 24.1 (CH(CH₃)₂); 6.0 (Si(CH₃)₃) ppm.

[{Carb^{DiPP}}BaCH(SiMe₃)₂·thf] (7)

Method A: To a Young's NMR tube loaded with [Ba{CH(SiMe₃)₂]₂·(thf)₂] (30 mg, 0.05 mmol) and {Carb^{DiPP}}H (28 mg, 0.04 mmol) was added 0.5 mL of [D₆]benzene. The Young's tube was sealed and briefly shaken resulting in a yellow solution. After 4 h at room temperature crystals suitable for an X-ray diffraction study began to grow. Yield: 28 mg (69%).

Method B: A Schlenk vessel was loaded with [Ba{CH(SiMe₃)₂]₂·(thf)₂] (300 mg, 0.50 mmol) and {Carb^{DiPP}}H (300 mg, 0.46 mmol) and dissolved in toluene (20 mL). The solution was left to stir at room temperature for 1 h before being

concentrated under reduced pressure to 5 mL. Crystallisation from the crude reaction mixture gave the desired compound in low yield. Attempts to completely remove the volatiles under reduced pressure resulted in the decomposition of the product to a mixture of inseparable products. Yield: 219 mg (43%).

^1H NMR (400.16 MHz, $[\text{D}_8]$ toluene): δ 8.63 (d, $J_{\text{HH}} = 2.1$ Hz, 2H, **CH**-Carb); 8.47 (s, 2H, **CH**=N); 7.62 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, **CH**-Carb); 7.07-7.03 (m, 6H, **Ar-H**); 3.29 (m, 4H, 2,5-**CH**₂, thf); 3.17 (hept, $J_{\text{HH}} = 7.0$ Hz 4H, **CH-CH**(**CH**₃)₂); 1.47 (s, 18H, **C**(**CH**₃)₃); 1.33 (m, 4H, 3,4-**CH**₂, thf); 1.23 (d, $J_{\text{HH}} = 6.2$ Hz, 12H, **CH**(**CH**₃)₂); 1.10 (d, $J_{\text{HH}} = 6.7$ Hz, 12H, **CH**(**CH**₃)₂); -0.16 (s, 18H, (**Si**(**CH**₃)₃)); -1.84 (s, 1H, **CH**(**Si**(**CH**₃)₃)₂ ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, $[\text{D}_8]$ toluene): δ 172.6 (**CH**=N); 150.0 (**Ar-C**); 148.9 (**Ar-C**); 140.9 (**C**4-H Carb); 139.1 (**Ar-C**); 132.3 (**C**2-H Carb); 129.5 (**Ar-C**); 126.3 (**Ar-C**); 124.5 (**Ar-C**); 123.2 (**Ar-C**); 120.1 (**Ar-C**); 68.2 (3,4-**CH**₂, thf); 34.9 (**C**(**CH**₃)₃); 32.9 (**CH**(**SiMe**₃)₂); 32.6 (**C**(**CH**₃)₃); 29.5 (**CH**(**CH**₃)₂); 26.0 (**CH**(**CH**₃)₂); 25.8 (3,4-**CH**₂, thf); 24.1 (**CH**(**CH**₃)₂); 5.79 (**Si**(**CH**₃)₃) ppm.

[{Carb^{DiPP}}BaN(SiMe₂H)₂·thf] (8a)

Method A: In a glove-box, a Young's NMR tube was loaded with [Ba(N(SiMe₂H)₂·(thf)₄] (36 mg, 0.05 mmol) and {Carb^{DiPP}}H (32 mg (0.05 mmol). The tube was removed from the glove-box, connected to a Schlenk line and the contents were dissolved in deuterated toluene (0.5 mL). The tube was sealed, shaken briefly and then heated to 50 °C overnight using an aluminium heating block. Small crystals had grown around the edge of the solvent that were suitable for an X-ray diffraction study.

Method B: A solution of {Carb^{DiPP}}H (440 mg, 0.67 mmol) in diethyl ether (10 mL) was added to a solution of [Ba{N(SiMe₂H)}]_n (300 mg, 0.75 mmol) in diethyl ether (20 mL) and thf (0.5 mL), and then stirring at room temperature overnight was ensured. The solution was concentrated to 5 mL and moved to a -30 °C freezer. Small crystals of the desired compound grew over 20 h, however they were contaminated with a small amount of [Ba{N(SiMe₂H)}₂]_n. Further recrystallisation did not purify the compound. As such, this method is not recommended for the synthesis of **8a**. Yield: 312 mg (47%).

Method C: A solution of {Carb^{DiPP}}H (216 mg, 0.33 mmol) in diethyl ether (10 mL) was added to a solution of [Ba{N(SiMe₂H)}]_n (132 mg, 0.33 mmol) in diethyl ether (20 mL) and stirred at room temperature overnight. The volatiles were removed under reduced pressure to give to give crude [{Carb^{DiPP}}Ba(N(SiMe₂H)₂·Et₂O]. The solid was redissolved in minimal thf and stirred for 30 min. Removal of the volatiles gave the desired product as a pale orange solid. Yield: 283 mg (87%).

^1H NMR (500.13 MHz, $[\text{D}_6]$ benzene): δ 8.70 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **Ar-H**); 8.47 (s, 2H, **CH**=N); 7.66 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **Ar-H**); 7.14-7.06 (m, 6H, **Ar-H**); 4.58 (hept, $^1J_{\text{HSi}} = 160.7$ Hz, $J_{\text{HH}} = 2.8$ Hz, 2H, **Si-H**); 3.21 (hept, $J_{\text{HH}} = 6.8$ Hz, 2H, **CH**(**CH**₃)₂); 2.99 (m, 4H, 2,5-**CH**₂, thf); 1.45 (s, 18H, **C**(**CH**₃)₃); 1.31 (d, $J_{\text{HH}} = 7.0$ Hz, 12H, **CH**(**CH**₃)₂); 1.13 (m, 16H, **CH**(**CH**₃)₂ and 3,4-**CH**₂, thf); -0.03 (d, 12H, $J_{\text{HH}} = 2.9$ Hz, **SiH**(**CH**₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $[\text{D}_6]$ benzene) δ 171.7 (**CH**=N); 149.2 (**Ar-C**); 148.8 (**Ar-C**); 140.4 (**Ar-C**); 138.4 (**Ar-C**); 132.0 (**Ar-C**); 128.6 (**Ar-C**); 125.9 (**Ar-C**); 124.2 (**Ar-C**); 122.7 (**Ar-C**); 119.9 (**Ar-C**); 67.7 (2,5-**CH**₂, thf); 34.5 (**C**(**CH**₃)₃); 32.2 (**C**(**CH**₃)₃); 28.9 (**CH**(**CH**₃)₂); 25.6 (**CH**(**CH**₃)₂); 25.3 (3,4 **CH**₂, thf); 23.7 (**CH**(**CH**₃)₂); 4.6 (**SiH**(**CH**₃)₂).

$^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (79.49 MHz, $[\text{D}_6]$ benzene, 298 K): δ -28.9 (**SiMe**₂H) ppm.

FTIR (Nujol mull in KBr): $\tilde{\nu}(\text{Si-H}) = 2949.3$ (s); 2898.1 (m); 2873.1 (m); 2857.7 (m); 2118.5 (w); 1998.3 (s); 1940.5 (m); 1456.3 (w); 1377.2 (w); 1290.9 (s); 1098.5 (s); 1044.5 (m); 972.1 (s); 887.2 (s); 832.3(s); 819.8 (s); 777.4 (s); 753.2 (s); 676.1 (w); 625.0 (w).

[{Carb^{DiPP}}BaN(SiMe₂H)₂·Et₂O] (8b)

A solution of {Carb^{DiPP}}H (793 mg, 1.21 mmol) in diethyl ether (10 mL) was added to a solution of [Ba{N(SiMe₂H)}]_n (500 mg, 1.25 mmol) in diethyl ether (20 mL) and stirred at room temperature overnight. The volatiles were removed under reduced pressure to give to give crude [{Carb^{DiPP}}Ba(N(SiMe₂H)₂·Et₂O)] as a yellow solid. Recrystallisation of the sample from hexanes gave crystals suitable for an X-ray diffraction study. Yield: 703 mg (58%).

¹H NMR (500.13 MHz, [D₆]benzene): δ 8.69 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, Ar-H); 8.43 (s, 2H, CH=N); 7.62 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, Ar-H); 7.20-7.17 (m, 6H, Ar-H); 4.44 (hept, $^1J_{\text{HSi}} = 160.0$ Hz, $J_{\text{HH}} = 2.8$ Hz, 2H, Si-H); 3.21-3.13 (m, 8H, CH(CH₃)₂ and CH₃CH₂O); 1.45 (s, 18H, C(CH₃)₃); 1.35 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, CH(CH₃)₂); 1.12 (d, $J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)); 1.04 (t, 6H, CH₃CH₂O); -0.11 (d, $J_{\text{HH}} = 2.9$ Hz, 12H, SiH(CH₃)₂).

¹³C{¹H} NMR (125.77 MHz, [D₆]benzene): δ 172.1 (CH=N); 149.9 (Ar-C); 148.6 (Ar-C); 140.4 (Ar-C); 138.5 (Ar-C); 132.0 (Ar-C); 128.5 (Ar-C); 126.2 (Ar-C); 124.3 (Ar-C); 122.6 (Ar-C); 119.8 (Ar-C); 65.6 (CH₃CH₂O); 34.5 (C(CH₃)₃); 32.2 (C(CH₃)₃); 28.9 (CH(CH₃)₂); 25.7 (CH(CH₃)₂); 23.5 (CH(CH₃)₂); 15.4 (CH₃CH₂O); 4.5 (SiH(CH₃)₂).

²⁹Si{¹H} INEPT NMR (79.49 MHz, [D₆]benzene, 298 K): δ -28.4 (SiMe₂H) ppm.

FTIR (Nujol mull in KBr): $\tilde{\nu}(\text{Si-H}) = 2969.6$ (s); 2870.0 (s); 2021.4(m); 1604.8 (s); 1558.4(s); 1465.9(s); 1373.3(m); 1234.4 (m); 1141.8 (s); 895.0(s); 756.1(m).

[{Carb^{DiPP}}SrN(SiMe₃)₂] (9)

To a stirred solution of [Sr{N(SiMe₃)₂}]₂ (300 mg, 0.73 mmol) in toluene (20 mL) at room temperature a solution of {Carb^{DiPP}}H (456 mg, 0.70 mmol) in toluene (10 mL) was added dropwise. The resulting bright yellow suspension was stirred at 60 °C for 2 days. The suspension was filtered off and the resulting yellow solution was concentrated to 3 mL and layered with hexanes (2 mL). After 2 days at room temperature, a crop of X-ray quality crystals was obtained as yellow blocks. Yield: (powder + crystals) 413 mg (65%).

¹H NMR (400.16 MHz, [D₆]benzene): δ 8.66 (d, $J_{\text{HH}} = 2.1$ Hz, 2H, CH-Carb); 8.53 (s, 2H, CH=N); 7.68 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, CH-Carb); 7.19-7.11 (m, 6H, Ar-H); 3.19 (hept, $J_{\text{HH}} = 6.8$ Hz 4H, CH(CH₃)₂); 1.43 (s, 18H, C(CH₃)₃); 1.36 (d, $J_{\text{HH}} = 6.7$ Hz, 12H, CH(CH₃)₂); 1.13 (d, $J_{\text{HH}} = 6.5$ Hz, 12H, CH(CH₃)₂); -0.15 (s, 18H, Si(CH₃)₃) ppm.

¹³C{¹H} NMR (100.63 MHz, [D₆]benzene): δ 173.7 (CH=N); 148.7 (Ar-C); 148.5 (Ar-C); 140.1 (C4-H Carb); 139.4 (Ar-C); 132.3 (C2-H Carb); 128.4 (Ar-C); 126.7 (Ar-C); 124.7 (Ar-C); 123.3 (Ar-C); 119.2 (Ar-C); 34.5 (C(CH₃)₃); 32.1 (C(CH₃)₃); 29.6 (CH(CH₃)₂); 25.8 (CH(CH₃)₂); 23.8 (CH(CH₃)₂); 5.4 (Si(CH₃)₃) ppm.

[{Carb^{DiPP}}SrN(SiMe₃)₂·thf] (10)

To a stirred solution of [Sr{N(SiMe₃)₂}₂.thf₂] (500 mg, 0.90 mmol) in toluene (20 mL), at room temperature, a solution of {Carb^{DiPP}}H (534 mg, 0.81 mmol) in toluene (20 mL) was added dropwise. The resulting bright yellow suspension was stirred at 60 °C for 4 days. The suspension was filtered off, and the resulting yellow solution was concentrated, layered with hexanes (2 mL) and left to crystallise. After 2 days at room temperature, a crop of X-ray quality crystals was obtained as yellow blocks. Yield (powder + crystals): 488 mg (62%).

¹H NMR (400.16 MHz, [D₈]toluene): δ 8.60 (d, *J*_{HH} = 2.0 Hz, 2H, Ar-H); 8.53 (s, 2H, CH=N); 7.66 (d, *J*_{HH} = 1.9 Hz, Ar-H); 7.15 (m, 6H, Ar-H); 3.43 (m, 4H, 2,5-CH₂, thf); 3.38 (hept, *J*_{HH} = 6.5 Hz, 4H, CH(CH₃)₂); 1.43 (s, 18H C(CH₃)₃); 1.37 (m, 4H, 3,4-CH₂, thf); 1.34 (d, *J*_{HH} = 7.1 Hz, 12H, CH(CH₃)₂); 1.12 (d, *J*_{HH} = 6.7 Hz, 12H, CH(CH₃)₂); -0.19 (s, 18H, Si(CH₃)₃) ppm.

¹³C{¹H} NMR (100.63 MHz, [D₈]toluene): δ 174.1 (CH=N); 149.6 (Ar-C); 149.2 (Ar-C); 140.5 (C4-H Carb); 139.6 (Ar-C); 132.5 (C2-H Carb); 129.6 (Ar-C); 127.0 (Ar-C); 125.0 (Ar-C); 123.3 (Ar-C); 119.6 (Ar-C); 68.3 (2,5-CH₂, thf); 34.9 (C(CH₃)₃); ; 32.5 (C(CH₃)₃); 29.8 (CH(CH₃)₂); 26.1 (CH(CH₃)₂); 26.0 (3,4-CH₂, thf); 24.1 (CH(CH₃)₂); 5.9 (Si(CH₃)₃) ppm.

[{Carb^{DiPP}}CaI.thf] (11)

A Schlenk vessel was loaded with CaI₂ (527 mg, 1.79 mmol) and [K{Carb^{DiPP}}.thf₂] (1.00 g, 1.20 mmol), suspended in thf (30 mL) and left to stir overnight. The volatiles were then removed under reduced pressure and the residue extracted into toluene (2 × 20 mL). The suspension was filtered to give a dark yellow solution and the volatiles were removed under reduced pressure. The resulting bright yellow powder was deemed suitably pure by ¹H NMR spectroscopy. Recrystallisation of this sample from hexanes gave crystal suitable for X-ray diffraction study. Yield: 920 mg (78%).

¹H NMR (300.13 MHz, [D₆]benzene): δ 8.64 (d, *J*_{HH} = 2.0 Hz, 2H, Carb-H); 8.44 (s, 2H, CH=N); 7.61 (d, *J*_{HH} = 1.9 Hz, 2H, Carb-H); 7.17-7.15 (m, 6H m-C₆H₃); 3.29-3.15 (m, 8H, CH(CH₃)₂, 2,5-CH₂, thf); 1.42 (s, 18H, C(CH₃)₃); 1.39 (d, *J*_{HH} = 7.0 Hz, 6H, CH(CH₃)₂); 1.11 (d, *J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂); 0.85 (m, 4H, 3,4-CH₂, thf) ppm.

¹³C{¹H} NMR (75.48 MHz, [D₆]benzene): δ 173.9 (CH=N); 149.7 (Ar-C); 148.3 (Ar-C); 140.4 (Ar-C); 139.7 (Ar-C); 131.7 (Ar-CH); 129.3 (Ar-C); 127.8 (C₆H₃); 126.5 (Ar-CH); 124.2 (Ar-C); 123.2 (Ar-C); 119.1 (Ar-C); (Ar-C); 69.7 (2,5-CH₂, thf); 34.6 (C(CH₃)₃); 32.1 (C(CH₃)₃); 29.5 (CH(CH₃)₂); 25.3 (CH(CH₃)₂); 24.8 (3,4-CH₂, thf); 23.5 (CH(CH₃)₂) ppm.

[{Carb^{DiPP}}CaCH(SiMe₃)₂.thf] (12)

Method A: To a Young NMR tube loaded with [Ca{CH(SiMe₃)₂}₂.(thf)₂] (30 mg, 0.06 mmol) and {Carb^{DiPP}}H (42 mg, 0.07 mmol) was added 0.5 mL of [D₈]toluene. The Young NMR tube was sealed and briefly shaken resulting in a yellow solution. After 2 days at room temperature, crystals suitable for an X-ray diffraction study began to grow on the walls of the tube.

Method B: [Ca{CH(SiMe₃)₂}₂.(thf)₂] (503 mg, 0.99 mmol) and the {Carb^{DiPP}}H (640 mg, 0.98 mol) were added to a Schlenk vessel with stir bar in a glovebox. The Schlenk flask was sealed and taken out of the glovebox and connected to a Schlenk manifold. Toluene (50 mL) was added via cannula. The reaction was heated to 80 °C and for 2 days. The volatiles were removed under reduced pressure, and the resulting yellow-orange solid was washed with hexane (2 × 4

mL). The resulting yellow powder was dried thoroughly under reduced pressure to give $[\{\text{Carb}^{\text{DiPP}}\}\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}\cdot\text{thf}]$. Yield: 847 mg (92%).

^1H NMR (400.16 MHz, $[\text{D}_6]$ benzene): δ 8.63 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **CH**-Carb); 8.54 (s, 2H, **CH**=N); 7.67 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **CH**-Carb); 7.12 (m, 6H, **Ar-H**); 3.24 (m, 4H, 2,5-**CH**₂, thf); 3.24 (hept, $J_{\text{HH}} = 6.3$ Hz, 4H, **CH**(CH₃)₂); 1.43 (s, 18H, C(CH₃)₃); 1.30 (d, $J_{\text{HH}} = 6.7$ Hz, 12H, CH(CH₃)₂); 1.12 (m, 4H, 3,4-**CH**₂, thf); 1.10 (d, $J_{\text{HH}} = 6.0$ Hz, 12H, CH(CH₃)₂); -0.10 (s, 18H, **SiMe**₃); -1.75 (s, 1H, **CH**(Si(CH₃)₃)₂) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, $[\text{D}_6]$ benzene): δ 174.1 (**CH**=N); 150.1 (**Ar-C**); 148.8 (**Ar-C**); 140.5 (**C4-H** Carb); 139.9 (**Ar-C**); 131.4 (**C2-H** Carb); 129.3 (**Ar-C**); 126.6 (**Ar-C**); 124.5 (**Ar-C**); 123.4 (**Ar-C**); 118.9 (**Ar-C**); 68.6 (2,5-**CH**₂, thf); 34.6 (C-(CH₃)₃); 32.1 (C(CH₃)₃); 29.4 (**CH**(CH₃)₂); 26.0 (CH(CH₃)₂); 25.3 (3,4-**CH**₂, thf); 23.5 (CH(CH₃)₂); 16.6 (**CH**(SiMe₃)₂); 5.7 (Si(CH₃)₃) ppm.

$[\{\text{Carb}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (13)

To a stirred solution of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{Et}_2\text{O})_2]$ (0.47 g, 0.92 mmol) in toluene (15 mL), at room temperature, a solution of the proligand $\{\text{Carb}^{\text{DiPP}}\}\text{H}$ (0.59 g, 0.92 mmol) in toluene (5 mL) was added. The resulting bright yellow suspension was stirred at 80 °C for 3 days. Removal of the solvent under reduced pressure gave the product as a yellow powder. The powder was washed with hexanes (3 × 10 mL) to give the crude compound. Crystals suitable for an X-ray diffraction study were recrystallised from a toluene solution layered with hexanes at -30 °C. Yield: 700 mg (79%).

^1H NMR (400.16 MHz, $[\text{D}_8]$ toluene): δ 8.57 (m, 4H **Ar-H**); 8.53 (s, 2H, **CH**=N); 7.66 (d, $J_{\text{HH}} = 1.6$ Hz, **Ar-H**); 7.15 (m, 6H, **Ar-H**); 3.23 (hept, $J_{\text{HH}} = 6.3$ Hz, 4H, **CH**(CH₃)₂); 1.41 (s, 18H, C(CH₃)₃); 1.38 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, CH(CH₃)₂); 1.12 (d, $J_{\text{HH}} = 6.6$ Hz, 12H, CH(CH₃)₂); -0.22 (s, 18H, (Si(CH₃)₃)) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63, $[\text{D}_8]$ toluene): δ 174.9 (**CH**=N); 150.3 (**Ar-C**); 148.9 (**Ar-C**); 140.6 (**C4-H**); 140.5 (**Ar-C**); 132.0 (**C2-H**); 128.4 (**Ar-C**); 127.2 (**Ar-C**); 125.0 (**Ar-C**); 123.7 (**Ar-C**); 119.0 (**Ar-C**); 34.9 (C(CH₃)₃); 32.4 (C(CH₃)₃); 30.0 (CH(CH₃)₂); 26.4 (CH(CH₃)₂); 24.0 (CH(CH₃)₂); 5.5 ((Si(CH₃)₃)) ppm.

$[\{\text{Carb}^{\text{DiPP}}\}\text{Mg}^n\text{Bu}]$ (14)

A solution of di-*n*-butyl-magnesium (0.5 M, 12.3 mL) in heptane was added dropwise to a solution of $\{\text{Carb}^{\text{DiPP}}\}\text{H}$ (1.00 g, 1.53 mmol) in hexanes (30 mL) at -78 °C. The bright yellow suspension was left to come to room temperature over 1 h, by which time the suspension had briefly become an orange solution before precipitating an orange powder. Stirring was continued at this temperature for 2 h, then the solid was isolated by filtration. Storage of the mother liquor in the freezer resulted in the formation of small orange crystals suitable for an X-ray diffraction study. Yield (powder + crystalline fraction): 1.02 g (91%).

^1H NMR (300.16 MHz, $[\text{D}_6]$ benzene): δ 8.61 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **CH**-Carb); 8.36 (s, 2H, **CH**=N); 7.58 (d, $J_{\text{HH}} = 1.9$ Hz, 2H, **CH**-Carb); 7.16-7.10 (m, 6H, (C₆H₃)₂); 3.19 (hept, $J_{\text{HH}} = 6.7$ Hz, 4H, **CH**(CH₃)₂); 1.43 (s, 18H, C(CH₃)₃); 1.30 (d, $J_{\text{HH}} = 6.9$ Hz, 12H, CH(CH₃)₂); 1.05 (d, $J_{\text{HH}} = 6.7$ Hz, 12H CH(CH₃)₂); 0.98 (m, 4H, MgCH₂CH₂CH₂CH₃); 0.75 (m, 3H, MgCH₂CH₂CH₂CH₃); -0.36 (m, 2H, MgCH₂CH₂CH₂CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, $[\text{D}_6]$ benzene): δ 171.9 (**CH**=N); 149.7 (**Ar-C**); 149.1 (**Ar-C**); 140.8 (**C4-H** Carb); 140.6 (**Ar-C**); 129.8 (**C2-H** Carb); 127.5 (**Ar-C**); 126.6 (**Ar-C**); 124.0 (**Ar-C**); 123.1 (**Ar-C**); 118.2 (**Ar-C**); 34.7 (C(CH₃)₃);

32.3 (MgCH₂CH₂CH₂CH₃); 32.2 (C(CH₃)₃); 29.4 (CH(CH₃)₂); 25.9 (CH(CH₃)₂); 23.4 (CH(CH₃)₂); 14.6(MgCH₂CH₂CH₂CH₃); 14.0 (MgCH₂CH₂CH₂CH₃) 11.0 (MgCH₂CH₂CH₂CH₃) ppm.

[Ba₂{Carb^{DiPP, red}}{Carb^{DiPP, silyl}}.(thf)₂] (15)

To a Schlenk vessel containing a solution of **6** (230 mg, 0.22 mmol) in toluene (30 mL), phenylsilane (56 μL, 0.46 mmol) was added dropwise via a microsyringe. The solution changed colour to orange and was stirred for 10 min. The volatiles were removed under reduced pressure and the residue was extracted with hexanes (2 × 10 mL) and filtered to give a clear yellow solution. The solution was concentrated to 10 mL and transferred to a -30 °C freezer. After 10 h, bright yellow crystals were isolated by filtration and submitted for an X-ray diffraction study. The remaining crystals were briefly dried under reduced pressure and submitted for NMR analysis. However, ¹H NMR analysis suggested a mixture of products which could not be purified from each other. Yield: 67 mg (30%).

[Ca₄{Carb^{DiPP, red}}₂H₂·(thf)₂] (16)

To a Schlenk vessel containing a solution of **12** (200 mg, 0.32 mmol) in toluene (30 mL), phenylsilane (84 μL, 0.68 mmol) was added dropwise via a microsyringe. The solution changed colour to orange and was stirred for 10 min. The volatiles were removed under reduced pressure and the residue was extracted with hexanes (2 × 10 mL) and filtered to give a clear yellow solution. The solution was concentrated to 10 mL and transferred to a +4 °C fridge. After 16 h, bright yellow crystals were isolated by filtration and submitted for an X-ray diffraction study. The remaining crystals were briefly dried under reduced pressure and used for NMR analysis, however suitable NMR results could not be obtained, as the sample contained an inseparable mixture of products.

[{Carb^{DiPP}}CaSn(SiMe₃)₃·thf] (17)

A Schlenk vessel was loaded with Sn(SiMe₃)₄ (220 mg, 0.53 mmol) and KO^tBu (60 mg, 0.54 mmol), dissolved in thf (10 mL) and left to stir for 1 h generating a pale yellow solution. This was added dropwise to a solution of [{Carb^{DiPP}}Ca(I)·(thf)₂] (515 mg, 0.48 mmol) in thf (30 mL) at -78 °C. The resulting yellow solution was left to stir for 2 h at room temperature, generating an orange suspension. The volatiles were removed under reduced pressure and the residue extracted into hexanes (30 mL). The suspension was filtered to give a dark orange solution which was concentrated to 5 mL and placed in a fridge at 4 °C. After 1 h, small crystals of the desired compound had started to form crystals which proved suitable for X-ray diffraction study. Yield: 215 mg (39%).

¹H NMR (400.13 MHz, [D₆]benzene): δ 8.65 (d, *J*_{HH} = 1.9 Hz, 2H, Carb-H); 8.50 (s, 2H, CH=N); 7.67 (d, *J*_{HH} = 1.9 Hz, 2H, Carb-H); 7.04 (m, 4H m-C₆H₃); 7.03 (t, *J*_{HH} = 8.1 Hz, 2H p-C₆H₃); 3.56 (hept, *J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₂); 3.04 (br m, 4H, 2,5-CH₂, thf); 2.97 (hept, *J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₂); 1.47 (s, 18H, C(CH₃)₃); 1.42 (d, *J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂); 1.34 (d, *J*_{HH} = 6.6 Hz, 6H, CH(CH₃)₂); 1.12 (m, 4H, 3,4-CH₂, thf); 1.03 (d, *J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂); 0.84 (d, *J*_{HH} = 6.8 Hz, 6H, CH(CH₃)₂); 0.30 (s, ²*J*_{H-Sn} = 10.7 Hz, 27H, Sn(Si(CH₃)₃) ppm.

¹³C{¹H} NMR (100.62 MHz, [D₆]benzene) δ 173.7 (CH=N); 149.8 (Ar-C); 148.2 (Ar-C); 141.2 (Ar-C); 140.6 (Ar-C); 140.1; 131.5 (Ar-CH); 128.4 (Ar-C); 126.2 (C₆H₃); 124.3 (C₆H₃); 123.8 (Ar-CH); 123.7 (Ar-C); 118.8 (Ar-C) 68.6 (2,5-CH₂, thf); 34.7 (C(CH₃)₃); 32.2 (C(CH₃)₃); 29.0 (CH(CH₃)₂); 28.7 (3,4-CH₂, thf); 27.3 (CH(CH₃)₂); 25.5 (CH(CH₃)₂); 23.6 (CH(CH₃)₂); 23.4 (CH(CH₃)₂); 7.5 (Sn(Si(CH₃)₃) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (79.49 MHz, $[\text{D}_6]$ benzene): $\delta -12.5$ ($^1J_{^{29}\text{Si}-^{119}\text{Sn}} = 27.1$ Hz, $^1J_{^{29}\text{Si}-^{117}\text{Sn}} = 26.0$ Hz) ppm.

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (142.50 MHz, $[\text{D}_6]$ benzene): $\delta -857.7$ ppm

Adapted procedure for the synthesis of $[\text{K}\{\text{CH}(\text{SiMe}_3)_2\}]_n$

In an appropriately sized Schlenk vessel, equimolar amounts of KO^tBu and $\text{CH}_2(\text{SiMe}_3)_2$ were combined. The contents were dissolved in thf (100 mL) to give a colourless solution. The solution was cooled to -78 °C and 1.01 mol equiv of $^n\text{BuLi}$ was added dropwise. The colourless solution turned to a pale-yellow solution over 1 h. The solution was then warmed up to room temperature over 40 min. The volatiles were removed under reduced pressure and the sticky residue was washed with petroleum ether (3×30 mL) to give an off-white powder. This powder was dissolved in minimal thf, and then crashed out of solution with the addition of petroleum ether (50 mL). The solid was isolated by filtration and dried under reduced pressure before being redissolved in thf and crashed out with hexanes again (for a total of 3 times). Finally, the white powder was isolated by filtration and dried at 50 °C under reduced pressure for at least 1 h to give the desired compound as a pyrophoric white powder.

For use in making the Ba species $[\text{Ba}\{\text{CH}(\text{SiMe}_3)_2\}_2 \cdot \text{thf}_x]$, it is important no lithium is present in the powder. This should be confirmed by ^7Li NMR is $[\text{D}_8]\text{thf}$.

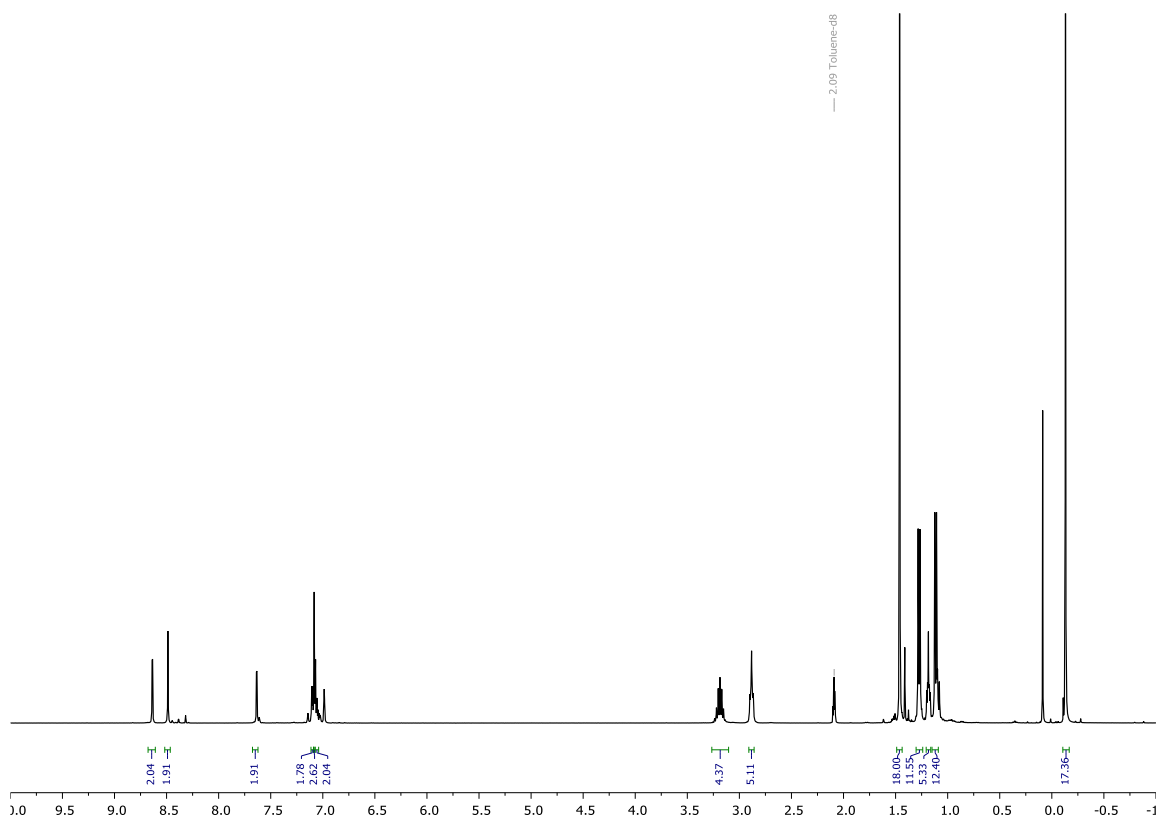


Figure S1. ^1H NMR spectrum (400.16 MHz, $[\text{D}_8]\text{toluene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_3)_2\cdot\text{thf}]$ (6).

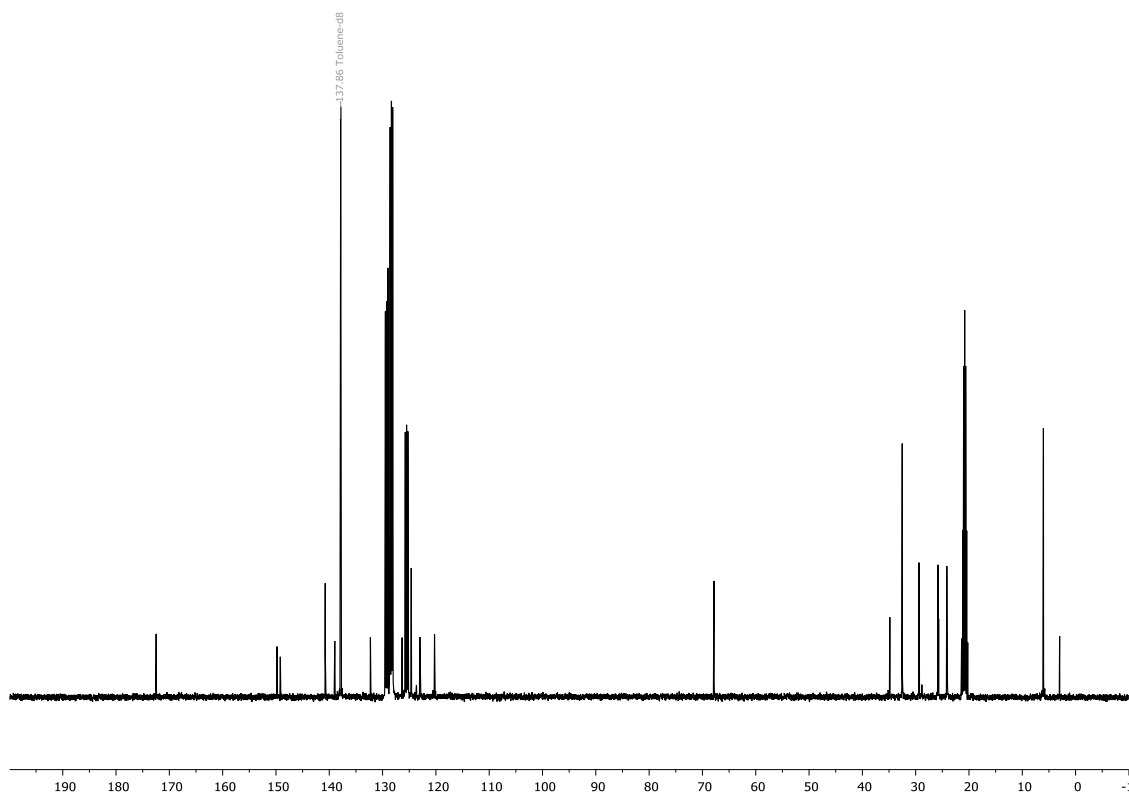


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_8]\text{toluene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_3)_2\cdot\text{thf}]$ (6).

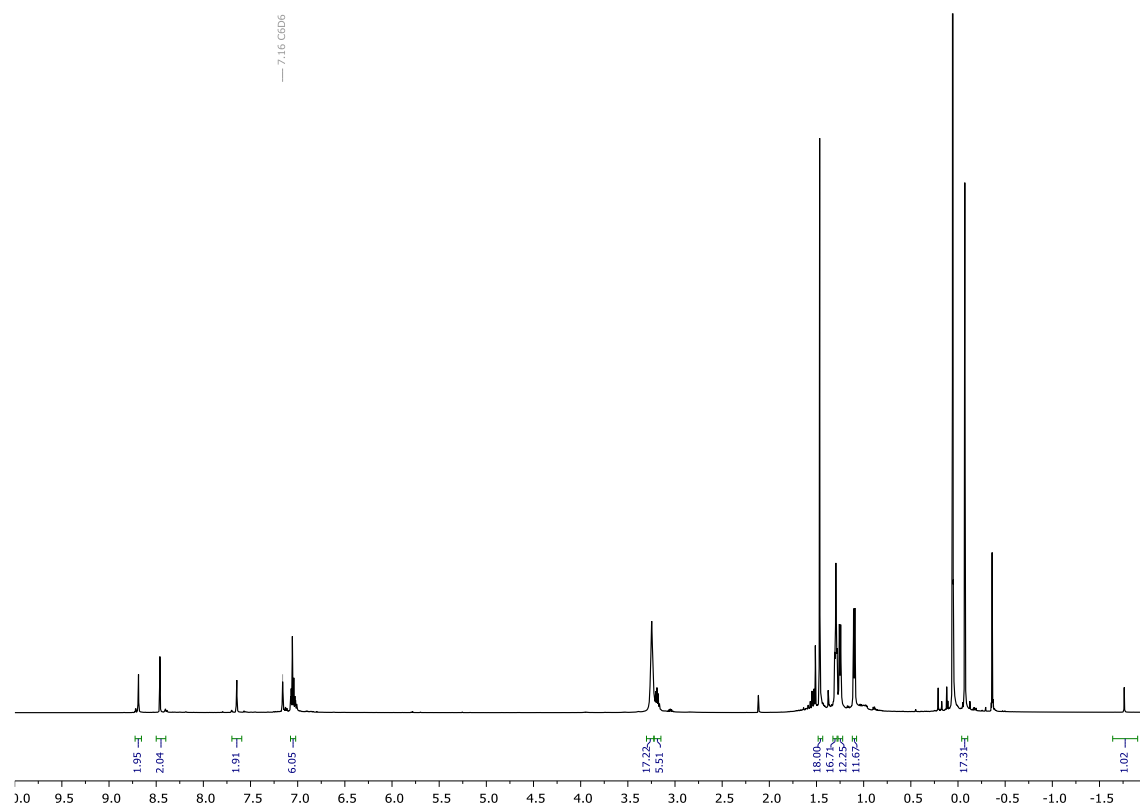


Figure S3. ^1H NMR spectrum (400.16 MHz, $[\text{D}_8]\text{toluene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaCH}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**7**).

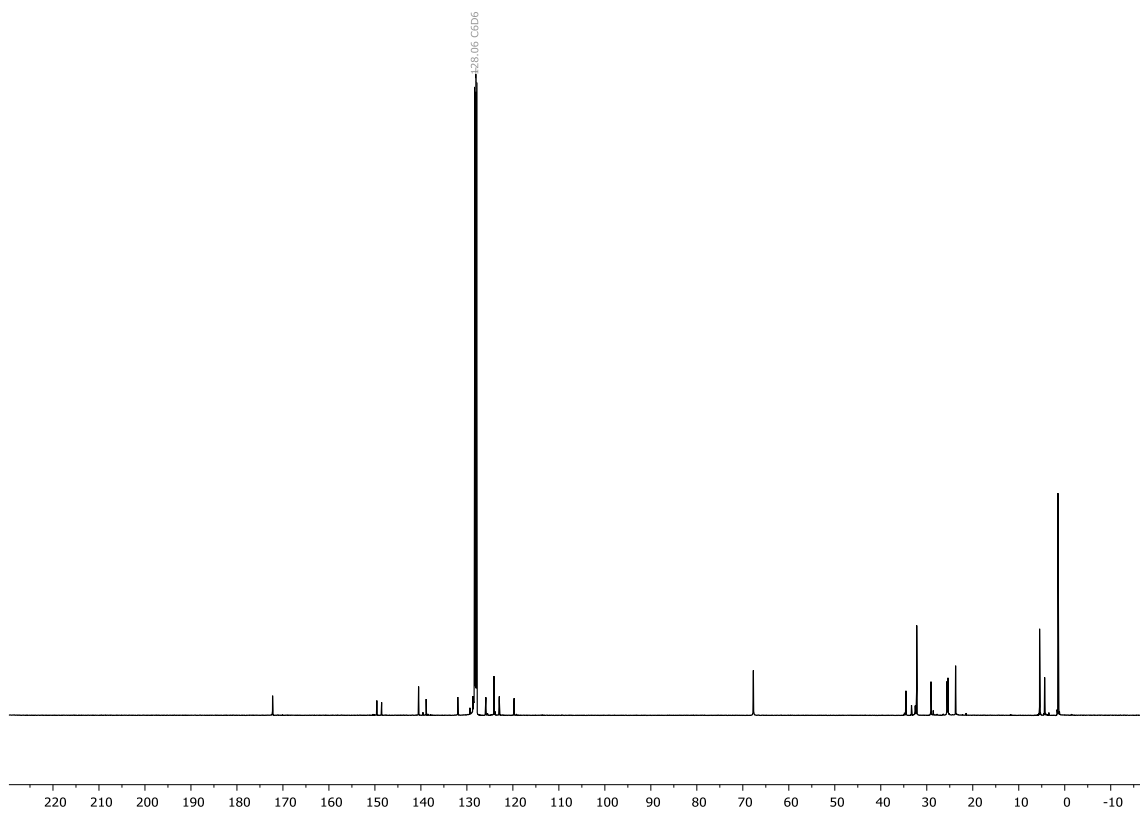


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_8]\text{toluene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaCH}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**7**).

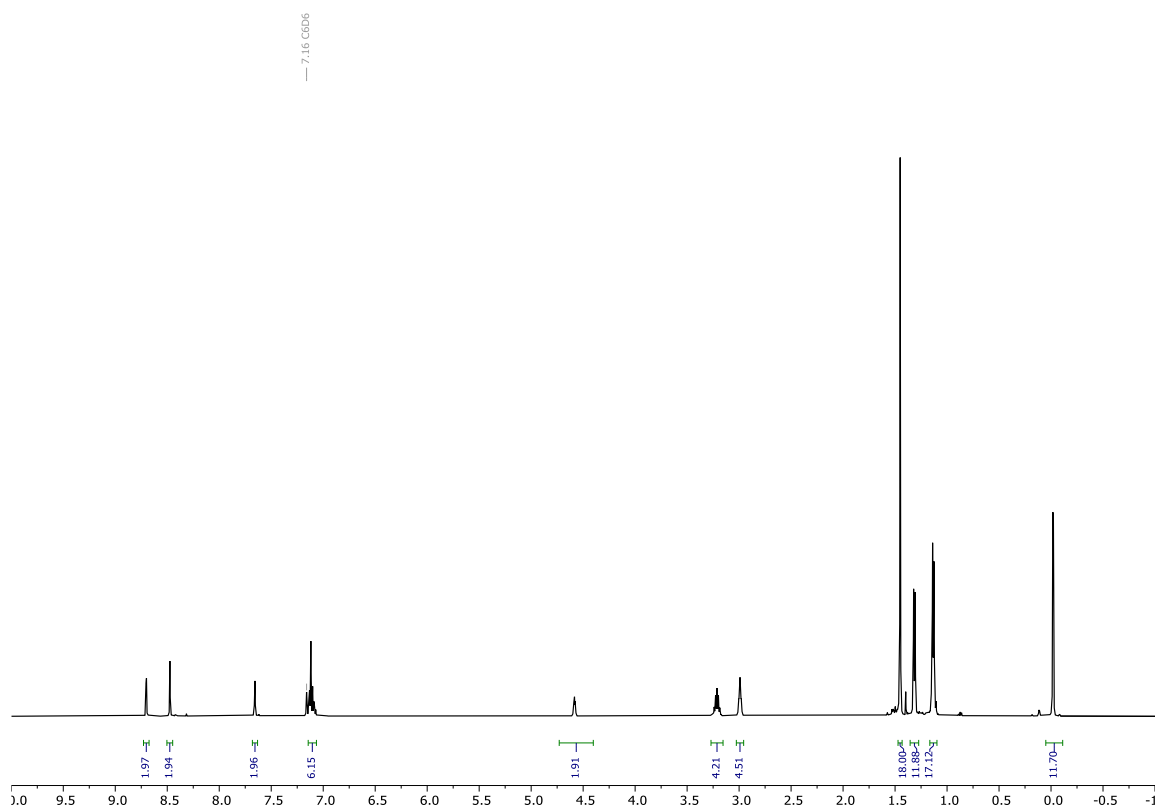


Figure S5. ^1H NMR spectrum (500.13 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DIPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{thf}]$ (**8a**).

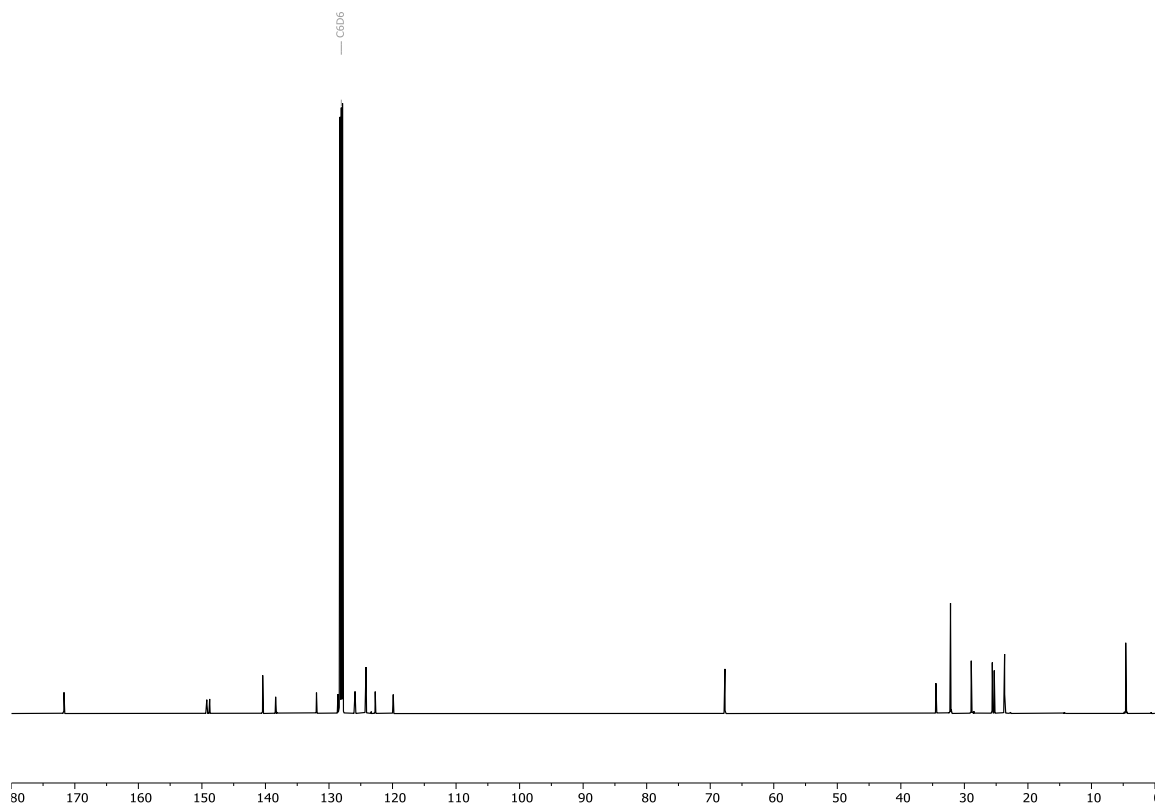


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.77 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DIPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{thf}]$ (**8a**).

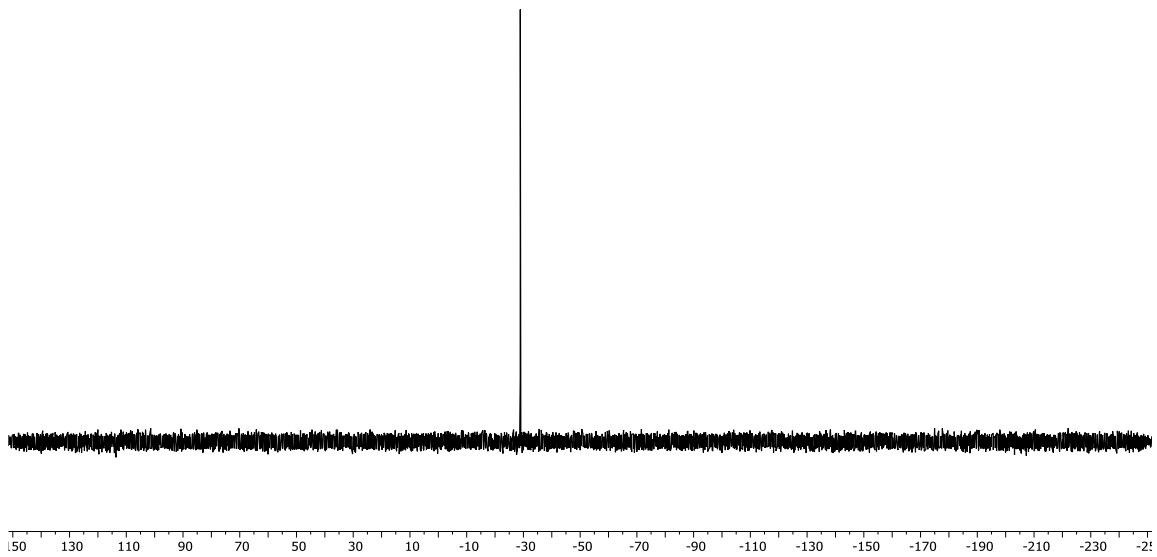


Figure S7. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (79.49 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{thf}]$ (**8a**).

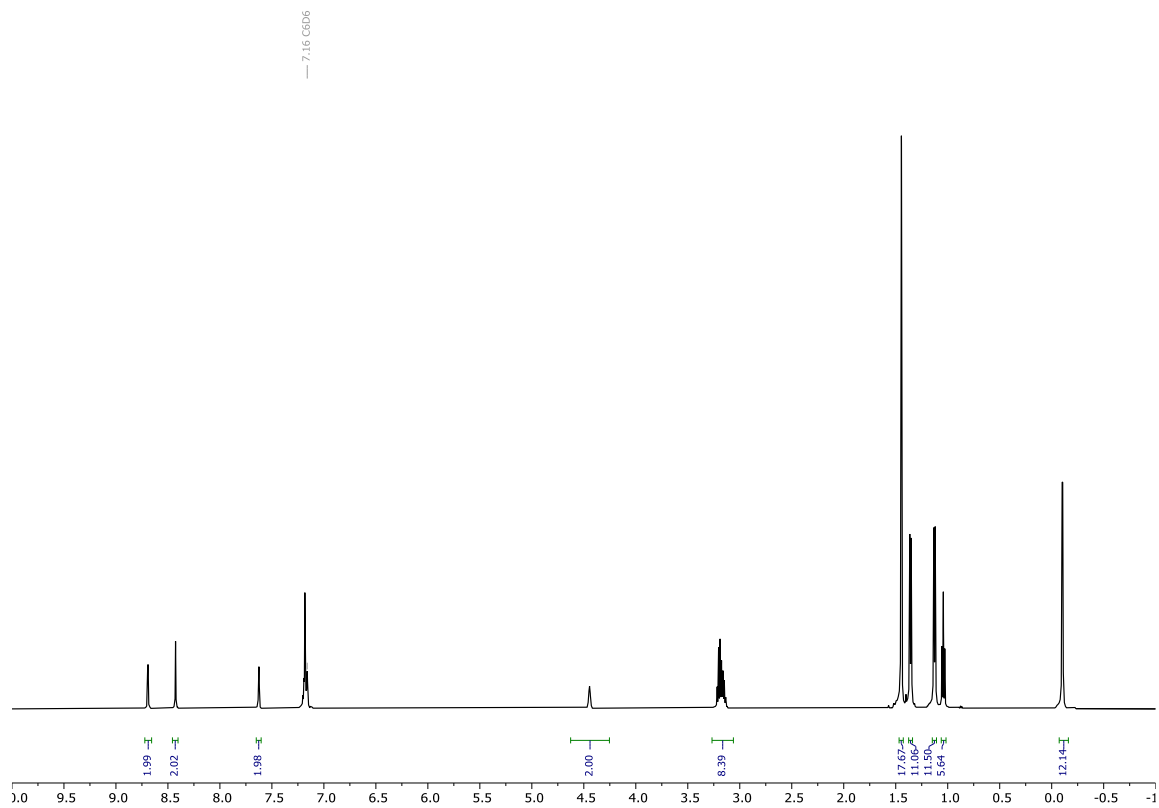


Figure S8. ^1H NMR spectrum (500.13 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{Et}_2\text{O}]$ (**8b**).

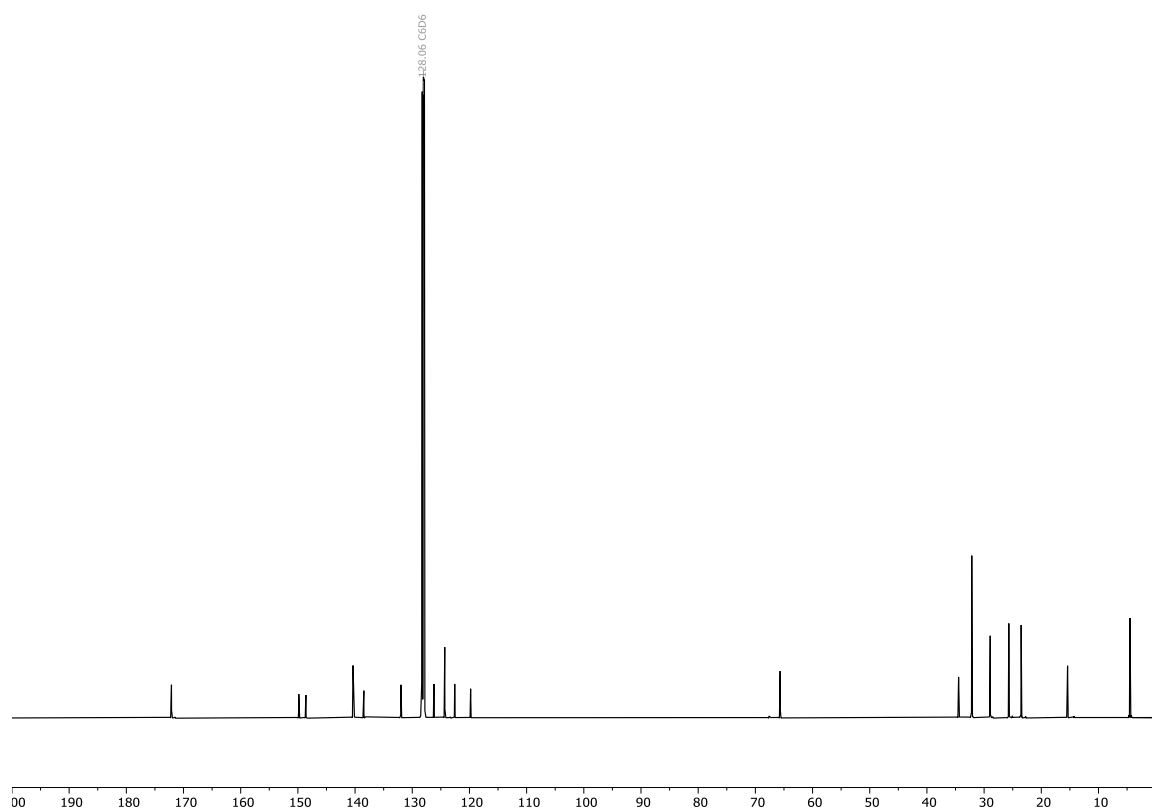


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.77 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{Et}_2\text{O}]$ (**8b**).

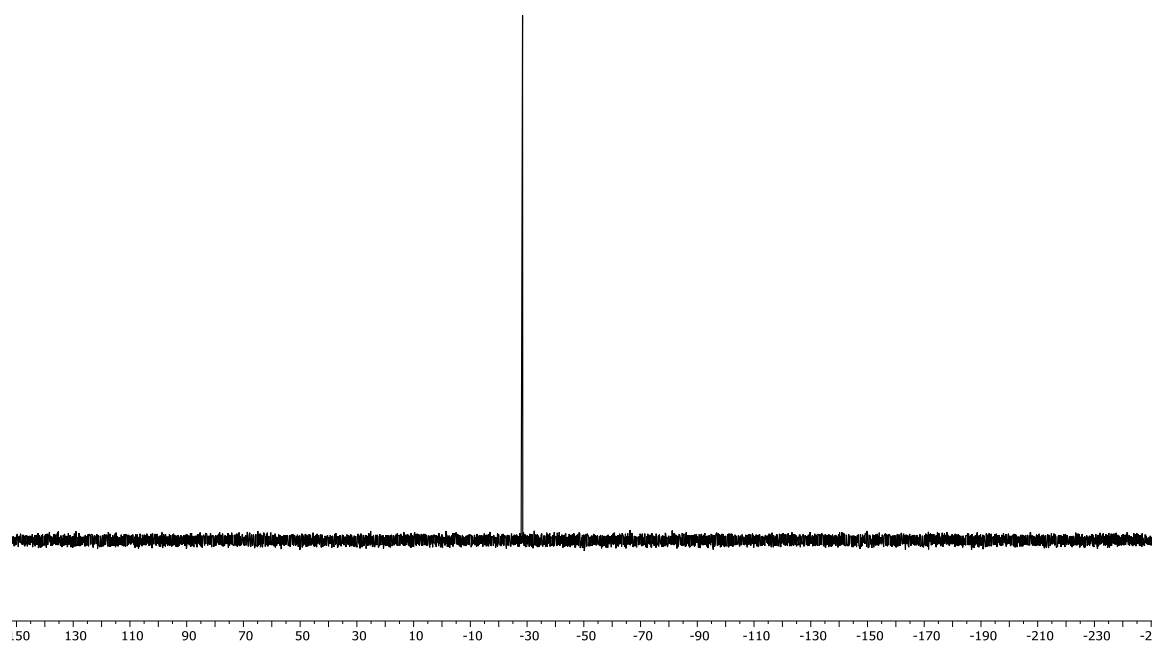


Figure S10. $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR spectrum (79.49 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{Et}_2\text{O}]$ (**8b**).

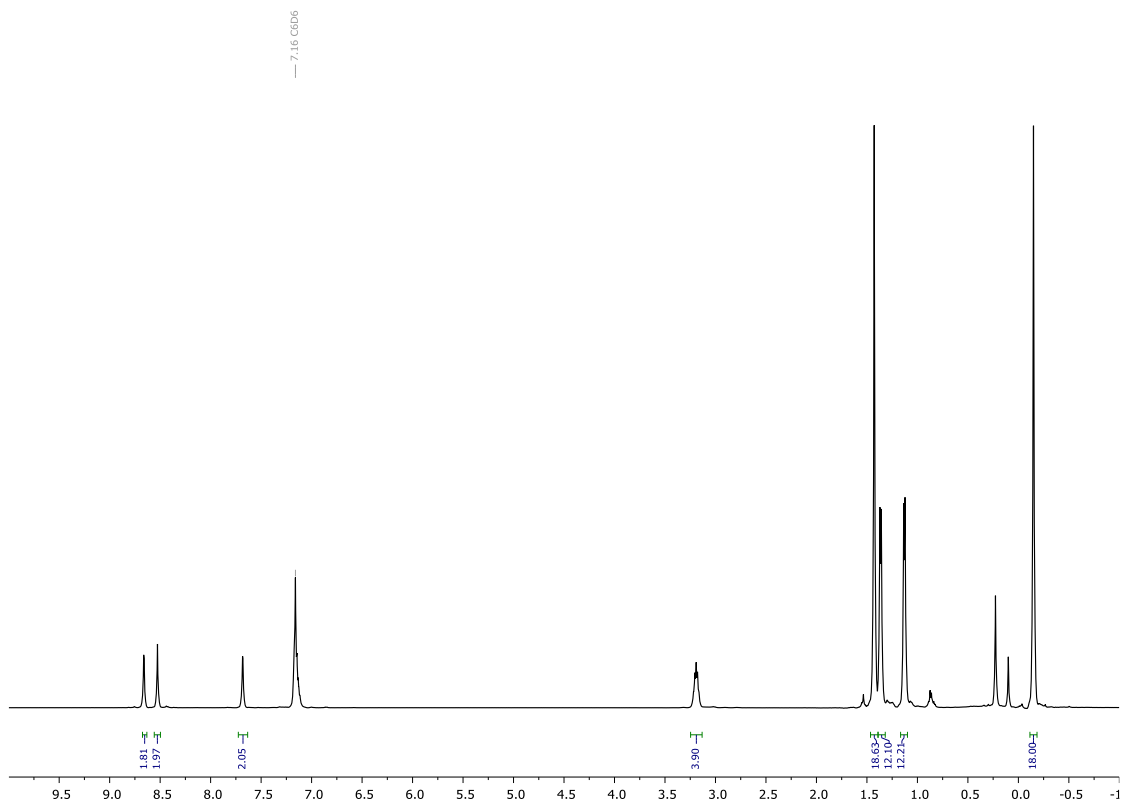


Figure S11. ^1H NMR spectrum (400.16 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{SrN}(\text{SiMe}_3)_2]$ (**9**).

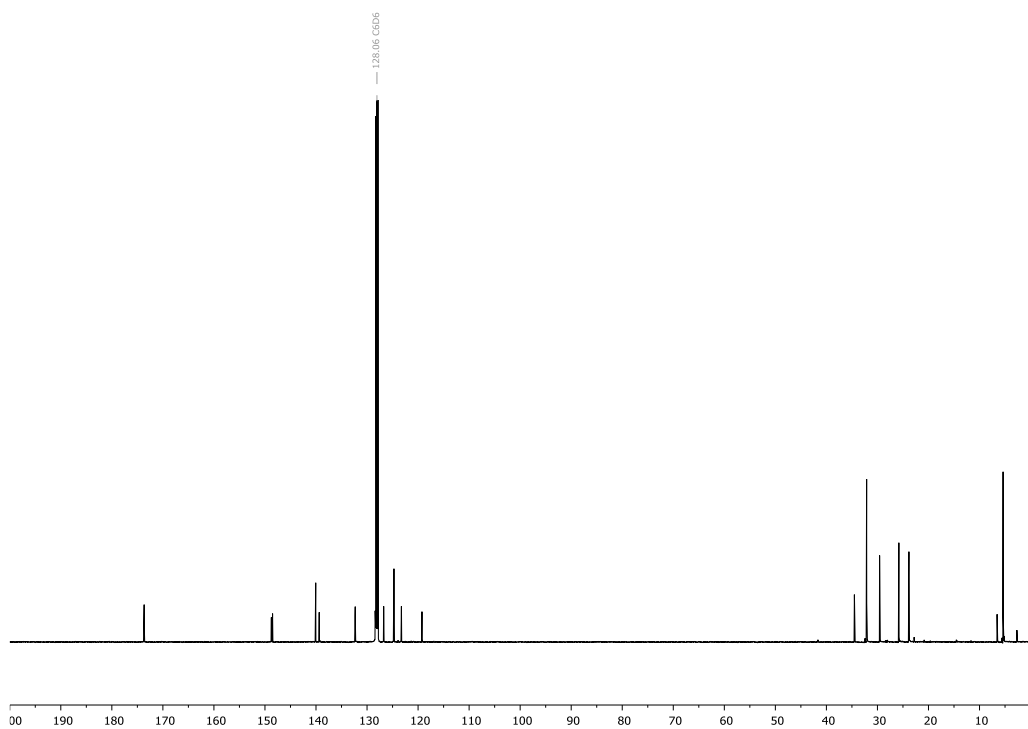


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{SrN}(\text{SiMe}_3)_2]$ (**9**).

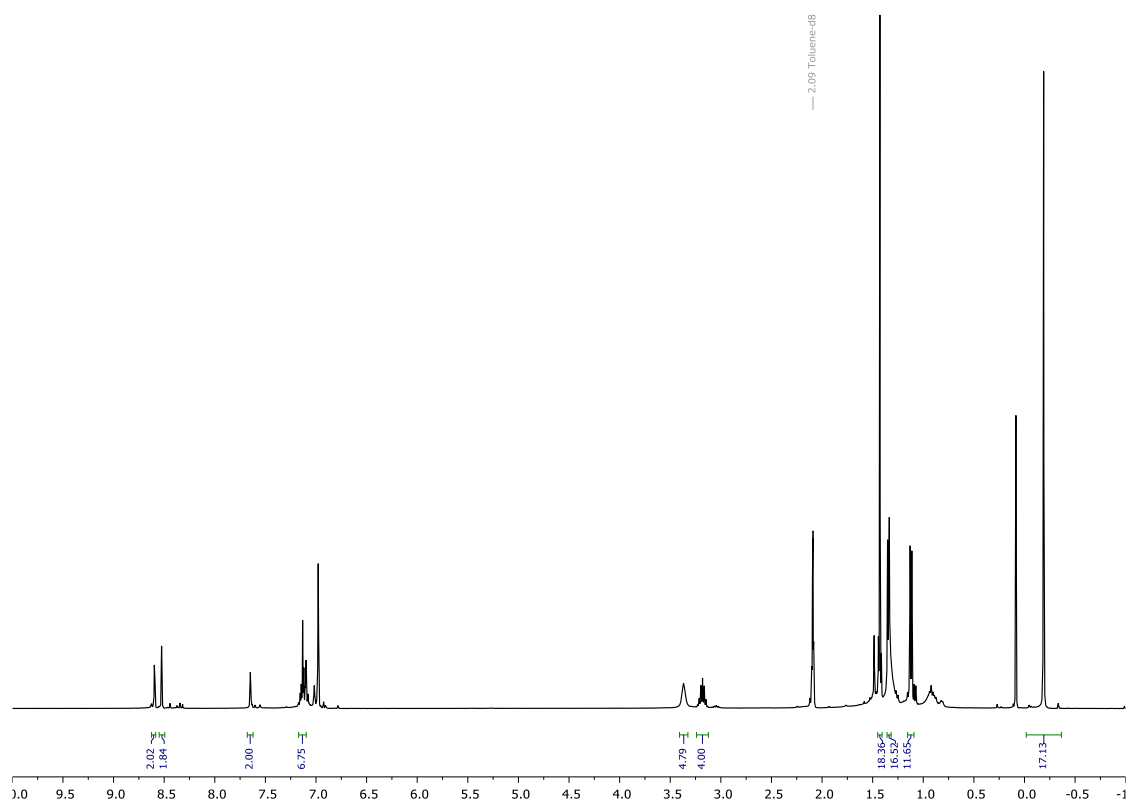


Figure S13. ^1H NMR spectrum (400.16 MHz, $[\text{D}_8]$ toluene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{SrN}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**10**).

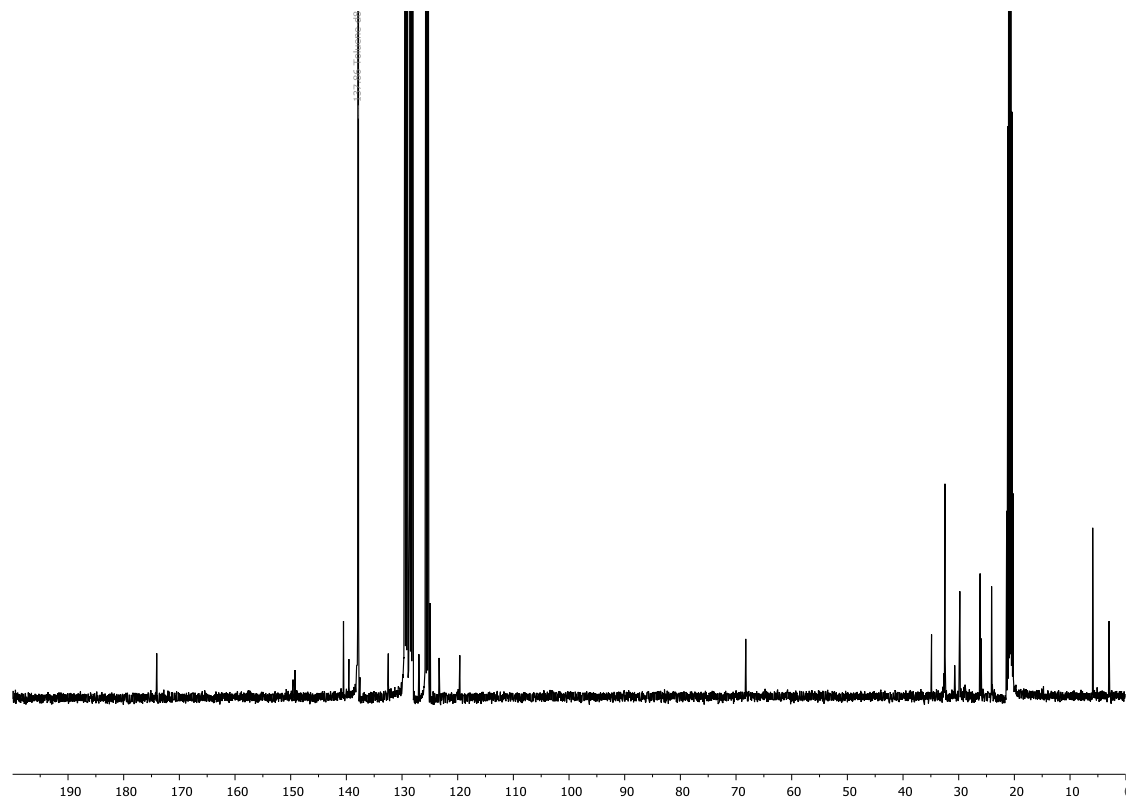


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_8]$ toluene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{SrN}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**10**).

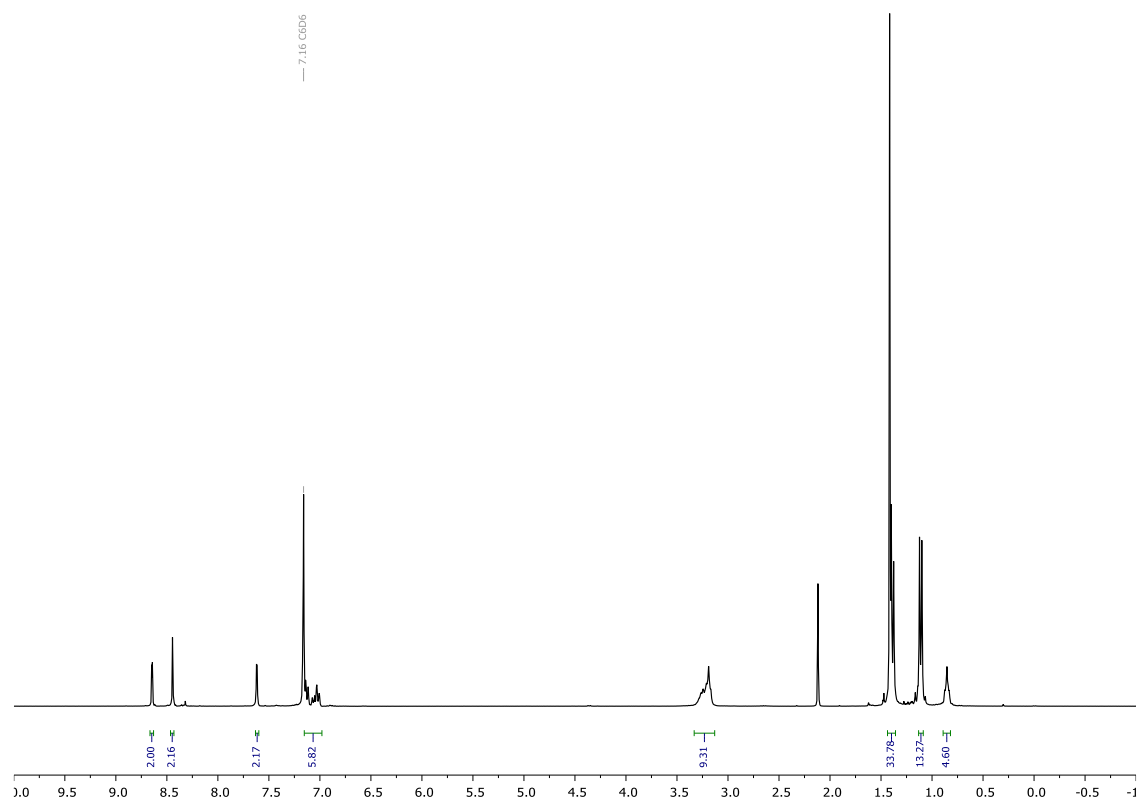


Figure S15. ^1H NMR spectrum (300.13 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaI}\cdot\text{thf}]$ (**11**).

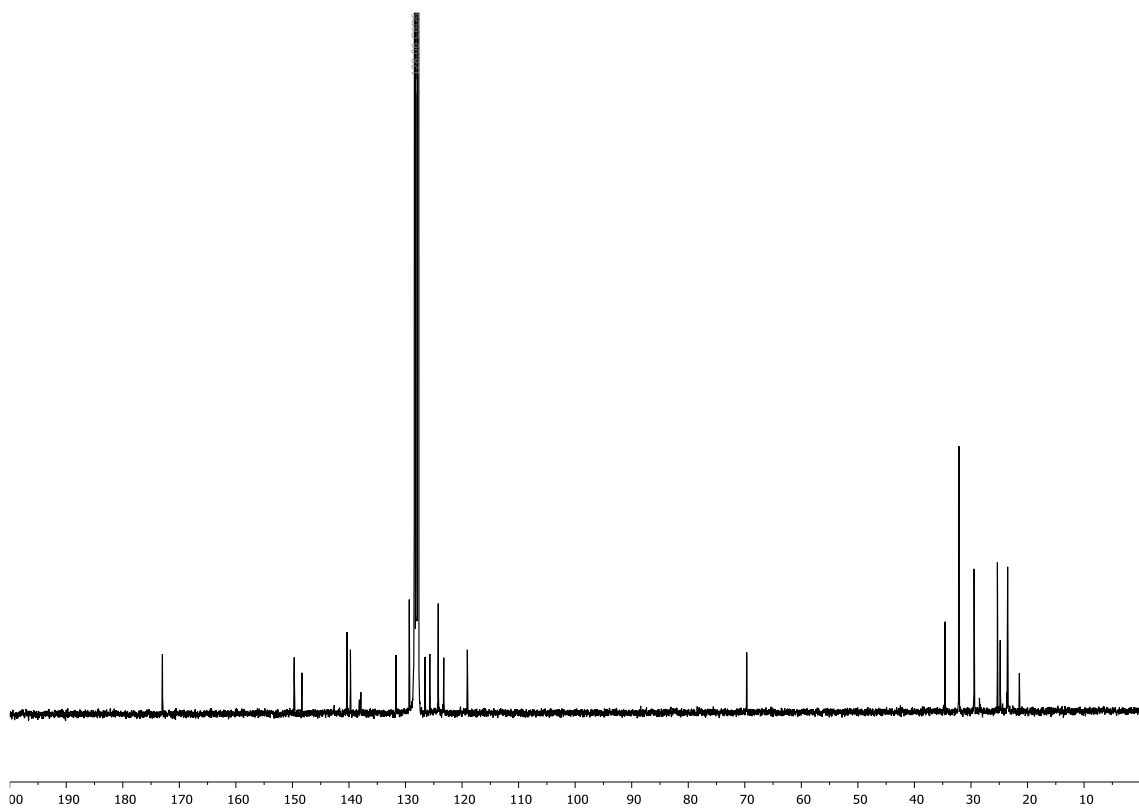


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.48 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaI}\cdot\text{thf}]$ (**11**).

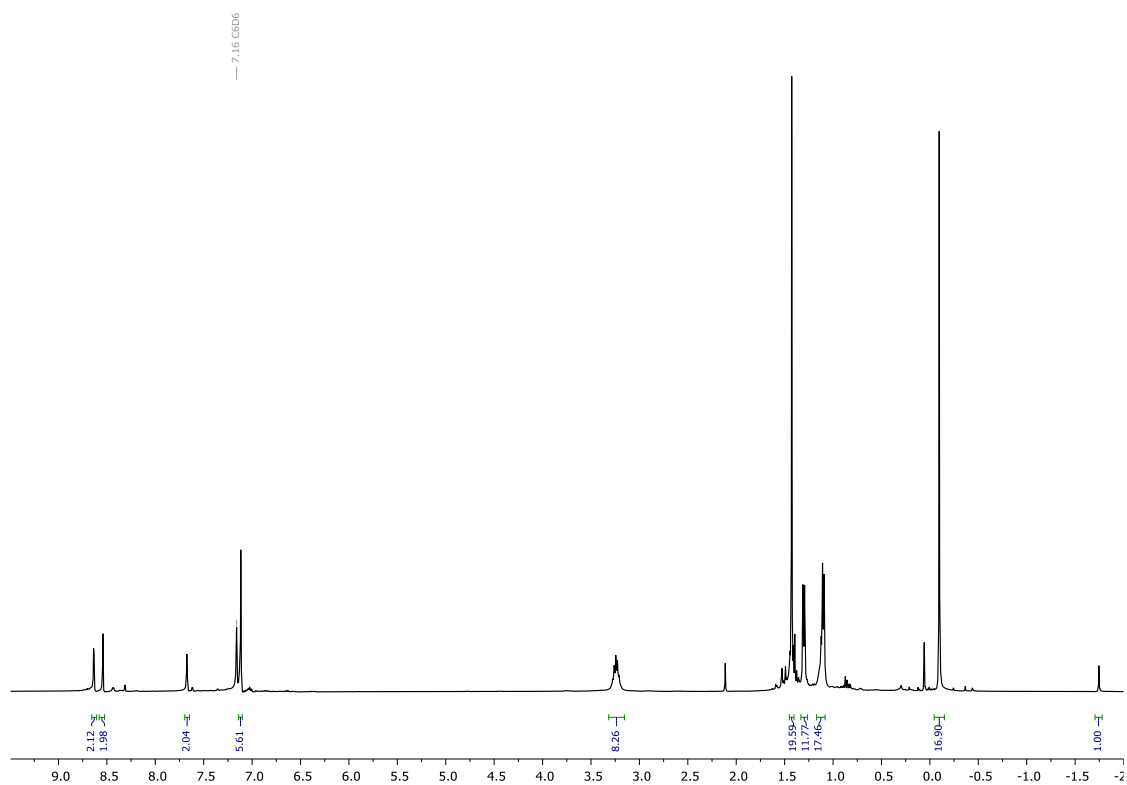


Figure S17. ^1H NMR spectrum (400.16 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaCH}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**12**).

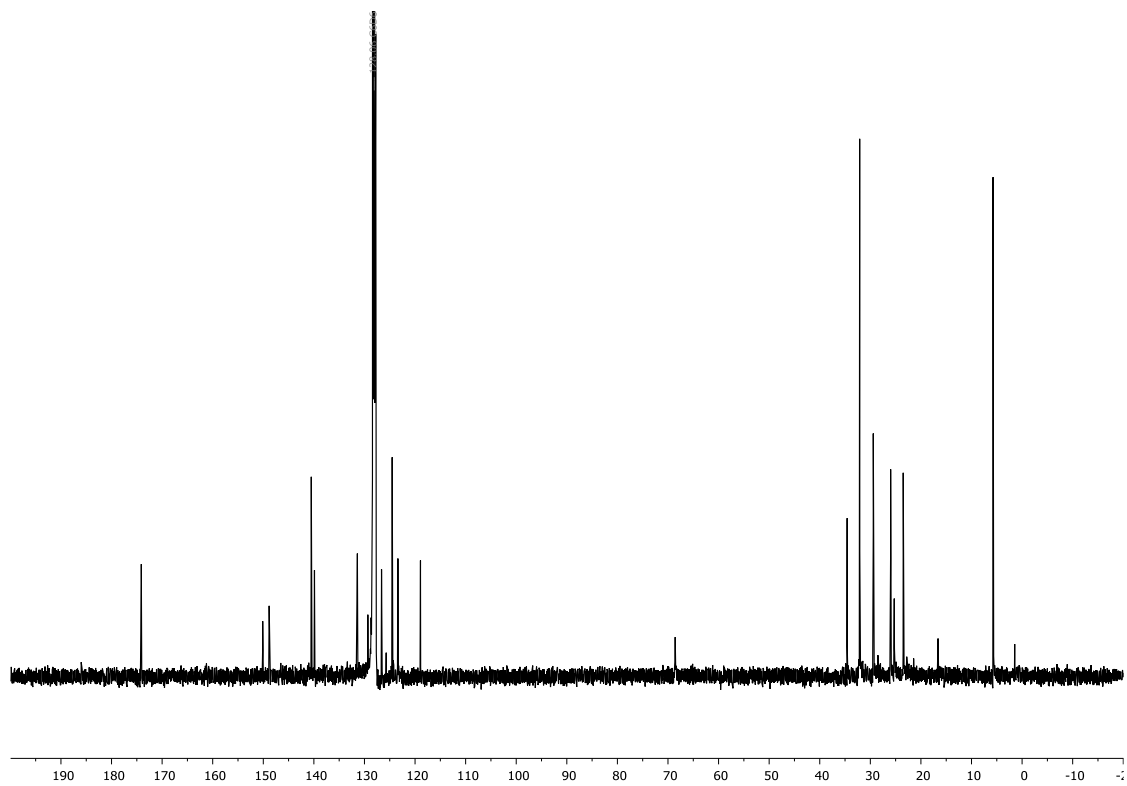


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaCH}(\text{SiMe}_3)_2\cdot\text{thf}]$ (**12**).

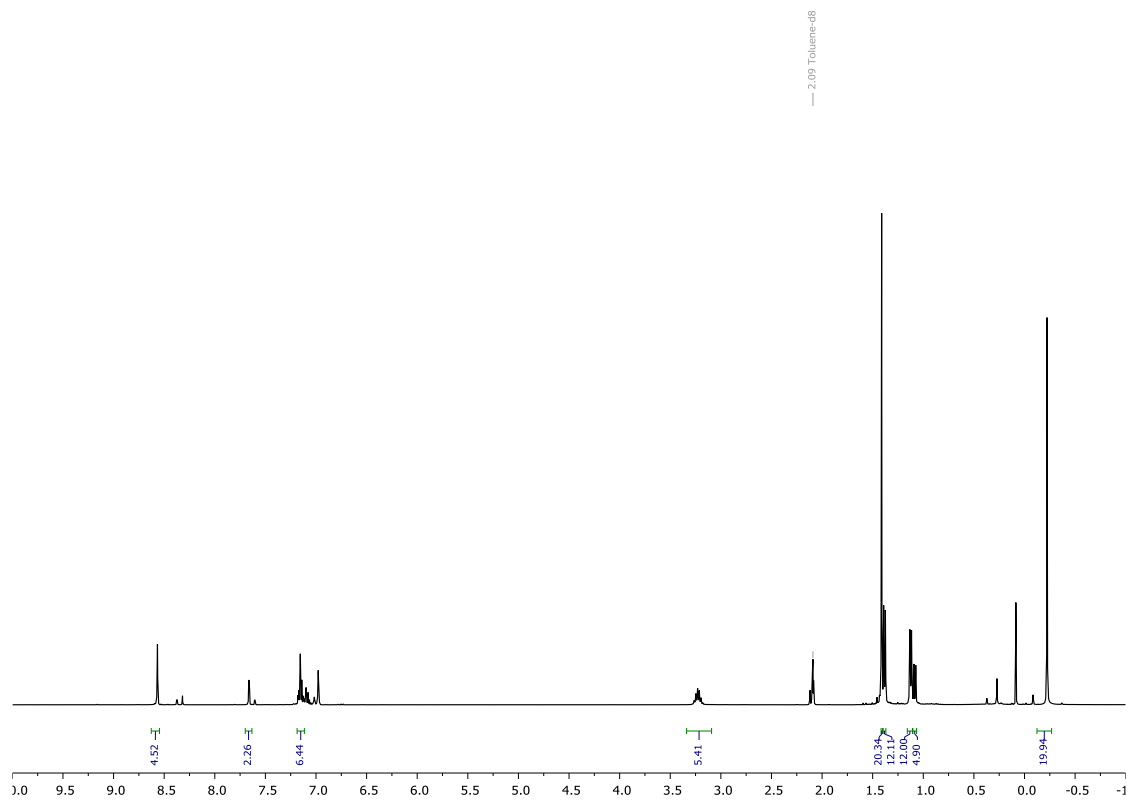


Figure S19. ^1H NMR spectrum (400.16 MHz, $[\text{D}_8]$ toluene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**13**).

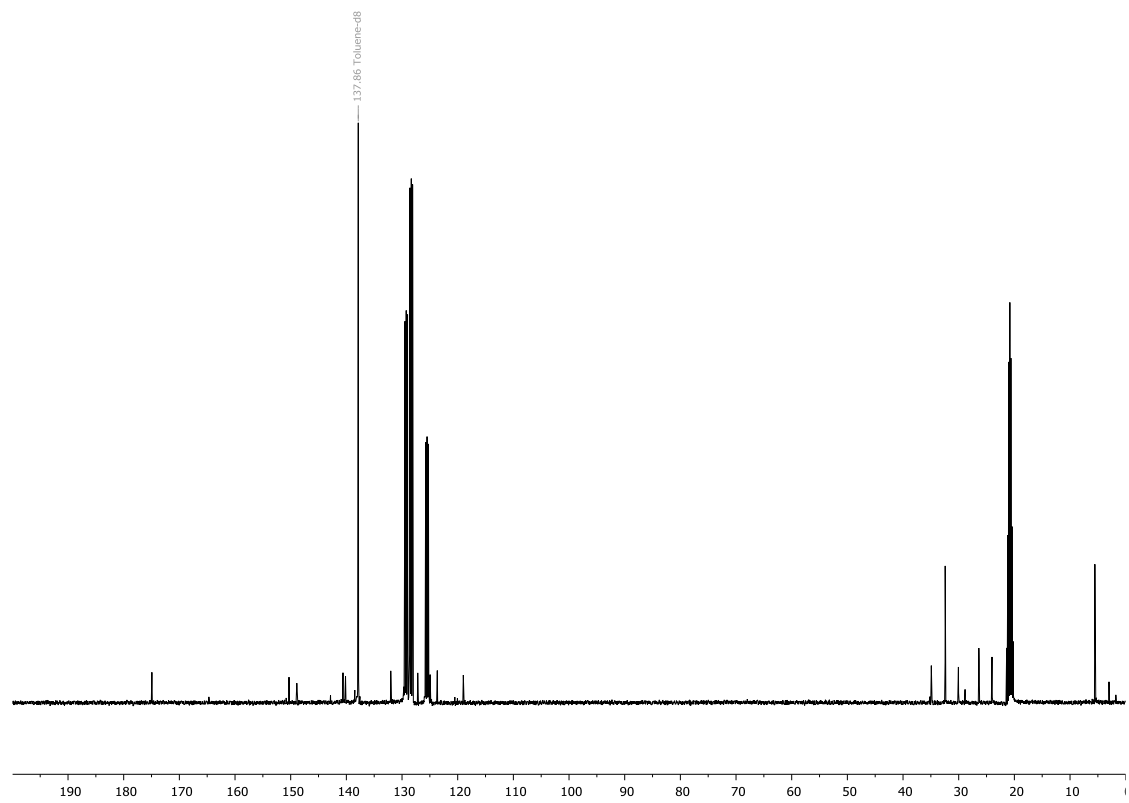


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.63 MHz, $[\text{D}_8]$ toluene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**13**).

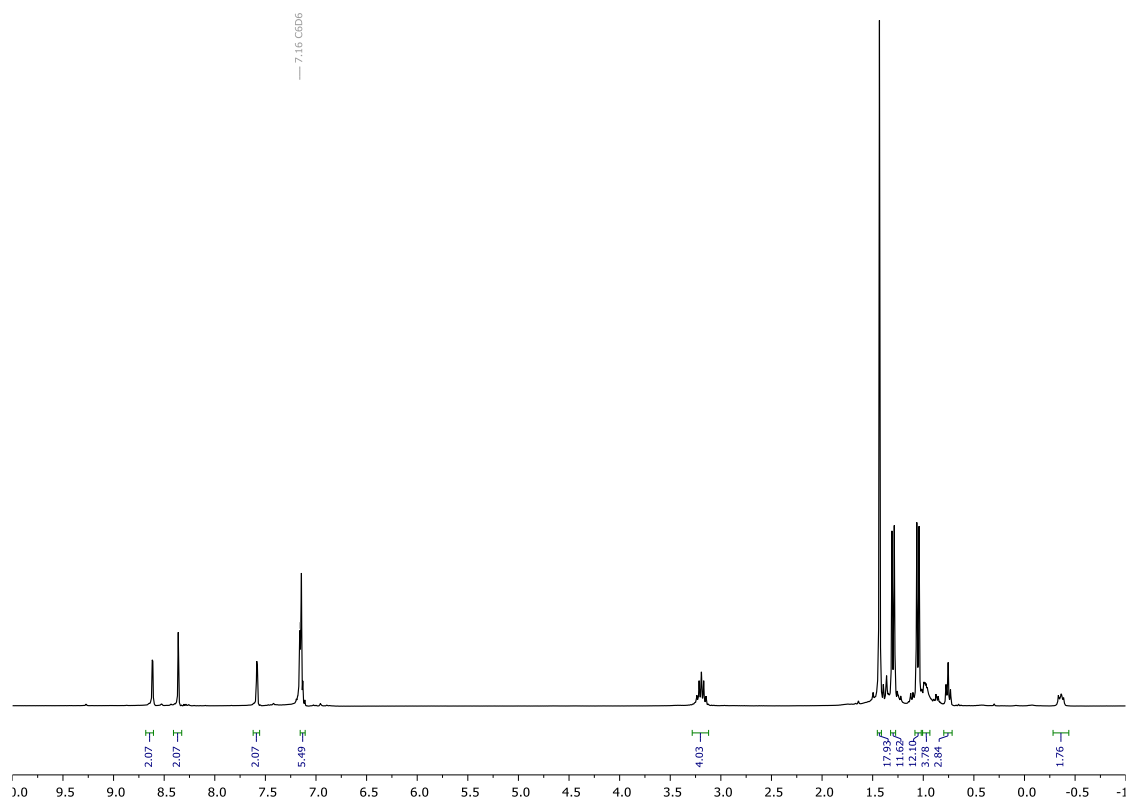


Figure S21. ^1H NMR spectrum (300.13 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{Mg}^n\text{Bu}]$ (14).

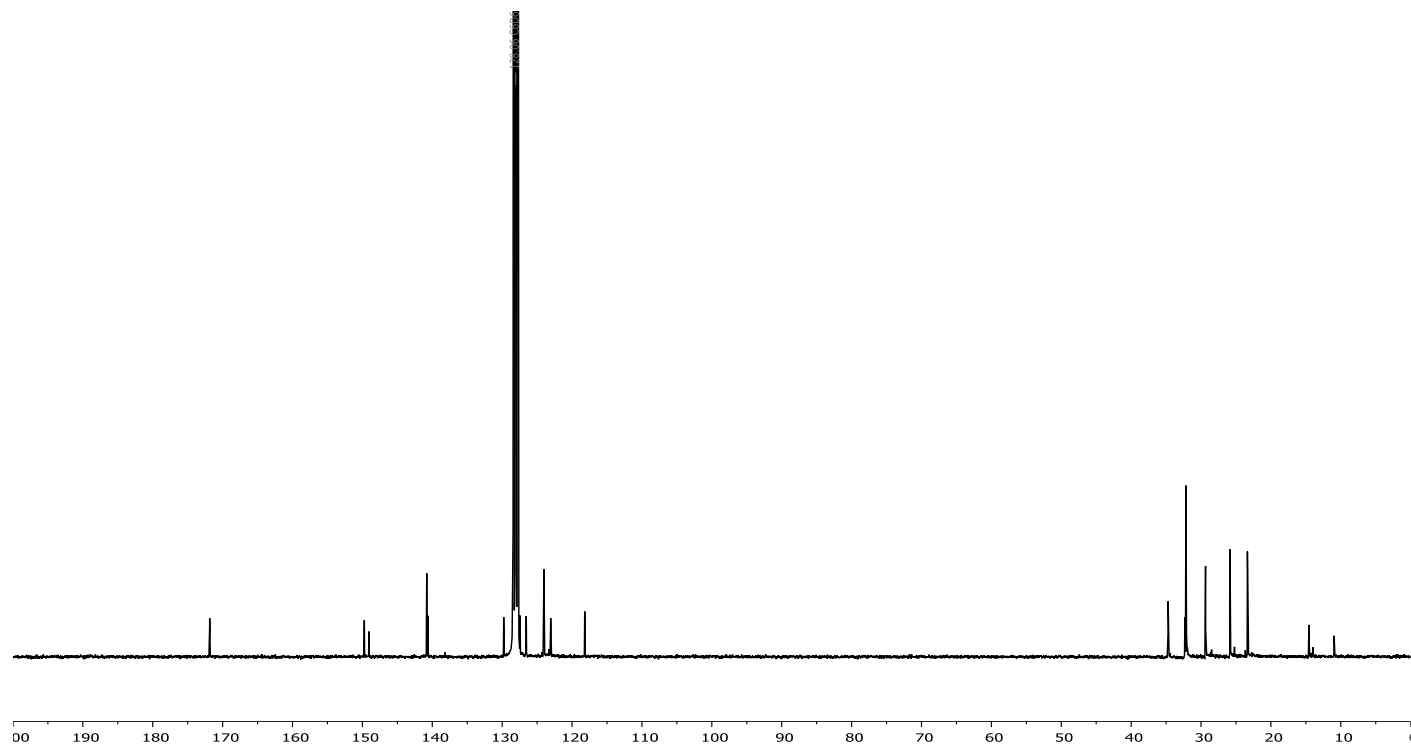


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.48 MHz, $[\text{D}_6]\text{benzene}$, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{Mg}^n\text{Bu}]$ (14).

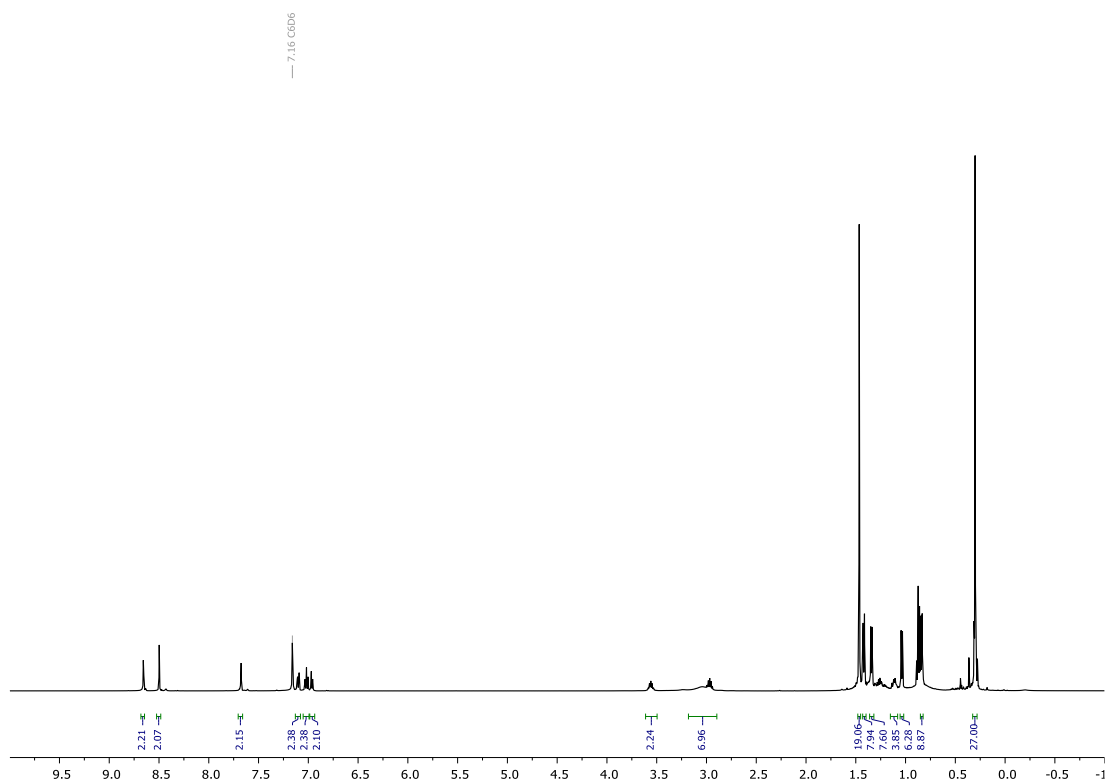


Figure S23. ^1H NMR spectrum (300.13 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaSn}(\text{SiMe}_3)_3\cdot\text{thf}]$ (**17**).

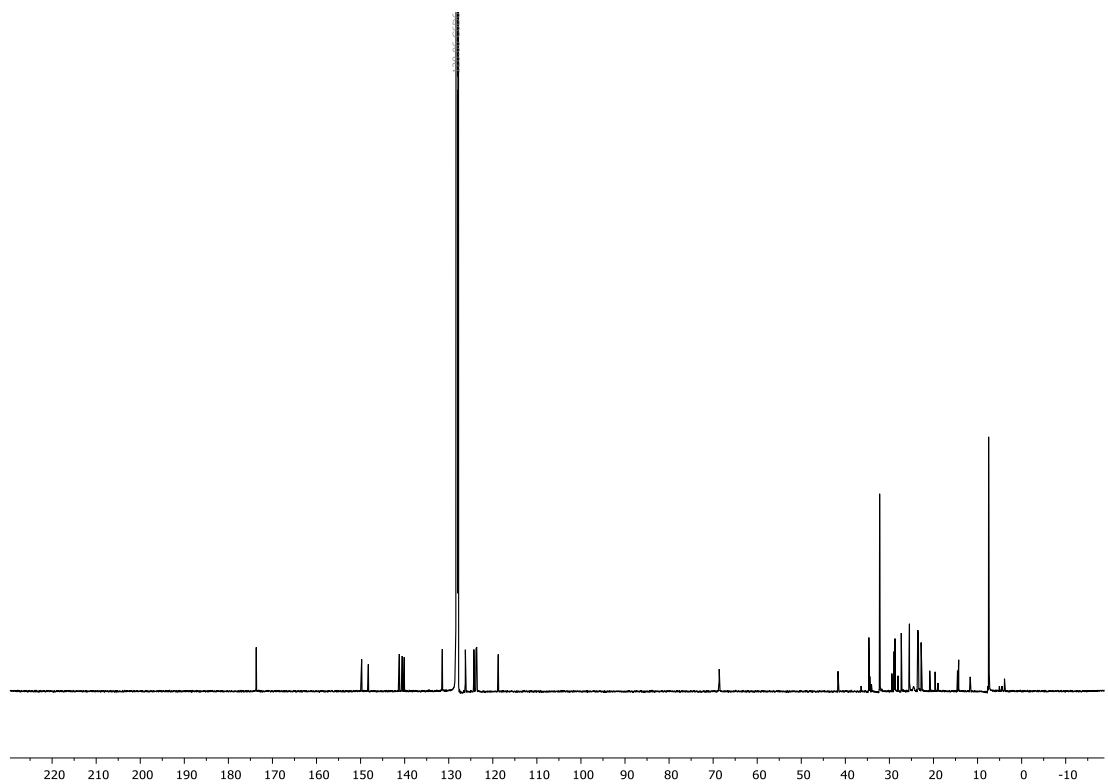


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75.48 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaSn}(\text{SiMe}_3)_3\cdot\text{thf}]$ (**17**).

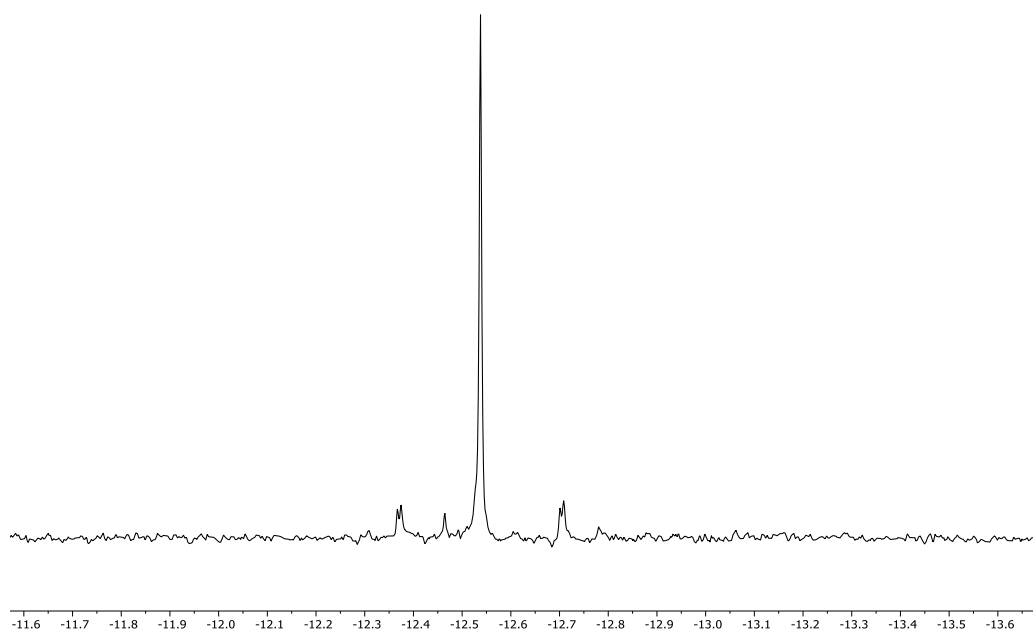


Figure S25. $^{29}\text{Si}\{\text{INEPT}\}$ NMR spectrum (79.49 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaSn}(\text{SiMe}_3)_3\cdot\text{thf}]$ (**17**).

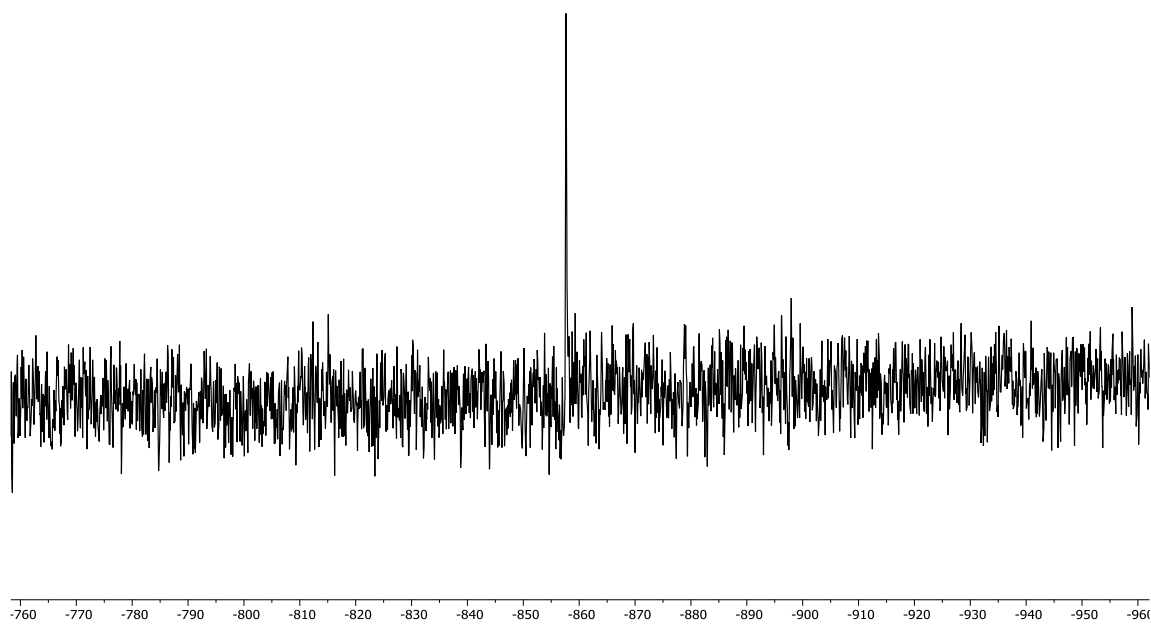


Figure S26. ^{119}Sn NMR spectrum (149.10 MHz, $[\text{D}_6]$ benzene, 298 K) of $[\{\text{Carb}^{\text{DiPP}}\}\text{CaSn}(\text{SiMe}_3)_3\cdot\text{thf}]$ (**17**).

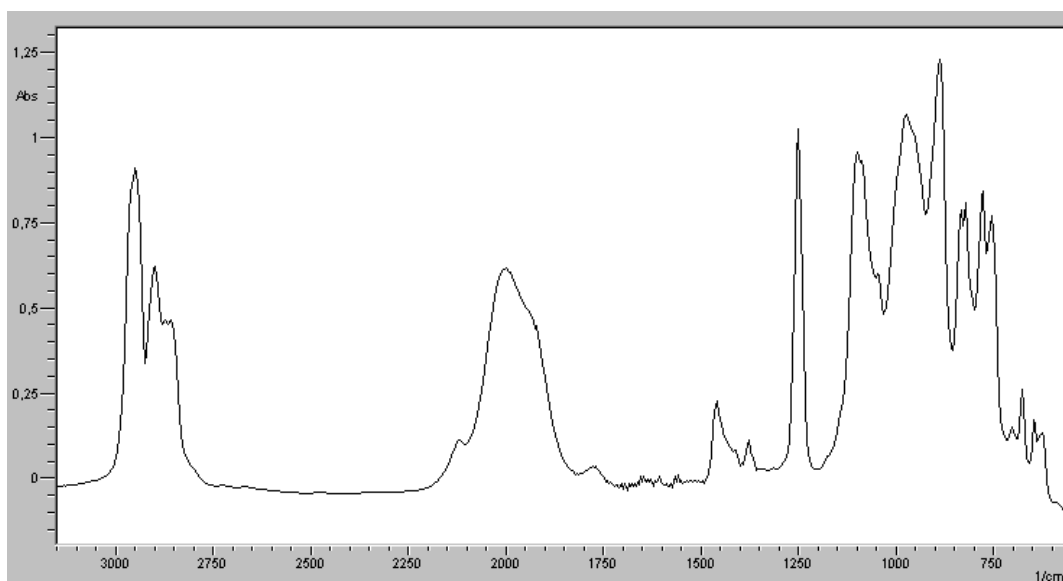


Figure S27. FTIR spectrum (Nujol mull in KBr) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{thf}]$ (**8a**).

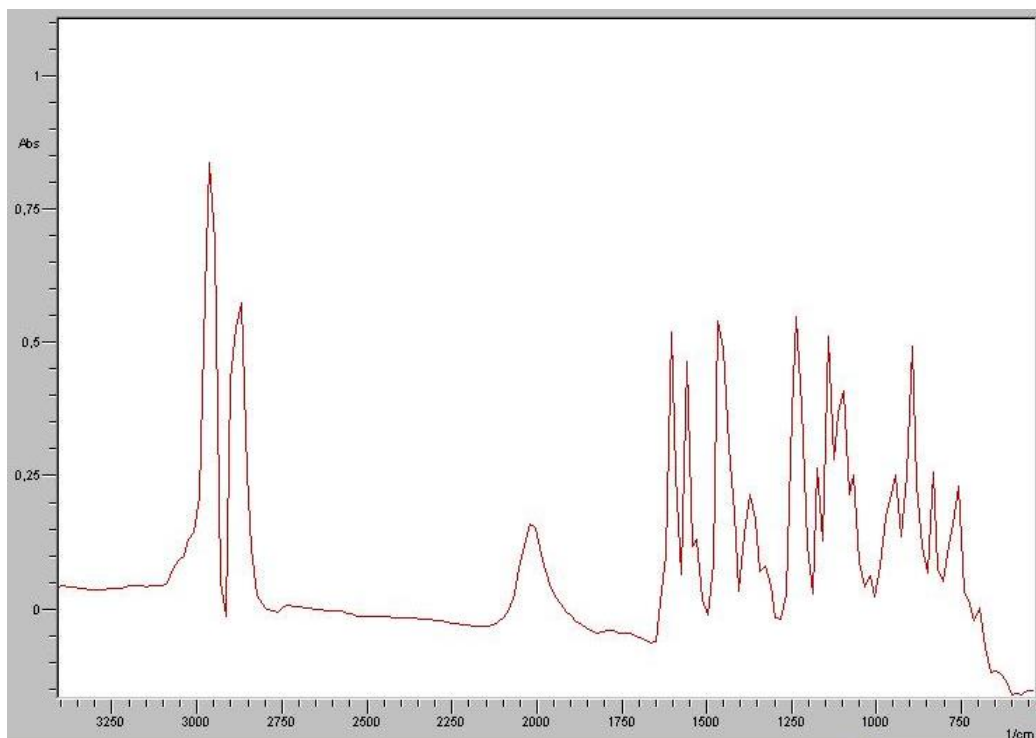


Figure S28. FTIR spectrum (Nujol mull in KBr) of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\cdot\text{Et}_2\text{O}]$ (**8b**).

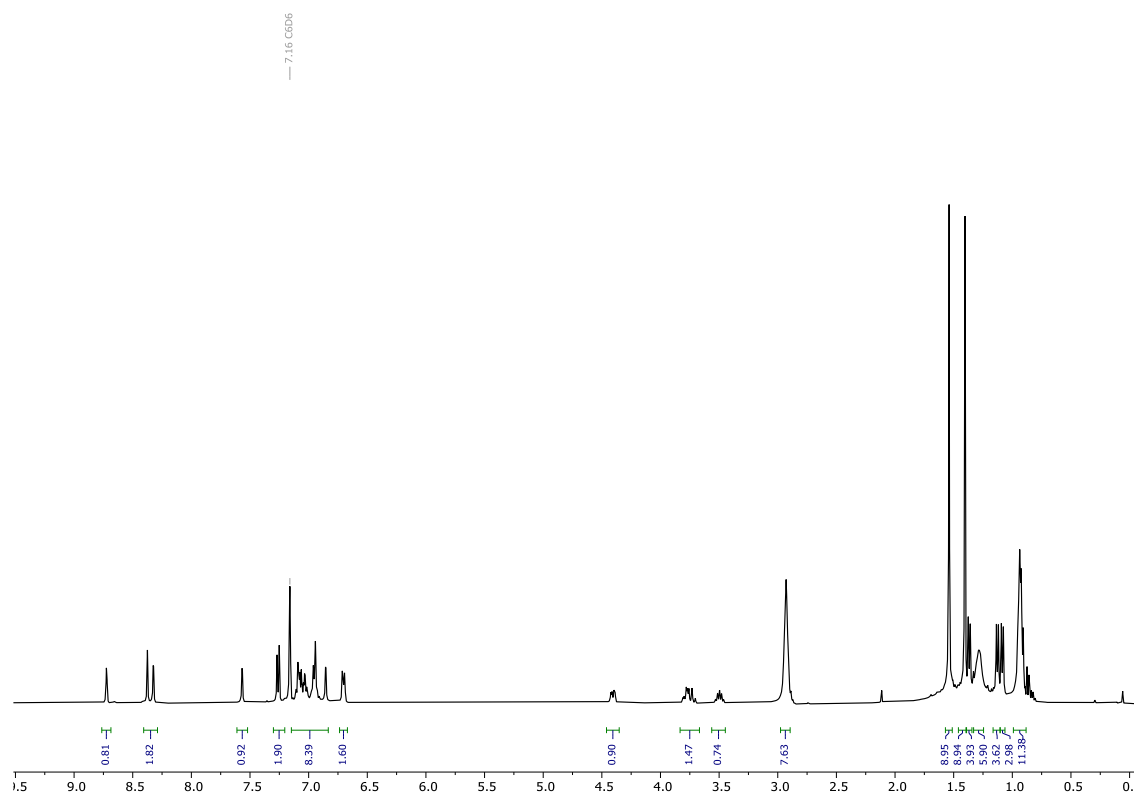


Figure S29. ¹H NMR spectrum (400.16 MHz, [D₆]benzene, 298 K) of [{Carb^{DiPP}}CaCH(SiMe₃)₂·thf] (**12**) after heating to 60 °C for 16 h.

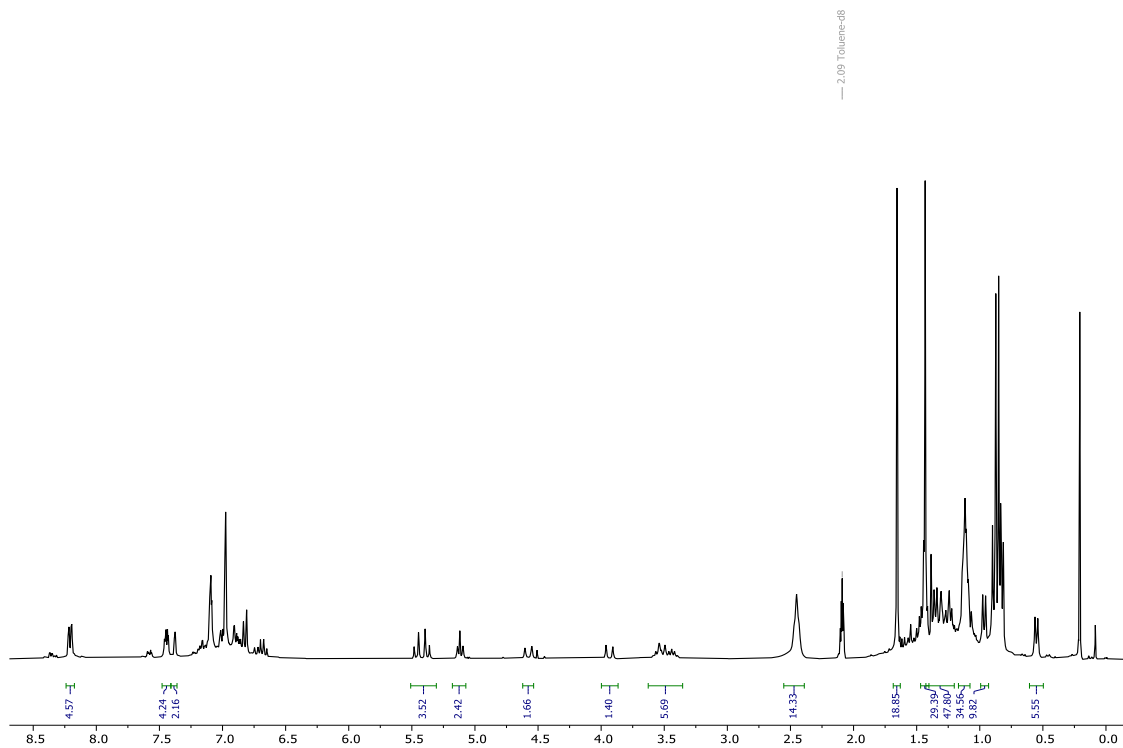


Figure S30. ¹H NMR spectrum (300.13 MHz, [D₈]toluene, 298 K) of crystals of [Ba₂{Carb^{DiPP,red}}]{Carb^{DiPP,silyl}}.(thf)₂ (**15**) dried briefly under vacuum.

X-ray diffraction crystallography details for complexes 6-17.

Compound	Complex Number	Experiment Number	CCDC Number
[{Carb ^{DiPP} }BaN(SiMe ₃) ₂ ·thf]	6	PC053	2003442
[{Carb ^{DiPP} }BaCH(SiMe ₃) ₂ ·thf]	7	PC084	2001221
[{Carb ^{DiPP} }BaN(SiMe ₂ H) ₂ ·thf]	8a	PC3013	2001222
[{Carb ^{DiPP} }BaN(SiMe ₂ H) ₂ ·Et ₂ O]	8b	PC05025	2009943
[{Carb ^{DiPP} }SrN(SiMe ₃) ₂]	9	PC2119	2003445
[{Carb ^{DiPP} }SrN(SiMe ₃) ₂ ·thf]	10	PC063	2001223
[{Carb ^{DiPP} }CaI·thf]	11	PC2099_2	2004124
[{Carb ^{DiPP} }CaCH(SiMe ₃) ₂ ·thf]	12	PC091	2001224
[{Carb ^{DiPP} }CaN(SiMe ₃) ₂]	13	PC06	2001225
[{Carb ^{DiPP} }Mg ⁿ Bu]	14	PC459	2004125
[Ba ₂ {Carb ^{DiPP,red} }{Carb ^{DiPP,silyl} }(thf) ₂]	15	PC0278	2003444
[Ca ₄ {Carb ^{DiPP,red} }] ₂ H ₂ ·(thf) ₂]	16	PC2170	2003446
[{Carb ^{DiPP} }CaSn(SiMe ₃) ₃ ·thf]	17	PC469_2	2004126

[{Carb^{DiPP}}BaN(SiMe₃)₂·thf] (CCDC 2003442, C₅₆H₈₄BaN₄OSi₂); $M = 1022.79$. 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 $P 2_1/n$ (I.T.#14), $a = 13.0335(16)$, $b = 22.924(3)$, $c = 19.431(2)$ Å, $\beta = 102.726(4)^\circ$, $V = 5663.0(11)$ Å³. $Z = 4$, $d = 1.200$ g·cm⁻³, $\mu = 0.782$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 12638 unique intensities and 623 parameters converged at $\omega R(F^2) = 0.0911$ ($R_F = 0.0431$) for 9542 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}BaCH(SiMe₃)₂·thf] (CCDC 2001221, C₅₇H₈₅BaN₃OSi₂); $M = 1021.79$. 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 $P 2_1/n$ (I.T.#14), $a = 13.0352(6)$, $b = 23.0649(12)$, $c = 19.3728(12)$ Å, $\beta = 102.726(2)^\circ$, $V = 5681.5(5)$ Å³. $Z = 4$, $d = 1.195$ g·cm⁻³, $\mu = 0.779$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 12927 unique intensities and 587 parameters converged at $\omega R(F^2) = 0.1239$ ($R_F = 0.0464$) for 10897 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}BaN(SiMe₂H)₂·thf] (CCDC 2001222, C₅₄H₈₀BaN₄OSi₂); $M = 994.74$. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.150 × 0.080 × 0.065 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150(2)$ K. Crystal structure has been described in monoclinic symmetry and $P 2_1/n$ (I.T.#14) centric space group. Cell parameters have been founded as follows: $a = 13.0429(4)$, $b = 22.7081(13)$, $c = 19.0827(7)$ Å, $\beta = 101.979(3)^\circ$, $V = 5528.8(4)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.195 g·cm⁻³ and 0.800 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program⁶). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except hydrogen atoms linked to silicon atom 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 12696 unique intensities and 568 parameters converged at $\omega R_F^2 = 0.0780$ ($R_F = 0.0338$) for 10928 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}BaN(SiMe₂H)₂·Et₂O] (CCDC 2009943, C₅₄H₈₂BaN₄OSi₂); $M = 996.75$. A suitable crystal for X-ray diffraction single crystal experiment (yellow prism, dimensions = 0.190 × 0.070 × 0.050 mm) was selected and mounted with a cryoloop on the goniometer head of a D8 Venture diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150(2)$ K. Crystal structure has been described in monoclinic symmetry and $P 2_1/n$ (I.T.#14) centric space group. Cell parameters have been founded as follows: $a = 13.4812(4)$, $b = 18.9373(7)$, $c = 22.0367(8)$ Å, $\beta = 100.3420(10)^\circ$, $V = 5534.5(3)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ

values are 1.196 g.cm^{-3} and 0.799 mm^{-1} respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL* program⁶). All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. Except Hydrogen atoms linked to silicon atoms of the main part of the disordered silicon group 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 12696 unique intensities and 601 parameters converged at $\omega R_F^2 = 0.1247$ ($R_F = 0.0511$) for 10369 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}SrN(SiMe₃)₂] (CCDC 2003445, C₅₈H₉₀N₄Si₂Sr); $M = 987.13$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator), $T = 150(2) \text{ K}$; monoclinic $P 2_1/n$ (I.T.#14), $a = 13.6245(15)$, $b = 17.4907(19)$, $c = 24.770(3) \text{ \AA}$, $\beta = 101.545(4)^\circ$, $V = 5783.2(11) \text{ \AA}^3$. $Z = 4$, $d = 1.134 \text{ g.cm}^{-3}$, $\mu = 1.011 \text{ mm}^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 13256 unique intensities and 622 parameters converged at $\omega R(F^2) = 0.0957$ ($R_F = 0.0407$) for 10164 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}SrN(SiMe₃)₂·thf] (CCDC 2001223, C₅₆H₈₄N₄OSi₂Sr); $M = 973.07$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator), $T = 150(2) \text{ K}$; monoclinic $P 2_1/n$ (I.T.#14), $a = 13.0440(9)$, $b = 22.7363(15)$, $c = 19.2821(13) \text{ \AA}$, $\beta = 103.267(3)^\circ$, $V = 5565.9(7) \text{ \AA}^3$. $Z = 4$, $d = 1.161 \text{ g.cm}^{-3}$, $\mu = 1.051 \text{ mm}^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 12729 unique intensities and 581 parameters converged at $\omega R(F^2) = 0.0971$ ($R_F = 0.0411$) for 10227 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}CaI·thf] (CCDC 2004124, C₆₂H₇₈CaIn₃O); $M = 1048.25$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator), $T = 150 \text{ K}$; tetragonal $I -4$ (I.T.#82), $a = 27.1903(5)$, $c = 15.5907(7) \text{ \AA}$, $V = 11526.4(7) \text{ \AA}^3$. $Z = 8$, $d = 1.208 \text{ g.cm}^{-3}$, $\mu = 0.685 \text{ mm}^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 13207 unique intensities and 645 parameters converged at $\omega R_F^2 = 0.0808$ ($R_F = 0.0346$) for 11796 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}CaCH(SiMe₃)₂·thf] (CCDC 2001224, C₅₇H₈₅CaN₃O Si₂); $M = 924.53$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator), $T = 150(2) \text{ K}$; monoclinic $P 2_1/n$ (I.T.#14), $a = 13.1266(12)$, $b = 22.5176(16)$, $c = 19.2806(17) \text{ \AA}$, $\beta = 103.089(3)^\circ$, $V = 5550.9(8) \text{ \AA}^3$. $Z = 4$, $d = 1.106 \text{ g.cm}^{-3}$, $\mu = 0.195 \text{ mm}^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 12532 unique intensities and 587 parameters converged at $\omega R(F^2) = 0.1443$ ($R_F = 0.0661$) for 8689 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}CaN(SiMe₃)₂] (CCDC 2001225, C₅₂H₇₆CaN₄Si₂·0.25(C₆H₁₄)); $M = 874.99$. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator), $T = 150(2) \text{ K}$; monoclinic $P 2_1/c$ (I.T.#14), $a = 15.3319(12)$, $b = 23.6745(16)$, $c = 16.1784(10) \text{ \AA}$, $\beta = 98.631(3)^\circ$, $V = 5805.9(7) \text{ \AA}^3$. $Z = 4$, $d = 1.001 \text{ g.cm}^{-3}$, $\mu = 0.183 \text{ mm}^{-1}$. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,⁷ implemented as the *SQUEEZE* option in *PLATON*.⁸ 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 13379 unique intensities and 533 parameters converged at $\omega R(F^2) = 0.1186$ ($R_F = 0.0466$) for 10381 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}MgⁿBu] (CCDC 2004125, C₅₀H₆₇MgN₃); $M = 734.37$. A suitable crystal for X-ray diffraction single crystal experiment (yellow prism, dimensions = 0.200 × 0.140 × 0.110 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150$ K; Crystal structure has been described in monoclinic symmetry and $P 2_1/n$ (I.T.#14) space group. Cell parameters have been refined as follows: $a = 13.2187(9)$, $b = 26.1942(16)$, $c = 13.5257(10)$ Å, $\beta = 109.095(3)^\circ$, $V = 4425.6(5)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.102 g.cm⁻³ and 0.076 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ 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 10030 unique intensities and 594 parameters converged at $\omega R_F^2 = 0.1461$ ($R_F = 0.0678$) for 6212 observed reflections with $I > 2\sigma(I)$.

[Ba₂{Carb^{DiPP,red}}{Carb^{DiPP,silyl}}.(thf)₂] (CCDC 2003444, C₁₁₂H₁₅₀Ba₂N₆O₂Si₂·0.5(C₅H₁₂)·0.5(C₆H₁₄)·0.5(C₇H₁₆)); $M = 2072.49$. 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; triclinic $P -1$ (I.T.#2), $a = 14.4116(14)$, $b = 14.4672(15)$, $c = 29.350(3)$ Å, $\alpha = 82.677(4)$, $\beta = 86.879(4)$, $\gamma = 67.857(4)^\circ$, $V = 5621.7(10)$ Å³. $Z = 2$, $d = 1.224$ g.cm⁻³, $\mu = 0.768$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,⁷ implemented as the *SQUEEZE* option in *PLATON*.⁸ 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. Except silicon-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 25526 unique intensities and 1135 parameters converged at $\omega R_F^2 = 0.1201$ ($R_F = 0.0553$) for 19055 observed reflections with $I > 2\sigma(I)$.

[Ca₄{Carb^{DiPP,red}}₂H₂.(thf)₂] (CCDC 2003446, C₁₀₀H₁₃₈Ca₄N₆O₂); $M = 1616.48$. 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; triclinic $P -1$ (I.T.#2), $a = 13.5213(19)$, $b = 13.6820(15)$, $c = 14.4001(16)$ Å, $\alpha = 62.706(4)$, $\beta = 71.846(5)$, $\gamma = 81.977(5)^\circ$, $V = 2249.5(5)$ Å³. $Z = 1$, $d = 1.193$ g.cm⁻³, $\mu = 0.292$ mm⁻¹. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except H1CA 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 10303 unique intensities and 523 parameters converged at $\omega R(F^2) = 0.2467$ ($R_F = 0.1180$) for 7498 observed reflections with $I > 2\sigma(I)$.

[{Carb^{DiPP}}CaSn(SiMe₃)₃.thf] (CCDC 2004126, C₅₉H₉₃CaN₃O₃Si₃Sn); $M = 1103.40$. A suitable crystal for X-ray diffraction single crystal experiment (orange prism, dimensions = 0.680 × 0.300 × 0.240 mm) was selected and mounted on the goniometer head of a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 150$ K; The crystal structure has been described in monoclinic symmetry and $P 2_1/c$ (I.T.#14) space group. Cell parameters have been refined as follows: $a = 13.0735(18)$, $b = 20.434(2)$, $c = 25.973(3)$ Å, $\beta = 91.784(5)^\circ$, $V = 6935.2(14)$ Å³. Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.105 g.cm⁻³ and 0.531 mm⁻¹ respectively. The structure was solved by dual-space algorithm using the *SHELXT* program,⁵ and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).⁶ The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,⁷ implemented as the *SQUEEZE* option in *PLATON*.⁸ 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 15634 unique intensities and 683 parameters converged at $\omega R_F^2 = 0.1304$ ($R_F = 0.0563$) for 11028 observed reflections with $I > 2\sigma(I)$.

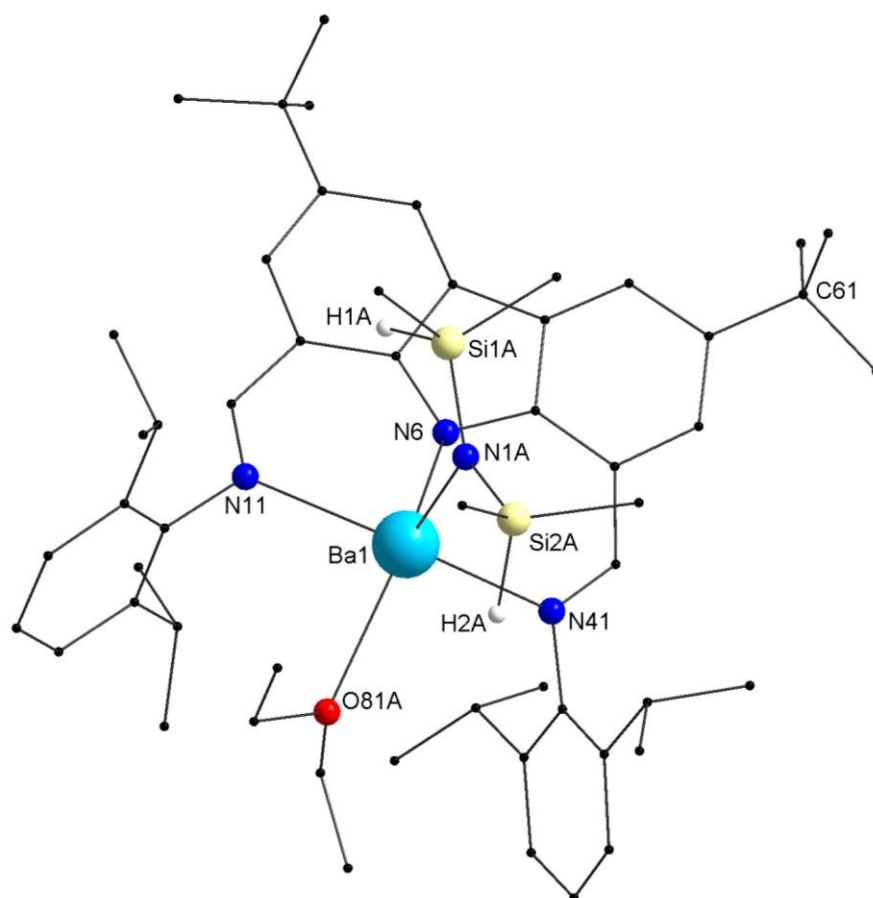


Figure S31. Representation of the molecular solid-state structure of $[\{\text{Carb}^{\text{DiPP}}\}\text{BaN}(\text{SiMe}_2\text{H})_2\text{-Et}_2\text{O}]$ (**8b**). H atoms other than SiH omitted for clarity. Only the main components of the disordered tBu group (for C61, 66% site occupation), $\text{N}(\text{SiMe}_2\text{H})_2$ (N1A, 87%) moiety and Et_2O molecule (O81A, 62%) are depicted. Selected interatomic distances (Å) and angles ($^\circ$): Ba1-N1A = 2.587(4), Ba1-N6 = 2.687(3), Ba1-N11 = 2.803(3), Ba1-N41 = 2.796(3), Ba1-O81A = 2.802(7); N1A-Ba1-N6 = 103.72(11), N1A-Ba1-N11 = 116.32(12), N1A-Ba1-N41 = 110.68(12), N1A-Ba1-O81A = 111.4(2), N6-Ba1-N11 = 69.27(8), N6-Ba1-N41 = 68.28(8), N6-Ba1-O81A = 144.8(2), N11-Ba1-N41 = 122.04(9), N11-Ba1-O81A = 94.22(17), N41-Ba1-O81A = 98.51(18). Torsion angles ($^\circ$): Ba1-N1A-Si1A-H1A = 10.03(230), Ba1A-N1A-Si2A-H2A = 9.19(246).

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