

Supplementary Material

Synthesis and Characterisation of Two Lithium Tetramethylberyllate Salts and a Series of β -Diketiminato Beryllium Alkyl Complexes

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Supplementary Material (45 pages)

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1. Experimental

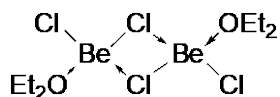
General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether was distilled over Na/K alloy (50:50), while *n*-hexane, toluene, and THF were distilled over molten potassium. Benzene-*d*₆ was stored over a mirror of sodium and degassed three times via freeze-pump-thaw. ¹H, ⁷Li, ⁹Be, ¹³C{¹H}, COSY, and HSQC NMR spectra were recorded on either Bruker Avance III 400 or Bruker Avance III 600 spectrometers and were referenced to the resonances of the solvent used, or to external reference solutions of 0.1 M LiCl in D₂O or Be(NO₃)₂ in H₂O/D₂O (90:10). The chemical shifts δ are reported in ppm. Mass spectra were collected using an Agilent Technologies 5975D inert MSD with a solid-state probe. FTIR spectra were collected for solid samples on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer, and the wavenumbers ν are reported in cm⁻¹. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined at ramp rates of 5 °C·min⁻¹ in sealed glass capillaries under dinitrogen and are uncorrected. The starting materials [BeX₂(OEt₂)₂] (X = Br, I),^[1] HC(MeCNPh){MeCN(H)Ph} ^{Ph}NacnacH,^[2] HC(MeCNXyl){MeCN(H)Xyl} ^{Xyl}NacnacH,^[3] HC(MeCNMes){MeCN(H)Mes} ^{Mes}NacnacH,^[4] HC(MeCNDep){MeCN(H)Dep} ^{Dep}NacnacH,^[5] and HC{MeCN(H)-(S)-(-)-CHMePh}(MeCNDip) ^{chiral}NacnacH^[6] were synthesised *via* reported methods. Diethyl ether solutions of LiMe·LiBr (1.5 mol L⁻¹), and *n*-hexane solutions of LiBu^{*n*} (1.6 mol L⁻¹) were purchased from Sigma Aldrich, and their concentrations regularly checked by titration.^[7] Tmeda was distilled from CaH₂ and stored over molecular sieves 4 Å. All other reagents were used as received from commercial sources.

CAUTION: Beryllium and its compounds are regarded as highly toxic and carcinogenic, and they also have an allergic potential if inhaled, with the risk of causing chronic beryllium disease.^[8] Suitable precautions (e.g., use of protective clothing, a breathing apparatus, and a well-ventilated fume cupboard) should be taken for all manipulations involving them.

[BeI₂(OEt₂)₂].

Prepared by a variation of the literature procedure.^[1] In a 3 L round-bottom Schlenk flask, iodine (15.1 g, 59.5 mmol) was added to a block of beryllium metal (15.42 g, ~2×2×2 cm³) in diethyl ether (200 mL) at 0 °C. The mixture was warmed slowly to room temperature and kept for 8 d with regular agitation. After one day, colourless crystal blocks had already formed on the glass walls and on the surface of the beryllium block. After 8 d, the solvent was decanted, and the red gluey residue extracted with hot toluene (50 mL). Volatiles were removed from the red filtrate under vacuum. The waxy residue was extracted with hot toluene (50 mL) and filtered. All volatiles were then removed

under vacuum, the residue extracted with hot toluene (50 mL), filtered, and stored at $-30\text{ }^{\circ}\text{C}$. The title compound was obtained as colourless crystalline material and isolated through decantation and drying under reduced pressure (20.9 g, 85 %). The remaining beryllium block was rinsed with isopropanol, ethanol, water and acetone, and dried under a stream of dinitrogen. This could be used for future preparations. NMR spectroscopic data for the title compound were identical to those reported.^[1]



In a 3 L round-bottom Schlenk flask, HCl in diethyl ether (20.0 mmol, 10.0 mL, 2.0 mol L⁻¹) was added dropwise to a block of beryllium metal (14.87 g, $\sim 2 \times 2 \times 2\text{ cm}^3$) in diethyl ether (200 mL) at $0\text{ }^{\circ}\text{C}$. An oil bubbler was connected to allow the formed dihydrogen gas to escape. The mixture was slowly warmed to room temperature and kept for 10 d with regular agitation. The yellowish liquid was then decanted off and all volatiles removed under reduced pressure. The residue was extracted with hot toluene ($2 \times 50\text{ mL}$) and the extract concentrated under vacuum to approx. 3 mL. Colourless crystalline blocks of the title compound formed after storing at $-30\text{ }^{\circ}\text{C}$ (464 mg, 15 %). M.p.: $102\text{-}104\text{ }^{\circ}\text{C}$ (colourless liquid); ¹H NMR (benzene-*d*₆, 600 MHz): $\delta = 0.88$ (t, ³*J*_{HH} = 7.1 Hz, 12H, OCH₂CH₃), 3.79 (t, ³*J*_{HH} = 7.1 Hz, 8H, OCH₂CH₃); ⁹Be NMR (benzene-*d*₆, 56 MHz): $\delta = 3.1$ (s, $\Delta\omega_{1/2} = 8\text{ Hz}$); ¹³C{¹H} NMR (benzene-*d*₆, 151 MHz): $\delta = 13.3$ (OCH₂CH₃), 68.7 (OCH₂CH₃); IR (ATR) ν (cm⁻¹) = 1739 w, 1197 w, 1151 m, 1092 m, 1026 m, 999 s, 894 s, 846 s, 780 very s, 706 s, 669 s; MS (EI 70 eV), *m/z* (%): 79.0 ([BeCl(OEt₂)-H]⁺, 29), 74.1 ([Et₂O]⁺, 72), 59.1 ([Et₂O-CH₃]⁺, 100); elemental analysis for C₈H₂₀O₂Be₂Cl₄ found (calcd.) in %: C 31.14 (31.19), H 6.41 (6.54).

S 4

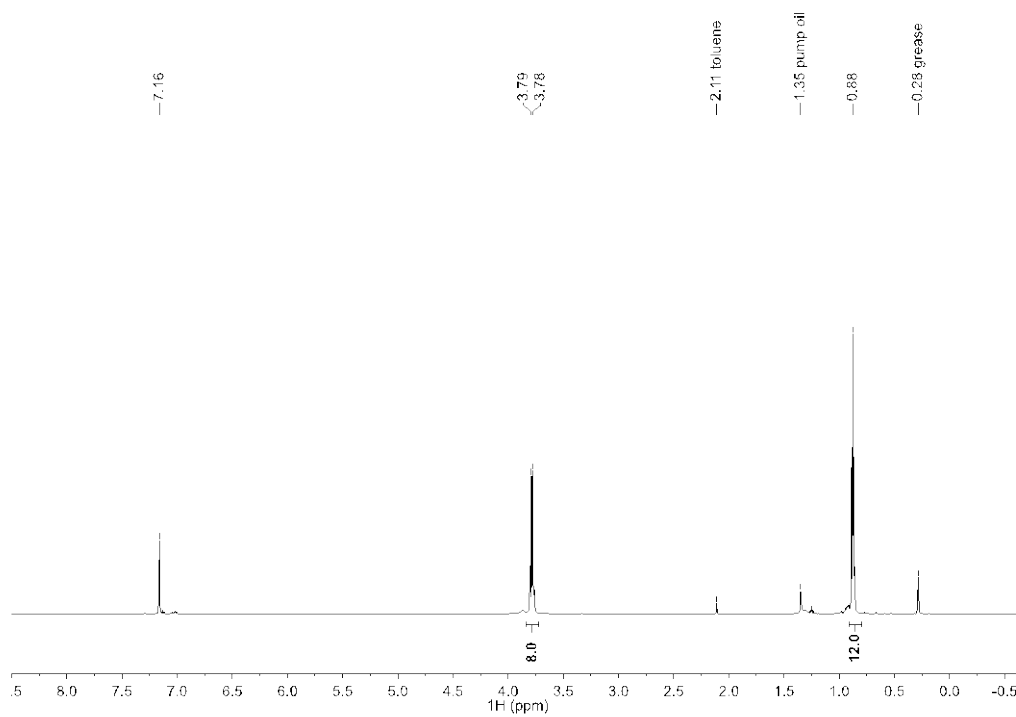


Figure S1. ^1H NMR spectrum of $[\{\text{BeCl}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ in benzene- d_6 at 298 K (600 MHz).

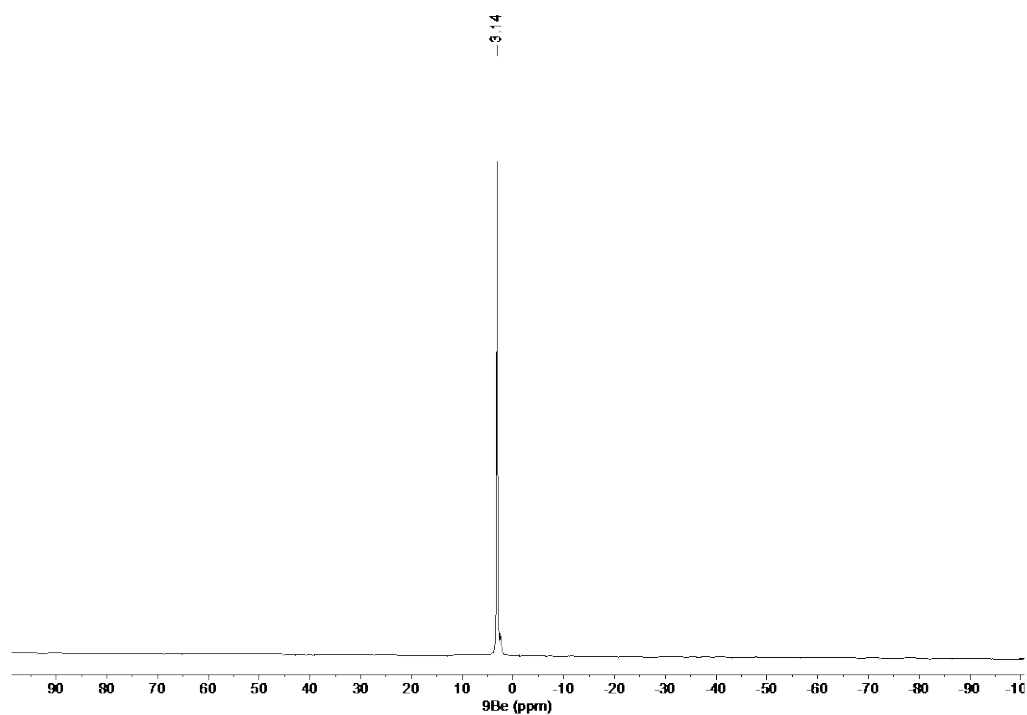


Figure S2. ^9Be NMR spectrum of $[\{\text{BeCl}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ in benzene- d_6 at 298 K (56 MHz).

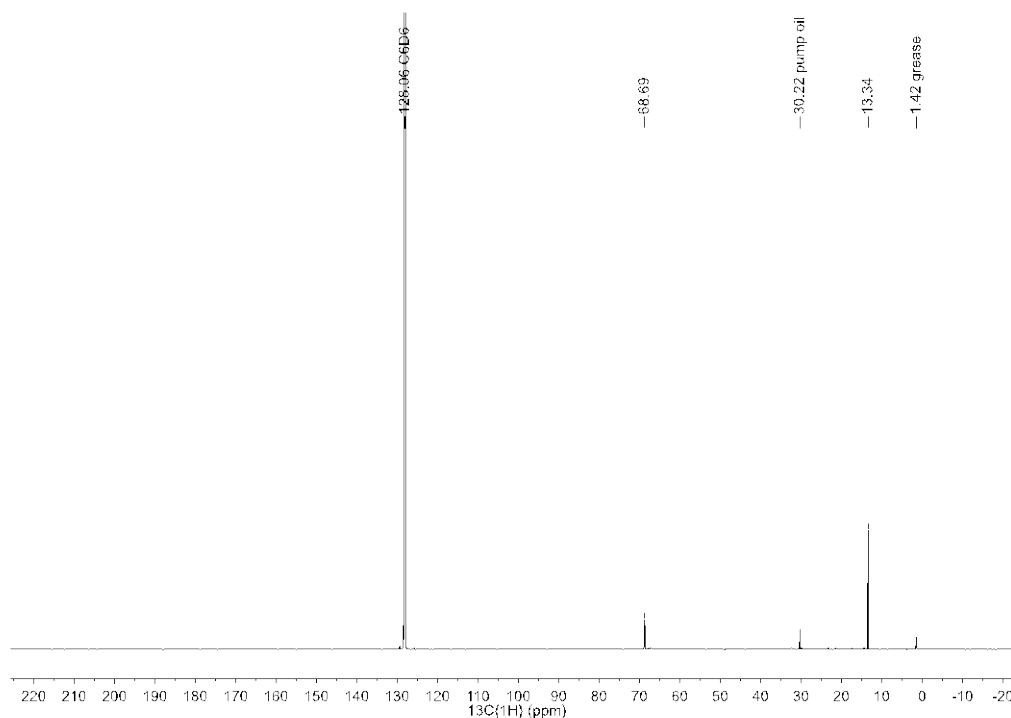


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\{\text{BeCl}(\text{OEt}_2)(\mu\text{-Cl})_2\}]$ in benzene- d_6 at 298 K (151 MHz).

“BeMe₂”.

Prepared *via* a variation of the literature procedure.^[9] LiMe·LiBr (1.74 mL, 1.5 mol·L⁻¹ in diethyl ether, 2.61 mmol, 2 equiv.) was added to a solution of $[\text{BeI}_2(\text{OEt}_2)_2]$ (510 mg, 1.24 mmol) in toluene (10 mL) at $-78\text{ }^\circ\text{C}$. The creamy white suspension was stirred for 16 h while slowly warming to room temperature. The mixture was then filtered, and volatiles removed from the filtrate under reduced pressure. The residue was extracted with boiling toluene (5 mL). Volatiles were removed from the extract under reduced pressure, and the colourless oil dried *in vacuo* for 12 h. The oily residue solidified overnight to a waxy solid when stored in a Schlenk flask at room temperature. NMR spectroscopic studies of the isolated material suggested it to contain a mixture of several products (see main text for further details). Titration as described below determined the total available methyl groups in the mixture to be 2.38 mmol (91 %). **CAUTION: The oily solid is extremely reactive. It ignites explosively upon exposure to air and moisture and forms toxic fumes!** ^1H NMR (benzene- d_6 , 400 MHz): $\delta = -0.67$ (br. s, BeCH_3), 0.69 (t, $^3J_{\text{HH}} = 7.1$ Hz, OCH_2CH_3), 2.93 (q, $^3J_{\text{HH}} = 7.0$ Hz, OCH_2CH_3); ^7Li NMR (benzene- d_6 , 156 MHz): $\delta = 0.45$ (s); ^9Be NMR (benzene- d_6 , 56 MHz): $\delta = 7.7$ (br. s, $\Delta\omega_{1/2} = 100$ Hz), 12.0 (br. s, $\Delta\omega_{1/2} = 100$ Hz), 22.4 (br. s, $\Delta\omega_{1/2} = 240$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 101 MHz): $\delta = -5.4$ (br., BeCH_3), 14.3 (OCH_2CH_3), 65.9 (OCH_2CH_3).

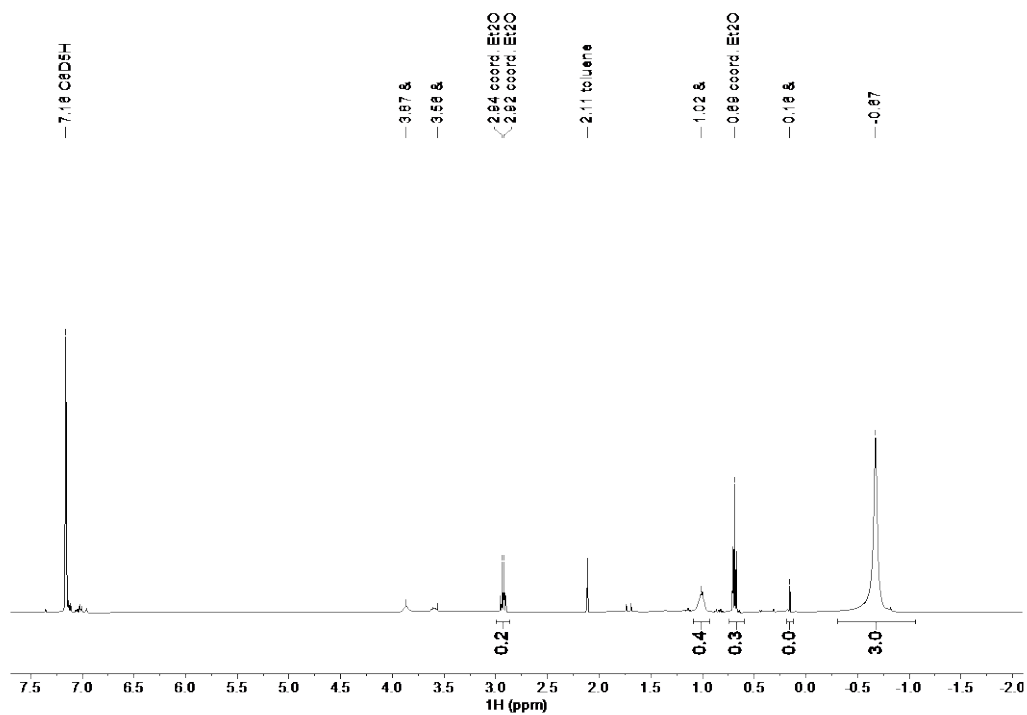


Figure S4. ^1H NMR spectrum of “BeMe₂” product mixture in benzene-*d*₆ at 298 K (400 MHz).

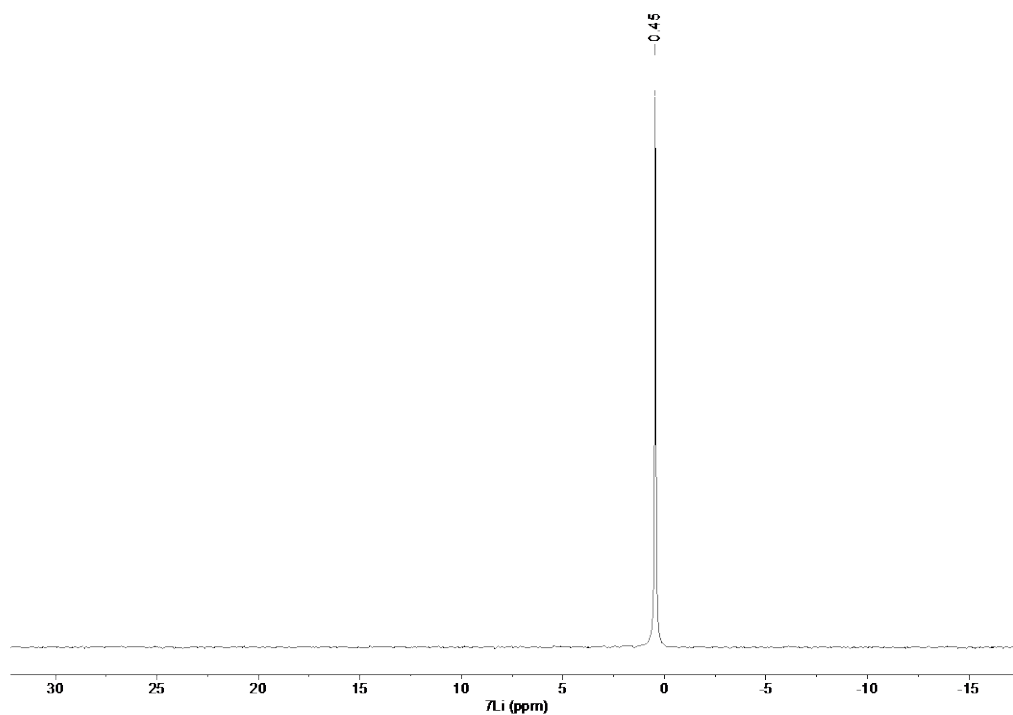


Figure S5. ^7Li NMR spectrum of “BeMe₂” product mixture in benzene-*d*₆ at 298 K (156 MHz).

S 7

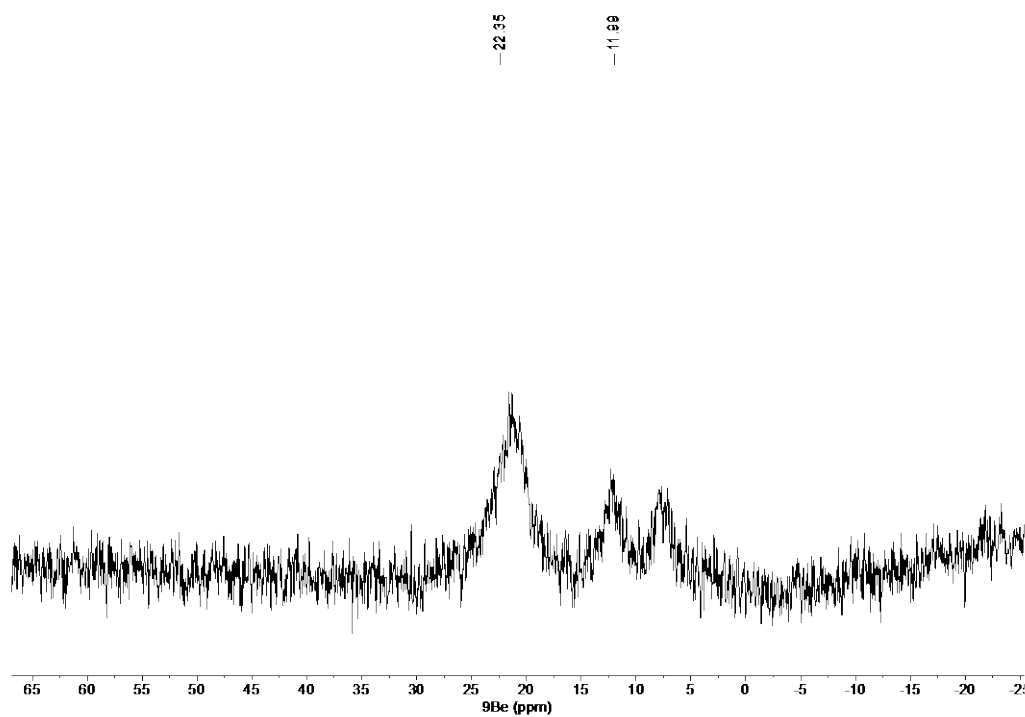


Figure S6. ^9Be NMR spectrum of “BeMe₂” product mixture in benzene-*d*₆ at 298 K (56 MHz).

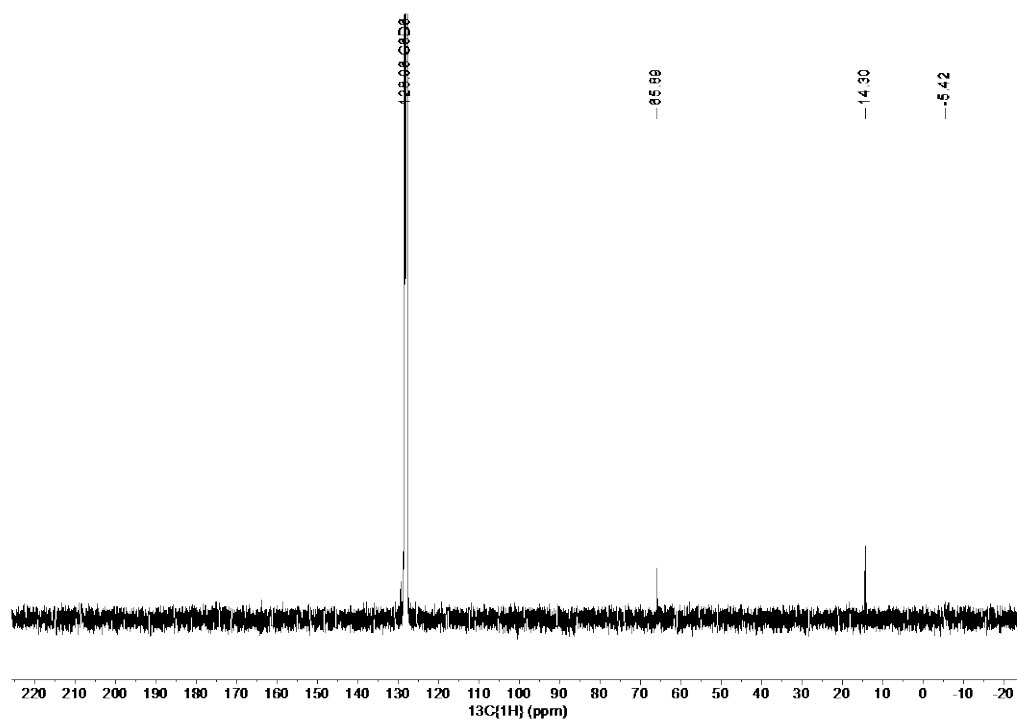


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of “BeMe₂” product mixture in benzene-*d*₆ at 298 K (101 MHz).

“BeBuⁿ”.

Prepared *via* a variation of the literature procedure.^[9] LiBuⁿ (1.52 mL, 1.6 mol·L⁻¹ in *n*-hexane, 2.43 mmol, 2 equiv.) was added to a solution of [BeI₂(OEt)₂] (500 mg, 1.22 mmol) in toluene (10 mL) at -78 °C. The creamy white suspension was stirred for 16 h while slowly warming to room temperature. The mixture was then filtered, and volatiles removed from the filtrate under reduced pressure. The residue was then extracted with warm toluene (5 mL). Volatiles were removed from the extract under reduced pressure, and the colourless oil dried *in vacuo* for 6 h. NMR spectroscopic studies of the isolated material suggested it to contain a mixture of several products. The oily residue solidified to a wax when stored in a Schlenk flask for several weeks at room temperature. Titration as described below determined the total available *n*-butyl groups in the mixture to be 2.30 mmol (94 %). **CAUTION: The oily solid ignites upon exposure to air and moisture and forms toxic fumes!** ¹H NMR (benzene-*d*₆, 400 MHz): δ = 0.16 (br. s, BeCH₂), 0.70 (t, ³J_{HH} = 7.1 Hz, OCH₂CH₃), 1.07 (br. s, 6H, CH₃), 1.54 (br. s, CH₂CH₂), 3.05 (m, OCH₂CH₃); ⁷Li NMR (benzene-*d*₆, 156 MHz): δ = -1.94 (s, Li-containing impurity); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 7.5 (br. sh.), 13.6 (br. s, Δω_{1/2} = 261 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = 12.4 (br., BeCH₂), 14.2 (OCH₂CH₃), 14.3 (br., CH₃), 29.3 (br., CH₂), 30.0 (br., CH₂), 66.4 (OCH₂CH₃); IR (ATR) ν (cm⁻¹) = 1454 w, 1271 w, 1213 w, 1183 m, 1125 m, 1068 w, 1042 m, 985 m, 947 m, 873 w, 850 m, 694 s, 672 s.

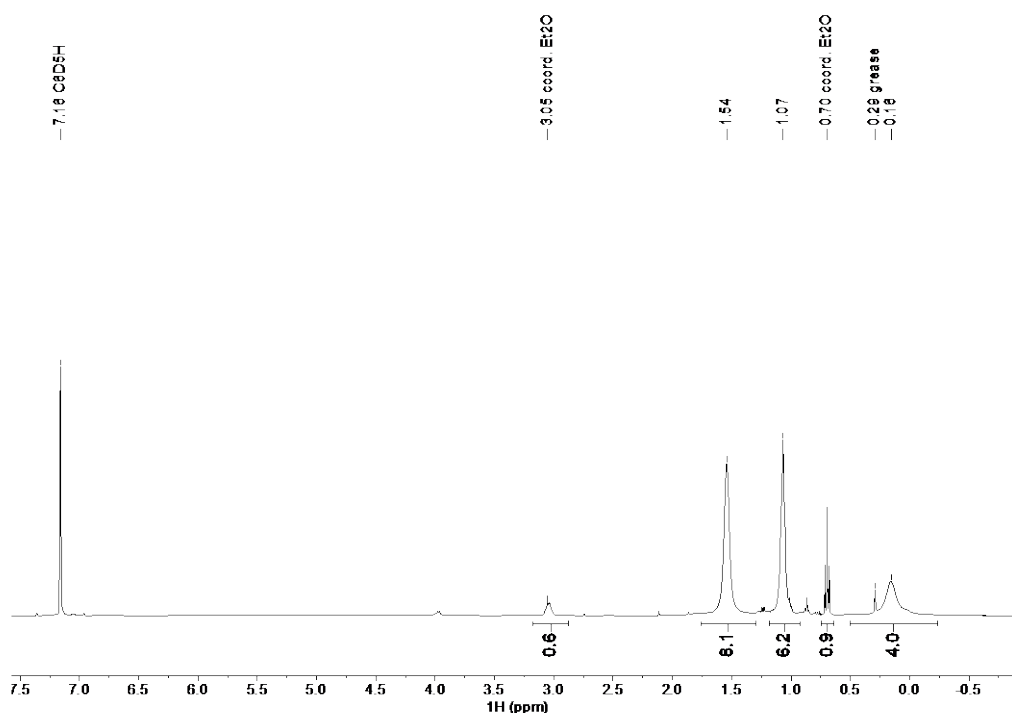


Figure S8. ¹H NMR spectrum of BeBuⁿ product mixture in benzene-*d*₆ at 298 K (400 MHz).

S 9

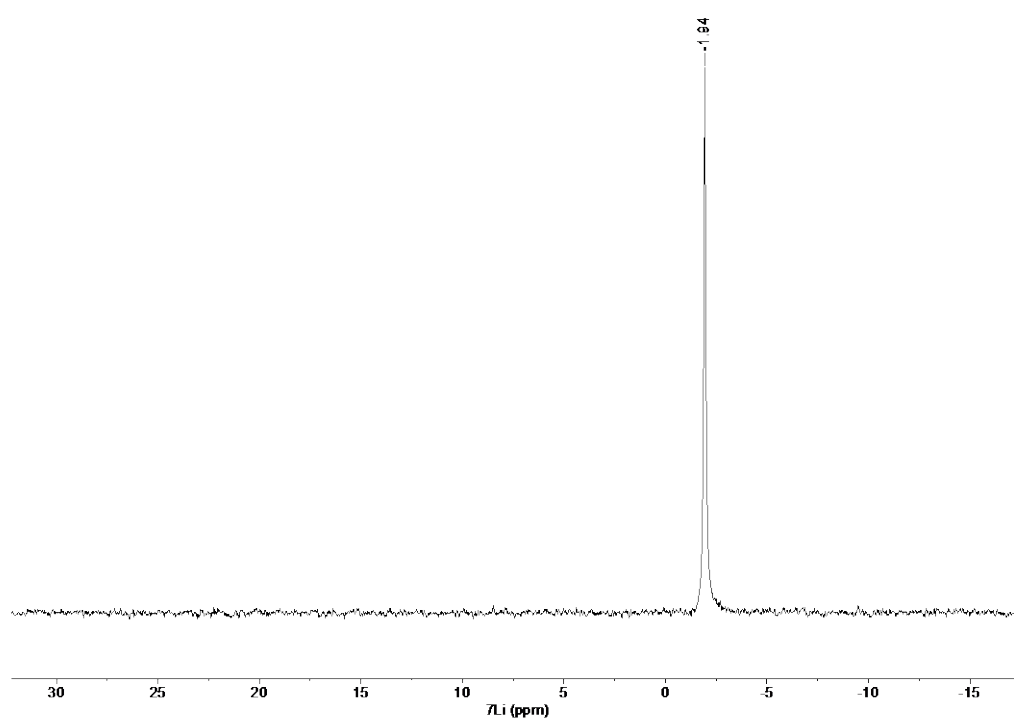


Figure S9. ${}^7\text{Li}$ NMR spectrum of “BeBu n ${}_2$ ” product mixture in benzene- d_6 at 298 K (156 MHz).

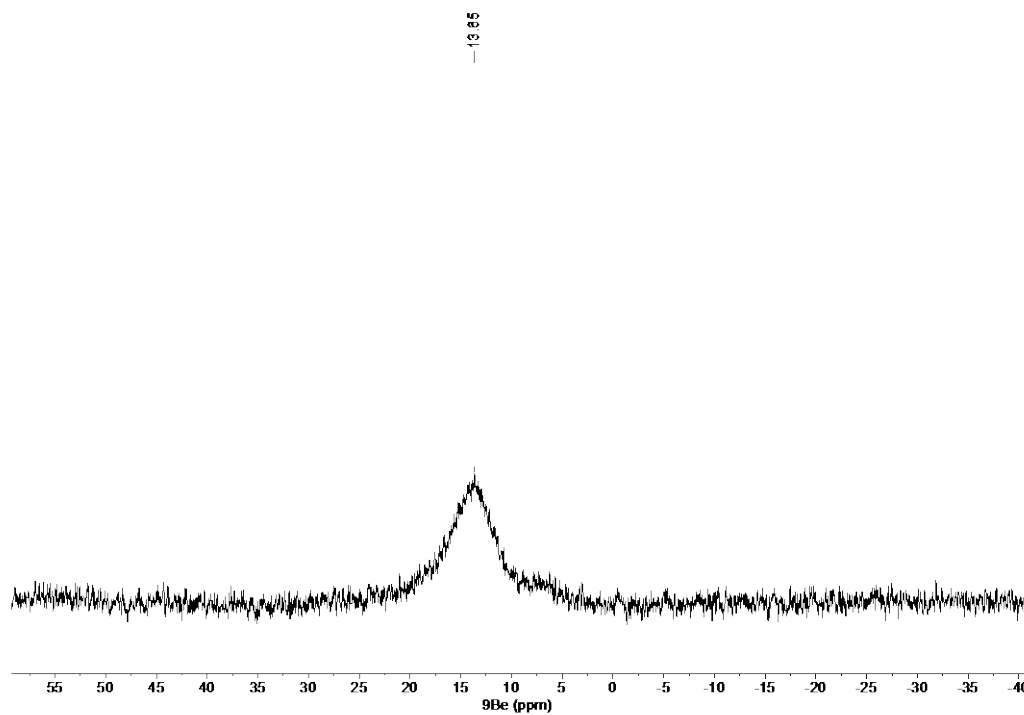


Figure S10. ${}^9\text{Be}$ NMR spectrum of “BeBu n ${}_2$ ” product mixture in benzene- d_6 at 298 K (56 MHz).

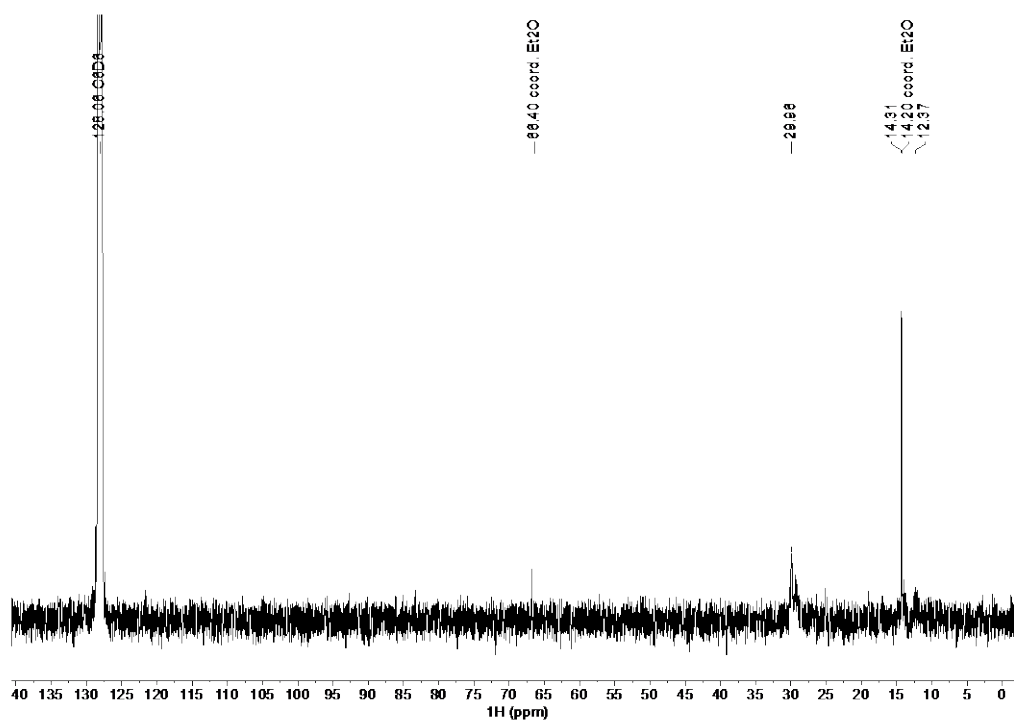


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of “BeBuⁿ₂” product mixture in benzene-*d*₆ at 298 K (101 MHz).

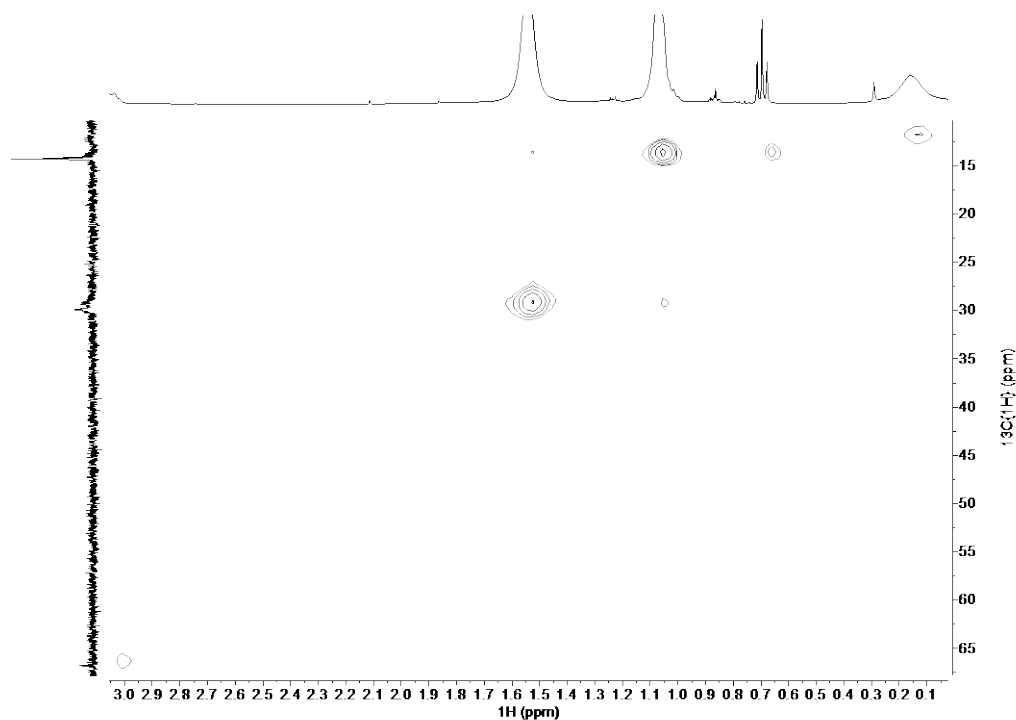


Figure S12. Excerpt from the HSQC NMR spectrum of “BeBuⁿ₂” product mixture in benzene-*d*₆ at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

Method for titrating available beryllium alkyl residues in “BeR₂” mixtures.

An oven-dried scintillation vial equipped with a small Teflon stir bar was stoppered with a septum and a stream of nitrogen was applied through needles piercing the septum (see Figure S13). After flushing with N₂ for 15 min, the septum was partially lifted and I₂ – typically 18-30 mg – was introduced. 3 mL of a saturated solution of LiCl in THF (500 mg in 100 mL) was added and a clear orange-red solution formed. The “BeR₂” mixture (R = Buⁿ or Me) solutions were added dropwise via a 1.00 mL syringe at room temperature. Upon reaction, the colour of the vigorously stirred solution changed from orange-red to yellow. As soon as the solution became very faintly yellow, addition was stopped for 15 seconds. Then a last drop was added, and the solution turned instantly colourless. The volume added and the amount of iodine used were employed for calculating the unknown “BeR₂” concentration in solution (Equation 1):^[7]

$$c(\text{BeR}_2) = \frac{1}{2} \frac{m(\text{I}_2)}{M(\text{I}_2) \cdot V(\text{BeR}_2\text{-solution})} \quad (\text{Equation 1})$$

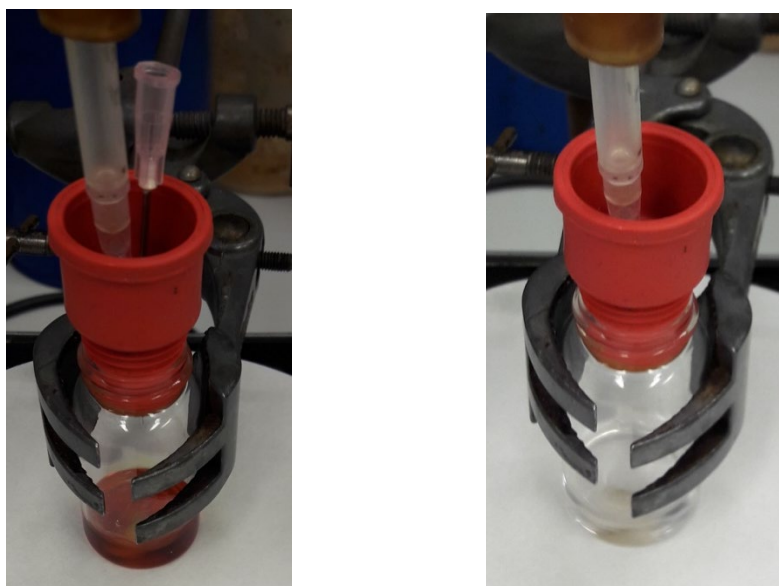
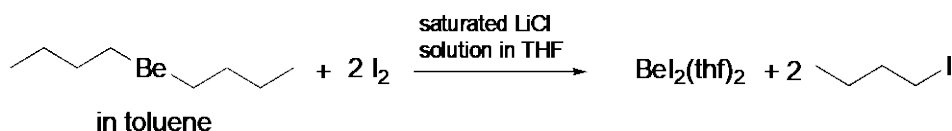
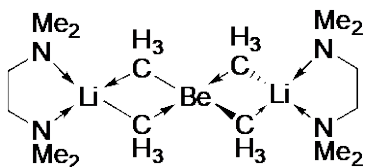


Figure S13. Titration of beryllium alkyls; I₂ solution (left) and solution after “BeR₂” addition end point reached (right).



Scheme S1. Titration of “BeR₂” exemplified using “BeBuⁿ”.

[{(tmeda)Li}₂(μ-BEMe₄)] (1).



A solution of [BeI₂(OEt₂)₂] (1.54 g, 3.75 mmol) in toluene (20 mL) was treated with LiMe·LiBr (5.0 mL, 1.5 mol L⁻¹ in diethyl ether, 7.5 mmol, 2 equiv.) at -78 °C. Upon warming to room temperature, a colourless solution formed. Volatiles were removed from the mixture under reduced pressure until most of the diethyl ether was removed. This led to the formation of a dense colourless suspension. Tmeda (0.6 mL, 3.8 mmol) was then added to the reaction mixture. Stirring was continued for 16 h before all volatiles were removed under vacuum. The residue was extracted with 2 × 10 mL warm toluene. The filtrate was concentrated under vacuum to incipient crystallisation. The solution was then kept at -30 °C. A colourless crystalline mixture of products, including **1** as the major component, was isolated. The other product(s) could not be separated after repeated recrystallisations (517 mg). M.p.: 161-163 °C (opaque liquid); ¹H NMR (benzene-*d*₆, 400 MHz): δ = -0.68 (br. s, 12H, BeCH₃), 1.81 (s, 8H, CH₂), 1.95 (s, 24H, CH₃); ⁷Li NMR (benzene-*d*₆, 156 MHz): δ = 1.54 (s); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 11.0 (v. br. s, Δω_{1/2} = 860 Hz) and/or 18.9 (s, Δω_{1/2} = 49 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = -3.7 (BeCH₃), 47.2 (CH₃), 56.5 (CH₂); IR (ATR) ν (cm⁻¹) = 1458 s, 1156 s, 1129 m, 1098 m, 1063 m, 1035 m, 1017 m, 947 s, 766 vs; MS (EI 70 eV), m/z (%): 123.2 ([{(tmeda)Li}]⁺, 39), 116.2 ([tmeda]⁺, 51), 72.2 ([Me₂NCH₂CH₂]⁺, 24), 58.2 ([Me₂NCH₃]⁺, 100).

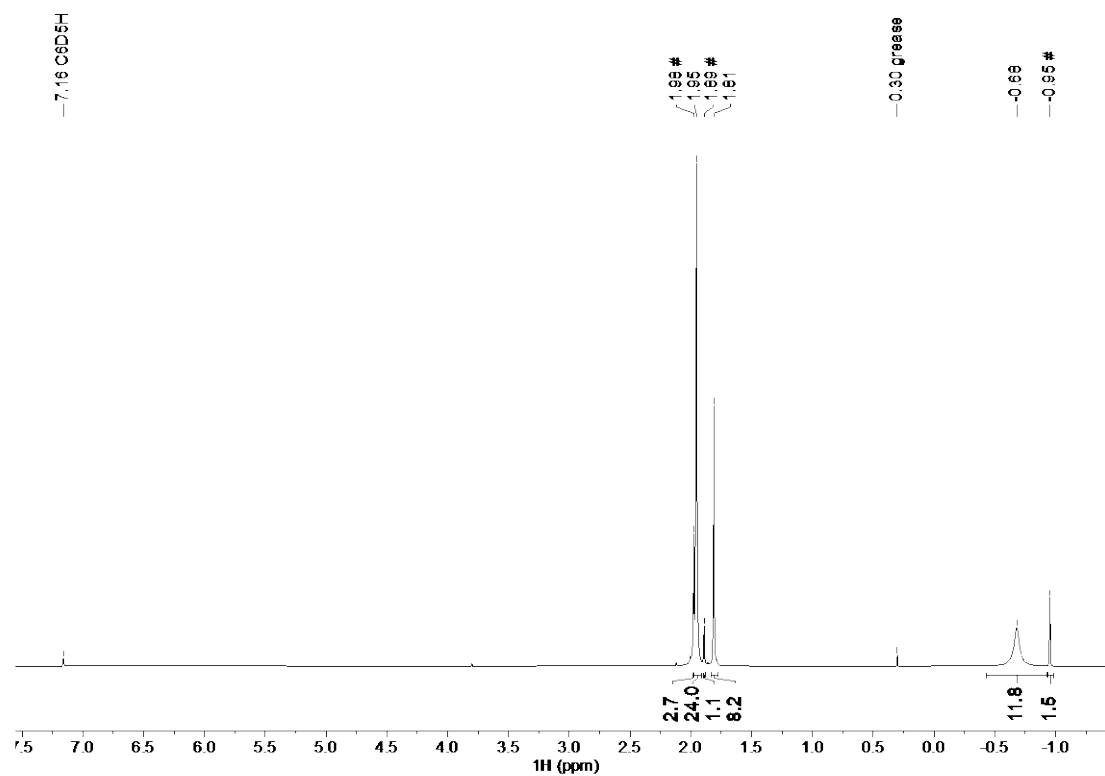


Figure S14. ^1H NMR spectrum of the crystalline mixture containing **1**, in benzene- d_6 at 298 K (400 MHz). #: unidentified species.

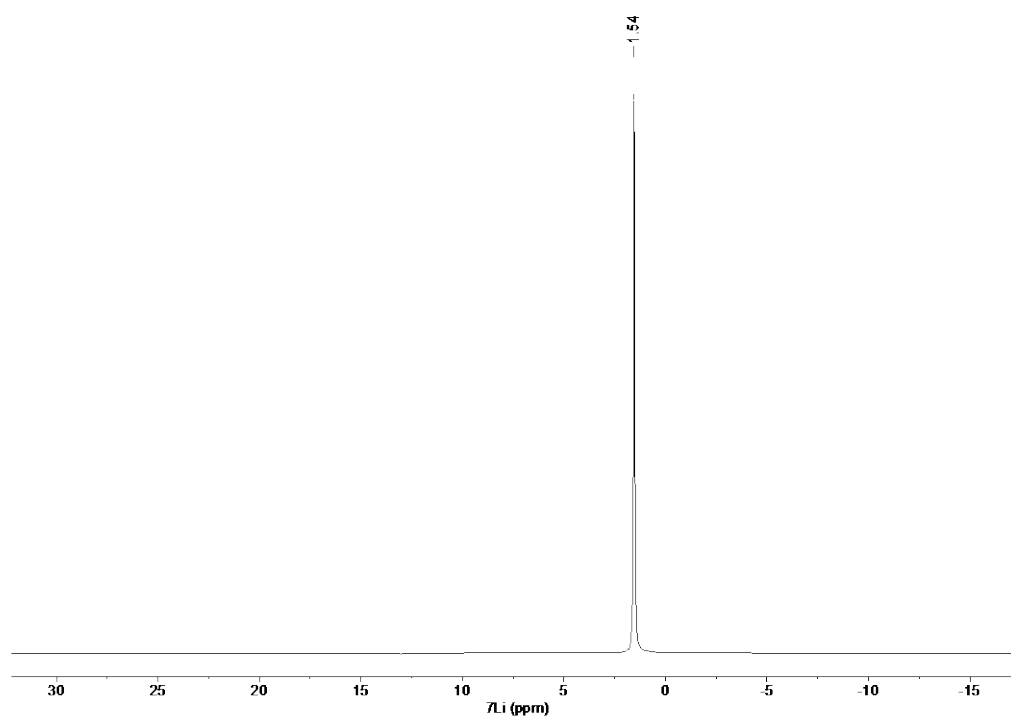


Figure S15. ^7Li NMR spectrum of the crystalline mixture containing **1**, in benzene- d_6 at 298 K (156 MHz).

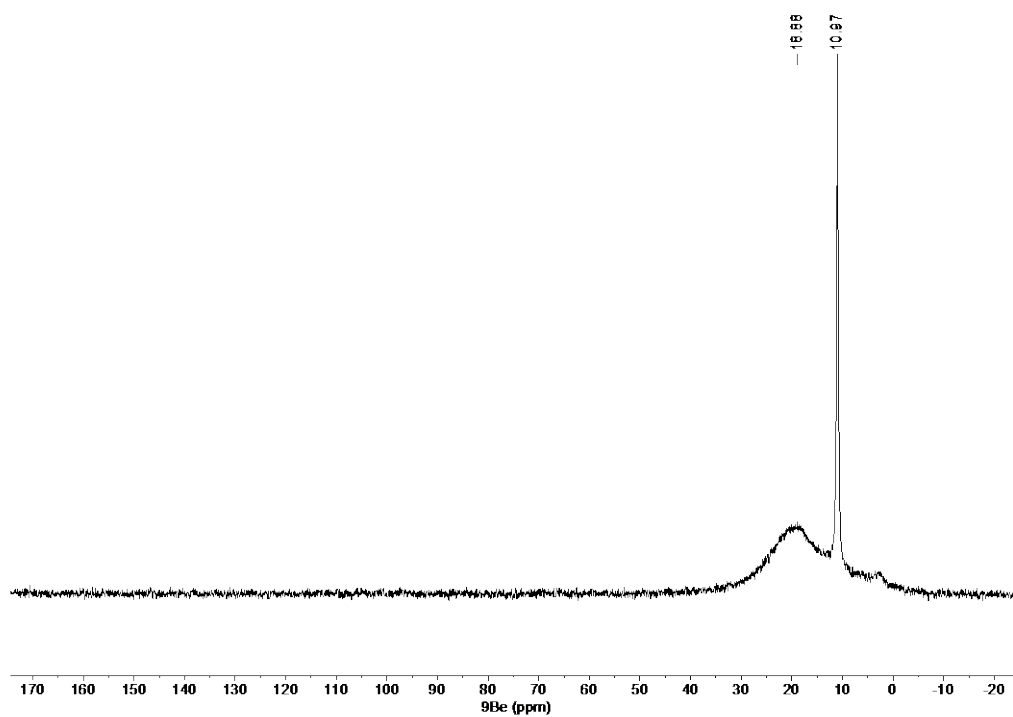


Figure S16. ^9Be NMR spectrum of the crystalline mixture containing **1**, in benzene- d_6 at 298 K (56 MHz).

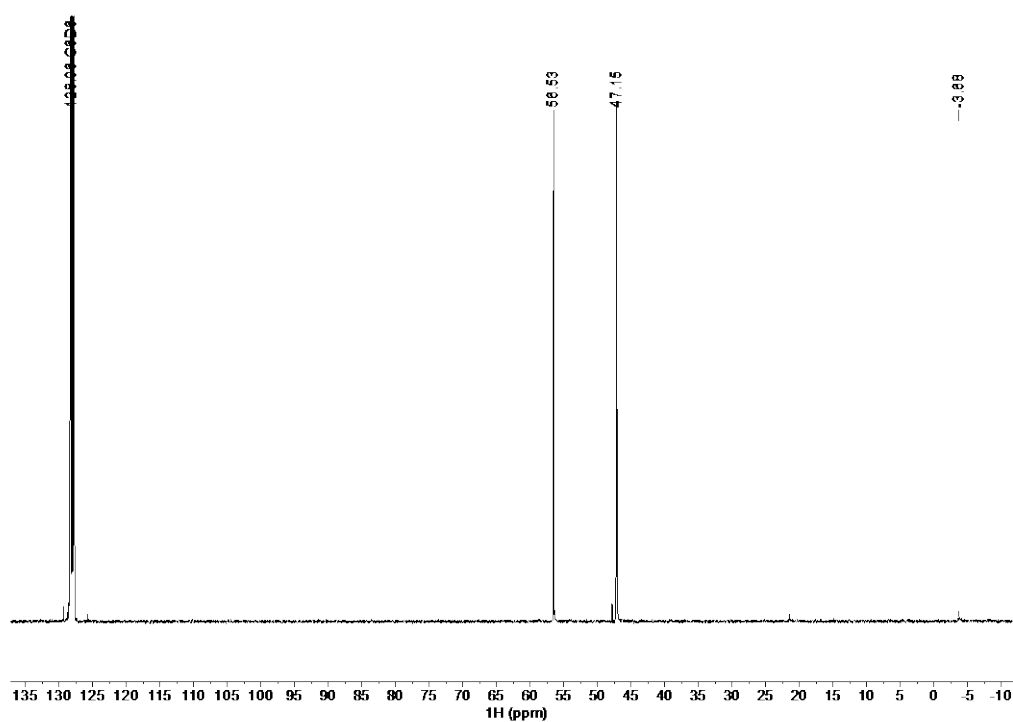


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the crystalline mixture containing **1**, in benzene- d_6 at 298 K (101 MHz).

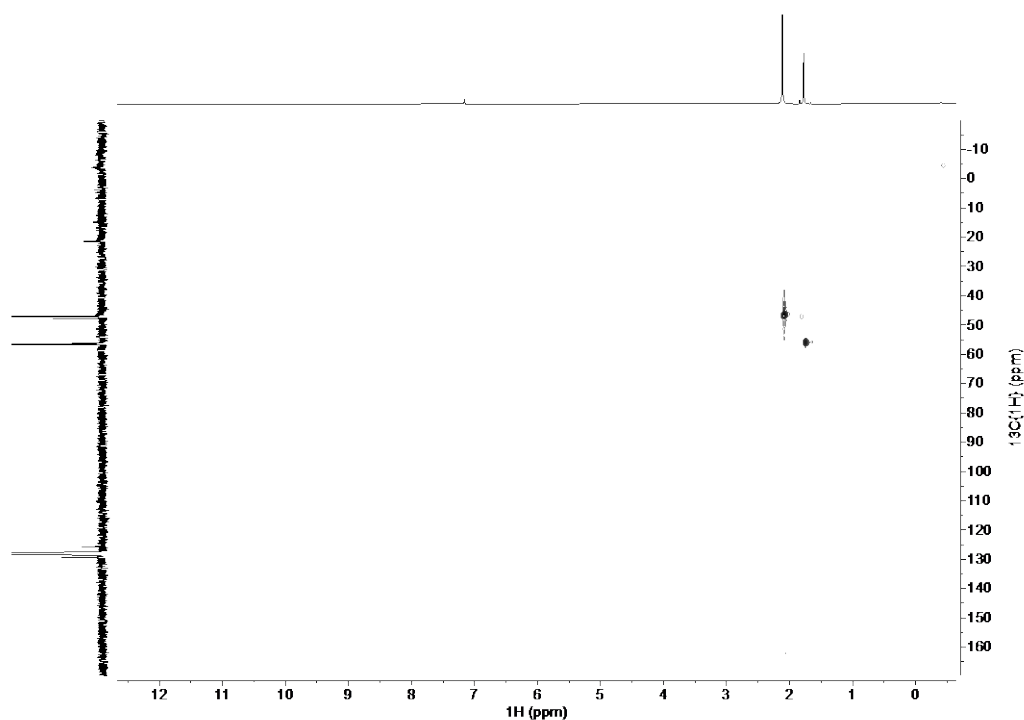
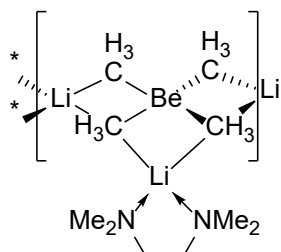


Figure S18. HSQC NMR spectrum of the crystalline mixture containing **1**, in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[{[(tmeda)Li](BeMe₄)(μ -Li)}_∞] (2**).**



Compound **2** was reproducibly obtained from attempted rational syntheses of **1**, as follows. A vigorously stirred solution of $[\text{BeI}_2(\text{OEt}_2)_2]$ (3.65 g, 8.88 mmol) in toluene (80 mL) was treated at room temperature with tmeda (2.7 mL, 18 mmol, 2 equiv.) which caused precipitation of a dense colourless solid. After stirring for 10 min, $\text{LiMe}\cdot\text{LiBr}$ (24.3 mL, 1.5 mol L^{-1} solution in diethyl ether, 36.4 mmol, 4.1 equiv.) was added dropwise at room temperature. The temperature of the reaction mixture increased slightly, and a colourless solution resulted after 15 min. Diethyl ether was then mostly removed under reduced pressure. The creamy colourless suspension was stirred for 16 h at room temperature. The suspension was filtered, and the lemon-coloured filtrate pumped to dryness under vacuum. The residue was then extracted with toluene (30 mL) and filtered. The filtrate was concentrated under vacuum and kept at $-30 \text{ }^\circ\text{C}$. Large colourless crystals formed within 20 min and were isolated through decantation. The mother liquor was kept at $-30 \text{ }^\circ\text{C}$ and another crop of pyrophoric colourless crystals of **2** was collected (1.18 g, 66 % based on $[\text{BeI}_2(\text{OEt}_2)_2]$).

M.p.: 100-103 °C (colourless liquid); ^1H NMR (benzene- d_6 , 400 MHz): $\delta = -0.36$ (br. s, BeCH_3), 1.68 (s, CH_2), 1.98 (s, CH_3); ^7Li NMR (benzene- d_6 , 156 MHz): $\delta = 1.81$ (s), 1.43 (br. sh); ^9Be NMR (benzene- d_6 , 56 MHz): $\delta = 3.8$ (s, $\Delta\omega_{1/2} = 211$ Hz), 23.6 (s, $\Delta\omega_{1/2} = 127$ Hz, major signal); $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 101 MHz): $\delta = -3.5$ (BeCH_3), 46.7 (CH_3), 56.5 (CH_2); IR (ATR) ν (cm^{-1}) = 1465 s, 1182 w, 1160 w, 1128 w, 1065 m, 1034 m, 1017 m, 948 s, 788 s br., 744 s br.; MS (EI 70 eV), m/z (%): 123.2 ($[(\text{tmeda})\text{Li}]^+$, 21), 116.2 ($[(\text{tmeda})]^+$, 34), 72.2 ($[\text{Me}_2\text{NCH}_2\text{CH}_2]^+$, 27), 58.2 ($[\text{Me}_2\text{NCH}_3]^+$, 100). N.B. the NMR spectra of the compound suggest the presence of another component in the crystalline mixture, though this could not be identified or separated.

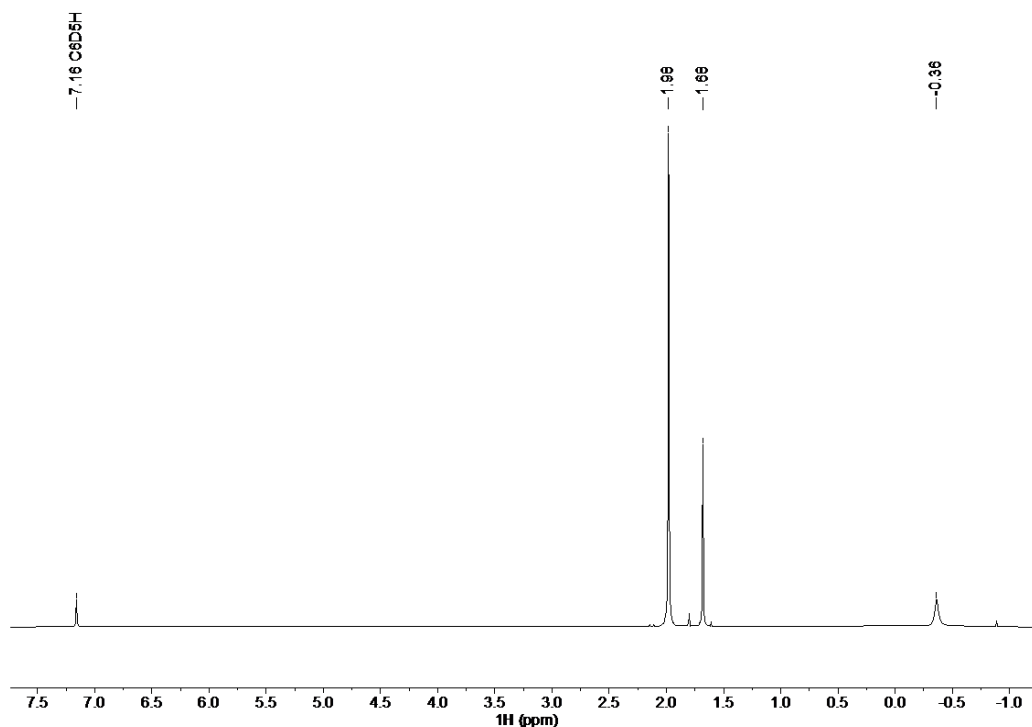


Figure S19. ^1H NMR spectrum of the crystalline mixture containing **2**, in benzene- d_6 at 298 K (400 MHz).

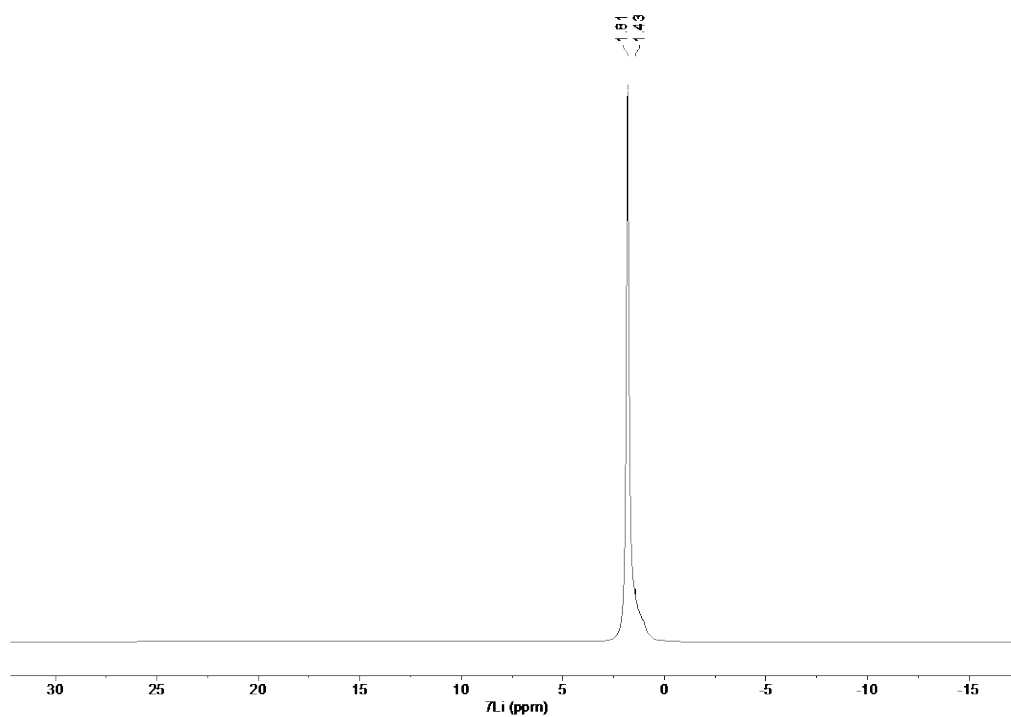


Figure S20. ${}^7\text{Li}$ NMR spectrum of the crystalline mixture containing **2**, in benzene- d_6 at 298 K (156 MHz).

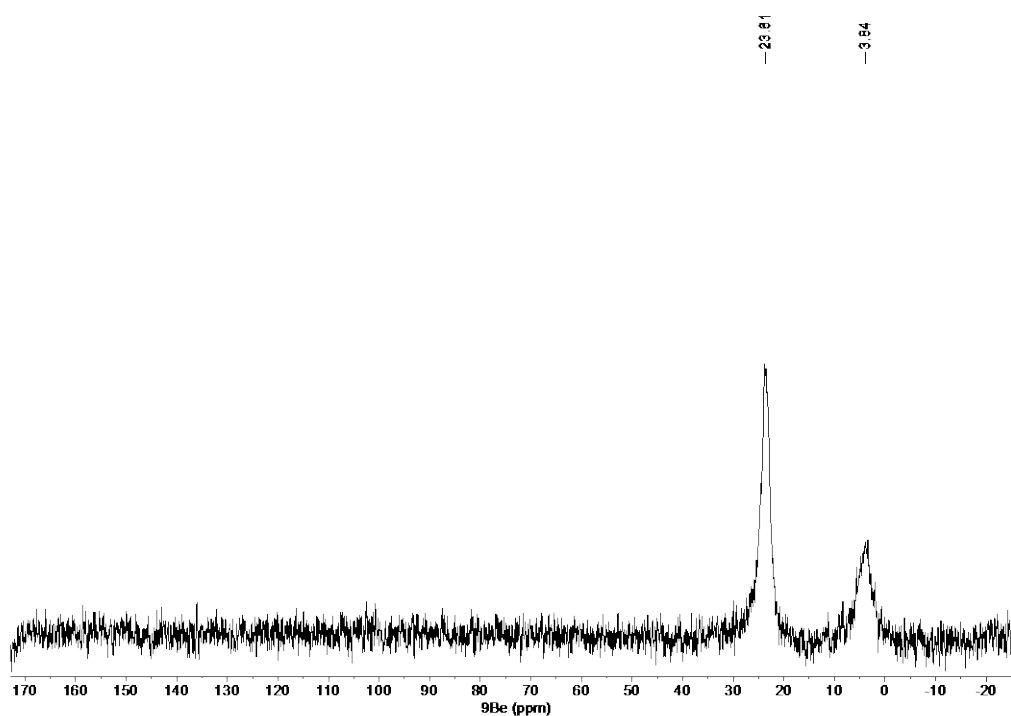


Figure S21. ${}^9\text{Be}$ NMR spectrum of the crystalline mixture containing **2**, in benzene- d_6 at 298 K (56 MHz).

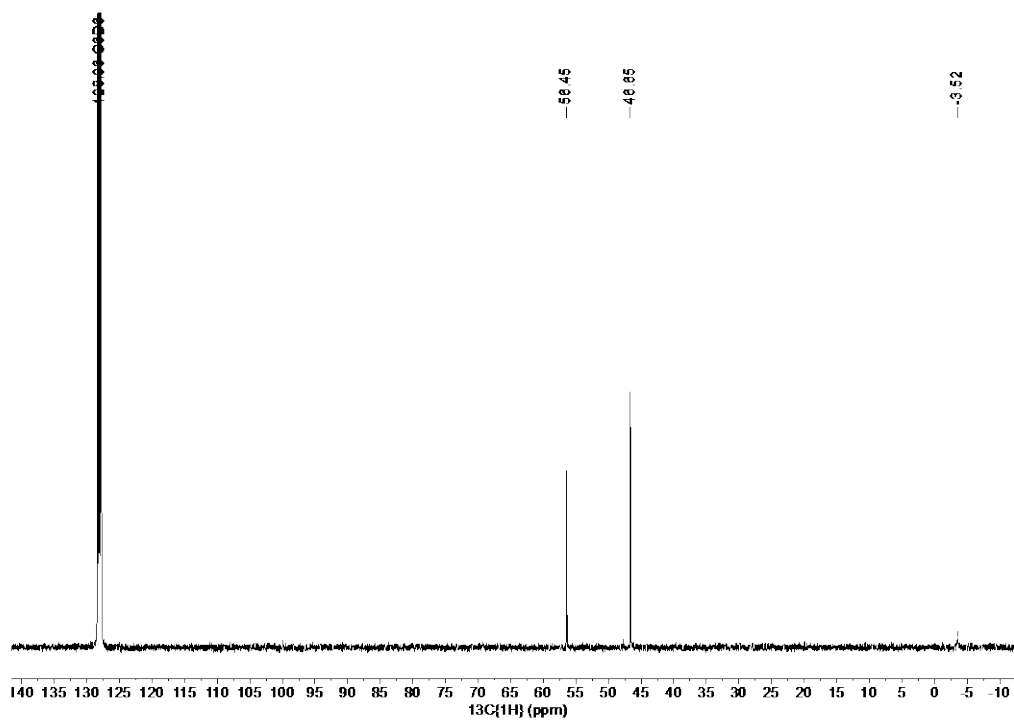


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the crystalline mixture containing **2**, in benzene- d_6 at 298 K (101 MHz).

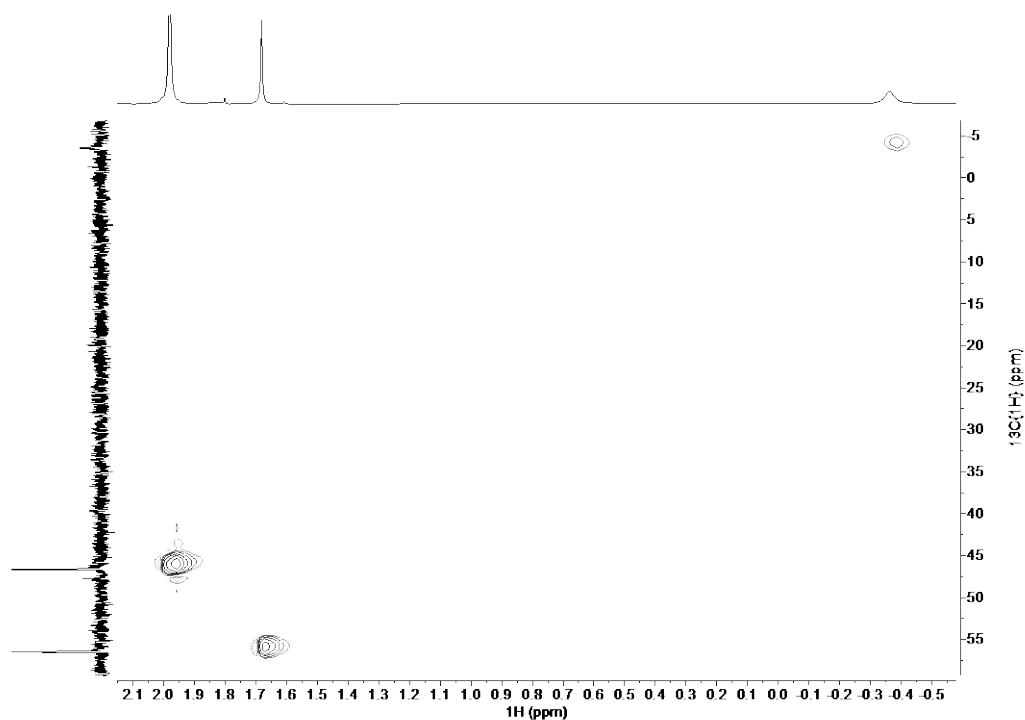
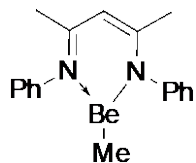


Figure S23. Excerpt from the HSQC NMR spectrum of the crystalline mixture containing **2**, in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[(^{Ph}Nacnac)BeMe] (3).



[BeBr₂(OEt₂)₂] (1.00 g, 3.15 mmol) was suspended in diethyl ether (20 mL) at room temperature, and treated with MeLi·LiBr (4.2 mL, 1.5 mol L⁻¹ solution in diethyl ether, 6.31 mmol, 2.0 equiv.). After stirring for 20 min at room temperature, the clear solution was added dropwise to a solution of ^{Ph}NacnacH (790 mg, 3.15 mmol) in diethyl ether (10 mL). The resultant yellow suspension was vigorously stirred for 16 h with the reaction flask being kept open to a nitrogen line. All volatiles were then removed under vacuum, and the residue extracted with boiling toluene (2 × 20 mL). The extract was filtered, and volatiles removed from the orange filtrate. The residue was dissolved in *n*-hexane:diethyl ether (10 mL, 9:1 v:v). This solution was filtered, and stored overnight at -30 °C. Red-orange crystals of the title compound were obtained and isolated through decantation, then dried under reduced pressure (770 mg, 89 %). M.p.: 259-260 °C (red liquid); ¹H NMR (benzene-*d*₆, 600 MHz): δ = -0.80 (s, 3H, BeCH₃), 1.70 (s, 6H, α-CH₃), 5.12 (s, 1H, β-CH), 6.89 (dm, ³J_{HH} = 7.3 Hz, 4H, *o*-CH), 6.98 (tt, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.2 Hz, 2H, *p*-CH), 7.12 (tm, ³J_{HH} = 7.8 Hz, 4H, *m*-CH); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 16.0 (s, Δω_{1/2} = 94 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 151 MHz): δ = -10.2 (br. s, BeCH₃), 22.3 (α-CH₃), 100.1 (β-CH), 125.3 (*p*-CH), 126.2 (*o*-CH), 129.0 (*m*-CH), 148.8 (*ipso*-C), 166.4 (α-C); IR (ATR) ν (cm⁻¹) = 1595 w, 1534 s, 1221 w, 1199 w, 1168 w, 1070 w, 1022 m, 1002 w, 990 m, 920 m, 869 m, 794 m, 755 s, 698 s, 657 m; MS (EI 70 eV), *m/z* (%): 258.2 ([M-Me]⁺, 69), 118.1 ([PhNCCCH₃]⁺, 100), 77.0 ([Ph]⁺, 66); elemental analysis for C₁₈H₂₀N₂Be found (calcd.) in %: C 78.86 (79.08), H 7.55 (7.37), N 9.98 (10.25).

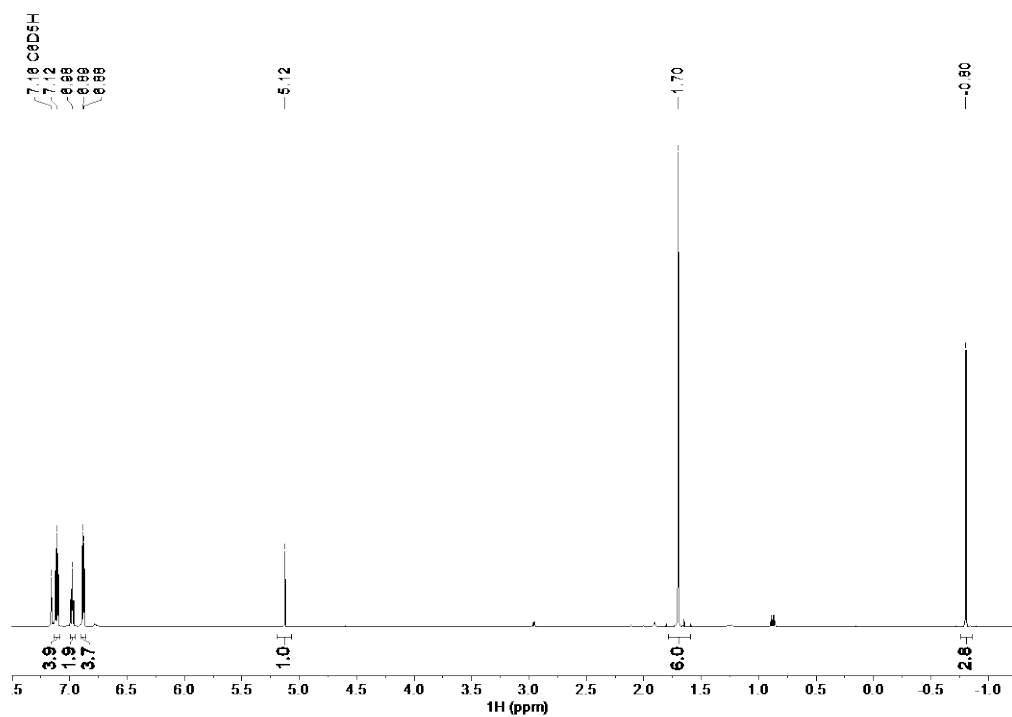


Figure S24. ^1H NMR spectrum of **3** in benzene- d_6 at 298 K (600 MHz).

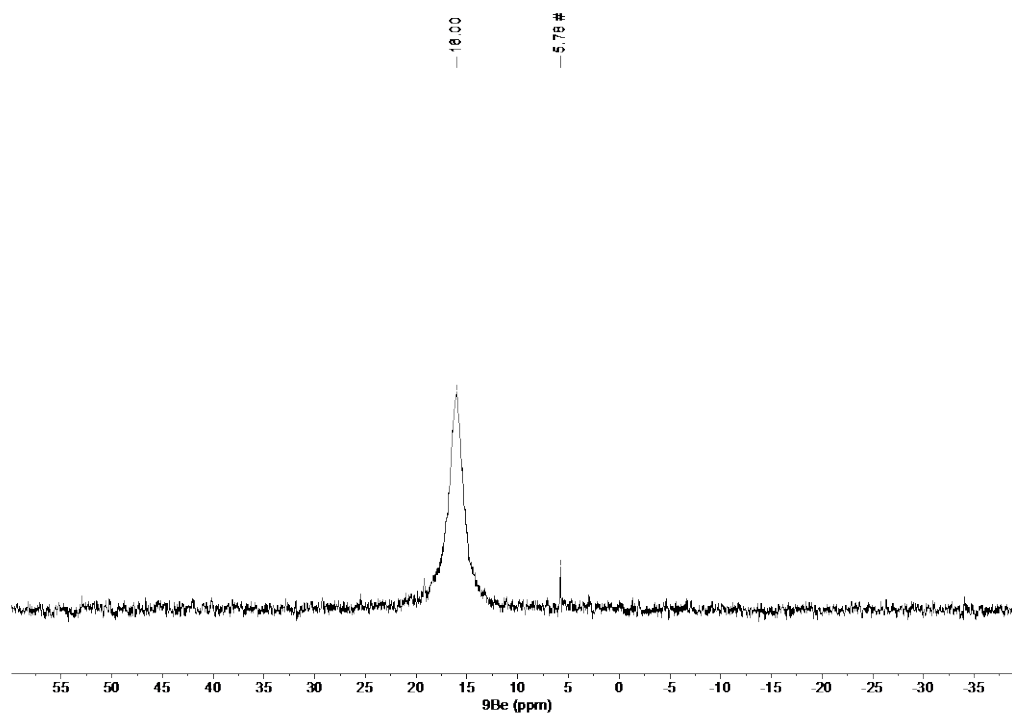


Figure S25. ^9Be NMR spectrum of **3** in benzene- d_6 at 298 K (56 MHz). #: minor contamination by $[(^{\text{Ph}}\text{Nacnac})_2\text{Be}]$.

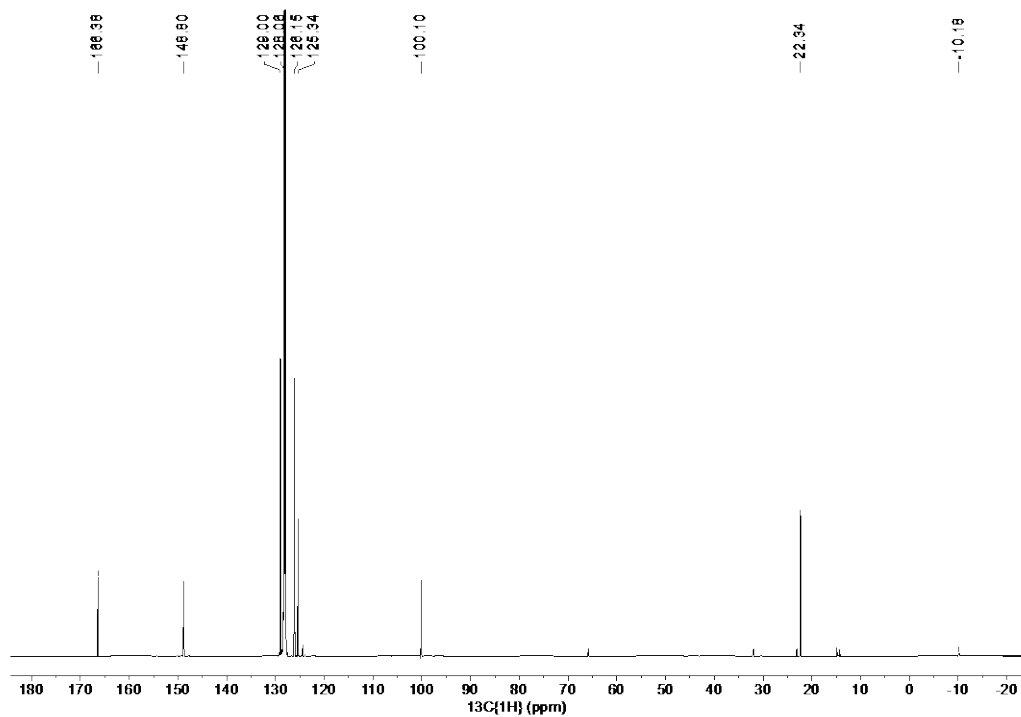


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in benzene- d_6 at 298 K (151 MHz).

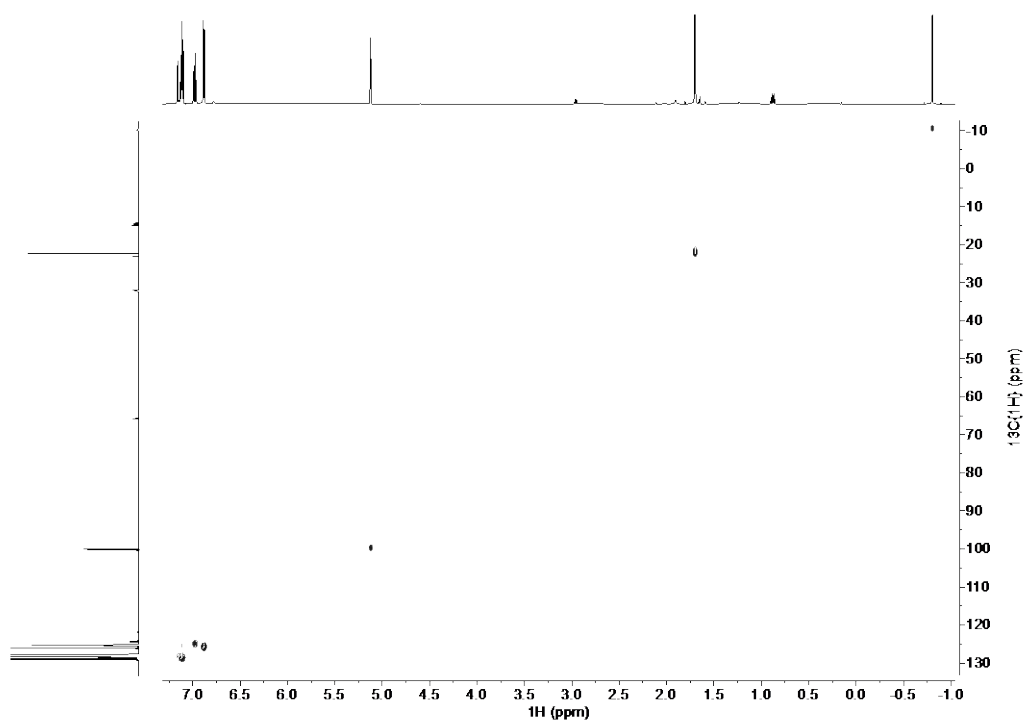
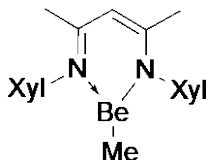


Figure S27. Excerpt from the HSQC NMR spectrum of **3** in benzene- d_6 at 298 K (^1H : 600 MHz; ^{13}C : 151 MHz).

[(^{Xyl}Nacnac)BeMe] (**4**).

[BeI₂(OEt₂)₂] (500 mg, 1.22 mmol) was dissolved in toluene (5 mL) and treated with MeLi·LiBr (1.7 mL, 1.5 mol L⁻¹ solution in diethyl ether, 2.55 mmol, 2.1 equiv.). The initially clear colourless solution was stirred vigorously for 1h, then added to a solution of ^{Xyl}NacnacH (373 mg, 1.22 mmol) in toluene (5 mL). After the initial gas formation ceased, diethyl ether was mostly removed under reduced pressure and the resulting creamy white suspension was stirred for 16 h. The suspension was filtered, and all volatiles removed under reduced pressure. The residue was extracted with toluene (15 mL), filtered, and the filtrate carefully concentrated under vacuum until incipient crystallisation occurred. The solution was stored at -30 °C affording colourless crystals of **4**. The product was isolated through decantation and dried under reduced pressure (234 mg, 58 %). M.p.: 134-135 °C (opaque colourless liquid); ¹H NMR (benzene-*d*₆, 400 MHz): δ = -1.08 (s, 3H, BeCH₃), 1.55 (s, 6H, α-CH₃), 2.07 (s, 12H, *o*-CH₃), 5.19 (s, 1H, β-CH), 6.98-7.04 (m, 6H, aryl); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 15.5 (s, Δω_{1/2} = 101 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = -12.9 (br. s, BeCH₃), 18.6 (*o*-CH₃), 21.4 (α-CH₃), 99.6 (β-CH), 125.6 (*p*-C), 128.6 (*m*-C), 132.2 (*o*-C), 146.6 (*ipso*-C), 166.6 (α-C); IR (ATR) ν (cm⁻¹) = 2916 br, 1624 w, 1537 s, 1237 m, 1189 m, 1162 m, 1092 m, 1055 m, 1020 m, 974 w, 917 w, 877 m, 833 m, 60 s, 749 v. s; MS (EI 70 eV), *m/z* (%): 314.3 ([M-Me]⁺, 100). A reproducible microanalysis of the compound could not be obtained due to its air sensitivity, and because it consistently crystallised with small amounts of unknown impurities.

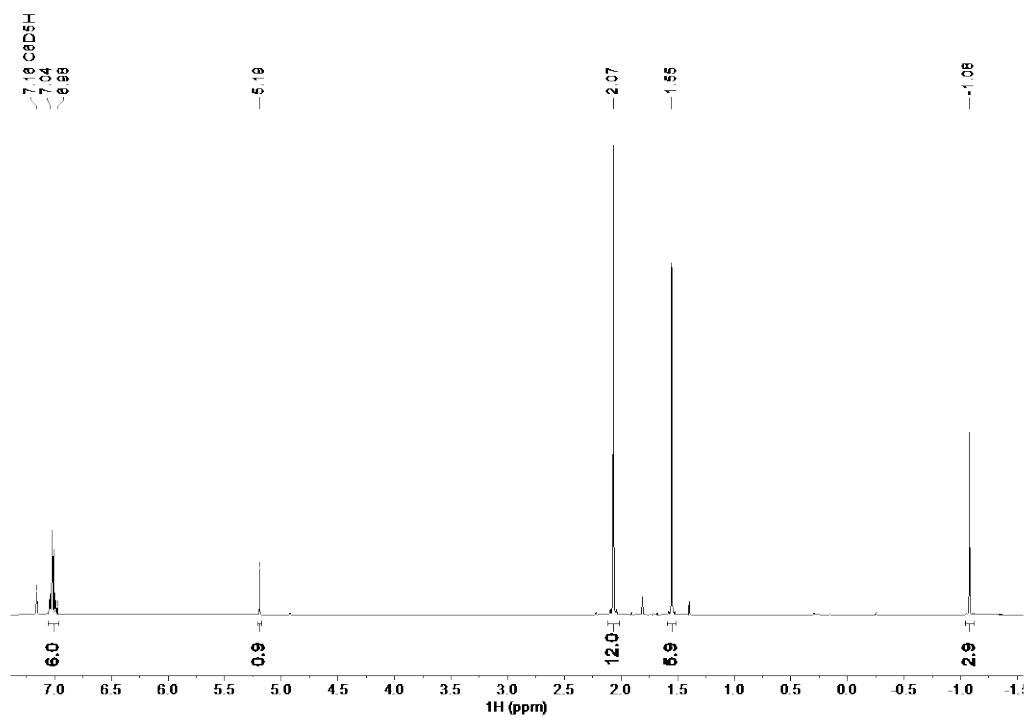


Figure S28. ^1H NMR spectrum of **4** in benzene- d_6 at 298 K (400 MHz).

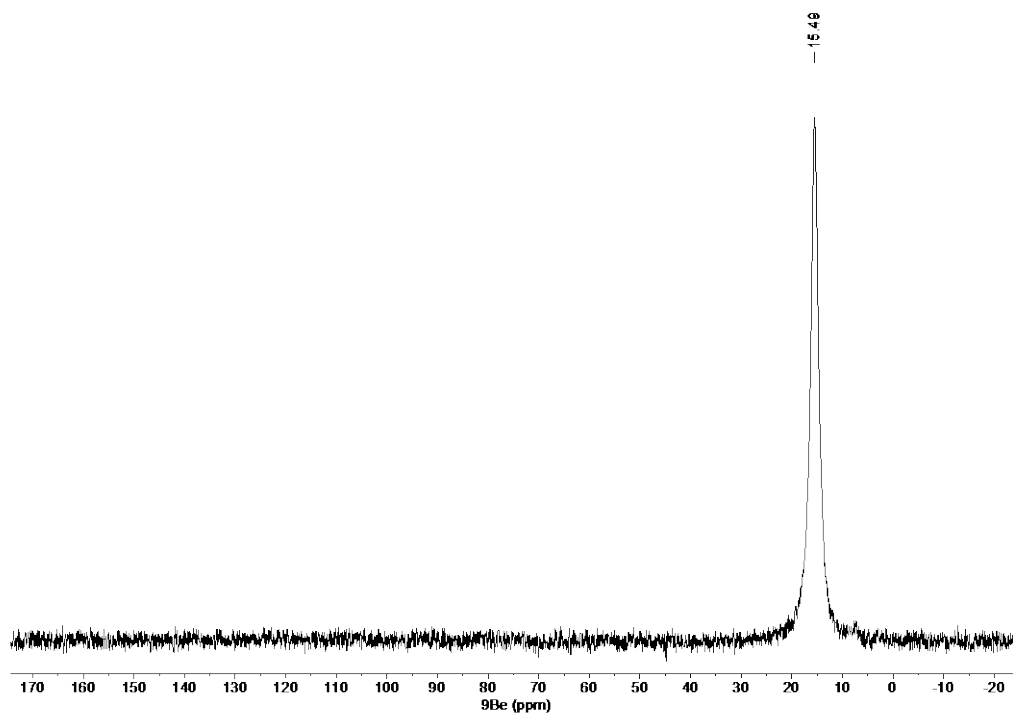


Figure S29. ^9Be NMR spectrum of **4** in benzene- d_6 at 298 K (56 MHz).

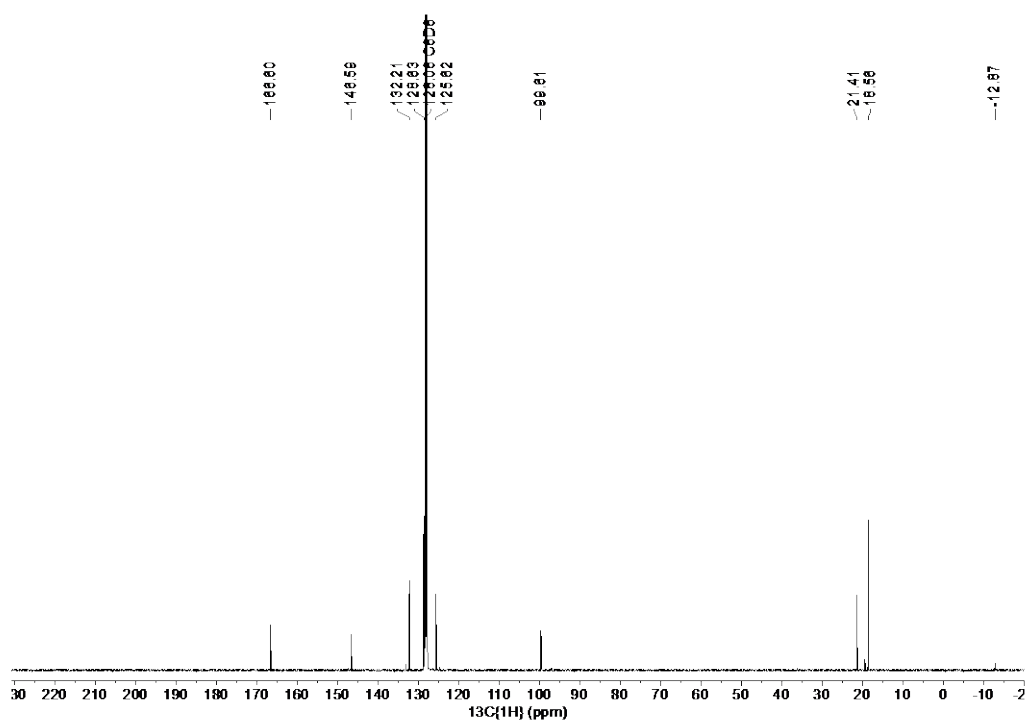


Figure S30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in benzene- d_6 at 298 K (101 MHz).

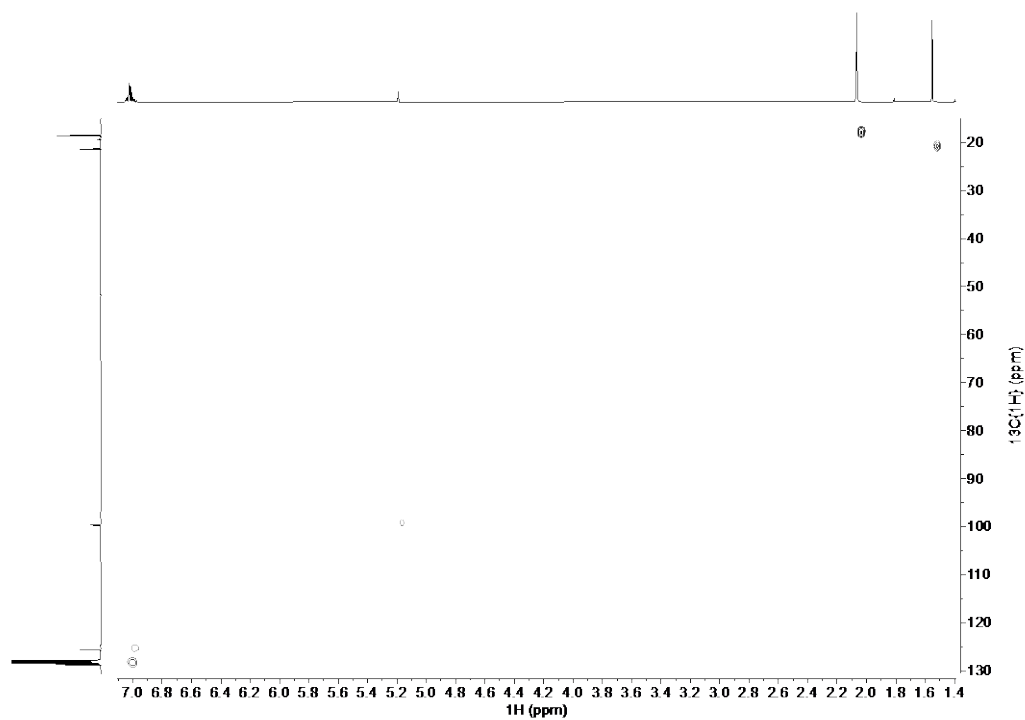
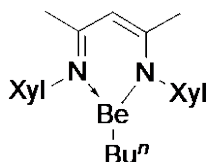


Figure S31. Excerpt from the HSQC NMR spectrum of **4** in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[(^{Xyl}Nacnac)BeBuⁿ] (**5**).

A solution of [BeBr₂(OEt)₂] (544 mg, 1.72 mmol) in toluene (10 mL) was treated with LiBuⁿ (2.3 mL, 1.6 mol L⁻¹ solution in *n*-hexane, 3.6 mmol, 2.1 equiv.). The resultant suspension was stirred for 16 h. The ligand ^{Xyl}NacnacH (526 mg, 1.72 mmol) was then added as a solid. The reaction mixture was stirred for another 24 h before all volatiles were removed *in vacuo*. The residue was extracted with *n*-hexane (10 mL), filtered, and the filtrate concentrated under vacuum to the point of incipient crystallisation. The solution was then kept for 1 h at -30 °C, during which time colourless crystals of **5** deposited. These were isolated and dried under vacuum. A second crop was isolated similarly (553 mg, 87 %). M.p.: 129-130 °C (colourless liquid); ¹H NMR (benzene-*d*₆, 400 MHz): δ = -1.09 (m, 2H, BeCH₂), 0.79 (t, ³J_{HH} = 7.3 Hz, 3H, CH₂CH₃), 0.94-1.02 (m, 2H, BeCH₂CH₂), 1.13-1.23 (m, 2H, CH₂CH₃), 1.54 (s, 6H, α-CH₃), 2.08 (s, 12H, *o*-CH₃), 5.19 (s, 1H, β-CH), 6.97-7.04 (m, 6H, aryl); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 14.8 (s, Δω_{1/2} = 137 Hz); ¹³C {¹H} NMR (benzene-*d*₆, 101 MHz): δ = 9.6 (br. s, BeCH₂), 14.4 (CH₂CH₃), 18.6 (*o*-CH₃), 21.4 (α-CH₃), 29.6 (CH₂), 30.1 (CH₂), 97.9 (β-CH), 125.3 (*p*-CH), 128.6 (*m*-CH), 132.4 (*o*-C), 142.9 (*ipso*-C), 165.3 (α-C); IR (ATR) ν (cm⁻¹) = 1540 s, 1193 m, 1094 m, 1072 m, 1026 m, 764 s; MS (EI 70 eV), *m/z* (%): 388.3 ([M+OH]⁺, 10), 342.3 ([M-C₂H₅]⁺, 26), 314.3 ([M-C₄H₉]⁺, 100). A reproducible microanalysis of the compound could not be obtained due to its air sensitivity, and because it consistently crystallised with small amounts of unknown impurities.

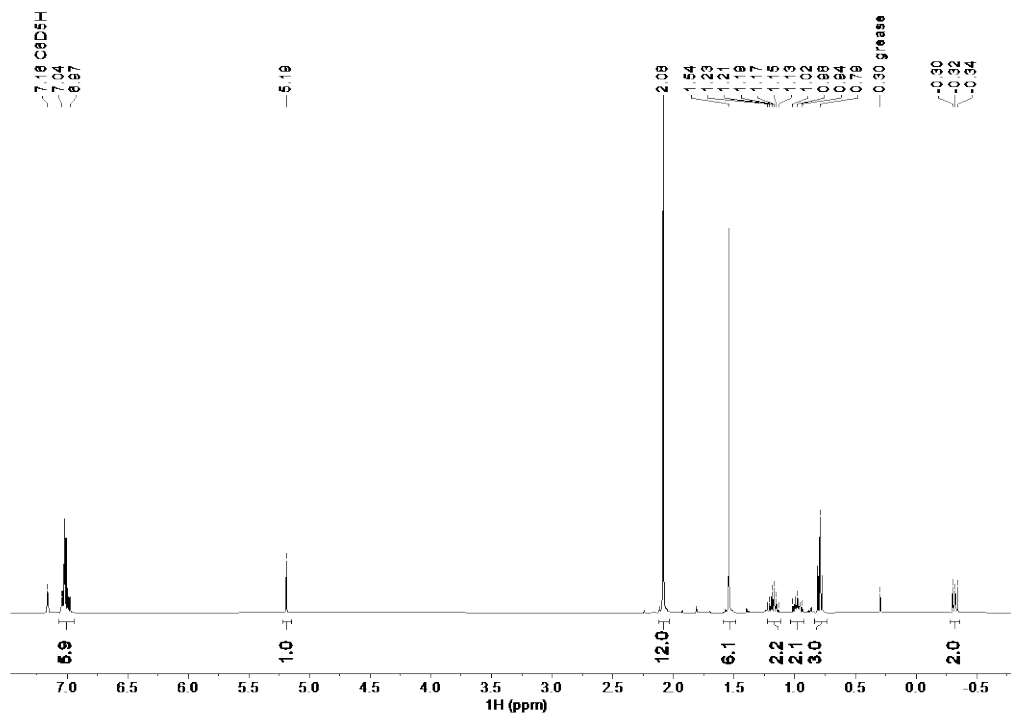


Figure S32. ^1H NMR spectrum of **5** in benzene- d_6 at 298 K (400 MHz).

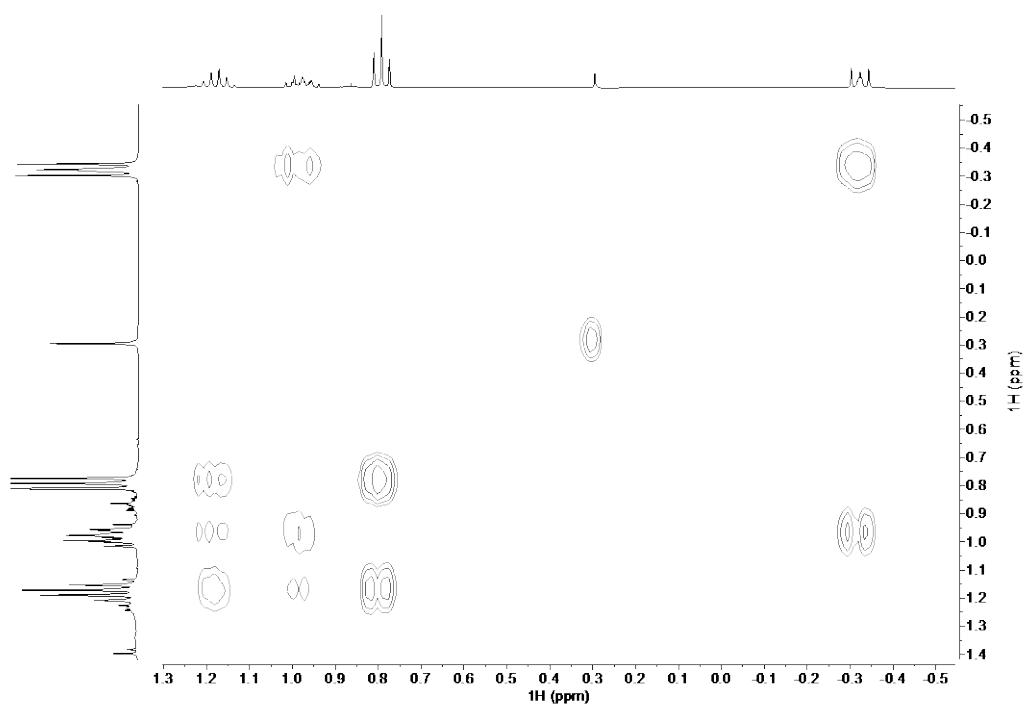


Figure S33. Excerpt from the COSY NMR spectrum of **5** in benzene- d_6 at 298 K (400 MHz).

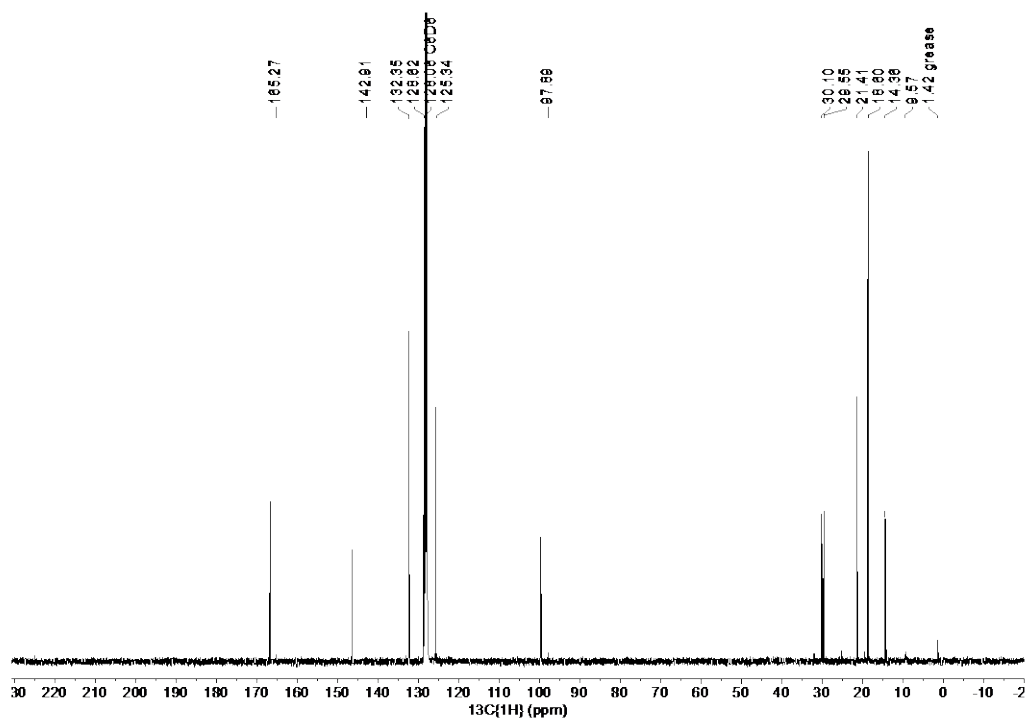


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in benzene- d_6 at 298 K (101 MHz).

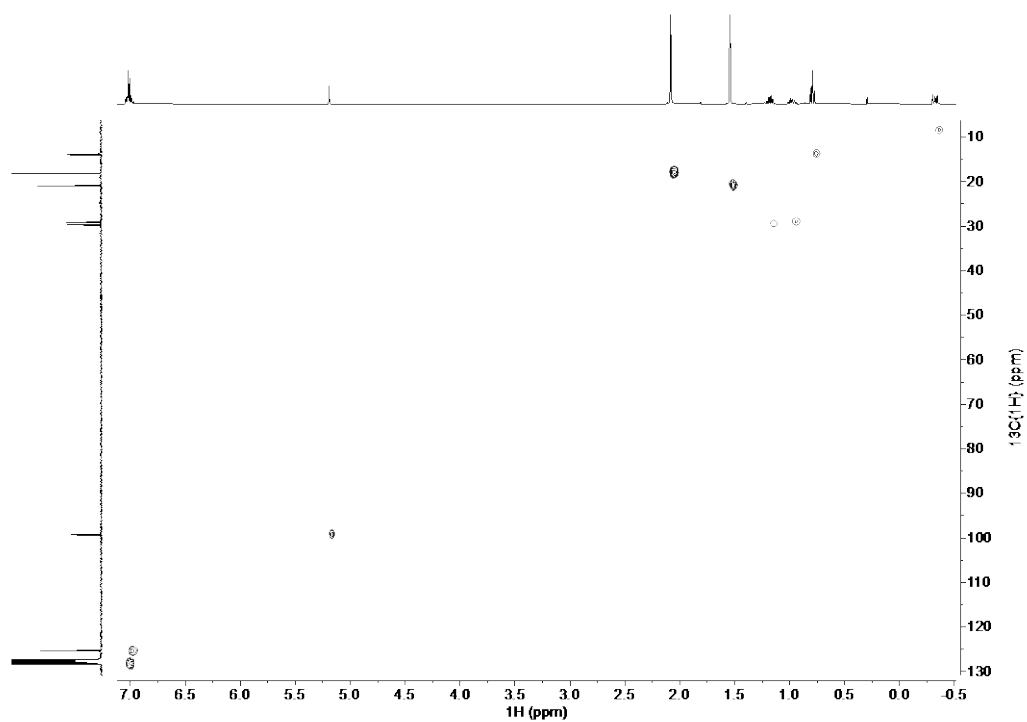
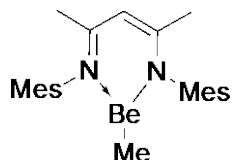


Figure S36. Excerpt from the HSQC NMR spectrum of **5** in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[(^{Mes}Nacnac)BeMe] (6).



A suspension of [BeBr₂(OEt)₂] (834 mg, 2.63 mmol) in diethyl ether (20 mL) was treated with LiMe·LiBr (3.5 mL, 1.5 mol L⁻¹ solution in Et₂O, 5.3 mmol, 2 equiv.) at -78 °C. The reaction mixture was then warmed to room temperature. After 20 min, the resultant solution was cooled to -78 °C, and a solution of ^{Mes}NacnacH (880 mg, 2.63 mmol) in diethyl ether (15 mL) was added. The reaction mixture was slowly warmed to room temperature and stirred for 16 h. All volatiles were then removed under vacuum and the colourless powdery residue extracted with boiling toluene (10 mL). The extract was filtered, and the filtrate kept at -30 °C. Large colourless crystalline blocks formed within minutes, and were isolated through decantation and then dried *in vacuo*. A second crop was collected similarly (377 mg, 40 %). M.p.: 142-146 °C (pale-yellow liquid); ¹H NMR (benzene-*d*₆, 600 MHz): δ = -1.02 (s, 3H, BeCH₃), 1.45 (s, 6H, α-CH₃), 2.09 (s, 12H, *o*-CH₃), 2.17 (s, 6H, *p*-CH₃), 5.24 (s, 1H, β-CH), 6.85 (s, 4H, *m*-CH); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 16.1 (s, Δω_{1/2} = 114 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = -12.6 (br. s, BeCH₃), 18.6 (*o*-CH₃), 21.0 (*p*-CH₃), 21.5 (α-CH₃), 99.6 (β-CH), 125.6 (*p*-C), 129.4 (*m*-CH), 131.8 (*o*-C), 134.5 (*p*-C), 144.1 (*ipso*-C), 166.8 (α-C); IR (ATR) ν (cm⁻¹) = 2922 br, 1623 w, 1534 m, 1231 m, 1200 m, 1185 m, 1147 m, 1021 br, 976 m, 878 m, 851 m, 822 m, 697 m; MS (EI 70 eV), *m/z* (%): 357.3 ([M]⁺, 7), 342.3 ([M-Me]⁺, 100); elemental analysis for C₂₄H₃₂N₂Be found (calcd.) in %: C 80.43 (80.62), H 9.19 (9.02), N 7.71 (7.84).

N.B. Compound **6** easily oxidises in the presence of adventitious oxygen and gives reddish solutions containing [^{Mes}Nacnac)Be(μ-OMe)₂], which were identified by a poor quality X-ray crystal structure.

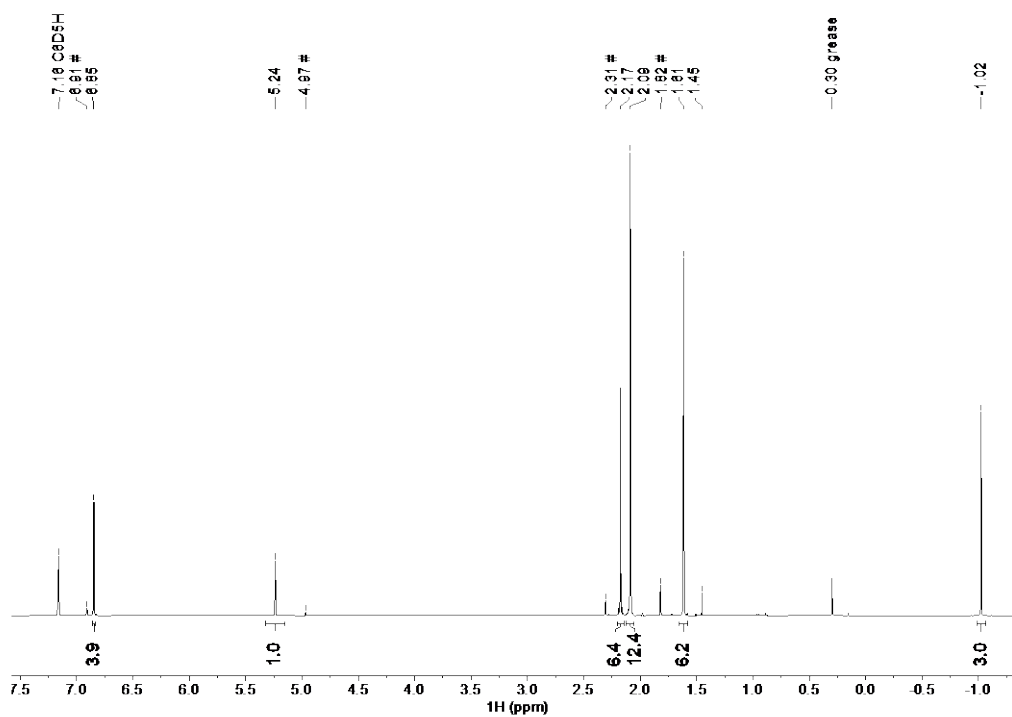


Figure S37. ^1H NMR spectrum of **6** in benzene- d_6 at 298 K (600 MHz). #: [$\{(\text{Mes}^{\text{Nacnac}}\text{Be}(\mu\text{-OMe})_2)\}_2$].

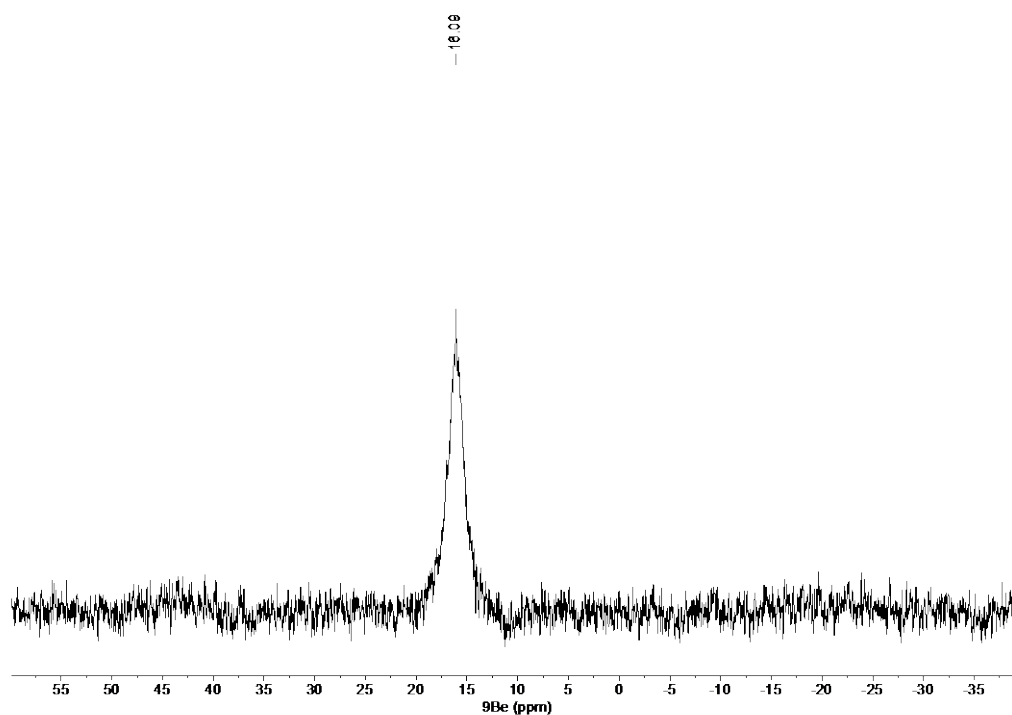


Figure S38. ^9Be NMR spectrum of **6** in benzene- d_6 at 298 K (56 MHz).

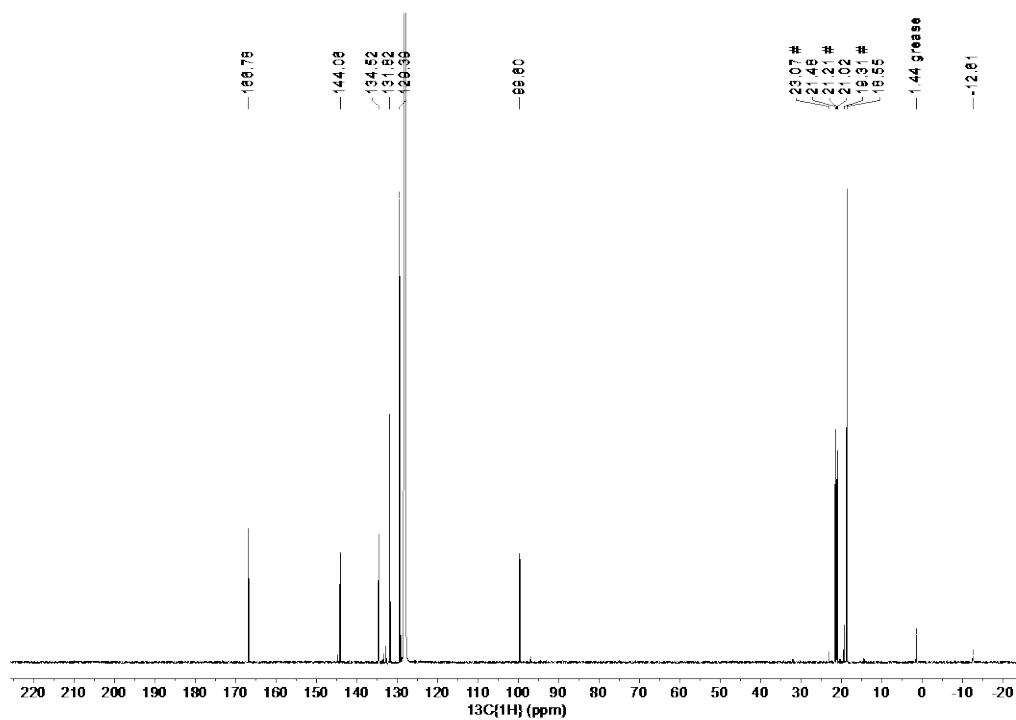


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** in benzene- d_6 at 298 K (151 MHz). #: $[\{(\text{Mes}^{\text{Nacnac}}\text{Be}(\mu\text{-OMe}))_2\}]$.

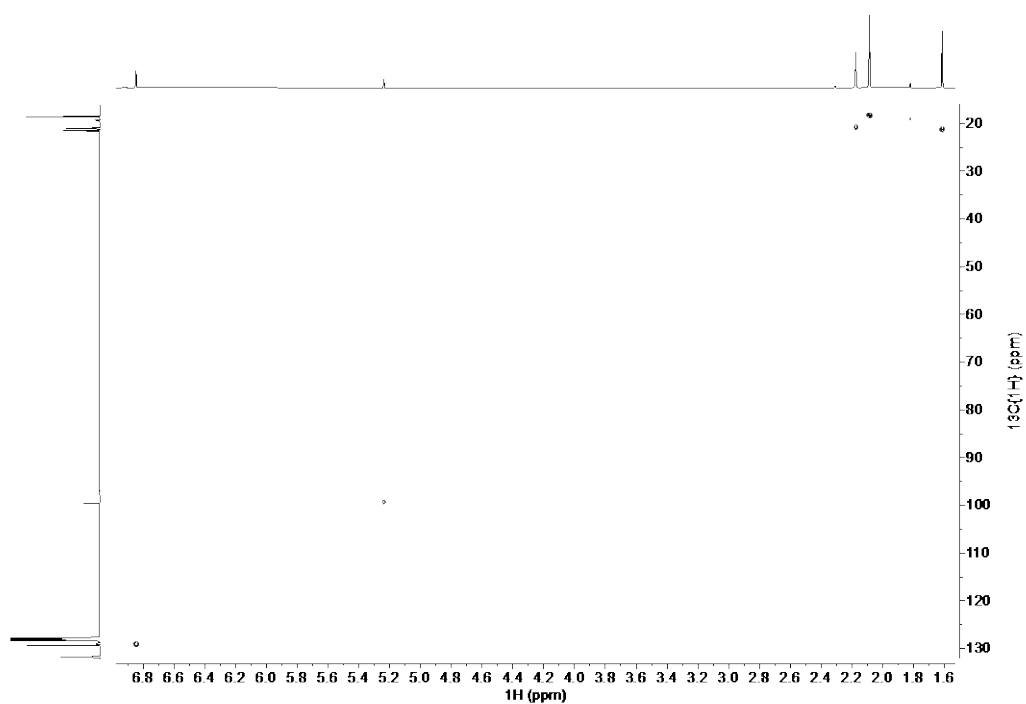
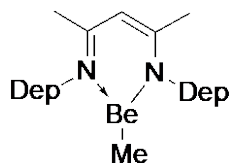


Figure S40. Excerpt from the HSQC NMR spectrum of **6** in benzene- d_6 at 298 K (^1H : 600 MHz; ^{13}C : 151 MHz).

[(^{Dep}Nacnac)BeMe] (**7**).

A solution of [BeI₂(OEt₂)₂] (500 mg, 1.22 mmol) in toluene (10 mL) was treated at room temperature with LiMe·LiBr (1.7 mL, 1.5 mol L⁻¹ solution in diethyl ether, 2.6 mmol, 2.1 equiv.). The resultant suspension was stirred for 16 h. A solution of ^{Dep}NacnacH (441 mg, 1.22 mmol) in toluene (5 mL) was then added to the reaction mixture. After the initial gas formation ceased, the reaction mixture was concentrated under vacuum until most of the diethyl ether had been removed. The mixture was stirred for a further 16 h. All volatiles were then removed under vacuum, and the residue was extracted with warm toluene (15 mL). The extract was filtered, and the filtrate placed at -30 °C for 20 min. This led to a colourless precipitate which was removed by filtration. The filtrate was concentrated under vacuum, and the process was repeated twice until no more precipitate formed. The resultant liquor was then stored overnight at -30 °C, yielding large colourless crystal blocks of **7**, which were isolated and dried *in vacuo*. A second crop was collected similarly (224 mg, 48 %). M.p.: 117-120 °C (colourless liquid); ¹H NMR (benzene-*d*₆, 400 MHz): δ = -1.07 (s, 3H, BeCH₃), 1.16 (t, ³J_{HH} = 7.6 Hz, 12H, CH₂CH₃), 1.62 (s, 6H, α-CH₃), 2.42 (dq, ³J_{HH} = 7.6 Hz, 4H, CH₂CH₃), 2.53 (dq, ³J_{HH} = 7.6 Hz, 4H, CH₂CH₃), 5.23 (s, 1H, β-CH), 7.10-7.15 (m, 6H, aryl); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 15.6 (s, Δω_{1/2} = 168 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = -10.7 (br. s, BeCH₃), 14.4 (CH₂CH₃), 22.0 (α-CH₃), 25.0 (CH₂CH₃), 99.6 (β-CH), 126.1 (*p*-CH), 126.6 (*m*-CH), 137.8 (*o*-C), 145.3 (*ipso*-C), 167.1 (α-C); IR (ATR) ν (cm⁻¹) = 1540 s, 1191 m, 1105 w, 1050 w, 1024 w, 975 w, 940 w, 866 w, 836 w, 803 w, 763 s, 718 w, 687 m; MS (EI 70 eV), m/z (%): 387.3 ([M+2H]⁺, 18) 370.3 ([M-Me]⁺, 24), 354.3 ([M-2×CH₄]⁺, 100), 105.1 ([PhMeCH]⁺, 100). A reproducible microanalysis of the compound could not be obtained due to its air sensitivity, and because it consistently crystallised with small amounts of unknown impurities.

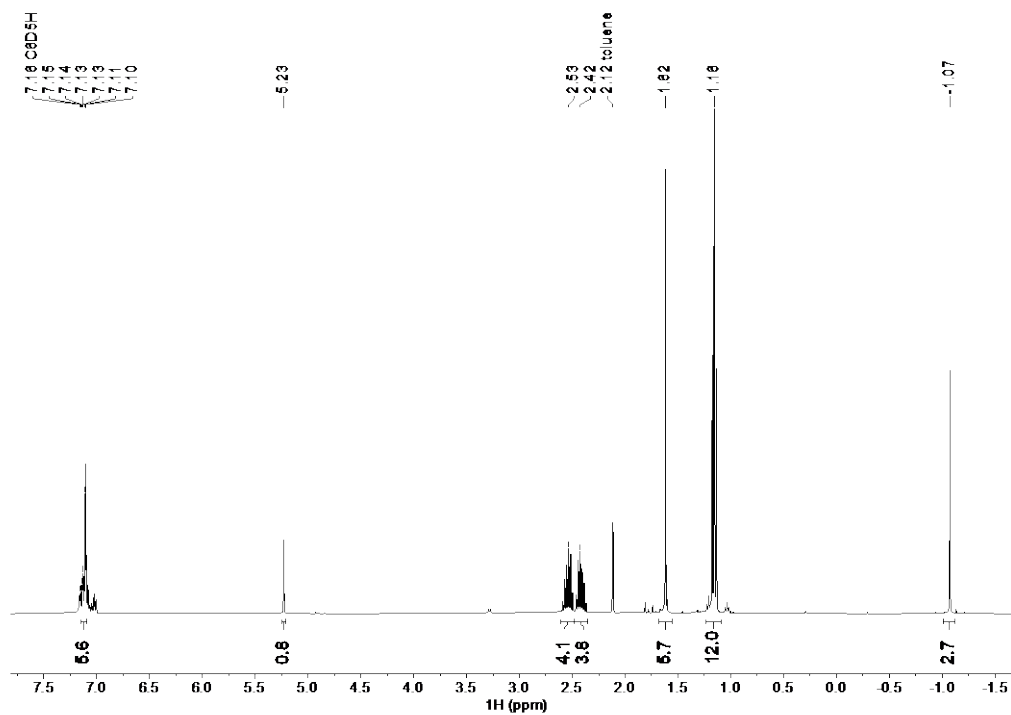


Figure S41 ^1H NMR spectrum of **7** in benzene- d_6 at 298 K (400 MHz).

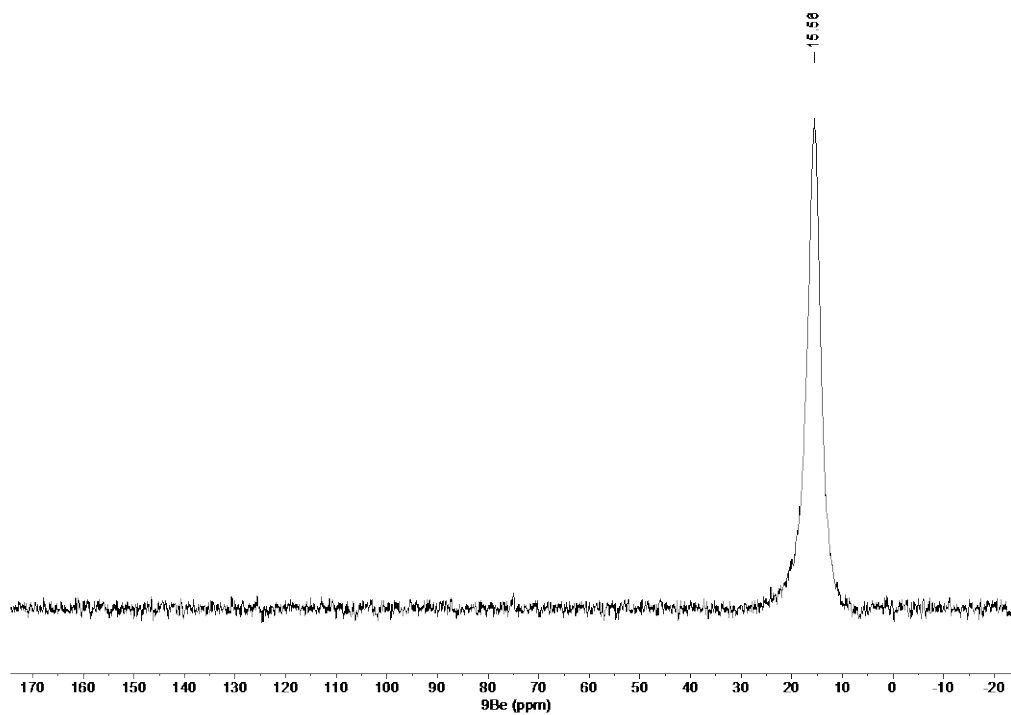


Figure S42. ^9Be NMR spectrum of **7** in benzene- d_6 at 298 K (56 MHz).

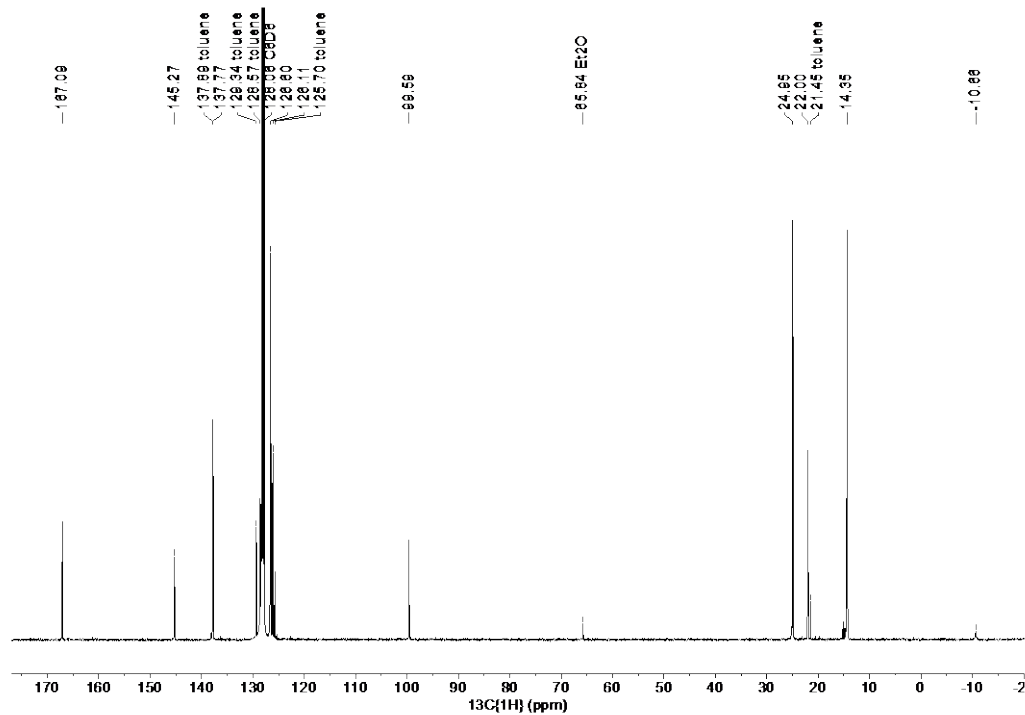


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in benzene- d_6 at 298 K (101 MHz).

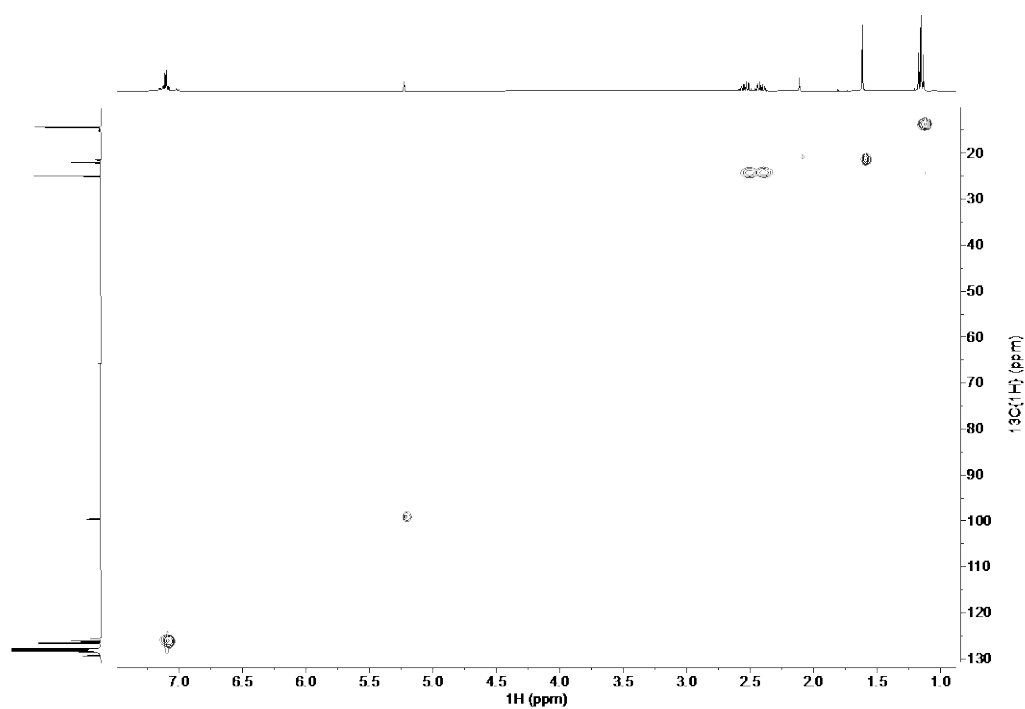
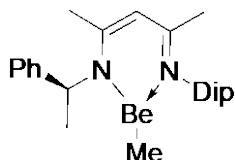


Figure S44. Excerpt from the HSQC NMR spectrum of **7** in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[(^{Chiral}Nacnac)BeMe] (8).

A solution of LiMe·LiBr (1.7 mL, 1.5 mol L⁻¹ solution in diethyl ether, 2.6 mmol, 2.1 equiv.) was added to a solution of [BeI₂(OEt₂)₂] (500 mg, 1.22 mmol) in toluene (10 mL) at room temperature. After stirring the colourless suspension for 1 h, a solution of ^{Chiral}NacnacH (442 mg, 1.22 mmol) in toluene (10 mL) was added to the reaction mixture. The resultant yellow suspension was stirred for another 16 h, and then filtered. The residue was extracted with warm toluene (5 mL), filtered, and the combined filtrates concentrated under vacuum. The residual foam was then extracted with *n*-hexane (10 mL) and volatiles removed from the extract *in vacuo*. The residue was extracted again with *n*-hexane (15 mL), filtered, and the filtrate concentrated under vacuum to give a viscous red solution. Storage of the solution at -30 °C overnight yielded large red crystals which were isolated through decantation and dried under vacuum (330 mg, 70 %). M.p.: 129-131 °C (yellow liquid); ¹H NMR (benzene-*d*₆, 400 MHz): δ = -0.99 (s, 3H, BeCH₃), 1.10 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.13 (d, ³J_{HH} = 7.0 Hz, 3H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.24 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.65 (s, 3H, α-CH₃), 1.71 (d, ³J_{HH} = 6.9 Hz, 3H, CHCH₃Ph), 1.79 (s, 3H, α-CH₃), 2.90 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂), 3.00 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂), 4.91 (q, ³J_{HH} = 6.9 Hz, 1H, CHCH₃Ph), 5.08 (s, 1H, β-CH), 7.07 (m, 1H, Ar-H), 7.10-7.14 (m, 2H, Ar-H), 7.17-7.21 (m, 3H, Ar-H), 7.24-7.26 (m, 2H, Ar-H); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 15.2 (s, Δω_{1/2} = 164 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = -7.0 (br. s, BeCH₃), 21.9 (CHCH₃Ph), 22.15 (α-CH₃), 22.16 (α-CH₃), 23.9 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 57.2 (CHCH₃Ph), 99.9 (β-CH), 123.7 (Ar-C), 123.8 (Ar-C), 126.5 (Ar-C), 126.6 (Ar-C), 126.6 (Ar-C), under C₆D₆ (Ar-C), 142.6 (Ar-C), 142.7 (Ar-C), 143.8 (Ar-C), 145.6 (Ar-C), 166.0 (α-C), 167.0 (α-C); IR (ATR) ν (cm⁻¹) = 1528 m, 1156 m, 1071 m, 1055 m, 1017 m, 962 m, 761 m, 742 m, 697 m, 684 m; MS (EI 70 eV), m/z (%): 370.3 ([M-Me]⁺, 91), 354.3 ([M-Me-CH₄]⁺, 75), 105.1 ([PhMeCH]⁺, 100). A reproducible microanalysis of the compound could not be obtained due to its air sensitivity, and because it consistently crystallised with small amounts of unknown impurities.

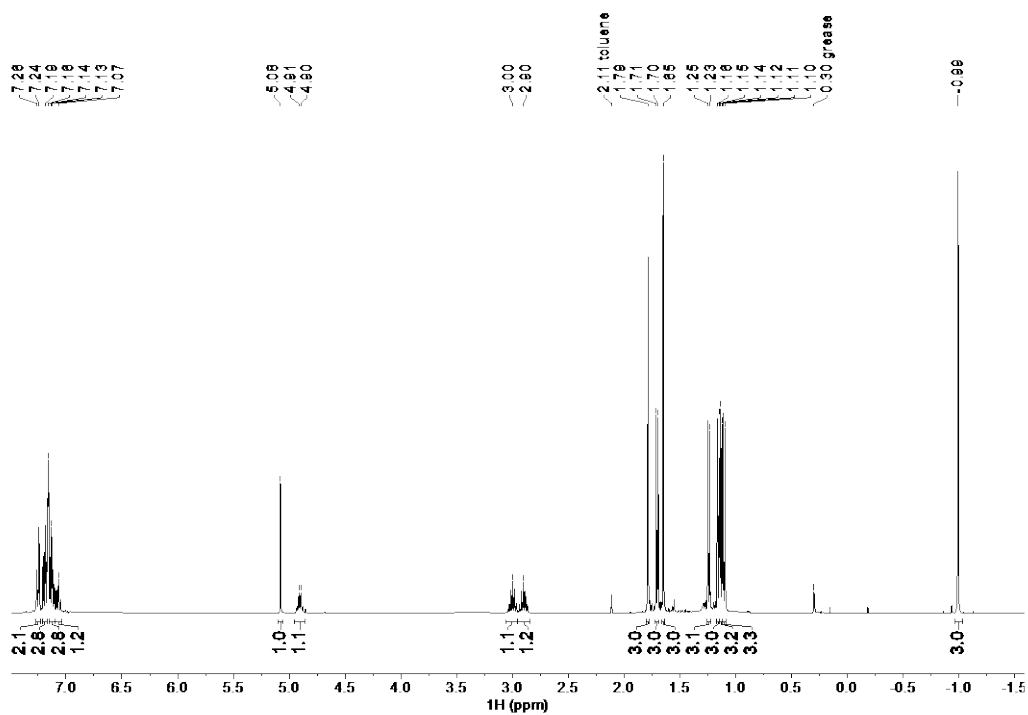


Figure S45. ^1H NMR spectrum of **8** in benzene- d_6 at 298 K (400 MHz).

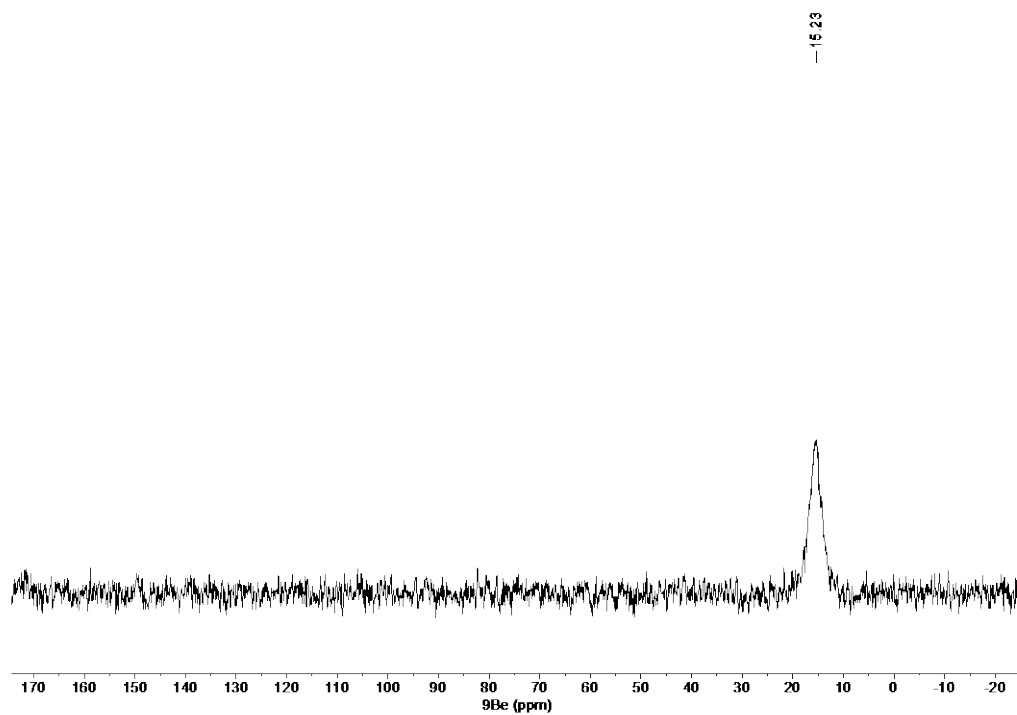


Figure S46. ^9Be NMR spectrum of **8** in benzene- d_6 at 298 K (56 MHz).

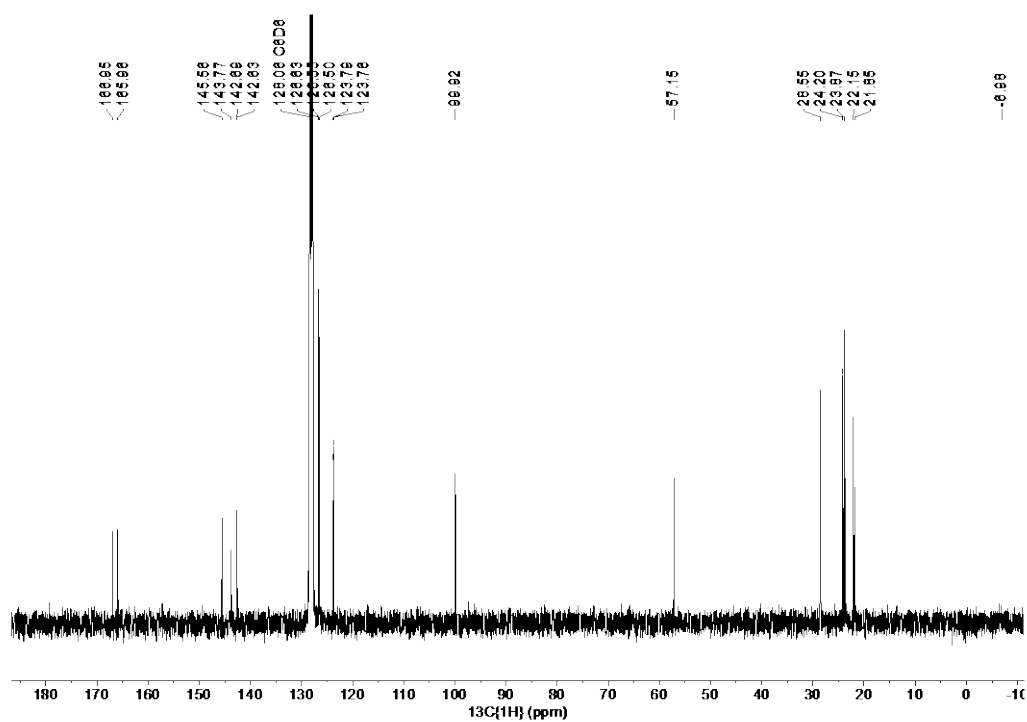


Figure S47. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** in benzene- d_6 at 298 K (101 MHz).

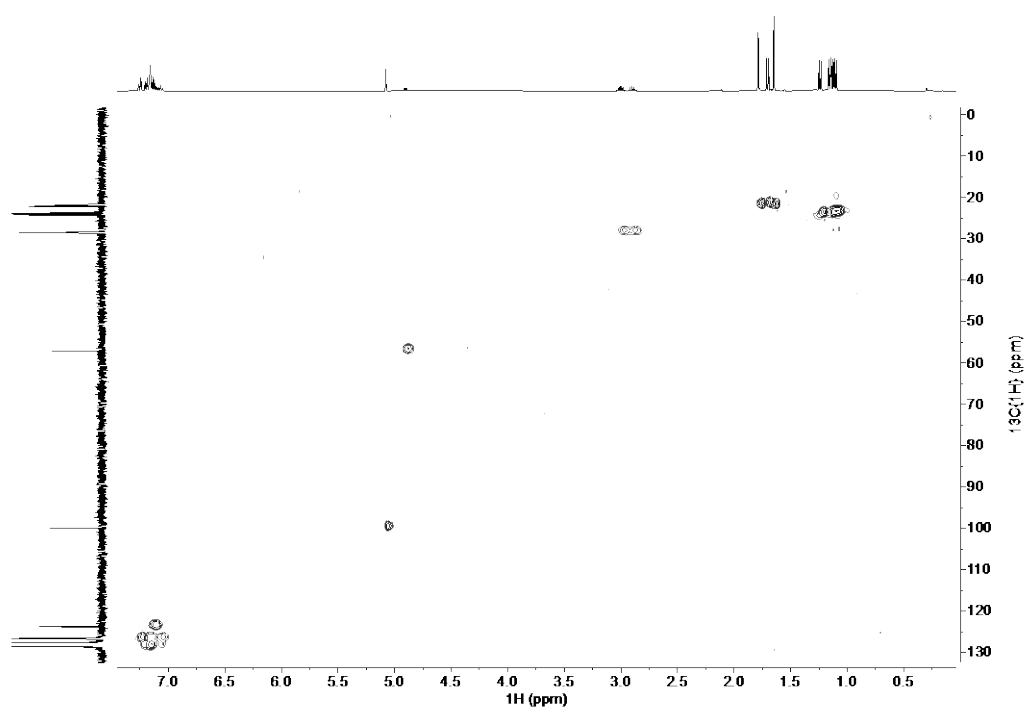
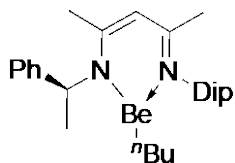


Figure S48. Excerpt from the HSQC NMR spectrum of **8** in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

[(^{Chiral}Nacnac)BeBuⁿ] (9).



A solution of LiBuⁿ (1.6 mL, 1.6 mol L⁻¹ solution in *n*-hexane, 2.6 mmol, 2.1 equiv.) was added to a solution of [BeL₂(OEt₂)₂] (500 mg, 1.22 mmol) in toluene (10 mL). After stirring the colourless suspension for 1 h, a solution of ^{Chiral}NacnacH (442 mg, 1.22 mmol) in toluene (10 ml) was added to the reaction mixture. The resultant yellow suspension was stirred for another 16 h, and then filtered and volatiles removed from the filtrate *in vacuo*. The residue was extracted with *n*-hexane (10 mL), filtered, and volatiles removed from the filtrate under vacuum. The product was obtained as a viscous orange oil (385 mg, 74 %). ¹H NMR (benzene-*d*₆, 400 MHz): δ = -0.28 (m, 2H, BeCH₂), 0.83 (t, ³J_{HH} = 7.3 Hz, 3H, Buⁿ-CH₃), 0.86-1.05 (m, 4H, Buⁿ-CH₂), 1.09 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.11 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.24 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.27 (d, ³J_{HH} = 6.9 Hz, 3H, CH(CH₃)₂), 1.65 (s, 3H, α-CH₃), 1.68 (d, ³J_{HH} = 7.0 Hz, 3H, CHCH₃Ph), 1.74 (s, 3H, α-CH₃), 2.95 (sept, ³J_{HH} = 6.9 Hz, 1H, CH(CH₃)₂), 2.99 (sept, ³J_{HH} = 7.0 Hz, 1H, CH(CH₃)₂), 5.07 (s, 1H, β-CH), 5.12 (q, ³J_{HH} = 7.0 Hz, 1H, CHCH₃Ph), 7.03-7.07 (m, 1H, ArH), 7.10-7.15 (m, 3H, ArH), 7.17-7.19 (m, 2H, ArH), 7.23-7.25 (m, 2H, ArH); ⁹Be NMR (benzene-*d*₆, 56 MHz): δ = 15.0 (s, Δω_{1/2} = 190 Hz); ¹³C{¹H} NMR (benzene-*d*₆, 101 MHz): δ = 12.6 (br. s, BeCH₂), 14.3 (Buⁿ-CH₃), 21.1 (CHCH₃Ph), 22.2 (α-CH₃), 22.5 (α-CH₃), 24.1 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 30.0 (Buⁿ-CH₂), 30.7 (CH(CH₃)₂), 56.8 (CHCH₃Ph), 100.4 (β-CH), 123.7 (Ar-C), 123.8 (Ar-C), 126.5 (Ar-C), 126.5 (Ar-C), 126.6 (Ar-C), 128.5 (Ar-C), 142.7 (Ar-C), 142.8 (Ar-C), 143.8 (Ar-C), 145.4 (Ar-C), 166.1 (α-C), 167.5 (α-C); IR (ATR, Nujol) ν (cm⁻¹) = 1558 m, 1538 m, 1100 br, 1023 m, 873 m, 801 m, 762 m, 698 m, 661 m; MS (EI 70 eV), m/z (%): 370.3 ([M-Buⁿ]⁺, 61), 354.3 ([M-Buⁿ-CH₄]⁺, 41), 105.1 ([PhMeCH]⁺, 100). A microanalysis of the compound was not obtained due to its air sensitivity, and because it could not be obtained as a crystalline solid.

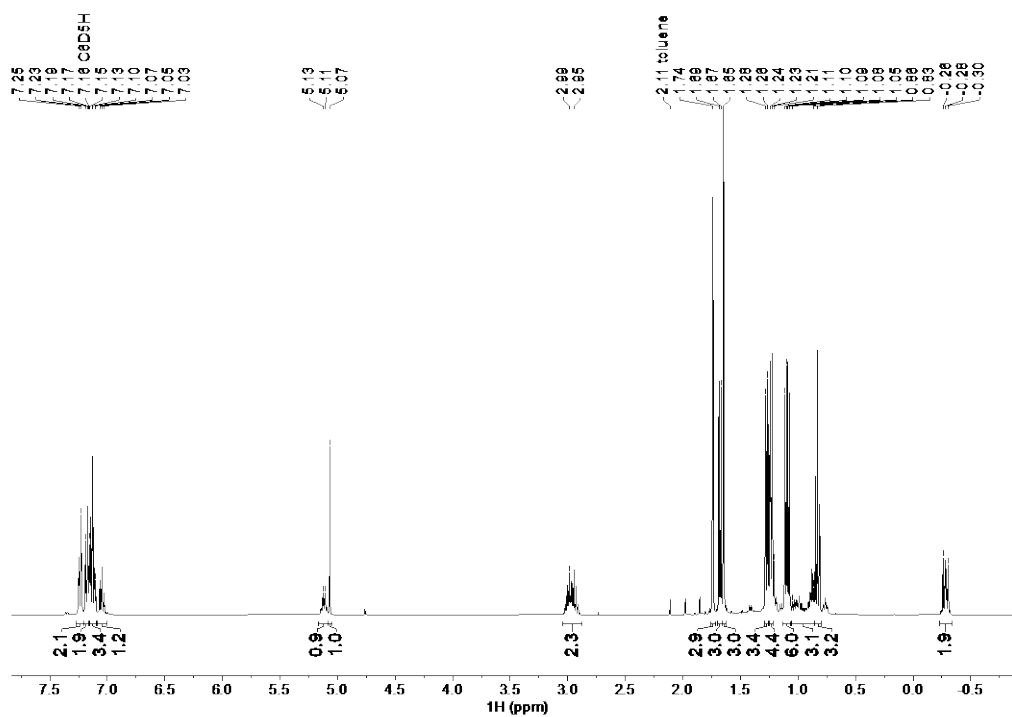


Figure S49. ^1H NMR spectrum of **9** in benzene- d_6 at 298 K (400 MHz).

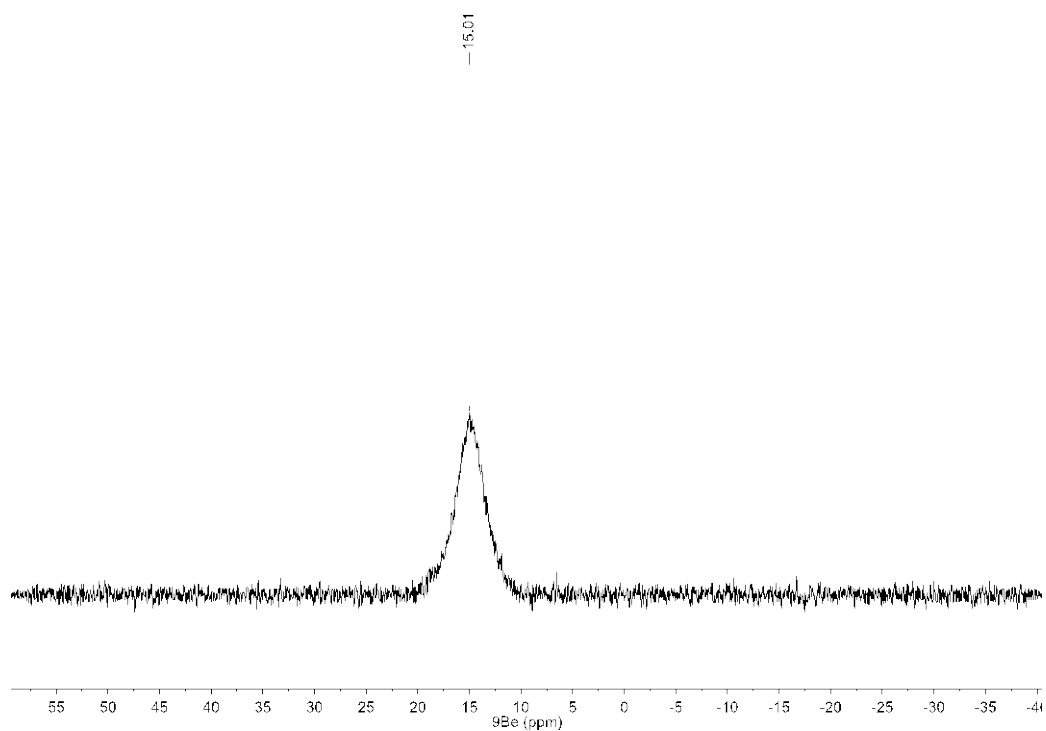


Figure S50. ^9Be NMR spectrum of **9** in benzene- d_6 at 298 K (56 MHz).

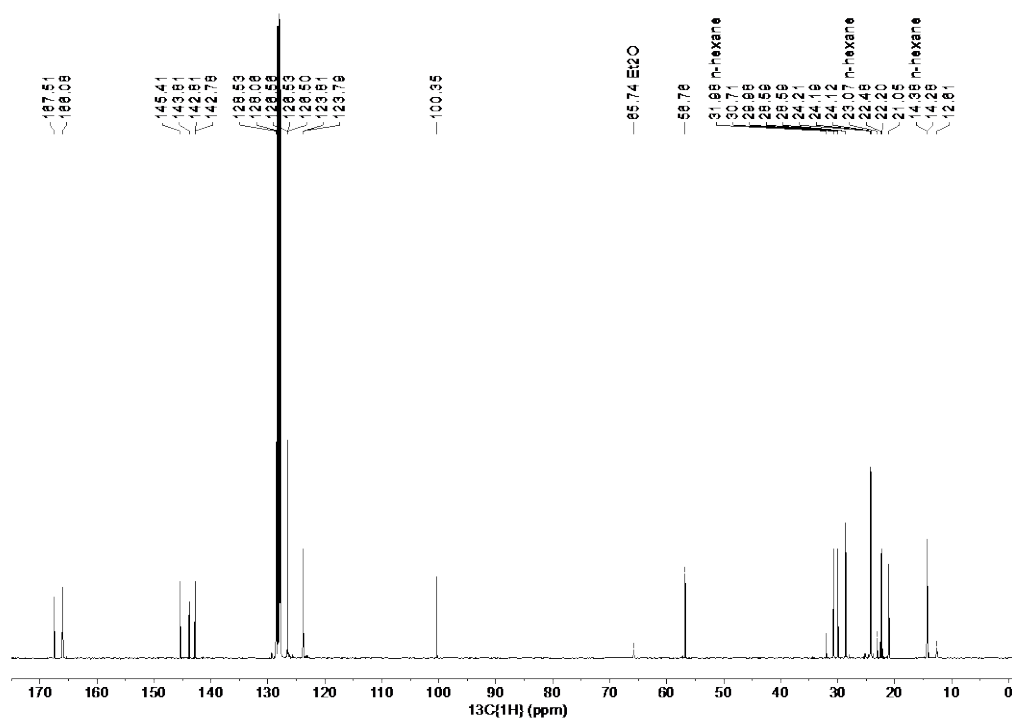


Figure S51. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** in benzene- d_6 at 298 K (101 MHz).

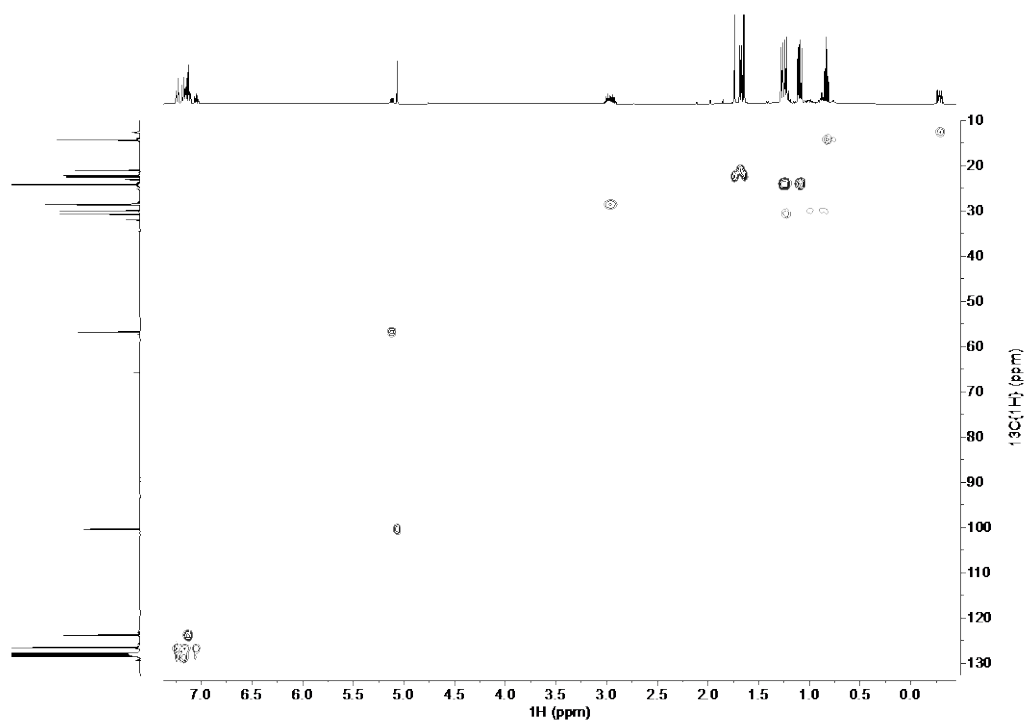


Figure S52. Excerpt from the HSQC NMR spectrum of **9** in benzene- d_6 at 298 K (^1H : 400 MHz; ^{13}C : 101 MHz).

2. X-Ray Crystallography

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made with either a Bruker Apex X8 diffractometer using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), a Rigaku Xtalab Synergy Dualflex diffractometer with a graphite monochromator with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu K α radiation (1.54180 \AA); or the MX1 beamline of the Australian Synchrotron ($\lambda = 0.71090 \text{ \AA}$). The software package Blu-Ice^[10] was used for synchrotron data acquisition, while the program XDS^[11] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F² by full matrix least squares (SHELX-16^[12]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). The absolute structure parameters refined as 0.15(13) for the structure of **2**, -0.6(9) for the structure of **5**, 0.0(3) for the structure of **7**, 0(4) for the structure of **8**, and 0.3(5) for the structure of ^{Chiral}NacnacH. The crystal structure of **8** included 8 crystallographically independent molecules in the asymmetric unit. There are no significant geometric differences between them. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal data for **1-2**, **5-8**, [$\{\text{BeCl}(\text{OEt}_2)(\mu\text{-Cl})\}_2$] and ChiralNacnacH .

	1	2	5	6
empirical formula	$\text{C}_{16}\text{H}_{44}\text{BeLi}_2\text{N}_4$	$\text{C}_{10}\text{H}_{28}\text{BeLi}_2\text{N}_2$	$\text{C}_{25}\text{H}_{34}\text{BeN}_2$	$\text{C}_{24}\text{H}_{32}\text{BeN}_2$
formula weight	315.44	199.23	371.55	357.52
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$
a (Å)	12.8044(10)	9.1798(7)	8.7480(17)	11.760(2)
b (Å)	14.8566(11)	9.6577(5)	15.711(3)	8.4800(17)
c (Å)	11.9470(8)	16.6288(12)	16.928(3)	22.650(5)
α (°)	90	90	90	90
β (°)	94.712(3)	90	90	90.26(3)
γ (°)	90	90	90	90
V (Å ³)	2265.0(3)	1474.24(17)	2326.6(8)	2258.7(8)
Z	4	4	4	4
T (K)	123(2)	123(2)	100(2)	123(2)
ρ_{calcd} (g·cm ³)	0.925	0.898	1.061	1.051
μ (mm ⁻¹)	0.053	0.350	0.060	0.060
F(000)	712	448	808	776
reflns collected	4250	9427	28968	55192
unique reflns	4250	2602	4311	4199
R _{int}	0.0776	0.0340	0.1137	0.0715
R1 [I > 2 σ (I)]	0.0651	0.0970	0.0431	0.0462
wR2 (all data)	0.1751	0.2707	0.1106	0.1281
largest peak and hole (e·Å ⁻³)	0.33, -0.28	1.42, -0.45	0.22, -0.30	0.25, -0.28
CCDC no.	1998149	1998150	1998153	1998154

	7	8	[{BeCl(OEt ₂)(μ-Cl)} ₂]	Chiral NacnacH
empirical formula	C ₂₆ H ₃₆ BeN ₂	C ₂₆ H ₃₆ BeN ₂	C ₈ H ₂₀ Be ₂ Cl ₄ O ₂	C ₂₅ H ₃₄ N ₂
formula weight	385.58	385.58	308.06	362.54
crystal system	orthorhombic	monoclinic	tetragonal	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 2 ₁
a (Å)	8.2382(3)	18.190(4)	14.2442(5)	8.3950(2)
b (Å)	13.6071(4)	24.705(5)	14.2442(5)	12.0810(3)
c (Å)	21.0084(4)	22.963(5)	7.6129(4)	11.1318(2)
α (°)	90	90	90	90
β (°)	90	113.03(3)	90	96.590(2)
γ (°)	90	90	90	90
V (Å ³)	2355.00(12)	9497(4)	1544.64(14)	1121.53(4)
Z	4	16	4	2
T (K)	123(2)	100(2)	123(2)	123(2)
ρ _{calcd} (g·cm ³)	1.087	1.079	1.325	1.074
μ (mm ⁻¹)	0.463	1.061	0.748	0.466
F(000)	840	3360	640	396
reflns collected	12519	116795	5817	11528
unique reflns	4134	34956	1444	3662
R _{int}	0.0442	0.0779	0.0561	0.0861
R1 [I > 2σ(I)]	0.0390	0.1086	0.0345	0.0494
wR2 (all data)	0.1018	0.3223	0.0893	0.1301
largest peak and hole (e·Å ⁻³)	0.14, -0.24	0.48, -0.38	0.38, -0.30	2.17, -0.20
CCDC no.	1998152	1998155	1998148	1998151

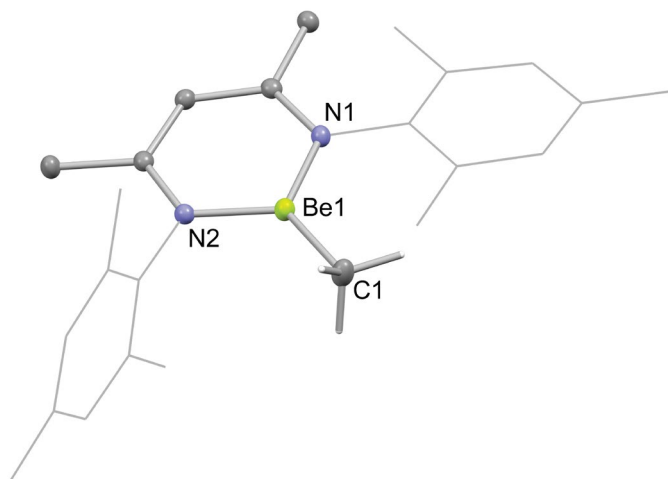


Figure S53. ORTEP diagram of compound **6** (25% thermal ellipsoids; hydrogen atoms, except Be methyl protons, omitted. N-substituents shown as wireframe for clarity). See main text for metrical parameters.

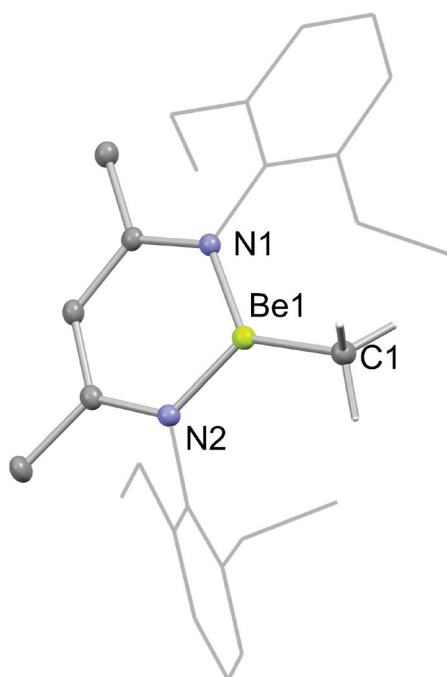


Figure S54. ORTEP diagram of compound **7** (25% thermal ellipsoids; hydrogen atoms, except Be methyl protons, omitted. N-substituents shown as wireframe for clarity). See main text for metrical parameters.

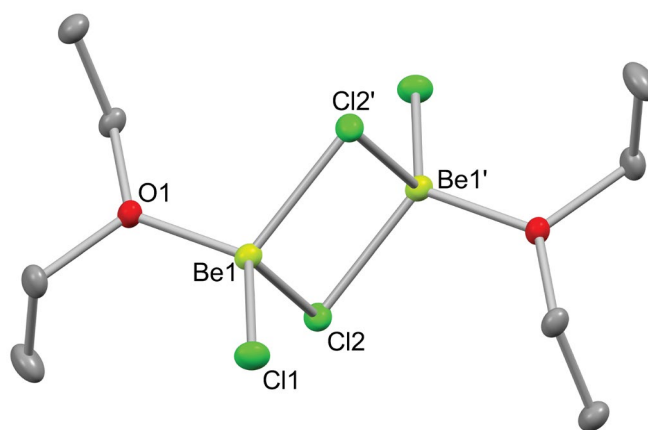


Figure S55. ORTEP diagram of $[\{\text{BeCl}(\text{OEt}_2)(\mu\text{-Cl})\}_2]$ (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Cl(1)-Be(1) 1.923(2), Cl(2)-Be(1) 2.073(2), Cl(2)-Be(1') 2.111(2), O(1)-Be(1) 1.621(3), Be(1)-Cl(2)-Be(1') 82.80(10), O(1)-Be(1)-Cl(1) 113.64(14), Cl(1)-Be(1)-Cl(2)' 113.08(11).

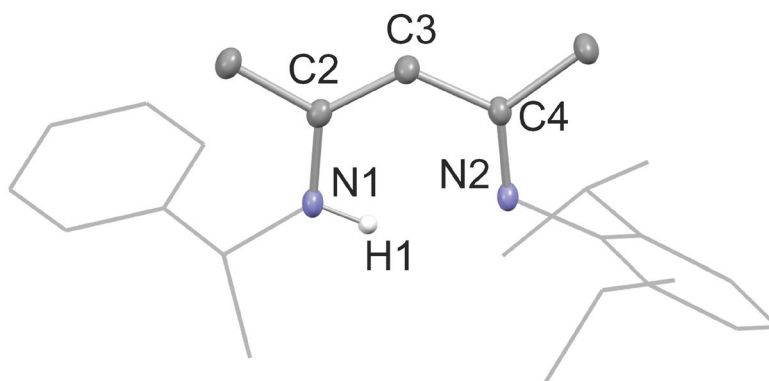


Figure S56. ORTEP diagram of $^{\text{Chiral}}\text{NacnacH}$ (25% thermal ellipsoids; hydrogen atoms, except N-H proton, omitted. N-substituents shown as wireframe for clarity). Selected bond lengths: N(1)-C(2) 1.351(4), N(2)-C(4) 1.291(4), C(2)-C(3) 1.369(4), C(3)-C(4) 1.439(4).

3. References

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