N-Heterocyclic Carbene, Carbodiphosphorane and Diphosphine Adducts of Beryllium Dihalides: Synthesis, Characterisation and Reduction Studies

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Supplementary Information (37 pages)

Contents

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 hexane, toluene, benzene and THF were distilled over molten potassium. ^{1}H, ^{13}C{^{1}H}and ^{9}Be 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 $Be(NO_3)_2$ in H_2O/D_2O (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 recorded as Nujol mulls, using an Agilent Cary 630 spectrometer operating in attenuated total reflectance (ATR) or transmission modes, and the wavenumbers ν are reported in cm^{-1}. Microanalyses were carried out at the Science Centre, London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials $[BeX_2(OEt_2)_2]$ (X = Br or I),[1,2] IPr,[3] IMes,[4] IPrIMe,[5] ::$C(PPh_3)_2$ (CDP),[6] [:Al(^{Dip}Nacnac)][7] and $[K_2(C_{10}H_8)_2(THF)]$[8] were prepared by literature procedures. All other reagents were used as received.

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.[9] 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.

Synthesis of $[(IPrIMe)_2BeI_2]$ 4. $[BeI_2(OEt_2)_2]$ (725 mg, 1.76 mmol) and IPrIMe (653 mg, 3.62 mmol) were combined as solids in a Schlenk tube and toluene (30 mL) was added at room temperature. A white suspension formed upon stirring. After 4.5 h all volatiles were removed under reduced pressure. The slightly yellowish residue was washed with cold toluene (−78 ºC, 10 mL) and dried *in vacuo* to yield **4** as an off-white powder (1.053 g, 96 %). Pale-yellow crystals of the compound were obtained by recrystallisation from toluene at −30 ºC. M.p.: 219-223 ºC (beige liquid); ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 1.17 (d, $^{3}J_{HH}$ = 7.2 Hz, 24H, $CH(CH_3)_2$), 1.64 (s, 12H, CH_3), 6.25 (m, 4H, $CH(CH_3)_2$); ^{9}Be NMR (benzene-d_6, 56 MHz, 303 K): δ = -3.4 (s, $\Delta\omega_{1/2}$ = 96 Hz); ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 298 K): δ = 10.0 (CH_3), 21.2 ($CH(CH_3)_2$), 52.0 ($CH(CH_3)_2$), 125.0 (CCH_3), 172.5 (br. s, NCN); IR (ATR) ν (cm^{-1}) = 1662 m, 1654 m, 1624 m, 1554 s, 354 m, 1230 v. s, 1190 v. s, 1136 m, 1111 s, 858 w, 826 w, 769 w, 751 w, 736 w; MS (EI 70 eV), m/z (%): 316.1 ([(IPrIMe)BeI]$^{+}$, 100), 180.2 ([IPrIMe]$^{+}$, 34); elemental analysis for $C_{22}H_{40}BeI_2N_4$ found (calcd.) in %: C 42.20 (42.39), H 6.59 (6.47), N 8.86 (8.99).

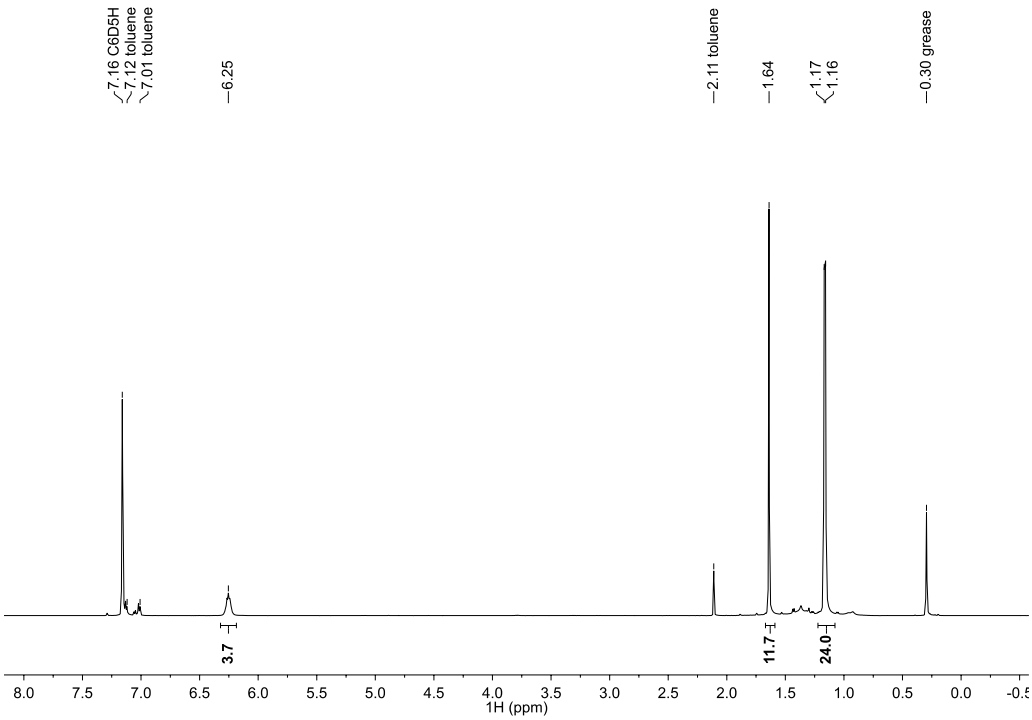


Figure S1. ^{1}H NMR spectrum of **4** in benzene-d_6 at 298 K (600 MHz).

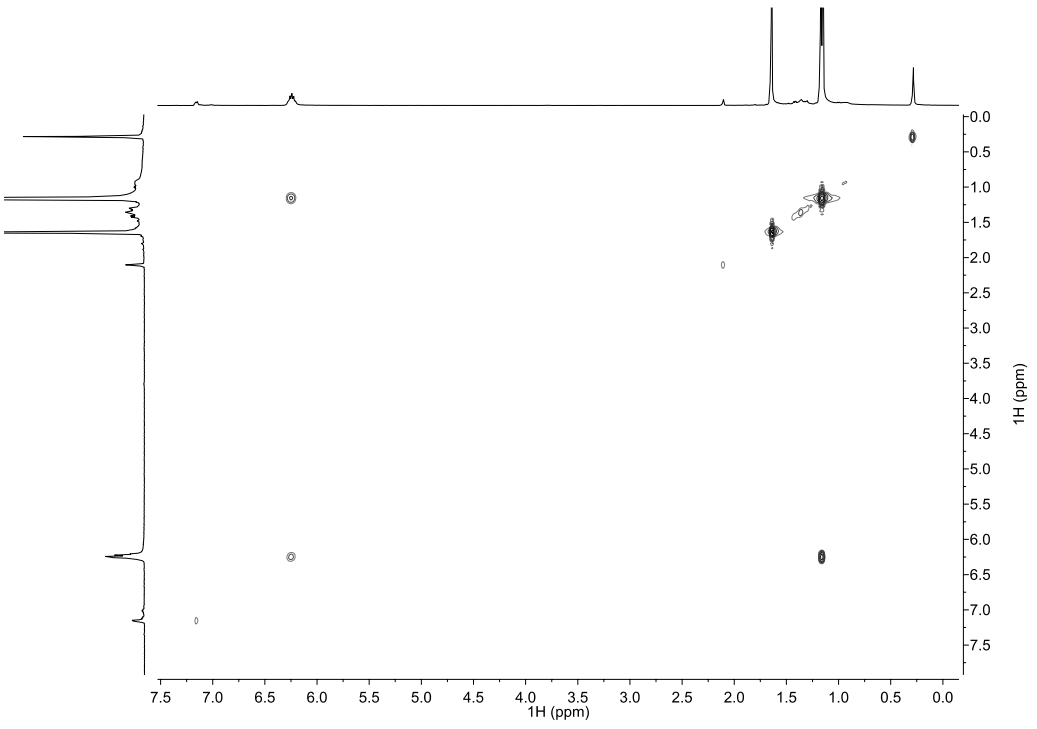


Figure S2. Excerpt from the COSY NMR spectrum of **4** in benzene-d_6 at 298 K (600 MHz).

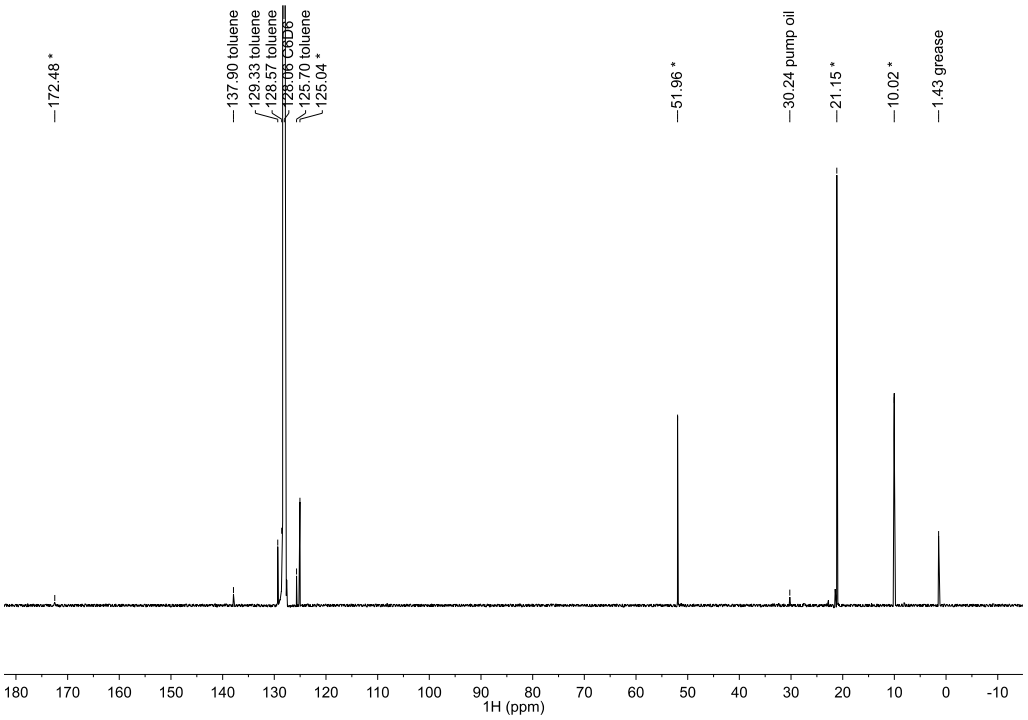


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in benzene-d_6 at 298 K (151 MHz).

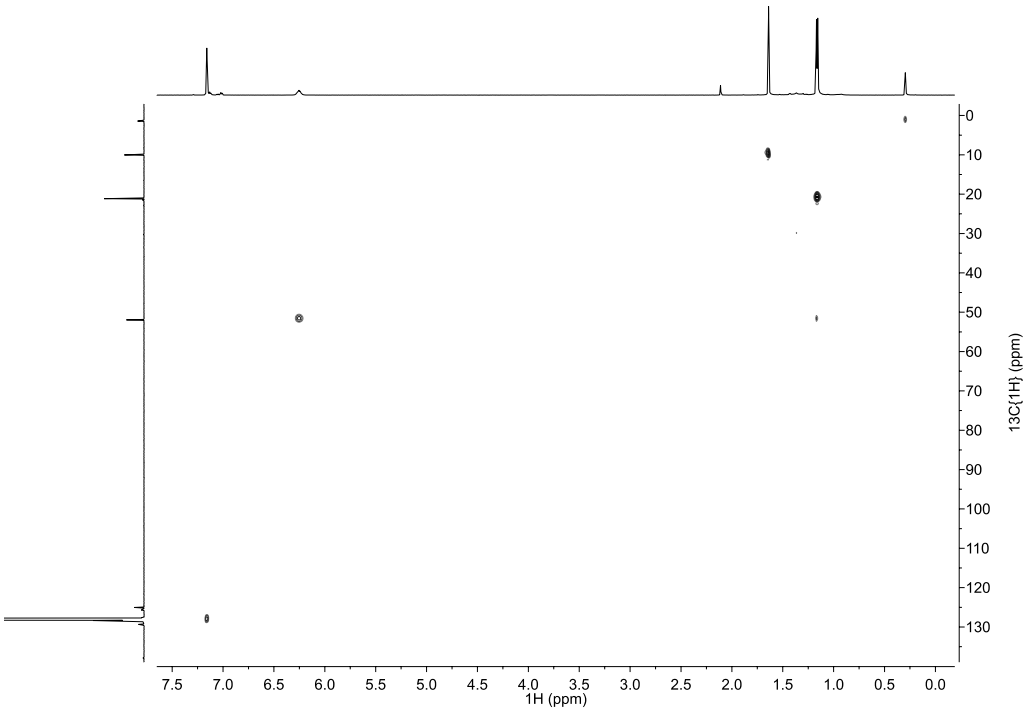


Figure S4. Excerpt from the HSQC NMR spectrum of **4** in benzene-d_6 at 298 K (^{1}H: 600 MHz, ^{13}C: 151 MHz).

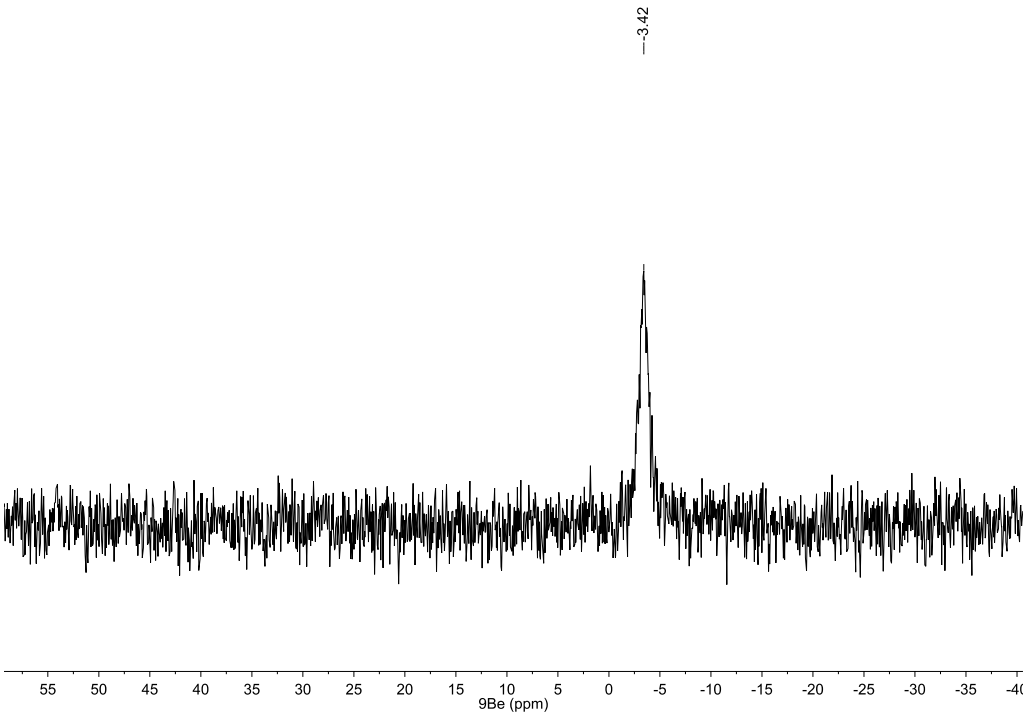


Figure S5. ^{9}Be NMR spectrum of **4** in benzene-d_6 at 303 K (56 MHz).

Synthesis of [(IMes)BeI$_2$] 5. [BeI$_2$(OEt$_2$)$_2$] (1.000 g, 2.43 mmol) and IMes (0.741 g, 2.43 mmol) were suspended in toluene (40 mL) at room temperature. The creamy beige suspension was stirred vigorously for 16 h. The resultant brown solution was then removed through filtration and the residue rinsed with toluene (20 mL) until the washings were clear and colourless. The remaining solids were dried under vacuum until the title compound was obtained as faintly peach-coloured powder. The washings were brought to dryness and suspended in a toluene/*n*-hexane mixture (1:1, 30 mL). This suspension was filtered, and the residue dried under vacuum, yielding a second crop of **5** (1.265 g, 92 %). M.p.: 248-250 ºC (turns brown-beige); ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 1.99 (s, 6H, *p*-C*H*$_3$), 2.14 (s, 12H, *o*-C*H*$_3$), 5.89 (s, 2H, NC*H*), 6.66 (s, 4H, *m*-C*H*); ^{9}Be NMR (benzene-d_6, 56 MHz, 298 K): δ = 11.7 (br. s, $\Delta\omega_{1/2}$ = 217 Hz); ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 298 K): δ = 18.7 (*o*-*C*H$_3$), 21.1 (*p*-*C*H$_3$), 122.6 (N*C*H), 129.9 (*m*-*C*H), 133.2 (*p*-*C*), 135.0 (*o*-*C*), 140.5 (*ipso*-*C*), 172.0 (br. s, N*C*N); IR (ATR) ν (cm^{-1}) = 1607, 1541, 1122, 1035 br, 985, 930, 851 s, 800, 746 s, 670; MS (EI 70 eV), m/z (%): 567.0 ([(IMes)BeI$_2$]$^+$, <1), 440.1 ([(IMes)BeI]$^+$, 100), 303.2 ([IMes –H]$^+$, 30); elemental analysis for C$_{21}$H$_{24}$BeI$_2$N$_2$ found (calcd.) in %: C 44.26 (44.46), H 4.35 (4.26), N 4.73 (4.94).

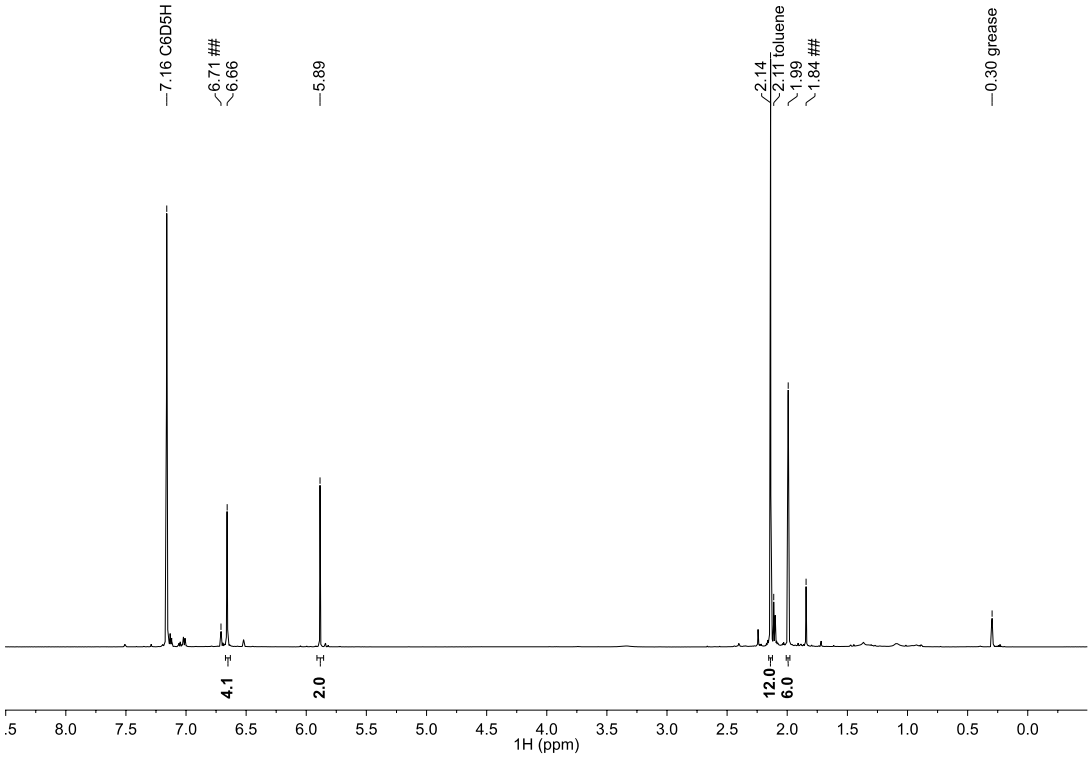


Figure S6. ^{1}H NMR spectrum of **5** in benzene-d_6 at 298 K (600 MHz). #: impurity.

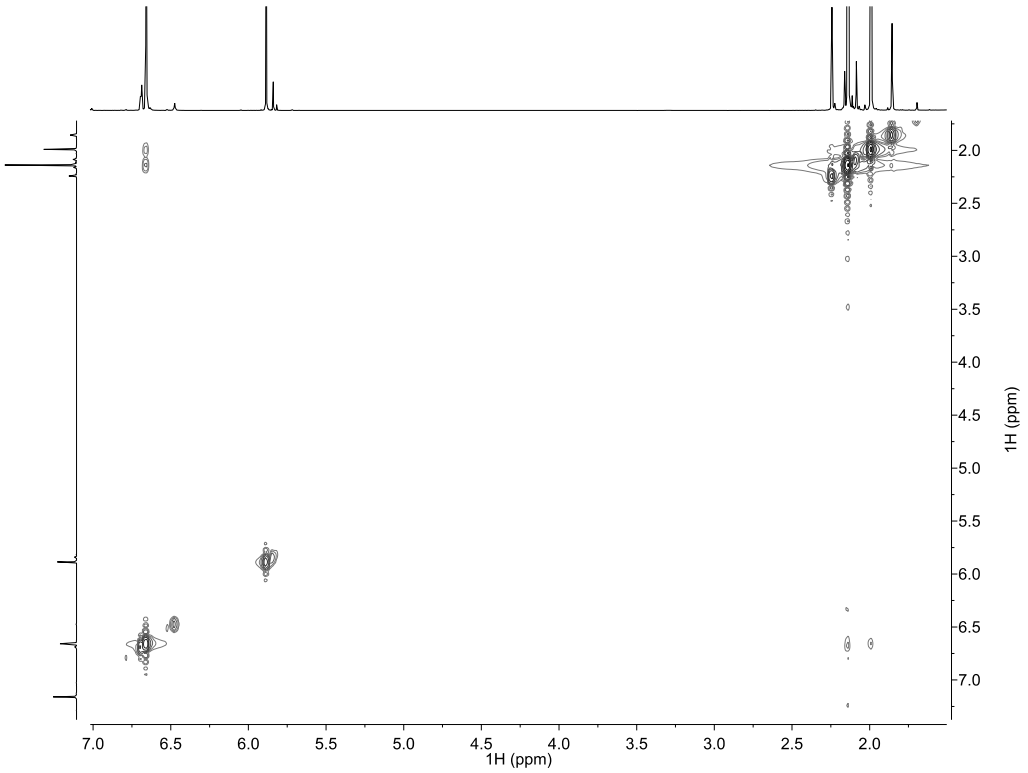


Figure S7. Excerpt from the COSY NMR spectrum of **5** in benzene-d_6 at 298 K (600 MHz).

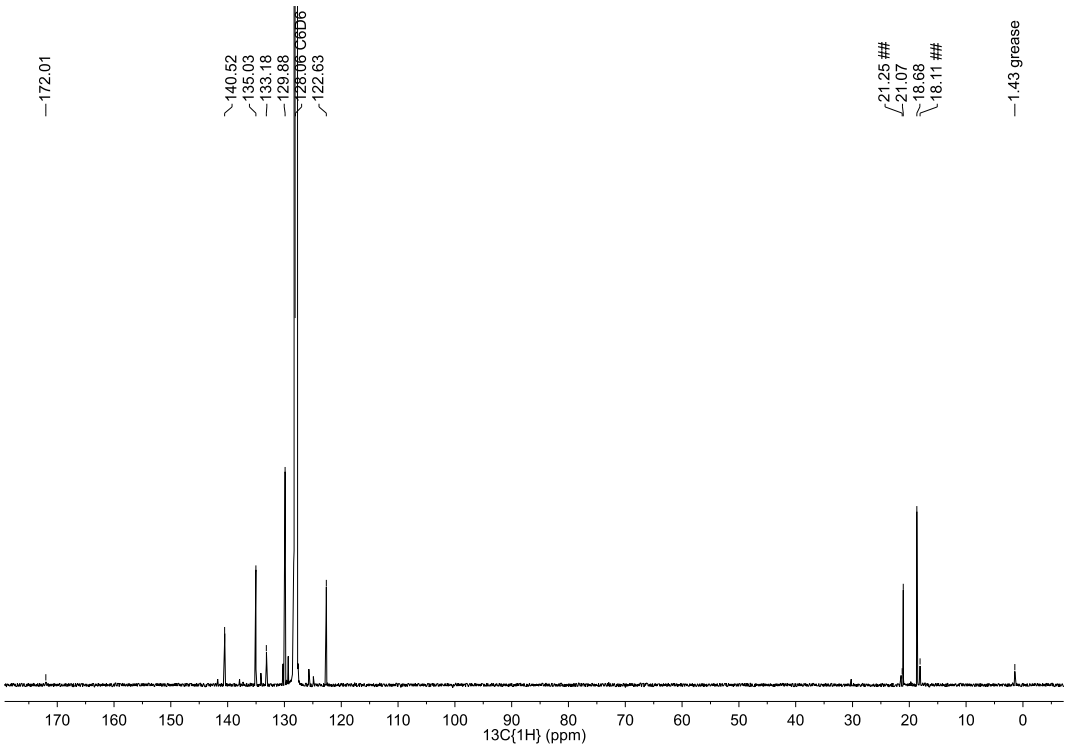


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in benzene-d_6 at 298 K (151 MHz). #: impurity.

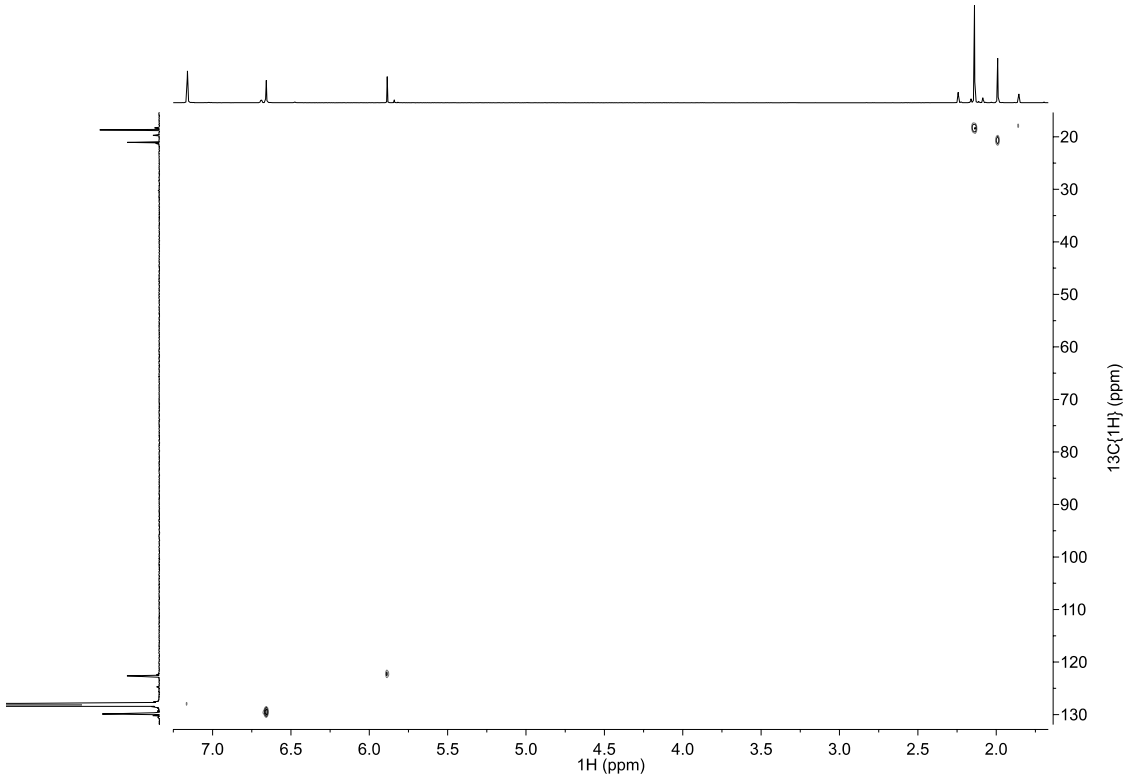


Figure S9. Excerpt from HSQC NMR spectrum of **5** in benzene-d_6 at 298 K (^{1}H: 600 MHz, ^{13}C: 151 MHz).

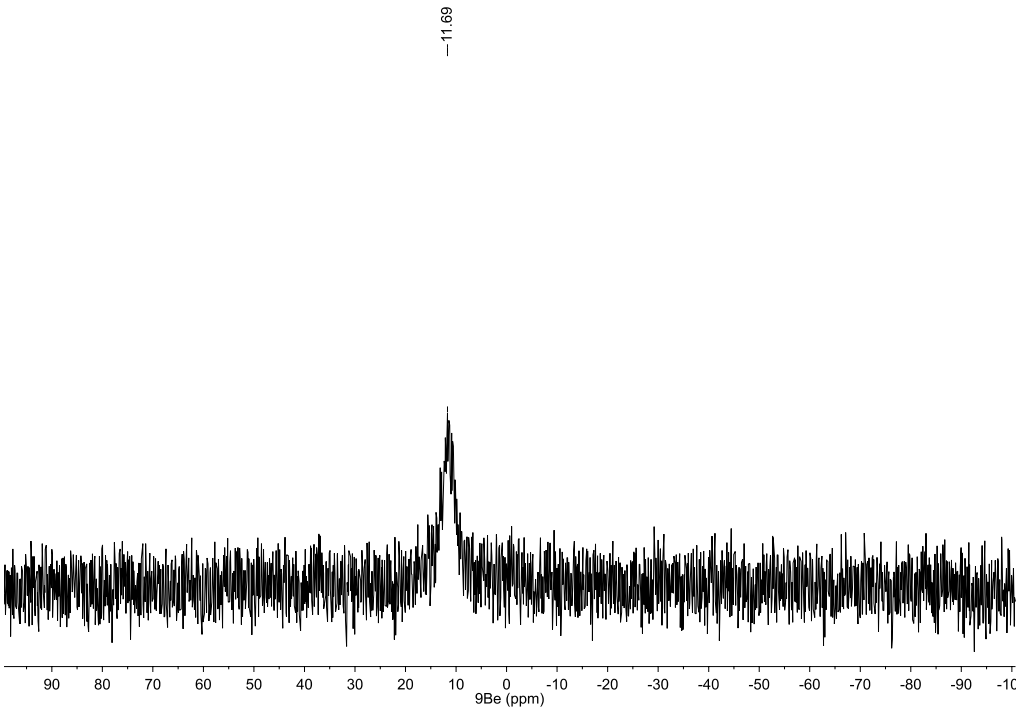


Figure S10. ^{9}Be NMR spectrum of **5** in benzene-d_6 at 298 K (56 MHz).

Synthesis of [(IPr)BeBr$_2$] 6. [$BeBr_2(OEt_2)_2$] (2.14 g, 6.75 mmol) and IPr (2.63 g, 6.75 mmol) were combined in a Schlenk tube, and toluene (100 mL) was added at room temperature. The ochre yellow suspension was stirred vigorously for 3.5 h. The liquor was decanted off and the residue rinsed with toluene (10 mL). Drying for 3 h under vacuum gave **6** as a fine ochre yellow powder. The filtrate was concentrated under vacuum until incipient crystallization occurred. The liquor was stored overnight at −30 ºC. Yellow crystals of the title compound were obtained (3.43 g, 91 %). M.p.: 229-231 ºC (beige liquid); ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 0.99 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH_3), 1.45 (br. d, $^{3}J_{HH}$ = 5.5 Hz, 12H, CH_3), 2.80 (br. m, 4H, CH(CH_3)$_2$), 6.41 (s, 2H, NCH), 7.07 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, *m*-CH), 7.19 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, *p*-CH); ^{9}Be NMR (benzene-d_6, 56 MHz, 300 K): δ = 14.1 (br. s, $\Delta\omega_{1/2}$ = 187 Hz); ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 298 K): δ = 23.2 (CH(*C*H$_3$)$_2$), 25.9 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 124.1 (N*C*H), 124.5, 131.3, 133.6, 145.8 (Ar-*C*), 200.4 (N*C*N); IR (ATR) ν (cm^{-1}) = 1594, 1118, 1061, 984, 949, 936, 800, 756, 675, 657; MS (EI 70 eV), m/z (%): 476.3 ([(IPr)BeBr]$^{+}$, 72), 387.3 ([(IPr)H]$^{+}$, 100); elemental analysis for $C_{27}H_{36}BeBr_2N_2$ found (calcd.) in %: C 58.09 (58.18), H 6.61 (6.51), N 4.94 (5.03).

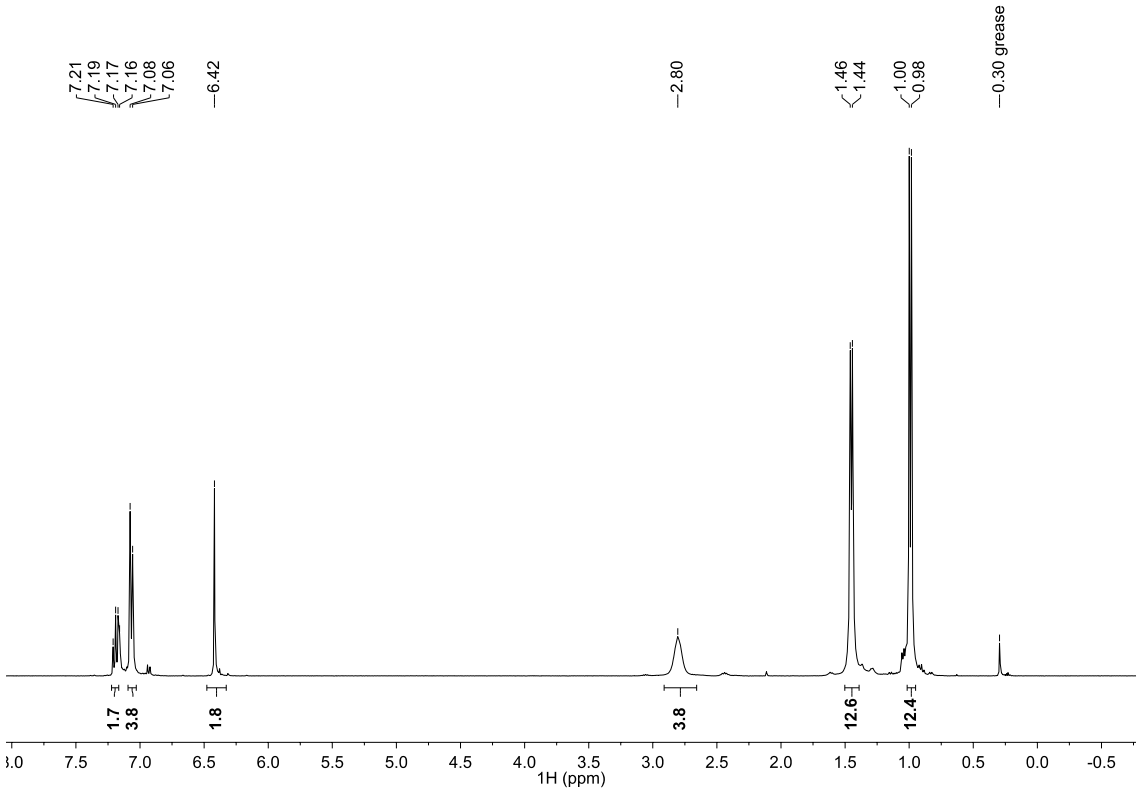


Figure S11. ^{1}H NMR spectrum of **6** in benzene-d_6 at 300 K (400 MHz).

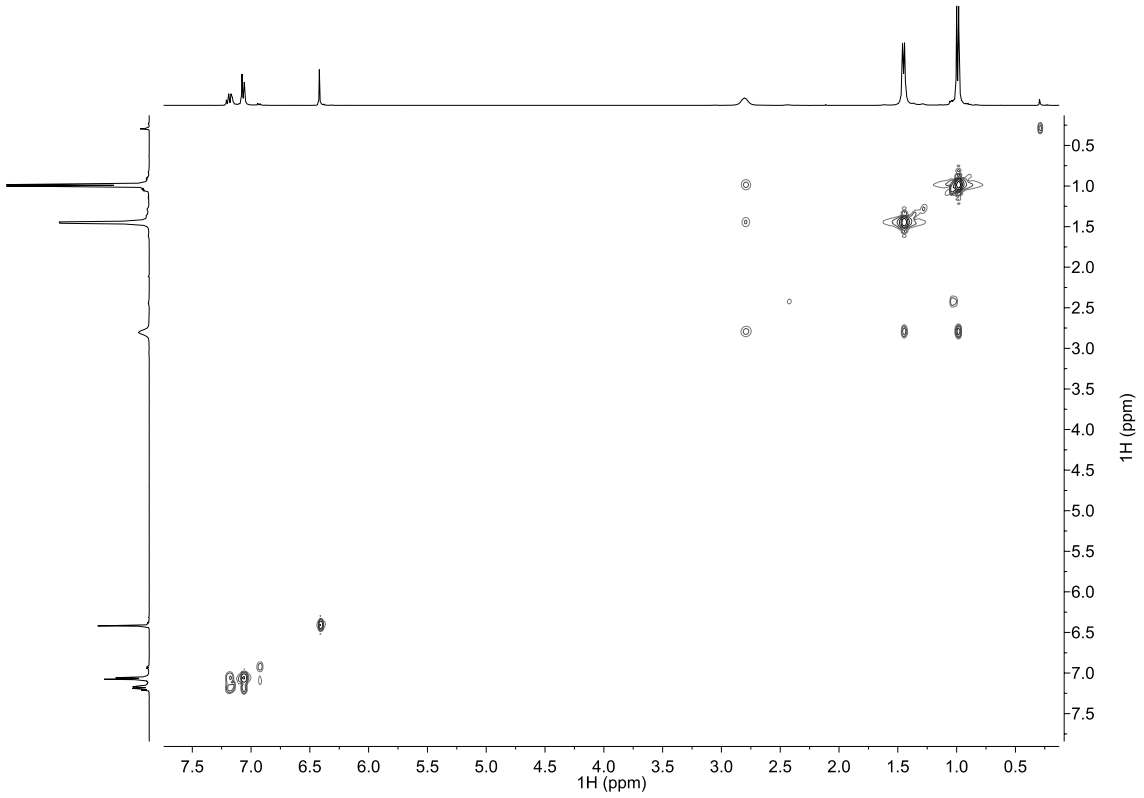


Figure S12. COSY NMR spectrum of **6** in benzene-d_6 at 298 K (600 MHz).

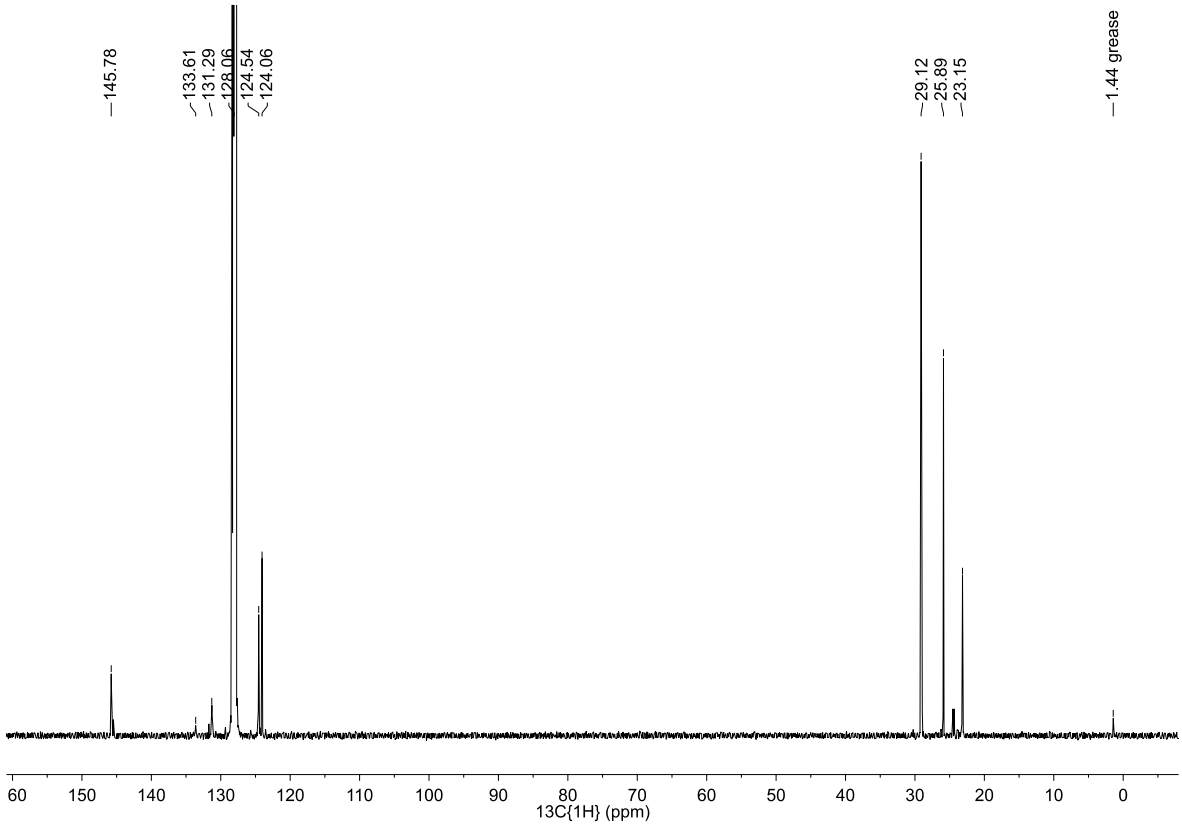


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in benzene-d_6 at 298 K (151 MHz).

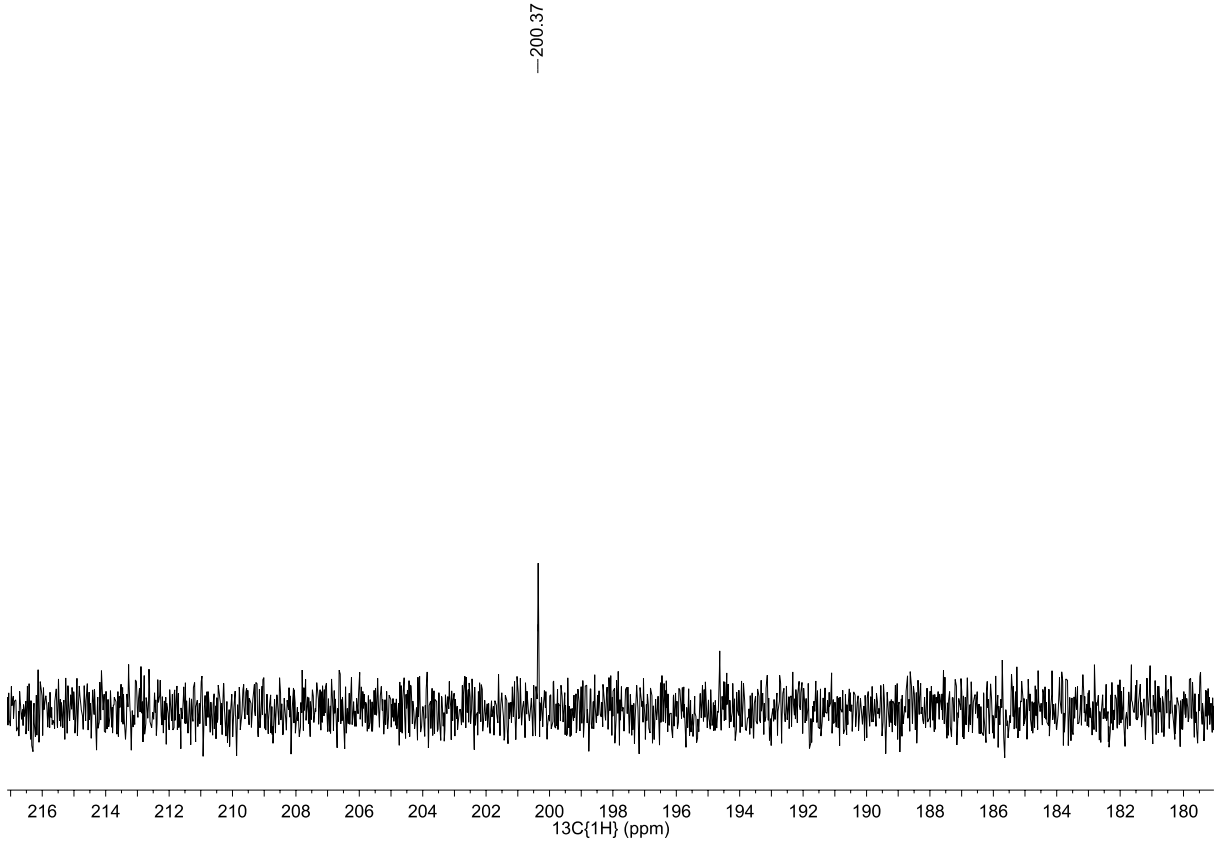


Figure S14. Excerpt from the $^{13}C\{^{1}H\}$ NMR spectrum of **6** in benzene-d_6 at 298 K (151 MHz).

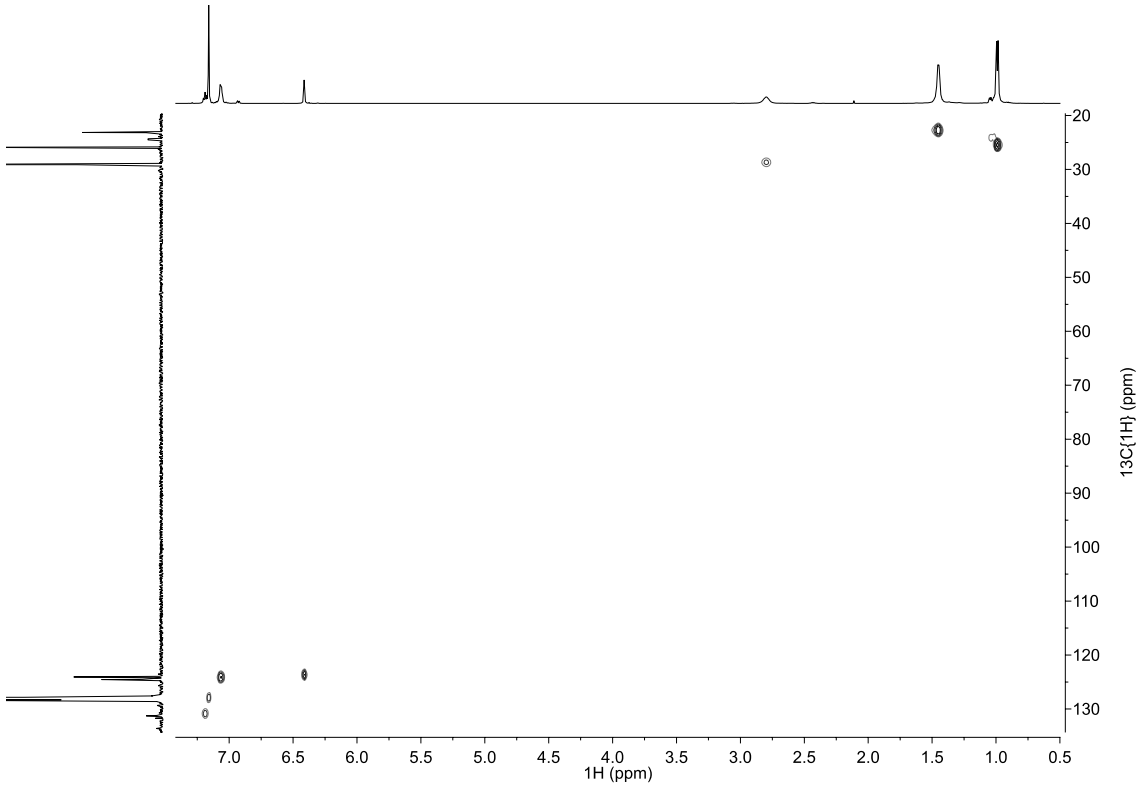


Figure S15. Excerpt from HSQC NMR spectrum of **6** in benzene-d_6 at 298 K (^{1}H: 600 MHz, ^{13}C: 151 MHz).

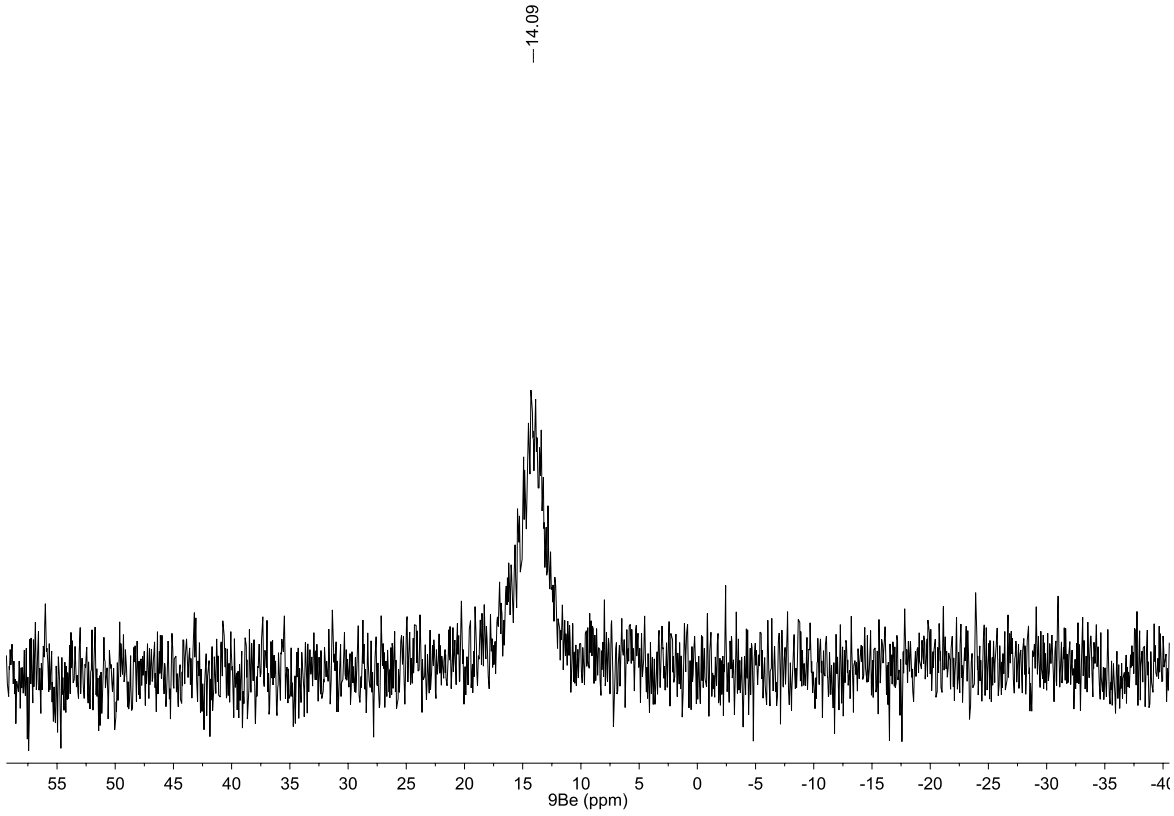


Figure S16. ^{9}Be NMR spectrum of **6** in benzene-d_6 at 300 K (56 MHz).

Synthesis of [(IPr)BeI$_2$] 7. [BeI$_2$(OEt$_2$)$_2$] (100 mg, 257 µmol) and IPr (103 mg, 250 µmol) were combined in a Schlenk tube and toluene (10 mL) was added at room temperature. A yellow suspension formed. After stirring for 5 h, the reaction mixture was filtered, and the residue dried under vacuum to yield **7** as pale-yellow powder (131 mg, 80 %). Crystals suitable for X-ray diffraction were obtained at room temperature by recrystallization from benzene. M.p.: >160 ºC (becomes beige) ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.47 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.87 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 6.42 (s, 2H, NCH), 7.05-7.19 (m, 6H, aryl); ^{9}Be NMR (benzene-d_6, 56 MHz, 300 K): δ = 11.8 (s, $\Delta\omega_{1/2}$ = 174 Hz); ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 298 K): δ = 23.3 (CH(*C*H$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 124.4 (N*C*H), 124.7, 131.5, 133.5, 145.6 (Ar-*C*), 198.4 (N*C*N); IR (ATR) ν (cm^{-1}) = 1593, 1209, 1182, 1131, 1118, 1061, 983, 800, 757, 661; MS (EI 70 eV), m/z (%): 524.3 ([(IPr)BeI]$^+$, 100), 476.3 (26), 387.3 ([IPr –H]$^+$, 12); elemental analysis for $C_{27}H_{36}BeI_2N_2$ found (calcd.) in %: C 49.59 (49.78), H 5.62 (5.57), N 4.19 (4.30).

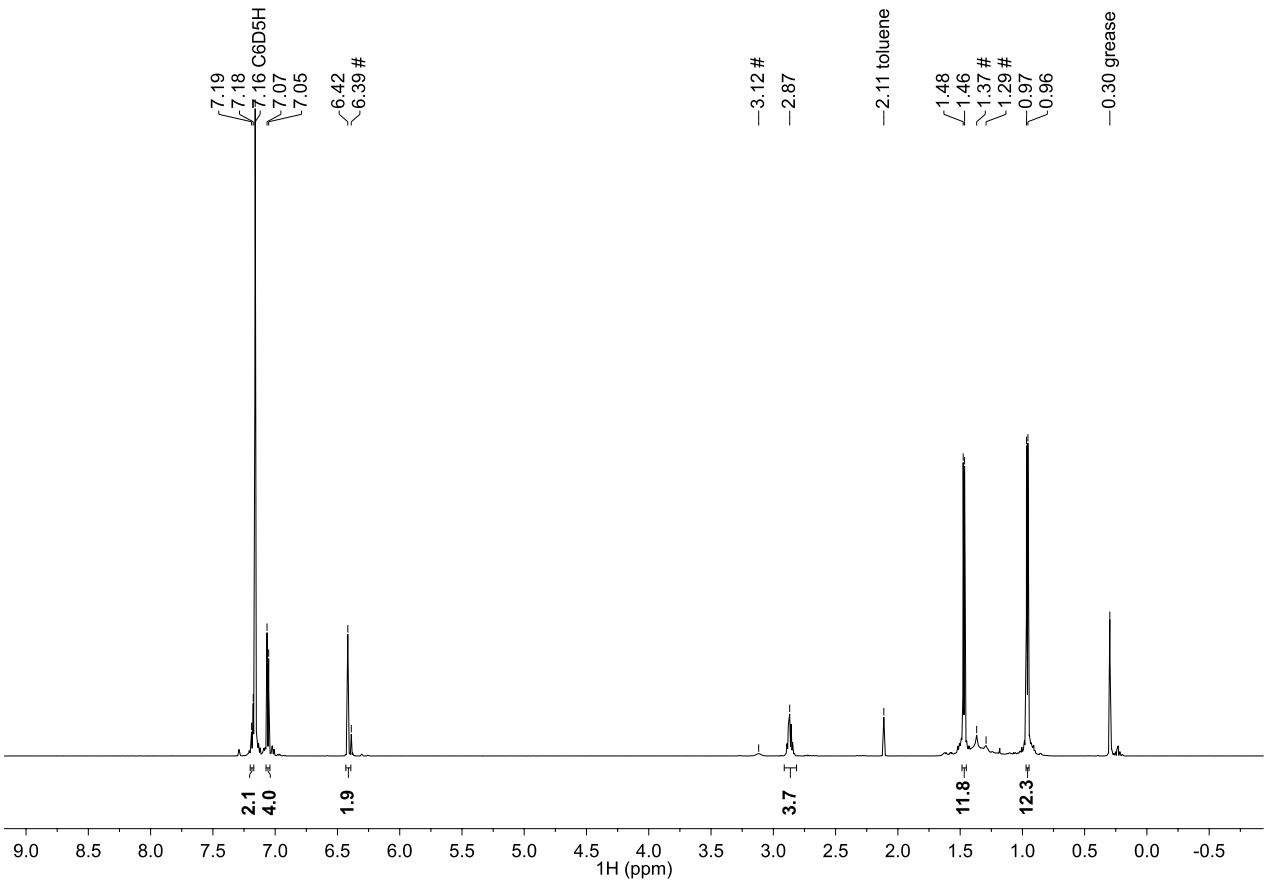


Figure S17. ^{1}H NMR spectrum of **7** in benzene-d_6 at 298 K (600 MHz). #: impurity.

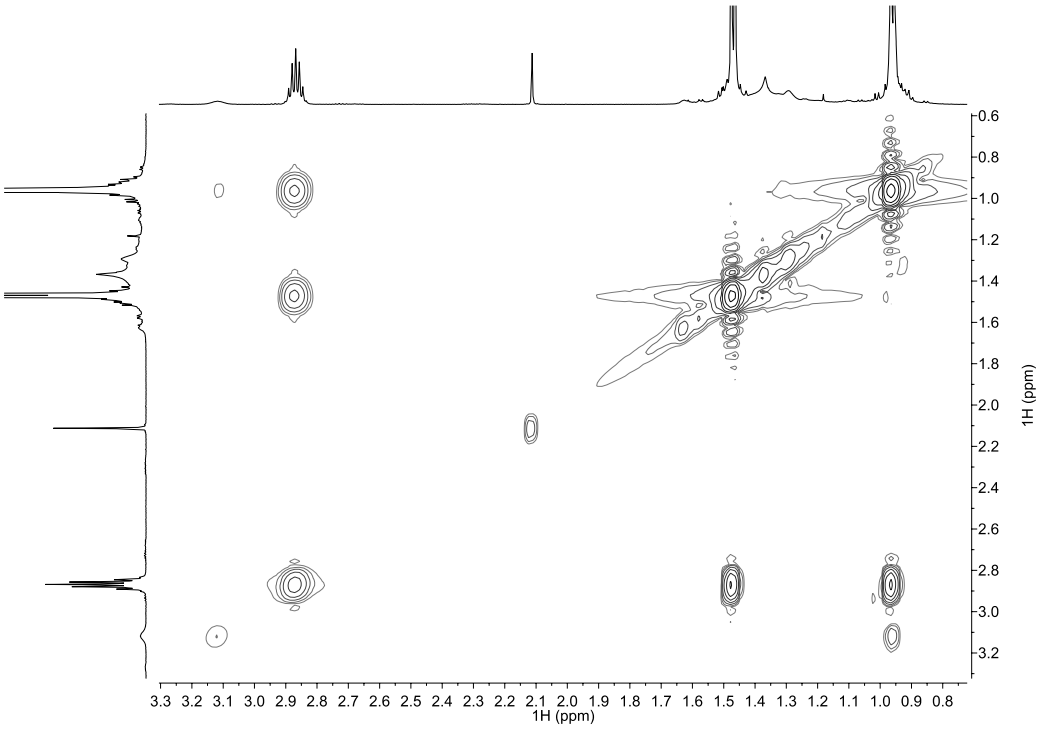


Figure S18. Excerpt from COSY NMR spectrum of **7** in benzene-d_6 at 298 K (600 MHz).

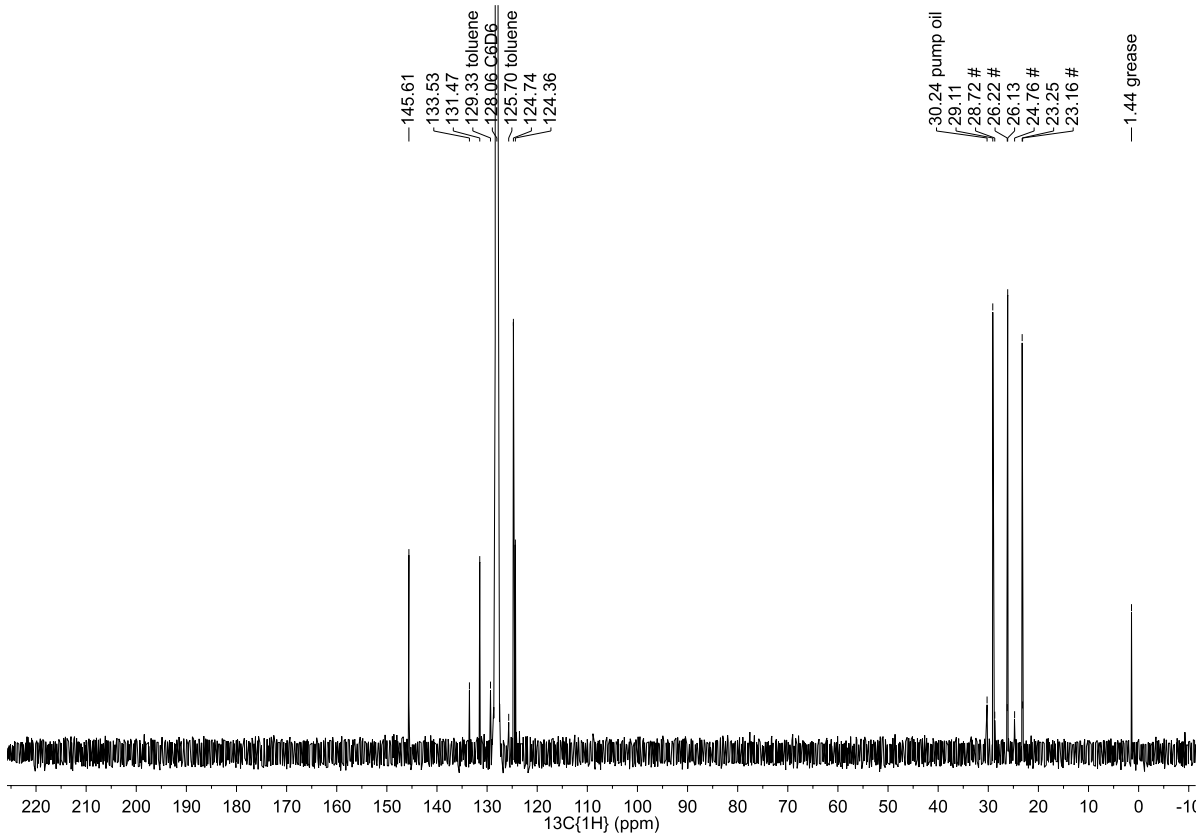


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in benzene-d_6 at 298 K (151 MHz). #: impurity.

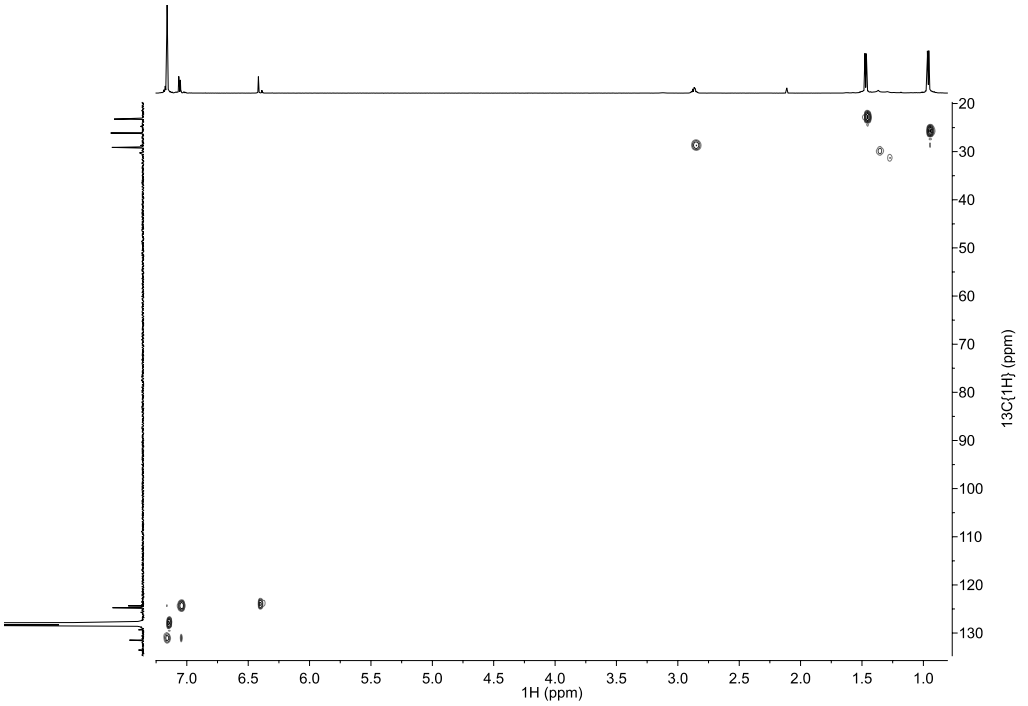


Figure S20. Excerpt from HSQC NMR spectrum of **7** in benzene-d_6 at 298 K (^{1}H: 600 MHz, ^{13}C: 151 MHz).

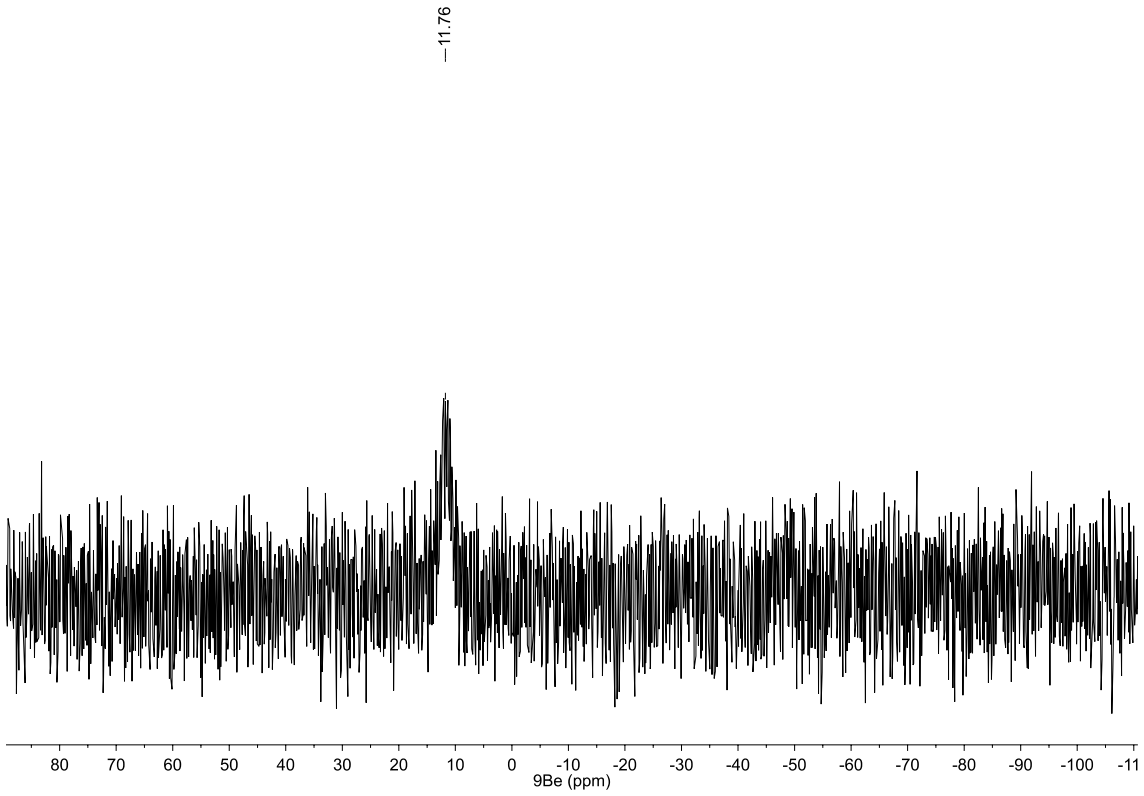


Figure S21. ^{9}Be NMR spectrum of **7** in benzene-d_6 at 300 K (56 MHz).

Synthesis of [(CDP)$BeBr_2$] 8. Toluene (5 mL) was added to a mixture of solid CDP (100 mg, 0.186 mmol) and [$BeBr_2(OEt_2)_2$] (62 mg, 0.196 mmol). A milky suspension formed immediately. After stirring for 1.5 h, all volatiles were removed *in vacuo* and the white powdery residue was rinsed with toluene (2 mL). The product was dried under reduced pressure (117 mg, 89 %). Colorless crystals were obtained by heating a suspension of the product (5 mg) in benzene (0.5 mL) for 2 days at 80 ºC, after which time the resultant solution was cooled to room temperature. M.p.: 214-219 ºC (decomp.); due to the extremely low solubility of the compound in non-coordinating solvents, no meaningful NMR spectroscopic data could be obtained; IR (ATR) ν (cm^{-1}) = 1585 w, 1480 w, 1435 s, 1213 w, 1184 w, 1159 w, 1098 s, 803 m, 736 s, 714 s, 684 s; MS (EI 70 eV), m/z (%): 624.1 ([$((Ph_3P)_2C)BeBr]^+$, 6), 535.3 ([$(Ph_3P)_2C–H]^+$, 41), 262.1 ([$PPh_3]^+$, 58), 183.1 ([PPh_2 –2H]$^+$, 100); elemental analysis for $C_{37}H_{30}BeBr_2P_2$ found (calcd.) in %: C 62.73 (63.00), H 4.45 (4.29).

Synthesis of [(CDP)BeI_2] 9. Toluene (5 mL) was added to a mixture of solid CDP (100 mg, 0.186 mmol) and [$BeI_2(OEt_2)_2$] (80 mg, 0.196 mmol). The suspension was stirred for 1.5 h. All volatiles were then removed *in vacuo* and the powdery residue rinsed with toluene (4 mL). The pale-yellow product was dried under reduced pressure (113 mg, 76 %). Colorless crystals were obtained by heating a suspension of the product (5 mg) in benzene (0.5 mL) for 2 days at 80 ºC, after which time the resultant solution was cooled to room temperature. M.p.: 198-201 ºC (red-brown liquid); due to the extremely low solubility of the compound in non-coordinating solvents, no meaningful NMR spectroscopic data could be obtained; IR (ATR) ν (cm^{-1}) = 1586 w, 1159 w, 1097 s, 1011 w, 906 br, 800 br, 737 s, 713 s, 684 s; MS (EI 70 eV), m/z (%): 671.2 ([$((Ph_3P)_2C)BeI–H]^+$, 4), 544.3 ([$((Ph_3P)_2C)Be–H]^+$, 32), 535.3 ([$(Ph_3P)_2C–H]^+$, 18), 273.1 ([$HCPPh_3]^+$, 12), 262.1 ([$PPh_3]^+$, 42), 183.1 ([PPh_2 –2H]$^+$, 100); elemental analysis for $C_{37}H_{30}BeI_2P_2$ found (calcd.) in %: C 55.30 (55.59), H 3.93 (3.78).

Synthesis of [{(DPPE)BeI_2}$_\infty$] 10. A solution of DPPE (970 mg, 2.43 mmol) in toluene (10 mL) was added to a solution of [$BeI_2(OEt_2)_2$] (1.000 g, 2.43 mmol) in toluene (15 mL), which afforded a yellow precipitate. After stirring for 2 h at room temperature, the yellow solids were isolated *via* filtration and rinsed with toluene (3 × 10 mL). The title compound was dried *in vacuo* (1.27 g, 79 %). X-ray quality crystals of the compound were obtained by boiling a suspension of it (5 mg) in benzene (0.5 mL) for 2 days, after which time the resultant solution was cooled to room temperature. M.p. unchanged at up to 260 °C; due to the extremely low solubility of the compound in non-coordinating solvents, no meaningful NMR spectroscopic data could be obtained; IR (ATR) ν (cm^{-1}) = 1480 w, 1433 w, 1093 br m, 1018 br m, 878 br, 796 br s, 739, 724 s, 688 s; MS (EI 70 eV), m/z (%): 534.1

([BeI]$^+$, 100), 398.2 ([DPPE]$^+$, 28), 262.1 ([BeI_2]$^+$, 26), 185.1 ([PPh_2]$^+$, 38), 183.1 ([PPh_2−2H]$^+$, 100); elemental analysis for $C_{26}H_{24}BeI_2P_2$ found (calcd.) in %: C 47.08 (47.23), H 3.77 (3.66).

Synthesis of [{(IPr)(Br)Be(μ-H)}$_2$] 11. An orange solution of [:Al(^{Dip}Nacnac)] (17 mg, 38 μmol) in toluene (3 mL) was added at −78 ºC to a turbid colorless solution of **6** (42 mg, 75 μmol) in toluene (3 mL). A yellow turbid reaction mixture formed immediately. The mixture was stirred at room temperature for 16 h, during which time a white precipitate formed, and was then isolated by filtration. The filtrate was concentrated under vacuum until incipient crystallization, then placed at −30 ºC. Small colorless crystals grew overnight (13 mg, 37 %). M.p.: > 260 ºC; Once crystallised the compound has negligible solubility in all common organic solvents. As a result, no meaningful NMR spectroscopic data could be obtained; IR (ATR) ν (cm^{-1}) = 1594 w, 1061 w, 980 w, 946 w, 938 w, 900 s, 841, 798 s, 765 w, 752 s, 710 w, 667 w; MS (EI 70 eV), m/z (%): 476.4 ([(IPr)BeBr]$^+$, 56), 387.4 ([(IPr) –H]$^+$, 100); As the compound could not be recrystallised from minor impurities, a satisfactory microanalysis could not be obtained.

Synthesis of [(IPr)Be($C_{10}H_8$)] 12. A vigorously stirred yellowish suspension of **6** (300 mg, 1.17 mmol) in toluene (20 mL) was treated with a dark-green solution of [$K_2(C_{10}H_8)_2$(THF)] (237 mg, 0.58 mmol) in THF (20 mL) at –78 ºC. Addition was complete within 30 min. The resulting turbid dark-orange reaction mixture was allowed to warm slowly to room temperature. After stirring for 16 h, the liquor was concentrated under vacuum to *ca.* 20 mL. After filtration, the orange solution was further concentrated under vacuum until incipient crystallization. The solution was kept for 2 d at –30 ºC, yielding **12** as an orange crystalline solid (124 mg, 20 %). M.p.: 225-229 ºC (red-orange liquid); ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 0.98 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.54 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 2.73 (m, 2H, naphth-CH), 5.53 (m, 2H, naphth-CH), 6.33 (s, 2H, NCH), 6.72 (m, 2H, naphth-CH), 6.85 (m, 2H, naphth-CH), 7.09 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Ar-CH), 7.25 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ar-CH); ^{9}Be NMR (benzene-d_6, 56 MHz, 296 K): δ = –4.2 (s, $\Delta\omega_{1/2}$ = 48 Hz); ^{13}C{^{1}H} NMR (benzene-d_6, 151 MHz, 298 K): δ = 23.0 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 57.3 (naphth-*C*H), 108.2 (naphth-*C*H), 117.7 (naphth-*C*H), 121.3 (naphth-*C*H), 123.4 (N*C*H), 124.2 (Ar-*C*H), 130.7 (Ar-*C*H), 134.9 (naphth-*C*), 145.7 (Ar-*C*), 148.4 (Ar-*C*), 172.7 (N*C*N); IR (ATR) ν (cm^{-1}) = 1685, 1676, 1591, 1541, 1253, 1060 m, 1006 m, 936 m, 887 m, 851 m, 802 s, 731 s, 710 s; MS (EI 70 eV), m/z (%): 525.5 ([(IPr)Be($C_{10}H_8$)]$^+$, 15), 387.3 ([IPr –H]$^+$, 22), 128.1 ([$C_{10}H_8$]$^+$, 100); a reproducible elemental analysis could not be obtained for the compound due to its very high air sensitivity.

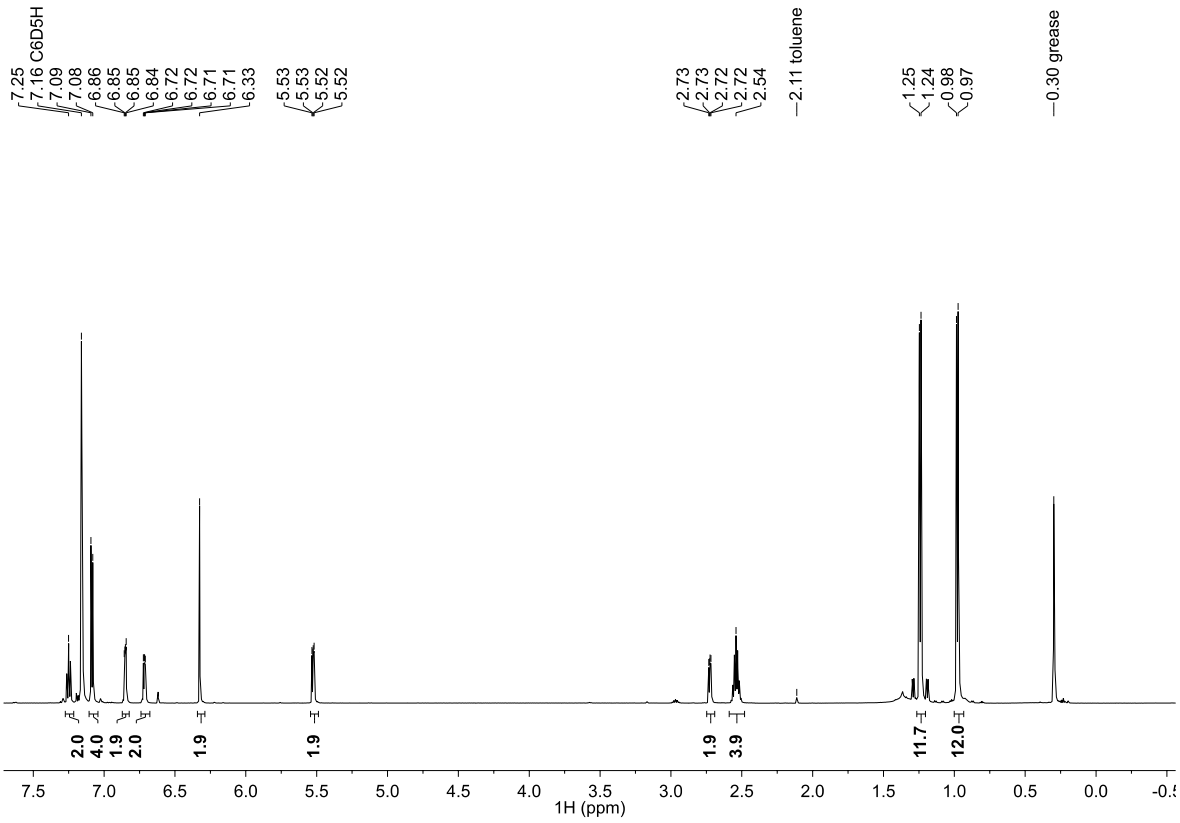


Figure S22. ^{1}H NMR spectrum of **12** in benzene-d_6 at 298 K (600 MHz).

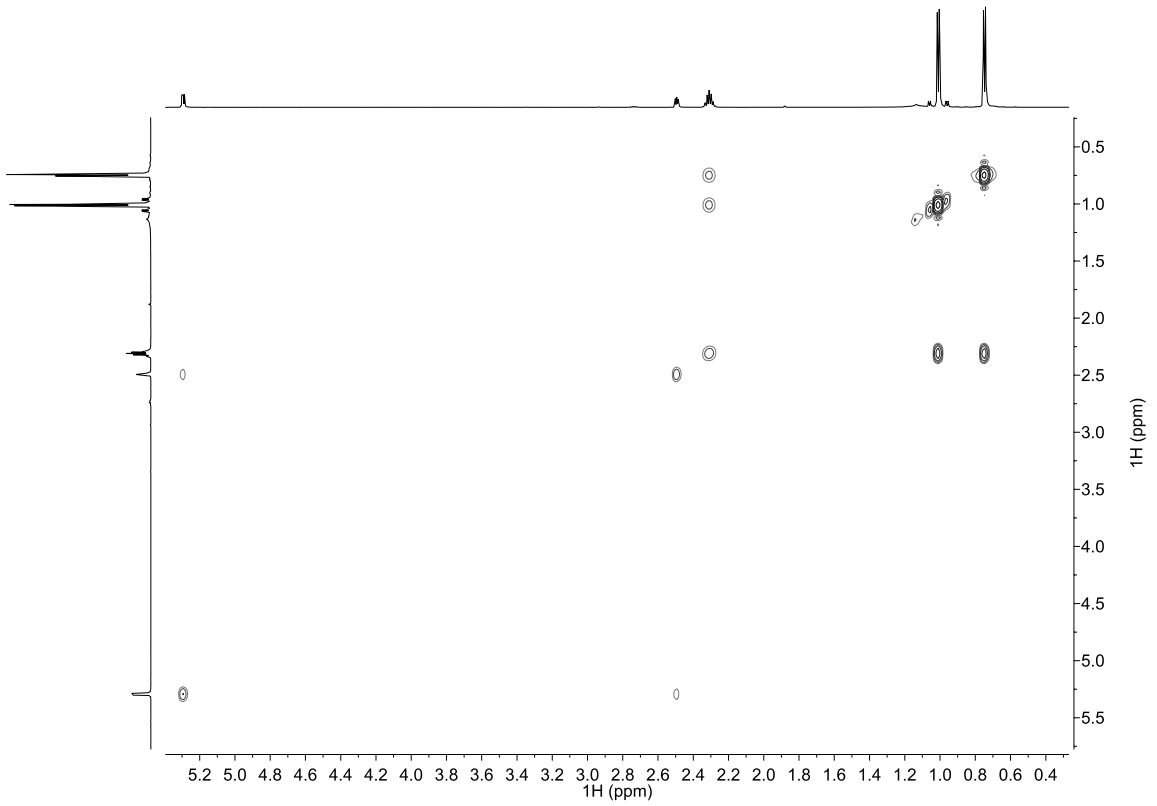


Figure S23. Excerpt from the COSY spectrum of **12** in benzene-d_6 at 298 K (600 MHz).

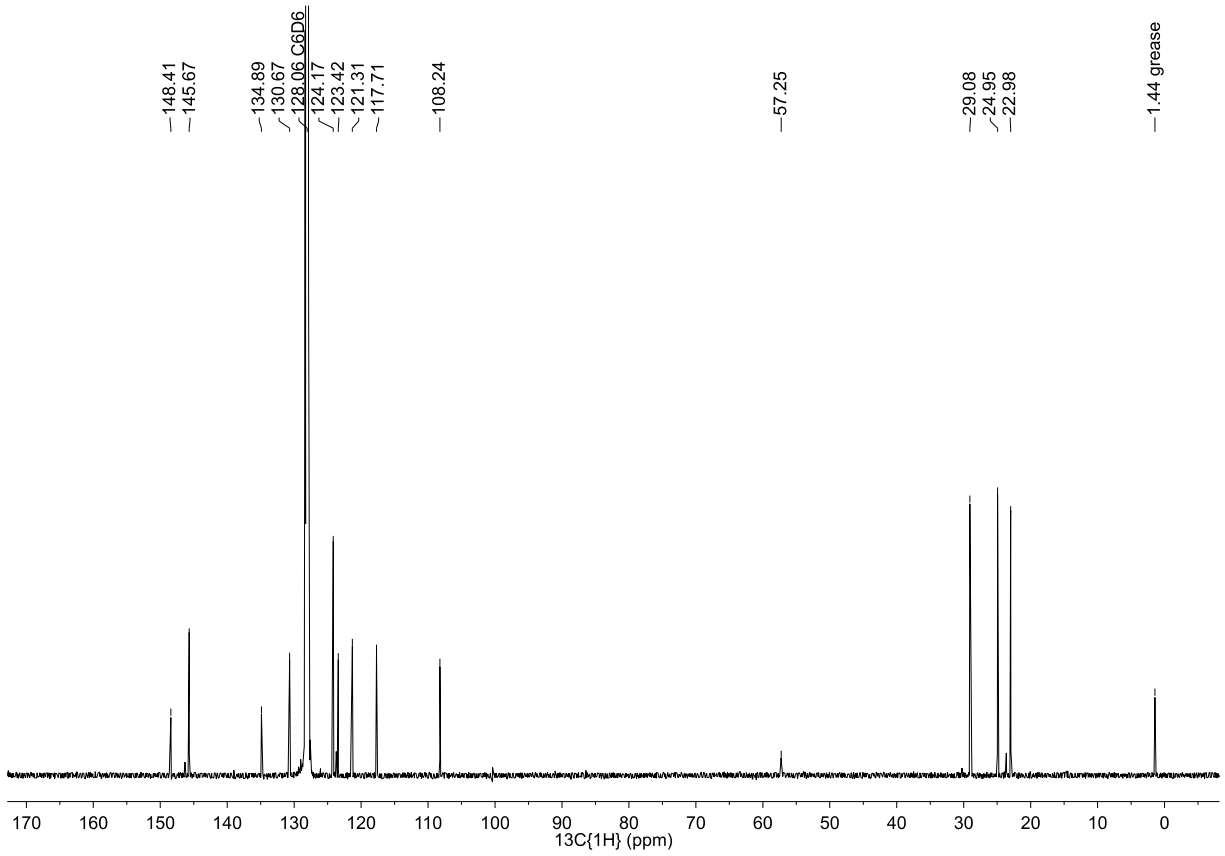


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **12** in benzene-d_6 at 298 K (151 MHz).

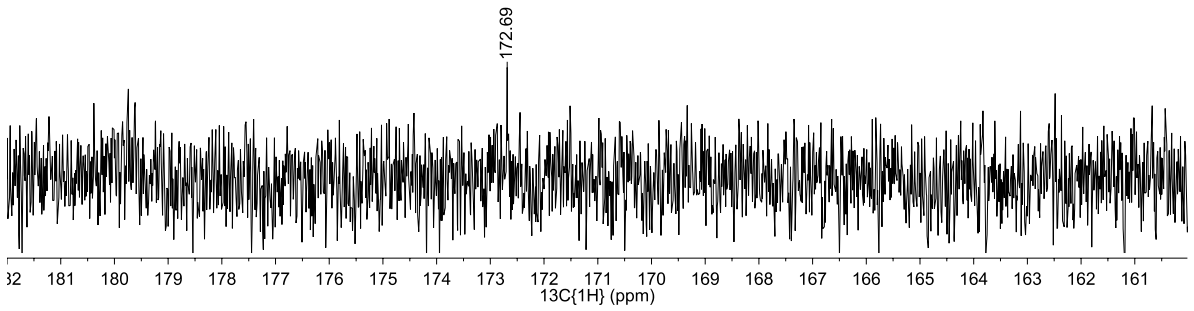


Figure S25. Excerpt from the $^{13}C\{^{1}H\}$ NMR spectrum of **12** in benzene-d_6 at 298 K (151 MHz).

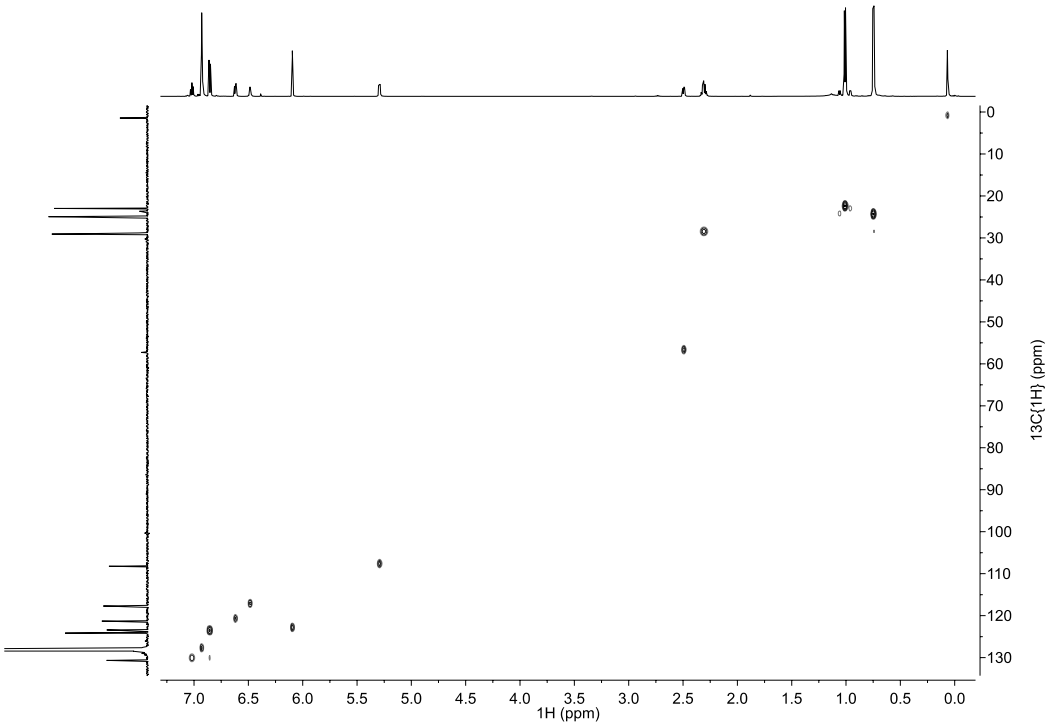


Figure S26. Excerpt from HSQC NMR spectrum of **12** in benzene-d_6 at 298 K (^{1}H: 600 MHz, ^{13}C: 151 MHz).

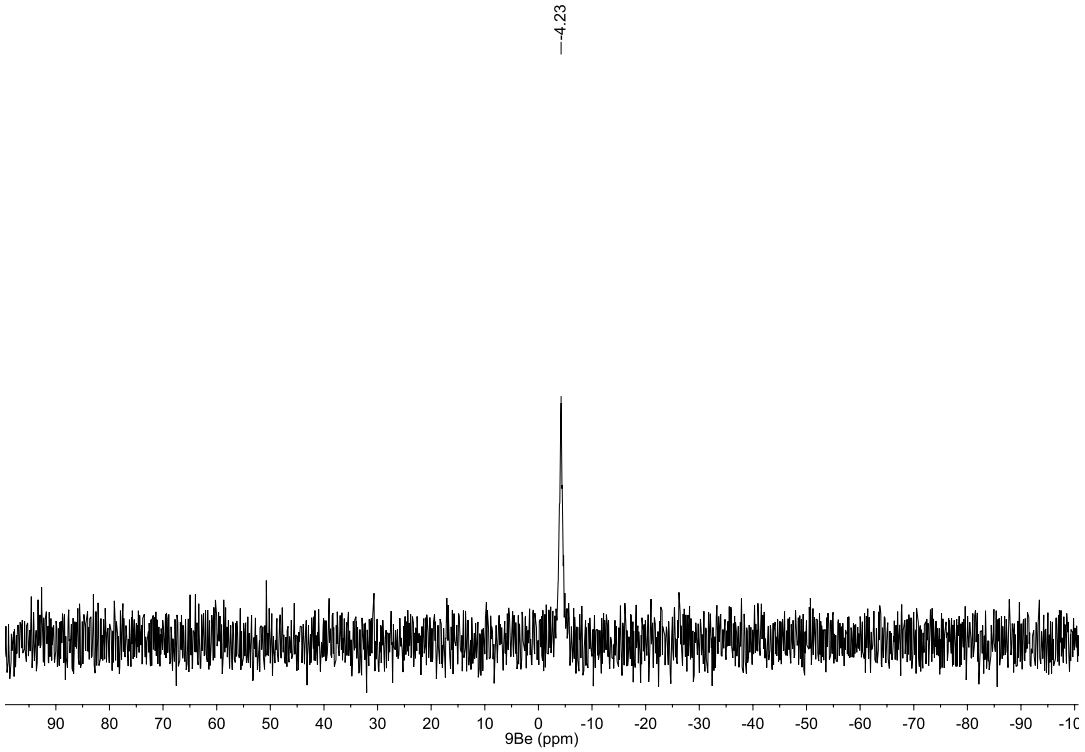


Figure S27. ^{9}Be NMR spectrum of **12** in benzene-d_6 at 296 K (56 MHz).

Synthesis of [(DPPE)(I)Be–Al(I)(DipNacnac)] 13. Compound **10** (489 mg, 740 μmol) and [:Al(DipNacnac)] (329 mg, 740 μmol) were combined in toluene (30 mL) and stirred for 16 h at 55 ºC. The mixture was then filtered, and the pale-yellow filtrate placed at −30 ºC for 12 h, which afforded a yellow mixture of free DPPE and [(DipNacnac)AlI$_2$]. The mother liquor was dried *in vacuo* and extracted with boiling hexane (5 mL), then filtered. The orange filtrate was concentrated *in vacuo* and placed at −30 ºC, yielding yellow crystals of **13** (15 mg, < 5%). Once crystallised the title compound had negligible solubility in common solvents at room temperature. Attempts to dissolve the compound in hot d_6-benzene led to its decomposition to free DPPE and [(DipNacnac)AlI$_2$]. The ^{1}H NMR spectrum of the compound was tentatively assigned from the spectrum of the reaction mixture (also containing DPPE and [(DipNacnac)AlI$_2$]) before crystallisation occurred; ^{1}H NMR (benzene-d_6, 600 MHz, 298 K): δ = 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.52 (s, 6H, α-CH_3), 3.32 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 3.37 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 4.90 (s, 1H, β-CH), 7.06-7.12 (m, 6H, Ar-H); IR (ATR) ν (cm^{-1}) = 1654 w, 1590 w, 1527 s, 1021 m, 935 m, 888 br. w, 798 s, 740 s, 694 s; MS (EI 70 eV), m/z (%): 571.3 ([(DipNacnac)AlI]$^+$, 46), 398.2 ([DPPE]$^+$, 21), 289.1, 183.1 ([PPh$_2$ −2H]$^+$, 100); As the compound could not be recrystallised from minor impurities, a satisfactory microanalysis could not be obtained.

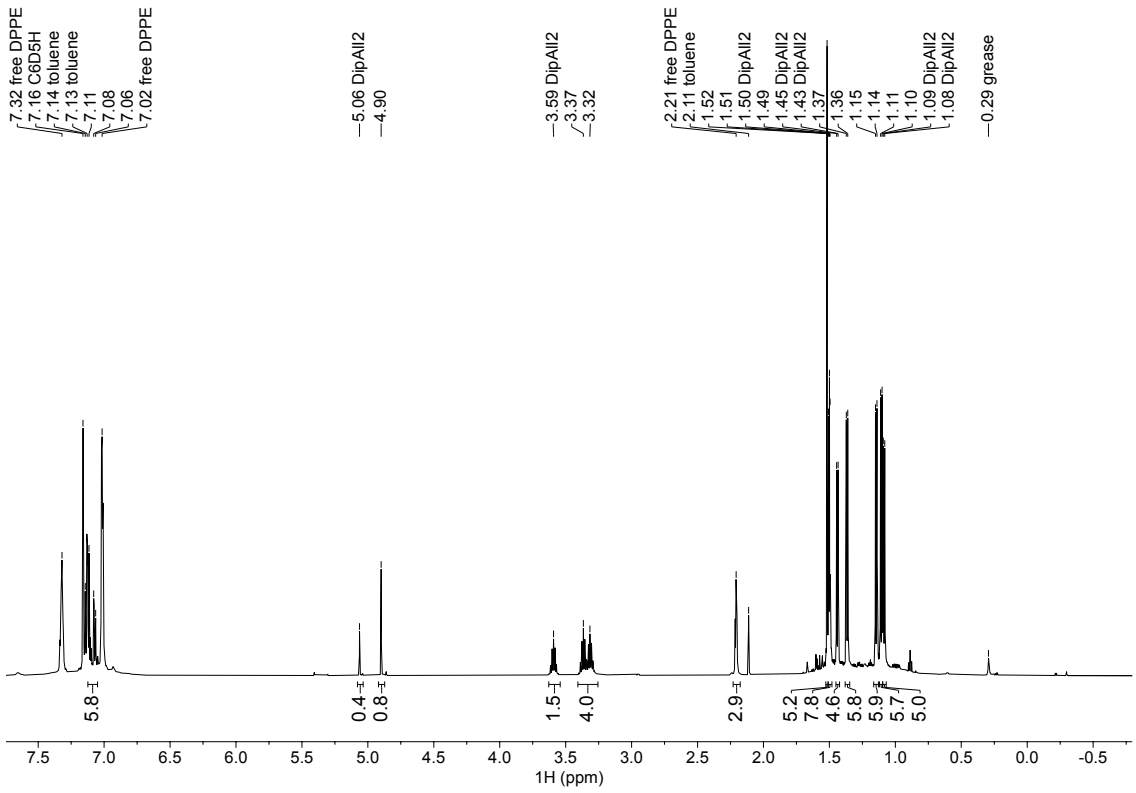


Figure S28. ^{1}H NMR spectrum of the reaction mixture containing **13** in benzene-d_6 at 298 K (600 MHz). "DipAlI2" = [(DipNacnac)AlI$_2$].

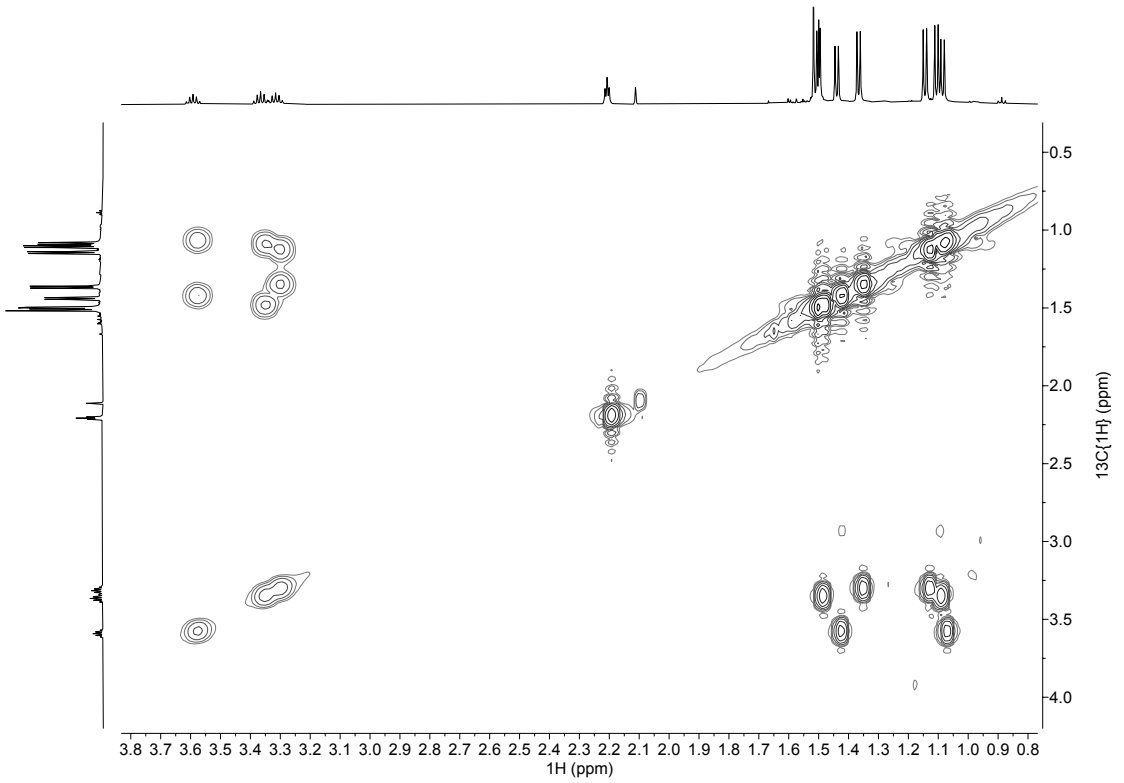


Figure S29. Excerpt from the COSY NMR spectrum of the reaction mixture containing **13** in benzene-d_6 at 298 K (600 MHz).

2. Crystallography

X-ray Diffraction Studies

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made with a Rigaku Xtalab Synergy Dualflex diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å), or the MX1 beamline of the Australian Synchrotron (λ = 0.71090 Å). 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 F^2 by full matrix least squares (SHELX-16[12]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). The atomic displacement parameters of the hydride ligand of **11** were freely refined isotropically, while its positional parameters were restrained using the DFIX command of SHELXL-16. Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Neutron Diffraction Study

A colourless square prismatic crystal of **11** (0.5 x 0.5 x 0.3 mm) was mounted on KOALA[13] and two sets of images in different mountings (shifted to complete the reciprocal lattice survey for a monoclinic crystal) with respect to the phi rotation axis of the instrument and with each exposure time of 1500s were recorded. It should be noted that the 0.075mm^3 crystal volume is below the specified minimum 0.1mm^3 volume for the instrument and the diffraction patterns recorded extended to relatively low resolution. Data were extracted from the 20 images by means of the LaueG software[14,15]. Intensities were recorded for diffraction spots with wavelengths $0.85 < \lambda < 1.70$ Å to a minimum *d* spacing of 1.0 Å. 20847 reflections were extracted of which 4177 were unique and 1166 satisfied the $I \geq 3\sigma I$ criterion of observability. The merging Rvalue for 4 sigma data of 6.7(6.3)% and weighted merging R of 8.3(7.5)% are indicative of well measured (reproducible) data for this instrument, the merge values for all data are much higher and indicate that the low intensity data are noisy, as is common with this method. It must be noted in this context that the final observed data are of relatively low "resolution" but that the effect being probed in this experiment is hydrogen atom presence/position which is predominantly encoded in this low resolution region of the diffraction pattern.

The neutron diffraction data thus obtained has been modelled using the CRYSTALS[16] software package. Refinement commenced from the original X-ray model in which the non-hydrogen atoms together with the hydrogens of the organic ligand were included. All atoms were modelled with positional and anisotropic displacement parameters refined. The model employed 447 distance, angle and displacement parameter restraints which impose chemically reasonable geometry on the model parameters and supplement the 1166 data which meet the three sigma criterion of observability. When the model approached convergence, all hydrogen atoms were deleted and a negative difference map returned all known hydrogen atom positions together with an unambiguous hydride location which was included in the final refinement cycles – no restraints were applied to the hydride location and the e.s.d.s on the hydride parameters and bonding geometry are as well determined as all others of this structure. The final model, refined against *F* and employing a 4 term Chebychev polynomial weighting scheme converged with $R = 0.046$ $R_w = 0.049$ $S = 1.49$, minimum and maximum residual nuclear densities were -0.45 and 0.65 fermi Å^3 and the final difference density map is featureless.

Full details of the experiment, data reduction and refinement are contained in the deposited CIF for this paper (CCDC deposition no.: 2079976)

Table S1. Crystal data for compounds **4-13** and [{(IPr)(Br)Be}$_2$(μ-O)] **1S.**

	4·(toluene)$_{0.75}$	**5**	**6**	**7**
empirical formula	$C_{27.25}H_{46}BeI_2N_4$	$C_{12}H_{24}BeI_2N_2$	$C_{27}H_{36}BeBr_2N_2$	$C_{27}H_{36}BeI_2N_2$
formula weight	692.49	567.23	557.41	651.39
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$Pnna$	$P2_1/n$	$P2_1/n$
a (Å)	16.9196(3)	18.8286(14)	10.1088(4)	10.4103(4)
b (Å)	9.8805(2)	14.4611(9)	17.9685(6)	17.6415(6)
c (Å)	19.4832(3)	8.3598(6)	15.4443(6)	15.9511(4)
α (°)	90	90	90	90
β (°)	101.905(2)	90	100.191(4)	99.948(3)
γ (°)	90	90	90	90
V (Å^3)	3187.03(10)	2276.2(3)	2761.04(18)	2885.43(17)
Z	4	4	4	4
T (K)	123(2)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.443	1.655	1.341	1.499
μ (mm^{-1})	1.994	2.769	2.952	2.195
F(000)	1390	1096	1144	1288
reflns collected	29180	13154	22453	23395
unique reflns	5923	2120	5131	5355
R_{int}	0.0318	0.0549	0.0457	0.0580
R1 [I > 2σ(I)]	0.0473	0.0284	0.0358	0.0304
wR2 (all data)	0.1042	0.0781	0.0891	0.0665
largest peak and hole (e·Å^{-3})	0.981, -1.006	0.929, -0.591	0.900, -0.676	0.565, -0.558
CCDC no.	2079971	2079970	2079972	2079981

	8	**9**	**10**	**11**
empirical formula	$C_{37}H_{30}BeBr_2P_2$	$C_{37}H_{30}BeI_2P_2$	$C_{26}H_{24}BeI_2P_2$	$C_{54}H_{74}Be_2Br_2N_4$
formula weight	705.38	799.36	661.20	957.01
crystal system	triclinic	triclinic	tetragonal	monoclinic
space group	P-1	P-1	$I4_1/acd$	$P2_1/n$
a (Å)	10.1607(5)	10.4186(2)	22.3321(7)	12.360(3)
b (Å)	10.8221(6)	10.7922(2)	22.3321(7)	14.990(3)
c (Å)	15.3532(7)	15.6804(3)	20.3419(11)	14.390(3)
α (°)	79.165(4)	78.741(2)	90	90
β (°)	84.319(4)	83.467(2)	90	105.21(3)
γ (°)	69.715(5)	70.283(2)	90	90
V (Å^3)	1554.26(15)	1625.59(6)	10145.0(11)	2572.8(10)
Z	2	2	16	2
T (K)	123(2)	123(2)	123(2)	100(2)
ρ_{calcd} (g·cm^3)	1.507	1.633	1.732	1.235
μ (mm^{-1})	2.737	2.058	2.618	1.613
F(000)	712	784	5120	1008
reflns collected	21335	23962	19373	41884
unique reflns	5775	6024	2371	4781
R_{int}	0.1191	0.0566	0.0805	0.1204
R1 [I > 2σ(I)]	0.0752	0.0471	0.1005	0.0439
wR2 (all data)	0.1978	0.1320	0.2251	0.1019
largest peak and hole (e·Å^{-3})	1.951, -1.197	3.170, -2.055 (near I1)	1.481, -0.820	1.121, -1.126
CCDC no.	2079974	2079973	2079975	2079980

	12	**13**·(benzene)	**1S**
empirical formula	$C_{37}H_{44}BeN_2$	$C_{61}H_{71}AlBeI_2N_2P_2$	$C_{54}H_{72}BeBr_2N_4O$
formula weight	525.75	1183.92	970.99
crystal system	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$	P-1	$P2_1/n$
a (Å)	12.2007(4)	11.70530(10)	12.230(2)
b (Å)	14.1881(4)	12.26950(10)	15.611(3)
c (Å)	17.9562(5)	20.3965(2)	14.194(3)
α (º)	90	94.4720(10)	90
β (º)	90	98.0260(10)	104.02(3)
γ (º)	90	102.9270(10)	90
V (Å^3)	3108.30(16)	2808.94(5)	2629.2(10)
Z	4	2	2
T (K)	123(2)	123(2)	100(2)
ρ_{calcd} (g·cm^3)	1.123	1.400	1.227
μ (mm^{-1})	0.064	1.232	1.581
F(000)	1136	1208	1020
reflns collected	19406	38111	18752
unique reflns	5749	10407	4844
R_{int}	0.0372	0.0278	0.0254
R1 [I > 2σ(I)]	0.0378	0.0218	0.0354
wR2 (all data)	0.0952	0.0545	0.0930
largest peak and hole (e·Å^{-3})	0.181, -0.193	0.650, -0.416	1.055, -0.519
CCDC no.	2079979	2079977	2079978

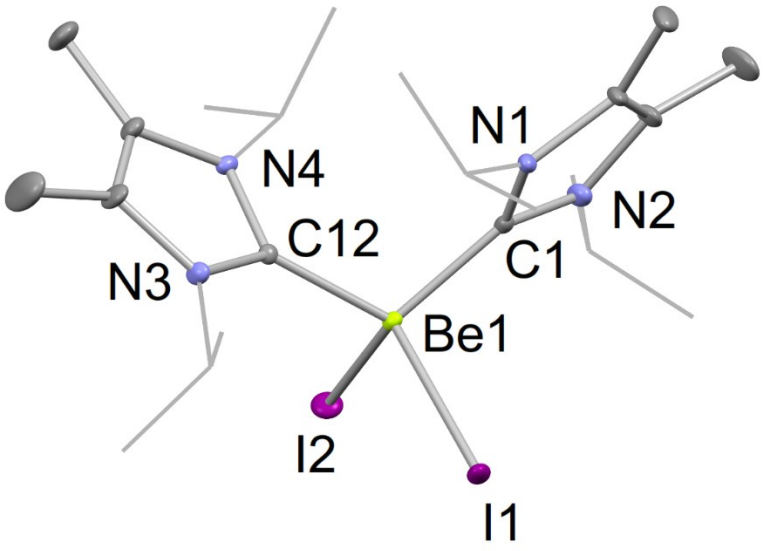


Figure S30. ORTEP diagram of compound **4**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Isopropyl groups displayed as wireframe for clarity. See main text for metrical parameters.

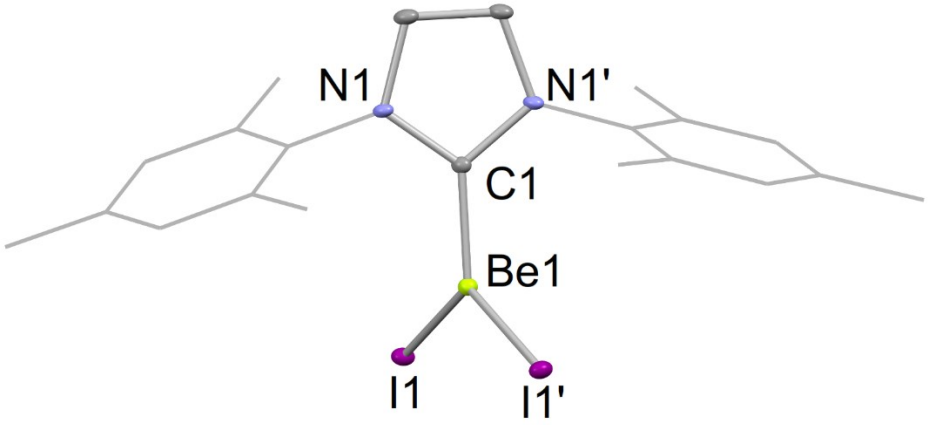


Figure S31. ORTEP diagram of compound **5**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Mes groups displayed as wireframe for clarity. See main text for metrical parameters.

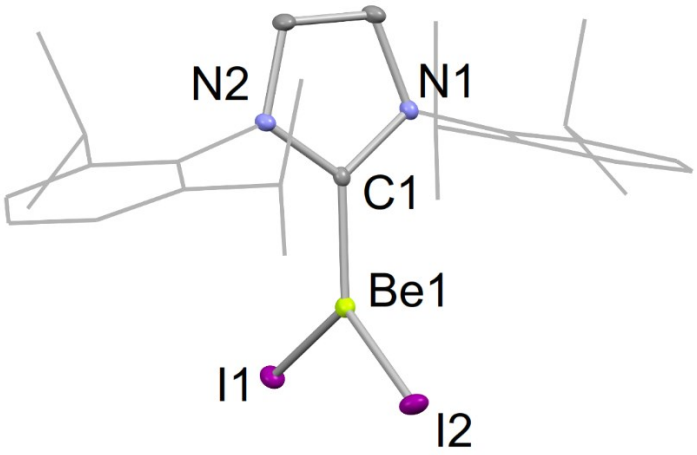


Figure S32. ORTEP diagram of compound **7**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Dip groups displayed as wireframe for clarity. See main text for metrical parameters.

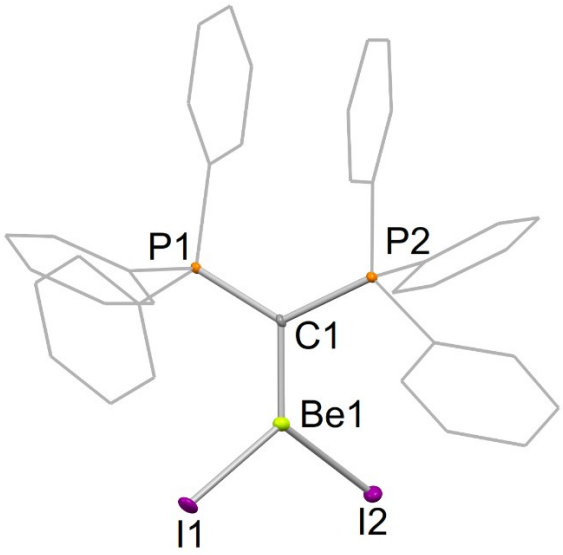


Figure S33. ORTEP diagram of compound **9**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Phenyl groups displayed as wireframe for clarity. See main text for metrical parameters.

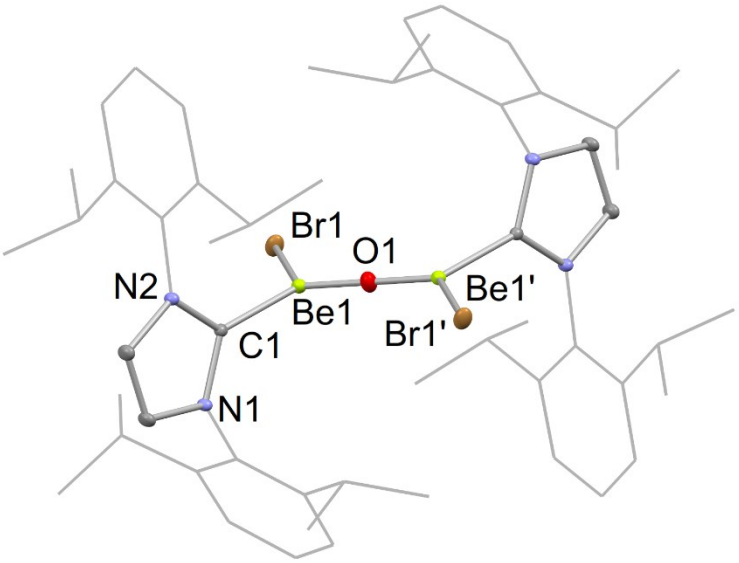


Figure S34. ORTEP diagram of compound [{(IPr)(Br)Be}$_2$(μ-O)] **1S**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms omitted. Dip groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (º): Br(1)-Be(1) 2.133(3), O(1)-Be(1) 1.408(3), C(1)-Be(1) 1.790(3), Be(1)'-O(1)-Be(1) 180.0, O(1)-Be(1)-C(1) 118.83(17), O(1)-Be(1)-Br(1) 126.75(15), C(1)-Be(1)-Br(1) 114.41(15).

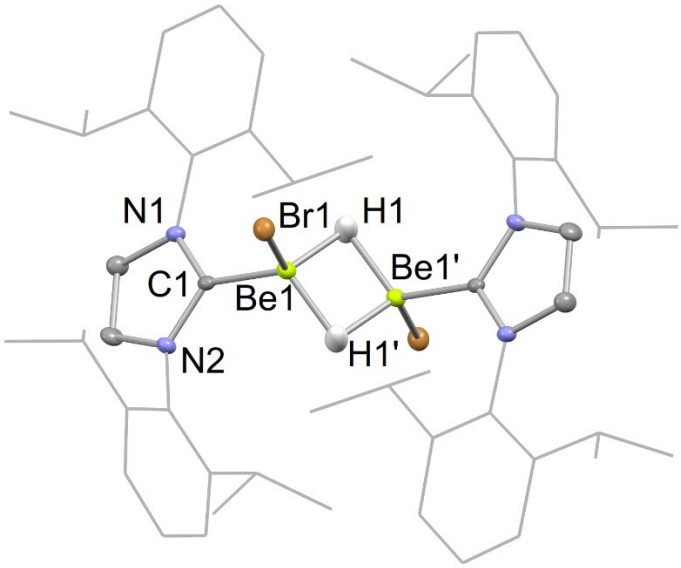
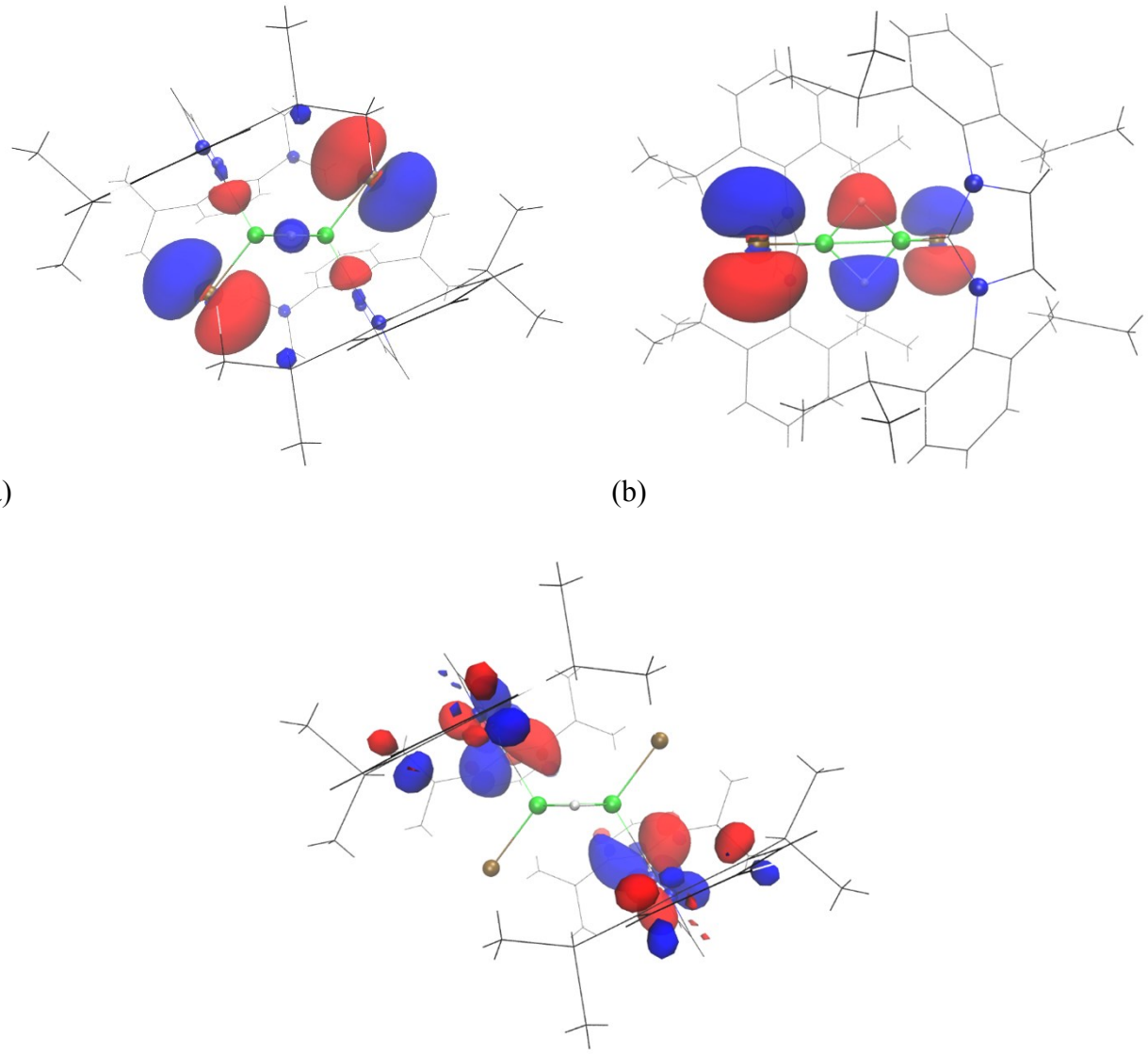


Figure S35. Molecular structure from the neutron diffraction study of **11**. Thermal ellipsoids drawn at the 25 % probability level. Hydrogen atoms, except the hydrides, omitted. Dip groups displayed as wireframe for clarity. Selected bond lengths (Å) and angles (°): C(1)-Be(1) 1.775(8), Be(1)-Br(1) 2.127(8), Be(1)-H(1) 1.480(13), C(1)-Be(1)-Br(1) 115.1(4), C(1)-Be(1)-H(1) 111.3(7), H(1)-Be(1)-Br(1) 114.3(8).

3. Computational Studies

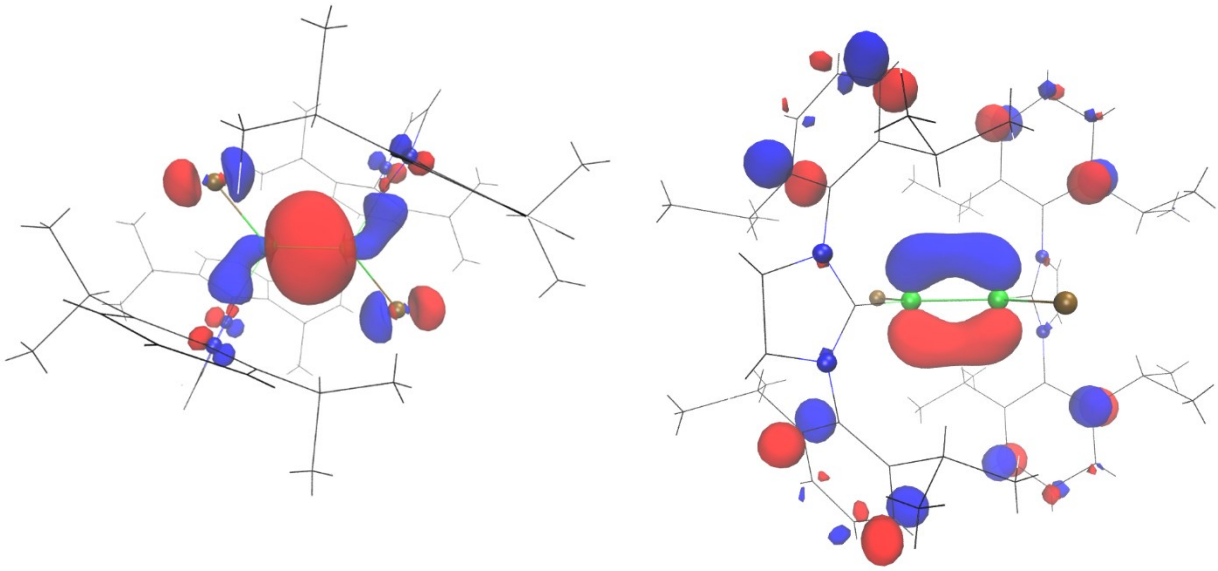
Geometry optimizations were performed using Becke's 3-parameter hybrid functional,[17] combined with the correlation functional provided by Lee, Yang, and Parr.[18] The 6-311+G(d) allelectron basis set was used for all atoms except iodine (where 6-311G(d) was used).[19] Dispersion effects were also considered using the third generation of Grimme's dispersion corrections with the Becke-Johnson damping model.[20] Natural bond order analysis (NBO) was performed using Weinhold's methodology.[21] All calculations were performed with the Gaussian16 suite of programs, with pictorial MO representations produced using VMD.[22]



(a) (b)

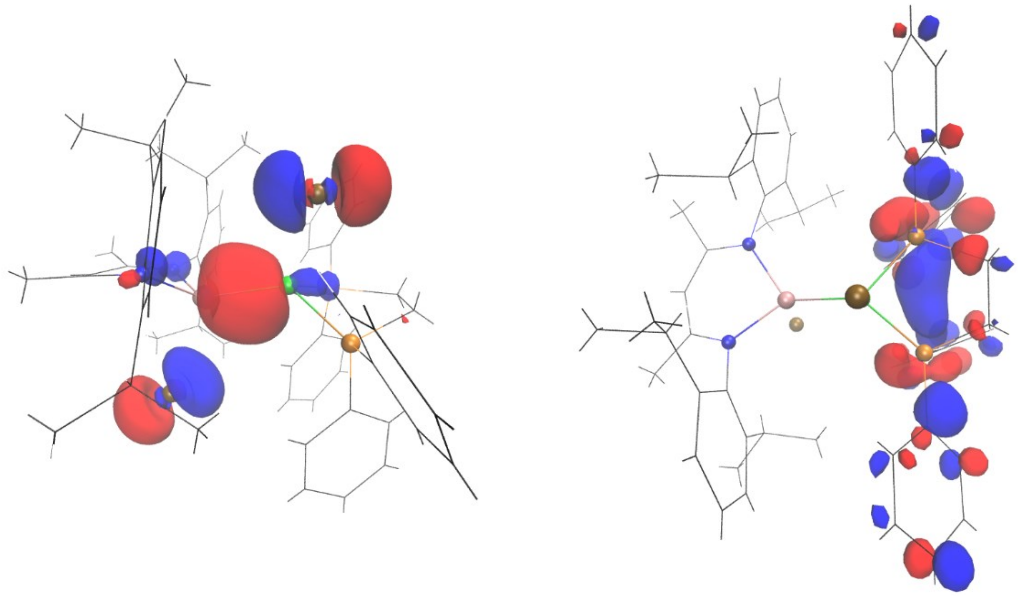
(c)

Figure S36. (a) HOMO-1, (b) HOMO, and (c) LUMO of [{(IPr)(Br)Be(μ-H)}$_2$] **11**.



(a) (b)

Figure S37. (a) HOMO, and (b) LUMO of [{(IPr)(Br)Be}$_2$].



(a) (b)

Figure S38. (a) HOMO, and (b) LUMO of [(DPPE)(I)Be–Al(I)(^{Dip}Nacnac)] **13**.

Table S2. Cartesian coordinates of optimised structures.

[(DPPE)(I)Be–Al(I)(DipNacnac)]
H = -17024.6597255 au

I	0.578037	0.694373	-3.022952
P	-1.695760	-1.562285	-1.544112
P	1.192194	-2.393977	-1.248848
C	1.298862	-3.595291	1.260629
H	1.778153	-2.679673	1.574072
C	-5.249307	0.548314	-3.620379
H	-6.084491	1.040652	-4.107380
C	-1.873982	-2.630998	1.016757
H	-1.063828	-1.956305	1.257967
C	-3.363567	-4.398404	1.694587
H	-3.716767	-5.094571	2.448179
C	0.392875	-5.754726	1.839265
H	0.192796	-6.523015	2.578692
C	3.687538	-3.675612	-1.415320
H	3.163195	-4.569188	-1.096507
C	-5.344618	0.165258	-2.285828
H	-6.248388	0.365888	-1.723026
C	5.052435	-1.374453	-2.187746
H	5.577993	-0.472213	-2.476287
C	-3.101686	-0.734012	-2.366207
C	-4.070365	0.309729	-4.324565
H	-3.977233	0.625724	-5.358100
C	-4.274972	-0.464288	-1.656086
H	-4.357403	-0.737738	-0.612072
C	0.425488	-2.975287	-2.833588
H	0.856855	-2.325760	-3.594397
H	0.734189	-3.996500	-3.064266
C	3.686499	-1.310408	-1.926464
H	3.167676	-0.364419	-2.010090
C	-3.504318	-3.494598	-0.540589
H	-3.971706	-3.483938	-1.519882
C	-0.029603	-5.925409	0.523485
H	-0.561101	-6.825245	0.232855
C	0.885562	-3.760584	-0.065892
C	5.738048	-2.579675	-2.060509
H	6.804096	-2.622915	-2.258567
C	2.994391	-2.466234	-1.551218
C	-3.961272	-4.376848	0.432358
H	-4.781248	-5.050863	0.206782
C	-1.107572	-2.824921	-2.812205
H	-1.597203	-3.768113	-2.570032
H	-1.469177	-2.518039	-3.792363
C	-2.322780	-3.523776	1.985027
H	-1.851345	-3.522834	2.960699
C	1.058912	-4.586736	2.204315
H	1.372215	-4.428406	3.230408
C	0.219355	-4.937131	-0.425253
H	-0.122004	-5.092499	-1.440135
C	5.054604	-3.730186	-1.667726
H	5.585908	-4.669439	-1.554916
C	-2.449218	-2.617448	-0.254056
C	-3.000992	-0.327201	-3.703689
H	-2.081036	-0.477310	-4.253596
Be	0.105328	-0.499485	-0.953065
I	0.519498	-0.507008	3.344451
Al	0.224539	0.808091	0.942559
N	-1.226442	2.025008	1.458195
N	1.639623	2.141327	1.163293
C	-4.192957	-0.905052	2.958202

H	-5.136126	-0.568542	3.398967
H	-3.784020	-1.668275	3.622524
H	-4.413710	-1.384939	2.002829
C	5.097443	1.348902	-0.057898
H	5.940175	0.721839	0.210665
C	3.953019	1.330939	0.744942
C	-2.952299	2.697203	-0.157050
C	-1.619141	4.804000	-0.637783
H	-2.546269	5.381148	-0.567075
H	-0.983400	5.290617	-1.380482
H	-1.103832	4.863798	0.320821
C	-2.098884	3.897579	2.831214
H	-2.380376	4.620027	2.061955
H	-1.774062	4.453678	3.709984
H	-2.998417	3.339787	3.076652
C	2.765031	3.672738	2.743945
H	3.235677	2.984893	3.452687
H	2.511566	4.585967	3.280928
H	3.503236	3.902779	1.978387
C	3.954732	0.459509	1.987339
H	3.036918	0.650070	2.540581
C	3.950002	-1.025164	1.610415
H	3.113166	-1.245567	0.950719
H	3.855333	-1.649163	2.502560
H	4.862804	-1.312798	1.081358
C	1.822459	3.965973	-1.095411
H	0.878979	3.493064	-0.823973
C	4.098009	2.965084	-1.519612
H	4.168578	3.598021	-2.395152
C	-4.309031	2.847118	-0.451533
H	-4.606381	3.441654	-1.306665
C	1.533005	3.008868	2.179267
C	-1.911440	3.352929	-1.051183
H	-0.989572	2.778324	-0.945885
C	-4.902135	1.392790	1.361423
H	-5.666593	0.868926	1.921580
C	2.933943	2.984917	-0.749987
C	1.760122	4.327940	-2.584211
H	2.584882	4.985020	-2.876144
H	0.834956	4.870337	-2.793891
H	1.779498	3.443708	-3.219402
C	0.311234	3.342399	2.773751
H	0.361415	4.060330	3.580491
C	-5.281253	2.237685	0.326927
H	-6.332830	2.384400	0.101308
C	-3.557296	1.208441	1.697386
C	1.957757	5.263694	-0.275774
H	1.805498	5.103592	0.789981
H	1.219435	5.999731	-0.603692
H	2.950541	5.702142	-0.415115
C	-3.184210	0.241450	2.814298
H	-2.225509	-0.203177	2.546887
C	2.858825	2.137627	0.380536
C	-2.985925	0.912109	4.183076
H	-2.120818	1.572068	4.198417
H	-2.810379	0.148016	4.944285
H	-3.873225	1.483687	4.474846
C	-0.978403	3.015519	2.325467
C	-2.299047	3.295181	-2.534016
H	-2.601585	2.291379	-2.830348
H	-1.442070	3.576118	-3.149180
H	-3.115115	3.984316	-2.771478
C	5.173080	2.150860	-1.184831

H	6.069213	2.153741	-1.797799
C	-2.590425	1.941594	0.975390
C	5.134047	0.774699	2.919818
H	6.091936	0.490695	2.474889
H	5.029743	0.219105	3.856099
H	5.188618	1.838550	3.162105

[{(IPr)(Br)Be}$_2$]
H = -7498.95809957 au

Br	1.766177	-0.000432	2.340180
N	2.881529	-1.077193	-1.413322
N	2.881880	1.076205	-1.413788
C	2.312587	-0.000252	-0.805813
C	3.790964	-0.676843	-2.389659
H	4.341814	-1.388631	-2.978801
C	3.791211	0.675147	-2.389946
H	4.342321	1.386514	-2.979352
C	2.726637	-2.443381	-0.966807
C	1.729755	-3.244994	-1.545156
C	1.650317	-4.573990	-1.119876
H	0.885799	-5.219531	-1.532271
C	2.528696	-5.077227	-0.168788
H	2.448749	-6.112901	0.145913
C	3.494168	-4.255714	0.398351
H	4.156138	-4.655135	1.157066
C	3.609047	-2.916458	0.020186
C	0.792104	-2.707179	-2.611573
H	0.640749	-1.643326	-2.420166
C	1.413794	-2.851121	-4.011256
H	2.368053	-2.326740	-4.092564
H	0.740961	-2.434334	-4.765539
H	1.587386	-3.903924	-4.255143
C	-0.589393	-3.365381	-2.574294
H	-0.554700	-4.414749	-2.882599
H	-1.261174	-2.842502	-3.255277
H	-1.030176	-3.316874	-1.578606
C	4.672663	-2.028565	0.644879
H	4.354981	-0.994392	0.514910
C	6.023013	-2.204676	-0.069743
H	6.389185	-3.230060	0.037424
H	6.773429	-1.533220	0.357745
H	5.949814	-1.986630	-1.137087
C	4.825589	-2.251703	2.153969
H	3.865665	-2.162502	2.662134
H	5.494907	-1.495439	2.572783
H	5.258221	-3.229488	2.383969
C	2.727785	2.442545	-0.967481
C	3.611676	2.915689	0.018109
C	3.497311	4.254932	0.396497
H	4.160461	4.654382	1.154180
C	2.531001	5.076408	-0.169247
H	2.451452	6.112072	0.145584
C	1.651396	4.573194	-1.119238
H	0.886406	5.218780	-1.530686
C	1.730237	3.244202	-1.544623
C	4.676746	2.028119	0.640753
H	4.360977	0.993668	0.508372
C	6.026622	2.208156	-0.073791
H	5.953402	1.992565	-1.141656
H	6.778277	1.536923	0.351861
H	6.391151	3.233882	0.035646
C	4.829406	2.248254	2.150320
H	5.259491	3.226666	2.382388

H	5.500838	1.492855	2.567342
C	0.791465	2.706421	-2.610057
H	0.639696	1.642741	-2.418053
C	1.412275	2.849301	-4.010235
H	1.586164	3.901888	-4.254848
H	0.738759	2.432352	-4.763817
H	2.366261	2.324453	-4.091856
C	-0.589648	3.365349	-2.572114
H	-1.029823	3.317350	-1.576131
H	-1.262115	2.842619	-3.252527
H	-0.554624	4.414611	-2.880731
Be	1.003232	-0.000088	0.352726
Br	-1.766043	-0.000273	-2.340007
N	-2.881581	1.077111	1.413591
N	-2.881925	-1.076282	1.413352
C	-2.312527	0.000381	0.805831
C	-3.791185	0.676442	2.389646
H	-4.342119	1.388052	2.978926
C	-3.791386	-0.675546	2.389521
H	-4.342567	-1.387105	2.978624
C	-2.726996	2.443408	0.967326
C	-1.729465	3.244828	1.544838
C	-1.650337	4.573877	1.119696
H	-0.885358	5.219285	1.531442
C	-2.529643	5.077379	0.169582
H	-2.449895	6.113099	-0.145016
C	-3.495853	4.256106	-0.396621
H	-4.158702	4.655753	-1.154463
C	-3.610473	2.916799	-0.018527
C	-0.790971	2.706714	2.610351
H	-0.639377	1.643033	2.418203
C	-1.411941	2.849499	4.010470
H	-2.365985	2.324741	4.091918
H	-0.738557	2.432387	4.764078
H	-1.585735	3.902078	4.255183
C	0.590278	3.365392	2.572712
H	0.555397	4.414599	2.881536
H	1.262566	2.842405	3.253105
H	1.030586	3.317517	1.576775
C	-4.675212	2.029351	-0.641921
H	-4.359176	0.994909	-0.510112
C	-6.025345	2.208624	0.072311
H	-6.390063	3.234343	-0.036579
H	-6.776715	1.537513	-0.354034
H	-5.952443	1.992333	1.140051
C	-4.827515	2.250318	-2.151408
H	-3.867711	2.158243	-2.659283
H	-5.498432	1.494829	-2.569084
H	-5.257998	3.228663	-2.383031
C	-2.727447	-2.442534	0.966887
C	-3.610242	-2.915468	-0.019823
C	-3.495607	-4.254705	-0.398123
H	-4.157861	-4.654018	-1.156648
C	-2.530040	-5.076349	0.168671
H	-2.450285	-6.112006	-0.146136
C	-1.651377	-4.573287	1.119590
H	-0.886854	-5.218957	1.531775
C	-1.730546	-3.244305	1.544966
C	-4.674141	-2.027520	-0.643952
H	-4.356822	-0.993312	-0.513364
C	-6.024368	-2.204502	0.070698
H	-5.951115	-1.987122	1.138180
H	-6.775045	-1.533011	-0.356277

H	-6.390228	-3.229934	-0.037067
C	-4.827120	-2.249862	-2.153154
H	-5.259256	-3.227744	-2.383658
H	-5.496914	-1.493728	-2.571455
H	-3.867302	-2.159863	-2.661373
C	-0.792684	-2.706671	2.611292
H	-0.640947	-1.642900	2.419730
C	-1.414458	-2.850170	4.010979
H	-1.588376	-3.902876	4.255053
H	-0.741532	-2.433440	4.765212
H	-2.368571	-2.325490	4.092149
C	0.588577	-3.365356	2.574122
H	1.029401	-3.317078	1.578444
H	1.260508	-2.842645	3.255086
H	0.553523	-4.414683	2.882515
Be	-1.003012	0.000117	-0.352546
H	3.869799	2.155426	2.658425

[{(IPr)(Br)Be(μ-H)}$_2$]

H = -7500.23253264 au

Br	-1.667488	0.000508	-2.338542
N	-2.883881	1.075387	1.410214
N	-2.884012	-1.075266	1.410376
C	-2.272100	-0.000042	0.850609
C	-3.544293	-2.915995	-0.051018
C	-2.704562	2.443876	0.972553
C	-1.725891	3.239885	1.586260
C	-3.399192	-4.250374	-0.436648
H	-4.025153	-4.648851	-1.225706
C	-4.593829	-2.036575	-0.711283
H	-4.295239	-0.998817	-0.563658
C	-2.705138	-2.443818	0.972746
C	-3.857761	0.677007	2.319331
H	-4.448339	1.389012	2.868051
C	-0.841196	2.704476	2.697251
H	-0.679314	1.640932	2.517485
C	-3.857861	-0.676638	2.319425
H	-4.448560	-1.388505	2.868197
C	-3.542901	2.916083	-0.051897
C	-1.614521	-4.563085	1.151067
H	-0.859802	-5.204017	1.587761
C	-1.726129	-3.239927	1.585808
C	-4.591871	2.036618	-0.712998
H	-4.292270	0.998955	-0.566735
C	-2.446558	-5.066050	0.159081
H	-2.340658	-6.096922	-0.163667
C	-5.969595	-2.235363	-0.052841
H	-6.317383	-3.264351	-0.183454
H	-6.710796	-1.570049	-0.505291
H	-5.943984	-2.026705	1.018490
C	-0.840708	-2.704591	2.696248
H	-0.678837	-1.641070	2.516369
C	-4.687063	-2.252854	-2.226414
H	-5.104930	-3.232080	-2.476708
H	-3.709216	-2.155011	-2.696703
H	-5.344981	-1.498695	-2.666578
C	-3.397327	4.250410	-0.437477
H	-4.022585	4.648918	-1.227070
C	-1.613816	4.563029	1.151559
H	-0.859310	5.203875	1.588745
C	-1.533201	2.851500	4.063465
H	-0.901120	2.435056	4.852496
H	-2.491701	2.328995	4.096209

H	-1.717639	3.904818	4.296689
C	-2.445054	5.066026	0.158945
H	-2.338799	6.096862	-0.163802
C	0.541741	3.359697	2.726344
H	1.029260	3.306780	1.753045
H	1.177634	2.835270	3.440178
H	0.494511	4.409360	3.032658
C	0.542178	-3.359946	2.724528
H	0.495020	-4.409650	3.030712
H	1.178512	-2.835695	3.438094
H	1.029190	-3.306929	1.750983
C	-5.967738	2.233467	-0.054180
H	-6.316325	3.262349	-0.183525
H	-5.941964	2.023482	1.016871
H	-6.708438	1.568139	-0.507435
C	-4.685661	2.254585	-2.227849
H	-5.104865	3.233559	-2.476913
H	-5.342682	1.500087	-2.668757
H	-3.707789	2.158558	-2.698460
C	-1.531980	-2.851465	4.062847
H	-2.490414	-2.328858	4.096054
H	-0.899427	-2.435021	4.851498
H	-1.716401	-3.904748	4.296245
Be	-0.958649	0.000069	-0.317507
Be	0.958970	0.000013	0.317966
Br	1.667882	0.000185	2.338957
C	2.272185	-0.000085	-0.850420
N	2.883888	1.075287	-1.410159
N	2.883848	-1.075372	-1.410374
C	2.704715	2.443804	-0.972529
C	3.857478	0.676855	-2.319572
C	2.704866	-2.443944	-0.972841
C	3.857470	-0.676795	-2.319682
C	1.726155	3.239926	-1.586281
C	3.543056	2.915909	0.051968
H	4.448028	1.388834	-2.868350
C	3.543916	-2.916246	0.050968
C	1.725885	-3.239955	-1.586057
H	4.447978	-1.388702	-2.868606
C	0.841399	2.704625	-2.697276
C	1.614200	4.563073	-1.151570
C	4.591952	2.036331	0.713072
C	3.397575	4.250243	0.437581
C	3.398679	-4.250627	0.436506
C	4.593452	-2.036924	0.711359
C	1.614168	-4.563154	-1.151429
C	0.840577	-2.704520	-2.696545
H	0.679571	1.641052	-2.517620
C	1.533240	2.851871	-4.063541
C	-0.541558	3.359828	-2.726110
H	0.859785	5.204006	-1.588794
C	2.445422	5.065962	-0.158888
H	4.292145	0.998703	0.566966
C	5.967763	2.232834	0.054024
C	4.685959	2.254441	2.227875
H	4.022801	4.648681	1.227231
H	4.024505	-4.649194	1.225627
C	2.446063	-5.066220	-0.159390
H	4.294675	-0.999153	0.564188
C	5.969125	-2.235275	0.052578
C	4.687038	-2.253776	2.226382
H	0.859470	-5.204021	-1.588257
H	0.678934	-1.640950	-2.516752

C	-0.542457	-3.359568	-2.724745
C	1.531803	-2.851661	-4.063133
H	0.901062	2.435536	-4.852550
H	2.491750	2.329402	-4.096501
H	1.717612	3.905232	-4.296624
H	-1.028931	3.306798	-1.752749
H	-1.177564	2.835467	-3.439896
H	-0.494375	4.409524	-3.032324
H	2.339249	6.096802	0.163873
H	6.316571	3.261673	0.183100
H	5.941766	2.022625	-1.016976
H	6.708410	1.567455	0.507292
H	5.105426	3.233337	2.476791
H	5.342828	1.499827	2.668808
H	3.708116	2.158697	2.698585
H	2.340084	-6.097107	0.163285
H	6.317063	-3.264273	0.182722
H	6.710325	-1.570045	0.505153
H	5.943296	-2.026198	-1.018664
H	5.105191	-3.233005	2.476196
H	3.709260	-2.156365	2.696904
H	5.344869	-1.499642	2.666717
H	-0.495551	-4.409292	-3.030891
H	-1.178698	-2.835187	-3.438296
H	-1.029401	-3.306414	-1.751176
H	2.490353	-2.329267	-4.096376
H	0.899341	-2.435134	-4.851812
H	1.715998	-3.904999	-4.296468
H	0.000194	1.062785	0.000287
H	0.000100	-1.062694	0.000222

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