Supplementary Information for

Alkali Metal Reduction of Crown Ether Encapsulated Alkali Metal Cations

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Synthetic Details

General Considerations

CAUTION: Beryllium and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, breathing apparatus, and a well-ventilated fume cupboard) should be taken for all manipulations involving these species.

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of argon. NMR experiments were conducted in J-Young tap NMR tubes prepared in a glovebox. NMR spectra were recorded on a Bruker BioSpin GmbH spectrometer operating at 400.13 MHz (^{1}H), 61.42 MHz (^{2}H), 100.62 MHz (^{13}C) and 56.2 MHz (^{9}Be) or on an Agilent ProPulse spectrometer operating at 194.3 MHz (^{7}Li). Elemental analyses were performed at Elemental Microanalysis Ltd., Okehampton, Devon, UK. Solvents were dried by passage through a commercially available solvent purification system and stored under argon in ampoules over 4 Å molecular sieves. C_6D_6, and C_6D_8 were purchased from Merck, dried over potassium before distilling and storage over molecular sieves. $\{CH_2SiMe_2N(H)Dipp\}_2$,[1] $[\{CH_2SiMe_2NDipp\}_2BeClLi]$,[2] and Na/NaCl were synthesised according to literature procedures.[3] Crown ethers: 12-cr-4, 15-cr-5 and 18-cr-6 were purchased from Merck and used without further purification.

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (1)

12-cr-4 (2.45 µl, 0.032 mmol) was added to a benzene solution (0.6 cm^3) of $[\{CH_2SiMe_2NDipp\}_2BeClLi]_2$ (**V^{Li}**) (10.2 mg, 0.018 mmol). the solution was then concentrated to afford **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$]** (**1**) as a colourless solid. Yield: 14.5 mg, 94%.

^{1}H NMR (C_6D_6): δ = 7.19-7.17 (*o*-Ar-H, 4H), 7.00 (br t, *p*-Ar-H, $^{3}J_{HH}$ = 7.50 Hz, 2H), 4.54 (sept, C<u>H</u>(CH$_3$)$_2$, $^{3}J_{HH}$ = 6.99 Hz, 4H), 3.13 (s, OCH$_2$CH$_2$O, 28H), 1.62 (d, CH(C<u>H</u>$_3$)$_2$, $^{3}J_{HH}$ = 6.94 Hz, 12H), 1.58 (d, CH(C<u>H</u>$_3$)$_2$, $^{3}J_{HH}$ = 6.94 Hz, 12H), 1.44 (s, SiCH$_2$, 4H), 0.48 (s, SiCH$_3$, 12H).

^{13}C{^{1}H} NMR (C_6D_6): δ = 154.0 (*i*-C_6H_3), 146.4 (*o*-C_6H_3), 122.3 (*m*-C_6H_3), 120.3 (*p*-C_6H_3), 67.7 (O<u>C</u>H$_2$<u>C</u>H$_2$O), 28.0 (<u>C</u>H(CH$_3$)$_2$), 26.0 (CH(<u>C</u>H$_3$)$_2$), 25.1 (CH(<u>C</u>H$_3$)$_2$), 15.6 (SiCH$_2$), 1.4 (SiCH$_3$).

^{9}Be NMR (C_6D_6) δ = 9.7 (br s, $\omega_{1/2}$ = 282 Hz).

Anal. Calc. for $Be_1Cl_1Li_1O_7Si_2N_2C_{44}H_{78}$: C, 61.83; H, 9.20; N, 3.28. Found: C, 62.05; H, 9.07; N, 3.29.

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Na(15-cr-5)$_2$] (2)

15-cr-5 (7.39 µl, 0.037 mmol) was added to a benzene solution (0.6 cm^3) of [{CH$_2$SiMe$_2$NDipp}$_2$BeClNa]$_2$ (**V^{Li}**) (10.5 mg, 0.018 mmol). The solution was then concentrated to afford **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Na(12-c-5)$_2$]** (**2**) as a colourless solid. Yield: 16.5 mg, 88%. Unable to remove [{CH$_2$SiMe$_2$NDipp}H]$_2$ impurity carried through from **[{CH$_2$SiMe$_2$NDipp}$_2$BeClNa]$_2$** (**V^{Na}**).

^{1}H NMR (C$_6$D$_6$): δ = 7.15-7.07 (*o*-Ar-H, 4H), 7.00 (br t, *p*-Ar-H, $^3J_{HH}$ = 7.31 Hz, 2H), 4.43 (sept, C<u>H</u>(CH$_3$)$_2$, $^3J_{HH}$ = 7.00 Hz, 4H), 3.4 (s, OC<u>H$_2$C</u>H$_2$O, 28H), 1.59 (d, CH(C<u>H$_3$</u>)$_2$, $^3J_{HH}$ = 7.04 Hz, 12H), 1.47 (d, CH(C<u>H$_3$</u>)$_2$, $^3J_{HH}$ = 6.81 Hz, 12H), 1.41 (s, SiCH$_2$, 4H), 0.49 (s, SiCH$_3$, 12H).

^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 153.8 (*i*-C$_6$H$_3$), 146.2 (*m*-C$_6$H$_3$), 122.2 (*o*-C$_6$H$_3$), 120.2 (*p*-C$_6$H$_3$), 70.6 (O<u>C</u>H$_2$<u>C</u>H$_2$O), 28.0 (<u>C</u>H(CH$_3$)$_2$), 25.5 (CH(<u>C</u>H$_3$)$_2$), 25.1 (CH(<u>C</u>H$_3$)$_2$), 15.4 (SiCH$_2$), 1.4 (SiCH$_3$)

^{9}Be NMR (C$_6$D$_6$) δ = 10.4 (br s, $\omega_{1/2}$ = 184 Hz).

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][K(18-cr-6]$_{1.5}$ (3)

[{CH$_2$SiMe$_2$NDipp}$_2$BeClK]$_2$ (**V^{K}**) (8.1 mg, 0.014 mmol) and 18-cr-6 (5.55 mg, 0.021 mmol) were introduced into a Young's NMR tube and dissolved in benzene (0.6 cm^3). The solution was then concentrated to afford **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**) as a colourless solid. Yield: 13 mg, 95%.

^{1}H NMR (C$_6$D$_6$): δ = 7.09 (d, *o*-Ar-H, $^3J_{HH}$ = 7.31 Hz, 4H), 6.90 (t, *p*-Ar-H, $^3J_{HH}$ = 7.47 Hz, 2H), 4.40 (sept, C<u>H</u>(CH$_3$)$_2$, $^3J_{HH}$ = 6.91 Hz, 4H), 3.10 (s, OC<u>H$_2$C</u>H$_2$O, 36H), 1.60 (d, CH(C<u>H$_3$</u>)$_2$, $^3J_{HH}$ = 6.36 Hz, 12H), 1.42 (overlapping and s, CH(C<u>H$_3$</u>)$_2$ and SiCH$_2$, respectively, 16H), 0.50 (s, SiCH$_3$, 12H).

^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 152.7 (*i*-C$_6$H$_3$), 144.9 (*m*-C$_6$H$_3$), 120.9 (*o*-C$_6$H$_3$), 118.8 (*p*-C$_6$H$_3$), 69.0 (O<u>C</u>H$_2$<u>C</u>H$_2$O), 26.8 (<u>C</u>H(CH$_3$)$_2$), 24.4 (CH(<u>C</u>H$_3$)$_2$), 24.0 (CH(<u>C</u>H$_3$)$_2$), 14.2 (SiCH$_2$), 0.2 (SiCH$_3$).

^{9}Be NMR (C$_6$D$_6$) δ = 10.5 (br s, $\omega_{1/2}$ = 201 Hz).

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Rb(18-cr-6)] (4)

First [{CH$_2$SiMe$_2$NDipp}$_2$BeClRb]$_2$ (**V^{Rb}**) was generated *in-situ* from [{CH$_2$SiMe$_2$NDipp}$_2$BeClLi]$_2$ (**V^{Li}**) (20 mg, 0.035 mmol) and Rb metal in d$_8$-toluene (0.6 cm^3). This solution was then filtered into a Young's NMR tube containing 18-cr-6 (9.36 mg, 0.035 mmol) in C$_6$D$_6$. The solution was concentrated, affording **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**) as a colourless solid. Yield: 19 mg, 61%.

^{1}H NMR (C_6D_8): δ = 7.10 (d, *o*-Ar-H, $^{3}J_{HH}$ = 7.52 Hz 4H), 6.92 (t, *p*-Ar-H, $^{3}J_{HH}$ = 7.52 Hz, 2H), 4.39 (sept, C<u>H</u>$(CH_3)_2$, $^{3}J_{HH}$ = 6.98 Hz, 4H), 3.06 (s, OC<u>H</u>$_2$C<u>H</u>$_2$O, 24H), 1.55 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 7.05 Hz, 12H), 1.45 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 6.99 Hz, 12H), 1.35 (s, $SiCH_2$, 4H), 0.41 (s, $SiCH_3$, 12H).

^{13}C{^{1}H} NMR (C_6D_8): δ = 154.0 (*i*-C_6H_3), 146.4 (*m*-C_6H_3), 122.0 (*o*-C_6H_3), 120.3 (*p*-C_6H_3), 69.7 (O<u>C</u>H$_2$<u>C</u>H$_2$O), 27.9 (<u>C</u>H$(CH_3)_2$), 25.6 (CH(<u>C</u>H$_3)_2$), 25.0 (CH(<u>C</u>H$_3)_2$), 15.3 ($SiCH_2$), 1.2 ($SiCH_3$).

^{9}Be NMR (C_6D_6) δ = 11.2 (br s, $\omega_{1/2}$ = 259 Hz).

Anal. Calc. for $Be_1Cl_1Rb_1O_6Si_2N_2C_{42}H_{74}$: C, 57.67; H, 8.07; N, 4.48. Found: C, 58.78; H, 8.62; N, 4.2**.**

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (5)

5 wt% Na/NaCl (0.26 g) was added to a benzene solution of [{$CH_2SiMe_2NDipp\}_2BeCl$][Li(12-cr-4)$_{1.75}$)] (**1**) (15.4 mg, 0.018 mmol). After sonicating for 15 minutes colourless crystals started to form. The suspension was agitated, filtered and concentrated, affording **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (5**) as a colourless solid. Yield: 9.2 mg, 62%. ^{13}C{^{1}H}, ^{9}Be and 2-dimensional spectroscopic data were not obtained due to the difficulty retaining **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Na(12-cr-4)$_2$]** (**5**) in solution as the product crystallises within the NMR tube. This compound can also be prepared by treating [{$CH_2SiMe_2NDipp\}_2BeCl$][Li(12-cr-4)$_{1.75}$)] (**1**) with metallic sodium.

^{1}H NMR (C_6D_6): δ = 7.19-7.17 (*o*-Ar-H, shoulders solvent peak, 4H), 6.99 (t, *p*-Ar-H, $^{3}J_{HH}$ = 7.43 Hz, 2H), 4.54 (sept, C<u>H</u>$(CH_3)_2$, $^{3}J_{HH}$ = 6.73 Hz, 4H), 3.36 (s, OC<u>H</u>$_2$C<u>H</u>$_2$O, 32H), 1.62 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 6.95 Hz, 12H), 1.57 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 6.95 Hz, 12H), 1.44 (s, $SiCH_2$, 4H), 0.48 (s, $SiCH_3$, 12H).

Anal. Calc. for $Be_1Cl_1Na_1O_8Si_2N_2C_{46}H_{82}$: C, 60.40; H, 9.04; N, 3.06. Found: C, 60.20; H, 8.29; N, 3.75.

Synthesis of [{CH$_2$SiMe$_2$NDipp}$_2$BeCl][K(12-cr-4)$_2$] (6)

First [{$CH_2SiMe_2NDipp\}_2BeCl]_2$[Li(12-cr-4)$_{1.75}$] (**1**) was generated *in-situ* from [{$CH_2SiMe_2NDipp\}_2BeClLi]_2$ (**V^{Li}**) (20 mg, 0.035 mmol) and 12-cr-4 in benzene (0.6 cm^3). The solution was then filtered into a Young's NMR tube containing KC_8 (23.96 mg, 0.18 mmol), and concentrated, affording **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][K(12-cr-4)$_2$]** (**6**) as a colourless solid. Yield: 18.2 mg, 56%.

^{1}H NMR (C_6D_6): δ = 7.14-7.10 (m, *o*-Ar-H, 4H), 6.97 (t, *p*-Ar-H, $^{3}J_{HH}$ = 7.61 Hz, 2H), 4.39 (sept, C<u>H</u>$(CH_3)_2$, $^{3}J_{HH}$ = 6.86 Hz, 4H), 3.28 (s, OC<u>H</u>$_2$C<u>H</u>$_2$O, 32H), 1.56 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 6.97 Hz, 12H), 1.49 (d, CH(C<u>H</u>$_3)_2$, $^{3}J_{HH}$ = 6.76 Hz, 12H), 1.39 (s, $SiCH_2$, 4H), 0.42 (s, $SiCH_3$, 12H).

$^{13}C\{^{1}H\}$ NMR (C_6D_6): δ = 154.2 (*i*-C_6H_3), 146.8 (*m*-C_6H_3), 122.4 (*o*-C_6H_3), 120.6 (*p*-C_6H_3), 69.3 (O<u>C</u>H$_2$<u>C</u>H$_2$O), 27.9 (<u>C</u>H(CH$_3$)$_2$), 25.7 (CH(<u>C</u>H$_3$)$_2$), 24.8 (CH(<u>C</u>H$_3$)$_2$), 15.4 ($SiCH_2$), 1.3 ($SiCH_3$).

^{9}Be NMR (C_6D_6) δ = 7.9 (br s, $\omega_{1/2}$ = 232 Hz).

This compound can also be prepared by treating [{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$)] (**6**) with metallic potassium.

Sequential Reduction Reaction from [{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_2$] (1) to (2) and attempted reaction of (2) with K.

A C_6D_6 solution of [{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (**1**, 5 mg, 0.006 mmol) was added to a J-Young's tube containing 5 % Na/NaCl (100 mg). The solution was sonicated for 5 minutes and filtered into a fresh J-Young's tube and analysed by ^{1}H NMR spectrosocopy, confirming the formation of [{CH_2SiMe_2NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (**2**). The solution was then introduced into an ampoule and vigorously stirred over a pre-formed K mirror for 8 hours before being filtered into a fresh J-Young's NMR tube. Analysis by ^{1}H NMR spectroscopy confirmed the retention of [{CH_2SiMe_2NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (**2)** as well as some decomposition as the only reaction outcome.

NMR Spectra

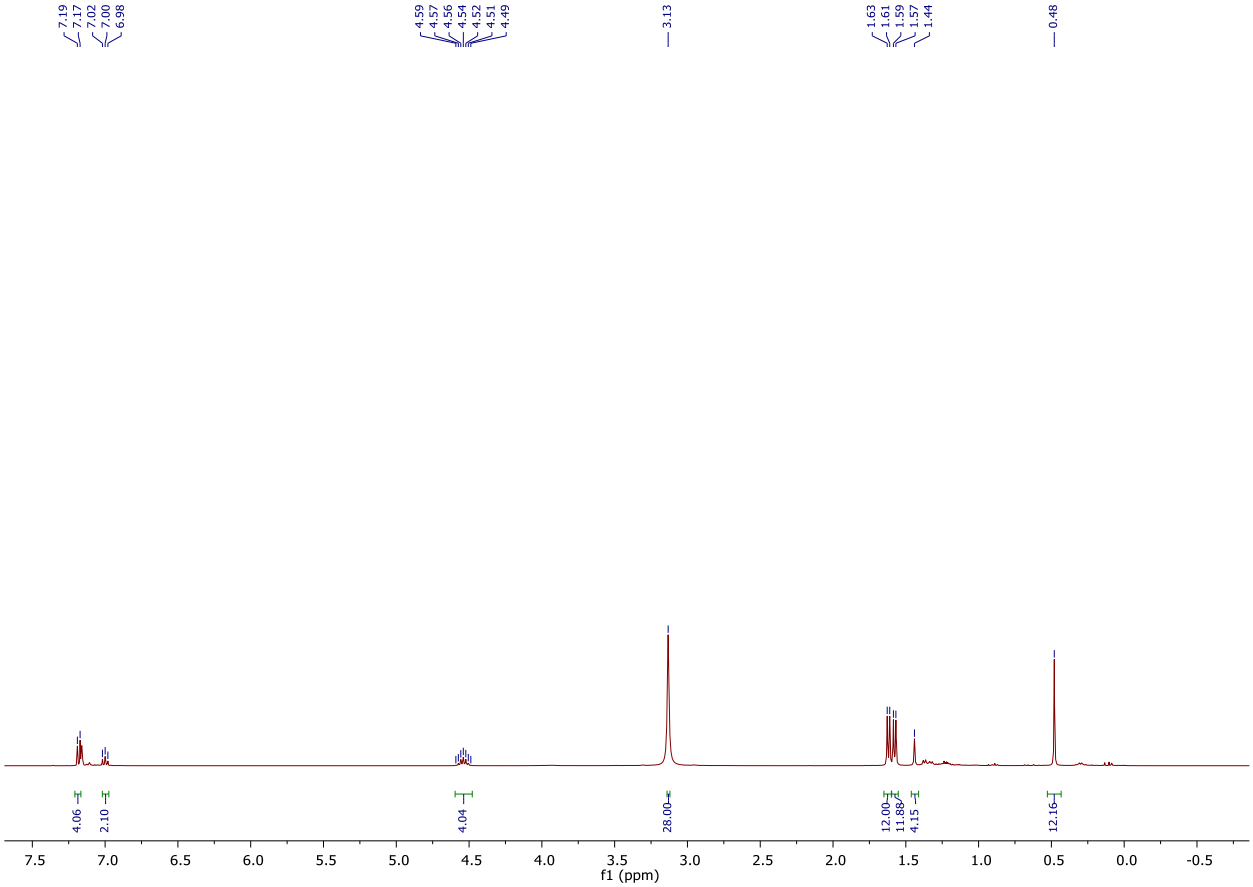

Figure S1. ^{1}H NMR Spectrum (C_6D_6, 298 K, 400.13 MHz) for **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (1).**

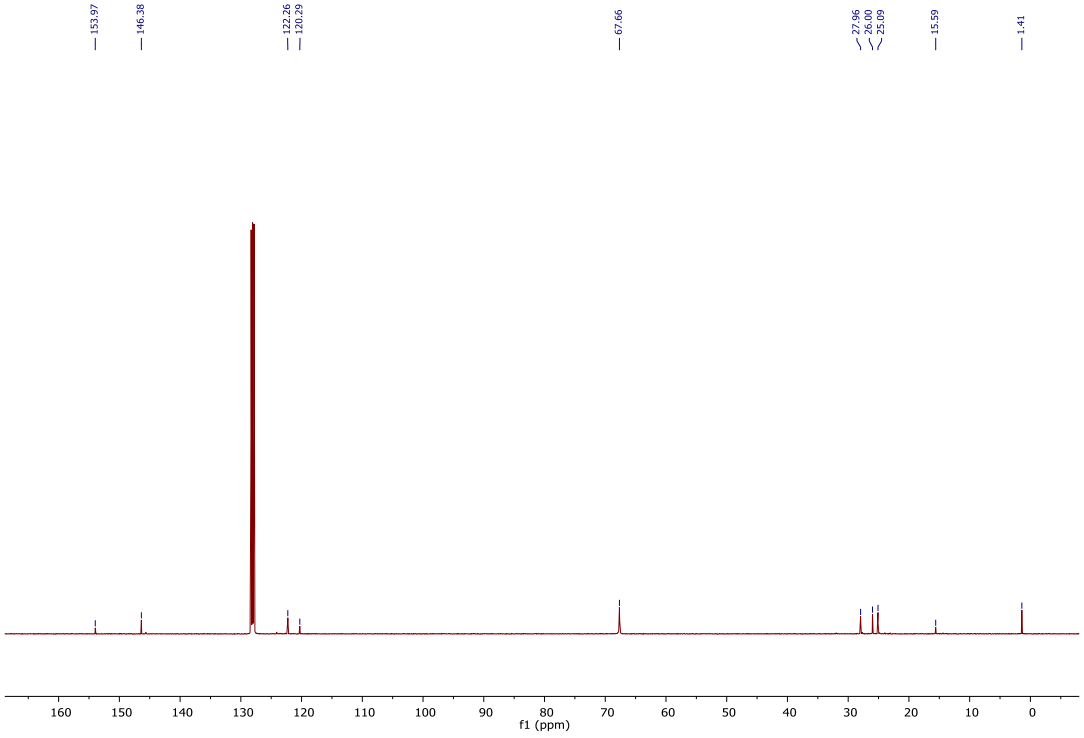

Figure S2. ^{13}C{^{1}H} NMR Spectrum (C_6D_6, 298 K, 100.62 MHz) for **[{CH$_2$SiMe$_2$NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (1).**

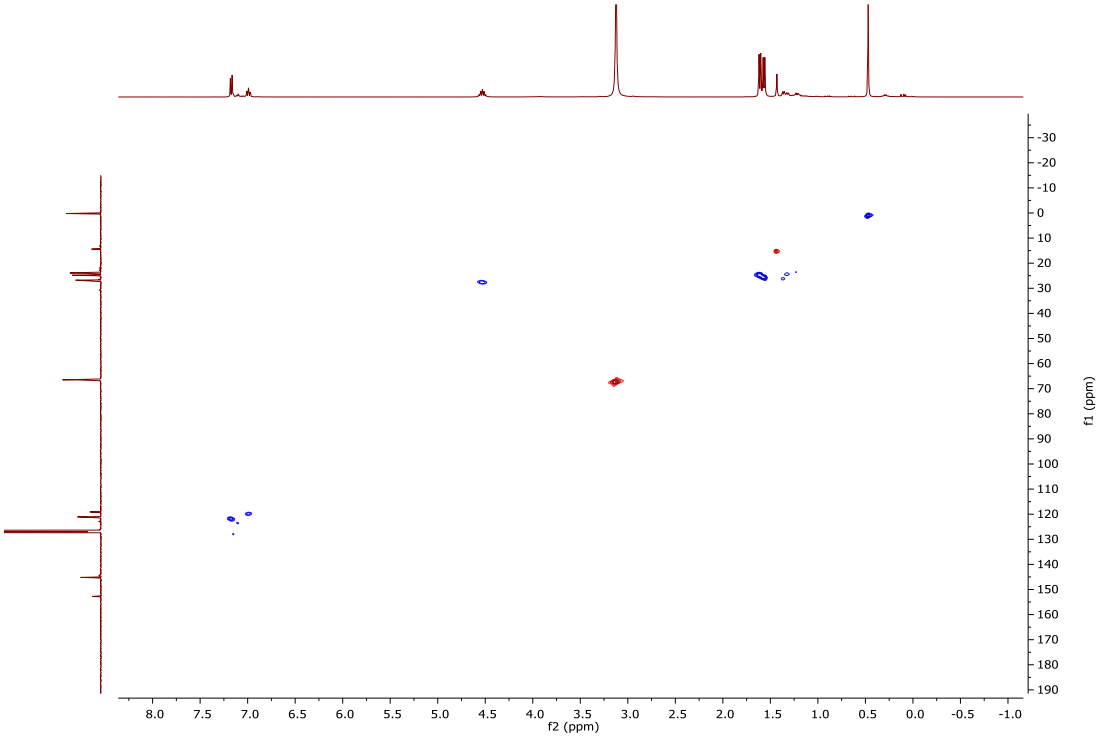

Figure S3. ^{1}H-^{13}C HSQC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (1).**

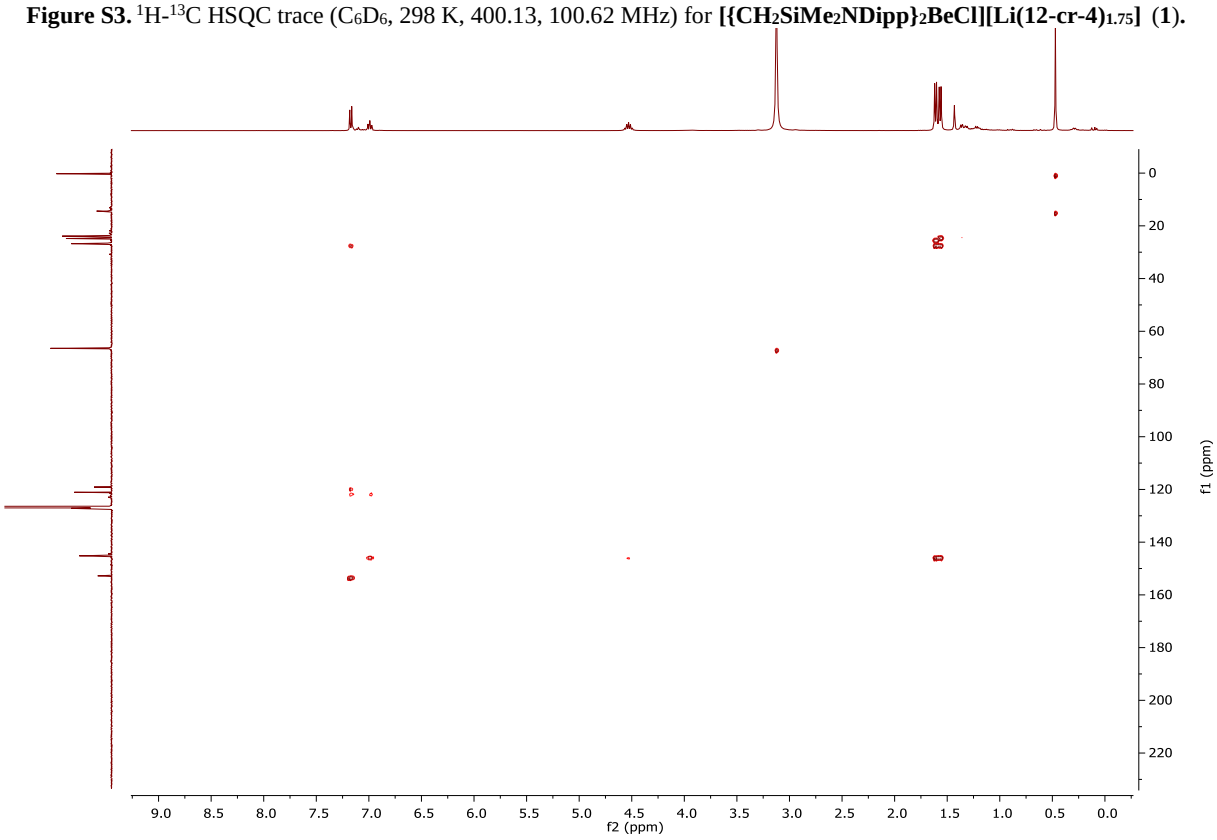

Figure S4. ^{1}H-^{13}C HMBC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$] (1).**

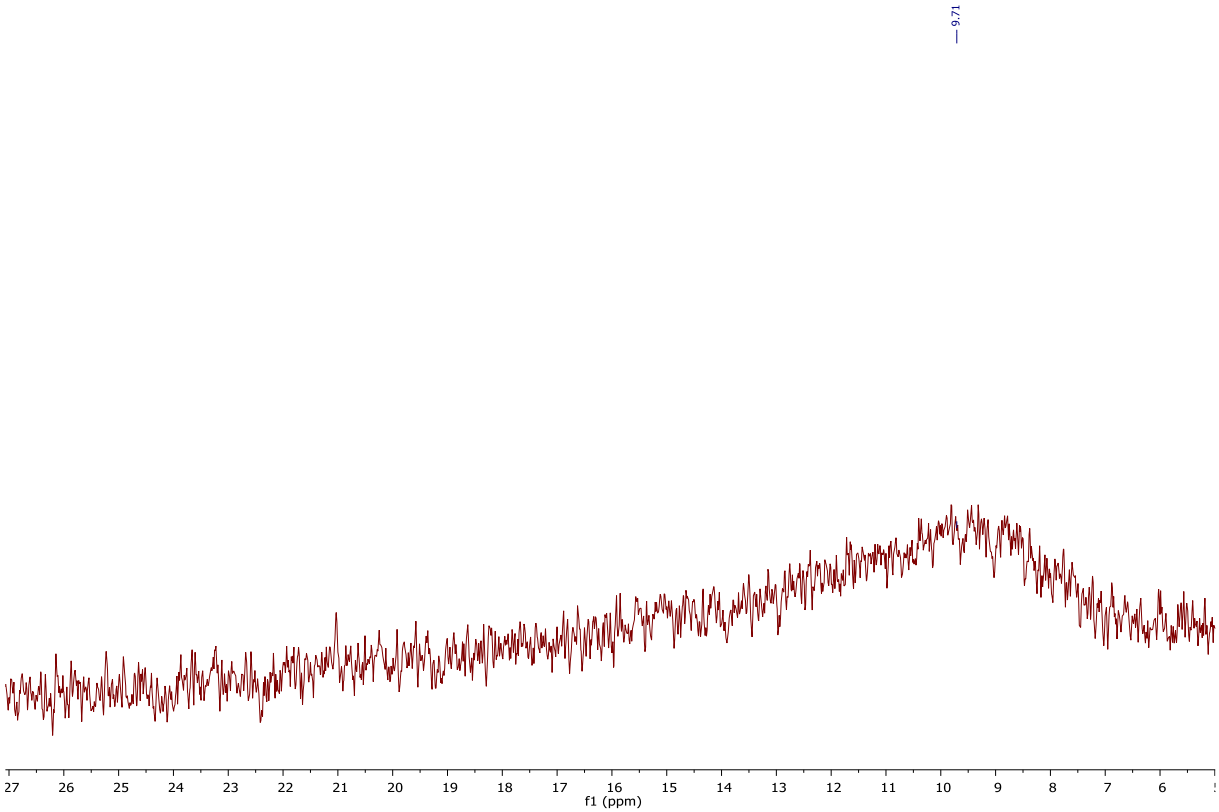

Figure S5. ^{9}Be NMR Spectrum (C_6D_6, 298 K, 56.2 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Li(12-cr-4)$_{1.75}$]** (**1**).

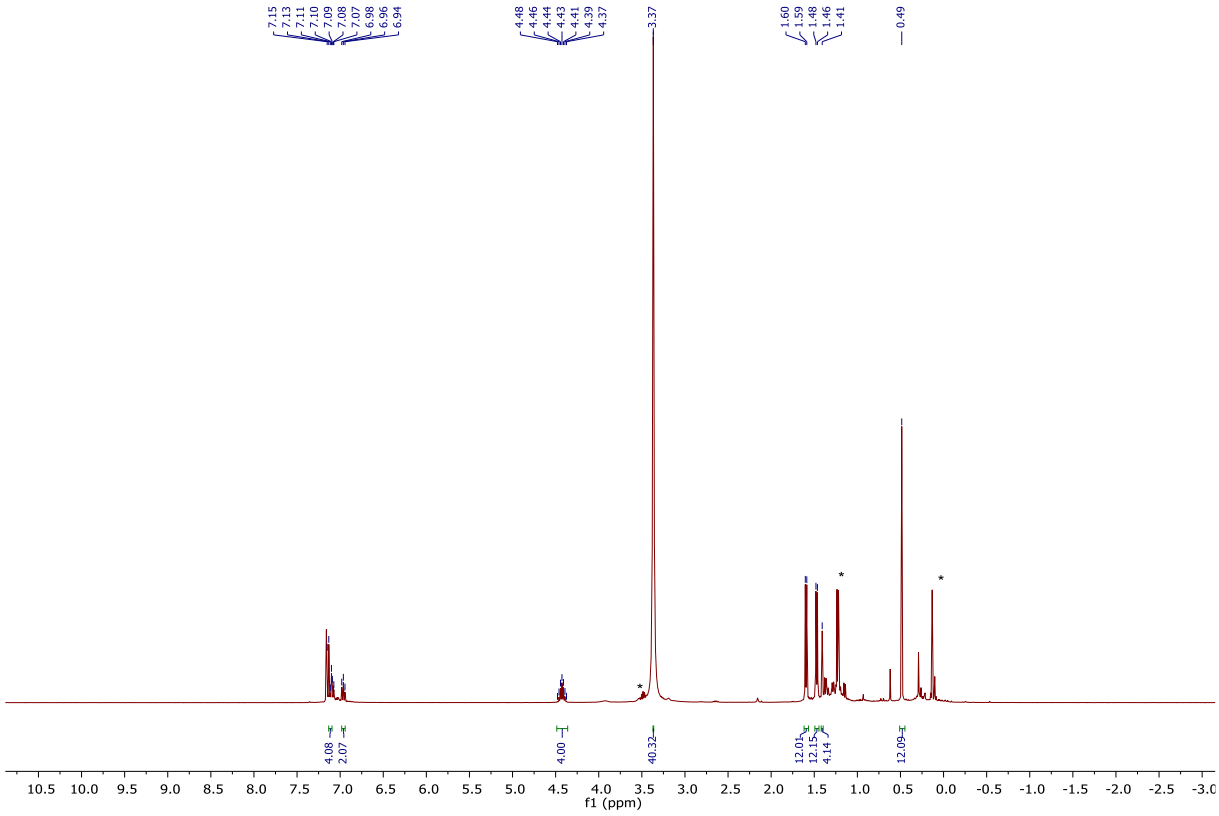

Figure S6. ^{1}H NMR Spectrum (C_6D_6, 298 K, 400.13 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(15-cr-5)$_2$]** (**2**). * = [{CH_2SiMe_2NDipp}H]$_2$.

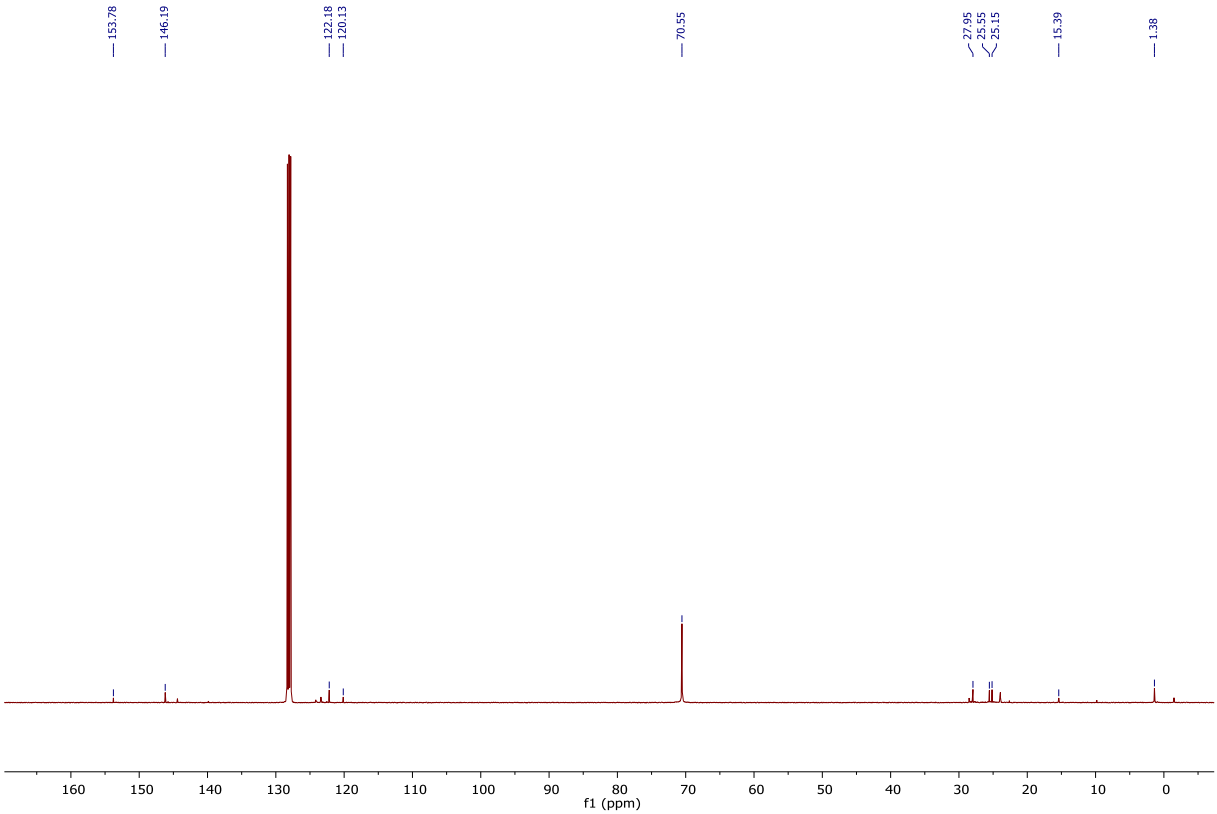

Figure S7. $^{13}C\{^{1}H\}$ NMR Spectrum (C_6D_6, 298 K, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(15-cr-5)$_2$]** (**2**).

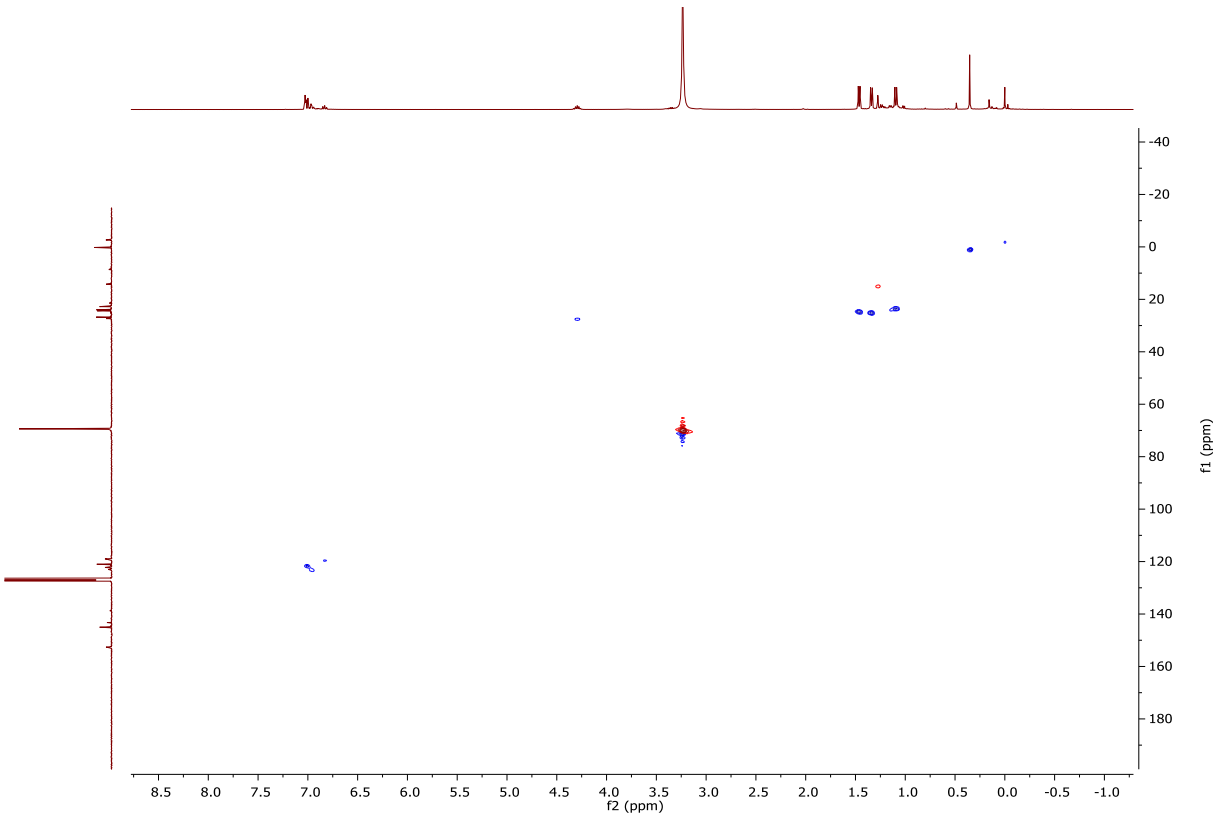

Figure S8. ^{1}H-^{13}C HSQC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(15-cr-5)$_2$]** (**2**).

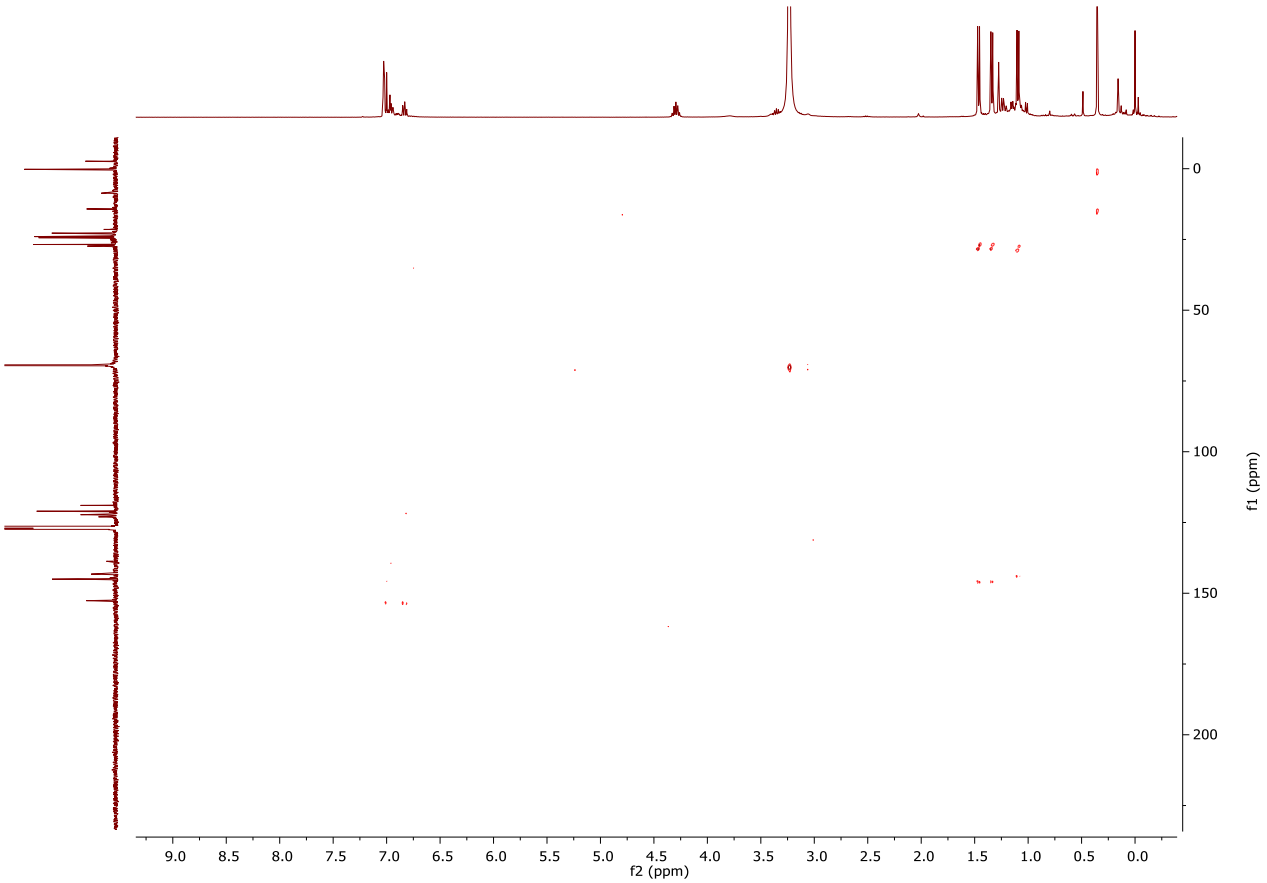

Figure S9. ^{1}H-^{13}C HMBC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(15-cr-5)$_2$]** (**2**).

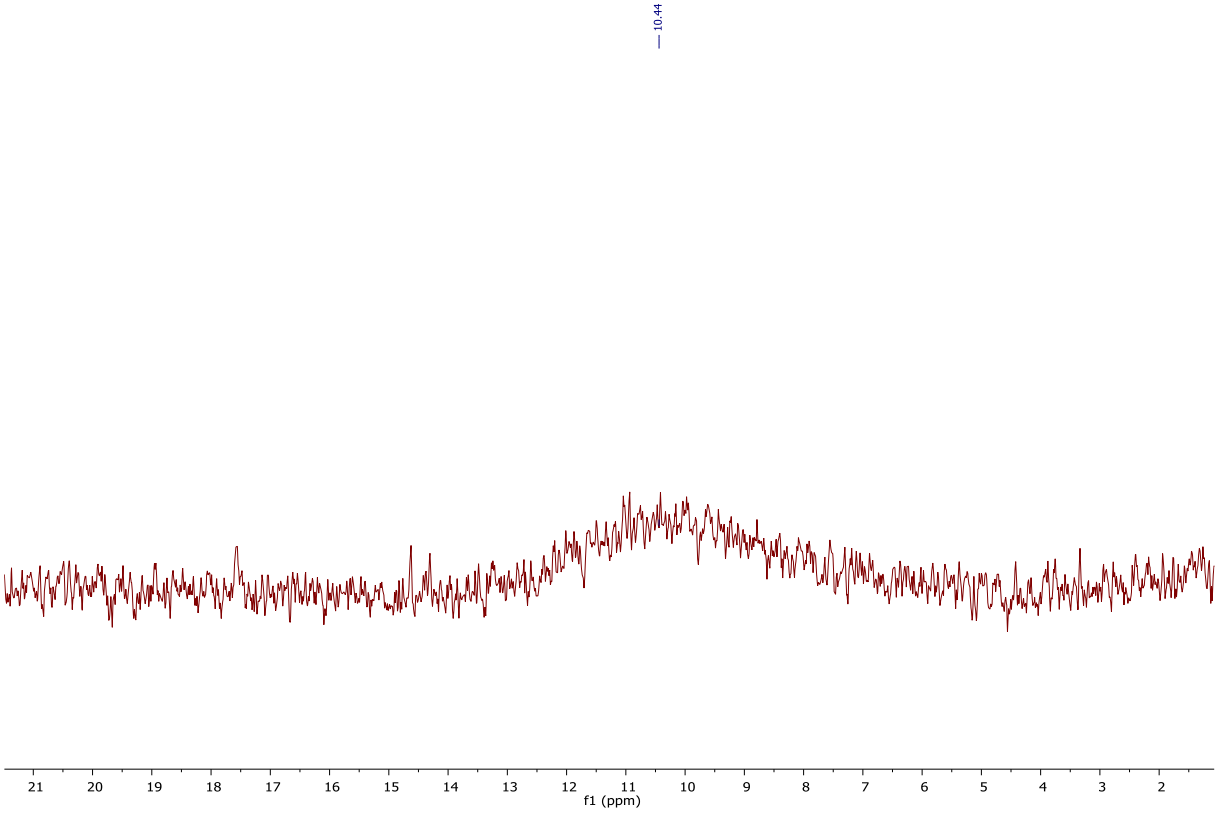

Figure S10. ^{9}Be NMR Spectrum (C_6D_6, 298 K, 56.2 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(15-cr-5)$_2$]** (**2**).

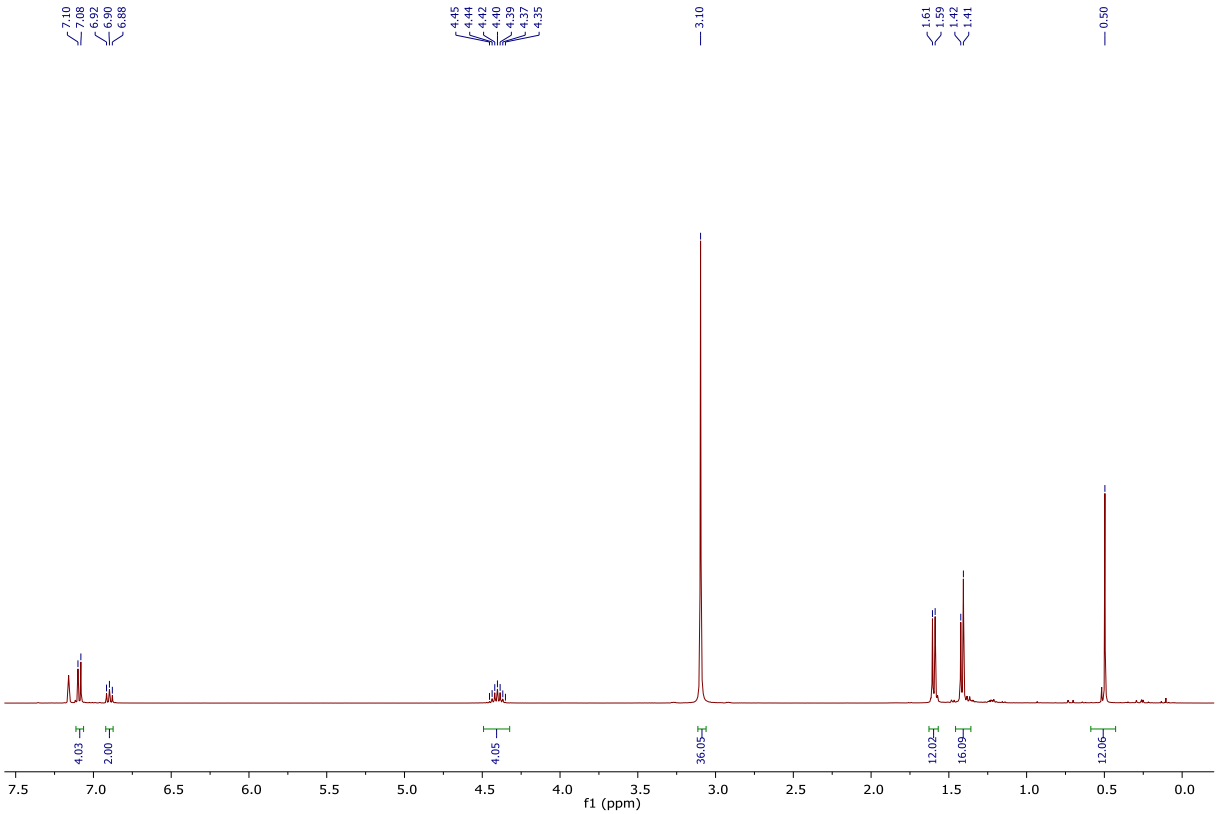

Figure S11. ^{1}H NMR Spectrum (C_6D_6, 298 K, 400.13 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**).

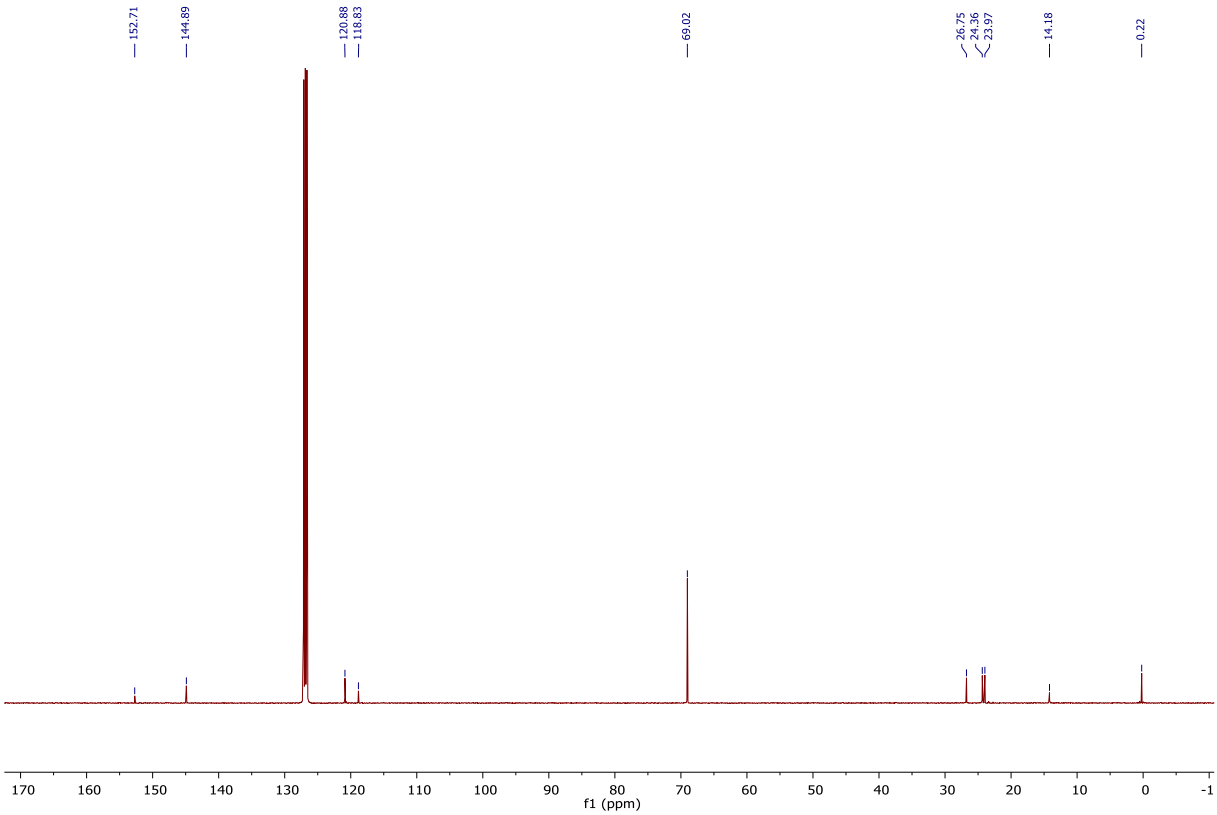

Figure S12. ^{13}C{^{1}H} NMR Spectrum (C_6D_6, 298 K, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**).

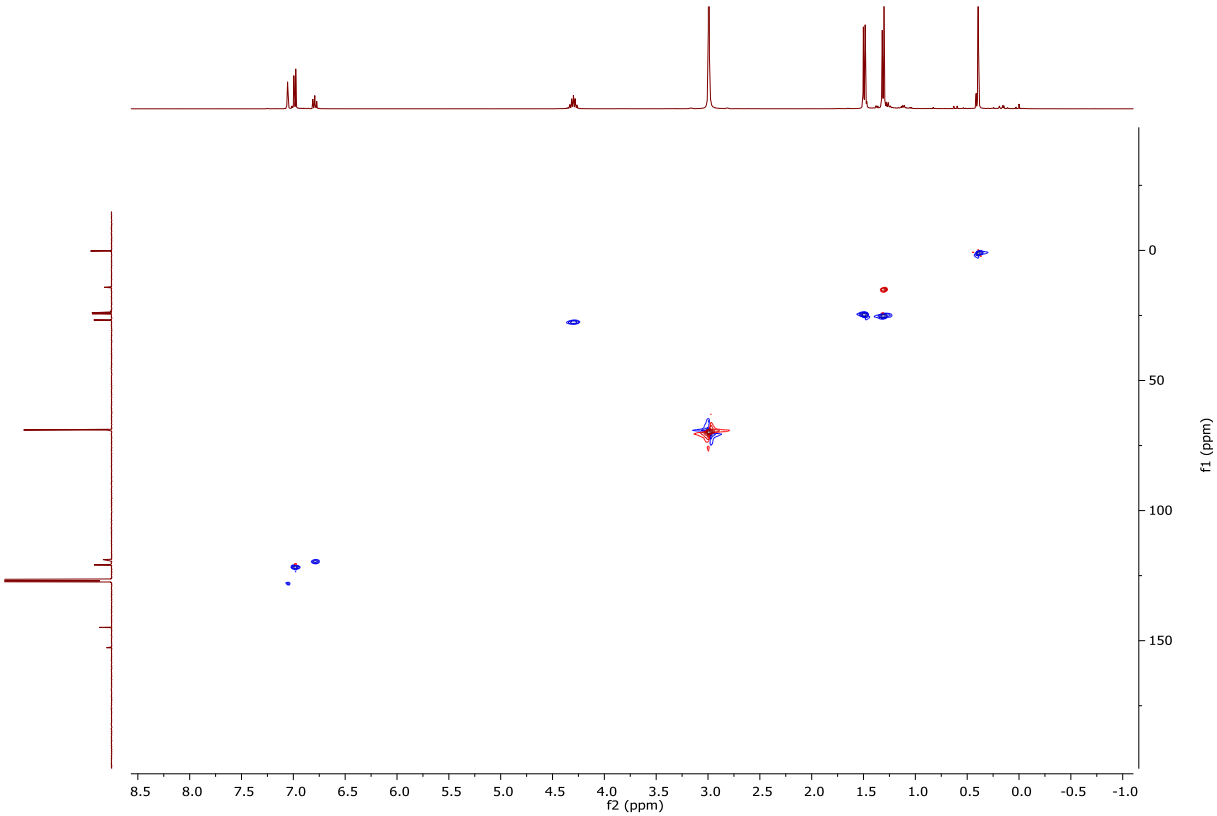

Figure S13. ^{1}H-^{13}C HSQC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**).

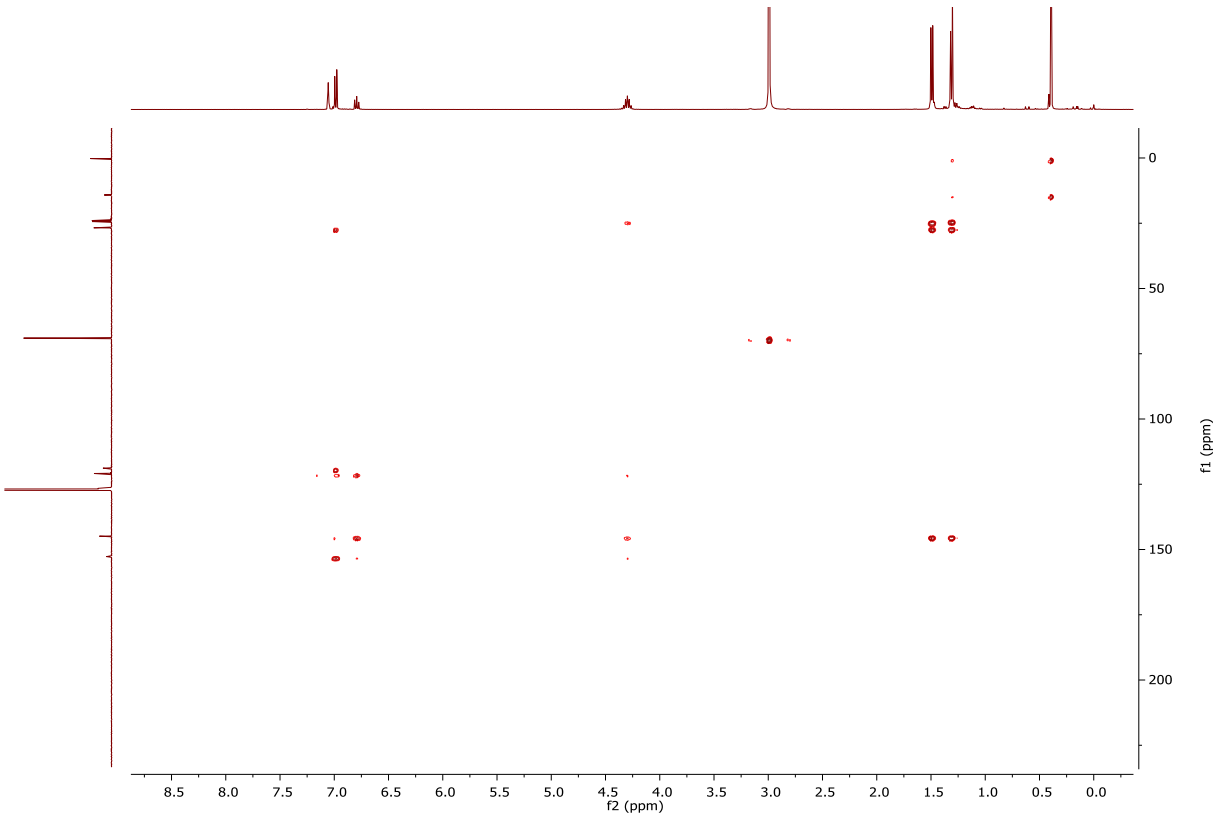

Figure S14. ^{1}H-^{13}C HMBC trace (C_6D_6, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**).

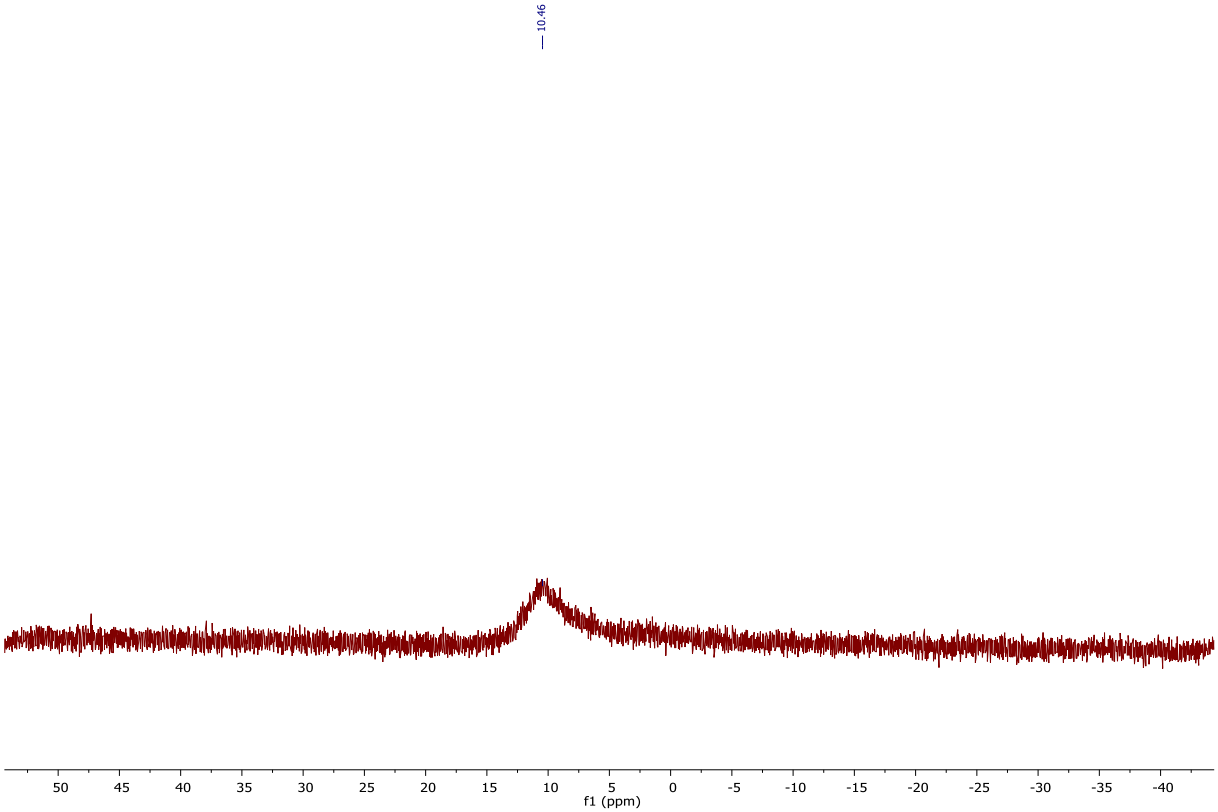

Figure S15. ^{9}Be NMR Spectrum (C_6D_6, 298 K, 56.2 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(18-cr-6)$_{1.5}$]** (**3**).

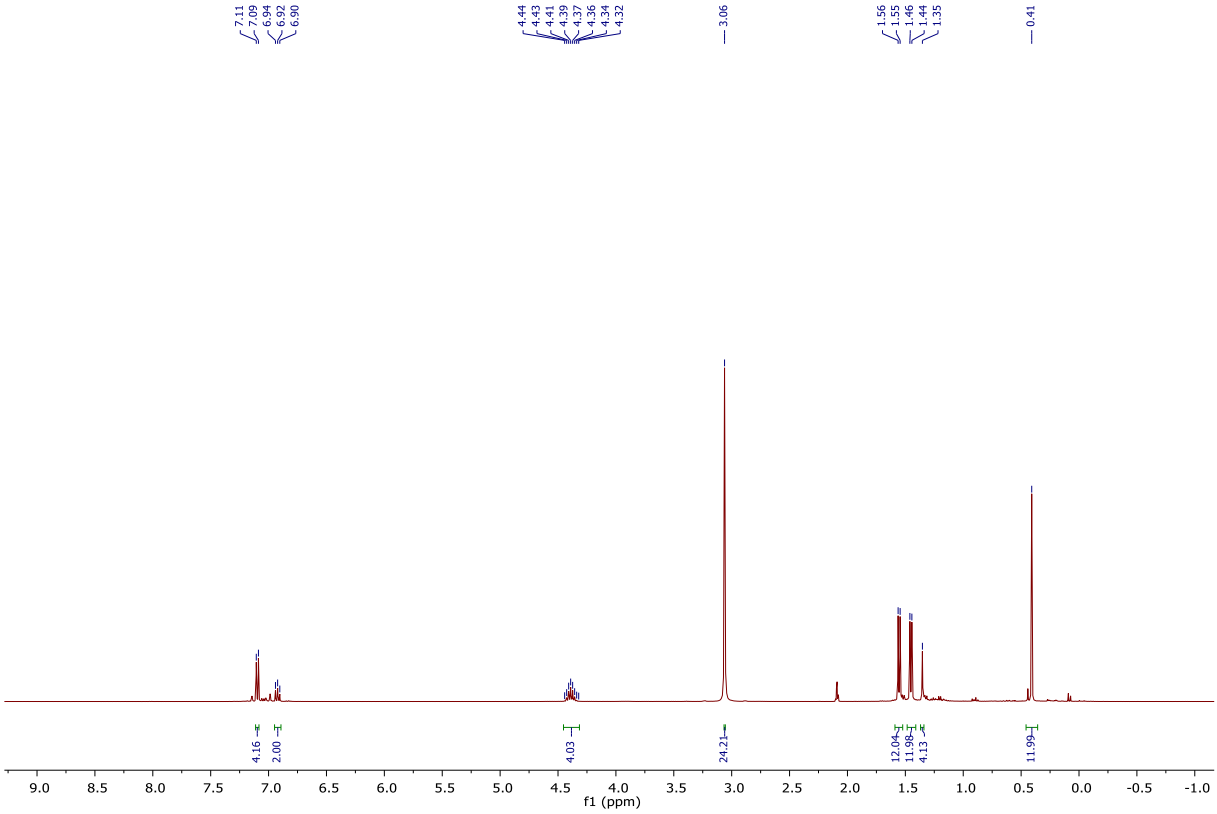

Figure S16. ^{1}H NMR Spectrum (C_6D_8, 298 K, 400.13 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**).

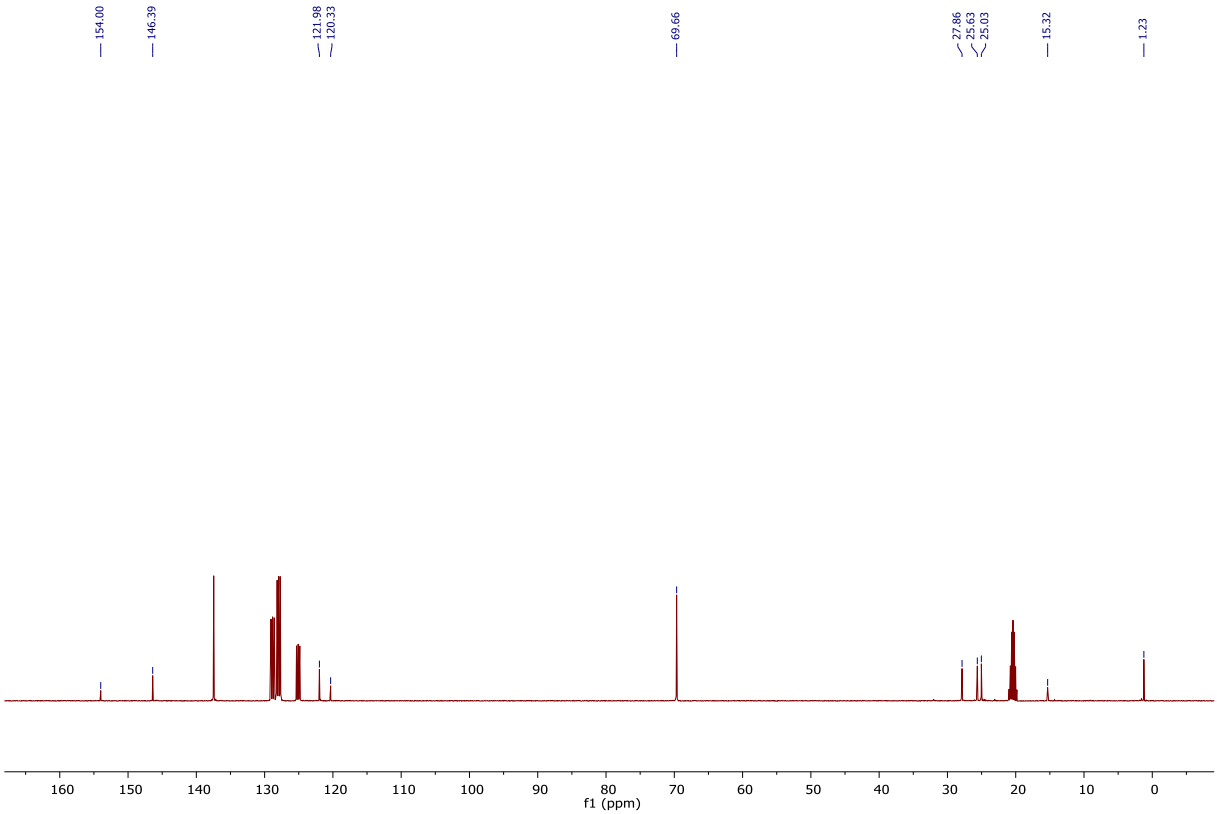

Figure S17. $^{13}C\{^{1}H\}$ NMR Spectrum (C_6D_8, 298 K, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**).

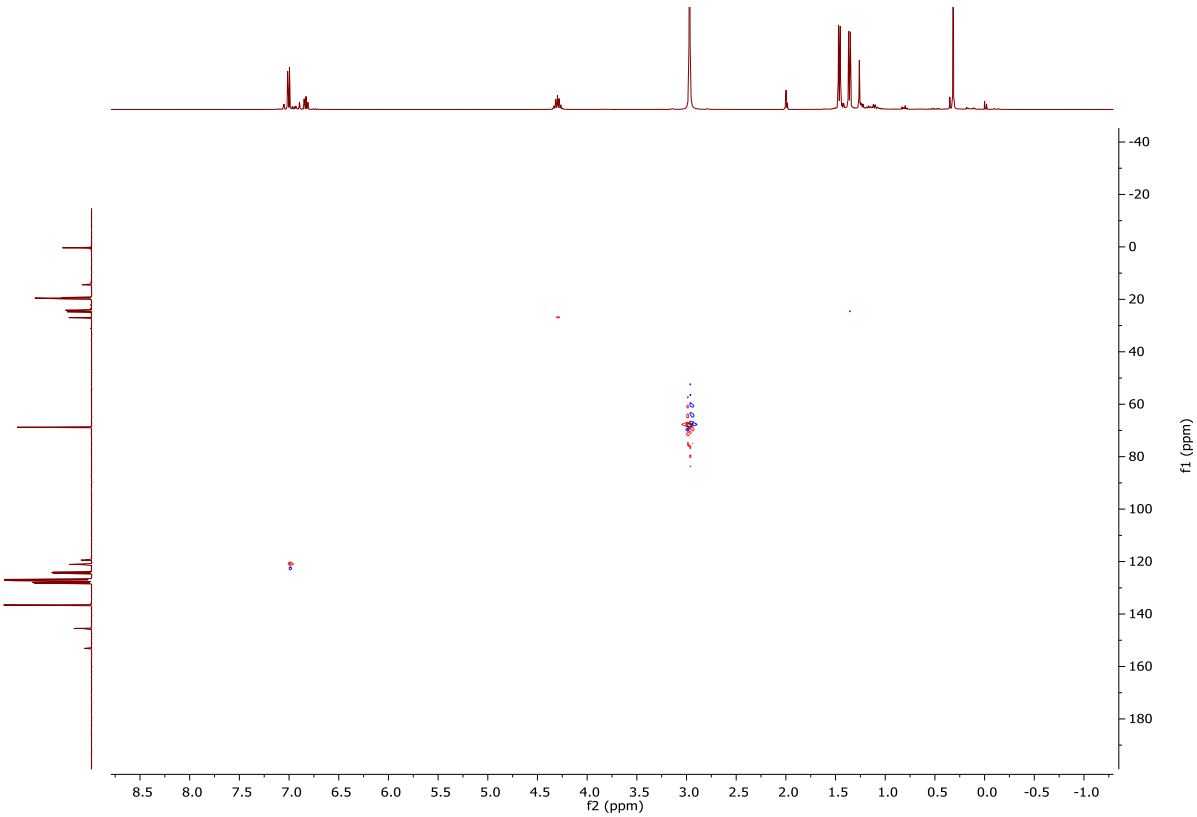

Figure S18. ^{1}H-^{13}C HSQC trace (C_6D_8, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**).

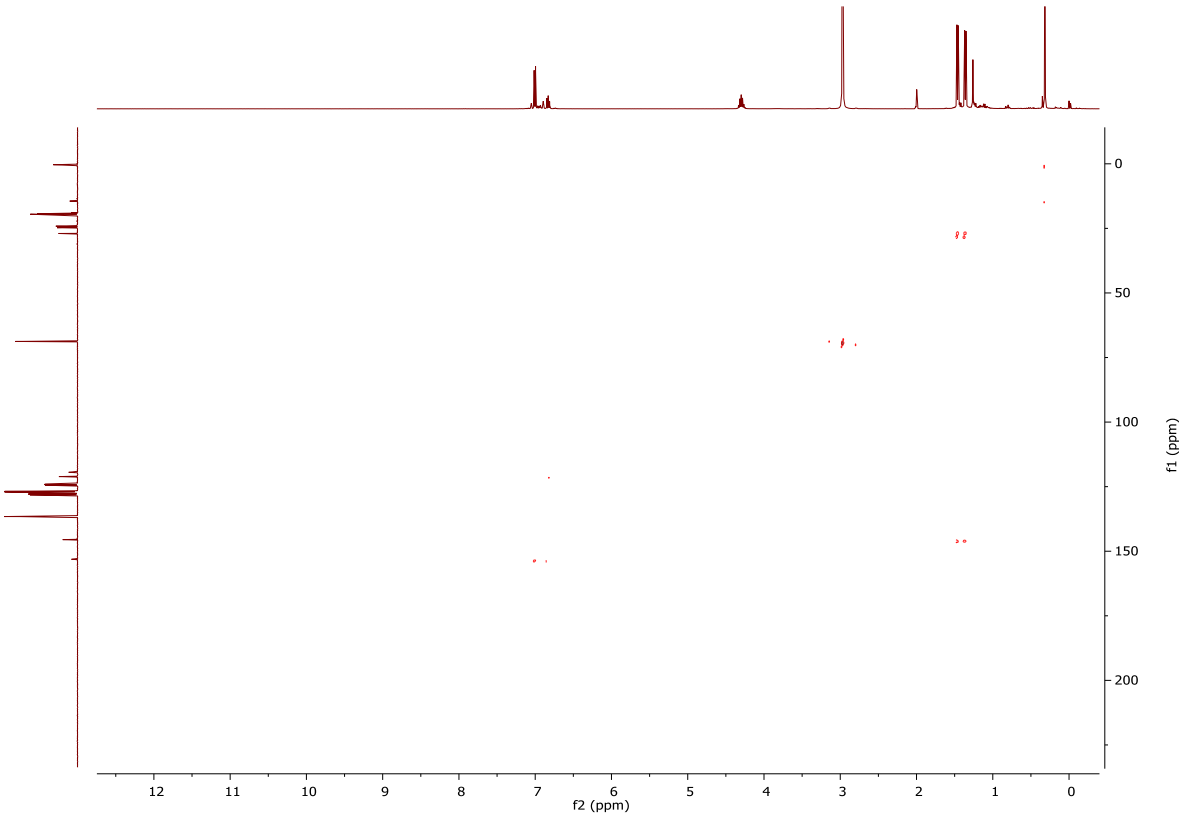

Figure S19. ^{1}H-^{13}C HMBC trace (C_6D_8, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**).

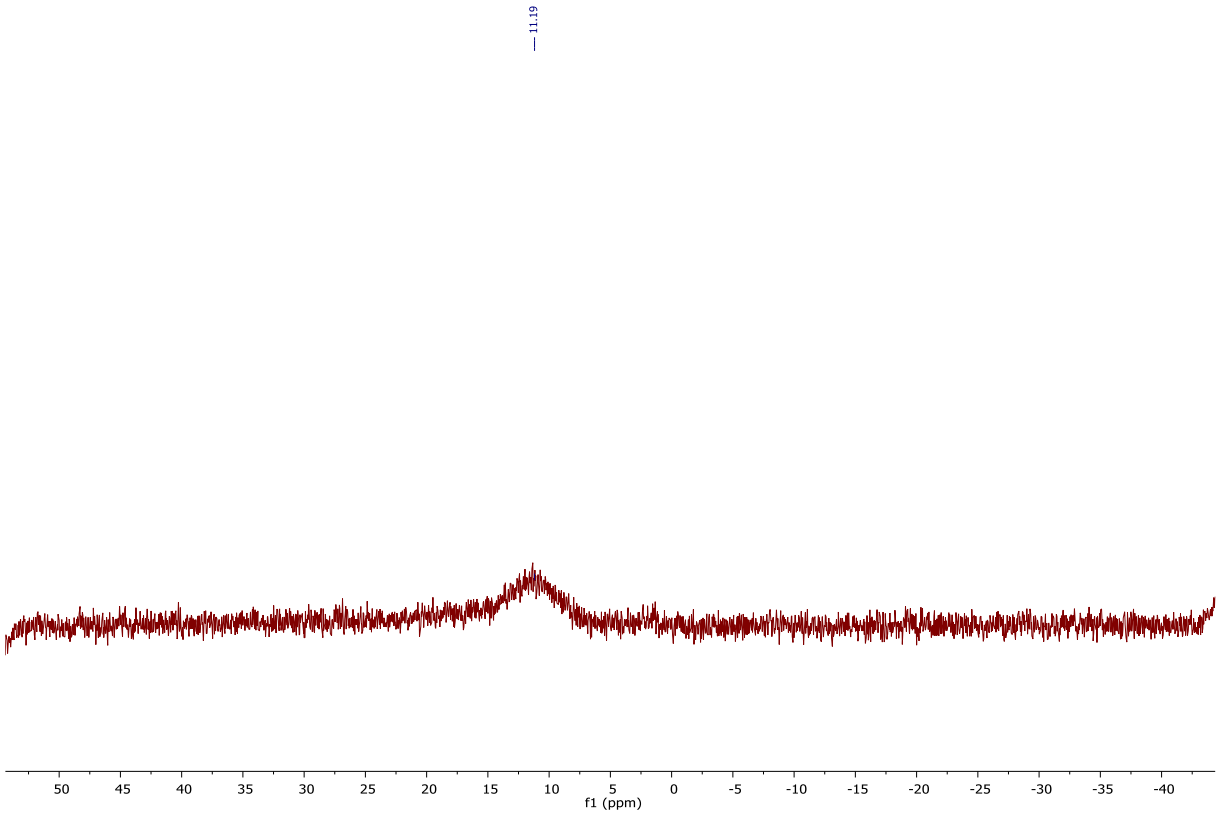

Figure S20. ^{9}Be NMR Spectrum (C_6D_6, 298 K, 56.2 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Rb(18-cr-6)]** (**4**).

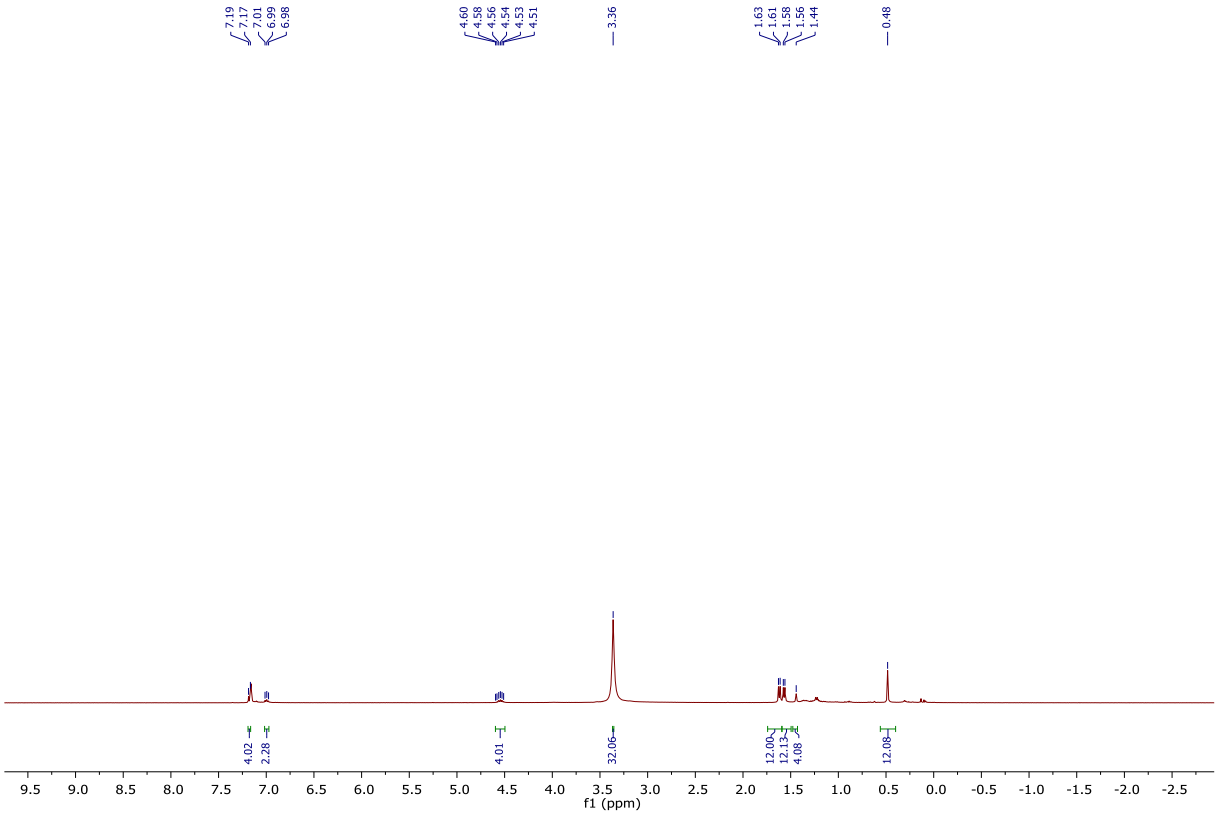

Figure S21. ^{1}H NMR Spectrum (C_6D_8, 298 K, 400.13 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (5).**

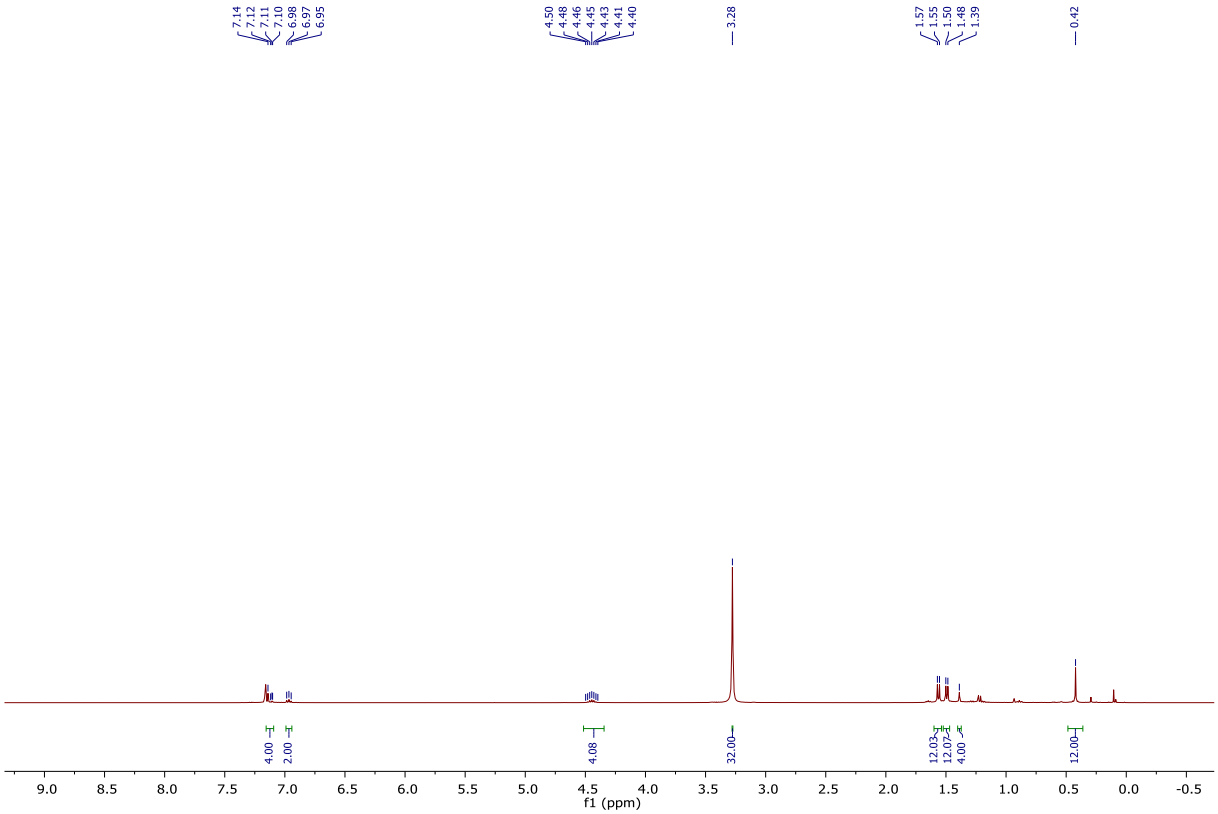

Figure S22. ^{1}H NMR Spectrum (C_6D_8, 298 K, 400.13 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$] (6).**

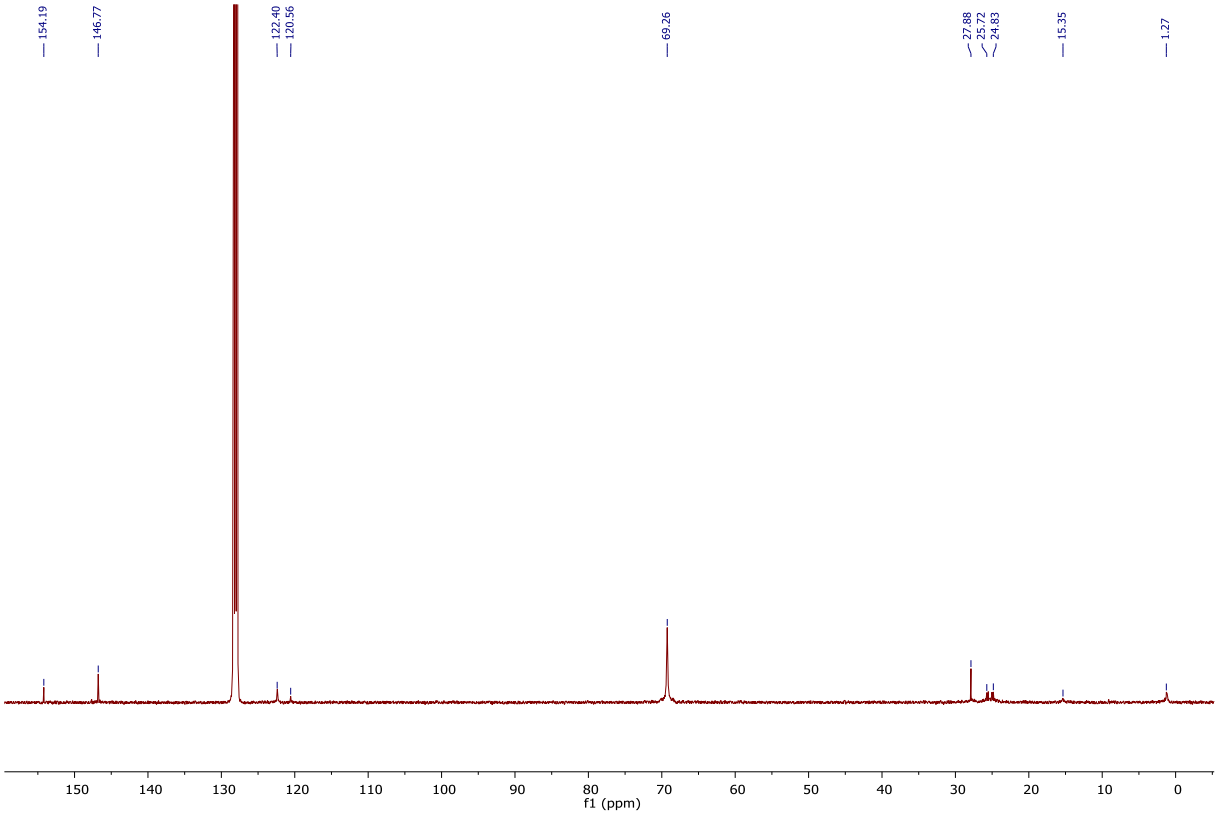

Figure S23. $^{13}C\{^{1}H\}$ NMR Spectrum (C_6D_8, 298 K, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$]** (**6**).

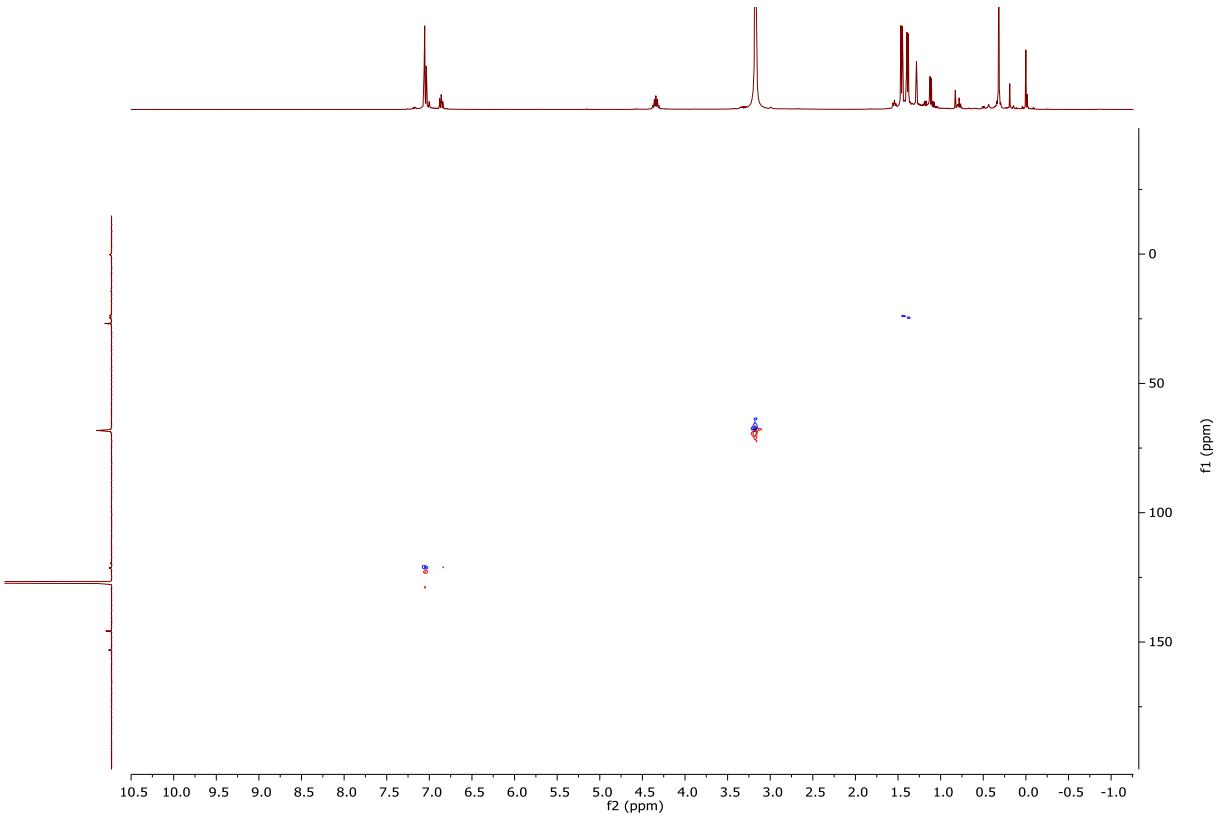

Figure S24. ^{1}H-^{13}C HSQC trace (C_6D_8, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$]** (**6**).

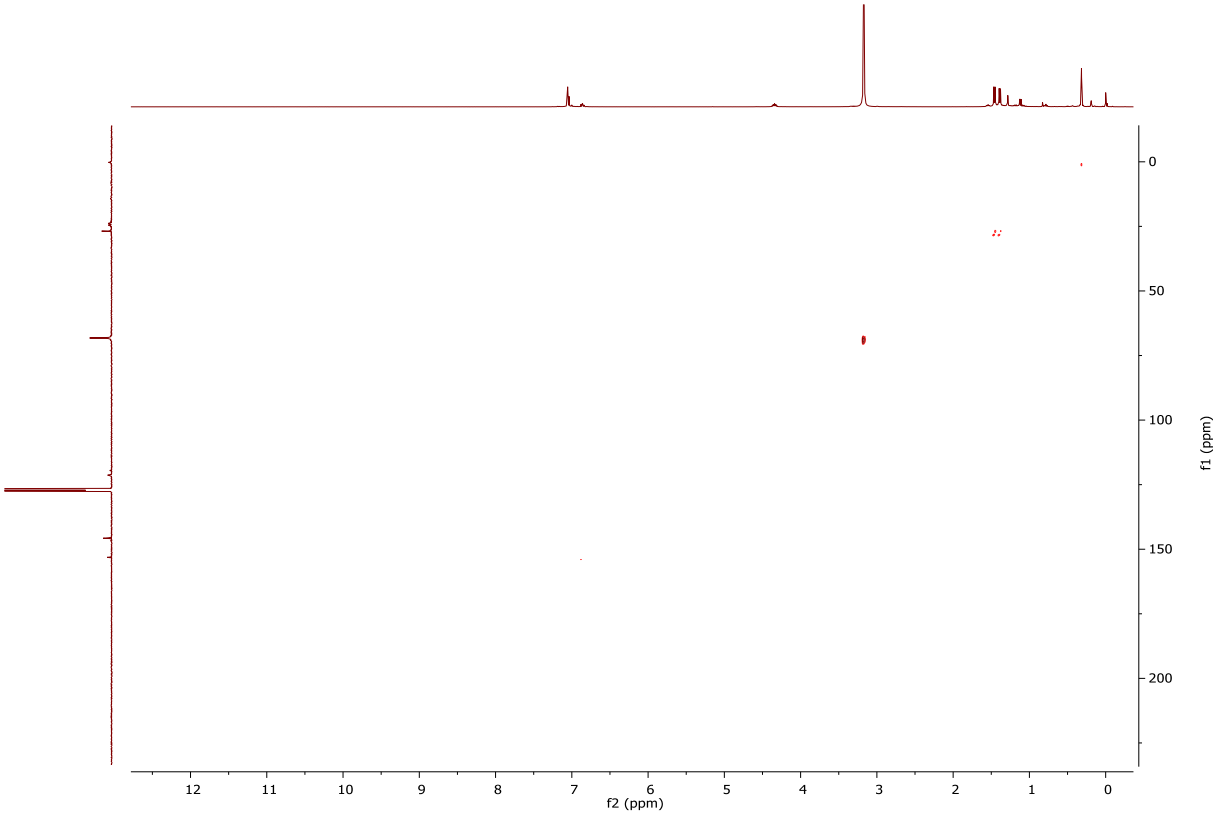

Figure S25. ^{1}H-^{13}C HMBC trace (C_6D_8, 298 K, 400.13, 100.62 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$]** (**6**).

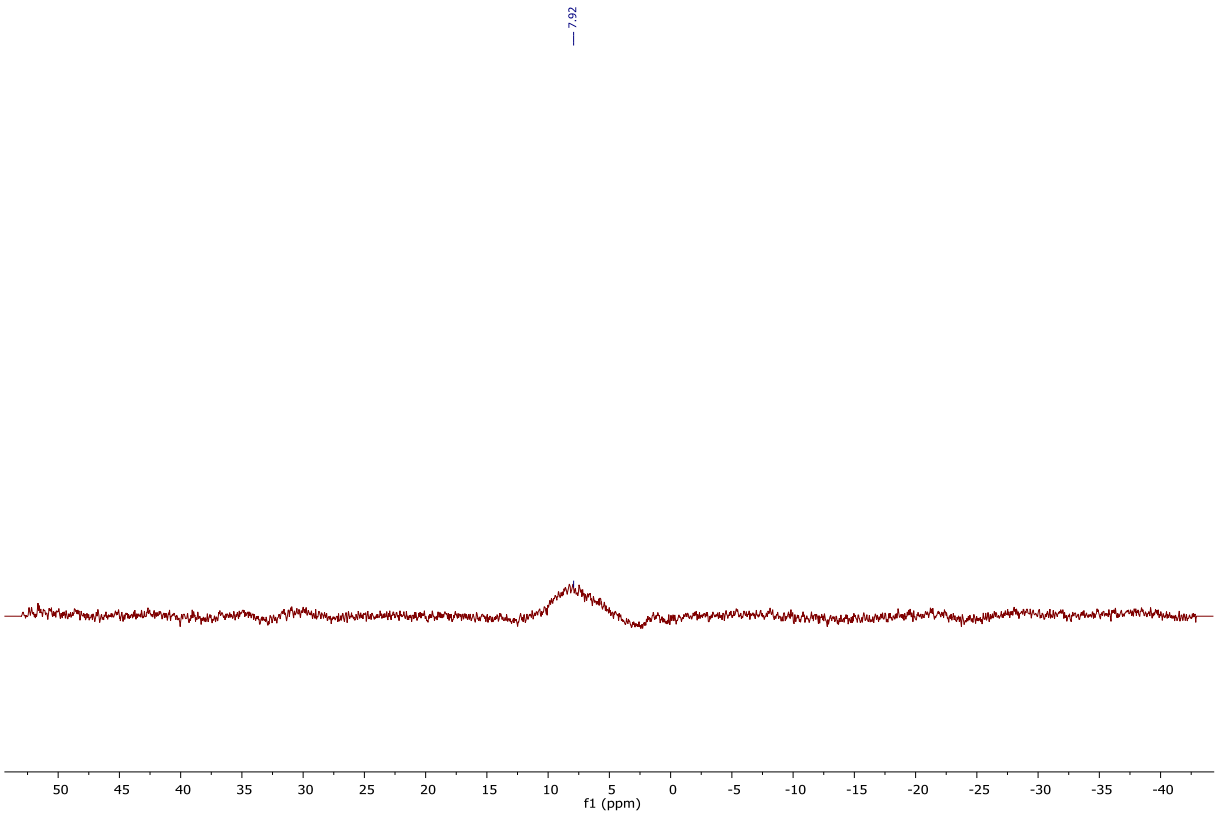

Figure S26. ^{9}Be NMR Spectrum (C_6D_6, 298 K, 56.2 MHz) for **[{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$]** (**6**).

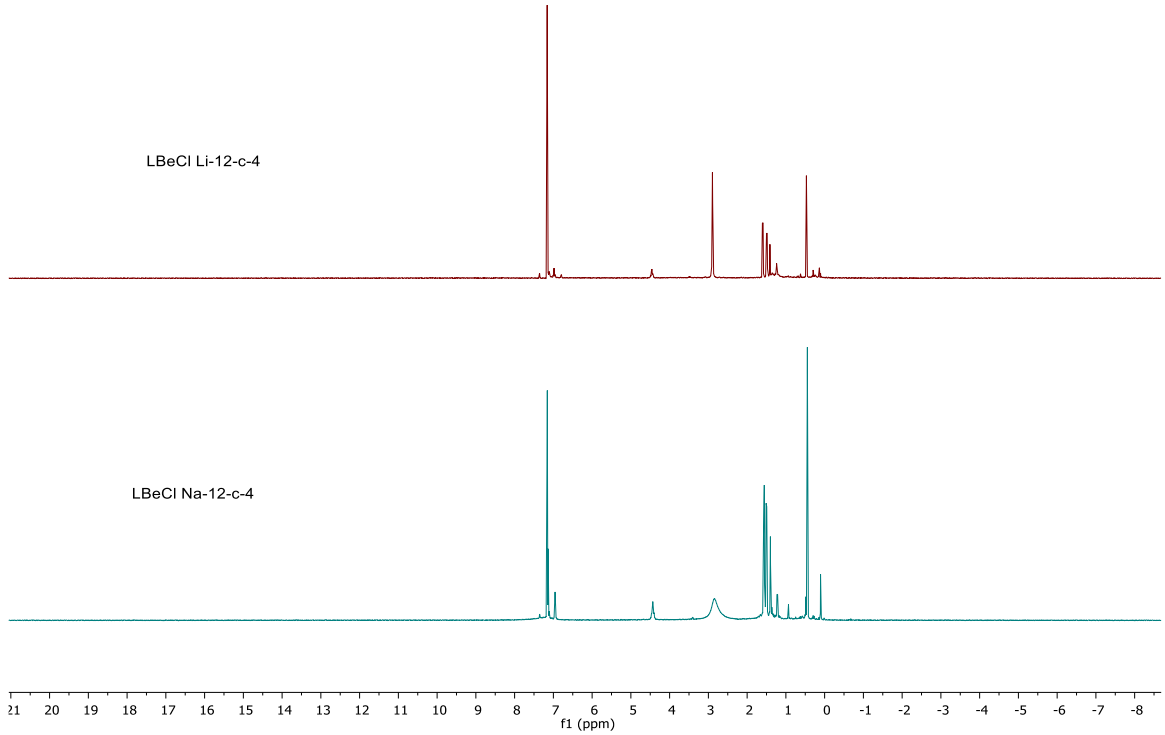

Figure S27. ^{1}H NMR Spectra (C_6D_6, 298 K, 400.13 MHz) for the Li (**1**) and Na (**5**) 12-crown-4 complexes.

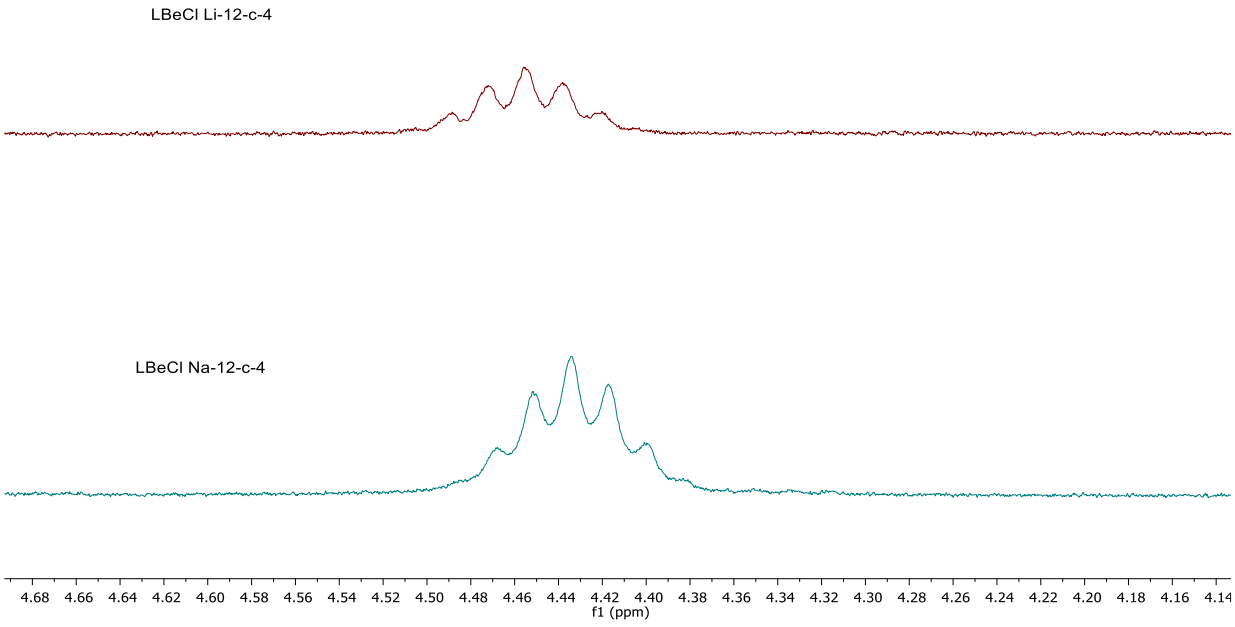

Figure S28. ^{1}H NMR Spectra (C_6D_6, 298 K, 400.13 MHz), expansion of the Dipp methine resonances for the Li (**1**) and Na (**5**) 12-crown-4 complexes.

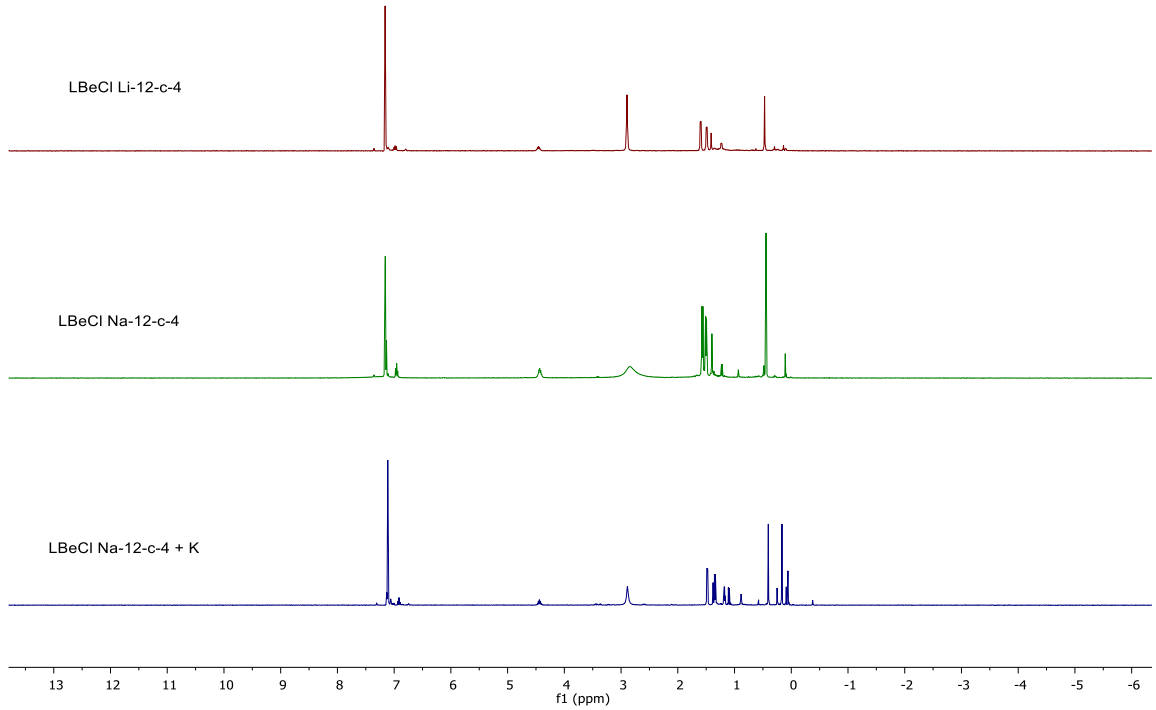

Figure S29. ^{1}H NMR Spectra (C_6D_6, 298 K, 400.13 MHz) for the Li (**1**) and Na (**5**) 12-crown-4 complexes and the attempted reduction of [{CH_2SiMe_2NDipp}$_2$BeCl][Na(12-cr-4)$_2$] (**5**) with K.

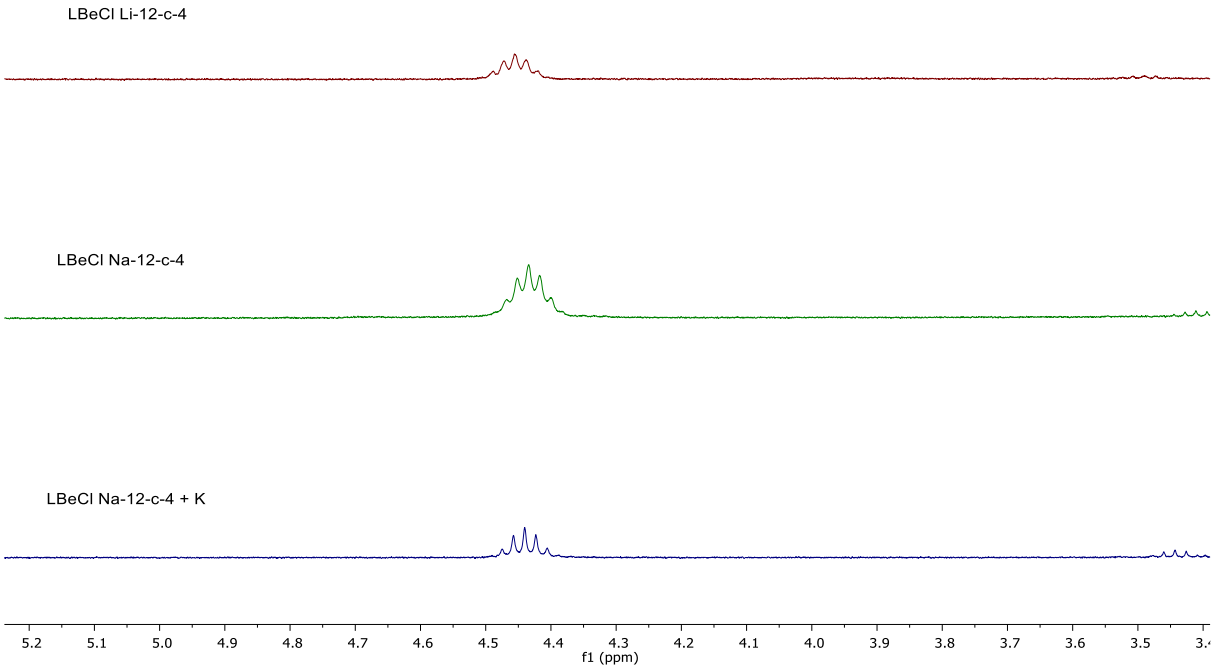

Figure S30. ^{1}H NMR Spectra (C_6D_6, 298 K, 400.13 MHz), expansion of the Dipp methine resonances for Li (**1**) and Na (**5**) 12-crown-4 complexes and the attempted reduction of [{CH_2SiMe_2NDipp}$_2$BeCl][K(12-cr-4)$_2$] with K.

Single Crystal X-ray Diffraction Analysis

Data for **6** were collected on an Agilent Xcalibur diffractometer (using Mo-Kα radiation) while those for **1** - **5** were obtained using an Agilent SuperNova instrument and a Cu-Kα source. All experiments were conducted at 150 K, solved using SHELXT[4] and refined using SHELXL[5] via the Olex2[6] interface. Refinements were unremarkable except for the points outlined hereafter.

The asymmetric unit in the structure of **1** contains two beryllium based anions, one (18-crown-6)$_2$Li species (based on Li1), half of an (18-crown-6)$_3$Li$_2$ moiety and one molecule of benzene. The electron density pertaining to the crown ether ligands in the molecule based on Li1 was smeared. Hence, one of these ligands was treated for 67:33 disorder and the other for 50:50 disorder. The O9 containing crown, bonded to Li2 was also treated for disorder, this time in a 75:25 ratio. Lastly, the solvent was also modelled as being split over two sites in equal portion. Distance and ADP restraints were employed, on merit, in disordered regions to assist convergence.

The diffraction ability of the sample in the structure of **2** suffered from rapid intensity fall off at higher Bragg angles. The asymmetric unit therein was seen to contain one beryllium-based anion and one [Na(15-crown-5)$_2$]$^+$ moiety, the latter being treated for 67:33 disorder in its entirety. This rampant disorder coupled with the fact that the crystals of this compound manifested as plates accounts for the afore mentioned decline in diffracting ability in the outer shells of raw data. The impact, in turn, is that the electron density in the disordered region is very smeared. Modelling as two components (with inclusion of distance and ADP restraints to assist convergence) is a best approximation, as the crown containing O6-O10 is most definitely further disordered but the data did not permit further deconvolution in this region of the electron density map. As such, no claims are being made about bond distances in the cation. However, overall, this experiment renders unambiguous assignment of this salt.

Disorder modelling (65:35) was confined to the crown ether containing O1 in the structure of **3**. Distance and ADP restraints were employed, on merit, in the disordered region to assist convergence. The asymmetric unit contains half of the moiety that contains the crowns with the full species being generated via inversion symmetry present in the space group. [Operation $1 - x$, $1 - y$, $1 - z$]

One cation, one anion, one disordered toluene moiety and a region of disordered solvent collectively constitute the asymmetric unit in the structure of **4**. The crown ether moiety was treated for 55:45 disorder and the toluene for 67:33 disorder. Distance and ADP restraints were employed, on merit, in disordered regions to assist convergence. The diffuse solvent area was treated with the solvent mask algorithm in Olex-2 and an allowance made, in the formula as presented, for two additional toluenes per unit cell.

In addition to one cation and one anion, the asymmetric unit plays host to a pair of benzene molecules in the structure of **5**.

There are two cations and two anions in the asymmetric unit of compound **6**. Given that there are four crown ether moieties present therein, the model is surprisingly ordered. Only the crown containing O8-O12 was treated for an 85:15 split across two proximate locations. Distance and ADP restraints were employed, on merit, in the disordered region to assist convergence.

Table S1: Crystal data and structure refinement for compounds **1 - 4**.

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{94}H_{162}Be_2Cl_2Li_2N_4O_{14}Si_4$	$C_{50}H_{90}BeClN_2NaO_{10}Si_2$	$C_{48}H_{88}BeClKN_2O_9Si_2$	$C_{52.5}H_{86}BeClN_2O_6RbSi_2$
Formula weight	1787.43	1002.86	976.94	1027.34
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/ Å	21.4089(2)	15.1421(6)	10.5322(1)	16.7051(3)
b/ Å	22.3190(2)	20.7692(7)	21.8852(2)	21.1030(3)
c/ Å	22.5227(2)	18.2654(5)	24.2440(2)	17.1977(3)
α/ °	90	90	90	90
β/ °	102.668(1)	91.531(3)	92.1130(10)	103.361(2)
γ/ °	90	90	90	90
U/ Å^3	10499.94(17)	5742.2(3)	5584.43(9)	5898.57(18)
Z	4	4	4	4
ρ_{calc}/ g cm^{-3}	1.131	1.160	1.162	1.157
μ/ mm^{-1}	1.444	1.482	2.081	2.302
F(000)	3880.0	2176.0	2120.0	2196.0
Crystal size/ mm^3	0.286 × 0.195 × 0.158	0.231 × 0.204 × 0.061	0.273 × 0.15 × 0.099	0.178 × 0.111 × 0.07
2θ range for data collection/°	7.566 to 146.872	7.226 to 146.782	7.298 to 145.44	6.864 to 146.832
Index ranges	$-25 \le h \le 26$ $-27 \le k \le 26$ $-27 \le l \le 27$	$-17 \le h \le 18$ $-25 \le k \le 25$ $-20 \le l \le 22$	$-12 \le h \le 12$ $-27 \le k \le 27$ $-29 \le l \le 17$	$-20 \le h \le 20$ $-26 \le k \le 24$ $-21 \le l \le 21$
Reflections collected	146394	46566	75169	78334
Independent reflections, R_{int}	21025, 0.0300	11441, 0.0604	11053, 0.0358	11800, 0.0463
Data/restraints/parameters	21025/1434/1477	11441/1280/895	11053/558/762	11800/894/762
Goodness–of–fit on F^2	1.013	1.027	1.016	1.025
Final R1, wR2 [I>=2σ(I)]	0.0425, 0.1115	0.0862, 0.2314	0.0388, 0.1068	0.0508, 0.1266
Final R1, wR2 [all data]	0.0470, 0.1155	0.1338, 0.2734	0.0443, 0.1121	0.0629, 0.1342
Largest diff. peak/hole/ e Å^{-3}	0.74/-0.41	0.55/-0.48	0.28/-0.43	0.85/-0.48

Table S2: Crystal data and structure refinement for compounds **5** and **6**.

Identification code	**5**	**6**
Empirical formula	$C_{58}H_{94}BeClN_2NaO_8Si_2$	$C_{46}H_{82}BeClKN_2O_8Si_2$
Formula weight	1070.98	930.87
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
a/ Å	12.1829(1)	14.9011(3)
b/ Å	17.5093(1)	19.7649(3)
c/ Å	29.9100(2)	18.0278(3)
α/ °	90	90
β/ °	96.725(1)	93.633(2)
γ/ °	90	90
U/ Å^3	6336.32(8)	5298.85(16)
Z	4	4
ρ_{calc}/ g cm^{-3}	1.123	1.167
μ/ mm^{-1}	1.350	0.244
F(000)	2320.0	2016.0
Crystal size/ mm^3	0.237 × 0.159 × 0.087	0.365 × 0.316 × 0.268
2θ range for data collection/°	7.56 to 146.706	5.854 to 58.256
Index ranges	$-14 \le h \le 14$ $-21 \le k \le 21$ $-37 \le l \le 29$	$-20 \le h \le 20$ $-27 \le k \le 25$ $-24 \le l \le 24$
Reflections collected	83688	61223
Independent reflections, R_{int}	12658, 0.0298	26216, 0.0305
Data/restraints/parameters	12658/0/670	26216/547/1232
Goodness–of–fit on F^2	1.038	1.041
Final R1, wR2 [I>=2σ(I)]	0.0368, 0.1026	0.0598, 0.1411
Final R1, wR2 [all data]	0.0414, 0.1065	0.0913, 0.1601
Largest diff. peak/hole/ e Å^{-3}	0.35/-0.62	0.46/-0.56
Flack parameter	-	0.094(15)

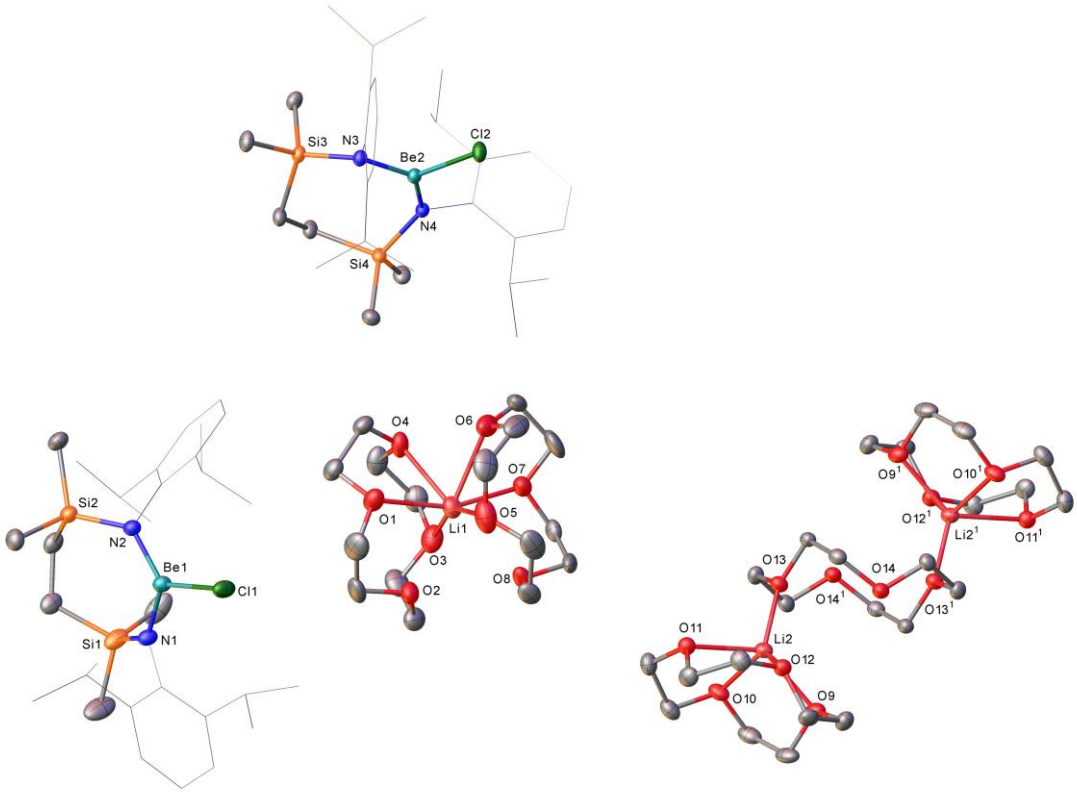

Figure S31. Molecular structure (30% probability ellipsoids) of compound **1**. For clarity, hydrogen atoms, disordered atoms and an occluded molecule of benzene have been omitted, while Dipp carbon atoms are presented as wireframe.

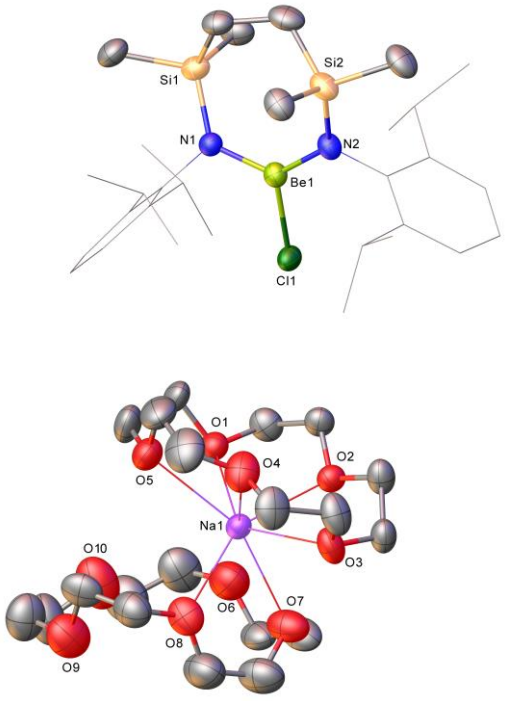

Figure S32. Molecular structure (30% probability ellipsoids) of compound **2**. For clarity, hydrogen and disordered atoms have been omitted, while Dipp carbon atoms are presented as wireframe.

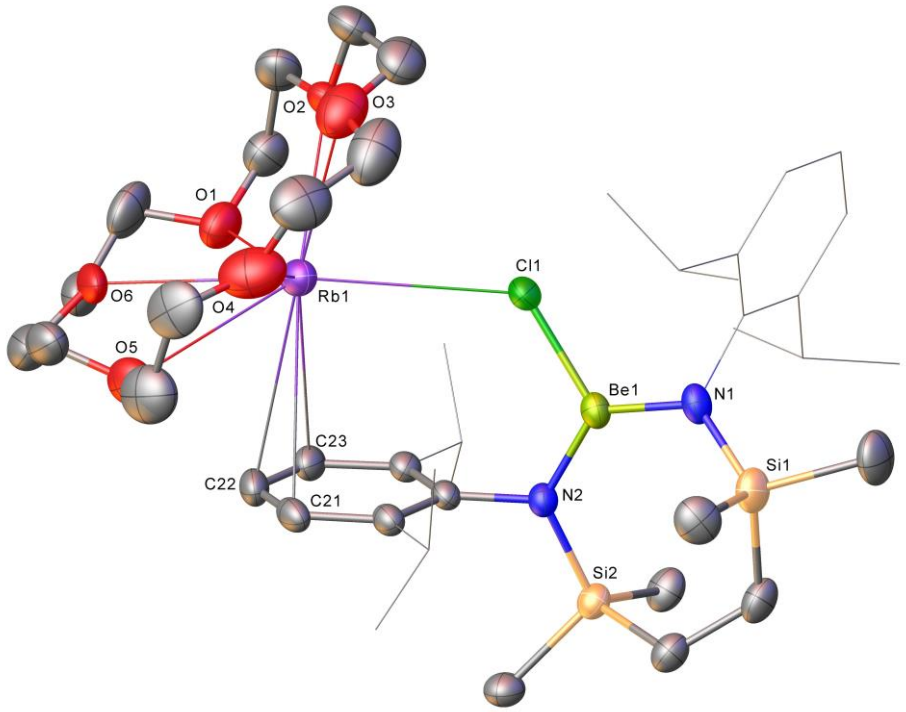

Figure S33. Molecular structure (30% probability ellipsoids) of compound **4**. For clarity, hydrogen atoms, disordered atoms and an occluded molecule of toluene have been omitted, while most Dipp carbon atoms are presented as wireframe.

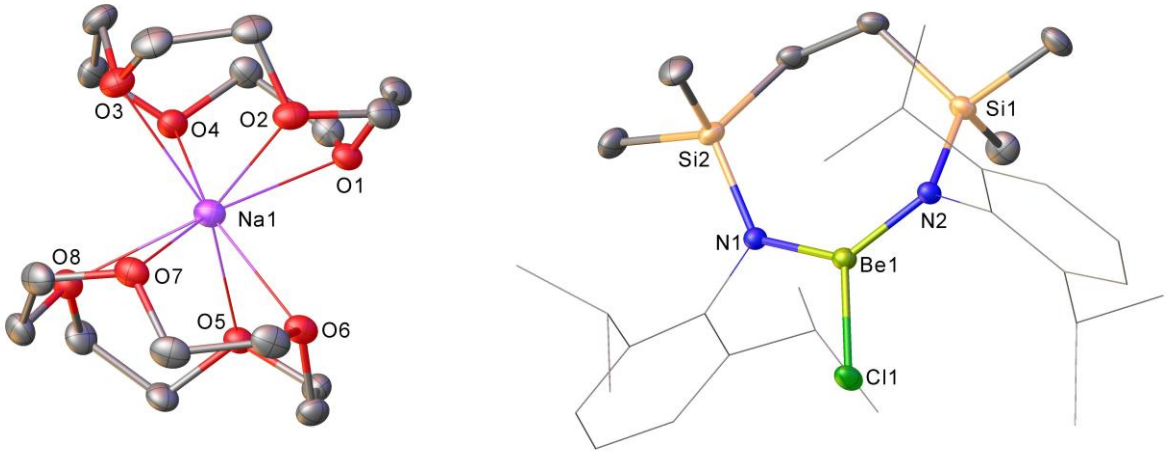

Figure S34. Molecular structure (30% probability ellipsoids) of compound **5**. For clarity, hydrogen atoms, disordered atoms and occluded benzene solvent have been omitted, while Dipp carbon atoms are presented as wireframe.

Computational Details

DFT calculations were performed with Gaussian 16 (C.01).[7] Initial optimizations were performed with the TPSS-D3BJ functional[8,9] and def2-TZVPP basis set[10] for all atoms (BS1), using the 'grid = ultrafine' option, with minima being confirmed *via* identification of all positive eigenvalues. Subsequent single-point calculations were performed at the DLPNO-CCSD(T0);TightPNO/def2-TZVPP[11-14] level of theory (with the default thresholds invoked using the "TightPNO" keyword), using ORCA version 5.0.2.[15,16-19] Solvation corrections (as well as atomic solvation energies used in the thermochemical model described below) were obtained by computing the electronic energy at the TPSS-D3BJ/def2-TZVPP level and subtracting it from the energy at the TPSS-D3BJ;CPCM=Benzene/def2-TZVPP level. This correction was then added to the DLPNO-CCSD(T0);TightPNO/def2-TZVPP energies along with free energy corrections obtained at the TPSS-D3BJ/def2-TZVPP level (herein referred to as "DLPNO-CCSD(T0);CPCM=Benzene/def2-TZVPP//TPSS-D3BJ/def2-TZVPP"). To obtain the overall free energies of reduction of the metal crown ether cations, the thermochemical approach outlined in earlier work was employed,[20] where experimentally derived enthalpies and entropies of atomisation are incorporated into the calculation to account for the heterogeneity of the reduction reaction systems.

Breakdown of Energy Contributions

Table S3 details contributions of relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

$\mathbf{\Delta E_{BS1}}$	SCF energy computed with the TPSS-D3BJ functional with BS1
$\mathbf{\Delta H_{BS1}}$	Enthalpy at 298.15 K with BS1
$\mathbf{\Delta G_{BS1}}$	Free energy at 298.15 K and 1 atm with BS1
$\mathbf{\Delta G_{BSI/C_6H_6}}$	Free energy corrected for Benzene solvent (calculated with CPCM in ORCA) with BS1
$\mathbf{\Delta E_{\mathit{DLPNO}}}$	SCF energy computed at the DLPNO-CCSD(T0);CPCM=Benzene/def2-TZVPP level
$\mathbf{\Delta G_{\mathit{DLPNO}}}$	Overall Free energy computed at the DLPNO-CCSD(T0);TightPNO;CPCM=Benzene/def2-TZVPP//TPSS-D3BJ/def2-TZVPP level.
$\mathbf{\Delta G_{\mathit{DLPNO+At.}}}$	Overall Free energy computed at the DLPNO-CCSD(T0);TightPNO;CPCM=Benzene/def2-TZVPP//TPSS-D3BJ/def2-TZVPP level, with enthalpies and entropies of atomization, along with atomic free energies of solvation for the alkali metals.

Table S3. Relative energies (kcal mol^{-1}) for computed reductions of cations $\mathbf{1}^+$ and $\mathbf{5}^+$. Data in bold are those used in the main text. Energies are quoted relative to $\mathbf{6}^+$ at 0.0 kcal/mol except for the last entry, which is relative to $\mathbf{10}^+$.

	ΔE_{BSI}	ΔH_{BSI}	ΔG_{BSI}	$\Delta G_{BSI/C_6H_6}$	ΔE_{DLPNO}	ΔG_{DLPNO}	$\Delta G_{DLPNO+At.}$
$\mathbf{1}^+$	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
$\mathbf{1}^+ \rightarrow \mathbf{5}^+$	9.7	9.2	10.3	9.8	4.1	4.2	**–7.5**
$\mathbf{1}^+ \rightarrow \mathbf{6}^+$	13.6	12.7	11.2	10.9	16.8	14.0	**–1.5**
$\mathbf{5}^+ \rightarrow \mathbf{6}^+$	3.9	3.5	1.0	1.1	12.7	9.9	**6.0**

Cartesian Coordinates and Computed Energies (in Hartrees) for Calculated Structures

Li
SCF (TPSS-D3BJ/def2-SVP) Energy (G16) = -7.488614825
Enthalpy 0K = -7.488615
Enthalpy 298K = -7.486254
Free Energy 298K = -7.502017
SCF (TPSS-D3BJ,CPCM=C_6H_6/def2-TZVPP) Energy (ORCA5) = -7.489048934
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -7.488633534
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -7.468124488

Li 0.0 0.0 0.0

Na
SCF (TPSS-D3BJ) Energy = -162.287474
Enthalpy 0K = -162.287474
Enthalpy 298K = -162.285114
Free Energy 298K = -162.302557
SCF (TPSS-D3BJ,CPCM=C_6H_6/def2-TZVPP) Energy (ORCA5) = -162.2875828
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -162.2874825
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -162.0166934

Na 0.0 0.0 0.0

K
SCF (TPSS-D3BJ) Energy = -599.9236842
Enthalpy 0K = -599.923684
Enthalpy 298K = -599.921324
Free Energy 298K = -599.939515
SCF (TPSS-D3BJ,CPCM=C_6H_6/def2-TZVPP) Energy (ORCA5) = -599.9237347
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -599.9236601
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -599.3263109

K 0.0 0.0 0.0

$[Li(12\text{-}cr\text{-}4)_2]^+$ / $\mathbf{1}^+$
SCF (TPSS-D3BJ) Energy = -1238.860285
Enthalpy 0K = -1238.372141
Enthalpy 298K = -1238.343739
Free Energy 298K = -1238.428283
SCF (TPSS-D3BJ,CPCM=C_6H_6/def2-TZVPP) Energy (ORCA5) = -1238.897575
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -1238.86155
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -1236.203307

Li 0.00013 0.00060 0.00119
O -1.35813 -1.92661 -0.33403
O -1.34480 0.33767 -1.91686
O -1.32808 1.93419 0.33794
O -1.33817 -0.32906 1.92365
O   1.33079 -1.40210 -1.36850

```
O   1.33872 -1.37213  1.39371
O   1.35173  1.39218  1.36473
O   1.34426  1.36379 -1.40050
C  -2.38898 -0.62482 -2.10856
H  -2.69486 -0.64791 -3.16377
H  -3.26900 -0.36310 -1.50498
C  -1.82160 -1.96907 -1.69257
H  -2.56770 -2.76261 -1.82459
H  -0.93859 -2.19876 -2.29127
C  -2.39053 -2.10732  0.64243
H  -2.70182 -3.16082  0.67546
H  -3.27091 -1.50032  0.39012
C  -1.80378 -1.68737  1.97681
H  -2.53928 -1.81444  2.78094
H  -0.91859 -2.28688  2.19696
C  -2.36835  0.64790  2.11751
H  -2.67168  0.67482  3.17341
H  -3.25295  0.39870  1.51544
C  -1.78432  1.98397  1.69926
H  -2.51938  2.78723  1.83387
H  -0.89518  2.20269  2.29329
C  -2.36323  2.13187 -0.63303
H  -2.65735  3.19027 -0.66422
H  -3.25162  1.53920 -0.37498
C  -1.79085  1.70211 -1.97059
H  -2.52959  1.83817 -2.77025
C   1.80375 -0.61869  2.52465
H   2.54175 -1.19342  3.09806
H   0.91987 -0.44595  3.14107
C   2.38767  0.70838  2.07931
H   2.70350  1.30016  2.94990
H   3.26365  0.55651  1.43354
C   1.81466  2.52171  0.60730
H   2.55861  3.09307  1.17619
H   0.93117  3.14053  0.44135
C   2.38715  2.07557 -0.72486
H   2.70076  2.94564 -1.31873
H   3.26302  1.42806 -0.58020
C   1.79714  0.60309 -2.53172
H   2.53778  1.16936 -3.11000
H   0.90832  0.43820 -3.14332
C   2.37112 -0.72881 -2.08697
H   2.67852 -1.32526 -2.95734
H   3.25042 -0.58396 -1.44422
C   1.78390 -2.53777 -0.61438
H   2.51663 -3.11863 -1.18828
H   0.89311 -3.14465 -0.44337
C   2.36867 -2.09938  0.71501
H   2.67167 -2.97366  1.30813
H   3.25298 -1.46418  0.56701
H  -0.89877  2.28838 -2.19755
```

[Na(12-cr-4)$_2$ / 5$^+$

```
SCF (TPSS-D3BJ) Energy = -1393.643689
Enthalpy 0K = -1393.156417
Enthalpy 298K = -1393.127896
Free Energy 298K = -1393.212466
SCF (TPSS-D3BJ,CPCM=C6H6/def2-TZVPP) Energy (ORCA5) = -1393.681167
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -1393.644657
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -1390.745326

Na -0.00089 -0.00058  0.00013
O  -1.49937 -1.51728  1.29931
O  -1.49889 -1.29910 -1.51677
O  -1.49822  1.51692 -1.29929
O  -1.49868  1.29898  1.51670
O   1.49898 -0.54800  1.92058
O   1.49942 -1.92124 -0.54798
```

```
O   1.49888  0.54784 -1.92046
O   1.49844  1.92085  0.54813
C  -2.53782 -2.14157  0.53437
H  -3.40259 -1.47083  0.43972
H  -2.87555 -3.06093  1.03354
C  -1.95840 -2.47514 -0.83071
H  -1.07180 -3.10217 -0.71285
H  -2.70018 -3.01226 -1.43582
C  -2.53708 -0.53429 -2.14166
H  -3.40210 -0.43946 -1.47127
H  -2.87446 -1.03368 -3.06102
C  -1.95749  0.83070 -2.47533
H  -1.07075  0.71271 -3.10212
H  -2.69914  1.43575 -3.01270
C  -2.53657  2.14188 -0.53477
H  -3.40176  1.47165 -0.44037
H  -2.87360  3.06139 -1.03415
C  -1.95747  2.47524  0.83049
H  -1.07055  3.10186  0.71298
H  -2.69926  3.01262  1.43535
C  -2.53740  0.53463  2.14122
H  -3.40227  0.44021  1.47056
H  -2.87488  1.03413  3.06050
C  -1.95859 -0.83063  2.47512
H  -1.07194 -0.71302  3.10210
H  -2.70068 -1.43524  3.01239
C   1.95836 -1.90301  1.78736
H   1.07156 -2.52189  1.94132
H   2.69991 -2.13909  2.56147
C   2.53803 -2.16894  0.40758
H   3.40236 -1.51928  0.21382
H   2.87640 -3.21251  0.33738
C   1.95841 -1.78742 -1.90307
H   1.07147 -1.94154 -2.52170
H   2.70018 -2.56120 -2.13957
C   2.53755 -0.40741 -2.16891
H   3.40221 -0.21355 -1.51969
H   2.87539 -0.33692 -3.21264
C   1.95764  1.90308 -1.78716
H   1.07057  2.52152 -1.94128
H   2.69923  2.13945 -2.56115
C   2.53699  2.16923 -0.40731
H   3.40168  1.52005 -0.21352
H   2.87478  3.21299 -0.33698
C   1.95743  1.78746  1.90325
H   1.07041  1.94122  2.52185
H   2.69883  2.56162  2.13969
C   2.53722  0.40774  2.16919
H   3.40202  0.21428  1.52006
H   2.87493  0.33734  3.21297
```

$[K(12\text{-}cr\text{-}4)_2]^+$ / 6^+

```
SCF (TPSS-D3BJ) Energy = -1831.27369426
Enthalpy 0K = -1830.78772
Enthalpy 298K = -1830.758547
Free Energy 298K = -1830.847906
SCF (TPSS-D3BJ,CPCM=C6H6/def2-TZVPP) Energy (ORCA5) = -1831.311083
SCF (TPSS-D3BJ/def2-TZVPP) Energy (ORCA5) = -1831.274836
SCF (DLPNO-CCSD(T0)/def2-TZVPP) Energy = -1828.034757

K  -0.00115 -0.01156 -0.43707
O  -2.04017 -1.95607 -0.58602
O  -2.31096  0.53249 -1.97249
O  -1.80886  1.95336  0.45624
O  -1.54406 -0.53795  1.86135
O   1.58447  0.99983  1.67201
O   1.74234 -1.76814  0.91147
O   2.26840 -0.99486 -1.79796
```

O	2.10622	1.75850	-1.04065
C	-2.77235	-1.80901	-1.81242
H	-3.56162	-2.56913	-1.88637
H	-2.04538	-1.98632	-2.60949
C	-3.37805	-0.42255	-1.96517
H	-3.94111	-0.36741	-2.90819
H	-4.07601	-0.21212	-1.14384
C	-2.73413	1.88614	-1.74657
H	-3.62175	2.12023	-2.34943
H	-1.90631	2.51151	-2.09129
C	-3.01792	2.16879	-0.27930
H	-3.35273	3.20981	-0.16194
H	-3.81751	1.51512	0.09402
C	-1.99663	1.80848	1.87288
H	-2.67575	2.58305	2.25391
H	-1.00646	1.95911	2.30972
C	-2.52163	0.43212	2.25306
H	-2.68530	0.38671	3.33978
H	-3.48239	0.23148	1.76069
C	-2.02874	-1.88803	1.80689
H	-2.61280	-2.12710	2.70603
H	-1.13206	-2.51308	1.79340
C	-2.86572	-2.15943	0.56658
H	-3.23255	-3.19594	0.58965
H	-3.73926	-1.49466	0.53501
C	1.88612	-0.06534	2.58689
H	0.91644	-0.40008	2.96259
H	2.48709	0.30591	3.42808
C	2.60654	-1.22485	1.91630
H	3.55237	-0.89012	1.46978
H	2.84309	-1.99400	2.66609
C	2.40351	-2.61471	-0.04077
H	1.60510	-3.18004	-0.52894
H	3.07199	-3.32272	0.46760
C	3.18679	-1.82632	-1.07907
H	3.96193	-1.21487	-0.59828
H	3.68647	-2.52137	-1.76936
C	2.89371	0.06684	-2.53574
H	2.14849	0.39380	-3.26578
H	3.77284	-0.30437	-3.07918
C	3.29284	1.23449	-1.64691
H	4.00606	0.90924	-0.87777
H	3.78219	2.01027	-2.25364
C	2.34997	2.61471	0.08626
H	1.41739	3.16433	0.23886
H	3.14829	3.33420	-0.14013
C	2.69991	1.83485	1.34457
H	3.60230	1.22897	1.18817
H	2.90434	2.53495	2.16789

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