Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Revealing the remarkable structural diversity of the alkali metal transfer agents of the *trans*-calix[2]benzene[2]pyrrolidide ligand

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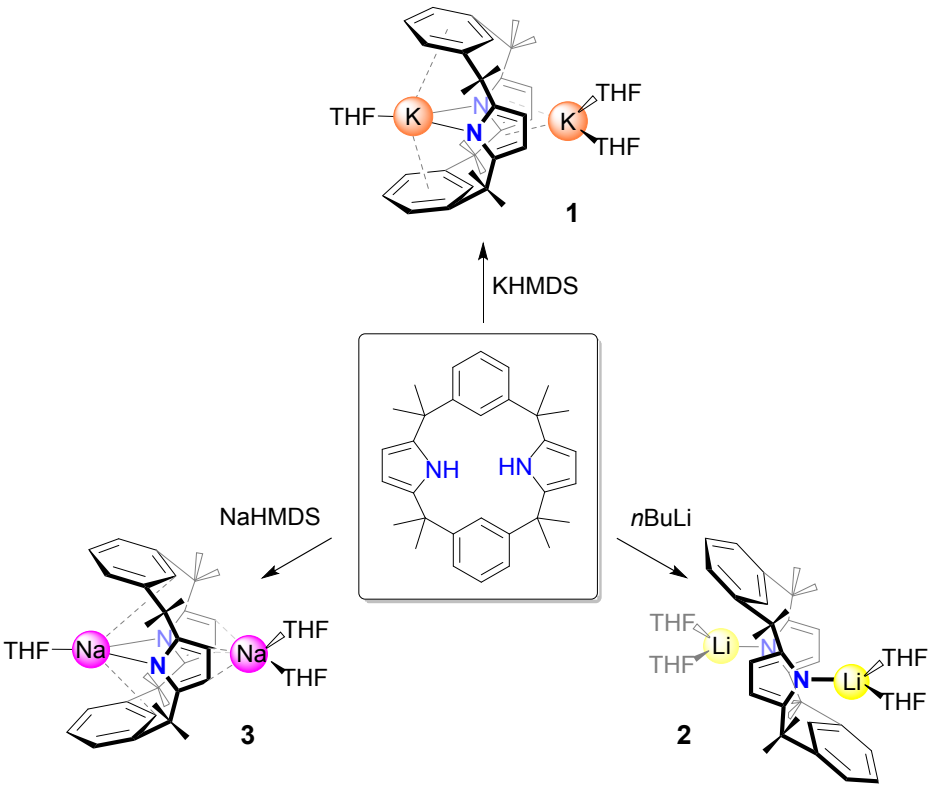
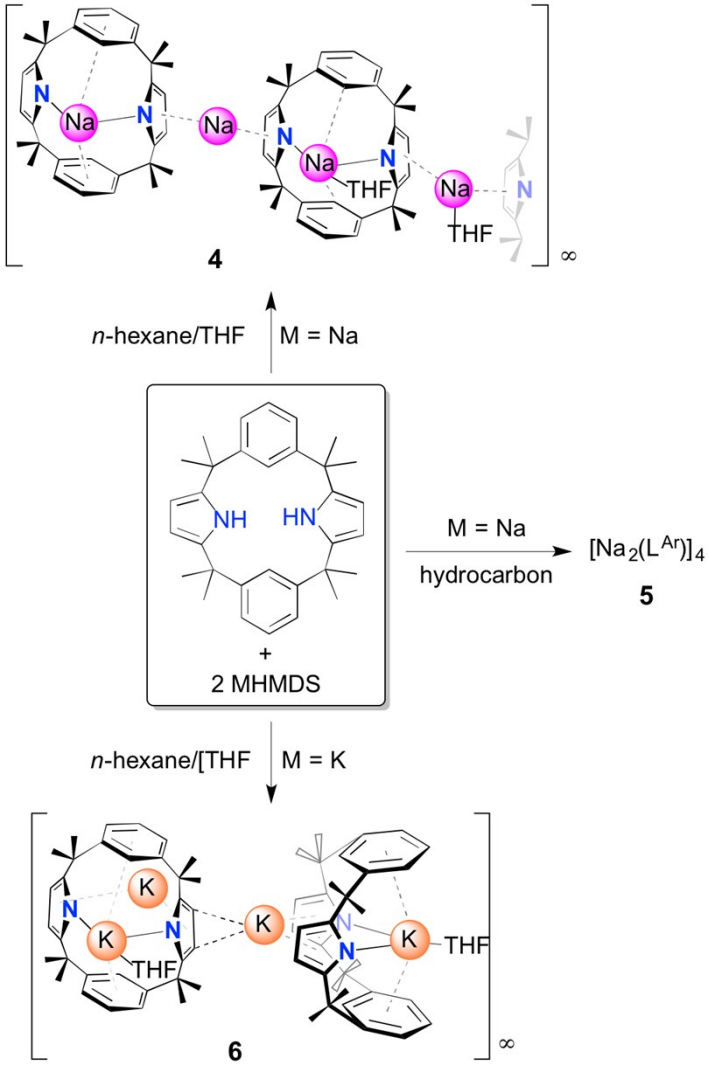
Contents



Scheme S1. Reaction scheme for discrete dinuclear monomers.



Scheme S2. Reaction scheme for polymers and tetramer.

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were performed under a protective atmosphere of dry pure argon gas using standard Schlenk tube or glovebox techniques. Solvents were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. Methylcyclohexane was distilled over sodium metal and stored with activated molecular sieves (4 Å) prior to use. Deuterated NMR solvents were degasified and stored over molecular sieves (4 Å) prior to use. *n*BuLi (1.6 M in *n*-hexane) solution was purchased from Aldrich and titrated prior to use. Sodium bis(trimethylsilyl)amide (NaHMDS) and potassium bis(trimethylsilyl)amide (KHMDS) were purchased from Aldrich and used as received. *trans*-Calix[2]benzene[2]pyrrole, H_2L^{Ar}, was prepared according to literature procedures.[1] NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer, operating at 400.1 MHz for ^{1}H, 155.5 MHz for ^{7}Li and 100.6 MHz for ^{13}C. ^{1}H and ^{13}C{^{1}H} spectra were referenced to the appropriate residual solvent signal, ^{7}Li NMR spectra were referenced against LiCl in D_2O (∂ = 0.00 ppm). Elemental analyses of the compounds **1** – **6** were carried out using a Perkin Elmer 2400 elemental analyser.

Crystal Structure Determinations. Single-crystal data were measured at 123(2) K on Oxford Diffraction Diffractometers with Cu-*Kα* radiation (λ = 1.5418 Å) for **1**, **2**, **4**, **5** and **6**. Measurements were at 170(2) K with Cu-*Kα* radiation (λ = 1.5418 Å) for **3**. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL programs.[2] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed and allowed to ride on their parent atoms. For **5**, the equivalent of 419 electrons were removed from approx 2600 Å^3 of "void" space per unit cell using the program SQUEEZE.[3] This electron density was believed to be due to disordered and partially present solvent molecules. Two $CH(CH_3)_2$ units of **5** were modelled as disordered over two sites as were tetrahydrofuran ligands of **1**, **3**, **4** and **6.** The geometries and displacement parameters of these groups were restrained to approximate typical values. In **4** the disorder of the thf ligands is associated with disordered positions for two of the four crystallographically independent Na sites. Caution is thus needed

when interpreting the geometric details of Na1 and Na4. CCDC-1499377 (**1**), CCDC-1499378 (**2**), CCDC-1499379 (**3**), CCDC-1499380 (**4**), CCDC-1499381 (**5**) and CCDC-1499382 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

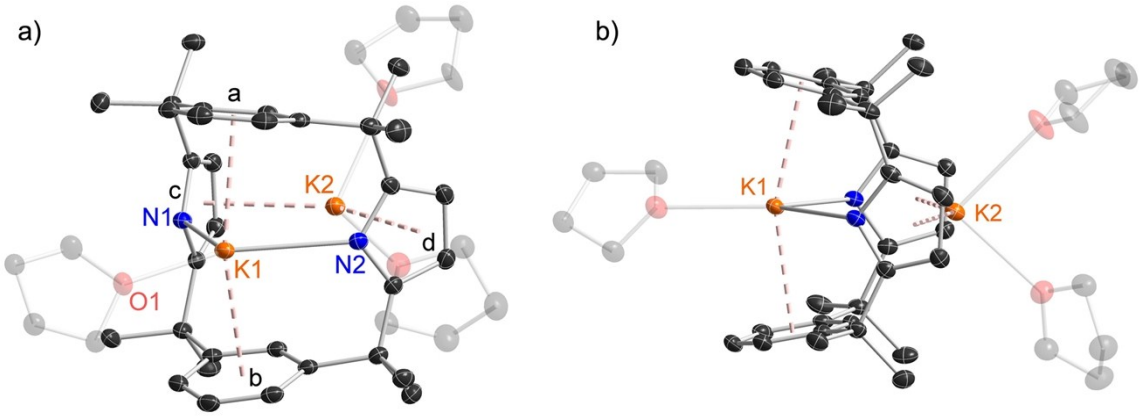


Figure 1. Molecular structure of $[K_2(L^{Ar})(thf)_3]$, **1**. Thermal ellipsoids are displayed at 35% probability, hydrogen atoms and one disordered component of two tetrahydrofuran ligands have been omitted for clarity. The dashed lines illustrate the K···C interactions. C_6H_4 and C_4H_2(pyrrolide) centroids are labelled as a – b and c – d, respectively. Selected bond lengths [Å] and angles [º]: K1-N1 2.8822(15); K1-N2 2.8815(14); K2-N1 3.3262(14) K2-N2 3.0667(15); K1-O1 2.8349(14); K1-a 2.9088; K1-b 2.8972; K2-c 2.9258; K2-d 2.8736; N2-K1-N1 102.00(4); a-K1-b 160.122; c-K2-d 144.563.

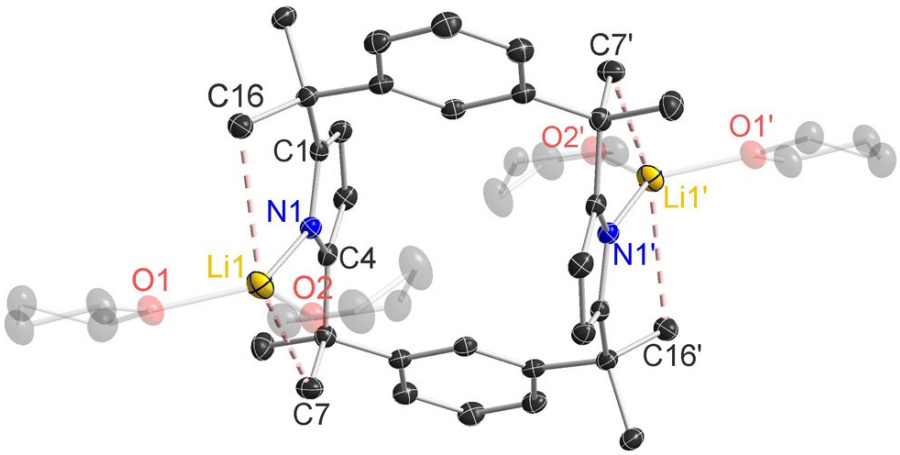


Figure 2. Molecular structure of $[Li_2(L^{Ar})(thf)_4]$, **2**. Thermal ellipsoids are displayed at 35% probability and hydrogen atoms have been omitted for clarity. The dashed lines represent short Li···Me contacts. The symmetry operation used to generate equivalent atoms denoted with ´ is -x+2,-y+1,-z+1. Selected bond lengths [Å] and angles [º]: Li1-N1 1.940(3); Li1-O1 1.944(3); Li1-O2 1.899(3); Li1-C7 2.727(3); Li1-C16 2.815(3); Li1-N1-C4 125.76(13); Li1-N1-C1 127.05(13); N1-Li1-C7 73.81(10); N1-Li1-C16 72.887(94); N1-Li1-O1 128.69(16); N1-Li1-O2 122.32(16); O1-Li1-O2 108.61(14); O1-Li1-C7 102.78(12); O2-Li1-C7 102.14(13); O1-Li1-C16 94.57(12); O2-Li1-C16 99.15(12); C7-Li1-C16 146.419; C4-N1-C1 105.68(12).

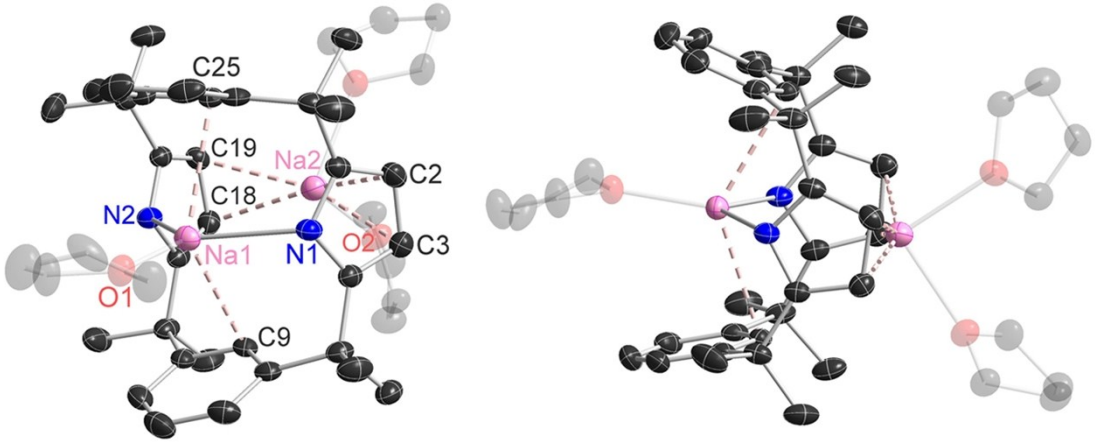


Figure 3. Molecular structure of $[Na_2(L^{Ar})(thf)_3]$, **3**. Thermal ellipsoids are displayed at 35% probability, hydrogen atoms and one disordered component of each tetrahydrofuran ligands have been omitted for clarity. The dashed lines represent short Na···C contacts. Selected bond lengths [Å] and angles [º]: Na1-O1 2.2467(14); Na1-N2 2.4867(16); Na1-N1 2.5006(16); Na1-C9 2.8254(17); Na1-C25 2.8509(16); Na2-O2 2.3547(15); Na2-C2 2.756(2); Na2-C18 2.8443(18); Na2-C19 2.8653(18); Na2-C3 2.8954(19); N2-Na1-N1 124.51(5); N2-Na1-C9 80.39(5); N1-Na1-C9 77.99(5); N2-Na1-C25 78.48(5); N1-Na1-C25 78.76(5); C9-Na1-C25 131.15(5); C2-Na2-C18 158.55(6); C2-Na2-C19 147.54(6); C18-Na2-C19 28.75(5); C2-Na2-C3 28.87(5); C18-Na2-C3 139.63(6); C19-Na2-C3 157.12(6).

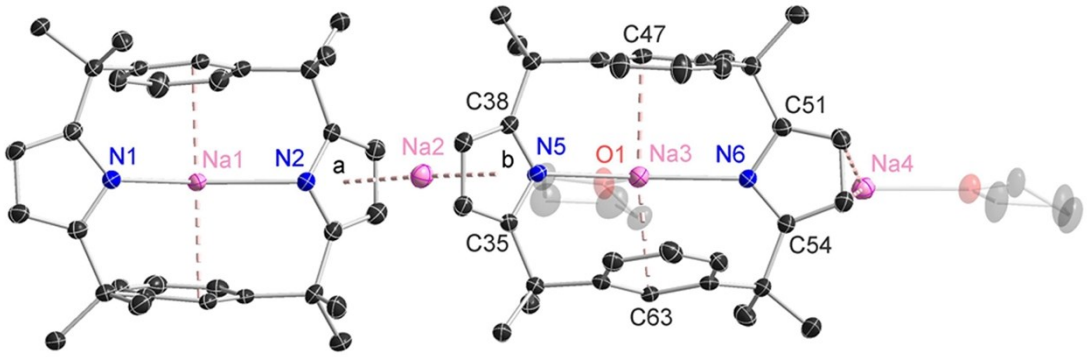


Figure 4. Molecular structure of $[\{Na_2(L^{Ar})(thf)_2\}\{Na_2(L^{Ar})\}]_\infty$, **4**, showing the contents of the asymmetric unit. Thermal ellipsoids are displayed at 35% probability. Hydrogen atoms, two disordered molecules of thf of crystallisation, and disordered components of a Na-thf moiety and a Na metal centre have been omitted for clarity. The disordered Na sites are Na1 and Na4. The dashed lines illustrate the Na···C interactions. a – b labels correspond to a centroid from C_4H_2N (pyrrolide). Selected bond lengths [Å] and angles [º]: Na2-N2 2.697(4); Na2-N5 2.716(4); Na2-a 2.3671 ; Na2-b 2.3582 ; Na3-O1 2.390(4); Na3-N5 2.435(3); Na3-N6 2.446(3); Na3-C47 2.718(4); Na3-C63 2.739(4); N2-Na2-N5 177.19(13); a-Na2-b 177.307; O1-Na3-N5 92.56(12); O1-Na3-N6 101.27(13); N5-Na3-N6 166.16(14); O1-Na3-C47 101.43(14); N5-Na3-C47 86.70(12); N6-Na3-C47 90.29(12); O1-Na3-C63 104.85(14); N5-Na3-C63 90.25(11); N6-Na3-C63 86.47(12); C47-Na3-C63 153.65(14); C35-N5-Na3 122.6(2); C38-N5-Na3 126.2(2); Na3-N5-Na2 138.96(14); C54-N6-Na3 126.3(3); C51-N6-Na3 122.5(3).

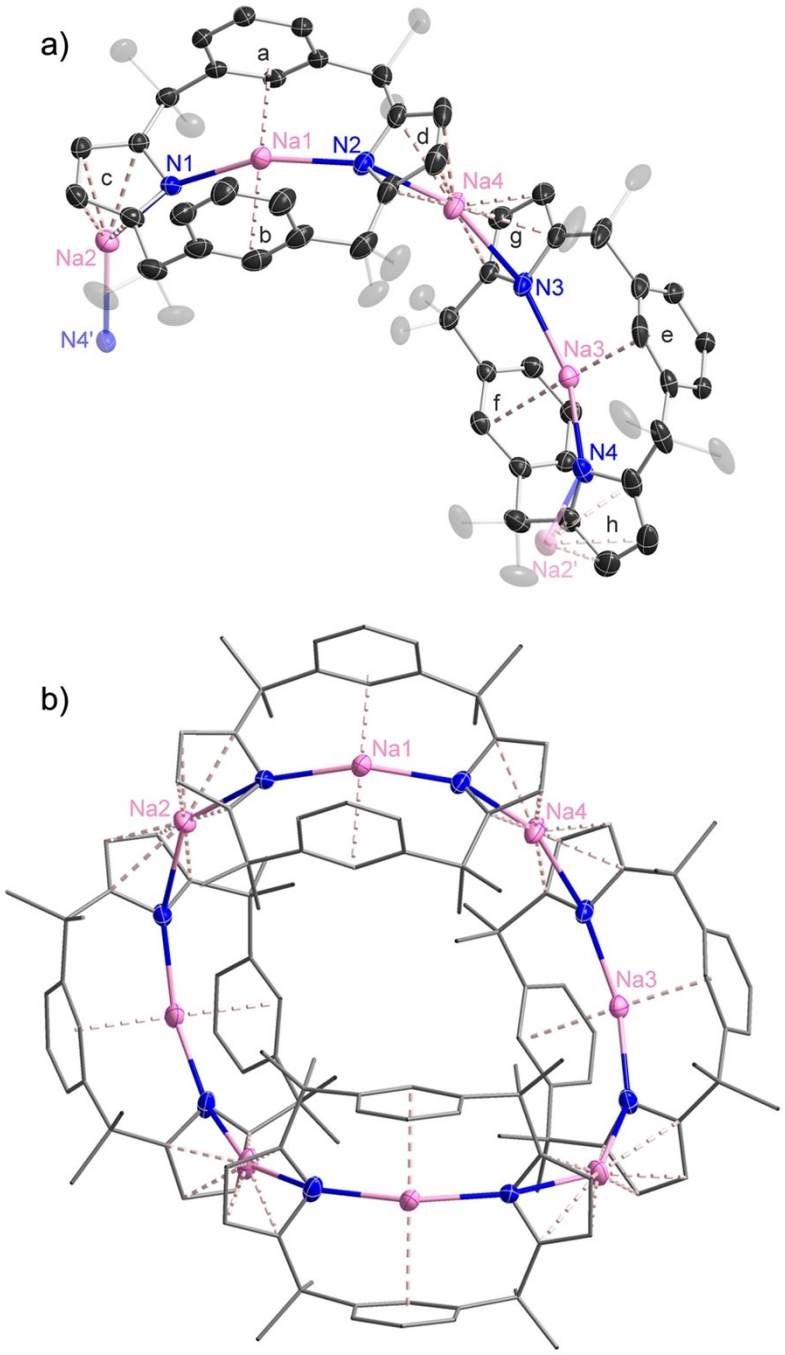


Figure 5. a) Molecular structure of $[Na_2(L^{Ar})]_4$, **5**, showing the contents of the asymmetric unit which corresponds to a quarter turn of the cyclic structure. b) Extended cyclic three dimensional structural framework of **5** showing atomic connectivity between the metal and the macrocyclic ligand. Thermal ellipsoids are displayed at 35% probability, hydrogen atoms and one disordered component of two $C(CH_3)_2$ groups have been omitted for clarity. The dashed lines represent Na···C contacts. The symmetry operation used to generate equivalent atoms denoted with ´ is -x+1,y,-z+3/2. a – b, e – f labels correspond to centroids $(C_q)_2CH$ whilst c – d, g – h labels correspond to a centroids C_4H_2 (pyrrolide). Selected bond lengths [Å] and angles [º]: Na1-N1 2.4063(18); Na1-N2 2.4046(18); Na3-N3 2.3935(17); Na3-N4 2.4070(16); Na2-N1 2.6623(17); Na4-N2 2.6104(17); Na4-N3 2.5496(18); Na2´-N4 2.6559(17); Na1-a 2.710(2)-2.8577(19); Na1-b 2.7186(18)-2.8670(18); Na2-c 2.659(2)-2.710(2); Na3-e 2.707(2)-2.870(2); Na3-f 2.722(2)-2.968(2); Na4-d 2.601(2)-2.787(3); Na4-g 2.601(2)-2.841(3); Na2´-h 2.656(2)-2.713(2); N1-Na1-N2 153.23(7); N3-Na3-N4 151.90(7); Na1-N1-Na2 145.29(8); Na1-N2-Na4 149.73(9); N4´-Na2-N1 139.29(6); Na3-N3-Na4 143.77(8); Na3-N4-Na2´ 153.69(8); N3-Na4-N2 158.03(7), a-Na1-b 174.3; c-Na2-h´ 164.0; e-Na3-f 178.4; d-Na4-g 154.1.

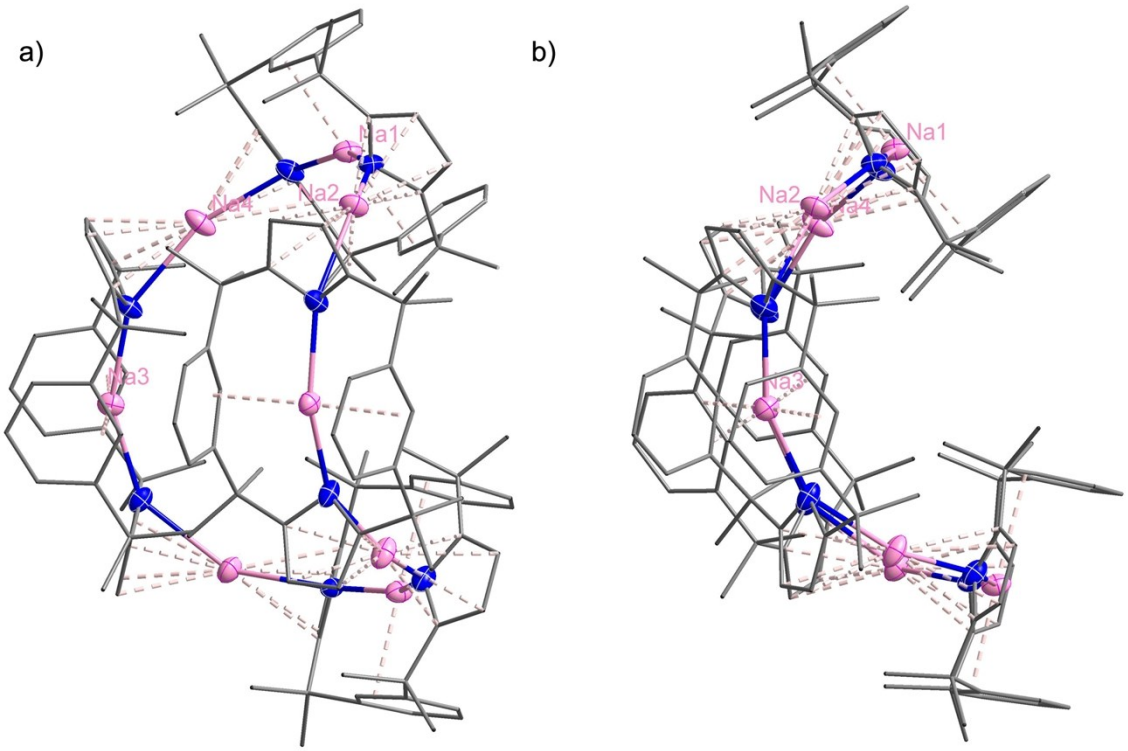


Figure 6. Side view of the core structure of $[Na_2(L^{Ar})]_4$, **5**. Thermal ellipsoids are displayed at 35% probability, hydrogen atoms have been omitted for clarity. C and N atoms are pictured as capped sticks. The dashed lines represent Na···C contacts.

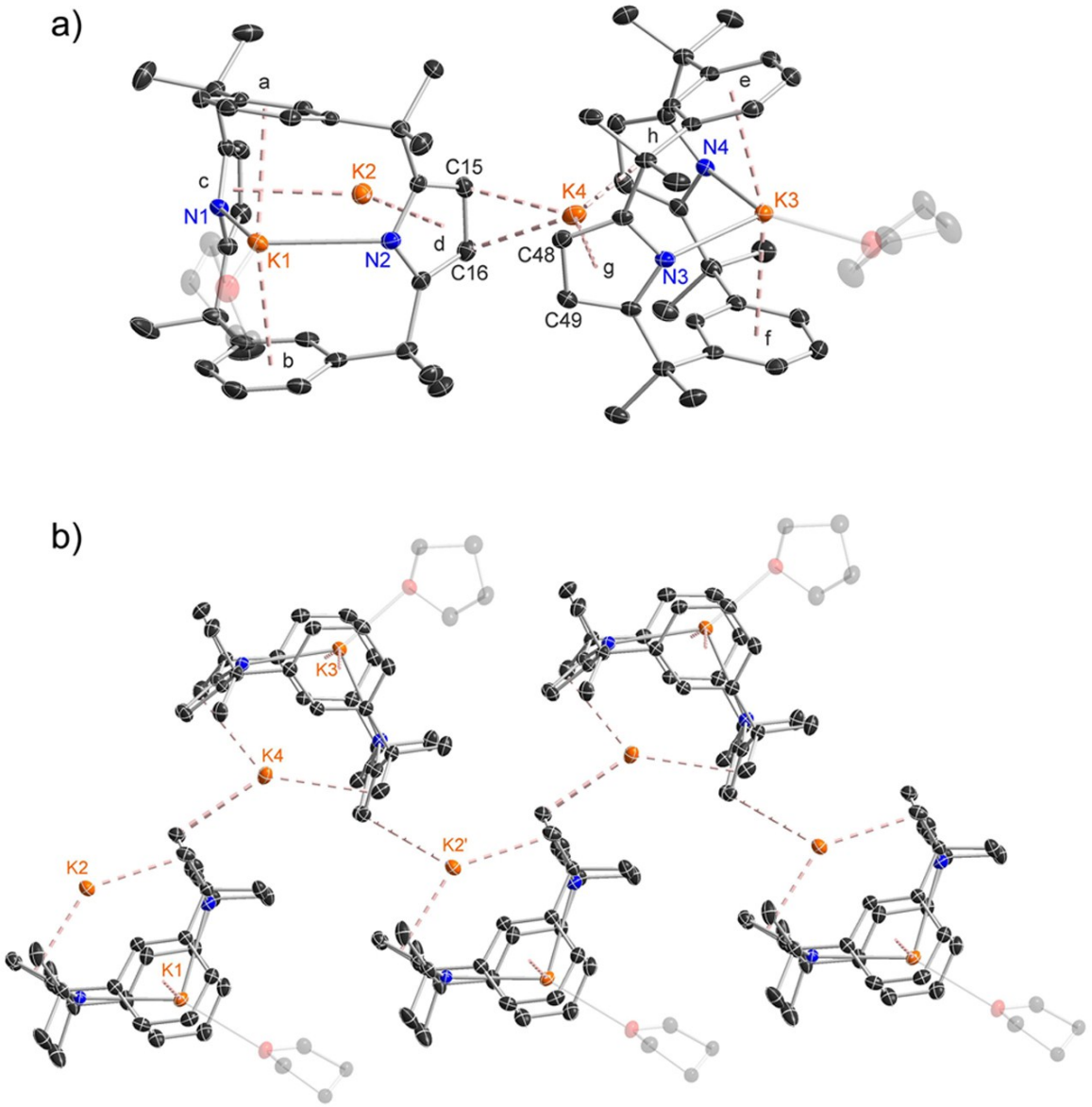


Figure 7. a) Molecular structure of $[K_2(L^{Ar})(thf)]_\infty$, **6**, showing the contents of the asymmetric unit. b) Section of the extended two dimensional structural framework showing the atomic connectivity between the metal and the macrocyclic ligand. Thermal ellipsoids are displayed at 35% probability, hydrogen atoms and one disordered component of tetrahydrofuran ligands have been omitted for clarity. The dashed lines illustrate the K···C interactions. a – b, e – f labels correspond to a centroid from C_6H_4 and c – d, g – h labels correspond to a centroid from C_4H_2 (pyrrolide). The symmetry operation used to generate equivalent atoms denoted with ´ is x+1,y,z. Selected bond lengths [Å] and angles [º]: K1-N1 2.8951(18); K1-N2 2.8503(18); K3-N3 2.8610(17); K3-N4 2.8187(18); K4-C15 3.046(2); K4-C16 3.309(2); K2´-C48 3.235(2); K2´-C49 3.089(2); K1-a 2.9161; K1-b 2.8715; K2-c 2.8490; K2-d 2.9886; K3-e 2.9325; K3-f 2.9175; K4-g 2.9674; K4-h 2.8759; N1-K1-N2 104.86(5); N3-K3-N4 105.24(5); C15-K2-C16 26.77(6); C15-K4-C16 25.34(5); C48-K2´-C49 25.91(5); C16-C15-K4 87.79(13); C15-C16-K4 66.87(12); a-K1-b 161.380; c-K2-d 140.055; e-K3-f 162.858; g-K4-h 137.746; C15-K4-g 138.213; C16-K4-g 130.261; C15-K4-h 83.837; C16-K4-h 88.851.

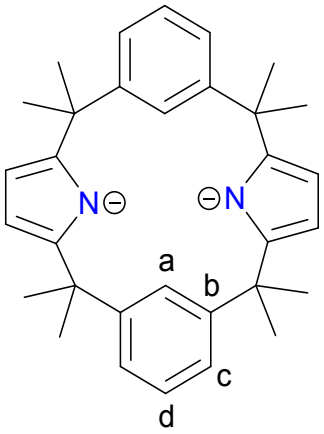
Table 1. Selected crystallographic and refinement data for **1** – **3**.

	1	**2**	**3**
Formula	C_{44} H_{60} K_2 N_2 O_3	C_{48} H_{68} Li_2 N_2 O_4	C_{44} H_{60} N_2 Na_2 O_3
Fw	743.14	750.92	710.92
Cryst. System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P\ 2_1/n$	$P\ 2_1/n$
Wavelength/Å	1.54184	1.54184	1.54184
a/Å	21.3422(2)	10.69220(10)	10.30734(17)
b/Å	9.86590(10)	15.3289(2)	27.6447(4)
c/Å	19.6135(2)	12.9982(2)	14.8943(3)
α/°	90	90	90
β/°	103.0860(10)	90.0580(10)	105.5875(17)
γ/°	90	90	90
Volume/Å^3	4022.57(7)	2130.40(5)	4087.94(12)
Z	4	2	4
Temp./K	123(2)	123(2)	170(2)
Refls. Collect.	27454	27244	28493
$2\theta_{max}$	139.98	139.99	146.09
R_{int}	0.0297	0.0536	0.0265
Goodness of fit	1.023	1.029	1.061
$R[F^2>2\sigma]$, F	0.0429	0.0522	0.0506
R_w(all data), F^2	0.1171	0.1456	0.1448

Table 2. Selected crystallographic and refinement data for **4** – **6**.

	4	**5**	**6**
Formula	C_{80} H_{104} N_4 Na_4 O_4	C_{128} H_{144} N_8 Na_8	C_{72} H_{88} K_4 N_4 O_2
Fw	1277.63	1978.42	1197.86
Cryst. System	Monoclinic	Orthorhombic	Triclinic
Space Group	C c	Pbcn	P -1
Wavelength/Å	1.54184	1.54184	1.54184
a/Å	10.2275(2)	19.8237(3)	10.4694(2)
b/Å	35.0736(6)	19.6671(3)	16.0165(4)
c/Å	19.9910(3)	32.4878(3)	20.7659(6)
α/°	90	90	109.148(3)
β/°	90.7580(10)	90	102.765(2)
γ/°	90	90	92.213(2)
Volume/Å^3	7170.4(2)	12666.2(3)	3184.73(15)
Z	4	4	2
Temp./K	123(2)	123(2)	123(2)
Refls. Collect.	17946	69945	32341
$2\theta_{max}$	139.99	139.99	139.98
R_{int}	0.0228	0.0271	0.0457
Goodness of fit	1.041	1.035	1.009
$R[F^2>2\sigma]$, F	0.0546	0.0526	0.0439
R_w(all data), F^2	0.1556	0.1484	0.1221

Synthesis of complexes 1 – 6



Synthesis of $[K_2(L^{Ar})(thf)_3]$, 1

Potassium bis(trimethylsilyl)amide (279.2 mg, 1.4 mmol) was added via solid addition tube to a solution of H_2L^{Ar} (315.4 mg, 0.7 mmol) in tetrahydrofuran (10 mL) under argon atmosphere at room temperature. The resulting solution was stirred for 3 h at room temperature and then it was filtered. The resulting colourless solution was concentrated under vacuum (2 mL). Suitable crystals of **1** for an X-ray diffraction study were obtained at -26°C. The crystalline material was filtered, washed with n-hexane (2 x 3 mL) and dried under vacuum for 20 min (115 mg, 0.15 mmol, 22%). ^{1}H NMR (400.13 MHz, [D_8]thf, 25°C): δ 7.16 – 7.12 (m, 4H; *c*-C*H*), 7.09 – 7.05 (m, 2H; *d*-C*H*), 6.69 (br t, *J*(H,H)=1.7 Hz, 2H; *a*-C*H*), 5.73 (s, 4H; C*H*-pyrrolide), 3.61 (m; OCH_2-thf), 1.77 (m; CH_2-thf), 1.42 ppm (s, 24H; CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, [D_8]thf, 25°C): δ 154.5 (*b*-C_q), 152.6 (C_q-pyrrolide), 129.5 (*a*-*C*H), 127.0 (*d*-*C*H), 122.0 (*c*-*C*H-Ar), 98.2 (*C*H-pyrrolide), 67.2 (O*C*H_2-thf), 41.7 (C_q-$(CH_3)_2$), 31.2 (CH_3), 25.1 ppm (CH_2-thf). We can observe by NMR spectroscopy that a small amount of thf was removed under vacuum. Present within the [D_8]thf solution is also a small amount of H_2L^{Ar} which is presumably a result of unavoidable hydrolysis. Elemental analysis calcd. (%) for $C_{35}H_{42}K_2N_2O_{0.75}$ $[K_2(L^{Ar})(thf)_{0.75}]$: C 72.36, H 7.29, N 4.82; found: C 71.65, H 7.29, N 5.28.

Synthesis of $[Li_2(L^{Ar})(thf)_4]$, 2

Commercial *n*-butyllithium (0.87 mL, 1.6M solution in *n*-hexane, 1.4 mmol) was added via syringe to a Schlenk tube containing a suspension of H_2L^{Ar} (315.4 mg, 0.7 mmol) in *n*-hexane (10 mL) under argon atmosphere at room temperature. The

resulting suspension was stirred for 3 h at room temperature and then the solvent was removed under vacuum to give a white solid. Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane (10 mL) into a tetrahydrofuran (5 mL) solution of **2**. The crystals were collected, washed with *n*-hexane (2 x 3 mL) and dried under vacuum for 20 min (410 mg, 0.55 mmol, 78%). ^{1}H NMR (400.13 MHz, C_6D_6/[D_8]thf, 25°C): δ 7.94 (br s, 2H; *a*-C*H*), 7.14 (m, overlapping with C_6D_6, 4H; *c*-C*H*), 7.01 (t, *J*(H,H)=7.7 Hz, 2H; *d*-C*H*), 6.08 (s, 4H; C*H*-pyrrolide), 3.50 (m, 12H; OCH_2-thf), 1.69 (s, 24H; CH_3), 1.48 ppm (m, 12H; CH_2-thf). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6/[D_8]thf, 25°C): δ 152.3 (*b*-C_q), 148.4 (C_q-pyrrolide), 128.0 (overlapping with C_6D_6, *d*-*C*H), 125.4 (br, *a*-*C*H), 122.1 (*c*-*C*H), 101.4 (*C*H-pyrrolide), 67.0 (O*C*H_2-thf), 41.2 (C_q-$(CH_3)_2$), 32.0 (*C*H_3), 24.8 ppm (*C*H_2-thf). ^{7}Li NMR (155.5 MHz, C_6D_6/[D_8]thf, 25°C): δ 4.67 ppm. Elemental analyses in combination with NMR spectroscopy reveal that the thf is partially removed under vacuum (*c.a.* 19%). Elemental analysis calcd. (%) for $C_{45}H_{62}Li_2N_2O_{3.25}$ [$Li_2(L^{Ar})(thf)_{3.25}$]: C 77.56, H 8.97, N 4.02; found: C 77.01, H 9.24, N 3.85.

Synthesis of [$Na_2(L^{Ar})(thf)_3$], 3

Sodium bis(trimethylsilyl)amide (256.7 mg, 1.4 mmol) was added via solid addition tube to a solution of H_2L^{Ar} (315.4 mg, 0.7 mmol) in tetrahydrofuran (10 mL) under argon atmosphere at room temperature. The resulting solution was stirred for 3 h at room temperature and it was filtered. The resulting colourless solution was concentrated under vacuum (2 mL) and **3** was crystallised as colourless crystals suitable for an X-ray diffraction study at -26°C for 48 h. **3** was filtered, washed with *n*-hexane (2 x 3 mL), and dried under vacuum for 20 min (175 mg, 0.24 mmol, 35%). ^{1}H NMR (400.13 MHz, [D_8]thf, 25°C): δ 7.10 – 7.08 (m, 4H; *c*+*d*-C*H*), 7.05 – 7.01 (m, 2H; *c*+*d*-C*H*), 6.88 (br t, *J*(H,H)=1.7 Hz, 2H; *a*-C*H*), 5.79 (s, 4H; C*H*-pyrrolide), 3.61 (m; OCH_2-thf), 1.77 (m; CH_2-thf), 1.42 ppm (s, 24H; CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, [D_8]thf, 25°C): δ 153.3 (*b*-C_q), 152.9 (C_q-pyrrolide), 128.0 (*d*-*C*H), 127.3 (*a*-*C*H), 121.8 (*c*-*C*H), 97.4 (*C*H-pyrrolide), 68.02 (O*C*H_2-thf), 41.7 (C_q-$(CH_3)_2$), 31.0 (*C*H_3), 26.1 (*C*H_2-thf) ppm. Elemental analyses in combination with NMR spectroscopy reveal the thf is partially removed under vacuum (*c.a.* 50%).

Elemental analysis calcd. (%) for $C_{38}H_{48}N_2Na_2O_{1.5}$ [$Na_2(L^{Ar})(thf)_{1.5}$]: C 75.72, H 8.03, N 4.65; found: C 75.30, H 8.30, N 4.66.

Synthesis of $[\{Na_2(L^{Ar})(thf)_2\}\{Na_2(L^{Ar})\}]_\infty$, 4

Sodium bis(trimethylsilyl)amide (256.7 mg, 1.4 mmol) was added via solid addition tube to a solution of H_2L^{Ar} (315.4 mg, 0.7 mmol) in tetrahydrofuran (10 mL) under argon atmosphere at room temperature. The resulting solution was stirred for 3 h at room temperature and then it was filtered. The resulting colourless solution was concentrated under vacuum (4 mL) and crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane (10 mL) into the tetrahydrofuran solution of **4**. The crystals were filtered, washed with *n*-hexane (2 x 3 mL), and dried under vacuum for 20 min (85 mg, 0.15 mmol, 21%). ^{1}H NMR (400.13 MHz, C_6D_6/[D_8]thf, 25°C): δ 7.18 (dd, *J*(H,H)=7.7 Hz, 1.8 Hz, 4H; *c*-C*H*), 7.03 (t, *J*(H,H)=7.7 Hz, 1H; *d*-C*H*), 7.00 (t, *J*(H,H)=7.7 Hz, 1H; *d*-C*H*), 6.93 (br s, 2H; *a*-C*H*), 6.01 (s, 4H; C*H*-pyrrolide), 3.53 (m; OCH_2-thf), 1.58 (s, 24H; CH_3), 1.49 ppm (m; CH_2-thf). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6/[D_8]thf, 25°C): δ 153.5 (C_q-pyrrolide), 153.2 (*b*-C_q), 127.9 (overlapping with C_6D_6, *d*-*C*H), 127.4 (*a*-*C*H), 121.4 (*c*-*C*H), 97.3 (*C*H-pyrrolide), 67.0 (O*C*H_2-thf), 41.7 (C_q-(CH_3)$_2$), 31.0 (*C*H_3), 24.8 ppm (*C*H_2-thf). Elemental analyses in combination with NMR spectroscopy reveal that 3 molecules of thf are present within the isolated compound **4** which is in agreement with the presence of several molecules of thf of crystallisation within the crystal lattice of **4**. This solvent is only partially removed under vacuum. Present within the C_6D_6/[D_8]thf solution are residual resonances for H_2L^{Ar} which is the result of unavoidable hydrolysis. Elemental analysis calcd. (%) for $C_{38}H_{48}N_2Na_2O_{1.5}$ $[\{Na_2(L^{Ar})(thf)_{1.5}\}\{Na_2(L^{Ar})\}]_\infty$: C 75.72, H 8.03, N 4.65; found: C 75.70, H 8.48, N 4.67.

Synthesis of $[Na_2(L^{Ar})]_4$, 5

Sodium bis(trimethylsilyl)amide (256.7 mg, 1.4 mmol) was added via solid addition tube to a diluted solution of H_2L^{Ar} (315.4 mg, 0.7 mmol) in methylcyclohexane (65 mL) under argon atmosphere. The reaction mixture was stirred for 6 h at room temperature. The reaction mixture was filtered to give a colourless solution which was concentrated under vacuum (c.a. 35 mL). Suitable crystals of **5** for an X-ray diffraction study were obtained at 4°C for 48 h. **5** was filtered, washed with n-hexane (2 x 3 mL) and dried under vacuum for 20 min (130 mg, 0.065 mmol, 38%). Alternatively, **5** can be crystallised by slow diffusion of *n*-hexane into the methylcyclohexane solution of **5** at room temperature. ^{1}H NMR (400.13 MHz,

C_6D_6/[D_8]thf, 25°C): δ 7.15 (dd, *J*(H,H)=7.6 Hz, 1.8 Hz, 4H; *c*-C*H*), 6.99 (t, *J*(H,H)=7.7 Hz, 2H; *d*-C*H*), 6.90 (br t, 2H; *a*-C*H*), 5.97 (s, 4H; C*H*-pyrrolide), 1.54 ppm (s, 24H; CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6/[D_8]thf, 25°C): δ 153.4 (C_q-pyrrolide), 153.2 (*b*-C_q), 127.9 (overlapping with C_6D_6, *d*-*C*H), 127.6 (*a*-*C*H), 121.4 (*c*-*C*H), 97.3 (*C*H-pyrrolide), 41.7 (C_q-$(CH_3)_2$), 31.0 ppm (CH_3). Present within the C_6D_6/[D_8]thf solution are residual resonances for H_2L^{Ar} which is the result of unavoidable hydrolysis, and for methylcyclohexane of crystallisation. Elemental analysis calcd. (%) for $C_{32}H_{36}N_2Na_2$: C 77.70, H 7.34, N 5.66; found: C 77.49, H 7.46, N 5.70.

Synthesis of $[K_2(L^{Ar})(thf)]_\infty$, 6

Potassium bis(trimethylsilyl)amide (279.2 mg, 1.4 mmol) was added via solid addition tube to a solution of H_2L^{Ar} (315.4 mg, 0.7 mmol) in tetrahydrofuran (10 mL) under argon atmosphere at room temperature. The resulting solution was stirred for 3 h at room temperature and then it was filtered. The solution was concentrated under vacuum (3 mL) and crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane (10 mL) into the tetrahydrofuran solution of **6**. The crystals were collected, washed with *n*-hexane (2 x 3 mL) and dried under vacuum (220 mg, 0.37 mmol, 53%). ^1H NMR (400.13 MHz, C_6D_6/[D_8]thf, 25°C): δ 7.21 (dd, *J*(H,H)=7.7 Hz, 1.8 Hz, 4H; *c*-C*H*), 6.98 (t, *J*(H,H)=7.7 Hz, 2H; *d*-C*H*), 6.86 (br t, *J*(H,H)=1.8 Hz, 2H; *a*-C*H*), 6.07 (s, 4H; C*H*-pyrrolide), 3.54 (m; OCH_2-thf), 1.66 (s, 24H; CH_3), 1.47 ppm (m; CH_2-thf). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6/[D_8]thf, 25°C): δ 154.6 (*b*-C_q), 152.9 (C_q-pyrrolide), 129.3 (*a*-*C*H), 127.0 (*d*-*C*H), 121.9 (*c*-*C*H), 98.5 (*C*H-pyrrolide), 67.0 (O*C*H_2-thf), 41.7 (C_q-$(CH_3)_2$), 31.2 (CH_3), 24.7 ppm (CH_2-thf). Elemental analysis calcd. (%) for $C_{36}H_{44}K_2N_2O$: C 72.19, H 7.40, N 4.68; found: C 72.14, H 7.70, N 4.74.

NMR SPECTRA

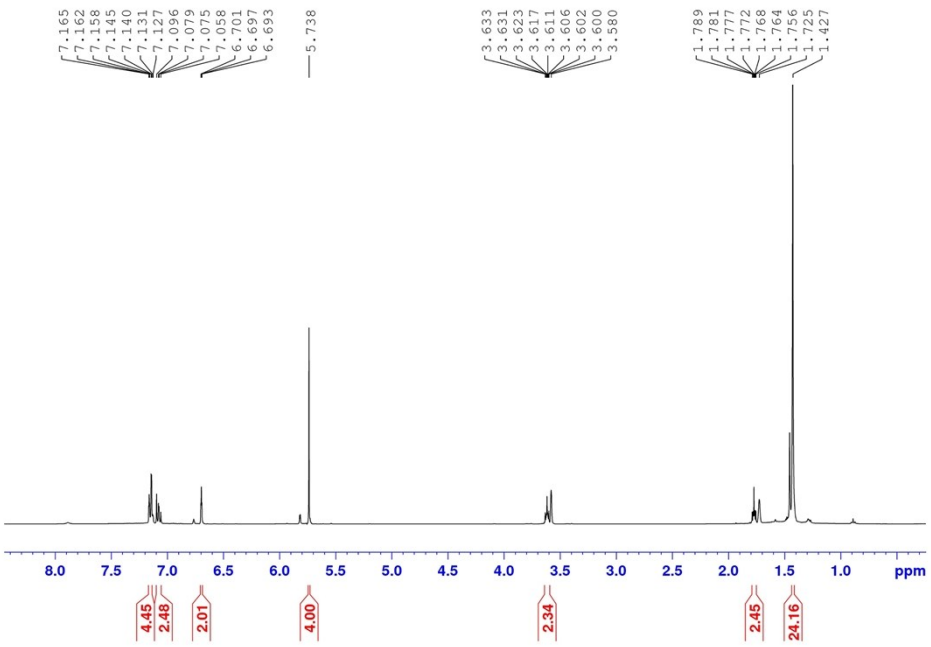


Figure 8. ^{1}H NMR spectrum of $[K_2(L^{Ar})(thf)_3]$, **1** (400.13 MHz, $[D_8]$thf, 25ºC).

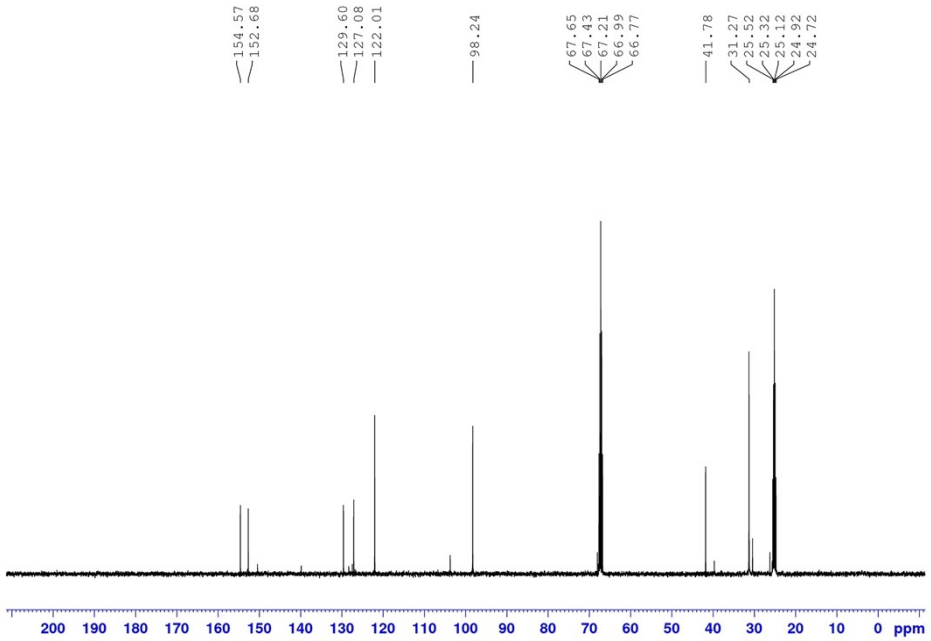


Figure 9. $^{13}C\{^{1}H\}$ NMR spectrum of $[K_2(L^{Ar})(thf)_3]$, **1** (100.6 MHz, $[D_8]$thf, 25ºC).

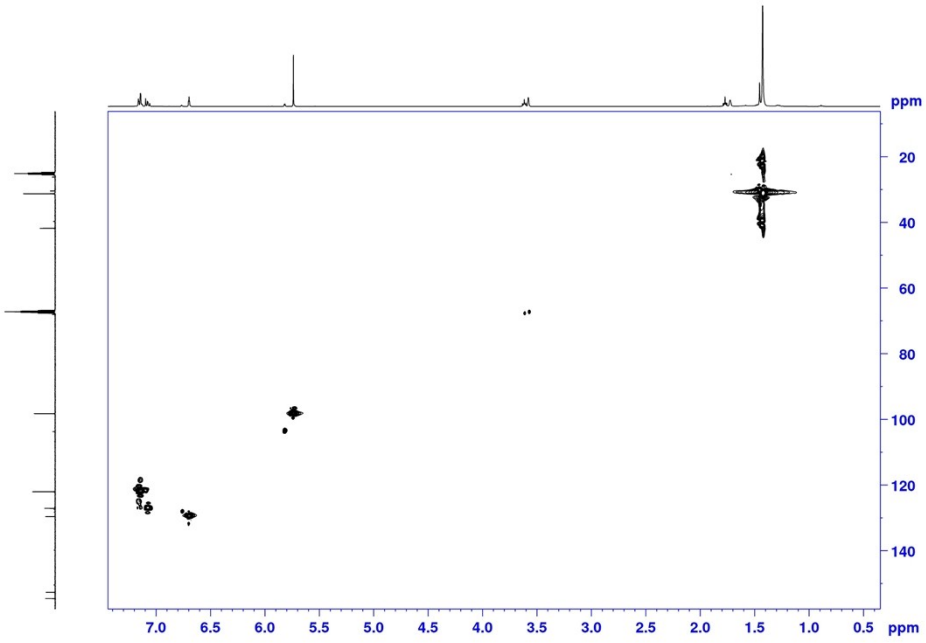


Figure 10. ^{1}H, ^{13}C-HSQC NMR spectrum of $[K_2(L^{Ar})(thf)_3]$, **1** (400.13 MHz, $[D_8]thf$, 25ºC).

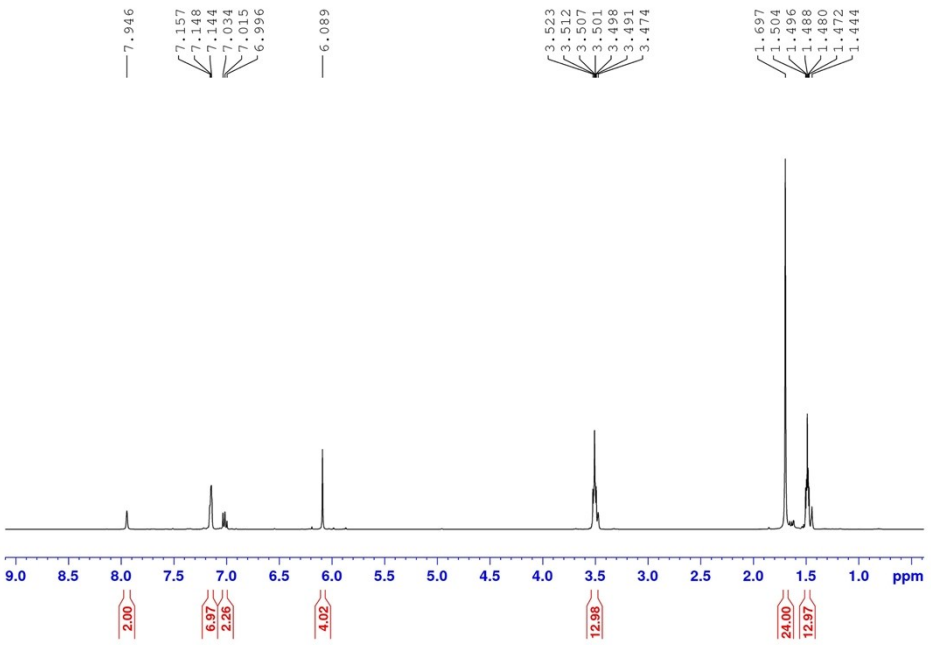


Figure 11. ^{1}H NMR spectrum of $[Li_2(L^{Ar})(thf)_4]$, **2** (400.13 MHz, $C_6D_6/[D_8]thf$, 25ºC).

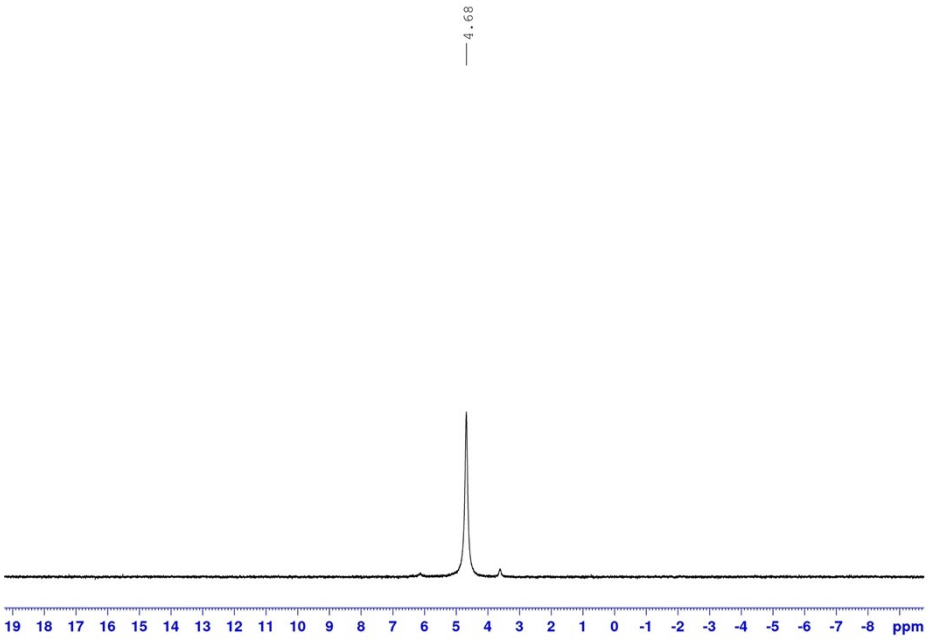


Figure 12. ^{7}Li NMR spectrum of [$Li_2(L^{Ar})(thf)_4$], **2** (155.5 MHz, C_6D_6/[D_8]thf, 25ºC).

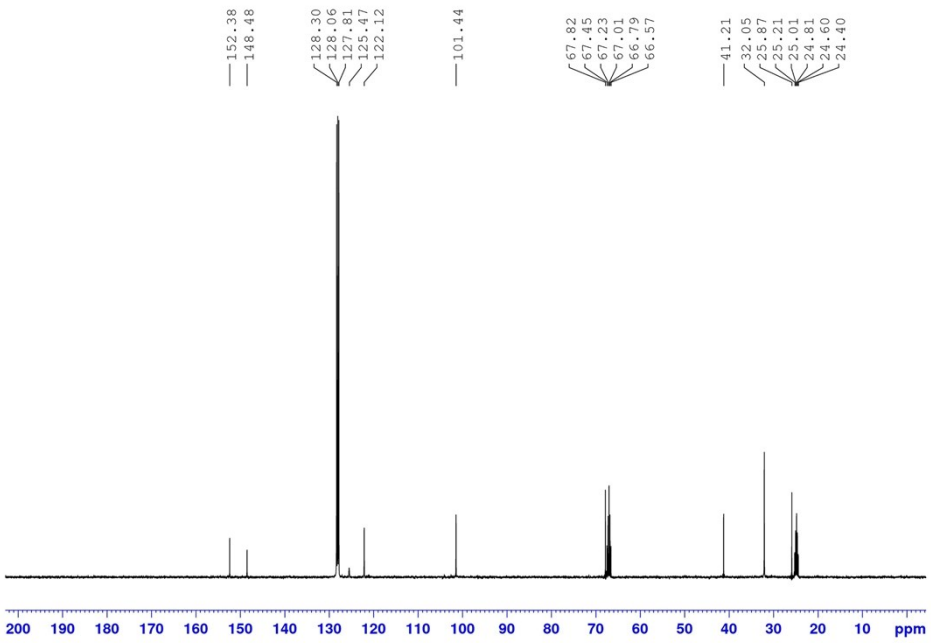


Figure 13. $^{13}C\{^{1}H\}$ NMR spectrum of [$Li_2(L^{Ar})(thf)_4$], **2** (100.6 MHz, C_6D_6/[D_8]thf, 25ºC).

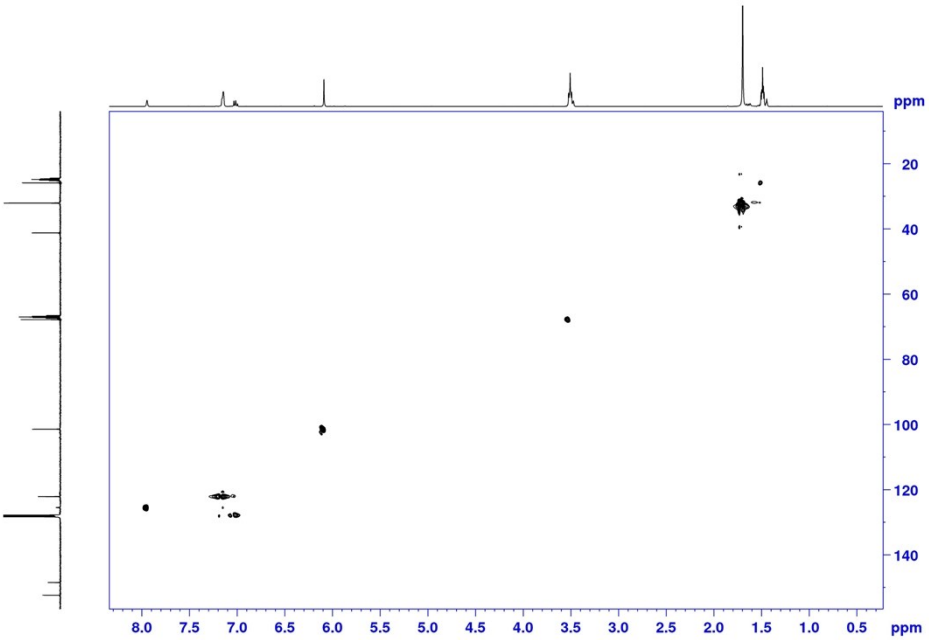


Figure 14. ^{1}H, ^{13}C-HSQC NMR spectrum of $[Li_2(L^{Ar})(thf)_4]$, **2** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

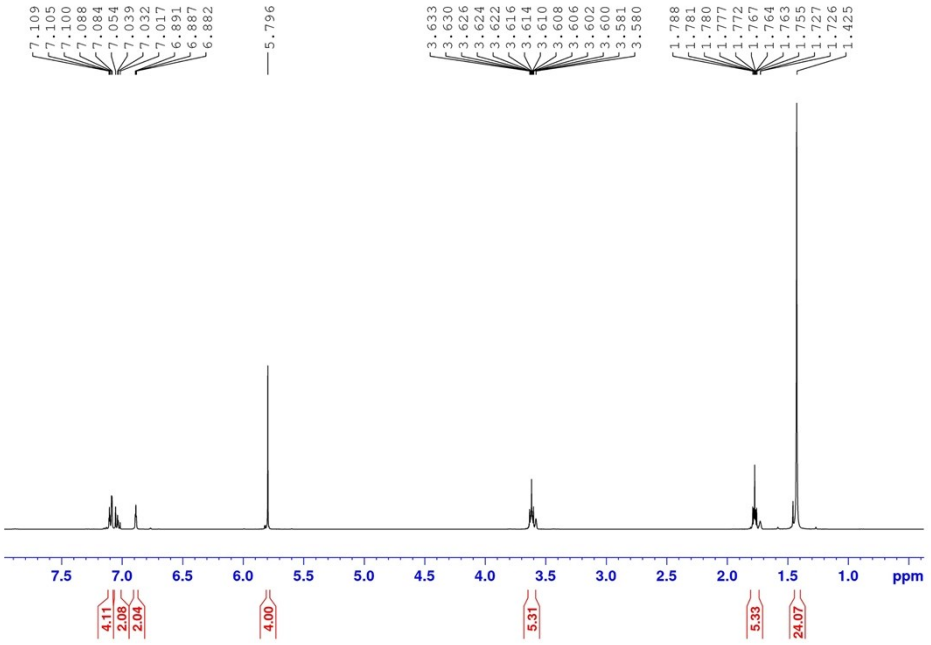


Figure 15. ^{1}H NMR spectrum of $[Na_2(L^{Ar})(thf)_3]$, **3** (400.13 MHz, [D_8]thf, 25ºC).

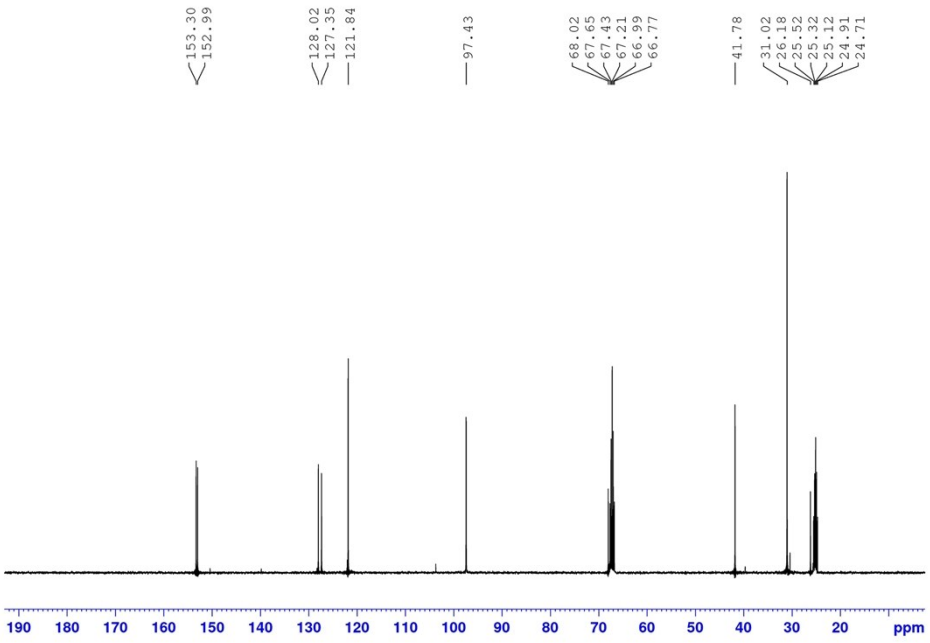


Figure 16. $^{13}C\{^{1}H\}$ NMR spectrum of $[Na_2(L^{Ar})(thf)_3]$, **3** (100.6 MHz, $[D_8]$thf, 25ºC).

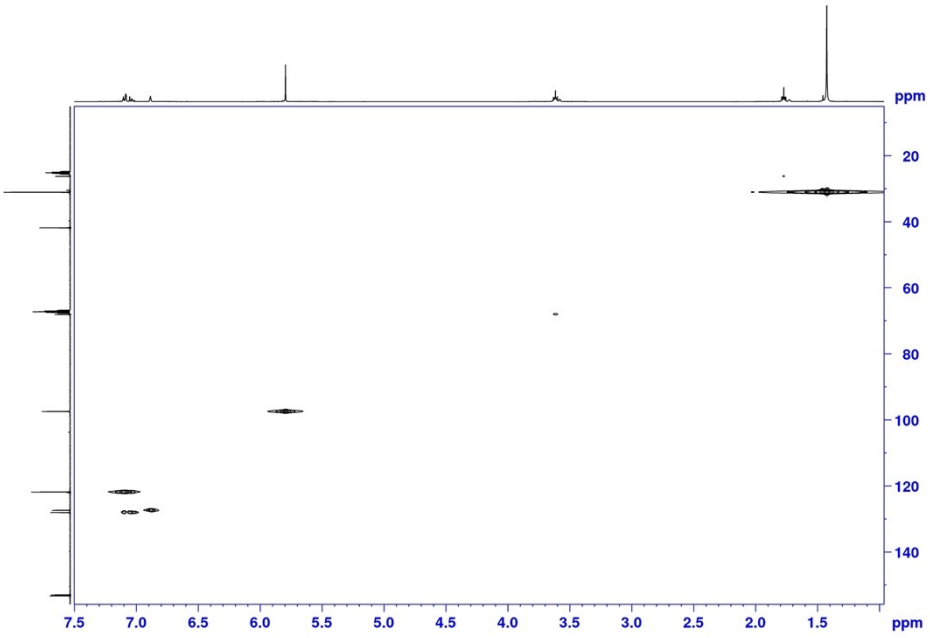


Figure 17. ^{1}H, ^{13}C-HSQC NMR spectrum of $[Na_2(L^{Ar})(thf)_3]$, **3** (400.13 MHz, $[D_8]$thf, 25ºC).

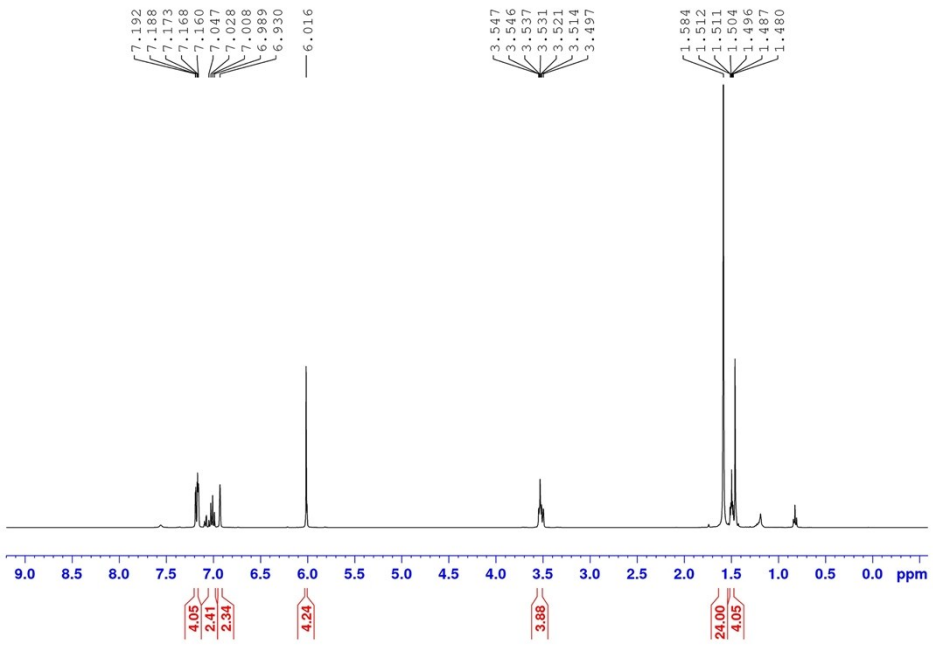


Figure 18. ^{1}H NMR spectrum of $[Na_2(L^{Ar})(thf)_3]_\infty$, **4** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

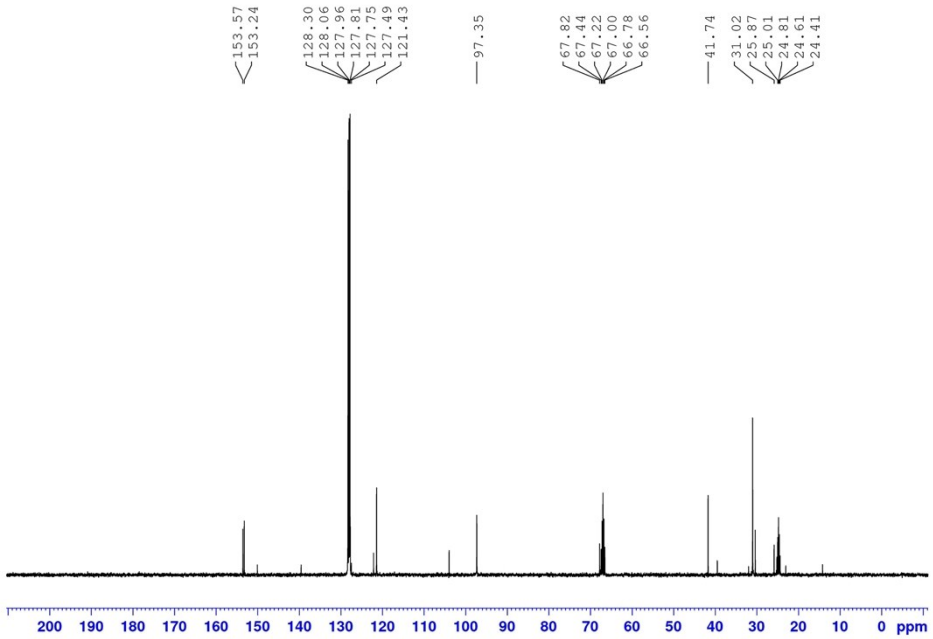


Figure 19. $^{13}C\{^{1}H\}$ NMR spectrum of $[Na_2(L^{Ar})(thf)_3]_\infty$, **4** (100.6 MHz, C_6D_6/[D_8]thf, 25ºC).

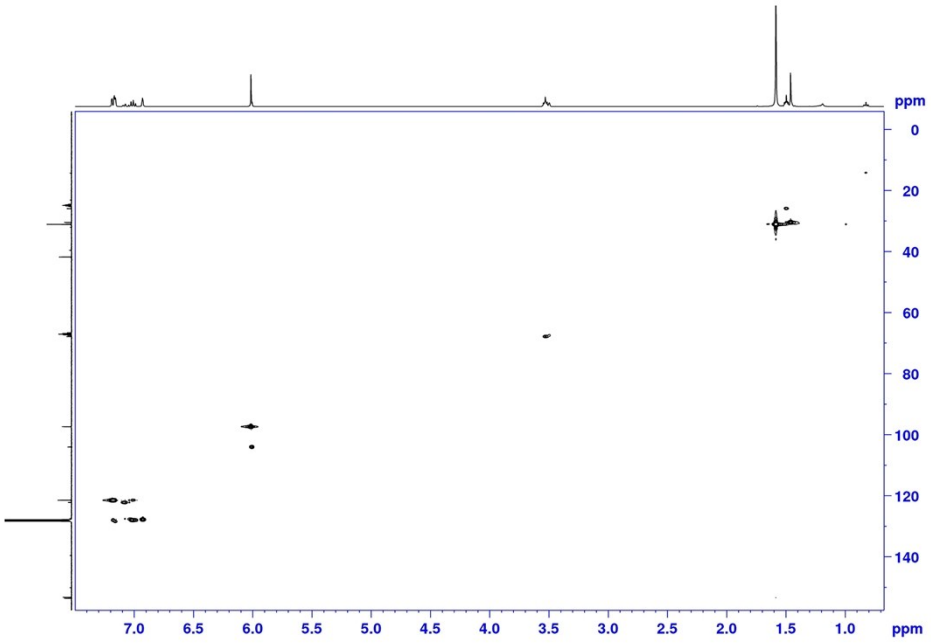


Figure 20. ^{1}H, ^{13}C-HSQC NMR spectrum of $[Na_2(L^{Ar})(thf)_3]_\infty$, **4** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

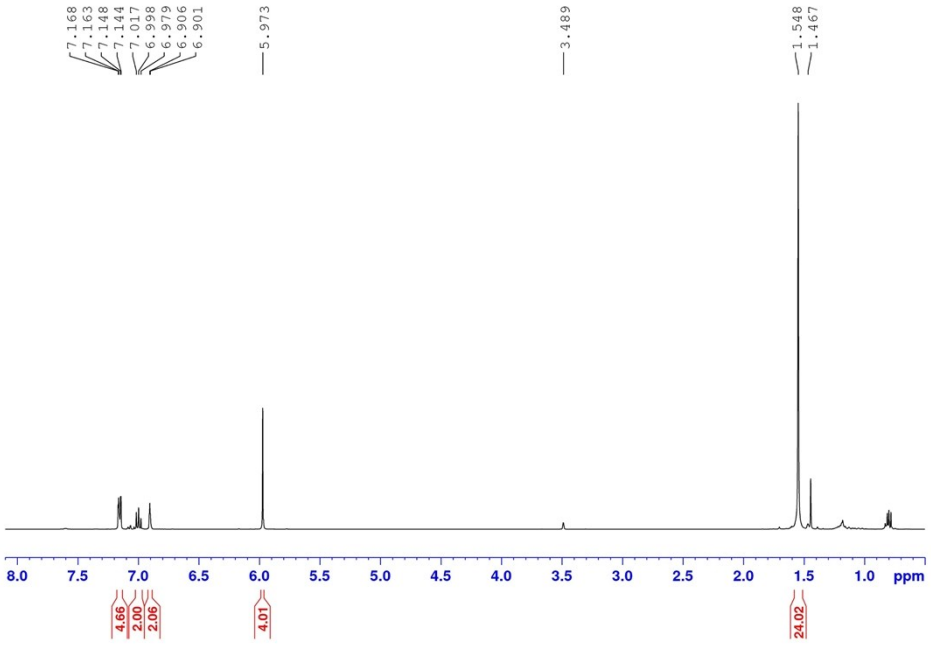


Figure 21. ^{1}H NMR spectrum of $[Na_2(L^{Ar})]_4$, **5** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

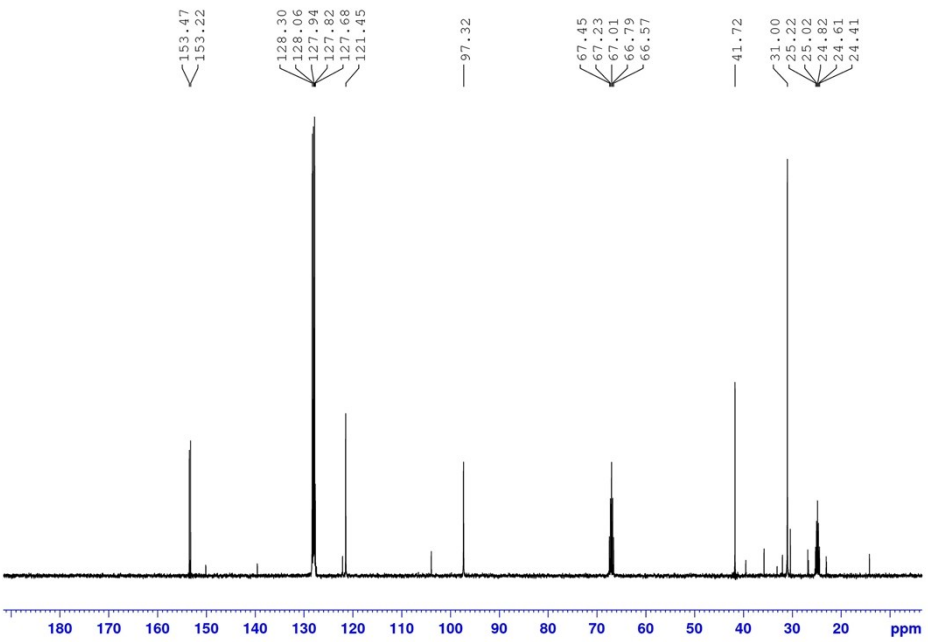


Figure 22. $^{13}C\{^{1}H\}$ NMR spectrum of $[Na_2(L^{Ar})]_4$, **5** (100.6 MHz, C_6D_6/$[D_8]$thf, 25ºC).

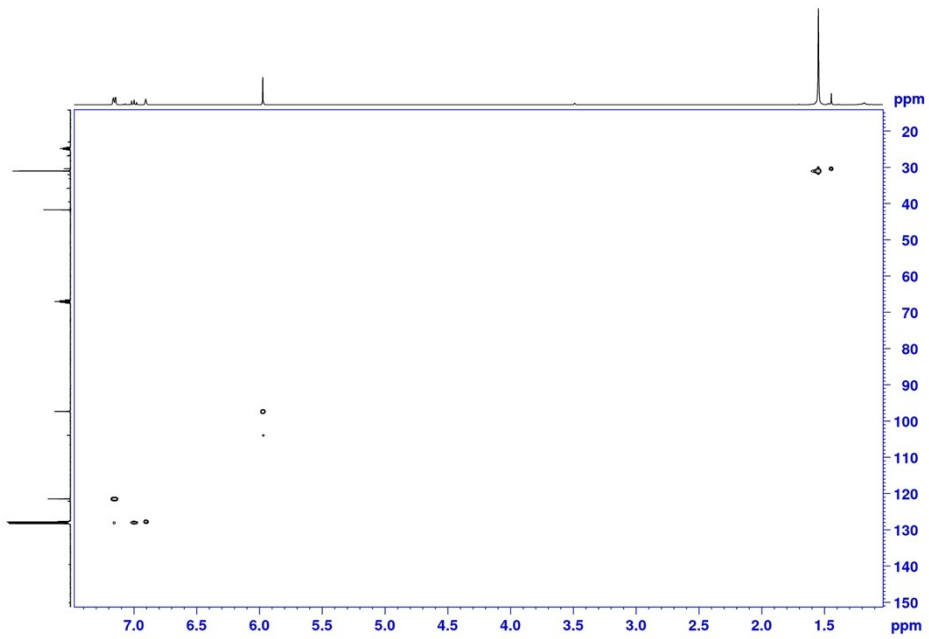


Figure 23. ^{1}H, ^{13}C-HSQC NMR spectrum of $[Na_2(L^{Ar})]_4$, **5** (400.13 MHz, C_6D_6/$[D_8]$thf, 25ºC).

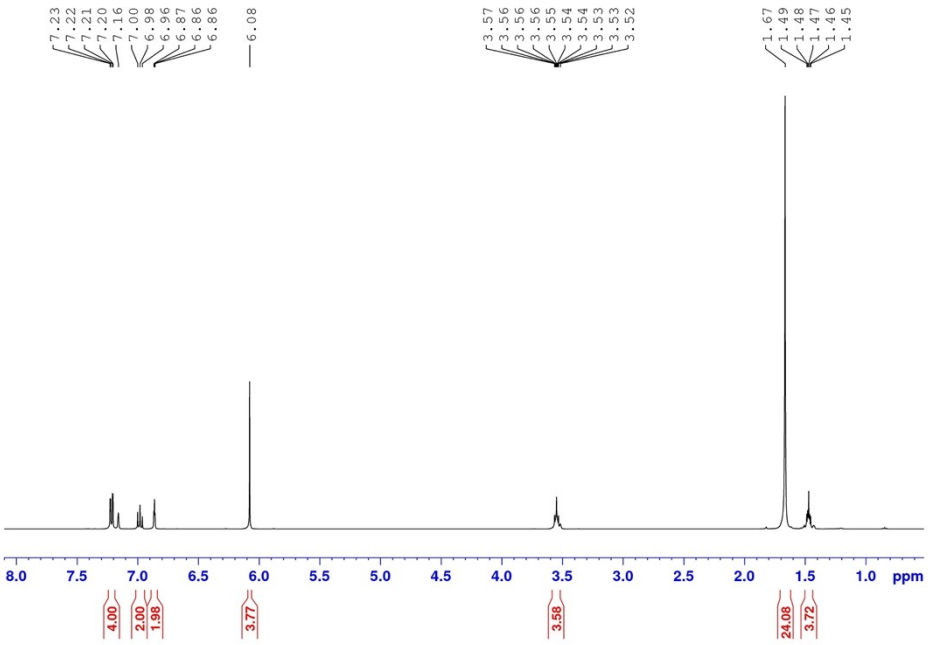


Figure 24. ^{1}H NMR spectrum of $[K_2(L^{Ar})(thf)]_\infty$, **6** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

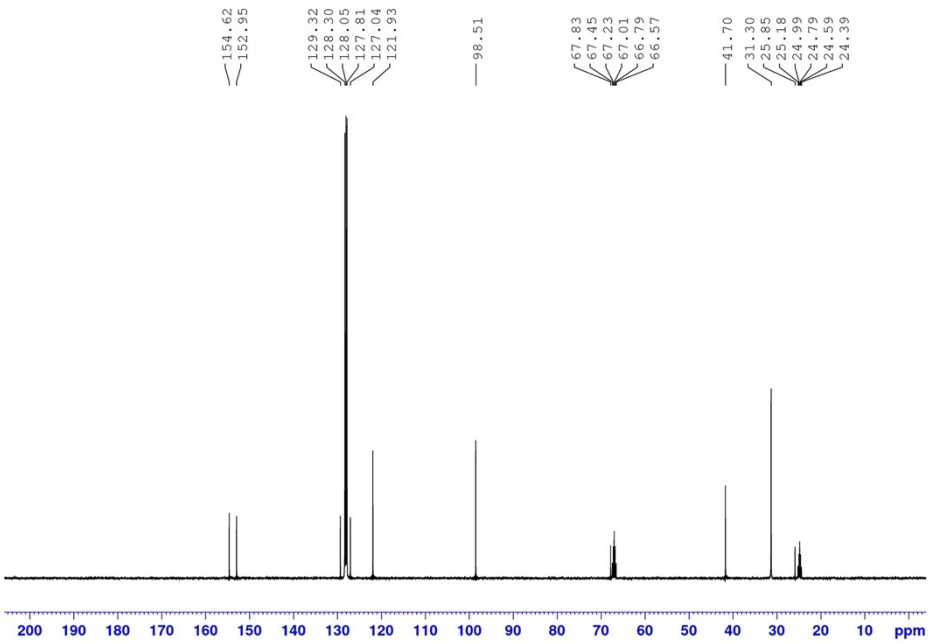


Figure 25. $^{13}C\{^{1}H\}$ NMR spectrum of $[K_2(L^{Ar})(thf)]_\infty$, **6** (100.6 MHz, C_6D_6/[D_8]thf, 25ºC).

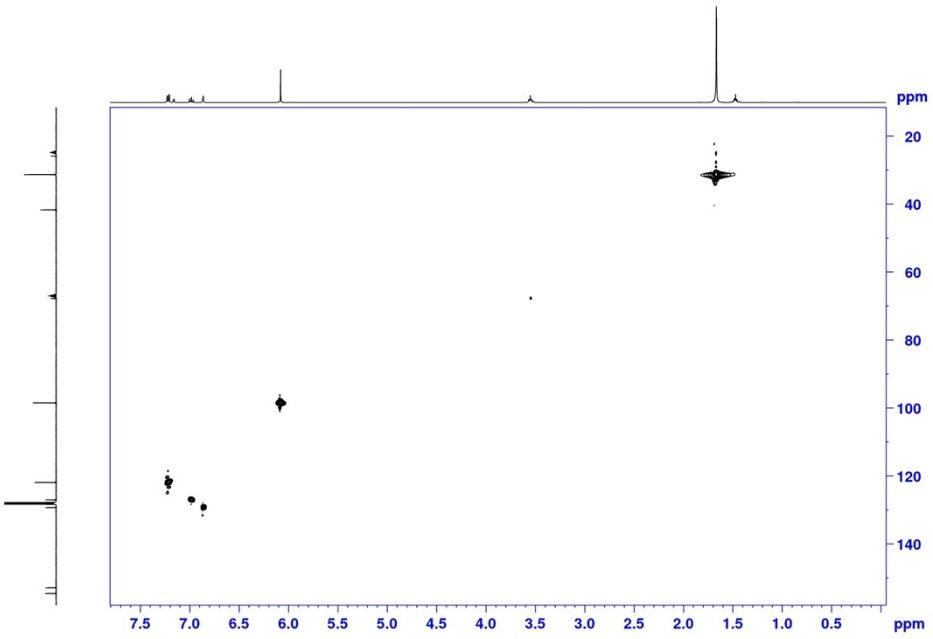


Figure 26. ^{1}H, ^{13}C-HSQC NMR spectrum of $[K_2(L^{Ar})(thf)]_\infty$, **6** (400.13 MHz, C_6D_6/[D_8]thf, 25ºC).

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