Contents

General Experimental

All reactions were performed under a protective argon atmosphere using either standard Schlenk or glove box techniques. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. C_6D_6, d_8-toluene and d_8-THF were degassed by freeze-pump-thaw methods and stored over activated 4 Å molecular sieves. ^{n}BuLi (1.6 M in hexane) was purchased commercially from Sigma-Aldrich and used as received. LiHMDS and NaHMDS were purchased from Fluorochem and Sigma-Aldrich respectively, stored in the glovebox and used as received. Diisopropylamine, TMEDA and PMDETA were purchased from Sigma-Aldrich and distilled under nitrogen and stored over activated 4 Å molecular sieves prior to use. 1H-pyrrole was purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves prior to use. All other reagents were purchased from commercial sources and were used as received.

NMR spectra were recorded on a Bruker AV3 or AV 400 MHz spectrometer operating at 400.13 MHz for ^{1}H, 155.47 MHz for ^{7}Li and 100.62 MHz for ^{13}C. All ^{13}C spectra were proton decoupled. ^{1}H, ^{13}C{1H} and ^{7}Li chemical shifts are expressed in parts per million (δ, ppm) and referenced to residual solvent peaks.

X-ray crystallography

Data for complexes 1-3 were collected on Oxford Diffraction Gemini S or Xcalibur E instruments with graphite-monochromated Mo Kα (λ = 0.71073 Å) or Cu Kα (λ 1.54184 Å) radiation. Data collection and processing used CrysalisPro software.[1] All structures were solved and refined to convergence on F^2 for all independent reflections by the full-matrix least squares method using SHELXL-2014[2] or by the Gauss Newton algorithm using OLEX2.[3] Two molecules of hexane co-crystallised in the unit cell of complex 2, with the corresponding electron density removed using the SQUEEZE routine implemented within the software program PLATON.[4] Approximately 102 electron equivalents were removed from 818 Å^3 of unit cell volume. Compound 3 was refined as an inversion twin, Flack parameter 0.27(6). Selected bond lengths and bond angles are presented in Figures 1 and 2, selected crystallographic data are shown in Table 1 and full details are presented in .cif format, available from the CCDC (1873068 – 1873070).

Synthesis of new compounds

Synthesis of [{(THF).Li($CO_2NC_4H_4$)}$_\infty$] (**1**)

^{n}BuLI (0.69 mL, 1.6 M in hexane, 1.1 mmol) was added *via* syringe to a cooled solution of 1H-pyrrole (0.07 mL, 1.0 mmol) in hexane (5 mL) at 0 ^{O}C, furnishing a grey suspension. After stirring for 15 minutes, CO_2 was bubbled through this suspension *via* a cannula and gas distribution tube from an adjacent Schlenk tube filled with dry ice. This formed a white precipitate with an exothermic reaction. After 10 minutes, the gas distribution tube was removed and THF was added with gentle heating to furnish a grey coloured solution. Upon cooling in a hot water Dewar overnight, a crop of X-ray quality colourless crystals had deposited (yield 0.0791 g, 0.42 mmol, 42 %).

^{1}H NMR (400.1 MHz, d_8-THF, 300 K): δ 7.27 (t, J = 2.2Hz, 2 H, CH_2), 5.94 (t, J = 2.2Hz, 2 H, CH_2), 3.61 (t, J = 6.64Hz, 4 H, 2 x CH_2), 1.77 (t, J = 6.62 Hz 4 H, 2 x CH_2) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF, 300 K): δ 155.1 (s, COO), 120.8 (s, CH_2), 109.2 (s, CH_2) ppm.

^{7}Li NMR (155.5 MHz, d_8-THF, 300 K): δ 2.18 (s) ppm.

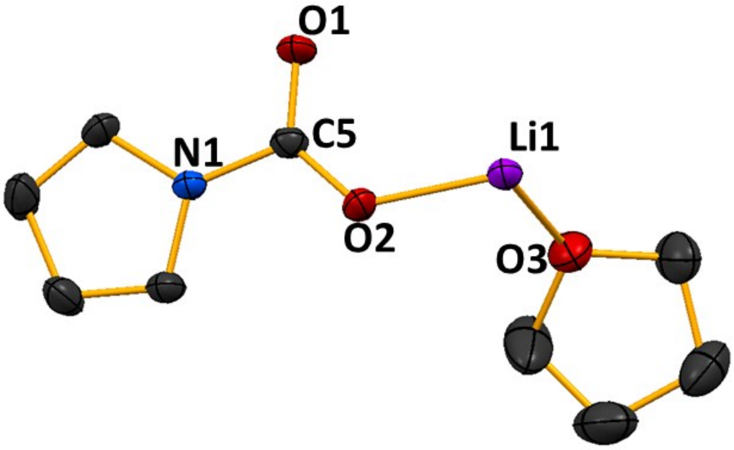
IR υ 1623 (br s, anti-symmetric COO), 1261.3 (s, symmetric COO) cm^{-1}

Melting point: Decomposes at 190 ^{O}C

Elemental analysis (%) for [{(THF).Li($CO_2NC_4H_4$)}$_\infty$]: calcd: C 57.15, H 6.40, N 7.41; found : C 55.85, H 6.04, N 7.58.

Figure 1: Molecular structure of [{(THF).Li(CO2NC4H4)}∞] (1)

Hydrogen atoms omitted for clarity



Selected bond lengths (Å) and bond angles (º)

N1 C5 1.424(4), C5 O1 1.234(3) C5 O2 1.262(3), O2 Li1 2.019(5), Li1 O3 1.959(6)

O1 C5 O2 127.8(3), N1 C5 O1 116.3(2), N1 C5 O2 115.9(2), O2 Li1 O3 100.8(2)

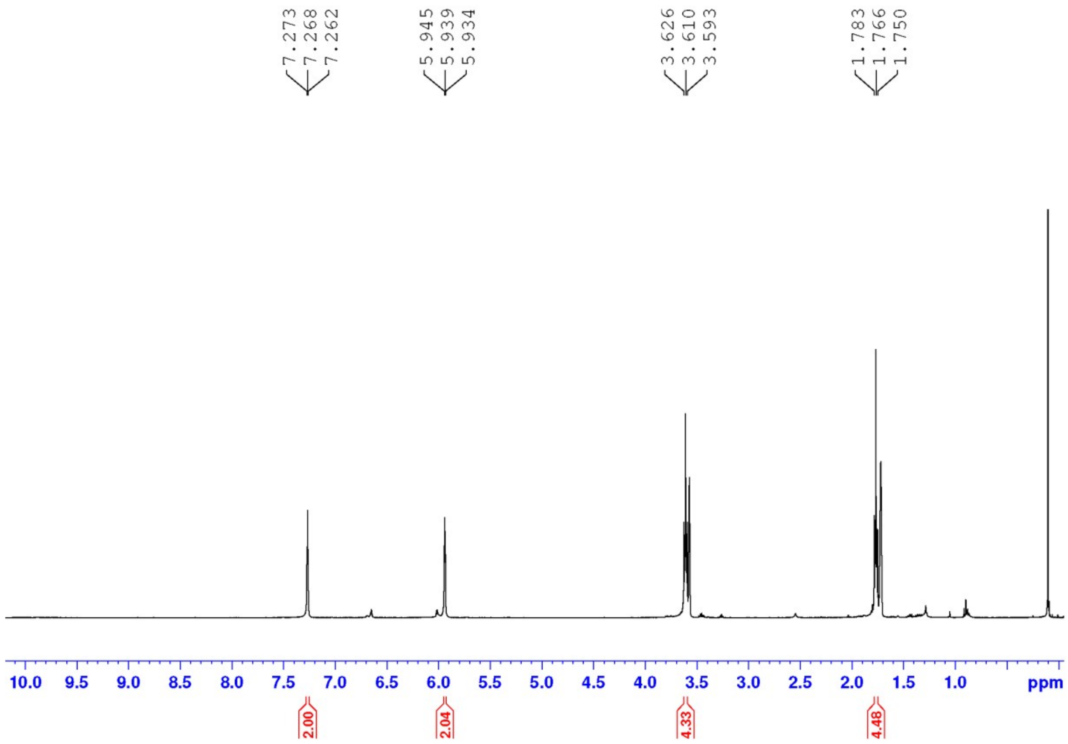
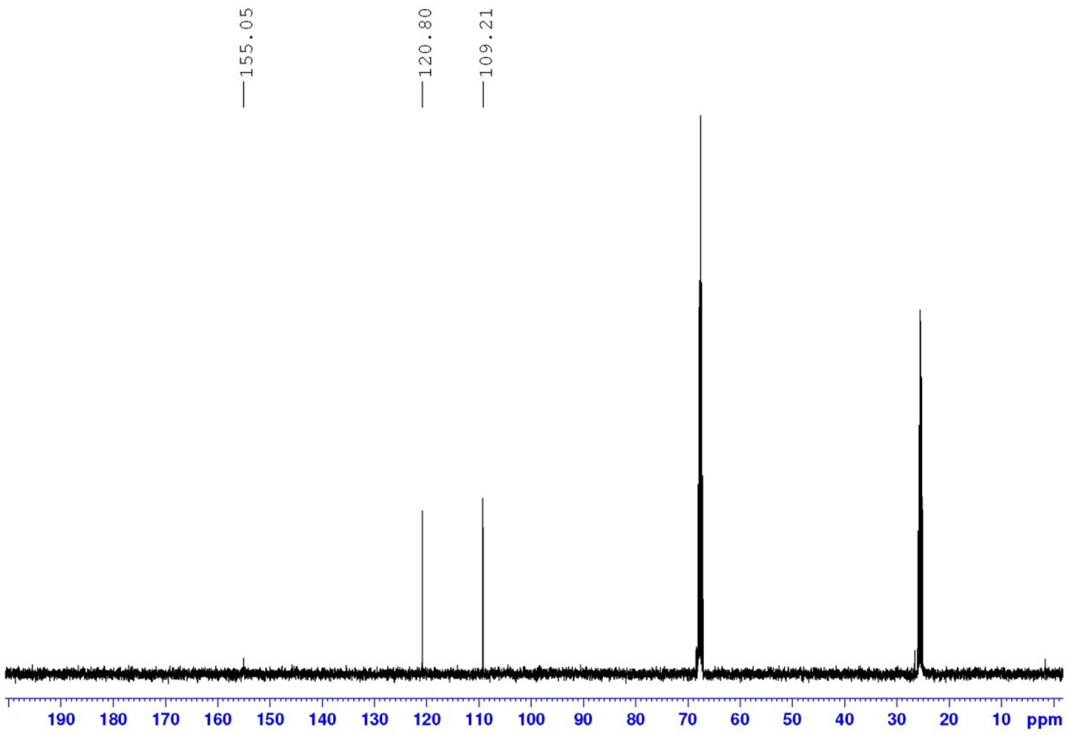


Figure 1.1: ^{1}H NMR in d_8-THF of compound **1**, [{(THF).Li($CO_2NC_4H_4$)}$_\infty$]



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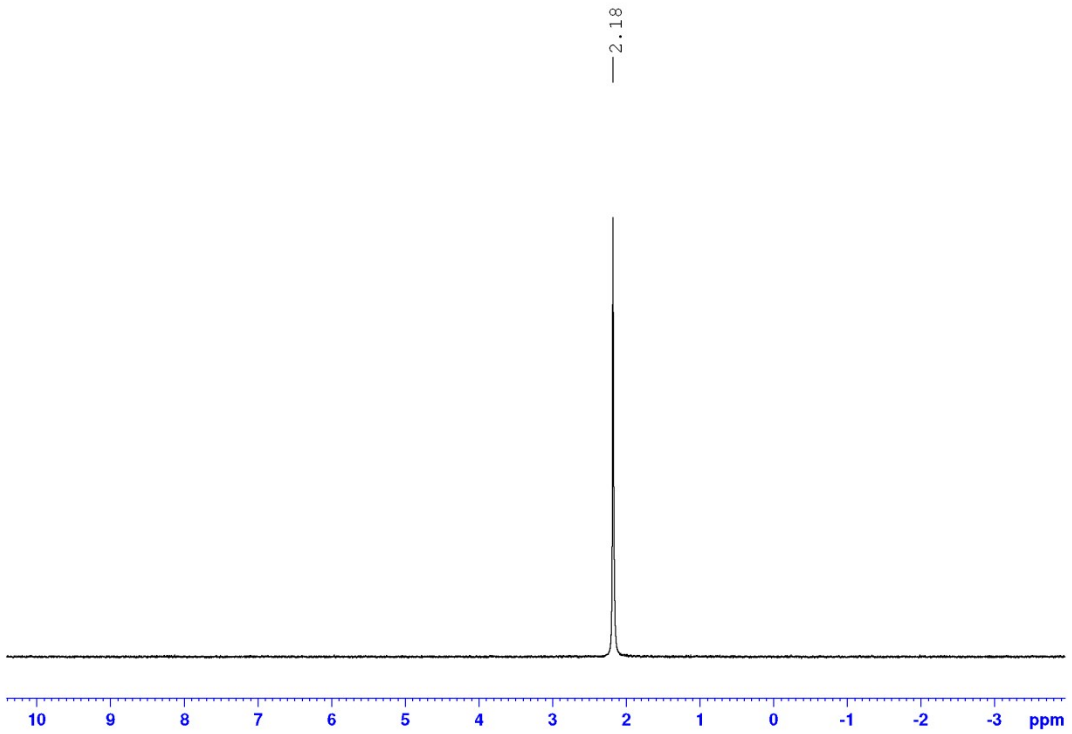


Figure 1.3: ^{7}Li NMR in d$_8$-THF of compound **1**, [{(THF).Li(CO$_2$NC$_4$H$_4$)}$_\infty$]

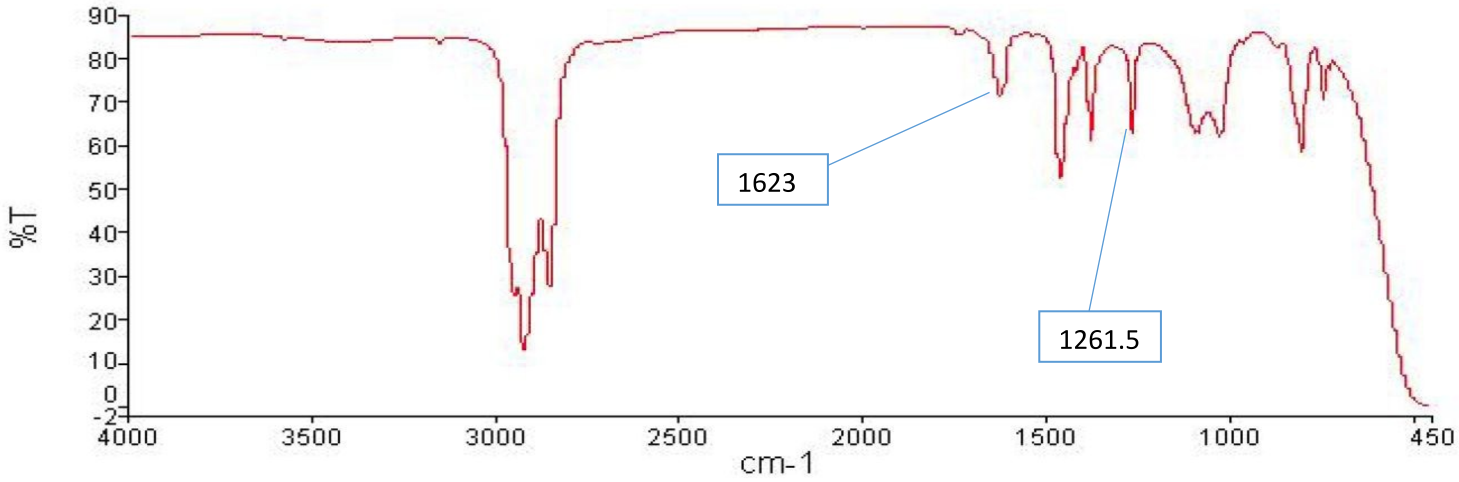


Figure 1.4: IR spectrum of compound **1**, [{(THF).Li(CO$_2$NC$_4$H$_4$)}$_\infty$], recorded as a nujol mull

Synthesis of [{(iPr$_2$NCOOLi)$_{12}$(iPr$_2$NCOOH)$_2$}] (**2**)

^{n}BuLi (0.69 mL, 1.6 M in hexane, 1.1 mmol) was added *via* syringe to a cooled solution of diisopropylamine (0.14 mL, 1 mmol) in hexane (5 mL) at 0 ^{O}C, furnishing a white precipitate. After stirring for 15 minutes, PMDETA (0.21 mL, 1 mmol) was added, furnishing a pale green solution. Upon stirring for a further 15 minutes, CO_2 was bubbled through this solution *via* a cannula and gas distribution tube from an adjacent Schlenk tube filled with dry ice. This furnished a homogenous colourless solution with exothermic reaction, which was subsequently placed at –33 ^{O}C. After a few days, colourless crystals had formed (yield 0.0580 g, 0.023 mmol, 33 % based on diisopropylamine).

^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.95 (d, J = 6.16Hz, 6H, CH_3), 2.79 (quintet, J = 5.92 Hz, 1H, CH) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): 45.4 (s, CH), 23.8 (s, CH_3) ppm.

^{7}Li NMR (155.5 MHz, d$_8$-toluene, 300 K): δ 0.50 (br s) ppm.

^{7}Li NMR (155.5 MHz, d$_8$-toluene, 350 K): δ 0.36 (s), 0.45 (s), 0.58 (s) ppm.

IR υ 1594.3 + 1545 (s, anti-symmetric COO), 1360 + 1265.6 (s, symmetric COO) cm^{-1}

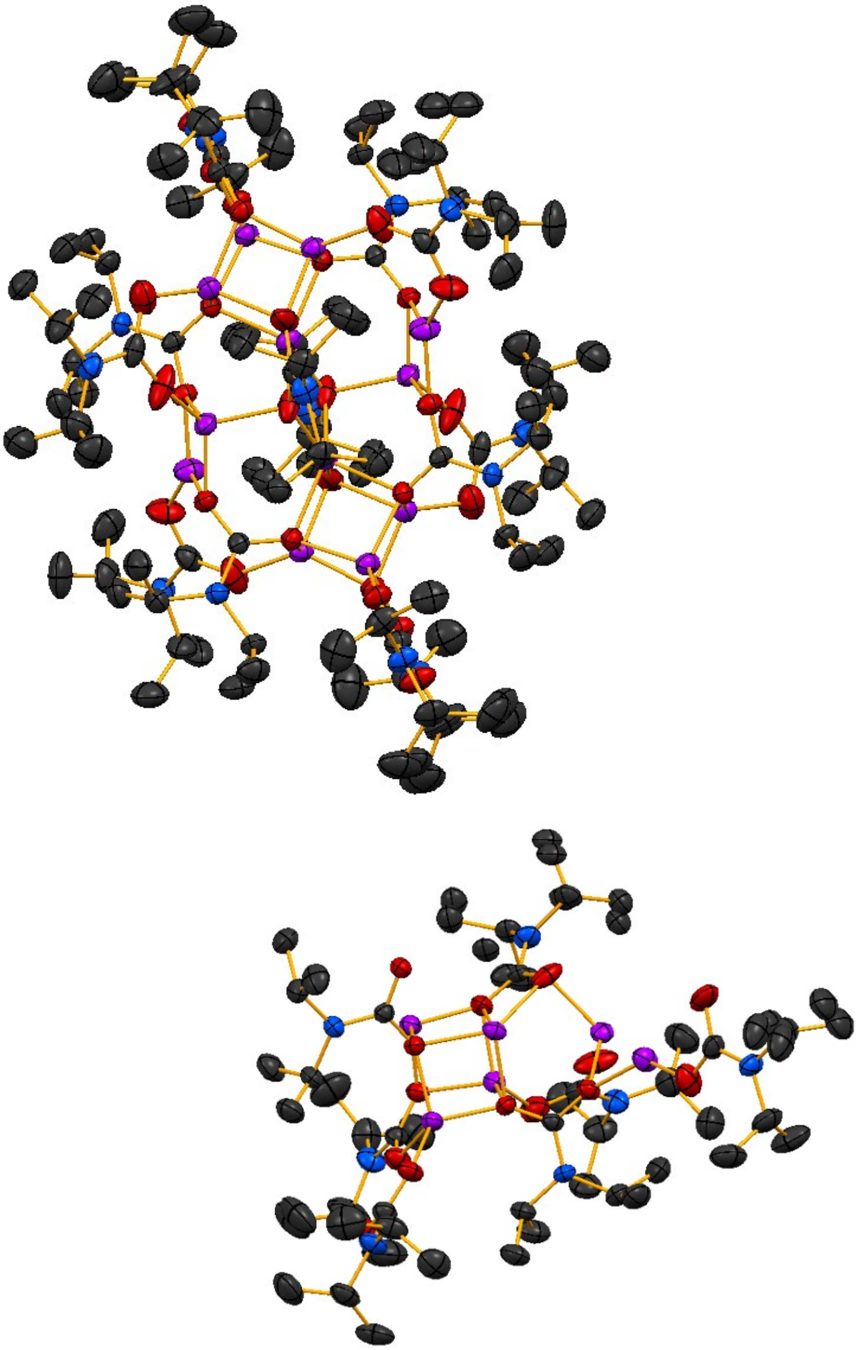
Melting point: Thermally stable up to 300 ^{O}C

Elemental analysis (%) for [{(iPr$_2$NCOOLi)$_{12}$(iPr$_2$NCOOH)$_2$}]: calcd: C 55.94, H 9.49, N 9.32; found : C 35.63, H 9.01, N 5.77.

Due to the extreme air- and moisture-sensitivity of this complex, satisfactory elemental analysis could not be obtained despite multiple attempts.

Figure 2: Molecular structure of [{(iPr$_2$NCOOLi)$_{12}$(iPr$_2$NCOOH)$_2$}] (2)

Hydrogen atoms omitted for clarity. Both centrosymmetric and asymmetric unit shown. Co-crystallised hexane solvent molecules omitted for clarity.



Selected bond lengths (Å) and bond angles (º)

C1 O1 1.262(3), C1 O2 1.263(3), C8 O3 1.227(3), C8 O4 1.320(3), C15 O5 1.262(4), C15 O6 1.264(4), C22 O7 1.271(3), C22 O8 1.279(3), C29 O9 1.251(3), C29 O10 1.261(3), C36 O11 1.267(3), C36 O12 1.289(3), C43 O13 1.236(4), C43 O14 1.274(4), Li1 O8 2.005(5), Li1 O9 2.221(5), Li1 O9' 1.941(4), Li1 O10 2.430(5), Li1 O12 2.061(5), Li 2 O2 1.906(5), Li2 O5 1.818(5), Li2 O10 1.894(5), Li2 O12 2.107(5), Li3 O2 1.982(5), Li3 O8 2.149(5), Li3 O10 1.984(5), Li3 O14 1.891(5), Li4 O1 1.944(5), Li4 O3 1.966(5), Li4 O8 1.966(5), Li4 O12 1.977(5), Li5 O6 1.793(5), Li5 O7 1.853(5), Li5 O11 1.912(5), Li6 O7 2.028(5), Li6 O9 2.019(5), Li6 O11 1.916(4), Li6 O13 1.800(5)

O1 C1 O2 121.0(2), O3 C8 O4 122.1(2), O5 C15 O6 123.2(3), O7 C22 O8 120.3(2), O9 C29 O10 121.2(2), O11, C36 O12 121.0(2), O13 C43 O14 125.0(3)

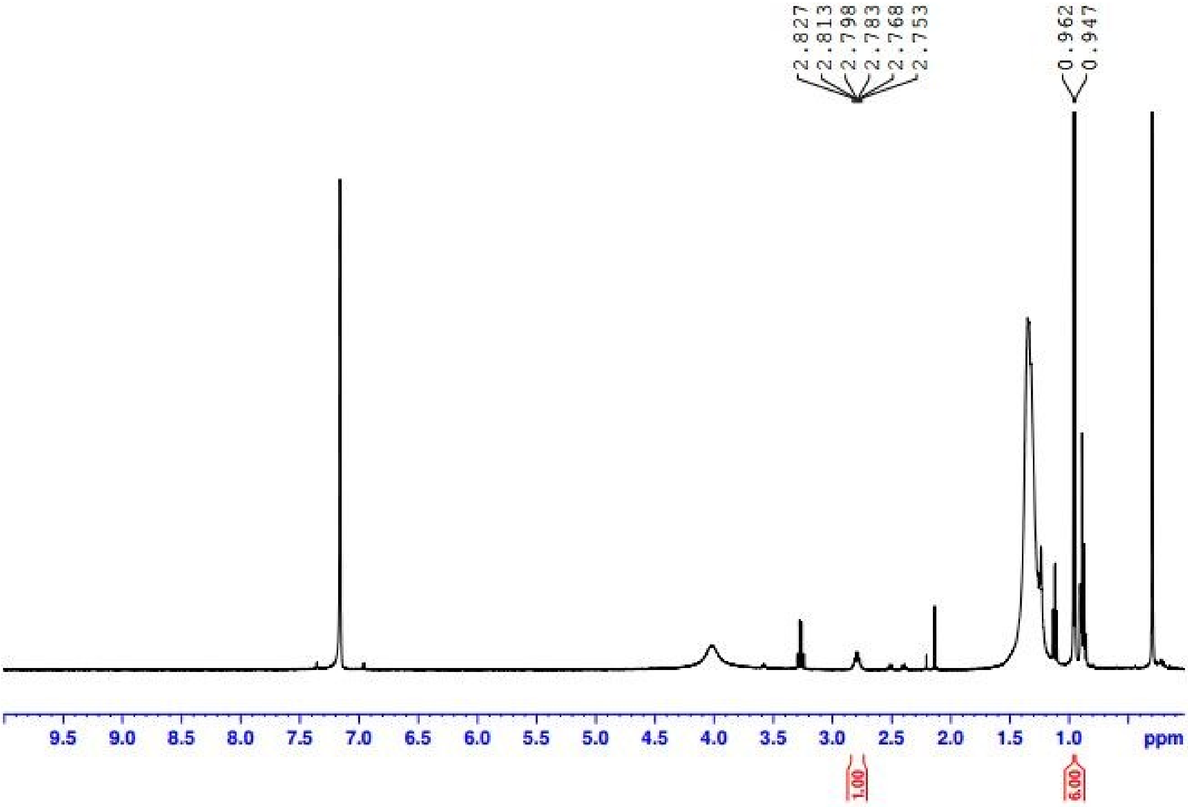
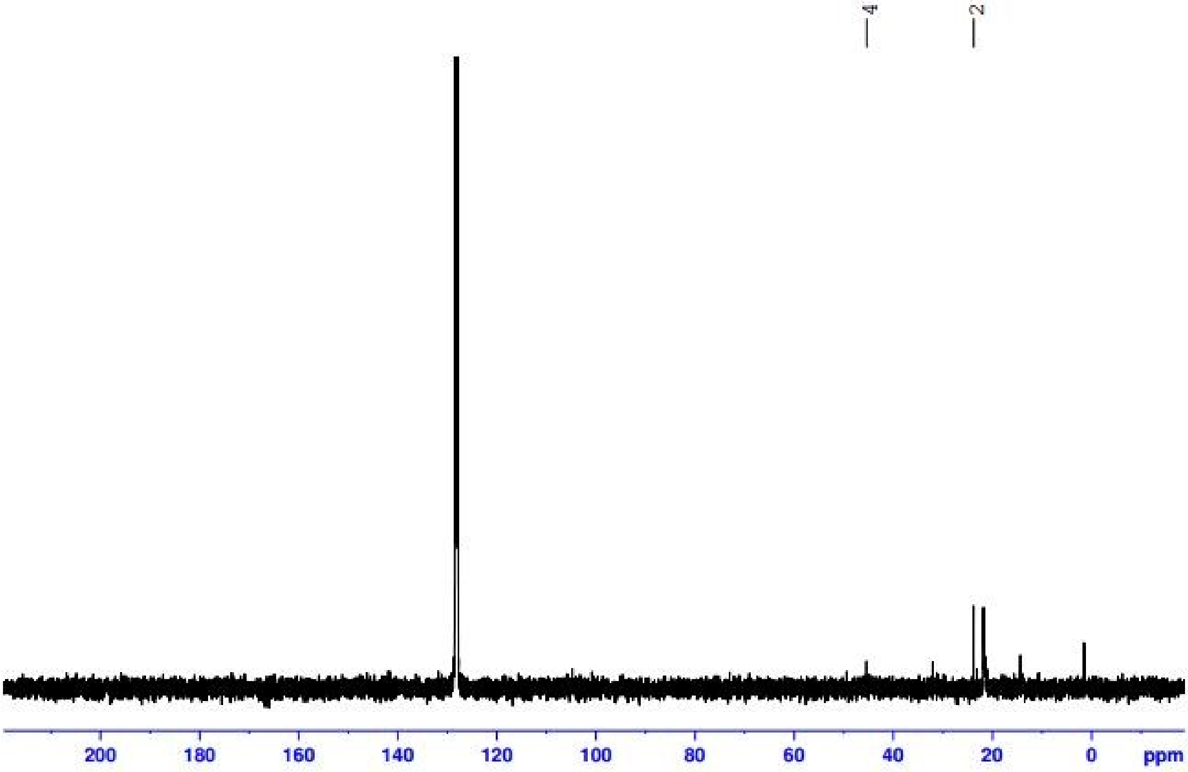


Figure 2.1: ${}^{1}H$ NMR in C_6D_6 of compound **2**, $[\{(i\mathrm{Pr}_2\mathrm{NCOOLi})_{12}(i\mathrm{Pr}_2\mathrm{NCOOH})_2\}]$

Figure 2.2: ${}^{13}C$ NMR in C_6D_6 of compound **2**, $[\{(i\mathrm{Pr}_2\mathrm{NCOOLi})_{12}(i\mathrm{Pr}_2\mathrm{NCOOH})_2\}]$



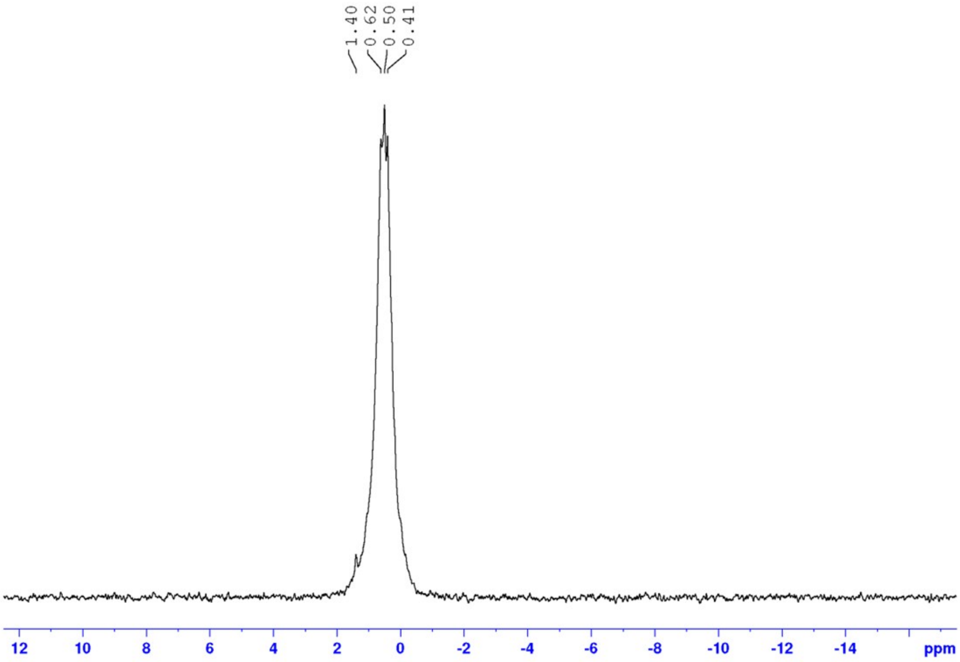
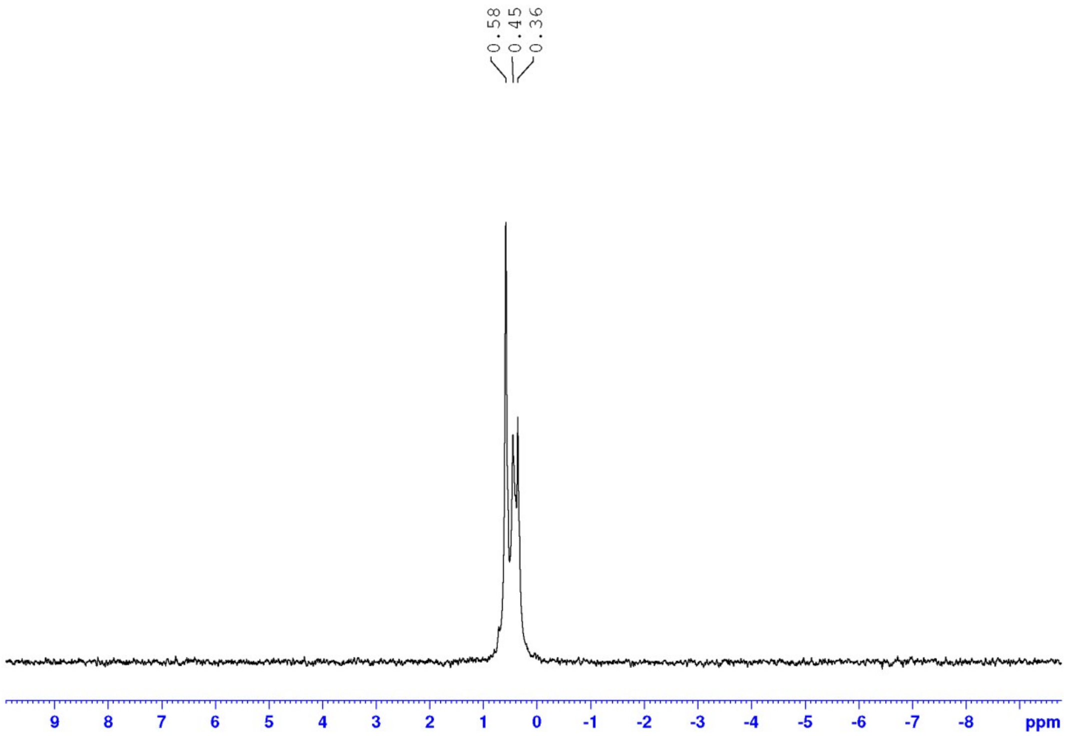


Figure 2.3: ^{7}Li NMR in d$_8$-toluene of compound **2**, [{(iPr$_2$NCOOLi)$_{12}$(iPr$_2$NCOOH)$_2$}] at 300 K

Figure 2.4: ^{7}Li NMR in d$_8$-toluene of compound **2**, [{(*i*Pr$_2$NCOOLi)$_{12}$(*i*Pr$_2$NCOOH)$_2$}] at 350 K



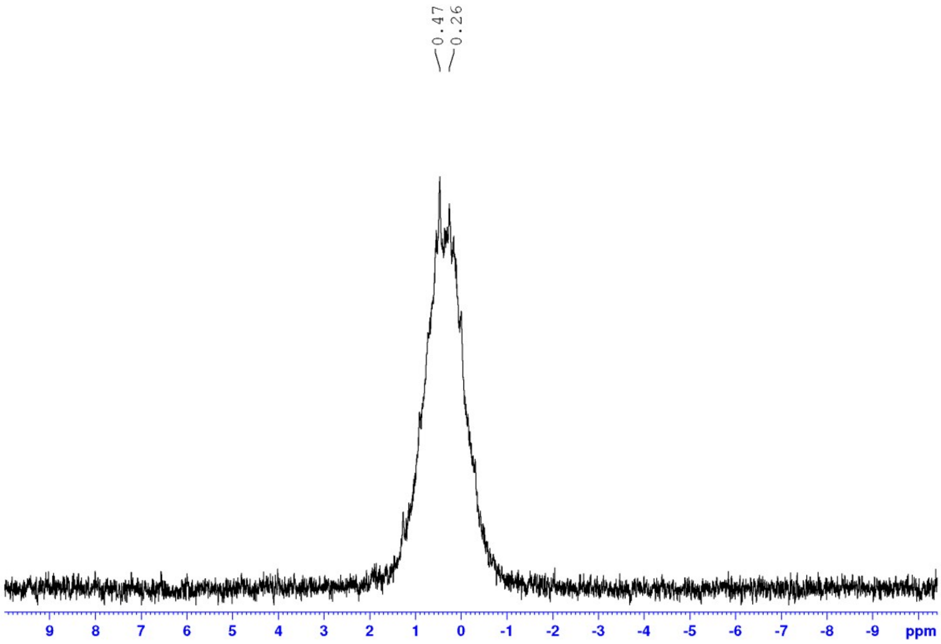


Figure 2.5: ^{7}Li NMR in d$_8$-toluene of compound **2**, [{(*i*Pr$_2$NCOOLi)$_{12}$(*i*Pr$_2$NCOOH)$_2$}] at 273 K

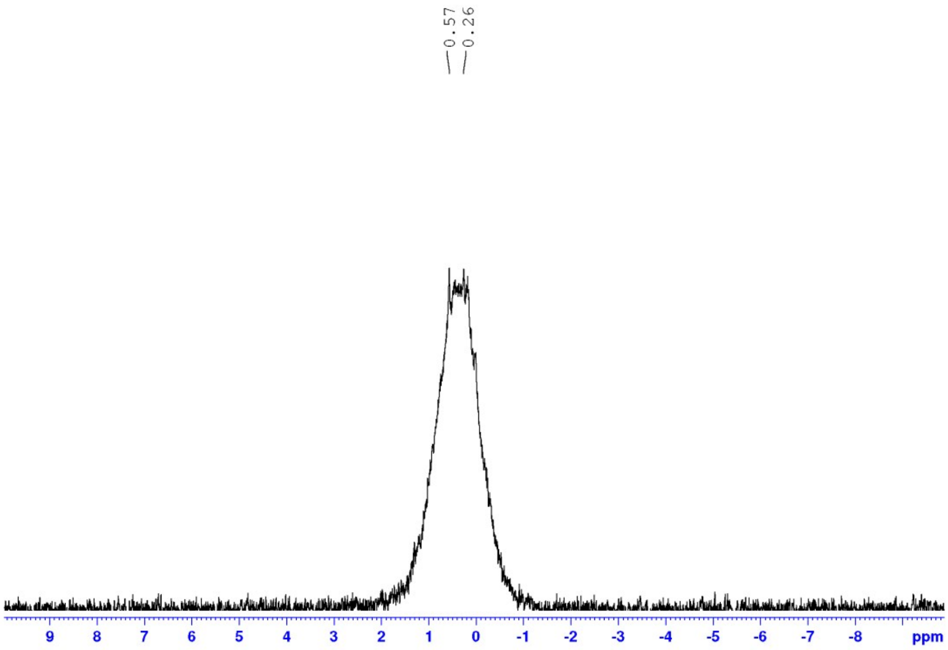


Figure 2.6: ^{7}Li NMR in d$_8$-toluene of compound **2**, $[\{(i\mathrm{Pr}_2\mathrm{NCOOLi})_{12}(i\mathrm{Pr}_2\mathrm{NCOOH})_2\}]$ at 253 K

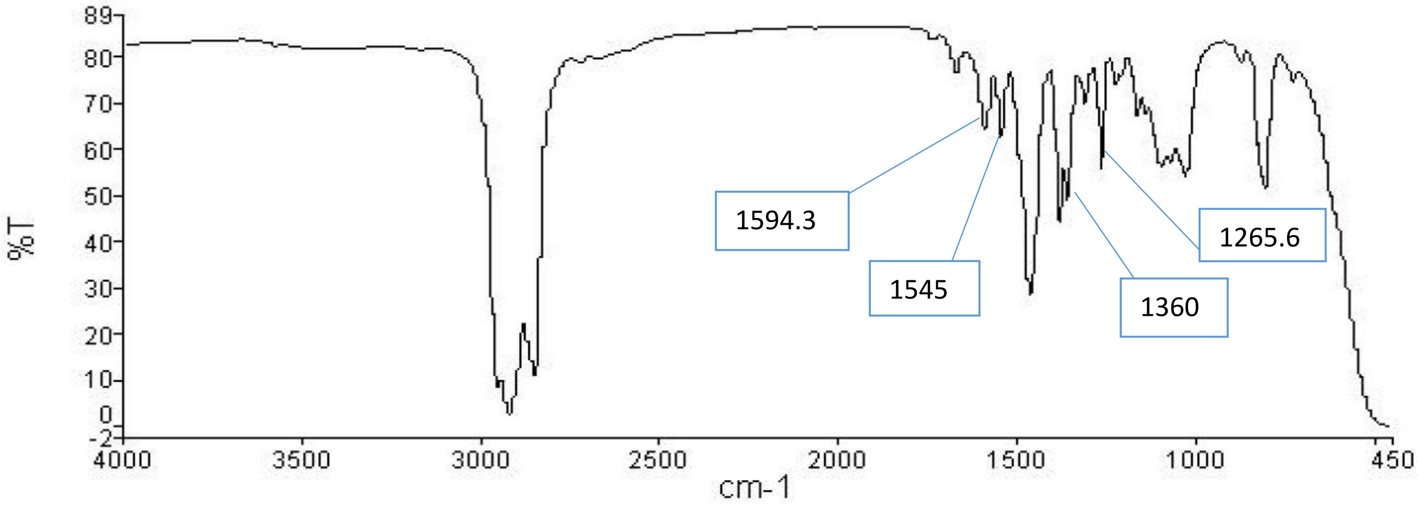


Figure 2.7: IR spectrum of compound **2**, $[\{(i\mathrm{Pr}_2\mathrm{NCOOLi})_{12}(i\mathrm{Pr}_2\mathrm{NCOOH})_2\}]$, recorded as a nujol mull

Synthesis of $[(Me_3Si)NC(=O)OC(=O)N(H)(SiMe_3)]_2LiNa(THF)_4$ (**3**)

LiHMDS (1 mmol, 0.1673 g) and NaHMDS(1 mmol, 0.1834 g) were added to a Schlenk within an Argon filled glovebox. They were then dissolved in THF (5 ml), giving a pale yellow solution which was stirred for 30 minutes. This solution was then cooled to -78 ^{O}C. Upon stirring for a further 15 minutes, CO_2 was bubbled through this solution *via* a cannula and gas distribution tube from an adjacent Schlenk tube filled with dry ice. This furnished a slightly more viscous solution, which was allowed to warm slowly to room temperature, whereupon a pale yellow solution reformed. This was placed at -33 ^{O}C. After a period of five days, a crop of X-ray quality colourless crystals had formed (yield 0.3746 g, 0.47 mmol, 51 %).

^{1}H NMR (400.1 MHz, d_8-THF, 300 K): δ 0.07 (s, 6 H, Me_3Si) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF, 300 K): δ 1.79 (s, Me_3Si) ppm.

^{7}Li NMR (155.5 MHz, d_8-THF, 300 K): δ -0.34 (s) ppm.

IR υ 3420.4 (broad, NH), 2245.5 (s, C-N), 1651.8 (s, C=O) cm^{-1}

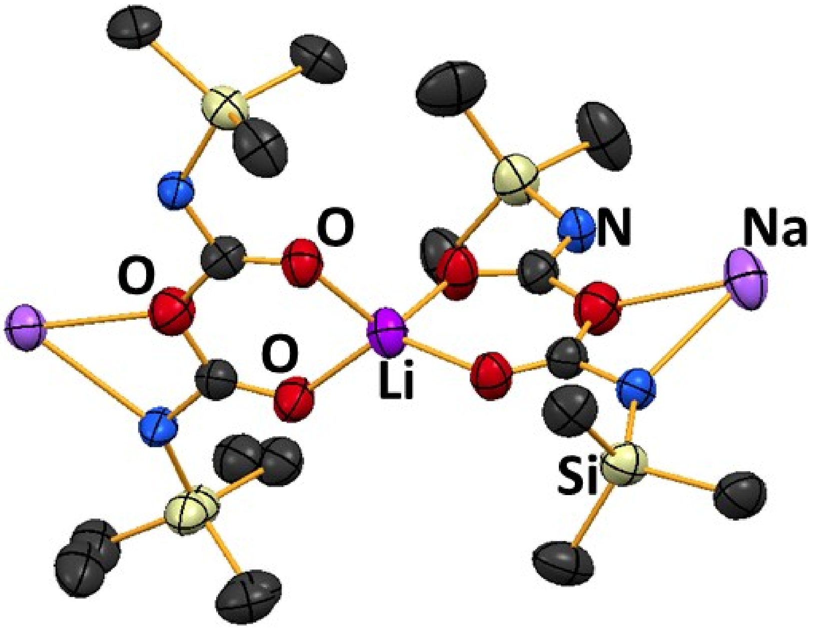
Melting point: Decomposes at 280 ^{O}C

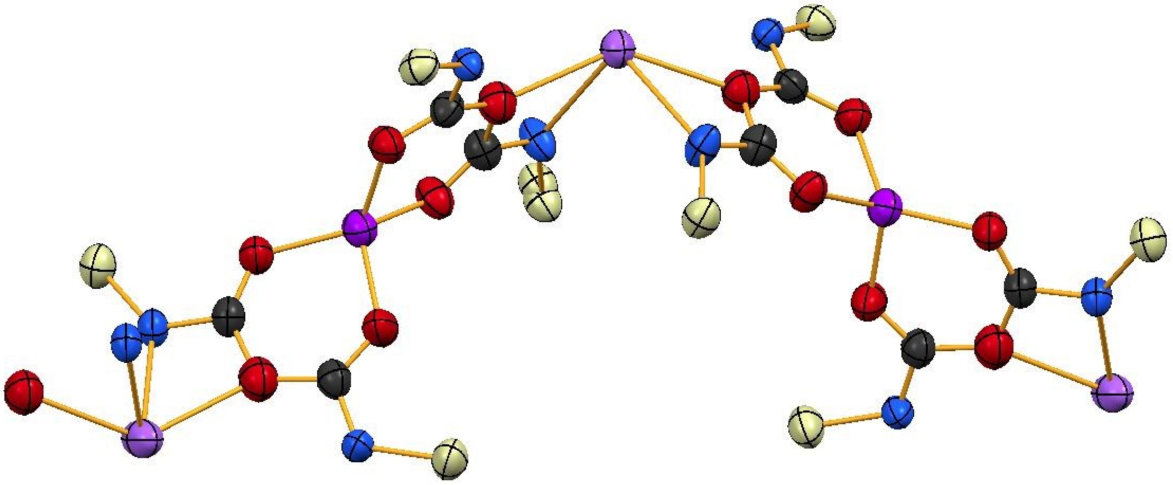
Elemental analysis (%) for $[(Me_3Si)NC(=O)OC(=O)N(H)(SiMe_3)]_2LiNa(THF)_4$: calcd: C 51.56, H 7.97, N 6.33; found : C 13.99, H 0.42, N 11.85.

Due to the extreme air- and moisture-sensitivity of this complex, satisfactory elemental analysis could not be obtained despite multiple attempts.

Figure 3: Molecular Structure of [(Me$_3$Si)NC(=O)OC(=O)N(H)(SiMe$_3$)]$_2$LiNa(THF)$_4$ (3)

Both hydrogen atoms and disordered THF solvent molecules omitted for clarity.





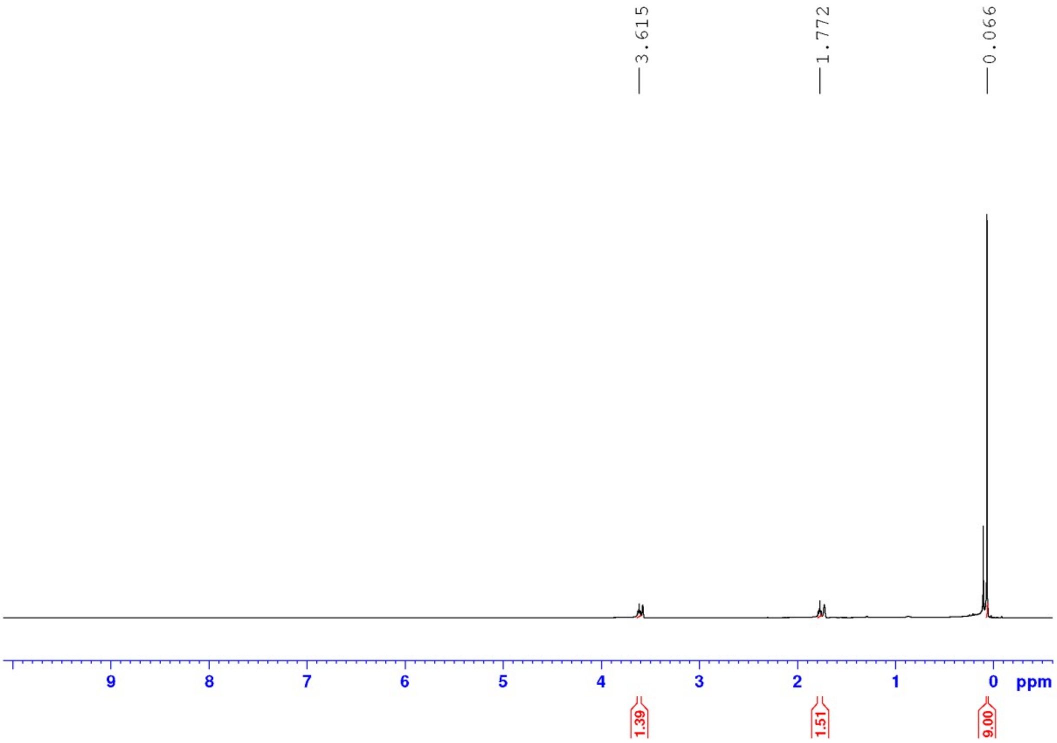


Figure 3.1: ^{1}H NMR in d$_8$-THF of compound **3**, [(Me$_3$Si)NC(=O)OC(=O)N(H)(SiMe$_3$)]$_2$LiNa(THF)$_4$

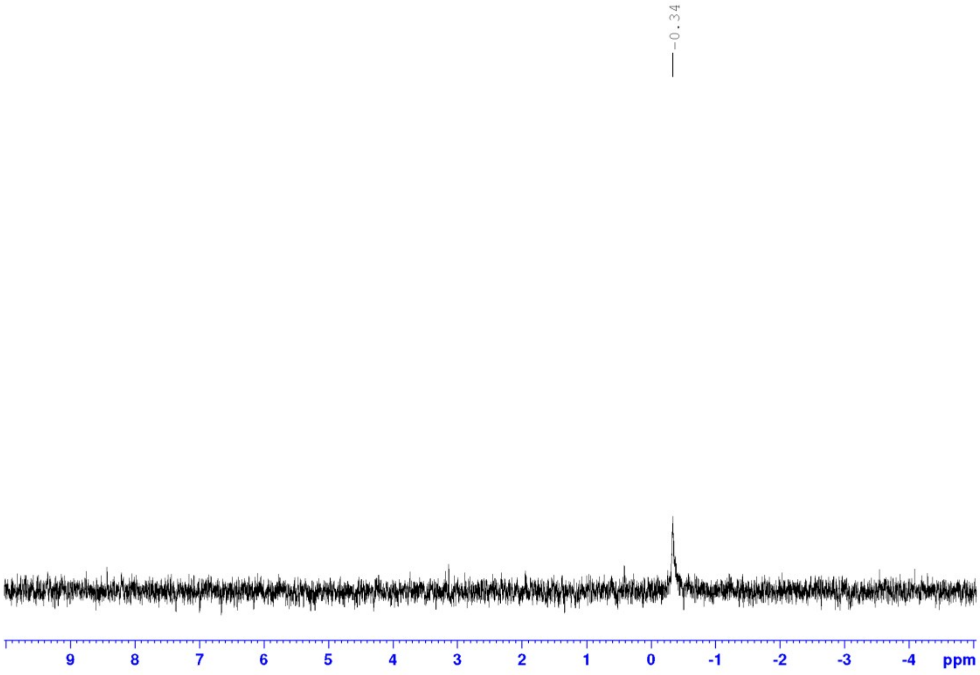
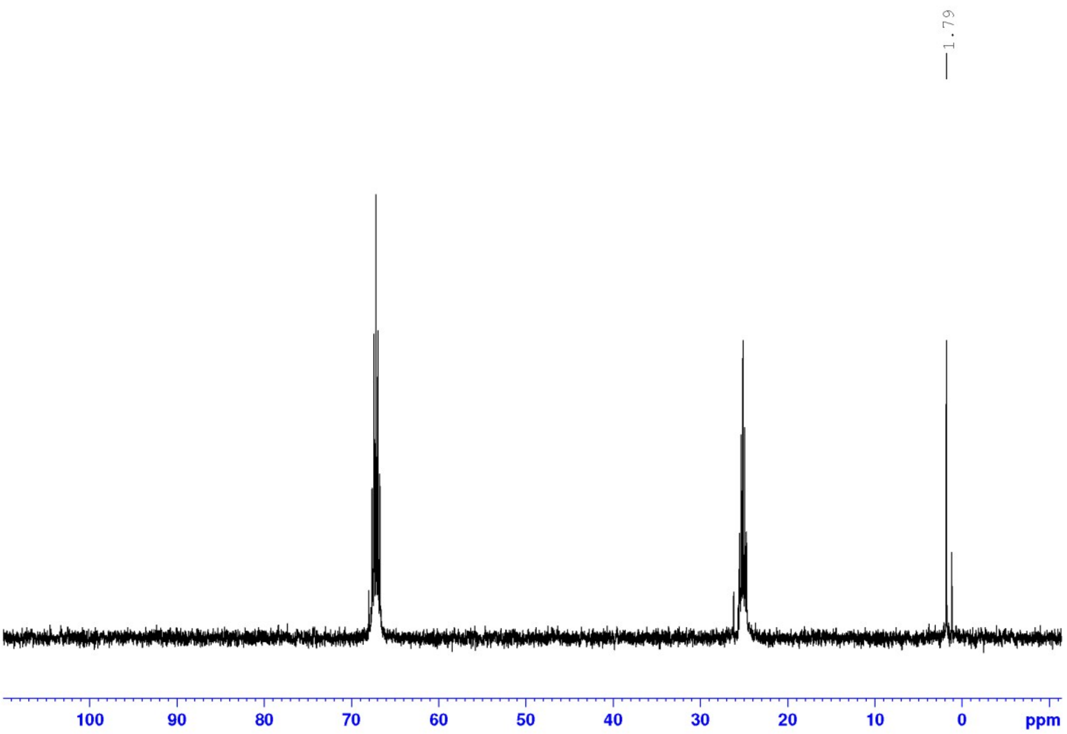


Figure 3.2: ^{7}Li NMR in d$_8$-THF of compound **3**, [(Me$_3$Si)NC(=O)OC(=O)N(H)(SiMe$_3$)]$_2$LiNa(THF)$_4$

Figure 3.3: -^{13}C NMR in d$_8$-THF of compound **3**, [(Me$_3$Si)NC(=O)OC(=O)N(H)(SiMe$_3$)]$_2$LiNa(THF)$_4$



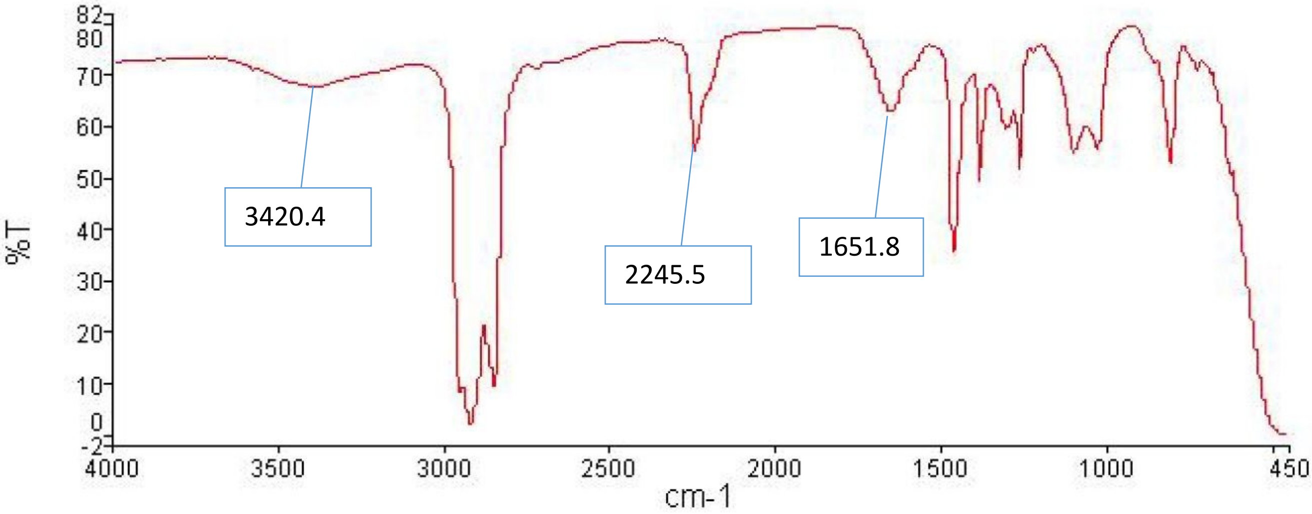


Figure 3.4: IR spectrum of compound **3**, [(Me$_3$Si)NC(=O)OC(=O)N(H)(SiMe$_3$)]$_2$LiNa(THF)$_4$recorded as a nujol mull

Table 1: X-ray crystal structural data and refinement details for compounds **1-3**

Compound	**[{(THF).Li($CO_2NC_4H_4$)}$_\infty$], 1**	**[{($i$$Pr_2$NCOOLi)$_{12}$($i$$Pr_2$NCOOH)$_2$}], 2**	**[(Me_3Si)NC(=O)OC(=O)N(H)($SiMe_3$)]$_2$LiNa(THF)$_4$, 3**
Empirical Formula	$C_9H_{12}LiNO_3$	$C_{98}H_{198}Li_{12}N_{14}O_{28}$	$C_{28}H_{62}LiN_4NaO_9Si_4$
Molecular Mass	189.14	2104.02	741.10
λ	Mo Kα (λ = 0.71073)	Cu Kσ (λ = 1.54184)	Cu Kσ (λ = 1.54184)
Space Group	P-1	P-1	C2
Crystal system	Triclinic	Triclinic	Monoclinic
Temperature (K)	153	153	123
a/Å	5.4312(10)	14.8500(7)	22.2504(11)
b/Å	7.6252(16)	15.5422(6)	13.1969(5)
c/Å	12.092(2)	17.5104(7)	17.7522(8)
α/°	84.577(15)	110.729(4)	90
β/°	87.445(14)	95.790(3)	112.116(5)
γ/°	76.369(17)	98.130(4)	90
Volume/Å^3	484.37(16)	3691.8(3)	4829.2(4)
Z	2	1	4
Measured Reflections	2777	34191	11971
Unique Reflections	1891	14449	6709
R_{int}	0.0239	0.0892	0.0400
Observed Reflections [I>2σI]	1145	9486	5340
Goodness of Fit	1.098	0.992	1.054
R [on F, obs refs only]	0.0641	0.0957	0.0891
ωR [on F^2, all data]	0.1939	0.3087	0.2660
Largest diff. peak /hole/Å^{-3}	0.38/-0.41	0.73/-0.56	0.68/-0.49

References

1. Agilent, CrysalisPrp, Agilent Technologies Ltd., Yarnton, Oxfordshire, England. 2014.
2. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
4. A. L. Spek, *Acta Crystallogr., Sect. C*, 2015, **71**, 9-18.
5.