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Electronic supporting information

Simplifying metal-'ate' chemistry: formation and comprehensive characterisation of a homo-metallic amido lithiate complex

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General Information

^{1}H NMR

Proton NMR (^{1}H NMR) spectra were recorded at 400 MHz on a BRUKER AUTO DRX 400 (400 MHz) spectrometer. Chemical shifts were recorded on the δ scale in parts per million (ppm). Spectra were measured in benzene-d_6 (C_6D_6) using the residual C_6D_6 signal (7.16 ppm) and tetrahydrofuran-d_8 (thf-d_8) using the residual thf-d_8 signal (3.58 ppm). The residual signal listed of each solvent was used as an internal reference. The resonance was reported according to the following convention: chemical shift (δ ppm) (number of hydrogens, multiplicity, coupling constant(s), assignment). Multiplicities are designated as s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), tt (triplet of triplet), q (quartet), dq (doublet of quartet) and m (multiplet).

^{13}C NMR

Carbon NMR (^{13}C NMR) spectra were recorded at 101 MHz on a BRUKER AUTO DRX 400 spectrometer. Chemical shifts were recorded on the δ scale in parts per million (ppm). Spectra were measured in benzene-d_6 (C_6D_6) using the triplet C_6D_6 signal (128.06 ppm), and tetrahydrofuran-d_8 (THF-d_8) using the pentet thf-d_8 signal (67.21 ppm).

^{7}Li NMR

Lithium NMR (^{7}Li NMR) spectra were recorded at 156 MHz on a BRUKER AUTO DRX 400 spectrometer to determine number of lithium environments, only.

Solvents and reagents

^{n}Hexane, tetrahydrofuran (thf), toluene, and diethyl ether (Et_2O) were degassed and dried using a MBRAUN SPS-800 solvent purification system and stored over 4Å molecular sieves under N_2. 1.6M ^{n}BuLi in hexane, 1-naphthylamine, allyl bromide, tmeda and pmdta were purchased from Aldrich. Allyl-1-naphthylamine was synthesized from from allyl bromide and 1-naphthylamine following the procedure described by Yus.[1]

Reaction under inert conditions – Schlenk protocol

All reactions requiring inert conditions were conducted using oven-dried glassware under a N_2 atmosphere using a vacuum/nitrogen line and Schlenk techniques. All glassware was dried at 120 °C for at least 24 hours prior to use. The Schlenk assembly was purged of air and moisture under high vacuum and backfilled with nitrogen three times. Liquids were transferred through rubber seals using oven dried nitrogen purged syringes or cannula. Filtering of solutions were carried out through rubber seals using oven dried nitrogen purged cannula with glass fibre microfilters (GF/A, circles ø 42.5 mm, Whatman®) which were fixed with Teflon tape. All manipulations of air-sensitive solids were carried out in a high-purity nitrogen recirculating dry box.

Single crystal x-ray diffraction

Crystallographic data for compounds **1, 2a** and **3** were obtained on a Bruker X8 APEXII CCD diffractometer[2] equipped with an OXFORD Cryosystems 700 and cooled to 123(1) K. Data was collected with monochromatic (graphite) Mo Kα radiation (λ = 0.71073 Å) and processed using the Bruker Apex2 v2012.2.0 software; Lorentz, polarization and absorption corrections (multi-scan – SADABS)[3] were applied. Compounds **1, 2a** and **6** were solved and refined with SHELX-97.[4] All non-hydrogen atoms were refined with anisotropic thermal parameters unless otherwise indicated and hydrogen atoms were placed in calculated positions using a riding model with C-H = 0.95-0.98 Å and U_{iso}(H)=xU_{iso}(C), x = 1.2 or 1.5. Data for **1, 2a** and **3** has been deposited with the Cambridge Crystallographic Database with CCDC numbers 1472608-1472610 respectively.

Compound	**1**	**2a**	**3**
Chemical formula	$C_{34}H_{44}Li_2N_2O_2$	$C_{38}H_{56}Li_2N_6$	$C_{22}H_{35}LiN_4$
Formula Mass	526.59	610.77	362.48
Crystal system	Triclinic	Orthorhombic	Orthorhombic
a/Å	7.9155(5)	9.170(3)	9.0445(8)
b/Å	9.4118(8)	24.337(9)	15.2792(11)
c/Å	10.9071(9)	33.568(11)	15.5861(13)
α/°	92.056(5)	90	90
β/°	96.772(4)	90	90
γ/°	108.249(4)	90	90
Unit cell volume/Å^3	763.83(10)	7492(4)	2153.9(3)
Temperature/K	173(2)	173(2)	173(3)
Space group	*P*-1	*Fdd2*	*P212121*
No. of formula units per unit cell, Z	1	8	4
No. of reflections measured	23211	15286	10724
No. of independent reflections	3965	3937	4211
R_{int}	0.1022	0.0376	0.0218
Final R_1 values ($I > 2\sigma(I)$)	0.0512	0.0837	0.0355
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1371	0.2386	0.0821
Final R_1 values (all data)	0.0810	0.1087	0.0434
Final $wR(F^2)$ values (all data)	0.1512	0.2653	0.0866

Summary of ^{1}H NMR Shifts in ppm (ally only)

H Environment	ally-1-naph	1	2a	3
NC<u>H</u>$_2$	3.49	3.85	4.01	4.17
C<u>H</u>=CH$_2$	5.72	6.09	6.50	6.34
CH=C<u>H</u>$_2$^{a}	5.11	5.13	5.38	5.44
CH=C<u>H</u>$_2$^{b}	4.99	4.89	5.06	5.19
ArH2	6.48	5.89	6.44	6.59
ArH3	7.32	6.92	7.60	7.68
ArH4	7.25	6.25	6.89	6.95
ArH5	7.43	7.34	7.81	7.89
ArH6	7.20	7.03	7.33	7.40
ArH7	7.39	6.87	7.07	7.08
ArH8	7.69	8.12	8.18	8.16

Summary of ^{13}C NMR Shifts in ppm (allyl only)

C Environment	ally-1-naph	1	2a	3
NC<u>H</u>$_2$	47.0	53.2	53.5	53.0
<u>C</u>H=CH$_2$	135.9	143.3	143.3	142.7
CH=<u>C</u>H$_2$	116.4	115.2	113.1	111.8
ArC1	143.9	158.4	157.3	159.2
ArC2	105.4	104.5	99.7	101.7
ArC3	126.2	129.2	130.0	130.5
ArC4	118.2	110.7	105.2	105.1
ArC5	135.3	140.7	136.6	138.1
ArC6	120.8	129.4	128.9	128.8
ArC7	125.0	123.7	129.4	124.5
ArC8	127.3	125.4	122.3	119.9
ArC9	129.3	121.4	120.7	123.8
ArC10	135.7	129.6	130.0	129.8

^{1}H NMR of allyl-1-naphthylamine ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 3.49 (2H, d, J = 4.93 Hz, NH-C<u>H</u>$_2$), 3.98 (1H, br s, NH), 4.99 (1H, ddt, J = 10.37 Hz, 1.52 Hz, 1.47 Hz, CH=C<u>H</u>$_2$^{a}), 5.11 (1H,

ddt, J = 17.29 Hz, 1.77 Hz, 1.62 Hz, CH=C$\underline{H}_2$[b]), 5.72 (1H, m, C$\underline{H}$=CH_2), 6.48 (1H, d, J = 7.42 Hz, ArH2), 7.20 (1H, ddd, J = 7.62, 6.66, 1.40 Hz, ArH6), 7.25 (1H, d, J = 8.17 Hz, ArH4), 7.29 (1H, ddd, J = 7.51, 6.72, 0.99 Hz, ArH7), 7.32 (1H, t, J = 8.11 Hz, ArH3), 7.43 (1H, d, J = 8.46 Hz, ArH5), 7.69 (1H, d, J = 8.11 Hz, ArH8); ^{13}C NMR (101 MHz, 25 °C, C_6D_6) δ 47.0 (N$\underline{C}H_2$), 116.4 (CH=$\underline{C}H_2$), 135.9 ($\underline{C}$H=CH_2), 143.9 (ArC1), 105.4 (ArC2), 126.2 (ArC3), 118.2 (ArC4), 135.7 (ArC5), 120.8 (ArC6), 125.0 (ArC7), 127.3 (ArC8), 129.3 (ArC9), 135.3 (ArC10)

Synthesis of [(1-naph)($CH_2CH=CH_2$)NLi.Et_2O]$_2$ 1 *N*-allyl-1-naphthylamine (0.53 mL, 3 mmol) was cooled to < -50 °C in Et_2O (12mL) followed by addition of 1.6M ^{n}BuLi in hexane (1.9 mL, 3mmol) dropwise and stirred for 1 hour. Solution quickly became yellow/orange and clear, some yellow precipitate was present below -50 °C. At 0 °C hexane (4mL) was added and the solution stirred for 5 mins proceeded by reduction of the volume by 1/3 *in vacuo* and placed in a freezer at -17 °C, within 1 hour crystals formed. Notes; if precipitate appears stir at room temperature and add minimum amount of Et_2O to dissolve precipitate, if not precipitate appears reduce solvent volume further *in vacuo*.

Elemental %: N: 6.80 C: 80.43 H: 6.37

Note; elemental affected by partial removal of Et_2O under vacuum prior to sample preparation.

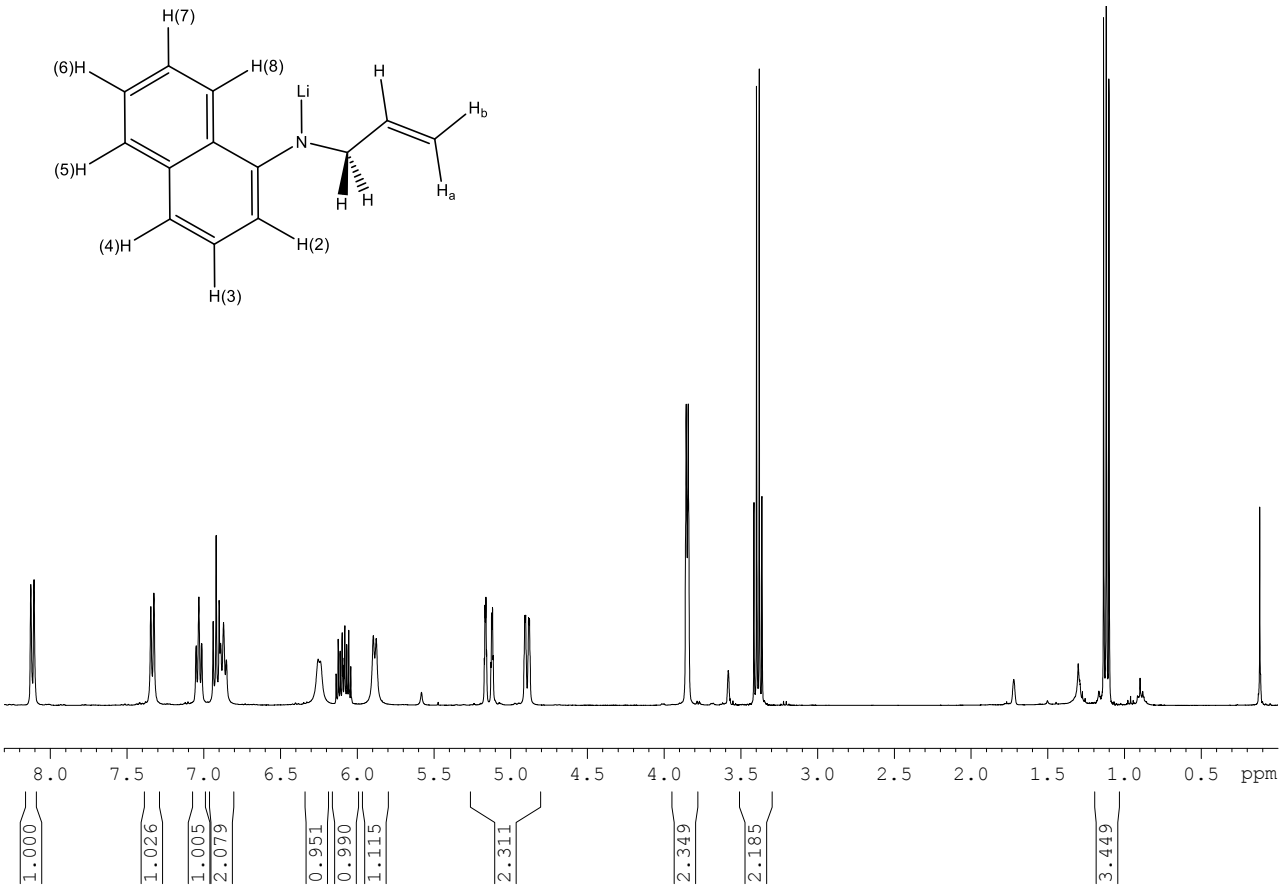

Figure 1 ^{1}H NMR of [(1-naph)($CH_2CH=CH_2$)NLi.Et_2O]$_2$ in D_8-thf. *Et_2O integrations are lower than expected due to vacuum treatment prior to being dissolved in NMR solvent.

^{1}H NMR of [(1-naph)($CH_2CH=CH_2$)NLi.Et_2O]$_2$ 1 ^{1}H NMR (400 MHz, 25 °C, D_8-thf) δ 1.12 (4H, t, J = 7.07, OC<u>H</u>$_2$) 3.39 (6H, q, J = 6.93, 7.03 Hz, CH_2C<u>H</u>$_3$), 3.85 (2H, dt, J = 5.26, 1.44 Hz, N-C<u>H</u>$_2$), 4.89 (1H, ddt, J = 10.15, 2.64, 1.42 Hz, CH=C<u>H</u>$_2^b$), 5.13 (1H, ddt, J = 17.19, 2.54, 1.81, CH=C<u>H</u>$_2^a$), 6.09 (1H, m, CH_2C<u>H</u>), 5.89 (1H, d, J = 7.66 Hz, ArH2), 6.25 (1H, d, J = 5.77 Hz, ArH4), 6.87 (1H, t, J = 7.76 Hz, ArH7), 6.92 (1H, t, J = 8.12 Hz, ArH3), 7.03 (1H, t, J = 7.29 Hz, ArH6), 7.34 (1H, d, J = 8.08 Hz, ArH5), 8.12 (1H, d, J = 8.38 Hz, ArH8); ^{13}C NMR (101 MHz, 25 °C, C_6D_6) δ 15.8 (O<u>C</u>H$_2$) 66.2 (OCH_2<u>C</u>H$_3$), 53.2 (N<u>C</u>H$_2$), 115.2 (CH=<u>C</u>H$_2$), 143.3 (<u>C</u>H=CH$_2$), 140.7 (ArC1), 104.5 (ArC2), 129.2 (ArC3), 110.7 (ArC4), 136.9 (ArC5), 129.4 (ArC6), 123.7 (ArC7), 125.4 (ArC8), 121.4 (ArC9), 129.6 (ArC10)

Synthesis of [Li·(TMEDA)$_2$]$^+$ [Li{N(1-naph)($CH_2CH=CH_2$)}$_2$]$^-$ 2a *N*-allyl-1-naphthylamine (0.53 mL, 3 mmol) was cooled to < -50 ^{o}C in hexane (12mL) followed by addition of 1.6M ^{n}BuLi in hexane (1.9 mL, 3mmol) dropwise. At 0 ^{o}C an equivalent of TMEDA was added dropwise and stirred for 1 hour forming a mixture of orange precipitate and a small amount of red oil. The solvent volume was reduced by half *in vacuo* and the products dissolved by addition of Et_2O (8mL) and the solution left stirring overnight (12 hours) The resulting solution was an intense red, when left standing at room temperature a yellow micro crystalline solid was deposited. Re-dissolving this solid into solution using a hot water bath (40 ^{o}C) and left standing once more allowed deposition of deep red cube-shaped crystals.

Elemental %: N: 13.88 C: 73.82 H: 8.96

Further notes; the yellow micro-crystalline solid has been isolated repeatedly and found to have the same crystal shape as the red crystals, but dissolves back into solution at room temperature before being re-deposited as the more intensely coloured red solid. ^{1}H NMR of solids ranging from yellow through to red showed a greater % conversion of the allyl amide to the aza-ally species. Isolation of the pure allyl amide species has proved difficult given the presence of the aza-ally species was seen in spectra made up from crystalline solids.

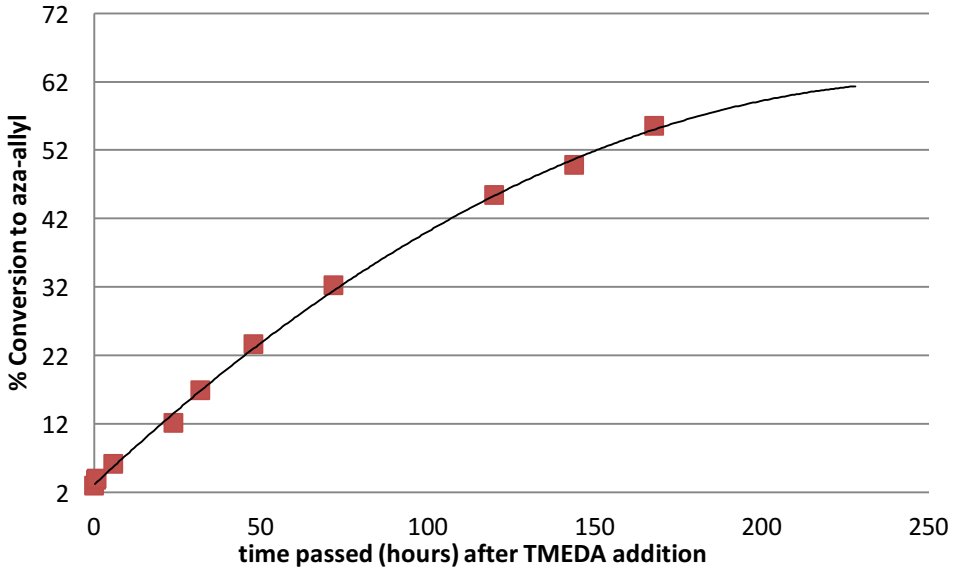

Figure 2 % Conversion of ally amide to aza-ally amide species in C_6D_6 over time (hours)

Figure 3 ^{1}H NMR of $[Li{\cdot}(TMEDA)_2]^+$ $[Li\{N(1\text{-naph})(CH_2CH{=}CH_2)\}_2]^-$ (aza-allyl) in C_6D_6, both **2a** and **2b** present in spectrum.

NMR of $[Li(TMEDA)_2][\ Li\{N(1\text{-naph})(CH_2CH{=}CH_2)\}_2]$ (allyl) 2a ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 1.60 (4H, brs, NC$\underline{H}_2$C$\underline{H}_2$N), 1.60 (12H, brs, NC$\underline{H}_3$), 4.01 (2H, d, J = 6.0 Hz, NC$\underline{H}_2$) , 6.50 (1H, m, C$\underline{H}$=CH$_2$), 5.06 (1H, d, J = 9.6 Hz, CH=C$\underline{H}_b$), 5.38 (1H, d, J = 17.2 Hz, CH=C$\underline{H}_a$), 6.44 (1H, d, J =

7.6 Hz, ArH2), 6.89 (1H, d, J = 8.0 Hz, ArH4), 7.07 (1H, dd, J = 8.0, 8.0 Hz, ArH7), 7.33 (1H, ddd, J = 8.0, 7.4, 1.6 Hz, ArH6), 7.60 (1H, t, J = 7.6 Hz, ArH3), 7.81 (1H, d, J = 9.0 Hz, ArH5), 8.18 (1H, d, J = 8.0 Hz, ArH8); ^{13}C NMR (101 MHz, 25 °C, C_6D_6) δ 44.6 (N<u>C</u>H$_3$) 53.5 (N<u>C</u>H$_2$), 55.8 (N<u>C</u>H$_2$), 143.3 (<u>C</u>H=CH$_2$), 113.1 (CH=<u>C</u>H$_2$), 136.6 (ArC1), 99.7 (ArC2), 130.0 (ArC3), 105.2 (ArC4), 130.0 (ArC5), 128.9 (ArC6), 129.4 (ArC7), 122.3 (ArC8), 120.7 (ArC9), 129.4 (ArC10)

^{1}H NMR of [Li(TMEDA)$_2$][Li{N(1-naph)(CH$_2$CH=CH$_2$)}$_2$] (aza-allyl) 2b ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 1.60 (4H, brs, NC<u>H</u>$_2$C<u>H</u>$_2$N), 1.60 (12H, brs, NC<u>H</u>$_3$), 7.60 (H, d, J = 7.6 Hz, NC<u>H</u>), 4.60 (1H, dq, J = 6.5, 7.2 Hz, CH=C<u>H</u>), 2.01 (3H, dd, J = 6.1, 1.4 Hz, CH-C<u>H</u>$_3$), 7.05 (1H, d, J = 7.9 Hz, ArH2), 7.11 (1H, d, J = 7.6 Hz, ArH4), 7.14 (1H, ddd, J = 8.4, 5.1, 1.7 Hz, ArH7), 7.34 (1H, ddd, J = 8.30, 6.50, 1.40 Hz, ArH6), 7.55 (1H, t, J = 7.8 Hz, ArH3), 7.81 (1H, d, J = 9.0 Hz, ArH5), 8.48 (1H, d, J = 8.2 Hz, ArH8)

Synthesis of [Li{(1-naph)(CH$_2$CH=CH$_2$)N}·PMDETA] 3 *N*-allyl-1-naphthylamine (0.53 mL, 3 mmol) was cooled to < -50 °C in Et$_2$O (12mL) followed by addition of 1.6M ^{n}BuLi in hexane (1.9 mL, 3mmol) dropwise and stirred for 1 hour. At 0 °C 1 equivalent of PMDETA was added dropwise, resulting in formation of an orange precipitate. The solvent was removed *in vacuo* and then dissolved in THF (6mL) followed by induced precipitation using hexane (6mL). The solution was stirred in a hot water bath (40 °C) then placed in the fridge at -5 °C. Yellow/orange diamond-shaped crystals formed within 1 hour.

Elemental %: N: 12.31 C: 65.20 H: 7.81

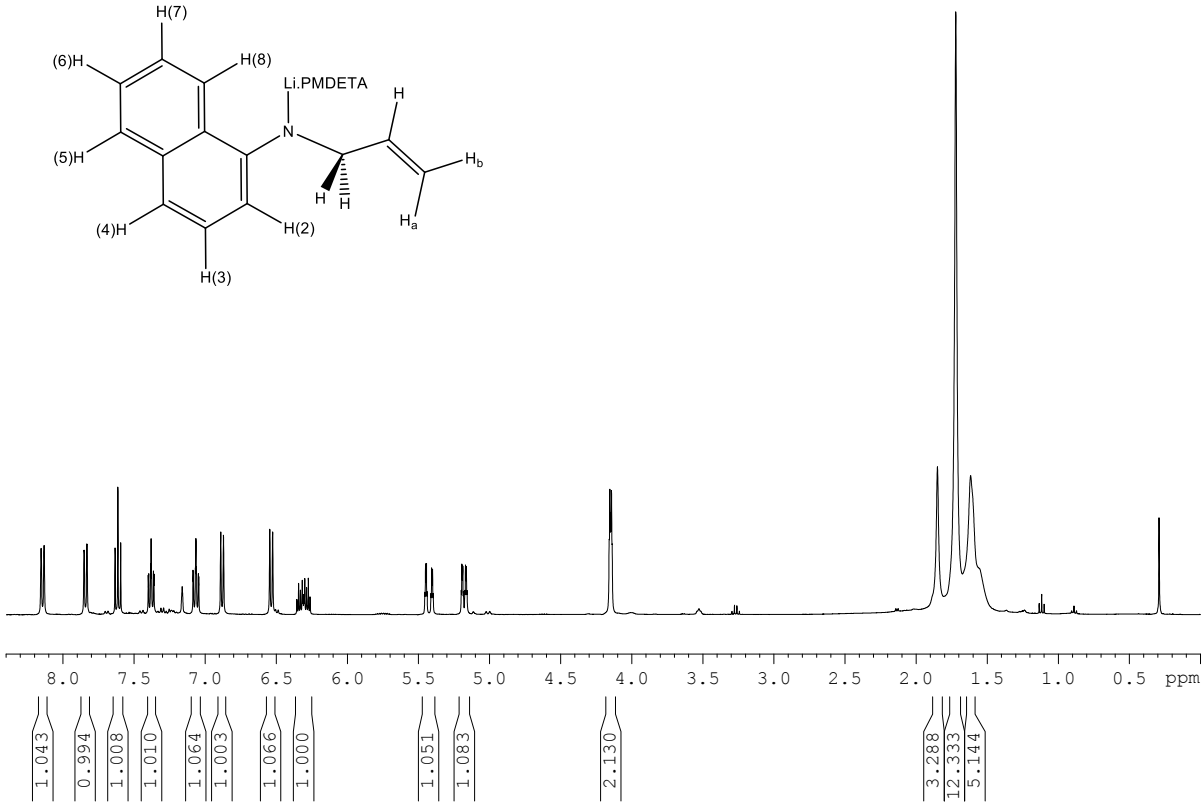

Figure 4 ^{1}H NMR of [Li{(1-naph)(CH$_2$CH=CH$_2$)N}·PMDETA] in C_6D_6.

^{1}H NMR of [Li{(1-naph)($CH_2CH=CH_2$)N}·PMDETA] 3 ^{1}H NMR (400 MHz, 25 °C, C_6D_6) δ 1.60 (8H, m, NC<u>H</u>$_2$C<u>H</u>$_2$N), 1.71 (12H, s, NC<u>H</u>$_3$), 1.84 (3H, s, NC<u>H</u>$_3$), 4.17 (2H, dt, J = 4.78, 2.45 Hz, NC<u>H</u>$_2$), 5.19 (1H, ddt, J = 10.25, 2.56, 1.98 Hz, CH=C<u>H</u>$_2$[c]), 5.44 (1H, ddt, J = 17.24, 2.56, 1.86 Hz, CH=C<u>H</u>$_2$[d]), 6.34 (1H, m, CH_2C<u>H</u>), 6.59 (1H, d, J = 8.04 Hz, ArH2), 6.95 (1H, d, J = 7.69 Hz, ArH4), 7.08 (1H, ddd, J = 8.10, 6.60, 1.40 Hz, ArH7), 7.40 (1H, ddd, J = 8.30, 6.60, 1.40 Hz, ArH6), 7.68 (1H, t, J = 7.92 Hz, ArH3), 7.89 (1H, d, J = 7.92 Hz, ArH5), 8.16 (1H, d, J = 8.15 Hz, ArH8); ^{13}C NMR (101 MHz, 25 °C, C_6D_6) δ 53.0 (N<u>C</u>H$_2$), 57.1 (H$_3$<u>C</u>N), 53.0 (N<u>C</u>H$_2$), 111.8 (CH=<u>C</u>H$_2$), 142.0 (<u>C</u>H=CH$_2$), 138.1 (ArC1), 101.0 (ArC2), 130.5 (ArC3), 101.7 (ArC4), 128.8 (ArC5), 128.8 (ArC6), 123.8 (ArC7), 119.9 (ArC8), 123.8 (ArC9), 128.5 (ArC10)

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