Electronic Supplementary Material (ESI) for Chemical Communications.

Dehydromethylation of utility amide 2,2,6,6-tetramethylpiperidide (TMP) to aza-allyl 2,2,6-trimethyl-1,2,3,4-tetrahydropyridide (TTHP): synthesis of a homologous series of alkali metal (Li, Na, K) TTHP compounds

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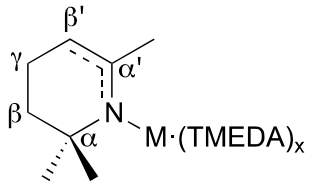
Contents

General Procedures

All reactions and manipulations were performed under a protective dry argon atmosphere using standard Schlenk techniques unless otherwise stated. Methylcyclohexane was distilled over sodium metal and stored with molecular sieves (4 Å) under nitrogen prior to use. *cyc*-C_6D_{12}, d_8-THF and C_6D_6 were degassed and stored over 4 Å molecular sieves prior to use. $CDCl_3$ was stored over 4 Å molecular sieves. NMR spectra were recorded at 300 K on Bruker Avance and DPX 400 MHz NMR spectrometers, operating at 400.1, 155.5 and 100.6 MHz for ^{1}H, ^{7}Li and ^{13}C, respectively. ^{1}H and ^{13}C chemical shifts (ppm) were referred to residual solvent signals, and ^{7}Li NMR spectra were referenced against an external standard solution of LiCl in D_2O (1 M, δ = 0 ppm). The assignments of the ^{1}H and ^{13}C{^{1}H} NMR spectra were made with the help of COSY, HMBC, and HSQC experiments. Despite several attempts, satisfactory elemental analyses of the compounds **1·TMEDA**, **2**, **2·TMEDA**, and **3**, carried out using a Perkin Elmer 2400 elemental analyser, could not be obtained due to their high air- and moisture-sensitive nature. Mass spectra (EI GCMS) for **4** was recorded on a Polaris Q from Thermo with helium as a carrier gas at 1ml/min and using an Agilent HP5-MS column (30m x 0.25mm x 0.25µm). Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrophotometer, and the samples were prepared within an argon-filled glove box using Nujol mulls between KBr plates. *n*BuLi (1.6M in hexanes, Aldrich) was titrated prior to use. TMEDA (N,N,N′,N′-tetramethylethylenediamine, Aldrich) was distilled over CaH_2 under nitrogen atmosphere and stored over activated molecular sieves (4 Å). TMP(H) (2,2,6,6-tetramethylpiperidine, Merck KGaA) was stored over activated molecular sieves (4 Å) prior to use. *n*-BuNa,[1] and Me_3SiCH_2K[2] were prepared according to literature methods.



TTHP–M·(TMEDA)$_x$

M	x	
Li	0	**1**
Li	1	**1·TMEDA**
Na	0	**2**
Na	1	**2·TMEDA**
K	0	**3**

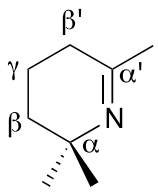


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Chart S1. Atom labelling used in NMR data (TTHP = 2,2,6-trimethyl-1,2,3,4-tetrahydropyridide).

***In situ* preparation of [Li(TTHP)] (1).**

To a Schlenk flask under argon was added *n*BuLi (2.5 mL of a 1.6M solution in hexane, 4 mmol) followed by TMP(H) (0.68 mL, 4mmol) via syringe. The resulting mixture was stirred for 15 min during which time an off-white precipitate formed in the mixture. Methylcyclohexane (20 mL) was added via syringe and the yellow solution was then heated to reflux. NMR spectroscopic analysis of an aliquot of the reaction mixture after 18h under reflux conditions showed a conversion of 25% (approx.) of LiTMP into **1** (see Fig. S3). Several attempts to improve the demethylation conditions and crystallization of **1** were unsuccessful. ^{1}H NMR (400.1 MHz, d_8-THF, 300 K, *reaction mixture*): δ, **1** (25% approx.), 1.02 (s, 6H, CMe_2), 1.17 (t, 2H, ^{3}J(H,H) = 6.6 Hz, β-CH_2), 1.57 (s, 3H, Me'), 2.05 (m, 2H, γ-CH_2), 3.37 (m, 1H, β'-CH); LiTMP (75% approx.), 1.08 (s, 12H, 4 x Me), 1.21 (t, 4H, ^{3}J(H,H) = 6.1 Hz, β-CH_2) 1.59-1.70 (m including 2H, γ-CH_2); signals for TMP(H) are also observed due to unavoidable hydrolysis of LiTMP during NMR analysis. ^{7}Li NMR (155.5 MHz, d_8-THF, 300 K, *reaction mixture*): δ, 1.12, 2.14 (v br).

Synthesis of [TMEDA·Li(TTHP)] (1·TMEDA).

To a Schlenk flask under argon was added *n*BuLi (2.5 mL of a 1.6M solution in hexane, 4 mmol) followed by TMP(H) (0.68 mL, 4 mmol) via syringe. The resulting pale yellow solution was stirred for 15 min during which time an off-white precipitate formed in the reaction mixture. Methylcyclohexane (20 mL) was added via syringe followed by TMEDA (1.2 mL, 8 mmol) to give a pale yellow solution (*c.a.* 2 equivalents was required). The reaction mixture was then heated to reflux for 18 h after which the mixture was a dark orange solution containing a brown oily material. NMR spectroscopic analysis of an aliquot of the reaction mixture showed quantitative dehydromethylation to TMEDA·LiTTHP (**1·TMEDA**, see Fig. S4). The solution was separated from the oil via cannula and cooled to -25 °C for 15 h to yield a small crop of suitable XRD quality orange crystals of **1·TMEDA** (typical yield 160 mg, 0.65 mmol, 16%). ^{1}H and ^{7}Li NMR spectroscopic analysis of the brown oil reveals the presence of a characteristic LiTTHP:TMEDA resonances in a 1:1 ratio (approx.) which resemble those signals of the crystalline material (see Fig. S9). ^{1}H NMR (400.1 MHz, d_8-THF, 300 K): δ 0.99 (s, 6H, CMe_2), 1.17 (t, 2H, ^{3}J(H,H) = 6.6 Hz, β-CH_2), 1.55 (s, 3H, α'-CMe), 2.07 (m, 2H, γ-CH_2), 2.15 (s, 12H, TMEDA-CH_3), 2.30 (s, 4H,

TMEDA-CH_2), 3.31 (m, 1H, *β'*-C*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, d_8-THF, 300 K): δ 23.2 (*γ*-*C*H_2), 26.1 (*α'*-C*Me*), 30.7 (*α*-C*Me*$_2$), 38.2 (*β*-*C*H_2), 46.0 (TMEDA-*C*H_3), 51.2 (*α*-*C*Me$_2$), 58.7 (TMEDA-*C*H_2), 76.5 (*β'*-*C*H), 149.4 (*α'*-*C*Me). ^{7}Li NMR (155.5 MHz, d_8-THF, 300 K): δ 1.10. IR (Nujol, cm^{-1}): *ν*(NC=C), 1575.

Synthesis of [Na(TTHP)] (2). Freshly prepared *n*-BuNa (320 mg, 4 mmol) was suspended in methylcyclohexane (20 mL) and TMP(H) (0.68 mL, 4 mmol) was added via syringe. The resulting pale yellow suspension was heated to reflux to give a solution which turned into a pale brown suspension after 5 min under reflux. The reaction mixture was refluxed for 12 h and the resulting suspension was filtered. The collected solid was washed with *n*-hexane (5 mL) and dried under vacuum to give **2** as a pale brown solid (480 mg, 3.26 mmol, 82%). ^{1}H NMR (400.1 MHz, d_8-THF, 300K): δ 0.98 (s, 6 H, C*Me*$_2$), 1.17 (t, 2 H, $^3J_{HH}$ = 6.5 Hz, *β*-CH_2), 1.58 (s, 3 H, *α'*-C*Me*), 2.09 (br m, 2 H, *γ*-CH_2), 3.27 (t, 1 H, $^3J_{HH}$ = 3.1 Hz, *β'*-C*H*). $^{13}C\{^1H\}$ NMR (100.8 MHz, d_8-THF, 300K): δ 23.5 (*γ*-*C*H_2), 27.3 (*α'*-C*Me*), 31.5 (C*Me*$_2$), 38.3 (*β*-*C*H_2), 51.2 (*C*Me$_2$), 74.9 (*β'*-*C*H), 150.8 (*α'*-C). IR (Nujol, cm^{-1}): *ν*(NC=C), 1538.

Synthesis of [TMEDA·Na(TTHP)]$_2$ (2·TMEDA) [equimolar amount of TMEDA]. Freshly prepared n-BuNa (400 mg, 5 mmol) was suspended in methylcyclohexane (20 mL) and TMP(H) (0.85 mL, 5 mmol) was added. The resulting pale yellow suspension was stirred for 30 min and then TMEDA (0.75 mL, 5 mmol) was added via syringe. The reaction mixture was stirred for 30 min at room temperature and then it was refluxed for 6 h to give a dark orange slight suspension which was filtered through Celite. The resulting orange solution was concentrated in vacuo (*c.a.* 5 mL) and upon standing at room temperature for 48 h afforded **2·TMEDA** as a crystalline material suitable for XRD studies. Crystalline **2·TMEDA** was filtered and washed with *n*-hexane (5 mL) and dried under vacuum (950 mg, 2.17 mmol, 87%). The filtrate was concentrated under vacuum to dryness to give a dark brown foam (90 mg, 0.21 mmol, 8%) which NMR data resembles that of the crystalline material, proving that the reaction is near quantitative (95%).

Synthesis of [TMEDA·Na(TTHP)]$_2$ (2·TMEDA) [excess of TMEDA (3 equiv)]. Freshly prepared n-BuNa (320 mg, 4 mmol) was suspended in methylcyclohexane (20 mL) and TMP(H) (0.68 mL, 4 mmol) was added. The resulting pale yellow

suspension was stirred for 30 min and then an excess of TMEDA (1.8 mL, 12 mmol) was added in order to achieve a solution which was additionally stirred for 30 min at room temperature and then refluxed for 6 h to give a dark orange solution. The reaction mixture was concentrated under vacuum (c.a. 5 mL) and placed at -27ºC for 24 h to give **2·TMEDA** as a crystalline material suitable for XRD studies. Crystalline **2·TMEDA** was filtered, washed with *n*-hexane (5 mL) and dried under vacuum (620 mg, 1.41 mmol, 71%). The filtrate was concentrated under vacuum to dryness to give a dark brown foam (103 mg, 0.23 mmol, 10%) which NMR data resembles that of the crystalline material, proving that the reaction is almost quantitative (81%). XRD studies isolated crystalline material revealed that **2·TMEDA** crystallise, in both cases, within the same dimeric structure. ^{1}H NMR (400.1 MHz, d_8-THF, 300K): δ 0.96 (s, 6 H, C*Me*$_2$), 1.16 (t, 2 H, $^{3}J_{HH}$ = 6.5 Hz, β-C*H*$_2$), 1.56 (s, 3 H, α'-C*Me*), 2.11 (br m, 2 H, γ-C*H*$_2$), 2.15 (s, 12 H, TMEDA-C*H*$_3$), 2.30 (s, 4 H, TMEDA-C*H*$_2$), 3.23 (t, 1 H, $^{3}J_{HH}$ = 3.3 Hz, β'-C*H*). ^{1}H NMR (400.1 MHz, C_6D_6, 300K): δ 1.31 (s, 6 H, C*Me*$_2$), 1.63 (t, 2 H, $^{3}J_{HH}$ = 6.5 Hz, β-C*H*$_2$), 1.97, 1.98 (both s, 3 H and 4 H, α'-C*Me* and TMEDA-C*H*$_2$, respectively), 2.05 (s, 12 H, TMEDA-C*H*$_3$), 2.73 (v br "dt", 2 H, γ-C*H*$_2$), 4.04 (v br t, 1 H, β'-C*H*). ^{13}C{^{1}H} NMR (100.8 MHz, d_8-THF, 300K): δ 23.4 (γ-*C*H$_2$), 28.5 (α'-C*Me*), 32.4 (C*Me*$_2$), 37.9 (β-*C*H$_2$), 46.0 (TMEDA-CH$_3$), 51.3 (α-*C*Me$_2$), 57.7 (TMEDA-CH$_2$), 76.8 (β'-*C*H), 151.4 (α'-C). IR (Nujol, cm^{-1}): ν(NC=C), 1569.

Synthesis of [K(TTHP)] (3). Freshly prepared KCH_2SiMe_3 (512 mg, 4 mmol) was suspended in methylcyclohexane (20 mL) and TMP(H) (0.68 mL, 4 mmol) was added via syringe. The resulting pale yellow suspension was stirred at room temperature for 30 min and then heated to reflux for 3h to give a pale brown suspension. The newly obtained suspension was filtered and the collected solid washed with n-hexane (5 mL) and dried under vacuum to give **3** as a pale brown solid (542 mg, 3.32 mmol, 83%). ^{1}H NMR (400.1 MHz, d_8-THF, 300K): δ 0.93 (s, 6 H, C*Me*$_2$), 1.11 (t, 2 H, $^{3}J_{HH}$ = 6.4 Hz, β-C*H*$_2$), 1.55 (s, 3 H, α'-C*Me*), 2.14 (br m, 2 H, γ-C*H*$_2$), 3.14 (t, 1 H, $^{3}J_{HH}$ = 3.2 Hz, β'-C*H*). ^{13}C{^{1}H} NMR (100.8 MHz, d_8-THF, 300K): δ 23.7 (γ-*C*H$_2$), 26.8 (α'-C*Me*), 31.3 (α-C*Me*$_2$), 38.1 (β-*C*H$_2$), 51.3 (α-*C*Me$_2$), 71.5 (β'-*C*H), 150.5 (α'-*C*Me). IR (Nujol, cm^{-1}): ν(NC=C), 1538.

Synthesis of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (4). Freshly prepared K(TTHP) **3** (1.63 g, 10 mmol) was suspended in *n*-hexane (20 mL) and distilled water was added dropwise (2 mL). The reaction mixture was stirred for 1h, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum to yield the titled compound **4** as a pale yellow liquid (1.1 g, 8.79 mmol, 88%).

Alternative synthesis of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (4). Freshly prepared K(TTHP) **3** (1.63 g, 10 mmol) was suspended in *n*-hexane (20 mL) and 2,2,6,6-tetramethylpiperidine (TMPH, 1.7 mL, 10 mmol) was added via syringe. The resulting pale yellow suspension was stirred at room temperature for 30 min and then heated to reflux for 5h to give a pale brown suspension. Distilled water was added dropwise (1.5 mL) and the reaction mixture was stirred for 30 min, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum to yield the titled compound **4** as a pale yellow liquid (821 mg, 6.56 mmol, 83%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ 1.12 (s, 6 H, CMe_2), 1.40 (m, 2 H, β-CH_2), 1.61 (m, 2 H, γ-CH_2), 1.86 (s, 3 H, α'-CMe), 2.00 (t, 1 H, $^3J_{HH}$ = 6.8 Hz, β'-CH_2). ^{13}C{^{1}H} NMR (100.8 MHz, $CDCl_3$, 300K): δ 16.5 (γ-CH$_2$), 27.5 (α'-CMe), 29.6 (β'-CH$_2$), 30.1 (α-CMe_2), 33.8 (β-CH$_2$), 53.2 (α-CMe$_2$), 164.9 (α'-CMe). IR (Nujol, cm^{-1}): ν(NC=C), 1662. LRMS (GC/EI) m/z calc. for $C_8H_{16}N$ [M+H-1e$^-$]$^+$, 126.13; found, 126.12; calc. for $C_7H_{12}N$ [M-CH_3-1e$^-$]$^+$, 110.09; found, 110.12; consistent with reported data.[3]

Control reaction in absence of alkali metal.

To a Schlenk flask under argon methylcyclohexane (20 mL) was added via syringe, followed by TMP(H) (1.36 mL, 8 mmol). The resulting solution was heated to reflux for 24 h after which ^{1}H NMR spectroscopic analysis of an aliquot of the reaction mixture was carried out. The spectrum obtained showed only signals due to TMP(H), indicating that no demethylation had occurred. ^{1}H NMR (400.1 MHz, $CDCl_3$, 300K): δ 1.09 (s, 12 H, Me), 1.29 (m, 4 H, β-CH_2), 1.62 (m, 2 H, γ-CH_2).

Crystal Structure Determinations

Single-crystal data were recorded at 123(2) K on Oxford Diffraction Xcalibur and Gemini Diffractometers with Mo-$K\alpha$ (λ = 0.71073 Å; for **1·TMEDA**, Figure S1) and Cu-$K\alpha$ (λ = 1.5418 Å; for **2·TMEDA**, Figure S2) radiation, respectively. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL programs.[4] Selected crystallographic parameters are given in Table S1 and full details are given in the deposited cif files. CCDC-1002045 (**1·TMEDA**) and CCDC-1002046 (**2·TMEDA**) 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.

Table S1. Selected crystallographic and refinement data for **1·TMEDA** and **2·TMEDA**.

Compound	**1·TMEDA**	**2·TMEDA**
Formula	$C_{14}H_{30}LiN_3$	$C_{28}H_{60}N_6Na_2$
MW	247.35	526.80
Cryst. System	Monoclinic	Orthorhombic
Space Group	$P2_1/c$	P*bca*
Wavelength/Å	0.71073	1.5418
a/Å	7.7542(7)	10.7005(3)
b/Å	12.7074(9)	15.6464(5)
c/Å	17.2355(15)	19.4063(7)
β/°	102.159(9)°	
Volume/Å^3	1660.2(2)	3249.09(18)
Z	4	4
Temp./*K*	123(2)	123(2)
Refls. Collect.	17768	22031
$2\theta_{max}$	52.0	146.3
R_{int}	0.0711	0.0369
Refls. Unique	3275	3254
Refls. Obs.	2186	2483
Goodness of fit	1.074	1.079
$R[F^2>2\sigma]$, *F*	0.0604	0.0527
R_w (all data), F^2	0.1295	0.1560
Largest diff. peak/hole/e Å^{-3}	0.198/-0.175	0.309/-0.201

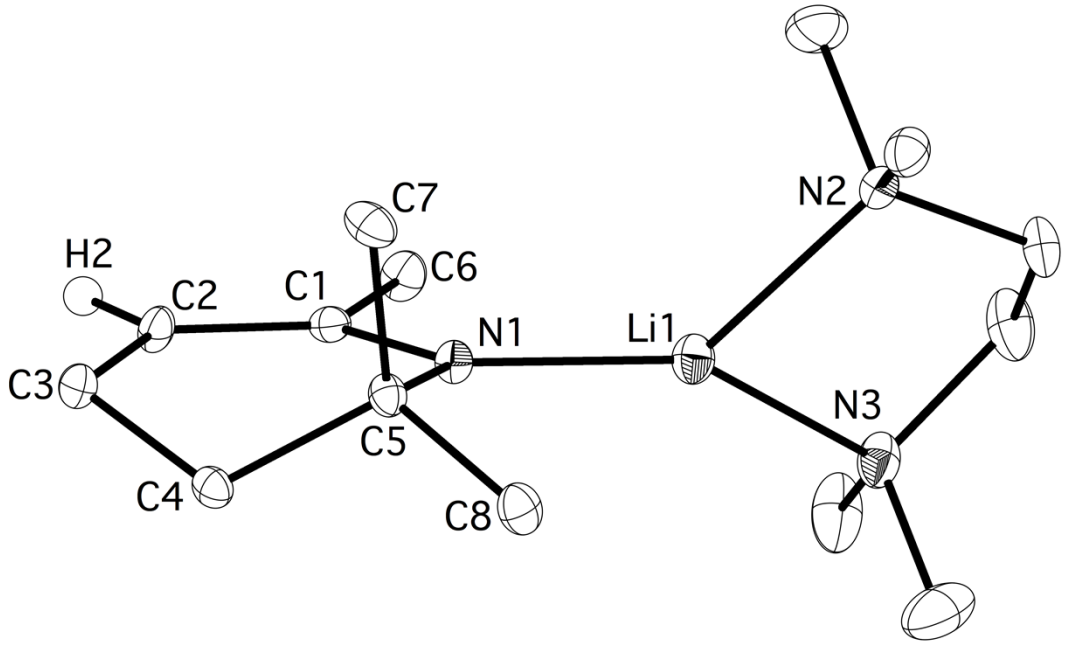

Figure S1. Molecular structure of **1·TMEDA**. Hydrogen atoms omitted for clarity with exception of the olefinic hydrogen on C2. Thermal ellipsoids are displayed at 30% probability.

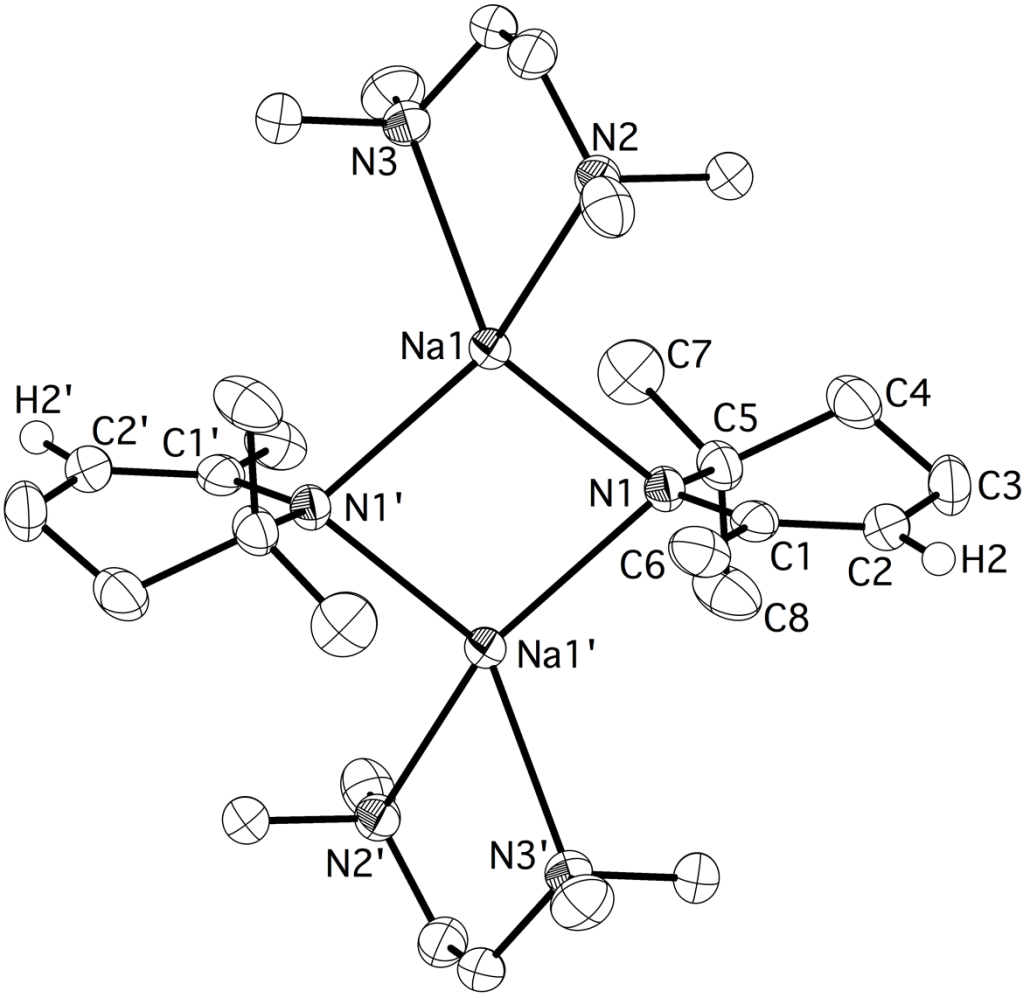

Figure S2. Molecular structure of **2·TMEDA**. Hydrogen atoms omitted for simplicity with exception of the olefinic hydrogen on C2. Thermal ellipsoids are displayed at 35% probability.

Table S2. Selected bond lengths (Å) and angles (°) for **1·TMEDA** and **2·TMEDA**.

1·TMEDA			
Li(1)-N(1)	1.883(4)		
Li(1)-N(3)	2.077(4)	N(1)-Li(1)-N(3)	141.48(18)
Li(1)-N(2)	2.078(3)	N(3)-Li(1)-N(2)	87.95(14)
N(1)-C(1)	1.363(2)	C(1)-N(1)-C(5)	114.44(15)
N(1)-C(5)	1.469(2)	C(2)-C(1)-N(1)	127.35(17)
C(1)-C(2)	1.357(3)	C(2)-C(1)-C(6)	119.49(16)
C(4)-C(5)	1.533(2)	N(1)-C(1)-C(6)	113.15(16)
2·TMEDA			
Na(1)-N(1)	2.4338(17)		
Na(1)-N(1)’	2.4835(16)	N(2)-Na(1)-N(3)	71.97(5)
Na(1)-N(2)	2.5262(17)	C(1)-N(1)-C(6)	113.71(17)
Na(1)-N(3)	2.5924(17)	N(1)-C(1)-C(2)	127.5(2)
N(1)-C(1)	1.356(2)	C(2)-C(1)-C(3)	118.0(2)
N(1)-C(6)	1.475(2)	C(1)-C(2)-C(4)	121.4(2)
C(1)-C(2)	1.370(3)	N(1)-Na(1)-N(1)’	100.90(5)
C(5)-C(6)	1.536(3)	Na(1)-N(1)-Na(1)’	79.10(5)

The symmetry operation to generate the equivalent atoms labelled with ’ is -x,-y,-z+2.

NMR Spectra

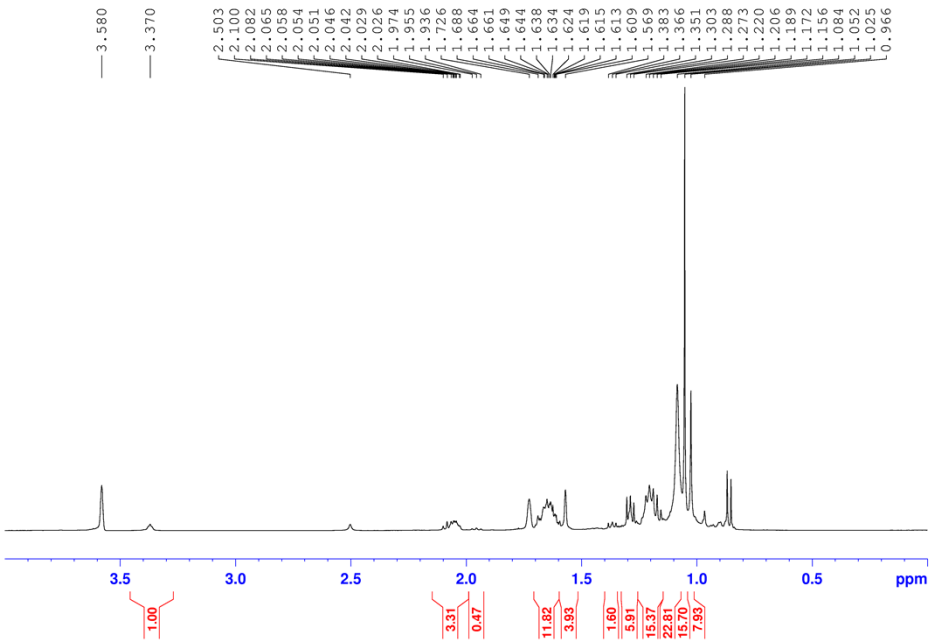

Figure S3. ^{1}H NMR Spectrum (d_8-THF, 300K, 400.1 MHz) of aliquot of reaction mixture in the absence of TMEDA after 18 h under reflux conditions in methylcyclohexane showing partial conversion of LiTMP to LiTTHP (**1**, 25% approx.). Conversion estimated as the ratio of signals of TTHP to LiTMP and TMPH (present from hydrolysis of LiTMP in d_8-THF).

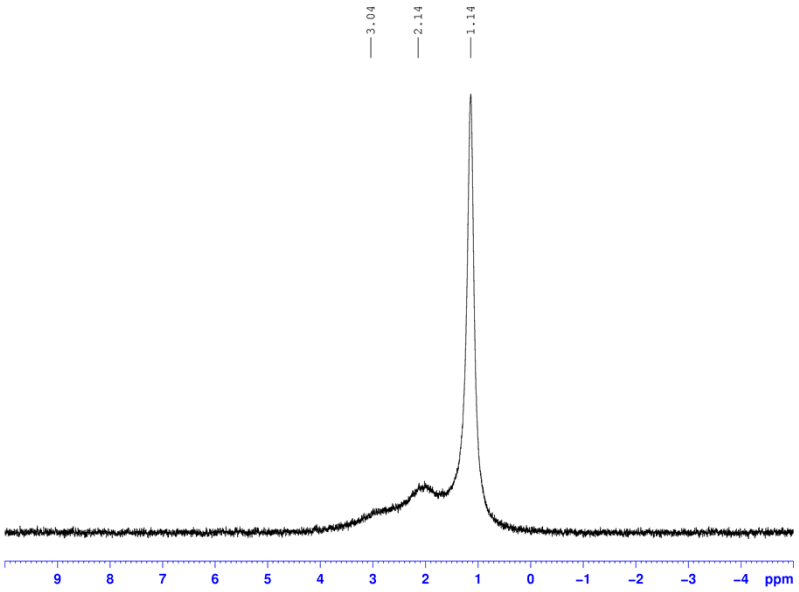

Figure S4. ^{7}Li NMR Spectrum (d_8-THF, 300K, 155.5 MHz) of aliquot of reaction mixture in the absence of TMEDA after 18 h under reflux conditions in methylcyclohexane showing partial conversion of LiTMP to LiTTHP (**1**, 25% approx., estimated by ^{1}H NMR study).

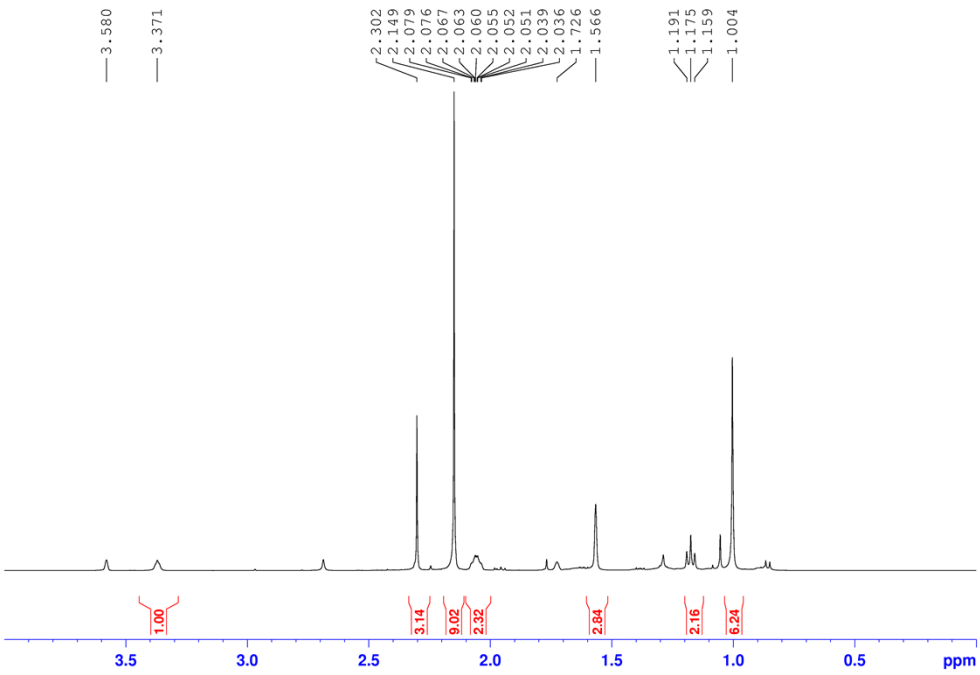

Figure S5. ^{1}H NMR Spectrum (d_8-THF, 300K, 400.1 MHz) of aliquot of reaction mixture showing quantitative conversion of TMEDA·LiTMP to TMEDA·Li(TTHP) (**1·TMEDA**).

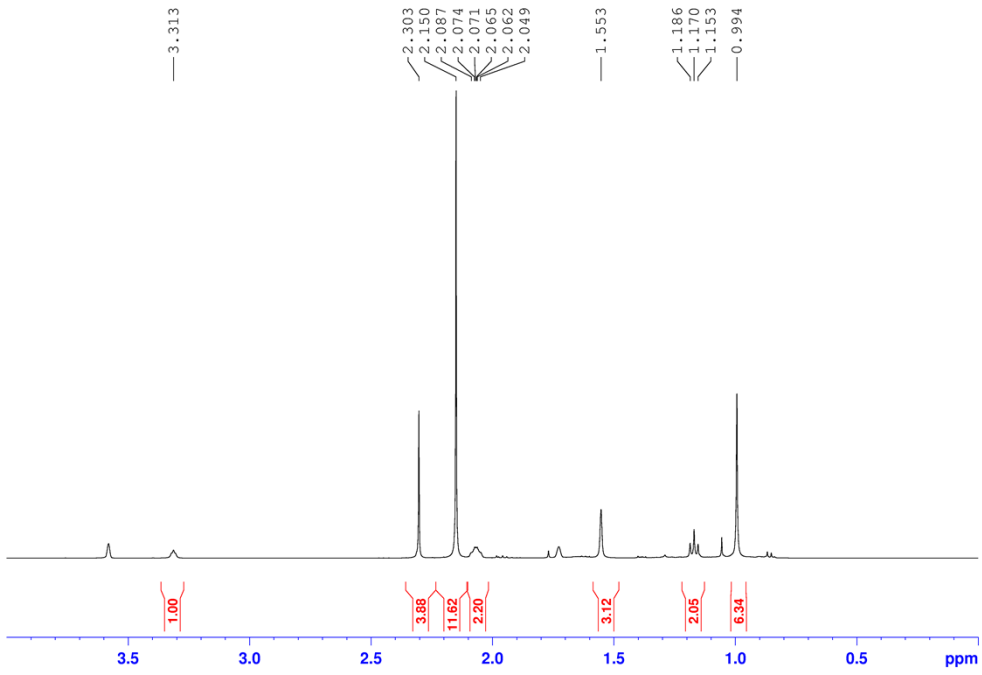

Figure S6. ^{1}H NMR spectrum (d_8-THF, 300K, 400.1 MHz) of isolated crystals of [TMEDA·Li(TTHP)] (**1·TMEDA**).

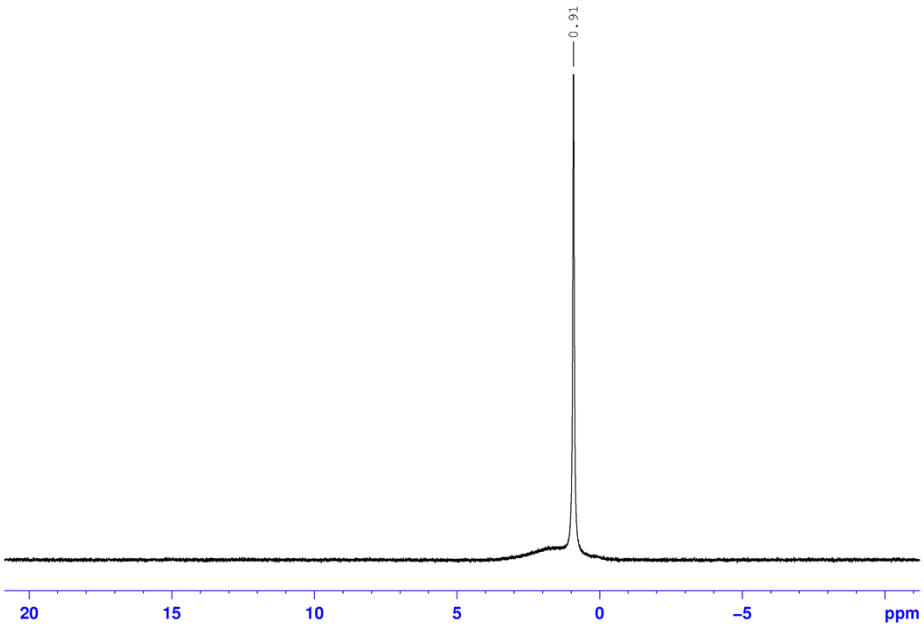

Figure S7. ^{7}Li NMR Spectrum (d_8-THF, 300K, 155.5 MHz) of isolated crystals of [TMEDA·Li(TTHP)] (**1·TMEDA**).

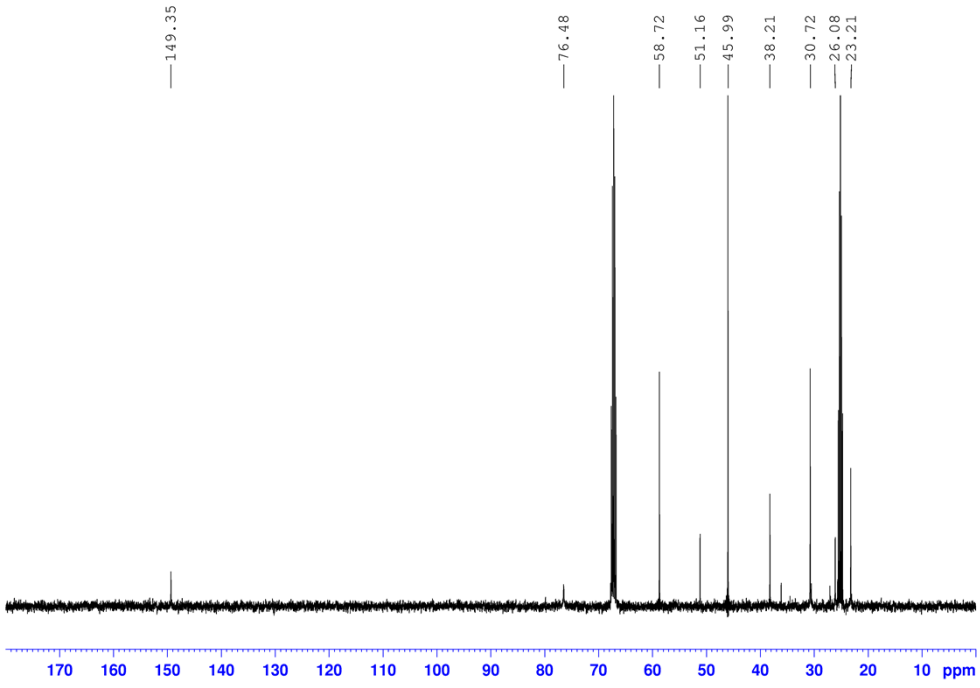

Figure S8. ^{13}C NMR Spectrum (d_8-THF, 300K, 100.60 MHz) of isolated crystals of [TMEDA·Li(TTHP)] (**1·TMEDA**).

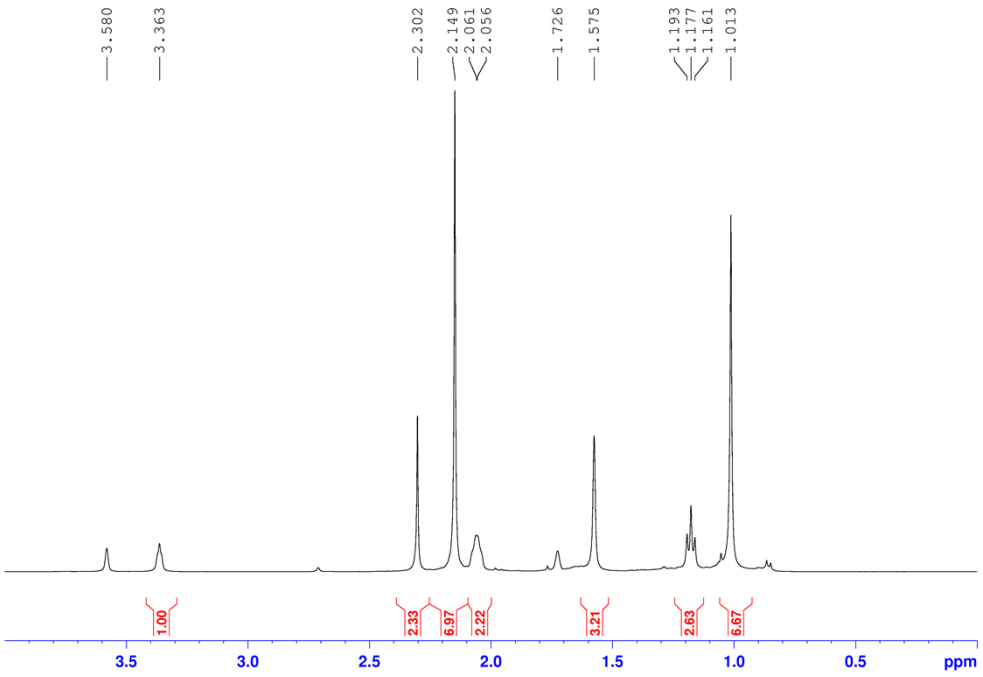

Figure S9. ^{1}H NMR Spectrum (d_8-THF, 300K, 400.1 MHz) of oil formed in reaction mixture of [TMEDA·Li(TTHP)] (**1·TMEDA**).

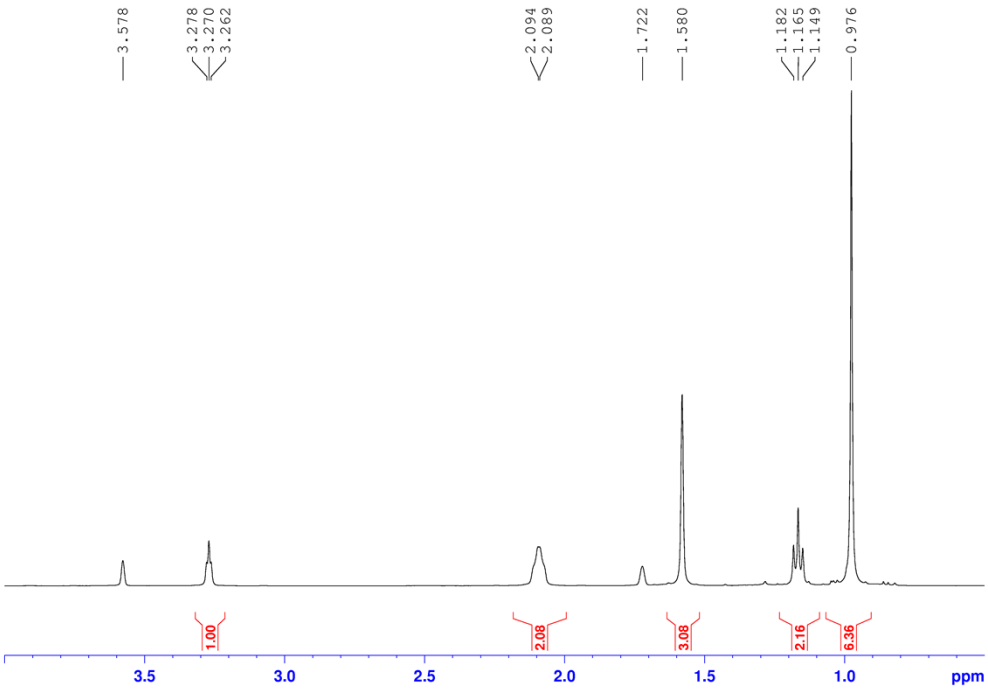

Figure S10. ^{1}H NMR spectrum (d_8-THF, 300K, 400.1 MHz) of isolated NaTTHP (**2**).

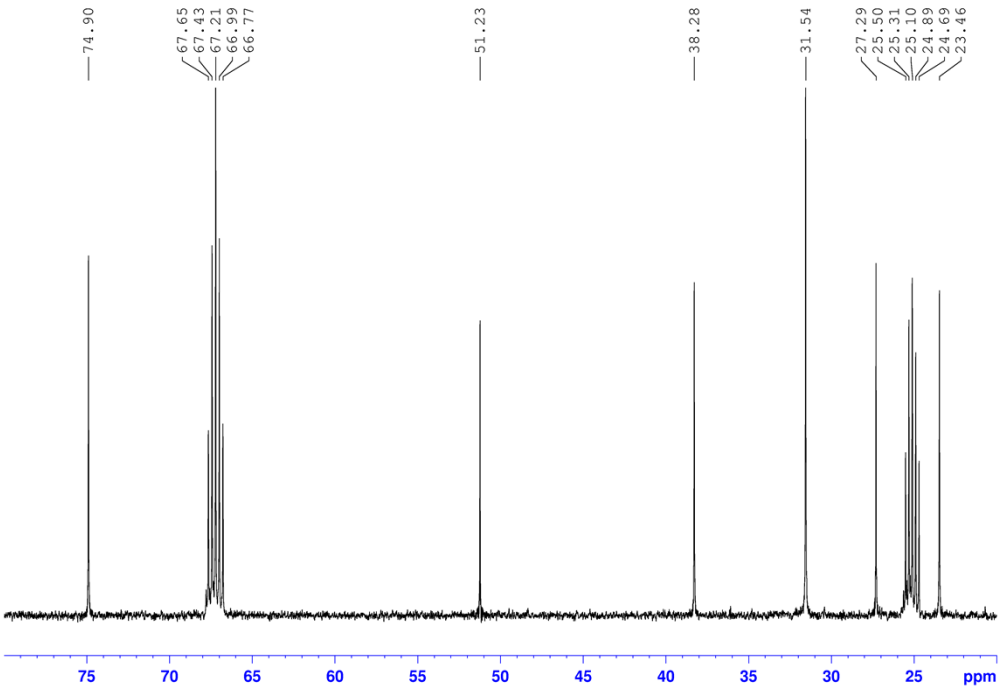

Figure S11. ^{13}C NMR Spectrum (d_8-THF, 300K, 100.60 MHz) of isolated NaTTHP (**2**).

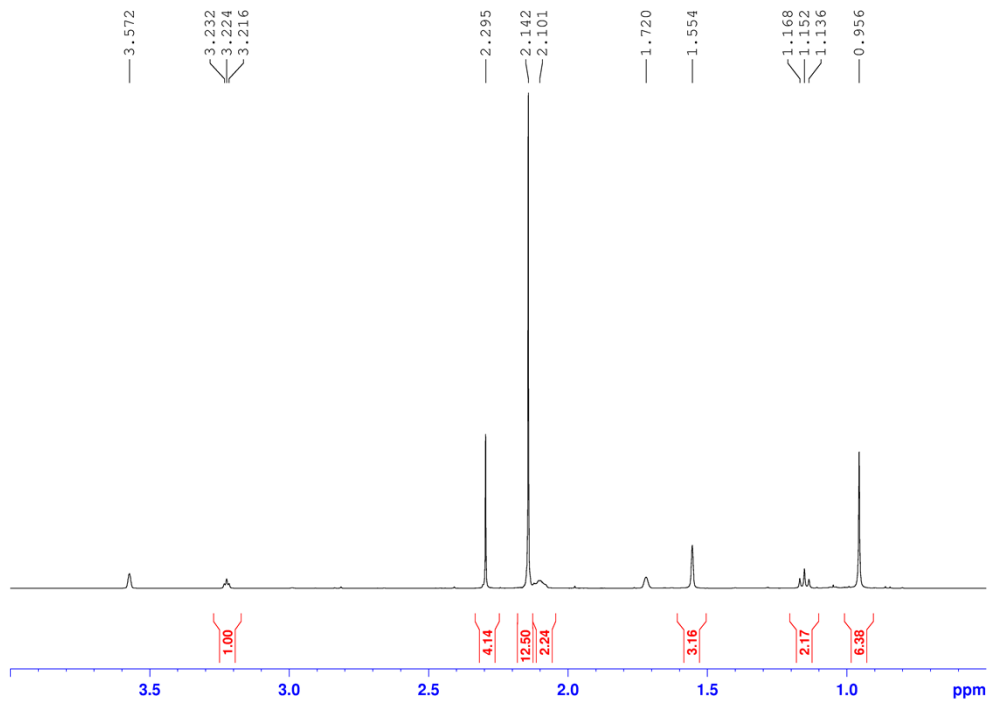

Figure S12. ^{1}H NMR spectrum (d_8-THF, 300K, 400.1 MHz) of isolated crystals of [TMEDA·Na(TTHP)] (**2·TMEDA**).

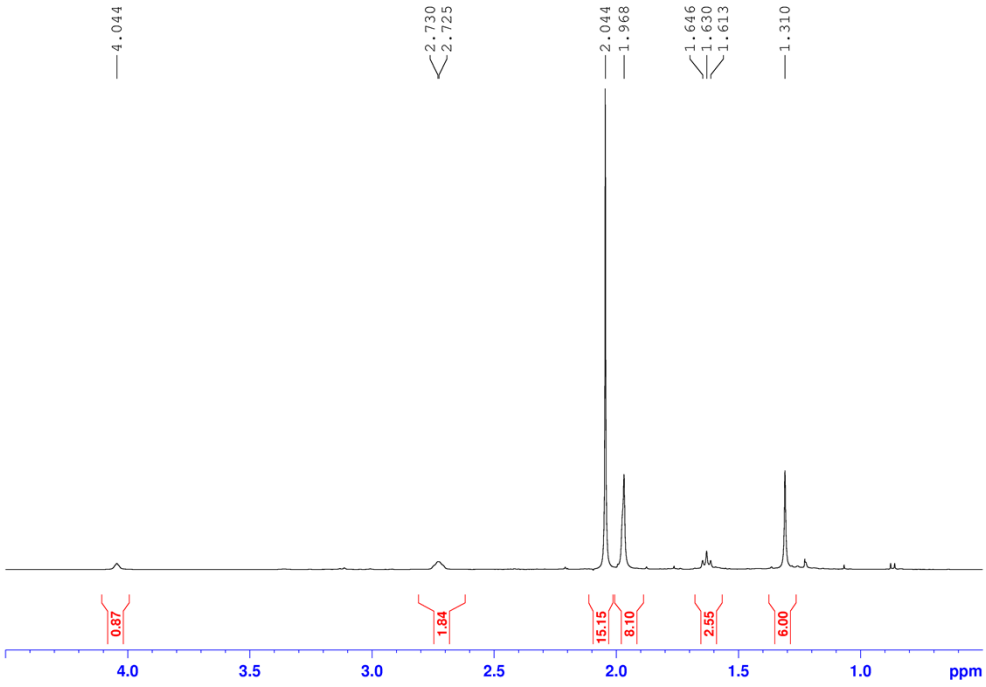

Figure S13. ^{1}H NMR spectrum (C_6D_6, 300K, 400.1 MHz) of isolated crystals of [TMEDA·Na(TTHP)] (**2·TMEDA**).

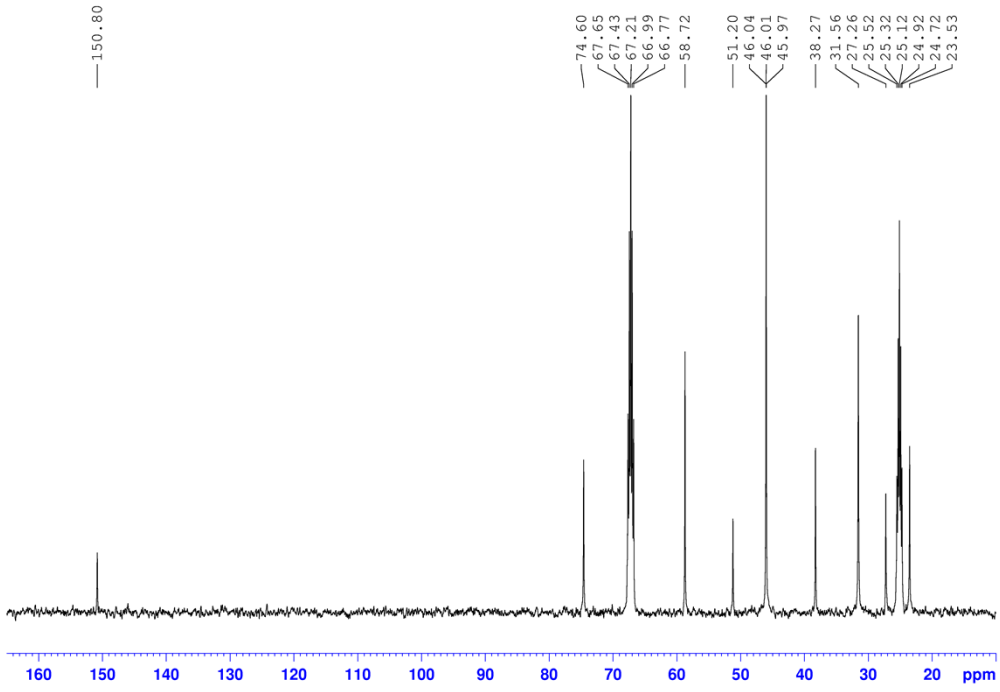

Figure S14. ^{13}C NMR Spectrum (d_8-THF, 300K, 100.60 MHz) of isolated crystals of [TMEDA·Na(TTHP)] (**2·TMEDA**).

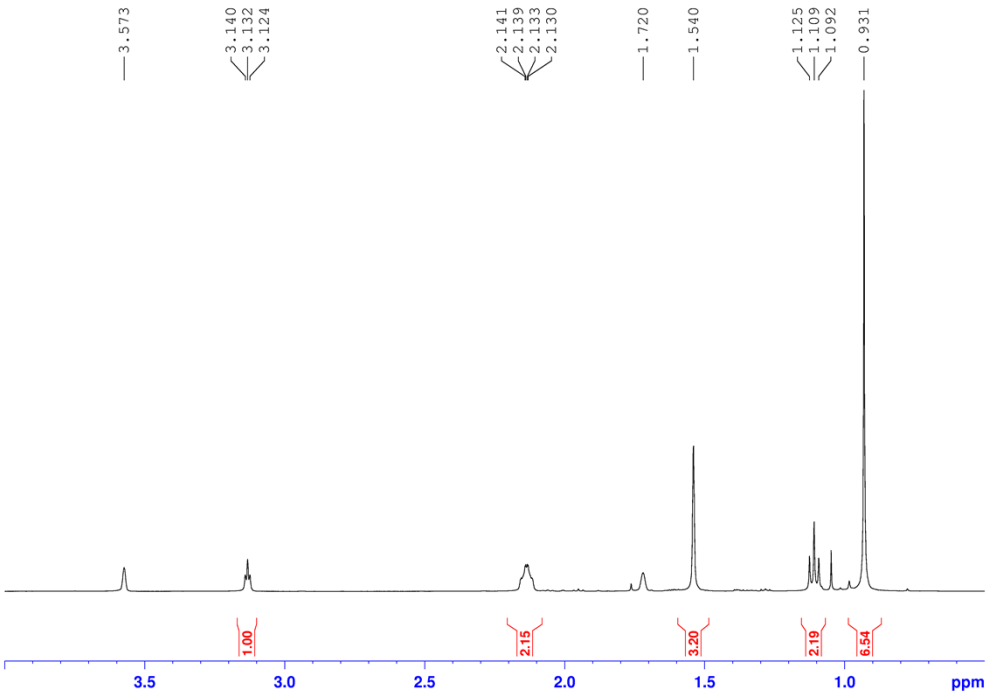

Figure S15. ^{1}H NMR spectrum (d_8-THF, 300K, 400.1 MHz) of KTTHP (**3**).

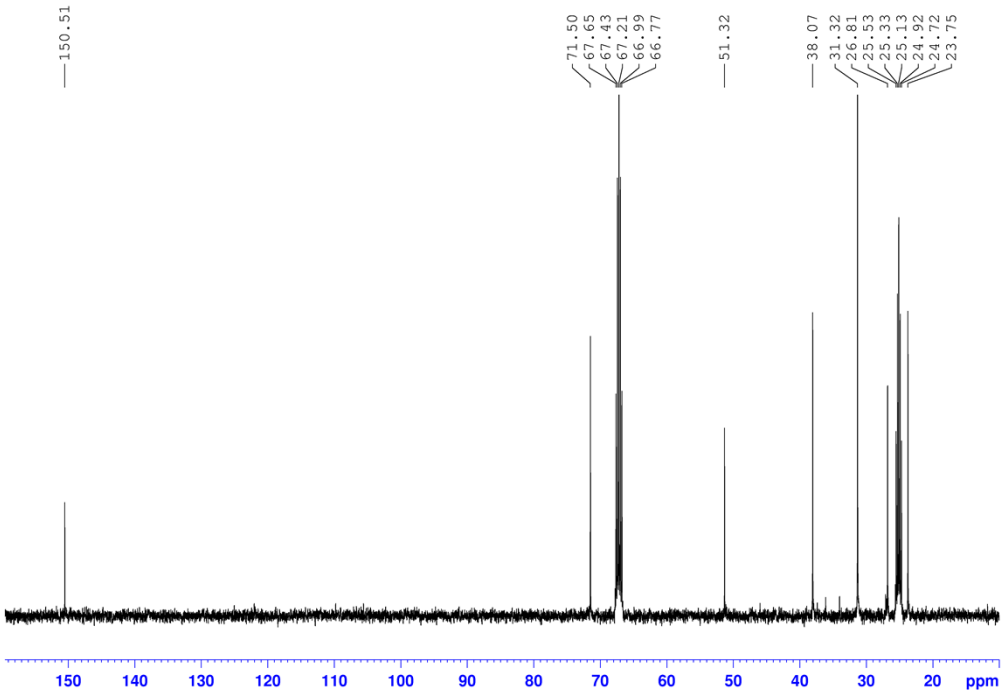

Figure S16. ^{13}C NMR Spectrum (d_8-THF, 300K, 100.60 MHz) of isolated KTTHP (**3**).

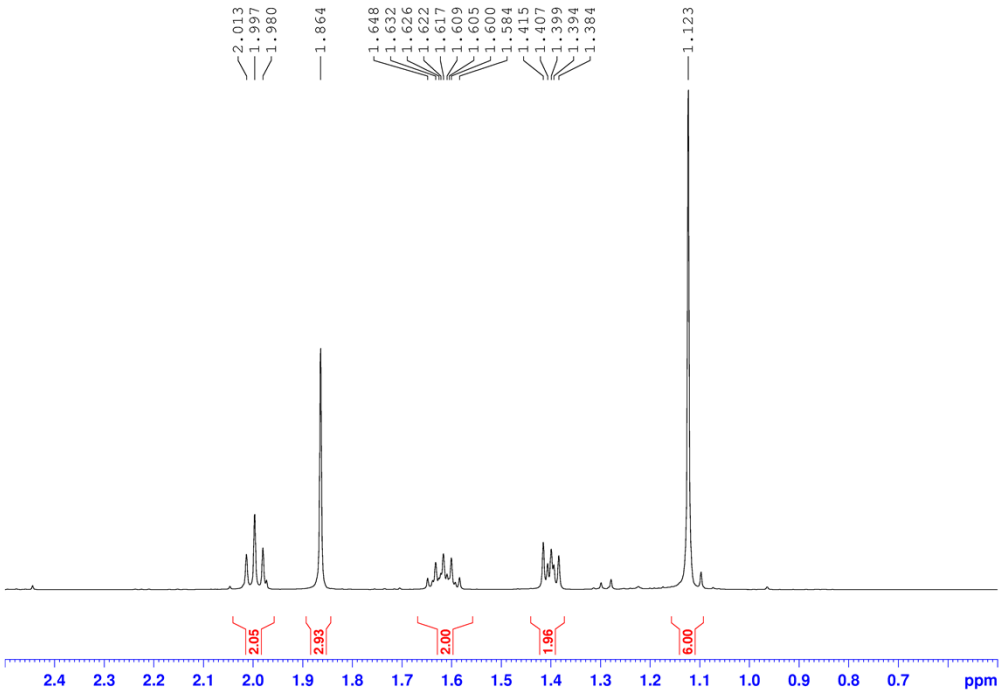

Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 300K, 400.1 MHz) of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**).

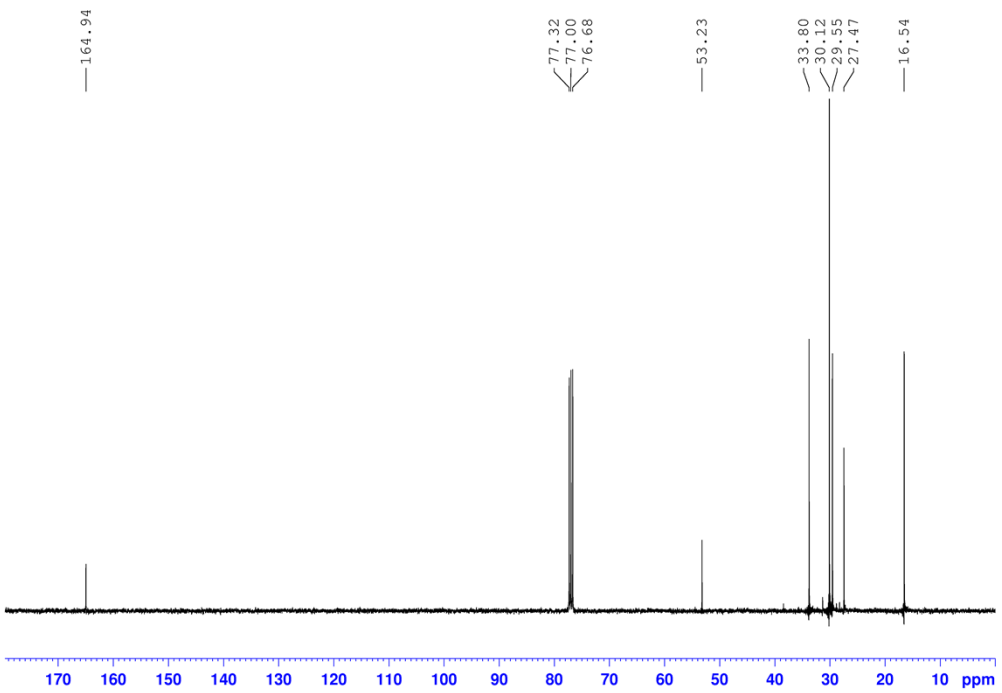

Figure S18. ^{13}C NMR Spectrum ($CDCl_3$, 300K, 100.60 MHz) of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**).

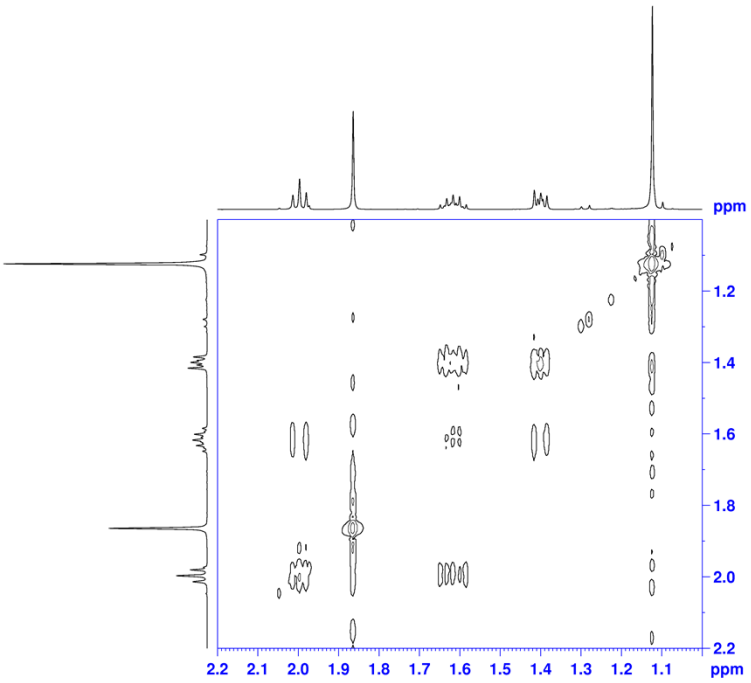

Figure S19. $^{1}H,^{1}H$-COSY NMR Spectrum ($CDCl_3$, 300K, 100.60 MHz) of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**).

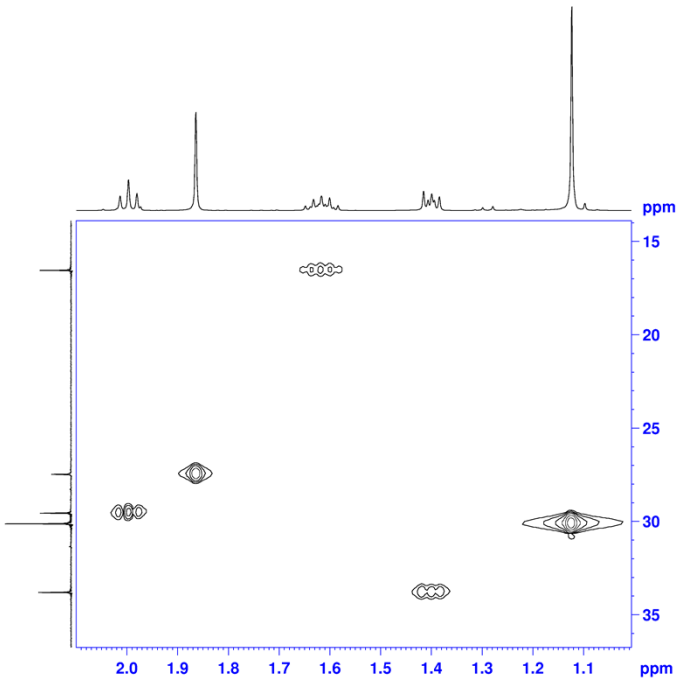

Figure S20. $^{1}H,^{13}C$-HSQC NMR Spectrum ($CDCl_3$, 300K, 100.60 MHz) of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**).

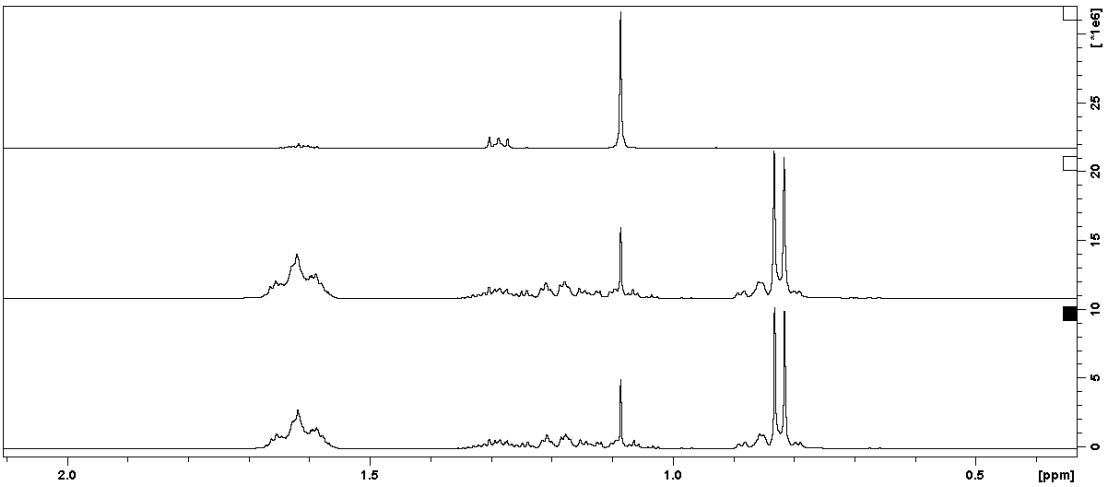

Figure S21. ^{1}H NMR study ($CDCl_3$, 300K, 400.1 MHz) of a control reaction in the absence of alkali metal. TMP(H) (top), *in situ* reaction mixture from TMP(H) and methylcyclohexane before (middle) and after 24 h at 101 ºC (bottom).

^{1}H DOSY NMR Studies

^{1}H DOSY NMR Analysis Details. The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed on a Bruker AVANCE 400 MHz NMR spectrometer at 300 K operating at 400.1 MHz for ^{1}H under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-*z*-atm probe with actively shielded *z*-gradient coil capable of delivering a maximum gradient strength of 54 G cm^{-1}. Diffusion-ordered NMR data were acquired using the Bruker pulse program *dstegp3s* with a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 4 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200 μs followed the application of each gradient pulse. Data were systematically accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. The signal decay dimension on the *pseudo*-2D data was generated by Fourier transformation of the time-domain data. DOSY plot were generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes. Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression. From the diffusion coefficients of the internal standards used (1,2,3,4-tetraphenylnaphthalene, 1-phenylnaphthalene and tetramethylsilane), linear calibration graphs were obtained by plotting *log*D versus *log*MW. Using the diffusion coefficients for the signals corresponding to the corresponding compound, an estimate of the MW of the species present in solution was obtained.

DOSY NMR Samples Preparation. To an NMR tube containing the corresponding compound to be analysed (typically, 20 mg) dissolved in the appropriate deuterated solvent (C_6D_6 or d_8-THF, 0.5 mL) was added inert internal standards 1,2,3,4-tetraphenylnaphthalene (TPhN, 15 mg), 1-phenylnaphthalene (PhN, 13.2 μL) and tetramethylsilane (TMS, 19.1 μL).

^{1}H DOSY NMR study of compound 1·TMEDA in C_6D_6 solution.

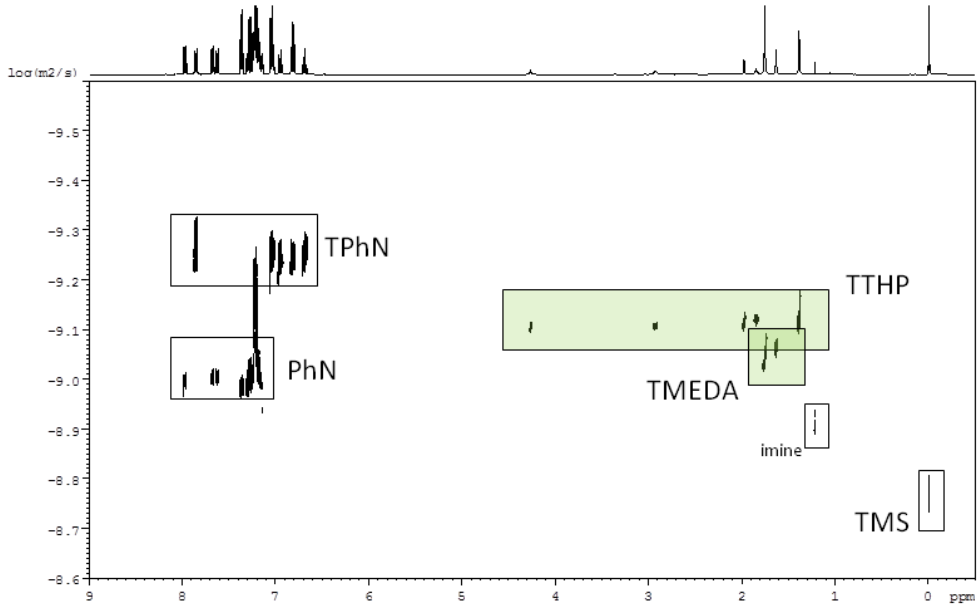

Figure S22. ^{1}H DOSY NMR plot of **1·TMEDA** in C_6D_6 solution. Small signals of 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**) due to unavoidable hydrolysis of **1·TMEDA** are detected (MW_{DOSY} found for **4**, 140.8 g mol^{-1}; calc. 125.21 g mol^{-1}, error 11.1%).

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure S21), with formula logD = -0.681(logMW) - 7.4378. Using the D values for **1·TMEDA** and the calibration graph, the MW of species in solution were estimated (Table S4).

Table S3. Diffusion coefficients and MW of internal standards.

Standard	**MW (gmol^{-1})**	**logMW**	**D (m^{2}s^{-1})**	**logD**
TPhN	432.55	2.636	5.74E-10	-9.241
PhN	204.27	2.310	1.01E-9	-8.996
TMS	88.22	1.946	1.70E-9	-8.770

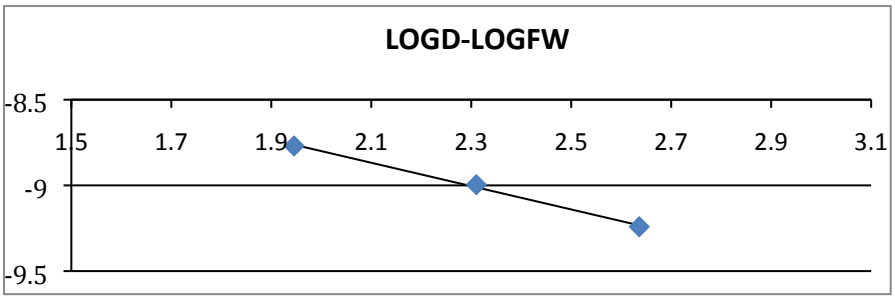

Figure S23. Calibration graph (logD = -0.681(logMW) - 7.4378, $R^2 = 0.997$) used to estimate of MW of compound **1·TMEDA** in C_6D_6 solution.

Table S4. Diffusion coefficients and corresponding calculated MW_{DOSY} for components present in C_6D_6 solution.

Component of spectrum	**D ($m^2 s^{-1}$)**	**MW_{DOSY}[a] (g mol^{-1})**
LiTTHP (**1**)	7.75E-10	286.1
TMEDA	8.74E-10	239.8
2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**)	1.26E-9	140.8

[a] MW from [logD = -0.681·logMW - 7.4378 ($r^2 = 0.997$)]

From the DOSY NMR study in C_6D_6 solution, the different components of the mixture are separated in the diffusion dimension in the size sequence TPhN > TTHP > TMEDA > PhN > TMS according to their increasing D values in the order TPhN < TTHP < TMEDA < PhN < TMS (see Tables S3 and S4).

The MW_{DOSY} values obtained were compared to the true MW of various species which may be present in the solution. The error of the MW_{DOSY} values with respect to these species was also determined. The results are shown in Table S5.

Table S5. Comparison of MW_{DOSY} to the MW of possible species.

Possible Species	**MW[a] (g mol^{-1})**	**MW_{DOSY}[b] (g mol^{-1})**	**Error (%) in MW_{DOSY}**

TMEDA·LiTTHP (**1·TMEDA**)	247.35	286.1	+13.54
LiTTHP (**1**)	131.15	286.1	+54.16
TMEDA	116.2	239.8	+51.54

[a] Real MW, [b] MW from [logD = -0.681·logMW - 7.4378 (r^2 = 0.997)]

As shown in Figure S20 and Table S4, the D value of the TMEDA in **1·TMEDA** (8.74E-10 m^2s^{-1}) is smaller than that determined for the TTHP component of **1·TMEDA** (7.75E-10 m^2s^{-1}), and corresponds to a MW_{DOSY} for the TMEDA which lies intermediate between the MW of free TMEDA (116.2 g mol^{-1}) and unsolvated LiTTHP (**1**, 131.15 g mol^{-1}). The data could be consistent with **1·TMEDA** existing in C_6D_6 solution as some mixture of the TMEDA solvated species, an unsolvated $[LiTTHP]_n$ and/or a species to which C_6D_6 is coordinated.

The D value of the TTHP signals gives a MW_{DOSY} which is greater than the MW of **1·TMEDA** (MW 247.35 g mol^{-1}; MW_{DOSY} 286.1 g mol^{-1}; error +13.5%), which could also be consistent with an equilibrium between TMEDA solvated **1·TMEDA** and a higher MW unsolvated or C_6D_6 solvated LiTTHP species.

^{1}H DOSY NMR study of compound 1·TMEDA in d_8-THF solution.

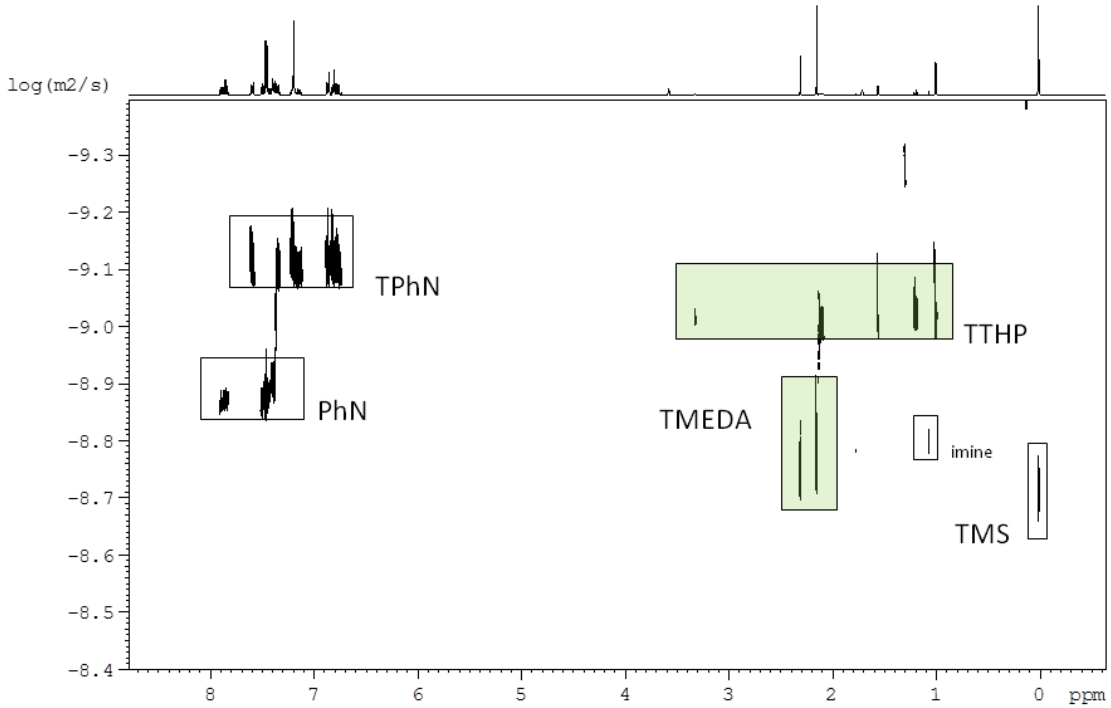

Figure S24. DOSY NMR plot of **1·TMEDA** in d_8-THF solution. Small signals of imine **4** due to unavoidable hydrolysis of **1·TMEDA** are detected (MW_{DOSY} found for imine **4**, 134.10 g mol^{-1}; calc. 125.21 g mol^{-1}, error 6.6%).

From the D values obtained for the internal standards (Table S6) a linear calibration graph of LogD versus LogMW was obtained (Figure S25), with formula logD = -0.5687(logMW) - 7.5763. Using the D values for **1·TMEDA** and the calibration graph, MW_{DOSY} was determined (Table S7).

Table S6. Diffusion coefficients and MW of internal standards.

Standard	**MW (gmol^{-1})**	**logMW**	**D (m^{2}s^{-1})**	**logD**
TPhN	432.55	2.636	8.14E-10	-9.089
PhN	204.27	2.310	1.37E-9	-8.864
TMS	88.22	1.946	2.02E-9	-8.695

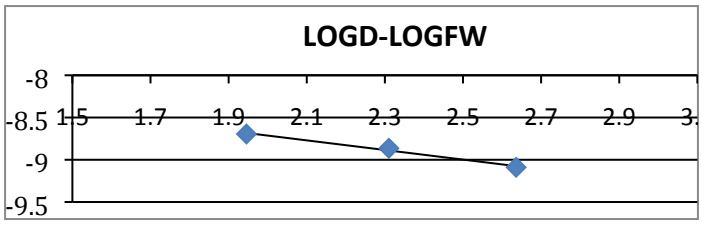

Figure S25. Calibration graph (logD = -0.5687(logMW) - 7.5763, $R^2 = 0.987$) used to estimate MW of compound **1·TMEDA** in d_8-THF solution.

Table S7. Diffusion coefficients and corresponding calculated MW_{DOSY} for components present in d_8-THF solution.

Component of spectrum	**D ($m^2 s^{-1}$)**	**MW_{DOSY}[a] ($g mol^{-1}$)**
LiTTHP (**1**)	9.95E-10	321.84
TMEDA	1.85E-9	108.20

[a] MW from [logD = -0.5687·logMW - 7.5763 ($r^2 = 0.987$)]

From the DOSY NMR study in d_8-THF solution, the different components of the mixture are separated in the diffusion dimension in the size sequence TPhN > TTHP > PhN > TMEDA > TMS according to their increasing D values in the order TPhN < TTHP < PhN < TMEDA < TMS (see Tables S6 and S7).

The MW_{DOSY} values obtained were compared to the true MW of various species which may be present in the solution. The error of the MW_{DOSY} values with respect to these species was also determined. The results are shown in Table S8.

Table S8. Comparison of W_{DOSY} to the MW of possible species.

Possible Species	**MW[a]**	**MW_{DOSY}[b] ($gmol^{-1}$)**	**Error (%) in MW_{DOSY}**
TMEDA·LiTTHP (**1·TMEDA**)	247.35	321.84	+23.15
LiTTHP (**1**)	131.15	321.84	-88.60

[LiTTHP·(d_8-THF)]$_2$	422.8	321.84	-31.37
[LiTTHP]$_2$·(d_8-THF)	342.5	321.84	-6.42
LiTTHP·(d_8-THF)$_2$	291.5	321.84	9.43
TMEDA	116.2	108.16	-7.43

[a] Real MW, [b] MW from [logD = -0.5687·logMW - 7.5763 (r^2 = 0.987)]

The DOSY NMR data would be consistent with TMEDA being free in d_8-THF solution as the MW_{DOSY} obtained from the D value of the TMEDA signals using the calibration graph (Figure S25) is comparable to the true MW of free TMEDA(with error of -7.4%).

It is possible the LiTTHP is solvated instead by d_8-THF molecules, present in vast excess, rather than TMEDA. The D values observed for the LiTTHP signals give a MW_{DOSY} value of 321.84 gmol^{-1}. Comparison of this value to the true MW of various possible d_8-THF solvated LiTTHP species was made (see Table S8).

The species for which MW_{DOSY} would have lowest error is the hemisolvate [(LiTTHP)$_2$]·(d_8-THF) (MW 342.5 g mol^{-1}; error -6.4%). The MW_{DOSY} would have a similar error for a possible bis-solvated species LiTTHP·(d_8-THF)$_2$ (MW 291.5 g mol^{-1}; error 9.4%).

^{1}H DOSY NMR study of compound Na·TTHP (2) in d_8-THF solution.

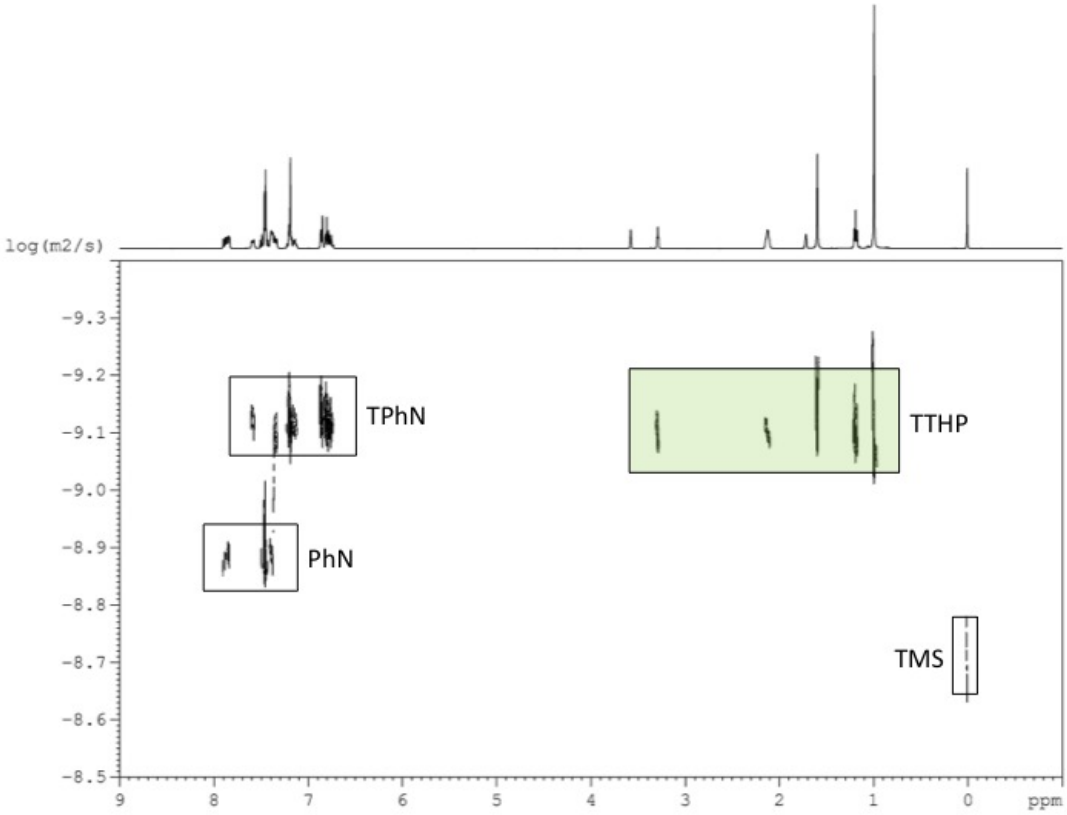

Figure S26. ^{1}H DOSY NMR plot of **2** in d_8-THF solution.

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure SX), with formula logD = -0.6075·logMW - 7.5061 (r^2 = 0.993). Using the D values for **2** and the calibration graph, the MW of species in solution were estimated (Table SX).

Table S9. Diffusion coefficients and MW of internal standards for **2**.

Standard	**MW (gmol^{-1})**	**logMW**	**D (m^{2}s^{-1})**	**logD**
TPhN	432.55	2.636	7.61E-10	-9.119
PhN	204.27	2.310	1.29E-9	-8.889
TMS	88.22	1.946	2.01E-9	-8.698

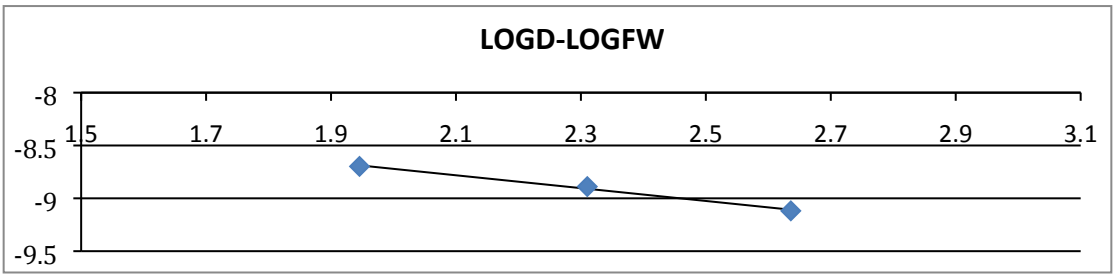

Figure S27. Calibration graph (logD = -0.6075·logMW - 7.5061 (r^2 = 0.993)) used to estimate MW of compound **2** in d_8-THF solution.

Table S10. Diffusion coefficients and corresponding calculated MW_{DOSY} for components present in d_8-THF solution.

Component of spectrum	**D (m^2 s^{-1})**	**MW_{DOSY}[a] (g mol^{-1})**
NaTTHP (**2**)	7.91E-10	423.2

[a] MW from [logD = -0.6075·logMW - 7.5061 (r^2 = 0.993)]

The MW_{DOSY} values obtained were compared to the true MW of various species which may be present in the solution. The error of the MW_{DOSY} values with respect to these species was also determined. The results are shown in Table S11.

Table S11. Comparison of MW_{DOSY} to the MW of possible species.

Possible Species	**MW[a] (g mol^{-1})**	**MW_{DOSY}[b] (g mol^{-1})**	**Error (%) in MW_{DOSY}**
[NaTTHP·(d_8-THF)]$_2$	454.70	423.20	+7%

[a] Real MW, [b] MW from [logD = -0.6075·logMW - 7.5061 (r^2 = 0.993)]

The D value of the TTHP signals gives a MW_{DOSY} which is comparable with the MW of [NaTTHP·(d_8-THF)]$_2$ (error +7%), which could also be consistent with the presence of a dimeric [NaTTHP]$_2$ solvated with two molecules of d_8-THF.

^{1}H DOSY NMR study of compound TMEDA·NaTTHP (2·TMEDA) in d_8-THF solution.

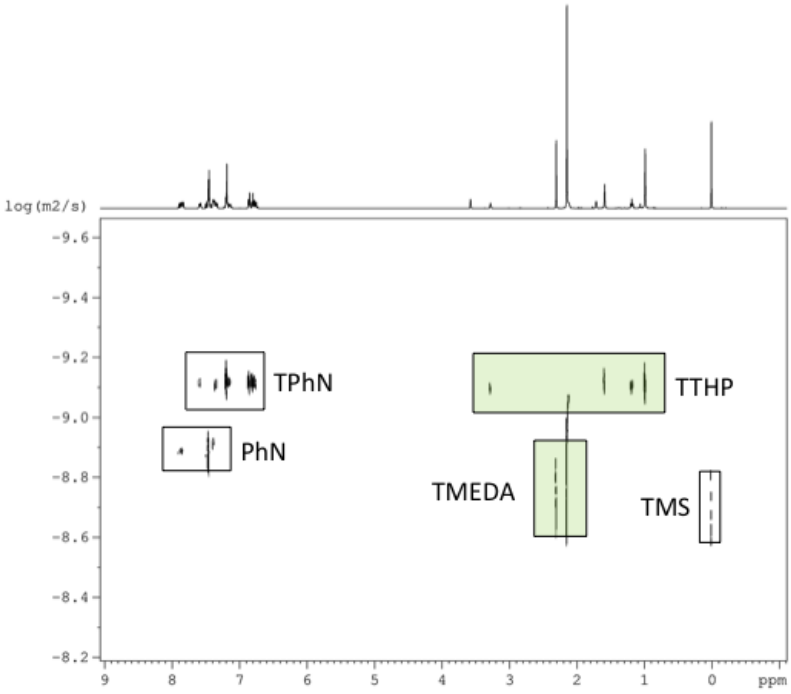

Figure S28. ^{1}H DOSY NMR plot of **2·TMEDA** in d_8-THF solution.

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure S29), with formula logD = -0.5975(logMW) - 7.532. Using the D values for **2·TMEDA** and the calibration graph, the MW of species in solution were estimated.

Table S12. Diffusion coefficients and MW of internal standards for **2b**.

Standard	MW (gmol^{-1})	logMW	D (m^{2}s^{-1})	logD
TPhN	432.55	2.636	7.57E-10	-9.121
PhN	204.27	2.310	1.30E-9	-8.885
TMS	88.22	1.946	1.96E-9	-8.707

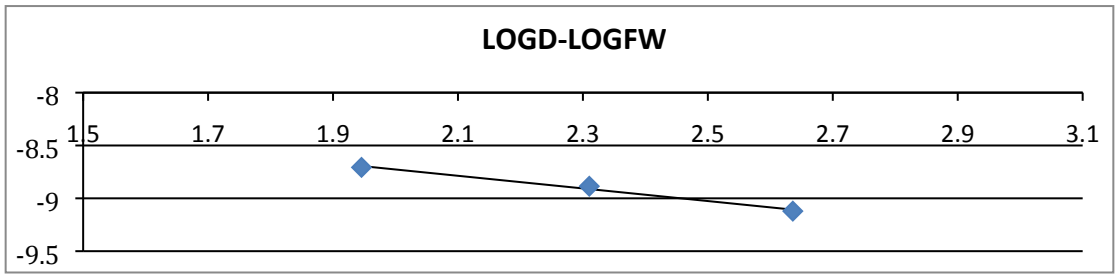

Figure S29. Calibration graph (logD = -0.5975(logMW) - 7.532, r^2 = 0.988) used to estimate MW of compound **2·TMEDA** in d_8-THF solution.

MW found by ^{1}H DOSY NMR for **2·TMEDA**, 432.4 g/mol; calc. for **2**·(d_8-THF)$_2$ ($C_{24}H_{28}D_{16}N_2Na_2O_2$), 454.70 g/mol; error, +5%.

The DOSY NMR data in d_8-THF suggest that TMEDA is replaced by d_8-THF in **2·TMEDA**, which is consistent with the MW observed. The MW_{DOSY} for non coordinated TMEDA found is 114.19 (MW calculated, 116.2; error: 1.7%).

^{1}H DOSY NMR study of compound TMEDA·NaTTHP (2·TMEDA) in C_6D_6 solution.

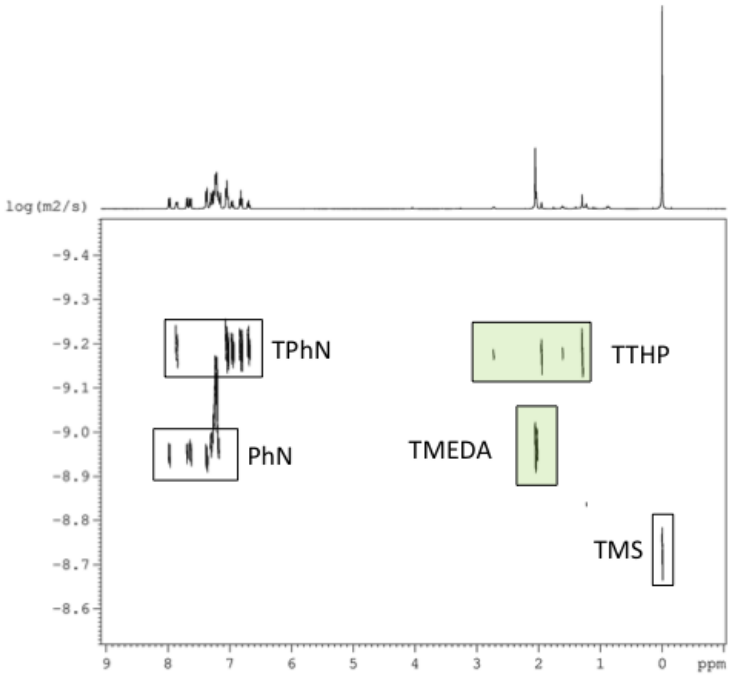

Figure S30. ^{1}H DOSY NMR plot of **2·TMEDA** in C_6D_6 solution.

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure S31), with formula logD = -0.6733(logMW) – 7.4069. Using the D values for **2·TMEDA** and the calibration graph, the MW of species in solution were estimated.

Table S13. Diffusion coefficients and MW of internal standards for **2·TMEDA**.

Standard	**MW (gmol^{-1})**	**logMW**	**D (m^{2}s^{-1})**	**logD**
TPhN	432.55	2.636	6.49E-10	-9.188
PhN	204.27	2.310	1.12E-9	-8.951
TMS	88.22	1.946	1.90E-9	-8.722

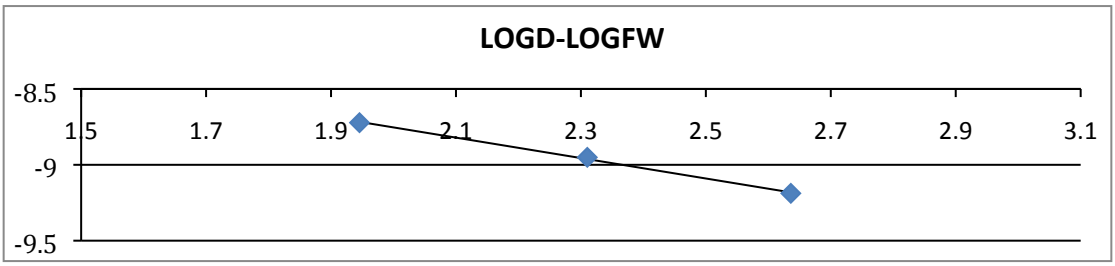

Figure S31. Calibration graph (logD = -0.6733(logMW) - 7.4069, r^2 = 0.988) used to estimate MW of compound **2·TMEDA** in C_6D_6 solution.

MW found by ^{1}H DOSY NMR for **2·TMEDA**, 430.5 g/mol; calc. for **2**.$(C_6D_6)_2$ ($C_{28}H_{28}D_{12}N_2Na_2$), 462.7 g/mol; error, +7%.

The DOSY NMR data in C_6D_6 solution suggest that TMEDA is replaced by C_6D_6 in **2·TMEDA**, which is consistent with the MW observed. The MW_{DOSY} for non coordinated TMEDA found is 207.4, slightly higher than the calculated (MW calculated, 116.2; error: +43.9%), possibly due to a dynamic equilibrium in C_6D_6 between C_6D_6 and TMEDA to coordinate to NaTTHP.

^{1}H DOSY NMR study of compound KTTHP (3) in d_8-THF solution.

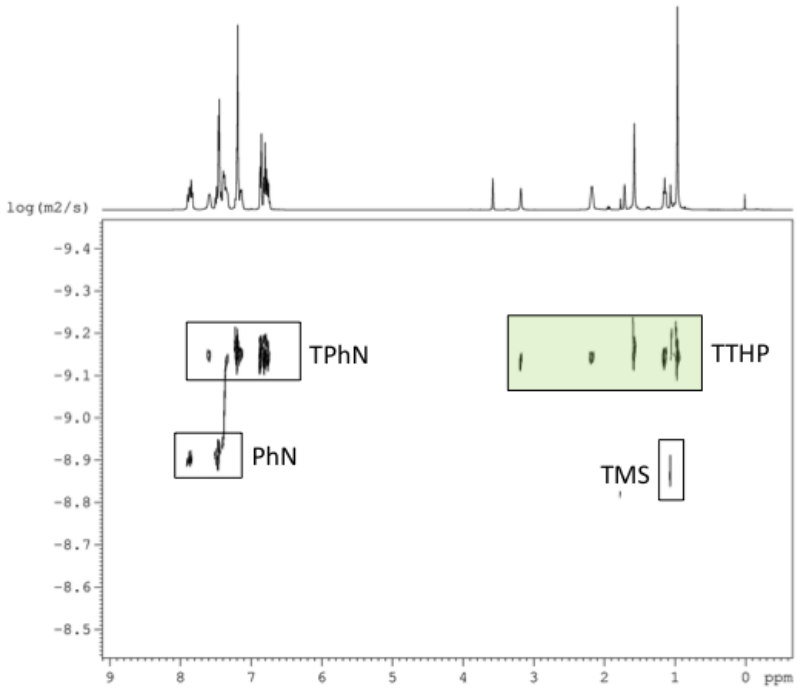

Figure S32. ^{1}H DOSY NMR plot of **3** in d_8-THF solution.

From the D values obtained for the internal standards a linear calibration graph of LogD versus LogMW was obtained (Figure S33), with formula logD = -0.5463(logMW) – 7.6796. Using the D values for **3** and the calibration graph, the MW of species in solution were estimated.

Table S14. Diffusion coefficients and MW of internal standards for **3**.

Standard	**MW (gmol^{-1})**	**logMW**	**D (m^{2}s^{-1})**	**logD**
TPhN	432.55	2.636	7.72E-10	-9.142
PhN	204.27	2.310	1.26E-9	-8.900
TMS	88.22	1.946	1.71E-9	-8.762

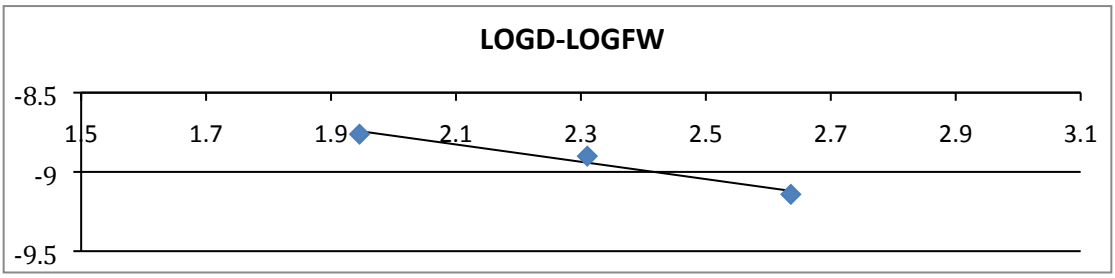

Figure S33. Calibration graph (logD = -0.6733(logMW) - 7.4069, r^2 = 0.988) used to estimate MW of compound **3** in d_8-THF solution.

MW found by ^{1}H DOSY NMR for **3**, 468.7 g/mol; calc. for **3**·(d_8-THF)$_2$ ($C_{24}H_{28}D_{16}N_2K_2O_2$), 486.9 g/mol; error, 4%.

The DOSY NMR data in d_8-THF solution suggest that **3** exists in d_8-THF solution as a dimeric KTTHP solvated by two molecules of d_8-THF.

IR Spectra

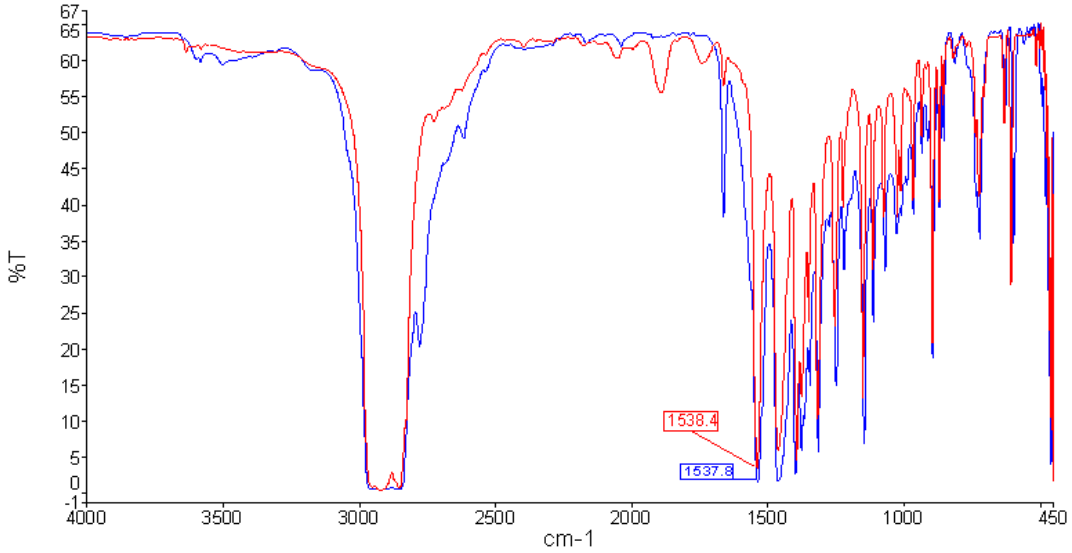

Figure S34. IR spectra (KBr, Nujol) for NaTTHP (**2**, red) and KTTHP (**3**, blue).

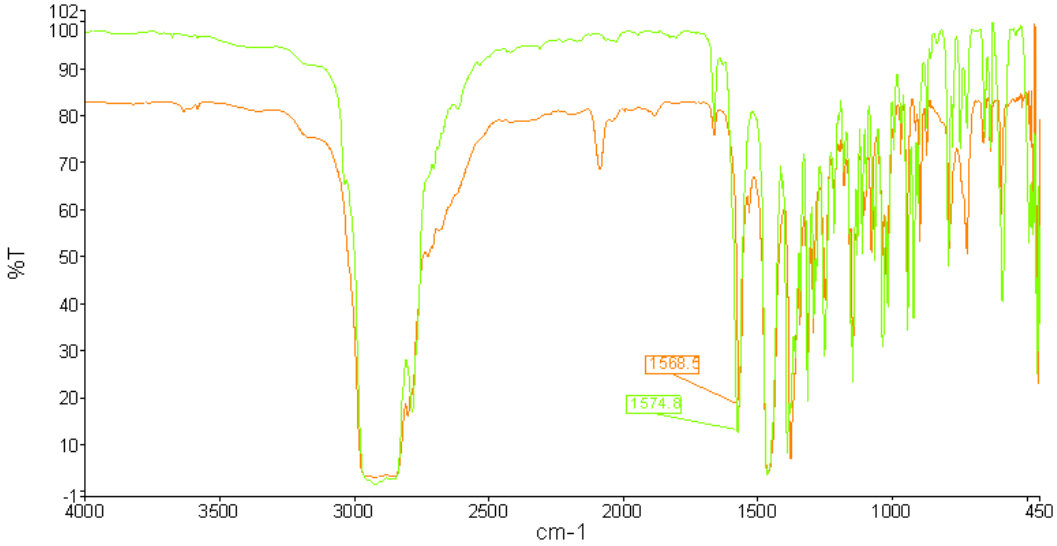

Figure S35. IR spectra (KBr, Nujol) for TMEDA·LiTTHP (**1·TMEDA**, green) and TMEDA·NaTTHP (**2·TMEDA**, orange).

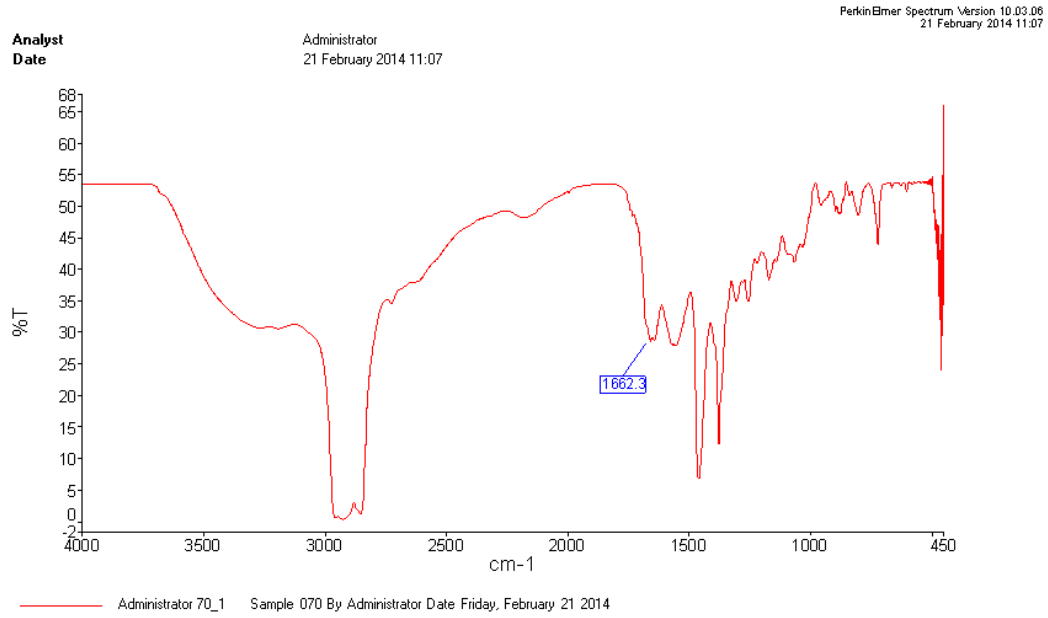

Figure S36. IR spectra (KBr, Nujol) for 2,2,6-trimethyl-2,3,4,5-tetrahydropyridine (**4**).

Thermal Volatilisation Analysis (TVA)

TVA is a form of evolved gas analysis, originally designed for the mechanistic characterization of polymer degradation behaviour but of much wider applicability. The Strathclyde system, built in-house, is based upon the apparatus and techniques originally described by I.C. McNeill in 1966 and developed subsequently.[5]
All TVA runs were conducted under vacuum using 50 mg samples, with the samples heated from ambient temperature to 240ºC at a rate of 5ºC min^{-1}.

Description of TVA Technique

The TVA apparatus consists primarily of a glass sample chamber connected to a primary liquid nitrogen cooled sub-ambient trap and a series of secondary liquid nitrogen cooled cold traps. The entire system is pumped to a vacuum of ~$1x10^{-4}$ Torr by the use of a two-stage rotary pump and an oil diffusion pumping system. As the sample is heated at a linear rate, using a programmable tube furnace, low volatility products (e.g. oligomers) condense at the water jacket cooled 'cold ring' placed directly above the sample tube or the liquid nitrogen cooled primary trap. In contrast, higher volatility degradation species with lower boiling points are collected in a primary liquid nitrogen sub-ambient trap, maintained at a temperature of -196ºC. These 'condensable' fractions are volatile at room temperature but non-volatile at liquid nitrogen temperatures, hence collect within the primary sub-ambient trap. Linear response Pirani gauges, positioned at both the entrance and exit of the primary sub-ambient trap, enables the evolution of both condensable and non-condensable volatiles to be continuously monitored as a function of pressure versus temperature. However, volatile products collected in the cold ring fraction are not detected by Pirani gauges as they condense prior to exiting the degradation tube. Subsequent sub-ambient differential distillation of the collected volatiles was carried out by heating the primary sub-ambient trap from -196°C to ambient temperature. A 1-300 amu Hiden single quadrapole RGA mass spectrometer samples a continuous product stream during both the degradation and sub-ambient distillation runs. This is particularly useful for the identification of non-condensable degradation products such as carbon monoxide and methane and condensable degradation products collected from the sub-ambient distillation procedure.

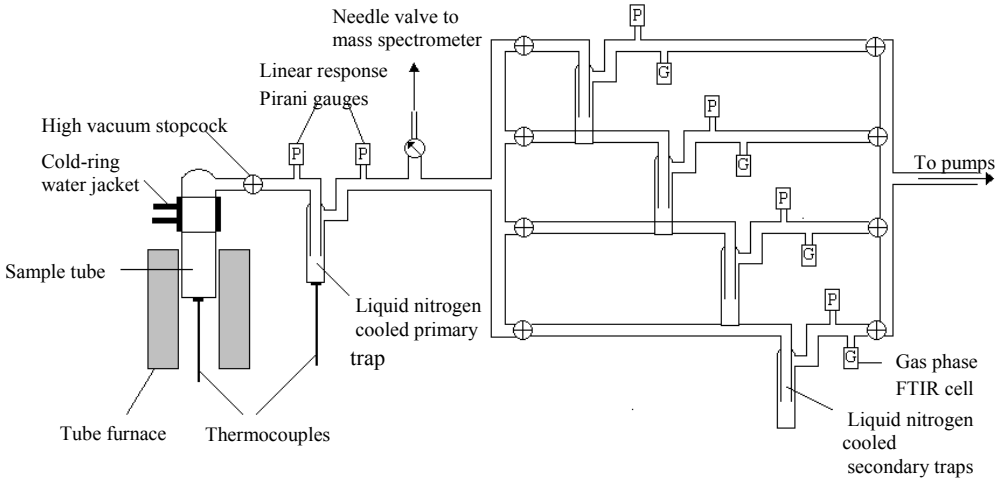

Figure S37. Schematic diagram of the TVA system.

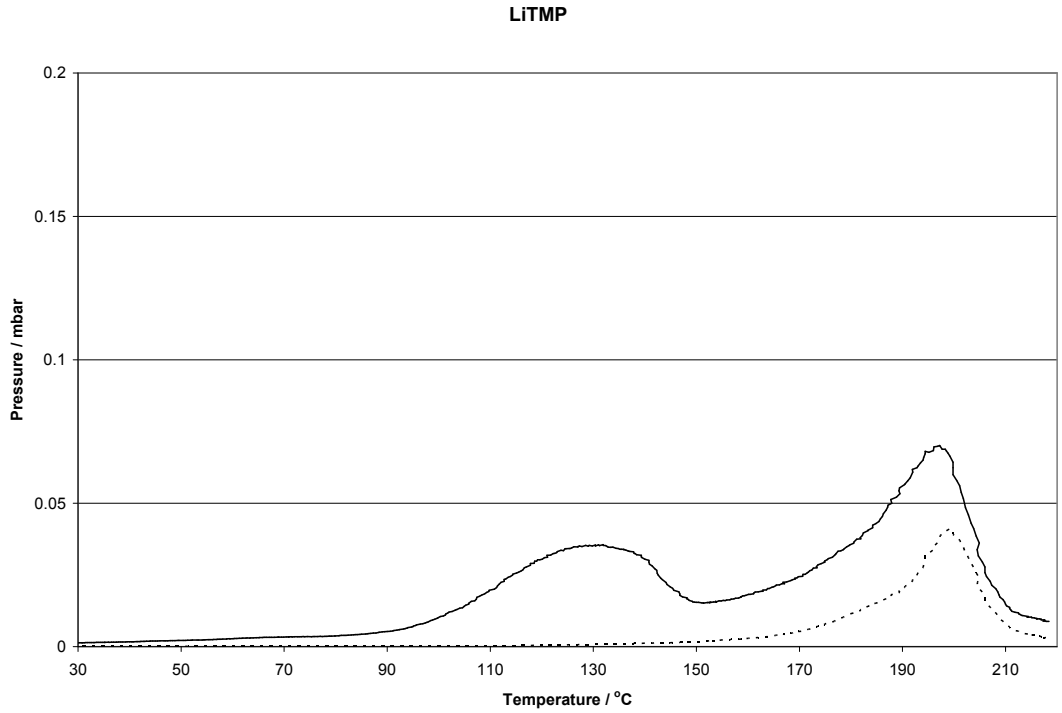

Figure S38. TVA thermogram for LiTMP. The solid line represents total volatile products, and the dashed line non-condensable volatile products.

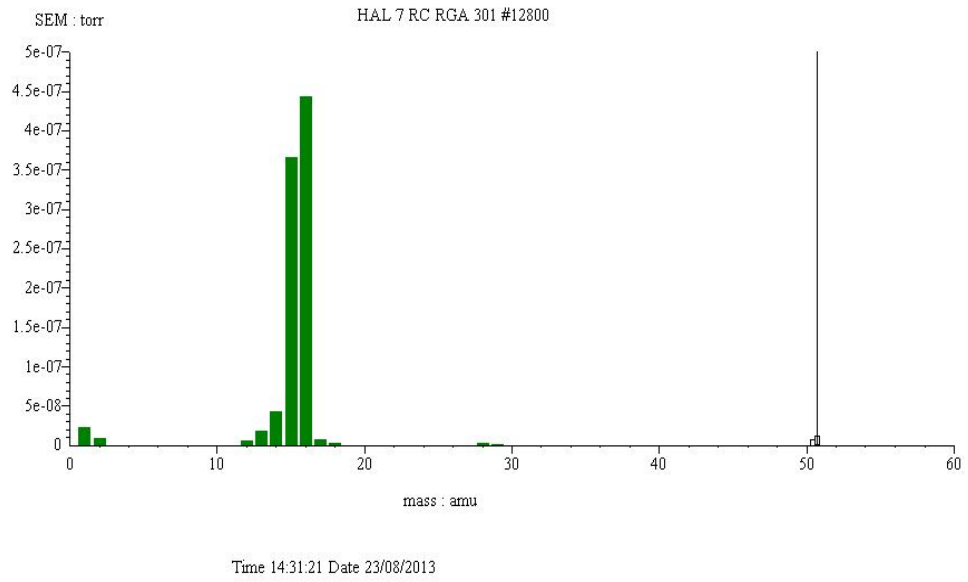

Figure S39. Mass spectrum (TVA) non-condensable products released from LiTMP.

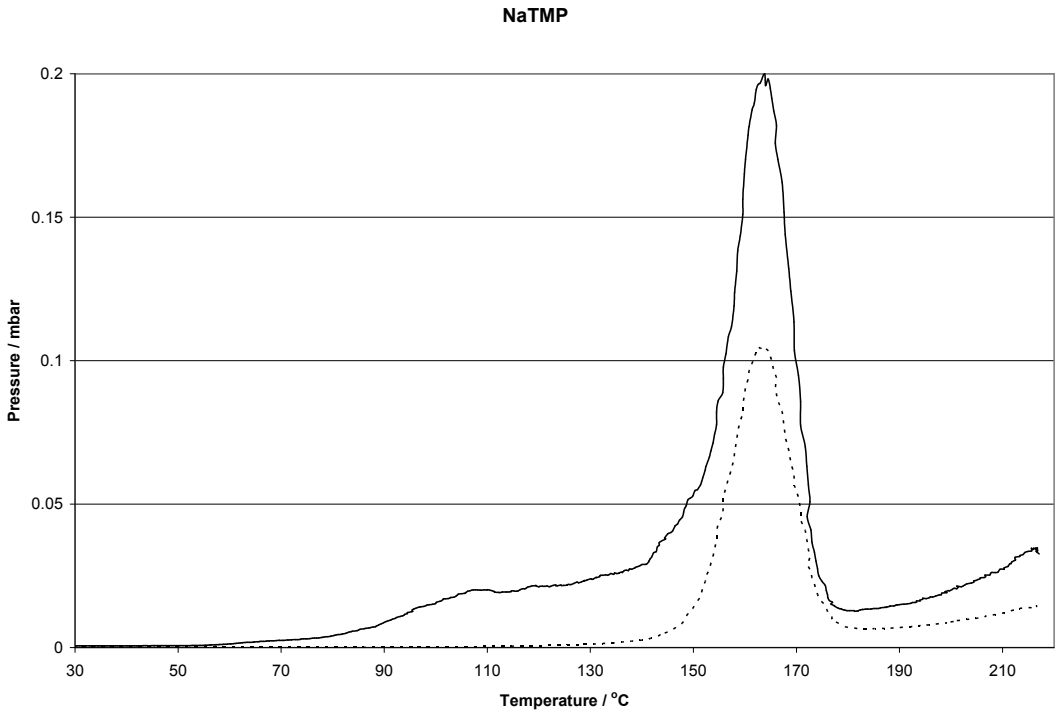

Figure S40. TVA thermogram for NaTMP. The solid line represents total volatile products, and the dashed line non-condensable volatile products.

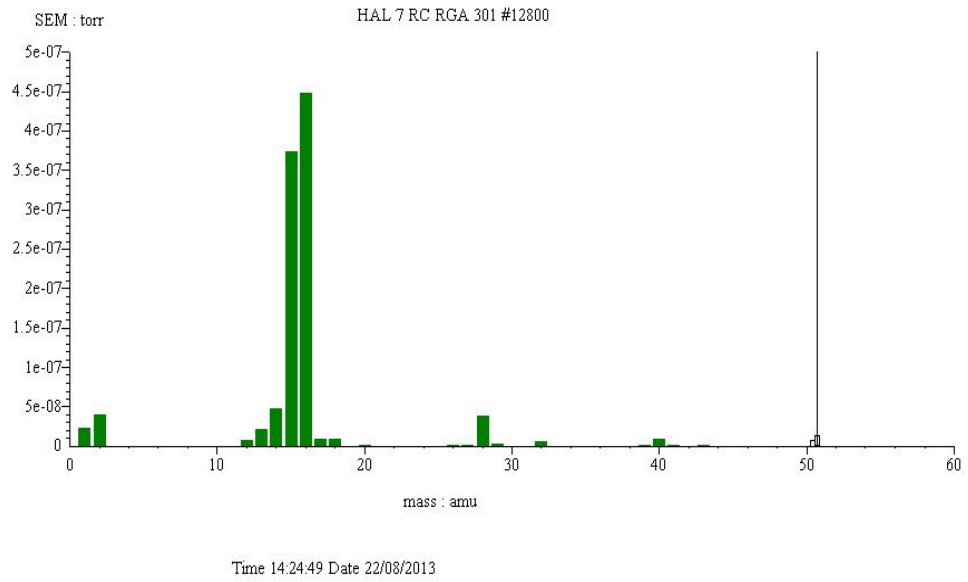

Figure S41. Mass spectrum (TVA) non-condensable products released from NaTMP.

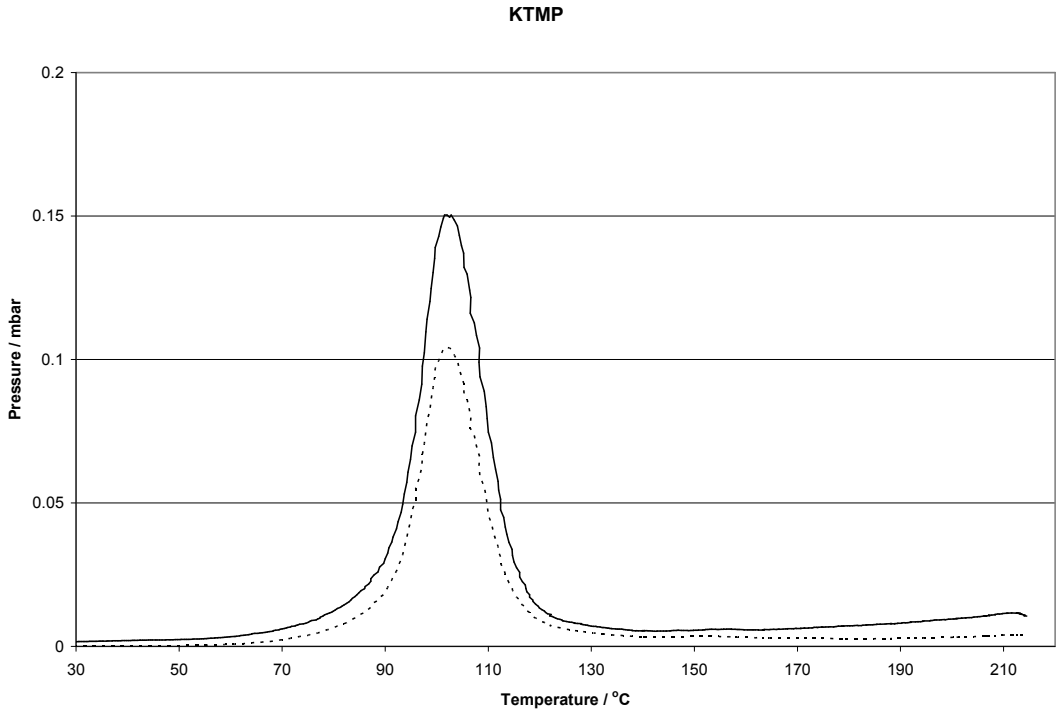

Figure S42. TVA thermogram for KTMP. The solid line represents total volatile products, and the dashed line non-condensable volatile products.

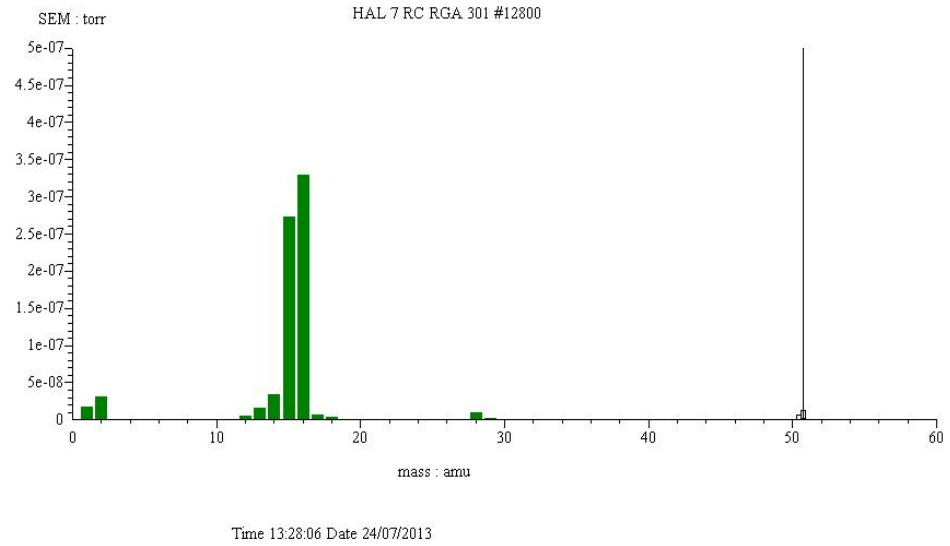

Figure S43. Mass spectrum (TVA) non-condensable products released from KTMP.

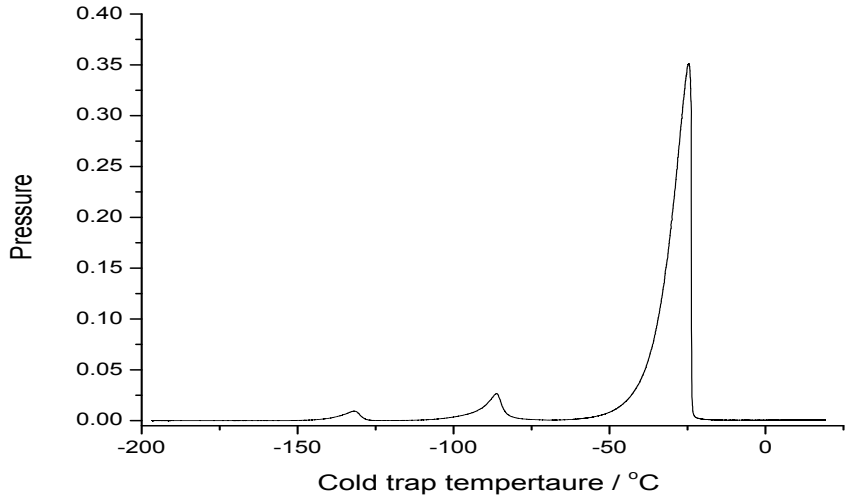

Figure S44. Sub-ambient TVA trace for LiTMP (condensable products).

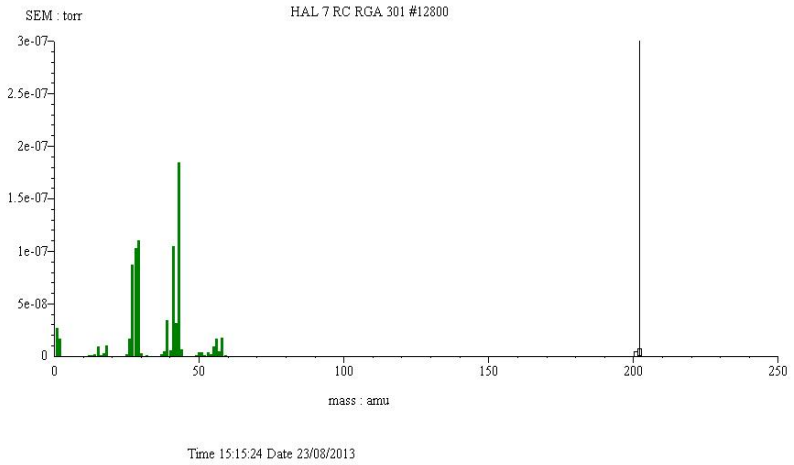

Figure S45. Mass spectrum (TVA) corresponding to the first condensable fraction being released from LiTMP.

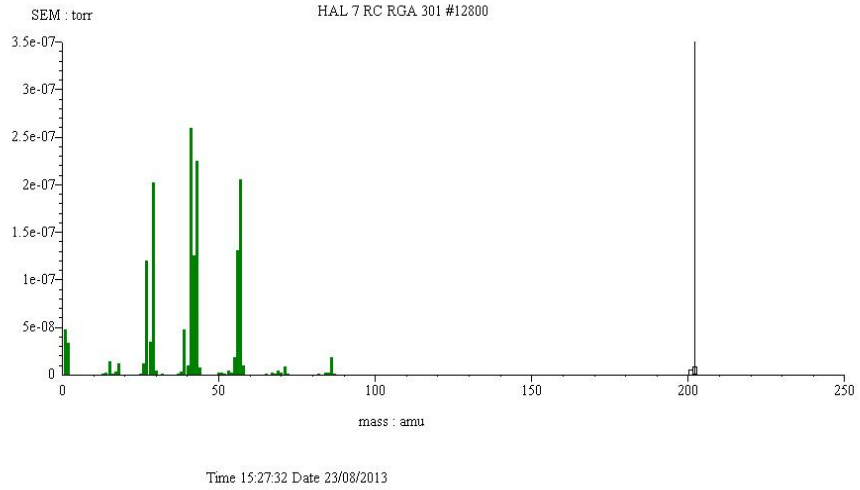

Figure S46. Mass spectrum (TVA) corresponding to the second condensable fraction released from LiTMP.

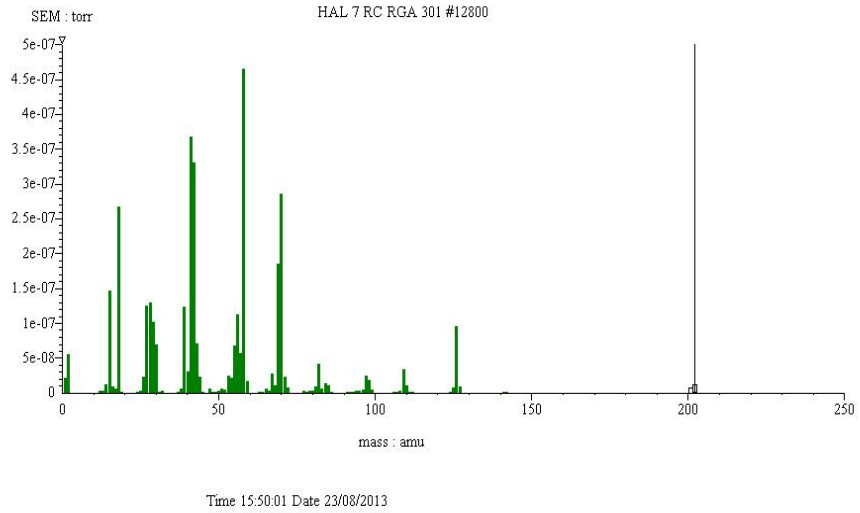

Figure S47. Mass spectrum (TVA) corresponding to the third condensable fraction released from LiTMP.

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