Facile synthesis of a genuinely alkane-soluble lithium hydride transfer reagent

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SUPPORTING INFORMATION

Graph S1 Plot of logD versus logFW from ^{1}H DOSY NMR data of the mixture of **3** and inert standards TPhN, PhN and TMS in C_6D_{12} solution at 300K

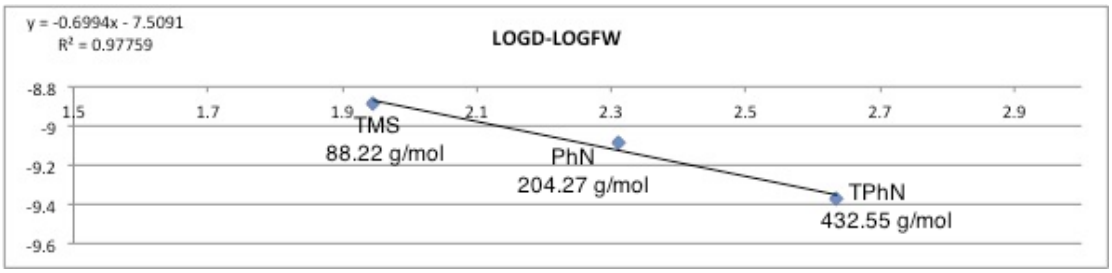

Table S1 D-FW analysis from the ^{1}H DOSY NMR data of the mixture of **3** and standards TPhN, PhN and TMS in C_6D_{12} solution at 300K

Compound	D_{Av} (x 10^{-10} m^2s^{-1})	Log D_{Av}	FW ($gmol^{-1}$)	Log FW
TPhN	4.22	-9.375047	432.55 [a]	2.636036
PhN	8.27	-9.082652	204.27 [a]	2.310204
TMS	12.89	-8.889747	88.22 [a]	1.945567
3	4.52	-9.344381	420.80 [b]	2.624079

[a] Theoretical FW [b] FW calculated from [log D = -0.6994·logFW-7.5091 (r^2 = 0.9775)]

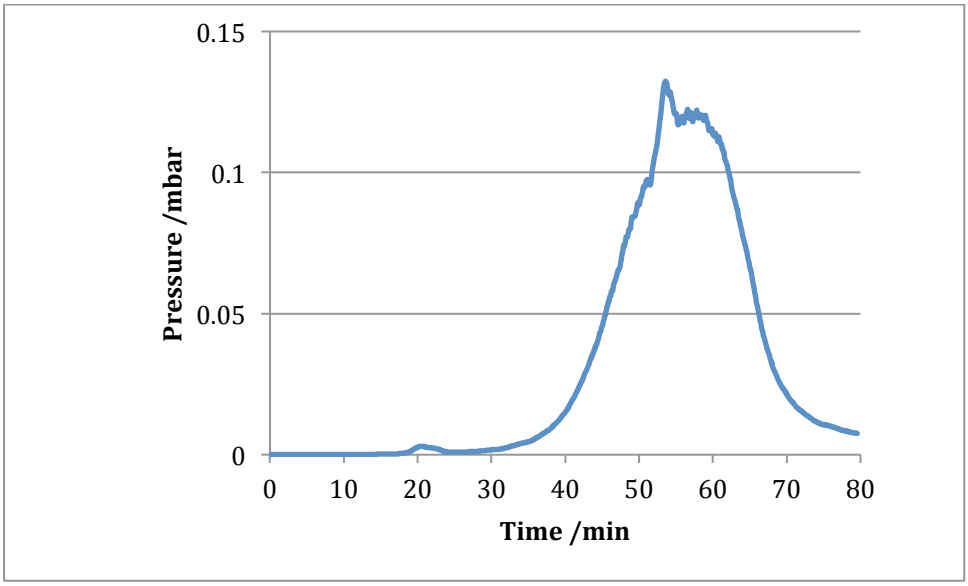

Figure S1 Sub-ambient distillation curve of products collected from thermolysis of complex **1**

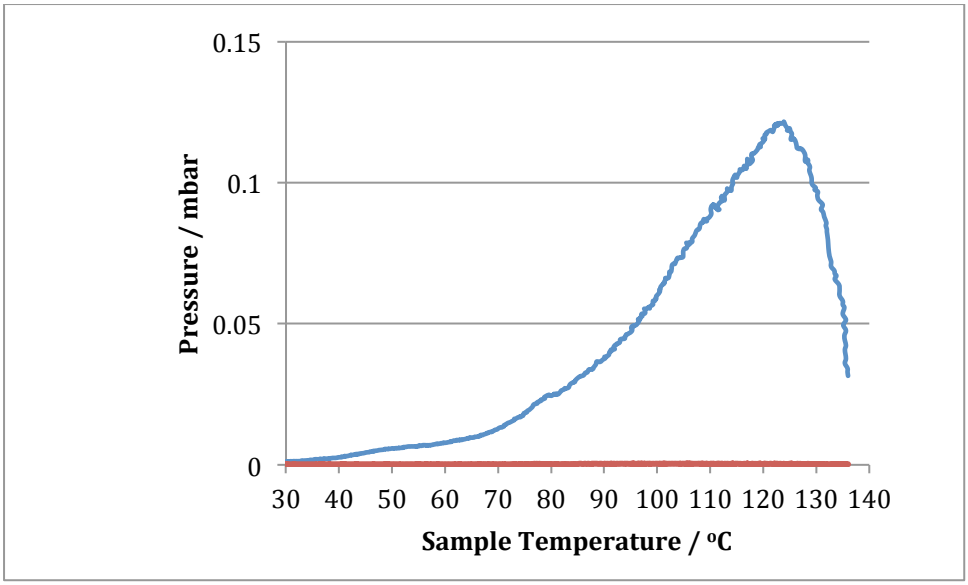

Figure S2 Thermal Volatility Analysis thermogram for **3**. The blue line represents total volatile products and the red line non-condensable volatile products.

Experimental

General Experimental

All reactions and manipulations were performed under a protective argon atmosphere using either standard Schlenk techniques or a MBraun glove box fitted with a gas purification and recirculation unit. Hexane was dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. *n*BuLi (1.6 M in hexanes), *t*BuLi (1.7 M in hexanes) and pyridine were purchased commercially from Sigma-Aldrich and used as received. Me_6TREN was prepared by a literature method.[1] NMR spectra were recorded on a Bruker 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.

DOSY NMR Spectroscopy

Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed on a Bruker AVANCE 400 NMR spectrometer operating at 400.13 MHz for proton resonance under TopSpin (version 2.0, Bruker Biospin, Karslruhe) and equipped with a BBFO-z-atm probe with actively shielded z-gradient coil capable of delivering a maximum gradient strength of 54 Gcm^{-1}. Diffusion-ordered NMR

data were acquired using the Bruker pulse program dstegp3s employing 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 of 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 plots 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.

Samples were prepared by introducing the desired complex (0.1 mmol) to a NMR tube containing 1,2,3,4-tetraphenylnaphthalene (TPhN, 15 mg), 1-phenylnaphthalene (PhN, 13.2 μL) and tetramethylsilane (TMS, 19.1 μL) as inert internal reference standards in 0.5 mL of the desired solvent for a concentration of 0.2 mol/l. The ^{1}H DOSY NMR data were recorded at 300 K. From the diffusion coefficients of the internal standards, linear calibration graphs were obtained by plotting logD versus logFW. Using the diffusion coefficients for the signals corresponding to the species under study an estimate of FW in solution was obtained.

X-ray crystallography

Crystallographic data were collected on Oxford Diffraction instruments with Mo Kα radiation (λ = 0.71073 Å). Structures were solved using *SHELXS-97*,[2] while refinement was carried out on F^2 against all independent reflections by the full-matrix least-squares method using the *SHELXL-97* program.[2] All non-hydrogen atoms were refined using anisotropic thermal parameters. Selected crystallographic details and refinement details are provided in table S2. CCDC-1017526 contains the supplementary crystallographic data for this structure. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2 Crystallographic data and refinement details for compounds **3**•Me_6TREN

	3•Me_6TREN
Empirical formula	$C_{21}H_{44}LiN_5$
Mol. mass	373.55
Crystal system	orthorhombic
Space group	P bca
a/Å	10.5102(3)
b/Å	18.8729(6)
c/Å	23.8796(6)
α/°	90
β/°	90
γ/°	90
V/Å^3	4736.7(4)
Z	8
λ/Å	0.71073
Measured reflections	38344
Unique reflections	5472
R_{int}	0.0515
Observed rflns [$I > 2\sigma(I)$]	3964
GooF	1.052
R [on F, obs rflns only]	0.0543
ωR [on F^2, all data]	0.1156
Largest diff. peak/hole e/Å^{-3}	0.261/-0.195

Thermal Volatility Analysis

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.[3]

All TVA runs were conducted under a vacuum of *ca*. 1 x 10^{-4} mbar using 200 mg samples, with the samples heated from ambient temperature to 140ºC at a rate

of 2.5 ºC min^{-1}. Evolved gases were condensed in a liquid-nitrogen cooled trap which was subsequently allowed to heat to RT over the period of 80 minutes.

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 $\sim 1 \times 10^{-4}$ 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 –196°C. These 'condensable' fractions are volatile at room temperature but involatile 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, the 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.

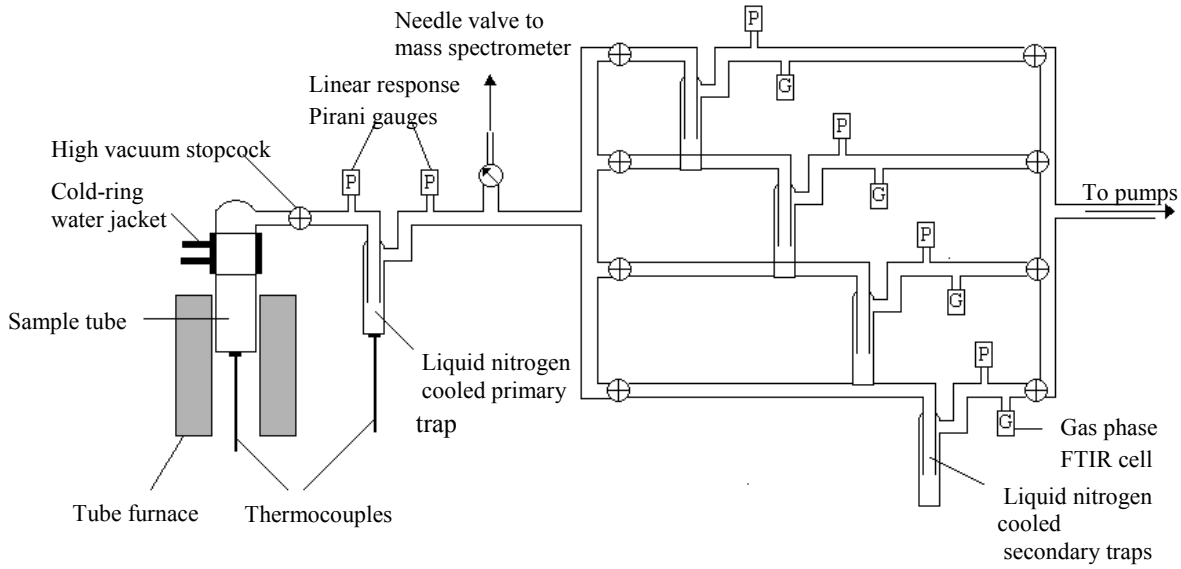

Figure S3 Schematic diagram of the TVA system

Synthesis of 2-*n*Bu(C_5H_5N)Li (**1**)

Pyridine (1.28 mL, 16 mmol) was added to a Schlenk flask containing hexane (10 mL). *n*BuLi (10 mL, 1.6 M in hexane, 16 mmol) was added via syringe, giving a yellow solution. A pale yellow precipitate formed almost immediately after the addition of *n*BuLi which was filtered and collected (yield 2.16 g, 15.04 mmol, 94 %).

^{1}H NMR (400.1 MHz, d_8-THF, 300 K): δ 6.55 (1H, d, $^3J_{H\text{-}H}$ = 5.49 Hz, H6), 5.72 (1H, t, $^3J_{H\text{-}H}$ = 5.49 Hz, H4), 4.29 (1H, t, $^3J_{H\text{-}H}$ = 5.49 Hz, H5), 4.08 (1H, t, $^3J_{H\text{-}H}$ = 5.32 Hz, H3), 3.54 (1H, quin, $^3J_{H\text{-}H}$ = 4.65 Hz, H2), 1.87 (1H, m, α-CH_2), 1.38 (1H, m, β-CH_2), 1.25 (2H, m, γ-CH_2), 1.18 (1H, m, β-CH_2), 0.89 (1H, m, α-CH_2), 0.86 ppm (3H, t, $C^3J_{H\text{-}H}$ = 7.06 Hz, CH_3).

^{13}C NMR (100.6 MHz, d_8-THF, 300 K): δ 150.0 (C6), 126.4 (C4), 96.7 (C3), 90.0 (C5), 57.6 (C2), 35.1 (α-CH_2), 28.5 (β-CH_2), 24.4 (γ-CH_2), 14.9 ppm (CH_3).

^{7}Li NMR (155.5 MHz, d_8-THF, 300 K): δ 2.17 ppm.

Elemental analysis (%) for $C_9H_{14}NLi$: calcd: C 75.51, H 9.86, N 9.78; found: C 75.19, H 9.95, N 9.81.

Synthesis of 2-*t*Bu(C_5H_5N)Li (**3**)

Pyridine (1.36 mL, 17 mmol) was added to a Schlenk flask containing hexane (5 mL). *t*BuLi (10 mL, 1.7 M in hexane, 17 mmol) was added via syringe, giving a yellow solution. A pale yellow precipitate formed after standing overnight at -30°C which was filtered and collected (yield 2.02 g, 14.11 mmol, 83 %).

^{1}H NMR (400.1 MHz, C_6D_{12}, 300 K): δ 6.85 (1H, d, $^3J_{H\text{-}H}$ = 5.09 Hz, H6), 6.12 (1H, t, $^3J_{H\text{-}H}$ = 6.11 Hz, H4), 4.92 (1H, br s, H5), 4.37 (1H, br s, H3), 3.12 (1H, br s, H2), 0.83 ppm (9H, s, CH_3).

^{13}C NMR (100.6 MHz, C_6D_{12}, 300 K): δ 150.0 (C6), 127.9 (C4), 95.1 (C3 + C5, confirmed by HSQC), 66.1 (C2), 39.3 (*t*Bu quaternary), 25.6 ppm (CH_3).

^{7}Li NMR (155.5 MHz, C_6D_{12}, 300 K): δ -1.79 ppm.

Elemental analysis (%) for $C_9H_{14}NLi$: calcd: C 75.51, H 9.86, N 9.78; found: C 75.39, H 9.94, N 9.80.

Synthesis of 2-*t*Bu(C_5H_5N)Li•Me_6TREN (**3**•Me_6TREN)

A sample of **3** (143 mg, 1 mmol) was added to a Schlenk flask and dissolved in hexane (5 mL) by gently warming with a heat gun for a few seconds. Me_6TREN (0.26 mL, I mmol) was added via syringe precipitating a yellow powder. THF was slowly added dropwise with stirring until a homogenous yellow solution was obtained. Yellow crystals formed after standing at -30°C for one week (yield 0.199 g, 53 %).

^{1}H NMR (400.1 MHz, C_6D_{12}, 300 K): δ 6.53 (1H, d, $^3J_{H\text{-}H}$ = 4.47 Hz, H6), 5.88 (1H, t, $^3J_{H\text{-}H}$ = 5.79 Hz, H4), 4.10 (1H, br t, $^3J_{H\text{-}H}$ = 4.74 Hz, H5), 4.02 (1H, br s, H3), 3.62 (1H, br d, $^3J_{H\text{-}H}$ = 5.00 Hz, H2), 2.77 (br s, 6H, CH_2 Me_6TREN), 2.52 (br s, 6H, CH_2 Me_6TREN), 2.29 (s, 18H, Me Me_6TREN), 0.86 ppm (9H, s, CH_3).

^{13}C NMR (100.6 MHz, C_6D_{12}, 300 K): δ 151.1 (C6), 128.7 (C4), 95.7 (C3), 88.2 (C5), 69.0 (C2), 58.5 (CH_2 Me_6TREN), 53.1 (CH_2 Me_6TREN), 46.0 (Me Me_6TREN), 42.1 (*t*Bu quaternary), 25.4 ppm (CH_3).

^{7}Li NMR (155.5 MHz, C_6D_{12}, 300 K): δ 0.81 ppm.

Elemental analysis (%) for $C_{21}H_{44}N_5Li$: calcd: C 67.52, H 11.87, N 18.75; found: C 66.40, H 11.99, N 18.56.

Hydrolithiation of benzophenone with **3**

Pyridine (0.27 mL, 3.4 mmol) was added to a Schlenk flask containing hexane (5 mL). *t*BuLi (2 mL, 1.7 M in hexane, 3.4 mmol) was added via syringe, giving a yellow solution. Solid benzophenone (619 mg, 3.4 mmol) was added from a solid addition tube and dissolved after approx. 1 minute. The yellow solution turned pale green then, after approx. 1 hour, a white precipitate formed alongside a colourless solution. The precipitate was filtered, washed with hexane, dried in vacuo and collected (535 mg, 83 %).

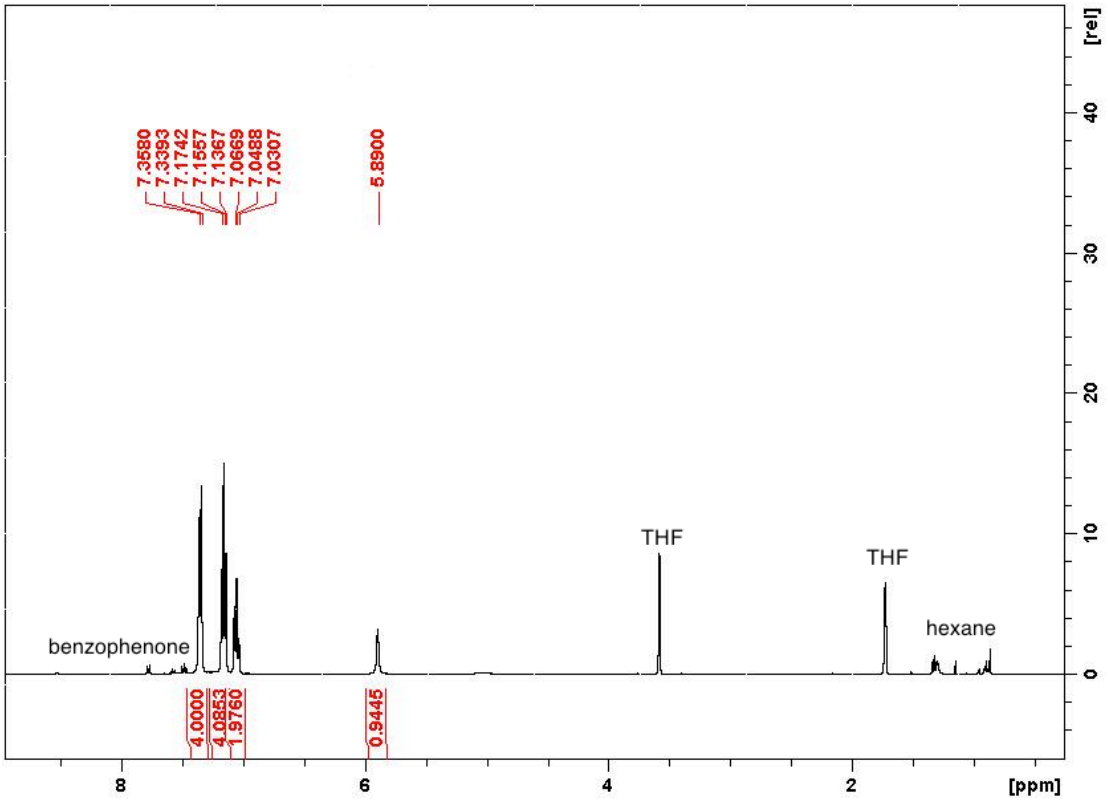

Figure S4 ^{1}H NMR spectrum of product obtained from hydrolithiation of benzophenone with complex **3**, recorded in d_8-THF at 300K with minor unknown protic impurity at approximately 5ppm.

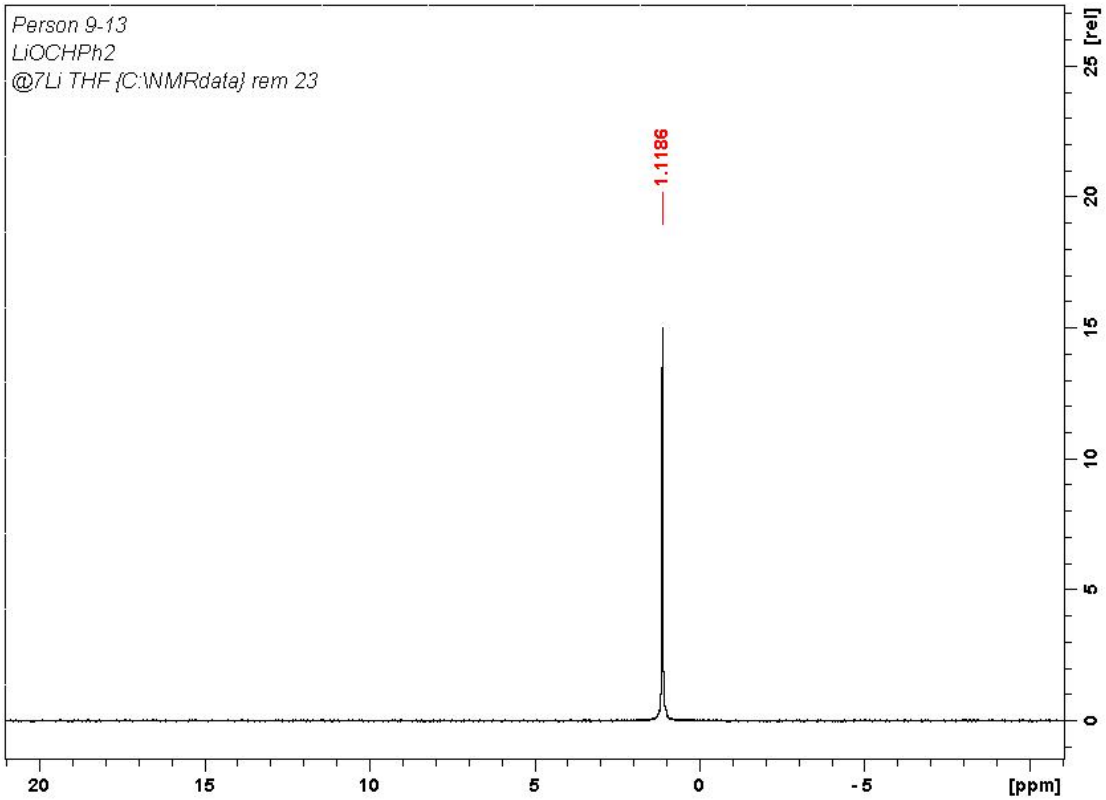

Figure S5 ^{7}Li NMR spectrum of product obtained from hydrolithiation of benzophenone with complex **3**, recorded in d_8-THF at 300K.

2-*n*butylpyridine

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.50 (1H, d, $^{3}J_{H\text{-}H}$ = 4.55 Hz, H6), 7.55 (1H, td, $^{3}J_{H\text{-}H}$ = 7.58, 1.77 Hz, H4), 7.11 (1H, d, $^{3}J_{H\text{-}H}$ = 7.83 Hz, H3), 7.06 (1H, dd, $^{3}J_{H\text{-}H}$ = 7.33, 5.05 Hz, H5), 2.77 (2H, t, $^{3}J_{H\text{-}H}$ = 7.74 Hz, α-CH_2), 1.70 (2H, quin, $^{3}J_{H\text{-}H}$ = 7.58 Hz, β-CH_2), 1.37 (2H, sxt, $^{3}J_{H\text{-}H}$ = 7.43 Hz, γ-CH_2), 0.92 ppm (3H, d, $^{3}J_{H\text{-}H}$ = 7.45 Hz, CH_3).

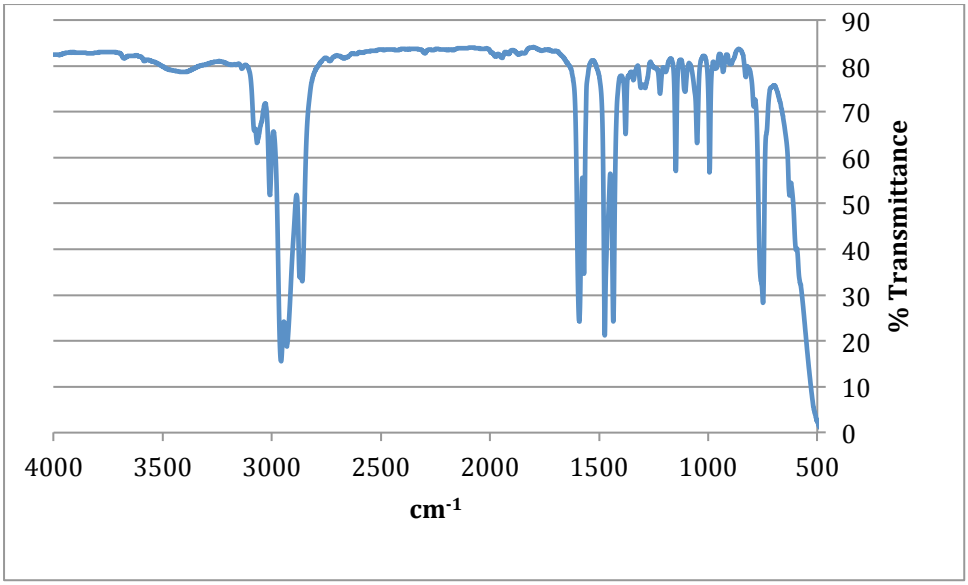

Figure S6 IR spectrum of 2-*n*butylpyridine

2-*t*butylpyridine

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.56 (1H, d, $^{3}J_{H\text{-}H}$ = 4.80 Hz, H6), 7.60 (1H, td, $^{3}J_{H\text{-}H}$ = 7.64, 1.77 Hz, H4), 7.33 (1H, d, $^{3}J_{H\text{-}H}$ = 8.08 Hz, H3), 7.06 (1H, m, H5), 1.37 ppm (9H, s, CH_3).

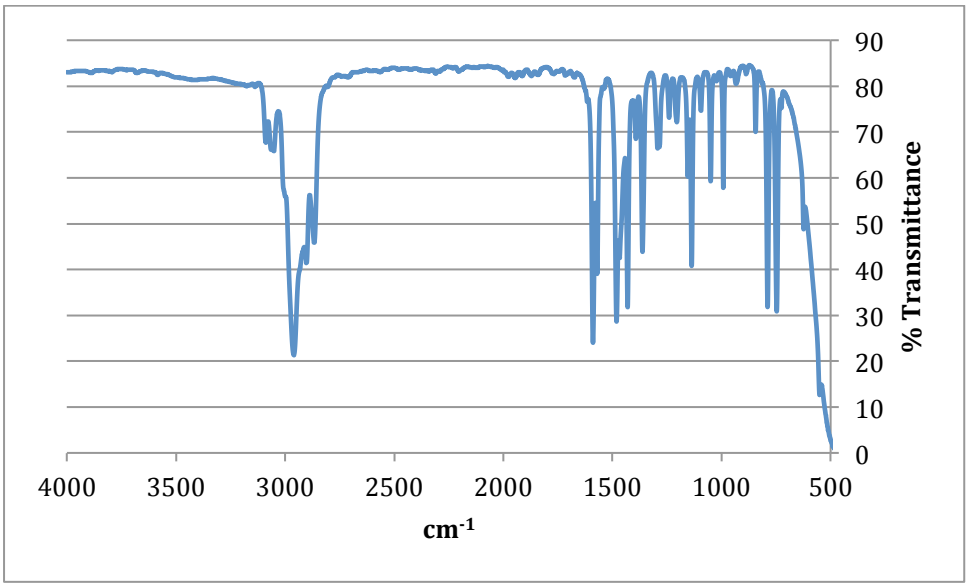

Figure S7 IR spectrum of 2-*t*butylpyridine

References

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2. G. M. Sheldrick, *Acta Crystallogr.*, 2007, **A64**, 112-122.
3. (a) I.C. McNeill, *J. Polym. Sci. A-1 Polym. Chem.*, 1966, **4**, 2479-2485; (b) I.C. McNeill, *Eur. Polym. J.*, 1967, **3**, 409-421; (c) I.C. McNeill, *Eur. Polym. J.*, 1970, **6**, 373–395; (d) I.C. McNeill, L. Ackerman, S.N. Gupta, M. Zulfiqar and S. Zulfiqar, *J. Polym. Sci. Polym. Chem. Ed.*, 1977, **15**, 2381–2392; L. Turnbull, J.J. Liggat and W.A. MacDonald, *Polym. Degrad. Stab.*, 2013, **98**, 2244-2258.