Electronic Supplementary Information

Isolation and Characterization of a Stable Pyridyllithium Compound – Aggregation in the Solid State and in Solution

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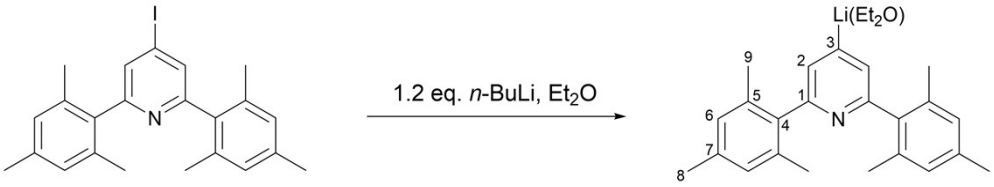
Experimental Procedures

General Remarks. All reactions were carried out under argon atmosphere using standard Schlenk techniques in flame dried glassware or in a glove box under argon or nitrogen (water and oxygen content below 1 ppm). Solvents were dried and distilled under an argon atmosphere: tetrahydrofuran and diethyl ether over sodium; pentane over CaH_2. Tetrohydrofuran-d_8 and DMSO-d_6 were dried over CaH_2. All solvents were stored over molecular sieves (Å3). NMR data were recorded either on a Bruker Avance II$^+$ Widebore 400 MHz spectrometer using J. Young NMR tubes for excluding air and moisture. Topspin 3.2 was used for manipulation of the spectra. Chemical shifts are reported in ppm relative to $Si(CH_3)_4$ for ^1H and ^{13}C, 9.7 M LiCl in D_2O for ^7Li. Coupling constant magnitudes, $|J|$, are given in Hz. Operating frequencies: Bruker Avance II$^+$ Widebore 400 MHz: ^1H 400.17 MHz, ^{13}C 100.62 MHz, ^7Li 155.52 MHz. ATR FTIR spectroscopy was performed at r.t. on a FTIR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside the glovebox. A KBr beam splitter was used for the spectra range from 4000 to 400 cm^{-1}. The spectra were recorded with 64 scans and a resolution of 2 cm^{-1}. Data processing was carried out with the OPUS 7.5 software package. The relative band intensities were described as follows: >0.66 = strong (s), >0.33 = medium (m) and >0.1 = weak (w). FT-Raman spectra were recorded on a Bruker Vertex 70 spectrometer equipped with a RAM II module using a Ge detector cooled with liquid nitrogen. Raman spectra were recorded (back-scattering mode) at room temperature in flame-sealed glass capillaries (1064 nm, 25-40 mW power, range 4000 to 200 cm^{-1}, resolution 4 cm^{-1}). Data processing was carried out with the OPUS 7.5 software package. The relative band intensities were described as follows: >0.66 = strong (s), >0.33 = medium (m) and >0.1 = weak (w). Melting points were determined on a Mel-Temp melting point device. 4-iodo-2,6-dimesitylpyridine was prepared according to a procedure given in the literature.[1]

Synthesis of 1(Et_2O).



To a suspension of 4-iodo-2,6-dimesitylpyridine (200 mg, 0.45 mmol) in Et_2O (10 ml) was added *n*-butyllithium (0.35 ml, 1.6 M in hexane, 0.56 mmol, 1.2 eq.) at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 1.5 h. The supernatant solution was filtered off to give a yellow solid. After drying *in vacuo* **1**(Et_2O) was obtained as pale yellow powder. Yield: 140 mg, 0.35 mmol, 78 %.

^1H NMR (400 MHz, THF-d_8, 203 K): δ = 7.50 (s, 2H, 2-*H*), 6.79 (s, 4H, 6-*H*), 3.36 (Et_2O), 2.25 (s, 6H, 8-*H*), 2.03 (s, 12H, 9-*H*), 1.12 (Et_2O) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, 203 K): δ = 209.0 (3-C), 152.0 (1-C), 143.2 (4-C), 137.5 (2-C), 136.1 (5-C), 134.9 (7-C), 128.0 (6-C), 66.67 (Et_2O), 21.4 (8- & 9-C), 15.94 (Et_2O) ppm.

^{7}Li (155 MHz, THF-d_8, 203 K): δ = 1.08 ppm.

ATR-IR (diamond): $\tilde{\nu}$ = 3039 (w), 2967 (m), 2916 (m), 2874 (w), 2858 (w), 2731 (w), 1613 (m), 1570 (w), 1539 (m), 1479 (m), 1471 (m), 1446 (m), 1398 (w), 1387 (w), 1376 (w), 1348 (w), 1301 (w), 1179 (w), 1165 (w), 1156 (w), 1103 (s), 1092 (m), 1066 (m), 1030 (s), 996 (w), 912 (w), 847 (s), 832 (w), 818 (w), 800 (w), 792 (w), 747 (w), 595 (w), 558 (m), 507 (m), 469 (s) cm^{-1}.

*a slight, but visible orange discoloration was visible after measurement

FT-Raman: $\tilde{\nu}$ = 3014 (w), 2968 (m), 2918 (m), 2858 (m), 1614 (s), 1570 (w), 1540 (w), 1503 (w), 1445 (w), 1380 (m), 1304 (m), 1030 (w), 996 (w), 582 (m), 565 (s), 526 (m), 510 (w), 482 (w), 456 (w), 440 (w) cm^{-1}.

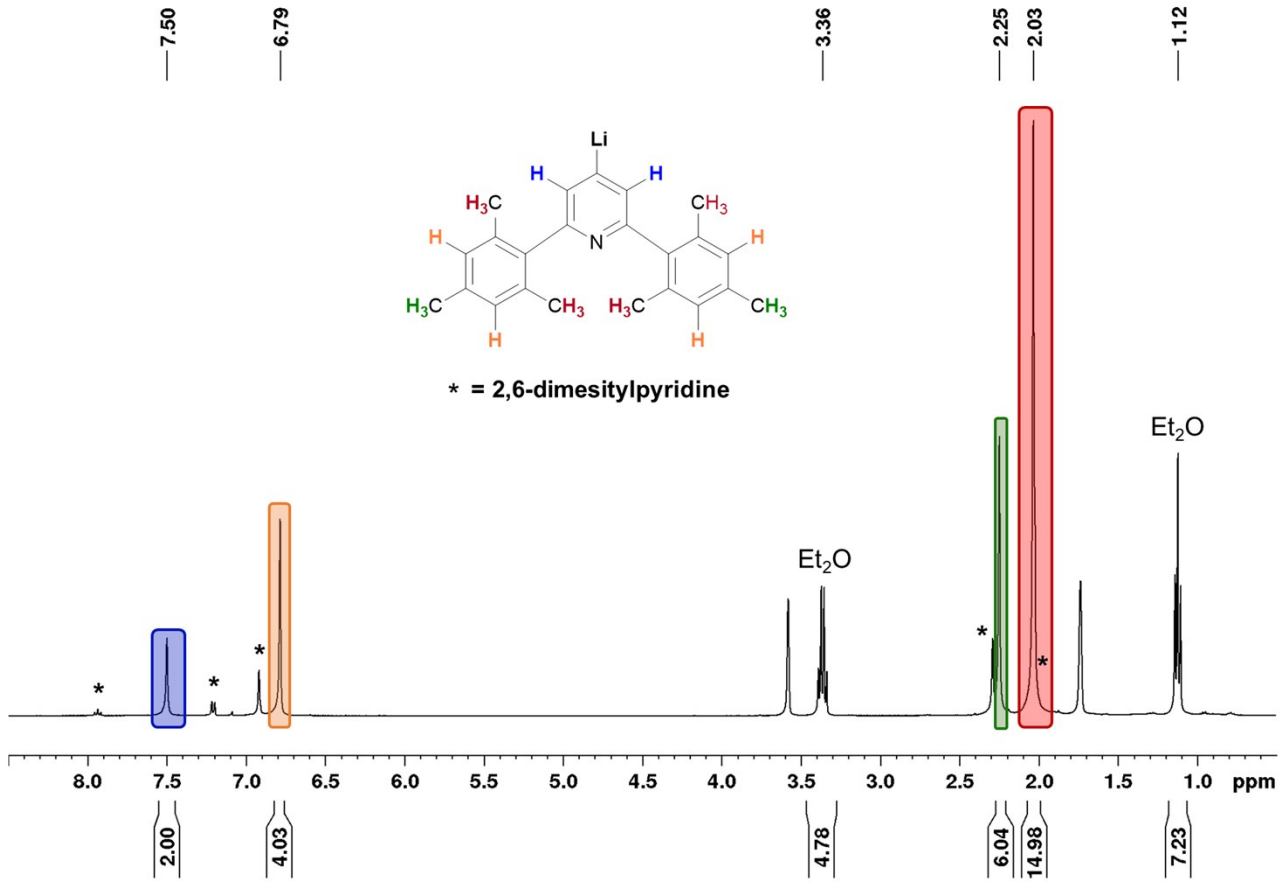


Figure S1. *^{1}H NMR (400 MHz, THF-d_8, 203 K) of compound **1** (* = 2,6-dimesitylpyridine).*

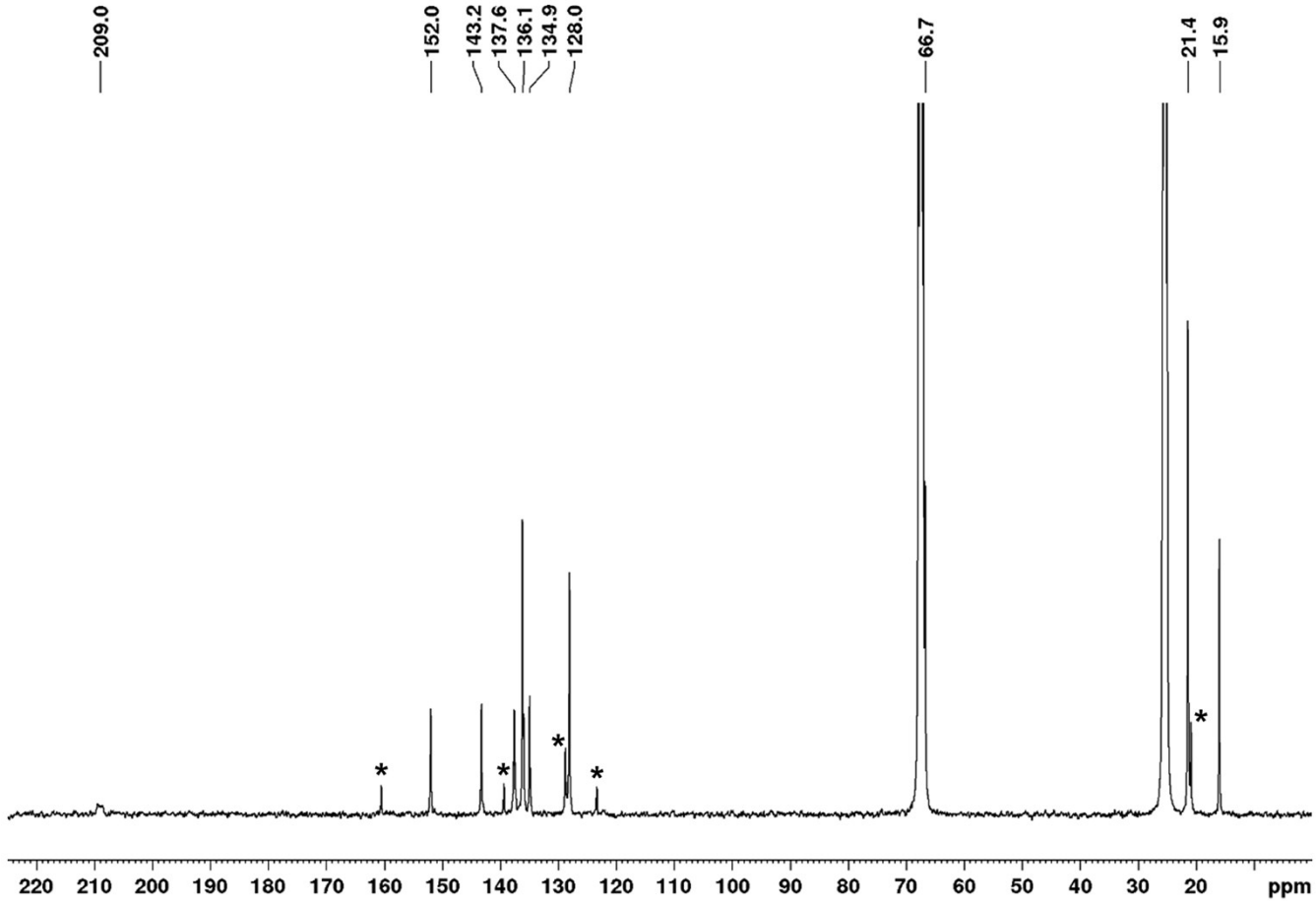


Figure S2. *$^{13}C\{^{1}H\}$ NMR (100 MHz, THF-d_8, 203 K) of **1**. (* = 2,6-dimesitylpyridine).*

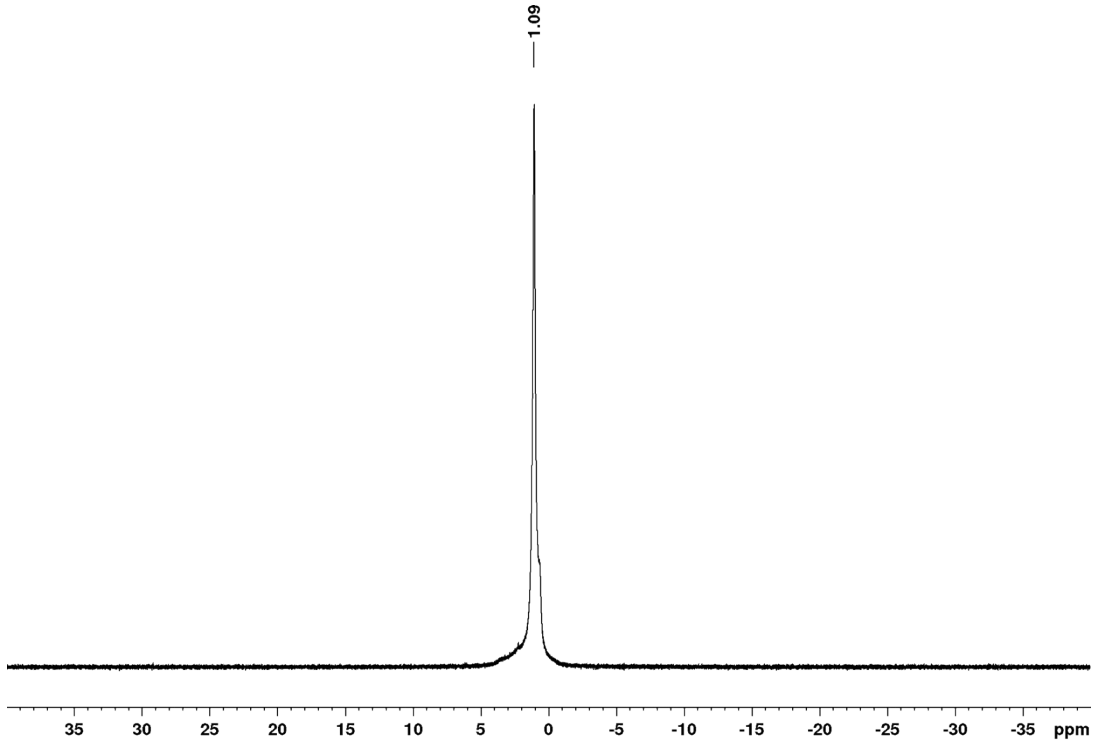


Figure S3. *^{7}Li NMR (155 MHz, THF-d_8, 203 K) spectrum of **1**.*

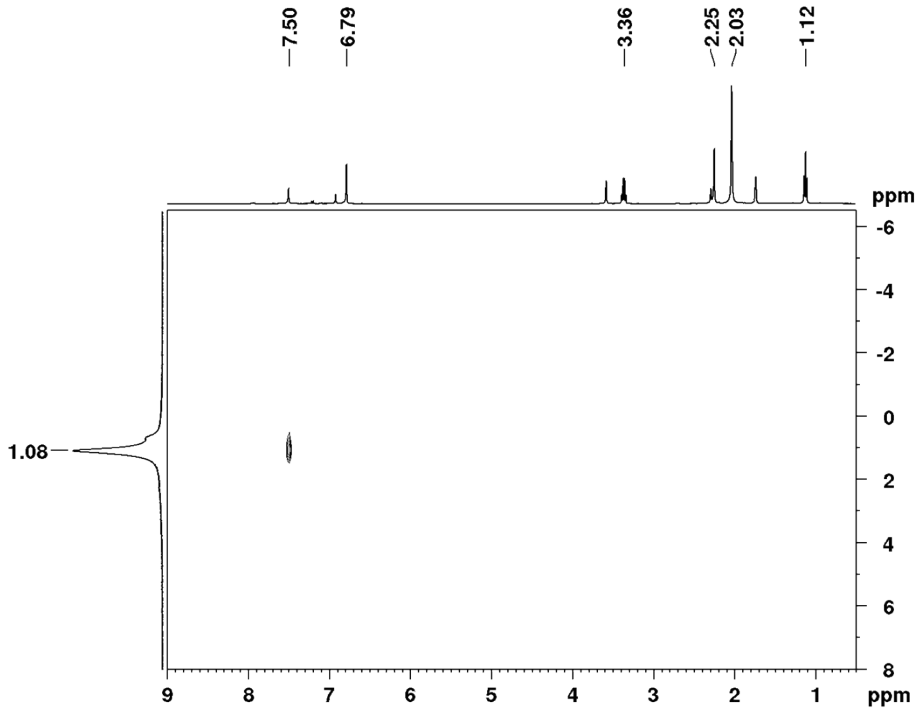
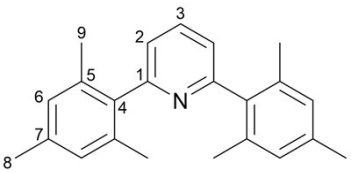


Figure S4. *$^{1}H,^{7}Li$ (400 MHz, 155 MHz, THF-d_8, 203 K) HSQC correlation NMR spectrum of **1**.*

Characterization of 2,6-dimesitylpyridine.

2,6-Dimesitylpyridine was synthesized according to a procedure in the literature.[2]



^{1}H NMR (400 MHz, 298 K, THF-d_8): δ = 7.81 (t, $^{3}J_{HH}$ = 7.74 Hz, 1H, 3-*H*), 7.13 (d, $^{3}J_{HH}$ = 7.74 Hz, 2H, 2-*H*), 6.87 (s, 4H, 6-*H*), 2.27 (s, 6H, 8-*H*), 2.02 (s, 12H, 9-*H*) ppm.

^{13}C{^{1}H} NMR (100 MHz, 298 K, THF-d_8): δ = 160.7 (1-C), 139.4 (4-C), 137.2 (7-C), 136.8 (3-C), 135.9 (5-C), 128.5 (6-C), 123.0 (2-C), 21.0 (8-C), 20.3 (9-C) ppm.

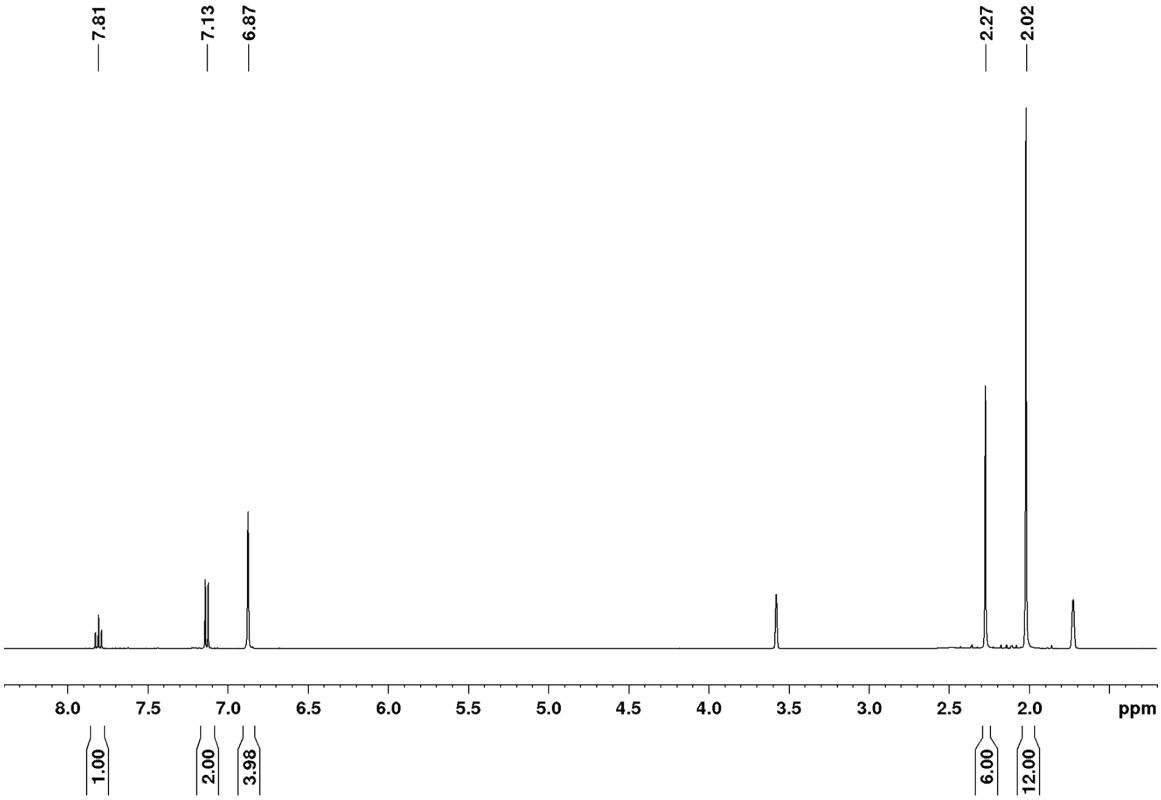


Figure S5. *^{1}H NMR (400 MHz, THF-d_8, 298 K) of 2,6-dimesitylpyridine.*

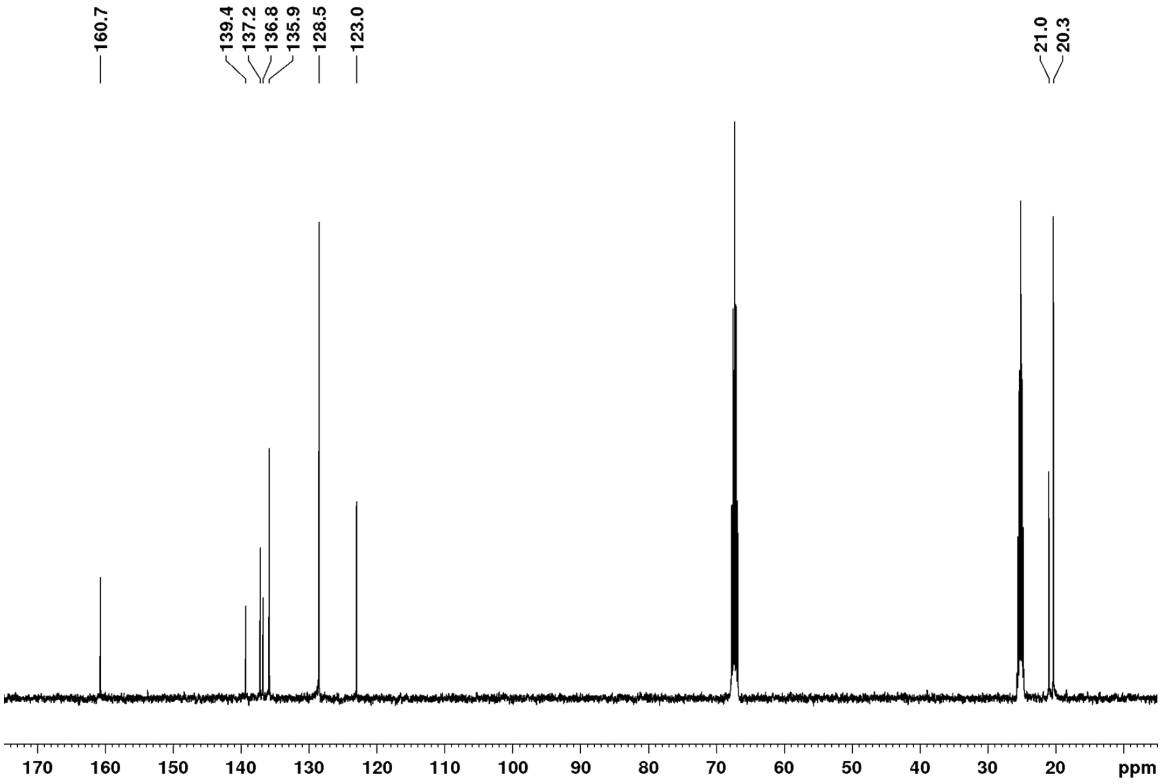
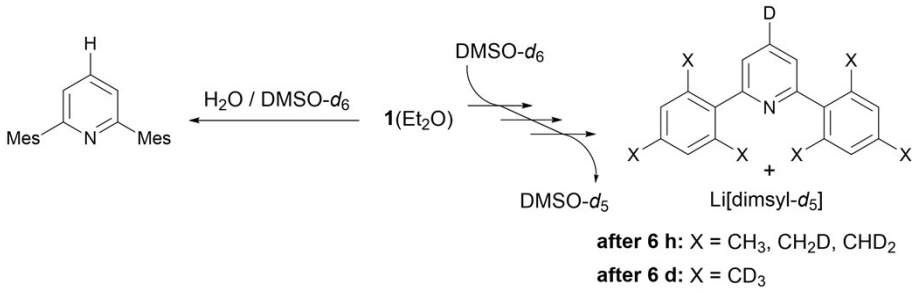


Figure S6. *^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 298 K) of 2,6-dimesitylpyridine.*

Deuteration of 1.



When a sample of **1**(Et_2O) was dissolved in aqueous DMSO-d_6, 2,6-Mes_2py was identified as the only product by NMR spectroscopy. However, when dry DMSO-d_6 was used instead, 4-D-2,6-Mes_2py was obtained with only partially deuterated methyl-groups. After keeping the sample for 6 days at ambient temperature, all methyl-groups were fully deuterated by the generated Li[dimsyl-d_5].

Figure S7, Bottom: ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of **1**(Et_2O) in DMSO-d_6 after 6 hours. The 4-position of 1(Et2O) is deuterated. The signal for the H-atom at the 4-position of the minor component Mes_2py (triplet, marked in turquois) is still detected. Already after 6 hours a partial deuteration of the methyl-groups at the mesityl-substituents is observed (marked in red and green).

Figure S7, Top: ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) spectrum of **1**(Et_2O) in DMSO-d_6 after 6 days. All of the methyl-groups at the mesityl-substituents are fully deuterated. Also, the 4-position of 2,6-Mes_2py is now deuterated. Only the signal for the H-atoms at the 3,5-positions at the pyridine (marked in blue) and the H-atoms at the mesityl-substituents (marked in orange) are detected.

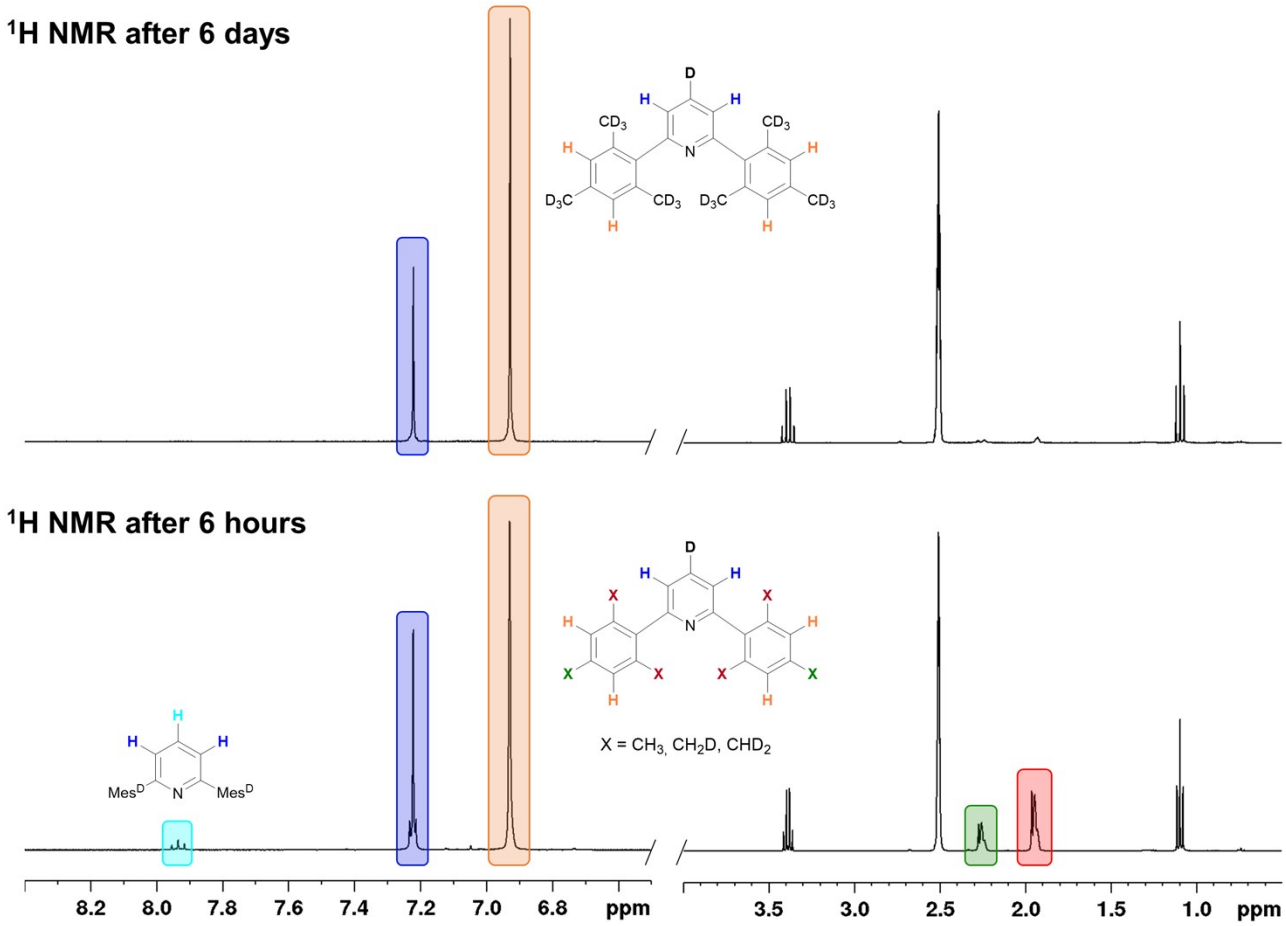


Figure S7. *Deuteration process of* ***1*** *in DMSO-d_6.*

ECC-DOSY NMR experiments and determination of the aggregation of 1 in THF

The DOSY NMR spectra were recorded on a Bruker AVANCE II$^+$ 400 MHz NMR spectrometer with a 5 mm BBFO probehead with a z-axis gradient coil with a maximum gradient strength of 50 G/cm^{-1}. The pyridyllithium compound **1** decomposes in solution at temperatures above −30 °C and therefore, the samples were prepared and kept permanently at temperatures below −30 °C in 5 mm NMR tubes with J. Young valves. In order to minimize convection an empty sealed 3 mm tube was placed inside the 5 mm tube to decrease the volume of the sample. Measurements were performed at 233 K and 243 K using a stimulated echo sequence. N_2 from vaporized liquid N_2 was used for cooling. For each DOSY NMR experiment, a series of 16 spectra on 64 K data points with 24 scans and a relaxation delay of 3 s was collected. The diffusion delay was varied between 0.2 and 0.6 s and the duration of the gradient pulses between 2.3 and 1.5 ms. The delay for gradient recovery was set to 0.2 ms. The pulse gradients were incremented from 2% to 95% of the maximum gradient strength in a linear ramp. The spectra were processed with the TOPSPIN 3.2 software. After Fourier transformation and baseline correction, diffusion coefficients were calculated by exponential fits with the T1/T2 module of TOPSPIN.

The obtained diffusion coefficients D are listed in Table S1 for 2,6-dimesitylpyridine (Mes_2py), **1** and THF. The software package "ECC-*MW* Estimation" (Version 1.3) obtained from http://www.stalke.chemie.uni-goettingen.de/mwestimation/ was used.[3]
The DOSY NMR measurements were performed at 233 K and 243 K. The authors stated that THF solutions may show discrepancies at lower temperatures. Compound Mes_2py was used as a benchmark and better results for its MW prediction were obtained for the measurements performed at 243 K. Therefore, only the results obtained at 243 K are given in the main manuscript.

ECC Models: CS = compact spheres, DSE = dissipated spheres and ellipsoids, ED = expanded discs, Merge = merged calibration curves.

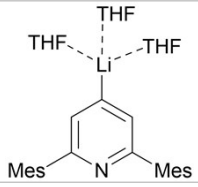
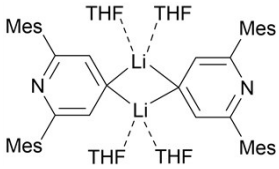
Table S1. *Diffusion coefficients D determined by DOSY experiments measured at 233 K and 243 K.*

	T = 233 K			**T = 243 K**		
Compound	**Mes_2py**	**1**	**THF**	**Mes_2py**	**1**	**THF**
D [10^{-10} m^2 s^{-1}]	2.98	2.41	7.3	4.09	3.28	9.36

Table S2. *Molecular weight determination (MW_{det}) and the percentage deviations (MW_{diff}) for compound **1** at 233 K and 243 K.*

MW(Mes_2py: $C_{23}H_{25}N$) = 315 g mol^{-1}				
ECC model	**T = 233 K**		**T = 243 K**	
	MW_{det} [g mol^{-1}]	**MW_{diff} [%]**	**MW_{det} [g mol^{-1}]**	**MW_{diff} [%]**
CS	395	−20	344	−8
Merge	374	−16	330	−4
DSE	353	−11	314	0
ED	339	−7	310	2

Table S3. *Molecular weight determination (MW_{det}) and the percentage deviations (MW_{diff}) for compound **1** at 243 K. Left: for the monomer **1**$(THF)_3$. Right: for the dimer [**1**$(THF)_2]_2$.*

1$(THF)_3$	[**1**$(THF)_2]_2$
	
MW(**1**$(THF)_3$: $C_{35}H_{48}NO_3Li$) MW = 538 g mol^{-1}	MW([**1**$(THF)_2]_2$: $C_{62}H_{80}N_2O_4Li_2$) MW = 931 g mol^{-1}

ECC model	**T = 243 K**		**T = 243 K**	
	MW_{det} [g mol^{-1}]	**MW_{diff} [%]**	**MW_{det} [g mol^{-1}]**	**MW_{diff} [%]**
CS	538	0	538	73
Merge	493	9	493	89
DSE	459	17	459	103
ED	415	30	415	124

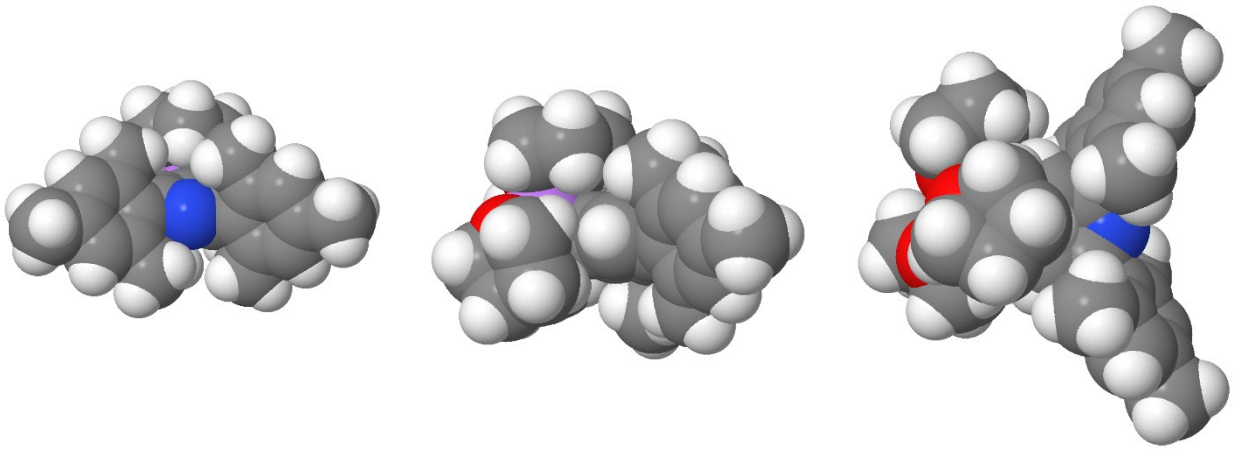


Figure S8. *Space-filling model of **1**$(THF)_3$. Front view (left), side view (middle) and top view (right).*

Crystallographic Section

Crystallization of $[1(THF)_2]_2$. 4-I-2,6-Mes_2py (200 mg, 0.453 mmol) were suspended in 2.5 ml THF in a long Schlenk-tube, equipped with a Teflon coated glass valve. At −78 °C *n*-butyllithium (0.35 ml, 1.6 м in hexane, 0.56 mmol, 1.2 eq.) were added. The reaction mixture was stirred for 0.5 h at −78 °C and was then slowly allowed to warm up to −30 °C. The reaction mixture was carefully layered with pentane and placed in a −40 °C freezer. After 7 days, yellow crystals were obtained from the sample and placed on a cooled (−40 °C) microscope-slide, allowing for the selection of a single crystal suitable for XRD.

Single Crystal X-Ray Diffraction. The data for the crystal structure of $[\mathbf{1}(THF)_2]_2$ was collected from a shock-cooled single crystal at 100 K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_α radiation, λ = 0.71073 Å. All data were integrated with SAINT,[4] and a multi-scan absorption correction using TWINABS was applied.[5] The structure was solved by direct methods using SHELXT 2014/5[6] and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3.[7] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.[8] The graphical representations were prepared with the Diamond 3.2k3 software.[9] The cif-files were prepared using the software FinalCif (https://www.xs3.uni-freiburg.de/research/finalcif). Crystallographic data (including structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre. CCDC No. 1981902 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S4. *Crystal data and structure refinement for* ***[1****$(THF)_2]_2$.*

CCDC number	1981902
Empirical formula	$C_{66}H_{88}Li_2N_2O_5$
Formula weight	1003.26
Temperature [K]	100.0
Crystal system	monoclinic
Space group (number)	$P2_1$ (4)
a [Å]	12.845(2)
b [Å]	16.759(3)
c [Å]	14.762(3)
α [Å]	90
β [Å]	107.779(9)
γ [Å]	90
Volume [Å^3]	3025.8(9)
Z	2
ρ_{calc} [g/cm^3]	1.101
μ [mm^{-1}]	0.067
F(000)	1088
Crystal size [mm^3]	0.361×0.318×0.252
Crystal colour	yellow
Crystal shape	block
Radiation	MoK_α (λ=0.71073)
2Θ range [°]	3.78 to 55.78
Index ranges	not applicable (twin)
Reflections collected	7419
Independent reflections	7419 R_{int} = 0.0392 R_{sigma} = 0.0202
Completeness to θ = 25.242°	99.90
Data / Restraints / Parameters	7419/1212/827
Goodness-of-fit on F^2	1.113
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0773 wR_2 = 0.2194
Final *R* indexes [all data]	R_1 = 0.0817 wR_2 = 0.2218
Largest peak/hole [eÅ^3]	0.35/-0.35
Flack X parameter	-3(2)

Twin law used for cell integration:

```
Transforms h1.1(1) → h1.2(2)
0.20004     -0.00037    -0.80077
-0.00001    -1.00000    0.00055
-1.19883    0.00006     -0.20004
```

The ratio of the twin domains is 0.48084

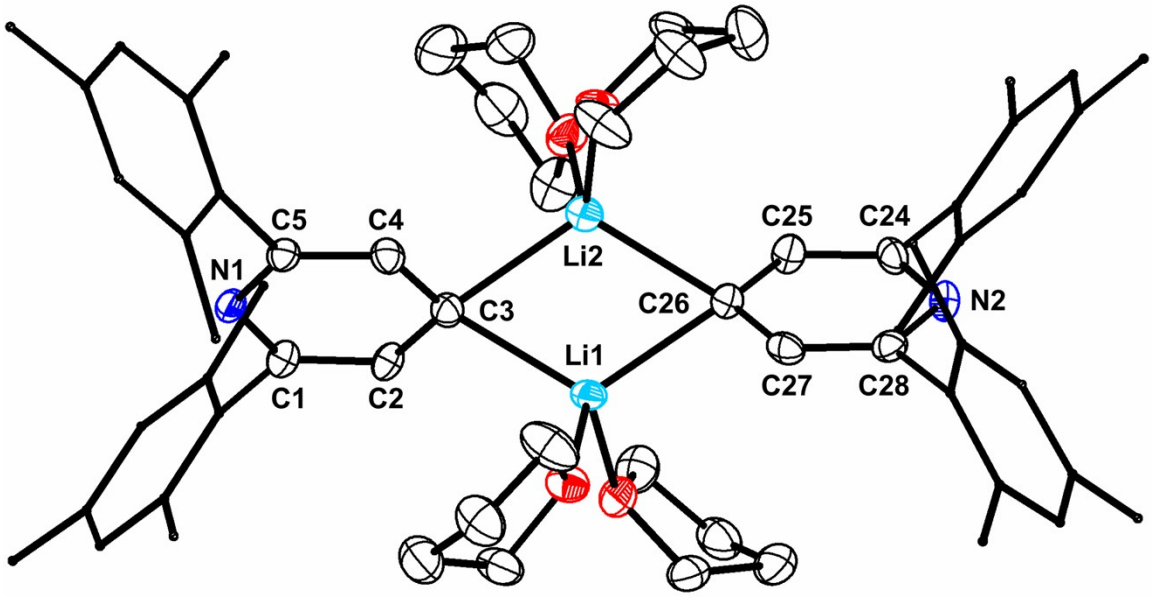


Figure S9. *Molecular structure of [**1**(THF)$_2$]$_2$ (50% probability ellipsoids, hydrogen atoms and a THF molecule omitted for clarity).*

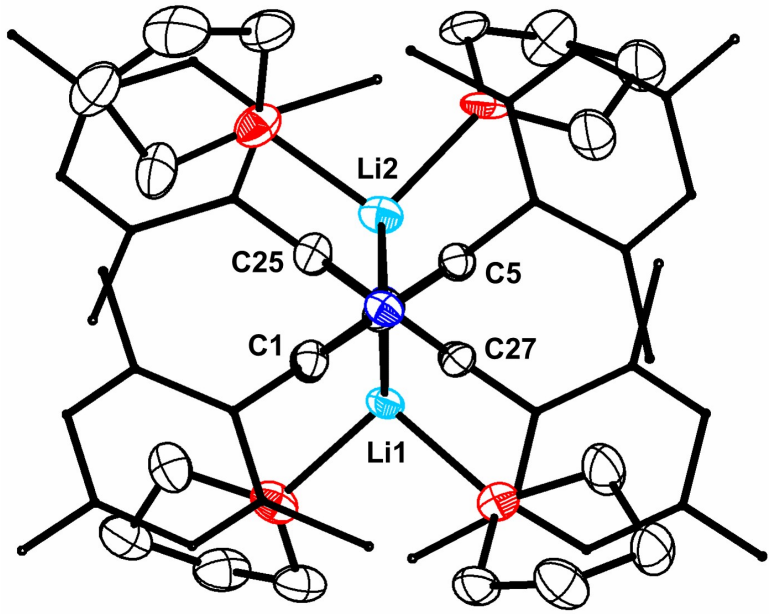


Figure S10. *Molecular structure of [**1**(THF)$_2$]$_2$ (50% probability ellipsoids, hydrogen atoms and a THF molecule omitted for clarity). View along the atoms N1–C3–C26–N2.*

Table S5. *Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* ***[1****(THF)$_2$]$_2$.*

Atom		***x***	***y***	***z***	U_{eq}
N1		0.5253(3)	0.6137(2)	0.5201(2)	0.0211(7)
Li1		0.7009(6)	0.3728(5)	0.6974(5)	0.0217(14)
C1		0.5821(4)	0.5573(3)	0.4911(3)	0.0215(8)
C2		0.6485(4)	0.5013(3)	0.5537(3)	0.0219(9)
H2		0.686549	0.464225	0.529102	0.026
N2		0.9744(3)	0.2450(2)	0.9697(3)	0.0227(8)
Li2		0.7982(7)	0.4859(5)	0.7889(6)	0.0273(17)
C3		0.6604(4)	0.4986(3)	0.6521(3)	0.0220(9)
C6		0.5689(4)	0.5612(3)	0.3867(3)	0.0230(9)
C5		0.5330(3)	0.6140(3)	0.6136(3)	0.0206(8)
C4		0.5974(4)	0.5592(3)	0.6783(3)	0.0223(9)
H4		0.599222	0.562493	0.741685	0.027
C7		0.4688(4)	0.5365(3)	0.3204(3)	0.0236(9)
C9		0.5342(5)	0.5774(3)	0.1890(4)	0.0336(11)
C8		0.4533(4)	0.5441(3)	0.2229(3)	0.0289(10)
H8		0.388162	0.526709	0.179807	0.035
C10		0.6328(4)	0.6012(3)	0.2548(3)	0.0311(11)
H10		0.687226	0.622993	0.232889	0.037
C13		0.5130(5)	0.5883(5)	0.0827(4)	0.0473(16)
H13A		0.574851	0.613802	0.071574	0.071
H13B		0.449144	0.620756	0.057330	0.071
H13C		0.501526	0.537079	0.052016	0.071
C12		0.3780(4)	0.5037(3)	0.3550(4)	0.0297(10)
H12A		0.319105	0.485628	0.301591	0.045
H12B		0.352071	0.544751	0.387982	0.045
H12C		0.405315	0.459764	0.397390	0.045
C11		0.6514(4)	0.5931(3)	0.3529(3)	0.0283(10)
C14		0.7583(4)	0.6221(4)	0.4226(4)	0.0368(12)
H14A		0.798084	0.652558	0.389052	0.055
H14B		0.801345	0.577036	0.452525	0.055
H14C		0.742915	0.654985	0.470212	0.055
C16		0.5189(4)	0.7563(3)	0.6600(3)	0.0235(9)
C15		0.4701(4)	0.6811(3)	0.6415(3)	0.0204(8)
C19		0.3028(4)	0.7353(3)	0.6582(3)	0.0246(9)
H19		0.231155	0.728109	0.658667	0.029
C18		0.3491(4)	0.8107(3)	0.6751(3)	0.0263(9)
C17		0.4568(4)	0.8206(3)	0.6765(3)	0.0243(9)
H17		0.488570	0.870908	0.688594	0.029
C21		0.6357(4)	0.7684(3)	0.6614(4)	0.0305(11)
H21A		0.652791	0.824341	0.667182	0.046
H21B		0.644897	0.748389	0.603437	0.046
H21C		0.683664	0.740362	0.714552	0.046
C22		0.2846(5)	0.8823(3)	0.6907(4)	0.0323(11)
H22A		0.324052	0.908441	0.748922	0.048
H22B		0.214771	0.864981	0.694493	0.048
H22C		0.273980	0.918829	0.638572	0.048
C23		0.3076(5)	0.5891(3)	0.6147(5)	0.0378(12)
H23A		0.236237	0.590500	0.622834	0.057
H23B		0.350993	0.548881	0.655461	0.057
H23C		0.300940	0.576807	0.549680	0.057
C24		1.0177(3)	0.3031(3)	0.9285(3)	0.0223(9)

C25		0.9537(4)	0.3584(3)	0.8643(3)	0.0242(9)
H25		0.989164	0.397506	0.840085	0.029
C26		0.8377(4)	0.3580(3)	0.8341(3)	0.0226(9)
C27		0.7966(3)	0.2952(3)	0.8790(3)	0.0219(9)
H27		0.721293	0.289063	0.863877	0.026
C28		0.8640(4)	0.2426(3)	0.9443(3)	0.0210(8)
C29		1.1418(4)	0.3044(3)	0.9595(3)	0.0262(9)
C30		1.1982(4)	0.3242(3)	1.0535(3)	0.0256(9)
C31		1.3132(4)	0.3253(3)	1.0828(4)	0.0329(11)
H31		1.351230	0.339732	1.144905	0.040
C32		1.3706(4)	0.3052(5)	1.0204(4)	0.0430(14)
C33		1.3129(4)	0.2862(5)	0.9272(4)	0.0441(15)
H33		1.351193	0.273366	0.884930	0.053
C34		1.1978(4)	0.2857(4)	0.8947(4)	0.0352(12)
C35		1.1382(4)	0.3454(3)	1.1238(4)	0.0303(10)
H35A		1.188108	0.369577	1.179034	0.045
H35B		1.108034	0.297838	1.142176	0.045
H35C		1.080213	0.382098	1.094835	0.045
C36		1.4957(4)	0.3066(6)	1.0524(5)	0.060(2)
H36A		1.521380	0.292217	1.000009	0.090
H36B		1.523306	0.269316	1.103476	0.090
H36C		1.520973	0.359302	1.073913	0.090
C37		1.1394(4)	0.2644(5)	0.7917(4)	0.0464(16)
H37A		1.191686	0.245554	0.762047	0.070
H37B		1.103215	0.310888	0.758614	0.070
H37C		1.086421	0.223447	0.789223	0.070
C38		0.8199(4)	0.1788(3)	0.9939(3)	0.0232(9)
C39		0.8176(4)	0.0985(3)	0.9659(4)	0.0306(10)
C40		0.7831(5)	0.0406(3)	1.0168(4)	0.0371(12)
H40		0.783579	-0.012493	0.998648	0.045
C41		0.7476(5)	0.0591(4)	1.0945(4)	0.0371(12)
C42		0.7473(4)	0.1389(3)	1.1205(4)	0.0320(11)
H42		0.722247	0.152633	1.171249	0.038
C43		0.7840(4)	0.1988(3)	1.0714(3)	0.0250(9)
C44		0.8498(6)	0.0773(4)	0.8791(5)	0.0445(14)
H44A		0.844239	0.020636	0.869386	0.067
H44B		0.923727	0.093982	0.887928	0.067
H44C		0.801904	0.103809	0.824498	0.067
C45		0.7079(6)	-0.0055(5)	1.1481(5)	0.0561(18)
H45A		0.632551	0.003887	1.142960	0.084
H45B		0.750983	-0.004509	1.213895	0.084
H45C		0.714947	-0.056674	1.121377	0.084
C46		0.7884(5)	0.2842(3)	1.1060(4)	0.0326(11)
H46A		0.757795	0.287090	1.157720	0.049
H46B		0.747101	0.317793	1.054954	0.049
H46C		0.862989	0.301946	1.127388	0.049
C20		0.3618(4)	0.6692(3)	0.6402(3)	0.0245(9)
O1_1		0.7449(3)	0.3005(2)	0.6107(3)	0.0311(8)
C1_1		0.7299(4)	0.2159(3)	0.6263(4)	0.0351(11)
H1A_1		0.680921	0.191477	0.569627	0.042
H1AB_1		0.700217	0.208297	0.678729	0.042
C2_1		0.8448(4)	0.1800(3)	0.6496(4)	0.0409(13)
H2A_1		0.886076	0.187573	0.716070	0.049

H2AB_1		0.842297	0.123655	0.634289	0.049
C3_1		0.8923(4)	0.2292(3)	0.5842(4)	0.0397(13)
H3A_1		0.971595	0.229413	0.606867	0.048
H3AB_1		0.868102	0.208955	0.519549	0.048
C4_1		0.8462(4)	0.3120(3)	0.5902(4)	0.0363(11)
H4A_1		0.896704	0.342828	0.640225	0.044
H4AB_1		0.833802	0.340107	0.530405	0.044
O1_2		0.5590(3)	0.3245(2)	0.6888(2)	0.0296(7)
C1_2		0.4881(4)	0.3103(4)	0.5925(4)	0.0349(11)
H1A_2		0.476686	0.253496	0.580773	0.042
H1AB_2		0.520066	0.332299	0.546370	0.042
C2_2		0.3815(5)	0.3513(4)	0.5858(4)	0.0441(14)
H2A_2		0.320725	0.326005	0.538711	0.053
H2AB_2		0.383853	0.407339	0.570290	0.053
C3_2		0.3737(4)	0.3402(4)	0.6851(4)	0.0417(13)
H3A_2		0.347374	0.287279	0.693523	0.050
H3AB_2		0.326327	0.379829	0.699876	0.050
C4_2		0.4919(4)	0.3516(5)	0.7455(4)	0.0467(15)
H4A_2		0.506286	0.407369	0.762145	0.056
H4AB_2		0.507283	0.320667	0.803668	0.056
O1_3		0.9181(3)	0.5488(2)	0.7634(3)	0.0333(8)
C1_3		0.9561(5)	0.5300(4)	0.6830(5)	0.0414(13)
H1A_3		0.895681	0.513645	0.628743	0.050
H1AB_3		1.009774	0.487405	0.698967	0.050
C2_3		1.0069(5)	0.6062(4)	0.6615(4)	0.0483(15)
H2A_3		1.083910	0.609037	0.697215	0.058
H2AB_3		0.998608	0.610605	0.594139	0.058
C3_3		0.9425(7)	0.6700(4)	0.6929(5)	0.0565(18)
H3A_3		0.873624	0.680342	0.644242	0.068
H3AB_3		0.983797	0.719276	0.707852	0.068
C4_3		0.9245(5)	0.6339(3)	0.7806(4)	0.0410(13)
H4A_3		0.984775	0.646591	0.836776	0.049
H4AB_3		0.857195	0.653577	0.789303	0.049
O1_4		0.7720(11)	0.5341(11)	0.9015(7)	0.030(2)
C1_4		0.8272(16)	0.5981(9)	0.9624(8)	0.081(5)
H1A_4		0.793470	0.648884	0.938754	0.097
H1AB_4		0.903515	0.600109	0.964874	0.097
C2_4		0.8174(9)	0.5813(6)	1.0605(6)	0.050(3)
H2A_4		0.767965	0.618875	1.075998	0.060
H2AB_4		0.888161	0.584629	1.108632	0.060
C3_4		0.7722(13)	0.4969(8)	1.0538(10)	0.048(3)
H3A_4		0.726299	0.489934	1.094552	0.057
H3AB_4		0.830475	0.457699	1.070344	0.057
C4_4		0.7060(10)	0.4914(7)	0.9493(10)	0.034(3)
H4A_4		0.695751	0.436297	0.928485	0.041
H4AB_4		0.634980	0.516436	0.937590	0.041
O1_5		0.7904(16)	0.5422(19)	0.9041(12)	0.029(4)
C1_5		0.8917(11)	0.5494(10)	0.9806(8)	0.032(3)
H1A_5		0.907760	0.605041	0.997375	0.038
H1AB_5		0.951715	0.526887	0.962102	0.038
C2_5		0.8752(12)	0.5037(12)	1.0637(10)	0.045(4)
H2A_5		0.922605	0.523496	1.123992	0.054
H2AB_5		0.887771	0.447059	1.058771	0.054

C3_5		0.7561(14)	0.5213(18)	1.0520(15)	0.045(5)
H3A_5		0.747575	0.572796	1.078935	0.054
H3AB_5		0.724146	0.480340	1.081628	0.054
C4_5		0.7055(15)	0.5211(18)	0.9447(15)	0.047(6)
H4A_5		0.676643	0.468666	0.922965	0.056
H4AB_5		0.646214	0.559450	0.925910	0.056
O1_6		0.9340(16)	-0.0866(14)	0.5253(11)	0.137(6)
C1_6		0.8834(10)	-0.0848(10)	0.6015(9)	0.068(4)
H1A_6		0.860409	-0.137732	0.613718	0.081
H1AB_6		0.820507	-0.049537	0.585339	0.081
C2_6		0.9718(10)	-0.0538(8)	0.6864(9)	0.057(3)
H2A_6		1.018583	-0.096951	0.719390	0.069
H2AB_6		0.940664	-0.027297	0.730503	0.069
C3_6		1.0350(9)	0.0043(7)	0.6454(9)	0.057(3)
H3A_6		1.110280	0.008836	0.685330	0.068
H3AB_6		1.001310	0.056664	0.636619	0.068
C4_6		1.0272(11)	-0.0349(11)	0.5506(9)	0.069(4)
H4A_6		1.019560	0.005605	0.501979	0.083
H4AB_6		1.093096	-0.065248	0.555816	0.083
O1_7		0.936(4)	-0.157(2)	0.529(3)	0.158(12)
C1_7		0.929(5)	-0.136(3)	0.623(3)	0.162(14)
H1A_7		0.969443	-0.173585	0.669949	0.195
H1AB_7		0.853143	-0.136201	0.622198	0.195
C2_7		0.976(4)	-0.053(3)	0.646(2)	0.126(11)
H2A_7		1.047609	-0.055290	0.693434	0.151
H2AB_7		0.928549	-0.019373	0.668603	0.151
C3_7		0.986(4)	-0.023(2)	0.552(3)	0.104(10)
H3A_7		1.061549	-0.021092	0.553093	0.125
H3AB_7		0.955030	0.030521	0.538845	0.125
C4_7		0.921(4)	-0.082(2)	0.477(2)	0.120(10)
H4A_7		0.843905	-0.067511	0.454251	0.144
H4AB_7		0.949356	-0.085090	0.423726	0.144
O1_8		1.048(3)	0.021(3)	0.719(3)	0.094(11)
C1_8		1.082(3)	0.007(4)	0.636(4)	0.088(11)
H1A_8		1.119784	-0.043937	0.639902	0.106
H1AB_8		1.129825	0.049089	0.626926	0.106
C2_8		0.975(5)	0.006(4)	0.555(3)	0.084(11)
H2A_8		0.982386	-0.020450	0.499525	0.101
H2AB_8		0.947964	0.059994	0.538513	0.101
C3_8		0.900(4)	-0.040(4)	0.599(4)	0.089(12)
H3A_8		0.825628	-0.020288	0.575572	0.107
H3AB_8		0.900317	-0.096514	0.584055	0.107
C4_8		0.948(4)	-0.026(5)	0.704(3)	0.094(12)
H4A_8		0.896958	0.003377	0.728398	0.113
H4AB_8		0.965149	-0.075955	0.738107	0.113

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S6. *Bond lengths and angles for [**1**(THF)$_2$]$_2$.*

Atom–Atom	**Length [Å]**
N1–C1	1.342(6)
N1–C5	1.353(6)

Li1–O1_2	1.963(8)
Li1–O1_1	1.966(8)
Li1–C3	2.225(9)
Li1–C26	2.249(8)
Li1–Li2	2.439(11)
C1–C2	1.407(6)
C1–C6	1.499(6)
C2–C3	1.414(6)
N2–C28	1.353(6)
N2–C24	1.354(6)
Li2–O1_4	1.967(16)
Li2–O1_5	1.97(2)
Li2–O1_3	1.995(9)
Li2–C3	2.253(9)
Li2–C26	2.256(10)
C3–C4	1.423(6)
C6–C11	1.407(7)
C6–C7	1.419(6)
C5–C4	1.401(6)
C5–C15	1.512(6)
C7–C8	1.398(6)
C7–C12	1.511(7)
C9–C10	1.398(7)
C9–C8	1.399(7)
C9–C13	1.520(7)
C10–C11	1.400(7)
C11–C14	1.523(7)
C16–C15	1.397(7)
C16–C17	1.406(6)
C16–C21	1.507(7)
C15–C20	1.400(7)
C19–C18	1.386(7)
C19–C20	1.414(6)
C18–C17	1.387(7)
C18–C22	1.515(6)
C23–C20	1.506(7)
C24–C25	1.398(6)
C24–C29	1.518(6)
C25–C26	1.419(6)
C26–C27	1.427(6)
C27–C28	1.395(6)
C28–C38	1.501(6)
C29–C30	1.395(7)
C29–C34	1.397(7)
C30–C31	1.406(7)
C30–C35	1.513(7)
C31–C32	1.386(8)
C32–C33	1.386(8)
C32–C36	1.530(7)
C33–C34	1.407(7)
C34–C37	1.519(8)
C38–C43	1.398(7)
C38–C39	1.406(7)
C39–C40	1.381(8)
C39–C44	1.505(8)
C40–C41	1.391(9)
C41–C42	1.391(9)
C41–C45	1.519(8)
C42–C43	1.403(7)
C43–C46	1.515(7)
O1_1–C4_1	1.437(6)
O1_1–C1_1	1.458(6)
C1_1–C2_1	1.532(7)
C2_1–C3_1	1.531(8)
C3_1–C4_1	1.521(7)
O1_2–C4_2	1.445(6)
O1_2–C1_2	1.455(5)
C1_2–C2_2	1.507(7)
C2_2–C3_2	1.511(7)
C3_2–C4_2	1.520(7)
O1_3–C4_3	1.447(6)
O1_3–C1_3	1.449(6)
C1_3–C2_3	1.510(7)
C2_3–C3_3	1.508(9)
C3_3–C4_3	1.510(8)
O1_4–C1_4	1.440(13)
O1_4–C4_4	1.447(10)
C1_4–C2_4	1.518(11)
C2_4–C3_4	1.519(12)
C3_4–C4_4	1.520(11)
O1_5–C4_5	1.440(13)
O1_5–C1_5	1.444(13)
C1_5–C2_5	1.515(12)
C2_5–C3_5	1.515(14)
C3_5–C4_5	1.517(13)
O1_6–C4_6	1.432(13)
O1_6–C1_6	1.461(12)
C1_6–C2_6	1.503(13)
C2_6–C3_6	1.507(11)
C3_6–C4_6	1.521(12)
O1_7–C1_7	1.454(15)
O1_7–C4_7	1.459(15)
C1_7–C2_7	1.510(15)
C2_7–C3_7	1.512(15)
C3_7–C4_7	1.532(15)
O1_8–C1_8	1.446(15)
O1_8–C4_8	1.451(15)
C1_8–C2_8	1.517(15)
C2_8–C3_8	1.519(15)
C3_8–C4_8	1.513(15)
Atom–Atom–Atom	**Angle [°]**
C1–N1–C5	116.8(4)
O1_2–Li1–O1_1	98.6(4)
O1_2–Li1–C3	104.1(4)
O1_1–Li1–C3	118.5(4)

O1_2–Li1–C26	117.9(4)
O1_1–Li1–C26	102.4(4)
C3–Li1–C26	114.9(4)
O1_2–Li1–Li2	131.6(4)
O1_1–Li1–Li2	129.8(4)
C3–Li1–Li2	57.5(3)
C26–Li1–Li2	57.4(3)
N1–C1–C2	122.7(4)
N1–C1–C6	113.3(4)
C2–C1–C6	124.0(4)
C1–C2–C3	123.3(4)
C28–N2–C24	115.9(4)
O1_4–Li2–O1_3	106.5(5)
O1_5–Li2–O1_3	98.9(8)
O1_4–Li2–C3	115.4(6)
O1_5–Li2–C3	119.7(8)
O1_3–Li2–C3	102.8(4)
O1_4–Li2–C26	102.8(6)
O1_5–Li2–C26	105.4(10)
O1_3–Li2–C26	116.1(4)
C3–Li2–C26	113.5(4)
O1_4–Li2–Li1	126.6(6)
O1_5–Li2–Li1	134.2(8)
O1_3–Li2–Li1	126.9(4)
C3–Li2–Li1	56.4(3)
C26–Li2–Li1	57.1(3)
C2–C3–C4	111.4(4)
C2–C3–Li1	106.3(4)
C4–C3–Li1	134.0(4)
C2–C3–Li2	137.1(4)
C4–C3–Li2	100.3(4)
Li1–C3–Li2	66.0(3)
C11–C6–C7	119.2(4)
C11–C6–C1	121.3(4)
C7–C6–C1	119.3(4)
N1–C5–C4	122.5(4)
N1–C5–C15	113.7(4)
C4–C5–C15	123.7(4)
C5–C4–C3	123.3(4)
C8–C7–C6	119.8(4)
C8–C7–C12	119.9(4)
C6–C7–C12	120.2(4)
C10–C9–C8	118.7(4)
C10–C9–C13	121.4(5)
C8–C9–C13	119.9(5)
C7–C8–C9	121.1(5)
C9–C10–C11	121.5(5)
C10–C11–C6	119.7(5)
C10–C11–C14	120.1(4)
C6–C11–C14	120.2(4)
C15–C16–C17	118.7(4)
C15–C16–C21	120.7(4)
C17–C16–C21	120.6(4)

C16–C15–C20	121.1(4)
C16–C15–C5	118.6(4)
C20–C15–C5	120.1(4)
C18–C19–C20	121.6(4)
C19–C18–C17	118.9(4)
C19–C18–C22	121.6(4)
C17–C18–C22	119.5(5)
C18–C17–C16	121.5(5)
N2–C24–C25	123.0(4)
N2–C24–C29	114.3(4)
C25–C24–C29	122.7(4)
C24–C25–C26	123.6(4)
C25–C26–C27	111.0(4)
C25–C26–Li1	137.7(4)
C27–C26–Li1	101.5(4)
C25–C26–Li2	102.1(4)
C27–C26–Li2	139.1(4)
Li1–C26–Li2	65.6(3)
C28–C27–C26	123.2(4)
N2–C28–C27	123.3(4)
N2–C28–C38	113.9(4)
C27–C28–C38	122.7(4)
C30–C29–C34	120.9(4)
C30–C29–C24	118.9(4)
C34–C29–C24	120.2(4)
C29–C30–C31	119.2(5)
C29–C30–C35	121.3(4)
C31–C30–C35	119.6(5)
C32–C31–C30	121.0(5)
C31–C32–C33	118.9(5)
C31–C32–C36	120.8(5)
C33–C32–C36	120.2(6)
C32–C33–C34	121.8(5)
C29–C34–C33	118.2(5)
C29–C34–C37	122.6(4)
C33–C34–C37	119.2(5)
C43–C38–C39	119.2(4)
C43–C38–C28	119.8(4)
C39–C38–C28	121.0(4)
C40–C39–C38	119.6(5)
C40–C39–C44	121.0(5)
C38–C39–C44	119.3(5)
C39–C40–C41	122.1(5)
C40–C41–C42	118.1(5)
C40–C41–C45	121.2(6)
C42–C41–C45	120.7(6)
C41–C42–C43	121.0(5)
C38–C43–C42	119.9(5)
C38–C43–C46	121.0(4)
C42–C43–C46	119.1(5)
C15–C20–C19	118.3(4)
C15–C20–C23	120.8(4)
C19–C20–C23	120.8(4)

C4_1–O1_1–C1_1	109.6(4)
C4_1–O1_1–Li1	120.9(4)
C1_1–O1_1–Li1	114.8(4)
O1_1–C1_1–C2_1	104.6(4)
C3_1–C2_1–C1_1	100.9(4)
C4_1–C3_1–C2_1	102.5(4)
O1_1–C4_1–C3_1	106.5(4)
C4_2–O1_2–C1_2	108.1(4)
C4_2–O1_2–Li1	122.6(4)
C1_2–O1_2–Li1	115.0(4)
O1_2–C1_2–C2_2	105.9(4)
C1_2–C2_2–C3_2	102.0(4)
C2_2–C3_2–C4_2	101.7(4)
O1_2–C4_2–C3_2	106.6(4)
C4_3–O1_3–C1_3	110.0(4)
C4_3–O1_3–Li2	119.5(4)
C1_3–O1_3–Li2	120.9(4)
O1_3–C1_3–C2_3	105.3(5)
C3_3–C2_3–C1_3	102.9(5)
C2_3–C3_3–C4_3	102.8(5)
O1_3–C4_3–C3_3	105.1(5)
C1_4–O1_4–C4_4	108.3(9)
C1_4–O1_4–Li2	130.9(10)
C4_4–O1_4–Li2	119.1(11)
O1_4–C1_4–C2_4	106.7(8)
C1_4–C2_4–C3_4	104.6(8)
C2_4–C3_4–C4_4	101.9(8)
O1_4–C4_4–C3_4	103.6(8)
C4_5–O1_5–C1_5	108.1(12)
C4_5–O1_5–Li2	119.0(17)
C1_5–O1_5–Li2	116.3(17)
O1_5–C1_5–C2_5	106.0(11)
C1_5–C2_5–C3_5	101.3(11)
C2_5–C3_5–C4_5	102.4(12)
O1_5–C4_5–C3_5	107.3(12)
C4_6–O1_6–C1_6	108.6(11)
O1_6–C1_6–C2_6	104.4(9)
C1_6–C2_6–C3_6	104.5(9)
C2_6–C3_6–C4_6	101.5(9)
O1_6–C4_6–C3_6	108.3(9)
C1_7–O1_7–C4_7	104.2(18)
O1_7–C1_7–C2_7	107.7(16)
C1_7–C2_7–C3_7	104.1(13)
C2_7–C3_7–C4_7	105.1(14)
O1_7–C4_7–C3_7	103.1(17)
C1_8–O1_8–C4_8	105.9(19)
O1_8–C1_8–C2_8	102.7(18)
C1_8–C2_8–C3_8	102.5(17)
C4_8–C3_8–C2_8	103.7(15)
O1_8–C4_8–C3_8	107.5(14)

Bonds to hydrogen atoms were omitted.

Table S7. *Torsion angles for [**1**(THF)$_2$]$_2$.*

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
C5–N1–C1–C2	-1.1(6)
C5–N1–C1–C6	179.9(4)
N1–C1–C2–C3	0.9(7)
C6–C1–C2–C3	179.8(4)
C1–C2–C3–C4	-0.2(6)
C1–C2–C3–Li1	152.9(4)
C1–C2–C3–Li2	-135.0(5)
N1–C1–C6–C11	103.4(5)
C2–C1–C6–C11	-75.6(6)
N1–C1–C6–C7	-72.9(5)
C2–C1–C6–C7	108.1(5)
C1–N1–C5–C4	0.6(6)
C1–N1–C5–C15	177.9(4)
N1–C5–C4–C3	0.0(7)
C15–C5–C4–C3	-176.9(4)
C2–C3–C4–C5	-0.3(6)
Li1–C3–C4–C5	-143.1(5)
Li2–C3–C4–C5	150.3(4)
C11–C6–C7–C8	0.0(7)
C1–C6–C7–C8	176.4(4)
C11–C6–C7–C12	-178.7(5)
C1–C6–C7–C12	-2.3(7)
C6–C7–C8–C9	-1.4(8)
C12–C7–C8–C9	177.3(5)
C10–C9–C8–C7	1.7(8)
C13–C9–C8–C7	-177.3(5)
C8–C9–C10–C11	-0.5(8)
C13–C9–C10–C11	178.4(6)
C9–C10–C11–C6	-0.9(8)
C9–C10–C11–C14	-178.0(5)
C7–C6–C11–C10	1.1(7)
C1–C6–C11–C10	-175.2(5)
C7–C6–C11–C14	178.3(5)
C1–C6–C11–C14	2.0(7)
C17–C16–C15–C20	-0.6(7)
C21–C16–C15–C20	179.9(4)
C17–C16–C15–C5	173.6(4)
C21–C16–C15–C5	-5.9(6)
N1–C5–C15–C16	-82.7(5)
C4–C5–C15–C16	94.5(5)
N1–C5–C15–C20	91.5(5)
C4–C5–C15–C20	-91.3(6)
C20–C19–C18–C17	-1.5(7)
C20–C19–C18–C22	177.6(4)
C19–C18–C17–C16	0.8(7)
C22–C18–C17–C16	-178.4(4)
C15–C16–C17–C18	0.2(7)
C21–C16–C17–C18	179.8(4)
C28–N2–C24–C25	0.7(7)
C28–N2–C24–C29	179.4(4)

N2–C24–C25–C26	-1.6(7)
C29–C24–C25–C26	179.8(4)
C24–C25–C26–C27	0.9(6)
C24–C25–C26–Li1	-136.7(5)
C24–C25–C26–Li2	156.5(4)
C25–C26–C27–C28	0.6(6)
Li1–C26–C27–C28	153.0(4)
Li2–C26–C27–C28	-141.2(5)
C24–N2–C28–C27	0.9(6)
C24–N2–C28–C38	-178.3(4)
C26–C27–C28–N2	-1.6(7)
C26–C27–C28–C38	177.5(4)
N2–C24–C29–C30	-66.8(6)
C25–C24–C29–C30	111.9(5)
N2–C24–C29–C34	113.0(5)
C25–C24–C29–C34	-68.3(7)
C34–C29–C30–C31	0.1(8)
C24–C29–C30–C31	179.9(4)
C34–C29–C30–C35	179.3(5)
C24–C29–C30–C35	-0.9(7)
C29–C30–C31–C32	-1.6(8)
C35–C30–C31–C32	179.2(5)
C30–C31–C32–C33	1.9(10)
C30–C31–C32–C36	179.9(6)
C31–C32–C33–C34	-0.8(11)
C36–C32–C33–C34	-178.8(7)
C30–C29–C34–C33	1.0(9)
C24–C29–C34–C33	-178.8(5)
C30–C29–C34–C37	-179.5(6)
C24–C29–C34–C37	0.7(9)
C32–C33–C34–C29	-0.6(10)
C32–C33–C34–C37	179.9(7)
N2–C28–C38–C43	100.5(5)
C27–C28–C38–C43	-78.6(6)
N2–C28–C38–C39	-77.2(6)
C27–C28–C38–C39	103.6(5)
C43–C38–C39–C40	-1.9(7)
C28–C38–C39–C40	175.8(5)
C43–C38–C39–C44	176.4(5)
C28–C38–C39–C44	-5.8(7)
C38–C39–C40–C41	1.6(8)
C44–C39–C40–C41	-176.7(6)
C39–C40–C41–C42	0.1(9)
C39–C40–C41–C45	178.7(6)
C40–C41–C42–C43	-1.5(8)
C45–C41–C42–C43	179.9(5)
C39–C38–C43–C42	0.6(7)
C28–C38–C43–C42	-177.2(4)
C39–C38–C43–C46	178.1(5)
C28–C38–C43–C46	0.2(7)
C41–C42–C43–C38	1.1(7)
C41–C42–C43–C46	-176.4(5)
C16–C15–C20–C19	-0.1(7)

C5–C15–C20–C19	-174.2(4)
C16–C15–C20–C23	176.5(5)
C5–C15–C20–C23	2.4(7)
C18–C19–C20–C15	1.2(7)
C18–C19–C20–C23	-175.4(5)
C4_1–O1_1–C1_1–C2_1	19.9(6)
Li1–O1_1–C1_1–C2_1	-119.9(4)
O1_1–C1_1–C2_1–C3_1	-36.1(5)
C1_1–C2_1–C3_1–C4_1	38.5(5)
C1_1–O1_1–C4_1–C3_1	5.1(6)
Li1–O1_1–C4_1–C3_1	142.0(4)
C2_1–C3_1–C4_1–O1_1	-27.8(5)
C4_2–O1_2–C1_2–C2_2	15.6(6)
Li1–O1_2–C1_2–C2_2	-125.5(5)
O1_2–C1_2–C2_2–C3_2	-34.2(6)
C1_2–C2_2–C3_2–C4_2	38.7(7)
C1_2–O1_2–C4_2–C3_2	9.5(7)
Li1–O1_2–C4_2–C3_2	147.0(5)
C2_2–C3_2–C4_2–O1_2	-30.4(7)
C4_3–O1_3–C1_3–C2_3	10.3(6)
Li2–O1_3–C1_3–C2_3	156.3(5)
O1_3–C1_3–C2_3–C3_3	-29.6(6)
C1_3–C2_3–C3_3–C4_3	37.2(6)
C1_3–O1_3–C4_3–C3_3	13.3(7)
Li2–O1_3–C4_3–C3_3	-133.2(5)
C2_3–C3_3–C4_3–O1_3	-31.4(7)
C4_4–O1_4–C1_4–C2_4	15(2)
Li2–O1_4–C1_4–C2_4	-150.0(13)
O1_4–C1_4–C2_4–C3_4	10.2(18)
C1_4–C2_4–C3_4–C4_4	-29.4(14)
C1_4–O1_4–C4_4–C3_4	-33.6(17)
Li2–O1_4–C4_4–C3_4	133.2(11)
C2_4–C3_4–C4_4–O1_4	38.4(14)
C4_5–O1_5–C1_5–C2_5	20(3)
Li2–O1_5–C1_5–C2_5	-116.9(16)
O1_5–C1_5–C2_5–C3_5	-36(2)
C1_5–C2_5–C3_5–C4_5	37(2)
C1_5–O1_5–C4_5–C3_5	4(3)
Li2–O1_5–C4_5–C3_5	139.8(19)
C2_5–C3_5–C4_5–O1_5	-26(3)
C4_6–O1_6–C1_6–C2_6	-20(2)
O1_6–C1_6–C2_6–C3_6	33.9(17)
C1_6–C2_6–C3_6–C4_6	-34.1(14)
C1_6–O1_6–C4_6–C3_6	-2(2)
C2_6–C3_6–C4_6–O1_6	22.6(19)
C4_7–O1_7–C1_7–C2_7	-34(5)
O1_7–C1_7–C2_7–C3_7	13(6)
C1_7–C2_7–C3_7–C4_7	12(5)
C1_7–O1_7–C4_7–C3_7	40(4)
C2_7–C3_7–C4_7–O1_7	-32(5)
C4_8–O1_8–C1_8–C2_8	39(5)
O1_8–C1_8–C2_8–C3_8	-41(5)
C1_8–C2_8–C3_8–C4_8	27(6)

C1_8–O1_8–C4_8–C3_8	-22(6)
C2_8–C3_8–C4_8–O1_8	-4(7)

Bonds to hydrogen atoms were omitted.

Computational Section

Calculations were performed with TURBOMOLE[10], except for the DLPNO-CCSD(T)[11] single point calculations which were done with ORCA.[12] DFT optimizations were carried out at the BP86-D3(BJ)[13]/def-TZVP[14] level with RI-J auxiliary bases[15] and D3[16](BJ)[17] dispersion correction and with TPSS[18]-D3(BJ)/def2-TZVPP[19] and corresponding RI-J[20] auxiliary bases. Vibrational frequencies were calculated analytically at the BP86-D3(BJ)/def-TZVP level with the AOFORCE[21] module and all structures represented true minima without imaginary frequencies on the respective hypersurface. Thermal contributions to *ab initio* reaction energies (see below) were calculated with inclusion of zero point energy, thermal contributions to the enthalpy/entropy (FREEH tool; unscaled[1] BP86-D3(BJ)/def-TZVP vibrational frequencies). For chiral molecules, standard entropies were corrected by adding *R*ln2 to account for the enantiomer. Entropies corrected this way are given in italics in Table S8.

***Ab initio* calculations:** MP2/A'VXZ and DLPNO-CCSD(T)/A'VXZ single point calculations with correlation-consistent basis sets were done with A'VXZ = cc-pVXZ for H and Li[22] and aug-cc-pVXZ for 2nd[23] row elements (X = D, Q) and corresponding RI-C auxiliary bases.[24] The DLPNO-CCSD(T) calculations were done with the same A'VDZ orbital and RI-C auxiliary basis set as the corresponding MP2 calculations. To improve accuracy, the "TIGHTPNO" truncation scheme defined by Liakos et al.[25] (TCutPNO 10^{-7}, TCutPairs 10^{-5}, TCutMKN 10^{-4}) was applied. The structures used for the single point calculations had TPSS-D3(BJ)/def2-TZVPP quality.

Ab initio reaction energies were calculated with a DLPNO-CCSD(T)-MP2 compound method, generating energies of almost CCSD(T)/A'VQZ quality. Typically the errors associated with the CCSD(T)/A'VDZ-MP2/A'VQZ addition scheme were found to be < 1 kJ mol^{-1} for a set of (non-isodesmic!) hydrogen bond dissociation energies (equation 1).[26]
This method has already been applied for the calculation of gas phase basicities for substituted pyridines, including benchmark calculations.[27]

The following compound addition scheme was applied:

$$E_{\text{comp}} = E_{\text{DLPNO-CCSD(T)/A'VDZ}} + E_{\text{MP2/A'VQZ}} - E_{\text{MP2/A'VDZ}} \approx E_{\text{CCSD(T)/A'VQZ}} \qquad (1)$$

Thermal contributions to reaction energies were calculated with inclusion of BP86-D3(BJ)/def-TZVP calculations at 1 bar, 298.15 K according to equation 2:

$$U^{p} = E_{\text{comp.}} + E_{\text{vrt}} \qquad (2)$$

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[1] By chance, scaling factors for BP86-D3(BJ)/def-TZVP frequencies were found to be very close to unity. Therefore, the contributions to entropy/enthalpy were not scaled.

(Where E_{vrt} = sum of translational, rotational, and vibrational energy incl. zero point vibrational energy @BP86-D3(BJ)/def–TZVP).

$U°$ was then corrected to the standard enthalpy $H°$ and Gibbs energy $G°$ by adding RT (equation 3); (*cf.* RT = 2.48 kJ mol^{-1} @ 298.15 K) as well as subtracting thereof $T \bullet S°$ (equation 4), and in turn generate $H°$ and corrected $G°$ values (Table S8).

$$H° = U° + RT \quad (3)$$

$$G° = H° - T \bullet S° \ (T = 298.15 \text{ K}) \quad (4)$$

Table S8-1. *Detailed data on the quantum chemical calculations for the gas phase basicities.*

	BP86-D3(BJ)/def-TZVP [H]	TPSS-D3(BJ)/def2-TZVPP [H]	DLPNO-CCSD(T) [H]	MP2DZ [H]	MP2QZ [H]
H^+	0	0	0	0	0
[**1**$(THF)_3$]	−1651.374763	−1651.645465	−1646.296526	−1645.778909	−1647.727122
[**1**$(THF)_3$]H^+	−1651.809867	−1652.086070	−1646.724498	−1646.198743	−1648.151207

Table S8-2*. Detailed data on the quantum chemical calculations for the gas phase basicities.*

	Ecomp [H]	Evrt [kJ mol^{-1}]	S0 [kJ mol^{-1} K^{-1}]	H° [kJ mol^{-1}]	G° [kJ mol^{-1}]	T1 diag
H^+	0	3.72	0.108854	6.20	-26.25	
[**1**$(THF)_3$]	−1648.244740	2057.04	*1.179943*	-4325406.22	−4325758.02	0.01
[**1**$(THF)_3$]H^+	−1648.676961	2095.11	*1.236413*	-4326502.95	−4326871.58	0.01

Optimized atomic coordinates (Å) for calculated molecules

TPSS-D3(BJ)/def2-TZVPP level of theory.

1$(THF)_3$, C_1

C	-1.96052	-0.11639	0.26400
N	-1.45079	-0.07909	1.51335
C	-1.15161	-0.14292	-0.88003
H	-1.67834	-0.19613	-1.83706
C	0.73218	-0.06521	0.49841
H	1.80552	-0.02690	0.70709
C	0.25938	-0.10817	-0.83265
C	-3.44935	-0.15789	0.15849
C	-0.10905	-0.06211	1.61779
C	-4.14918	-1.29039	0.62163
C	-5.53884	-1.33484	0.49146
H	-6.07032	-2.21906	0.83976
C	-6.26121	-0.27873	-0.07199
C	-5.55121	0.83834	-0.51419
H	-6.09390	1.67778	-0.94599
C	-4.15792	0.91498	-0.41197
C	-3.41213	-2.45151	1.24418
H	-4.08694	-3.29816	1.39970
H	-2.97790	-2.16085	2.20567
H	-2.58051	-2.77695	0.60916
C	-7.76684	-0.33349	-0.16970
H	-8.14002	0.36399	-0.92551
H	-8.23338	-0.06629	0.78686
H	-8.11191	-1.33938	-0.42993
C	-3.44558	2.15969	-0.88971
H	-2.92605	1.98879	-1.83914
H	-2.69035	2.48367	-0.16736

H	-4.15890	2.97540	-1.03950
C	0.46757	-0.02959	2.99568
C	1.01288	-1.19721	3.55893
C	1.58230	-1.13835	4.83495
H	1.99279	-2.04762	5.27121
C	1.62306	0.05065	5.56715
C	1.06183	1.19584	4.99512
H	1.06933	2.13002	5.55443
C	0.48343	1.17420	3.72319
C	0.94092	-2.51393	2.82121
H	-0.10144	-2.80913	2.65654
H	1.43908	-3.30479	3.38897
H	1.40342	-2.44887	1.83115
C	2.26934	0.10136	6.93074
H	1.77526	0.83375	7.57661
H	3.32565	0.38989	6.85662
H	2.22948	-0.87443	7.42422
C	-0.12610	2.42504	3.13789
H	0.33612	2.67491	2.17571
H	0.00057	3.27445	3.81482
H	-1.19407	2.28018	2.94613
H	0.41702	4.35417	-0.85209
H	2.66222	3.66603	-1.02789
H	1.93093	3.79443	-3.61454
C	0.49479	3.30982	-1.16494
C	1.95755	2.82860	-1.11193
H	-0.43854	3.98494	-3.05847
H	-0.13310	2.70007	-0.51474
C	0.08660	3.11903	-2.64768
H	2.14254	2.10635	-0.31638
C	1.41767	2.85800	-3.35333
O	2.20837	2.14754	-2.37132
H	4.57135	1.04699	-1.79750
H	1.35438	2.21863	-4.23494
H	-0.56047	2.24355	-2.73873
C	4.68978	0.04152	-1.39140
H	5.77987	0.13712	0.50902
H	4.10393	0.71056	0.57322
H	5.55139	-0.44905	-1.86701
C	4.76961	-0.03484	0.12964
Li	1.77616	0.17706	-2.26078
O	3.48531	-0.68746	-1.71476
O	1.41135	-0.45548	-4.13050
H	3.12337	-1.58053	-4.20260
C	4.25761	-1.46261	0.42669
C	2.10988	-1.63182	-4.60114
H	2.14274	-1.60276	-5.69845
C	3.41781	-1.83113	-0.81698
H	-0.28142	-0.66504	-5.32149
H	5.09265	-2.15816	0.54458
C	0.00425	-0.77721	-4.26621
H	3.66101	-1.49361	1.34011
H	2.35885	-1.98720	-0.60389
H	-0.54589	-0.06479	-3.65166
H	3.82600	-2.70596	-1.33730
C	1.28621	-2.83035	-4.09377
C	-0.11225	-2.22610	-3.78632
H	1.72854	-3.25122	-3.18842
H	-0.92043	-2.75902	-4.29279
H	1.24051	-3.62194	-4.84587
H	-0.30386	-2.23269	-2.71153

$[\mathbf{1}(\mathrm{THF})_3\mathrm{H}]^+$, C_1

C	-1.90917	-0.12501	-0.48754
N	-1.81029	-0.10862	0.87226
C	-0.72284	-0.11208	-1.20965
H	-0.84026	-0.13615	-2.29153
C	0.53411	-0.07491	0.79567
H	1.46020	-0.04353	1.36750
C	0.56583	-0.08013	-0.62236
C	-3.27446	-0.17034	-1.05803
C	-0.62945	-0.08682	1.55079
C	-4.05549	-1.33403	-0.90092
C	-5.33284	-1.36268	-1.46413
H	-5.92965	-2.26605	-1.36307
C	-5.85683	-0.27126	-2.16204
C	-5.05952	0.86951	-2.30200
H	-5.45083	1.72852	-2.84198
C	-3.77224	0.94169	-1.76860
C	-3.52880	-2.54836	-0.16920
H	-4.08015	-3.44212	-0.46900
H	-3.64187	-2.45097	0.91800
H	-2.46669	-2.71446	-0.37503
C	-7.25214	-0.31344	-2.73032
H	-7.33234	0.29911	-3.63223
H	-7.97461	0.07550	-2.00275
H	-7.54981	-1.33623	-2.97528
C	-2.95255	2.19861	-1.94531
H	-2.14653	2.05326	-2.67301
H	-2.48512	2.51203	-1.00609
H	-3.58127	3.01658	-2.30361
C	-0.69875	-0.04728	3.03056
C	-0.43200	-1.21555	3.77253
C	-0.48763	-1.14659	5.16493
H	-0.29514	-2.04800	5.74205
C	-0.78873	0.04448	5.83506
C	-1.04697	1.18675	5.07270
H	-1.28053	2.12168	5.57660
C	-1.01020	1.16489	3.67648
C	-0.11314	-2.52186	3.08445
H	-0.90141	-2.80828	2.37929
H	-0.00448	-3.32517	3.81598
H	0.81741	-2.45683	2.51030
C	-0.80794	0.09768	7.34144
H	-1.42345	0.92573	7.70170
H	0.20575	0.24204	7.73397
H	-1.19311	-0.83362	7.76577
C	-1.28946	2.42369	2.88762
H	-0.57796	2.54634	2.06428
H	-1.22565	3.30307	3.53188
H	-2.29458	2.41311	2.44822
H	0.87953	4.52114	-0.82750
H	3.00350	3.71666	-0.17289
H	3.38768	3.70529	-2.76769
C	1.02549	3.47276	-1.09659
C	2.31441	2.91440	-0.46422
H	1.04967	4.20116	-3.18969
H	0.15322	2.90884	-0.76141
C	1.24354	3.28799	-2.62306
H	2.14047	2.25700	0.38869
C	2.70598	2.84607	-2.72724
O	2.94758	2.11800	-1.49673
H	4.96952	1.04861	-0.08739
H	2.92472	2.16552	-3.55009
H	0.58686	2.50310	-3.00730
C	4.96605	0.02752	0.29427
H	5.55612	0.00472	2.40462

H	3.94056	0.65327	2.08514
H	5.90600	-0.47117	0.02201
C	4.66522	-0.10855	1.78342
Li	2.50176	0.17427	-1.49815
O	3.86119	-0.65872	-0.34343
O	2.80094	-0.47942	-3.34279
H	4.46923	-1.53654	-2.77813
C	4.04629	-1.52446	1.88554
C	3.71994	-1.58038	-3.56800
H	4.20206	-1.43388	-4.54197
C	3.61020	-1.85474	0.43958
H	1.81916	-0.63560	-5.16869
H	4.78096	-2.25140	2.23836
C	1.62160	-0.82945	-4.10632
H	3.20327	-1.54292	2.57943
H	2.54736	-2.07936	0.33143
H	0.81220	-0.18349	-3.76458
H	4.19829	-2.67928	0.01992
C	2.84587	-2.84769	-3.55241
C	1.40917	-2.32047	-3.82871
H	2.89388	-3.34360	-2.58069
H	0.93136	-2.82729	-4.66966
H	3.17547	-3.56198	-4.30958
H	0.77833	-2.44902	-2.94605
H	-2.67106	-0.11080	1.41217

2,6-Dimesitylpyridine, C_2

C	1.19682	0.07597	2.52887
C	1.15856	0.06740	1.12863
N	0.00000	0.00000	0.44637
C	-1.15856	-0.06740	1.12863
C	-1.19682	-0.07597	2.52887
C	0.00000	0.00000	3.23504
C	-2.40729	-0.14888	0.31894
C	2.40729	0.14888	0.31894
C	2.60745	1.24747	-0.54193
C	3.78258	1.31267	-1.29299
C	4.75760	0.31337	-1.22921
C	4.52954	-0.77338	-0.38359
C	3.37444	-0.87111	0.39853
C	-3.37444	0.87111	0.39853
C	-4.52954	0.77338	-0.38359
C	-4.75760	-0.31337	-1.22921
C	-3.78258	-1.31267	-1.29299
C	-2.60745	-1.24747	-0.54193
C	3.17959	-2.08639	1.27712
C	1.58315	2.35057	-0.65841
C	6.02730	0.41568	-2.03831
C	-1.58315	-2.35057	-0.65841
C	-3.17959	2.08639	1.27712
C	-6.02730	-0.41568	-2.03831
H	-1.27887	-2.71699	0.32819
H	-1.98950	-3.19015	-1.22877
H	-3.82524	2.90289	0.94238
H	-3.43102	1.87527	2.32316
H	-6.79698	-0.97271	-1.48952
H	-6.43504	0.57442	-2.26237
H	1.98950	3.19015	-1.22877
H	0.67750	1.99046	-1.15543
H	3.82524	-2.90289	0.94238
H	3.43102	-1.87527	2.32316
H	5.85450	0.94013	-2.98282

H	6.79698	0.97271	-1.48952
H	2.14896	0.14752	3.04415
H	-2.14896	-0.14752	3.04415
H	0.00000	-0.00000	4.32129
H	3.93639	2.16640	-1.95019
H	5.26338	-1.57586	-0.33698
H	-5.26338	1.57586	-0.33698
H	-3.93639	-2.16640	-1.95019
H	2.14269	-2.43401	1.25922
H	1.27887	2.71699	0.32819
H	6.43504	-0.57442	-2.26237
H	-0.67750	-1.99046	-1.15543
H	-2.14269	2.43401	1.25922
H	-5.85450	-0.94013	-2.98282

Natural Population Analysis

TPSS-D3(BJ)/def2-TZVPP level of theory.

Table S9. *Distribution of Natural Charges of* ***1****$(THF)_3$ and 2,6-Dimesitylpyridin.*

1$(THF)_3$				**2,6-Dimesitylpyridine**		
No.	**Atom**	**Natural Charge**		**No.**	**Atom**	**Natural Charge**
{Mes_2py}-moiety				{Mes_2py}-moiety		
1	C	0.15333		1	C	-0.23348
2	N	-0.44185		2	C	0.19114
3	C	-0.29669		3	N	-0.413
4	H	0.17035		4	C	0.19114
5	C	-0.31577		5	C	-0.23348
6	H	0.16775		6	C	-0.16458
7	C	-0.4658		7	C	-0.07675
8	C	-0.05649		8	C	-0.07675
9	C	0.15358		9	C	0.02726
10	C	0.02128		10	C	-0.20449
11	C	-0.20692		11	C	-0.0069
12	H	0.19004		12	C	-0.20663
13	C	-0.01781		13	C	0.01165
14	C	-0.20929		14	C	0.01165
15	H	0.18866		15	C	-0.20663
16	C	0.00472		16	C	-0.0069
17	C	-0.60012		17	C	-0.20449
18	H	0.19417		18	C	0.02726
19	H	0.22686		19	C	-0.59717
20	H	0.20707		20	C	-0.60039
21	C	-0.58849		21	C	-0.59029
22	H	0.19989		22	C	-0.60039
23	H	0.20567		23	C	-0.59717
24	H	0.20221		24	C	-0.59029
25	C	-0.59398		25	H	0.20591
26	H	0.20266		26	H	0.19921
27	H	0.21127		27	H	0.20507
28	H	0.19861		28	H	0.20519
29	C	-0.0529		29	H	0.20825
30	C	0.00523		30	H	0.20375
31	C	-0.21008		31	H	0.19921
32	H	0.18954		32	H	0.22855
33	C	-0.01885		33	H	0.20507
34	C	-0.20725		34	H	0.20519
35	H	0.1904		35	H	0.20476
36	C	0.01469		36	H	0.20825
37	C	-0.59704		37	H	0.21186
38	H	0.21673		38	H	0.21186
39	H	0.197		40	H	0.19386
40	H	0.20514		41	H	0.19305
41	C	-0.58822		42	H	0.19305
42	H	0.20289		43	H	0.19386
43	H	0.20343		44	H	0.21191
44	H	0.20164		45	H	0.20591
45	C	-0.59905		46	H	0.20375
46	H	0.20335		47	H	0.22855
47	H	0.19641		48	H	0.21191

48	H	0.22579		49	H	0.20476
{Li(THF)$_3$}-moiety				4-H		
49	H	0.20034		39	H	0.20695
50	H	0.15742				
51	H	0.15473				
52	C	-0.42191				
53	C	-0.07858				
54	H	0.20704				
55	H	0.23072				
56	C	-0.41115				
57	H	0.19889				
58	C	-0.07665				
59	O	-0.5438				
60	H	0.20068				
61	H	0.1972				
62	H	0.20943				
63	C	-0.0726				
64	H	0.21057				
65	H	0.2028				
66	H	0.15333				
67	C	-0.40765				
68	Li	0.8455				
69	O	-0.55063				
70	O	-0.54141				
71	H	0.19579				
72	C	-0.42184				
73	C	-0.07609				
74	H	0.15681				
75	C	-0.08268				
76	H	0.15576				
77	H	0.19984				
78	C	-0.07725				
79	H	0.22279				
80	H	0.20942				
81	H	0.20112				
82	H	0.15975				
83	C	-0.41436				
84	C	-0.41901				
85	H	0.20336				
86	H	0.20612				
87	H	0.20331				
88	H	0.22908				

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