Supplementary Information

Synthesis and reactivity of Li and $TaMe_3$ complexes supported by *N,N'*-bis(2,6-diisopropylphenyl)-*o*-phenylenediamido ligands

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1. NMR Spectra

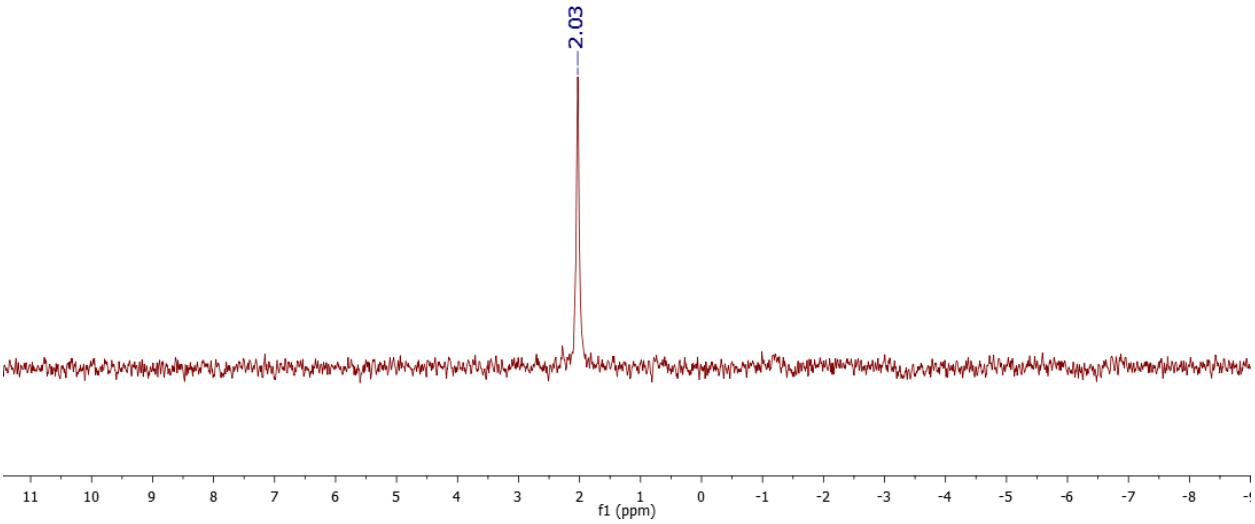

Figure S1. ^{7}Li NMR Spectrum (233 MHz, 25 °C) of **2** in C_6D_6

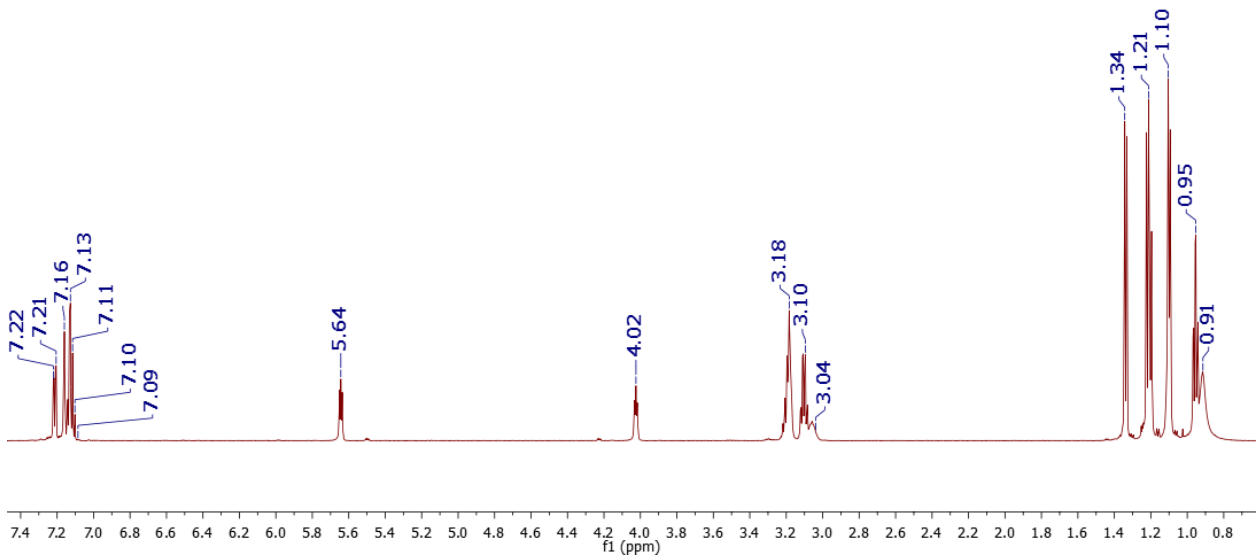

Figure S2. ^{1}H NMR Spectrum (600 MHz, 25 °C) of **2** in C_6D_6

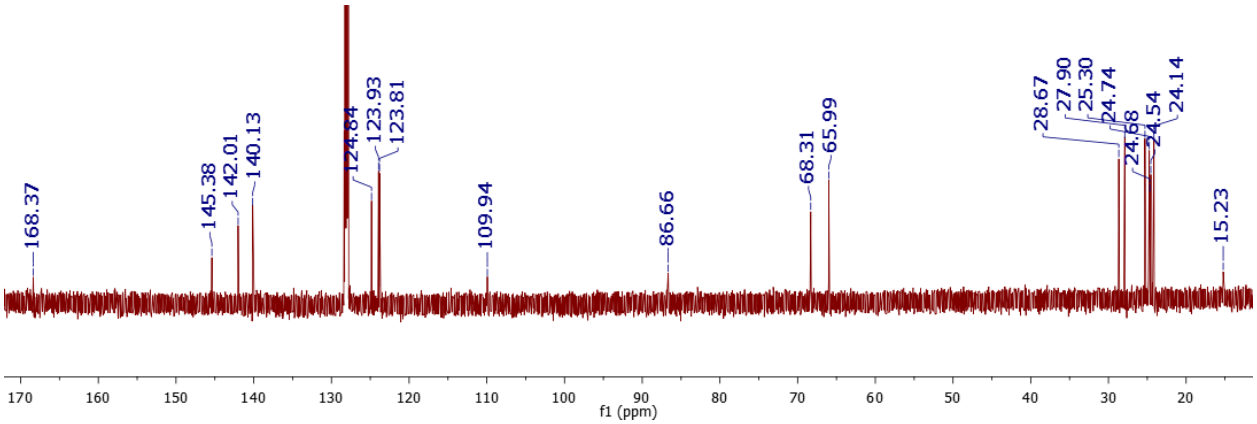

Figure S3. ^{13}C NMR Spectrum (151 MHz, 25 °C) of **2** in C_6D_6

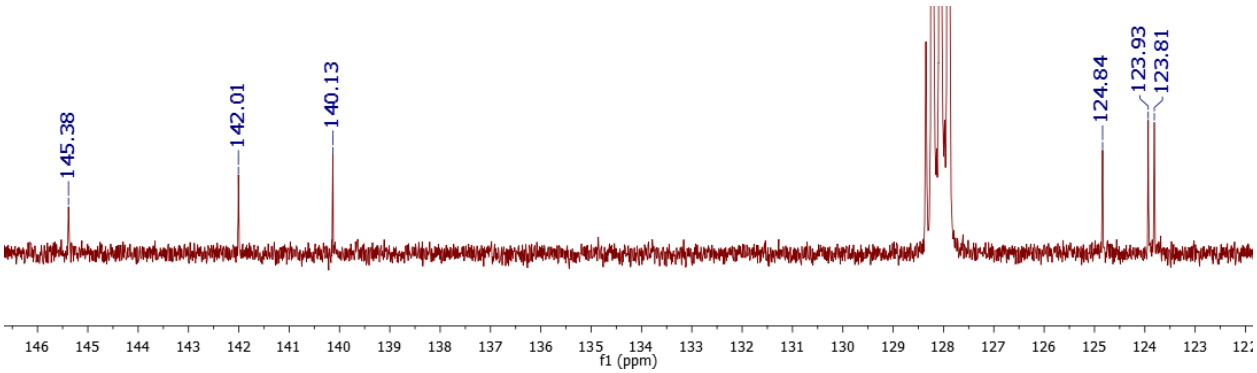

Figure S4. Aryl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **2** in C_6D_6

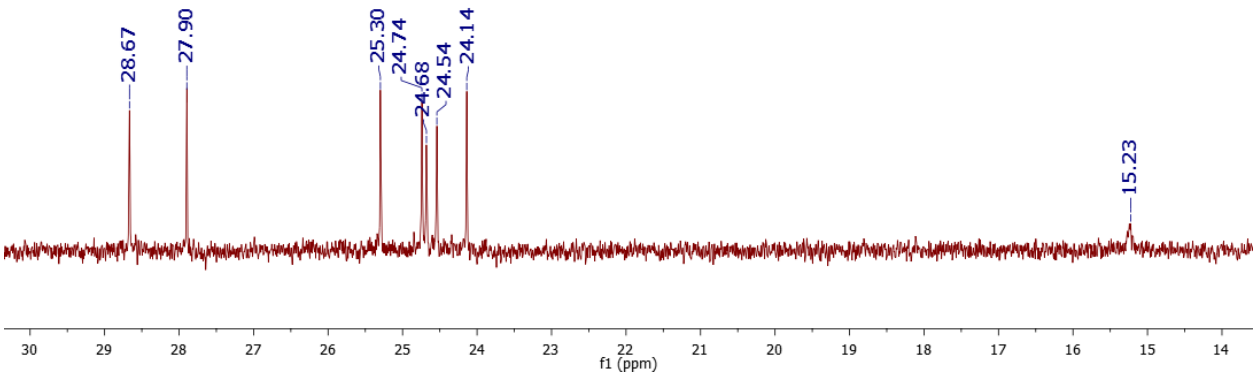

Figure S5. Alkyl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **2** in C_6D_6

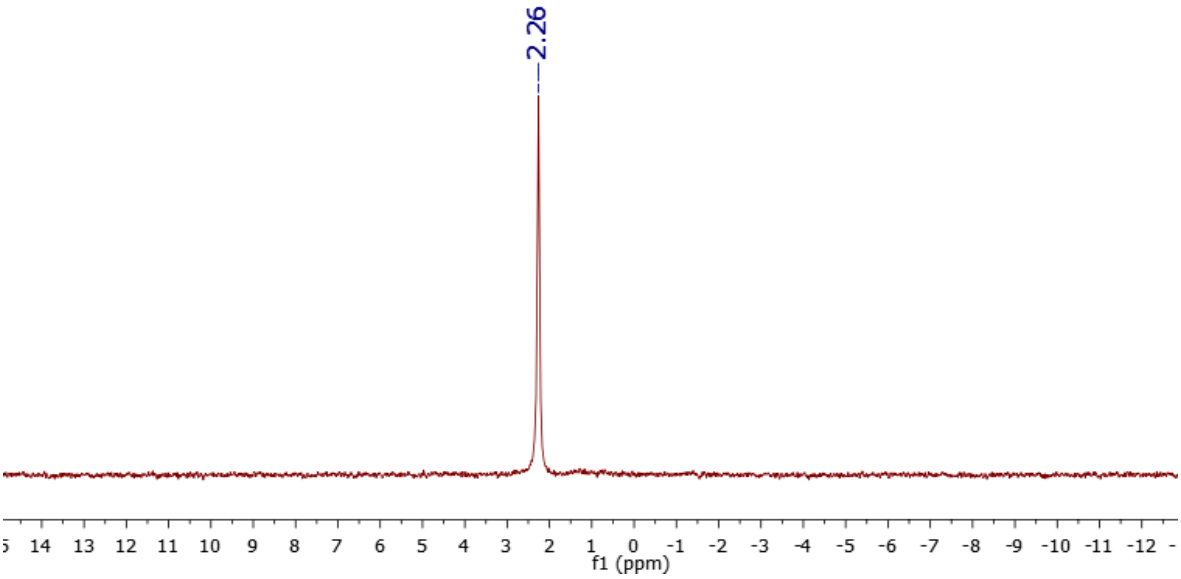

Figure S6. ^{7}Li NMR Spectrum (194 MHz, 25 °C) of **3**(thf) in C_6D_6

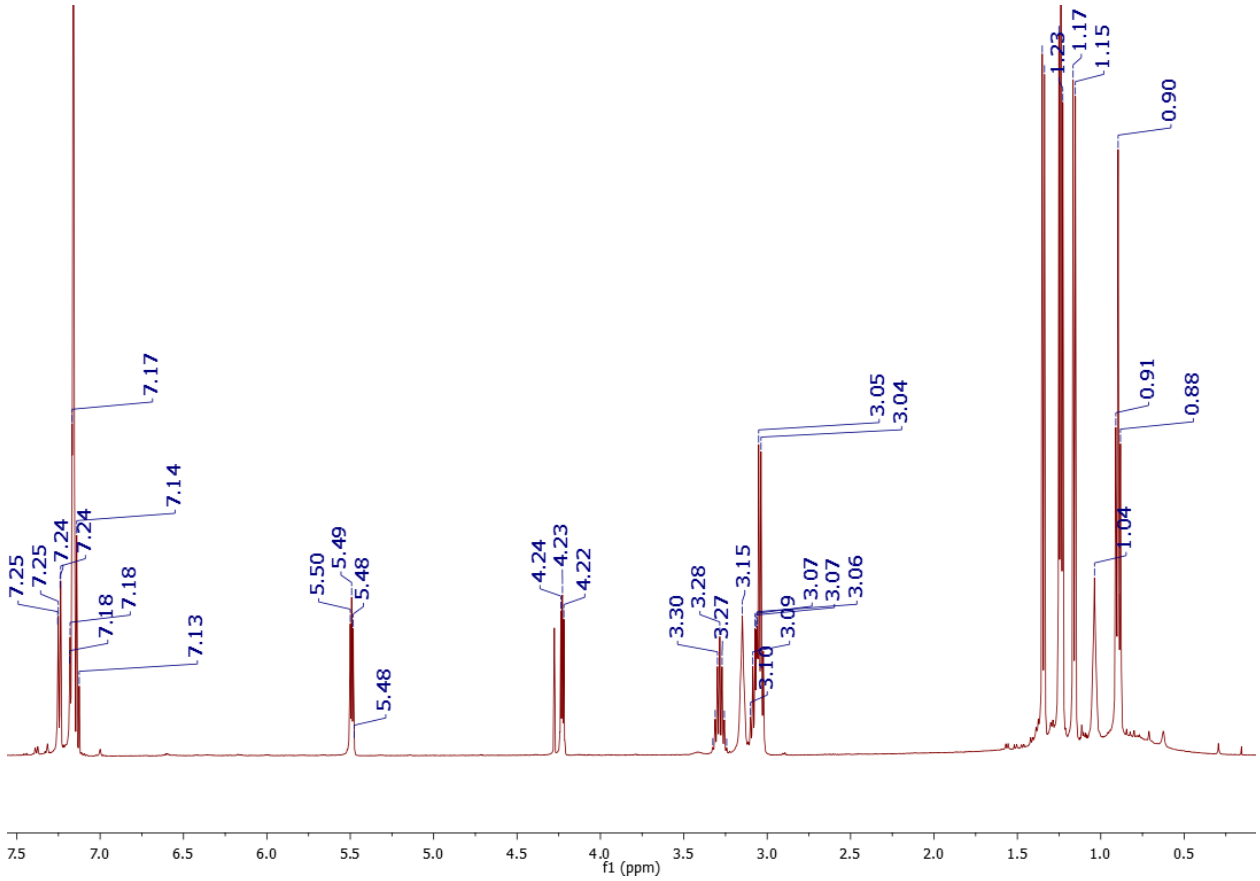

Figure S7. ^{1}H NMR Spectrum (500 MHz, 25 °C) of **3**(thf) in C_6D_6. Note: spectrum contains dichloromethane at 4.28 ppm

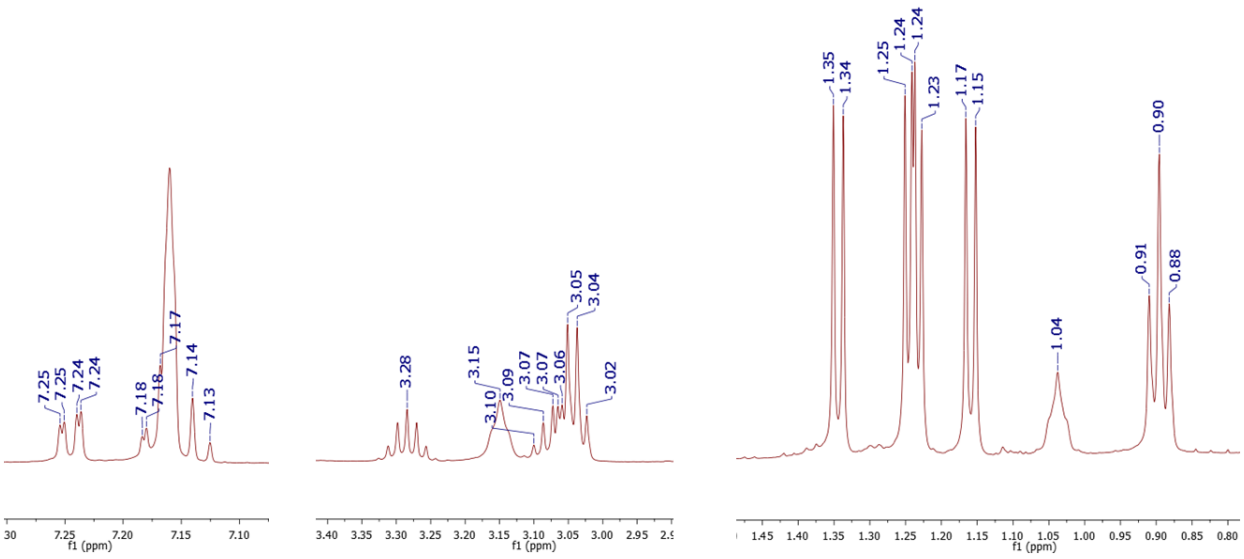

Figure S8. Expansion of selected regions of ^{1}H NMR Spectrum (500 MHz, 25 °C) of **3**(thf) in C_6D_6.

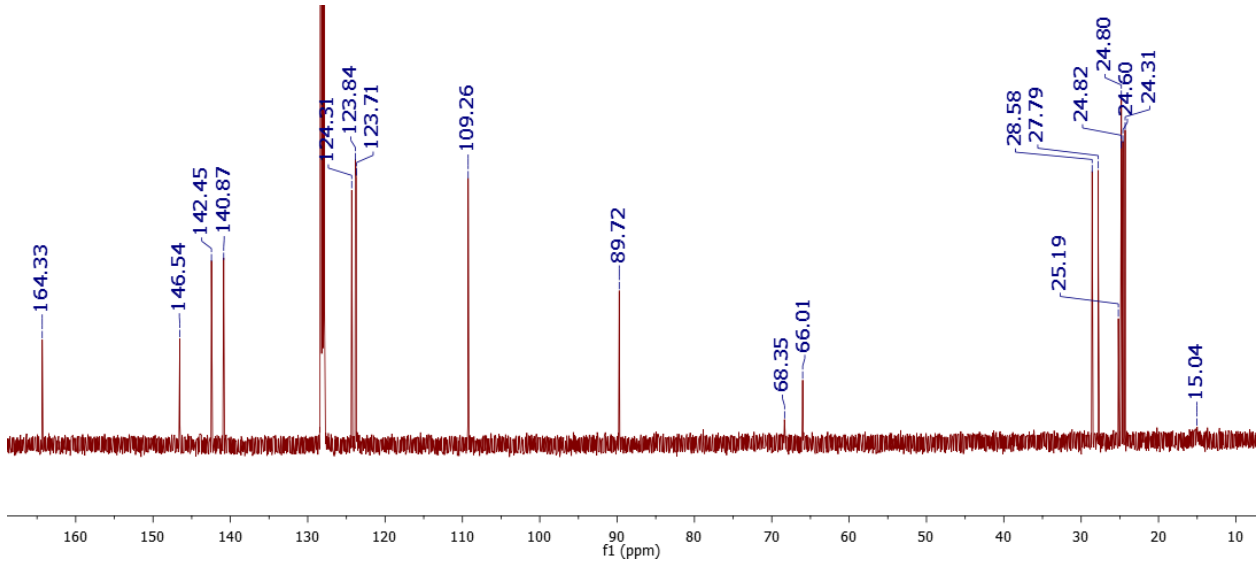

Figure S9. ^{13}C NMR Spectrum (126 MHz, 25 °C) of **3**(thf) in C_6D_6

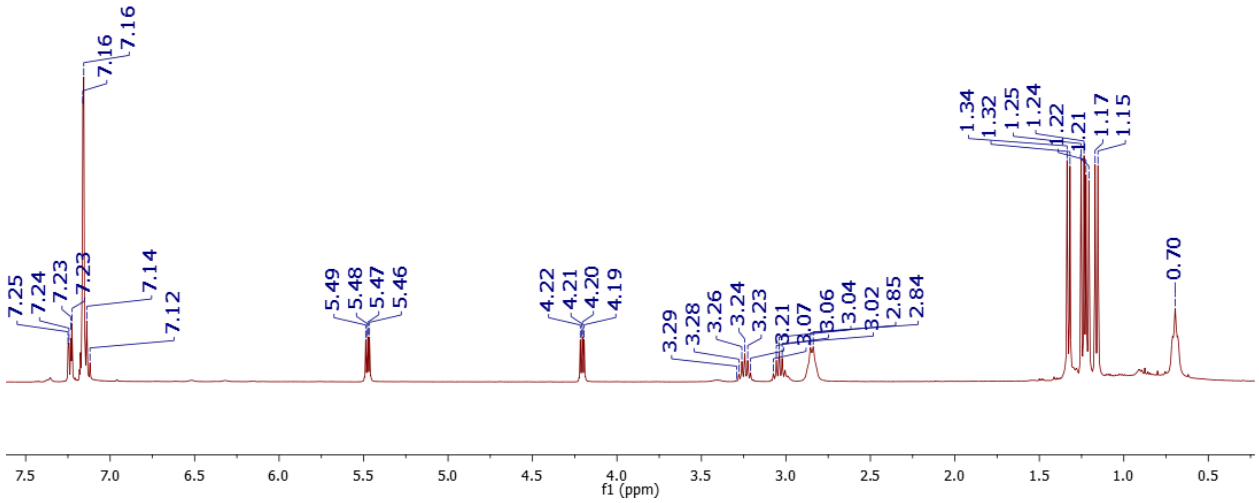

Figure S10. ^{1}H NMR Spectrum (400 MHz, 25 °C) of **3** in C_6D_6

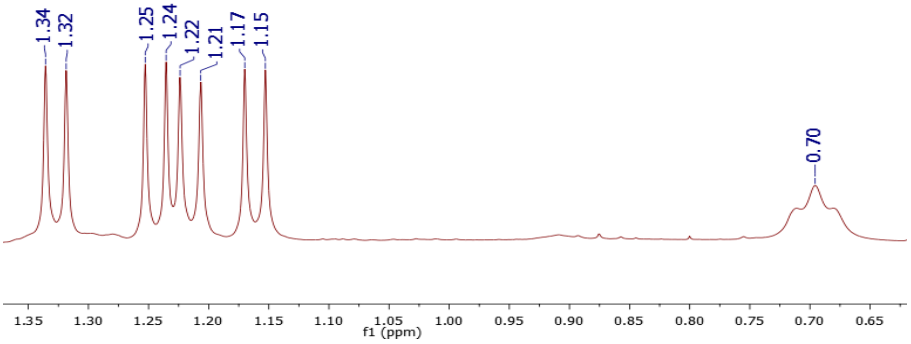

Figure S11. Expansion of the alkyl region of ^{1}H NMR Spectrum (400 MHz, 25 °C) of **3** in C_6D_6

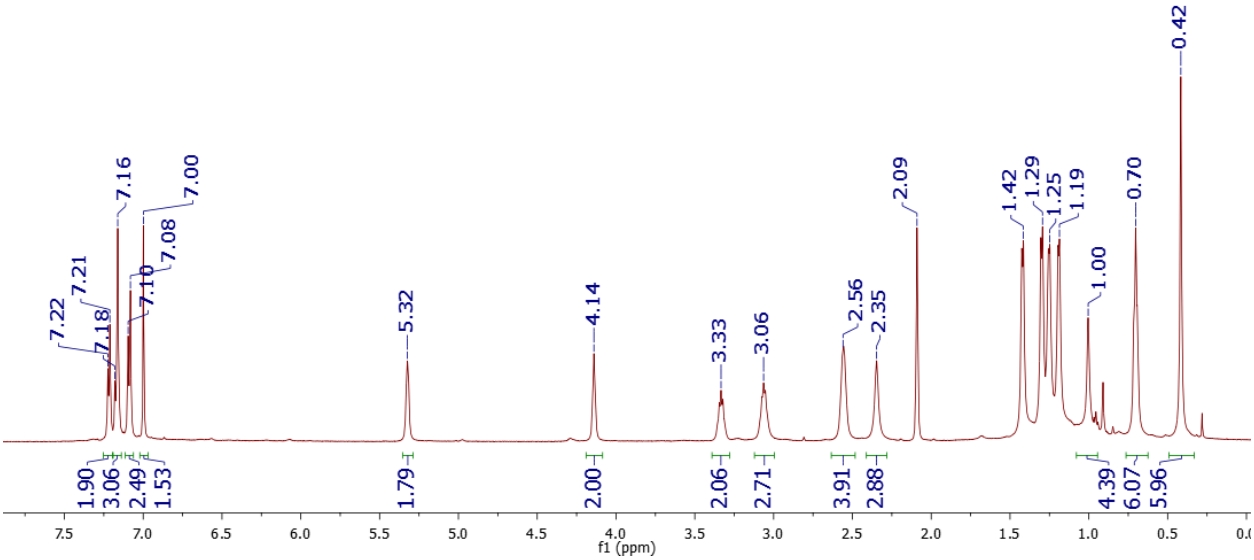

Figure S12. ^{1}H NMR Spectrum (600 MHz, -80 °C) of **3** in $C_6D_5CD_3$

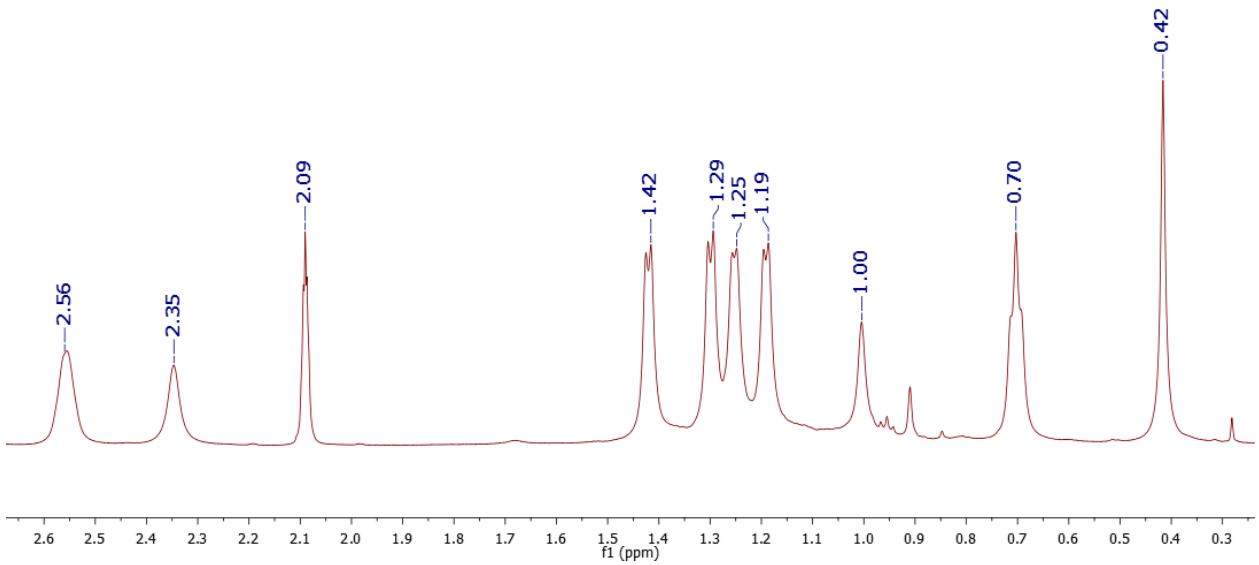

Figure S13. Expansion of the alkyl region of ^{1}H NMR Spectrum (600 MHz, 25 °C) of **3** in $C_6D_5CD_3$

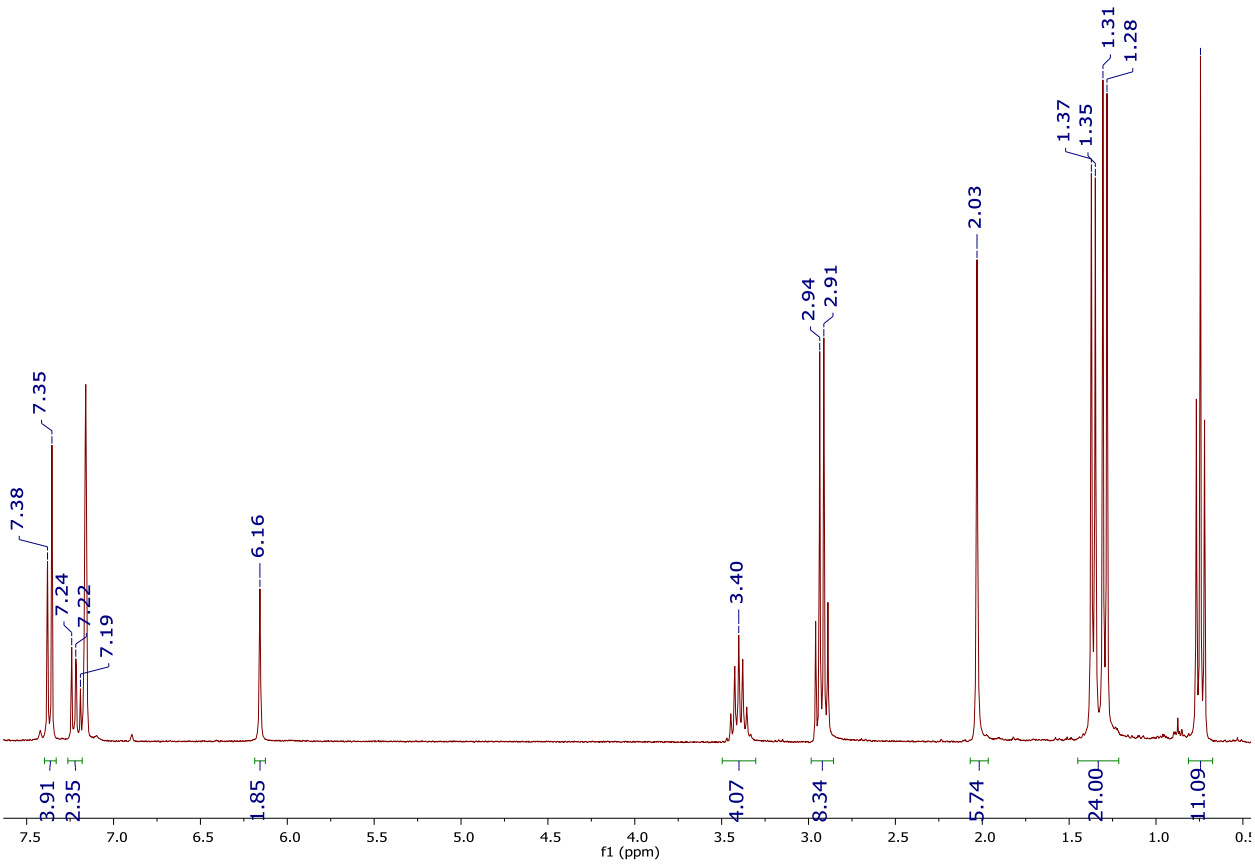

Figure S14. ^{1}H NMR Spectrum (300 MHz, 25 °C) of **5** in C_6D_6

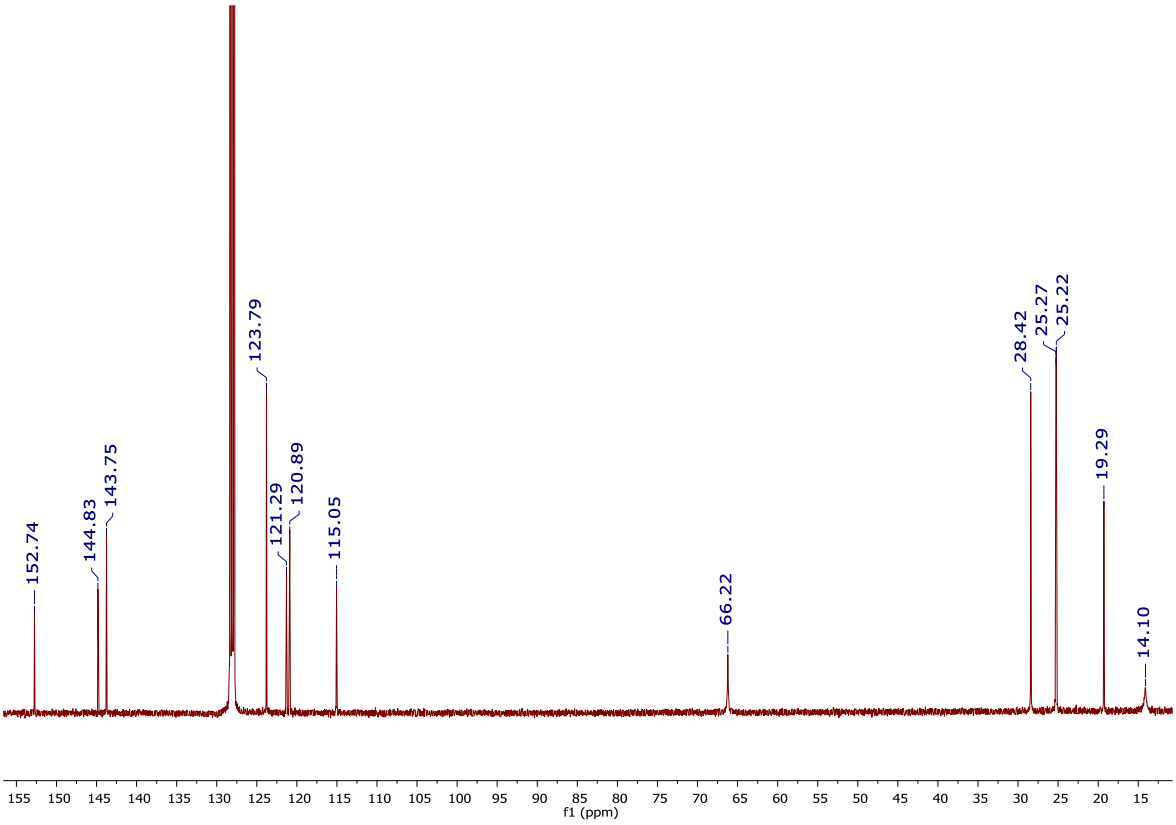

Figure S15. ^{13}C NMR Spectrum (101 MHz, 25 °C) of **5** in C_6D_6

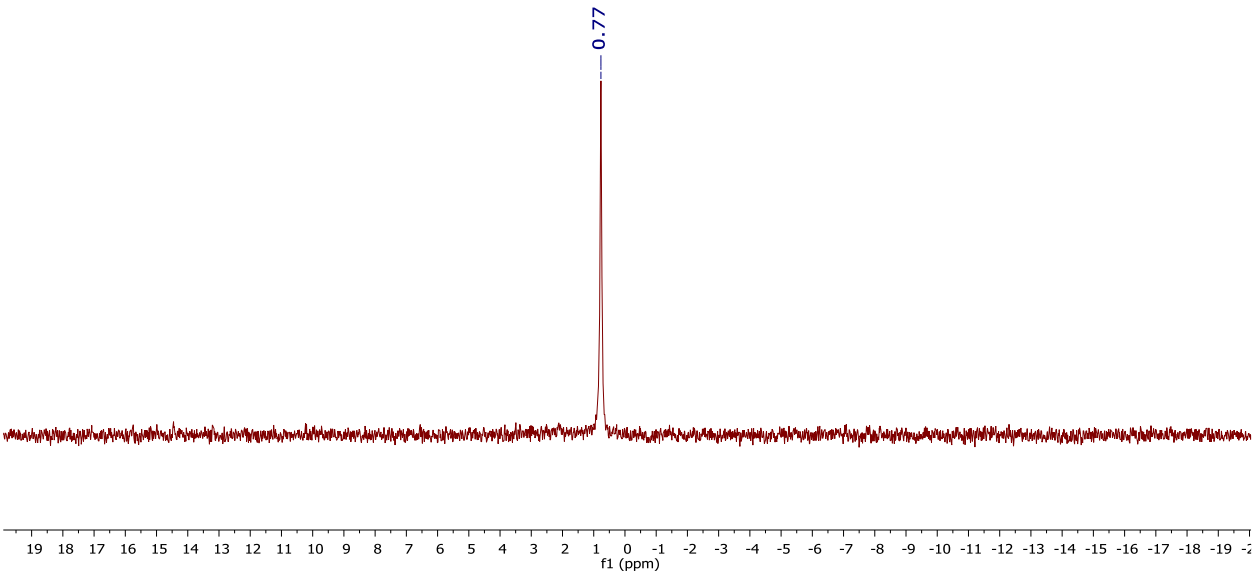

Figure S16. ^{7}Li NMR Spectrum (194 MHz, 25 °C) of **5** in C_6D_6

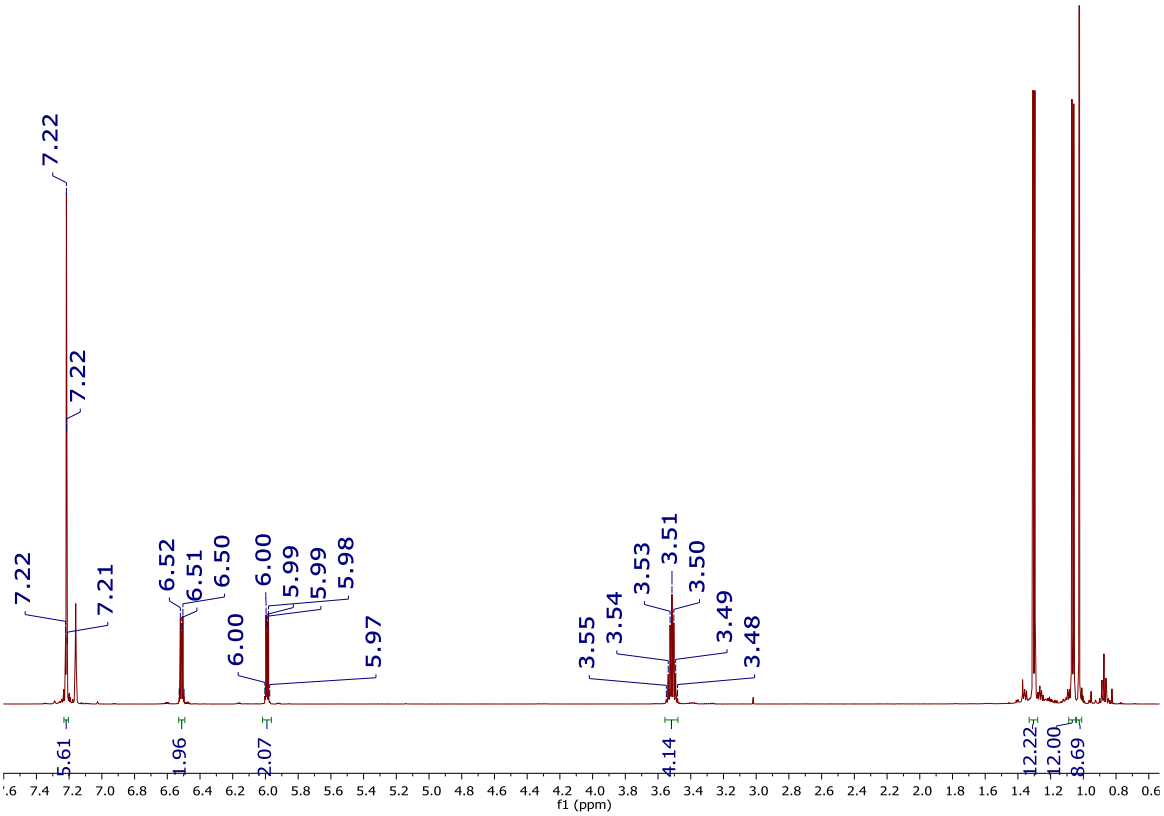

Figure S17. ^{1}H NMR Spectrum (600 MHz, 25 °C) of **8** in C_6D_6 spectrum contains pentane at 1.26 and 0.87

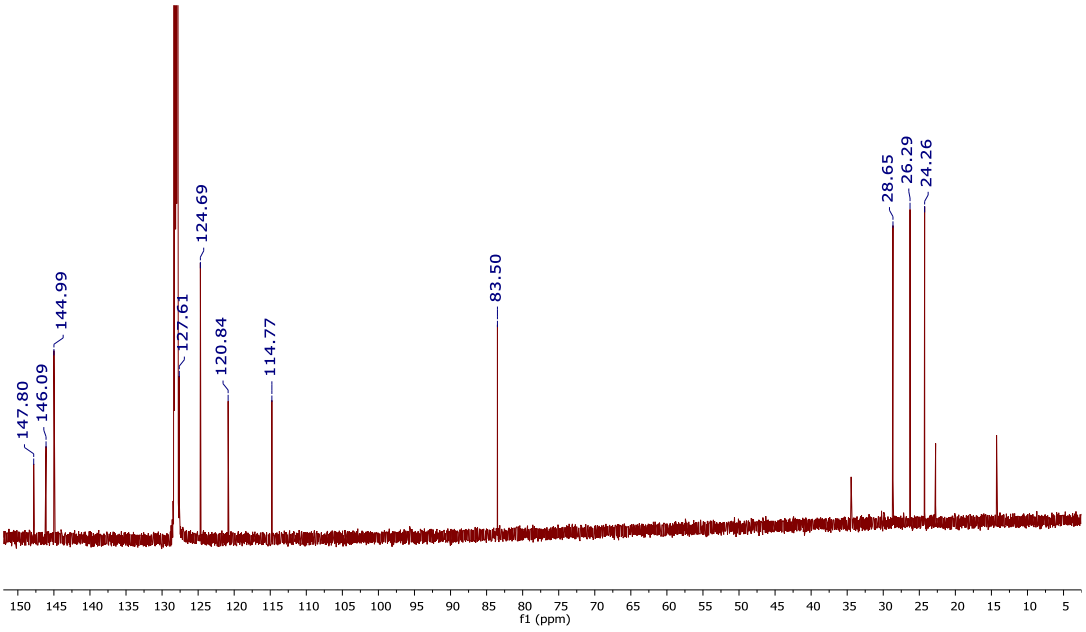

Figure S18. ^{13}C NMR Spectrum (151 MHz, 25 °C) of **8** in C_6D_6 Note: spectrum contains pentane at 34.45, 22.73, and 14.30.

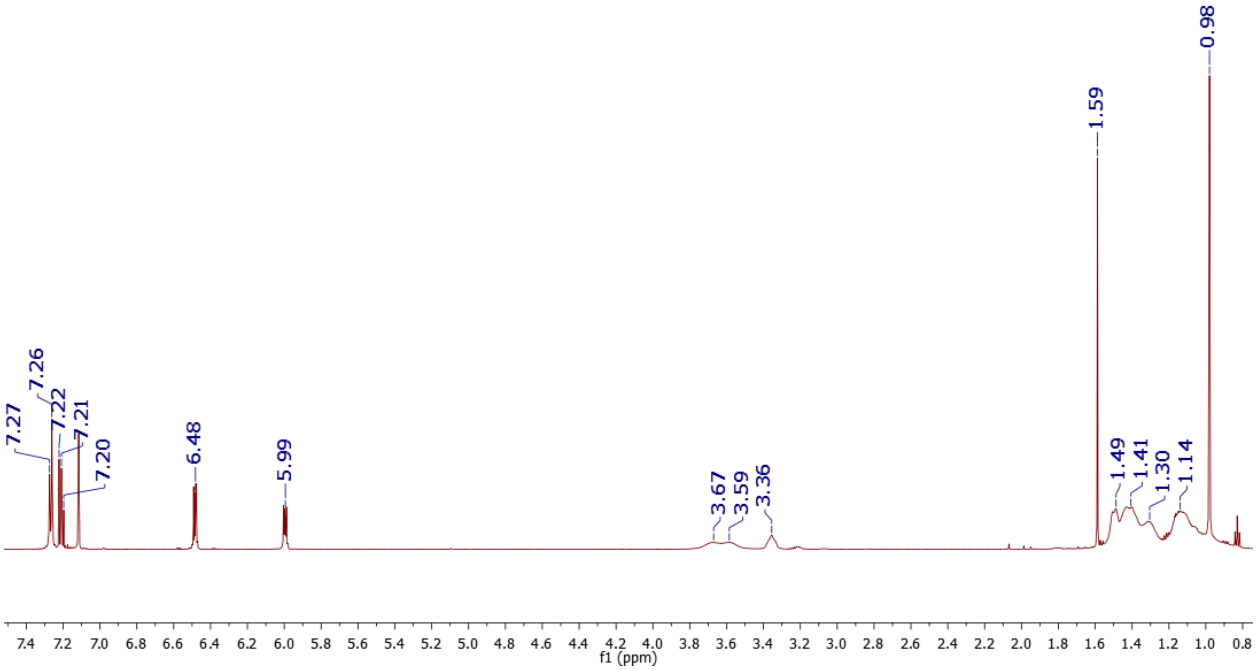

Figure S19. ^{1}H NMR Spectrum (600 MHz, 25 °C) of **9** in C_6D_6

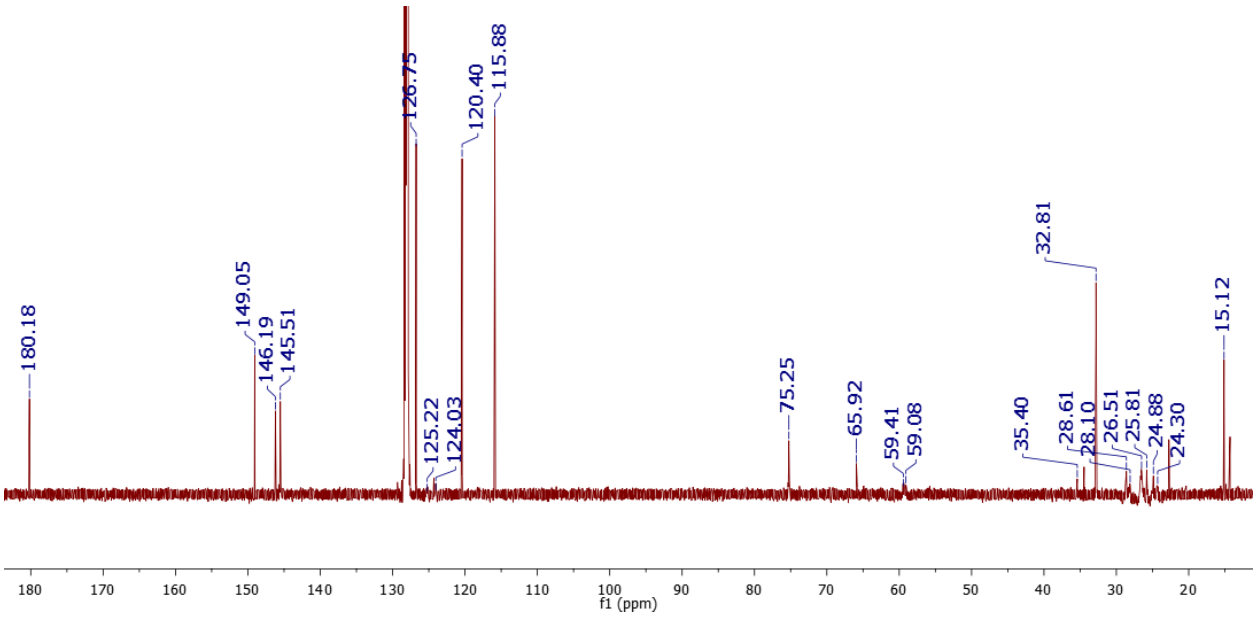

Figure S20. ^{13}C NMR Spectrum (151 MHz, 2 °C) of **9** in C_6D_6.

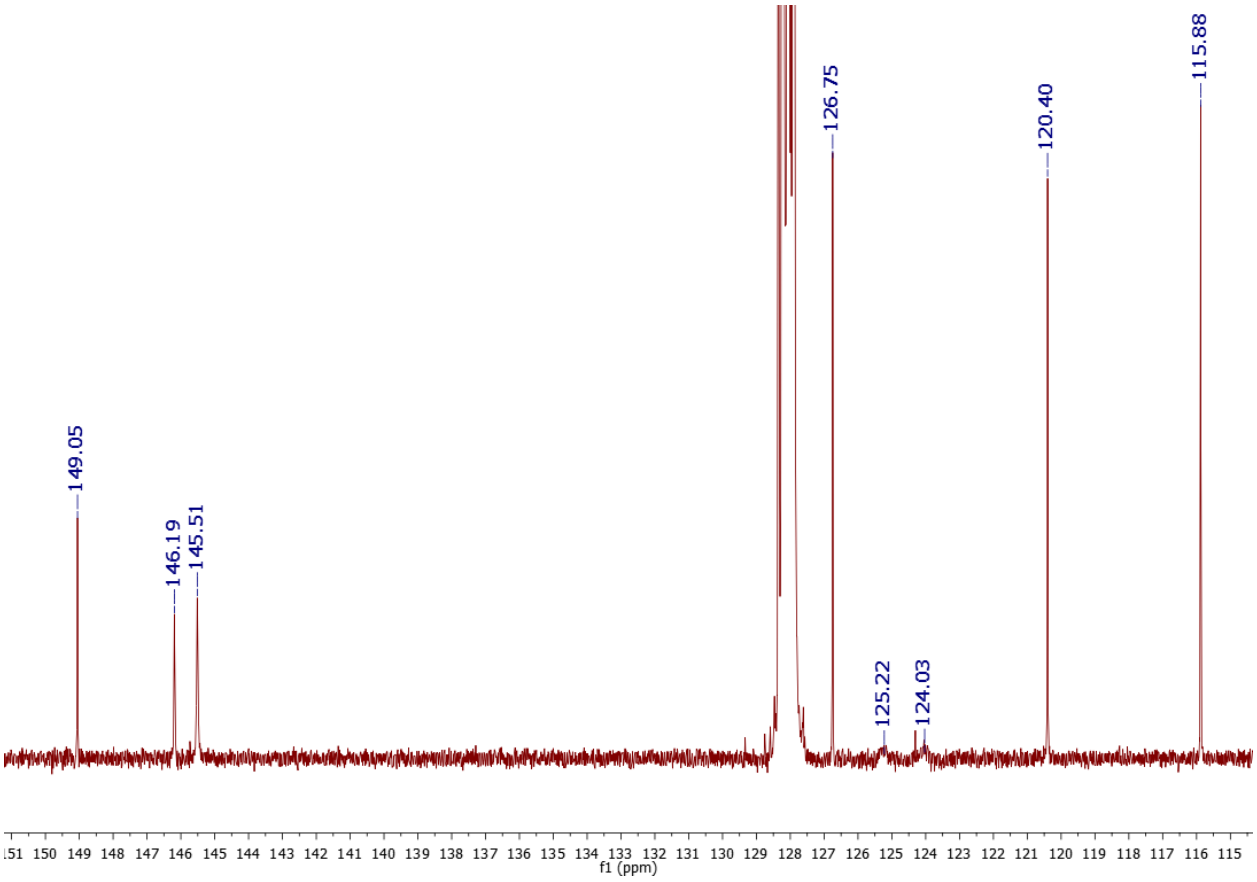

Figure S21. Aryl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **9** in C_6D_6.

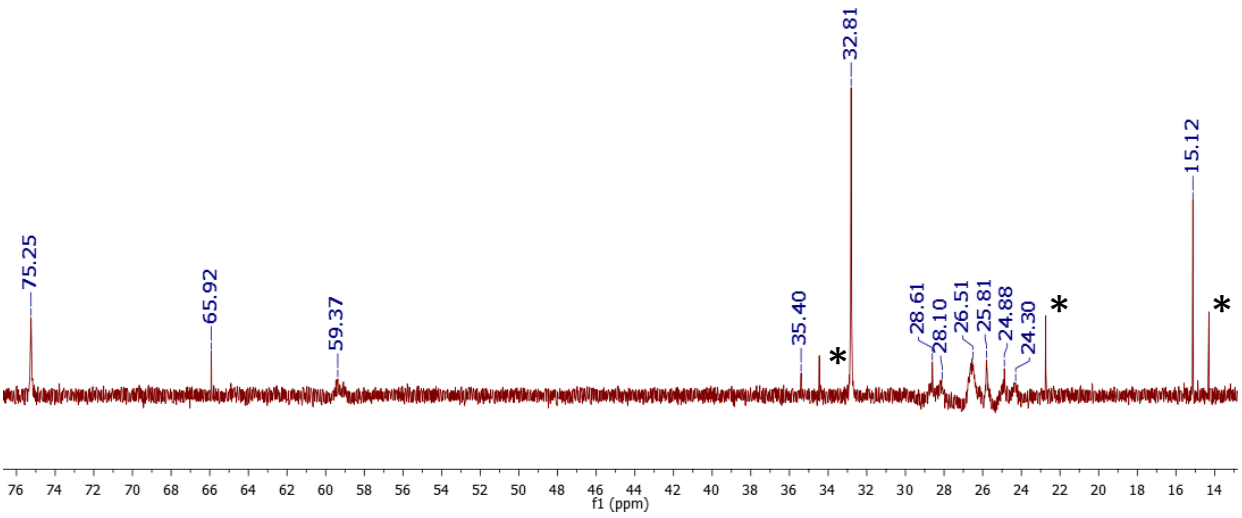

Figure S22. Alkyl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **9** in C_6D_6. Peaks due to residual pentane are marked with an asterisk.

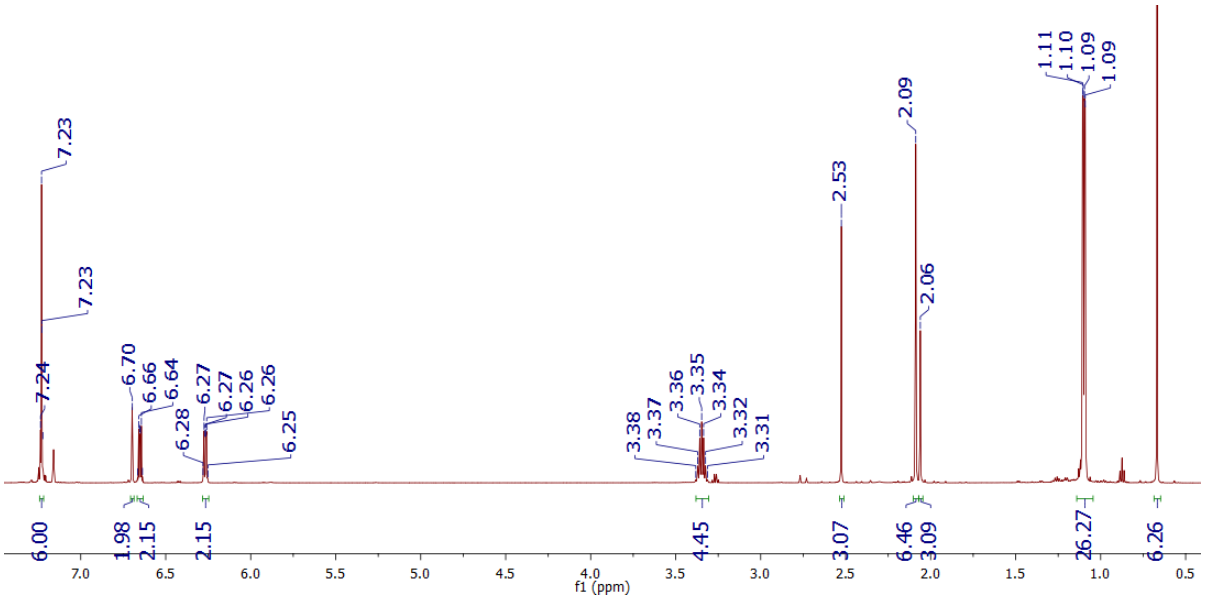

Figure S23. ^{1}H NMR Spectrum (600 MHz, 25 °C) of **10** in C_6D_6

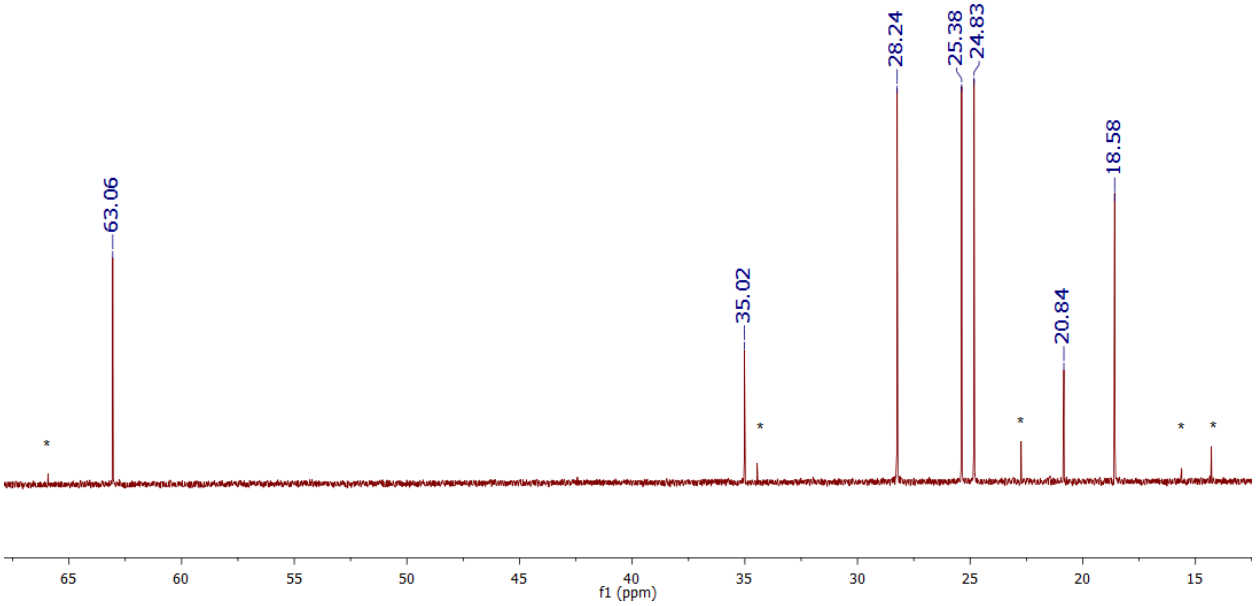

Figure S24. Alkyl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **10** in C_6D_6. Peaks due to residual pentane and Et_2O are marked with an asterisk.

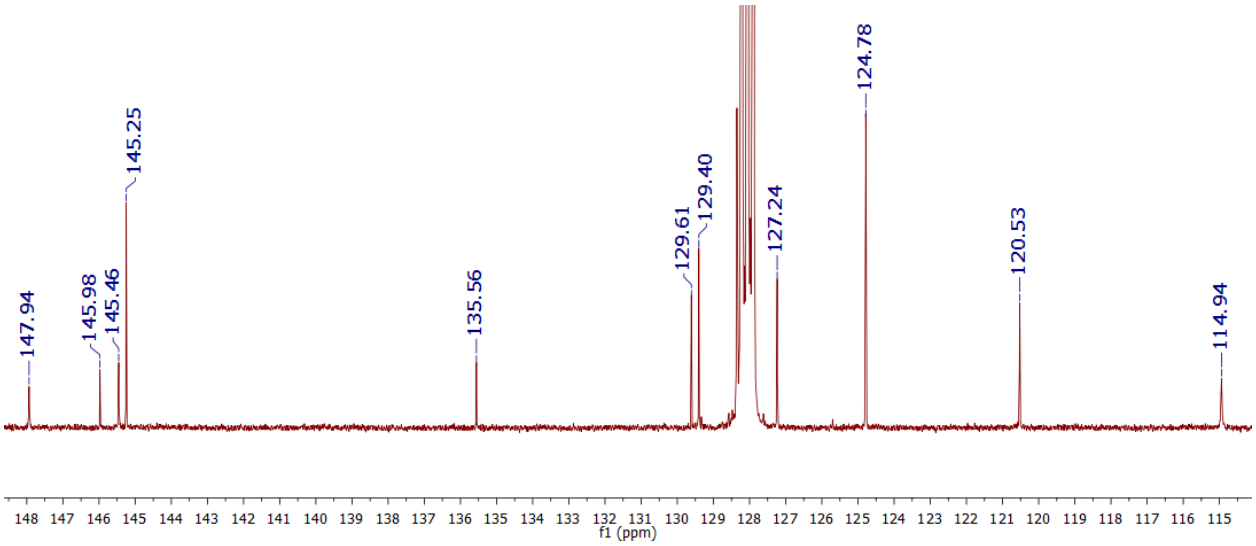

Figure S25. Aryl region of ^{13}C NMR Spectrum (151 MHz, 25 °C) of **10** in C_6D_6.

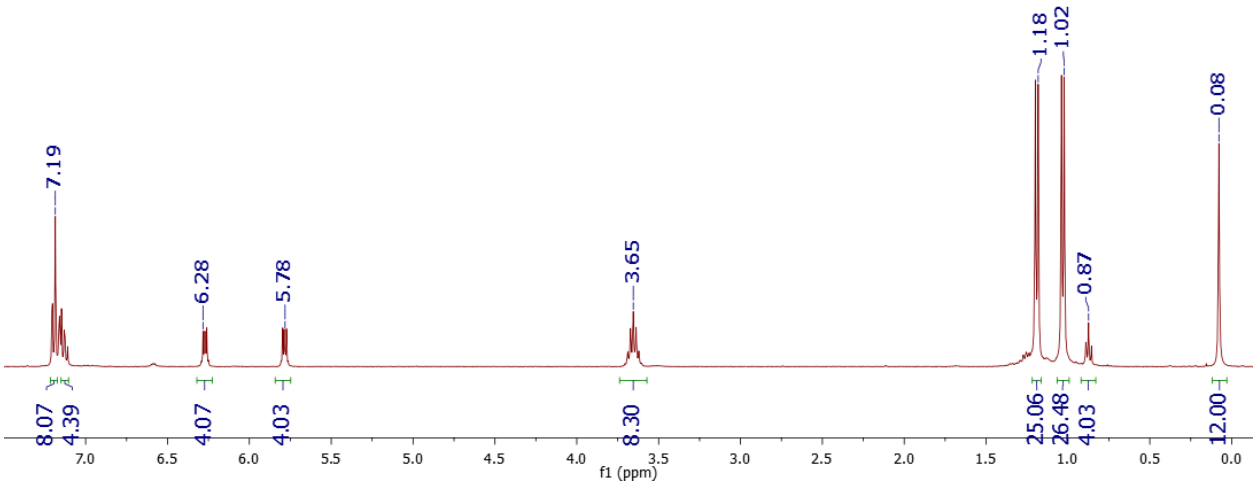

Figure S26. ^{1}H NMR Spectrum (400 MHz, 25 °C) of **11**(pentane)$_{2/3}$ in C_6D_6.

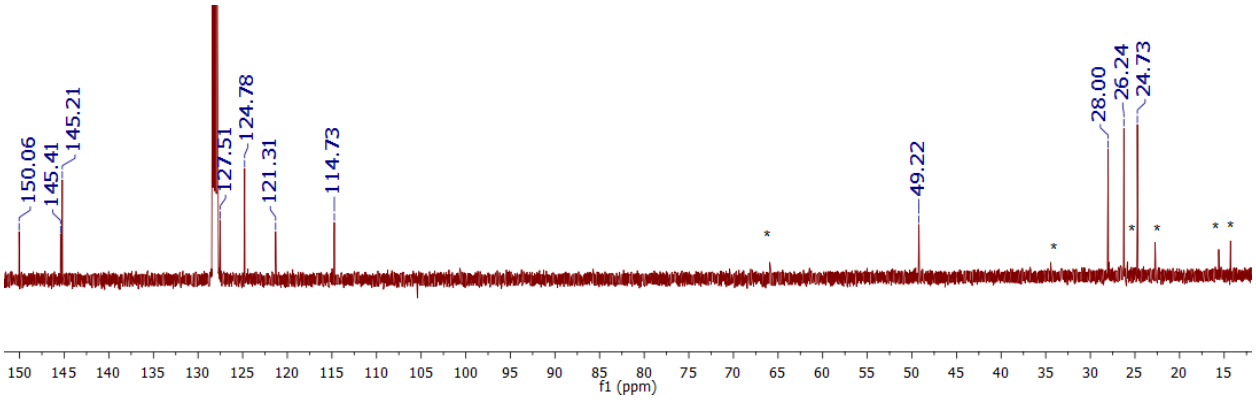

Figure S27. ^{13}C NMR Spectrum (500 MHz, 25 °C) of **11** in C_6D_6 Note: volatile impurities in the NMR solvent (THF, Et_2O, pentane) are marked with an asterisk

2. X-ray Crystallography

The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 2 software package.[1] The structures were solved by direct methods and refined using SHELXL-2013 and SHELXL-2014.[2,3] All non-hydrogen atoms were refined anisotropically, except for a few atoms involved in the disordered portions. All hydrogen atoms were calculated using the riding model. The diffuse residual electron density from a disordered cocrytallized pentane molecule in the lattice of **11** was removed with the SQUEEZE function of PLATON,[4] and was not included in the formula or the refinement. Selected crystallographic data are listed in Table 1S.

Synthesis of $K_2L(dme)_4$:

K_2L (130 mg, 0.258 mmol) was recrystallized from cold 1,2-dimethoxyethane (dme, 5 mL). The supernatant was decanted from the yellow crystals, which were washed with cold dme (2 x 2 mL) and pentane (3 x 2 mL). Drying *in vacuo* yielded yellow $K_2L(dme)_4$ (110 mg, 0.127 mmol, 49%), which is insoluble in C_6D_6.

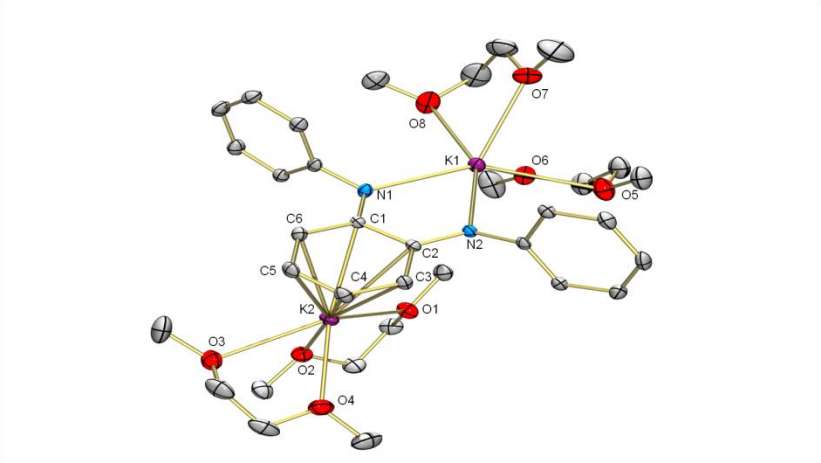

Figure S28 Molecular structure of $K_2L(dme)_4$ with 30% probability ellipsoids. Isopropyl groups and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C2 1.462(3), C2-C3 1.412(3), C3-C4 1.410(3), C4-C5 1.371(4), C5-C6 1.413(3), C1-N1 1.362(3), C2-N2 1.362(3), K1-N1 2.719(2), K1-N2 2.713(2), K1-O5 2.974(2), K1-O6 2.787(2), K1-O7 2.879(3), K1-O8 2.850(2), K2-C1 3.077(2), K2-C2 3.231(2), K2-C3 3.204(2), K2-C4 3.168(2), K2-C5 3.101(2), K2-C6 3.021(2), K2-O1 2.743(2), K2-O2 2.880(2), K2-O3 2.858(2), K2-O4 2.670(2), N1-K1-N2 61.24(6), O5-K1-O6 57.66(6), O7-K1-O8 61.68(7), O1-K2-O2 60.04(6), O3-K2-O4 59.84(6).

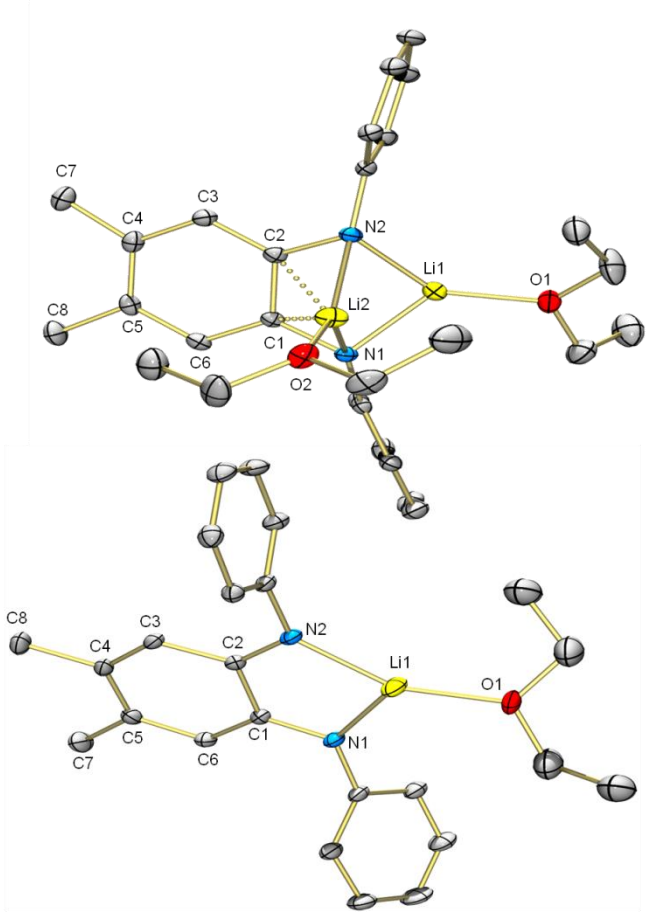

Figure S29 Molecular structures of $[Li_2L'(Et_2O)_2]$, **5** (top), and $[LiL'(Et_2O)]$, **6** (bottom) with 30% probability ellipsoids. Only one disordered component of Et_2O molecules is shown. Isopropyl groups and hydrogen atoms are omitted for clarity. Selected bond angles (°) for **5**: N1-Li1-N2 85.4(1), O1-Li1-N1 129.4(2), O1-Li1-N2 141.6(2), N1-Li2-N2 80.6(1), O2-Li2-N1 134.5(2), O2-Li2-N2 144.9(2). Selected bond angles (°) for **6**: O1-Li1-N1 118.7(2), O1-Li1-N2 153.8(3), N1-Li1-N2 87.0(1)

Table 1S Selected bond lengths in **5** and **6**

Bond	Length in **5** (Å)	Length in **6** (Å)	Bond	Length in **5** (Å)	Length in **6** (Å)
C1-C2	1.442(2)	1.464(2)	Li1-N1	1.961(3)	1.950(3)
C2-C3	1.404(3)	1.426(2)	Li1-N2	1.968(4)	1.960(3)
C3-C4	1.405(3)	1.374(2)	Li1-O1	1.871(3)	1.901(6)
C4-C5	1.404(2)	1.426(2)	Li2-N1	2.056(4)	
C5-C6	1.405(3)	1.374(2)	Li2-C1	2.291(4)	
C1-C6	1.394(2)	1.427(2)	Li2-C2	2.324(4)	
C1-N1	1.417(2)	1.337(2)	Li2-N2	2.064(4)	
C2-N2	1.407(2)	1.339(2)	Li2-O2	1.997(4)	

Discussion of the molecular structures of 5 and 6.

Different from the solution data, the solid state structure of **5** (Figure S29) reveals that the two Li atoms occupy distinct coordination environments. Li1 resides in a distorted trigonal planar geometry: two amido nitrogen donor atoms and one oxygen from a terminal diethylether ligand occupy the three coordination sites. Li2 is tetracoordinate, engaging in an η^4- interaction with the two diamido nitrogen donor atoms and the two N-bound *o*-phenylene carbons. The coordination sphere of Li2 is completed by a terminal diethylether ligand. The NN chelate forms longer N-Li bonds with Li2 (2.056(4) and 2.064(4) Å) than with Li1 ((1.961(3) and 1.968(4) Å). Li1 sits on one side of the C1-C2-N1-N2 plane with a dihedral angle between this plane and N1-Li1-N2 plane of 37°; Li2 sits on the other side of the C1-C2-N1-N2 plane, with a dihedral angle between this plane and N1-Li2-N2 plane of 80°. Among related dilithium complexes of o-phenylenediamido ligands such as **1**, the *N,N'*-disilyl versions by Lappert,[5] or the *N,N'*-2,4,6-triisopropylphenyl version by Liddle,[6] **5** is structurally unique in that Et_2O is used as a co-ligand instead of THF and that among these related complexes, the *ipso* carbons in **5** are bound the closest to Li (C1-Li2, 2.291(4) Å; C2-Li2, 2.324(4) Å).

The solid-state molecular structure of **6** (Figure S29) reveals that Li1 is chelated by the **L'**$^{\cdot-}$ ligand and is bound to a terminal disordered solvent molecule modelled as a 70/30 ratio of Et_2O/THF. The sum of the angles around Li is 359.5(4)°, consistent with a distorted trigonal planar geometry. One electron oxidation of **L'**$^{2-}$ led to a pronounced decrease in the respective C1-N1 and C2-N2 bond lengths to 1.337(2) and 1.339(2) Å relative to the counterparts in **5** (1.417(2) and 1.407(2) Å). Akin to the structure of [LiL(OEt_2)],[7] elongation of the C1-C6 and C2-C3 bonds to 1.427(2) and 1.426(2) Å and compression of the C5-C6 and C3-C4 bonds each to 1.374(2) Å is also observed. In the starting diamido complex **5** these bond lengths are statistically similar.

Table 2S. Crystallographic data for **2, 3(thf)$_2$, 5, 6, 8, 9, 10, 11,** and **K$_2$L(dme)$_4$**.

	2	**3(thf)$_2$**	**5**	**6**	**8**
Formula	$C_{41}H_{66}ClLiN_2O_2Ta$	$C_{42}H_{66}LiN_2O_2Ta$	$C_{40}H_{62}Li_2N_2O_2$	$C_{36}H_{51.4}LiN_2O$	$C_{33}H_{47}N_2Ta$
FW	842.29	818.85	616.79	535.13	652.67
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P2_1/n$	Pcba	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	11.0302(4)	21.1920(16)	11.4110(15)	8.9697(4)	10.6170(19)
b (Å)	23.2106(8)	18.2269(12)	19.573(3)	21.8449(8)	17.966(3)
c (Å)	17.0382(7)	21.3088(16)	17.749(2)	17.0042(7)	16.185(3)
α (deg)	90	90	90	90	90
β (deg)	108.6064(15)	90	93.323(6)	94.395(2)	98.038(7)
γ (deg)	90	90	90	90	90
V (Å^3)	4134.1(3)	8230.8(10)	3957.6(9)	3322.0(2)	3056.8(9)

Z	4	8	4	4	4
D_c (g·cm^{-3})	1.353	1.322	1.035	1.070	1.418
μ (mm^{-1})	2.757	2.705	0.061	0.063	3.618
no. of refln collected	39363	70581	19128	28427	24798
no. of indept refln	9494	9454	8876	7647	7023
GOF on F^2	1.183	1.150	1.010	1.040	1.128
R [$I > 2\sigma(I)$]	R_1 = 0.0233[a)]	R_1 = 0.0318	R_1 = 0.0579	R_1 = 0.0623	R_1 = 0.0290
	wR_2 = 0.0577 [b)]	wR_2 = 0.0797	wR_2 = 0.1525	wR_2 = 0.1718	wR_2 = 0.0441
R (all data)	R_1 = 0.0339	R_1 = 0.0647	R_1 = 0.1088	R_1 = 0.0865	R_1 = 0.0683
	wR_2 = 0.0799	wR_2 = 0.1160	wR_2 = 0.1884	wR_2 = 0.1896	wR_2 = 0.0889

	9	**10**	**11**	**$K_2L(dme)_4$**
Formula	$C_{46}H_{69}N_4Ta$	$C_{42}H_{58}N_5Ta$	$C_{64}H_{88}N_4Ta_2$	$C_{46}H_{78}N_2O_8K_2$
FW	859.00	813.88	1275.28	865.30
T (K)	150(2)	150(2)	150(2)	149(2)
space group	$P2_1/n$	P-1	$P2_1/c$	$P2_1/n$
a (Å)	14.1372(15)	10.4591(8)	15.9017(5)	10.8034(7)
b (Å)	15.1014(15)	12.8533(10)	19.5480(4)	27.6688(19)
c (Å)	20.108(2)	16.2426(13)	22.0555(5)	17.1421(12)
α (deg)	90	69.066(3)	90	90
β (deg)	96.647(4)	82.852(4)	92.2620(11)	98.503(2)
γ (deg)	90	76.536(3)	90	90
V (Å^3)	4264.1(8)	1981.3(3)	6850.5(3)	5067.7(6)
Z	4	2	4	4
D_c (g·cm^{-3})	1.338	1.364	1.236	1.070
μ (mm^{-1})	2.613	2.808	3.227	0.235
no. of refln collected	37634	23806	65508	33778
no. of indept refln	9755	9050	15746	8874
GOF on F^2	0.956	1.040	0.933	1.039
R [$I > 2\sigma(I)$]	R_1 = 0.0407[a]	R_1 = 0.0209	R_1 = 0.0356	R_1 = 0.0519
	wR_2= 0.0839[b]	wR_2 = 0.0482	wR_2 = 0.0791	wR_2 = 0.1425
R (all data)	R_1 = 0.0893	R_1 = 0.0257	R_1 = 0.0595	R_1 = 0.0715
	wR_2 = 0.0990	wR_2 = 0.0499	wR_2 = 0.0853	wR_2 = 0.1600

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$ [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

3. EPR Spectroscopy

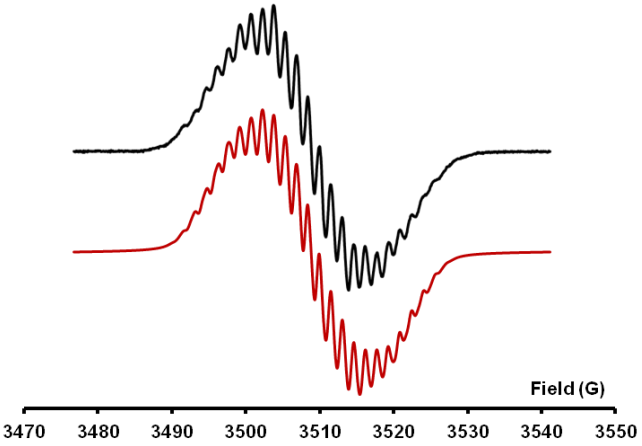

Figure S30 Experimental (top) and simulated (bottom) EPR spectrum of **6** (thf solution, room temperature) X-band microwave frequency 9.856 GHz. Parameters used in simulation: 100% Lorentzian lineshape, g = 2.0075, a_N = 4.58 G, a_H = 3.39 and 1.53 G, a_{Li} = 0.85 G,

The room temperature EPR spectrum of a THF solution of **6** is shown in Figure S30. The *g* factor of **6** is 2.0075; it is close to the free electron value of 2.0036, which is expected for an organic radical with negligible spin-orbit coupling. The multiplet pattern was simulated taking into account hyperfine coupling to a pair of equivalent ^{14}N nuclei, a pair of equivalent *o*-phenylene ^{1}H nuclei, the six equivalent 4,5-dimethyl ^{1}H nuclei, and one ^{7}Li nucleus. The multiplet pattern is consistent with delocalization of the unpaired electron throughout the *o*-phenylene framework, which has been observed in EPR spectra of [LiL(OEt$_2$)].[7]

4. References:

1. Apex 2 Software Package; Bruker AXS Inc., Madison, WI, 2013.
2. Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.
3. http://shelx.uni-ac.gwdg.de/SHELX/index.php (accessed July 4, 2013 and September 4, 2015).
4. Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7.
5. S. Daniele, C. Drost, B. Gehrhus, S. M. Hawkins, P. B. Hitchcock, M. F. Lappert, P. G. Merle and S. G. Bott, *J. Chem. Soc., Dalton Trans.*, 2001, 3179.
6. S. Robinson, E. S. Davies, W. Lewis, A. J. Blake and S. T. Liddle, *Dalton Trans.*, 2014, **43**, 4351-4360
7. T. Janes, J. M. Rawson and D. Song, *Dalton Trans.*, 2013, **42**, 10640-10648.