Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

for

α-CC Agostic Structures and Aggregation Diversity in Cyclopropyllithium Derivatives

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1. Experimental section

All operations were performed with rigorous exclusion of air and moisture, using standard Schlenk techniques and an Ar filled Jacomex glovebox (O_2<5 ppm, H_2O<1 ppm). Cyclopropylbenzene, tmeda and *n*-butyllithium (2.5 M solution in hexanes) were purchased from Aldrich. All solvents were pre-dried by passing through a Puresolv MD 7 solvent purification machine, dried over molecular sieves, filtered and degassed by freeze–pump–thaw cycles. Deuterated solvents and cyclopropylbenzene were dried over molecular sieves, filtered, and degassed by several freeze–pump–thaw cycles and stored in sealed ampoules in the glovebox. Tmeda was distilled over Na and further degassed by freeze–pump–thaw cycles. 1-chlorophenylcyclopropane was prepared according to a literature procedure.[1]

NMR spectra were recorded by using J. Young valve NMR tubes using Bruker Avance III 400 (^{1}H, 400.16; ^{19}F, 376.49; ^{7}Li, 155.52; ^{13}C, 100.6 MHz) or Avance 500 (^{1}H, 500.33;^{13}C 125.82 MHz) spectrometers. Chemical shifts for ^{1}H NMR were determined using residual proton signals in the deuterated solvents and reported versus $SiMe_4$. Chemical shifts for ^{13}C NMR spectra were that of the solvent referenced to $SiMe_4$.^{19}F NMR spectra were referenced versus external $CFCl_3$. ^{7}Li NMR spectra were referenced versus external LiCl. DOSY NMR experiments were carried out on a Bruker Avance 400 spectrometer equipped with a 5 mm triple resonance inverse Z-gradient probe (TBI ^{1}H, ^{31}P, BB). The DOSY spectra were acquired at room temperature, without temperature regulation to avoid convection, with the stebpgp1s pulse program from Bruker topspin software. All spectra were recorded with 16 K time domain data point in the t2 dimension and 16 t1 increments. The strength of the gradient was linearly incremented in 16 steps from 2 up to 95% of the maximum gradient strength. All measurements were performed with a compromise diffusion delay D ranging from 90 to 130 ms and a gradient pulse length d ranging from 1.8 to 2.4 ms. Elemental analyses (Analytical service of the LCC) are the average of at least two independent measurements.

Synthesis of [Li(*c*-CPhC$_2$H$_4$)(tmeda)] (3) and [Li(NMe$_2$)(tmeda)] (4). Cyclopropylbenzene (505 mg, 4.27 mmol), tmeda (494 mg, 4.25 mmol) and pentane (6 mL) were mixed together. The mixture was cooled down to 0°C and *n*BuLi in hexanes (2.4 mL, 6.0 mmol) was slowly added. The mixture was slowly warmed to room temperature affording a red solution from which a yellow solid gradually precipitated over a period of 5 days. The precipitate was collected by filtration and washed with cold (–40°C) pentane (3 x 1 mL) to give a *ca* 4:1 mixture of **3** and **4** (548 mg, 1.94 mmol in **3**, 45% for **3**). ^{1}H NMR ([D$_6$]benzene, 298 K) δ = 7.47 (br s, 2 H, *o/m*-C$_6$*H*$_5$), 7.30 (t, 2 H, *m/o*-C$_6$*H*$_5$), 6.88 (t, 1 H, *p*-C$_6$*H*$_5$), 2.95 (br s, 1.5 H, LiN(C*H*$_3$)$_2$), 1.82 (s, 12 H, C*H*$_3$N-tmeda), 1.67 (s, 4 H, C*H*$_2$N-tmeda), 1.26 (br s, 2 H, *H*β), 0.95 (br s, 2 H, *H*β) ppm; ([D$_8$]thf, 298 K) δ = 6.63 (m, 4 H, (*o*,*m*)-C$_6$*H*$_5$), 6.09 (tt, 1 H, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.9 Hz, *p*-C$_6$*H*$_5$), 2.74 (br s, 1.6 H, LiN(C*H*$_3$)$_2$), 2.30 (s, 4 H, C*H*$_2$N-tmeda), 2.15 (s, 12 H, C*H*$_3$N-tmeda), 0.43 (br s, 4 H, *H*β) ppm. Single crystals of **1** and **5** suitable for X-ray diffraction were obtained by suspending the mixture of **3** and **4** in hexane followed by slow addition of thf until dissolution and storage at –40°C overnight.

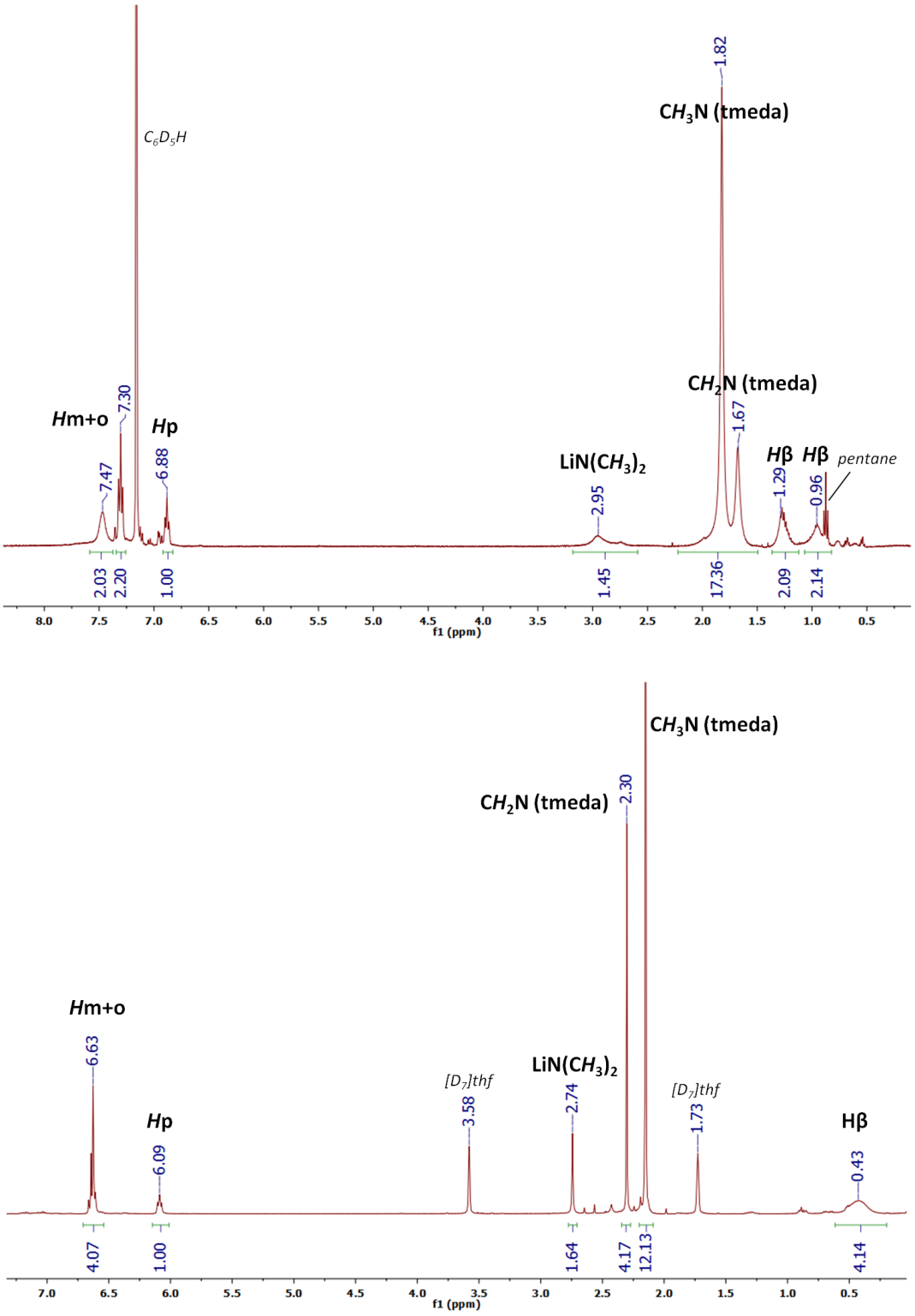


Figure F1. ^{1}H NMR spectrum of the *ca* 4:1 mixture of **3** and **4** at 298 K in [D_6]benzene (top) and [D_8]thf (bottom).

Synthesis of [Li(thf)$_2$(μ-*c*-CPhC$_2$H$_4$)$_2$Li(thf)] (1): 1-Chlorophenylcyclopropane (200 mg, 1.31 mmol), *n*BuLi in hexanes (0.6 mL, 1.5 mmol,) and pentane (4 mL) were mixed together in a Schlenk flask. Thf (0.2 mL, 2.5 mmol) was quickly added via a syringe and the reaction mixture was stirred at room temperature. A white solid started to precipitate almost immediately and stirring was maintained for 10 min. The reaction slurry was then stored at –40°C overnight. After filtration, the solid was washed with pentane and dried under vacuum, to give an analytically pure white powder (130 mg, 0.280 mmol, 43%). Elemental Analysis: Calcd for $C_{30}H_{42}Li_2O_3$: C, 77.57; H, 9.11; N 0.00. Found: C, 77.70; H, 9.18; N 0.00. **1** gave **2** upon dissolution in [D$_8$]thf (see main text). ^{1}H NMR ([D$_8$]thf, 298 K) δ = 6.62 (m, 8 H, (*o*,*m*)-C$_6$*H*$_5$), 6.08 (tt, 2 H, $^3J_{HH}$ = 6.3, $^4J_{HH}$ = 1.9 Hz, *p*-C$_6$*H*$_5$), 3.62 (m, 12 H, CH$_2$C*H*$_2$O-thf), 1.77 (m, 12 H, C*H*$_2$CH$_2$O-thf), 0.42 (br s, 8 H, *H*β) ppm. ^{7}Li NMR ([D$_8$]thf, 298 K) δ = 0.35 (s, *Li*) ppm. ^{13}C NMR ([D$_8$]thf, 298 K) δ = 167.88 (s, *ipso*-*C*$_6$H$_5$), 127.58 (d, J_{CH} = 151 Hz, *m*-*C*$_6$H$_5$), 125.21 (d, J_{CH} = 152 Hz, *o*-*C*$_6$H$_5$), 113.60 (d, J_{CH} = 157 Hz, *p*-*C*$_6$H$_5$), 68.39 (t, J_{CH} = 144 Hz, CH$_2$*C*H$_2$O-thf), 28.03 (s, *C*α) 26.53 (t, J_{CH} = 132 Hz, *C*H$_2$CH$_2$O-thf), 11.21 (t, J_{CH} = 153 Hz, *C*β) ppm. The *ipso*-*C*$_6$H$_5$, *m*-*C*$_6$H$_5$, *o*-*C*$_6$H$_5$, *p*-*C*$_6$H$_5$ and *C*α were assigned thanks to a HMBC analysis. Single crystals of **1** suitable for X-ray diffraction analysis were obtained directly from the reaction mixture after storage at –40°C. **1** reacted slowly with protio-thf (several hours at room temperature, $t_{1/2} \approx 24$ h) according to classical thf cleavage pathways.

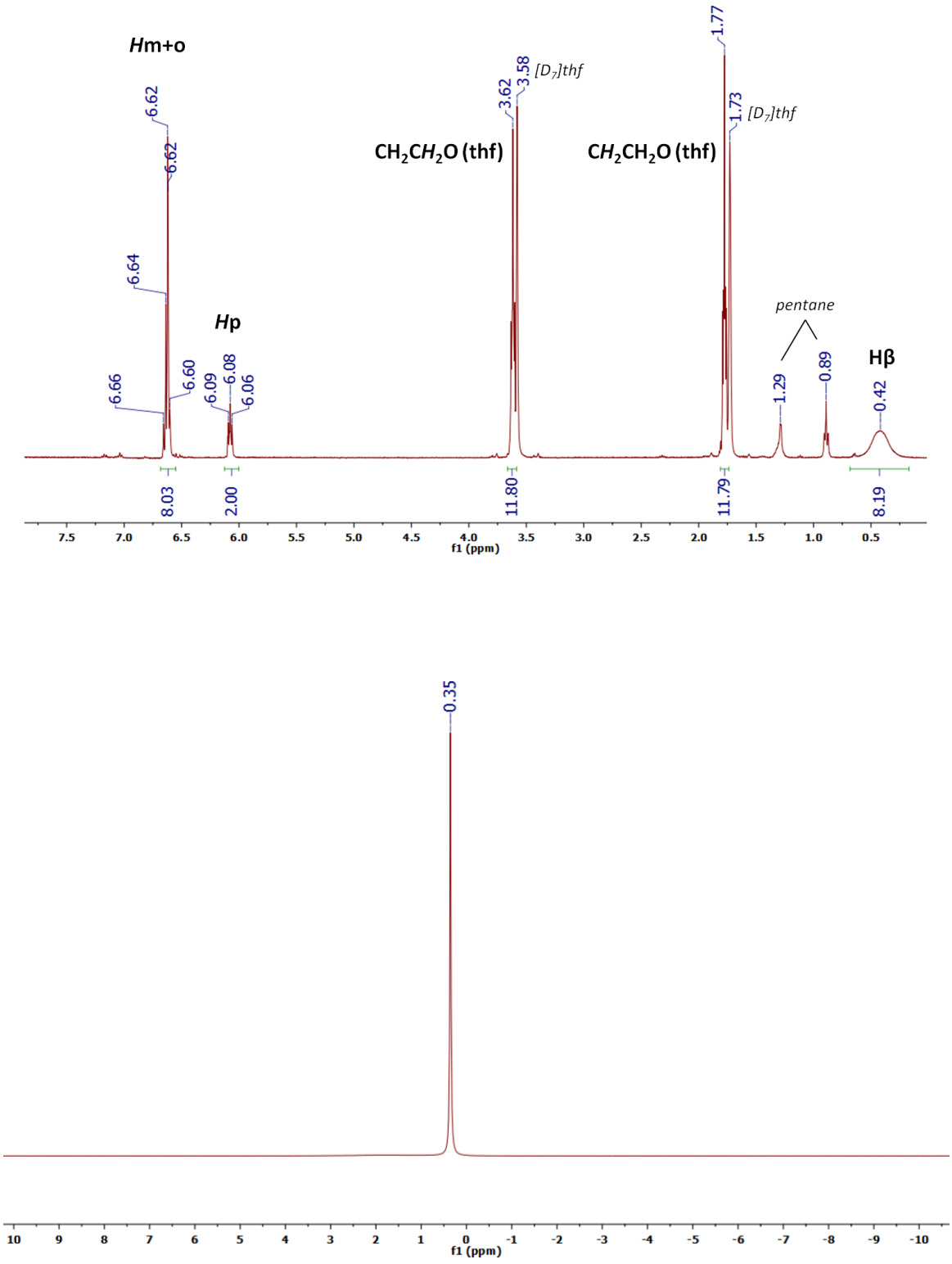


Figure F2. ^{1}H (top) and ^{7}Li (bottom) NMR spectrum of **1** at 298 K in [D_8]thf.

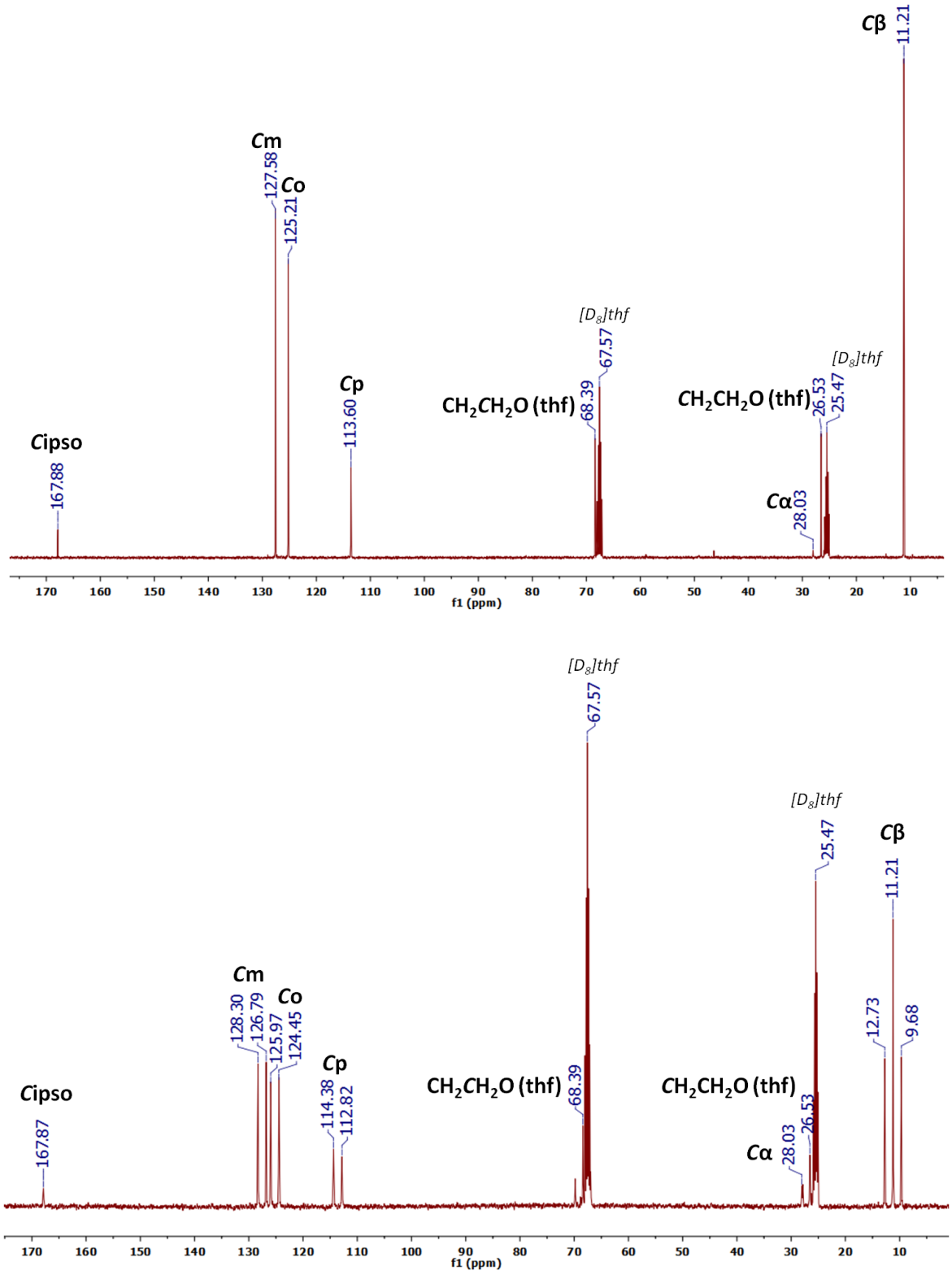


Figure F3. $^{13}C\{^{1}H\}$ (top) and ^{13}C (bottom) NMR spectrum of **1** at 298 K in $[D_8]$thf.

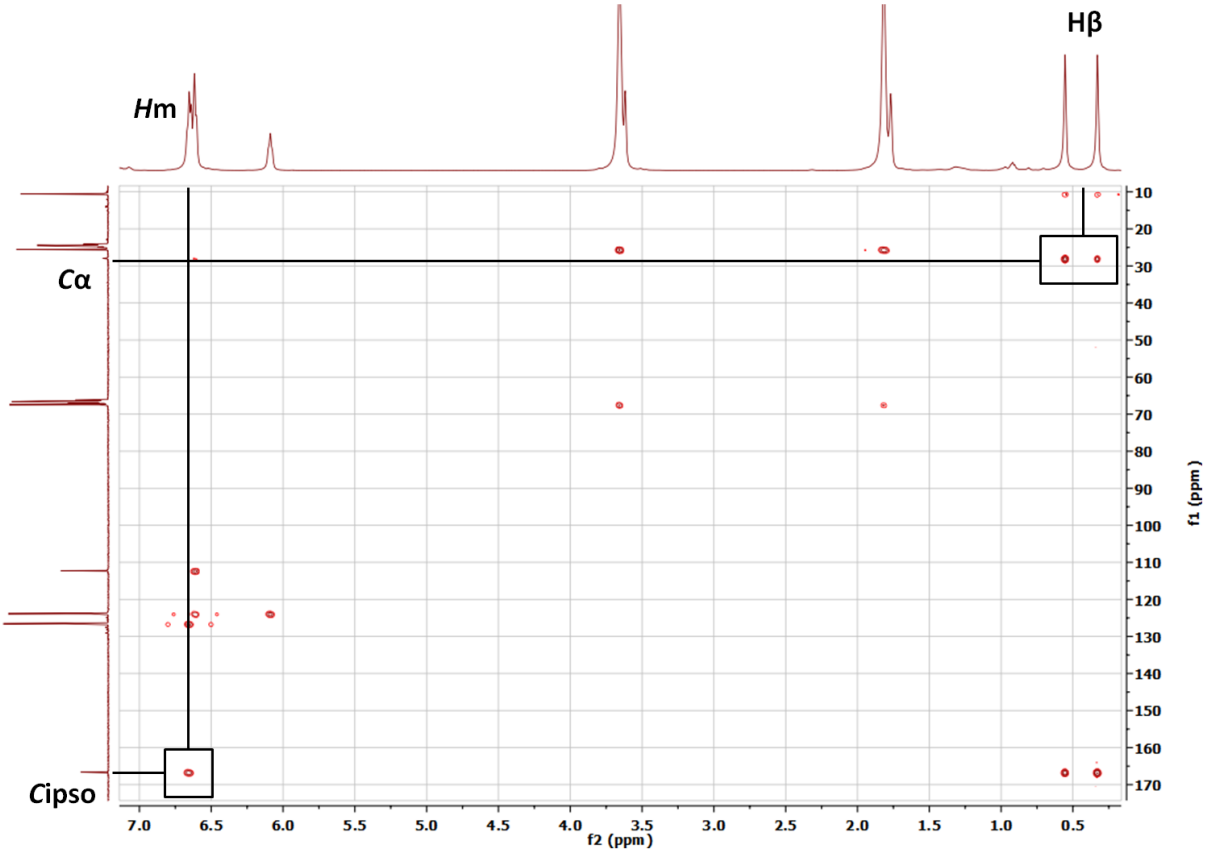


Figure F4. HMBC ^{1}H-^{13}C NMR spectrum of **1** at 193 K in [D_8]thf.

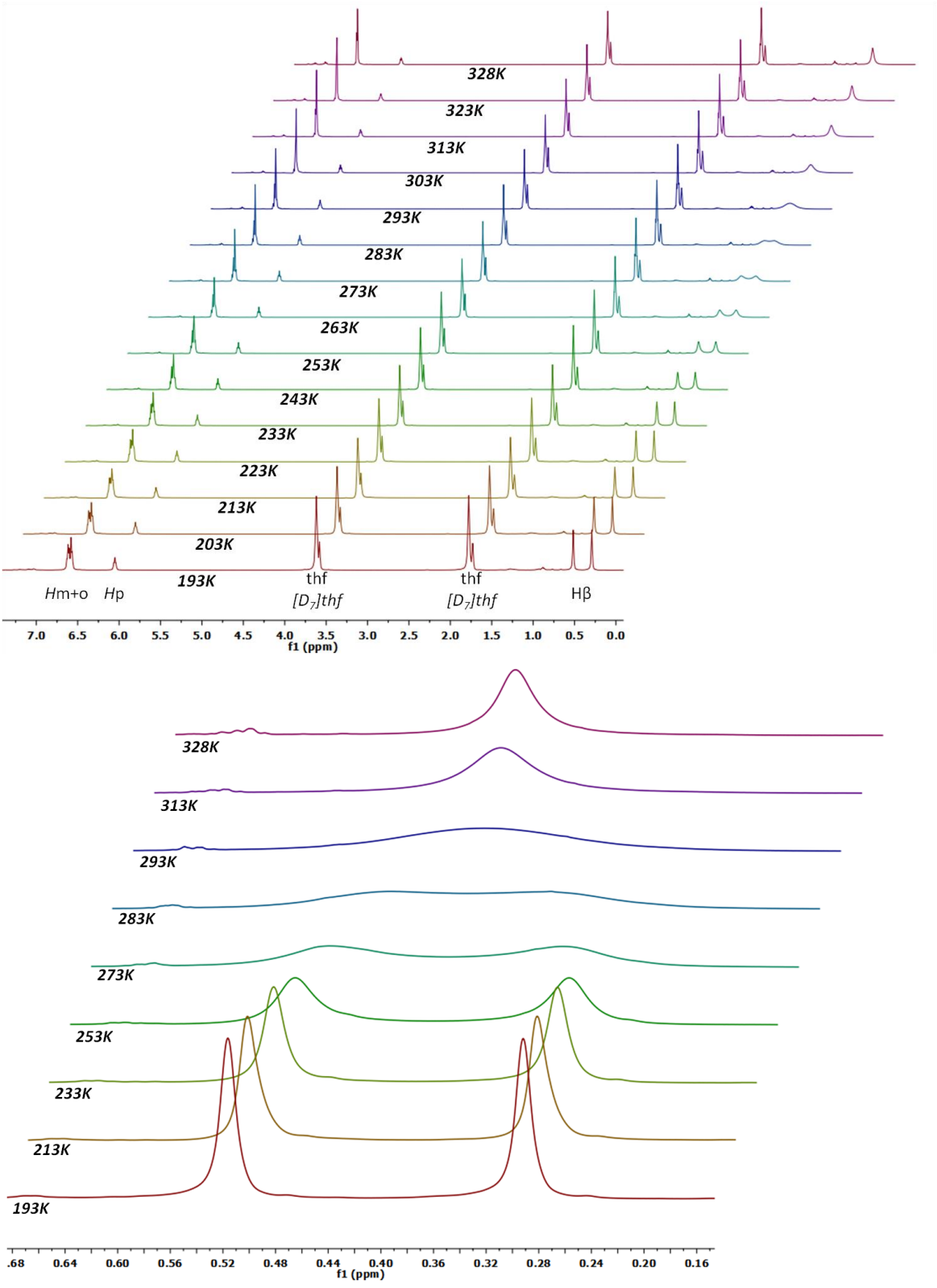
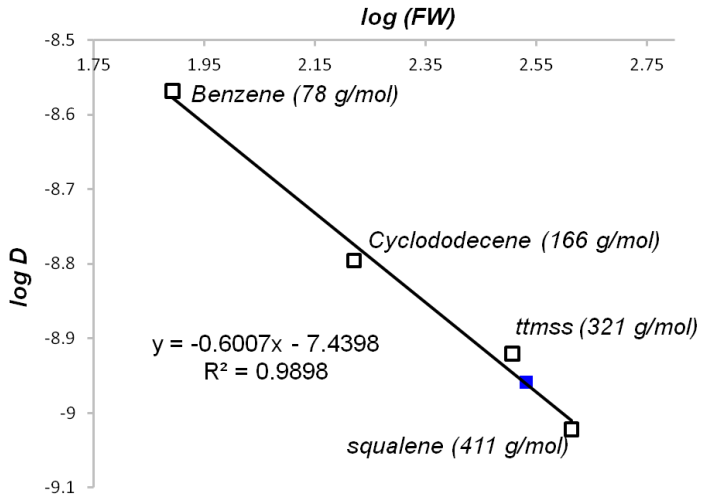


Figure F5. ^{1}H NMR variation temperature experiment for **1** in [D_8]thf (193 – 328 K); full (top) and expansion (Hβ region, bottom) plots.



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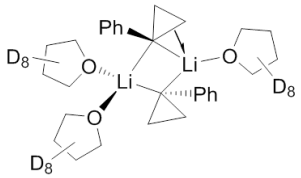
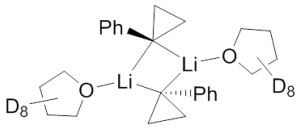
log FW	1.8927066	2.220892249	2.50628851	2.61354585	2.531478917
log D	-8.5686362	-8.795880017	-8.92081875	-9.02227639	-8.958607315
***FW* / g mol^{-1}**	78.11	166.3	320.84	410.72	**340**
***D* / m^2 s^{-1}**	2.7E-09	1.6E-09	1.2E-09	9.5E-10	1.1E-09

Figure F6. Diffusion-formula weight analysis of **1**.



FW = 488.69 g/mol



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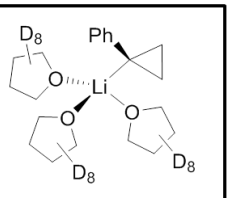
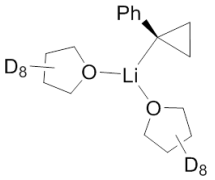


FW = 364.58 g/mol

2



FW = 284.42 g/mol

Figure F7. Putative structures for **2** (see Figure F6).

2. X-ray crystallography. A summary of crystal, acquisition and refinement data can be found in **Table 1** below. Data for **1** and **5** were collected at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a Mo-Kα radiation (λ = 0.71073Å) micro-source and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by direct methods using SIR92[2] or SHELXS-97,[3] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97[3] included in the software package WinGX version 1.63.[4] All hydrogens atoms were placed geometrically, and refined by using a riding model. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ where $P=(Fo^2+2Fc^2)/3$. Ellipsoids are drawn at the 30% probability level for non-hydrogen atoms.

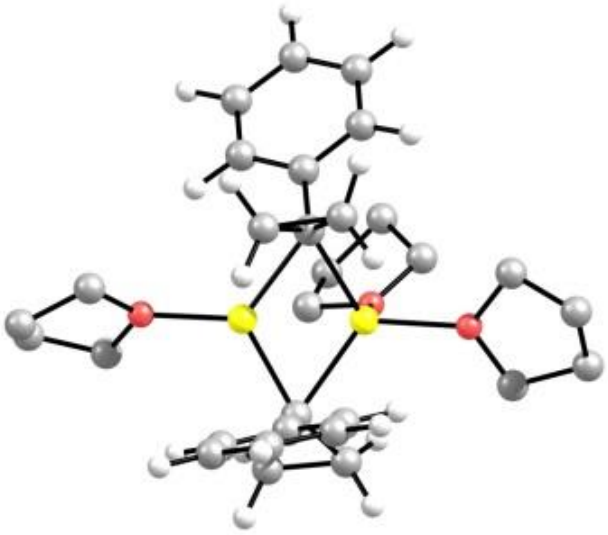
For **1**, the checkcif presents one Alert B due to the thermal disorder on one of the thf (O2-based) coordinated to Li2. This disorder has been well treated with the Part instructions of the SHELXL-97 refinement program. However, there is still one Alert B due to the position of two hydrogen atoms of this THF.

Table T1. Table of crystallographic data.

	1	**5**
Formula	$C_{30}H_{42}Li_2O_3$, $0.5(C_6H_{14})$	$C_{38}H_{62}Li_4N_2O_4$
CCDC	1465291	1465290
Mol. wt.	507.60	638.66
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a(Å)	8.5802(5)	8.7871(10)
b(Å)	9.4380(5)	9.5833(11)
c(Å)	20.2265(11)	13.1959(13)
α(°)	80.998(2)	104.353(4)
β(°)	82.494(2)	93.696(4)
γ(°)	70.198(2)	116.282(4)
V(Å^3)	1516.79(15)	945.63(18)
Z	2	1
Density (g/cm^3)	1.111	1.121
Abs. coeff., (mm^{-1})	0.068	0.069
F(000)	554	348
Crystal size, mm	0.2 x 0.12 x 0.03	0.18 x 0.12 x 0.08
θ range, deg	2.31 to 25.35	1.63 to 26.37
Limiting indices	-10<=h<=9	-10<=h<=10
	-11<=k<=11	-11<=k<=11
	-24<=l<=24	-16<=l<=14
R(int)	0.0362	0.0259
Reflections collected	27496	23990
Reflec. Unique [$I>2\sigma(I)$]	5557	3853
Completeness to θ	99.9 %	99.8 %
Data/restraints/param.	5557 / 0 / 346	3853 / 3 / 227
Goodness-of-fit	1.040	1.028
R_1 [$I>2\sigma(I)$] (all data)	0.0548	0.0415
wR_2 [$I>2\sigma(I)$] (all data)	0.1340	0.1044
Largest diff. e·Å^{-3}	0.376 and -0.326	0.469 and -0.289

3. Computational details. Calculations were performed at the DFT level with the PBE1PBE functional as implemented in Gaussian09, revision D.01,[5] using the def2TZVP basis set (N, O, C, Li and H).[6] Structure optimizations were carried out without symmetry constraints. The nature of the stationary points was ascertained by a vibrational analysis within the harmonic approximation (1 atm and 298 K). Minima were identified by a full set of real frequencies. Electronic and free energies are reported in hartree with zero-point energy correction. Computation of NMR coupling constants used the same functional associated with the IGLO-II basis set for C and H.[7] NBO calculations were carried out with NBO 6.0 as implemented in Gaussian 09.[8]

$[Li(thf)_2(\mu\text{-}c\text{-}CPhC_2H_4)_2Li(thf)]$ (1).



Electronic and zero-point energy -1407.313903 Free energy -1407.392831 hartree

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6	8.439493000	6.968535000	4.825696000
1	8.957427000	7.312603000	5.715751000
6	7.438570000	7.748402000	4.264487000
1	7.157809000	8.694846000	4.711293000
6	6.810382000	7.294874000	3.109447000
1	6.033060000	7.896124000	2.648268000
6	7.164478000	6.086036000	2.538630000
1	6.656685000	5.747431000	1.640454000
6	8.467690000	3.940764000	2.556630000
6	9.905768000	3.590019000	2.310687000
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1	10.264353000	2.579461000	2.494182000
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6	4.185371000	-1.438483000	4.405882000
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1	2.653406000	-0.974070000	2.976063000
6	3.888307000	0.726072000	3.383123000
1	3.328613000	1.369710000	2.711207000
6	5.415779000	2.651676000	3.884811000
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1	4.473321000	4.604394000	3.283333000
1	3.332085000	3.448122000	4.106864000
6	5.304891000	3.593628000	5.073603000
1	4.883529000	3.223209000	6.005785000
1	6.020721000	4.406996000	5.226083000
6	8.093570000	0.181657000	2.034471000
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1	7.843189000	0.236412000	3.099784000
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1	8.256002000	-1.978956000	2.259927000
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1	5.220116000	0.442090000	0.765013000
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1	11.300460000	1.803636000	7.283570000
8	5.547477000	3.419239000	0.391721000
3	6.620792000	2.779081000	1.989159000
3	7.438014000	3.168647000	4.247514000
6	8.201333000	3.035079000	7.143023000
1	7.790715000	4.045756000	7.102591000
6	9.522449000	2.949247000	7.884772000
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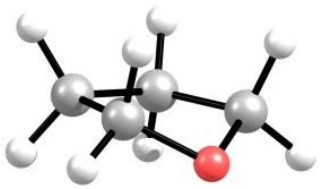
thf



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6	6.246514000	0.096420000	0.605750000
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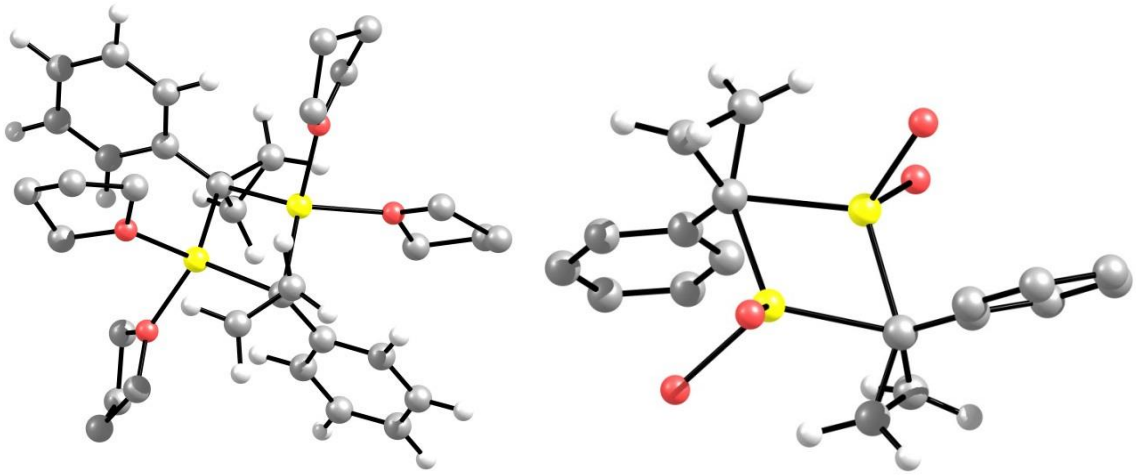
1	5.223463000	0.451733000	0.757519000
8	7.137800000	0.955562000	1.301542000

[Li(thf)$_2$(μ-*c*-CPhC$_2$H$_4$)$_2$Li(thf)$_2$] (4).



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1	9.606153000	6.331300000	3.454239000
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6	6.827753000	8.094833000	2.663945000
1	6.447570000	9.109874000	2.669886000
6	6.043231000	7.043175000	2.201884000
1	5.034649000	7.236432000	1.849228000
6	6.531385000	5.748245000	2.197794000
1	5.893458000	4.940014000	1.854761000
6	8.303832000	4.034122000	2.614871000
6	9.795709000	3.839328000	2.522001000
1	10.468130000	4.694368000	2.497336000
1	10.245064000	2.970218000	2.996085000
6	8.964416000	3.637778000	1.297368000
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1	3.647105000	-1.934626000	2.136790000

6	4.515327000	-0.164838000	2.972855000
1	3.817849000	0.487498000	2.458072000
6	5.613239000	1.856734000	4.009340000
6	4.330483000	2.637836000	4.134098000
1	4.291150000	3.660944000	3.765597000
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6	7.032893000	-0.149438000	0.361267000
1	5.964483000	-0.198889000	0.575426000
1	7.182412000	0.322623000	-0.617614000
6	7.714006000	-1.504411000	0.437321000
1	7.712046000	-2.024264000	-0.521790000
1	7.209238000	-2.132832000	1.174881000
6	9.109285000	-1.130865000	0.922625000
1	9.638507000	-1.957582000	1.398459000
6	8.801698000	-0.006032000	1.892719000
1	8.546948000	-0.394369000	2.884934000
1	9.609959000	0.723583000	1.985620000
6	4.224054000	2.696460000	0.471600000
1	3.812495000	2.887180000	1.463098000
1	3.967254000	1.670601000	0.177649000
6	3.793767000	3.689867000	-0.587534000
1	2.829061000	3.439705000	-1.030772000
1	3.726559000	4.694132000	-0.160375000
6	4.955331000	3.603421000	-1.570674000
1	4.839273000	2.727955000	-2.215555000
1	5.051791000	4.482620000	-2.208535000
6	6.149502000	3.434640000	-0.643400000
1	6.933249000	2.797991000	-1.060725000
1	6.594823000	4.395702000	-0.371486000
8	7.658782000	0.663168000	1.357779000
8	8.601638000	2.081083000	5.800568000
6	9.923002000	1.574151000	5.610615000
1	10.624707000	2.415464000	5.572159000
1	9.959916000	1.051682000	4.652727000
6	10.196938000	0.672605000	6.801096000
1	9.820241000	-0.335966000	6.610076000
1	11.260041000	0.600713000	7.033801000
8	5.644482000	2.822630000	0.551678000
3	6.815312000	2.376812000	2.179919000
3	7.427504000	3.155900000	4.485658000

6	8.146820000	1.792876000	7.126889000
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6	9.376417000	1.344803000	7.895073000
1	9.129668000	0.680372000	8.723941000
1	9.914744000	2.207354000	8.298442000
1	7.390612000	1.002023000	7.079165000
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1	8.617589000	7.416454000	6.049027000
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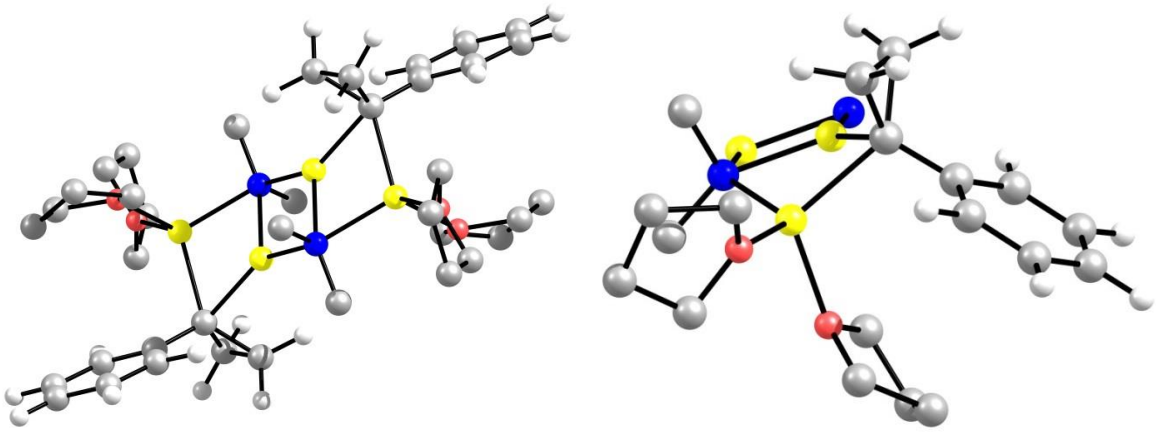
1	6.390627000	7.739976000	6.945383000
1	9.721251000	-0.763825000	0.093662000

$[Li(thf)_2(\mu\text{-}c\text{-}CPhC_2H_4)(\mu\text{-}NMe_2)Li]_2$ (5)



Electronic and zero-point energy -1923.320204 Free energy -1923.422440 hartree

6	1.682369000	-0.511175000	-2.802848000
6	1.878545000	0.695567000	-3.681876000
6	2.538045000	0.649072000	-2.339009000
6	2.384083000	-1.736413000	-3.187695000
6	2.299289000	-2.263915000	-4.487208000
6	2.922664000	-3.451253000	-4.838270000
6	3.663387000	-4.166198000	-3.905737000

6	3.770497000	-3.661166000	-2.614927000
6	3.145368000	-2.476042000	-2.265603000
6	-1.170646000	1.568750000	-1.625301000
6	-2.555938000	-0.251866000	-1.156429000
6	-2.763549000	-1.200748000	-4.869655000
6	-3.505076000	-0.023284000	-5.492191000
6	-2.377026000	0.824187000	-6.112168000
6	-1.102411000	0.082204000	-5.709417000
6	-0.413033000	-3.435115000	-1.282796000
6	-0.382741000	-4.937657000	-1.489171000
6	-0.066925000	-5.036862000	-2.976344000
6	-0.867279000	-3.879287000	-3.540173000
7	-1.184389000	0.203289000	-1.143224000
8	-1.463189000	-0.704215000	-4.579749000
8	-0.879503000	-2.876774000	-2.517157000
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3	-0.491048000	-0.914712000	-2.809364000
6	-1.682393000	0.511165000	2.802832000
6	-1.878594000	-0.695548000	3.681896000
6	-2.538126000	-0.649062000	2.339046000
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6	1.170530000	-1.568824000	1.625297000
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6	2.376770000	-0.824149000	6.112284000
6	1.102235000	-0.082057000	5.709497000
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1	3.220806000	-0.314556000	0.476020000
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1	0.360139000	-5.424046000	-0.856234000
1	-1.360633000	-5.376171000	-1.270017000

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