Solution Structures of Lithium Amino Alkoxides
Used in Highly Enantioselective 1,2-Additions

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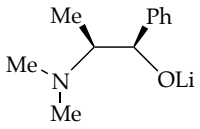
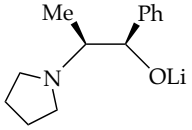
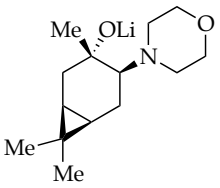
Chart 1:



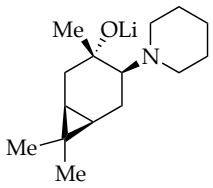
2a



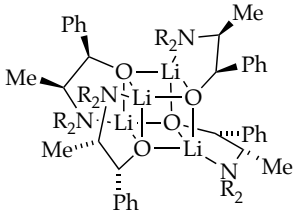
2b



3a

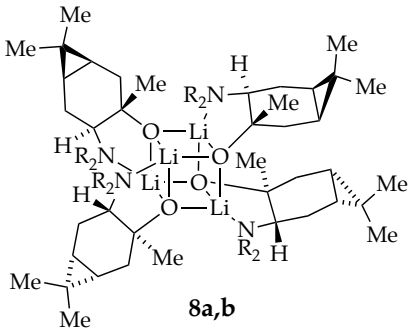


3b



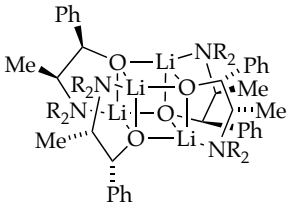
7a,b

a; $R_2N = NMe_2$; **b;** R_2N= 



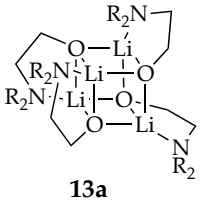
8a,b

a; R_2N =  **b**; R_2N = 

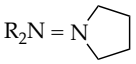


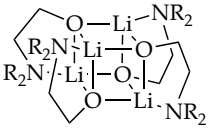
9a,b

a; $R_2N = NMe_2$; **b;** R_2N= 

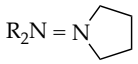


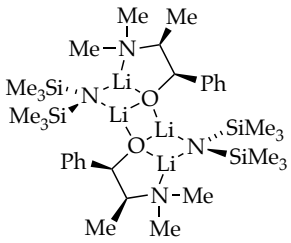
13a

R_2N = 

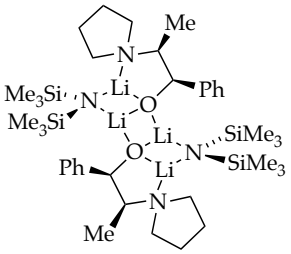


13b

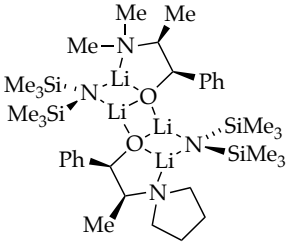
R_2N = 



12a



12b



12c

Part 1: NMR Spectroscopic Studies

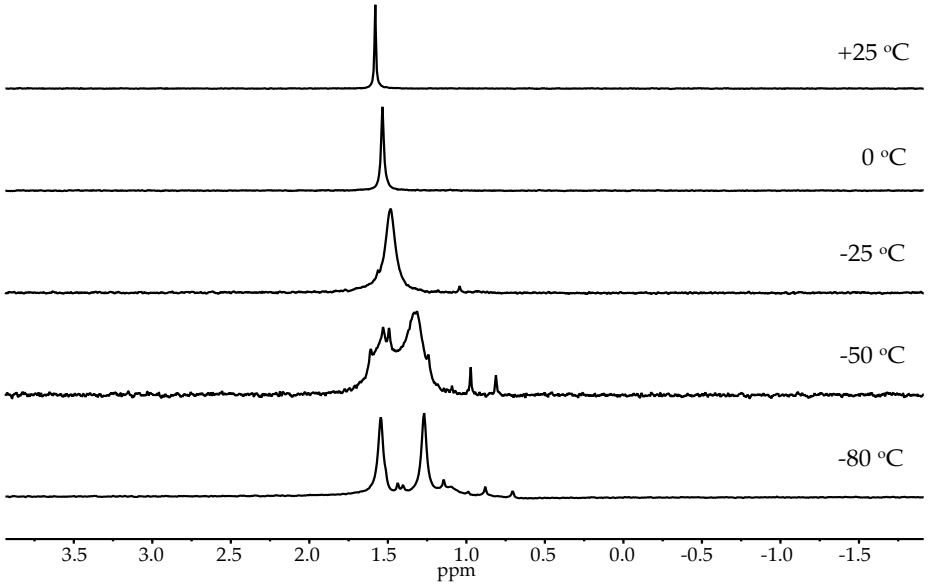


Figure S1. ^{6}Li NMR spectra of [^{6}Li]**2a** (0.10 M) in toluene showing coalescence with increasing temperature and evidence of structural asymmetry of the homoaggregate at low temperature.

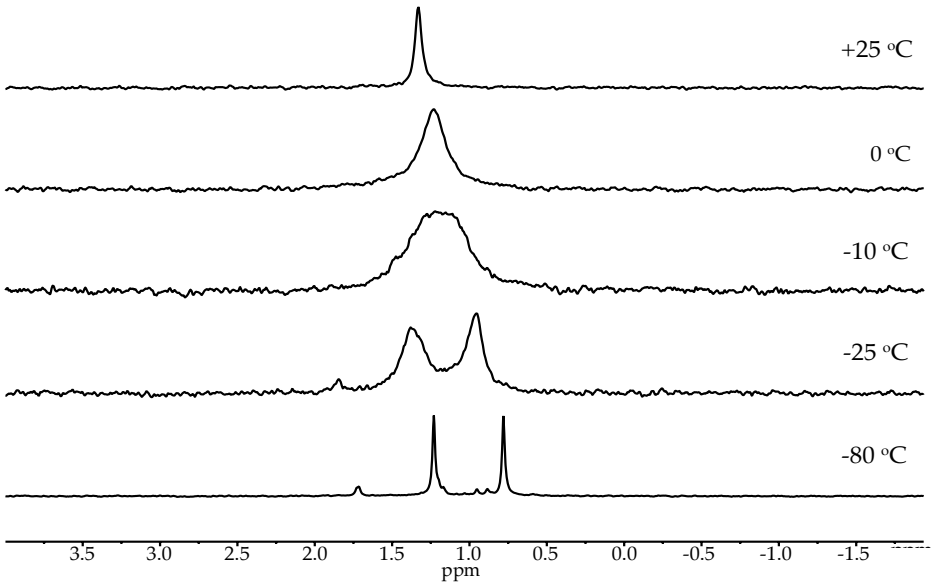


Figure S2. ^{6}Li NMR spectra of [^{6}Li]**2b** (0.10 M) in toluene showing coalescence with increasing temperature and evidence of structural asymmetry of the homoaggregate at low temperature.

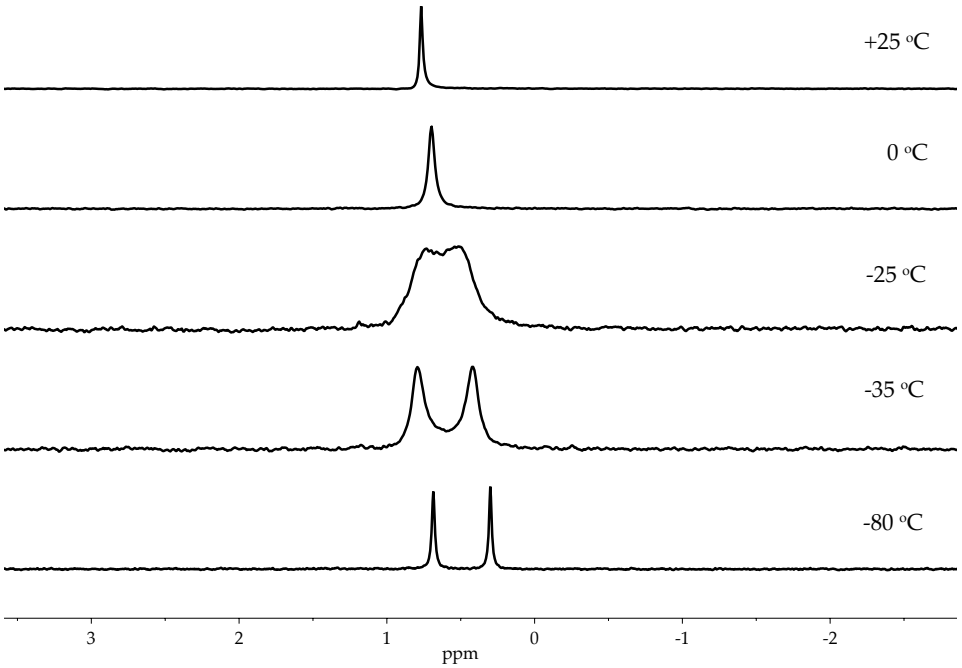


Figure S3. ^{6}Li NMR spectra of [^{6}Li]**3a** (0.10 M) in toluene showing coalescence with increasing temperature and evidence of structural asymmetry of the homoaggregate at low temperature.

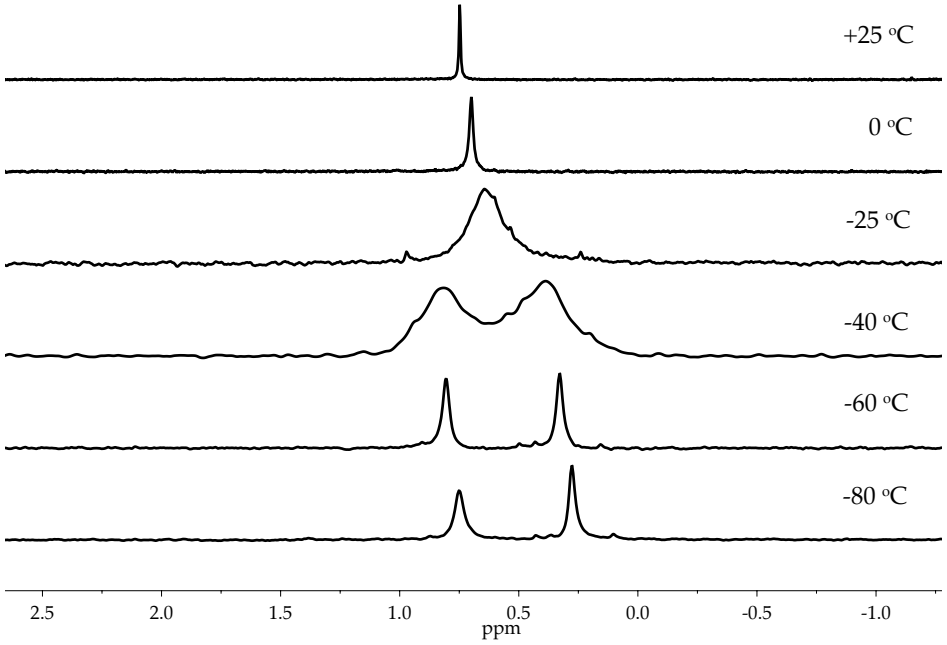


Figure S4. ^{6}Li NMR spectra of [^{6}Li]**3b** (0.10 M) in toluene showing coalescence with increasing temperature and evidence of structural asymmetry of the homoaggregate at low temperature.

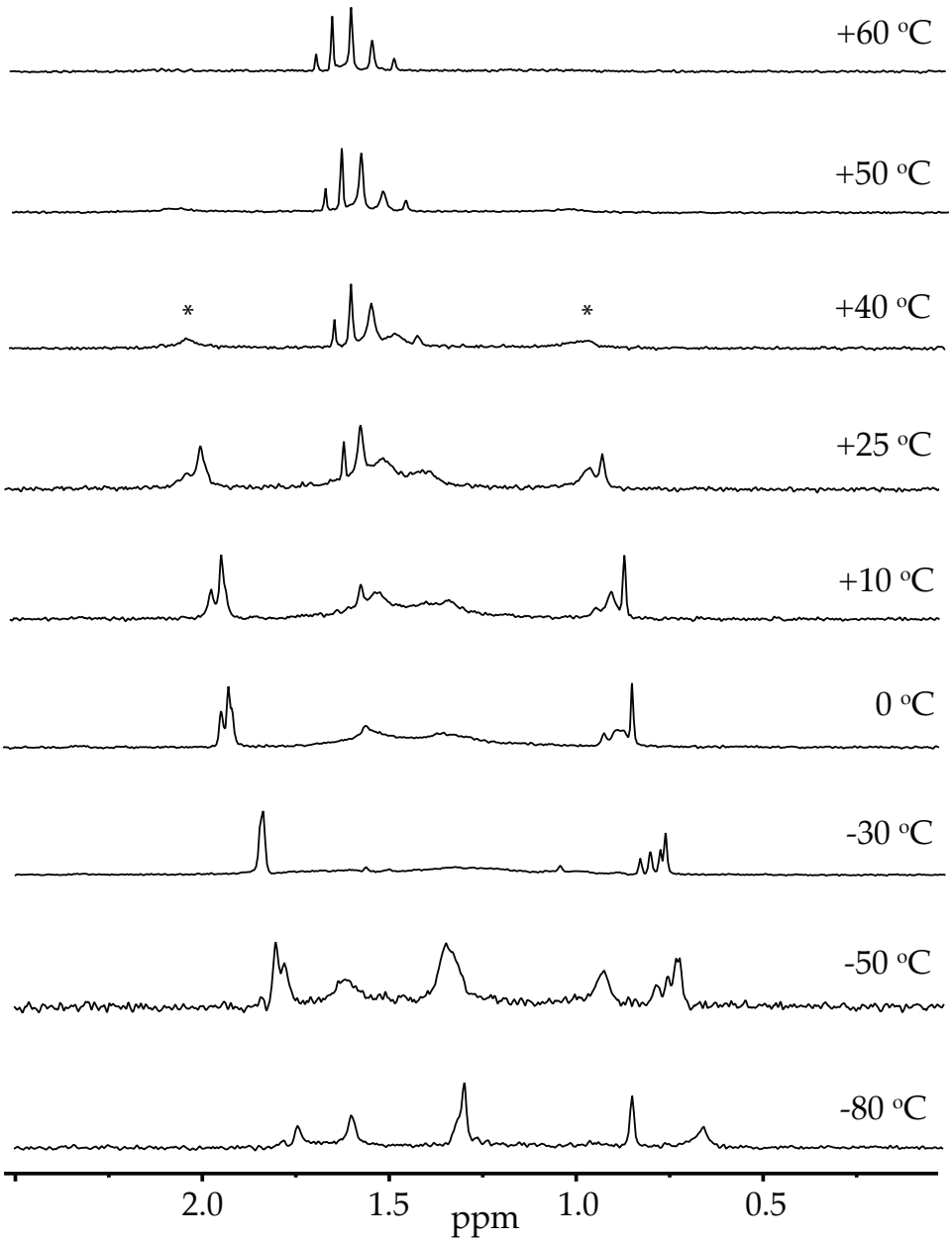


Figure S5. ^{6}Li NMR spectra of [^{6}Li]**2a** (0.050 M) and [^{6}Li]**2b** (0.050 M) with 0.020 M excess [^{6}Li]LiHMDS in toluene showing coalescence behavior with changing temperature. Asterisks (*) denote mixed aggregates of amino alkoxides and [^{6}Li]LiHMDS that occur under conditions of excess base (see figures 12-15).

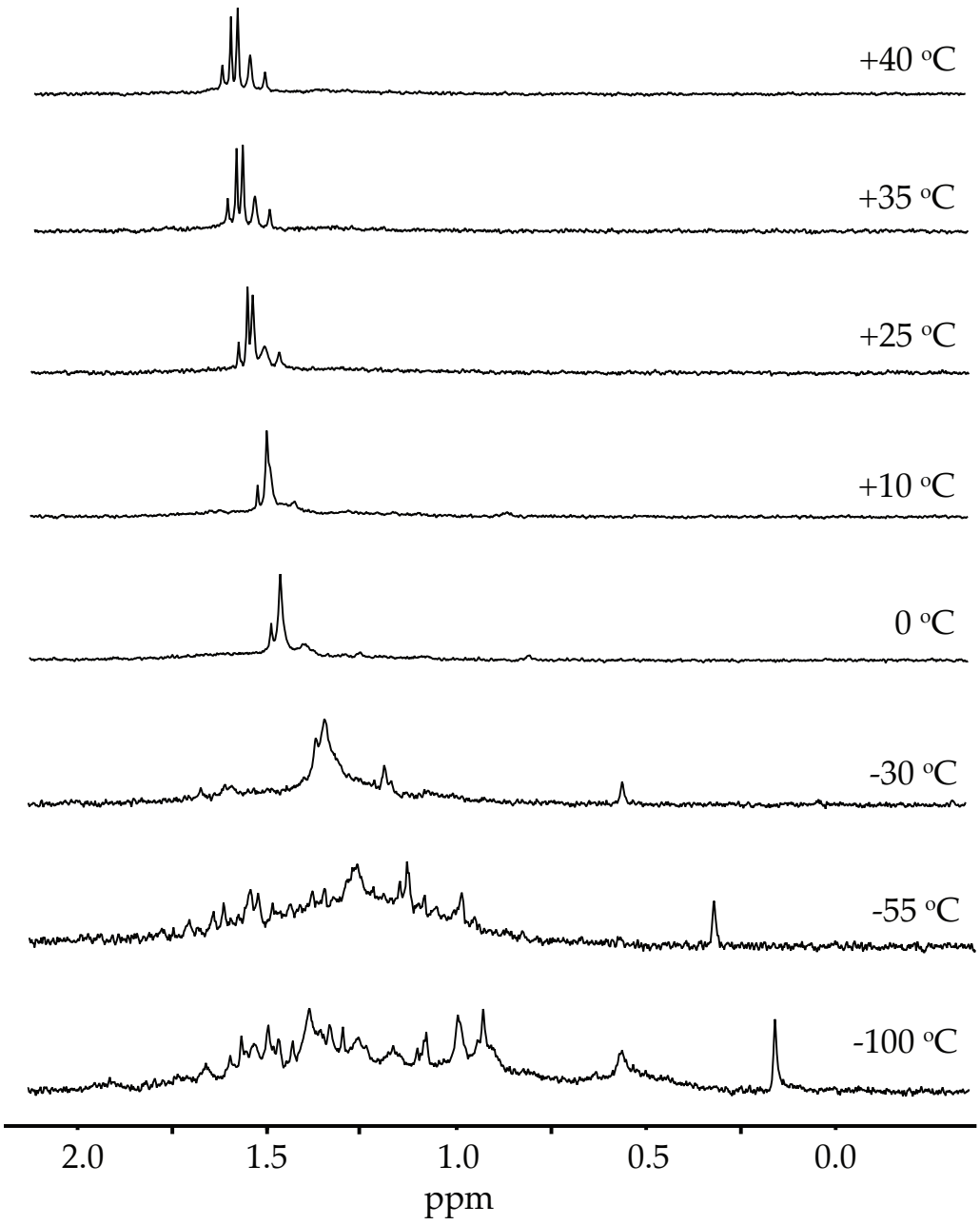


Figure S6. ^{6}Li NMR spectra of [^{6}Li]**2a** (0.050 M) and [^{6}Li]**2b** (0.050 M) with 0.020 M excess [^{6}Li]LiHMDS in THF (6.0 M) with toluene cosolvent showing coalescence behavior with changing temperature. The coalescence temperature is approximately 20 °C lower than in pure toluene.

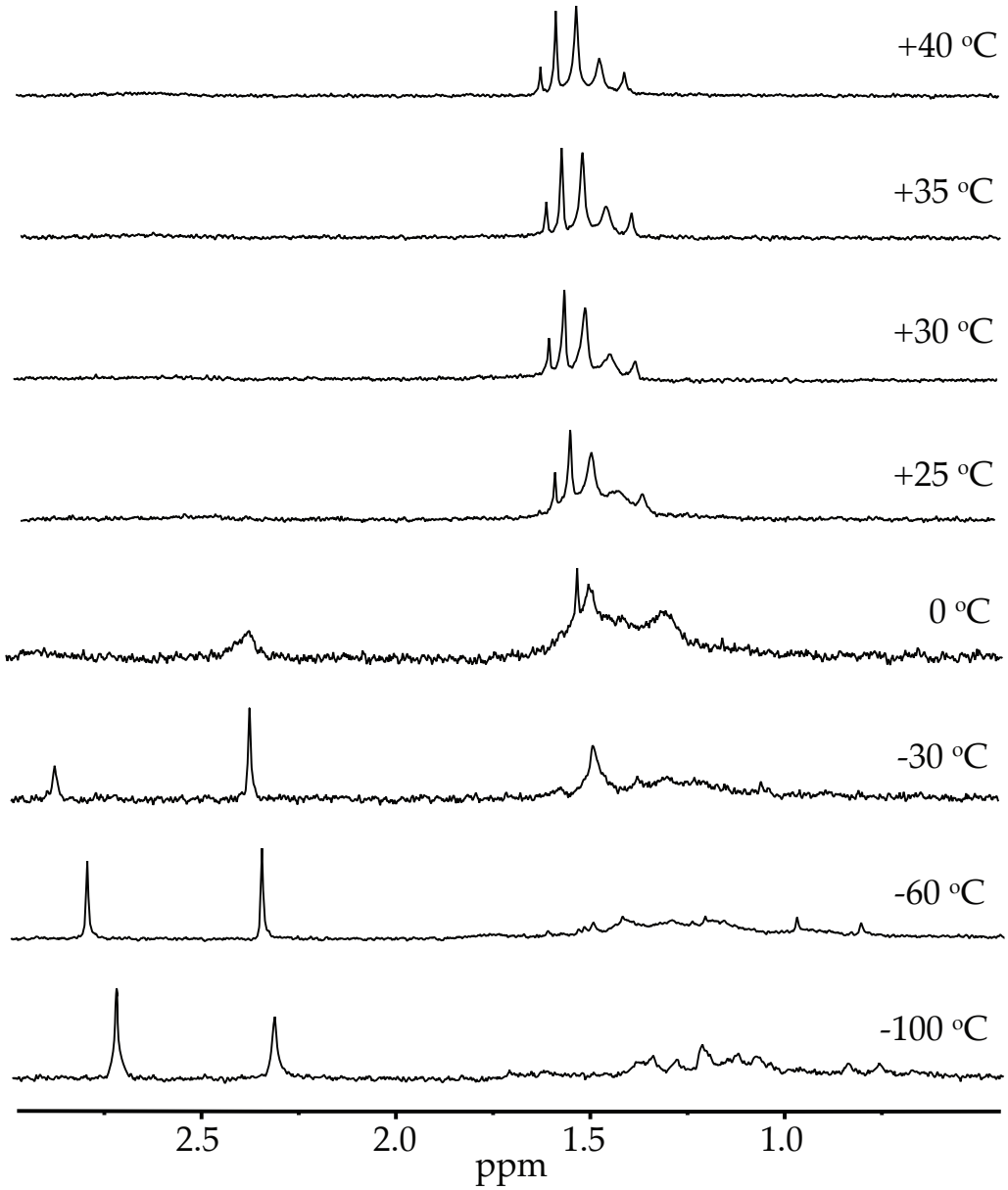


Figure S7. ^{6}Li NMR spectra of [^{6}Li]**2a** (0.050 M) and [^{6}Li]**2b** (0.050 M) with 0.020 M excess [^{6}Li]LiHMDS in pyridine (1.20 M) with toluene cosolvent showing coalescence behavior with changing temperature. The coalescence temperature is approximately 20 °C lower than in pure toluene.

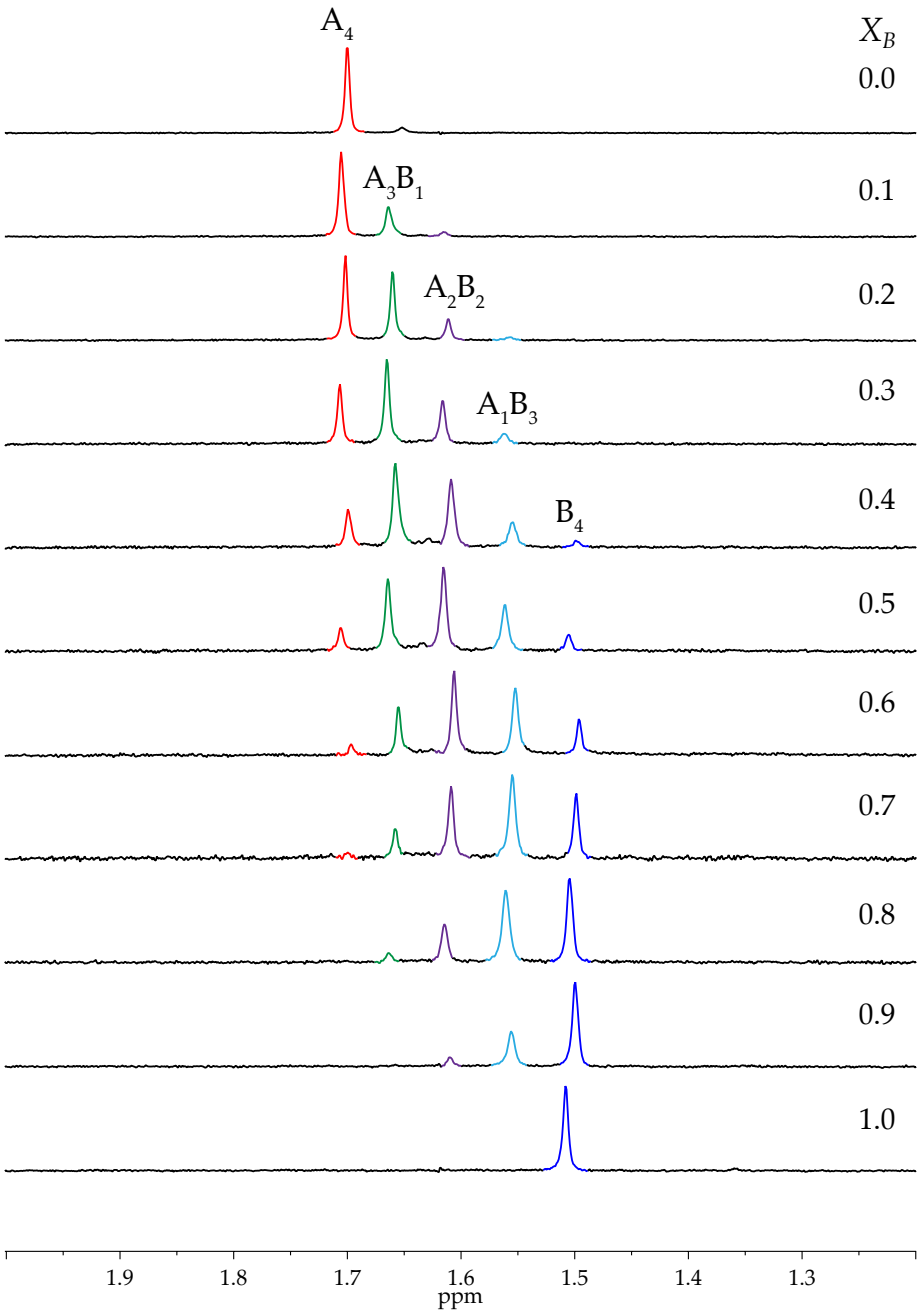


Figure S8. ^{6}Li NMR spectra of 0.10 M solutions of amino alkoxides [^{6}Li]**2b** (**A**) and [^{6}Li]**2a** (**B**) with varying mole fractions of **B** (X_B) in toluene at +60 °C.

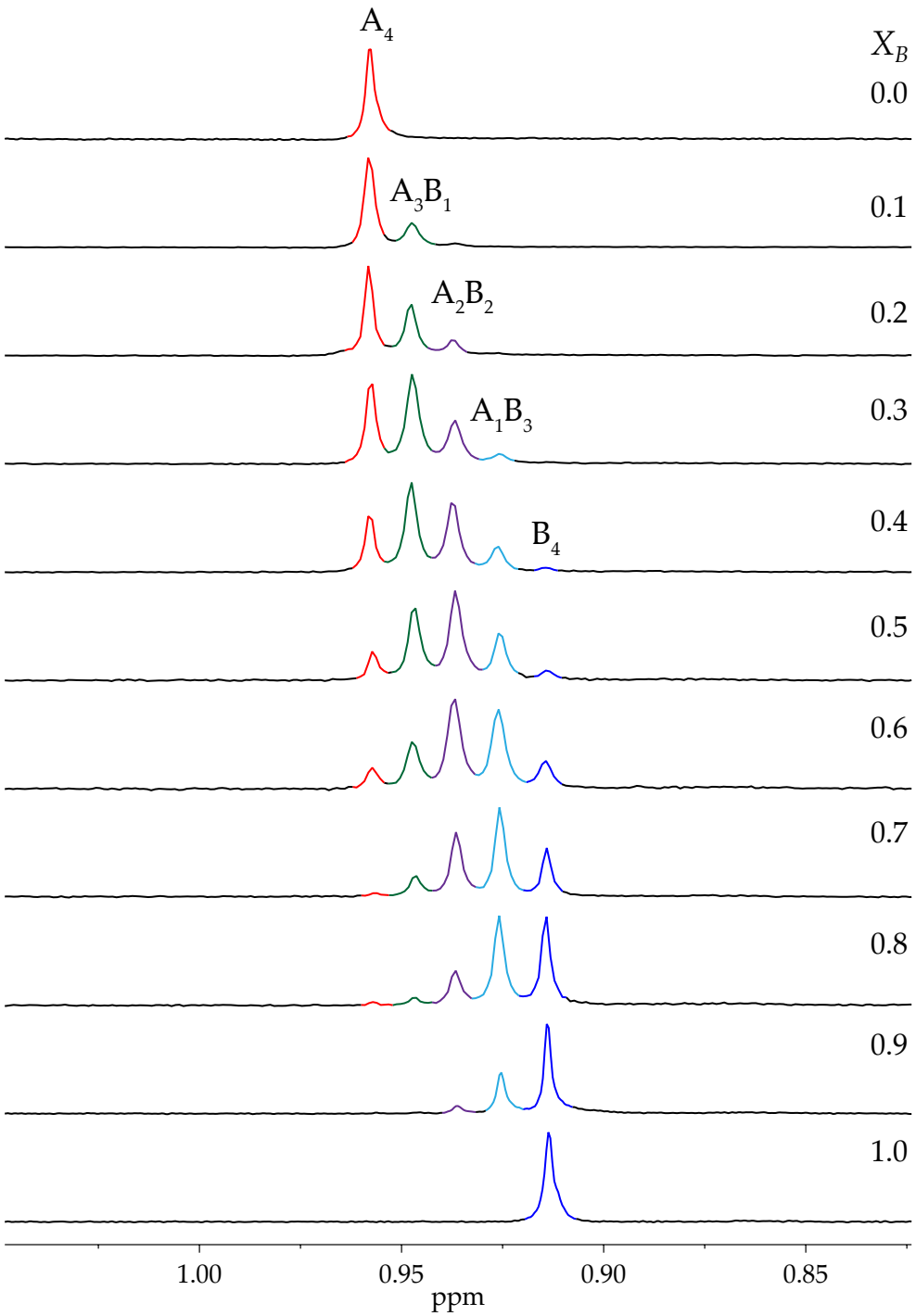


Figure S9. ^{6}Li NMR spectra for 0.10 M solutions of amino alkoxides [^{6}Li]**3a** (**A**) and [^{6}Li]**3b** (**B**) with varying mole fractions of **B** (X_B) in toluene at +60 °C.

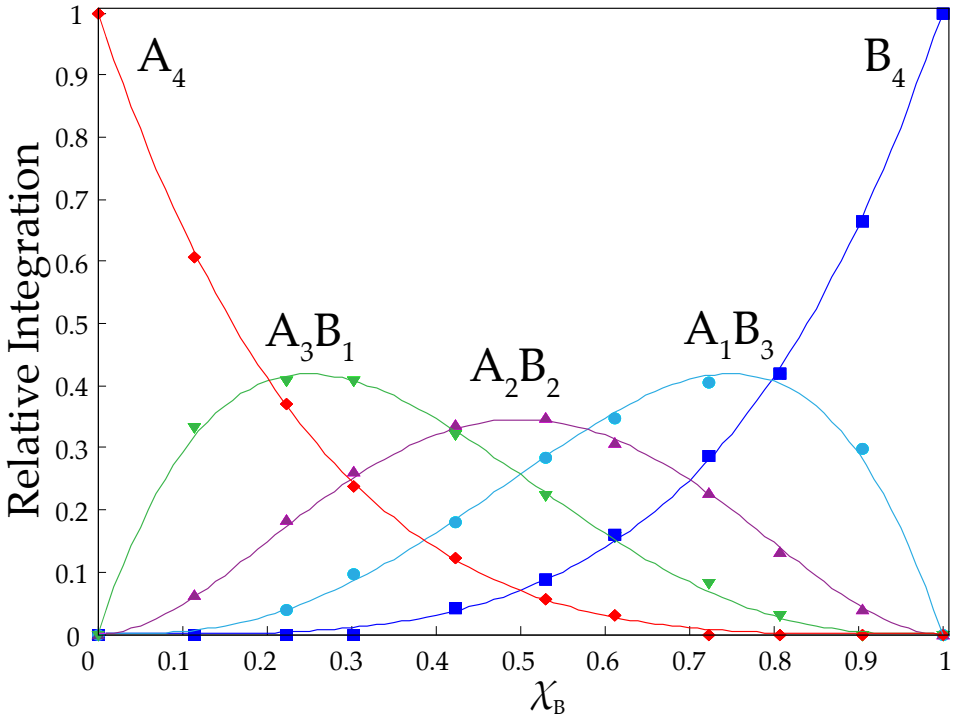


Figure S10. Job plot showing the relative integrals versus measured mole fractions of [^{6}Li]**2a** (X_B) for 0.10 M mixtures of amino alkoxides [^{6}Li]**2b** (**A**) and [^{6}Li]**2a** (**B**) in toluene at +60 °C.

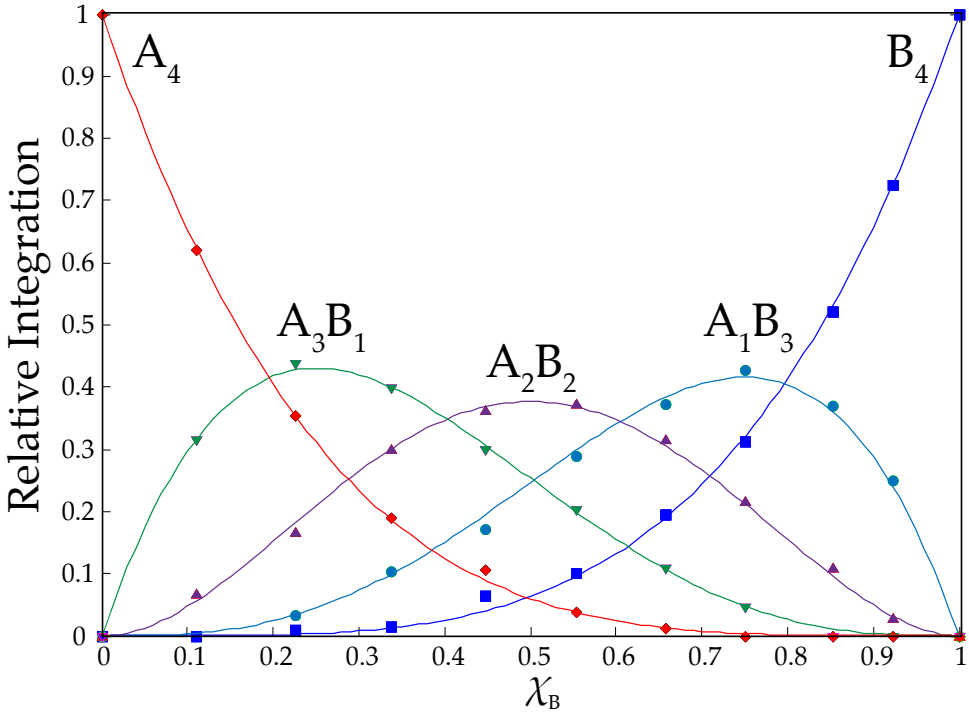


Figure S11. Job plot showing the relative integrals versus measured mole fractions of [^{6}Li]**3b** (X_B) for 0.10 M mixtures of amino alkoxides [^{6}Li]**3a** (**A**) and [^{6}Li]**3b** (**B**) in toluene at +80 °C.

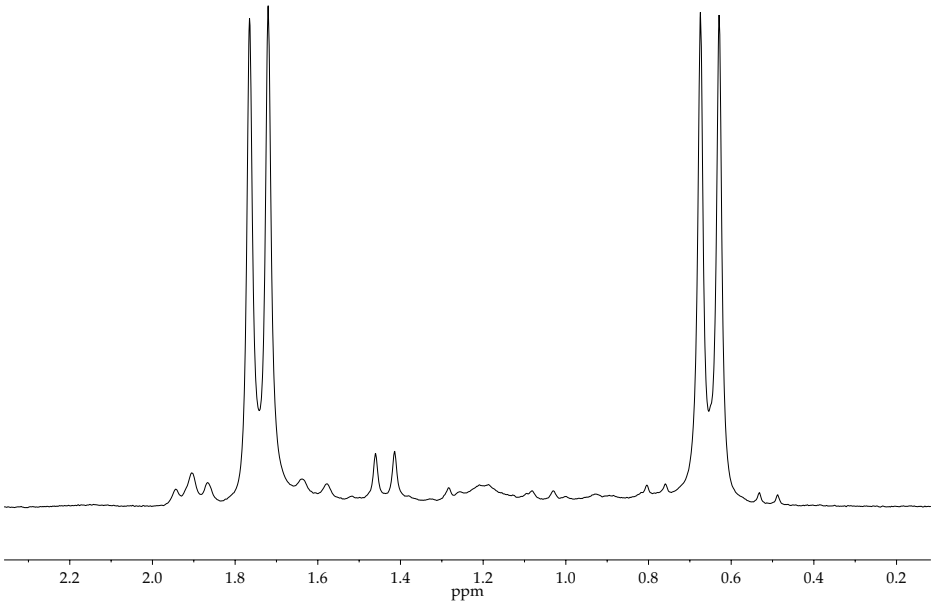


Figure S12. ^{6}Li NMR spectrum of **12b** formed by mixing [^{6}Li,^{15}N]LiHMDS (0.20 M) and **2b** (0.10 M) in d_8-toluene at -80 °C. δ 1.74 (d, $^{2}J_{\text{Li-N}}$ = 4.0 Hz), δ 0.65 (d, $^{2}J_{\text{Li-N}}$ = 4.0 Hz).

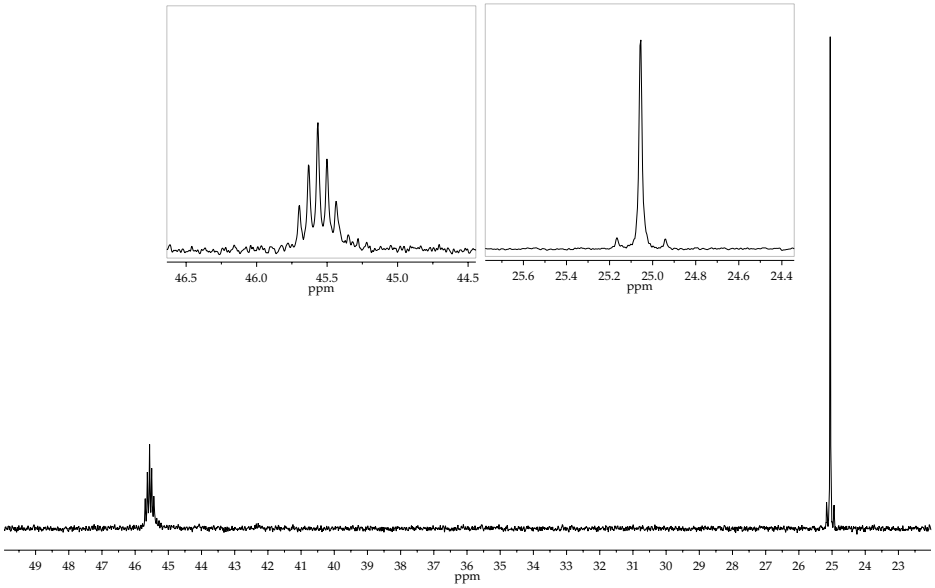


Figure S13. ^{15}N NMR spectrum of **12b** formed by mixing [^{6}Li,^{15}N]LiHMDS (0.20 M) and **2b** (0.10 M) in d_8-toluene at -80 °C. The apparent pentet at δ 45.6 corresponds to the nitrogen in mixed aggregate **12b**, and the singlet at δ 25.1 to free [^{15}N]HMDS.

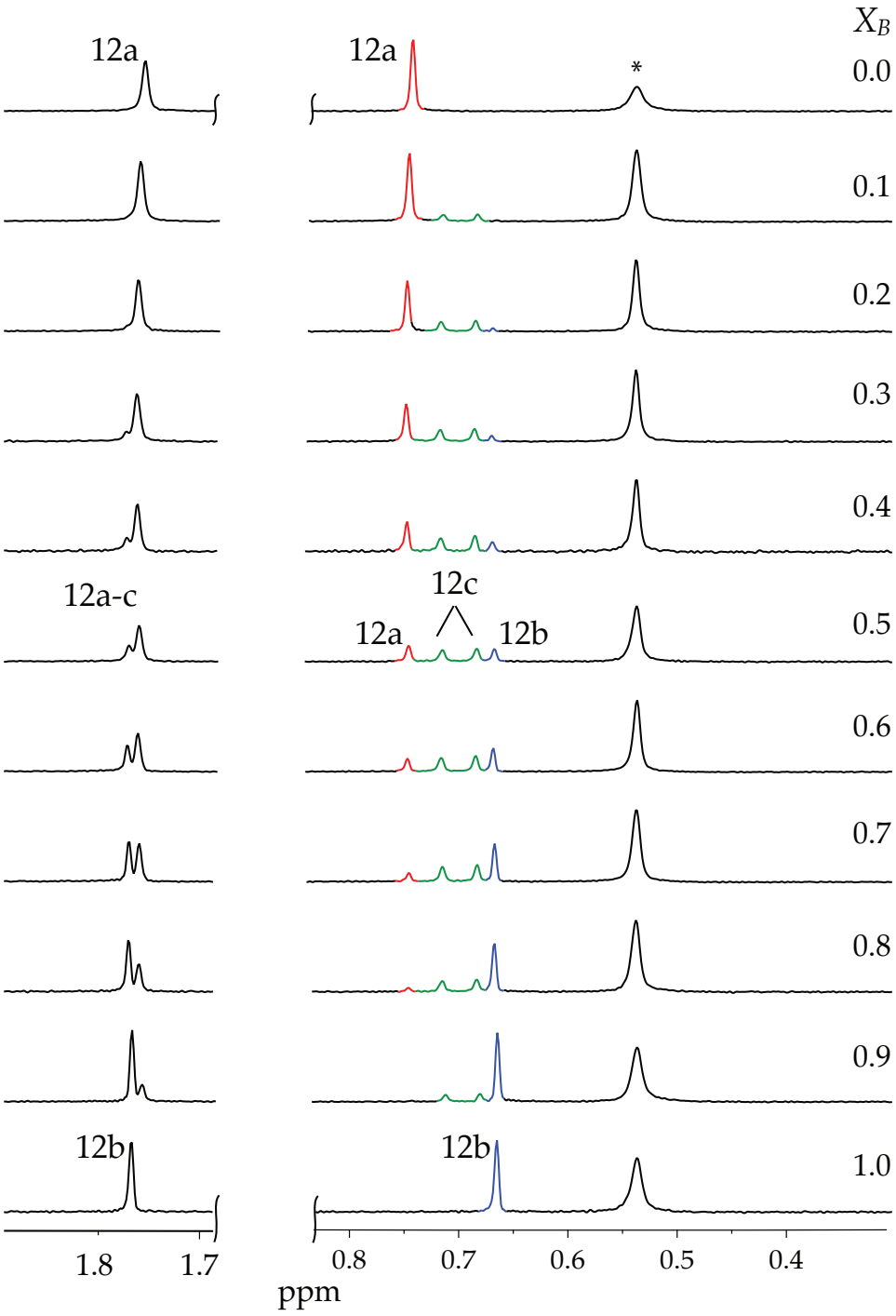


Figure S14. ^{6}Li NMR spectra of a mixture of [^{6}Li]**12a** and [^{6}Li]**12b** at 0.10 M total concentration with 0.20 M additional [^{6}Li]LiHMDS in toluene at -30 °C with varying measured mole fraction of **12b** (X_B). Asterisk (*) denotes excess [^{6}Li]LiHMDS.

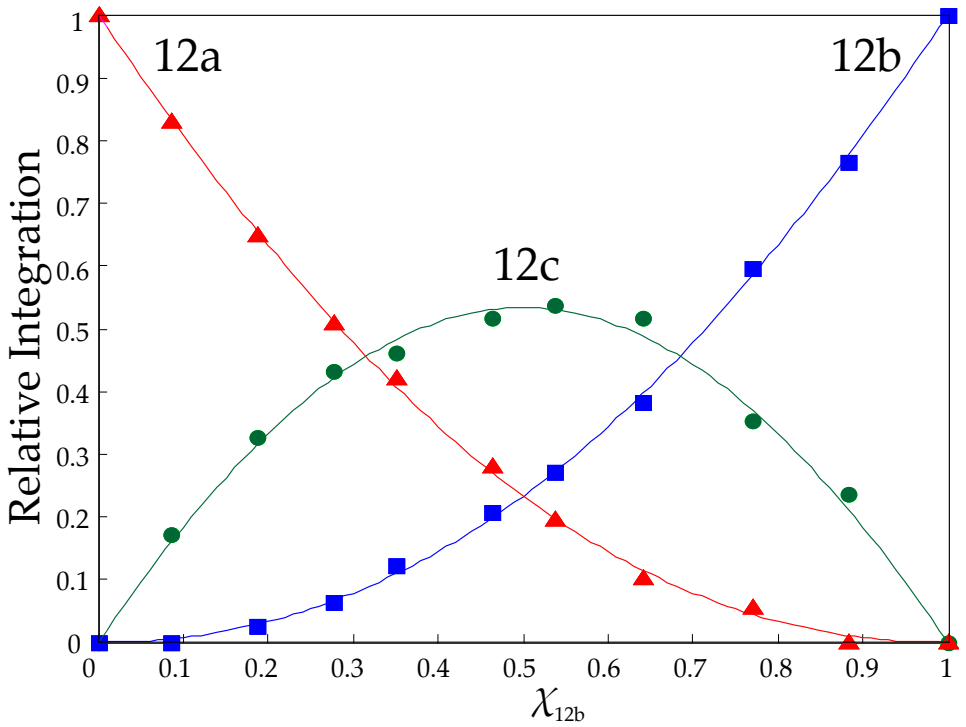


Figure S15. Job plot showing the relative integrals versus measured mole fractions of [^{6}Li]**12b** for 0.10 M mixtures of [^{6}Li]**12a** and [^{6}Li]**12b** with 0.20 M excess [^{6}Li]LiHMDS in toluene at -30 °C.

Part 2: X-Ray Characterization

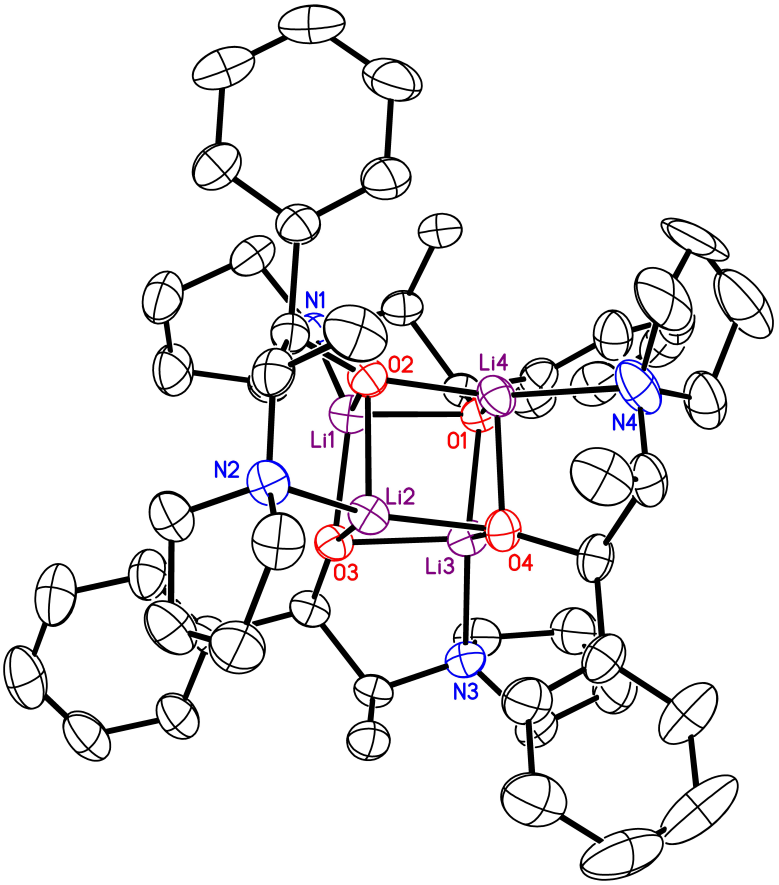


Figure S16. X-ray crystal structure of **2b**. Crystal data: $C_{52}H_{72}Li_4N_4O_4$, FW 844.90, Monoclinic, Space group P2(1), a = 10.6188(7) Å, b = 21.6666(15) Å, c = 21.4263(13) Å, V = 4951.4(6) Å^3, F(000) = 1824, Z = 4, T = 223(2) K, μ = 0.070 mm^{-1}, D_{calc} = 1.133 Mg/m^3, Crystal size 0.50 x 0.25 x 0.03 mm^3, θ = 0.95 to 23.25°, 1222 parameters, GOF = 1.051, wR(F^2) = 0.0738, R_1 = 0.0339 [6463 data with I > 2 σ(I).

Table S1. Crystal data and structure refinement for lithium enolate **2b**.

Identification code	2b	
Empirical formula	C52 H72 Li4 N4 O4	
Formula weight	844.90	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.6188(7) Å	a= 90°.
	b = 21.8666(15) Å	b= 95.593(2)°.
	c = 21.4263(13) Å	g = 90°.
Volume	4951.4(6) $Å^3$	
Z	4	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	1824	
Crystal size	0.50 x 0.25 x 0.03 mm^3	
Theta range for data collection	0.95 to 23.25°.	
Index ranges	-11<=h<=11, -23<=k<=22, -23<=l<=23	
Reflections collected	60393	
Independent reflections	6463 [R(int) = 0.0485]	
Completeness to theta = 23.25°	88.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9983 and 0.9661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6463 / 15 / 1222	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0339, wR2 = 0.0738	
R indices (all data)	R1 = 0.0491, wR2 = 0.0810	
Absolute structure parameter	0(10)	
Largest diff. peak and hole	0.109 and -0.165 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	5290(5)	9001(3)	5021(2)	41(1)
Li(2)	6724(5)	9942(3)	5067(2)	40(1)
Li(3)	5821(4)	9541(3)	6051(2)	38(1)
Li(4)	7494(5)	8932(3)	5583(2)	42(1)
O(1)	5867(2)	8668(1)	5883(1)	38(1)
O(2)	6915(2)	9121(1)	4739(1)	40(1)
O(3)	4914(2)	9820(1)	5256(1)	38(1)
O(4)	7486(2)	9775(1)	5895(1)	38(1)
N(1)	4092(2)	8258(1)	4793(1)	41(1)
N(2)	7406(2)	10232(1)	4173(1)	42(1)
N(3)	4728(2)	10107(1)	6548(1)	40(1)
N(4)	9319(2)	8874(2)	6158(2)	59(1)
C(1)	4567(3)	7872(2)	5334(2)	42(1)
C(2)	5751(3)	7519(2)	5207(2)	56(1)
C(3)	4831(3)	8288(2)	5929(1)	37(1)
C(4)	4880(3)	7893(2)	6509(2)	43(1)
C(5)	5962(4)	7605(2)	6761(2)	62(1)
C(6)	5950(5)	7201(2)	7256(2)	82(1)
C(7)	4820(6)	7092(2)	7517(2)	81(2)
C(8)	3762(5)	7385(2)	7292(2)	69(1)
C(9)	3777(4)	7776(2)	6787(2)	54(1)
C(10)	4045(3)	7953(2)	4177(2)	54(1)
C(11)	3220(4)	8367(2)	3752(2)	70(1)
C(12)	2223(4)	8581(2)	4161(2)	71(1)
C(13)	2765(3)	8445(2)	4828(2)	52(1)
C(14)	7837(3)	9652(2)	3905(2)	46(1)
C(15)	9229(3)	9513(2)	4100(2)	69(1)

C(16)	6971(3)	9129(2)	4096(2)	38(1)
C(17)	7363(3)	8511(2)	3851(2)	44(1)
C(18)	8114(4)	8110(2)	4217(2)	61(1)
C(19)	8415(4)	7540(2)	3998(2)	76(1)
C(20)	7964(5)	7346(2)	3414(2)	77(1)
C(21)	7228(4)	7742(2)	3036(2)	71(1)
C(22)	6938(3)	8314(2)	3252(2)	57(1)
C(23)	6291(3)	10484(2)	3804(2)	56(1)
C(24)	6143(4)	11123(2)	4054(2)	69(1)
C(25)	7490(4)	11312(2)	4277(2)	72(1)
C(26)	8299(3)	10748(2)	4181(2)	60(1)
C(27)	4161(3)	10503(2)	6032(2)	38(1)
C(28)	5049(3)	11016(2)	5893(2)	48(1)
C(29)	3834(3)	10102(2)	5443(2)	38(1)
C(30)	3086(3)	10453(2)	4907(2)	41(1)
C(31)	3183(3)	10275(2)	4299(2)	59(1)
C(32)	2512(4)	10566(3)	3798(2)	79(1)
C(33)	1732(4)	11052(2)	3897(3)	78(1)
C(34)	1611(4)	11228(2)	4490(2)	71(1)
C(35)	2276(3)	10935(2)	4996(2)	60(1)
C(36)	5317(3)	10447(2)	7097(2)	53(1)
C(37)	5523(4)	9963(2)	7605(2)	69(1)
C(38)	4523(4)	9480(2)	7429(2)	71(1)
C(39)	3801(3)	9715(2)	6829(2)	54(1)
C(40)	9626(3)	9519(2)	6307(2)	53(1)
C(41)	10271(3)	9833(2)	5791(2)	68(1)
C(42)	8368(3)	9857(2)	6408(1)	43(1)
C(43)	8631(3)	10519(2)	6576(2)	49(1)
C(44)	8459(3)	10979(2)	6138(2)	56(1)
C(45)	8685(4)	11590(2)	6298(3)	81(1)
C(46)	9089(5)	11737(3)	6910(4)	106(2)
C(47)	9285(6)	11289(4)	7350(3)	119(2)
C(48)	9051(4)	10684(3)	7184(2)	85(2)
C(49)	8910(20)	8604(8)	6803(10)	64(5)
C(50)	9501(10)	7955(6)	6779(10)	112(6)
C(51)	9932(11)	7863(5)	6177(7)	82(4)

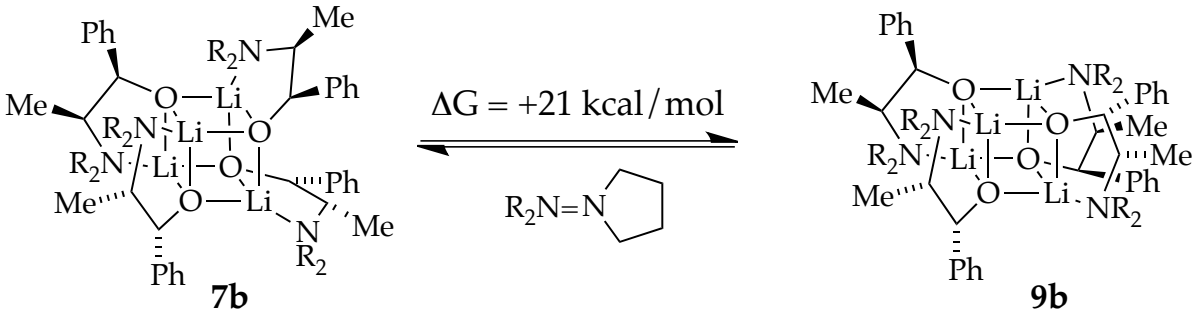
C(52)	10345(10)	8507(5)	6053(7)	77(3)
C(49A)	9080(30)	8439(12)	6609(12)	62(5)
C(50A)	9091(16)	7795(5)	6344(8)	75(5)
C(51A)	10131(9)	7864(4)	5859(7)	57(3)
C(52A)	10392(8)	8539(4)	5802(6)	43(3)
Li(1')	2559(5)	9533(3)	909(3)	43(1)
Li(2')	572(5)	8924(3)	846(2)	42(1)
Li(3')	1766(5)	9062(3)	-135(3)	44(1)
Li(4')	587(4)	9943(3)	272(2)	40(1)
O(1')	2274(2)	9895(1)	54(1)	41(1)
O(2')	913(2)	9778(1)	1155(1)	42(1)
O(3')	2252(2)	8702(1)	689(1)	41(1)
O(4')	-64(2)	9132(1)	3(1)	39(1)
N(1')	4325(2)	10038(1)	1016(1)	48(1)
N(2')	-344(2)	8717(1)	1659(1)	44(1)
N(3')	2606(2)	8261(1)	-513(1)	45(1)
N(4')	-877(3)	10345(1)	-293(1)	49(1)
C(1')	4407(3)	10246(2)	357(2)	45(1)
C(2')	4981(3)	9775(2)	-47(2)	56(1)
C(3')	3056(3)	10406(2)	63(2)	38(1)
C(4')	3119(3)	10709(2)	-566(2)	43(1)
C(5')	2709(3)	10418(2)	-1119(2)	53(1)
C(6')	2744(4)	10703(2)	-1695(2)	66(1)
C(7')	3228(4)	11279(3)	-1723(2)	77(1)
C(8')	3665(4)	11573(2)	-1184(3)	78(1)
C(9')	3603(3)	11300(2)	-609(2)	61(1)
C(10')	4194(4)	10562(2)	1442(2)	61(1)
C(11')	4433(5)	10294(2)	2091(2)	79(1)
C(12')	5247(4)	9734(2)	2008(2)	72(1)
C(13')	5451(3)	9724(2)	1311(2)	62(1)
C(14')	-24(3)	9288(2)	2011(2)	45(1)
C(15')	1258(3)	9259(2)	2390(2)	61(1)
C(16')	-72(3)	9819(2)	1535(1)	39(1)
C(17')	-177(3)	10436(2)	1843(2)	43(1)
C(18')	686(4)	10895(2)	1783(2)	63(1)
C(19')	521(4)	11474(2)	2034(2)	81(1)

C(20')	-506(5)	11584(2)	2358(2)	77(1)
C(21')	-1390(5)	11135(3)	2409(2)	82(1)
C(22')	-1219(4)	10571(2)	2165(2)	69(1)
C(23')	-61(3)	8145(2)	2014(2)	58(1)
C(24')	-780(4)	7665(2)	1617(2)	72(1)
C(25')	-1993(4)	7992(2)	1353(2)	68(1)
C(26')	-1718(3)	8665(2)	1465(2)	58(1)
C(27')	3222(3)	7957(2)	51(2)	45(1)
C(28')	4593(3)	8152(2)	215(2)	59(1)
C(29')	2425(3)	8081(2)	607(2)	41(1)
C(30')	2970(3)	7753(2)	1198(2)	42(1)
C(31')	3571(3)	8072(2)	1694(2)	55(1)
C(32')	4057(4)	7776(2)	2233(2)	67(1)
C(33')	3942(4)	7156(3)	2290(2)	73(1)
C(34')	3353(4)	6829(2)	1803(2)	79(1)
C(35')	2874(4)	7131(2)	1263(2)	63(1)
C(36')	1496(4)	7910(2)	-793(2)	64(1)
C(37')	1209(4)	8154(2)	-1449(2)	73(1)
C(38')	2385(4)	8506(2)	-1588(2)	73(1)
C(39')	3359(4)	8327(2)	-1051(2)	66(1)
C(40')	-1311(3)	9817(2)	-694(2)	45(1)
C(41')	-494(4)	9718(2)	-1229(2)	65(1)
C(42')	-1291(3)	9247(2)	-268(2)	39(1)
C(45')	-2162(4)	7586(2)	-587(2)	66(1)
C(46')	-3027(4)	7611(2)	-1106(2)	67(1)
C(47')	-3364(3)	8170(2)	-1357(2)	67(1)
C(48')	-2814(3)	8702(2)	-1099(2)	55(1)
C(43')	-1903(3)	8685(2)	-590(2)	42(1)
C(44')	-1603(3)	8113(2)	-340(2)	52(1)
C(49')	-493(4)	10896(2)	-628(2)	65(1)
C(50')	-373(4)	11368(2)	-108(2)	79(1)
C(51')	-1434(4)	11211(2)	299(2)	75(1)
C(52')	-1877(3)	10582(2)	77(2)	59(1)

Part 3: DFT Computations

Geometries are optimized at the B3LYP level of theory using the 6-31G(d) basis set. Numbers above equilibrium arrows are ΔG_{MP2}. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation. [i.e. $G_{MP2} = (E_{HF} + E2 + \text{thermal correction})$]

a)



b)

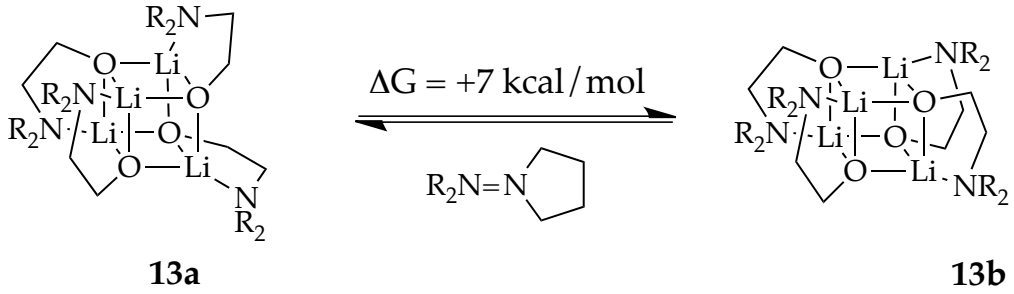
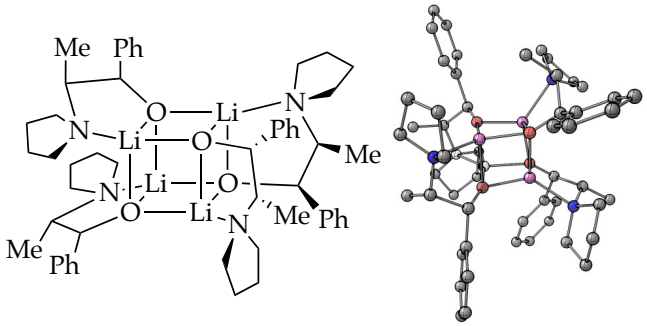


Figure S17.
Comparison of the relative free energies (ΔG_{MP2}, kcal/mol) at -78 °C of a) observed S_4 core pyrrolidinyl ephedrate **7b** and unobserved D_{2d} core structure **9b**, and b) analogous unsubstituted S_4 core **13a** and D_{2d} core **13b**.

Table S3. Optimized geometries, coordinates and energies for observed S_4 core tetramer **7b**.

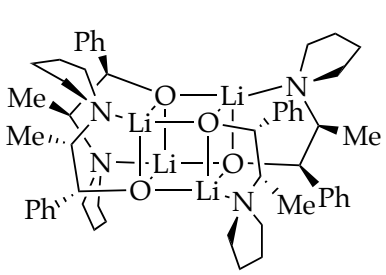


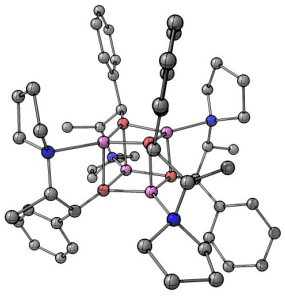
G = -2574.184593 Hartree
G_{MP2} = -2565.598563 Hartree

Atom	X	Y	Z	Atom	X	Y	Z
Li	0.841170	1.046029	-0.412403	H	4.343868	1.335696	-1.925817
Li	-1.042599	0.383821	1.210918	H	3.682964	1.346559	-0.294504
O	0.929614	0.289166	1.353827	C	2.700831	4.070609	-1.033620
Li	0.622382	-1.387823	0.422334	H	0.799794	3.410965	-1.923421
O	-1.343876	-1.360187	0.436360	H	2.143886	3.589491	-3.066918
Li	-1.094105	-0.371657	-1.191787	H	4.669047	3.506021	-0.196860
O	0.822351	-0.624707	-1.403988	H	4.624451	3.691718	-1.955584
C	1.684324	-0.546783	-2.489739	H	2.255273	3.988006	-0.034198
C	1.929813	0.955207	-2.919584	H	2.764463	5.133185	-1.288399
O	-1.069629	1.465685	-0.454728	N	2.253704	1.860422	-1.783194
C	-1.685766	2.168851	-1.481899	C	1.276449	-4.399412	1.638646
C	-3.010679	1.471939	-1.949113	C	0.698731	-4.136621	-0.640083
H	-3.479142	2.100043	-2.728892	C	2.586815	-4.514287	0.865852
C	-1.822427	-2.642969	0.209838	H	0.860804	-5.405894	1.832609
C	-1.046788	-3.709863	1.059538	H	1.386769	-3.891030	2.600330
H	-1.411345	-4.709608	0.753505	C	2.116411	-4.756973	-0.581424
C	1.293822	1.099762	2.419989	H	0.633271	-3.317998	-1.361762
C	0.445694	0.774651	3.700964	H	-0.043877	-4.898734	-0.927458
H	0.760621	1.462330	4.507512	H	3.144235	-3.574029	0.930531
C	-1.976509	0.412011	4.294408	H	3.229955	-5.312748	1.250015
C	-1.314060	2.484808	3.525270	H	2.793327	-4.312287	-1.314122
C	-3.293680	1.148174	3.991738	H	2.064380	-5.831309	-0.790216
H	-1.694076	0.564674	5.351874	N	0.400563	-3.622943	0.733581
H	-2.037460	-0.663456	4.114161	C	-3.822509	-0.755752	-2.752937
C	-2.848384	2.545950	3.480021	C	-2.103509	0.264593	-3.918496
H	-0.828729	3.071338	2.742859	C	-3.286339	-1.855090	-3.685314
H	-0.944693	2.862794	4.497092	H	-4.654940	-0.215950	-3.240530
H	-3.864267	0.619919	3.221324	H	-4.180397	-1.144234	-1.798962
H	-3.928547	1.205159	4.881242	C	-2.125229	-1.173775	-4.460805
H	-3.202002	2.719931	2.459533	H	-1.100371	0.696168	-3.898956
H	-3.229974	3.363160	4.099849	H	-2.739026	0.923347	-4.539622
N	-0.989237	1.046949	3.392300	H	-2.919572	-2.705793	-3.102573
C	3.658419	1.863868	-1.257177	H	-5.905160	-4.867521	-0.483983
C	1.877907	3.274944	-2.043486	H	-7.168878	-3.297929	0.979029
C	4.052323	3.344370	-1.086183	C	2.789967	1.073821	2.754596
N	-2.669667	0.153320	-2.555338	C	3.405323	2.203265	3.311608
H	0.933086	1.291685	-3.234128	C	3.576101	-0.064001	2.533005

H	1.072849	2.161305	2.185020
H	-1.646907	-2.936634	-0.846730
H	-1.035405	2.178203	-2.380628
H	1.214545	-0.981580	-3.396834
C	-1.945357	3.652278	-1.185587
C	-2.302414	4.536408	-2.215807
C	-1.814056	4.165375	0.106545
C	-2.539207	5.886145	-1.955631
H	-2.387567	4.167419	-3.236551
C	-2.049122	5.516552	0.374971
H	-1.514437	3.482834	0.891533
C	-2.416718	6.382608	-0.655035
H	-2.813974	6.552963	-2.769461
H	-1.941447	5.892849	1.389844
H	-2.598449	7.434622	-0.450765
C	-3.999202	1.335459	-0.789151
H	-4.127956	2.310492	-0.309056
H	-4.983394	0.999445	-1.128456
H	-3.633196	0.627510	-0.042075
C	-1.329263	-3.554177	2.554199
H	-1.033045	-2.565727	2.909707
H	-2.401632	-3.669641	2.732983
H	-0.814668	-4.310599	3.153402
C	-3.332106	-2.808157	0.421603
C	-4.056931	-1.932944	1.237574
C	-4.021400	-3.863900	-0.192607
C	-5.427890	-2.106425	1.440124
H	-3.528938	-1.110404	1.708666
C	-5.391207	-4.044029	0.005991
H	-3.478936	-4.551060	-0.839966
C	-6.101243	-3.163708	0.825516
H	-5.972177	-1.412802	2.076928
C	4.761658	2.198733	3.643186
H	2.813979	3.101728	3.481812
C	4.932898	-0.075901	2.863647
H	3.111457	-0.942219	2.095828
C	5.532122	1.056052	3.419933
H	5.217292	3.089092	4.069796
H	5.524013	-0.971845	2.687852
H	6.589136	1.049211	3.672978
C	0.700844	-0.653111	4.183241
H	0.105680	-0.908109	5.064534
H	0.489139	-1.374818	3.392024
H	1.753847	-0.755872	4.459449
H	-4.072434	-2.231083	-4.347237
H	-1.173554	-1.675497	-4.256660
H	-2.273786	-1.187006	-5.545031
C	2.855066	1.091562	-4.141241
H	2.467772	0.491510	-4.972814
H	2.909950	2.129671	-4.486871
H	3.872275	0.744461	-3.938769
C	2.982076	-1.343760	-2.299105
C	3.655818	-1.373397	-1.071182
C	3.531708	-2.070252	-3.365266
C	4.856412	-2.070272	-0.923611
H	3.236339	-0.835937	-0.227291
C	4.726893	-2.779249	-3.222609
H	3.013488	-2.084122	-4.322191
C	5.399689	-2.776202	-1.999611
H	5.368810	-2.060043	0.035577
H	5.129043	-3.336083	-4.065611
H	6.332091	-3.322815	-1.884097

Table S4. Optimized geometries, coordinates and energies at the B3LYP level of theory with 6-31G(d) basis set for unobserved D_{2d} core tetramer **9b**.



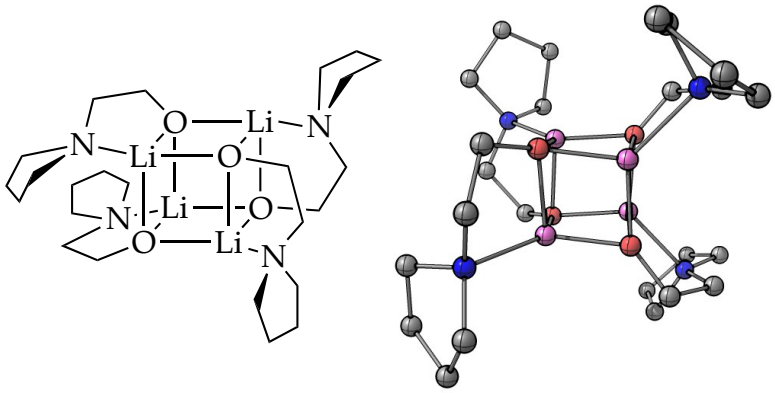


G = -2574.158243 Hartree
G_{MP2} = -2565.564775 Hartree

Atom	X	Y	Z	Atom	X	Y	Z
Li	0.653718	0.707339	-1.117836	C	1.491132	3.150891	-3.468372
Li	-0.653704	0.706364	1.118512	H	-0.322499	1.916048	-3.702389
O	1.265338	0.889929	0.690588	H	0.855514	1.767930	-5.022967
Li	1.136432	-1.099835	0.565175	H	3.151163	2.865308	-2.063061
O	-0.673091	-1.222092	1.290804	H	3.692583	3.092216	-3.725125
Li	-1.136607	-1.099181	-0.566151	H	0.998665	3.585026	-2.592267
O	0.672929	-1.220935	-1.291924	H	1.503107	3.919055	-4.247620
C	1.016268	-1.698751	-2.549296	N	1.408836	0.786243	-3.197718
C	0.936914	-0.561268	-3.638907	C	3.889570	-2.296403	1.150981
O	-1.265295	0.890715	-0.689734	C	2.874857	-1.611299	3.093064
C	-2.225425	1.128548	-1.654076	C	4.992695	-2.479328	2.214869
C	-3.469469	0.179847	-1.499737	H	4.253636	-2.074140	0.149765
H	-4.181527	0.420890	-2.305623	H	3.294626	-3.214975	1.074045
C	2.225548	1.126792	1.655091	C	4.274150	-2.122341	3.542284
C	3.469428	0.178012	1.499898	H	2.133946	-2.415246	3.179218
H	4.181578	0.418289	2.305931	H	2.515239	-0.769635	3.688106
C	-1.016424	-1.701049	2.547742	H	5.399987	-3.495437	2.210122
C	-0.936968	-0.564576	3.638392	H	5.827329	-1.794390	2.027323
H	0.145801	-0.412000	3.720942	H	4.177352	-2.985684	4.208543
C	-2.843330	1.112236	3.332416	H	4.821078	-1.351957	4.095543
C	-0.745604	1.887776	3.933063	N	2.983552	-1.236585	1.659469
C	-2.912186	2.635820	3.108648	C	-3.889958	-2.294794	-1.152816
H	-3.218331	0.862809	4.339288	C	-2.875134	-1.608258	-3.094339
H	-3.437244	0.562336	2.603589	C	-4.993082	-2.476756	-2.216877
C	-1.491072	3.147746	3.471227	H	-4.254028	-2.073269	-0.151438
H	0.322529	1.912637	3.704104	H	-3.295130	-3.213499	-1.076577
H	-0.855459	1.763381	5.024576	C	-4.274496	-2.118722	-3.543989
H	-3.151246	2.863518	2.065806	H	-2.134346	-2.412251	-3.181133
H	-3.692497	3.088888	3.728132	H	-2.515373	-0.766166	-3.688690
H	-0.998645	3.582608	2.595460	H	-5.400442	-3.492842	-2.212976
H	-1.502958	3.915243	4.251134	H	-5.827675	-1.791921	-2.028778
N	-1.408858	0.783352	3.198457	H	-4.177823	-2.981499	-4.211001
C	2.843322	1.115219	-3.331330	H	-4.821321	-1.347781	-4.096573
C	0.745638	1.891353	-3.931346	N	-2.983799	-1.234691	-1.660443
C	2.912199	2.638590	-3.106140	H	-0.145845	-0.408573	-3.721370
H	3.218350	0.866722	-4.338421	H	-0.231871	-2.398964	2.913144
H	3.437204	0.564638	-2.602994	H	1.822433	0.889143	2.661775
H	-1.822311	0.891669	-2.660942	H	2.489576	-1.207627	-5.075082

H	0.231688	-2.396283	-2.915365
C	4.174803	0.401785	0.165173
H	3.559178	0.033938	-0.658267
H	4.344663	1.472476	0.018798
H	5.148017	-0.097208	0.122730
C	2.665664	2.596005	1.747309
C	3.479550	3.046234	2.798343
C	2.231418	3.531304	0.801501
C	3.866291	4.383705	2.887974
H	3.808887	2.345446	3.563610
C	2.614719	4.872827	0.887042
H	1.575727	3.188946	0.007708
C	3.437626	5.303983	1.928043
H	4.497773	4.709432	3.711226
H	2.263743	5.582394	0.141247
H	3.735396	6.347085	1.997760
C	2.261218	-2.605922	-2.480729
C	2.042769	-3.904569	-1.986660
C	3.575922	-2.266122	-2.823948
C	3.082319	-4.819202	-1.831585
H	1.028633	-4.196516	-1.720542
C	4.626476	-3.179803	-2.677592
H	3.801936	-1.286871	-3.225503
C	4.387405	-4.458936	-2.178884
H	2.873784	-5.816850	-1.452199
H	5.633772	-2.885880	-2.963632
H	5.202717	-5.169682	-2.071262
C	1.414347	-1.021095	-5.027901
H	0.914837	-1.962055	-5.285954
H	1.159870	-0.293077	-5.806092
C	-1.414350	-1.025652	5.026990
H	-0.914861	-1.966866	5.284160
H	-1.159807	-0.298354	5.805832
H	-2.489583	-1.212189	5.074057
C	-2.261422	-2.608093	2.478370
C	-2.043059	-3.906268	1.983023
C	-3.576090	-2.268572	2.822003
C	-3.082658	-4.820706	1.827126
H	-1.028953	-4.197997	1.716552
C	-4.626691	-3.182066	2.674825
H	-3.802037	-1.289703	3.224527
C	-4.387707	-4.460723	2.174858
H	-2.874189	-5.817994	1.446757
H	-5.633957	-2.888379	2.961214
H	-5.203055	-5.171330	2.066595
C	-2.665282	2.597914	-1.745081
C	-3.479063	3.049159	-2.795760
C	-2.230891	3.532351	-0.798486
C	-3.865569	4.386772	-2.884290
H	-3.808504	2.349065	-3.561616
C	-2.613957	4.874012	-0.882922
H	-1.575275	3.189221	-0.004965
C	-3.436764	5.306177	-1.923585
H	-4.496973	4.713293	-3.707286
H	-2.262875	5.582898	-0.136530
H	-3.734350	6.349389	-1.992441
C	-4.174901	0.402674	-0.164885
H	-3.559330	0.034223	0.658323
H	-4.344723	1.473268	-0.017753
H	-5.148141	-0.096301	-0.122845

Table S5. Optimized geometries, coordinates and energies at the B3LYP level of theory with 6-31G(d) basis set for unsubstituted S_4 core tetramer **13a**.

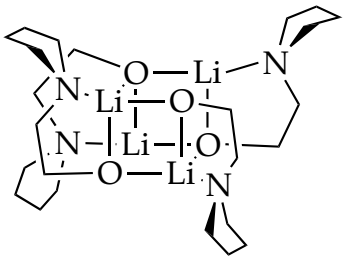


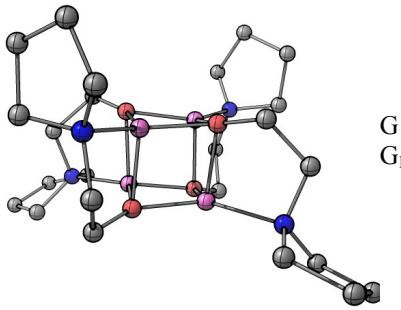
G = -1493.16961 Hartree
G_{MP2} = -1488.098718 Hartree

Atom	X	Y	Z	Atom	X	Y	Z
Li	0.066950	-0.694590	1.293791	H	-3.538680	0.230250	1.314494
Li	1.432836	-0.166526	-0.772256	H	2.620757	1.960899	2.050245
O	1.281372	0.755823	1.007120	H	3.263212	2.102795	-0.292531
Li	-0.214339	1.531845	0.127754	H	-3.066399	-0.946539	3.423497
O	0.063531	0.778220	-1.697593	H	-2.423976	1.154038	2.319981
Li	-1.052418	-0.588095	-0.968048	H	1.164017	-3.577028	-0.873196
O	-1.564328	0.270218	0.655001	H	0.139858	-2.512077	-2.821140
C	-2.491837	0.247761	1.681692	H	0.487390	1.689642	-3.520329
C	-2.334544	-0.985620	2.591790	H	1.246272	3.228057	-1.796359
O	0.443666	-1.721815	-0.262460	C	-0.573185	-0.105327	4.095505
C	0.223159	-3.006745	-0.727755	C	-0.732095	-2.406780	3.804027
C	-0.500830	-3.016924	-2.087420	C	0.708754	-0.671317	4.738244
H	-0.661833	-4.056528	-2.436622	H	-1.368553	0.020420	4.854180
C	-0.142763	1.794912	-2.613768	H	-0.414715	0.857901	3.604162
C	0.174295	3.184707	-2.028397	C	0.622937	-2.207391	4.502322
H	-0.040592	3.976333	-2.774110	H	-0.739995	-3.236175	3.089039
C	2.564431	1.032589	1.445683	H	-1.527863	-2.594497	4.549589
C	3.558418	1.215632	0.282639	H	1.596377	-0.254573	4.253282
H	4.580361	1.393275	0.673962	H	0.764733	-0.414192	5.800525
C	4.339752	0.309180	-1.867386	H	1.438475	-2.542530	3.853229
C	4.108093	-1.170569	-0.089987	H	0.686284	-2.783226	5.430696
C	4.439046	-1.080322	-2.517856	N	-0.965253	-1.130321	3.108749
H	5.346772	0.689000	-1.610328	C	-0.104989	4.668304	-0.086533
H	3.851594	1.057306	-2.500741	C	-2.002619	3.628281	-0.932489
C	4.326467	-2.070350	-1.322378	C	-1.176178	4.900447	0.992766
H	3.421549	-1.606134	0.640201	H	-0.077735	5.520101	-0.792140
H	5.068814	-0.964429	0.418369	H	0.904238	4.534931	0.316841
H	3.614613	-1.231573	-3.222398	C	-2.454375	4.226986	0.413339
H	5.372073	-1.196899	-3.077740	H	-2.488195	2.676405	-1.160972
H	3.477087	-2.746346	-1.457789	H	-2.210239	4.329857	-1.762397
H	5.221666	-2.689122	-1.206519	H	-0.882431	4.423248	1.933402
N	3.548751	0.076416	-0.647717	H	-1.315458	5.966375	1.197561
H	-2.668896	-2.972916	-0.252718	H	-2.811615	3.437494	1.081250
H	-2.938901	-4.017751	-1.665325	H	-3.276243	4.936481	0.276017
H	-3.814412	-0.450820	-3.042188	N	-0.547553	3.443280	-0.772886
H	-4.466878	-1.853965	-3.887498	C	-2.341414	-2.021525	-3.384776

H	-4.324838	-1.393436	-0.977196	C	-2.860062	-2.966336	-1.329110
H	-5.002970	-2.822439	-1.758807	C	-3.776075	-1.543488	-3.097657
N	-1.773974	-2.278966	-2.049896	H	-2.357883	-2.950693	-3.984976
H	-2.550875	-1.885225	2.001127	H	-1.730355	-1.286708	-3.918360
H	2.955578	0.231512	2.108119	C	-4.122257	-2.174187	-1.716942
H	-1.188168	1.808143	-2.987364				
H	-0.372613	-3.610488	-0.011362				

Table S6. Optimized geometries, coordinates and energies with 6-31G(d) basis set for unsubstituted D_{2d} core tetramer **13b**.



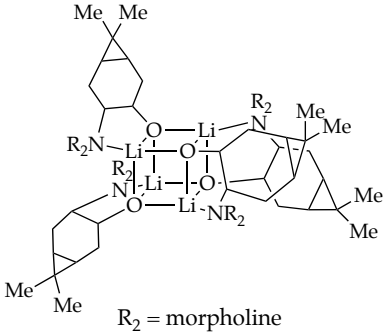


G = -1493.158199 Hartree
G_{MP2} = -1488.087406 Hartree

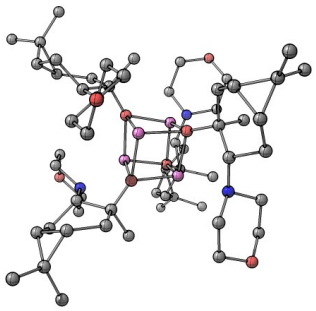
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.035758	1.250456	0.793171	C	-3.692535	-0.430867	0.183822
Li	-0.035613	-1.250942	0.792414	H	-4.751687	-0.260469	0.450574
O	1.432165	-0.029686	0.963734	C	2.771796	-0.204505	1.246377
Li	1.253162	-0.032524	-1.038260	C	3.692682	0.430047	0.184082
O	-0.034228	-1.427976	-1.197798	H	4.751803	0.259288	0.450715
Li	-1.253199	0.032448	-1.038272	C	-0.120350	-2.774819	-1.497050
O	0.034116	1.427818	-1.197255	C	0.552774	-3.652906	-0.423501
C	0.119148	2.774659	-1.496758	H	1.622532	-3.410826	-0.402845
C	-0.553848	3.652362	-0.422818	C	-1.319977	-3.938934	1.171997
O	-1.432115	0.028977	0.963729	C	0.845300	-3.976901	2.002201
C	-2.771780	0.203178	1.246569	C	-1.493497	-3.829588	2.697843
H	-1.368733	-4.996014	0.847773	H	-0.367514	3.034027	-2.459425
H	-2.074100	-3.381832	0.610075	H	3.071370	0.244297	2.216524
C	-0.040530	-3.859316	3.255594	H	3.521958	1.512969	0.189220
H	1.797044	-3.442468	2.086188	H	-0.458300	4.726718	-0.679039
H	1.069633	-5.038409	1.785286	H	1.172585	3.110068	-1.606526
H	-1.986889	-2.888517	2.959851	H	-3.071193	-0.246467	2.216381
H	-2.111393	-4.644154	3.088296	H	-3.521619	-1.513762	0.188219
H	0.182025	-2.935443	3.798828	H	5.782749	0.437847	-3.443784
H	0.129132	-4.692546	3.944419	H	6.108245	0.922114	-1.781517
N	0.026174	-3.392073	0.926451	H	5.677088	-1.848754	-2.744699
C	1.319910	3.938778	1.171333	H	6.117790	-1.319814	-1.125364
C	-0.844842	3.976923	2.002935	N	3.371889	-0.044953	-1.186063
C	1.494386	3.830210	2.697145	C	-3.970864	-0.794532	-2.245868
H	1.368485	4.995694	0.846562	C	-3.945060	1.381001	-1.472226
H	2.073674	3.381387	0.609219	C	-5.438040	-0.326108	-2.410897
C	0.041757	3.859583	3.255787	H	-3.866088	-1.854328	-1.998089
H	-1.796565	3.442569	2.087642	H	-3.413024	-0.614486	-3.174309

H	-1.069253	5.038393	1.785904	C	-5.409390	1.153890	-1.942079
H	1.988392	2.889515	2.959349	H	-3.355370	1.839003	-2.275598
H	2.112135	4.645261	3.086816	H	-3.862727	2.026265	-0.594685
H	-0.180248	2.935636	3.799126	H	-5.782906	-0.435745	-3.443941
H	-0.127698	4.692752	3.944736	H	-6.108460	-0.921260	-1.782048
N	-0.026393	3.391803	0.926834	H	-5.677072	1.850286	-2.743038
C	3.970672	0.795426	-2.245399	H	-6.117540	1.320118	-1.124036
C	3.945241	-1.380636	-1.473238	N	-3.371864	0.045051	-1.186026
C	5.437910	0.327349	-2.410822	H	-1.623477	3.409764	-0.401562
H	3.865727	1.855044	-1.996932	H	0.365420	-3.034589	-2.460049
H	3.412801	0.615879	-3.173917	H	3.039106	-1.280478	1.335584
C	5.409478	-1.153009	-1.943150	H	-3.039420	1.278991	1.336637
H	3.355506	-1.838192	-2.276829	H	0.456554	-4.727208	-0.679685
H	3.863121	-2.026494	-0.596115	H	-1.174103	-3.109521	-1.605975

Table S7. Optimized geometries, coordinates and energies at the B3LYP level of theory with 6-31G(d) basis set for unsubstituted D_{2d} core tetramer **8a**.



R_2 = morpholine



G = -3041.437536 Hartree
G_{MP2} = -2988.763774Hartree

Atom	X	Y	Z	Atom	X	Y	Z
Li	-1.208837	0.631033	0.399523	H	7.603116	-1.796532	-1.870020
Li	-0.477234	-1.211903	-1.177998	O	-1.389289	-1.310039	0.525708
Li	0.477426	-1.212021	1.177841	C	-2.407886	-2.266672	0.634369
Li	1.208822	0.631198	-0.399541	C	-3.218566	-2.320873	-0.706116
O	0.466889	0.744722	1.408468	C	-3.393838	-1.851673	1.811068
C	-0.645963	2.765133	2.168884	H	-3.545913	-1.283525	-0.854999
H	-0.095304	3.216703	1.336363	C	-4.502026	-3.179968	-0.592615
C	-0.697006	3.835138	3.283791	H	-3.144919	-2.440542	2.704790
H	-1.414829	4.622782	3.026766	H	-3.104873	-0.824826	2.047916
H	-1.052842	3.399277	4.223503	C	-4.908557	-1.848342	1.586827
C	0.219407	1.512805	2.556190	H	-4.974824	-3.287985	-1.575414
C	1.594567	1.999111	3.190462	H	-4.255212	-4.196143	-0.267134
H	1.738814	1.491461	4.153323	C	-5.490916	-2.519620	0.356806
H	2.361072	1.594011	2.524432	C	-5.825167	-3.052126	1.738818
O	1.389525	-1.309773	-0.525929	C	-5.298874	-4.386212	2.233589
C	2.408139	-2.266373	-0.634688	C	-7.233718	-2.761617	2.238490
C	3.218729	-2.320757	0.705847	H	-5.336932	-4.425437	3.330056
C	3.394183	-1.851206	-1.811265	H	-5.913190	-5.213922	1.854910

H	3.546056	-1.283426	0.854888
C	4.502215	-3.179810	0.592297
H	3.145461	-2.440084	-2.705034
H	3.105121	-0.824389	-2.048125
C	4.908875	-1.847722	-1.586833
H	4.974916	-3.288051	1.575116
H	4.255471	-4.195914	0.266540
C	5.491161	-2.519191	-0.356874
C	5.825609	-3.051403	-1.738946
C	5.299455	-4.385443	-2.233994
C	7.234196	-2.760704	-2.238405
H	5.337790	-4.424561	-3.330454
H	5.913680	-5.213185	-1.855240
H	4.265824	-4.577761	-1.942035
H	7.938663	-3.534792	-1.905686
H	7.267123	-2.732606	-3.335746
C	-1.578639	4.260944	-4.647402
C	-2.523401	5.409181	-4.970959
H	-2.032636	6.159001	-5.605698
H	-3.412009	5.050515	-5.506890
H	-2.866308	5.917194	-4.062314
C	-2.236267	-4.057477	-2.220273
C	-2.971758	-1.956400	-3.105707
C	-1.443791	-4.279540	-3.504515
H	-3.219486	-4.534645	-2.355998
H	-1.732380	-4.560812	-1.394441
C	-2.182084	-2.264544	-4.375941
H	-4.014819	-2.281887	-3.264456
H	-2.979026	-0.873954	-2.938737
H	-1.390268	-5.349056	-3.730412
H	-0.416267	-3.894534	-3.395040
H	-2.686610	-1.831691	-5.245373
H	-1.172682	-1.830132	-4.308234
N	-2.378046	-2.613622	-1.918504
O	-2.078256	-3.659826	-4.612681
C	-0.493063	0.623066	3.602377
H	-1.348699	0.106849	3.160348
H	0.204197	-0.147484	3.944887
H	-0.828200	1.170426	4.492688
C	0.493287	0.623454	-3.602249
H	1.348992	0.107390	-3.160178
H	-0.203795	-0.147236	-3.944806
H	0.828362	1.170898	-4.492535
C	1.757266	-3.618800	-1.002113
H	0.946723	-3.851319	-0.309609
H	1.319685	-3.535968	-2.003585
H	2.451860	-4.466300	-1.015311
C	-1.756985	-3.619159	1.001511
H	-0.946523	-3.851563	0.308874
H	-1.319300	-3.536504	2.002950
H	-2.451589	-4.466653	1.014634
C	-3.083527	2.297479	2.549861
C	-2.379079	3.436169	0.573930
C	-4.397157	1.965123	1.847925
H	-3.225648	3.240956	3.100117
H	-2.854506	1.517858	3.276784
H	-4.265319	-4.578506	1.941352
H	-7.938159	-3.535710	1.905727
H	-7.266515	-2.733702	3.335839
H	-7.602763	-1.797415	1.870307
O	-0.466944	0.744840	-1.408457
C	-0.219434	1.513026	-2.556105
C	0.645736	2.765443	-2.168585
C	-1.594563	1.999179	-3.190582
H	0.095024	3.216750	-1.335960
C	0.696555	3.835658	-3.283303
H	-1.738352	1.491916	-4.153714
H	-2.361165	1.593573	-2.524964
C	-1.860999	3.496588	-3.360688
H	1.414266	4.623384	-3.026204
H	1.052394	3.400010	-4.223114
C	-0.684525	4.454721	-3.438600
H	1.614193	3.488026	0.205789
H	5.211698	1.923565	-2.577604
H	4.322683	0.988075	-1.347792
H	4.027685	3.882285	0.752068
H	3.625906	2.149179	0.639285
O	4.749281	2.963829	-0.901291
N	1.979117	2.414281	-1.568587
C	2.236306	-4.057569	2.219675
C	2.971859	-1.956646	3.105476
C	1.443900	-4.279851	3.503924
H	3.219511	-4.534809	2.355241
H	1.732335	-4.560721	1.393780
C	2.182212	-2.265012	4.375673
H	4.014920	-2.282156	3.264167
H	2.979140	-0.874171	2.938692
H	1.390383	-5.349407	3.729630
H	0.416370	-3.894824	3.394574
H	2.686757	-1.832301	5.245165
H	1.172800	-1.830610	4.308073
N	2.378141	-2.613662	1.918155
O	2.078418	-3.660338	4.612169
C	1.860640	3.496528	3.361116
H	2.729882	3.858794	2.814659
C	0.683963	4.454397	3.439305
H	0.802246	5.405838	2.920974
C	1.578075	4.260391	4.648072
C	2.522584	5.408719	4.972046
H	2.031637	6.158217	5.607025
H	3.411255	5.050064	5.507881
H	2.865402	5.917108	4.063582
C	1.086956	3.538191	5.889353
H	0.437189	2.688029	5.668491
H	1.936575	3.154533	6.469309
H	0.527869	4.222574	6.540776
C	-1.087399	3.539268	-5.888940
H	-0.528452	4.223983	-6.540132
H	-0.437465	2.689156	-5.668377
H	-1.936953	3.155646	-6.469015
H	-2.730297	3.858482	-2.814078
H	-0.802968	5.405958	-2.919932

C	-3.719666	3.087020	-0.066319
H	-2.462485	4.434673	1.037845
H	-1.614399	3.487992	-0.205394
H	-5.211841	1.922570	2.577523
H	-4.322665	0.987427	1.347568
H	-4.027907	3.882103	-0.751691
H	-3.625926	2.149020	-0.639263
N	-1.979268	2.413863	1.568763
O	-4.749467	2.963220	0.901439
C	3.083344	2.298241	-2.549760
C	2.378849	3.436444	-0.573575
H	6.299850	-1.988132	0.144258
H	5.381777	-0.909114	-1.870563
H	-5.381513	-0.909835	1.870799
H	-6.299714	-1.988545	-0.144135
C	4.397043	1.965879	-1.847960
H	3.225339	3.241866	-3.099791
H	2.854377	1.518779	-3.276866
C	3.719506	3.087314	0.066539
H	2.462118	4.435048	-1.037299

Part 4. Full References

Reference 24. Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.;Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.;Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.