Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The Smaller, the better? How aggregate size affects the reactivity of (trimethylsilyl)methyllithium

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Content:

A. General procedures

All experiments were performed under an atmosphere of argon by using standard Schlenk techniques. *n*-heptane was dried by refluxing over sodium and distilled under an atmosphere of argon prior to use. All reagents were used as commercial products without further purification. NMR spectra were recorded on a *Bruker AV Avance III HD* spectrometer. All NMR spectra were recorded at room temperature (ca. 22 °C). ^{1}H NMR and {^{1}H}^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) and referred to tetramethylsilane (TMS, δ = 0.0 ppm) with the deuterium signal of the solvent serving as internal lock and residual solvent signals as an additional reference. {^{1}H}^{29}Si NMR chemical shifts are reported in ppm, referenced to an external standard of TMS (δ = 0.0 ppm), and measured via the INEPT puls sequence. For the assignment of the multiplicities the following abbreviations were used: s = singlet, m = multiplet.

B. Experimental Details

Crystallization of Me_3SiCH_2Li·(*R*,*R*)-TMCDA (2)

A solution of 0.170 g (1 mmol, 1 eq.) (*R*,*R*)-TMCDA in 3 mL dry *n*-pentane was cooled to −30 °C. After the addition of 1 mL (1 mmol, 1 eq.) of a 1 M solution of Me_3SiCH_2Li in pentane, the mixture was stored at −80 °C for crystallization. After one week colorless needles of compound **2** were obtained.

^{1}H NMR	(400.25 MHz, C_6D_6): δ = −1.54 (s, 2H, SiC*H*$_2$), 0.44 [s, 12 H; $CH_2Si(CH_3)_3$], 0.58 – 0.70 [m, 4 H; $(CH_3)_2NCHCH_2CH_2$], 1.33 – 1.43 [m, 4 H; $(CH_3)_2NCHCH_2CH_2$], 1.79 – 1.81 [m, 2 H; $(CH_3)_2NCHCH_2CH_2$], 1.93 [s, 12 H; $(CH_3)_2N$] ppm.
{^{1}H}^{13}C NMR	(100.64 MHz, C_6D_6): δ = −5.7 [1C; $(CH_3)SiCH_2$], 6.6 [3C; $(CH_3)SiCH_2$], 22.0 [2C; $(CH_3)_2NCHCH_2CH_2$], 25.3 [2C; $(CH_3)_2NCHCH_2CH_2$], 40. 5 [4C; $(CH_3)_2N$], 64.2 [2C; $(CH_3)_2NCHCH_2CH_2$] ppm.
^{7}Li NMR	(155.55 MHz, C_6D_6): δ = 2.8 [1Li; $(CH_3)SiCH_2Li$] ppm.
{^{1}H}^{29}Si NMR	(79.52 MHz, C_6D_6): δ = −3.6 [1 Si; $(CH_3)SiCH_2Li$] ppm.

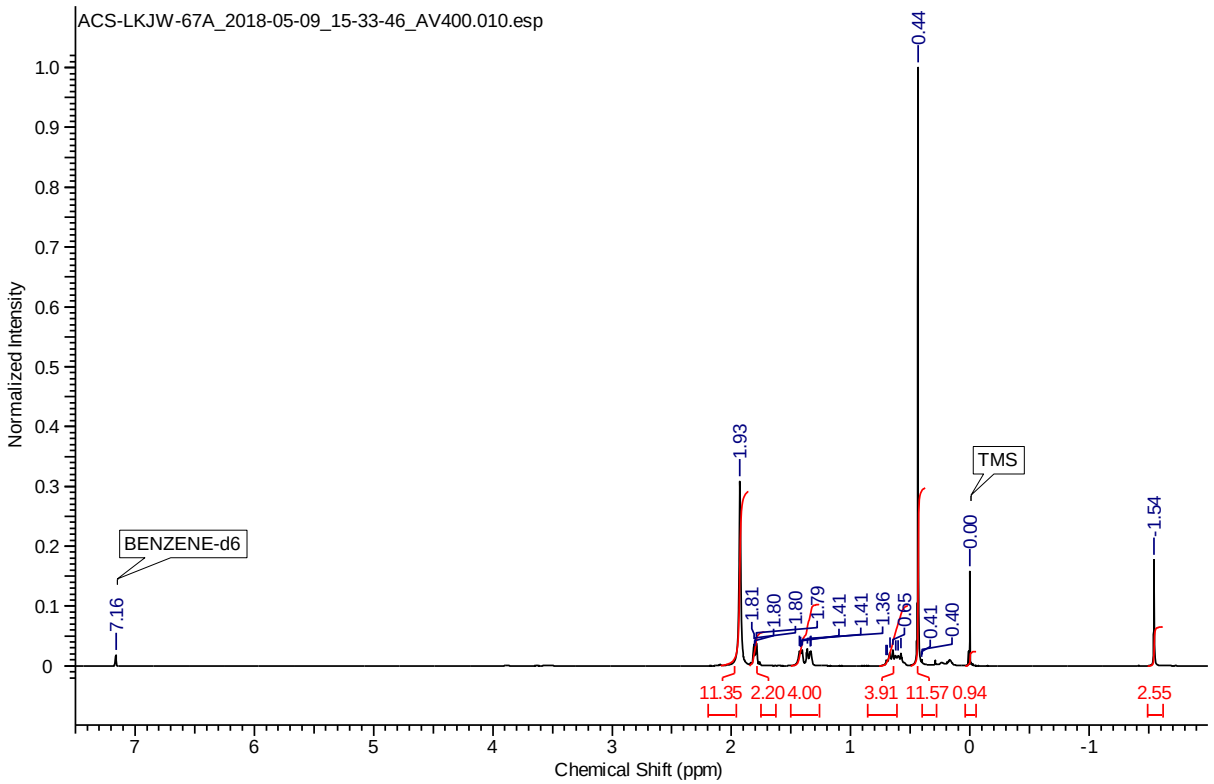


Figure 1: ^{1}H NMR spectrum of **2**.

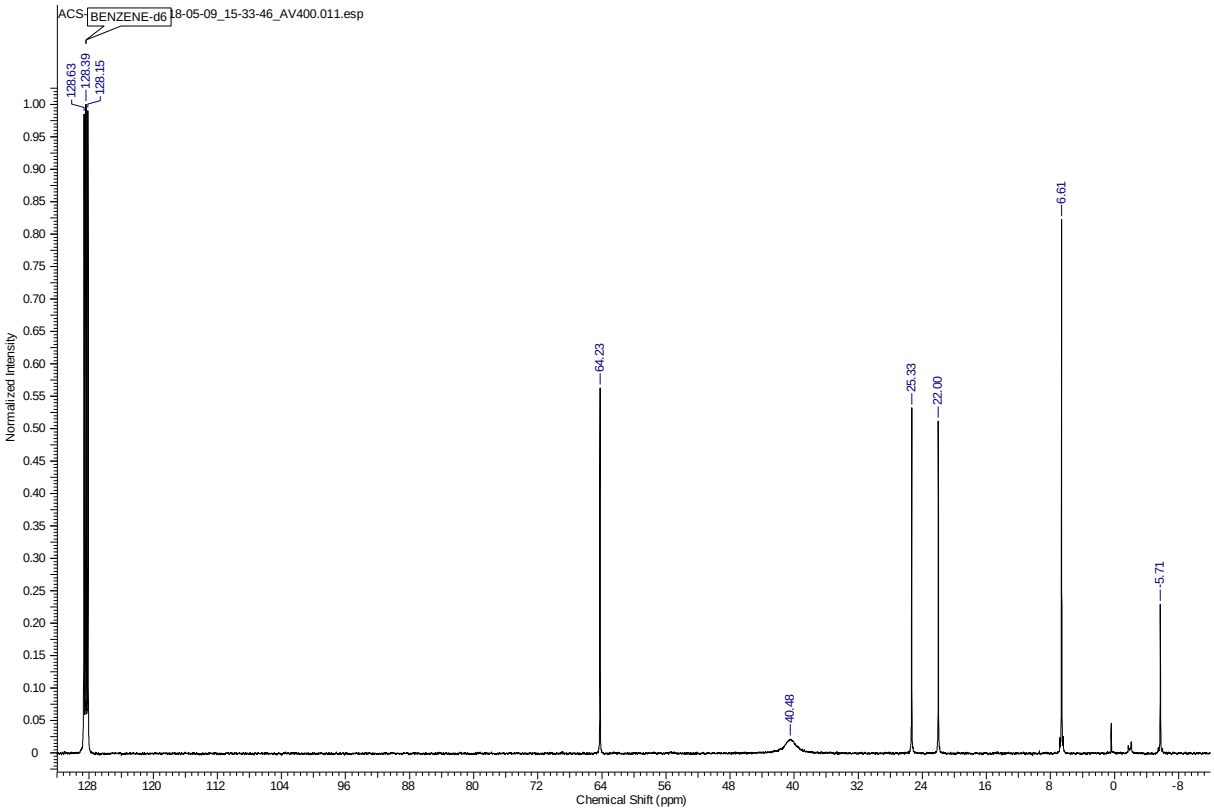


Figure 2: {^{1}H}^{13}C NMR spectrum of **2**.

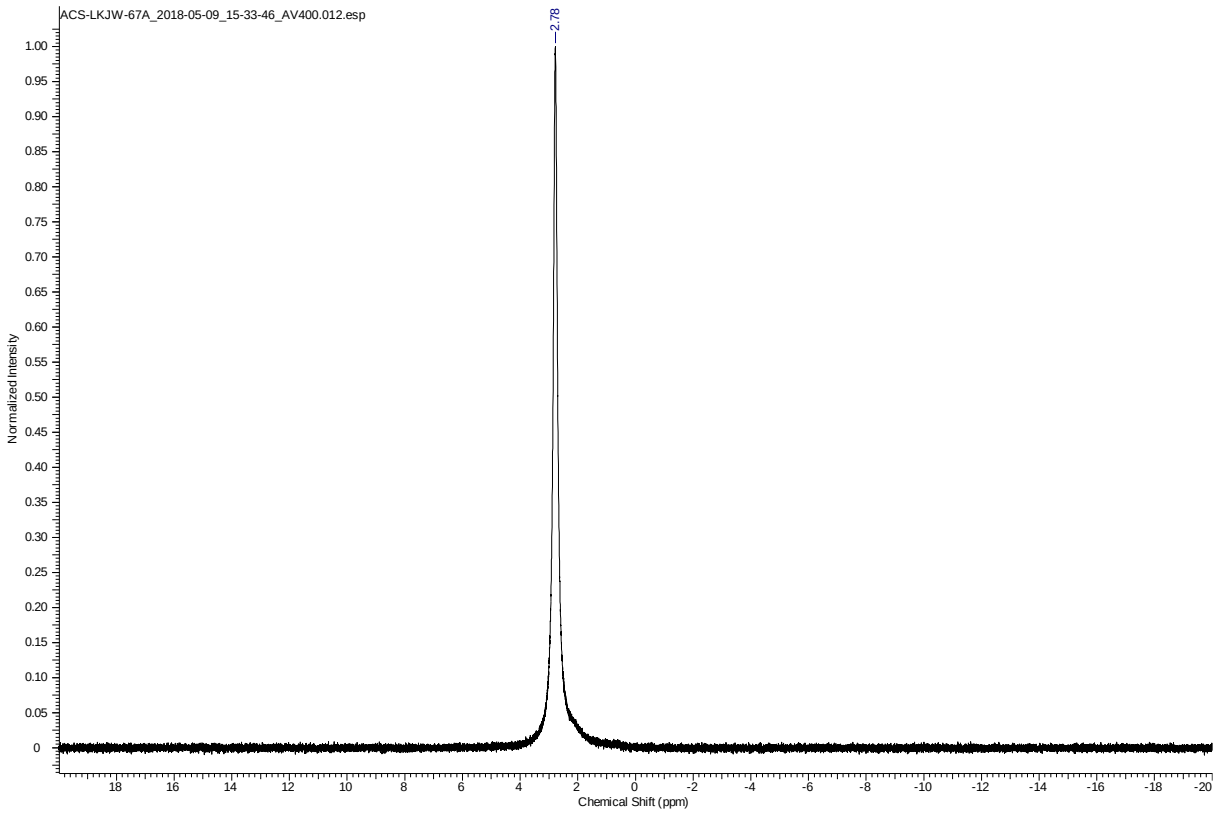


Figure 3: ^{7}Li NMR spectrum of **2**.

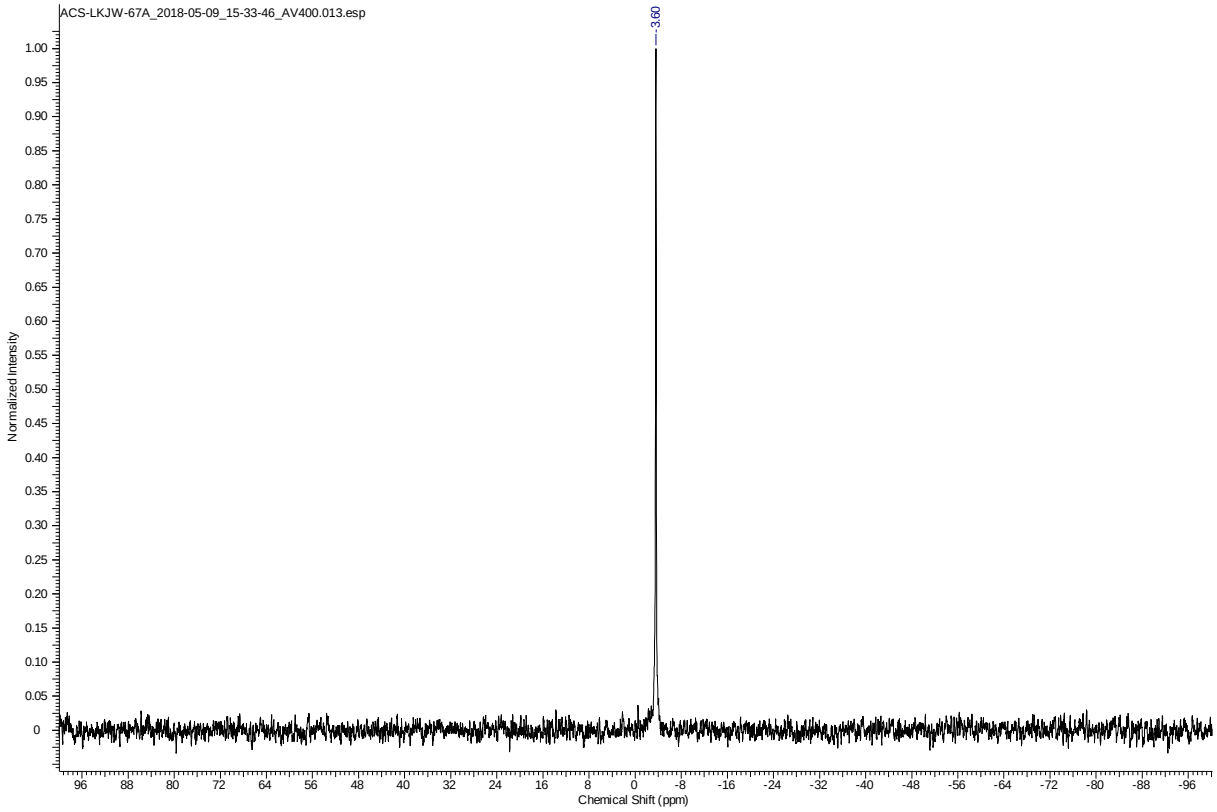


Figure 4: $\{^{1}H\}^{29}$Si NMR spectrum of **2**.

Crystallization of $(Me_3SiCH_2)_2 \cdot$ n quinuclidine (3: n=2; 4: n=3)

A solution of 0.111 g (1 mmol, 1 eq.) quinuclidine in 3 mL dry *n*-pentane was cooled to –50 °C. At this temperature, 1 mL (1 mmol, 1 eq.) of a 1 M solution of Me_3SiCH_2Li in pentane was added. Upon warming to –20 °C, crystallization began. The solution was stored at –80 °C. After two weeks, colorless diamond-shaped plates of **3** and hexagonal plates of **4** were obtained.

^{1}H NMR	(400.25 MHz, C_6D_6): δ = –1.87 (s, 2H; SiC*H*$_2$), 0.35 [s, 9H; $CH_2Si(CH_3)_3$], 1.12 – 1.17 (m, 6H; NCH_2CH_2CH), 1.35 – 1.38 (m, 1H; NCH_2CH_2CH), 2.69 – 2.73 (m, 6H; NCH_2CH_2CH) ppm.
$\{^1H\}^{13}$C NMR	(100.64 MHz, C_6D_6): δ = –5.8 (1C; Si*C*H$_2$), 5.5 [3C; $CH_2Si(CH_3)_3$], 20.9 (1C; NCH_2CH_2CH), 26.3 (3C; NCH_2CH_2CH), 48.0 (3C; NCH_2CH_2CH) ppm.
^{7}Li NMR	(155.55 MHz, C_6D_6): δ = 2.7 [1Li; $(CH_3)_3SiCH_2Li$] ppm.
$\{^1H\}^{29}$Si NMR	(79.52 MHz, C_6D_6): δ = –1.22 [1Si; $(CH_3)_3SiCH_2Li$] ppm.

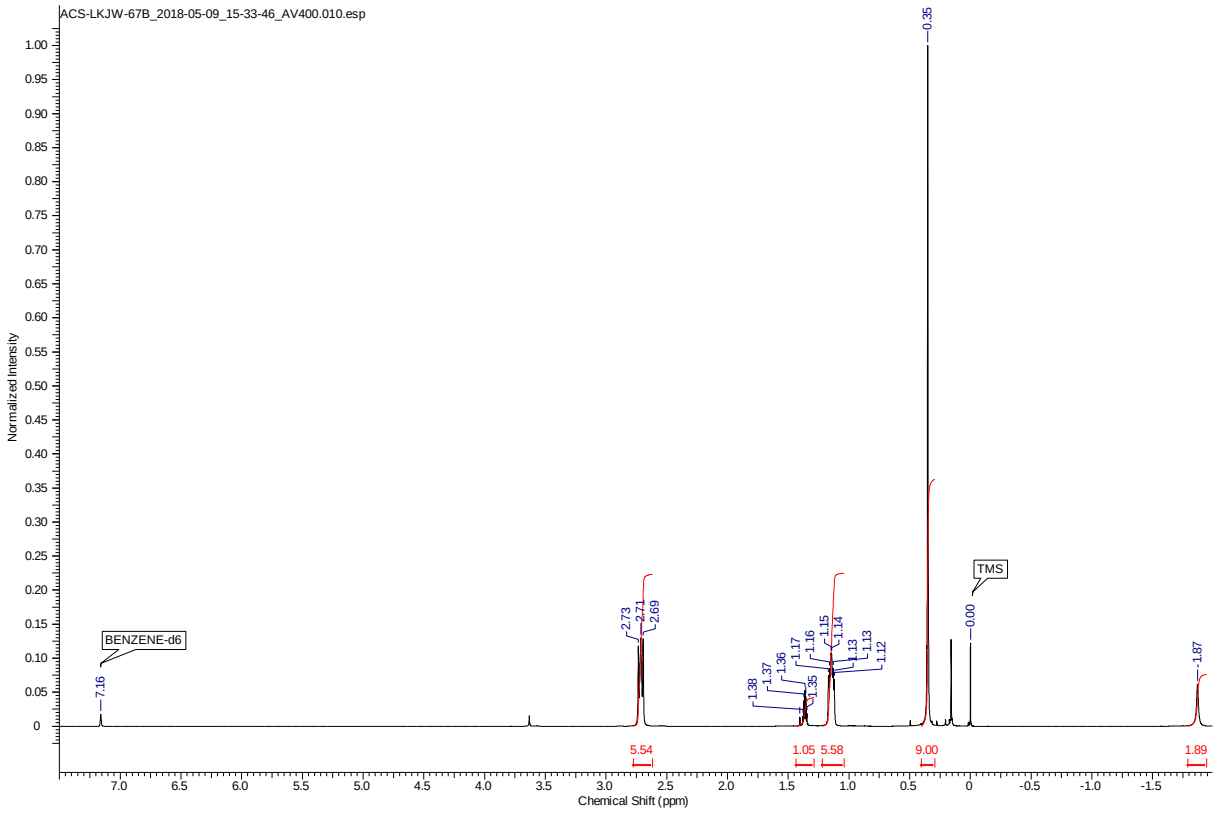


Figure 5: ^{1}H NMR spectrum of **3** and **4**.

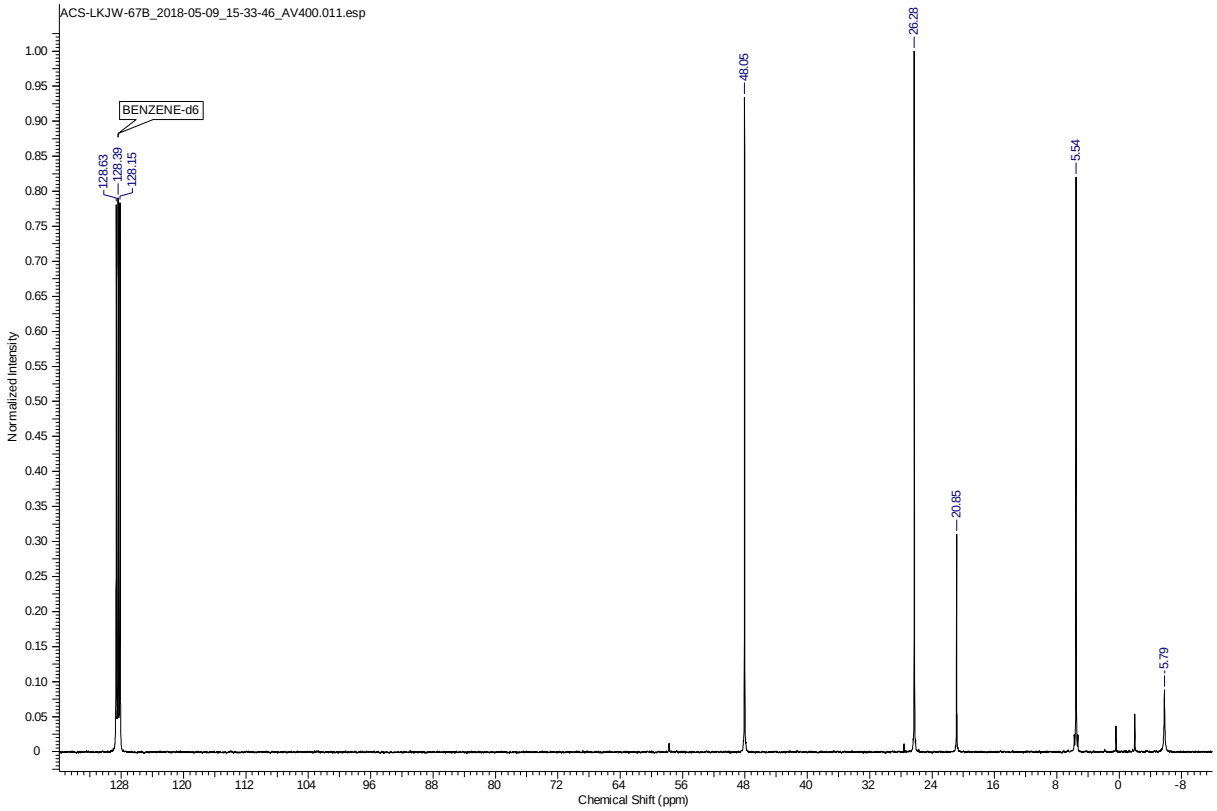


Figure 6: $\{^{1}H\}^{13}C$ NMR spectrum of **3** and **4**.

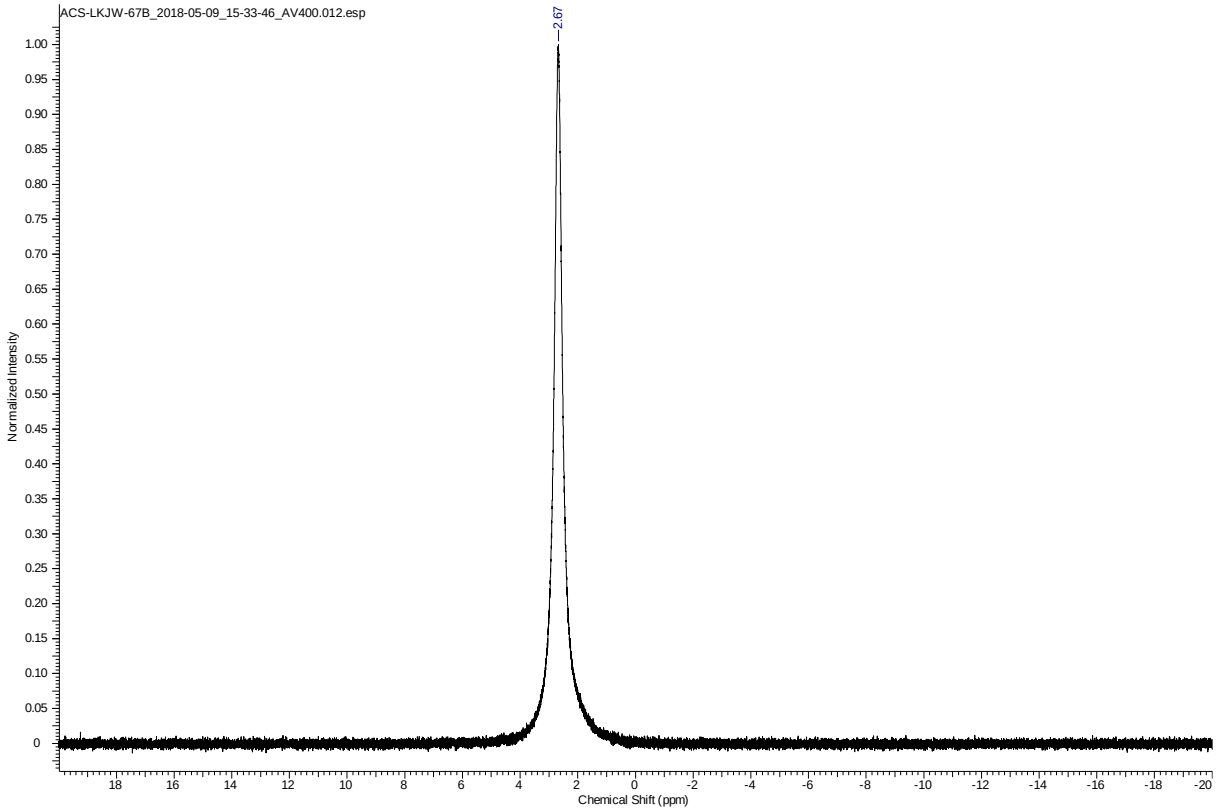


Figure 7: ^{7}Li NMR spectrum of **3** and **4**.

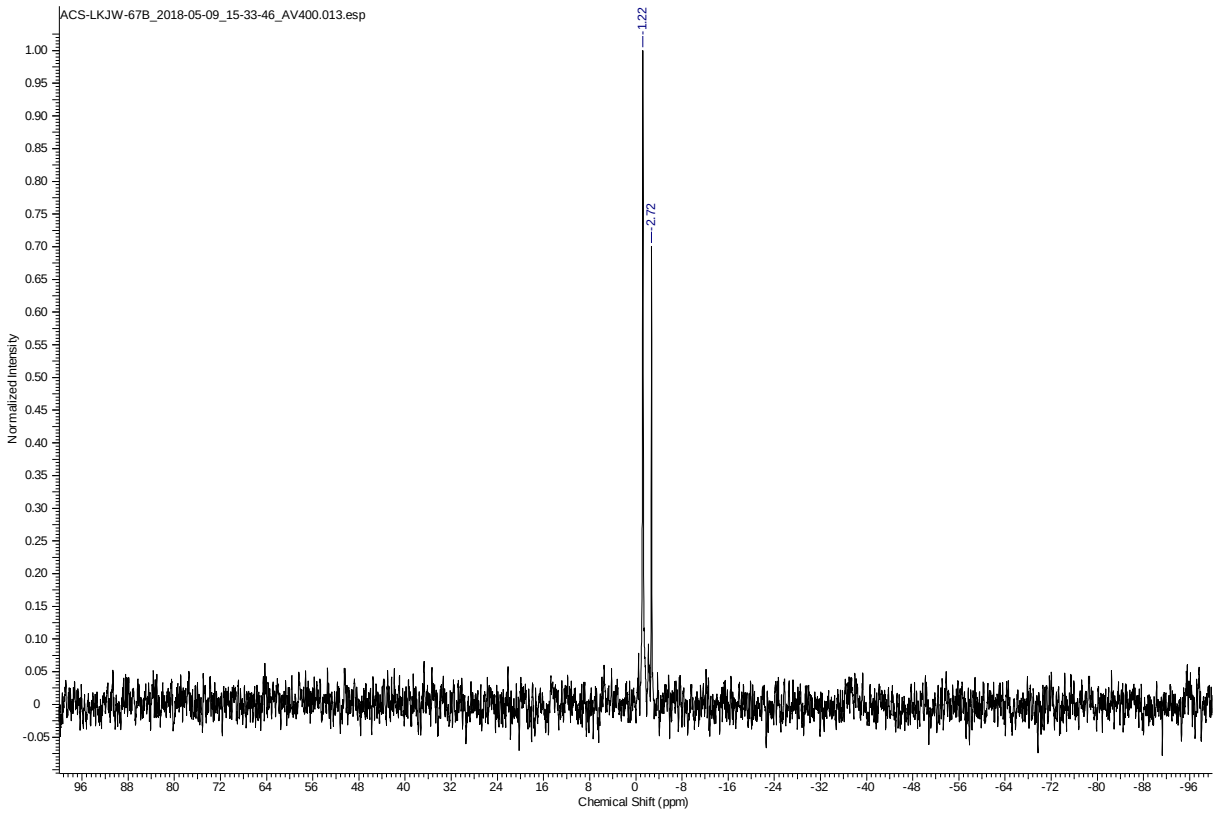


Figure 8: $\{^1H\}^{29}Si$ NMR spectrum of **3** and **4**.

Deprotonation of *N*,*N*-Dimethylbenzylamine

A solution of 0.83 g (7.5 mmol, 1.5 eq.) quinuclidine and 0.75 mL (5 mmol, 1 eq.) *N*,*N*-dimethylbenzylamine in 40 mL dry *n*-heptane was cooled to 0 °C and added 7.5 mL (7.5 mmol, 1.5 eq.) of a 1 M solution of Me_3SiCH_2Li in pentane. After warming to rt the solution was stirred for 1 h and then refluxed for 4 h. After cooling to −50 °C, 0.65 mL (5 mmol, 1 eq.) Me_3SiCl was added. The solution was left to warm to rt and stirred overnight. The reaction was quenched by the addition of 40 mL of 2 M aqueous HCl and the phases were separated. The aqueous layer was cooled by the addition of ice and brought to pH 14 by the addition of KOH. It was then extracted with 3x 40 mL Et_2O. The combined organic layers were dried over Na_2SO_4 and the volatiles were removed under reduced pressure. The residue was distilled by Kugelrohr distillation at 40 °C and $9.8 \cdot 10^{-1}$ mbar to give 3-trimethylsilyl-*N*,*N*-dimethylbenzylamine as a yellowish oil (0.85 g, 4.1 mmol, 82%). Spectral data was consistent with previously reported data.[§1]

C. X-Ray Crystallographic Analyses

Data collection was conducted on a *Bruker D8 Venture* four-circle diffractometer by Bruker AXS GmbH using a *PHOTON II* CPAD detector by *Bruker AXS GmbH* for compound **2** and a *PHOTON100* CMOS area detector by *Bruker AXS GmbH* for compounds **3** and **4**. X-ray radiation was generated by microfocus source *IμS* Mo by *Incoatec GmbH* with *HELIOS* mirror optics and a single-hole collimator by *Bruker AXS GmbH*.

For the data collection, the programs APEX 3 Suite (v.2017.3-0) with the integrated programs SAINT (integration) and SADABS (adsorption correction) by Bruker AXS GmbH were used. Using Olex[2],[§2] the structures were solved with the ShelXT[§3] structure solution program using Intrinsic Phasing and refined with the XL[§4] refinement package using Least Squares minimization. In the structure refinement of aggregate **4**, co-crystallized and disordered pentane was suppressed by the SQUEEZE instruction.

Crystallographic data have been deposited at the CCDC (Cambridge Crystallographic Data Centre). These data can be obtained free of charge from the CCDC, Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). CCDC deposition numbers are 1908867 (compound **2**), 1908868 (compound **3**), 1908869 (compound **4**).

Table 1: Crystal data and structure refinements for compounds **2**–**4** .

Compound	**2**	**3**	**4**
Empirical formula	$C_{14}H_{33}LiN_2Si$	$C_{22}H_{48}Li_2N_2Si_2$	$C_{65}H_{135}Li_4N_7Si_4$
Formula weight	264.45	410.68	1154.91
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$C2/c$	$C2/c$
a/Å	7.4127(3)	16.995(2)	21.750(3)
b/Å	12.3217(5)	16.128(2)	12.1145(15)
c/Å	10.0582(4)	12.3697(14)	31.140(5)
α/°	90	90	90
β/°	105.694(2)	128.118(4)	105.610(4)
γ/°	90	90	90
Volume/Å^3	884.44(6)	2667.6(6)	7902.4(19)
Z	2	4	4
ρ_{calc}g/cm^3	0.993	1.023	0.971
μ/mm^{-1}	0.121	0.142	0.113
F(000)	296.0	912.0	2568.0
Crystal size/mm^3	0.773 × 0.15 × 0.141	0.271 × 0.195 × 0.167	0.771 × 0.459 × 0.174
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.206 to 59.984	5.052 to 66.488	5.03 to 61.152
Index ranges	−10 ≤ h ≤ 10 −17 ≤ k ≤ 17	−25 ≤ h ≤ 25 −24 ≤ k ≤ 24	−31 ≤ h ≤ 30 −17 ≤ k ≤ 16

	−14 ≤ l ≤ 14	−18 ≤ l ≤ 18	−44 ≤ l ≤ 43
Reflections collected	5139	52393	50164
Independent reflections	5139 [R_{int} = 0.0369, R_{sigma} = 0.0242]	4883 [R_{int} = 0.0689, R_{sigma} = 0.0368]	11922 [R_{int} = 0.0602, R_{sigma} = 0.0580]
Data/restraints/parameters	5139/1/171	4883/0/223	11922/0/386
Goodness-of-fit on F^2	1.047	1.054	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0885	R_1 = 0.0460, wR_2 = 0.1183	R_1 = 0.0667, wR_2 = 0.1861
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0898	R_1 = 0.0602, wR_2 = 0.1263	R_1 = 0.0880, wR_2 = 0.1988
Largest diff. peak/hole / e $Å^{-3}$	0.35/−0.18	0.59/−0.51	0.97/−0.49
Flack parameter	0.03(6)	–	–

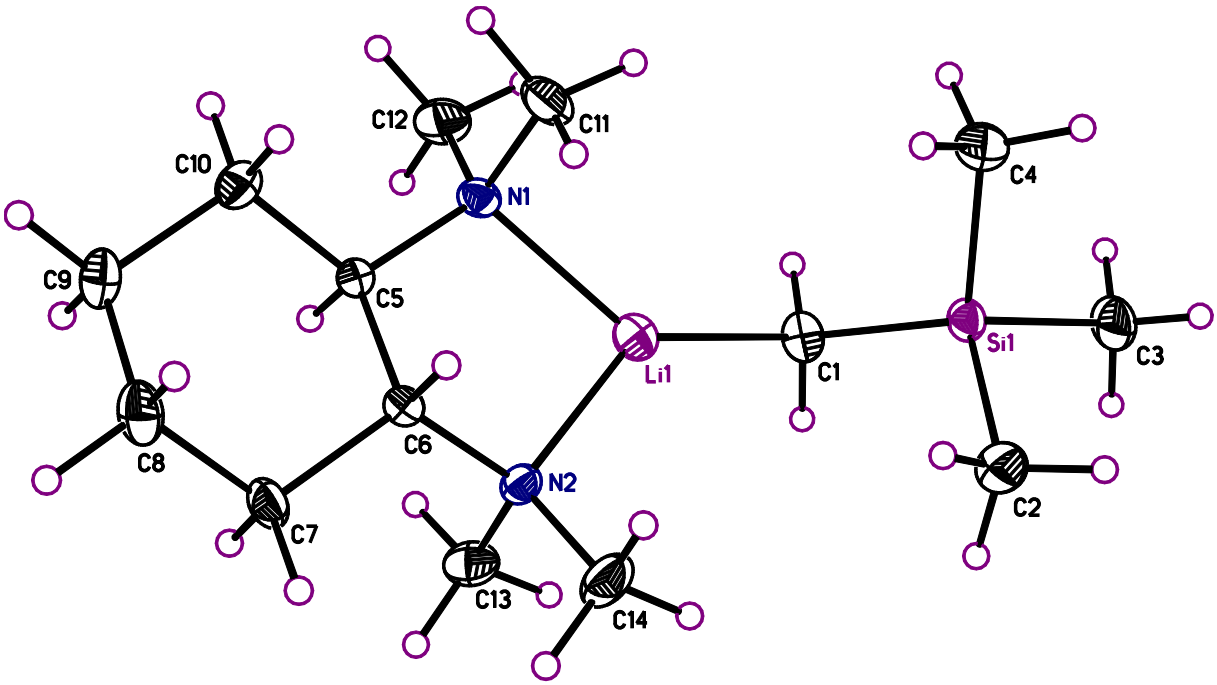


Figure 9: Ortep[$5] plot and numbering scheme of compound **2**. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths [A] and angles [°]: C1-Li1 2.069(3), N1-Li1 2.050(2), N2-Li1 2.049(4), Si1-C1 1.8075(17), Si1-C2 1.887(2),

Si1-C3 1.8958(18), Si1-C4 1.887(2); Si1-C1-Li1 114.64(12), C1-Si1-C2 110.44(10), C1-Si1-C3 117.89(9), C1-Si1-C4 110.37(10), C2-Si1-C3 105.09(12), C2-Si1-C4 107.60(10), C3-Si1-C4 104.84(11).

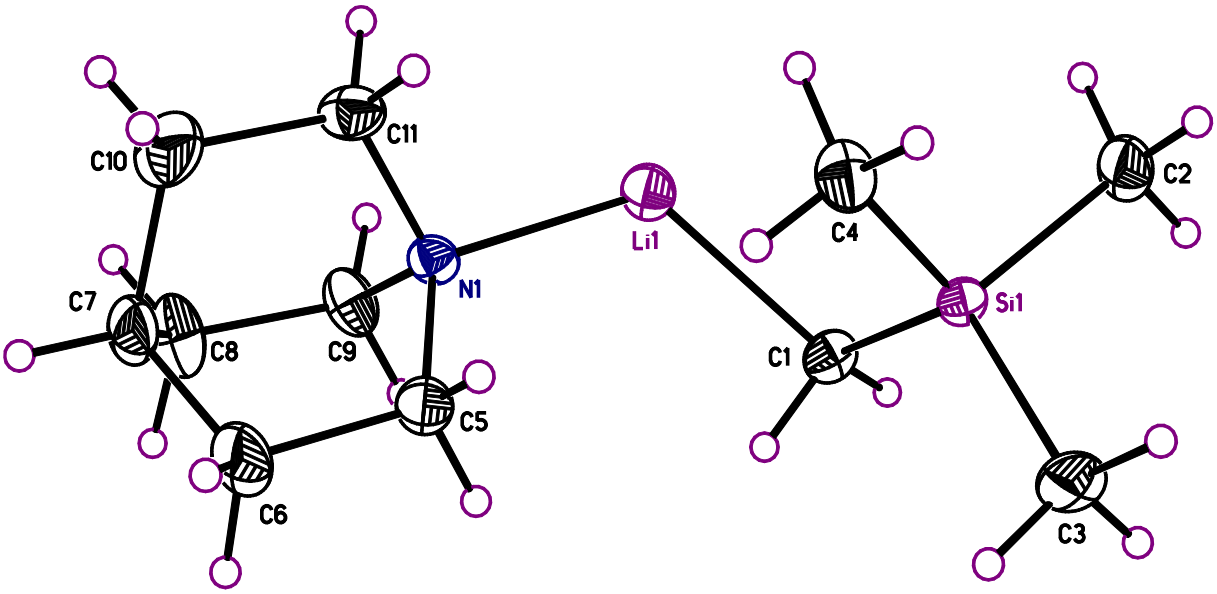


Figure 10: Ortep[$5] plot and numbering scheme of compound **3**. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Si1-C1 1.8306(10), Si1-C2 1.8878(11), Si1-C3 1.8855(11), Si1-C4 1.8971(11), N1-Li1 2.0822(19), C1-Li1 2.185(2), Si1-C1-Li1 94.79(6), N1-Li1-C1 123.67(9), C2-Si1-C4 107.80(5), C2-Si1-C3 104.87(5), C1-Si1-C3 117.29(5).

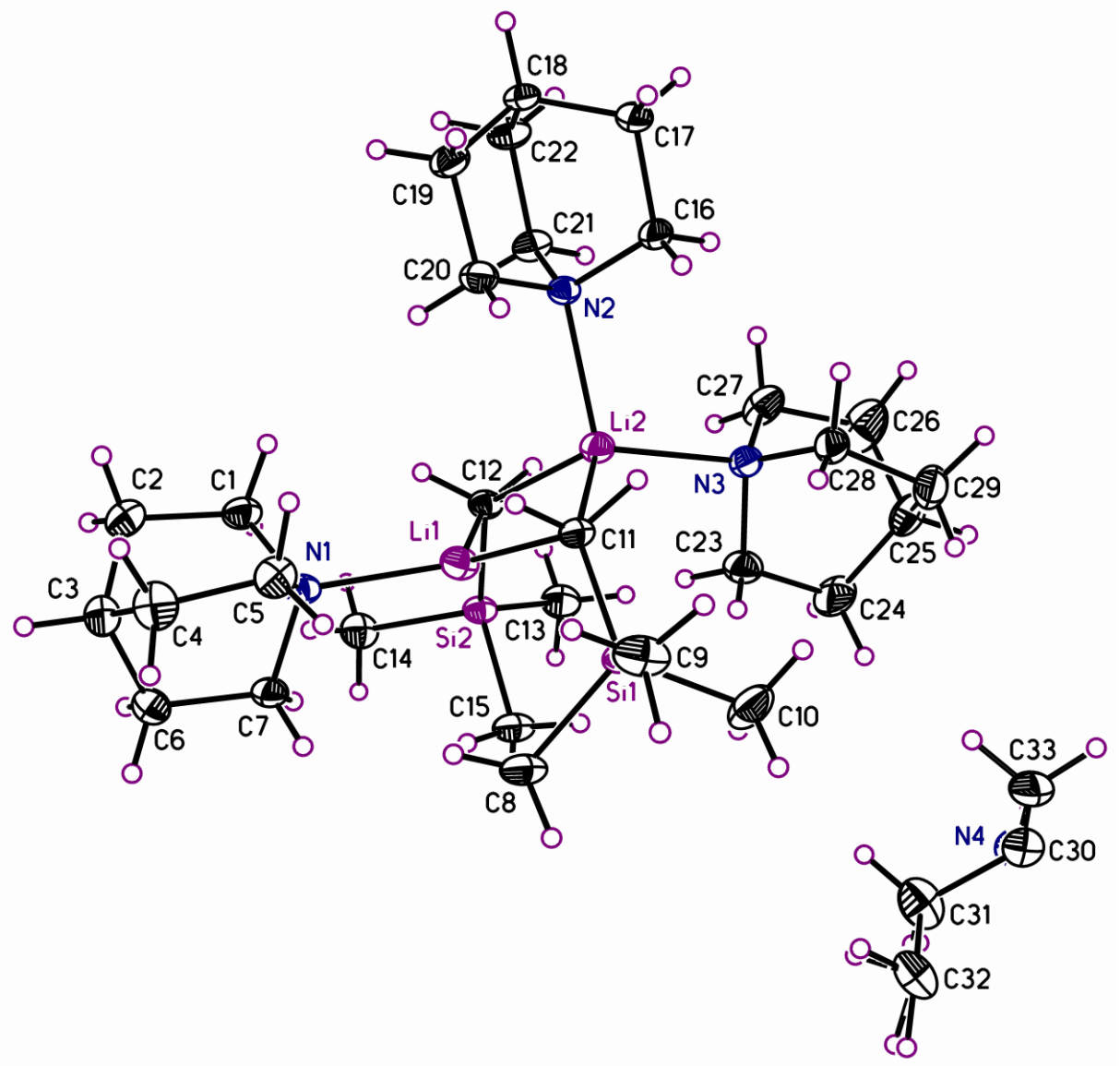


Figure 11: Ortep[§5] plot and numbering scheme of compound **4**. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Si1-C8 1.887(2), Si1-C9 1.885(2), Si1-C10 1.885(2), Si1-C11 1.837(2), Si2-C12 1.8331(19), Si2-C13 1.885(2), Si2-C14 1.883(2), Si2-C15 1.896(2), N1-Li1 2.123(4), N2-Li2 2.141(4), N3-Li2 2.164(4), C11-Li1 2.169(4), C11-Li2 2.280(4), C12-Li1 2.181(4), C12-Li2 2.284(4), Li1-C11-Li2 65.84(14), Li1-C12-Li2 65.60(14), C11-Li1-C12 117.95(17), C11-Li2-C12 109.55(15), N2-Li2-N3 109.14(16), N1-Li1-C11 121.00(18), N1-Li1-C12 115.71(17), N2-Li2-C11 108.15(16), N2-Li2-C12 106.86(16).

D. Quantum chemical calculations

Optimization and additional harmonic vibrational frequency analyses were performed with the software package *Gaussian 09* (Revision E.01).[§6] The GJF input files were created with the program *GaussView* 5.0. The ground state structures were optimized without symmetry restrictions. Vibrational frequency analysis showed no imaginary frequency in the harmonical approximation in case of ground states and one imaginary frequency in case of transition states. The calculated standard orientations of the optimized structures can be found in Tables 4–10. The visualization of the optimized structures was performed with the program *Molekel* V. 4.3 (Figures 12–18).[§7]

Evaluation of functional

Table 2: Comparison of experimental and theoretical N–Li bond lengths (in Å) obtained by three different quantum chemical functionals.

bond	experimental	M062X	deviation [%]	B3LYP	deviation [%]	B3LYP/gd3	deviation [%]
N1–Li1	2.127(5)	2.08299	−2.07	2.18599	2.77	2.11668	−0.49
N2–Li2	2.139(5)	2.05839	−3.77	2.24321	4.87	2.12325	−0.74
N3–Li2	2.161(5)	2.08207	−3.65	2.20008	1.81	2.11099	−2.31

To obtain a high correspondence of experimental and theoretical data an evaluation of three quantum chemical levels was performed. Using the basis set 6-31+G(d), geometry optimizations of the structure of compound **4** were used to determine the most fitting method by comparing Li–N distances. Additional gd3 dispersion correction on the B3LYP functional[§8] gave the best accordance of theory and experiment (see Table 2), so all following calculations were performed on the B3LYP/6-31+G(d)/gd3 level of theory.

Calculations on the deprotonation reaction of benzylamine (7)

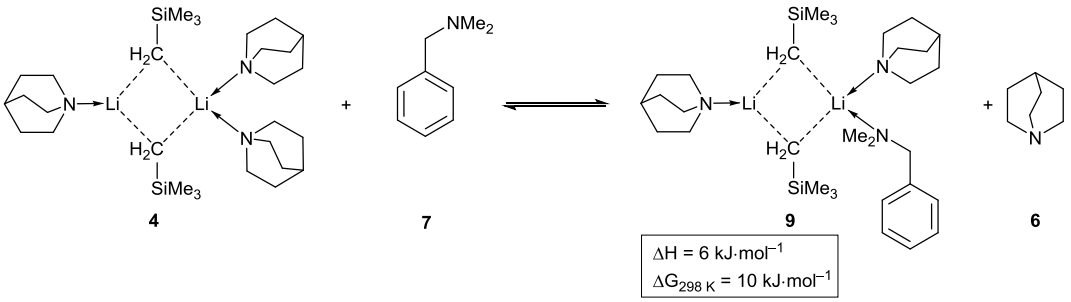
In the course of our studies, we were interested in the activation energy of the deprotonation reaction of benzylamine (**7**) by quinuclidine-stabilizes Me_3SiCH_2Li. In Table 3, the obtained energies in Hartree of the necessary molecules are listed.

Table 3: Total (SCF), ground state (ZPE) and Gibbs ($\Delta G_{298\,K}$) energies of the optimized structures.

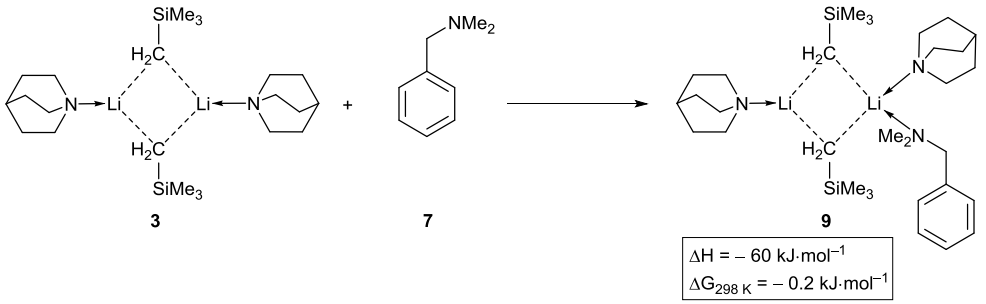
Optimized structure	Functional/Basis set	SCF [Hartree]	ZPE [Hartree]	$\Delta G_{298\,K}$ [Hartree]
Monomer **2**	B3LYP/6-31+G(d)	−959.951710402	−959.495280	−959.551621
Symmetric Dimer **3**	B3LYP/6-31+G(d)[a]	−1571.02561393	−1570.354612	−1570.425178
Asymmetric Dimer **4**	B3LYP/6-31+G(d)	−1900.39123530	−1899.520883	−1899.600875
Benzylamine (**7**)	B3LYP/6-31+G(d)	−405.557719682	−405.355117	−405.390299
Quinuclidine (**6**)	B3LYP/6-31+G(d)	−329.336876645	−329.141073	−329.171614
Mixed Dimer **9**	B3LYP/6-31+G(d)	−1976.61029923	−1975.732526	−1975.815567
Transition state **9-TS**	B3LYP/6-31+G(d)	−1976.56850696	−1975.695857	−1975.777331

[a] Residual imaginary frequency was proved to be an artefact by repeating the calculation with setting the calculation grid to *ultrafine*.

As stated in the publication, we assumed the mixed dimer **9** to be the starting aggregate. It can be formed by the replacement of one molecule of quinuclidine in the asymmetric dimer **4** with an energy need of 6 kJ/mol (process 1, see Scheme 1). Alternatively, it can be formed by the addition of benzylamine (**7**) to the symmetric dimer **3** (process 2, see Scheme 2). Here, an energy gain of 60 kJ/mol is observed.



Scheme 1: Formation of the mixed aggregate **9** by replacement of quinuclidine (**6**) by benzylamine (**7**) in the asymmetric dimer **4** (**process 1**).



Scheme 2: Formation of the mixed aggregate **9** by addition of benzylamine (**7**) to the symmetric dimer **3** (**process 2**).

In this consideration based on ΔH, process 2 shown in Scheme 2 would be favored. Since the deprotonation reactions were performed at high temperatures (refluxing *n*-heptane), changes in entropy are of increased importance. This can be considered by using $\Delta G_{298\ K}$ values in the calculation of the processes. For process 1, an energy need of 10 kJ/mol was obtained based on $\Delta G_{298\ K}$. Due to an unfavorable change in entropy of process 2, the energy gain is decreased to 0.2 kJ/mol with $\Delta G_{298\ K}$. This shows that both processes are of comparable probability. It should be noted that all $\Delta G_{298\ K}$ values given here are calculated for room temperature (298 K). At elevated temperatures, entropic changes become more relevant, so the observed tendencies are expected to be even more pronounced. Additionally, entropic changes in the surrounding solvent sphere also have influence on the $\Delta G_{298\ K}$ values. By this, the underlying processes become too complex for a precise theoretical description.

When considering $\Delta G_{298\ K}$, the activation energy of the deprotonation of benzylamine (**7**) starting from mixed aggregate **9** was calculated to 100 kJ/mol, which is only insignificantly higher than in the former calculations based on ΔH.

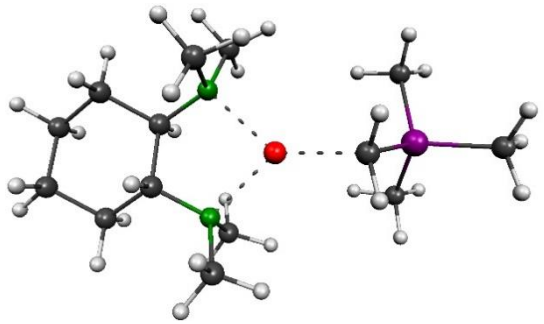


Figure 12: Molekel plot of Monomer **2** [B3LYP/6-31+G(d)/gd3].

Table 4: Standard orientation of Monomer **2** [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
Si	3.87244	-0.013025	-0.037362
N	-0.920835	-1.470984	0.258515
N	-0.829388	1.400836	0.270068
C	2.542686	-0.185914	1.224622
H	2.668899	0.581687	2.010767
H	2.63586	-1.162514	1.736035
C	3.808734	1.708189	-0.876406
H	3.882489	2.51254	-0.130745
H	2.869548	1.85593	-1.427764
H	4.633869	1.845826	-1.58865
C	5.682459	-0.211012	0.567781
H	5.920461	0.537005	1.336791
H	6.415698	-0.09943	-0.244541
H	5.836509	-1.199706	1.022055
C	3.66882	-1.311291	-1.433101
H	4.48181	-1.253536	-2.169998
H	2.722754	-1.175734	-1.976652
H	3.670533	-2.33228	-1.025148
C	-2.198285	-0.706455	0.328922
H	-2.403427	-0.592488	1.402323
C	-2.038936	0.716397	-0.268076
H	-1.84434	0.601522	-1.343274
C	-3.352198	1.517464	-0.120864
H	-3.562375	1.683899	0.944601
H	-3.2325	2.508388	-0.57602
C	-4.549521	0.788299	-0.747748
H	-5.462872	1.378597	-0.600878
H	-4.404013	0.702588	-1.835075
C	-4.71021	-0.611435	-0.142744
H	-5.542135	-1.144608	-0.620164
H	-4.967281	-0.521943	0.923458
C	-3.415694	-1.423628	-0.296978
H	-3.232256	-1.589753	-1.367287
H	-3.534042	-2.414405	0.159077
C	-0.593014	-2.007025	-1.073728

H	-1.242555	-2.845948	-1.371506
H	0.441748	-2.364021	-1.065755
H	-0.67138	-1.224567	-1.834615
C	-0.844974	-2.542354	1.262888
H	-1.027392	-2.130095	2.260416
H	0.162684	-2.968321	1.254135
H	-1.567526	-3.355717	1.079372
C	-0.970511	1.920389	1.641602
H	-1.628599	2.802316	1.700611
H	0.019482	2.205153	2.011655
H	-1.367047	1.14858	2.307985
C	-0.341181	2.466557	-0.618333
H	-1.035311	3.321498	-0.684214
H	-0.18199	2.068339	-1.625556
H	0.619401	2.832597	-0.244354
Li	0.611218	-0.082369	0.572962

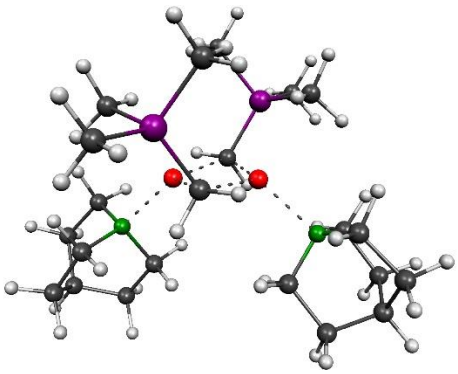


Figure 13: Molekel plot of Symmetric Dimer **3** [B3LYP/6-31+G(d)].

Table 5: Standard orientation of Symmetric Dimer **3** [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
Si	-1.172908	2.221301	2.194737
N	-2.62061	-0.888328	-0.364493
C	-1.863407	-2.111576	-0.742514
H	-1.258914	-2.393849	0.126448
H	-1.169682	-1.836661	-1.542937
C	-2.133063	2.252945	3.843498
H	-2.841689	1.414767	3.898326
H	-2.705057	3.182587	3.974226
H	-1.448341	2.156323	4.696662
C	-0.221286	0.681184	1.804916
C	-0.020436	3.734839	2.169315
H	0.800646	3.618313	2.88963
H	-0.563685	4.652274	2.432212

H	0.42715	3.888685	1.179863
C	-3.518024	-0.507276	-1.486247
H	-2.886573	-0.34566	-2.366002
H	-3.976967	0.455159	-1.234547
C	-4.266333	-2.826831	-0.878422
H	-4.962452	-3.645232	-1.09492
C	-3.443045	-1.184446	0.836026
H	-4.029388	-0.288013	1.060929
H	-2.762324	-1.342067	1.678511
C	-2.5143	2.554317	0.855345
C	-2.817521	-3.266022	-1.16885
H	-2.70311	-3.49085	-2.237014
H	-2.582141	-4.186541	-0.619925
C	-4.594736	-1.601248	-1.754064
H	-5.598511	-1.229327	-1.512288
H	-4.603531	-1.883423	-2.814146
C	-4.368502	-2.416665	0.604047
H	-4.068497	-3.256231	1.244167
H	-5.407267	-2.173898	0.860145
Li	-1.120839	0.50788	-0.125424
H	0.713175	0.721033	2.394181
H	-2.97609	3.535263	1.029458
H	-3.327185	1.816709	0.881299
H	-0.751197	-0.215871	2.175632
H	-2.115254	2.587679	-0.169753
Si	1.172908	2.221298	-2.194738
N	2.62061	-0.888328	0.364494
C	1.863406	-2.111576	0.742512
H	1.258914	-2.393849	-0.12645
H	1.16968	-1.836662	1.542935
C	2.133064	2.252941	-3.843499
H	2.84169	1.414762	-3.898325
H	2.705058	3.182583	-3.974227
H	1.448343	2.156319	-4.696663
C	0.221286	0.681182	-1.804917
C	0.020437	3.734837	-2.169318
H	-0.800645	3.618311	-2.889634
H	0.563687	4.652272	-2.432215
H	-0.42715	3.888683	-1.179867
C	3.518023	-0.507276	1.48625
H	2.88657	-0.345661	2.366003
H	3.976966	0.455159	1.234551
C	4.266333	-2.826831	0.878424
H	4.962451	-3.645232	1.094922
C	3.443047	-1.184444	-0.836024
H	4.02939	-0.288011	-1.060926
H	2.762327	-1.342065	-1.67851

C	2.5143	2.554315	-0.855346
C	2.81752	-3.266023	1.168849
H	2.703108	-3.490851	2.237012
H	2.582141	-4.186541	0.619923
C	4.594734	-1.601249	1.754067
H	5.598509	-1.229327	1.512293
H	4.603528	-1.883424	2.814148
C	4.368503	-2.416663	-0.604045
H	4.068499	-3.256229	-1.244166
H	5.407269	-2.173897	-0.860142
Li	1.120839	0.50788	0.125424
H	-0.713175	0.721031	-2.394181
H	2.97609	3.53526	-1.029459
H	3.327185	1.816707	-0.881299
H	0.751197	-0.215873	-2.175632
H	2.115254	2.587678	0.169752

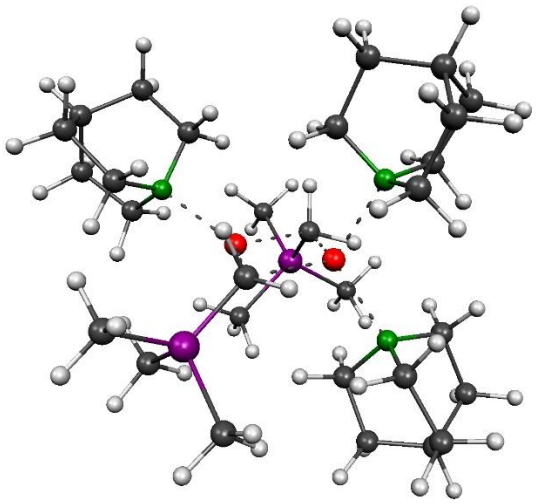


Figure 14: Molekel plot of Asymmetric Dimer **4** [B3LYP/6-31+G(d)/gd3].

Table 6: Standard orientation of Asymmetric Dimer **4** [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
Si	-0.494344	-1.277366	-3.028364
Si	-0.382326	-1.739365	2.853576
N	1.285771	2.543633	0.147243
N	-3.207726	-0.153274	0.067542
N	2.878254	-0.617762	-0.050708
C	-0.079445	-0.184058	1.884179
C	1.346926	5.136787	0.250165
H	1.374738	6.231761	0.293775
C	-0.887151	-2.961959	-2.205746
H	-0.053698	-3.302675	-1.577222

H	-1.06302	-3.737717	-2.963922
H	-1.777166	-2.929358	-1.56395
C	1.844858	3.085862	-1.115755
H	1.185765	2.763145	-1.926981
H	2.816464	2.608826	-1.282403
C	-0.116262	0.077904	-1.815906
C	-3.713409	0.017863	1.455244
H	-3.065994	0.738653	1.963183
H	-3.586723	-0.939413	1.968656
C	-0.088192	3.077053	0.331482
H	-0.466018	2.676079	1.276555
H	-0.705268	2.659722	-0.468662
C	-1.994985	-0.858998	-4.133707
H	-2.285438	-1.709526	-4.765377
H	-1.757927	-0.015677	-4.796281
H	-2.877151	-0.569302	-3.54758
C	-1.263677	-3.100203	1.834002
H	-2.268062	-2.795517	1.511389
H	-1.383631	-4.018904	2.424408
H	-0.699254	-3.362167	0.928951
C	2.131821	2.98464	1.282114
H	3.144636	2.609757	1.097601
H	1.761357	2.490682	2.18648
C	-3.968497	-1.250109	-0.588256
H	-3.696266	-2.189317	-0.096757
H	-3.619992	-1.315746	-1.622013
C	-5.744707	0.413682	0.031243
H	-6.814282	0.652624	0.016258
C	0.961858	-1.657914	-4.208382
H	1.8651	-1.947865	-3.652859
H	1.218141	-0.773427	-4.807026
H	0.728309	-2.478292	-4.90129
C	2.130874	4.536242	1.433957
H	1.662881	4.834767	2.38074
H	3.156517	4.92648	1.44596
C	-5.505298	-1.002948	-0.525182
H	-5.952213	-1.100968	-1.522315
H	-5.993251	-1.744343	0.120358
C	1.977384	4.63883	-1.065748
H	3.030768	4.944242	-1.112736
H	1.471612	5.098379	-1.924223
C	-4.959429	1.418582	-0.833477
H	-5.177864	2.446202	-0.516808
H	-5.271955	1.331811	-1.881988
C	-3.440566	1.108911	-0.68479
H	-2.950875	1.01653	-1.657599
H	-2.925806	1.906935	-0.139035

C	3.794322	-0.243431	-1.15597
H	4.207609	0.743073	-0.916044
H	3.200685	-0.134758	-2.069423
C	2.393506	-2.004829	-0.289133
H	1.93892	-2.014796	-1.281413
H	1.596456	-2.209048	0.429333
C	3.633585	-0.57675	1.227717
H	2.96033	-0.919391	2.016174
H	3.875577	0.46992	1.44083
C	4.921416	-1.450658	1.163147
H	5.822798	-0.823984	1.183153
H	4.97467	-2.119754	2.03078
C	-0.108298	4.634773	0.319306
H	-0.673277	5.011661	-0.5432
H	-0.599515	5.024476	1.220062
C	-1.467312	-1.492819	4.406702
H	-0.964599	-0.835623	5.129071
H	-1.689294	-2.44265	4.913217
H	-2.426148	-1.02039	4.153378
C	4.881198	-2.269291	-0.142306
H	5.728104	-2.963724	-0.183019
C	-5.202602	0.474491	1.472265
H	-5.796838	-0.172089	2.129839
H	-5.29286	1.496927	1.86131
C	3.548042	-3.041193	-0.189773
H	3.442813	-3.658073	0.712083
H	3.528415	-3.721977	-1.049935
C	1.231562	-2.56688	3.456667
H	1.852241	-2.933491	2.629086
H	0.998902	-3.431875	4.092576
H	1.841783	-1.874187	4.051778
C	4.929012	-1.295467	-1.337492
H	4.796685	-1.850561	-2.27501
H	5.908536	-0.803549	-1.390701
Li	-1.109822	-0.429689	0.015252
Li	1.052407	0.434582	0.072252
H	-0.660632	0.982269	-2.142597
H	0.896213	0.212207	2.22182
H	-0.80778	0.575828	2.22432
H	0.948095	0.329856	-1.978191

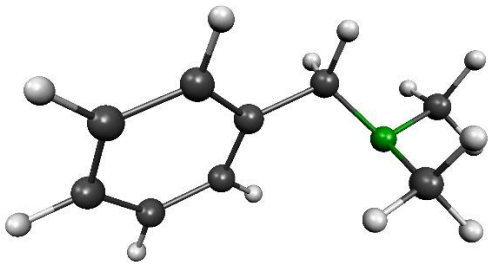


Figure 15: Molekel plot of Benzylamine (**7**) [B3LYP/6-31+G(d)/gd3].

Table 7: Standard orientation for Benzylamine (**7**) [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
C	-3.060645	0.280355	-0.227788
C	-2.180321	1.35031	-0.02647
C	-0.842177	1.109026	0.288548
C	-0.361445	-0.20366	0.406779
C	-1.246714	-1.266866	0.197042
C	-2.590166	-1.029863	-0.115242
H	-4.102842	0.468478	-0.473591
H	-2.538551	2.373204	-0.115549
H	-0.151231	1.935833	0.431008
H	-0.883022	-2.289669	0.274502
H	-3.263907	-1.867972	-0.276218
N	2.028075	0.291778	-0.069787
C	3.383589	0.223521	0.461444
H	3.785049	-0.810759	0.483911
H	4.051807	0.833485	-0.156301
H	3.404866	0.621191	1.482272
C	1.982202	-0.150961	-1.45994
H	2.651647	0.47047	-2.064421
H	2.290885	-1.210357	-1.576795
H	0.966902	-0.045008	-1.852531
C	1.088849	-0.452932	0.772452
H	1.25661	-0.131977	1.809253
H	1.296238	-1.542947	0.742014

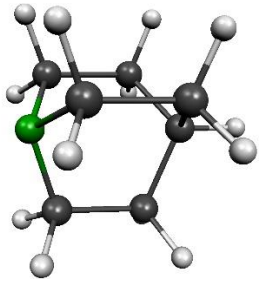


Figure 16: Molekel plot of Chinuclidine (**6**) [B3LYP/6-31+G(d)/gd3].

Table 8: Standard orientation for Chinuclidine (**6**) [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
N	-1.293679	-0.005685	0.000182
C	-0.804012	1.00218	-0.957195
H	-1.227952	1.971258	-0.668205
H	-1.21475	0.753165	-1.942879
C	-0.793356	-1.335349	-0.391535
H	-1.212893	-1.573146	-1.376303
H	-1.201235	-2.066689	0.316371
C	1.295729	0.005318	-0.000514
H	2.392206	0.010068	-0.000862
C	-0.800303	0.323296	1.349498
H	-1.217292	-0.413486	2.046369
H	-1.215665	1.29928	1.627448
C	0.758587	1.056939	-0.993328
H	1.136862	0.846639	-2.002427
H	1.124099	2.054291	-0.715098
C	0.769331	-1.38384	-0.416171
H	1.150462	-2.150054	0.271761
H	1.139802	-1.639287	-1.417651
C	0.762482	0.336549	1.408916
H	1.136113	1.317836	1.729874
H	1.135247	-0.40064	2.132312

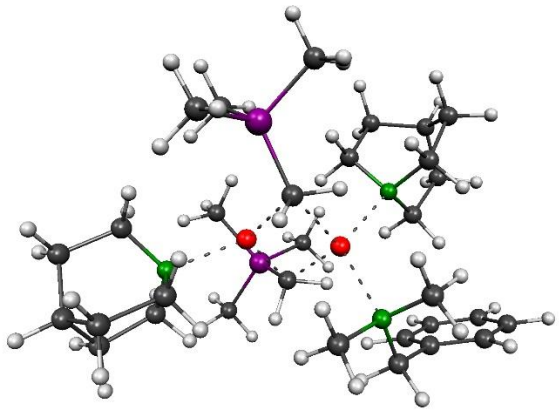


Figure 17: Molekel plot for Mixed Dimer **9** [B3LYP/6-31+G(d)/gd3].

Table 9: Standard orientation for Mixed Dimer **9** [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
N	-3.561655	-0.676784	0.108699
N	2.197018	1.306584	-0.143816
N	1.13156	-1.029275	2.515255

C	-4.581465	0.155709	-0.581575
C	-6.016867	-0.423307	-0.402096
C	-5.940004	-1.620326	0.56528
C	-5.046124	-2.705993	-0.06489
C	-3.660954	-2.072517	-0.392609
C	-3.843302	-0.666871	1.568968
C	-5.290881	-1.150352	1.880917
C	3.329229	0.494269	-0.658087
C	4.373717	1.370142	-1.410472
C	3.795914	2.790459	-1.56083
C	2.419014	2.68415	-2.243879
C	1.466274	1.906821	-1.292599
C	2.74725	2.404469	0.691061
C	3.59986	3.395551	-0.156285
C	-0.190647	-1.292877	3.109434
C	3.148243	-2.321185	1.637586
C	4.349918	-1.894991	2.224687
C	5.544908	-1.902439	1.500424
C	1.84722	-2.330199	2.412275
C	1.861128	-0.066456	3.352697
C	5.56066	-2.360283	0.178892
C	4.377675	-2.82026	-0.404866
C	-0.118013	-1.401955	-0.721213
C	-0.995899	1.601445	1.254144
Li	-1.580211	0.028347	-0.078799
Li	0.64061	0.109761	0.699699
C	3.184161	-2.801461	0.320593
H	-4.305606	0.214226	-1.639326
H	-4.508083	1.167248	-0.173756
H	-6.694396	0.342449	-0.004361
H	-6.429371	-0.748291	-1.365708
H	-6.943044	-2.018204	0.757485
H	-5.514669	-3.102169	-0.974407
H	-4.935441	-3.547714	0.630861
H	-2.840291	-2.645575	0.04886
H	-3.48252	-2.0445	-1.471023
H	-3.6715	0.348606	1.934827
H	-3.097355	-1.310023	2.047948
H	-5.277815	-1.97003	2.610365
H	-5.88417	-0.338844	2.321287
H	2.910244	-0.272725	-1.312679
H	3.784604	-0.020881	0.190126
H	5.321303	1.406284	-0.856866
H	4.594738	0.943151	-2.396709
H	4.470706	3.417986	-2.154438
H	2.518995	2.165672	-3.206363
H	2.017761	3.683093	-2.45638

H	0.704574	2.563996	-0.873354
H	0.939709	1.103153	-1.811528
H	3.351777	1.941938	1.47878
H	1.91198	2.91664	1.177791
H	3.096799	4.367809	-0.236732
H	4.571649	3.575049	0.320921
H	-0.760213	-1.94983	2.445311
H	-0.738142	-0.355308	3.21745
H	-0.104584	-1.77522	4.100585
H	4.354539	-1.56551	3.260987
H	6.463823	-1.561317	1.97083
H	1.156561	-3.022771	1.922672
H	2.03138	-2.718688	3.432126
H	1.272348	0.851189	3.442416
H	2.816836	0.184519	2.889188
H	2.053027	-0.462548	4.367547
H	6.489522	-2.367883	-0.385651
H	4.379418	-3.187722	-1.427968
H	0.969663	-1.462541	-0.553058
H	2.266738	-3.150815	-0.14485
H	-0.001718	1.897479	1.636672
Si	-1.785601	3.155315	0.605238
Si	-0.33324	-1.640823	-2.549062
C	1.312605	-1.395954	-3.491054
H	2.095096	-2.061649	-3.102087
H	1.190717	-1.61285	-4.560971
H	1.686179	-0.366987	-3.409529
C	-1.539612	-0.388813	-3.351841
H	-2.565731	-0.49598	-2.974642
H	-1.232659	0.648625	-3.160701
H	-1.583604	-0.523073	-4.441452
C	-0.988619	-3.368285	-3.03323
H	-1.190668	-3.445339	-4.110683
H	-0.258064	-4.146071	-2.772311
H	-1.91989	-3.6094	-2.503008
C	-2.20801	3.102796	-1.263623
H	-2.725867	4.02249	-1.56963
H	-1.307073	3.016182	-1.884591
H	-2.860053	2.261667	-1.531287
C	-0.681921	4.704968	0.794377
H	-0.430102	4.880459	1.848941
H	0.263729	4.599276	0.244812
H	-1.179997	5.606953	0.412688
C	-3.433064	3.541801	1.491849
H	-3.941247	4.408339	1.047228
H	-4.133031	2.696329	1.451648
H	-3.255836	3.763836	2.552719

H	-1.562486	1.316845	2.158341
H	-0.529443	-2.280252	-0.189696

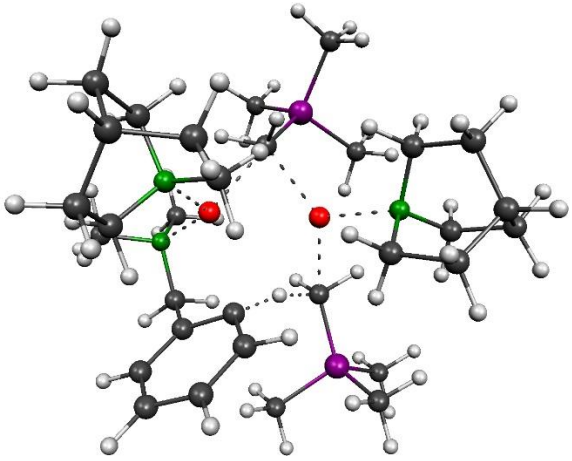


Figure 18: Molekel plot for Transition State **9-TS** [B3LYP/6-31+G(d)/gd3].

Table 10: Standard orientation for Transition State **9-TS** [B3LYP/6-31+G(d)/gd3].

Atomic Symbol	x	y	z
N	2.310474	-1.423078	-0.848906
N	-2.894892	-0.801771	-0.413794
N	-1.923726	1.482834	2.285055
C	3.781767	-1.204003	-0.819742
C	4.490932	-1.922022	-2.005358
C	3.409668	-2.452881	-2.966639
C	2.573465	-3.514436	-2.224464
C	2.039883	-2.882564	-0.905177
C	1.765972	-0.780493	-2.073753
C	2.48602	-1.283265	-3.358842
C	-3.861624	0.186148	-0.964825
C	-4.756476	-0.448904	-2.068773
C	-4.550446	-1.976076	-2.038337
C	-3.095693	-2.276005	-2.44682
C	-2.156674	-1.421737	-1.547307
C	-3.649486	-1.861749	0.303692
C	-4.765028	-2.475022	-0.594759
C	-1.36344	1.165661	3.60521
C	-1.398364	2.750313	0.218704
C	-2.262748	3.643442	-0.427591
C	-2.327422	3.679139	-1.825004
C	-1.314301	2.722822	1.731496
C	-3.382068	1.626892	2.373539
C	-1.518846	2.813792	-2.567297
C	-0.663463	1.922326	-1.905129

C	-0.275555	-1.630613	1.610286
C	1.964137	1.5645	0.872088
Li	1.199184	-0.446373	0.653029
Li	-1.397056	0.033794	0.817662
C	-0.57752	1.847397	-0.50281
Si	0.813455	-2.394961	2.919275
C	0.195243	-2.001527	4.677868
C	2.624143	-1.778779	2.880141
C	0.928218	-4.293551	2.770001
Si	2.753964	3.107361	0.184791
C	3.040297	2.909286	-1.688302
C	4.449844	3.501848	0.960371
C	1.644185	4.625513	0.447526
H	4.159861	-1.556856	0.144445
H	3.948963	-0.123909	-0.854341
H	5.159589	-1.228633	-2.530019
H	5.108545	-2.754402	-1.644604
H	3.873427	-2.888784	-3.858813
H	3.1855	-4.399305	-2.009673
H	1.743052	-3.846422	-2.861224
H	0.961186	-3.0286	-0.797523
H	2.510247	-3.334506	-0.026225
H	1.872914	0.299662	-1.951724
H	0.694932	-1.002336	-2.107206
H	1.755483	-1.609074	-4.109937
H	3.075658	-0.476252	-3.811944
H	-3.29721	1.041647	-1.341693
H	-4.472917	0.537863	-0.128626
H	-5.811862	-0.200288	-1.900937
H	-4.487689	-0.056756	-3.05819
H	-5.250177	-2.471781	-2.720867
H	-2.938266	-2.035225	-3.505676
H	-2.887163	-3.347096	-2.325246
H	-1.346598	-2.025669	-1.128537
H	-1.70152	-0.602606	-2.11071
H	-4.07097	-1.418516	1.213385
H	-2.9263	-2.618857	0.621206
H	-4.728861	-3.570999	-0.559295
H	-5.760757	-2.175413	-0.24277
H	-0.288184	0.994796	3.511396
H	-1.819325	0.24827	3.989166
H	-1.538147	1.977748	4.333506
H	-2.878718	4.324824	0.159447
H	-2.993507	4.378244	-2.325251
H	-0.261909	2.727226	2.024731
H	-1.784687	3.613482	2.183245
H	-3.835998	0.66963	2.652958

H	-3.779518	1.935822	1.403954
H	-3.673432	2.384328	3.123749
H	-1.550586	2.83872	-3.655672
H	-0.035807	1.277366	-2.519053
H	-1.238059	-1.47896	2.135705
H	-0.488353	-2.424217	0.872091
H	0.629234	1.477805	0.141253
H	1.732388	1.710195	1.940735
H	2.748979	0.785982	0.841352
H	-0.855076	-2.294773	4.808062
H	0.787924	-2.54226	5.427869
H	0.273475	-0.93205	4.908793
H	3.152086	-2.085769	1.968531
H	2.700079	-0.685374	2.955016
H	3.182309	-2.201294	3.726617
H	1.619477	-4.723912	3.507715
H	-0.056053	-4.756971	2.920607
H	1.278865	-4.592401	1.772589
H	2.090755	2.753864	-2.215073
H	3.695629	2.05589	-1.911604
H	3.515267	3.803733	-2.112958
H	5.153937	2.669508	0.824518
H	4.357496	3.677487	2.040595
H	4.90283	4.39822	0.513587
H	1.429729	4.783017	1.513473
H	0.686266	4.514671	-0.072726
H	2.130598	5.535821	0.072392

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