Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Normal to abnormal I^{t}Bu·AlH_3 isomerization in solution and in the solid state

Anna M. Chernysheva,[a] Michael Weinhart,[b] Manfred Scheer,[b] Alexey Y. Timoshkin *[a]

CONTENTS

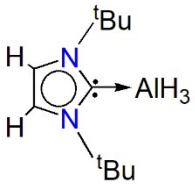
EXPERIMENTAL SECTION

General procedures

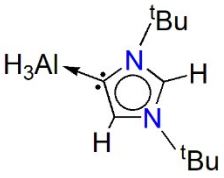
All manipulations were performed under dry argon using standard Schlenk and glove-box techniques. All solvents were purified and degassed by standard procedures.[1] The I^{t}Bu (1,3-di-*tert*-butylimidazolin-2-ylidene) was prepared according to literature procedure from the corresponding imidazolium salt.[2] $LiAlH_4$ was obtained from Sigma-Aldrich (95%) and used without further purification.

Deuterated solvents (benzene-d^6, dichloromethane-d^2 and tetrahydrofuran-d^8) were purchased from Sigma Aldrich, distilled, degased and stored over activated molecular sieves (4Å). The NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. ^{1}H NMR spectra were calibrated using residual proton signals of the solvent: (δ $^1H(C_6D_5H)$ = 7.16; δ ^1H(THF) = 1.72, 3.58; δ $^1H(CHDCl_2)$ = 5.32 ppm). ^{13}C NMR spectra were calibrated using the solvent signals (δ $^{13}C(C_6D_6)$ = 128.06; δ $^{13}C(d_8$-THF) = 67.21, 25.31; δ $^{13}C(CD_2Cl_2)$ = 53.84 ppm).

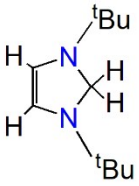
Elemental analyses (C, H, N) were performed on a Vario micro cube instrument.



1



1a



I^{t}BuH$_2$

Synthesis of 1/1a

First attempt: 0.50 g (2.8 mmol) I^{t}Bu was dissolved in 5 ml of Et_2O and added to a suspension of 0.32 g (8.3 mmol) $LiAlH_4$ in 12 ml Et_2O at −30 °C. The mixture was stirred and allowed to reach room temperature with additional stirring for 2 days. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene (320 mg, 54 %). **^{1}H NMR** (400 MHz, C_6D_6, 298 K) showed that during this attempt not all of the I^{t}Bu has reacted and the product mixture consisted of **1** (62% of the mix, δ = 6.41 (s, 2H, NC_2H_2N), 5.42 (br, AlH_3), 1.55 (s, 18H, ^{t}Bu) ppm), I^{t}Bu (35% of the mix, δ = 6.50 (s, 2H, NC_2H_2N), 1.37 (s, 18H, ^{t}Bu) ppm) and the side product I^{t}BuH$_2$ (3% of the mix, δ = 5.49 (s, 2H, NC_2H_2N), 4.25 (s, 2H, NCH_2N), 1.00 (s, 18H, ^{t}Bu) ppm). After the subsequent syntheses (attempts 2 and 3) no free I^{t}Bu was observed. Colorless crystals of **1a** were obtained by dissolving small amount of product mixture in THF layered with *n*-hexane and storing the solution at 6°C for a week (Fig. S10).

Second attempt: 0.10 g (0.56 mmol) I^{t}Bu was dissolved in 5 ml of Et_2O and added to a suspension of 76 mg (2.0 mmol) $LiAlH_4$ in 10 ml Et_2O at 0 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene (61 mg). The product is a mixture of isomers: normal (**1**) (46%) and abnormal (**1a**) (1%). The side product I^{t}BuH$_2$ (5%) is observed as in the first attempt. The attempt to obtain the crystals of **1** or **1a** from hexane solution at −27 °C failed. The isomers **1** and **1a** can be distinguished by the singlets of the tert-butyl protons: in case of **1** one singlet at 1.55 ppm for 18 tert-butyl protons is observed in C_6D_6, while **1a** gives two singlets at 1.47 and 0.68 ppm since the two ^{t}Bu-groups are non-equivalent. **^{1}H NMR** (400 MHz, C_6D_6, 298 K) of **1**: δ = 6.41 (s, 2H, NC_2H_2N), 5.42 (br, AlH_3), 1.55 (s, 18H, ^{t}Bu) ppm; **1a**: δ = 7.26 (s, 1H, NCHN), 6.75 (s, 2H, NC_2HN), 4.34 (br, AlH_3), 1.47 (s, 9H, ^{t}Bu), 0.68 (s, 9H, ^{t}Bu) ppm (Fig. S1). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 298 K) of **1**: δ = 30.61 (CH_3-^{t}Bu), 59.94 ($C(CH_3)_3$), 117.23 (N*C*H*C*HN) ppm (Fig. S1).

Third attempt: 0.50 g (2.8 mmol) I^{t}Bu was dissolved in 10 ml of Et_2O and added to a suspension of 0.21 g (5.6 mmol) $LiAlH_4$ in 10 ml Et_2O at −50 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene. The small amount of white product was dissolved again in toluene and within 3 days at 6 °C crystals of **1** were obtained (Fig. S11) (180 mg, 31

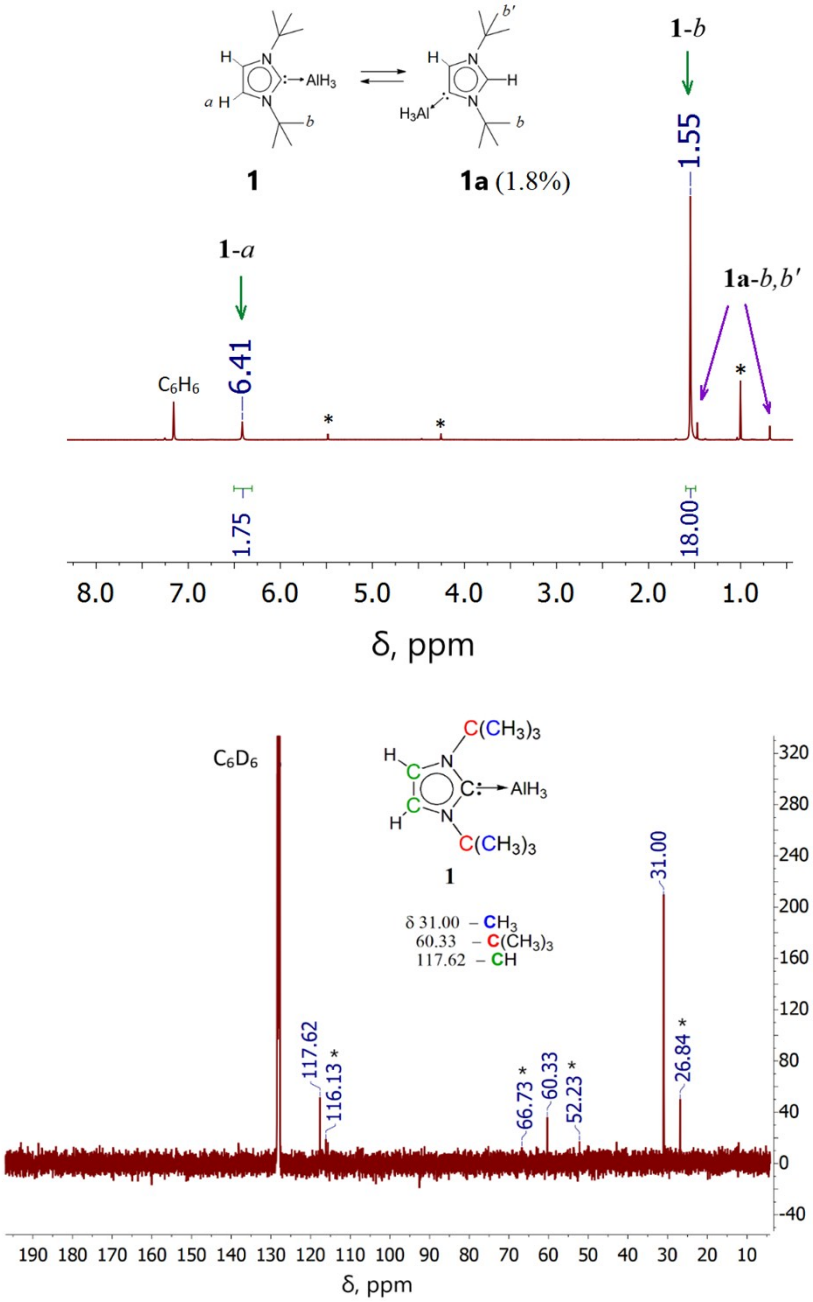


Figure S1. ^{1}H NMR (C_6D_6, 400 MHz) of product mixture with **1** form predominance; * denotes I^{t}BuH_2 (top); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz) of product mixture (bottom).

%). **CHN** (%) calc. for $C_{11}H_{23}AlN_2$: C 62.83, H 11.02, N 13.32; found: C 63.15, H 10.20, N 13.33.

The role of the solvent in the isomerization

In order to understand the role of the solvent in the formation of abnormal isomer, the synthesis was repeated and NMR studies were carried out.

0.20 g (1.1 mmol) I^{t}Bu was dissolved in 4 ml of Et_2O and added to a suspension of 0.14 g (3.7 mmol) $LiAlH_4$ in 10 ml Et_2O at −20 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 40 ml of toluene and filtered to remove LiH and the excess of $LiAlH_4$. The resulting white solid was obtained after removing of toluene (0.15 g, 65%).

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were measured in C_6D_6 and CD_2Cl_2 just after the synthesis. In nonpolar C_6D_6 the content of abnormal isomer **1a** is the lowest and equals 1.8% (Fig. S2 + S3). Amount of **1a** increases in the case of more polar solvent dichloromethane (14%) (Fig. S4 + S5). NMR measurements were carried out at room temperature ca. 2 hours after the addition of the solvent.

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) of **1**: δ = 7.20 (s, 2H, NC_2H_2N), 4.41 (br, AlH_3), 1.80 (s, 18H, CH_3-^{t}Bu) ppm; **1a**: δ 8.01 (d, $^4J_{HH}$=1.8 Hz, 1H, NC*H*N), 7.28 (d, $^4J_{HH}$=2Hz, 1H, 1H, NC_2HN), 3.19 (br, AlH_3), 1.73 (s, 9H, CH_3-^{t}Bu), 1.60 (s, 9H, CH_3-^{t}Bu) ppm. For comparison the **^{1}H NMR** (400 MHz, CD_2Cl_2, 298 K) for I^{t}Bu·$AlMe_3$/*a*I^{t}Bu·$AlMe_3$[3]: I^{t}Bu·$AlMe_3$: δ = 7.17 ppm (s, 2H, NCHCHN), 1.73 (s, 18H, CH_3-^{t}Bu), -0.73 (s, 9H, $AlMe_3$); aI^{t}Bu·$AlMe_3$: δ = 7.92 (d, $^4J_{HH}$=2Hz, 1H, NC*H*N), 7.10 (d, $^4J_{HH}$=2Hz, 1H, NC*H*CN), 1.65 (s, 9H, CH_3-^{t}Bu), 1.59 (s, 9H, CH_3-^{t}Bu), -0.96 (s, 9H, $AlMe_3$) ppm.

^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz, 298 K) of **1**: δ = 31.33 (*C*H_3-^{t}Bu), 60.67 (*C*$(CH_3)_3$), 118.51 (N*C*H*C*HN) ppm; **1a**: δ 30.31 (*C*H_3-^{t}Bu), 30.47 (*C*H_3-^{t}Bu), 58.15 (*C*$(CH_3)_3$), 63.09 (*C*$(CH_3)_3$), 153.91 ($C_{carbene}$) ppm. For comparison the **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2, 298 K) for I^{t}Bu·$AlMe_3$/*a*I^{t}Bu·$AlMe_3$[3]: I^{t}Bu·$AlMe_3$: δ = -0.8 ($AlMe_3$), 31.4 (CH_3-^{t}Bu), 59.1 ($C(CH_3)_3$), 117.4 (NCHCHN), 174.3 ppm ($C_{carbene}$); aI^{t}Bu·$AlMe_3$: δ = -6.1 ($AlMe_3$), 29.9 (CH_3-^{t}Bu), 30.4 (CH_3-^{t}Bu), 57.2 ($C(CH_3)_3$), 59.1 ($C(CH_3)_3$), 126.8 (NCHCN), 128.6 (NCHN), 155.9 ppm ($C_{carbene}$).

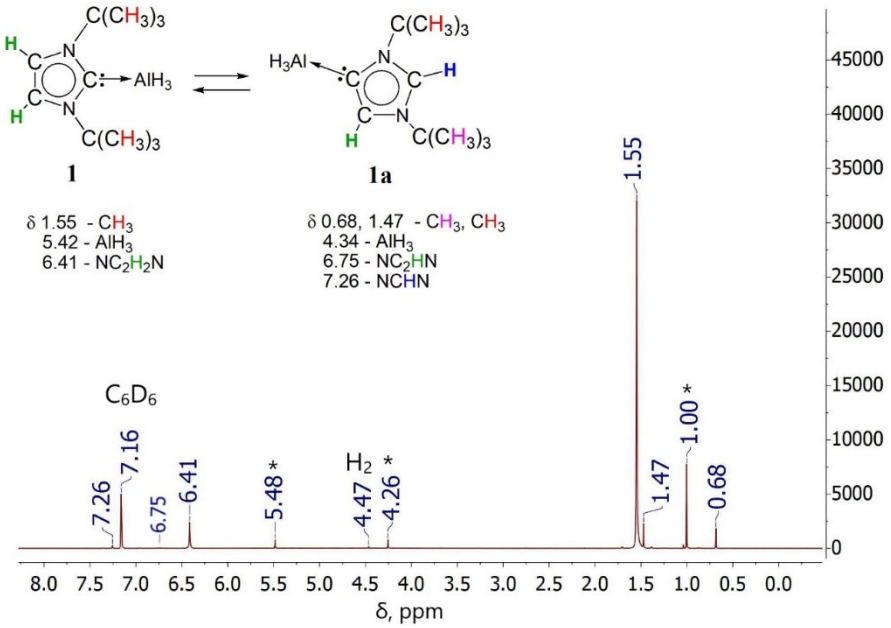


Figure S2. ^{1}H NMR (C_6D_6, 400 MHz) of product mixture with isomer **1** predominance; * denotes I^{t}BuH_2 (8 %).

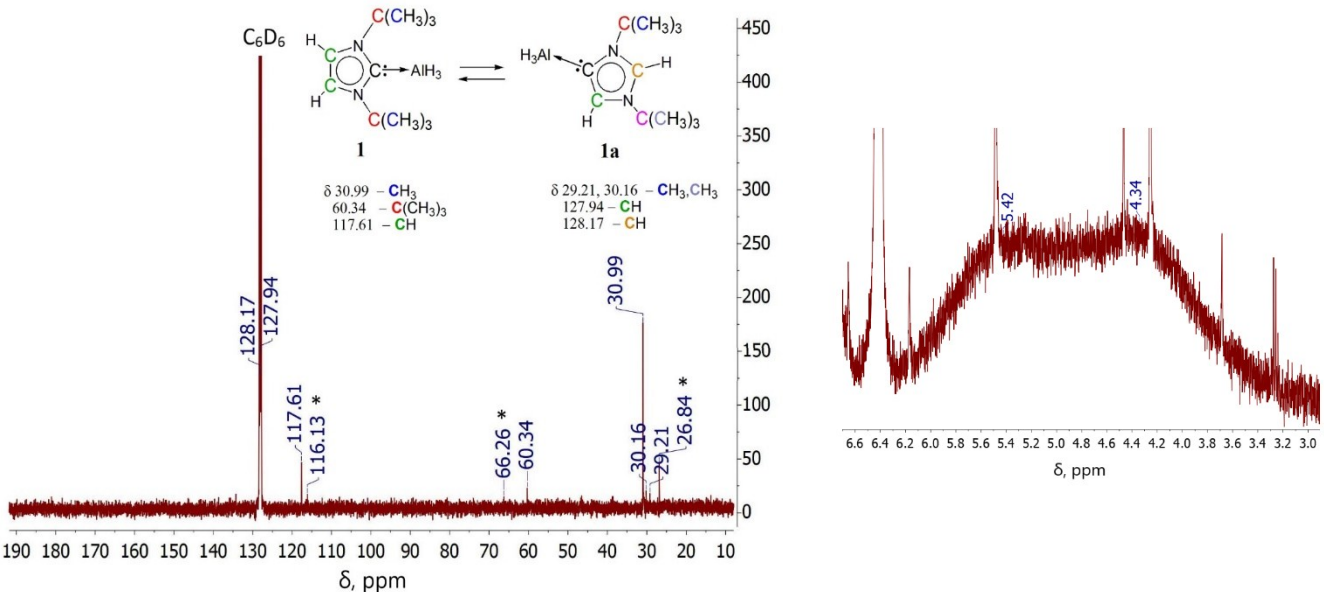


Figure S3. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz) (left); ^{1}H NMR (C_6D_6, 400 MHz) of product mixture: fragment with AlH_3-signals (right); * denotes I^{t}BuH_2 (8 %).

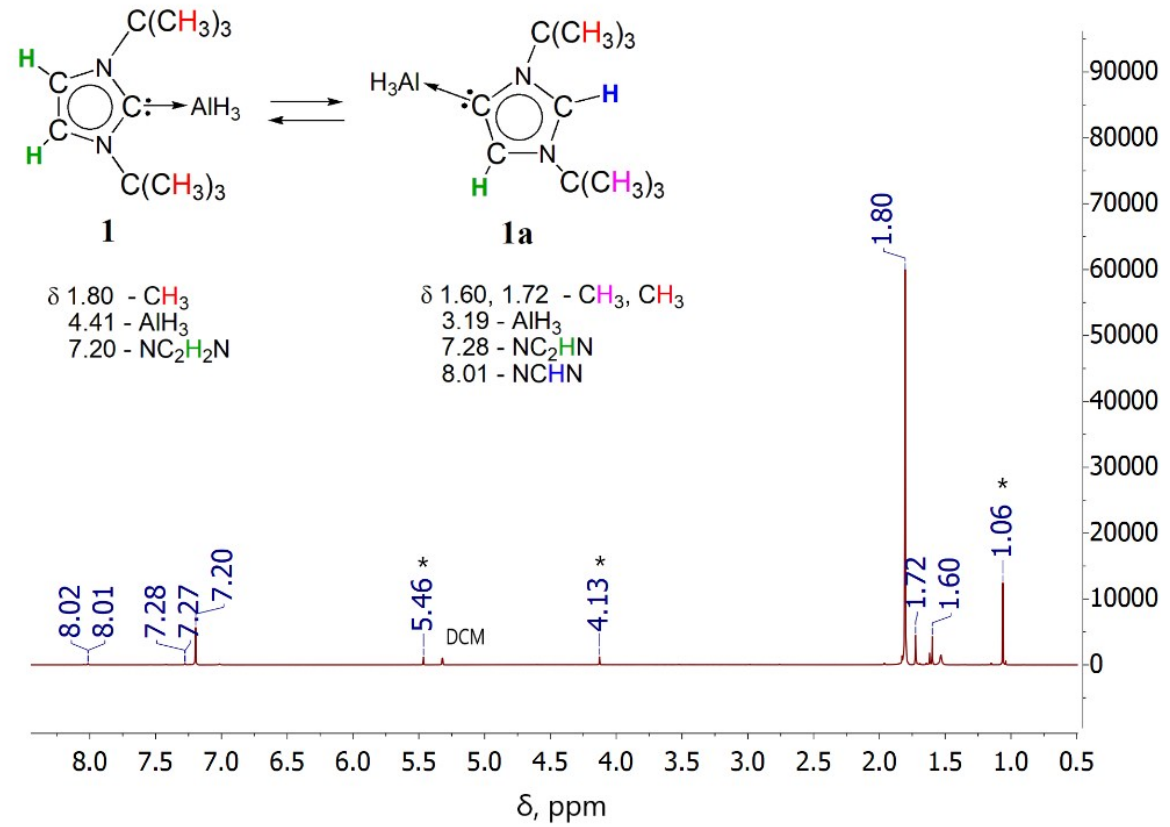


Figure S4. ^{1}H NMR (CD_2Cl_2, 400 MHz) of product mixture; * denotes I^{t}BuH_2 signals.

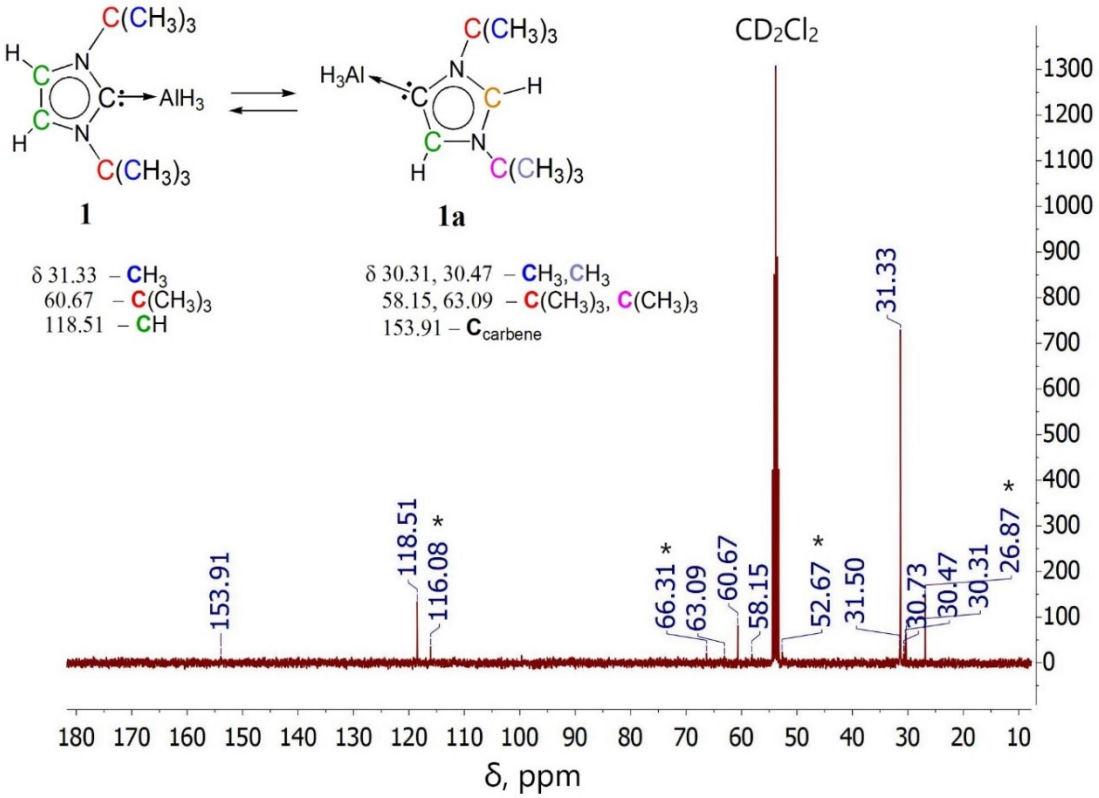


Figure S5. ^{13}C{^{1}H} NMR (CD_2Cl_2, 400 MHz) of product mixture; * denotes I^{t}BuH_2 signals: δ 26.87 (CH_3-^{t}Bu), 52.67 (NCH_2N), 66.31 ($C(CH_3)_3$), 116.08 (NCHCHN) ppm.

The NMR spectra were measured also in d_8-THF after 3 weeks of storing the product under argon. **^{1}H NMR** (d_8-THF, 400 MHz, 298 K) of **1**: δ = 7.33 (s, 2H, NC_2H_2N), 4.13 (br, AlH_3), 1.74 (s, 18H, ^{t}Bu) ppm; **1a**: δ 8.39 (s, 1H, NCHN), 7.27 (s, 2H, NC_2HN), 3.34 (br, AlH_3), 1.73 (s, 9H, ^{t}Bu), 1.60 (s, 9H, ^{t}Bu) ppm. **^{13}C{^{1}H} NMR** (d_8-THF, 100 MHz, 298 K) of **1**: δ = 31.22 (CH_3-^{t}Bu), 59.66 ($C(CH_3)_3$), 118.14 (NCHCHN) ppm, **1a**: δ 29.77 (CH_3-^{t}Bu), 30.29 (CH_3-^{t}Bu), 57.96 ($C(CH_3)_3$), 60.27 ($C(CH_3)_3$), 128.52 (NCHCN), 130.92 (NCHN) (Fig. S6 +S7).

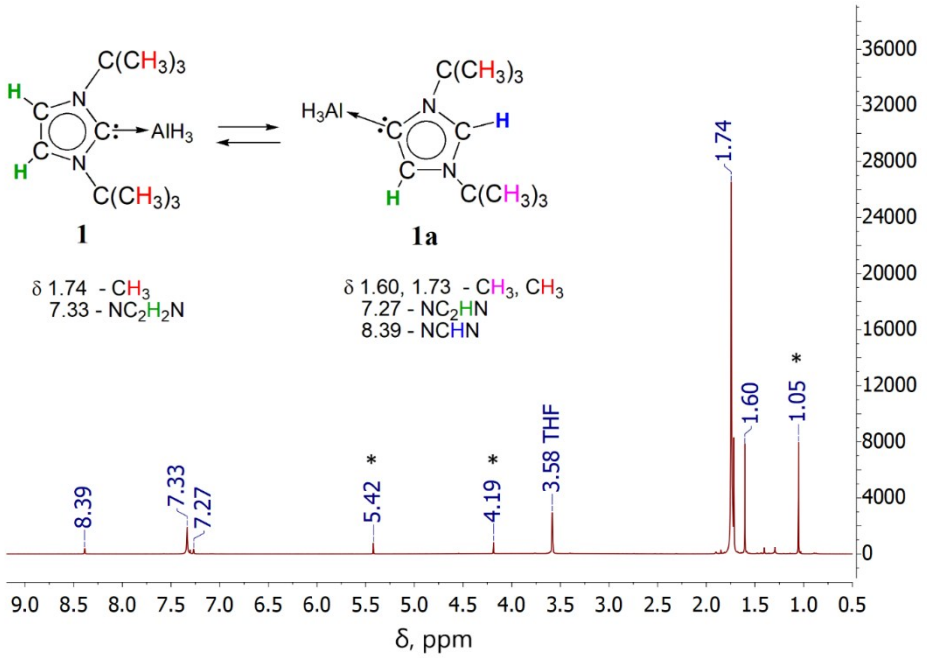


Figure S6. ^{1}H NMR (d^8-THF, 400 MHz) of product mixture. * denotes I^tBuH_2 signals.

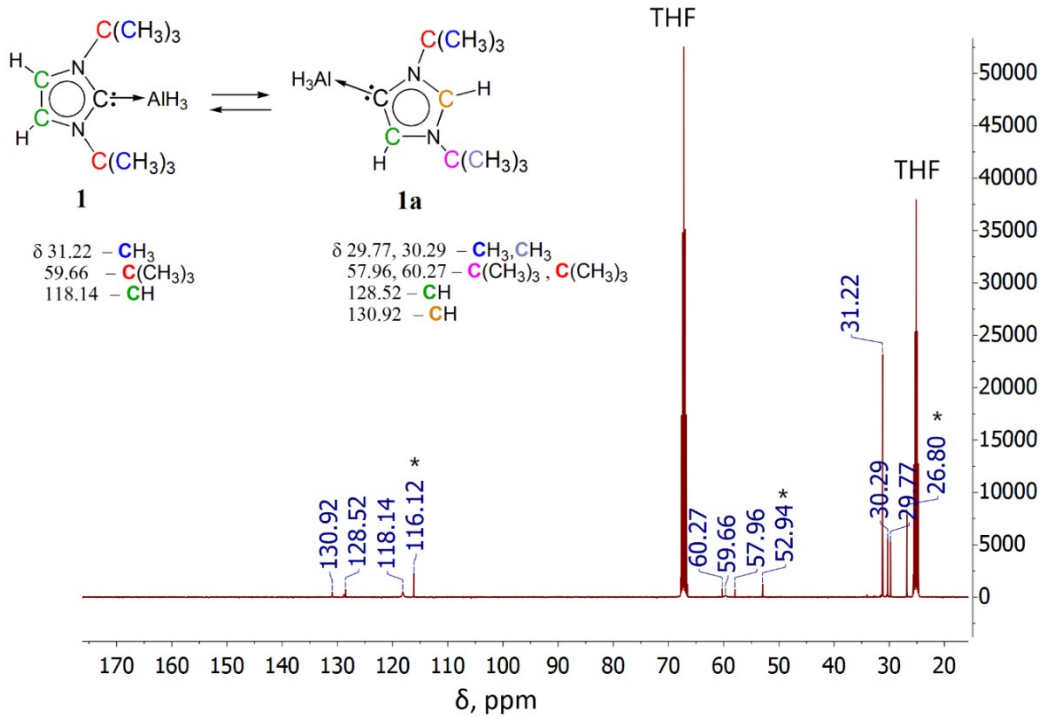


Figure S7. $^{13}C\{^{1}H\}$ NMR (d^8-THF, 400 MHz) of product mixture; * denotes I^tBuH_2 signals.

THF as medium has lower dielectric constant ε=7.43[4] than the dichloromethane (ε=8.93)[4] and the content of form **1a** was expected to be lower than in case of CD_2Cl_2 (see DFT computations on page S21, Table S5), but it equaled 19% (Fig. S4 + S5). This fact points on the specific joint of THF in isomerization process or the isomerization in the solid state during storing.

Isomerization in the solid state

We decided to check if **1** isomerizes into **1a** in the solid state. According to ^{1}H NMR in CD_2Cl_2 NMR after 2 hours after the synthesis and isolation of **1** the content of **1a** in the mixture of isomers was only 14% (NMR control). After 32 days of storage of the product in the solid state under argon the amount of **1a** increased up to 89 %, and after 81 days only isomer **1a** is present in the solid state (Fig. S8, Fig. S9). The signals of ^{t}Bu protons are the most representative (1.80 ppm for **1**, 1.72 and 1.60 ppm for **1a**).

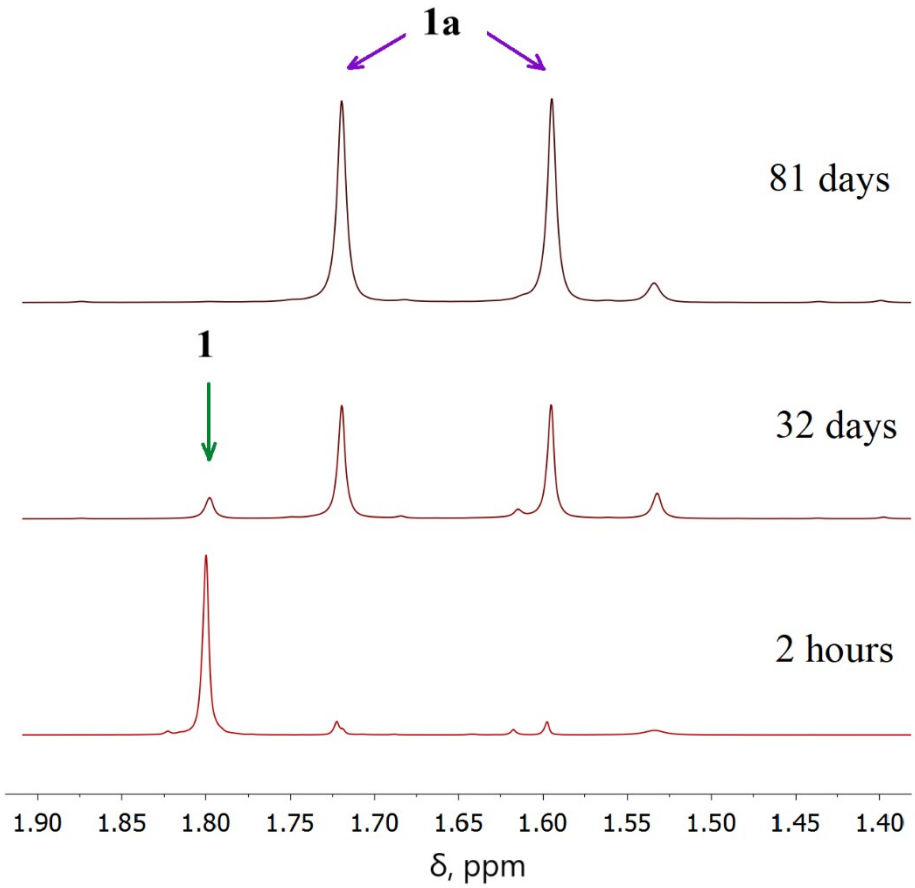


Figure S8. Section of ^{1}H NMR spectra (CD_2Cl_2, 400 MHz): the increase of the contents of **1a** after 32 days and 81 days of storing the product mixture in the solid state under argon.

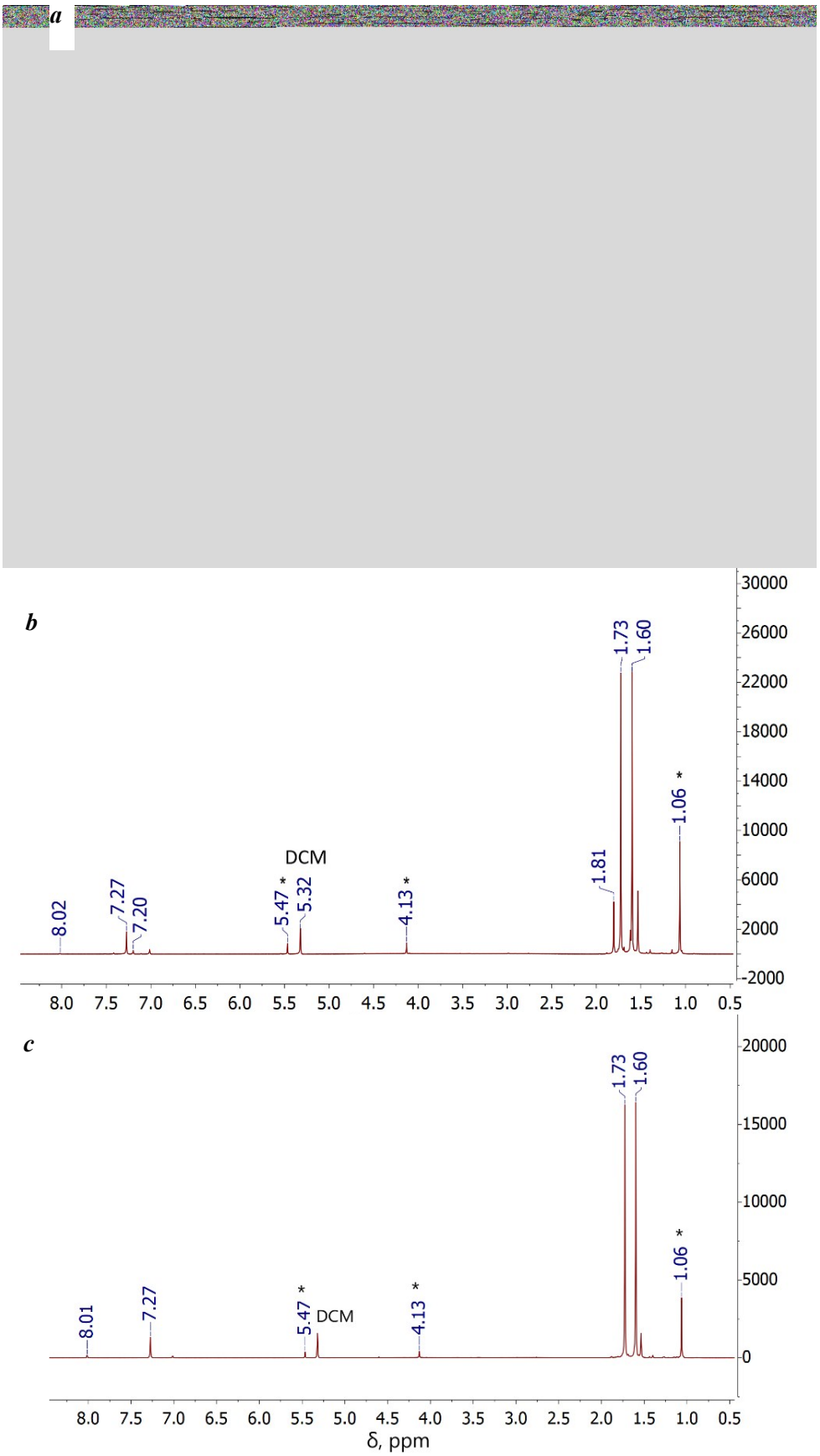


Figure S9. ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of product mixture: a) 2 hours after the synthesis; b) after 32 days; c) after 81 days.

Crystallographic details

The single crystal X-Ray structure analysis was performed on a Rigaku Oxford Diffraction SuperNova and a Rigaku Oxford Diffraction GeminiUltra diffractometers applying Cu-Kα radiation (λ = 1.54178 Å) at 123 K. All crystallographic manipulations were performed under mineral oil. Crystals were selected from the ampule in an inert atmosphere and placed into dehydrated and deoxygenated mineral oil. A selected crystal was mounted on a plastic MiTeGen CryoMounts® loop under a stream of cold N_2. The structure was solved using the Olex2 program[5] and refined anisotropically against F2 using the SHELXT program.[6] Crystallographic data together with the details of the experiment are given in Table S1. All cif-files (CCDC 1966204 (**1**) and 1966205 (**1a**)) are available online from the Cambridge Crystallographic Data Centre.

Table S1. Summary of crystallographic data and structure refinement for complex **1** and **1a** characterized by single crystal X-ray structure determination.

	1	**1a**
Empirical formula	$C_{11}H_{23}AlN_2$	$C_{11}H_{23}AlN_2$
Formula weight	210.29	210.29
Temperature [K]	122.98(10)	123.0(2)
Wavelength [Å]	1.54184	1.54184
Crystal system	tetragonal	monoclinic
Space group	$P4_2/n$	$P2_1/n$
a [Å]	13.99950(10)	8.5552(5)
b [Å]	13.99950(10)	11.6275(7)
c [Å]	13.7306(2)	13.9902(8)
α/β/γ [°]	90/90/90	90/102.264(6)/90
Volume [Å^3]	2691.00(5)	1359.92(14)
Z	8	4
ρ_{calc} [g/cm^3]	1.038	1.027
μ [mm^{-1}]	1.061	1.050
F(000)	928.0	464.0
2Θ-area [°]	8.934 to 146.88	9.986 to 149.402
Index ranges	$-12 \le h \le 16$, $-16 \le k \le 16$, $-16 \le l \le 12$	$-10 \le h \le 7$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	7413	7331
Unique reflections	2605	2672
R_{int}	0.0187	0.0731
Data / restraints / parameters	2605/0/146	2672/0/146
Goodness-of-fit on F^2	1.047	1.058
R_1 [I>=2σ(I)]	0.0317	0.0599
wR_2 [I>=2σ(I)]	0.0867	0.1670
R_1 (all data)	0.0330	0.0649
wR_2 (all data)	0.0877	0.1755
Largest diff. peak and hole max. / min. [e·Å^{-3}]	0.261/-0.232	0.438/−0.461

CCDC-1966204 (**1**) and CCDC-1966205 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

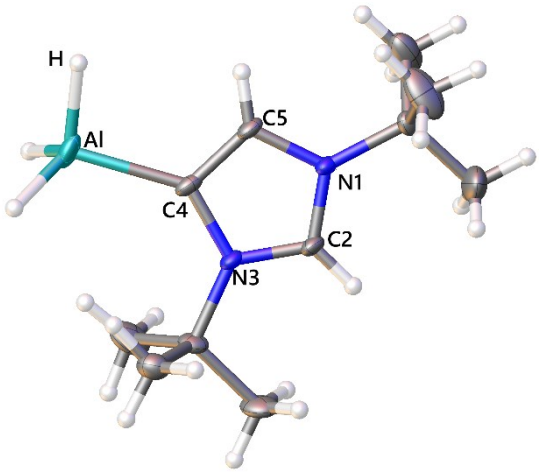
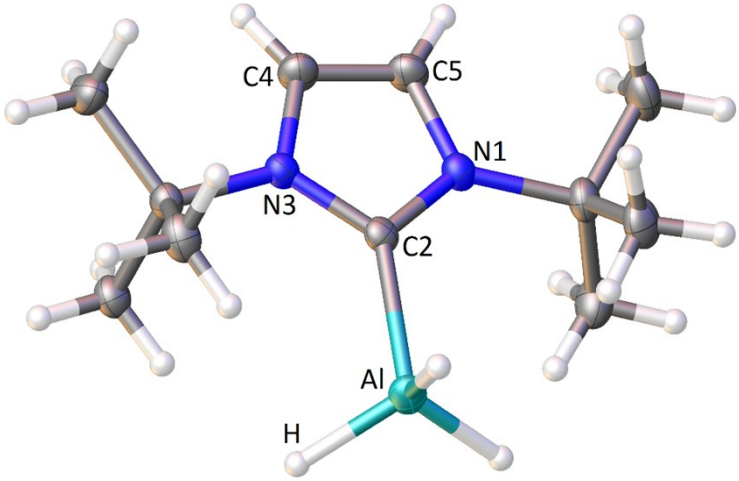


Figure S10. Molecular structure of complex **1a**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental bond distances (Å) and angles (°): Al–C4 2.026(2); Al–H 1.56(3); C2–N1 1.326(3); C2–N3 1.332(3); N3–C4 1.411(2); N1–C5 1.383(3); C4–C5 1.355(3); N1–C2–N3 109.35(17); N3–C4–C5 103.39(16).



1

Figure S11. Molecular structure of complex **1**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental bond distances (Å) and angles (°): Al–C2 2.0838(11); Al–H 1.50(2); C2–N1 1.3684(14); C2–N3 1.3694(14); N3–C4 1.3790(15); N1–C5 1.3787(15); C4–C5 1.3406(17); N1–C2–N3 104.45(9); N3–C4–C5 107.28(10).

COMPUTATIONAL SECTION

Computational details

Density functional theory in form of B3LYP-D3[7] functional with conjunction of def2-SVPD[8] basis set was used as implemented in Gaussian-16 software suite[9] to locate minima and transition states on the respective potential energy surfaces of the studied systems. Vibrational frequency computations were performed to verify that obtained stationary points are either true minima (Nimag=0) or transition states (Nimag=1) and to obtain the thermodynamic characteristics. Intrinsic reaction coordinate (IRC[10]) scans were performed to prove that the transition state connects the corresponding reactants and products. In order to take into account solvent effects, the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)[11] was used.

Mechanistic studies

We considered two pathways of solvent-free isomerization. The first includes H-transfer via in situ H_2 formation and subsequent reaction (pathway 1). The second pathway consists of dissociation and NHC-assisted proton transfer (pathway 2). Computed reaction pathways are depicted in Fig. S12 and Fig. S13.

Pathway 1:

As a starting point for the geometry optimization, geometry of the one asymmetric unit of **1a** that contains two neighboring *a*I^{t}Bu·AlH_3 molecules was used. We succeeded in locating the transition state **TS4** (Fig. S12) featuring the hydrogen expulsion reaction which leads to the intermediate **4**, which was confirmed by the intrinsic reaction coordinate (IRC) scan. In the same manner we located transition state **TS3** and suggested the reaction pathway up to **1** through 8 steps forming 3 intermediates. The reaction starts with interaction of the hydridic H on aluminum in **1** with the hydrogen atom in the NHC backbone of the neighboring molecule. Passing through the transition state **TS1** results in the dihydrogen molecule formation along with intermediate **2**. The formation of **2** is thermodynamically favored ($\Delta G^\circ_{298} = -31$ kJ·mol^{-1}) but the activation barrier is very high (413 kJ·mol^{-1}). Then the reaction with hydrogen leads to cleavage of Al-C bond and formation of ion-pair **3** passing the **TS2**. Next step was suggested in an assumption that hydride in anion of ion-pair **3** interacts with proton in the backbone of the cation of the ion-pair via transition state **TS3**, resulting the hydrogen expulsion and formation of **4**. Finally, **4** reacts with molecular H_2 with cleavage of the Al-C bond via **TS4** and formation of the product **1a** (Fig. S12).

At B3LYP-D3/def2-SVPD level of theory several attempts of localizing **TS2** failed. The Synchronous Transit-guided Quasi-Newton method (QST2 and QST3 options)[12] did not help:

the predicted **TS2** reorganizes into the product **3**. **TS2** was localized on a RHF/3-21G* level of theory with subsequent SP-computation on B3LYP-D3/def2-SVPD level of theory.

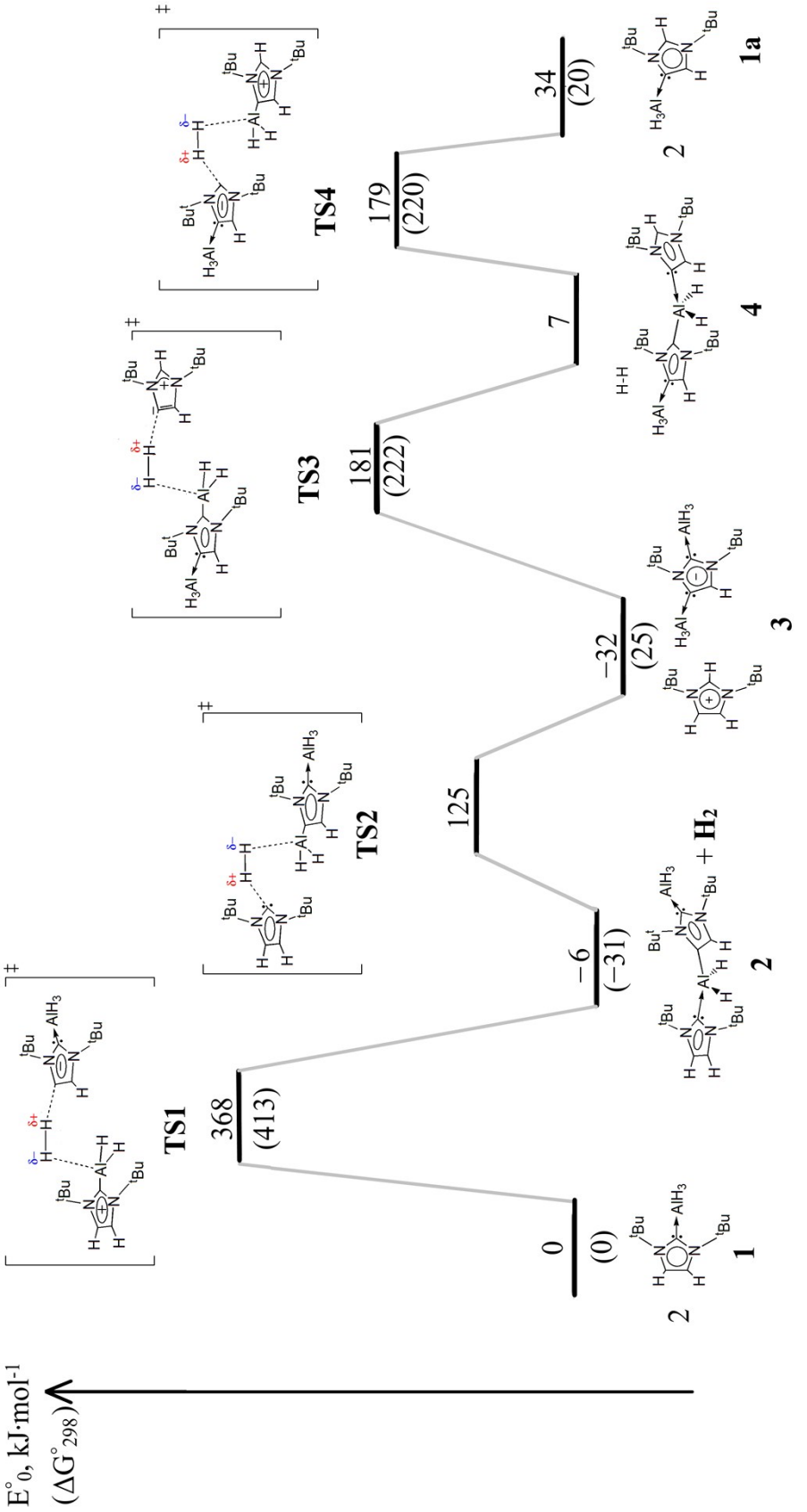


Figure S12. Energy profile for the isomerization process (pathway 1). The relative energies (ΔE°_{298}, in kJ·mol^{-1}) and Gibbs free energy values (ΔG°_{298}, in kJ·mol^{-1}, in parentheses) are given with respect to two isolated molecules of **1**. B3LYP-D3/def2-SVPD level of theory.

Pathway 2:

For pathway 2 the dissociation of one molecule of **1** is considered as a first step (Fig. S13). Then the free carbene I^{t}Bu attacks the hydrogen atom in the NHC backbone of the neighboring molecule **1**, passing the **TS5** and forming the ion-pair **5**. The association of an anion with AlH_3 leads to formation of a more stable ion-pair **3**. The dissociation of AlH_3 from C2-carbone of anion leads to the new ion-pair **6**. Then the proton in the backbone of cationic part of **6** interacts with the carbene site of anionic part, passing **TS6** (**TS6′**) and forming **1a** and *a*I^{t}Bu. The latter forms complex with AlH_3 on the last step. The energy barrier of 425 kJ·mol^{-1} is very high to make the isomerization through this pathway operational.

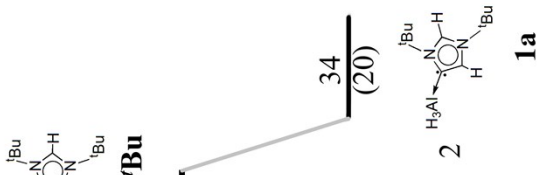


Figure S13. Energy profile for the isomerization process (pathway 2). The relative energies (ΔE°_{0}, in kJ·mol^{-1}) and Gibbs free energy values (ΔG°_{298}, in kJ·mol$^{-1,}$ in parentheses) are given with respect to two isolated molecules of **1**. B3LYP-D3/def2-SVPD level of theory.

Thermodynamic characteristics

Table S2. Total energies E°_0, sum of electronic and thermal enthalpies H°_{298}, standard Gibbs free energies (Hartree) and standard entropies S°_{298} (cal·mol^{-1}K^{-1}).

	B3LYP-D3/def2-SVPD level of theory				RHF/3-21G* level of theory		
Compound	E°_0	H°_{298}	S°_{298}	G°_{298}	E°_0	H°_{298}	S°_{298}
1	-784.5702435	-784.233327	126.598	-784.293478			
1a	-784.5638492	-784.227324	131.430	-784.289771			
H_2	-1.1738579	-1.160603	31.224	-1.175438			
AlH_3	-244.1458501	-244.123270	49.545	-244.146810			
I^{t}Bu	-540.3622556	-540.052199	118.815	-540.108653			
*a*I^{t}Bu	-540.3357863	-540.025745	118.924	-540.082250			
I^{t}BuH$_2$	-541.5740532	-541.240872	118.168	-541.297018			
TS1	-1569.0003509	-1568.328925	211.650	-1568.429487			
2	-1567.9739281	-1567.316767	204.045	-1567.413715			
TS2[a)]	-1569.0927777				-1552.9072531	-1552.189447	214.757
3	-1569.1527897	-1568.476936	211.831	-1568.577584			
TS3	-1569.0715338	-1568.399416	216.520	-1568.502292			
4	-1569.1379301	-1568.400758	215.706	-1568.503246			
TS4	-1569.0724876	-1568.400758	215.706	-1568.503246			
TS5[a)]	-1324.8315682				-1310.518006	-1309.827722	193.472
5[a)]	-1569.0169065				-1552.8699562	-1552.149126	226.906
6	-1569.0999114	-1568.425537	217.381	-1568.528822			
TS6	-1569.0037432	-1568.334568	211.167	-1568.434900			
TS6′[a)]	-1324.8969215				-1310.5049524	-1309.815808	198.651

[a)] SP energy on B3LYP-D3/def2-SVPD with optimized on RHF/3-21G* geometry.

Table S3. Total energies E°_0, sum of electronic and thermal enthalpies H°_{298} (Hartree) and standard entropies S°_{298} (cal·mol^{-1}K^{-1}) of **1** and **1a** in gas phase and in different solvents. B3LYP-D3/def2-SVPD level of theory.

	compound	E°_0	H°_{298}	S°_{298}
gas phase	**1**	-784.5702440	-784.233327	126.598
	1a	-784.5638492	-784.227324	131.430
n-hexane (ε=1,8819)	**1**	-784.5750926	-784.238259	126.340
	1a	-784.5729135	-784.236457	132.216
C_6H_6 (ε=2,2706)	**1**	-784.5763670	-784.239567	126.335
	1a	-784.5751887	-784.23872	131.258
THF (ε=7,4257)	**1**	-784.5820578	-784.245467	126.470
	1a	-784.5848261	-784.248497	132.121
DCM (ε=8,93)	**1**	-784.5826012	-784.246041	126.491
	1a	-784.5857036	-784.249407	132.211

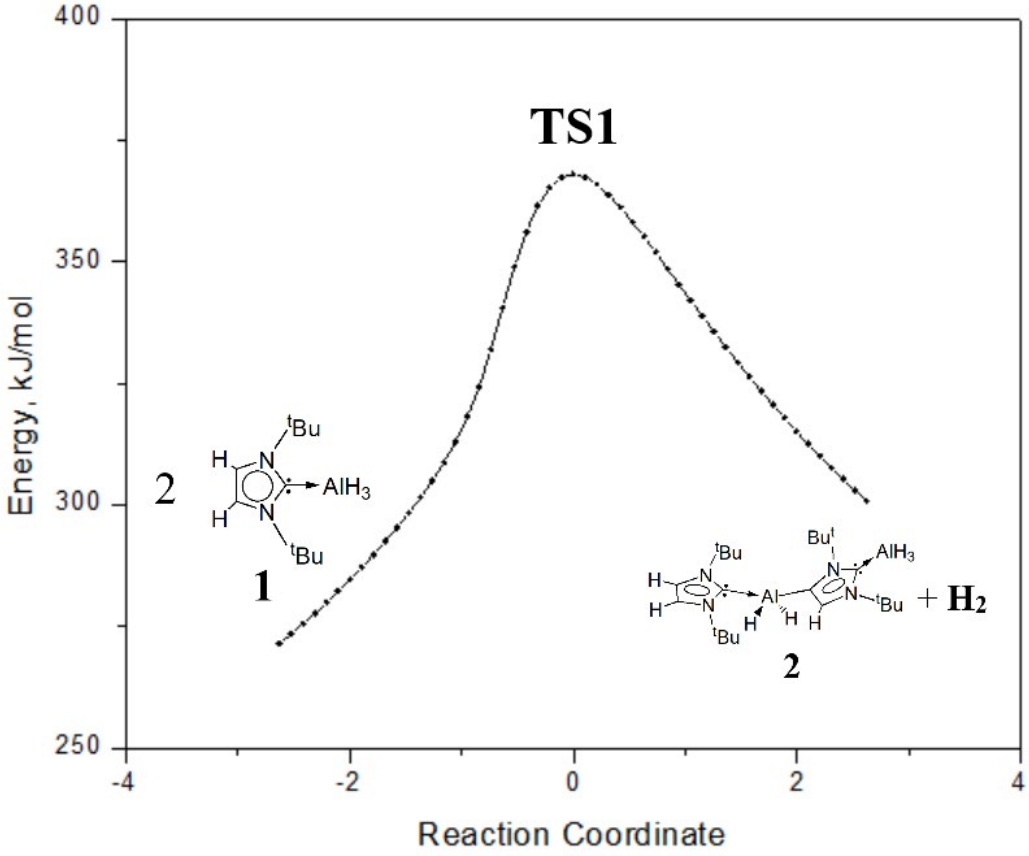
Table S4. Computed energies ΔE°_{0} (in kJ·mol^{-1}), standard enthalpies $\Delta H°_{298}$, standard entropies $\Delta S°_{298}$ (cal·mol^{-1}K^{-1}) and Gibbs free energies $\Delta G°_{298}$ (in kJ·mol^{-1}) for processes (1)-(4) in the gas phase. B3LYP-D3/def2-SVPD, PCM level of theory.

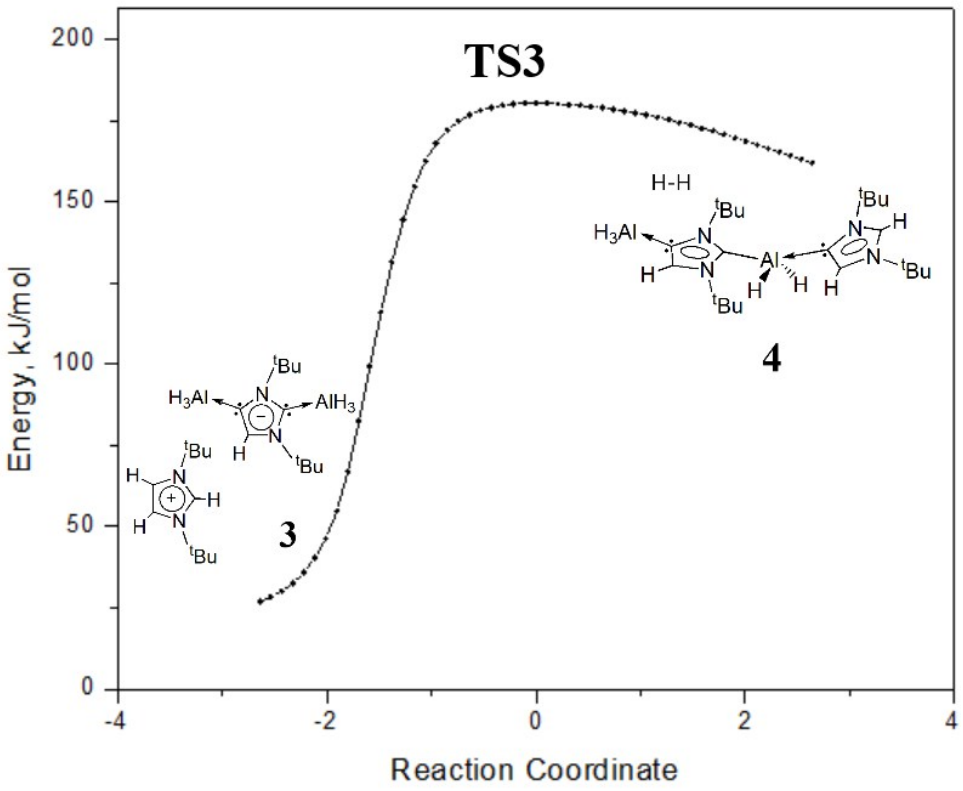
	Process	ΔE°_{0}	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
(1)	**1** = I^{t}Bu + AlH_3	163.1	151.9	174.7	99.8
(2)	**1a** = *a*I^{t}Bu + AlH_3	215.8	205.6	155.0	159.4
(3)	I^{t}Bu = *a*I^{t}Bu	69.5	69.5	0.5	69.3
(4)	**1** = **1a**	16.8	15.8	20.2	9.7

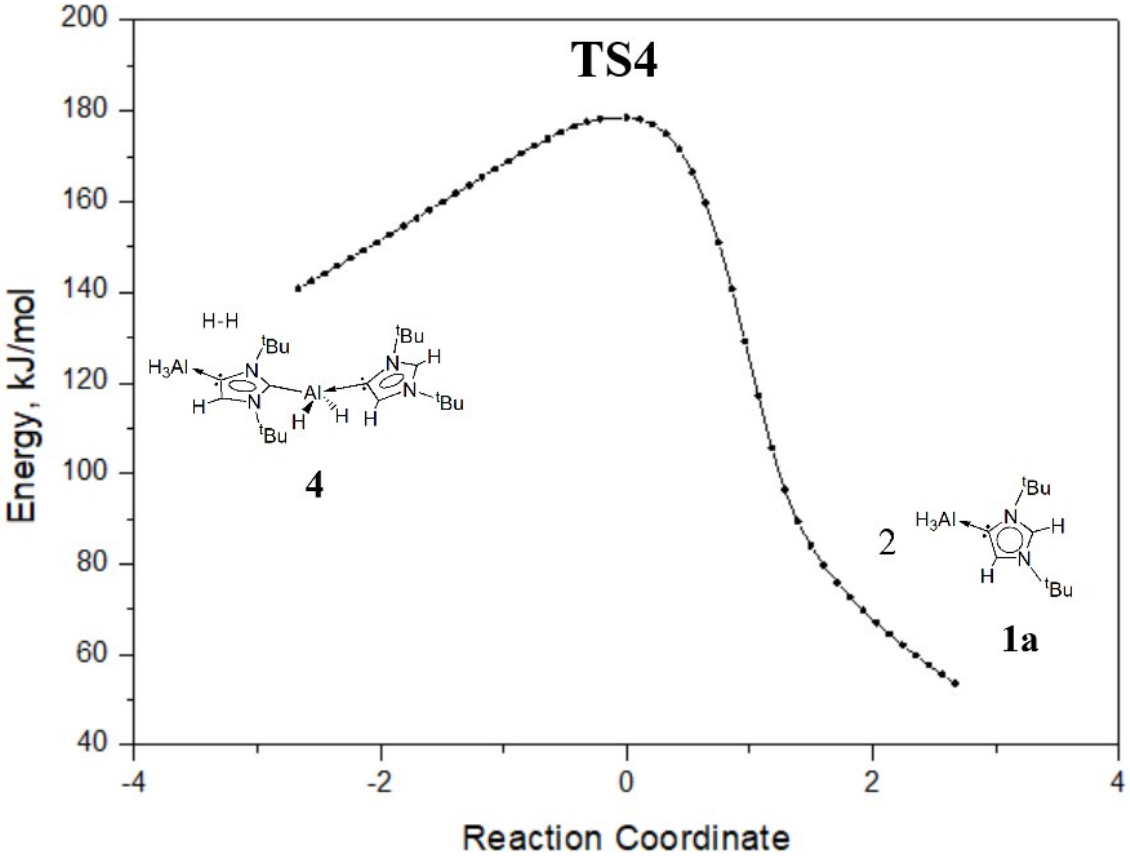
Table S5. Computed ΔE°_{0} (in kJ·mol^{-1}) of isomer **1a** with respect to **1**, standard enthalpies $\Delta H°_{298}$, standard Gibbs free energies $\Delta G°_{298}$ (in kJ·mol^{-1}), equilibrium constants K_{298} for the process **1** = **1a** and dielectric permittivity of the solvent ε[4] and dipole moments μ[4]. B3LYP-D3/def2-SVPD level of theory, PCM for solvents.

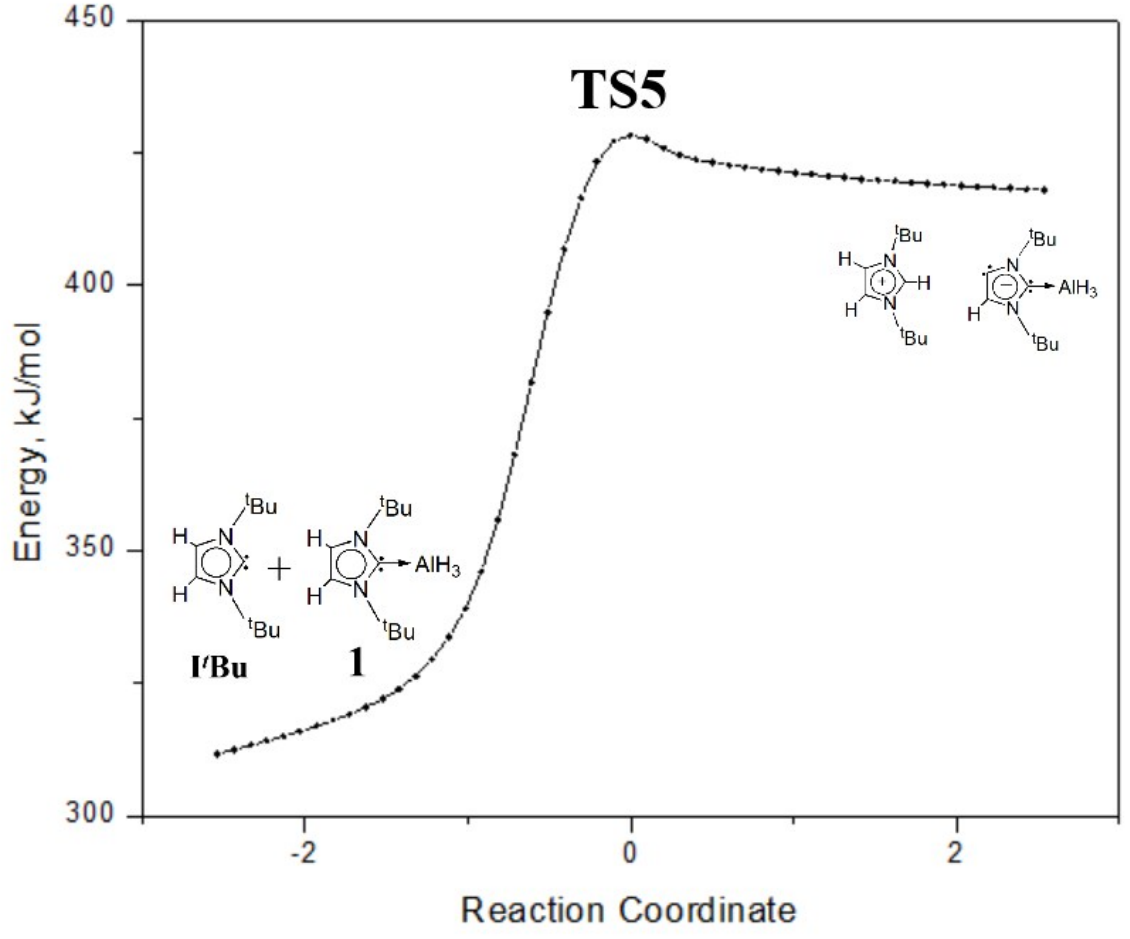
Medium	ΔE°_{0}	ΔH°_{298}	ΔG°_{298}	K_{298}	ε	μ
gas phase	16.8	15.8	9.7	0.02		
n-hexane	5.7	4.7	−2.6	2.9	1.8819	0.08
benzene	3.1	2.2	−3.9	4.9	2.2706	0
THF	−7.3	−8.0	−15.0	426.7	7.4257	1.75
dichloromethane	−8.1	−8.8	−16.0	630.8	8.93	1.14

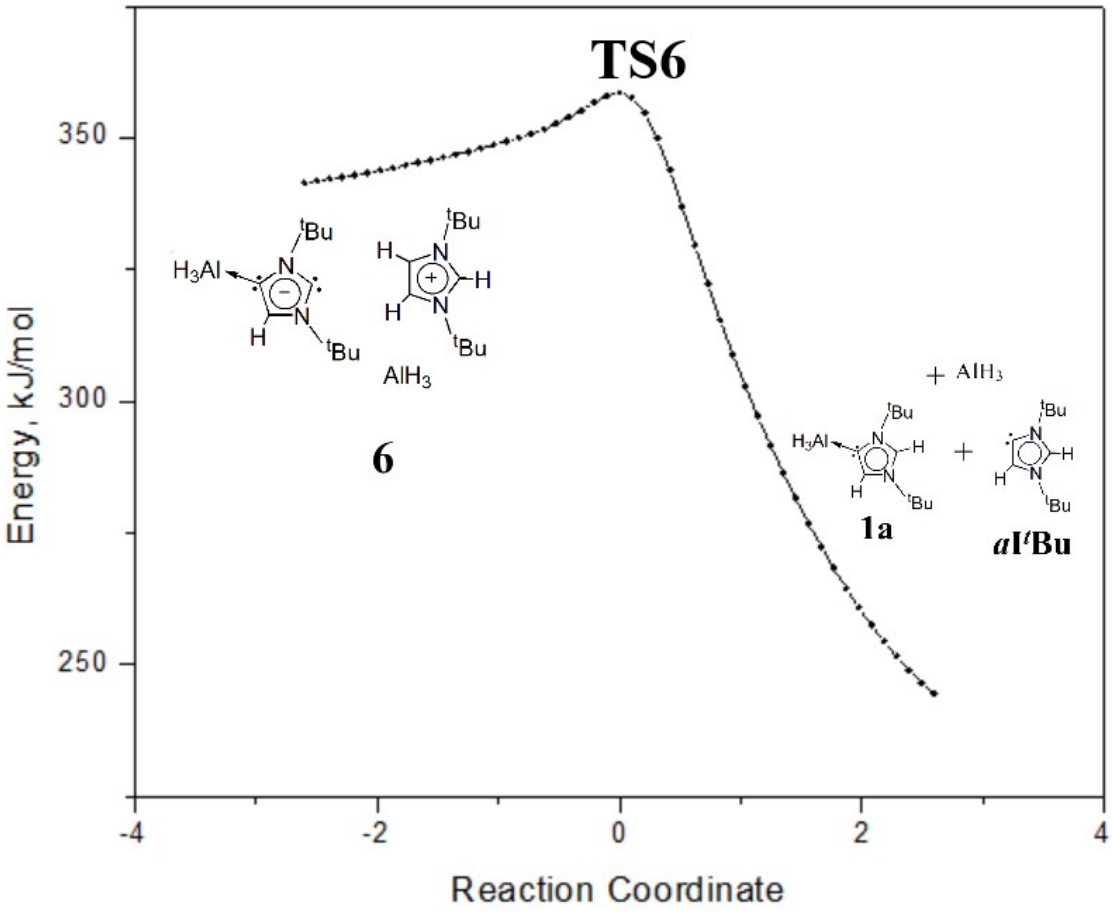
Figure S14. IRC scans. Relative energies are given with respect to two isolated molecules of **1**.




TS3
Energy, kJ/mol
Reaction Coordinate
200
150
100
50
0
-4
-2
0
2
4
H-H
3
4


TS4
Energy, kJ/mol
Reaction Coordinate
H-H
4
2
1a


TS5
Energy, kJ/mol
Reaction Coordinate
AlH3
I'Bu
1


TS6
Energy, kJ/mol
350
300
250
-4
-2
0
2
4
Reaction Coordinate
6
AlH3
+ AlH3
1a
aI'Bu

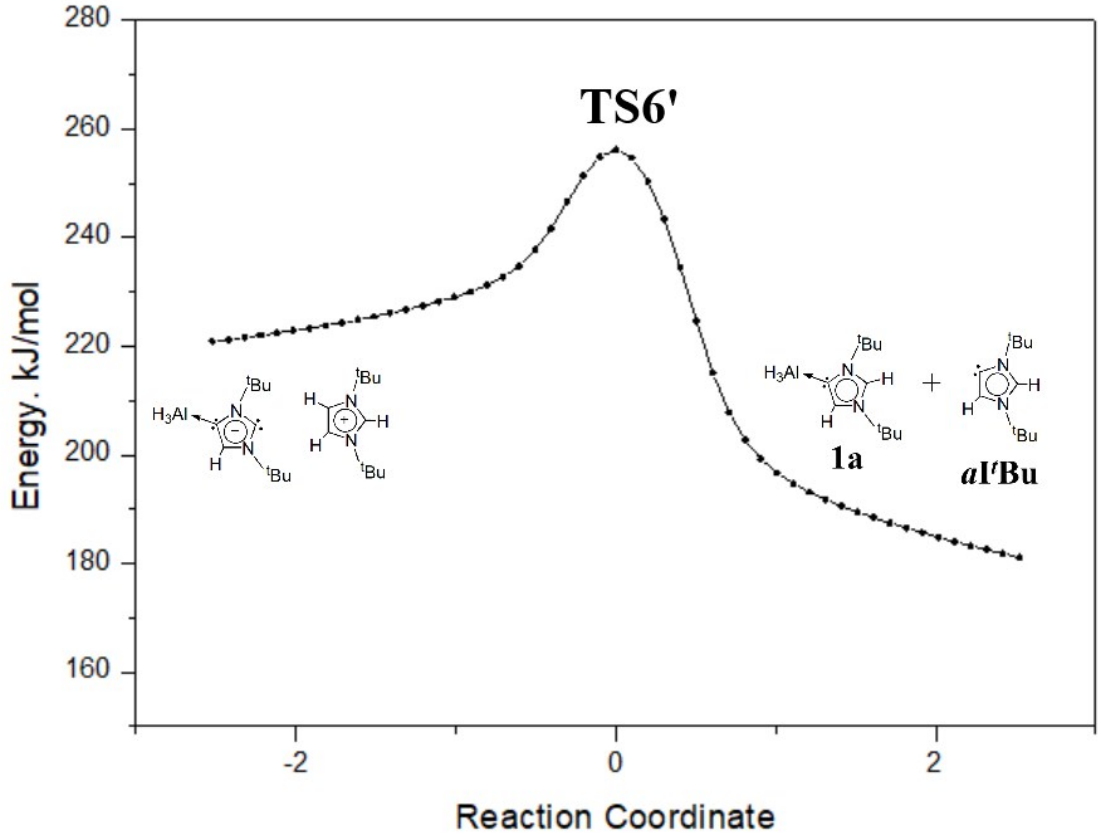

TS6'
Energy. kJ/mol
280
260
240
220
200
180
160
-2
0
2
Reaction Coordinate
1a
aI'Bu

Table S6. Summary of reaction path following. Energies reported relative to the TS energy (ΔE, Hartree).

TS1		**TS3**	
ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.02561	-2.62159	-0.05850	-2.63909
-0.02477	-2.51670	-0.05795	-2.53387
-0.02390	-2.41183	-0.05727	-2.42884
-0.02300	-2.30697	-0.05633	-2.32368
-0.02207	-2.20212	-0.05506	-2.21824
-0.02111	-2.09724	-0.05335	-2.11279
-0.02012	-1.99235	-0.05109	-2.00772
-0.01910	-1.88743	-0.04787	-1.90297
-0.01805	-1.78249	-0.04321	-1.79748
-0.01698	-1.67753	-0.03734	-1.69175
-0.01586	-1.57258	-0.03091	-1.58598
-0.01472	-1.46760	-0.02452	-1.48020
-0.01354	-1.36264	-0.01868	-1.37442
-0.01235	-1.25765	-0.01372	-1.26866
-0.01111	-1.15287	-0.00978	-1.16294
-0.00989	-1.04865	-0.00681	-1.05726
-0.00864	-0.94455	-0.00467	-0.95160
-0.00737	-0.83981	-0.00316	-0.84593
-0.00612	-0.73488	-0.00210	-0.74023
-0.00489	-0.62986	-0.00136	-0.63451
-0.00371	-0.52486	-0.00084	-0.52877
-0.00259	-0.41984	-0.00048	-0.42302
-0.00160	-0.31485	-0.00025	-0.31727
-0.00078	-0.20986	-0.00010	-0.21151
-0.00021	-0.10494	-0.00002	-0.10576
0.00000	0.00000	0.00000	0.00000
-0.00025	0.10499	-0.00002	0.10575
-0.00105	0.20995	-0.00007	0.21149
-0.00245	0.31494	-0.00016	0.31726
-0.00451	0.41995	-0.00026	0.42302
-0.00725	0.52497	-0.00040	0.52880
-0.01045	0.62998	-0.00055	0.63457
-0.01372	0.73495	-0.00072	0.74035
-0.01665	0.83976	-0.00092	0.84612
-0.01902	0.94418	-0.00114	0.95190
-0.02091	1.04872	-0.00138	1.05768
-0.02254	1.15350	-0.00164	1.16346
-0.02399	1.25838	-0.00193	1.26924
-0.02531	1.36329	-0.00224	1.37502
-0.02653	1.46823	-0.00257	1.48081
-0.02767	1.57321	-0.00293	1.58659
-0.02876	1.67820	-0.00329	1.69238
-0.02979	1.78319	-0.00368	1.79817
-0.03078	1.88817	-0.00408	1.90396
-0.03174	1.99302	-0.00449	2.00974
-0.03264	2.09784	-0.00490	2.11553
-0.03353	2.20276	-0.00532	2.22132
-0.03438	2.30777	-0.00574	2.32710
-0.03520	2.41277	-0.00616	2.43288
-0.03599	2.51777	-0.00658	2.53865
-0.03675	2.62278	-0.00699	2.64441
TS4		**TS5**	

ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.04757	-2.66990	-0.00395	-2.53590
-0.04682	-2.56307	-0.00390	-2.43426
-0.04603	-2.45631	-0.00384	-2.33260
-0.04521	-2.34961	-0.00378	-2.23094
-0.04435	-2.24286	-0.00371	-2.12926
-0.04343	-2.13602	-0.00364	-2.02765
-0.04247	-2.02915	-0.00357	-1.92606
-0.04143	-1.92229	-0.00349	-1.82453
-0.04031	-1.81546	-0.00341	-1.72291
-0.03906	-1.70868	-0.00333	-1.62125
-0.03764	-1.60195	-0.00324	-1.51957
-0.03598	-1.49527	-0.00314	-1.41789
-0.03395	-1.38881	-0.00304	-1.31620
-0.03132	-1.28268	-0.00294	-1.21452
-0.02777	-1.17606	-0.00283	-1.11284
-0.02344	-1.06918	-0.00271	-1.01117
-0.01880	-0.96224	-0.00258	-0.90951
-0.01438	-0.85529	-0.00245	-0.80787
-0.01048	-0.74834	-0.00230	-0.70626
-0.00719	-0.64140	-0.00214	-0.60471
-0.00458	-0.53447	-0.00196	-0.50327
-0.00266	-0.42756	-0.00175	-0.40230
-0.00135	-0.32066	-0.00145	-0.30335
-0.00054	-0.21378	-0.00094	-0.20306
-0.00012	-0.10691	-0.00031	-0.10162
0.00000	0.00000	0.00000	0.00000
-0.00010	0.10688	-0.00043	0.10170
-0.00036	0.21377	-0.00189	0.20338
-0.00075	0.32071	-0.00449	0.30507
-0.00122	0.42764	-0.00817	0.40677
-0.00177	0.53459	-0.01272	0.50846
-0.00236	0.64151	-0.01780	0.61015
-0.00299	0.74845	-0.02295	0.71183
-0.00365	0.85525	-0.02762	0.81344
-0.00432	0.96213	-0.03133	0.91477
-0.00501	1.06892	-0.03402	1.01567
-0.00570	1.17569	-0.03605	1.11700
-0.00639	1.28203	-0.03763	1.21848
-0.00708	1.38855	-0.03885	1.31990
-0.00778	1.49533	-0.03976	1.42117
-0.00846	1.60226	-0.04047	1.52231
-0.00915	1.70911	-0.04105	1.62350
-0.00984	1.81595	-0.04155	1.72491
-0.01051	1.92273	-0.04200	1.82638
-0.01118	2.02947	-0.04241	1.92797
-0.01184	2.13618	-0.04279	2.02951
-0.01249	2.24289	-0.04315	2.13105
-0.01313	2.34964	-0.04349	2.23255
-0.01376	2.45645	-0.04381	2.33408
-0.01439	2.56330	-0.04412	2.43564
-0.01500	2.67019	-0.04441	2.53725

TS6		TS6′	
ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.04347	-2.59480	-0.01344	-2.52329
-0.04265	-2.49112	-0.01330	-2.42217
-0.04178	-2.38848	-0.01316	-2.32105
-0.04080	-2.28569	-0.01301	-2.21994
-0.03972	-2.18216	-0.01285	-2.11882
-0.03853	-2.07843	-0.01268	-2.01771
-0.03725	-1.97457	-0.01250	-1.91659
-0.03587	-1.87068	-0.01231	-1.81549
-0.03439	-1.76675	-0.01212	-1.71438
-0.03281	-1.66279	-0.01191	-1.61336
-0.03113	-1.55883	-0.01169	-1.51247
-0.02936	-1.45488	-0.01146	-1.41161
-0.02749	-1.35092	-0.01121	-1.31068
-0.02552	-1.24696	-0.01094	-1.20964
-0.02343	-1.14299	-0.01064	-1.10871
-0.02124	-1.03904	-0.01032	-1.00775
-0.01892	-0.93510	-0.00995	-0.90698
-0.01646	-0.83123	-0.00951	-0.80646
-0.01384	-0.72743	-0.00895	-0.70611
-0.01106	-0.62359	-0.00815	-0.60551
-0.00825	-0.51969	-0.00703	-0.50488
-0.00560	-0.41576	-0.00549	-0.40426
-0.00329	-0.31181	-0.00364	-0.30332
-0.00146	-0.20786	-0.00183	-0.20224
-0.00034	-0.10392	-0.00050	-0.10114
0.00000	0.00000	0.00000	0.00000
-0.00023	0.10372	-0.00055	0.10115
-0.00072	0.20743	-0.00220	0.20227
-0.00128	0.31102	-0.00486	0.30339
-0.00179	0.41470	-0.00827	0.40451
-0.00224	0.51847	-0.01203	0.50562
-0.00263	0.62207	-0.01559	0.60667
-0.00296	0.72552	-0.01842	0.70740
-0.00326	0.82858	-0.02034	0.80739
-0.00353	0.93186	-0.02168	0.90804
-0.00378	1.03563	-0.02266	1.00865
-0.00403	1.13955	-0.02340	1.10921
-0.00426	1.24347	-0.02400	1.20995
-0.00448	1.34740	-0.02452	1.31084
-0.00469	1.45133	-0.02499	1.41178
-0.00489	1.55527	-0.02541	1.51266
-0.00508	1.65920	-0.02580	1.61358
-0.00527	1.76313	-0.02617	1.71458
-0.00545	1.86705	-0.02652	1.81566
-0.00562	1.97095	-0.02685	1.91673
-0.00579	2.07484	-0.02717	2.01781
-0.00595	2.17872	-0.02747	2.11889
-0.00611	2.28259	-0.02776	2.21998
-0.00626	2.38646	-0.02804	2.32106
-0.00640	2.49034	-0.02832	2.42215
-0.00654	2.59422	-0.02858	2.52323

Cartesian coordinates for the optimized geometries

xyz coordinates in Å, B3LYP-D3/def2-SVPD level of theory, gas phase.

H_2

H	0.000000000	0.000000000	0.380080000
H	0.000000000	0.000000000	-0.380080000

AlH_3

Al	0.000000000	0.000000000	0.000000000
H	0.000000000	1.584301000	0.000000000
H	1.372045000	-0.792151000	0.000000000
H	-1.372045000	-0.792151000	0.000000000

I^{t}Bu

N	1.068692000	-0.213795000	-0.000012000
C	0.000004000	0.632250000	-0.000109000
C	0.678815000	-1.549641000	0.000211000
C	-0.678825000	-1.549634000	0.000211000
N	-1.068695000	-0.213790000	0.000006000
H	-1.371671000	-2.382359000	0.000346000
H	1.371658000	-2.382367000	0.000354000
C	2.489564000	0.217087000	-0.000016000
C	3.170909000	-0.335490000	-1.264634000
C	3.170634000	-0.334646000	1.265118000
H	2.665516000	0.042202000	2.164133000
H	3.150124000	-1.432398000	1.292121000
H	4.221895000	-0.017241000	1.295601000
H	3.150554000	-1.433262000	-1.290860000
H	4.222136000	-0.017981000	-1.295161000
H	2.665909000	0.040649000	-2.164013000
C	-2.489562000	0.217102000	-0.000029000
C	-3.170710000	-0.334751000	1.265012000
C	-3.170840000	-0.335347000	-1.264740000
H	-2.665806000	0.040902000	-2.164053000
H	-3.150455000	-1.433116000	-1.291083000
H	-4.222073000	-0.017857000	-1.295280000
H	-3.150239000	-1.432507000	1.291898000
H	-4.221961000	-0.017317000	1.295477000
H	-2.665625000	0.041983000	2.164094000
C	2.566352000	1.747219000	-0.000529000
H	2.072964000	2.168415000	0.882601000
H	3.623267000	2.047028000	-0.000513000
H	2.073164000	2.167810000	-0.884062000
C	-2.566342000	1.747235000	-0.000391000
H	-2.073002000	2.168338000	0.882811000
H	-2.073103000	2.167914000	-0.883852000
H	-3.623256000	2.047049000	-0.000402000

***a*I^{t}Bu**

N	-1.088795000	-0.299292000	0.000026000
C	0.004004000	0.484562000	0.000107000
C	-0.768415000	-1.666269000	-0.000079000
C	0.613906000	-1.628321000	-0.000029000
N	1.083787000	-0.307539000	0.000178000
H	1.313216000	-2.454744000	-0.000054000
C	-2.497506000	0.187984000	-0.000074000
C	-3.181363000	-0.360197000	1.261674000
C	-3.181044000	-0.359907000	-1.262121000
H	-2.703356000	0.042183000	-2.166632000
H	-3.097752000	-1.452596000	-1.282020000
H	-4.242019000	-0.073032000	-1.269229000
H	-3.097987000	-1.452881000	1.281383000
H	-4.242362000	-0.073403000	1.268530000
H	-2.703967000	0.041759000	2.166399000
C	2.484560000	0.195985000	-0.000002000
C	2.706423000	1.039538000	-1.267220000
C	3.454310000	-0.991517000	0.000770000
H	3.322489000	-1.616089000	0.893194000
H	3.322924000	-1.616940000	-0.891119000
H	4.482765000	-0.610714000	0.000818000
H	2.509816000	0.440002000	-2.165512000
H	3.745021000	1.396078000	-1.304865000
H	2.048264000	1.917968000	-1.288107000
C	-2.542320000	1.720550000	0.000097000
H	-2.063930000	2.142110000	-0.895315000
H	-3.589623000	2.045758000	0.000054000
H	-2.064065000	2.141897000	0.895680000

C	2.706305000	1.041001000	1.266261000
H	2.048265000	1.919543000	1.286072000
H	2.509554000	0.442532000	2.165233000
H	3.744927000	1.397498000	1.303606000
H	0.037073000	1.565201000	0.000187000

I^{t}BuH$_2$

N	0.044318000	0.688355000	-1.157849000
C	-0.759587000	0.276283000	0.000000000
C	1.364540000	0.820788000	-0.671581000
C	1.364540000	0.820788000	0.671581000
N	0.044318000	0.688355000	1.157849000
H	2.195023000	1.034699000	1.333369000
H	2.195023000	1.034699000	-1.333369000
C	-0.210864000	0.021173000	-2.453103000
C	0.285424000	-1.440754000	-2.450782000
C	0.511670000	0.813900000	-3.554645000
H	0.197428000	1.865551000	-3.533785000
H	1.602348000	0.775222000	-3.437636000
H	0.272736000	0.392646000	-4.540371000
H	1.365353000	-1.481357000	-2.254645000
H	0.090532000	-1.916781000	-3.421751000
H	-0.220522000	-2.035086000	-1.677925000
C	-0.210864000	0.021173000	2.453103000
C	0.511670000	0.813901000	3.554645000
C	0.285424000	-1.440753000	2.450782000
H	-0.220521000	-2.035086000	1.677925000
H	1.365353000	-1.481357000	2.254645000
H	0.090532000	-1.916781000	3.421751000
H	1.602348000	0.775222000	3.437636000
H	0.272736000	0.392647000	4.540371000
H	0.197428000	1.865551000	3.533785000
C	-1.723169000	0.063967000	-2.727398000
H	-2.093763000	1.095989000	-2.664919000
H	-1.932696000	-0.322313000	-3.733240000
H	-2.286389000	-0.553745000	-2.015109000
C	-1.723169000	0.063967000	2.727398000
H	-2.093763000	1.095989000	2.664919000
H	-2.286389000	-0.553745000	2.015109000
H	-1.932696000	-0.322312000	3.733240000
H	-1.745981000	0.758688000	0.000000000
H	-0.925306000	-0.828638000	0.000000000

1

N	-1.085145000	-0.569759000	-0.014838000
C	0.000002000	0.267199000	0.004748000
C	-0.677282000	-1.889729000	-0.023760000
C	0.677227000	-1.889749000	-0.023762000
N	1.085124000	-0.569789000	-0.014844000
H	1.353384000	-2.730270000	-0.037288000
H	-1.353463000	-2.730233000	-0.037282000
C	-2.541135000	-0.174999000	0.007440000
C	-2.877716000	0.378217000	1.400659000
C	-3.414452000	-1.413150000	-0.258458000
H	-3.178650000	-1.882898000	-1.222919000
H	-3.337651000	-2.162243000	0.540542000
H	-4.460059000	-1.087467000	-0.294161000
H	-2.675334000	-0.379914000	2.169785000
H	-3.944389000	0.637860000	1.442677000
H	-2.298811000	1.280372000	1.618484000
C	2.541119000	-0.175050000	0.007436000
C	2.812494000	0.842560000	-1.109411000
C	3.414431000	-1.413201000	-0.258480000
H	3.337640000	-2.162298000	0.540517000
H	3.178615000	-1.882944000	-1.222941000
H	4.460038000	-1.087520000	-0.294195000
H	2.535314000	0.424186000	-2.085880000
H	3.883699000	1.082492000	-1.123213000
H	2.270015000	1.779497000	-0.964341000
C	-2.812510000	0.842593000	-1.109424000
H	-2.535334000	0.424201000	-2.085886000
H	-3.883714000	1.082527000	-1.123227000
H	-2.270029000	1.779532000	-0.964371000
C	2.877702000	0.378153000	1.400659000
H	2.298798000	1.280307000	1.618491000
H	2.675317000	-0.379984000	2.169779000
H	3.944376000	0.637792000	1.442680000
H	-1.326932000	2.866934000	0.781435000
Al	0.000052000	2.409997000	0.011040000
H	1.327155000	2.866854000	0.781280000
H	-0.000031000	2.748666000	-1.560807000

TS1

N	-3.181353000	-1.088183000	0.387001000
C	-4.356913000	-0.385561000	0.332243000

N	-4.011687000	0.816966000	-0.226935000
Al	0.231138000	-0.343052000	-0.782238000
C	-2.082463000	-0.332168000	-0.066777000
C	-2.645879000	0.859450000	-0.435271000
H	-2.153086000	1.720512000	-0.867046000
C	-4.918071000	1.960112000	-0.597863000
C	-3.037030000	-2.500100000	0.888519000
C	-2.945437000	-2.473007000	2.422915000
H	-3.866226000	-2.069300000	2.863897000
H	-2.796809000	-3.494229000	2.808187000
H	-2.089387000	-1.857130000	2.743149000
C	-4.210853000	-3.363101000	0.400260000
H	-4.306987000	-3.302391000	-0.694111000
H	-4.022368000	-4.411655000	0.676876000
H	-5.167452000	-3.081680000	0.852403000
C	-1.753299000	-3.119113000	0.314876000
H	-0.844766000	-2.658161000	0.722337000
H	-1.725284000	-4.182036000	0.596887000
H	-1.721467000	-3.048603000	-0.780488000
C	-4.202734000	2.869431000	-1.615605000
H	-3.870288000	2.308480000	-2.502292000
H	-4.912833000	3.640488000	-1.947529000
H	-3.338178000	3.393748000	-1.182416000
C	-6.188254000	1.420951000	-1.271750000
H	-6.804555000	0.823432000	-0.590962000
H	-6.804345000	2.267382000	-1.611838000
H	-5.930305000	0.802160000	-2.144615000
C	-5.235129000	2.778008000	0.664402000
H	-4.303352000	3.148530000	1.121232000
H	-5.860128000	3.645812000	0.400587000
H	-5.780578000	2.169485000	1.397078000
H	-0.060040000	1.031093000	-1.514237000
H	-0.752247000	-0.579522000	0.710847000
H	0.226356000	-1.724608000	-1.532159000
C	2.283430000	0.047918000	-0.149092000
N	3.363495000	-0.796180000	-0.156261000
N	2.721877000	1.170053000	0.510610000
H	0.130475000	-0.721675000	1.030641000
C	4.439192000	-0.213408000	0.488304000
C	4.039465000	1.013231000	0.902967000
H	4.604631000	1.763539000	1.439268000
C	1.971438000	2.465597000	0.721365000
C	3.432148000	-2.170167000	-0.777930000
C	3.105000000	-2.052505000	-2.274726000
H	2.084426000	-1.688975000	-2.440032000
H	3.185052000	-3.042864000	-2.747922000
H	3.815691000	-1.372836000	-2.770122000
C	2.470429000	-3.108942000	-0.032684000
H	2.726521000	-3.149457000	1.037348000
H	2.552412000	-4.124799000	-0.447591000
H	1.426813000	-2.793080000	-0.136416000
C	4.857422000	-2.731247000	-0.640411000
H	5.604801000	-2.101097000	-1.145927000
H	4.881433000	-3.719125000	-1.121269000
H	5.152995000	-2.873304000	0.410100000
C	2.766068000	3.366803000	1.682820000
H	2.923413000	2.888691000	2.661911000
H	2.186546000	4.285258000	1.849867000
H	3.737856000	3.673029000	1.268670000
C	0.599863000	2.197021000	1.359672000
H	-0.111407000	1.740945000	0.662583000
H	0.154465000	3.153952000	1.668431000
H	0.693050000	1.554608000	2.247118000
C	1.839201000	3.174489000	-0.635828000
H	2.833765000	3.377690000	-1.062873000
H	1.317819000	4.135117000	-0.503479000
H	1.263282000	2.563584000	-1.342575000
Al	-6.244016000	-0.884107000	1.198842000
H	-6.906034000	0.512169000	1.645230000
H	-5.920695000	-1.792460000	2.485935000
H	-7.074742000	-1.641373000	0.045871000
H	5.401995000	-0.690598000	0.613370000

2

N	1.232739000	-1.280230000	0.051229000
C	2.515931000	-0.924349000	-0.264712000
N	2.890967000	-0.068919000	0.730011000
Al	-1.063136000	-0.076950000	1.927454000
C	0.736145000	-0.554861000	1.151648000
C	1.817846000	0.173270000	1.565977000
H	1.876753000	0.861865000	2.397066000
C	4.231143000	0.563948000	0.952415000
C	0.467768000	-2.403947000	-0.591437000
C	-0.605947000	-1.826039000	-1.524210000
H	-0.139570000	-1.217679000	-2.306628000

H	-1.159359000	-2.645900000	-2.000569000	H	-6.487841000	-1.090511000	0.517311000
H	-1.325202000	-1.213877000	-0.972706000	H	-5.789105000	-0.955071000	-1.094643000
C	1.403535000	-3.334268000	-1.376483000	C	-0.979363000	3.805659000	-1.484778000
H	2.258725000	-3.645701000	-0.765469000	H	-1.104818000	3.622714000	-2.558593000
H	0.837885000	-4.231688000	-1.658199000	H	-0.163499000	4.530276000	-1.382429000
H	1.772880000	-2.882416000	-2.299647000	H	-1.895638000	4.262314000	-1.088279000
C	-0.162886000	-3.249958000	0.528663000	C	0.558069000	1.819293000	-1.406465000
H	-0.838726000	-2.681180000	1.169804000	H	0.836515000	0.910144000	-0.878436000
H	-0.730791000	-4.073842000	0.077698000	H	1.437615000	2.472882000	-1.448048000
H	0.620779000	-3.679697000	1.166366000	H	0.288099000	1.543510000	-2.433042000
C	4.477218000	0.655268000	2.471251000	C	-0.224408000	2.968712000	0.718846000
H	4.358772000	-0.326458000	2.948341000	H	-1.078765000	3.428428000	1.230921000
H	5.503911000	1.000528000	2.641805000	H	0.585873000	3.705178000	0.656697000
H	3.809534000	1.370375000	2.966857000	H	0.135236000	2.144384000	1.331054000
C	5.338348000	-0.308438000	0.347486000	Al	3.302558000	-0.898465000	-2.242049000
H	5.295193000	-0.340567000	-0.743935000	H	4.021808000	0.537817000	-2.335901000
H	6.312650000	0.114485000	0.623745000	H	1.973149000	-0.894555000	-3.153914000
H	5.280261000	-1.333369000	0.735067000	H	4.285972000	-2.145785000	-2.456587000
C	4.218879000	1.972311000	0.337384000	H	-4.552013000	0.478818000	-1.982670000
H	3.412381000	2.574716000	0.777877000				
H	5.174643000	2.474778000	0.540329000			**3**	
H	4.075640000	1.913216000	-0.746613000	N	-2.139800000	-1.098118000	0.349009000
H	-0.834664000	1.056443000	3.028792000	C	-2.854878000	0.061790000	0.234250000
H	-1.868410000	-1.337260000	2.461528000	N	-2.480384000	0.586290000	-0.967415000
C	-2.215550000	0.753075000	0.317123000	Al	0.431794000	-2.406921000	-1.018707000
N	-3.414338000	0.263171000	-0.141880000	C	-1.208365000	-1.252960000	-0.694064000
N	-1.794447000	1.610975000	-0.667501000	C	-1.458341000	-0.179533000	-1.507218000
C	-3.676509000	0.741362000	-1.409653000	H	-0.964642000	0.084623000	-2.432752000
C	-2.663850000	1.578417000	-1.737530000	C	-3.132916000	1.707184000	-1.718238000
H	-2.519390000	2.151963000	-2.640180000	C	-2.447402000	-2.194864000	1.335968000
C	-0.597517000	2.535072000	-0.698888000	C	-1.389431000	-2.242612000	2.446306000
C	-4.390694000	-0.631053000	0.584082000	H	-1.408201000	-1.318901000	3.033566000
C	-4.540091000	-0.144707000	2.033311000	H	-1.611913000	-3.082526000	3.118199000
H	-3.611875000	-0.238427000	2.600405000	H	-0.387814000	-2.398927000	2.030334000
H	-5.295086000	-0.759028000	2.540281000	C	-3.842125000	-1.992085000	1.946001000
H	-4.873280000	0.901261000	2.052463000	H	-4.604971000	-1.871263000	1.167437000
C	-3.912902000	-2.087114000	0.489377000	H	-4.092239000	-2.880500000	2.539643000
H	-3.805344000	-2.385624000	-0.561603000	H	-3.887587000	-1.132858000	2.620504000
H	-4.652115000	-2.746108000	0.963280000	C	-2.469812000	-3.527235000	0.564934000
H	-2.958844000	-2.226175000	0.999776000	H	-1.488773000	-3.814039000	0.174091000
C	-5.772486000	-0.521319000	-0.086709000	H	-2.802108000	-4.324100000	1.242788000
H	-6.122951000	0.518235000	-0.132837000	H	-3.169627000	-3.474781000	-0.279158000

C	-4.542298000	1.969942000	-1.172188000
H	-4.526039000	2.394690000	-0.164925000
H	-5.043278000	2.695622000	-1.825744000
H	-5.135868000	1.047900000	-1.155524000
C	-2.272423000	2.975600000	-1.625900000
H	-1.263169000	2.793338000	-2.018061000
H	-2.730527000	3.773618000	-2.225656000
H	-2.202365000	3.315804000	-0.587835000
C	-3.268197000	1.270460000	-3.191078000
H	-3.801178000	0.313829000	-3.265686000
H	-3.839694000	2.030689000	-3.737973000
H	-2.297630000	1.167740000	-3.690781000
H	1.310979000	-1.479261000	-2.030460000
H	1.275601000	-2.433288000	0.388236000
H	0.156383000	-3.890846000	-1.560229000
C	2.914847000	0.037050000	0.347973000
N	4.045921000	0.122958000	-0.370411000
N	2.515415000	1.273545000	0.675610000
H	2.374010000	-0.885860000	0.565815000
C	4.357918000	1.459901000	-0.529668000
C	3.402054000	2.177867000	0.125613000
H	3.288388000	3.246833000	0.242706000
C	1.286489000	1.657162000	1.460856000
C	4.811592000	-1.017007000	-0.984164000
C	4.440101000	-1.077540000	-2.472381000
H	3.363996000	-1.257574000	-2.589933000
H	4.991329000	-1.897176000	-2.951732000
H	4.705727000	-0.141341000	-2.982558000
C	4.429892000	-2.317228000	-0.270652000
H	4.655260000	-2.261155000	0.803209000
H	5.018337000	-3.136091000	-0.700110000
H	3.370619000	-2.565981000	-0.396051000
C	6.310566000	-0.742466000	-0.792708000
H	6.650815000	0.138710000	-1.351470000
H	6.876031000	-1.602912000	-1.170043000
H	6.556036000	-0.606782000	0.268849000
C	1.715891000	2.614600000	2.580095000
H	2.455641000	2.143753000	3.240702000
H	0.832135000	2.870440000	3.176925000
H	2.133775000	3.552551000	2.192152000
C	0.656188000	0.401144000	2.052675000
H	0.328111000	-0.289458000	1.272105000
H	-0.234689000	0.690320000	2.619469000
H	1.344170000	-0.124289000	2.728164000
C	0.310752000	2.327764000	0.490105000
H	0.735062000	3.239460000	0.048727000
H	-0.608369000	2.597282000	1.023612000
H	0.042731000	1.633972000	-0.313260000
Al	-3.470927000	1.244146000	1.869221000
H	-2.925224000	2.709591000	1.450555000
H	-2.565717000	0.688942000	3.085594000
H	-5.053458000	1.172074000	2.103325000
H	5.223303000	1.795865000	-1.083475000

TS3

N	-3.200438000	-1.161648000	0.281900000
C	-4.427257000	-0.695953000	-0.003092000
N	-4.361622000	0.636800000	-0.107081000
H	-5.322984000	-1.284956000	-0.127110000
Al	0.447162000	0.481626000	-0.273638000
C	-2.269168000	-0.116931000	0.366071000
C	-3.037245000	0.999525000	0.121836000
H	-2.726223000	2.035438000	0.074039000
C	-5.474672000	1.576465000	-0.419137000
C	-2.843904000	-2.605440000	0.419088000
C	-2.015992000	-2.773960000	1.701136000
H	-2.586385000	-2.441180000	2.578107000
H	-1.754151000	-3.831407000	1.833619000
H	-1.088125000	-2.198952000	1.655354000
C	-4.113683000	-3.460526000	0.517123000
H	-4.715981000	-3.413792000	-0.400463000
H	-3.823403000	-4.507750000	0.659315000
H	-4.736326000	-3.164975000	1.372874000
C	-2.031101000	-3.006756000	-0.821396000
H	-1.175919000	-2.338237000	-0.958882000
H	-1.664117000	-4.036144000	-0.714985000
H	-2.652593000	-2.950430000	-1.725345000
C	-5.121802000	2.314934000	-1.720778000
H	-5.001820000	1.604381000	-2.548815000
H	-5.924987000	3.018360000	-1.976719000
H	-4.190133000	2.884499000	-1.618890000
C	-6.783256000	0.798784000	-0.599289000
H	-7.062612000	0.256850000	0.314335000
H	-7.588647000	1.507267000	-0.824549000

H	-6.721961000	0.089053000	-1.435236000
C	-5.609855000	2.562295000	0.752765000
H	-4.687545000	3.136735000	0.901684000
H	-6.422559000	3.271415000	0.547857000
H	-5.838550000	2.028363000	1.684310000
H	-0.194762000	1.923163000	-0.272203000
H	-0.647487000	-0.062407000	1.231094000
H	0.120500000	-0.522030000	-1.446207000
C	2.451535000	0.416429000	0.159135000
N	3.284476000	-0.672249000	0.060345000
N	3.293826000	1.486085000	0.294707000
H	0.119581000	0.031057000	1.546184000
C	4.633975000	-0.313127000	0.059388000
Al	6.472055000	-1.203896000	-0.291743000
C	4.600934000	1.048541000	0.215730000
H	5.447976000	1.716034000	0.263282000
C	2.924192000	2.923378000	0.509620000
C	2.852627000	-2.106449000	-0.072712000
C	2.756291000	-2.446645000	-1.567864000
H	2.005874000	-1.822123000	-2.067252000
H	2.470153000	-3.501129000	-1.689874000
H	3.732019000	-2.295729000	-2.045854000
C	1.514117000	-2.341595000	0.639032000
H	1.548311000	-1.987668000	1.676935000
H	1.302581000	-3.417287000	0.649902000
H	0.673273000	-1.879686000	0.116953000
C	3.886237000	-3.017533000	0.607755000
H	4.827282000	-3.067830000	0.055123000
H	3.480017000	-4.036806000	0.648982000
H	4.102320000	-2.682907000	1.629431000
C	4.174659000	3.723976000	0.914899000
H	4.648892000	3.308553000	1.813049000
H	3.865744000	4.752015000	1.138220000
H	4.917835000	3.771230000	0.109874000
C	1.912731000	3.023622000	1.663866000
H	0.968653000	2.523341000	1.435009000
H	1.684627000	4.080014000	1.859104000
H	2.337275000	2.585089000	2.576233000
C	2.378141000	3.511737000	-0.802427000
H	3.123004000	3.402273000	-1.601343000
H	2.167089000	4.581919000	-0.669040000
H	1.449589000	3.024697000	-1.113486000
H	7.383655000	0.109830000	-0.549086000
H	6.272406000	-2.144018000	-1.597559000
H	6.913711000	-2.052222000	1.009517000

4

N	-2.257124000	-0.581766000	0.167705000
C	-3.487532000	-0.103134000	0.394890000
N	-3.698646000	0.958785000	-0.391457000
H	-4.201258000	-0.506560000	1.095073000
Al	0.185008000	0.263358000	-1.843608000
C	-1.609372000	0.195961000	-0.806285000
C	-2.549097000	1.145431000	-1.138727000
H	-2.457904000	1.958108000	-1.847577000
C	-4.906195000	1.832489000	-0.437465000
C	-1.712712000	-1.826553000	0.814311000
C	-0.373064000	-1.490409000	1.472010000
H	-0.488254000	-0.697051000	2.220429000
H	0.040675000	-2.376867000	1.964286000
H	0.358794000	-1.165871000	0.736397000
C	-2.684435000	-2.334901000	1.886232000
H	-3.657155000	-2.629135000	1.468159000
H	-2.244005000	-3.226978000	2.344704000
H	-2.836817000	-1.596155000	2.685277000
C	-1.561738000	-2.881648000	-0.290327000
H	-0.970052000	-2.497247000	-1.125751000
H	-1.055399000	-3.766015000	0.113161000
H	-2.545733000	-3.181188000	-0.676189000
C	-5.974895000	1.291206000	0.518058000
H	-5.628531000	1.292818000	1.560308000
H	-6.858454000	1.936904000	0.462484000
H	-6.287280000	0.274808000	0.242954000
C	-4.480109000	3.245890000	-0.007209000
H	-3.717852000	3.656896000	-0.680286000
H	-5.349050000	3.916308000	-0.027818000
H	-4.071157000	3.234507000	1.011367000
C	-5.440637000	1.831116000	-1.878272000
H	-5.718223000	0.815615000	-2.188933000
H	-6.330112000	2.470951000	-1.941211000
H	-4.696519000	2.217453000	-2.585358000
H	0.008857000	1.656468000	-2.618454000
H	0.299719000	-5.103158000	1.670029000
H	0.198281000	-1.041528000	-2.751946000
C	1.777192000	0.329723000	-0.511746000

N	2.546575000	-0.742346000	-0.136190000	Al	-0.138270000	0.234740000	-0.419510000
N	1.836464000	1.188642000	0.556019000	C	-2.213250000	0.023184000	-0.384611000
H	0.897804000	-4.684787000	1.888827000	C	-2.965816000	1.169558000	-0.506821000
C	2.972539000	-0.654202000	1.193807000	H	-2.620536000	2.192859000	-0.577599000
Al	3.538181000	-2.011279000	2.643451000	C	-5.430145000	1.832954000	-0.676391000
C	2.527326000	0.580462000	1.588859000	C	-2.886465000	-2.467972000	-0.208662000
H	2.652147000	1.035366000	2.560212000	C	-2.180943000	-2.690250000	1.136556000
C	1.462872000	2.644086000	0.558142000	H	-2.828926000	-2.387001000	1.969606000
C	3.009000000	-1.841068000	-1.059986000	H	-1.935860000	-3.753354000	1.252615000
C	3.222413000	-1.268160000	-2.471324000	H	-1.249357000	-2.123816000	1.205025000
H	2.294252000	-0.939358000	-2.943753000	C	-4.197931000	-3.264784000	-0.229667000
H	3.649639000	-2.052253000	-3.109472000	H	-4.742831000	-3.136891000	-1.175085000
H	3.928395000	-0.428118000	-2.438629000	H	-3.955413000	-4.328951000	-0.134546000
C	1.996266000	-2.993066000	-1.055669000	H	-4.856769000	-3.003327000	0.610059000
H	1.821323000	-3.338076000	-0.030022000	C	-2.007466000	-2.901488000	-1.390138000
H	2.397579000	-3.833876000	-1.636722000	H	-1.073697000	-2.333203000	-1.434823000
H	1.052024000	-2.690886000	-1.513596000	H	-1.758868000	-3.965643000	-1.288796000
C	4.368442000	-2.363529000	-0.569261000	H	-2.539880000	-2.758206000	-2.339805000
H	5.077472000	-1.543706000	-0.403828000	C	-6.773079000	1.094991000	-0.674298000
H	4.778757000	-3.030004000	-1.338721000	H	-6.935715000	0.547661000	0.264077000
H	4.292510000	-2.939941000	0.356564000	H	-7.579645000	1.830160000	-0.772319000
C	2.015675000	3.312274000	1.828074000	H	-6.856064000	0.397967000	-1.519123000
H	1.545313000	2.921299000	2.739488000	C	-5.357818000	2.797795000	0.517820000
H	1.796124000	4.385183000	1.774509000	H	-4.406066000	3.342600000	0.538367000
H	3.102799000	3.195528000	1.910885000	H	-6.167544000	3.535118000	0.444282000
C	-0.060932000	2.828497000	0.539986000	H	-5.466195000	2.253788000	1.465113000
H	-0.477256000	2.600325000	-0.441903000	C	-5.243386000	2.582890000	-2.005005000
H	-0.305564000	3.874291000	0.769023000	H	-5.269838000	1.885900000	-2.852591000
H	-0.540890000	2.185508000	1.288340000	H	-6.051067000	3.315431000	-2.130443000
C	2.107678000	3.310494000	-0.668789000	H	-4.289492000	3.123620000	-2.032026000
H	3.198650000	3.194175000	-0.635254000	H	-0.106068000	1.806280000	-0.584245000
H	1.871949000	4.383633000	-0.672176000	H	-0.255148000	-0.211728000	1.414569000
H	1.734705000	2.875034000	-1.601269000	H	0.375766000	-0.816010000	-1.471194000
H	3.121094000	-1.202040000	3.984345000	C	2.172291000	0.202742000	0.608098000
H	5.097128000	-2.405324000	2.567408000	N	3.077008000	-0.690495000	0.103816000
H	2.563310000	-3.283491000	2.358766000	N	2.844770000	1.387103000	0.645961000
				H	0.596256000	-0.104711000	1.268280000
		TS4		C	4.287359000	-0.085447000	-0.268495000
N	-3.174559000	-1.000928000	-0.346291000	Al	6.042789000	-0.623504000	-1.223173000
C	-4.406179000	-0.479756000	-0.440756000	C	4.102727000	1.225593000	0.089772000
N	-4.313544000	0.850626000	-0.542259000	H	4.802346000	2.044609000	-0.015754000
H	-5.330451000	-1.035449000	-0.438044000	C	2.423290000	2.657744000	1.296569000

C	2.891904000	-2.174680000	0.078796000	H	3.087064000	0.283020000	1.316922000
C	2.912961000	-2.670841000	-1.374781000	H	3.794055000	-1.351060000	1.298432000
H	2.081921000	-2.233559000	-1.941491000	H	2.275844000	-1.044088000	2.180363000
H	2.813857000	-3.765658000	-1.390396000	C	-2.810505000	-0.083782000	0.001723000
H	3.850046000	-2.401400000	-1.874533000	C	-3.196017000	-0.957004000	-1.203451000
C	1.569811000	-2.579054000	0.743069000	C	-3.509742000	1.276165000	-0.098899000
H	1.487019000	-2.181318000	1.762534000	H	-3.267250000	1.920316000	0.755602000
H	1.532199000	-3.673905000	0.801106000	H	-3.241791000	1.799977000	-1.025242000
H	0.706824000	-2.260479000	0.154044000	H	-4.594135000	1.115761000	-0.101806000
C	4.033473000	-2.808376000	0.894501000	H	-2.885217000	-0.479510000	-2.141572000
H	5.019710000	-2.570885000	0.483520000	H	-4.284804000	-1.095568000	-1.226440000
H	3.916013000	-3.901140000	0.896784000	H	-2.734525000	-1.951824000	-1.150135000
H	4.000856000	-2.452167000	1.933833000	C	1.733503000	-2.651685000	0.032117000
C	3.551320000	3.100704000	2.250803000	H	1.175137000	-2.962661000	-0.862075000
H	3.765219000	2.313602000	2.985658000	H	2.675194000	-3.211961000	0.040372000
H	3.240368000	4.007007000	2.787448000	H	1.172437000	-2.940989000	0.931892000
H	4.479523000	3.331531000	1.716502000	C	-3.188597000	-0.769830000	1.324662000
C	1.152931000	2.449672000	2.130972000	H	-2.716063000	-1.756713000	1.416395000
H	0.281937000	2.242105000	1.504414000	H	-2.878268000	-0.156004000	2.179945000
H	0.944609000	3.370373000	2.690725000	H	-4.276344000	-0.911504000	1.373172000
H	1.285729000	1.631887000	2.850654000	H	1.052157000	3.868548000	-0.060200000
C	2.192760000	3.726557000	0.215940000	Al	2.087758000	2.628932000	-0.043268000
H	3.103408000	3.883079000	-0.376270000	H	2.973598000	2.501655000	1.299558000
H	1.921374000	4.682334000	0.686308000	H	2.974859000	2.466360000	-1.381388000
H	1.386013000	3.422543000	-0.459947000	H	-0.681387000	-1.922898000	0.024260000
H	6.786562000	0.812779000	-1.322672000				
H	5.645837000	-1.255587000	-2.660441000			**6**	
H	6.835785000	-1.698696000	-0.308643000	N	1.780725000	0.424912000	1.274536000
				C	2.041224000	-0.913824000	1.234353000
		1a		C	2.039686000	1.099149000	0.057929000
N	0.800466000	-0.347407000	0.000419000	C	2.491731000	0.094368000	-0.756461000
C	-0.432869000	-0.872613000	0.005216000	N	2.475369000	-1.107522000	-0.045250000
C	0.731638000	1.052821000	-0.022657000	H	2.797492000	0.164997000	-1.792582000
C	-0.621898000	1.311881000	-0.030897000	C	1.308121000	1.109052000	2.508036000
N	-1.331214000	0.119925000	-0.015490000	C	-0.090742000	1.703218000	2.264868000
H	-1.108305000	2.277405000	-0.048841000	C	2.305262000	2.223979000	2.865718000
C	2.065665000	-1.153161000	0.014058000	H	3.302386000	1.797389000	3.035625000
C	2.852134000	-0.786674000	1.280944000	H	2.388182000	2.972162000	2.069114000
C	2.858762000	-0.819463000	-1.257787000	H	1.982854000	2.735783000	3.783163000
H	2.287730000	-1.101209000	-2.153266000	H	-0.081492000	2.426715000	1.443775000
H	3.093053000	0.249075000	-1.321328000	H	-0.445675000	2.212519000	3.171378000
H	3.801277000	-1.383145000	-1.255205000	H	-0.802636000	0.906044000	2.023580000

C	3.042239000	-2.398695000	-0.515064000
C	2.107963000	-3.545356000	-0.103064000
C	4.423338000	-2.576324000	0.137969000
H	5.078093000	-1.733280000	-0.120294000
H	4.318860000	-2.610426000	1.229427000
H	4.897511000	-3.505929000	-0.207482000
H	1.908717000	-3.507118000	0.972841000
H	2.573446000	-4.508818000	-0.349418000
H	1.157111000	-3.481628000	-0.648029000
C	1.234370000	0.111007000	3.671525000
H	2.211923000	-0.339613000	3.873242000
H	0.893318000	0.643600000	4.570131000
H	0.539346000	-0.708884000	3.458232000
C	3.181051000	-2.388709000	-2.044055000
H	2.224597000	-2.158641000	-2.532759000
H	3.930496000	-1.662823000	-2.383259000
H	3.504399000	-3.381376000	-2.380654000
H	1.599031000	2.642642000	-2.288862000
Al	1.799560000	2.978182000	-0.700875000
H	0.368294000	3.572551000	-0.193254000
H	3.014621000	3.962975000	-0.335762000
H	0.143627000	-1.125067000	-0.281545000
N	-1.923977000	-0.679515000	0.219287000
C	-2.725085000	0.341236000	-0.098064000
C	-0.732667000	-0.517033000	-0.469461000
C	-0.847673000	0.643779000	-1.203115000
N	-2.104432000	1.155850000	-0.958468000
H	-0.097473000	1.153199000	-1.799203000
C	-2.308766000	-1.818264000	1.129579000
C	-1.110894000	-2.757609000	1.275669000
C	-3.490552000	-2.550859000	0.476632000
H	-4.374481000	-1.904797000	0.388546000
H	-3.221051000	-2.910083000	-0.523619000
H	-3.765215000	-3.413856000	1.095667000
H	-0.864645000	-3.233169000	0.320080000
H	-1.378365000	-3.548576000	1.985243000
H	-0.216988000	-2.242266000	1.654066000
C	-2.705752000	2.414088000	-1.533485000
C	-4.117730000	2.073136000	-2.032567000
C	-1.830736000	2.881184000	-2.699537000
H	-0.822336000	3.158308000	-2.370286000
H	-1.759639000	2.109402000	-3.477538000
H	-2.294679000	3.769383000	-3.143124000
H	-4.089282000	1.245295000	-2.752274000
H	-4.540079000	2.955473000	-2.527762000
H	-4.797610000	1.807225000	-1.211650000
C	-2.700084000	-1.237125000	2.495174000
H	-3.535320000	-0.528334000	2.421245000
H	-3.019172000	-2.056563000	3.150210000
H	-1.850593000	-0.731530000	2.966269000
C	-2.734109000	3.464378000	-0.415417000
H	-3.341187000	3.124429000	0.435376000
H	-1.714120000	3.681234000	-0.073066000
H	-3.178900000	4.390133000	-0.802391000
H	-3.731630000	0.476111000	0.269721000
Al	-1.236218000	-1.591143000	-2.894012000
H	-2.758493000	-1.136692000	-2.788750000
H	-0.256026000	-0.890602000	-3.915508000
H	-0.839256000	-2.966837000	-2.209626000

TS6

N	1.698267000	0.616489000	1.047358000
C	1.726961000	-0.700581000	0.687103000
C	2.370179000	1.450907000	0.133640000
C	2.885162000	0.559890000	-0.778053000
N	2.497059000	-0.731050000	-0.432886000
H	3.512263000	0.771059000	-1.639370000
C	1.131637000	1.096868000	2.342194000
C	-0.067352000	2.022490000	2.085806000
C	2.237225000	1.850176000	3.103543000
H	3.110265000	1.195284000	3.248940000
H	2.562616000	2.749657000	2.563927000
H	1.862565000	2.156344000	4.093152000
H	0.207453000	2.866461000	1.438817000
H	-0.442582000	2.425892000	3.038963000
H	-0.889287000	1.473231000	1.603723000
C	3.049298000	-1.966158000	-1.055306000
C	2.254242000	-3.189689000	-0.585119000
C	4.513832000	-2.097204000	-0.594999000
H	5.107107000	-1.226011000	-0.911429000
H	4.565209000	-2.167480000	0.502355000
H	4.970226000	-3.001400000	-1.027139000
H	2.303593000	-3.303870000	0.506103000
H	2.673820000	-4.092602000	-1.053523000

H	1.196649000	-3.126607000	-0.873675000	H	-1.305580000	-3.462647000	0.860357000
C	0.685049000	-0.099005000	3.190228000	H	-2.033183000	-3.617846000	2.479536000
H	1.520475000	-0.780308000	3.401868000	H	-0.686274000	-2.486166000	2.213526000
H	0.279655000	0.270792000	4.144713000	C	-2.344664000	2.127833000	-1.614630000
H	-0.096781000	-0.676806000	2.687622000	C	-3.691422000	1.828739000	-2.290936000
C	2.982553000	-1.849682000	-2.585791000	C	-1.278150000	2.450583000	-2.664903000
H	1.947612000	-1.703687000	-2.925199000	H	-0.313304000	2.698588000	-2.196697000
H	3.597021000	-1.018299000	-2.960809000	H	-1.154380000	1.625195000	-3.382619000
H	3.365161000	-2.775057000	-3.042529000	H	-1.603552000	3.338965000	-3.224538000
H	3.319594000	3.574866000	-1.568237000	H	-3.615382000	0.943623000	-2.940060000
Al	2.385503000	3.471098000	-0.253496000	H	-3.987623000	2.692391000	-2.903766000
H	0.819849000	3.806948000	-0.600882000	H	-4.494482000	1.655853000	-1.557260000
H	2.868064000	4.331653000	1.023738000	C	-3.038166000	-1.071811000	2.721754000
H	0.340148000	-1.254799000	0.398251000	H	-3.821760000	-0.323473000	2.525505000
N	-2.041106000	-0.843599000	0.476670000	H	-3.441261000	-1.783563000	3.456855000
C	-2.685178000	0.239124000	0.035160000	H	-2.175354000	-0.561868000	3.171122000
C	-0.798446000	-0.948932000	-0.178267000	C	-2.455233000	3.275213000	-0.600944000
C	-0.759029000	0.176097000	-0.998600000	H	-3.178835000	3.043893000	0.197049000
N	-1.926256000	0.882798000	-0.868037000	H	-1.473792000	3.492330000	-0.155392000
H	0.071186000	0.524641000	-1.605694000	H	-2.801872000	4.181771000	-1.118534000
C	-2.636762000	-1.831669000	1.447131000	H	-3.678997000	0.551514000	0.338184000
C	-1.593433000	-2.908829000	1.763221000	Al	-1.280327000	-2.307885000	-2.119964000
C	-3.869771000	-2.473275000	0.788593000	H	-2.740074000	-1.669649000	-2.291599000
H	-4.639315000	-1.723839000	0.547003000	H	-0.179560000	-1.916252000	-3.192507000
H	-3.596268000	-2.997529000	-0.137360000	H	-1.210594000	-3.741338000	-1.427874000
H	-4.314650000	-3.200607000	1.483666000				

RHF/3-21G* for **TS2, 5**, **TS5** and **TS6′**, gas phase.

TS2

N	2.516178000	-1.241219000	-0.127330000	H	1.662563000	-2.796895000	-3.052861000
C	3.528211000	-0.329667000	-0.175762000	H	0.864272000	-1.447334000	-2.251320000
N	3.280821000	0.529487000	0.855426000	C	3.714383000	-3.154665000	-1.189672000
Al	-0.113608000	-1.553340000	1.683625000	H	4.087664000	-3.431131000	-0.211297000
C	1.587374000	-0.933503000	0.901441000	H	3.561344000	-4.055336000	-1.772430000
C	2.097593000	0.169135000	1.482662000	H	4.458446000	-2.566013000	-1.693786000
H	1.695710000	0.720198000	2.293219000	C	1.376034000	-3.432466000	-0.453186000
C	4.098332000	1.705797000	1.320974000	H	0.364435000	-3.053680000	-0.447282000
C	2.367819000	-2.422838000	-1.049139000	H	1.380855000	-4.314348000	-1.081950000
C	1.816625000	-1.943247000	-2.402333000	H	1.658385000	-3.725979000	0.548364000
H	2.500366000	-1.264001000	-2.884485000	C	5.586388000	1.325252000	1.380957000
				H	6.000094000	1.130712000	0.407904000

H	6.139047000	2.149907000	1.815597000
H	5.720679000	0.448423000	2.002089000
C	3.836666000	2.905584000	0.396367000
H	2.778433000	3.142458000	0.394510000
H	4.383359000	3.767767000	0.761488000
H	4.157495000	2.694889000	-0.610760000
C	3.668493000	2.088637000	2.753634000
H	3.748293000	1.244342000	3.427414000
H	4.336455000	2.866109000	3.101699000
H	2.662241000	2.485870000	2.788194000
H	-0.691871000	-0.394416000	2.610449000
H	-1.246111000	-1.420664000	0.137414000
H	-0.508036000	-3.057870000	1.988236000
C	-3.326792000	0.269028000	-0.176877000
N	-4.631324000	-0.024858000	0.097339000
N	-3.377130000	1.525583000	-0.694718000
H	-1.837084000	-0.896394000	0.094273000
C	-5.470694000	1.041740000	-0.241894000
C	-4.693295000	2.003787000	-0.733688000
H	-4.952141000	2.965468000	-1.102088000
C	-2.220437000	2.329865000	-1.163626000
C	-5.063499000	-1.313020000	0.705002000
C	-4.486099000	-1.406373000	2.126297000
H	-3.406743000	-1.363502000	2.103619000
H	-4.786533000	-2.339560000	2.588140000
H	-4.847531000	-0.582801000	2.730454000
C	-4.557758000	-2.471297000	-0.170405000
H	-4.945098000	-2.372774000	-1.177341000
H	-4.893211000	-3.414748000	0.243984000
H	-3.478821000	-2.480862000	-0.214039000
C	-6.598121000	-1.372925000	0.774947000
H	-6.997046000	-0.593669000	1.413205000
H	-6.886195000	-2.328019000	1.195975000
H	-7.039699000	-1.291305000	-0.211242000
C	-2.445151000	2.706837000	-2.639044000
H	-2.559002000	1.811040000	-3.236767000
H	-1.592896000	3.266261000	-3.005433000
H	-3.329138000	3.320423000	-2.762572000
C	-0.930614000	1.512498000	-1.040015000
H	-0.737179000	1.240117000	-0.013048000
H	-0.102937000	2.113716000	-1.396620000
H	-0.983732000	0.611856000	-1.636295000
C	-2.113652000	3.592906000	-0.290805000
H	-3.002130000	4.206981000	-0.375347000
H	-1.262027000	4.184269000	-0.605407000
H	-1.984033000	3.313670000	0.747467000
Al	5.113174000	-0.138898000	-1.634673000
H	5.396431000	1.437162000	-1.772526000
H	4.559509000	-0.727532000	-3.022688000
H	6.330815000	-0.978276000	-0.992025000
H	-6.522721000	1.025228000	-0.110485000

TS5

N	3.028344000	1.227348000	0.321607000
C	2.370775000	0.124421000	-0.086710000
C	4.378478000	1.121309000	-0.011219000
C	4.540584000	-0.052006000	-0.624737000
N	3.287713000	-0.665429000	-0.677350000
H	5.418928000	-0.491068000	-1.022946000
H	5.093125000	1.870906000	0.211646000
C	2.393723000	2.419203000	0.980001000
C	1.512098000	3.135765000	-0.054209000
C	3.491327000	3.371779000	1.478692000
H	4.157146000	2.876321000	2.175343000
H	4.066059000	3.788386000	0.660256000
H	3.012886000	4.193067000	1.996480000
H	2.100399000	3.418464000	-0.919484000
H	1.092709000	4.031367000	0.388838000
H	0.698147000	2.496145000	-0.363823000
C	3.045338000	-2.031187000	-1.248389000
C	4.125800000	-2.338955000	-2.299902000
C	1.669952000	-2.060496000	-1.927289000
H	0.869545000	-1.837963000	-1.238982000
H	1.636252000	-1.337924000	-2.734384000
H	1.507046000	-3.048284000	-2.341385000
H	4.159440000	-1.565054000	-3.057036000
H	3.874861000	-3.276313000	-2.779849000
H	5.107279000	-2.452392000	-1.856681000
C	1.555974000	1.937854000	2.171190000
H	2.175539000	1.391839000	2.872741000
H	1.130078000	2.796291000	2.676691000
H	0.747422000	1.306580000	1.836885000
C	3.125538000	-3.051763000	-0.103183000
H	4.097179000	-3.007904000	0.374976000

H	2.364660000	-2.850466000	0.636533000
H	2.975190000	-4.051560000	-0.492756000
N	-1.579816000	-0.559656000	0.819626000
C	-2.779107000	-0.225122000	0.252507000
C	-0.466341000	-0.139783000	0.032089000
C	-1.052470000	0.427518000	-1.039473000
H	-0.587215000	0.855115000	-1.890748000
H	1.104228000	-0.076314000	0.051968000
C	-1.392832000	-1.313109000	2.098130000
C	-1.631114000	-0.384134000	3.301324000
C	0.050922000	-1.840762000	2.163060000
H	0.257168000	-2.473828000	1.311054000
H	0.773297000	-1.039381000	2.189666000
H	0.156156000	-2.428883000	3.067696000
H	-0.951381000	0.457875000	3.255804000
H	-1.449035000	-0.927071000	4.222652000
H	-2.645445000	-0.019530000	3.313044000
C	-3.368607000	0.914256000	-1.976693000
C	-4.486590000	-0.094671000	-2.289304000
C	-2.576082000	1.129369000	-3.284267000
H	-1.836109000	1.913004000	-3.186476000
H	-2.093162000	0.214295000	-3.604146000
H	-3.277077000	1.433463000	-4.051597000
H	-4.055641000	-1.050374000	-2.561087000
H	-5.072380000	0.276440000	-3.122651000
H	-5.152921000	-0.237857000	-1.457582000
C	-2.318041000	-2.543352000	2.140640000
H	-2.169114000	-3.146318000	1.253139000
H	-2.074269000	-3.138151000	3.013875000
H	-3.357539000	-2.276048000	2.207911000
C	-3.925554000	2.273830000	-1.521321000
H	-4.524995000	2.166033000	-0.631947000
H	-3.105462000	2.953954000	-1.319841000
H	-4.542487000	2.696069000	-2.307175000
H	-4.633861000	-0.425681000	2.668401000
Al	-4.748471000	-0.471548000	1.062935000
H	-5.633435000	0.770317000	0.542330000
H	-5.245523000	-1.900804000	0.492024000
N	-2.453410000	0.369679000	-0.921476000

5

N	4.057971000	-0.376228000	1.056448000
C	3.270000000	-0.608039000	-0.011255000
C	5.145665000	0.385821000	0.668549000
C	5.013169000	0.615528000	-0.668547000
N	3.847303000	-0.011206000	-1.071401000
H	5.662062000	1.153977000	-1.344875000
H	5.928981000	0.691522000	1.347687000
C	3.716433000	-0.776910000	2.460761000
C	2.790472000	0.301273000	3.045163000
C	5.010400000	-0.885176000	3.276324000
H	5.724374000	-1.571372000	2.801608000
H	5.494077000	0.089454000	3.423067000
H	4.767708000	-1.278526000	4.270076000
H	3.270145000	1.288478000	3.015196000
H	2.556804000	0.058119000	4.090176000
H	1.850997000	0.344727000	2.481811000
C	3.232292000	0.062856000	-2.436798000
C	4.345415000	0.241773000	-3.476038000
C	2.271134000	1.260277000	-2.451177000
H	1.460479000	1.109018000	-1.729392000
H	2.795874000	2.191307000	-2.203152000
H	1.826267000	1.369457000	-3.448743000
H	4.844681000	1.215828000	-3.390092000
H	3.902449000	0.192966000	-4.477394000
H	5.097398000	-0.554309000	-3.394823000
C	3.003984000	-2.133985000	2.419416000
H	3.641303000	-2.901052000	1.960560000
H	2.767383000	-2.445857000	3.443818000
H	2.061719000	-2.064313000	1.864239000
C	2.468676000	-1.240184000	-2.695466000
H	3.135734000	-2.109278000	-2.626381000
H	1.646608000	-1.359856000	-1.980131000
H	2.039695000	-1.209726000	-3.704322000
N	-2.456890000	-1.142592000	-0.356528000
C	-3.576179000	-0.441223000	0.023882000
C	-1.326006000	-0.336490000	-0.531732000
C	-1.800560000	0.915337000	-0.260252000
H	-1.244657000	1.840601000	-0.257753000
H	2.142718000	-1.014079000	0.033957000
C	-2.376859000	-2.629759000	-0.531557000
C	-2.365628000	-3.294073000	0.855176000
C	-1.075123000	-2.990719000	-1.266296000
H	-1.050413000	-2.548565000	-2.268204000

H	-0.182256000	-2.667549000	-0.722795000
H	-1.036334000	-4.082540000	-1.372560000
H	-1.497945000	-2.947235000	1.432439000
H	-2.293947000	-4.385390000	0.746175000
H	-3.282082000	-3.066483000	1.407828000
C	-3.960035000	2.063512000	0.425163000
C	-5.256539000	2.103265000	-0.397342000
C	-3.163343000	3.343668000	0.085760000
H	-2.269032000	3.425094000	0.724358000
H	-2.902505000	3.360923000	-0.985266000
H	-3.793658000	4.212979000	0.296764000
H	-5.029025000	2.071317000	-1.470967000
H	-5.802273000	3.031274000	-0.179024000
H	-5.919488000	1.268638000	-0.157776000
C	-3.544257000	-3.131073000	-1.395650000
H	-3.590971000	-2.566663000	-2.335992000
H	-3.391817000	-4.192828000	-1.632030000
H	-4.509817000	-3.047373000	-0.892014000
C	-4.230382000	2.060370000	1.938163000
H	-4.842645000	1.197840000	2.216722000
H	-3.281474000	2.026190000	2.491515000
H	-4.770112000	2.973890000	2.225363000
H	-5.333568000	-2.639766000	1.131138000
Al	-5.509186000	-1.179430000	0.485520000
H	-6.164289000	-0.166670000	1.550481000
H	-6.285795000	-1.175381000	-0.927184000
N	-3.155256000	0.858340000	0.062967000
Al	0.978099000	4.093620000	0.000435000
H	0.656108000	3.991651000	-1.546105000
H	2.010875000	3.060716000	0.623365000
H	0.485518000	5.329880000	0.853317000

TS6′

N	-2.542082000	-1.552508000	-1.329872000
C	-2.927455000	-0.313532000	-0.944437000
C	-1.638178000	-2.153044000	-0.398248000
C	-1.481778000	-1.198589000	0.537951000
N	-2.255826000	-0.073392000	0.202174000
H	-0.887307000	-1.237399000	1.414425000
C	-3.036702000	-2.250360000	-2.547590000
C	-4.159843000	-3.219234000	-2.140438000
C	-1.883291000	-3.021495000	-3.209902000
H	-1.042309000	-2.362714000	-3.384174000
H	-1.549131000	-3.847493000	-2.605994000
H	-2.226583000	-3.416587000	-4.160049000
H	-3.787157000	-3.938212000	-1.424155000
H	-4.526044000	-3.750576000	-3.012513000
H	-4.982600000	-2.668115000	-1.697556000
C	-2.358990000	1.155737000	1.022384000
C	-2.332895000	2.382535000	0.098881000
C	-1.161143000	1.244913000	1.985123000
H	-1.186314000	0.457822000	2.726663000
H	-0.226990000	1.186019000	1.441172000
H	-1.203035000	2.195272000	2.504185000
H	-1.425406000	2.381257000	-0.492250000
H	-2.366530000	3.288601000	0.693592000
H	-3.182716000	2.375436000	-0.565428000
C	-3.563937000	-1.228611000	-3.565834000
H	-2.789176000	-0.512249000	-3.810181000
H	-3.847219000	-1.756141000	-4.469540000
H	-4.428814000	-0.703204000	-3.194006000
C	-3.664177000	1.115180000	1.836670000
H	-4.521059000	1.102747000	1.176570000
H	-3.683756000	0.223846000	2.452036000
H	-3.731147000	1.986191000	2.479673000
H	-0.214035000	-3.874738000	1.404414000
Al	-0.721252000	-3.983230000	-0.141125000
H	-1.848879000	-5.142424000	-0.367651000
H	0.510110000	-4.149668000	-1.191012000
H	-4.098798000	0.471494000	-1.395462000
N	-6.048631000	1.879265000	-2.367221000
C	-7.363484000	1.745085000	-2.221311000
C	-5.377211000	0.906716000	-1.585578000
C	-6.382987000	0.215677000	-0.995686000
N	-7.617916000	0.745168000	-1.399046000
H	-6.323876000	-0.615380000	-0.337219000
C	-5.400406000	2.965819000	-3.171236000
C	-4.056128000	2.454513000	-3.701748000
C	-5.202021000	4.183649000	-2.254787000
H	-6.155824000	4.542794000	-1.885008000
H	-4.579456000	3.922560000	-1.411315000
H	-4.723250000	4.982999000	-2.807325000
H	-3.394814000	2.167442000	-2.898681000
H	-3.584774000	3.245844000	-4.271871000

H	-4.203731000	1.600165000	-4.347648000
C	-8.956643000	0.231329000	-0.972358000
C	-10.064939000	1.081048000	-1.610329000
C	-9.038137000	0.329799000	0.559124000
H	-8.275854000	-0.275109000	1.031500000
H	-8.913474000	1.356784000	0.878934000
H	-10.006350000	-0.025264000	0.889770000
H	-9.999010000	2.116899000	-1.297939000
H	-11.022398000	0.695994000	-1.284607000
H	-10.035176000	1.023915000	-2.692264000
C	-6.305283000	3.335693000	-4.359886000
H	-7.228622000	3.806683000	-4.042710000
H	-5.780649000	4.046913000	-4.984757000
H	-6.533054000	2.459852000	-4.955389000
C	-9.078510000	-1.227340000	-1.441280000
H	-8.986294000	-1.286753000	-2.518484000
H	-8.312879000	-1.847558000	-0.994841000
H	-10.045770000	-1.618130000	-1.150360000
H	-8.096913000	2.346883000	-2.692700000

References

[1] D. D. Perrin and W. L. F. Armarego, Purification of Laboratory Chemicals, 1988 (Pergamon Press: Oxford).

[2] J. W. Runyon, O. Steinhof, H. V. R. Dias, J. C. Calabrese, W. J. Marshall and A. J. Arduengo III, *Austr. J. Chem.*, 2011, **64**, 1165.

[3] G. Schnee, O. Nieto Faza, D. Specklin, B. Jacques, L. Karmazin, R. Welter, C. Silva López and S. Dagorne, *Chem. − Eur. J.*, 2015, **21**, 17959.

[4] David R. Lide, ed., CRC Handbook of Chemistry and Physics, Internet Version 2005, CRC Press, Boca Raton, FL, 2005.

[5] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

[6] G.M. Sheldrick, *Acta Cryst.*, 2015, **C27**, 3.

[7] (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648. (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785. (c) S. Grimme, *J. Comput. Chem.* 2004, **25**, 1463.

[8] D. Rappoport and F. Furche, *J. Chem. Phys.*, 2010, **133**, 134105.

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revis. A.03. Gaussian, Inc., Wallingford CT, 2016.

[10] K. Fukui, *Acc. Chem. Res*., 1981, **14**, 363.

[11] (a) S. Miertuš, E. Scrocco and J.Tomasi, *Chem. Phys.*, 1981, **55**, 117; (b) E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3032; (c) B. Mennucci, R. Cammi and J. Tomasi, *J. Chem. Phys.*, 1998, **109**, 2798; (d) M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43.

[12] C. Peng and H. B. Schlegel, *Israel J. Chem.*, 1993, **33**, 449.