Supporting information for;

Reversible 1,1-hydroaluminations and C-H activation in reactions of a cyclic (alkyl)(amino) carbene with alane

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1. Syntheses

General Considerations: All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (Innovative Technology glovebox equipped with a -35 °C freezer). Toluene (tol) and pentane were collected from a Grubbs-type column system manufactured by Innovative Technology, and stored over 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 minutes and cooling under vacuum. The process was repeated until no further moisture was released upon heating. Benzene-d_6 (C_6D_6) and toluene-d_8 purchased from Cambridge Isotope Laboratories, were degassed and stored over 4 Å molecular sieves in the glovebox for at least 8 h prior to use. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich, Strem Chemical or TCI. $cAAC^{Et}$ was prepared using literature methods.[1] NMR Spectra were recorded on a Bruker Avance III 400 MHz, or an Agilent DD2 600 MHz, spectrometer and spectra were referenced to residual solvents of toluene-d_8 (^1H = 2.08 ppm for *methyl* proton, ^{13}C = 122.4 ppm for *ipso* carbon) and C_6D_6 (^1H = 7.16 ppm, ^{13}C = 128.06 ppm for carbon). Chemical shifts (δ) are reported in ppm. In some instances, signal and/or coupling assignments were derived from 2D NMR experiments. IR spectra were recorded on a Bruker ALPHA spectrometer equipped with an ATR sampling unit. Elemental analysis (C, H, N) were performed in house.

Synthesis of ($cAAC^{Et}H$)AlH_2·$NEtMe_2$ (1) and ($cAAC^{Et}H$)$_2$Al(μ-H)$_2$$AlH_2$·$NEtMe_2$ (2)
A solution of AlH_3·$NEtMe_2$ in toluene (0.5 M, 0.57 mL, 0.29 mmol) was added dropwise to a solution of $cAAC^{Et}$ (90 mg, 0.29 mmol) in 2 mL of pentane while stirring at room temperature/-35/-78 ºC. The reaction mixture was allowed to slowly warm up to room temperature and stirred for another 2 h. The solvent was removed in *vacuo* to yield orange oil, which was dissolved in minimum amount of pentane, and left in the freezer overnight to obtain crystalline products that was suitable for single x-ray studies for **1** and **2**. Attempts to isolate the clean product of **1** and **2** are unsuccessful due to the similar solubility as well as **1** and **2** release $NEtMe_2$ slowly at room temperature.

Synthesis of (($cAAC^{Menthyl}H$)AlH_2)$_2$ (*meso*-3) and (*rac*-3)
A solution of AlH_3·$NEtMe_2$ in toluene (0.5 M, 1.7 mL, 0.85 mmol) was added dropwise to a solution of $cAAC^{Et}$ (534 mg, 1.70 mmol) in 6 mL of pentane while stirring at room temperature. The reaction mixture was stirred at room temperature for another 2 h. The solvent was removed in *vacuo* to yield white powder, which was dissolved in minimum amount of pentane, and left in the freezer overnight to obtain crystalline products that was suitable for single x-ray studies. The resulting compound were washed with 3 × 2 mL cold pentane and dried in *vacuo* to yield white powder (328 mg, 59 % Yield).

^{1}H NMR (600 MHz, Toluene-d_8, 253K, dr(*meso*-**3**:*rac*-**3**) = 1: 0.6): δ 7.12 – 6.92 (m, 12H), 4.89 (s, br, 1H, *rac*-**3**-Al*H*), 4.29 (p, *J* = 6.8 Hz, 2H, *rac*-**3**- *H*^{i}Pr), 4.20 (p, *J* = 6.7 Hz, 2H, *meso*-**3** - *H*^{i}Pr), 3.91 (s, br, 1H, *meso*-**3** -Al*H*), 3.61 (s, 2H, *meso*-**3** – *H*C_{cAAC}), 3.46 (p, *J* = 6.8 Hz, 2H, *meso*-**3** - *H*^{i}Pr), 3.22 (p, *J* = 6.7 Hz, 2H, *rac*-**3** - *H*^{i}Pr), 3.10 (d, *J* = 2.5 Hz, 2H, *rac*-**3** -*H*C_{cAAC}), 1.98 (m, 3H), 1.78 – 1.12 (m, 54H), 1.06 (s, 4H), 0.92 – 0.85 (m, 12H), 0.78 (t, *J* = 7.4 Hz, 4H), 0.70 (d, *J* = 7.6 Hz, 6H), 0.46 (t, *J* = 7.3 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298K): δ 152.0 (-Ph*C*), 151.0 (-Ph*C*), 149.7 (-Ph*C*), 144.8 (-Ph*C*), 148.0 (-Ph*C*), 143.7 (-Ph*C*), 126.6 (-Ph*C*), 125.7 (-Ph*C*), 125.2 (-Ph*C*), 124.7 (-Ph*C*), 73.7 (-HC_{cAAC} (*meso*-**3**)), 70.2 (-HC_{cAAC} (*rac*-**3**)), 66.2, 64.3, 55.6, 52.3, 49.5, 48.6, 34.3, 33.8, 33.5, 32.5, 32.1, 29.4, 29.0, 28.3, 27.7, 27.3, 26.4, 25.7, 25.5, 25.2, 24.7, 14.3, 10.7, 10.3, 10.0.

^{27}Al{^{1}H} NMR (128 MHz, C_6D_6, 298K): silent.

Anal. Calcd. For $C_{44}H_{73}AlN_2$: C 80.43%, H 11.20%, N 4.26 %. Found: C 80.65%, H 11.85%, N 3.86 %.

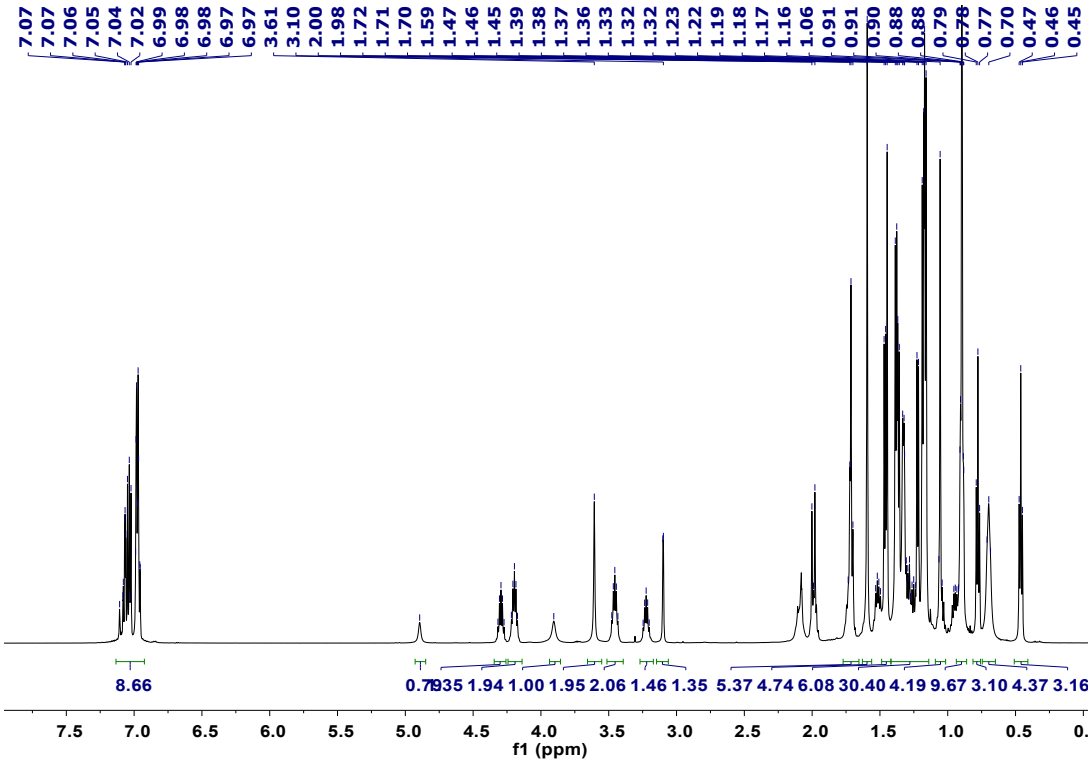


Figure S1. ^{1}H NMR of *meso*-**3** and *rac*-**3** at -20 °C

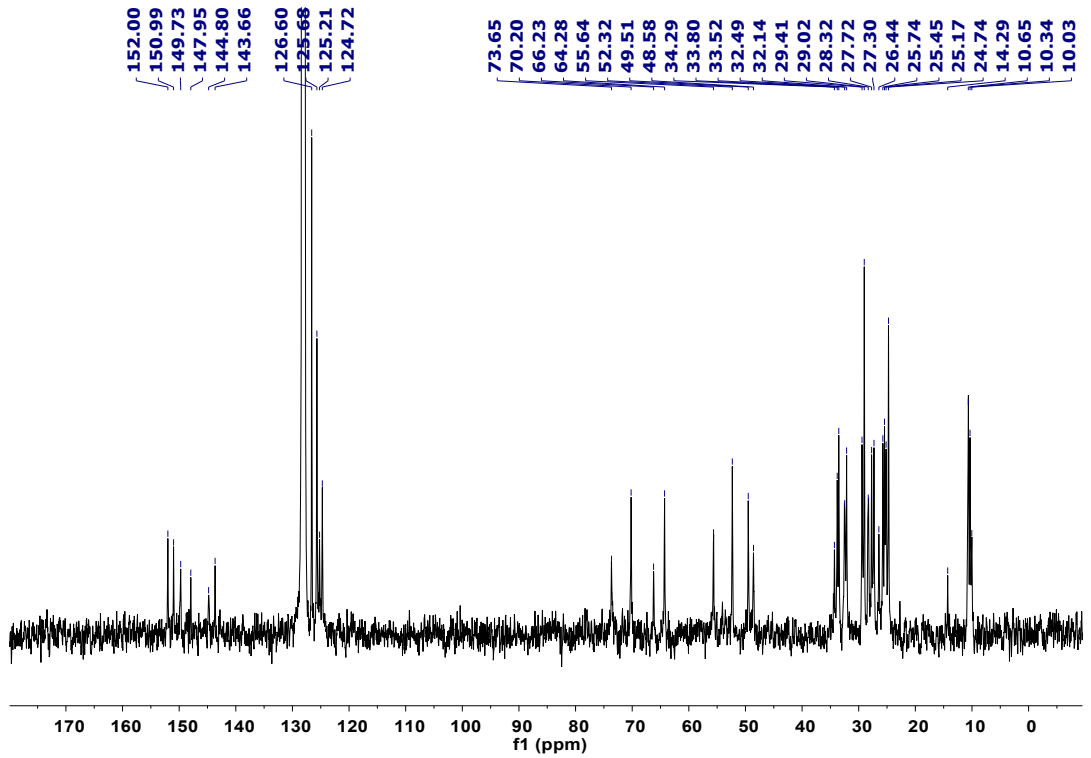


Figure S2. ^{13}C{^{1}H} NMR of *meso*-**3** and *rac*-**3**

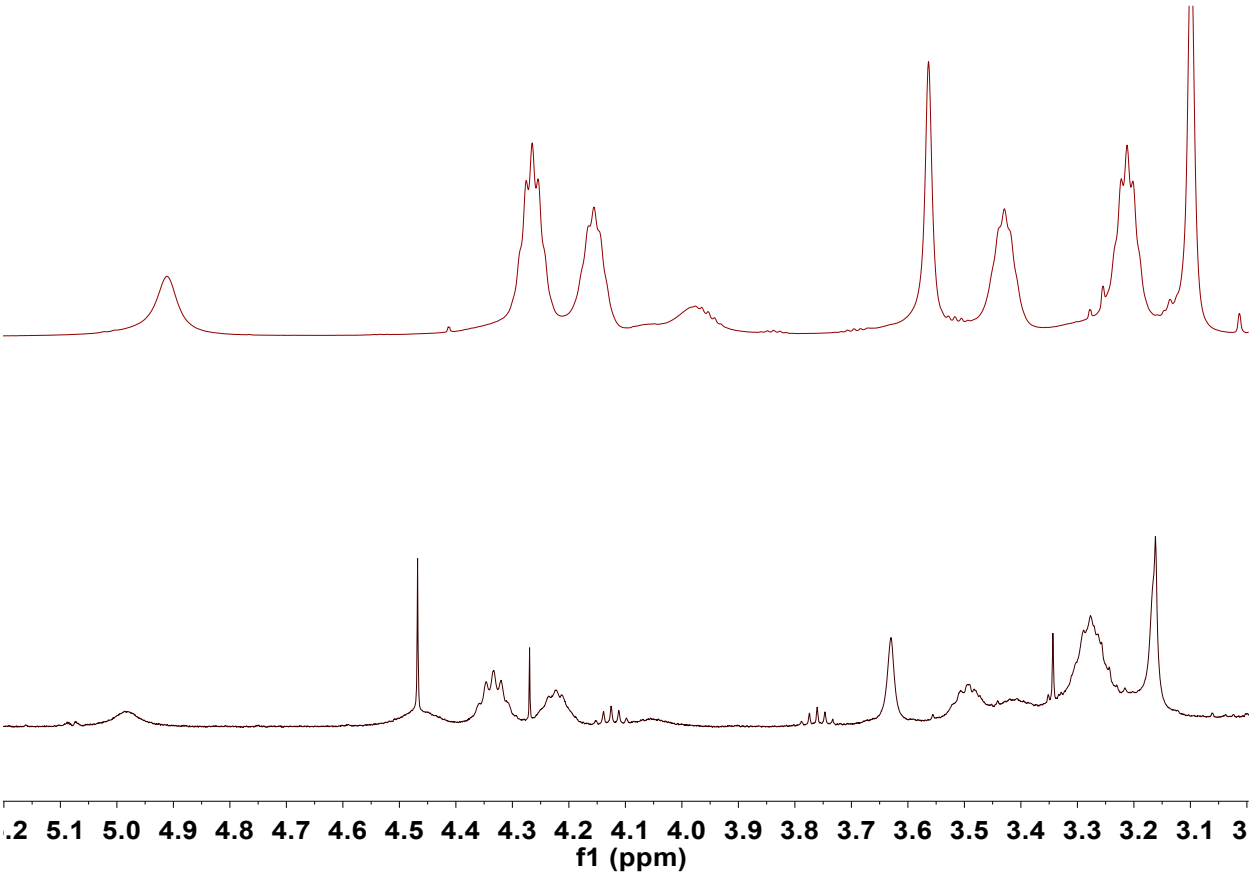


Figure S3. ^{1}H NMR range from 3.0 to 5.2 ppm for (a) bulk compound **3** in C_6D_6 at room temperature and (b) crystal of *meso*-**3** covered with Paratone-N oil dissolved in C_6D_6 at room temperature

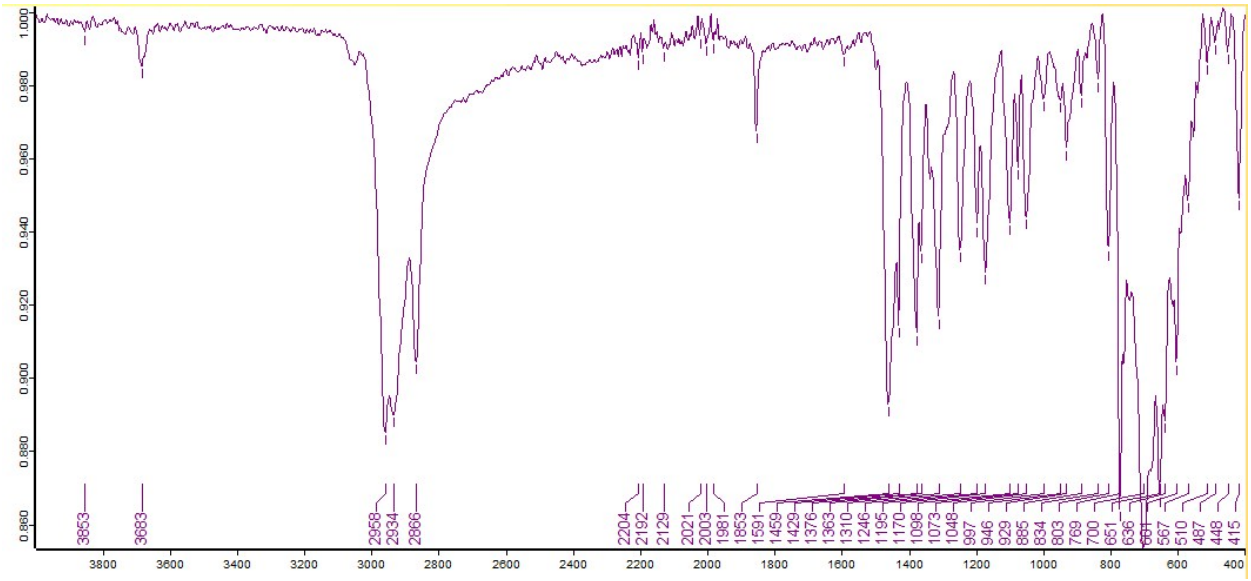


Figure S4. IR spectrum of crystalline *meso*-**3**

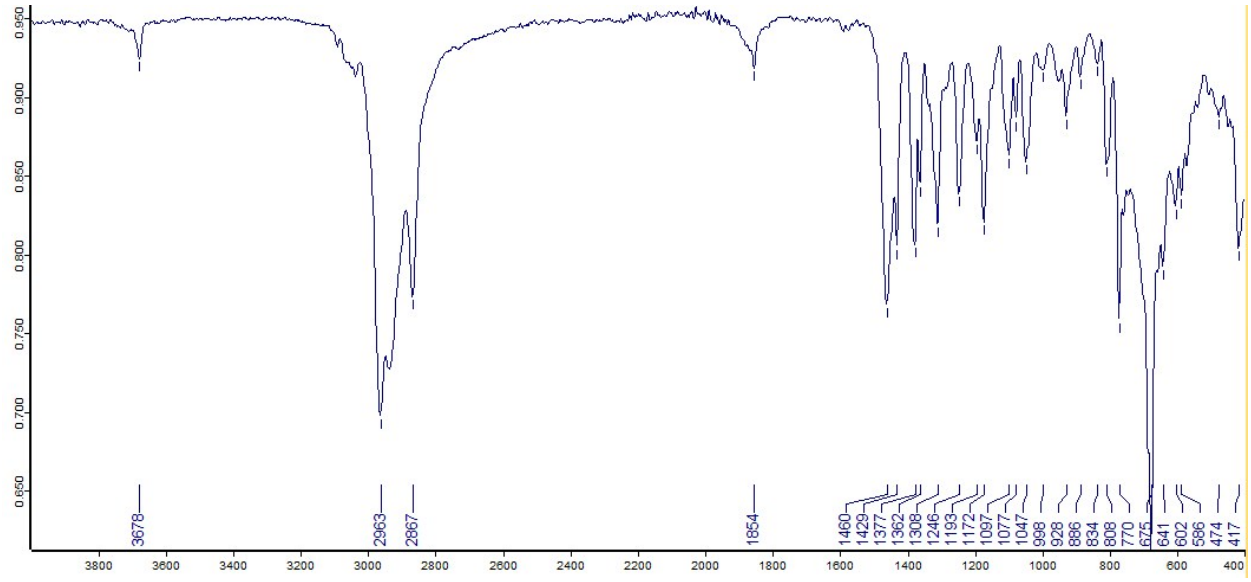


Figure S5. IR spectrum of compound **3** in benzene

Synthesis of (cAAC^{Et}H)Al(CHC(Et)$_2$CH$_2$C(Me)$_2$NC$_6$H$_3$(*i*Pr)C(Me)CH$_2$ (4)
Compound **3** (45 mg, 0.068 mmol) was dissolved in 0.5 mL of toluene-d_8 in a sealed 5 mm NMR tube and heated at 100 °C for 90 mins, the crude reaction ^{1}H NMR spectroscopy (Figure S5) were collected after the reaction cooled down to room temperature. The NMR tube was then brought into a glovebox, and the reaction mixture was transferred out with 2 mL of pentane, and in *vacuo* to yield colorless crystals that is suitable for x-ray studies. The crystalline product was then washed with 3 × 2 mL of cold pentane and dried to yield **4** (44 mg, >95% Yield).

^{1}H NMR (400MHz, C_6D_6, 298 K): δ 7.33–7.07 (m, 6H, Ar*H*), 4.18 (m, br, 1H, -C*H*(CH_2)(CH_3)), 4.07 (hept, *J* = 6.9 Hz, 1H, -*H*^{i}Pr), 3.64 (hept, *J* = 6.8 Hz, 1H, -*H*^{i}Pr), 3.37 (s, 1H, *H*C$_{cAAC}$), 3.26 (hept, *J* = 6.4 Hz, 1H, -*H*^{i}Pr), 3.13 (s, 1H, *H*C$_{cAAC}$), 2.00 – 1.56 (m, 12H), 1.55 – 1.03 (m, 35H), 0.99 (t, *J* = 7.4 Hz, 3H, -CH_2C*H*$_3$), 0.87 (t, *J* = 7.4 Hz, 3H, -CH_2C*H*$_3$), 0.66 (t, *J* = 7.0 Hz, 3H, -CH_2C*H*$_3$), 0.48 (t, *J* = 7.2 Hz, 3H, -CH_2C*H*$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298K): δ 153.8 (-Ph*C*), 153.4 (-Ph*C*), 151.2 (-Ph*C*), 150.2 (-Ph*C*), 145.0 (-Ph*C*), 141.5 (-Ph*C*), 127.0 (-Ph*C*), 126.2 (-Ph*C*), 125.7 (-Ph*C*), 124.2 (-Ph*C*), 124.1 (-Ph*C*), 123.2 (-Ph*C*), 70.2 (-H*C*$_{cAAC}$), 66.7 (-H*C*$_{cAAC}$), 64.2, 63.5, 54.8, 54.5, 50.0, 49.7, 35.4, 33.1, 33.0, 33.0, 32.2, 32.0, 29.4, 29.0, 28.8, 28.7, 28.4, 28.3, 27.4, 27.3, 26.1, 26.0, 25.5, 25.3, 25.1, 25.0, 11.0, 10.9, 10.6, 10.5.

^{27}Al{^{1}H} NMR (128 MHz, C_6D_6, 298K): silent.

Anal. Calcd. For $C_{44}H_{71}AlN_2$: C 80.68%, H 10.93%, N 4.28 %. Found: C 81.04%, H 11.47%, N 3.92 %.

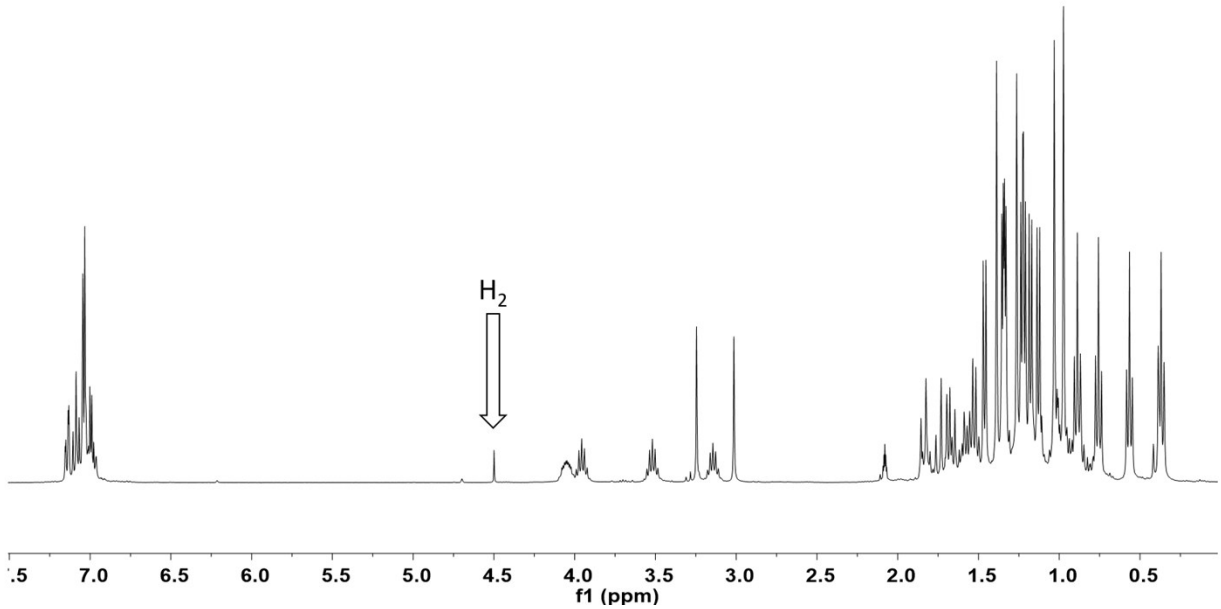


Figure S6. ^{1}H NMR of crude reaction for synthesis of **4**.

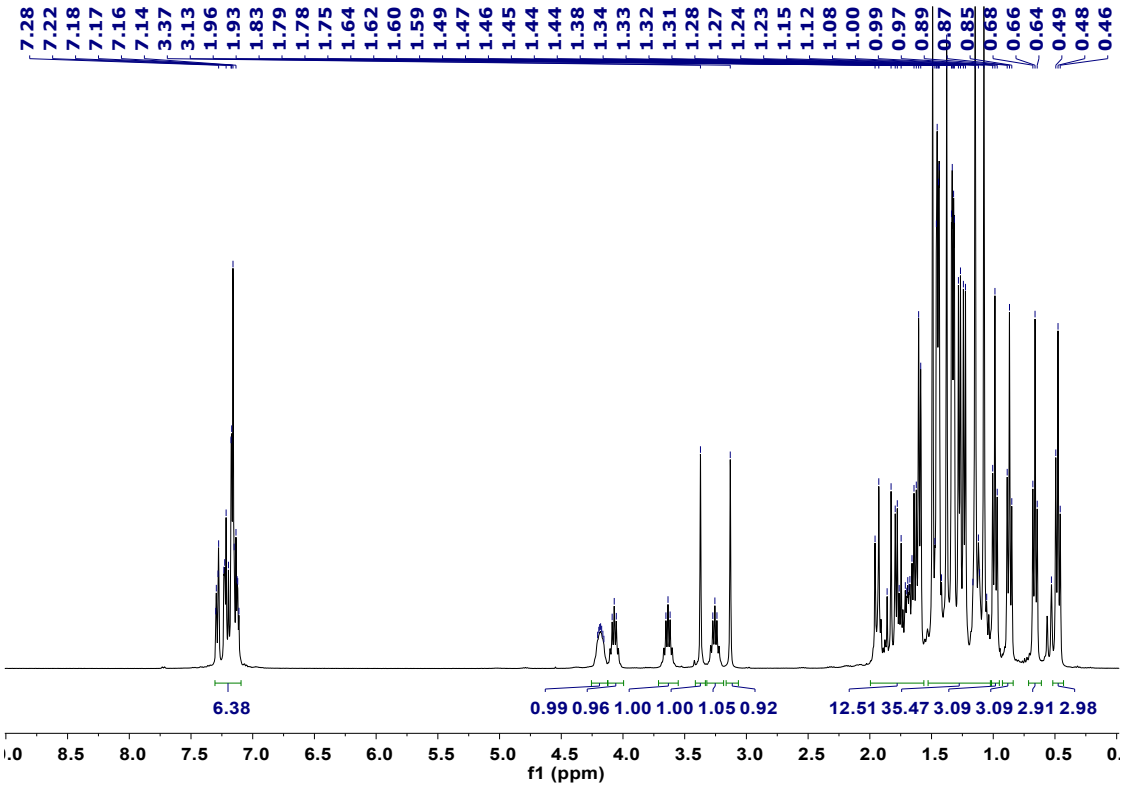


Figure S7. ^{1}H NMR of **4**

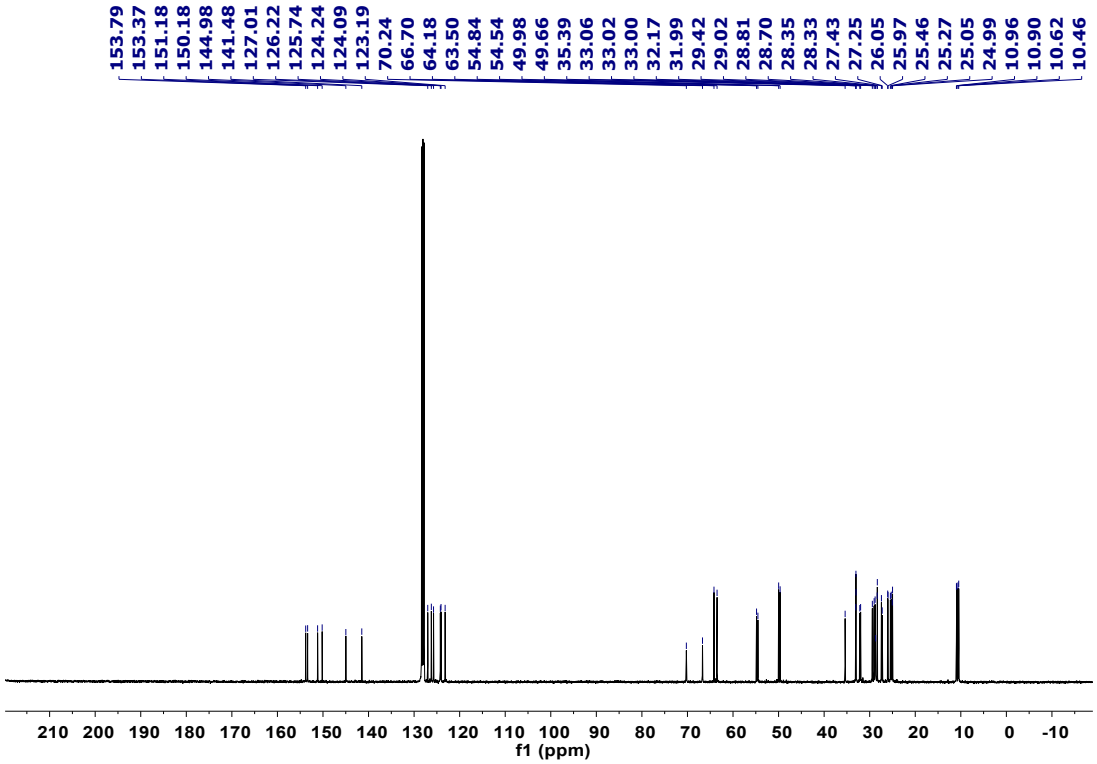
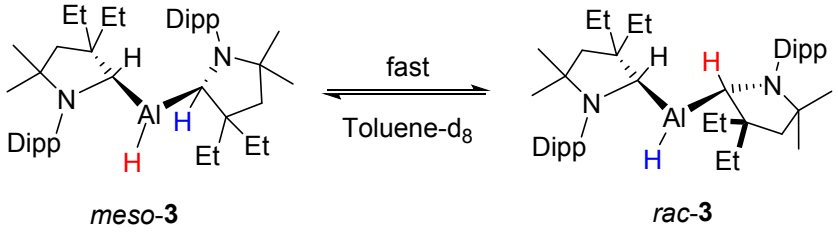


Figure S8. $^{13}C\{^{1}H\}$ NMR of **4**

2. Thermodynamic Calculations



meso-**3** *rac*-**3**

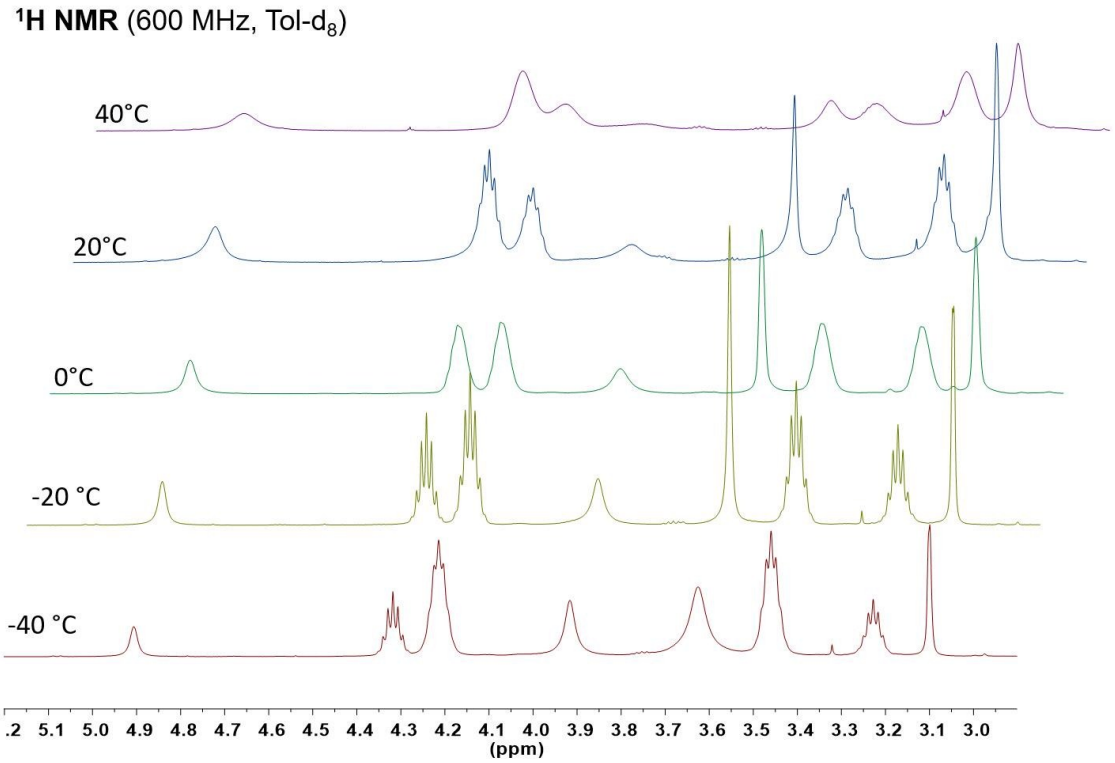


Figure S9. ^{1}H VT-NMR spectra (range: 2.8 to 5.2 ppm) of **3** in toluene-d_8

Table S1. Average ratio between *meso*-**3** and *rac*-**3** at different temperature

Temperature	*meso*-**3**	*rac*-**3**
-40 °C	2.50	1.0
-20 °C	1.60	1.0
0 °C	1.05	1.0
20 °C	0.75	1.0
40 °C	0.50	1.0

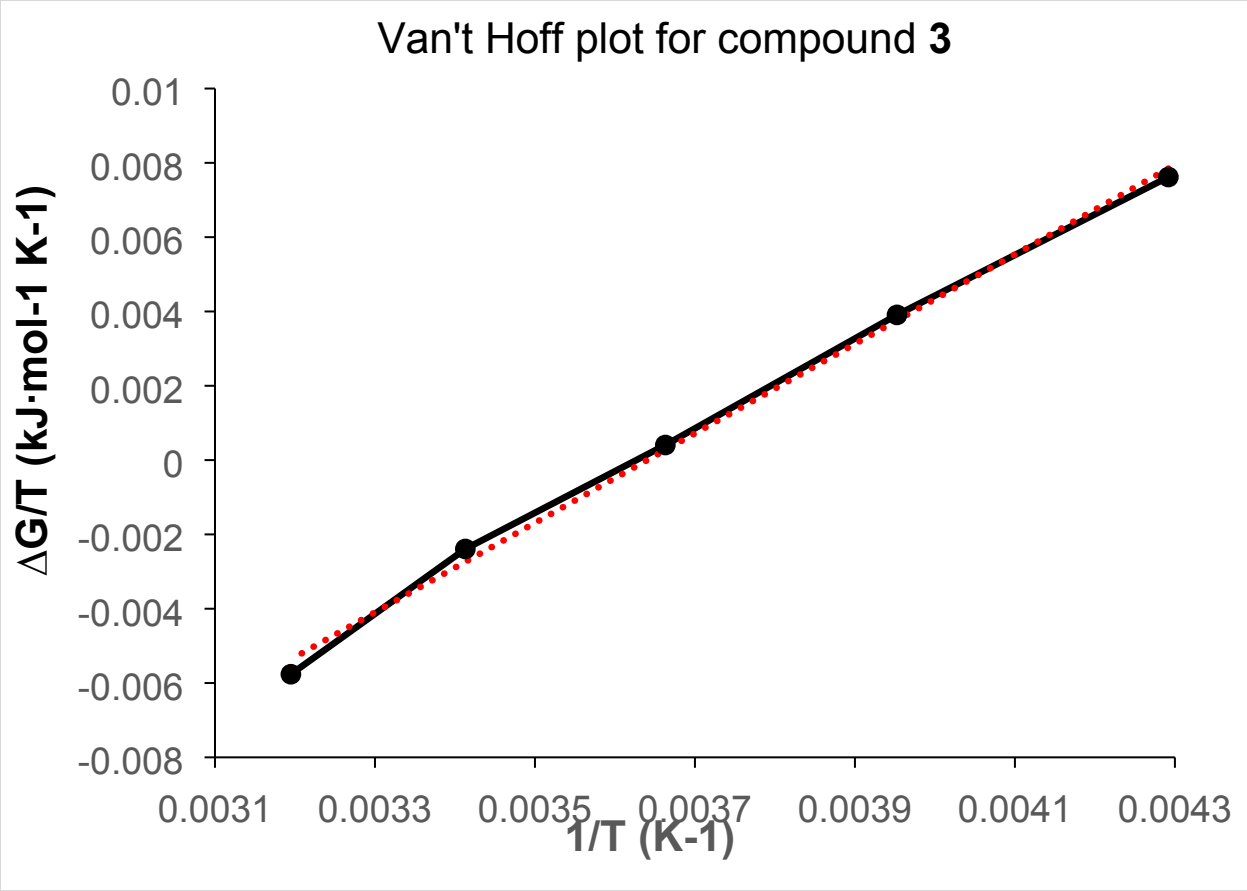


Figure S10. Van't Hoff plot for **3**

ΔH = 12.042 kJ/mol = 2.88 kcal/mol

ΔS = 43.8 J/mol = 0.01 kcal/mol

3. X-ray Crystallography

X-ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in an N_2 filled glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure Solution and Refinement. The structures of **1** & **2**, *meso*-**3**, and **4** were solved by intrinsic phasing using XS. All the structures were subjected to full-matrix least-squares refinement on F^2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined with anisotropically thermal parameters. Carbon bound hydrogen atoms were placed in geometrically calculated positions and refined using an appropriate riding model and coupled isotropic thermal parameters. The Al-bound hydrogen atoms were located in difference Fourier maps and refined in an unrestrained manner.

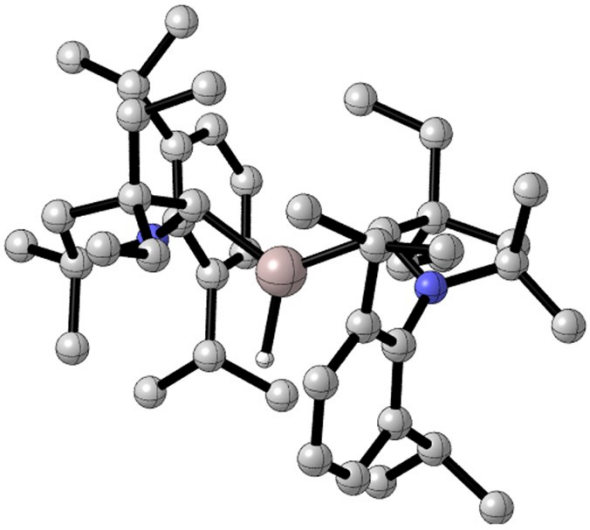
Table S2. Summary of crystallographic data for compound **1 & 2, *meso*-3, and 4**

	1 & 2	*meso*-**3**	**4**
Moiety formula	C74 H135 Al3 N5	C44 H73 Al N2	C44 H71 Al N2
Sum formula weight	1175.80	657.02	655.00
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.636(3)	9.4074(6)	11.9225(9)
b (Å)	18.707(4)	11.4610(8)	13.304(1)
c (Å)	19.303(5)	19.170(2)	13.382(1)
α (deg.)	66.586(7)	92.871(2)	79.775(3)
β (deg.)	76.109(8)	98.051(2)	80.203(2)
γ (deg.)	86.462(8)	101.380(2)	79.872(3)
vol (Å^3)	3741(2)	1999.8(2)	2035.1(3)
Z	2	2	2
ρ (calcd) (Mg·cm^3)	1.044	1.091	1.069
μ (mm^{-1})	0.092	0.082	0.080
F(000)	1306	728	724
Theta range (°)	2.195 to 27.102	2.038 to 28.281	1.573 to 27.877
T(K)	150(2)	150(2)	150(2)
reflections collected	44237	42000	45138
unique reflections	15956	9933	9692
R_{int}	0.0593	0.0428	0.0696
GOF (F^2)	1.022	1.024	1.024
R1 indices [I>2σ(I)]	0.0569	0.0450	0.0536
wR2 indices (all data)	0.1733	0.1295	0.1557
Largest diff. peak and hole (e. Å^{-3})	0.544 & -0.477	0.310 & -0.320	0.271 & -0.298
CCDC No.	1850755	1850754	1850753

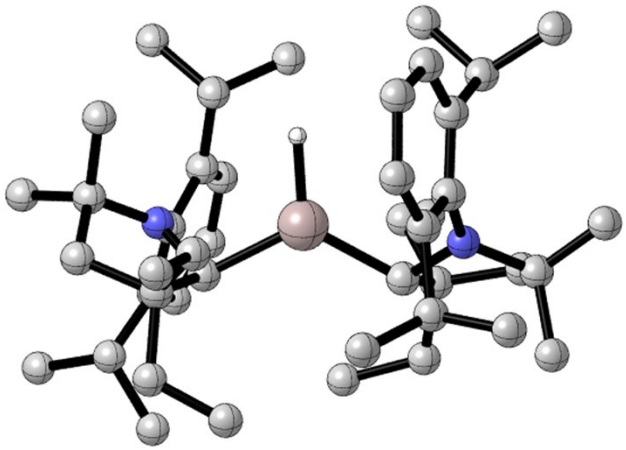
4. Computational Chemistry

All calculations were computed using the Gaussian 09 program.[2] Geometry optimizations were performed at M06-2X functional with the crystallographic coordinates used as starting geometries when available.[3] The Def2-SVP basis set was used for all atoms. The stationary nature of the converged geometry was confirmed by carrying out a frequency calculation and ensuring the absence of imaginary frequencies Optimized structures were visualized using CYLview softwares.[4]

Table S3. Calculated enthalpy for *meso*-**3**, (R, R)-**3**, and (S, S)-**3**



(R,R)-3



(S,S)-3

	Relative calculated enthalpy (kcal/mol)	Experimental (kcal/mol)
meso-**3**	0	0
(R, R)-**3**	3.41717922	
(S, S)-**3**	3.41592888	2.88

Table S4. Cartesian coordinates of *meso*-**3**, (R, R)-**3**, and (S, S)-**3**

meso-**3**:

Al	-0.16703	0.43978	0.31782	C	0.00017	-2.23565	2.98785
H	-0.65493	0.97374	1.72087	H	-0.62646	-1.86016	3.81034
N	2.23815	0.46801	0.86465	H	0.19079	-3.30418	3.17319
N	-2.16448	0.09198	-0.61716	H	-0.57754	-2.14476	2.05928
C	1.59197	1.07957	-0.35240	C	2.68045	2.88788	-1.80307
H	1.94182	0.53809	-1.24019	H	3.53995	2.21782	-1.96378
C	2.05997	2.56060	-0.42823	H	3.10172	3.90637	-1.76329
C	3.16042	2.65338	0.65428	C	1.74070	2.76925	-2.99590
H	3.16748	3.62932	1.16226	H	2.25767	3.03538	-3.92888
H	4.14893	2.54140	0.18039	H	0.86303	3.42661	-2.90226
C	2.95656	1.50391	1.66174	H	1.37634	1.73627	-3.10769
C	4.30352	0.99880	2.17582	C	0.89241	3.52474	-0.13249
H	4.80392	1.80169	2.73676	H	0.51694	3.30708	0.87950
H	4.95768	0.69529	1.34857	H	0.06250	3.27492	-0.81554
H	4.17889	0.13656	2.84516	C	1.19543	5.01441	-0.25957
C	2.12389	1.97352	2.86563	H	0.33990	5.61473	0.08311
H	2.59189	2.85702	3.32531	H	1.39670	5.30037	-1.30244
H	2.06572	1.18864	3.63282	H	2.06759	5.31214	0.34192
H	1.09659	2.22940	2.57388	C	-1.18814	-1.07400	-0.39128
C	2.69015	-0.89061	0.80020	H	-1.62984	-1.76648	0.33109
C	3.60530	-1.33176	-0.19145	C	-0.95618	-1.77826	-1.75515
C	3.89703	-2.69492	-0.29739	C	-2.05017	-1.17796	-2.66480
H	4.58567	-3.03228	-1.07571	H	-2.92987	-1.84128	-2.68169
C	3.35909	-3.62286	0.58727	H	-1.71623	-1.08035	-3.70905
H	3.60204	-4.68237	0.49165	C	-2.46723	0.19431	-2.09292
C	2.52928	-3.18057	1.60863	C	-1.65019	1.34293	-2.69492
H	2.12976	-3.90067	2.32652	H	-1.70333	1.32987	-3.79383
C	2.17919	-1.83185	1.73229	H	-0.59342	1.28243	-2.40193
C	4.35667	-0.37765	-1.10875	H	-2.03612	2.31295	-2.34694
H	4.10105	0.64306	-0.79955	C	-3.94556	0.44669	-2.37898
C	5.87476	-0.54043	-0.94866	H	-4.09104	0.50040	-3.46793
H	6.40284	0.25776	-1.49204	H	-4.29301	1.38855	-1.93531
H	6.21694	-1.50236	-1.35895	H	-4.57310	-0.36264	-1.98676
H	6.18157	-0.50414	0.10598	C	-3.24832	0.29912	0.32580
C	3.98014	-0.54170	-2.58478	C	-4.11800	-0.74799	0.72664
H	4.55965	0.15603	-3.20906	C	-5.09399	-0.49935	1.69709
H	2.91264	-0.35387	-2.76519	H	-5.74308	-1.31823	2.01433
H	4.20287	-1.56382	-2.92962	C	-5.27762	0.76395	2.23846
C	1.29779	-1.42882	2.90532	H	-6.05156	0.93994	2.98697
H	1.01920	-0.37839	2.76167	C	-4.47319	1.80351	1.79524
C	2.06898	-1.54099	4.22626	H	-4.62988	2.80672	2.19584
H	1.44704	-1.19251	5.06490	C	-3.45703	1.60011	0.85590
H	2.99214	-0.94442	4.21542	C	-4.11208	-2.14331	0.11967
H	2.35154	-2.58665	4.42590	H	-3.41261	-2.13516	-0.71947

C	-3.66042	-3.21045	1.12335
H	-3.60921	-4.19922	0.64147
H	-4.37736	-3.28078	1.95569
H	-2.67498	-2.98881	1.55647
C	-5.48334	-2.52834	-0.45152
H	-5.40662	-3.47787	-1.00282
H	-5.87481	-1.76391	-1.13728
H	-6.22793	-2.67055	0.34522
C	-2.65519	2.82760	0.44644
H	-1.80540	2.48838	-0.15845
C	-2.10151	3.59440	1.65184
H	-1.45431	4.41591	1.31007
H	-1.51591	2.93597	2.30755
H	-2.90980	4.04638	2.24546
C	-3.48821	3.78062	-0.42059
H	-2.87769	4.64163	-0.73484
H	-4.34929	4.16584	0.14724
H	-3.87941	3.29301	-1.32374
C	0.44709	-1.49235	-2.34007
H	1.19972	-1.67541	-1.55492
H	0.51452	-0.41791	-2.57242
C	0.81021	-2.29013	-3.59038
H	1.74480	-1.91532	-4.03074
H	0.03049	-2.21915	-4.36438
H	0.96003	-3.35590	-3.36612
C	-1.13359	-3.30425	-1.61034
H	-1.09906	-3.76806	-2.61004
H	-2.14316	-3.51147	-1.22396
C	-0.10621	-3.96454	-0.69734
H	-0.31555	-5.03746	-0.57766
H	-0.11116	-3.50731	0.30437
H	0.91873	-3.86423	-1.08506

(R, R)-**3**:

Al	0.16943	0.13124	0.22804
N	2.86489	-0.53575	-0.74371
N	-2.59160	0.53830	0.79028
C	1.49806	-0.31625	-1.19965
H	1.45983	0.48091	-1.98123
C	1.13283	-1.67364	-1.91111
C	2.51539	-2.35376	-2.12571
H	2.63415	-2.74480	-3.14793
H	2.63109	-3.20452	-1.43469
C	3.58370	-1.29381	-1.77841
C	4.88385	-1.90759	-1.27503
H	5.40984	-2.39500	-2.10856
H	4.70734	-2.66228	-0.49998
H	5.54742	-1.13159	-0.86155
C	3.90007	-0.44783	-3.02757
H	4.24407	-1.09728	-3.84644
H	4.69204	0.28302	-2.82094
H	3.01457	0.09771	-3.38285
C	3.38403	0.08802	0.42556
C	3.50074	-0.64598	1.63521
C	3.84269	0.02536	2.81409
H	3.91454	-0.53962	3.74638
C	4.06976	1.39551	2.82827
H	4.31388	1.90389	3.76256
C	4.00256	2.11035	1.63764
H	4.21714	3.18086	1.64089
C	3.68507	1.47507	0.43279
C	3.29482	-2.15076	1.70869
H	2.99991	-2.48048	0.70280
C	2.18480	-2.56156	2.68014
H	2.04757	-3.65397	2.65855
H	2.43834	-2.27915	3.71397
C	4.60181	-2.85311	2.10233
H	4.49875	-3.94502	2.00742
H	4.85431	-2.63350	3.15121
H	5.44887	-2.52679	1.48405
C	3.79164	2.26452	-0.86075
H	3.21723	1.72701	-1.62886
C	3.25887	3.69616	-0.76439
H	3.19408	4.14708	-1.76555
H	3.92454	4.33429	-0.16389
H	2.26300	3.73505	-0.30387
C	5.26467	2.30059	-1.29521
H	5.37368	2.75061	-2.29423
H	5.70538	1.29443	-1.31459
H	5.85015	2.90105	-0.58162
C	0.26729	-2.52041	-0.95516
H	-0.65404	-1.95842	-0.67991
H	0.84705	-2.64650	-0.02284
C	-0.18296	-3.88027	-1.47539
H	-0.68744	-4.45391	-0.68451
H	0.67416	-4.47222	-1.83174
H	-0.89393	-3.77319	-2.30729
C	0.42977	-1.46641	-3.26064
H	0.29295	-2.44922	-3.74131
H	1.11139	-0.90454	-3.92016
C	-0.90620	-0.74083	-3.18789
H	-1.35520	-0.63324	-4.18581

H	-0.77311	0.27169	-2.77914	C	-0.11146	2.92396	1.05952
H	-1.64165	-1.26093	-2.55139	H	0.73125	2.54090	0.44482
C	-1.54024	1.12478	-0.07170	H	-0.08855	2.34014	1.99287
H	-1.87788	1.06476	-1.11936	C	0.18512	4.38525	1.37846
C	-1.43782	2.63489	0.31750	H	1.11016	4.46991	1.96623
C	-2.66355	2.85319	1.23108	H	-0.62701	4.84219	1.96336
H	-3.49673	3.24685	0.62660	H	0.31525	4.98314	0.46422
H	-2.47260	3.59068	2.02570	C	-1.55208	3.51830	-0.93835
C	-3.07609	1.48199	1.81181	H	-1.62504	4.57696	-0.63616
C	-2.40186	1.23807	3.17600	H	-2.50927	3.27708	-1.42979
H	-2.59161	2.07800	3.86166	C	-0.41828	3.34620	-1.94287
H	-1.31630	1.10560	3.06678	H	-0.61636	3.91178	-2.86420
H	-2.79851	0.32643	3.64399	H	-0.29396	2.28828	-2.22474
C	-4.58963	1.40520	2.00356	H	0.54513	3.69487	-1.54439
H	-4.90221	2.11199	2.78628	H	0.38796	-0.32754	1.72547
H	-4.89878	0.39602	2.31257	H	1.23031	-2.08430	2.42736
H	-5.12339	1.65792	1.07833	(S, S)-**3**:			
C	-3.30313	-0.56663	0.24825	N	-2.85618	-0.08837	0.54713
C	-4.08976	-0.41658	-0.92600	N	2.67675	-0.09796	-0.61182
C	-4.61330	-1.55090	-1.55250	C	-2.86781	1.23036	-0.00318
H	-5.20567	-1.43351	-2.46342	C	2.81634	0.99568	0.29491
C	-4.40910	-2.82338	-1.03008	C	-3.34352	1.49833	-1.30965
H	-4.82179	-3.69877	-1.53431	C	3.15288	0.78393	1.66149
C	-3.69962	-2.96669	0.15610	C	2.58826	2.32568	-0.15017
H	-3.57165	-3.96221	0.58644	C	-1.98948	-1.13441	-0.03299
C	-3.14495	-1.86054	0.81033	H	-2.40363	-1.48569	-1.00475
C	-4.45217	0.94617	-1.50032	C	-3.29600	2.80768	-1.80280
H	-3.99803	1.70764	-0.85157	H	-3.65640	3.00997	-2.81386
C	-3.92990	1.16199	-2.92406	C	-3.85819	0.41682	-2.24997
H	-4.22770	2.15582	-3.29238	H	-3.92950	-0.51574	-1.68263
H	-4.34680	0.41200	-3.61432	C	-2.31505	2.29182	0.76315
H	-2.83554	1.09305	-2.97811	C	-4.04972	-0.66634	1.22237
C	-5.97314	1.15128	-1.47618	C	1.65846	-1.13901	-0.32519
H	-6.22654	2.18554	-1.75430	H	1.81977	-1.58971	0.66746
H	-6.39683	0.94290	-0.48394	C	2.67952	3.38522	0.76089
H	-6.46968	0.48164	-2.19466	H	2.50329	4.40363	0.40803
C	-2.44677	-2.07015	2.14346	C	-2.30469	3.58655	0.23751
H	-1.86737	-1.16025	2.34795	H	-1.88661	4.40562	0.82252
C	-1.47897	-3.25420	2.15830	C	1.95861	-2.23176	-1.38242
H	-0.95609	-3.29890	3.12524	C	3.20227	1.87164	2.53868
H	-0.71815	-3.16515	1.37186	H	3.44221	1.69706	3.59004
H	-2.00014	-4.21467	2.02462	C	-2.79620	3.84995	-1.03656
C	-3.49034	-2.24447	3.25505	H	-2.77142	4.86550	-1.43527
H	-3.00325	-2.30875	4.24024	C	-2.18525	-2.30006	0.96459
H	-4.06650	-3.16996	3.09724	C	2.96912	3.16928	2.10094
H	-4.20511	-1.41023	3.27715	H	3.02091	4.00650	2.79902

C	3.48335	-0.58433	2.24689	H	-0.37931	0.35755	1.49572
H	3.54601	-1.30257	1.42007	C	1.55898	-3.65732	-0.95322
C	-5.25173	0.73524	-2.80017	H	2.02290	-4.36005	-1.66535
H	-5.63064	-0.11255	-3.39097	H	0.47226	-3.77554	-1.09506
H	-5.22936	1.61295	-3.46326	C	1.20960	-1.89064	-2.69454
H	-5.96892	0.94115	-1.99358	H	1.27183	-0.80588	-2.87278
C	2.23923	2.67688	-1.58688	H	0.13498	-2.10757	-2.51779
H	2.10207	1.72971	-2.12441	C	-1.48712	3.26251	2.98212
C	3.83381	-0.61991	-1.39292	H	-2.44204	3.79543	3.09761
C	3.48788	-2.11161	-1.51368	H	-0.74691	3.96568	2.57028
H	3.88069	-2.55946	-2.43890	H	-1.13480	2.96834	3.98108
H	3.95039	-2.65285	-0.67304	C	5.18150	-0.41502	-0.69308
C	-3.69302	-2.16762	1.27003	H	5.99012	-0.81085	-1.32536
H	-3.97550	-2.62604	2.23001	H	5.22439	-0.93378	0.27232
H	-4.25539	-2.69887	0.48629	H	5.37683	0.65480	-0.52180
C	-1.63696	2.02337	2.10042	C	2.38664	-1.05609	3.20861
H	-2.24551	1.29469	2.64443	H	2.58448	-2.08115	3.55884
C	-5.37587	-0.44670	0.47874	H	1.39619	-1.03771	2.73211
H	-5.55979	0.62628	0.31394	H	2.34033	-0.40047	4.09268
H	-6.20539	-0.84404	1.08266	C	3.95327	0.02425	-2.78533
H	-5.40226	-0.96105	-0.48997	H	4.74878	-0.47718	-3.35781
C	-1.32394	-2.06765	2.22144	H	4.22122	1.08442	-2.70516
H	-1.53696	-1.05965	2.60873	H	3.02089	-0.04668	-3.35833
H	-0.26965	-2.05316	1.89124	C	-2.29971	-3.98174	-1.03705
C	-1.86939	-3.69761	0.39918	H	-2.13930	-5.04159	-1.28163
H	-2.34610	-4.43888	1.06189	H	-1.72727	-3.38855	-1.76573
H	-0.78681	-3.88026	0.49306	H	-3.36546	-3.76168	-1.20066
C	-4.23599	-0.08790	2.63311	C	-1.46265	-3.08647	3.34785
H	-3.38010	-0.31515	3.28291	H	-0.82086	-2.80870	4.19652
H	-5.13533	-0.51772	3.09824	H	-1.16382	-4.09534	3.02770
H	-4.36918	1.00418	2.59015	H	-2.49482	-3.14529	3.72448
C	-2.87502	0.17822	-3.40222	C	1.64070	-2.63607	-3.95279
H	-3.22931	-0.63869	-4.04940	H	0.97213	-2.39798	-4.79190
H	-1.87265	-0.07716	-3.03000	H	1.61994	-3.72639	-3.81061
H	-2.77163	1.08273	-4.02146	H	2.65941	-2.35359	-4.25565
C	0.93254	3.47181	-1.68766	C	4.84258	-0.58971	2.95633
H	0.66326	3.62493	-2.74411	H	5.11223	-1.61460	3.25315
H	1.03160	4.46705	-1.22581	H	4.82339	0.02318	3.86968
H	0.09771	2.94789	-1.20369	H	5.63724	-0.19512	2.30776
C	3.37643	3.47574	-2.23871	C	1.92065	-4.09076	0.46571
H	3.20743	3.58329	-3.32103	H	1.71102	-5.16169	0.60061
H	4.35745	3.00470	-2.08414	H	1.34102	-3.54781	1.22723
H	3.43202	4.48747	-1.80732	H	2.98658	-3.93481	0.69057
C	-0.26142	1.38781	1.88087	Al	-0.18415	-0.37415	-0.53578
H	0.28721	1.26751	2.82763	H	-0.25421	0.86429	-1.50864
H	0.36332	1.99079	1.20550				

4. References

1. V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed. Engl.*, 2005, **44**, 5705-5709.
2. 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, M. C. X. Li, 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. J. A. Montgomery, 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, 2016, *Gaussian 09, Revision E.01*. , Wallingford CT.
3. Y. Zhao and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2007, **120**, 215-241.
4. Legault C. Y., CYLview, 1.0b; Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009; www.cylview.org.