Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

[(Flu)-$(CH_2)_2$-(NHC)-CH_2-(NHC)-$(CH_2)_2$-(Flu)]$^{2-}$: an 'all-organic' hybrid and flexible ligand that enwraps a Ca^{2+} pseudo-tetrahedrally.

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General Procedure

All reactions were performed under a dry N_2/Ar atmosphere using the standard Schlenk technique or inside a glovebox, unless otherwise stated. Prior to use, glassware were dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. Bis(1*H*-imidazole-1-yl)methane[1] and 9-(2-bromoethyl)-9*H*-fluorene[2] were prepared following the literature procedure. All other reagents are available commercially. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker (Avance NEO) or a Bruker (Avance III) spectrometer operating at 500 MHz, at ambient temperature unless otherwise mentioned. Chemical shifts (δ in ppm) in the ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual signals of the deuterated solvents. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), br (broad). Mass spectrometric analyses were done on a Bruker micrOTOF–Q II Spectrometer. X-ray diffraction data were collected on a Rigaku Synergy xtalab diffractometer. Single crystal diffraction data are reported in crystallographic information files (cif) accompanying this document.

1. Experimental Procedure.

1.1. Synthesis of LH_4Br_2 (1)

A 50 ml round bottom flask fitted with a reflux condenser was charged with bis(1*H*-imidazole-1-yl)methane (1.100 g, 7.42 mmol), 9-(2-bromoethyl)-9*H*-fluorene (4.060 g, 14.80 mmol), and 20 mL of dry acetonitrile under a N_2 atmosphere and heated at 120 °C for 6 days. The reaction progress was monitored by TLC. It should be noted that a <1 g scale preparation is nearly completed within 2 days. However, in upscaled reactions, extra time is required to ensure the reaction completion. Upon completion, all volatiles were removed under vacuum to obtain a sticky solid which was vigorously stirred overnight with excess of Et_2O and sonicated for two more hours to obtain a free-flowing white suspension. Subsequent filtration followed by washing the white solid residue three more times with excess of Et_2O afforded **1** (59% yield) as a white powder.

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.26 (s, 2H, imidazolium-*H*), 7.91 (d, *J* = 7.5 Hz, 4H, Flu), 7.87 (br, 2H, imidazole backbone-*H*), 7.82 (br, 2H, imidazole backbone-*H*), 7.63 (d, *J* = 7.5 Hz, 4H, Flu), 7.41 (t, *J* = 7.5 Hz, 4H, Flu), 7.33 (t, *J* = 7.3 Hz, 4H, Flu), 6.46 (s, 2H, Imd-C*H*$_2$-Imd), 4.18 (t, *J* = 5.7 Hz, 2H, 9C*H*-Flu), 4.10-4.05 (m, 4H, Imd-C*H*$_2$-CH$_2$-Flu), 2.66-2.60 (m, 4H, Imd-CH$_2$-C*H*$_2$-Flu).^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 145.3, 140.4, 137.4, 127.5, 127.2, 124.6, 123.1, 121.9, 120.3, 57.8 (Imd-*C*H$_2$-Imd), 46.8 (Imd-*C*H$_2$-CH$_2$-Flu), 44.3 (9*C*H-Flu), 31.7(Imd-CH$_2$-*C*H$_2$-Flu). HRMS-(m/z): $[M]^{2+}$ calc. for $[C_{37}H_{34}N_4]^{2+}$, 267.14 found 267.14.

1.2. Synthesis of [(LH)Ca(HMDS)] (2).

Inside the glovebox, a 5 mL screw cap vial fitted with a magnetic bead was charged with CaI_2 (0.100 g, 0.340 mmol), KHMDS (0.136 g, 0.681 mmol), and 2 mL of toluene and stirred at room temperature for 36 hours. The resulting white suspension was filtered directly onto **1** (0.118 g, 0.170 mmol) in another 10 mL screw cap vial fitted with a magnetic bead. The reaction mixture which immediately turned orange was stirred for two hours at room temperature. Subsequent

filtration and storing the filtrate in the −40 °C freezer for 48 h afforded orange crystals of **2** (25 % yield) which are of X-ray quality. After isolating the crystals, excess hexane was added to the remaining mother liquor to precipitate out the rest of **2** as an orange solid. The solid was further washed with hexane and benzene consecutively to remove any soluble impurities. The orange reside was finally dried under high vacuum to afford **2** in overall 85% yield.

^{1}H NMR (500 MHz, DMSO) δ 7.89 (d, J = 7.6 Hz, flu-H, 5H), 7.35 (d, J = 8.1 Hz, Imidazole backbone-*H*, 4H), 7.26 (s, 1H), 6.87 (t, J = 7.8 Hz, 5H), 6.42 (t, J = 7.1 Hz, 5H), 6.15 (s, N-CH_2-N, 2H), 4.21 – 4.11 (m, N-CH_2-CH$_2$-Flu, 4H), 3.48 – 3.39 (m, N-CH$_2$-CH_2-Flu, 4H), 0.01 (s, 19H). ^{13}C{^{1}H} NMR (126 MHz, DMSO) δ 134.3, 120.9, 118.7, 118.5, 113.1, 107.4, 89.0, 51.7, 29.5, 2.8. Elemental analysis for $C_{43}H_{49}N_5CaSi_2$: Calcd. C, 70.54; H, 6.75; N, 9.57; Found C, 68.62; H, 6.55; N, 9.22.

1.3. Synthesis of [(L)Ca] (3).

Heating a benzene suspension of **2** (30mg) in a teflon-stoppered storage tube at 80 °C for 12 h resulted in a quantitative conversion of **2** into **3** as red crystals which are of X-ray quality. The crystals were isolated by washing with fresh benzene to remove the HN(SiMe$_3$)$_2$ byproduct and dried under vacuum.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88 (d, *J* = 7.6 Hz, flu-*H*, 4H), 7.37 (residual benzene), 7.35 (d, *J* = 8.1 Hz, flu-*H*, 4H), 7.28 (d, *J* = 14.0 Hz, Imidazole backbone-*H*, 4H), 6.86 (t, *J* = 7.3 Hz, flu-*H*, 4H), 6.42 (t, *J* = 7.0 Hz, flu-*H*, 4H), 6.14 (s, N-CH_2-N, 2H), 4.22 – 4.12 (m, N-CH_2-CH$_2$-Flu, 4H), 3.50 – 3.38 (m, N-CH$_2$-CH_2-Flu, 4H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 134.3, 128.3(residual benzene), 120.9, 118.7, 118.5, 113.1, 107.4, 89.0, 51.7, 29.5. Elemental analysis for $C_{37}H_{31}CaN_4$,2(C_6H_6): Calcd C, 80.84; H, 5.95; N, 7.70; Found C, 77.92; H, 6.23; N, 7.44.

1.4. Synthesis of Compound [(LH)Li$_2$(HMDS)] (4).

Inside the glovebox, a 5 mL screw cap vial fitted with a magnetic bead was charged with **1** (0.150 g, 0.216 mmol), LiHMDS (0.145 g, 0.864 mmol), and 4 mL of toluene and stirred at room temperature for 2 hours, during which the reaction color turned orange. It was then filtered into another 10 mL screw cap vial. Subsequent cooling at −40 °C afforded dark orange crystals of **4** (20 % yield) which are of X-ray quality. After isolating the crystals, excess hexane was added to the remaining mother liquor to precipitate out the rest of **4** as an orange solid. The solid was further washed with hexane to remove any soluble impurities. The orange reside was finally dried under high vacuum to afford **4** in overall 57% yield.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.5 Hz, flu-*H*, 5H), 7.37 (d, *J* = 8.1 Hz, Imidazole backbone-*H*, 4H), 7.27 (s, 1H), 6.92 (t, *J* = 7.8 Hz, flu-*H,* 5H), 6.48 (t, *J* = 7.1 Hz, flu-*H*, 5H), 6.15 (s, N-CH_2-N, 2H), 4.19-4.12 (m, N-CH_2-CH$_2$-Flu, 4H), 3.47-3.41 (m, N-CH$_2$-CH_2-Flu, 4H), 0.03 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 134.4, 120.9, 118.7, 118.5, 113.1, 107.4, 89.1, 51.6, 29.6, 3. Elemental analysis for $C_{43}H_{49}Li_2N_5Si_2$,3(C_7H_8): Calcd C, 76.90; H, 7.36; N, 7.87; Found C, 74.72; H, 7.13; N, 7.39.

2. Spectroscopic Data.

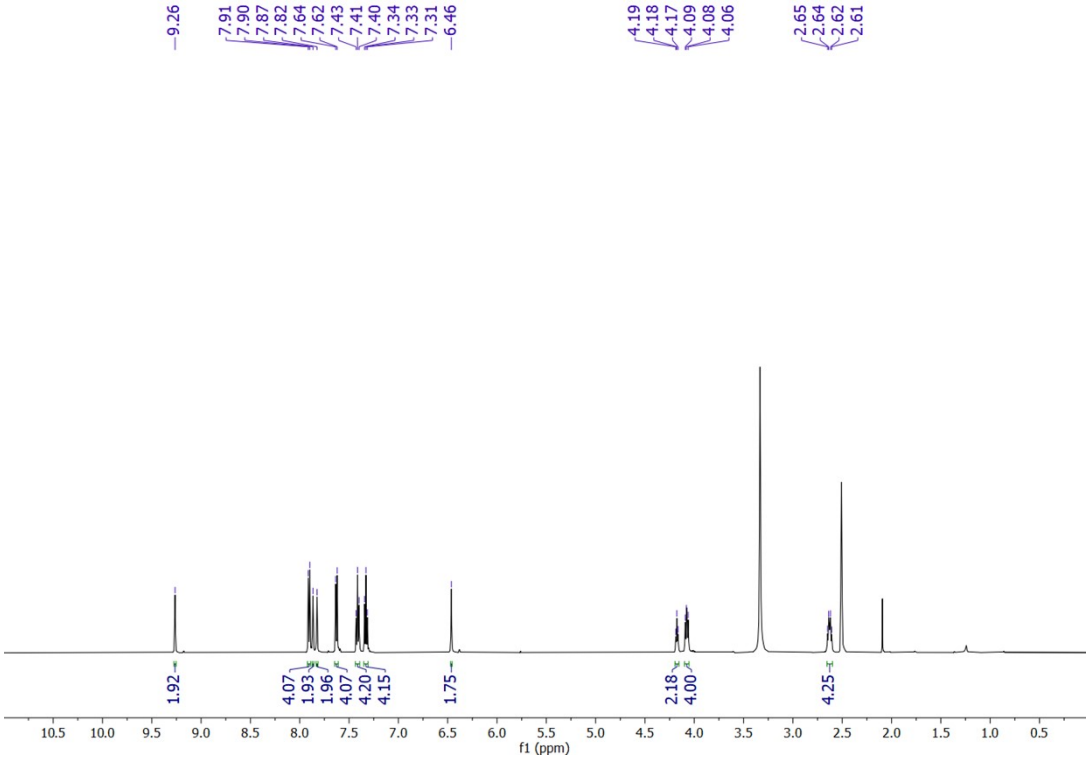


Fig-1. ^{1}H NMR spectrum of **1** in DMSO-d_6.

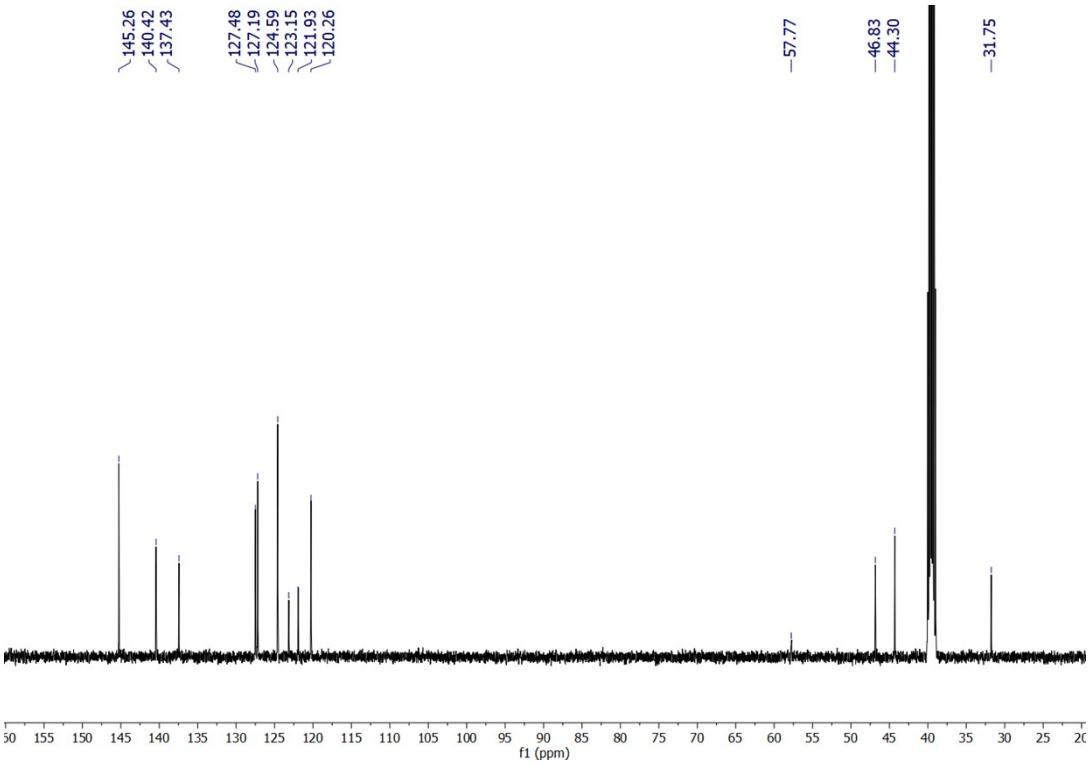


Fig-2. ^{13}C{^{1}H} NMR spectrum of **1** in DMSO-d_6.

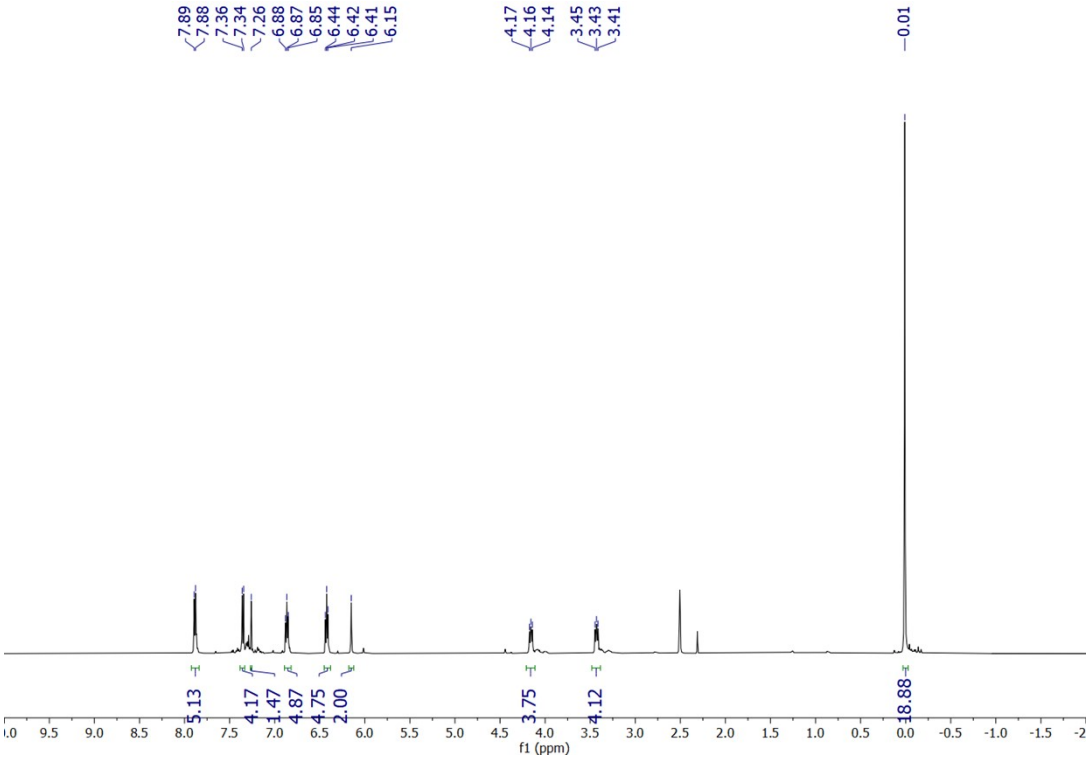


Fig-3. ^{1}H NMR spectrum of **2** in DMSO-d_6.

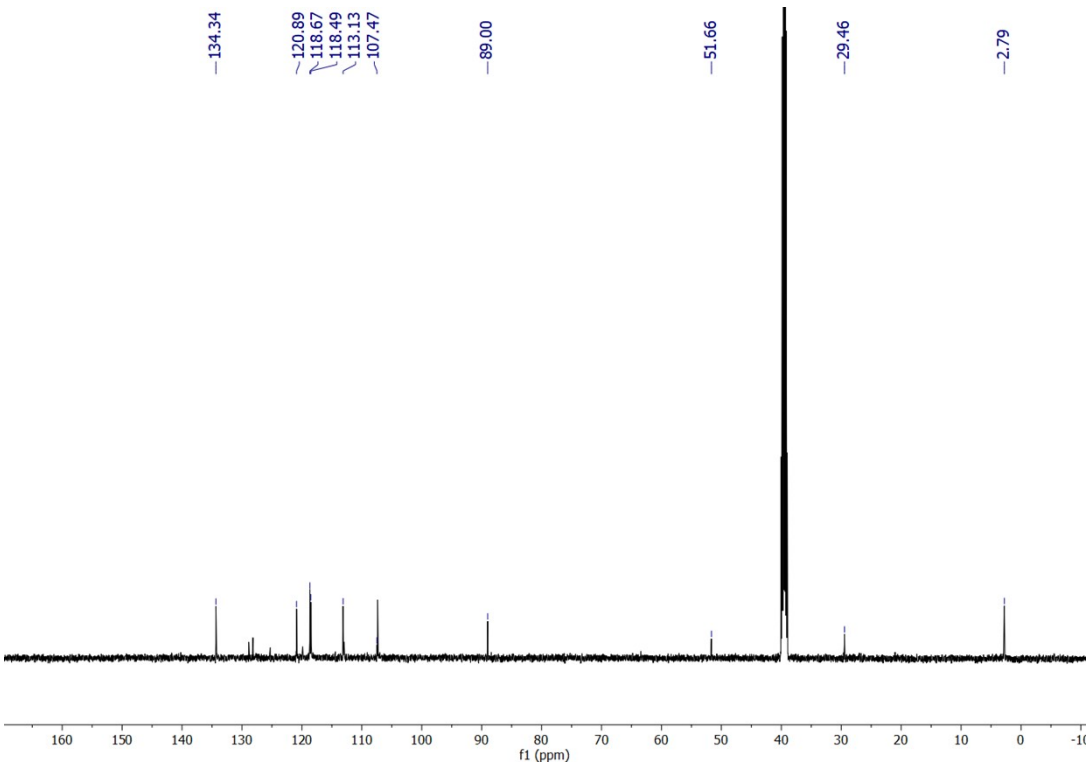


Fig-4. ^{13}C NMR spectrum of **2** in DMSO-d_6.

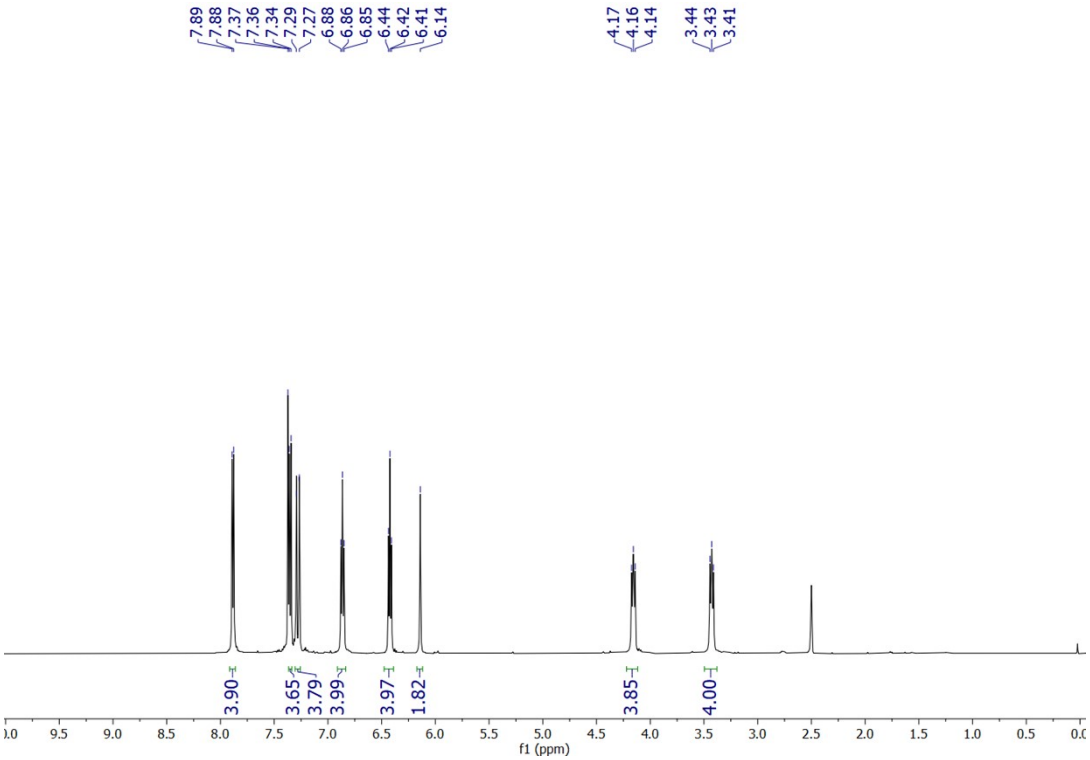


Fig-5. ^{1}H NMR spectrum of **3** in DMSO-d_6.

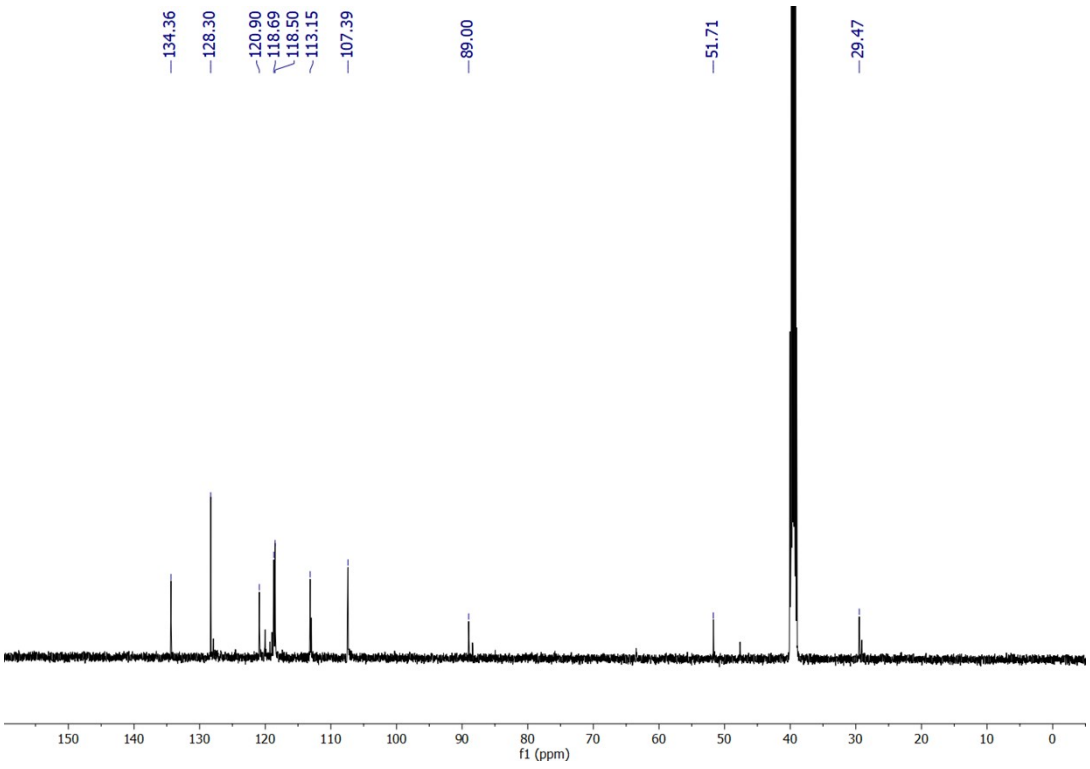


Fig-6. ^{13}C{^{1}H} NMR spectrum of **3** in DMSO-d_6.

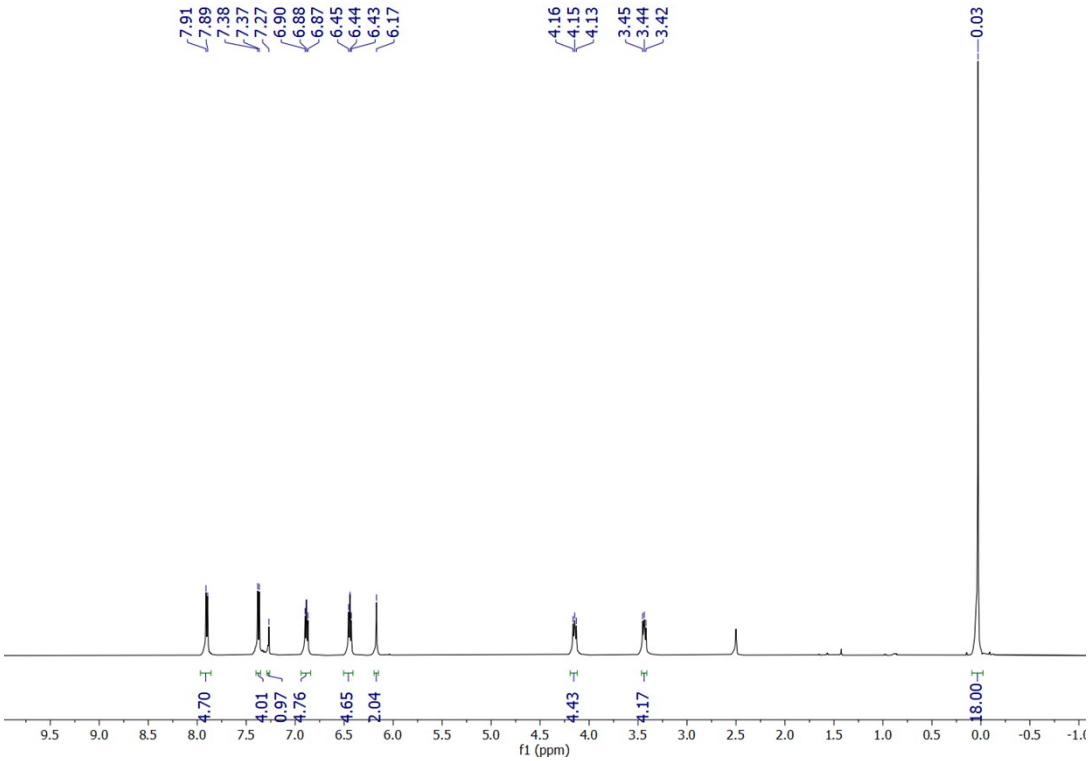


Fig-7. ^{1}H NMR spectrum of **4** in DMSO-d_6.

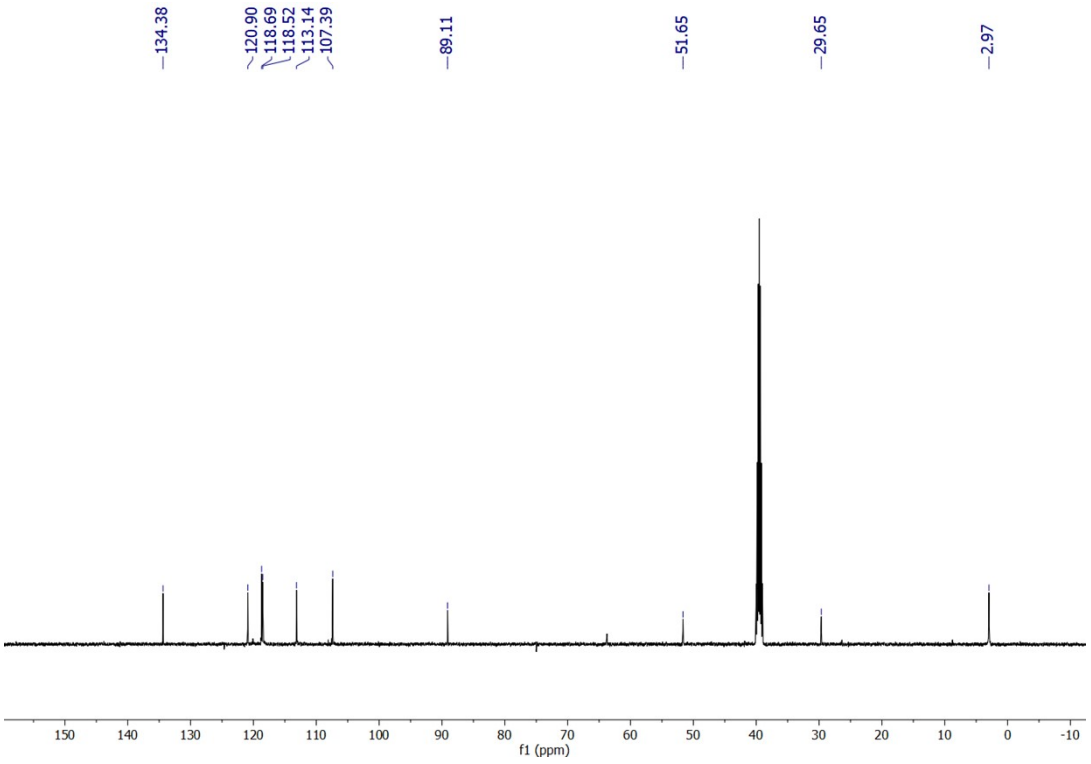


Fig-8. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in DMSO-d_6.

3. Crystallographic Data.

X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex four-circle diffractometer with HyPix3000 detector and Cu-K_α radiation. Measurements were carried out at 100 K (**2**), (**3**) and (**4**) respectively. The structures were solved by intrinsic phasing using SHELXT.[3] all refinements were carried out against F^2 with ShelXL[4] as implemented in the program system Olex2.[5] The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions and treated as riding throughout the refinement. Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.[6] CCDC- 2168390 (**2**), CCDC-2168389 (**3**) and CCDC- 2177822 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystallographic data of **2, 3** and **4**.

	2	**3**	**4**
formula	$C_{43}H_{49}CaN_5Si_2$	$C_{49}H_{43}CaN_4$	$C_{57}H_{65}Li_2N_5Si_2$
Fw /g·mol^{-1}	732.13	727.95	890.20
cryst. color, habit	Dark orange	Dark red	Dark Orange
crystal size / mm	0.15 × 0.14 × 0.09	0.5 × 0.096 × 0.083	0.6 × 0.34 × 0.18
crystal system	triclinic	monoclinic	orthorhombic
space group	*P-1*	*P2$_1$/n*	*Pna2$_1$*
a / Å	9.5409(2)	18.9502(2)	12.11370(10)
b / Å	15.2405(2)	9.61450(10)	30.6579(3)
c / Å	15.8200(2)	21.1384(2)	15.47960(10)
α / °	111.179(2)	90	90
β / °	105.9930(10)	104.1130(10)	90
γ / °	97.2430(10)	90	90
V / Å^3	1995.57(6)	3735.10(7)	5748.82(8)
Z	2	4	4
d_{calc}/Mg·m^{-3}	1.218	1.295	1.029
μ(CuKα)/mm^{-1}	2.205	1.759	0.834
F(000)	780.0	1540.0	1904.0
2θ range / °	6.388 to 136.486	5.622 to 136.46	6.396 to 136.396
index ranges	*-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -19 ≤ l ≤ 18*	*-22 ≤ h ≤ 22, -11 ≤ k ≤ 10, -25 ≤ l ≤ 19*	*-14 ≤ h ≤ 14, -36 ≤ k ≤ 32, -18 ≤ l ≤ 18*
refln.	27262	27961	57785
independ. reflns (R_{int})	7241 [R_{int} = 0.0371, R_{sigma} = 0.0314]	6796 [R_{int} = 0.0521, R_{sigma} = 0.0388]	10110 [R_{int} = 0.0448, R_{sigma} = 0.0265]
observed reflns	6345	6281	9412
data/ restr./ param.	7241/0/477	6796/0/488	10110/49/603
*R*1, *wR*2 [*I*> 2σ(*I*)]	R_1 = 0.0352, wR_2 = 0.0908	R_1 = 0.0355, wR_2 = 0.0951	R_1 = 0.0526, wR_2 = 0.1424
*R*1, *wR*2 (all data)	R_1 = 0.0413, wR_2 = 0.0944	R_1 = 0.0380, wR_2 = 0.0974	R_1 = 0.0555, wR_2 = 0.1450
GooF on F^2	1.063	1.060	1.055
largest diff. peak, hole/ e·Å^3	0.30/-0.28	0.26/-0.82	0.49/-0.24
CCDC number	2168390	2168389	2177822

4. DFT Analysis:

(a) Theoretical method:

The geometries of the studied system were optimized at the CAM-B3LYP level[7] with Pople basis sets 6-31G(d,p) for all the atoms using Gaussian 16 program[8] suite for electronic structure and harmonic frequencies calculation. Energy decomposition analysis were performed by the Amsterdam Density Functional (ADF) program package[9-10] at the B3LYP-D3/TZ2P level by using Ca^{+2} (for **2** and **3**) or Li_2^{2+}(for **4**) as a **fragment1** and $[L]^{-2}$ (for **3**) or $[(LH)(HMDS)]^{-2}$ (for **2** and **4**) as a **fragment2** where relativistic effects were incorporated by the zeroth-order regular approximation (ZORA).

In the EDA method, the interaction energy (ΔE_{int}) between two fragments is splitted into four energy terms, viz., the electrostatic interaction energy (ΔE_{elstat}), the Pauli repulsion(ΔE_{Pauli}), the orbital interaction energy(ΔE_{orb}) and the dispersion energy (ΔE_{dis}). Thus the interaction energy can be defined as follows:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{dis}$$

The first term ΔE_{elstat} is the electrostatic interactions between two fragments in their position within the molecules and it is usually attractive. The next ΔE_{Pauli} corresponds to destabilizing interaction between the occupied orbitals of the fragments. The ΔE_{orb} originates from the polarization and mixing of orbitals between the two fragments. Finally, the term ΔE_{dis} is the dispersion energy between the two fragments. The results are summarized in Table S2.

Table S2. EDA-NOCV analyses for the metal complexes **2** to **4** at the B3LYP-D3/TZ2P-ZORA level taking Ca^{2+} or Li_2^{2+} as **fragment 1** and $[L]^{2-}$ or $[(LH)(HMDS)]^{2-}$ as **fragment 2**, respectively.

[a]Energy Term	Ca^{2+} + $[(LH)(HMDS)]^{2-}$ (**2**)	Ca^{2+} + $[L]^{2-}$ (**3**)	Li_2^{2+} + $[(LH)(HMDS)]^{2-}$ (**4**)
ΔE_{Pauli}	69.4	57.2	51.2
ΔE_{elstat}[b]	−430.8 (66.9%)	−400.2 (66.5%)	−425.6 (68.5%)
ΔE_{orb}[b]	−202.7 (31.5%)	−201.1 (33.4%)	−195.3 (31.4%)
ΔE_{dis}[b]	−9.7 (0.01%)	−8.2 (0.01%)	−7.2 (0.01%)
ΔE_{int}[c]	−573.8	−552.3	−576.9
ΔE_{prep} (metal)[d]	416.0 (414.8)[e]	416.0 (414.8)[e]	392.5
ΔE_{prep} (ligand)[f]	−29.8	−25.9	−28.2
ΔE_{Total} (= $-D_e$)[g]	−187.6	−162.2	−212.6

[a] Energy values are in kcal/mol; [b] Values in the parentheses indicate the percentage contribution to the total attractive interaction $\Delta E_{orb} + \Delta E_{elstat} + \Delta E_{dis}$; [c] $\Delta E_{int} = \Delta E_{pauli} + \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{dis}$; [d] $Ca \rightarrow Ca^{2+}$ and $Li_2 \rightarrow Li_2^{2+}$; [e] ΔE_{prep} (Ca^{2+}; experimental)[11]; [f] Preparation of $[L]^{2-}$ (for **3**) and Preparation of $[LH)(HMDS)]^{2-}$ (for **2** and **4**); [g] ΔE_{Total} (ΔE_{int} + ΔE_{prep} (fluorenyls metal) + ΔE_{prep} (ligand))= $-D_e$).

(b) Cartesian Coordinates:

Energies in Hartrees and Cartesian coordinates of calculated molecules for the favourable (indirect) pathway at the CAM-B3LYP/6-31G(d,p) level of theory:

2

Energy: -3197.546175 a.u.

Ca	1.37915700	0.94692100	9.29674300
Si	2.54703500	-0.31461200	12.30945500
Si	1.67803000	-2.47023200	10.39845600
N	4.22690600	3.56152200	9.63043400
N	3.79105400	0.45305400	6.78372300
N	4.76215700	1.84209500	8.50641000
N	1.94683600	0.29617600	5.73935700
N	1.92610800	-0.83132700	10.80995800
C	-0.16259200	2.94360500	7.82776800
C	-0.51229800	1.70942700	7.21238300
C	3.26378800	7.98614200	11.99827200
C	2.45372500	0.33528500	6.98847700
C	-0.64602100	2.96080400	9.18691400
C	2.04025000	7.33505600	12.48699800
C	3.75588600	2.34199700	9.28130000
C	4.32956900	7.08502200	12.13420700
C	0.52679600	4.08643900	7.34429300
H	0.89617900	4.11072500	6.32251200
C	-1.26525800	0.97210000	8.17079100
C	2.36505100	6.03896500	12.91430000
C	2.93871400	0.39736100	4.77588800
H	2.72545500	0.37182300	3.71925800

C	3.47303500	9.25696900	11.47495000
H	2.65109400	9.95821400	11.36984800
C	3.84928100	5.77741600	12.73586700
H	4.31138700	5.64591500	13.72308600
C	5.47767100	3.81807300	9.08969600
H	6.00216400	4.74443600	9.26162200
C	4.11244600	0.50189700	5.43619700
H	5.12459700	0.58701400	5.07450600
C	4.71652300	0.52787700	7.89417300
H	4.40485000	-0.19587500	8.64655500
H	5.71639400	0.27015000	7.54656500
C	0.69590800	5.17972400	8.16198900
H	1.20583100	6.05888900	7.77780200
C	3.56240500	4.51037800	10.52112900
H	2.50882400	4.23978500	10.57057200
H	3.61966800	5.49792800	10.05588100
C	5.60909900	7.44914000	11.74501100
H	6.44185400	6.75991500	11.85379400
C	5.81696700	2.72948400	8.37151600
H	6.69762900	2.50786300	7.79013200
C	0.21240100	5.19187500	9.49248000
H	0.35774600	6.07008900	10.11280200
C	-1.33425500	1.71585800	9.40546900
C	-0.44289000	4.09100300	10.00122000
H	-0.81866800	4.10625800	11.02072600
C	-0.33466900	1.35929000	5.76284300
H	0.08610400	2.21354400	5.22178300
H	-1.31213400	1.16477600	5.29908500
C	0.73471100	7.80521400	12.57482900
H	0.48067600	8.80903600	12.24881300
C	4.75914300	9.61763500	11.08453500
H	4.93903100	10.60565500	10.67343000
C	4.21152000	4.53424900	11.90576700
H	3.93515300	3.62804400	12.45241200
H	5.30057700	4.50625800	11.79383500
C	0.52302800	0.12530800	5.45018700
H	0.17380600	-0.73801600	6.01940300
H	0.44354800	-0.12487100	4.38974900
C	1.38587100	5.20612600	13.43225400
H	1.62638500	4.20056200	13.76312200
C	5.81907900	8.72260000	11.21753300
H	6.81635200	9.02085600	10.91086500
C	-1.91738400	-0.28707000	8.10630800
H	-1.91189800	-0.86191500	7.18443100
C	-0.24600300	6.96433500	13.09263500
H	-1.27018600	7.31468400	13.16802200
C	0.07612200	5.67664500	13.51826100
H	-0.69955800	5.03498600	13.92359100
C	4.43944000	-0.15254300	12.32436400
H	4.91404400	-1.12046800	12.13186300
H	4.81607100	0.21663700	13.28480600
H	4.77553400	0.53988700	11.54464700

C	1.87405500	1.41474500	12.73308900
H	2.30333900	1.77629400	13.67443000
H	0.78521000	1.39473700	12.85274200
C	-2.01415100	1.18614400	10.51857500
H	-2.06871300	1.75450400	11.44371100
C	3.21622700	-3.55801700	10.65359400
H	4.05768700	-3.19719200	10.05169300
H	3.02654500	-4.59830700	10.36712600
H	3.54285900	-3.56020300	11.69881800
C	2.10268700	-1.38403700	13.81190300
H	1.01876200	-1.44761400	13.94861900
H	2.52886400	-0.95858200	14.72723200
H	2.48243600	-2.40632600	13.71908600
C	-2.63003000	-0.04334500	10.42221200
H	-3.16291900	-0.45417700	11.27327000
C	1.21327300	-2.66693100	8.56950200
H	0.27055000	-2.15662800	8.34193000
H	1.07634400	-3.72666000	8.32760600
H	1.98175800	-2.26562600	7.90199600
C	-2.58216600	-0.77104200	9.21043400
H	-3.08521700	-1.73171500	9.15164700
C	0.26374800	-3.30803800	11.34596700
H	0.45249700	-3.34207300	12.42259500
H	0.11103300	-4.33746400	11.00261600
H	-0.67468300	-2.76441700	11.19286300
H	2.11314900	2.16360500	11.96888400

TS1

Energy: -3197.504386 a.u.

Ca	1.20252800	1.13580500	9.38832400
Si	2.86736400	-0.34440600	12.15286200
Si	1.88267400	-2.47727800	10.16681100
N	4.27867000	3.45531500	9.75614700
N	3.49921700	0.12353500	7.25832800
N	4.50130500	1.48639900	8.94991000
N	1.87972400	0.31867900	5.87141900
N	2.38103600	-0.83035800	10.53662500
C	-0.29869900	3.10277700	7.91555200
C	-0.58171600	1.91492000	7.18776100
C	3.16380400	8.14124000	11.85237900
C	2.17002600	0.35585600	7.19024400
C	-0.85087600	3.00494200	9.24628100
C	2.02704600	7.43374100	12.45842200
C	3.59041800	2.30436000	9.53914800
C	4.29473900	7.31573300	11.93326600
C	0.40788300	4.28499600	7.56715000
H	0.82804600	4.39813700	6.57177100
C	-1.34852600	1.08212600	8.04698800
C	2.46793900	6.17593000	12.89530900
C	3.00920800	0.03928500	5.11852400
H	2.98191200	-0.06048900	4.04466500

C	3.24650800	9.40134200	11.27123800
H	2.37402100	10.04419500	11.20866100
C	3.95115000	6.00935900	12.62419400
H	4.47781400	5.97215700	13.58752300
C	5.58998400	3.35562200	9.32299600
H	6.29601600	4.16585700	9.41609800
C	4.03637600	-0.06889200	5.99587200
H	5.08374200	-0.26748800	5.83183200
C	4.17332200	0.11020900	8.55995700
H	3.19209800	-0.50734100	9.73223500
H	5.11995000	-0.42180900	8.43642000
C	0.54127700	5.29831500	8.48611700
H	1.07300700	6.20391800	8.20791800
C	3.75610700	4.62270700	10.45631800
H	2.67076700	4.52463000	10.49280900
H	3.98754600	5.51485700	9.86775000
C	5.51281600	7.74510500	11.43042400
H	6.39479900	7.11404700	11.49277000
C	5.72454500	2.11446800	8.80357700
H	6.57235400	1.62777500	8.34807800
C	-0.00107800	5.19424500	9.79089100
H	0.11956300	6.01251800	10.49216000
C	-1.50794200	1.72853300	9.33214400
C	-0.68493000	4.05891800	10.16704900
H	-1.10884500	3.98536400	11.16555500
C	-0.24292600	1.68870000	5.73812900
H	0.33301000	2.54322300	5.36816200
H	-1.16142300	1.66843500	5.13366000
C	0.70566400	7.82520400	12.64252400
H	0.36201000	8.80036900	12.31177300
C	4.47108400	9.82710100	10.76571700
H	4.55202700	10.80707200	10.30677700
C	4.35495300	4.74028300	11.85788500
H	4.07071800	3.85886600	12.44202700
H	5.44737600	4.71703500	11.78232900
C	0.51790100	0.41091800	5.35129200
H	-0.03142100	-0.47495500	5.67929500
H	0.58914300	0.36004300	4.26208700
C	1.58825200	5.30021300	13.51138300
H	1.92088400	4.32465200	13.85382100
C	5.59508600	9.00684700	10.84318400
H	6.54266600	9.35434200	10.44463100
C	-1.92928800	-0.20340500	7.87162000
H	-1.86139400	-0.71051900	6.91403700
C	-0.17452400	6.94235600	13.26190500
H	-1.20933000	7.23182500	13.41290800
C	0.26144500	5.68980700	13.69090400
H	-0.43688100	5.01447800	14.17460000
C	4.73036500	-0.08262000	12.23764900
H	5.26329300	-1.01675600	12.03435800
H	5.03067800	0.26139500	13.23275900
H	5.06651000	0.65724800	11.50685000

C	2.00795000	1.27041200	12.64872300
H	2.27975200	1.52655000	13.67866800
H	0.91593700	1.16811400	12.62844800
C	-2.20709100	1.08685800	10.37333400
H	-2.33379300	1.58651400	11.33090300
C	3.26096200	-3.71725900	10.53295600
H	4.15332600	-3.47829200	9.94525500
H	2.95221600	-4.73317800	10.26526900
H	3.55490300	-3.72892000	11.58592000
C	2.39808800	-1.55598300	13.52246300
H	1.31639500	-1.60849600	13.67115400
H	2.83736900	-1.19864500	14.46022700
H	2.76547400	-2.57134400	13.35708600
C	-2.74874300	-0.16400600	10.16628900
H	-3.29796800	-0.65935500	10.96019600
C	1.47603500	-2.66122300	8.33763600
H	0.62246900	-2.04348900	8.04452400
H	1.21397500	-3.70653100	8.13949700
H	2.31804400	-2.39549400	7.69474000
C	-2.60849900	-0.79973900	8.90919200
H	-3.05533700	-1.77845500	8.76067900
C	0.32313100	-2.97625900	11.10183500
H	0.47180100	-3.06312700	12.17970500
H	-0.02295900	-3.94991400	10.73849600
H	-0.48481600	-2.25791600	10.92730700
H	2.29680900	2.11885100	12.02176800

Intermediate (Int)

Energy: -3197.505738 a.u.

Ca	-0.61464500	-1.37907200	-0.67794200
Si	0.88483900	-2.70437000	2.36710900
Si	-0.15627000	-4.97836400	0.47150300
N	2.34901900	1.10610500	-0.26629800
N	1.56159100	-2.16255100	-2.85795200
N	2.55153400	-0.84675800	-1.12177000
N	-0.04633200	-1.95845100	-4.26171500
N	0.39343700	-3.31923900	0.77906200
C	-2.20290200	0.65068500	-2.05735100
C	-2.49386100	-0.49704200	-2.84338600
C	1.27102500	5.73241500	1.92967800
C	0.21571000	-2.08280800	-2.94334900
C	-2.70756300	0.46760900	-0.71650300
C	0.14636500	5.00850100	2.53889500
C	1.66647700	-0.05036600	-0.46987100
C	2.40926600	4.91516400	1.98890600
C	-1.53769700	1.86819300	-2.36304800
H	-1.15337900	2.04538600	-3.36362200
C	-3.21696700	-1.39002100	-2.00898300
C	0.60256100	3.75021300	2.95818600
C	1.12267600	-1.97913900	-5.00645000
H	1.12636400	-1.92324100	-6.08414900

C	1.33776400	7.00052500	1.36415600
H	0.45948500	7.63688600	1.31845900
C	2.08280000	3.59589800	2.66364700
H	2.62538900	3.54276100	3.61722200
C	3.63758200	1.03017300	-0.76772100
H	4.33907300	1.84638500	-0.69134400
C	2.13931800	-2.09565400	-4.11736600
H	3.20524000	-2.14821600	-4.27439800
C	2.19213700	-2.21592400	-1.52942000
H	1.12776600	-3.07800700	0.05223500
H	3.13407400	-2.76208000	-1.63882900
C	-1.40253600	2.83582200	-1.39644500
H	-0.90442000	3.76946100	-1.64249800
C	1.84322800	2.25352700	0.47625700
H	0.75994100	2.14902800	0.53990400
H	2.05535800	3.15993000	-0.09766300
C	3.61879900	5.36098500	1.47983300
H	4.50624300	4.73617000	1.52505400
C	3.75787400	-0.19943200	-1.31881200
H	4.58759500	-0.66680500	-1.82529800
C	-1.90077100	2.64943300	-0.08322000
H	-1.78198000	3.43484600	0.65516000
C	-3.34115000	-0.82323600	-0.68308100
C	-2.54104300	1.47666400	0.25291400
H	-2.93265900	1.33948600	1.25803900
C	-2.19722700	-0.63853900	-4.31299100
H	-1.66081200	0.25255000	-4.65543900
H	-3.13317700	-0.65928000	-4.89005300
C	-1.17640700	5.38658800	2.74037300
H	-1.53201500	6.36157100	2.42198900
C	2.55391300	7.44295800	0.85264500
H	2.62249000	8.42950700	0.40593300
C	2.47689700	2.34365500	1.86408000
H	2.20997800	1.44896500	2.43632800
H	3.56740400	2.32809900	1.76202100
C	-1.40542100	-1.87055400	-4.78511300
H	-1.93167100	-2.78811600	-4.51305700
H	-1.33276200	-1.85040200	-5.87531500
C	-0.26289900	2.86193000	3.57633300
H	0.08153700	1.88599900	3.90502700
C	3.68522000	6.63103800	0.90870200
H	4.62610600	6.99155800	0.50586400
C	-3.78948800	-2.66961300	-2.24237200
H	-3.74530800	-3.11797100	-3.23032300
C	-2.04213500	4.49086000	3.36151300
H	-3.07778700	4.76980800	3.52589600
C	-1.59062700	3.23855200	3.77485700
H	-2.27778300	2.55274600	4.25977900
C	2.73831200	-2.39981700	2.36420800
H	3.28939400	-3.33557900	2.23024200
H	3.06251700	-1.95352800	3.30977100
H	3.02397400	-1.72410300	1.55357000

C	-0.01636900	-1.08759700	2.73329100
H	0.23357000	-0.74156300	3.74193500
H	-1.10385700	-1.21951900	2.69717600
C	-4.00185000	-1.53302200	0.33875700
H	-4.10438000	-1.09192400	1.32759600
C	1.20366000	-6.22454600	0.85989600
H	2.09001600	-6.02848200	0.24824200
H	0.86878300	-7.24315900	0.63832900
H	1.51316200	-6.19980300	1.90815500
C	0.45466800	-3.86442900	3.78528600
H	-0.62376300	-3.94058700	3.94430800
H	0.88941300	-3.45499800	4.70340000
H	0.85229700	-4.87402900	3.65867100
C	-4.53933700	-2.77512100	0.07390800
H	-5.06114600	-3.32160000	0.85275600
C	-0.58719700	-5.15604600	-1.34731300
H	-1.48823600	-4.59277600	-1.60833300
H	-0.77818700	-6.21050800	-1.57377100
H	0.22182300	-4.80765400	-1.99361100
C	-4.43164000	-3.33390200	-1.22247800
H	-4.87410600	-4.30686100	-1.41568400
C	-1.69839400	-5.36747100	1.47278200
H	-1.50911100	-5.45891100	2.54382600
H	-2.11537400	-6.32069000	1.13104300
H	-2.46726700	-4.60307100	1.32270700
H	0.26260800	-0.29002800	2.03800500

Rearranged Intermediate

Energy: -3197.512772 a.u.

Ca	-0.34784800	-0.80161900	-1.14405000
Si	-0.71125900	-1.16210600	2.45069400
Si	-1.91219100	-3.66624500	0.94327000
N	2.58605500	1.53649900	-0.61812900
N	2.65389300	-2.48937600	-1.96000200
N	3.20633800	-0.49615200	-0.70726300
N	1.27092000	-3.05994500	-3.47042800
N	-0.74503600	-2.31073200	1.05262200
C	-0.67464100	0.36400700	-3.75089000
C	-1.10687100	-0.98708300	-3.89995200
C	0.43860200	2.85535700	3.88482500
C	1.32269600	-2.51625100	-2.23582200
C	-1.59728100	1.07527900	-2.90283300
C	1.77176700	2.39490600	4.15732800
C	2.08554200	0.28323100	-0.64073500
C	0.43653800	3.36152900	2.53516600
C	0.42485600	1.07566300	-4.29733000
H	1.13690700	0.57088700	-4.94448100
C	-2.34812500	-1.09545200	-3.20864500
C	2.54949300	2.62033300	2.96362100
C	2.53332300	-3.35152200	-3.96137900
H	2.68914300	-3.80174200	-4.92861600

C	-0.72578400	2.89588000	4.65710800
H	-0.71733600	2.51477000	5.67672100
C	1.72699300	3.20787500	1.96943600
C	3.96822200	1.54622600	-0.68279200
H	4.54263400	2.45764400	-0.67731900
C	3.41441900	-2.98698800	-3.00539300
H	4.48999800	-3.05370200	-2.96976100
C	3.17704200	-1.94281800	-0.72398000
H	0.18030700	-2.74319500	1.01405400
H	4.19041000	-2.31307400	-0.57362500
C	0.55809900	2.42128900	-4.04521100
H	1.38439900	2.96782300	-4.49051500
C	1.79533500	2.77021000	-0.57117300
H	0.74853100	2.47132800	-0.53569200
H	1.95369300	3.29226300	-1.51922100
C	-0.76124500	3.91953800	2.02900400
H	-0.79277300	4.33180700	1.02205700
C	4.36587100	0.25943700	-0.74004300
H	5.34975600	-0.17920600	-0.78550700
C	-0.36339700	3.11644100	-3.22643900
H	-0.23044200	4.17914300	-3.05322100
C	-2.64571300	0.15299400	-2.55081700
C	-1.42075600	2.44988500	-2.64949500
H	-2.13313200	2.98547600	-2.02752300
C	-0.54180000	-2.00505000	-4.84832500
H	0.23759700	-1.54888400	-5.46787300
H	-1.32068800	-2.34027600	-5.54716400
C	2.36074600	1.82946400	5.29290100
H	1.76668600	1.66775900	6.19051900
C	-1.89008400	3.43573800	4.13077800
H	-2.79424000	3.47714000	4.73079200
C	2.13609000	3.68681700	0.61418200
H	3.21063800	3.90931100	0.59024200
H	1.64248200	4.64168500	0.38439500
C	0.03247200	-3.28049400	-4.21599600
H	-0.68892100	-3.72872000	-3.53137900
H	0.25461200	-4.01814100	-4.99057800
C	3.91738400	2.25818700	2.98222100
H	4.53841400	2.41603700	2.10338400
C	-1.89419600	3.95333700	2.81867300
H	-2.80863500	4.38986100	2.42405600
C	-3.29847300	-2.14624100	-3.12237300
H	-3.12743100	-3.08415100	-3.64380700
C	3.70122200	1.48019000	5.27899100
H	4.16322300	1.04358000	6.15933200
C	4.47093500	1.70225900	4.11843700
H	5.52421700	1.43141700	4.12155000
C	1.10379600	-0.86965100	2.78286300
H	1.59358800	-1.79573400	3.10373900
H	1.24268700	-0.12392500	3.57046000
H	1.62404400	-0.48747300	1.90063900
C	-1.63671800	0.36701000	1.89308100

H	-1.87344900	1.01155400	2.74483500
H	-2.57753700	0.10493800	1.39603000
C	-3.83643100	0.30449100	-1.81472700
H	-4.06035400	1.25113800	-1.33001200
C	-1.56035100	-4.95298800	2.26888900
H	-0.51866700	-5.28814100	2.23315600
H	-2.19090300	-5.83361600	2.10894900
H	-1.75837800	-4.58241700	3.27659300
C	-1.50321300	-1.83488100	4.01568200
H	-2.55461700	-2.10834800	3.90162700
H	-1.45348800	-1.04871300	4.77633600
H	-0.96318500	-2.70146700	4.40597800
C	-4.73529300	-0.73892300	-1.74908200
H	-5.66411700	-0.62348000	-1.20048800
C	-1.67954800	-4.49600300	-0.72465700
H	-2.04247500	-3.86062700	-1.53629800
H	-2.24417500	-5.43307300	-0.76095200
H	-0.62798700	-4.73291300	-0.91418300
C	-4.46397100	-1.95718400	-2.41512900
H	-5.19585200	-2.75816500	-2.36841500
C	-3.65103000	-2.99556200	1.11110800
H	-3.83485100	-2.54733700	2.09039400
H	-4.36964000	-3.81206700	0.98674100
H	-3.87147800	-2.24739200	0.34546400
H	-1.04557800	1.00357200	1.22567500
H	2.55682300	-2.29670800	0.09817300

TS 2
Energy: -3197.511720 a.u.

Ca	-0.47329700	-0.21616500	-0.04309700
Si	1.49090400	-2.93076500	1.79574500
Si	3.17981900	-1.71664100	-0.49703400
N	-1.33005000	3.12198400	-0.85654000
N	-0.25020000	0.13772100	-3.65737800
N	-0.48198700	2.32638300	-2.63472700
N	-0.81522500	-1.87390900	-3.27045800
N	1.82458100	-1.56586800	0.67321800
C	-3.25914000	-0.69830200	-1.05434700
C	-2.66038500	-1.97526300	-0.80763100
C	2.13329900	1.14909100	2.87413100
C	-0.26283900	-0.79977500	-2.66598000
C	-3.62281400	-0.08606900	0.19146400
C	2.75066900	1.64748100	1.66472200
C	-0.81339600	1.98657900	-1.36325600
C	0.75019100	1.50634800	2.82072200
C	-3.59384900	-0.03278000	-2.25726500
H	-3.34076400	-0.47422200	-3.21689100
C	-2.76893300	-2.19827400	0.60456800
C	1.72750200	2.29126400	0.90105900
C	-1.15478300	-1.62050700	-4.58876400
H	-1.60567100	-2.36375300	-5.22661500

C	2.67756500	0.55253600	4.01688400
H	3.73433600	0.29787300	4.05130600
C	0.44581000	2.15660900	1.56083400
C	-1.31389600	4.15501200	-1.77523400
H	-1.69781800	5.13753700	-1.55253200
C	-0.79645200	-0.34344000	-4.83682300
H	-0.86475700	0.24907800	-5.73512600
C	0.30764100	1.46261700	-3.49381800
H	2.06025000	-0.76185000	1.27091700
H	0.37938800	1.92982400	-4.47644700
C	-4.28229800	1.15932200	-2.21147600
H	-4.56011100	1.65197200	-3.13911100
C	-1.73259200	3.23504000	0.54375900
H	-2.36985600	2.38089800	0.76400400
H	-2.35228600	4.13213900	0.63149000
C	-0.04377700	1.27543900	3.96065500
H	-1.09485000	1.55260900	3.96342700
C	-0.77248400	3.65468200	-2.90782000
H	-0.58373900	4.11341300	-3.86527900
C	-4.65694700	1.74466000	-0.98394500
H	-5.22039300	2.67226000	-0.97982200
C	-3.28516600	-1.01600200	1.23947500
C	-4.33340300	1.12491100	0.20532800
H	-4.65445500	1.55536100	1.15090700
C	-2.49048900	-3.04830900	-1.84637800
H	-3.26835300	-2.94882700	-2.61562300
H	-2.64710100	-4.03405200	-1.39183400
C	4.08750900	1.69980400	1.26001200
H	4.85840500	1.22189800	1.85869300
C	1.87449500	0.33983000	5.12464800
H	2.29019800	-0.10365500	6.02357500
C	-0.55154000	3.30437800	1.51276800
H	-0.01110100	4.24041900	1.31179700
H	-0.99596200	3.42874000	2.50758800
C	-1.13319300	-3.10839000	-2.56101800
H	-0.32832300	-3.28237700	-1.84589300
H	-1.11307000	-3.92418600	-3.28995100
C	2.10970800	3.02022800	-0.24384900
H	1.37122700	3.57793200	-0.81244200
C	0.51951000	0.71312500	5.09094900
H	-0.09743500	0.55187600	5.97013000
C	-2.59347500	-3.35880700	1.39662900
H	-2.27071900	-4.29000200	0.94156500
C	4.43415400	2.40976900	0.12182700
H	5.47267100	2.47230800	-0.18725900
C	3.44313800	3.07808300	-0.61433200
H	3.73078300	3.66157600	-1.48488100
C	3.05377300	-3.56290800	2.63383400
H	2.79289700	-4.38799800	3.30501600
H	3.51982800	-2.78313300	3.24291300
H	3.80236000	-3.93653900	1.93026400
C	0.34301400	-2.28885600	3.11399600

H	0.05479600	-3.10814400	3.78005500
H	-0.59199300	-1.87631300	2.72834900
C	-3.52438100	-0.99533200	2.62434700
H	-3.91285000	-0.09641400	3.09614300
C	4.84985600	-1.59639000	0.38032300
H	4.75118700	-1.54707900	1.46647100
H	5.38111800	-0.69694100	0.06100900
H	5.47860900	-2.46139600	0.14702100
C	0.71289000	-4.35850100	0.85361000
H	-0.11160900	-4.02623200	0.22083900
H	0.29404300	-5.06588200	1.57623600
H	1.42719100	-4.90262100	0.23392500
C	-3.32186400	-2.13717500	3.36997300
H	-3.52099500	-2.13512700	4.43626100
C	3.08827200	-0.38248300	-1.80528400
H	2.27907100	-0.59416800	-2.50633700
H	4.03075700	-0.36130100	-2.36255400
H	2.94461500	0.61002400	-1.37086400
C	-2.88217400	-3.32151800	2.74232400
H	-2.76405200	-4.22242700	3.33753700
C	3.08341800	-3.37531800	-1.38052800
H	3.32793300	-4.22293400	-0.73622600
H	3.81793000	-3.36532200	-2.19300000
H	2.10366300	-3.55728800	-1.82990300
H	0.83160400	-1.52438000	3.72052600
H	1.31103700	1.36994800	-3.07638600

3

Energy: -3197.532505 a.u.

Ca	-1.00333100	0.06883500	0.91249700
Si	3.22882400	-4.09680000	0.90946800
Si	4.32309800	-2.81059800	-1.78560000
N	-0.93446400	3.50309700	-0.44541500
N	0.36080100	-0.13254800	-2.35347000
N	0.14889700	2.21684900	-1.75165100
N	-0.55791900	-2.01391000	-1.98194700
N	3.19379200	-3.02786300	-0.47075100
C	-3.45932700	-0.40443700	-0.50697700
C	-3.01753400	-1.70425600	-0.11983500
C	1.47241300	1.05863400	2.23177700
C	-0.03208000	-0.94946600	-1.33733900
C	-3.88186300	0.32776400	0.65944900
C	2.40955800	1.74594900	1.39422900
C	-0.53815600	2.21665700	-0.57641200
C	0.42834300	2.01643200	2.56886900
C	-3.54829900	0.22964400	-1.77209400
H	-3.24074500	-0.29908000	-2.67042700
C	-3.21922900	-1.80097800	1.28866200
C	1.91437900	3.08171500	1.22149000
C	-0.51285600	-1.86669700	-3.35762000
H	-0.87931400	-2.62098000	-4.03543700

C	1.40149500	-0.26040200	2.68775800
H	2.18549700	-0.96732900	2.42903800
C	0.69512700	3.24406300	1.94032000
C	-0.49441900	4.29085000	-1.49750300
H	-0.71506000	5.34421700	-1.56410800
C	0.07084600	-0.67211000	-3.59566500
H	0.32010400	-0.17680300	-4.52044100
C	1.03461400	1.13096500	-2.14071600
H	2.38548200	-2.41461600	-0.50973500
H	1.53592500	1.41582000	-3.06488800
C	-4.04137900	1.51134300	-1.86013900
H	-4.12090700	1.98720900	-2.83343800
C	-1.43357100	4.04369500	0.81283200
H	-2.10173900	3.29827100	1.24485800
H	-2.03144100	4.93261100	0.59423100
C	-0.65713200	1.56075200	3.36600400
H	-1.45577800	2.24245500	3.64689600
C	0.19163200	3.47919600	-2.32695300
H	0.69569900	3.67963400	-3.25878600
C	-4.45050800	2.22608000	-0.71062700
H	-4.83627900	3.23496300	-0.81564800
C	-3.74156600	-0.55505700	1.78815300
C	-4.37003400	1.64207500	0.53533200
H	-4.70231100	2.18463700	1.41713200
C	-2.70307700	-2.84888500	-1.03901500
H	-3.19436200	-2.69619100	-2.00750300
H	-3.12389300	-3.77747800	-0.63344300
C	3.59942700	1.33242600	0.77879800
H	3.97174700	0.32137200	0.92870500
C	0.31609400	-0.67938000	3.45442300
H	0.25691400	-1.70164400	3.81088100
C	-0.27334300	4.37538500	1.78534000
H	0.24408000	5.26830000	1.41803700
H	-0.73299700	4.66292600	2.73943600
C	-1.21517900	-3.12183200	-1.29777600
H	-0.68544900	-3.28222200	-0.35785600
H	-1.08562400	-4.01627900	-1.91299000
C	2.65115000	3.96557300	0.39984400
H	2.30585400	4.98337300	0.24063900
C	-0.69819700	0.24559200	3.80168200
H	-1.53720400	-0.09369000	4.39818800
C	-3.03023000	-2.87085600	2.20127200
H	-2.64258200	-3.82488900	1.85346500
C	4.29760000	2.22019100	-0.01817000
H	5.22494000	1.91551200	-0.49306300
C	3.81472100	3.53493900	-0.20147500
H	4.37867300	4.22195100	-0.82653900
C	4.35428300	-3.45386800	2.27495400
H	5.38360400	-3.34849200	1.91929200
H	4.36721200	-4.13659200	3.13091500
H	4.03145500	-2.47330700	2.63791300
C	1.47419200	-4.23650300	1.57459400

H	1.45473000	-4.81723400	2.50201500
H	0.81833800	-4.73729400	0.85613400
C	-4.08380900	-0.42254900	3.14576300
H	-4.50160900	0.51146100	3.51315500
C	6.08725500	-2.82351000	-1.13320500
H	6.24762700	-2.01205800	-0.41734300
H	6.80359000	-2.69676800	-1.95115600
H	6.33258800	-3.76377800	-0.62996900
C	3.84469800	-5.79757900	0.39248500
H	3.19464400	-6.23968200	-0.36806000
H	3.86702100	-6.47595900	1.25129000
H	4.85879200	-5.76050200	-0.01702300
C	-3.90798400	-1.48798700	4.00264100
H	-4.18169200	-1.39701700	5.04879900
C	3.95422200	-1.15537500	-2.59747600
H	2.94874500	-1.14730700	-3.03012800
H	4.66159800	-0.95905900	-3.40930700
H	4.02663600	-0.32978600	-1.88285200
C	-3.37571300	-2.70793000	3.52359900
H	-3.24845000	-3.53616200	4.21470500
C	4.15460000	-4.16611100	-3.08244000
H	4.35095200	-5.15389200	-2.65514100
H	4.85823800	-4.01561800	-3.90781300
H	3.14439700	-4.18295800	-3.50317500
H	1.04791600	-3.25258700	1.79620200
H	1.78712500	0.99715400	-1.36325000

Energies in Hartrees and Cartesian coordinates of calculated molecules for the unfavourable (direct) pathway at the CAM-B3LYP/6-31G(d,p) level of theory:

TS 1_d

Energy: -3197.467329 a.u.

Ca	1.56509200	1.37694200	9.03812900
Si	1.71409500	0.74560700	12.85423600
Si	4.15230800	0.21660800	11.21970500
N	3.69792900	4.11410200	7.81324300
N	2.85616600	0.43449300	5.75994900
N	3.92685900	2.52932800	6.40717800
N	1.07685600	-0.66546600	6.12974400
N	2.70412200	1.18397100	11.45688100
C	-0.48799800	2.32868400	7.30227000
C	-0.97807000	1.05485500	7.73973700
C	4.07574000	5.01987300	13.44966900
C	2.05338300	0.00656100	6.77725400
C	-0.77012100	3.32347500	8.30485100
C	2.64019200	5.24205000	13.53871200
C	3.34961000	2.82465300	7.60054200
C	4.33397600	4.33216600	12.23560000
C	0.15759600	2.74189500	6.11116700
H	0.35752100	2.02417900	5.32034500
C	-1.67728500	1.30129100	8.96895700

C	2.04701600	4.67780500	12.38326700
C	1.24660100	-0.65097200	4.75578400
H	0.56413500	-1.14115200	4.08016100
C	5.11515400	5.40323000	14.29293800
H	4.90444200	5.91864300	15.22605200
C	3.06291800	3.96747200	11.59185200
H	2.91010400	2.51203700	11.70771000
C	4.45684600	4.62017500	6.77092700
H	4.81891900	5.63585800	6.75609200
C	2.37768500	0.04534300	4.51906100
H	2.88828900	0.27542600	3.59763400
C	4.09377500	1.15865800	5.94986600
H	4.70263600	0.61796900	6.67542800
H	4.62770100	1.18036200	5.00065800
C	0.51101900	4.06479900	5.94476000
H	0.99446300	4.37515100	5.02255000
C	3.44587100	4.83170200	9.08083200
H	2.73655400	5.64241500	8.90094400
H	4.39435600	5.26371500	9.40850200
C	5.66273900	4.10987900	11.86141700
H	5.89858100	3.64653200	10.90968100
C	4.61252100	3.61579500	5.88172000
H	5.14457300	3.57668000	4.94441400
C	0.26419100	5.02527400	6.94750700
H	0.55884500	6.05775300	6.78899100
C	-1.54677600	2.68042900	9.33601200
C	-0.37341400	4.65764100	8.11690000
H	-0.59216400	5.40250200	8.87795300
C	-1.23093600	-0.14514900	6.86664900
H	-1.46024600	0.17221200	5.84017400
H	-2.12647600	-0.66793000	7.22214200
C	1.86801300	5.90845700	14.48853000
H	2.33006700	6.33081700	15.37673800
C	6.42760700	5.14200900	13.91974600
H	7.24677900	5.44257600	14.56516800
C	2.92628300	3.81946400	10.09826700
H	1.85653900	3.68572300	9.88608600
H	3.44332000	2.89583600	9.84283800
C	-0.11498900	-1.19320700	6.78571000
H	0.17821000	-1.52843000	7.78252900
H	-0.44261300	-2.06962600	6.21981200
C	0.67448900	4.84142800	12.17833400
H	0.19361400	4.43794700	11.29225100
C	6.69534500	4.51185100	12.70162900
H	7.72512300	4.33913600	12.40266800
C	-2.49333000	0.46369000	9.76394800
H	-2.62109200	-0.58481300	9.50683900
C	0.50252600	6.04649400	14.27786900
H	-0.10962200	6.57022500	15.00512900
C	-0.08501500	5.52217200	13.12169100
H	-1.15172400	5.64797700	12.95947600
C	2.38436200	1.51822800	14.43888000

H	3.39215400	1.16861100	14.67737200
H	1.73574600	1.26267100	15.28380600
H	2.41844400	2.60827500	14.36479300
C	-0.05535300	1.32130400	12.63891500
H	-0.63631700	1.04351000	13.52540800
H	-0.55211100	0.86278600	11.77894300
C	-2.23087800	3.18784500	10.45058200
H	-2.15397800	4.24166200	10.70558700
C	5.20890200	-0.00719700	12.76773100
H	5.50652300	0.96370100	13.17521100
H	6.12296300	-0.55610600	12.51739300
H	4.69901700	-0.56040400	13.56039700
C	1.58704600	-1.11994000	13.16341800
H	1.12264000	-1.64899700	12.32538300
H	0.94366200	-1.27175400	14.03697700
H	2.54329700	-1.60312500	13.37820000
C	-3.03906000	2.35264000	11.19501600
H	-3.58196800	2.74040800	12.05065200
C	5.32528300	0.93003000	9.91684700
H	4.82890400	1.23590800	8.99184300
H	6.05063600	0.15014300	9.65976400
H	5.88879900	1.78585100	10.28940900
C	-3.16483900	0.99271000	10.84622400
H	-3.80841700	0.35077000	11.44100600
C	3.74665500	-1.50207200	10.52275600
H	3.05915600	-2.07858600	11.14271500
H	4.67338200	-2.07937700	10.43028100
H	3.31657500	-1.43667800	9.51598100
H	-0.13265000	2.40365100	12.52951000

Intermediate (Int_d)

Energy: -3197.505792 a.u.

Ca	1.54376500	1.41367800	9.09250200
Si	2.23010100	0.53515300	12.80624500
Si	4.31324000	-0.55523200	10.71186200
N	3.39076200	4.35542900	7.93027200
N	2.95925900	0.56785400	5.89560300
N	3.83008100	2.73208300	6.62403300
N	1.28973500	-0.71204700	6.19256700
N	3.11234700	0.66593200	11.23568600
C	-0.57757800	2.08468700	7.27375300
C	-0.89987200	0.77762400	7.74869800
C	3.44034600	5.63283500	13.74401400
C	2.14518200	0.08162300	6.87190100
C	-0.75502300	3.03988700	8.33567400
C	2.20354000	6.33073800	13.51489600
C	3.25367300	3.01710900	7.82877700
C	3.71249700	4.85877100	12.55951100
C	-0.14835500	2.55456500	6.00638000
H	-0.00960500	1.85819500	5.18373700
C	-1.33703600	0.93011600	9.09801000

C	1.74422600	5.96246100	12.20172500
C	1.54423100	-0.71322000	4.83163100
H	0.96273400	-1.29183900	4.13188500
C	4.31080500	5.58288500	14.83377500
H	4.10055300	6.16977600	15.72546400
C	2.67176700	5.06139000	11.61912300
H	3.61051100	1.55944600	11.28595200
C	4.02027500	4.89837800	6.82361800
H	4.21390900	5.95499800	6.73084000
C	2.60695700	0.09701300	4.64077300
H	3.14489000	0.36084600	3.74432600
C	4.12291100	1.38660200	6.16541100
H	4.73082400	0.88157600	6.91492000
H	4.70525500	1.46378700	5.24838400
C	0.07106600	3.89984500	5.81567800
H	0.38398700	4.25670800	4.83849000
C	3.04068600	5.17630000	9.10338700
H	2.27729300	5.89799200	8.80269800
H	3.93904400	5.73068500	9.38345500
C	4.87827200	4.05795300	12.53198900
H	5.14072900	3.49066000	11.63917900
C	4.30341600	3.87254400	5.99537600
H	4.79942800	3.85043300	5.03818800
C	-0.11035800	4.83344800	6.86213700
H	0.06193700	5.88859500	6.67632700
C	-1.24280100	2.31542000	9.48185200
C	-0.51942800	4.40921100	8.10775600
H	-0.68176300	5.12830400	8.90577600
C	-1.07143700	-0.45551100	6.91035200
H	-1.36600000	-0.17773400	5.89076000
H	-1.89512700	-1.06205300	7.30546900
C	1.45547300	7.20799500	14.30411900
H	1.80821800	7.48444300	15.29554500
C	5.44272400	4.78193200	14.78551900
H	6.12116000	4.74233900	15.63208300
C	2.56707500	4.36055600	10.30669900
H	1.52867300	4.04355600	10.11795700
H	3.19219600	3.46060600	10.34967100
C	0.14996100	-1.37803300	6.81296500
H	0.46427200	-1.70826200	7.80509500
H	-0.07779200	-2.26818700	6.22085600
C	0.52619500	6.50720400	11.73658800
H	0.16005900	6.26327600	10.74136300
C	5.71802000	4.02375800	13.63165000
H	6.61635100	3.41178200	13.59976700
C	-1.85719800	0.00036700	10.03571000
H	-1.94250200	-1.05156900	9.77533700
C	0.26263000	7.72555200	13.82529000
H	-0.32127000	8.40795900	14.43528600
C	-0.19457600	7.36816100	12.54177600
H	-1.13012200	7.78436500	12.17649500
C	3.40751100	0.54278600	14.26933700

H	3.99688500	-0.37028600	14.36736100
H	2.82595000	0.66321700	15.18928900
H	4.09429500	1.39315800	14.20830400
C	1.12694900	2.03051100	12.95309800
H	0.69301100	2.06956600	13.95767100
H	0.29281200	2.01263100	12.24813500
C	-1.70411700	2.73689900	10.74278600
H	-1.64787400	3.78554700	11.02282300
C	5.23286100	-1.40199900	12.11305400
H	5.75145800	-0.68782700	12.75716300
H	5.98694300	-2.06901300	11.68138300
H	4.57889100	-2.01342700	12.74026200
C	1.23801900	-1.05864500	12.75395900
H	0.50430000	-1.04821300	11.94185700
H	0.68312200	-1.17412900	13.69025100
H	1.86843600	-1.94527400	12.63979800
C	-2.23869700	1.81340300	11.61560500
H	-2.60241000	2.13185600	12.58662800
C	5.56285100	0.38974300	9.67331700
H	5.07232000	1.11006100	9.01249400
H	6.16807500	-0.28696000	9.06234900
H	6.24686500	0.95322800	10.31567200
C	-2.30487100	0.44697400	11.25893600
H	-2.72669700	-0.26294400	11.96439000
C	3.43743600	-1.88336500	9.71498200
H	2.61352200	-2.32652000	10.28262600
H	4.13827800	-2.68851800	9.47230700
H	3.03754000	-1.49508300	8.77400300
H	1.68694600	2.96062600	12.80257300

Cartesian coordinates of molecule 4 at the CAM-B3LYP/6-31G(d,p) level of theory:

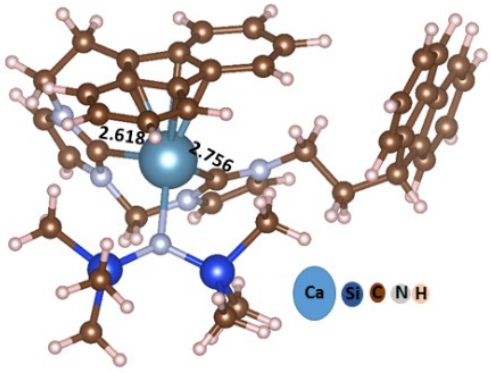
Energy: -2535.0285319 a.u**.**

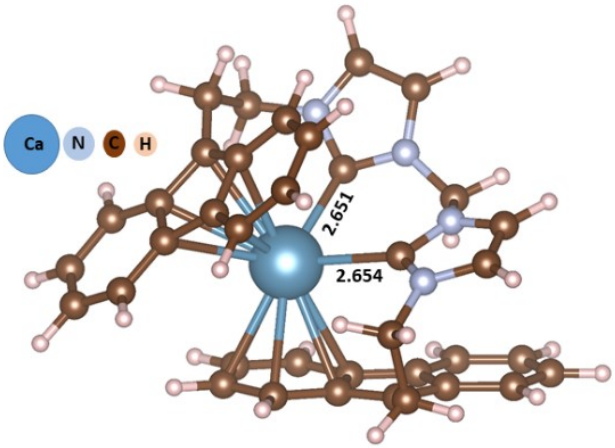
Si	9.81481400	19.55412800	11.79132600
Si	10.71446500	17.47509100	9.76332300
N	7.42512700	20.39603100	6.80836300
N	6.40005100	18.53702800	6.99698000
N	4.93084900	17.53093300	10.84864700
N	5.29989400	17.28720200	8.76338800
N	9.50018800	18.17264300	10.78951900
C	6.75790100	15.78068900	12.83983400
C	7.15269800	14.86161400	11.81475300
C	7.11146400	13.44165600	9.84649600
H	6.58041900	13.04063900	8.98596500
C	10.48434900	24.66484400	7.00665600
C	10.92377500	23.33216300	6.86582000
C	7.39591100	19.27696200	7.58108300
C	7.82917900	15.82550100	13.79175300
C	3.75465100	17.03943500	10.29273600
H	2.87080400	16.84758100	10.88037800

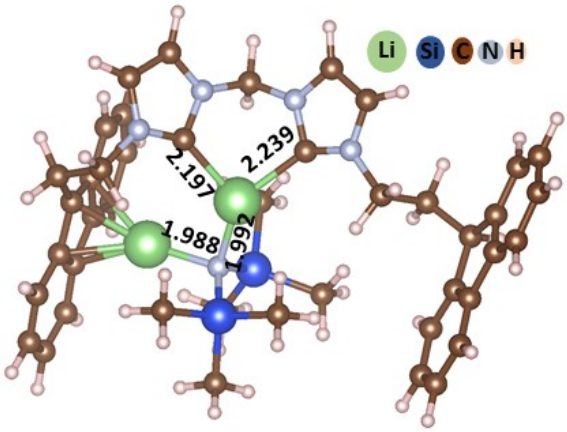
C	5.91208800	17.68911000	9.92221300
C	8.49816300	14.39187700	12.08509200
C	5.82246000	19.18197000	5.90928500
H	5.01714200	18.75645200	5.33103600
C	9.42350300	23.82298900	5.10107900
C	7.97382800	16.49966000	15.03391400
H	7.16390800	17.11106000	15.42535700
C	6.47994300	20.36026300	5.78662200
H	6.36144700	21.16566300	5.07871400
C	6.47835000	14.35576900	10.67099300
H	5.45611000	14.65980900	10.45946900
C	8.92299400	14.99811300	13.32364700
C	6.01054100	17.22704800	7.49663200
H	6.90884200	16.62177300	7.62615900
H	5.36810900	16.74705100	6.75717700
C	3.98458300	16.88699000	8.96531300
H	3.34373700	16.53998000	8.16975700
C	9.54922000	24.96821700	5.91437300
C	10.10777100	14.89144800	14.08033400
H	10.92456300	14.26551300	13.72852600
C	8.39694800	21.48755700	6.94004600
H	8.79547600	21.45304400	7.95381300
H	7.85630400	22.43121000	6.81982900
C	9.14434400	16.36168400	15.75845000
H	9.24441800	16.87224800	16.71292800
C	11.83770600	22.79292200	7.76486800
H	12.18451900	21.76793700	7.66484900
C	5.39718100	16.38844800	13.04067700
H	5.25158400	16.60408500	14.10704900
H	4.60647400	15.67095900	12.77583100
C	9.51723800	21.37408600	5.89204200
H	9.08124800	21.04972800	4.93959300
H	10.21544300	20.58602700	6.19445500
C	10.21721700	15.56665500	15.28522700
H	11.12319300	15.47969800	15.87762900
C	9.11899200	13.47375700	11.21443400
H	10.12547000	13.11943500	11.42486400
C	8.43345700	13.00263300	10.10605000
H	8.90292200	12.28517300	9.43950700
C	9.86694400	16.39043400	8.44501300
H	9.24356000	15.60753800	8.89290200
H	10.61274100	15.88887600	7.81671700
H	9.24417200	17.00029500	7.77726700
C	10.28768100	22.69123700	5.64015900
H	11.07400500	22.45648200	4.90764200
C	5.10552300	17.71081700	12.29441100
H	4.18534000	18.16893000	12.67554300
H	5.92209900	18.41858500	12.43646000
C	12.30814200	23.59182200	8.81353100
H	13.01857300	23.18104800	9.52431100
C	11.87037500	24.91275100	8.95485700
H	12.24610000	25.51820300	9.77436200

C	10.95660800	25.46028000	8.05251100
H	10.62392400	26.48835100	8.16481800
C	9.73072400	21.19260700	10.81630000
H	10.46971400	21.23681800	10.01032900
H	9.90488800	22.05673900	11.46881600
H	8.73777100	21.32833500	10.36639100
C	8.60018800	23.84256900	3.98009700
H	8.50941300	22.96853200	3.33926300
C	11.74677500	18.75398000	8.78976100
H	11.09722200	19.40149500	8.18921700
H	12.44355900	18.25243100	8.10737200
H	12.33895000	19.39751900	9.44981000
C	11.48997400	19.51559000	12.69157800
H	11.56725300	18.63043500	13.33286000
H	11.60976200	20.39904500	13.33012900
H	12.33751100	19.49572900	11.99751400
C	7.89517100	25.01251200	3.67286800
H	7.25210600	25.04115100	2.79813700
C	8.84705700	26.13516500	5.60522400
H	8.94091700	27.02186000	6.22570000
C	11.95313900	16.36492100	10.68146200
H	12.51770000	16.92680400	11.43269600
H	12.67368800	15.91722000	9.98613100
H	11.43964100	15.54755800	11.19886900
C	8.01872800	26.14746700	4.48088300
H	7.46716800	27.04859000	4.22924700
C	8.48237300	19.73566300	13.13618700
H	7.49107400	19.91134600	12.70017600
H	8.70742700	20.60084200	13.77160700
H	8.42043700	18.85921500	13.79033200
Li	8.59885400	16.72818700	11.81652800
Li	7.92445000	18.51894700	9.62115800

(C) Computationally optimized structures of 2, 3, and 4:







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