Experimental and Supplementary Information for

Cooperative Dihydrogen Activation at a $Na(I)_2/Mg(I)_2$ Ensemble

Han-Ying Liu, Samuel E. Neale, Michael S. Hill,* Mary F. Mahon, Claire L. McMullin* and Ben Morrison

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

1 Experimental and Supplementary Information

1.1. General information

Unless stated otherwise, all the experiments were conducted using standard Schlenk line and/or glovebox techniques under an inert atmosphere of argon. NMR spectra were recorded with an Agilent ProPulse spectrometer (^{1}H at 500 MHz, ^{13}C at 126 MHz). The spectra are referenced relative to residual protio solvent resonances. Elemental analyses were performed at Elemental Microanalysis Ltd., Okehampton, Devon, UK. Solvents were dried by passage through a commercially available solvent purification system and stored under argon in ampoules over 4 Å molecular sieves. C_6D_6 was purchased from Sigma-Aldrich, dried over a potassium mirror before distilling and storage over molecular sieves. $[\{SiN^{Dipp}\}MgNa]_2$ (**6**),[1] was prepared according to reported procedures. All other chemicals were purchased from Sigma-Aldrich Merck and used without further purification.

*Synthesis of $[\{SiN^{Dipp}\}Mg(H)Na_2\{SiN^{Dipp}\}Na_2(H)Mg\{SiN^{Dipp}\}]$ (**9**)*

In a J Young's tube, $[\{SiN^{Dipp}\}MgNa]_2$ (**6**, 21.6 mg, 0.02 mmol) was dissolved in 0.4 mL of d_6-benzene. The bright yellow solution was degassed by three freeze-pump-thaw cycles, before being charged with 2 atm. of hydrogen gas. The reaction mixture was observed to develop into a colourless solution with black precipitates after being kept at 40 °C for 3 days. The reaction mixture was then filtered and removal of all volatiles of the filtrate *under vacuo* afforded **6** as a colorless powder. Yield 17.9 mg, 78 %. The reaction was also carried out in the same procedure with $^2H_2$, and the resulting powder was dissolved in C_6H_6 to record a ^{2}H NMR spectrum. Anal Calc'd for $C_{96}H_{166}Mg_2N_6Na_4Si_6$ (**6**, 1713. 51): C, 67.29; H, 9.77; N, 4.90 %. Found: C, 66.82; H, 9.42; N, 4.82 %. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a hexane solution of **6** at room temperature. ^{1}H NMR (500 MHz, 298 K, Benzene-d_6) δ 7.03 – 6.93 (m, 4H, *m*-C_6H_3), 6.90 (d, J = 7.5 Hz, 8H, *m*-C6*H*3 on $\{SiN^{Dipp}\}Mg$), 6.82 – 6.78 (m, 2H, *p*-C_6H_3), 6.74 (t, J = 7.5Hz, 4H, *p*-C_6H_3 on $\{SiN^{Dipp}\}Mg$), 3.96 (sept, J = 7.0 Hz, 8H, C*H*Me$_2$ on $\{SiN^{Dipp}\}Mg$), 3.90 (sept, J = 6.9 Hz, 4H, C*H*Me$_2$), 1.28 (d, J = 7.0 Hz, 24H, CH*Me*$_2$ on $\{SiN^{Dipp}\}Mg$), 1.23 (d, J = 6.9 Hz, 12H, CH*Me*$_2$), 1.19 (d, J = 6.9 Hz, 12H, CH*Me*$_2$), 1.17 (s, 8H, SiCH_2 on $\{SiN^{Dipp}\}Mg$), 1.13 (s, 4H, SiCH_2), 0.87 (d, J = 7.0 Hz, 24H, CH*Me*$_2$

on {SiN^{Dipp}}Mg), 0.25 (s, 36H, SiMe$_2$)*overlapping peaks. ^{2}H NMR (77 MHz, 298 K, C_6H_6) δ 4.16. ^{13}C NMR (126 MHz, 298 K, Benzene-d_6) δ 156.6 (*i*-C_6H_3), 152.1 (*i*-C_6H_3 on {SiN^{Dipp}}Mg), 147.1 (*o*-C_6H_3), 146.0 (*o*-C_6H_3 on {SiN^{Dipp}}Mg), 129.3 (m-C_6H_3), 123.1 (*p*-C_6H_3), 122.7 (*m*-C_6H_3 on {SiN^{Dipp}}Mg), 119.9 (*p*-C_6H_3 on {SiN^{Dipp}}Mg), 27.4 (*C*HMe$_2$), 27.1 (*C*HMe$_2$ on {SiN^{Dipp}}Mg), 25.6 (CH*Me*$_2$ on {SiN^{Dipp}}Mg), 25.2 (CH*Me*$_2$), 24.0 (CH*Me*$_2$), 23.8 (CH*Me*$_2$ on {SiN^{Dipp}}Mg), 13.2 (Si*C*H$_2$ on {SiN^{Dipp}}Mg), 13.0 (Si*C*H$_2$), 1.2 (Si*Me*$_2$)*overlapping peaks.

Figure S1. ^{1}H NMR (500 MHz, 298 K, d_6-benzene) spectrum of **9**. *toluene †excess H_2

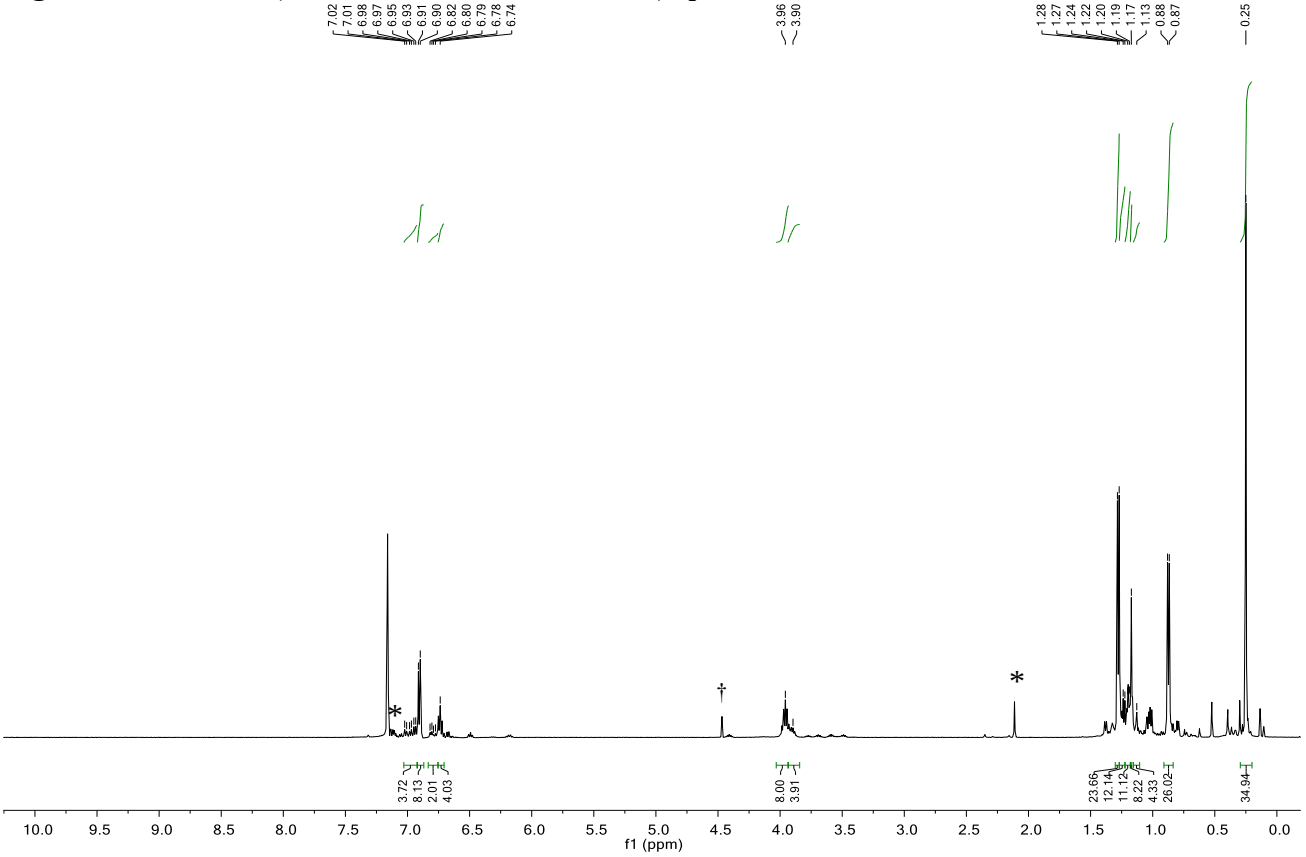


Figure S2. Expansion of the aliphatic region of the ^{1}H NMR (500 MHz, 298 K, d_6-benzene) spectrum of **9**.

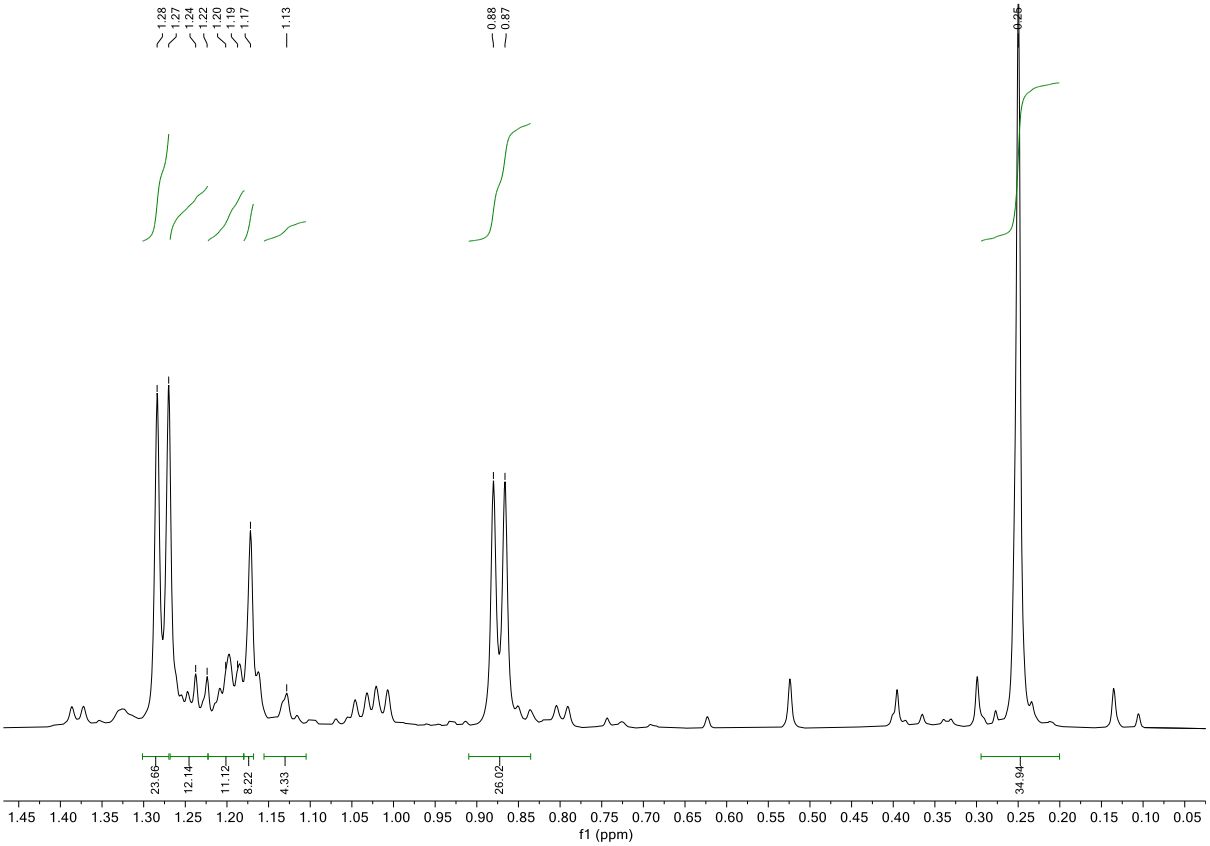


Figure S3. ^{2}H NMR (77 MHz, 298 K, benzene) spectrum of **9**

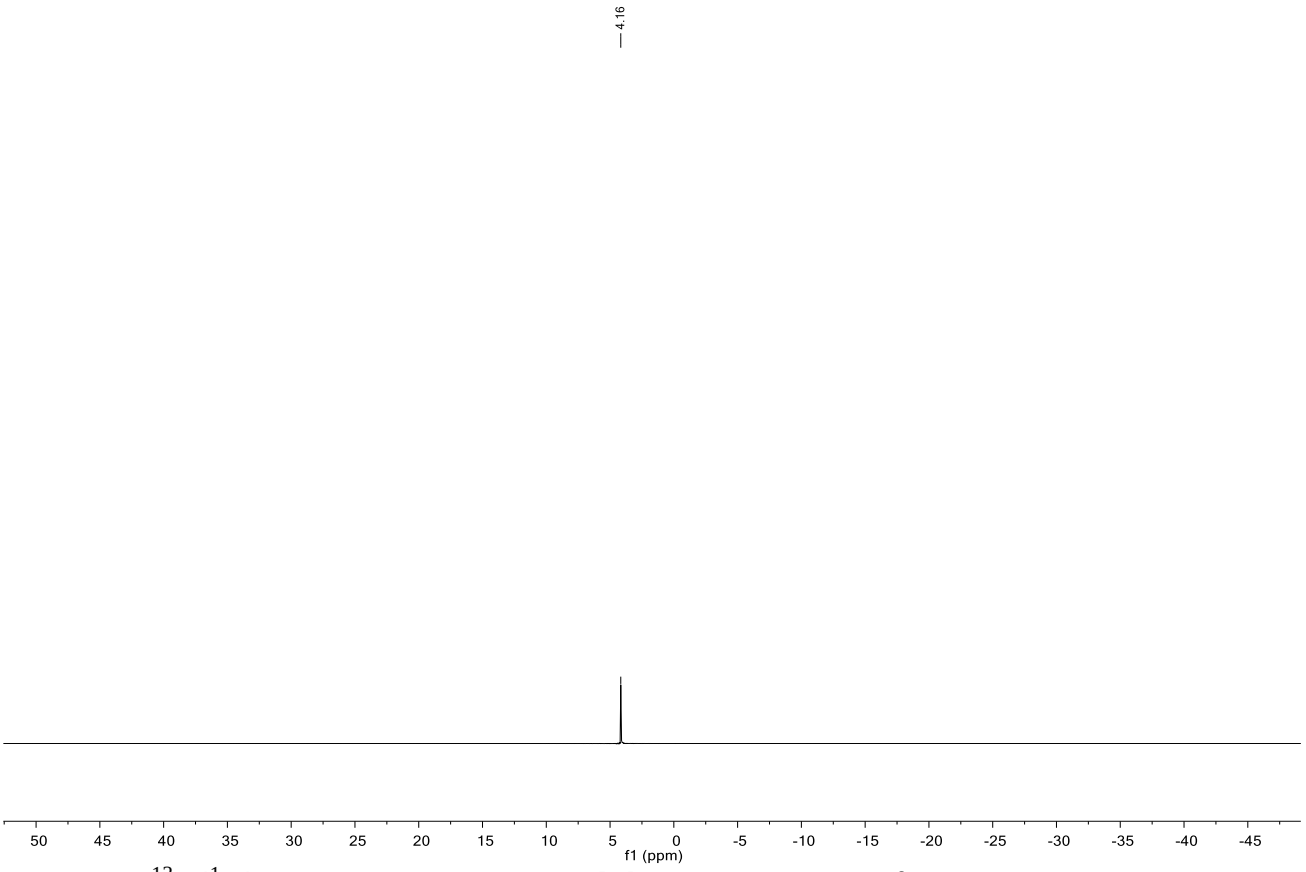


Figure S4. ^{13}C{^{1}H} NMR (126 MHz, 298 K, d$_6$-benzene) spectrum of **9**.

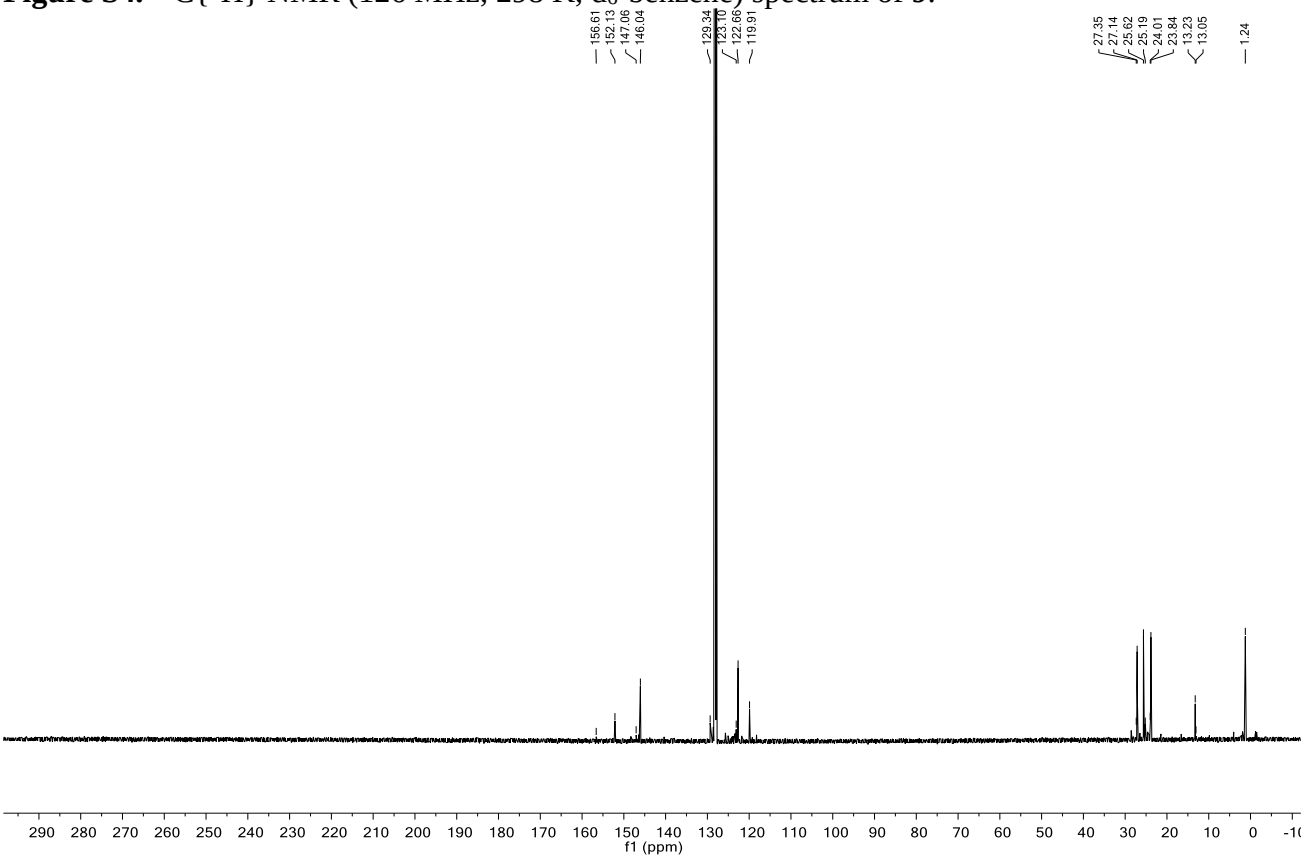


Figure S5. Expansion of the aliphatic region of the $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, d_6-benzene) spectrum of **9**.

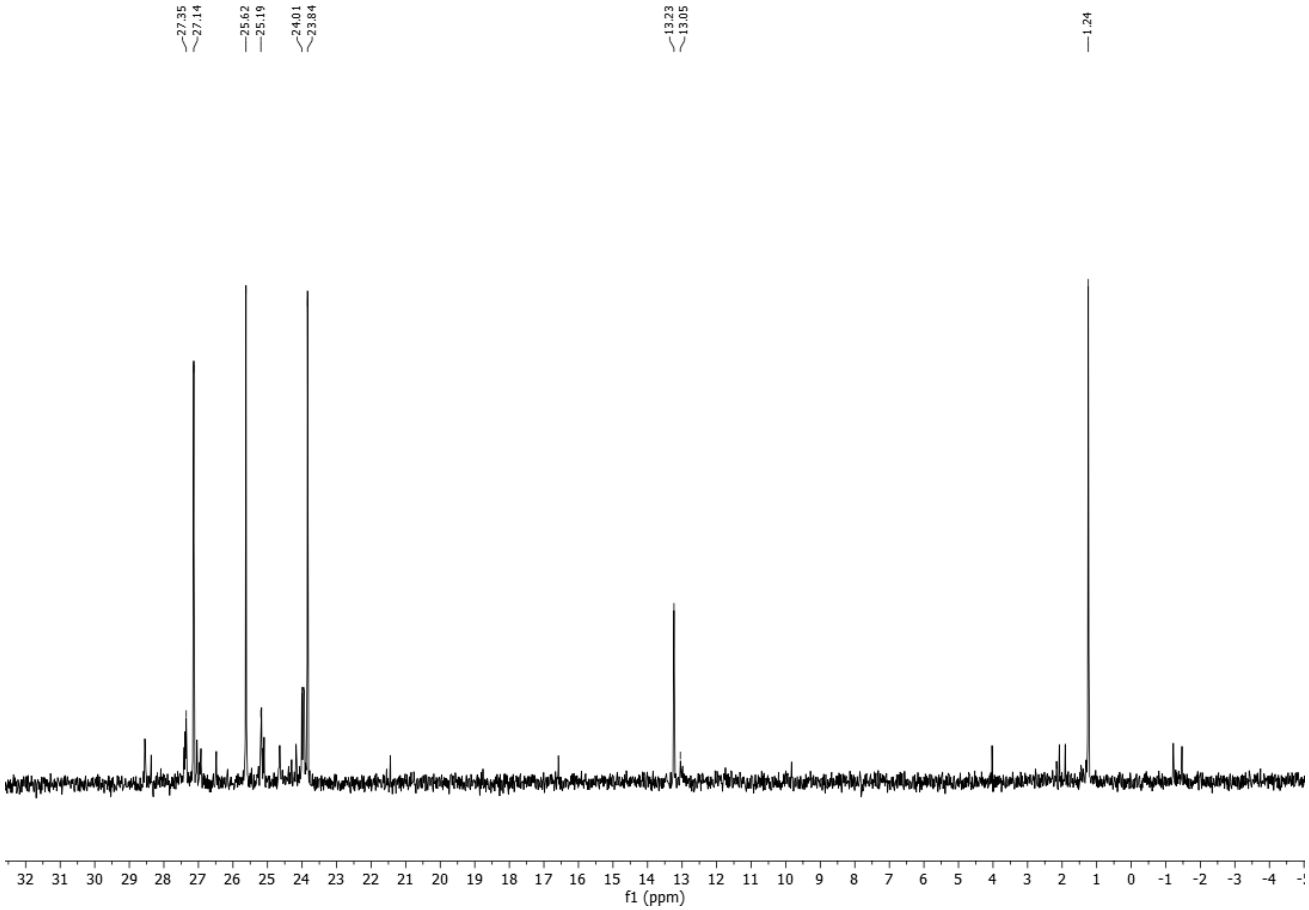


Figure S6. ^{1}H-^{13}C HSQC spectrum of **9**.

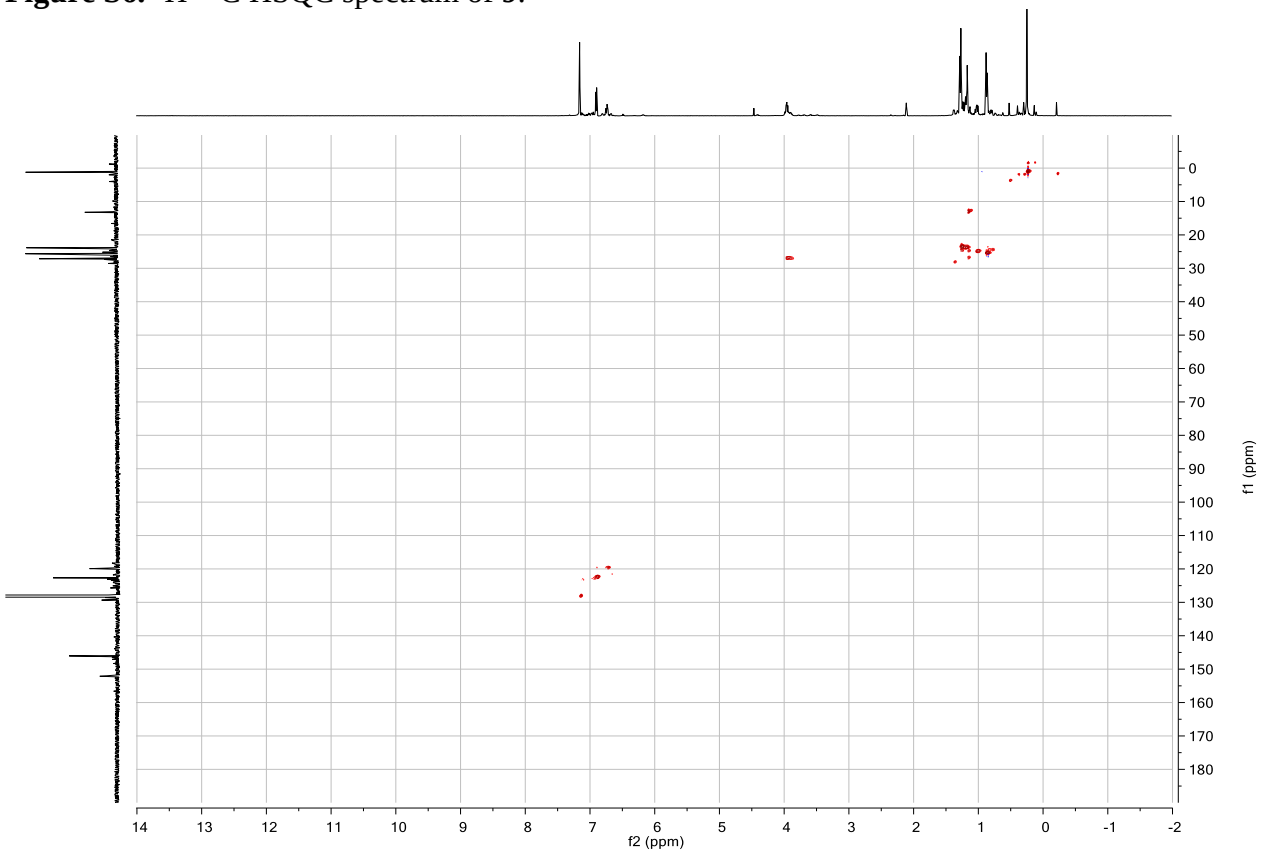
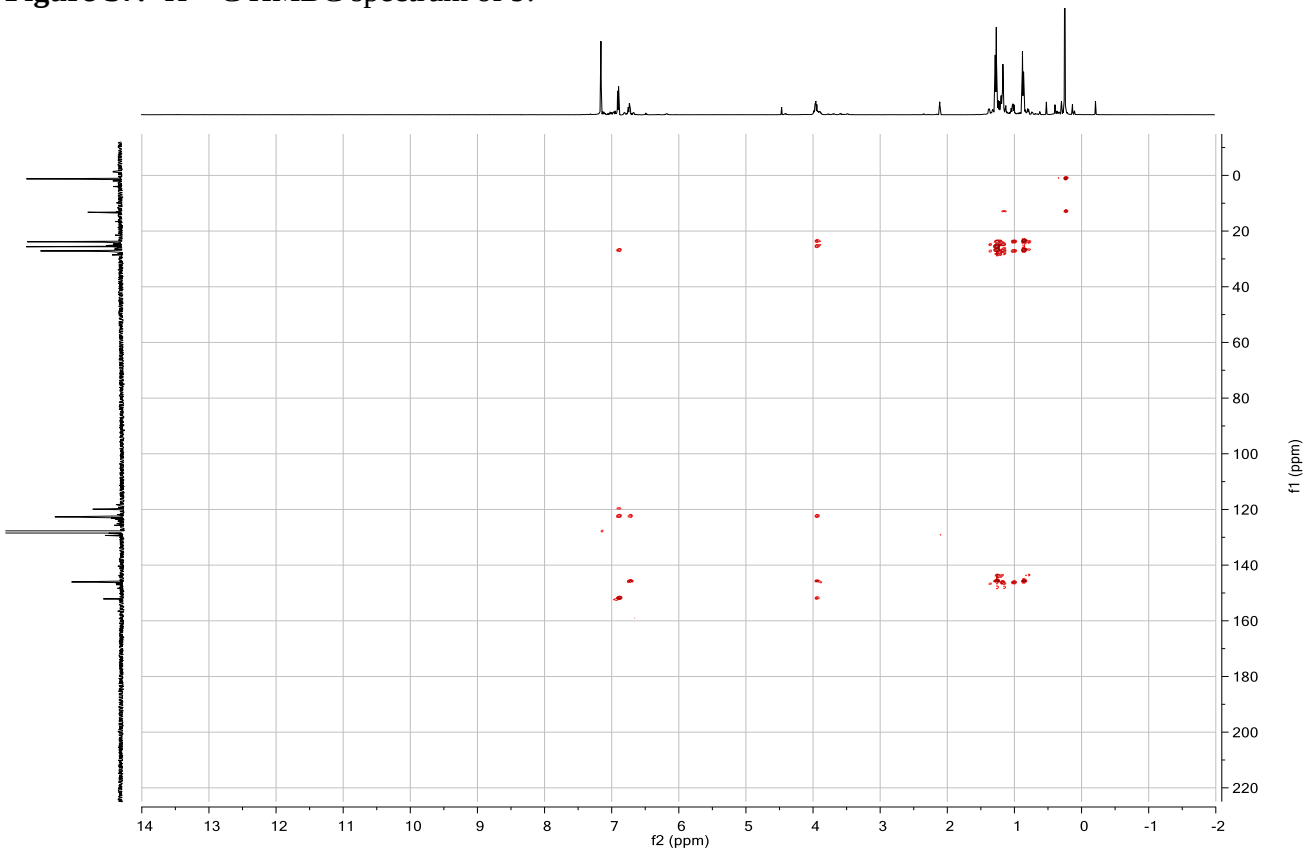


Figure S7. ^{1}H-^{13}C HMBC spectrum of **9**.



1.4. ICP-OES Details (Conducted at Butterworth Lab.)

The metallic solid deposited from a reaction of **6** and H_2 performed as described above was isolated by careful decantation and washed with toluene (0.5 mL x2) and hexane (0.5 mL x2). The resultant powdery deposit was then collected, and all volatiles were removed under vacuum. The vial was then removed from the glovebox, 1mL of deionised water was then slowly added to the powder along with a few drops of HCl(aq.). Bubbles were observed during this process. After all the metal had dissolved, the solution was further diluted deionised water to 5 mL in total volume. The sample was then kept under ambient conditions and shipped to Butterworth Lab. Ltd., Teddington, for ICPOES analysis.

BUTTERWORTH
LABORATORIES

Certificate of Analysis

Department of Chemistry
University of Bath
Bath
UK
BA2 7AY

Job Ref: **2206-0034**
Report Ref: RN-01783-22
Date Issued: 30 June 2022
Order Ref: 27505526

For attention of H. Liu

Sample of:	Acidified Aqueous Solution of Metallic Mirror		
BLL Ref:	**06-0122-22**	Date Received:	7 June 2022
Analysis Started:	15 June 2022	Analysis Completed:	17 June 2022
Sample Reference:	HYDL789		

Test	Result	Units
Magnesium expressed as Mg	110	mg/L
	110	mg/L
Sodium expressed as Na	<5	mg/L
	<5	mg/L

Results relate to sample as received.

Sample analysed in accordance with in house method BLM 537G (revision 7).

Andrew Milne
Team Leader - QC

Craig McConville
Analytical Operations Manager
Issued for and on behalf of Butterworth Laboratories

Encl. Raw Data Pack

1.5. Single Crystal X-ray Diffraction Analysis

Data were collected for compound **9** on a Rigaku Xcalibur diffractometer (Mo Kα; λ = 0.71073 Å). The sample was maintained at 150(2) K during data collection. Using Olex2,[2] the structure were solved with the using ShelXT and refined with the ShelxL[4] refinement package using Least Squares minimization.

The asymmetric unit in **9** comprises half of a dimer (the remainder of which is generated *via* a crystallographic inversion centre) plus half of a molecule of hexane which is disordered in a 70:30 ratio. The latter fragments are also proximate to a centre of inversion, which serves to complete both moieties. With the inclusion of distance and ADP restraints, this region of the electron density map modelled well. The hydride at the centre of the metal triangle was located and refined with a riding U_{iso} value.

Table S1: Crystal data and structure refinement for compound **9**.

Empirical formula	$C_{48}H_{83}MgN_3Na_2Si_3$
Formula weight	856.73
Crystal system	triclinic
Space group	*P*-1
a/Å	10.4759(3)
b/Å	12.0459(4)
c/Å	23.1083(8)
α/°	76.271(3)
β/°	78.238(3)
γ/°	69.189(3)
Volume/Å^3	2624.90(16)
Z	2
ρ_{calc}g/cm^3	1.084
μ/mm^{-1}	0.152
F(000)	936.0
Crystal size/mm^3	0.53 × 0.391 × 0.144
2Θ range for data collection/°	5.922 to 60.634
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 17$, $-32 \leq l \leq 32$
Reflections collected	45674
Independent reflections	13937 [R_{int} = 0.0357, R_{sigma} = 0.0456]
Data/restraints/parameters	13937/116/564
Goodness-of-fit on F^2	1.027
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1096
Final *R* indexes [all data]	R_1 = 0.0700, wR_2 = 0.1213
Largest diff. peak/hole / e Å^{-3}	0.60/-0.33

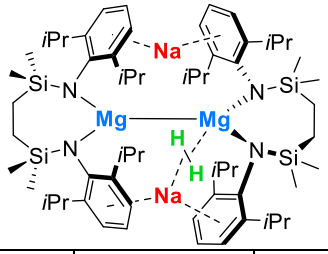
2.0 Computational Details

DFT calculations were run with Gaussian 16 (C.01)[5] using BP86.[6-7] The Na, Mg, and Si centres were described with the Stuttgart RECPs and associated basis sets,[8] and the 6-31G** basis set was used for all other atoms (BS1).[9-10] A polarization function was also added to Si ($\zeta d = 0.284$). Initial BP86 optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues) or transition structures (one negative eigenvalue). Natural Bond Orbital analyses were carried out with NBO (version 7)[11] within Gaussian 16 (C.01) also at the BP86/6-311++G** level. The energies of donor-acceptor interactions (i.e. "$\Delta E^{(2)}$") between the various molecular fragments (automatically designated during the NBO procedure itself) within **III** were also estimated with second-order perturbation theory analysis of the Fock matrix in the NBO basis, as is performed in NBO7. Key donor-acceptor NBO interactions between each designated fragment as part of the analyses, are provided in Table S2 and outlined in Figure S6.

2.1 NBO data

Second Order Perturbation Theory Analysis of Donor Acceptor NBO interactions between molecular fragments

Table S2. Selected donor acceptor interaction energies, $\Delta E^{(2)}$, for **III.**



*Left & right Mg (**1**) = Orange*
*Top & bottom Na (**2&3**) = Red*
*H_2 moiety (**4**) = Purple*

Donor NBO (Unit)	Acceptor NBO (Unit)	$\Delta E^{(2)}$ (kcal/mol)
$\Omega_{Mg5\text{-}Mg172}$ (1)	n^*_{Na6} (3)	16.7
$\Omega_{Mg5\text{-}Mg172}$ (1)	$AB_{H173\text{-}H174}$ (4)	9.2
$\Omega_{Mg5\text{-}Mg172}$ (1)	R^*_{H173} (4)	2.3

Donor NBO (Unit)	Acceptor NBO (Unit)	$\Delta E^{(2)}$ (kcal/mol)
$\Omega_{Mg5\text{-}Mg172}$ (1)	n^*_{Na7} (2)	30.1
$\Omega_{Mg5\text{-}Mg172}$ (1)	R^*_{Na7} (2)	2.0
$\Omega_{H173\text{-}H174}$ (4)	n^*_{Na6} (3)	1.6

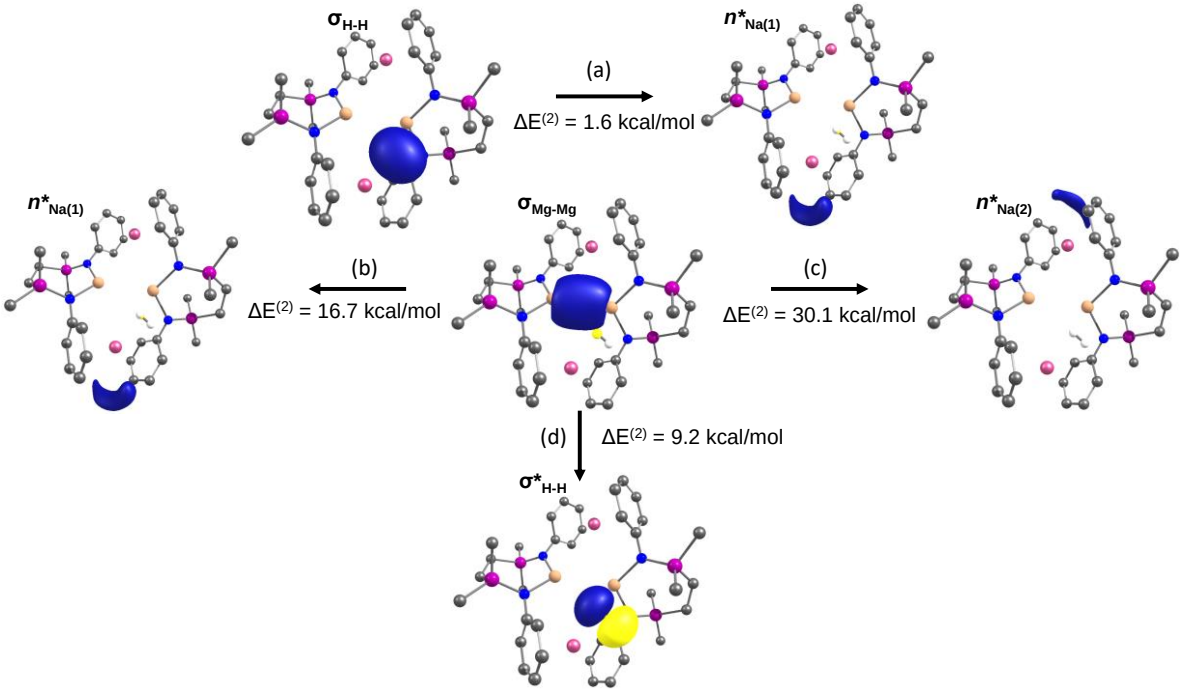


Figure S8. Overview of key NBO donor acceptor interactions between the H_2 fragment and the Mg_2Na_2 tetrametallic core fragment (*a*, *d*) along with interactions within the Mg_2Na_2 fragment itself (*b*, *c*).

2.2 Cartesian Coordinates and Computed Energies (in Hartrees)

H_2
SCF (BP86) Energy = -1.17646512696
Enthalpy 0K = -1.164184
Enthalpy 298K = -1.163240
Free Energy 298K = -1.178052
Lowest Frequency = 4354.5793 cm^{-1}
SCF (BP86-D3BJ) Energy = -1.17657513946
SCF (C6H6) Energy = -1.17652524941
SCF (BS2) Energy = -1.17751849719

H	0.00000	0.00000	0.37532
H	0.00000	0.00000	-0.37532

TS(I-II)
SCF (BP86) Energy = -2584.87178002
Enthalpy 0K = -2583.331117
Enthalpy 298K = -2583.330172
Free Energy 298K = -2583.559461
Lowest Frequency = -80.7041 cm^{-1}
Second Frequency = 14.5354 cm^{-1}
SCF (BP86-D3BJ) Energy = -2585.37776370
SCF (C6H6) Energy = -2584.88633265
SCF (BS2) Energy = -4450.66763207

Si	-4.67452	-0.55866	1.60309
Si	-4.33679	1.61798	-1.66751
Si	4.35527	-1.49471	-1.70324
Si	4.74408	0.64482	1.58499
Mg	1.75685	-0.17019	0.05293
Na	-0.40162	-3.46098	0.04585
Na	0.41401	3.45253	0.10139
N	-3.12941	-1.17001	0.95808
N	-2.72646	1.78447	-0.91776
N	3.14294	1.14823	0.97586
N	2.77166	-1.75520	-0.93060
C	-2.85649	-2.54157	1.12806
C	2.11649	-2.97362	-1.17516
C	-1.16026	3.16562	-2.29052
C	-3.20828	-3.52753	0.12037
C	-2.06283	3.00225	-1.16475
C	-2.20239	-3.04853	2.32047
C	2.77108	2.47569	1.27067
C	1.19998	-3.13515	-2.29190
C	2.31523	-4.13584	-0.32589
C	3.18819	3.59523	0.44504
C	-1.80202	-4.40060	2.39910
H	-1.28916	-4.74891	3.30363
C	-1.99833	-2.17271	3.55749
H	-2.52200	-1.22268	3.35556
C	5.99176	0.11636	0.22664
H	6.04605	0.92945	-0.52261
H	6.97590	0.13911	0.74162
C	-2.24771	4.15949	-0.30787
C	-2.80888	-4.87512	0.26133
H	-3.08952	-5.59455	-0.51674
C	-0.48161	4.38792	-2.49035
H	0.18289	4.48878	-3.35630
C	5.81284	-1.24538	-0.47843
H	5.77251	-2.06386	0.26645
H	6.71446	-1.46285	-1.08996
C	-5.94795	-0.04308	0.25994
H	-6.00185	-0.84922	-0.49561
H	-6.92957	-0.06973	0.77821
C	0.99035	-2.01762	-3.31400
H	1.42554	-1.10519	-2.86898
C	1.94060	2.79020	2.41938
C	-5.77488	1.32509	-0.43318
H	-5.72991	2.13408	0.32200
H	-6.68160	1.55071	-1.03453
C	0.54634	-4.36799	-2.50857
H	-0.11968	-4.46980	-3.37319
C	-2.08109	-5.32132	1.37631
H	-1.77180	-6.36789	1.46338
C	2.76004	4.90699	0.74517

H	3.09449	5.73195	0.10470
C	3.33155	-4.12312	0.81527
H	3.63930	-3.06825	0.93320
C	-1.54056	5.35700	-0.55327
H	-1.70768	6.21568	0.10824
C	1.93761	5.18669	1.84750
H	1.62609	6.21253	2.06922
C	1.63053	-5.34340	-0.58824
H	1.81732	-6.20901	0.05841
C	-3.23321	4.13757	0.85997
H	-3.72453	3.15092	0.82326
C	-0.98613	2.06691	-3.34033
H	-1.47598	1.16584	-2.93067
C	4.10662	3.40575	-0.76286
H	4.38696	2.33923	-0.77151
C	1.54570	4.12194	2.67409
H	0.93191	4.33328	3.55731
C	0.74403	-5.47508	-1.66807
H	0.23347	-6.42381	-1.86191
C	4.65878	-0.80212	2.83857
H	3.98263	-0.57804	3.68035
H	5.66887	-0.97379	3.25279
H	4.33321	-1.75166	2.38338
C	-0.65169	5.48577	-1.63210
H	-0.12094	6.42610	-1.81276
C	-4.37231	0.95193	2.73478
H	-3.92989	0.63915	3.69612
H	-5.31611	1.48272	2.95410
H	-3.68446	1.67416	2.26685
C	-5.56405	-1.87328	2.67657
H	-6.61719	-1.57776	2.82698
H	-5.10048	-1.95394	3.67308
H	-5.55832	-2.87897	2.22517
C	4.29242	0.03802	-2.84400
H	3.65288	-0.14916	-3.72306
H	5.30144	0.30342	-3.20832
H	3.88805	0.91572	-2.31355
C	-4.09758	-3.15894	-1.06511
H	-4.12525	-2.05628	-1.09163
C	4.88559	-2.99921	-2.78078
H	4.07548	-3.72936	-2.93766
H	5.73337	-3.53620	-2.32132
H	5.22516	-2.65368	-3.77314
C	-2.60765	-2.81906	4.82412
H	-3.64759	-3.14480	4.66132
H	-2.59806	-2.09886	5.66101
H	-2.02953	-3.70300	5.14863
C	1.54733	1.71578	3.43482
H	1.79373	0.74479	2.96902
C	-4.35327	0.20909	-2.96343
H	-3.81696	0.51639	-3.87723
H	-5.38748	-0.05255	-3.25129
H	-3.86822	-0.70625	-2.58778
C	-0.51606	-1.83910	3.80694
H	0.09825	-2.75569	3.87641
H	-0.38888	-1.28542	4.75370
H	-0.12033	-1.20950	2.99175
C	1.74444	-2.32133	-4.63120
H	2.82044	-2.47984	-4.46277
H	1.62787	-1.48606	-5.34489
H	1.34264	-3.23132	-5.11285
C	0.49040	1.73234	-3.62439
H	1.04897	2.60472	-4.00688
H	0.57072	0.94120	-4.38915
H	0.99890	1.36631	-2.71404
C	-0.49448	-1.75057	-3.62354
H	-0.98665	-2.62501	-4.08481
H	-0.59894	-0.91487	-4.33561
H	-1.05489	-1.47907	-2.71046
C	-4.86112	3.21771	-2.58601
H	-5.31359	3.94725	-1.89349
H	-5.62551	2.96938	-3.34366
H	-4.02717	3.72284	-3.09852
C	0.04607	1.72994	3.78166
H	-0.27365	2.69507	4.21283
H	-0.18536	0.95200	4.52768
H	-0.57286	1.52770	2.88831

C 5.61717 2.07363 2.51843
H 4.93932 2.64394 3.17359
H 6.08370 2.79149 1.82438
H 6.42346 1.65541 3.14645
C 3.37940 3.71847 -2.08848
H 2.48211 3.09123 -2.22045
H 4.04056 3.53219 -2.95307
H 3.06276 4.77685 -2.13099
C 4.59280 -4.93965 0.44584
H 4.34322 -6.00736 0.30823
H 5.34891 -4.87084 1.24788
H 5.04870 -4.57978 -0.48902
C -5.54161 -3.66981 -0.84191
H -5.56240 -4.77343 -0.78613
H -6.19430 -3.36171 -1.67800
H -5.97737 -3.27887 0.09104
C 2.76063 -4.63910 2.15467
H 1.84549 -4.10085 2.45599
H 3.50261 -4.51210 2.96226
H 2.51572 -5.71542 2.10562
C -3.57612 -3.67444 -2.42164
H -2.53772 -3.35853 -2.61119
H -4.20051 -3.28421 -3.24406
H -3.61007 -4.77741 -2.48313
C -2.51982 4.27083 2.22296
H -1.77833 3.46831 2.37912
H -3.24532 4.21283 3.05328
H -1.99313 5.23930 2.30696
C -1.69256 2.44766 -4.66403
H -2.76329 2.65701 -4.51459
H -1.60444 1.62743 -5.39884
H -1.23449 3.34813 -5.11205
C 2.38338 1.85059 4.73056
H 3.46435 1.79005 4.52844
H 2.12397 1.04776 5.44348
H 2.18809 2.81793 5.22784
C 5.39571 4.25303 -0.67226
H 5.17532 5.33426 -0.73206
H 6.07225 4.00913 -1.50999
H 5.94034 4.07743 0.26876
C -4.32065 5.22795 0.73127
H -3.89127 6.24252 0.81849
H -5.07065 5.11749 1.53400
H -4.84359 5.17064 -0.23663
Mg -1.73167 0.17402 0.04913
H 2.26728 -1.83469 1.92671
H 1.56971 -1.62233 2.11948

II
SCF (BP86) Energy = -2584.87310933
Enthalpy 0K = -2583.331090
Enthalpy 298K = -2583.330146
Free Energy 298K = -2583.558413
Lowest Frequency = 23.2516 cm^{-1}
Second Frequency = 26.0922 cm^{-1}
SCF (BP86-D3BJ) Energy = -2585.38267179
SCF (C6H6) Energy = -2584.89308127
SCF (BS2) Energy = -4450.66800297

Si -4.52323 -1.16899 1.56604
Si -4.45678 0.95825 -1.77364
Si 4.49381 -0.86444 -1.64278
Si 4.43578 1.16063 1.70698
Mg 1.66829 0.06866 -0.01109
Na 0.16700 -3.51922 0.05856
Na -0.08147 3.56036 0.03562
N -2.88052 -1.51624 0.96368
N -2.91242 1.40760 -1.00871
N 2.83774 1.52830 1.00208
N 2.95006 -1.40030 -0.92692
C -2.34827 -2.79114 1.22767
C 2.50264 -2.69787 -1.23368
C -1.54839 3.01070 -2.35018
C -2.57663 -3.91573 0.33620
C -2.44425 2.71189 -1.24612
C -1.54549 -3.05545 2.41052
C 2.30746 2.79909 1.30000

C	1.57708	-2.93984	-2.32827
C	2.92089	-3.86311	-0.46785
C	2.64467	3.97758	0.52047
C	-0.95978	-4.32560	2.60654
H	-0.36446	-4.50072	3.51055
C	-1.43275	-2.02940	3.54156
H	-1.82207	-1.07820	3.13855
C	5.82803	0.84324	0.42400
H	5.83325	1.69850	-0.27920
H	6.76472	0.95471	1.01086
C	-2.82678	3.82782	-0.39980
C	-1.98135	-5.17118	0.59206
H	-2.18434	-6.00310	-0.09294
C	-1.07194	4.32540	-2.54825
H	-0.41136	4.52662	-3.39974
C	5.87132	-0.48647	-0.35949
H	5.92283	-1.34174	0.34150
H	6.81547	-0.53818	-0.94213
C	-5.83481	-0.82777	0.20523
H	-5.78699	-1.66328	-0.52015
H	-6.80092	-0.96906	0.73542
C	1.19914	-1.82700	-3.30648
H	1.50074	-0.87734	-2.82986
C	1.38446	2.99731	2.40437
C	-5.85545	0.52394	-0.53646
H	-5.92479	1.35834	0.18837
H	-6.78371	0.59720	-1.14265
C	1.09181	-4.24158	-2.58193
H	0.41045	-4.39783	-3.42593
C	-1.15585	-5.38717	1.70748
H	-0.70446	-6.36763	1.89091
C	2.06586	5.23007	0.82159
H	2.34695	6.10098	0.21720
C	3.98976	-3.77074	0.62458
H	4.13003	-2.69476	0.83194
C	-2.31893	5.12288	-0.64379
H	-2.63822	5.94753	0.00507
C	1.16221	5.39599	1.88226
H	0.73422	6.37813	2.10761
C	2.39814	-5.14119	-0.76654
H	2.73834	-6.00151	-0.17837
C	-3.82541	3.65087	0.74275
H	-4.06173	2.57362	0.77111
C	-1.16681	1.94069	-3.37345
H	-1.49563	0.97717	-2.94573
C	3.64577	3.91984	-0.63316
H	4.01535	2.88176	-0.66606
C	0.84059	4.27486	2.66332
H	0.16206	4.39893	3.51503
C	1.47922	-5.34572	-1.80688
H	1.09343	-6.34671	-2.02534
C	4.36386	-0.35331	2.87355
H	3.69569	-0.16250	3.73045
H	5.37118	-0.57129	3.27212
H	4.00641	-1.26099	2.36230
C	-1.43944	5.38734	-1.70590
H	-1.06612	6.40065	-1.88624
C	-4.48682	0.33154	2.75029
H	-3.98810	0.06409	3.69766
H	-5.50935	0.67425	2.99111
H	-3.94147	1.18378	2.31323
C	-5.26100	-2.65196	2.55086
H	-6.17205	-3.03257	2.05743
H	-5.55575	-2.33139	3.56540
H	-4.56157	-3.49722	2.65503
C	4.20350	0.70752	-2.68901
H	3.62444	0.46659	-3.59671
H	5.16141	1.15817	-3.00629
H	3.64643	1.47225	-2.12428
C	-3.52612	-3.80066	-0.85530
H	-3.78084	-2.73017	-0.93647
C	5.24336	-2.18204	-2.83140
H	4.62779	-3.09234	-2.91360
H	6.25141	-2.48733	-2.50161
H	5.35270	-1.75851	-3.84512
C	-2.32480	-2.45506	4.73465
H	-3.36889	-2.61960	4.42943

```
H  -2.31404 -1.67803  5.51977
H  -1.95559 -3.39361  5.18659
C   1.03893  1.86249  3.36910
H   1.39420  0.93173  2.89057
C  -4.21307 -0.52869 -2.95173
H  -3.64446 -0.22726 -3.84791
H  -5.18578 -0.93163 -3.28718
H  -3.66069 -1.35051 -2.46718
C   0.00572 -1.79544  4.04408
H   0.51051 -2.73558  4.32968
H  -0.00136 -1.15454  4.94290
H   0.62368 -1.28670  3.28671
C   1.99124 -1.97669 -4.62813
H   3.07801 -1.99398 -4.45466
H   1.76497 -1.13969 -5.31294
H   1.71908 -2.91510 -5.14456
C   0.34956  1.86577 -3.63309
H   0.75088  2.80830 -4.04619
H   0.58045  1.07143 -4.36352
H   0.90224  1.63195 -2.70505
C  -0.30784 -1.75932 -3.61314
H  -0.67912 -2.67940 -4.09838
H  -0.52467 -0.92590 -4.30245
H  -0.89832 -1.59007 -2.69454
C  -5.19189  2.39305 -2.81825
H  -5.92396  2.97666 -2.23453
H  -5.72967  1.97848 -3.68934
H  -4.43220  3.09706 -3.19330
C  -0.47353  1.73323  3.63071
H  -0.89628  2.64074  4.09700
H  -0.67836  0.89530  4.31658
H  -1.02649  1.53695  2.69407
C   5.09524  2.62158  2.75967
H   4.30924  3.13113  3.33943
H   5.58768  3.38354  2.13302
H   5.85180  2.24531  3.47080
C   2.98129  4.23878 -1.99042
H   2.14424  3.55441 -2.20941
H   3.70882  4.14190 -2.81526
H   2.58875  5.27209 -2.01137
C   5.34232 -4.33390  0.12417
H   5.25559 -5.41156 -0.10450
H   6.12043 -4.21516  0.89891
H   5.68592 -3.82492 -0.78833
C  -4.83303 -4.58904 -0.60384
H  -4.63098 -5.67252 -0.52024
H  -5.53894 -4.44325 -1.44061
H  -5.33022 -4.26925  0.32468
C   3.60537 -4.48635  1.93939
H   2.63227 -4.15013  2.33447
H   4.36657 -4.28882  2.71386
H   3.55522 -5.58228  1.80833
C  -2.89471 -4.25700 -2.18682
H  -1.96329 -3.71112 -2.41017
H  -3.59282 -4.07931 -3.02340
H  -2.65984 -5.33703 -2.17986
C  -3.24131  4.05875  2.11221
H  -2.32425  3.49488  2.35310
H  -3.97018  3.86345  2.91825
H  -2.99418  5.13571  2.14404
C  -1.91169  2.15749 -4.71273
H  -3.00457  2.16196 -4.57955
H  -1.65854  1.35604 -5.42991
H  -1.62535  3.12045 -5.17337
C   1.78668  2.02900  4.71379
H   2.87831  2.06815  4.57452
H   1.55909  1.18539  5.38954
H   1.47927  2.96021  5.22339
C   4.85291  4.86019 -0.41589
H   4.54683  5.92197 -0.42856
H   5.59581  4.72173 -1.22093
H   5.35288  4.67047  0.54695
C  -5.13592  4.42823  0.48226
H  -4.95843  5.51904  0.46769
H  -5.87240  4.22104  1.27856
H  -5.58734  4.15167 -0.48331
Mg -1.69680 -0.02211 -0.00925
```

H   2.13084 -2.05404 1.28138
H   1.63957 -2.08404 1.85657

TS(II-III)
SCF (BP86) Energy = -2584.87294852
Enthalpy 0K = -2583.332091
Enthalpy 298K = -2583.331147
Free Energy 298K = -2583.558890
Lowest Frequency = -58.5131 cm^{-1}
Second Frequency = 22.9393 cm^{-1}
SCF (BP86-D3BJ) Energy = -2585.38264686
SCF (C6H6) Energy = -2584.89285512
SCF (BS2) Energy = -4450.66814089

Si -4.55067 -1.10828 1.54632
Si -4.42818 1.01948 -1.79659
Si 4.48735 -0.92261 -1.66481
Si 4.44368 1.07133 1.71694
Mg 1.67465 0.04481 -0.02023
Na 0.08592 -3.54952 0.01606
Na -0.03194 3.54651 0.04423
N -2.90006 -1.47137 0.97445
N -2.88333 1.44555 -1.02042
N   2.85704 1.47711 1.01032
N   2.92917 -1.42056 -0.95994
C -2.38280 -2.75078 1.24633
C   2.45591 -2.71050 -1.24915
C -1.48989 3.03359 -2.35005
C -2.63542 -3.88078 0.36827
C -2.39545 2.74368 -1.25160
C -1.56973 -3.01319 2.42440
C   2.34528 2.75510 1.30662
C   1.53575 -2.95026 -2.34905
C   2.84334 -3.87300 -0.46345
C   2.69781 3.92604 0.52348
C -1.00669 -4.29159 2.63012
H -0.40294 -4.46691 3.52782
C -1.43238 -1.97034 3.53804
H -1.69905 -0.99718 3.08877
C   5.83458 0.74400 0.43511
H   5.85616 1.61171 -0.25261
H   6.77010 0.83147 1.02814
C -2.76619 3.86159 -0.40289
C -2.06352 -5.14487 0.63662
H -2.28797 -5.98160 -0.03595
C -0.99594 4.34277 -2.54204
H -0.32869 4.53805 -3.38967
C   5.86288 -0.57190 -0.37132
H   5.90373 -1.43916 0.31568
H   6.80824 -0.62487 -0.95215
C -5.84147 -0.74562 0.17052
H -5.79971 -1.58067 -0.55585
H -6.81304 -0.87618 0.69363
C   1.18060 -1.83895 -3.33693
H   1.49761 -0.89200 -2.86501
C   1.42789 2.96790 2.41260
C -5.84101 0.60717 -0.56883
H -5.90274 1.44151 0.15668
H -6.76488 0.69346 -1.17995
C   1.03896 -4.24856 -2.59847
H   0.36581 -4.40363 -3.44938
C -1.23307 -5.36138 1.74764
H -0.79911 -6.34784 1.94088
C   2.13804 5.18761 0.82293
H   2.43159 6.05336 0.21703
C   3.89308 -3.77680 0.64584
H   4.05044 -2.69784 0.82563
C -2.24060 5.15070 -0.64045
H -2.55164 5.97730 0.00994
C   1.23821 5.36810 1.88456
H   0.82431 6.35661 2.10840
C   2.31137 -5.14830 -0.75816
H   2.63375 -6.00716 -0.15772
C -3.77108 3.69271 0.73512
H -4.01903 2.61797 0.75897
C -1.11447 1.96080 -3.37264
H -1.45285 0.99999 -2.94626

C	3.70504	3.84986	-0.62304
H	4.02556	2.79630	-0.67719
C	0.90220	4.25350	2.66926
H	0.22700	4.38937	3.52179
C	1.40567	-5.35156	-1.81089
H	1.01411	-6.35050	-2.02859
C	4.32055	-0.45369	2.86519
H	3.69070	-0.23260	3.74370
H	5.32311	-0.73996	3.23136
H	3.89169	-1.33096	2.35533
C	-1.35363	5.40691	-1.69827
H	-0.96626	6.41574	-1.87392
C	-4.51545	0.38905	2.73403
H	-4.02517	0.11965	3.68492
H	-5.53764	0.73888	2.96579
H	-3.96100	1.23707	2.30020
C	-5.33085	-2.58798	2.50436
H	-6.22066	-2.96615	1.97184
H	-5.67021	-2.26486	3.50413
H	-4.64013	-3.43553	2.64121
C	4.24435	0.64806	-2.72571
H	3.67214	0.41132	-3.63893
H	5.21533	1.07607	-3.03435
H	3.69510	1.42971	-2.17651
C	-3.57559	-3.76115	-0.83084
H	-3.83379	-2.69125	-0.90811
C	5.21886	-2.26924	-2.83197
H	4.58115	-3.16454	-2.91155
H	6.21458	-2.59672	-2.48624
H	5.35117	-1.86052	-3.84901
C	-2.44668	-2.27529	4.66940
H	-3.47851	-2.33716	4.29522
H	-2.40793	-1.48870	5.44422
H	-2.20797	-3.23890	5.15524
C	1.07375	1.83975	3.38199
H	1.41045	0.90256	2.90265
C	-4.19827	-0.47712	-2.96501
H	-3.60585	-0.19413	-3.85165
H	-5.17394	-0.85871	-3.31646
H	-3.67501	-1.30928	-2.46564
C	-0.02539	-1.86382	4.15974
H	0.32284	-2.82463	4.57890
H	-0.03863	-1.14477	4.99697
H	0.73072	-1.51311	3.44058
C	1.97454	-2.01064	-4.65471
H	3.06025	-2.04578	-4.47675
H	1.76558	-1.17386	-5.34526
H	1.68816	-2.94713	-5.16697
C	0.40207	1.87303	-3.62776
H	0.81174	2.81039	-4.04454
H	0.62853	1.07335	-4.35368
H	0.95104	1.63969	-2.69741
C	-0.32446	-1.74801	-3.64729
H	-0.71097	-2.66596	-4.12485
H	-0.52575	-0.91688	-4.34427
H	-0.91300	-1.56029	-2.73100
C	-5.13278	2.46465	-2.84840
H	-5.87430	3.04754	-2.27581
H	-5.65373	2.06012	-3.73428
H	-4.36144	3.16763	-3.20081
C	-0.43768	1.73294	3.65881
H	-0.84299	2.64674	4.12849
H	-0.64664	0.89857	4.34800
H	-1.00320	1.54365	2.72832
C	5.13223	2.50332	2.79563
H	4.34492	3.13169	3.24131
H	5.79317	3.16576	2.21170
H	5.73859	2.08493	3.61838
C	3.07754	4.23536	-1.98025
H	2.20982	3.60040	-2.22748
H	3.81235	4.12055	-2.79624
H	2.73883	5.28763	-1.98344
C	5.24279	-4.37920	0.18586
H	5.13999	-5.46190	-0.01031
H	6.01110	-4.24999	0.96861
H	5.60910	-3.90540	-0.73696
C	-4.88107	-4.55910	-0.60552

H -4.67596 -5.64293 -0.53489
H -5.57763 -4.40505 -1.44857
H -5.39053 -4.25447 0.32127
C   3.46772 -4.44936 1.97123
H   2.50197 -4.07217 2.34831
H   4.22533 -4.26085 2.75141
H   3.38022 -5.54540 1.86266
C -2.92289 -4.20200 -2.15781
H -1.99740 -3.64098 -2.36971
H -3.61327 -4.03053 -3.00210
H -2.67180 -5.27839 -2.15210
C -3.18811 4.08999 2.10816
H -2.27919 3.51393 2.35184
H -3.92291 3.90173 2.91048
H -2.92748 5.16363 2.14398
C -1.85275 2.18438 -4.71448
H -2.94604 2.19710 -4.58568
H -1.60285 1.38175 -5.43150
H -1.55717 3.14556 -5.17300
C   1.83774 1.99969 4.71853
H   2.92805 2.03078 4.56731
H   1.61026 1.15824 5.39701
H   1.54350 2.93368 5.23088
C   4.95213 4.72424 -0.35957
H   4.69387 5.79859 -0.33832
H   5.69954 4.57908 -1.15933
H   5.42699 4.47744 0.60284
C -5.07219 4.48421 0.47027
H -4.88320 5.57313 0.45773
H -5.81434 4.28373 1.26302
H -5.52209 4.21335 -0.49771
Mg -1.69537 0.00157 -0.00847
H   1.98852 -2.14850 1.35259
H   1.33350 -1.91561 1.65349

III
SCF (BP86) Energy = -2584.87309567
Enthalpy 0K = -2583.331369
Enthalpy 298K = -2583.330424
Free Energy 298K = -2583.559487
Lowest Frequency = 22.7234 cm^{-1}
Second Frequency = 24.0395 cm^{-1}
SCF (BP86-D3BJ) Energy = -2585.38316163
SCF (C6H6) Energy = -2584.89625844
SCF (BS2) Energy = -4450.66818486

Si 4.55735 0.99226 1.55275
Si 4.38868 -1.12992 -1.78903
Si -4.45546 1.02418 -1.69999
Si -4.47649 -0.95271 1.69700
Mg -1.68625 -0.02411 -0.04391
Na 0.03217 3.60552 0.00345
Na -0.06103 -3.53862 0.06350
N   2.91191 1.40823 0.99908
N   2.83454 -1.51504 -1.00889
N -2.90164 -1.41182 0.99920
N -2.88110 1.46682 -0.99757
C   2.44685 2.71217 1.25576
C -2.37060 2.74611 -1.26250
C   1.39774 -3.06303 -2.34185
C   2.75843 3.82494 0.37446
C   2.31228 -2.79982 -1.24414
C   1.62888 3.01780 2.42123
C -2.41855 -2.69540 1.31650
C -1.44366 2.97804 -2.35812
C -2.72895 3.90655 -0.46105
C -2.79001 -3.86788 0.54487
C   1.12908 4.32345 2.61766
H   0.51693 4.52836 3.50261
C   1.38946 1.97333 3.51459
H   1.46234 0.98500 3.02570
C -5.85119 -0.59217 0.40649
H -5.89190 -1.46335 -0.27614
H -6.79120 -0.65259 0.99582
C   2.65596 -3.93037 -0.40083
C   2.24872 5.11742 0.63436
H   2.51957 5.93898 -0.03986

```
C   0.86710 -4.35757 -2.53506
H   0.19317 -4.53260 -3.38171
C  -5.84347  0.71899 -0.40809
H  -5.86417  1.59106  0.27344
H  -6.78566  0.79228 -0.99194
C   5.83868  0.61364  0.17068
H   5.81273  1.44772 -0.55703
H   6.81311  0.72613  0.69266
C  -1.10923  1.86760 -3.35364
H  -1.45401  0.92558 -2.89167
C  -1.51170 -2.91189  2.43036
C   5.81150 -0.74049 -0.56581
H   5.85994 -1.57416  0.16153
H   6.73179 -0.84544 -1.17946
C  -0.92423  4.26954 -2.59781
H  -0.24977  4.41958 -3.44871
C   1.42148  5.37904  1.73715
H   1.03604  6.38670  1.92404
C  -2.25441 -5.13593  0.86042
H  -2.56069 -6.00308  0.26283
C  -3.77070  3.81240  0.65409
H  -3.94454  2.73376  0.81585
C   2.09339 -5.20373 -0.63882
H   2.38349 -6.03987  0.00904
C  -1.36169 -5.32023  1.92759
H  -0.96576 -6.31332  2.16334
C  -2.17822  5.17585 -0.74730
H  -2.48484  6.03495 -0.13877
C   3.66894 -3.79383  0.73403
H   3.96536 -2.73155  0.74470
C   1.05253 -1.98011 -3.36425
H   1.41367 -1.02839 -2.93615
C  -3.79044 -3.78318 -0.60719
H  -4.09390 -2.72481 -0.66942
C  -1.00952 -4.20364  2.70247
H  -0.34009 -4.34237  3.55915
C  -1.27283  5.37321 -1.80231
H  -0.86799  6.36791 -2.01524
C  -4.29622  0.57276  2.83721
H  -3.73295  0.31149  3.74921
H  -5.28722  0.95032  3.14752
H  -3.76511  1.40082  2.34084
C   1.19616 -5.43287 -1.69400
H   0.77952 -6.42990 -1.87007
C   4.48680 -0.53592  2.69868
H   4.01224 -0.28886  3.66273
H   5.50029 -0.92428  2.90611
H   3.90433 -1.35068  2.23912
C   5.38328  2.43285  2.53373
H   6.26575  2.81151  1.98955
H   5.74312  2.07517  3.51448
H   4.71113  3.28683  2.71445
C  -4.26616 -0.55757 -2.75541
H  -3.66981 -0.34899 -3.66006
H  -5.25034 -0.94304 -3.07792
H  -3.76087 -1.36168 -2.19599
C   3.69019  3.65567 -0.82508
H   3.89864  2.57475 -0.89756
C  -5.13795  2.39767 -2.86536
H  -4.48153  3.28140 -2.91927
H  -6.13388  2.74000 -2.53473
H  -5.25752  2.00612 -3.89065
C   2.50282  2.05742  4.58869
H   3.50643  1.93802  4.15951
H   2.35963  1.27308  5.35368
H   2.46964  3.03699  5.09929
C  -1.14467 -1.77963  3.39071
H  -1.46687 -0.84160  2.90379
C   4.19637  0.36348 -2.96873
H   3.59479  0.09078 -3.85231
H   5.18168  0.71525 -3.32444
H   3.69728  1.21378 -2.47514
C   0.02974  2.08509  4.23599
H  -0.03642  3.00388  4.84647
H  -0.09055  1.23980  4.93532
H  -0.82869  2.07282  3.54885
C  -1.88902  2.06926 -4.67546
```

H	-2.97470	2.12973	-4.50406
H	-1.69616	1.23288	-5.37118
H	-1.57635	3.00224	-5.17871
C	-0.46016	-1.85356	-3.62554
H	-0.89151	-2.77863	-4.04787
H	-0.66293	-1.04558	-4.34923
H	-1.00773	-1.61050	-2.69680
C	0.39550	1.74184	-3.65243
H	0.80904	2.65441	-4.11754
H	0.58228	0.91241	-4.35559
H	0.97100	1.53093	-2.73287
C	5.05968	-2.59949	-2.82810
H	5.77624	-3.20222	-2.24435
H	5.60300	-2.21467	-3.70928
H	4.27122	-3.27999	-3.18659
C	0.36714	-1.68960	3.67211
H	0.75845	-2.60183	4.15668
H	0.58412	-0.84774	4.35062
H	0.93936	-1.52165	2.74145
C	-5.21540	-2.35594	2.77883
H	-4.44948	-2.99028	3.25258
H	-5.87312	-3.01587	2.18853
H	-5.83398	-1.91482	3.58038
C	-3.16231	-4.18624	-1.95903
H	-2.28504	-3.56464	-2.20685
H	-3.89193	-4.06721	-2.77909
H	-2.83763	-5.24292	-1.95348
C	-5.11159	4.44966	0.21658
H	-4.99012	5.53401	0.04081
H	-5.87743	4.31948	1.00164
H	-5.49301	4.00129	-0.71304
C	5.03095	4.39494	-0.60834
H	4.87525	5.48752	-0.54739
H	5.71911	4.20190	-1.45025
H	5.52673	4.07630	0.32113
C	-3.32006	4.45282	1.98669
H	-2.35896	4.04877	2.35115
H	-4.07387	4.26749	2.77120
H	-3.20628	5.54824	1.89646
C	3.05413	4.11862	-2.15296
H	2.10193	3.60122	-2.35835
H	3.73199	3.90840	-2.99865
H	2.85511	5.20582	-2.15390
C	3.06697	-4.14564	2.11144
H	2.18861	-3.52094	2.34857
H	3.81001	-3.98647	2.91241
H	2.75133	-5.20406	2.15764
C	1.78913	-2.22253	-4.70389
H	2.88124	-2.26605	-4.57190
H	1.56395	-1.41270	-5.42103
H	1.46827	-3.17472	-5.16416
C	-1.91372	-1.91940	4.72677
H	-3.00398	-1.93905	4.57326
H	-1.67819	-1.07509	5.39902
H	-1.63173	-2.85240	5.24771
C	-5.05220	-4.63643	-0.34450
H	-4.81129	-5.71468	-0.31711
H	-5.79413	-4.48330	-1.14785
H	-5.52675	-4.37750	0.61494
C	4.93295	-4.64657	0.48048
H	4.69752	-5.72644	0.48685
H	5.68483	-4.46536	1.26865
H	5.39212	-4.41176	-0.49271
Mg	1.68312	-0.04029	0.00450
H	-1.71415	2.23918	1.50513
H	-1.09079	1.80384	1.45091

References

1. H.-Y. Liu, R. J. Schwamm, S. E. Neale, M. S. Hill, C. L. McMullin and M. F. Mahon M., *J. Am. Chem. Soc.*, 2021, **143**, 17851–17856.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, H. *J. Appl. Cryst*., 2009, **42**, 339-341.
3. G. M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3-8.
4. G. M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3-8.
5. Gaussian 16, Revision C.01, 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. V. 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. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. 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, Inc., Wallingford CT, 2016.
6. A. D. Becke, *Physical Review A* 1988, **38**, 3098-3100.
7. J. P. Perdew, *Physical Review B* 1986, **33**, 8822-8824.
8. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H Preuß, H., *Theoretica chimica acta* 1990, **77**, 123-141.
9. P. C. Hariharan and J. A. Pople, *Theoretica chimica acta* 1973, **28**, 213-222.
10. W. J. Hehre, R. Ditchfield and J. A. Pople, *The Journal of Chemical Physics* 1972, **56**, 2257-2261.
11. NBO 7.0, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, USA, 2003.