Supporting Information

S–H Bond Activation in Hydrogen Sulfide by NHC-stabilized Silyliumylidene Ions

Amelie Porzelt [1], Julia I. Schweizer [2], Ramona Baierl [1], Philipp J. Altmann [1], Max C. Holthausen [2] and Shigeyoshi Inoue [1,*]

[1] WACKER-Institute of Silicon Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85748 Garching bei München, Germany; amelie.porzelt@tum.de (A.P.); ga67liz@mytum.de (R.B.); philipp.altmann@mytum.de (P.J.A.)

[2] Institut für Anorganische Chemie, Goethe-Universität, Max-von-Laue-Straße 7, 60438 Frankfurt/Main, Germany; schweizer@chemie.uni-frankfurt.de (J.I.S.); Max.Holthausen@chemie.uni-frankfurt.de (M.C.H.)

* Correspondence: s.inoue@tum.de; Tel.: +49-89-289-13596

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1. NMR Spectra

Thiosilaaldehyde B

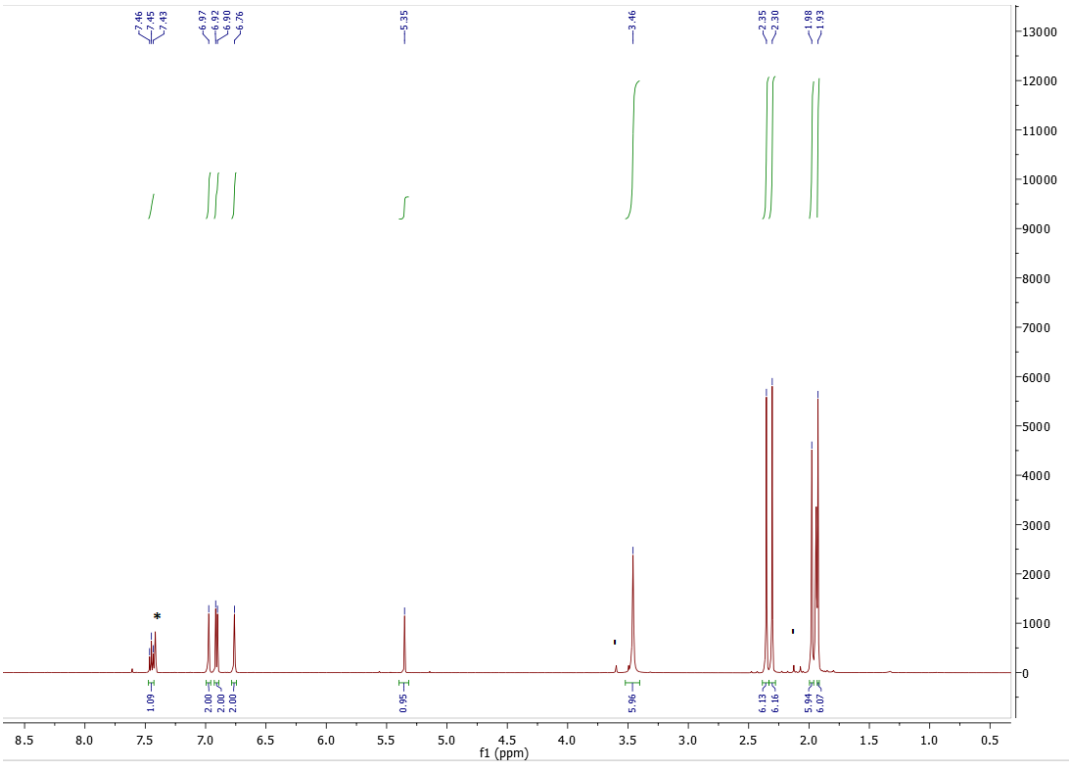


Figure S1: ^{1}H NMR spectrum of compound **B**, * benzene, ‘ traces of imidazolium salt.

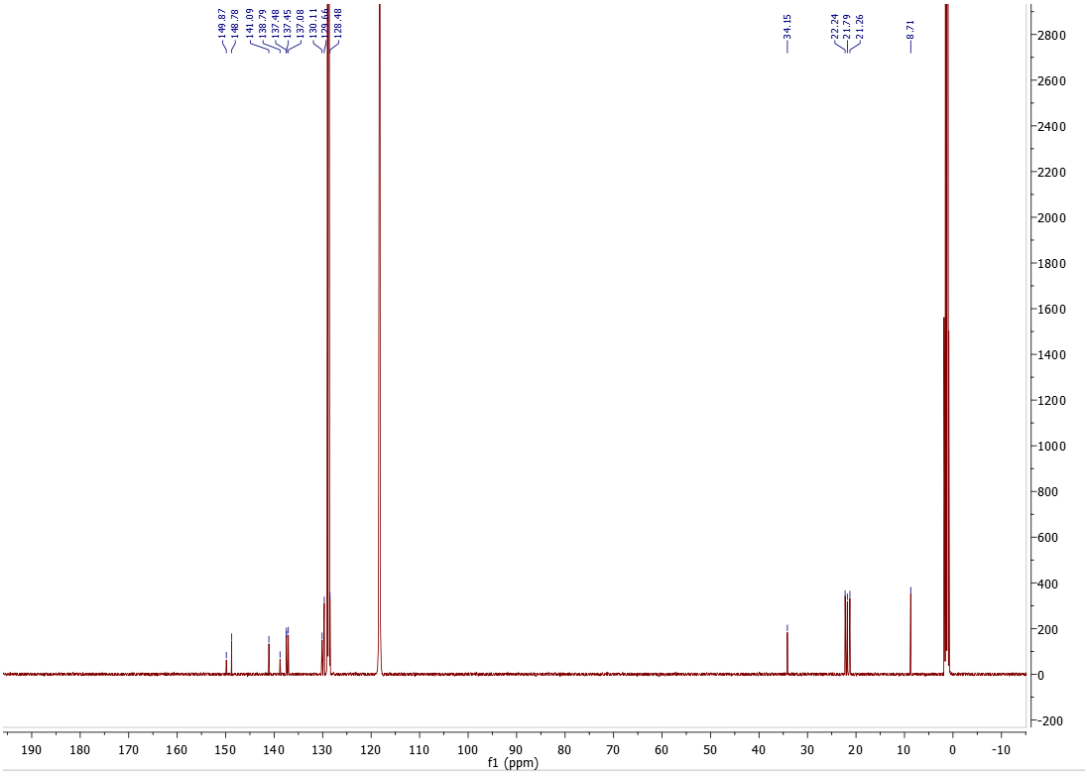


Figure S2: ^{13}C NMR spectrum of compound **B.**

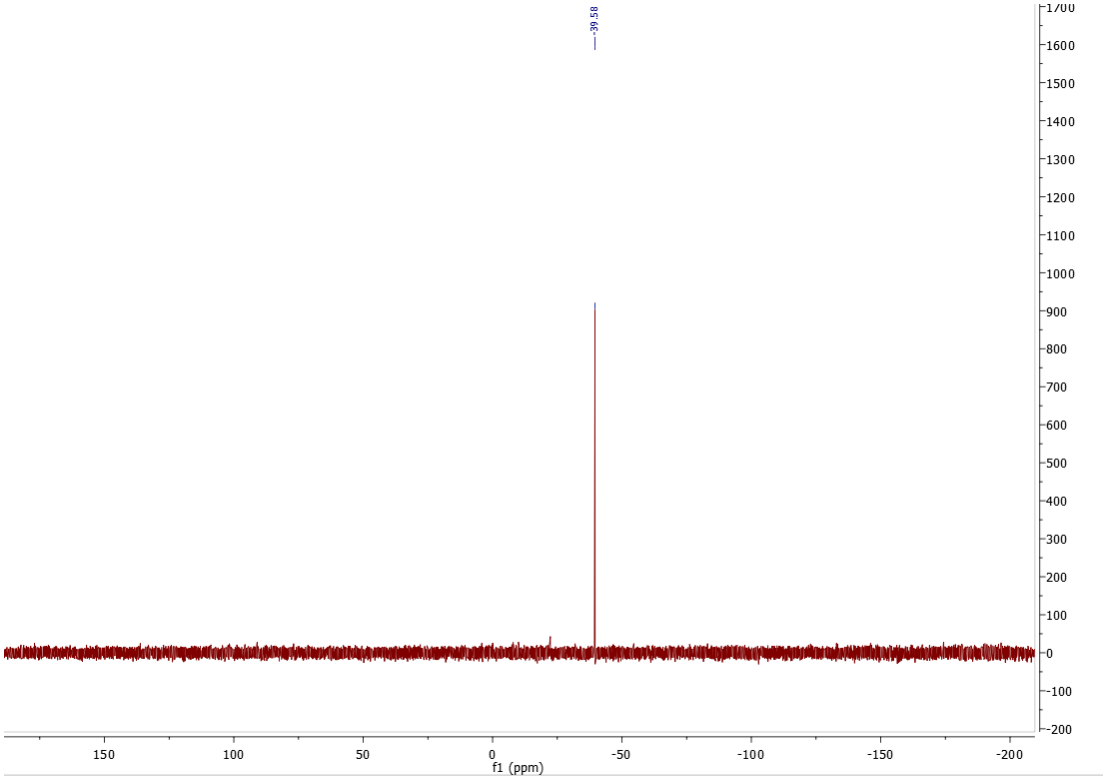


Figure S3: ^{29}Si NMR spectrum of compound **B.**

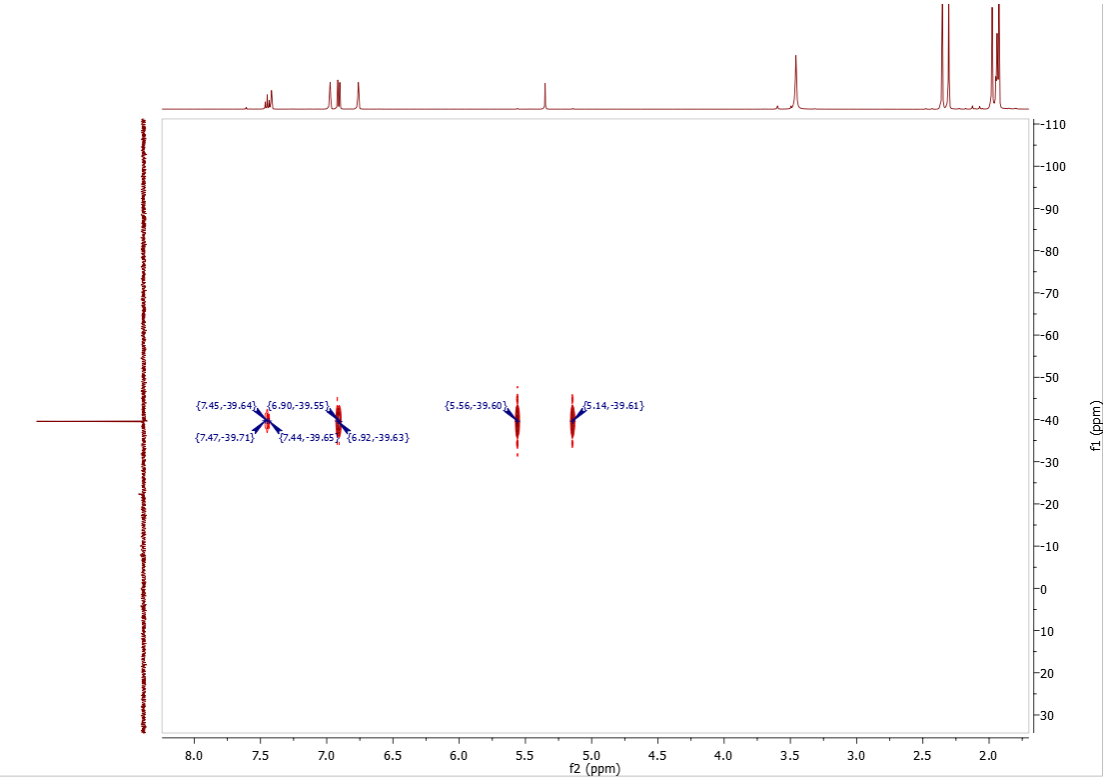


Figure S4: ^{1}H/^{29}Si-HMBC-NMR spectrum of compound **B.**

2. X-ray Crystallographic Data

General Information

The X-ray intensity data of **B** was collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), an IMS microsource with MoKα radiation (λ = 0.71073 Å) and a Helios mirror optic by using the APEX III software package.[S1] The measurement was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on the top of a microsampler, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[S2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[S2] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the APEX III software in conjunction with SHELXL-2014[S3] and SHELXLE[S4]. The H atom bound to the silicon atom was allowed to refine freely. Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and U_{iso}(H) = 1.5·U_{eq}(C). Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and U_{iso}(H) = 1.2·U_{eq}(C). Full-matrix least-squares refinements were carried out by minimizing $\Delta w(F_o^2-F_c^2)^2$ with SHELXL-97[S5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[S6] The image of the crystal structure was generated byPlaton.[S7] CCDC 1839062 contains the supplementary data for the structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

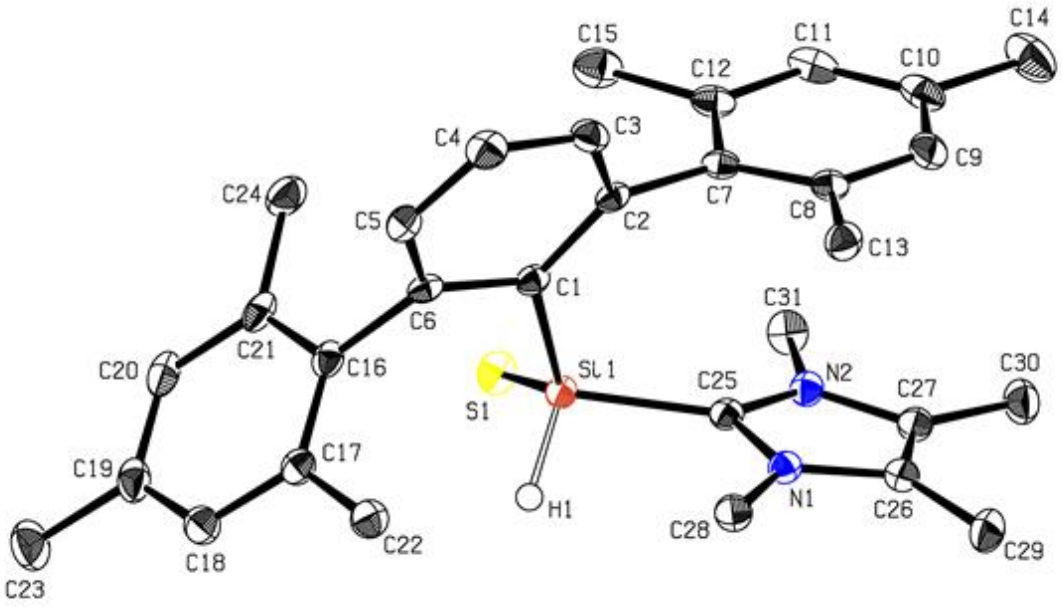


Figure S5: Molecular structure of thiosilaaldehyde **B** in the solid state with ellipsoids set at the 50% probability level. For clarity, hydrogen atoms have been omitted for clarity with exception of the Si-H proton. Selected bond lengths (Å) and angles (deg): S1–Si1 2.0227(9), Si1–C1 1.902(2), Si1–C25 1.934(2), Si1–H1 1.41(3), C1–Si1–C25 104.52(11), C1–Si1–S1 121.14(8), C25–Si1–S1 113.40(8), C1–Si1–H1 103.3(11), C25–Si1–H1 98.1(11), S1–Si1–H1 113.5(11).

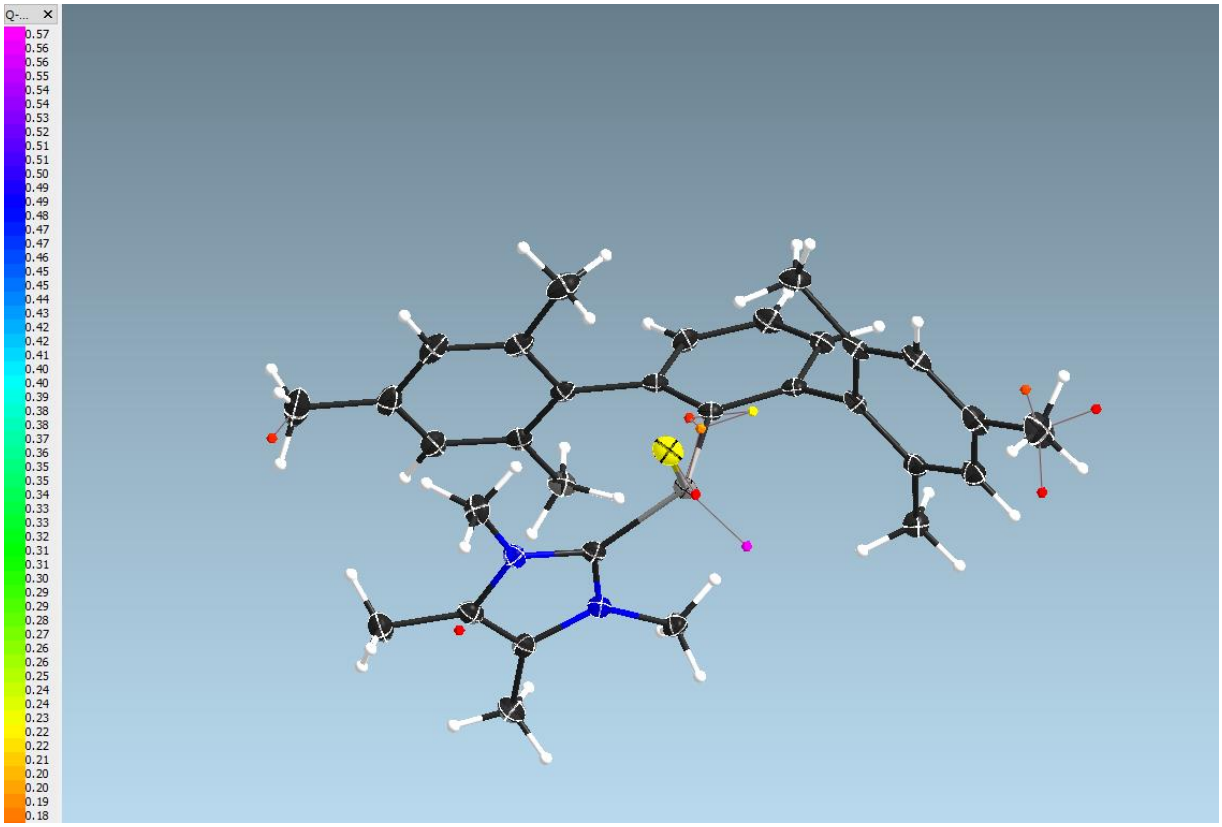


Figure S6: Screenshot of the refined structure of **B** showing a residual electron density of 0.57 close to the Si1 atom (pink dot) that suggests the presence of an H atom in this position. Accordingly, an H atom was placed in this position and refined freely.

Table S1: Sample and crystal data for **B**.

Identification code	**PorAm7_2**	
Chemical formula	$C_{31}H_{38}N_2SSi$	
Formula weight	498.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.064 mm x 0.097 mm x 0.116 mm	
Crystal habit	clear colorless fragment	
Crystal system	orthorhombic	
Space group	*P* 21 21 21	
Unit cell dimensions	*a* = 9.1908(5) Å	α = 90°
	b = 12.7408(6) Å	β = 90°
	c = 23.2296(12) Å	γ = 90°
Volume	2720.1(2) Å^3	
Z	4	
Density (calculated)	1.218 g/cm^3	
Absorption coefficient	0.185 mm^{-1}	
F(000)	1072	

Table S2: Data collection and structure refinement for **B**.

Diffractometer	**Bruker D8 Venture, CMOS detector (Bruker Photon-100)**
Radiation source	IMS microsource, Mo
Theta range for data collection	2.32 to 25.03°
Index ranges	-10<=*h*<=10, -15<=*k*<=15, -27<=*l*<=27
Reflections collected	51362
Independent reflections	4804 [R(int) = 0.0437]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.6679 and 0.7453
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	4804 / 0 / 330
Goodness-of-fit on F^2	1.050
Δ/σ_{max}	0.007
Final R indices	4590 data; $I>2\sigma(I)$ $R1 = 0.0294$, $wR2 = 0.0698$
	all data $R1 = 0.0322$, $wR2 = 0.0717$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0319P)^2+1.3450P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.218 and −0.233 eÅ^{-3}
R.M.S. deviation from mean	0.041 eÅ^{-3}

3. Computational Details

A) Evaluation of the computational model

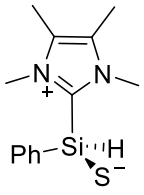
Table S3. Comparison of selected bond lengths (Å) and angles (°) for the computed and experimental structures of **B**. Geometries are calculated at the M06-L/6-31+G(d,p) level of theory, $\mathbf{B^{Model}}$: R = Ph, **11**: R = 2,6-Ph_2-C_6H_3; both $ImMe_2H_2$. Experimental data taken from the single-crystal X-ray analysis of **B**.

bond/angle	exp.	calc. B^{Model}	Δ(calc.-exp.)	calc. 11	Δ(calc.-exp.)
Si-S	2.0227(9)	2.01	-0.01	2.01	-0.01
Si-H	1.41(3)	1.50	0.09	1.50	0.09
Si-C^{NHC}	1.934(2)	1.94	0.01	1.97	0.04
Si-$C^{Ph/mTer}$	1.902(2)	1.89	-0.01	1.92	0.01
S-Si-H	113.5(11)	120.9	7.4	118.2	4.7
$C^{Ph/mTer}$-Si-S	121.14(8)	119.2	-1.9	123.2	2.1
$C^{Ph/mTer}$-Si-H	113.3(11)	106.0	-7.3	101.4	-11.9

B) NBO and QTAIM results

NBO Analyses of B^{Model} and 12

Table S4. Selected results of the NBO and NRT analysis of $\mathbf{B^{Model}}$; wave functions computed at the M06-L/6-311++G(2d,2p)//M06-L/6-31+G(d,p) level of DFT.



Bond	NBO analysis (NLMOs)[a]			NRT analysis[b]	
	pol.	hybr.	WBI	bond	tot/cov/ionic
Si-S	38% (Si)	$sp^{2.13}$(Si)	1.38	Si-S	1.28/0.80/0.48
	62% (S)	$sp^{3.55}$(S)			
Si-H	41% (Si)	$sp^{2.76}$ (Si)	0.84	Si-H	0.96/0.78/0.18
	59% (H)	$sp^{0.01}$ (H)			
Si-C^{NHC}	23% (Si)	$sp^{5.27}$ (Si)	0.63	Si-C^{NHC}	0.76/0.34/0.42
	77% (C^{NHC})	$sp^{1.31}$ (C^{NHC})			
Si-C^{Ph}	28% (Si)	$sp^{2.80}$ (Si)	0.72	Si-C^{Ph}	0.98/0.53/0.45
	72% (C^{Ph})	$sp^{2.29}$ (C^{NHC})			

[a] pol. =polarization, hybr. = hybridization, WBI = Wiberg bond index.
[b] Natural bond order (tot/cov/ionic: total/covalent/ionic).

Table S5. Results of NRT analysis of $\mathbf{B^{Model}}$.

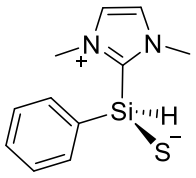
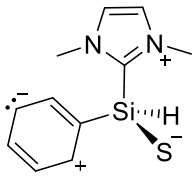
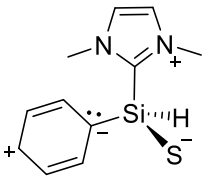
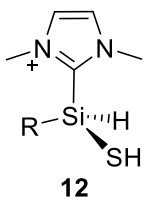
Lewis structure			
Resoance weight	10.4 %	8.9 %	8.9 %

Table S6. Fragment charges obtained from NPA analysis of **12**; wave functions computed at the M06-L/6-311++G(2d,2p)//M06-L/6-31+G(d,p) level of DFT.



12

Bond	NPA charge / e
Si	1.25
S	-0.38
H_1	0.18
H_2	-0.17

QTAIM Analyses of B^{Model} and 1-4

Table S7. Selected properties of the electron density distribution of $\mathbf{B^{Model}}$ and **1-4**: Bond path lengths $d_{A–B}$, and distances to bcps $d_{A–bcp}$ and $d_{bcp–B}$, the electron density ρ_{bcp}, the Laplacian of the electron density $\nabla^2\rho_{bcp}$, the total energy density H_{bcp}, the bond ellipticity $\varepsilon_{bcp} = \lambda_1/\lambda_2 - 1$ (derived from the two negative eigenvalues of the Hessian matrix of the electron density at the bcp with $\lambda_1 \geq \lambda_2$), delocalization index $\delta_{Si,S}$ (number of electrons shared between two atoms).

	$d_{Si\text{-}S}$ [Å]	$d_{Si\text{-}bcp}$ [Å]	$d_{bcp\text{-}S}$ [Å]	ρ_{bcp} [eÅ^{-3}]	$\nabla^2\rho_{bcp}$ [eÅ^{-5}]	H_{bcp} [E_hÅ^{-3}]	ε_{bcp}	$\delta_{Si,S}$
B^{Model}								
Si-S	2.00	0.75	1.26	0.78	3.33	-0.52	0.01	0.78
Si-H	1.47	0.72	0.74	0.79	3.15	-0.51	0.01	0.48
Si-C^{NHC}	1.94.	0.75	1.20	0.65	4.69	-0.36	0.09	0.35
Si-C^{Ph}	1.89	0.73	1.16	0.81	4.05	-0.54	0.07	0.46
1								
Si-S	2.13	0.77	1.36	0.66	1.36	-0.43	0.12	0.56
Si-H	1.47	0.72	0.74	0.83	3.54	-0.55	0.02	0.52
Si-C^{NHC}	1.91	0.73	1.18	0.72	4.73	-0.43	0.07	0.40
Si-C^{Ph}	1.85	0.72	1.13	0.87	4.23	-0.61	0.09	0.52
S-H	1.33	0.82	0.51	1.40	-13.00	-1.30	0.07	1.13
2								
Si-S	1.95	0.73	1.22	0.83	5.24	-0.55	0.21	1.15
Si-H	1.47	0.73	0.75	0.82	3.20	-0.54	0.05	0.58
Si-C^{Ph}	1.84	0.72	1.13	0.86	4.76	-0.09	0.17	0.58
3								
Si-S	2.14	0.78	1.37	0.64	1.36	-0.40	0.10	0.57
Si-H	1.47	0.73	0.74	0.82	3.75	-0.53	0.01	0.55
Si-H	1.47	0.73	0.74	0.82	3.75	-0.53	0.01	0.55
Si-H	1.46	0.72	0.74	0.82	3.93	-0.53	0.00	0.54
S-H	1.33	0.81	0.52	1.39	-12.77	-1.32	0.08	1.16
4								
Si-S	1.94	0.73	1.21	0.83	5.39	-0.56	0.23	1.25
Si-H	1.47	0.73	0.74	0.83	3.27	-0.55	0.05	0.60
Si-H	1.47	0.73	0.74	0.83	3.27	-0.55	0.05	0.60

C) Mechanistic investigations

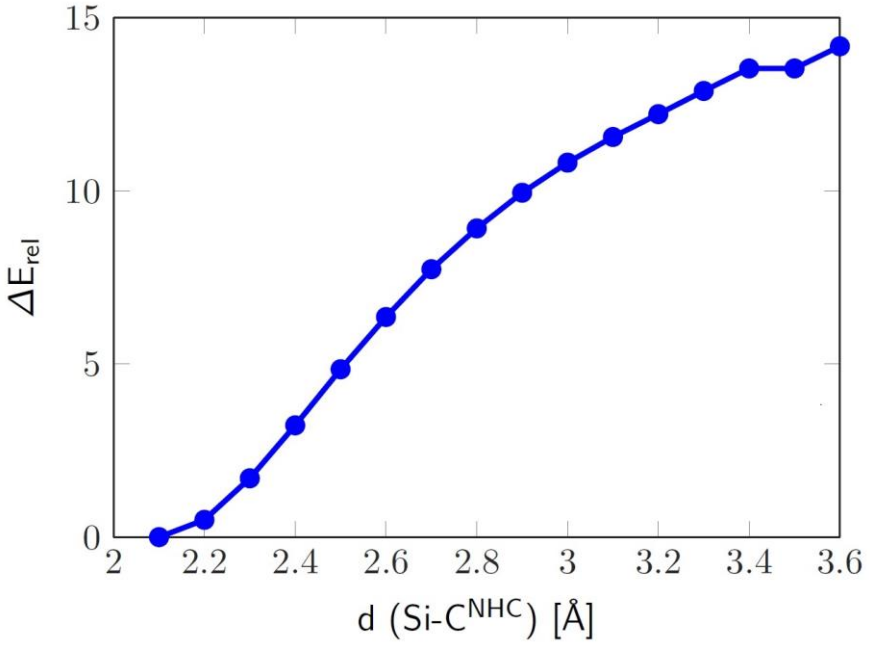


Figure S7. Results for the relaxed scan along the Si-C^{NHC} bond in **10**.

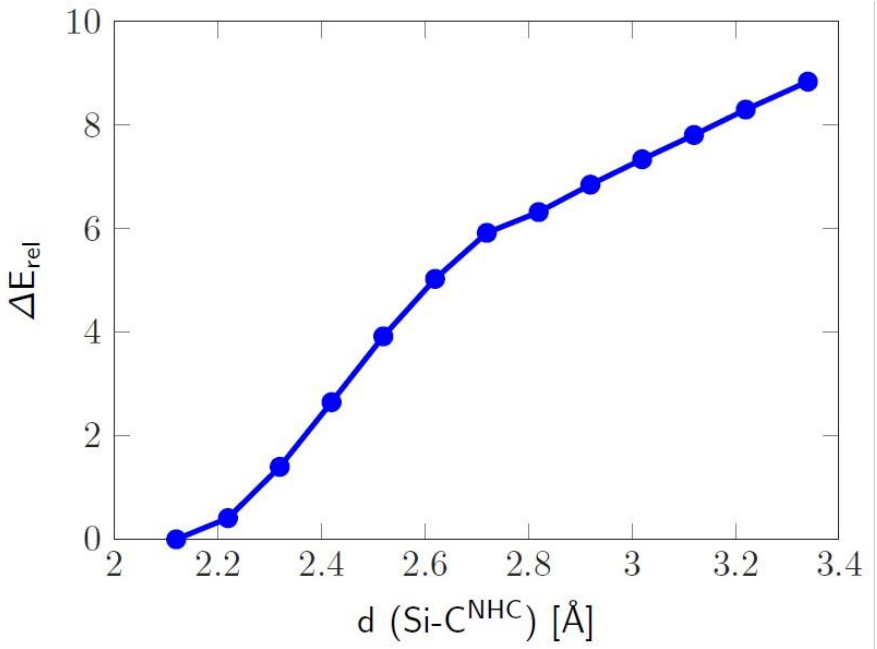


Figure S8. Results for the relaxed scan along the second Si–C^{NHC} bond in **10**.

D) Calculated structures & energies

Table S8. Calculated energies at the M06-L/6-311+G(d,p)(SMD: acetonitrile/benzene) level of density functional theory

Structure	E(SCF) [H/particle]
5	-1748.1361
IMe$_2$H$_2$	-304.7491
TS56	-2052.8550
6	-2052.8551
TS67	-2052.8399
7	-2052.8858
8	-1592.5187
H$_2$S	-399.4053
TS89	-1991.9189
TS^{2}89	-2391.3115
9	-1991.9379
TS910	-1991.9137
10	-1991.9348
TS1011	-1991.9238
11	-1686.7544
$^+$H-IMe$_2$H$_2$	-305.2407
12	-1687.1978
IMe$_2$H$_2$	-304.7540
TS1211	-1991.9379
TS1213	-1991.9143
13	-1686.7039
TS1311	-1686.6685
TS^{H2S}1311	-2086.1036

Table S9: Cartesian coordinated (x,y,z) for the optimized structure of **B^{Model}**.

C 1.34530 -0.35618 0.17422
N 1.19755 -1.44885 -0.61580
C -0.02488 -1.80957 -1.31980
H -0.33932 -0.98033 -1.95746
H -0.82648 -2.03185 -0.61306
H 0.17955 -2.68573 -1.93432
C 2.39747 -2.11483 -0.75036
C 3.31569 -1.42295 -0.02522
N 2.65313 -0.35448 0.53527
H 4.36772 -1.59402 0.13745
H 2.48855 -3.01055 -1.34358
C 3.27938 0.73108 1.27493
H 2.87529 0.78575 2.28712
H 3.07326 1.67302 0.75435

H 4.35306 0.55170 1.31658
Si 0.16495 1.15905 0.46692
C -1.56708 0.41799 0.40167
C -4.11312 -0.76084 0.18776
C -2.03168 -0.47799 1.37654
C -2.41407 0.72353 -0.67181
C -3.67545 0.14066 -0.78166
C -3.29106 -1.06734 1.27260
H -3.63528 -1.75928 2.03759
H -1.39947 -0.72037 2.23170
H -5.09629 -1.21710 0.10496
H -4.31968 0.39029 -1.62112
H -2.06199 1.42827 -1.42554
S 0.70564 2.51007 -0.91861
H 0.46372 1.38434 1.91684

Table S10: Cartesian coordinated (x,y,z) for the optimized structure of **1**.

C 1.40679 -0.33924 0.09931
N 1.25336 -1.50239 -0.57851
C 0.01798 -1.98733 -1.19351
H -0.33388 -1.27446 -1.94045
H -0.75487 -2.12655 -0.43662
H 0.23130 -2.93855 -1.67747
C 2.45216 -2.16905 -0.64346
C 3.37276 -1.40251 0.00530
N 2.71514 -0.28446 0.45027
H 4.42571 -1.55597 0.18030
H 2.54909 -3.11955 -1.14343
C 3.33677 0.80798 1.19503
H 3.04128 0.76612 2.24474
H 3.03445 1.76385 0.76266
H 4.41769 0.70843 1.11913
Si 0.12979 1.01884 0.51703
C -1.59733 0.36969 0.38462
C -4.15970 -0.73834 0.14973
C -2.13641 -0.41128 1.42255
C -2.37131 0.59837 -0.76360
C -3.64463 0.04762 -0.88010
C -3.40834 -0.96503 1.30263
H -3.81724 -1.56334 2.11130
H -1.56553 -0.58556 2.33379
H -5.15386 -1.16562 0.05983
H -4.23798 0.23735 -1.76940
H -1.97459 1.21455 -1.56936
H 0.49690 1.40180 1.89659
S 0.65727 2.50842 -0.91434
H -0.08379 3.48170 -0.35388

Table S11: Cartesian coordinated (x,y,z) for the optimized structure of **2**.

Si -1.48831 -0.72395 0.00018
C 0.29580 -0.25770 -0.00011
C 3.01005 0.43130 0.00007
C 1.28794 -1.25399 -0.00013

C 0.69052 1.09176 0.00008
C 2.03781 1.43311 0.00005
C 2.63690 -0.91201 -0.00011
H 3.39612 -1.68907 -0.00022
H 0.99966 -2.30399 -0.00023
H 4.06293 0.69937 0.00007
H 2.33438 2.47789 0.00006
H -0.07232 1.86809 0.00004
S -3.00298 0.50575 -0.00012
H -1.59099 -2.20386 0.00058

Table S12: Cartesian coordinated (x,y,z) for the optimized structure of **3**.

Si -0.03669 1.03236 0.00000
S -0.03669 -1.11090 0.00000
H 1.30122 -1.23771 0.00000
H 0.63164 1.57644 1.20250
H 0.63164 1.57644 -1.20250
H -1.46392 1.40624 0.00000

Table S13: Cartesian coordinated (x,y,z) for the optimized structure of **4**.

Si 0.00000 0.00000 -0.91900
H 0.00000 1.21141 -1.76996
H 0.00000 -1.21141 -1.76996
S 0.00000 0.00000 1.02537

Table S14: Cartesian coordinated (x,y,z) for the optimized structure of **5**.

Si 0.21821 -0.97178 -0.88903
C 0.56957 0.84109 -0.21600
C 0.92135 3.34750 1.08521
C 1.86005 1.30964 0.14122
C -0.51540 1.73656 -0.02081
C -0.33687 2.95919 0.64026
C 2.01307 2.53536 0.80731
H -1.19560 3.61329 0.78065
H 1.05648 4.29566 1.59824
H 3.01544 2.86124 1.07756
C -1.26441 -1.28846 0.41039
N -1.36280 -1.03360 1.74151
C -0.36300 -0.35605 2.55516
H -0.49829 0.72819 2.50344
H 0.63194 -0.61409 2.19097
H -0.47290 -0.69554 3.58590
C -2.57053 -1.47331 2.23661
C -3.24487 -2.02813 1.19630
N -2.43044 -1.90834 0.09230
C -2.77788 -2.42033 -1.22359
H -2.84844 -3.51014 -1.18996
H -1.98889 -2.12757 -1.92084
H -3.73102 -1.99388 -1.54201
Cl 1.55335 -2.18445 0.37926
C -1.88304 1.42976 -0.50782
C -4.48438 0.91624 -1.45832
C -2.10102 1.05034 -1.84206
C -2.99803 1.55941 0.33350

C -4.28427 1.29818 -0.13237
C -3.38748 0.80003 -2.31214
C 3.09419 0.56635 -0.19945
C 5.44933 -0.81051 -0.87378
C 4.12369 0.40476 0.73648
C 3.27772 0.04529 -1.48694
C 4.44220 -0.63772 -1.82119
C 5.28648 -0.28389 0.40655
H 2.49541 0.18080 -2.23125
H 4.56221 -1.03778 -2.82426
H 6.35546 -1.35191 -1.13092
H 6.06406 -0.41910 1.15370
H 3.98894 0.79180 1.74454
H -1.25057 0.97249 -2.51452
H -3.53351 0.51934 -3.35225
H -5.48848 0.72275 -1.82647
H -2.84470 1.84999 1.37188
H -5.13200 1.39370 0.54146
H -4.21661 -2.49252 1.14367
H -2.83709 -1.36038 3.27570

Table S15: Cartesian coordinated (x,y,z) for the optimized structure of **ImMe$_2$H$_2$**.

C -0.00000 0.99032 0.00001
N -1.05965 0.12162 0.00002
C -2.43525 0.56631 -0.00003
H -2.96202 0.20807 -0.88965
H -2.43052 1.65574 -0.00031
H -2.96196 0.20854 0.88983
C -0.67880 -1.21081 0.00000
C 0.67881 -1.21080 0.00002
N 1.05965 0.12162 0.00001
H 1.38522 -2.02771 -0.00004
H -1.38521 -2.02771 0.00014
C 2.43525 0.56631 -0.00002
H 2.96196 0.20848 0.88980
H 2.43051 1.65574 -0.00022
H 2.96202 0.20815 -0.88968

Table S16: Cartesian coordinated (x,y,z) for the optimized structure of **TS56**.

Si -0.14785 0.29215 -0.88827
Cl 1.46334 -0.34241 -2.22595
C 0.86377 2.53761 -0.33911
C 0.30186 -0.37294 0.89908
C 0.49616 -1.40930 3.55743
C 1.54993 -0.77758 1.44605
C -0.83412 -0.49783 1.74763
C -0.73399 -1.01975 3.04409
C 1.62195 -1.28210 2.75796
H -1.63390 -1.09323 3.65175
H 0.57745 -1.79553 4.56994
H 2.59683 -1.56850 3.14735
C -0.08396 4.57950 -0.77942
C -0.05778 4.43582 0.57121
C 0.53838 3.10874 -2.70782
H -0.43755 5.39198 -1.39664

H 0.48165 4.01774 -3.30950
H 1.46112 2.57066 -2.92959
H -0.30122 2.44088 -2.94795
C 0.79641 2.69758 2.14834
H -0.37391 5.10152 1.36053
H -0.11298 2.30271 2.61632
H 1.20296 3.49365 2.77798
H 1.52259 1.88705 2.07795
N 0.50223 3.44398 -1.30425
N 0.53393 3.20612 0.81740
C -1.12710 -1.49664 -1.27492
N -0.79143 -2.79916 -1.07298
C 0.45955 -3.24579 -0.48333
H 1.26448 -2.58135 -0.80462
H 0.66719 -4.25995 -0.82806
H 0.39481 -3.23188 0.60882
C -1.79440 -3.64680 -1.49177
C -2.79067 -2.85945 -1.97598
N -2.36149 -1.55701 -1.83980
H -3.74915 -3.10674 -2.40443
H -1.70901 -4.72003 -1.42003
C -3.15856 -0.40376 -2.22319
H -2.57489 0.49295 -1.99490
H -4.08752 -0.39035 -1.64756
H -3.38100 -0.44495 -3.29236
C 2.85230 -0.77477 0.72481
C 5.39651 -0.83893 -0.47774
C 3.60605 -1.95821 0.68657
C 3.40553 0.37916 0.15854
C 4.66555 0.34636 -0.43040
C 4.85892 -1.99687 0.08083
C -2.20987 -0.09870 1.33465
C -4.86823 0.66074 0.79263
C -3.25367 -1.03227 1.39223
C -2.52337 1.22440 0.98475
C -3.83963 1.60079 0.72365
C -4.57068 -0.66141 1.11897
H 3.19071 -2.86338 1.12852
H 5.41521 -2.93020 0.04773
H 6.37615 -0.86185 -0.94770
H 5.07253 1.25378 -0.86945
H 2.81444 1.29256 0.14085
H -4.05974 2.63474 0.47061
H -5.89466 0.95783 0.59359
H -1.73032 1.96576 0.93950
H -5.36334 -1.40369 1.17186
H -3.01963 -2.06441 1.64934

Table S17: Cartesian coordinated (x,y,z) for the optimized structure of **6**.

Si -0.03808 0.55446 -0.71842
Cl 1.35156 -0.37093 -2.13009
C 1.24520 2.11479 -0.19647
C 0.15926 -0.44108 0.94805
C 0.07314 -1.98988 3.34759
C 1.29954 -1.15183 1.41149

C -1.02022 -0.54198 1.73799
C -1.05560 -1.30845 2.91144
C 1.23613 -1.90872 2.59604
H -1.97715 -1.34446 3.48897
H 0.04886 -2.57003 4.26630
H 2.13225 -2.43098 2.92520
C 1.53176 4.36496 -0.51958
C 1.39446 4.17011 0.81424
C 1.41298 2.90104 -2.53754
H 1.68744 5.26651 -1.09182
H 1.54660 3.85294 -3.05360
H 2.17863 2.19048 -2.85336
H 0.43268 2.46835 -2.79132
C 1.17948 2.20904 2.32559
H 1.41783 4.86669 1.63801
H 0.16028 1.91778 2.59821
H 1.54450 2.93579 3.05392
H 1.80296 1.31376 2.37192
N 1.47101 3.12015 -1.11384
N 1.24607 2.80488 1.00565
C -1.45071 -1.02404 -1.36472
N -1.44684 -2.38207 -1.27493
C -0.37067 -3.15287 -0.67933
H 0.58083 -2.66948 -0.91194
H -0.37904 -4.15907 -1.10225
H -0.48887 -3.20987 0.40779
C -2.59184 -2.93423 -1.81413
C -3.34180 -1.89547 -2.26566
N -2.62791 -0.74777 -1.98460
H -4.30189 -1.87145 -2.75751
H -2.76599 -3.99917 -1.83887
C -3.09632 0.58807 -2.30853
H -2.38799 1.29982 -1.87374
H -4.08936 0.74417 -1.87977
H -3.13620 0.72090 -3.39330
C 2.60531 -1.24860 0.69875
C 5.10138 -1.57663 -0.56801
C 3.07483 -2.52020 0.33618
C 3.43420 -0.14966 0.44659
C 4.66628 -0.31170 -0.18019
C 4.30065 -2.68526 -0.30173
C -2.29502 0.13302 1.37448
C -4.76755 1.36674 0.81950
C -3.47808 -0.61594 1.30330
C -2.37660 1.51771 1.15567
C -3.60267 2.12834 0.89092
C -4.70201 -0.01180 1.01944
H 2.45347 -3.38952 0.54706
H 4.62949 -3.67998 -0.59111
H 6.05928 -1.69893 -1.06614
H 5.28801 0.55960 -0.36949
H 3.10366 0.84508 0.72302
H -3.64379 3.20397 0.74122
H -5.72125 1.84513 0.61142
H -1.48021 2.12718 1.22331

H -5.60258 -0.61771 0.95956
H -3.42511 -1.69322 1.45351

Table S18: Cartesian coordinated (x,y,z) for the optimized structure of **TS67**.

Si 0.16589 -0.59789 0.63530
Cl -0.45603 -2.74610 -1.30244
C -1.76253 -0.75164 1.18562
C 0.09785 1.19619 -0.09496
C 0.28243 3.90427 -0.99764
C -1.01664 1.86541 -0.67531
C 1.30474 1.95078 0.01751
C 1.38822 3.26936 -0.44307
C -0.90873 3.20283 -1.09798
H 2.33208 3.80064 -0.33921
H 0.35114 4.93030 -1.34824
H -1.77899 3.67607 -1.54741
C -3.62685 -1.43708 2.29482
C -3.27408 -0.24460 2.82229
C -2.84206 -2.97405 0.55310
H -4.44842 -2.09804 2.51899
H -3.74333 -3.47436 0.91207
H -2.92173 -2.76991 -0.51339
H -1.97222 -3.61360 0.69724
C -1.43154 1.36342 2.54020
H -3.71878 0.35353 3.60148
H -0.36497 1.13312 2.64396
H -1.82779 1.69940 3.49963
H -1.54168 2.16105 1.80135
N -2.70892 -1.73841 1.30788
N -2.14221 0.16448 2.15289
C 1.61912 -1.13759 -0.63080
N 1.98164 -0.75676 -1.88603
C 1.15552 0.00588 -2.80070
H 0.12860 -0.35653 -2.72273
H 1.51402 -0.17083 -3.81536
H 1.19255 1.07567 -2.57815
C 3.17378 -1.34460 -2.24993
C 3.58565 -2.08835 -1.19298
N 2.63707 -1.93247 -0.20630
H 4.46371 -2.69709 -1.04854
H 3.61860 -1.18002 -3.21870
C 2.65103 -2.66667 1.04455
H 2.21745 -2.04123 1.82801
H 3.68391 -2.91924 1.29068
H 2.05297 -3.57731 0.94626
C -2.35534 1.25436 -0.89804
C -4.93315 0.23174 -1.40059
C -2.52967 0.06009 -1.60910
C -3.50159 1.92625 -0.44782
C -4.77687 1.41710 -0.68589
C -3.80202 -0.44094 -1.86387
C 2.56312 1.39741 0.59619
C 4.99227 0.42521 1.63980
C 3.71642 1.33166 -0.19704
C 2.66139 0.99699 1.93692

C 3.86300 0.51725 2.45321
C 4.91734 0.84209 0.31277
H -1.66570 -0.51294 -1.93384
H -3.90221 -1.36766 -2.42410
H -5.92638 -0.16341 -1.59638
H -5.64819 1.95026 -0.31407
H -3.38552 2.85550 0.10871
H 3.91719 0.21807 3.49685
H 5.92717 0.04475 2.04288
H 1.79000 1.07229 2.57971
H 5.79185 0.78339 -0.33016
H 3.65664 1.64800 -1.23715

Table S19: Cartesian coordinated (x,y,z) for the optimized structure of **7**.

Si 0.16060 -0.10930 0.94001
C 1.32506 -1.07138 -0.30011
C 0.17422 1.66970 0.19273
C 0.48003 4.21822 -1.04716
C 1.45596 2.28131 0.04764
C -0.95276 2.44806 -0.18873
C -0.78287 3.69064 -0.82026
C 1.59150 3.52178 -0.58465
Cl -0.46695 -3.70396 -1.26311
H -1.66688 4.25709 -1.10504
H 0.59581 5.18162 -1.53523
H 2.58738 3.94736 -0.69049
C 2.78731 -2.69157 -0.85204
C 2.71218 -1.83887 -1.90245
C 1.61582 -2.94320 1.31360
H 2.46368 -3.56750 1.59942
H 1.37680 -2.24103 2.11749
H 0.74671 -3.56570 1.06022
C 1.45984 0.19417 -2.48917
H 0.78019 0.90096 -2.02240
H 0.98382 -0.25172 -3.36673
H 2.35808 0.73235 -2.80348
N 1.96912 -2.19187 0.12517
N 1.81810 -0.85224 -1.55266
C -1.48122 -1.02228 0.40636
N -2.18510 -1.79091 1.28168
C -1.85067 -2.04953 2.66856
H -2.70521 -1.80686 3.30564
H -0.99518 -1.42563 2.93895
H -1.59136 -3.10434 2.79208
C -3.28275 -2.34478 0.66935
C -3.27445 -1.90527 -0.61456
N -2.18851 -1.08348 -0.74761
C -1.69452 -0.62603 -2.02649
H -1.24842 0.36313 -1.91151
H -2.53067 -0.55876 -2.72419
H -0.96546 -1.37200 -2.37450
C 2.71012 1.64026 0.53077
C 5.10449 0.46971 1.44234
C 2.85852 1.25388 1.87168
C 3.80277 1.46460 -0.32899

C 4.98515 0.87701 0.11596
C 4.04074 0.67340 2.32105
C -2.34606 2.02421 0.07993
C -5.01079 1.28304 0.61367
C -3.34317 2.15712 -0.89753
C -2.71921 1.52887 1.33764
C -4.03481 1.15945 1.60136
C -4.65947 1.78628 -0.63769
H 3.71570 1.78474 -1.36579
H 5.81183 0.73700 -0.57546
H 6.02409 0.00943 1.79285
H 4.13349 0.38536 3.36482
H 2.03598 1.41380 2.56220
H -6.03680 0.99040 0.81811
H -5.41180 1.88587 -1.41568
H -3.07106 2.53389 -1.88187
H -1.96205 1.43913 2.11655
H -4.30058 0.77890 2.58486
H 3.32206 -3.61837 -0.72651
H 3.19170 -1.85318 -2.86782
H -3.92431 -2.12799 -1.44498
H -3.94894 -3.01394 1.18857

Table S20: Cartesian coordinated (x,y,z) for the optimized structure of **8**.

Si -0.13583 -0.52394 -0.77445
C -1.27928 -1.20692 0.66973
C -0.11462 1.35144 -0.35023
C -0.39053 4.04465 0.50132
C -1.38845 1.99195 -0.33231
C 1.02265 2.14343 -0.04637
C 0.86675 3.46588 0.39822
C -1.50690 3.31550 0.10797
H 1.75414 4.05183 0.62517
H -0.49571 5.07152 0.83771
H -2.49108 3.77842 0.11487
C -2.86542 -2.59526 1.49515
C -2.77555 -1.53272 2.33427
C -1.76502 -3.28970 -0.63173
H -3.49403 -3.47077 1.52362
H -2.65957 -3.90215 -0.74335
H -1.59470 -2.69659 -1.53515
H -0.90186 -3.93961 -0.46325
C -1.43704 0.53297 2.50779
H -3.31562 -1.29499 3.23721
H -0.57192 0.98140 2.02938
H -1.21675 0.31419 3.55519
H -2.26285 1.24587 2.45547
N -1.95537 -2.38192 0.48766
N -1.80096 -0.70132 1.82858
C 1.50156 -1.36948 -0.09162
N 2.24029 -2.21495 -0.86535
C 2.05514 -2.45535 -2.28893
H 2.82181 -1.92164 -2.85622
H 1.06871 -2.08355 -2.57539
H 2.13390 -3.52489 -2.48965

C 3.28585 -2.75072 -0.15110
C 3.19824 -2.25085 1.10913
N 2.10518 -1.41725 1.12684
H 3.81469 -2.40915 1.97984
H 3.99616 -3.42806 -0.59754
C 1.67291 -0.67226 2.29290
H 1.39149 0.33672 1.98685
H 2.50211 -0.60685 2.99734
H 0.82448 -1.16743 2.77282
C -2.64222 1.30230 -0.74414
C -5.03413 0.02936 -1.52079
C -3.77406 1.31736 0.08412
C -2.75298 0.67443 -1.99499
C -3.93306 0.04231 -2.37664
C -4.95493 0.68144 -0.29228
C 2.40807 1.65146 -0.22274
C 5.06937 0.81744 -0.61600
C 2.79230 1.00055 -1.40448
C 3.39102 1.88789 0.75063
C 4.70513 1.46892 0.56173
C 4.10863 0.58979 -1.60021
H -3.72888 1.84173 1.03727
H -1.91078 0.70282 -2.67980
H -3.99912 -0.42364 -3.35587
H -5.95537 -0.46077 -1.82150
H -5.81578 0.70566 0.36995
H 2.04966 0.84544 -2.18780
H 4.39340 0.11388 -2.53565
H 6.09757 0.50530 -0.77270
H 5.44909 1.66167 1.32959
H 3.11380 2.40209 1.66935

Table S21: Cartesian coordinated (x,y,z) for the optimized structure of **H_2S**.

S 0.00000 0.00000 0.10330
H 0.00000 0.96768 -0.82641
H 0.00000 -0.96768 -0.82641

Table S22: Cartesian coordinated (x,y,z) for the optimized structure of **TS89**.

Si 0.14540 -0.36126 0.32368
C -0.03317 1.51496 0.25577
C -0.00492 4.34295 0.35400
C -1.23688 2.25646 0.14281
C 1.18606 2.23304 0.42703
C 1.18605 3.63083 0.43857
C -1.20438 3.65572 0.22207
H 2.13204 4.15332 0.55602
H 0.00147 5.42790 0.39266
H -2.13982 4.20326 0.13936
C 1.28627 -0.86893 -1.11569
N 1.60557 -0.22217 -2.27060
C 0.98346 0.99500 -2.76626
H 1.43394 1.87535 -2.29947
H -0.08012 0.98998 -2.52203
H 1.11308 1.04130 -3.84725
C 2.63822 -0.86602 -2.90899

C 2.96377 -1.94583 -2.14585
N 2.13395 -1.93016 -1.05435
H 3.71338 -2.70897 -2.28186
H 3.05027 -0.50490 -3.83794
C 2.19860 -2.87965 0.05454
H 2.88279 -3.68173 -0.21657
H 1.20986 -3.30090 0.25374
H 2.54506 -2.37854 0.96393
H 0.62406 -1.15484 1.69446
S 0.95606 -2.20348 3.18044
H 0.85994 -1.12678 3.98093
C -1.46398 -1.33784 0.04608
N -2.35502 -1.52816 1.05229
N -1.87249 -2.16138 -0.95758
C -3.00938 -2.84335 -0.58060
C -3.31000 -2.44116 0.68243
C -2.27404 -0.91018 2.37232
C -1.29136 -2.23802 -2.28579
H -1.85707 0.09553 2.27771
H -3.28153 -0.82668 2.77984
H -1.62442 -1.51614 3.01754
H -0.37014 -2.82670 -2.28646
H -2.01183 -2.70805 -2.95458
H -1.07594 -1.23082 -2.65177
H -3.50092 -3.54126 -1.23915
H -4.11597 -2.72054 1.34181
C 2.49305 1.53693 0.57600
C 4.95858 0.20693 0.82634
C 2.74388 0.68510 1.66176
C 3.51756 1.74076 -0.36080
C 4.73764 1.07899 -0.23978
C 3.96094 0.01807 1.78185
C -2.56932 1.64318 -0.09498
C -5.13217 0.58561 -0.58117
C -2.84431 0.92640 -1.26673
C -3.61400 1.84290 0.81691
C -4.88097 1.31155 0.58131
C -4.10876 0.39876 -1.51047
H -2.05396 0.79824 -2.00620
H -5.67612 1.47547 1.30322
H -3.42330 2.41446 1.72307
H -6.12209 0.18157 -0.77062
H -4.30118 -0.14326 -2.43364
H 1.98847 0.54714 2.43053
H 4.11947 -0.64174 2.63072
H 5.91187 -0.30455 0.92326
H 5.51935 1.25165 -0.97449
H 3.35425 2.42863 -1.18984

Table S23: Cartesian coordinated (x,y,z) for the optimized structure of **TS²89**.

Si -0.17921 0.21071 -0.21729
C 1.50114 0.97458 0.26915
C -0.11738 -1.67287 -0.42428
C -0.38262 -4.46824 -0.80705

C -1.38827 -2.26807 -0.66699
C 1.01913 -2.51942 -0.40780
C 0.86932 -3.89706 -0.62180
C -1.50767 -3.65266 -0.82020
H 1.75752 -4.52376 -0.60956
H -0.47949 -5.54001 -0.95017
H -2.49383 -4.07779 -0.98966
C 3.49833 1.93565 -0.10116
C 3.18793 2.12858 1.20625
C 2.38449 0.91667 -2.08267
H 4.35567 2.24022 -0.67939
H 2.21671 1.82835 -2.66173
H 3.31631 0.43841 -2.38701
H 1.56292 0.22250 -2.26667
C 1.29543 1.51728 2.70509
H 3.71844 2.63906 1.99369
H 1.99007 1.87876 3.46233
H 0.99868 0.49639 2.95888
H 0.41459 2.16529 2.69522
N 2.45501 1.24383 -0.66302
N 1.96389 1.53568 1.41875
C -1.32283 0.45400 1.30361
N -2.23944 1.45305 1.39676
C -2.37932 2.55119 0.44409
H -2.48794 2.13957 -0.56199
H -1.50271 3.20641 0.47372
H -3.27453 3.11507 0.70259
C -3.05499 1.26148 2.48181
C -2.65367 0.10732 3.08190
N -1.59245 -0.37195 2.35348
H -3.03061 -0.40778 3.95139
H -3.84894 1.94853 2.72735
C -0.92107 -1.62645 2.65455
H 0.11814 -1.57296 2.32916
H -1.39811 -2.45488 2.12225
H -0.96394 -1.80072 3.72984
S 0.82797 4.25096 -0.39719
H 0.24500 3.63869 -1.48022
H -0.55791 1.20954 -1.61716
S -0.68235 2.15100 -3.04958
H -1.97727 2.43308 -2.82917
H 0.43877 5.47711 -0.77370
C 2.40940 -2.05274 -0.15836
C 5.08597 -1.32448 0.32127
C 3.38240 -2.19447 -1.15539
C 2.81089 -1.56122 1.09071
C 4.13202 -1.19611 1.33081
C 4.70713 -1.82697 -0.92134
C -2.63684 -1.46263 -0.76291
C -5.02538 0.00704 -0.96595
C -3.67954 -1.65602 0.15462
C -2.82224 -0.53811 -1.80230
C -4.00656 0.18903 -1.90107
C -4.86064 -0.92263 0.05992
H 6.11956 -1.04921 0.50869

H 2.07801 -1.47851 1.89245
H 4.42181 -0.82773 2.31193
H 5.44594 -1.94609 -1.70886
H 3.09101 -2.59446 -2.12447
H -2.04496 -0.39765 -2.55058
H -4.13707 0.88445 -2.72653
H -5.95191 0.56737 -1.05084
H -5.65742 -1.08748 0.78020
H -3.56003 -2.39149 0.94973

Table S24: Cartesian coordinated (x,y,z) for the optimized structure of **9**.

Si 0.11258 -0.32663 0.25422
C -0.04864 1.54244 0.30003
C -0.01558 4.35735 0.50558
C -1.25301 2.28475 0.22963
C 1.17498 2.24568 0.49496
C 1.17535 3.64211 0.55944
C -1.21934 3.67885 0.35967
H 2.12161 4.15938 0.69588
H -0.00662 5.44010 0.58426
H -2.15482 4.23009 0.31112
C 1.29449 -0.79962 -1.15695
N 1.59521 -0.13014 -2.30290
C 0.98576 1.11196 -2.75220
H 1.45802 1.96915 -2.26409
H -0.07540 1.11835 -2.49646
H 1.10250 1.19003 -3.83279
C 2.62181 -0.75992 -2.96298
C 2.95747 -1.85253 -2.22200
N 2.14128 -1.86050 -1.12064
H 3.70655 -2.61197 -2.37988
H 3.02539 -0.37854 -3.88750
C 2.18425 -2.86964 -0.06220
H 3.03783 -3.51982 -0.24470
H 1.26756 -3.46605 -0.07394
H 2.27758 -2.40236 0.92748
H 0.60831 -1.04541 1.50222
S 1.05262 -2.42747 3.14454
H 1.19695 -1.51094 4.11760
C -1.47078 -1.34102 -0.02982
N -2.30504 -1.64356 0.99423
N -1.91198 -2.06595 -1.09163
C -3.01540 -2.80450 -0.73175
C -3.25920 -2.53654 0.58033
C -2.15615 -1.14807 2.36061
C -1.36526 -2.02340 -2.43595
H -2.00110 -0.06648 2.33635
H -3.07673 -1.35581 2.90384
H -1.29067 -1.64861 2.83612
H -0.43452 -2.59302 -2.50388
H -2.09389 -2.45190 -3.12334
H -1.17862 -0.98632 -2.72664
H -3.52574 -3.44645 -1.43174
H -4.02405 -2.90071 1.24720

C 2.47537 1.53484 0.62243
C 4.92304 0.16697 0.82392
C 2.70746 0.62668 1.66643
C 3.51052 1.77684 -0.29460
C 4.72208 1.09706 -0.19671
C 3.91525 -0.06126 1.75943
C -2.58319 1.66528 -0.00150
C -5.13475 0.57671 -0.46276
C -2.88865 1.03418 -1.21387
C -3.59045 1.76546 0.96652
C -4.85217 1.21748 0.74207
C -4.14933 0.49100 -1.44569
H -2.12930 0.99438 -1.99522
H -5.61920 1.30193 1.50634
H -3.37519 2.27256 1.90475
H -6.12161 0.16080 -0.64212
H -4.36926 0.01736 -2.39976
H 1.94593 0.45238 2.42228
H 4.05508 -0.77057 2.57070
H 5.86950 -0.36016 0.90123
H 5.51257 1.29905 -0.91436
H 3.36143 2.50811 -1.08841

Table S25: Cartesian coordinated (x,y,z) for the optimized structure of **TS910**.

Si -0.26861 0.29164 0.56522
C -0.80251 1.89528 -0.29293
C -0.56822 -1.27349 -0.40518
C -1.24506 -2.91857 -2.58351
C -1.92042 -1.67676 -0.60898
C 0.44699 -1.82914 -1.23174
C 0.08770 -2.61927 -2.32712
C -2.23305 -2.48802 -1.70641
H 0.87317 -3.02485 -2.95865
H -1.50853 -3.53440 -3.43815
H -3.26415 -2.80056 -1.84939
C -1.22816 4.08208 -0.54158
C -1.77303 3.42278 -1.59634
C 0.00211 3.41632 1.52791
H 1.08495 3.48457 1.39855
H -0.36767 4.36842 1.90606
H -0.23349 2.64068 2.26017
C -1.94693 1.06210 -2.37426
H -1.12678 0.35919 -2.53070
H -2.15382 1.55411 -3.32278
H -2.84418 0.56194 -2.00386
N -0.65724 3.12612 0.26740
N -1.52402 2.08593 -1.42260
C 1.41714 0.45545 1.46794
N 2.58305 1.11023 1.26412
C 2.94208 1.95981 0.13207
H 2.17706 1.89913 -0.66352
H 3.88854 1.60296 -0.27791
H 3.06508 2.98917 0.47811
C 3.45050 0.86567 2.29940

C 2.81457 0.04627 3.17714
N 1.56444 -0.18788 2.66356
C 0.59405 -1.07818 3.28667
H 0.19881 -1.77623 2.54335
H -0.23133 -0.51241 3.72439
H 1.09949 -1.64622 4.06638
S 1.13084 1.60267 -2.64777
H 2.39595 1.42457 -3.06353
H -1.10325 0.36761 1.78793
C -3.03049 -1.30326 0.30069
C -5.18344 -0.73472 2.02318
C -2.92415 -1.51010 1.68405
C -4.25427 -0.83665 -0.20262
C -5.31713 -0.54765 0.64896
C -3.98415 -1.22576 2.53812
C 1.88873 -1.70151 -0.92273
C 4.63154 -1.62353 -0.32810
C 2.36752 -2.14517 0.31826
C 2.81079 -1.25773 -1.87912
C 4.16914 -1.20776 -1.57723
C 3.72800 -2.10720 0.61727
H 2.44188 -0.92066 -2.84306
H 4.87104 -0.84682 -2.32391
H 5.69421 -1.59830 -0.10325
H 4.08411 -2.48052 1.57421
H 1.66237 -2.56616 1.03422
H -2.00576 -1.93886 2.07975
H -3.88388 -1.40527 3.60506
H -6.01521 -0.51874 2.68669
H -6.25425 -0.18623 0.23642
H -4.37685 -0.70985 -1.27641
H 3.13958 -0.39003 4.10820
H -1.18699 5.13176 -0.30128
H -2.29718 3.78791 -2.46416
H 4.44173 1.28980 2.31195

Table S26: Cartesian coordinated (x,y,z) for the optimized structure of **10**.

Si -0.00107 0.36840 -0.72577
C -1.37480 -1.07246 -1.38239
C 0.10303 -0.44532 0.99148
C -0.00129 -1.94334 3.39669
C -1.08558 -0.51607 1.76418
C 1.24646 -1.14551 1.46090
C 1.16987 -1.88221 2.65406
C -1.12619 -1.26324 2.94843
H 2.05759 -2.40886 2.99558
H -0.03492 -2.51191 4.32120
H -2.04763 -1.28552 3.52513
C -3.25955 -1.98987 -2.22565
C -2.48708 -3.00394 -1.75692
C -3.07811 0.48800 -2.36085
H -4.03937 0.35155 -2.85539
H -3.21894 1.10383 -1.47034
H -2.39282 0.98664 -3.04836

C -0.25303 -3.18390 -0.66332
H 0.69454 -2.70202 -0.91132
H -0.26099 -4.19107 -1.08042
H -0.36578 -3.23566 0.42346
N -2.56371 -0.82422 -1.99378
N -1.34366 -2.42455 -1.25413
C 1.08575 2.11536 -0.21052
N 1.32266 3.10636 -1.11718
C 1.09968 3.01939 -2.55388
H 0.17016 2.48525 -2.75330
H 1.91578 2.49026 -3.04792
H 1.02730 4.03131 -2.95189
C 1.77396 4.25825 -0.50979
C 1.81197 4.00242 0.82017
N 1.38416 2.70017 0.99024
C 1.28251 2.11202 2.32336
H 1.95128 1.25700 2.43165
H 0.26438 1.78201 2.53251
H 1.56397 2.87620 3.04676
S 1.28392 -0.33638 -2.31254
H 2.43690 0.23431 -1.91490
H -1.01370 1.37513 -1.12038
C -2.33591 0.19084 1.38350
C -4.75629 1.52627 0.85162
C -2.36676 1.57996 1.19393
C -3.54482 -0.51558 1.29592
C -4.74076 0.14157 1.02093
C -3.56495 2.24426 0.93929
C 2.54942 -1.24096 0.74223
C 5.03549 -1.56106 -0.55322
C 3.36592 -0.13775 0.46142
C 3.03125 -2.51280 0.39579
C 4.24988 -2.67274 -0.25691
C 4.59454 -0.29458 -0.17721
H 2.43131 -3.38814 0.63771
H 4.58935 -3.66814 -0.52738
H 5.99009 -1.68243 -1.05553
H 5.21298 0.57749 -0.37140
H 3.05261 0.85942 0.74818
H -1.44383 2.15281 1.27124
H -3.56881 3.32401 0.82117
H -5.69176 2.04302 0.65947
H -5.66477 -0.42574 0.95435
H -3.53689 -1.59468 1.43955
H 2.09626 4.62332 1.65468
H -4.22488 -1.99530 -2.70639
H -2.64147 -4.07117 -1.75049
H 2.02053 5.14523 -1.07131

Table S27: Cartesian coordinated (x,y,z) for the optimized structure of **TS1011**.

Si -0.23055 0.31473 -0.73725
C -0.98144 2.12537 -0.71301
C -0.12355 -0.21111 1.06907
C 0.06199 -0.98464 3.78405

C 1.02839 0.10928 1.83822
C -1.18923 -0.89791 1.70542
C -1.06835 -1.30050 3.04180
C 1.09100 -0.26713 3.18676
H -1.89469 -1.83843 3.49954
H 0.13662 -1.28551 4.82488
H 1.97825 -0.00570 3.75820
C -1.67019 4.11183 -1.51515
C -1.76724 4.15743 -0.16145
C -0.90126 2.45157 -3.20461
H -1.90080 4.84653 -2.26993
H -0.71526 3.34405 -3.80103
H -0.01549 1.81621 -3.22142
H -1.74327 1.89510 -3.61791
C -1.20510 2.67868 1.74799
H -2.09156 4.94435 0.50019
H -1.67914 1.73800 2.02567
H -1.68565 3.49668 2.28279
H -0.14863 2.63670 2.02039
N -1.18007 2.86851 -1.83390
N -1.34037 2.93897 0.31609
C 1.27348 -2.10905 -1.20047
N 2.19783 -2.02484 -2.20620
C 2.03555 -1.19624 -3.38470
H 2.76239 -0.37713 -3.38282
H 1.02527 -0.78384 -3.38228
H 2.17061 -1.79139 -4.29112
C 3.32352 -2.78971 -1.96113
C 3.11453 -3.39378 -0.76268
N 1.87123 -2.97307 -0.32803
H 3.72664 -4.08341 -0.20180
H 4.14992 -2.85482 -2.65268
C 1.29287 -3.37070 0.94112
H 0.24588 -3.07087 0.95188
H 1.80893 -2.88029 1.77273
H 1.36168 -4.45332 1.06381
S -1.58697 -0.60147 -2.10984
H -0.83725 -1.72543 -2.05647
H 1.04928 0.65542 -1.38013
C 2.19149 0.88680 1.32492
C 4.45311 2.34384 0.49926
C 2.53357 2.09960 1.94174
C 3.02446 0.40432 0.30742
C 4.14221 1.12479 -0.10214
C 3.64736 2.82737 1.52759
C -2.48082 -1.20860 1.03639
C -4.93277 -1.82328 -0.18552
C -2.83894 -2.53723 0.78290
C -3.38529 -0.19672 0.69438
C -4.60257 -0.49901 0.09168
C -4.04830 -2.84192 0.16374
H -3.14020 0.84291 0.90348
H -5.29417 0.29980 -0.16058
H -5.87874 -2.06141 -0.66198
H -4.30283 -3.87758 -0.04138

H -2.15403 -3.33670 1.05909
H 1.93029 2.46445 2.77196
H 3.89298 3.76397 2.01980
H 5.32791 2.90348 0.18255
H 4.78167 0.72215 -0.88384
H 2.80119 -0.55389 -0.14988

Table S28: Cartesian coordinated (x,y,z) for the optimized structure of **11**.

Si 0.39490 -1.14381 -0.08690
C -1.12927 -0.93345 1.13570
N -2.34651 -1.52540 1.16181
C -2.83471 -2.54660 0.24082
H -2.91102 -3.50005 0.76857
H -2.12516 -2.64440 -0.58554
H -3.81537 -2.24455 -0.13034
C -3.08702 -1.06694 2.22803
C -2.31376 -0.16923 2.89139
N -1.11566 -0.10748 2.21583
C -0.01830 0.76929 2.59906
H -0.08661 1.72466 2.07056
H 0.93271 0.29605 2.34845
H -0.06847 0.93577 3.67565
C 0.68850 0.70925 -0.49770
C 1.12862 3.51166 -0.51307
C -0.37905 1.61843 -0.70831
C 1.99373 1.24729 -0.35457
C 2.19435 2.63571 -0.35537
C -0.15035 3.00217 -0.70062
H -0.98824 3.67531 -0.86927
H 1.29732 4.58514 -0.51967
H 3.20661 3.02040 -0.25304
S 0.17075 -2.54191 -1.51477
H 1.40482 -1.38190 0.99016
C -1.77474 1.16941 -0.92659
C -4.43805 0.38752 -1.37845
C -2.82698 1.73757 -0.19196
C -2.08178 0.20412 -1.89732
C -3.40205 -0.17818 -2.12083
C -4.14565 1.34702 -0.40920
C 3.18287 0.38285 -0.18078
C 5.44324 -1.24794 0.17098
C 3.39750 -0.73007 -1.00578
C 4.13054 0.67293 0.81174
C 5.24860 -0.13611 0.98972
C 4.51511 -1.53984 -0.82666
H 2.67787 -0.96760 -1.78632
H 4.65601 -2.40319 -1.47065
H 6.31342 -1.88319 0.31109
H 5.96493 0.09645 1.77328
H 3.97027 1.52973 1.46407
H -2.59924 2.48364 0.56855
H -4.94516 1.79319 0.17703
H -5.46768 0.08855 -1.55778
H -3.61729 -0.92583 -2.88013

H -1.28004 -0.24825 -2.47433
H -4.08949 -1.41790 2.41383
H -2.50350 0.42074 3.77381

Table S29: Cartesian coordinated (x,y,z) for the optimized structure of $^{+}$**H-ImMe$_2$H$_2$**.

C 0.00000 -0.86341 -0.00085
N -1.08655 -0.08406 -0.00036
C -2.47156 -0.54885 0.00061
H -2.97663 -0.18868 0.89703
H -2.48282 -1.63693 -0.00789
H -2.98198 -0.17502 -0.88709
C -0.68116 1.23291 0.00001
C 0.68116 1.23291 -0.00000
N 1.08655 -0.08406 -0.00036
H 1.38909 2.04605 0.00006
H -1.38909 2.04605 0.00008
C 2.47156 -0.54885 0.00061
H 2.98197 -0.17503 -0.88709
H 2.48282 -1.63693 -0.00788
H 2.97664 -0.18868 0.89703
H 0.00000 -1.94230 -0.00140

Table S30: Cartesian coordinated (x,y,z) for the optimized structure of **12**.

Si 0.31198 -0.87469 -0.47179
C -1.30606 -1.28025 0.46859
C 0.61925 0.95957 -0.20677
C 0.97744 3.50438 0.93551
C -0.48203 1.84180 -0.05905
C 1.91750 1.42650 0.11421
C 2.07670 2.68556 0.70497
C -0.28888 3.09843 0.52679
H 3.07798 3.03299 0.94593
H 1.11388 4.48236 1.38702
H -1.13718 3.77111 0.62660
C -3.30983 -2.09874 1.02476
C -2.80952 -1.45480 2.11358
C -2.48599 -2.60705 -1.28756
H -4.23832 -2.62637 0.87657
H -3.51943 -2.91656 -1.43456
H -2.21996 -1.88560 -2.06053
H -1.83047 -3.47807 -1.34902
C -0.72813 -0.16892 2.63962
H -3.21831 -1.30671 3.10018
H -0.91922 -0.46851 3.66932
H -0.95318 0.89356 2.51250
H 0.32293 -0.34578 2.40609
N -2.37214 -1.98446 0.02638
N -1.57298 -0.97005 1.75870
S 1.52160 -2.26326 0.62083
H 2.67026 -2.09200 -0.06002
H 0.08767 -1.33408 -1.85652
C 3.10426 0.61655 -0.21529
C 5.29726 -1.01173 -0.85746
C 3.20319 0.01380 -1.47997

C 4.13912 0.41921 0.70857
C 5.22184 -0.39499 0.39259
C 4.29138 -0.79631 -1.79877
C -1.83078 1.48372 -0.54917
C -4.38690 0.83666 -1.52716
C -1.99576 0.96767 -1.84510
C -2.97364 1.68485 0.23971
C -4.23758 1.35590 -0.24060
C -3.26317 0.65372 -2.33124
H -1.12479 0.86347 -2.48950
H -3.37493 0.28640 -3.34796
H -5.37591 0.60071 -1.90838
H -5.11039 1.51355 0.38656
H -2.86392 2.09542 1.24237
H 2.43584 0.21246 -2.22702
H 4.07042 0.87636 1.69281
H 6.00696 -0.55627 1.12496
H 6.14444 -1.64501 -1.10154
H 4.36019 -1.24737 -2.78418

Table S31: Cartesian coordinated (x,y,z) for the optimized structure of **TS1211**.

Si -0.56598 -0.39292 -0.17937
C -1.97812 -1.26865 0.78054
C -1.14288 1.38994 -0.35980
C -2.01748 4.00996 0.18046
C -2.52425 1.71105 -0.41259
C -0.20836 2.43442 -0.15794
C -0.65738 3.72718 0.13658
C -2.94211 3.01700 -0.12607
H 0.07197 4.51834 0.28994
H -2.35718 5.01767 0.40062
H -4.00127 3.25681 -0.18153
C -3.50163 -2.75798 1.46073
C -3.45772 -1.76048 2.38381
C -2.27254 -3.28690 -0.65826
H -4.09540 -3.65673 1.41406
H -1.29320 -3.75128 -0.52673
H -3.03548 -4.05999 -0.73398
H -2.28206 -2.69036 -1.57126
C -2.19803 0.38448 2.65027
H -4.00824 -1.61655 3.29949
H -2.34407 0.23245 3.71888
H -2.85155 1.18551 2.29415
H -1.15813 0.65977 2.46868
N -2.58488 -2.44083 0.48614
N -2.50834 -0.86164 1.95705
S 0.93003 -0.85237 1.27224
H 2.12605 -0.59319 0.66281
H -0.40280 -1.17819 -1.42277
C 1.23317 2.17624 -0.31940
C 3.96248 1.64682 -0.68138
C 1.67983 1.44119 -1.43007
C 2.17788 2.65483 0.59683
C 3.53037 2.38217 0.42187

C 3.03564 1.18370 -1.61149
C -3.54707 0.71841 -0.80791
C -5.51311 -1.12318 -1.62056
C -3.35759 -0.08057 -1.94701
C -4.74877 0.58662 -0.09494
C -5.71724 -0.33067 -0.49067
C -4.33455 -0.98763 -2.35236
H -2.45719 0.05286 -2.54420
H -4.18495 -1.57390 -3.25527
H -6.27853 -1.82373 -1.94087
H -6.63811 -0.42165 0.07848
H -4.91732 1.20684 0.78420
H 0.95843 1.12007 -2.18055
H 1.84125 3.21251 1.46758
H 4.24960 2.73684 1.15464
H 5.01821 1.42839 -0.81768
H 3.37292 0.63101 -2.48432
C 4.43264 -1.30992 0.46481
N 5.71078 -0.85294 0.64519
N 4.48527 -1.77490 -0.82274
C 6.50586 -1.00572 -0.47888
H 7.54280 -0.70469 -0.51174
C 5.72233 -1.59374 -1.41906
H 5.94314 -1.90348 -2.42981
C 6.19557 -0.27910 1.88351
H 5.38115 -0.28876 2.60624
H 7.03074 -0.86534 2.27673
H 6.53517 0.75034 1.72891
C 3.36595 -2.42192 -1.46960
H 2.55271 -2.48851 -0.74488
H 3.02990 -1.85470 -2.34415
H 3.63777 -3.43255 -1.78830

Table S32: Cartesian coordinated (x,y,z) for the optimized structure of **TS1213**.

N 2.47271 0.84417 1.91935
C 1.70720 -0.16387 1.43337
N 2.36001 -1.30408 1.76887
C 3.52312 -1.01470 2.44463
C 3.59647 0.34041 2.53280
Si -0.01858 -0.09007 0.54582
H -0.81843 -1.70829 0.22975
S -1.11696 0.88369 2.20873
H -0.58128 0.06321 3.13314
C 0.28627 1.27619 -0.75075
C -0.67158 2.29556 -0.97247
C -0.31714 3.44791 -1.68575
C 0.95308 3.58534 -2.23248
C 1.86470 2.54119 -2.12119
C 1.53940 1.38103 -1.40709
C 1.86344 -2.65069 1.52111
C 2.19986 2.26670 1.75667
C -1.78718 -2.67496 -0.06305
N -3.00144 -2.59311 0.54256
C -4.02881 -2.85097 -0.34262

C -3.45050 -3.08625 -1.55034
N -2.08777 -2.96843 -1.35797
C -3.19126 -2.24086 1.93902
C -1.09267 -3.09331 -2.40483
H 2.83153 2.60406 -2.61537
H 1.21470 4.48131 -2.78718
H -1.06363 4.22384 -1.83697
H 1.15278 -2.94576 2.29806
H 2.70688 -3.34081 1.51693
H 1.36766 -2.68392 0.55041
H 2.68710 2.80789 2.56729
H 1.12201 2.43268 1.80251
H 2.58169 2.61736 0.79376
H -1.32978 -3.93972 -3.05104
H -0.12025 -3.26608 -1.94267
H -1.05085 -2.18252 -3.01066
H -3.86425 -2.95520 2.41703
H -3.59787 -1.22943 2.02403
H -2.22368 -2.27211 2.43908
H 4.18778 -1.78666 2.79801
H 4.34227 0.98216 2.97452
H -5.06508 -2.86375 -0.04128
H -3.88405 -3.34167 -2.50482
C 2.52165 0.27323 -1.38600
C 4.36806 -1.85287 -1.39245
C 3.87397 0.49347 -1.08668
C 2.11941 -1.03204 -1.71059
C 3.03219 -2.08364 -1.71812
C 4.78540 -0.55908 -1.08068
C -2.06501 2.15049 -0.50089
C -4.71905 1.84975 0.37056
C -2.76874 0.95886 -0.73780
C -2.72442 3.19476 0.16173
C -4.03482 3.04252 0.60221
C -4.08494 0.81197 -0.30917
H 4.20733 1.50100 -0.84271
H 5.82689 -0.36836 -0.83751
H 5.08350 -2.66980 -1.40380
H -2.18802 4.12001 0.35916
H -4.52377 3.85563 1.13027
H -5.74553 1.73688 0.70642
H -2.28548 0.15702 -1.29681
H -4.62134 -0.10905 -0.52456
H 1.08296 -1.20082 -1.99493
H 2.70655 -3.08364 -1.99570

Table S33: Cartesian coordinated (x,y,z) for the optimized structure of **13**.

Si 0.49657 -1.16370 0.23501
C -1.20178 -0.86207 1.13255
N -2.38763 -1.53775 1.18045
C -2.81627 -2.57459 0.25820
H -2.73900 -2.21985 -0.76840
H -3.85441 -2.82047 0.48580
H -2.19418 -3.46609 0.36421

C -3.15351 -1.11871 2.24957
C -2.44561 -0.15905 2.89427
N -1.25623 -0.01816 2.21217
C -0.18205 0.86331 2.62642
H -0.16392 1.77916 2.02849
H 0.77497 0.34371 2.49333
H -0.32062 1.11139 3.67966
C 0.72952 0.66282 -0.41164
C 1.19227 3.47352 -0.49951
C -0.32656 1.58297 -0.65450
C 2.04009 1.20637 -0.30417
C 2.25307 2.59166 -0.34022
C -0.08931 2.96610 -0.67234
H -0.92332 3.64080 -0.85538
H 1.36689 4.54582 -0.52433
H 3.26978 2.97035 -0.26032
S -0.01728 -2.32894 -1.58439
H 0.72116 -3.40164 -1.25325
C -1.72161 1.15843 -0.92617
C -4.37651 0.43554 -1.51949
C -2.00736 0.27167 -1.97356
C -2.79406 1.69296 -0.19752
C -4.10728 1.32647 -0.48119
C -3.32094 -0.08138 -2.27083
C 3.22889 0.33965 -0.14470
C 5.50423 -1.28810 0.13321
C 4.22204 0.64731 0.79487
C 3.40347 -0.79430 -0.95151
C 4.53052 -1.59878 -0.81473
C 5.34610 -0.16131 0.93830
H 2.65023 -1.03012 -1.70090
H 4.64893 -2.47050 -1.45278
H 6.38194 -1.91904 0.24290
H 6.09798 0.08588 1.68309
H 4.09386 1.51744 1.43592
H -2.58685 2.38603 0.61682
H -4.92203 1.73945 0.10841
H -5.40130 0.15659 -1.74955
H -3.51834 -0.76322 -3.09448
H -1.18843 -0.11990 -2.57107
H -2.67561 0.42983 3.76773
H -4.13016 -1.53235 2.44387

Table S34: Cartesian coordinated (x,y,z) for the optimized structure of **TS1311**.

S 1.50263 -2.39767 0.34870
Si 0.24967 -0.94297 -0.63640
H 0.77952 -2.30473 -1.22690
N -2.47559 -1.87593 0.03772
N -1.46956 -1.04539 1.75326
C 0.60575 0.88903 -0.19445
C -0.47820 1.79057 -0.02232
C -0.28411 3.02319 0.61356
H -1.13458 3.69011 0.74073
C 0.98157 3.40883 1.04205

H 1.12636 4.36828 1.53075
C 2.06797 2.58447 0.78028
H 3.07300 2.91177 1.03732
C 1.90599 1.34256 0.14778
C -1.32894 -1.26282 0.42180
C -3.31998 -2.04336 1.11457
C -2.68630 -1.51469 2.19438
C -2.74369 -2.37284 -1.30000
H -1.99744 -1.94789 -1.97552
H -3.74440 -2.06701 -1.61053
H -2.66159 -3.46267 -1.31666
C -0.44335 -0.44959 2.59383
H -0.42240 0.63670 2.46870
H 0.52705 -0.87210 2.30893
H -0.65973 -0.69845 3.63292
H -4.28354 -2.51693 1.01695
H -2.98821 -1.43704 3.22680
C -1.84482 1.48474 -0.50919
C -4.44313 0.97070 -1.46185
C -2.05647 1.07264 -1.83438
C -2.96225 1.64533 0.32273
C -4.24791 1.38282 -0.14442
C -3.34240 0.82409 -2.30620
C 3.12387 0.57356 -0.18340
C 5.45707 -0.83861 -0.85560
C 4.18117 0.46176 0.72847
C 3.26656 -0.01985 -1.44462
C 4.42185 -0.71663 -1.77966
C 5.33205 -0.24681 0.40040
H -2.81135 1.95744 1.35502
H -5.09856 1.50002 0.52207
H -5.44657 0.77614 -1.83117
H -3.48543 0.51859 -3.33980
H -1.20043 0.96445 -2.49589
H 4.07783 0.90062 1.71858
H 6.13070 -0.34606 1.13059
H 6.35506 -1.39431 -1.11047
H 4.50978 -1.17293 -2.76167
H 2.45970 0.07490 -2.16979

Table S35: Cartesian coordinated (x,y,z) for the optimized structure of **TS^{H2S}1311**.

Si 0.27511 0.73726 -0.01843
S 1.51340 1.29635 1.69712
H 1.77157 2.50942 1.16145
H 0.51327 2.21574 -0.96636
S 0.97403 3.77306 -1.41308
H 2.25327 3.48088 -1.12260
C -1.39477 0.79290 0.96460
N -1.82264 0.06399 2.02531
C -1.11658 -1.07381 2.58628
H -0.04104 -0.90253 2.51402
H -1.36427 -1.98952 2.04100
H -1.39549 -1.17883 3.63492
C -3.02520 0.54701 2.49035

C -3.34774 1.61223 1.70892
N -2.34001 1.74428 0.78110
H -4.19341 2.28034 1.73271
H -3.53787 0.09959 3.32695
C -2.24854 2.80534 -0.21416
H -2.04343 2.37080 -1.19450
H -1.43570 3.49523 0.03392
H -3.20014 3.33554 -0.24261
C 0.49113 -1.13760 -0.32707
C 0.73641 -3.95973 -0.36271
C -0.62972 -1.96779 -0.59827
C 1.76492 -1.76013 -0.24476
C 1.86367 -3.15790 -0.23071
C -0.49930 -3.36239 -0.58581
H -1.37478 -3.97515 -0.79129
H 0.82867 -5.04206 -0.35425
H 2.84931 -3.61145 -0.15218
C 3.01518 -0.97032 -0.22955
C 5.37990 0.54615 -0.22395
C 4.06167 -1.27953 0.64816
C 3.18873 0.09388 -1.12700
C 4.35736 0.84811 -1.12174
C 5.22989 -0.52400 0.65681
C -1.95567 -1.40668 -0.95107
C -4.47093 -0.37671 -1.69101
C -2.06682 -0.41388 -1.93846
C -3.13434 -1.88591 -0.36056
C -4.37795 -1.37210 -0.71949
C -3.31047 0.09324 -2.30541
H 6.29032 1.13863 -0.21310
H 4.46814 1.67005 -1.82390
H 2.40137 0.32854 -1.84150
H -1.16635 -0.05513 -2.43329
H -3.37290 0.85069 -3.08268
H -5.44123 0.01876 -1.97802
H -5.27672 -1.75045 -0.23953
H -3.06797 -2.66231 0.40050
H 3.93673 -2.09519 1.35718
H 6.02174 -0.76394 1.36121

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