Electronic Supplementary Material (ESI) for Dalton Transactions.

Activation of carbon disulfide by a hypersilyl germylene

V. S. Ajithkumar,[a,b†] Nripen Khilari,[c†] Pratiksha B. Ghanwat,[a,b] Geethu Venugopal,[b,d] Debasis Koley*[c] and Sakya S. Sen*[a,b]

[a]Inorganic Chemistry and Catalysis Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India).

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002 (India).

[c]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur,741246 (India).

[d]Organic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008 (India).

Content

General Experimental Information. All experiments were carried out under argon atmosphere using Schlenk techniques or inside a MBRAUN or VTPL glove box. Toluene and hexane, were purified by MBRAUN solvent purification system MB SPS-800 and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 was distilled over Na/benzophenone and stored over activated 4 Å molecular sieves prior to use. The precursor, [PhC(N*t*Bu)$_2$GeSi(SiMe$_3$)$_3$] (**1**)[S1] was synthesized by reported literature procedure. Chemicals purchased from Sigma Aldrich and TCI Chemicals were used without further purification. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6 using a Bruker Advance DPX 200 or a Bruker Advance DRX 400 or 500 spectrometers. Melting points were measured in a sealed glass tube using Stuart SMP-30 melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were obtained using a Q Exactive Thermo Scientific.

Spectroscopic data of compounds 2 and 3

Synthesis of compound [PhC(N*t*Bu)$_2$]GeCS$_2$Si(SiMe$_3$)$_3$ (2). To a toluene (10 mL) solution of **1** (0.15 g, 0.3 mmol), CS_2 was added (0.02 mL, 0.02 g, 0.3 mmol) drop by drop via a syringe at room temperature. Upon addition, the solution showed an instantaneous color change from yellow to purple, and the reaction was over in two minutes. The solution was filtered through a celite pad, and the filtrate was concentrated to ~3 mL to yield purple coloured crystals of **2** (0.14 g, 79 %), Mp: 91-92 °C.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.68-7.66 (d, 2H, *Ph*), 7.11-6.96 (m, 3H, *Ph*), 1.10 (s, 18H, *t*Bu), 0.40 (s, 27H, Si*Me*$_3$) ppm.

^{13}C{^{1}H} NMR (100.66 MHz, C_6D_6, 298 K): *δ* 308.7 (*C*S$_2$), 170.0 (N*C*N), 153.3 (*Ph*), 141.1 (*Ph*), 136.0 (*Ph*), 130.1 (*Ph*), 129.4 (*Ph*), 53.5 (*C*Me$_3$), 31.8 (C*Me*$_3$), 2.1 (Si*Me*$_3$), 1.4 (Si*Me*$_3$) ppm.

^{29}Si{^{1}H} NMR (79.53 MHz, C_6D_6, 298 K): *δ* -8.8 {s, Si(*Si*Me$_3$)$_3$}, *δ* -62.8 {s, *Si*(SiMe$_3$)$_3$} ppm.

Elemental analysis: $C_{25}H_{50}GeN_2S_2Si_4$; Calculated: C, 47.83; H, 8.03; N, 4.46; Found: C, 47.71; H, 7.89; N, 4.30.

HRMS (CH_3CN): m/z calcd for $C_{25}H_{50}GeN_2S_2Si_4$ $[M+H]^+$, 628.17; found, 628.551.

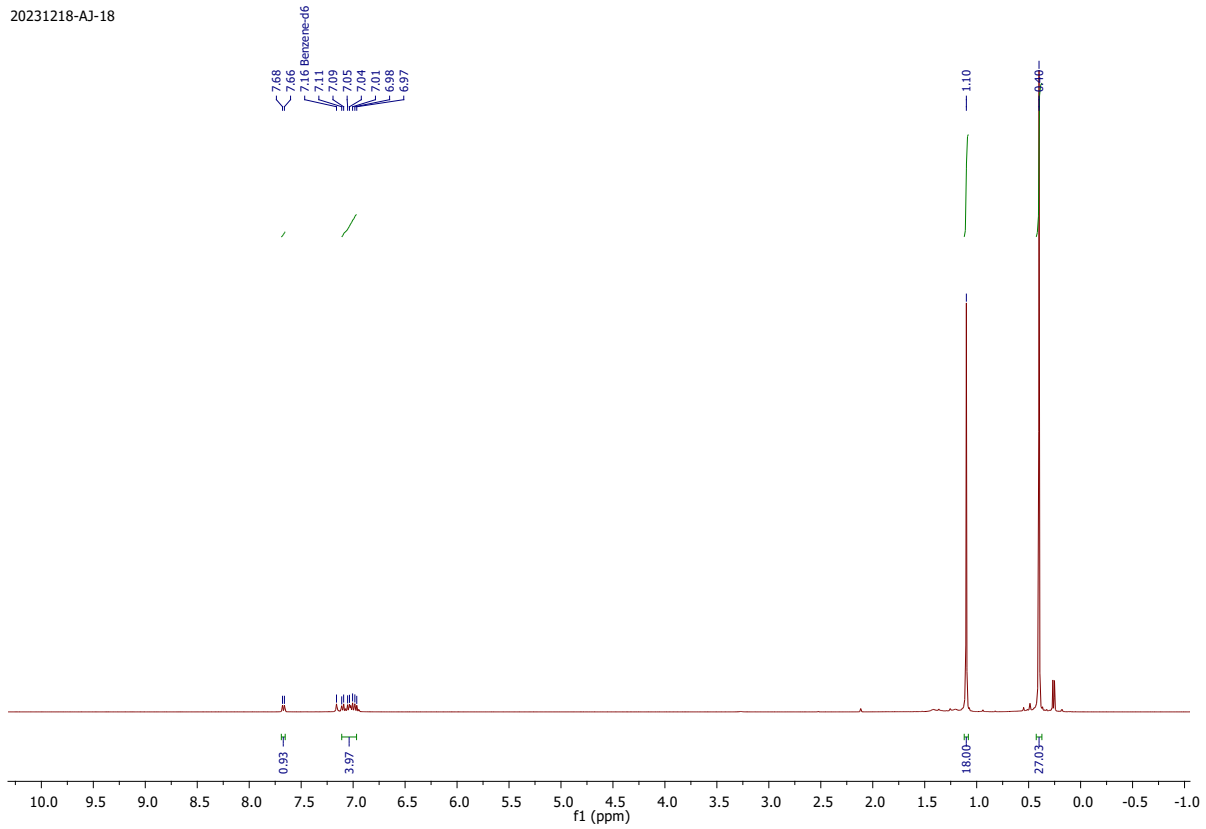

Figure S1. ^{1}H NMR Spectrum of **2** (C_6D_6, 400 MHz, 298 K)

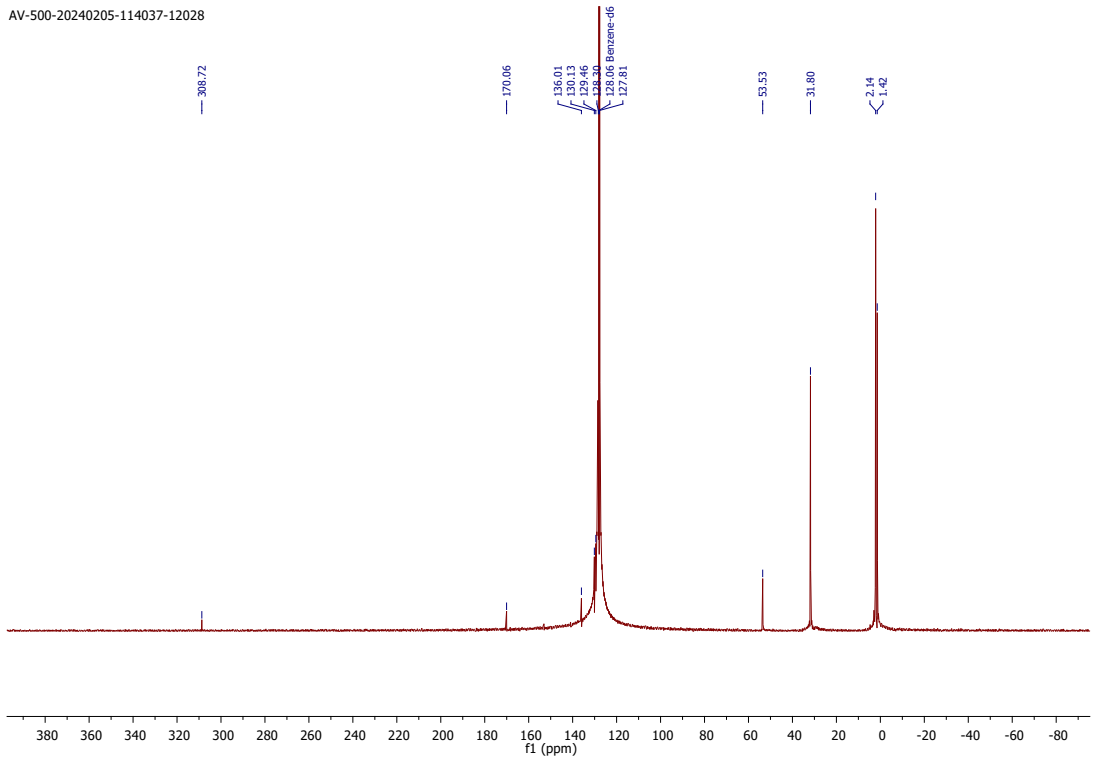

Figure S2. ^{13}C NMR Spectrum of **2** (C_6D_6, 100.66 MHz, 298 K)

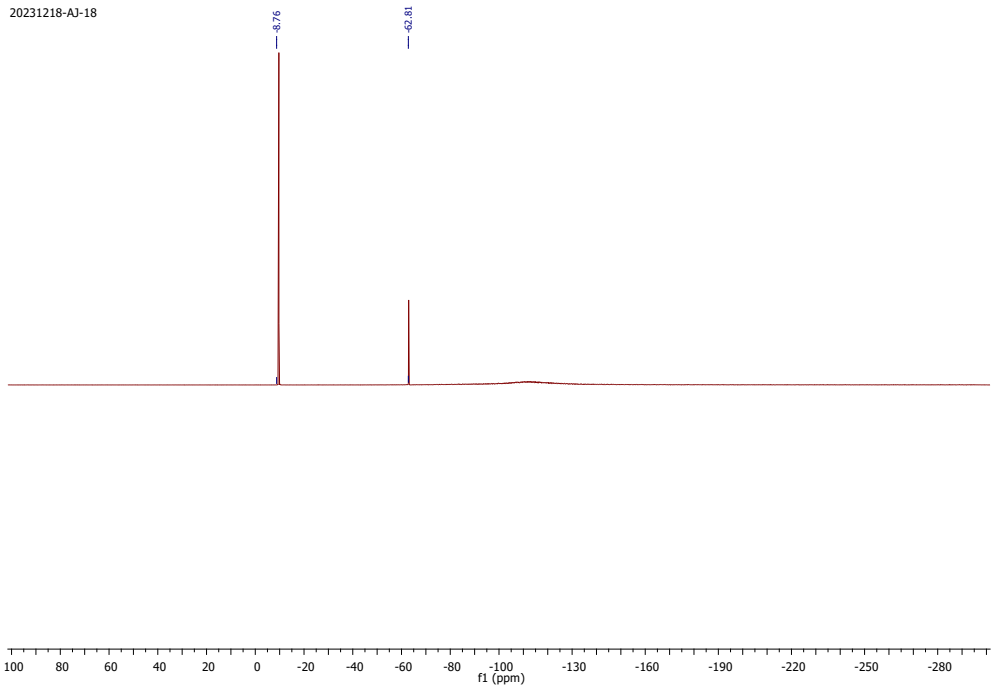

Figure S3. ^{29}Si NMR Spectrum of **2** (C_6D_6, 79.49 MHz, 298 K)

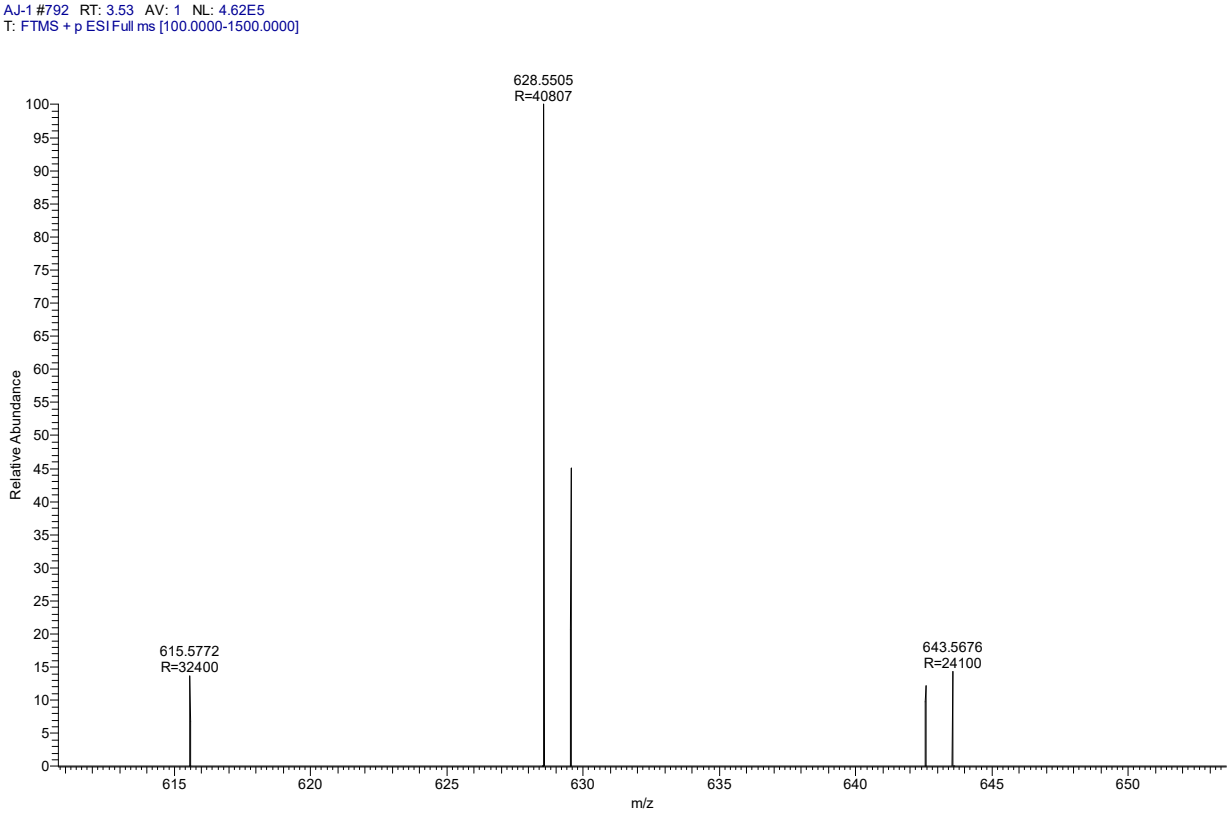

Figure S4. HRMS Spectrum of **2**

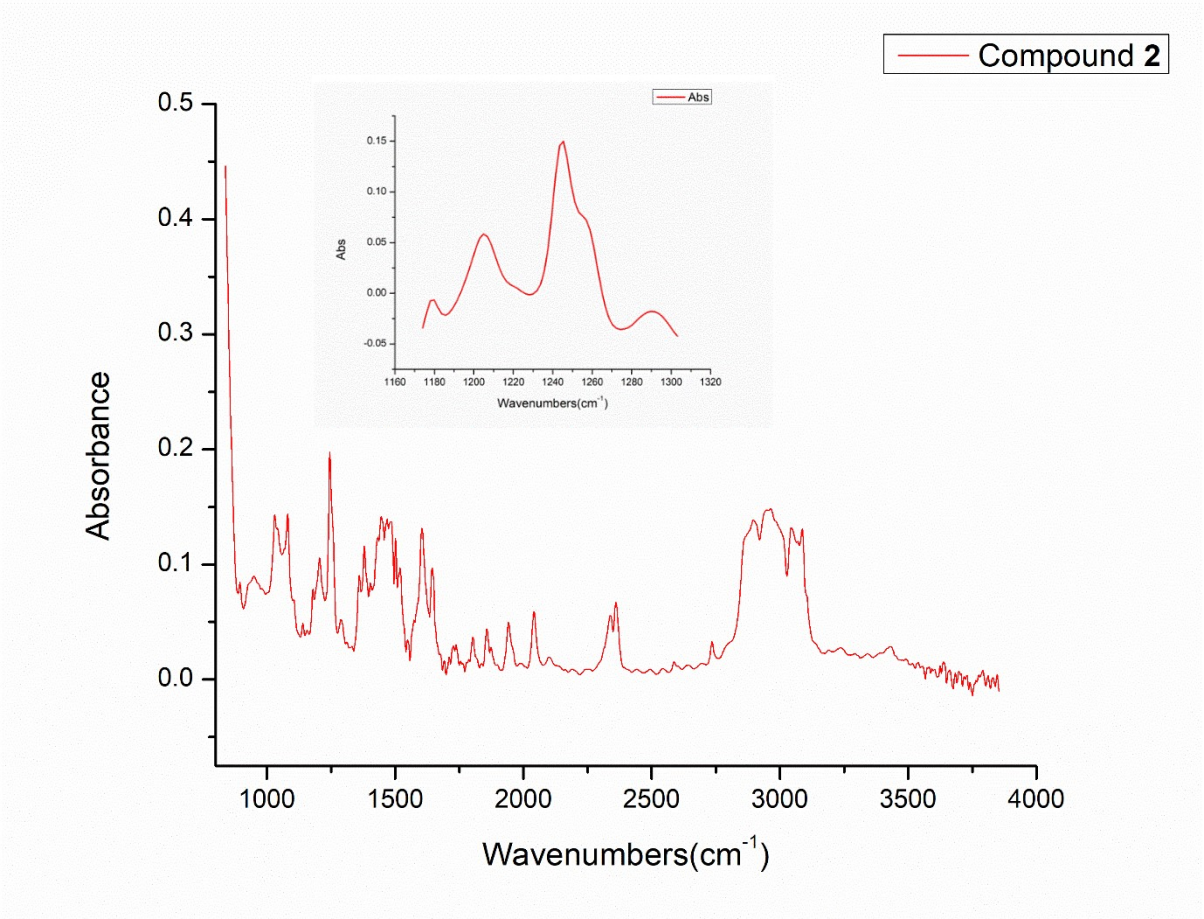

Figure S5. IR Spectrum of **2**

Synthesis of compound PhC(N*t*Bu)$_2$Ge(=S)Si(SiMe$_3$)$_3$ (3). To a toluene (5 mL) solution of **2** (0.15 g, 0.2 mmol), one equivalent of **1** (0.13 g, 0.2 mmol) dissolved in toluene (5 mL) was added drop by drop via a cannula at −78 °C. The reaction mixture was allowed to reach room temperature slowly, and stirred further for 12 hrs. After that, all the volatiles were removed in vacuum and the residue was extracted with toluene (8 mL). The filtrate was collected through a cannula, and concentrated to ~2 mL to yield colorless crystals of **3** (0.07 g, 50 %). Mp: 150-151 °C.

It must be noted that formation of **3** is accompanied by another side product, which we could not isolate or characterize.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.03-7.01 (m, 2H, Ph), 6.99-6.97 (m, 1H, Ph), 6.94-6.91 (m, 1H, *Ph*), 6.89–6.86 (m, 1H, *Ph*), 1.11 (s, 18H, *tBu*), 0.49 (s, 27H, Si*Me*$_3$) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): *δ* 168.4 (N*C*N), 153.0 (*Ph*), 141.2 (*Ph*), 135.7 (*Ph*), 129.6 (*Ph*), 129.2 (*Ph*), 128.5 (*Ph*), 127.5 (*Ph*), 54.3 (*C*Me$_3$), 31.7 (*C*Me$_3$), 5.2, 4.7, 2.9, 1.6, 1.0, 0.4 (Si*Me*$_3$ and C*Me*$_3$) ppm.

^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): *δ* -10.7 {s, Si(*Si*Me$_3$)$_3$}, -61.7 {s, *Si*(SiMe$_3$)$_3$} ppm.

HRMS (CH_3CN): m/z calcd for $C_{24}H_{50}GeN_2SSi_4$ $[M+H]^+$, 584.20; found, 585.339.

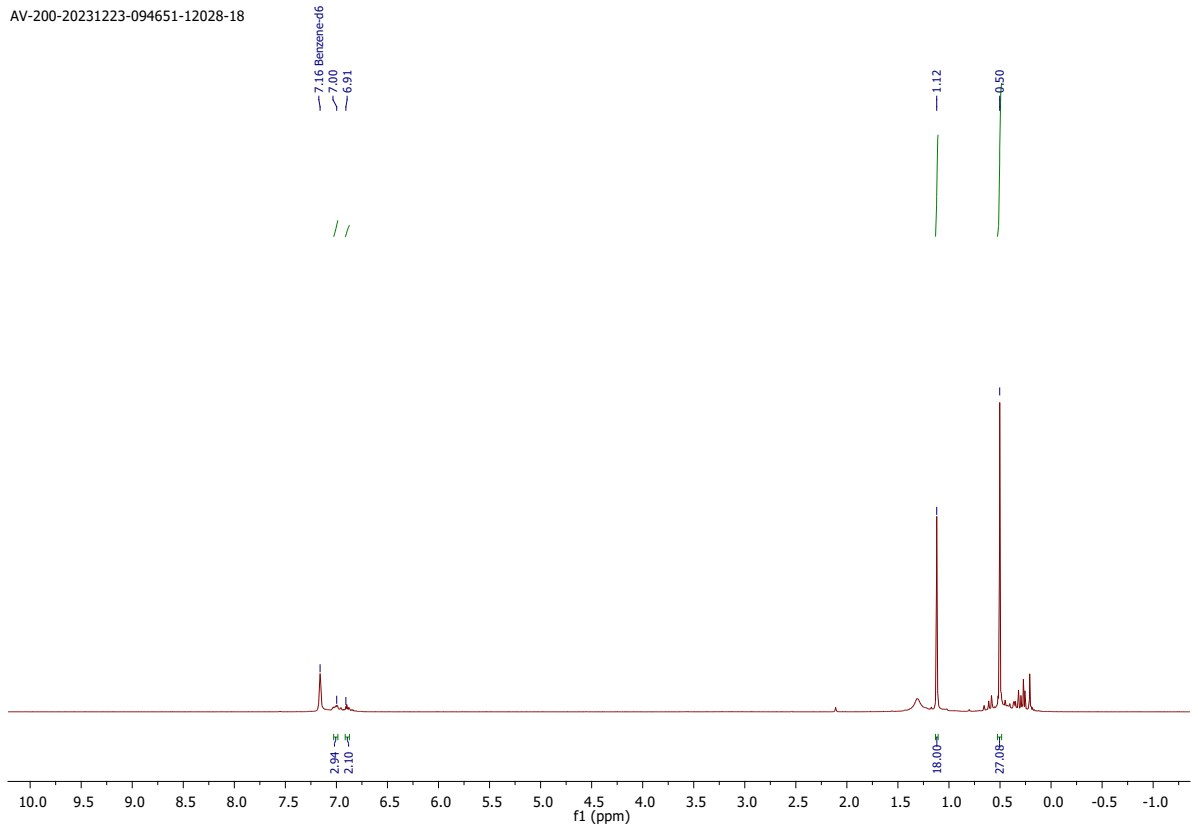

Figure S6. ^{1}H NMR Spectrum of **3** (C_6D_6, 400 MHz, 298 K)

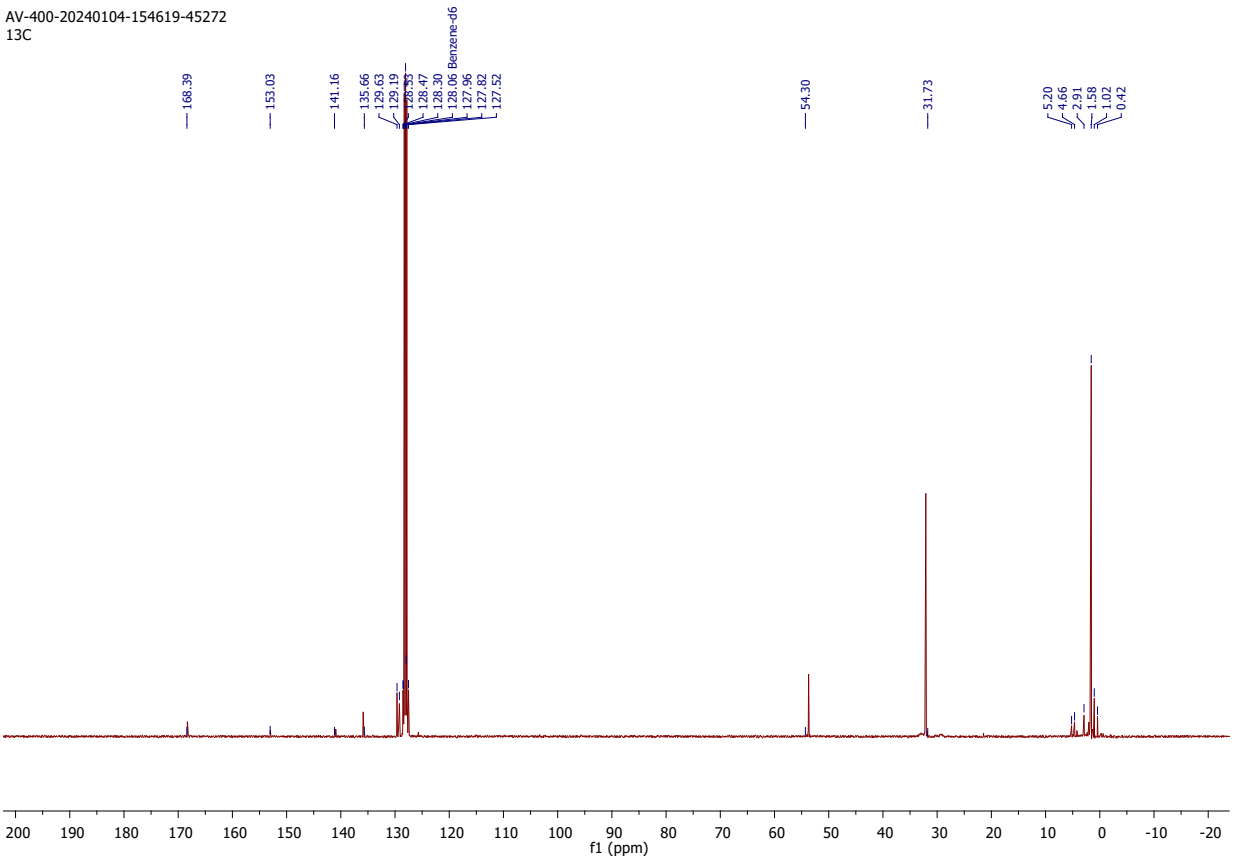

Figure S7. ^{13}C NMR Spectrum of **3** (C_6D_6, 100.61 MHz, 298 K)

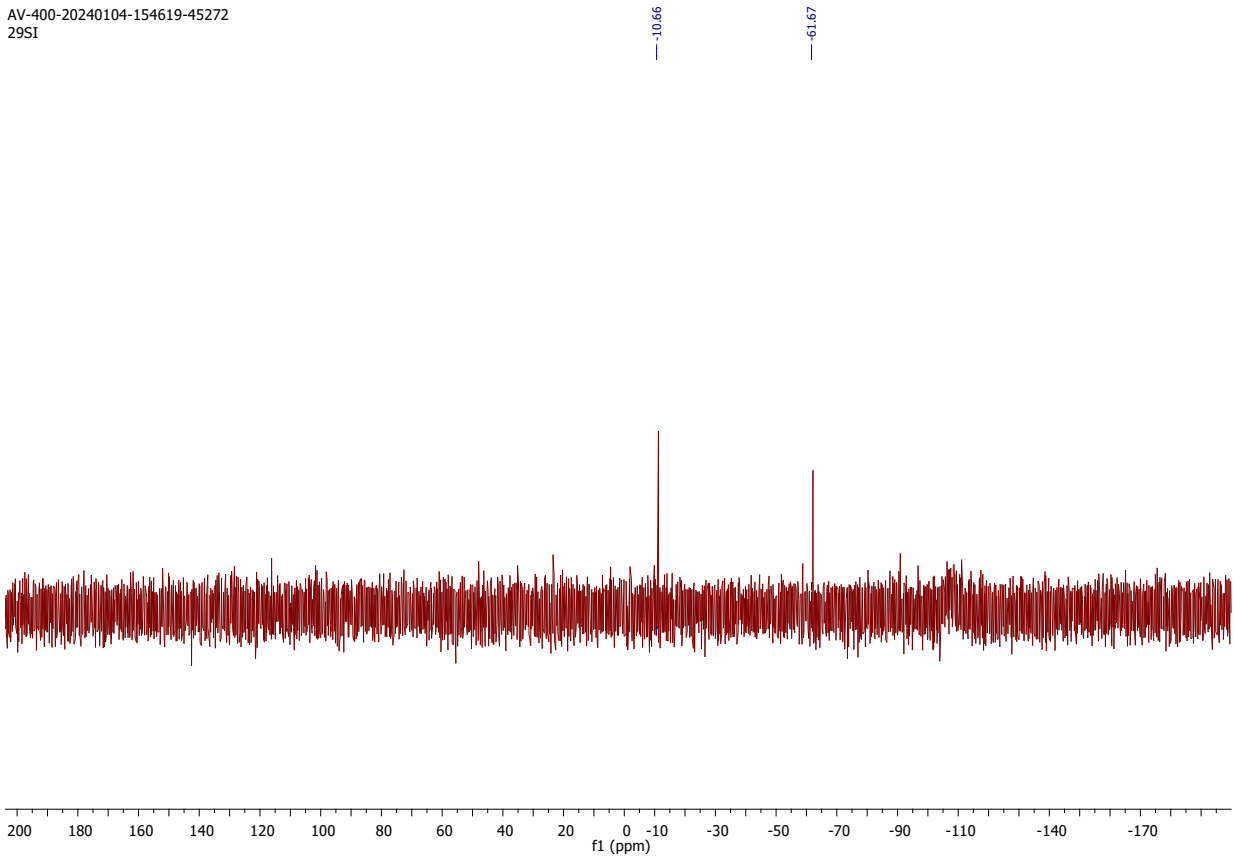

Figure S8. ^{29}Si NMR Spectrum of **3** (C_6D_6, 79.49 MHz, 298 K)

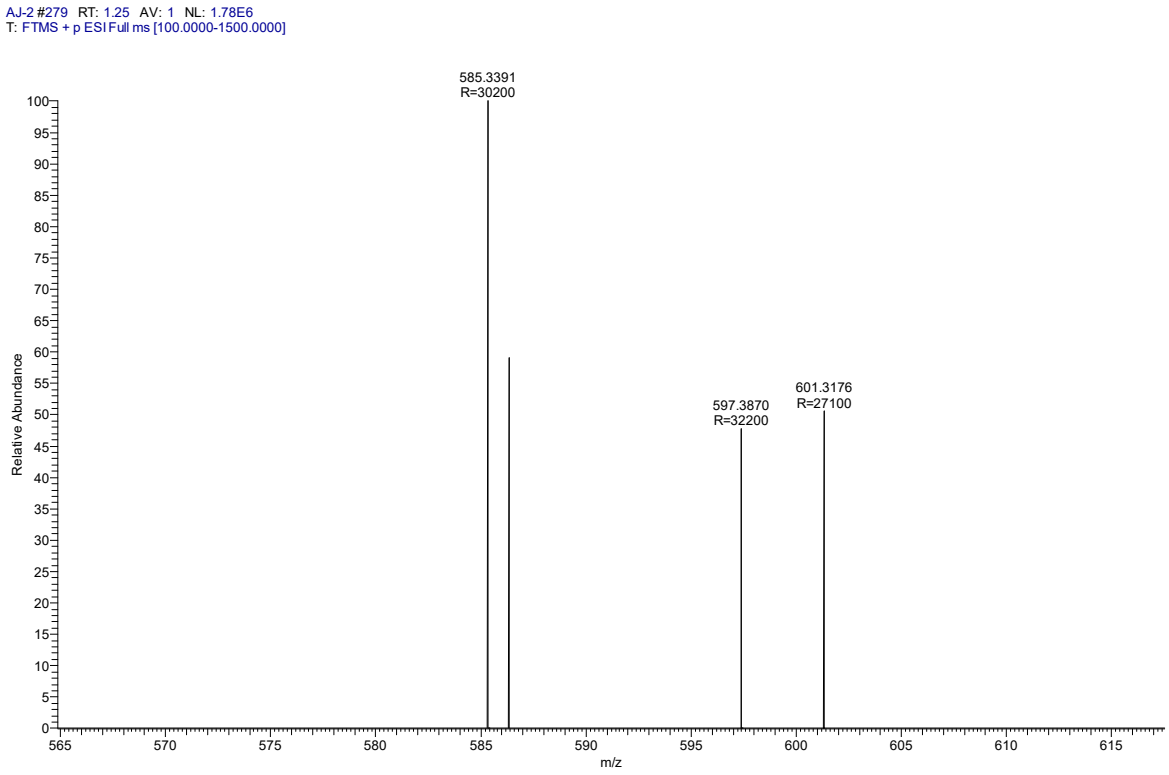

Figure S9. HRMS Spectrum of **3**

Synthesis of compound PhC(N*t*Bu)$_2$Si(=S)Si(SiMe$_3$)$_3$ (4). To a toluene (5 mL) solution of **2** (0.15 g, 0.24 mmol), one equivalent of silylene, (PhC(NtBu)$_2$Si-Si(SiMe$_3$)$_3$)[S2] (0.12 g, 0.24 mmol) dissolved in toluene (5 mL) was added dropwise via a cannula at −78 °C. The reaction mixture was allowed to reach room temperature slowly and stirred further for 12 hr. After that, all the volatiles were removed in vacuum and the residue was extracted with toluene (8 mL). The filtrate was collected through a cannula and concentrated to ~3 mL to yield colorless crystals of **4** (0.06 g, 47 %). Compound **4** was previously reported by us in a different synthetic procedure and its characterization is given in ref. S2.

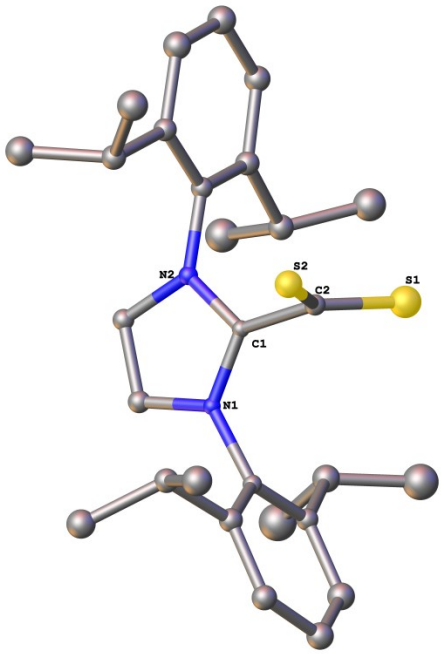

Figure S10. The molecular structure of IDipp·CS$_2$.

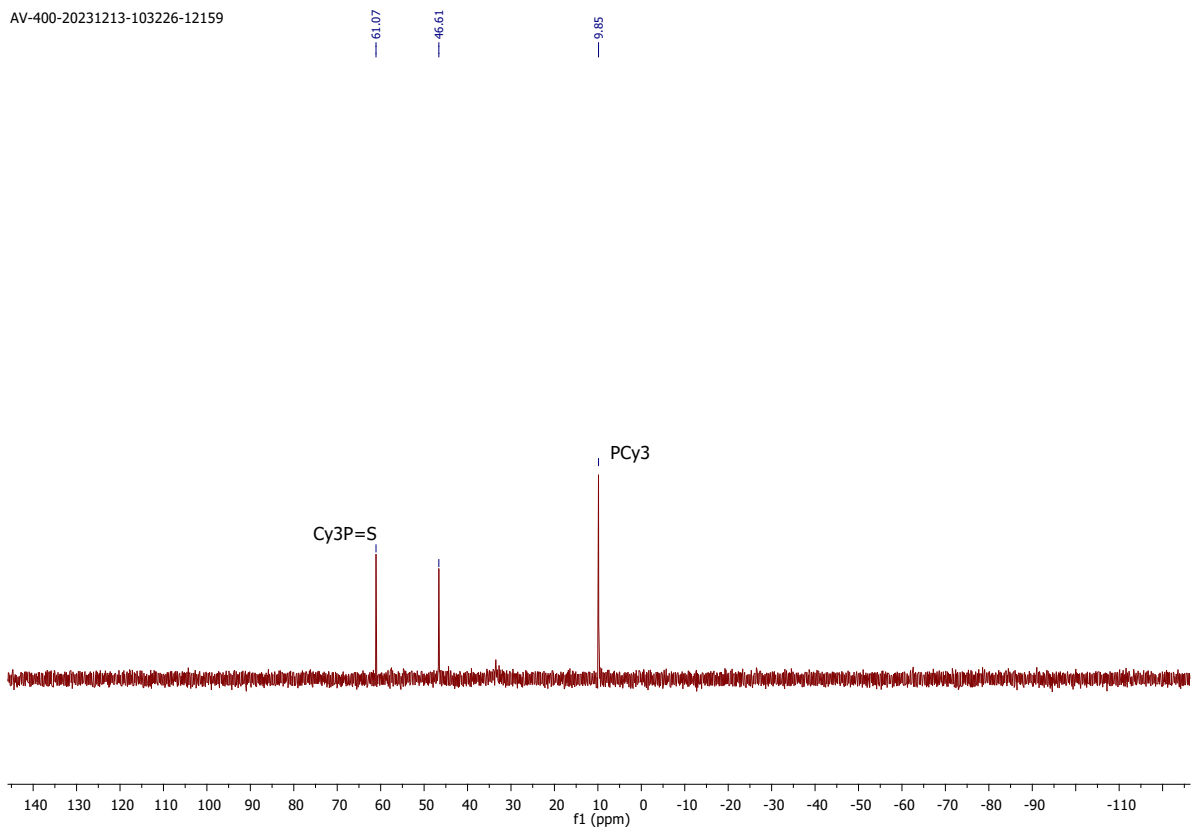

Figure S11. ^{31}P NMR Spectrum for reaction of **2** with PCy_3 indicating formation of $Cy_3P{=}S$ at 61.1 ppm ($CDCl_3$, 161.98 MHz, 298 K)

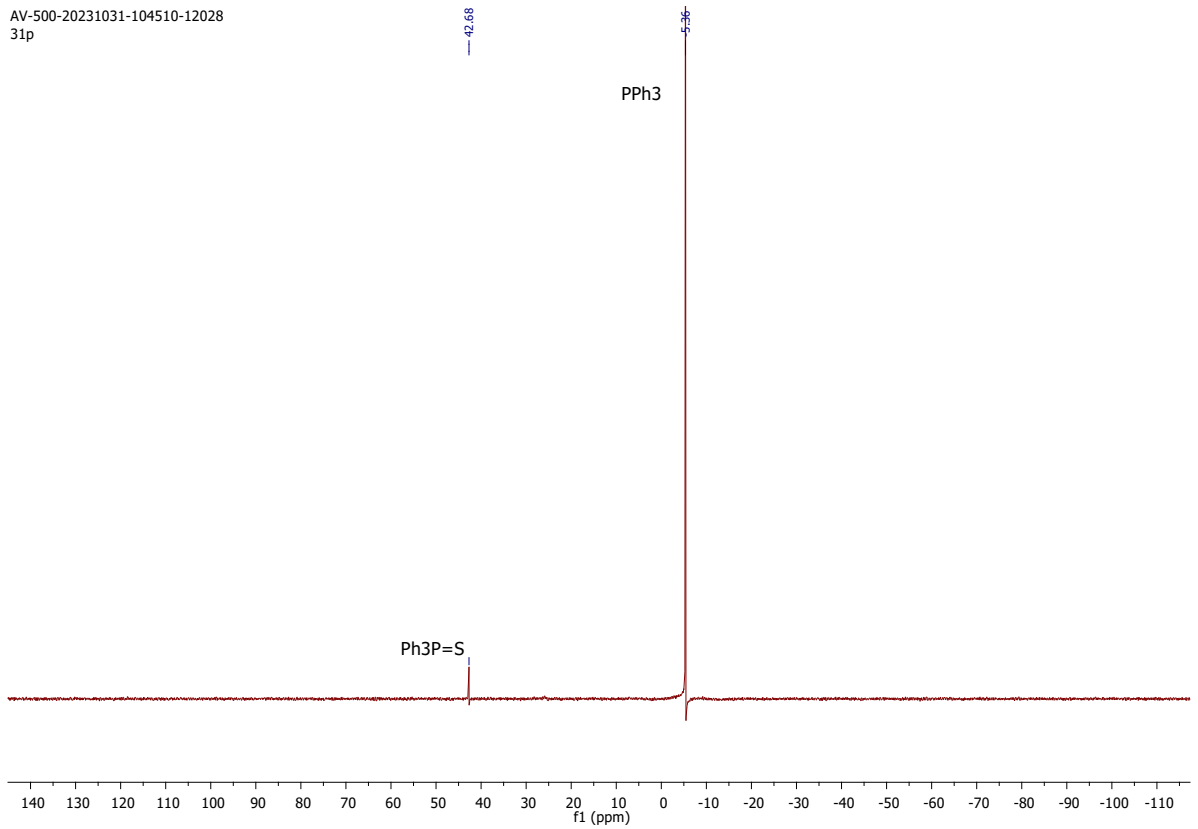

Figure S12. ^{31}P NMR Spectrum for reaction of **2** with PPh_3 indicating formation of $Ph_3P=S$ at 42.7 ppm ($CDCl_3$, 161.98 MHz, 298 K)

Details of photophysical experiments

Absorption measurements of solid compounds were carried out with the help of an integrating sphere (ISR-603), attached to a Shimadzu UV-3600 Plus spectrophotometer. The photoluminescence experiments were performed on Flurolog-3 spectrofluorometer (HORIBA Scientific) with Xe-lamp as excitation source for fluorescence and Xe flash lamp for phosphorescence emission. Phosphorescence lifetime was measured using spectrofluorometer (Horiba scientific) with spectra LED excitation source of 525 nm (77 K). The quality of the fit has been judged by fitting parameters such as χ^2 (<1.2) as well as visual inspection of the residuals.

Crystallographic data for the structural analysis of compounds 2 and 3. X-ray intensity data measurements of compounds **2** and **3** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoKα= 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S4] All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on *F*2.[S5] All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP* III[S6] view of compounds **2** and **3** were drawn with 50% probability displacement ellipsoids and H atoms omitted for clarity.

Table S1. Crystal data parametrs of compounds **2** and **3**

Identification code	**2**	**3**
Empirical formula	$C_{25}H_{50}GeN_2S_2Si_4$	$C_{24}H_{50}GeN_2SSi_4$
Formula weight	627.74	583.69
Temperature/K	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	P1	Pc
a/Å	9.8098(14)	21.115(2)
b/Å	23.143(4)	9.6030(11)
c/Å	24.199(3)	16.2157(19)

α/°	87.922(5)	90
β/°	79.937(4)	93.596(4)
γ/°	79.857(5)	90
Volume/Å^3	5324.7(13)	3281.5(6)
Z	6	1
ρ_{calc}g/cm^3	1.175	1.181
μ/mm^{-1}	1.132	1.158
F(000)	2004.0	1248.0
Crystal size/mm^3	0.11 × 0.06 × 0.02	0.11 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.954 to 56	4.242 to 56.696
Index ranges	-12 ≤ h ≤ 12, -30 ≤ k ≤ 30, -31 ≤ l ≤ 31	-28 ≤ h ≤ 28, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21
Reflections collected	123414	136918
Independent reflections	49867 [R_{int} = 0.0725, R_{sigma} = 0.1061]	16323 [R_{int} = 0.0776, R_{sigma} = 0.0444]
Data/restraints/parameters	49867/431/1952	16323/2/610
Goodness-of-fit on F^2	1.053	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0837, wR_2 = 0.2113	R_1 = 0.0404, wR_2 = 0.0869
Final R indexes [all data]	R_1 = 0.1044, wR_2 = 0.2283	R_1 = 0.0552, wR_2 = 0.0934
Largest diff. peak/hole / e Å$^-$	2.77/-1.08	0.87/-0.64

3		
CCDC No.	2339965	2339967

Details of theoretical calculations

Photophysical TDDFT data for complex 1 and 2:

Table S2. Calculated singlet triplet gap values (vertical) and oscillator strengths of **1** and **2**.

Species	Calc. wavelength (Expt value)	Oscillator strength
2	399 nm (408 nm)	0.0163
	571 nm (570 nm)	0.0014
1	327 nm (412 nm)	0.1785

Species	S_1	T_1	E_{S1-T1}
2	2.17 eV	1.82 eV	0.35 eV
1	2.61 eV	2.51 eV	0.10 eV

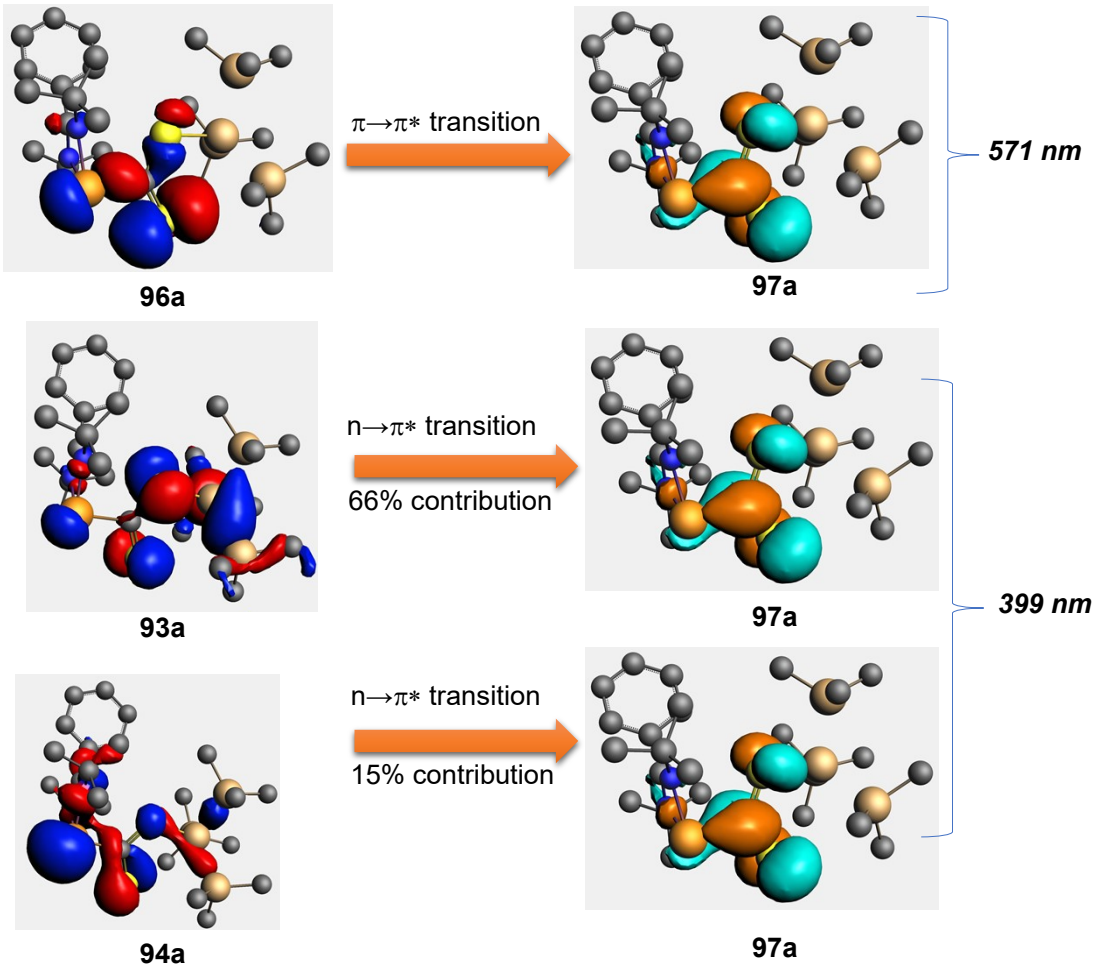

Figure S13. Some selected NTOs with their corresponding excitation energies for **2**.

All calculations were performed employing density functional theory (DFT) implemented in the Gaussian 09 program package.[S7] Geometry optimizations of the reactants, transition states, and intermediates were carried out using gradient-corrected BP86 functional[S8] in conjunction with Ahlrichs' split valence plus polarization basis set (def2-SVP)[S9] for all the atoms. The frequency calculations were performed on the optimized geometries at the same level to determine the nature of stationary points on the potential energy surface either as minima or the transition states and to obtain the thermochemical energy values. Transition states are characterized by first-order saddle points. The minima were identified by having a complete set of real frequencies and transition states own only one imaginary

frequency. The transition states were searched using the linear synchronous transit (LST) method,[S10] and optimizations were performed by utilizing the default Berny algorithm, implemented in the Gaussian 09 quantum code. Intrinsic reaction coordinate (IRC) calculations were carried out to verify the connectivity between the transition state and the corresponding intermediates.[S11]

Furthermore, to improve the energy values obtained at the R-BP86/def2-SVP level, single-point calculations were conducted on the optimized geometries with the same functional, employing the triple-ζ valence plus polarization basis set (def2-TZVP) for all the atoms. Tight wave function convergence criteria and “ultrafine” (99,950) grid were used in numerical integration during single-point calculations. Additionally, to incorporate the London dispersion effects, we used Grimme's D3 empirical correction.[S12] Solvation energies (E_L^S) were evaluated by a self-consistent reaction field (SCRF) method for all the intermediates and transition states, using the SMD continuum solvation model[S13] for toluene solvent (dielectric constant ε= 2.374).

The concentration correction was conducted in the Gaussian 09 program by converting the concentration value to the corresponding pressure value according to the ideal gas equation, $p_i = RTn_i/V$, where p_i is the pressure, R is the gas constant, T is the absolute temperature, n_i is the molar quantity, and V is the reaction volume. At the reaction temperature, the partial pressures of the reactants and catalyst were estimated from the approximate experimental concentrations as follows: the partial pressure of species **1**: 0.27 mM ≙ 0.0066 atm;, CS_2: 0.27 mM ≙ 0.0066 atm;, and alphatic/aromatic isocyanate: 0.27 mM ≙ 0.0066 atm. The partial pressure of the intermediates in the reaction system was estimated according to the partial pressures of the reactants. We have focused on the energy terms H_L^S and G_L^S which represent the enthalpy and Gibbs free energy respectively in the solution phase at the higher

basis set mentioned earlier. The Gibbs free energy in the solution phase (G_L^S) was calculated according to the following equation: $G_L^S = H_L^S - TS_L^S$ where, H_L^S was calculated from E_L^S (single point energy at higher basis set) and the H_{corr} (enthalpy corrections at the lower basis set), while the solvation entropy (S_L^S) was estimated as two-thirds of the gas-phase value to consider the solvation entropy contribution.[S14] Optimized geometries were rendered using the CYLview and Chemcraft visualization programs.[S15, S16] All the reported energy values (ΔG_L^S) were obtained at the R-BP86-D3 (SMD(Toluene))/def2-TZVP//R-BP86/def2-SVP level.

To explore the photophysical properties, crystal structures **1** and **2** were used as the initial input for the geometry optimization. The structures of **1** and **2** were relaxed via density functional theory (DFT) using the BP86 functional in the Gaussian 09 suite of programs. These calculations used the Def2-TZVP basis for all atoms during the calculation. Additionally, to incorporate the London dispersion effects, we used Grimme's D3 empirical correction.

Time-dependent DFT (TDDFT) calculations were carried out with the Amsterdam Density Functional (ADF2022.01) program.[S17] As with the geometry optimization, the BP86-D3 functional was used. Based on the one-component zeroth-order regular approximation (ZORA),[S18,S19] the 10 lowest scalar relativistic singlet and triplet excitations were calculated. Spin-orbit coupling (SOC) was included perturbatively around the one-component TDDFT calculations, [S20,S21] leading to a total of 40 spin-mixed excitations. The calculations were performed with a Slater-type TZP basis set [S22] and a frozen core approximation.

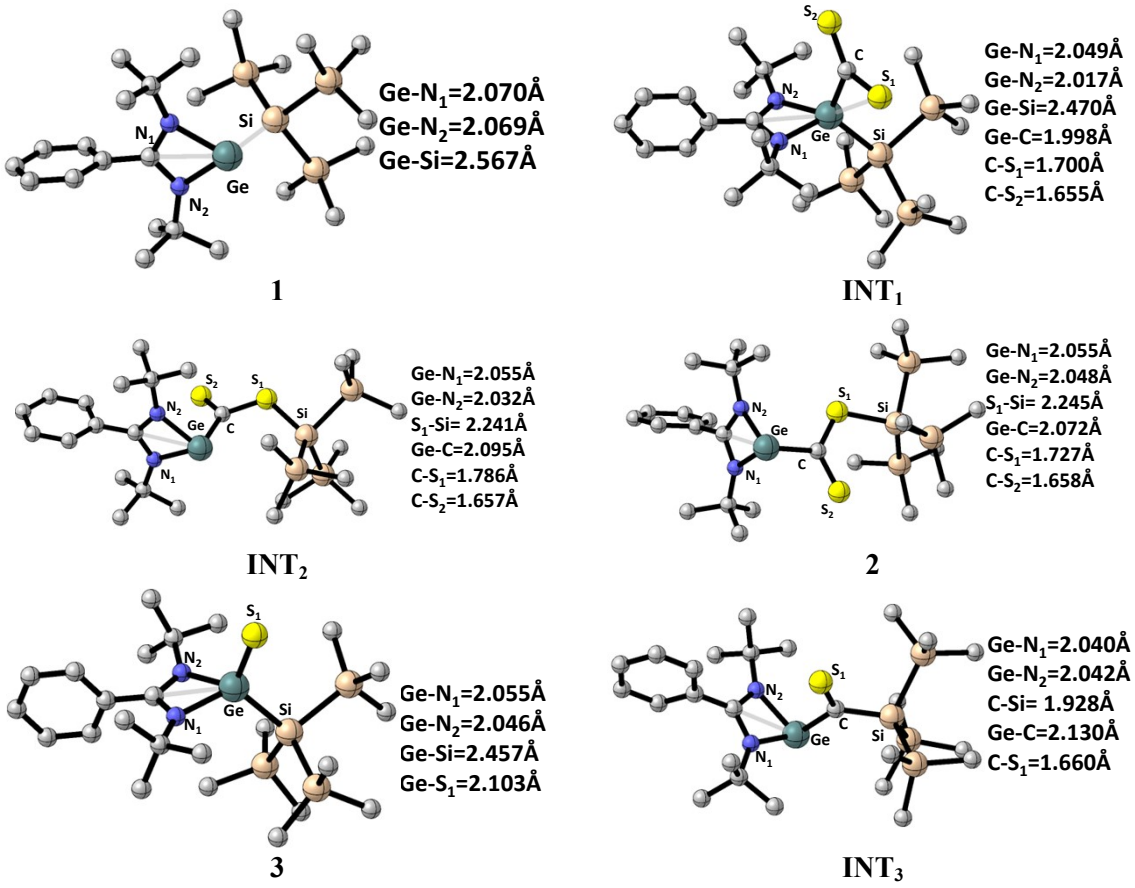

Figure S14. Optimized geometries of the intermediates and transition states involved in the CS_2 activation reaction by **1**. The key geometrical parameters of the structures are also provided. Less pertinent hydrogen atoms are removed for clarity.

Table S3**.** Absolute energies (in Hartree) of all the intermediates and transition states.

E_e = Electronic energy at the optimization level of theory, H_{298} *and* G_{298} are Enthalpy and Gibbs free energy at the optimization level of theory at 298 K, and E_L^S = Electronic energy at the single-point level of theory. $H_L^S = E_L^S + H_{corr}$ Where H_{corr} is the enthalpy correction value at a given concentration. $G_L^S = H_L^S - 0.67(H_{298}-G_{298})$. Concentration terms are added as mentioned in the Computational Methodology. Imig = Imaginary Frequency.

Species	E_e	H_{298}	G_{298}	E_L^S	H_L^S	G_L^S	imig
1	-4288.24491	-4287.52762	-4287.65880	-4290.19273	-4289.54278	-4289.63067	0
CS_2	-834.30675	-834.29585	-834.32289	-834.62646	-834.61615	-834.63427	0
TS_1	-5122.54031	-5121.81172	-5121.95272	-5124.81983	-5124.15918	-5124.25365	1
INT_1	-5122.55351	-5121.82358	-5121.96282	-5124.83963	-5124.17774	-5124.27103	0
TS_2	-5122.53592	-5121.80774	-5121.94644	-5124.81520	-5124.15494	-5124.24787	1
INT_2	-5122.57392	-5121.84458	-5121.98819	-5124.84480	-5124.18342	-5124.27964	0
2	-5122.55621	-5121.82704	-5121.97128	-5124.83030	-5124.16905	-5124.26570	0
3	-4686.39924	-4685.67789	-4685.81296	-4688.49717	-4687.84336	-4687.93385	0
INT_3	-4724.41143	-4723.68597	-4723.82609	-4726.54160	-4725.88392	-4725.97779	0

Table S4. Cartesian coordinates of all the intermediates and transition states

1			
Ge	-0.090389	-0.015762	-1.567824
Si	1.885455	-0.015184	0.070902
Si	1.591484	-0.720142	2.334536
Si	3.537688	-1.435821	-0.941214
Si	2.999013	2.111996	0.156972
N	-1.578140	1.106104	-0.668137
N	-1.559351	-1.087367	-0.578075
C	-2.300636	0.016559	-0.346488
C	-3.711229	0.025284	0.178779
C	-3.942221	0.082604	1.572087
H	-3.083860	0.118821	2.260795
C	-1.955019	-2.512803	-0.631861
C	-4.822816	-0.021981	-0.693220
H	-4.659303	-0.052545	-1.781336
C	-1.940571	2.539885	-0.672258
C	-2.982894	-2.776551	-1.759908
H	-2.608754	-2.379270	-2.726279
H	-3.153465	-3.867348	-1.878507
H	-3.961735	-2.307760	-1.540047
C	-6.350789	0.033645	1.204944
H	-7.377613	0.035377	1.603652
C	-2.513993	-3.004255	0.723660
H	-3.477357	-2.520740	0.976450
H	-2.686894	-4.100106	0.685835
H	-1.795151	-2.797793	1.542687
C	-0.750802	3.275937	-1.319081
H	-0.611724	2.951915	-2.371863
H	-0.915440	4.372369	-1.314108
H	0.182708	3.064245	-0.762883
C	-2.136841	3.059329	0.771479
H	-1.240772	2.842878	1.387771
H	-2.302070	4.157137	0.769150
H	-3.013989	2.586857	1.256367
C	-0.667671	-3.294450	-0.955283
H	0.110343	-3.104256	-0.190280
H	-0.865335	-4.384823	-0.993850
H	-0.262667	-2.987009	-1.942264
C	-0.026169	0.010589	3.034557
H	-0.190132	-0.312928	4.085649
H	-0.015484	1.120058	3.013135
H	-0.886113	-0.333400	2.423235
C	-5.252437	0.086387	2.080666
H	-5.414131	0.129749	3.169397
C	3.022516	-0.174802	3.478952
H	3.995640	-0.591041	3.144924
H	3.123063	0.929403	3.524219
C	2.863896	-3.126020	-1.521435
H	2.419423	-3.712648	-0.691424
H	2.095873	-3.016550	-2.314518
H	3.701350	-3.722898	-1.945505
C	-6.132269	-0.019545	-0.183037
H	-6.987588	-0.057243	-0.876266
C	3.071756	2.972206	-1.548117
H	3.625492	2.352318	-2.282817
H	2.069208	3.177072	-1.973949
H	3.605208	3.943735	-1.454224
C	-3.203341	2.831131	-1.519642
H	-4.122051	2.424891	-1.055382
H	-3.339716	3.927757	-1.626783
H	-3.098818	2.398607	-2.536278
C	4.287228	-0.609557	-2.492448
H	3.499626	-0.341504	-3.227919
H	4.849323	0.314546	-2.244958
H	4.993393	-1.309142	-2.991237
C	2.165710	3.300019	1.403309
H	1.103409	3.506540	1.161714
H	2.200896	2.887317	2.433263
C	4.814255	1.948247	0.734480
H	5.259789	2.963158	0.829776
H	4.898287	1.447011	1.720226
H	5.430743	1.380401	0.007538
H	2.835875	-0.538198	4.513714
C	4.963287	-1.827709	0.271058
H	4.602300	-2.409058	1.145472
H	5.735580	-2.441669	-0.242820
H	5.456118	-0.911828	0.654712
C	1.478928	-2.621176	2.493192
H	2.397584	-3.119739	2.119390
H	1.354186	-2.904147	3.561501
H	0.617255	-3.038180	1.932557
H	2.704137	4.273170	1.413128
TS_1			
Ge	-0.085686	0.684628	-0.780214
Si	1.978733	-0.380970	0.304826
Si	1.670213	-2.470392	1.424196
Si	3.537725	-0.647543	-1.502521
Si	3.098520	1.097310	1.833160
N	-1.547823	0.949008	0.627527
N	-1.597019	-0.699751	-0.824714
C	-2.313621	-0.026730	0.102311
C	-3.733944	-0.326894	0.492111
C	-3.999301	-1.237003	1.540093
H	-3.160077	-1.721598	2.063084
C	-2.010415	-1.732773	-1.804009
C	-4.818984	0.289388	-0.171674
H	-4.618676	1.006158	-0.982440
C	-1.865539	2.008011	1.613522
C	-3.144203	-1.240121	-2.734486
H	-2.879108	-0.262110	-3.185754
H	-3.305421	-1.971554	-3.553965
H	-4.103318	-1.129656	-2.192664
C	-6.396178	-0.911600	1.246993
H	-7.433253	-1.139228	1.540236
C	-2.438342	-3.034583	-1.087120
H	-3.356574	-2.887973	-0.485285
H	-2.648470	-3.828274	-1.834100
H	-1.634701	-3.397937	-0.414816
C	-0.639327	2.940882	1.641015
H	-0.492377	3.436911	0.659280

H	-0.764461	3.730110	2.409495
H	0.276149	2.367253	1.884009
C	-2.069052	1.392464	3.017767
H	-1.188030	0.785451	3.310372
H	-2.206464	2.194071	3.773227
H	-2.965642	0.742126	3.049395
C	-0.763896	-2.014698	-2.664588
H	0.089437	-2.330389	-2.031908
H	-0.967226	-2.817815	-3.401332
H	-0.462986	-1.105775	-3.226442
C	0.084113	-2.420466	2.480890
H	-0.067835	-3.385861	3.011138
H	0.129926	-1.614094	3.241871
H	-0.800749	-2.231872	1.838332
C	-5.322945	-1.526829	1.914330
H	-5.514619	-2.238621	2.732791
C	3.136954	-2.876766	2.578849
H	4.092714	-2.941289	2.018444
H	3.261298	-2.118460	3.379165
C	2.772637	-1.416581	-3.071305
H	2.348190	-2.424691	-2.887015
H	1.972400	-0.776735	-3.496691
H	3.565057	-1.520493	-3.844894
C	-6.140700	-0.003159	0.204266
H	-6.976914	0.484682	-0.321206
C	3.155141	2.899978	1.214256
H	3.718698	2.972912	0.261879
H	2.151794	3.334491	1.036048
H	3.674359	3.533910	1.966321
C	-3.102762	2.845316	1.209945
H	-4.043371	2.268415	1.294578
H	-3.190387	3.727196	1.878405
H	-3.001992	3.209513	0.167122
C	4.252752	1.043121	-2.017394
H	3.444347	1.758246	-2.279216
H	4.864399	1.499782	-1.212052
H	4.905821	0.922688	-2.909329
C	2.299727	1.054349	3.568668
H	1.236393	1.368439	3.562915
H	2.347500	0.036410	4.008812
C	4.916479	0.558310	2.068883
H	5.394513	1.214453	2.829415
H	5.004898	-0.489374	2.421126
H	5.499962	0.655945	1.130357
H	2.965212	-3.859932	3.070142
C	4.979296	-1.787982	-0.981662
H	4.625626	-2.817313	-0.762448
H	5.719102	-1.857578	-1.809312
H	5.509415	-1.413264	-0.082821
C	1.529208	-3.927269	0.199434
H	2.448632	-4.034020	-0.413311
H	1.386011	-4.877684	0.758818
H	0.672268	-3.813245	-0.495262
C	-0.585974	2.830408	-2.382225
S	0.788251	3.664740	-2.376645
S	-2.125694	2.623593	-2.808995
H	2.849360	1.740644	4.249638

INT_1

Ge	-0.091168	-0.467276	0.597474
Si	2.066097	0.311656	-0.320554
Si	1.781670	2.461090	-1.348394
Si	3.514274	0.424293	1.600699
Si	3.147207	-1.096500	-1.946704
N	-1.635160	-0.972052	-0.597364
N	-1.667406	0.840089	0.662812
C	-2.393662	0.050835	-0.148744
C	-3.829749	0.282187	-0.514753
C	-4.157089	1.213484	-1.524996
H	-3.353524	1.760581	-2.041808
C	-2.084473	1.921551	1.596709
C	-4.864811	-0.425779	0.135496
H	-4.617307	-1.137270	0.937924
C	-1.971956	-2.133674	-1.464234
C	-3.270647	1.492198	2.491039
H	-3.036103	0.531318	2.994301
H	-3.438230	2.260741	3.274097
H	-4.212358	1.389984	1.918339
C	-6.524381	0.713252	-1.239157
H	-7.575523	0.879544	-1.523056
C	-2.433922	3.210131	0.818219
H	-3.333779	3.073484	0.186098
H	-2.644976	4.036460	1.528511
H	-1.592658	3.523861	0.167139
C	-0.636207	-2.686510	-1.994295
H	0.022276	-2.979662	-1.151153
H	-0.815127	-3.578394	-2.628236
H	-0.111854	-1.924743	-2.605082
C	-2.849406	-1.736103	-2.673159
H	-2.403153	-0.884804	-3.227482
H	-2.912451	-2.598789	-3.368081
H	-3.882486	-1.465377	-2.385816
C	-0.867416	2.171995	2.509107
H	0.033482	2.419475	1.911640
H	-1.065892	3.019232	3.196448
H	-0.657899	1.267364	3.119039
C	0.239009	2.442570	-2.468474
H	0.117392	3.421937	-2.980546
H	0.311558	1.655439	-3.247243
H	-0.676289	2.249403	-1.870874
C	-5.498198	1.423822	-1.886558
H	-5.741800	2.146622	-2.681119
C	3.302387	2.878788	-2.423515
H	4.231421	2.919866	-1.817909
H	3.460061	2.150048	-3.244268
C	2.618569	1.038814	3.160337
H	2.196513	2.056121	3.029371
H	1.797741	0.355772	3.463300
H	3.348088	1.081335	3.998795
C	-6.204846	-0.208455	-0.226260

H	-7.004618	-0.762809	0.289576
C	3.139184	-2.943311	-1.514018
H	3.548948	-3.120495	-0.499558
H	2.122729	-3.380910	-1.539323
H	3.773126	-3.488068	-2.247854
C	-2.669951	-3.229570	-0.623406
H	-3.648087	-2.880247	-0.237453
H	-2.854644	-4.129007	-1.247295
H	-2.033196	-3.526847	0.234063
C	4.265436	-1.279701	1.975211
H	3.464774	-2.024004	2.170394
H	4.890876	-1.655833	1.139470
H	4.910494	-1.212835	2.878496
C	2.436833	-0.850850	-3.701174
H	1.366095	-1.129748	-3.774106
H	2.538046	0.199601	-4.043800
C	4.976543	-0.549178	-2.012039
H	5.492856	-1.118974	-2.815780
H	5.094823	0.530506	-2.233663
H	5.502826	-0.765945	-1.059762
H	3.157907	3.879984	-2.885715
C	4.921664	1.652724	1.205466
H	4.538600	2.681487	1.041026
H	5.627946	1.691624	2.063753
H	5.499732	1.354774	0.306977
C	1.618028	3.894224	-0.102305
H	2.500878	3.955091	0.567456
H	1.550806	4.855804	-0.656813
H	0.715711	3.811099	0.535533
C	-0.102838	-1.755052	2.125227
S	0.832062	-3.033080	1.506366
S	-0.909862	-1.527111	3.563085
H	2.998329	-1.492048	-4.415487

TS_2			
Ge	-0.309067	-0.192265	-0.296509
Si	2.416348	0.038240	0.374927
Si	2.195919	-1.995350	1.654443
Si	3.666308	-0.463945	-1.604965
Si	3.697669	1.548832	1.742139
N	-1.898908	0.349365	0.856930
N	-2.069920	-1.096037	-0.797948
C	-2.755071	-0.372360	0.104762
C	-4.250555	-0.367246	0.244693
C	-4.899248	-1.305397	1.077604
H	-4.302307	-2.039186	1.641241
C	-2.500423	-2.001190	-1.886878
C	-5.022167	0.575045	-0.471450
H	-4.513804	1.294510	-1.132294
C	-2.138466	1.374154	1.903739
C	-3.482046	-1.307194	-2.860132
H	-3.069604	-0.328393	-3.180968
H	-3.634366	-1.943226	-3.757027
H	-4.473278	-1.139629	-2.396320
C	-7.062987	-0.354648	0.484541
H	-8.160432	-0.348970	0.578778
C	-3.124328	-3.292235	-1.307808
H	-4.068833	-3.079520	-0.768707
H	-3.357220	-4.005175	-2.126205
H	-2.422795	-3.789325	-0.606087
C	-0.749254	1.775845	2.440306
H	-0.117848	2.202236	1.633527
H	-0.853581	2.542292	3.234691
H	-0.224173	0.900187	2.872037
C	-2.971355	0.799282	3.072974
H	-2.494860	-0.114220	3.485021
H	-3.035782	1.549251	3.888598
H	-4.005181	0.549619	2.765936
C	-1.216339	-2.362441	-2.663549
H	-0.474658	-2.856604	-2.001418
H	-1.448498	-3.059999	-3.493329
H	-0.752628	-1.453739	-3.099949
C	0.866291	-1.844070	3.016971
H	0.749504	-2.817308	3.542146
H	1.137865	-1.080437	3.775210
H	-0.123270	-1.569118	2.594531
C	-6.299738	-1.297145	1.195837
H	-6.796432	-2.031371	1.849675
C	3.820416	-2.527103	2.512482
H	4.654186	-2.644897	1.790137
H	4.136364	-1.793643	3.283278
C	2.535733	-1.128418	-2.985149
H	2.022080	-2.064014	-2.682636
H	1.763826	-0.381385	-3.263825
H	3.137330	-1.349087	-3.894013
C	-6.421818	0.579411	-0.348671
H	-7.015086	1.317356	-0.911385
C	3.762458	3.337312	1.091878
H	4.149450	3.390821	0.053694
H	2.763611	3.819449	1.102677
H	4.440084	3.935178	1.740664
C	-2.828527	2.626557	1.312360
H	-3.867602	2.407295	0.997788
H	-2.871537	3.432028	2.075035
H	-2.268944	3.004459	0.433217
C	4.553916	1.087441	-2.262726
H	3.829499	1.891236	-2.507144
H	5.283029	1.490820	-1.529648
H	5.112837	0.831978	-3.189643
C	3.037601	1.605325	3.531951
H	2.003804	2.005735	3.575717
H	3.035011	0.601530	4.005640
C	5.493524	0.896241	1.813448
H	6.091264	1.530011	2.505065
H	5.549630	-0.148980	2.179667
H	5.981626	0.935186	0.817292
H	3.673150	-3.504730	3.021943
C	4.996673	-1.781727	-1.229642
H	4.552493	-2.747708	-0.911935
H	5.599917	-1.974177	-2.143959
H	5.692079	-1.446951	-0.432136

C	1.653668	-3.423751	0.508112
H	2.428795	-3.668829	-0.247337
H	1.461479	-4.339775	1.108311
H	0.715374	-3.178027	-0.033016
C	-0.161911	1.482612	-1.428921
S	1.331192	2.136441	-0.897551
S	-1.290764	2.082810	-2.491352
H	3.682779	2.267219	4.150262
INT_2			
Ge	0.813719	0.186834	0.764209
Si	-3.039967	-0.048663	-0.055931
Si	-2.889117	-0.301531	2.325472
Si	-3.599098	2.186312	-0.680510
Si	-4.644571	-1.604727	-0.930667
N	2.365250	-1.099797	0.360577
N	2.608434	1.079625	0.429469
C	3.245870	-0.090133	0.239888
C	4.711324	-0.242063	-0.058714
C	5.655841	-0.421934	0.975880
H	5.316636	-0.459800	2.022841
C	3.091247	2.472835	0.507743
C	5.155939	-0.199790	-1.399247
H	4.416070	-0.050714	-2.201455
C	2.496588	-2.558568	0.164151
C	3.807803	2.903596	-0.793831
H	3.171255	2.673938	-1.672165
H	4.008745	3.995311	-0.772779
H	4.778343	2.385625	-0.919910
C	7.457705	-0.516163	-0.662298
H	8.528577	-0.623186	-0.897447
C	4.020729	2.672231	1.728910
H	4.957314	2.089233	1.624290
H	4.299985	3.742046	1.832164
H	3.512593	2.356002	2.663677
C	1.112090	-3.163504	0.480818
H	0.329098	-2.740315	-0.182415
H	1.128577	-4.262625	0.334389
H	0.824510	-2.963545	1.533710
C	3.534946	-3.171098	1.134755
H	3.295447	-2.902372	2.184589
H	3.524851	-4.278250	1.052123
H	4.563386	-2.827418	0.910126
C	1.831446	3.346999	0.688346
H	1.280798	3.064868	1.610778
H	2.108156	4.417634	0.770504
H	1.147332	3.233808	-0.177400
C	-1.943730	-1.857396	2.866611
H	-2.034390	-1.987306	3.967086
H	-2.335472	-2.772474	2.377194
H	-0.866316	-1.763294	2.620845
C	7.022159	-0.556473	0.673978
H	7.750360	-0.695306	1.488865
C	-4.699180	-0.461995	2.920626
H	-5.323423	0.397418	2.598510
H	-5.179183	-1.392555	2.553456
C	-2.082384	3.310037	-0.445197
H	-1.732010	3.317658	0.607500
H	-1.242156	2.970058	-1.085760
H	-2.328744	4.355543	-0.732755
C	6.522112	-0.338253	-1.697123
H	6.857574	-0.304471	-2.745847
C	-4.488074	-1.753821	-2.821308
H	-4.671078	-0.783945	-3.327434
H	-3.478273	-2.102567	-3.119985
H	-5.234273	-2.486214	-3.200319
C	2.867218	-2.895472	-1.300435
H	3.882428	-2.532594	-1.555262
H	2.853137	-3.994805	-1.455752
H	2.144915	-2.431781	-2.001786
C	-4.107300	2.237695	-2.513775
H	-3.318766	1.788500	-3.152529
H	-5.053423	1.686689	-2.695957
H	-4.259231	3.289179	-2.841660
C	-4.353192	-3.328459	-0.171534
H	-3.320373	-3.680825	-0.374648
H	-4.505837	-3.332647	0.927751
C	-6.416850	-1.029320	-0.522680
H	-7.148758	-1.777394	-0.898656
H	-6.583847	-0.910807	0.567275
H	-6.649670	-0.059929	-1.011243
H	-4.716668	-0.491080	4.032326
C	-5.039489	2.839268	0.387418
H	-4.768861	2.884094	1.463102
H	-5.314056	3.868321	0.067759
H	-5.944244	2.203613	0.290340
C	-2.154344	1.230410	3.180988
H	-2.729397	2.149213	2.941917
H	-2.182929	1.090348	4.283771
H	-1.097974	1.385866	2.880605
C	0.201069	0.150089	-1.238625
S	-1.406989	-0.570269	-1.527208
S	1.110933	0.494071	-2.580606
H	-5.057347	-4.066833	-0.613494
2			
Ge	1.634933	-1.067308	-1.952948
S	-0.865179	-2.488676	-0.652845
S	-0.828478	0.530889	-0.454137
Si	-2.938232	0.166984	0.293040
Si	-4.244823	-0.854213	-1.443888
Si	-3.473216	2.497173	0.505878
Si	-2.872274	-0.857136	2.458269
N	2.862380	-1.309948	-0.320838
N	2.504389	0.657750	-1.232635
C	4.201954	0.606598	0.646608
C	3.753061	1.140400	1.875338
C	4.665582	1.714443	2.777238
C	6.034385	1.765687	2.460645
C	6.488359	1.238303	1.238425
C	5.579121	0.660325	0.336803
C	3.206526	-0.010126	-0.296849

C	3.213193	-2.457065	0.543994
C	4.727687	-2.540736	0.847033
C	2.801733	-3.726978	-0.234466
C	2.413155	-2.383911	1.866889
C	2.657708	2.020901	-1.786532
C	1.594981	2.152951	-2.900188
C	2.388243	3.098108	-0.709800
C	4.058054	2.225887	-2.413617
C	-0.132129	-1.007257	-0.872629
C	-1.214247	-0.408395	3.277852
C	-3.076702	-2.745492	2.436989
C	-4.290544	-0.137679	3.516764
C	-4.669255	-2.673184	-1.088658
C	-5.903703	0.083341	-1.588588
C	-3.330189	-0.704148	-3.103166
C	-3.246834	3.368864	-1.174904
C	-5.268099	2.769105	1.088316
C	-2.304671	3.322291	1.768077
H	-5.246133	-3.093260	-1.941533
H	-3.752647	-3.280345	-0.951350
H	-5.295141	-2.775167	-0.177490
H	-5.761061	1.150236	-1.858262
H	-6.522709	-0.384478	-2.385499
H	-6.487603	0.042439	-0.645213
H	-4.048043	-3.048818	1.995262
H	-2.270058	-3.224223	1.846725
H	-3.038490	-3.135591	3.477755
H	-1.091992	0.690221	3.374738
H	-1.154918	-0.853290	4.295043
H	-0.362262	-0.794087	2.681222
H	-4.185051	0.956714	3.667195
H	-5.285041	-0.326043	3.060298
H	-4.286919	-0.616960	4.520317
H	-5.462648	3.859098	1.192007
H	-6.003375	2.362674	0.364334
H	-5.462461	2.296560	2.072830
H	-2.515850	4.412201	1.832193
H	-2.430649	2.894305	2.784625
H	-1.241341	3.196815	1.476085
H	-3.468154	4.454360	-1.078215
H	-2.206721	3.263020	-1.546876
H	-3.925993	2.953430	-1.948401
H	-3.080630	0.350957	-3.338390
H	-2.387383	-1.287799	-3.090277
H	-3.970676	-1.097330	-3.922649
H	1.642702	3.159090	-3.364267
H	1.763331	1.400386	-3.699685
H	0.575021	2.004685	-2.489945
H	4.856333	2.211478	-1.645828
H	4.271770	1.433219	-3.160549
H	4.108381	3.207071	-2.930936
H	3.159511	3.087928	0.085112
H	2.392417	4.107797	-1.171352
H	1.397023	2.932519	-0.241164
H	6.748950	2.216747	3.167252
H	4.303019	2.125924	3.732566
H	2.679508	1.108578	2.118446
H	7.559961	1.273423	0.985557
H	5.940485	0.235054	-0.612177
H	5.074581	-1.724660	1.508877
H	4.945980	-3.501570	1.358039
H	5.321522	-2.511315	-0.089893
H	1.718850	-3.709770	-0.480507
H	3.374192	-3.810400	-1.181795
H	3.003316	-4.632463	0.373764
H	2.686262	-1.479530	2.448006
H	1.324727	-2.357346	1.658940
H	2.624793	-3.271345	2.499794

3

Ge	-0.017077	-0.043355	-1.129406
Si	1.982750	-0.018180	0.297578
Si	1.598270	-0.711692	2.553243
Si	3.559567	-1.435959	-0.835203
Si	2.971420	2.170782	0.322953
N	-1.621437	1.102059	-0.549316
N	-1.594359	-1.093876	-0.357244
C	-2.338289	0.019254	-0.207287
C	-3.749969	0.042261	0.309685
C	-3.980589	0.138782	1.700578
H	-3.123766	0.199924	2.389305
C	-1.991542	-2.521711	-0.434663
C	-4.856275	-0.036323	-0.565355
H	-4.689326	-0.099960	-1.651198
C	-1.989984	2.534558	-0.636948
C	-2.921227	-2.760089	-1.650017
H	-2.460508	-2.342968	-2.568752
H	-3.083870	-3.848079	-1.799895
H	-3.914156	-2.292088	-1.502024
C	-6.387724	0.066193	1.328850
H	-7.415262	0.073681	1.725408
C	-2.662374	-3.008327	0.869504
H	-3.635123	-2.511924	1.051371
H	-2.848892	-4.100828	0.808054
H	-2.006459	-2.822192	1.744995
C	-0.774381	3.249431	-1.259411
H	-0.549617	2.837162	-2.264309
H	-0.971984	4.336293	-1.353996
H	0.123503	3.120017	-0.624120
C	-2.279411	3.127396	0.761306
H	-1.419030	2.964485	1.442505
H	-2.456930	4.220584	0.685060
H	-3.178191	2.670914	1.221362
C	-0.689373	-3.313578	-0.661464
H	0.034045	-3.130485	0.158399
H	-0.899669	-4.401419	-0.702710
H	-0.214518	-3.012894	-1.616755
C	-0.040737	0.015762	3.198956
H	-0.205228	-0.269026	4.260972
H	-0.053276	1.123347	3.133263
H	-0.890119	-0.374242	2.600265

C	-5.291569	0.150552	2.205384
H	-5.455952	0.224754	3.291980
C	3.015460	-0.111161	3.681599
H	3.996193	-0.517172	3.357303
H	3.094111	0.995308	3.703169
C	2.830770	-3.092769	-1.414340
H	2.385309	-3.683631	-0.588439
H	2.056596	-2.920261	-2.189770
H	3.642944	-3.701240	-1.869489
C	-6.166273	-0.026291	-0.056311
H	-7.019650	-0.089553	-0.749832
C	3.015601	2.961229	-1.408030
H	3.725733	2.418062	-2.064004
H	2.031942	2.950000	-1.917033
H	3.358492	4.016240	-1.331256
C	-3.201859	2.748824	-1.575948
H	-4.140754	2.354184	-1.142867
H	-3.347467	3.834322	-1.756248
H	-3.021991	2.256799	-2.553503
C	4.240107	-0.547456	-2.370724
H	3.396159	-0.242799	-3.025609
H	4.834432	0.353160	-2.113017
H	4.898513	-1.236336	-2.943724
C	2.080496	3.333227	1.548974
H	1.010765	3.487631	1.301284
H	2.132938	2.939229	2.585405
C	4.778688	2.036658	0.923713
H	5.217168	3.056911	0.987364
H	4.858873	1.570902	1.927008
H	5.403195	1.448706	0.220076
H	2.834793	-0.456592	4.723188
C	4.987065	-1.818587	0.376244
H	4.636037	-2.407508	1.249719
H	5.763797	-2.422024	-0.142981
H	5.474268	-0.898979	0.759627
C	1.516659	-2.608163	2.733300
H	2.447288	-3.095609	2.375202
H	1.386072	-2.877137	3.804357
H	0.667246	-3.046843	2.170790
H	2.573637	4.330003	1.543518
S	0.227938	-0.199881	-3.211754

INT_3

Ge	-0.631159	0.045404	1.458113
N	-2.170912	1.107521	0.643586
N	-2.138948	-1.082853	0.668905
C	-2.857690	-0.001893	0.314201
C	-4.221497	-0.028359	-0.317388
C	-5.391643	-0.019075	0.473920
H	-5.306744	0.004553	1.571646
C	-2.413111	-2.529526	0.590733
C	-4.342256	-0.060781	-1.725150
H	-3.425752	-0.065253	-2.335635
C	-2.482057	2.543522	0.525277
C	-2.685258	-2.983145	-0.863462
H	-1.871932	-2.638066	-1.533354
H	-2.739176	-4.090904	-0.914235
H	-3.643794	-2.581359	-1.245795
C	-6.772248	-0.074035	-1.533649
H	-7.766490	-0.091809	-2.007695
C	-3.597029	-2.924312	1.506746
H	-4.547181	-2.473671	1.157516
H	-3.729620	-4.026818	1.514847
H	-3.412182	-2.590528	2.548890
C	-1.199949	3.290073	0.955104
H	-0.356629	3.036273	0.279976
H	-1.353482	4.387599	0.918525
H	-0.912930	3.017912	1.993027
C	-3.636529	2.941591	1.476853
H	-3.400674	2.647918	2.520734
H	-3.798326	4.040027	1.453790
H	-4.587491	2.454897	1.182049
C	-1.134715	-3.231849	1.098697
H	-0.903635	-2.923414	2.140276
H	-1.262566	-4.333253	1.088225
H	-0.265532	-2.981071	0.456056
C	-6.659895	-0.041910	-0.132691
H	-7.565496	-0.034791	0.494584
C	-5.611149	-0.083356	-2.327571
H	-5.693091	-0.107964	-3.425886
C	-2.823572	2.942609	-0.929989
H	-3.791018	2.515083	-1.257599
H	-2.897164	4.047188	-1.014462
H	-2.033918	2.586141	-1.622037
C	0.549792	0.020752	-0.314559
S	-0.107583	0.027571	-1.839229
Si	2.470341	-0.020914	-0.148826
Si	3.259680	2.168873	-0.747588
Si	3.273048	-1.576042	-1.796313
Si	3.302791	-0.578038	2.035836
C	5.068762	-2.101222	-1.415622
H	5.148944	-2.633498	-0.445056
H	5.427423	-2.794260	-2.208129
H	5.760701	-1.233925	-1.389365
C	3.226990	-0.854493	-3.557390
H	3.549617	-1.624406	-4.292429
H	2.195490	-0.532986	-3.808218
H	3.900142	0.021206	-3.667043
C	2.183042	-3.138452	-1.756462
H	2.218748	-3.638155	-0.766008
H	1.125523	-2.888791	-1.980363
H	2.530926	-3.867839	-2.520256
C	5.107597	2.064286	-1.212018
H	5.722859	1.666471	-0.378727
H	5.271156	1.414384	-2.096515
H	5.490067	3.078171	-1.462229
C	2.293886	2.844430	-2.238683
H	2.404998	2.189290	-3.126308
H	1.208971	2.926250	-2.021712
H	2.670309	3.857046	-2.503016
C	3.087888	3.398137	0.699670

H	3.718479	3.102764	1.563817
H	3.413555	4.410883	0.375441
H	2.039794	3.476414	1.055253
C	5.203806	-0.387256	2.030243
H	5.611560	-0.711861	3.012708
H	5.693281	-0.995165	1.242763
H	5.503966	0.671102	1.879802
C	2.885050	-2.390401	2.460958
H	3.302843	-2.659118	3.455840
H	1.787430	-2.550452	2.501116
H	3.305142	-3.097241	1.715026
C	2.643274	0.531777	3.437234
H	1.543883	0.433267	3.550989
H	3.121778	0.235501	4.396744
H	2.873710	1.602570	3.259485

References:

[S1] M. K. Bisai, V. S. Ajithkumar, R. G. Gonnade and S. S. Sen, *Organometallics* 202**1**, **40**, 2651−2657.

[S2] M. K. Bisai, V. S. V. S. N. Swamy, T. Das, K. Vanka, R. G. Gonnade and S. S. Sen, *Inorg. Chem.* 2019, **58**, 10536−10542.

[S3] M. K. Barman, A. Baishya, T. Peddarao and S. Nembenna, *J. Organomet. Chem.* 2014, *772–773*, 265–270.

[S4] Bruker (2006). APEX2, SAINT and SADABS. Bruker AXS Inc. Madison, Wisconsin, USA.

[S5] G. M. Sheldrick, *Acta Crystallogr*, 2008, **A64**, 112-122.

[S6] L. J. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565–565.

[S7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, G. H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels ,

O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc., Wallingford, CT, 2013.

[S8] (a) A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098−3100; (b) J. P. Perdew, *Phys. Rev. B:* 1986, **33**, 8822−8824.

[S9] (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*. 2005, **7**, 3297−3305; (b) F. Weigend, *Phys. Chem. Chem. Phys*. 2006, **8**, 1057−1065.

[S10] T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett*. 1977, **49**, 225−232.

[S1] (a) H. P. Hratchian and H. B. Schlegel, *J. Chem. Phys*. 2004, **120**, 9918−9924; (b) K. Fukui, *Acc. Chem. Res*. 1981, **14**, 363−368.

[S12] S. Grimme, J. Antony, S. Ehrlich and H. Krieg*, J. Chem. Phys*. 2010, **132**, 154104−154122.

[S13] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378–6396.

[S 4] (a) J. Cooper and T. Ziegler, *Inorg. Chem.*, 2002, **41**, 6614–6622.; (b) S. Tobisch, *Chem. Eur. J.*, 2005, **11**, 3113–3126; (c) S. D. Tommaso, V. Tognetti, E. Sicilla, C. Adamo and N. Russo, *Inorg. Chem.*, 2010, **49**, 9875–9883; (d) B. Maity, L. J. Gooßen and D. Koley, *Chem. Sci*. 2015*,* **6**, 2532–2552.

[S 5] C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke, 2009. http://www.cylview.org.

[S 6] Chemcraft - graphical software for visualization of quantum chemistry computations. Version 1.8, build 682. https://www.chemcraftprog.com.

[S17] E. J. Baerends, T. Ziegler, A. J. Atkins, J. Autschbach, O. Baseggio, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, C. Cappelli, L. Cavallo, C. Daul, D. P. Chong, D. V. Chulhai, L. Deng, R. M. Dickson, J. M. Dieterich, F. Egidi, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, A. Förster, C. Fonseca

Guerra, M. Franchini, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. Goez, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, Z. Hu, C. R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J. W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M. V. Krykunov, P. Lafiosca, E. van Lenthe, D. A. McCormack, M. Medves, A. Michalak, M. Mitoraj, S. M. Morton, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, M. Pavanello, C. A. Peeples, P. H. T. Philipsen, D. Post, C. C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, M. Reimann, J. I. Rodríguez, P. Ros, R. Rüger, P. R. T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Stener, M. Swart, D. Swerhone, V. Tognetti, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo and A. L. Yakovlev, ADF 2020.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com, 2020.

[S18] E. van Lenthe, E. J. Baerends and J. G. Snijders*, J. Chem. Phys*., 1993, **99**, 4597–4610.

[S19] E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys*., 1994, **101**, 9783–9792.

[S20]. F. Wang, T. Ziegler, E. van Lenthe, S. J. A. van Gisbergen and E. J. Baerends*, J. Chem. Phys*., 2005, **122**, 204103.

[S21] F. Wang and T. Ziegler*, J. Chem. Phys*., 2005, **123**, 154102.

[S22] E. van Lenthe and E. J. Baerends, *J. Comput. Chem*., 2003, **24**, 1142–1156.