Supporting Information

for

NHC-Stabilized 1-Hydrosilaimine: Synthesis, Structure and Reactivity

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Experimental section

All experiments were carried out under argon atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox. *n*-Hexane, diethyl ether, THF, toluene were dried by A131 Innovative Technology solvent purification system. Benzene was refluxed over sodium/benzophenone, then distilled and stored under argon. Starting compounds $TerSiHCl_2$,[S1] NHC^{Me4},[S2] and DipNHLi[S3] were prepared according to known literature procedures. Benzene-d6 was dried and distilled over potassium under argon. NMR spectra were recorded with Bruker NanoBay 300 MHz NMR machine. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent (^1H) or the deuterated solvent itself (^{13}C). ^{29}Si and $^{29}Si\{^1H\}$ NMR spectra were referenced to external $SiMe_4$. UV/Vis spectra were acquired using a Jasco V-670 spectrometer using quartz cells with a path length of 0.1 cm. IR spectra were recorded on a Bruker–Alpha spectrometer. Melting points were determined in closed NMR tubes under argon atmosphere and are uncorrected. Elemental analyses were performed on an Elemental Analyzer from Elementar (Vario Micro Cube).

Synthesis of 1: In a dried 100 mL Schlenk flask, 2.85 g (4.9 mmol) of $TerSiHCl_2$ and 0.897 g (4.9 mmol) of DipNHLi were taken and 70 mL of toluene was added to it at −78 °C. The reaction mixture was brought to room temperature over a period of 3 hrs. Then it was heated at 80 °C for 12 hrs. Subsequently all volatiles including solvents were removed and extracted with 60 mL of *n*-hexane. After removal of solvents under vacuum off-white solid compound **1** was formed. Yield of the crude product: 3.2 g (90.2 %). We were unable to get pure compound of it as it is highly soluble even in *n*-pentane. However we have measured the purity of **1** using mesitylene as an external standard which shows the crude product was 70 % pure. We have proceeded to the next step with crude product. **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 4.81 (d, $^3J_{(H, H)}$ = 8.56 Hz, 1H, Si–*H*). ppm. **^{29}Si NMR** (59.6 MHz, C_6D_6, 298K): δ = −19.83 (d, $^1J_{(Si, H)}$ = 277 Hz.) ppm. **IR** (KBr, cm^{-1}): $\bar{\upsilon}$ = 420 (s), 432 (w), 450 (w), 460 (s), 475 (m), 499 (w), 520 (m), 594 (w), 650 (w), 722 (w), 743 (s), 786 (s), 805 (s), 872 (s), 905 (w), 936 (w), 1052(m), 1076 (w), 1107 (m), 1122 (w), 1168 (m), 1186 (m), 1253 (m), 1320 (m), 1360 (m), 1385 (w), 1431 (m), 1474 (s), 1568 (m), 1605 (m), 1767 (w), 2241(s, Si-*H*), 2723 (w), 2751 (w), 2809 (m), 3003 (s), 3060 (s), 3181(w), 3364 (s, N-*H*).

Synthesis of 2: In a100 mL Schlenk flask 1.19 g of compound **1** was dissolved in 10 mL of *n*-hexane and in another 25 ml Schlenk flask 0.415 g of NHC^{Me4} was dissolved in 7 mL of toluene. The toluene solution of NHC^{Me4} was added to the *n*-hexane solution of **1** at −78 °C. Subsequently the reaction mixture was allowed to warm to room temperature slowly over a period of 4 hrs and then stirred for another 12 hrs at room temperature. The reaction mixture was dried thoroughly and extracted with 50 mL of warm *n*-hexane using D4 filtration unit. The filtrate was kept at −20 °C. After one day yellow block shaped crystals were formed and 0.570 g of compound **2** collected. The resulting mother liquor was concentrated to about 25 mL of volume, kept at −20 °C for another two days and yielded 0.110 g of compound **2**. Yield: 0.680 g (51%). Single crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of *n*-pentane at 0 °C after one day. **M.P.**: 153 °C (decomposed; color changed at 145 °C from deep yellow to light yellow). **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 1.04–1.06 (6H, $CH(CH_3)_2$, 6H, C–CH_3 of NHC^{Me4}), 1.11 (d, 6H, $CH(CH_3)_2$), 1.18–1.21 (m, 18H, $(CH(CH_3)_2)$, 1.25–1.29 (m, 12H, $(CH(CH_3)_2)$), 1.43 (d, 6H, $CH(CH_3)_2$), 2.85 (sep, 2H, $CH(CH_3)_2$) 3.05–3,09 (6H, N-CH_3, 2H, $CH(CH_3)_2$), 3.28 (sep, 2H, $CH(CH_3)_2$), 3.56 (sep, 2H, CH(CH3)2), 6.43 (s, 1H, Si–*H*), 6.78 (t, 1H, Ar–*H*), 7.00 (br, 2H, Ar–*H*), 7.13–7.15 (m, 5H, Ar–*H*), 7.19 (br, 2H, Ar–*H*). ppm. **^{13}C NMR** (75.43 MHz, C_6D_6, 298K): δ = 7.96 (2C, CH_3, C-CH_3 of NHC^{Me4}), 22.99 (2C, $CH(CH_3)_2$), 24.12 (2C, $CH(CH_3)_2$), 24.72 (2C, $CH(CH_3)_2$), 24.94 (2C, $CH(CH_3)_2$), 25.24 (2C, $CH(CH_3)_2$), 25.70 (2C, $CH(CH_3)_2$), 26.55 (2C, $CH(CH_3)_2$), 26.90 (2C, $CH(CH_3)_2$), 27.89 (2C, $CH(CH_3)_2$), 31.66 (2C, $CH(CH_3)_2$), 31.89 (2C, $CH(CH_3)_2$), 33.26 (2C, N–CH_3), 35.01 (2C, $CH(CH_3)_2$), 113.02 (1C, Ar–CH), 120.76 (2C, Ar–CH), 121.03 (2C, Ar–CH), 122.92 (2C, Ar–CH), 126.00 (2C, CH_3–C of NHC^{Me4}), 127.12 (1C, Ar–CH), 132.55(2C, Ar–CH), 139.80 (1C), 139.88 (2C), 140.26 (2C), 147.46 (2C), 147.51 (2C), 147.57 (2C), 148.13 (2C), 152.06 (1C), 155.57 (1C, NCN), ppm. **^{29}Si NMR** (59.6 MHz, C_6D_6, 298K): δ = −76.46 ($^{1}J_{(Si,\ H)}$ = 199.26) ppm. **UV/Vis** (*n*-hexane): $\lambda_{max}(\varepsilon)$ = 271 (13530), 318 (5341), 373 (sh, 2448), and 440 (sh, 1464) nm ($Lmol^{-1}cm^{-1}$). **IR** (KBr, cm^{-1}): $\bar{\upsilon}$ = 744 (m), 804 (w), 834 (w), 907 (w), 995 (m), 1047 (w), 1144(w), 1286(m), 1353 (s), 1414 (s), 1460 (1460), 1581(vw), 1646 (vw), 2112(m, Si-*H*), 2866 (vs), 2901(vs), 2905(vs), 2918(vs), 29 41(s), 2950 (vs), 2954 (vs), 2999 (w). Elemental

Analysis: Calcd. for $C_{55}H_{79}N_3Si_2$ (809.60): C, 81.52; H, 9.83; N, 5.19. Found: C, 80.94; H, 10.059; N, 5.33.

Synthesis of 3: In a 25 mL Schlenk flask, 0.248 g (0.28 mmol) of compound **2** was suspended with 12 mL *n*-hexane and 5 μL (0.28 mmol) water added at 0 °C. Then the reaction mixture was allowed to stir at the same temperature for another 2 hrs and the yellow color of the solution slowly turns into colorless. Subsequently all volatiles were removed under high vacuum and the residue washed with *n*-pentane to give compound **3** as a white solid. Yield: 0.195 g (85 %). Single crystals suitable for X-ray structural analysis were obtained from saturated toluene solution at −20 °C after 2 days. **M.P.**: 140 °C (decomposed). **^{1}H NMR** (300 MHz, C_6D_6, 298K): δ = 1.05 (d, 6H, CH(CH_3)$_2$), 1.12 (s, 6H, C–CH_3), 1.17–1.1.20 (m, 12H, CH(CH_3)$_2$), 1.26–1.34(m, 18 H, CH(CH_3)$_2$), 1.45 (d, 6H, CH(CH_3)$_2$), 1.64 (d, 6H, CH(CH_3)$_2$), 2.74 (s, 6H, N–CH_3), 2.92 (sep, 2H, C*H*(CH$_3$)$_2$), 3.06 (d, 1H, $^3J_{(H,H)}$ = 6.45Hz, N–*H*), 3.45 (m, 6H, C*H*(CH$_3$)$_2$), 4.93 (d, $^3J_{(H,H)}$ = 6.51Hz, 1H, Si–*H*) , 6.88–6.93 (m, 1H, Ar–*H*), 6.98–7.01 (m, 2 H, Ar–*H*), 7.20 (br, 5H, Ar–*H*), 7.34 (br, 2H, Ar–*H*), 13.27 (br, 1H, C^{imid}–*H*) ppm. **^{13}C NMR** (75.43 MHz, C_6D_6, 298K): δ = 7.51 (2C, C–*C*H$_3$), 23.33 (2C, CH(*C*H$_3$)$_2$), 23.55 (2C, CH(*C*H$_3$)$_2$), 24.35 (2C, CH(*C*H$_3$)$_2$), 24.44 (2C, CH(*C*H$_3$)$_2$), 25.06 (2C, CH(*C*H$_3$)$_2$), 25.22 (2C, CH(*C*H$_3$)$_2$), 26.14 (2C, CH(*C*H$_3$)$_2$), 26.18 (2C, CH(*C*H$_3$)$_2$), 27.42 (2C, *C*H(CH$_3$)$_2$), 31.20 (2C, *C*H(CH$_3$)$_2$), 31.23 (2C, *C*H(CH$_3$)$_2$), 32.71 (2C, N–*C*H$_3$), 34.62 (2C, *C*H(CH$_3$)$_2$), 120.55(2C, Ar–*C*H), 121.04 (2C, Ar–*C*H), 122.20 (1C, Ar–*C*H), 123.08 (2C, CH$_3$–*C*), 123.25 (2C, Ar–*C*H), 126.83 (1C, Ar–*C*H), 128.34 (1C, Ar–*C*H), 130.00 (1C, Ar–*C*H), 140.39 (2C), 141.55 (1C), 141.70 (1C), 144.62 (2C), 146.68 (2C), 147.45 (1C), 147.61 (2C), 147.67 (1C), ppm. **^{29}Si NMR** (59.6 MHz, C_6D_6, 298K): δ = –42.46 (d, $^1J_{(Si,\ H)}$ = 220.81) ppm. **IR** (KBr, cm^{-1}): $\bar{\upsilon}$ = 523 (w), 596 (w), 632 (w), 653 (vw), 673 (vw), 715 (w), 736 (w), 758 (m), 803 (m), 834 (m), 855 (m), 874 (w), 940 (vw), 1003(m), 1076 (vw), 1103 (w), 1168 (w), 1243 (m), 1314 (m), 1359 (m), 1380 (m), 1460 (s), 1566 (m), 1605 (m), 1640 (w), 1756 (w), 2125 (s, Si–*H*), 2883 (vs), 2973 (vs), 3024(w), 3363 (s, N–*H*). Elemental Analysis: Calcd. for $C_{55}H_{81}N_3OSi$ (827.61): C, 79.75; H, 9.86; N, 5.07. Found: C, 78.10; H, 9.896; N, 5.42.

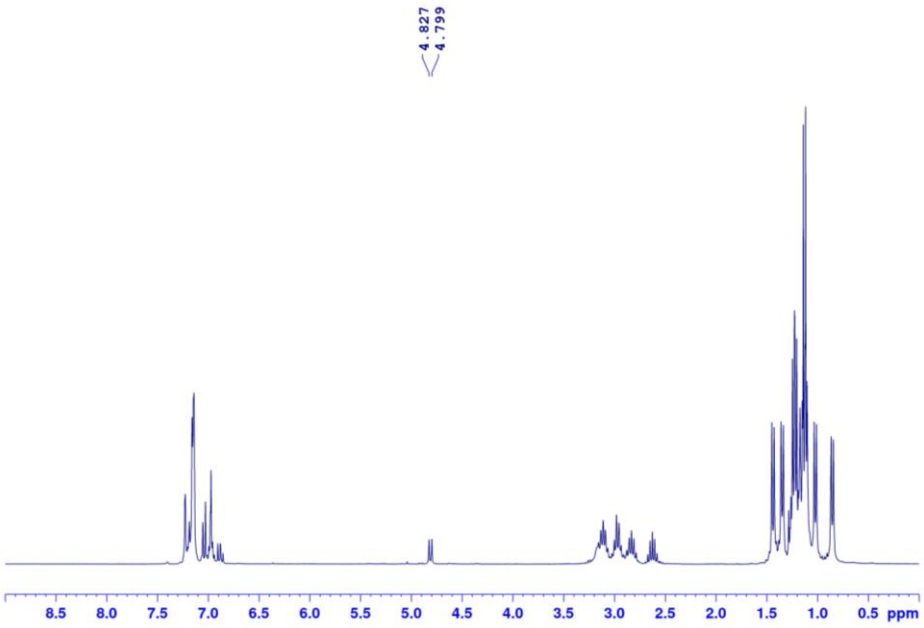


Figure S1: ^{1}H NMR of **1** in [D6]-benzene at RT.

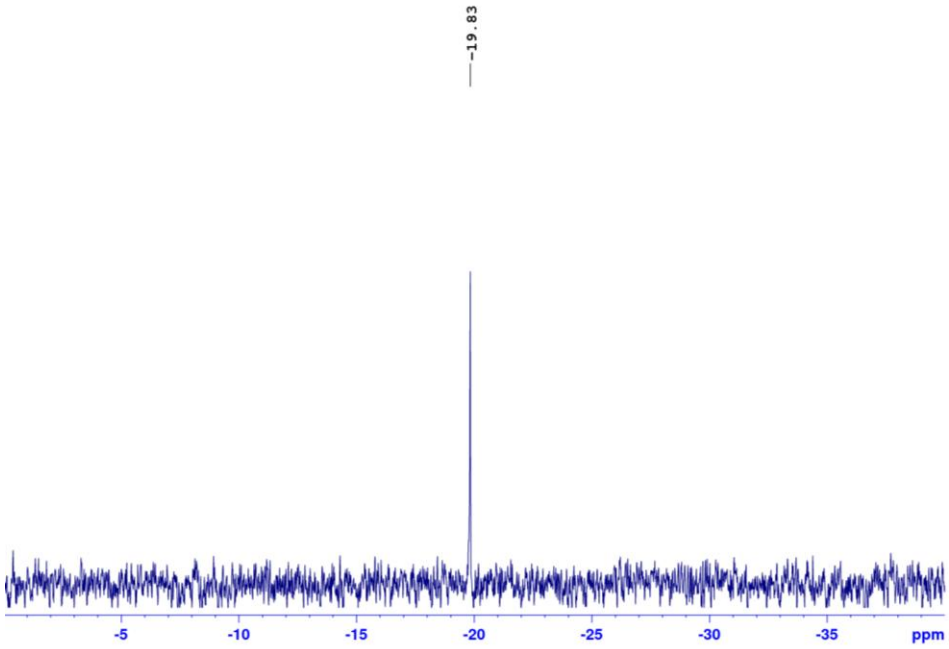


Figure S2: ^{29}Si{^{1}H} NMR of **1** in [D6]-benzene at RT.

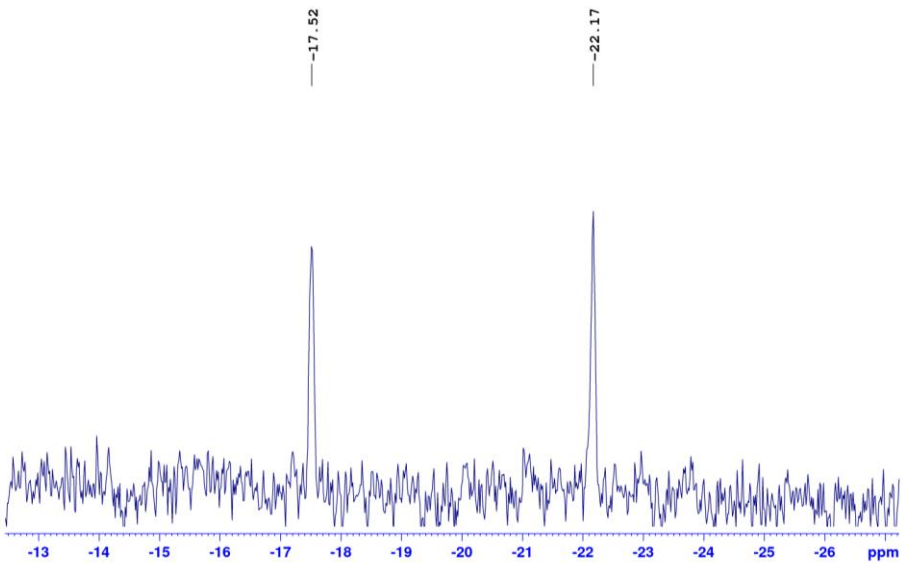


Figure S3: ^{29}Si NMR of **1** in [D6]-benzene at RT.

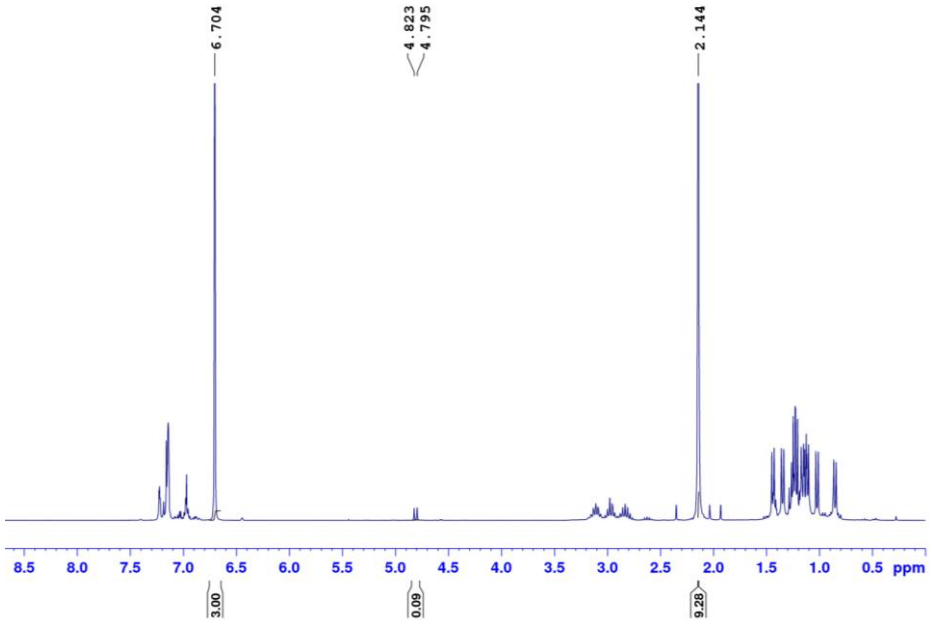


Figure S4: ^{1}H NMR of **1** with mesitylene in [D6]-benzene at RT.

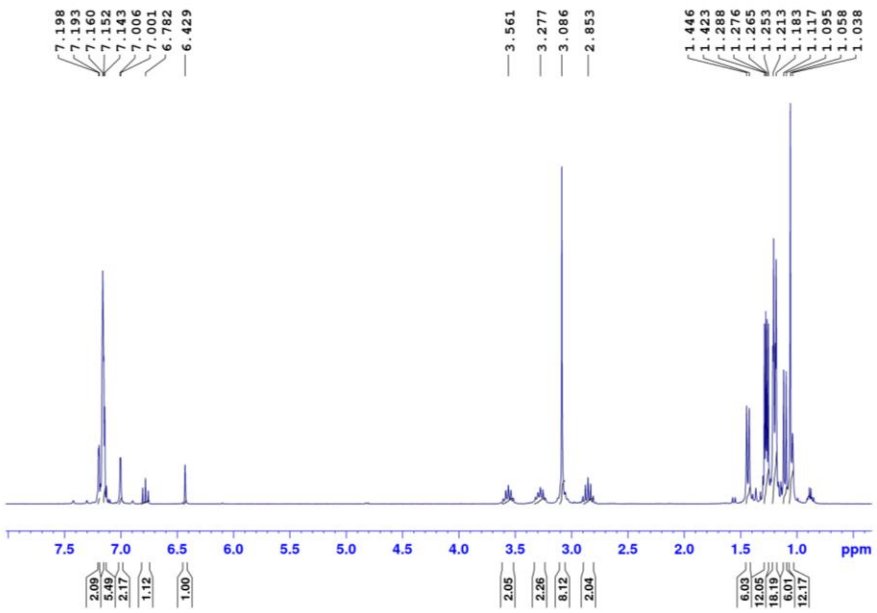


Figure S5: ^{1}H NMR of **2** in [D6]-benzene at RT.

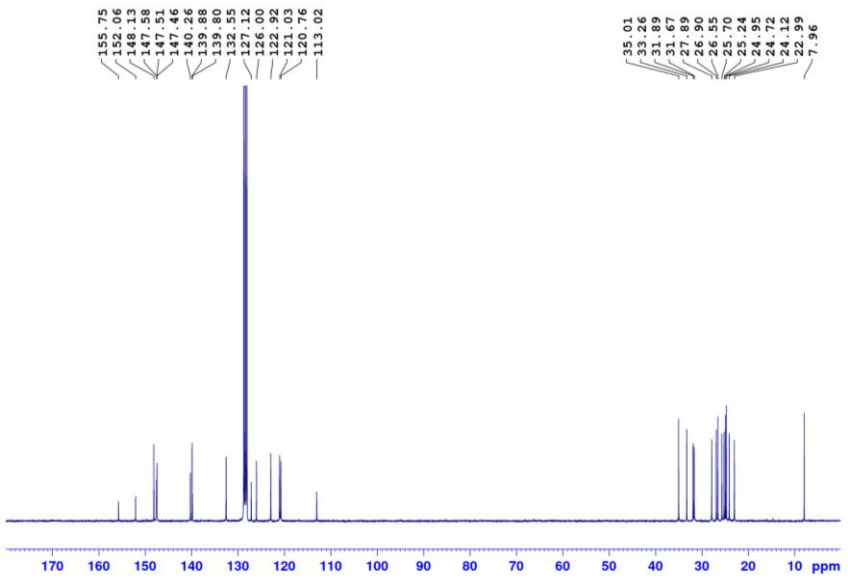


Figure S6: ^{13}C{^{1}H} NMR of **2** in [D6]-benzene at RT.

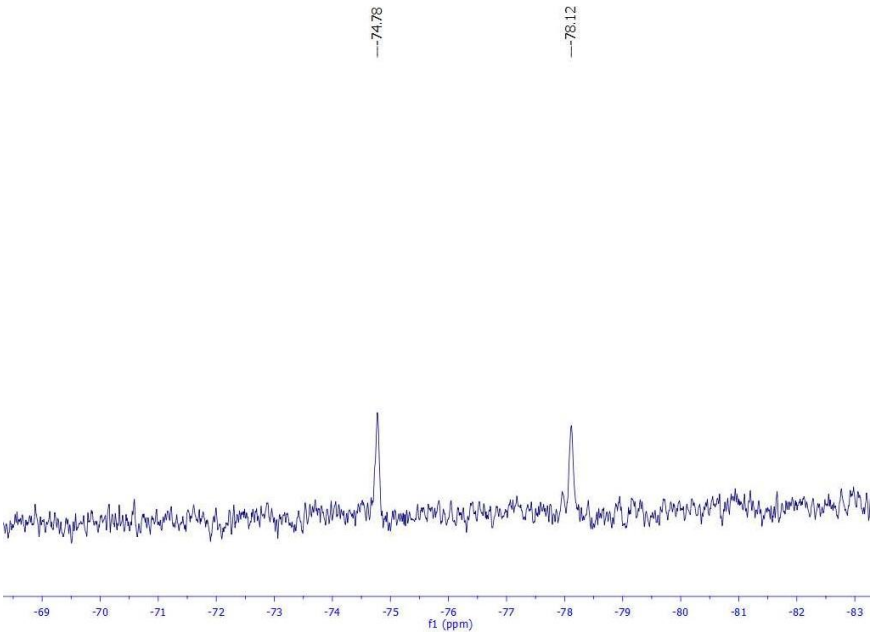


Figure S7: ^{29}Si NMR of **2** in [D6]-benzene at RT.

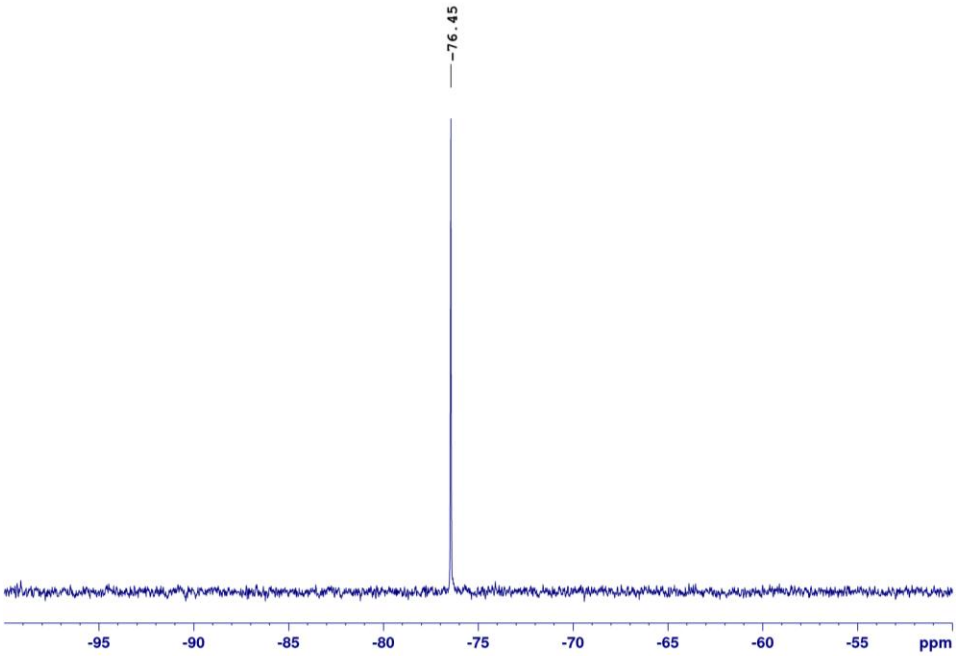


Figure S8: ^{29}Si{H} NMR of **2** in [D6]-benzene at RT.

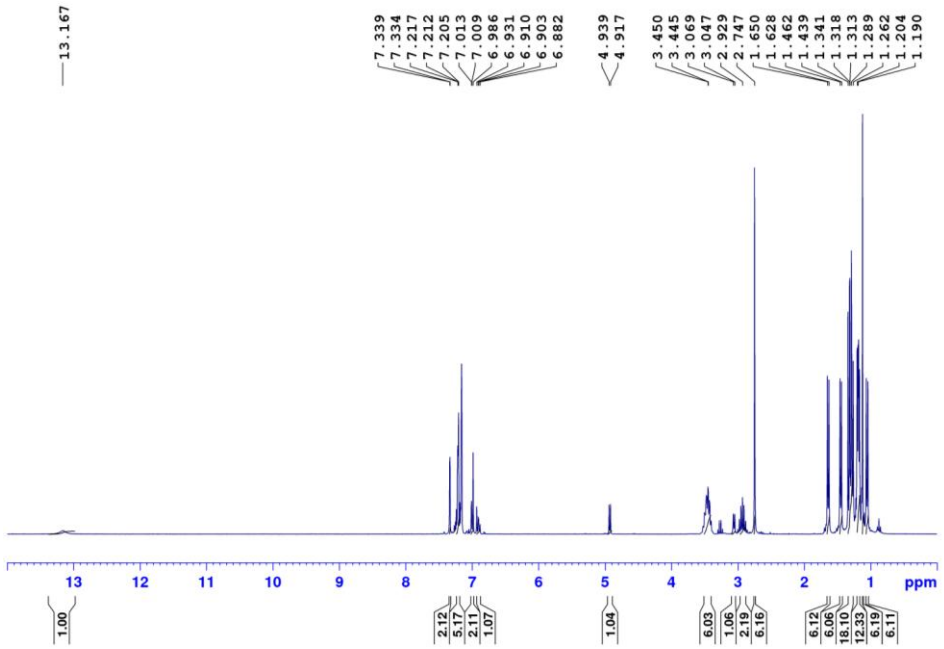


Figure S9: ^{1}H NMR of **3** in [D6]-benzene at RT.

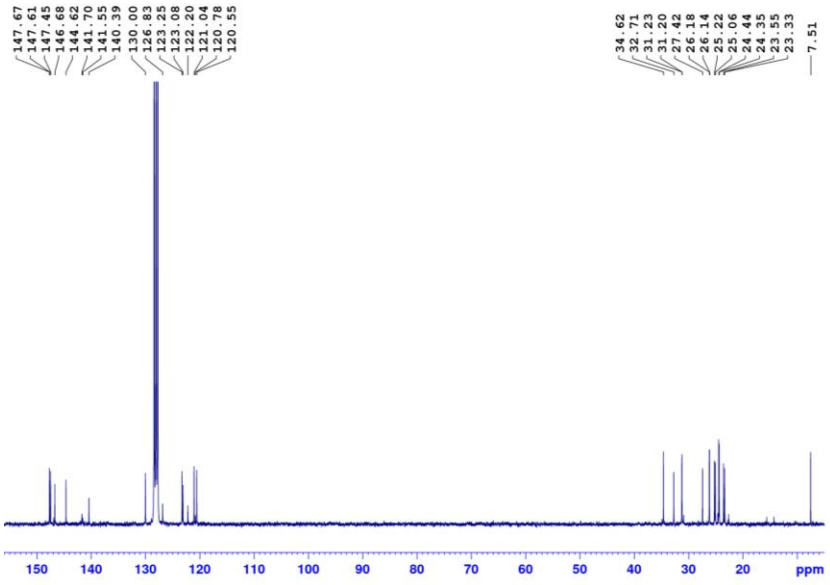


Figure S10: ^{13}C{^{1}H} NMR of **3** in [D6]-benzene at RT.

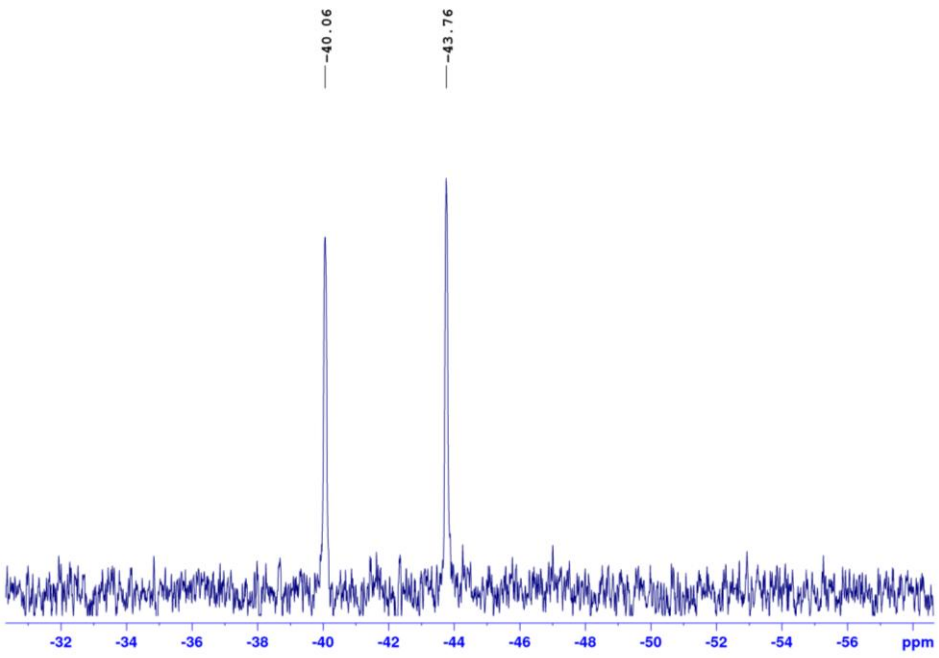


Figure S11: ^{29}Si NMR of **3** in [D6]-benzene at RT.

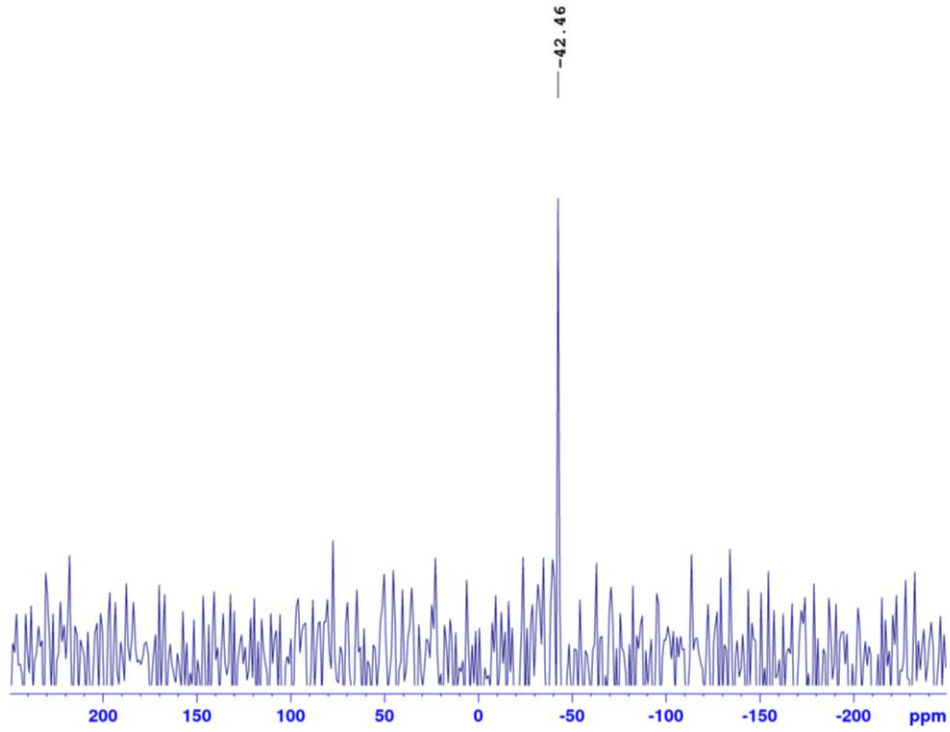


Figure S12: ^{29}Si{H} NMR of **3** and NHC^{Me}_4 in [D6]-benzene at RT.

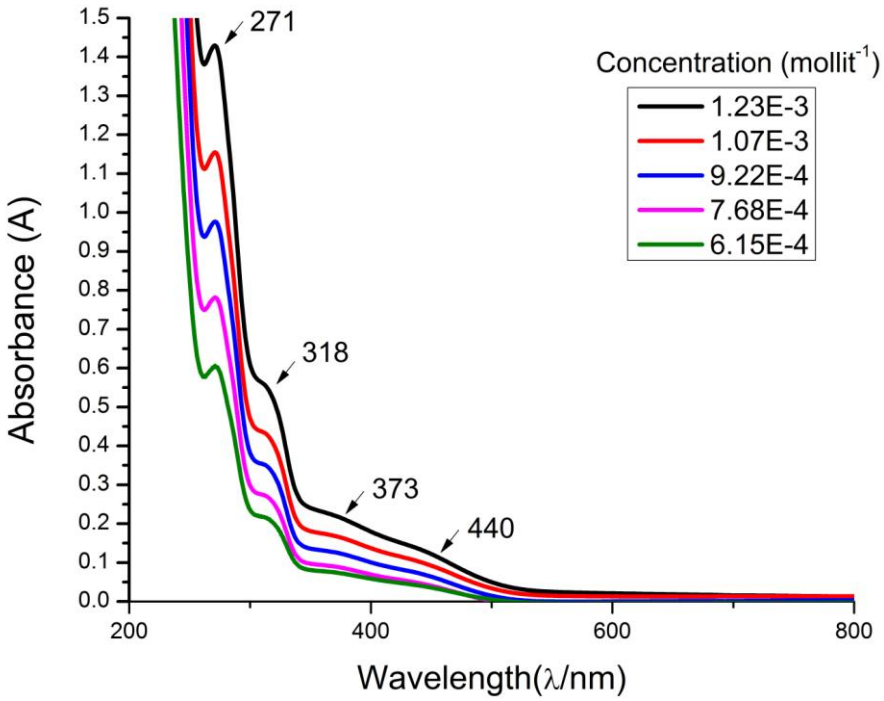


Figure S13: UV/Vis spectrum of compound **2**.

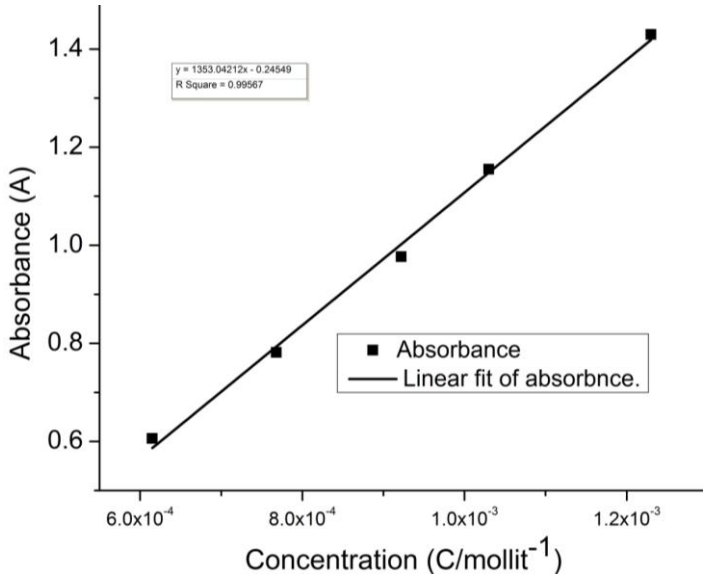


Figure S14: Linear regression of compound **2** at 271 nm.

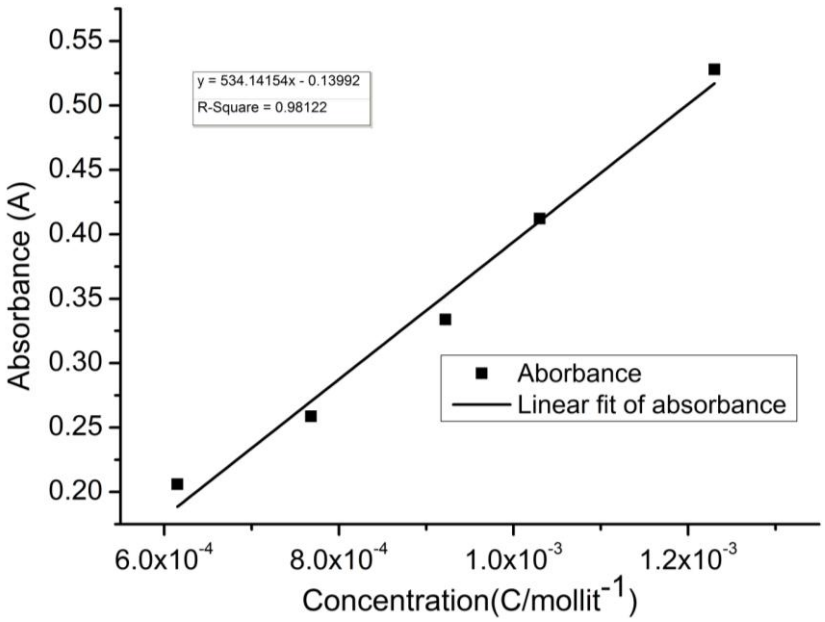


Figure S15: Linear regression of compound **2** at 318 nm.

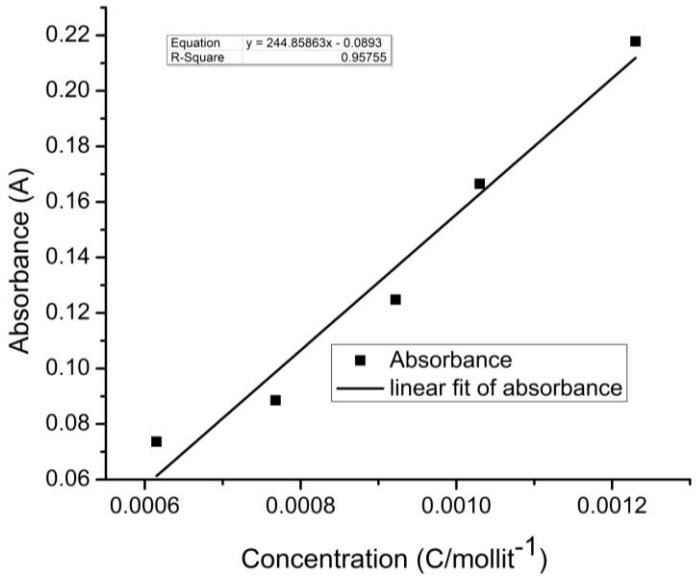


Figure S16: Linear regression of compound **2** at 373 nm.

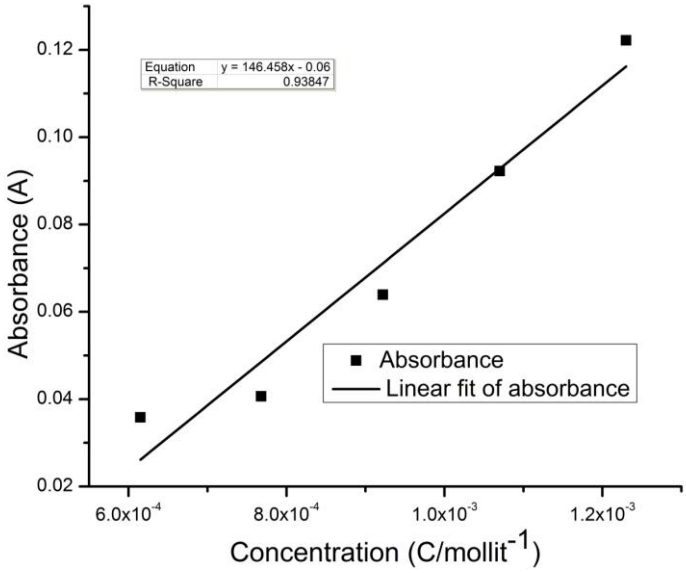


Figure S17: Linear regression of compound **2** at 440 nm.

X-ray structural Analysis

Diffraction data were collected at low temperature (-103.0 °C) using a STOE-IPDS 2T diffractometer with graphite-monochromated molybdenum *Kα* radiation, λ = 0.71073 Å. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques (SHELXL-2013).[S4] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to nitrogen or silicon atoms of **3** were located and refined freely. All other hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for the aromatic carbon atoms. The crystal and refinement data are summarized in Tables S1 and S2. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. These data can be obtained free of charge on quoting the depository numbers CCDC 1542299 (**2·0.5*n*-pentane**) and 1542300 (**3**) by FAX (+44-1223-336-033), email (deposit@ccdc.cam.ac.uk) or their web interface (at http://www.ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for **2•0.5*n*-pentane** (CCDC: 1542299)

Identification code	DD 491A
Empirical formula	$C_{57.50}H_{85}N_3Si$
Formula weight	846.37
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*P*bca
Unit cell dimensions	*a* = 19.358 (4) Å
	b = 21.667 (3) Å
	c = 27.029 (5) Å
Volume	11337 (3) Å^3
Z	8
Density (calculated)	0.992 Mg/m^3.
Absorption coefficient	0.076 mm^{-1}
F(000)	3720
Crystal size	0.29 x 0.23 x 0.18 mm^3
Theta range for data collection	4.131 to 25.026 deg.
Index ranges	-11<=h<=22, -25<=k<=25, -12<=l<=32
Reflections collected	25584
Independent reflections	9947 [*R*(int) = 0.1462]
Completeness to theta = 25.242°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.744 and 0.633
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9947 / 219/ 595
Goodness-of-fit on F^2	1.021
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.1168, *wR*2 = 0.2818
R indices (all data)	*R*1 = 0.2221, *wR*2 = 0.3407
Extinction coefficient	0.0028 (6)
Largest diff. peak and hole	0.827 and -0.684 e.Å^{-3}

Table S2. Crystal data and structure refinement for **3** (CCDC: 1542300)

Identification code	DD 491B
Empirical formula	$C_{55}H_{81}N_3OSi$
Formula weight	828.31
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.730 (6) Å
	b = 17.458 (8) Å β = 91.470(9)°.
	c = 24.128 (5) Å
Volume	6202 (5) Å^3
Z	4
Density (calculated)	0.887 g/cm^3.
Absorption coefficient	0.070 mm^{-1}
F(000)	1816.0
Crystal size	0.17 x 0.12 x 0.09 mm^3
Theta range for data collection	2.766 to 57.168 deg.
Index ranges	-16<=h<=19, -23<=k<=23, -32<=l<=32
Reflections collected	108845
Independent reflections	15682 [R(int) = 0.1534]
Completeness to theta = 25.242°	99.0 %
Absorption correction	multi-scan
Max. and min. transmission	0.647 and 0.746
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15682 / 6/ 566
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0731, wR2 = 0.1926
R indices (all data)	R1 = 0.1841, wR2 = 0.0.2444
Largest diff. peak and hole	0.0.71 and -0.40 e.Å^{-3}

Computational Calculation:

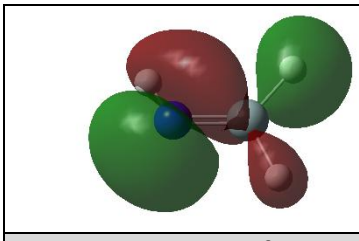
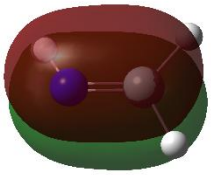
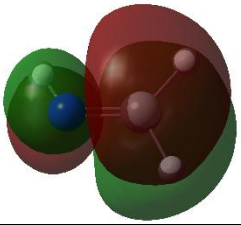
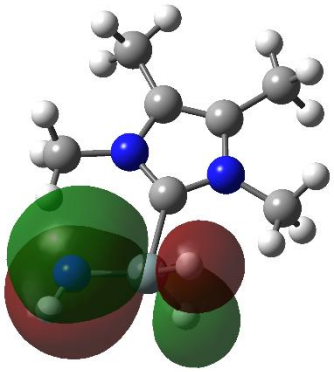
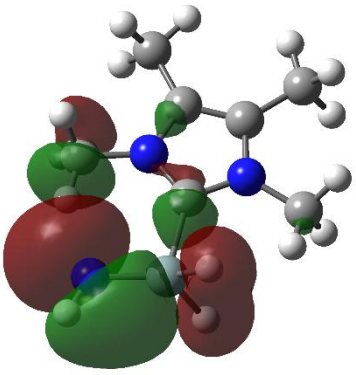
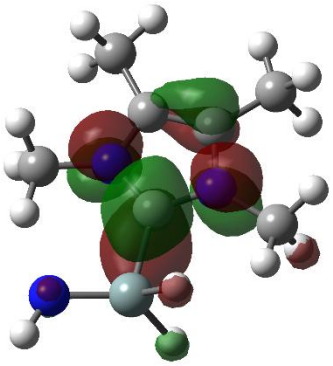
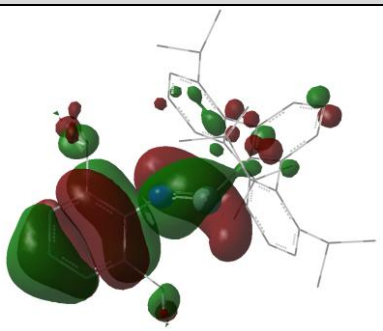
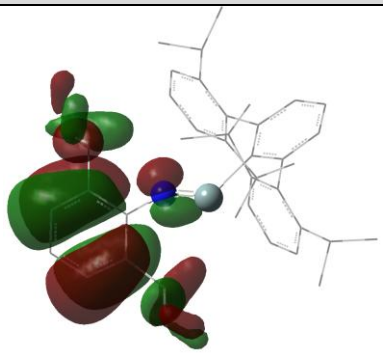
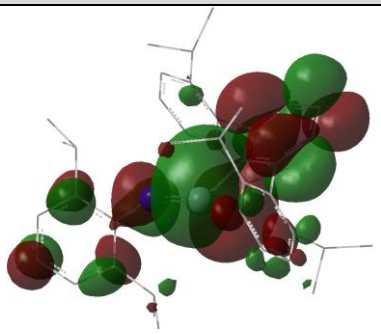
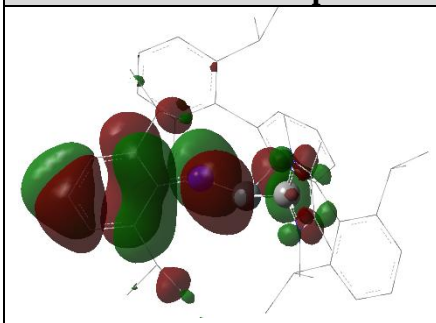
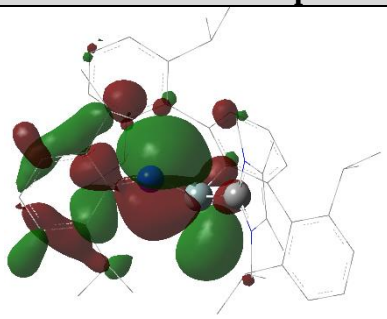
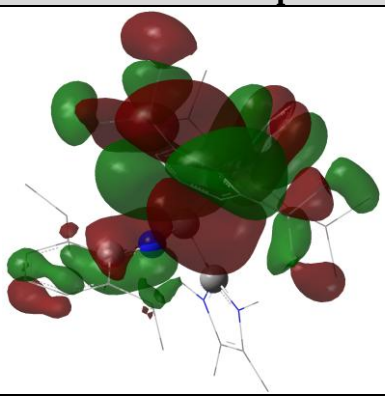
Computational Method:

All theoretical calculations, in this paper are carried out using the Gaussian03 suite of programs.[S5] The Full geometry optimizations of **IV**, **V**, **2-Dip**, **2-Dip'**, and **3-Dip** were performed at B3LYP/6-311G(d,p) level of theory. Frequency analyses were performed to determine the relative energies of **2-Dip** and **3-Dip** in solution (CPCM method, heptane) at B3LYP/6-311G(d,p) level of theory.[S6] Wiberg bond orders (WBI) as a criterion to estimate the bond orders of chemical structures were also calculated within the natural bond orbital (NBO) analysis for **IV**, **V**, **2-Dip**, and **2-Dip'**.[S7] The electronic absorption spectrums for **IV**, **V**, **2-Dip**, and **2-Dip'** were predicted with using the optimized geometry at time-dependent density functional theory (TD-DFT) method in solution (heptane) at B3LYP/6-311G(d,p) level of theory. ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts were calculated by the GIAO method in solution (benzene) at B3LYP/6-311+2df level of theory. The proposed O-H bond activation mechanism for the formation of **3** was modelled using simplified model systems **2-Dip*** and **3-Dip*** (Dip group instead of Ter) at B3LYP/6-311G(d,p). The chemical reaction channels have been checked by the intrinsic reaction coordinate (IRC) method to verify the energy profiles at the B3LYP/6-311G(d,p) level of theory for the processes from transition state to intermediates, by using the second-order Gonzalez-Schlegel method.[S8, S9] The relative Gibbs free energies are given in kcal/mol. The GaussView 5.0 program was employed for visualization of the final geometries of the optimized structures.[S10]

Table S3. The calculated NMR, UV/Vis, WBO, and NBO results for the compounds of $H_2Si{=}NH$, **IV**, $H_2Si(NHC^{Me_4}){=}NH$, **V**, **2-Dip'** (NHC free form of **2-Dip**), **2-Dip**, and **3-Dip**. NMR results of **2-Dip** at the B3LYP/6-311G(d,p) level of theory (solvent: benzene for NMR and *n*-heptane for UV/Vis).

	IV		**V**		**2-Dip'**		**2-Dip**		**3-Dip**
^{1}H of *H*-Si	7.2		6.7				7.2		5.1
^{1}H of *H*-NHC	-		-		-		-		15.4
^{13}C of NH*C*	-		164.2		-		166.4		159.8
^{29}Si	-74.7		-78.7				-92.9		-53.3
Si=N Bond length	1.601		1.639		1.593		1.624		-
Si=N (WBI)	1.686		1.176		1.340		0.981		-
Si-NHC Bond length	-		1.962		-		1.984		-
Si-NHC (WBI)	-		0.670		-		0.617		-
UV/Vis	222, 184, 119		347, 267, 213, 185				479, 428, 317, 263		-
	Si	**N**	**Si**	**N**	**Si**	**N**	**Si**	**N**	**-**
Hybrids	$sp^{1.63}$	$sp^{1.63}$	$sp^{1.83}$	$sp^{1.78}$	p	p	$sp^{2.27}$	$sp^{1.37}$	-
Charges	1.225	-1.204	1.246	-1.476	1.546	-1.075	1.584	-1.196	-

Table S4. Frontier Molecular Orbitals of $H_2Si{=}NH$, **IV**, $H_2Si(NHC^{Me_4}){=}NH$, **V, 2-Dip'**, and **2-Dip** at the B3LYP/6-311G(d,p) level of theory.

		
HOMO of **IV**	HOMO-1 of **IV**	LUMO of **IV**
		
HOMO of **V**	HOMO-1 of **V**	LUMO of **V**
		
HOMO of **2-Dip'**	HOMO-1 of **2-Dip'**	LUMO of **2-Dip'**
		
HOMO of **2-Dip**	HOMO-1 of **2-Dip**	HOMO-3 of **2-Dip**

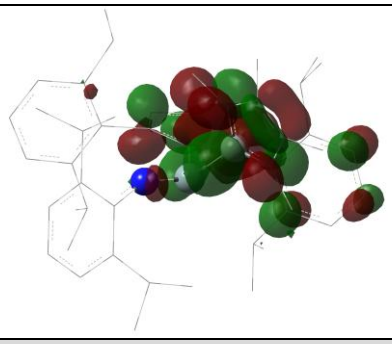
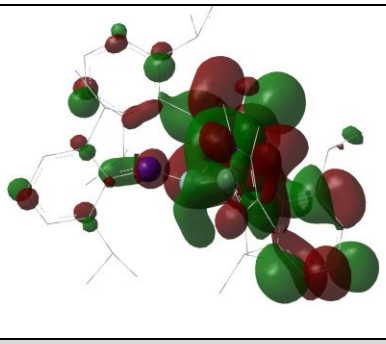
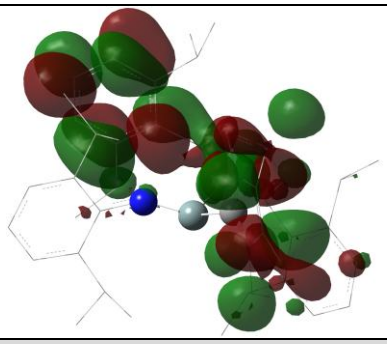
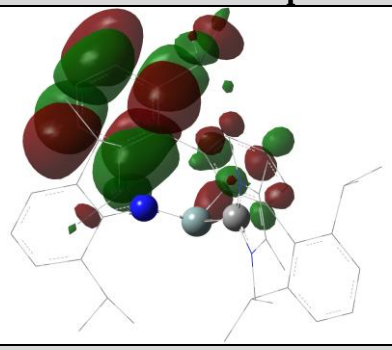
		
LUMO of **2-Dip**	LUMO+1 of **2-Dip**	LUMO+7 of **2-Dip**
		
LUMO+8 of **2-Dip**		

Figure S18. The relative free energy of **2-Dip** and **3-Dip** at B3LYP/6-311G(d,p) level of theory. ΔG energy values at 298 K are given in kcal mol^{-1} (Dip instead of Tip, Solvent = Heptane).

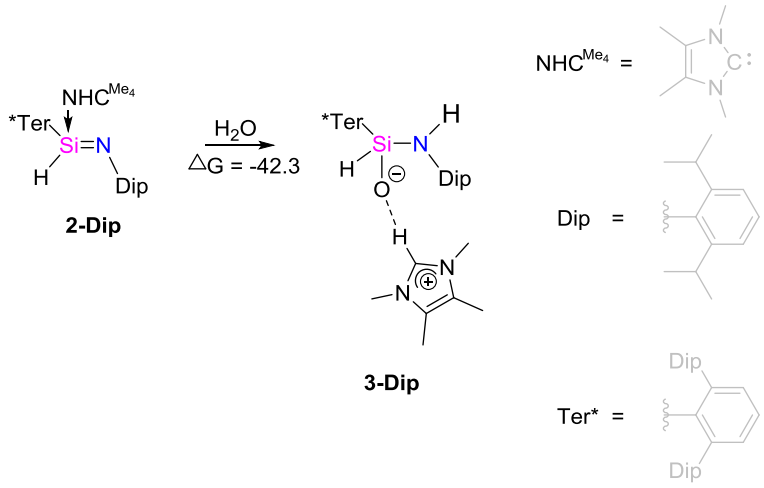


Figure S19. Proposed reaction mechanism of **2-Dip*** with H_2O to furnish **3-Dip*** using simplified model system (Dip group instead of Ter) at B3LYP/6-311G(d,p) level of theory. ΔG energy values at 298 K are given in kcal mol^{-1}.

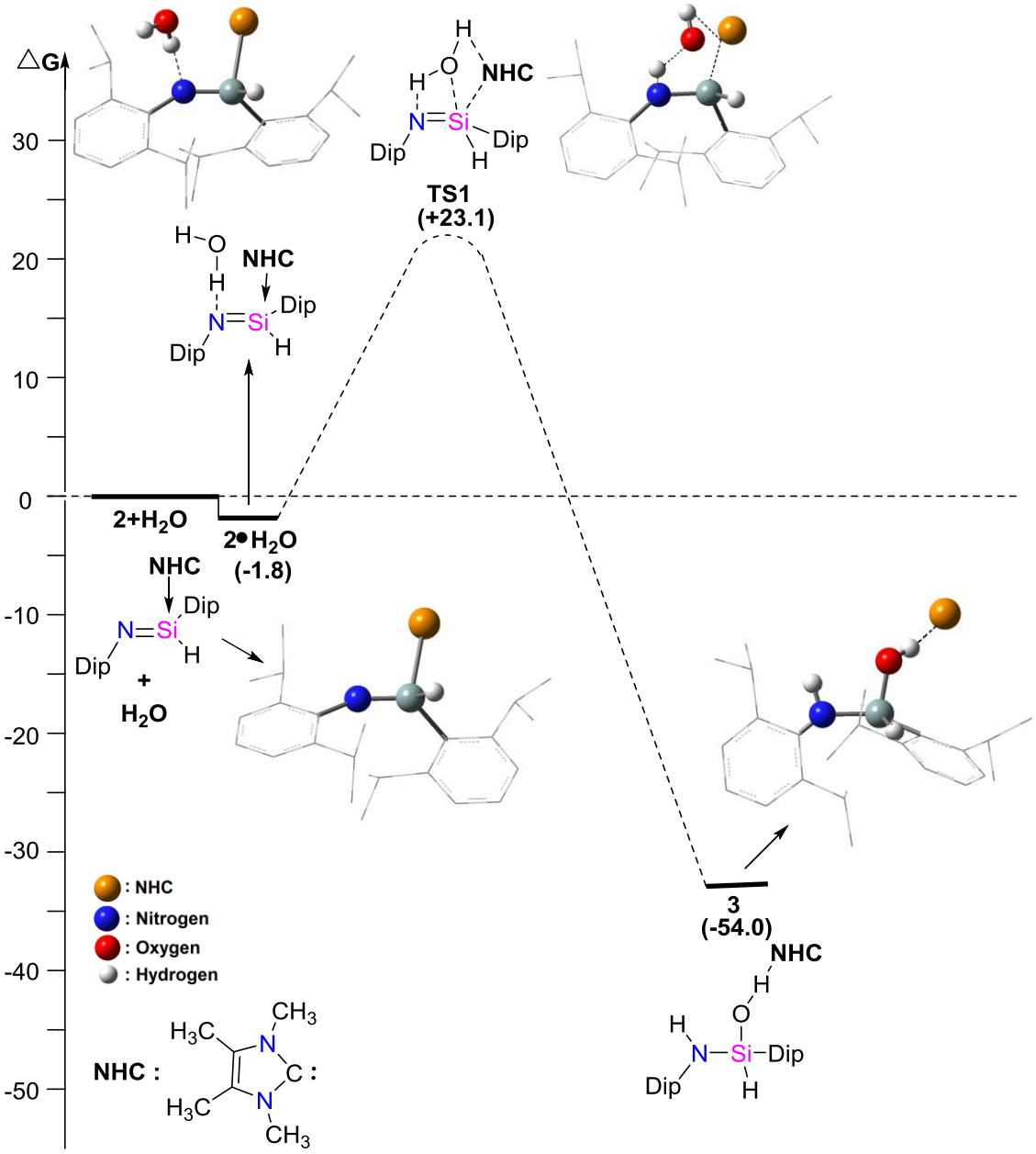


Table S5. Cartesian coordinates of **IV**.

Si,0,0.488774,0.014562,-0.000533
H,0,1.339054,1.23669,0.003304
N,0,-1.106255,-0.127286,0.00095
H,0,-1.723704,0.676172,-0.003247
H,0,1.285595,-1.225731,0.000764

Table S6. Cartesian coordinates of **V**.

Si,0,2.440232,-0.671806,0.010063
H,0,2.437577,-1.658535,-1.144546
N,0,3.211135,0.774865,-0.012671
C,0,0.532212,-0.212911,-0.011101
N,0,-0.050065,1.004218,-0.002096
C,0,-1.437642,0.885113,0.002992
C,0,-1.717654,-0.450306,-0.002843
N,0,-0.487809,-1.103496,-0.016073
C,0,0.669701,2.286517,-0.002596
H,0,0.397672,2.850087,0.89225
H,0,0.387594,2.854921,-0.891263
H,0,1.748706,2.054664,-0.008928
C,0,-2.341612,2.070812,0.009395
H,0,-2.189343,2.697428,-0.87437
H,0,-2.174876,2.698811,0.889454
H,0,-3.384708,1.754239,0.017743
C,0,-3.018869,-1.178748,-0.001926
H,0,-3.151965,-1.777772,-0.908544
H,0,-3.846215,-0.471086,0.048072
H,0,-3.107299,-1.852135,0.856173
C,0,-0.321206,-2.554442,0.004592
H,0,0.70189,-2.795876,-0.271871
H,0,-0.998401,-3.012626,-0.71691
H,0,-0.529344,-2.950444,1.000695
H,0,4.221519,0.82566,0.000209
H,0,2.421545,-1.617363,1.195774

Table S7. Cartesian coordinates and energy values for the **2-Dip'**.

Si,-0.0329117134,-0.2264851764,0.8449730475
H,0.9386838647,0.1049875592,1.906446231
N,-1.3574792874,0.612671182,0.5600653737
C,-2.1948681542,1.6338930926,0.9561063686
C,-3.0066578342,2.2649276287,-0.0346833826
C,-3.8800819947,3.2839127506,0.3374885208
H,-4.4821118366,3.7710441415,-0.4208685843
C,-4.0054757414,3.6840742702,1.6624718489
H,-4.696879846,4.4739071835,1.9348402379
C,-3.233561661,3.0622010584,2.6348084277
H,-3.3342970359,3.3778624192,3.6665085775
C,-2.3184365721,2.0576100709,2.3164845167
C,-2.8689466539,1.8681848659,-1.4949165322
H,-2.4767621455,0.8495629696,-1.4943853227
C,-1.8394271316,2.7730676439,-2.201481215
H,-2.1784138922,3.8139932748,-2.2088967322
H,-1.6888721001,2.4622858959,-3.2405057661
H,-0.8727637951,2.7406891106,-1.6932617706
C,-4.2003503096,1.8603680212,-2.2612141761
H,-4.9453312342,1.243506496,-1.7528891378
H,-4.0515900212,1.4526523429,-3.2655503644
H,-4.6162674752,2.865374882,-2.3814414671
C,-1.4471622205,1.4762510749,3.4199347725
H,-1.1390731806,0.4741341865,3.1052731186
C,-2.1690812554,1.3011178856,4.7668584419
H,-2.4152128568,2.2605431296,5.2300466921
H,-1.5254304714,0.7616868718,5.4680883781
H,-3.0966110633,0.7349871893,4.652087088
C,-0.1698449405,2.3209051871,3.6011485198
H,0.3702605013,2.4433646684,2.6599517876
H,0.5091447573,1.8575396643,4.3245186305
H,-0.4259334705,3.3198381995,3.9669244103
C,0.4929840353,-1.8216250472,0.0145874705
C,-0.4045206167,-2.7926185747,-0.5037197629
C,0.0889256271,-4.043502159,-0.8898581187
H,-0.6085792959,-4.7843792988,-1.2627741021
C,1.4445238442,-4.340072873,-0.8211302474
H,1.8054734001,-5.3135178122,-1.13453639
C,2.3359412508,-3.3774151764,-0.3663250413

H,3.3990210084,-3.5870479566,-0.3396241313
C,1.8821367027,-2.1264173573,0.0610272429
C,-1.8762788068,-2.55574023,-0.7058899165
C,-2.7870151545,-2.7300438478,0.3590666155
C,-4.1508540302,-2.556190002,0.1108499248
H,-4.8630518036,-2.6825388653,0.9176062416
C,-4.6138452284,-2.2279589579,-1.1563797928
C,-3.7145810015,-2.0847041028,-2.2038837084
H,-4.0870268273,-1.8439063962,-3.1930554994
C,-2.3408903661,-2.2504958449,-2.005780309
C,-2.3308795111,-3.1733473456,1.7476190585
H,-1.2562590771,-2.9880016731,1.8239052011
C,-3.0097535121,-2.3946839075,2.8871348139
H,-2.9250960572,-1.3166579542,2.7373304042
H,-2.5455784335,-2.647860475,3.844798573
H,-4.0723744876,-2.6387978904,2.9697885383
C,-2.5361014073,-4.6909688159,1.9284956816
H,-3.5956635302,-4.9513486047,1.8489738611
H,-2.1812776818,-5.013881538,2.9122025654
H,-1.9942873856,-5.2600128175,1.1692022431
C,-1.4030640643,-2.1510453902,-3.2100829831
H,-0.3763786581,-2.1819188657,-2.84088625
C,-1.5563326583,-0.8343963117,-3.990042795
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H,-1.4256673811,-4.3040561184,-3.6268753944
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H,-2.5975086942,-3.3807648973,-4.569184909
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C,4.3785554847,0.7404148172,0.0630797324
H,4.7435985707,1.5069388884,-0.6107997048
C,3.3836601526,-0.1422708115,-0.3721856832
C,3.0278640725,-2.3224710543,2.8071305647
H,2.1638527414,-2.8336351775,2.3773395951

C,2.5781714709,-1.7287119578,4.1550587133
H,2.1829940312,-2.5175171634,4.8018330041
H,1.7963031103,-0.9781065778,4.0190734808
H,3.4075002366,-1.2539265012,4.6865219593
C,4.124800387,-3.3833013753,3.020497279
H,5.0230192316,-2.9398767819,3.4602262303
H,4.4140022584,-3.8533032778,2.0774217688
H,3.7732183205,-4.1684852911,3.6964461094
C,2.8908453193,-0.0400270581,-1.8152332012
H,2.0364380636,-0.7090692078,-1.9297265194
C,3.9767933613,-0.5246160908,-2.7961855377
H,4.8668920405,0.1092909118,-2.7458297177
H,3.6036385685,-0.4991451899,-3.8243365156
H,4.2836922624,-1.5492887011,-2.5720051944
C,2.4111809475,1.3751134485,-2.1835422612
H,1.6270379711,1.7219659732,-1.5058418119
H,2.0038727031,1.3835421568,-3.1983478922
H,3.2259569508,2.1035196723,-2.1511456363
H,-5.6759749891,-2.0925388807,-1.3287921801
H,5.6886242656,1.3378090279,1.6560617662

Table S8. Cartesian coordinates and energy values of **2-Dip** in heptane.

Si,10.4155749612,13.344247903,19.7326838881
H,10.2245187445,14.7248699648,19.2007883233
N,9.7403001364,12.8660222696,21.1307824204
C,8.9410941958,13.0910182165,22.2171667064
C,8.5655881932,11.9888771686,23.0590586584
C,7.7864355243,12.1974702581,24.1943966713
H,7.5215609203,11.3499360321,24.8173934878
C,7.3352687654,13.4616845791,24.5557719936
H,6.7367695608,13.6045525426,25.4487356148
C,7.6614333555,14.5362826852,23.7389462534
H,7.2977768618,15.5225049479,24.0057079789
C,8.435970928,14.3860808956,22.5877803524
C,8.9577161795,10.5724431589,22.6671284832
H,9.8882897952,10.6614186088,22.1023843157
C,7.8812446178,9.9700301662,21.7396602698
H,6.927618867,9.8856147768,22.2702116198

H,8.1603280971,8.9645693006,21.3992595685
H,7.719136503,10.6070518365,20.8668705928
C,9.2156877672,9.6297562463,23.8520863927
H,9.9345930715,10.0624260971,24.5501926214
H,9.621170902,8.6767130266,23.4963173114
H,8.2990065189,9.40125833,24.4046245052
C,8.6673934227,15.5917121906,21.6879956495
H,9.6454089694,15.4664609486,21.2166966391
C,8.6928944549,16.9492465915,22.4094229845
H,7.7056795048,17.2323721614,22.785960502
H,9.0087009785,17.7353044972,21.716150498
H,9.3852293746,16.9437907073,23.2538360884
C,7.6059772263,15.6219533681,20.5692112249
H,7.5647033685,14.6652104971,20.044776077
H,7.8105818779,16.413788496,19.8392557193
H,6.6162080745,15.8054898973,20.998866854
C,9.3916883318,12.345881459,18.3566847803
N,9.2400306086,11.0008954064,18.3293620381
C,8.1828209214,10.6281241244,17.507441757
C,7.6652551728,11.7841236321,17.0021611977
N,8.4279780674,12.8238423224,17.5297753821
C,10.1012371092,10.0706893727,19.0505354017
H,10.9423214341,9.7637351256,18.4258035749
H,9.5256329605,9.1958083647,19.3413480154
H,10.4555998161,10.5652239328,19.9510842879
C,7.7794404886,9.207891308,17.2997892841
H,7.4285487354,8.7494247111,18.2294054432
H,8.6083191543,8.6032432281,16.9205231656
H,6.9676752138,9.1488051792,16.5748755491
C,6.5236889262,12.0166294784,16.0717721164
H,5.7392331424,12.6206375157,16.537659635
H,6.0776417328,11.0665395183,15.7783996879
H,6.8413403032,12.5316968326,15.1600393397
C,8.2006970864,14.2251446401,17.1801997581
H,8.9232462367,14.8412610357,17.7020550808
H,7.19268301,14.5228062748,17.4715048764
H,8.3347960642,14.3598831078,16.107031347
C,12.3113195867,13.0932724353,19.4090913886
C,13.2445285905,12.6067503495,20.369609991
C,14.6216014148,12.6505303898,20.0974479451

H,15.3066540076,12.2968242449,20.8584568446
C,15.1203626103,13.1540031223,18.9084476474
H,16.1892392968,13.1882273644,18.7279705927
C,14.2279363153,13.629675167,17.9616756273
H,14.5970480613,14.0458363062,17.0314798531
C,12.8464070786,13.607490764,18.1889732511
C,12.9461163852,12.0604548408,21.7496826101
C,12.8379390369,12.9539400519,22.840988293
C,12.7446785152,12.4349063345,24.1344302339
H,12.6466557981,13.110826154,24.9749845563
C,12.7854533061,11.0676823511,24.3674239755
C,12.9241616633,10.195204231,23.2985711826
H,12.9699751199,9.1295078789,23.4900709191
C,13.0116807575,10.6661120572,21.9844895185
C,12.915542061,14.468419453,22.6601698806
H,12.6433163798,14.6964396927,21.6274956653
C,11.9471435047,15.2423594092,23.5683436974
H,10.9319085883,14.8503796126,23.4972949214
H,11.9334683846,16.2977293983,23.2806918605
H,12.2541432216,15.2023184961,24.6175576085
C,14.3592266534,14.9689000371,22.8761659526
H,14.6916325593,14.7555772769,23.8967271137
H,14.4159195897,16.0513683005,22.7229371993
H,15.0607504857,14.4935858924,22.1874136694
C,13.2359476633,9.6480310981,20.863671056
H,13.003163131,10.1404125096,19.9159804478
C,12.3313615198,8.4065215745,20.9876235716
H,12.6428655767,7.764931242,21.8160421837
H,12.3908455743,7.8020014025,20.0769750699
H,11.2881570725,8.6751721869,21.1607255181
C,14.7082124812,9.192002733,20.7934365908
H,15.3826566591,10.0267317356,20.6001148259
H,14.8449233021,8.4570691809,19.9933571459
H,15.0119417717,8.7249636751,21.734916377
C,12.0469651348,14.1997225656,17.0467265941
C,11.7936529922,15.5938858745,17.0183929196
C,11.1888074141,16.1503685481,15.8874290451
H,10.9966119571,17.2164681581,15.8558675995
C,10.8514429511,15.3668023136,14.7913281996
C,11.127207912,14.006121901,14.8095961161

H,10.8903716693,13.4066091953,13.9382166968
C,11.7321198325,13.4033387202,15.9189236011
C,12.2410088033,16.5218633313,18.1476640428
H,12.4457566219,15.9037594928,19.0233870764
C,11.1726219698,17.551068033,18.5544028265
H,11.5079691831,18.1072002457,19.4341649811
H,10.2268822949,17.0673836571,18.8066331526
H,10.9840864402,18.2823791706,17.7631082922
C,13.5541074599,17.2388409648,17.7718971146
H,13.4165810795,17.8690713792,16.887962562
H,14.3520847997,16.5258533952,17.5557366055
H,13.8875780924,17.8789884245,18.5941396389
C,12.1190618916,11.9257744429,15.8367381056
H,12.282028002,11.5721513204,16.8577752389
C,13.4434186991,11.7429194234,15.0658637385
H,13.3433519797,12.1027582824,14.0373367585
H,13.720030598,10.6846712644,15.0274210919
H,14.2639527487,12.2865856228,15.534740898
C,11.0356451937,11.0392319194,15.1980046869
H,10.0612629673,11.178376278,15.6678499045
H,11.3135593585,9.9850154653,15.2922164924
H,10.9239820275,11.2429570446,14.1292133849
H,12.7153238839,10.6844653753,25.3796299541
H,10.3935743235,15.8192492547,13.9178909111

Zero-point correction= 1.044090 (Hartree/Particle)
Thermal correction to Energy= 1.102579
Thermal correction to Enthalpy= 1.103523
Thermal correction to Gibbs Free Energy= 0.951623
Sum of electronic and zero-point Energies= -2360.841490
Sum of electronic and thermal Energies= -2360.783001
Sum of electronic and thermal Enthalpies= -2360.782057
Sum of electronic and thermal Free Energies= -2360.933956

Table S9. Cartesian coordinates and energy values of **3-Dip** in heptane.

Si,0,0.228816,0.207544,0.146732
H,0,0.218151,1.256785,1.20034
O,0,-1.007144,0.328813,-0.866532

N,0,0.222191,-1.302324,1.121226
H,0,0.464116,-2.11082,0.562332
C,0,-0.852094,-1.596915,2.00612
C,0,-0.894987,-0.989316,3.290897
C,0,-1.959557,-1.276289,4.150906
H,0,-1.978923,-0.816369,5.1334
C,0,-2.965804,-2.166584,3.800127
H,0,-3.769951,-2.392385,4.492574
C,0,-2.904708,-2.788294,2.559646
H,0,-3.672442,-3.505511,2.288704
C,0,-1.878708,-2.517494,1.649896
C,0,0.236131,-0.110784,3.817513
H,0,0.947967,0.019912,3.00433
C,0,-0.25001,1.283126,4.251339
H,0,-0.708515,1.817007,3.4158
H,0,0.587287,1.888293,4.610487
H,0,-0.980914,1.222855,5.064005
C,0,0.979167,-0.81507,4.969879
H,0,0.325737,-0.969888,5.834049
H,0,1.832714,-0.214578,5.299791
H,0,1.35341,-1.792419,4.655597
C,0,-1.880998,-3.272053,0.322428
H,0,-1.090122,-2.866431,-0.308719
C,0,-1.588908,-4.769665,0.539121
H,0,-0.63453,-4.916782,1.049654
H,0,-1.541985,-5.295374,-0.418797
H,0,-2.369366,-5.239326,1.146009
C,0,-3.191813,-3.084722,-0.462258
H,0,-3.131732,-3.599212,-1.426126
H,0,-3.378263,-2.026332,-0.65662
H,0,-4.05276,-3.492091,0.076546
C,0,1.921429,0.377853,-0.773639
C,0,2.514554,1.66688,-0.879416
C,0,3.645695,1.873062,-1.680214
H,0,4.066272,2.870609,-1.743312
C,0,4.234288,0.828165,-2.377346
H,0,5.109922,1.000429,-2.993918
C,0,3.689671,-0.442727,-2.265368
H,0,4.142537,-1.274815,-2.793346
C,0,2.550553,-0.677314,-1.483749

C,0,2.022937,2.887715,-0.139032
C,0,1.046078,3.730153,-0.714706
C,0,0.66214,4.886241,-0.027662
H,0,-0.086053,5.541422,-0.459049
C,0,1.231414,5.220465,1.193766
C,0,2.213987,4.405148,1.739486
H,0,2.670168,4.682663,2.683104
C,0,2.630315,3.24057,1.088354
C,0,0.457223,3.449277,-2.095978
H,0,0.643605,2.400055,-2.330167
C,0,1.161042,4.304383,-3.168613
H,0,1.010479,5.372168,-2.980172
H,0,0.765403,4.077286,-4.164015
H,0,2.236815,4.1161,-3.183569
C,0,-1.065106,3.648794,-2.155811
H,0,-1.556699,3.017672,-1.414345
H,0,-1.43452,3.366035,-3.146838
H,0,-1.354857,4.690531,-1.986983
C,0,3.767625,2.418663,1.695275
H,0,3.806051,1.46394,1.167938
C,0,3.560664,2.10182,3.185583
H,0,3.579861,3.004285,3.803515
H,0,4.358829,1.444713,3.543974
H,0,2.607548,1.598811,3.352211
C,0,5.124175,3.119451,1.480904
H,0,5.320823,3.292515,0.420694
H,0,5.94011,2.509503,1.881387
H,0,5.147585,4.088904,1.988188
C,0,2.086116,-2.111685,-1.464509
C,0,2.63512,-3.011482,-0.518556
C,0,2.285638,-4.363624,-0.591869
H,0,2.70187,-5.063024,0.124267
C,0,1.424917,-4.831112,-1.577189
C,0,0.899226,-3.946272,-2.508661
H,0,0.240053,-4.321118,-3.283956
C,0,1.219475,-2.584436,-2.475777
C,0,3.645346,-2.559721,0.53553
H,0,3.625568,-1.469007,0.562874
C,0,3.304281,-3.051717,1.952644
H,0,2.305367,-2.725455,2.246775

H,0,4.020565,-2.642044,2.671346
H,0,3.352797,-4.141836,2.032811
C,0,5.072332,-2.988095,0.139933
H,0,5.157092,-4.078433,0.09588
H,0,5.798843,-2.623704,0.8729
H,0,5.350831,-2.590396,-0.838615
C,0,0.675749,-1.66918,-3.571288
H,0,0.950591,-0.645007,-3.315534
C,0,1.322307,-1.996967,-4.93113
H,0,2.411554,-1.92277,-4.881393
H,0,0.971269,-1.300525,-5.699207
H,0,1.071565,-3.01077,-5.258673
C,0,-0.858846,-1.704411,-3.658785
H,0,-1.234624,-2.705191,-3.894136
H,0,-1.19929,-1.032388,-4.45441
H,0,-1.288722,-1.36628,-2.714213
C,0,-3.592726,0.857875,-0.536095
H,0,-2.454616,0.61781,-0.538428
N,0,-4.439953,1.003558,0.489467
C,0,-5.720992,1.292293,0.014858
N,0,-4.298822,1.047266,-1.657951
C,0,-5.631346,1.318971,-1.349085
C,0,-4.054159,0.864756,1.893977
H,0,-3.008053,0.571921,1.93886
H,0,-4.648523,0.087352,2.372901
H,0,-4.191347,1.812383,2.417446
C,0,-6.88173,1.507491,0.92529
H,0,-7.781375,1.721305,0.348407
H,0,-6.713068,2.35022,1.602594
H,0,-7.082229,0.62421,1.539228
C,0,-6.661839,1.571336,-2.396354
H,0,-6.773717,0.713879,-3.066954
H,0,-6.409319,2.441509,-3.009981
H,0,-7.63191,1.760683,-1.936898
C,0,-3.70366,0.955177,-2.991059
H,0,-2.640777,0.758343,-2.858799
H,0,-3.841406,1.893935,-3.529393
H,0,-4.162624,0.139773,-3.552594
H,0,0.919915,6.121036,1.712641
H,0,1.170151,-5.884583,-1.621506

Zero-point correction= 1.068234 (Hartree/Particle)
Thermal correction to Energy= 1.129386
Thermal correction to Enthalpy= 1.130330
Thermal correction to Gibbs Free Energy= 0.967766
Sum of electronic and zero-point Energies= -2437.350468
Sum of electronic and thermal Energies= -2437.289315
Sum of electronic and thermal Enthalpies= -2437.288371
Sum of electronic and thermal Free Energies= -2437.450935

Table S10. Cartesian coordinates and energy values for the **H_2O** in heptane.

O,0.,0.,0.118665
H,0.,0.756944,-0.474661
H,0.,-0.756944,-0.474661

Zero-point correction= 0.021121 (Hartree/Particle)
Thermal correction to Energy= 0.023956
Thermal correction to Enthalpy= 0.024901
Thermal correction to Gibbs Free Energy= 0.003474
Sum of electronic and zero-point Energies= -76.431946
Sum of electronic and thermal Energies= -76.429110
Sum of electronic and thermal Enthalpies= -76.428166
Sum of electronic and thermal Free Energies= -76.449592

Table S11. Cartesian coordinates and energy values for the **2-Dip*** in gas phase.

Si,-0.3608383238,-0.2801415756,-0.6129670291
H,-0.6961887523,-0.5515459932,-2.0509409439
N,1.0950320319,0.3503586855,-0.2701237703
C,2.4578176369,0.3461293339,-0.3082662336
C,3.1747387434,1.2452148876,0.5496978359
C,4.5659400793,1.2955242586,0.5054909301
H,5.0947070455,1.9861177493,1.1543256089
C,5.3001311327,0.4776882844,-0.3482125945
H,6.383083915,0.5306265861,-0.3694775773
C,4.6191193736,-0.4165798334,-1.1661601423

H,5.191667794,-1.0615663816,-1.8244157479
C,3.2267190984,-0.5093503909,-1.1643409965
C,2.3898706652,2.1674697649,1.472546117
H,1.4559433013,1.644122451,1.6972365637
C,2.0075969078,3.4736114992,0.7484162509
H,2.9027217988,4.0451490171,0.482287047
H,1.3758319142,4.1097915697,1.3803981897
H,1.4628627256,3.2510836658,-0.1715897046
C,3.091715899,2.4780842822,2.8032980507
H,3.3958432146,1.5617704431,3.3162243808
H,2.4191370139,3.0317647787,3.4671397643
H,3.9851243157,3.0950960842,2.6656270184
C,2.5289909019,-1.4797760711,-2.1067322873
H,1.5775425848,-1.7565165007,-1.6388287281
C,3.2943896938,-2.7914816528,-2.346739285
H,4.2084995875,-2.6333960545,-2.9265564482
H,2.6723250137,-3.4931096865,-2.9114357209
H,3.5750828693,-3.2678470751,-1.4039772555
C,2.1969901674,-0.8052169794,-3.4524945497
H,1.6181853715,0.108201757,-3.3012425331
H,1.6172938997,-1.472295192,-4.1001122726
H,3.1178908297,-0.5341783876,-3.9784969007
C,-1.5365135121,1.2873946638,-0.3236594813
N,-2.3611435522,1.6429941221,0.6880581767
C,-2.8624470248,2.9293905101,0.4912734147
C,-2.3309142084,3.3762366463,-0.68233289
N,-1.5180461062,2.3522356117,-1.1599276193
C,-2.6445524819,0.8495774787,1.8829010777
H,-3.7227126862,0.7560482311,2.0199540641
H,-2.2085857035,1.3313439272,2.7600275228
H,-2.2153545669,-0.1399134327,1.7627186822
C,-3.7890588646,3.5876114481,1.4565234191
H,-3.3360871727,3.6892123735,2.447378929
H,-4.7214382261,3.026753662,1.573824158
H,-4.0469222947,4.5877617918,1.1090277682
C,-2.5068338182,4.6753479267,-1.3933172692
H,-1.5705795673,5.2394005256,-1.4452876879
H,-3.2344173052,5.2947512873,-0.8691258516
H,-2.8683376302,4.5318702151,-2.4156061475
C,-0.6943114455,2.4320313658,-2.3691850849

H,-1.219251692,2.0059765432,-3.225634715
H,0.2305579816,1.8865341126,-2.1862017417
H,-0.4573763586,3.47502943,-2.56906505
C,-1.1583717871,-1.7618736429,0.3315920222
C,-0.5250591574,-2.3975930658,1.4347211321
C,-1.1028545728,-3.5422722229,1.9991713031
H,-0.6140296201,-4.0269612887,2.8368615556
C,-2.2825885636,-4.0758228672,1.5055135793
H,-2.7090702101,-4.9682968286,1.9515579132
C,-2.9169600506,-3.4568947971,0.4370315891
H,-3.8411662963,-3.8782439149,0.0570167338
C,-2.3827025259,-2.308323669,-0.1527414218
C,0.7776946768,-1.8968631542,2.0609980115
H,1.0747184429,-0.9888827076,1.540024067
C,-3.1670892611,-1.7011165932,-1.3213956928
H,-2.7210418453,-0.7409083633,-1.5807871531
C,0.5967864701,-1.5326722774,3.5469727725
H,0.3400758694,-2.4040020091,4.1575055013
H,1.5238294834,-1.1105206613,3.9452877167
H,-0.1934892533,-0.788197287,3.6832895495
C,1.9177914569,-2.916956884,1.8842406039
H,2.8549936445,-2.5072357176,2.2700388423
H,1.7123802486,-3.8521347651,2.4154927694
H,2.0699110496,-3.1555948184,0.829416893
C,-4.6381891627,-1.4138614441,-0.9655890752
H,-5.1336811918,-0.8993072416,-1.7947210036
H,-5.2002535643,-2.3300446111,-0.767603673
H,-4.718415238,-0.7797409191,-0.0782244308
C,-3.0692286197,-2.586883036,-2.5773266
H,-3.5081583433,-3.5728074527,-2.3990427384
H,-3.6008508327,-2.1288566935,-3.4175924171
H,-2.0275384607,-2.7317458308,-2.8715830603

Zero-point correction= 0.714692 (Hartree/Particle)
Thermal correction to Energy= 0.755700
Thermal correction to Enthalpy= 0.756644
Thermal correction to Gibbs Free Energy= 0.638812
Sum of electronic and zero-point Energies= -1663.029461
Sum of electronic and thermal Energies= -1662.988453
Sum of electronic and thermal Enthalpies= -1662.987509

Sum of electronic and thermal Free Energies= -1663.105341

Table S12. Cartesian coordinates and energy values for the **2-Dip*·H_2O** in gas phase.

Si,-0.3758812492,0.3691706243,0.6177562362
H,-0.7227669747,0.7471360358,2.0251194258
N,0.9864976663,-0.5145608911,0.3510953028
C,2.3654946746,-0.5269337796,0.3812501925
C,3.0670211832,-1.4010600296,-0.5098155179
C,4.4589483136,-1.4752786876,-0.4632975025
H,4.9748644562,-2.1500435023,-1.1398248274
C,5.2034580522,-0.7071815289,0.4230922273
H,6.2856561453,-0.7745918996,0.4409522227
C,4.5343012568,0.1493891156,1.2904800302
H,5.114793937,0.7456407755,1.9852944166
C,3.1426911431,0.2545379735,1.2972936353
C,2.3071076147,-2.2800349957,-1.49746395
H,1.2690778029,-1.9440077789,-1.459451207
C,2.3246122815,-3.7622813435,-1.0746256368
H,3.3487759359,-4.145252313,-1.0209377289
H,1.7756943215,-4.3799327207,-1.7951063424
H,1.8570931114,-3.8922092285,-0.0966663052
C,2.8077439847,-2.1239428596,-2.944342388
H,2.7895489058,-1.0783410875,-3.2613644703
H,2.1800522569,-2.7000693842,-3.633412257
H,3.8332678645,-2.4870243869,-3.0615488525
C,2.4526873399,1.1407618451,2.3263458995
H,1.5541755718,1.5573726498,1.8563577133
C,3.2842532359,2.3428809074,2.8007116778
H,4.14285952,2.0340218172,3.4040256646
H,2.6706056202,2.9973893875,3.4271395067
H,3.6592282532,2.9315526586,1.9597305027
C,1.9888848528,0.307249649,3.5384541358
H,1.3789513435,-0.5416745673,3.2255516928
H,1.401357123,0.9153547434,4.2347371646
H,2.8580053484,-0.0819160006,4.0788687169
C,-1.7370998587,-0.9993526796,0.2401301679
N,-2.0834568386,-1.4479827264,-0.9875183487
C,-2.9562948351,-2.5277020472,-0.8907073449

C,-3.1441302761,-2.7517034647,0.4420864845
N,-2.3947540222,-1.7914303112,1.1152895214
C,-1.587432461,-0.8888815891,-2.2454641416
H,-2.2249027614,-0.0715527994,-2.5858495155
H,-1.5616066111,-1.6746837004,-2.9980836324
H,-0.576106022,-0.5237340347,-2.0883672235
C,-3.5099542989,-3.2350341541,-2.081298287
H,-2.7256845588,-3.7330563198,-2.6597919745
H,-4.0367730699,-2.5497971704,-2.7516574135
H,-4.2202799148,-3.999020618,-1.7660730501
C,-3.9391013409,-3.7966602743,1.1484588906
H,-3.3023860841,-4.414706901,1.7878922628
H,-4.4218464771,-4.4546818439,0.4261929329
H,-4.7233803763,-3.3611387948,1.7752424795
C,-2.2394366212,-1.7633249393,2.5735180775
H,-1.9359510276,-0.7659705455,2.8788201345
H,-1.4594399575,-2.4714536053,2.8572465828
H,-3.1925103189,-2.0085243184,3.0398513622
C,-0.9437154033,1.9068726008,-0.4145731362
C,-0.1345749003,2.5327144066,-1.4012031834
C,-0.6201629923,3.6492096336,-2.09387451
H,0.0056225844,4.1249062824,-2.8402609501
C,-1.8797185608,4.1680346162,-1.8409106259
H,-2.2372402089,5.033157618,-2.3894627401
C,-2.6742220291,3.5761700304,-0.8699851581
H,-3.6537778212,3.9926205129,-0.6618442916
C,-2.2286586225,2.4635127758,-0.1504865423
H,0.6992802997,-2.1271247854,1.3264618194
O,0.5556233648,-2.9056795894,1.9165826129
H,1.4263606596,-3.072236623,2.28975154
C,1.287544923,2.0810186485,-1.7333704241
H,1.4813440845,1.1480213466,-1.2095609211
C,-3.1790284327,1.9232486231,0.9230541201
H,-2.7243396935,1.0492620481,1.3854004927
C,1.4871764594,1.8065499166,-3.2356970127
H,1.3793475821,2.7129193063,-3.8387626721
H,2.491394828,1.4123301641,-3.4126678336
H,0.7682574547,1.072631054,-3.6112791354
C,2.3206762865,3.1095242552,-1.233364756
H,3.3359392098,2.7406832377,-1.4010785333

H,2.2147264519,4.0671428738,-1.753307214
H,2.2042446952,3.2959538565,-0.1634406816
C,-4.5270625129,1.4636225001,0.3368686669
H,-5.1564771878,1.027816257,1.1192504268
H,-5.0812713283,2.295750828,-0.105250532
H,-4.3848821181,0.7101132692,-0.4426223417
C,-3.3878418307,2.9460903705,2.0558138908
H,-3.8691134681,3.8569049016,1.6892513046
H,-4.0235836282,2.5261342042,2.8418550854
H,-2.4336383057,3.2306684995,2.5052598924

Zero-point correction= 0.740718 (Hartree/Particle)
Thermal correction to Energy= 0.784030
Thermal correction to Enthalpy= 0.784974
Thermal correction to Gibbs Free Energy= 0.663830
Sum of electronic and zero-point Energies= -1739.475065
Sum of electronic and thermal Energies= -1739.431754
Sum of electronic and thermal Enthalpies= -1739.430810
Sum of electronic and thermal Free Energies= -1739.551953

Table S13. Cartesian coordinates and energy values for the **TS1** in gas phase.

Si,0.4128363948,0.0512240178,-0.737783194
H,0.747596292,0.7727227563,-1.9746273544
N,-1.1224767304,-0.7497330039,-0.6310692611
C,-2.512361495,-0.4469443511,-0.5798859256
C,-3.3587219238,-1.4064072933,0.0338837907
C,-4.7374134133,-1.1856246646,0.0586567464
H,-5.3883741755,-1.9143680057,0.5272350311
C,-5.2917239998,-0.0450280322,-0.5063290096
H,-6.3636159464,0.1173424618,-0.4737531099
C,-4.4630421837,0.8794601948,-1.1288661547
H,-4.9066470283,1.7546807139,-1.5870389555
C,-3.0782709774,0.6993462939,-1.1908313559
C,-2.7732741638,-2.6928154849,0.6043265762
H,-1.7549743245,-2.4550224383,0.9235996088
C,-2.660722815,-3.7751012682,-0.4902346136
H,-3.6519075193,-4.0403827604,-0.8710527036
H,-2.1988846067,-4.6845411599,-0.0902714673

H,-2.0582731905,-3.4342766295,-1.3351987186
C,-3.5302747988,-3.2422901779,1.8234857611
H,-3.656404453,-2.480426179,2.5974570404
H,-2.9782730395,-4.0806281221,2.2594141618
H,-4.5228162792,-3.6175083073,1.5578163461
C,-2.2197602455,1.6744445403,-1.9905802133
H,-1.268668962,1.7957066956,-1.4654688432
C,-2.8081675632,3.0884402769,-2.1124290777
H,-3.702309337,3.1084806042,-2.7423845845
H,-2.0741970181,3.7529928429,-2.576608974
H,-3.0703290411,3.5067980481,-1.1369349573
C,-1.9161613,1.0939725857,-3.3878316248
H,-1.4105360479,0.1283982013,-3.3264231998
H,-1.2748996812,1.7764274278,-3.9553900954
H,-2.846639043,0.9598185112,-3.9486675511
C,1.9557690087,-1.0673862017,-0.3093507508
N,2.2005613814,-1.7165326624,0.8510834102
C,3.4442482006,-2.345271708,0.8200731527
C,3.9802432818,-2.067892984,-0.4017561485
N,3.0494229327,-1.2872582018,-1.0824962142
C,1.3031730712,-1.7415550842,1.9995699383
H,1.6503829869,-1.0510243011,2.7692006938
H,1.2574266817,-2.752056761,2.4061476028
H,0.308981284,-1.4532956,1.6725522938
C,3.9707867378,-3.1475818204,1.961496279
H,3.3510121488,-4.027461849,2.1621308909
H,4.0215457766,-2.5600651638,2.8831078141
H,4.9775447039,-3.5008458112,1.7390726088
C,5.2837546856,-2.4774554229,-0.9997364057
H,5.1489447015,-3.148171535,-1.8539363858
H,5.8877062695,-3.0036496406,-0.2604675292
H,5.8565751621,-1.6120412046,-1.3441137354
C,3.1735686897,-0.892724623,-2.4915579587
H,3.6533862635,0.0832644655,-2.5811958364
H,2.157949686,-0.9113329892,-2.9023298777
H,3.7796553774,-1.6368961035,-3.0060515242
C,0.6600500399,1.4551455946,0.6421295011
C,-0.1209591632,1.6579733101,1.8213777935
C,0.1578378342,2.7294820367,2.6813118009
H,-0.4543261271,2.8704274515,3.564497803

C,1.182365473,3.6238884892,2.4303384493
H,1.3719860358,4.4518794855,3.1053072099
C,1.9622914718,3.4395778262,1.3016056697
H,2.7688728991,4.1353697385,1.099440682
C,1.7319714595,2.3783171193,0.4206204124
H,-0.9117535304,-1.4995411367,-1.326614909
O,0.4018491746,-1.7090017141,-2.368029301
H,0.7632522235,-2.5913273771,-2.2267450201
C,-1.3168090464,0.7989953508,2.2456247525
H,-1.4069091795,-0.0351608732,1.5556904028
C,2.697537846,2.30980115,-0.7692879531
H,2.4998268768,1.4020507673,-1.3288229077
C,-1.1662411876,0.2135565426,3.6660117686
H,-1.1925791509,0.9943242759,4.4307657499
H,-1.9919790999,-0.4730344641,3.8756988207
H,-0.2312010917,-0.3351265168,3.7969593705
C,-2.6304111144,1.6038569645,2.1731431996
H,-3.4884776893,0.9552091465,2.3678725408
H,-2.637510352,2.4086650217,2.914666073
H,-2.7708284546,2.0489083878,1.1887358006
C,4.1720972097,2.2395783896,-0.3277935686
H,4.8234473178,2.0974849022,-1.1966538288
H,4.4961966699,3.1558510911,0.1719198522
H,4.3401365931,1.4095119385,0.3638324962
C,2.4670945404,3.4750726925,-1.7494872787
H,2.6544414941,4.4406602274,-1.2713785602
H,3.1336866188,3.3941684635,-2.6143108322
H,1.4375529042,3.478540136,-2.1146815654

Zero-point correction= 0.741109 (Hartree/Particle)
Thermal correction to Energy= 0.782679
Thermal correction to Enthalpy= 0.783624
Thermal correction to Gibbs Free Energy= 0.667930
Sum of electronic and zero-point Energies= -1739.441984
Sum of electronic and thermal Energies= -1739.400414
Sum of electronic and thermal Enthalpies= -1739.399469
Sum of electronic and thermal Free Energies= -1739.515163

Table S14. Cartesian coordinates and energy values for the **3-Dip*** in gas phase.

Si,-0.2236382165,0.6402804699,-1.054940356
H,-0.1945612252,1.7269474088,-2.0564095439
N,-1.7846847421,-0.1595653379,-1.2060045578
C,-3.1466079985,0.0250109593,-0.915138512
C,-3.9738424229,-1.1295053043,-0.7865364198
C,-5.3276476231,-0.9655981546,-0.4967163173
H,-5.958959589,-1.8398848191,-0.3972134186
C,-5.8887510964,0.2925793082,-0.3201516647
H,-6.9417557596,0.3981020062,-0.0854302235
C,-5.0803353968,1.4122132223,-0.4539555549
H,-5.5205566856,2.3939830639,-0.3298873685
C,-3.7206283657,1.3123882119,-0.7579138726
C,-3.4041327135,-2.5306326983,-1.0061250277
H,-2.3852084774,-2.5491371415,-0.5993650399
C,-3.3181574241,-2.8631077684,-2.5122996233
H,-4.3226196691,-2.9094837491,-2.9429707997
H,-2.8333494637,-3.8312251287,-2.6735428159
H,-2.7588244877,-2.106753941,-3.0680704023
C,-4.1591775127,-3.6452147161,-0.2648315089
H,-4.2648354543,-3.4203055784,0.79934298
H,-3.6135753524,-4.5882430291,-0.360492897
H,-5.1583875591,-3.8082575469,-0.6779262959
C,-2.9148856846,2.5816649516,-1.0090724052
H,-1.882558214,2.4034117167,-0.6977954177
C,-3.3745847536,3.7992069517,-0.1908533994
H,-4.3524732061,4.1669992189,-0.5136131669
H,-2.6641116708,4.6205278762,-0.3191956513
H,-3.4325677694,3.5672986894,0.8753937015
C,-2.8983155698,2.913808347,-2.5139404893
H,-2.5221424324,2.0736162358,-3.1004280415
H,-2.2630354052,3.7818196309,-2.7171333311
H,-3.9105667235,3.1428299105,-2.8610743539
C,3.1550126441,-1.4706337947,-0.2595833747
N,3.9273287836,-1.374900879,0.8540511721
C,5.0308101946,-2.2337151769,0.8117860822
C,4.9470037026,-2.894100477,-0.3770189331
N,3.7966628874,-2.4081337858,-1.0047881077
C,3.6269185421,-0.4756370028,1.9600256916
H,4.4441430901,0.2325852258,2.1169151354

H,3.4632936629,-1.0366610007,2.8834268338
H,2.7224348837,0.0749535143,1.7141606446
C,6.0353593269,-2.3227344776,1.9111385118
H,5.577637899,-2.6283795195,2.8577303302
H,6.5363240997,-1.3645541571,2.0843090733
H,6.8046256222,-3.0561284111,1.6662304096
C,5.8305713219,-3.9315892732,-0.9840561185
H,5.2952531659,-4.8703337349,-1.161189143
H,6.6697094546,-4.1517320522,-0.323014482
H,6.2436535139,-3.6042179779,-1.9437860814
C,3.3171886489,-2.8377495459,-2.3124695648
H,4.0586103392,-2.6250350332,-3.0868849474
H,2.4040889848,-2.2873617049,-2.5289395735
H,3.1016722015,-3.9092828825,-2.3137257149
C,0.262416401,1.4041299546,0.6338097063
C,-0.2339551427,0.9418667892,1.882779703
C,0.1121889678,1.6156792071,3.0598924018
H,-0.2749958822,1.2651167095,4.0100744281
C,0.9433655244,2.7258396531,3.0368795304
H,1.1886257737,3.2450818059,3.9575861328
C,1.4759582764,3.1542020408,1.8292330067
H,2.1488762093,4.0044910798,1.8203714422
C,1.1684163498,2.5032687645,0.6302248155
H,-1.577150801,-1.1202325947,-1.4398916399
O,0.7993789612,-0.5732529052,-1.4846821117
H,1.6212621712,-0.7967993319,-0.9392966658
C,-1.0963093955,-0.3129141226,2.0266760753
H,-1.3580041243,-0.6575157545,1.0288448511
C,1.8694271907,3.0121902336,-0.6343176398
H,1.6423298417,2.336197866,-1.4576493859
C,-0.3047184201,-1.4511743288,2.7011966223
H,-0.0024434778,-1.1812272546,3.7178414687
H,-0.9192848496,-2.3544987109,2.7657295086
H,0.5960264913,-1.6962814601,2.1326715487
C,-2.4180288983,-0.0474577337,2.7698142666
H,-3.0331444185,-0.9516056643,2.7785196087
H,-2.2497611579,0.2467922711,3.8099916503
H,-2.9948346259,0.739880871,2.2806520635
C,3.4035310306,2.9983364611,-0.4913868245
H,3.8694479371,3.3017481198,-1.4338007412

H,3.7526116123,3.6851863217,0.284715829
H,3.7637374473,1.9961844437,-0.2465618545
C,1.3640471335,4.4070195411,-1.0444966
H,1.5738432646,5.1498509129,-0.269239593
H,1.8512591673,4.7378282447,-1.9668032328
H,0.2850521375,4.4000434507,-1.215886419

Zero-point correction= 0.741323 (Hartree/Particle)
Thermal correction to Energy= 0.784255
Thermal correction to Enthalpy= 0.785199
Thermal correction to Gibbs Free Energy= 0.661997
Sum of electronic and zero-point Energies= -1739.521809
Sum of electronic and thermal Energies= -1739.478877
Sum of electronic and thermal Enthalpies= -1739.477933
Sum of electronic and thermal Free Energies= -1739.601136

Table S15. Cartesian coordinates and energy values for the **H_2O** in gas phase.

O,1.3621370635,1.7748753051,-0.0235142
H,2.3227245901,1.8225433143,-0.0235142
H,1.0864201971,2.6962768706,-0.0235142

Zero-point correction= 0.021325 (Hartree/Particle)
Thermal correction to Energy= 0.024160
Thermal correction to Enthalpy= 0.025104
Thermal correction to Gibbs Free Energy= 0.003679
Sum of electronic and zero-point Energies= -76.426123
Sum of electronic and thermal Energies= -76.423288
Sum of electronic and thermal Enthalpies= -76.422343
Sum of electronic and thermal Free Energies= -76.443769

Table S16. Imaginary frequencies and vibrational frequencies (cm^{-1}) of optimized structures at B3LYP/6-311G(d,p).

	2-Dip	**3-Dip**	**H_2O**	**2-Dip***	**2-Dip*·H_2O**	**TS1**	**3-Dip***	**H_2O (Gas)**
Vibrational Frequencies	17.40	2.30	1606.97	12.23	10.31	-124.53	9.99	1637.92
Imaginary Frequencies	0	0	0	0	0	1	0	0

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