Supporting Information

Synthesis, characterisation and electronic properties of naphthalene bridged disilanes

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(i) Spectra of synthesised compounds

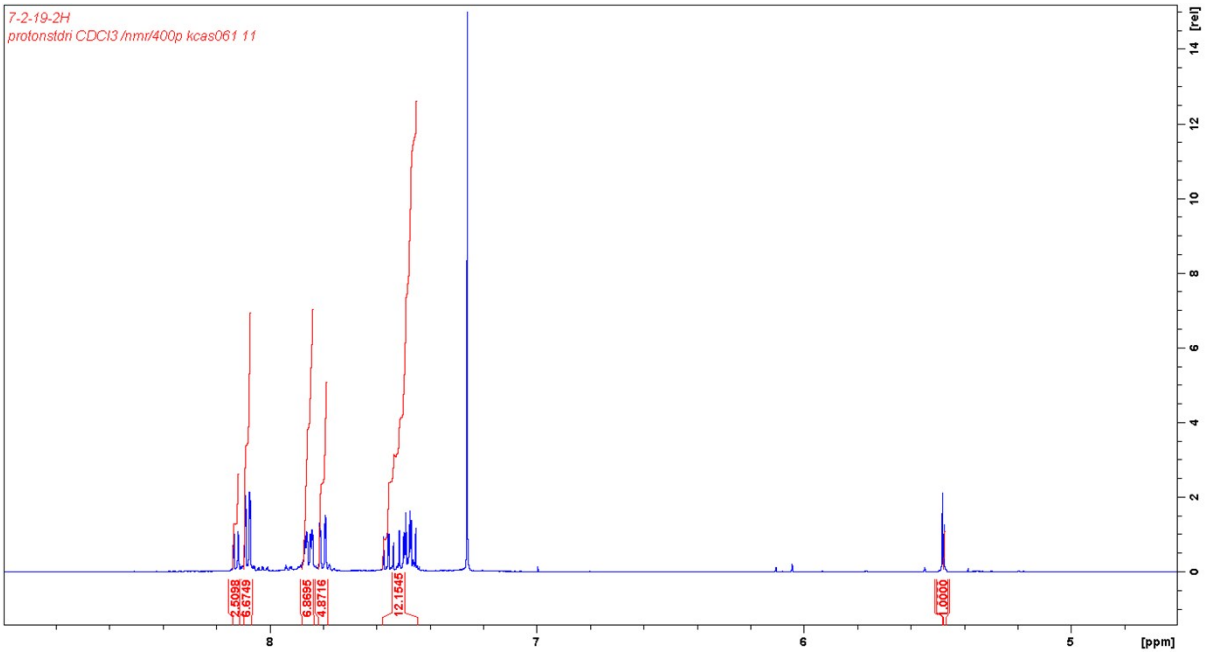

Figure S1- ^{1}H NMR spectrum of the product obtained after reacting stoichiometric amounts of 1,8-dilthionaphthalene and $Cl_3SiSiCl_3$ in $CDCl_3$

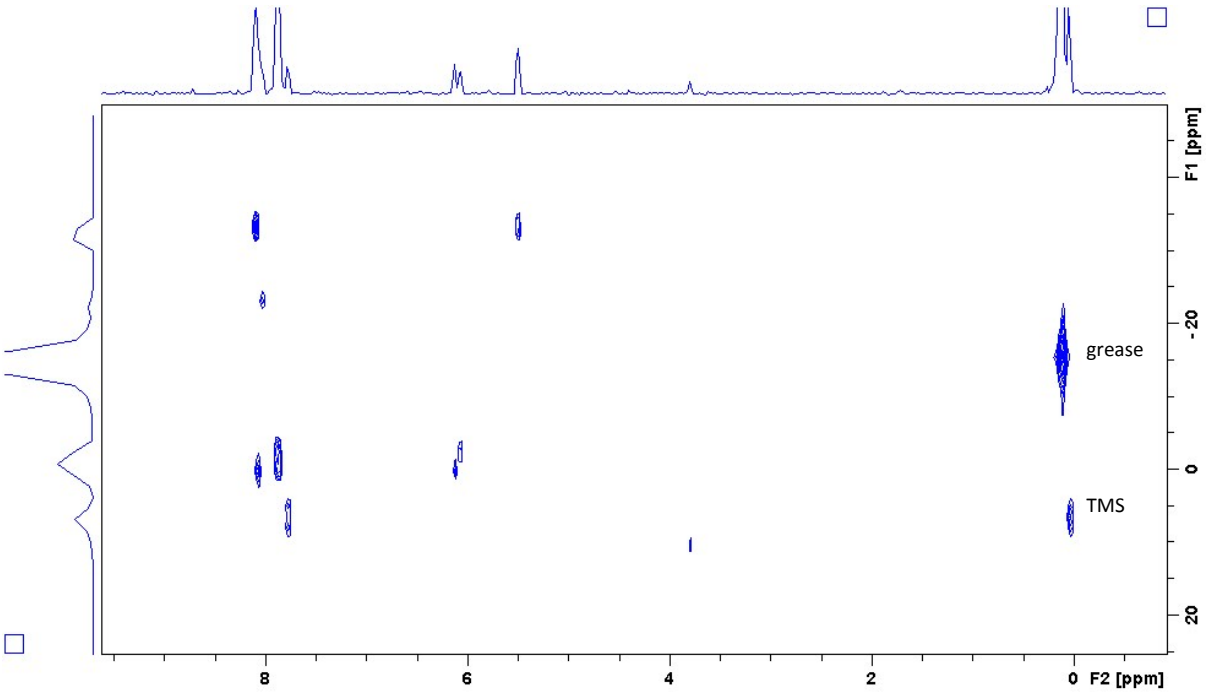

Figure S2- $^{29}Si\{^{1}H\}$ NMR (2D-HMBC) spectrum of the product obtained after reacting stoichiometric amounts of 1,8-dilthionaphthalene and $Cl_3SiSiCl_3$ in $CDCl_3$

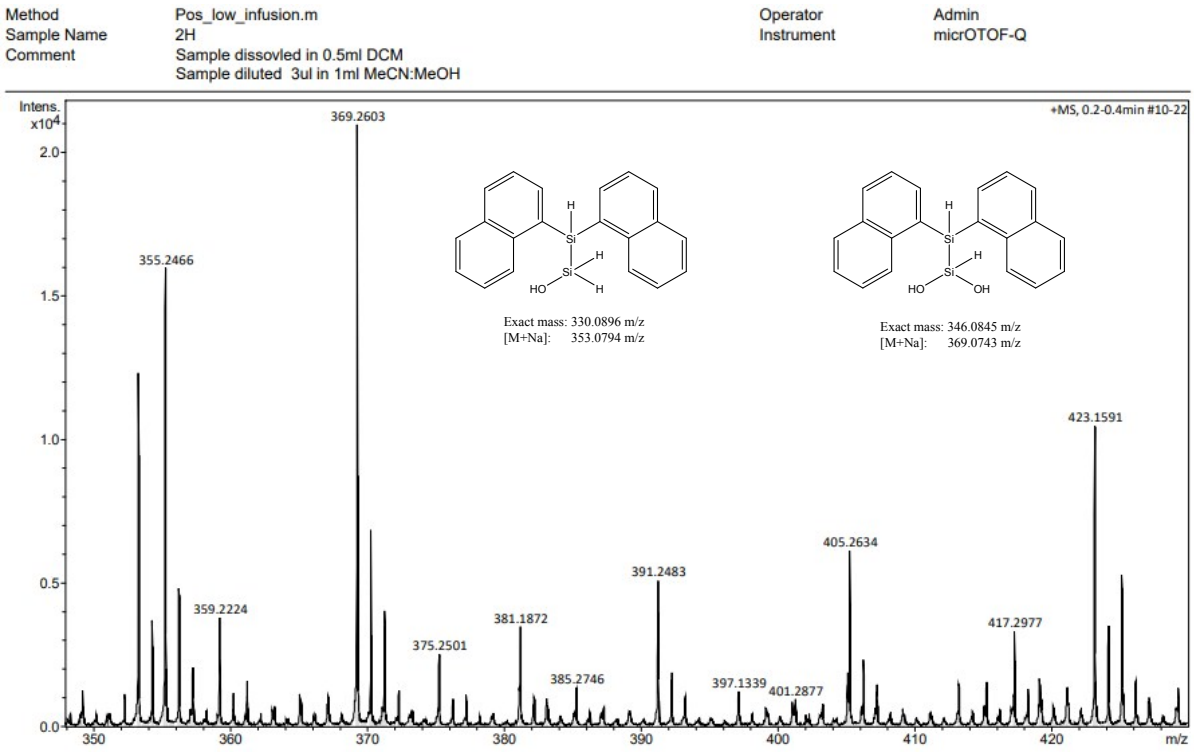

Figure S3- MS-ESI spectrum of the product obtained after reacting stoichiometric amounts of 1,8-dilthionaphthalene and $Cl_3SiSiCl_3$ in $CDCl_3$

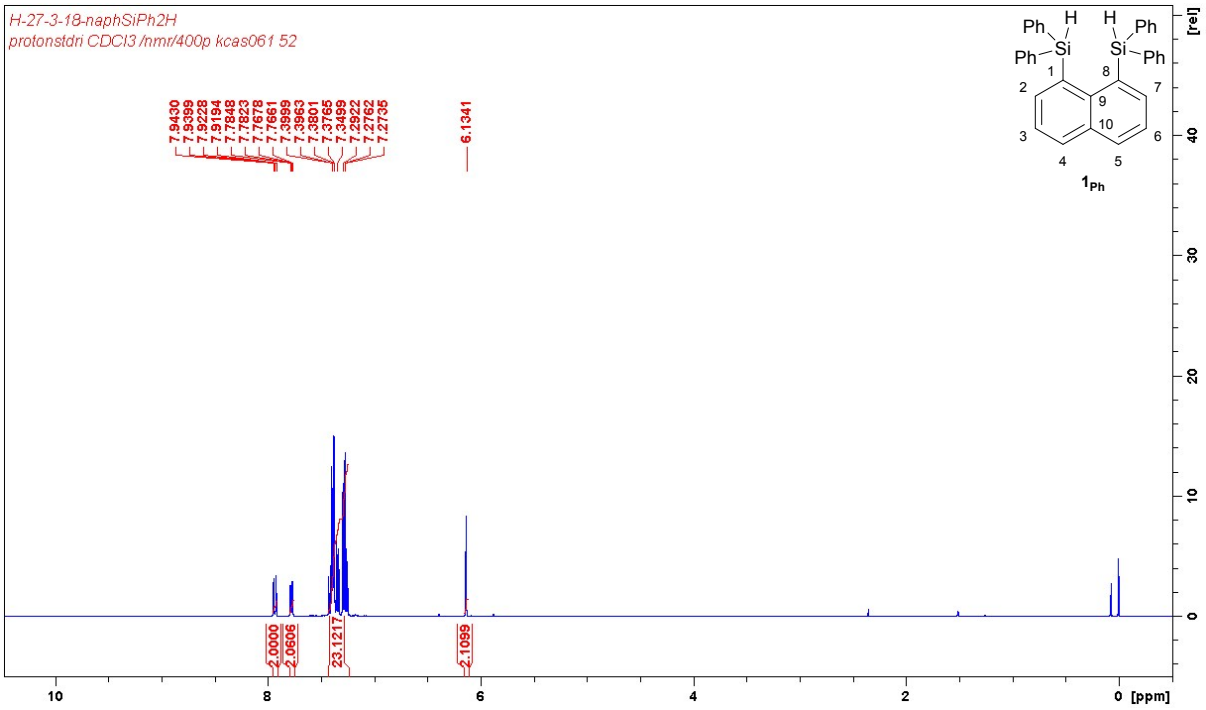

Figure S4- ^{1}H NMR spectrum of $\mathbf{1_{Ph}}$ in $CDCl_3$ (residual grease at 0.07 ppm, TMS at 0.0 ppm)

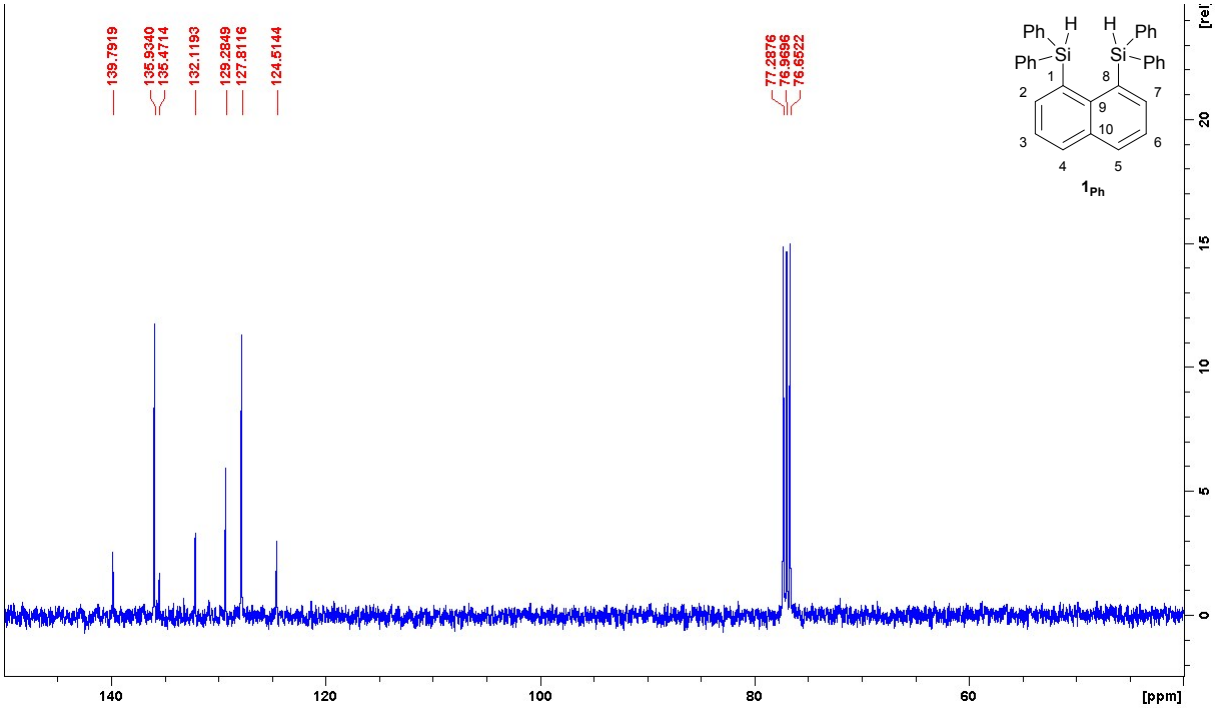

Figure S5- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{1_{Ph}}$ in $CDCl_3$

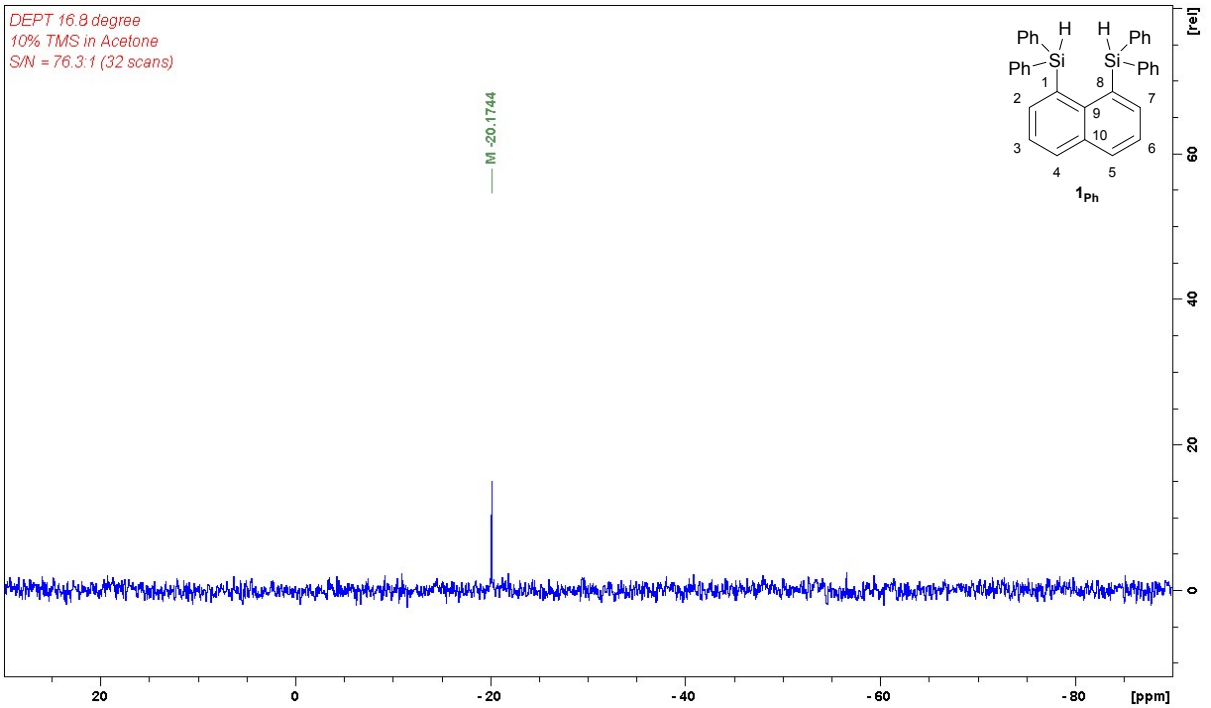

Figure S6- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{1_{Ph}}$ in $CDCl_3$

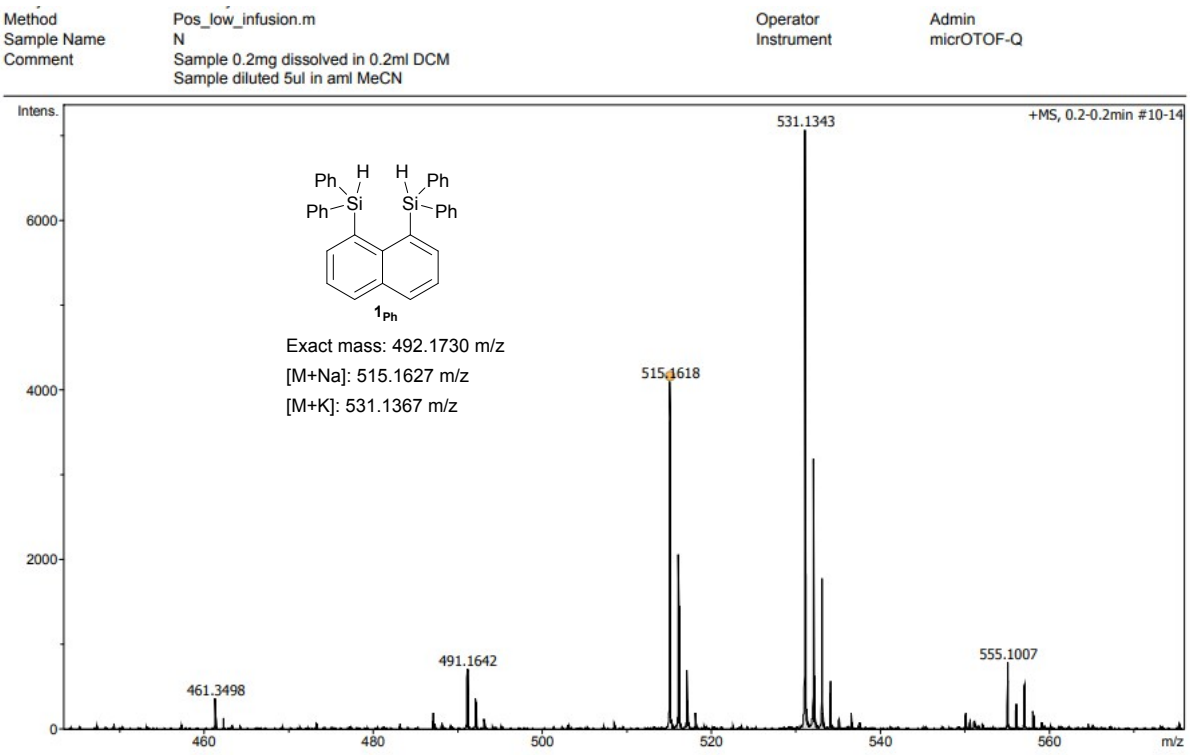

Figure S7- MS-ESI spectrum of $\mathbf{1_{Ph}}$

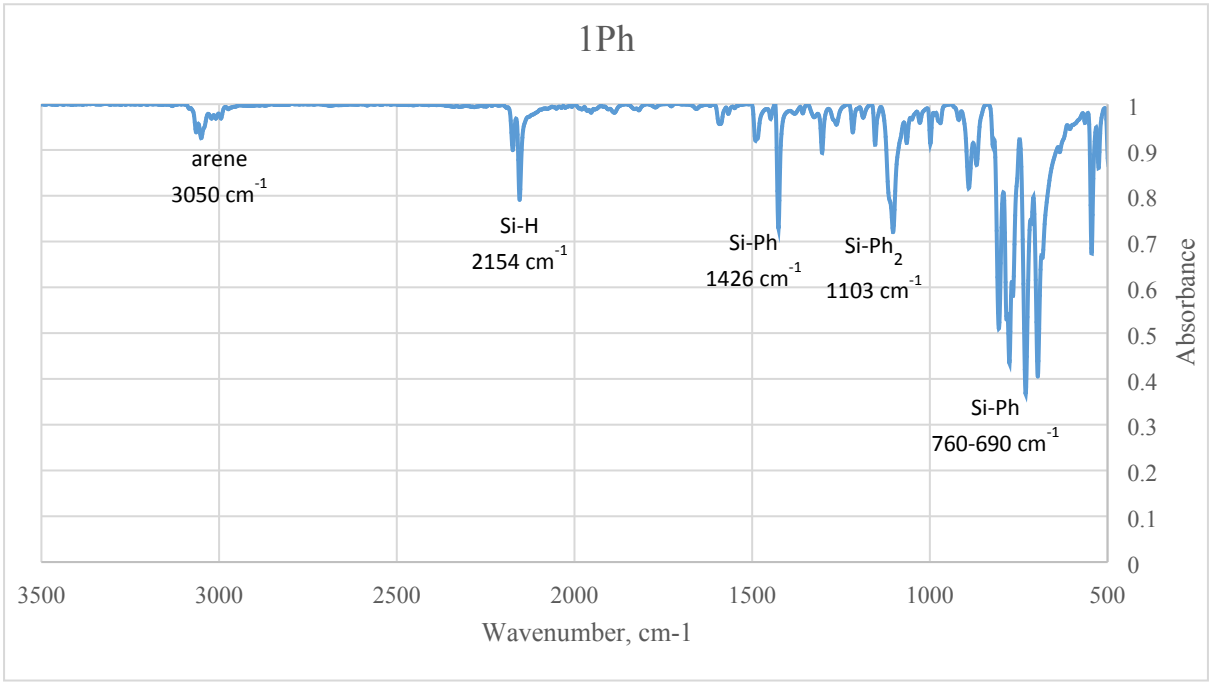

Figure S8- Infrared spectrum of $\mathbf{1_{Ph}}$

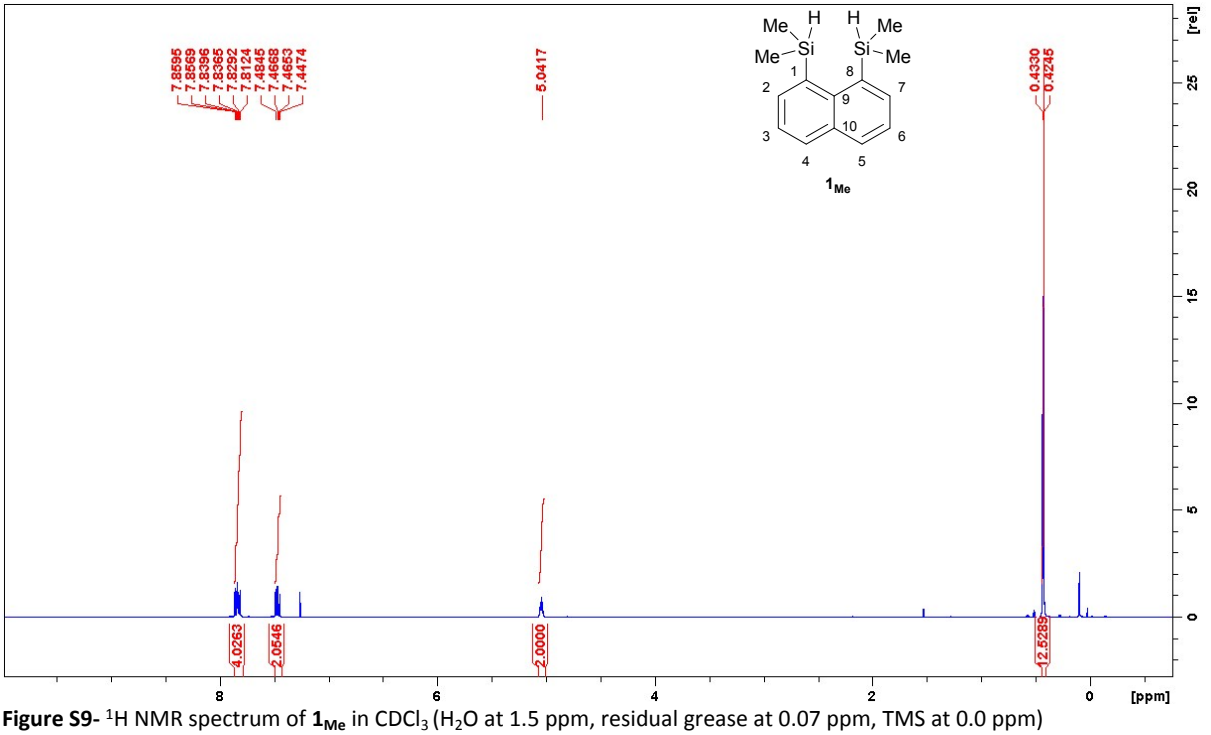

Figure S9- ^{1}H NMR spectrum of $\mathbf{1_{Me}}$ in $CDCl_3$ (H_2O at 1.5 ppm, residual grease at 0.07 ppm, TMS at 0.0 ppm)

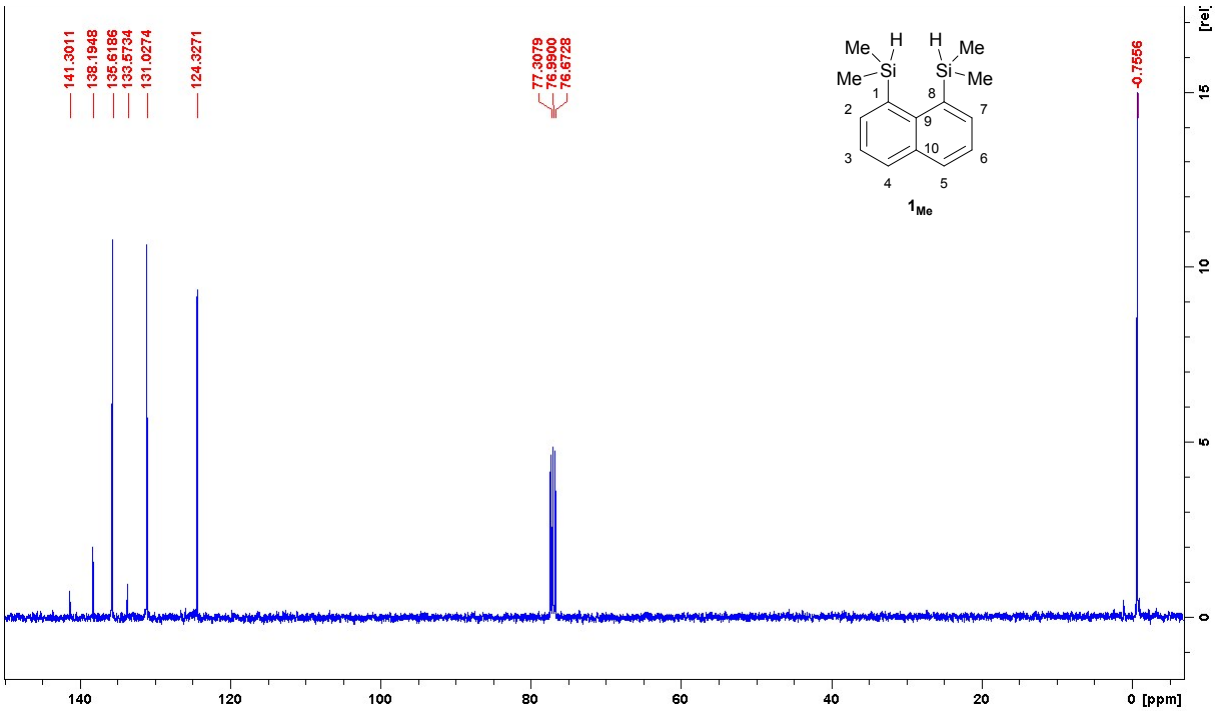

Figure S10- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{1_{Me}}$ in $CDCl_3$

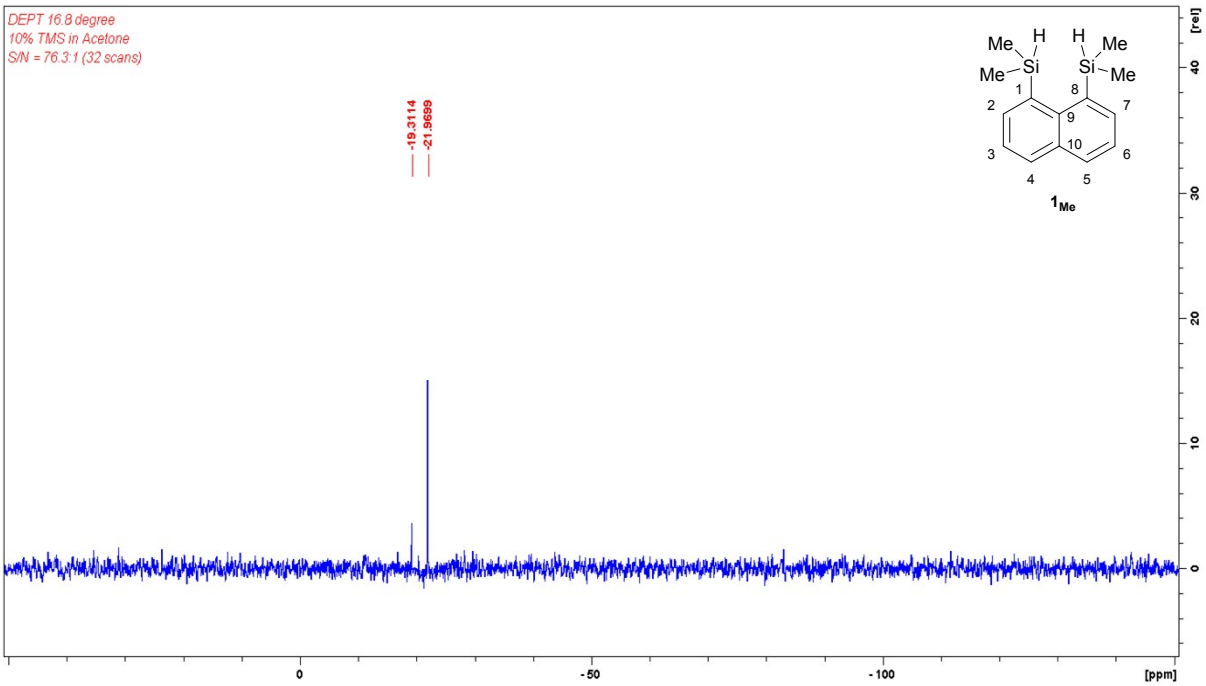

Figure S11- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{1_{Me}}$ in $CDCl_3$. [Note: the peak at -19.3 ppm is residual grease]

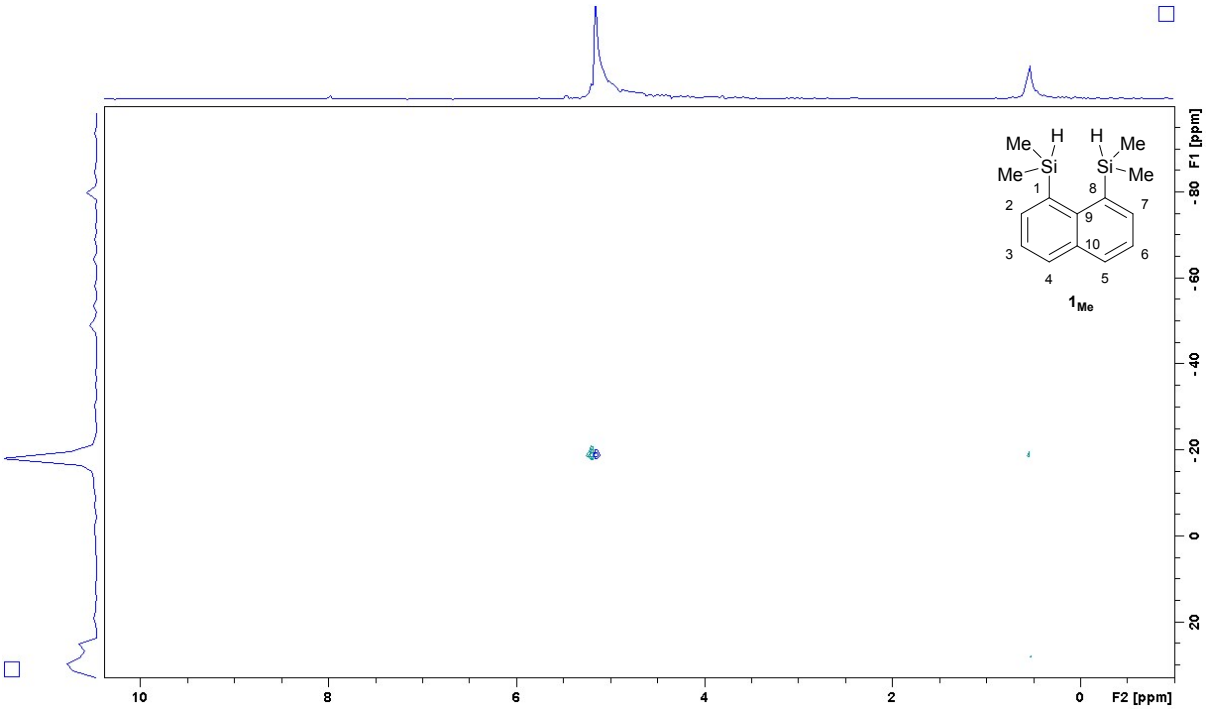

Figure S12- $^{29}Si\{^{1}H\}$ NMR (2D-HSQC) spectrum of $\mathbf{1_{Me}}$ in $CDCl_3$

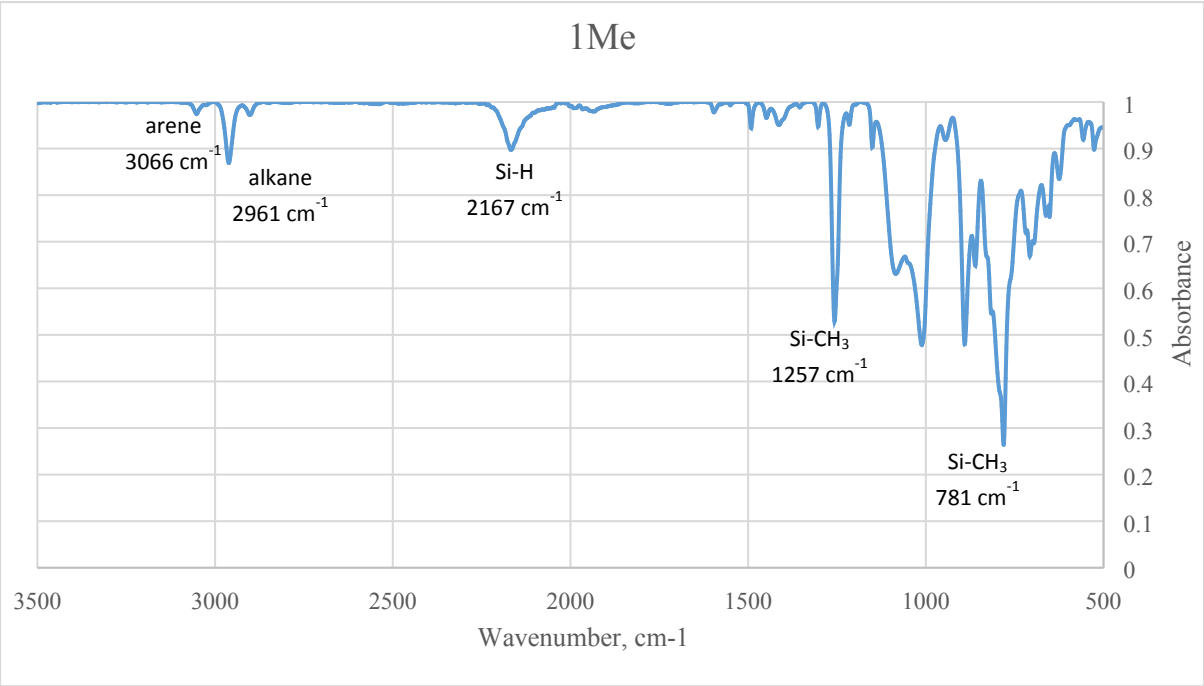

Figure S13- Infrared spectrum of $\mathbf{1_{Me}}$

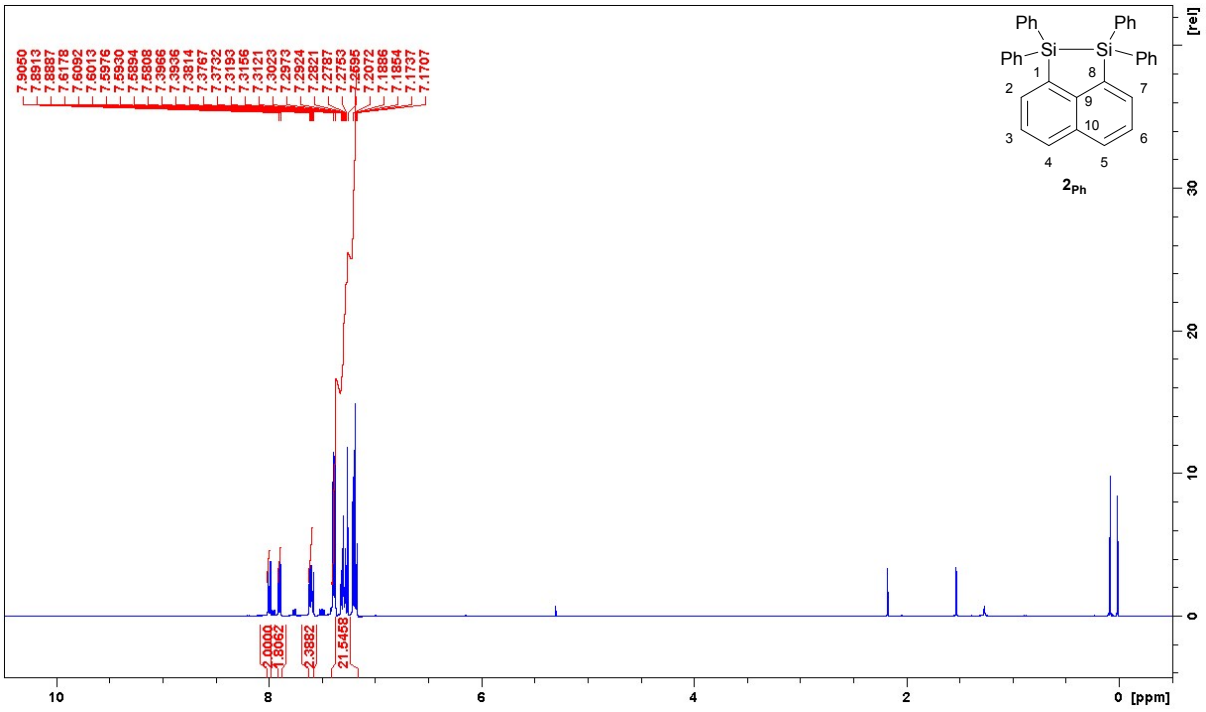

Figure S14- ^{1}H NMR spectrum of $\mathbf{2_{Ph}}$ in $CDCl_3$ (toluene at 2.4 ppm, H_2O at 1.5 ppm, residual grease at 0.07 ppm, TMS at 0.0 ppm)

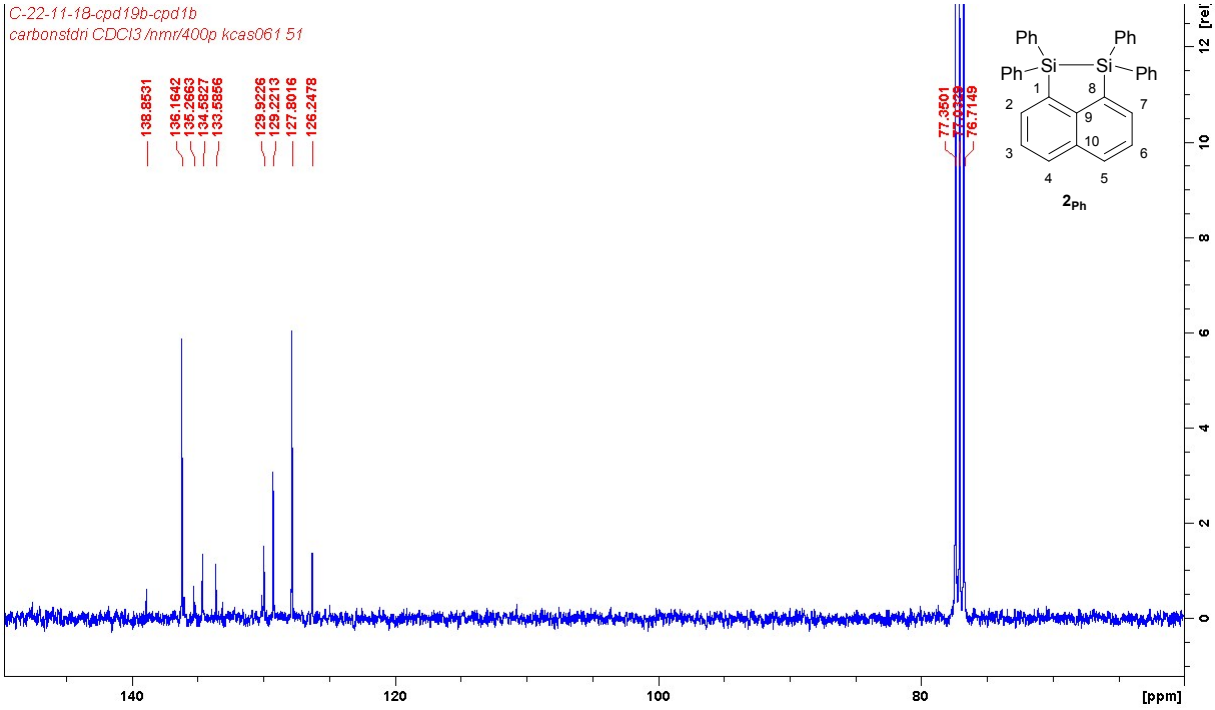

Figure S15- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2_{Ph}}$ in $CDCl_3$

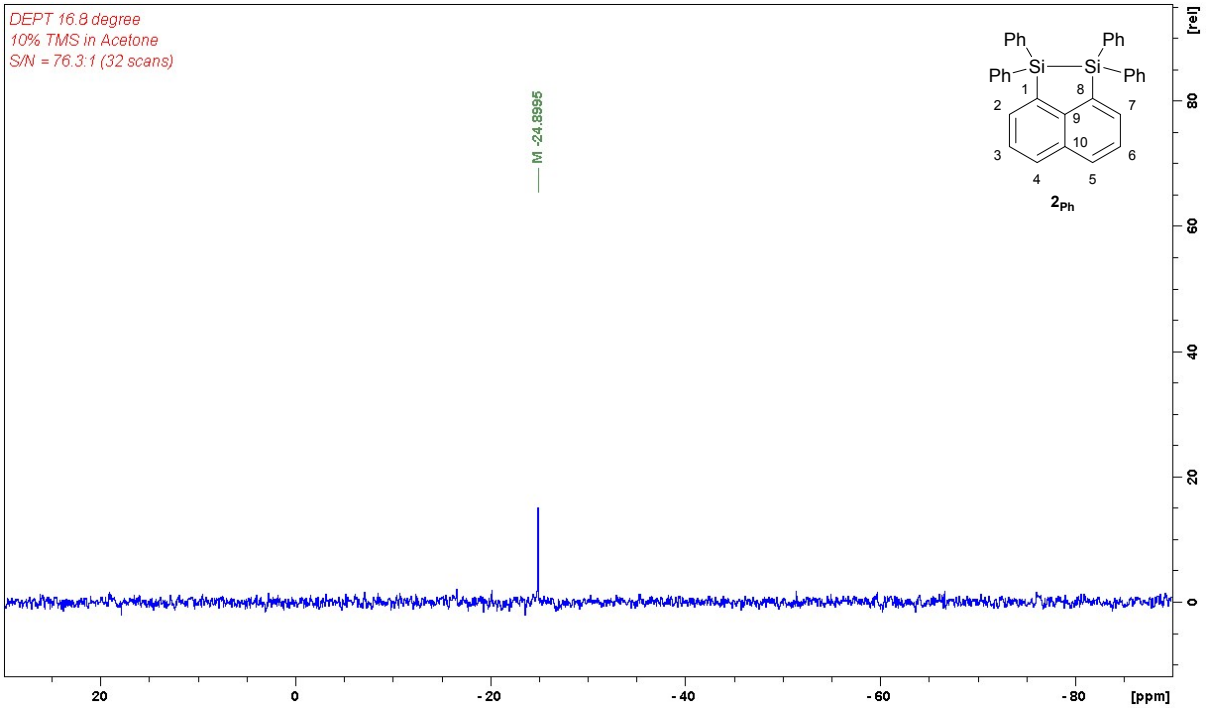

Figure S16- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{2_{Ph}}$ in $CDCl_3$

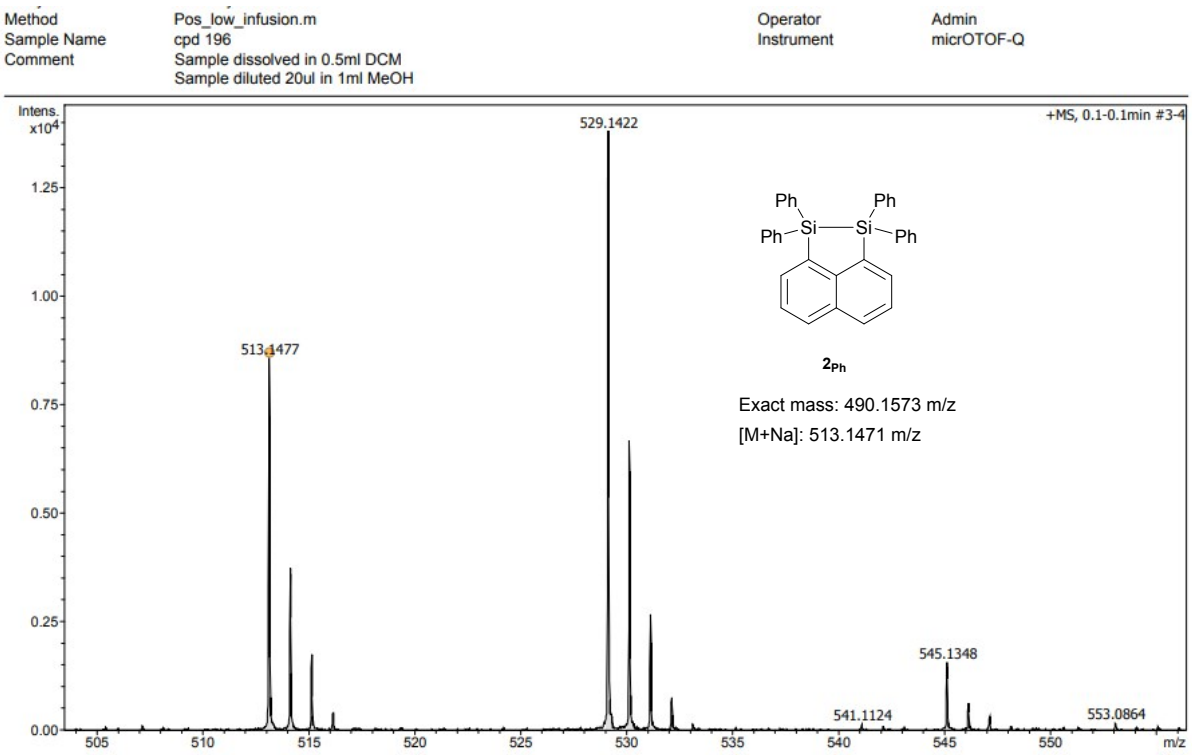

Figure S17- MS-ESI spectrum of $\mathbf{2_{Ph}}$

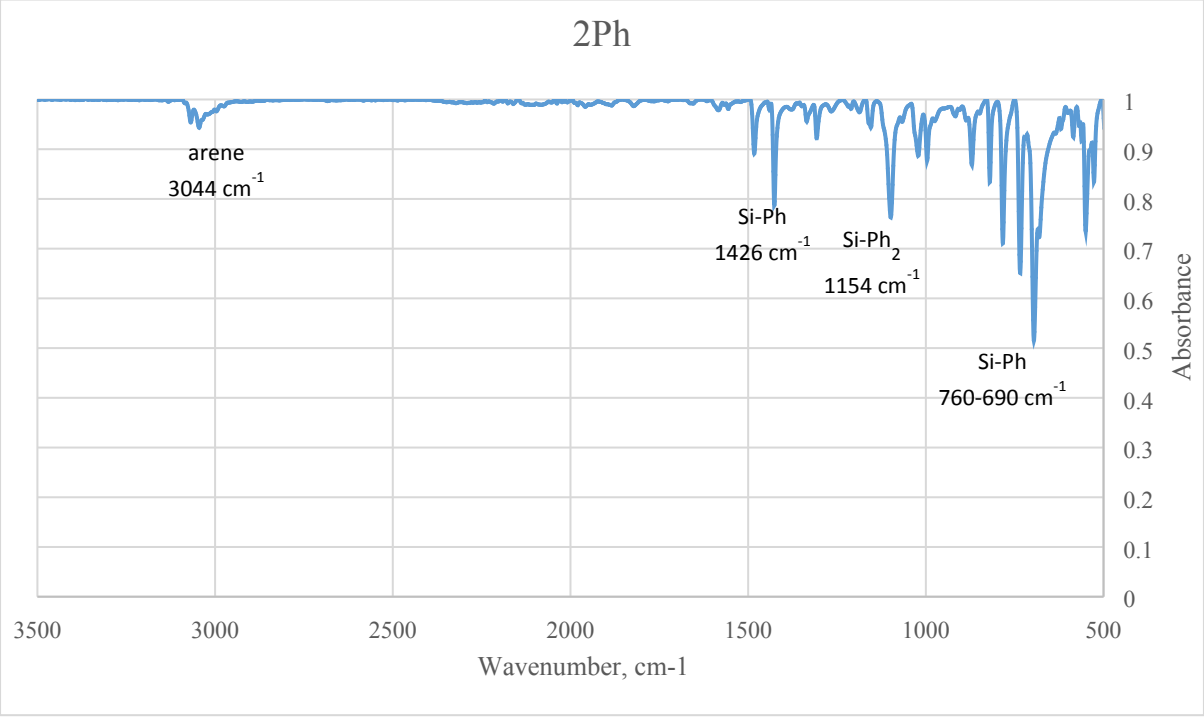

Figure S18- Infrared spectrum of $\mathbf{2_{Ph}}$

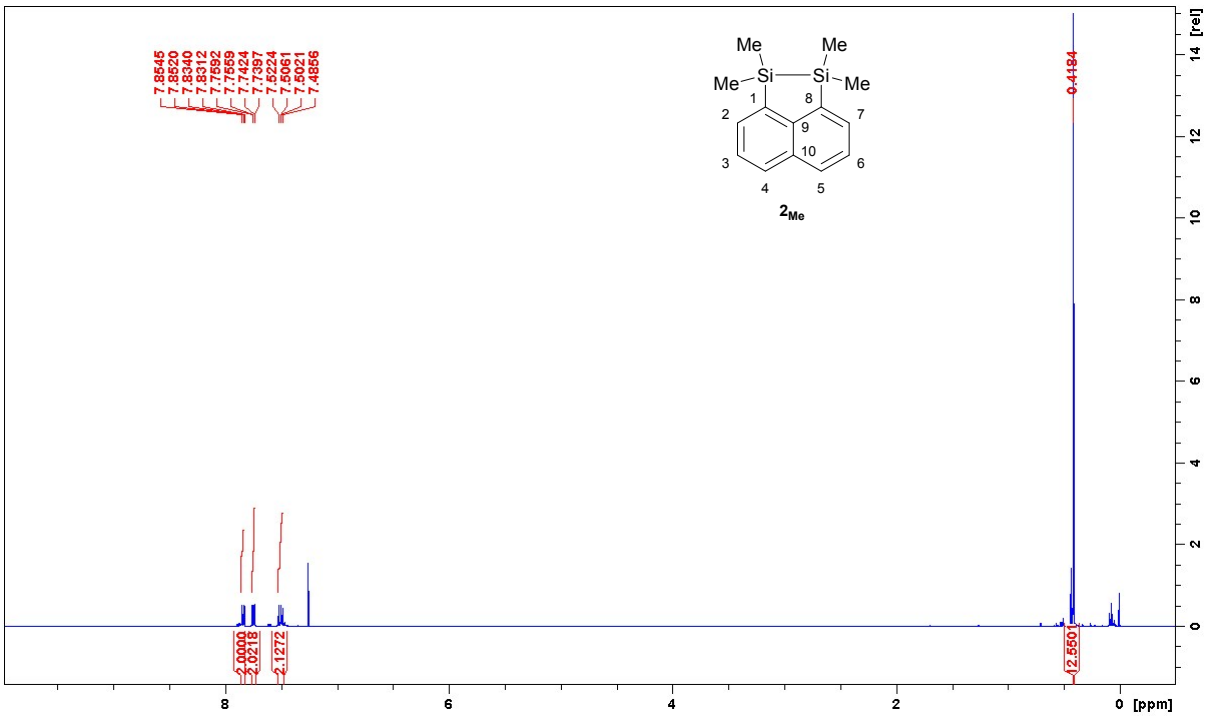

Figure S19- ^{1}H NMR spectrum of $\mathbf{2_{Me}}$ in $CDCl_3$ (residual grease at 0.07 ppm, TMS at 0.0 ppm)

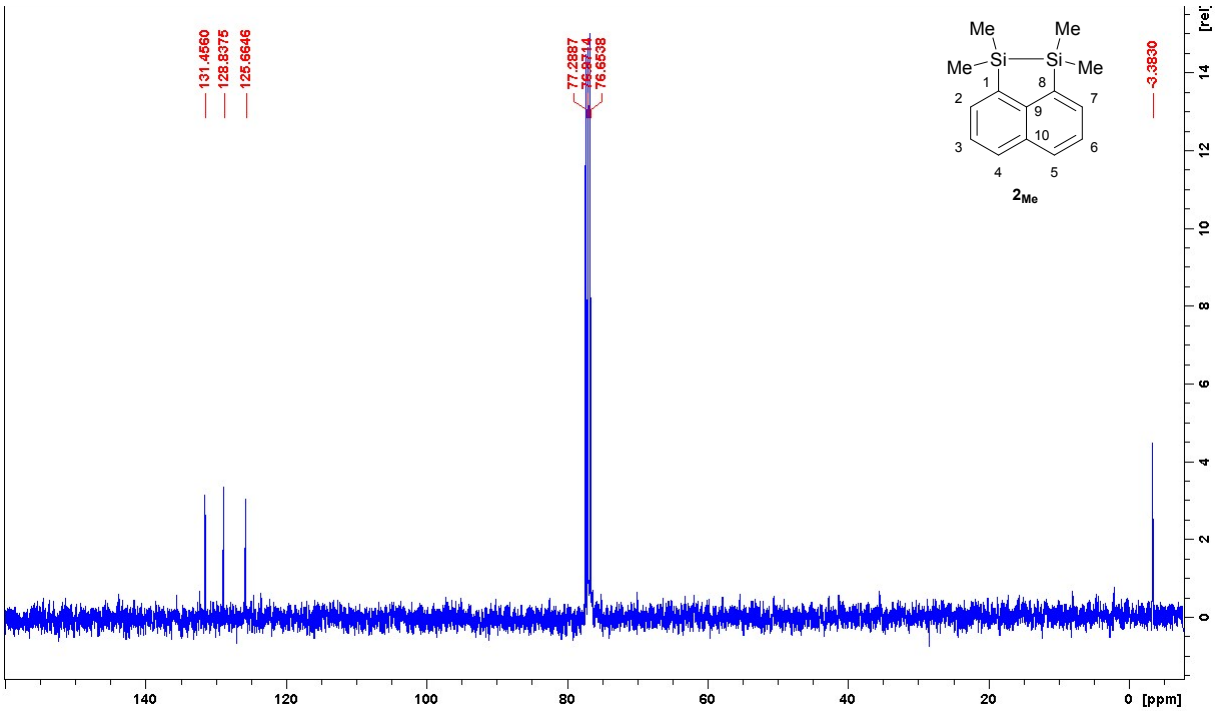

Figure S20- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2_{Me}}$ in $CDCl_3$

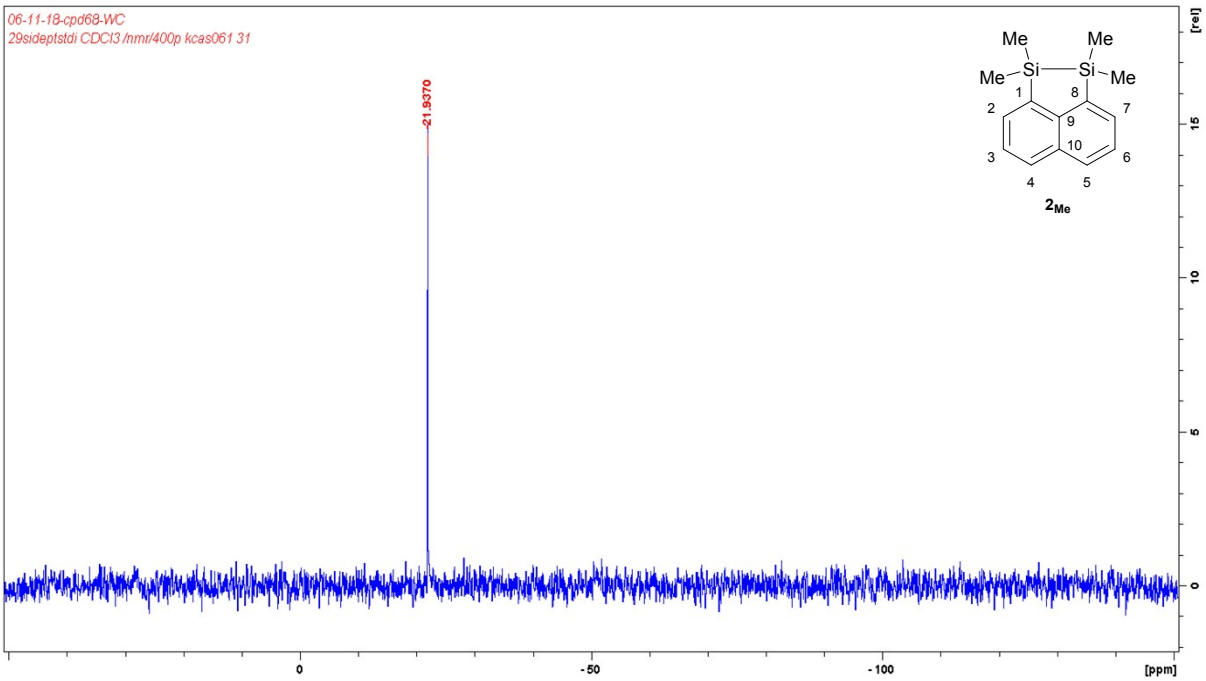

Figure S21- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{2_{Me}}$ in $CDCl_3$

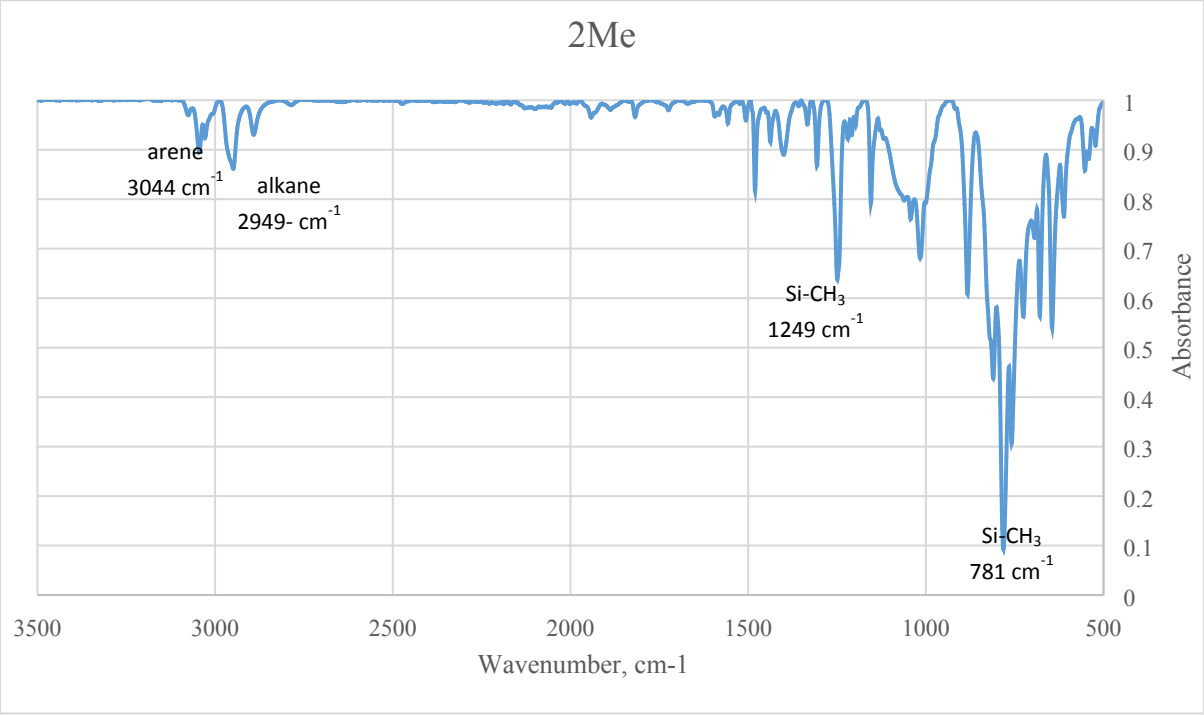

Figure S22- Infrared spectrum of $\mathbf{2_{Me}}$

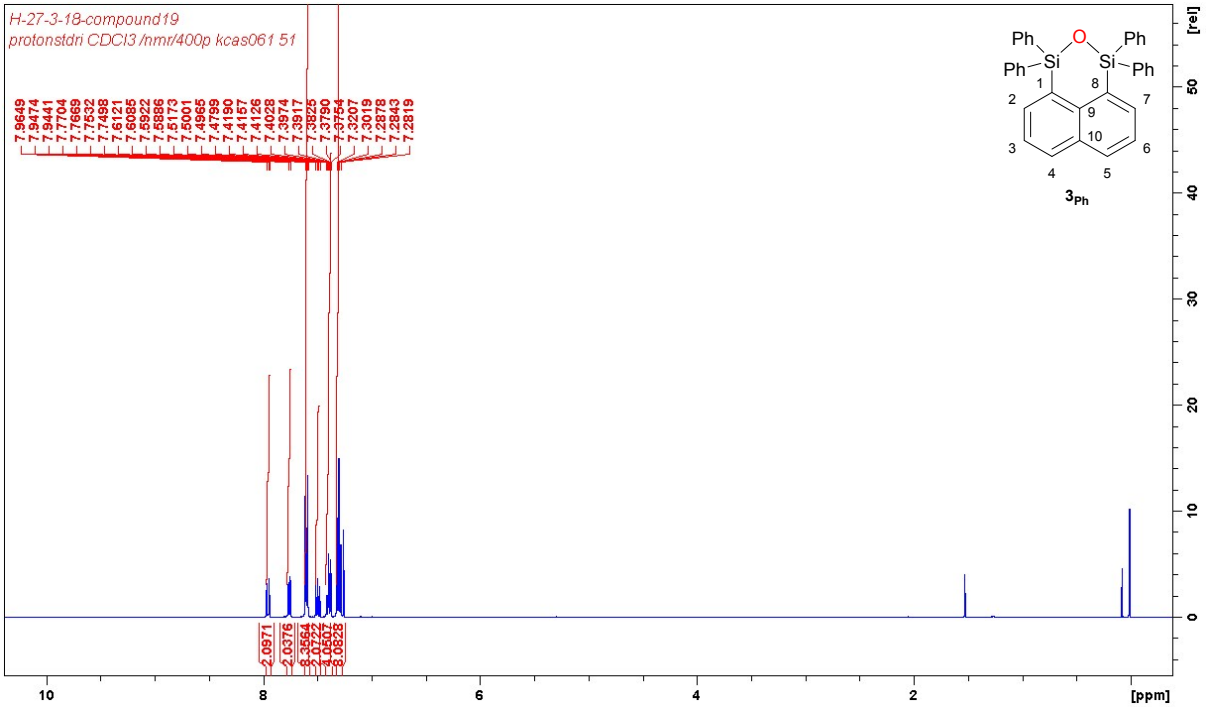

Figure S23- ^{1}H NMR spectrum of $\mathbf{3_{Ph}}$ in $CDCl_3$ (H_2O at 1.5 ppm, residual grease at 0.07 ppm, TMS at 0.0 ppm)

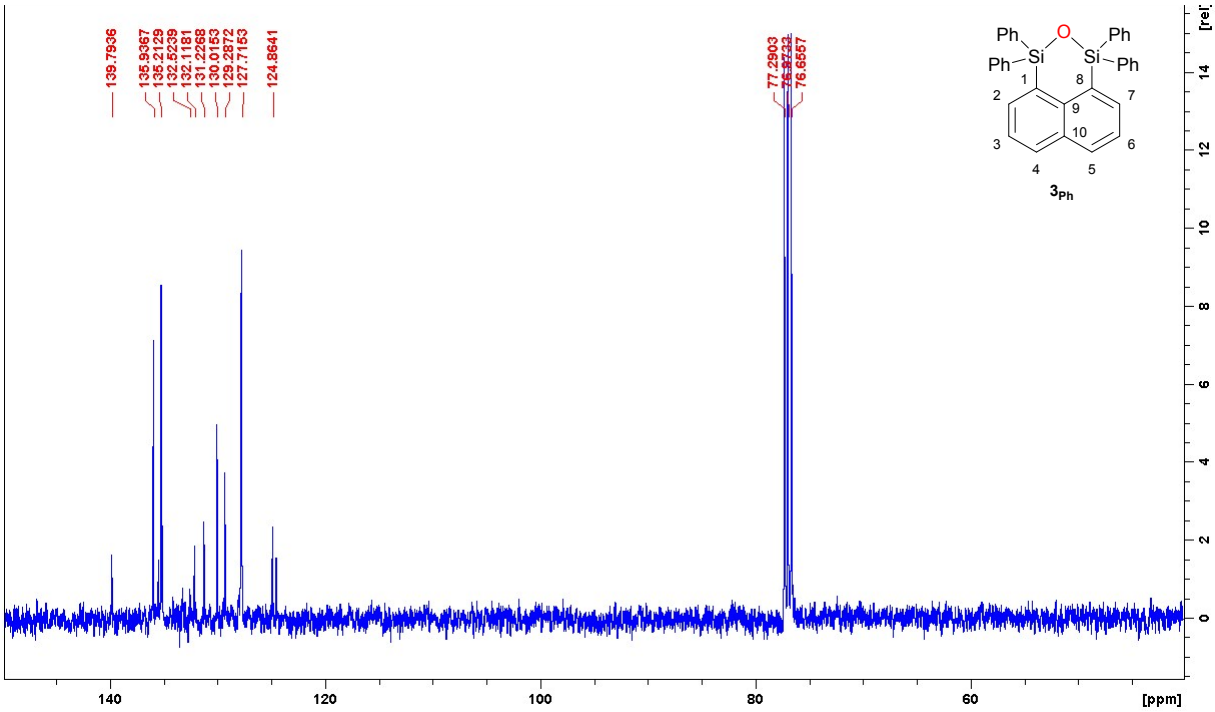

Figure S24- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3_{Ph}}$ in $CDCl_3$

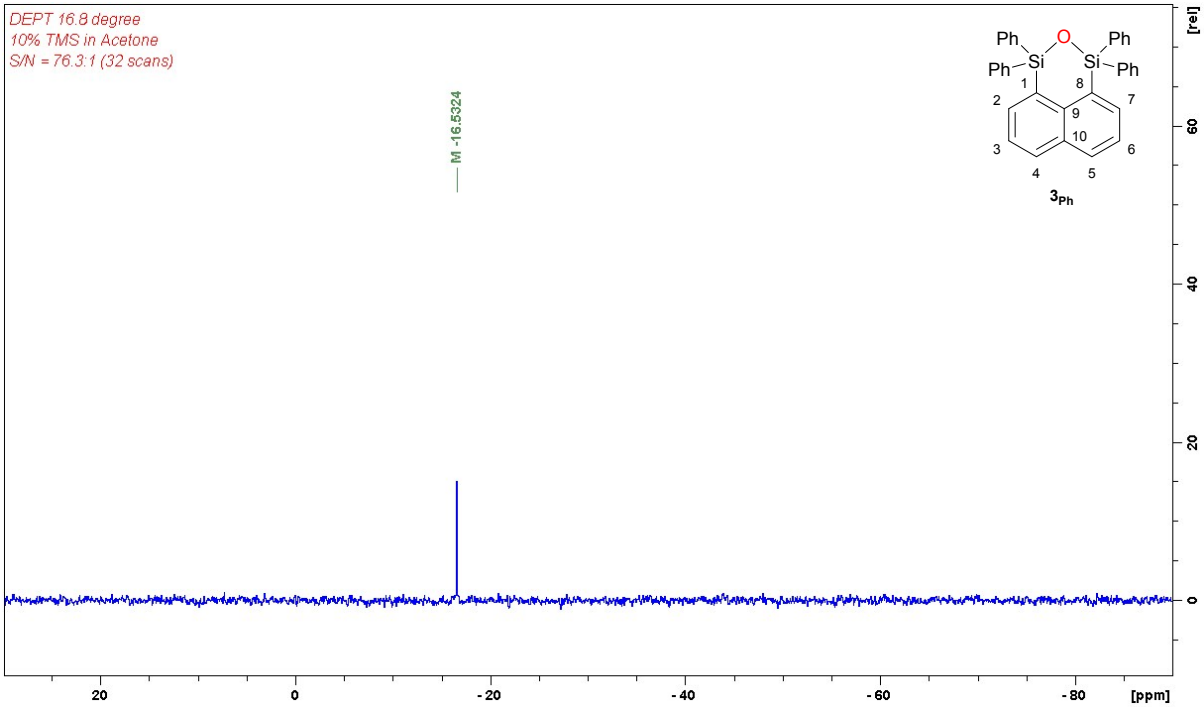

Figure S25- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{3_{Ph}}$ in $CDCl_3$

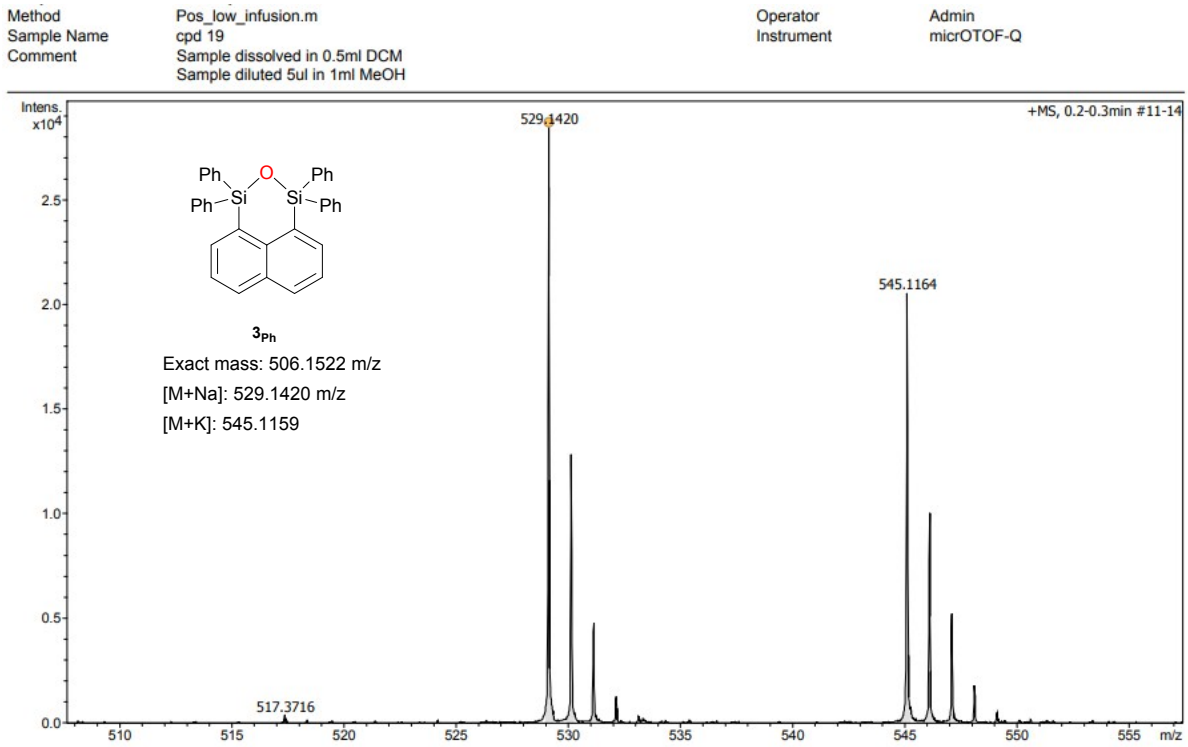

Figure S26- MS-ESI spectrum of $\mathbf{3_{Ph}}$

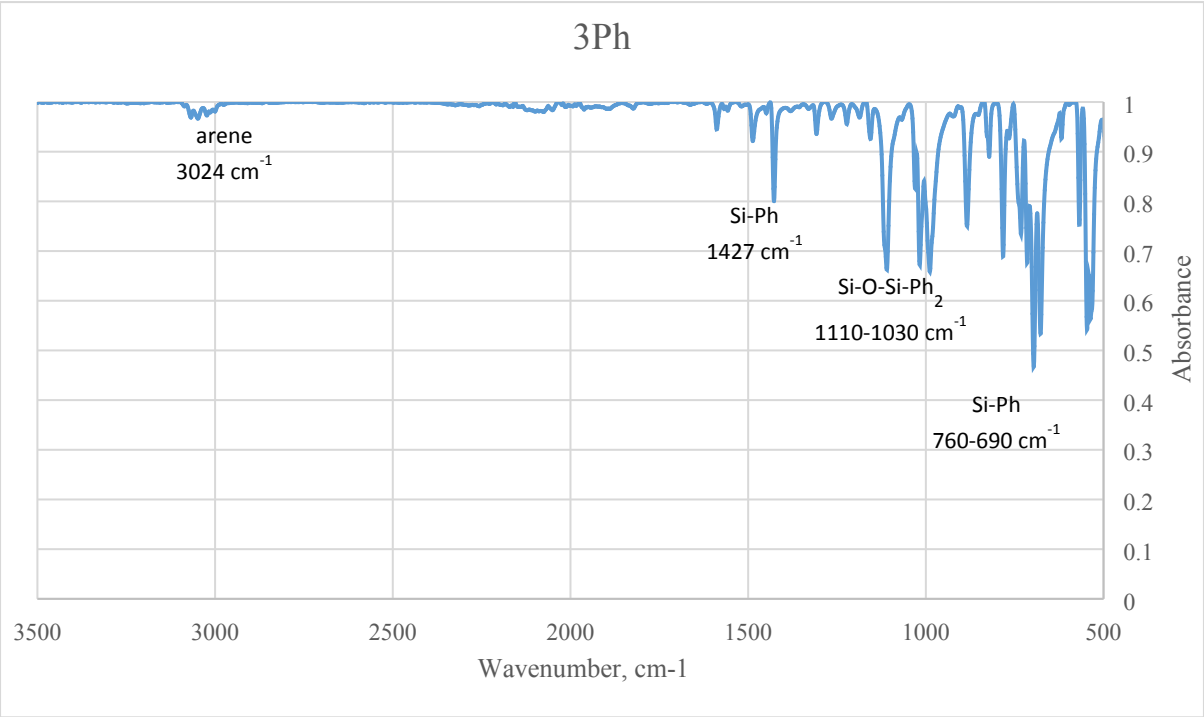

Figure S27- Infrared spectrum of $\mathbf{3_{Ph}}$

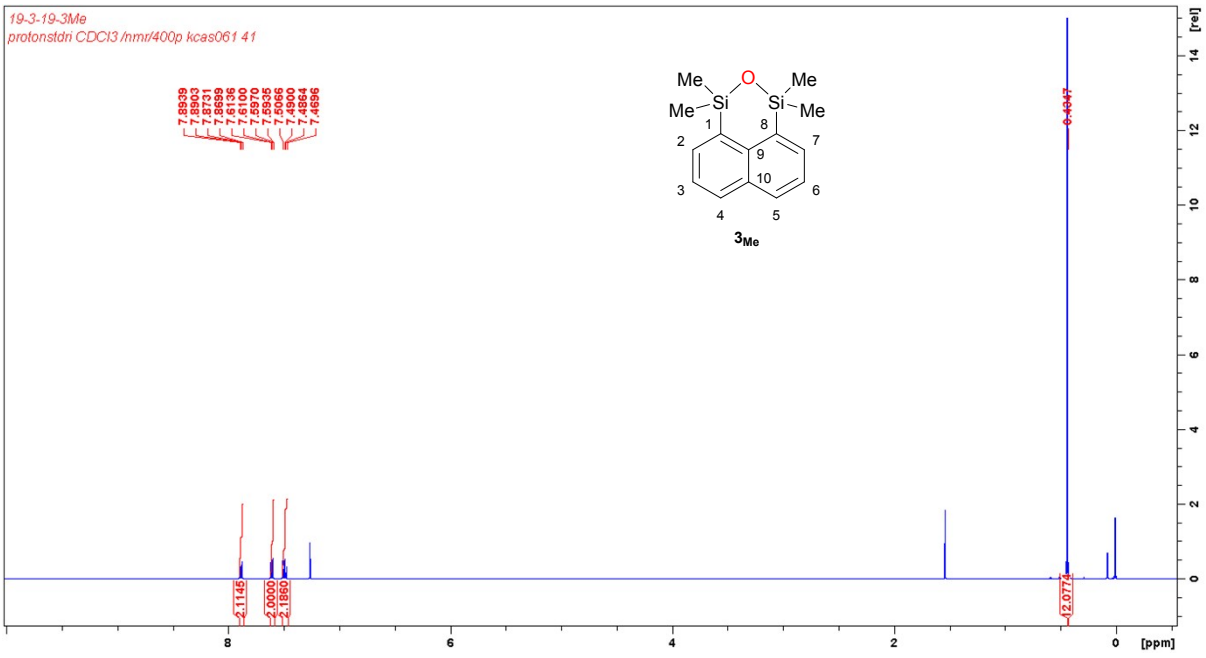

Figure S28- ^{1}H NMR spectrum of $\mathbf{3_{Me}}$ in $CDCl_3$

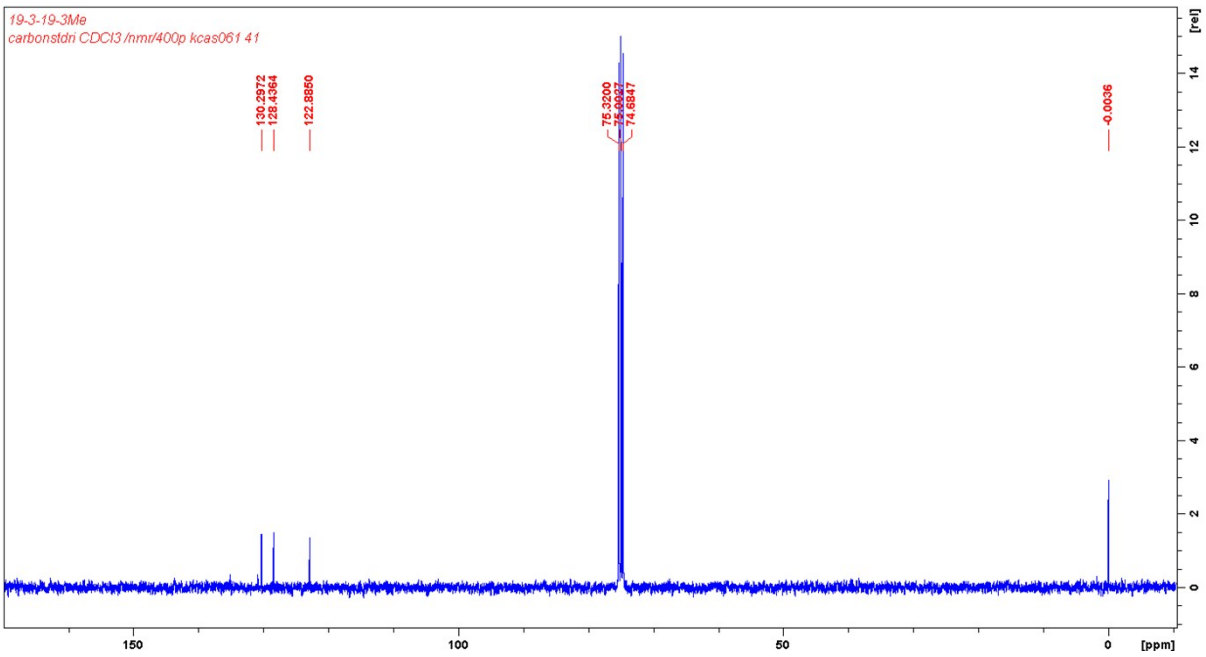

Figure S29- $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3_{Me}}$ in $CDCl_3$

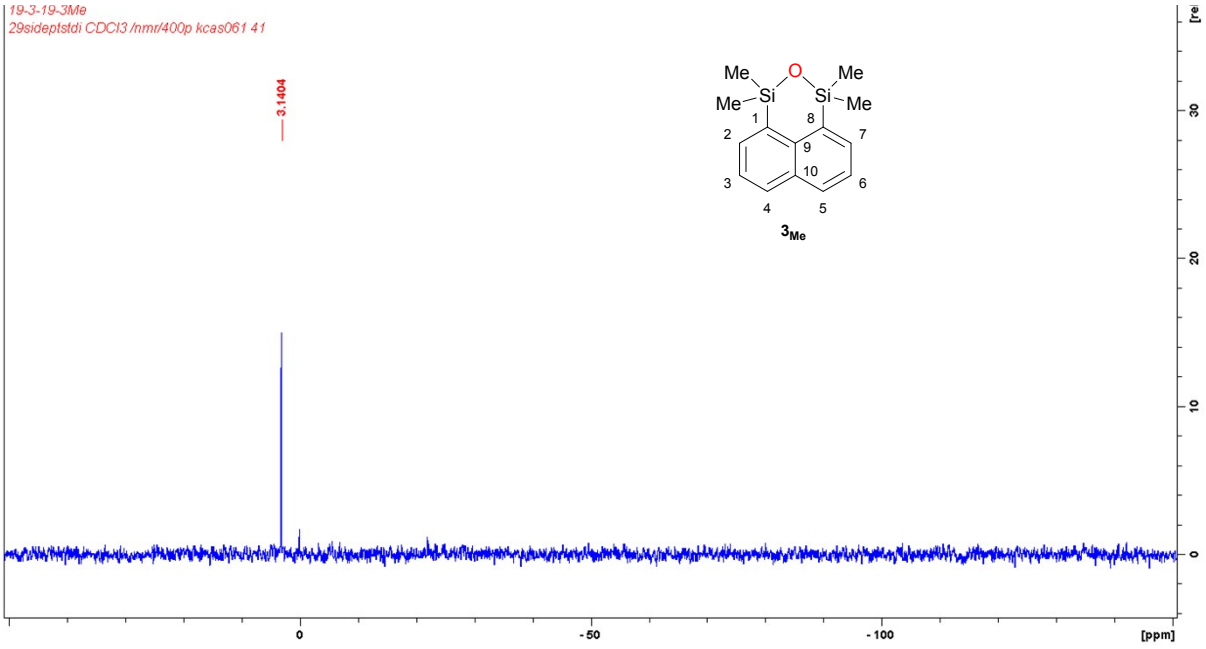

Figure S30- $^{29}Si\{^{1}H\}$ NMR spectrum of $\mathbf{3_{Me}}$ in $CDCl_3$

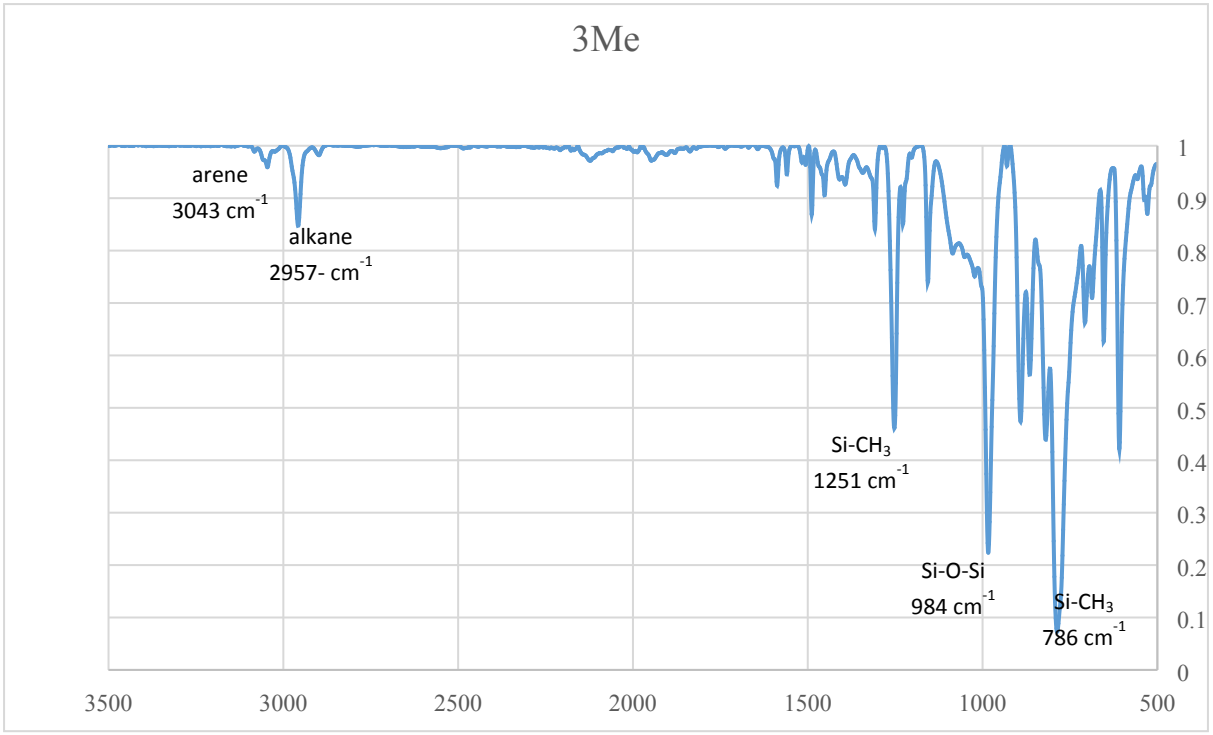

Figure S31- Infrared spectrum of $\mathbf{3_{Me}}$

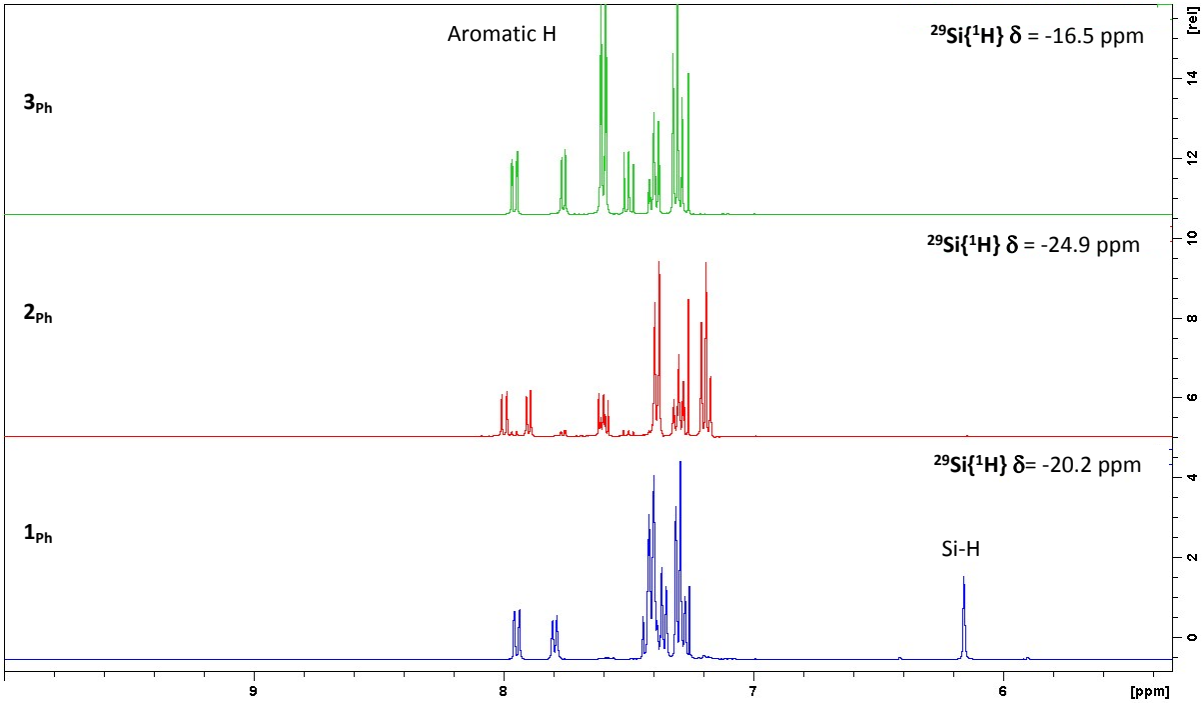

Figure S32- ^{1}H NMR spectra of $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$ and $\mathbf{3_{Ph}}$ in $CDCl_3$

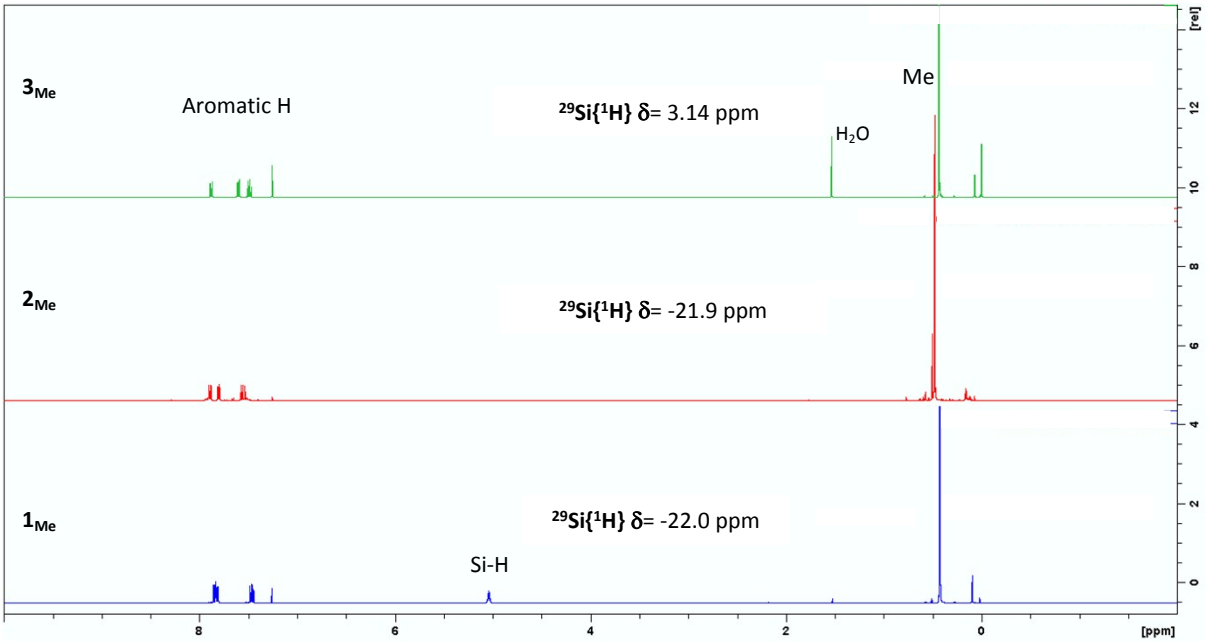

Figure S33- ^{1}H NMR spectra of $\mathbf{1_{Me}}$, $\mathbf{2_{Me}}$ **and** $\mathbf{3_{Me}}$ in $CDCl_3$

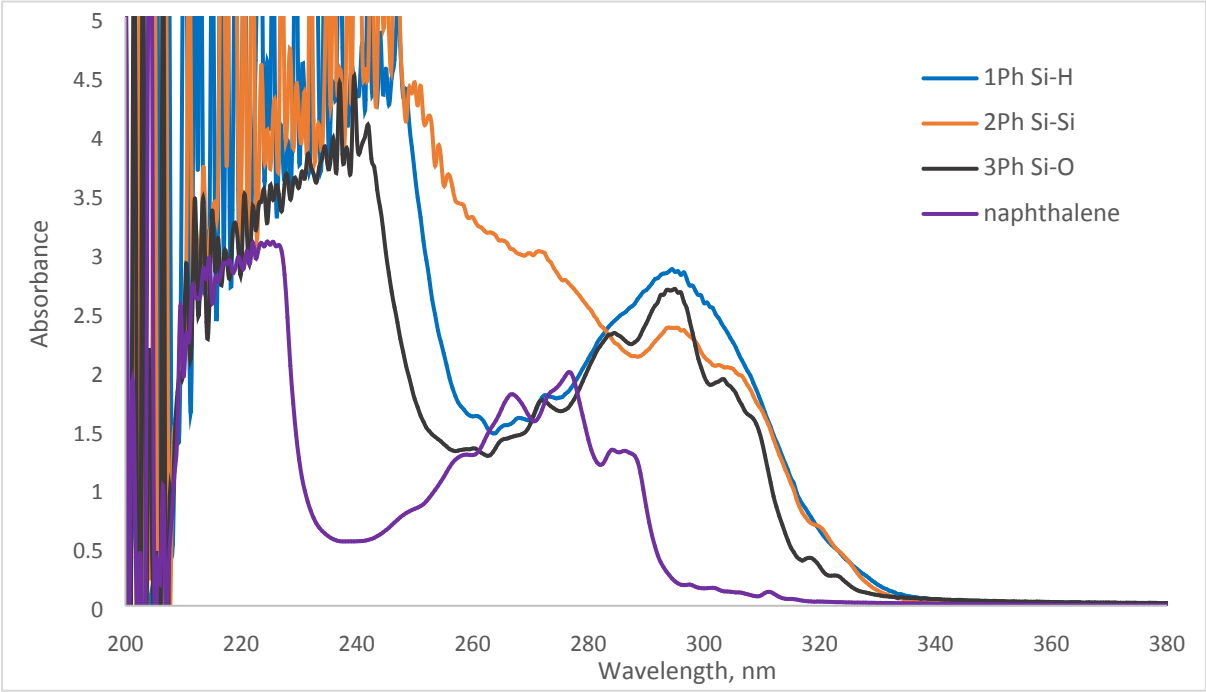

Figure S34- UV-Vis spectra of $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$ **and** $\mathbf{3_{Ph}}$ in THF (0.33 mM)

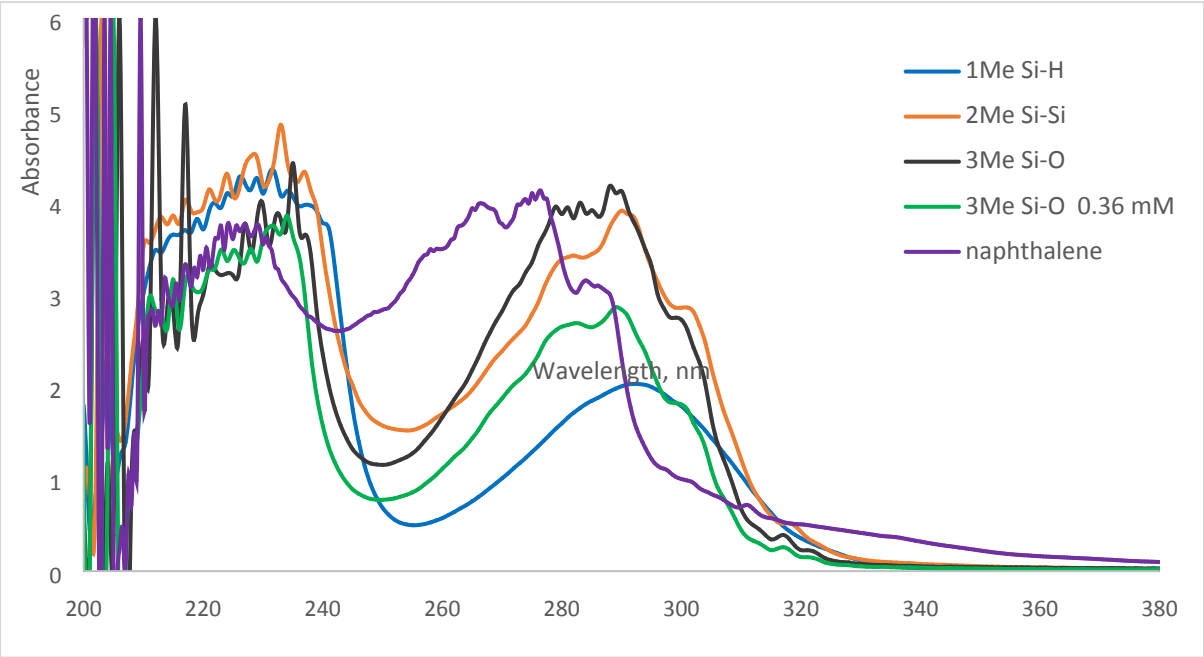

Figure S35- UV-Vis spectra of **1_{Me}, 2_{Me} and 3_{Me}** in THF (0.50 mM)

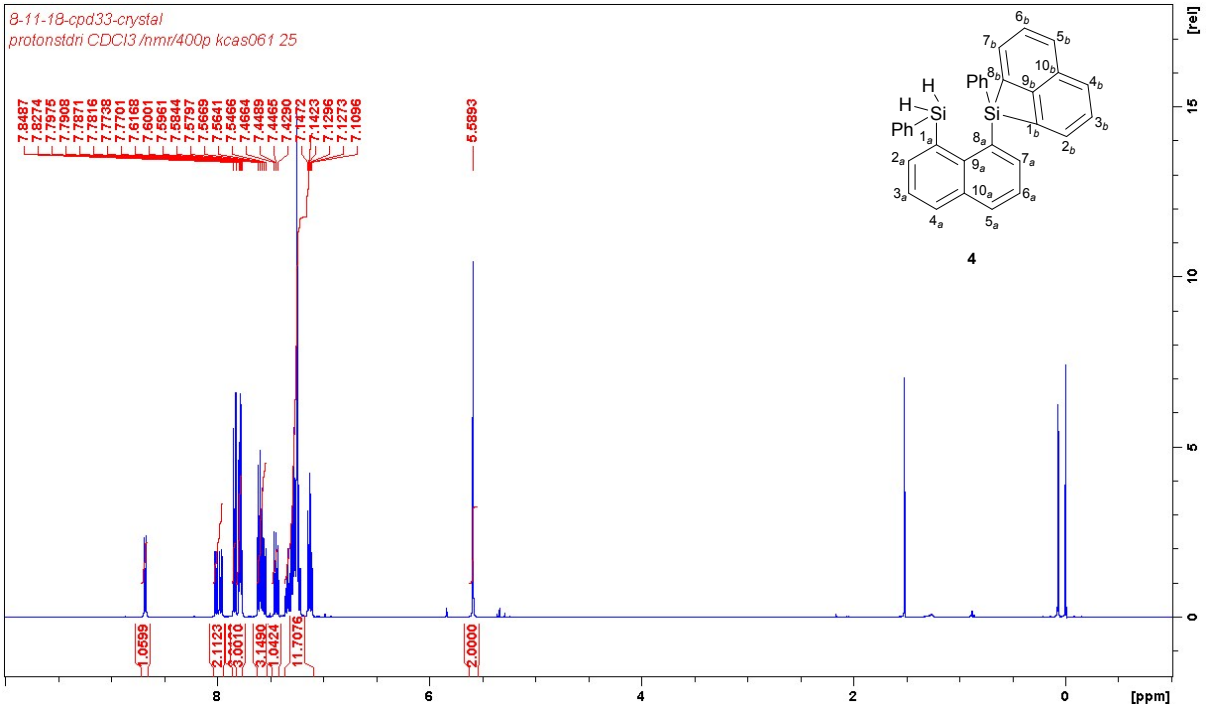

Figure S36- ^{1}H NMR spectrum of **4** in $CDCl_3$ (H_2O at 1.5 ppm, residual grease at 0.07 ppm, TMS at 0.0 ppm)

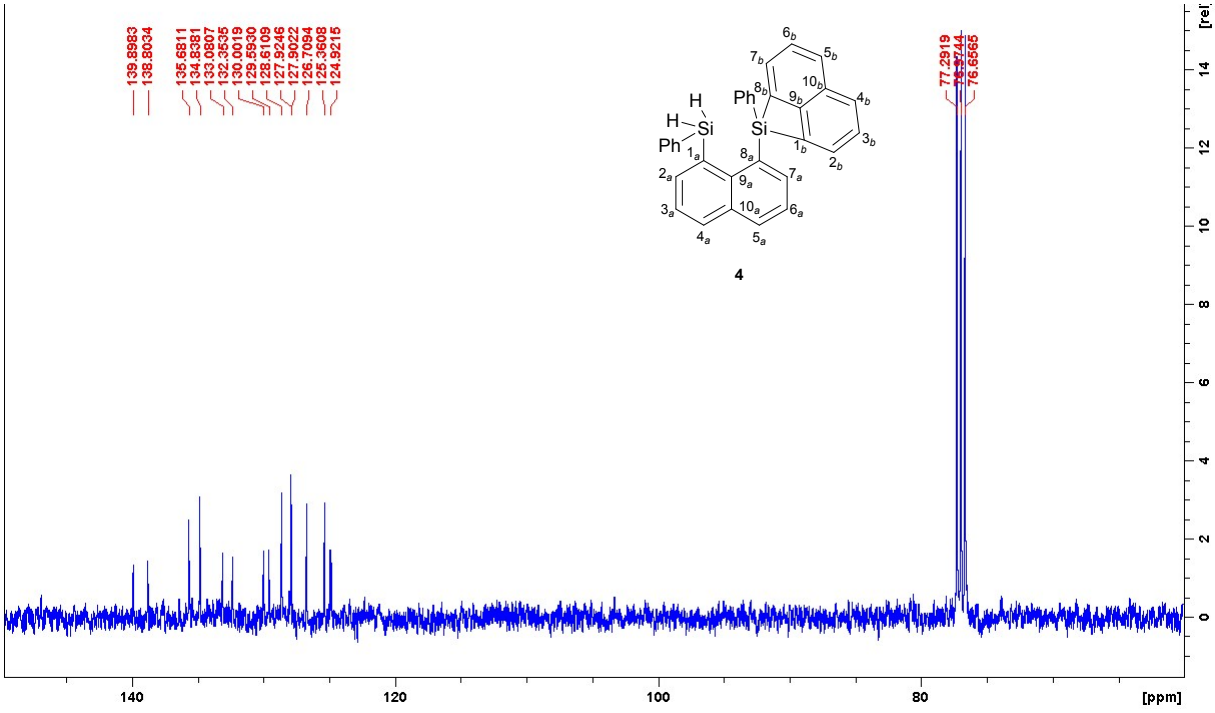

Figure S37- $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$

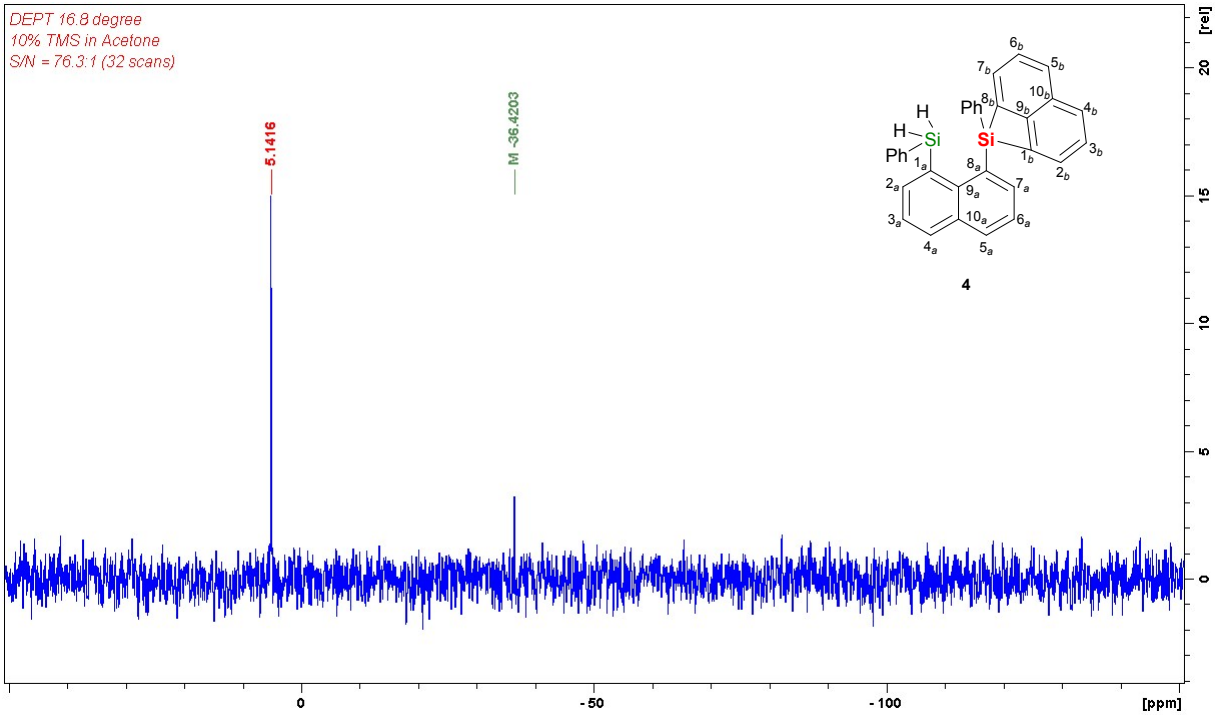

Figure S38-$^{29}Si\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$

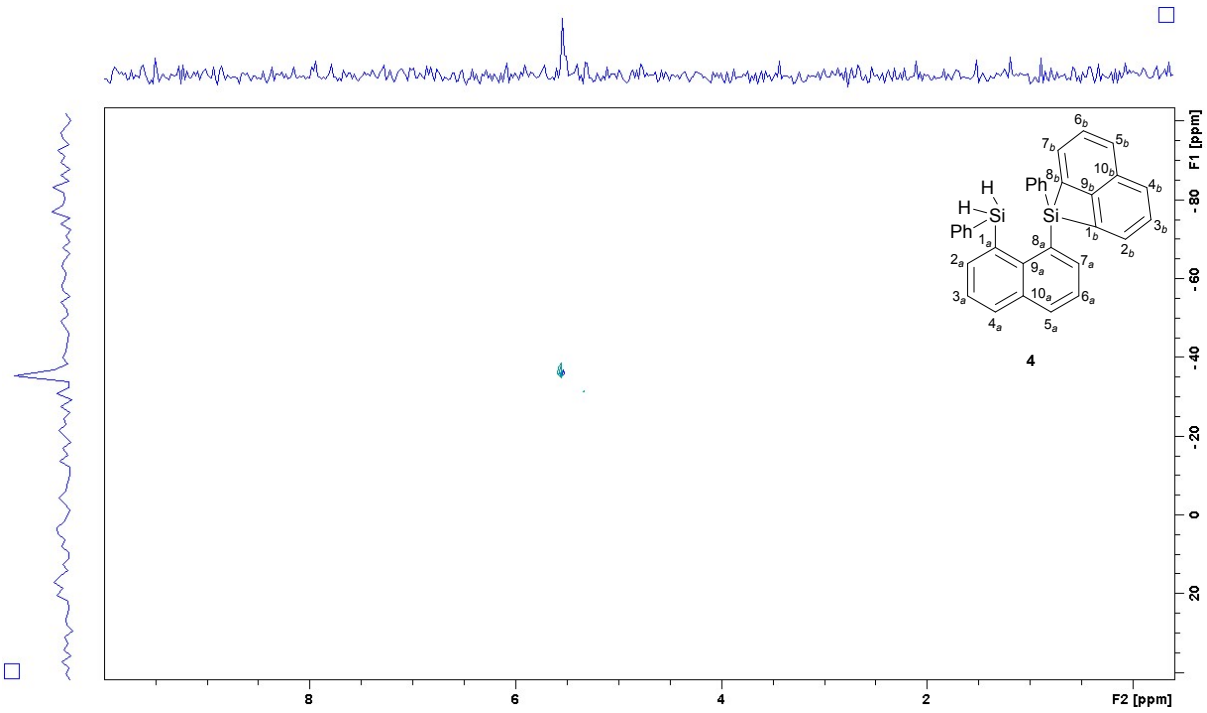

Figure S39- $^{29}Si\{^{1}H\}$ NMR (2D-HSQC) spectrum of **4** in $CDCl_3$

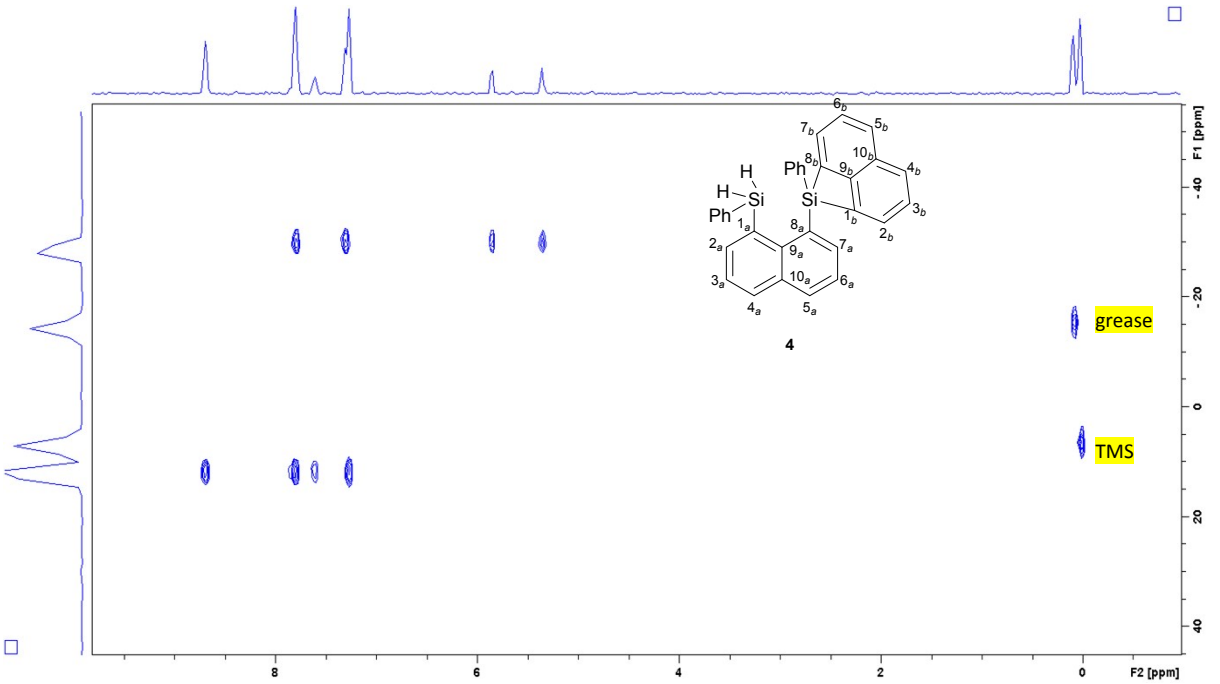

Figure S40- $^{29}Si\{^{1}H\}$ NMR (2D-HMBC) spectrum of **4** in $CDCl_3$

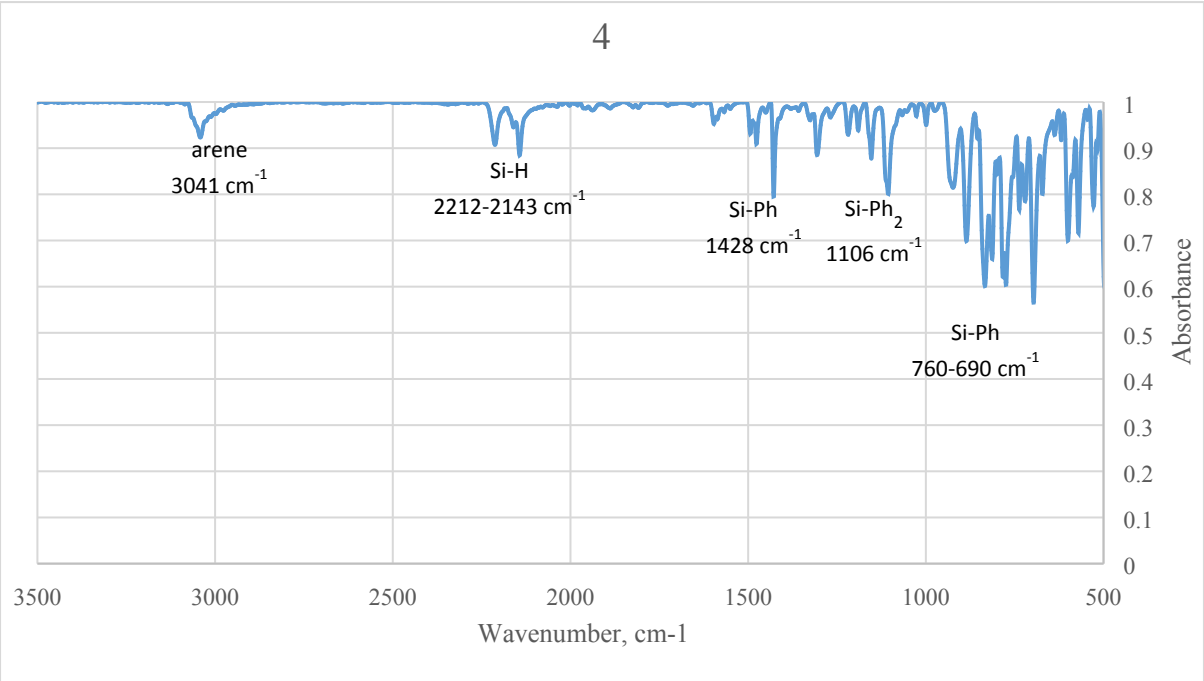

Figure S41- Infrared spectrum of **4**

(ii) Crystallographic Information

Table S1. Structural factors from datablock shelx for compounds $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$, $\mathbf{2_{Me}}$, $\mathbf{3_{Ph}}$, $\mathbf{3_{Me}}$ and **4**

Compound	$\mathbf{1_{Ph}}$	$\mathbf{2_{Ph}}$	$\mathbf{2_{Me}}$	$\mathbf{3_{Ph}}$	$\mathbf{3_{Me}}$	**4**
CCDC	1886586	1886587	1937006	1886595	1937007	1886596
Chemical Formula	$C_{34}H_{28}Si_2$	$C_{34.1}H_{26}O_{0.1}Si_2$	$C_{14}H_{18}O_{0.1}Si_2$	$C_{34}H_{26}OSi_2$	$C_{14}H_{18}OSi_2$	$C_{32}H_{24}Si_2$
M (g mol^{-1})	492.74	493.60	243.98	506.73	258.46	464.69
Temperature (K)	100(1)	110(1)	99.97(13)	100(1)	101(2)	100(1)
Crystal size (mm)	0.32 × 0.2 × 0.2	0.14 × 0.05 × 0.05	0.2 × 0.15 × 0.1	0.34 × 0.14 × 0.12	0.15 × 0.12 × 0.1	0.14 × 0.12 × 0.1
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$I2/a$	P-1	P-1
a (Å)	11.9187(1)	15.6489(3)	8.35819(19)	20.0464(2)	12.20007(13)	7.9022(1)
b (Å)	12.6618(1)	8.81950(10)	8.27537(16)	8.7971(1)	12.30177(13)	9.3800(1)
c (Å)	17.4771(2)	19.3548(3)	19.9683(4)	44.8873(6)	12.38995(13)	16.7481(1)
α (º)	90	90	90	90	116.7870(10)	105.275(1)
β (º)	93.383(1)	106.959(2)	94.0488(19)	95.644(1)	96.6352(9)	90.621(1)
γ (º)	90	90	90	90	112.9004(10)	96.144(1)
V (A^3)	2632.91(4)	2555.10(7)	1377.70(5)	7877.51(16)	1430.24(3)	1189.69(2)
Z	4	4	4	12	4	2
ρ_{calc} (mg m^{-3})	1.243	1.283	1.176	1.282	1.200	1.297
μ (mm^{-1})	1.370	1.417	2.102	1.419	2.102	1.485
F (000)	1040	1038	523	3192	552	488
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
Θ range (deg)	11.198 to 135.47	11.112 to 135.47	8.88 to 148.392	11.298 to 136.49	13.088 to 136.456	11.272 to 136.49
h range	-11≤ h ≤ 14	-17 ≤ h ≤ 18	-10 ≤ h ≤ 10	-12 ≤ h ≤ 12	-14 ≤ h ≤ 14	-9 ≤ h ≤ 9
k range	-15 ≤ k ≤ 15	-9 ≤ k ≤ 10	-10 ≤ k ≤ 9	-13 ≤ k ≤ 11	-14 ≤ k ≤ 14	11 ≤ k ≤ 11
l range	-20 ≤ l ≤ 19	-23 ≤ l ≤ 23	-24 ≤ l ≤ 24	-25 ≤ l ≤ 25	-13 ≤ l ≤ 14	-20 ≤ l ≤ 20
Reflections collected	28300	19186	14649	26277	43511	32410
Data/restraints/ parameters	4763/0/333	4633/6/360	2767/6/205	7144/0/502	5232/0/315	4358/0/315
Independent reflections (R_{int})	4763 (0.0315)	4633 (0.0356)	2767 (0.0326)	7144 (0.0242)	5232 (0.0392)	4358 (0.0391)
R_1, wR_2 (obs., I>=2σ (I))	0.0297, 0.0773	0.0326, 0.0892	0.0296, 0.0734	0.0298, 0.0761	0.0265, 0.0722	0.0299, 0.0788
R_1, wR_2 (all data)	0.0311, 0.0784	0.0354, 0.0914	0.0334, 0.0756	0.0306, 0.0766	0.0287, 0.0735	0.0322, 0.0803
S on F^2	1.042	1.044	1.055	1.038	1.076	1.067

Table S2. Selected metrical parameters for $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$, $\mathbf{2_{Me}}$, $\mathbf{3_{Ph}}$, $\mathbf{3_{Me}}$ and **4.**

Parameter		$\mathbf{1_{Ph}}$	$\mathbf{2_{Ph}}$	$\mathbf{2_{Me}}$	$\mathbf{3_{Ph}}$*	$\mathbf{3_{Me}}$*	**4**
Si-naph /Å	Si1-C13 or Si1-C5[a] or Si3-C27[b]	1.8864(13)	1.8717(17)	1.8817(16)[a]	1.8747(13) 1.8730(13)	1.8800(14)[a] 1.8738(13)[b]	1.8798(14)
	Si2-C22 or Si2-C13[c] or Si4-C19[d]	1.8916(13)	1.8793(16)	1.8745(15)[c]	1.8732(13) 1.8730(13)	1.8716(13)[c] 1.8747(13)[d]	1.8796(14)
	Si2-C23	-	-	-	-	-	1.8940(14)
	Si2-C32	-	-	-	-	-	1.9096(14)
Si-E /Å	Si1-Si2	3.419(6)	2.3512(13)	2.329(2)	2.9721(7) / 2.9515(14)		3.4809(6)
	C13-C22 or C13-C5[e]	2.5698(17)	2.505(2)	2.501(2)[e]	2.5352(17) / 2.527(3)	2.524(3)[e]	2.561(3)
	C23 – C32	-	-	-	-	-	2.315(3)
	Si1-H	1.365(16)	-	-	-	-	1.379(15)
	Si2-H or Si1-H1B[f]	1.371(16)		-	-	-	1.371(19)[f]
	Si1-O1 / Si2-O1	-	-	-	1.6353(9) / 1.6355(9) 1.6413(6) / 1.6413(6)	1.6384(10) / 1.6336(10) 1.6367(9) / 1.6394(9)	-
Si-E-E /°	Si1-C13-C18	123.36(12)	117.30(10)	116.76(10)	124.57(10) / 123.70(11)	125.34(9) / 124.75(9)	128.85(10)
	Si2-C22-C18	129.35(9)	116.50(10)	117.06(10)	125.49(10) / 123.70(11)	125.24(9) / 125.07(10)	132.08(10)
	C13-Si1-Si2	-	92.15(5)	92.58(6)	83.59(5) / 82.70(5)	-	76.32(5)
	C22-Si2-Si1	-	92.44(5)	92.69(6)	82.99(5) / 82.70(5)	-	74.48(5)
	Si1-O1-Si2	-	-	-	130.65(6) / 128.05(8)	130.31(6) / 129.75(6)	-
	C13-Si1-O1	-	-	-	107.82(5) / 108.44(6)	107.57(5) / 108.15(5)	-
	C22-Si2-O1	-	-	-	107.38(5) / 108.44(6)	108.27(5) / 107.86(5)	-
	C28-C32-Si2	-	-	-	-	-	87.39(9)
	C28-C23-Si2	-	-	-	-	-	88.21(9)
Torsion /°	Si1-C13-C18-C22	12.7(2)	0.54(17)	2.9(4)	3.0(2) / 10.95(6)	4.87(17) / -8.14(18)	15.7(2)
	Si2-C22-C18-C13	17.0(2)	3.80(17)	-1.03(16)	0.2(2) / 10.95(6)	-1.49(17) / -4.65(18)	4.7(2)
	C13-Si1-Si2-C22	17.50(6)	-	-	2.21(6) / 15.68(9)	-	11.86(6)
	C23-C28-C32-Si2	-	-	-	-	-	4.2(1)

*two crystallographically independent molecules; $\mathbf{3_{Ph}}$: molecule 1 has C_1 symmetry, molecule 2 has C_2 symmetry; $\mathbf{3_{Me}}$ both molecules have C_1 symmetry

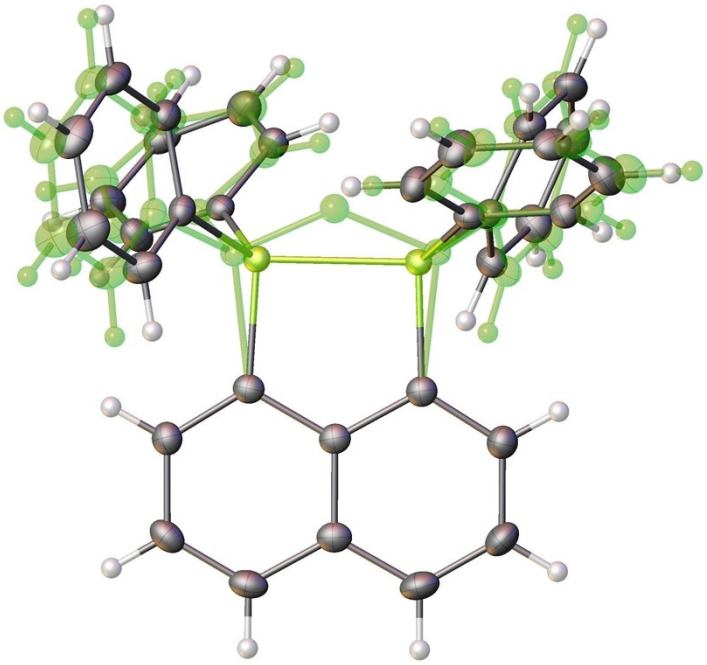

Figure S42- Refined structure of $\mathbf{2}_{\mathbf{Ph}}$ containing co-crystallisation from $\mathbf{3}_{\mathbf{Ph}}$ (10.3(2)%) demonstrating the source of the extra electron density above the Si-Si bond

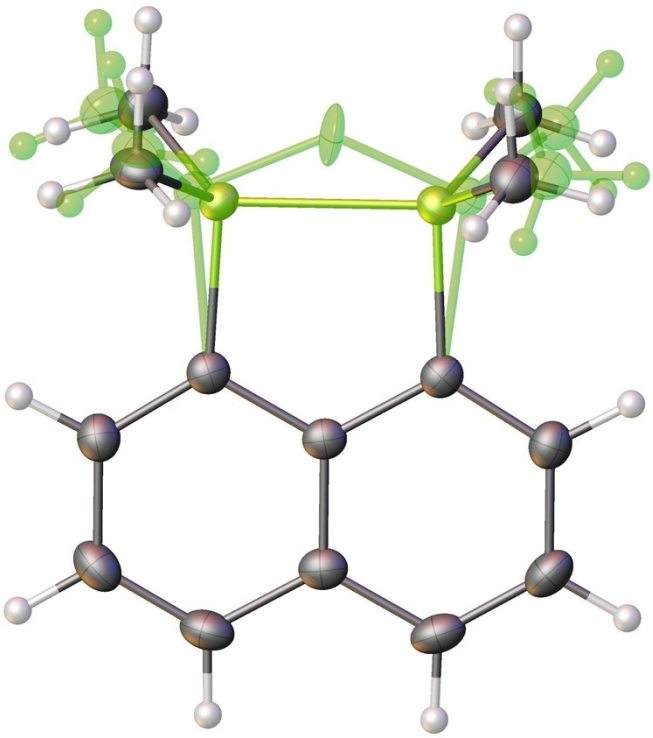

Figure S43- Refined structure of $\mathbf{2}_{\mathbf{Me}}$ containing co-crystallisation from $\mathbf{3}_{\mathbf{Me}}$ (9.4(4)%) demonstrating the source of the extra electron density above the Si-Si bond

(iii) Computational Information

Images of Optimized Geometries and HOMOs:

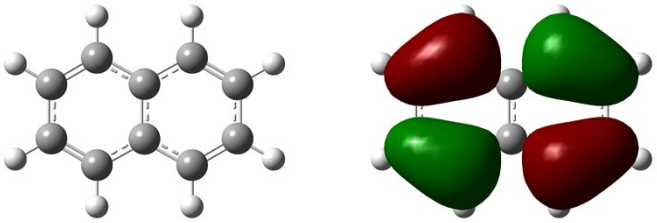

Figure S44- naphthalene

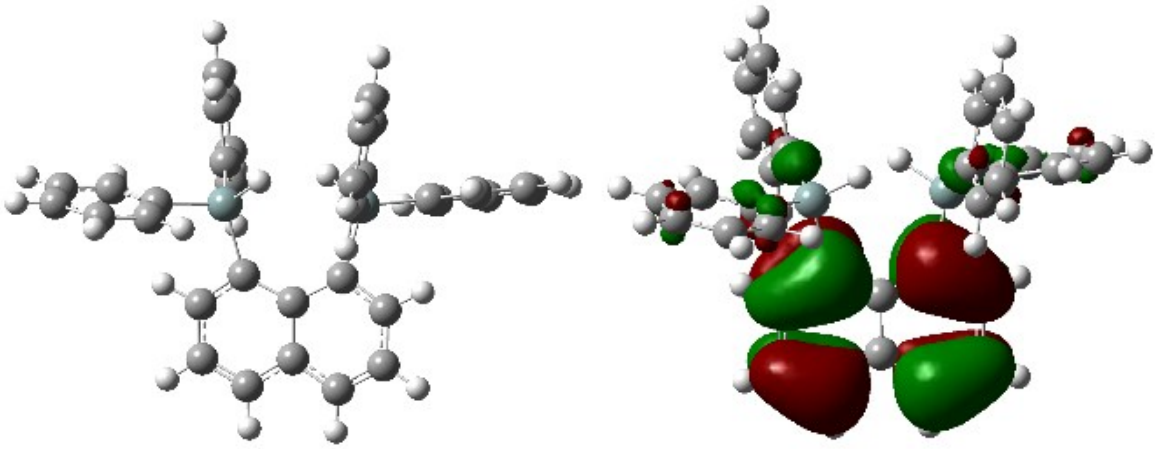

Figure S45- 1_{Ph}

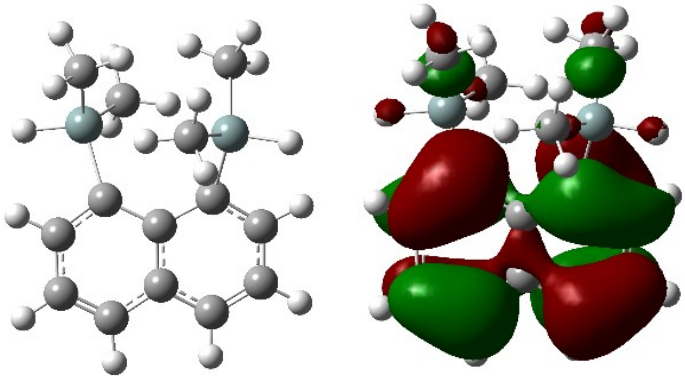

Figure S46- 1_{Me}

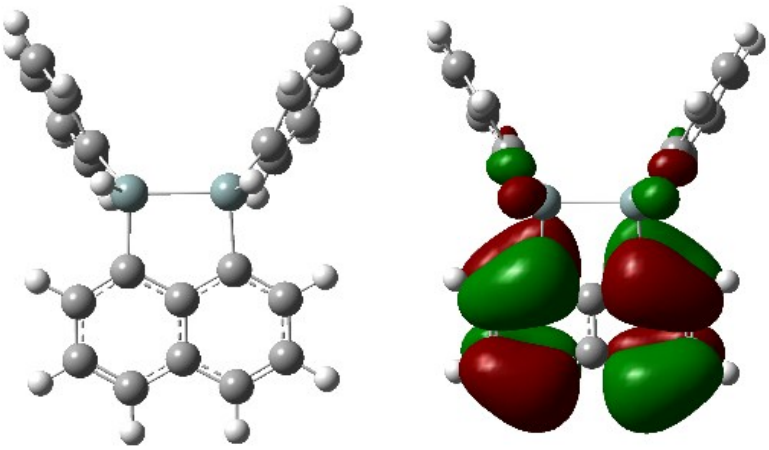

Figure S47- $2_{Ph'}$

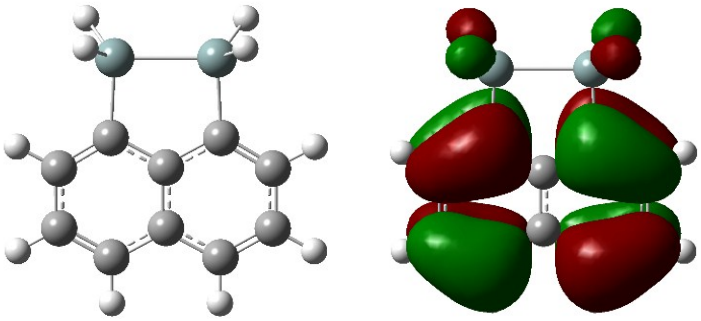

Figure S48- 2_{H}

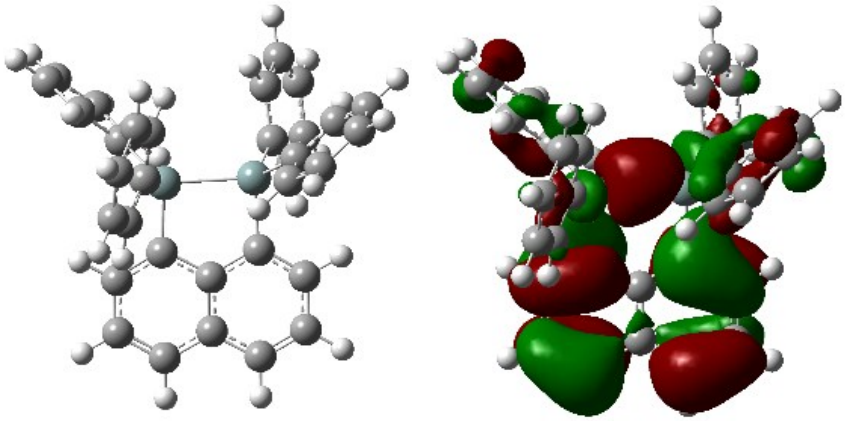

Figure S49- 2_{Ph}

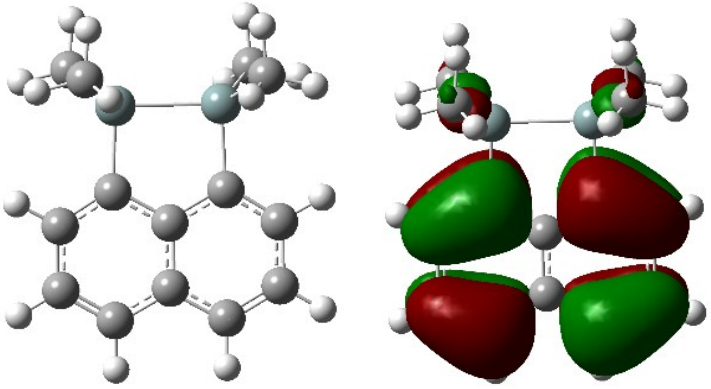

Figure S50- 2_{Me}

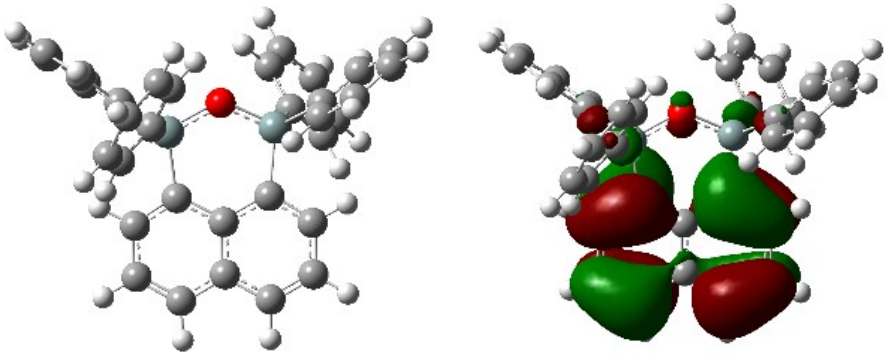

Figure S51- 3_{Ph}

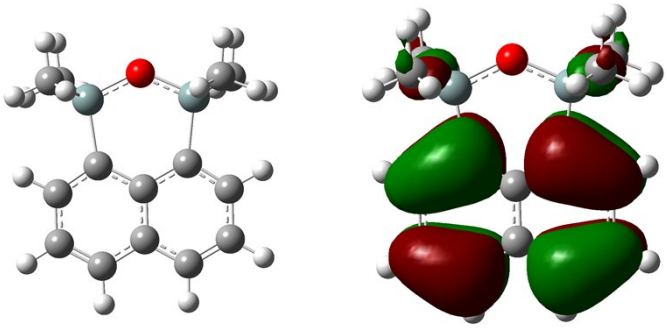

Figure S52- 3_{Me}

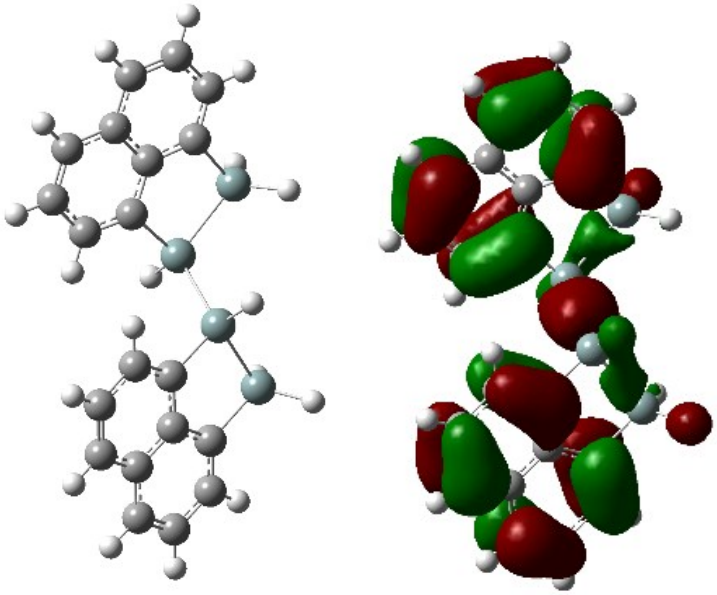

Figure S53- 2_{H}-dimer

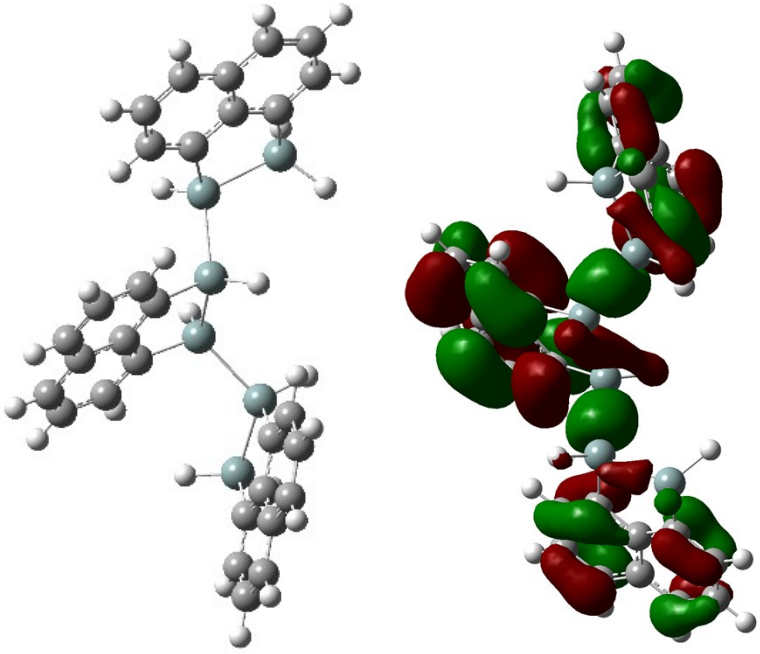

Figure S54- 2_H-trimer

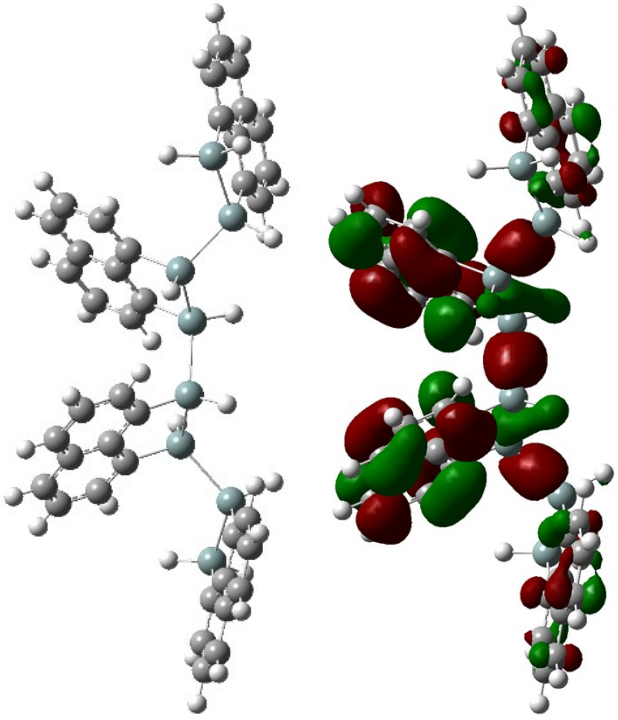

Figure S55- 2_H-tetramer

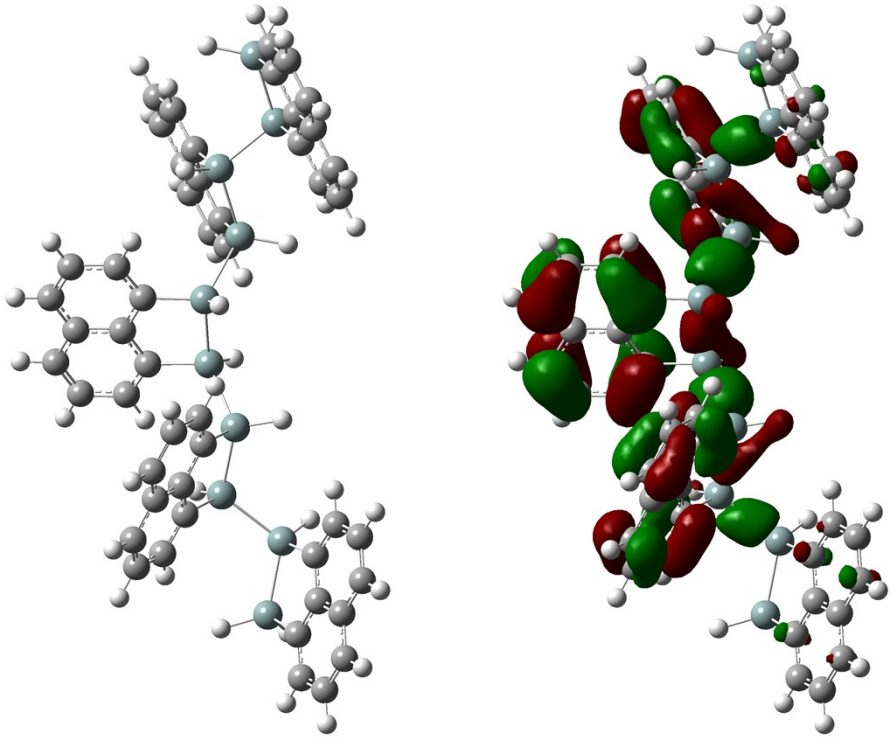

Figure S56- 2_H-pentamer

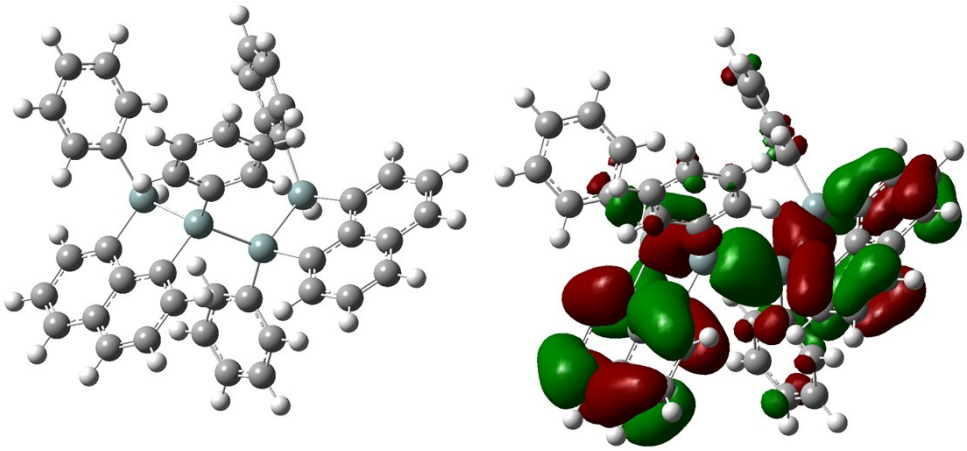

Figure S57- $2_{Ph'}$-dimer

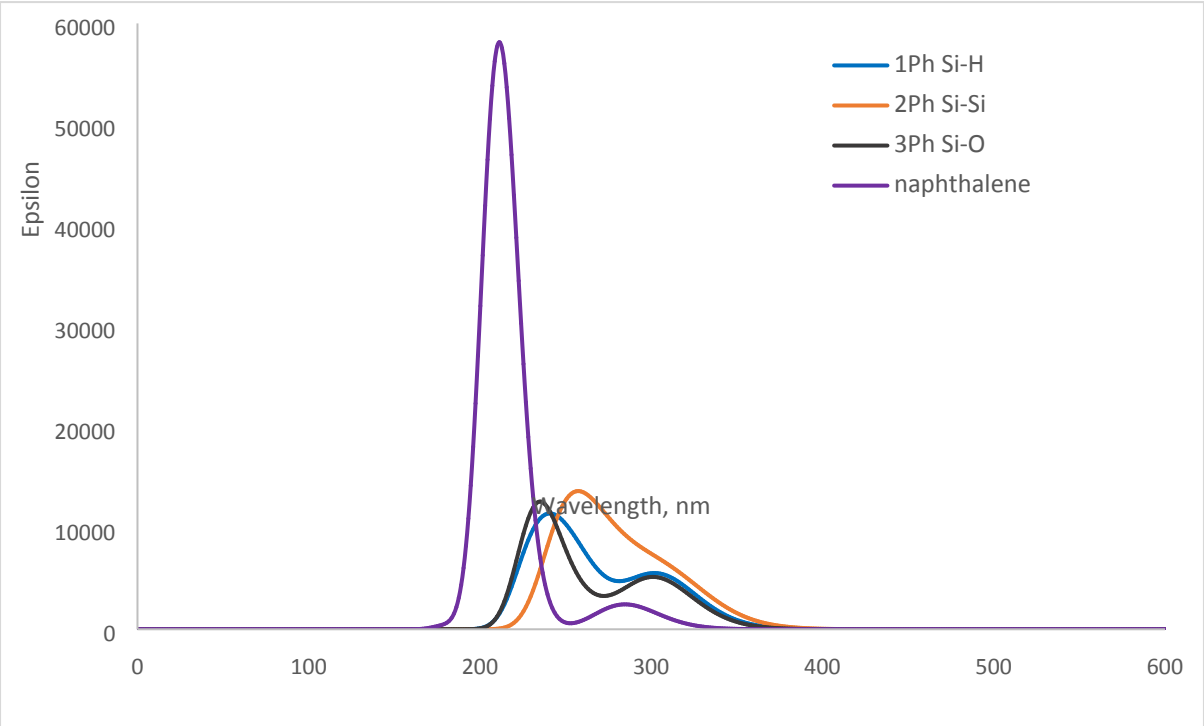

Figure S58- Calculated UV-Vis spectra (gas phase) of $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$ **and** $\mathbf{3_{Ph}}$ using TD-SCF, B3LYP/6-31(++)G**

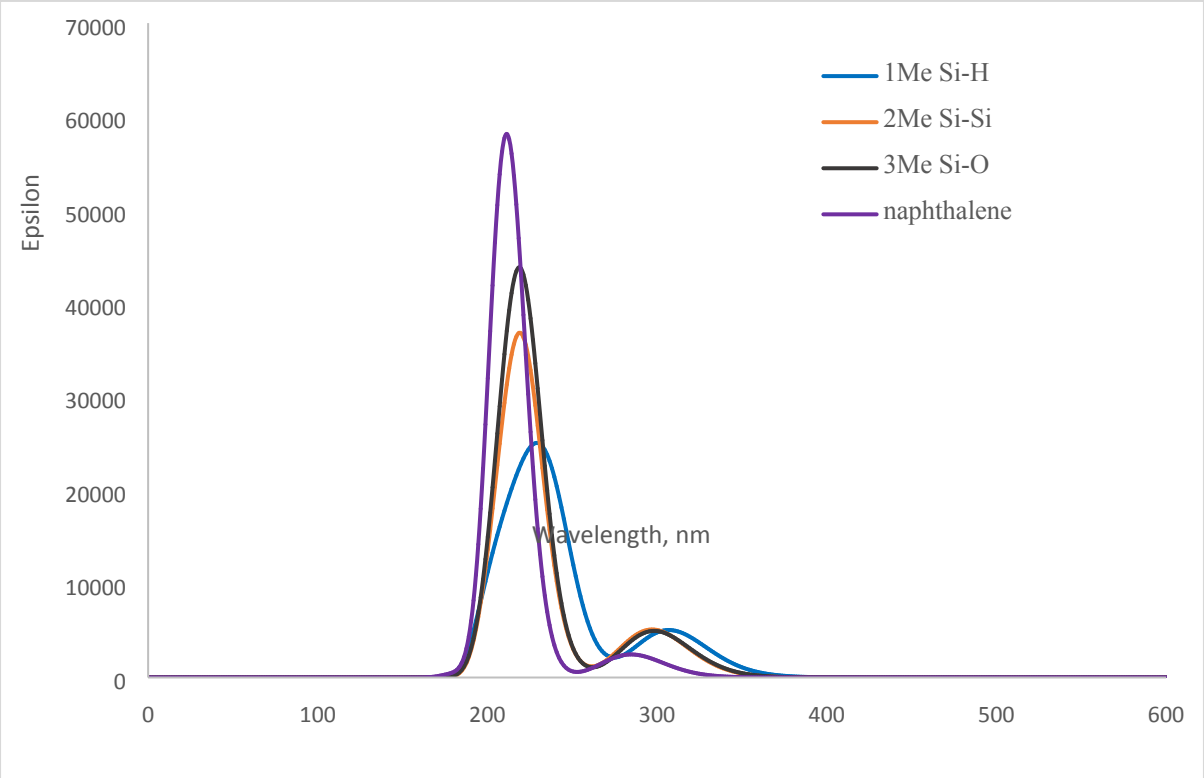

Figure S59- Calculated UV-Vis spectra (gas phase) of $\mathbf{1_{Me}}$, $\mathbf{2_{Me}}$ **and** $\mathbf{3_{Me}}$ using TD-SCF, B3LYP/6-31(++)G**

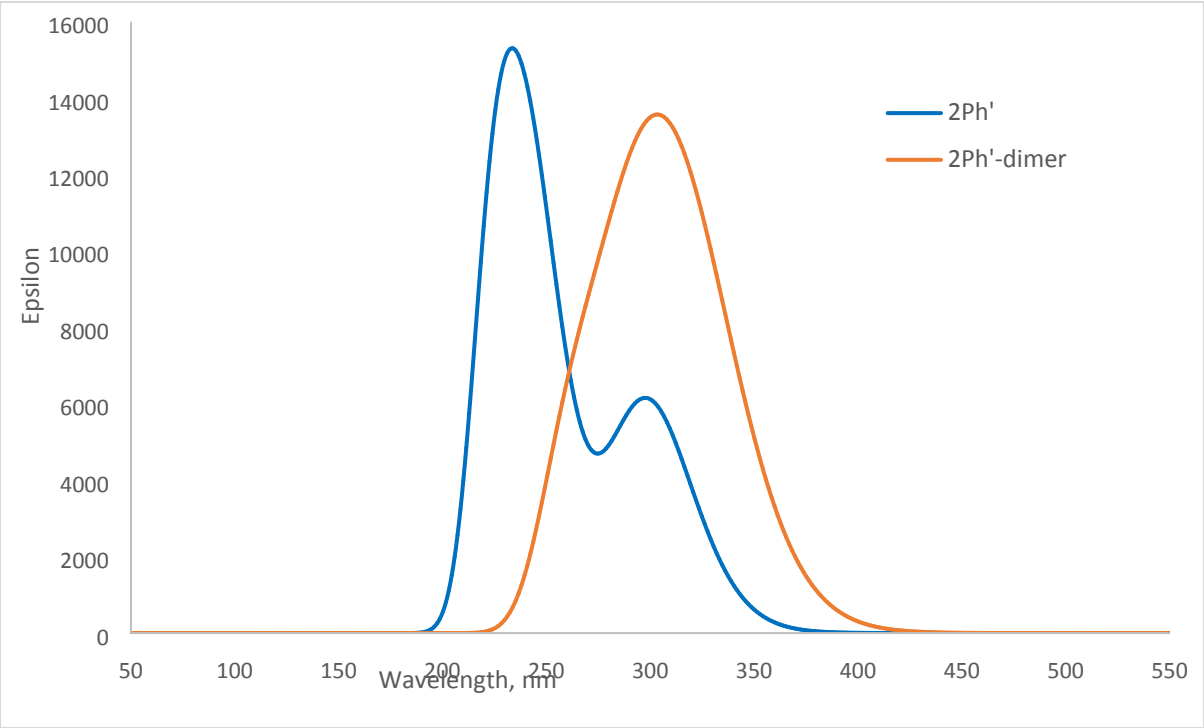

Figure S60- Calculated UV-Vis spectra (gas phase) of **$2_{Ph'}$ and $2_{Ph'}$-dimer** using TD-SCF, B3LYP/6-31(++)G**

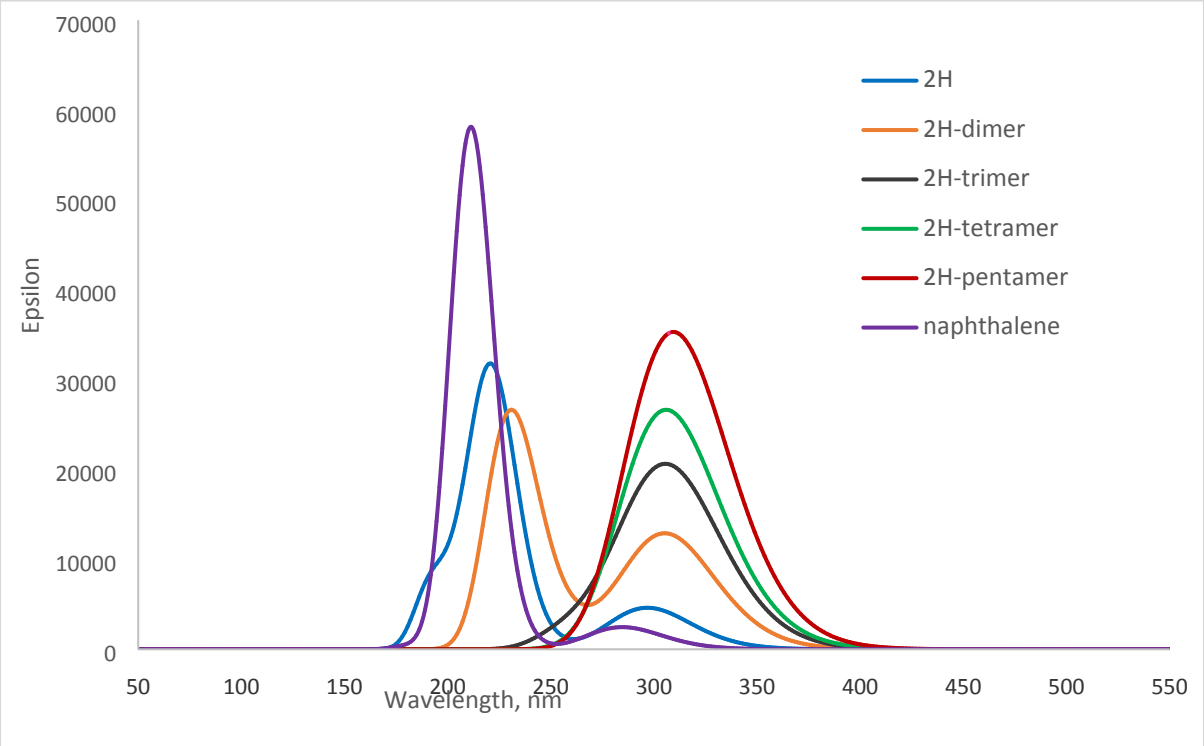

Figure S61- Calculated UV-Vis spectra (gas phase) of **2_H, 2_H-dimer, 2_H-trimer, 2H-tetramer and 2_H-pentamer** using TD-SCF, B3LYP/6-31(++)G**

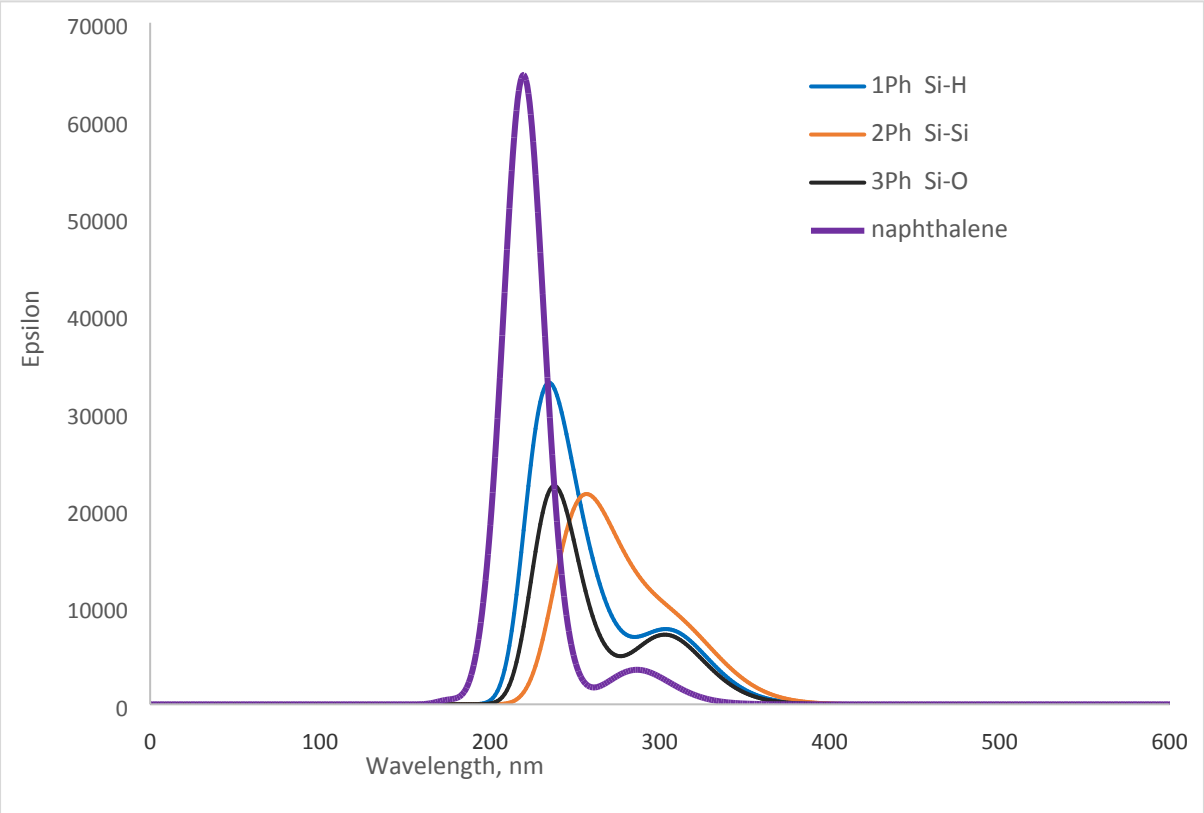

Figure S62- Calculated UV-Vis spectra (in THF) of $\mathbf{1_{Ph}}$, $\mathbf{2_{Ph}}$ **and** $\mathbf{3_{Ph}}$ using TD-SCF, B3LYP/6-31(++)G**

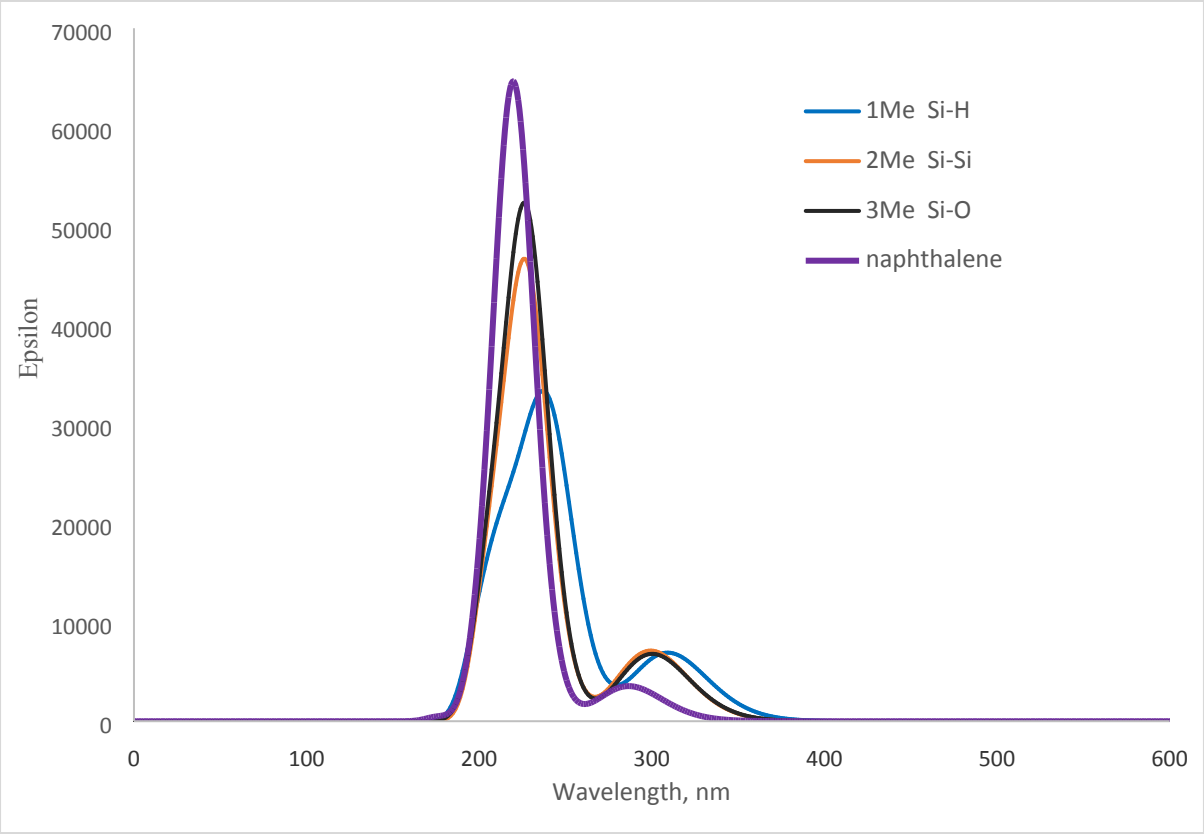

Figure S63- Calculated UV-Vis spectra (in THF) of $\mathbf{1_{Me}}$, $\mathbf{2_{Me}}$ **and** $\mathbf{3_{Me}}$ using TD-SCF, B3LYP/6-31(++)G**

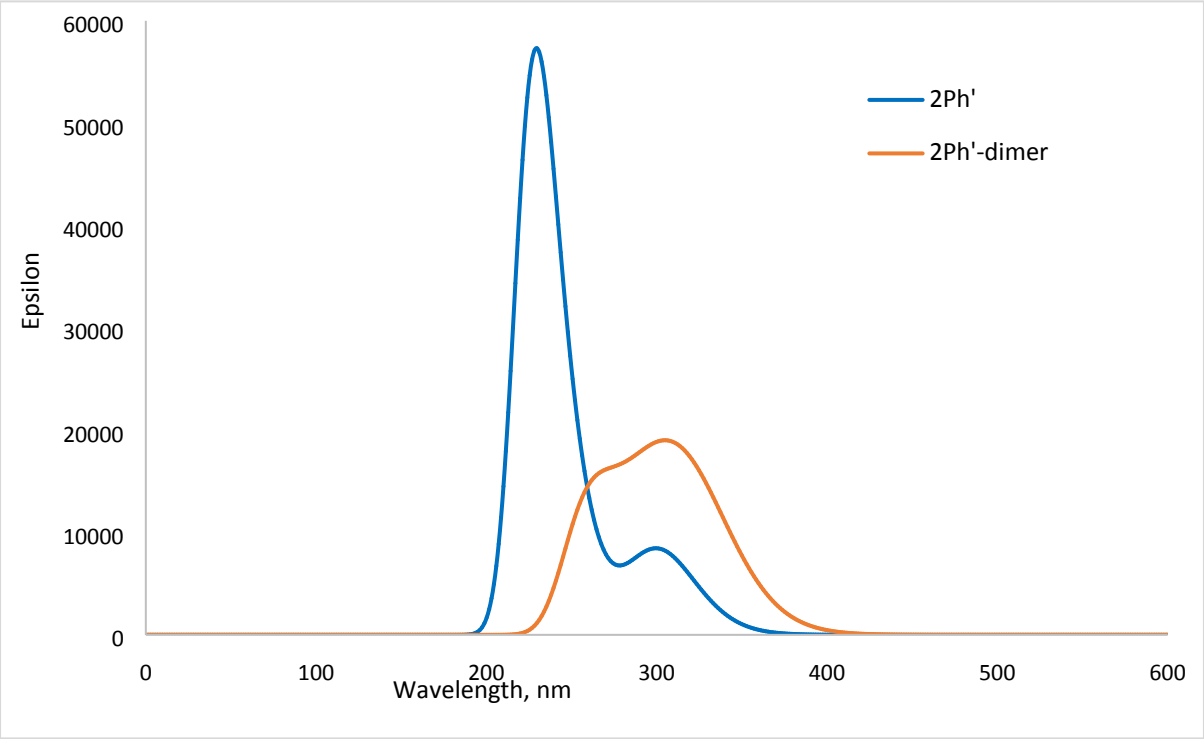

Figure S64- Calculated UV-Vis spectra (in THF) of **$2_{Ph'}$ and $2_{Ph'}$-dimer** using TD-SCF, B3LYP/6-31(++)G**

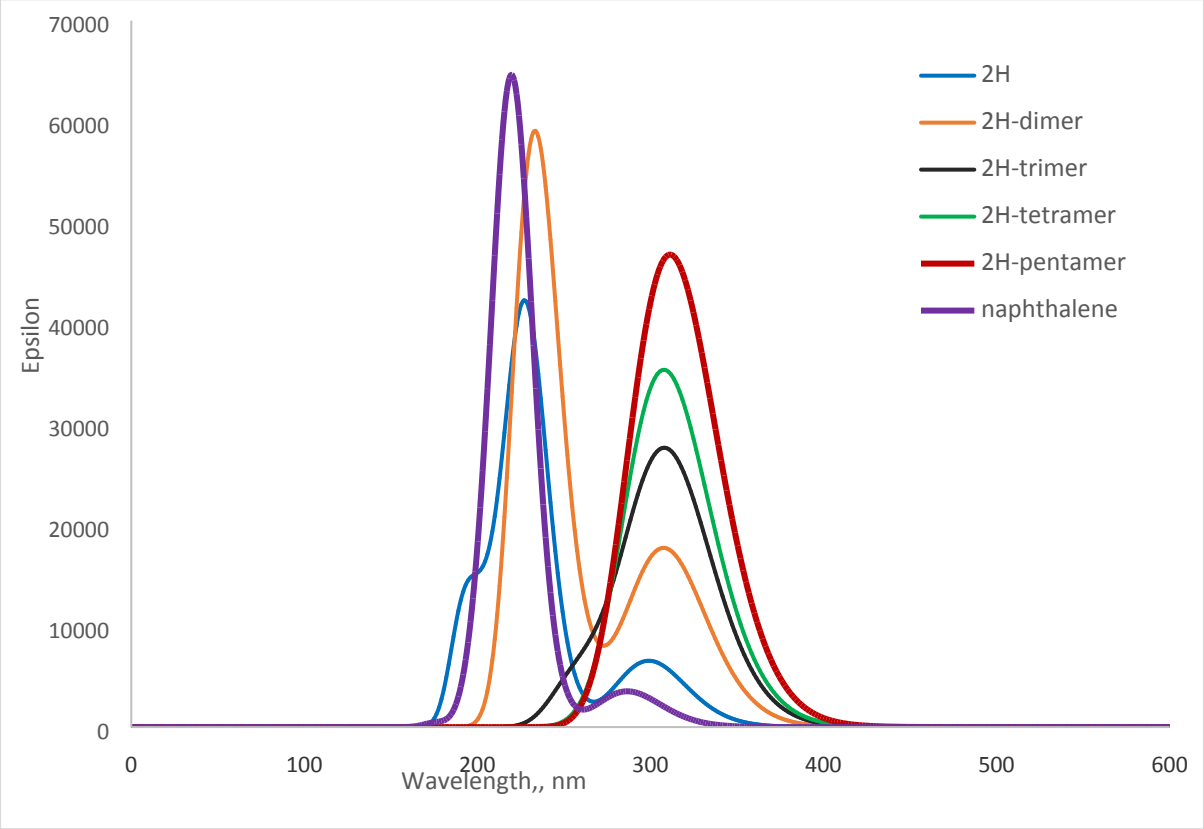

Figure S65- Calculated UV-Vis spectra (in THF) of **2_H, 2_H-dimer, 2_H-trimer, 2H-tetramer and 2_H-pentamer** using TD-SCF, B3LYP/6-31(++)G**