Electronic Supporting Information (ESI)

What do we know about bifunctional cage-like T_8 silsesquioxanes? Theory *versus* lab routine

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4. Quantum calculations

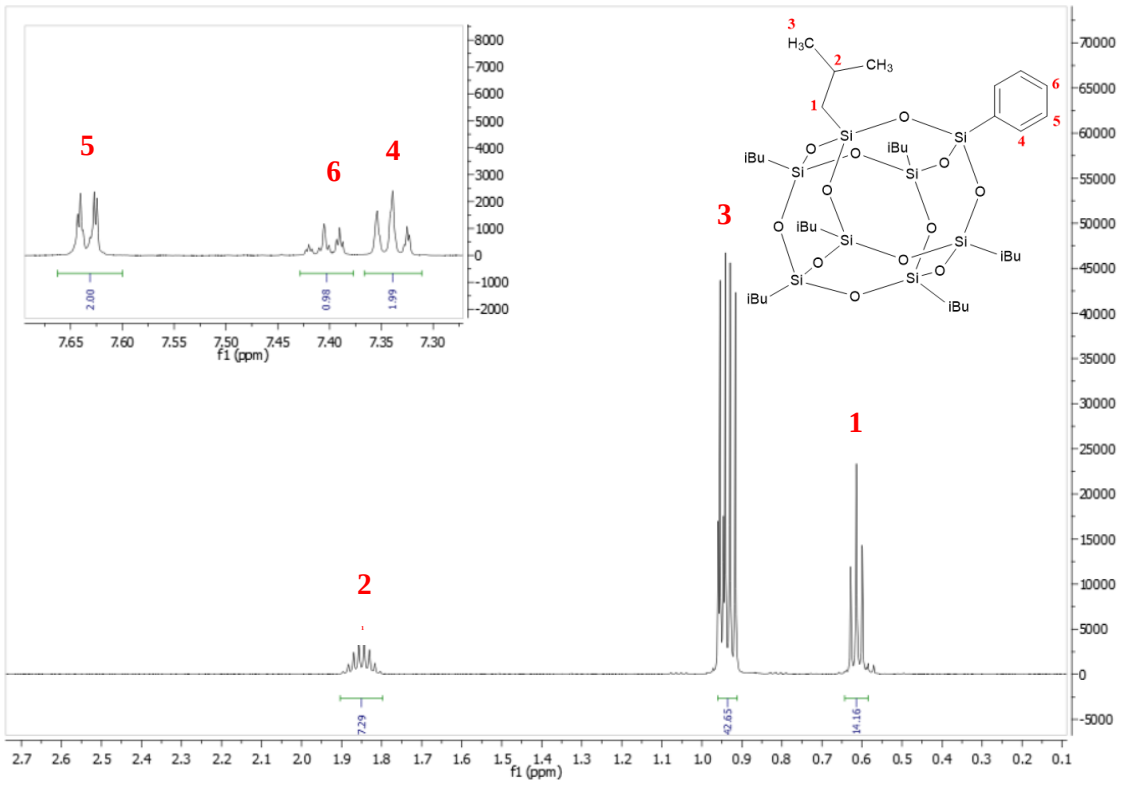


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **1**.

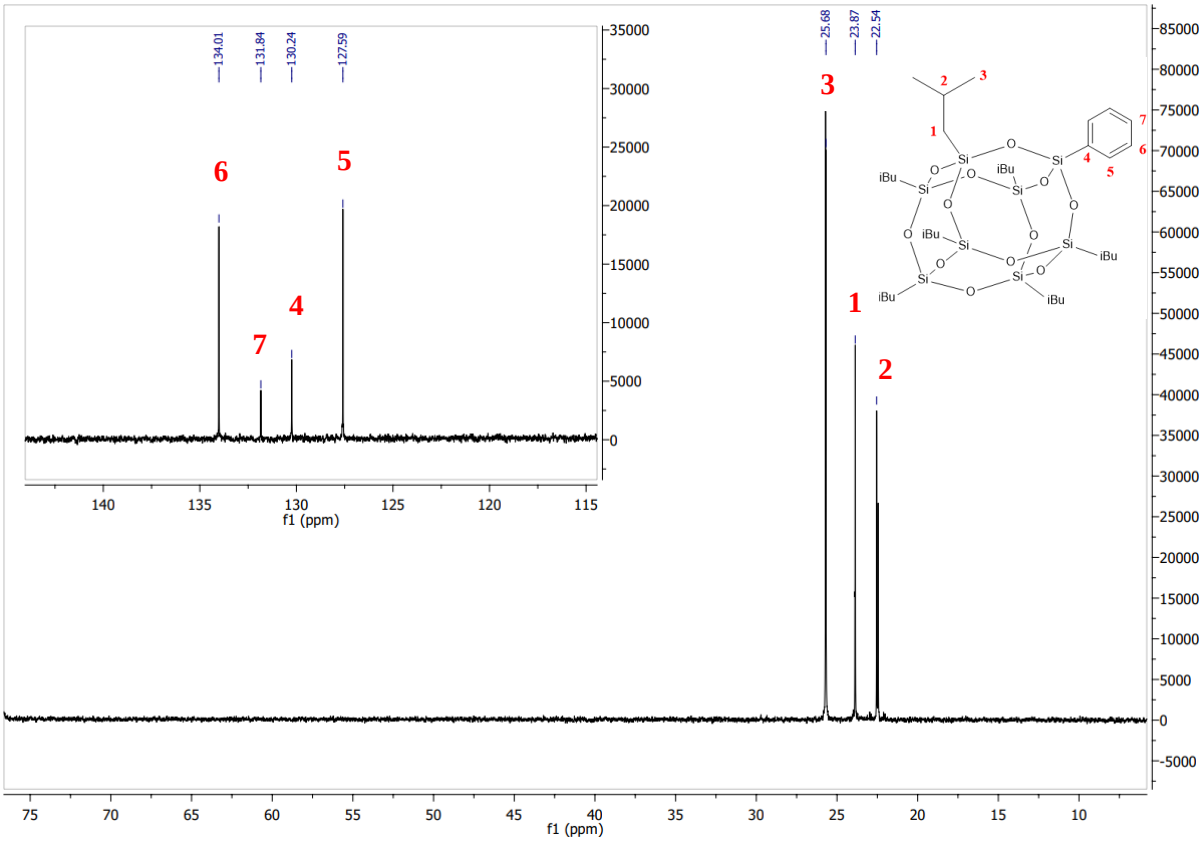


Figure S2. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **1**.

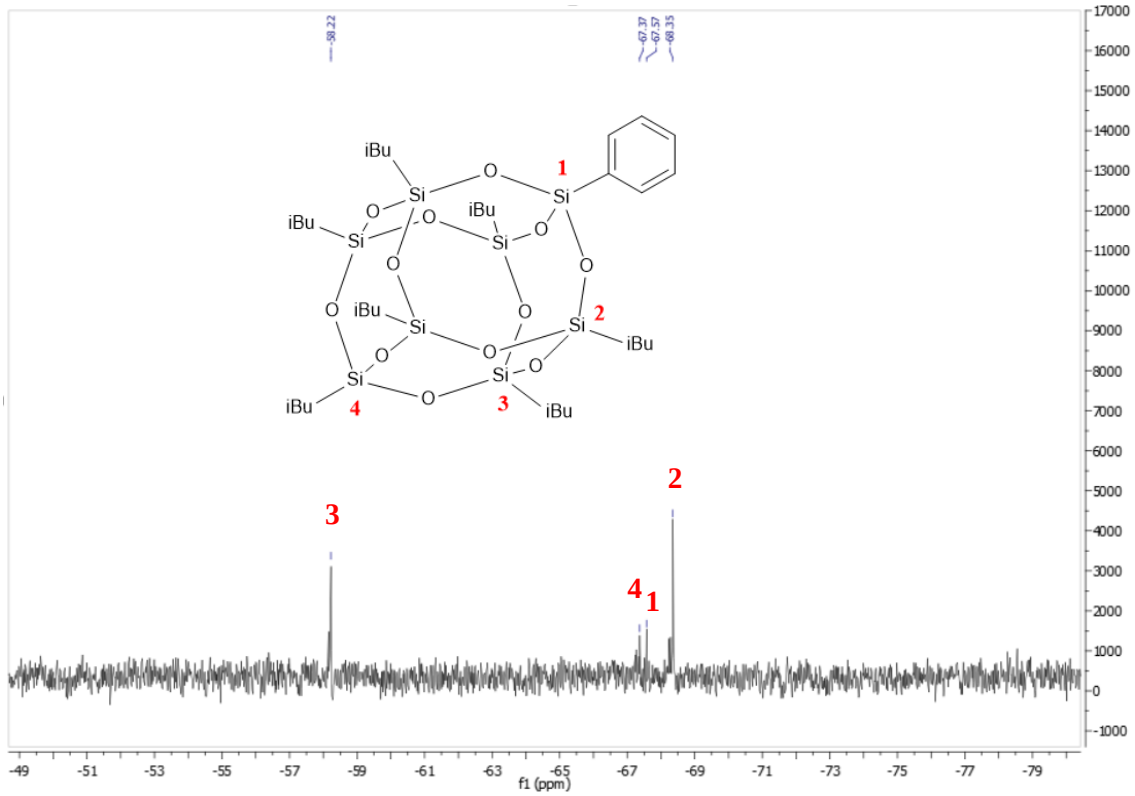


Figure S3. ^{29}Si NMR (600 MHz, $CDCl_3$, 300 K) spectrum of **1**.

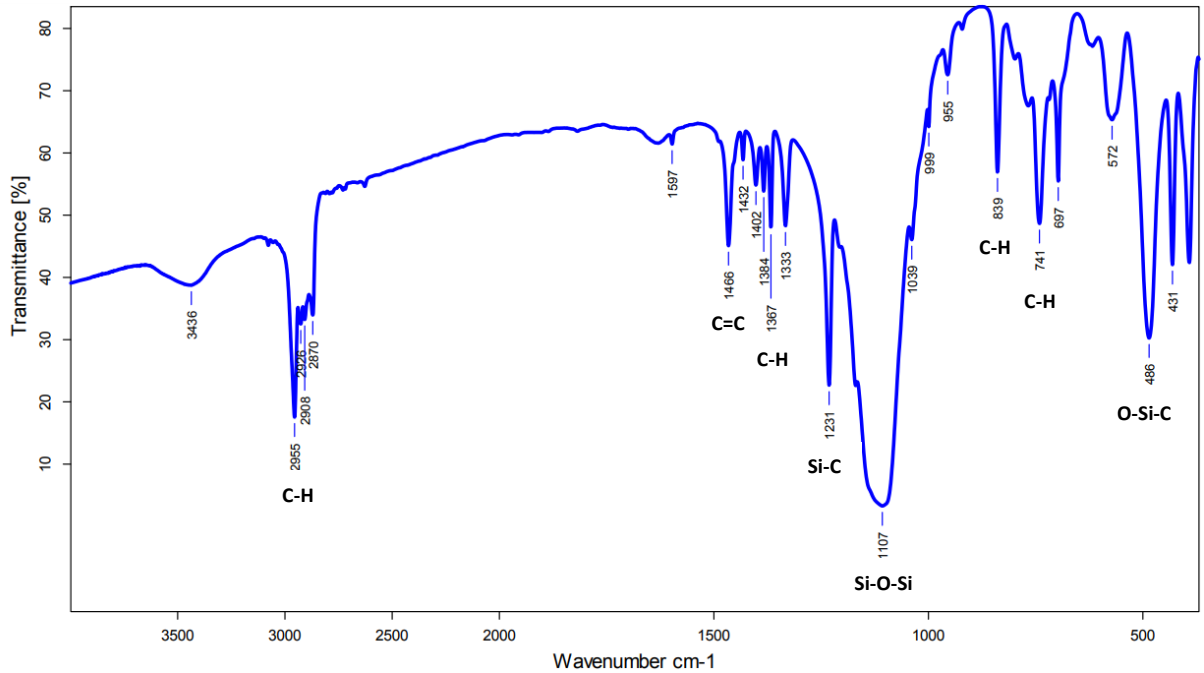


Figure S4. FT-IR spectrum (KBr pellet) of **1**.

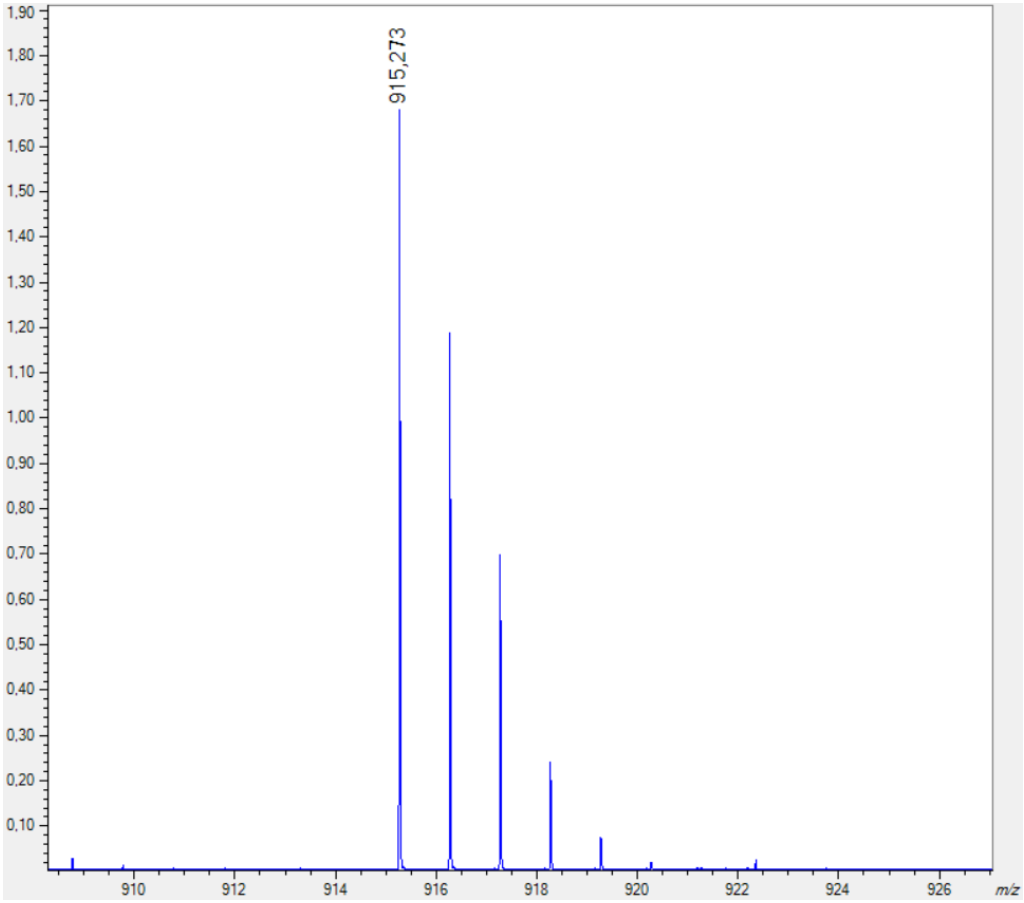


Figure S5. MALDI-MS of **1**.

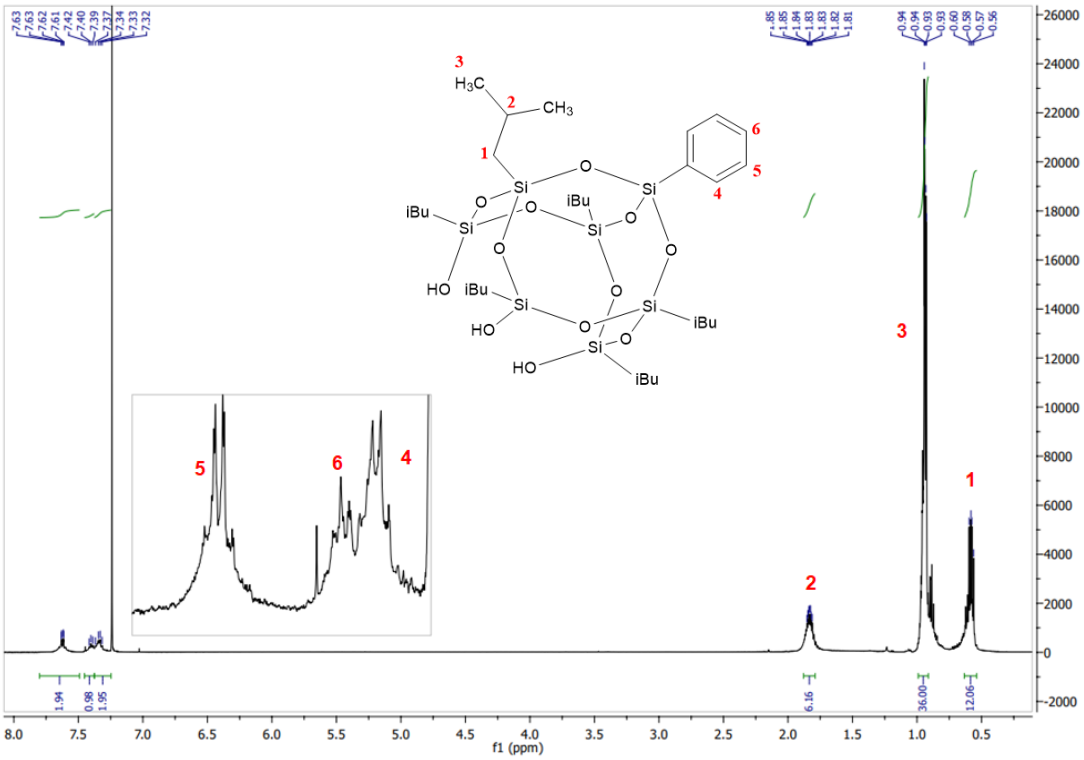


Figure S6. ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) spectrum of **2**.

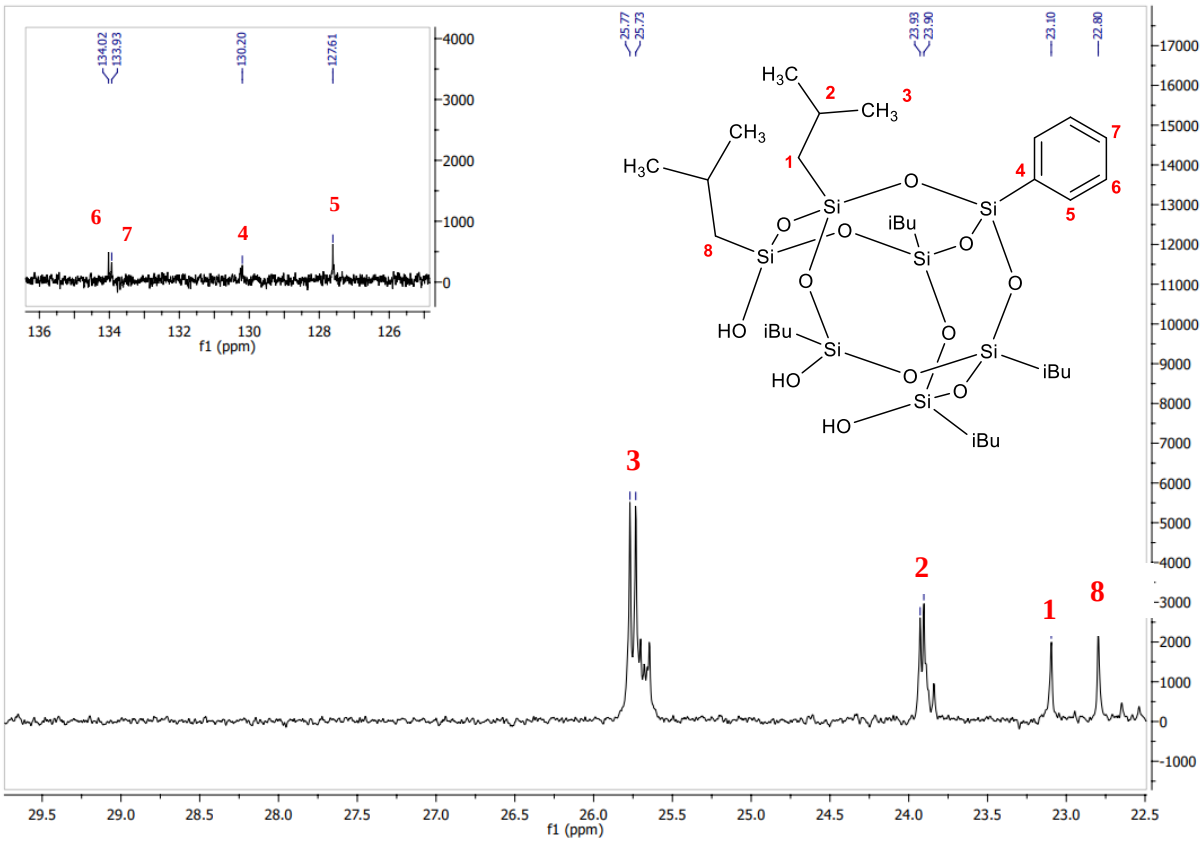


Figure S7. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **2**.

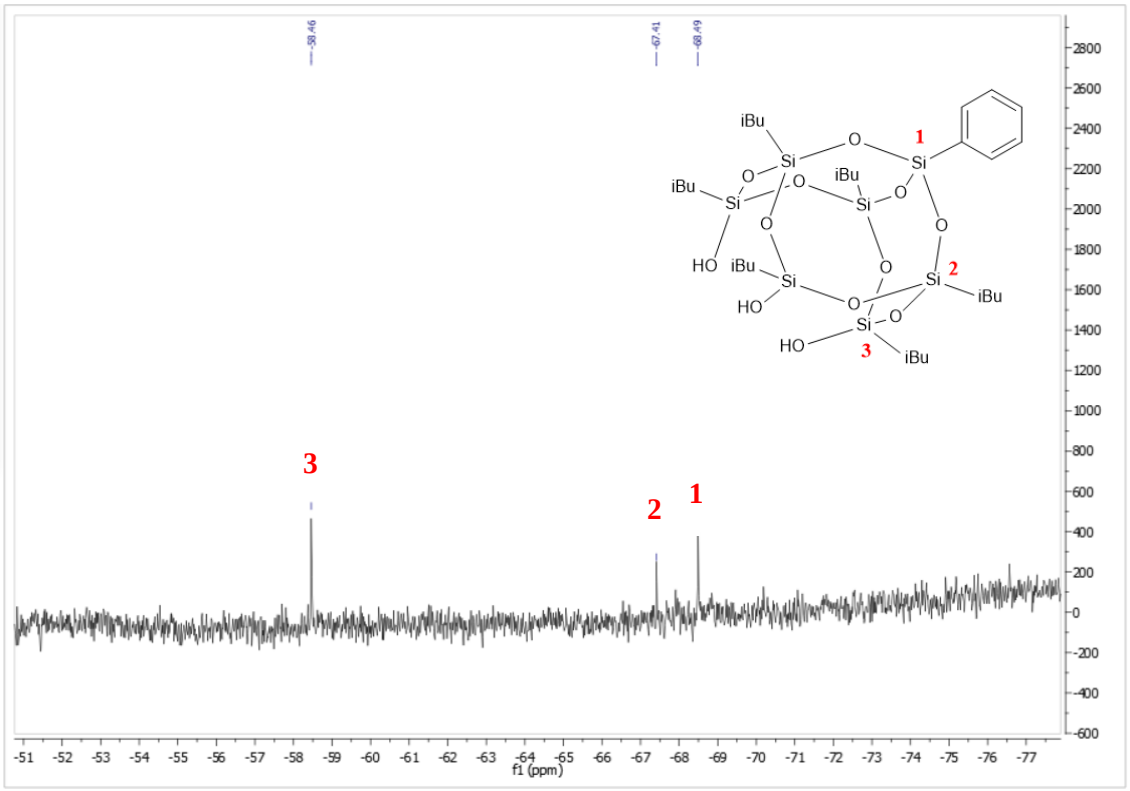


Figure S8. ^{29}Si NMR (600 MHz, $CDCl_3$, 300K) spectrum of **2**.

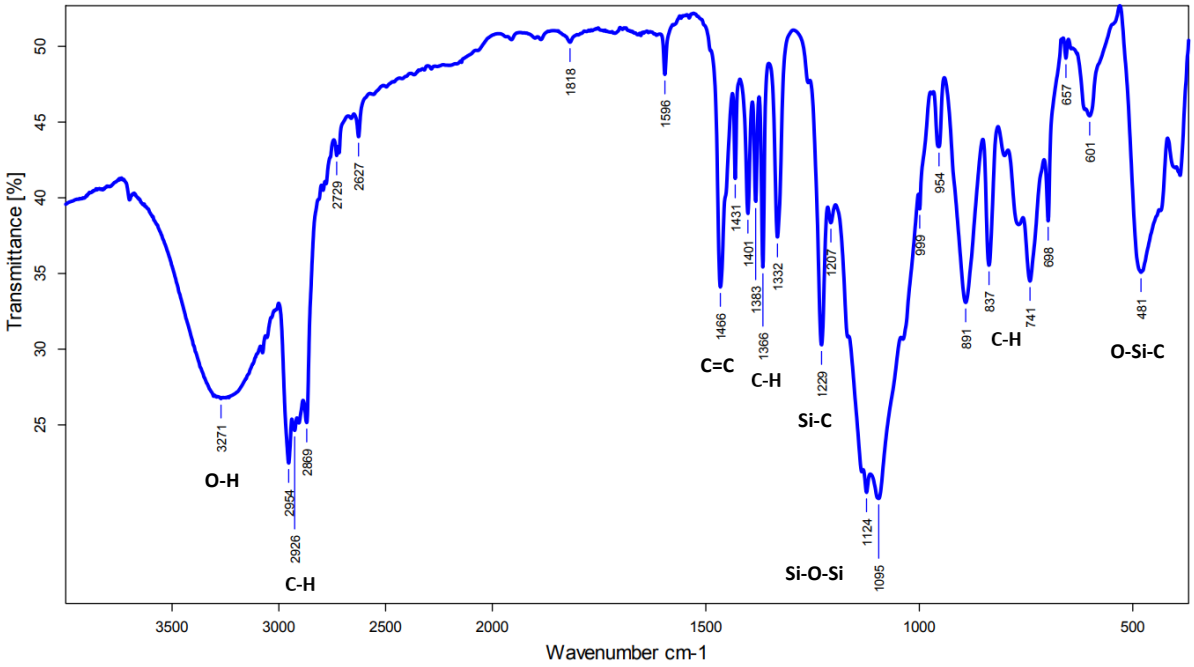


Figure S9. FT-IR spectrum (KBr pellet) of **2**.

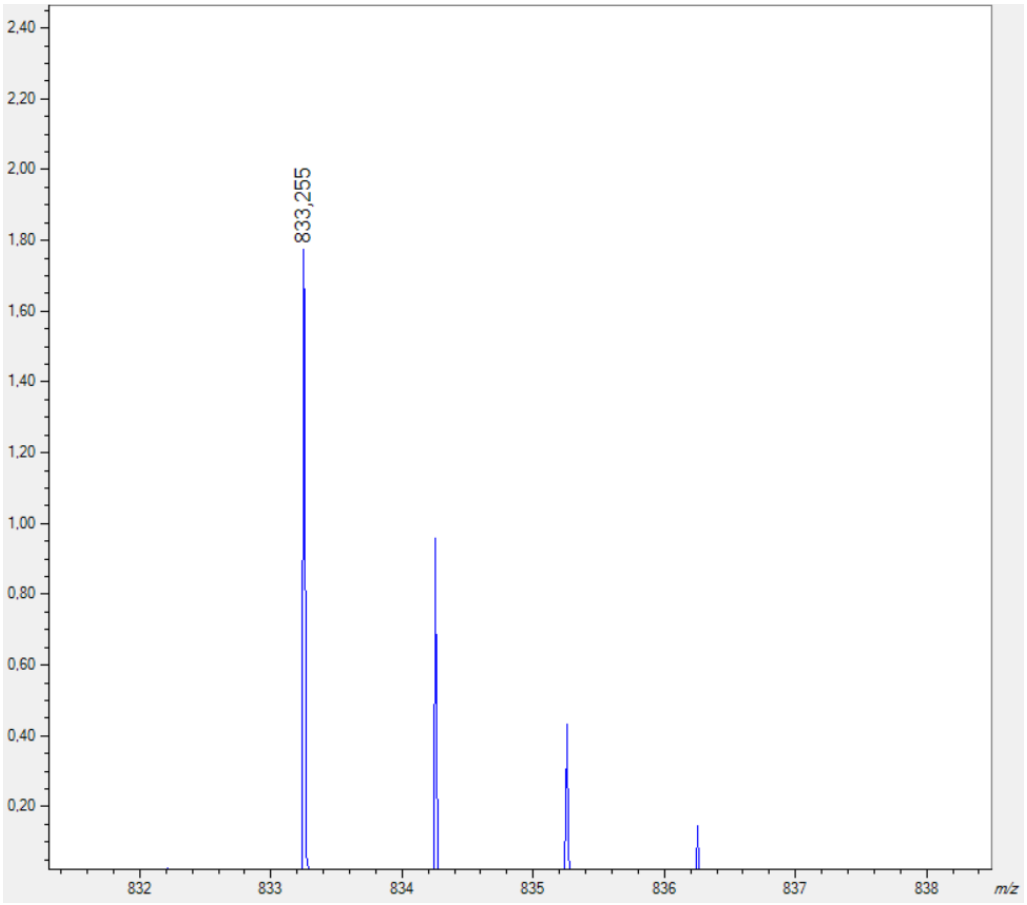


Figure S10. MALDI-MS of **2**.

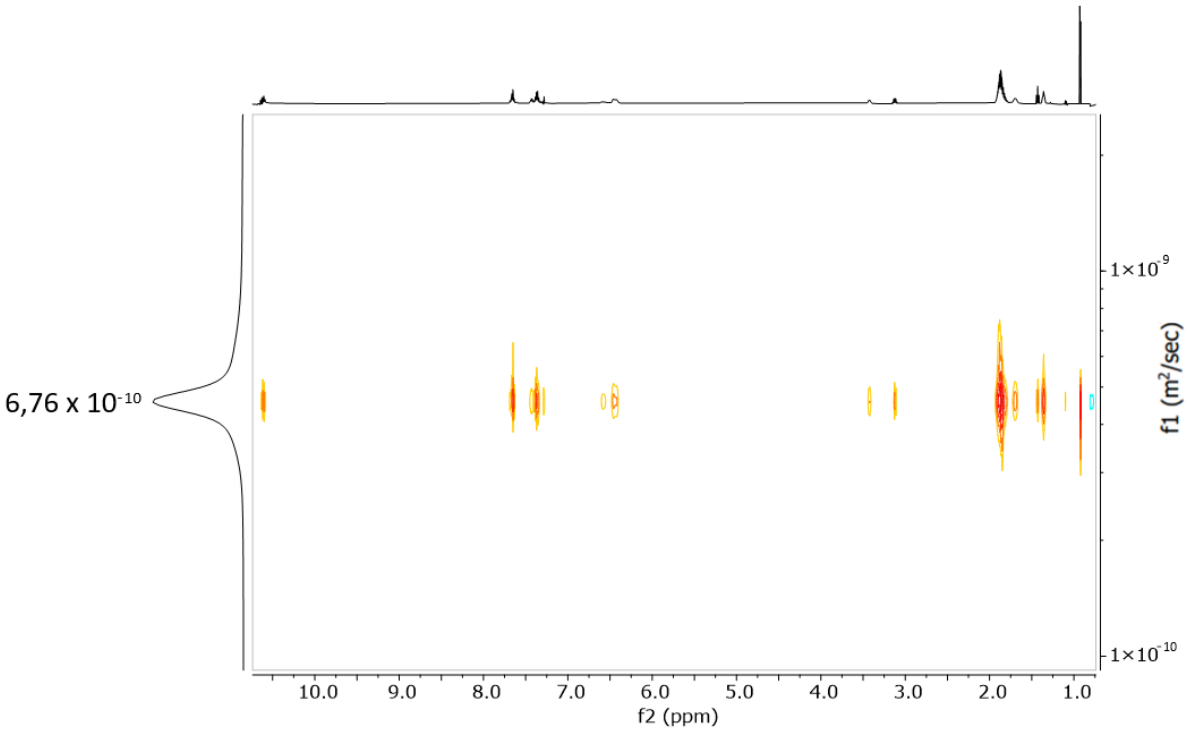


Figure S11. DOSY NMR of **2**.

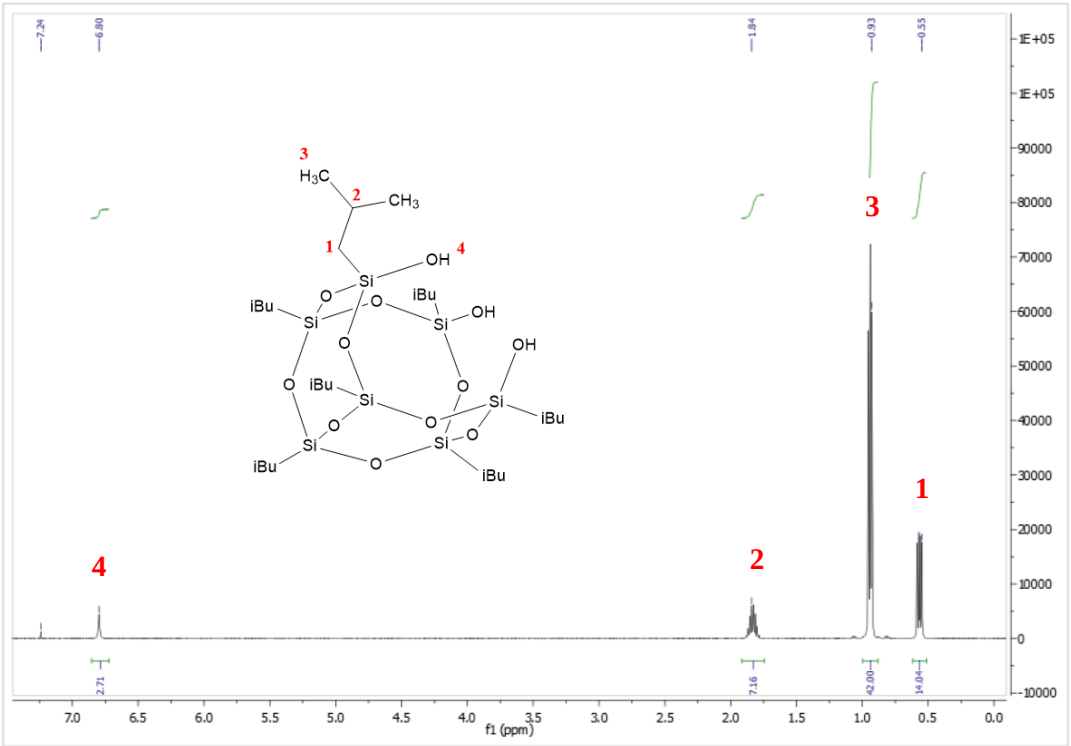


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **3**.

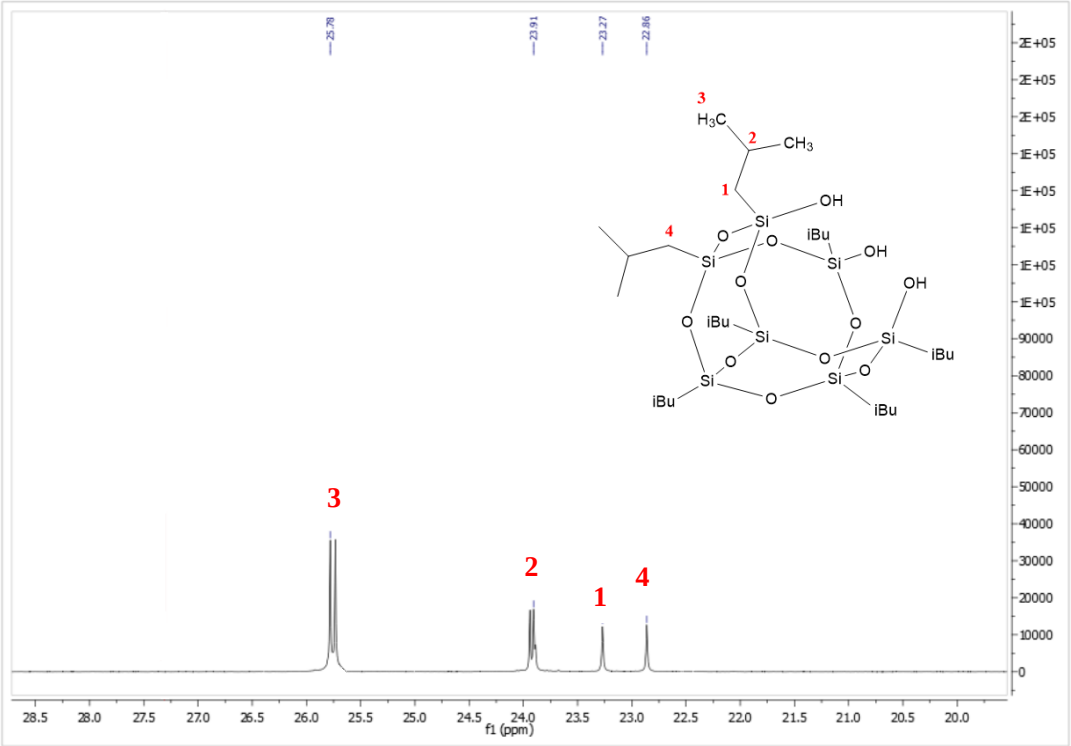


Figure S13. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **3**.

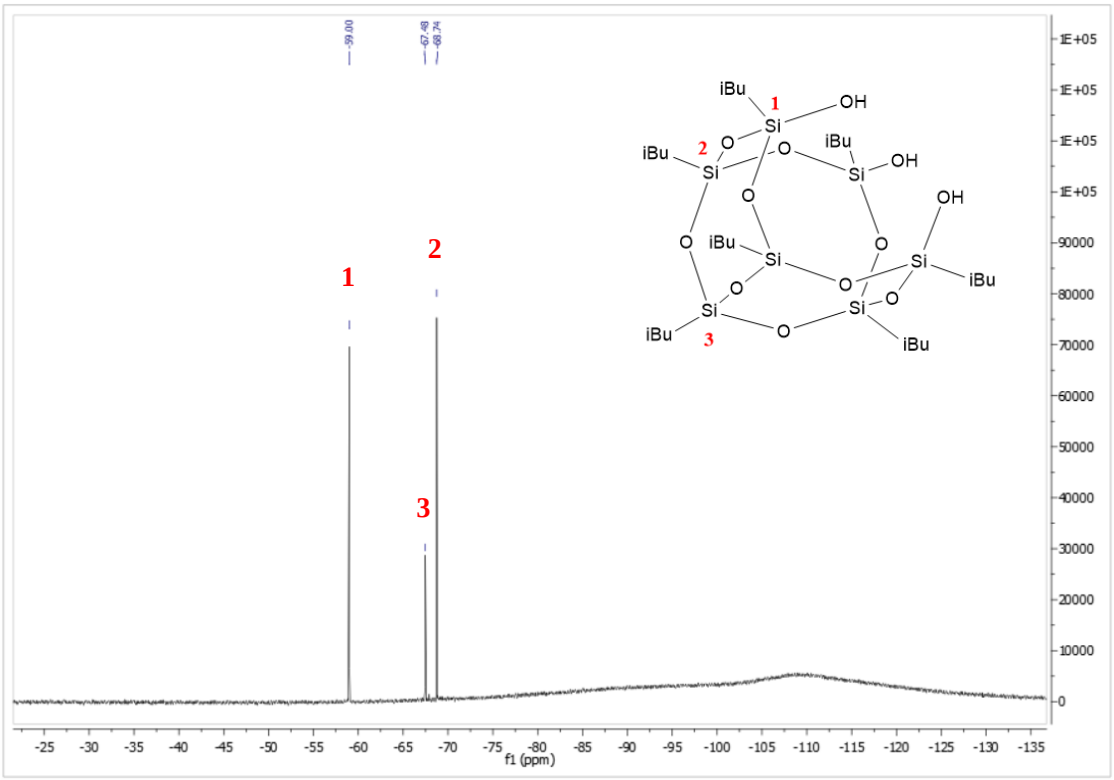


Figure S14. ^{29}Si NMR (600 MHz, $CDCl_3$, 300K) spectrum of **3**.

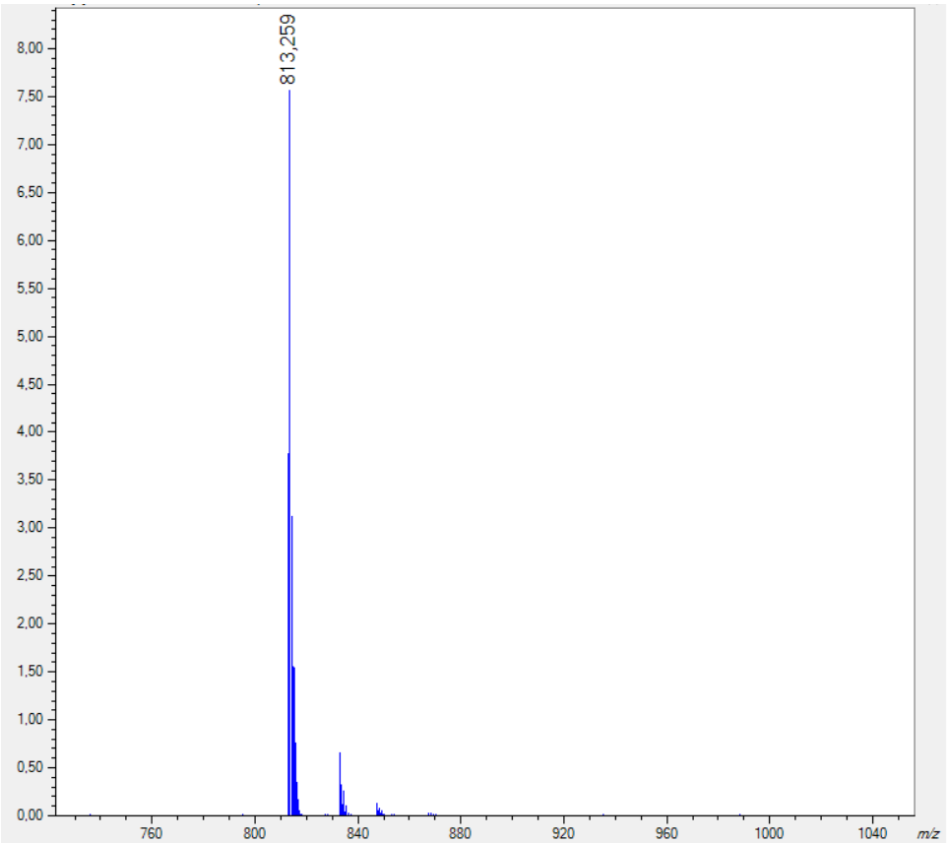


Figure S15. MALDI-MS of **3**.

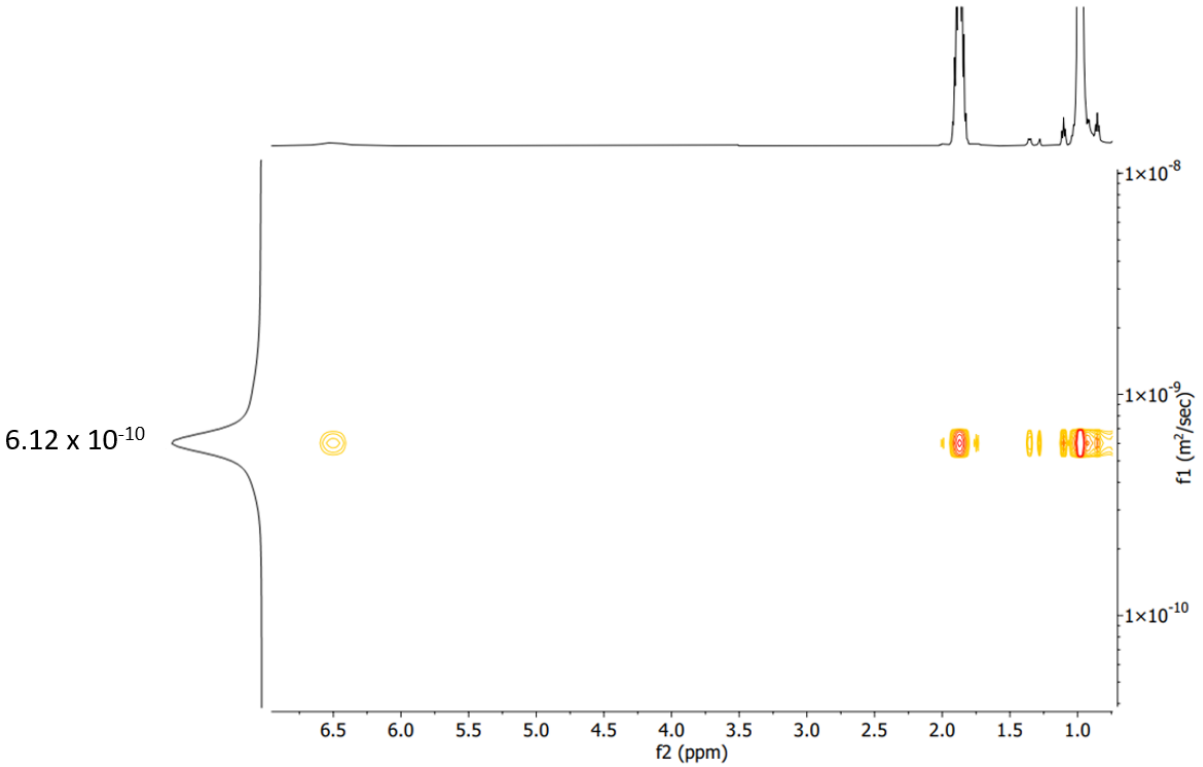


Figure S16. DOSY NMR of **3**.

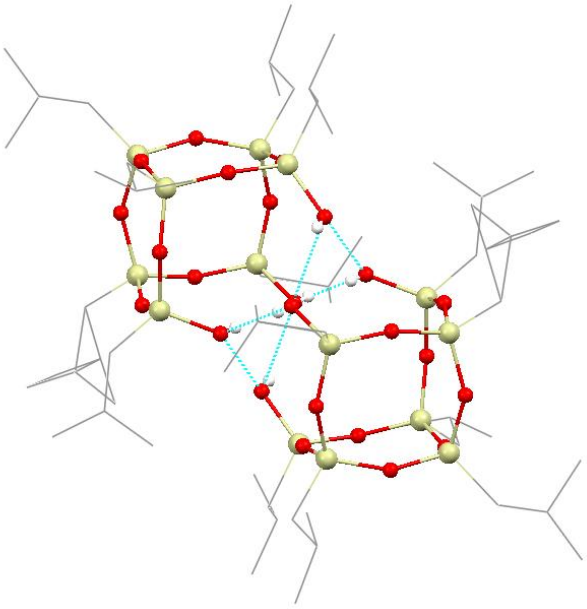
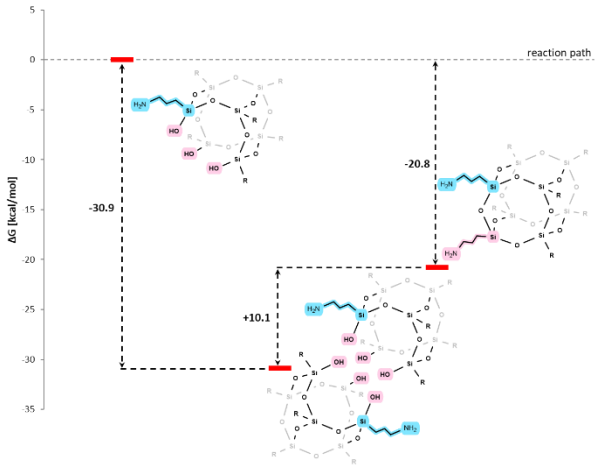
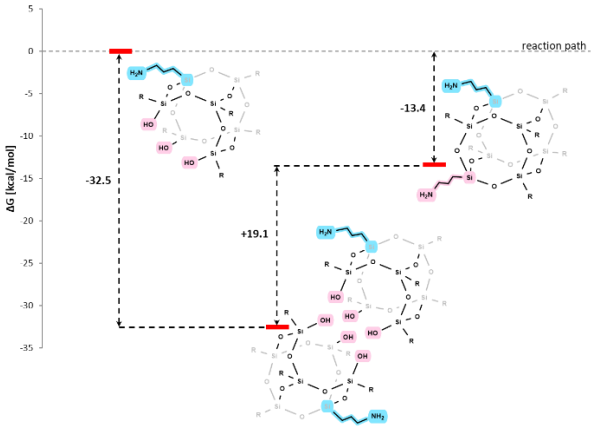


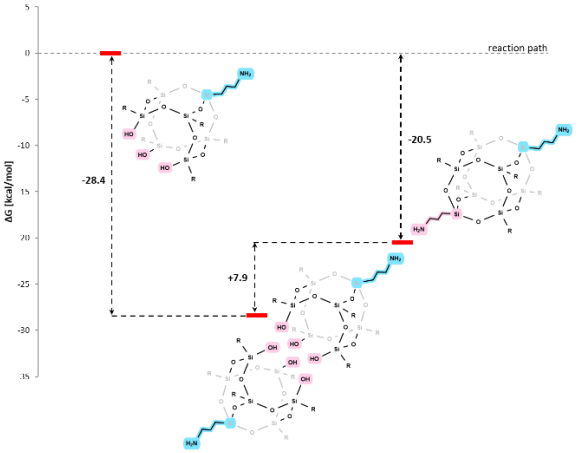
Figure S17. Molecular structure of **3**.



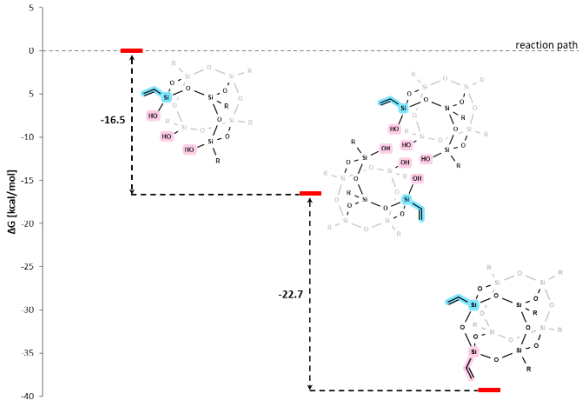
***ortho*-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$**



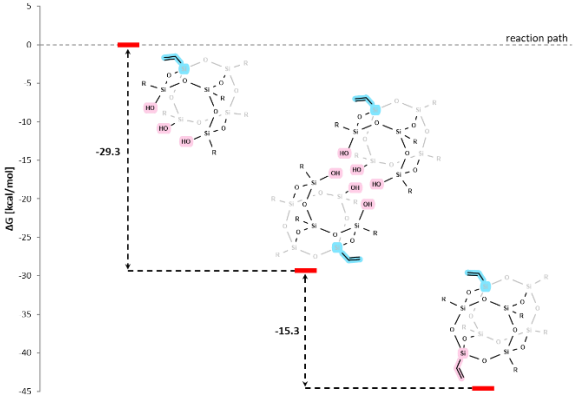
***meta*-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$**



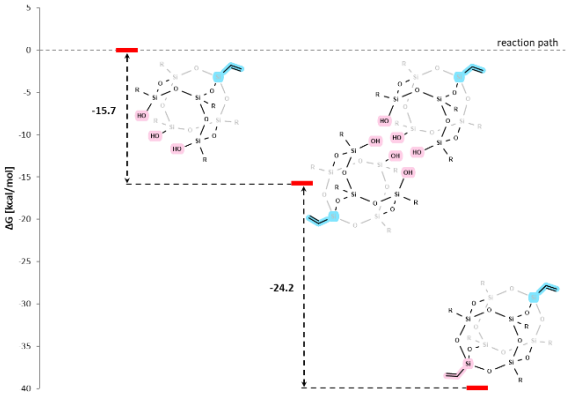
***para*-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$**



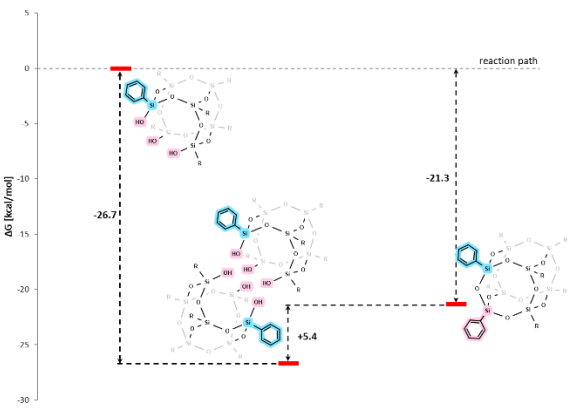
***ortho*-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$**



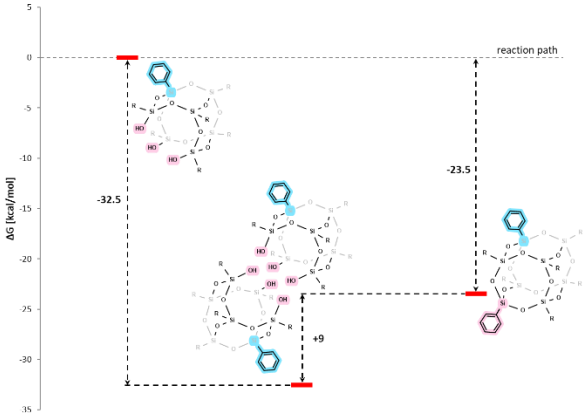
***meta*-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$**



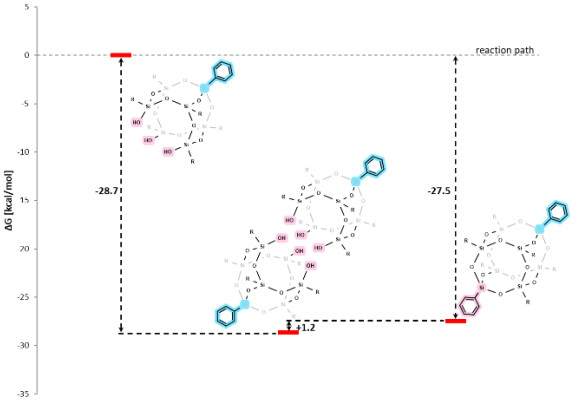
***para*-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$**



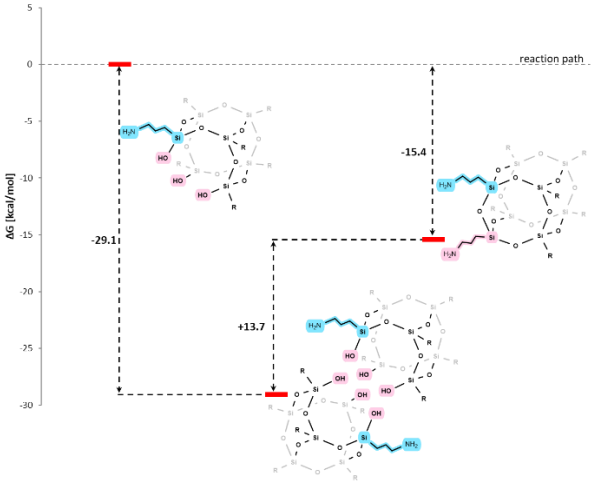
***ortho*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**



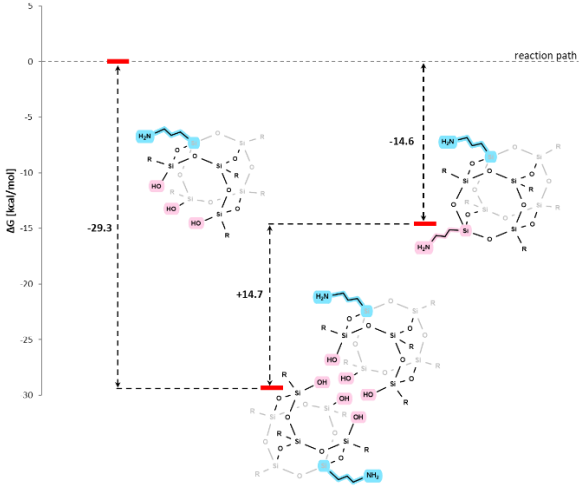
***meta*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**



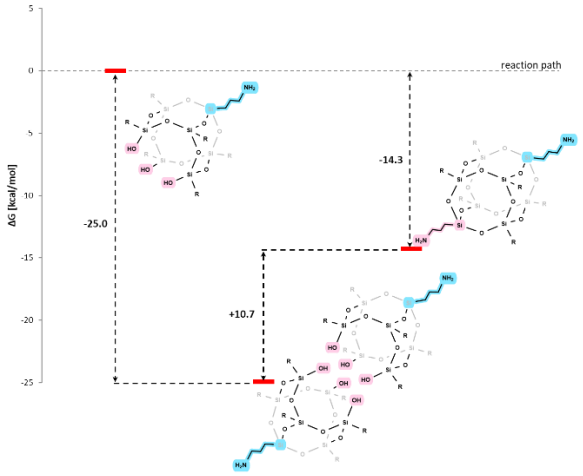
***para*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**



***ortho*-T_7(Ph)$_6$($C_3H_6NH_2$)(OH)$_3$**



***meta*-T_7(Ph)$_6$($C_3H_6NH_2$)(OH)$_3$**



***para*-T_7(Ph)$_6$($C_3H_6NH_2$)(OH)$_3$**

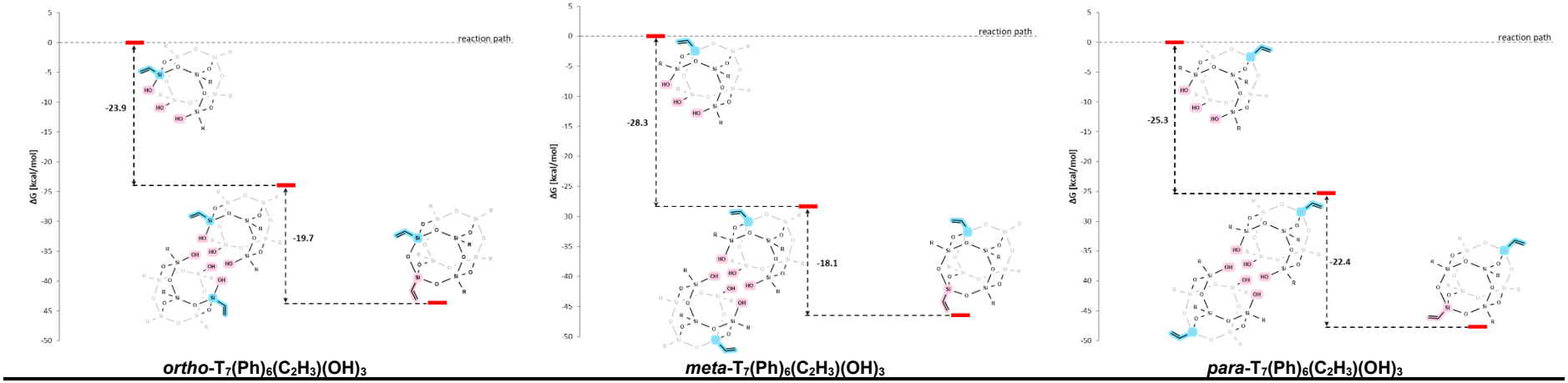


Figure S18. Relative Gibbs free energies (kcal/mol) for DFT optimized POSS structures.

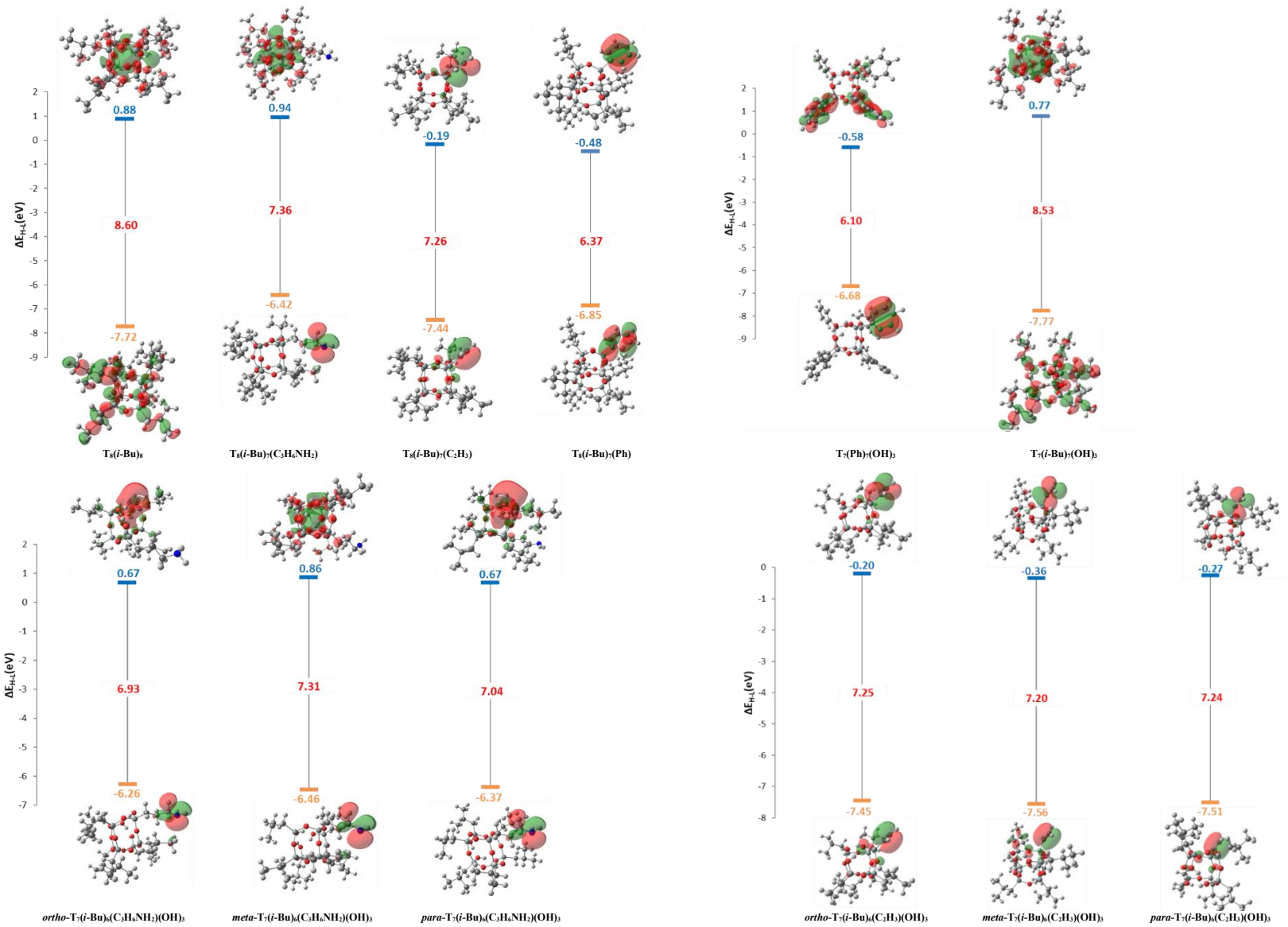
Table S1. The calculated HOMO-LUMO energy gaps and quantum chemical properties of POSS complexes. Data are given in eV.

	Molecular Orbitals	Energy	Energy gap	Ionization potential (I)	Electron affinity (A)	Global hardness (η)	Electronegativity (χ)	Chemical potential (μ_c)	Global softness (σ)[a]	Global electrophilicity (ω)
T_8(*i*-Bu)$_8$	HOMO LUMO	-7.72 0.88	8.60	7.72	-0.88	4.30	3.42	-3.42	0.12	1.36
T_8(*i*-Bu)$_8$	HOMO LUMO	-7.77 0.77	8.53	7.77	-0.77	4.27	3.50	-3.50	0.12	1.44
T_8(*i*-Bu)$_7$($C_3H_6NH_2$)	HOMO LUMO	-6.42 0.94	7.36	6.42	-0.94	3.68	2.74	-2.74	0.14	1.02
***ortho*-T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	HOMO LUMO	-6.26 0.67	6.93	6.26	-0.67	3.47	2.80	-2.80	0.14	1.13
***meta*-T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	HOMO LUMO	-6.46 0.86	7.31	6.46	-0.86	3.66	2.80	-2.80	0.14	1.07
***para*-T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	HOMO LUMO	-6.37 0.67	7.04	6.37	-0.67	3.52	2.85	-2.85	0.14	1.15
T_8(*i*-Bu)$_7$(C_2H_3)	HOMO LUMO	-7.44 -0.19	7.26	7.44	0.19	3.63	3.82	-3.82	0.14	2.01
***ortho*-T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	HOMO LUMO	-7.45 -0.20	7.25	7.45	0.20	3.63	3.82	-3.82	0.14	2.02
***meta*-T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	HOMO LUMO	-7.56 -0.36	7.20	7.56	0.36	3.60	3.96	-3.96	0.14	2.17
***para*-T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	HOMO LUMO	-7.51 -0.27	7.24	7.51	0.27	3.62	3.89	-3.89	0.14	2.09
T_8(*i*-Bu)$_7$(Ph)	HOMO LUMO	-6.85 -0.48	6.37	6.85	0.48	3.19	3.66	-3.66	0.16	2.10
***ortho*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**	HOMO LUMO	-6.81 -0.42	6.39	6.81	0.42	3.19	3.61	-3.61	0.16	2.04
***meta*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**	HOMO LUMO	-6.92 -0.55	6.37	6.92	0.55	3.18	3.73	-3.73	0.16	2.19
***para*-T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**	HOMO LUMO	-6.86 -0.48	6.38	6.86	0.48	3.19	3.67	-3.67	0.16	2.12
T_8(Ph)$_8$	HOMO LUMO	-6.69 -0.56	6.12	6.69	0.56	3.06	3.62	-3.62	0.16	2.14
T_7(Ph)$_7$()H)$_3$	HOMO LUMO	-6.68 -0.58	6.10	6.68	0.58	3.05	3.63	-3.63	0.16	2.17

$T_8(Ph)_7(C_3H_6NH_2)$	HOMO LUMO	-6.24 -0.52	5.72	6.24	0.52	2.86	3.38	-3.38	0.17	2.00
***ortho*-$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$**	HOMO LUMO	-6.21 -0.59	5.62	6.21	0.59	2.81	3.40	-3.40	0.18	2.06
***meta*-$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$**	HOMO LUMO	-6.19 -0.59	5.60	6.19	0.59	2.80	3.39	-3.39	0.18	2.05
***para*-$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$**	HOMO LUMO	-6.37 -0.58	5.79	6.37	0.58	2.89	3.47	-3.47	0.17	2.09
$T_8(Ph)_7(C_2H_3)$	HOMO LUMO	-6.67 -0.56	6.11	6.67	0.56	3.06	3.61	-3.61	0.16	2.13
***ortho*-$T_7(Ph)_6(C_2H_3)(OH)_3$**	HOMO LUMO	-6.68 -0.59	6.09	6.68	0.59	3.04	3.64	-3.64	0.16	2.17
***meta*-$T_7(Ph)_6(C_2H_3)(OH)_3$**	HOMO LUMO	-6.65 -0.60	6.04	6.65	0.60	3.02	3.62	-3.62	0.17	2.17
***para*-$T_7(Ph)_6(C_2H_3)(OH)_3$**	HOMO LUMO	-6.63 -0.61	6.02	6.63	0.61	3.01	3.62	-3.62	0.17	2.18

[a] data are given in eV^{-1}

$I = -E_{HOMO}; A = -E_{LUMO}; \eta = \frac{I-A}{2}; \chi = \frac{I+A}{2}; \mu_c = -\chi; \sigma = \frac{1}{2\eta}; \omega = \frac{\mu^2}{2\eta}$



$T_8(i\text{-Bu})_8$ $T_8(i\text{-Bu})_7(C_3H_6NH_2)$ $T_8(i\text{-Bu})_7(C_2H_3)$ $T_8(i\text{-Bu})_7(Ph)$

$T_7(Ph)_7(OH)_3$ $T_7(i\text{-Bu})_7(OH)_3$

ortho-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$ *meta*-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$ *para*-$T_7(i\text{-Bu})_6(C_3H_6NH_2)(OH)_3$

ortho-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$ *meta*-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$ *para*-$T_7(i\text{-Bu})_6(C_2H_3)(OH)_3$

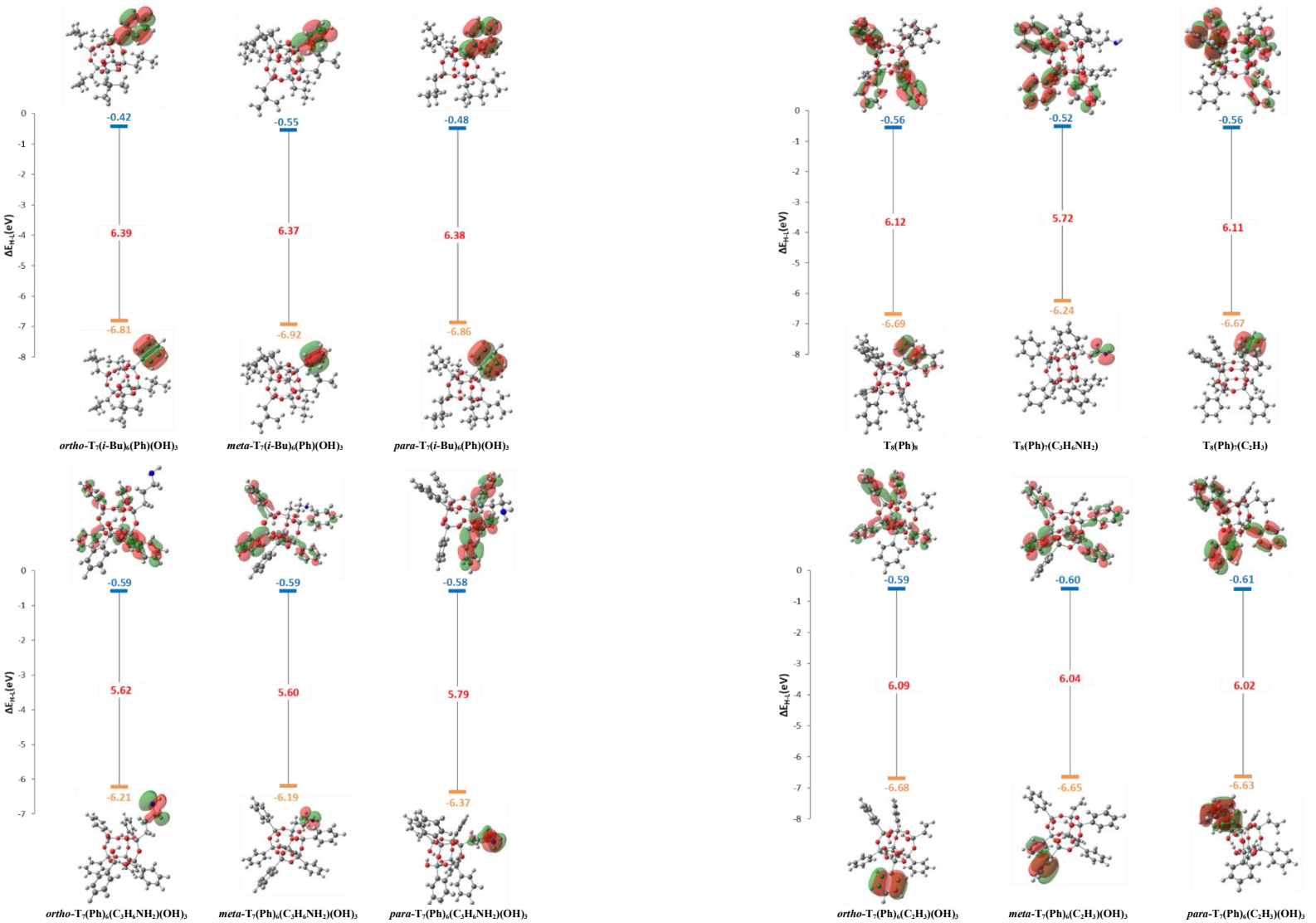


Figure S19. The calculated HOMO (orange) and LUMO (blue) energy levels and their visualization, and HOMO-LUMO energy gaps (red) of optimized POSS models. HOMO – orange; LUMO – blue; $\Delta E_{H\text{-}L}$ – red

Table S2. Energies of calculated POSS models. Data are given in kcal/mol.

		E_{tot}	E_{tot} + ZPE	H	G	S[a]
	T_8(*i*-Bu)$_8$	-2813122	-2812459	-2812416	-2812524	0.365
	T_7(*i*-Bu)$_7$(OH)$_3$	-2533419	-2532815	-2532775	-2532877	0.344
	[T_7(*i*-Bu)$_7$(OH)3]$_2$	-5066879	-5065669	-5065589	-5065776	0.625
T_8(*i*-Bu)$_7$($C_3H_6NH_2$)		-2823175	-2822518	-2822475	-2822584	0.365
ortho	**T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	-2543470	-2542872	-2542833	-2542935	0.342
ortho	[T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$]$_2$	-5086989	-5085792	-5085712	-5085901	0.631
ortho	**T_8(*i*-Bu)$_6$($C_3H_6NH_2$)$_2$**	-2833231	-2832580	-2832537	-2832646	0.364
meta	**T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	-2543473	-2542875	-2542836	-2542938	0.344
meta	[T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$]$_2$	-5086997	-5085800	-5085721	-5085909	0.631
meta	**T_8(*i*-Bu)$_6$($C_3H_6NH_2$)$_2$**	-2833229	-2832579	-2832536	-2832646	0.368
para	**T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$**	-2543470	-2542873	-2542833	-2542935	0.340
para	[T_7(*i*-Bu)$_6$($C_3H_6NH_2$)(OH)$_3$]$_2$	-5086989	-5085792	-5085713	-5085898	0.619
para	**T_8(*i*-Bu)$_6$($C_3H_6NH_2$)$_2$**	-2833229	-2832579	-2832536	-2832645	0.367
T_8(*i*-Bu)$_7$(C_2H_3)		-2762997	-2762384	-2762343	-2762449	0.358
ortho	**T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	-2483295	-2482742	-2482704	-2482805	0.338
ortho	[T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$]$_2$	-4966633	-4965524	-4965448	-4965626	0.595
ortho	**T_8(*i*-Bu)$_6$(C_2H_3)$_2$**	-2712874	-2712312	-2712273	-2712373	0.337
meta	**T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	-2483297	-2482743	-2482706	-2482803	0.326
meta	[T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$]$_2$	-4966644	-4965534	-4965460	-4965635	0.589
meta	**T_8(*i*-Bu)$_6$(C_2H_3)$_2$**	-2712875	-2712312	-2712273	-2712374	0.339
para	**T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$**	-2483297	-2482744	-2482706	-2482804	0.330
para	[T_7(*i*-Bu)$_6$(C_2H_3)(OH)$_3$]$_2$	-4966635	-4965525	-4965450	-4965625	0.586
para	**T_8(*i*-Bu)$_6$(C_2H_3)$_2$**	-2712874	-2712312	-2712273	-2712373	0.338
T_8(*i*-Bu)$_7$(Ph)		-2859426	-2858782	-2858740	-2858849	0.365
ortho	**T_7(*i*-Bu)$_6$(Ph)(OH)$_3$**	-2579723	-2579139	-2579100	-2579202	0.344
ortho	**[T_7(*i*-Bu)$_6$(Ph)(OH)$_3$]$_2$**	-5159491	-5158322	-5158243	-5158431	0.631
ortho	**T_8(*i*-Bu)$_6$(Ph)$_2$**	-2905731	-2905108	-2905066	-2905175	0.364

meta	$T_7(i\text{-}Bu)_6(Ph)(OH)_3$	-2579723	-2579139	-2579100	-2579203	0.344
	$[T_7(i\text{-}Bu)_6(Ph)(OH)_3]_2$	-5159503	-5158333	-5158255	-5158438	0.613
	$T_8(i\text{-}Bu)_6(Ph)_2$	-2905731	-2905108	-2905066	-2905176	0.369
para	$T_7(i\text{-}Bu)_6(Ph)(OH)_3$	-2579718	-2579135	-2579095	-2579198	0.346
	$[T_7(i\text{-}Bu)_6(Ph)(OH)_3]_2$	-5159491	-5158320	-5158243	-5158425	0.613
	$T_8(i\text{-}Bu)_6(Ph)_2$	-2905731	-2905107	-2905065	-2905174	0.363
	$T_8(Ph)_8$	-3183560	-3183058	-3183018	-3183126	0.363
	$T_7(Ph)_7(OH)_3$	-2857554	-2857091	-2857054	-2857156	0.339
	$[T_7(Ph)_7(OH)_3]_2$	-5715163	-5714235	-5714163	-5714342	0.599
$T_8(Ph)_7(C_3H_6NH_2)$		-3147310	-3146794	-3146755	-3146863	0.363
ortho	$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$	-2821304	-2820827	-2820790	-2820892	0.341
	$[T_7(Ph)_6(C_3H_6NH_2)(OH)_3]_2$	-5642666	-5641710	-5641637	-5641813	0.590
	$T_8(Ph)_6(C_3H_6NH_2)_2$	-3111059	-3110530	-3110489	-3110600	0.372
meta	$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$	-2821304	-2820827	-2820790	-2820891	0.339
	$[T_7(Ph)_6(C_3H_6NH_2)(OH)_3]_2$	-5642662	-5641706	-5641633	-5641812	0.599
	$T_8(Ph)_6(C_3H_6NH_2)_2$	-3111062	-3110532	-3110492	-3110599	0.358
para	$T_7(Ph)_6(C_3H_6NH_2)(OH)_3$	-2821305	-2820828	-2820791	-2820891	0.336
	$[T_7(Ph)_6(C_3H_6NH_2)(OH)_3]_2$	-5642655	-5641700	-5641627	-5641808	0.608
	$T_8(Ph)_6(C_3H_6NH_2)_2$	-3111060	-3110531	-3110491	-3110599	0.363
$T_8(Ph)_7(C_2H_3)$		-3087132	-3086660	-3086623	-3086726	0.348
ortho	$T_7(Ph)_6(C_2H_3)(OH)_3$	-2761127	-2760694	-2760660	-2760756	0.323
	$[T_7(Ph)_6(C_2H_3)(OH)_3]_2$	-5522304	-5521437	-5521368	-5521535	0.563
	$T_8(Ph)_6(C_2H_3)_2$	-2990705	-2990263	-2990227	-2990327	0.333
meta	$T_7(Ph)_6(C_2H_3)(OH)_3$	-2761127	-2760694	-2760659	-2760755	0.321
	$[T_7(Ph)_6(C_2H_3)(OH)_3]_2$	-5522300	-5521433	-5521364	-5521538	0.583
	$T_8(Ph)_6(C_2H_3)_2$	-2990705	-2990263	-2990227	-2990327	0.335
para	$T_7(Ph)_6(C_2H_3)(OH)_3$	-2761127	-2760694	-2760660	-2760754	0.317
	$[T_7(Ph)_6(C_2H_3)(OH)_3]_2$	-5522300	-5521433	-5521363	-5521534	0.573
	$T_8(Ph)_6(C_2H_3)_2$	-2990705	-2990263	-2990227	-2990327	0.336

[a] data are given in kcal/mol