Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

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Supporting Information

NMR spectra of 1

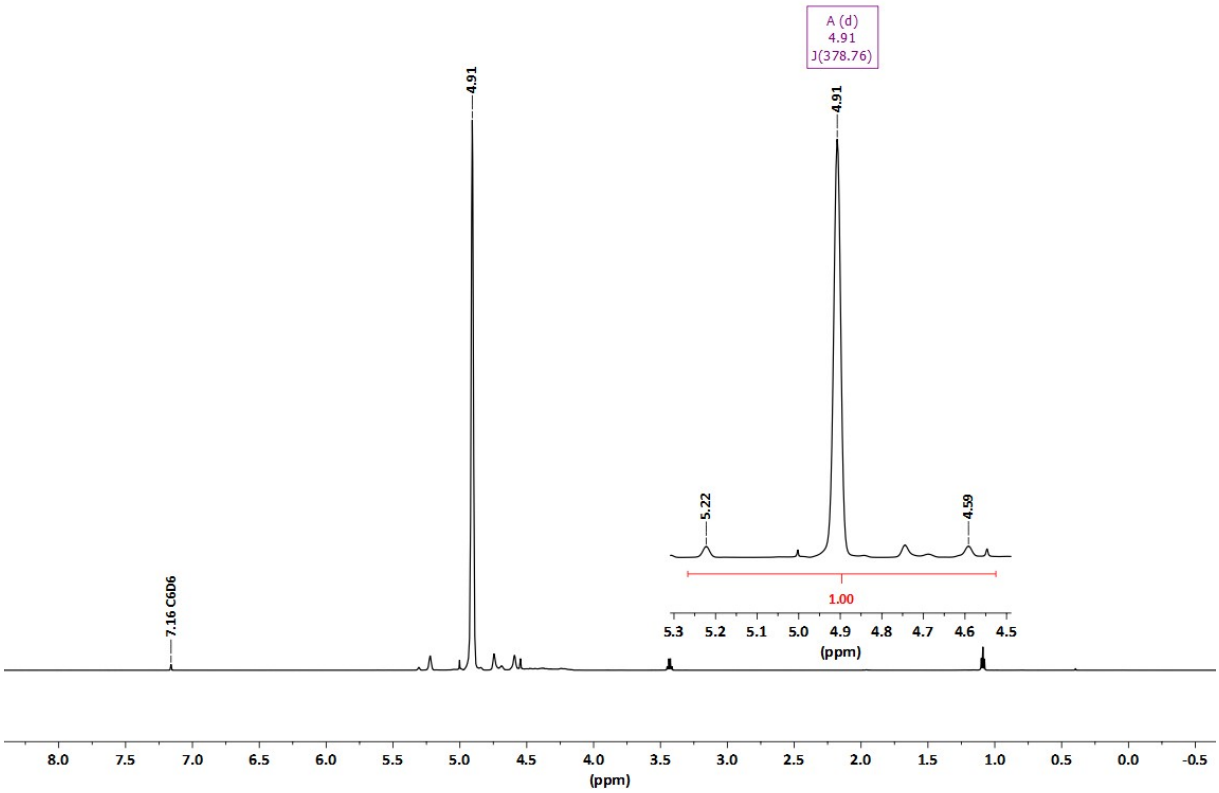

Figure S1. ^{1}H–NMR spectrum (600.2 MHz, C_6D_6) of $\{(F_3C)_3CO\}_3SiH$ (**1**).

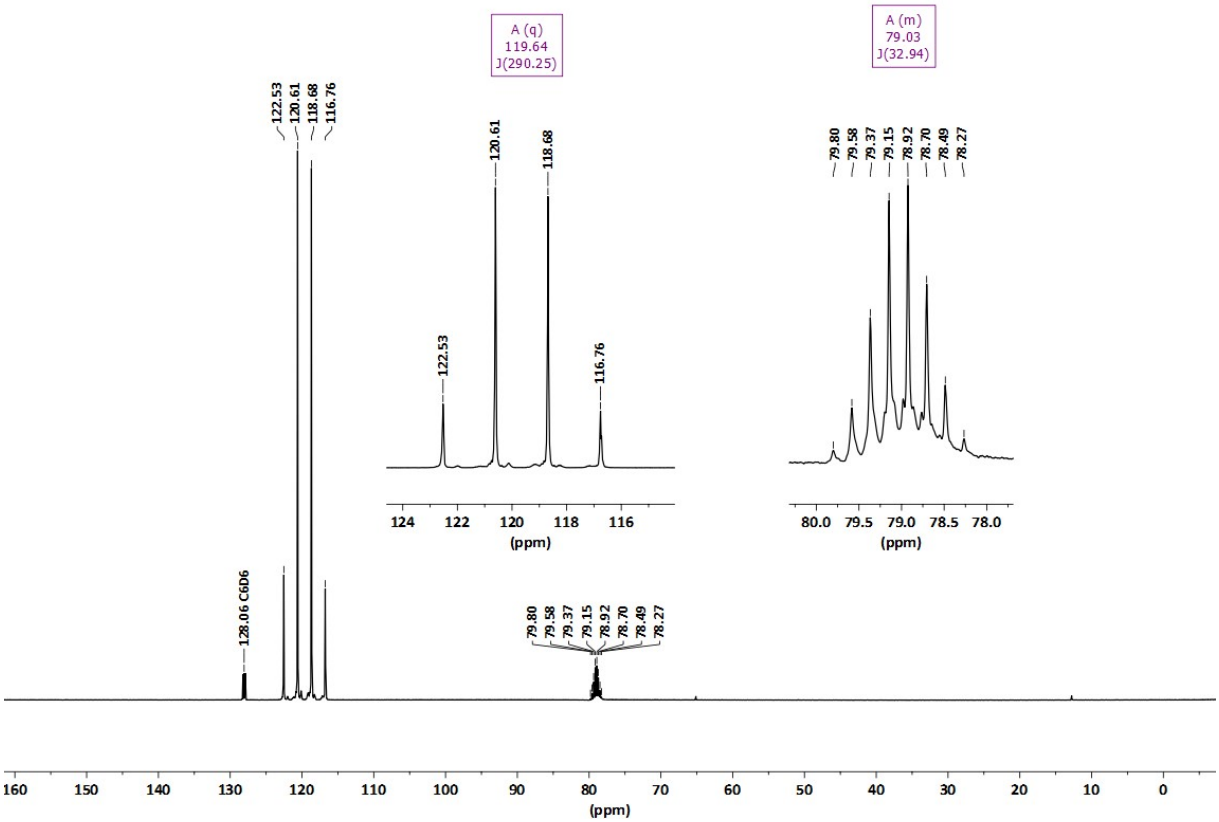

Figure S2. ^{13}C–$\{^{1}$H$\}$–NMR spectrum (151.0 MHz, C_6D_6) of $\{(F_3C)_3CO\}_3SiH$ (**1**).

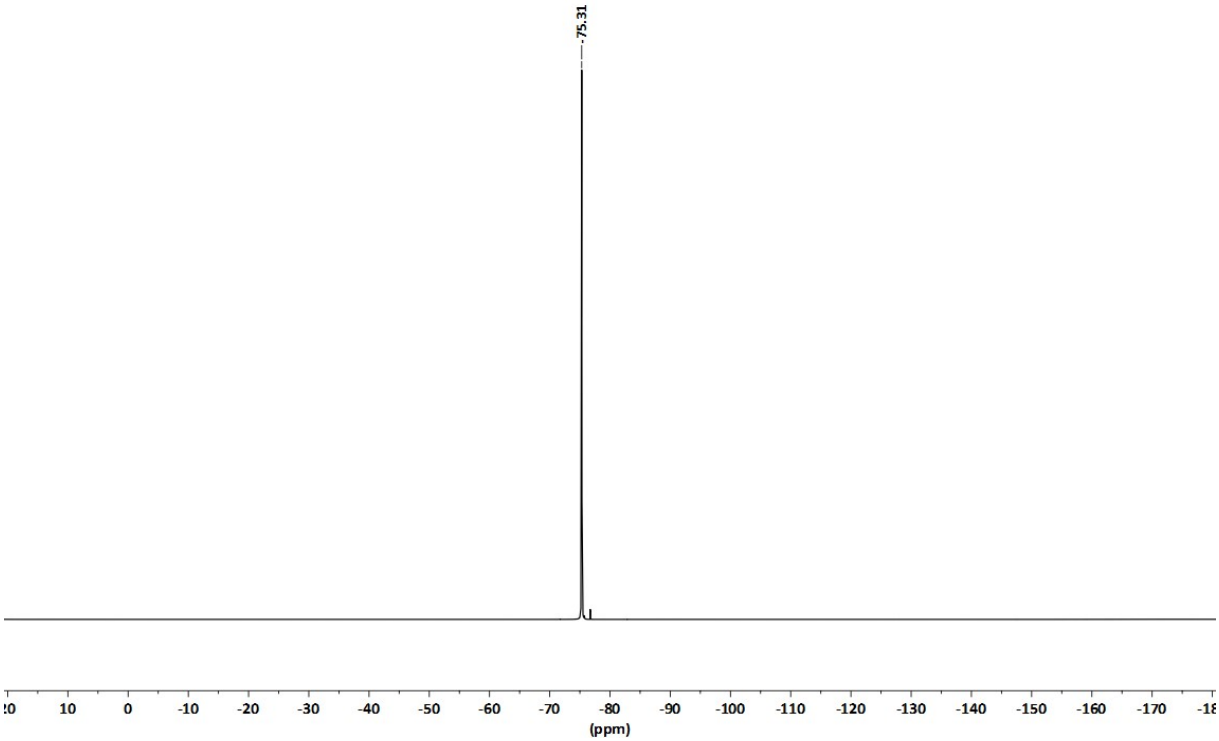

Figure S3. ^{19}F–NMR spectrum (565.0 MHz, C_6D_6) of $\{(F_3C)_3CO\}_3SiH$ (**1**).

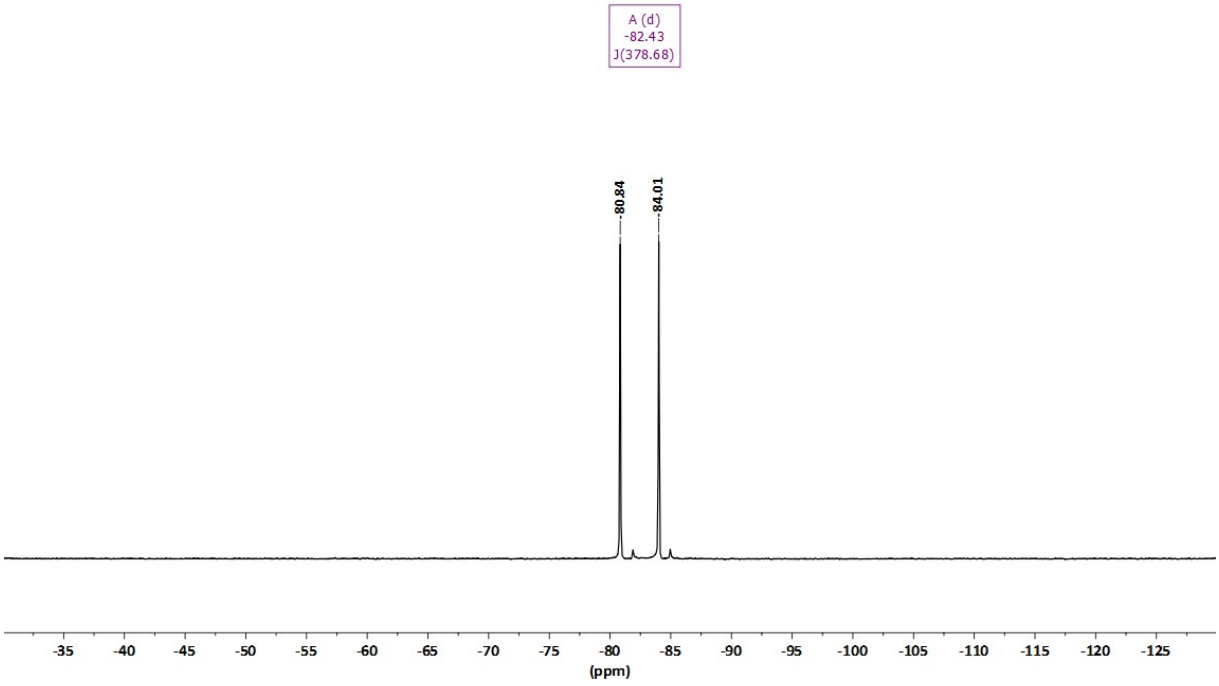

Figure S4. ^{29}Si–DEPT45–NMR spectrum (119.2 MHz, $CDCl_3$) of $\{(F_3C)_3CO\}_3SiH$ (**1**).

IR and Raman spectra of 1

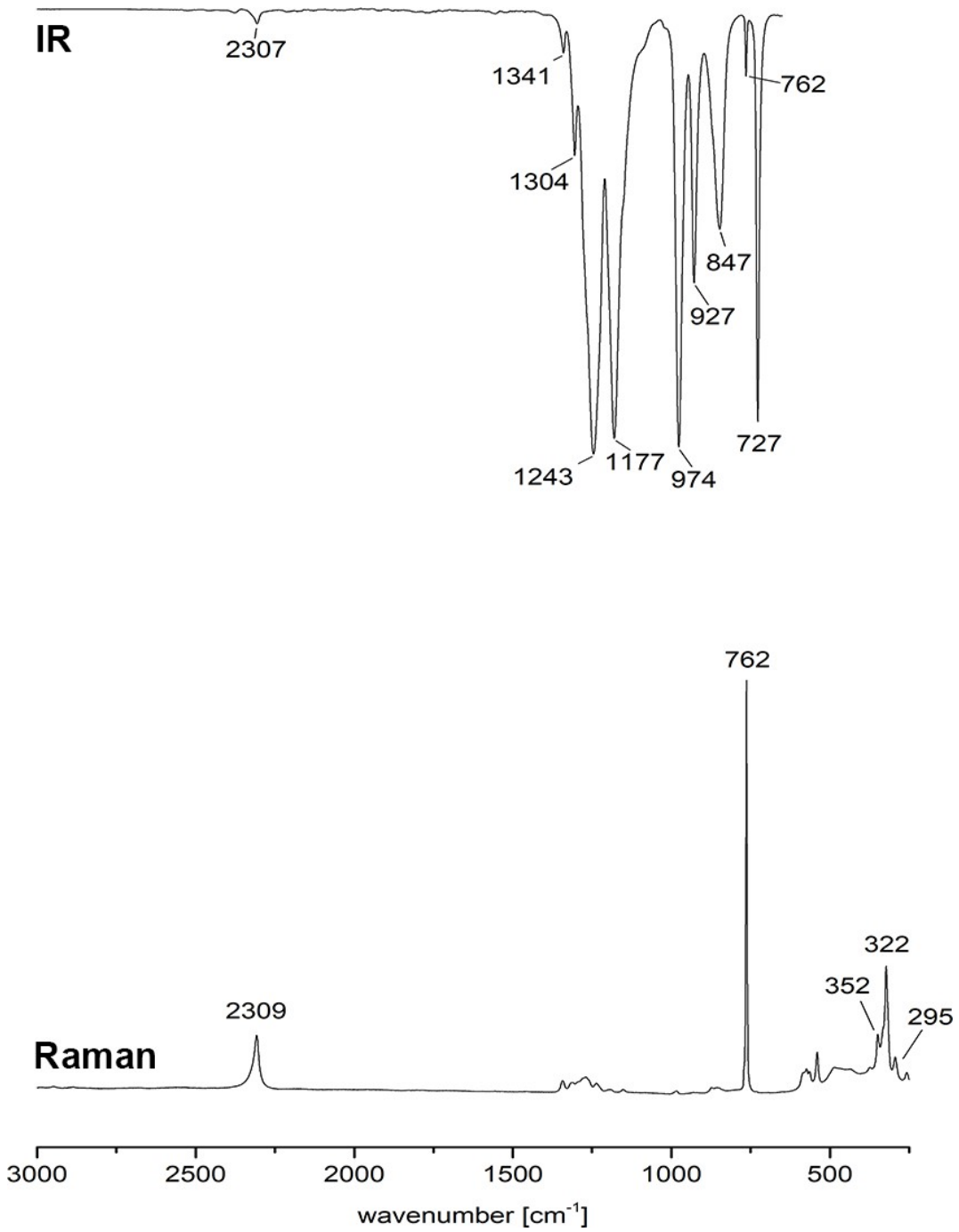

Figure S5. IR and Raman spectra of $\{(F_3C)_3CO\}_3SiH$ (**1**).

NMR spectra of 2

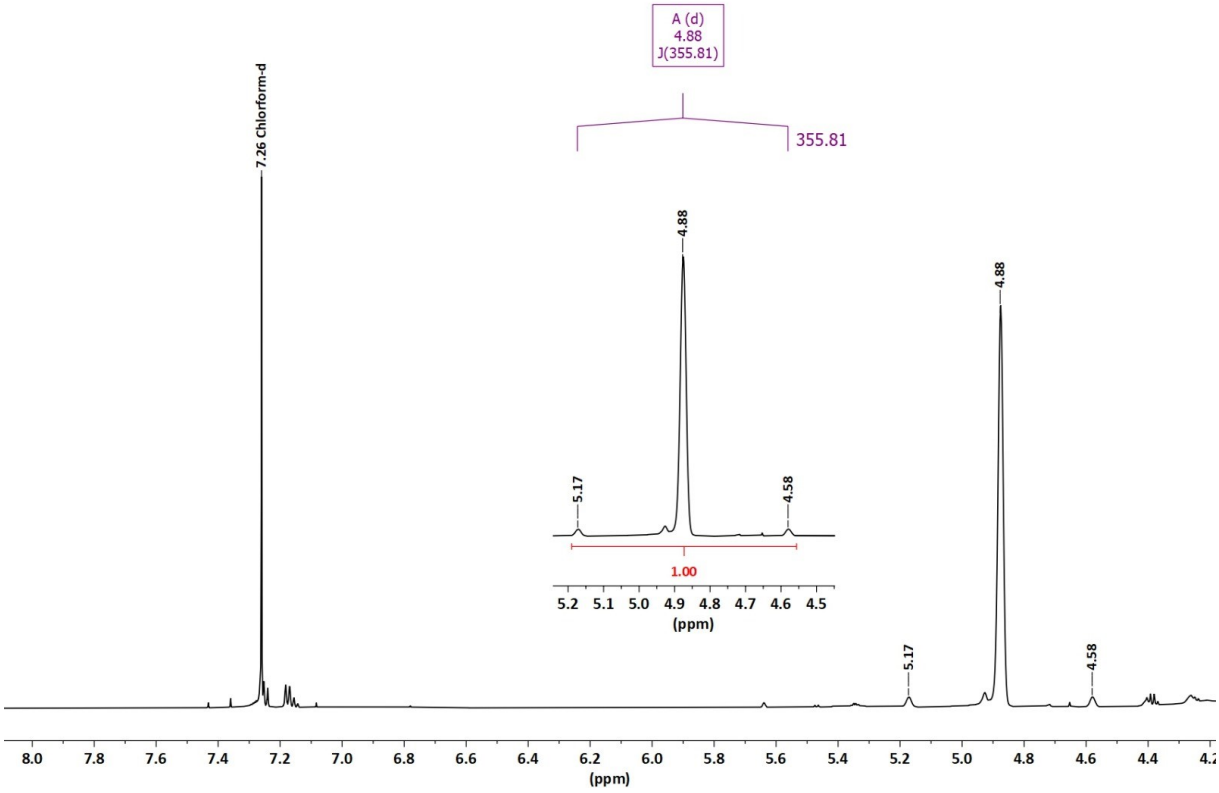

Figure S6. ^{1}H–NMR spectrum (600.2 MHz, $CDCl_3$) of $\{(F_5C_6)_3CO\}_2SiHCl$ (**2**).

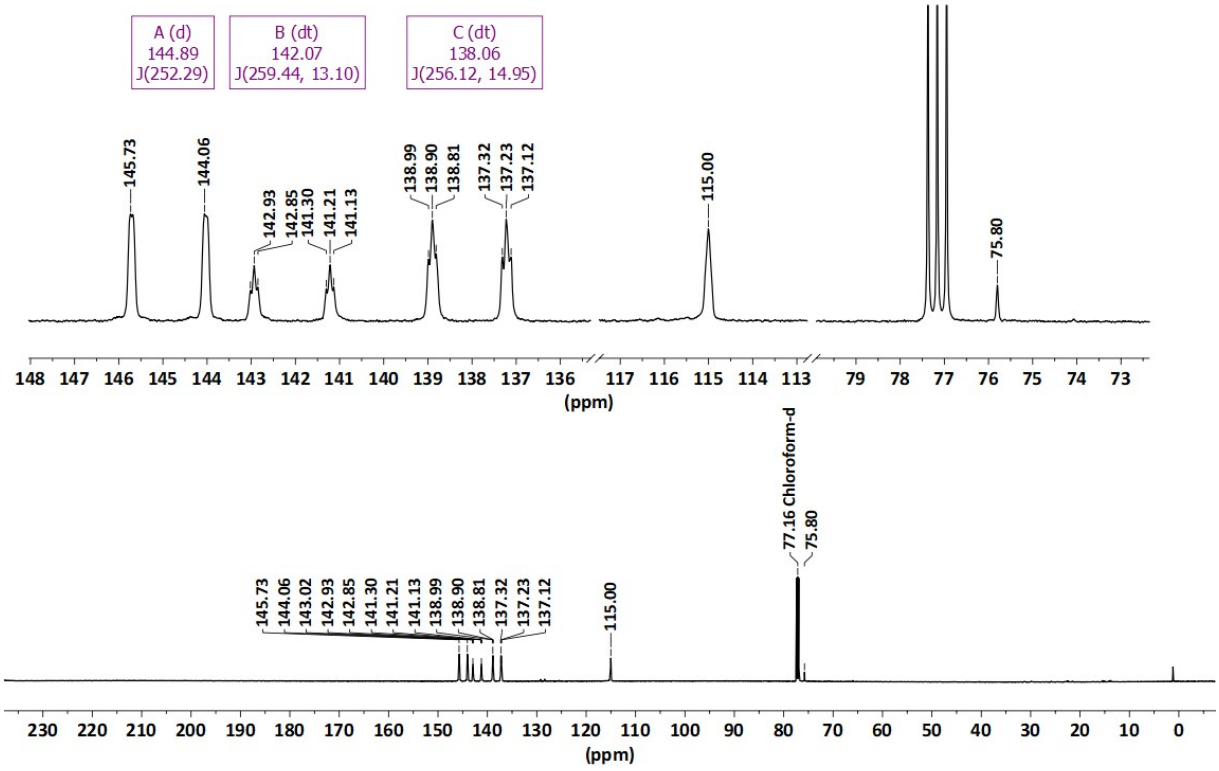

Figure S7. ^{13}C–NMR spectrum (150.9 MHz, $CDCl_3$) of $\{(F_5C_6)_3CO\}_2SiHCl$ (**2**).

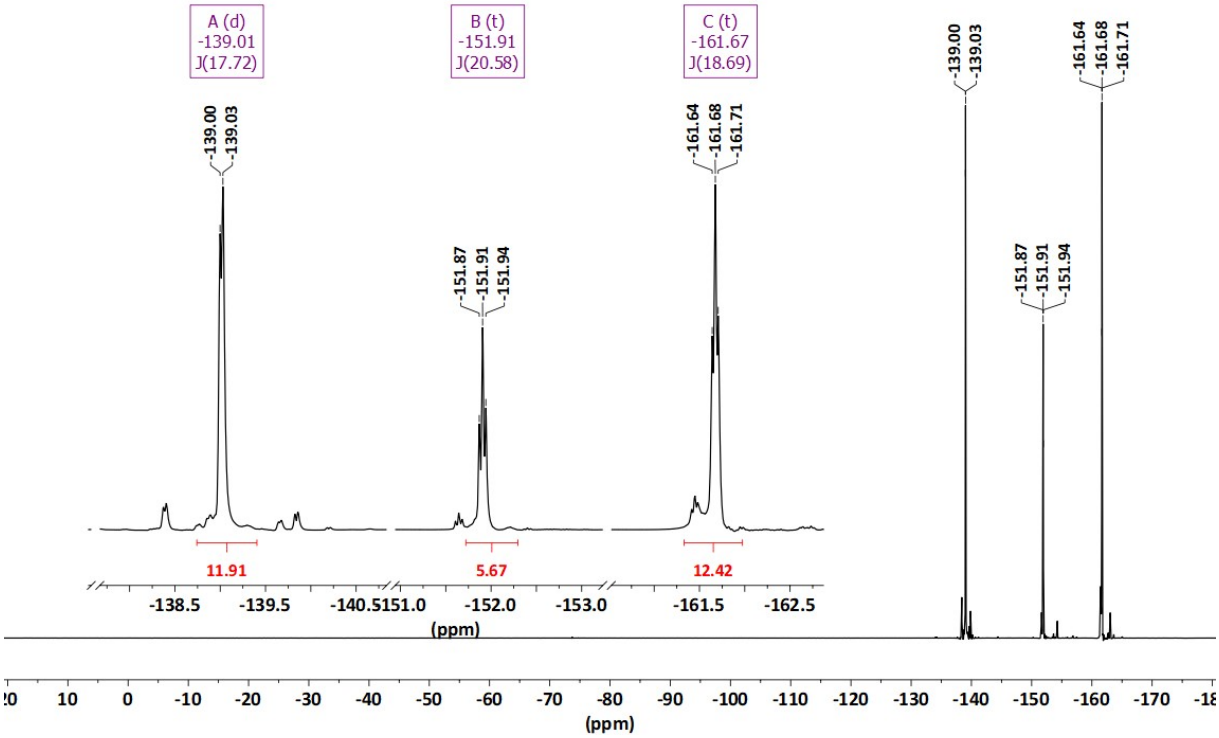

Figure S8. ^{19}F–NMR spectrum (565.0 MHz, $CDCl_3$) of $\{(F_5C_6)_3CO\}_2SiHCl$ (**2**).

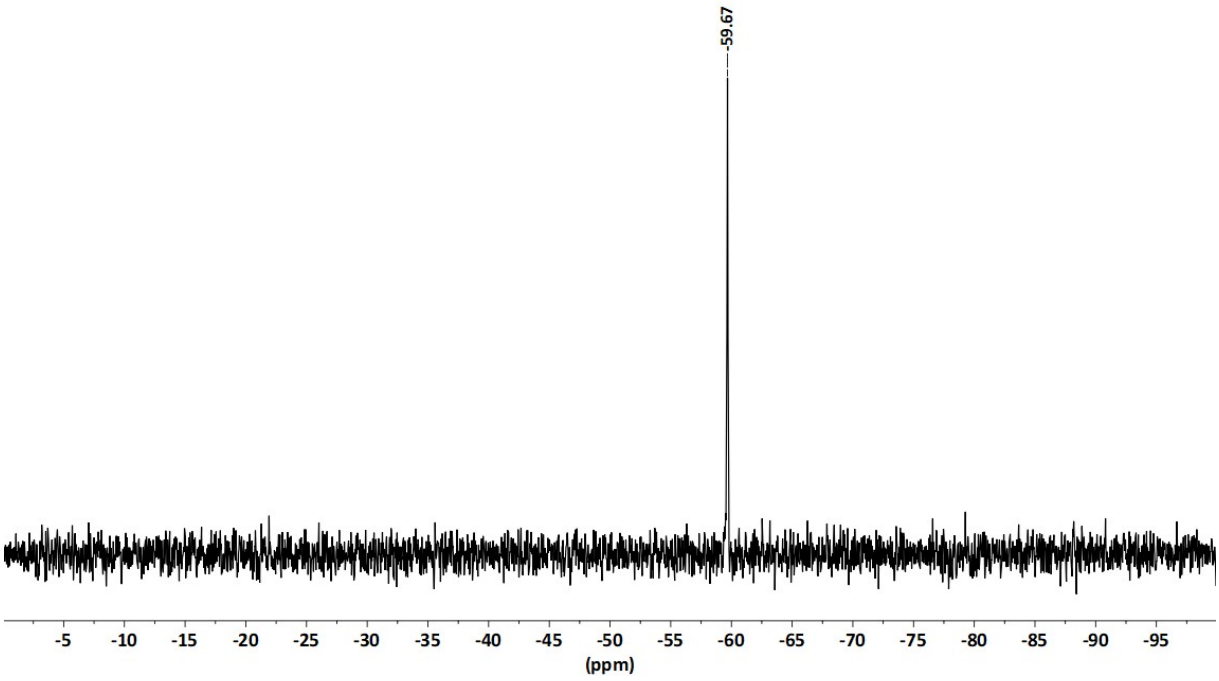

Figure S9. ^{29}Si–NMR spectrum (119.2 MHz, $CDCl_3$) of $\{(F_5C_6)_3CO\}_2SiHCl$ (**2**).

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IR spectrum of 2

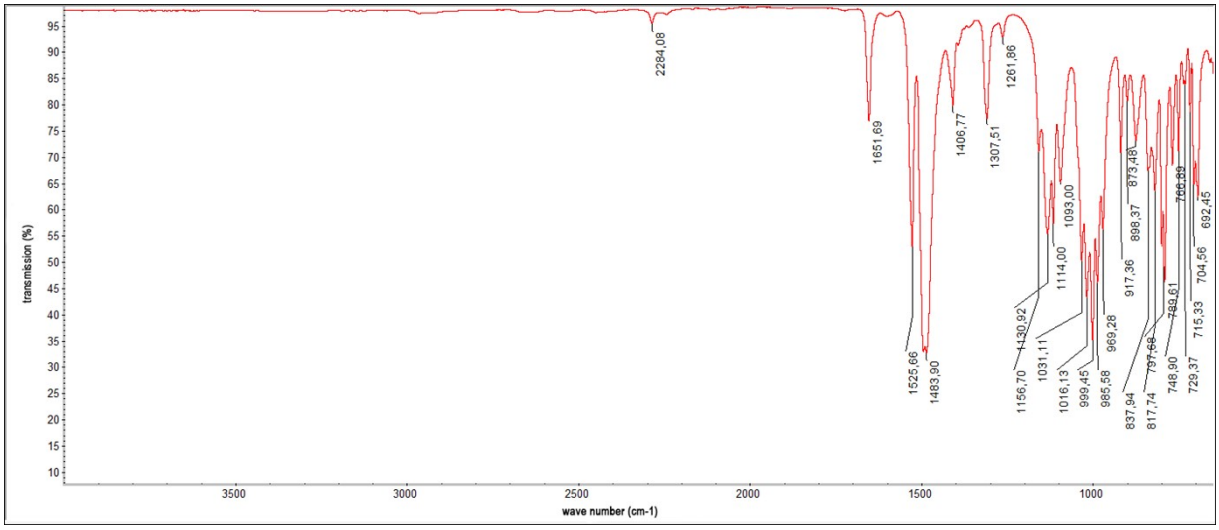

Figure S10. IR spectrum of $\{(F_5C_6)_3CO\}_2SiHCl$ (**2**).

Supporting Information

Crystallographic Data of 1 and 2

Table S1. Crystal data and structure refinement of **1** after IAM and **2** after HAR.

	1	**2**
Formula	$C_{12}HF_{27}O_3Si$	$C_{38}HClF_{30}O_2Si$
Formula weight, g mol^{-1}	734.18	1122.92
Crystal system	trigonal	monoclinic
Crystal size, mm	0.29 × 0.26 × 0.22	0.31 × 0.19 × 0.07
Space group	$P\bar{3}$	$P2_1/n$
a, Å	10.4987(3)	13.2008(4)
b, Å	10.4987(3)	14.2304(4)
c, Å	11.6734(4)	20.1079(6)
α, º	90	90
β, º	90	103.8710(10)
γ, º	120	90
V, Å^3	1114.29(7)	3667.17(19)
Z	2	4
Temperature, K	120	100
ρ_{calcd}, Mg m^{-3}	2.188	2.034
μ (Mo *K*α), mm^{-1}	0.348	0.331
F(000)	708	2187
θ range, deg	2.24 to 30.50	2.09 to 28.28
Index ranges	–14 ≤ h ≤ 14	–18 ≤ h ≤ 18
	–14 ≤ k ≤ 14	–20 ≤ k ≤ 20
	–16 ≤ l ≤ 16	–28 ≤ l ≤ 28
No. of reflns collected	53400	120588
Completeness to θ_{max}	99.6%	99.9%
No. indep. Reflns	2264	9084
No. obsd reflns with($I>2\sigma(I)$)	1881	7687
No. refined params	336	667
GooF (F^2)	1.032	1.072
R_1 (F) ($I > 2\sigma(I)$)	0.0298	0.0198
wR_2 (F^2) (all data)	0.0925	0.0369
Largest diff peak/hole, e Å^{-3}	0.190 / –0.165	0.310 / –0.312
CCDC number	2127793	2127794

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Computational Data

Table S2. Topological and integrated bond properties from AIM and ELI-D of **1**, **2**, **1a**, **2a**, Me_3SiH, $(Cl_3Si)_3SiH$ and $(C_2F_5)_3SiH$.

Contact or basin	d [Å]	ρ(r) [eÅ^{-3}]	$\nabla^2\rho(r)$ [eÅ^{-5}]	ε	G/ρ(r) [a.u.]	H/ρ(r) [a.u.]	δ(Si|X)	N_{ELI} [e]
1								
Si-H	1.459	0.91	4.2	0.00	1.04	–0.71	0.47	
Si-O1	1.639	0.92	21.7	0.05	2.06	–0.41	0.33	1.49
Si-O2	1.643	0.91	21.4	0.05	2.05	–0.41	0.34	1.60
Si-O3	1.640	0.92	21.6	0.05	2.05	–0.41	0.34	1.57
LP_H								2.02
LP_O1								4.92
LP_O2								4.82
LP_O3								4.84
2								
Si-H	1.463	0.89	4.5	0.02	1.04	–0.69	0.47	
Si-Cl	2.047	0.69	5.7	0.04	1.14	–0.56	0.41	1.59
Si-O1	1.637	0.92	22.0	0.05	2.06	–0.39	0.36	1.56
Si-O2	1.638	0.93	21.8	0.05	2.04	–0.40	0.37	1.57
LP_H								2.02
LP_O1								4.89
LP_O2								4.87
LP_Cl								6.33
Me_3SiH								
Si-H	1.495	0.80	4.4	0.00	1.02	–0.63	0.48	
$(Cl_3Si)_3SiH$								
Si-H	1.486	0.80	4.5	0.00	1.02	–0.63	0.68	
$(C_2F_5)_3SiH$								
Si-H	1.473	0.86	4.4	0.01	1.03	–0.67	0.54	

Table S2 cont. Topological and integrated bond properties from AIM and ELI-D of **1**, **2**, **1a**, **2a**, Me_3SiH, $(Cl_3Si)_3SiH$ and $(C_2F_5)_3SiH$.

Contact or basin	d [Å]	ρ(r) [eÅ^{-3}]	$\nabla^2\rho(r)$ [eÅ^{-5}]	ε	G/ρ(r) [a.u.]	H/ρ(r) [a.u.]	δ(Si|X)	N_{ELI} [e]
1a								
Si-O1	1.782	0.67	11.9	0.04	1.61	–0.36	0.44	1.32
Si-O2	1.781	0.67	11.9	0.04	1.61	–0.36	0.44	1.32
Si-O3	1.781	0.67	11.9	0.04	1.62	–0.36	0.44	1.32
LP_O1								4.99
LP_O2								4.99
LP_O3								4.99
LP_Si								2.04
2a								
Si-O1	1.823	0.57	10.1	0.04	1.45	–0.21	0.46	
Si-O2	1.787	0.59	12.0	0.06	1.59	–0.16	0.46	1.35
Si-Cl	2.235	0.48	1.8	0.14	0.73	–0.47	0.56	1.14
LP_O1								6.28
LP_O2								4.99
LP_Si								2.02
LP_Cl								6.51

Table S3. AIM derived atomic charges [in e] of **1**, **2**, **1a**, **2a**, Me_3SiH, $(Cl_3Si)_3SiH$ and $(C_2F_5)_3SiH$.

Compound	q(Si)	q(H)	q(O1)	q(O2)	q(O3)	q(Cl)
1	3.19	–0.65	–1.40	–1.40	–1.39	
2	3.10	–0.66	–1.38	–1.38		–0.76
1a	1.75		–1.33	–1.33	–1.34	
2a	1.64		–1.27	–1.28		–0.76
Me_3SiH	2.84	–0.70				
$(Cl_3Si)_3SiH$	1.57	–0.62				
$(C_2F_5)_3SiH$	2.74	–0.63				

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Table S4. Calculation of Interaction Energies (kJ mol^{-1})

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	6	x, y, z	10.50	B3LYP/6-31G(d,p)	0.1	-0.0	-17.7	2.5	-13.8
	3	-x, -y, -z	8.15	B3LYP/6-31G(d,p)	0.4	-0.2	-32.8	3.4	-26.2
	3	-x, -y, -z	8.69	B3LYP/6-31G(d,p)	-0.2	-0.0	-18.4	4.3	-13.6

R is the distance between molecular centroids (mean atomic position) in Å. Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below).

Cohesive energy = ½ (–13.8 · 6 – 26.2 · 3 – 13.6 · 3) kJ mol^{-1}

Table S5. Scaling factor for benchmarked energy models

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

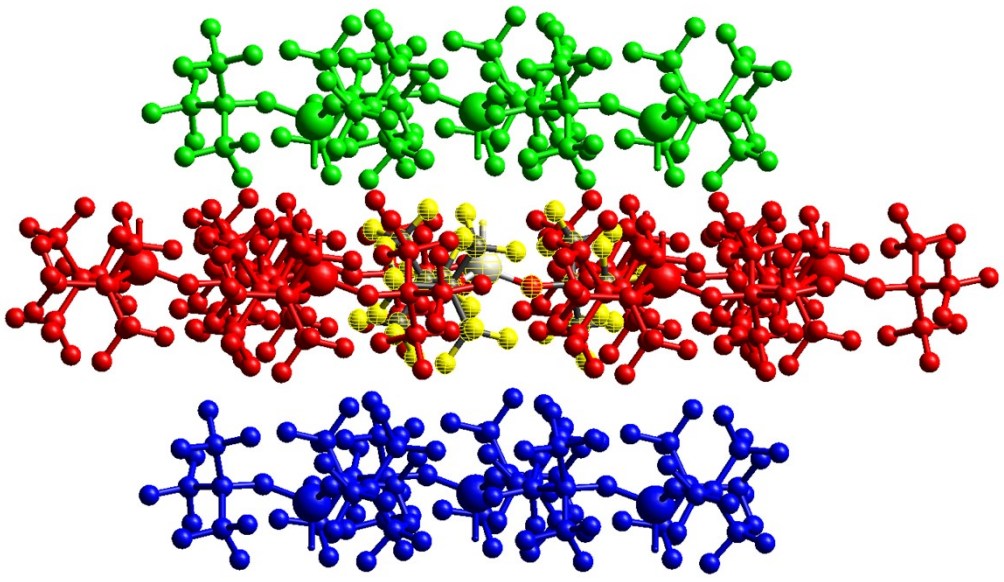

Figure S11. Cluster of symmetry-generated molecules with any atom within 3.8 Å radius around the central molecule used for estimating the cohesive energy. Colour code according to the symmetry operation given in Table S4.