Electronic Supplementary Information

Hydroperoxo double hydrogen bonding: Stabilization of hydroperoxo complexes exemplified by triphenylsilicon and triphenylgermanium hydroperoxides

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Contents

X-ray analysis

Table S1. Crystal data, data collection and refinement parameters for **1**, **2** and **3**.

	1	**2**	**3**
formula	$C_{18}H_{16}O_2Si$	$C_{18}H_{16}Ge_1O_2$	$C_{36}H_{30}Ge_2O_2$
fw	292.40	336.90	639.78
colour, habit	colourless, prism	colourless, plate	colourless, plate
cryst size, mm	0.40×0.20×0.05	0.40×0.25×0.01	0.60×0.50×0.05
cryst syst	triclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*-1
a, Å	9.8022(3)	9.8517(3)	8.6748(2)
b, Å	11.3939(3)	11.4503(3)	9.4769(2)
c, Å	14.9070(4)	15.0058(4)	11.2572(3)
α, deg	88.3116(11)	88.4868(9)	65.780(1)
β, deg	89.7934(11)	89.8466(10)	88.888(1)
γ, deg	65.7475(10)	65.3416(9)	66.382(1)
V, Å^3	1517.23(7)	1537.77(7)	761.58(3)
Z	4	4	1
ρ_{calc}, g/cm^3	1.280	1.455	1.395
μ, mm^{-1}	0.156	1.993	2.003
F(000)	616	688	326
θ range, deg	2.28 to 27.00	2.27 to 27.00	2.01 to 27.99
total no. of reflns	17101	15171	8232
unique reflns, R_{int}	6582, 0.0281	6668, 0.0257	3637, 0.0244
reflns. with $I>2\sigma(I)$	5395	5425	3432
no. of variables	507	507	241
R_1 ($I>2\sigma(I)$)	0.0412	0.0394	0.0237
wR_2 (all data)	0.0971	0.1052	0.0628
GoF on F^2	1.037	1.069	1.066
largest diff peak/hole, e/Å^3	0.366 / -0.251	0.939 / -0.590	0.394 / -0.374

X-ray powder diffraction

Triphenylsilyl hydroperoxide Ph_3SiOOH (**1**), triphenylgermyl hydroperoxide Ph_3GeOOH (**2**) and bis(triphenylgermyl)peroxide $(Ph_3GeO)_2$ (**3**) crystals were carefully ground in a mortar. Resulting powders were placed to low background Si sample holder. X-ray powder diffractograms of **1-3** are presented in the **Figure S1a-c** respectively. The calculated diffractograms were obtained using Mercury CCDC software. The peak position mismatch caused by different temperatures of X-ray analysis (150 K) and powder diffraction (298 K) experiments.

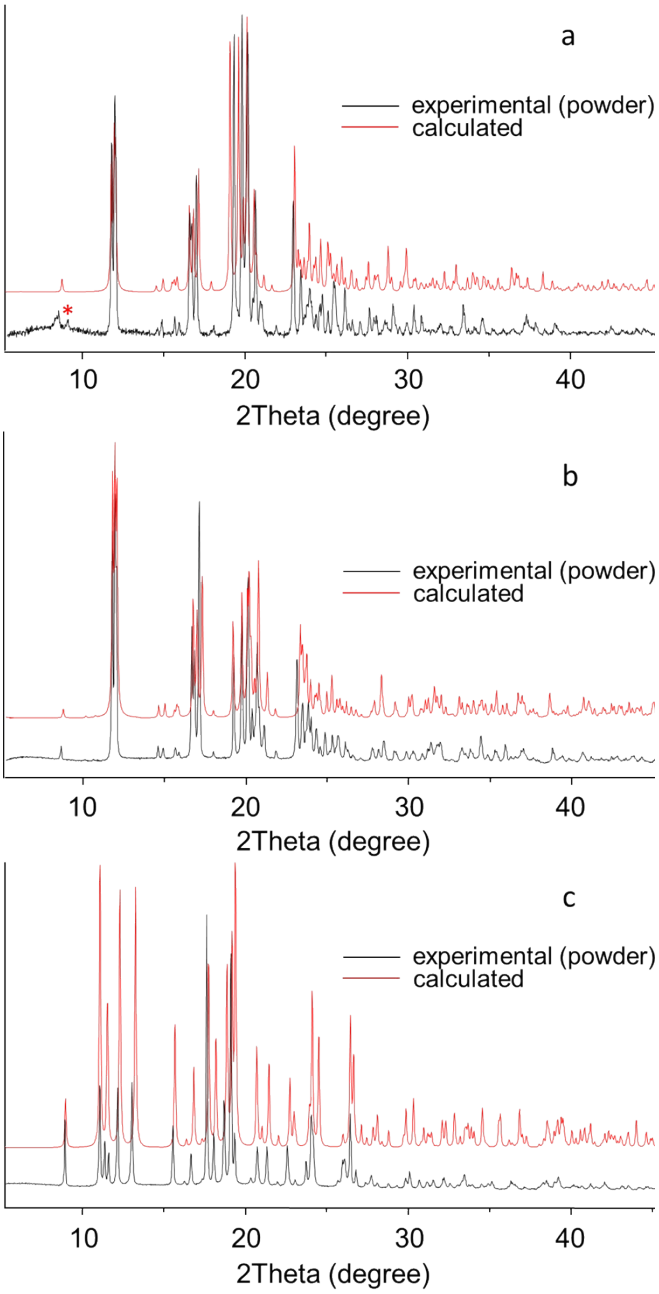

Figure S1. X-ray powder diffractograms of Ph_3SiOOH, **1** (a); Ph_3GeOOH, **2** (b) and $(Ph_3GeO)_2$, **3** (c). * - unidentified peak. Calculated powder diffractograms were obtained using Mercury (CCDC) software.

Graphical representations of the Rietweld refinement results obtained for **1**-**3** are presented in **Figure S2a-c,** respectively. Zero error (mm) and unit cell parameters were refined, spherical harmonics was applied for preferred orientation correction. Sample **1** contains small amount of an unidentified phase after grinding which can be attributed to the possible decomposition product. Rietweld refinement results presented in Table S2.

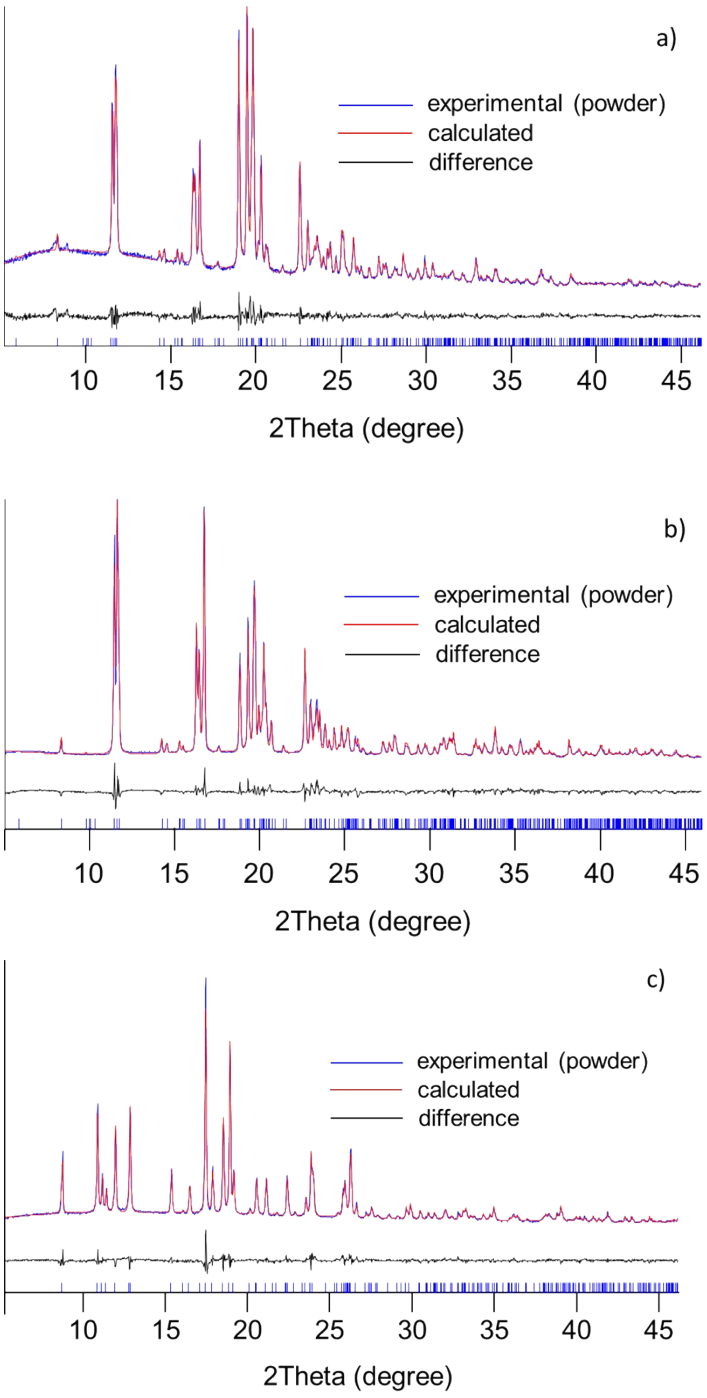

Figure S2. Rietweld refinement results for Ph_3SiOOH, **1** (a); Ph_3GeOOH, **2** (b) and $(Ph_3GeO)_2$, **3** (c). the vertical bars show the calculated positions of the Bragg reflections.

Table S2. Rietweld refinement results for **1-3.**

Compound	Results
1	**R-Values** Rexp : 4.22 Rwp : 6.20 Rp : 4.86 GOF : 1.47 Rexp`: 10.27 Rwp`: 15.08 Rp` : 15.85 DW : 1.17 **Quantitative Analysis - Rietveld** Phase 1 : Structure 100.000 % **Background** One on X 0(2400) Chebychev polynomial, Coefficient 0 440(120) 1 -450(140) 2 173(83) 3 -2(48) **Instrument** Primary radius (mm) 280 Secondary radius (mm) 280 **Corrections** Zero error -0.00562(87) LP Factor 0 **Structure 1** Phase name Structure R-Bragg 1.542 Spacegroup P-1 Scale 0.0002073(24) Cell Mass 1169.640 Cell Volume (Å^3) 1562.46(14) Wt% - Rietveld 100.000 Crystallite Size Cry size Lorentzian (nm) 10000(52000) Crystal Linear Absorption Coeff. (1/cm) 13.3822(12) Crystal Density (g/cm^3) 1.24306(11) Preferred Orientation Spherical Harmonics Order 8 y00 1 y20 -0.160(27) y21m 0.069(21) y21p 0.138(32) y22m -0.009(20) y22p -0.008(22) y40 0.118(31) y41m 0.107(32) y41p 0.000(41) y42m 0.026(30) y42p -0.083(22) y43m -0.184(25) y43p 0.075(26) y44m -0.152(20) y44p 0.193(29) y60 -0.0081(31) y61m -0.302(33) y61p 0.040(52) y62m 0.016(37) y62p 0.014(24)

Compound	Results
	y63m 0.165(38) y63p 0.024(31) y64m 0.050(19) y64p 0.156(28) y65m 0.180(26) y65p -0.025(30) y66m 0(3900000) y66p 0(3900000) y80 -0.085(42) y81m 0.107(38) y81p -0.138(51) y82m 0.002(37) y82p 0.133(32) y83m -0.156(31) y83p 0.186(35) y84m -0.045(24) y84p 0.003(26) y85m 0.146(25) y85p -0.096(34) y86m 0.104(28) y86p 0.031(18) y87m 0.181(28) y87p -0.074(27) y88m -0.348(40) y88p -0.096(17) Lattice parameters a (Å) 9.81058(48) b (Å) 11.58381(63) c (Å) 14.99700(75) alpha (°) 88.7575(26) beta (°) 89.4753(42) gamma (°) 66.4890(28)
2	**R-Values** Rexp : 1.98 Rwp : 4.01 Rp : 3.03 GOF : 2.03 Rexp`: 4.73 Rwp`: 9.62 Rp` : 8.33 DW : 0.89 **Quantitative Analysis - Rietveld** Phase 1 : Structure 100.000 % **Background** One on X 12000(11000) Chebychev polynomial, Coefficient 0 1430(580) 1 -170(670) 2 -450(390) 3 430(230) **Instrument** Primary radius (mm) 280 Secondary radius (mm) 280 Linear PSD 2Th angular range (°) 2.915693 FDS angle (°) 0.34 Beam spill, sample length (mm) 10.5 Intensity not corrected Full Axial Convolution Filament length (mm) 12 Sample length (mm) 15 Receiving Slit length (mm) 12 Primary Sollers (°) 2.5

Compound	Results	
	Secondary Sollers (°)	2.5
	Corrections	
	Zero error	-0.002(31)
	LP Factor	0
	Structure 1	
	Phase name	Structure
	R-Bragg	1.251
	Spacegroup	P-1
	Scale	0.001039(11)
	Cell Mass	639.855
	Cell Volume (Å^3)	785.642(47)
	Wt% - Rietveld	100.000
	Crystallite Size	
	Cry size Lorentzian (nm)	191.9(23)
	Crystal Linear Absorption Coeff. (1/cm)	25.8535(16)
	Crystal Density (g/cm^3)	1.352404(81)
	Preferred Orientation Spherical Harmonics	
	Order	8
	y00	1
	y20	0.475(25)
	y21m	0.016(27)
	y21p	0.190(23)
	y22m	-0.022(19)
	y22p	0.003(22)
	y40	0.540(32)
	y41m	-0.128(39)
	y41p	-0.131(26)
	y42m	0.067(24)
	y42p	0.156(27)
	y43m	0.089(18)
	y43p	-0.054(28)
	y44m	0.019(26)
	y44p	0.009(22)
	y60	0.0389(33)
	y61m	-0.021(49)
	y61p	0.185(32)
	y62m	0.005(29)
	y62p	-0.027(34)
	y63m	-0.063(22)
	y63p	0.022(33)
	y64m	-0.006(25)
	y64p	-0.101(26)
	y65m	-0.020(20)
	y65p	0.062(26)
	y66m	0(470000)
	y66p	0(470000)
	y80	0.229(36)
	y81m	0.176(45)
	y81p	-0.016(34)
	y82m	-0.154(33)
	y82p	0.160(38)
	y83m	0.229(30)
	y83p	0.130(34)
	y84m	0.022(24)
	y84p	0.001(27)
	y85m	-0.011(27)

Compound	Results
	y85p -0.017(31) y86m 0.110(30) y86p -0.016(22) y87m -0.008(26) y87p 0.035(21) y88m -0.012(30) y88p -0.029(21) Lattice parameters a (Å) 8.86418(30) b (Å) 9.50865(27) c (Å) 11.37092(27) alpha (°) 65.8214(25) beta (°) 89.2051(22) gamma (°) 66.0565(22)
3	**R-Values** Rexp : 1.48 Rwp : 4.64 Rp : 3.49 GOF : 3.13 Rexp`: 3.93 Rwp`: 12.31 Rp` : 13.04 DW : 0.54 **Quantitative Analysis - Rietveld** Phase 1 : Structure 100.000 % **Background** One on X 0.0001 Chebychev polynomial, Coefficient 0 3281.104 1 -1131.11 2 -50.1102 3 111.481 **Instrument** Primary radius (mm) 280 Secondary radius (mm) 280 Linear PSD 2Th angular range (°) 2.915693 FDS angle (°) 0.34 Beam spill, sample length (mm) 10.5 Intensity not corrected Full Axial Convolution Filament length (mm) 12 Sample length (mm) 15 Receiving Slit length (mm) 12 Primary Sollers (°) 2.5 Secondary Sollers (°) 2.5 **Corrections** Zero error -0.02491449 LP Factor 0 **Structure 1** Phase name Structure R-Bragg 1.896 Spacegroup P-1 Scale 0.000685835113 Cell Mass 1347.739 Cell Volume (Å^3) 1584.79438 Wt% - Rietveld 100.000

Compound	Results	
	Crystallite Size	
	Cry size Lorentzian (nm)	230.9
	Crystal Linear Absorption Coeff. (1/cm)	26.405
	Crystal Density (g/cm^3)	1.412
	Preferred Orientation Spherical Harmonics	
	Order	8
	y00	0
	y20	0
	y21m	0
	y21p	0
	y22m	0
	y22p	0
	y40	0
	y41m	0
	y41p	0
	y42m	0
	y42p	0
	y43m	0
	y43p	0
	y44m	0
	y44p	0
	y60	0
	y61m	0
	y61p	0
	y62m	0
	y62p	0
	y63m	0
	y63p	0
	y64m	0
	y64p	0
	y65m	0
	y65p	0
	y66m	0
	y66p	0
	y80	0
	y81m	0
	y81p	0
	y82m	0
	y82p	0
	y83m	0
	y83p	0
	y84m	0
	y84p	0
	y85m	0
	y85p	0
	y86m	0
	y86p	0
	y87m	0
	y87p	0
	y88m	0
	y88p	0
	Lattice parameters	
	a (Å)	9.8907050
	b (Å)	11.6080450
	c (Å)	15.1267971
	alpha (°)	88.67264
	beta (°)	89.59911
	gamma (°)	65.88993

Solid-state DFT calculations

The space groups and unit cell parameters of the considered two-component obtained in the single-crystal X-ray studies are fixed and structural relaxations are limited to the positional parameters of atoms. The atomic positions from experiment are used as the starting point in the solid-state DFT computations. Density functional theory computations with periodic boundary conditions (solid-state DFT) were performed in the Crystal09[1,2] software package using B3LYP in the localized basis sets 6-31G** for C,O,H atoms and 6-31G* for Si and Ge atoms. The B3LYP/6-31G** approximation provides reliable and consistent results in studying the intermolecular interactions in crystals.[3,4] The mixing coefficient of Hartree-Fock/Kohn-Sham matrices is set to 25%. Tolerance on energy controlling the self-consistent field convergence for geometry optimizations and frequencies computations is set to 10^{-8} and 10^{-10} hartree respectively. The shrinking factor of the reciprocal space net is set to 3. All the optimized structures are found to correspond to the minimum point on the potential energy surface.

Evaluation of H-bond enthalpies/energies

The optimized structures were used in B3LYP/6-31G** computations of the periodic electronic wave-functions by CRYSTAL98.[5] The quantum theory of atoms in molecules and crystals (Bader) analysis of the periodic electron density[6] is performed with TOPOND.[7] The calculation methodology is presented elsewhere.[8] The energy of the considered hydrogen bond, energy E_{HB}, is evaluated according to ref. [9] as

$$E_{HB}\ [\text{kJ mol}^{-1}] = 1124 \cdot G_b\ [\text{atomic units}], \qquad (1)$$

where G_b is the positively-defined local electronic kinetic energy density at the H···O bond critical point. Eq. (1) yields reasonable E_{HB} values for molecular crystals with intermolecular H-bonds.[10]

Table S3. Selected computed parameters of hydroperoxo double hydrogen bonding motif for **1** and **2** at the B3LYP/6-31G** level.

Compound	*d*(M-O), Å	*d*(O-O), Å	∠(O-O-H), °	∠(M-O-O-H), °	*d*(M…M), Å	*d*(O…O)/ *d*(O…H), Å	∠(O-H..O), °
1	1.770 1.773	1.473 1.471	98 99	-115.6 129.2	6.005 5.786	2.719/1.783 2.721/1.792	157.1 155.5
2	1.869 1.874	1.472 1.471	98 99	-112.2 125.5	5.881 6.103	2.714/1.774 2.722/1.786	157.9 157.0

The list of hydroperoxocomplexes

Table S4. The list of p- and d-block hydroperoxocomplexes in CSD and ICSD*.

Database Identifier, element (**M**)	Ref.
ICSD 260828, (**Sn)**	11
MAJROH, (**B)**	12
GULKED, (**Pt)**	13
HADZAQ, (**Co**)	14
NOBCIQ, (**Cu**)	15
QORKEN, (**Co**)	16
RAVKOO01, (**Pd**)	17
RECKUG, (**Pd)**	18
TAYLAH, **(Rh)**	19
TITLIT, (**Pt)**	20

* with localized proton of OOH-group.

NMR spectra

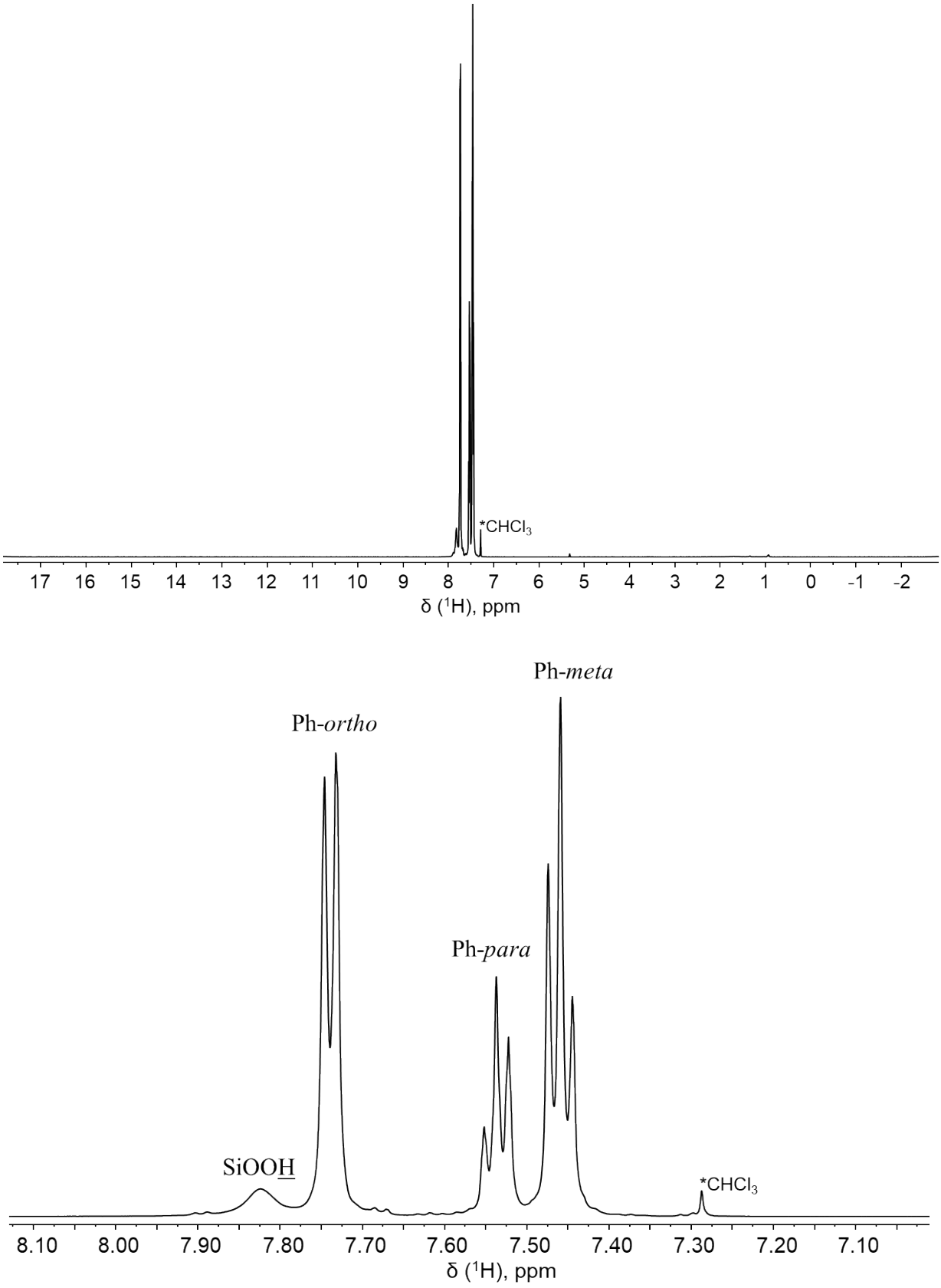

Figure S3. ^{1}H-NMR spectrum of Ph_3SiOOH in $CDCl_3$. (* solvent peaks). Lower – magnified spectrum.

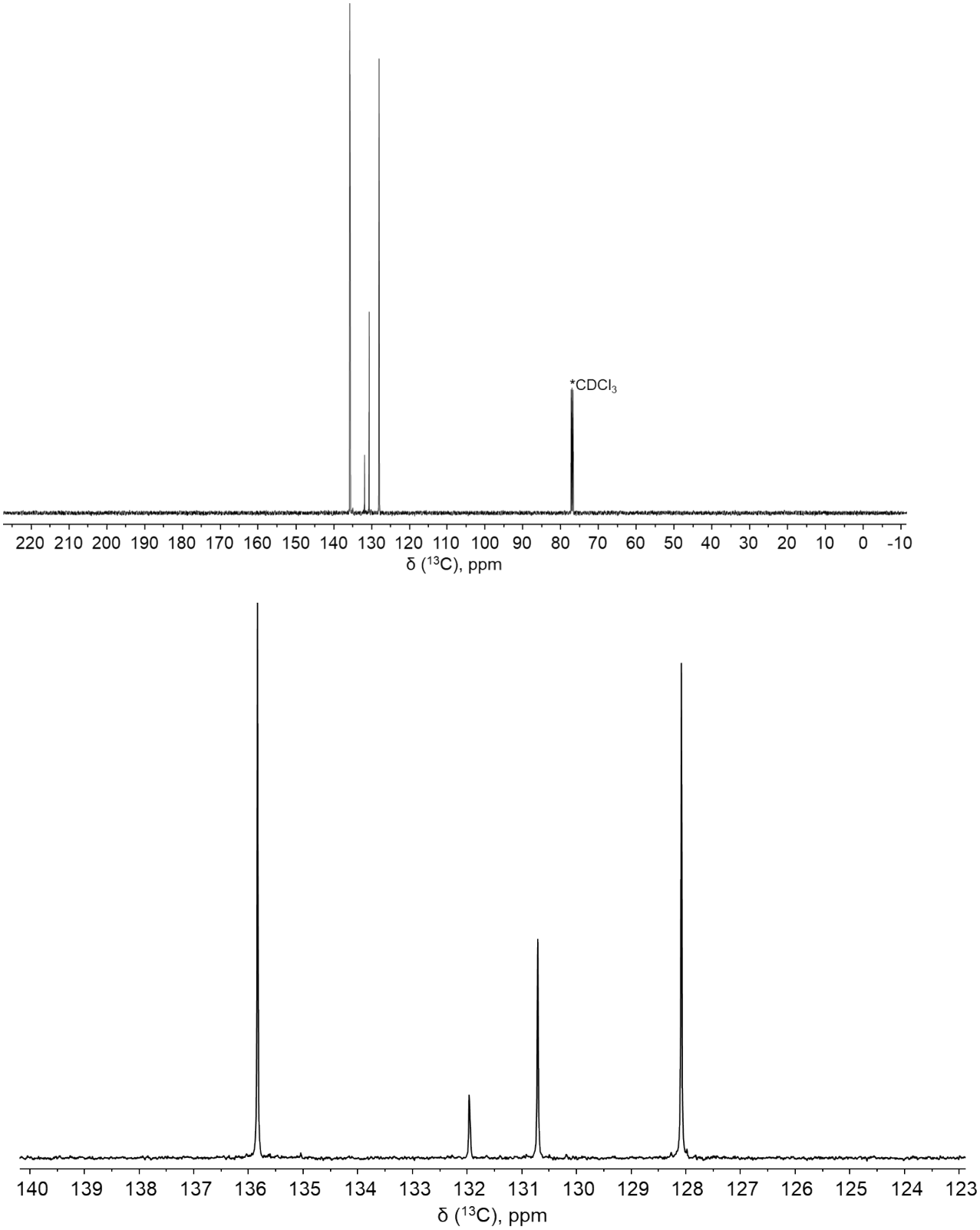

Figure S4. ^{13}C-NMR spectrum of Ph_3SiOOH in $CDCl_3$. (* solvent peaks). Lower – magnified spectrum.

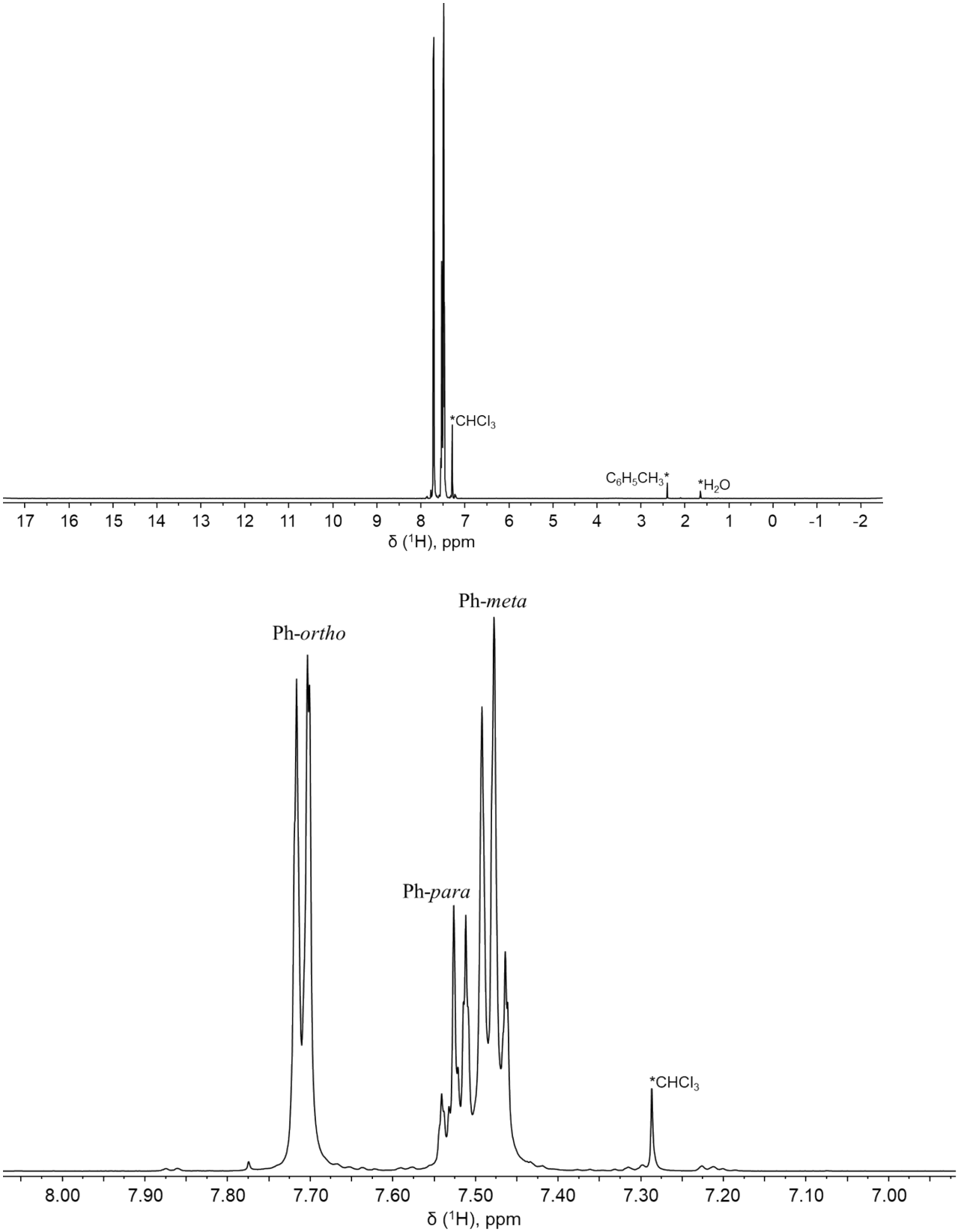

Figure S5. ^{1}H-NMR spectrum of Ph_3GeOOH in $CDCl_3$. (* solvent peaks). Lower – magnified spectrum.

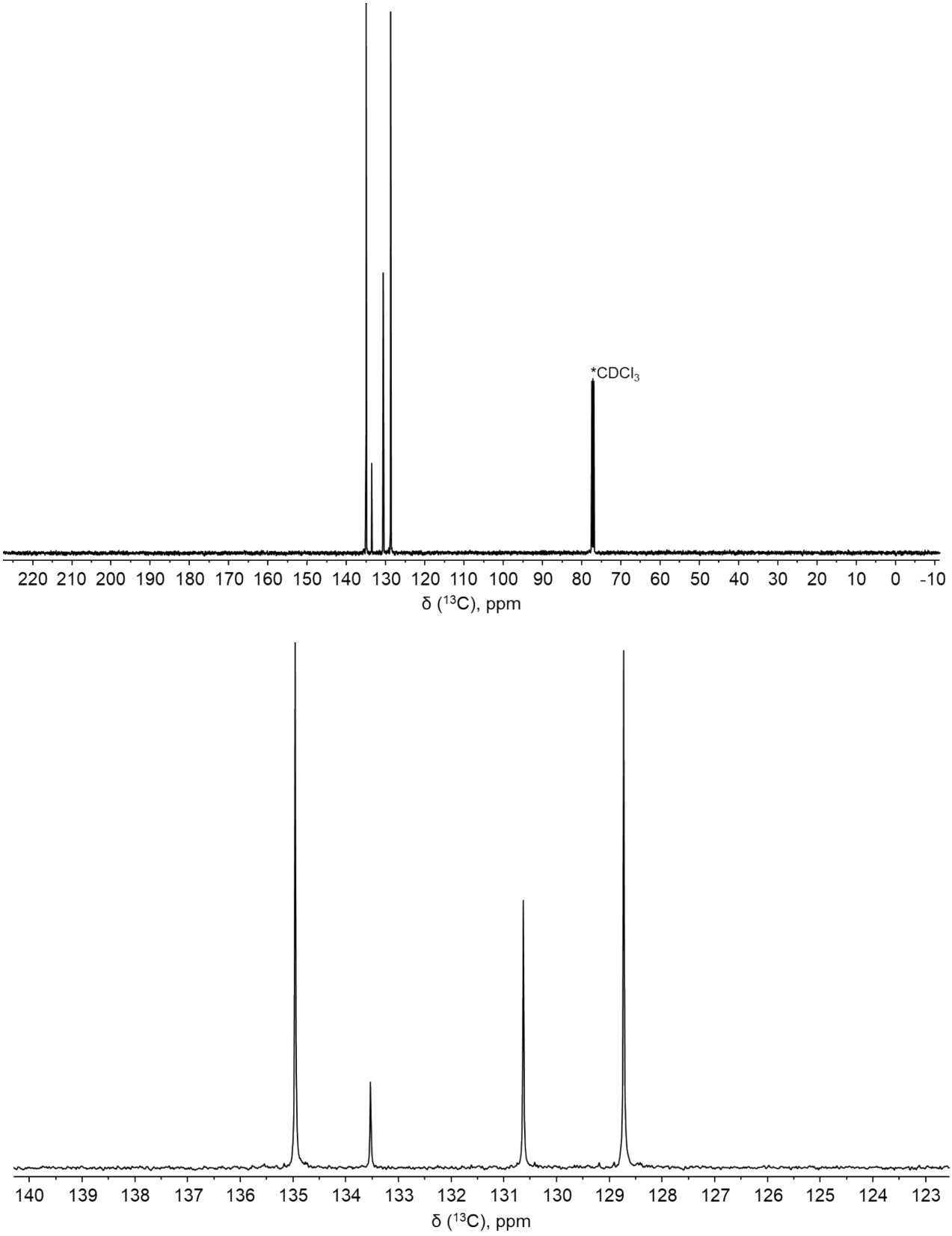

Figure S6. ^{13}C-NMR spectrum of Ph_3GeOOH in $CDCl_3$. (* solvent peaks). Lower – magnified spectrum.

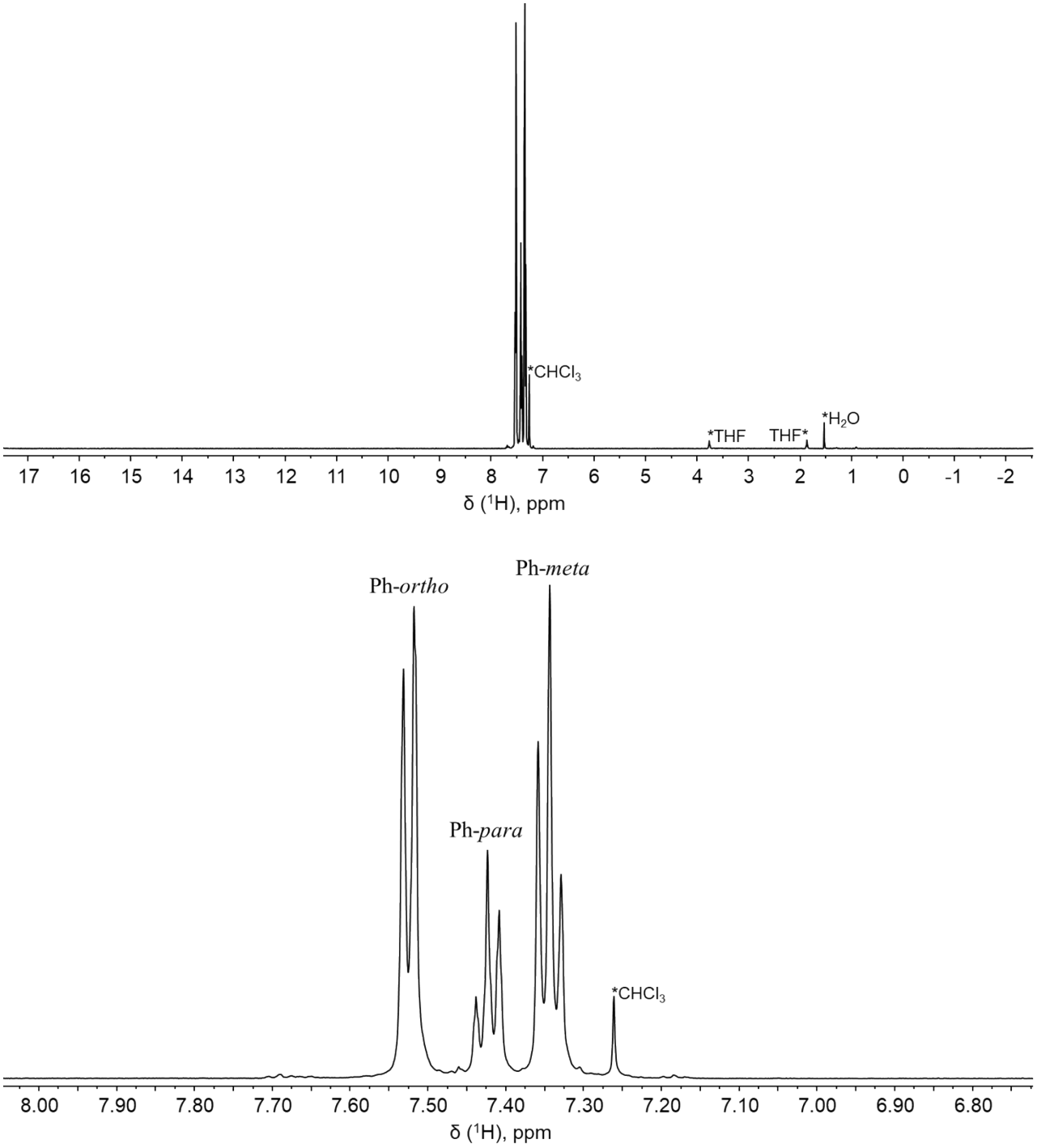

Figure S7. ^{1}H-NMR spectrum of $(Ph_3GeO)_2$ in $CDCl_3$ (* solvent peaks). Lower – magnified spectrum.

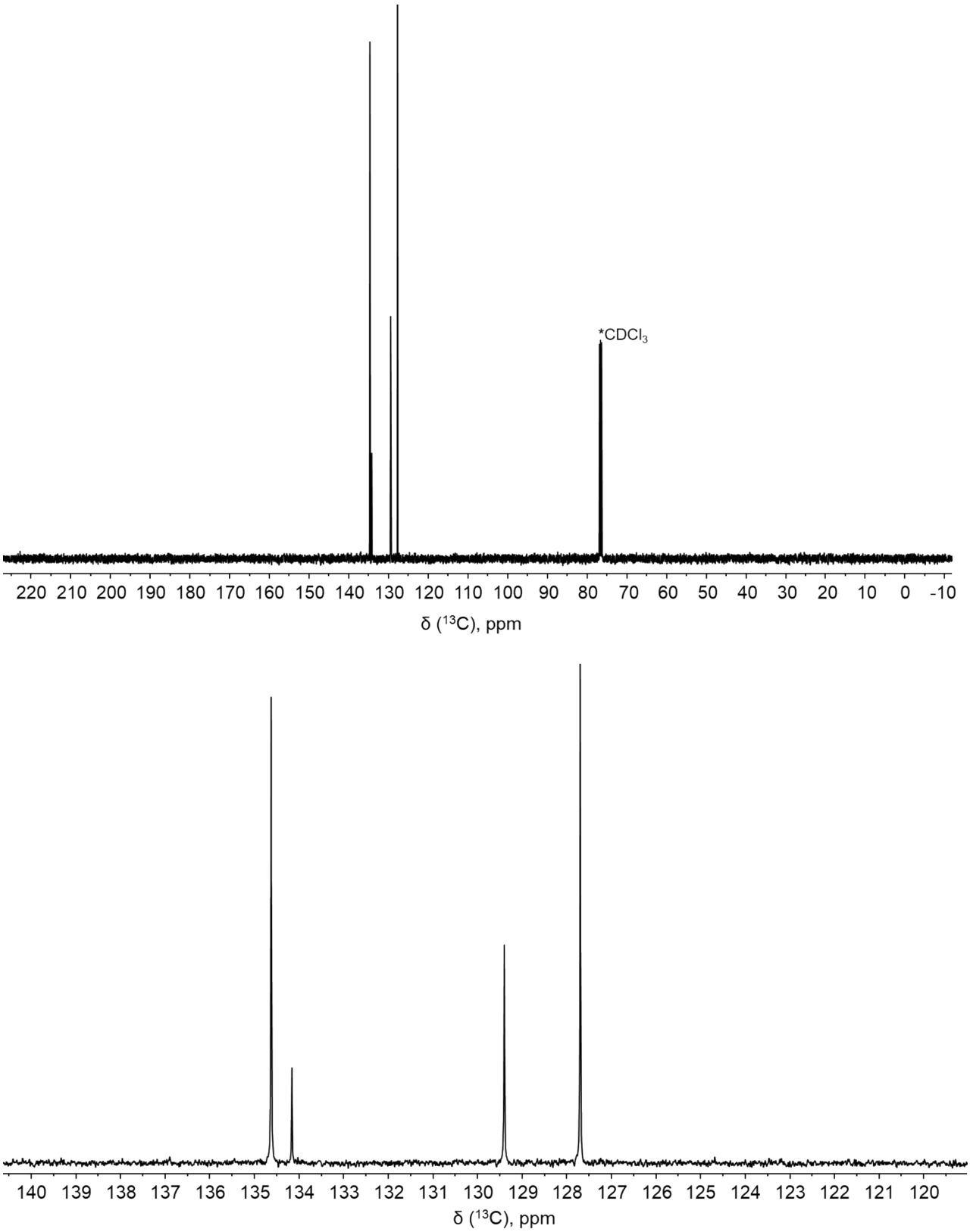

Figure S8. ^{13}C-NMR spectrum of $(Ph_3GeO)_2$ in $CDCl_3$. (* solvent peaks). Lower – magnified spectrum.

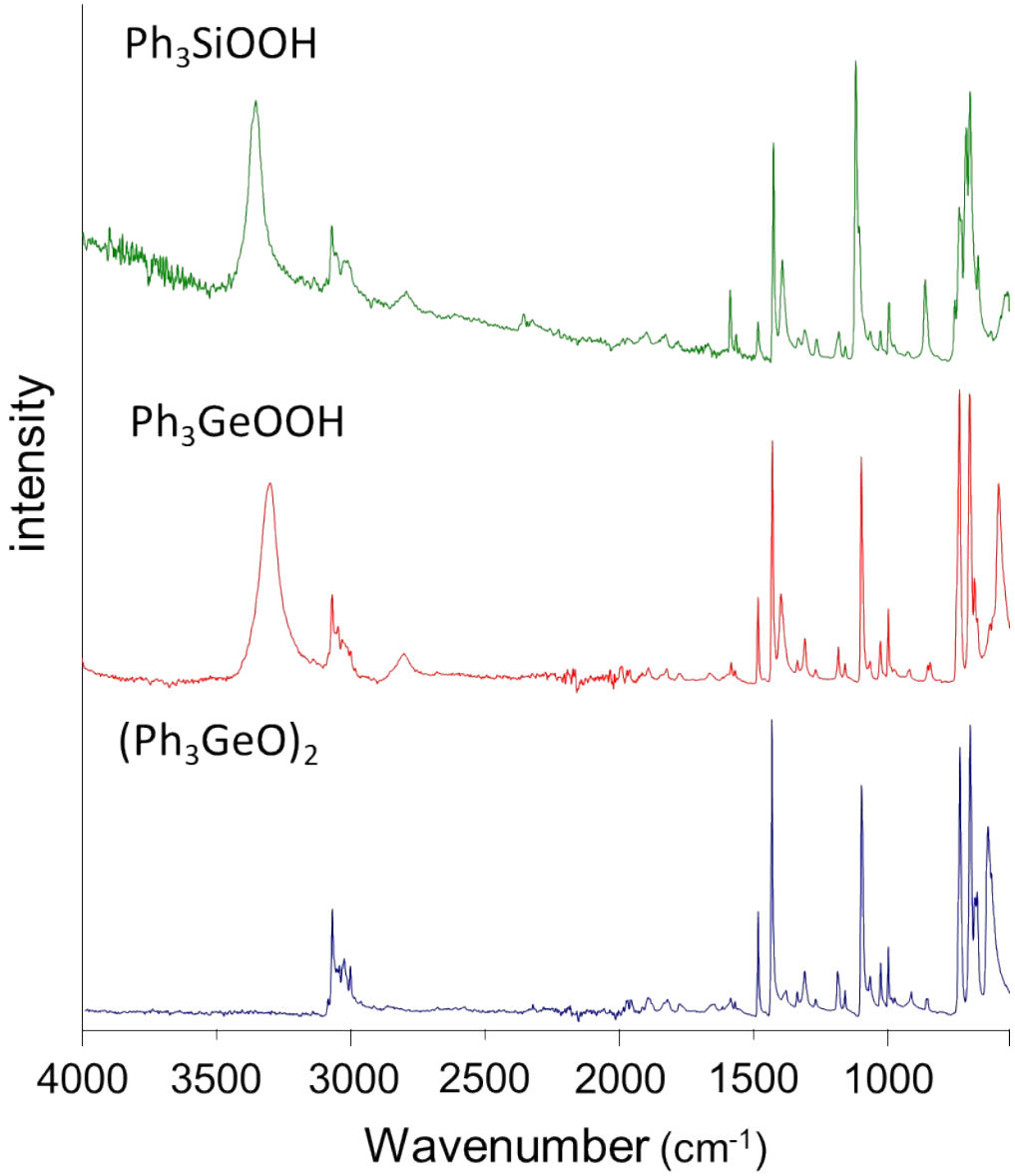

Figure S9. FTIR spectra of **1**-**3**.

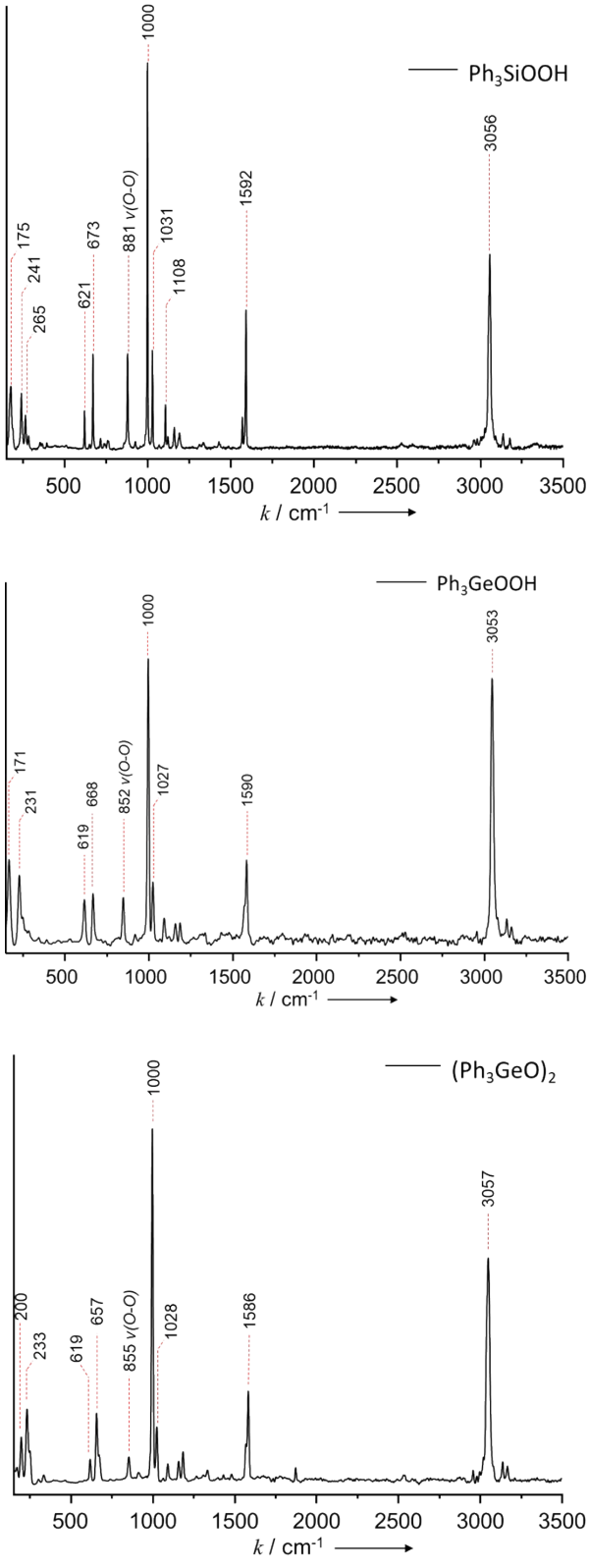

Figure S10. Raman spectra of **1-3**.

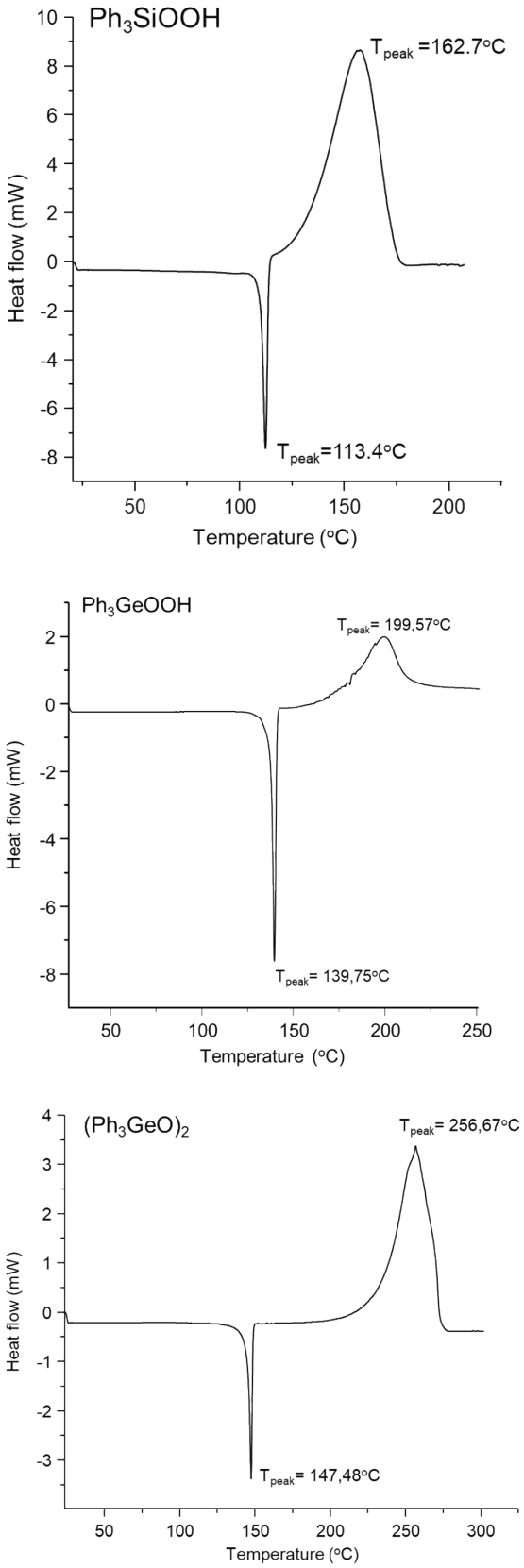

Figure S11. DSC of **1-3**.

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