Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022

Electronic Supplementary Material (ESI) for New Journal of Chemistry

# Cooperative assembly of redistributed aryl-germanium bearing alkoxysilane in mesostructured siloxane network

Nadia Katir,[a] Jamal El Haskouri,[b] Pedro Amoros,[b] and Abdelkrim El Kadib.[a,*]

[a.] *Euromed Research Center, Engineering Division, Euro-Med University of Fes (UEMF), Route de Meknes, Rond-point de Bensouda, 30070, Fès, Morocco.* a.elkadib@ueuromed.org

[b.] *Instituto de Ciència de los Materials de la Universidad de Valencia, Calle catedratico José Beltran, 2 CP 46980 Paterna Valencia, Spain.*

**S1: Experimental section: Synthesis and characterization of $Ph_3GeSi$**, **$Ph_2GeSi_2$** and **$PhGeSi_3$**

**S2.** Infrared spectra of bimetallic silyl-germyl precursors **$Ph_3GeSi$**, **$Ph_2GeSi_2$** and **$PhGeSi_3$**

**S3.** $^1H$, $^{13}C$ and $^{29}Si$ NMR spectra of bimetallic silyl-germyl precursors **$Ph_3GeSi$**, **$Ph_2GeSi_2$** and **$PhGeSi_3$**

**S4.** CP MAS $^{13}C$ and $^{29}Si$ NMR spectra of **$Ph_3GeSi@SiO_2$**, **$Ph_2GeSi_2@SiO_2$** and **$PhGeSi_3@SiO_2$**

**S5.** TGA curves of **$Ph_3GeSi@SiO_2$**, **$Ph_2GeSi_2@SiO_2$** and **$PhGeSi_3@SiO_2$**

**S6.** Scanning electronic microscopy analyses of ***$Ph_3GeSi@PhSiO_2$***

**S7.** Digital photos of **CS-$Ph_3GeSi@SiO_2$**, **CS-$Ph_2GeSi_2@SiO_2$** and **CS-$PhGeSi_3@SiO_2$** solutions

**S8.** Infrared spectra of **CS-$Ph_3GeSi@SiO_2$-*f***, **CS-$Ph_2GeSi_2$@ $SiO_2$-*f*** and **CS-$PhGeSi_3$@ $SiO_2$-*f***

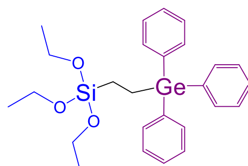
**S9.** EDX of **CS-$Ph_3GeSi$@ $SiO_2$-*f***, **CS-$Ph_2GeSi_2$@ $SiO_2$-*f*** and **CS-$PhGeSi_3$@ $SiO_2$-*f***

**S10.** Digital photos and Infrared spectra of **CS-$Ph_3GeSi$@ $SiO_2$-*f*-150°C**, **CS-$Ph_2GeSi_2$@ $SiO_2$-*f*-150°C** and **CS-$PhGeSi_3$@ $SiO_2$-*f*-150°C**

# S1: Experimental section:

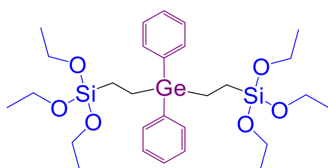
## S1a: Synthesis and characterization of $Ph_3GeSi$, $Ph_2GeSi_2$ and $PhGeSi_3$

***Synthesis and characterization of $Ph_3GeSi$***



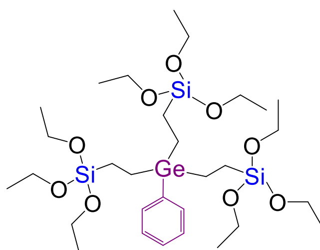

A solution of triethoxyvinylsilane (0.46 g, 2.42 mmol) and triphenylgermane (0.75 g, 2.45 mmol) in toluene (2 ml) was heated in the presence of AIBN at 90°C for 2h. After evaporation of solvent, $\mathbf{Ph_3GeSi_1}$ (1.10 g, 91%) was obtained as a white powder. M.p. 57 °C; $\delta_H$(300.13 MHz; $CDCl_3$; $Me_4Si$) 0.69-0.75 (2 H, m, $CH_2$-Si), 1.12 (9 H, t, *J* 7.0 , $OCH_2$-$C\mathit{H}_3$), 1.48-1.54 (2 H, m, ($C\mathit{H}_2$-Ge), 3.71 (6 H, q, *J* 7.0, $OC\mathit{H}_2$-$CH_3$), 7.25-7.41 (15 H, m, $C_6H_5$); $\delta_c$(75.48 MHz; $CDCl_3$; $Me_4Si$) 4.71 ($\mathit{C}H_2$-Si), 5.84 ($\mathit{C}H_2$-Ge), 18.51 ($OCH_2\mathit{C}H_3$), 58.62 ($O\mathit{C}H_2CH_3$), 128.36 ($C_m$), 129.04 ($C_p$), 135.19 ($C_o$), 137.11 ($C_{ipso}$); $\delta_{Si}$(59.62 MHz; $CDCl_3$; $Me_4Si$) -45.88; MS (EI): *m/z* = 496 (1) $[M]^+$.

***Synthesis and characterization of $Ph_2GeSi_2$***




A solution of triethoxyvinylsilane (1.86 g, 9.78 mmol) and diphenylgermane (1.13 g, 4.91 mmol) in toluene (5 mL) was heated in the presence of AIBN at 90°C for 2h. After evaporation of solvent and distillation under reduced pressure, $\mathbf{Ph_2GeSi_2}$ (2.70 g, 90%) was obtained as a colorless liquid. Bp: 140°C / 0.3 mmHg; $\delta_H$(300.13 MHz; $CDCl_3$; $Me_4Si$) 0.59-0.64 (4 H, m, $CH_2$-Si), 1.13 (18 H, t, *J* 7.0 , $OCH_2$-$C\mathit{H}_3$), 1.20-1.27 (4 H, m, ($C\mathit{H}_2$-Ge), 3.72 (12 H, q, *J* 7.0, $OC\mathit{H}_2$-$CH_3$), 7.24-7.27 (6 H, m, $C_6H_5$), 7.36-7.38 (4 H, m, $C_6H_5$); $\delta_c$(75.48 MHz; $CDCl_3$; $Me_4Si$) 4.28 (Si-$\mathit{C}H_2$-$\mathit{C}H_2$-Ge), 18.40 ($OCH_2\mathit{C}H_3$), 58.51 ($O\mathit{C}H_2CH_3$), 128.11 ($C_m$), 128.66 ($C_p$), 134.71($C_o$), 137.93 ($C_{ipso}$); $\delta_{Si}$(59.62 MHz; $CDCl_3$; $Me_4Si$) -45.77; MS (EI): *m/z* = 533 (3) $[M-Ph]^+$.

***Synthesis and characterization of $PhGeSi_3$***




A solution of triethoxyvinylsilane (2.36 g, 12.42 mmol) and phenylgermane (0.63 g, 4.12 mmol) in toluene (5 ml) was heated in the presence of AIBN at 90°C for 3h. After evaporation of solvent and distillation under reduced pressure, $\mathbf{PhGeSi_3}$ (2.62 g, 88 %) was obtained as a colorless liquid. Bp: 140°C/0.04 mmHg; $\delta_H$(300.13 MHz; $CDCl_3$; $Me_4Si$) 0.55-0.61 (6 H, m, $CH_2$-Si), 0.96-1.02 (6 H, m, $C\mathit{H}_2$-Ge), 1.15 (27 H, t, *J* 7.0 , $OCH_2$-$C\mathit{H}_3$), 3.71 (18 H, q, *J* 7.0, $OC\mathit{H}_2$-$CH_3$), 7.22-7.26 (3 H, m, $C_6H_5$), 7.33-7.35 (2 H, m, $C_6H_5$); $\delta_c$(75.48 MHz; $CDCl_3$; $Me_4Si$) 2.14, 3.16 (Si-$\mathit{C}H_2$-$\mathit{C}H_2$-Ge), 17.27 ($OCH_2\mathit{C}H_3$), 57.35

($OCH_2CH_3$), 126.81 ($C_m$), 127.18 ($C_p$), 133.07 ($C_o$), 137.98 ($C_{ipso}$); $\delta_{Si}$(59.62 MHz; $CDCl_3$; $Me_4Si$) -45.72; MS (EI): *m/z* = 724 (1) $[M]^+$.

## S1b: Synthesis of $Ph_3GeSi@SiO_2$, $Ph_2GeSi_2@SiO_2$ and $PhGeSi_3@SiO_2$

### *Synthesis of $Ph_3GeSi@SiO_2$*

The Pluronic P123 (0.9 g) was dissolved in an aqueous HCl solution (5.1 g of HCl 37%, in 25 g $H_2O$) with stirring at room temperature for 4 h. TEOS (1.89 g, 9.09 mmol) was added dropwise to this homogeneous solution. After 15 min, the **$Ph_3GeSi$** precursor (0.5 g, 1.01 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 1.6 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.

### *Synthesis of $Ph_2GeSi_2@SiO_2$*

The Pluronic P123 (1.46 g) was dissolved in an aqueous HCl solution (8.18 g of HCl 37%, in 36 g $H_2O$) with stirring at room temperature for 4 h. TEOS (3.07 g, 14.76 mmol) was added dropwise to this homogeneous solution. After 15 min, the **$Ph_2GeSi_2$** precursor (0.5 g, 0.82 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 2.2 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.

### *Synthesis of $PhGeSi_3@SiO_2$*

The Pluronic P123 (1.84 g) was dissolved in an aqueous HCl solution (10.28 g of HCl 37%, in 46 g $H_2O$) with stirring at room temperature for 4 h. TEOS (3.88 g, 18.65 mmol) was added dropwise to this homogeneous solution. After 15 min, the **$PhGeSi_3$** precursor (0.5 g, 0.69 mmol of Si) was added to the reaction mixture. The resulting mixture was kept stirring at 40 °C for 20 h and heated at 100°C under static conditions for an additional 24 h. After cooling, the solid product was recovered by filtration, successively washed with deionized water and ethanol to neutrality, and drying in air at 60 °C for 12 h giving 2.33 g of material as a white powder. The surfactant was removed by extraction in a Soxhlet with 250 mL of ethanol containing 2 mL of 37 % HCl aqueous solution at reflux temperature for 72 h. The recovered solid was washed with ethanol and air-dried at 60 °C.

### S1c: Preparation of Chitosan–$Ph_nGeSi_{4-n}$@$SiO_2$ Films.

***Preparation of CS–$Ph_3GeSi$@$SiO_2$-f***

50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (7 mg) and **$Ph_3GeSi$** (7 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.

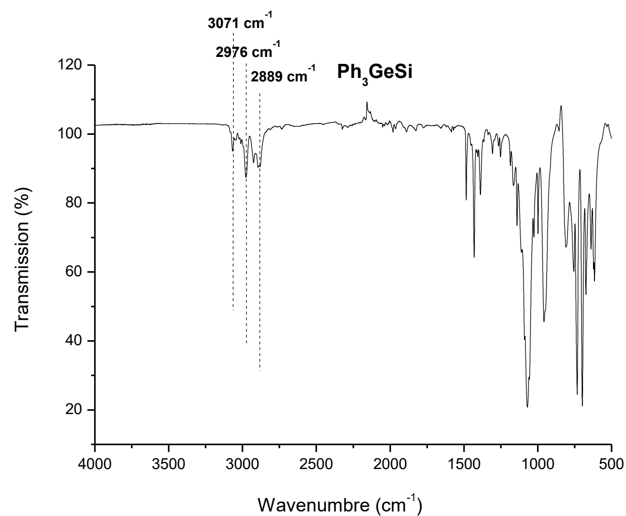
***Preparation of CS–$Ph_2GeSi_2$@$SiO_2$-f***

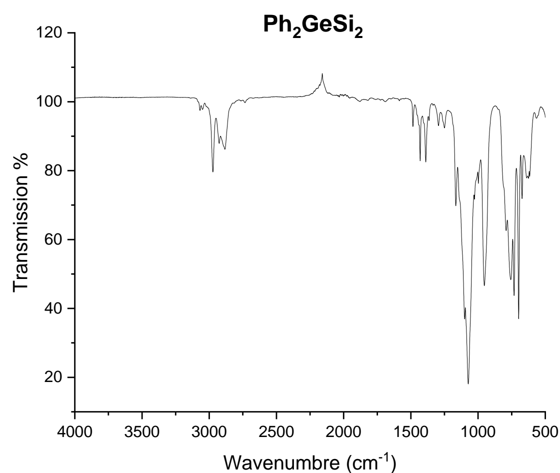
50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (8.8 mg) and **$Ph_2GeSi_2$** (8.8 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.

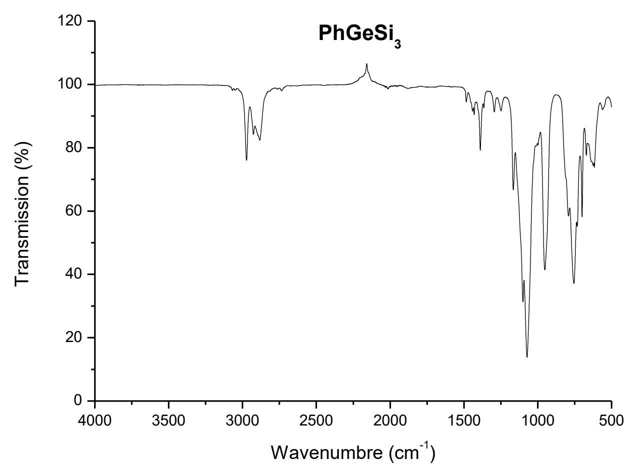
***Preparation of CS–$PhGeSi_3$@$SiO_2$-f***

50 mg of chitosan was completely dissolved in 4 mL of 1% (v/v) acetic acid solution, and the mixture was kept under vigorous stirring for 120 min. tetraethylorthosilicate (10.5 mg) and **$PhGeSi_3$** (10.5 mg) were added to the chitosan solution, and the resulting mixture was stirred for an additional 90 min. The resulting solution was cast into plastic Petri dishes allowing solvent removal and film formation after complete drying.

**S2.** Infrared spectra of bimetallic silyl-germyl precursors **$Ph_3GeSi$**, **$Ph_2GeSi_2$** and **$PhGeSi_3$**

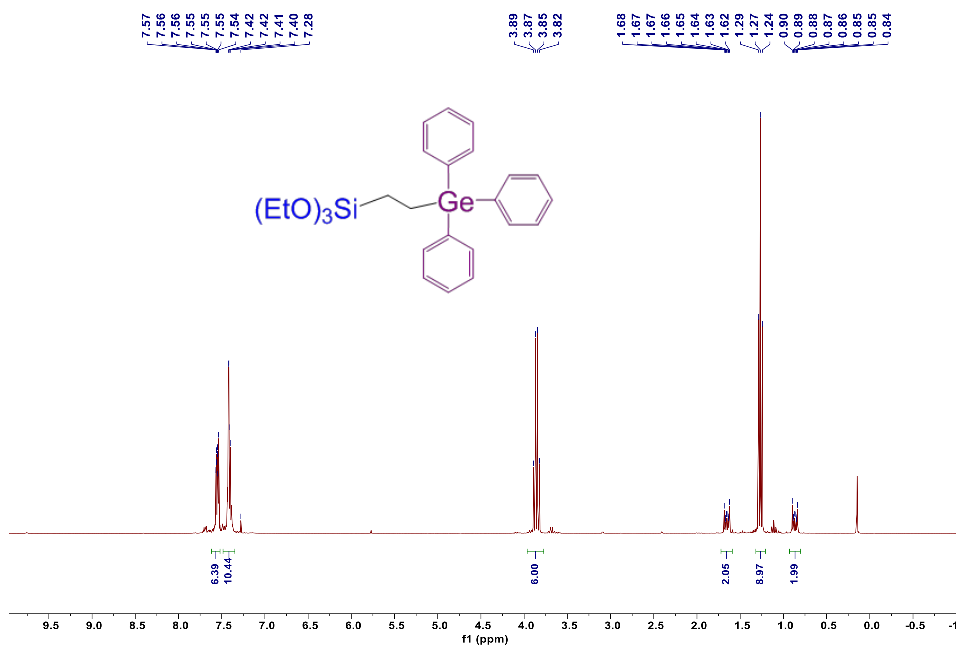


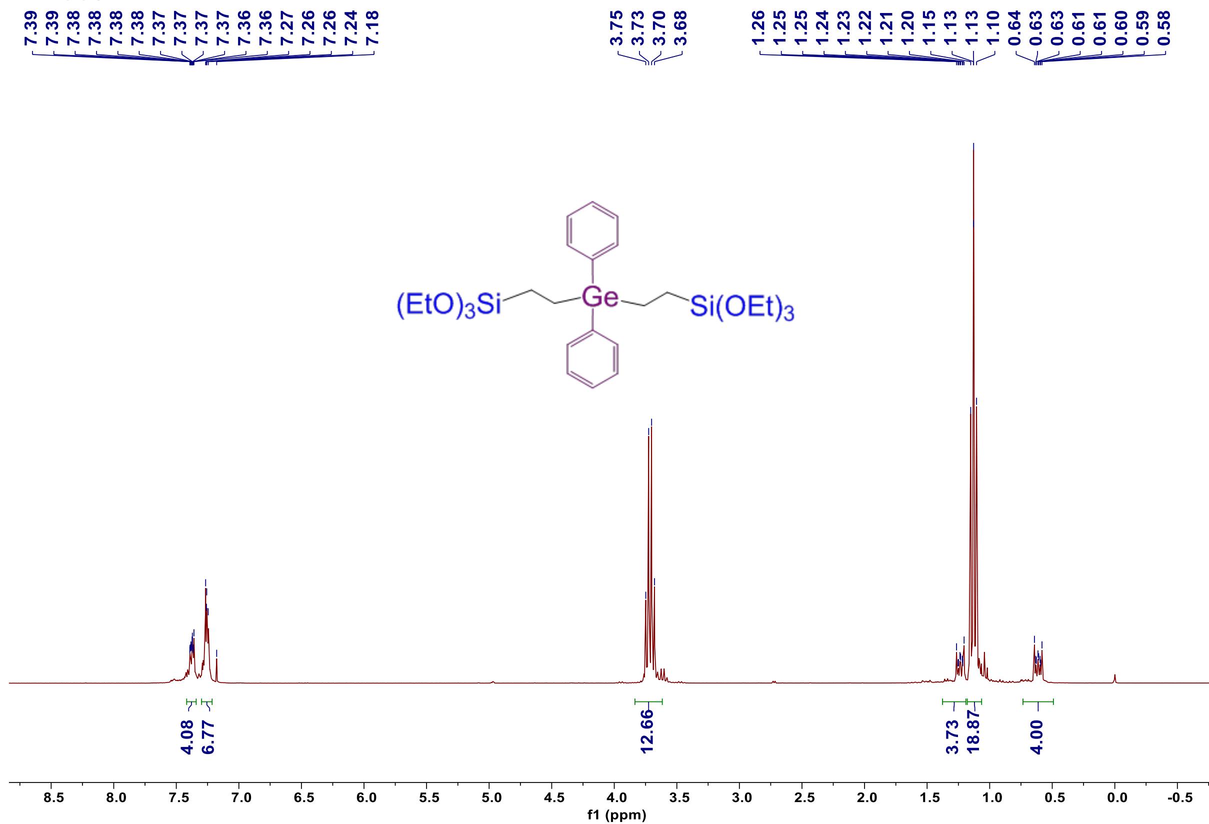



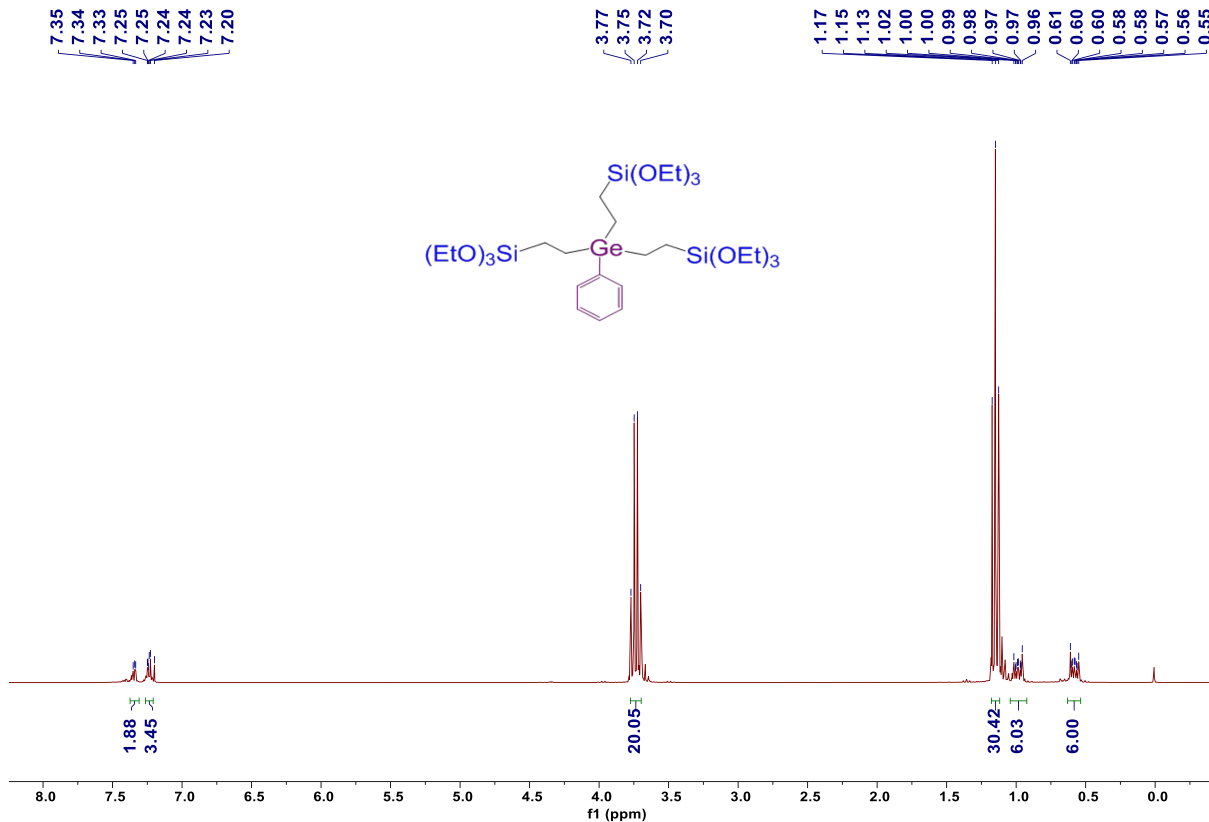
**S3.** $^{1}H$, $^{13}C$ and $^{29}Si$ NMR spectra of bimetallic silyl-germyl precursors **$Ph_3GeSi$**, **$Ph_2GeSi_2$** and **$PhGeSi_3$**

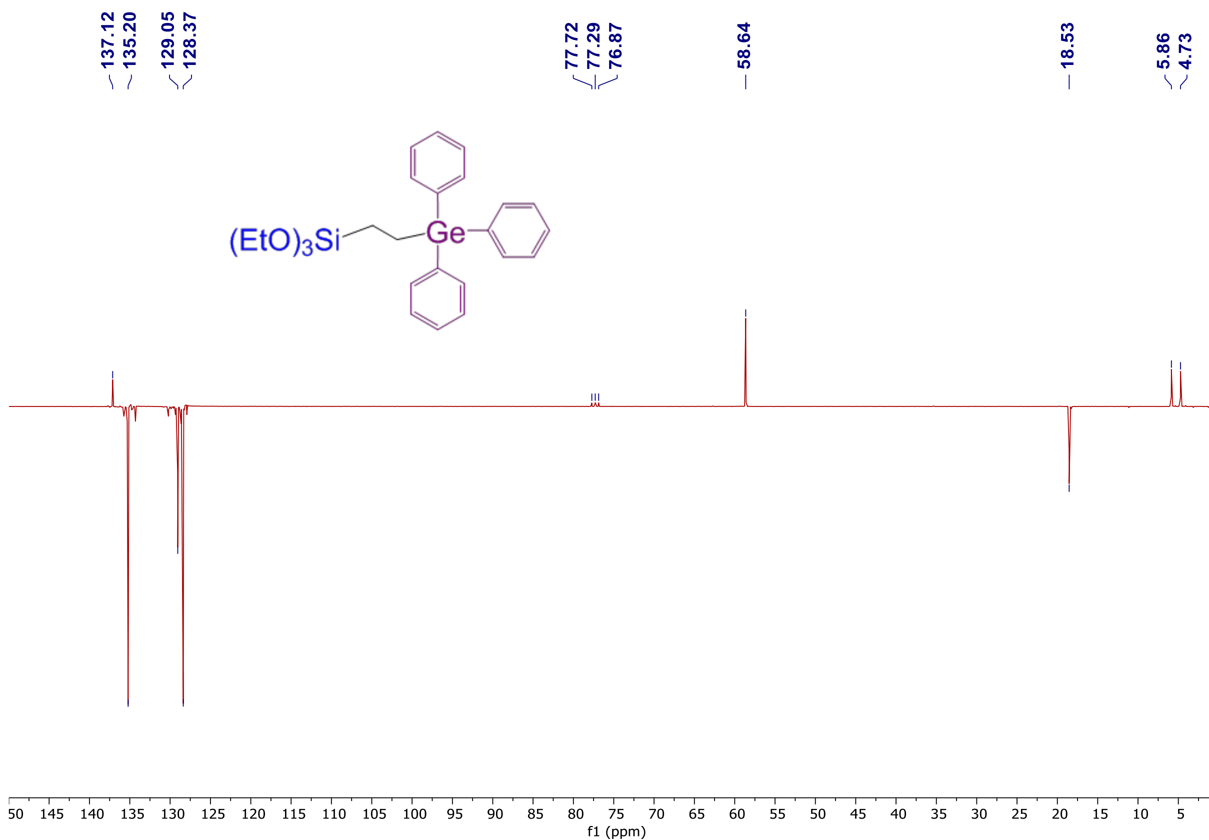
**Ph3GeSi**

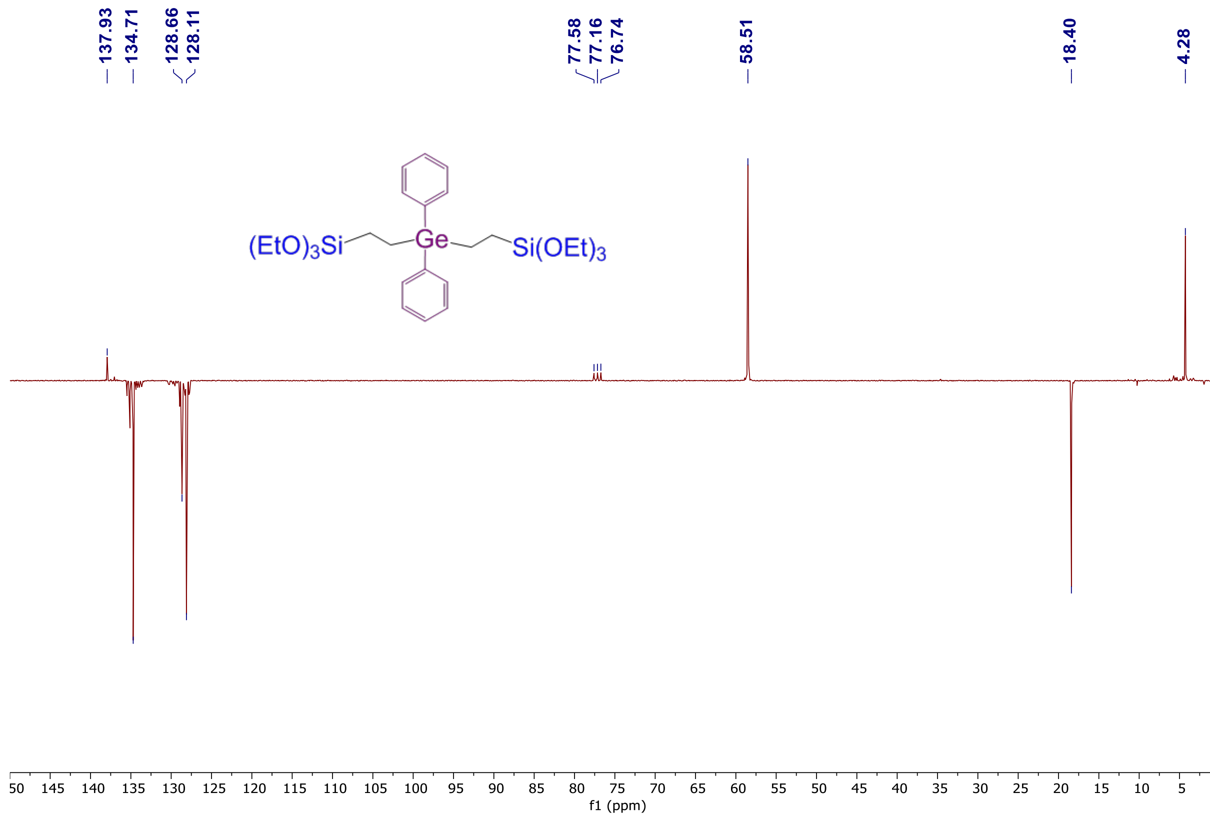


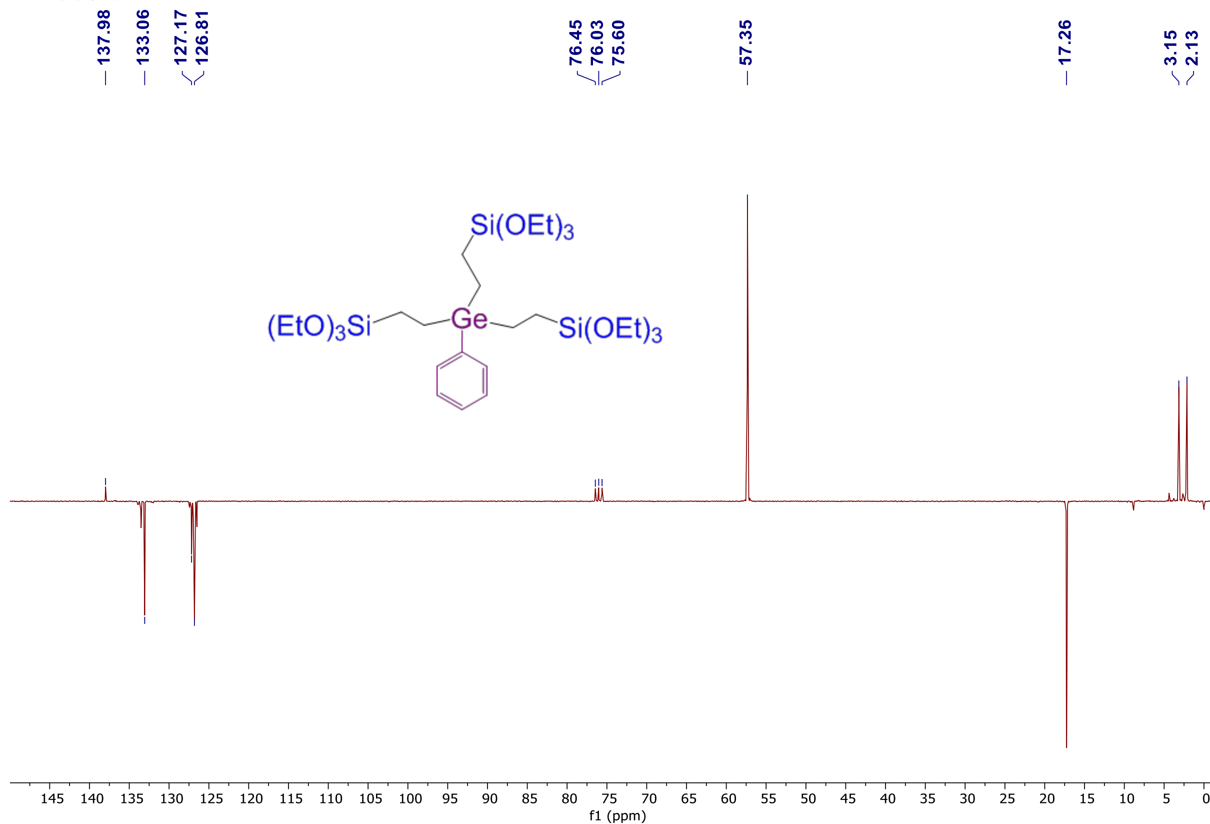

**Ph2GeSi**

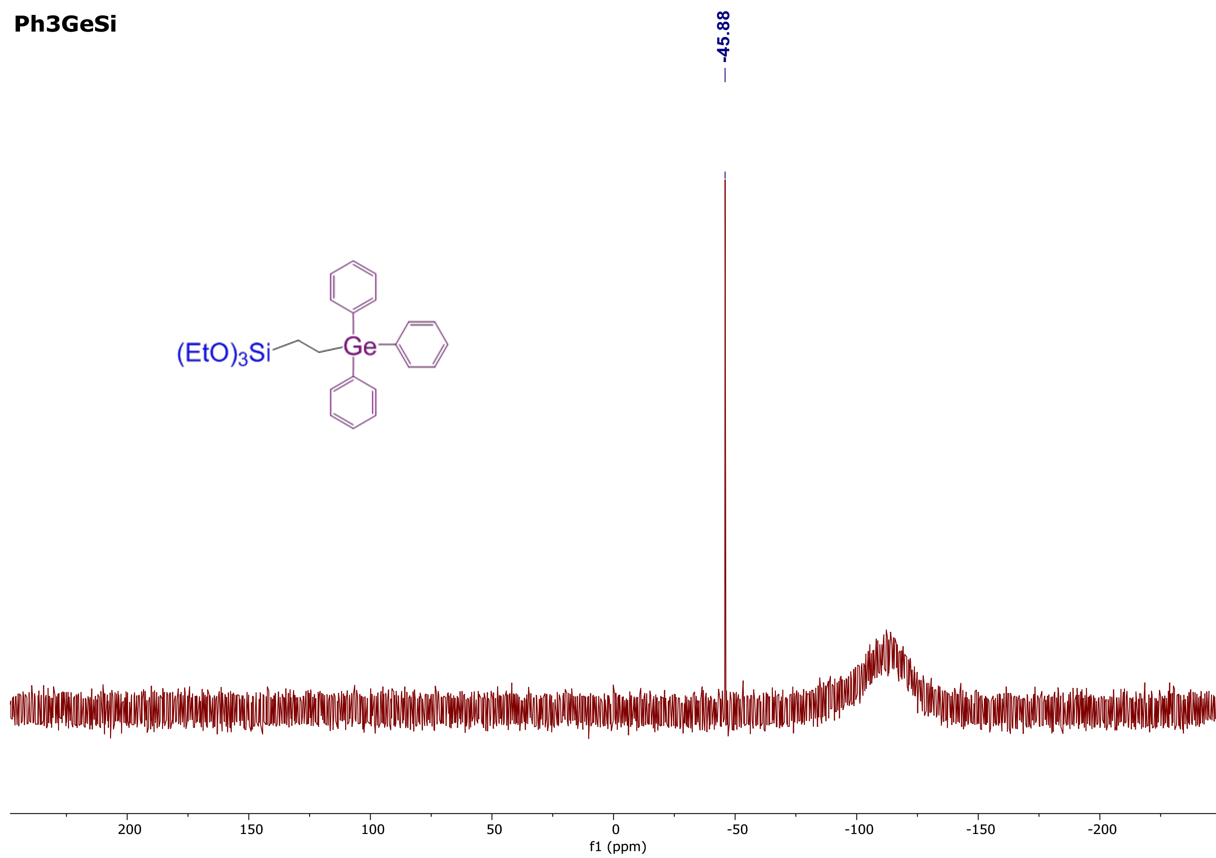


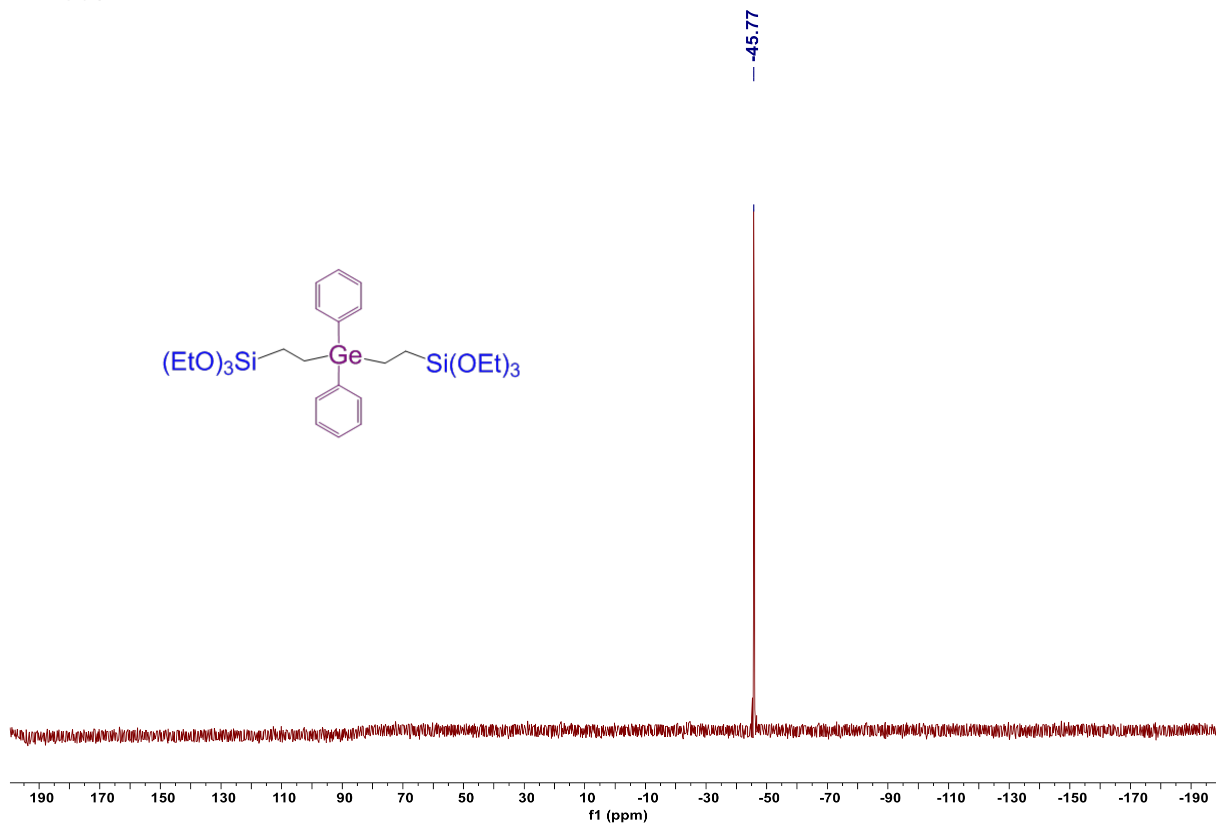

PhGeSi3
7.35
7.34
7.33
7.25
7.25
7.24
7.24
7.23
7.20
3.77
3.75
3.72
3.70
1.17
1.15
1.13
1.02
1.00
1.00
0.99
0.98
0.97
0.97
0.96
0.61
0.60
0.60
0.58
0.58
0.57
0.56
0.55
Si(OEt)3
(EtO)3Si
Ge
Si(OEt)3
1.88
3.45
20.05
30.42
6.03
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph3GeSi
137.12
135.20
129.05
128.37
77.72
77.29
76.87
58.64
18.53
5.86
4.73
(EtO)3Si
Ge
50
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

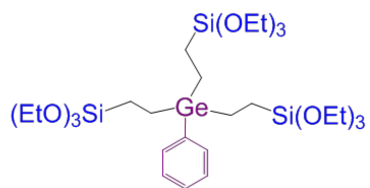

Ph2GeSi2
137.93
134.71
128.66
128.11
77.58
77.16
76.74
58.51
18.40
4.28
(EtO)3Si
Ge
Si(OEt)3
f1 (ppm)

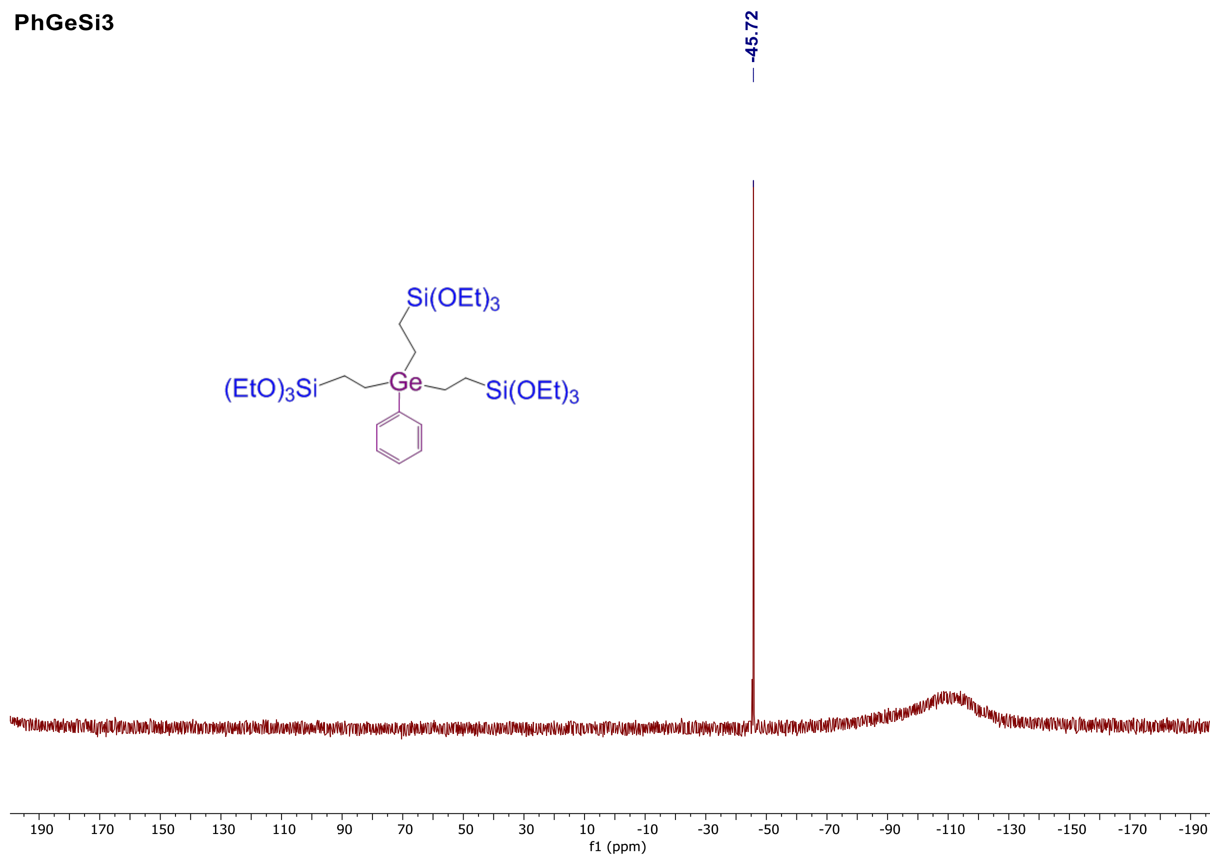

PhGeSi3
137.98
133.06
127.17
126.81
76.45
76.03
75.60
57.35
17.26
3.15
2.13
Si(OEt)3
(EtO)3Si
Ge
Si(OEt)3
f1 (ppm)


Ph3GeSi
-45.88
(EtO)3Si
Ge
200
150
100
50
0
-50
-100
-150
-200
f1 (ppm)

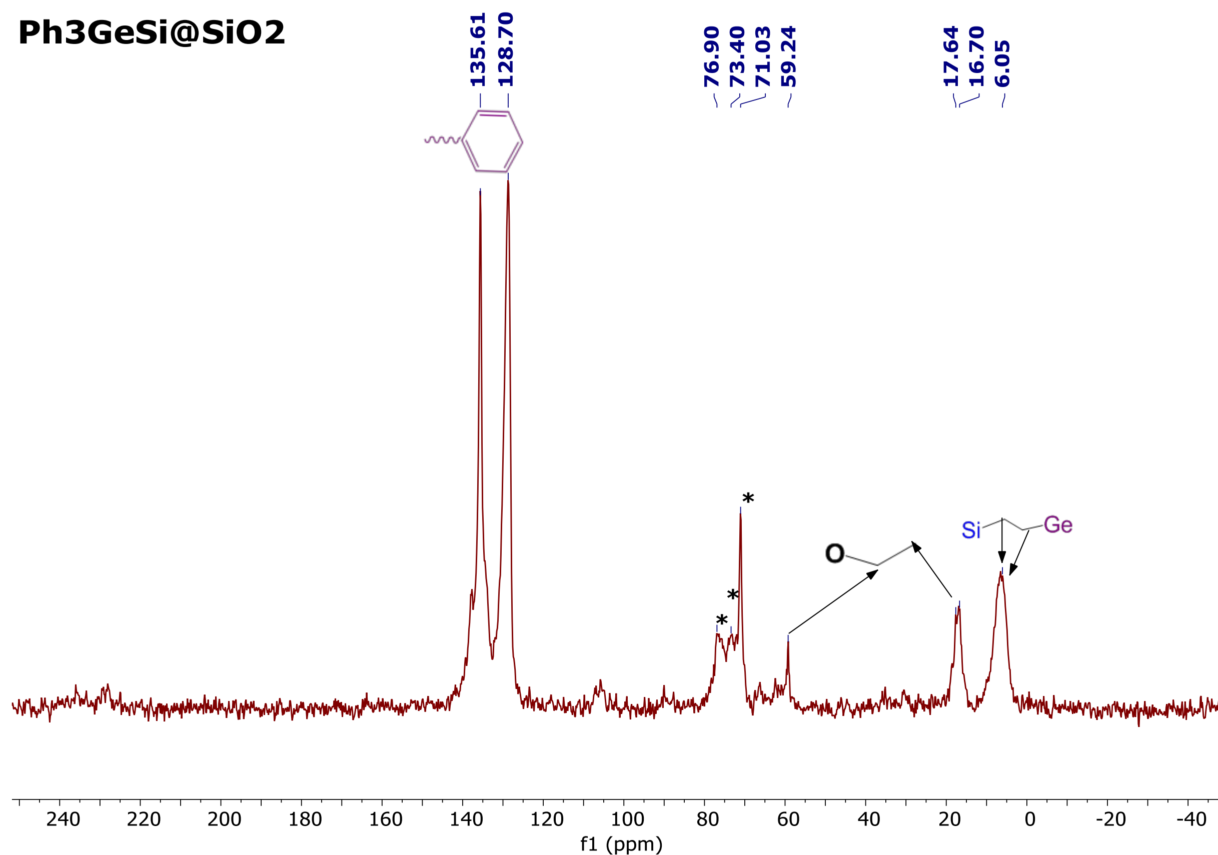

Ph2GeSi2
-45.77
(EtO)3Si
Ge
Si(OEt)3
190
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

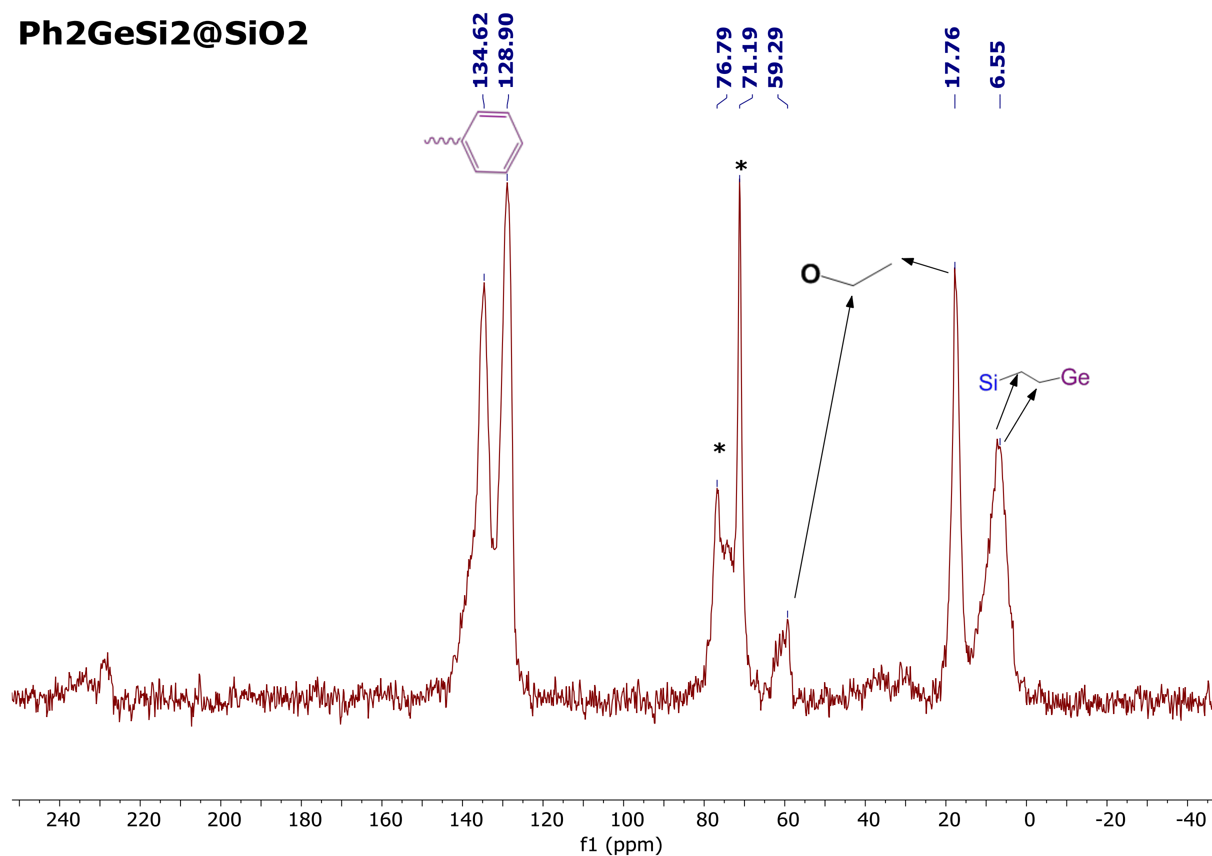
**PhGeSi3**

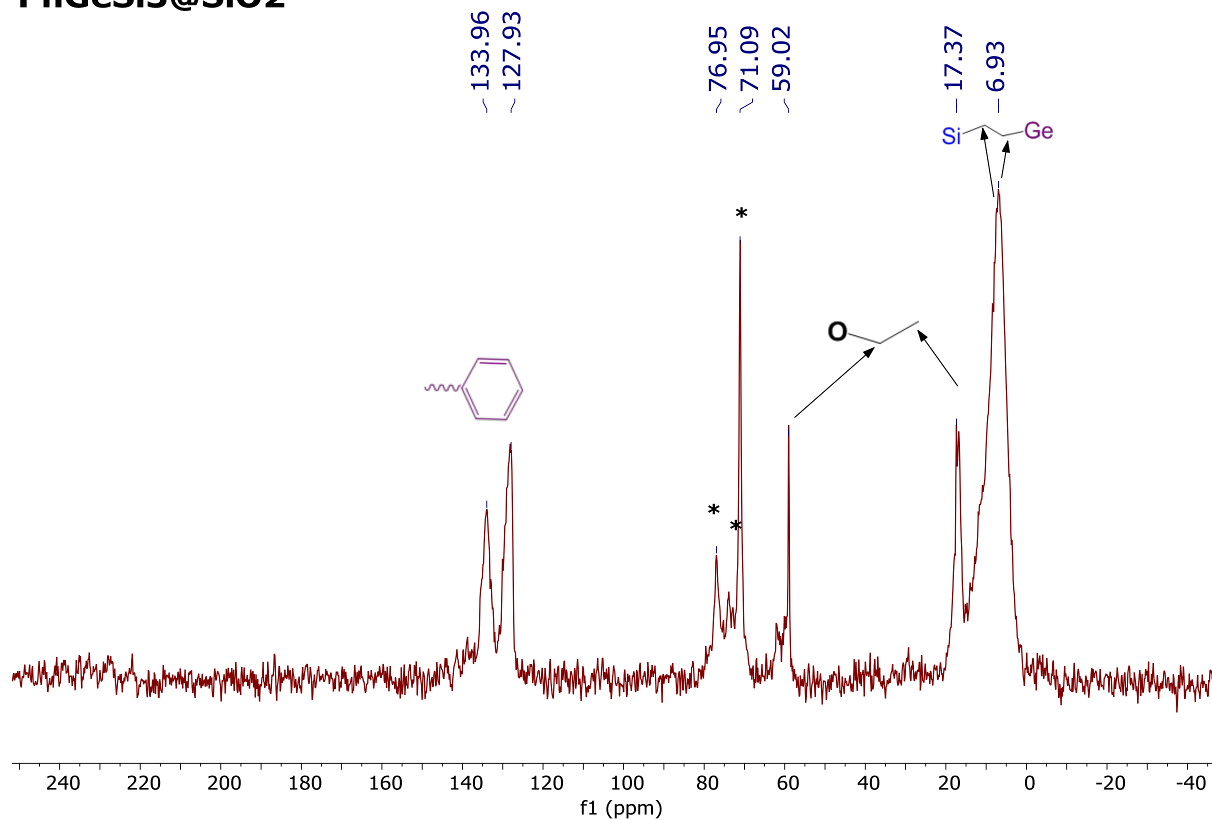


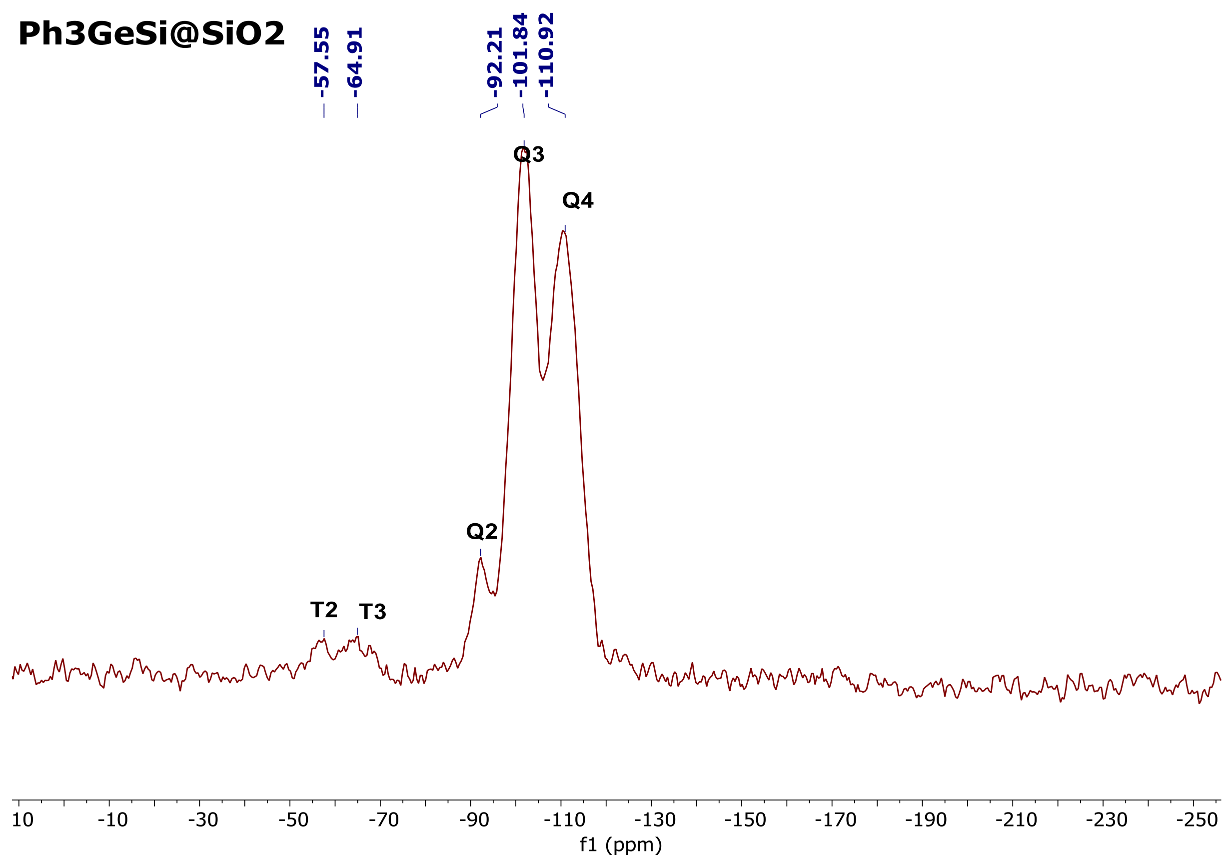



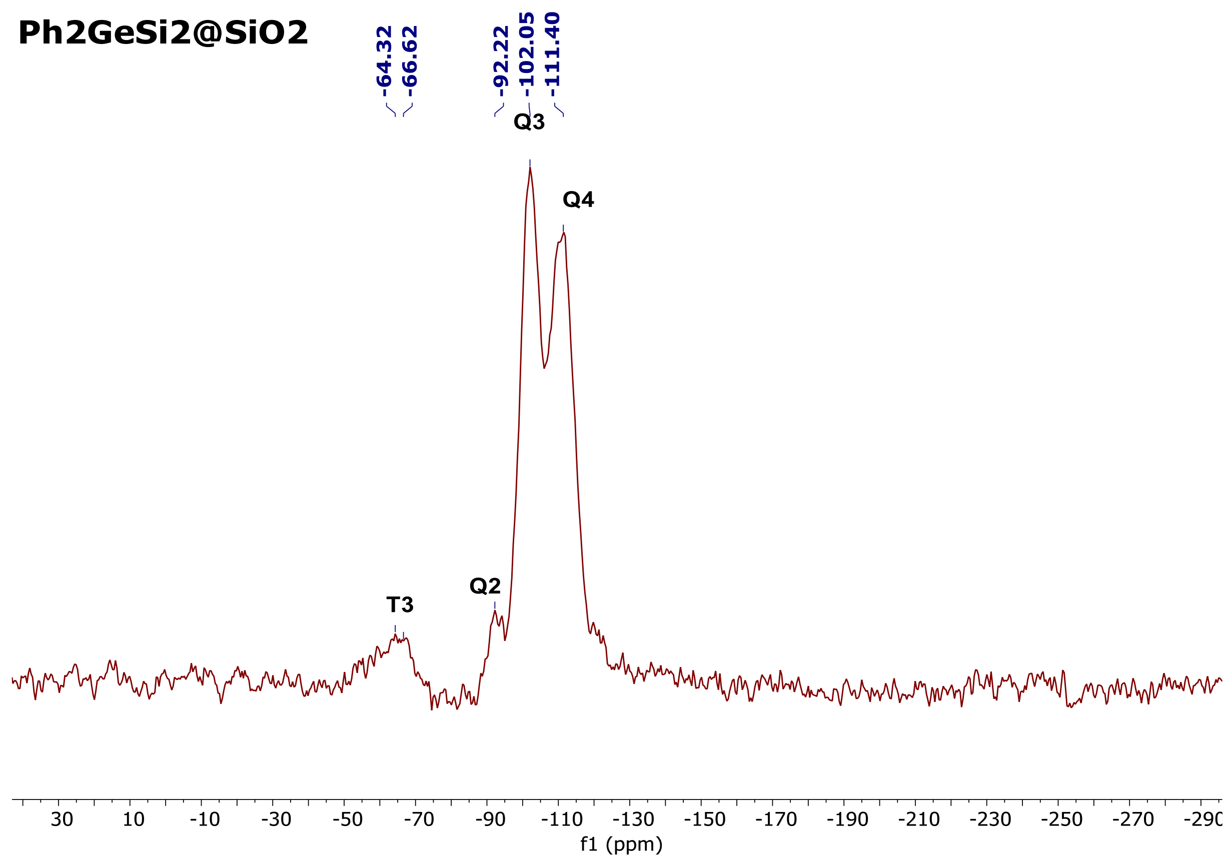
**S4.** CP MAS $^{13}C$ and $^{29}Si$ NMR spectra of **$Ph_3GeSi@SiO_2$**, **$Ph_2GeSi_2@SiO_2$** and **$PhGeSi_3@SiO_2$**

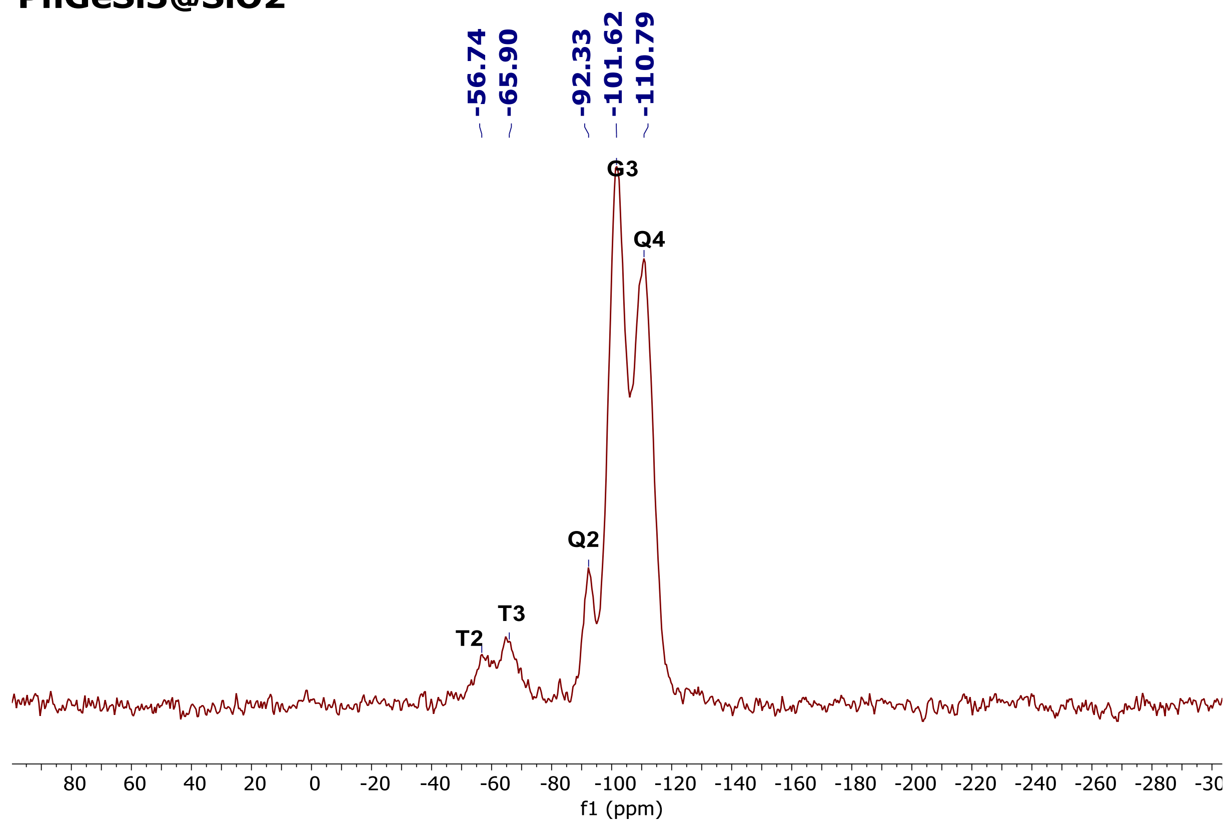



Ph2GeSi2@SiO2
134.62
128.90
76.79
71.19
59.29
17.76
6.55
*
*
O
Si
Ge
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)


PhGeSi3@SiO2
133.96
127.93
76.95
71.09
59.02
17.37
6.93
Si
Ge
*
*
*
O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)

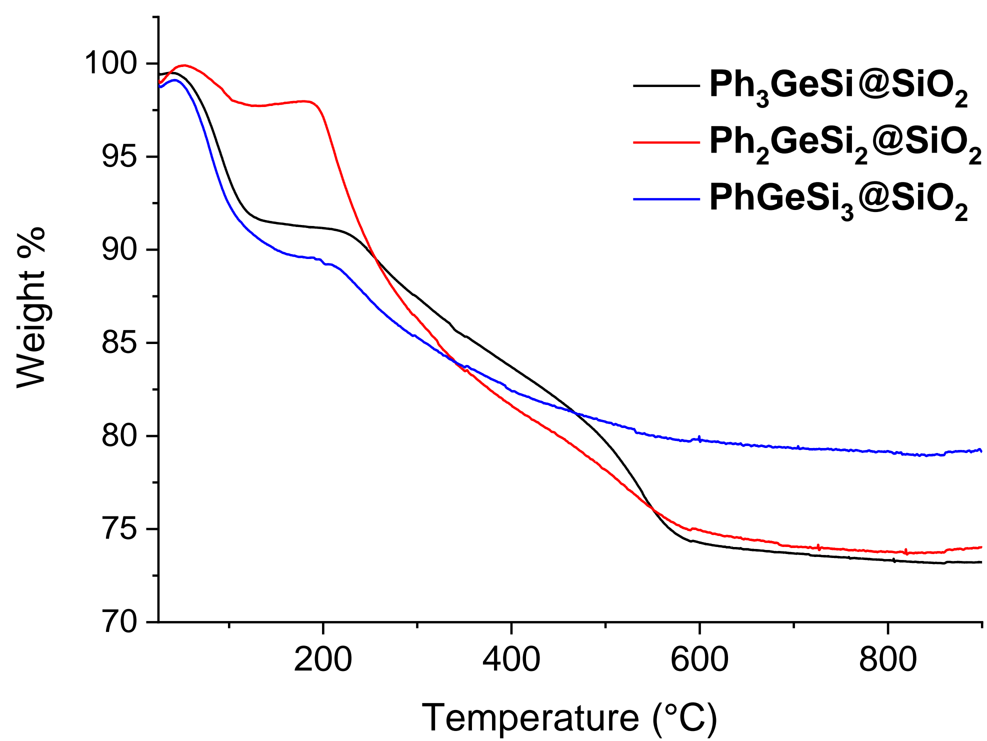

Ph3GeSi@SiO2
-57.55
-64.91
-92.21
-101.84
-110.92
Q3
Q4
Q2
T2
T3
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)


Ph2GeSi2@SiO2
-64.32
-66.62
-92.22
-102.05
-111.40
Q3
Q4
T3
Q2
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

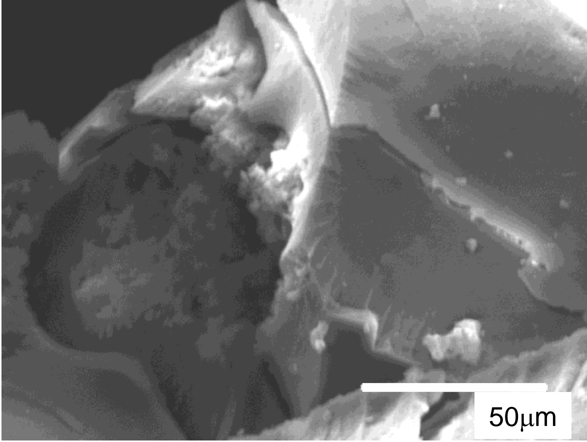


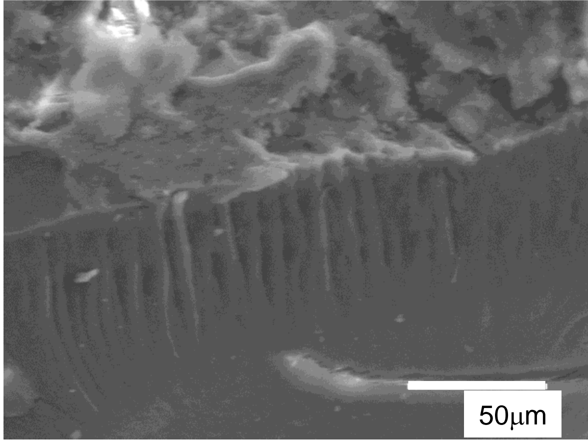
PhGeSi3@SiO2
-56.74
-65.90
-92.33
-101.62
-110.79
G3
Q4
Q2
T3
T2
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

**S5.** TGA curves of **$Ph_3GeSi@SiO_2$**, **$Ph_2GeSi_2@SiO_2$** and **$PhGeSi_3@SiO_2$**



**S6.** Scanning electronic microscopy analyses of ***$Ph_3GeSi@PhSiO_2$***

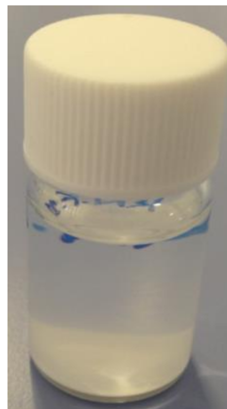


**S7.** Digital photos of, **CS-$Ph_3GeSi$@SiO**, **CS-$Ph_2GeSi_2$@$SiO_2$** and **CS-$PhGeSi_3$@$SiO_2$** solutions

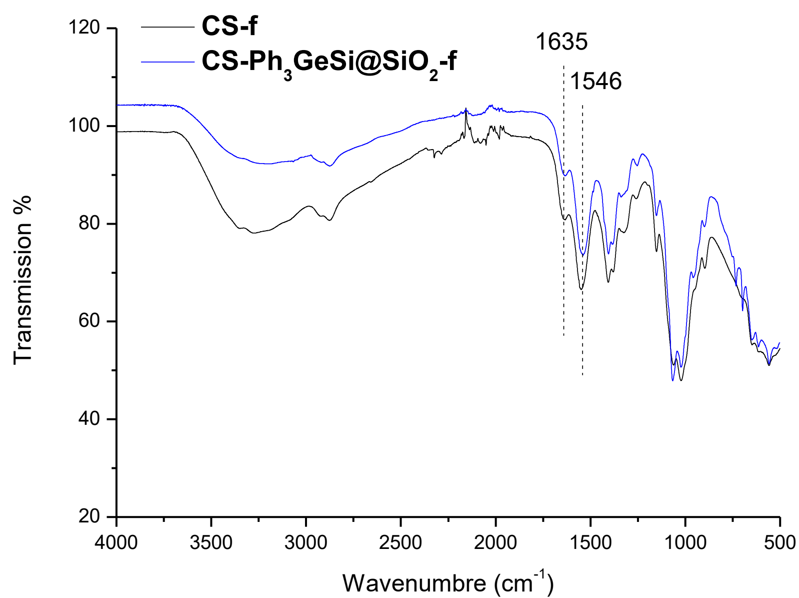
**CS-$Ph_3GeSi$@$SiO_2$**

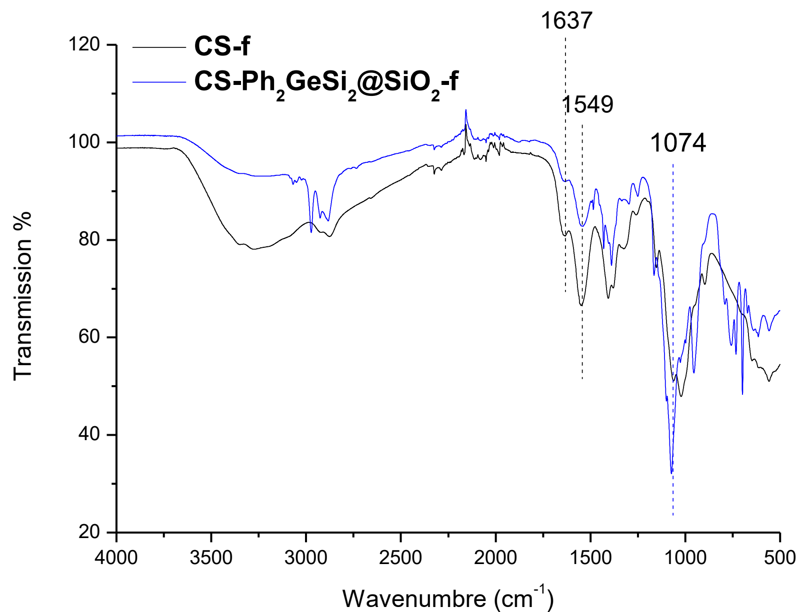
**CS-$Ph_2GeSi_2$@$SiO_2$**

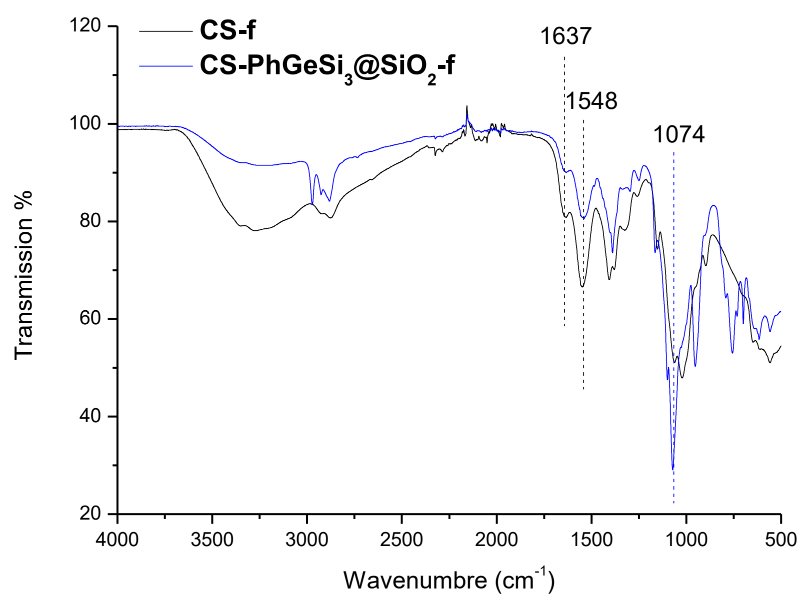


**CS-$PhGeSi_3$@$SiO_2$**

**S8.** Infrared spectra of **CS-$Ph_3GeSi@SiO_2$-*f***, **CS-$Ph_2GeSi_2@SiO_2$-*f*** and **CS-$PhGeSi_3@SiO_2$-*f***

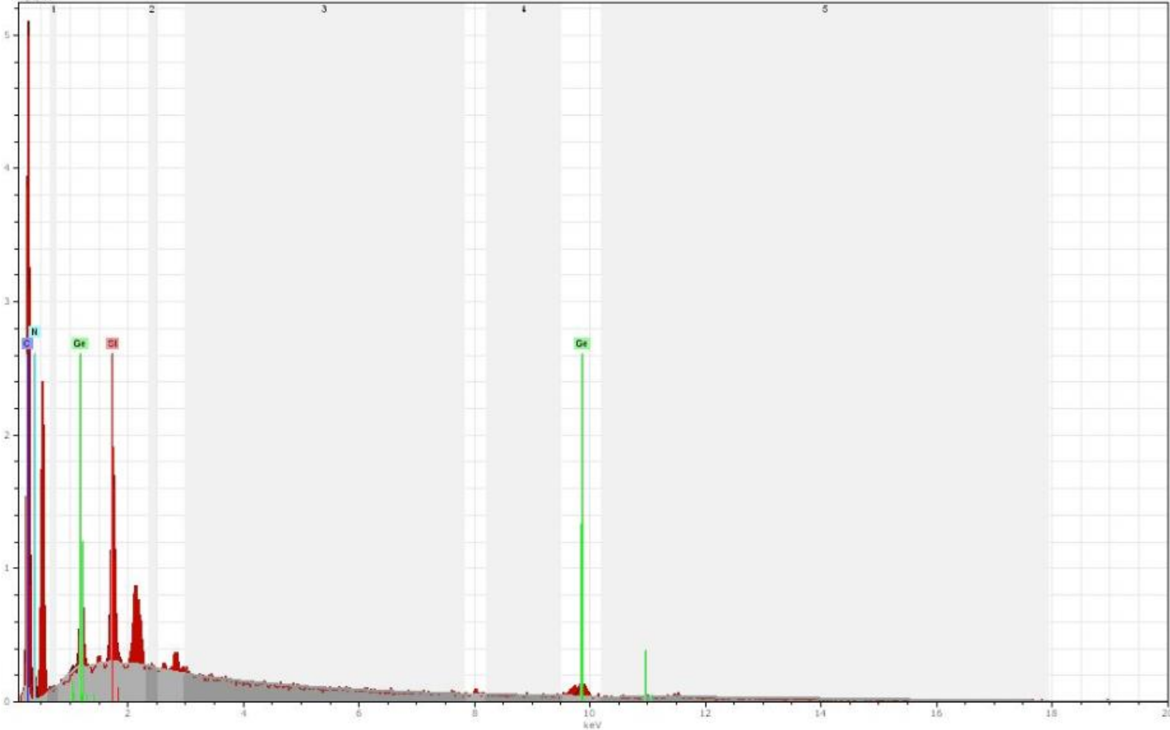


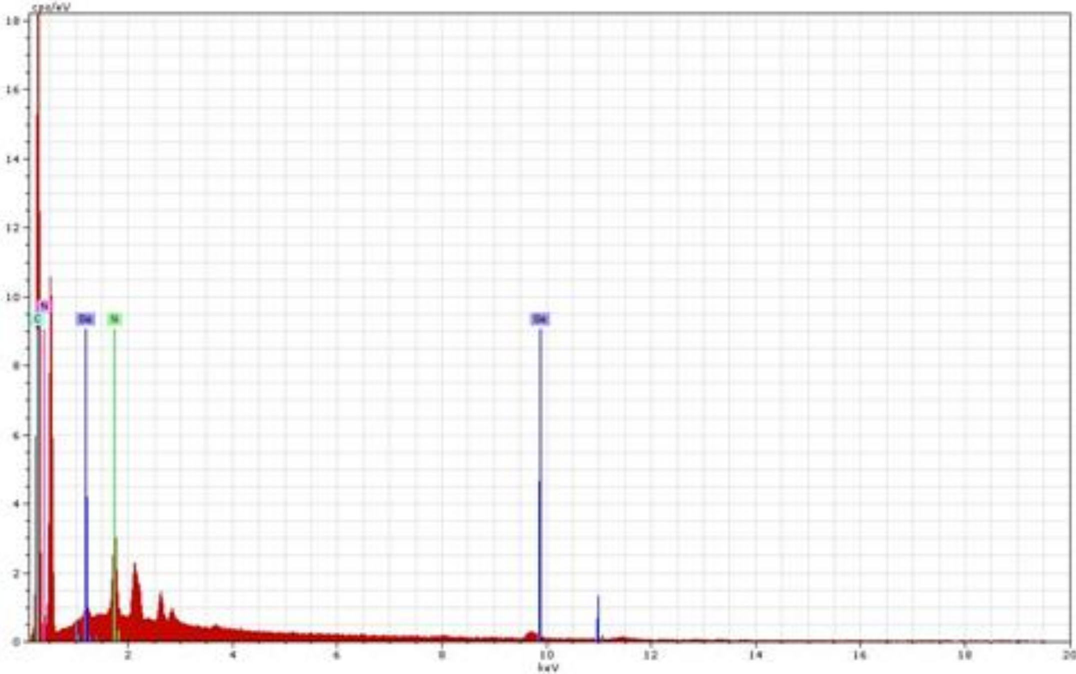


CS-f
CS-PhGeSi3@SiO2-f
1637
1548
1074
Transmission %
120
100
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbre (cm-1)

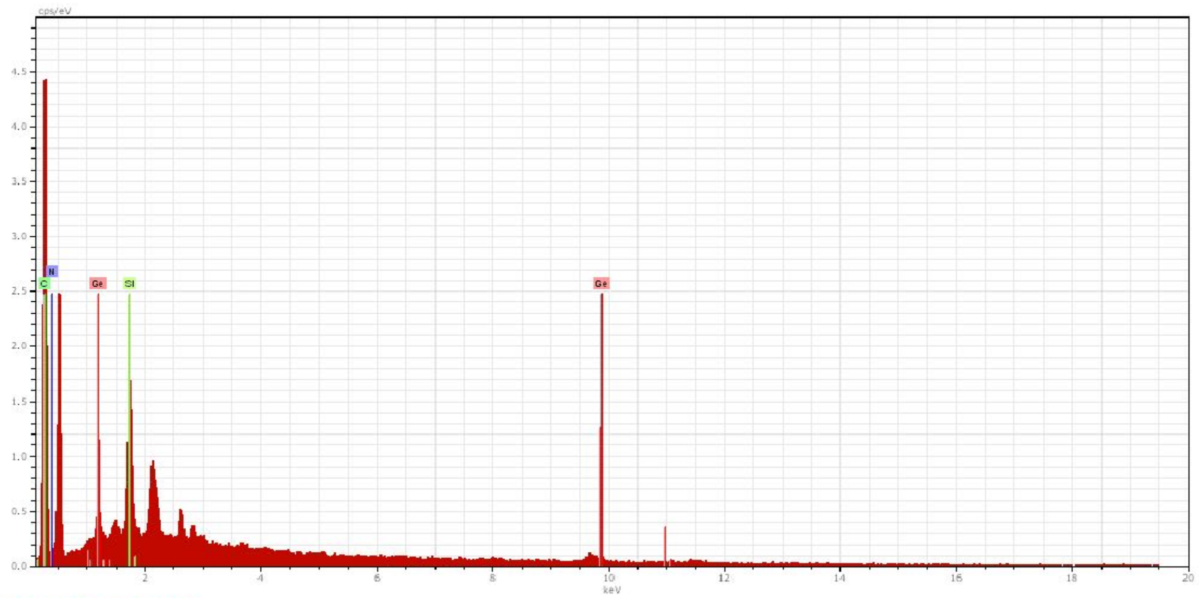
**S9.** EDX of **CS-$Ph_3GeSi$@$SiO_2$-*f***, **CS-$Ph_2GeSi_2$@$SiO_2$-*f*** and **CS-$PhGeSi_3$@$SiO_2$-*f***



**CS-$Ph_3GeSi$@$SiO_2$-*f***



**CS-$Ph_2GeSi_2$@$SiO_2$-*f***



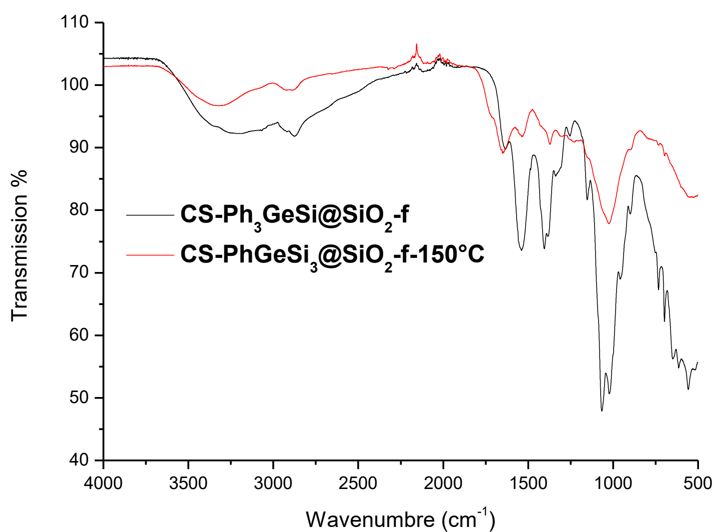

**CS-PhGeSi$_3$@SiO$_2$-*f***

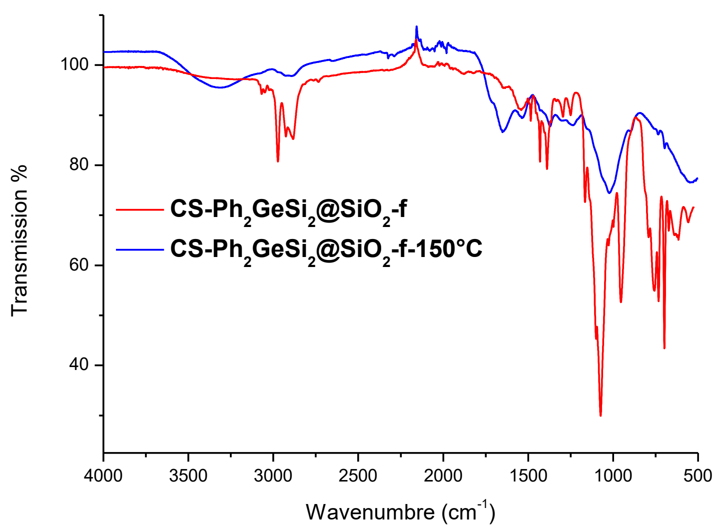
**S10.** Digital photos and Infrared spectra of **CS-$Ph_3GeSi@SiO_2$-*f*-150°C**, **CS-$Ph_2GeSi_2@SiO_2$-*f*-150°C** and **CS-$PhGeSi_3@SiO_2$-*f*-150°C**

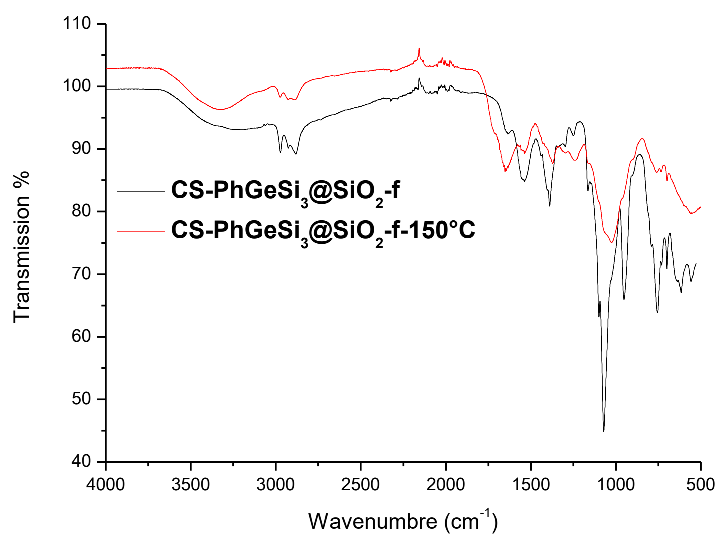
**CS-$Ph_3GeSi@SiO_2$-*f*-150°C**

**CS-$Ph_2GeSi_2@SiO_2$-*f*-150°C**

**CS-$PhGeSi_3@SiO_2$-*f*-150°C**




110
100
90
80
70
60
50
40
Transmission %
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbre (cm-1)
CS-PhGeSi3@SiO2-f
CS-PhGeSi3@SiO2-f-150°C