Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information

Room Temperature Silylation of Alcohols Catalyzed by Metal Organic Frameworks

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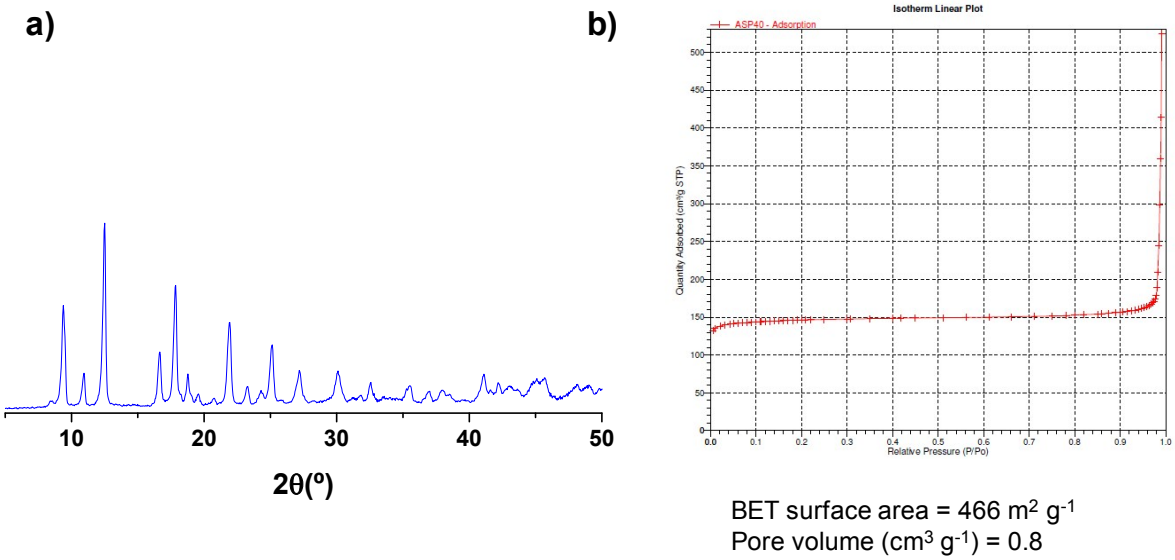
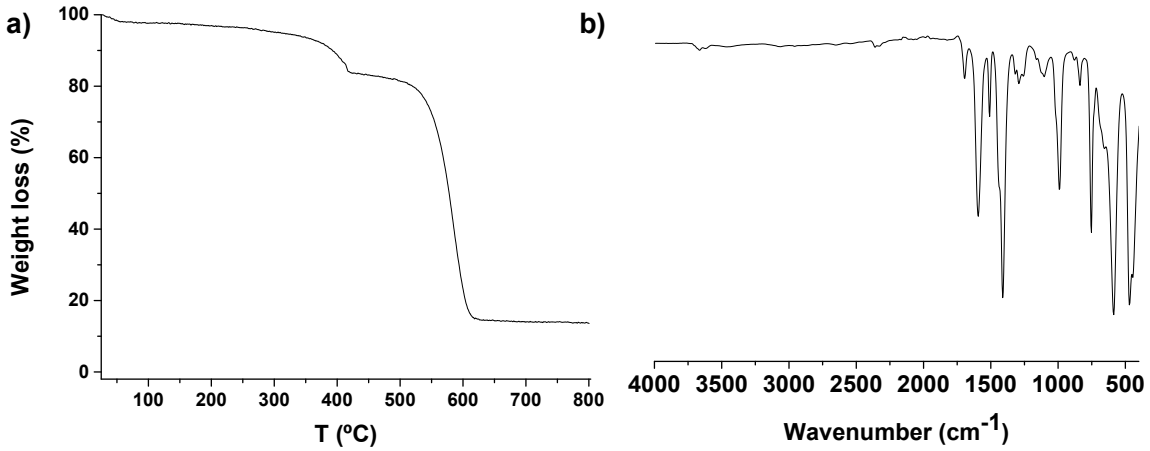


Fig S1. Powder XRD (left) and N_2 isothermal adsorption (right) of MIL-53(Al) sample. Note: PXRD patterns of MIL-53(Al) was recorded on a Philips XPert diffractometer equipped with a graphite monochromator (40 kV and 45 mA) employing Ni filtered CuKα radiation. N_2 adsorption isotherms at 77 K was recorded using a Micromeritics ASAP 2010 device.



Catalyst	Formula	Al (%)	
		Calc	Theorethical
MIL-53 (Al)	Al(OH)(CO_2-C_6H_4-CO_2)	10.6	12.6

Fig S2. Termogravimetry (a) and FT-IR (b) of MIL-53(Al) sample. Note: Termogravimetric analyses were performed on a TGA/SDTA851e METTLER TOLEDO station. ATR-FTIR spectra of MIL-53(Al) was recorded using a Bruker Tensor27 instrument after heating the samples were heated in an oven (100 ºC for 12 h) to remove physisorbed water.

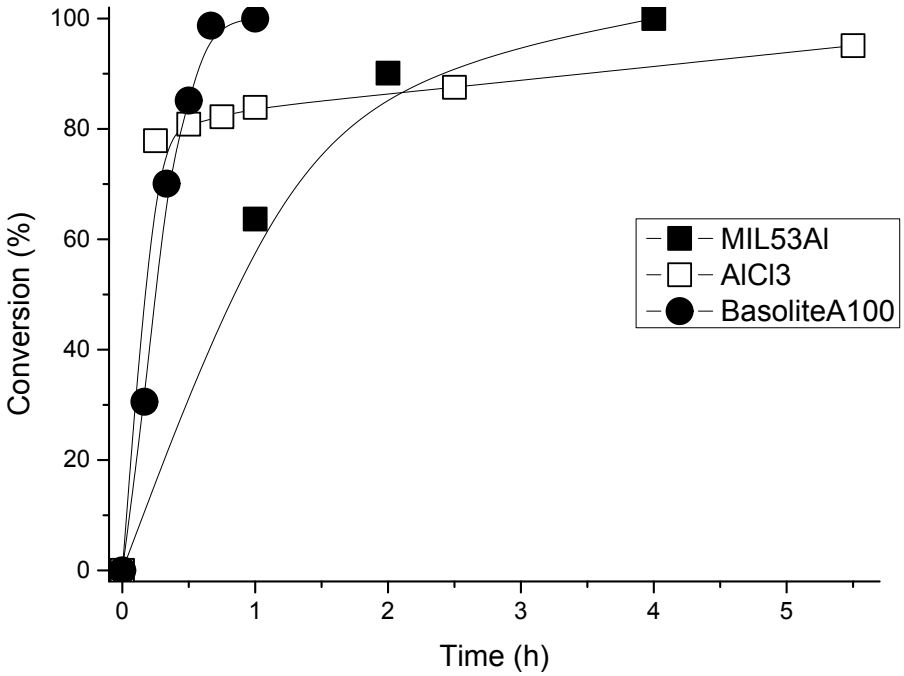


Figure S3. Time conversion plot for the silylation of benzyl alcohol with HMDS using commercial Al(OH(BDC) (■), synthetic MIL-53(Al) (□) and $AlCl_3$ (■) as catalysts. Reaction

conditions: benzyl alcohol (1 mmol), HMDS (1 mmol), catalyst (50 mg of Basolite A100 and MIL-53(Al) or equivalent in mmol of Al for $AlCl_3$), toluene (2 mL), r.t.

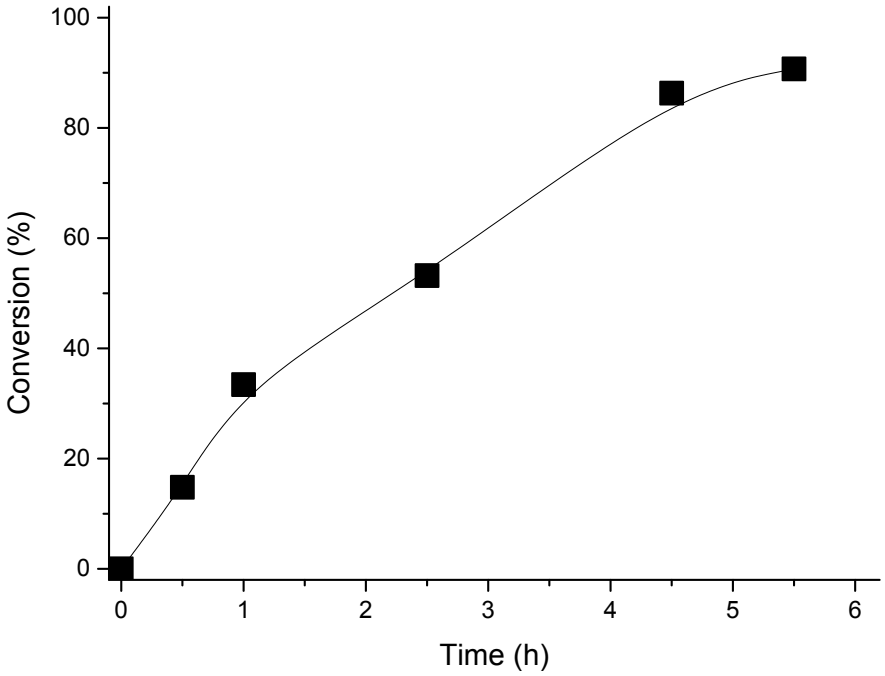


Figure S4. Time conversion plot of the reaction of HDMS and 2-phenyl-2-propanol catalyzed by Basolite A100. Reaction conditions: 2-phenyl-2-propanol (1 mmol), HMDS (1 mmol), Basolite A100 (50 mg), toluene (2 mL), r.t.

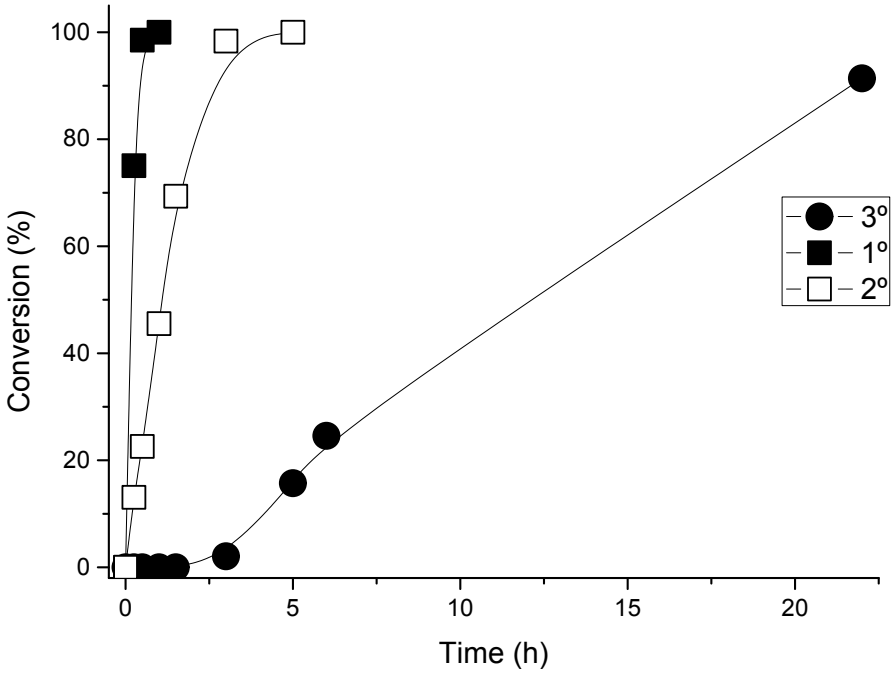


Figure S5. Competitive silylation of benzyl alcohol, 1-phenylethanol and 2-phenyl-2-propanol by HDMS in the presence of Basolite A100 as catalyst. Reaction conditions: benzyl alcohol (1 mmol), 1-phenylethanol (1 mmol), 2-phenyl-2-propanol (1 mmol), HMDS (1 mmol), Basolite A100 (50 mg), toluene (2 mL), r.t. up to 5 h, then 50 ^{o}C until final reaction time.

Experimental section.

IR spectra were recorded with a Nexus 8700 FTIR spectrometer using a DTGS detector and acquiring at 4 cm^{-1} resolution. An IR cell allowing in situ treatments in controlled atmospheres and temperatures from 25 ºC to 500 ºC has been connected to a vacuum system with gas dosing facility. The samples were pressed into self-supported wafers and pre-treated at 150 ºC in vacuum (10^{-4} mbar) for 1h. For the adsorption study, each reactant was adsorbed separately at 25ºC on the pre-activated samples at increasing dosing from 0.2 to 2mbar. Spectra were acquired after each dosing. For the "in situ" study, both HDMS (2mbar) and benzyl-alcohol (2mbar) was co-adsorbed on the pre-activated sample at 25ºC. Spectra were acquired after 3h.

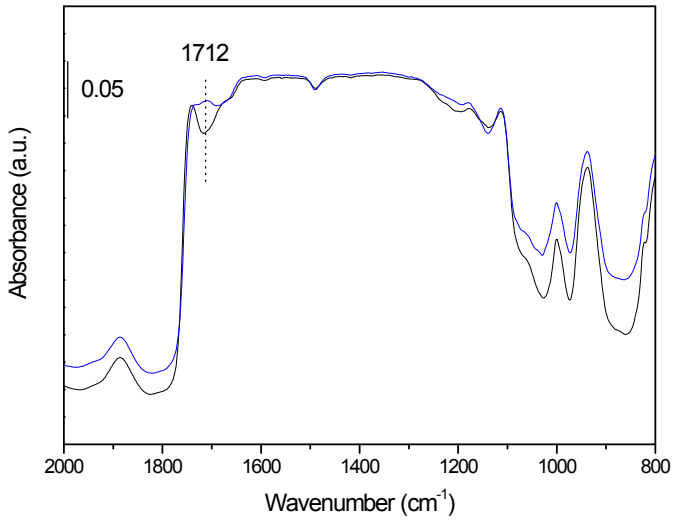


Fig.S6 IR spectra of benzyl-alcohol adsorbed on Fe (BTC) at 2mbar and 25ºC (blue line). Black line Fe(BTC) before adsorption.

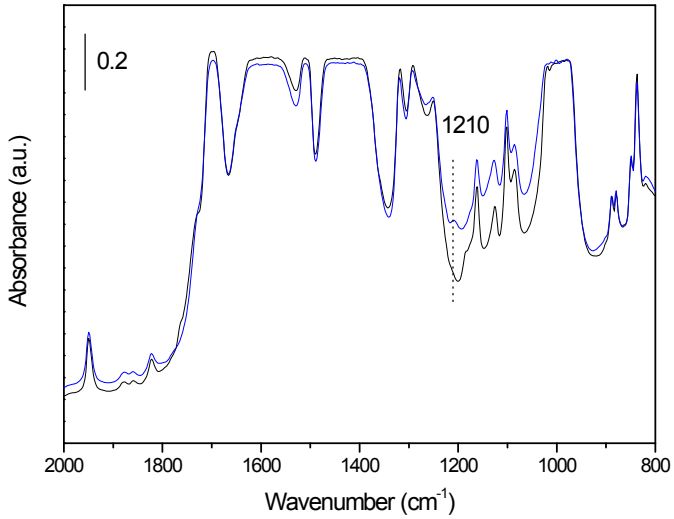


Fig.S7 IR spectra of benzyl-alcohol adsorbed on Al(OH)(BDC) at 2mbar and 25ºC (blue line). Black line Al(OH)(BDC) before adsorption.

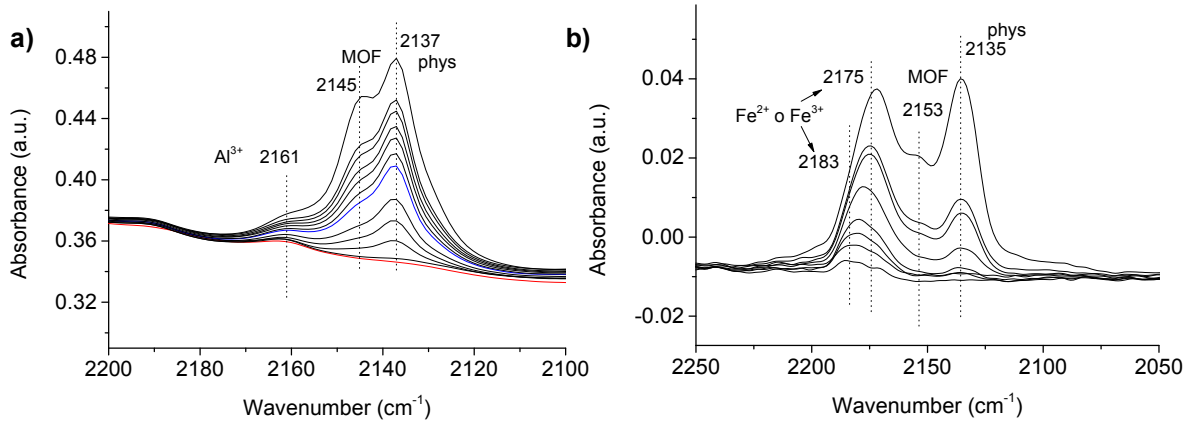
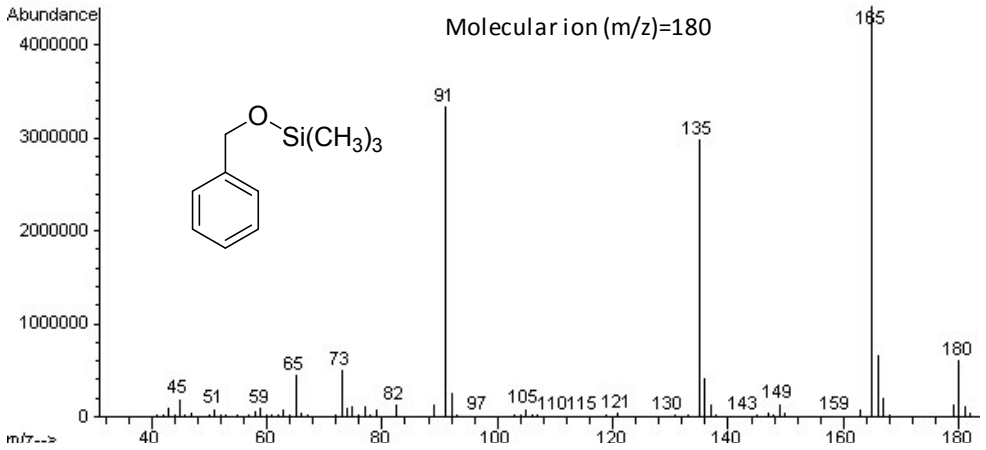


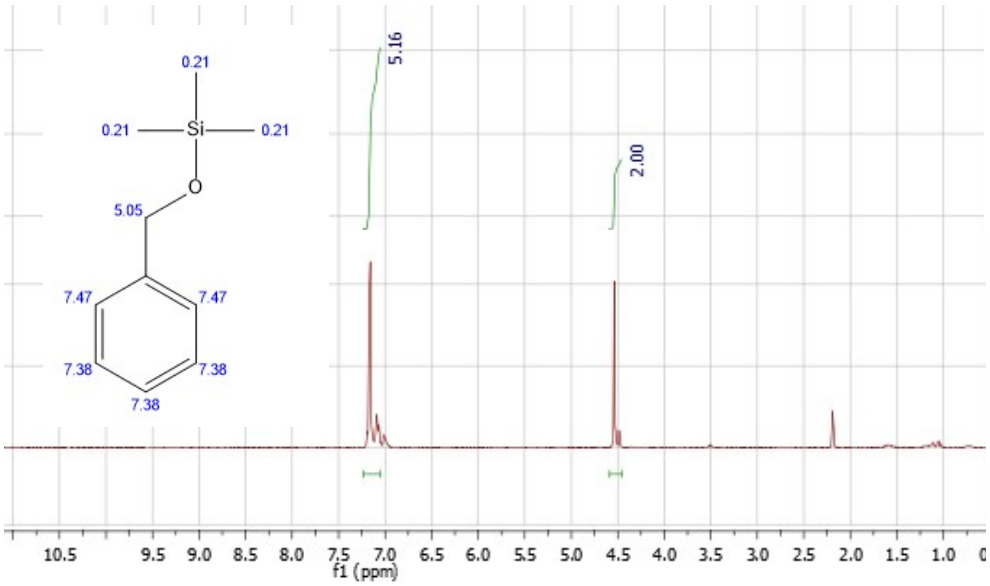
Fig S8. CO adsorption at low temperature using Basolite A-100 (a) and Fe(BTC)(b)

Table S1. Mass spectrum (a), ^{1}H-NMR (b) and ^{13}C-NMR (Bruker Advance 400 MHz) of the different products under study. Note that the numbers appearing in the chemical structure of ^{1}H- and ^{13}C-NMR represents the NMR shifts in ppm estimated using ChemDraw® software. $CDCl_3$ was employed as solvent.

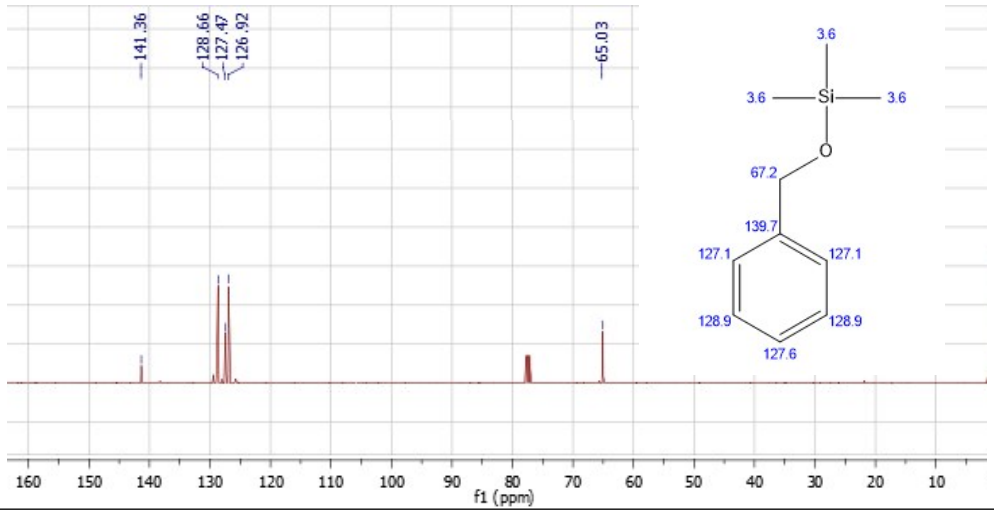
a)



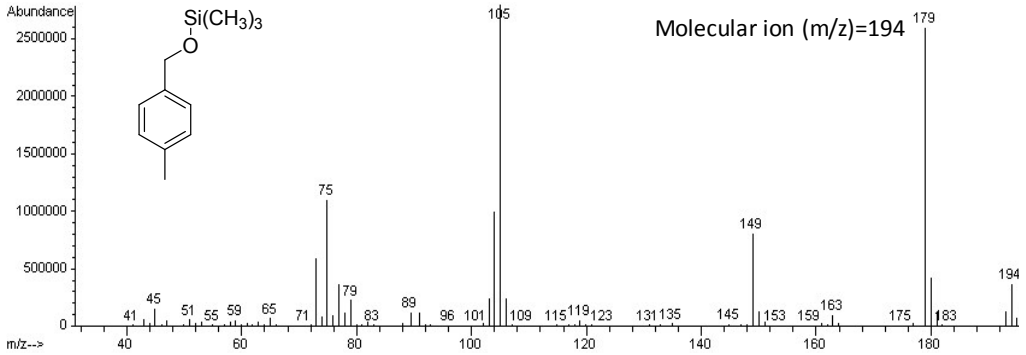
b)



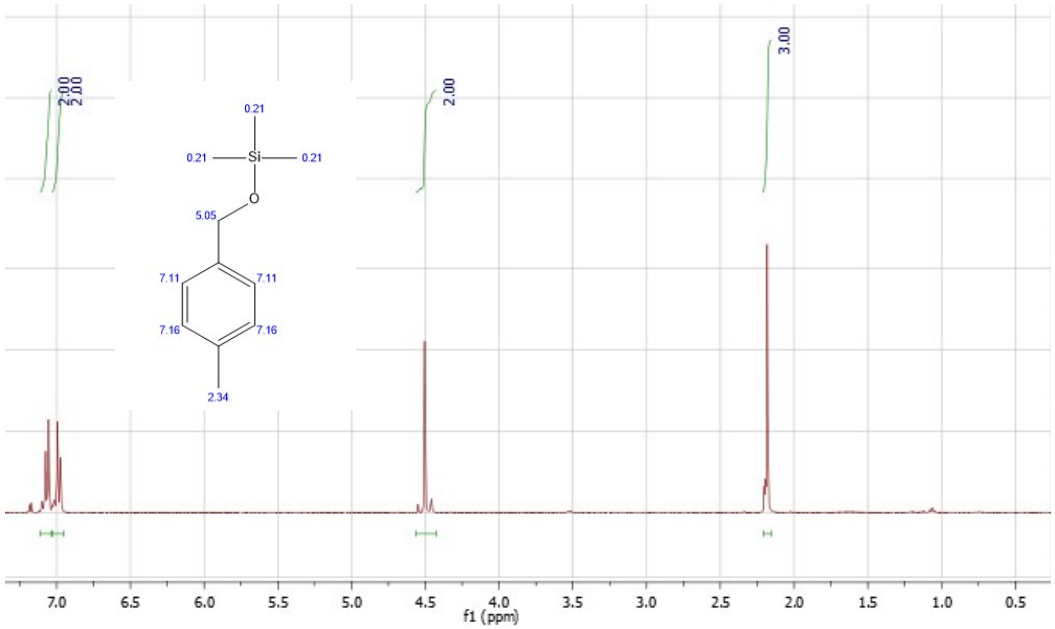
c)



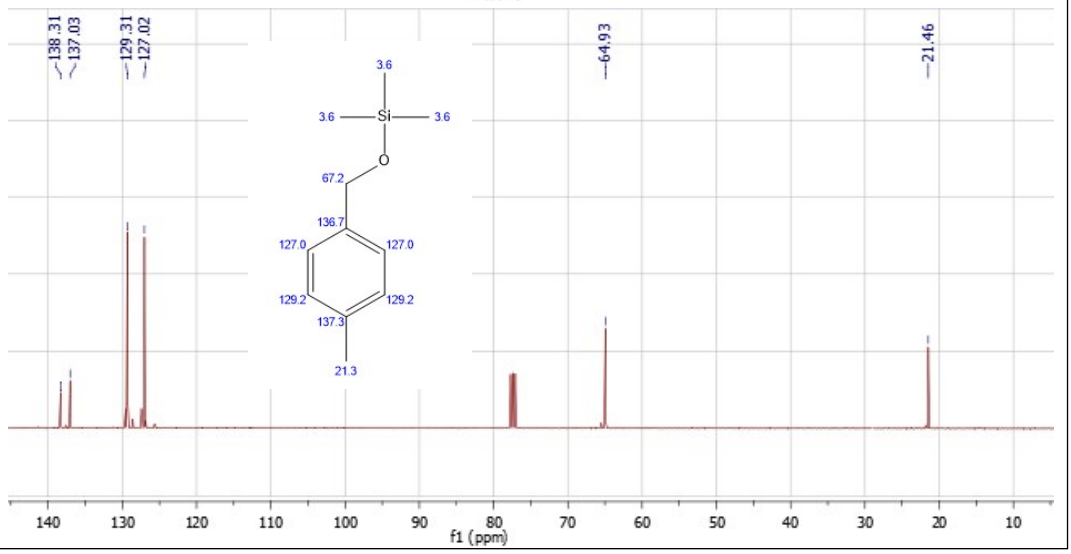
a)


Abundance
2500000
2000000
1500000
1000000
500000
0
m/z-->
Si(CH3)3
O
Molecular ion (m/z)=194
105
179
75
149
194
45
79
89
41
51
55
59
65
71
83
96
101
109
115
119
123
131
135
145
153
159
163
175
183
40
60
80
100
120
140
160
180

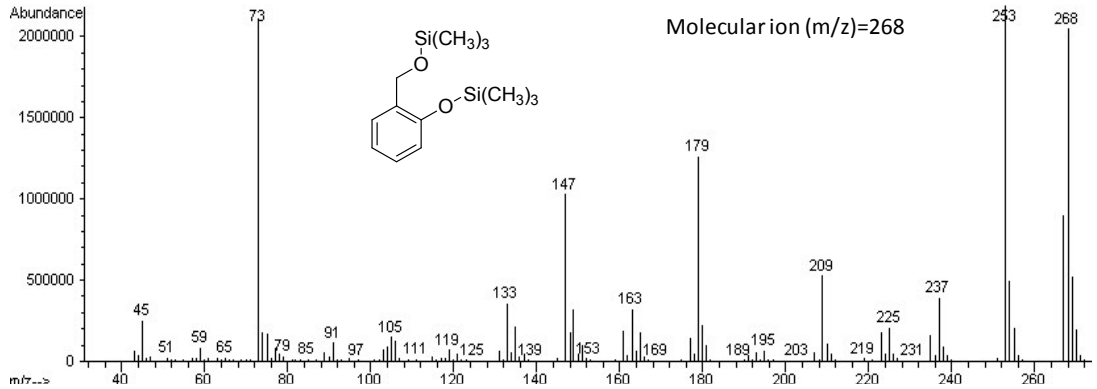
b)


2.00
2.00
2.00
3.00
0.21
0.21
0.21
Si
O
5.05
7.11
7.11
7.16
7.16
2.34
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
f1 (ppm)

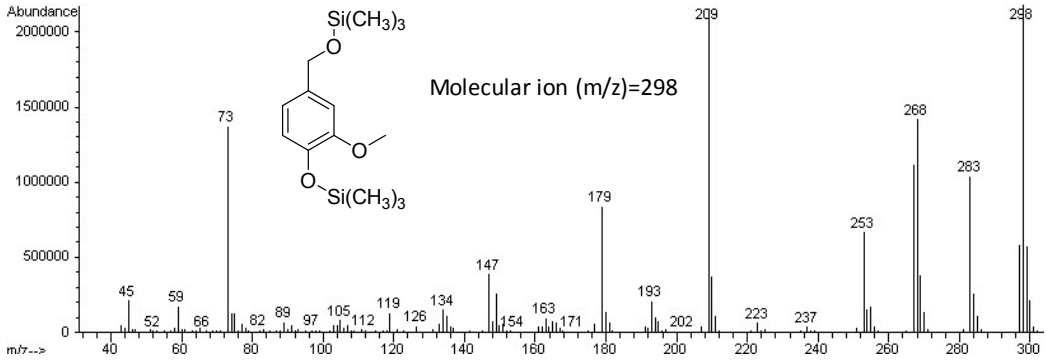
c)


138.31
137.03
129.31
127.02
64.93
21.46
3.6
3.6
3.6
Si
O
67.2
136.7
127.0
127.0
129.2
129.2
137.3
21.3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

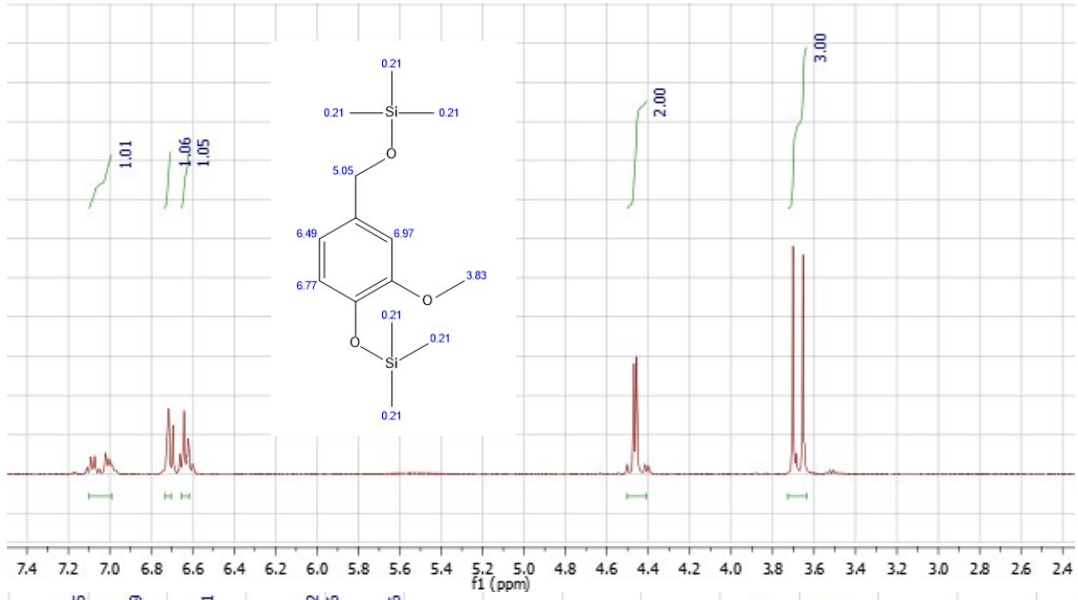
a)


Abundance
Molecular ion (m/z)=268
Si(CH3)3
O
Si(CH3)3

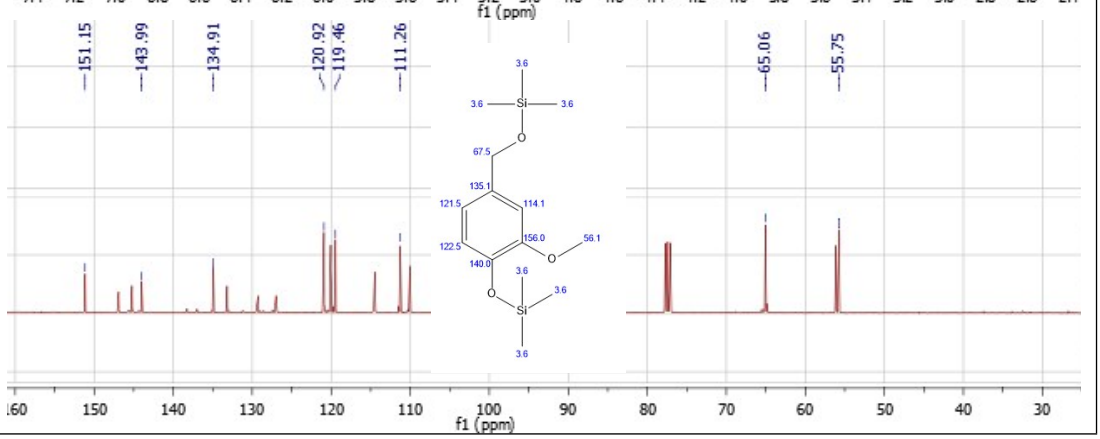
a)


Abundance
Molecular ion (m/z)=298
Si(CH3)3
O
Si(CH3)3

b)

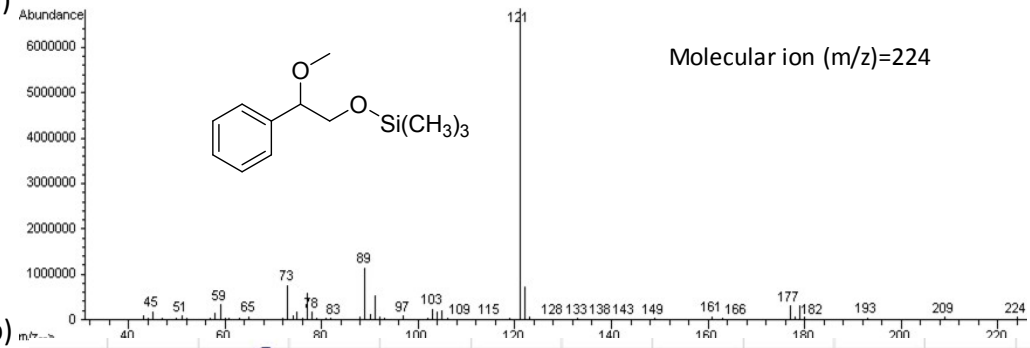

1.01
1.06
1.05
2.00
3.00
f1 (ppm)

c)


151.15
143.99
134.91
120.92
119.46
111.26
65.06
55.75
f1 (ppm)

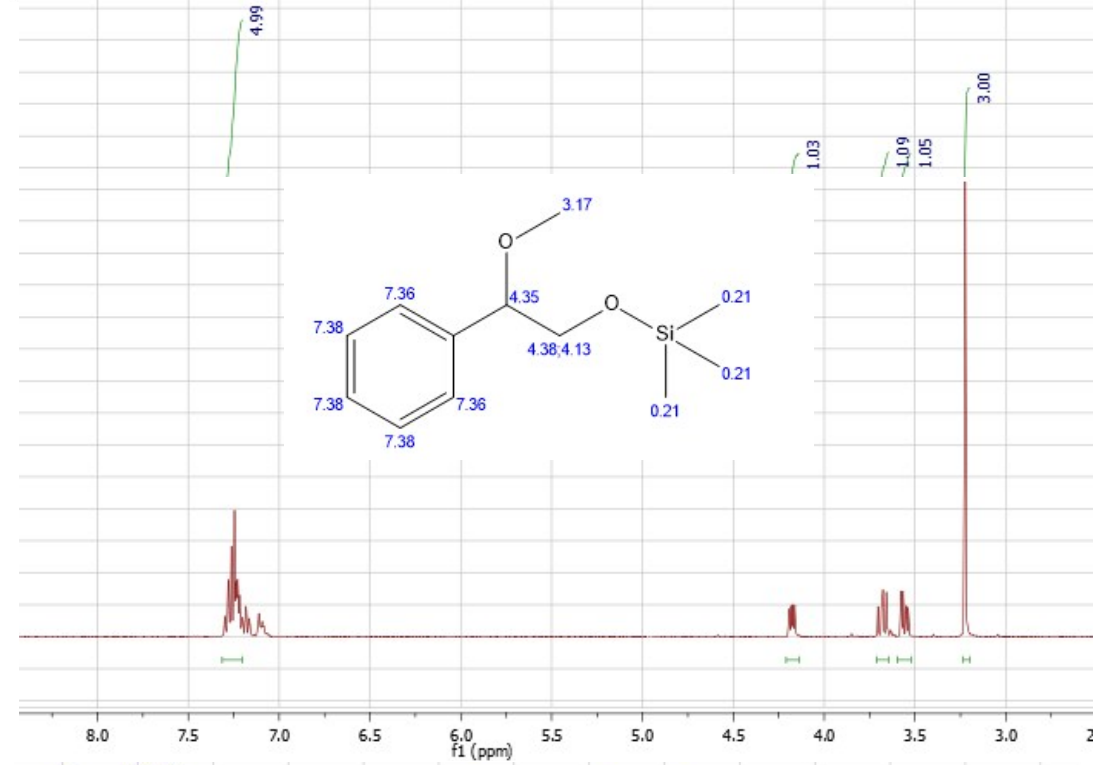
^{1}H and ^{13}C-NMR shows signals of the mono- and bis-silylated compound

a)

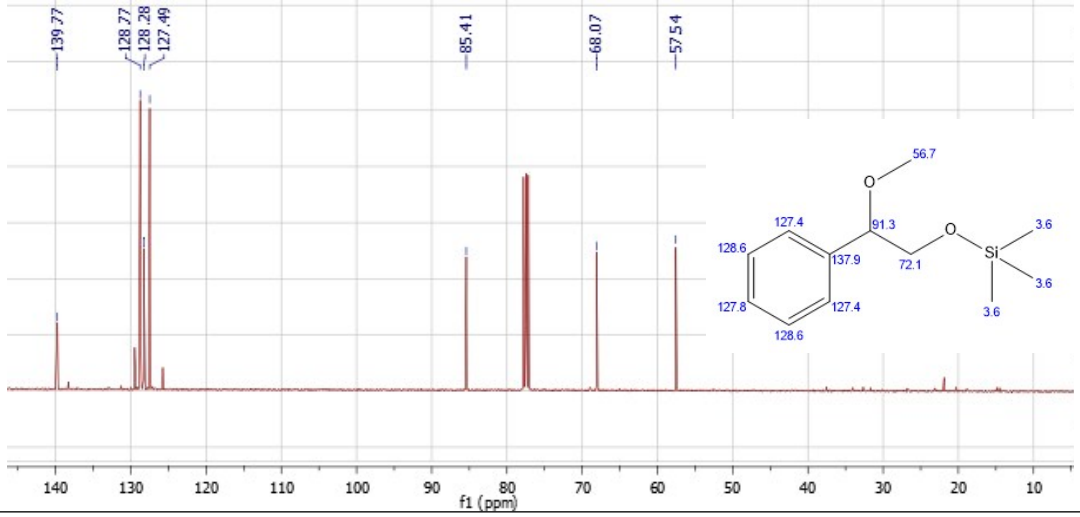


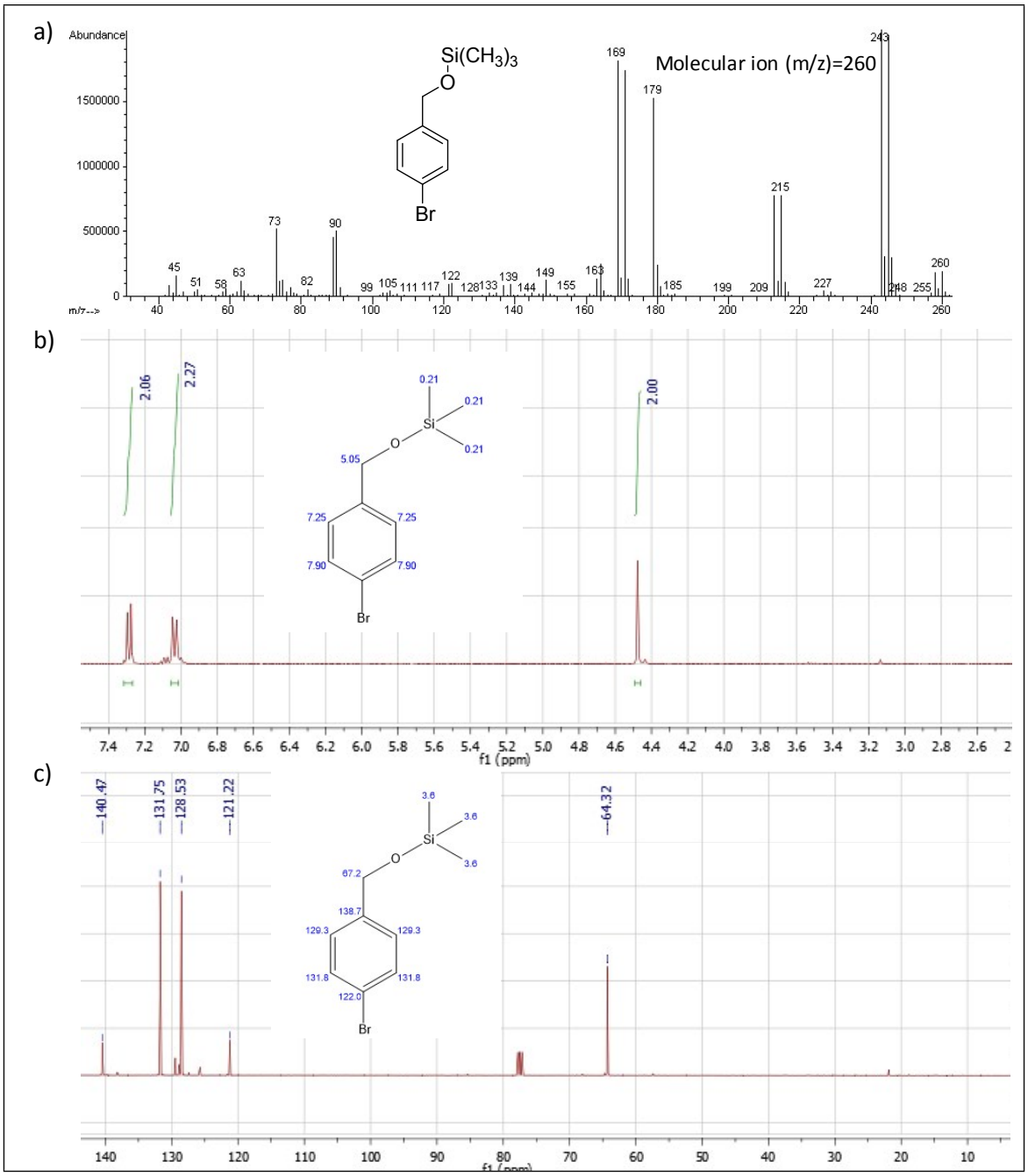
Molecular ion (m/z)=224

b)

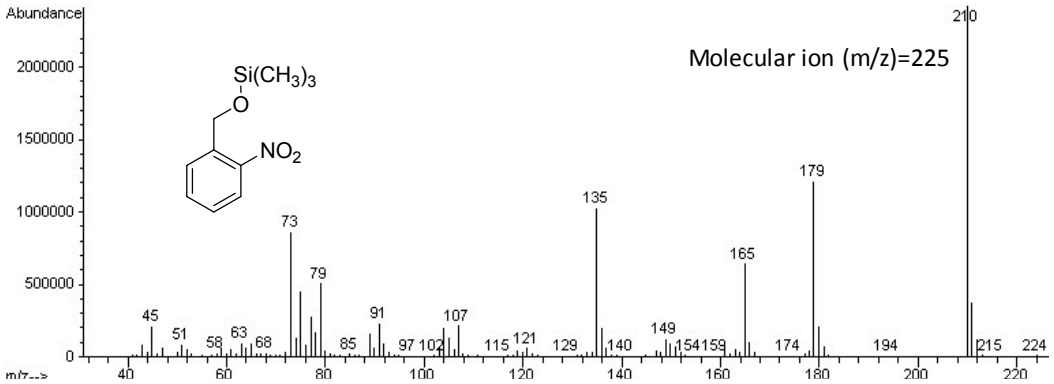


c)

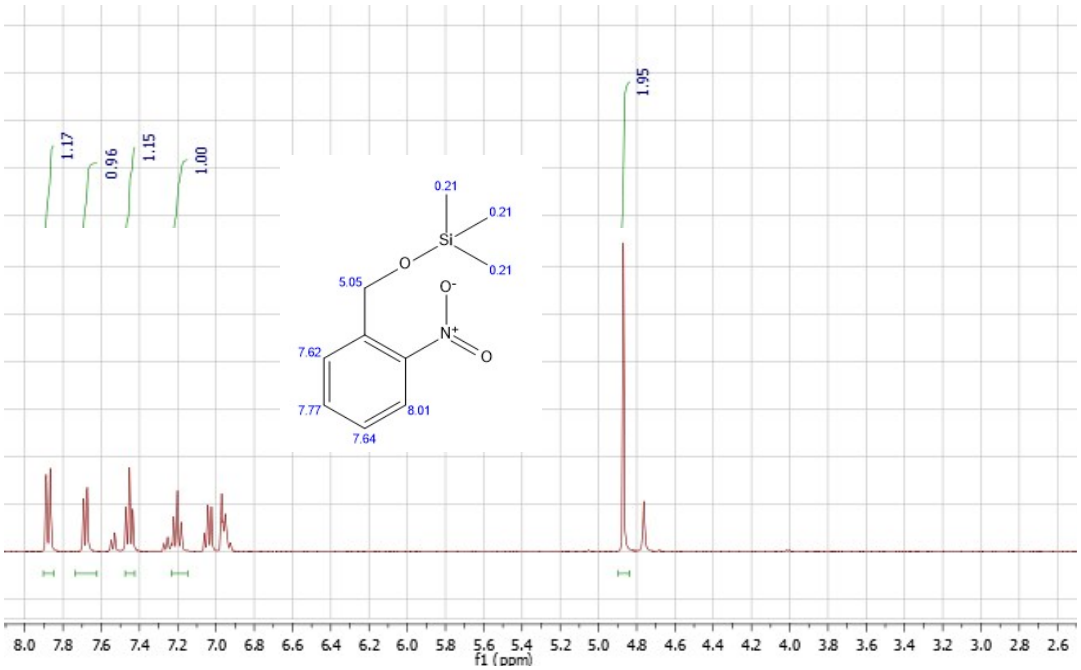



a)
Abundance
Si(CH3)3
O
Br
Molecular ion (m/z)=260
169
179
243
215
260
73
90
45
63
82
122
139
149
163
b)
2.06
2.27
2.00
0.21
0.21
0.21
Si
O
5.05
7.25
7.25
7.90
7.90
Br
f1 (ppm)
c)
140.47
131.75
128.53
121.22
64.32
3.6
3.6
3.6
Si
O
67.2
138.7
129.3
129.3
131.8
131.8
122.0
Br
f1 (ppm)

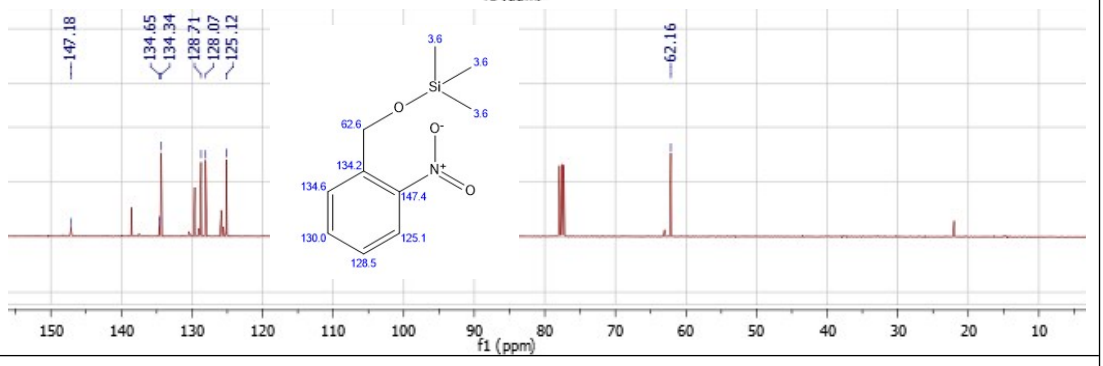
a)


Abundance
Molecular ion (m/z)=225
Si(CH3)3
O
NO2
210
179
135
165
73
79
91
107
45
51
58
63
68
85
97
102
115
121
129
140
149
154
159
174
194
215
224
m/z-->

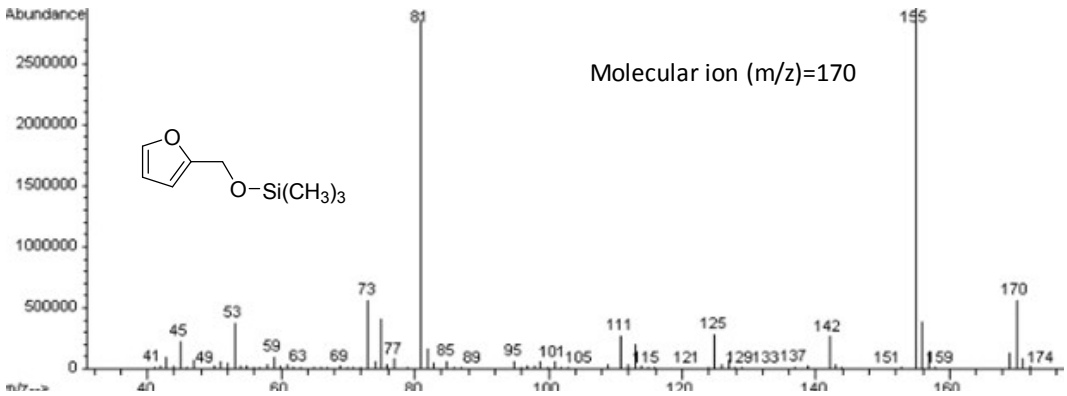
b)


1.17
0.96
1.15
1.00
1.95
0.21
0.21
0.21
Si
O
5.05
O-
N+
O
7.62
7.77
8.01
7.64
f1 (ppm)

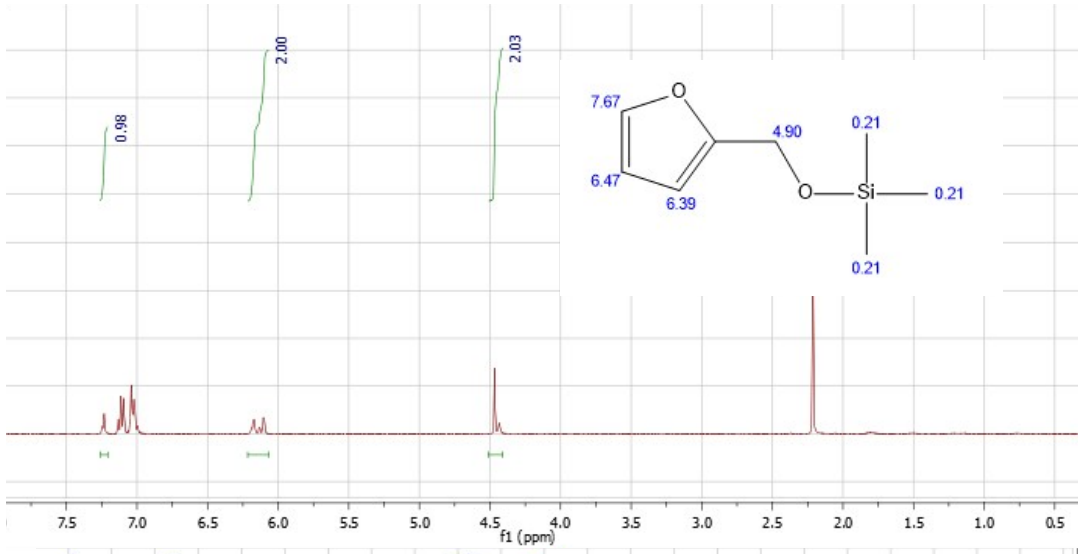
c)


147.18
134.65
134.34
128.71
128.07
125.12
62.16
3.6
3.6
3.6
Si
O
62.6
O-
N+
O
134.2
134.6
147.4
130.0
125.1
128.5
f1 (ppm)

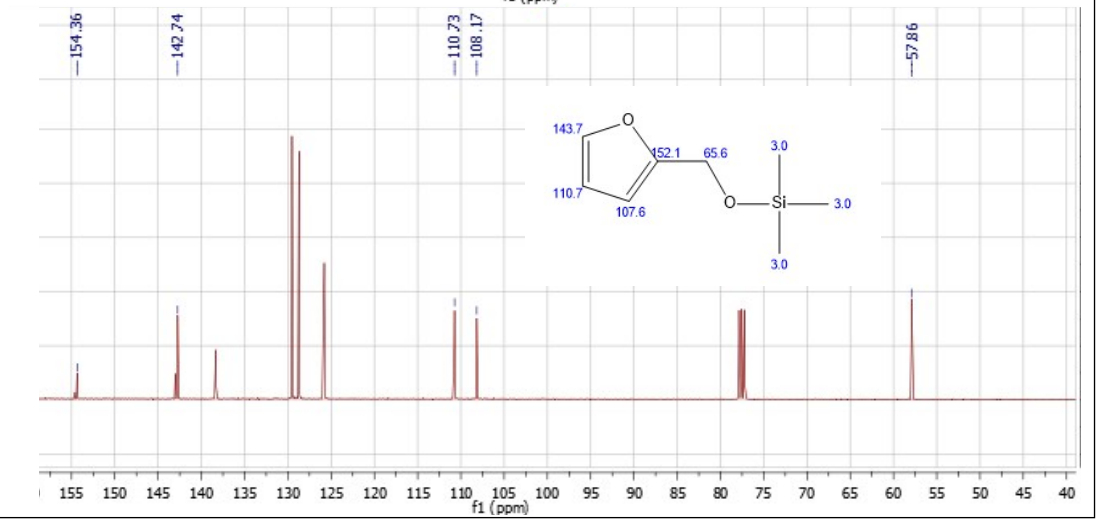
a)

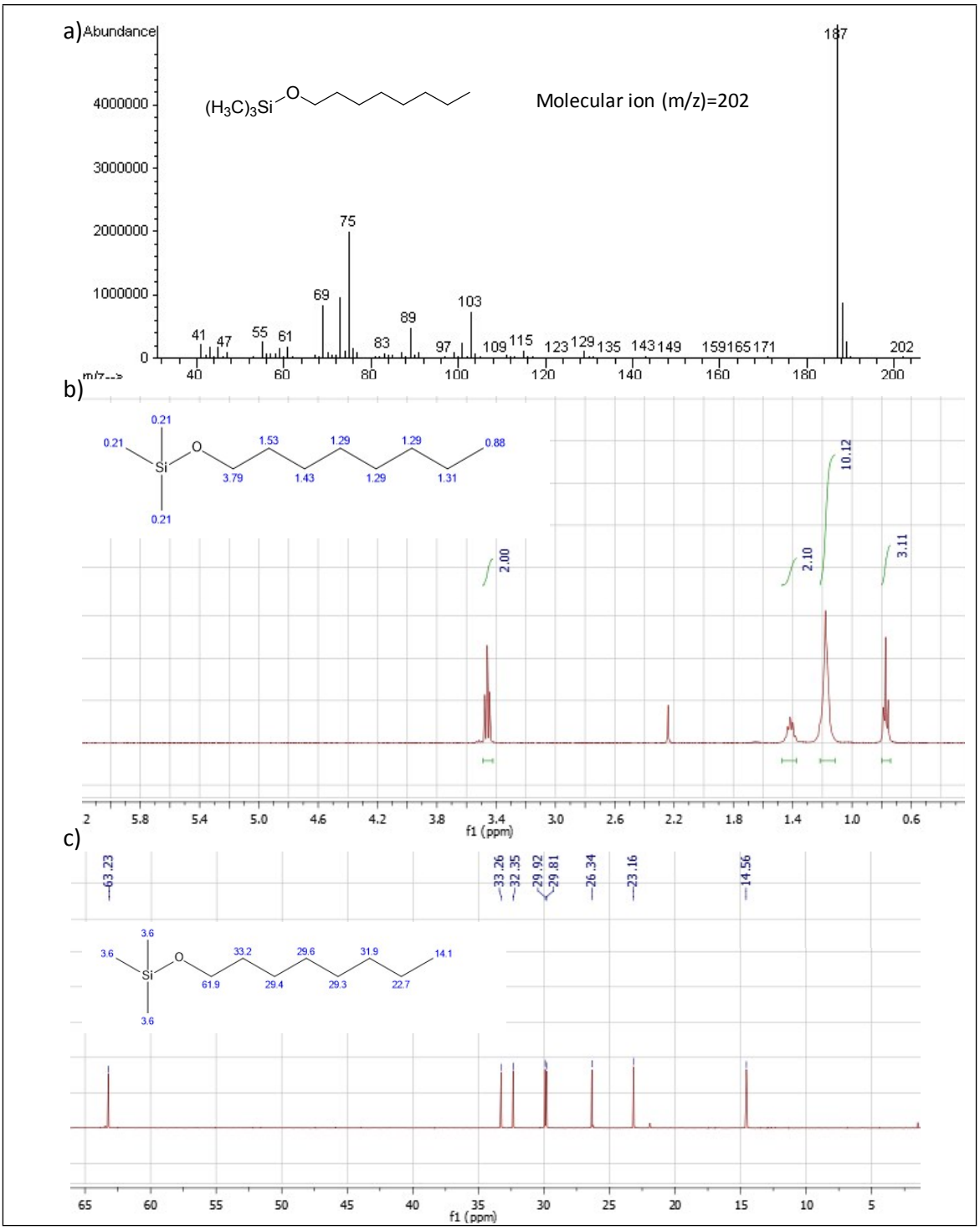

Abundance
Molecular ion (m/z)=170
O
O−Si(CH3)3

b)

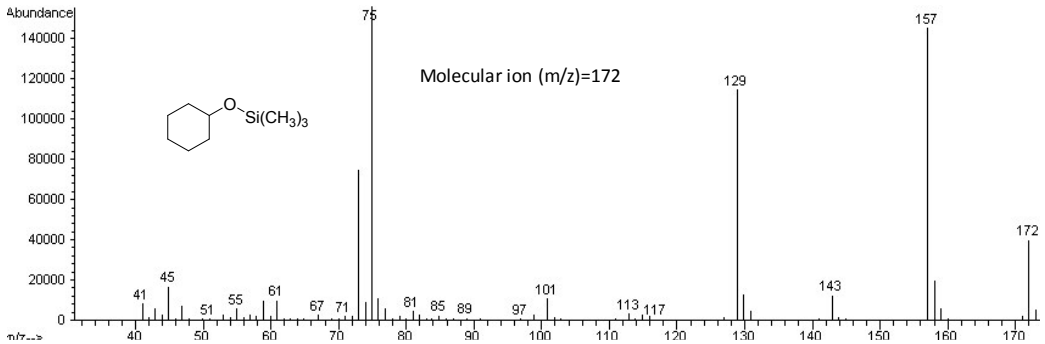

0.98
2.00
2.03
7.67
4.90
0.21
6.47
6.39
Si
0.21
0.21
f1 (ppm)

c)

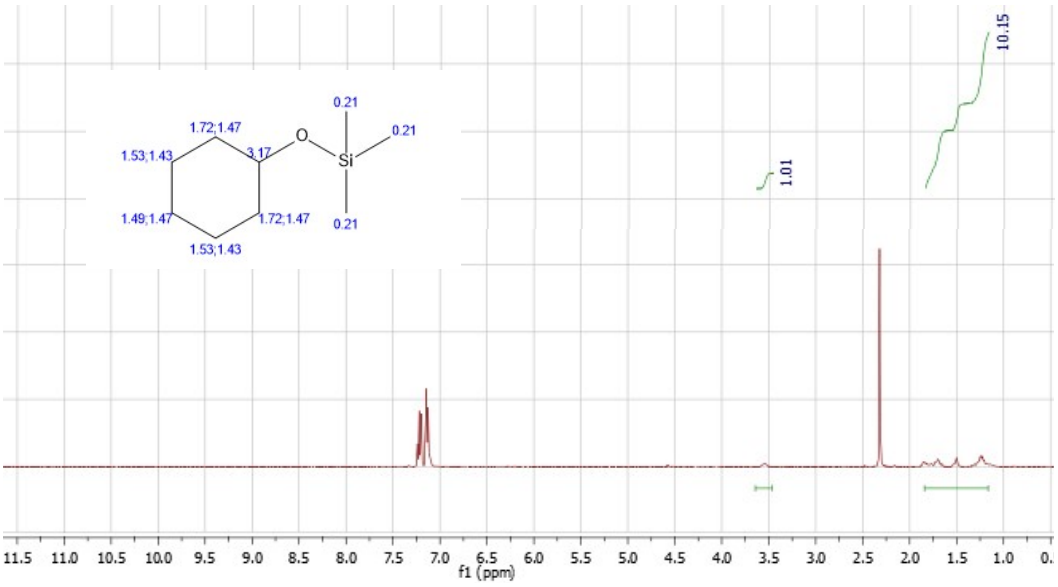

154.36
142.74
110.73
108.17
57.86
143.7
152.1
65.6
3.0
110.7
107.6
Si
3.0
3.0
f1 (ppm)


a)
Abundance
4000000
3000000
2000000
1000000
0
(H3C)3Si
O
Molecular ion (m/z)=202
187
75
69
103
89
41
47
55
61
83
97
109
115
123
129
135
143
149
159
165
171
202
40
60
80
100
120
140
160
180
200
b)
0.21
0.21
Si
O
0.21
1.53
1.29
1.29
0.88
3.79
1.43
1.29
1.31
2.00
2.10
10.12
3.11
2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
f1 (ppm)
c)
63.23
33.26
32.35
29.92
29.81
26.34
23.16
14.56
3.6
3.6
Si
O
3.6
33.2
29.6
31.9
14.1
61.9
29.4
29.3
22.7
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

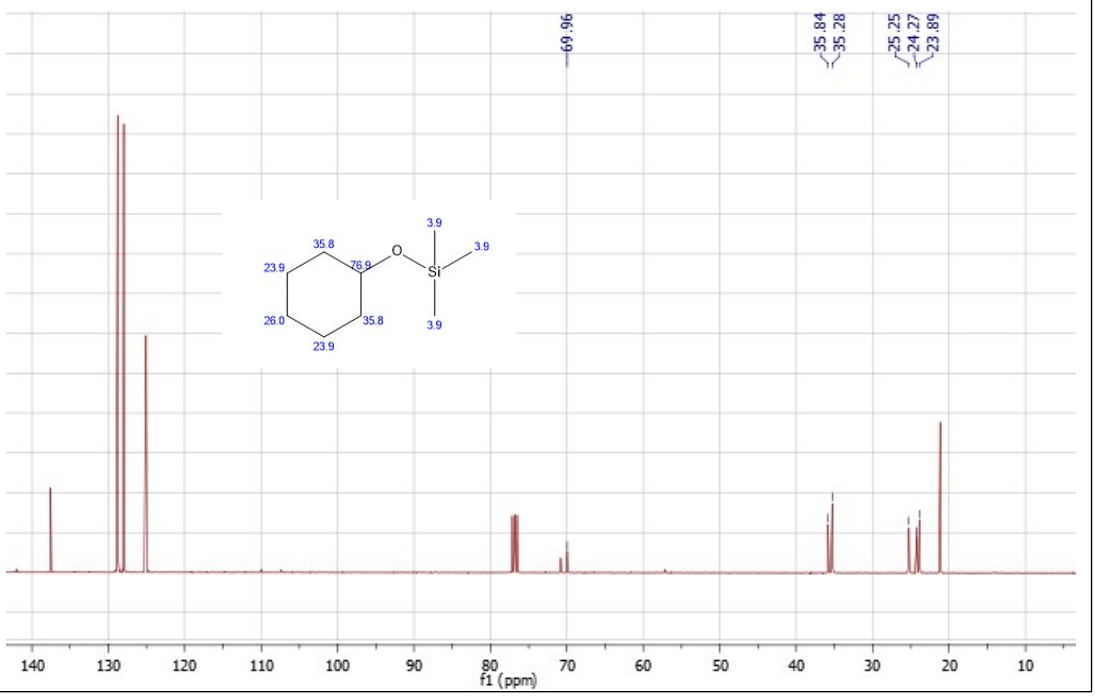
a)

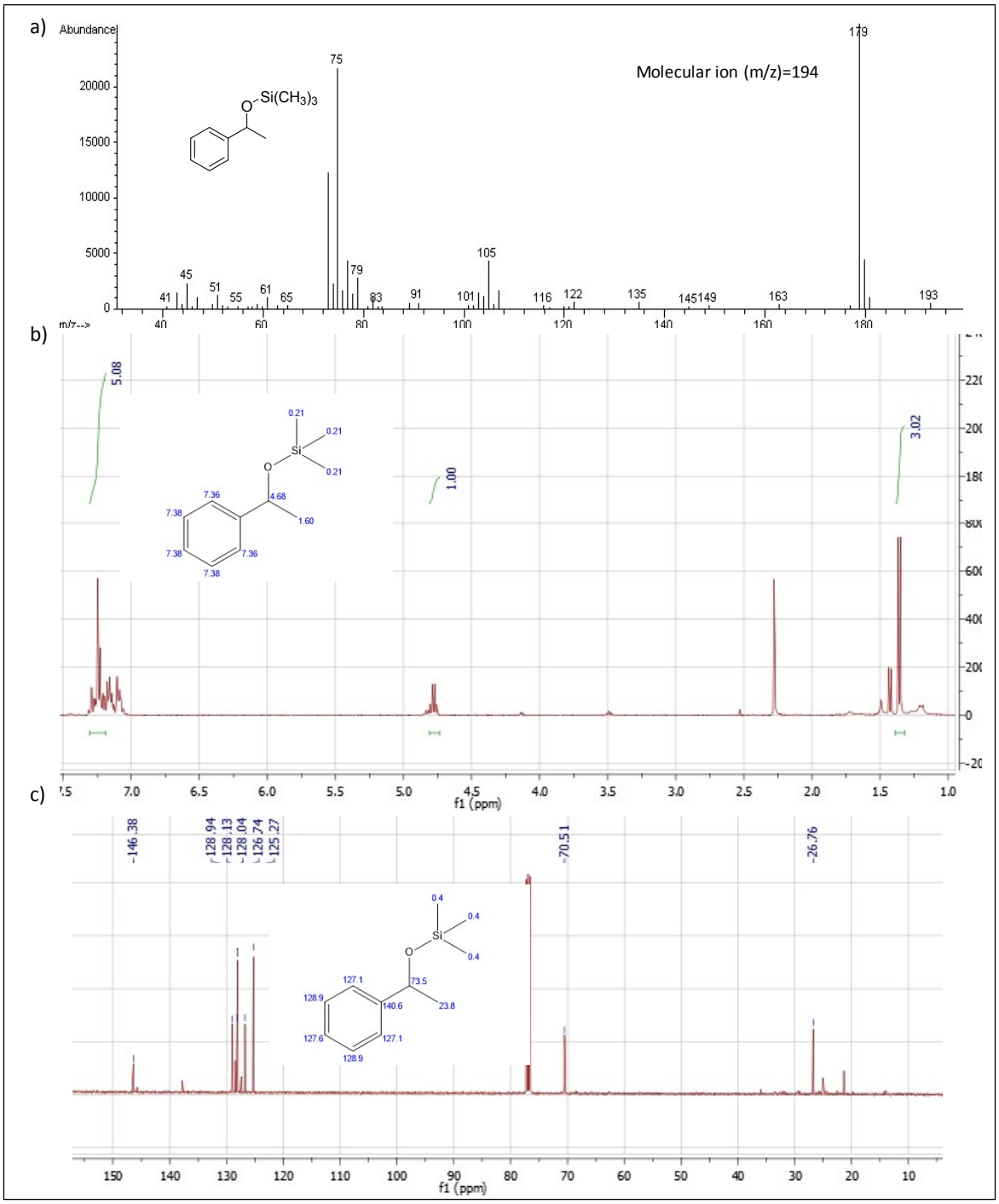

Abundance
140000
120000
100000
80000
60000
40000
20000
0
Molecular ion (m/z)=172
O
Si(CH3)3
75
157
129
172
143
101
45
41
51
55
61
67
71
81
85
89
97
113
117
40
50
60
70
80
90
100
110
120
130
140
150
160
170

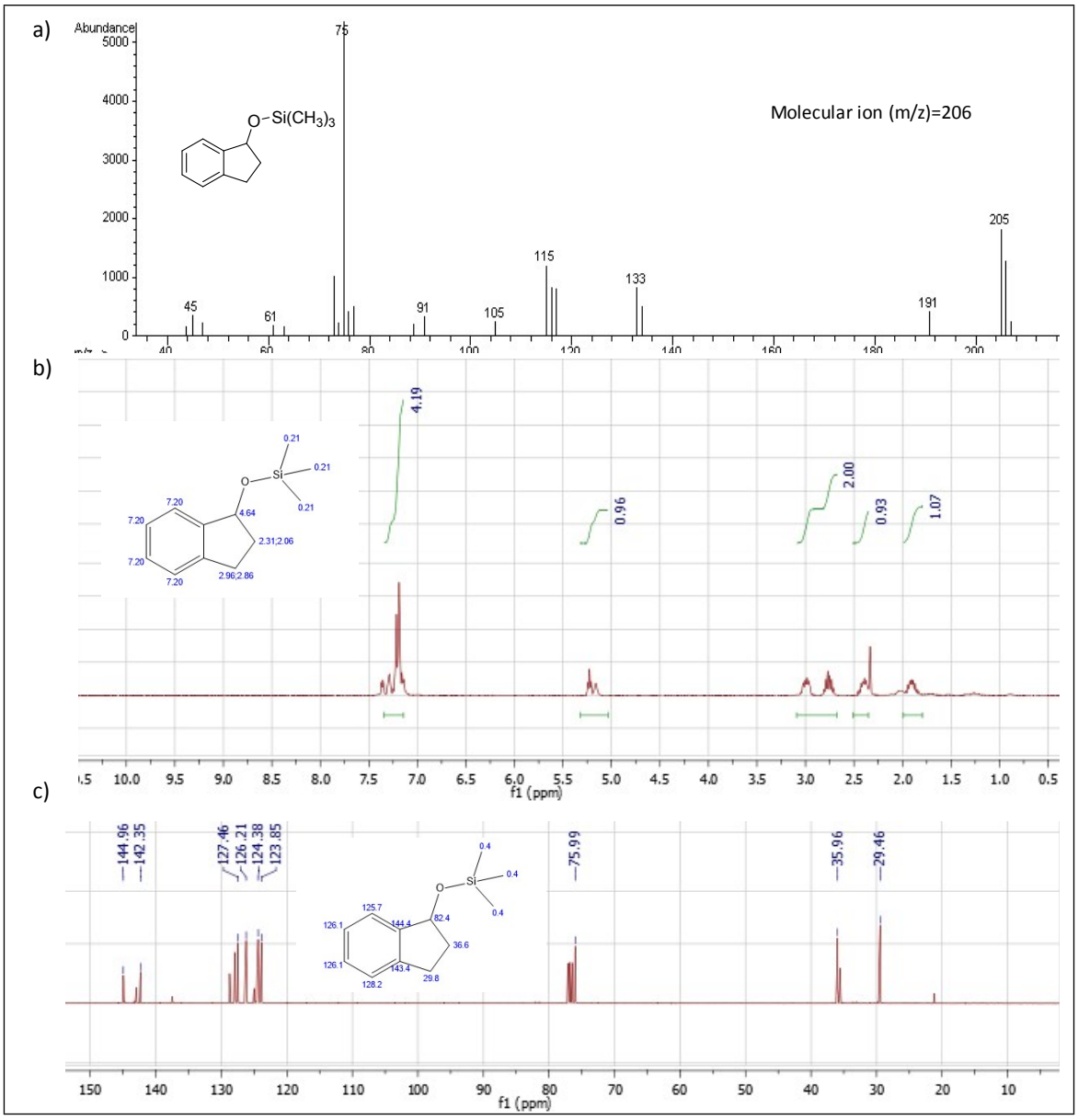
b)


0.21
1.72;1.47
0.21
1.53;1.43
3.17
O
Si
1.49;1.47
1.72;1.47
0.21
1.53;1.43
1.01
10.15
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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
f1 (ppm)

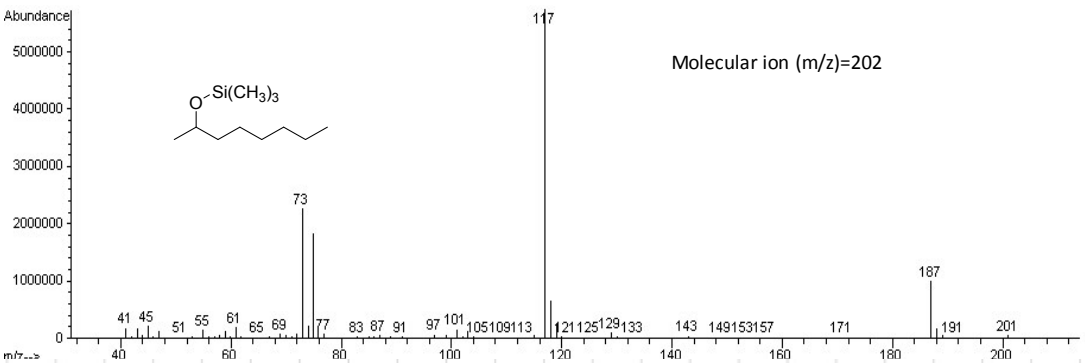
c)


69.96
35.84
35.28
25.25
24.27
23.89
3.9
35.8
3.9
23.9
76.9
O
Si
26.0
35.8
3.9
23.9
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

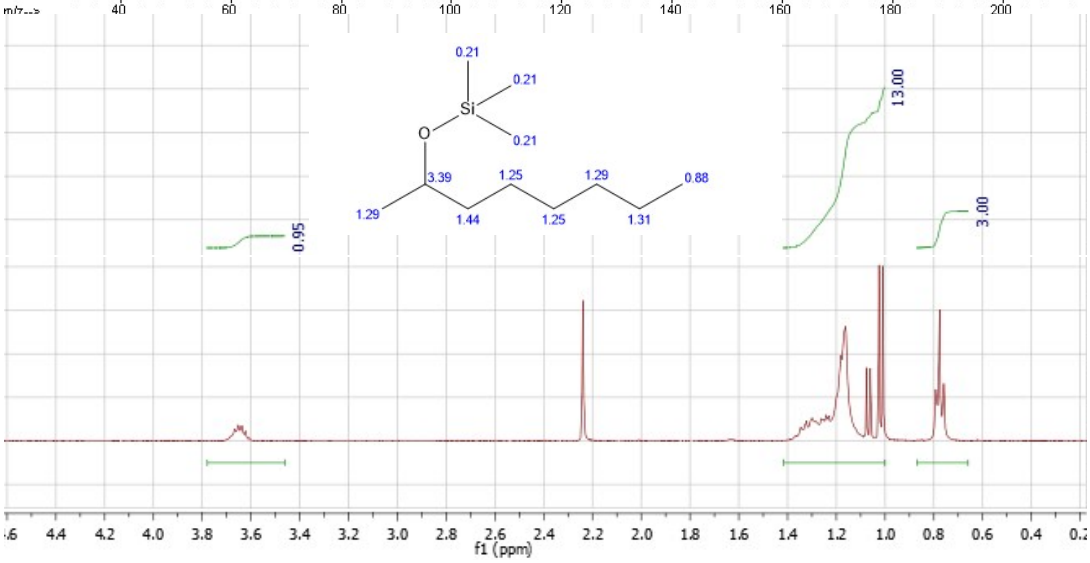

a)
Abundance
Molecular ion (m/z)=194
O-Si(CH3)3
b)
5.08
1.00
3.02
f1 (ppm)
c)
-146.38
128.94
128.13
128.04
126.74
125.27
-70.51
-26.76
f1 (ppm)


a)
Abundance
5000
4000
3000
2000
1000
0
O–Si(CH3)3
Molecular ion (m/z)=206
75
45
61
91
105
115
133
191
205
b)
4.19
0.96
2.00
0.93
1.07
0.21
0.21
0.21
7.20
7.20
7.20
7.20
4.64
2.31;2.06
2.96;2.86
f1 (ppm)
c)
144.96
142.35
127.46
126.21
124.38
123.85
75.99
35.96
29.46
0.4
0.4
0.4
125.7
126.1
126.1
144.4
82.4
36.6
143.4
29.8
128.2
f1 (ppm)

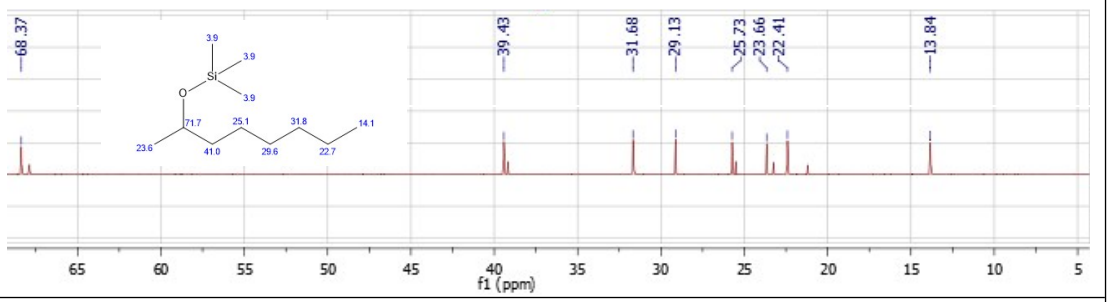
a)

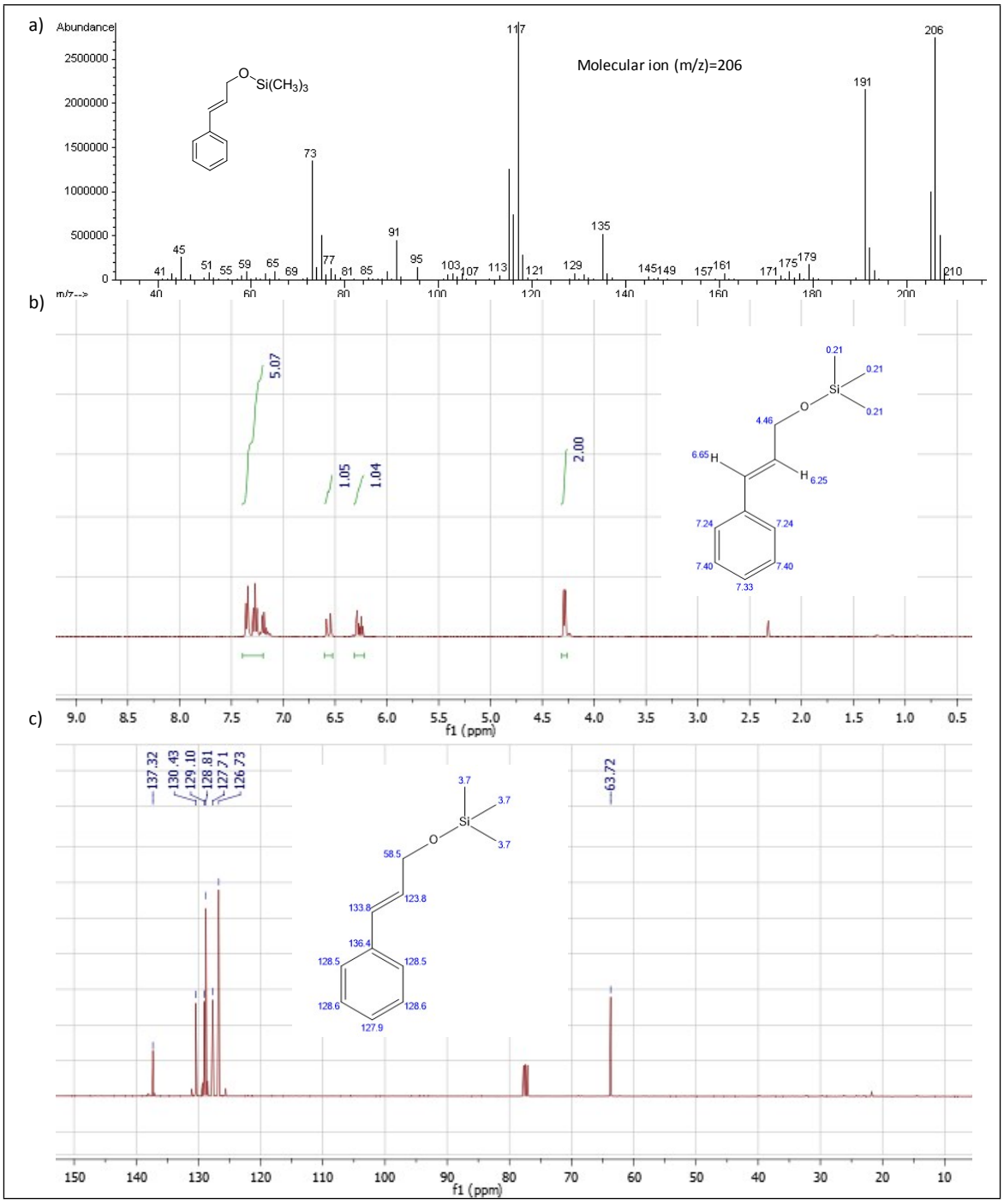

Abundance
5000000
4000000
3000000
2000000
1000000
0
Si(CH3)3
O
117
73
187
Molecular ion (m/z)=202
41 45 51 55 61 65 69 77 83 87 91 97 101 105 109 113 121 125 129 133 143 149 153 157 171 191 201
40 60 80 100 120 140 160 180 200

b)

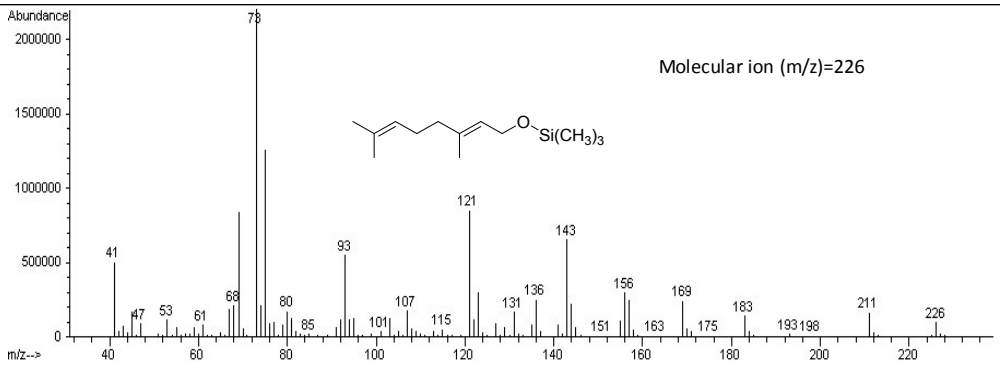

0.21
0.21
0.21
Si
O
3.39
1.25
1.29
0.88
1.29
1.44
1.25
1.31
0.95
13.00
3.00
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4
f1 (ppm)

c)


68.37
39.43
31.68
29.13
25.73
23.66
22.41
13.84
3.9
3.9
3.9
Si
O
71.7
25.1
31.8
14.1
23.6
41.0
29.6
22.7
65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

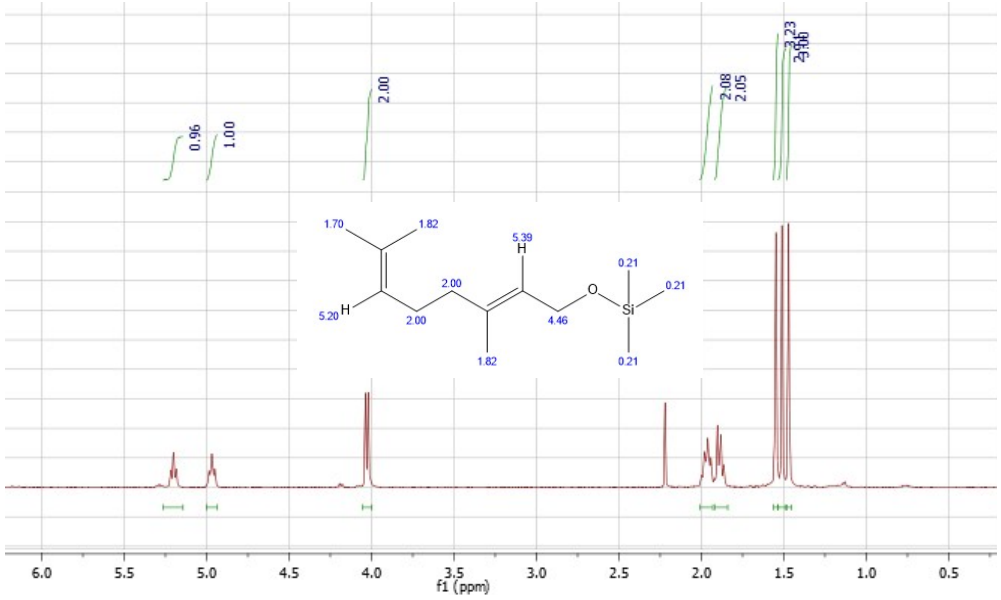

a)
Abundance
Molecular ion (m/z)=206
Si(CH3)3
b)
5.07
1.05
1.04
2.00
f1 (ppm)
c)
137.32
130.43
129.10
128.81
127.71
126.73
63.72
f1 (ppm)

a)

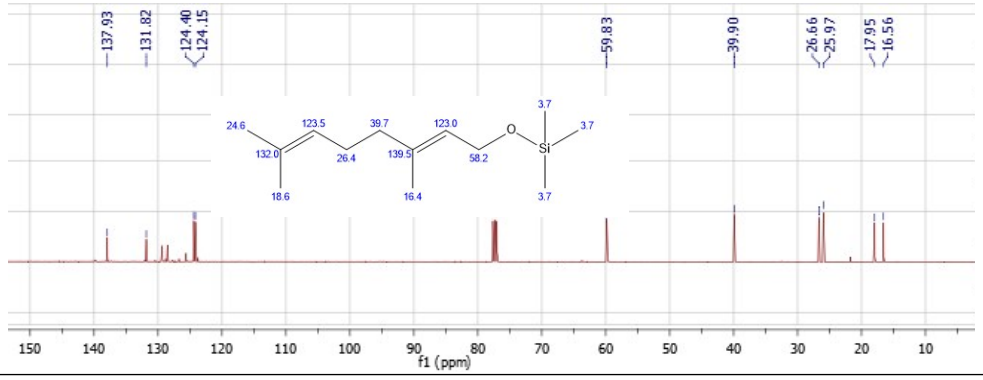


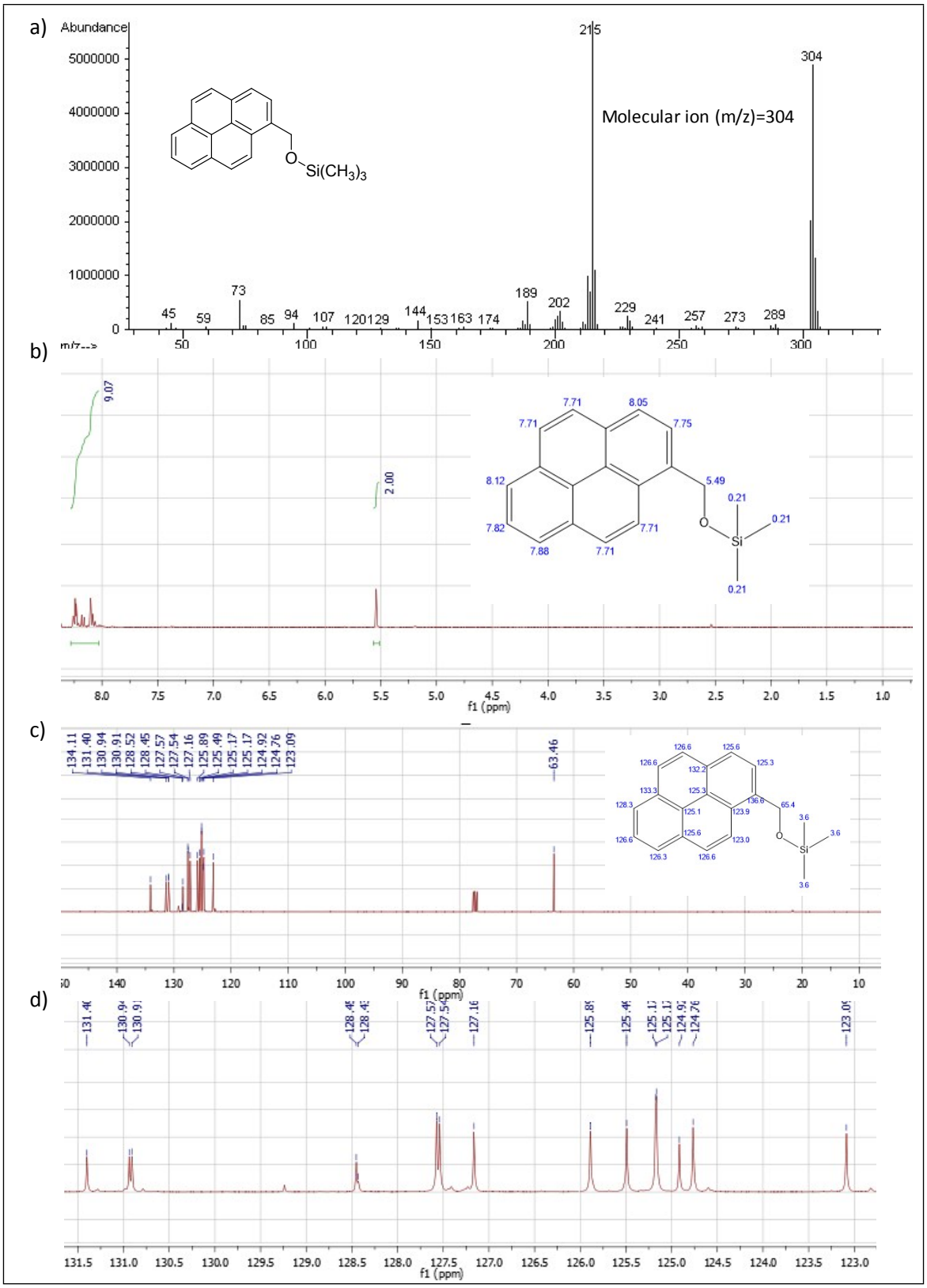
Molecular ion (m/z)=226

b)

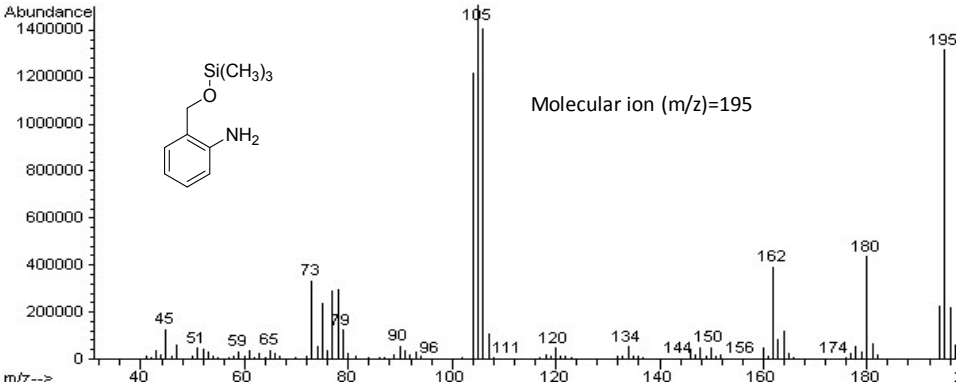


c)

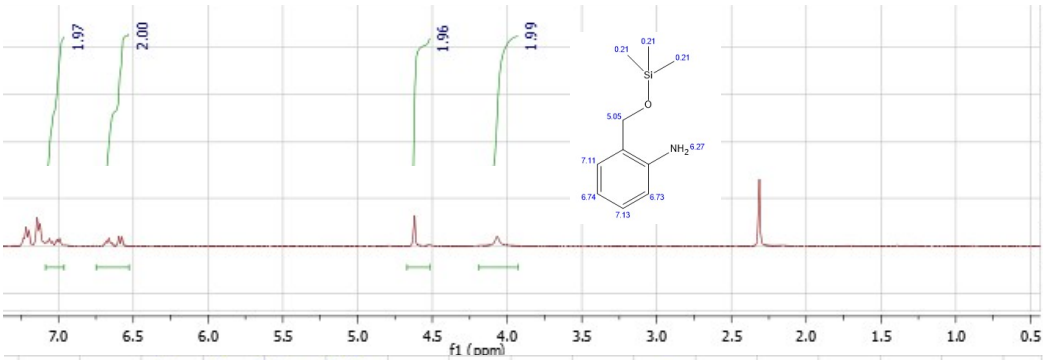



a)
Abundance
5000000
4000000
3000000
2000000
1000000
0
215
304
Molecular ion (m/z)=304
O
Si(CH3)3
73
45
59
85
94
107
120129
144
153163
174
189
202
229
241
257
273
289
50
100
150
200
250
300
b)
9.07
2.00
7.71
8.05
7.71
7.75
8.12
5.49
0.21
0.21
7.82
7.71
O
Si
7.88
7.71
0.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
c)
134.11
131.40
130.94
130.91
128.52
128.45
127.57
127.54
127.16
125.89
125.49
125.17
125.17
124.92
124.76
123.09
63.46
126.6
125.6
126.6
125.3
132.2
133.3
125.3
136.8
65.4
128.3
125.1
123.9
125.6
126.6
123.0
O
Si
3.6
3.6
3.6
126.3
126.6
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
d)
131.4
130.9
130.9
128.4
128.4
127.5
127.5
127.1
125.8
125.4
125.1
125.1
124.9
124.7
123.0
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
123.0
f1 (ppm)

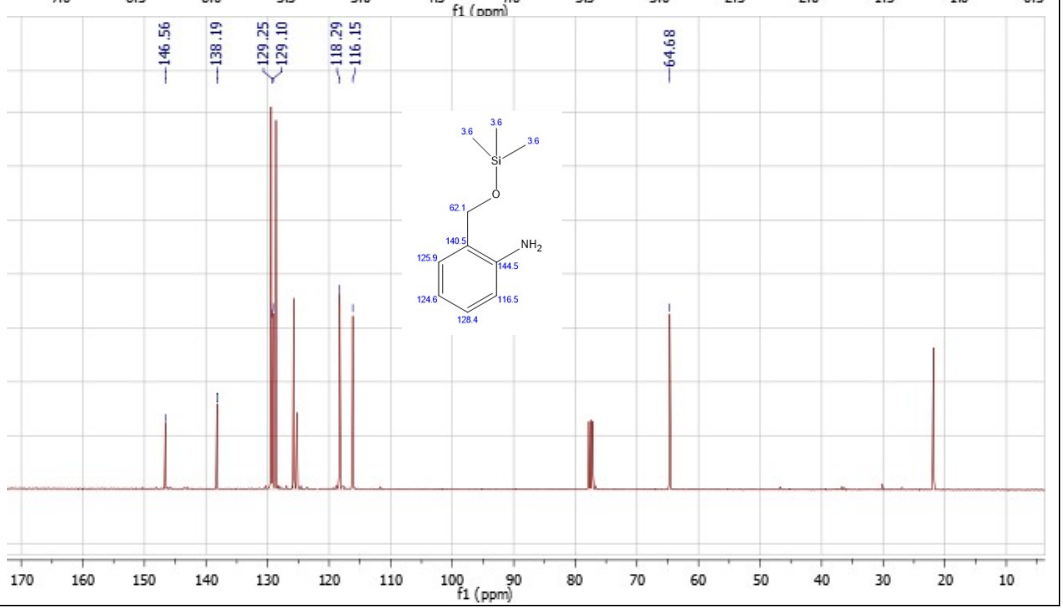
a)


Abundance
1400000
1200000
1000000
800000
600000
400000
200000
0
Si(CH3)3
O
NH2
Molecular ion (m/z)=195
105
195
73
79
45
51
59
65
90
96
111
120
134
144
150
156
162
174
180
m/z-->
40
60
80
100
120
140
160
180

b)


1.97
2.00
1.96
1.99
f1 (ppm)

c)


146.56
138.19
129.25
129.10
118.29
116.15
64.68
f1 (ppm)

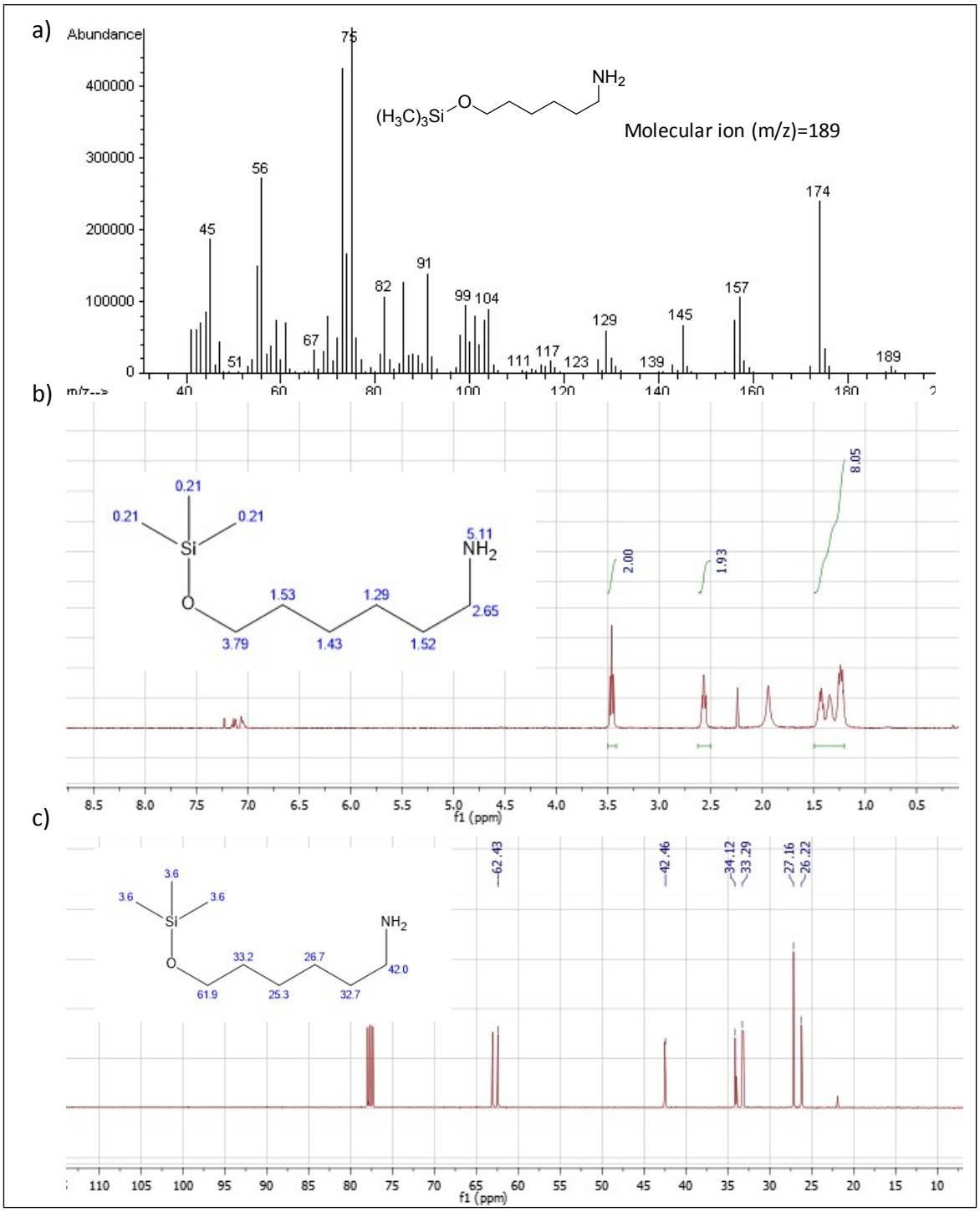
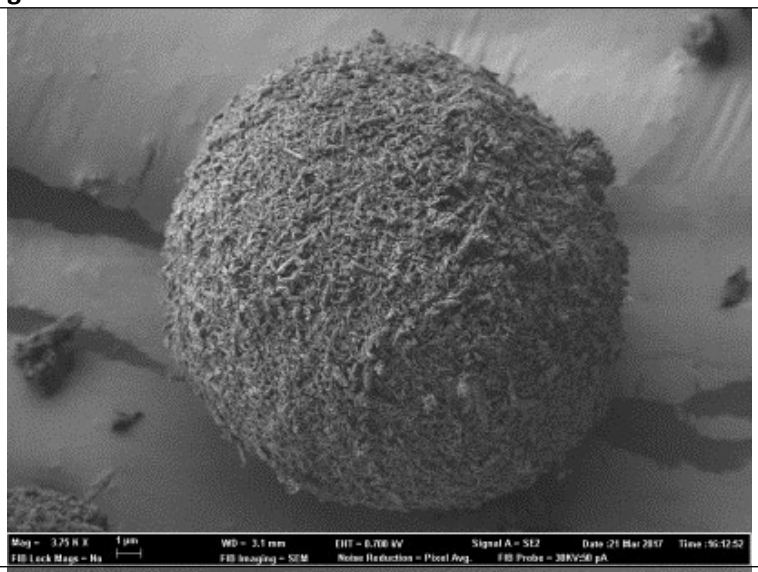
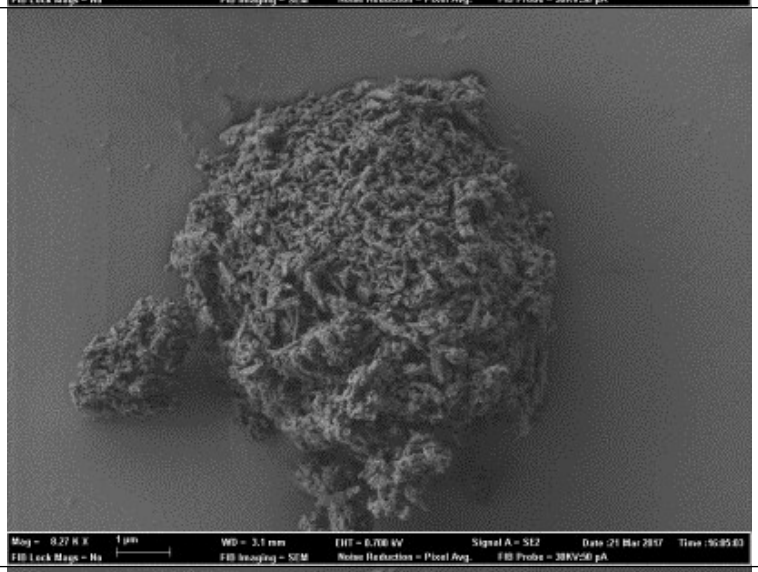
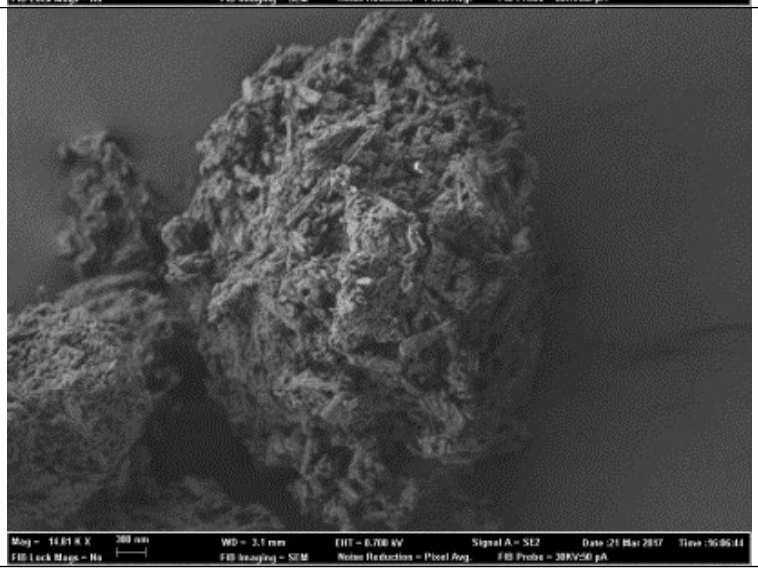
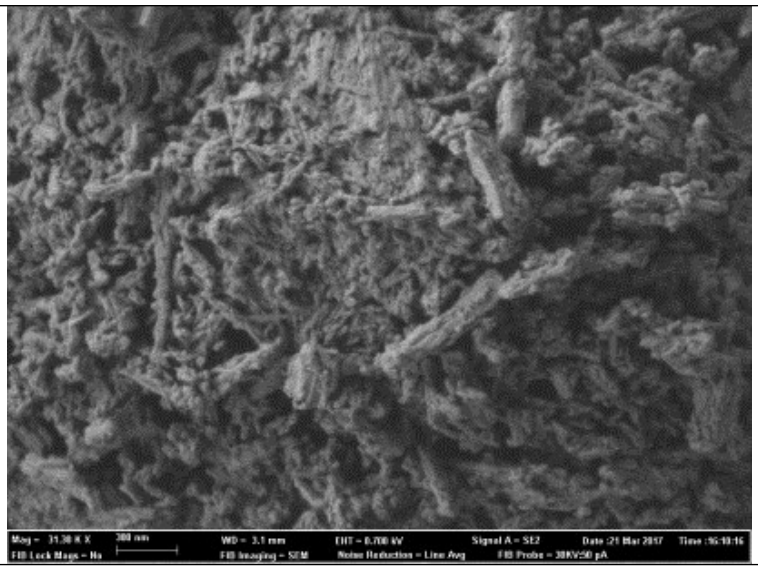
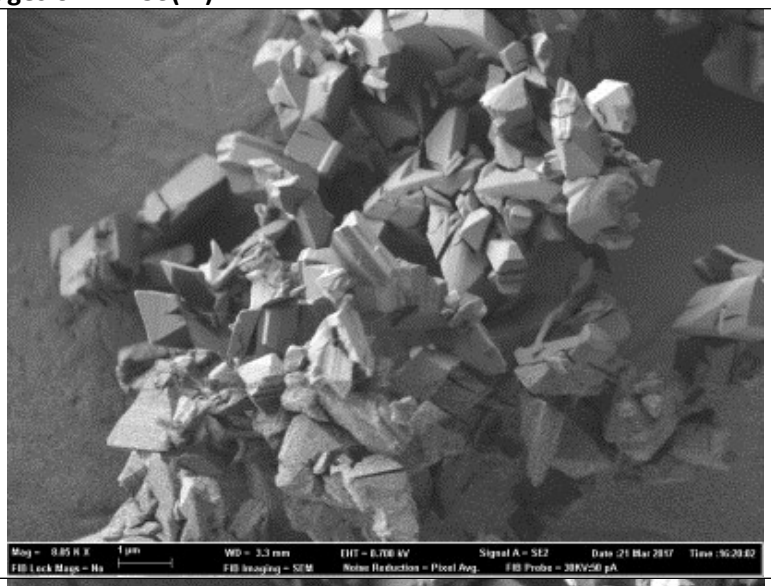
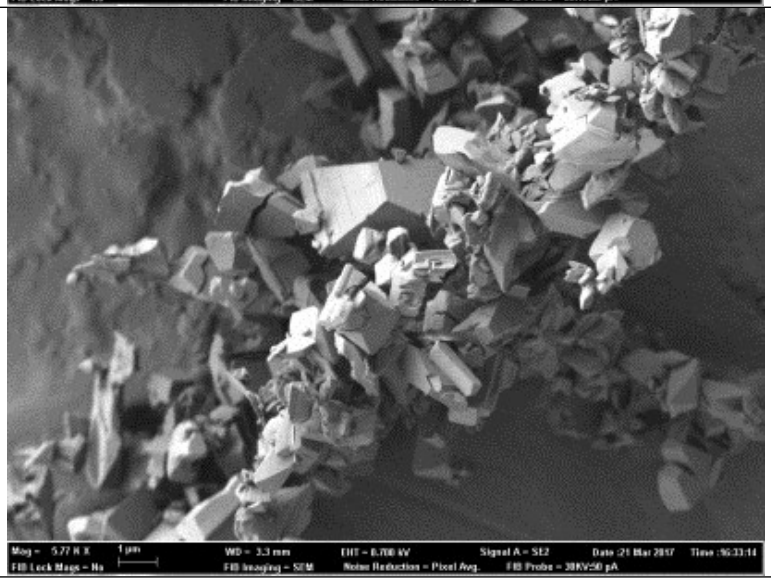
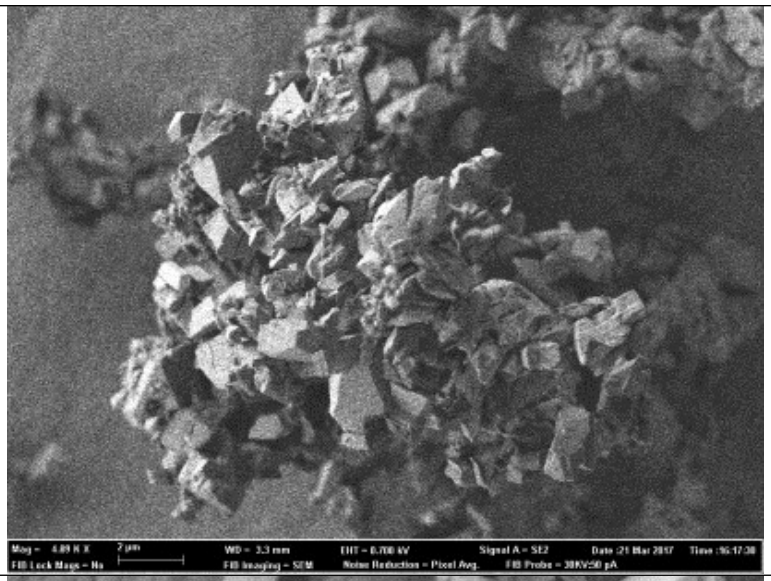

a)
Abundance
400000
300000
200000
100000
0
45
56
75
67
51
82
91
99
104
111
117
123
129
139
145
157
174
189
NH2
(H3C)3Si
O
Molecular ion (m/z)=189
b)
0.21
0.21
0.21
Si
O
5.11
NH2
1.53
1.29
2.65
3.79
1.43
1.52
2.00
1.93
8.05
f1 (ppm)
c)
3.6
3.6
3.6
Si
O
NH2
33.2
26.7
42.0
61.9
25.3
32.7
62.43
42.46
34.12
33.29
27.16
26.22
f1 (ppm)

Table S2. Representative SEM images of Basolite A100 and MIL-53(Al) samples. SEM images were collected using a Zeiss instrument.

Representative SEM images of Basolite A100	
Scale bar: 1 μm	
Scale bar: 1 μm	
Scale bar: 300 nm	

Scale bar: 300 nm	
Representative SEM images of MIL-53(Al)	
Scale bar: 1 µm	
Scale bar: 1 µm	

Scale bar: 300 nm	
Scale bar: 300 nm