The β Effect of Silicon in Phenyl Cations.

Valentina Dichiarante, Andrea Salvaneschi, Stefano Protti,
Daniele Dondi, Maurizio Fagnoni*, and Angelo Albini.

Dipartimento di Chimica Organica, Università, V. Taramelli 10, 27100 Pavia, Italy

fagnoni@unipv.it

SUPPORTING INFORMATION

47 PAGES

TABLE OF CONTENTS

1) Experimental details

General

NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15 W phosphor coated lamps (maximum of emission 310 nm) for the irradiation.

The progress of the reaction was followed by GC (HP5 column) except when **15** was formed where HPLC analysis (AQUASIL C18 (250×4.6 mm) column, MeCN/ water 70:30, flux 1 mL/min) with UV detection at λ = 270 nm was adopted. Products **5, 7-8**, **9a**, **10**, **11a**, **14**, **14a**, **15**, and **16** were isolated from preparative irradiations and characterized. Workup of the photolytes involved concentration in vacuo and chromatographic separation using Millipore 60 Å 35-70 μm silica gel. The yields of products **5a**, **6a**, **7a**, **12a**, **13a**, **16a**, **18a** were determined by comparison with either commercial standards or by their independent syntheses. Products **9**, **11**, **12** and **13** were identified by GC-MS analysis and determined after desilylation by treating the end mixture with a large excess of Bu_4NF.

9: MS (m/z): 278 (M^+, 100), 237 (5), 214 (10), 199 (60), 167 (30), 139 (10), 121 (25), 105 (10), 91 (5), 73 (2).

11: MS (m/z): 264 (M^+, 95), 185 (60), 167 (20), 153 (85), 125 (90), 107 (100), 77 (50), 47 (10).

12: MS (m/z): 256 (M^+, 30), 241 (100), 225 (50), 210 (5), 195 (10), 182 (10), 152 (2).

13: MS (m/z): 242 (M^+, 20), 227 (100), 211 (90), 181 (10), 165 (15), 152 (10), 106 (5), 45 (5).

Synthesis of 3-trimethylsilyl-4-chloro-anisole (1). 3-Trimethylsilyl-anisole (**5**, colorless oil) was obtained in 87% yield from 3-bromo-anisole and chlorotrimethylsilane through a Grignard reaction[S1] and was used for the next step without further purification. The title compound was obtained by

treating **5** with SO_2Cl_2 at room temperature.[S2] Purification by distillation under reduced pressure afforded **1** (colorless oil) in 60% yield.

5: ^{1}H NMR (δ, $CDCl_3$): 0.35 (s, 9H), 3.90 (s, 3H), 6.90-6.95 (m, 1H), 7.10-7.20 (m, 2H), 7.30-7.40 (m., 1H); ^{13}C NMR ($CDCl_3$), δ: -1.6 (CH_3), 54.6 (CH_3), 113.4 (CH), 118.5 (CH), 125.1 (CH), 128.5 (CH), 141.7, 158.5; IR (neat), υ/cm^{-1}: 838, 1046, 1228, 1247, 1409, 1570, 2955; MS (m/z): 180 (M^+, 20), 165 (100), 135 (25), 121 (5), 107 (5), 91 (10), 77 (5), 51 (2), 43 (5); Anal. Calcd for $C_{10}H_{16}OSi$: C 66.61, H 8.94; found: C 66.7, H 8.8.

1: ^{1}H NMR (δ, $CDCl_3$): 0.40 (s, 9H), 3.80 (s, 3H), 6.80 (dd, 1H, *J* = 8.7 and 3 Hz), 7.00 (d, 1H, *J* = 3Hz), 7.25 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR (δ, $CDCl_3$): -0.98 (CH_3), 55.3 (CH_3), 115.1 (CH), 121.4 (CH), 129.9 (CH), 132.1, 139.7, 157.5; IR (neat) ν/cm^{-1}: 2956, 1471, 1285, 1237, 840; MS (m/z): 214 (100, M^+), 199 (40), 184 (25), 121 (80), 105 (60), 91 (10); Anal. Calcd. For $C_{10}H_{15}ClSiO$: C, 55.93; H, 7.04; found: C, 55.6; H, 7.4.

Synthesis of 3,5-*bis*(trimethylsilyl)-4-chloroanisole. (2) 3,5-Dibromo-4-chloroanisole was obtained starting from 3,5-dibromo-4-amino-anisole[S3] through a Sandmeyer reaction with cuprous chloride. After purification by column chromatography (eluant: cyclohexane) the title compound was isolated in 52% yield as a colorless solid. mp 69-71°C; ^{1}H NMR (δ, $CDCl_3$): 3.80 (s, 3H), 7.20 (s, 2H); ^{13}C NMR (δ, $CDCl_3$): 55.9 (CH_3), 118.7 (CH), 123.2, 135.1, 158.1; IR (neat) ν/cm^{-1}: 2956, 1582, 1419, 1039, 841; Anal. Calcd. For $C_7H_5Br_2ClO$: C, 27.99; H, 1.68; found: C, 26.9; H, 1.5.

To a solution of 3,5-dibromo-4-chloroanisole (1.1 g, 3.6 mmol) in dry THF (10 mL) was added trimethysilylchloride (1.4 mL, 11.34 mmol) and Mg (212 mg, 8.72 mmol). The resulting mixture was refluxed for 48 hours, then water (10 mL) was added. The organic layer was washed with brine (2×10 mL) and water (2×10 mL), dried and then evaporated. Purification by column chromatography (eluant: cyclohexane) afforded 650 mg of **2** (colorless solid, 69 % yield).

2: mp 61-64 °C; ^{1}H NMR (δ, $CDCl_3$): 0.40 (s, 18H), 3.80 (s, 3H), 6.95 (s, 2H); ^{13}C NMR (δ, $CDCl_3$): -0.67 (CH_3), 55.2 (CH_3), 121.8 (CH), 139.2, 140.1, 156.9; IR (neat) ν/cm^{-1}: 2950, 1425, 1027, 820; Anal. Calcd. For $C_{13}H_{23}OSi_2$: C, 54.41; H, 8.08; found: C, 54.0; H, 8.2.

Synthesis of 3-trimethylsilyl-4-chloro-phenol (3). 1.2 g of **1** were dissolved in 20 mL of dry CH_2Cl_2 and the resulting solution was cooled to -78 °C and 5.7 mL of BBr_3 (1M solution in CH_2Cl_2) were added. The mixture was stirred for 2 hours at room temperature and 10 mL of water were then added. The separated organic layer was washed with water (2×20 mL), dried over $MgSO_4$ and then the solvent was eliminated in vacuo. Purification by column chromatography (eluant cyclohexane/ethyl acetate 9:1) afforded 600 mg of **3** (colorless oil, 54% yield).

3: ^{1}H NMR (δ, $CDCl_3$): 0.40 (s, 9H), 5.10-5.20 (bs, 1H), 6.75-6.80 (dd, 1H, *J* = 8 and 3 Hz), 7.00-7.10 (d, 1H, *J* = 3 Hz), 7.25-7.35 (d, 1H, *J* = 8 Hz); ^{13}C NMR (δ, $CDCl_3$): -1.2 (CH_3), 116.9 (CH), 121.8 (CH), 129.8 (CH), 131.8, 139.8, 153.1; IR (neat) ν/cm^{-1}: 3344, 2956, 1417, 1250, 839. Anal. Calcd. For $C_9H_{13}OSi$: C, 53.85; H, 6.53; found: C, 53.2; H, 6.4.

Synthesis of 3-trimethylsilyl-4-chloro-*N*,*N*-dimethylaniline (4). 3-Iodo-4-chloronitrobenzene[S4] (1.8 g, 6.3 mmol) was treated with an ethanol:ethylacetate 5:2 solution of $SnCl_2$ as previously reported.[S5] Purification with column chromatography yielded 1 g (63% yield) of 3-iodo-4-chloroaniline as a solid.

mp 68-70 °C. ^{1}H NMR (δ, $CDCl_3$): 3.60-3.75 (bs, 2H), 6.50-6.60 (dd, 1H, *J* = 9 and 3 Hz), 7.10-7.15 (m, 2H); IR (neat) ν/cm^{-1}: 3458, 2926, 1458, 1123, 909; Anal. Calcd. For $C_6H_5ICl N$: C, 28.43; H, 1.99; found: C, 28.1; H, 1.5.

3-Iodo-4-chloro-*N*,*N*-dimethylaniline was obtained from the above iodoaniline (1g, 4 mmol) by reacting with formaldehyde and $NaBH_4$.[S6] Purification by column chromatography (eluant:

cyclohexane: ethylacetate 95:5) afforded 0.7 g (51 % yield) of the methylated derivative (colorless solid).

mp 53-54 °C; ^{1}H NMR (δ, $CDCl_3$): 2.95 (s, 6H), 6.60-6.65 (dd, 1H, *J* = 9 and 3 Hz), 7.10-7.15 (d, 1H, *J* = 3 Hz), 7.20-7.25 (d, 1H, *J* = 9 Hz); ^{13}C NMR (δ, $CDCl_3$): 40.0 (CH_3), 98.2, 113.0 (CH), 122.7, 124.7, 128.4 (CH), 149.1; IR (neat) ν/cm^{-1}: 2938, 1460, 1119, 880; Anal. Calcd. For C_8H_9ICl: C, 34.13; H, 3.22; found: C, 34.1; H, 3.3.

The title compound (**4**) was obtained by a silylation reaction as previously described for the synthesis of **1**.[S1] Purification by column chromatography (eluant: cyclohexane:ethylacetate 99:1) afforded 3-trimethylsilyl-4-chloro-*N*,*N*-dimethylaniline (oil) in 31% yield.

4: ^{1}H NMR (δ, CD_3COCD_3): 0.35 (s, 9H), 2.80 (s, 6H), 6.70-6.75 (dd, 1H, *J* = 3 and 8 Hz), 6.80-6.85 (d, 1H, *J* = 3 Hz), 7.15-7.20 (d, 1H, *J* = 8 Hz); ^{13}C NMR (δ,CD_3COCD_3): -0.15 (CH_3), 40.8 (CH_3), 116.1 (CH), 120.6 (CH), 129.8, 130.7 (CH), 139.1, 150.3; IR (neat) ν/cm^{-1}: 2933, 1505, 1249, 840; Anal. Calcd. For $C_{11}H_{18}ClNSi$: C, 58.00; H, 7.96; found: C, 57.5; H, 7.5.

Synthesis of 3-trimethylsilylphenol (6). The title compound was obtained starting from 3-bromophenol following the procedure described by Noda.[S7]

6: ^{1}H NMR (δ, CD_3COCD_3): 0.40 (s, 9H), 6.80-6.85 (m, 1H), 6.95-7.05 (m, 2H), 7.20 (m, 1H), 8.15 (bs, 1H); ^{13}C NMR (δ, CD_3COCD_3), δ: -0.6 (CH_3), 117.0 (CH), 121.1 (CH), 125.5 (CH), 130.2 (CH), 142.8, 158.0; IR (neat), υ/cm^{-1}: 837, 1112, 1248, 1425, 1573, 2956, 3327; MS (m/z): 166 [M^+] (25), 151 (100), 123 (10), 91 (15), 73 (10), 45 (5); Anal. Calcd. for $C_9H_{14}OSi$: C 65.00, H 8.49; found: C 64.8, H 8.6.

Synthesis of 3-trimethylsilyl-*N,N*-dimethylaniline (16). Compound **16** was synthesized starting from 3-bromo-*N,N*-dimethylaniline[S8] (800 mg, 4 mmol) by the usual Grignard reaction.[S1] Purification by column chromatography afforded 450 mg of the title compound (pale yellow oil, 59% yield).

16: ^{1}H NMR[S9] (δ, CD_3COCD_3): 0.25 (s, 9H), 2.95 (s, 6H), 6.60-6.70 (dd, 1H, *J* = 2 and 7 Hz), 6.80-6.85 (dd, 1H, *J* = 1 and 6 Hz), 6.90-6.95 (d, 1H, *J* = 2 Hz), 7.15-7.20 (m, 1H); ^{13}C NMR (δ,CD_3COCD_3): -0.6 (CH_3), 41.0 (CH_3), 114.5 (CH), 118.3 (CH), 122.6 (CH), 129.6 (CH), 141.4, 151.4; IR (neat) ν/cm^{-1}: 2930, 1506, 1242, 910, 844; MS (m/z): 193 (M^+ , 100), 178 (22), 163 (28); Anal. Calcd. For $C_{11}H_{19}NSi$: C, 68.33; H, 9.90; found: C, 68.3; H, 9.5.

(S1) Eaborn, C.; Jaura, K. L.; Walton, D. R. M. *J. Chem. Soc.* **1964**, 1198-1199.

(S2) Sato, H.; Dan, T.; Onuma, E.; Tanaka, H.; Aoki, B.; Joga, H. *Chem. Pharm. Bull.* **1992**, *40*, 109-116.

(S3) Cossy, J.; Poitevin, C.; Gomez Pardo, D.; Peglion, J. L. *Synth. Comm.* **1997**, *27*, 3525-3527.

(S4) Olah, G. A.; Wang, Q.; Sandford, G.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 3194-3195.

(S5) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, 839-842.

(S6) Campus, F.; Call, J.; Messenguer, A.; Pericas, M. A. *Synthesis*, **1980**, 743-746.

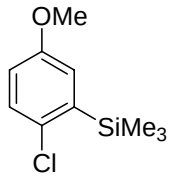
(S7) Nishide, K.; Ohsugi, S.; Miyamoto, T.; Kumar, K.; Node, M., *Monatsh. Chem.* **2004**, *135*, 189-200

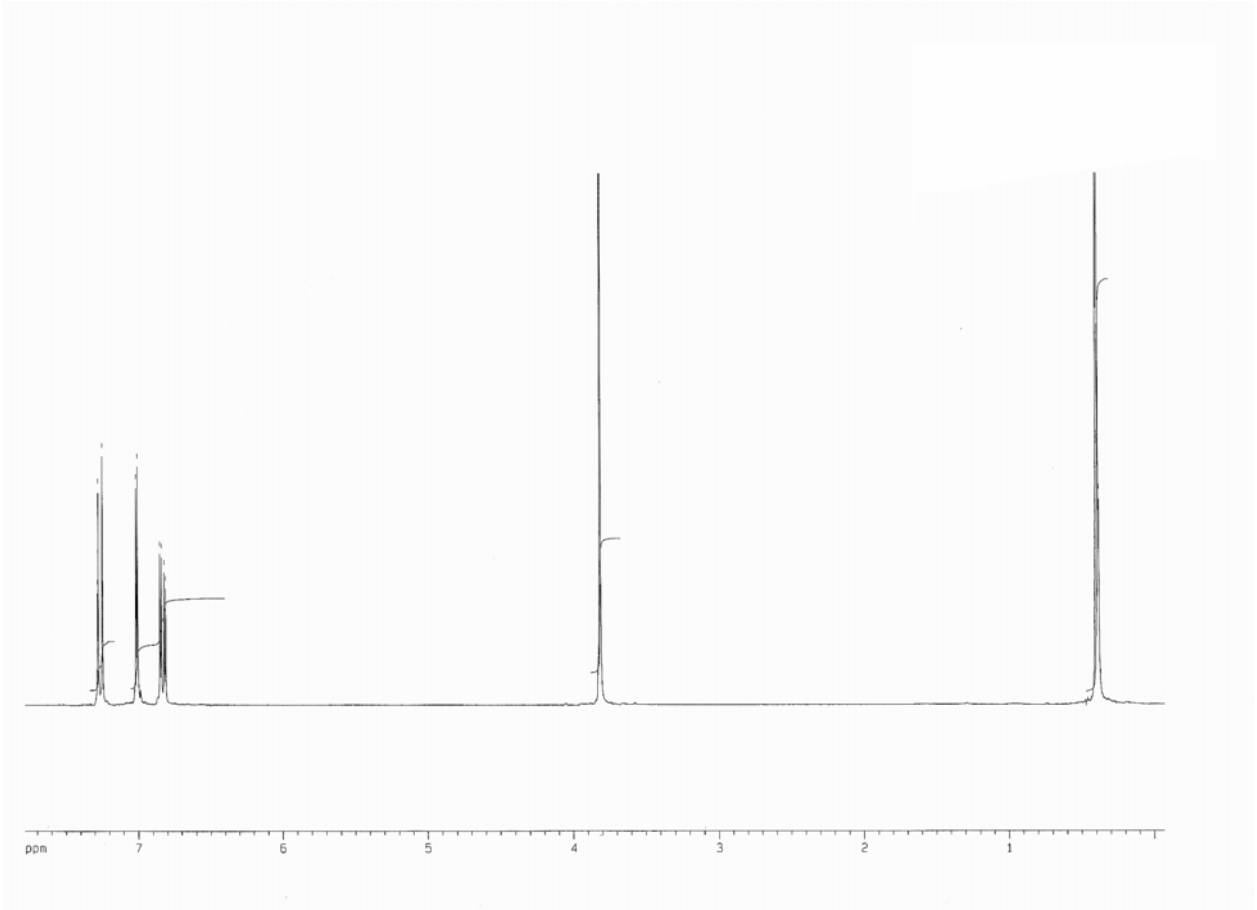
(S8) Manring L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6452-6458.

(S9) Jaggard, J. F. R.; Pidcock, A. *J. Organomet. Chem.* **1969**, *16*, 324-326.

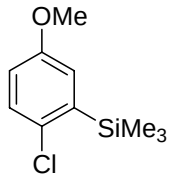
2) ^{1}H-NMR and ^{13}C-NMR spectra of compounds 1-8, 10, 11a, 15, 16

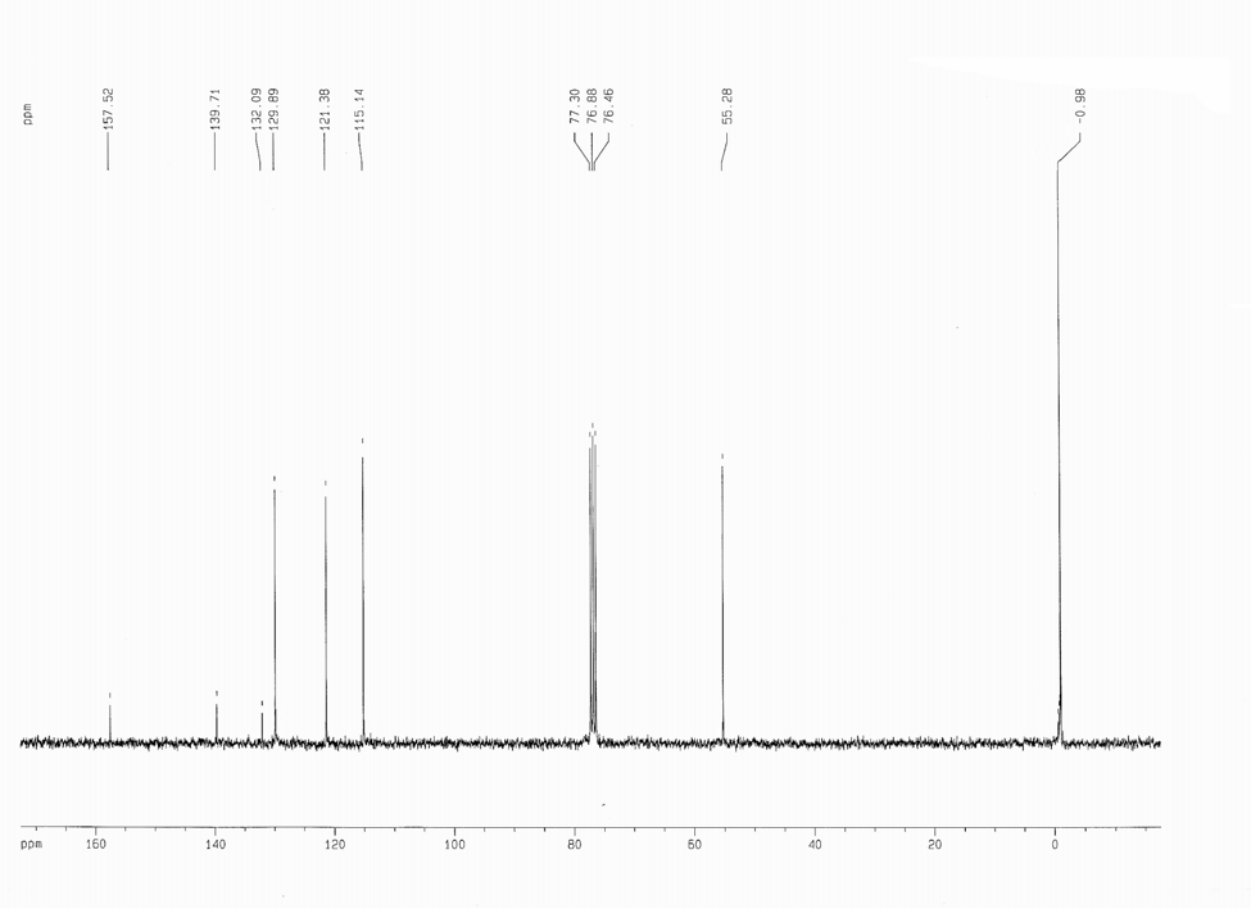
Compound **1**



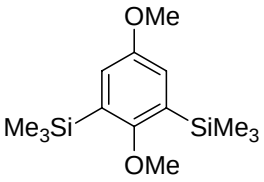


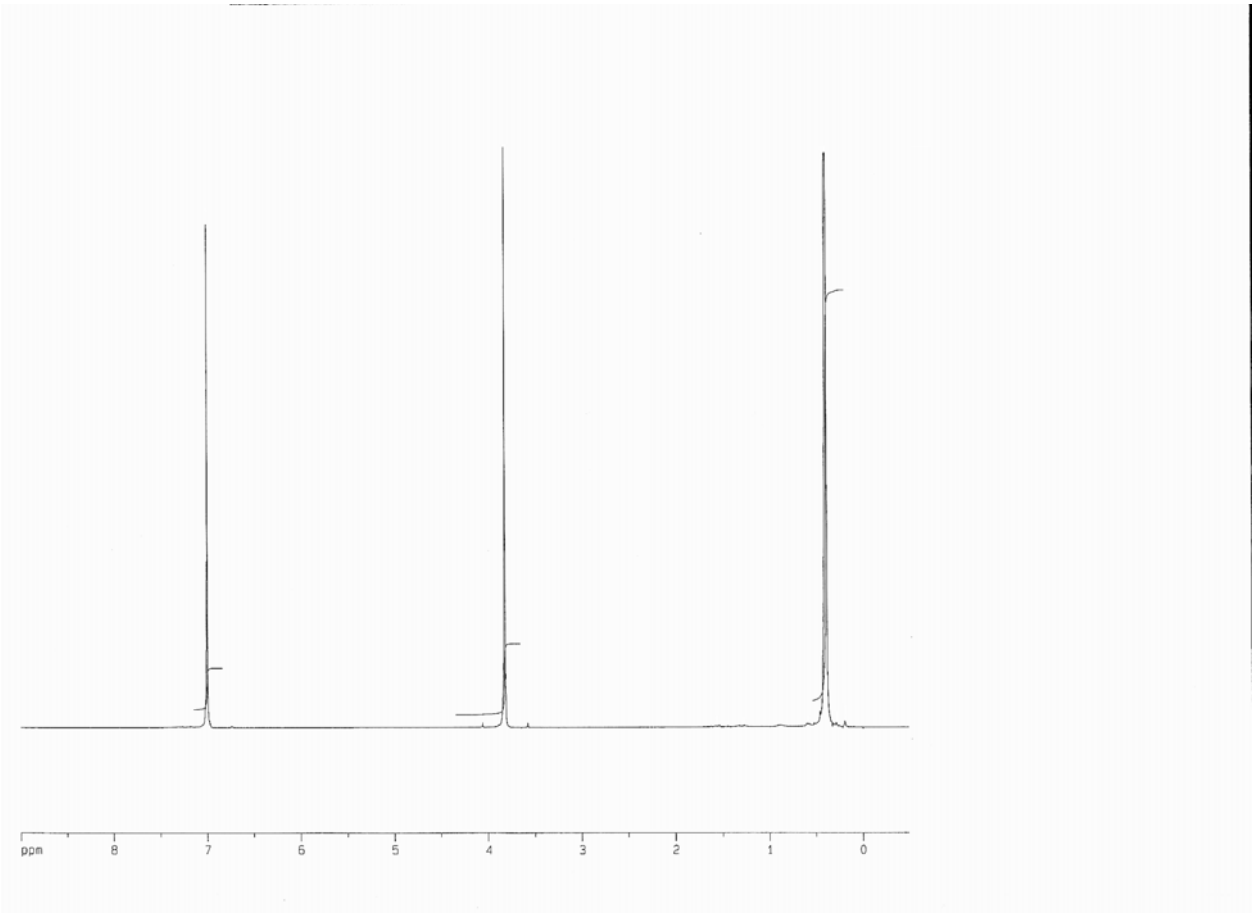
Compound **1**


OMe
SiMe3
Cl

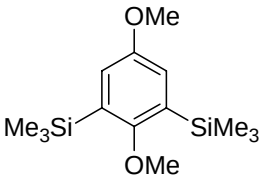

ppm
157.52
139.71
132.09
129.89
121.38
115.14
77.30
76.88
76.46
55.28
-0.98
ppm
160
140
120
100
80
60
40
20
0

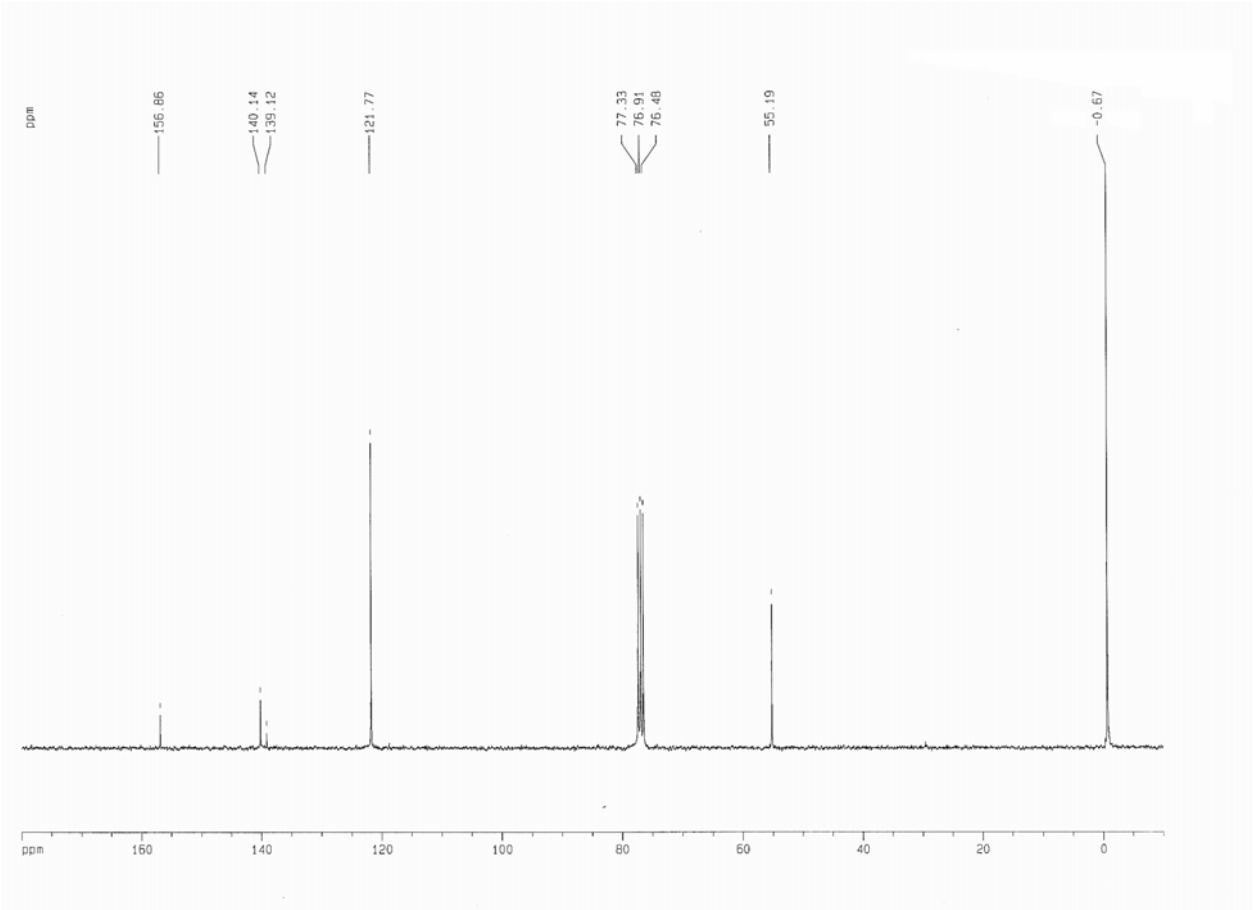
Compound **2**



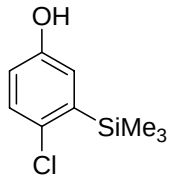


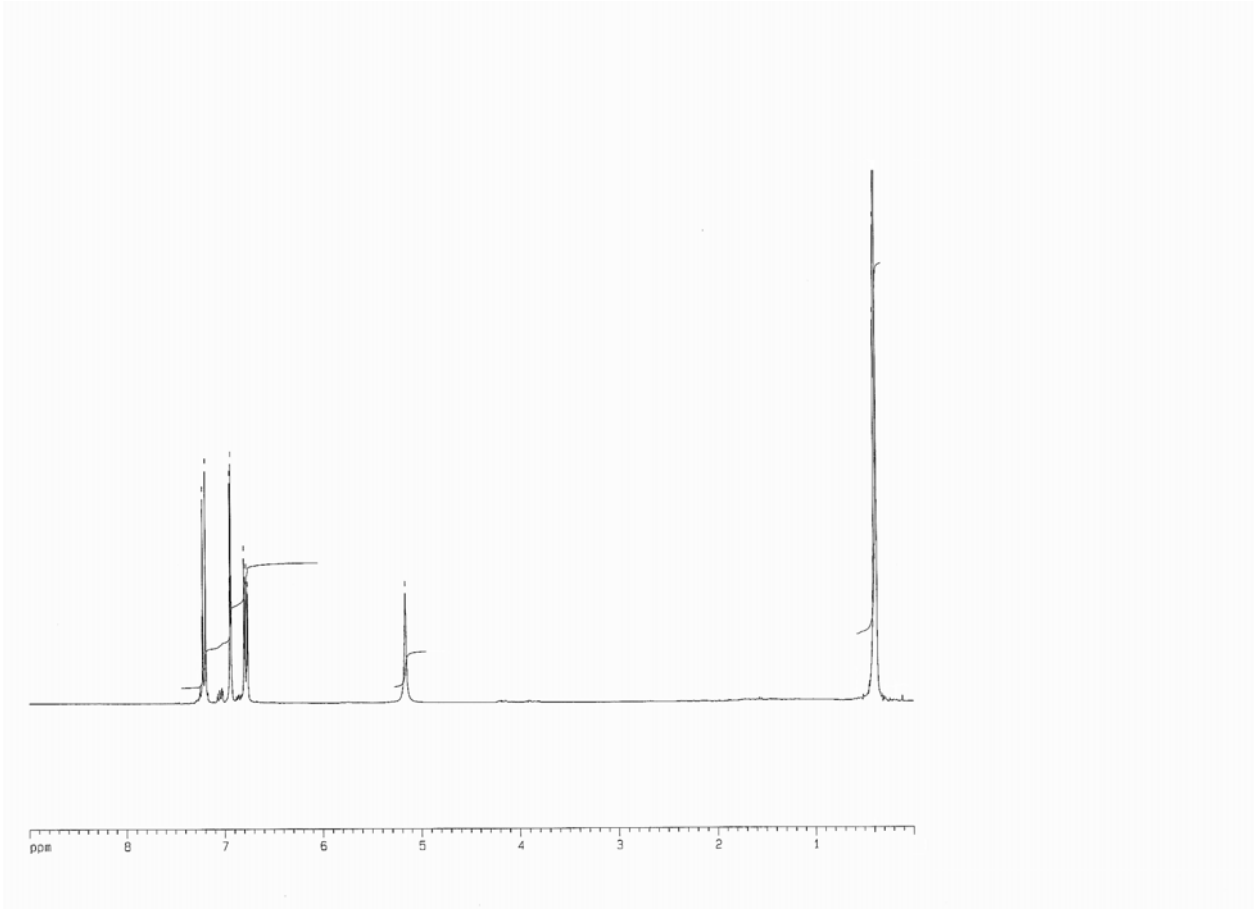
Compound **2**


OMe
Me3Si
SiMe3
OMe

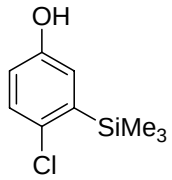

ppm
156.86
140.14
139.12
121.77
77.33
76.91
76.48
55.19
-0.67
ppm
160
140
120
100
80
60
40
20
0

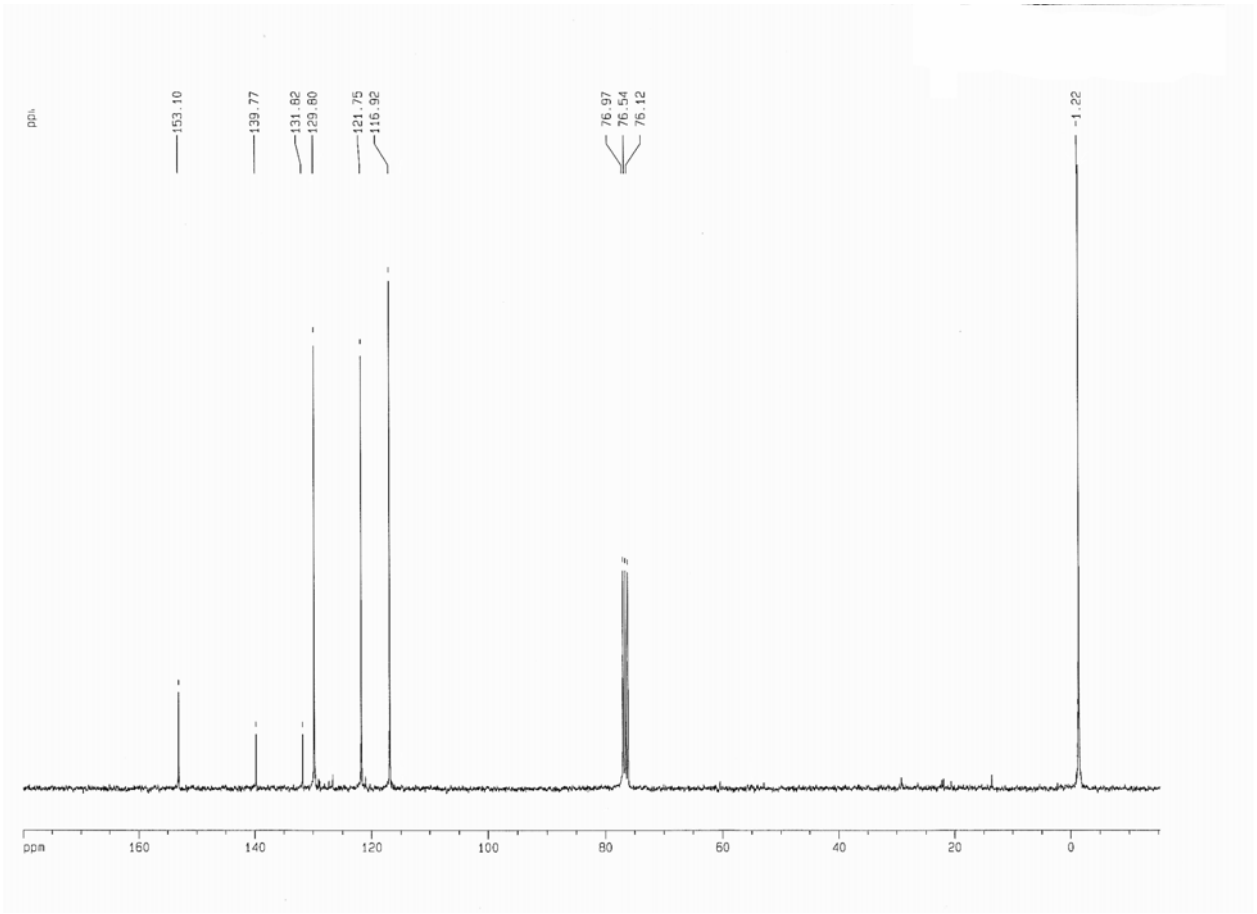
Compound **3**



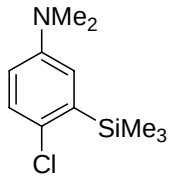


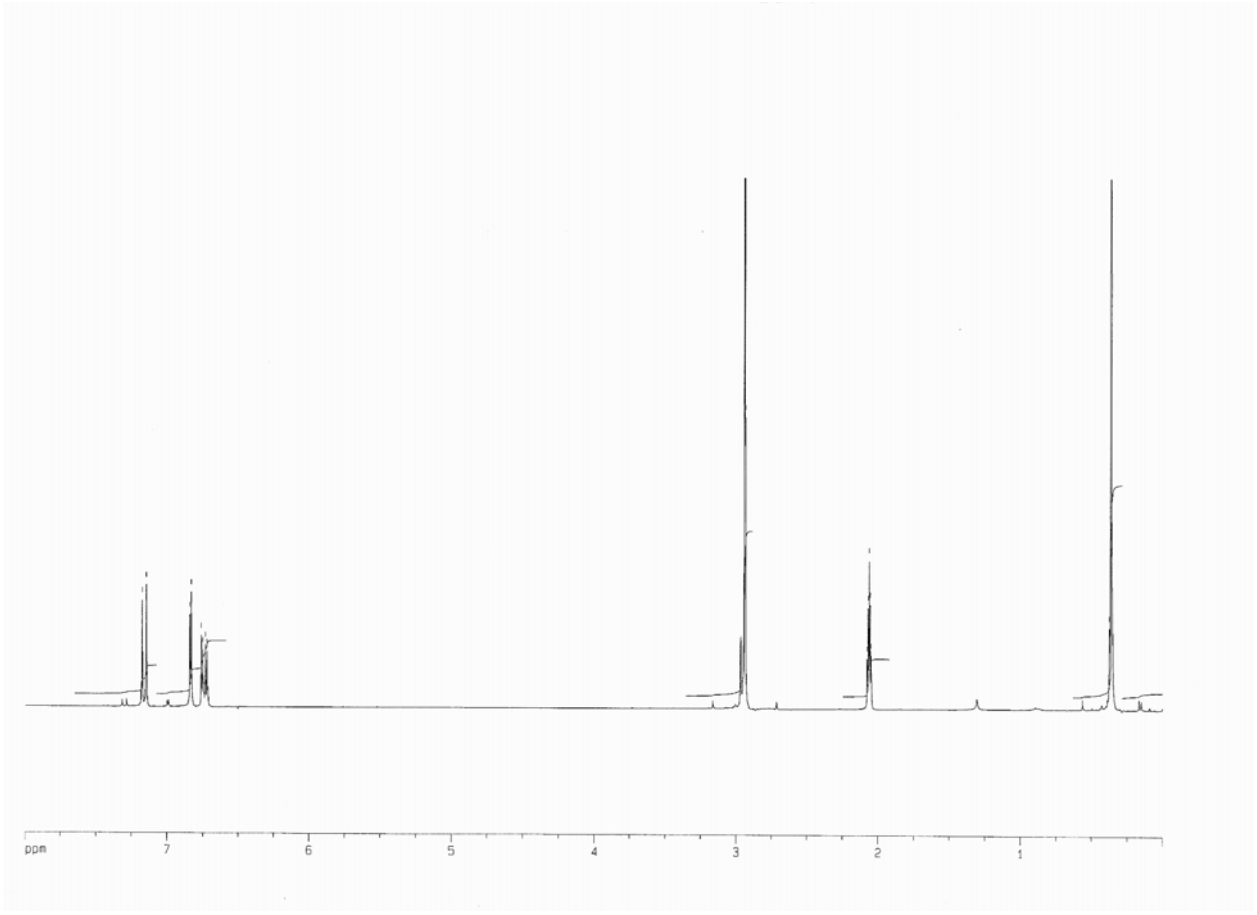
Compound **3**


OH
SiMe3
Cl

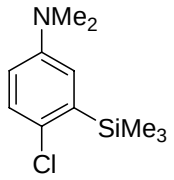

153.10
139.77
131.82
129.80
121.75
116.92
76.97
76.54
76.12
-1.22
ppm
160
140
120
100
80
60
40
20
0

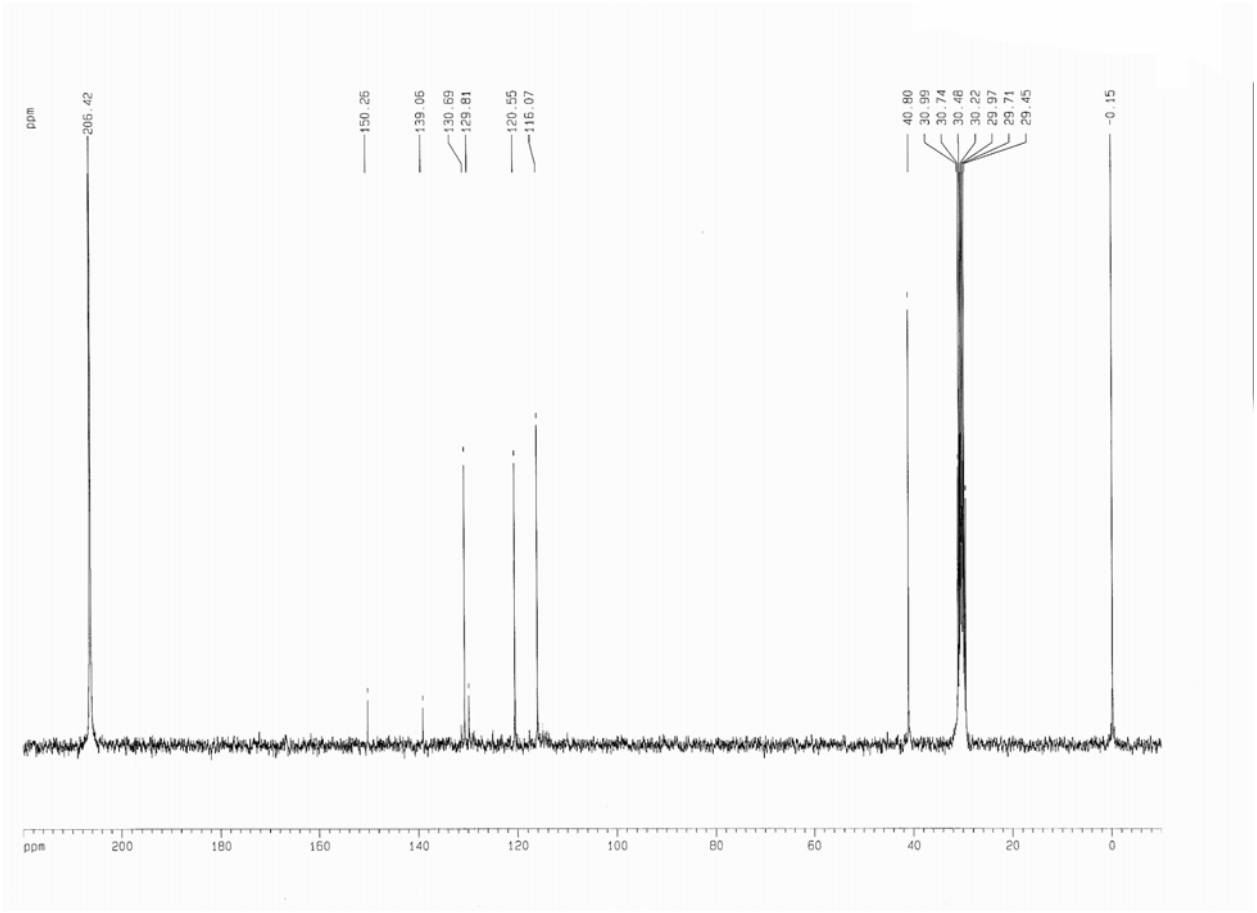
Compound **4**



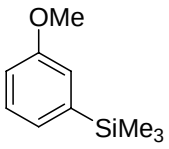


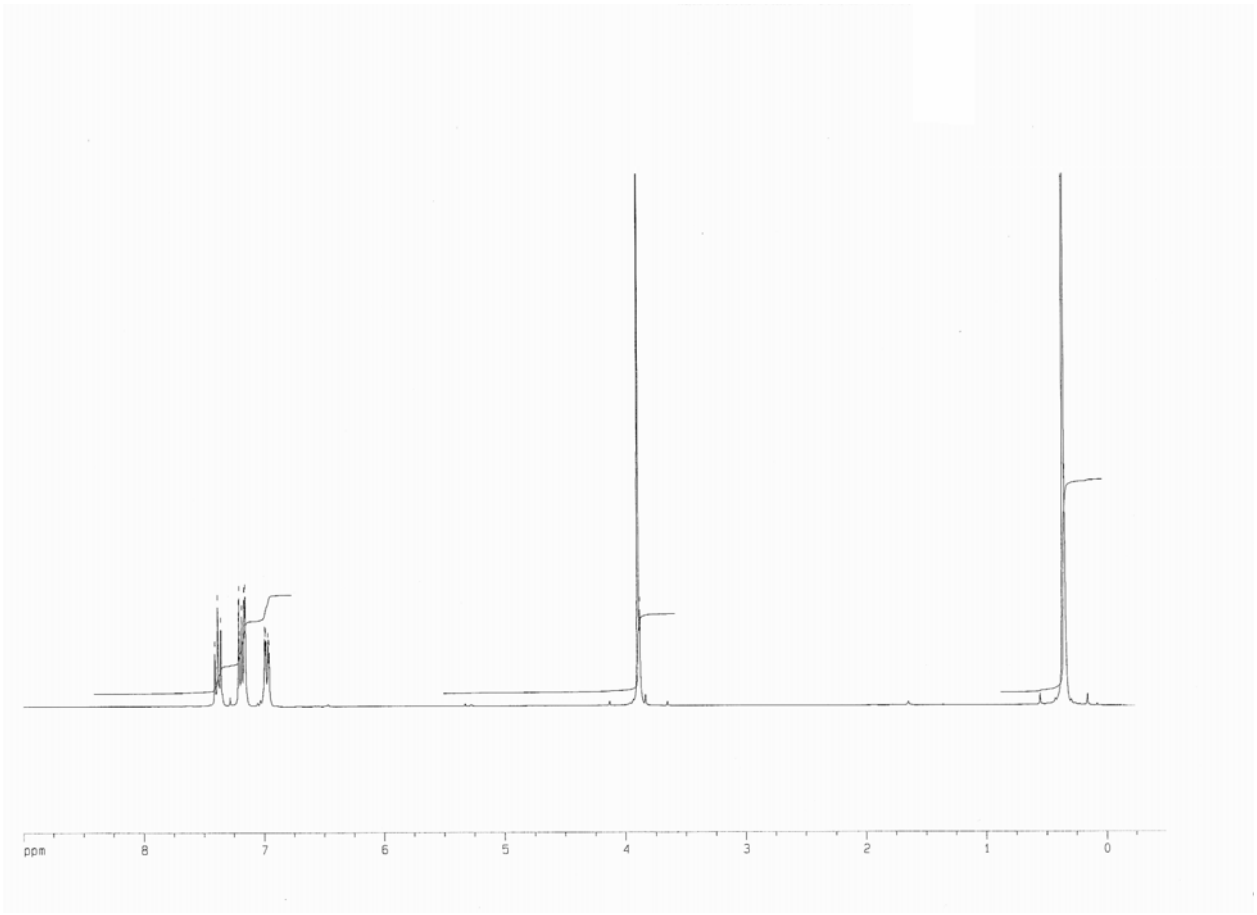
Compound **4**


NMe2
SiMe3
Cl

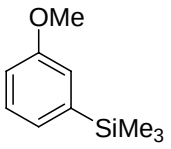

ppm
206.42
150.26
139.06
130.69
129.81
120.55
116.07
40.80
30.99
30.74
30.48
30.22
29.97
29.71
29.45
-0.15
ppm
200
180
160
140
120
100
80
60
40
20
0

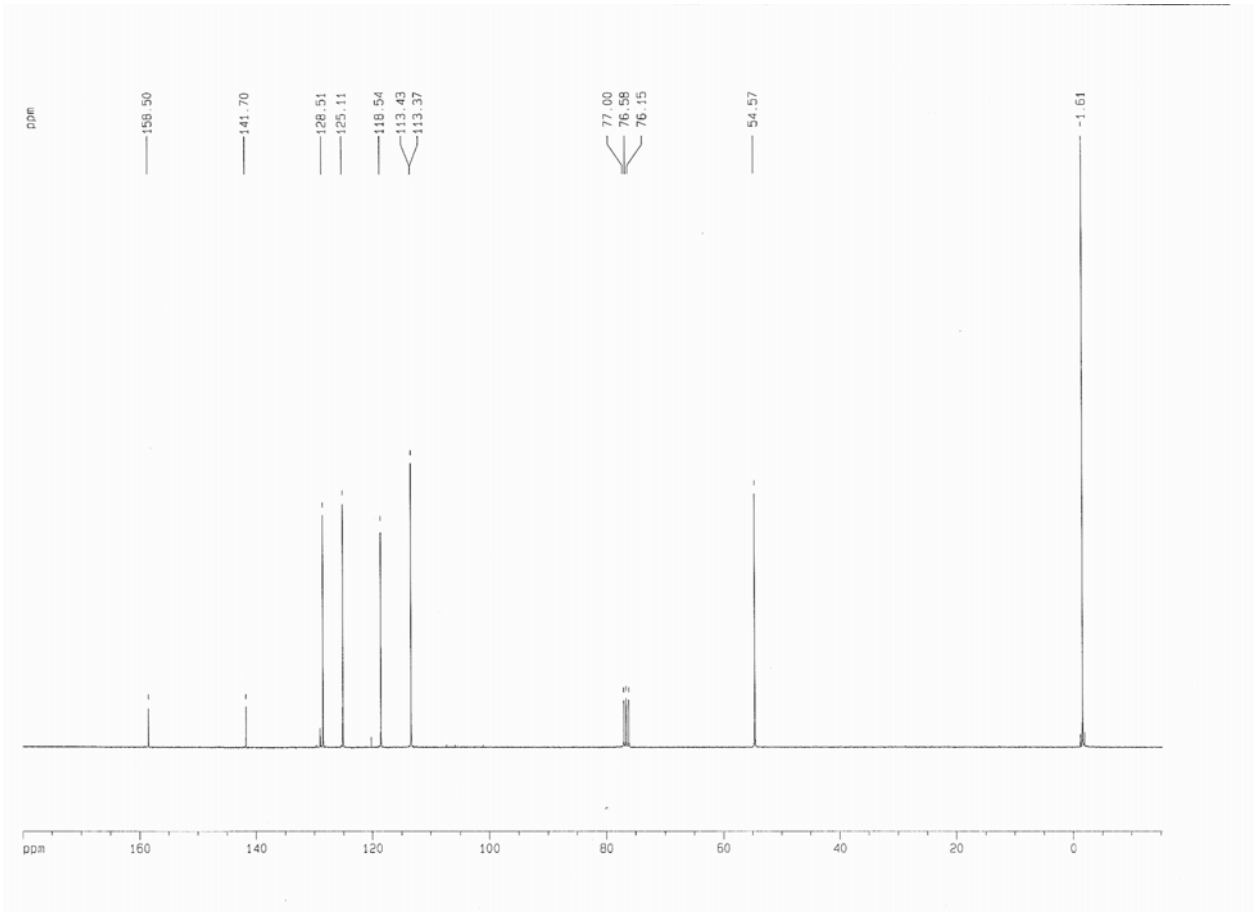
Compound **5**



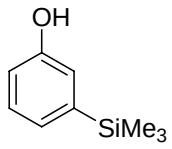


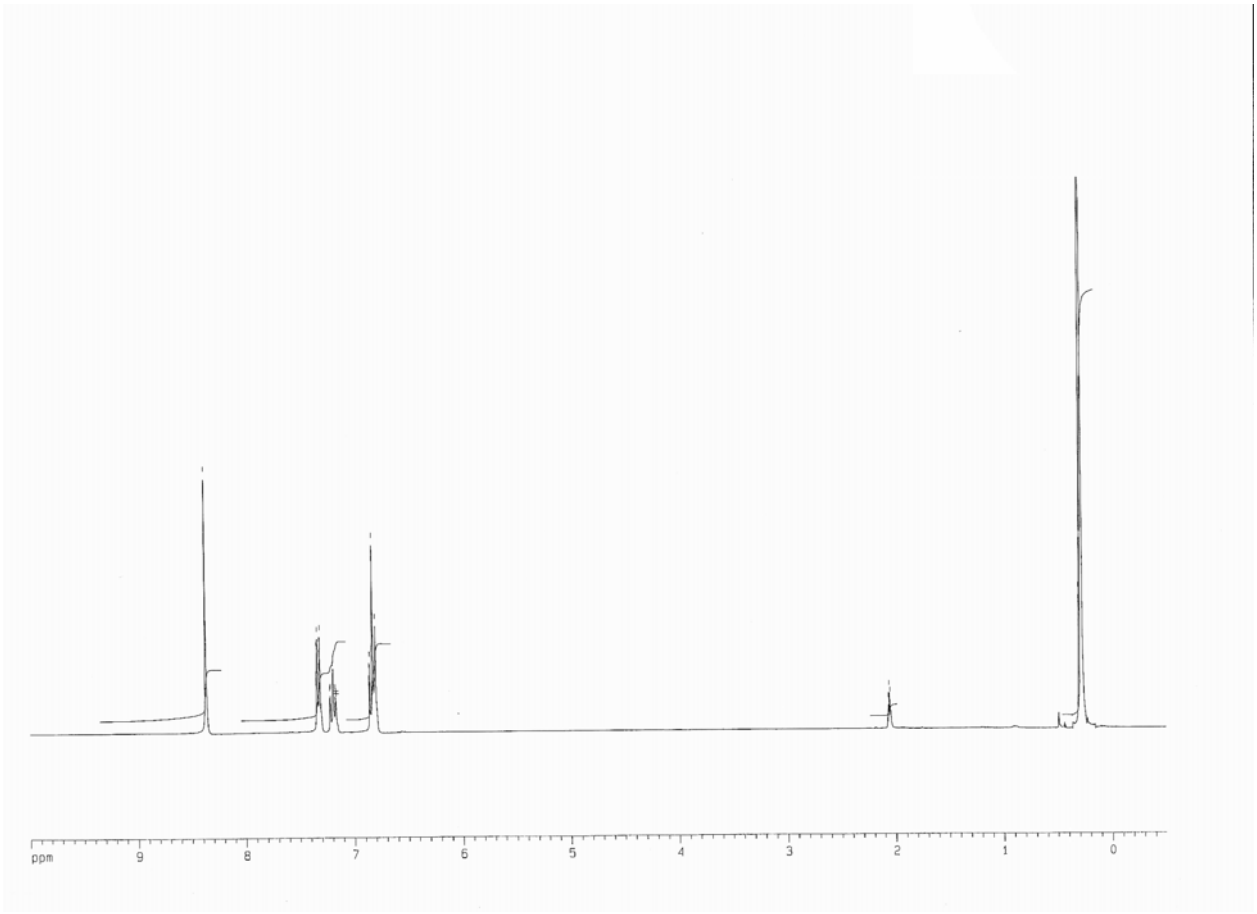
Compound **5**


OMe
SiMe3

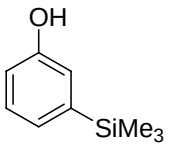

ppm
158.50
141.70
128.51
125.11
118.54
113.43
113.37
77.00
76.58
76.15
54.57
-1.61
ppm
160
140
120
100
80
60
40
20
0

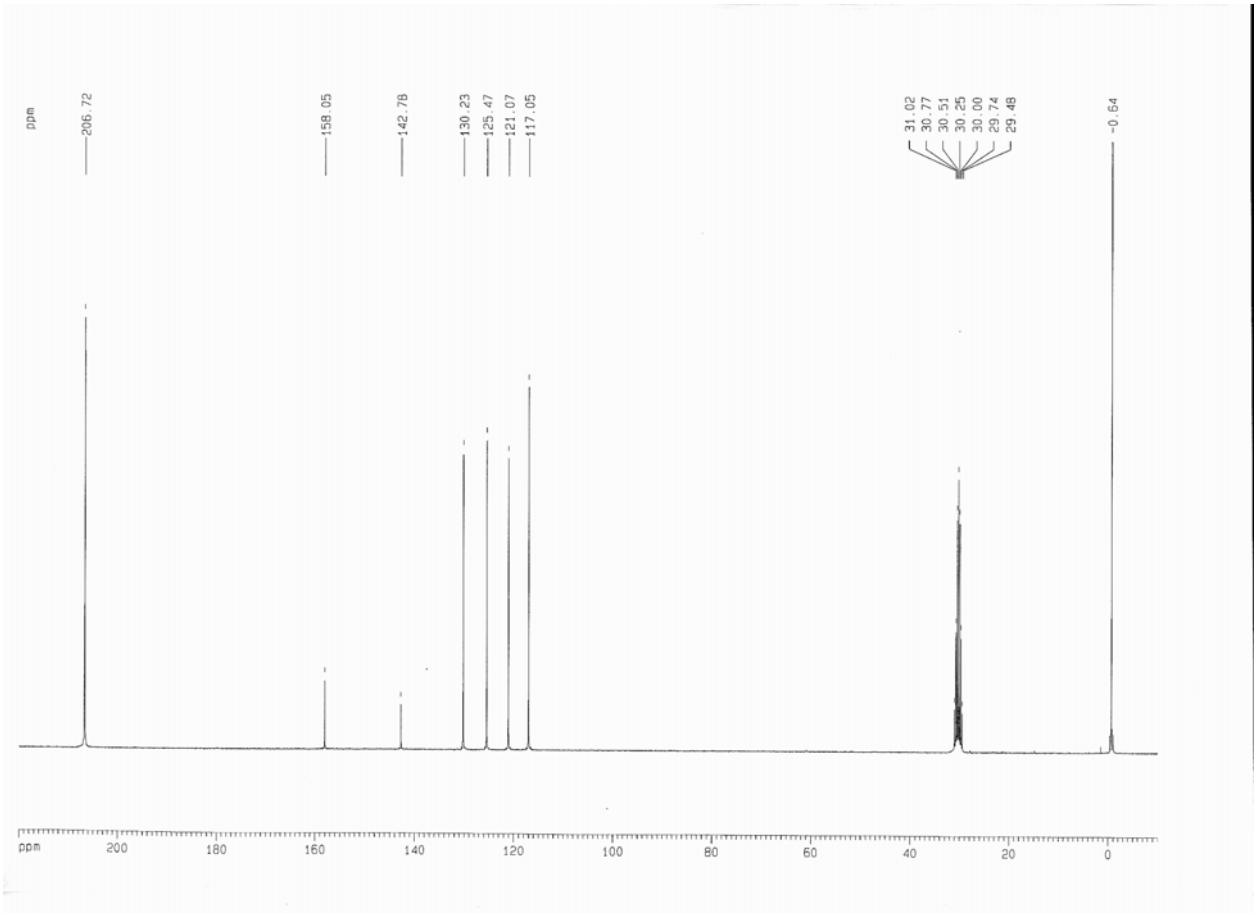
Compound **6**



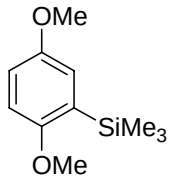


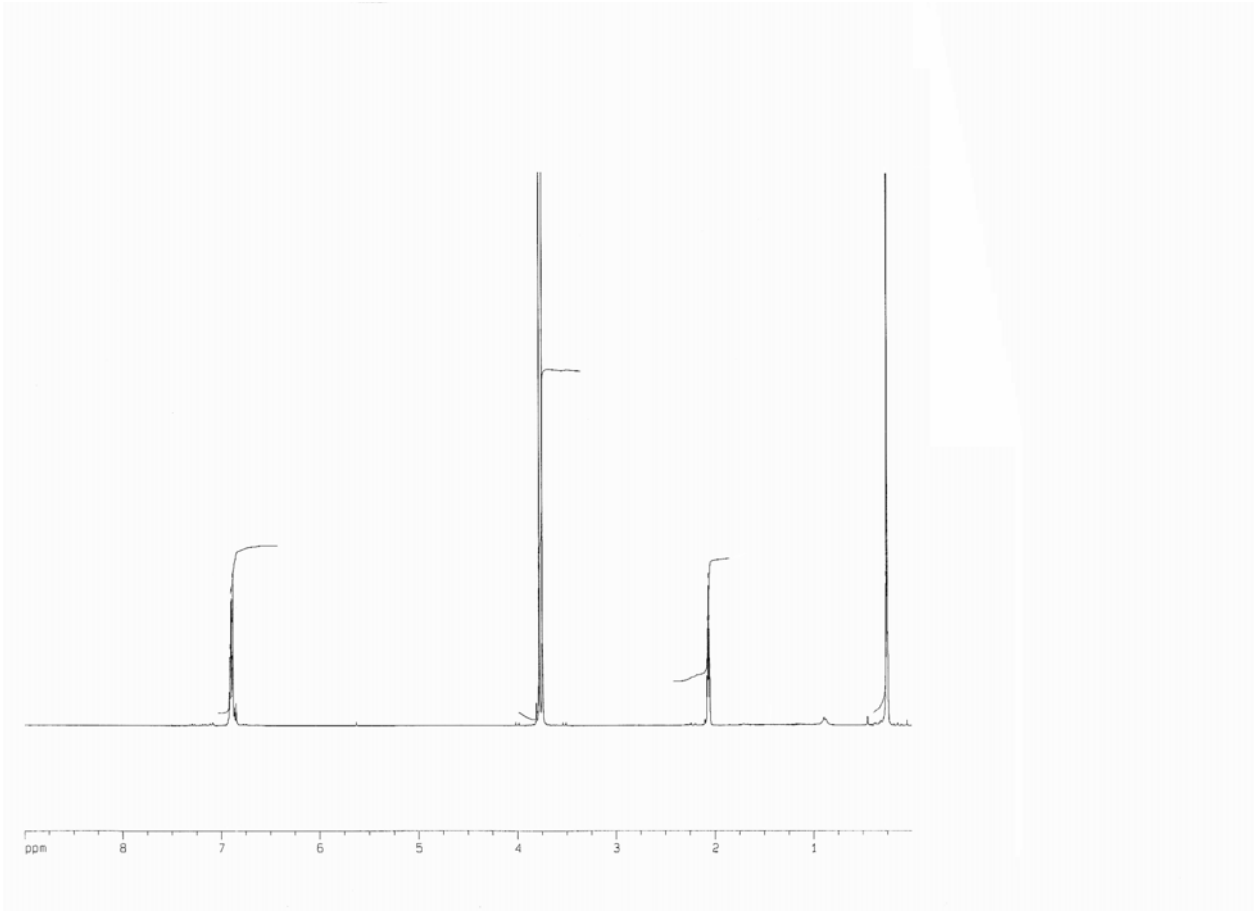
Compound **6**


OH
SiMe3

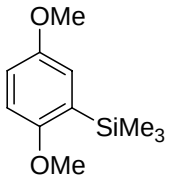

ppm
206.72
158.05
142.78
130.23
125.47
121.07
117.05
31.02
30.77
30.51
30.25
30.00
29.74
29.48
-0.64
ppm
200
180
160
140
120
100
80
60
40
20
0

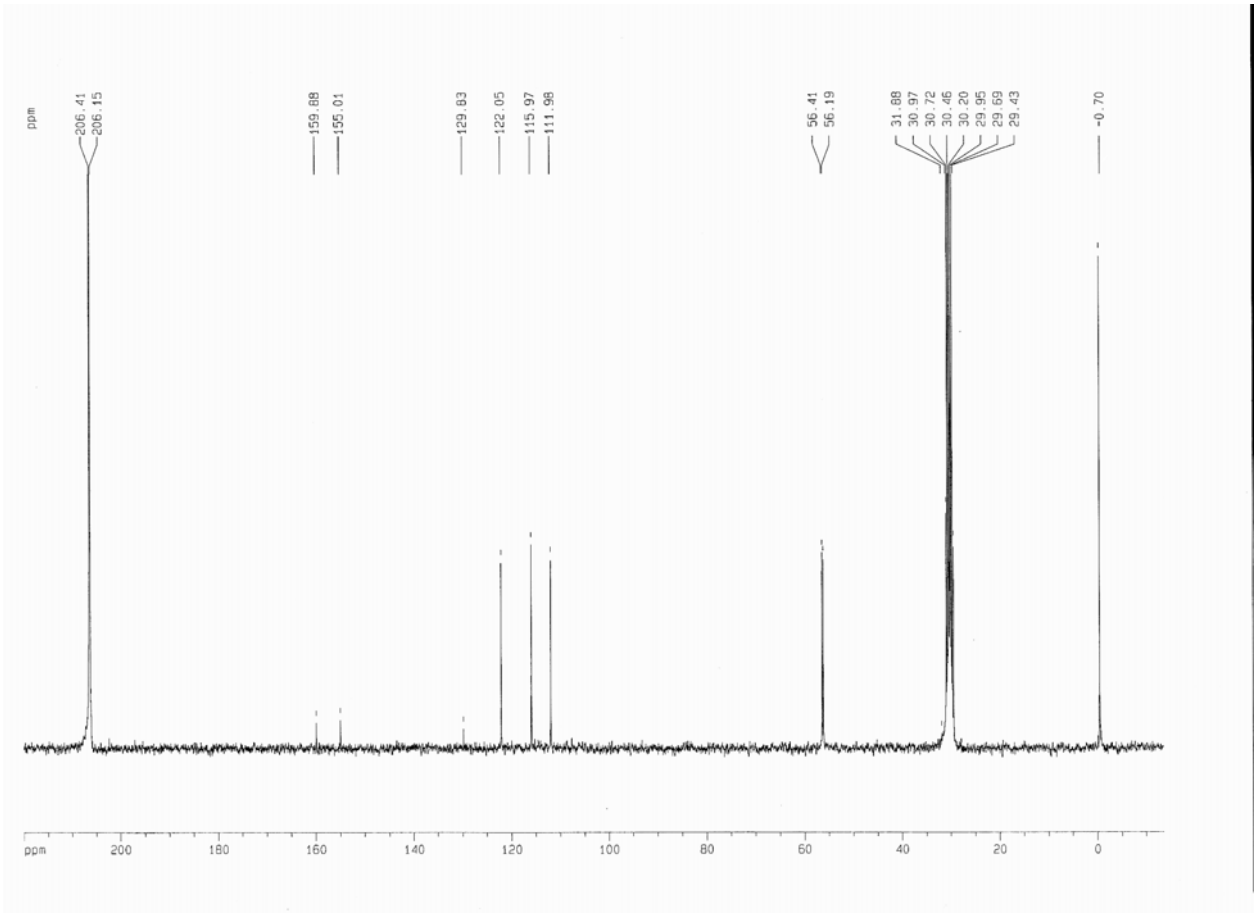
Compound **7**



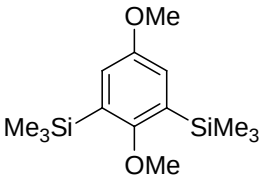


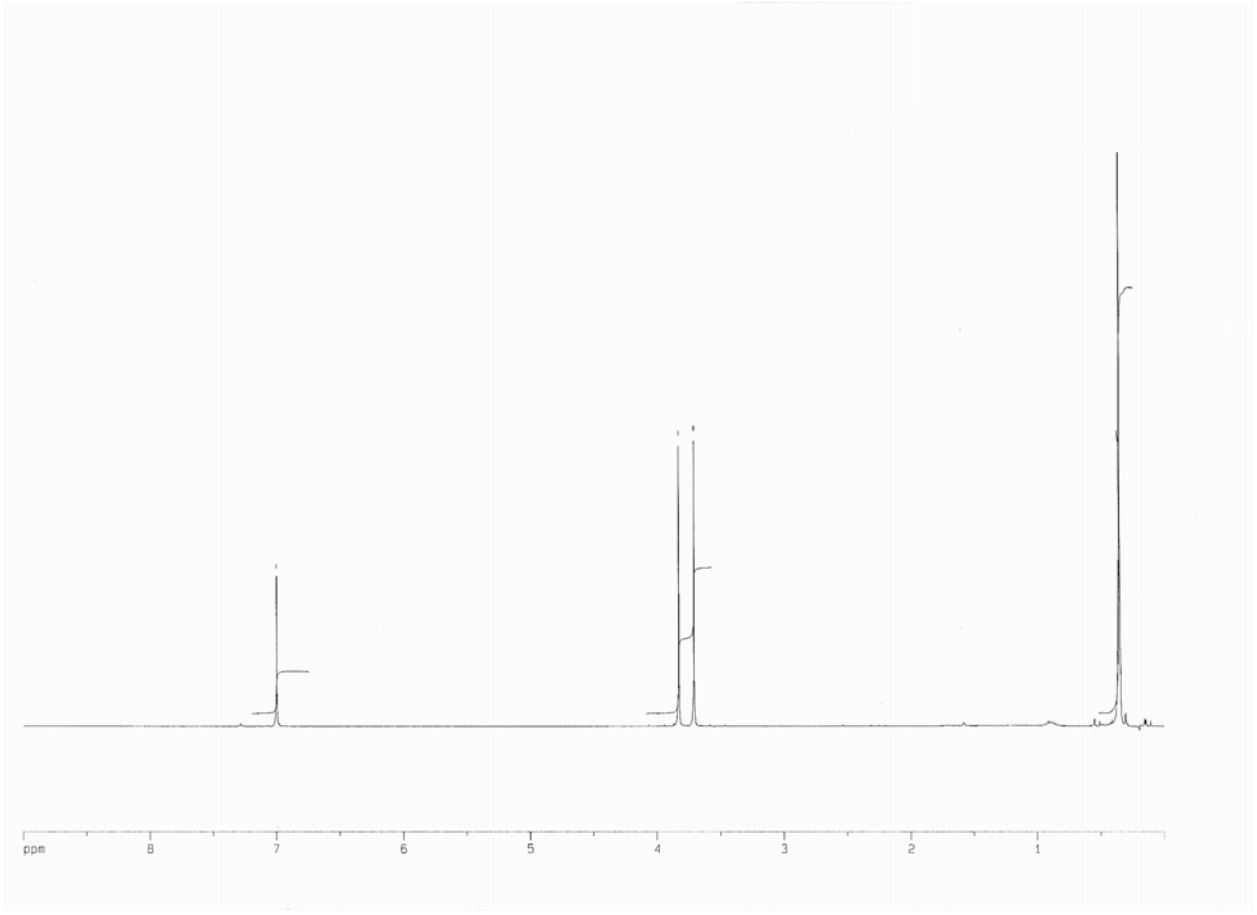
Compound **7**


OMe
SiMe3
OMe

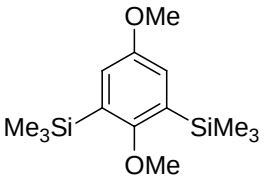

ppm
206.41
206.15
159.88
155.01
129.83
122.05
115.97
111.98
56.41
56.19
31.88
30.97
30.72
30.46
30.20
29.95
29.69
29.43
-0.70
ppm
200
180
160
140
120
100
80
60
40
20
0

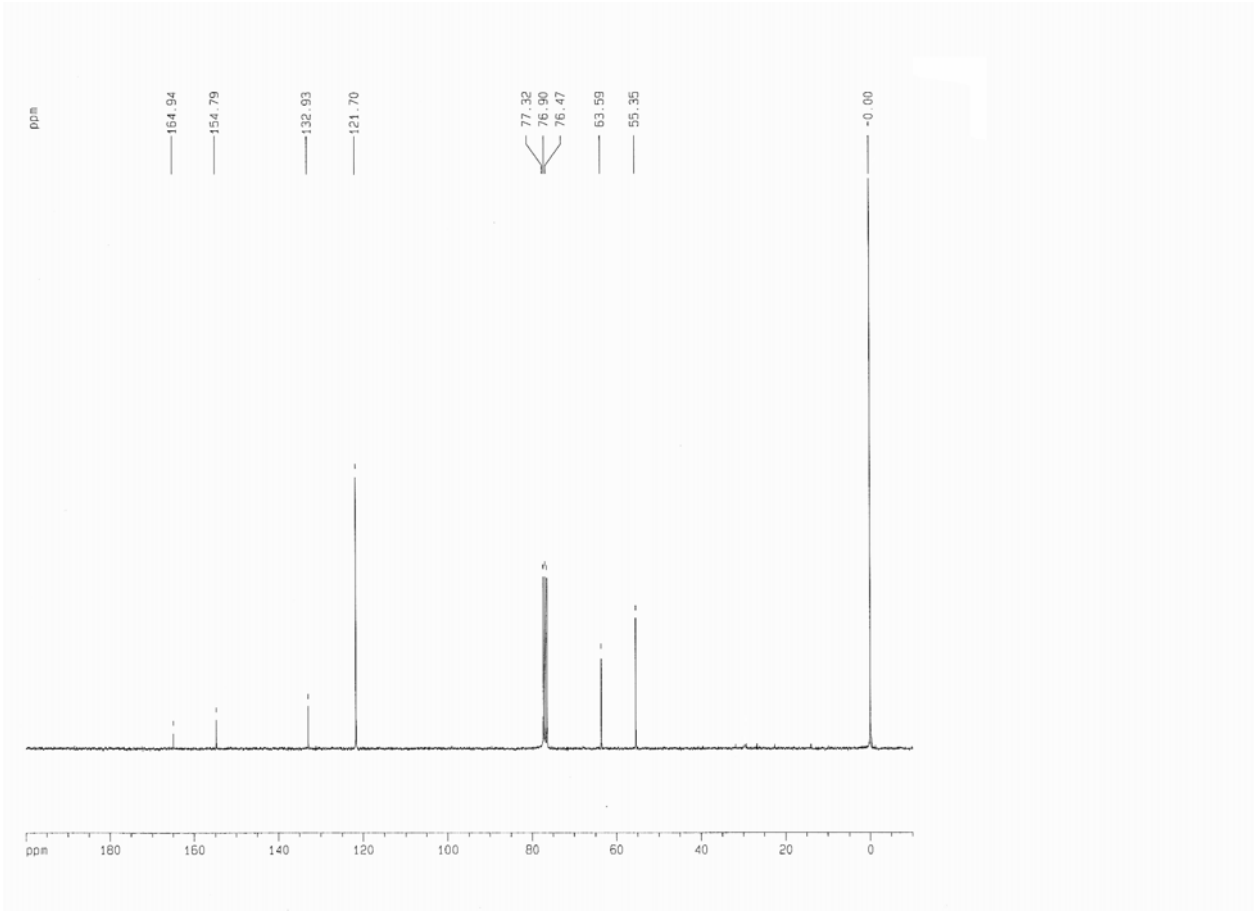
Compound **8**



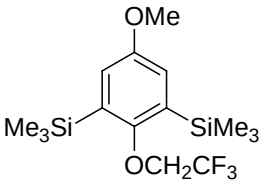


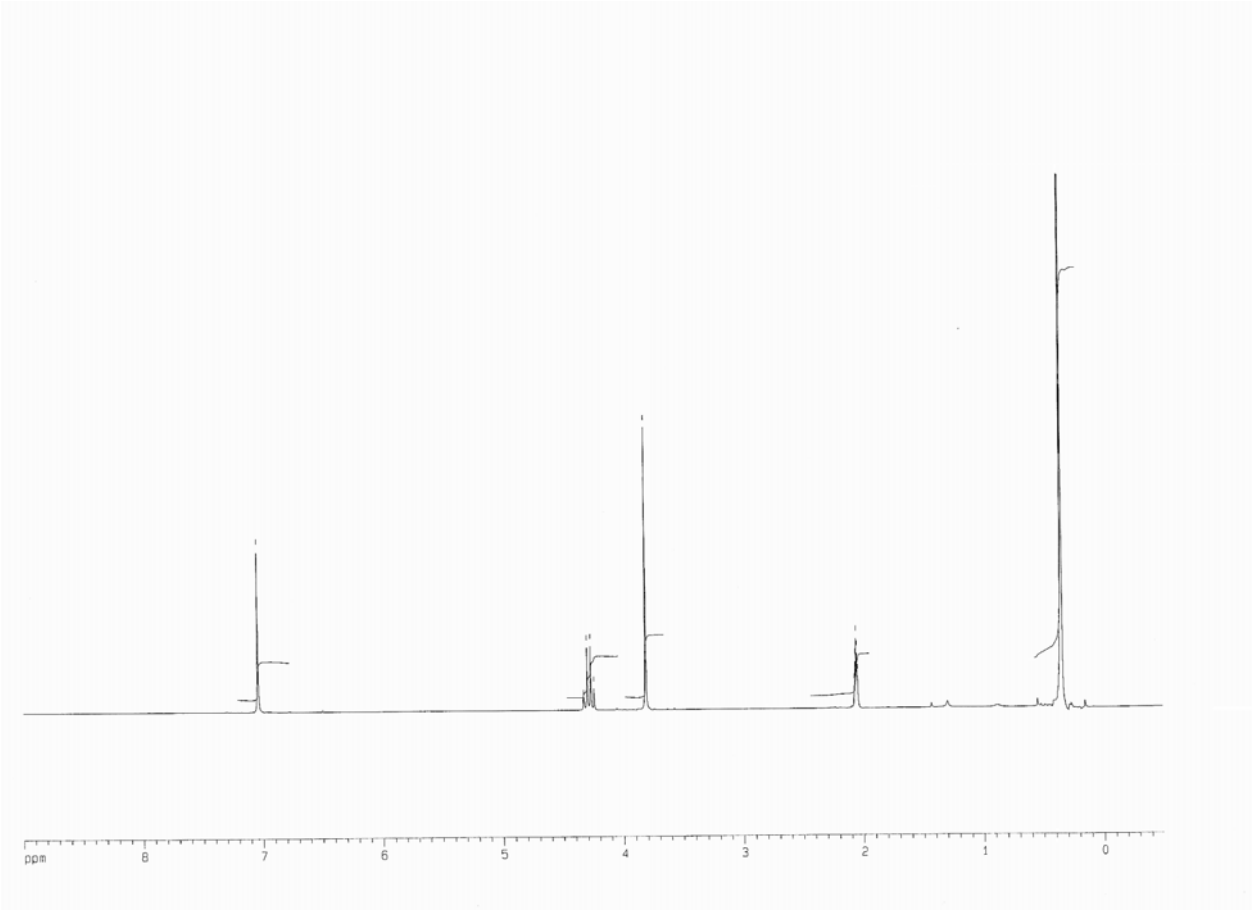
Compound **8**


OMe
Me3Si
SiMe3
OMe

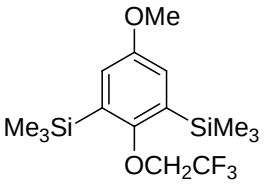

ppm
164.94
154.79
132.93
121.70
77.32
76.90
76.47
63.59
55.35
-0.00
ppm
180
160
140
120
100
80
60
40
20
0

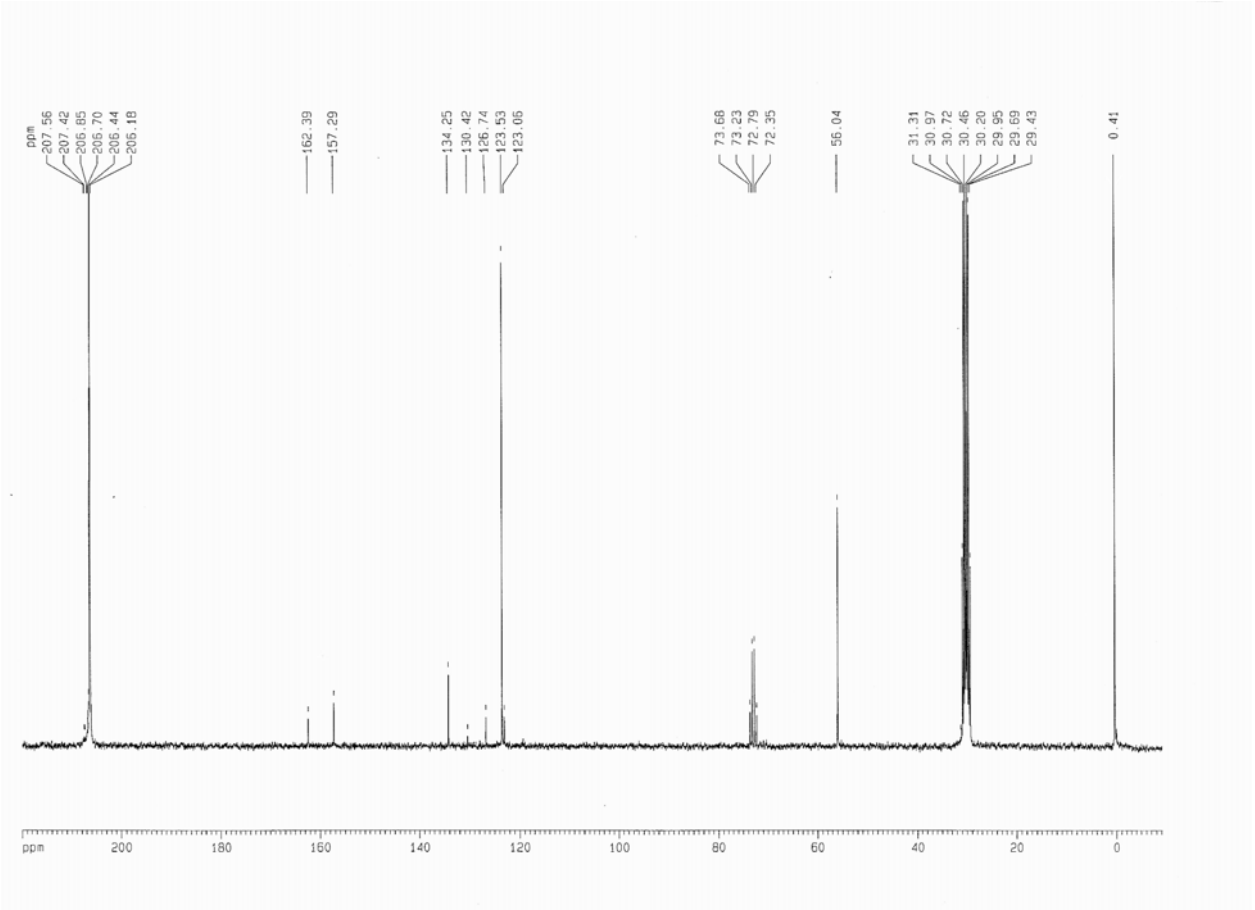
Compound **10**



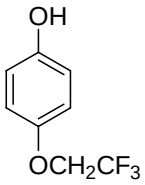


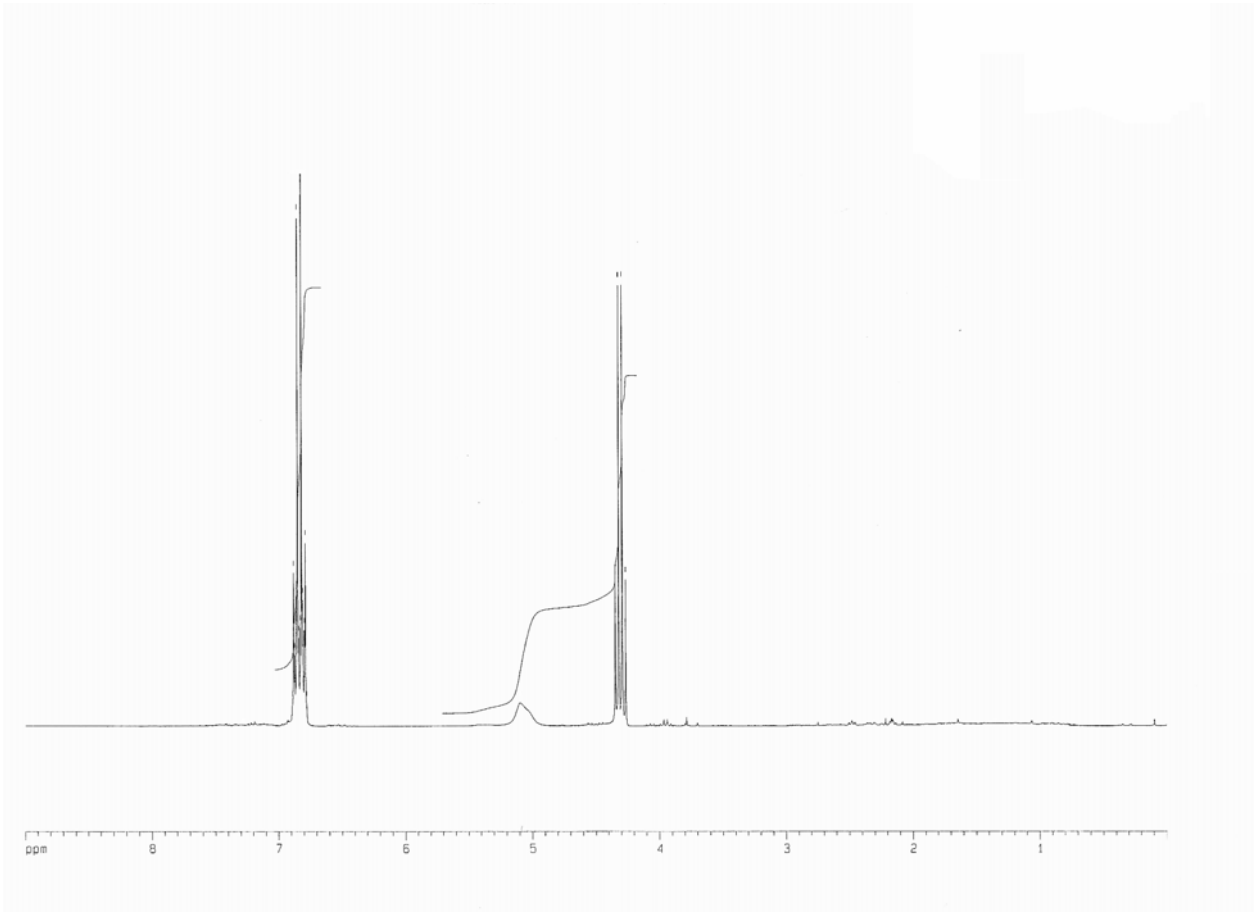
Compound **10**


OMe
Me3Si
SiMe3
OCH2CF3

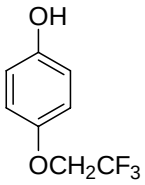

ppm
207.56
207.42
206.85
206.70
206.44
206.18
162.39
157.29
134.25
130.42
126.74
123.53
123.06
73.68
73.23
72.79
72.35
56.04
31.31
30.97
30.72
30.46
30.20
29.95
29.69
29.43
0.41
ppm
200
180
160
140
120
100
80
60
40
20
0

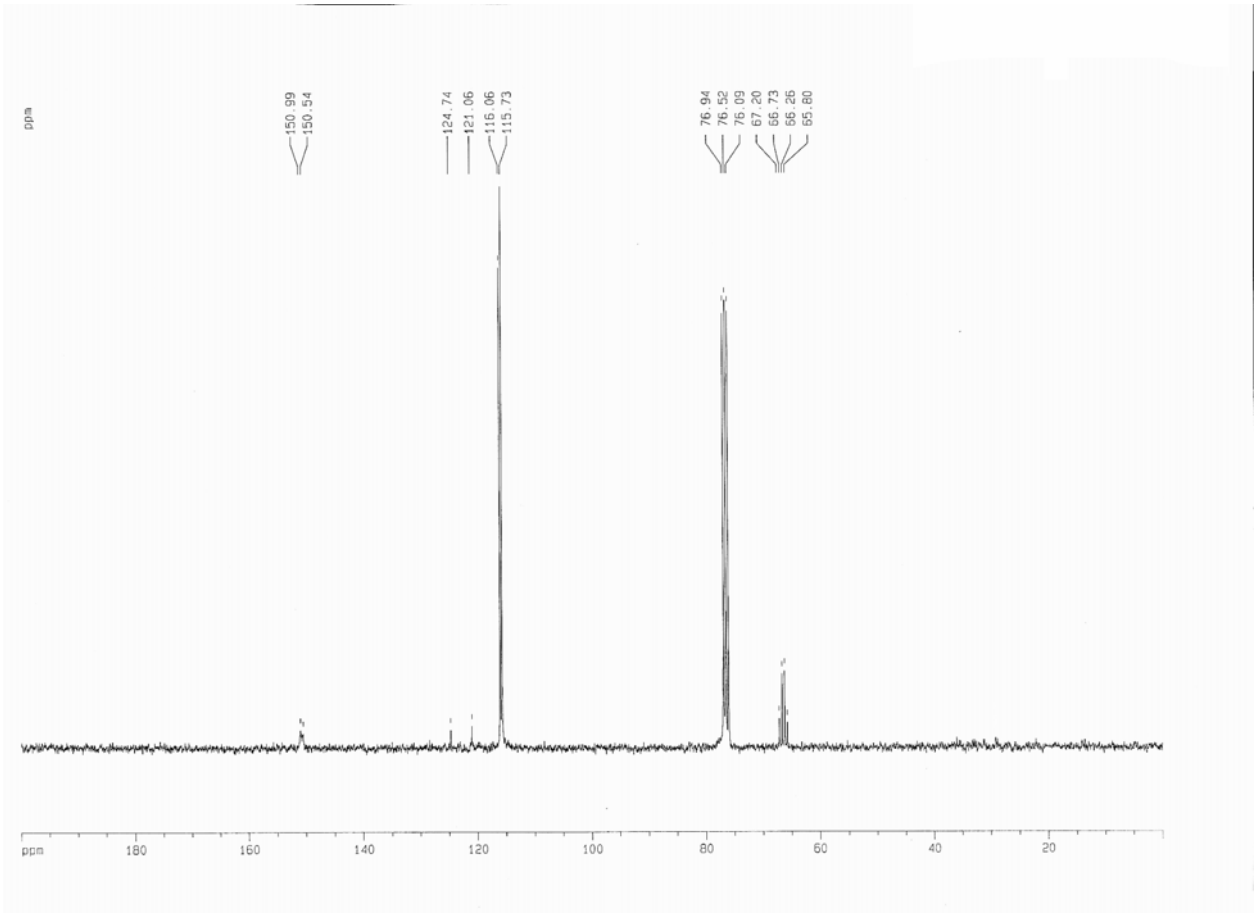
Compound **11a**



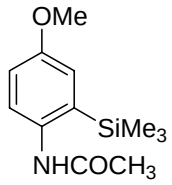


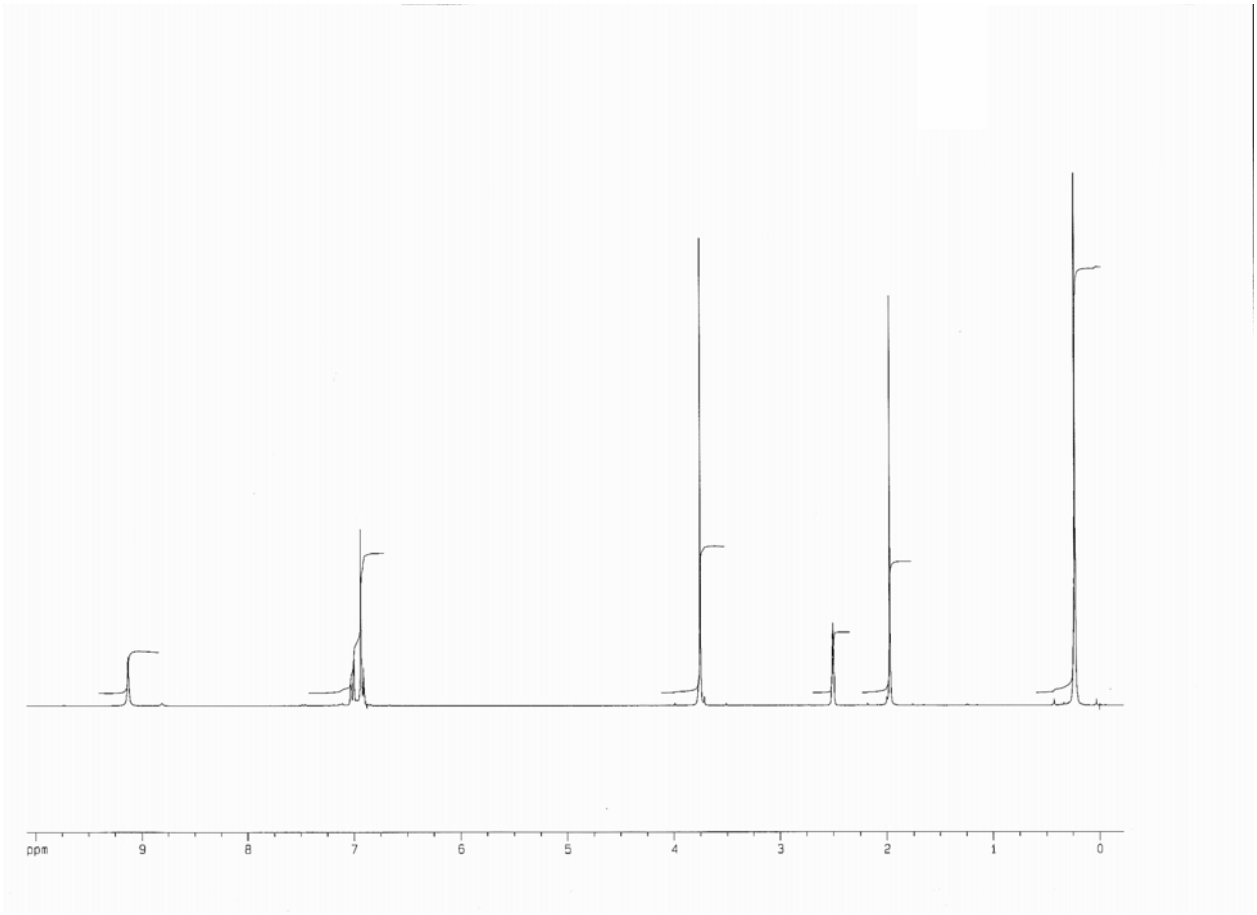
Compound **11a**



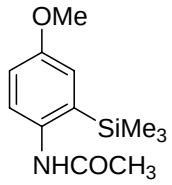


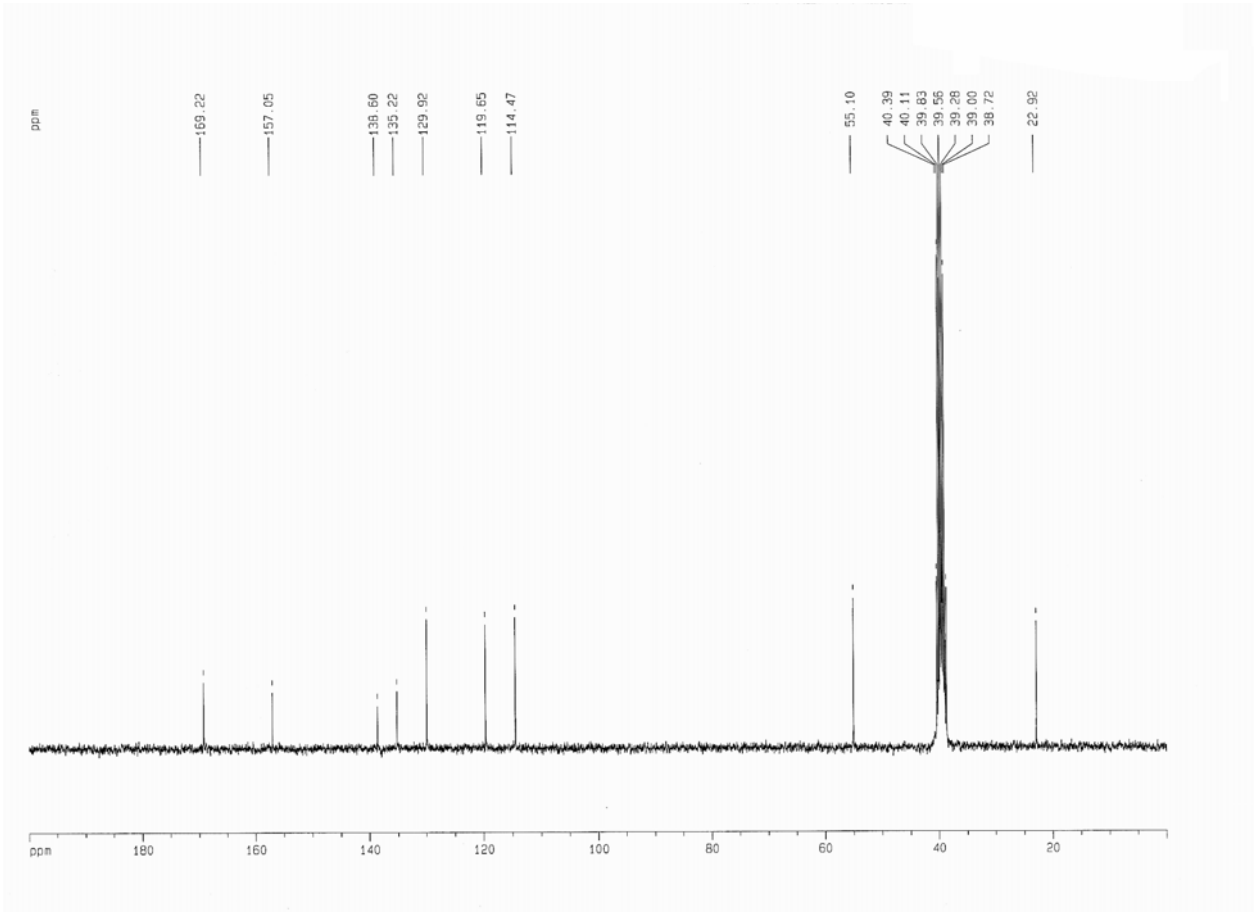
Compound **15**



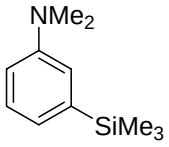


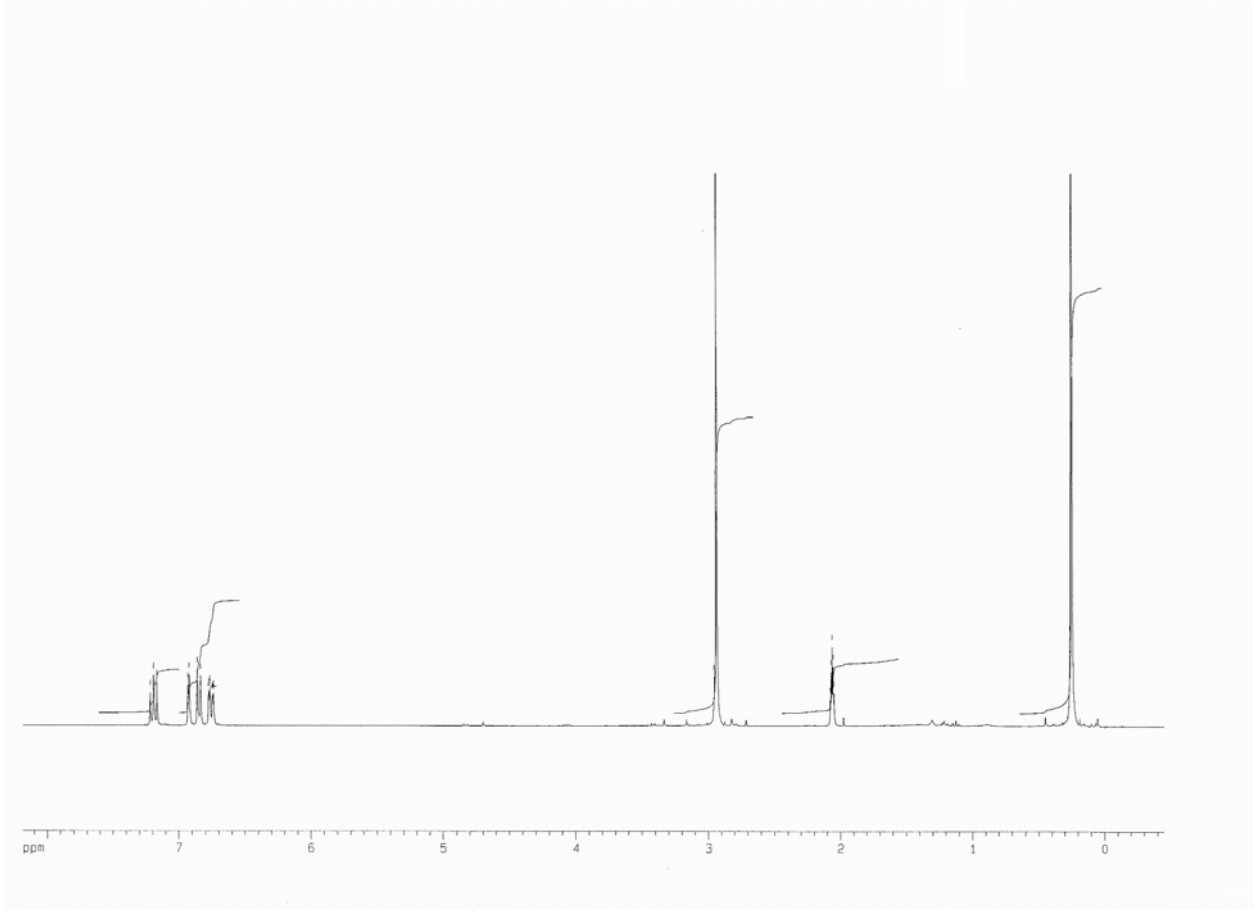
Compound **15**


OMe
SiMe3
NHCOCH3

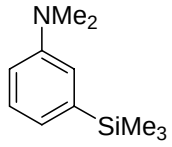

ppm
169.22
157.05
138.60
135.22
129.92
119.65
114.47
55.10
40.39
40.11
39.83
39.56
39.28
39.00
38.72
22.92
ppm
180
160
140
120
100
80
60
40
20

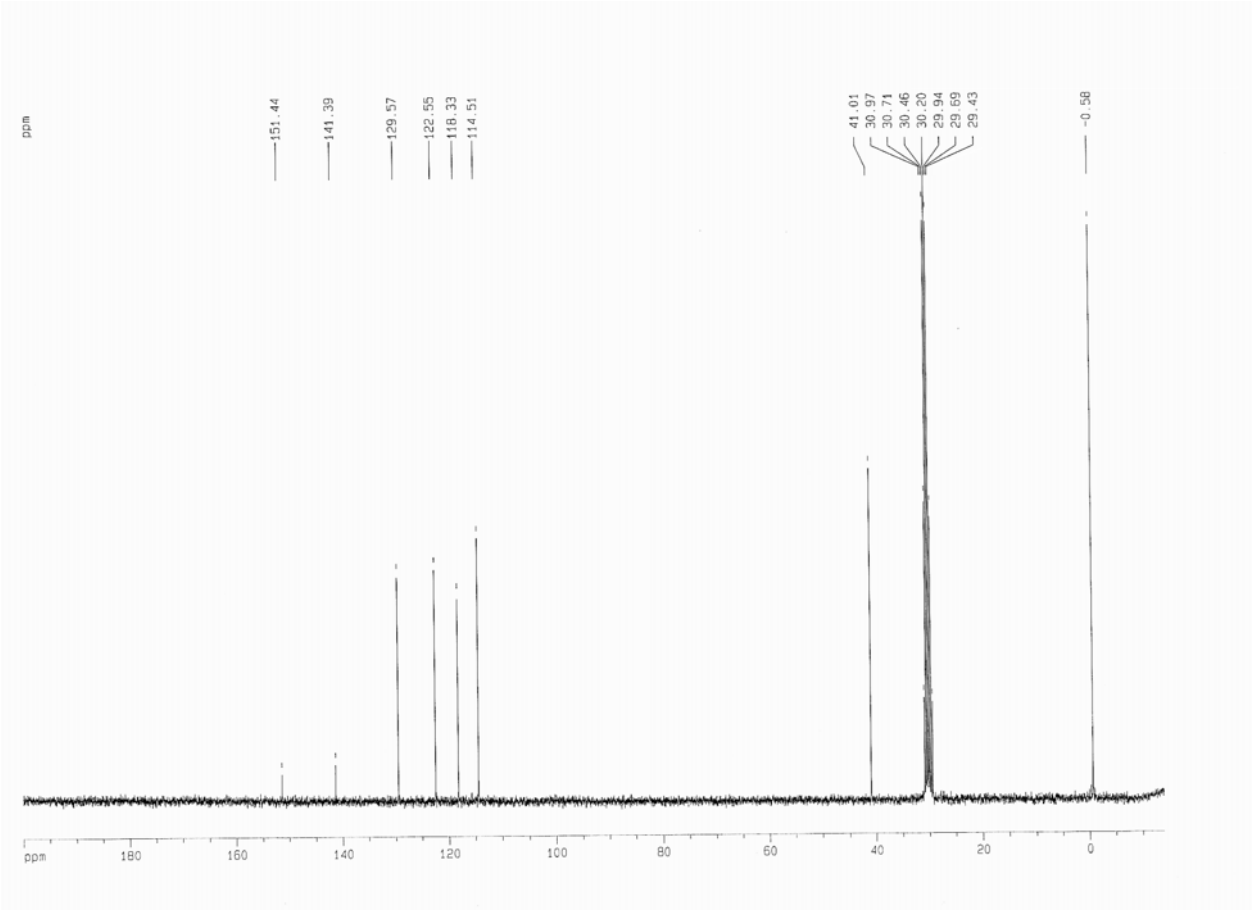
Compound **16**





Compound **16**


NMe2
SiMe3


ppm
151.44
141.39
129.57
122.55
118.33
114.51
41.01
30.97
30.71
30.46
30.20
29.94
29.69
29.43
-0.58
ppm
180
160
140
120
100
80
60
40
20
0

Calculations

Analogously to previous works,[S10] the level of theory chosen for the optimization of all the stationary points in our investigation was [UB3LYP/6-311+G(2d,p)]. All calculations were carried out by using the Gaussian 03[S11] program package.

Frequency calculations were performed in vacuo to check that energy minima and transition states have respectively zero and one imaginary frequencies. Solvent effect was calculated by CPCM-UB3LYP/6-311+G(2d,p) method (methanol bulk) on the optimized geometries obtained in vacuo. Reported energies were evaluated by adding ZPE energies obtained in vacuo with CPCM energies.

Optimized geometry listed in cartesian format, and minimum energies (in Hartree) are reported below.

^{3}1

E(gas phase) = -1215.1293088 Ha
E(MeOH)=-1215.1379519 Ha

C	0.293301	-0.122065	0.108777
C	-0.768918	-0.901570	-0.258866
C	-2.115772	-0.489858	-0.036849
C	-2.396465	0.671859	0.728533
C	-1.364778	1.478621	1.114629
C	-0.044140	1.232588	0.552089
H	-0.631666	-1.896833	-0.668967
H	-3.406364	0.888841	1.051688
H	-1.529850	2.334559	1.757890
O	-3.056733	-1.344530	-0.496022
C	-4.434316	-1.062737	-0.258382
H	-4.712858	-0.091744	-0.674953
H	-4.987075	-1.849951	-0.765231
H	-4.662409	-1.087839	0.810063
Si	2.087360	-0.729131	0.065371
C	2.083101	-2.608520	-0.083180
H	3.110091	-2.984643	-0.071606
H	1.547855	-3.080872	0.744073
H	1.626193	-2.944266	-1.017773
C	2.915396	-0.206921	1.673635
H	3.963921	-0.517260	1.687604
H	2.886716	0.878618	1.794433
H	2.421315	-0.653747	2.539978
C	3.013481	0.004704	-1.399991
H	3.044590	1.094095	-1.346321
H	4.042231	-0.367283	-1.422667
H	2.535647	-0.267810	-2.344171
Cl	0.405715	2.560801	-0.697849

^{1}19^{+}
E(gas phase)=-754.6630471 Ha
E(MeOH)=-754.7320978 Ha

C	0.382487	0.323514	-0.000285
C	-0.711739	-0.602638	-0.000367
C	-2.056068	-0.181652	-0.000187
C	-2.376875	1.189288	0.000047
C	-1.351127	2.167078	0.000088
C	-0.213666	1.478606	-0.000460
H	-0.484966	-1.661861	-0.000518
H	-3.396813	1.548320	0.000109
H	-1.519522	3.233684	0.000316
O	-2.958724	-1.168765	-0.000229
C	-4.358716	-0.846818	0.000312
H	-4.624374	-0.285906	-0.898327
H	-4.874342	-1.802294	0.000304
H	-4.623760	-0.286239	0.899337
Si	2.286139	-0.214708	0.000071
C	2.267623	-2.077700	-0.000383
H	3.303976	-2.429480	-0.000373
H	1.788591	-2.493884	0.888325
H	1.788751	-2.493446	-0.889381
C	2.990132	0.523938	1.562652
H	4.044017	0.243348	1.648797
H	2.940971	1.615149	1.558016
H	2.477641	0.158616	2.454757
C	2.990958	0.524721	-1.561768
H	4.045149	0.245003	-1.647002
H	2.479557	0.159118	-2.454384
H	2.940912	1.615891	-1.557027

^{3}19^{+}
E(gas phase)=-754.6503057 Ha
E(MeOH)=-754.7191192 Ha

C	0.356396	0.272922	-0.000022
C	-0.689891	-0.626537	-0.000053
C	-2.054182	-0.174628	-0.000035
C	-2.382315	1.219584	-0.000002
C	-1.352991	2.125630	0.000016
C	-0.055856	1.602157	0.000018
H	-0.532928	-1.699172	-0.000088
H	-3.412853	1.546949	0.000013
H	-1.538101	3.193111	0.000038
O	-2.943431	-1.132009	-0.000017

C	-4.374397	-0.871761	0.000030
H	-4.646436	-0.323155	-0.900670
H	-4.832507	-1.854951	0.000003
H	-4.646392	-0.323224	0.900786
Si	2.232909	-0.221536	-0.000008
C	2.303445	-2.091483	-0.000785
H	3.348582	-2.412695	-0.000962
H	1.836413	-2.526036	0.886519
H	1.836328	-2.525338	-0.888384
C	2.965011	0.523254	1.554596
H	4.033300	0.295263	1.602656
H	2.860978	1.610628	1.571156
H	2.500537	0.121302	2.457678
C	2.965386	0.524636	-1.553768
H	2.860710	1.611957	-1.569719
H	4.033839	0.297328	-1.601416
H	2.501614	0.122959	-2.457332

5
E(gas phase)=-755.620062 Ha
E(MeOH)=-755.6261136 Ha

C	-0.044469	1.857129	-0.000003
C	-0.249838	0.476637	-0.000002
C	0.876944	-0.363790	0.000000
C	2.166051	0.164031	0.000002
C	2.349808	1.549874	0.000000
C	1.247464	2.385401	-0.000002
H	-0.888680	2.536101	-0.000005
H	0.740176	-1.437778	0.000002
H	3.359308	1.942007	0.000000
H	1.392835	3.459765	-0.000004
O	3.311307	-0.581691	0.000004
Si	-1.982790	-0.282629	-0.000003
C	-2.193023	-1.356483	1.536831
H	-3.180840	-1.825691	1.553901
H	-1.447189	-2.154812	1.572895
H	-2.086511	-0.763803	2.448852
C	-2.192998	-1.356506	-1.536825
H	-3.180815	-1.825714	-1.553911
H	-2.086461	-0.763842	-2.448852
H	-1.447165	-2.154837	-1.572857
C	-3.286857	1.076893	-0.000007
H	-3.208099	1.714473	0.884130
H	-3.208096	1.714477	-0.884140
H	-4.287956	0.636818	-0.000007
C	3.197876	-1.996268	0.000006
H	2.677586	-2.355700	0.893239

H	2.677598	-2.355703	-0.893236
H	4.217171	-2.376927	0.000007

^{1}20^{+}
E(gas phase)=-1163.43250120 Ha
E(MeOH)=-1163.4895217 Ha

Si	-3.069925	-0.727856	-0.000144
Si	2.726255	-1.306115	0.000549
C	0.144407	2.154932	-0.000198
C	-0.092613	-0.288311	-0.000881
C	1.294923	1.348843	-0.003336
C	-1.140359	1.572969	0.001571
C	-1.328894	0.159442	0.000387
C	1.199920	-0.087583	-0.003524
C	4.236660	-0.228648	-0.211423
C	2.456267	-2.466607	-1.439175
C	2.679341	-2.172891	1.655484
C	-3.109841	-1.766866	1.553127
C	-3.115661	-1.752197	-1.562966
C	-4.335909	0.643185	0.008540
H	-4.263056	1.272256	0.898341
H	2.288502	1.773694	-0.008980
H	-2.012779	2.214886	0.003127
H	-5.334904	0.197525	0.009928
H	3.529252	-2.856603	1.735008
H	1.769413	-2.764281	1.780178
H	2.743951	-1.466284	2.485477
H	5.122379	-0.870173	-0.236528
H	4.373074	0.470228	0.616852
H	4.219290	0.332996	-1.148012
H	3.295443	-3.164127	-1.510151
H	2.391499	-1.929453	-2.387648
H	1.547455	-3.061078	-1.318608
H	-2.341310	-2.522867	-1.569814
H	-2.993539	-1.135436	-2.455735
H	-4.082035	-2.258372	-1.639898
H	-2.336910	-2.539016	1.548799
H	-4.076682	-2.272161	1.629894
H	-2.982411	-1.158915	2.451176
H	-4.268383	1.278385	-0.877314
O	0.158116	3.497702	0.000109
C	1.414361	4.186661	0.000160
H	1.165507	5.243773	0.002347
H	1.989349	3.944012	0.896959
H	1.987740	3.947411	-0.898554

^{3}20^{+}
E(gas phase)=-1163.4067631 Ha
E(MeOH)=-1163.4895217 Ha

Si	3.035644	-0.698555	-0.000005
Si	-2.698935	-1.274001	0.000006
C	-0.158523	2.146017	0.000035
C	0.113072	-0.494764	0.000006
C	-1.334721	1.336895	0.000000
C	1.157643	1.567095	0.000025
C	1.323206	0.198515	0.000009
C	-1.213734	-0.038948	-0.000031
C	-4.275788	-0.262544	-0.001029
C	-2.525043	-2.307460	1.554000
C	-2.523780	-2.308709	-1.553002
C	3.087873	-1.745905	-1.553047
C	3.087975	-1.745639	1.553219
C	4.358707	0.627148	-0.000157
H	4.309423	1.263576	-0.887197
H	-2.308860	1.807672	0.000013
H	1.994305	2.256508	0.000029
H	5.344538	0.154310	-0.000286
H	-3.327507	-3.048847	-1.594553
H	-1.575757	-2.850887	-1.572953
H	-2.587525	-1.699332	-2.457172
H	-5.136875	-0.936348	-0.002472
H	-4.364978	0.369074	-0.888520
H	-4.366918	0.367754	0.887210
H	-3.329933	-3.046269	1.596386
H	-2.587668	-1.697088	2.457578
H	-1.577880	-2.851120	1.574225
H	2.283720	-2.484790	1.571370
H	3.011294	-1.136010	2.456322
H	4.035072	-2.289811	1.601000
H	2.283700	-2.485153	-1.570950
H	4.035027	-2.289975	-1.600860
H	3.010997	-1.136456	-2.456253
H	4.309646	1.263556	0.886909
O	-0.166669	3.456862	0.000049
C	-1.398825	4.223091	-0.000040
H	-1.079917	5.260016	-0.000220
H	-1.971471	4.000734	-0.899551
H	-1.971377	4.001024	0.899608

3,5-*bis*(trimethylsilyl)anisole
E(gas phase)=-1164.363118 Ha
E(MeOH)=-1164.3681859 Ha

C	1.302666	0.157659	0.000015
C	1.129763	1.537590	0.000062
C	-0.148432	2.106368	0.000013
C	-1.272159	1.286990	-0.000080
C	-1.135846	-0.112284	-0.000111
C	0.150551	-0.650185	-0.000062
H	1.975632	2.215268	0.000133
H	-2.260642	1.729001	-0.000172
O	-0.183151	3.473519	0.000071
C	-1.447543	4.117219	-0.000058
H	-2.026834	3.862183	0.892981
H	-1.238882	5.185137	-0.000040
H	-2.026655	3.862179	-0.893211
Si	3.021646	-0.633663	-0.000008
Si	-2.680629	-1.203649	0.000008
C	-3.709523	-0.829557	-1.536608
H	-3.149484	-1.053649	-2.448026
H	-4.626006	-1.426400	-1.549635
H	-4.000375	0.223342	-1.578822
C	-2.194644	-3.024095	-0.001724
H	-3.091284	-3.650210	-0.001948
H	-1.609648	-3.288111	-0.886320
H	-1.609056	-3.289630	0.882027
C	-3.707561	-0.831947	1.538503
H	-3.146320	-1.057268	2.448878
H	-3.998425	0.220873	1.582577
H	-4.623965	-1.428904	1.551873
C	3.210584	-1.709550	-1.537637
H	2.448755	-2.492457	-1.573376
H	3.115455	-1.113750	-2.448922
H	4.189184	-2.197686	-1.555540
C	3.210591	-1.709697	1.537517
H	4.189160	-2.197900	1.555328
H	3.115547	-1.113971	2.448858
H	2.448715	-2.492561	1.573226
C	4.351035	0.701806	0.000069
H	4.284207	1.340976	0.884123
H	5.344050	0.243745	0.000022
H	4.284193	1.341127	-0.883874
H	0.266762	-1.729029	-0.000102

^{1}21^{+}
E(gas phase)=-695.4842496 Ha
E(MeOH)=-695.5609701 Ha

C	0.051105	0.230025	0.055295
C	1.048027	-0.792172	0.057477
C	2.425633	-0.483233	0.005517

C	2.836569	0.874273	-0.046682
C	1.905533	1.926750	-0.042648
C	0.711839	1.350708	0.152759
H	0.716118	-1.823414	0.088627
H	3.887541	1.139207	-0.032138
H	2.170661	2.973350	-0.071537
N	3.358000	-1.475314	0.024477
H	3.074443	-2.437984	-0.058184
H	4.316510	-1.277145	-0.212160
Si	-1.891230	-0.108223	-0.012418
C	-2.390491	-0.366947	1.767909
H	-3.463044	-0.579956	1.810023
H	-1.867285	-1.210878	2.221735
H	-2.204393	0.520634	2.375756
C	-2.081333	-1.631064	-1.073058
H	-3.148030	-1.850622	-1.180117
H	-1.673982	-1.486178	-2.075584
H	-1.616708	-2.515236	-0.631763
C	-2.637769	1.421325	-0.779259
H	-3.722587	1.302441	-0.847612
H	-2.448516	2.314123	-0.177854
H	-2.264183	1.595996	-1.790543

^{3}**21**$^{+}$
E(gas phase)=-695.4854777 Ha
E(MeOH)=-695.5699098 Ha

C	0.070231	-0.191378	0.000000
C	1.020250	0.810629	0.000005
C	2.420340	0.498310	0.000002
C	2.871347	-0.863954	-0.000006
C	1.940203	-1.871010	-0.000010
C	0.605007	-1.476548	-0.000007
H	0.730268	1.856646	0.000012
H	3.934425	-1.077192	-0.000008
H	2.233649	-2.913722	-0.000016
N	3.318113	1.484969	0.000007
H	3.033832	2.456093	0.000012
H	4.312449	1.297282	0.000005
Si	-1.845465	0.105614	0.000005
C	-2.499450	-0.706417	1.555370
H	-2.080066	-0.255416	2.457477
H	-3.585745	-0.591544	1.602608
H	-2.281525	-1.776695	1.575619
C	-2.118431	1.958974	-0.000362
H	-1.703689	2.442040	-0.888753
H	-3.192698	2.162808	-0.000117
H	-1.703230	2.442535	0.887548

C	-2.499543	-0.707008	-1.555006
H	-3.585819	-0.591978	-1.602352
H	-2.080051	-0.256491	-2.457305
H	-2.281799	-1.777332	-1.574757

3-Trimethylsilylaniline
E(gas phase)=-696.4378361 Ha
E(MeOH)=-696.4499411 Ha

C	-0.551916	1.593314	-0.009794
C	-0.083879	0.273376	-0.006696
C	-1.027478	-0.759224	0.001898
C	-2.403252	-0.507716	0.007014
C	-2.841368	0.821293	0.005813
C	-1.919057	1.856879	-0.003510
H	0.144733	2.422832	-0.019249
H	-0.699864	-1.795941	0.007594
H	-3.904817	1.036663	0.015277
H	-2.271973	2.882176	-0.007292
Si	1.763634	-0.131120	0.000530
C	2.160074	-1.288370	-1.435986
H	3.222010	-1.550209	-1.443577
H	1.591535	-2.219740	-1.373003
H	1.922529	-0.819925	-2.394451
C	2.211225	-0.981640	1.623332
H	3.271004	-1.251060	1.647077
H	2.010462	-0.328943	2.476630
H	1.631361	-1.897240	1.765387
C	2.772828	1.450020	-0.179876
H	2.537664	1.975092	-1.109091
H	2.600585	2.139922	0.650080
H	3.840638	1.214468	-0.194870
N	-3.323310	-1.561108	0.074851
H	-4.241921	-1.347695	-0.286558
H	-2.984720	-2.444547	-0.278498

^{1}19a^{+}
E(gas phase)=-345.8853901 Ha
E(MeOH)=-345.9696932 Ha

C	-1.364945	1.470239	0.037275
C	0.000397	1.100752	-0.013790
C	0.367903	-0.259365	-0.004009
C	-0.622545	-1.271143	0.017764
C	-1.998060	-0.970725	0.055352
C	-2.067729	0.350995	-0.099313
H	-1.717211	2.489630	0.123919

H	0.726297	1.901328	-0.063599
H	-0.332122	-2.312763	-0.067306
H	-2.782082	-1.715623	0.049910
O	1.617472	-0.701435	-0.023393
C	2.715274	0.233833	0.017956
H	2.686717	0.811422	0.942847
H	3.611050	-0.378163	-0.010306
H	2.685800	0.888132	-0.855726

^{3}19a^{+}
E(gas phase)=-345.8911661 Ha
E(MeOH)=-345.9702825 Ha

C	-1.341396	1.438587	0.000000
C	-0.004955	1.127049	0.000020
C	0.376422	-0.252933	0.000010
C	-0.606521	-1.304805	0.000010
C	-1.940022	-0.984851	-0.000012
C	-2.243698	0.371927	-0.000021
H	-1.682414	2.467040	0.000011
H	0.744707	1.906326	0.000061
H	-0.253468	-2.328993	0.000020
H	-2.709906	-1.746793	-0.000020
O	1.610319	-0.670844	0.000024
C	2.750963	0.236600	-0.000030
H	2.728050	0.847151	0.901546
H	3.617966	-0.414871	-0.000277
H	2.727757	0.847454	-0.901390

5a
E(gas phase)=-346.8770869 Ha
E(MeOH)=-346.8842909 Ha

C	-1.848319	-0.995653	0.000071
C	-0.496918	-1.299357	-0.000002
C	0.451109	-0.271848	-0.000078
C	0.032056	1.058280	-0.000112
C	-1.332466	1.347447	-0.000028
C	-2.277338	0.331664	0.000077
H	-2.573987	-1.800575	0.000139
H	-0.149274	-2.324963	0.000003
H	0.747571	1.868515	-0.000232
H	-1.650212	2.383673	-0.000048
H	-3.334487	0.565975	0.000154
O	1.756982	-0.670931	-0.000219
C	2.767424	0.325245	0.000204
H	2.708061	0.955081	0.893336

H	3.714523	-0.210187	0.000458
H	2.708657	0.955258	-0.892846

^{1}21a^{+}
E(gas phase)=-286.7116121 Ha
E(MeOH)=-286.803846 Ha

C	1.253858	1.246358	-0.068740
C	-0.139689	1.232615	-0.028498
C	-0.854309	-0.000025	-0.004655
C	-0.139529	-1.232558	-0.028505
C	1.254060	-1.246276	-0.068814
C	1.703392	0.000050	0.194829
H	1.842856	2.152526	-0.134541
H	-0.665282	2.178459	0.038728
H	-0.664999	-2.178454	0.038993
H	1.843033	-2.152465	-0.134490
N	-2.196397	-0.000111	0.030424
H	-2.723803	0.859197	0.002381
H	-2.723714	-0.859470	0.002261

^{3} 21a^{+}
E(gas phase)=-286.7273734 Ha
E(MeOH)=-286.8222685 Ha

C	-1.219111	1.244131	0.000002
C	0.153376	1.247858	-0.000008
C	0.862354	0.000023	-0.000010
C	0.153370	-1.247848	-0.000009
C	-1.219100	-1.244148	0.000001
C	-1.840292	-0.000004	0.000016
H	-1.787107	2.166535	-0.000007
H	0.710415	2.177996	-0.000034
H	0.710468	-2.177952	-0.000017
H	-1.787094	-2.166553	0.000009
N	2.194371	-0.000007	-0.000005
H	2.724591	0.862814	0.000100
H	2.724544	-0.862855	0.000036

Aniline
E(gas phase)=-287.6948929 Ha
E(MeOH)=-287.7076336 Ha

C	-0.219900	-1.203615	-0.004882
C	-0.934380	0.000002	-0.007976
C	-0.219912	1.203609	-0.004859

C	1.168704	1.198682	0.003460
C	1.876045	0.000008	0.007752
C	1.168701	-1.198682	0.003458
H	-0.759057	-2.145189	-0.013327
H	-0.759056	2.145192	-0.013263
H	1.701713	2.142554	0.007443
H	2.958738	-0.000002	0.014750
H	1.701731	-2.142542	0.007423
N	-2.332381	-0.000028	-0.077235
H	-2.776481	-0.834432	0.278206
H	-2.776476	0.834595	0.277697

$^{1}C_6H_5^+$
E(gas phase)=-231.3231006 Ha
E(MeOH)=-231.4152169 Ha

C	-1.210258	0.612703	0.000005
C	-1.266155	-0.818270	0.000001
C	-0.000062	-1.187092	-0.000009
C	1.266068	-0.818355	0.000004
C	1.210338	0.612600	-0.000004
C	0.000062	1.294378	-0.000001
H	-2.169403	1.120235	0.000004
H	-2.179896	-1.396334	-0.000003
H	2.179728	-1.396550	0.000023
H	2.169518	1.120061	-0.000001
H	0.000100	2.376807	-0.000001

Benzene
E(gas phase)=-232.3174261 Ha
E(MeOH)=-232.3235018 Ha

C	-1.388380	0.100920	-0.000001
C	-0.606654	1.252606	-0.000009
C	0.781532	1.151688	-0.000001
C	1.388376	-0.100980	-0.000002
C	0.606708	-1.252579	-0.000001
C	-0.781582	-1.151655	0.000005
H	-2.469207	0.179658	0.000009
H	-1.078998	2.227969	0.000014
H	1.390016	2.048444	0.000027
H	2.469212	-0.179578	0.000009
H	1.078931	-2.228001	-0.000006
H	-1.389952	-2.048488	-0.000001

Stationary points involved in addition of phenyl cations ^{1}**19**$^{+}$, ^{3}**19**$^{+}$, ^{1}**21**$^{+}$, ^{3}**21**$^{+}$ to ethylene in neat methanol.

^{1}19^{+} + ethylene.
E = -833.3816287 Ha

C	2.377184	1.505674	0.103666
C	1.225987	2.219145	0.097049
C	-0.065072	1.584785	0.000222
C	-0.143373	0.135108	-0.057432
C	1.045988	-0.558448	-0.064258
C	2.302167	0.093386	0.010533
H	3.350075	1.974092	0.169571
H	1.265544	3.301402	0.153534
H	1.034577	-1.636862	-0.118646
C	-1.269950	2.418180	0.596179
C	-1.121565	2.452231	-0.840494
H	-0.964488	3.269671	1.188571
H	-1.770865	1.858391	-1.463575
H	-0.683004	3.317199	-1.317664
H	-2.049730	1.814024	1.035434
O	3.459824	-0.528217	0.005451
C	3.544526	-1.968682	-0.090916
H	4.607701	-2.186259	-0.086373
H	3.064198	-2.432739	0.770355
H	3.095777	-2.311594	-1.022939
C	-2.227674	-1.059401	1.837789
C	-3.163471	-0.258396	-1.008847
C	-1.312835	-2.656264	-0.635982
H	-1.406158	-1.448947	2.443050
H	-2.533526	-0.102577	2.265480
H	-3.071619	-1.746518	1.946907
H	-2.894098	-0.142035	-2.061411
H	-3.985539	-0.979268	-0.972033
H	-3.561915	0.689231	-0.642451
H	-2.224149	-3.259665	-0.670223
H	-0.912158	-2.620062	-1.651744
H	-0.605317	-3.194232	-0.001408
Si	-1.756098	-0.955816	0.021922

^{3}19^{+} + ethylene (transition state)
E = -833.2678227 Ha

C	0.900364	-0.990130	-0.201700
C	-0.230629	-0.247477	0.099716
C	0.034247	1.077643	0.503386
C	1.309618	1.625660	0.764273

C	2.421505	0.871046	0.467116
C	2.220856	-0.449606	-0.039551
H	0.840324	-2.019926	-0.542308
H	1.409526	2.634069	1.153689
H	3.419962	1.265713	0.616573
C	-1.361859	2.824464	-0.505543
C	-0.659263	3.977958	-0.388343
H	-2.137386	2.567294	0.209812
H	0.041834	4.297641	-1.154553
H	-0.769619	4.626799	0.476459
H	-1.333729	2.246370	-1.424278
O	3.193519	-1.277798	-0.358325
C	4.588043	-0.913188	-0.214062
H	5.141599	-1.783953	-0.559718
H	4.814398	-0.045791	-0.839495
H	4.813627	-0.711404	0.836132
C	-1.765978	-2.900461	-0.028550
C	-2.888128	-0.504051	1.614505
C	-2.897300	-0.427799	-1.510658
H	-1.279687	-3.233655	-0.953013
H	-1.186920	-3.280467	0.820851
H	-2.747151	-3.389225	0.006089
H	-2.991064	0.584325	1.692482
H	-3.898862	-0.928814	1.635206
H	-2.366557	-0.857107	2.511257
H	-3.843097	-0.974675	-1.610124
H	-3.144284	0.638103	-1.475727
H	-2.316437	-0.615708	-2.420762
Si	-2.003106	-1.032968	0.037464

^{3}19^{+} + ethylene

E = -833.3206375 Ha

C	-0.872477	-0.929029	-0.000212
C	0.228369	-0.110113	-0.000477
C	-0.021234	1.311122	-0.000775
C	-1.356294	1.809128	-0.000839
C	-2.441322	0.980873	-0.000539
C	-2.208642	-0.420189	-0.000193
H	-0.781230	-2.007784	0.000020
H	-1.500237	2.882595	-0.001154
H	-3.444700	1.382519	-0.000504
C	1.127140	2.289815	-0.001823
C	0.813213	3.743678	0.002259
H	1.748062	2.038658	-0.872538
H	0.713915	4.286892	0.932017
H	0.726960	4.295303	-0.923769
H	1.753345	2.034990	0.864092

O	-3.150477	-1.331500	0.000266
C	-4.558065	-0.978994	0.000130
H	-5.082352	-1.928705	0.000015
H	-4.796760	-0.413035	0.899839
H	-4.796604	-0.412885	-0.899519
C	1.690747	-2.807829	-0.002670
C	2.907623	-0.461575	-1.557567
C	2.903488	-0.465717	1.561569
H	1.156082	-3.155974	0.884432
H	1.155312	-3.153353	-0.890330
H	2.663144	-3.307972	-0.003839
H	3.258229	0.571794	-1.549477
H	3.793035	-1.096513	-1.653325
H	2.302834	-0.611966	-2.454922
H	3.789499	-1.099801	1.657388
H	3.252764	0.568137	1.557886
H	2.296658	-0.619783	2.456915
Si	1.980041	-0.954868	0.000104

^{1}21^{+} + ethylene.
E = -774.2114197 Ha

C	0.982331	-1.114675	-0.089948
C	0.104378	-0.067426	-0.063344
C	0.671950	1.278099	0.007073
C	2.106620	1.421536	0.104094
C	2.946424	0.362371	0.089407
C	2.398588	-0.947353	-0.023814
H	0.615086	-2.132172	-0.153917
H	2.515308	2.423507	0.177324
H	4.019221	0.496801	0.154058
N	3.200182	-2.010503	-0.061881
H	4.203592	-1.916193	-0.012545
H	2.828968	-2.945117	-0.144482
C	-0.009944	2.455030	-0.819702
C	-0.161660	2.458224	0.623806
H	-0.829916	2.139555	-1.444903
H	0.412312	3.153428	1.221108
H	-1.105827	2.162384	1.056300
H	0.692781	3.130373	-1.287144
C	-1.948117	-2.292607	-0.632528
C	-2.271116	-0.468391	1.829932
C	-2.862264	0.593664	-1.020790
H	-1.565266	-2.398245	-1.650327
H	-1.460287	-3.036078	0.001592
H	-3.010353	-2.550733	-0.658519
H	-2.222767	0.535918	2.255292
H	-3.303183	-0.814702	1.934975

H	-1.641641	-1.120300	2.439727
H	-3.881588	0.197890	-0.987979
H	-2.913108	1.620813	-0.655277
H	-2.563293	0.610226	-2.071607
Si	-1.781032	-0.539619	0.016742

^{3}21^{+} + ethylene (transition state)
E=-774.1012023 Ha

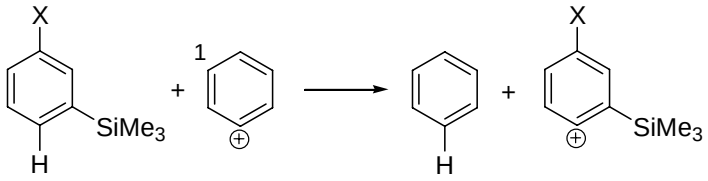
C	-1.091514	-1.325909	-0.125113
C	-0.119734	-0.349063	0.030358
C	-0.613967	0.961072	0.219339
C	-1.970208	1.317430	0.336994
C	-2.921807	0.337229	0.187809
C	-2.491412	-1.009103	-0.060367
H	-0.815865	-2.366138	-0.284532
H	-2.256531	2.348154	0.519392
H	-3.983875	0.560420	0.249995
N	-3.400285	-1.980049	-0.214996
H	-4.395620	-1.792604	-0.161762
H	-3.125641	-2.941496	-0.384592
C	0.703313	2.978912	-0.388635
C	-0.063471	4.044608	-0.068181
H	0.716796	2.582443	-1.400160
H	-0.002026	4.518780	0.907682
H	-0.771377	4.470877	-0.774321
H	1.484912	2.632424	0.280457
C	2.579406	-0.075323	-1.494141
C	2.497812	-0.137515	1.637344
C	1.865599	-2.693543	-0.008757
H	2.089879	-0.408042	-2.416514
H	2.589389	1.018985	-1.490336
H	3.623340	-0.409158	-1.540814
H	2.024064	-0.583496	2.519159
H	3.567189	-0.376209	1.683477
H	2.402499	0.950531	1.721312
H	2.918573	-2.996760	0.034840
H	1.363335	-3.166334	0.843334
H	1.454377	-3.117062	-0.932885
Si	1.762463	-0.811267	0.037953

^{3}21^{+} + ethylene.
E = -774.1543065 Ha

C	-0.949111	-1.274086	0.030081
C	-0.087201	-0.204547	-0.033763

C	-0.670922	1.107099	-0.121565
C	-2.084101	1.261392	-0.142091
C	-2.926674	0.191986	-0.080067
C	-2.368368	-1.115775	0.011007
H	-0.564652	-2.285331	0.098946
H	-2.491550	2.262500	-0.210181
H	-4.002475	0.321583	-0.097294
N	-3.164640	-2.185859	0.081060
H	-4.171878	-2.097420	0.068286
H	-2.784928	-3.120565	0.149111
C	0.175460	2.345746	-0.251038
C	-0.385829	3.594813	0.340992
H	0.354672	2.499205	-1.326538
H	-0.836079	3.582794	1.325377
H	-0.149644	4.553022	-0.098807
H	1.170465	2.143917	0.164435
C	2.623857	0.127552	-1.535748
C	2.541500	0.136610	1.590271
C	2.020979	-2.440340	0.020988
H	2.137529	-0.238787	-2.443149
H	2.629163	1.217778	-1.569879
H	3.666182	-0.201670	-1.570335
H	2.036116	-0.264823	2.471883
H	3.594351	-0.151839	1.657696
H	2.502342	1.225583	1.648314
H	3.090115	-2.669602	0.028224
H	1.592597	-2.910310	0.909836
H	1.600317	-2.919690	-0.866526
Si	1.817307	-0.573431	0.008485

Table S1: ΔE values for the isodesmic reactions corrected with ZPVE.



Cation	ΔE (kcal mol^{-1})
^{1}**C$_6$H$_5$$^+$**	0.00
^{1}**19a$^+$**	3.97
^{3}**19a$^+$**	5.24
^{1}**19$^+$**	-8.15
^{3}**19$^+$**	0.92
^{1}**20$^+$**	-17.11
^{3}**20$^+$**	-2.41
^{1}**21a$^+$**	-2.15
^{3}**21a$^+$**	-12.22
^{1}**21$^+$**	-11.67
^{3}**21$^+$**	-15.70

(S10) Guizzardi, B.; Mella, M.; Fagnoni, M.; Freccero, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 6353-6363 and references cited therein.

(S11) Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, **2003**.