

## SUPPORTING INFORMATION

### Gold nanoparticles-catalyzed activation of 1,2-disilanes: Hydrolysis, silyl protection of alcohols and reduction of *tert*- benzylic alcohols

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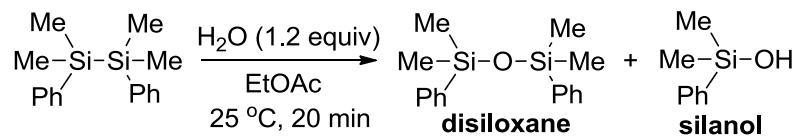
### 1,2-Disilanes

Hexamethyldisilane, 1,2-diphenyl-1,1,2,2-tetramethyldisilane, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, and hexaphenyldisilane are commercially available. Hexaethyldisilane, was synthesized in 63% isolated yield by the reaction between triethylsilyl chloride and Na metal (2 equiv) in the absence of solvent, at 120 °C for 12 h.<sup>1</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.97 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 8.4, 4.1.

### Typical procedure for the homogeneous Ph<sub>3</sub>PAuNTf<sub>2</sub>-catalyzed hydrolysis of PhMe<sub>2</sub>SiSiMe<sub>2</sub>Ph

To a tube containing 1,1,2,2-tetramethyl-1,2-diphenyldisilane (10 mg, 0.037 mmol) and H<sub>2</sub>O (1 μL, 0.055 mmol) in 0.3 mL of chloroform-D was added Ph<sub>3</sub>PAuNTf<sub>2</sub> (4 mg, 15 mol%). The reaction was stirred at room temperature and monitored by <sup>1</sup>H NMR. After 40 h the starting material had been completely consumed providing the corresponding 1,3-disiloxane as a single product. Under the same conditions, [(2-biphenyl)di-*tert*-butylphosphine]AuSbF<sub>6</sub> (15 mol%) provided traces of products.

### Screening of catalysts during the hydrolysis of Me<sub>2</sub>PhSiSiPhMe<sub>2</sub>



Entry	Catalyst	Conversion <sup>a</sup>	disiloxane/silanol <sup>a</sup>
1	Au/TiO <sub>2</sub> (1%)	99%	80/20 <sup>b</sup>
2	Au/Al <sub>2</sub> O <sub>3</sub> (1%)	72%	20/80 <sup>c</sup>
3	Au/ZnO (1%)	55%	40/60 <sup>d</sup>

<sup>a</sup> Based on GC analysis. <sup>b</sup> PhMe<sub>2</sub>SiH was also seen in 11% relative yield. <sup>c</sup> PhMe<sub>2</sub>SiH was also seen in 9% relative yield. <sup>d</sup> PhMe<sub>2</sub>SiH was also seen in 13% relative yield.

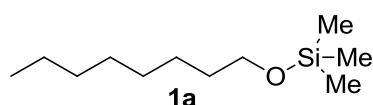
### General procedure for the Au/TiO<sub>2</sub>-catalyzed silylative protection of alcohols with hexamethyldisilane

To a vial containing 0.5 mmol of an alcohol, 0.3 mmol of hexamethyldisilane, and 1 mL of dry ethyl acetate under an inert atmosphere are added 100 mg of Au/TiO<sub>2</sub> (~1.0 mol% in Au). The gradual evolution of hydrogen gas is immediately obvious. In case of using non-dried solvent and open air conditions, 1-2 mmol of disilane should be used, to compensate its competing hydrolytic destruction. After a certain period of time (see Table 2) and at

room temperature, the reaction is complete (TLC, GC-MS). The slurry is filtered with the aid of ethyl acetate (3 mL) under a low pressure through a short pad of silica gel, and the filtrate is evaporated to afford the TMS-protected alcohols in high yields and purity.

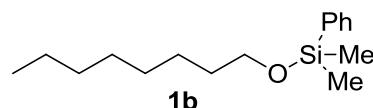
### Spectroscopic data of silylated products from the alcoholysis of 1,2-disilanes

#### Trimethyl(octyloxy)silane (**1a**)<sup>2</sup>



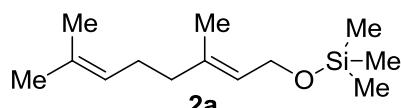
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 3.56 (t, *J* = 6.5 Hz, 2H), 1.52 (m, 2H), 1.27 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H), 0.11 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 62.8, 32.8, 31.8, 29.4, 29.3, 25.8, 22.7, 14.1, -0.5.

#### Dimethyl(octyloxy)(phenyl)silane (**1b**)<sup>3</sup>



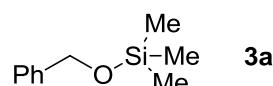
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.55-7.62 (m, 2H), 7.34-7.43 (m, 3H), 3.59 (t, *J*=6.5 Hz, 2H), 1.53 (m, 2H), 1.26 (m, 10H), 0.88 (t, *J*=6.5 Hz, 3H), 0.38 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 138.1, 133.5, 129.5, 127.8, 63.2, 32.6, 31.8, 29.3, 25.8, 22.6, 14.1, -1.8.

#### (E)-(3,7-Dimethylocta-2,6-dienyloxy)trimethylsilane (**2a**)<sup>4</sup>



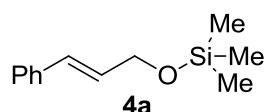
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.32 (t, *J* = 6.5 Hz, 1H), 5.09 (t, *J* = 6.5 Hz, 1H), 4.15 (d, *J* = 6.5 Hz, 2H), 2.09 (m, 2H), 2.03 (m, 2H), 1.67 (br s, 3H), 1.64 (br s, 3H), 1.60 (br s, 3H), 0.13 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 137.6, 131.5, 124.1, 123.8, 59.5, 39.6, 26.3, 25.6, 17.6, 16.2, -0.3.

#### Benzyoxytrimethylsilane (**3a**)<sup>4</sup>



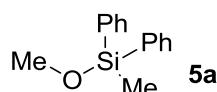
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.24-7.38 (m, 5H), 4.71 (s, 2H), 0.16 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 141.0, 128.3, 127.1, 126.5, 64.6, -0.4.

#### (Cinnamyoxy)trimethylsilane (**4a**)<sup>5</sup>



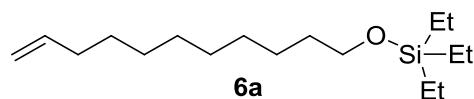
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.19-7.42 (m, 5H), 6.60 (d,  $J = 16.0$  Hz, 1H), 6.31 (dt,  $J_1 = 16.0$  Hz,  $J_2 = 5.5$  Hz, 1H), 4.33 (dd,  $J_1 = 5.5$  Hz,  $J_2 = 1.5$  Hz, 2H), 0.19 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 137.0, 130.1, 128.8, 128.5, 127.4, 126.4, 63.4, -0.3.

**Methoxy(methyl)diphenylsilane (5a)<sup>6</sup>**



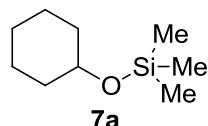
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.62-7.69 (m, 4H), 7.39-7.50 (m, 6H), 3.60 (s, 3H), 0.70 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 135.6, 134.3, 129.8, 127.9, 51.2, -3.4.

**Triethyl(undec-10-enyloxy)silane (6a)<sup>7</sup>**



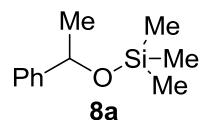
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 5.74-5.88 (m, 1H), 4.99 (dd,  $J_1 = 17.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 4.93 (dd,  $J_1 = 10.5$  Hz,  $J_2 = 2.0$  Hz, 1H), 3.59 (t,  $J = 6.5$  Hz, 2H), 2.04 (m, 2H), 1.46-1.57 (m, 2H), 1.24-1.42 (m, 12H), 0.96 (t,  $J = 8.0$  Hz, 9H), 0.60 (q,  $J = 8.0$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 139.2, 114.1, 63.0, 33.8, 32.9, 29.6, 29.4, 29.1, 28.9, 25.8, 6.8, 4.4.

**(Cyclohexyloxy)trimethylsilane (7a)<sup>8</sup>**



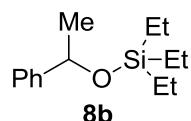
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 3.53 (m, 1H), 1.74 (m, 4H), 1.52 (m, 1H), 1.22 (m, 5H), 0.10 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 71.1, 36.1, 25.5, 24.5, 0.2.

**Trimethyl(1-phenylethoxy)silane (8a)<sup>9</sup>**



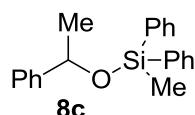
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.20-7.38 (m, 4H), 4.87 (q,  $J = 6.5$  Hz, 1H), 1.45 (d,  $J = 6.5$  Hz, 3H), 0.09 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 146.4, 128.1, 126.8, 125.3, 70.6, 26.8, 0.1.

**Triethyl(1-phenylethoxy)silane (8b)<sup>10</sup>**



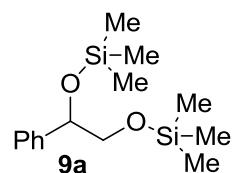
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.19-7.38 (m, 5H), 4.86 (q, *J* = 6.5 Hz, 1H), 1.43 (d, *J* = 6.5 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.57 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 146.9, 128.1, 126.7, 125.2, 70.5, 27.2, 6.8, 4.8.

**Methyldiphenyl(1-phenylethoxy)silane (8c)<sup>11</sup>**



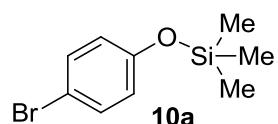
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.22-7.65 (m, 15H), 4.97 (q, *J* = 6.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.58 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 146.1, 136.5, 136.4, 134.4, 134.3, 129.7, 128.1, 127.8, 127.7, 126.9, 125.4, 71.5, 26.9, -2.4.

**2,2,7,7-Tetramethyl-4-phenyl-3,6-dioxa-2,7-disilaoctane (9a)<sup>5</sup>**



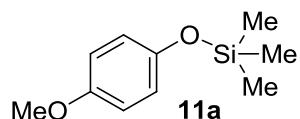
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.21-7.39 (m, 5H), 4.71 (dd, *J*<sub>1</sub> = 6.5 Hz, *J*<sub>2</sub> = 5.0 Hz, 1H), 3.63 (dd, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 6.5 Hz, 1H), 3.59 (dd, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 5.0 Hz, 1H), 0.09 (s, 9H), 0.06 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 142.2, 128.0, 127.3, 126.3, 75.8, 69.1, 0.2, -0.5.

**(4-Bromobenzyloxy)trimethylsilane (10a)<sup>5</sup>**



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.33 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 0.26 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 154.4, 132.3, 121.9, 113.8, 0.1.

**(4-Methoxybenzyloxy)trimethylsilane (11a)<sup>5</sup>**

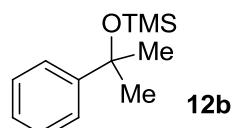


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 6.78 (br s, 4H), 3.76 (s, 3H), 0.24 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 154.2, 148.8, 120.7, 114.5, 55.6, 0.1.

**Spectroscopic data of products from the reaction of hexamethyldisilane with tertiary alcohols**

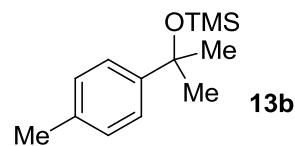
Among the products of Table 2, cumene (**12a**) *p*-cymene (**13a**), and triphenylmethane (**15a**) are commercially available substances.

**Trimethyl(2-phenylpropan-2-yloxy)silane (**12b**)<sup>5</sup>**



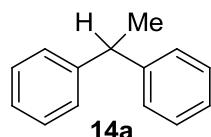
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.45 (d, *J* = 7.5 Hz, 2H), 7.18-7.33 (m, 3H), 1.60 (s, 6H), 0.10 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 150.1, 127.9, 126.3, 124.7, 75.2, 32.5, 2.4.

**Trimethyl(2-*p*-tolylpropan-2-yloxy)silane (**13b**)**



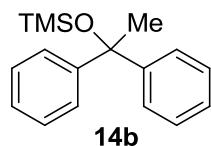
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.38 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.62 (s, 6H), 0.14 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 147.1, 135.1, 128.5, 124.6, 75.0, 32.5, 20.9, 2.4; MS (EI): 222 (M<sup>+</sup>, 1%), 207 (M<sup>+</sup>-Me, 31%), 132 (22%), 91 (34%), 75 (100%).

**Ethane-1,1-diyldibenzene (**14a**)**



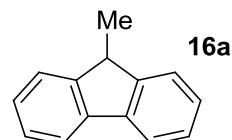
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.20-7.34 (m, 10H), 4.18 (q, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 146.3, 128.3, 127.6, 126.0, 44.8, 21.8.

**(1,1-Diphenylethoxy)trimethylsilane (**14b**)<sup>4</sup>**



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.40 (d, *J* = 7.5 Hz, 4H), 7.17-7.32 (m, 6H), 1.97 (s, 3H), 0.01 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 149.3, 127.8, 126.5, 126.1, 78.4, 30.6, 2.0.

**9-Methyl-9*H*-fluorene (**16a**)**



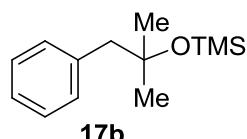
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.69 (d, *J* = 7.0 Hz, 2H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.32-7.43 (m, 4H), 3.97 (q, *J* = 7.5 Hz, 1H), 1.55 (d, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 148.9, 140.5, 126.9, 124.0, 119.8, 42.4, 18.2.

**Trimethyl(9-methyl-9*H*-fluoren-9-yloxy)silane (16b)**



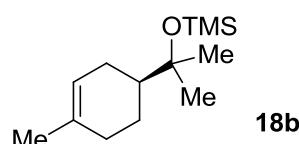
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.63 (d, *J* = 7.0 Hz, 2H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.29-7.36 (m, 4H), 1.72 (s, 3H), -0.34 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 150.1, 138.9, 128.6, 127.6, 123.9, 119.9, 81.2, 29.3, 1.3; MS (EI): 268 (M<sup>+</sup>, 4%), 253 (M<sup>+</sup>-Me, 27%), 178 (56%), 152 (17%), 75 (100%).

**Trimethyl(2-methyl-1-phenylpropan-2-yloxy)silane (17b)<sup>12</sup>**



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.15-7.35 (m, 5H), 2.73 (s, 2H), 1.22 (s, 6H), 0.07 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 138.8, 130.7, 127.5, 125.9, 74.1, 51.1, 29.7, 2.5.

**(S)-Trimethyl(2-(4-methylcyclohex-3-enyl)propan-2-yloxy)silane (18b)<sup>2</sup>**



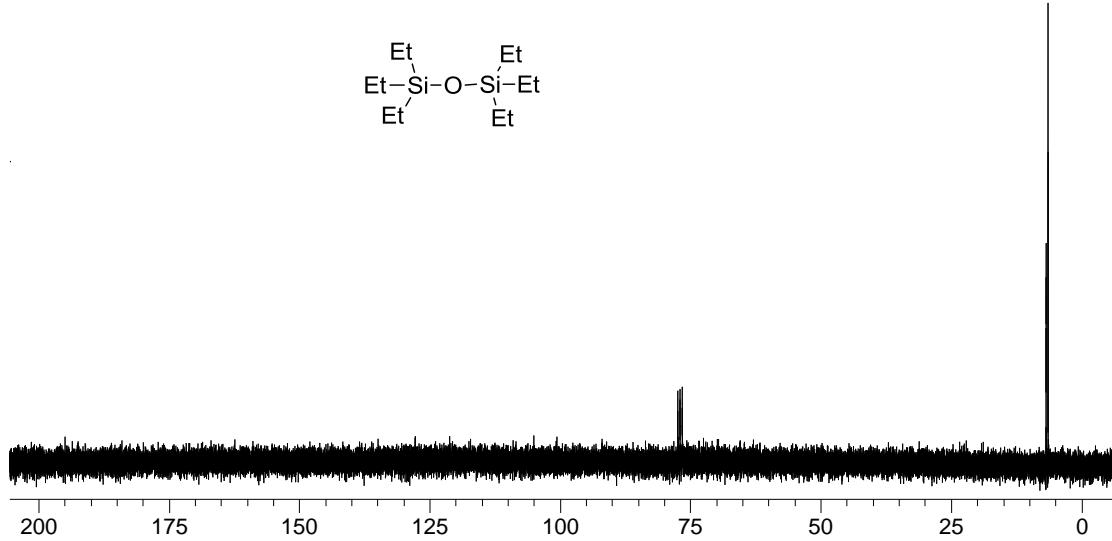
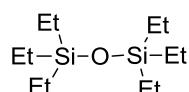
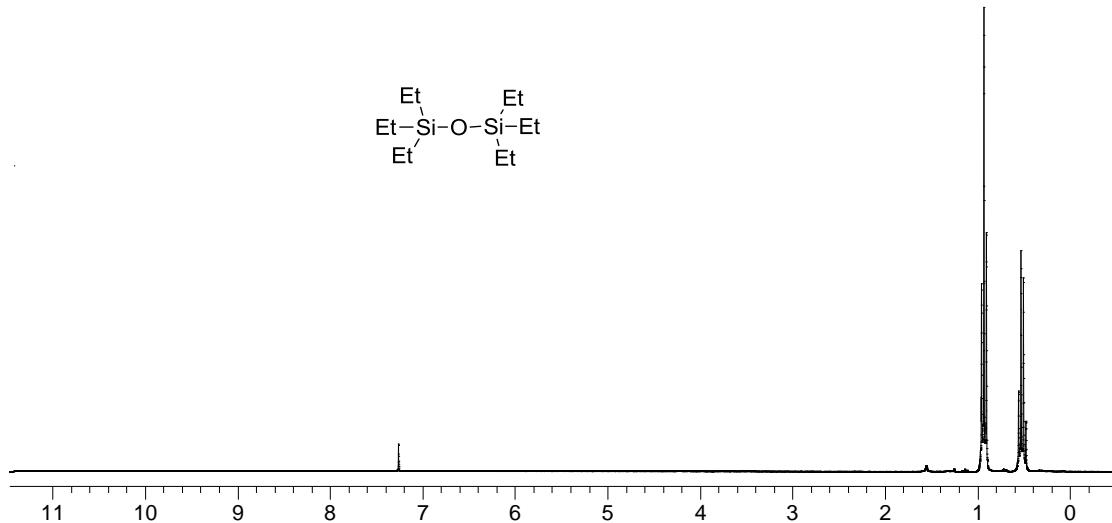
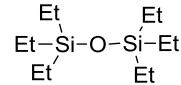
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.38 (br s, 1H), 1.97 (m, 2H), 1.72-2.10 (m, 5H), 1.65 (br s, 3H), 1.45 (m, 1H), 1.18-1.24 (m, 1H), 1.18 (s, 3H), 1.16 (s, 3H), 0.09 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 133.9, 121.1, 75.7, 45.8, 31.2, 27.7, 27.0, 26.9, 24.0, 23.4, 2.6.

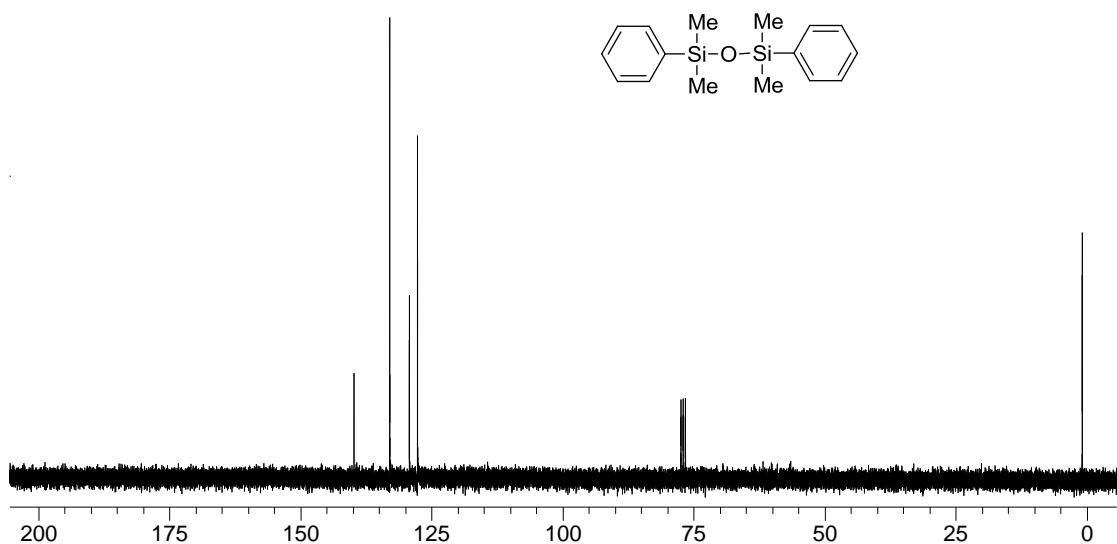
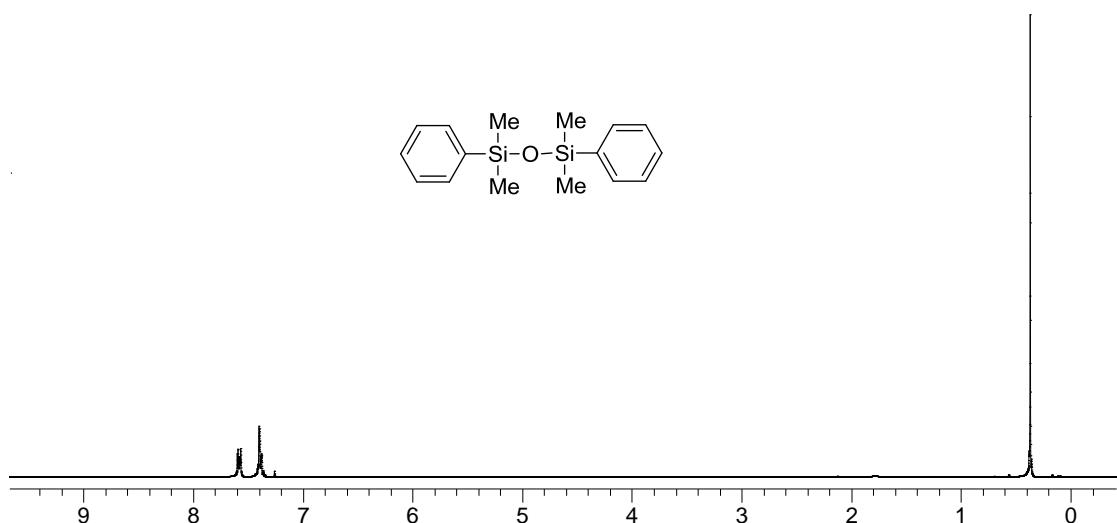
## References

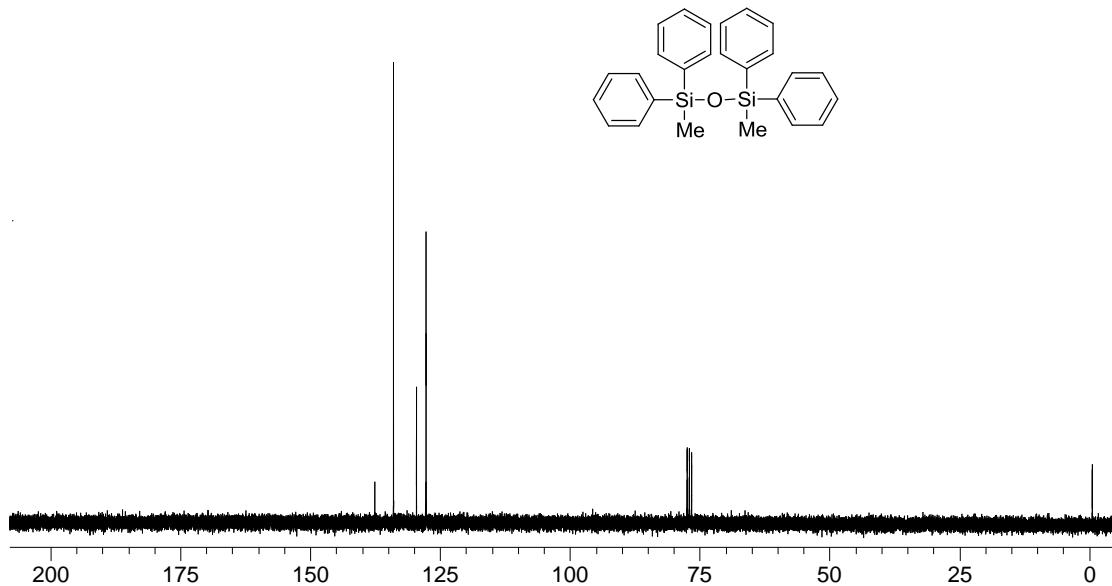
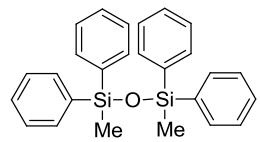
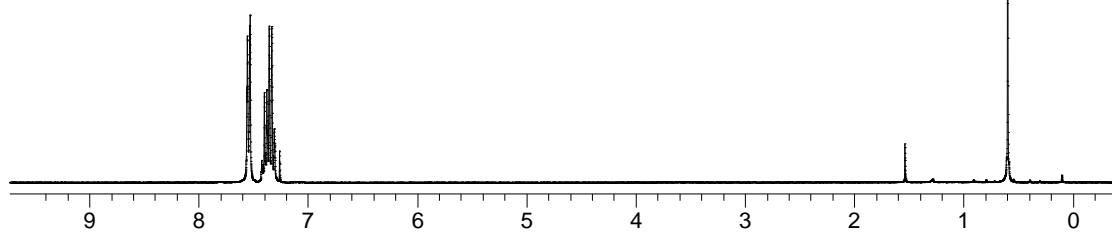
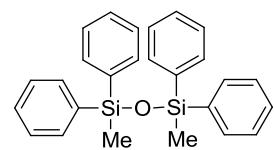
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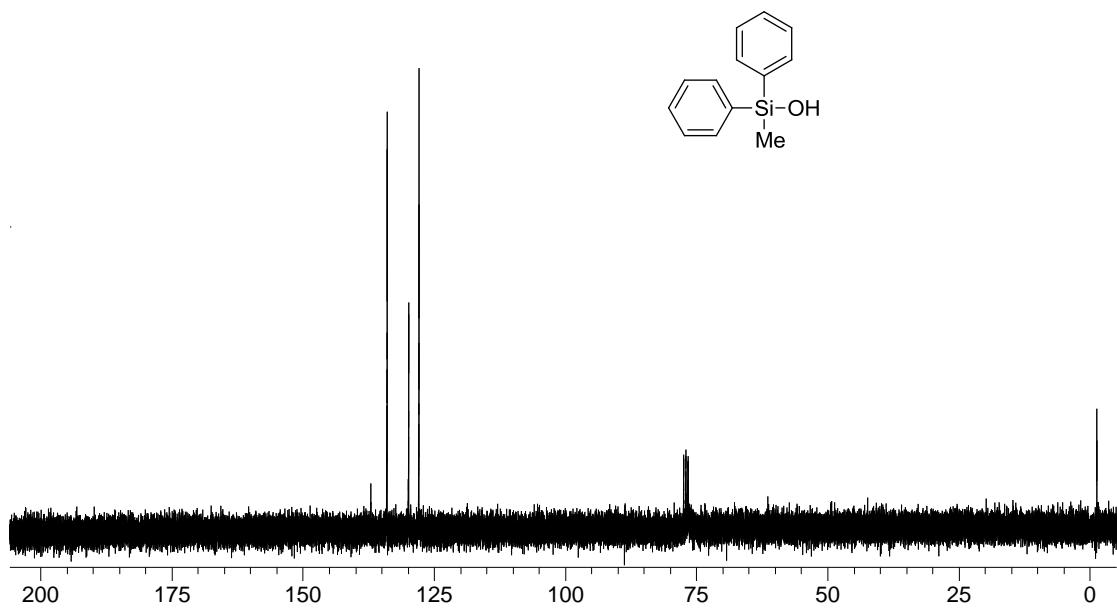
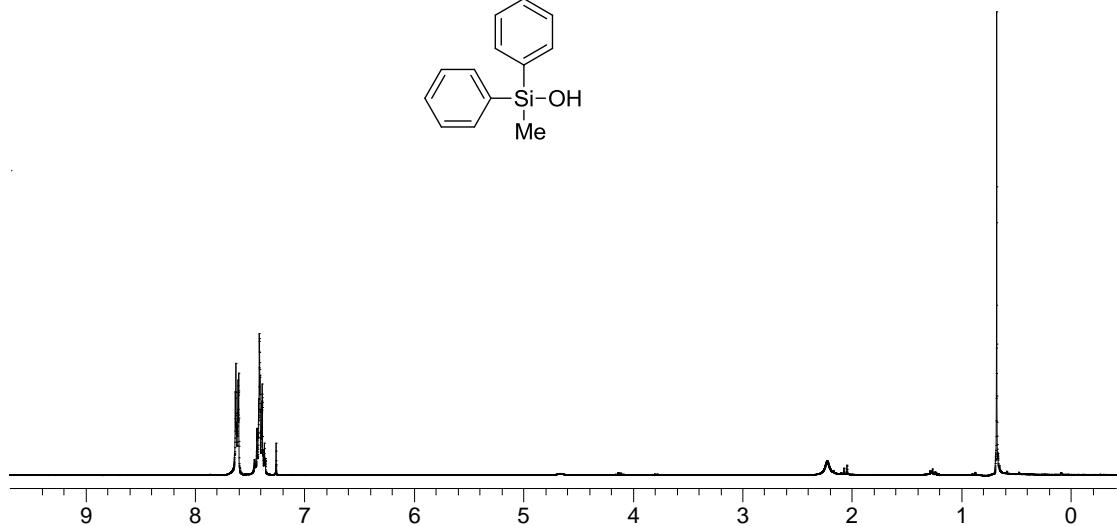
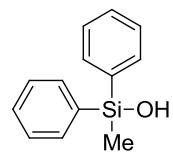
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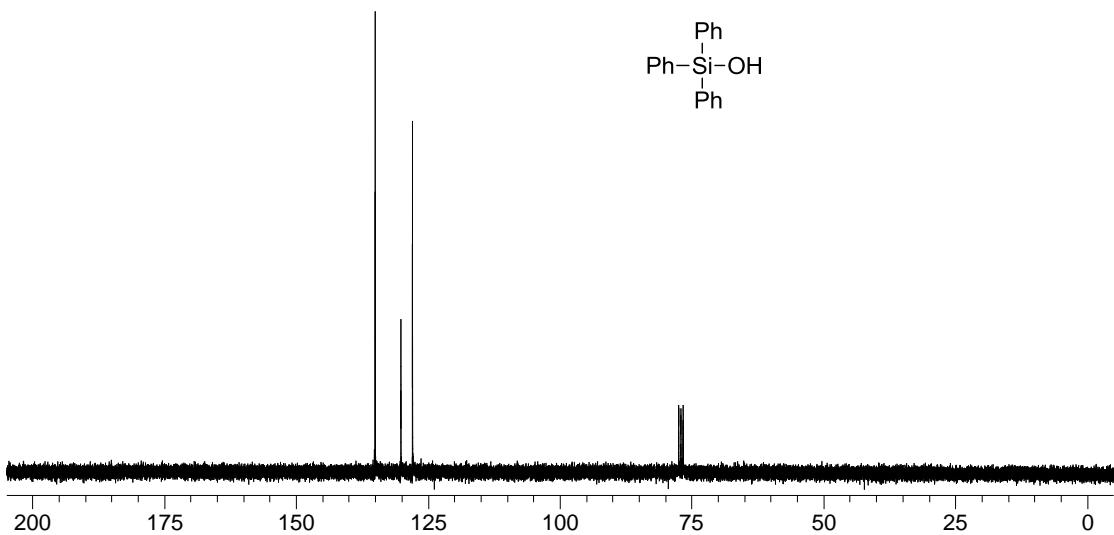
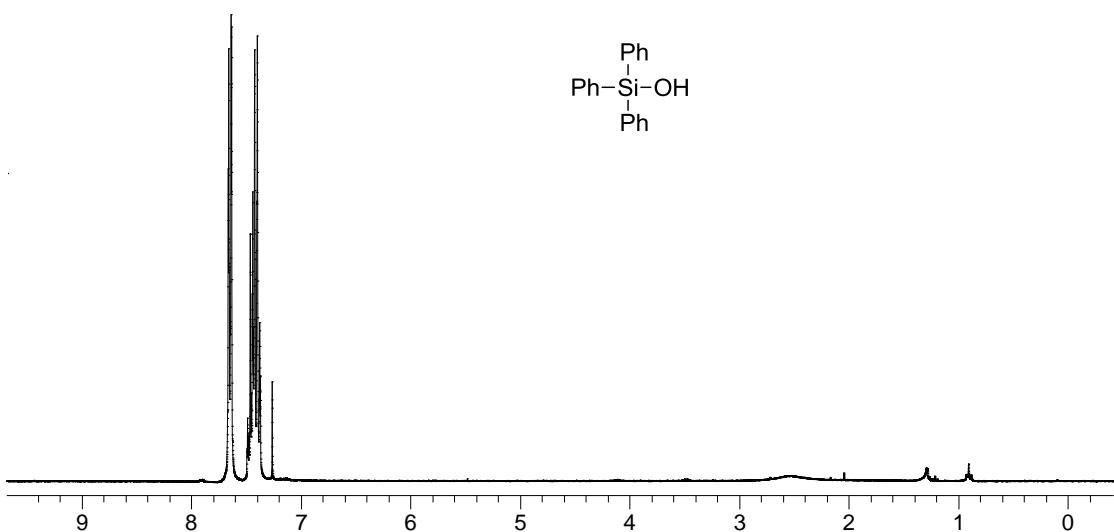
**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra**

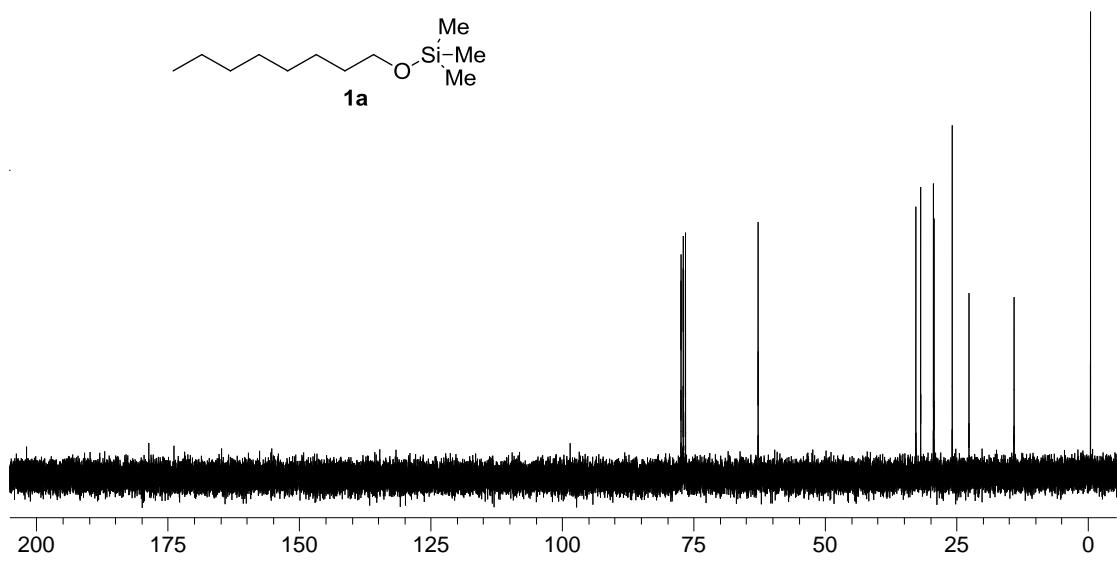
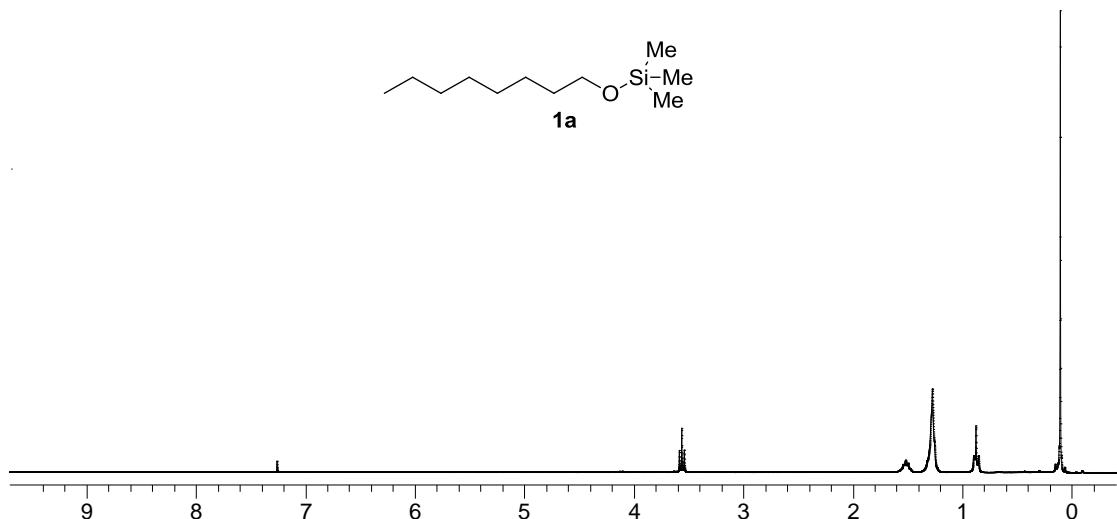


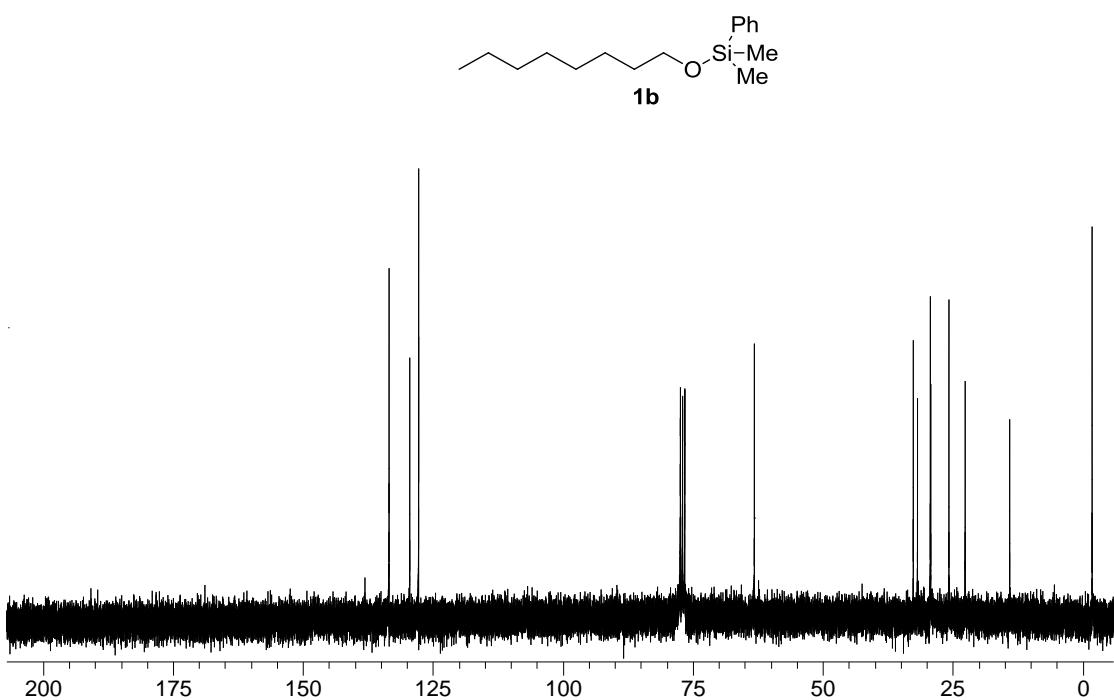
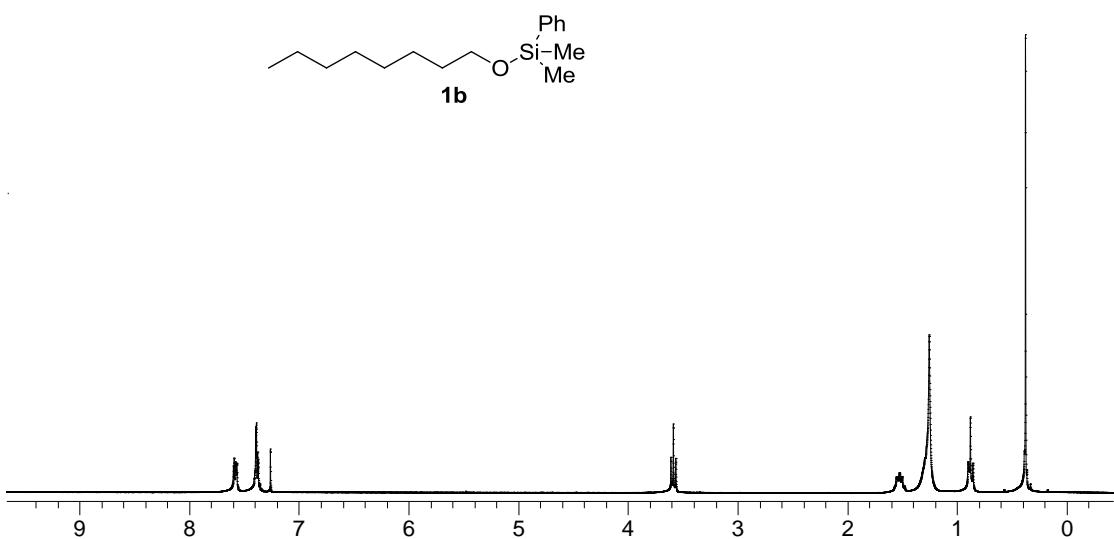


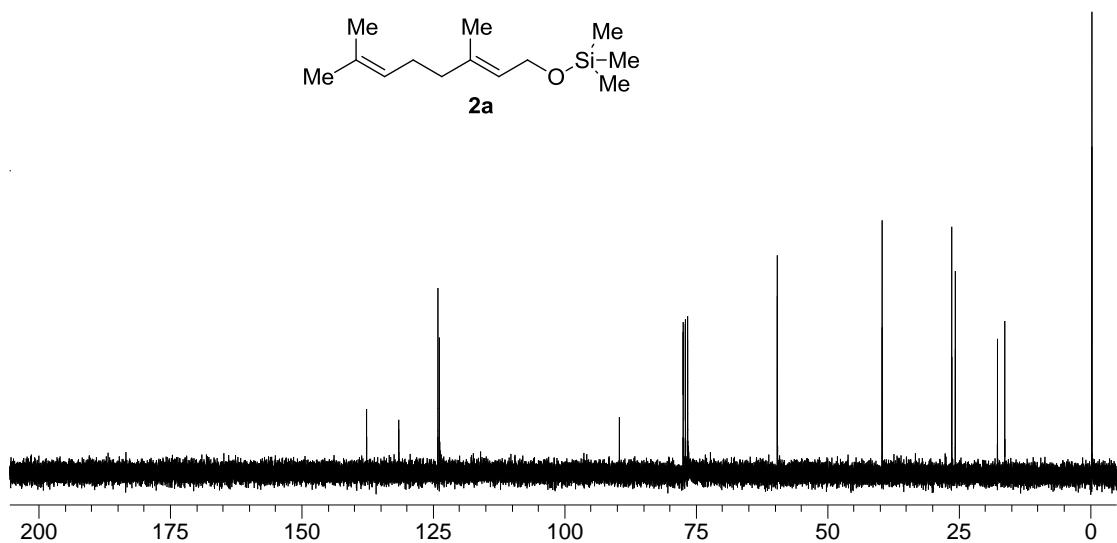
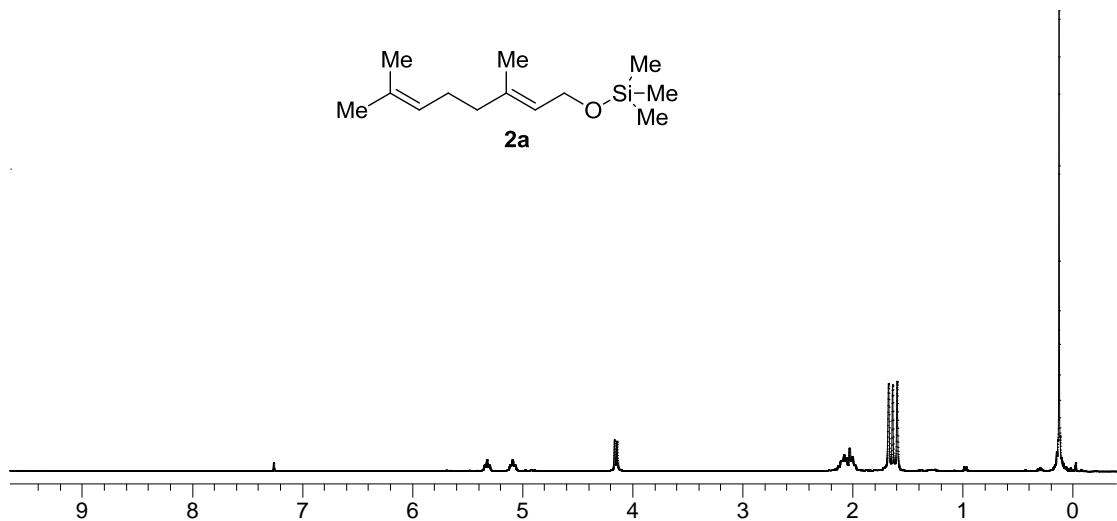


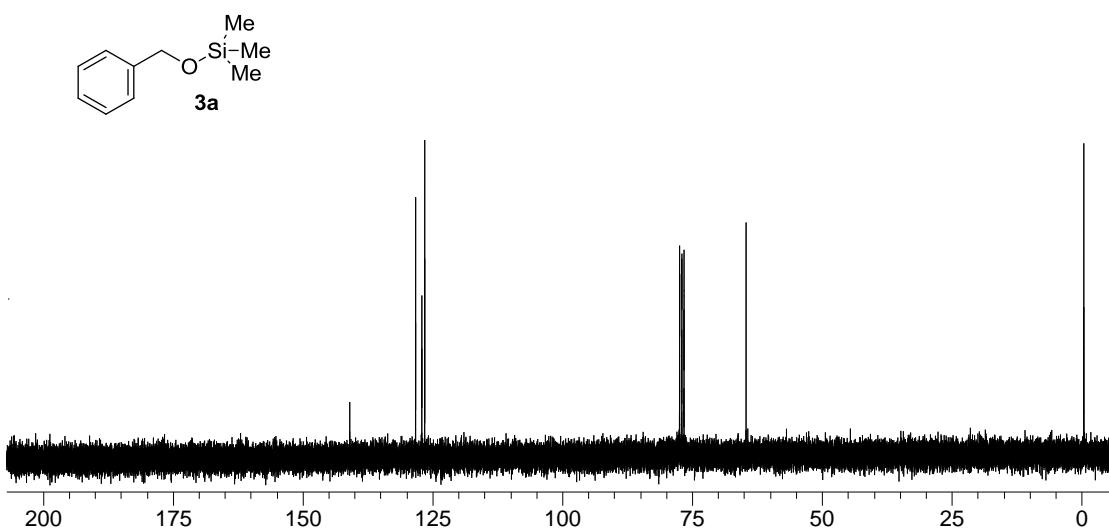
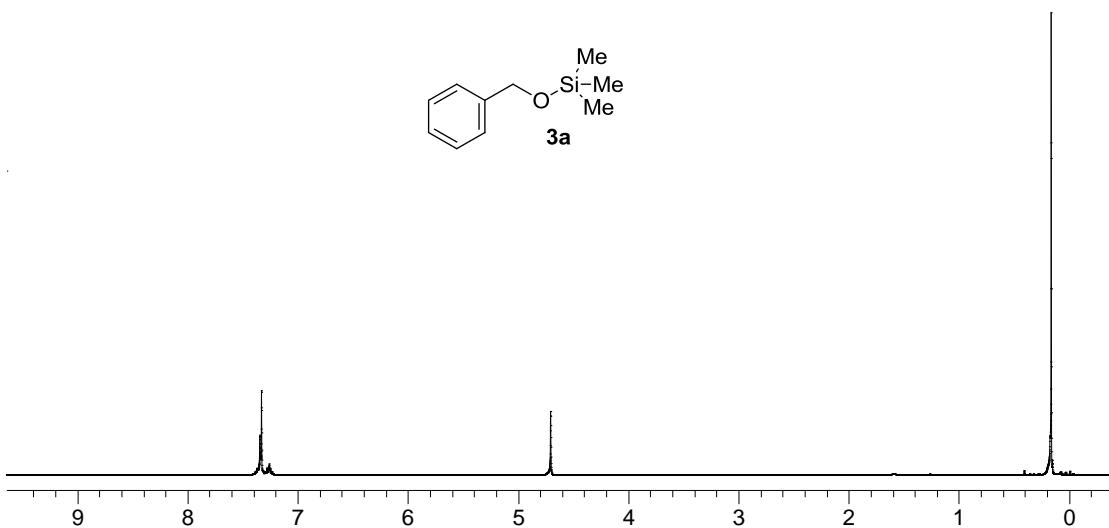


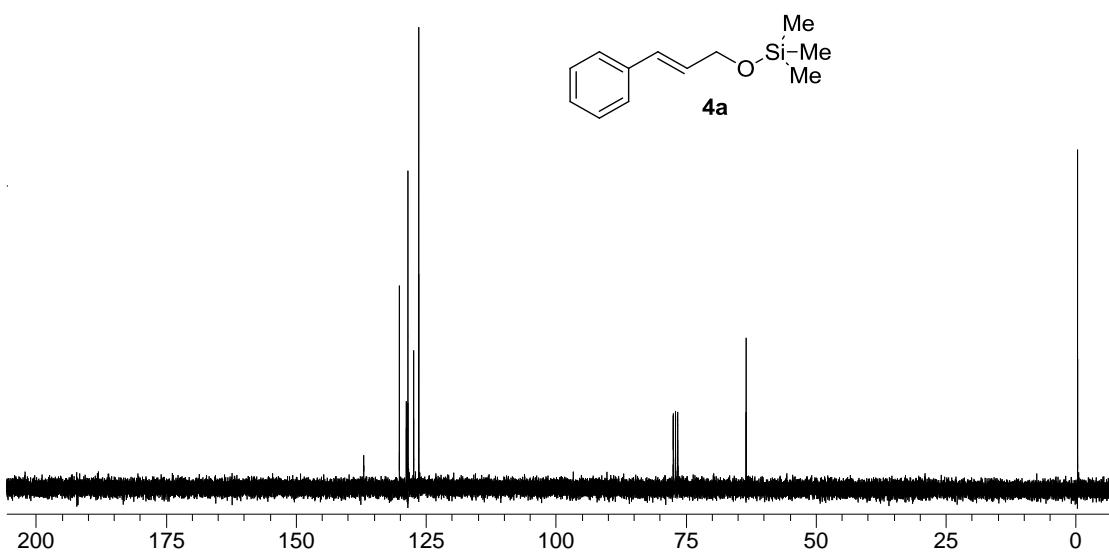
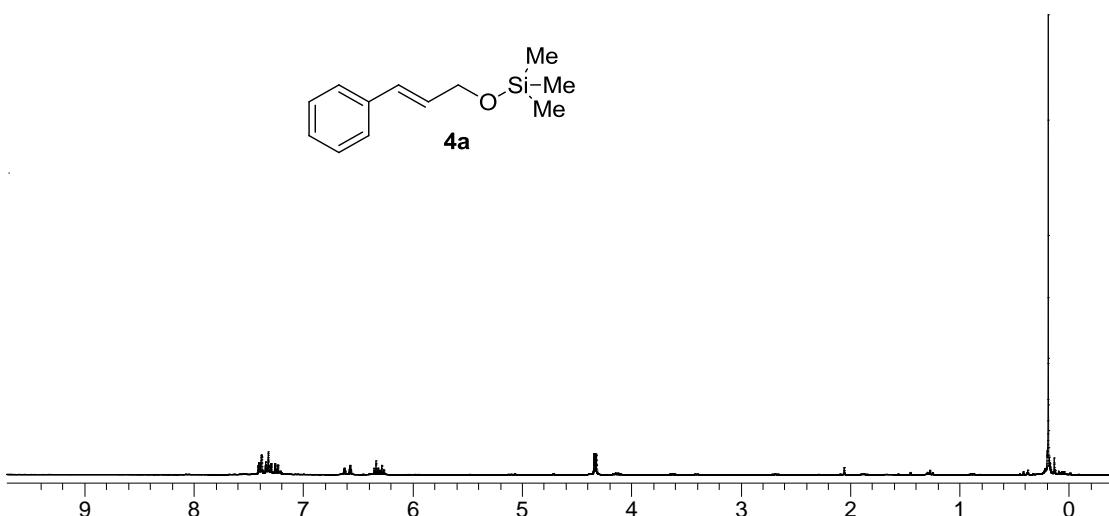


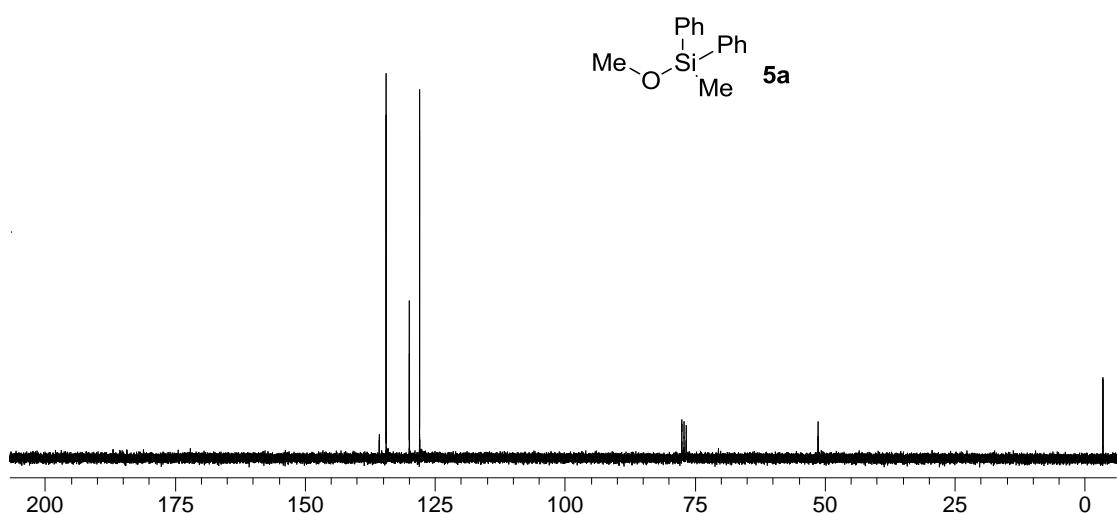
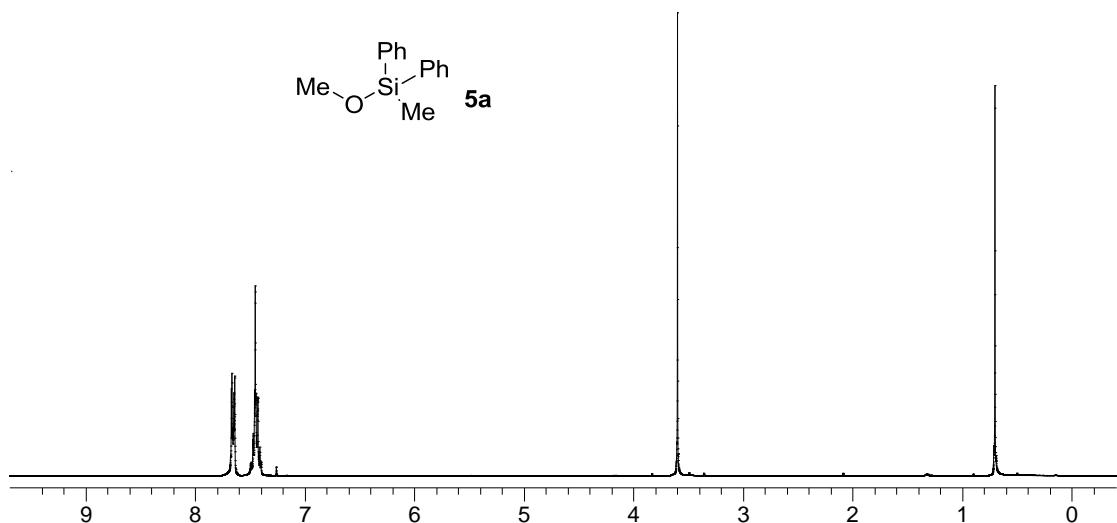


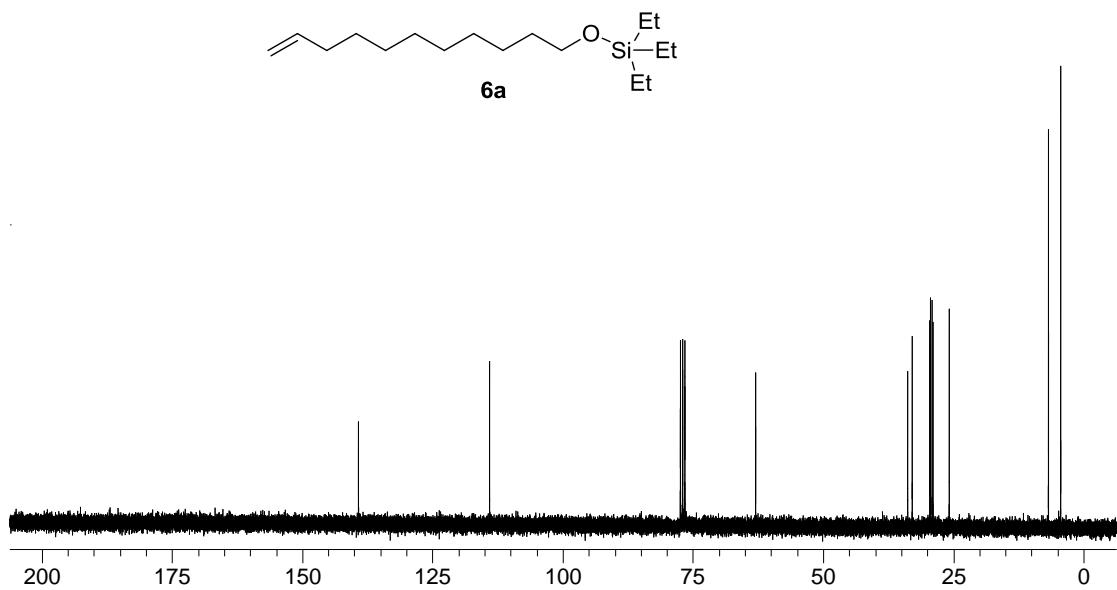
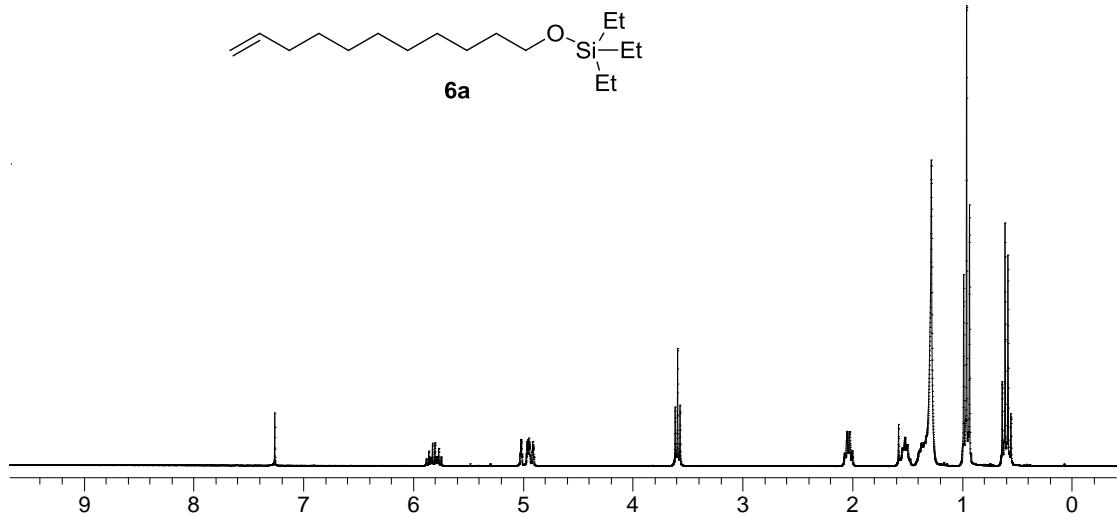


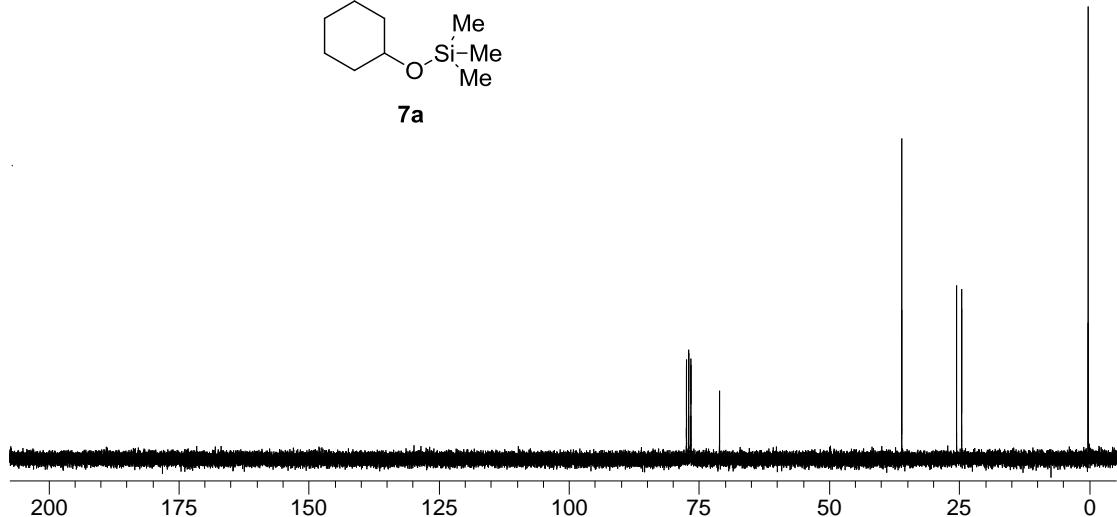
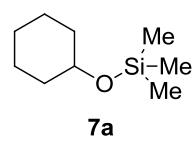
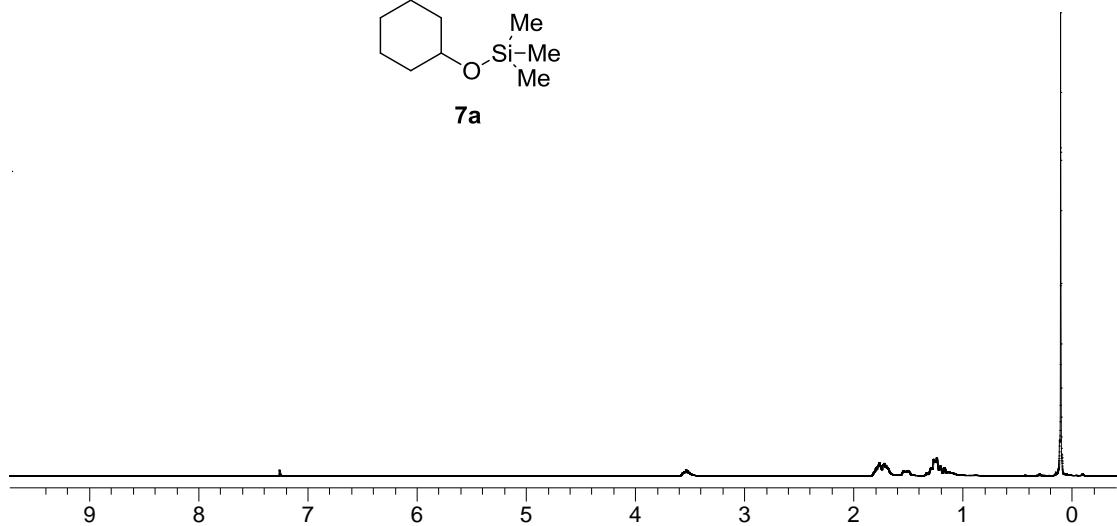
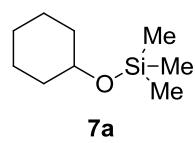


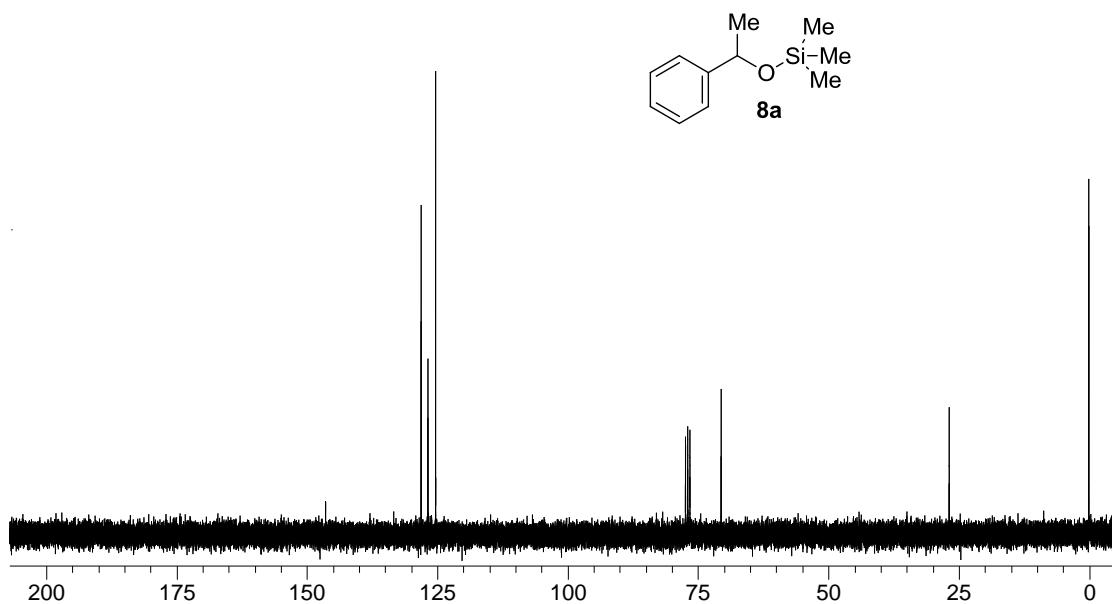
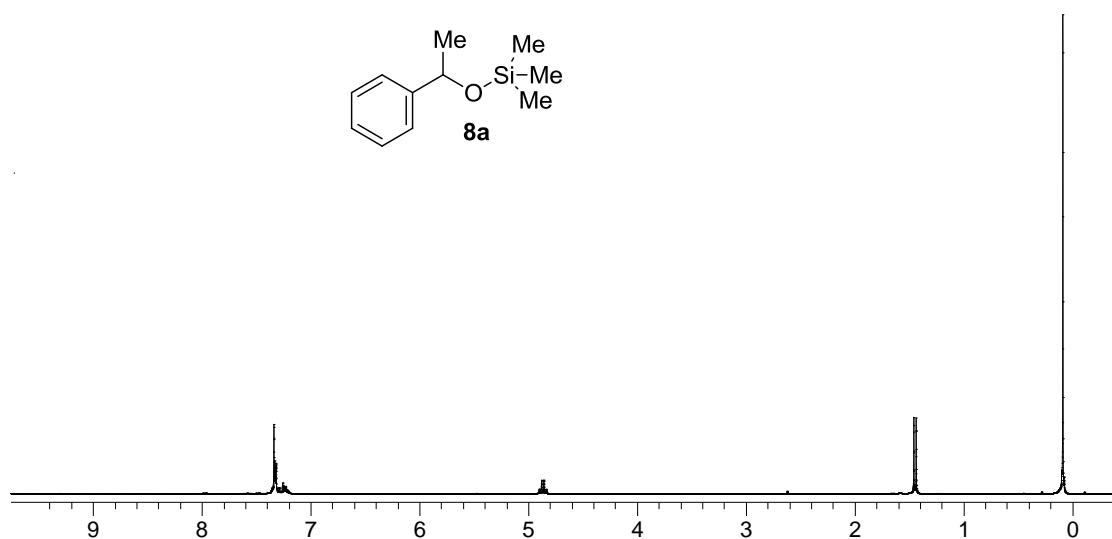


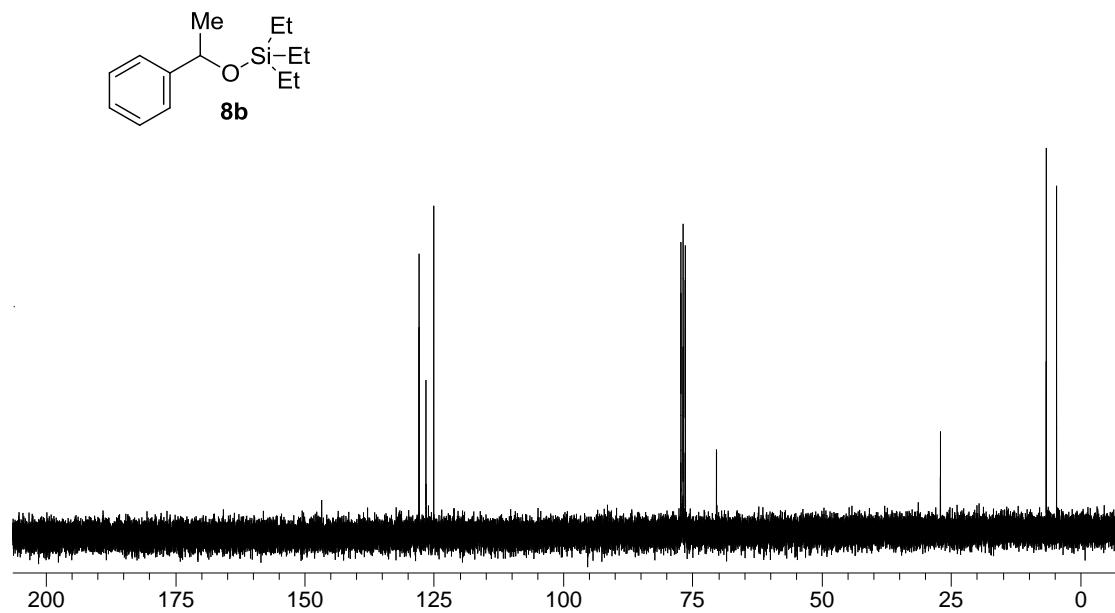
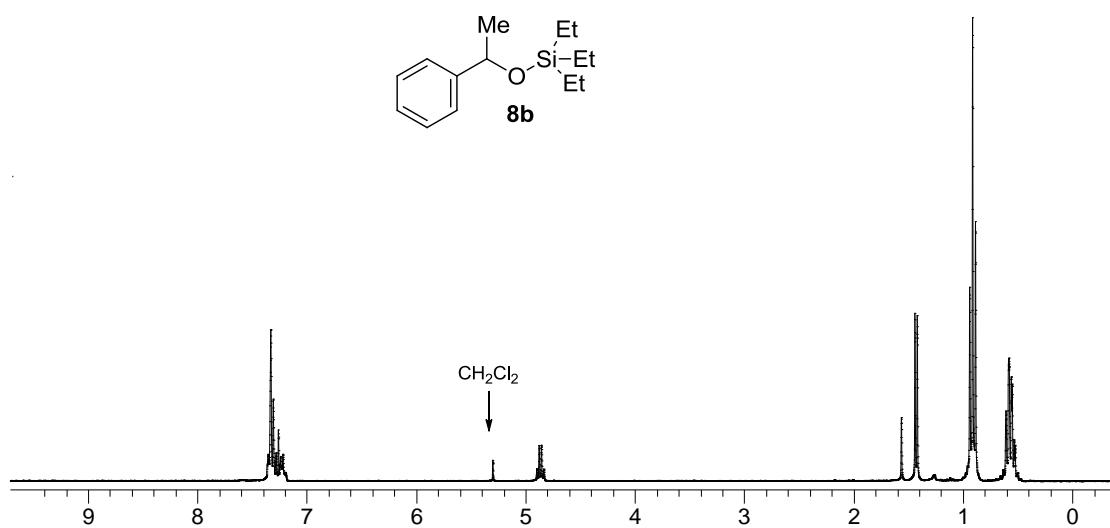


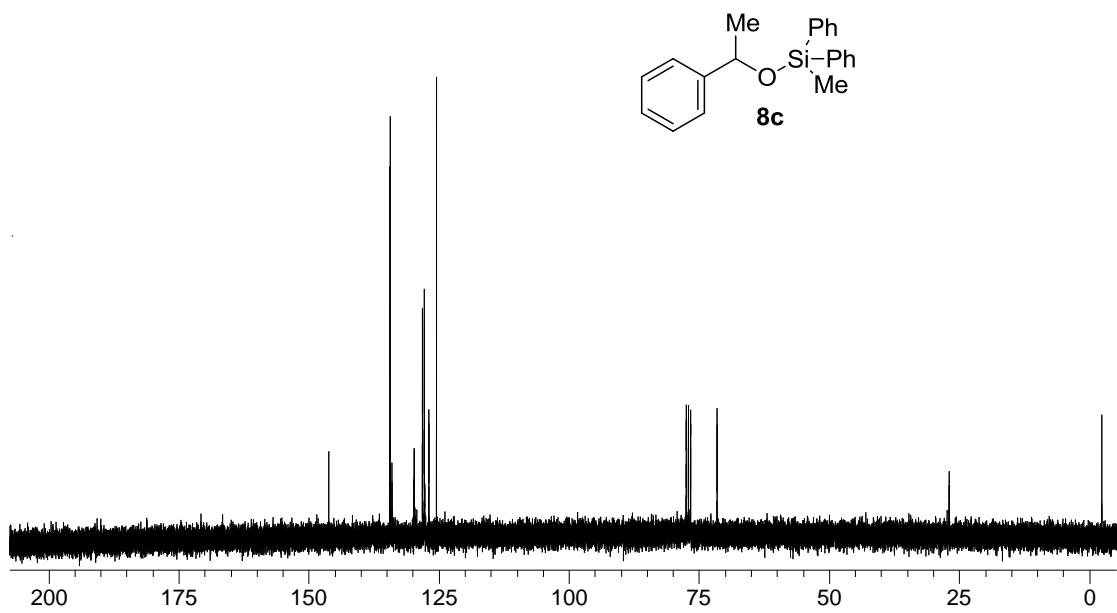
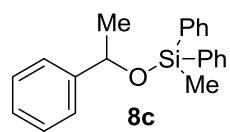
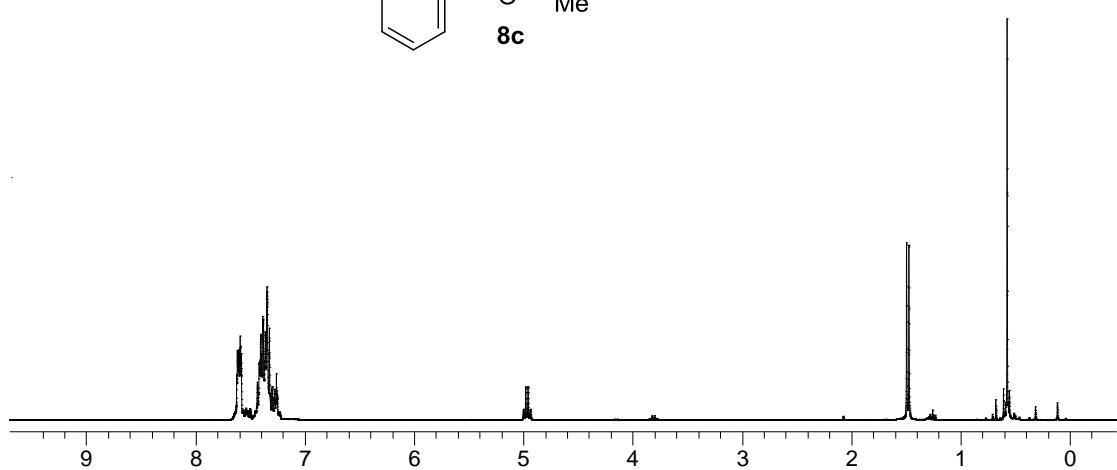
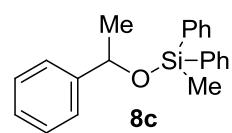


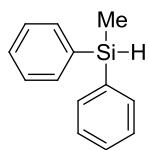




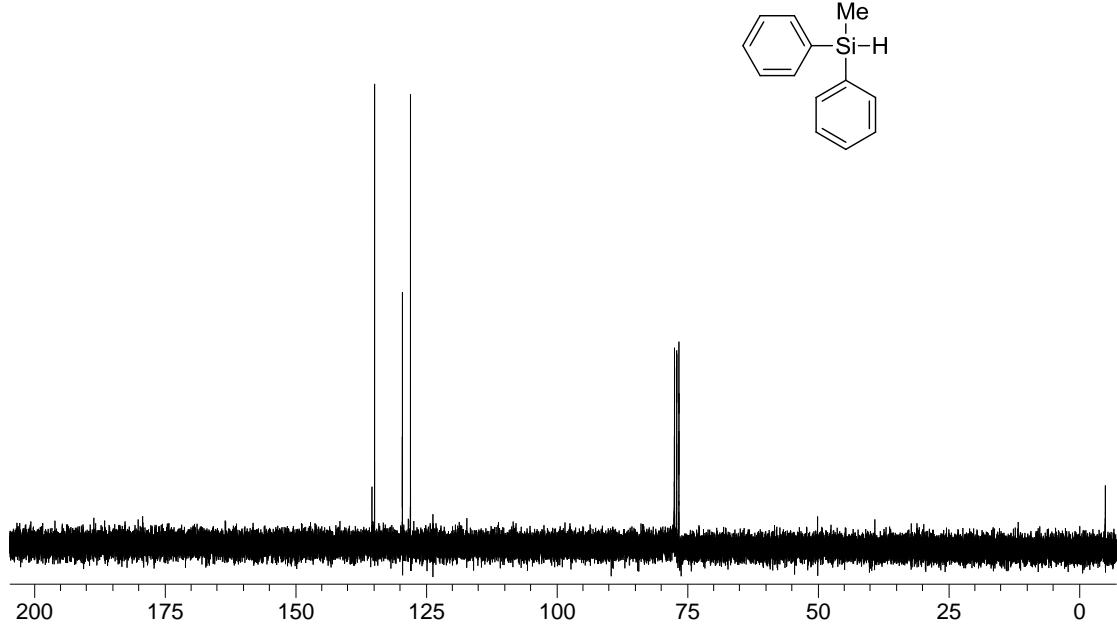
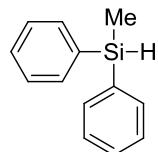
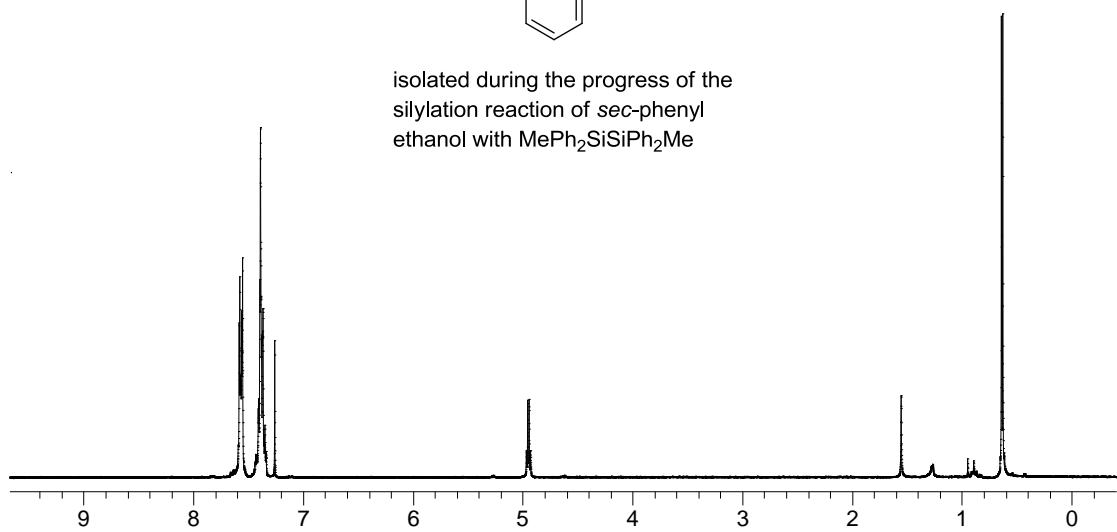


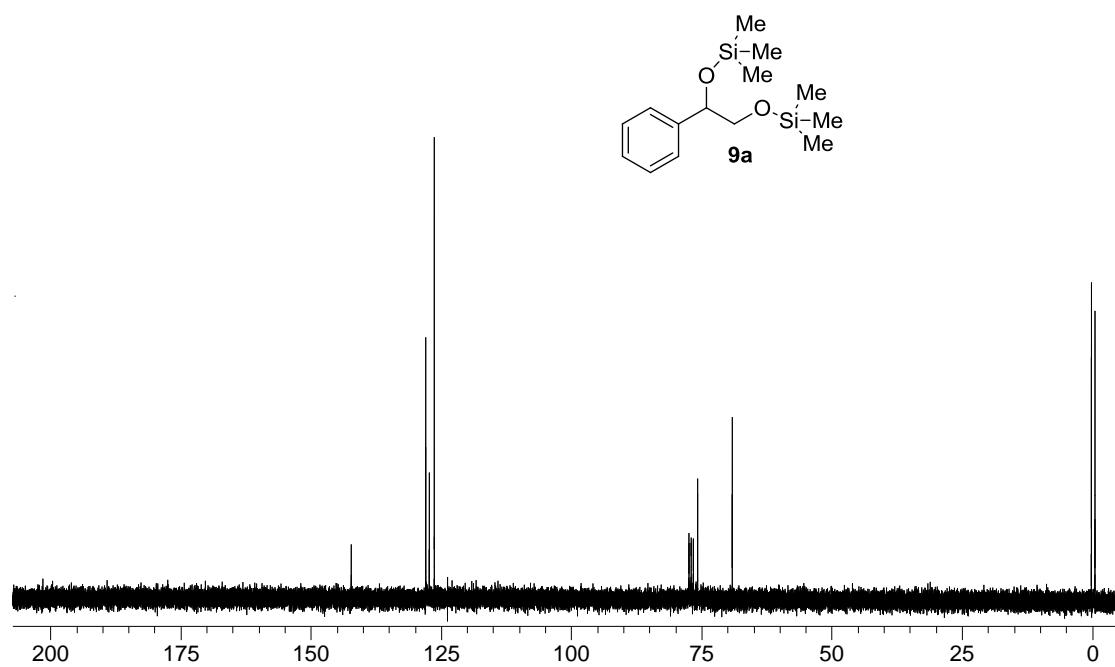
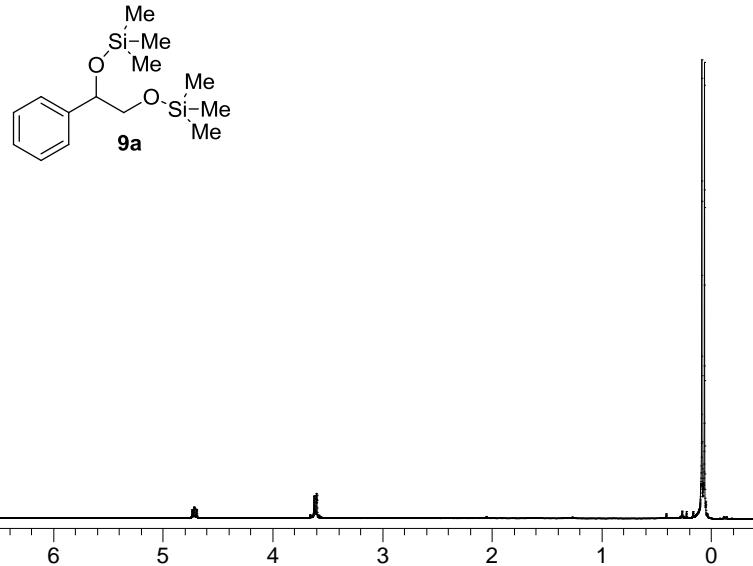


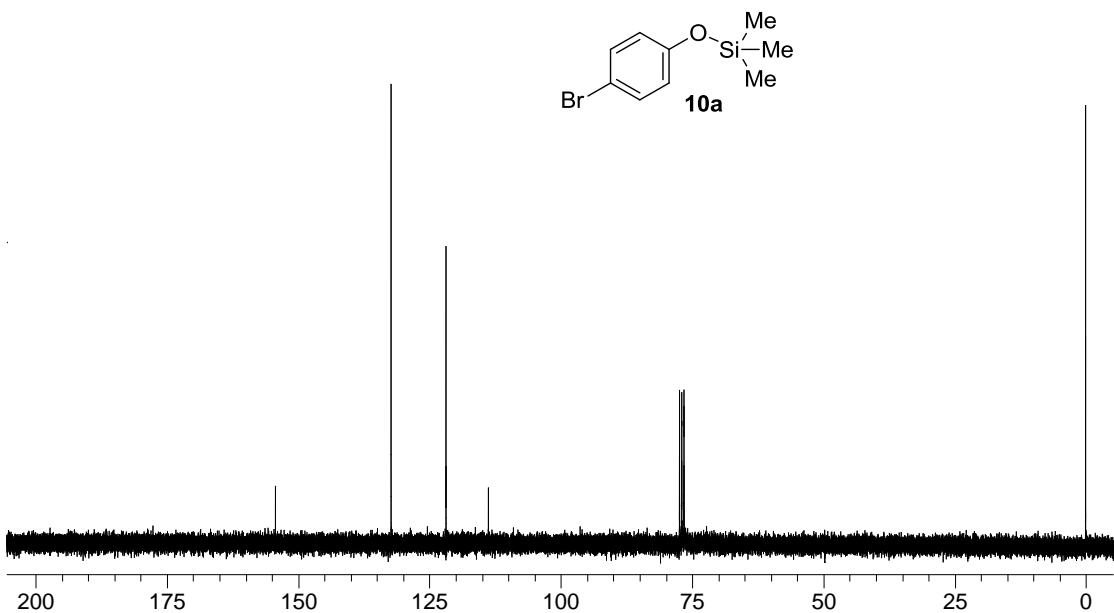
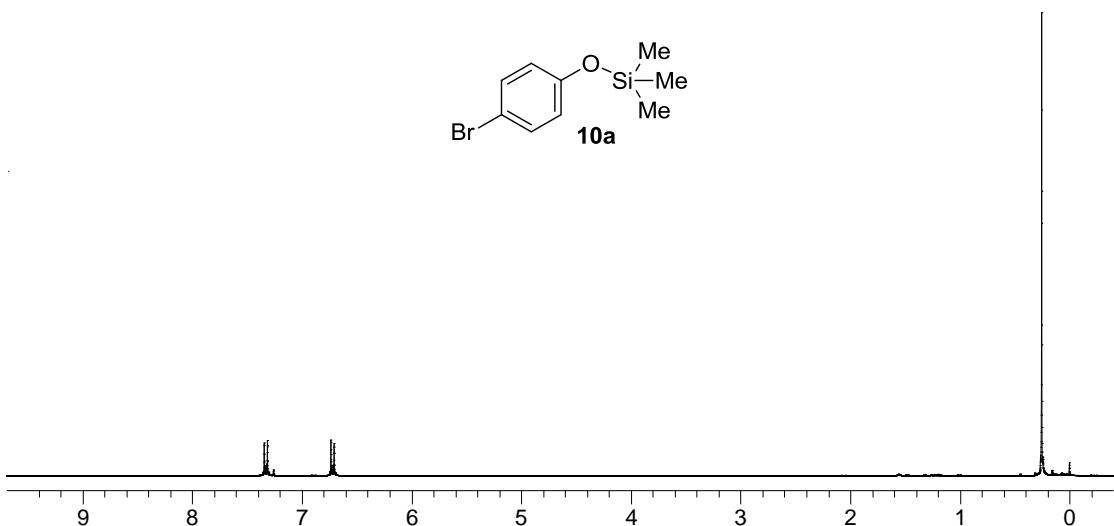


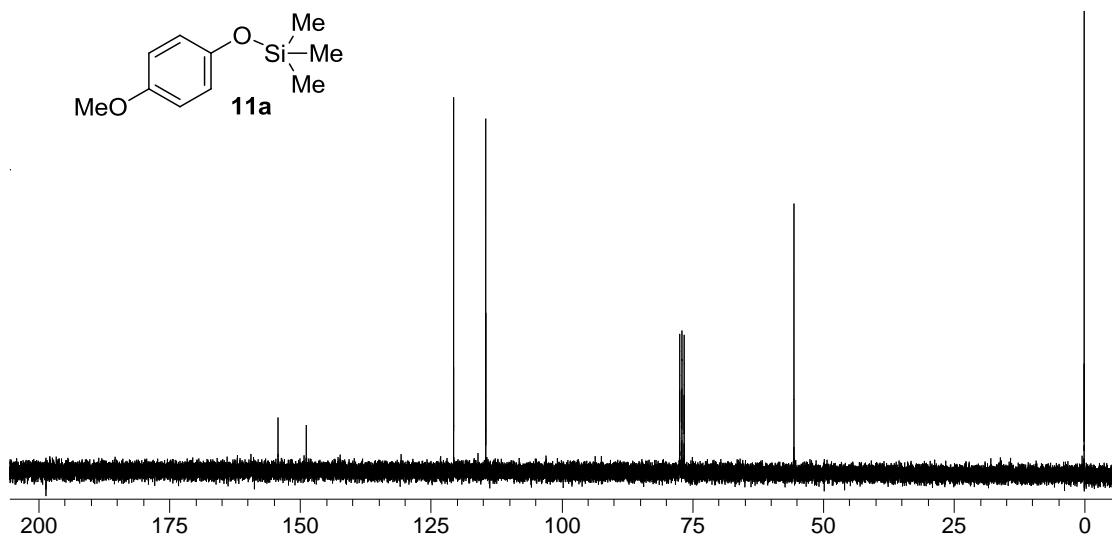
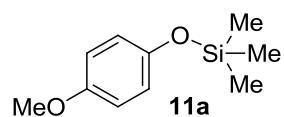
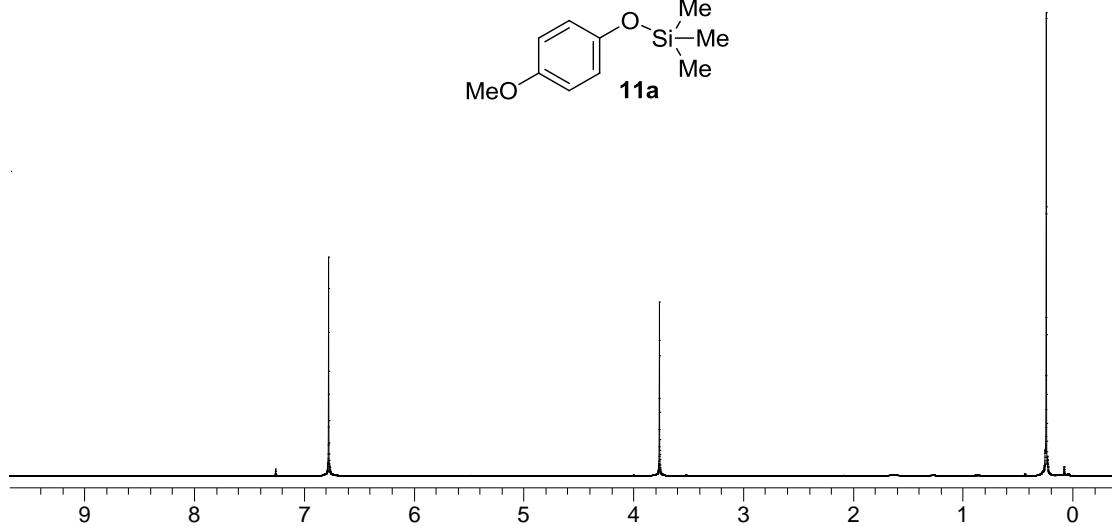
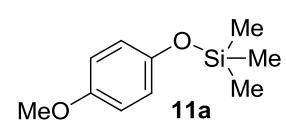


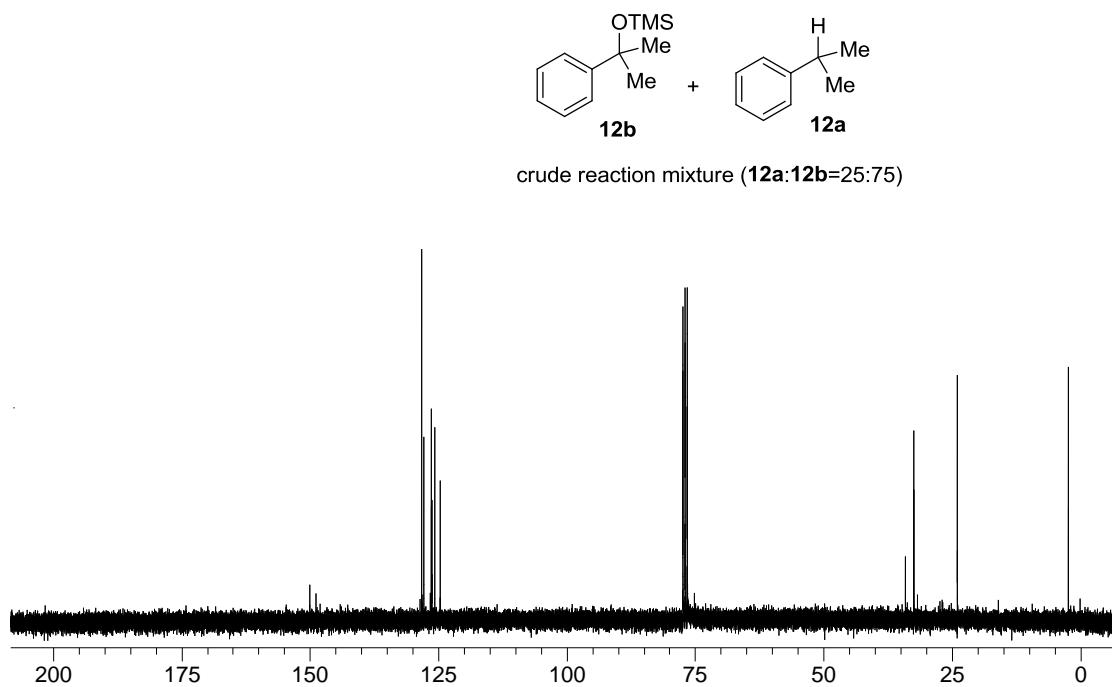
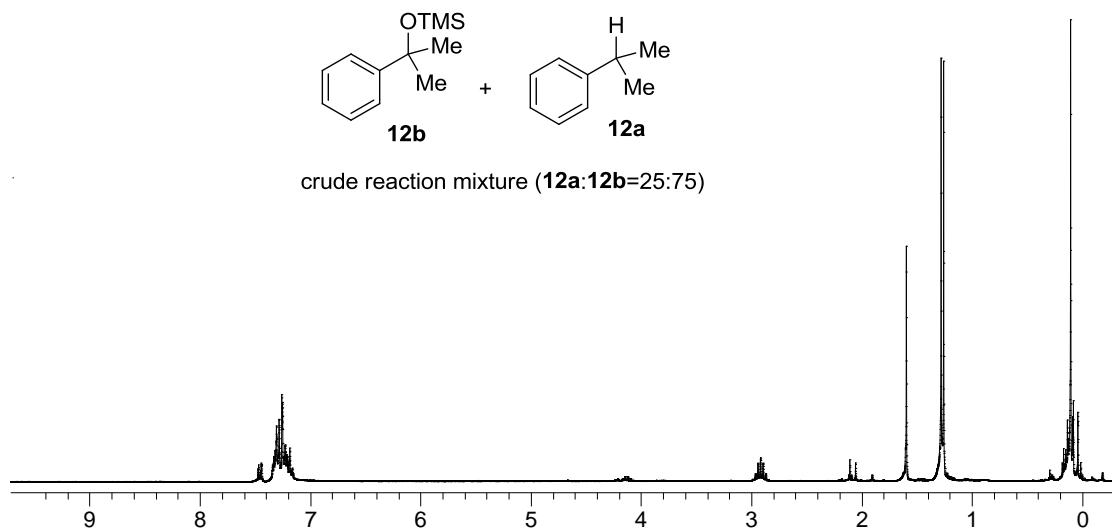
isolated during the progress of the silylation reaction of sec-phenyl ethanol with MePh<sub>2</sub>SiSiPh<sub>2</sub>Me

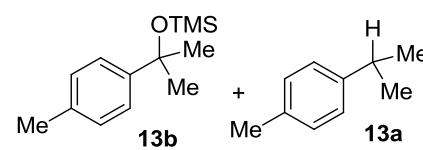




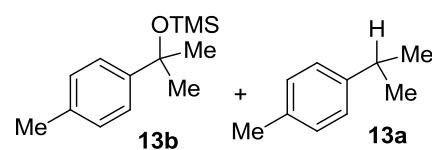
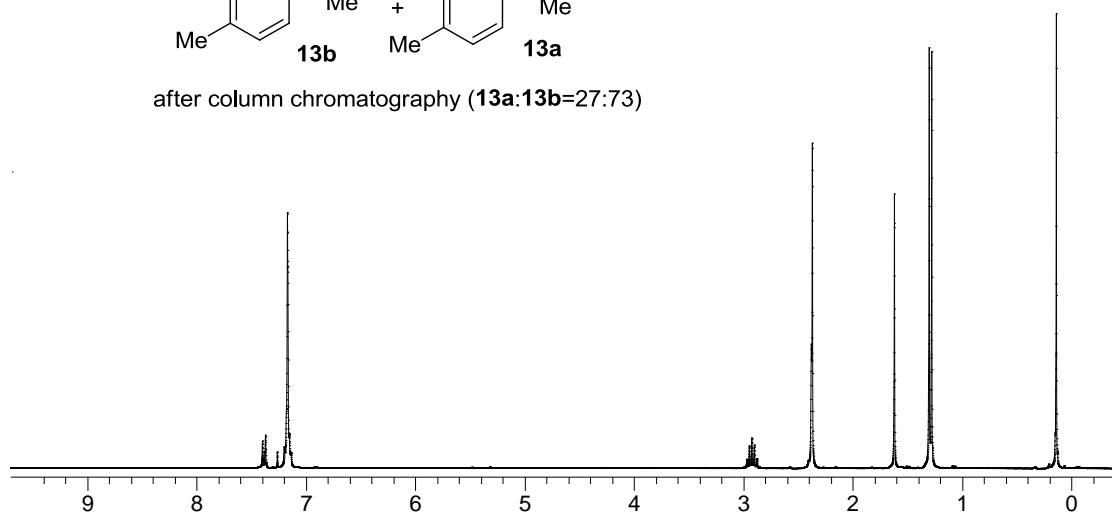




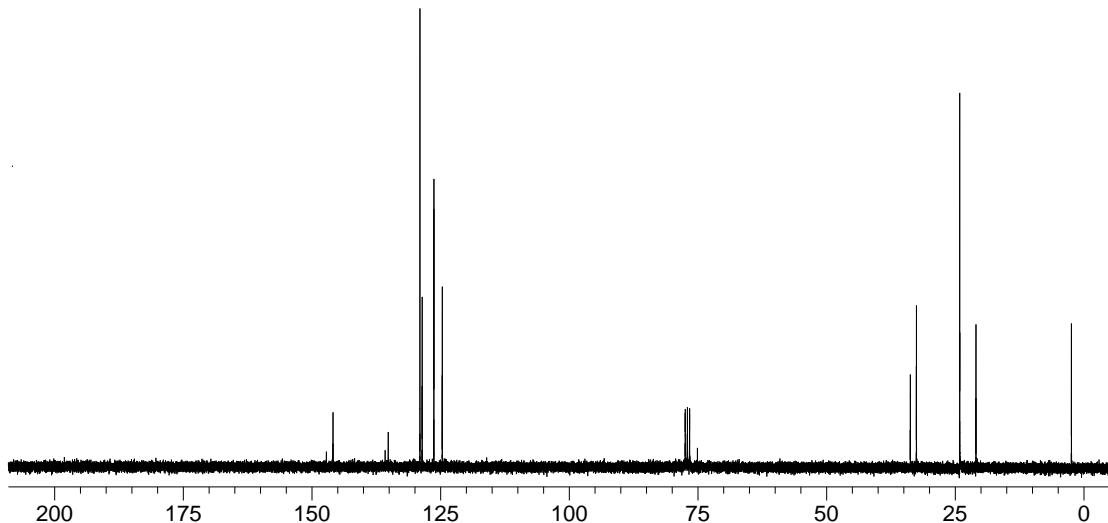


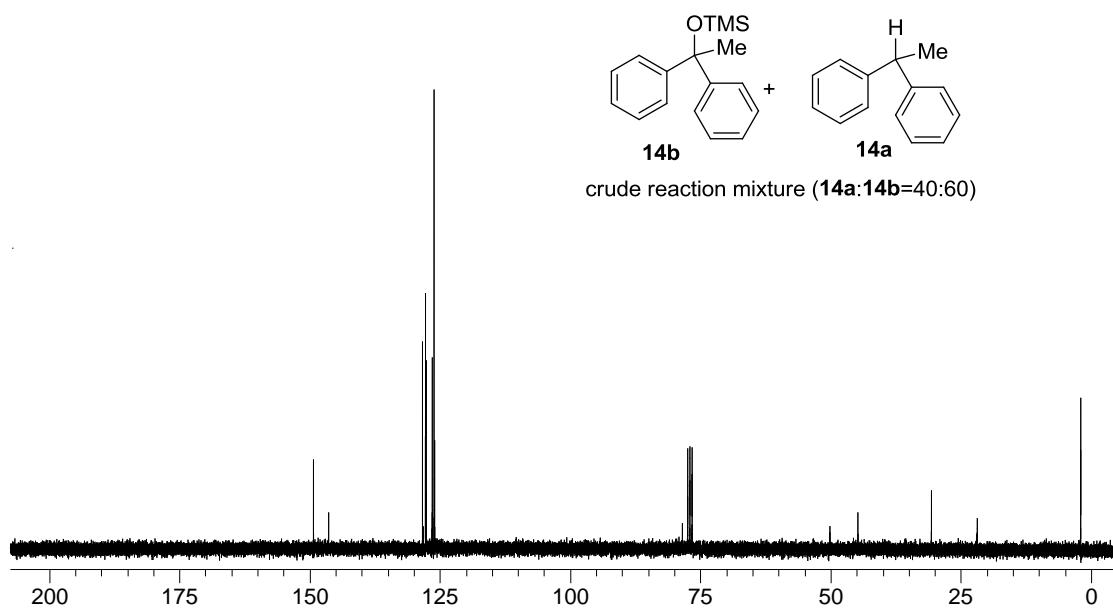
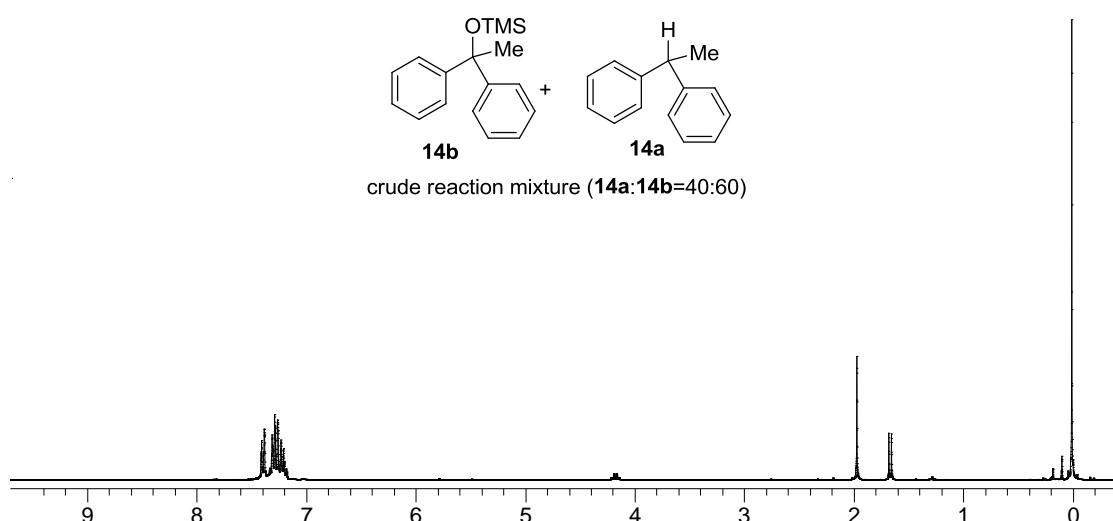


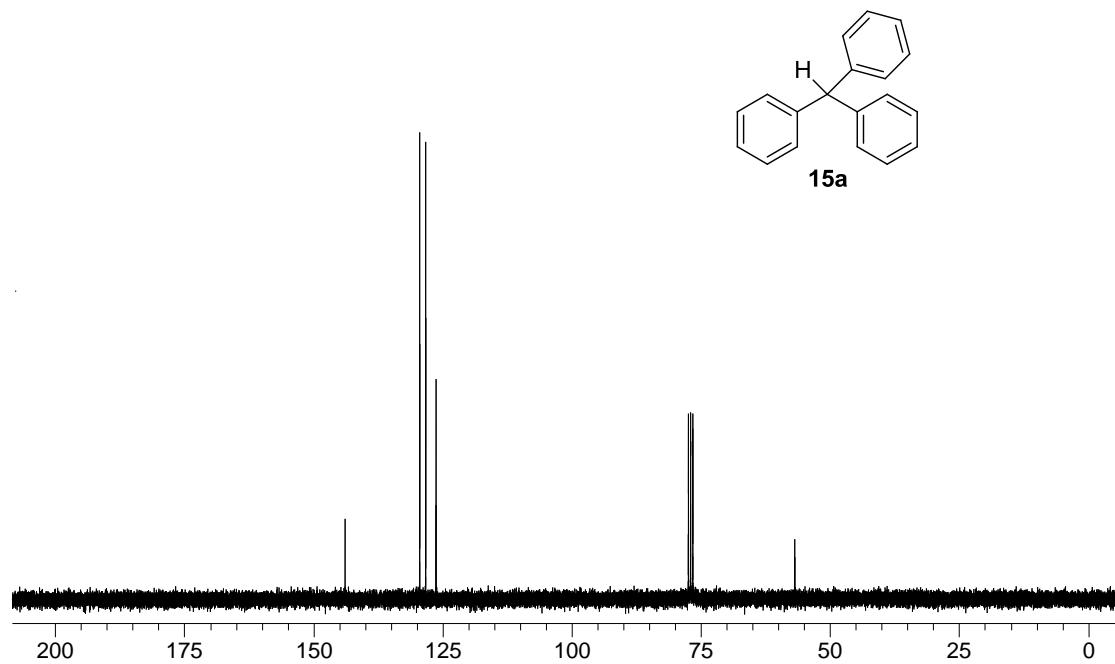
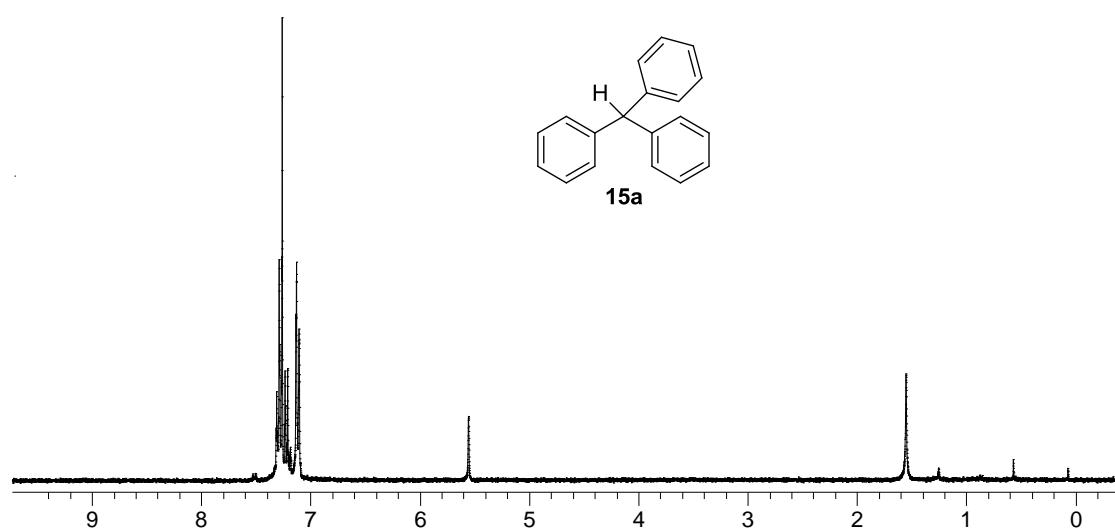
after column chromatography (**13a**:**13b**=27:73)

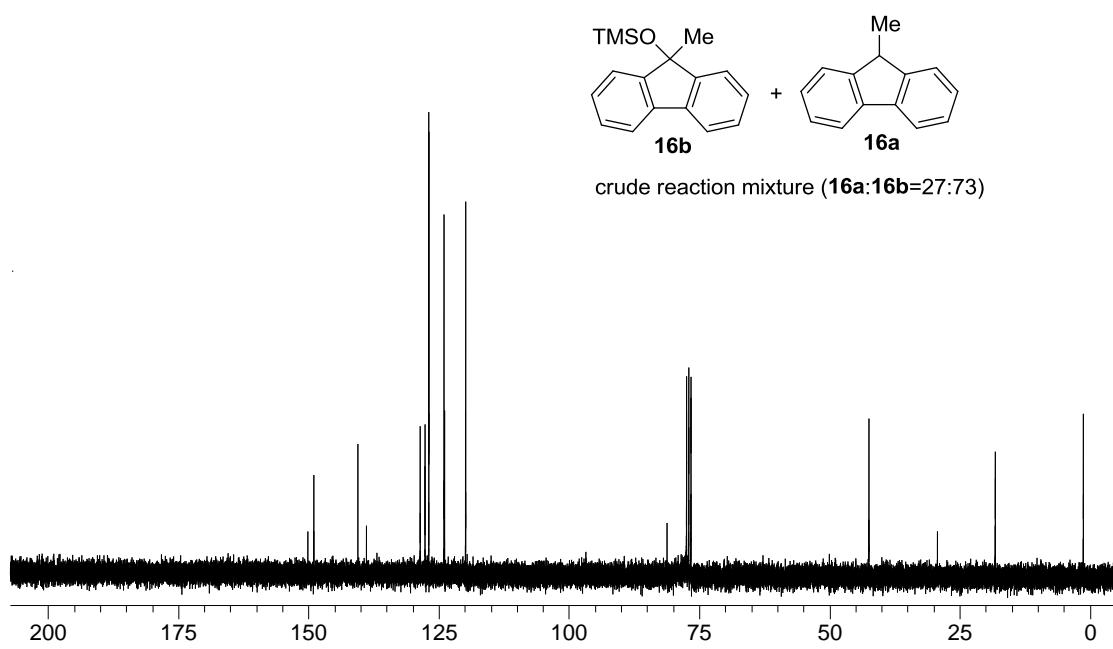
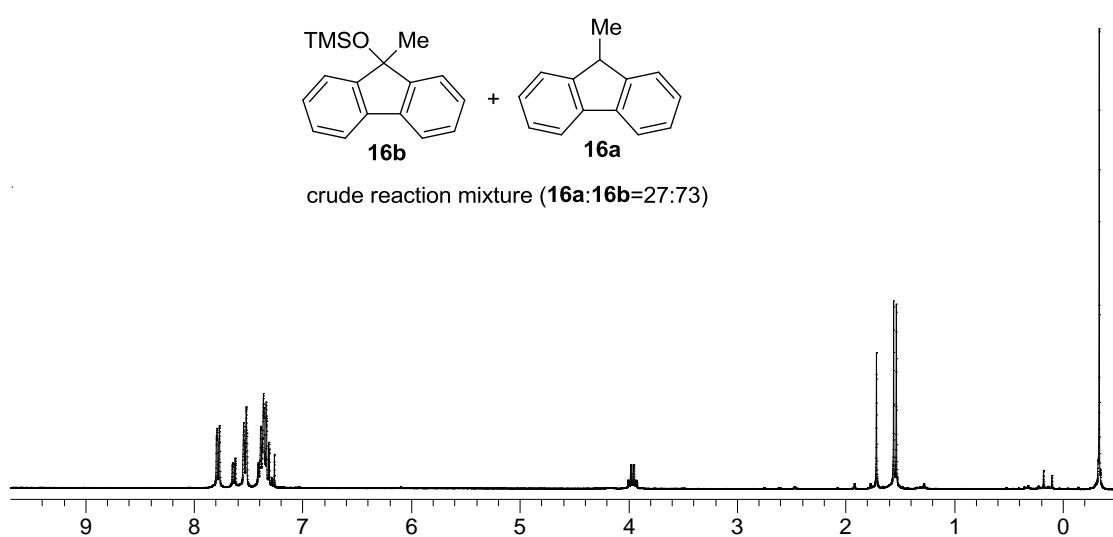


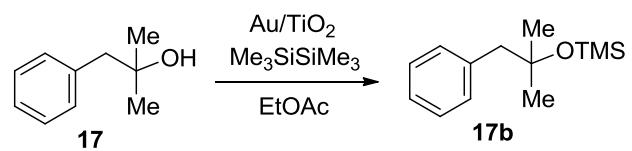
after column chromatography (**13a**:**13b**=27:73)



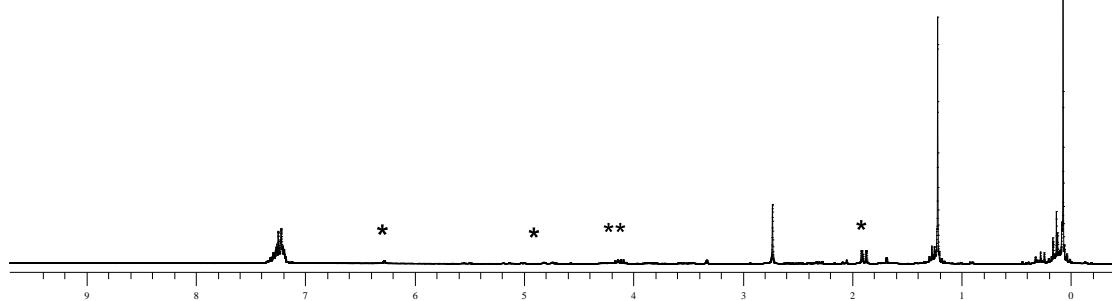






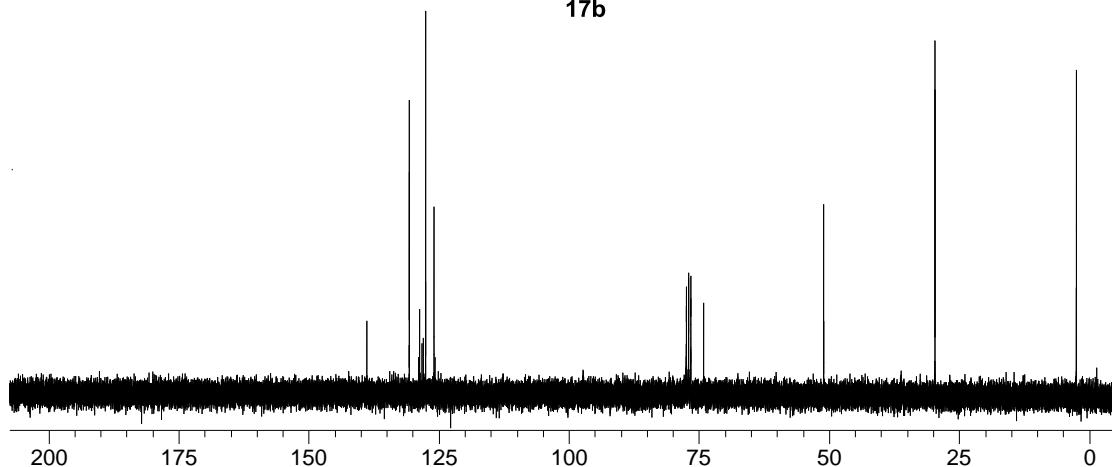
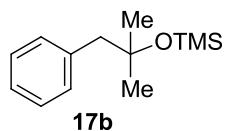


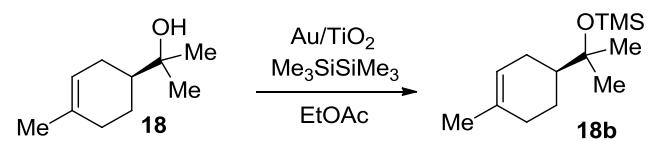
crude reaction mixture



\*: Dehydration products from starting material

\*\*: Solvent impurities





crude reaction mixture

