

# Lewis Base-Promoted Carbon-Carbon $sp^3$ - $sp^3$ Coupling Reactions of $\alpha$ -Silyl Silylethers

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## Supporting Information

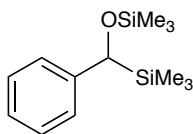
|   |     |
|---|-----|
| General Information .....   | S2  |
| General Procedure (I) for Synthesis of $\alpha$ -Silyl silylether ..... | S2  |
| General Procedure (II) for the $sp^3$ - $sp^3$ coupling .....           | S5  |
| Labeling Experiments .....  | S18 |
| Crossover Experiment.....   | S20 |
| Selected NMR Spectra .....  | S25 |
| Selected Mass Spectra.....  | S64 |

## General Information

All reactions were carried out under a nitrogen atmosphere using Schlenk or glovebox techniques in flame-dried glassware with magnetic stirring. THF, Et<sub>2</sub>O, toluene, DMF, MeOH, and CH<sub>2</sub>Cl<sub>2</sub> were purified by passage through a bed of activated alumina.<sup>1</sup> DMA, DMSO and other reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.<sup>2</sup> Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and visualizing stains (anisaldehyde, ceric ammonium nitrate, potassium permanganate, or phosphomolybdic acid) followed by heating. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. <sup>1</sup>H-NMR spectra were recorded on an AVANCE III 500 MHz w/ direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 7.26 ppm). Data are reported as (app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz), integration. Proton-decoupled <sup>13</sup>C-NMR spectra were recorded on an AVANCE III 500 MHz w/ direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 77.0 ppm). Mass spectra data were obtained on a Varian 1200 Quadrupole Mass Spectrometer and Micromass Quadro II Spectrometer. Aldehydes, alcohols, fluorides, and alkyl halides were purchased from Sigma-Aldrich Company unless otherwise noted.

## General Procedure (I) for Synthesis of α-Silyl silylether

To a flame-dried round bottom flask containing a magnetic stirring bar under nitrogen was added distilled diisopropyl amine (1.3 equiv) and THF (0.2 M). The solution was cooled to -78 °C and freshly titrated *n*-butyl lithium in hexane (1.3 equiv) was added. The solution was warmed to room temperature for 15 minutes and then cooled to -78 °C. To the stirred solution was added benzyloxytrimethylsilane (1 equiv) in THF dropwise. The reaction was warmed and stirred for 2 hours or until disappearance of the TMS-benzylether by TLC. The solution was then cooled to -78 °C and trimethylsilyl chloride (1.3 equiv) was added slowly. The reaction was stirred at ambient temperature for 0.5 hours and then treated with 1N NaCl. After stirring at room temperature for 15 min, this solution was diluted with diethyl ether. The aqueous layer was discarded and the resulting ether layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated in vacuo to provide the unpurified α-silyl silylether. The α-silyl silylether was purified by flash chromatography.

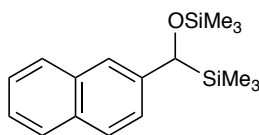


## α-Trimethylsilyl-α-trimethylsiloxytoluene (1a) Prepared according to the general procedure

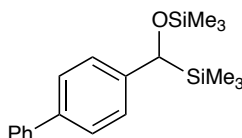
<sup>1</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

<sup>2</sup> Perrin, D. D. and Armarego, W. L. *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford. **1988**.

(I) using benzyloxytrimethylsilane (2.35 g, 13.0 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine (2.2 mL, 16.9 mmol, 1.3 equiv) and 2.7 M *n*-butyl lithium (6.27 mL, 16.9 mmol, 1.3 equiv)), and trimethylsilyl chloride (2.17 mL, 16.4 mmol, 1.3 equiv). The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 2.48 g (75%) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>); δ 7.26–7.23 (m, 3H), 7.12 (dd, *J* = 13.9, 7.0 Hz, 2H), 4.43 (s, 1H), 0.01 (s, 9H), –0.06 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>); δ 144.3, 127.6(2C), 125.0, 124.8(2C), 70.2, 0.0(3C), –4.1(3C). Spectroscopy is identical to previously reported data.<sup>3</sup>

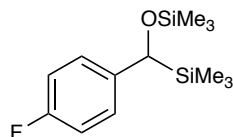


**Trimethyl(naphthalen-2-yl(trimethylsilyl)methoxy)silane (1b)** Prepared according to the general procedure (I) using trimethyl(naphthalen-2-ylmethoxy)silane (1.50 g, 6.52 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine 1.08 mL, 8.48 mmol, 1.3 equiv and 2.7 M *n*-butyl lithium, 3.14 mL, 8.48 mmol, 1.3 equiv) and trimethylsilyl chloride (1.08 mL, 8.48 mmol, 1.3 equiv). The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 1.58 g (80%) as a white solid. FTIR (film); 3056, 2956, 2898, 2833, 1247, 1051, 863, 840, 740 cm<sup>–1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>); δ 7.99–7.96 (m, 2H), 7.93 (d, *J* = 8.5, 1H), 7.81 (s, 1H), 7.61 (ddd, *J* = 8.1, 6.9, 1.3, 1H), 7.56 (ddd, *J* = 7.5, 5.5, 1.2, 1H), 7.51 (dd, *J* = 8.5, 1.6, 1H), 4.83 (s, 1H), 0.26 (s, 9H), 0.20 (s, 9H). <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>); δ 142.2, 133.5, 132.0, 127.66, 127.56, 127.2, 125.7, 124.7, 124.3, 122.5, 70.5, 0.1(3C), –3.9(3C). MS (EI); *m/z* calcd for [M]<sup>+</sup> (C<sub>17</sub>H<sub>26</sub>OSi<sub>2</sub>)<sup>+</sup>: 302 Found: [M]<sup>+</sup> 302.

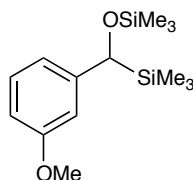


**(Biphenyl-4-yl(trimethylsilyl)methoxy)trimethylsilane (1c)** Prepared according to the general procedure (I) using (biphenyl-4-ylmethoxy)trimethylsilane (1.0 g, 3.9 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine 0.70 mL, 5.07 mmol, 1.3 equiv and 2.5 M *n*-butyl lithium, 2.03 mL, 5.07 mmol, 1.3 equiv) and trimethylsilyl chloride (0.64 mL, 5.07 mmol, 1.3 equiv). The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 810 mg (65%) as a colorless oil. FTIR (film); 3028, 2957, 2898, 2828, 1486, 1249, 1052, 1249, 1052, 871, 840, 752 cm<sup>–1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>); δ 7.63–7.62 (m, 2H), 7.52 (d, *J* = 8.2, 2H), 7.43 (t, *J* = 7.7, 2H), 7.33 (d, *J* = 7.4, 1H), 7.22 (d, *J* = 8.1, 2H), 4.51 (s, 1H), 0.05 (s, 9H), 0.00 (s, 9H). <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>); δ 143.6, 141.1, 137.7, 128.6, 126.8, 126.3, 125.2, 70.1, 0.1(3C), –4.1(3C). MS (EI); *m/z* calcd for [M]<sup>+</sup> (C<sub>19</sub>H<sub>28</sub>OSi<sub>2</sub>)<sup>+</sup>: 328 Found: [M]<sup>+</sup> 328.

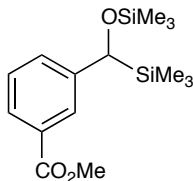
<sup>3</sup> Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, 96, 3214–3222.



**((4-Fluorophenyl)(trimethylsilyl)methoxy)trimethylsilane (1d)** Prepared according to the general procedure (I) using (3-fluorobenzoyloxy)trimethylsilane (0.5 g, 2.33 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine 0.35 mL, 2.4 mmol, 1.03 equiv and 2.5 M *n*-butyl lithium, 0.96 mL, 2.4 mmol, 1.03 equiv) and trimethylsilyl chloride (0.3 mL, 2.4 mmol, 1.03 equiv). The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 75 mg (15%) as a colorless oil. FTIR (film); 2958, 2926, 2901, 2851, 1604, 1506, 1250, 1222, 1052, 870, 841 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>); δ 7.08 (dd, *J* = 8.8, 5.5, 2H), 6.94 (t, *J* = 8.8, 2H), 4.40 (s, 1H), 0.00 (s, 9H), -0.07 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>); δ 160.8 (d, *J* = 242 Hz, 1C), 140.0, 126.1 (d, *J* = 8 Hz, 2C), 114.5 (d, *J* = 21 Hz, 2C), 69.6, 0.0 (3C), -4.2(3C). MS (EI); *m/z* calcd for [M]<sup>+</sup> (C<sub>13</sub>H<sub>23</sub>FOSi<sub>2</sub>)<sup>+</sup>: 270 Found: [M]<sup>+</sup> 270.



**((3-Methoxyphenyl)(trimethylsilyl)methoxy)trimethylsilane (1e)** Prepared according to the general procedure (I) using (3-methoxybenzoyloxy)trimethylsilane (0.70 g, 3.33 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine 0.6 mL, 4.33 mmol, 1.3 equiv and 2.5 M *n*-butyl lithium, 2.0 mL, 4.33 mmol, 1.3 equiv) and trimethylsilyl chloride (0.55 mL, 4.33 mmol, 1.3 equiv). The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 715 mg (76%) as a colorless oil. FTIR (film); 3380, 2927, 2865, 1952, 1799, 1757, 1452, 1392, 1065, 1027, 762, 700 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>); δ 7.15 (t, *J* = 7.9 Hz, 1H), 6.72-6.72 (m, 1H), 6.69 (dt, *J* = 7.6, 0.7 Hz, 1H), 6.65 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.41 (s, 1H), 3.79 (s, 3H), 0.01 (s, 9H), -0.06 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>); δ 159.2, 146.2, 128.5, 117.3, 110.4, 110.4, 70.2, 55.1, 0.0 (3C), -4.1 (3C). MS (EI); *m/z* calcd for [M]<sup>+</sup> (C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>Si<sub>2</sub>)<sup>+</sup>: 282 Found: [M]<sup>+</sup> 282.



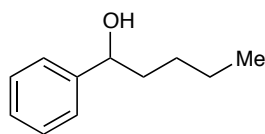
**Methyl 3-((trimethylsilyl)(trimethylsilyloxy)methyl)benzoate (1f)** Methyl 3-((trimethylsilyl)carbonyl)benzoate was prepared from corresponding benzoyl chloride with hexamethyldisilane in the presence of palladium (II) acetate as a catalyst.<sup>4</sup> Methyl 3-

<sup>4</sup> Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, 6, 974-979.

((trimethylsilyl)carbonyl)benzoate (1.006 g, 4.26 mmol, 1.0 equiv) was then reduced with sodium borohydride (0.048 g, 1.28 mmol, 0.3 equiv) in methanol (21 mL), quenched after 20 minutes with saturated  $\text{NH}_4\text{Cl}$  (20 mL), and extracted with EtOAc (30 mL x 2). The combined organic layers were washed with brine, dried over  $\text{MgSO}_4$ , and filtered. The filtrate was concentrated under reduced pressure and subjected to the next step without further purification. To a 0.125M solution of the alcohol (1.0 equiv) in THF was added  $\text{TMSCl}$  (0.648 mL, 5.11 mmol, 1.2 equiv) followed by imidazole (0.58 g, 8.51 mmol, 2.0 equiv.) The mixture was stirred at  $0^\circ\text{C}$  followed by overnight stirring at rt. The mixture was then diluted with EtOAc (30 mL) and washed with brine (20 mL x 3). The combined aqueous phases were extracted with EtOAc (30 mL x 2), and the combined organic layers were dried over  $\text{MgSO}_4$  and then concentrated in vacuo. The crude product was purified by flash chromatography (5% EtOAc/hexanes, 2%  $\text{Et}_3\text{N}$ ) on silica gel to afford 1.11 g (84%) as a colorless oil. FTIR (film); 3411, 2955, 2900, 2848, 1726, 1603, 1440, 1284, 1056, 840, 746  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.81-7.79 (m, 2H), 7.38-7.32 (m, 2H), 4.49 (s, 1H), 3.91 (s, 3H), 0.01 (s, 9H), -0.05 (s, 9H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  167.4, 144.9, 129.55, 129.40, 127.9, 126.5, 125.7, 69.9, 52.0, -0.03(3C), -4.2(3C). MS (EI);  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{15}\text{H}_{27}\text{O}_3\text{Si}_2$ ) $^+$ : 311 Found:  $[\text{M}]^+$  311.

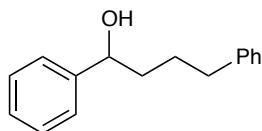
### General Procedure (II) for the $sp^3$ - $sp^3$ coupling

To a flame-dried 2 dram vial containing a magnetic stirring bar in a glove box was added  $\alpha$ -silyl silylether (1 equiv), electrophile and solvent. To the stirred solution was added tetramethylammonium fluoride. The vial was capped and stirred for 16 hours at ambient temperature. The vial was removed from the glove box and diluted with THF (0.5 mL). To the stirring solution was added 1 equivalent of TBAF (1M in THF) and allowed to stir at room temperature for 15 minutes. This solution was diluted with diethyl ether (5 mL) and washed with brine (2 x 5 mL). The aqueous layer was discarded and the resulting organic layer was dried over anhydrous  $\text{MgSO}_4$  filtered, and concentrated in vacuo to provide the unpurified secondary alcohols. The products were purified by flash chromatography on silica gel.

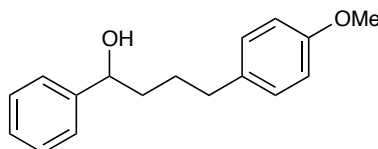


**1-Phenylpentan-1-ol (3)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL) to afford 107 mg (65%) of **5a** after flash chromatography (20% EtOAc/hexanes) as a volatile, colorless oil.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.35–7.34 (m, 4H), 7.30–7.26 (m, 1H), 4.67 (dd,  $J = 7.5, 5.9$  Hz, 1H), 1.85–1.77 (m, 2H), 1.75–1.68 (m, 2H), 1.44–1.22 (m, 5H), 0.89 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.9, 128.3(2C), 127.4, 125.9(2C), 74.6, 38.8, 27.9, 22.6, 14.0. Spectroscopy is equivalent to previously reported data.<sup>5</sup>

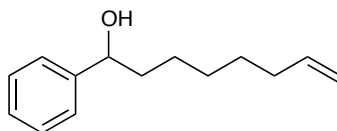
<sup>5</sup> Suh, Y.; Lee, J. S.; Kim, S. H.; Rieke, R. D. *J. Organomet. Chem.* **2003**, 684, 20–36.



**1,4-Diphenylbutan-1-ol (5)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (3-bromopropyl)benzene (179 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 138 mg (61%) of **5** after flash chromatography (20% EtOAc/hexanes) as a white solid. FTIR (film); 3366, 3084, 3061, 3026, 2937, 2859, 1947, 1879, 1807, 1750, 1602, 1494, 1452, 1061, 1027, 748, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.38–7.32 (m, 4H), 7.31–7.27 (m, 3H), 7.21–7.17 (m, 3H), 4.69 (t,  $J = 5.1$ , 1H), 2.65 (t,  $J = 7.4$ , 2H), 1.95 (d,  $J = 2.4$ , 1H), 1.89–1.82 (m, 1H), 1.81–1.75 (m, 2H), 1.66–1.61 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.6, 142.2, 128.41 (2C), 128.36 (2C), 128.24 (2C), 127.5, 125.84 (2C), 125.69, 74.5, 38.5, 35.7, 27.6. MS (EI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{18}\text{ONa}$ ) $^+$ : 249, 250 Found:  $[\text{M}+\text{Na}]^+$  249, 250.

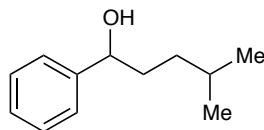


**4-(4-Methoxyphenyl)-1-phenylbutan-1-ol (6)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-(3-bromopropyl)-4-methoxybenzene (205 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 100 mg (65%) of **6** after flash chromatography (20% EtOAc/hexanes) as a colorless oil. FTIR (film); 3400, 3029, 2935, 2858, 2835, 2059, 1951, 1881, 1812, 1737, 1611, 1512, 1454, 1245, 1178, 1038, 701  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.37–7.32 (m, 4H), 7.30–7.26 (m, 1H), 7.08 (ddd,  $J = 5.0, 3.0, 3.0$  Hz, 2H), 6.83 (ddd,  $J = 5.0, 3.0, 3.0$  Hz, 2H), 5.67 (dd,  $J = 7.0, 5.5$  Hz, 1H), 3.79 (s, 3H), 2.58 (t,  $J = 7.4$  Hz, 2H), 2.02 (s, 1H), 1.88–1.82 (m, 1H), 1.78–1.71 (m, 2H), 1.58 (ddd,  $J = 10.8, 7.5, 3.1$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  157.6, 144.7, 133.7, 129.2(2C), 128.4(2C), 127.5, 125.8(2C), 113.6(2C), 73.8, 55.2, 40.7, 31.1 MS (EI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{18}\text{ONa}$ ) $^+$ : 256 Found:  $[\text{M}+\text{Na}]^+$ : 256.

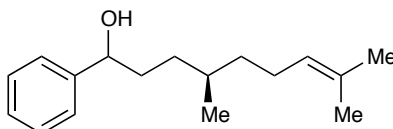


**1-Phenyloct-7-en-1-ol (7)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 7-bromohept-1-ene (159 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 70 mg (57%) of **7** after flash chromatography (20% EtOAc/hexanes) as a colorless oil. FTIR (film); 3352, 3075, 3029, 2976, 2929, 2856, 1958, 1876, 1818, 1640, 1493, 1453, 1027, 995, 910, 761, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ); 7.37–7.33 (m, 4H), 7.29–7.26 (m, 1H), 5.79 (dddd,  $J = 13.5, 10.5, 6.8, 6.5$ , 1H), 4.98 (ddd,  $J = 17.5, 2, 2$ , 1H), 4.93 (ddd,  $J = 10.2, 1, 1$ , 1H), 4.66 (ddd,  $J = 7.6, 5.6, 3.1$ , 1H), 2.03 (q,  $J = 7.1$  Hz, 2H), 1.86–1.77 (m, 2H), 1.74–1.68 (m, 1H), 1.45–1.26 (m, 6H).  $^{13}\text{C}$

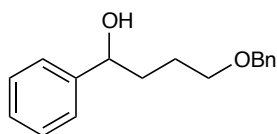
NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.8, 139.0, 128.4(2C), 127.5(2C), 125.9, 114.2, 74.6, 39.0, 33.7, 29.0, 28.8, 25.6. MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{14}\text{H}_{20}\text{O}$ ) $^+$ : 204 Found:  $[\text{M}]^+$  204.



**4-Methyl-1-phenylpentan-1-ol (8)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-bromo-3-methyl-butane (136 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 55 mg (52%) of **8** after flash chromatography (20% EtOAc/hexanes) as a colorless oil. FTIR (film); 3362, 3346, 2954, 2933, 2869, 1946, 1883, 1801, 1751, 1452, 1391, 1367, 1058, 1027, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.34–7.37 (m, 4H), 7.27–7.30 (m, 1H), 4.62–4.65 (m, 1H), 1.87 (d,  $J = 2.1$  Hz, 1H), 1.76–1.83 (m, 1H), 1.71 (m, 1H), 1.55 (m, 1H), 1.29–1.37 (m, 1H), 1.11–1.17 (m, 1H), 0.88 (d,  $J = 3.1$  Hz, 3H), 0.87 (d,  $J = 3.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.9, 128.4 (2C), 127.5, 125.9 (2C), 75.0, 36.9, 34.9, 28.0, 22.6, 22.5. MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{12}\text{H}_{18}\text{O}$ ) $^+$ : 178 Found:  $[\text{M}]^+$  178.



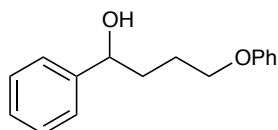
**(4R)-4,8-Dimethyl-1-phenylnon-7-en-1-ol (9)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (*R*)-8-bromo-2,6-dimethyloct-2-ene (197 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 73 mg (50%) of **9** as an inseparable mixture of diastereomers (1:1) after flash chromatography (20% EtOAc/hexanes) as a white solid. FTIR (film) 3350, 2961, 2925, 2855, 1946, 1875, 1806, 1752, 1453, 1377, 1057, 1028, 763, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ); 7.37–7.33 (m, 9H), 7.30–7.26 (m, 2H), 5.10–5.07 (m, 2H), 4.64–4.61 (m, 2H), 1.94 (tq,  $J = 16.5, 8.2$  Hz, 6H), 1.85–1.73 (m, 3H), 1.71–1.68 (m, 8H), 1.59 (s, 6H), 1.48–1.40 (m, 3H), 1.36–1.25 (m, 5H), 1.17–1.04 (m, 3H), 0.87 (d,  $J = 6.6$  Hz, 5H), 0.87 (d,  $J = 6.6$  Hz, 5H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.91, 144.85, 131.1, 128.4, 127.47, 127.44, 125.89, 125.84, 124.8, 75.1, 36.91, 36.86, 36.59, 36.46, 32.91, 32.87, 32.3, 25.7, 25.46, 25.44, 19.48, 19.46, 17.6. MS (ESI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{17}\text{H}_{26}\text{O}$ ) $^+$ : 246 Found:  $[\text{M}]^+$  246.



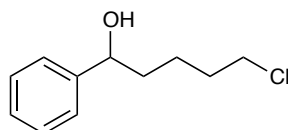
**4-(Benzyloxy)-1-phenylbutan-1-ol (10)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), ((3-bromopropoxy)methyl)benzene (205 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to isolate 86 mg (56%)



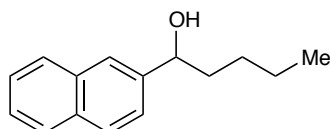
of **10** as a colorless oil. FTIR (film); 3412, 3086, 3063, 3030, 2919, 2854, 2795, 2245, 1951, 1880, 1811, 1756, 1586, 1603, 1495, 1453, 1028, 1101, 913, 744, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ); 7.37-7.27 (m, 10H), 4.70 (t,  $J = 6.8$  Hz, 1H), 4.52 (s, 2H), 3.52 (t,  $J = 6.1$  Hz, 2H), 2.82 (s, 1H), 1.87 (q,  $J = 7.1$  Hz, 2H), 1.80-1.65 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.8, 138.2, 128.4(2C), 128.3(2C), 127.7(2C), 127.3, 126.9, 125.8(2C), 74.1, 73.0, 70.3, 36.5, 26.2. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{NaC}_{17}\text{H}_{20}\text{O}_2$ ) $^+$ : 279 Found:  $[\text{M}+\text{Na}]^+$  279.



**4-Phenoxy-1-phenylbutan-1-ol (11)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (3-bromopropoxy)benzene (193 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to afford 90 mg (62%) of **11** as a colorless oil. FTIR (film); 3391, 3062, 3029, 2922, 2872, 1599, 1586, 1496, 1471, 1453, 1245, 1033, 754, 700, 692  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.37 (m, 4H), 7.29 (m, 3H), 6.94 (t,  $J = 7.3$  Hz, 1H), 6.89 (d,  $J = 8.0$  Hz, 2H), 4.77 (bm, 1H), 4.00 (m, 2H), 2.09 (bs, 1H), 1.99-1.93 (m, 3H), 1.83 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  158.8, 144.5, 129.4(2C), 128.5(2C), 127.6, 125.8(2C), 120.6, 114.4(2C), 74.2, 67.6, 35.8, 25.7. MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{16}\text{H}_{18}\text{O}_2$ ) $^+$ : 242 Found:  $[\text{M}]^+$  242.



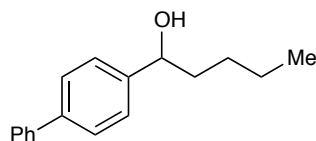
**5-Chloro-1-phenylpentan-1-ol (12)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-bromo-4-chlorobutane (153 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to isolate **12** as a colorless oil (81.0 mg, 68%). FTIR (film); 3380, 2927, 2865, 1952, 1799, 1757, 1452, 1392, 1065, 1027, 762, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.37-7.33 (m, 4H), 7.29 (m, 1H), 4.68 (ddd,  $J = 7.7, 5.5, 2.5$  Hz, 1H), 3.52 (t,  $J = 6.7$  Hz, 2H), 1.90 (d,  $J = 3.0$  Hz, 1H), 1.86-1.69 (m, 4H), 1.63-1.54 (m, 1H), 1.48-1.40 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.5, 128.5(2C), 127.7, 125.8(2C), 74.4, 44.9, 38.2, 32.4, 23.2. MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{11}\text{H}_{15}\text{ClO}$ ) $^+$ : 198, 200 Found:  $[\text{M}]^+$  198, 200.



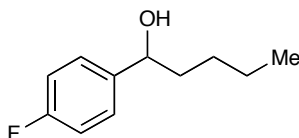
**1-(Naphthalen-2-yl)pentan-1-ol (13)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4a** (181 mg, 0.6 mmol), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 137 mg (64%)



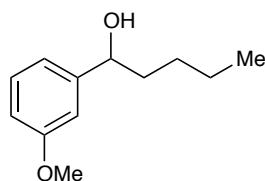
of **13** after flash chromatography (20% EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.86–7.76 (m, 4H), 7.52–7.47 (m, 3H), 4.80 (t,  $J = 6.7$  Hz, 1H), 2.29 (s, 1H), 1.89–1.78 (m, 2H), 1.44–1.25 (m, 4H), 0.91 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  142.2, 133.2, 132.9, 128.1, 127.8, 127.6, 126.0, 125.7, 124.5, 124.1, 74.7, 38.6, 27.9, 22.6, 14.0. Spectroscopy is equivalent to previously reported data.<sup>6</sup>



**1-(Biphenyl-4-yl)pentan-1-ol (14)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4b** (197 mg, 0.6 mmol), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 89 mg (61%) of **14** after flash chromatography (20% EtOAc/hexanes). FTIR (film); 3427, 2958, 2930, 2859, 1638, 1510, 1223, 836  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.61 (m, 4H), 7.48–7.42 (m, 4H), 7.39–7.35 (m, 1H), 4.73–4.70 (m, 1H), 2.09 (d,  $J = 2.8$  Hz, 1H), 1.88–1.82 (m, 1H), 1.80–1.74 (m, 1H), 1.47–1.29 (m, 4H), 0.93 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  143.9, 140.8, 140.3, 128.7(2C), 127.2, 127.1(2C), 127.0(2C), 126.3(2C), 74.4, 38.7, 28.0, 22.6, 14.0. MS (ESI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{17}\text{H}_{20}\text{O}$ )<sup>+</sup>: 240 Found:  $[\text{M}]^+$  240.



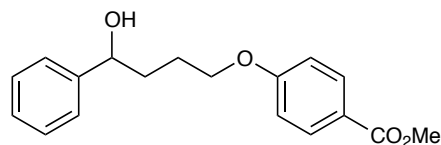
**1-(4-Fluorophenyl)pentan-1-ol (15)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4d** (162.3 mg, 0.6 mmol), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 50 mg (37%) of **16** after flash chromatography (20% EtOAc/hexanes). FTIR (film); 3427, 2958, 2930, 2859, 1638, 1510, 1223, 836  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.32 (m, 2H), 7.03 (m, 2H), 4.65 (t,  $J = 6.6$  Hz, 1H), 1.82–1.75 (bm, 2H), 1.71–1.64 (bm, 1H), 1.41–1.29 (bm, 2H), 1.26–1.19 (bm, 2H), 0.88 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  162.1 (d,  $J = 245.0$  Hz, 1C), 140.6, 127.5 (d,  $J = 7.9$  Hz, 2C), 115.2 (d,  $J = 21.0$  Hz, 2C), 74.1, 38.9, 27.9, 22.6, 14.0. MS (ESI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{11}\text{H}_{15}\text{FO}$ )<sup>+</sup>: 182 Found:  $[\text{M}]^+$  182.



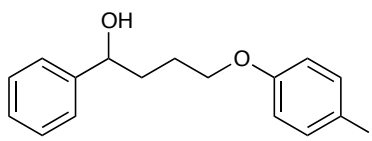
**1-(3-Methoxyphenyl)pentan-1-ol (16)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4c** (169 mg, 0.6 mmol), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 75 mg (64%) of

<sup>6</sup> Tanoue, Y.; Terada, A.; Seto, I.; Umezue, Y.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1221–1224.

**15** after flash chromatography (20% EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.27 (t,  $J$  = 8.1 Hz, 1H), 6.94-6.92 (m, 2H), 6.83 (ddd,  $J$  = 8.2, 2.4, 1.1 Hz, 1H), 4.65 (ddd,  $J$  = 2.5, 5.5, 2.5 Hz, 1H), 3.83 (s, 3H), 1.87-1.78 (m, 2H), 1.72 (dd,  $J$  = 10.2, 5.7 Hz, 1H), 1.40-1.26 (m, 5H), 0.90 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  159.7, 146.7, 129.4, 118.2, 112.8, 111.3, 74.6, 55.2, 38.8, 28.0, 22.6, 14.0. Spectroscopy is equivalent to previously reported data.<sup>7</sup>

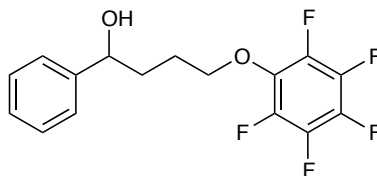


**Methyl 4-(4-hydroxy-4-phenylbutoxy)benzoate (17)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), methyl 4-(3-bromopropoxy)benzoate (246 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to afford 114 mg (63%) of **17** as a yellowish oil. FTIR (film); 3401, 2950, 2927, 2874, 1715, 1605, 1511, 1282, 1254, 1027, 846, 770  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.98-7.95 (m, 2H), 7.38-7.34 (m, 4H), 7.28 (ddd,  $J$  = 8.9, 5.7, 3.0 Hz, 1H), 6.89-6.86 (m, 2H), 4.76 (t,  $J$  = 5.8 Hz, 1H), 4.05-3.98 (m, 2H), 3.87 (s, 3H), 2.13 (s, 1H), 1.99-1.90 (m, 3H), 1.85-1.81 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  166.9, 162.7, 144.4, 131.5, 128.5, 127.7, 125.8, 122.4, 114.0, 74.2, 67.9, 51.8, 35.5, 25.5. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{18}\text{H}_{20}\text{O}_4\text{Na}$ ) $^+$ : 323 Found:  $[\text{M}+\text{Na}]^+$  323.

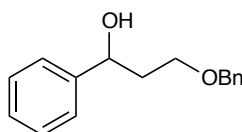


**4-(4-Iodophenoxy)-1-phenylbutan-1-ol (18)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-(3-bromopropoxy)-4-iodobenzene (307 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to afford 122 mg (55%) of **18** as a colorless oil. FTIR (film); 3400, 3083, 3061, 3028, 2923, 2872, 1585, 1485, 1282, 1174, 1028, 999, 819, 761, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.55-7.52 (m, 2H), 7.36 (d,  $J$  = 4.3 Hz, 4H), 7.29 (dq,  $J$  = 8.5, 4.3 Hz, 1H), 6.67-6.64 (m, 2H), 4.74 (t,  $J$  = 6.2 Hz, 1H), 3.97-3.89 (m, 2H), 2.12 (s, 1H), 1.96-1.89 (m, 3H), 1.83-1.77 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  158.7, 144.4, 138.1, 128.5, 127.6, 125.8, 116.8, 82.6, 74.2, 67.8, 35.5, 25.5. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{17}\text{IO}_2\text{Na}$ ) $^+$ : 391 Found:  $[\text{M}+\text{Na}]^+$  391.

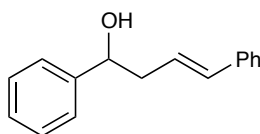
<sup>7</sup> Li, N. S.; Yu, S.; Kabalka, G. W. *J. Organomet. Chem.* **1997**, 531, 101–105.



**4-(Perfluorophenoxy)-1-phenylbutan-1-ol (19)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-(3-bromopropoxy)-2,3,4,5,6-pentafluorobenzene (275 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (20% EtOAc:hexanes) to afford 98 mg (49%) of **19** as a colorless oil. FTIR (film); 3369, 3087, 3064, 3031, 2956, 2887, 2661, 1514, 1158, 1029, 995, 763, 701  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.38-7.34 (m, 4H), 7.32-7.28 (m, 1H), 4.79-4.75 (m, 1H), 4.21-4.14 (m, 2H), 1.97-1.88 (m, 4H), 1.82-1.81 (m, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ );  $\delta$  144.32, 142.84-142.71 (m, 1C), 140.87-140.74 (m, 1C), 139.05-138.81 (m, 1C), 137.04-136.79 (m, 1C), 133.66-133.40 (m, 1C), 128.56 (2C), 127.74, 125.76 (2C), 75.50 (t,  $J = 2.7$ , 1C), 74.07, 34.94, 26.21. MS (ESI);  $m/z$  calcd for  $[\text{M-OH}]^+$  ( $\text{C}_{16}\text{H}_{12}\text{F}_5\text{O}$ ) $^+$ : 315 Found:  $[\text{M}]^+$  315.

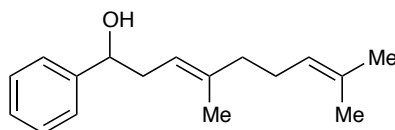


**3-(Benzyloxy)-1-phenylpropan-1-ol (20)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), ((2-bromoethoxy)methyl)benzene (194 mg, 0.9 mmol), and tetramethylammonium fluoride (55.0 mg, 0.6 mmol) in THF (1.5 mL). The crude product was purified via column chromatography (15% EtOAc:hexanes) to afford 110 mg (76%) of **20** as a colorless oil. FTIR (film); 3342, 2945, 2832, 1461, 1425, 1114, 1026  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.43-7.29 (m, 10H), 4.97 (dd,  $J = 8.3$ , 3.8 Hz, 1H), 4.58 (s, 2H), 3.75-3.67 (m, 2H), 3.42 (br s, 1H), 2.14-2.02 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  144.3, 137.8, 128.4(2C), 128.3(2C), 127.74, 127.71, 127.70, 127.2, 125.6(2C), 73.4, 73.3, 68.61, 38.56. MS (EI);  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}$ ) $^+$ : 265 Found:  $[\text{M}+\text{Na}]^+$  265.

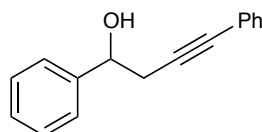


**(E)-1,4-Diphenylbut-3-en-1-ol (21)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (*E*)-(3-bromoprop-1-enyl)benzene (91 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 150 mg (67%) of **21** after flash chromatography (20% EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.42-7.36 (m, 6H), 7.34-7.30 (m, 3H), 7.26-7.23 (m, 1H), 6.52 (d,  $J = 15.9$  Hz, 1H), 6.23 (ddd,  $J = 7.5$ , 14.5, 7.5 Hz, 1H), 4.82 (t,  $J = 6.4$  Hz, 1H), 2.70-2.66 (m, 2H), 2.21 (s, 1H).  $^{13}\text{C}$  NMR (125

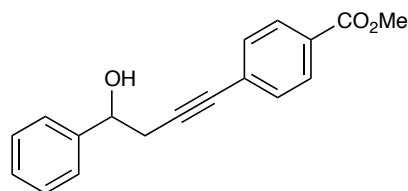
MHz, CDCl<sub>3</sub>);  $\delta$  143.8, 137.1, 133.3, 128.5 (2C), 128.4 (2C), 127.3, 126.1 (2C), 125.84, 125.75 (2C), 73.7, 43.0. Spectroscopy is equivalent to previously reported data.<sup>8</sup>



**(E)-4,8-Dimethyl-1-phenylnona-3,7-dien-1-ol (22)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (*E*)-1-chloro-3,7-dimethylocta-2,6-diene (104 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 191 mg (78%) of **22** after flash chromatography (20% EtOAc/hexanes). FTIR (film); 3368, 2966, 2915, 2855, 1958, 1875, 1805, 1493, 1452, 1382, 1048, 756, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>);  $\delta$  7.38–7.33 (m, 4H), 7.29–7.26 (m, 1H), 5.17 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 5.08–5.05 (m, 1H), 4.68 (ddd, *J* = 7.9, 5.1, 2.8 Hz, 1H), 2.55–2.40 (m, 2H), 2.12–2.02 (m, 5H), 1.69 (s, 3H), 1.61 (s, 6H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>);  $\delta$  144.2, 139.6, 131.8, 128.3 (2C), 127.4, 125.8 (2C), 124.1, 119.6, 73.9, 39.9, 38.3, 26.5, 25.8, 17.8, 16.3. MS (ESI); *m/z* calcd for [M]<sup>+</sup> (C<sub>17</sub>H<sub>24</sub>O)<sup>+</sup>: 244 Found: [M]<sup>+</sup> 244.



**1,4-Diphenylbut-3-yn-1-ol (23)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), (3-chloroprop-1-ynyl)benzene (90.0 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 142 mg (64%) of **23** after flash chromatography (20% EtOAc/hexanes). FTIR (film); 3370, 3061, 3031, 2925, 2853, 1598, 1490, 1453, 1442, 1384, 1048, 1027, 755, 692 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>);  $\delta$  7.45 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.40–7.37 (m, 4H), 7.33–7.28 (m, 4H), 4.97 (ddd, *J* = 3.4, 6.5, 10.0 Hz, 1H), 2.88–2.86 (m, 2H), 2.44 (d, *J* = 3.5 Hz, 1H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>);  $\delta$  142.6, 131.6 (2C), 128.4 (2C), 128.2 (2C), 128.0, 127.9, 125.8 (2C), 123.2, 85.9, 83.2, 72.6, 30.6. Spectroscopy is equivalent to previously reported data.<sup>9</sup>

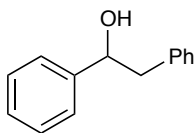


**Methyl 4-(4-hydroxy-4-phenylbut-1-ynyl)benzoate (24)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), methyl 4-(3-chloroprop-1-ynyl)benzoate (188 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in

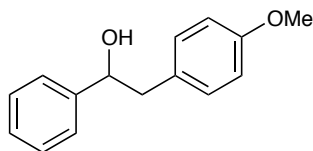
<sup>8</sup> Selander, N.; Szabo, K. J. *J. Org. Chem.* **2009**, 74, 5695–5698.

<sup>9</sup> Chini, M.; Crotti, P.; Favero, L.; Macchia, F. *Tetrahedron Lett.* **1991**, 32, 6617–6620.

THF (1.5 mL) to afford 100 mg (60%) of **24** after flash chromatography (20% EtOAc/hexanes). FTIR (film); 3434, 3062, 3030, 2951, 2224, 1948, 1720, 1605, 1494, 1277, 1018, 858, 769, 698  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.97–7.95 (m, 2H), 7.45–7.42 (m, 4H), 7.41–7.38 (m, 2H), 7.34–7.31 (m, 1H), 4.98 (td,  $J = 6.3, 3.1$  Hz, 1H), 3.91 (s, 3H), 2.90 (d,  $J = 6.3$  Hz, 2H), 2.37 (d,  $J = 3.4$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  166.6, 142.5, 131.6(2C), 129.4(2C), 129.3, 128.5(2C), 128.1, 128.0, 125.8(2C), 89.4, 82.5, 72.6, 52.2, 30.6. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{18}\text{H}_{17}\text{O}_3$ ) $^+$ : 281 Found:  $[\text{M}+\text{H}]^+$  281.

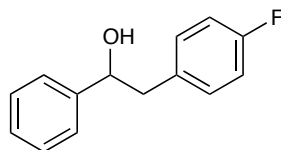


**1,2-Diphenylethanol (25)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), benzyl chloride (76.0 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in DMSO (1.5 mL) to afford 154 mg (75%) of **16** after flash chromatography (20% EtOAc/hexanes) as a white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.40 (m, 4H), 7.39–7.25 (m, 7H), 4.94 (ddd,  $J = 8.0, 5.2, 2.4$  Hz, 1H), 3.10 (dd,  $J = 13.7, 4.9$  Hz, 1H), 3.04 (dd,  $J = 13.6, 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  143.7, 137.9, 129.5(2C), 128.5(2C), 128.4(2C), 127.6, 127.6, 126.6, 125.8(2C), 75.3, 46.1. Spectroscopy is equivalent to previously reported data.<sup>5</sup>

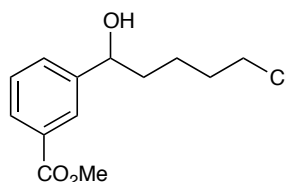


**2-(4-Methoxyphenyl)-1-phenylethanol (26)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-(chloromethyl)-4-methoxybenzene (94 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in DMSO (1.5 mL) to afford 150 mg (66%) of **26** after flash chromatography (20% EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.37–7.27 (m, 5H), 7.15–7.11 (m, 2H), 7.00–6.95 (m, 2H), 4.87 (ddd,  $J = 3.0, 7.0, 7.0$  Hz, 1H), 3.00 (d,  $J = 6.7$  Hz, 2H), 1.92 (d,  $J = 3.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  161.7, 143.6, 133.6, 130.9, 128.4 (2C), 127.7, 125.9 (2C), 115.2, 75.4, 45.0. Spectroscopy is equivalent to previously reported data.<sup>10</sup>

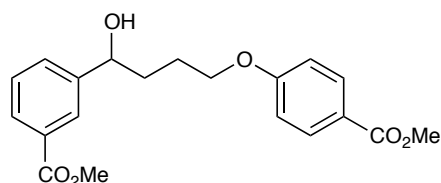
<sup>10</sup> Barrero, A. F.; Herrador, M. M.; del Moral, J. F. Q.; Arteaga, P.; Akssira, M.; El Hanbali, F.; Arteaga, J. F.; Dieguez, H. R.; Sanchez, E. M. *J. Org. Chem.* **2007**, 72, 2251–2254.



**2-(4-Fluorophenyl)-1-phenylethanol (27)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 1-(chloromethyl)-4-fluorobenzene (87.0 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in DMSO (1.5 mL) to afford 151 mg (70%) of **27** after flash chromatography (10% EtOAc/hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  7.37–7.27 (m, 5H), 7.15–7.11 (m, 2H), 7.00–6.95 (m, 2H), 4.87 (ddd,  $J = 3.0, 7.0, 7.0$  Hz, 1H), 3.00 (d,  $J = 6.7$  Hz, 2H), 1.92 (d,  $J = 3.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  162.7, 160.7, 143.6, 133.6 (d,  $J = 3.0$  Hz, 1C), 130.9 (d,  $J = 8.0$  Hz, 1C), 128.4 (2C), 127.7, 125.9 (2C), 115.3, 115.1, 75.4, 45.0. Spectroscopy is equivalent to previously reported data.<sup>3</sup>

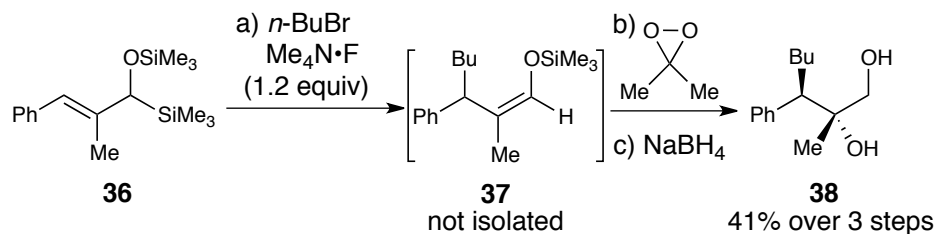


**Methyl 3-(5-chloro-1-hydroxypentyl)benzoate (28)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4e** (186 mg, 0.6 mmol), 1-bromo-4-chlorobutane (154 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 71 mg (46%) of **28** after flash chromatography (25% EtOAc/hexanes). FTIR (film); 3430, 2995, 2950, 2866, 1721, 1605, 1589, 1434, 1287, 1201, 1108, 913, 756  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  8.01 (t,  $J = 1.7$  Hz, 1H), 7.95 (dt,  $J = 7.7, 1.4$  Hz, 1H), 7.55 (dt,  $J = 7.7, 1.2$  Hz, 1H), 7.43 (t,  $J = 7.7$  Hz, 1H), 4.75 (ddd,  $J = 7.7, 5.1, 3.0$  Hz, 1H), 3.92 (s, 3H), 3.52 (t,  $J = 6.7$  Hz, 2H), 2.00 (d,  $J = 3.3$  Hz, 1H), 1.84–1.70 (m, 4H), 1.63–1.54 (m, 1H), 1.48–1.40 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  167.0, 145.0, 130.37, 130.31, 128.8, 128.6, 127.0, 73.9, 52.2, 44.8, 38.3, 32.4, 23.1. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{13}\text{H}_{18}\text{ClO}_3$ )<sup>+</sup>: 257 Found:  $[\text{M}+\text{H}]^+$  257.

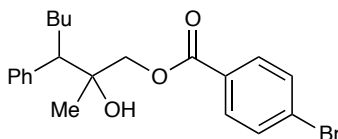


**Methyl 3-(1-hydroxy-4-(4-(methoxycarbonyl)phenoxy)butyl)benzoate (29)** Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **4e** (186 mg, 0.6 mmol), methyl 4-(3-bromopropoxy)benzoate (246 mg, 0.9 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford 123 mg (57%) of **29** after flash chromatography (25% EtOAc/hexanes). FTIR (film); 3479, 2996, 2951, 2875, 1718, 1605, 1511, 1434, 1284, 1254, 1169, 969, 847, 771, 756  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ );  $\delta$  8.04 (t,  $J = 1.7$  Hz, 1H), 7.98–7.94 (m, 3H), 7.59–7.58 (m, 1H), 7.43 (t,  $J = 7.7$  Hz, 1H), 6.90–6.87 (m, 2H), 4.84 (dt,  $J = 6.9, 3.7$  Hz, 1H), 4.07–4.00 (m, 2H), 3.93 (s, 3H), 3.87 (s, 3H), 2.17 (d,  $J = 3.4$  Hz, 1H), 1.99–1.93

(m, 3H), 1.88-1.83 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  166.96, 166.85, 162.6, 144.8, 131.6(2C), 130.37, 130.33, 128.84, 128.64, 127.0, 122.5, 114.0(2C), 73.7, 67.8, 52.2, 51.9, 35.6, 25.4. MS (ESI);  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{20}\text{H}_{23}\text{O}_6$ ): 359 Found:  $[\text{M}+\text{H}]^+$  359.



**2-Methyl-3-phenylheptane-1,2-diol (38)** To a flame-dried 2 dram vial containing a magnetic stirring bar in a glove box was added  $\alpha$ -silyl silylether **36** (176 mg, 0.6 mmol, 1 equiv), butyl bromide (100  $\mu\text{L}$ , 0.9 mmol), and THF (1.5 mL). To the stirred solution was added TMAF (66.0 mg, 0.72 mmol, 1.2 equiv). The vial was capped and the reaction was allowed to stir at ambient temperature overnight (~14 hours). The reaction was removed from the glove box and filtered quickly through a pad of celite into a 10 mL round-bottom flask with magnetic stirbar. The pad was rinsed with ~5 mL dry THF. The flask was capped, purged with nitrogen and cooled to  $-78^\circ\text{C}$  by dry ice/acetone bath. To the cooled solution was added DMDO (0.07 M in Acetone) at  $-78^\circ\text{C}$  dropwise via cannula. The reaction was allowed to stir for 3 hours at which point 0.5 mL 1M HCl was added and the reaction was extracted with diethyl ether (3 x 5 mL). The organic fractions were combined and the solvent was removed by rotary evaporation. The crude residue was diluted with methanol (5 mL), treated with sodium borohydride (30 mg, 0.8 mmol) and allowed to stir at ambient temperature for 1 hour. The solvent was removed and the residue was subject to flash chromatography (15 to 50% EtOAc/hexanes) on silica gel to afford the inseparable products as a 1:1 mixture of diastereomers (55 mg, 41%).  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.26 (s, 10H), 3.55 (dd,  $J = 11.1, 5.2$  Hz, 1H), 3.42 (ddd,  $J = 18.2, 11.1, 4.1$  Hz, 2H), 3.23 (dd,  $J = 10.7, 4.7$  Hz, 1H), 2.79 (ddd,  $J = 13.8, 11.8, 3.2$  Hz, 2H), 1.94-1.87 (m, 2H), 1.84-1.69 (m, 5H), 1.33-1.18 (m, 5H), 1.15 (s, 3H), 1.14 (s, 3H), 1.04 (m, 4H), 0.81 (d,  $J = 7.4$  Hz, 3H), 0.80 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  140.9, 140.1, 129.7(2C), 129.2, 128.37(2C), 128.23(2C), 126.9, 126.6(2C), 74.9, 74.5, 68.77, 68.71, 52.8, 52.3, 30.32, 30.19, 28.9, 28.2, 22.77, 22.70, 21.6, 20.6, 13.98, 13.93.



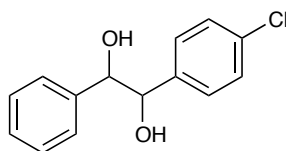
**2-Hydroxy-2-methyl-3-phenylheptyl 4-bromobenzoate** To a flame-dried 5 mL round-bottom flask with stirbar was added **38** (35 mg, 0.16 mmol) in pyridine (2.5 mL). 4-Bromobenzoylchloride (48 mg, 0.22 mmol), triethylamine (76 mL, 0.59 mmol) and a spatula tip of 4-dimethylaminopyridine (~2 mg, cat.) were added sequentially. The reaction was capped, purged with nitrogen and stirred at ambient temperature for 3 hours. The solution was diluted with water (3 mL) extracted with diethyl ether (3 x 4 mL). The organic fractions were combined and washed with (aq. 3 mL) 0.2 M copper sulfate followed by water (3 mL) then brine (3 mL).



The ethereal solution was dried with anhydrous magnesium sulfate, filtered and concentrated. The crude benzoate products were separated by preparative reverse-phase HPLC.

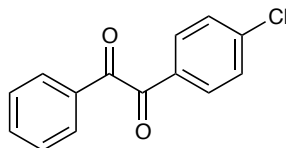
**Diastereomer 1:** FTIR (film); 3475, 2955, 2928, 2870, 2856, 1721, 1590, 1453, 1398, 1271, 1116, 1103, 1012, 996, 756, 702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.89 (ddd,  $J = 2.0, 9.0, 4.0$  Hz, 2H), 7.61 (ddd,  $J = 2.0, 9.0, 4.0$  Hz, 2H), 7.32-7.28 (m, 2H), 7.24 (m, 3H), 4.13 (s, 2H), 2.82 (dd,  $J = 12.0, 3.1$  Hz, 1H), 1.99-1.80 (m, 3H), 1.35-1.19 (m, 2H), 1.25 (s, 3H), 1.06 (m, 2H), 0.81 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ );  $\delta$  165.8, 140.3, 131.8(2C), 131.1(2C), 129.3, 128.8, 128.4(2C), 128.3, 126.9, 74.0, 70.8, 53.6, 30.3, 29.7, 28.3, 22.7, 21.8, 14.0. MS (ESI)  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{21}\text{H}_{25}\text{BrO}_3$ ) $^+$ : 404, 406 Found:  $[\text{M}]^+$  404, 406.

**Diastereomer 2:** FTIR (film); 3495, 2955, 2930, 2856, 1720, 1590, 1454, 1397, 1383, 1271, 1116, 1012, 756, 702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.75 (ddd,  $J = 3.0, 10.0, 5.0$  Hz, 2H), 7.46 (ddd,  $J = 3.0, 10.0, 5.0$  Hz, 2H), 7.19 (m, 2H), 7.12-7.10 (m, 3H), 4.06 (d,  $J = 11.0$  Hz, 1H), 4.00 (d,  $J = 11.0$  Hz, 1H), 2.67 (t,  $J = 7.7$  Hz, 1H), 1.74-1.69 (m, 2H), 1.20-1.14 (m, 1H), 1.16 (s, 3H), 1.13-1.05 (m, 2H), 0.94-0.87 (m, 2H), 0.66 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  165.8, 139.9, 131.8(2C), 131.1(2C), 129.5(C), 128.8, 128.40(2C), 128.3, 127.0, 73.7, 70.7, 53.2, 30.2, 28.7, 23.0, 22.7, 13.9. MS (ESI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{21}\text{H}_{25}\text{BrO}_3$ ) $^+$ : 404, 406 Found:  $[\text{M}]^+$  404, 406.

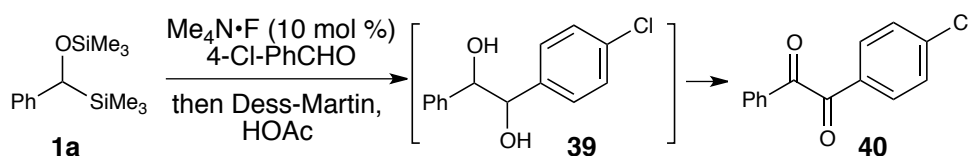


**1-(4'-chlorophenyl)-2-phenylethane diol (39)** To a flame-dried 2 dram vial containing a magnetic stirring bar in a glove box was added  $\alpha$ -silyl silylether **1** (150 mg, 0.6 mmol), 4-chlorobenzaldehyde (84.0 mg, 0.6 mmol), and DMA (1.0 mL). To the stirred solution was added TMAF (6.0 mg, .06 mmol). The vial was capped and stirred for 12 hours. The vial was removed from the glove box and treated with 1N HCl (1mL). After stirring at room temperature for 15 min, this solution was diluted with diethyl ether (20 mL) and brine (10 mL). The aqueous layer was discarded and the resulting ether layer was dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated in vacuo to provide the unpurified diol. The product was purified by flash chromatography (20% EtOAc/hexanes) on silica gel to afford 108 mg (72%) of **39**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ); 7.32-7.11 (bm, 7H), 7.05 (d,  $J = 2.1$  Hz, 1H), 7.03 (d,  $J = 1.9$  Hz, 1H), 4.86-4.83 (m, 2H), 4.71 (dd,  $J = 7.5, 2.1$  Hz, 1H), 4.65 (dd,  $J = 7.6, 2.5$  Hz, 1H), 2.92 (d,  $J = 1.7$  Hz, 1H), 2.72 (d,  $J = 2.5$  Hz, 1H), 2.24 (d,  $J = 2.7$  Hz, 1H), 2.19 (d,  $J = 2.6$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  139.45, 139.32, 138.18, 138.12, 133.69, 133.56, 128.41, 128.29, 128.25, 128.23, 128.21, 128.15, 126.96(2C), 126.92(2C), 79.2, 78.5, 77.93, 77.91. Spectroscopy is equivalent to previously reported data.<sup>11</sup>

<sup>11</sup> Bustillo, A. J.; Garcia-Pajon, C. M.; Aleu, J.; Hernandez-Galan, R.; Collado, I. G. *Tetrahedron: Asymmetry* **2003**, *14*, 3755-3760.



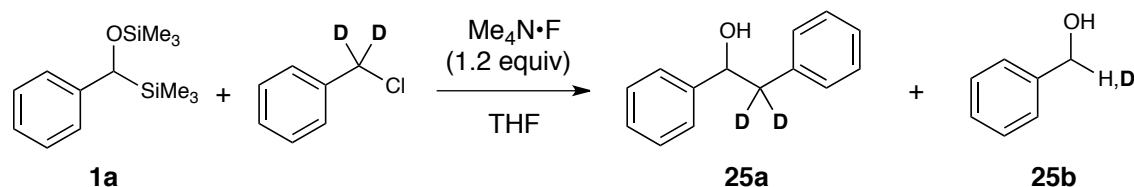
**1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (40)** To a flame dried 2-dram vial with stirbar was added **39** (35 mg, 0.14 mmol) and THF (1.5 mL). To the stirring colorless solution was added Dess-Martin periodinane (122 mg, 0.28 mmol) in one portion. The yellow solution was capped and allowed to stir at room temperature for 1 hour. The reaction was poured onto a 1:1 aqueous mixture of sodium bicarbonate/sodium thiosulfate (5 mL) and stirred for 20 minutes. The aqueous mixture was extracted with diethyl ether (3 x 3 mL). The organic fractions were combined, dried with anhydrous  $\text{MgSO}_4$ , filtered and concentrated to yield 26 mg (76%) the **40** as a yellow solid.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.97 (q,  $J = 1.4$  Hz, 1H), 7.95 (t,  $J = 1.6$  Hz, 1H), 7.93 (t,  $J = 2.1$  Hz, 1H), 7.92 (t,  $J = 2.1$  Hz, 1H), 7.67 (app tt,  $J = 7.5, 1.3$  Hz, 1H), 7.54-7.49 (bm, 3H), 7.48 (t,  $J = 1.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  193.8, 193.0, 141.6, 135.1, 132.7, 131.25, 131.19(2C), 129.9(2C), 129.4(2C), 129.0(2C). Spectroscopy is equivalent to previously reported data.<sup>12</sup>



**1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (40)** To a flame-dried 2 dram vial containing a magnetic stirring bar in a glove box was added  $\alpha$ -silyl silylether **1a** (150 mg, 0.6 mmol), 4-chlorobenzaldehyde (84 mg, 0.6 mmol), and DMA (1.5 mL). To the stirred solution was added TMAF (6 mg, 0.06 mmol). The vial was capped and stirred for 16 hours. The vial was removed from the glove box, and treated Dess-Martin periodinane (505 mg, 1.2 mmol) and acetic acid (0.5 mL). After stirring at room temperature for 1 hour, the yellowish solution was poured onto a 1:1 aqueous mixture of sodium bicarbonate/sodium thiosulfate (5 mL) and stirred for 20 minutes. The aqueous mixture was extracted with diethyl ether (3 x 3 mL). The organic fractions were combined, dried with anhydrous  $\text{MgSO}_4$ , filtered and concentrated. The product was purified by flash chromatography (20% EtOAc/hexanes) on silica gel to afford 76 mg (53%) of **40** as a yellow solid. Spectra were identical to above.

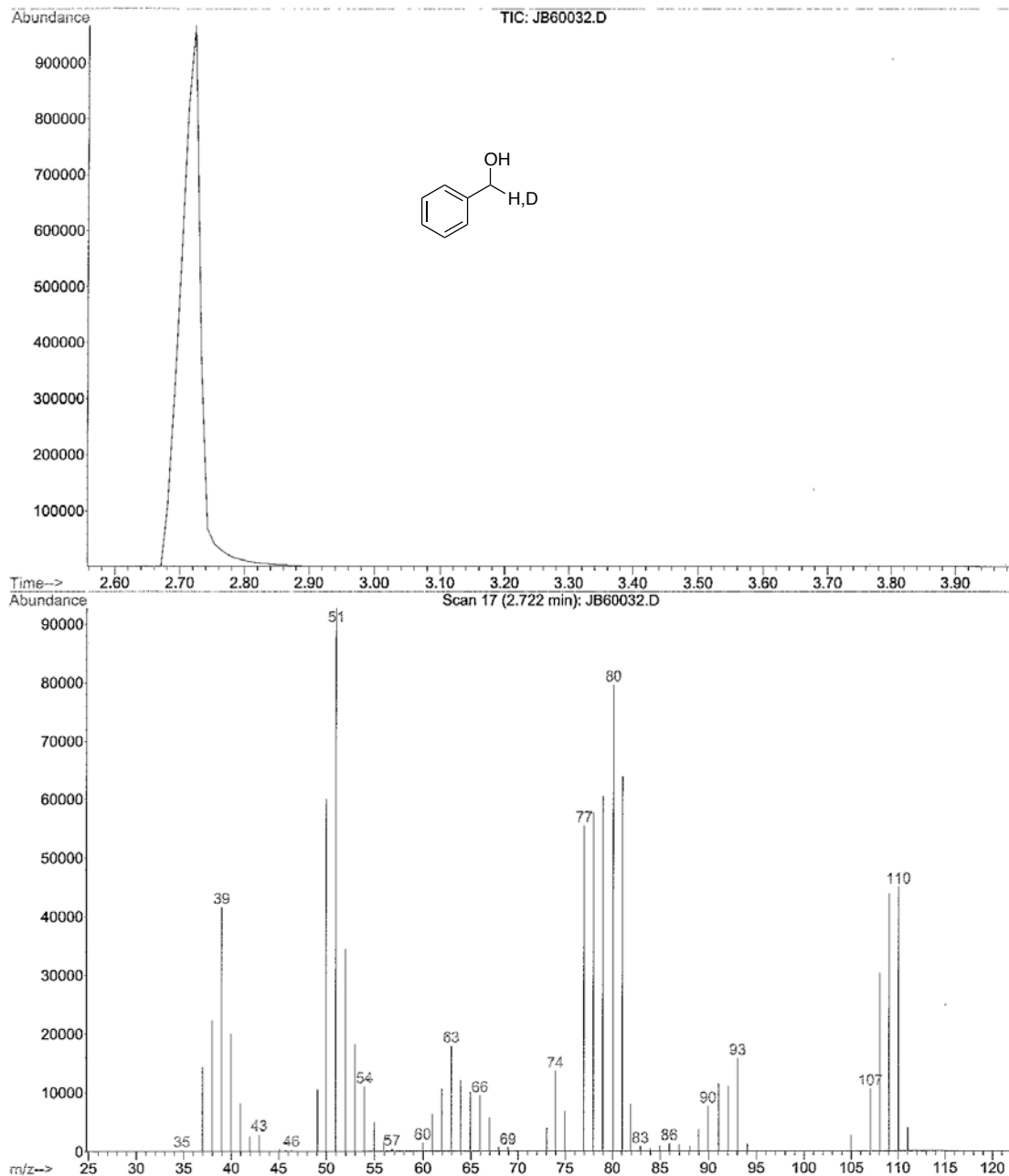
<sup>12</sup> Wan, Z. H.; Jones, C. D.; Mitchell, D.; Pu, J. Y.; Zhang, T. Y. *J Org Chem* **2006**, 71, 826-828.

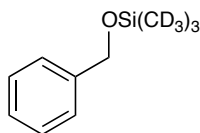
## Labeling Experiments



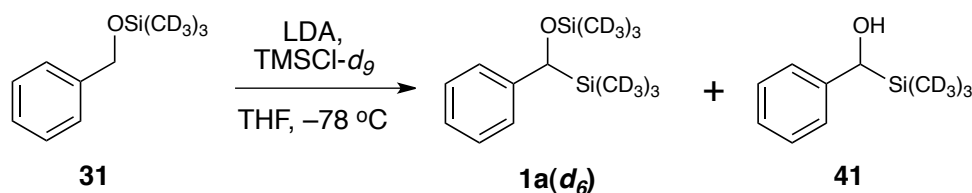
Prepared according to the general procedure (II) using  $\alpha$ -silyl silylether **1a** (150 mg, 0.6 mmol), benzyl- $\alpha,\alpha$ - $d_2$  chloride (76 mg, 0.6 mmol), and tetramethylammonium fluoride (66.0 mg, 0.72 mmol) in THF (1.5 mL) to afford after flash chromatography (20% EtOAc/hexanes) 40 mg (33%) of **25a** as a white solid as well as 5.0 mg (8%) of **25b** as a colorless oil. **25a**: FTIR (film); 3393, 3060, 3027, 2879, 1949, 1878, 1807, 1753, 1603, 1494, 1449, 1091, 1056, 755, 698  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.38-7.34 (m, 4H), 7.33-7.28 (m, 3H), 7.27-7.23 (m, 1H), 7.21 (dt,  $J$  = 8.1, 1.8 Hz, 2H), 4.89 (s, 1H), 1.99 (d,  $J$  = 2.5 Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ );  $\delta$  143.7, 137.9, 129.5, 128.48(2C), 128.38(2C), 127.6, 126.6(2C), 125.9(2C), 75.2, 45.6(m, 1C). MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_{14}\text{H}_{12}\text{D}_2\text{O}$ ) $^+$ : 200 Found:  $[\text{M}]^+$  200. **25b**:  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ );  $\delta$  7.37 (m, 5H), 7.30 (m, 2H), 4.69 (s, 2H), 4.67 (s, 1H), 1.79 (s, 1H). MS (EI);  $m/z$  calcd for  $[\text{M}]^+$  ( $\text{C}_7\text{H}_6\text{DO}$ ) $^+$ : 108 Found:  $[\text{M}]^+$  108.

File : C:\HPCHEM\1\DATA\BREKAN\JB60032.D  
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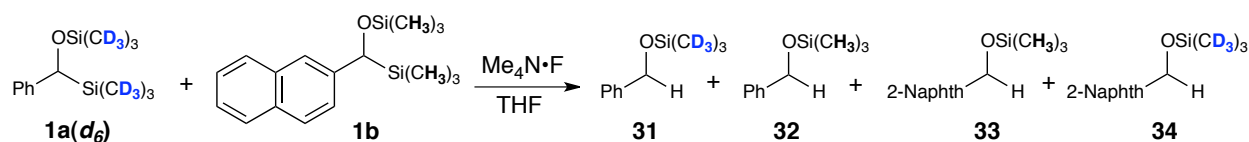


**Benzyloxy- $d_9$ -trimethylsilane (**31**)** In a 5 mL round-bottomed flask was added benzyl alcohol (88.0 mg, 0.8 mmol) and chlorotrimethylsilane- $d_9$  (100 mg, 0.85 mmol) in THF (2.0 mL). Imidazole (110 mg, 1.6 mmol) was added against a positive flow of nitrogen. The cloudy solution was stirred for 30 minutes. The reaction mixture was diluted with diethyl ether (5 mL). The organic solution was washed with brine (3 mL), H<sub>2</sub>O (3 mL), dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated. The product was purified by flash chromatography (5% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford 117 mg (76%) of **31** as colorless oil. FTIR (film); 3065, 3031, 2859, 2212, 1496, 1454, 1379, 1306, 1255, 1207, 1096, 1003, 835, 813, 729, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>);  $\delta$  7.35–7.32 (m, 4H), 7.28–7.23 (m, 1H), 4.70 (s, 2H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>);  $\delta$  140.9, 128.3(2C), 127.1, 126.5(2C), 64.6, -1.3(m, 3C). MS (ES);  $m/z$  calcd for [M]<sup>+</sup> (C<sub>10</sub>H<sub>7</sub>D<sub>9</sub>OSi)<sup>+</sup>: 189 Found: [M]<sup>+</sup> 189.



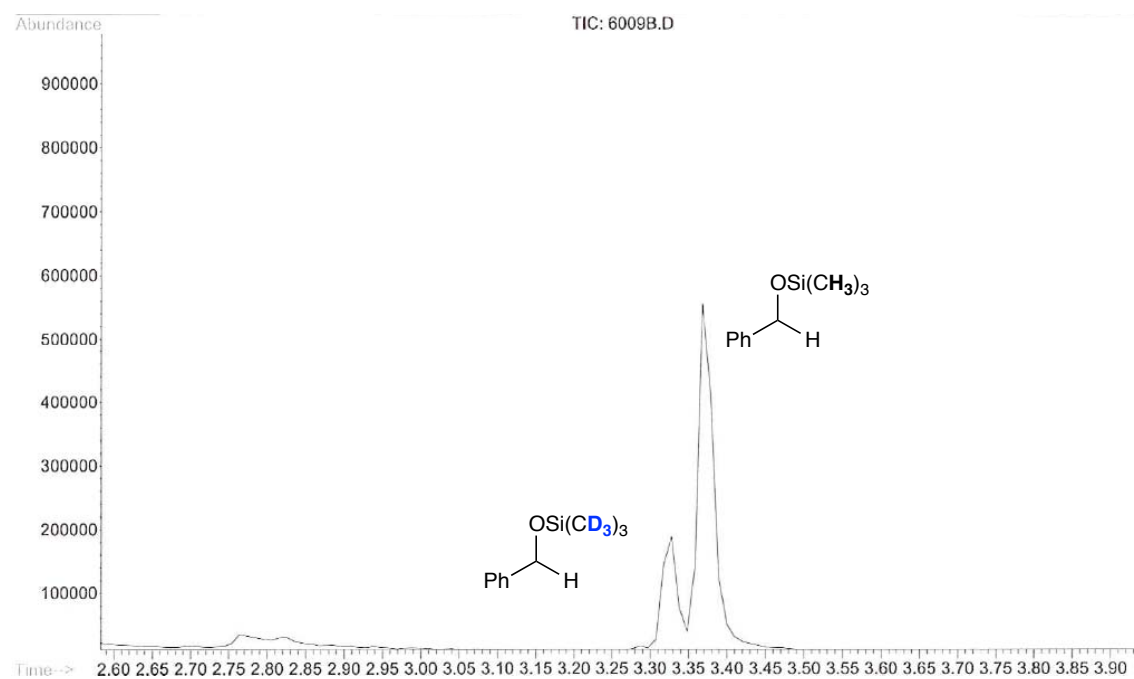
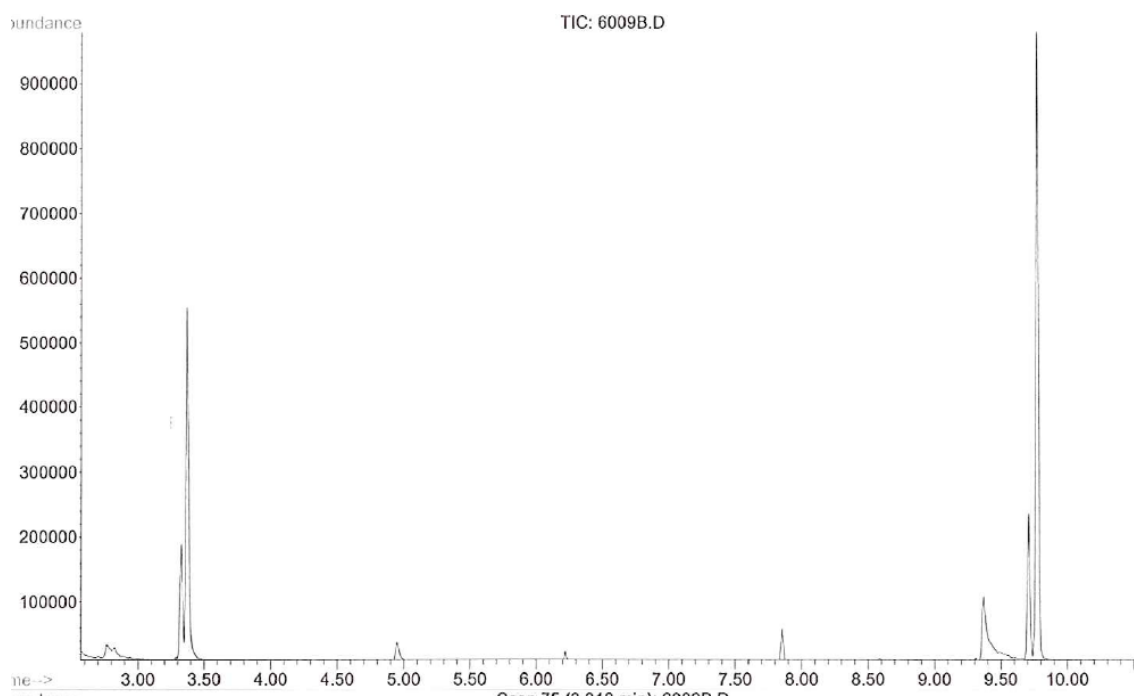
**$\alpha$ - $d_9$ -Trimethylsilyl- $\alpha$ - $d_9$ -trimethylsiloxytoluene (**1a(d<sub>6</sub>)**)** Prepared according to the general procedure (I) using **31** (117 mg, 0.62 mmol, 1 equiv), lithium diisopropylamide (generated from diisopropyl amine 115  $\mu$ L, 0.80 mmol, 1.3 equiv and 2.5 M *n*-butyllithium, 321  $\mu$ L, 0.80 mmol, 1.3 equiv) and chlorotrimethylsilane- $d_9$  (80.0 mg, 0.68 mmol, 1.1 equiv). The product was purified by flash chromatography (1% EtOAc/hexanes, 2% Et<sub>3</sub>N) on silica gel to afford **1a(d<sub>6</sub>)** (10 mg, 6%), **41** (52 mg, 45%), and **31** (25 mg, 21% recovery). (**1a(d<sub>6</sub>)**) <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>);  $\delta$  7.32–7.29 (m, 2H), 7.20–7.15 (m, 3H), 4.49 (s, 1H). (C<sub>13</sub>H<sub>6</sub>D<sub>18</sub>OSi<sub>2</sub>)<sup>+</sup>: 270 Found: [M]<sup>+</sup> 270. (**1a(d<sub>3</sub>)**) FTIR (film); 3415, 3061, 3025, 2836, 2211, 1599, 1492, 1449, 996, 774, 740, 701, 643 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>);  $\delta$  7.33–7.30 (m, 2H), 7.20–7.16 (m, 3H), 4.52 (s, 1H), 1.76 (s, 1H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>);  $\delta$  144.2, 128.1(2C), 125.7, 124.8(2C), 70.5, -5.1(3C). (ES);  $m/z$  calcd for [M]<sup>+</sup> (C<sub>10</sub>H<sub>7</sub>D<sub>9</sub>OSi)<sup>+</sup>: 189 Found: [M]<sup>+</sup> 189.

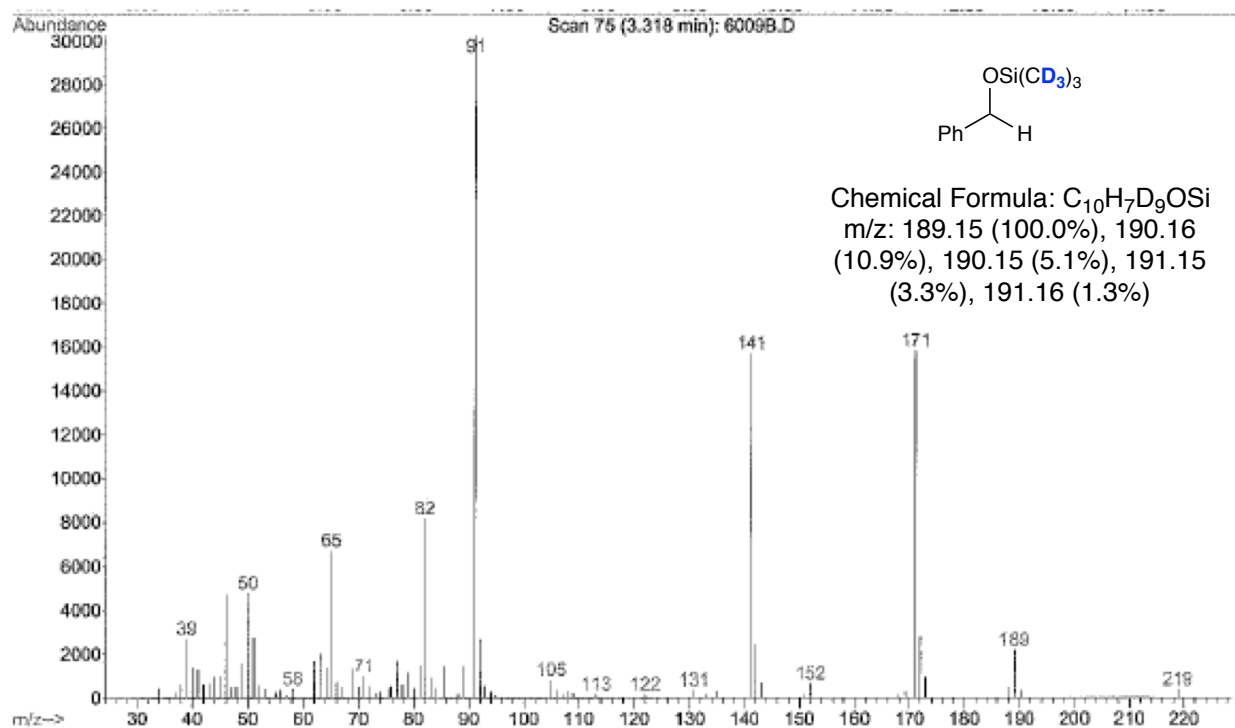
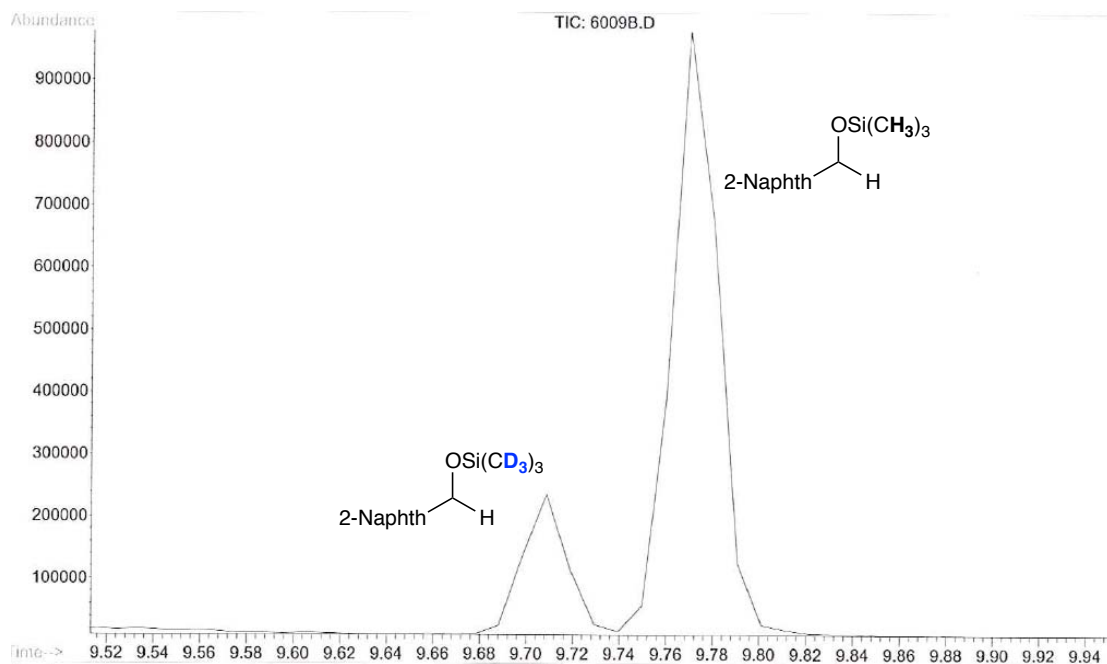
### Crossover Experiment



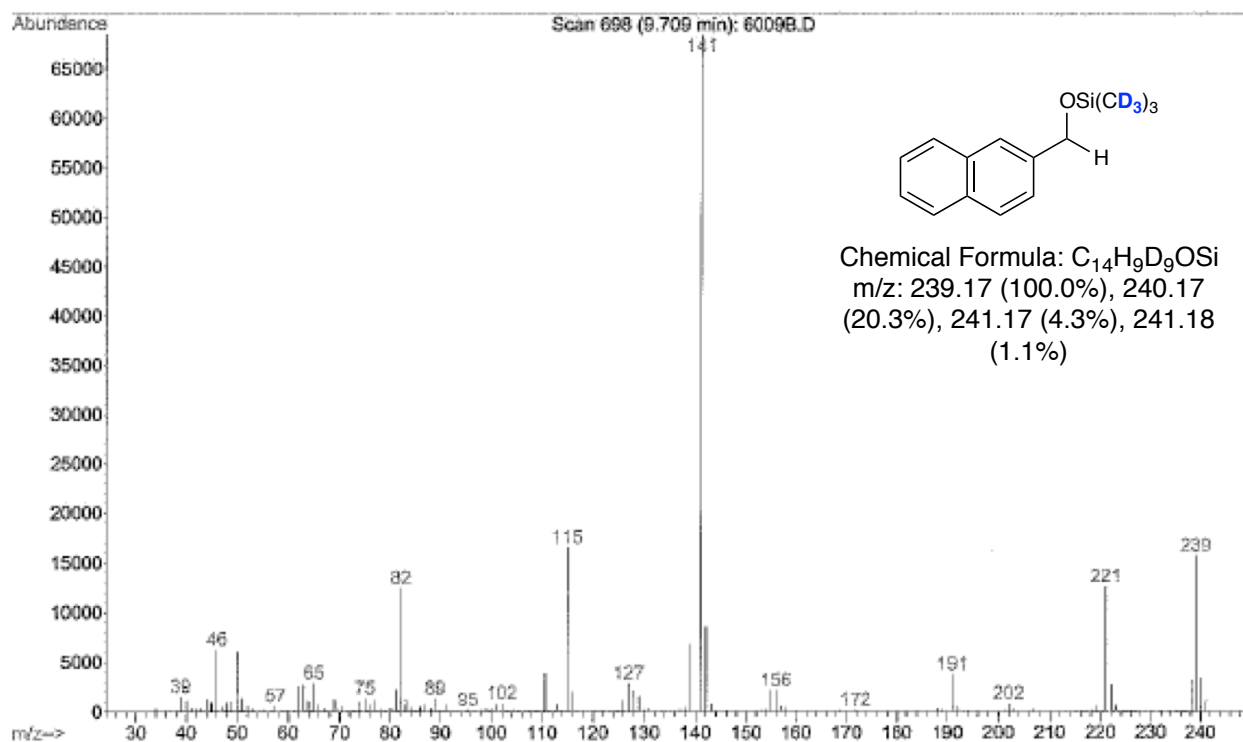
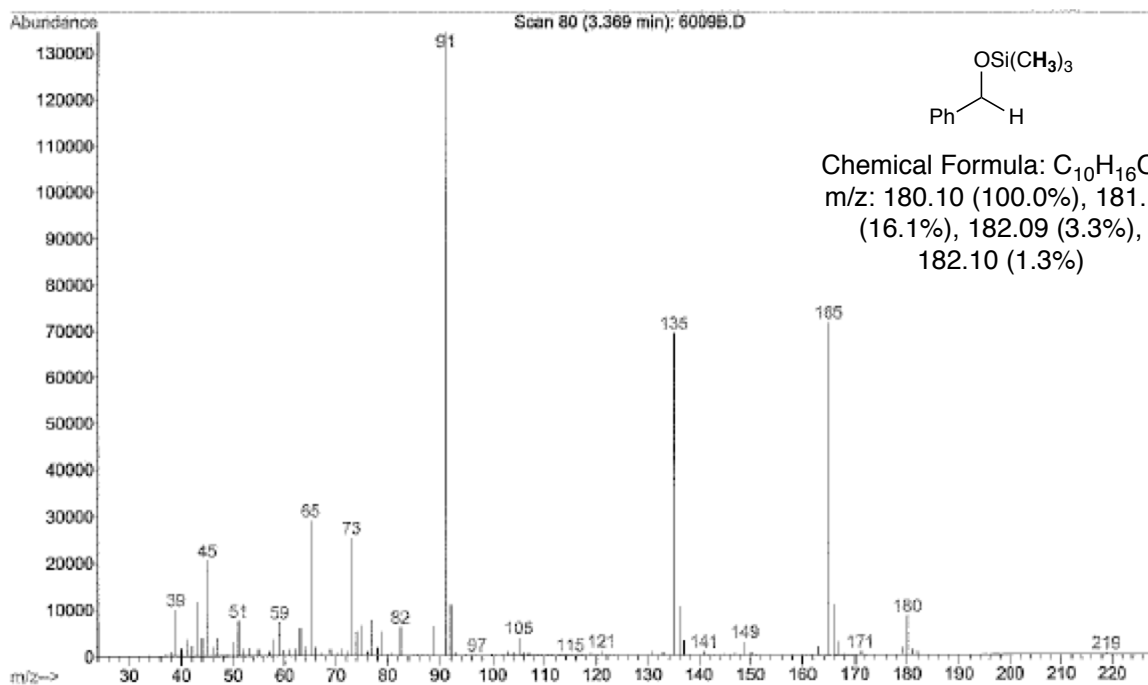
To a flame-dried 2 dram vial containing a magnetic stirring bar in a glove box was added  $\alpha$ -( $d_9$ )-silyl-( $d_9$ ) silylether **1a(d<sub>6</sub>)** (10.0 mg, 1 equiv),  $\alpha$ -silyl silylether **1b** (11.0 mg, 1 equiv) and THF (0.4 mL). Tetramethylammonium fluoride (4.0 mg, 1.1 equiv) was added in one portion. The yellow solution was capped and allowed to stir at ambient temperature. After one hour a 50  $\mu$ L

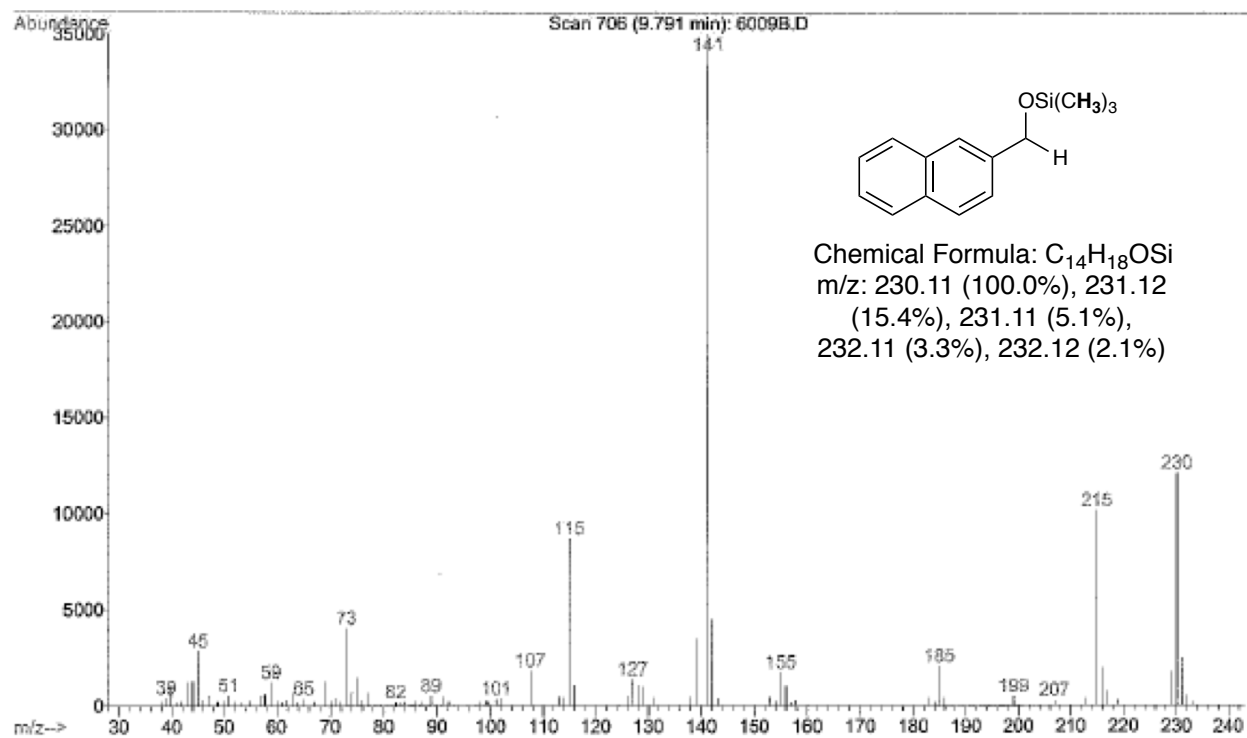
aliquot was taken, diluted with THF (0.5 mL) and analyzed by gas chromatography. HP-6890 gas chromatograph with 5972A mass spectrometer. DB-XLB column (30 meter, 0.25 I.D., 250 micron film thickness) Method: (start at 100 °C ramp to 140 °C @ 14 °C/min, hold at 140 °C for 2 min, then ramp to 250 °C @ 14 °C/min, hold at 250 °C for 5 min.)



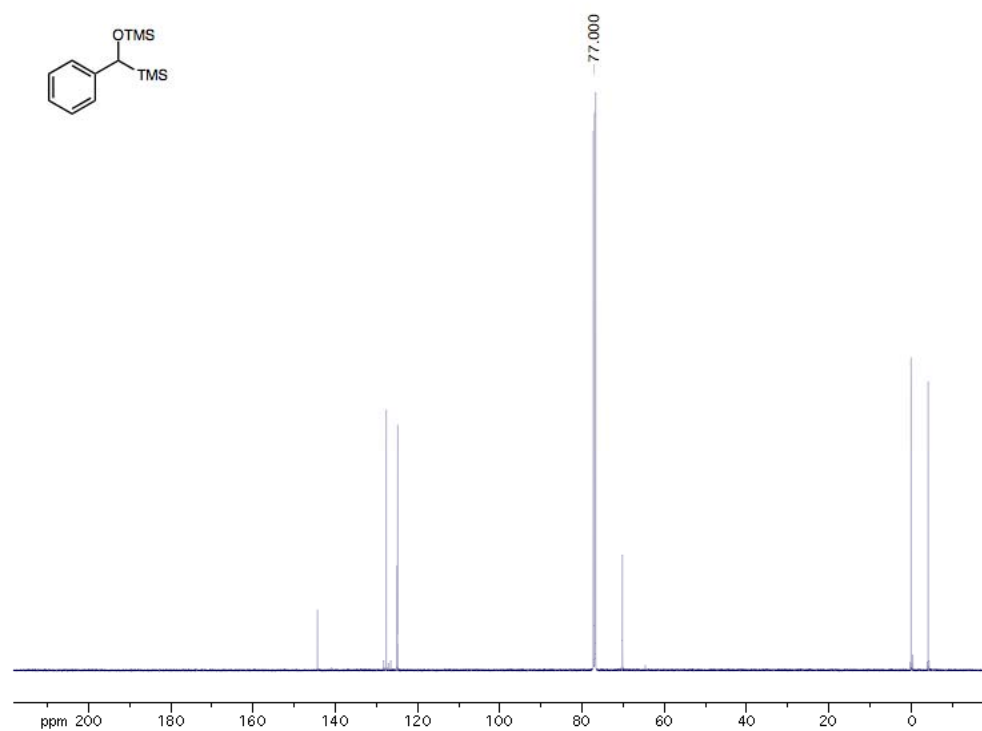
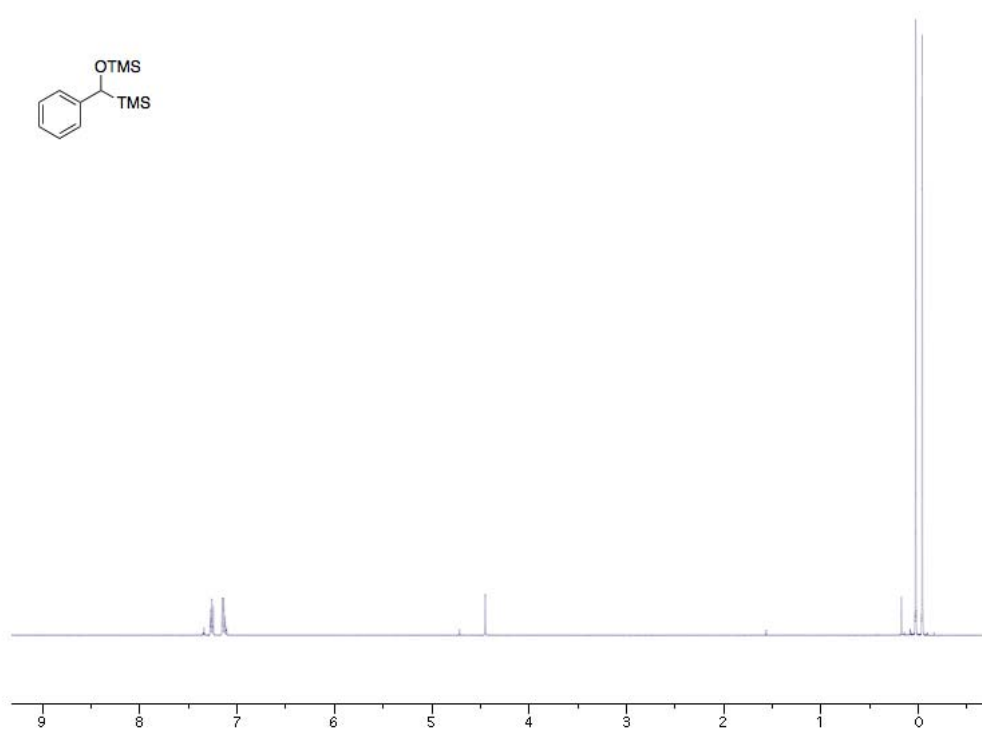


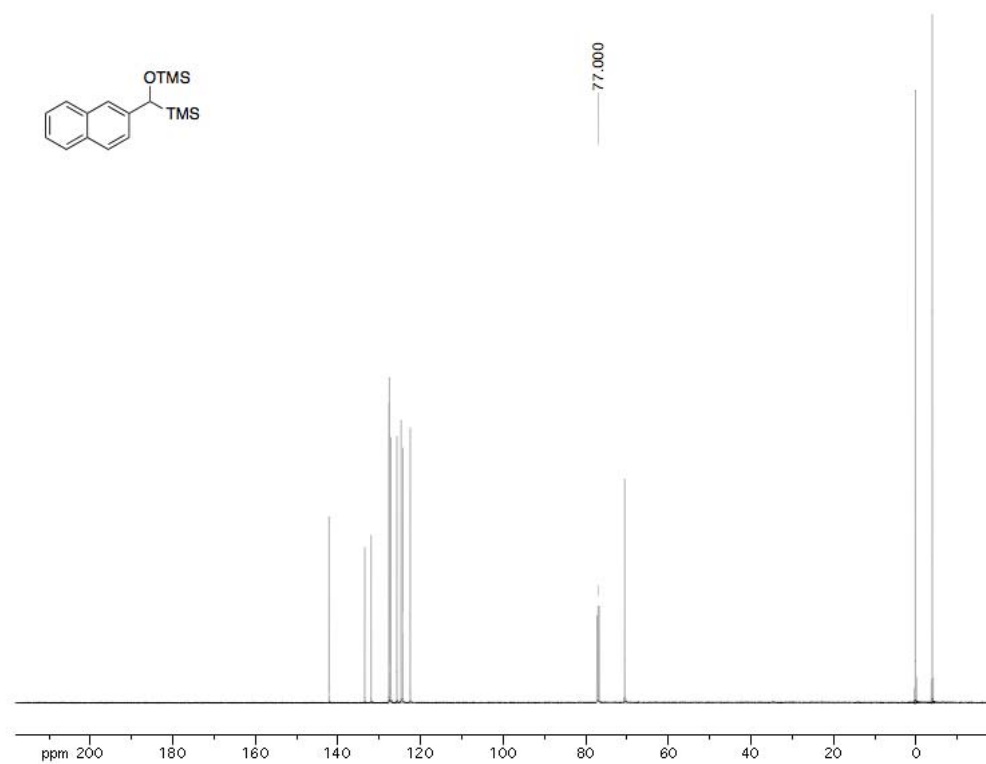
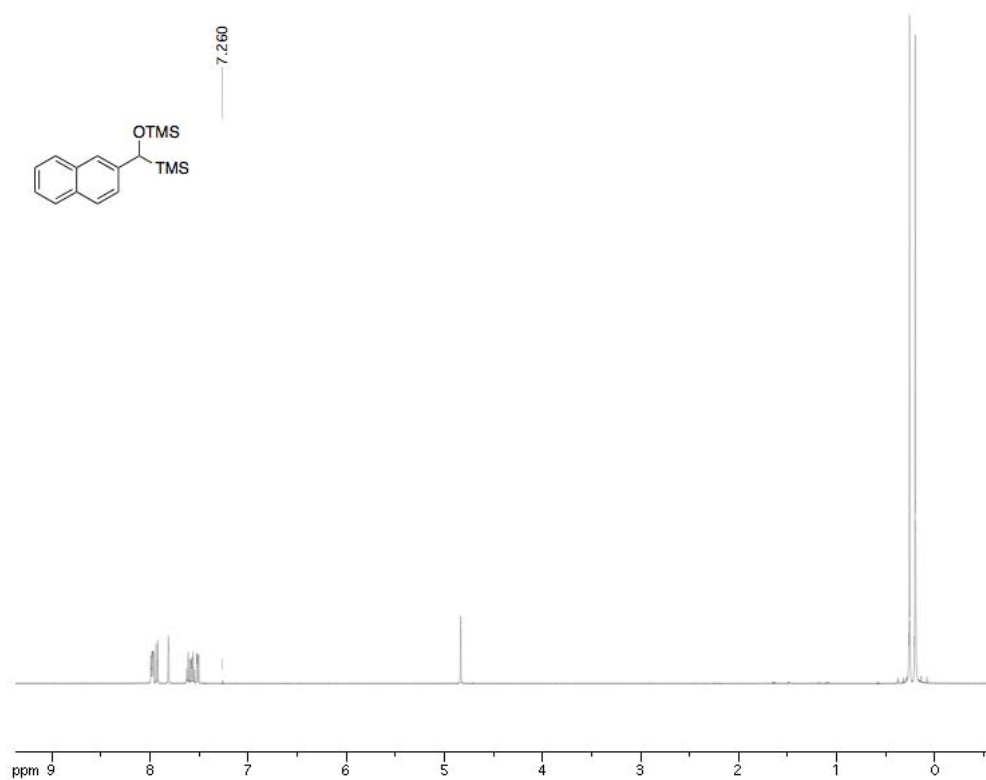


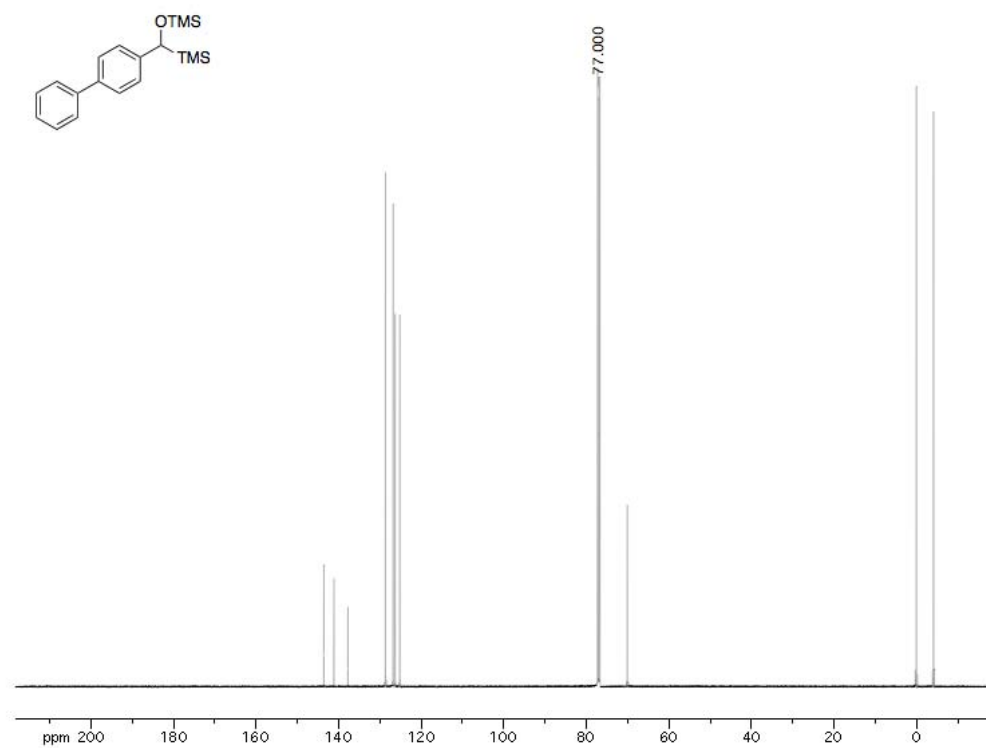
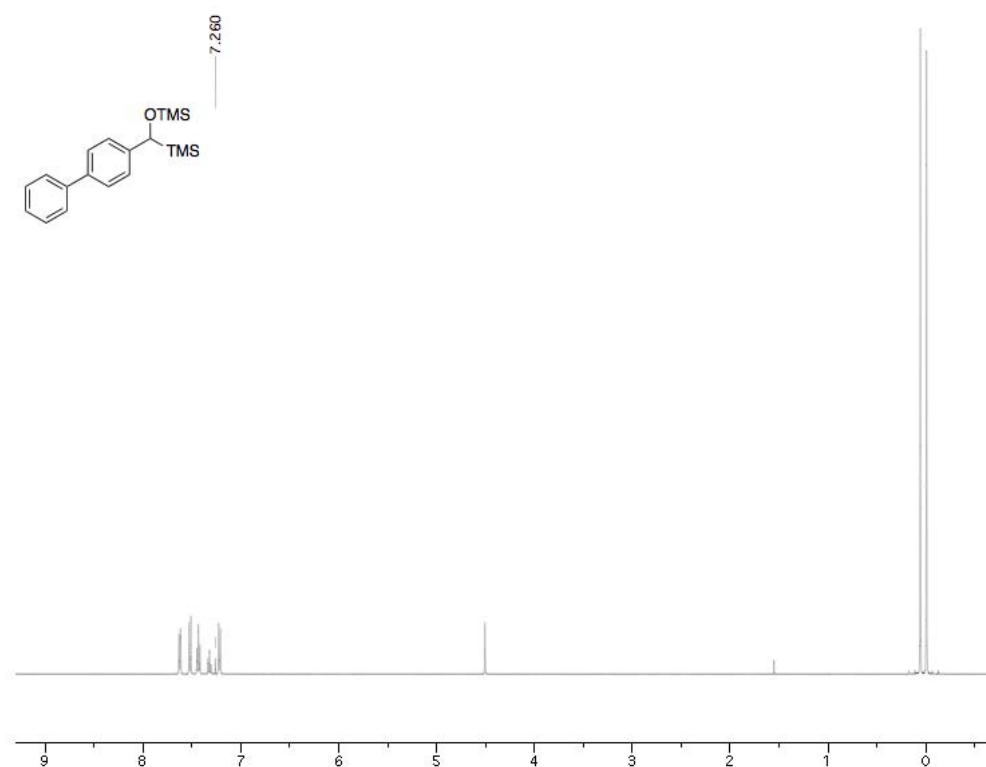


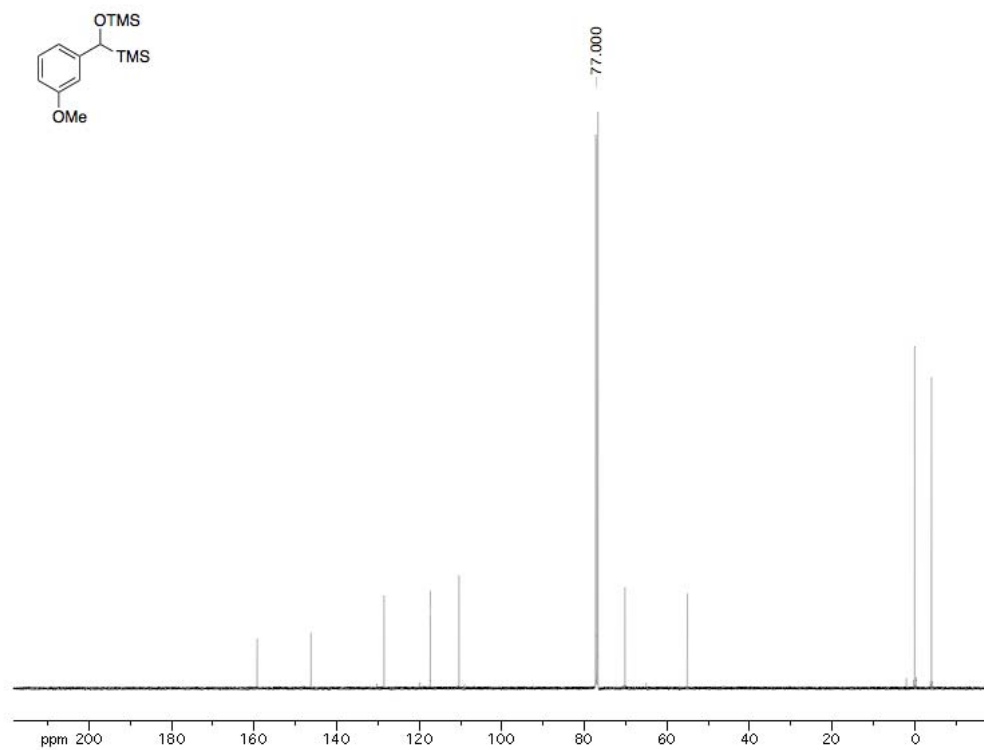
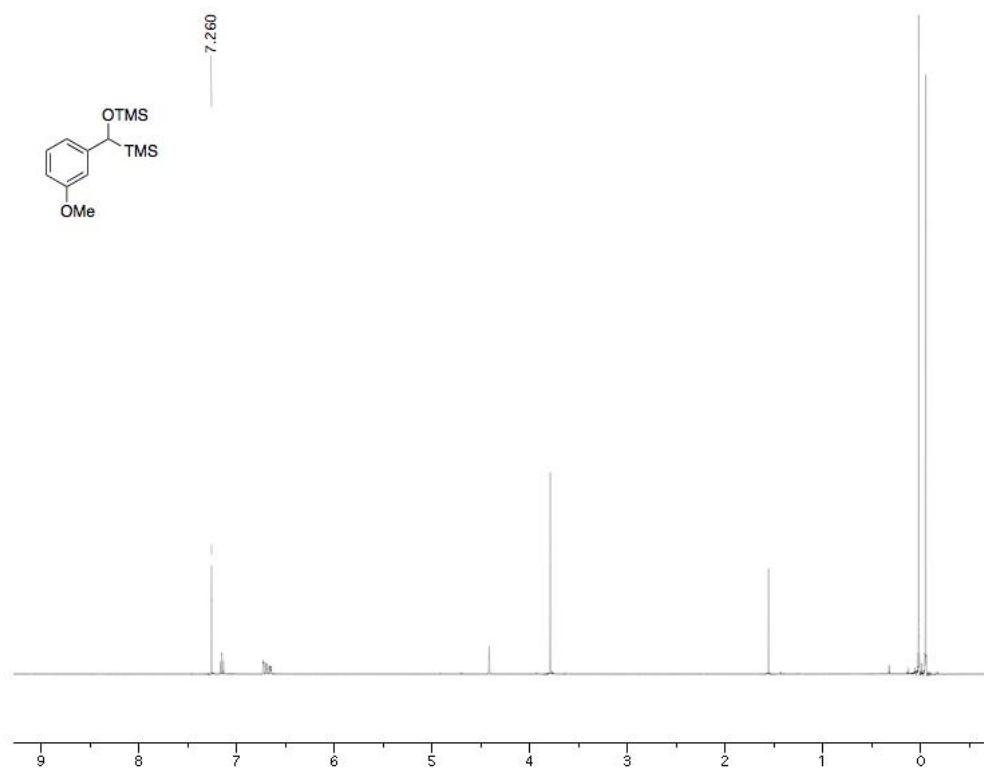


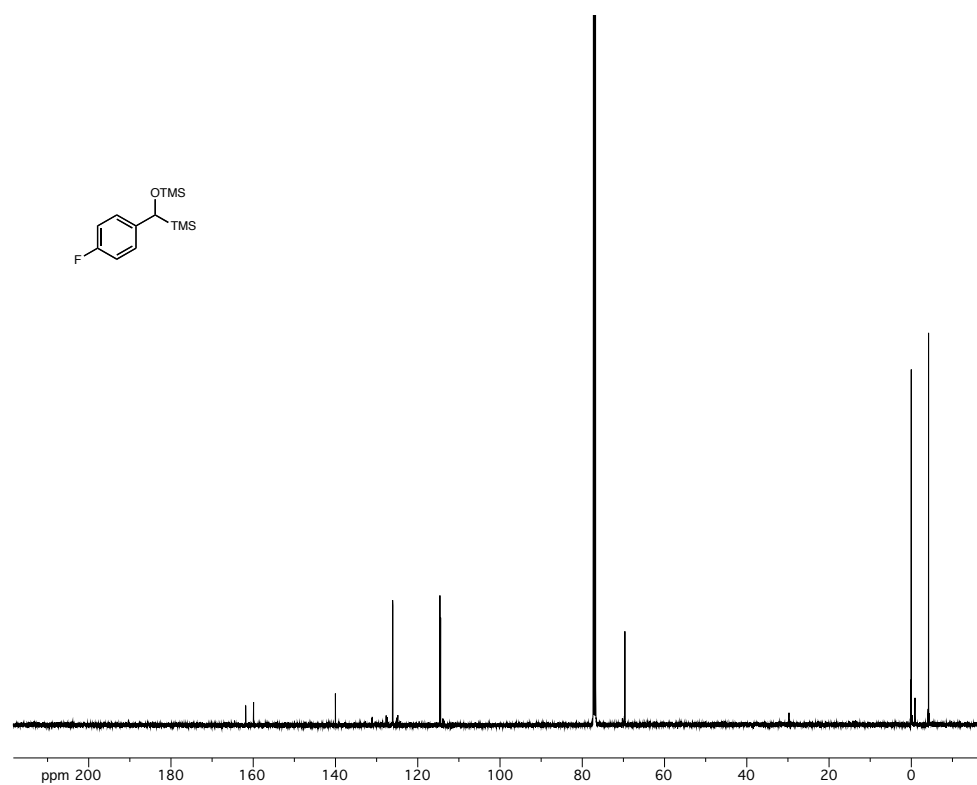
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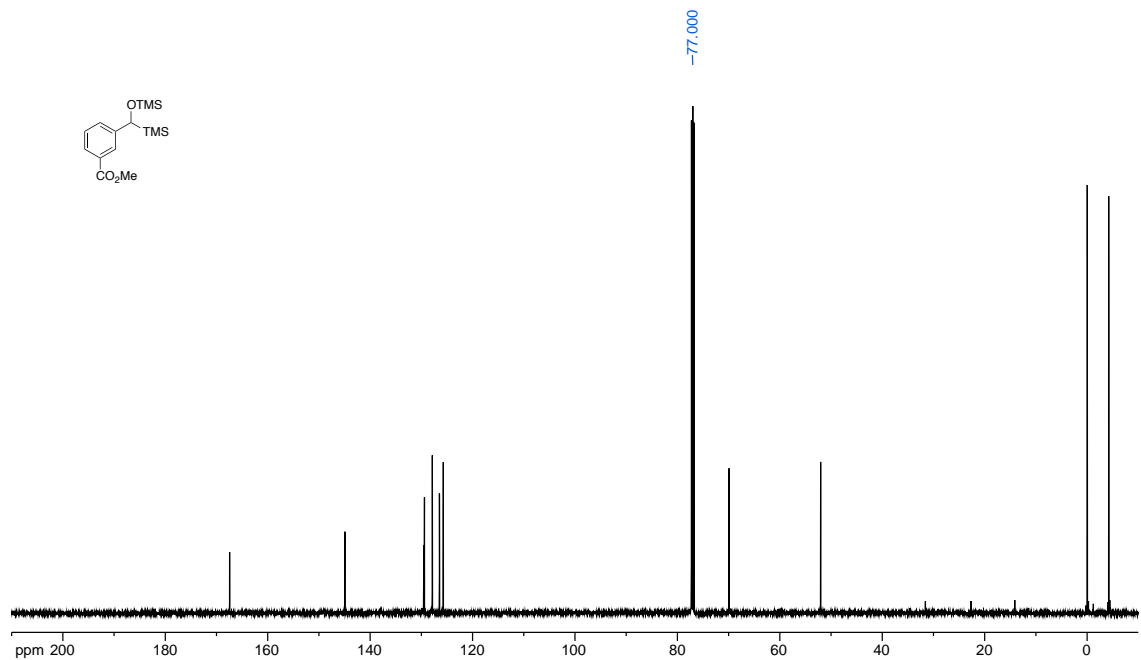
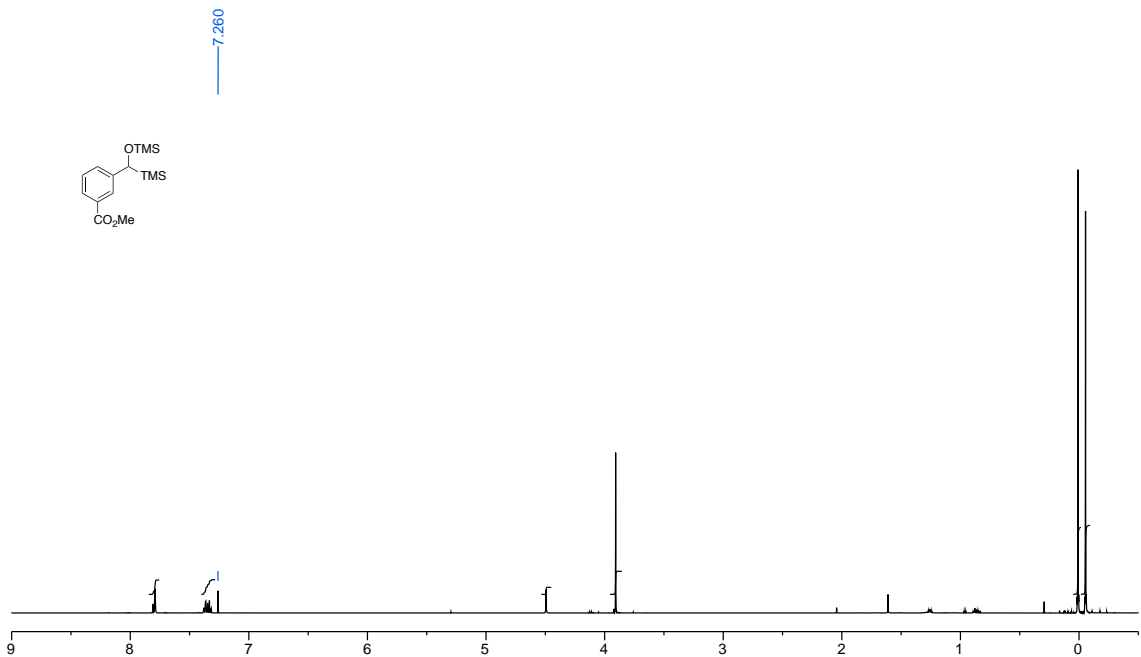


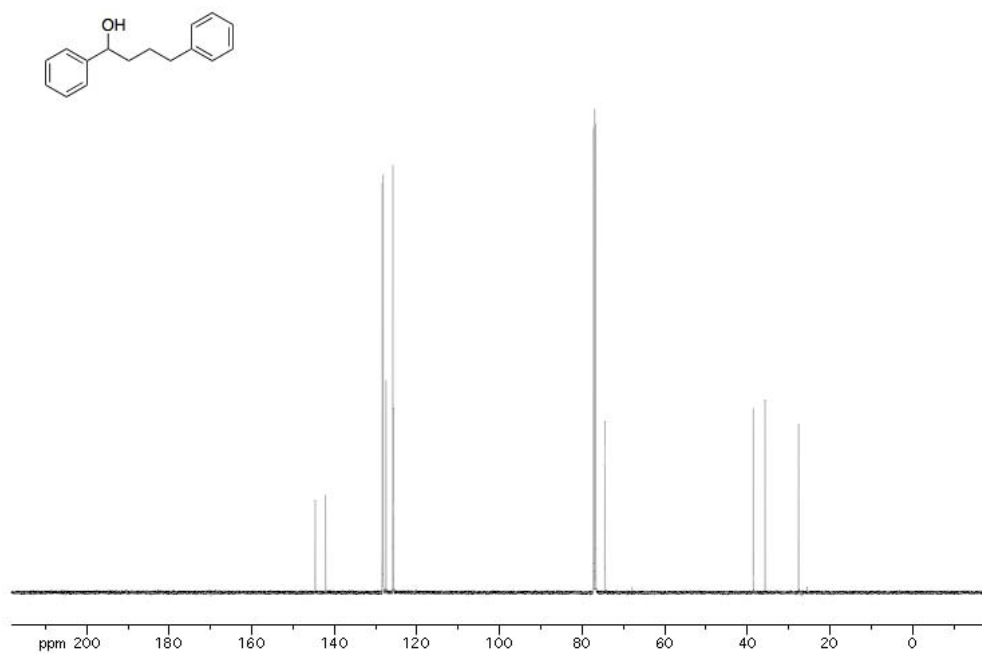
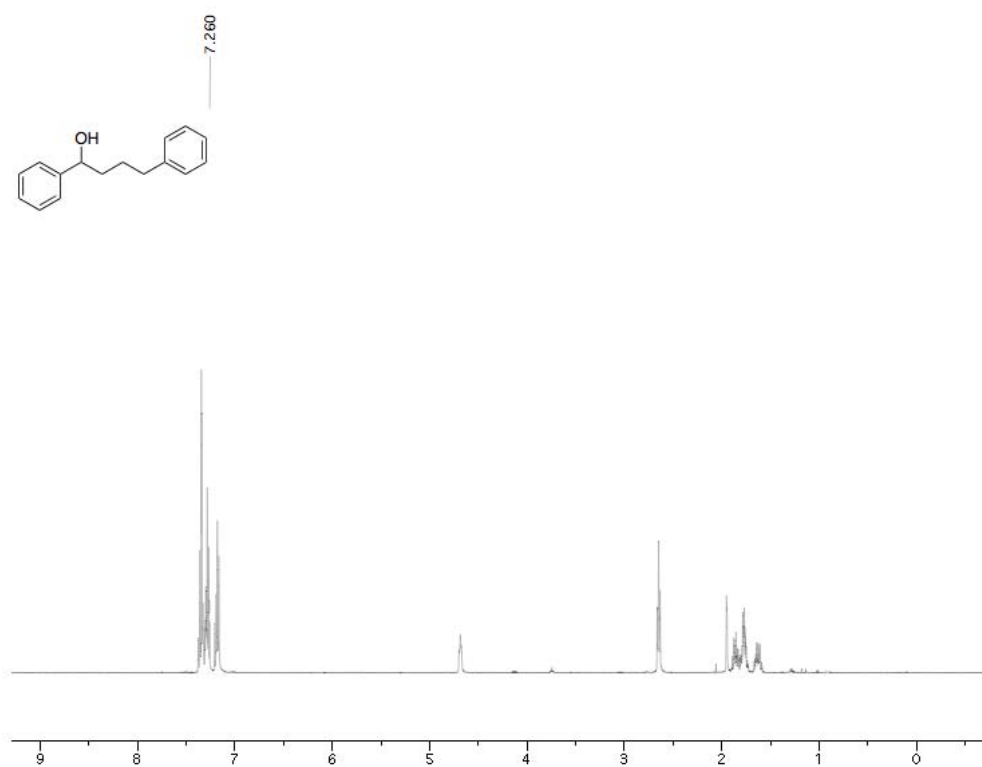


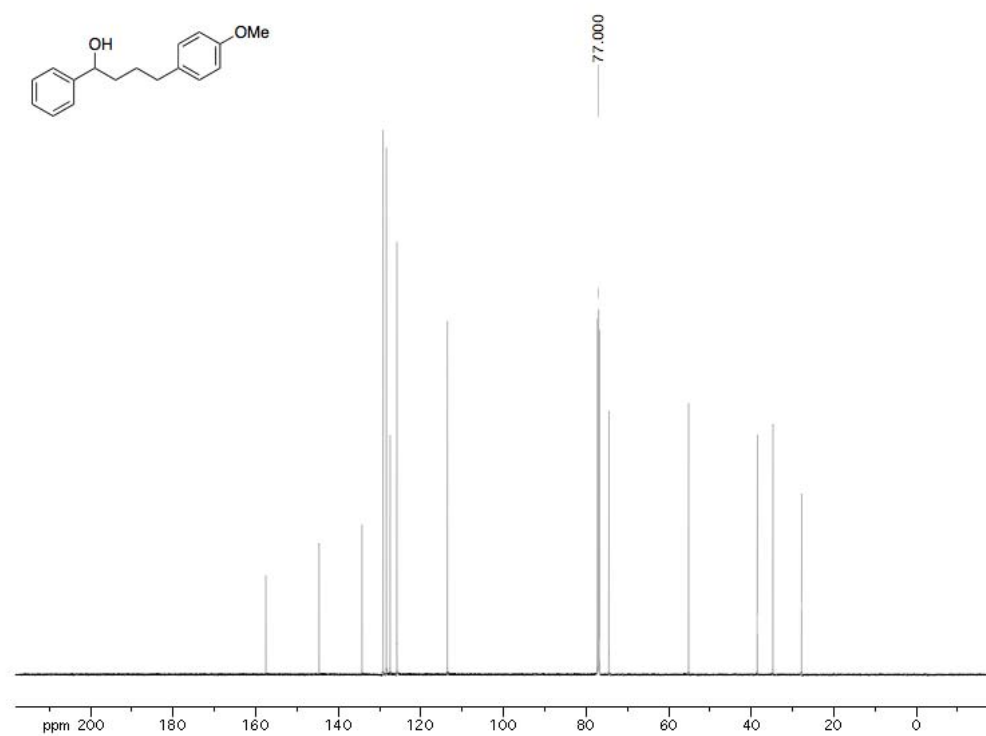
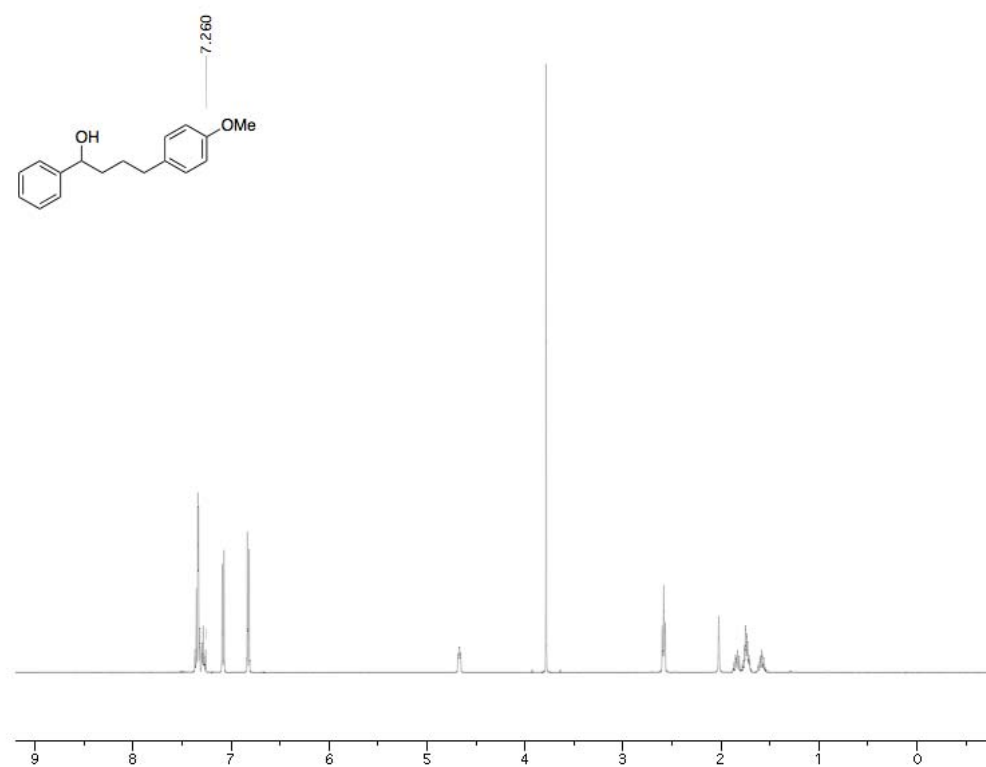


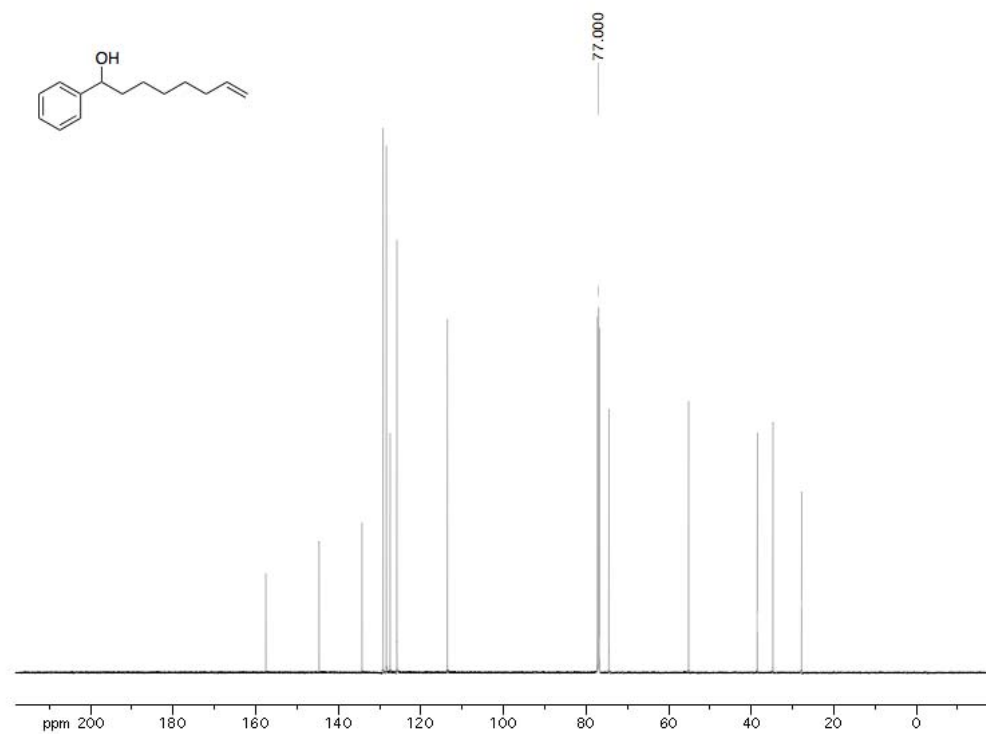
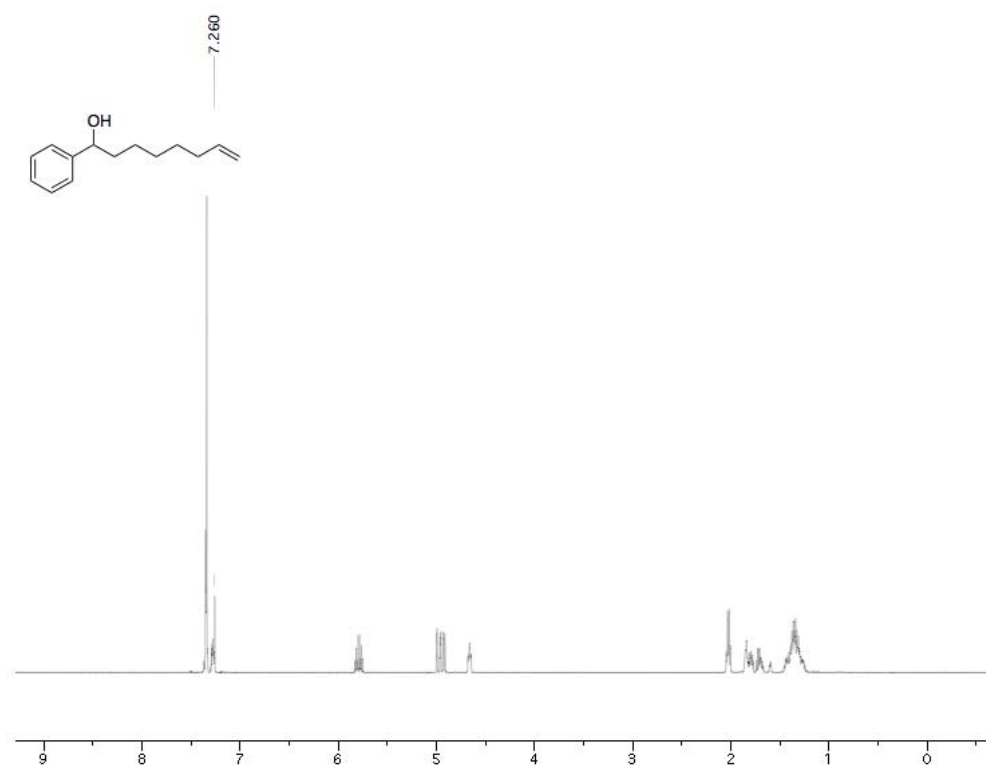


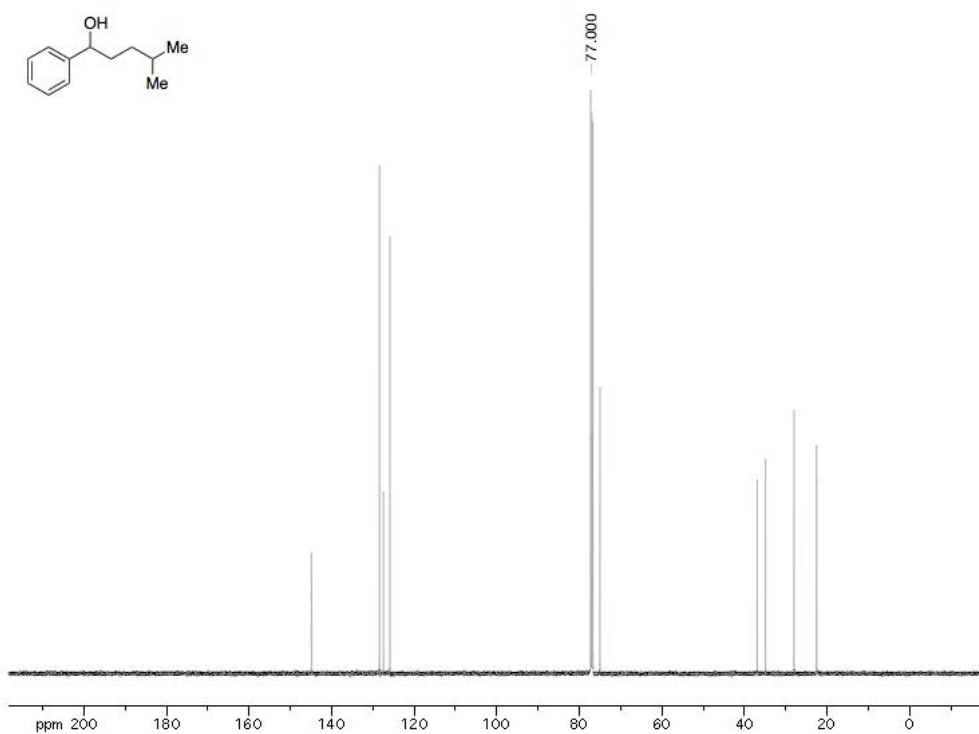
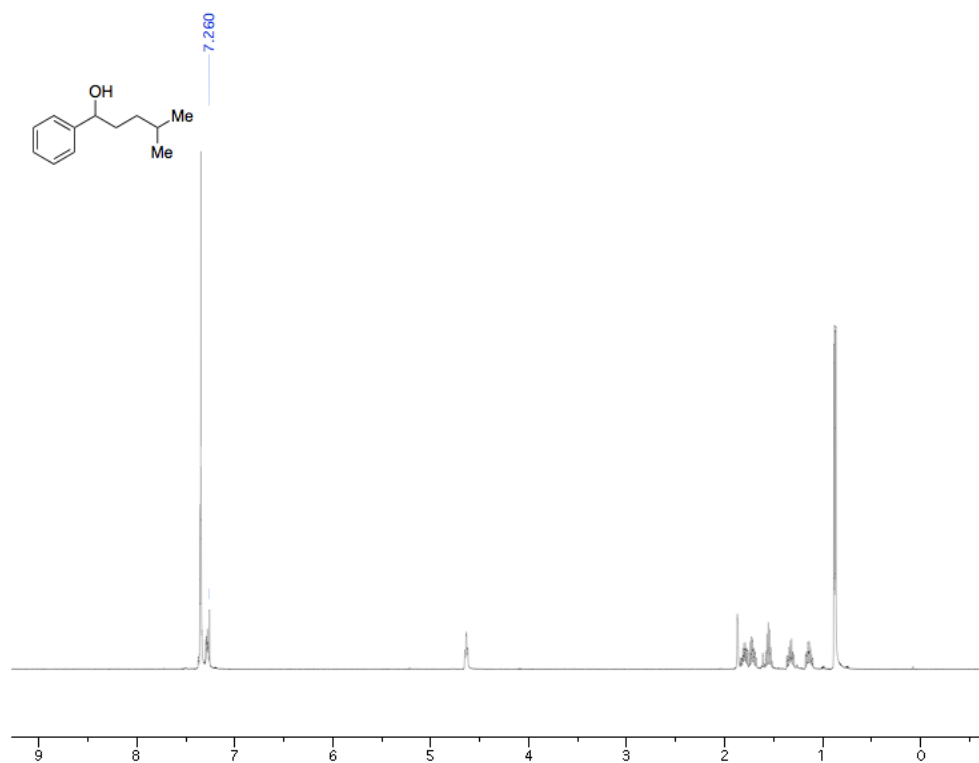


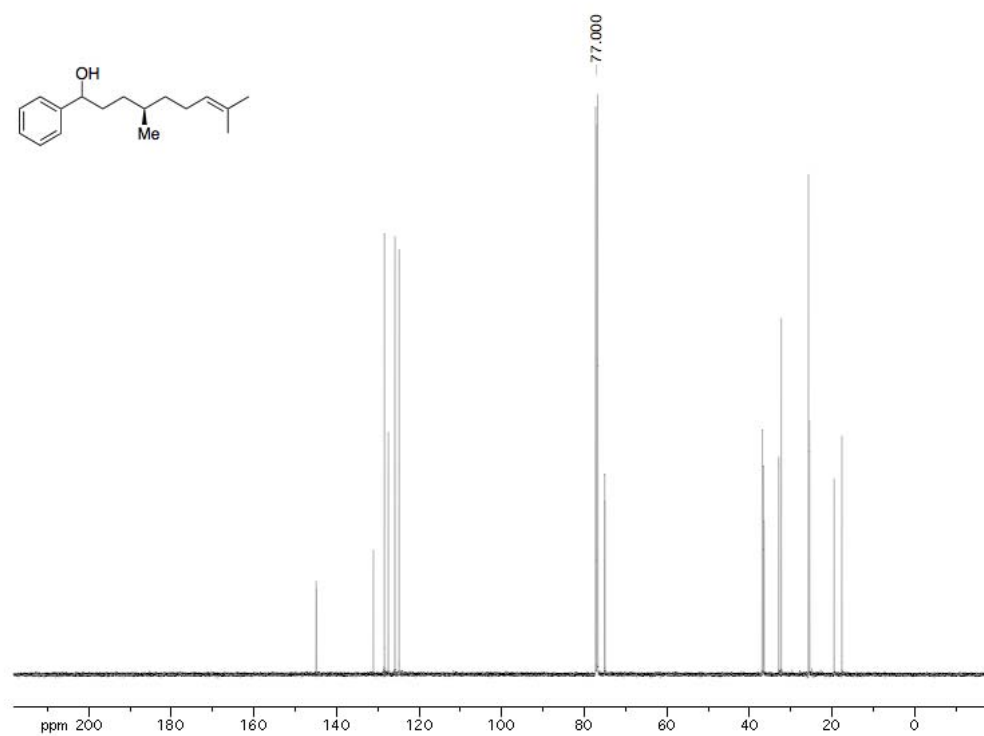
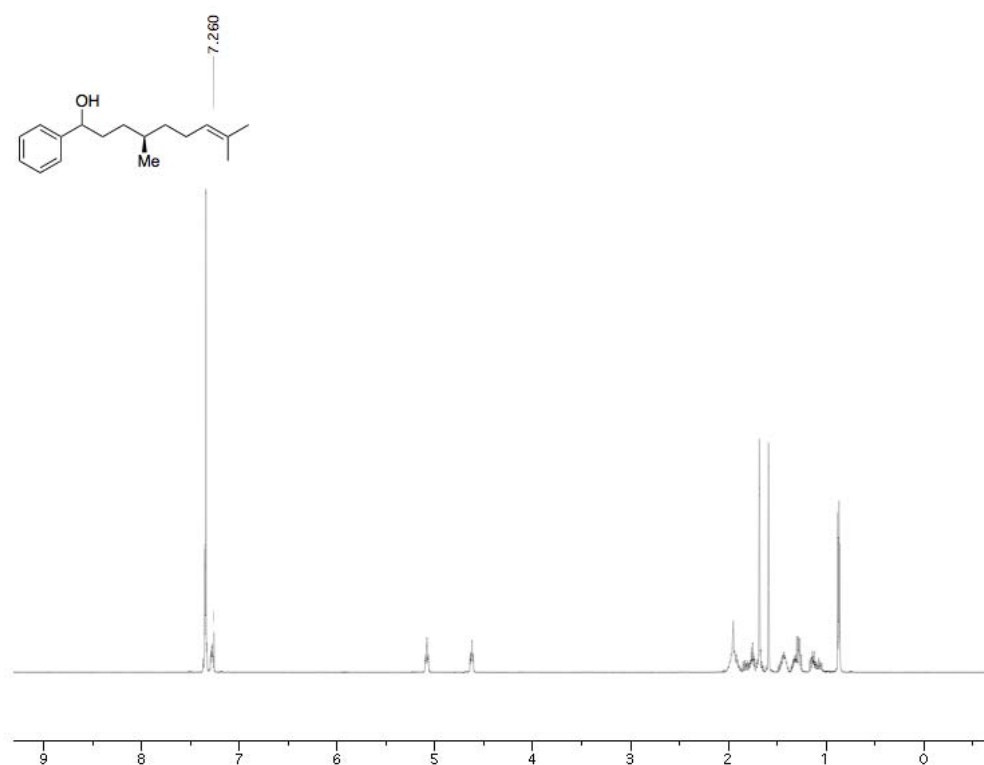


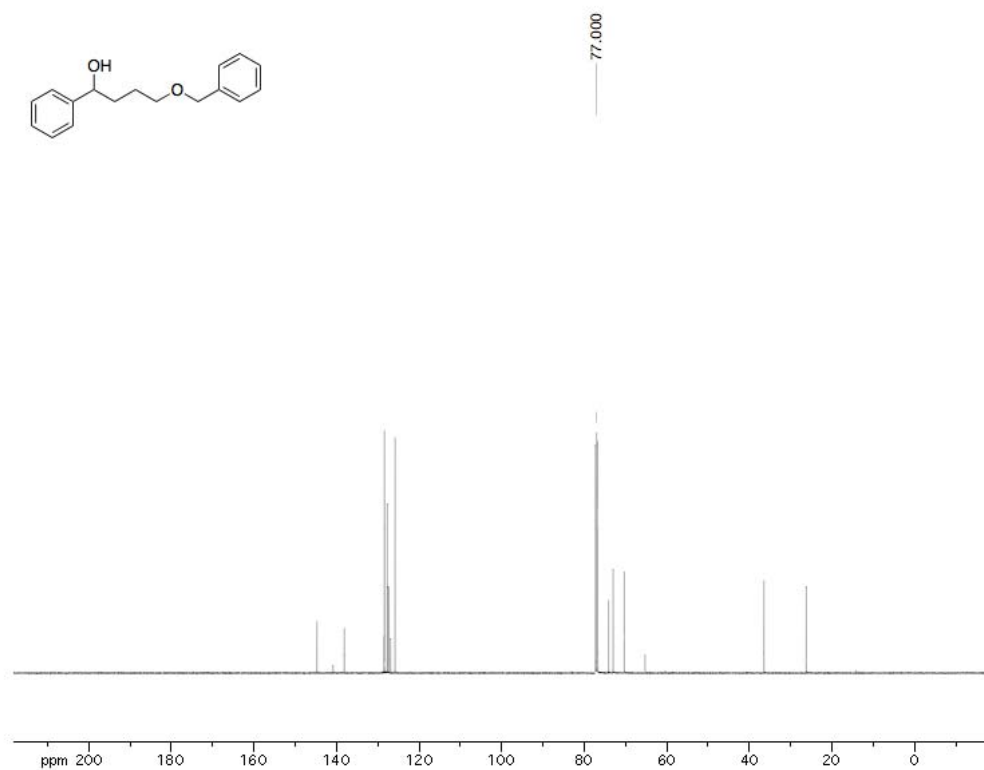
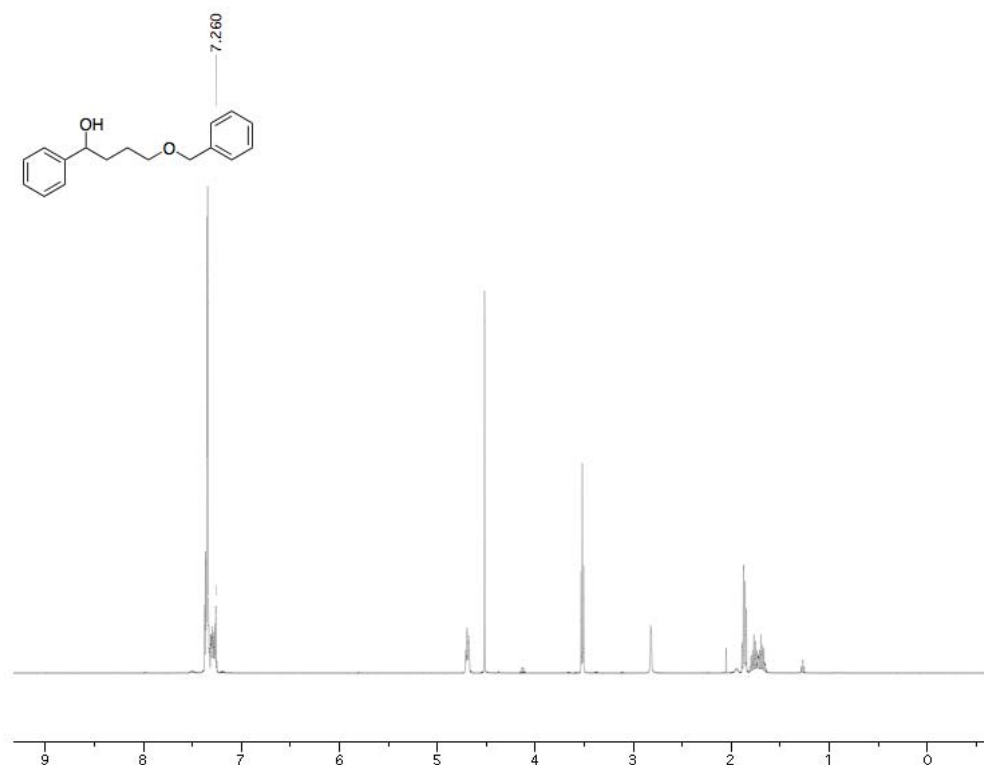




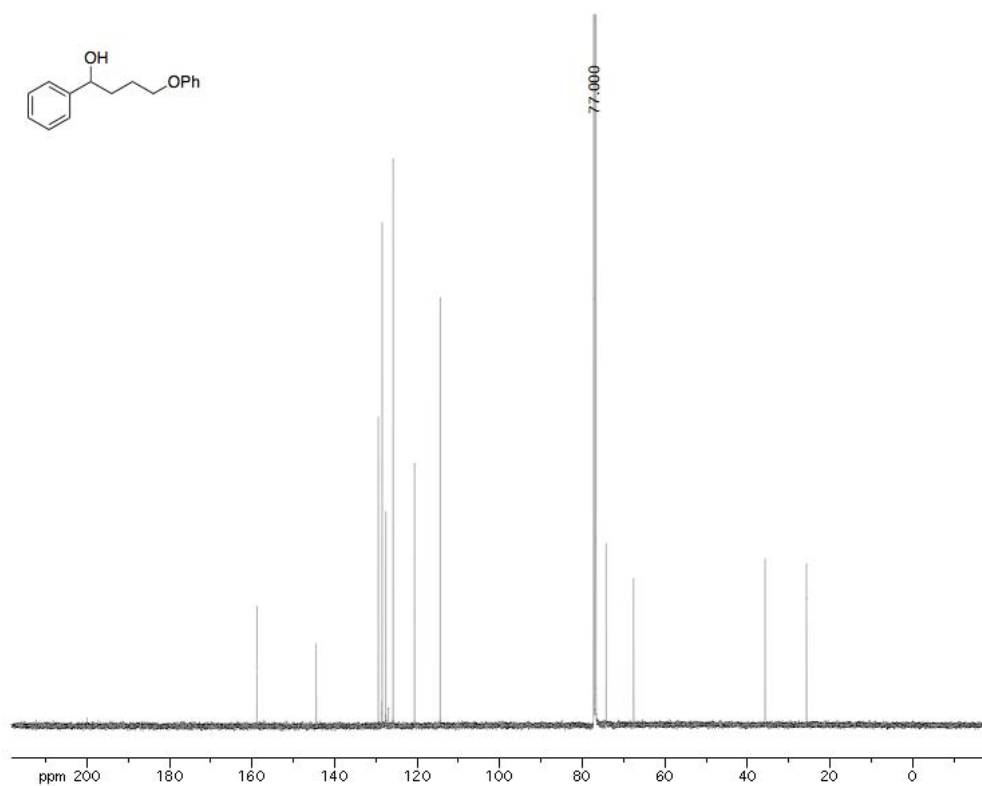
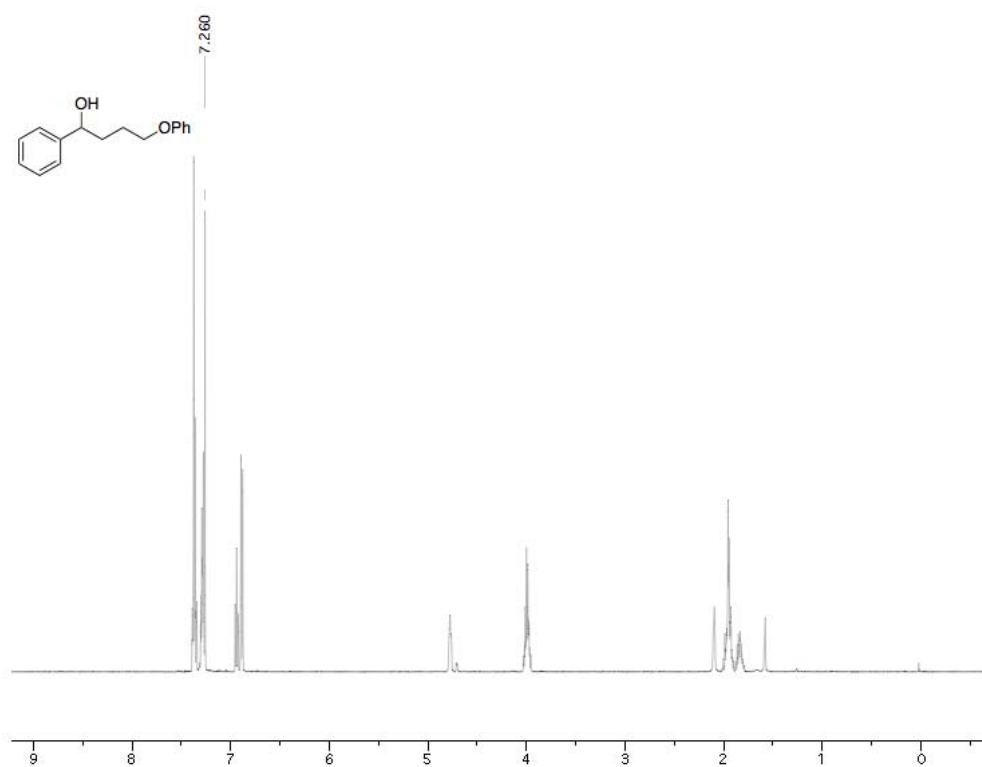


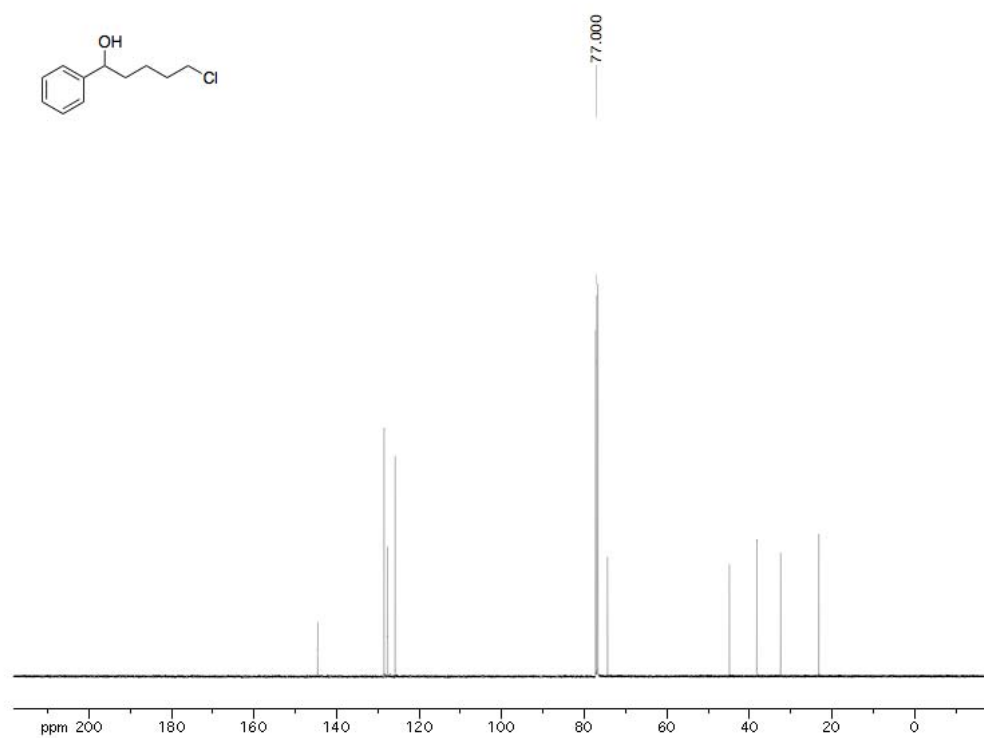
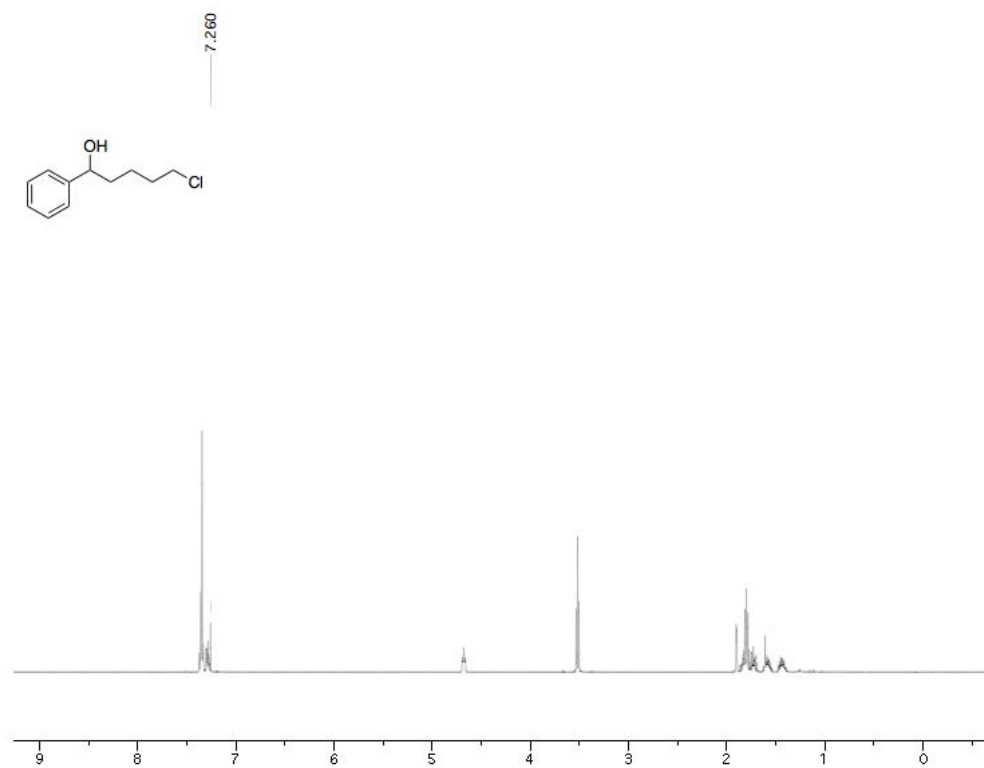


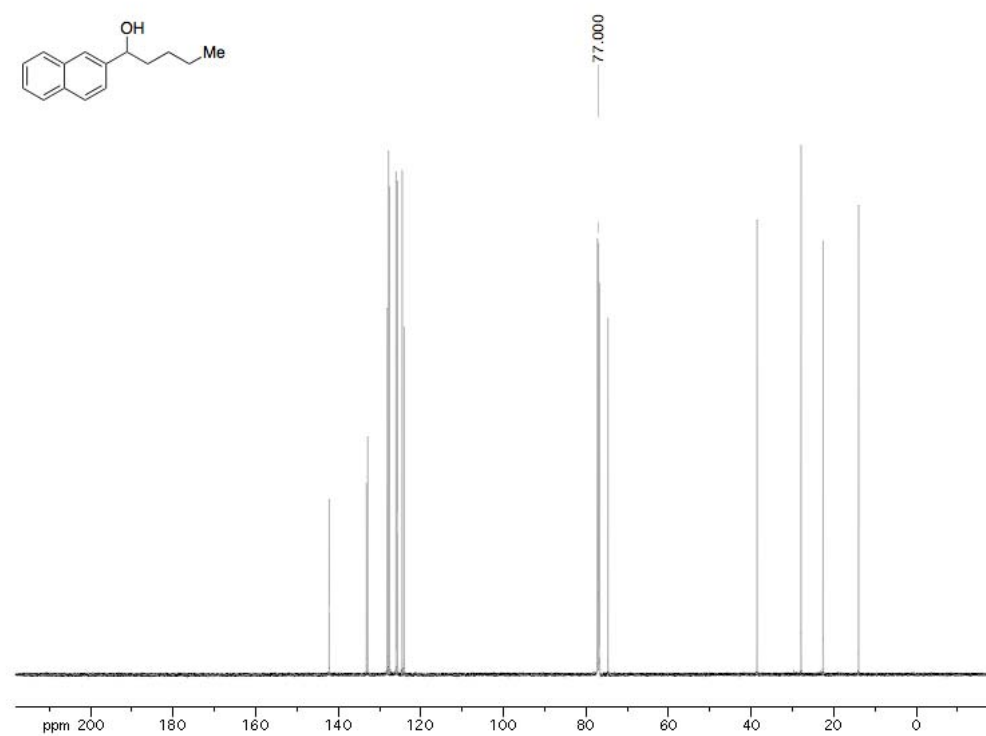
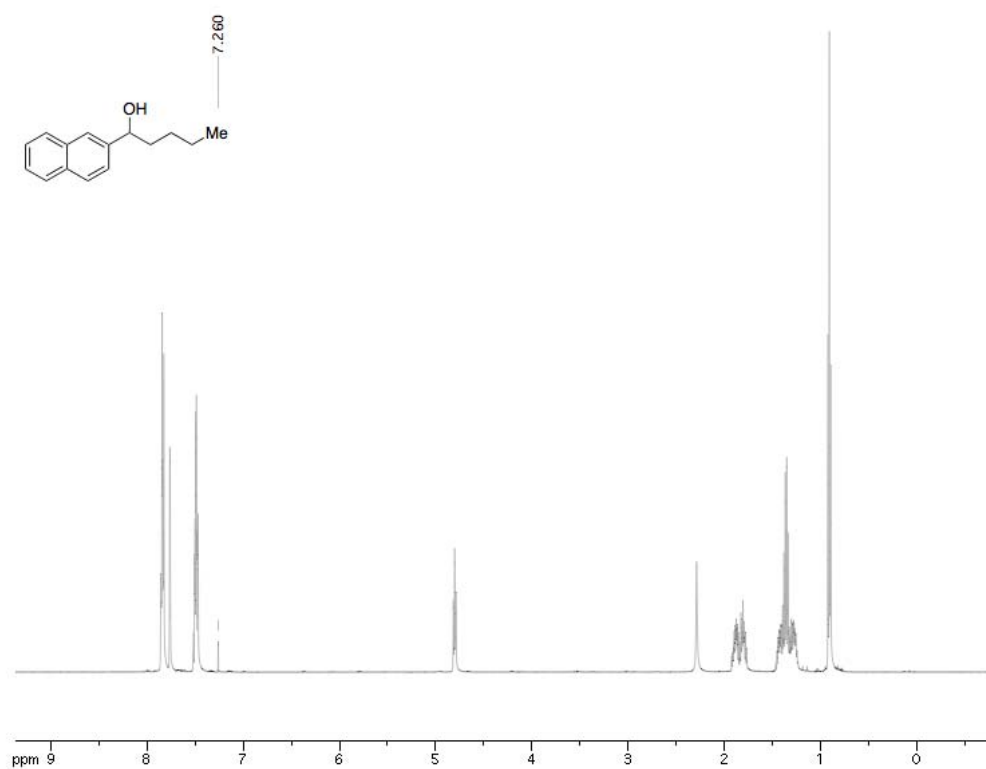


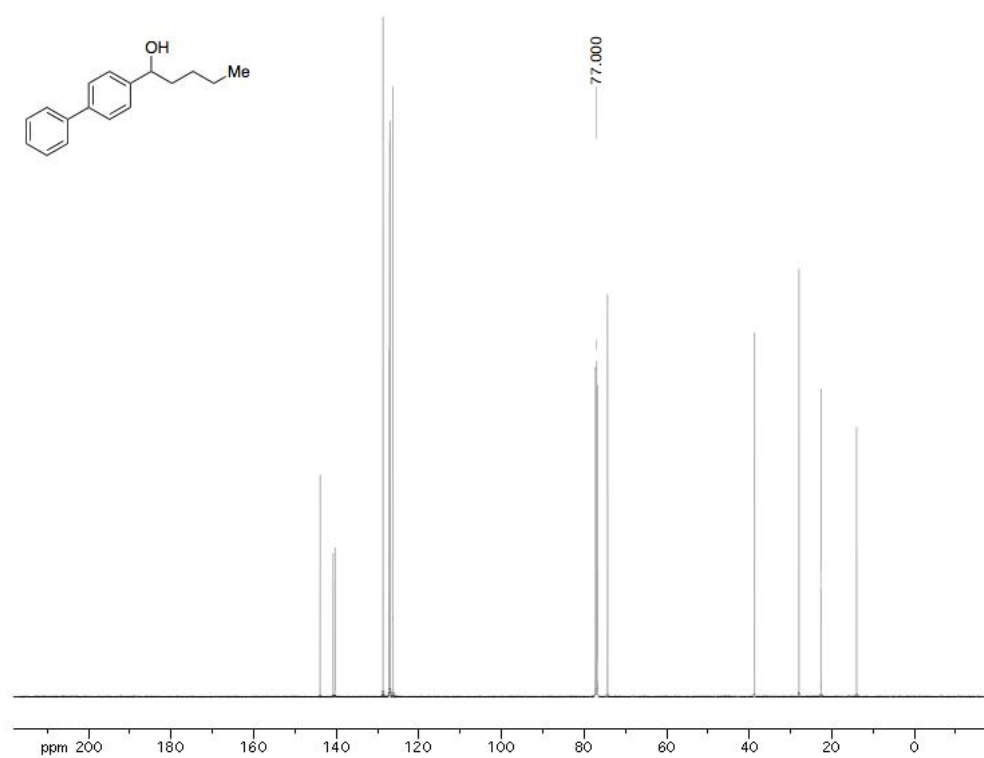
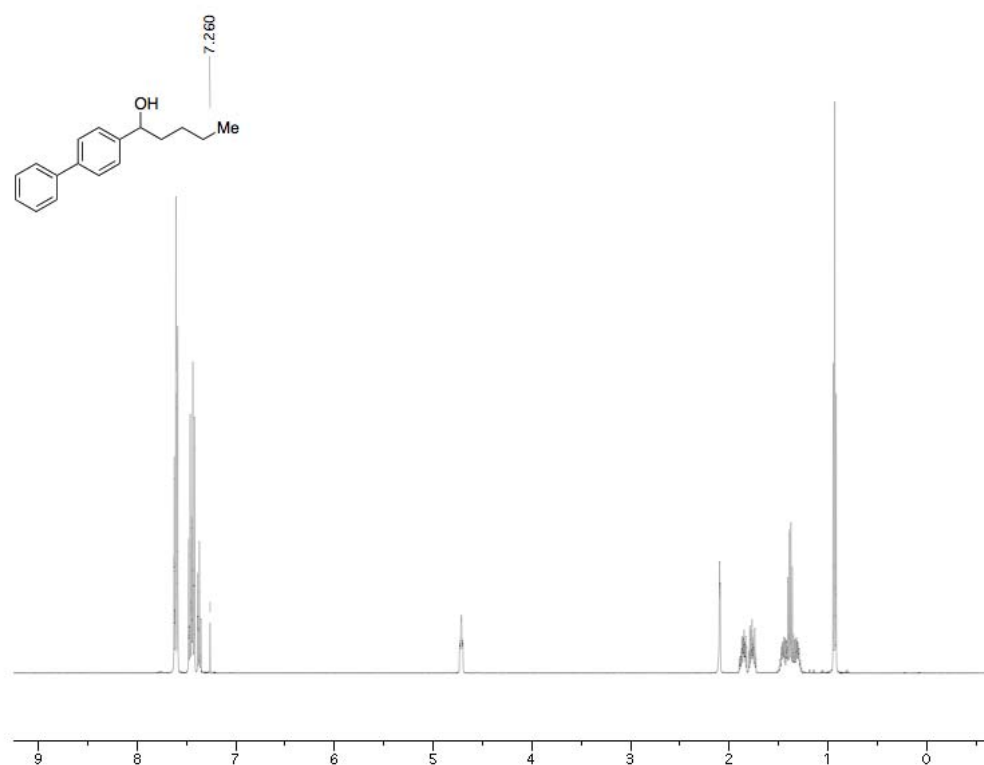


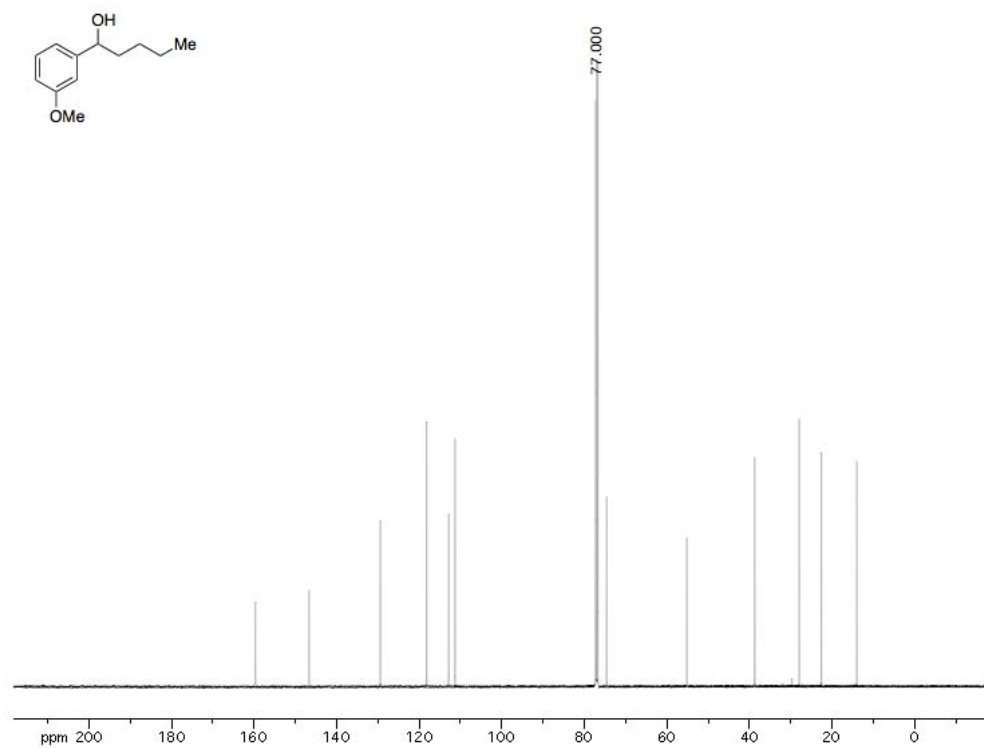
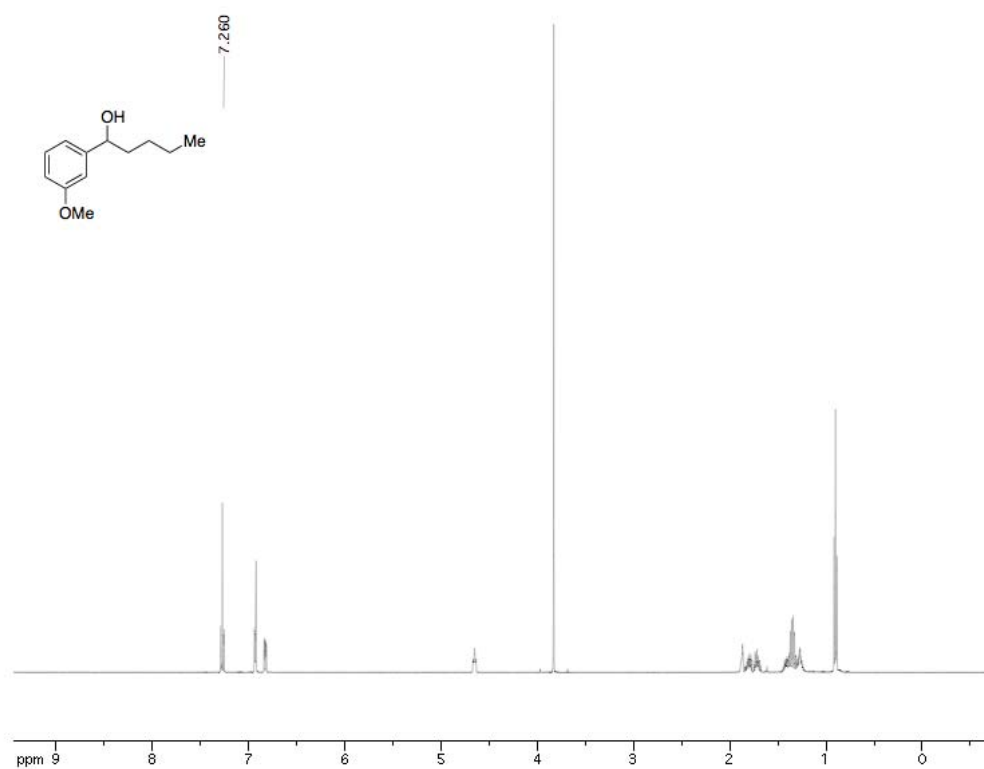


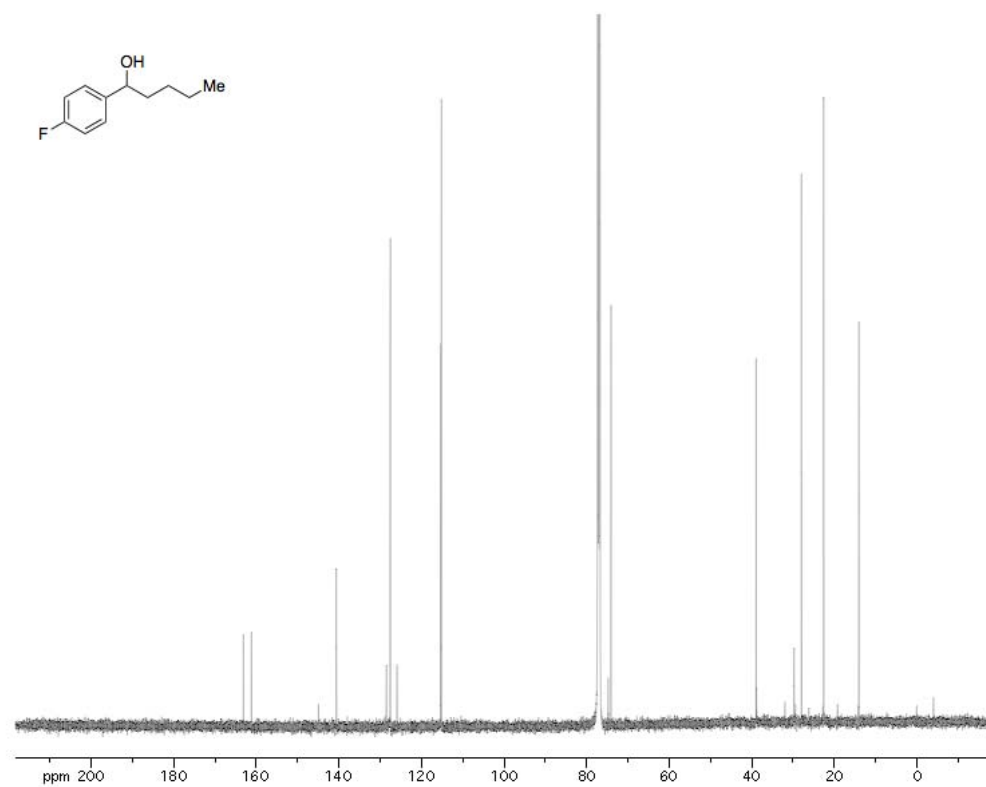
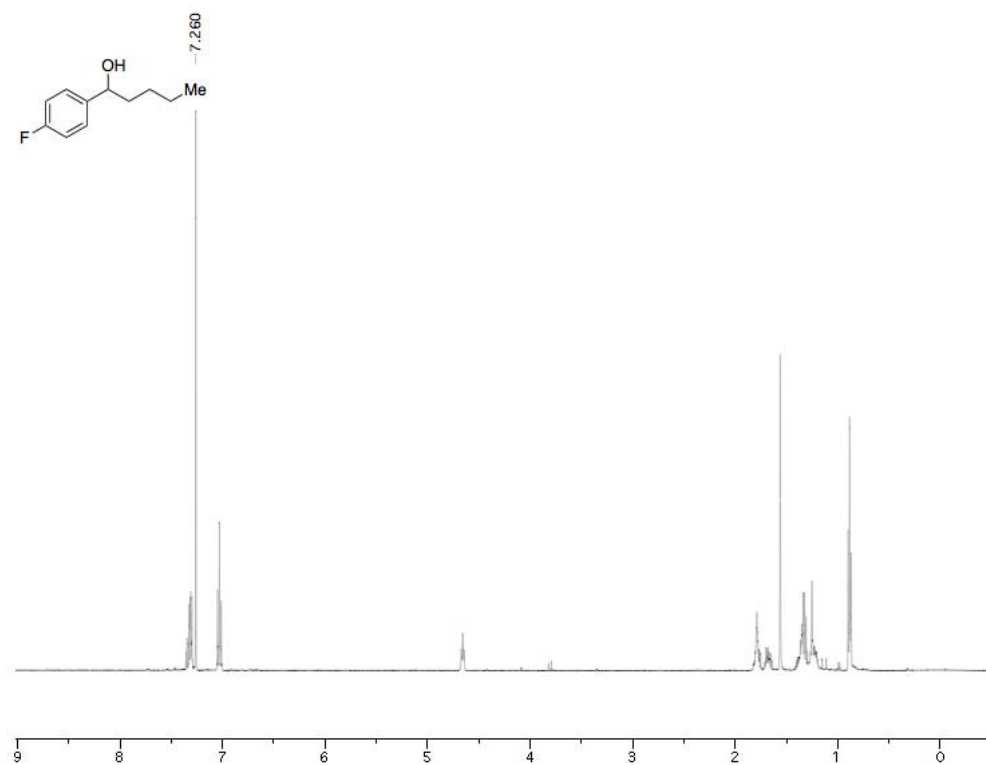


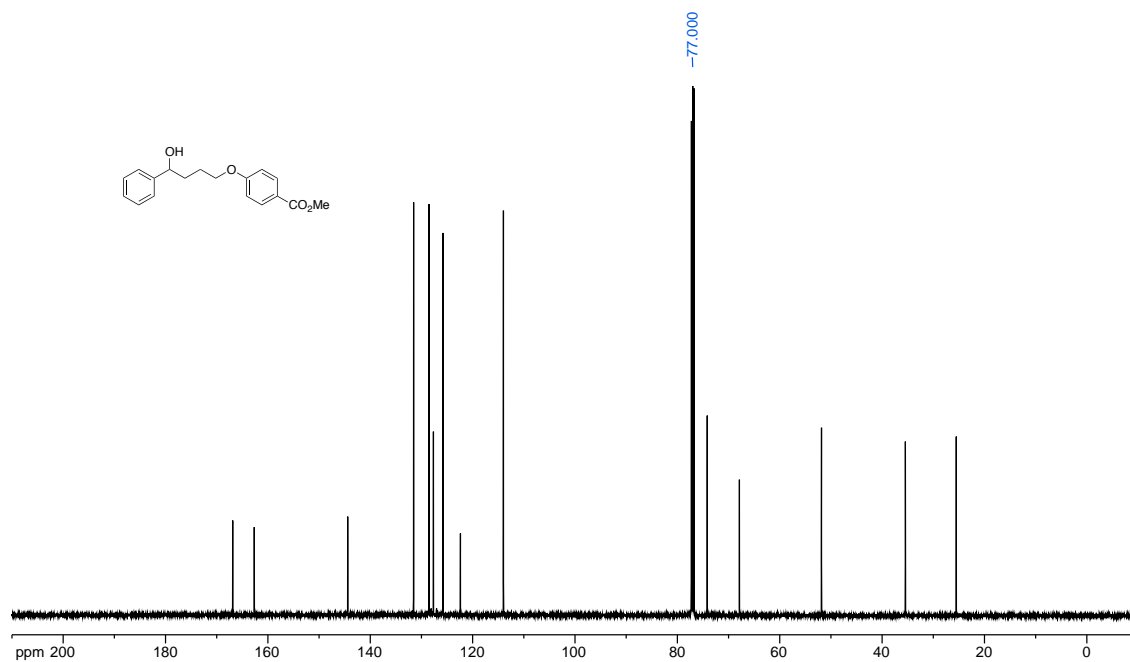
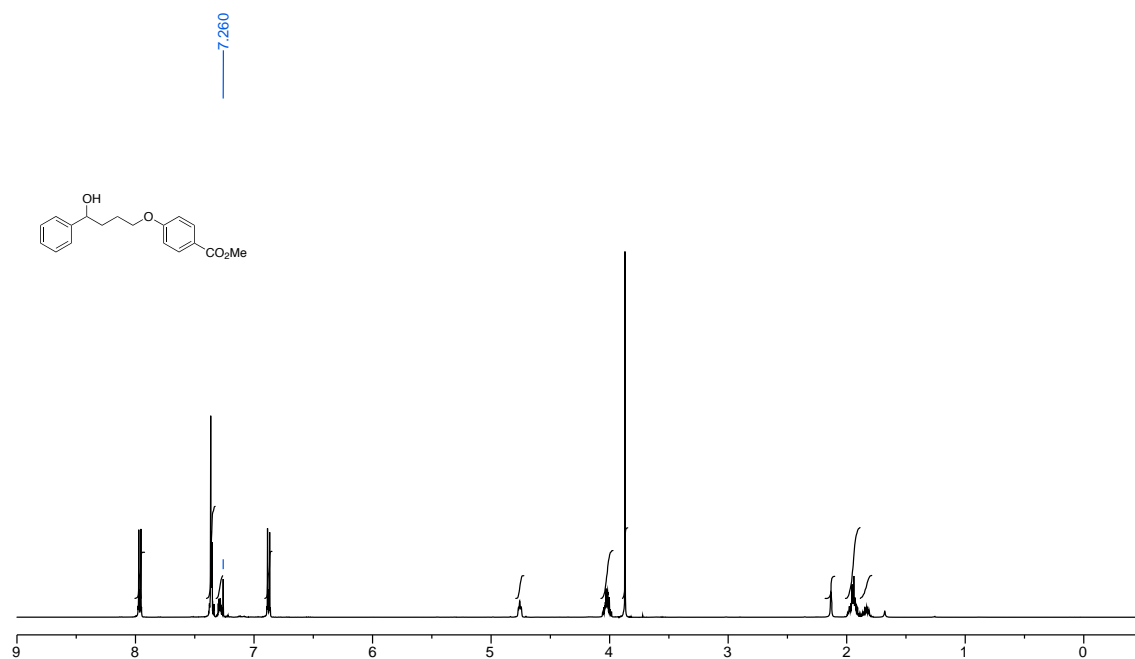


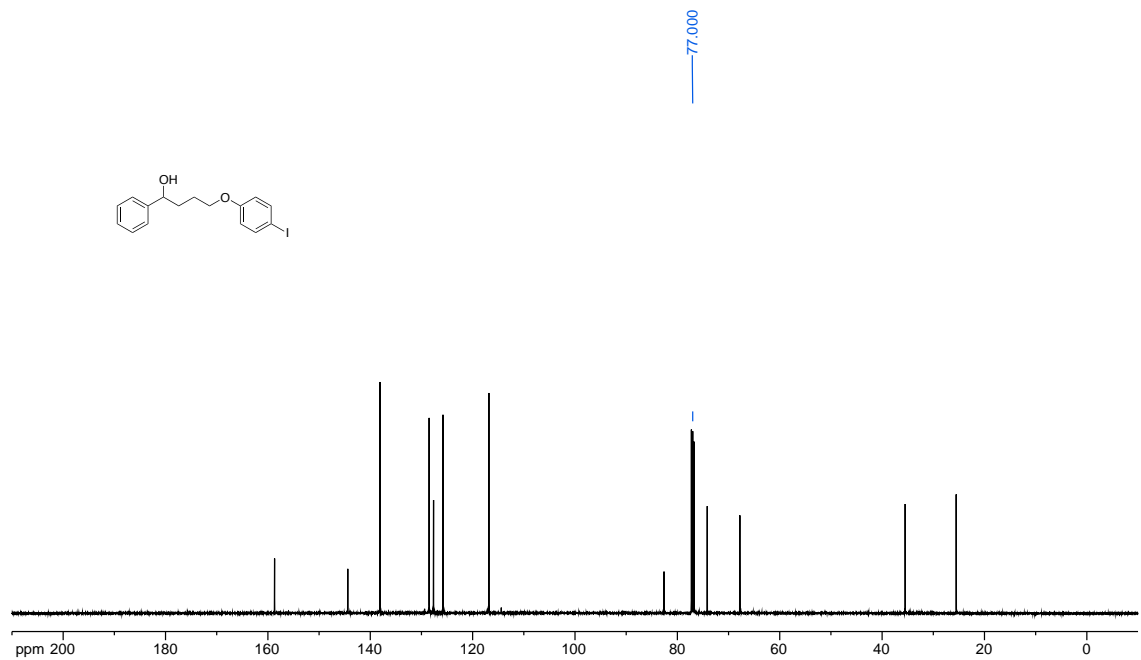
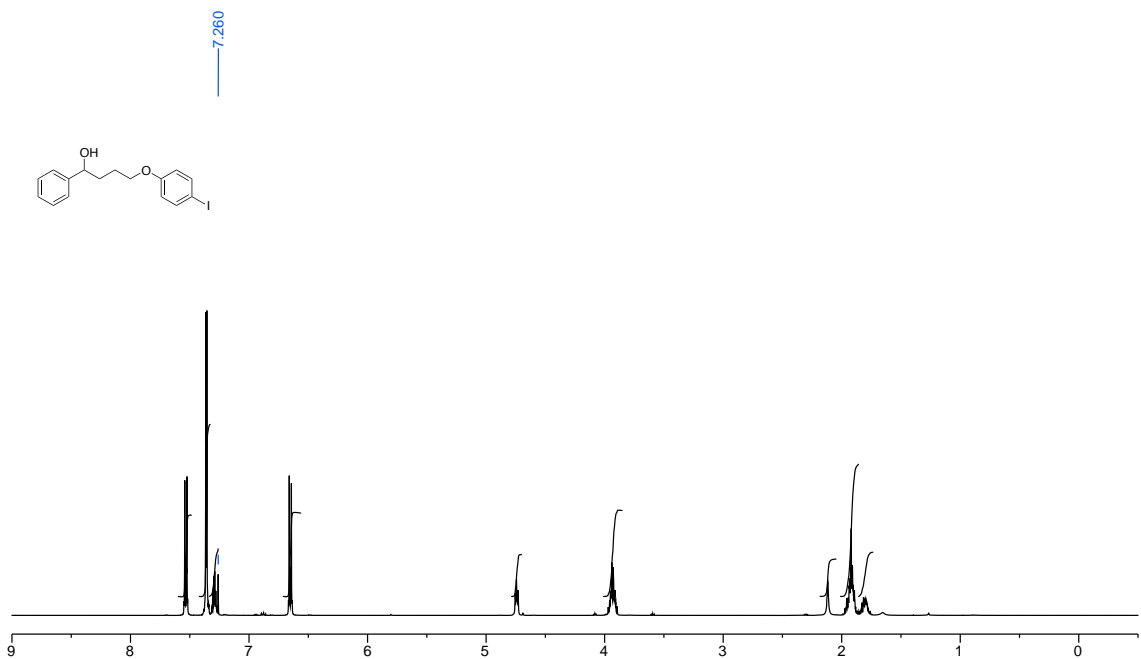




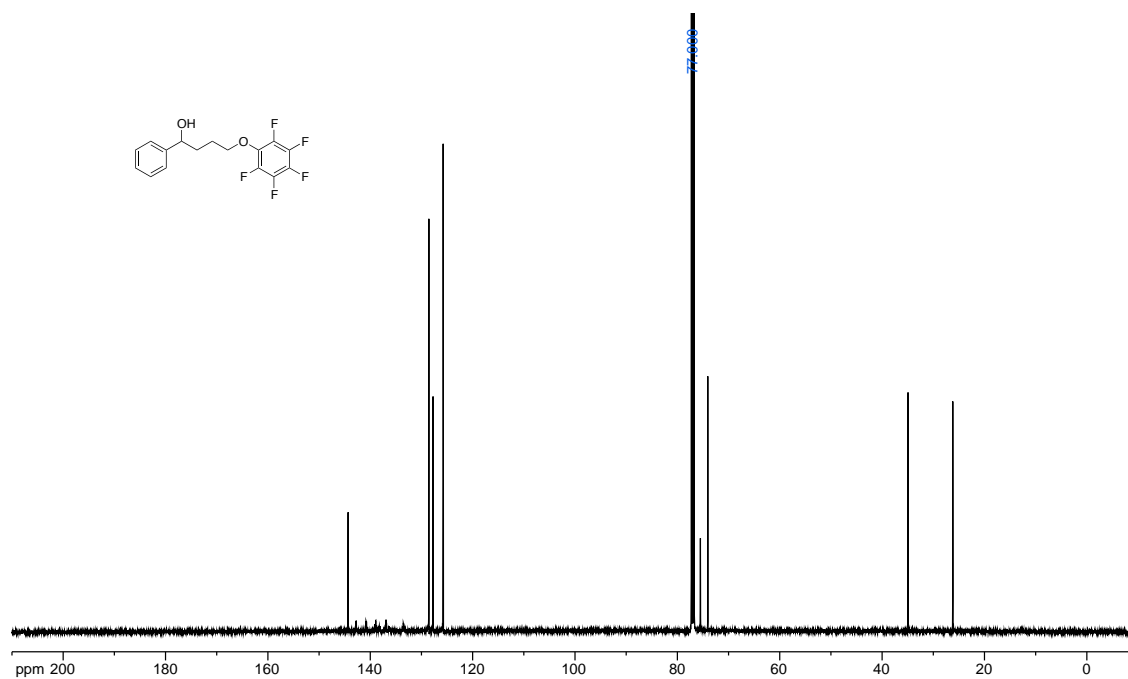
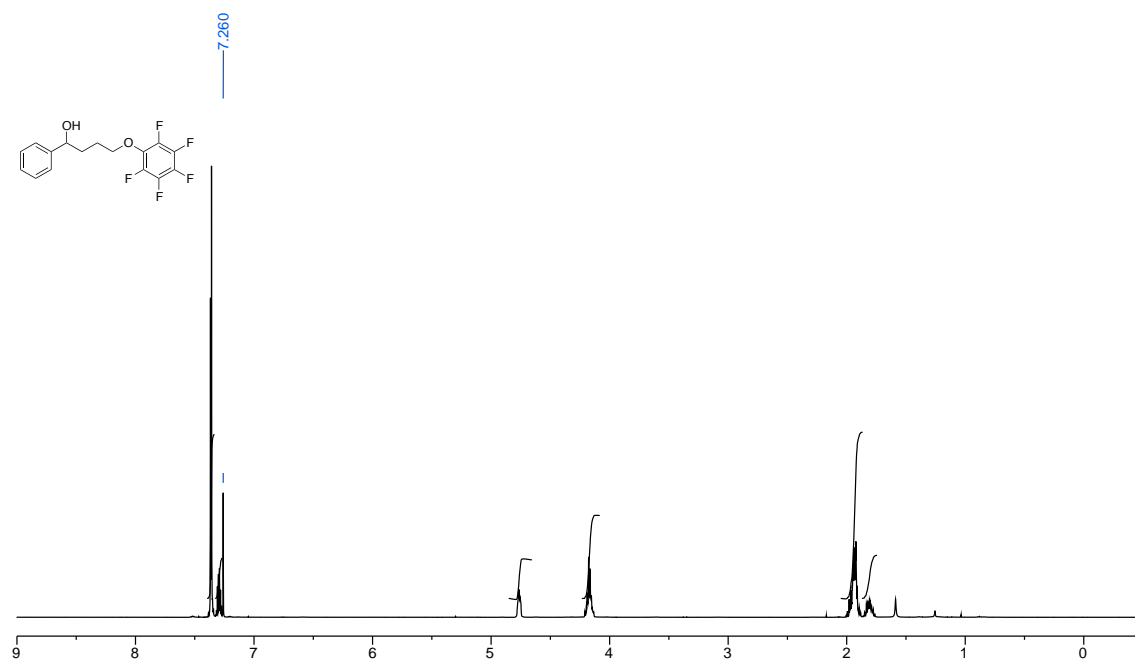


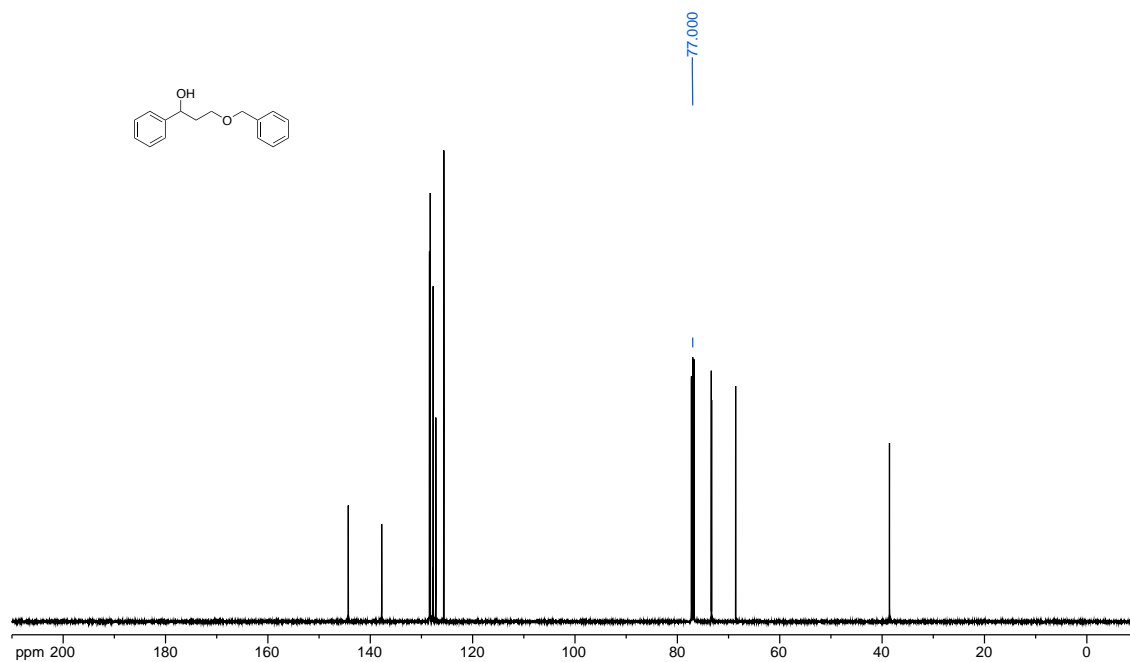
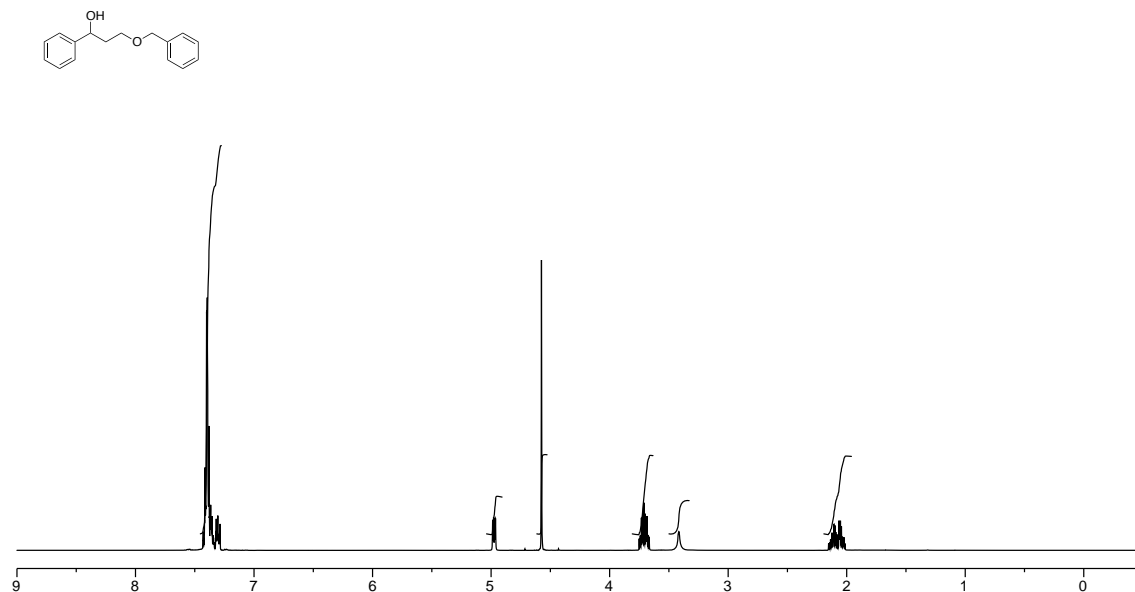


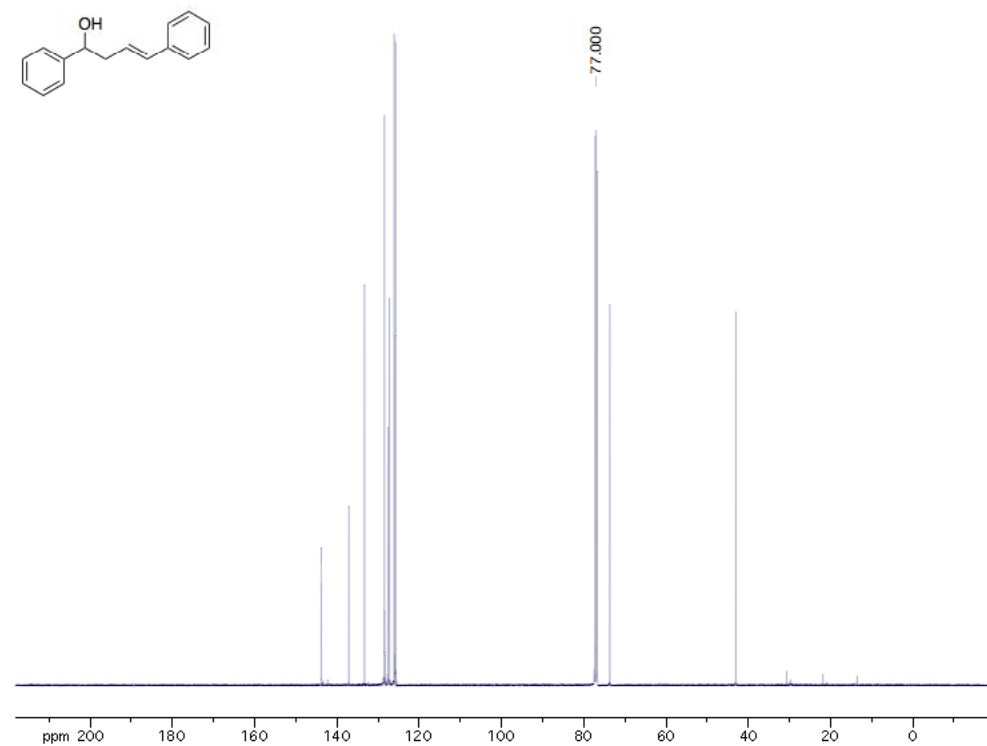
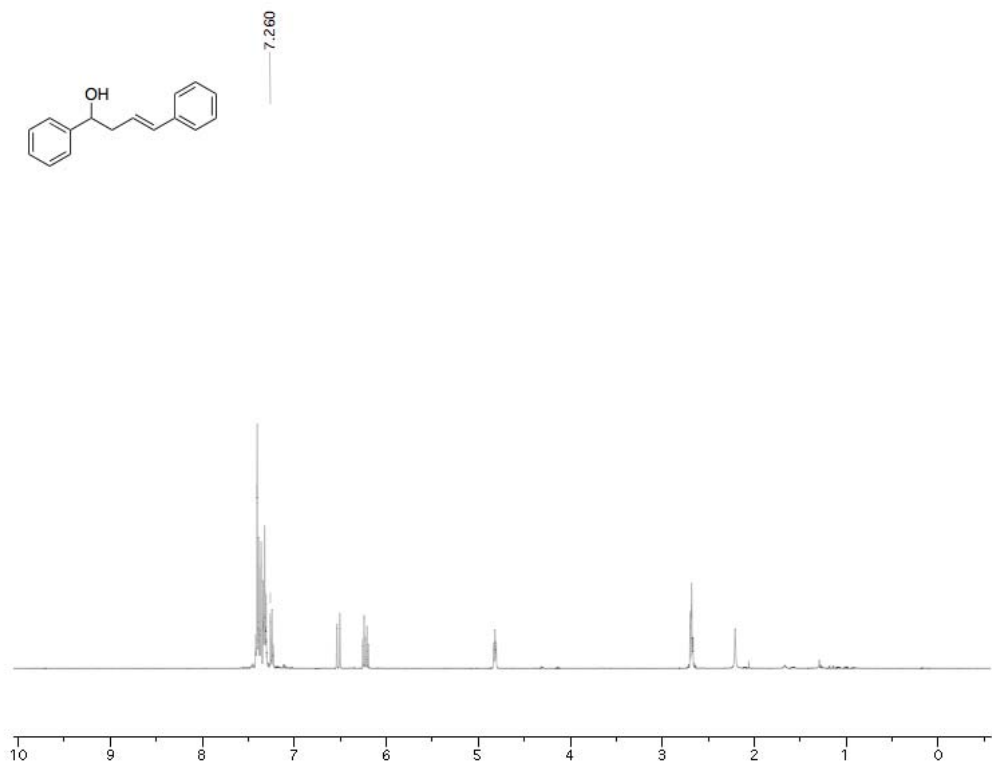


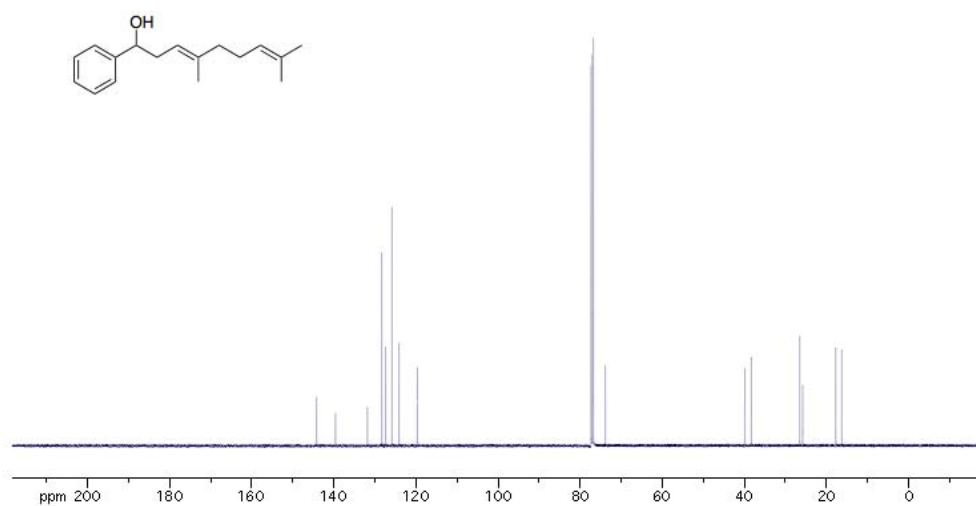
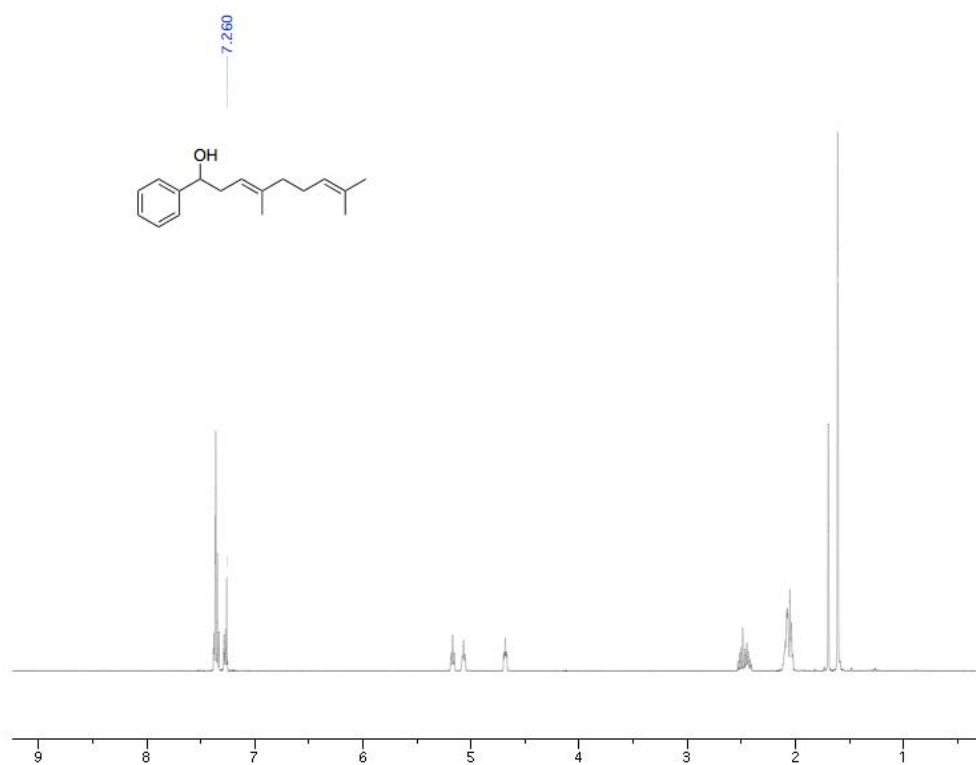


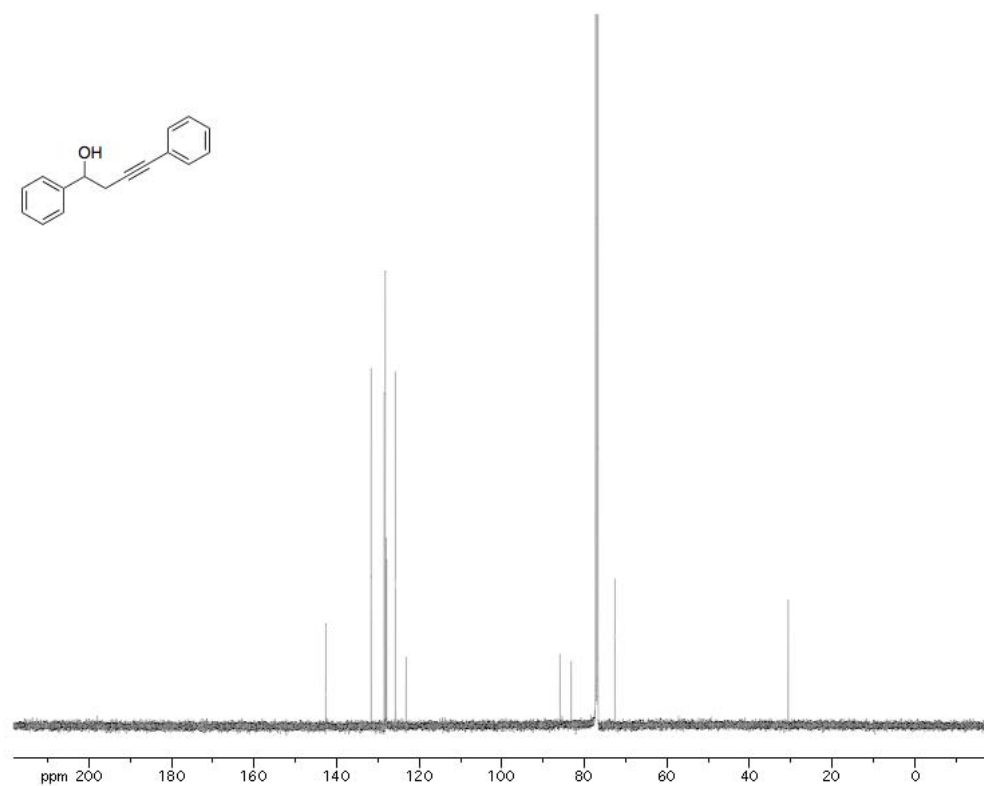
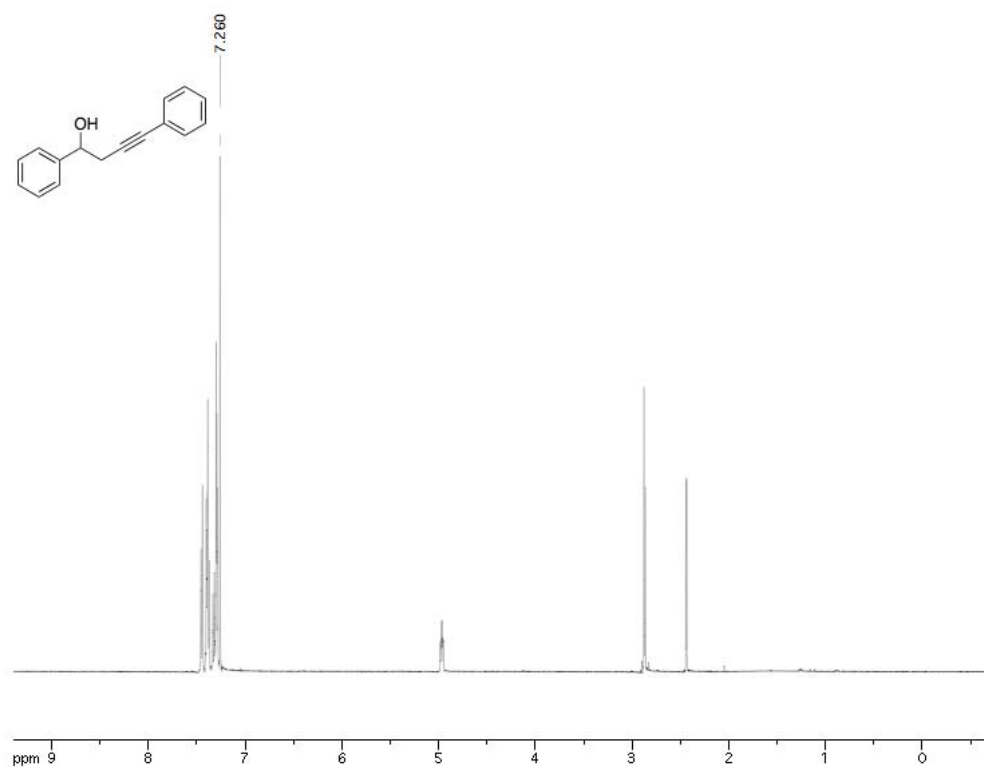


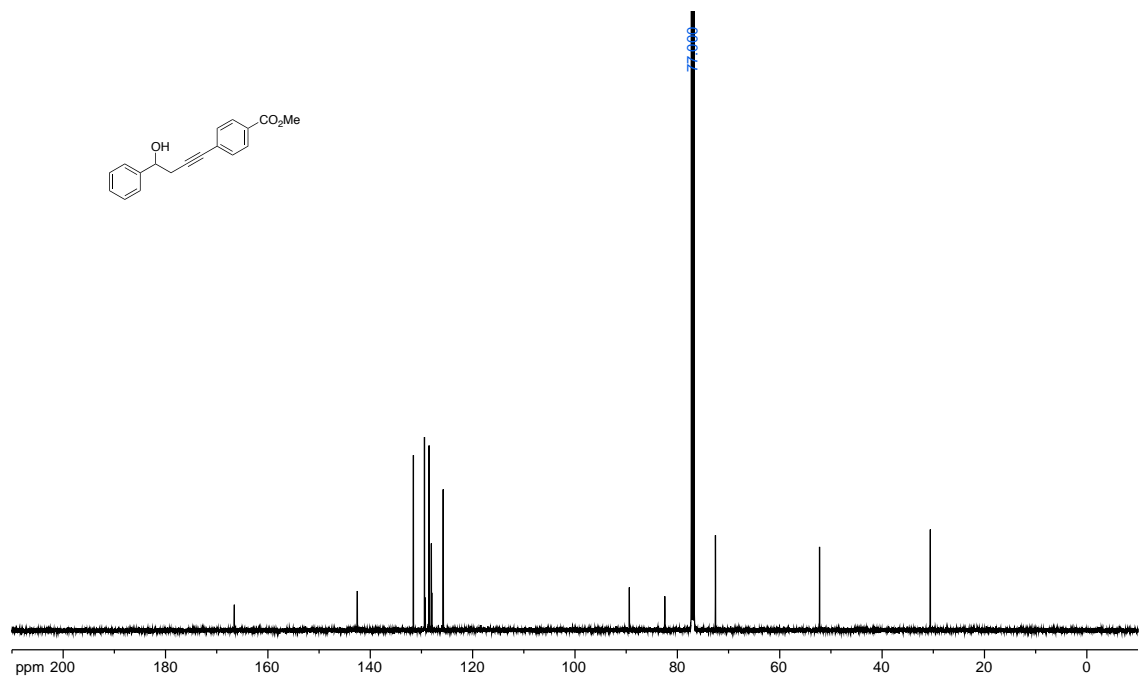
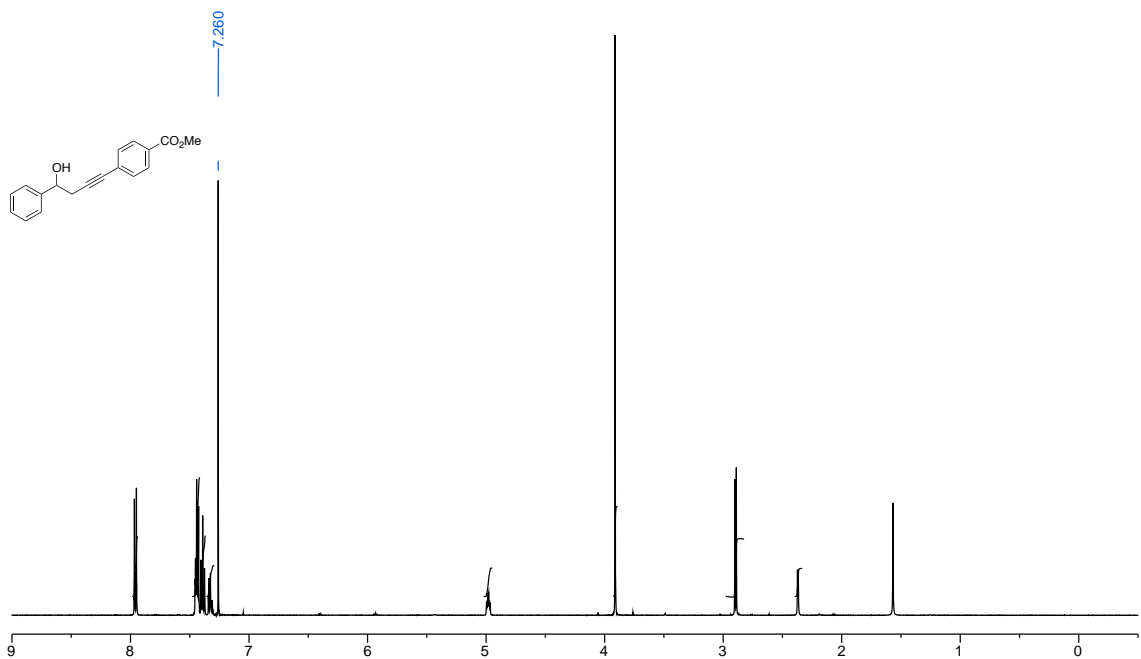


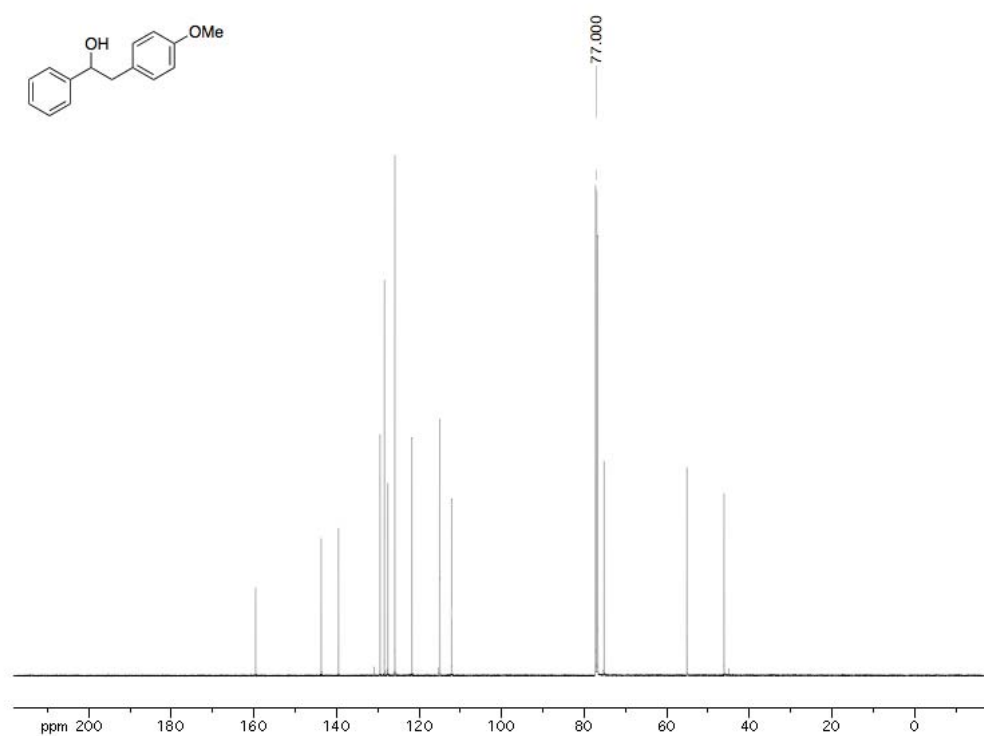
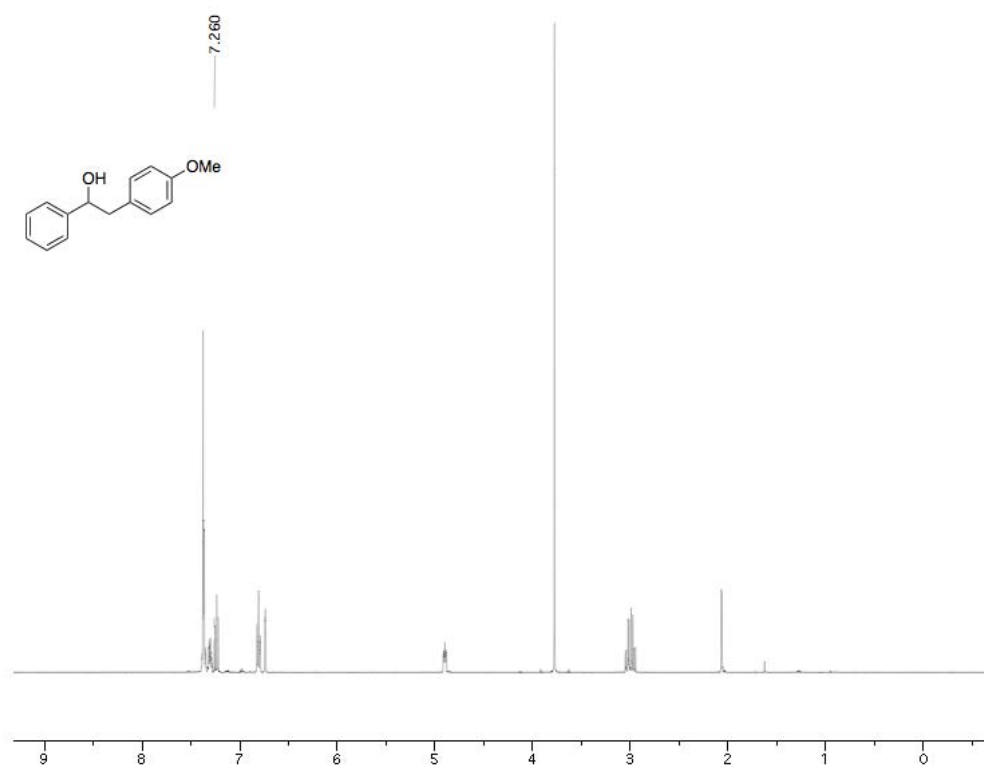


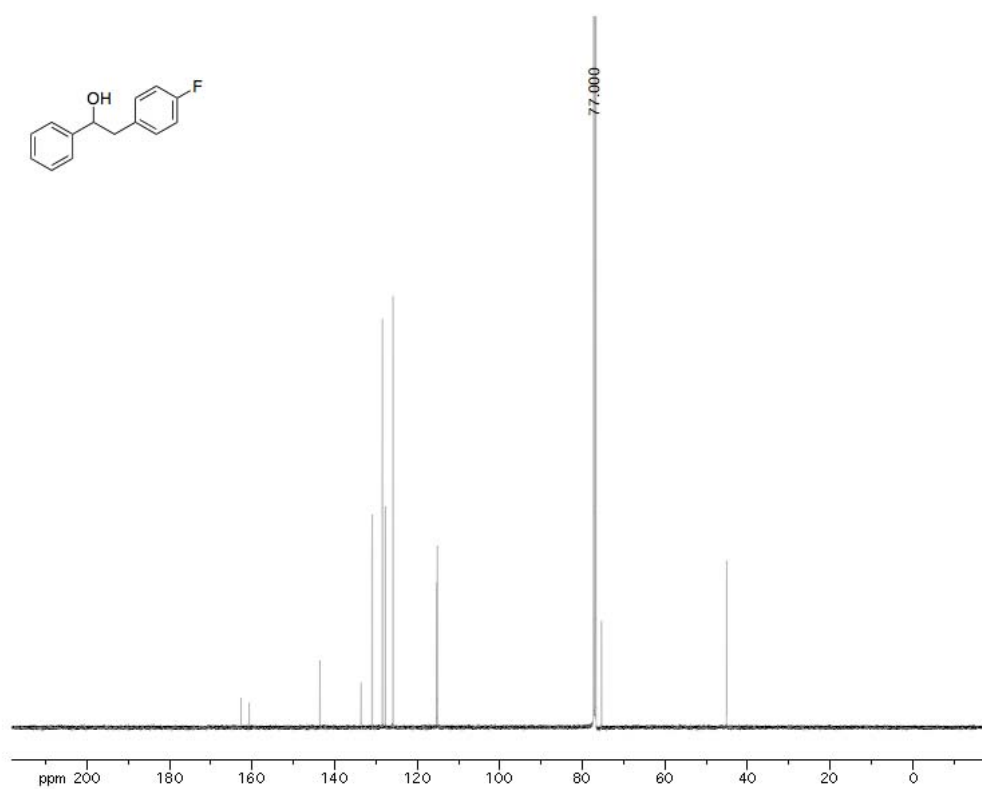
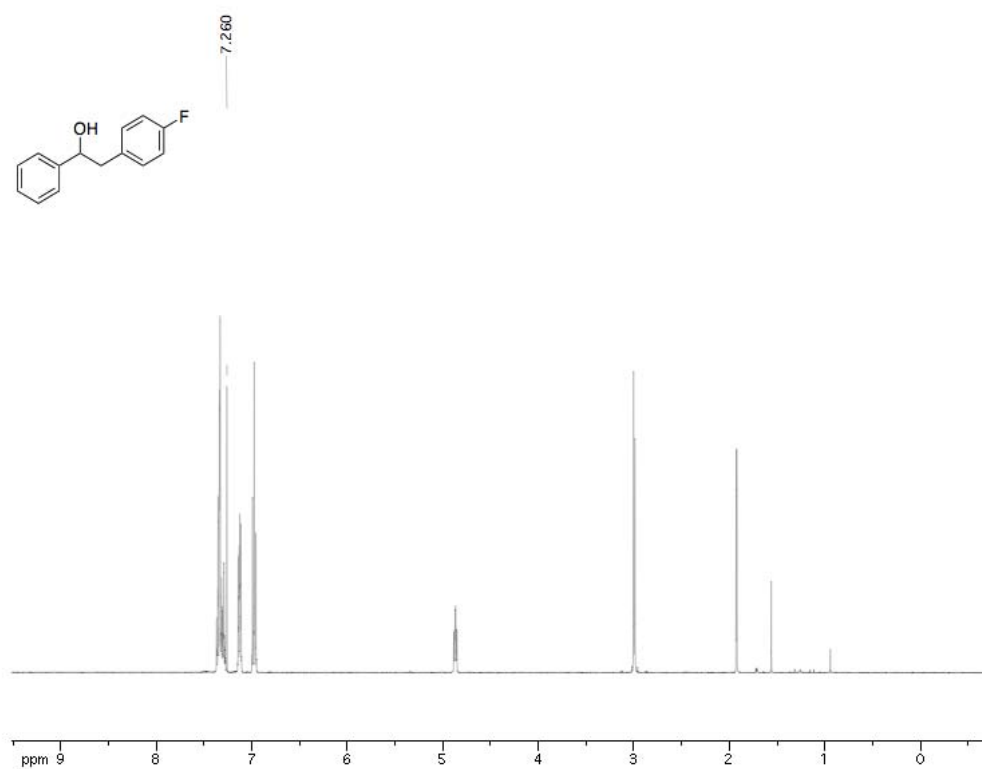




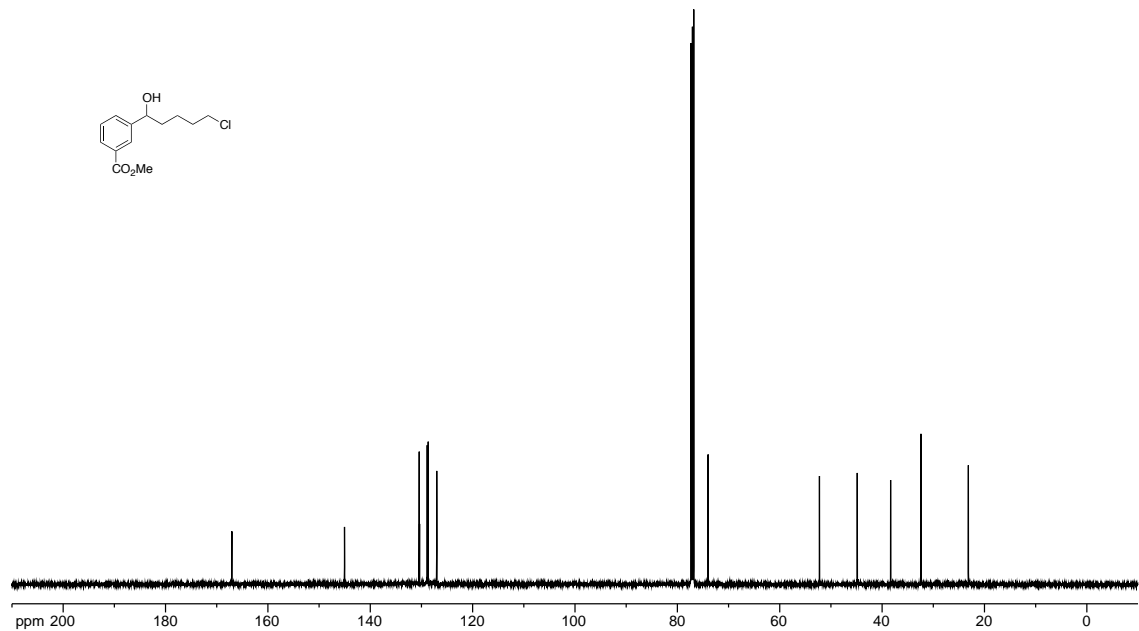
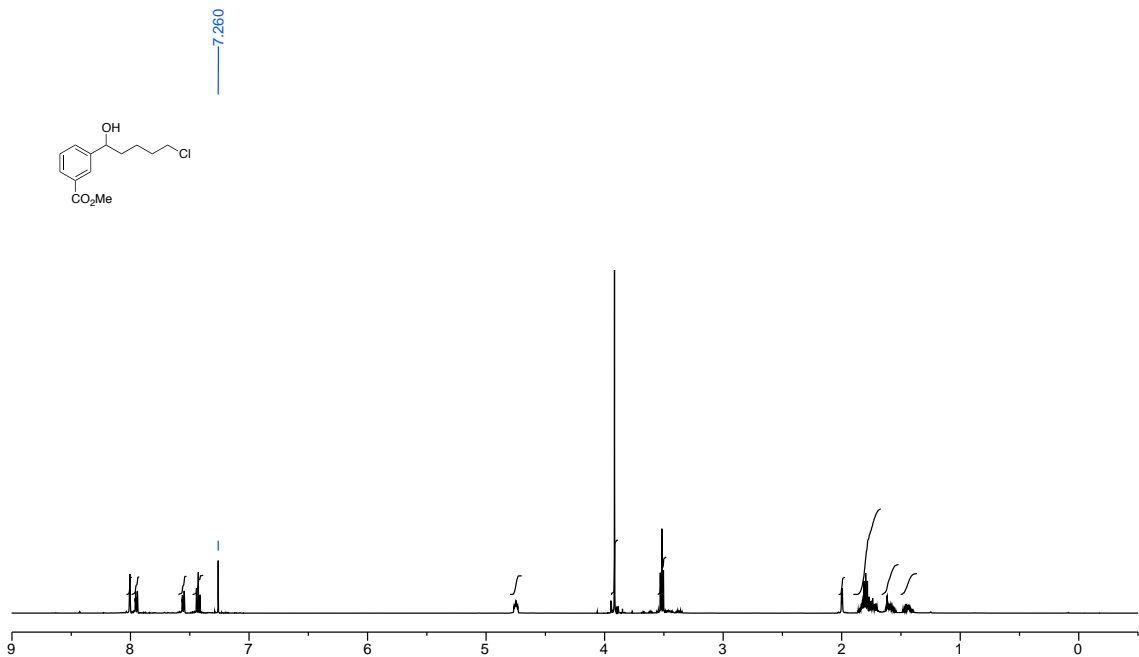


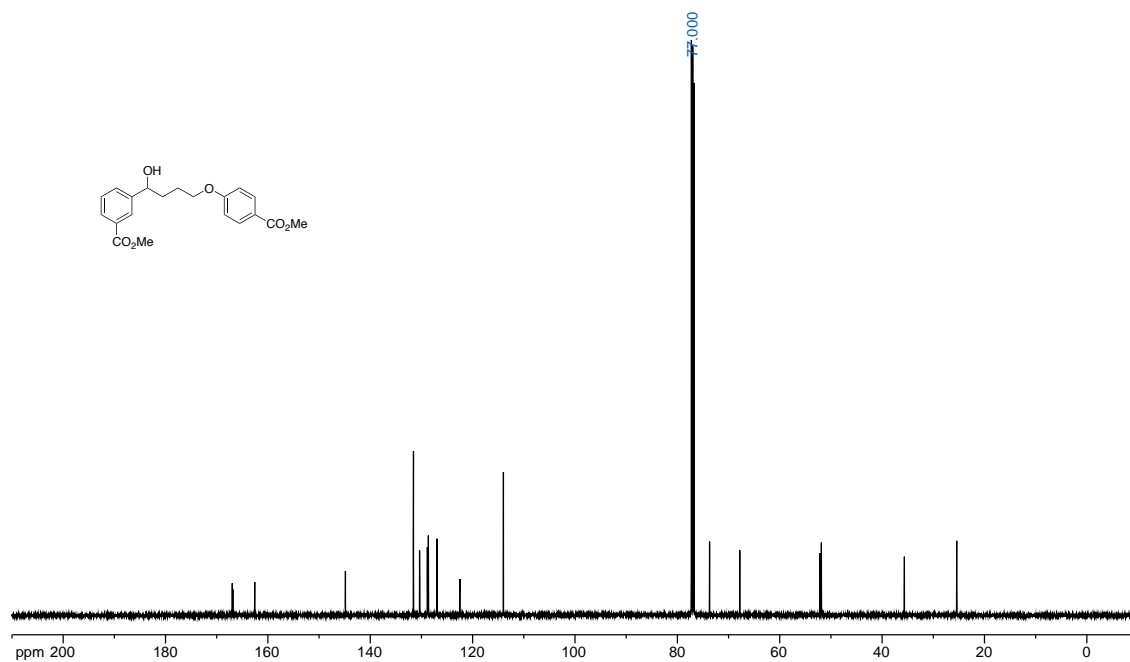
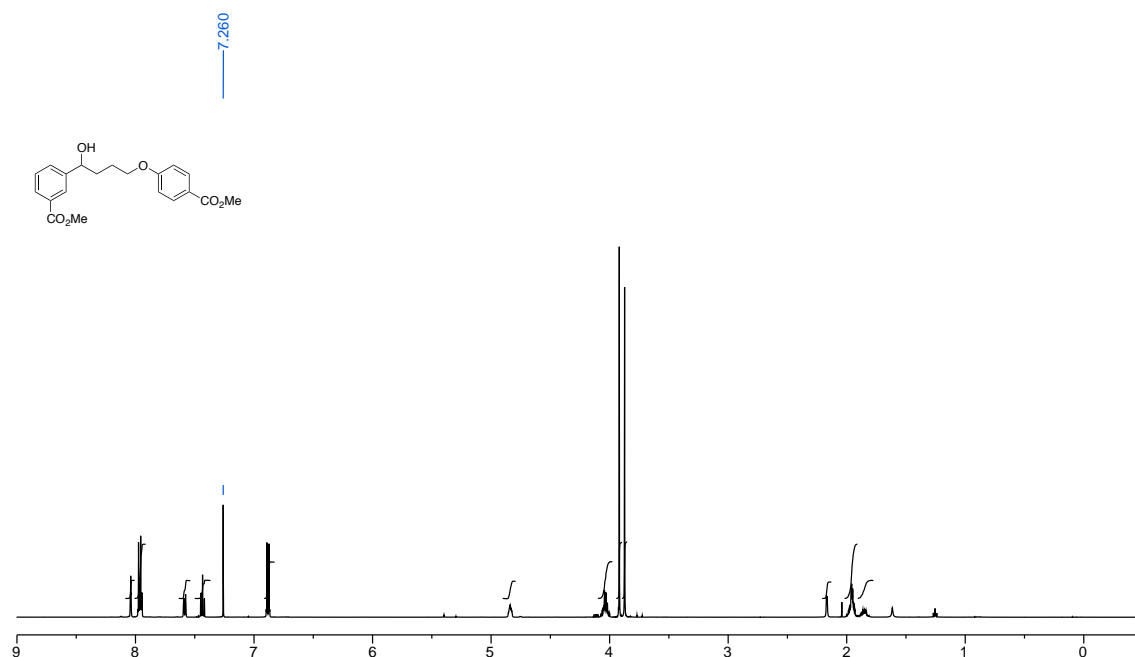


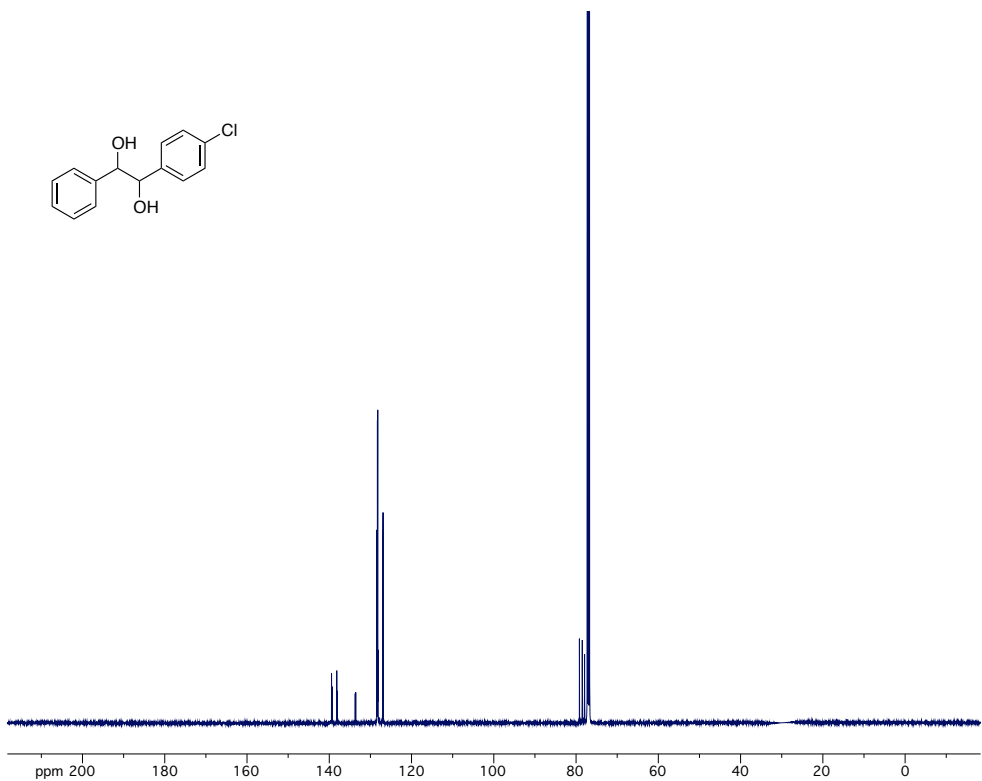
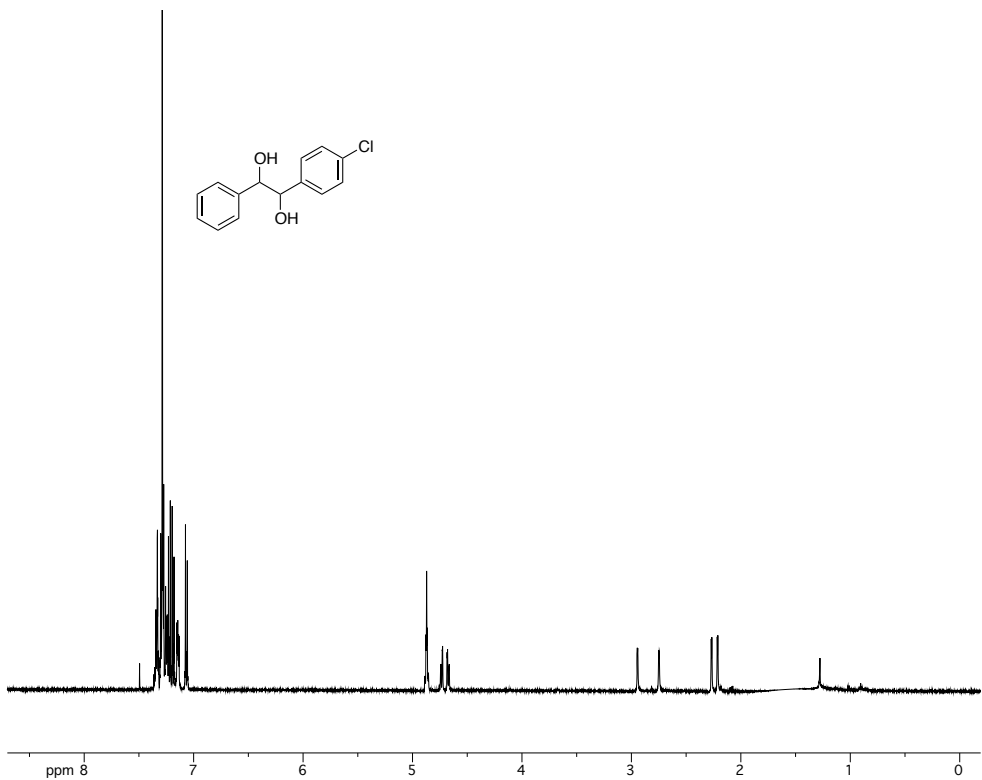


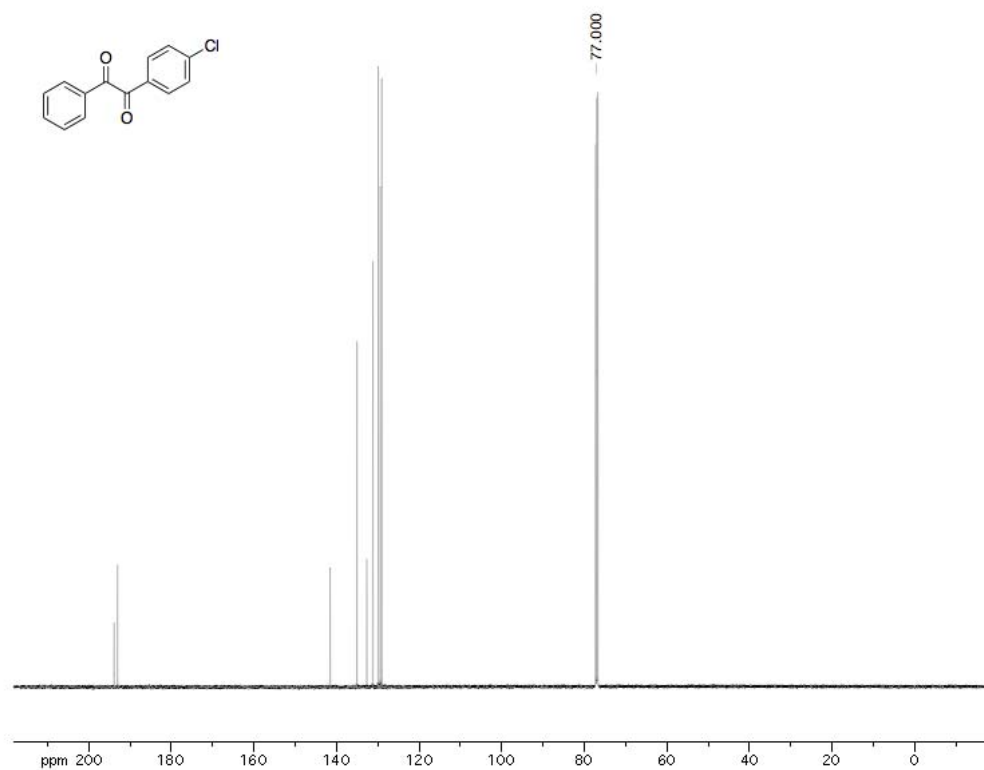
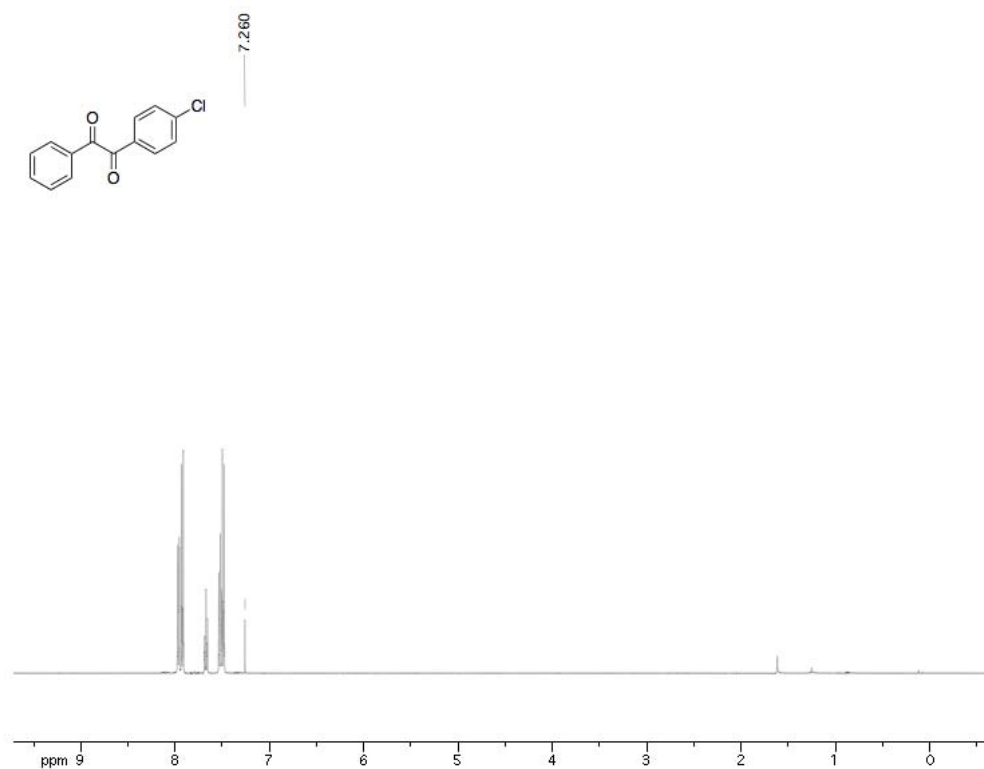


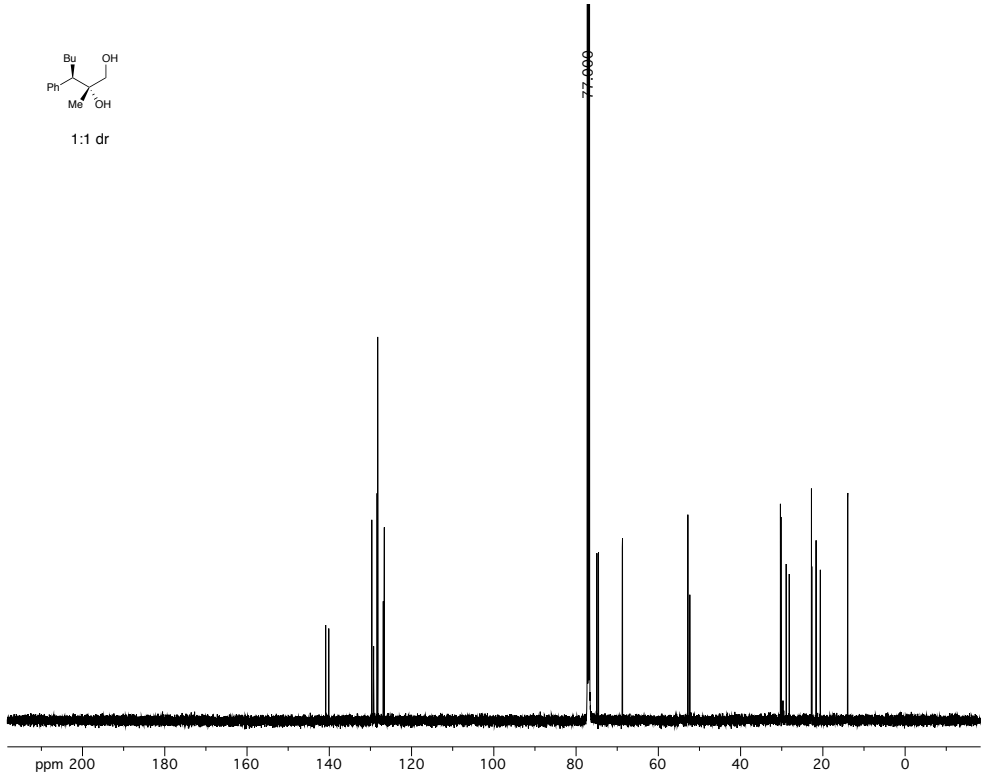
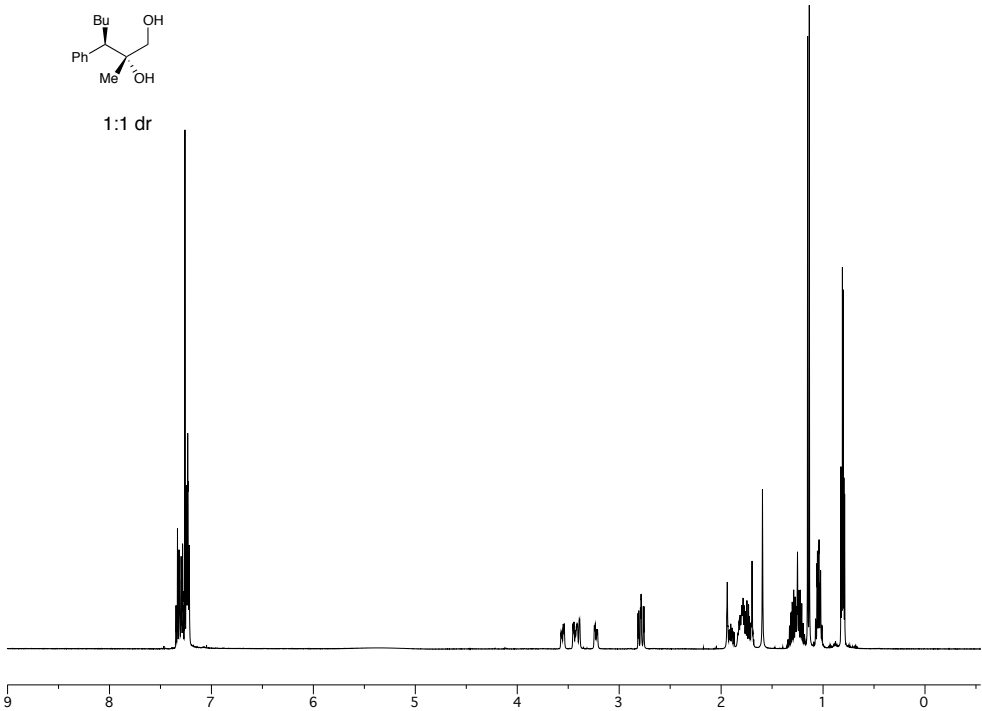


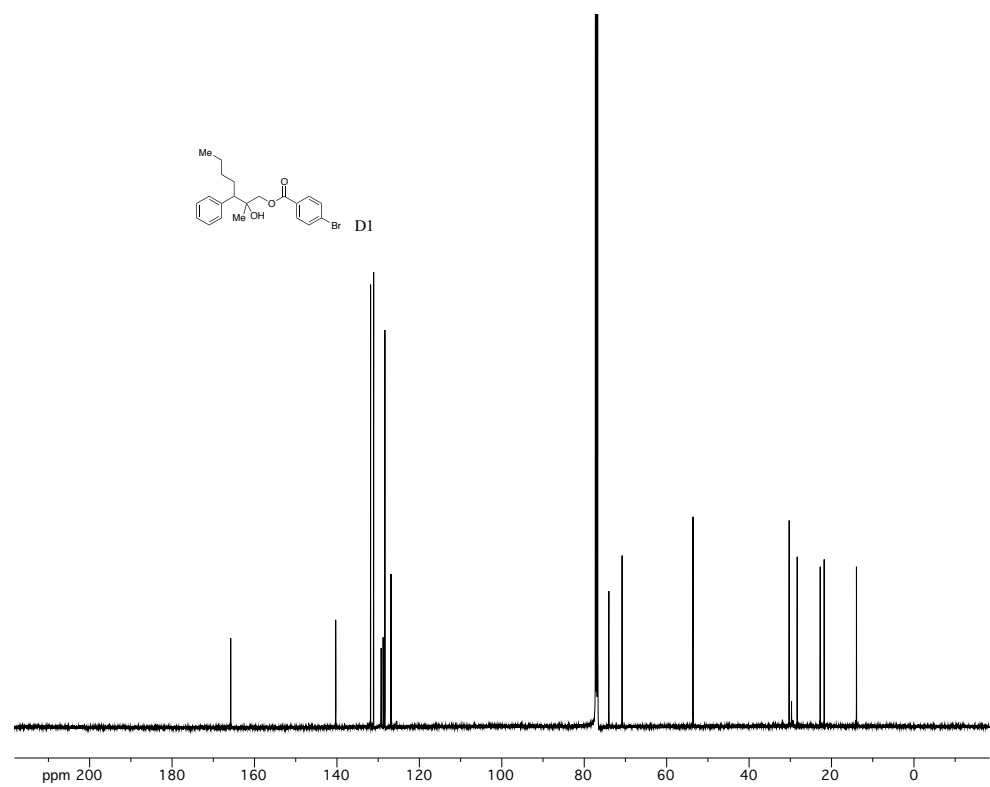
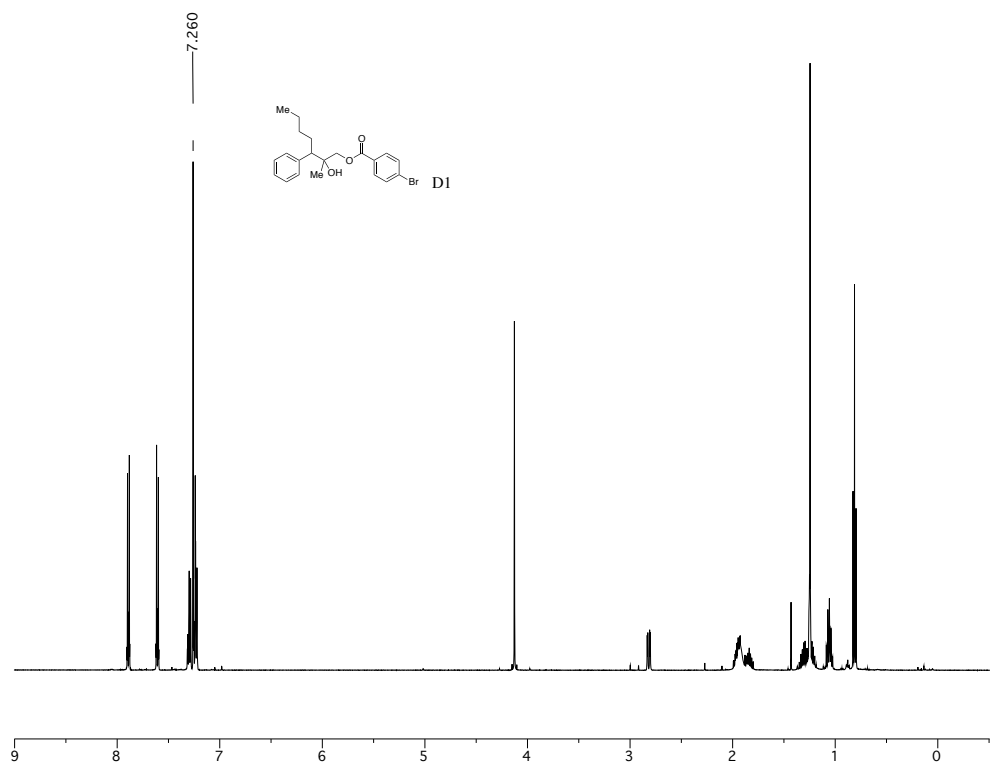


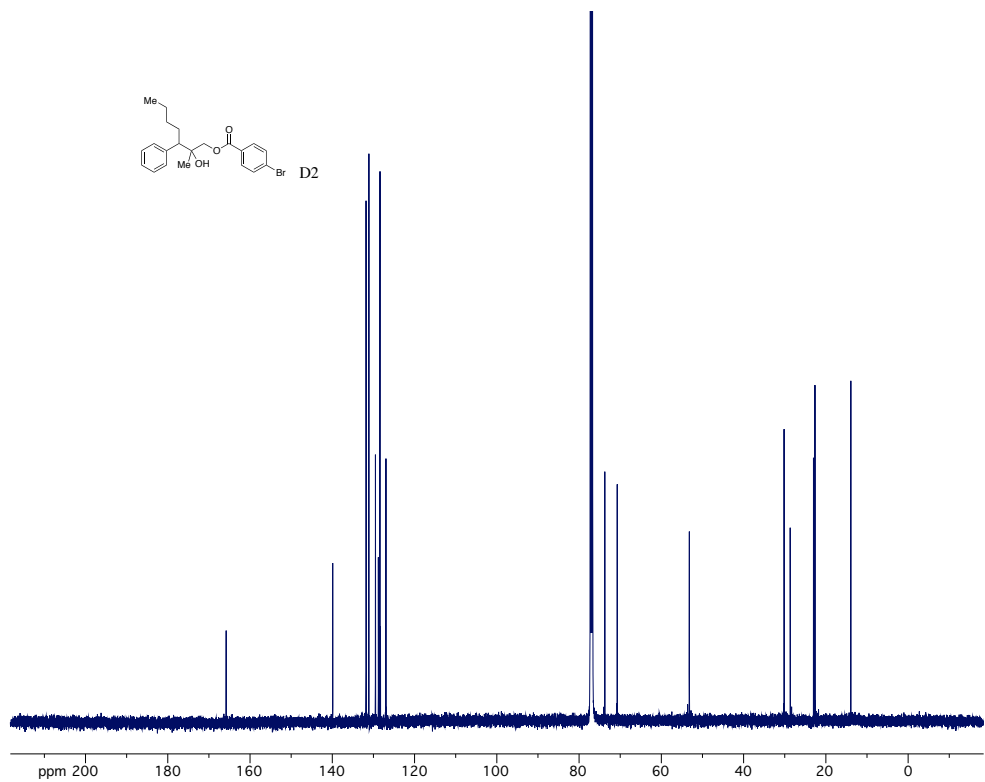
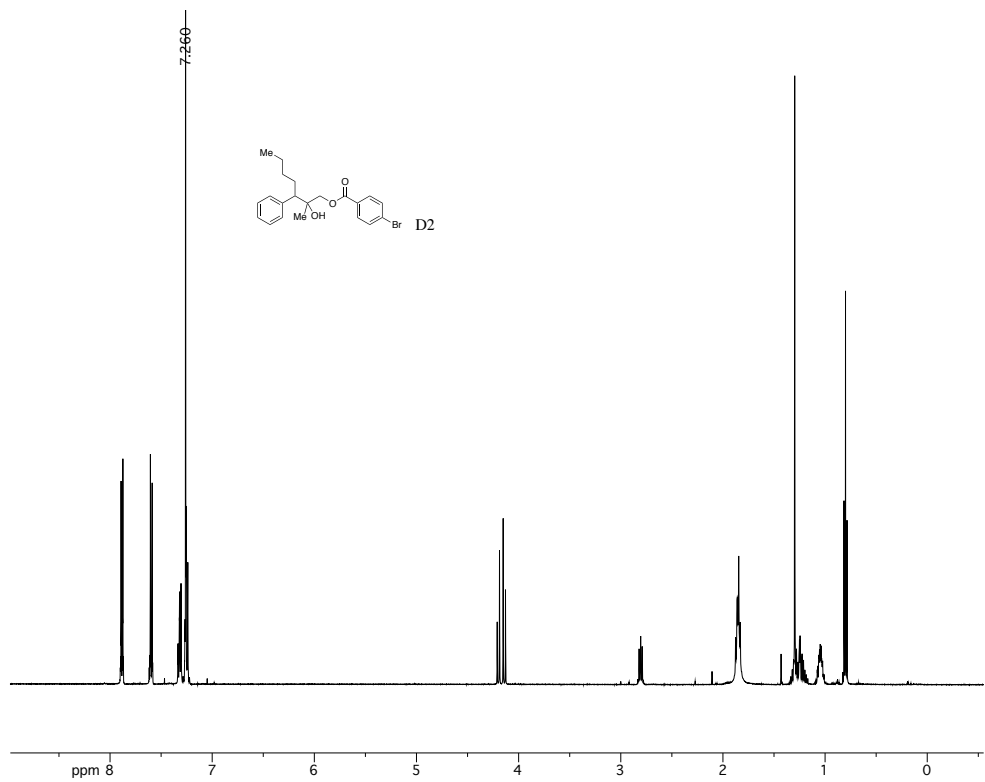


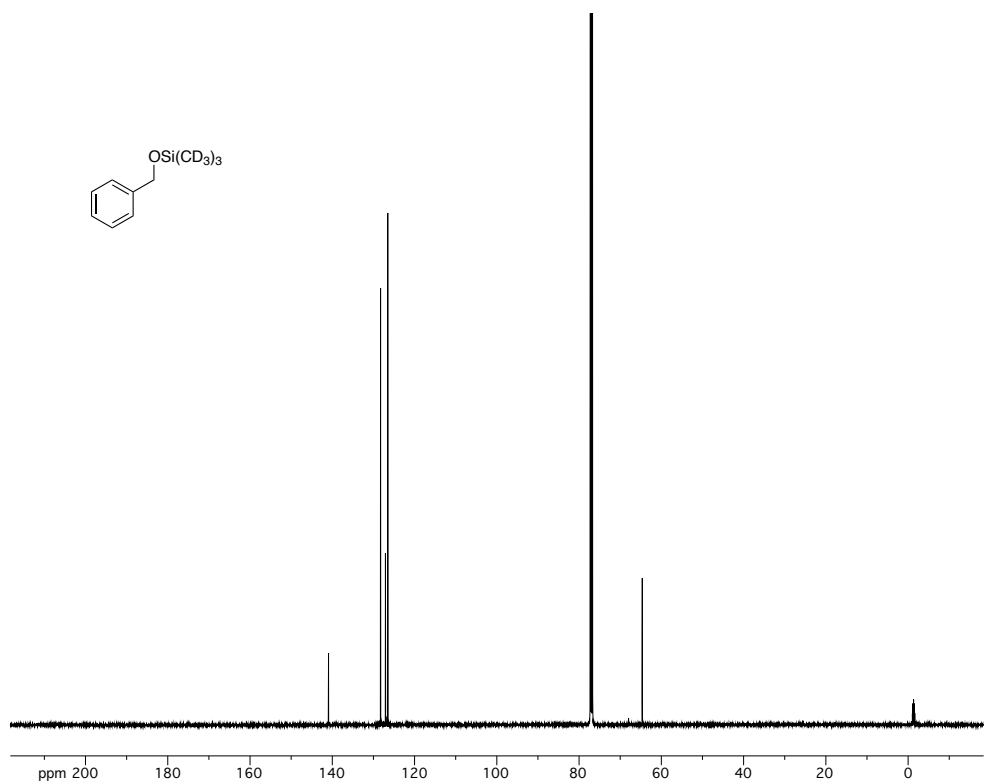




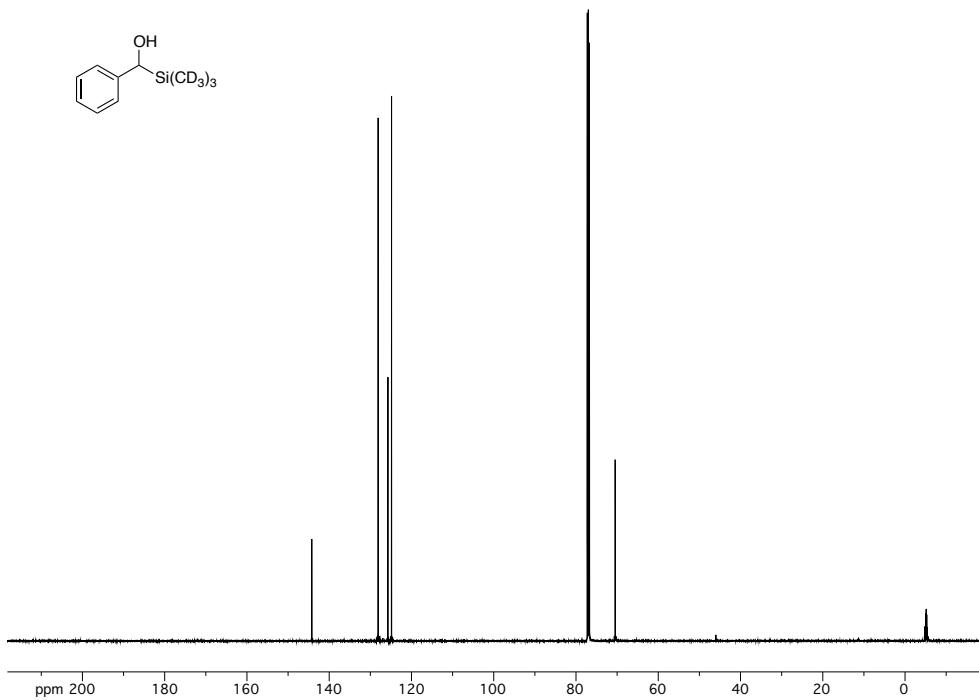
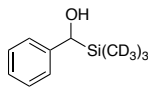
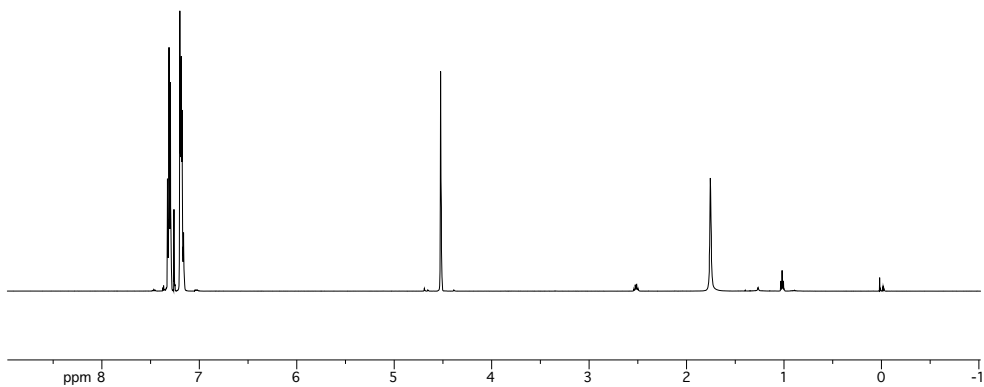
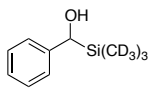


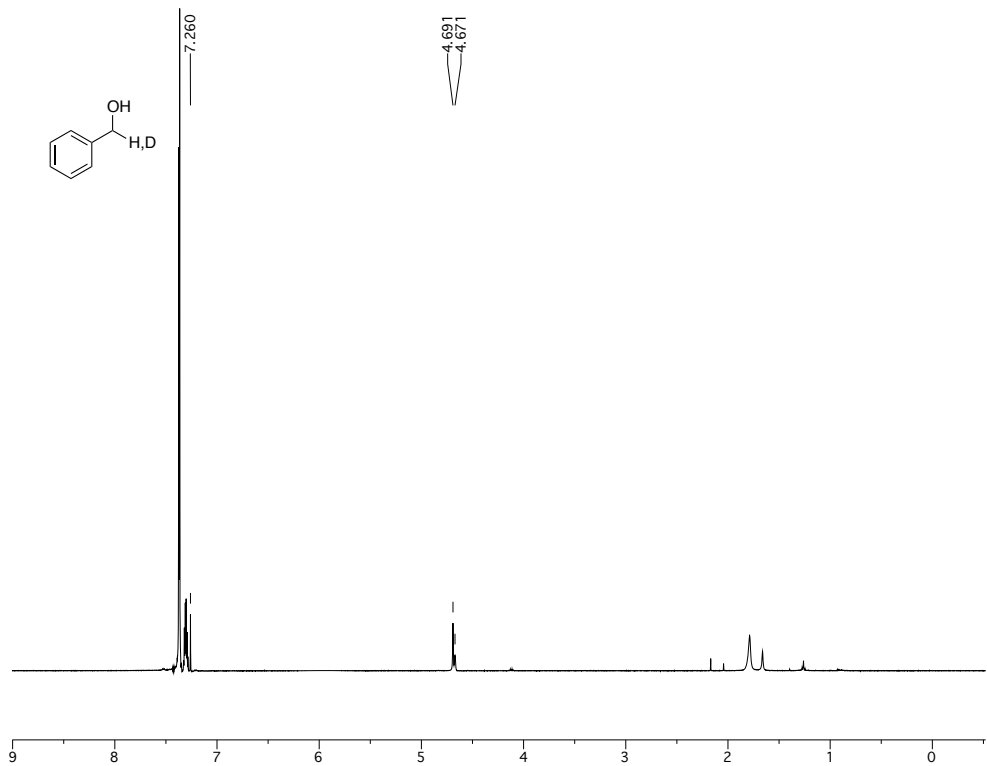
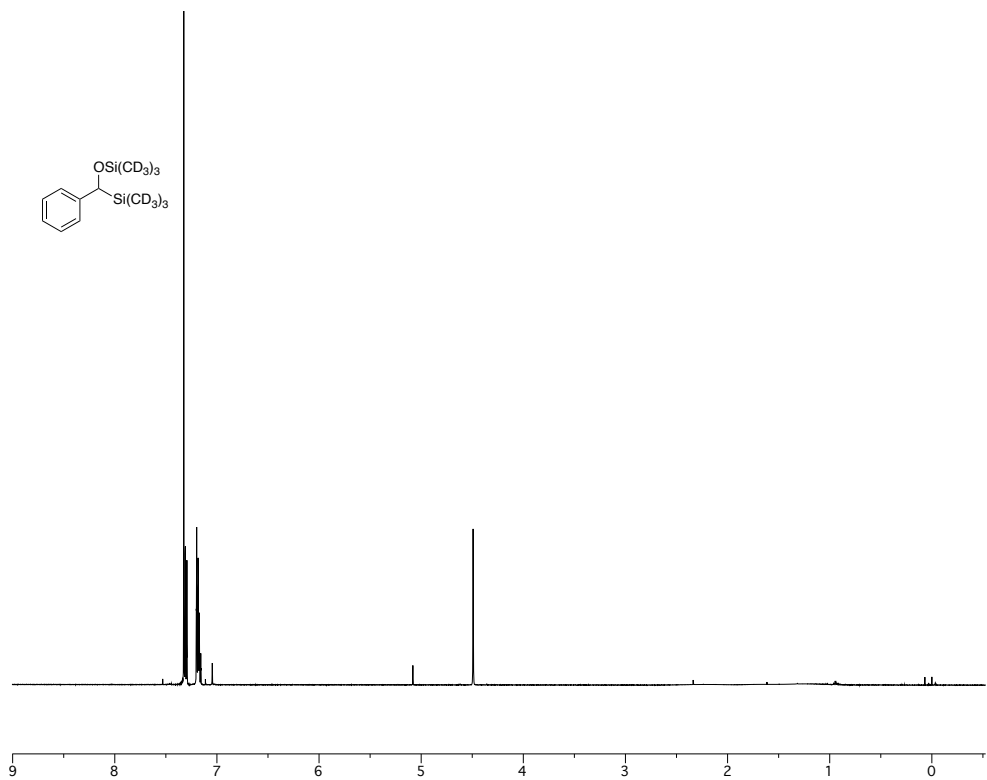


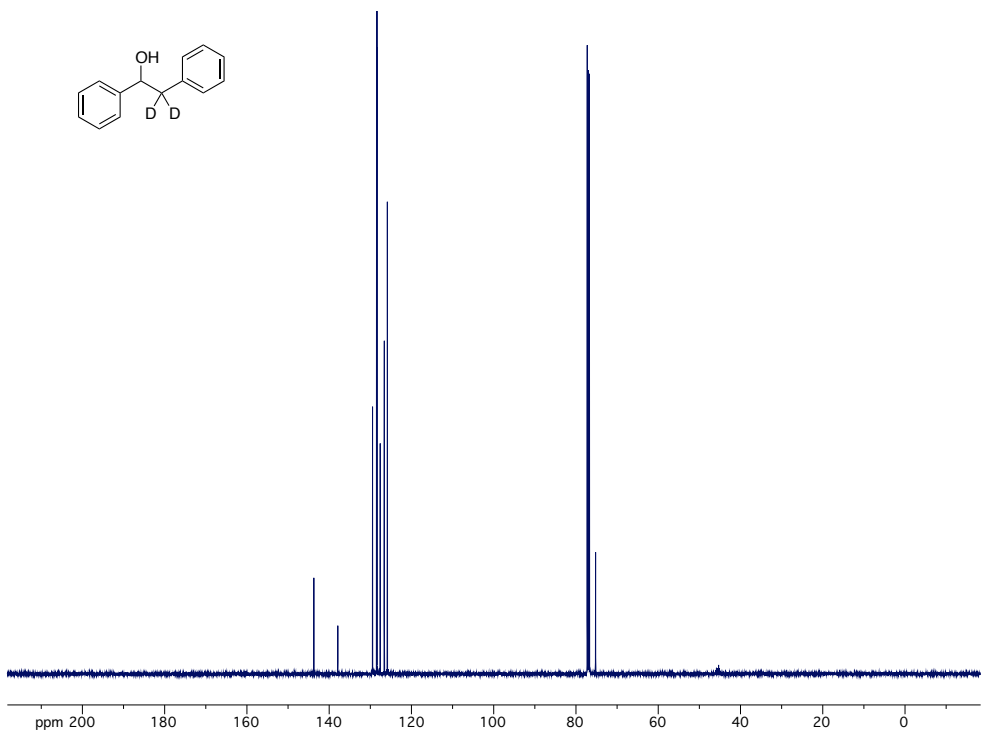
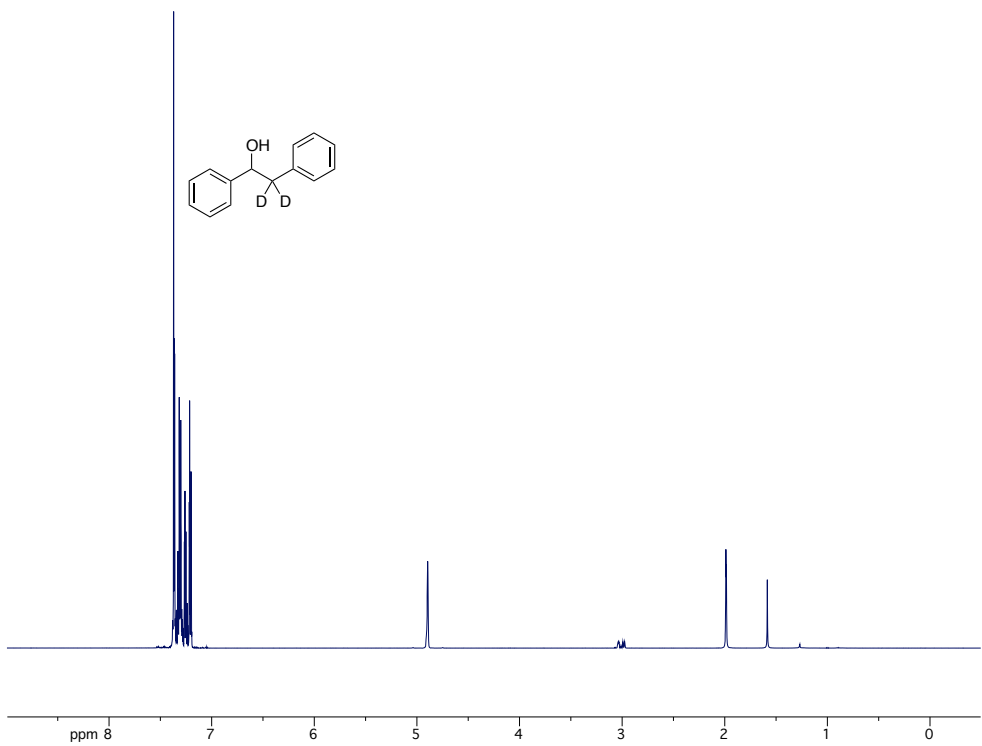






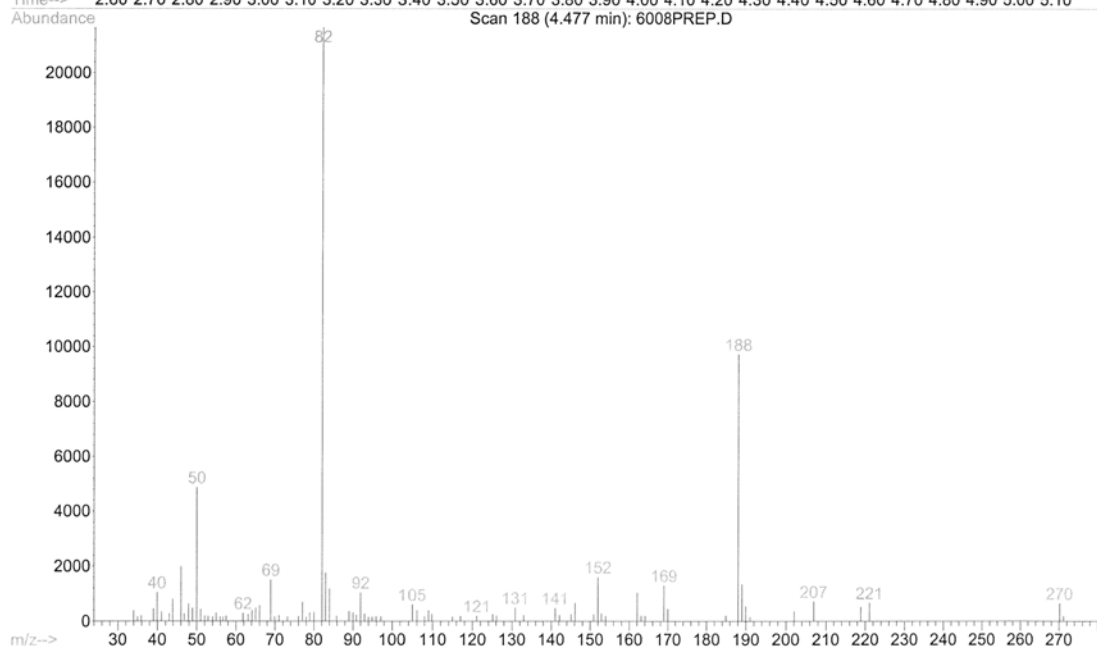
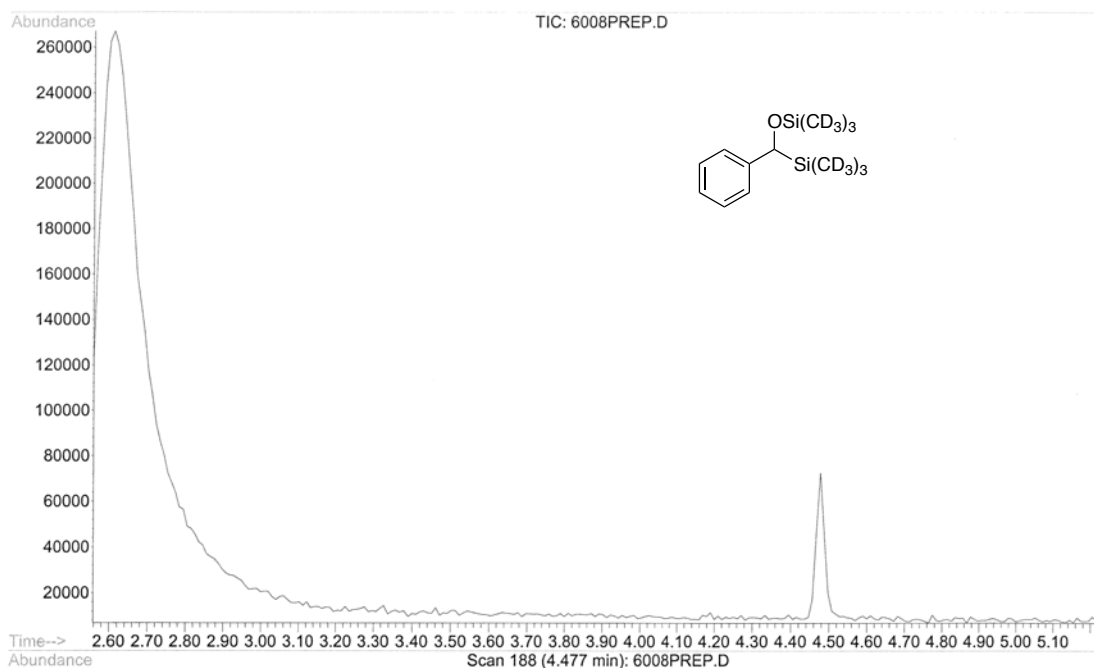






## Selected Mass Spectra

File : C:\HPCHEM\1\DATA\BREKAN\6008PREP.D  
Operator : brekan  
Acquired : 15 May 2011 18:06 using AcqMethod JAB\_3  
Instrument : GC/MS Ins  
Sample Name: jb-6-008.prep  
Misc Info :  
Vial Number: 1



File : C:\HPCHEM\1\DATA\BREKAN\6007.D  
Operator : brekan  
Acquired : 14 May 2011 11:34 using AcqMethod JAB\_3  
Instrument : GC/MS Ins  
Sample Name: jb-6-007  
Misc Info :  
Vial Number: 1

