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Supplementary Material for  
**O–H Hydrogen bonding promotes H-atom transfer from  $\alpha$  C–H bonds  
for C-Alkylation of alcohols**

Jenna L. Jeffrey, Jack A. Terrett, David W. C. MacMillan\*

\*Corresponding author. E-mail: [dmacmill@princeton.edu](mailto:dmacmill@princeton.edu)

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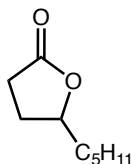
Materials and Methods  
Supplementary Text  
Data  
DFT Calculations

## Materials and Methods

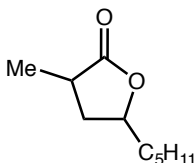
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego (46). Solvents were purified by passage through columns of activated alumina, or according to the method of Grubbs (47). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow column chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still (48). Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed using a UV lamp, *p*-anisaldehyde, potassium permanganate, or ceric ammonium molybdate stain.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker UltraShield Plus (500 and 125 MHz, respectively) instrument, and are internally referenced to residual protio solvent signals. Data for  $^1\text{H}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet), coupling constant (Hz), and integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift relative to  $\text{CDCl}_3$  (77 ppm) and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of wavenumbers ( $\text{cm}^{-1}$ ). High Resolution Mass spectra were obtained from the Princeton University Mass Spectrometry Facility.

## Supplementary Text

**General  $\alpha$ -Alkylation Procedure:** An 8-mL glass vial equipped with a Teflon septum and magnetic stir bar was charged with Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.8 mg, 2.5  $\mu$ mol, 1 mol%), quinuclidine (2.8 mg, 25  $\mu$ mol, 10 mol%), and either tetra-*n*-butylammonium phosphate (21 mg, 63  $\mu$ mol, 25 mol%) or tetra-*n*-butylammonium trifluoroacetate (63  $\mu$ mol, 25 mol%), followed by CH<sub>3</sub>CN (0.31 mL, 0.8 M), 1-hexanol (63  $\mu$ L, 0.50 mmol, 2.0 equiv) and methyl acrylate (23  $\mu$ L, 0.25 mmol, 1.0 equiv). The resulting solution was then sparged with N<sub>2</sub> for 3 minutes. The vial was sealed and placed approximately 3 inches away from a Kessil<sup>®</sup> LED illuminator (model H150 blue, <http://www.kessil.com/horticulture/H150.php>). The reaction mixture was stirred and irradiated for 24 h. The internal temperature was maintained at approximately 27 °C by an electric fan placed approximately 10 inches above the vial. Upon completion, Amberlyst<sup>®</sup> 15 (dry, 100 mg) was added to the reaction mixture in one portion. The resulting mixture was heated with stirring at 50 °C for 3 h. After cooling to room temperature, the Amberlyst<sup>®</sup> 15 beads were removed by filtration and the reaction mixture was concentrated *in vacuo*. Purification of the crude product by flash column chromatography on silica gel using the indicated solvent system afforded the desired product.

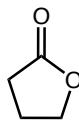


**5-Pentyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0  $\mu$ mol, 1 mol%), quinuclidine (11.1 mg, 100  $\mu$ mol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250  $\mu$ mol, 25 mol%), 1-hexanol (251  $\mu$ L, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0  $\mu$ L, 1.00 mmol, 1.0 equiv), and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) as a colorless liquid (126 mg, 81% yield). Spectral data were identical to those of commercially available material and consistent with previous report (49).

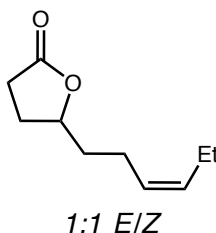


**3-Methyl-5-pentyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0  $\mu$ mol, 1 mol%), quinuclidine (11.1 mg, 100  $\mu$ mol, 10 mol%), tetra-*n*-butylammonium trifluoroacetate (89.0 mg, 250  $\mu$ mol, 25 mol%), 1-hexanol (251  $\mu$ L, 2.00 mmol, 2.0 equiv), isobornyl methacrylate (226  $\mu$ L, 1.00 mmol, 1.0 equiv), and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) as a colorless liquid (141 mg, 83% yield) consisting of two diastereomers (1.7:1 ratio, as determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.50 (tt, *J* = 7.7, 5.3 Hz, 1H), 4.33 (ddt, *J* = 10.7, 7.5, 5.5 Hz, 1H), 2.74–2.60 (m, 2H), 2.48 (ddd, *J* = 12.4, 8.5, 5.4 Hz,

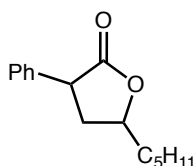
1H), 2.15–2.06 (m, 1H), 2.04–1.94 (m, 1H), 1.79–1.64 (m, 2H), 1.63–1.41 (m, 5H), 1.41–1.23 (m, 14H), 0.93–0.84 (m, 5H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 180.1, 179.6, 78.7, 78.5, 37.4, 35.9, 35.5, 35.4 (2), 34.0, 31.5 (2), 25.0, 24.9, 22.5 (2), 15.9, 15.1, 13.9 ppm; IR (film) 2932, 2862, 1765, 1456, 1378, 1355, 1291, 1188, 1171, 1126, 1081, 1038, 1008 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>19</sub>O<sub>2</sub> [(M+H)<sup>+</sup>] 171.1380, found 171.1378.



**Dihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv), methanol (202 μL, 5.00 mmol, 5.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were subjected to irradiation for 12 h. Upon completion, Amberlyst 15 beads (400 mg) were added and the reaction mixture was heated at 45 °C for 3 h. After cooling the reaction mixture to 23 °C, methyl benzoate (126 μL, 1.00 mmol, 1.0 equiv) was added as an internal standard and <sup>1</sup>H NMR analysis showed the desired product (61% yield), which was not isolated due to its volatility. Data were consistent with previous reports (50, 51).

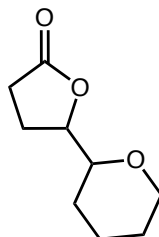


**(Z/E)-5-(Hex-3-en-1-yl)dihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), (*Z*)-hept-4-en-1-ol (134 μL, 1.00 mmol, 1.0 equiv), methyl acrylate (450 μL, 5.00 mmol, 5.0 equiv) and CH<sub>3</sub>CN (3.33 mL, 0.3 M) were used (40 h reaction time). The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (127 mg, 75% yield) consisting of two diastereomers (~1:1 ratio, as determined by <sup>1</sup>H NMR). Spectral data were consistent with previous reports (53, 54).

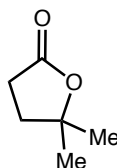


**5-Pentyl-3-phenyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 1-hexanol (251 μL, 2.00 mmol, 2.0 equiv), methyl 2-phenylacrylate (162 mg, 1.00 mmol, 1.0 equiv), and CH<sub>3</sub>CN

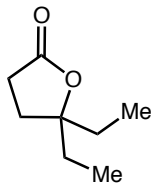
(1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexane) as a colorless oil (176 mg, 76% yield) consisting of two diastereomers (2.2:1 ratio, as determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, single diastereomer) δ 7.40–7.32 (m, 2H), 7.32–7.26 (m, 3H), 4.64 (tt, *J* = 7.5, 5.7 Hz, 1H), 3.90 (dd, *J* = 9.5, 6.8 Hz, 1H), 2.50 (dt, *J* = 13.1, 7.0 Hz, 1H), 2.42–2.34 (m, 1H), 1.87–1.74 (m, 1H), 1.69–1.60 (m, 1H), 1.56–1.46 (m, 1H), 1.46–1.38 (m, 1H), 1.38–1.30 (m, 4H), 0.94–0.87 (m, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.2, 137.2, 128.9, 127.6, 127.5, 79.0, 45.7, 36.4, 35.4, 31.5, 25.0, 22.5, 13.9 ppm; IR (film) 2956, 2930, 2859, 1761, 1605, 1498, 1455, 1364, 1256, 1232, 1155, 1080, 1049, 1031, 1009 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>21</sub>O<sub>2</sub> [(M+H)<sup>+</sup>] 233.1536, found 233.1537.



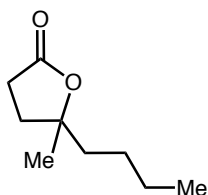
**5-(Tetrahydro-2H-pyran-2-yl)dihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (7.80 mg, 7.00 μmol, 1 mol%), quinuclidine (7.80 mg, 70.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (59.4 mg, 175 μmol, 25 mol%), (tetrahydro-2H-pyran-2-yl)methanol (158 μL, 1.40 mmol, 2.0 equiv), methyl acrylate (63.4 μL, 0.70 mmol, 1.0 equiv) and CH<sub>3</sub>CN (0.88 mL, 0.8 M) were used (48 h reaction time). The product was isolated by flash column chromatography (10:1 hexanes/EtOAc) as a colorless oil (86 mg, 72% yield) consisting of two diastereomers (2:1 ratio, as determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, single diastereomer) δ 4.33 (td, *J* = 6.7, 4.5 Hz, 1H), 4.02–3.91 (m, 1H), 3.50–3.34 (m, 2H), 2.65–2.51 (m, 1H), 2.50–2.36 (m, 1H), 2.22 (td, *J* = 8.4, 6.7 Hz, 2H), 1.94–1.81 (m, 1H), 1.69–1.62 (m, 1H), 1.59–1.43 (m, 3H), 1.29 (tdd, *J* = 12.6, 11.3, 4.0 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.5, 82.0, 78.3, 68.4, 28.2, 27.5, 25.8, 22.9, 22.8 ppm; HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>15</sub>O<sub>3</sub> [(M+H)<sup>+</sup>] 171.1021, found 171.1021.



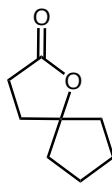
**5,5-Dimethyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), isopropanol (153 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. Analysis of the crude reaction mixture using <sup>1</sup>H NMR with an internal standard (methyl benzoate, 126 μL, 1.00 mmol, 1.0 equiv) indicated 93% yield of the desired product, which was not isolated due to its volatility. Spectral data were consistent with previous report (54).



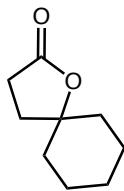
**5,5-Diethyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 0.25 mol%), quinuclidine (2.80 mg, 25.0 μmol, 2.5 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 2-hexanol (252 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used (40 h reaction time). The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (108 mg, 76% yield). Spectral data were consistent with previous report (55).



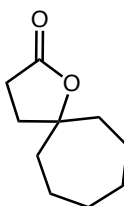
**5-Butyl-5-methyldihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 2-hexanol (252 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (125 mg, 80% yield). Spectral data were consistent with previous report (56).



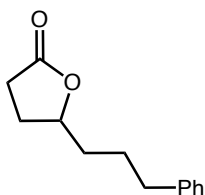
**1-Oxaspiro[4.4]nonan-2-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), cyclopentanol (182 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (111 mg, 79% yield). Spectral data were consistent with previous reports (55, 57, 58).



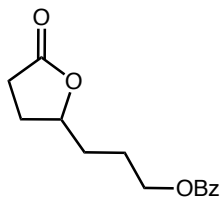
**1-Oxaspiro[4.5]decan-2-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), cyclohexanol (211 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (139 mg, 90% yield). Spectral data were consistent with previous reports (58, 59).



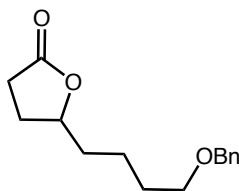
**1-Oxaspiro[4.6]undecan-2-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), cycloheptanol (241 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (151 mg, 90% yield). Spectral data were consistent with previous report (56).



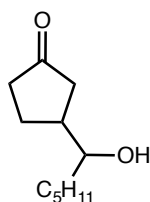
**5-(3-Phenylpropyl)dihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 4-phenylbutan-1-ol (305 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) as a colorless oil (150 mg, 73% yield). Spectral data were consistent with previous reports (60).



**3-(5-Oxotetrahydrofuran-2-yl)propyl benzoate:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 4-hydroxybutyl benzoate (194 mg, 1.00 mmol, 1.0 equiv), methyl acrylate (450 μL, 5.00 mmol, 5.0 equiv), and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) as a colorless oil (201 mg, 81% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.05–7.98 (m, 2H), 7.60–7.51 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 4.59–4.50 (m, 1H), 4.42–4.28 (m, 2H), 2.54 (dd, *J* = 9.6, 6.8 Hz, 2H), 2.35 (dq, *J* = 13.4, 6.8 Hz, 1H), 2.04–1.73 (m, 5H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.9, 166.4, 132.9, 130.0, 129.4, 128.3, 80.2, 64.1, 32.2, 28.7, 27.9, 24.8 ppm; IR (film) 2953, 1768, 1712, 1602, 1584, 1492, 1452, 1421, 1385, 1349, 1314, 1271, 1221, 1175, 1113, 1070, 1025 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>17</sub>O<sub>4</sub> [(M+H)<sup>+</sup>] 249.1121, found 249.1121.



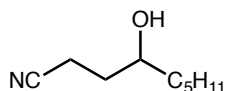
**5-(4-(Benzyloxy)butyl)dihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 5-(benzyloxy)pentan-1-ol (389 mg, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (6:3:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes/EtOAc) as a colorless oil (186 mg, 75% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37–7.26 (m, 5H), 4.54–4.43 (m, 3H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.56–2.49 (m, 2H), 2.31 (dq, *J* = 12.9, 6.8 Hz, 1H), 1.90–1.70 (m, 2H), 1.70–1.42 (m, 5H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.2, 138.4, 128.3, 127.6, 127.5, 80.8, 72.9, 69.9, 35.3, 29.4, 28.8, 27.9, 22.1 ppm; IR (film) 3030, 2933, 2859, 1767, 1496, 1454, 1421, 1360, 1217, 1178, 1098, 1019 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>20</sub>NaO<sub>3</sub> [(M+Na)<sup>+</sup>] 271.13047, found 271.13034.



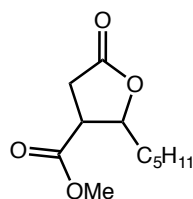
**3-(1-Hydroxyhexyl)cyclopentan-1-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium trifluoroacetate (89.0 mg, 250 μmol, 25 mol%), cyclopent-2-



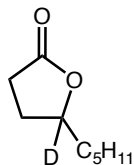
enone (84.0  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv), 1-hexanol (251  $\mu\text{L}$ , 2.00 mmol, 2.0 equiv) and  $\text{CH}_3\text{CN}$  (1.25 mL, 0.8 M) were used (70 h reaction time). The product was isolated by flash column chromatography (2:1 hexanes/EtOAc) as a colorless oil (155 mg, 84% yield) consisting of two diastereomers and the corresponding ketals.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.68–3.47 (m, 1H), 2.40–2.09 (m, 5H), 2.08–1.98 (m, 1H), 1.81–1.68 (m, 1H), 1.56–1.38 (m, 4H), 1.37–1.28 (m, 4H), 0.94–0.85 (m, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  219.3, 219.1, 74.5, 74.3, 42.8, 42.7, 41.8, 40.4, 38.6, 38.5, 35.8, 35.8, 31.8, 31.8, 26.0, 25.3, 25.3, 24.6, 22.6, 14.0 ppm; IR (film) 3431, 2956, 2928, 2859, 1733, 1461, 1403, 1378, 1282, 1162, 1126, 1053, 1024  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{20}\text{O}_2$   $[(\text{M})^+]$  184.1463, found 184.1462. A portion of the product mixture (38 mg) was heated in acetic anhydride (20 equiv) at 80  $^\circ\text{C}$  for 12 h. Upon completion, the reaction mixture was cooled to 25  $^\circ\text{C}$  and the solvent was removed *in vacuo* to afford the acetate as a colorless oil consisting of two diastereomers (~1:1 ratio).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.00–4.89 (m, 1H), 2.44–2.23 (m, 3H), 2.22–2.06 (m, 2H), 2.05 (s, 1.5H), 2.03 (s, 1.5H), 1.94–1.85 (m, 0.5 H), 1.78–1.66 (m, 0.5H), 1.65–1.44 (m, 3H), 1.36–1.13 (m, 6H), 0.90–0.82 (m, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  218.0, 217.9, 170.7, 170.7, 75.8, 75.7, 41.5, 40.6, 40.5, 40.4, 38.4, 38.0, 32.8, 32.7, 31.6, 25.9, 24.9, 24.8, 22.4, 21.0, 21.0, 13.9 ppm; IR (film) 2932, 2862, 1734, 1461, 1406, 1372, 1235, 1160, 1130, 1049, 1022  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{22}\text{NaO}_3$   $[(\text{M}+\text{Na})^+]$  249.1467, found 249.1467.



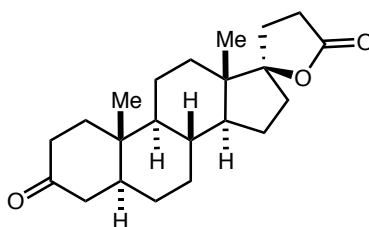
**4-Hydroxynonanenitrile:** According to the general procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (11.2 mg, 10.0  $\mu\text{mol}$ , 1 mol%), quinuclidine (11.1 mg, 100  $\mu\text{mol}$ , 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250  $\mu\text{mol}$ , 25 mol%), 1-hexanol (251  $\mu\text{L}$ , 2.00 mmol, 2.0 equiv), acrylonitrile (66.0  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv) and  $\text{CH}_3\text{CN}$  (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1  $\rightarrow$  1:1 hexanes/EtOAc) as a colorless oil (117 mg, 75% yield). Spectral data were consistent with previous reports (61, 62).



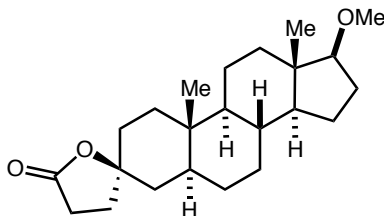
**Methyl 5-oxo-2-pentyltetrahydrofuran-3-carboxylate:** According to the general procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (11.2 mg, 10.0  $\mu\text{mol}$ , 1 mol%), quinuclidine (11.2 mg, 100  $\mu\text{mol}$ , 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250  $\mu\text{mol}$ , 25 mol%), 1-hexanol (314  $\mu\text{L}$ , 2.5 mmol, 2.5 equiv), dimethyl fumarate (144 mg, 1.00 mmol, 1.0 equiv), and  $\text{CH}_3\text{CN}$  (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (141 mg, 66% yield) consisting of two diastereomers (1.4:1 ratio, as determined by  $^1\text{H}$  NMR). Spectral data were consistent with previous reports (63).



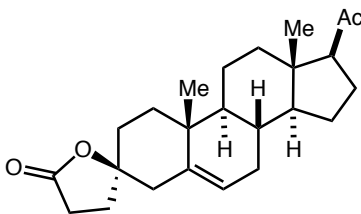
**5-Pentyl-2,3-dihydrofuran-2-one-5-*d***: According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), hexan-1,1-*d*<sub>2</sub>-1-ol (52.0 mg, 0.50 mmol, 2.0 equiv), methyl acrylate (23.0 μL, 0.250 mmol, 1.0 equiv) and CH<sub>3</sub>CN (0.31 mL, 0.8 M) were used. Purification by silica gel column chromatography (9:1→2:1 hexanes/EtOAc) afforded the product (72.5 mg, 80% yield) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.55–2.50 (m, 2H), 2.31 (dt, *J* = 13.4, 6.9 Hz, 1H), 1.84 (dt, *J* = 12.7, 9.4 Hz, 1H), 1.73 (ddd, *J* = 14.5, 9.9, 5.1 Hz, 1H), 1.63–1.53 (m, 1H), 1.51–1.25 (m, 6H), 0.93–0.84 (m, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.3, 80.6 (t), 35.4, 31.5, 28.8, 27.8, 24.8, 22.5, 13.9 ppm. IR (film) 2931, 2861, 1769, 1460, 1422, 1379, 1280, 1254, 1197, 1175, 1128, 1046 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>9</sub>H<sub>16</sub>DO<sub>2</sub> [(M+H)<sup>+</sup>] 158.1291, found 158.1289.



**(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethylhexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-17,2'-furan]-3,5'(2*H*)-dione**: According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), dihydrotestosterone (72.6 mg, 0.25 mmol, 1.0 equiv), methyl acrylate (68.0 μL, 0.750 mmol, 3.0 equiv) and DMF (0.50 mL, 0.5 M) were used. Purification by silica gel column chromatography (9:1→2:1 hexanes/EtOAc) followed by recrystallization from hexanes afforded the product (45.3 mg, 53% yield, >20:1 dr as determined by <sup>1</sup>H NMR) as a colorless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.60–2.44 (m, 2H), 2.43–2.34 (m, 2H), 2.33–2.19 (m, 3H), 2.09 (ddd, *J* = 15.0, 3.9, 2.3 Hz, 1H), 2.02 (ddd, *J* = 13.1, 6.5, 2.4 Hz, 1H), 1.90 (ddd, *J* = 12.8, 9.3, 7.5 Hz, 1H), 1.80 (ddd, *J* = 14.1, 9.6, 5.8 Hz, 1H), 1.73 (dq, *J* = 13.1, 3.5 Hz, 1H), 1.70–1.61 (m, 2H), 1.56 (dt, *J* = 12.0, 3.2 Hz, 1H), 1.53–1.48 (m, 1H), 1.47–1.26 (m, 6H), 1.14 (ddd, *J* = 12.2, 10.6, 7.4 Hz, 1H), 1.02 (s, 3H), 0.94 (s, 3H), 0.93–0.84 (m, 1H), 0.72 (ddd, *J* = 12.3, 10.8, 4.3 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 211.7, 176.8, 96.0, 53.4, 49.6, 46.6, 45.7, 44.6, 38.5, 38.1, 35.7, 35.7, 35.6, 31.8, 31.2, 31.2, 29.3, 28.6, 22.9, 20.8, 14.6, 11.5 ppm; IR (film) 2929, 2854, 1767, 1737, 1709, 1446, 1420, 1385, 1264, 1214, 1187, 1152, 1076, 1055, 1025 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>32</sub>O<sub>3</sub> [(M+H)<sup>+</sup>] 345.2424, found 345.2424.

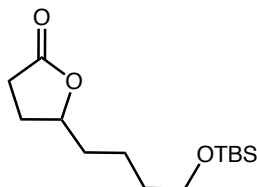


**(5S,8R,9S,10S,13S,14S,17S)-17-Methoxy-10,13-dimethyloctadecahydro-5'H-spiro[cyclopenta[a]phenanthrene-3,2'-furan]-5'-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), (5S,8R,9S,10S,13S,14S,17S)-17-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (77.0 mg, 0.250 mmol, 1.0 equiv), methyl acrylate (45.0 μL, 0.50 mmol, 2.0 equiv) and CH<sub>3</sub>CN (0.31 mL, 0.8 M) were used (48 h reaction time). The product was isolated by silica gel column chromatography (9:1→2:1 hexanes/EtOAc) as a colorless solid (69.0 mg, 77% yield, >20:1 dr as determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.33 (s, 3H), 3.20 (t, *J* = 8.3 Hz, 1H), 2.57 (t, *J* = 8.3 Hz, 2H), 2.14–1.95 (m, 3H), 1.94–1.85 (m, 2H), 1.80 (t, *J* = 13.1 Hz, 1H), 1.74 (dt, *J* = 13.6, 3.7 Hz, 1H), 1.68 (dt, *J* = 13.0, 3.6 Hz, 1H), 1.61 (dq, *J* = 12.8, 3.2 Hz, 1H), 1.58–1.49 (m, 2H), 1.48–1.34 (m, 3H), 1.34–1.20 (m, 4H), 1.14 (td, *J* = 12.7, 4.0 Hz, 2H), 1.07–0.90 (m, 2H), 0.84 (s, 4H), 0.74 (s, 3H), 0.65 (td, *J* = 11.5, 4.1 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.6, 90.7, 87.4, 57.8, 54.4, 51.2, 43.4, 42.9, 39.3, 38.0, 35.6, 35.6, 35.2, 32.3, 31.5, 31.3, 28.6, 28.4, 27.6, 23.3, 20.9, 11.7, 11.6 ppm; IR (film) 2923, 2847, 1773, 1451, 1361, 1294, 1265, 1212, 1188, 1172, 1141, 1117, 1103, 1082, 1023 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd for C<sub>23</sub>H<sub>37</sub>O<sub>3</sub> [(M+H)<sup>+</sup>] 361.2737, found 361.2737.

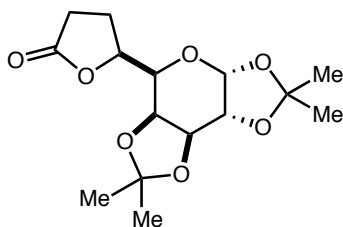


**(8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-1,2,3',4,4',7,8,9,10,11,12,13,14,15,16,17-hexadecahydro-5'H-spiro[cyclopenta[a]phenanthrene-3,2'-furan]-5'-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (5.60 mg, 5.00 μmol, 1 mol%), quinuclidine (5.60 mg, 50.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (42.4 mg, 125 μmol, 25 mol%), 3β-hydroxypregn-5-en-20-one (158 mg, 0.50 mmol, 1.0 equiv), methyl acrylate (362 μL, 4.00 mmol, 8.0 equiv) and DMF (1.25 mL, 0.4 M) were used (48 h reaction time). Purification by silica gel column chromatography (2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes), followed by recrystallization from ethanol, afforded the title compound (129 mg, 70% yield, >20:1 dr as determined by <sup>1</sup>H NMR) as a colorless solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.40–5.35 (m, 1H), 2.68 (dq, *J* = 13.4, 2.8 Hz, 1H), 2.63–2.46 (m, 3H), 2.21–2.13 (m, 1H), 2.11 (s, 3H), 2.10–1.97 (m, 5H), 1.93–1.80 (m, 2H), 1.73–1.38 (m, 8H), 1.28–1.18 (m, 1H), 1.17–1.08 (m, 2H), 1.03 (s, 3H), 1.02–0.95 (m, 1H), 0.62 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 209.4, 176.5, 139.0, 123.4, 87.3, 63.6, 56.7, 50.0, 43.9, 42.8, 38.7, 36.4, 35.6, 33.1, 31.7, 31.7, 31.5, 29.6, 28.4, 24.4, 22.7, 21.0, 19.0, 13.2 ppm; IR (film) 2965, 2939, 2892, 2866, 2852, 2825, 1775, 1701, 1447,

1383, 1356, 1294, 1265, 1245, 1223, 1204, 1186, 1164, 1152, 1130, 1096, 1073, 1038, 1018  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{35}\text{O}_3$   $[(\text{M}+\text{H})^+]$  371.2586, found 371.2586.

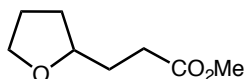


**5-((*tert*-Butyldimethylsilyloxy)butyl)dihydrofuran-2(3*H*)-one:** According to the general procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.80 mg, 2.50  $\mu\text{mol}$ , 0.25 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 2.50 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250  $\mu\text{mol}$ , 25 mol%), 5-((*tert*-butyldimethylsilyloxy)pentan-1-ol (437 mg, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv) and  $\text{CH}_3\text{CN}$  (1.25 mL, 0.8 M) were used (40 h reaction time). The product was isolated by silica gel column chromatography (10:1 hexanes/EtOAc) as a colorless oil (199 mg, 73% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.53–4.44 (m, 1H), 3.61 (t,  $J$  = 6.2 Hz, 2H), 2.57–2.49 (m, 2H), 2.32 (ddt,  $J$  = 13.0, 7.4, 6.5 Hz, 1H), 1.85 (dtd,  $J$  = 12.8, 9.5, 8.0 Hz, 1H), 1.80–1.72 (m, 1H), 1.67–1.40 (m, 5H), 0.89 (s, 9H), 0.04 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2, 80.9, 62.8, 35.3, 32.4, 28.8, 28.0, 25.9, 21.7, 18.3, -5.3 ppm; IR (film) 2932, 2858, 1776, 1462, 1360, 1254, 1178, 1097, 1007  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{29}\text{O}_3\text{Si}$   $[(\text{M}+\text{H})^+]$  273.1886, found 273.1885. Spectral data were consistent with previous reports (64, 65).

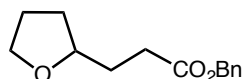


**(*S*)-5-((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)dihydrofuran-2(3*H*)-one:** According to the general procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.80 mg, 2.50  $\mu\text{mol}$ , 1 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0  $\mu\text{mol}$ , 25 mol%), 1,2:3,4-Di-*O*-isopropylidene- $\alpha$ -D-galactopyranose (65.0 mg, 0.25 mmol, 1.0 equiv), methyl acrylate (227  $\mu\text{L}$ , 2.50 mmol, 8.0 equiv) and  $\text{CH}_3\text{CN}$  (0.50 mL, 0.5 M) were used. The product was isolated by silica gel column chromatography (4:1 hexanes/EtOAc) as a colorless viscous oil (67.3 mg, 85% yield) consisting of two diastereomers (~1:1 ratio). The diastereomers were separated by a second flash column (silica gel, 4:1 hexanes/EtOAc  $\rightarrow$  2:1 hexanes/EtOAc). Diastereomer 1:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.52 (d,  $J$  = 4.9 Hz, 1H), 4.69 (q,  $J$  = 7.1 Hz, 1H), 4.62 (dd,  $J$  = 8.0, 2.4 Hz, 1H), 4.36 (dd,  $J$  = 8.0, 1.9 Hz, 1H), 4.32 (dd,  $J$  = 5.0, 2.4 Hz, 1H), 3.74 (dd,  $J$  = 7.5, 1.9 Hz, 1H), 2.55–2.49 (m, 2H), 2.42–2.32 (m, 1H), 2.28–2.17 (m, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 109.5, 108.8, 96.2, 77.5, 70.6, 70.5, 70.4, 69.0, 27.9, 26.1, 25.8, 24.8, 24.7, 24.1 ppm; IR (film) 2988, 2938, 1779, 1459, 1382, 1373, 1254, 1211, 1164, 1106, 1063  $\text{cm}^{-1}$ ; Diastereomer 2:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.56 (d,  $J$  = 5.0 Hz, 1H), 4.70–4.57 (m, 2H), 4.34 (dd,  $J$  = 5.0, 2.5 Hz, 1H), 4.26 (dd,  $J$  = 7.9, 2.0

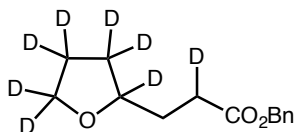
Hz, 1H), 3.79 (dd,  $J = 7.5, 1.9$  Hz, 1H), 2.59–2.49 (m, 2H), 2.43–2.33 (m, 1H), 2.07 (dq,  $J = 12.9, 9.8$  Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.32 (s, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 109.8, 108.8, 96.2, 79.5, 70.7, 70.3, 70.2, 69.9, 28.5, 26.1, 25.9, 24.9, 24.5, 24.1 ppm; IR (film) 2987, 2937, 1774, 1458, 1377, 1253, 1210, 1166, 1104, 1067, 1047, 1023  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{23}\text{O}_7$  [(M+H) $^+$ ] 315.1444, found 315.1445.



**Methyl 3-(tetrahydrofuran-2-yl)propanoate:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0  $\mu\text{mol}$ , 1 mol%), quinuclidine (11.1 mg, 100  $\mu\text{mol}$ , 10 mol%), tetrahydrofuran (164  $\mu\text{L}$ , 2.00 mmol, 2.0 equiv), methyl acrylate (90.0  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv) and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used. Methyl benzoate (126  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv) was added as an internal standard and  $^1\text{H}$  NMR analysis showed the desired product (64% yield). The volatile product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.87–3.78 (m, 2H), 3.70 (td,  $J = 8.0, 6.3$  Hz, 1H), 3.66 (s, 3H), 2.51–2.32 (m, 2H), 1.98 (dddd,  $J = 11.7, 8.5, 6.5, 5.0$  Hz, 1H), 1.94–1.75 (m, 4H), 1.46 (ddt,  $J = 12.0, 8.7, 7.4$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 78.1, 67.7, 51.6, 31.2, 30.9, 30.7, 25.7 ppm; IR (film) 2953, 2872, 1735, 1438, 1356, 1260, 1195, 1164, 1069, 1017  $\text{cm}^{-1}$ .

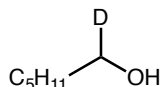


**Benzyl 3-(tetrahydrofuran-2-yl)propanoate:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50  $\mu\text{mol}$ , 1 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 10 mol%), benzyl acrylate (37.5  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv), tetrahydrofuran (61.0  $\mu\text{L}$ , 0.75 mmol, 3.0 equiv), and CH<sub>3</sub>CN (0.63 mL, 0.3 M) were used. The product was isolated by flash column chromatography (6:1 hexanes/EtOAc) as a colorless oil (20.6 mg, 35% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.27 (m, 5H), 5.12 (s, 2H), 3.87–3.78 (m, 2H), 3.70 (td,  $J = 8.0, 6.3$  Hz, 1H), 2.57–2.38 (m, 2H), 2.02–1.93 (m, 1H), 1.93–1.78 (m, 4H), 1.46 (ddt,  $J = 11.9, 8.7, 7.4$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 136.0, 128.5, 128.1, 128.1, 78.1, 67.7, 66.1, 31.1, 31.1, 30.6, 25.7 ppm; IR (film) 2955, 2869, 1733, 1498, 1457, 1419, 1379, 1350, 1258, 1213, 1157, 1110, 1069, 1017  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{18}\text{NaO}_3$  [(M+Na) $^+$ ] 257.1154, found 257.1155.

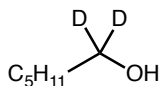


**Benzyl 3-(tetrahydrofuran-2-yl-*d*<sub>7</sub>)propanoate-2-*d*:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50  $\mu\text{mol}$ , 1 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 10 mol%), benzyl acrylate (37.5  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv), tetrahydrofuran-*d*<sub>8</sub> (61.0  $\mu\text{L}$ , 0.75 mmol, 3.0 equiv), and CH<sub>3</sub>CN (0.63 mL, 0.3 M) were used. The product was isolated by flash column chromatography (6:1 hexanes/EtOAc) as a colorless oil (24.5 mg, 41% yield), which was partially deuterated (23%) at the carbon position  $\alpha$  to the carbonyl.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

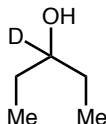
$\delta$  7.40–7.28 (m, 5H), 5.12 (s, 2H), 2.56–2.39 (m, 1.55H, 23% D incorporation), 1.90–1.76 (m, 2H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 136.0, 128.5, 128.1, 128.1, 77.5 (m), 66.8 (m), 66.1, 31.1, 30.8 (m), 30.8 (m), 30.5, 30.4, 24.6 (m) ppm; IR (film) 2941, 1732, 1498, 1456, 1381, 1355, 1242, 1214, 1164, 1106, 1027  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{D}_8\text{NaO}_3$  [(M+Na) $^+$ ] 265.1656, found 265.1656.



**Hexan-1-*d*-1-ol:** To a suspension of  $\text{LiAlD}_4$  (342 mg, 8.14 mmol, 0.5 equiv) in dry THF (5 mL) at 0 °C was added a solution of hexanal (2.00 mL, 16.3 mmol, 1.0 equiv) in THF (5 mL) dropwise. The mixture was warmed to 23 °C and stirred an additional 3 h at 23 °C. Upon completion, the solution was cooled to 0 °C and quenched by addition of 1 M aqueous HCl. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 15 mL). The combined organic extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/ $\text{Et}_2\text{O}$ ) afforded the pure product as a colorless liquid (1.4 g, 83% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.62 (ddd,  $J = 8.3, 4.9, 1.6$  Hz, 1H), 1.56 (q,  $J = 7.0$  Hz, 2H), 1.42–1.24 (m, 6H), 0.89 (t,  $J = 6.8$  Hz, 3H) ppm; IR (film) 3320, 2957, 2927, 2859, 2163, 1463, 1379, 1343, 1131, 1066, 1033  $\text{cm}^{-1}$ . Spectral data were consistent with previous report (66).

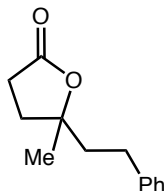


**Hexan-1,1-*d*<sub>2</sub>-1-ol:** To a suspension of  $\text{LiAlD}_4$  (504 mg, 12.0 mmol, 0.5 equiv) in dry THF (5 mL) at 0 °C was added a solution of methyl hexanoate (3.53 mL, 24.0 mmol, 1.0 equiv) in THF (5 mL) dropwise. The mixture was warmed to 23 °C and stirred an additional 3 h at 23 °C. Upon completion, the solution was cooled to 0 °C and quenched by addition of 1 M aqueous HCl. The mixture was extracted with  $\text{Et}_2\text{O}$  (3 x 15 mL). The combined organic extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/ $\text{Et}_2\text{O}$ ) afforded the pure product as a colorless liquid (2.25 g, 90% yield). Spectral data were consistent with previous report (67).

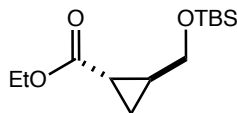


**Pentan-3-*d*-3-ol:** To a suspension of  $\text{LiAlD}_4$  (323 mg, 7.69 mmol, 0.25 equiv) in dry THF (5 mL) at 0 °C was added a solution of 3-pentanone (3.25 mL, 30.8 mmol, 1.0 equiv) in THF (5 mL) dropwise. The mixture was warmed to 23 °C and stirred an additional 3 h at 23 °C. Upon completion, the solution was cooled to 0 °C and quenched by addition of 1 M aqueous HCl. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 15 mL). The combined organic extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/ $\text{Et}_2\text{O}$ ) afforded the pure product as a colorless liquid (2.2 g, 80% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.57–1.37 (m, 4H), 1.34 (brs, 1H), 0.94 (t,  $J = 7.5$

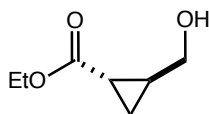
Hz, 6H) ppm; IR (film) 3351, 2963, 2930, 2877, 2149, 1460, 1378, 1328, 1266, 1173, 1147, 1040  $\text{cm}^{-1}$ . Spectral data were consistent with previous report (68).



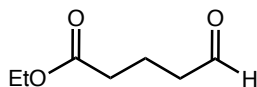
**5-Methyl-5-phenethylidihydrofuran-2(3H)-one:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (11.2 mg, 10.0  $\mu\text{mol}$ , 1 mol%), quinuclidine (11.1 mg, 100  $\mu\text{mol}$ , 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250  $\mu\text{mol}$ , 25 mol%), 4-phenylbutan-2-ol (307  $\mu\text{L}$ , 2.00 mmol, 2.0 equiv), methyl acrylate (90.0  $\mu\text{L}$ , 1.00 mmol, 1.0 equiv), and CH<sub>3</sub>CN (1.25 mL, 0.8 M) were used (30 h reaction time). The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless oil (120 mg, 59% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.27 (m, 2H), 7.23–7.16 (m, 3H), 2.82–2.53 (m, 4H), 2.14 (ddd,  $J$  = 12.9, 9.5, 7.9 Hz, 1H), 2.07–1.92 (m, 3H), 1.47 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  176.6, 141.2, 128.5, 128.2, 126.1, 86.3, 42.9, 33.1, 30.2, 29.1, 25.6 ppm; IR (film) 3027, 2975, 2934, 1762, 1603, 1497, 1455, 1421, 1383, 1290, 1252, 1206, 1172, 1142, 1116, 1088, 1031, 1011  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$  calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>2</sub> [(M+Na)<sup>+</sup>] 227.1048, found 227.1049.



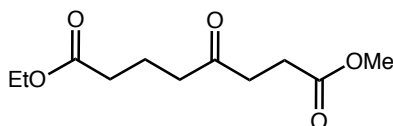
**Ethyl (1S,2S)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopropane-1-carboxylate:** To a solution of ethyl 2-(diethoxyphosphoryl)acetate (4.21 mL, 21.2 mmol, 2.0 equiv) in DME (43 mL) at 25 °C was added *n*-BuLi (8.71 mL, 21.8 mmol, 2.05 equiv, 2.5 M solution in hexanes) dropwise over 10 minutes, according to the procedure of Bray and Minicone (69). To the resulting solution was added *tert*-butyldimethylsilyl (S)-(-)-glycidyl ether (2.00 g, 10.6 mmol, 1.0 equiv). The reaction mixture was heated to 130 °C for 20 h in a sealed pressure vessel. Upon completion, the reaction mixture was cooled to 25 °C, and saturated aqueous ammonium chloride (80 mL) was added. The mixture was extracted with diethyl ether (3 x 100 mL). The combined organic extracts were dried (MgSO<sub>4</sub>), filtered and concentrated under reduced pressure. The residue was dry-loaded onto silica and purified by flash column chromatography (10:1 hexanes/EtOAc), which gave the silyl ether product as a colorless oil (2.74 g, 40% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.12 (q,  $J$  = 7.1 Hz, 2H), 3.62 (qd,  $J$  = 10.8, 5.0 Hz, 2H), 1.70–1.49 (m, 2H), 1.25 (t,  $J$  = 7.1 Hz, 3H), 1.13 (ddd,  $J$  = 8.9, 4.9, 4.1 Hz, 1H), 0.93–0.84 (m, 10H), 0.04 (s, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 63.3, 60.4, 25.9, 24.1, 18.3, 17.6, 14.3, 12.3, -5.3, -5.3 ppm. IR (film) 2956, 2931, 2858, 1726, 1467, 1380, 1316, 1255, 1177, 1089, 1039, 1006  $\text{cm}^{-1}$ . HRMS (ESI)  $m/z$  calcd for C<sub>13</sub>H<sub>27</sub>O<sub>3</sub>Si [(M+H)<sup>+</sup>] 259.1729, found 259.1728.



**Ethyl (1*S*,2*S*)-2-(hydroxymethyl)cyclopropane-1-carboxylate (70):** To a solution of the silyl ether (329 mg, 1.27 mmol, 1.0 equiv) in THF (25.4 mL, 0.05 M) at 0 °C was added tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 1.40 mL, 1.40 mmol, 1.1 equiv) dropwise. The resulting solution was stirred at 0 °C for 1.5 h. Following addition of hexane (10 mL), Et<sub>2</sub>O (20 mL) and water (50 mL), the organic layer was separated, dried (MgSO<sub>4</sub>), filtered and concentrated *in vacuo*. The residue was dry-loaded onto silica and purified by flash column chromatography (4:1→2:1 hexanes/EtOAc), which gave the product as a colorless liquid (160 mg, 87% yield). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 3.94 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.22 (dd, *J* = 11.4, 5.5 Hz, 1H), 3.02 (dd, *J* = 11.4, 6.6 Hz, 1H), 1.67 (dtdd, *J* = 8.8, 6.4, 5.5, 4.1 Hz, 1H), 1.51 (brs, 1H), 1.49 (ddd, *J* = 8.6, 4.8, 4.0 Hz, 1H), 1.15 (ddd, *J* = 8.9, 4.8, 4.1 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H), 0.51 (ddd, *J* = 8.4, 6.3, 4.1 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 174.1, 64.1, 60.8, 24.8, 18.7, 14.6, 12.8 ppm. IR (film) 3424, 2985, 1713, 1451, 1409, 1375, 1316, 1267, 1202, 1180, 1091, 1027 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd for C<sub>7</sub>H<sub>12</sub>NaO<sub>3</sub> [(M+Na)<sup>+</sup>] 167.0684, found 167.0684.



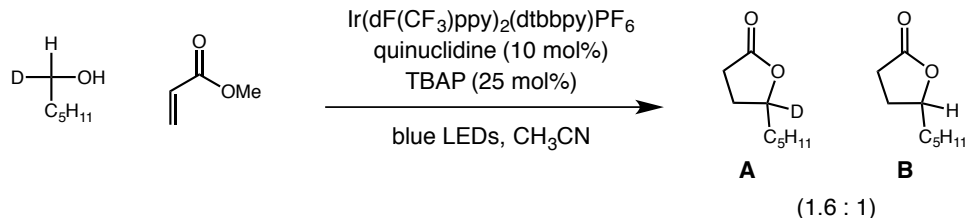
**Ethyl 5-oxopentanoate:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), ethyl (1*S*,2*S*)-2-(hydroxymethyl)cyclopropane-1-carboxylate (36.0 mg, 250 μmol, 1.0 equiv) and CH<sub>3</sub>CN (313 μL, 0.8 M) were used (18 h reaction time). The product was isolated by flash column chromatography (4:1 hexanes/EtOAc) as a colorless liquid (8.0 mg, 22% yield), along with recovered starting material. Spectral data were consistent with previous report (71).



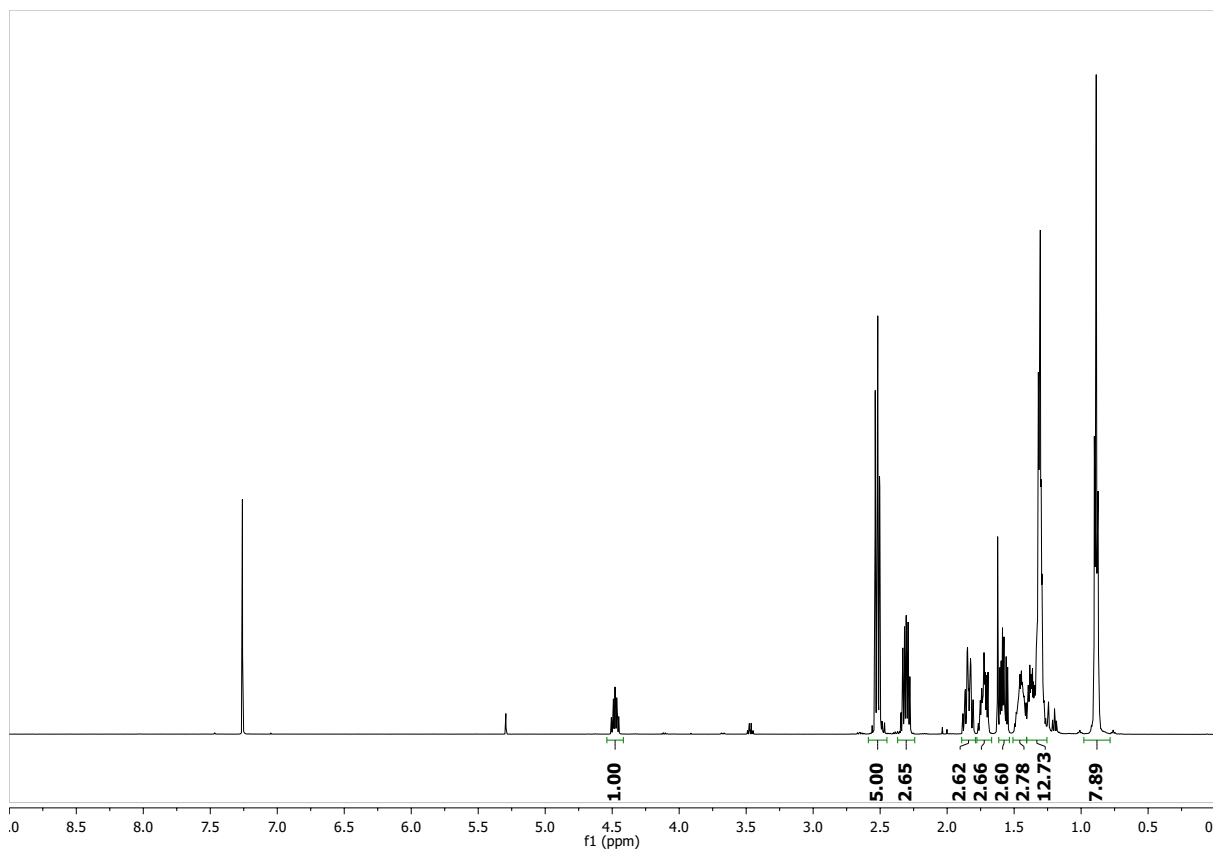
**8-Ethyl 1-methyl 4-oxooctanedioate:** According to the general procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (1.60 mg, 1.46 μmol, 1 mol%), quinuclidine (1.60 mg, 15.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (12.4 mg, 36.0 μmol, 25 mol%), ethyl (1*S*,2*S*)-2-(hydroxymethyl)cyclopropane-1-carboxylate (21.0 mg, 146 μmol, 1.0 equiv), methyl acrylate (13.2 μL, 146 μmol, 1.0 equiv), and CH<sub>3</sub>CN (364 μL, 0.4 M) were used (24 h reaction time). The product was isolated by flash column chromatography (2:1 hexanes/EtOAc) as a colorless oil (6.3 mg, 30% yield), along with ethyl 5-oxopentanoate (6.1 mg, 29% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.12 (q, *J* = 7.2 Hz, 2H), 3.67 (s, 3H), 2.74–2.68 (m, 2H), 2.59 (t, *J* = 6.5 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.32 (t, *J* = 7.3 Hz, 2H), 1.91 (p, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.1, 173.2, 173.1, 60.3, 51.8, 41.5, 37.0, 33.2, 27.7, 18.8, 14.2 ppm. IR (film) 2934, 1732, 1439, 1414, 1373, 1242, 1176, 1100, 1044 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>18</sub>NaO<sub>5</sub> [(M+Na)<sup>+</sup>] 253.1052, found 253.1054. The formation of this hydroacylation product presumably involves C–H abstraction from ethyl 5-oxopentanoate to generate the corresponding nucleophilic acyl radical.

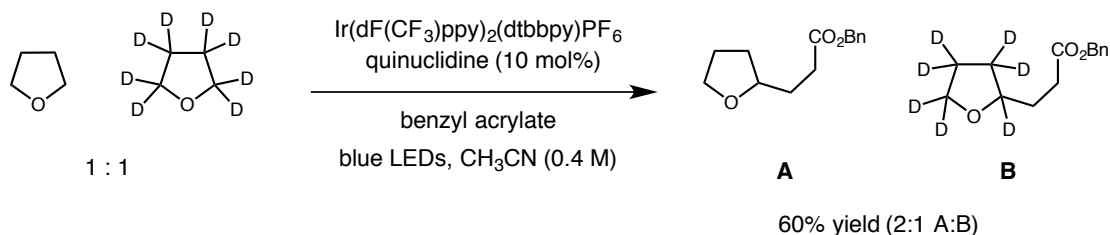


## Kinetic Isotope Effects

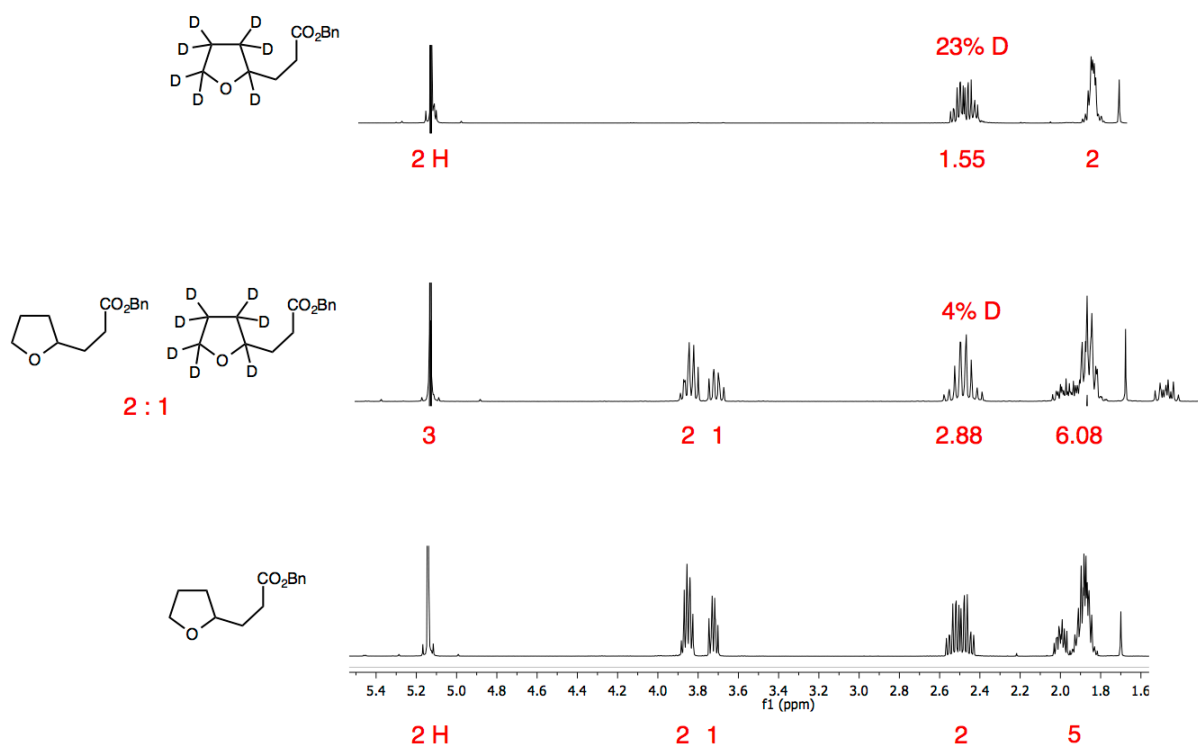


Procedure: According to the General  $\alpha$ -Alkylation Procedure, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (5.60 mg, 5.00  $\mu$ mol, 1 mol%), quinuclidine (5.60 mg, 50.0  $\mu$ mol, 10 mol%), tetra-*n*-butylammonium phosphate (42.0 mg, 125  $\mu$ mol, 25 mol%), hexan-1-*d*-1-ol (103 mg, 1.00 mmol, 2.0 equiv), methyl acrylate (45.0  $\mu$ L, 0.50 mmol, 1.0 equiv) and CH<sub>3</sub>CN (0.63 mL, 0.8 M) were used. The products were isolated by flash column chromatography (18:2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes/EtOAc) in the form of a colorless liquid, which consisted of a 1.6:1 ratio of A to B, as determined by NMR analysis (relative integrations of the signals at 4.5, 2.3 and 0.93–0.84 ppm were used).



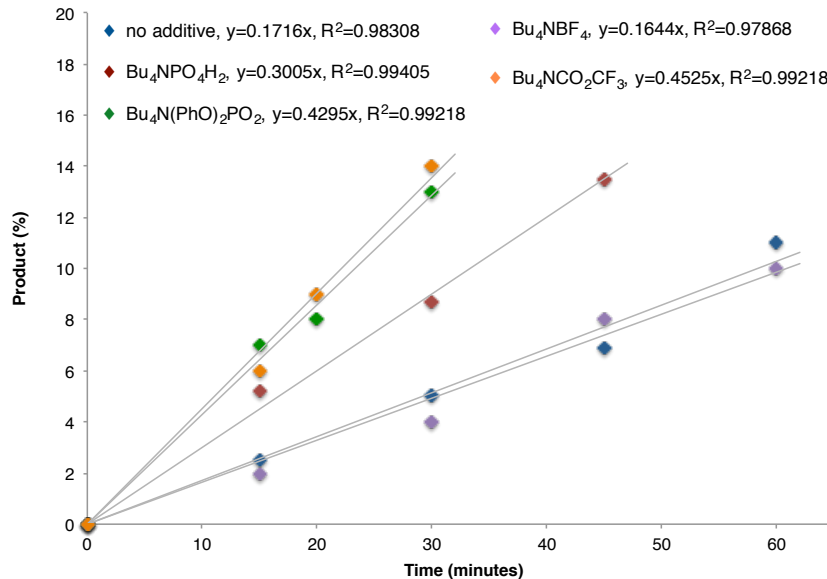
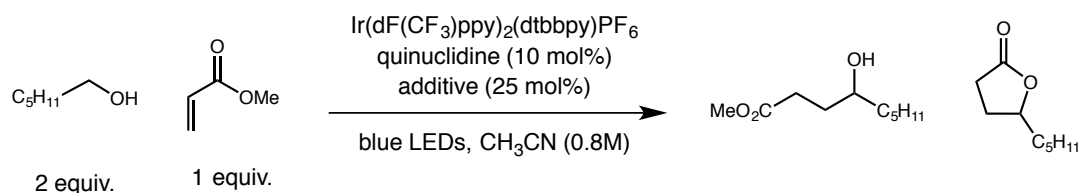


Procedure: According to the General  $\alpha$ -Alkylation Procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.80 mg, 2.50  $\mu\text{mol}$ , 1 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 10 mol%), tetrahydrofuran (61.0  $\mu\text{L}$ , 0.75 mmol, 3.0 equiv),  $d_8$ -tetrahydrofuran (61.0  $\mu\text{L}$ , 0.75 mmol, 3.0 equiv), benzyl acrylate (37.5  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv) and  $\text{CH}_3\text{CN}$  (0.63 mL, 0.4 M) were irradiated for 24 h. Purification by flash column chromatography (6:1 hexanes/EtOAc) afforded the products (**A** and **B**) in the form of a colorless oil (36.0 mg, 60% yield), which consisted of a 2:1 ratio of A to B (as determined by NMR analysis).

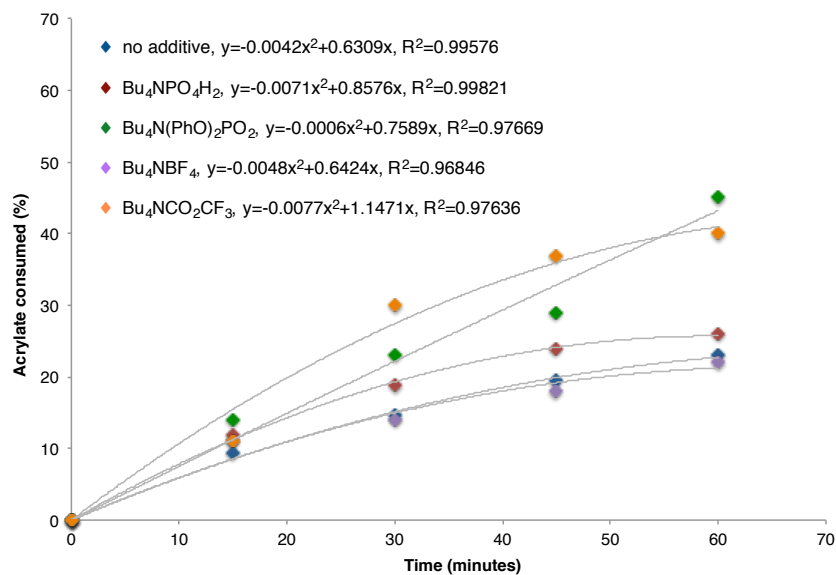
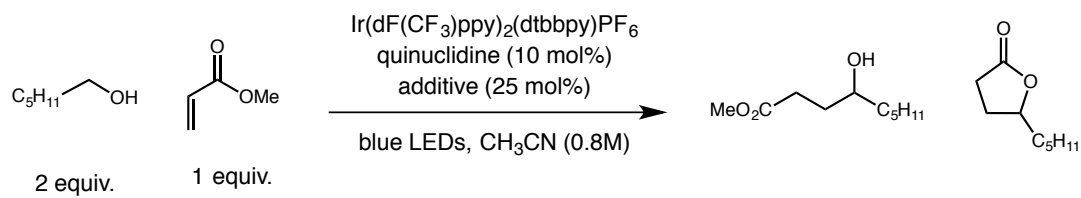


## Kinetics Experiments

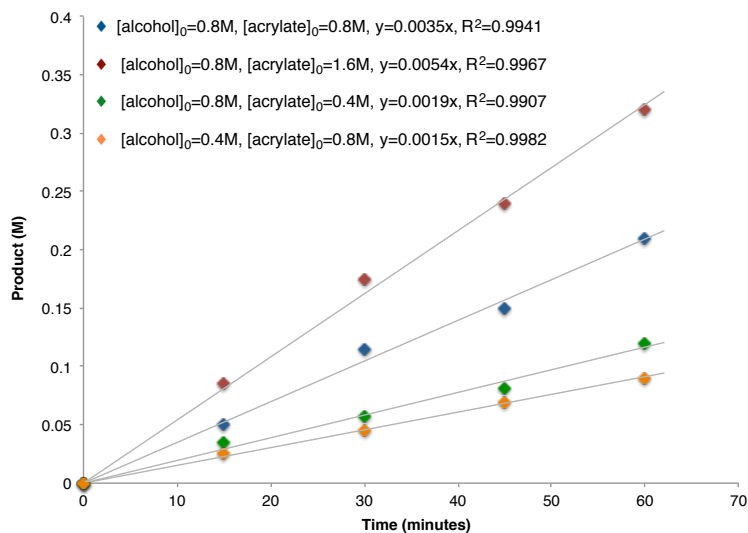
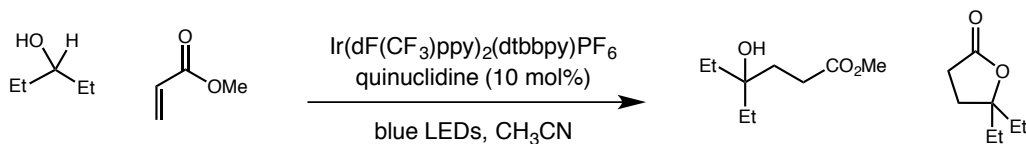
Typical procedure: An 8-mL glass vial equipped with a Teflon septum and magnetic stir bar was charged with Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (5.60 mg, 5.00 μmol, 1 mol%), quinuclidine (5.60 mg, 50.0 μmol, 10 mol%), the indicated tetra-*n*-butylammonium additive (125 μmol, 25 mol%), the indicated alcohol (1.00 mmol, 2.0 equiv), methyl acrylate (45.0 μL, 0.50 mmol, 1.0 equiv), methyl benzoate (32.0 μL, 0.5 equiv) as internal standard, and CH<sub>3</sub>CN (0.63 mL, 0.8 M). The resulting solution was then sparged with N<sub>2</sub> for 2 minutes. The vial was sealed and placed approximately 3 inches away from a Kessil<sup>®</sup> LED illuminator (model H150 blue, <http://www.kessil.com/horticulture/H150.php>). The reaction mixture was stirred and irradiated for the indicated period of time, with the internal temperature maintained at approximately 27 °C by an electric fan placed approximately 10 inches above the vial. At the indicated time points, the reaction mixture was placed in the dark and an aliquot was removed by syringe and analyzed by <sup>1</sup>H NMR and/or GC. The reaction mixture was then degassed by N<sub>2</sub> bubbling for 2 minutes prior to resuming irradiation. Each data point represents an average value determined from at least three separate experiments.



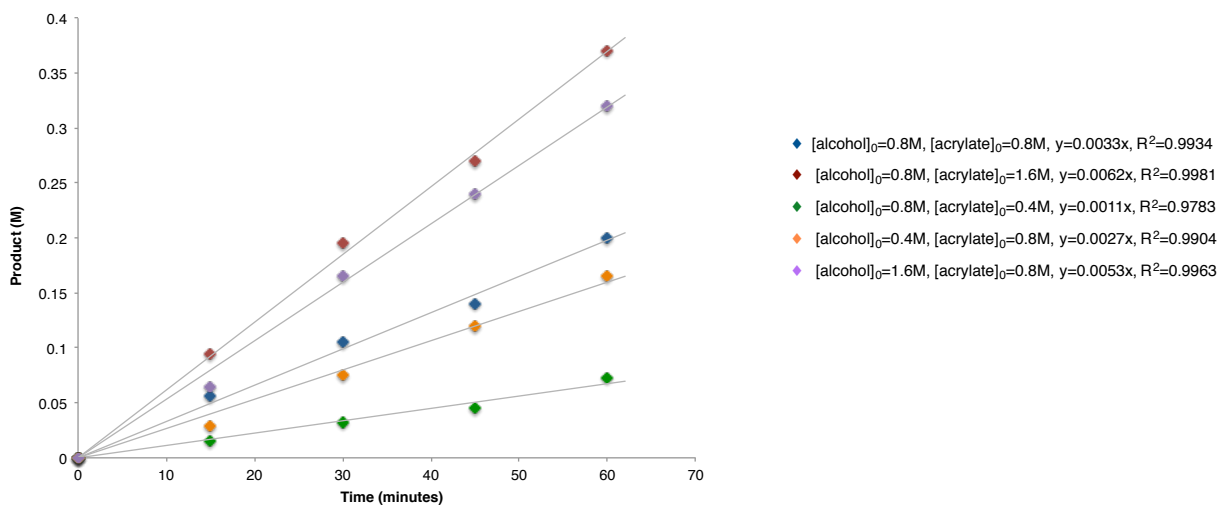
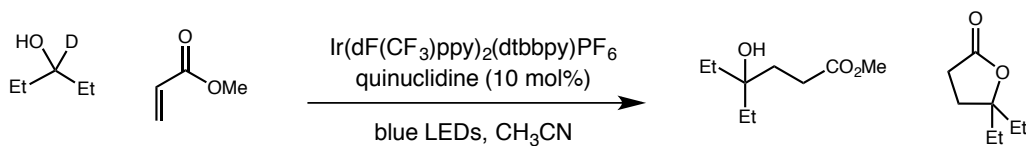
**Figure S1.** Initial rate of alkylation of 1-hexanol with methyl acrylate in the presence of additives.



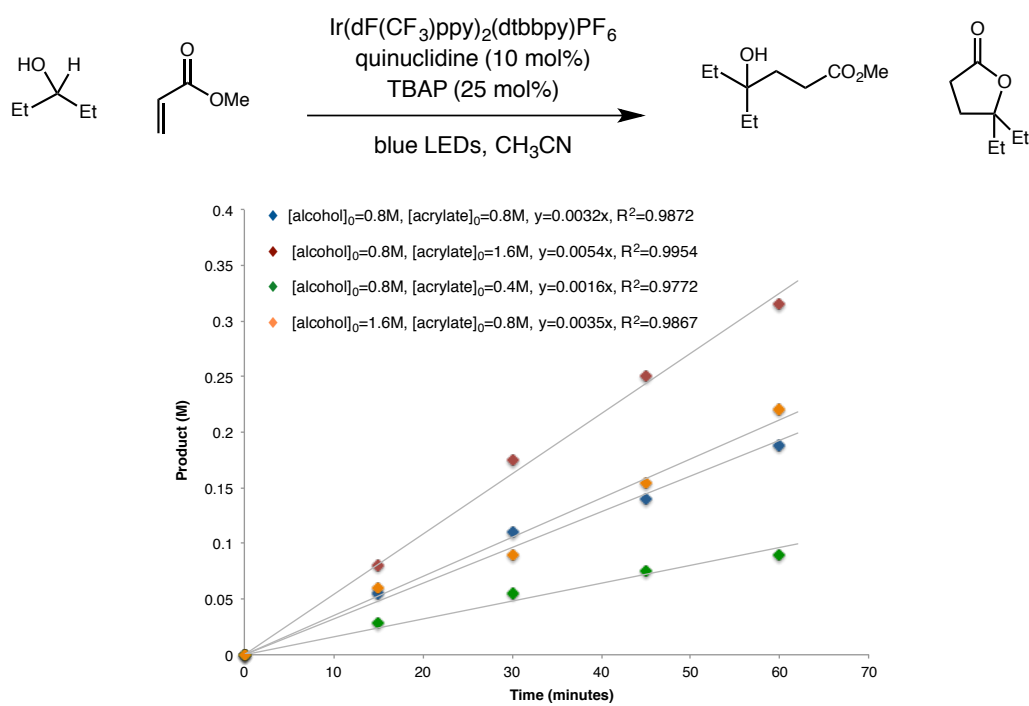
**Figure S2.** Initial rate of acrylate consumption in the reaction of 1-hexanol with methyl acrylate in the presence of additives.



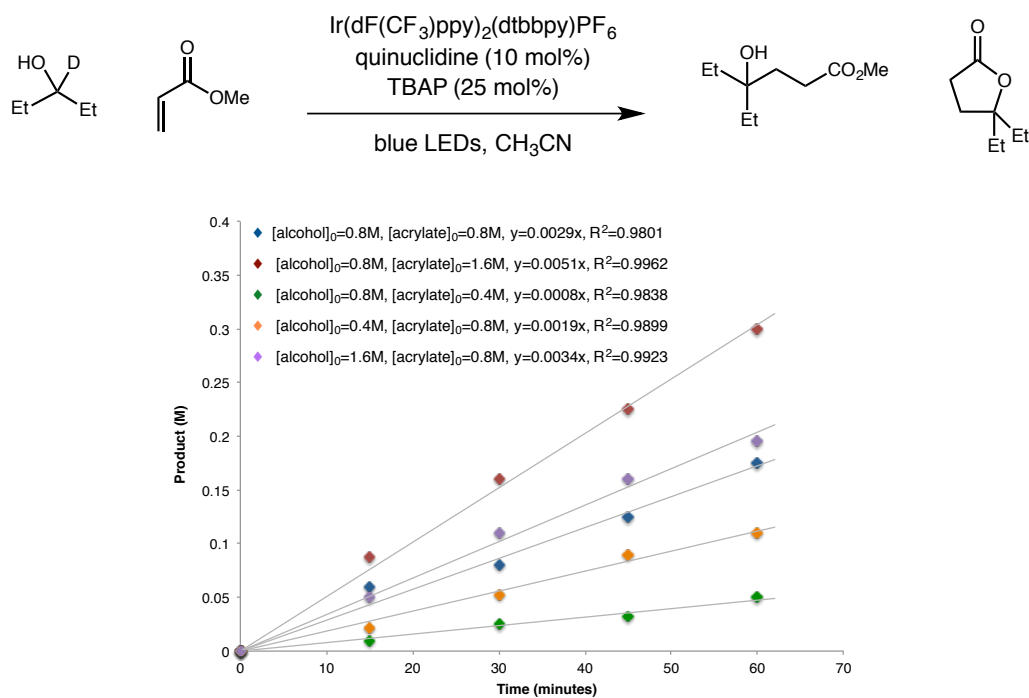
**Figure S3.** Initial rate of alkylation of 3-pentanol as a function of initial conditions.  
 $\text{rate} = k[\text{alcohol}][\text{acrylate}]$ ,  $k = 0.0051 \pm 0.0007\text{M}^{-1}\text{s}^{-1}$



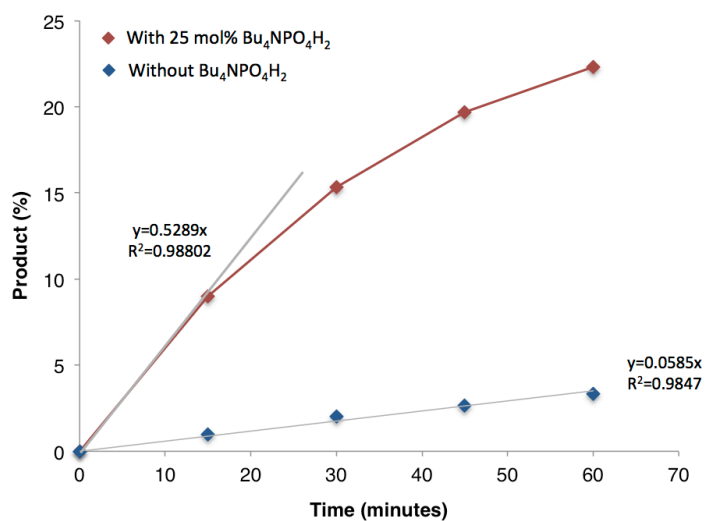
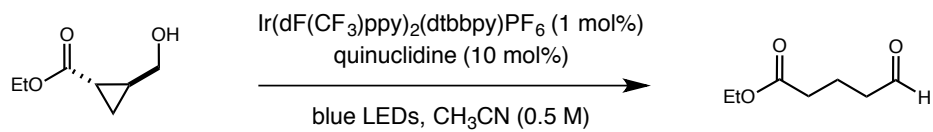
**Figure S4.** Initial rate of alkylation of D-3-pentanol as a function of initial conditions.  
 $\text{rate} = k[\text{alcohol}][\text{acrylate}]$ ,  $k = 0.0044 \pm 0.0008\text{M}^{-1}\text{s}^{-1}$ ;  $\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1$



**Figure S5.** Initial rate of alkylation of 3-pentanol as a function of initial conditions with 25 mol% TBAP.  $\text{rate} = k[\text{alcohol}][\text{acrylate}]$ ,  $k = 0.004 \pm 0.001 \text{ M}^{-1}\text{s}^{-1}$



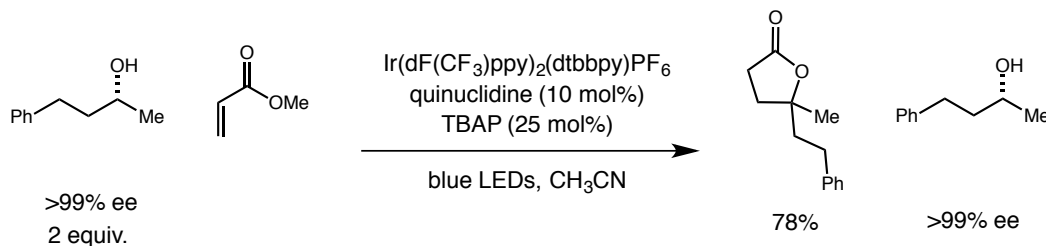
**Figure S6.** Initial rate of alkylation of D-3-pentanol as a function of initial conditions with 25 mol% TBAP.  $\text{rate} = k[\text{alcohol}][\text{acrylate}]$ ,  $k = 0.004 \pm 0.001 \text{ M}^{-1}\text{s}^{-1}$ ,  $\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1$



**Figure S7.** Initial rate of conversion of **36** to **37** in the presence and absence of  $\text{Bu}_4\text{NPO}_4\text{H}_2$  (average of three experiments).

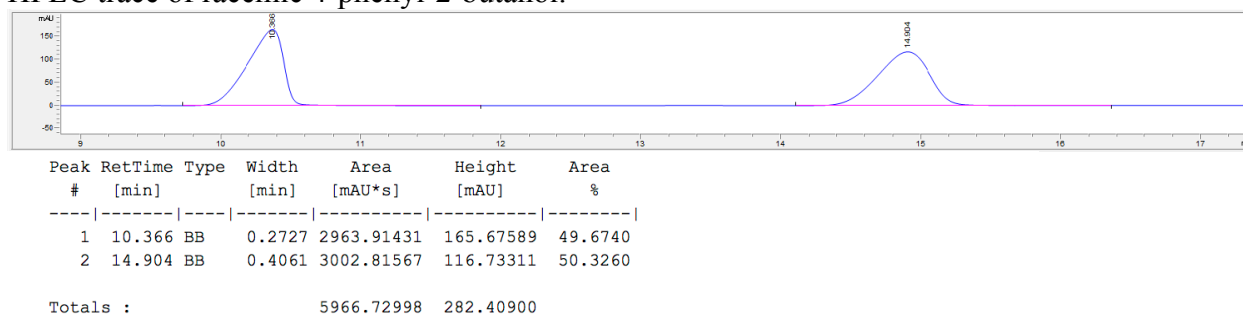
## HPLC Data

High-performance liquid chromatography (HPLC) was performed on an Agilent Technologies 1260 Infinity using a Chiralcel OD-H column.

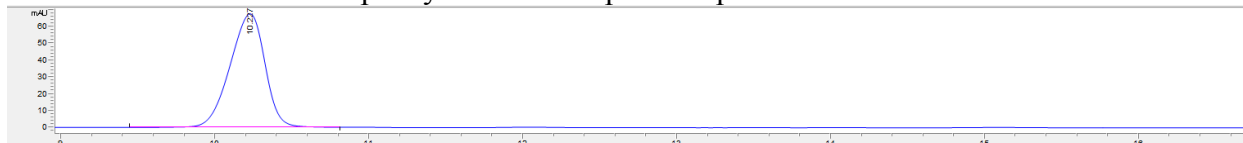


According to the general  $\alpha$ -alkylation procedure,  $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$  (2.80 mg, 2.50  $\mu\text{mol}$ , 1 mol%), quinuclidine (2.80 mg, 25.0  $\mu\text{mol}$ , 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0  $\mu\text{mol}$ , 25 mol%), (*R*)-4-phenylbutan-2-ol (77.0  $\mu\text{L}$ , 0.50 mmol, 2.0 equiv), methyl acrylate (23.0  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv), and  $\text{CH}_3\text{CN}$  (0.31 mL, 0.8 M) were used. Upon completion, the solvent was removed under reduced pressure, the reaction mixture was diluted with hexanes/EtOAc, filtered over a short pad of silica gel, concentrated and analyzed by HPLC (OD, 5% IPA/hexanes, 1.0 mL/min, 270 nm), which indicated >99% ee of the unreacted (*R*)-4-phenylbutan-2-ol ( $t_R = 10.2$  minutes).

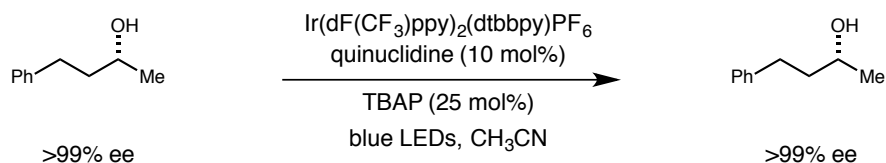
HPLC trace of racemic 4-phenyl-2-butanol:



HPLC trace of unreacted 4-phenyl-2-butanol upon completion of the reaction:

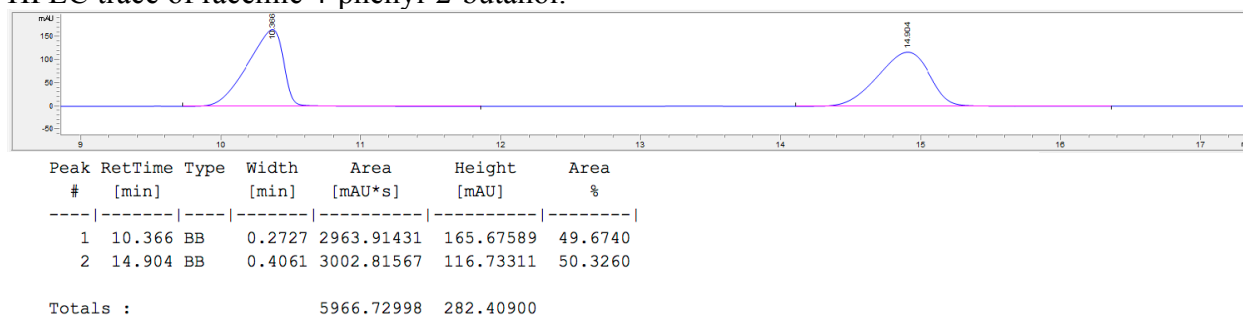




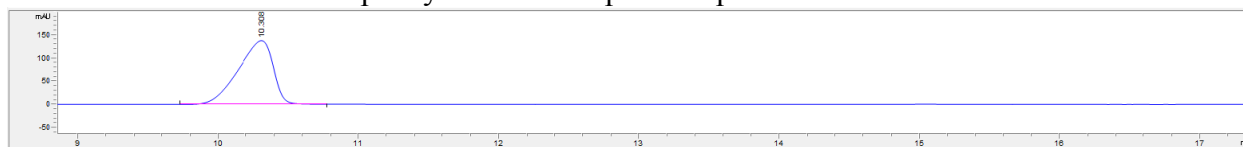


Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.50 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0 μmol, 25 mol%), (*R*)-4-phenylbutan-2-ol (77.0 μL, 0.50 mmol, 2.0 equiv), and CH<sub>3</sub>CN (0.31 mL, 0.8 M) were subjected to the standard conditions in the absence of methyl acrylate. After 24 h, the solvent was removed under reduced pressure, the reaction mixture was diluted with hexanes/EtOAc, filtered over a short pad of silica gel, concentrated and analyzed by HPLC (OD, 5% IPA/hexanes, 1.0 mL/min, 270 nm), which indicated >99% ee of the unreacted (*R*)-4-phenylbutan-2-ol (*t*<sub>R</sub> = 10.2 minutes).

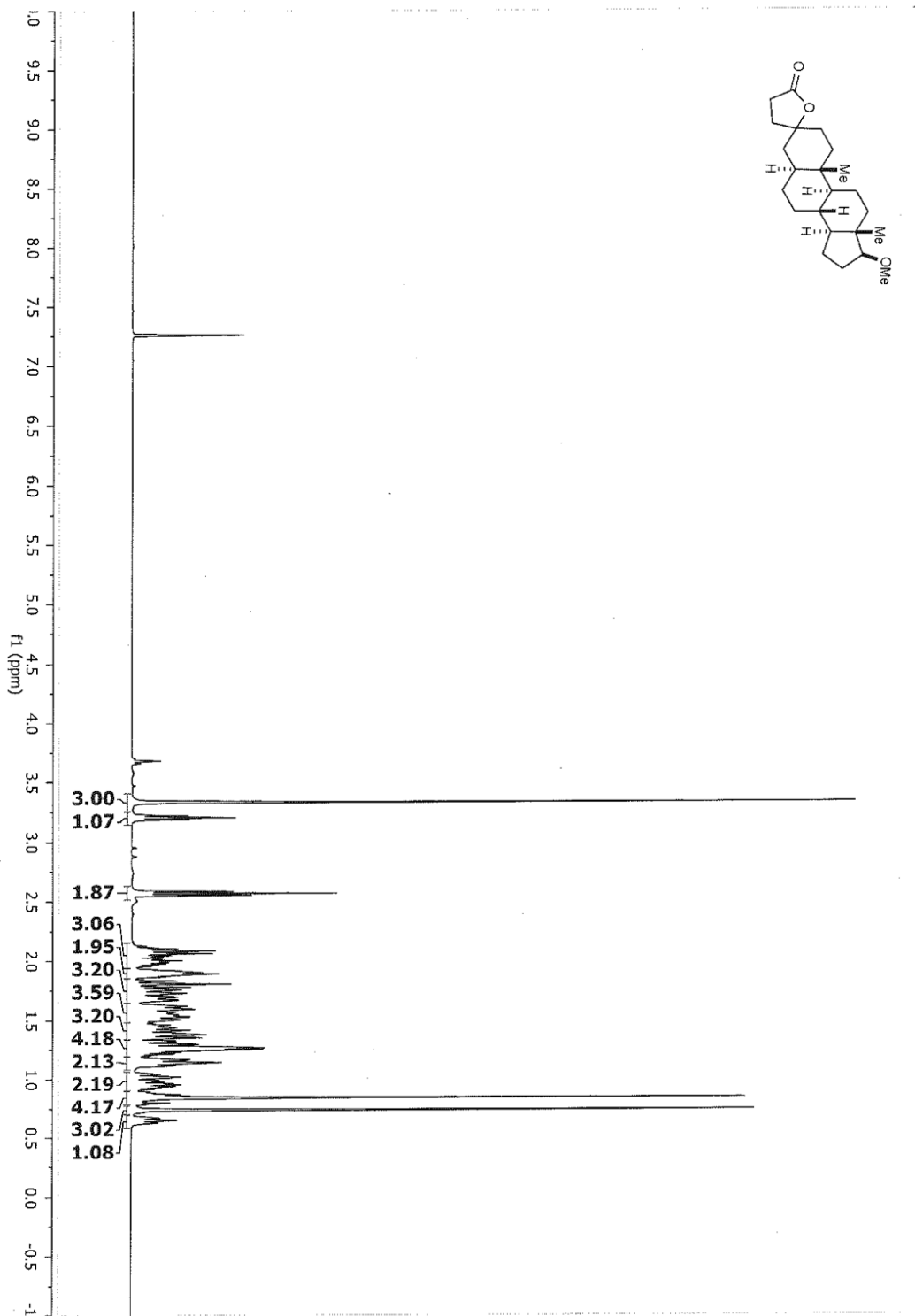
HPLC trace of racemic 4-phenyl-2-butanol:

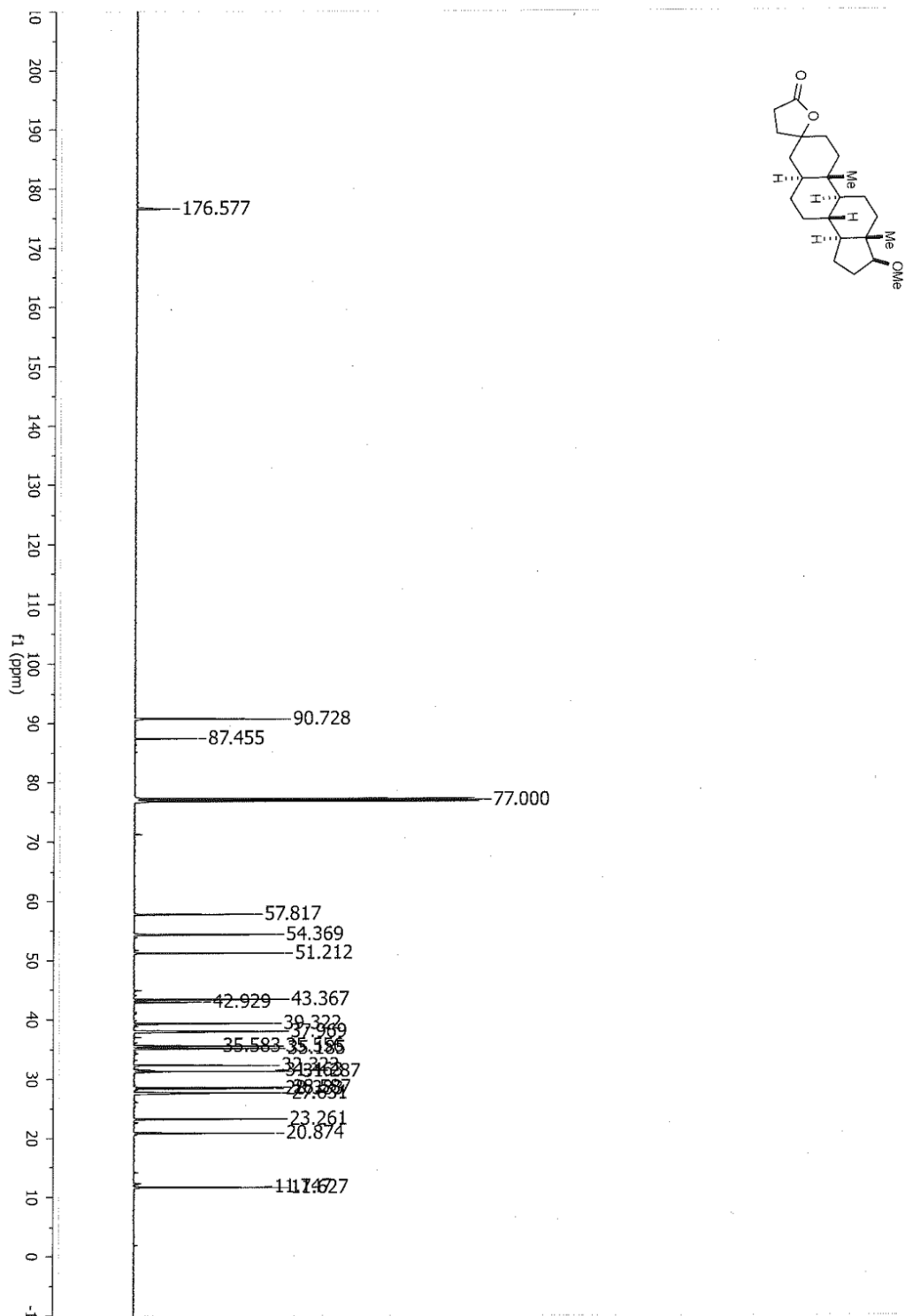


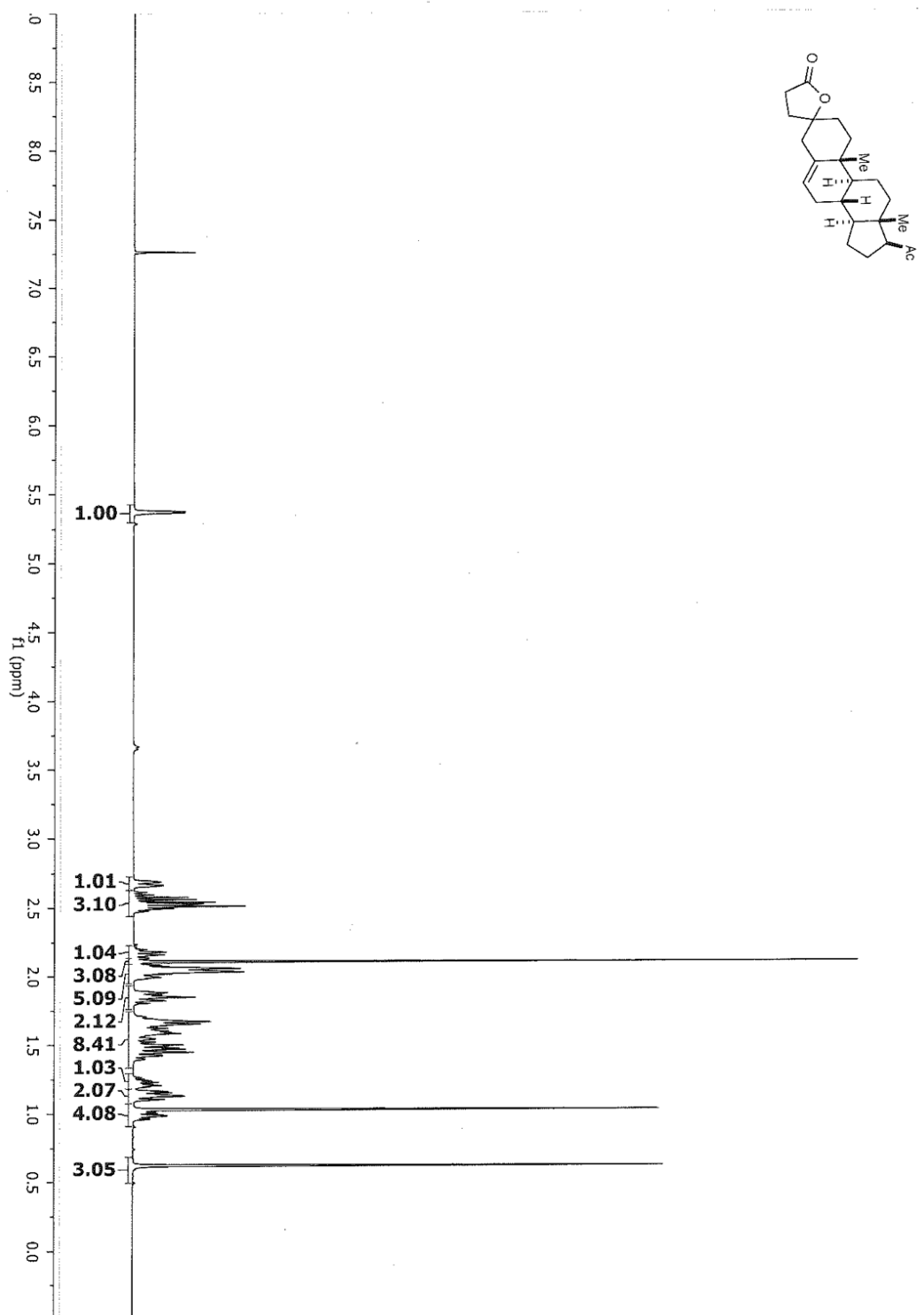
HPLC trace of unreacted 4-phenyl-2-butanol upon completion of the reaction:

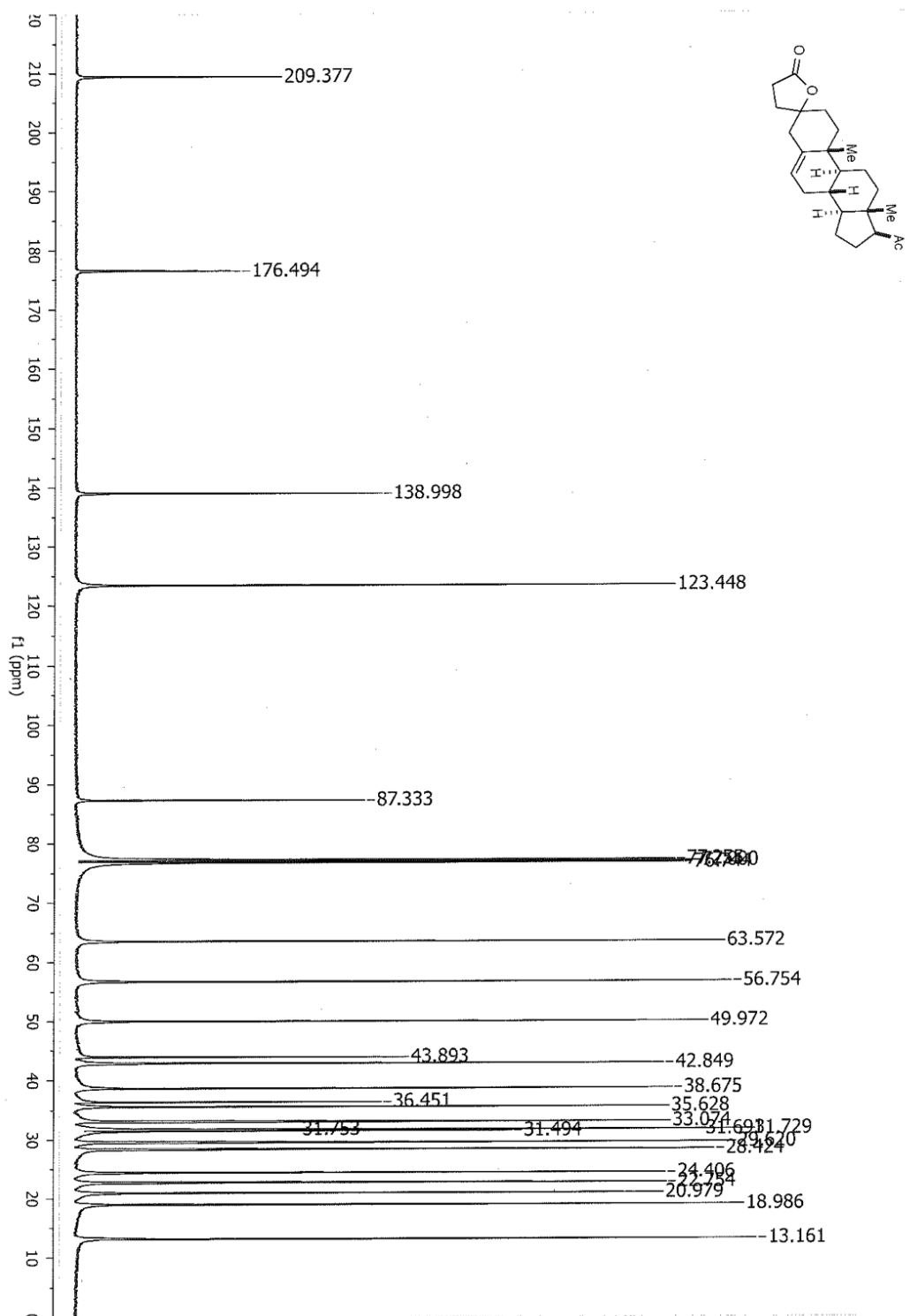


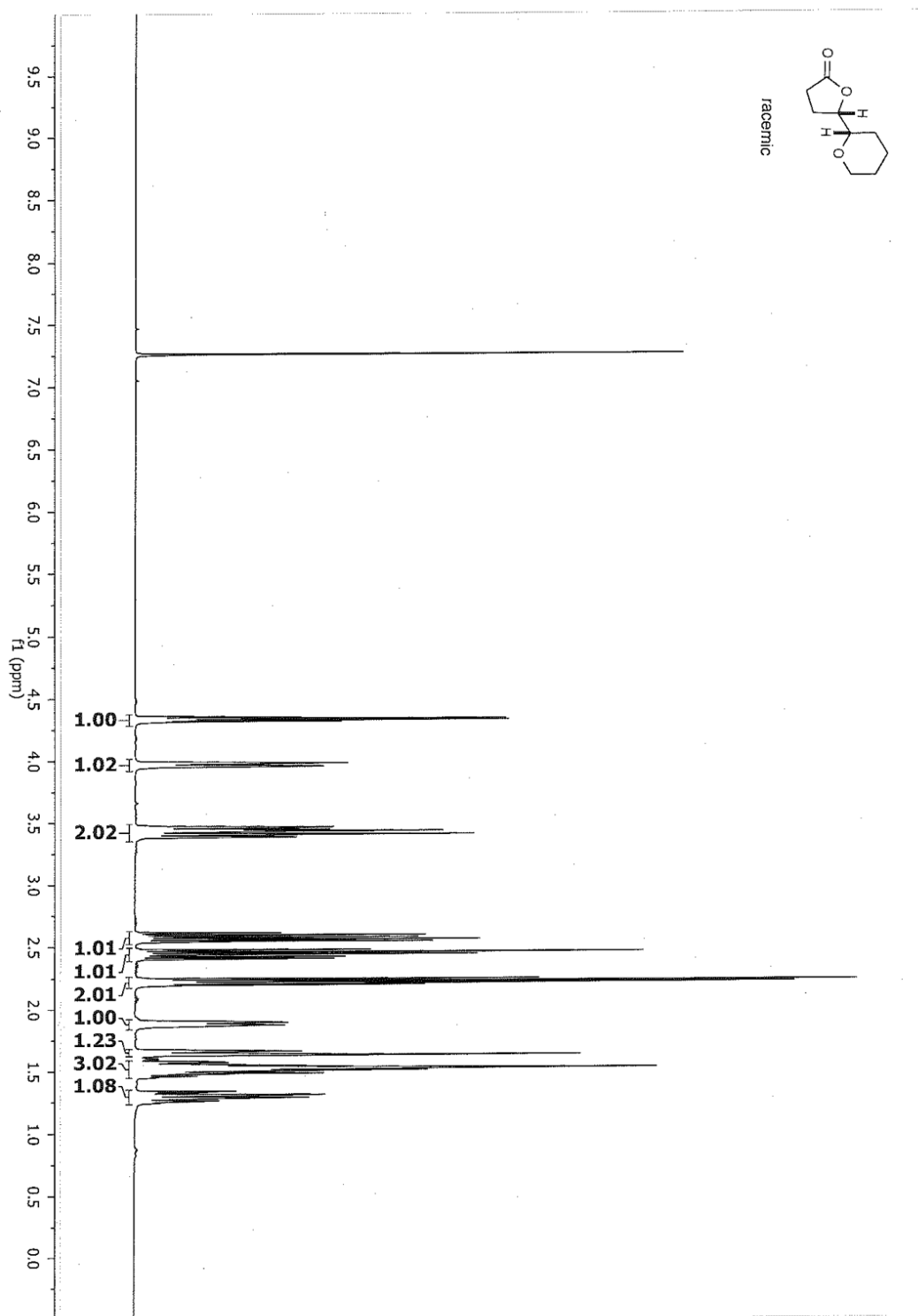
## NMR Spectra

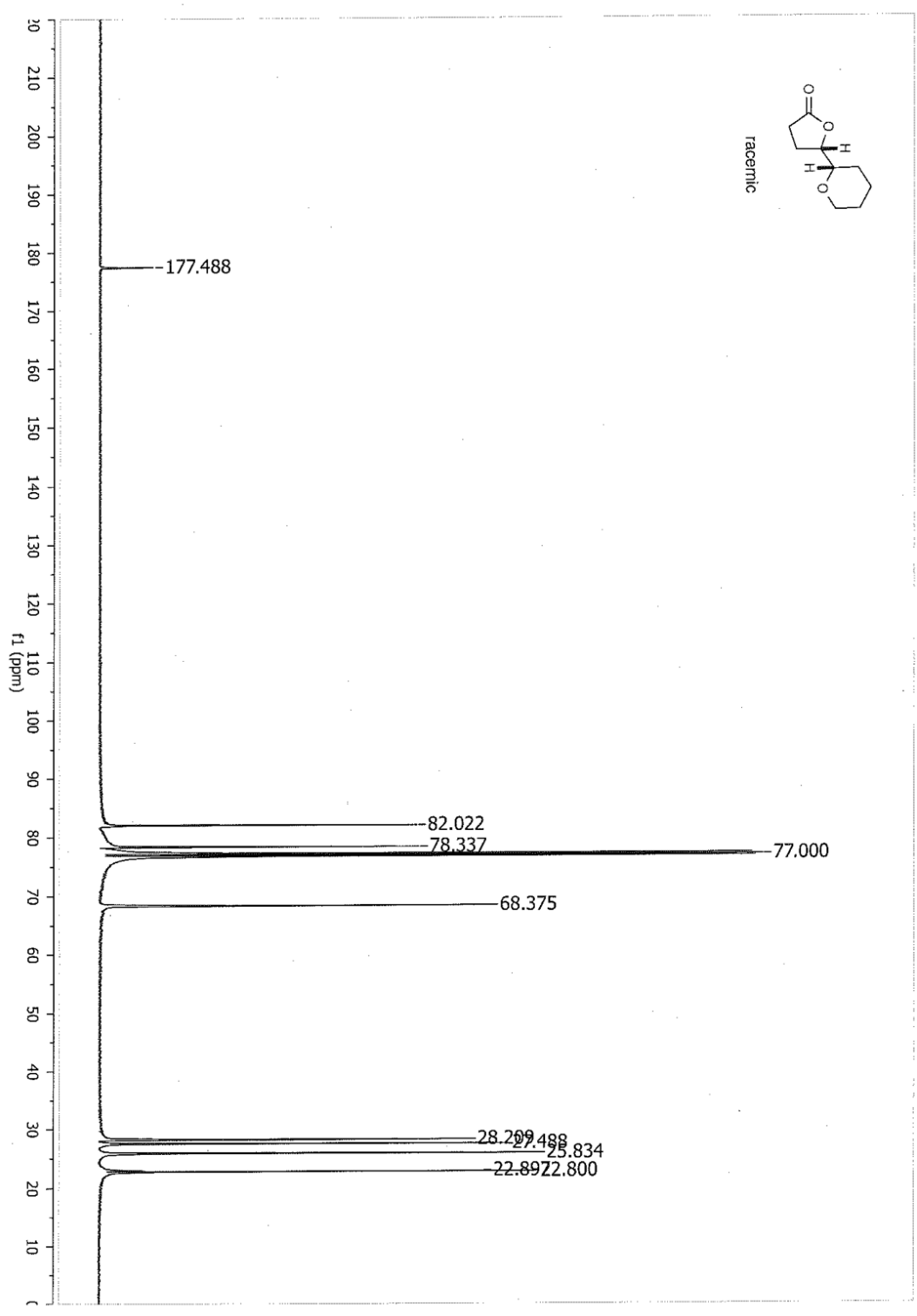


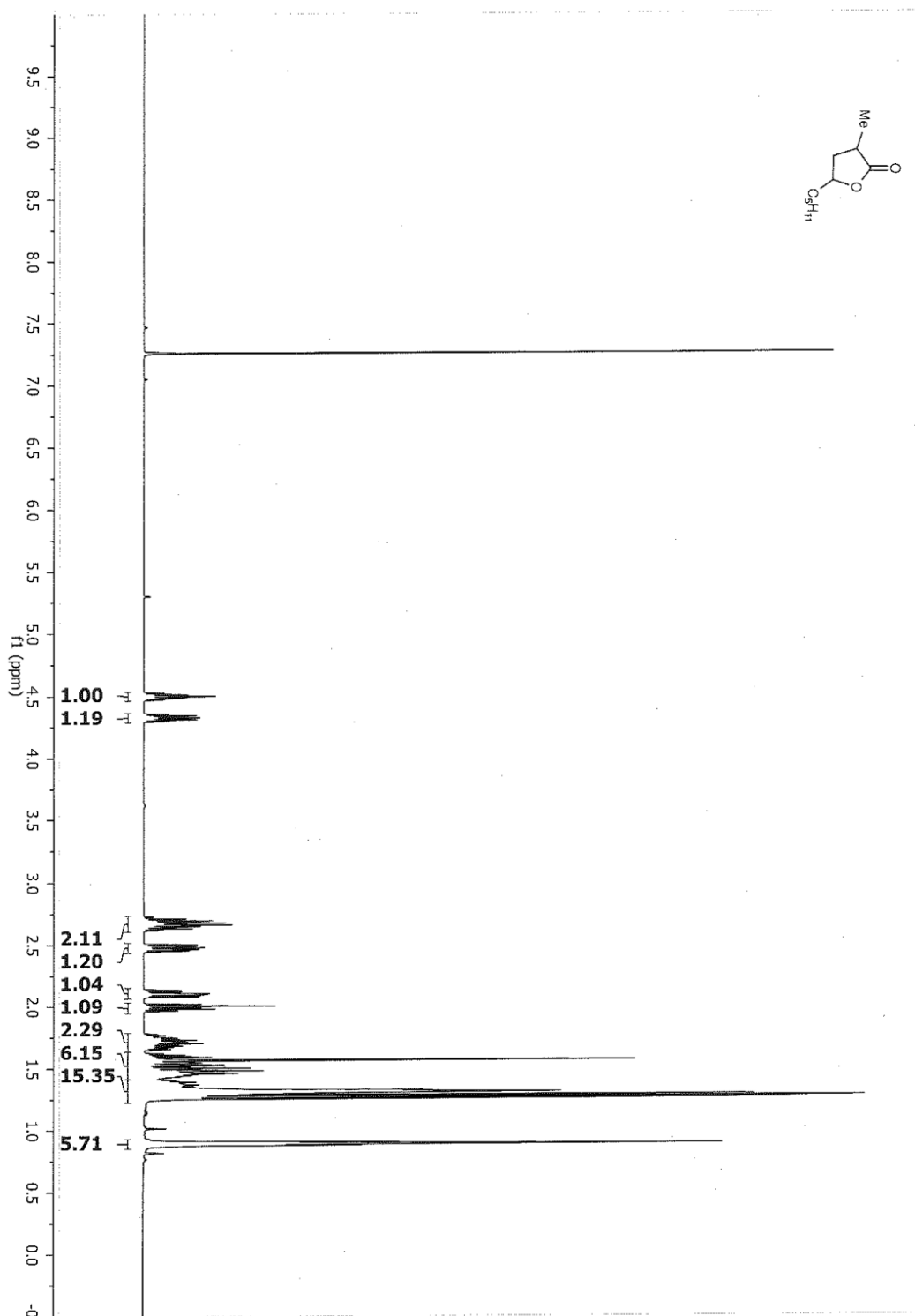




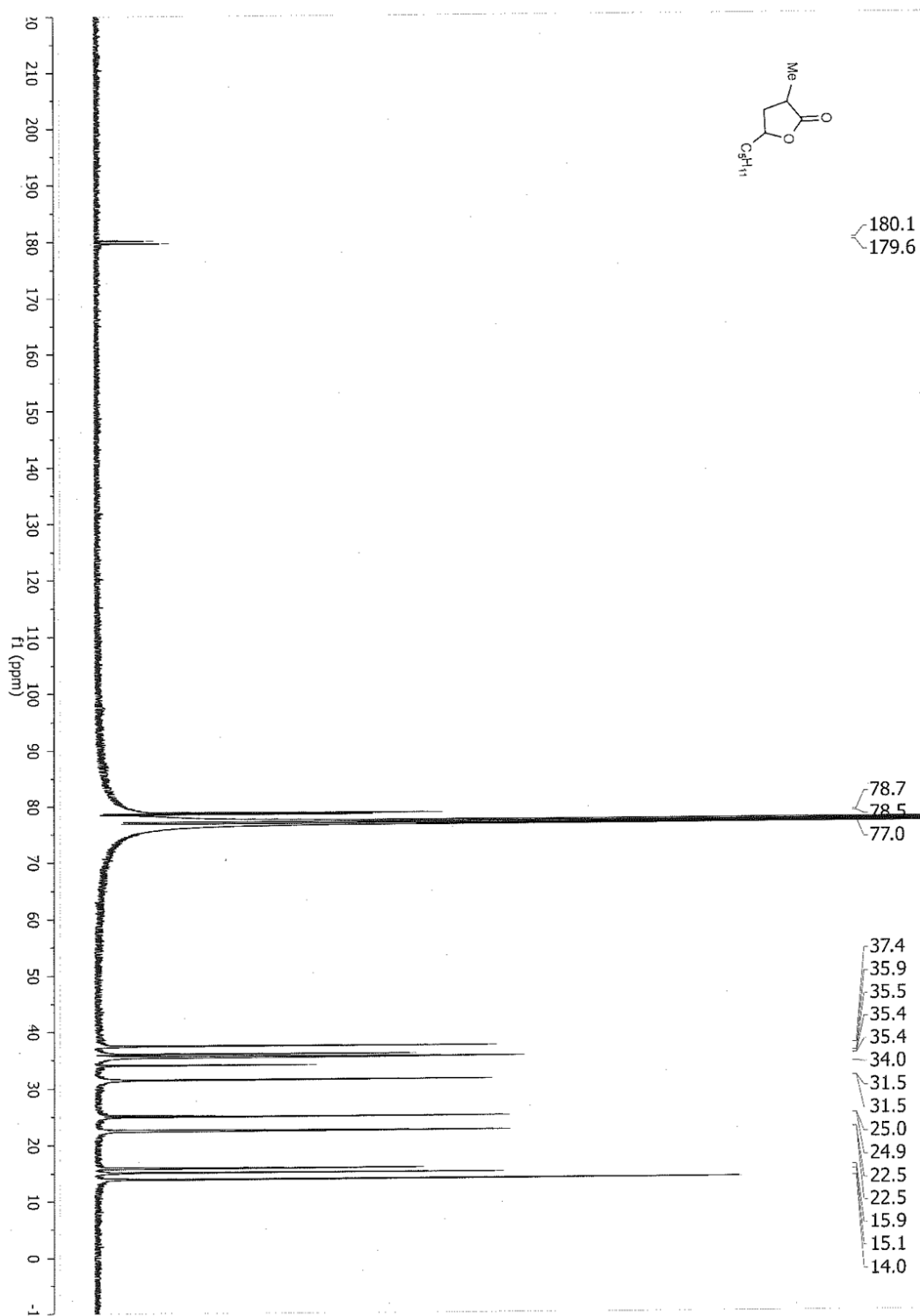


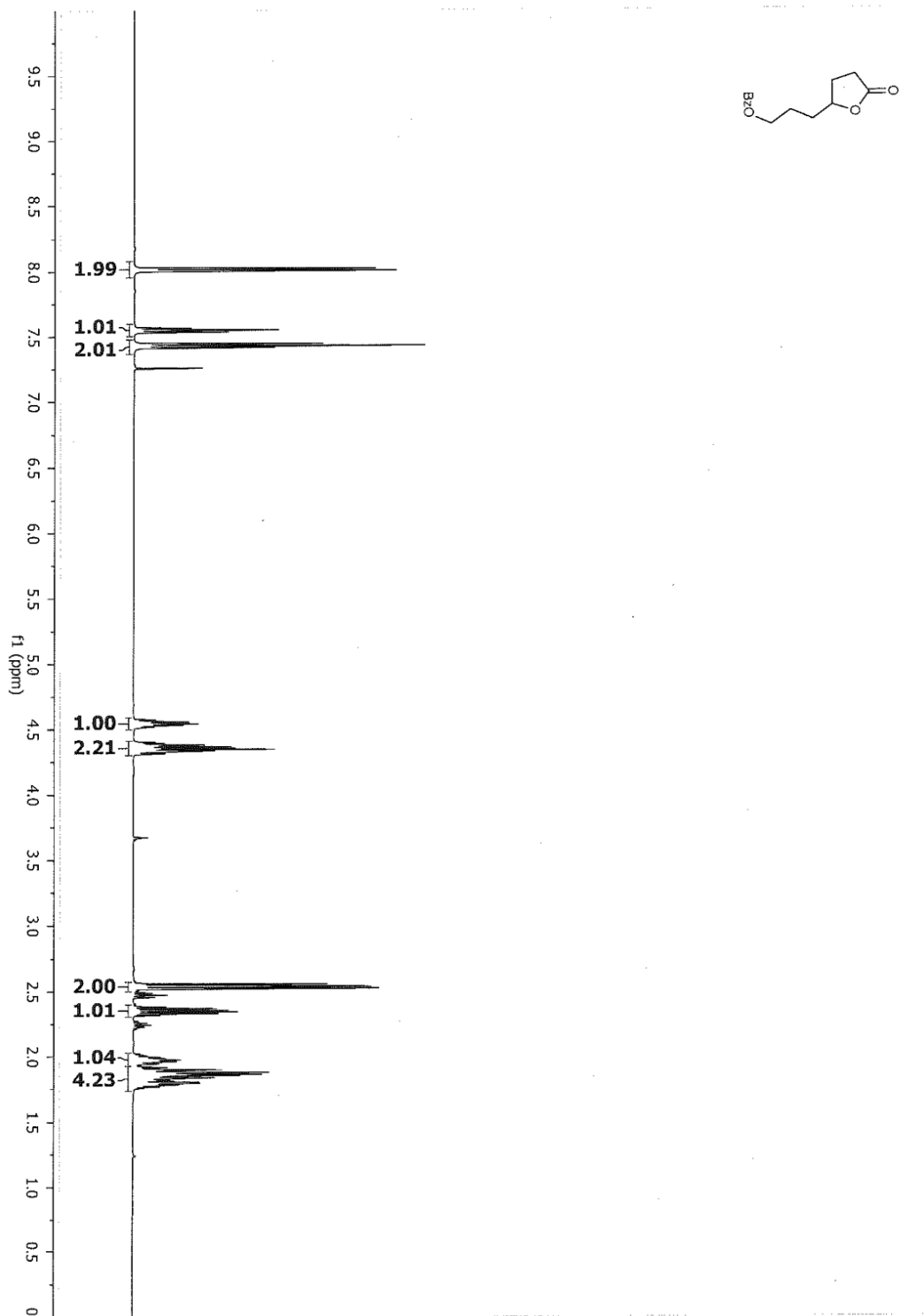


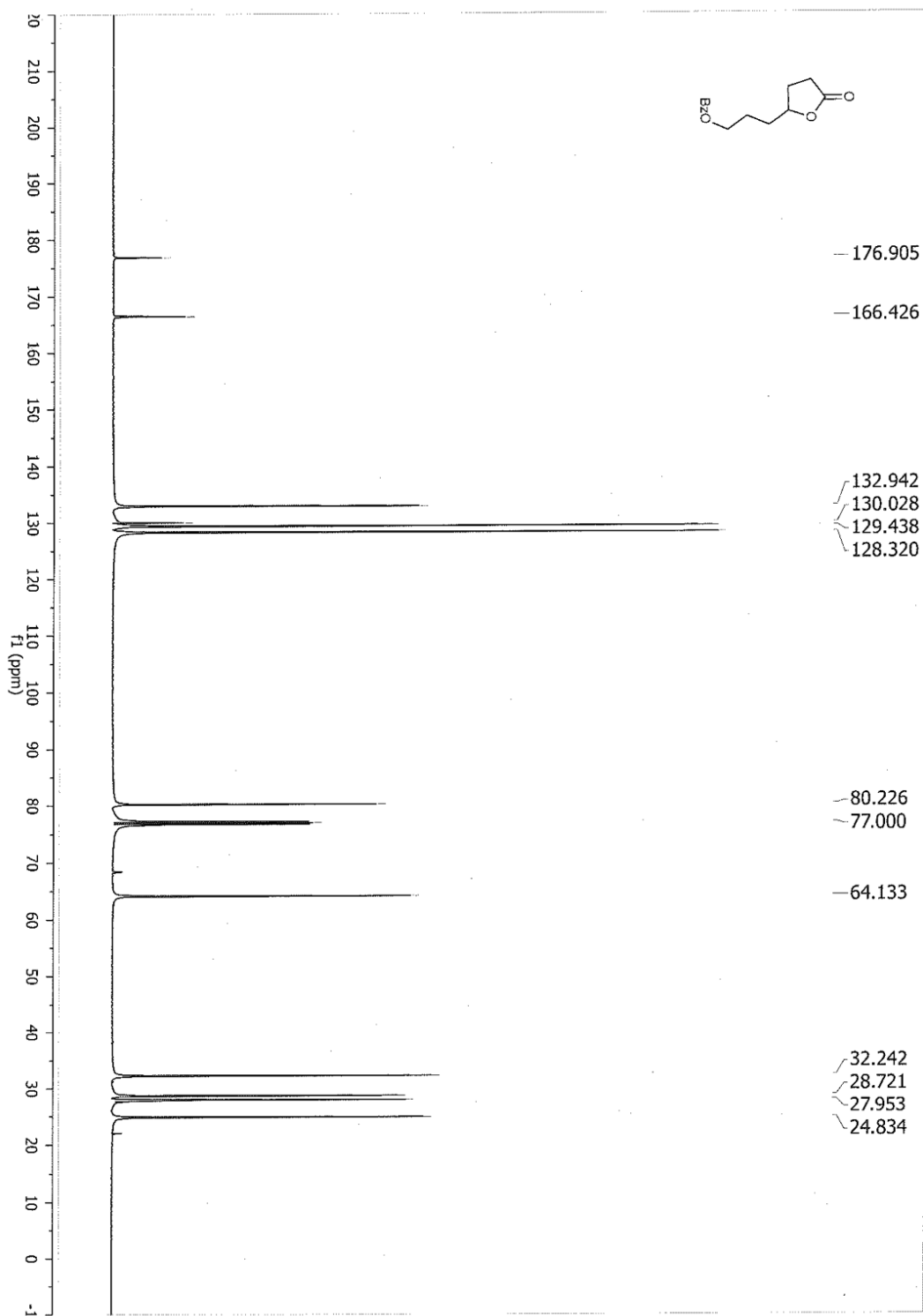


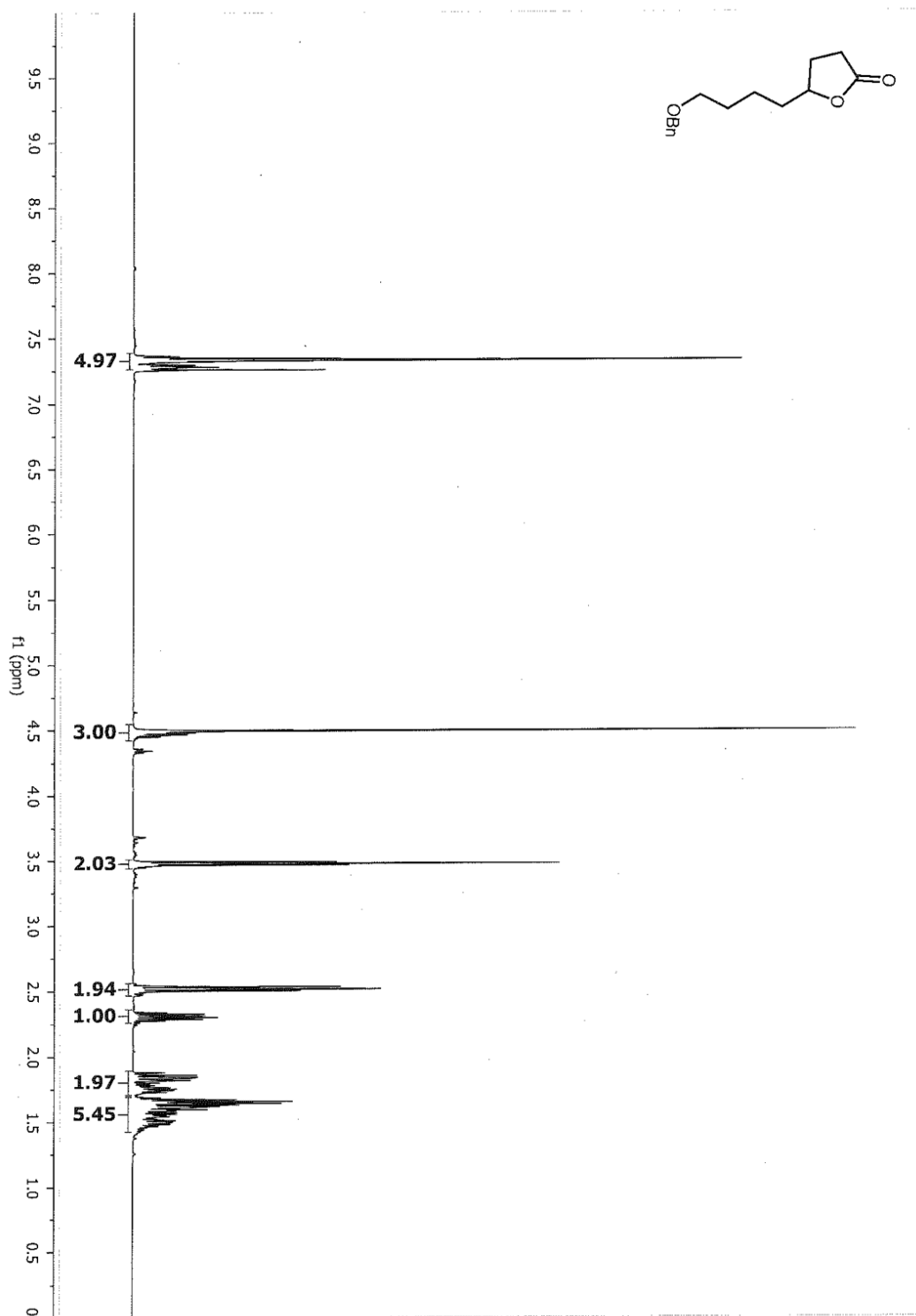


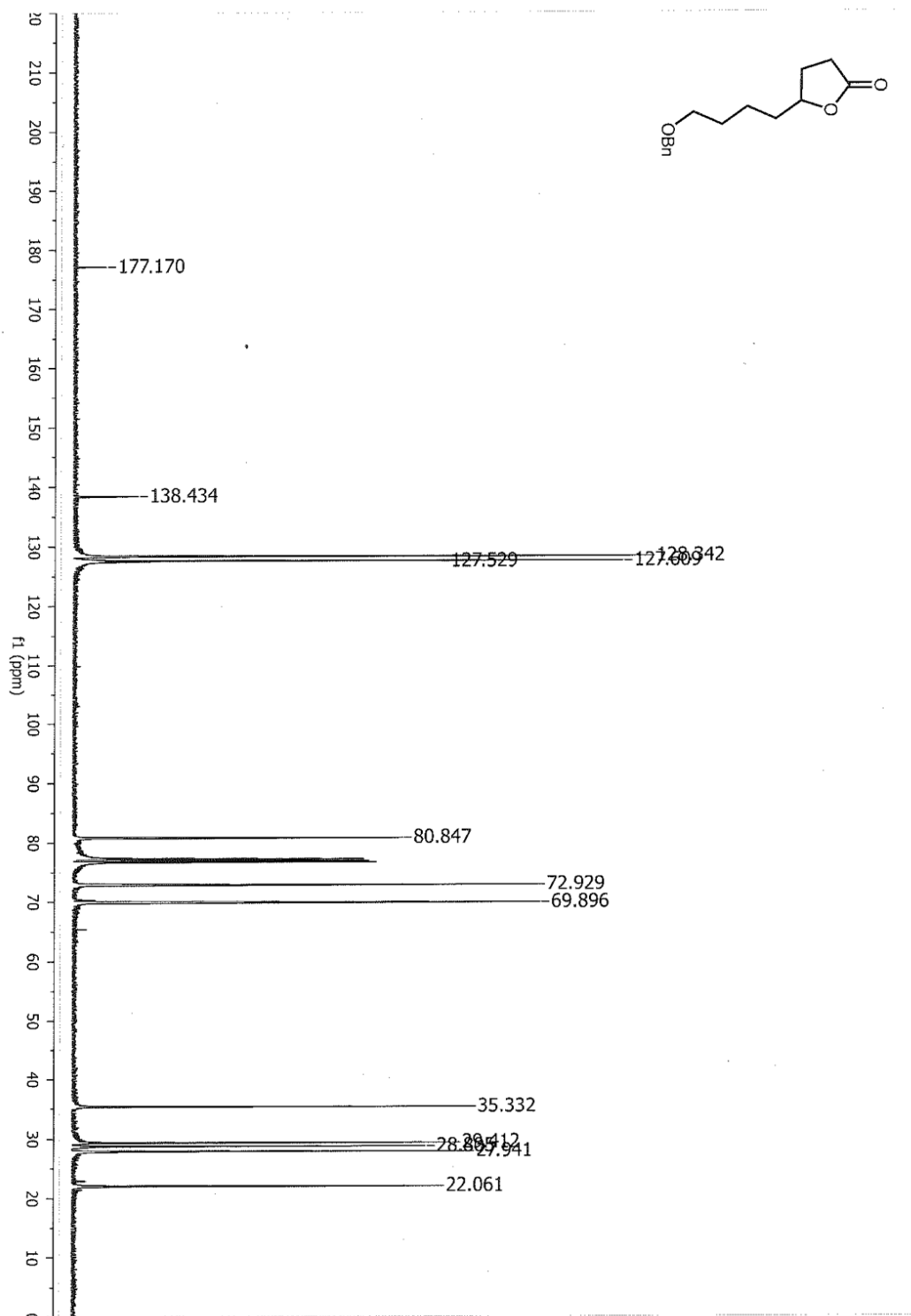


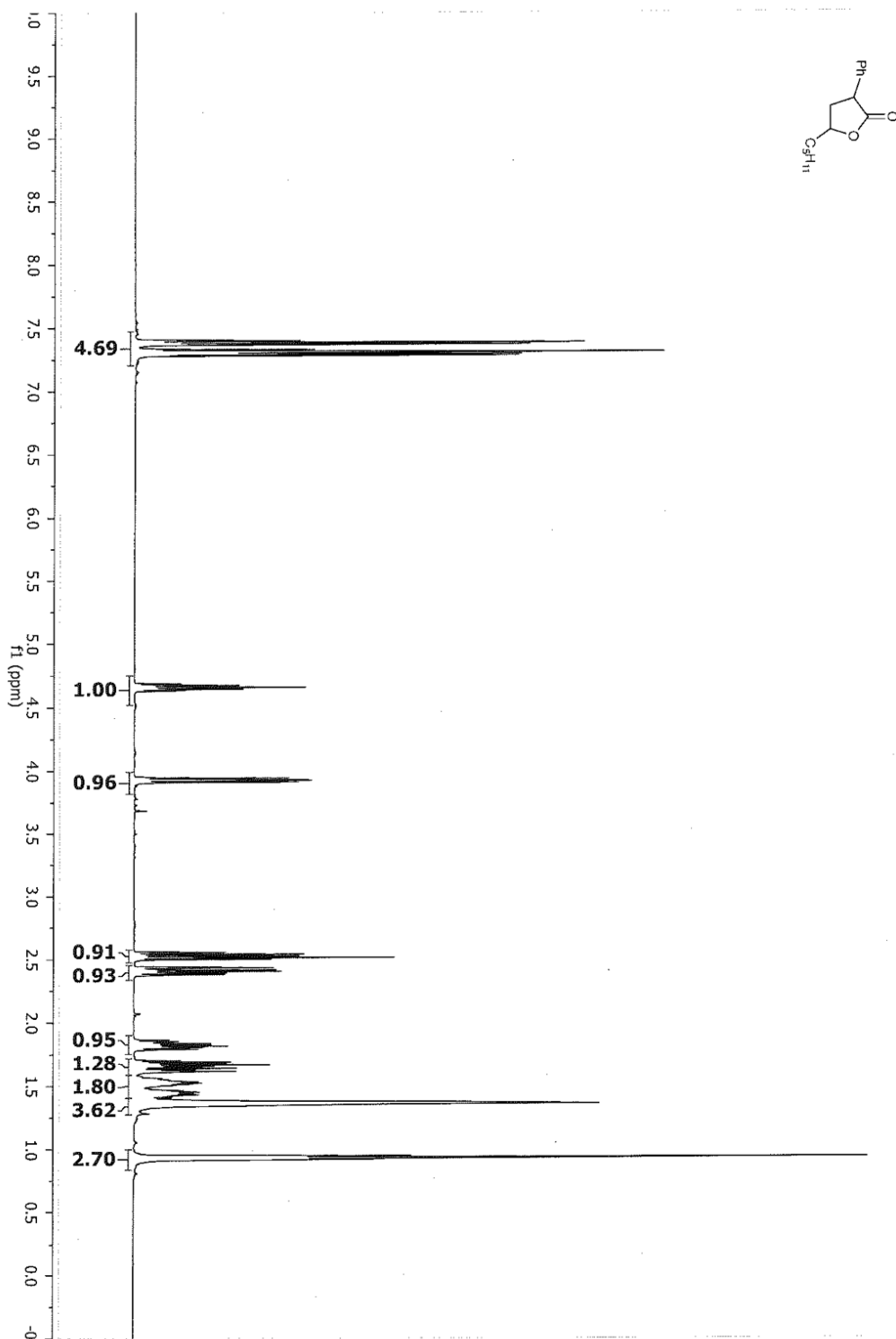


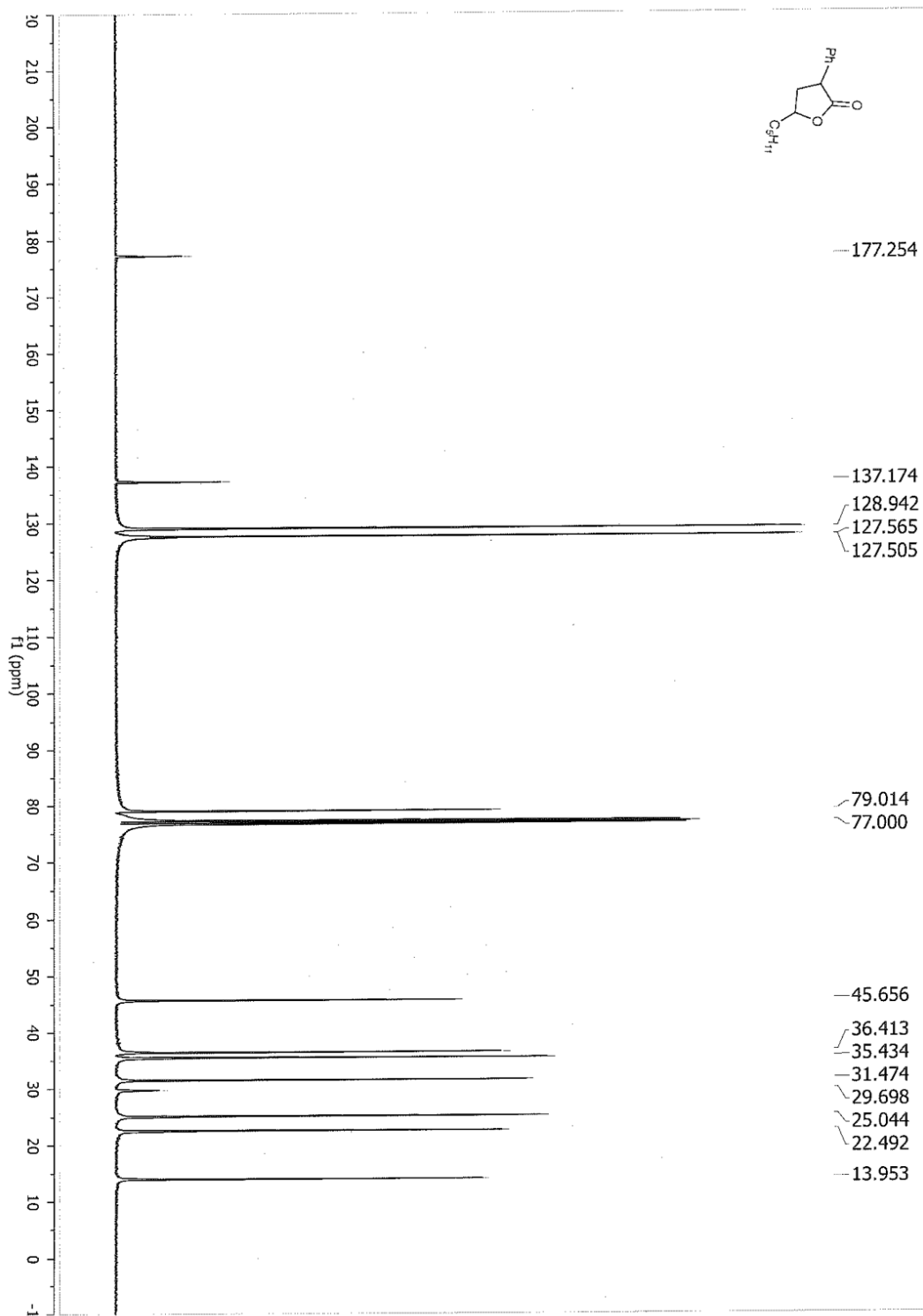


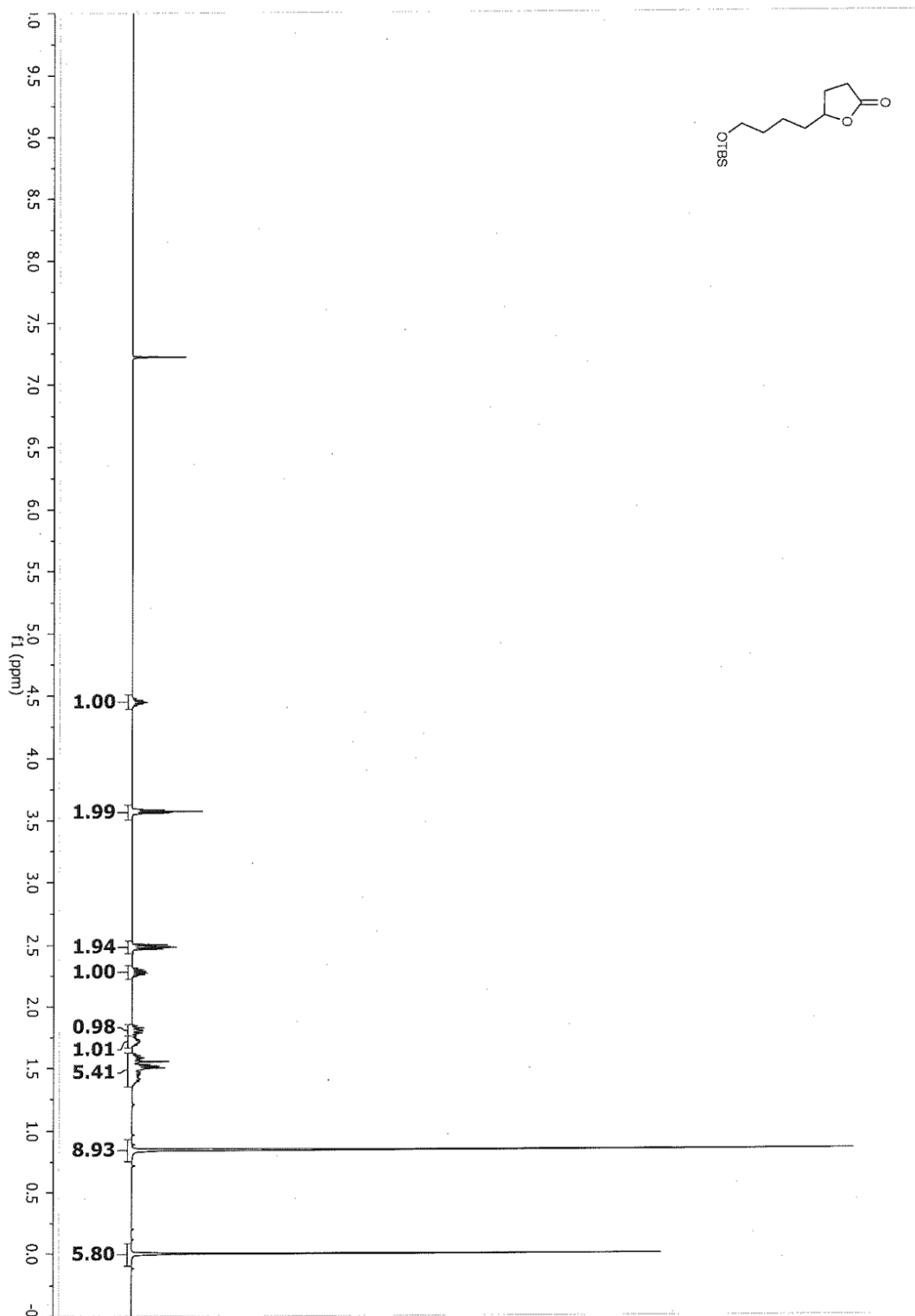




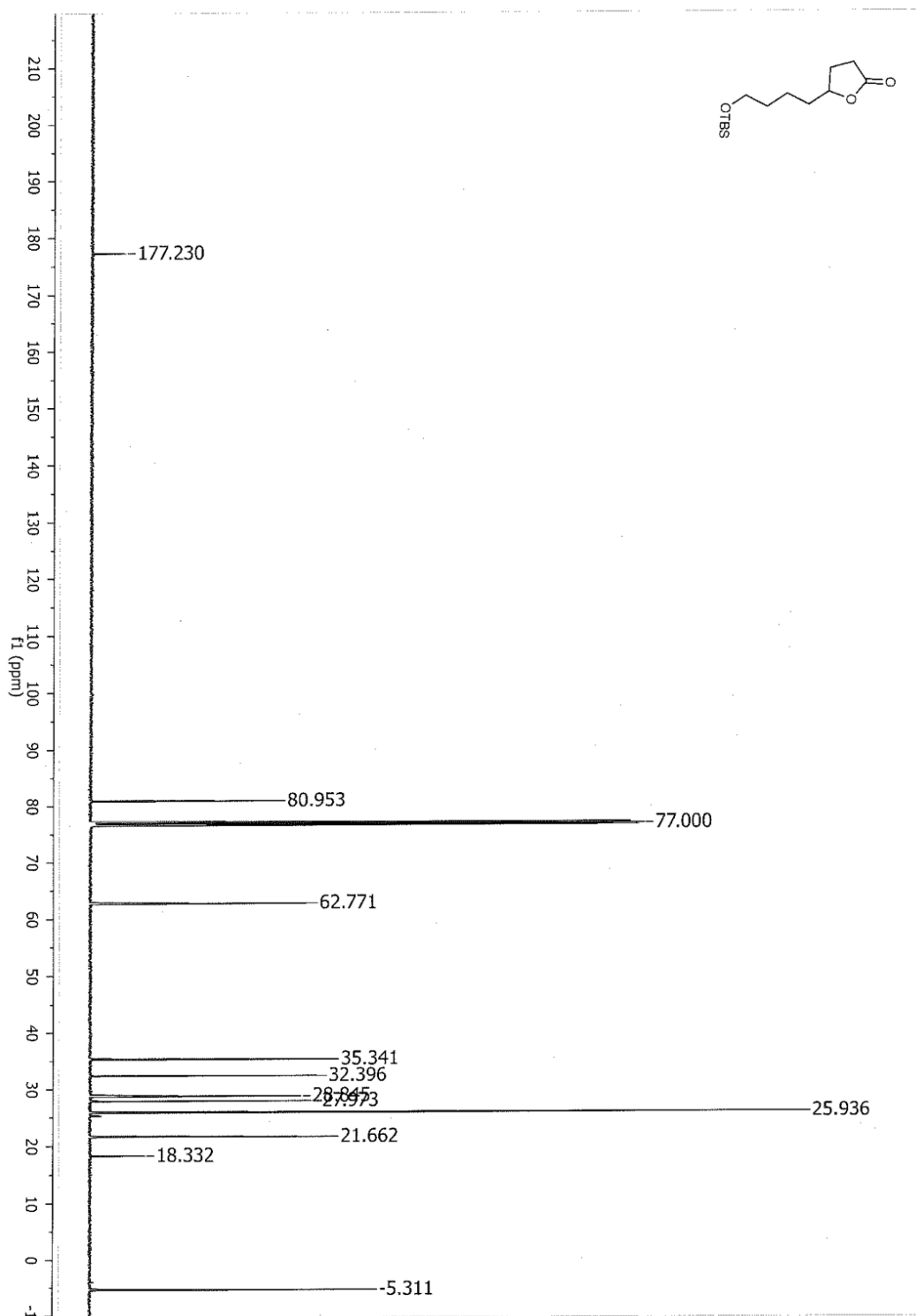


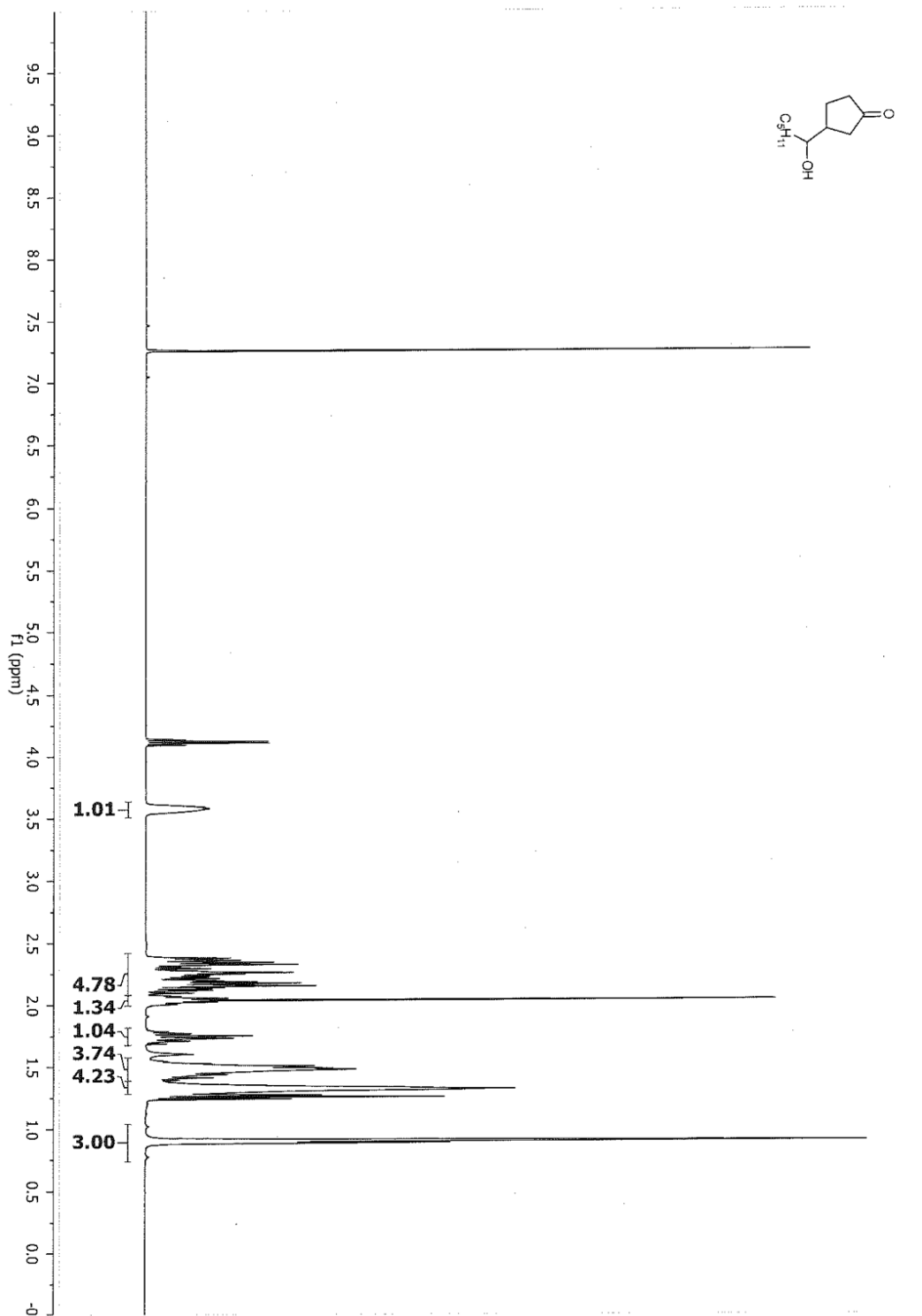


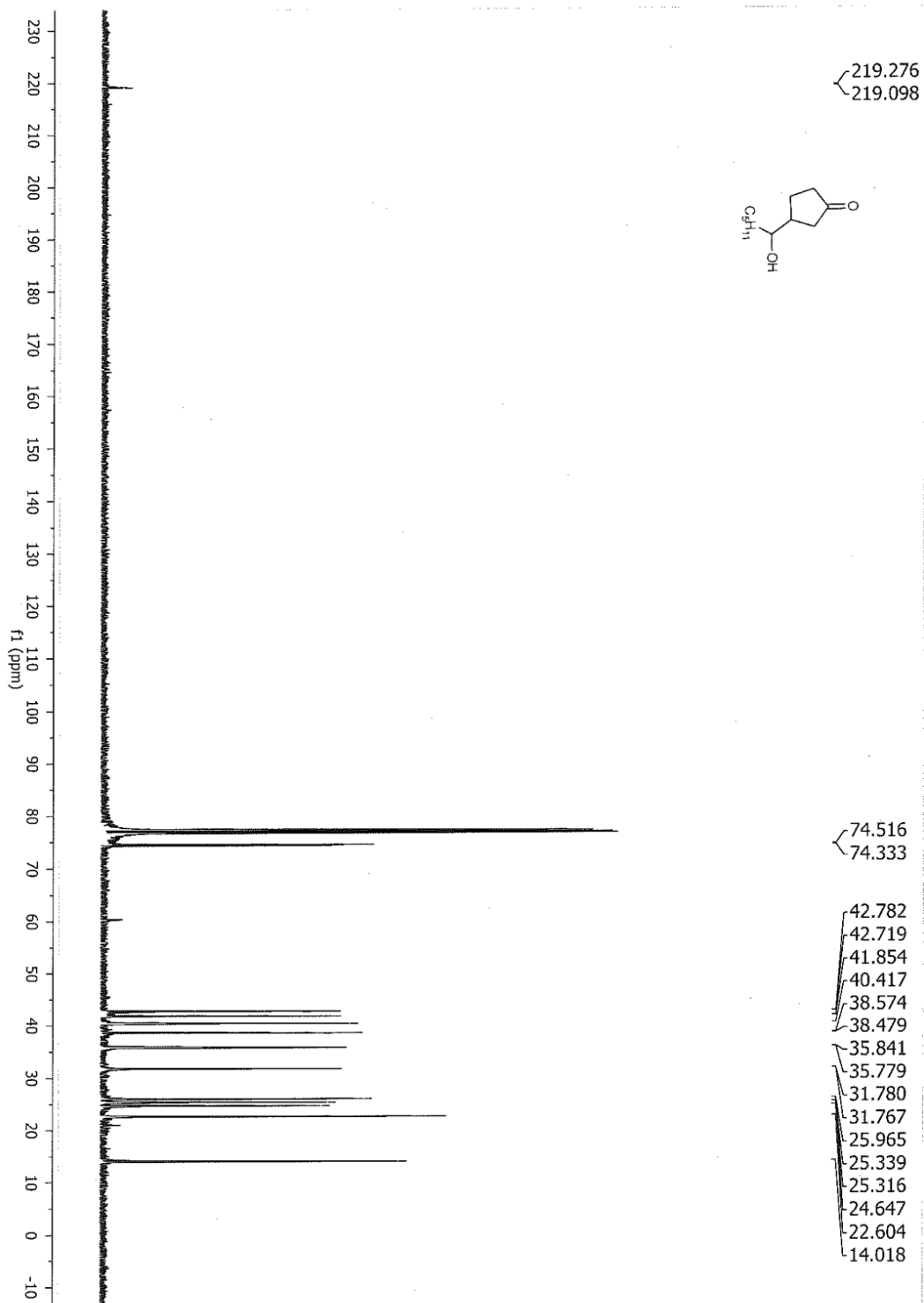


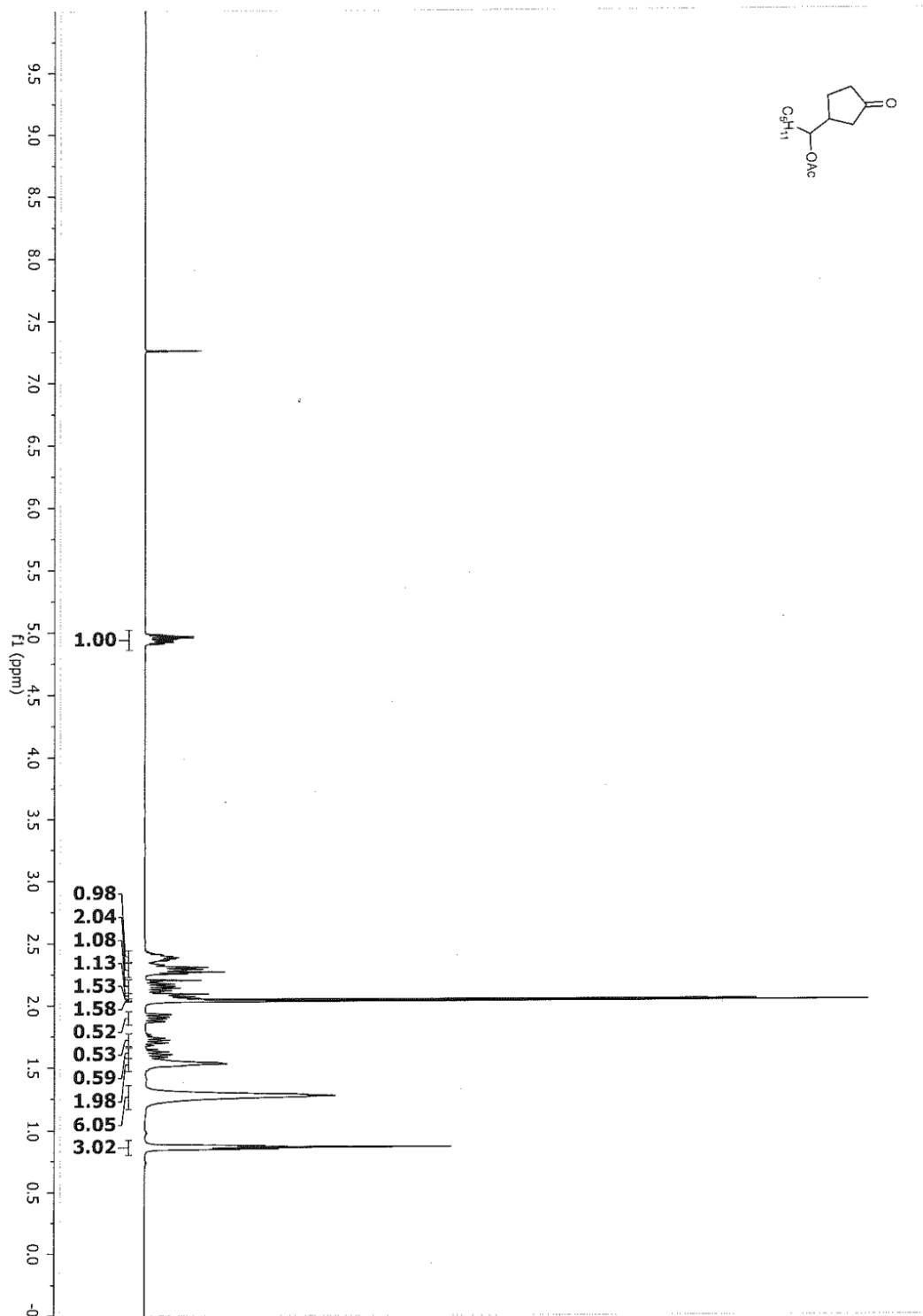


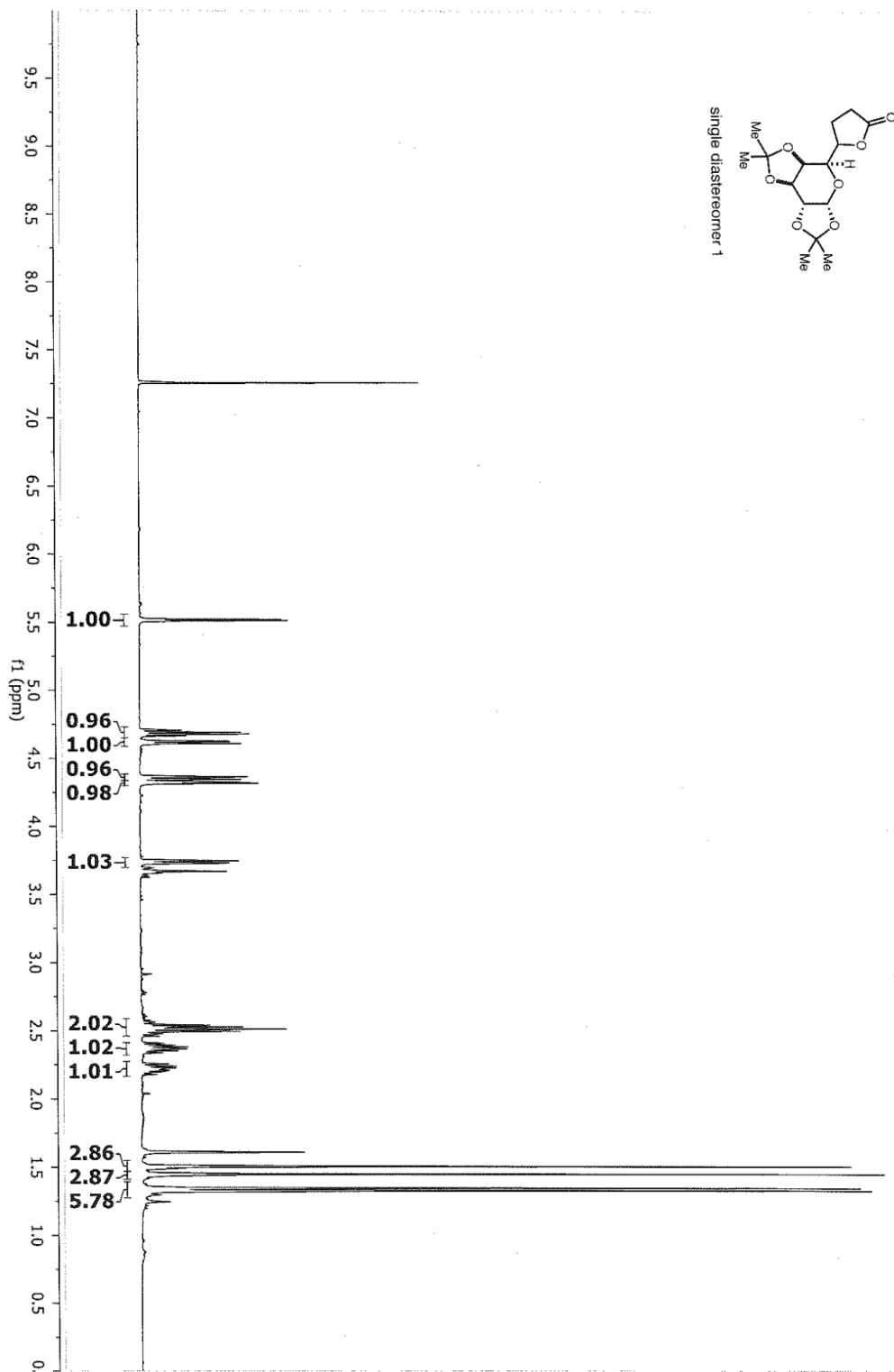


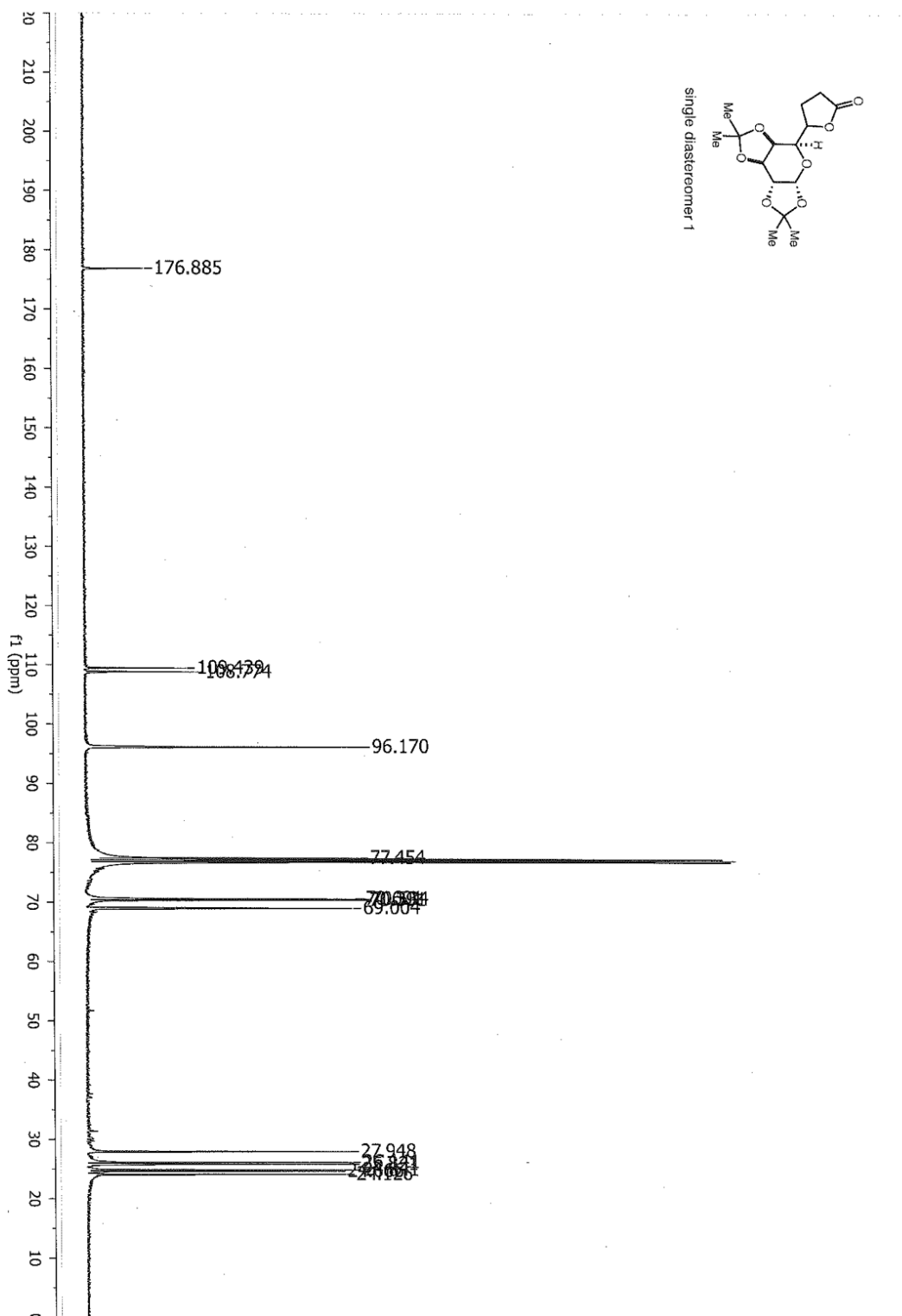


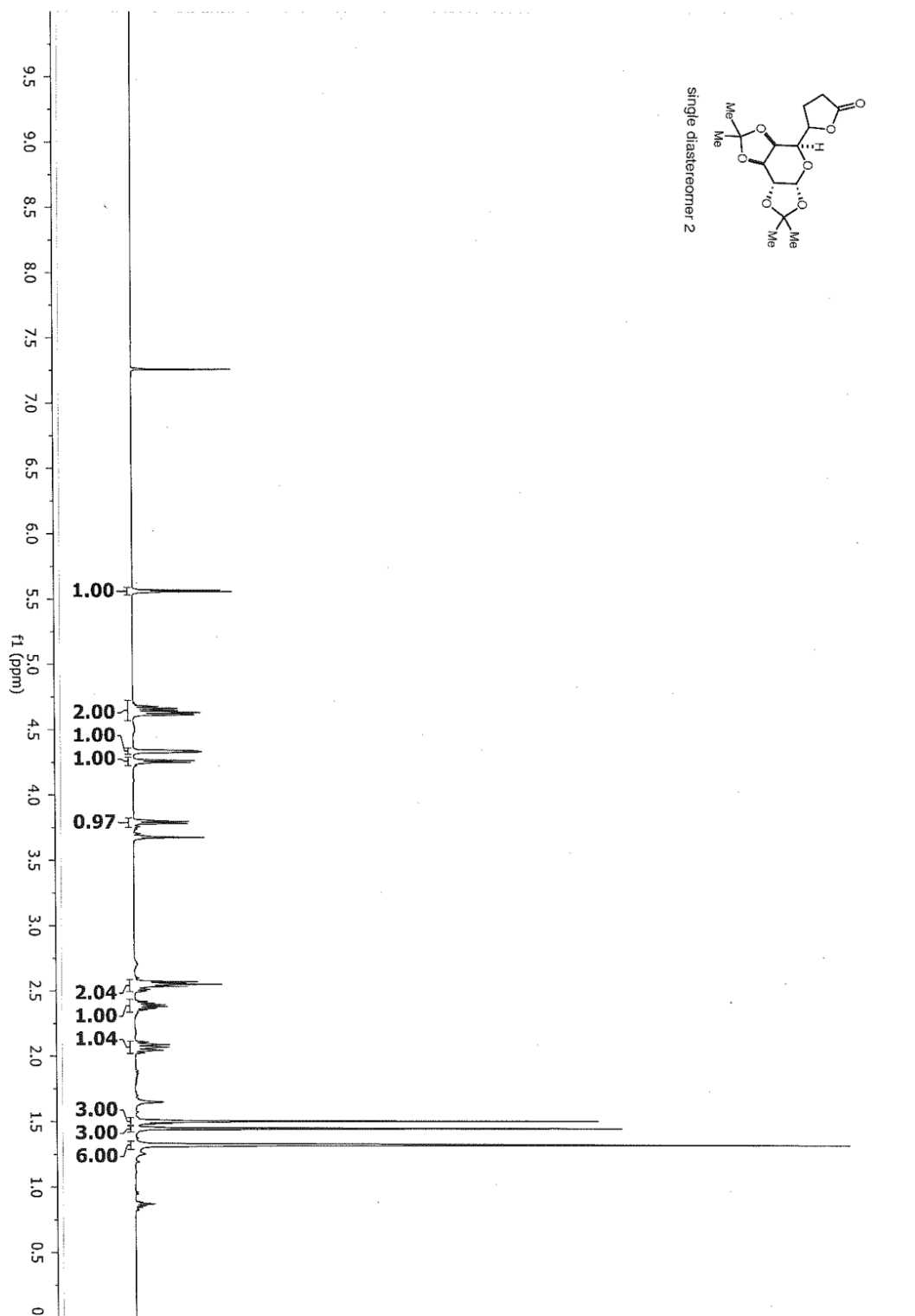


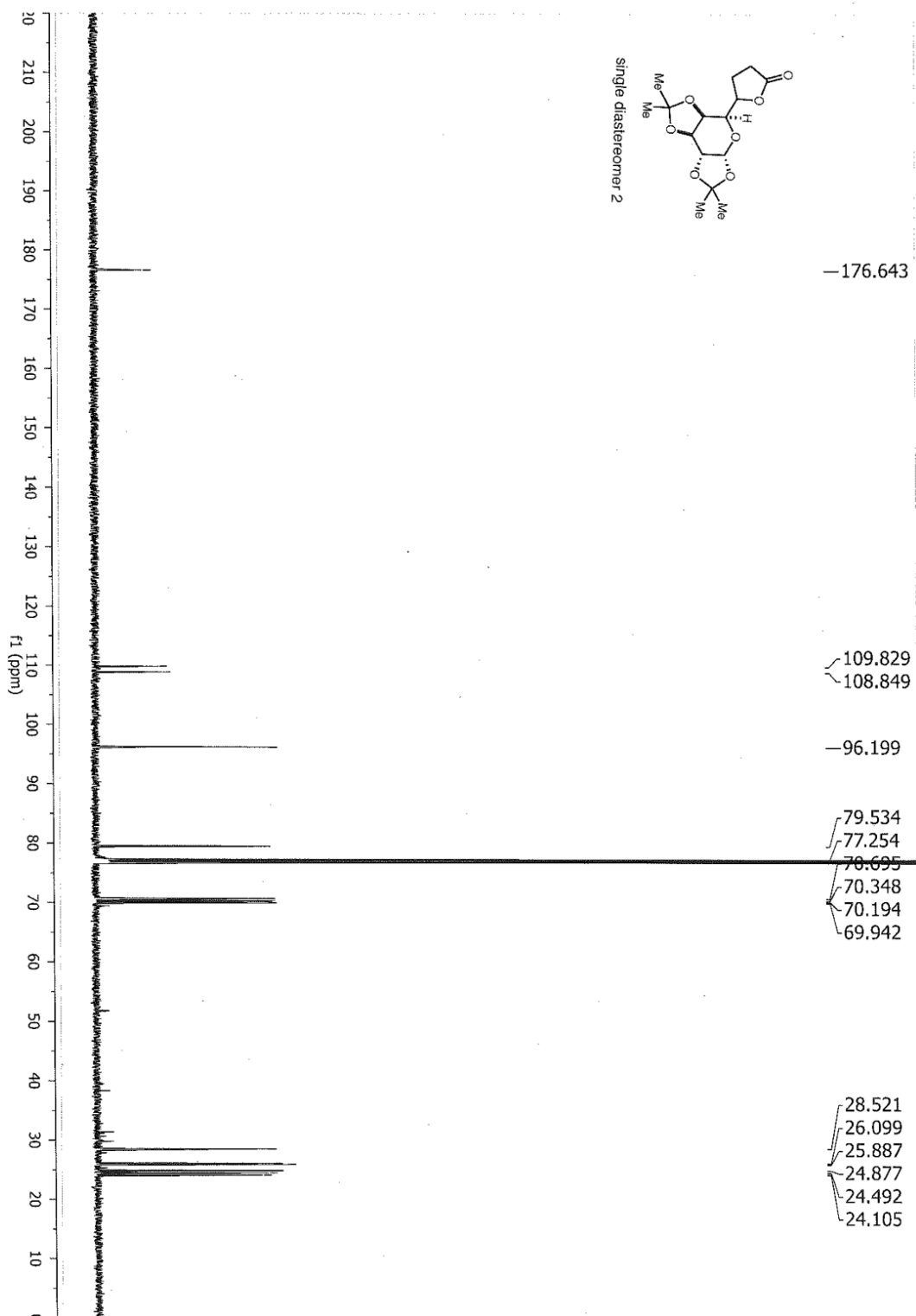




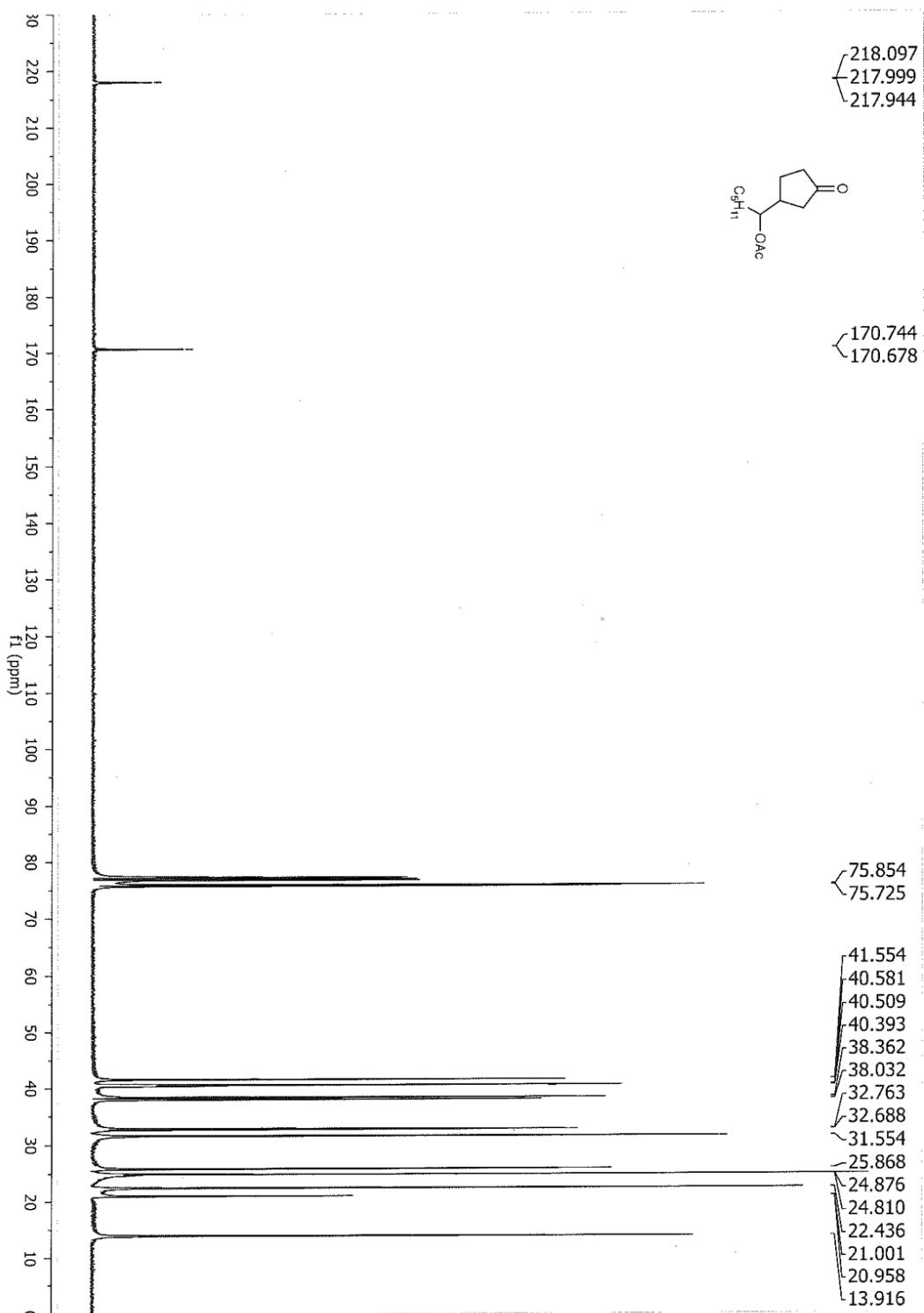


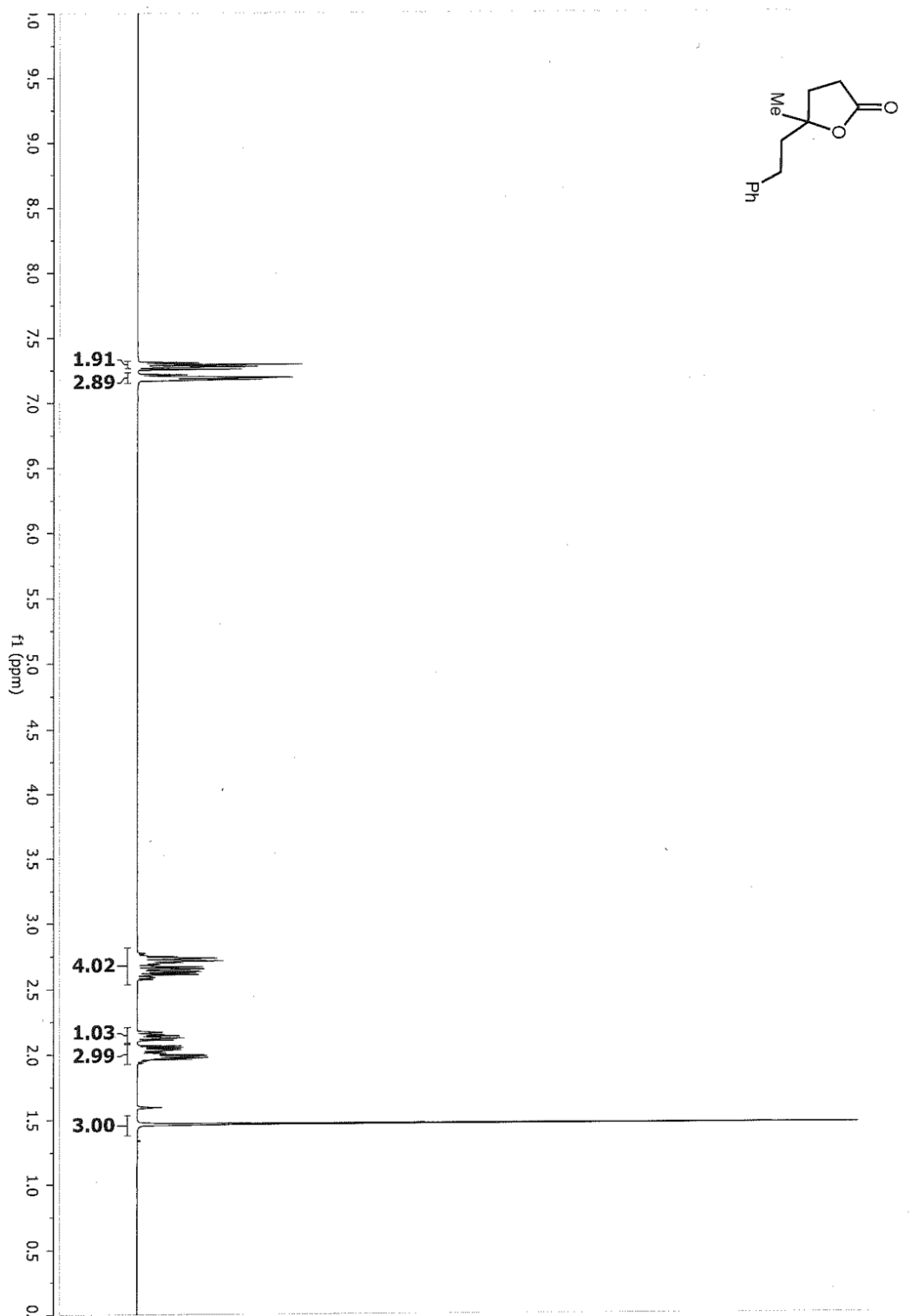


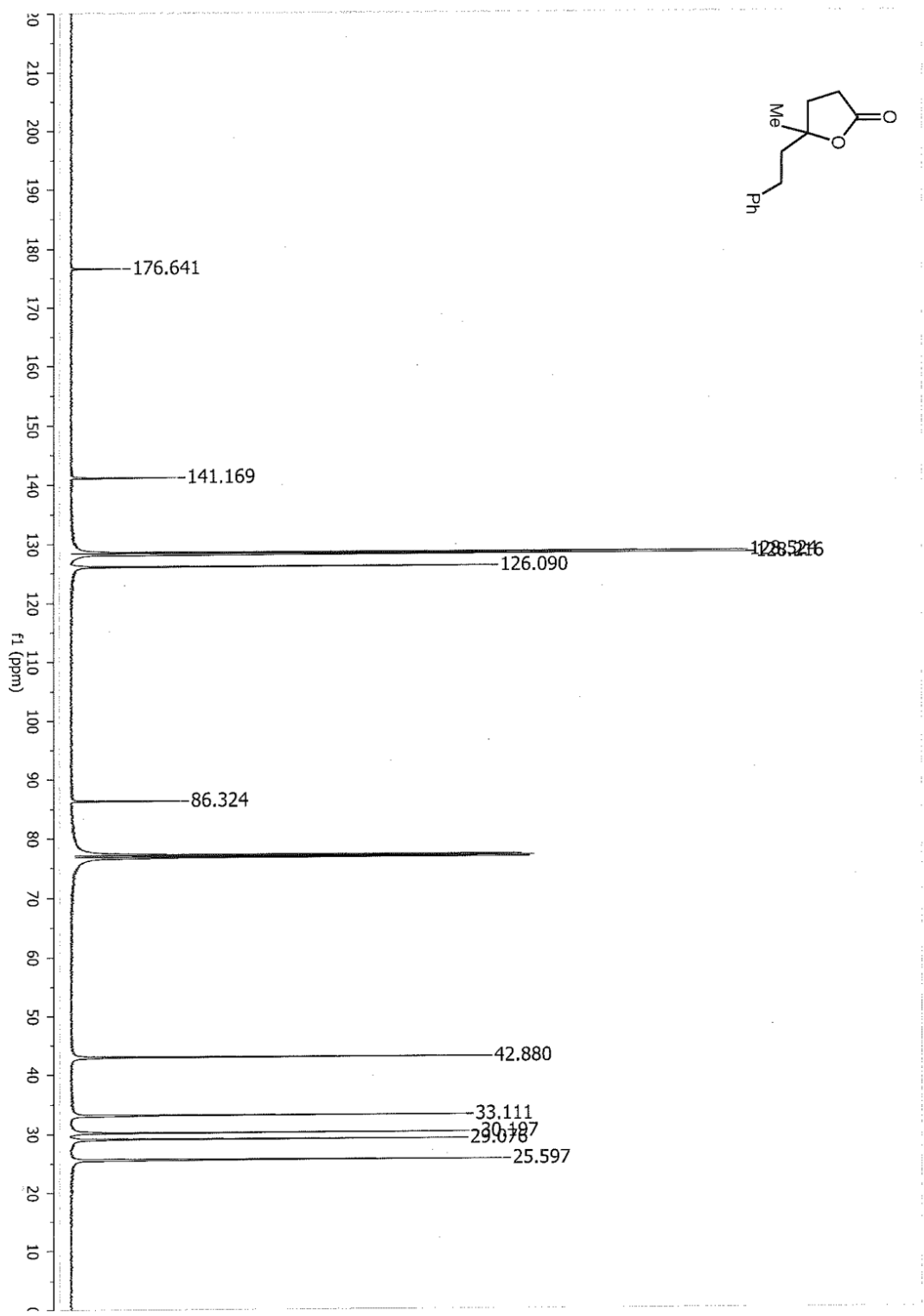


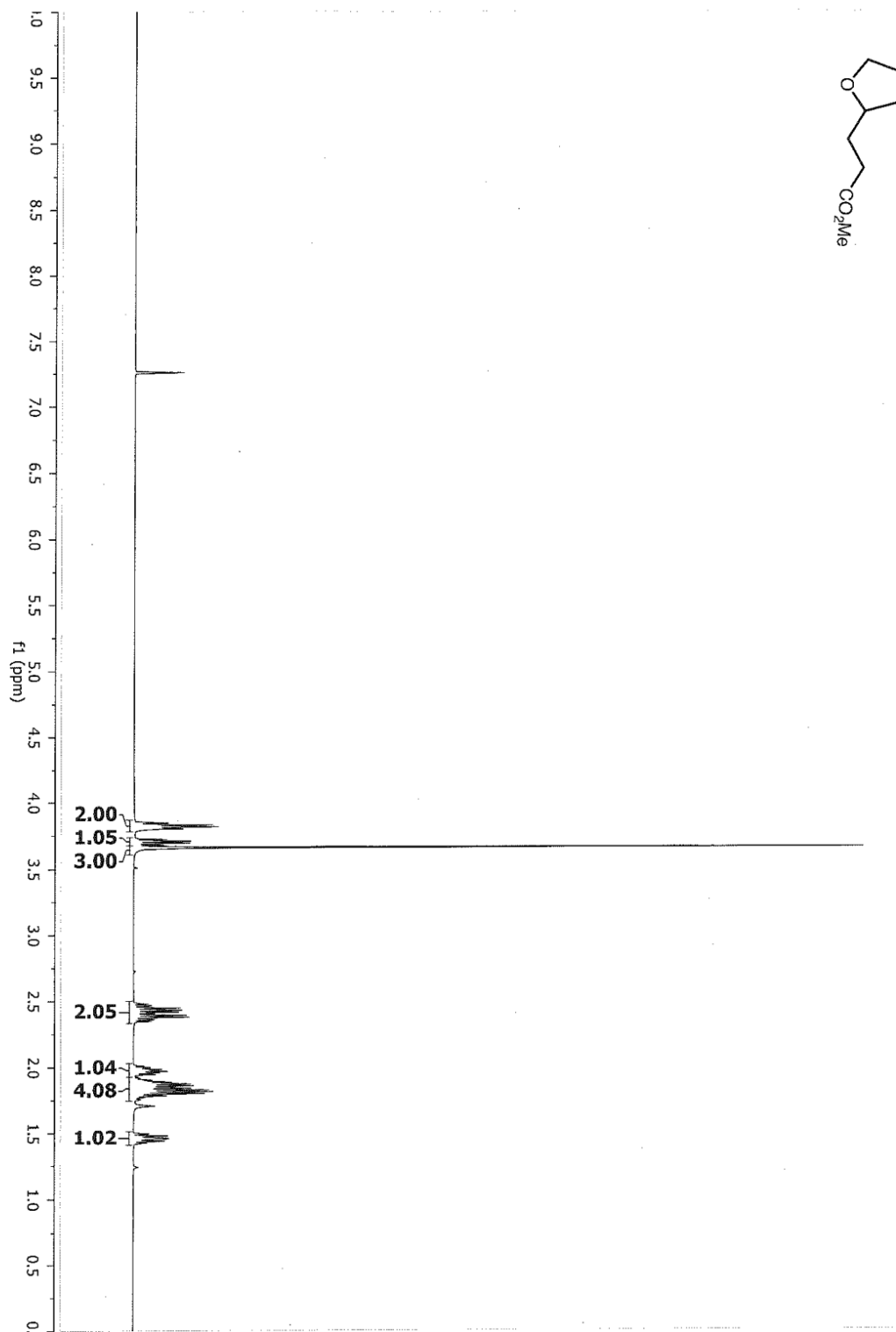


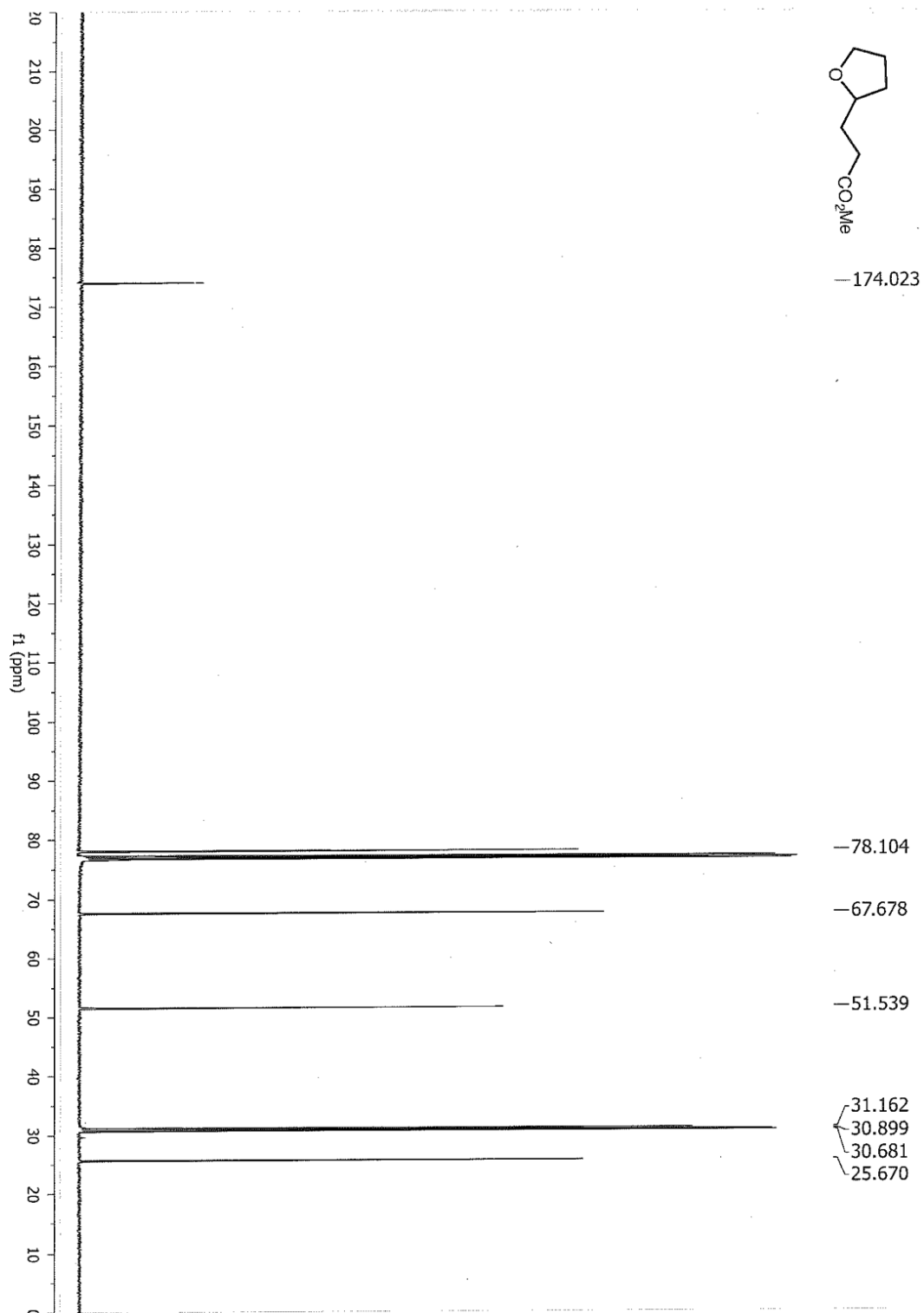


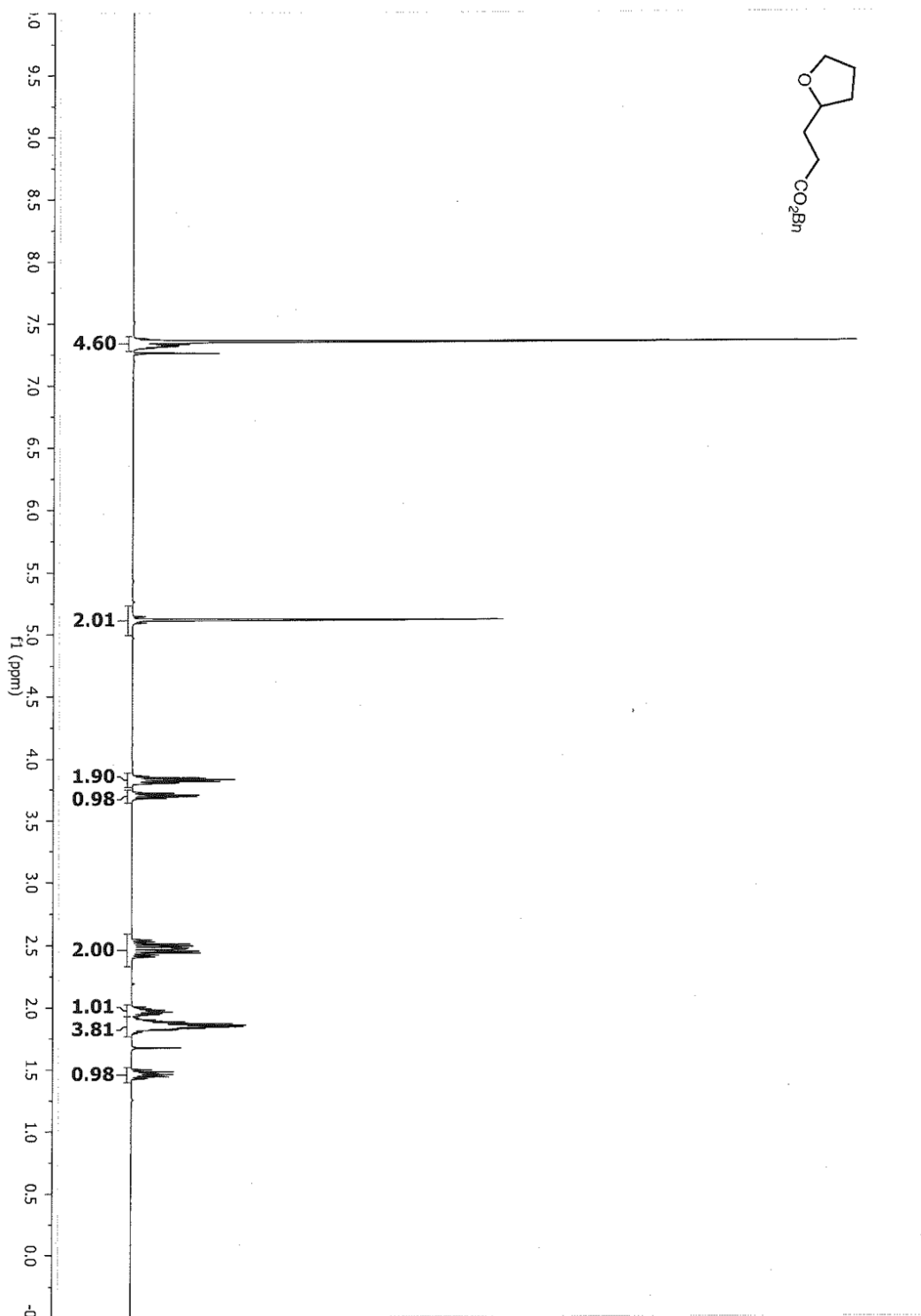


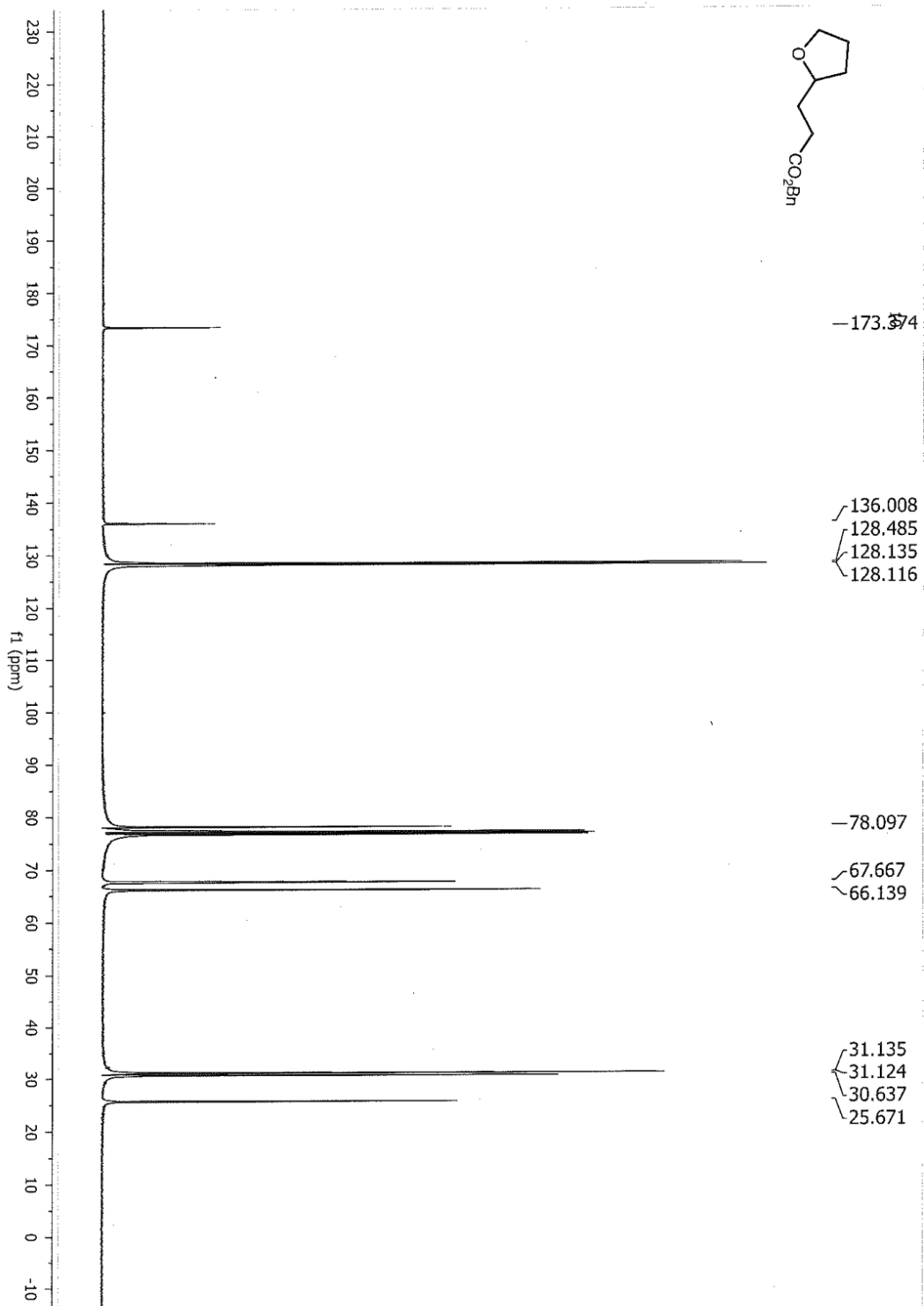


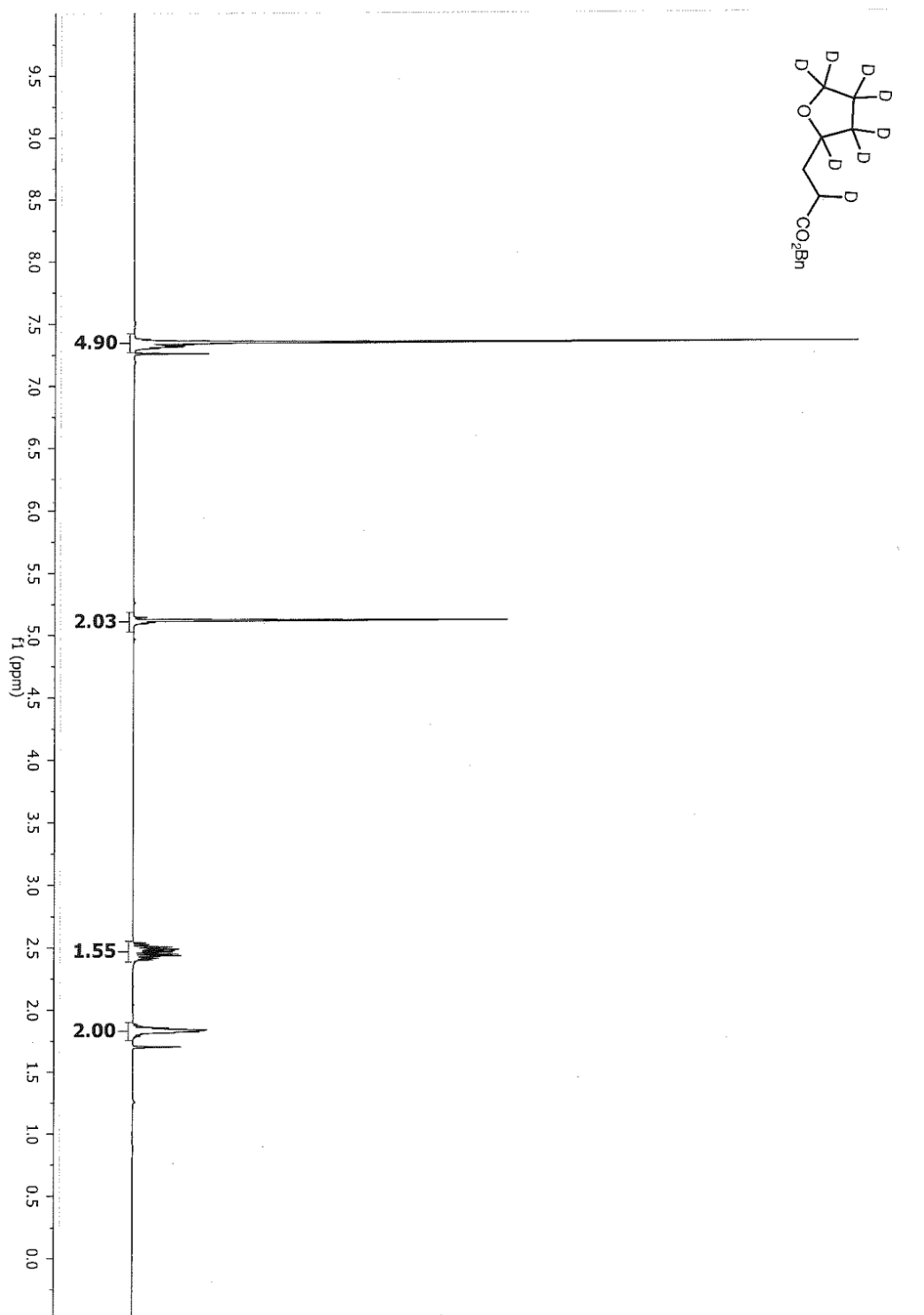






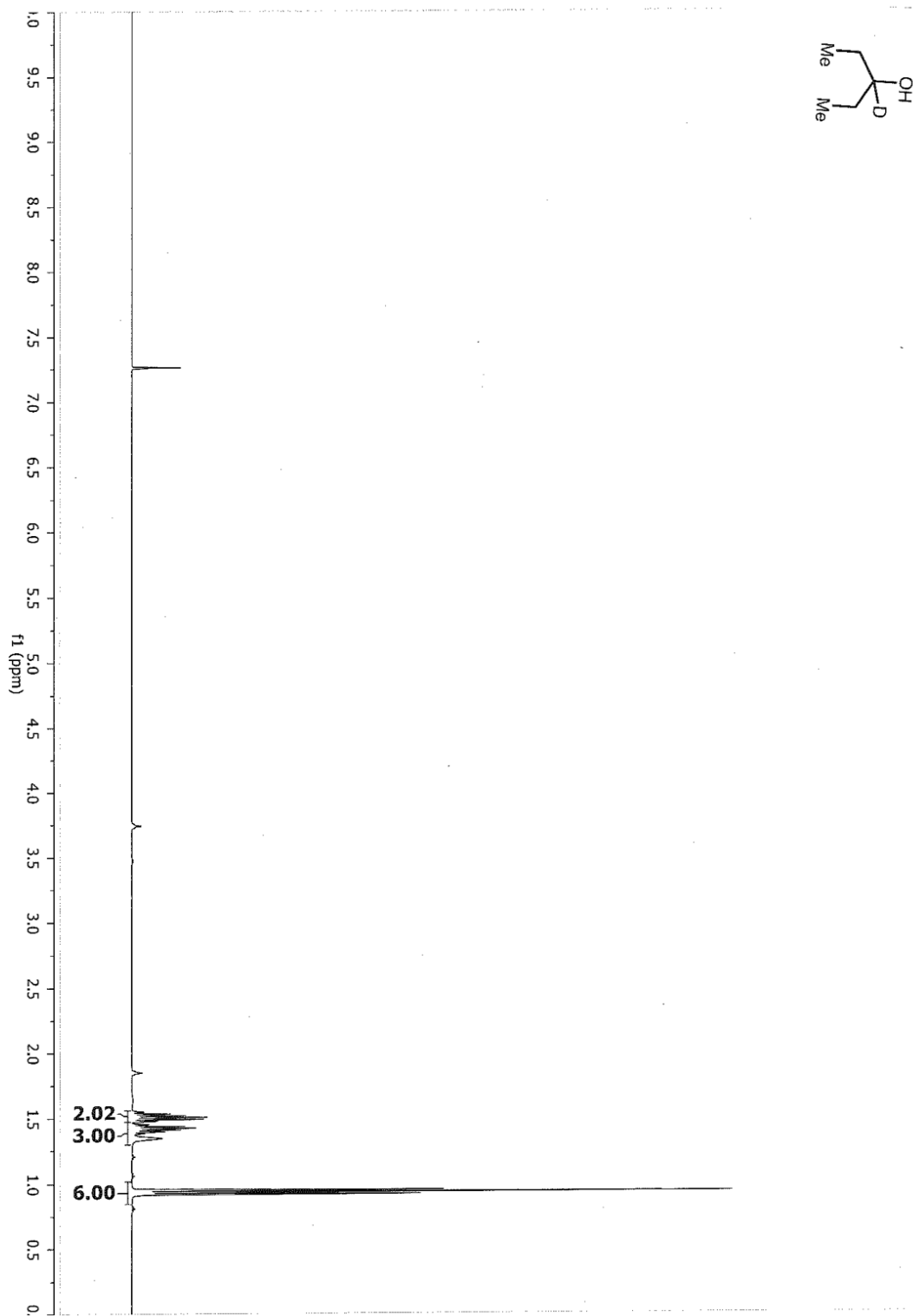


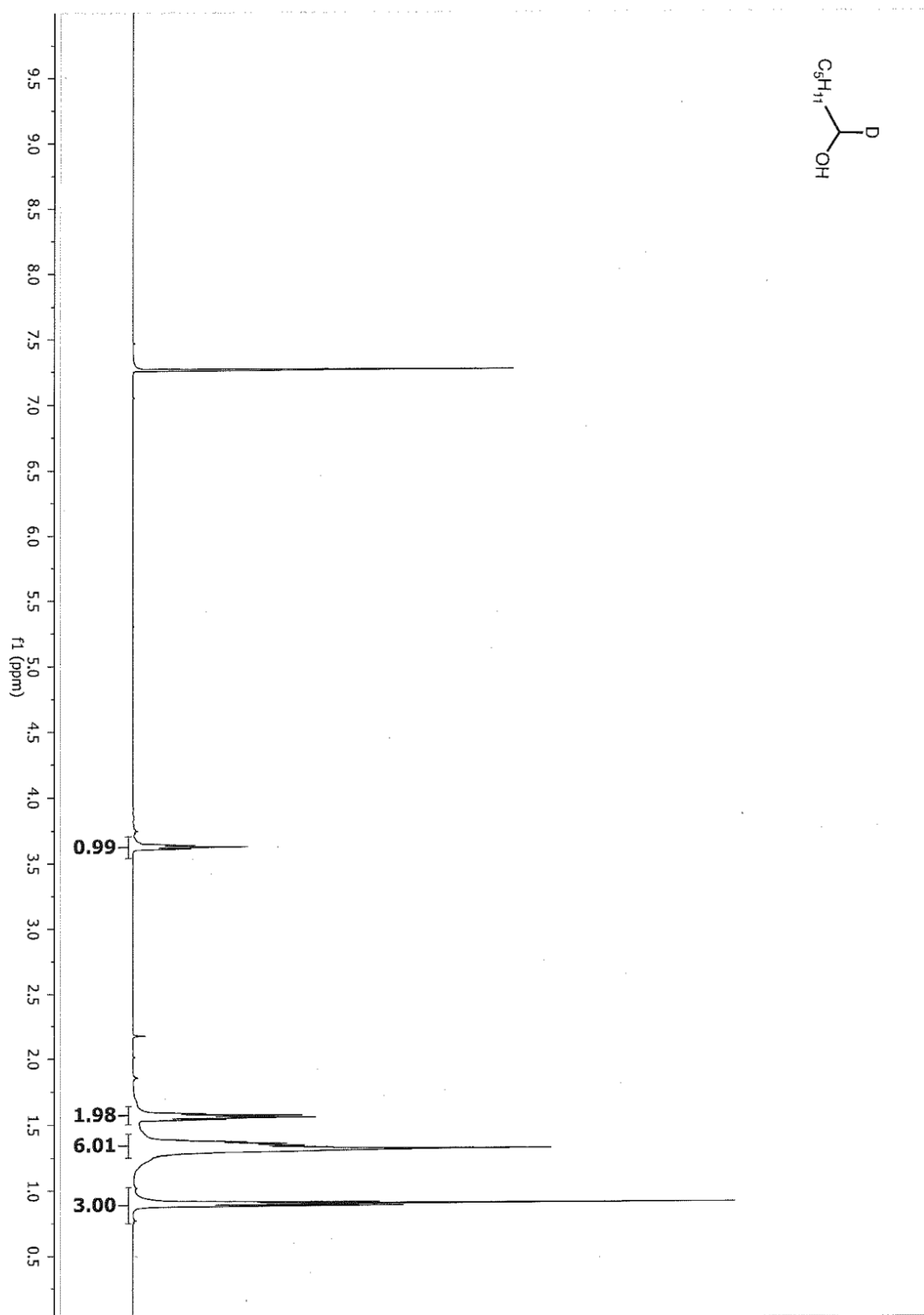


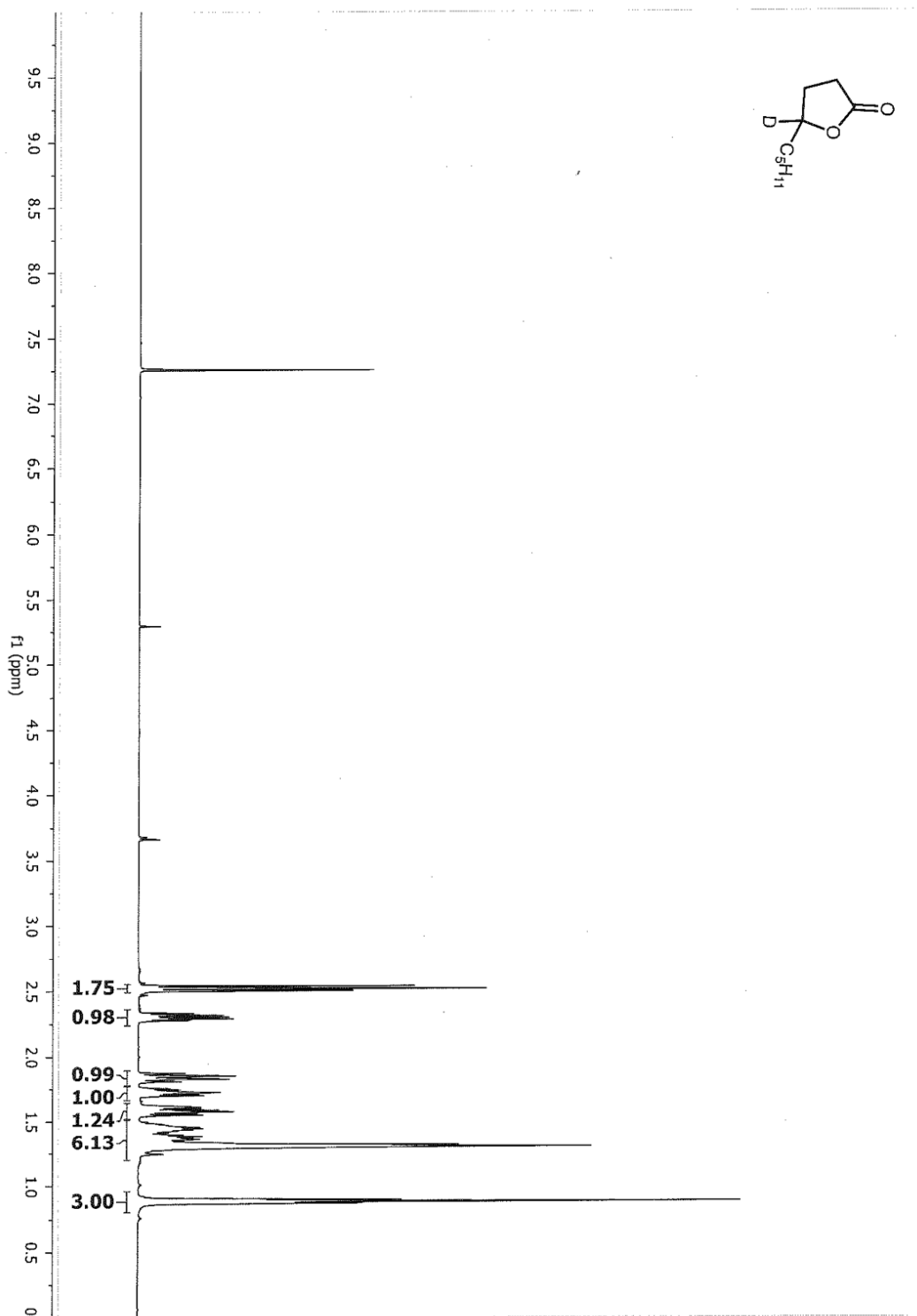


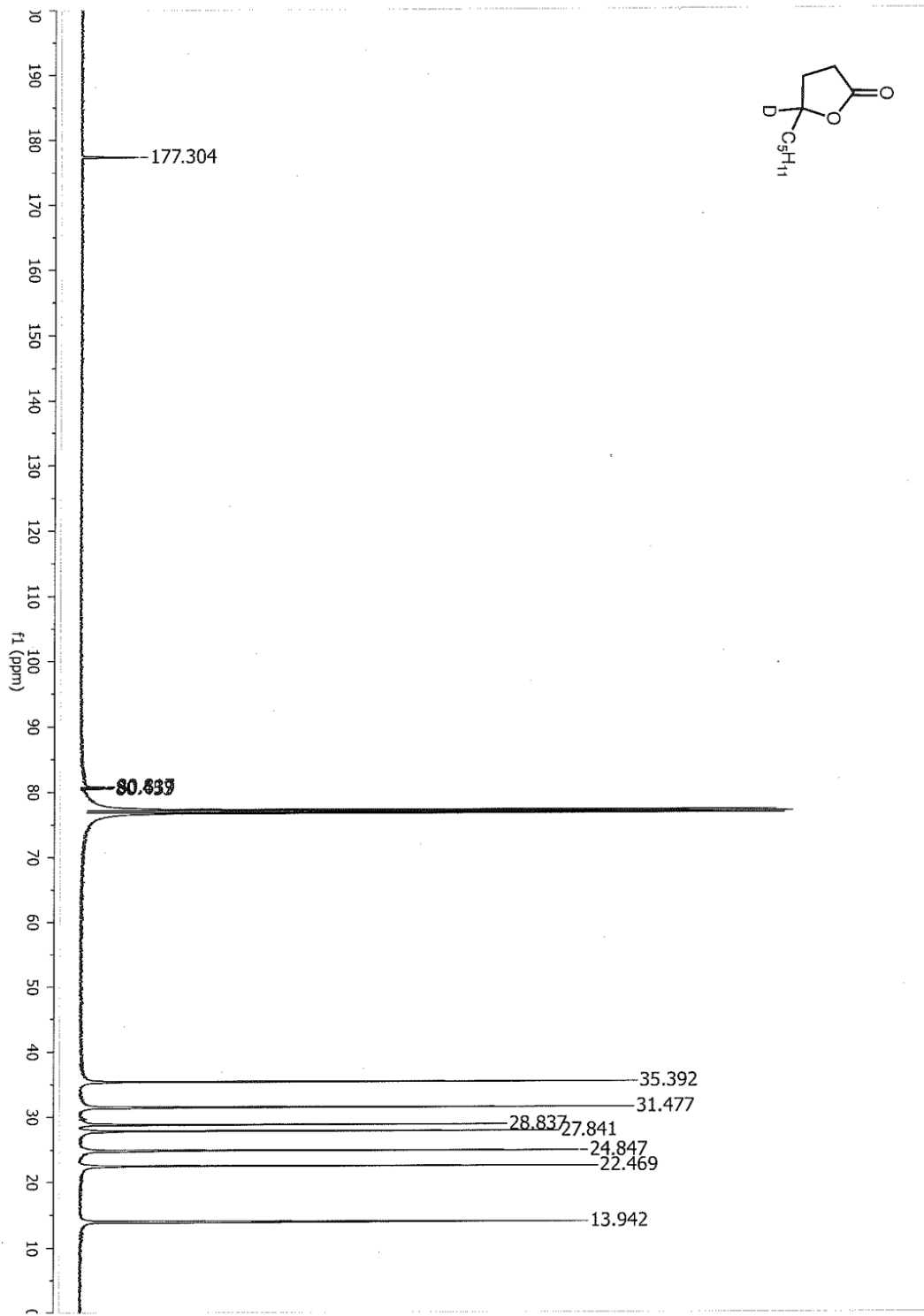


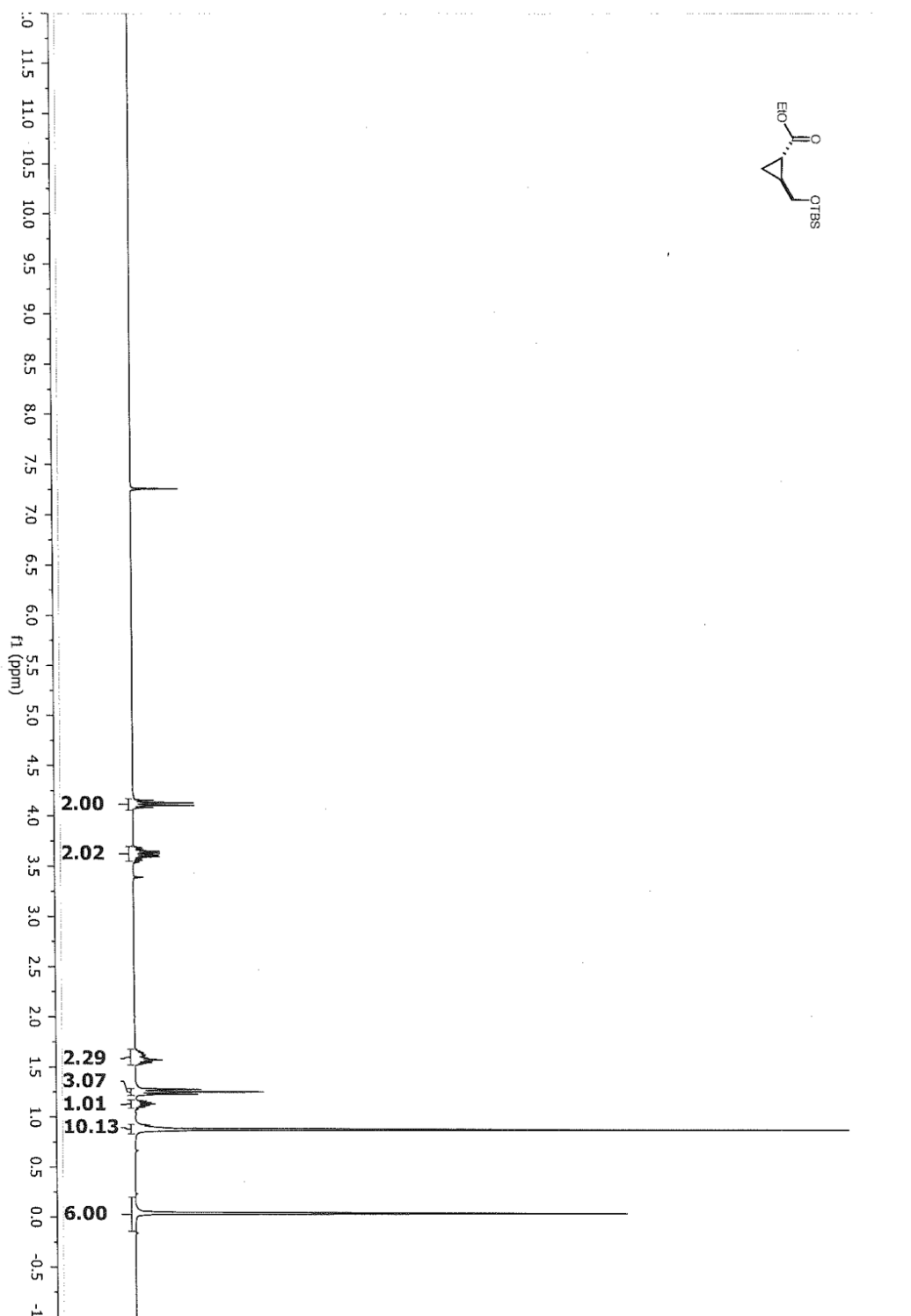


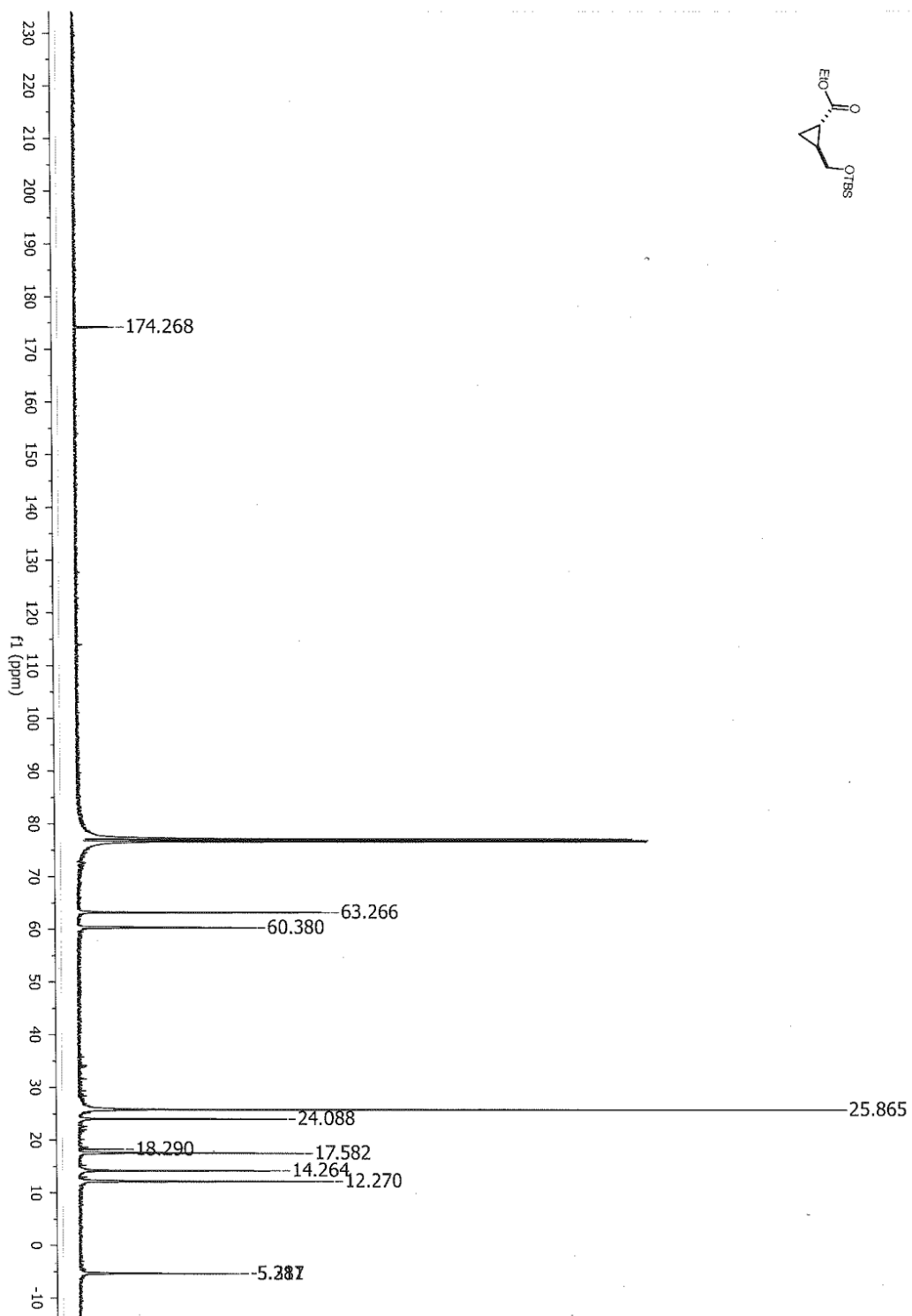


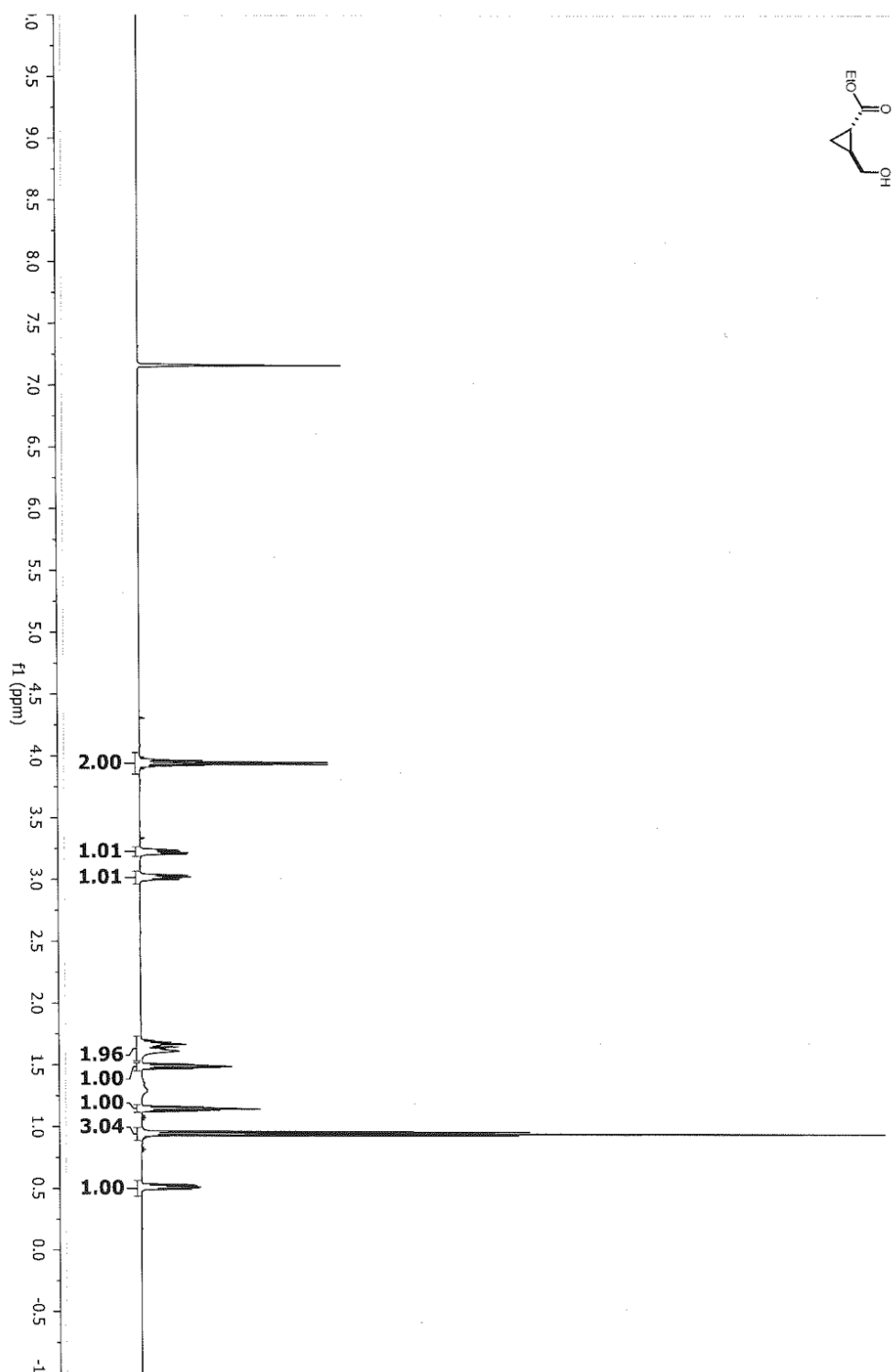




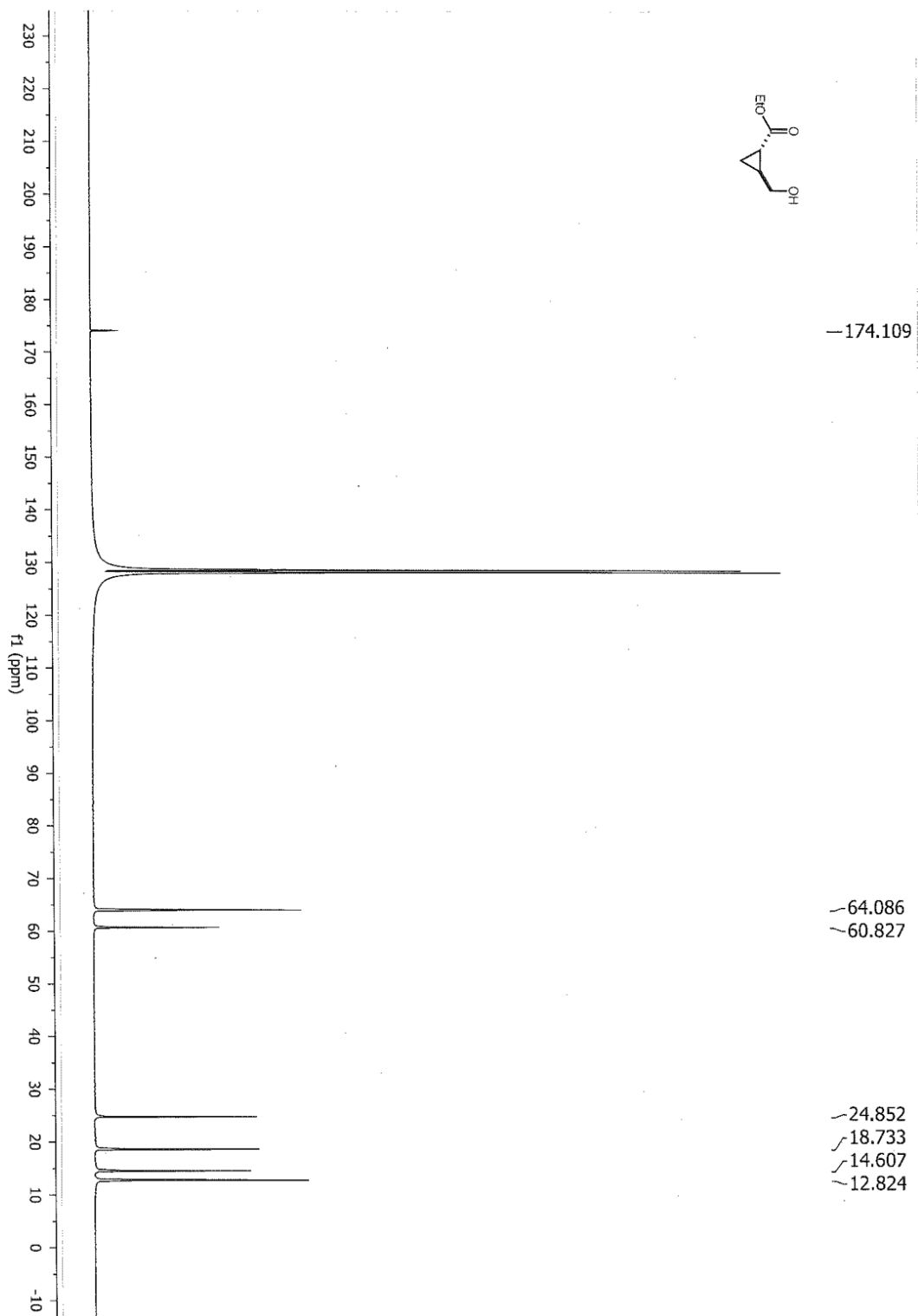


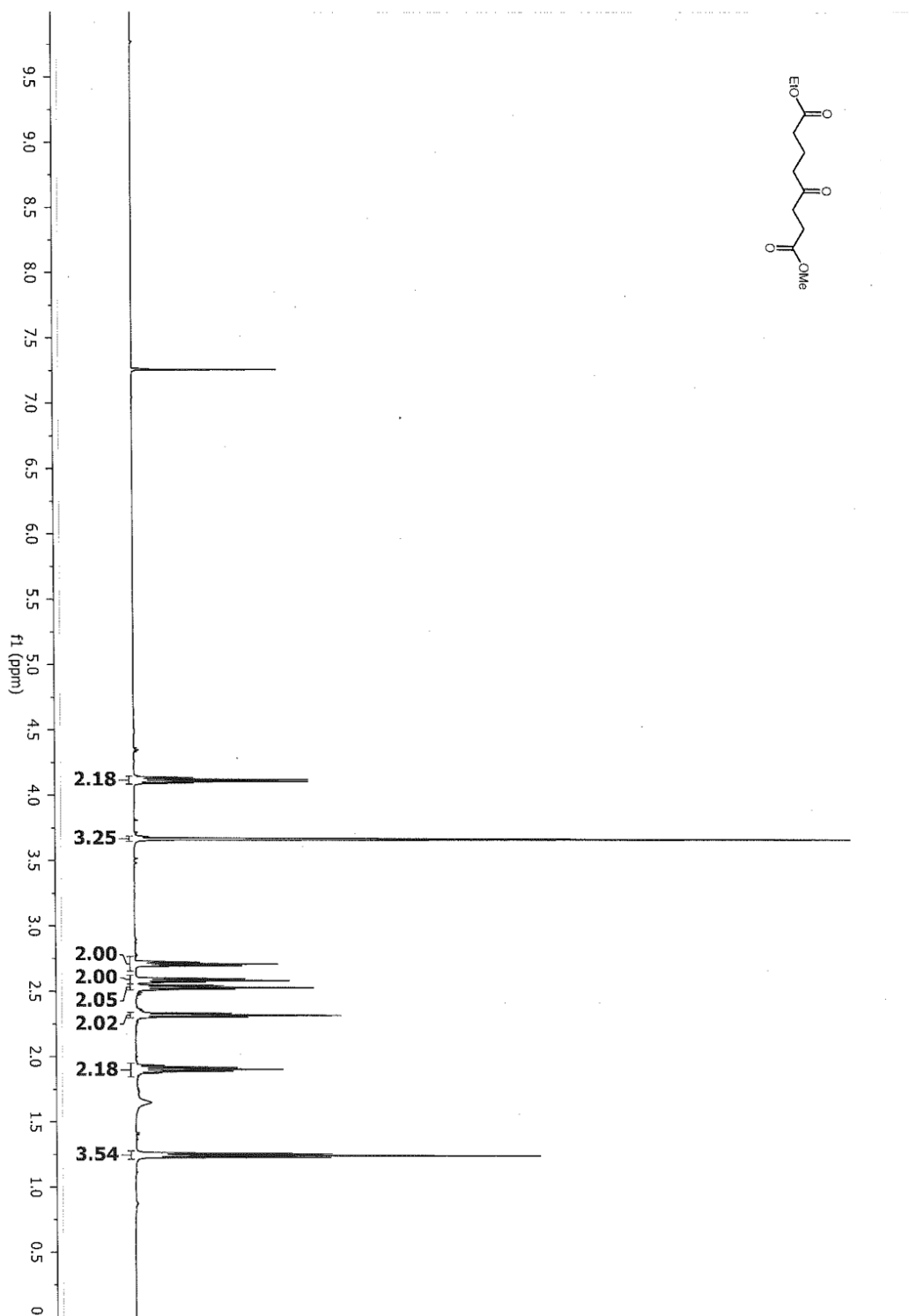


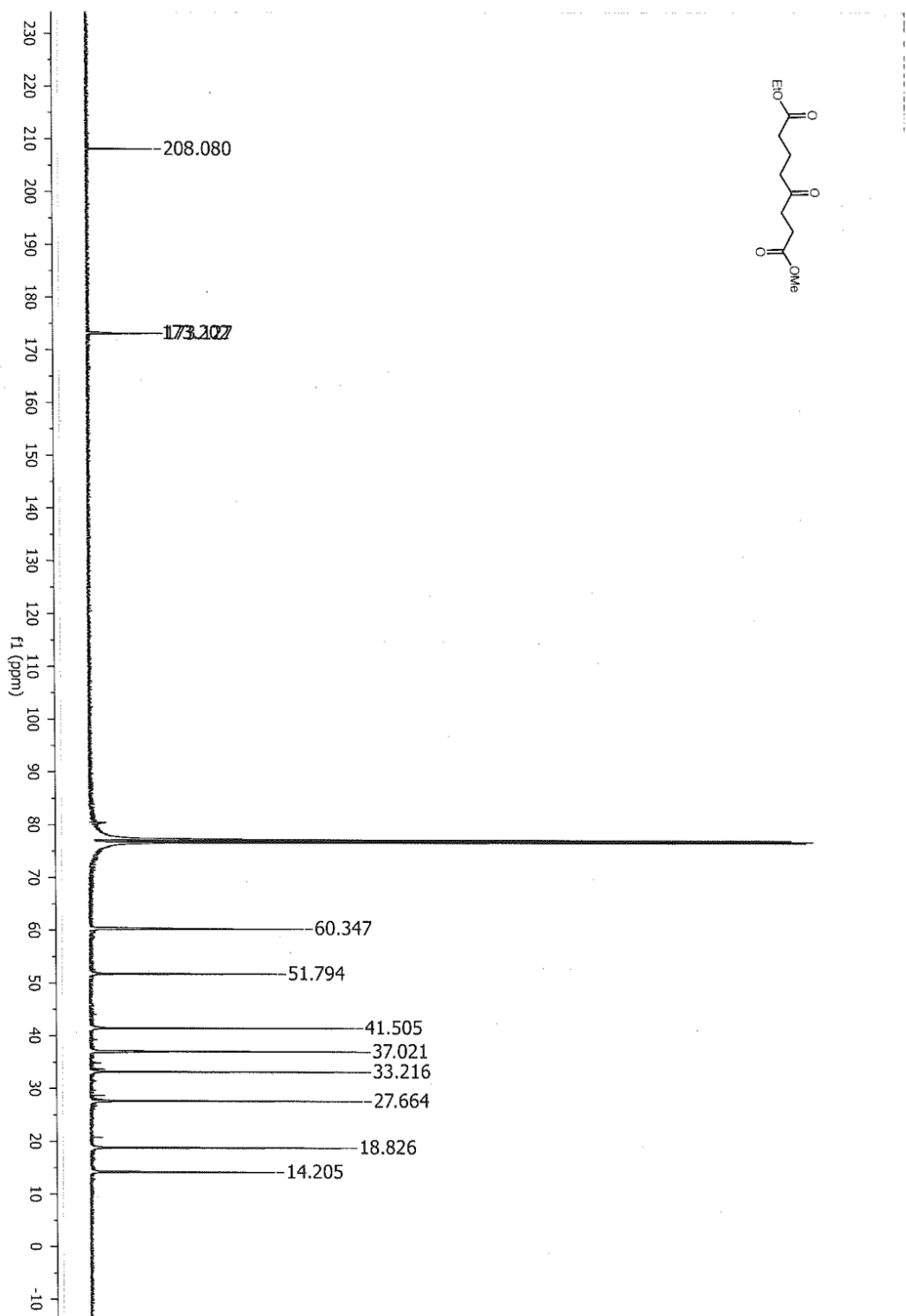






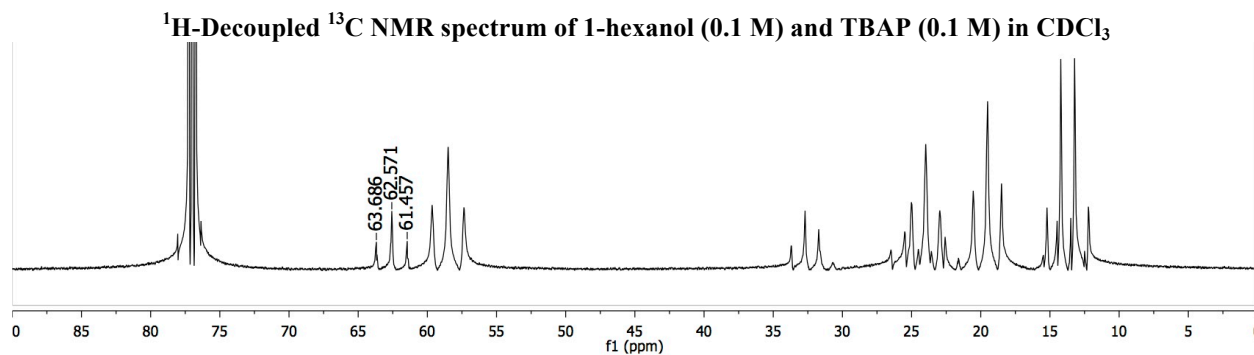
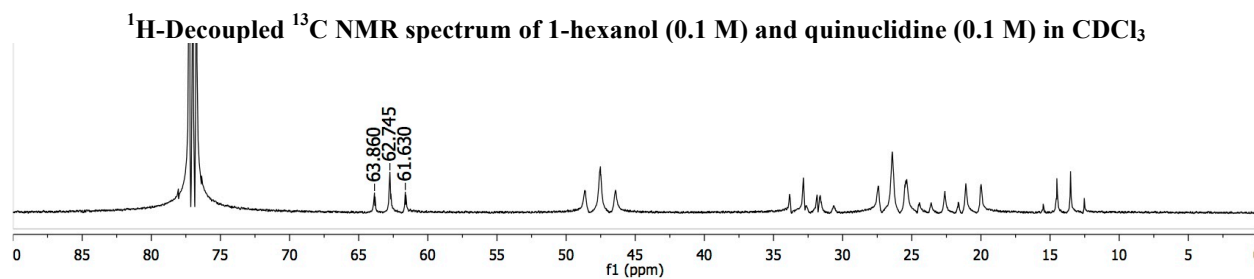
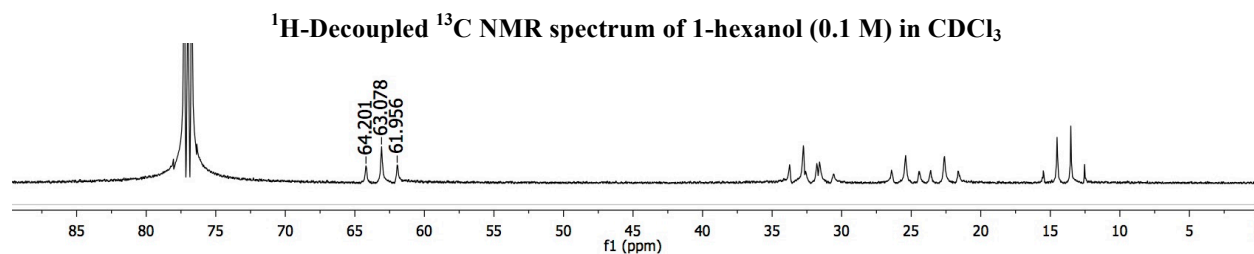




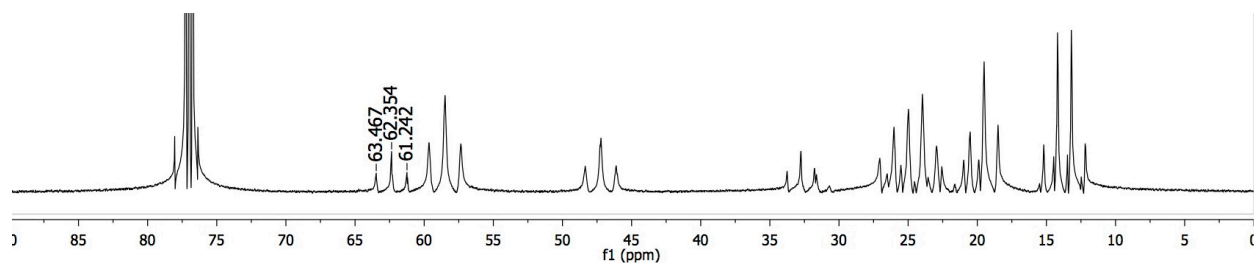


**Determination of  $^1J_{CH}$** 

Solutions of 1-hexanol (10  $\mu$ L) in  $CDCl_3$  (0.8 mL, 0.1 M) were prepared and either quinuclidine (8.9 mg, 0.1 M), tetra-*n*-butylammonium phosphate (27 mg, 0.1 M), or both quinuclidine and tetra-*n*-butylammonium phosphate were added. Proton-decoupled  $^{13}C$  NMR spectra were acquired at 125.85 MHz. Data were recorded using a 31,250 Hz spectral width and a 1.05 ms acquisition time.



**$^1H$ -Decoupled  $^{13}C$  NMR spectrum of 1-hexanol (0.1 M), quinuclidine (0.1 M) and TBAP (0.1 M) in  $CDCl_3$**



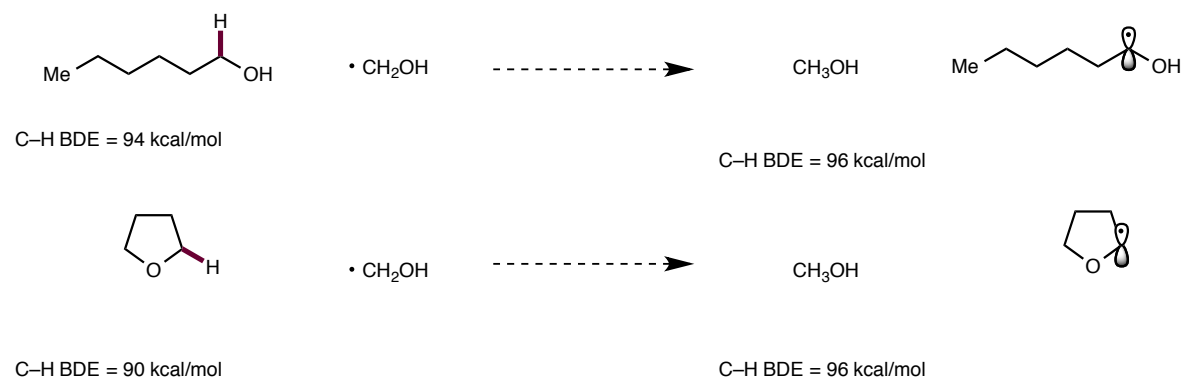
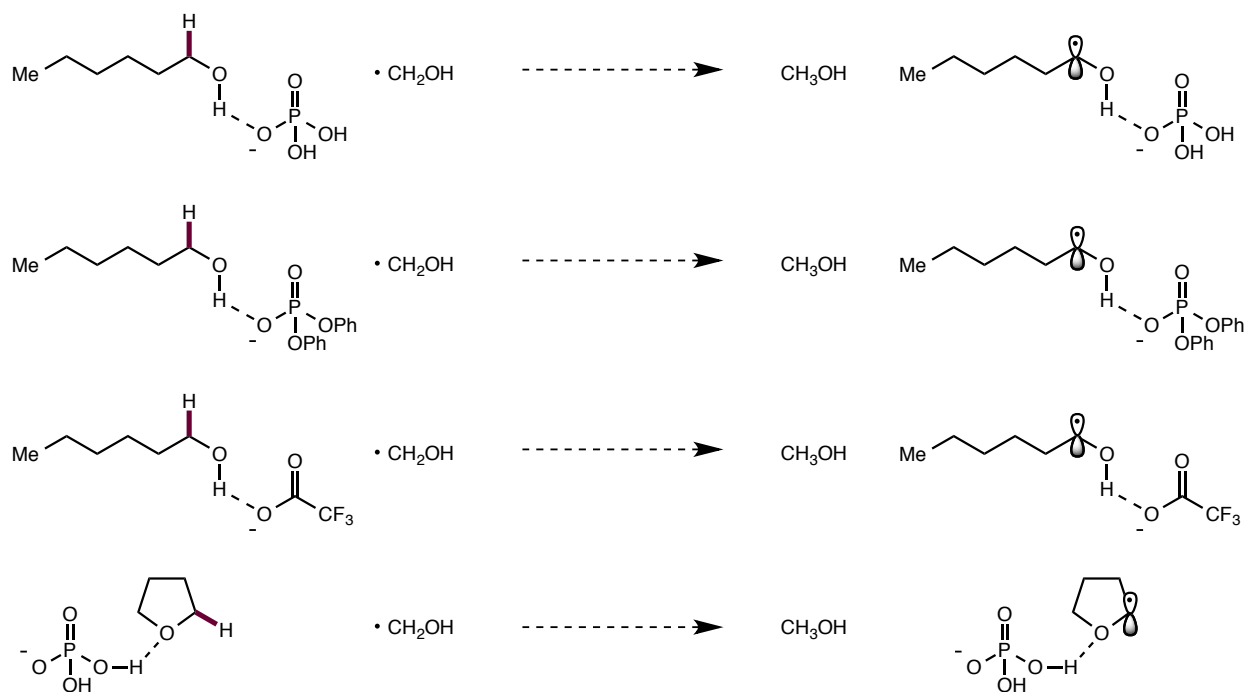
## DFT Computational Information

### Computational Details

All calculations used DFT methodology as implemented in the Gaussian 09 series of computer programs (72, 73). We employed the unrestricted B3LYP functional (74–78). All-electron, split-valence double- $\zeta$  plus polarization function 6-31G(d,p) basis sets were used (79–82). Calculations were performed using the CPCM solvation model in acetonitrile. All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis.

**Table S1:** Thermodynamic parameters; geometries and frequencies were calculated with UB3LYP/6-31G(d,p) in all cases. Energies are given in hartree particle<sup>-1</sup>.

Entry	Job Name	E+ZPE	G	H	S
1	Hexanol	-312.139768	-312.174368	-312.129280	94.896
2	Hexanol radical	-311.493696	-311.529223	-311.483120	97.033
3	Hexanol–dihydrogen phosphate	-955.856757	-955.908365	-955.838840	146.327
4	Hexanol–dihydrogen phosphate radical	-955.214722	-955.262616	-955.197645	136.744
5	Hexanol–diphenyl phosphate	-1417.801803	-1417.865799	-1417.775091	190.912
6	Hexanol–diphenyl phosphate radical	-1417.159623	-1417.225504	-1417.132786	195.141
7	Hexanol–trifluoroacetate	-838.512028	-838.563924	-838.493766	147.660
8	Hexanol–trifluoroacetate radical	-837.869935	-837.919945	-837.852523	141.901
9	Tetrahydrofuran	-232.352810	-232.379496	-232.348279	65.702
10	Tetrahydrofuran radical	-231.713892	-231.742085	-231.708105	71.517
11	Tetrahydrofuran–dihydrogen phosphate	-876.073258	-876.115974	-876.060250	117.283
12	Tetrahydrofuran–dihydrogen phosphate radical	-875.427628	-875.468069	-875.415398	110.856
13	Methanol	-115.689753	-115.712526	-115.685469	56.947
14	Methanol radical	-115.040577	-115.063574	-115.036284	57.438

**Figure S8.** Isodesmic reactions used for our thermochemical analyses of bond weakening.**A. Isodesmic reactions for C–H BDE determination****B. DFT estimates of C–H bond weakening**

**Table S2.** Analysis of the isodesmic reactions above. Energies are provided in kcal mol<sup>-1</sup> using the conversion factor 627.509 kcal mol<sup>-1</sup> per hartree and are rounded off after the third decimal place. Entropies are provided in e.u. and are rounded off after the third decimal place.

Rxn	Entries for $\Delta$	$\Delta E+ZPE$	$\Delta G$	$\Delta H$	$\Delta S$
A. Hexanol	=(2+13)-(1+14)	-1.948	-2.389	-1.898	1.646
B. Hexanol-dihydrogen phosphate	=(4+13)-(3+14)	-4.481	-2.010	-5.014	-10.074
B. Hexanol-diphenyl phosphate	=(6+13)-(5+14)	-4.390	-5.432	-4.317	3.738
B. Hexanol-trifluoroacetate	=(8+13)-(7+14)	-4.445	-3.121	-4.984	-6.250
A. Tetrahydrofuran	=(10+13)-(9+14)	-6.437	-7.242	-5.654	5.324
B. Tetrahydrofuran-dihydrogen phosphate	=(12+13)-(11+14)	-2.225	-0.657	-2.719	-6.918

Computed values for the bond weakening or strengthening of hexanol and tetrahydrofuran can be determined by taking the  $\Delta\Delta$  of the Reactions A and B above; the results are shown below:

Quantity	$\Delta\Delta E+ZPE$	$\Delta\Delta G$	$\Delta\Delta H$	$\Delta\Delta S$
<b>Hexanol</b>				
Dihydrogen phosphate Bond Weakening	-2.533	0.379	<b>-3.116</b>	-11.720
Diphenyl phosphate Bond Weakening	-2.442	-3.043	<b>-2.419</b>	2.092
Trifluoroacetate Bond Weakening	-2.497	-0.732	<b>-3.086</b>	-7.896
<b>Tetrahydrofuran</b>				
Dihydrogen phosphate Bond Strengthening	4.212	6.585	<b>2.935</b>	-12.242

Taking the known literature value of 96 kcal mol<sup>-1</sup> as the BDE of the  $\alpha$ -C-H bond in methanol (83), the corresponding  $\alpha$ -C-H bond BDE in hexanol is calculated to be ~94.1 kcal mol<sup>-1</sup>. The tabulated  $\Delta H$  values at 6-31G(d,p) predicts hexanol  $\alpha$ -C-H BDE bond-weakening of 3.1, 2.4, and 3.1 kcal mol<sup>-1</sup> when OH-hydrogen bound to dihydrogen phosphate, diphenyl phosphate, and trifluoroacetate, respectively. This decrease in BDE corresponds to an  $\alpha$ -C-H BDE of 91.0, 91.7, and 91.0 kcal mol<sup>-1</sup>, respectively.

The  $\alpha$ -oxy C-H bond of tetrahydrofuran is calculated to have a BDE of ~90.3 kcal mol<sup>-1</sup>. Conversely, when hydrogen-bound to dihydrogen phosphate, the tabulated  $\Delta H$  values at 6-31G(d,p) predict a tetrahydrofuran  $\alpha$ -C-H BDE bond-strengthening of 2.9 kcal mol<sup>-1</sup>. This increase in BDE corresponds to an  $\alpha$ -C-H BDE of 93.2 kcal mol<sup>-1</sup>.

**Table S3:** Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points. All energies and frequencies calculated at UB3LYP/6-31G(d,p); all geometries optimized at UB3LYP/6-31G(d,p).

**Hexanol (entry 1)**

E (UB3LYP)	-312.333243
Zero-point correction=	0.193474
Thermal correction to Energy=	0.203018
Thermal correction to Enthalpy=	0.203962
Thermal correction to Gibbs Free Energy=	0.158874
Sum of electronic and zero-point Energies=	-312.139768
Sum of electronic and thermal Energies=	-312.130224
Sum of electronic and thermal Enthalpies=	-312.129280
Sum of electronic and thermal Free Energies=	-312.174368

Charge = 0; Multiplicity = 1

C	-2.58511700	0.46825200	0.00445100
H	-2.60950800	1.09009700	0.91085600
O	-3.78265400	-0.32152700	-0.08128900
H	-3.82036700	-0.90208600	0.69161700
C	-1.31044500	-0.37288300	-0.02686900
H	-1.31584500	-1.06410900	0.82838300
H	-1.31663600	-0.99031900	-0.93489800
C	-0.03589900	0.48216700	0.01473000
H	-0.03768700	1.17767500	-0.83672100
H	-0.04322600	1.10423800	0.92117700
C	1.25408600	-0.34846800	-0.01597800
H	1.26288800	-0.97073700	-0.92264700
H	1.25677600	-1.04513500	0.83491900
C	2.53108900	0.50139800	0.02472900
H	2.52764200	1.19859900	-0.82461000
H	2.52219700	1.12242000	0.93127600
C	3.81561900	-0.33509700	-0.00779700
H	3.86993200	-0.94007400	-0.92092000
H	4.70758600	0.30031000	0.02465600
H	3.86255100	-1.02011000	0.84735300
H	-2.62107400	1.13923600	-0.85972500



**Hexanol radical (entry 2)**

E(UB3LYP)	-311.673144
Zero-point correction=	0.179447
Thermal correction to Energy=	0.189079
Thermal correction to Enthalpy=	0.190024
Thermal correction to Gibbs Free Energy=	0.143920
Sum of electronic and zero-point Energies=	-311.493696
Sum of electronic and thermal Energies=	-311.484064
Sum of electronic and thermal Enthalpies=	-311.483120
Sum of electronic and thermal Free Energies=	-311.529223

Charge = 0; Multiplicity = 2

C	-2.60619800	0.41371400	0.01798500
H	-2.69096500	1.34772800	0.57289100
O	-3.76588000	-0.33036400	-0.09543800
H	-4.53603100	0.24763100	-0.00405900
C	-1.35186000	-0.39062500	0.06198800
H	-1.30669500	-0.97870400	0.99850000
H	-1.37046600	-1.13049200	-0.75134600
C	-0.08489400	0.47246800	-0.04706400
H	-0.10532000	1.02501700	-0.99610400
H	-0.09214000	1.22775400	0.75150000
C	1.21120100	-0.34304700	0.04131900
H	1.21697600	-1.10209900	-0.75451000
H	1.22947100	-0.89496700	0.99236900
C	2.48045200	0.51204900	-0.06948400
H	2.46137600	1.06442400	-1.01923800
H	2.47551900	1.26988900	0.72618400
C	3.77262700	-0.30869500	0.01680600
H	3.82127200	-1.05446600	-0.78580800
H	4.65860700	0.33025900	-0.06780600
H	3.83747600	-0.84424800	0.97164000

**Hexanol-dihydrogen phosphate (entry 3)**

E(UB3LYP)	-956.087841
Zero-point correction=	0.231084
Thermal correction to Energy=	0.248057
Thermal correction to Enthalpy=	0.249001
Thermal correction to Gibbs Free Energy=	0.179476
Sum of electronic and zero-point Energies=	-955.856757
Sum of electronic and thermal Energies=	-955.839784
Sum of electronic and thermal Enthalpies=	-955.838840
Sum of electronic and thermal Free Energies=	-955.908365

Charge = -1; Multiplicity = 1

C	0.66095700	1.79763200	0.37859900
H	1.13511200	2.72408900	0.72552400
H	0.33042200	1.24709200	1.27300700
O	-0.46504300	2.18665500	-0.40686200
H	-1.07071900	1.41361700	-0.50185900
C	1.67855600	0.95887900	-0.39937800
H	1.18790400	0.04415400	-0.75973700
H	1.98915500	1.52323900	-1.28933400
C	2.91095200	0.58839900	0.43696000
H	3.38620500	1.50744100	0.81002200
H	2.59272600	0.02470100	1.32591400
C	3.94970300	-0.23561700	-0.33605100
H	4.26934300	0.32737600	-1.22510100
H	3.47748800	-1.15615400	-0.70929300
C	5.18476300	-0.60527800	0.49616100
H	5.65543200	0.31428300	0.87100600
H	4.86642700	-1.17025200	1.38329700
C	6.21868500	-1.42434600	-0.28572900
H	6.58015800	-0.87117000	-1.16100400
H	7.08734500	-1.67065200	0.33501300
H	5.78696800	-2.36667800	-0.64420500
P	-3.37144600	-0.38819600	0.07668900
O	-2.15641500	0.07215600	-0.71527900
O	-3.98923700	0.44169000	1.16873300
O	-4.57954200	-0.73515600	-0.99746200
O	-3.02410300	-1.86200700	0.74148400
H	-2.38876800	-2.35212500	0.19884200
H	-4.22047100	-1.02073600	-1.85070800

**Hexanol–dihydrogen phosphate radical (entry 4)**

E(UB3LYP)	-955.431557
Zero-point correction=	0.216835
Thermal correction to Energy=	0.232968
Thermal correction to Enthalpy=	0.233912
Thermal correction to Gibbs Free Energy=	0.168941
Sum of electronic and zero-point Energies=	-955.214722
Sum of electronic and thermal Energies=	-955.198589
Sum of electronic and thermal Enthalpies=	-955.197645
Sum of electronic and thermal Free Energies=	-955.262616

Charge = -1; Multiplicity = 2

C	0.68321900	0.44986500	-0.16005000
H	0.43403000	-0.31888200	-0.89441800
O	-0.28379000	1.38855700	0.08070100
H	-1.18115700	1.03043400	-0.17146600
C	2.09416300	0.92094400	-0.02116900
H	2.33837800	1.64983000	-0.81896300
H	2.19573600	1.47586800	0.92324000
C	3.12105700	-0.22117300	-0.06367500
H	2.91619600	-0.92126000	0.75790800
H	2.98975900	-0.79121800	-0.99468200
C	4.57315300	0.26414000	0.02981500
H	4.70427200	0.83877000	0.95849700
H	4.77657700	0.96329400	-0.79450600
C	5.60413900	-0.87179900	-0.00818300
H	5.40066000	-1.57137000	0.81447100
H	5.47517800	-1.44492900	-0.93686300
C	7.05239600	-0.37791600	0.08940200
H	7.21974200	0.17180600	1.02356600
H	7.76285600	-1.21154200	0.06124100
H	7.29625200	0.29667900	-0.74025100
P	-3.76848100	-0.17406200	0.12235600
O	-2.64734500	0.49291600	-0.66651700
O	-3.90713300	-0.02053600	1.61116000
O	-5.20044100	0.30050400	-0.54840800
O	-3.72183100	-1.79588000	-0.18418100
H	-3.38872900	-1.98139300	-1.07476600
H	-5.09698100	0.51599800	-1.48722600

**Hexanol-diphenyl phosphate (entry 5)**

E (UB3LYP)	-1418.194737
Zero-point correction=	0.392933
Thermal correction to Energy=	0.418702
Thermal correction to Enthalpy=	0.419646
Thermal correction to Gibbs Free Energy=	0.328937
Sum of electronic and zero-point Energies=	-1417.801803
Sum of electronic and thermal Energies=	-1417.776035
Sum of electronic and thermal Enthalpies=	-1417.775091
Sum of electronic and thermal Free Energies=	-1417.865799

Charge = -1; Multiplicity = 1

C	-3.00010200	-1.65209000	1.74769700
H	-3.60910200	-2.00746300	2.58785800
H	-2.70757600	-0.61509200	1.97395400
O	-1.84641800	-2.49195600	1.70073800
H	-1.16077700	-2.05788900	1.14238900
C	-3.82601700	-1.68855800	0.45935300
H	-3.19589100	-1.35967800	-0.37850500
H	-4.10836300	-2.73010300	0.25339200
C	-5.08457300	-0.81316200	0.53223000
H	-5.70219100	-1.13425700	1.38376300
H	-4.79370900	0.22695900	0.73892800
C	-5.93204200	-0.85402500	-0.74660100
H	-6.22679500	-1.89334000	-0.95270800
H	-5.31585300	-0.53507300	-1.59995900
C	-7.18996300	0.02214600	-0.67871500
H	-7.80576500	-0.29631800	0.17399800
H	-6.89544300	1.06067200	-0.47298500
C	-8.03101600	-0.02478500	-1.95985900
H	-8.36593300	-1.04669700	-2.17508600
H	-8.92199000	0.60753400	-1.87709400
H	-7.45371400	0.32391900	-2.82465900
P	1.09222100	-0.25465300	0.47531300
O	0.08875400	-1.33277500	0.13759200
O	1.65287500	-0.10961200	1.86232100
O	2.32955400	-0.29277900	-0.64451500
O	0.39966800	1.14663900	-0.06416200
C	0.88208300	2.43550100	0.06442900
C	-0.00762500	3.45156900	-0.30676700
C	2.16984600	2.75310400	0.51126800
C	0.39226500	4.78688500	-0.23335500
H	-1.00109400	3.18156100	-0.65075100
C	2.55611600	4.09628400	0.58175400
H	2.85634700	1.96987700	0.80607600
C	1.67714800	5.11807500	0.21208400
H	-0.30398300	5.56824300	-0.52420900
H	3.55640600	4.33839000	0.92960700
H	1.98752900	6.15680300	0.26991000
C	3.36223400	-1.20638900	-0.65768300
C	4.47967400	-0.86249200	-1.42936400
C	3.32370300	-2.43156300	0.01974900
C	5.55843700	-1.74384200	-1.52097500
H	4.48818500	0.09068400	-1.94857100
C	4.41423000	-3.30265600	-0.07631500
H	2.45647400	-2.70638100	0.60919700
C	5.53386700	-2.96845500	-0.84341800

H	6.42064700	-1.46939900	-2.12198000
H	4.37975300	-4.25075700	0.45279700
H	6.37446500	-3.65182300	-0.91391400

**Hexanol-diphenyl phosphate radical (entry 6)**

E (UB3LYP)	-1417.538299
Zero-point correction=	0.378676
Thermal correction to Energy=	0.404569
Thermal correction to Enthalpy=	0.405513
Thermal correction to Gibbs Free Energy=	0.312795
Sum of electronic and zero-point Energies=	-1417.159623
Sum of electronic and thermal Energies=	-1417.133730
Sum of electronic and thermal Enthalpies=	-1417.132786
Sum of electronic and thermal Free Energies=	-1417.225504

Charge = -1; Multiplicity = 2

C	3.26312500	-0.85400300	-0.01598800
H	2.98462600	-0.19872900	0.81170800
O	2.31361500	-1.75800700	-0.41269000
H	1.41085800	-1.45626300	-0.11922200
C	4.68191400	-1.29363400	-0.17573600
H	4.90643000	-2.12547700	0.52069600
H	4.81726900	-1.71191100	-1.18418600
C	5.69699000	-0.16448100	0.05837800
H	5.51805900	0.63881000	-0.66941500
H	5.52596800	0.27544100	1.05145800
C	7.15549200	-0.62892300	-0.04187100
H	7.32712800	-1.07464200	-1.03272200
H	7.33185800	-1.43106400	0.68963500
C	8.17527400	0.49415500	0.18825700
H	8.00223700	1.29493900	-0.54415500
H	8.00239300	0.94108700	1.17725000
C	9.63039500	0.02086500	0.09089000
H	9.84398000	-0.39933000	-0.89935800
H	10.33150000	0.84546100	0.26116600
H	9.84334700	-0.75697600	0.83413100
P	-1.17639600	-0.20937200	-0.17801900
O	-0.07388000	-1.02260700	0.46618700
O	-1.39718000	-0.23943700	-1.66401500
O	-2.60581500	-0.50201400	0.62497200
O	-0.94763800	1.32205700	0.39709600
C	-1.70673200	2.44807200	0.13274500
C	-1.35982400	3.59180900	0.86251500
C	-2.75367100	2.49086300	-0.79492400
C	-2.06421200	4.78079300	0.66569100
H	-0.54349100	3.53441500	1.57560900
C	-3.45229500	3.68929900	-0.97955700
H	-3.00774900	1.60888600	-1.36948300
C	-3.11649000	4.83669500	-0.25562700
H	-1.78926200	5.66348500	1.23588000
H	-4.26483300	3.71905200	-1.70006700
H	-3.66460300	5.76145500	-0.40741100
C	-3.42274500	-1.59155900	0.39272500
C	-4.79264300	-1.40363200	0.60928700
C	-2.93167700	-2.84482500	0.00806300
C	-5.67385900	-2.47335900	0.43690000
H	-5.15019800	-0.42407100	0.91036600
C	-3.82611900	-3.90548500	-0.16924500
H	-1.86781000	-2.99086300	-0.14307600
C	-5.19670600	-3.72884300	0.04350100

H	-6.73592000	-2.32163000	0.60676000
H	-3.44224800	-4.87601900	-0.47038600
H	-5.88370900	-4.55825000	-0.09332200

**Hexanol-trifluoroacetate (entry 7)**

E (UB3LYP)	-838.732165
Zero-point correction=	0.220137
Thermal correction to Energy=	0.237455
Thermal correction to Enthalpy=	0.238399
Thermal correction to Gibbs Free Energy=	0.168241
Sum of electronic and zero-point Energies=	-838.512028
Sum of electronic and thermal Energies=	-838.494710
Sum of electronic and thermal Enthalpies=	-838.493766
Sum of electronic and thermal Free Energies=	-838.563924

Charge = -1; Multiplicity = 1

C	1.23743100	2.23653900	0.41416200
H	1.89411000	3.11481200	0.43493500
H	1.01978400	1.96867000	1.45981100
O	0.04123100	2.64197200	-0.25167600
H	-0.65862900	1.96670000	-0.08700600
C	1.95133500	1.07402300	-0.28010400
H	1.27504900	0.20867400	-0.31469700
H	2.15414900	1.35915000	-1.32152800
C	3.26111900	0.67666300	0.41484600
H	3.93019900	1.54864000	0.45456600
H	3.05150600	0.40253700	1.45899700
C	3.98976700	-0.48548700	-0.27297000
H	4.19951400	-0.21389600	-1.31787200
H	3.32299600	-1.35927800	-0.31110200
C	5.30160900	-0.88334200	0.41693100
H	5.96903300	-0.01099200	0.45242600
H	5.09268200	-1.15190200	1.46188500
C	6.02124300	-2.04772300	-0.27372800
H	6.27233300	-1.79721700	-1.31149700
H	6.95323600	-2.30445800	0.24206000
H	5.39208600	-2.94582600	-0.29234600
O	-1.94082300	0.83329600	0.38040900
O	-2.50626600	0.14976400	-1.71408600
C	-3.64748900	-0.78646700	0.17716900
C	-2.58200200	0.16665300	-0.47284700
F	-4.57861900	-0.08301400	0.88053000
F	-4.32864300	-1.53795700	-0.71949500
F	-3.07265600	-1.65580700	1.05379200



**Hexanol-trifluoroacetate radical (entry 8)**

E (UB3LYP)	-838.075951
Zero-point correction=	0.206016
Thermal correction to Energy=	0.222483
Thermal correction to Enthalpy=	0.223428
Thermal correction to Gibbs Free Energy=	0.156006
Sum of electronic and zero-point Energies=	-837.869935
Sum of electronic and thermal Energies=	-837.853468
Sum of electronic and thermal Enthalpies=	-837.852523
Sum of electronic and thermal Free Energies=	-837.919945

Charge = -1; Multiplicity = 2

C	1.12654700	0.56641900	0.23502300
H	0.75681500	-0.45126500	0.09394800
O	0.20700800	1.56830000	0.07491300
H	-0.71622100	1.20798500	0.19471200
C	2.53210300	0.90664000	-0.14000400
H	2.61125400	1.06766900	-1.23322700
H	2.80387500	1.86915200	0.31833000
C	3.54468400	-0.17106800	0.27662600
H	3.50749600	-0.29826100	1.36727800
H	3.24402000	-1.13588600	-0.15662900
C	4.98343200	0.14601300	-0.15032600
H	5.28421400	1.11333200	0.27831800
H	5.01988000	0.27008100	-1.24253900
C	5.99726600	-0.92696200	0.26840800
H	5.96027100	-1.05190900	1.35959700
H	5.69762900	-1.89320400	-0.16083000
C	7.43380900	-0.60371500	-0.15897100
H	7.77473900	0.34034500	0.28300400
H	8.13086200	-1.38901200	0.15400400
H	7.50912100	-0.50585100	-1.24872900
O	-2.25491900	0.64959000	0.50528500
O	-2.67748000	-0.11870400	-1.59318900
C	-4.35002500	-0.36336300	0.10958200
C	-2.94215700	0.10383500	-0.40072800
F	-5.05412000	0.66549800	0.65482900
F	-5.12917700	-0.89488000	-0.86037800
F	-4.23167900	-1.31322300	1.07877300

**Tetrahydrofuran (entry 9)**

E(UB3LYP)	-232.469114
Zero-point correction=	0.116304
Thermal correction to Energy=	0.119890
Thermal correction to Enthalpy=	0.120834
Thermal correction to Gibbs Free Energy=	0.089617
Sum of electronic and zero-point Energies=	-232.352810
Sum of electronic and thermal Energies=	-232.349224
Sum of electronic and thermal Enthalpies=	-232.348279
Sum of electronic and thermal Free Energies=	-232.379496

Charge = 0; Multiplicity = 1

C	-1.19219200	0.45845900	0.00000000
O	0.00000000	1.26210700	-0.00000200
C	1.19219200	0.45846000	0.00000000
C	0.77463100	-1.02598200	0.00000100
C	-0.77463100	-1.02598300	0.00000000
H	-1.78158400	0.71892200	0.88754500
H	-1.78158600	0.71892100	-0.88754300
H	1.78158500	0.71892100	-0.88754400
H	1.78158500	0.71892300	0.88754300
H	1.16863800	-1.54056800	-0.88045100
H	1.16863700	-1.54056600	0.88045500
H	-1.16863700	-1.54056800	-0.88045300
H	-1.16863800	-1.54056800	0.88045300

**Tetrahydrofuran radical (entry 10)**

E(UB3LYP)	-231.816865
Zero-point correction=	0.102973
Thermal correction to Energy=	0.107816
Thermal correction to Enthalpy=	0.108760
Thermal correction to Gibbs Free Energy=	0.074780
Sum of electronic and zero-point Energies=	-231.713892
Sum of electronic and thermal Energies=	-231.709049
Sum of electronic and thermal Enthalpies=	-231.708105
Sum of electronic and thermal Free Energies=	-231.742085

Charge = 0; Multiplicity = 2

C	0.60097800	-1.09784000	0.04962400
O	-0.76630000	-0.99398500	-0.11679000
C	-1.14991800	0.37553700	0.17224200
C	0.07414800	1.20924400	-0.21244700
C	1.24671800	0.25904300	0.13561300
H	1.02966100	-1.98374400	-0.40653900
H	-2.04941000	0.59022000	-0.40751400
H	-1.37962900	0.45564300	1.24244000
H	0.06131100	1.42128100	-1.28650400
H	0.11406200	2.15930400	0.32622300
H	2.09523700	0.36690100	-0.55024100
H	1.62760600	0.46638100	1.14626300

**Tetrahydrofuran–dihydrogen phosphate (entry 11)**

E (UB3LYP)	-876.228231
Zero-point correction=	0.154973
Thermal correction to Energy=	0.167037
Thermal correction to Enthalpy=	0.167981
Thermal correction to Gibbs Free Energy=	0.112256
Sum of electronic and zero-point Energies=	-876.073258
Sum of electronic and thermal Energies=	-876.061194
Sum of electronic and thermal Enthalpies=	-876.060250
Sum of electronic and thermal Free Energies=	-876.115974

Charge = -1; Multiplicity = 1

C	-2.54631200	1.24920400	0.06601500
O	-1.49691400	0.42012800	-0.50558800
C	-1.91733000	-0.96991900	-0.52320400
C	-3.11407200	-1.04671000	0.42283200
C	-3.76319200	0.33386400	0.22798100
H	-2.19365400	1.63211100	1.03139800
H	-2.71912900	2.09253800	-0.60855300
H	-2.19594300	-1.23618800	-1.55061700
H	-1.06536800	-1.58184000	-0.21574400
H	-3.78364300	-1.87565500	0.17808800
H	-2.77613000	-1.17006200	1.45778100
H	-4.37392800	0.34289800	-0.68146100
H	-4.39581600	0.63541600	1.06708000
O	0.98330900	0.98873100	0.47802300
H	0.11045400	0.74222200	0.08157500
P	2.22285000	0.05598000	-0.05419500
O	3.48970200	0.67045000	0.50419600
O	1.94634500	-1.39876400	0.70969300
O	2.06623100	-0.24003600	-1.53066000
H	2.18646800	-1.34384300	1.64631700

**Tetrahydrofuran–dihydrogen phosphate radical (entry 12)**

E (UB3LYP)	-875.568646
Zero-point correction=	0.141018
Thermal correction to Energy=	0.152304
Thermal correction to Enthalpy=	0.153248
Thermal correction to Gibbs Free Energy=	0.100576
Sum of electronic and zero-point Energies=	-875.427628
Sum of electronic and thermal Energies=	-875.416342
Sum of electronic and thermal Enthalpies=	-875.415398
Sum of electronic and thermal Free Energies=	-875.468069

Charge = -1; Multiplicity = 2

C	-2.39773800	1.21083000	0.12213300
O	-1.55835200	0.20722700	0.58173000
C	-2.05539800	-1.06813400	0.08178100
C	-3.56427600	-0.85942500	-0.04678200
C	-3.66719600	0.63563100	-0.43847100
H	-2.29035700	2.14744800	0.65742300
H	-1.58117500	-1.26752400	-0.88616200
H	-1.75742600	-1.83315800	0.80002700
H	-4.00989500	-1.52888000	-0.78642300
H	-4.05132500	-1.03531300	0.91756400
H	-3.71467300	0.74792500	-1.53135600
H	-4.56274700	1.11786400	-0.03033600
O	1.18016300	0.72592200	0.96118400
H	0.23997900	0.52355500	0.76409300
P	2.21160400	0.09177600	-0.15221300
O	3.58355600	0.63232500	0.18880200
O	2.16847100	-1.53617400	0.19333800
O	1.62394900	0.21670400	-1.54091000
H	2.67892400	-1.72999300	0.99324100

**Methanol (entry 13)**

E(UB3LYP)	-115.740948
Zero-point correction=	0.051195
Thermal correction to Energy=	0.054535
Thermal correction to Enthalpy=	0.055479
Thermal correction to Gibbs Free Energy=	0.028421
Sum of electronic and zero-point Energies=	-115.689753
Sum of electronic and thermal Energies=	-115.686413
Sum of electronic and thermal Enthalpies=	-115.685469
Sum of electronic and thermal Free Energies=	-115.712526

Charge = 0; Multiplicity = 1

C	0.67261600	-0.02001600	0.00000200
H	1.09060400	0.98877300	-0.00115900
H	1.02497200	-0.54815300	0.89430800
H	1.02479100	-0.55011600	-0.89320500
O	-0.75320500	0.12340300	0.00000400
H	-1.15042300	-0.75763400	0.00000900

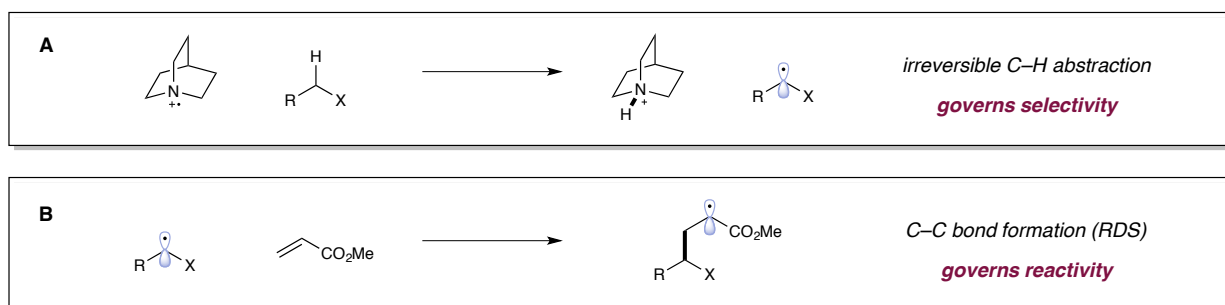
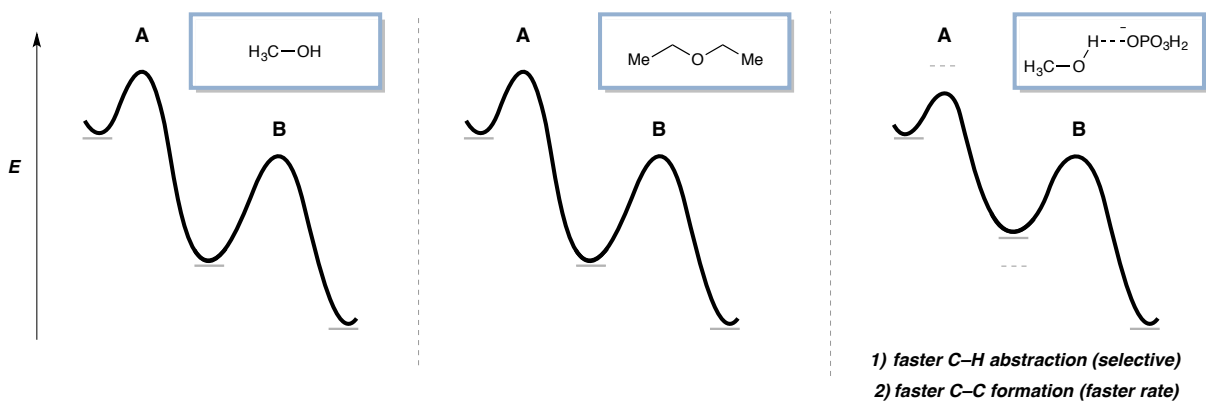
**Methanol radical (entry 14)**

E(UB3LYP)	-115.077784
Zero-point correction=	0.037207
Thermal correction to Energy=	0.040556
Thermal correction to Enthalpy=	0.041500
Thermal correction to Gibbs Free Energy=	0.014209
Sum of electronic and zero-point Energies=	-115.040577
Sum of electronic and thermal Energies=	-115.037228
Sum of electronic and thermal Enthalpies=	-115.036284
Sum of electronic and thermal Free Energies=	-115.063574

Charge = 0; Multiplicity = 2

C	0.68871700	0.02802900	-0.06361500
H	1.23909500	-0.88747800	0.11253400
H	1.11332800	1.00117500	0.16024700
O	-0.67209300	-0.12706800	0.01883900
H	-1.10797900	0.73467200	-0.04180700

## Energetic Profiles for Alcohol, Ether, and Hydrogen-Bonded Alcohol Substrates



**Figure S9.** Reaction coordinate diagram showing the proposed effect of TBAP on C-H abstraction and C-C bond formation.