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Supplementary Material for

O–H Hydrogen bonding promotes H-atom transfer from α C–H bonds for C-Alkylation of alcohols

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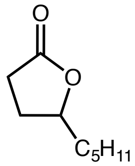
Materials and Methods

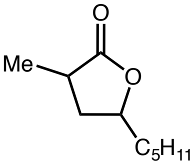
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego (*46*). Solvents were purified by passage through columns of activated alumina, or according to the method of Grubbs (*47*). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator 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}H and ^{13}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}H NMR are reported as follows: chemical shift (δ 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}C NMR are reported in terms of chemical shift relative to $CDCl_3$ (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 (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectrometry Facility.

Supplementary Text

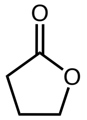
General α-Alkylation Procedure: An 8-mL glass vial equipped with a Teflon septum and magnetic stir bar was charged with Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.8 mg, 2.5 μmol, 1 mol%), quinuclidine (2.8 mg, 25 μmol, 10 mol%), and either tetra-*n*-butylammonium phosphate (21 mg, 63 μmol, 25 mol%) or tetra-*n*-butylammonium trifluoroacetate (63 μmol, 25 mol%), followed by CH$_3$CN (0.31 mL, 0.8 M), 1-hexanol (63 μL, 0.50 mmol, 2.0 equiv) and methyl acrylate (23 μL, 0.25 mmol, 1.0 equiv). The resulting solution was then sparged with N$_2$ for 3 minutes. The vial was sealed and placed approximately 3 inches away from a Kessil® 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® 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® 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.



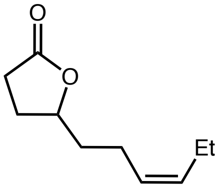
5-Pentyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 1-hexanol (251 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv), and CH$_3$CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH$_2$Cl$_2$/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(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (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%), 1-hexanol (251 μL, 2.00 mmol, 2.0 equiv), isobornyl methacrylate (226 μL, 1.00 mmol, 1.0 equiv), and CH$_3$CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH$_2$Cl$_2$/hexanes) as a colorless liquid (141 mg, 83% yield) consisting of two diastereomers (1.7:1 ratio, as determined by ^{1}H NMR). ^{1}H NMR (500 MHz, CDCl$_3$) δ 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for $C_{10}H_{19}O_2$ [(M+H)$^+$] 171.1380, found 171.1378.

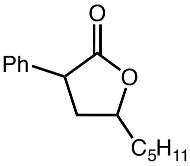


Dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv), methanol (202 μL, 5.00 mmol, 5.0 equiv) and CH_3CN (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 ^{1}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*).



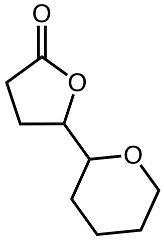
1:1 E/Z

(*Z*/*E*)-5-(Hex-3-en-1-yl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (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_3CN (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 ^{1}H NMR). Spectral data were consistent with previous reports (*53*, *54*).

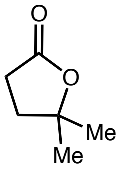


5-Pentyl-3-phenyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 1-hexanol (251 μL, 2.00 mmol, 2.0 equiv), methyl 2-phenylacrylate (162 mg, 1.00 mmol, 1.0 equiv), and CH_3CN

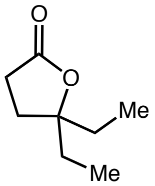
(1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH_2Cl_2/hexane) as a colorless oil (176 mg, 76% yield) consisting of two diastereomers (2.2:1 ratio, as determined by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$, single diastereomer) δ 7.40–7.32 (m, 2H), 7.32–7.26 (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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{21}O_2$ [$(M+H)^+$] 233.1536, found 233.1537.



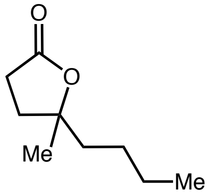
5-(Tetrahydro-2*H*-pyran-2-yl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7.80 mg, 7.00 μmol, 1 mol%), quinuclidine (7.80 mg, 70.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (59.4 mg, 175 μmol, 25 mol%), (tetrahydro-2H-pyran-2-yl)methanol (158 μL, 1.40 mmol, 2.0 equiv), methyl acrylate (63.4 μL, 0.70 mmol, 1.0 equiv) and CH_3CN (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 ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$, 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_9H_{15}O_3$ [$(M+H)^+$] 171.1021, found 171.1021.



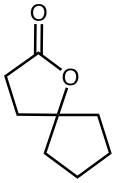
5,5-Dimethyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), isopropanol (153 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH_3CN (1.25 mL, 0.8 M) were used. Analysis of the crude reaction mixture using ^{1}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*).



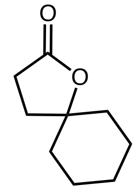
5,5-Diethyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 0.25 mol%), quinuclidine (2.80 mg, 25.0 µmol, 2.5 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 2-hexanol (252 µL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv) and CH$_3$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*).



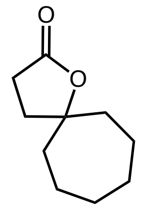
5-Butyl-5-methyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.1 mg, 100 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 2-hexanol (252 µL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv) and CH$_3$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*).



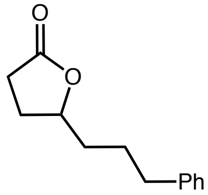
1-Oxaspiro[4.4]nonan-2-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.1 mg, 100 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), cyclopentanol (182 µL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv) and CH$_3$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*).



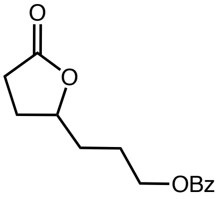
1-Oxaspiro[4.5]decan-2-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), cyclohexanol (211 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH$_3$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*).



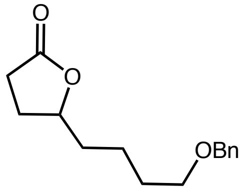
1-Oxaspiro[4.6]undecan-2-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), cycloheptanol (241 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH$_3$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*).



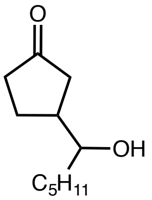
5-(3-Phenylpropyl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 4-phenylbutan-1-ol (305 μL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH$_3$CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH$_2$Cl$_2$/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$_3$)ppy]$_2$(dtbbpy)PF$_6$ (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$_3$CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (2:1 CH$_2$Cl$_2$/hexanes) as a colorless oil (201 mg, 81% yield). ^{1}H NMR (500 MHz, CDCl$_3$) 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; ^{13}C NMR (125 MHz, CDCl$_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for C$_{14}$H$_{17}$O$_4$ [(M+H)$^+$] 249.1121, found 249.1121.

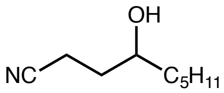


5-(4-(Benzyloxy)butyl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 μmol, 25 mol%), 5-(benzyloxy)pentan-1-ol (389 mg, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 μL, 1.00 mmol, 1.0 equiv) and CH$_3$CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (6:3:1 CH$_2$Cl$_2$/hexanes/EtOAc) as a colorless oil (186 mg, 75% yield). ^{1}H NMR (500 MHz, CDCl$_3$) 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; ^{13}C NMR (125 MHz, CDCl$_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{20}$NaO$_3$ [(M+Na)$^+$] 271.13047, found 271.13034.

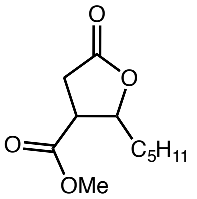


3-(1-Hydroxyhexyl)cyclopentan-1-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 μmol, 1 mol%), quinuclidine (11.1 mg, 100 μmol, 10 mol%), tetra-*n*-butylammonium trifluoroacetate (89.0 mg, 250 μmol, 25 mol%), cyclopent-2-

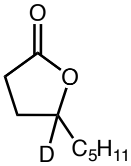
enone (84.0 µL, 1.00 mmol, 1.0 equiv), 1-hexanol (251 µL, 2.00 mmol, 2.0 equiv) and CH_3CN (1.25 mL, 0.8 M) were used (70 h reaction time). The product was isolated by flash column chromatography (2:1 hexanes/EtOAc) as a colorless oil (155 mg, 84% yield) consisting of two diastereomers and the corresponding ketals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 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 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{20}O_2$ $[(M)^+]$ 184.1463, found 184.1462. A portion of the product mixture (38 mg) was heated in acetic anhydride (20 equiv) at 80 °C for 12 h. Upon completion, the reaction mixture was cooled to 25 °C and the solvent was removed *in vacuo* to afford the acetate as a colorless oil consisting of two diastereomers (~1:1 ratio). ^{1}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 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 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{22}NaO_3$ $[(M+Na)^+]$ 249.1467, found 249.1467.



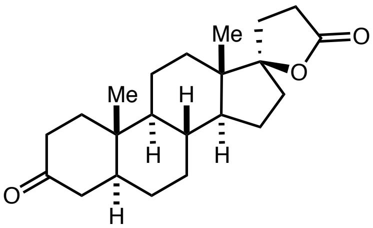
4-Hydroxynonanenitrile: According to the general procedure, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.1 mg, 100 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 1-hexanol (251 µL, 2.00 mmol, 2.0 equiv), acrylonitrile (66.0 µL, 1.00 mmol, 1.0 equiv) and CH_3CN (1.25 mL, 0.8 M) were used. The product was isolated by flash column chromatography (4:1→1:1 hexanes/EtOAc) as a colorless oil (117 mg, 75% yield). Spectral data were consistent with previous reports (*61*, *62*).



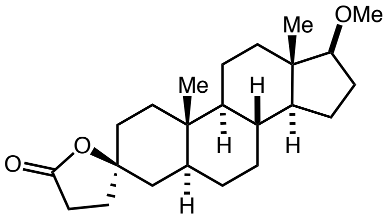
Methyl 5-oxo-2-pentyltetrahydrofuran-3-carboxylate: According to the general procedure, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.2 mg, 100 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 1-hexanol (314 µL, 2.5 mmol, 2.5 equiv), dimethyl fumarate (144 mg, 1.00 mmol, 1.0 equiv), and CH_3CN (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}H NMR). Spectral data were consistent with previous reports (*63*).



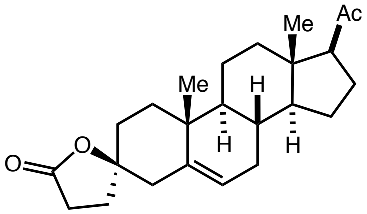
5-Pentyldihydrofuran-2(3*H*)-one-5-*d*: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), hexan-1,1-d_2-1-ol (52.0 mg, 0.50 mmol, 2.0 equiv), methyl acrylate (23.0 μL, 0.250 mmol, 1.0 equiv) and CH_3CN (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. ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_{16}DO_2$ [(M+H)$^+$] 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_3)ppy]$_2$(dtbbpy)PF_6 (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 ^{1}H NMR) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{32}O_3$ [(M+H)$^+$] 345.2424, found 345.2424.

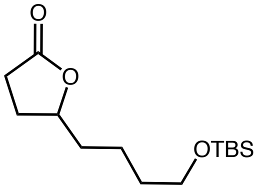


(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-17-Methoxy-10,13-dimethyloctadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-3,2'-furan]-5'-one: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), (5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*S*)-17-methoxy-10,13-dimethylhexadecahydro-1*H*-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_3CN (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 ^1H NMR). ^1H NMR (500 MHz, $CDCl_3$) 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{37}O_3$ [$(M+H)^+$] 361.2737, found 361.2737.

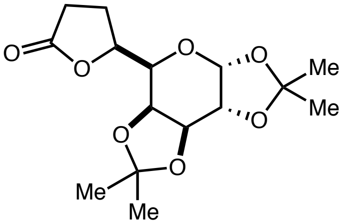


(8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-10,13-dimethyl-1,2,3',4,4',7,8,9,10,11,12,13,14,15,16,17-hexadecahydro-5'*H*-spiro[cyclopenta[*a*]phenanthrene-3,2'-furan]-5'-one:

According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (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_2Cl_2/hexanes), followed by recrystallization from ethanol, afforded the title compound (129 mg, 70% yield, >20:1 dr as determined by ^1H NMR) as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$) 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{35}O_3$ [(M+H)$^+$] 371.2586, found 371.2586.

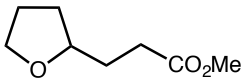


5-(4-((*tert*-Butyldimethylsilyl)oxy)butyl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 0.25 mol%), quinuclidine (2.80 mg, 25.0 µmol, 2.50 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 5-((*tert*-butyldimethylsilyl)oxy)pentan-1-ol (437 mg, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv) and CH_3CN (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}H NMR (500 MHz, CDCl$_3$) δ 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}C NMR (125 MHz, CDCl$_3$) δ 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 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{29}O_3Si$ [(M+H)$^+$] 273.1886, found 273.1885. Spectral data were consistent with previous reports (*64*, *65*).

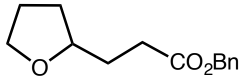


(*S*)-5-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)dihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.80 mg, 25.0 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0 µmol, 25 mol%), 1,2:3,4-Di-*O*-isopropylidine-α-D-galactopyranose (65.0 mg, 0.25 mmol, 1.0 equiv), methyl acrylate (227 µL, 2.50 mmol, 8.0 equiv) and CH_3CN (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 → 2:1 hexanes/EtOAc). Diastereomer 1: ^{1}H NMR (500 MHz, CDCl$_3$) δ 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}C NMR (125 MHz, CDCl$_3$) δ 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 cm^{-1}; Diastereomer 2: ^{1}H NMR (500 MHz, CDCl$_3$) δ 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

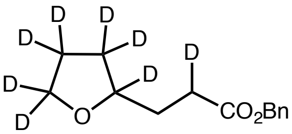
Hz, 1H), 3.79 (dd, *J* = 7.5, 1.9 Hz, 1H), 2.59–2.49 (m, 2H), 2.43–2.33 (m, 1H), 2.07 (dq, *J* = 12.9, 9.8 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.32 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 109.8, 108.8, 96.2, 79.5, 70.7, 70.3, 70.2, 69.9, 28.5, 26.1, 25.9, 24.9, 24.5, 24.1 ppm; IR (film) 2987, 2937, 1774, 1458, 1377, 1253, 1210, 1166, 1104, 1067, 1047, 1023 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{23}O_7$ [$(M+H)^+$] 315.1444, found 315.1445.



Methyl 3-(tetrahydrofuran-2-yl)propanoate: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.1 mg, 100 µmol, 10 mol%), tetrahydrofuran (164 µL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv) and CH_3CN (1.25 mL, 0.8 M) were used. Methyl benzoate (126 µL, 1.00 mmol, 1.0 equiv) was added as an internal standard and ^{1}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}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 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 cm^{-1}.

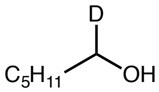


Benzyl 3-(tetrahydrofuran-2-yl)propanoate: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.80 mg, 25.0 µmol, 10 mol%), benzyl acrylate (37.5 µL, 0.25 mmol, 1.0 equiv), tetrahydrofuran (61.0 µL, 0.75 mmol, 3.0 equiv), and CH_3CN (0.63 mL, 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}H NMR (500 MHz, $CDCl_3$) δ 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}C NMR (125 MHz, $CDCl_3$) δ 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 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{18}NaO_3$ [$(M+Na)^+$] 257.1154, found 257.1155.

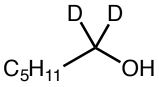


Benzyl 3-(tetrahydrofuran-2-yl-*d*$_7$)propanoate-2-*d*: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.80 mg, 25.0 µmol, 10 mol%), benzyl acrylate (37.5 µL, 0.25 mmol, 1.0 equiv), tetrahydrofuran-*d*$_8$ (61.0 µL, 0.75 mmol, 3.0 equiv), and CH_3CN (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 α to the carbonyl. ^{1}H NMR (500 MHz, $CDCl_3$)

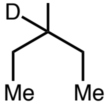
δ 7.40–7.28 (m, 5H), 5.12 (s, 2H), 2.56–2.39 (m, 1.55H, 23% D incorporation), 1.90–1.76 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 136.0, 128.5, 128.1, 128.1, 77.5 (m), 66.8 (m), 66.1, 31.1, 30.8 (m), 30.8 (m), 30.5, 30.4, 24.6 (m) ppm; IR (film) 2941, 1732, 1498, 1456, 1381, 1355, 1242, 1214, 1164, 1106, 1027 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}D_8NaO_3$ [(M+Na)$^+$] 265.1656, found 265.1656.



Hexan-1-*d*-1-ol: To a suspension of $LiAlD_4$ (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 CH_2Cl_2 (3 x 15 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/Et_2O) afforded the pure product as a colorless liquid (1.4 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 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 cm^{-1}. Spectral data were consistent with previous report (*66*).

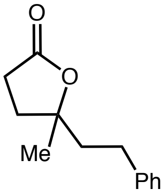


Hexan-1,1-*d*₂-1-ol: To a suspension of $LiAlD_4$ (504 mg, 12.0 mmol, 0.5 equiv) in dry THF (5 mL) at 0 °C was added a solution of methyl hexanoate (3.53 mL, 24.0 mmol, 1.0 equiv) in THF (5 mL) dropwise. The mixture was warmed to 23 °C and stirred an additional 3 h at 23 °C. Upon completion, the solution was cooled to 0 °C and quenched by addition of 1 M aqueous HCl. The mixture was extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/Et_2O) afforded the pure product as a colorless liquid (2.25 g, 90% yield). Spectral data were consistent with previous report (*67*).

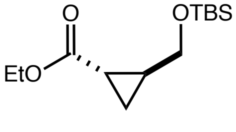


Pentan-3-*d*-3-ol: To a suspension of $LiAlD_4$ (323 mg, 7.69 mmol, 0.25 equiv) in dry THF (5 mL) at 0 °C was added a solution of 3-pentanone (3.25 mL, 30.8 mmol, 1.0 equiv) in THF (5 mL) dropwise. The mixture was warmed to 23 °C and stirred an additional 3 h at 23 °C. Upon completion, the solution was cooled to 0 °C and quenched by addition of 1 M aqueous HCl. The mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash column chromatography (1:1 pentane/Et_2O) afforded the pure product as a colorless liquid (2.2 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57–1.37 (m, 4H), 1.34 (brs, 1H), 0.94 (t, *J* = 7.5

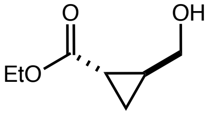
Hz, 6H) ppm; IR (film) 3351, 2963, 2930, 2877, 2149, 1460, 1378, 1328, 1266, 1173, 1147, 1040 cm^{-1}. Spectral data were consistent with previous report (*68*).



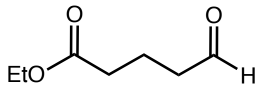
5-Methyl-5-phenethyldihydrofuran-2(3*H*)-one: According to the general procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (11.2 mg, 10.0 µmol, 1 mol%), quinuclidine (11.1 mg, 100 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (85.0 mg, 250 µmol, 25 mol%), 4-phenylbutan-2-ol (307 µL, 2.00 mmol, 2.0 equiv), methyl acrylate (90.0 µL, 1.00 mmol, 1.0 equiv), and CH$_3$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). ^{1}H NMR (500 MHz, CDCl$_3$) δ 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; ^{13}C NMR (125 MHz, CDCl$_3$) δ 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 cm^{-1}; HRMS (ESI) *m/z* calcd for C$_{13}$H$_{16}$NaO$_2$ [(M+Na)$^+$] 227.1048, found 227.1049.



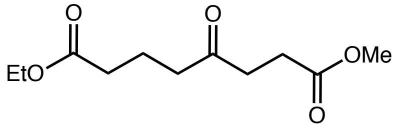
Ethyl (1*S*,2*S*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)cyclopropane-1-carboxylate: To a solution of ethyl 2-(diethoxyphosphoryl)acetate (4.21 mL, 21.2 mmol, 2.0 equiv) in DME (43 mL) at 25 °C was added *n*-BuLi (8.71 mL, 21.8 mmol, 2.05 equiv, 2.5 M solution in hexanes) dropwise over 10 minutes, 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$_4$), 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). ^{1}H NMR (300 MHz, CDCl$_3$) δ 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; ^{13}C NMR (125 MHz, CDCl$_3$) δ 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 cm^{-1}. HRMS (ESI) *m/z* calcd for C$_{13}$H$_{27}$O$_3$Si [(M+H)$^+$] 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_2O (20 mL) and water (50 mL), the organic layer was separated, dried ($MgSO_4$), 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). ^{1}H NMR (500 MHz, C_6D_6) 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; ^{13}C NMR (125 MHz, C_6D_6) 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^{-1}. HRMS (ESI) *m/z* calcd for $C_7H_{12}NaO_3$ $[(M+Na)^+]$ 167.0684, found 167.0684.

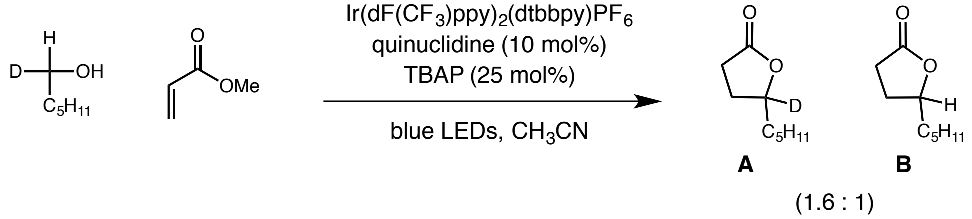


Ethyl 5-oxopentanoate: According to the general procedure, Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2.80 mg, 2.50 μmol, 1 mol%), quinuclidine (2.80 mg, 25.0 μmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.2 mg, 63.0 μmol, 25 mol%), ethyl (1*S*,2*S*)-2-(hydroxymethyl)cyclopropane-1-carboxylate (36.0 mg, 250 μmol, 1.0 equiv) and CH_3CN (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_3)ppy]$_2$(dtbbpy)PF_6 (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_3CN (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). ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{13}C NMR (125 MHz, $CDCl_3$) 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^{-1}. HRMS (ESI) *m/z* calcd for $C_{11}H_{18}NaO_5$ $[(M+Na)^+]$ 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 α-Alkylation Procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5.60 mg, 5.00 µmol, 1 mol%), quinuclidine (5.60 mg, 50.0 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (42.0 mg, 125 µmol, 25 mol%), hexan-1-*d*-1-ol (103 mg, 1.00 mmol, 2.0 equiv), methyl acrylate (45.0 µL, 0.50 mmol, 1.0 equiv) and CH$_3$CN (0.63 mL, 0.8 M) were used. The products were isolated by flash column chromatography (18:2:1 CH$_2$Cl$_2$/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).

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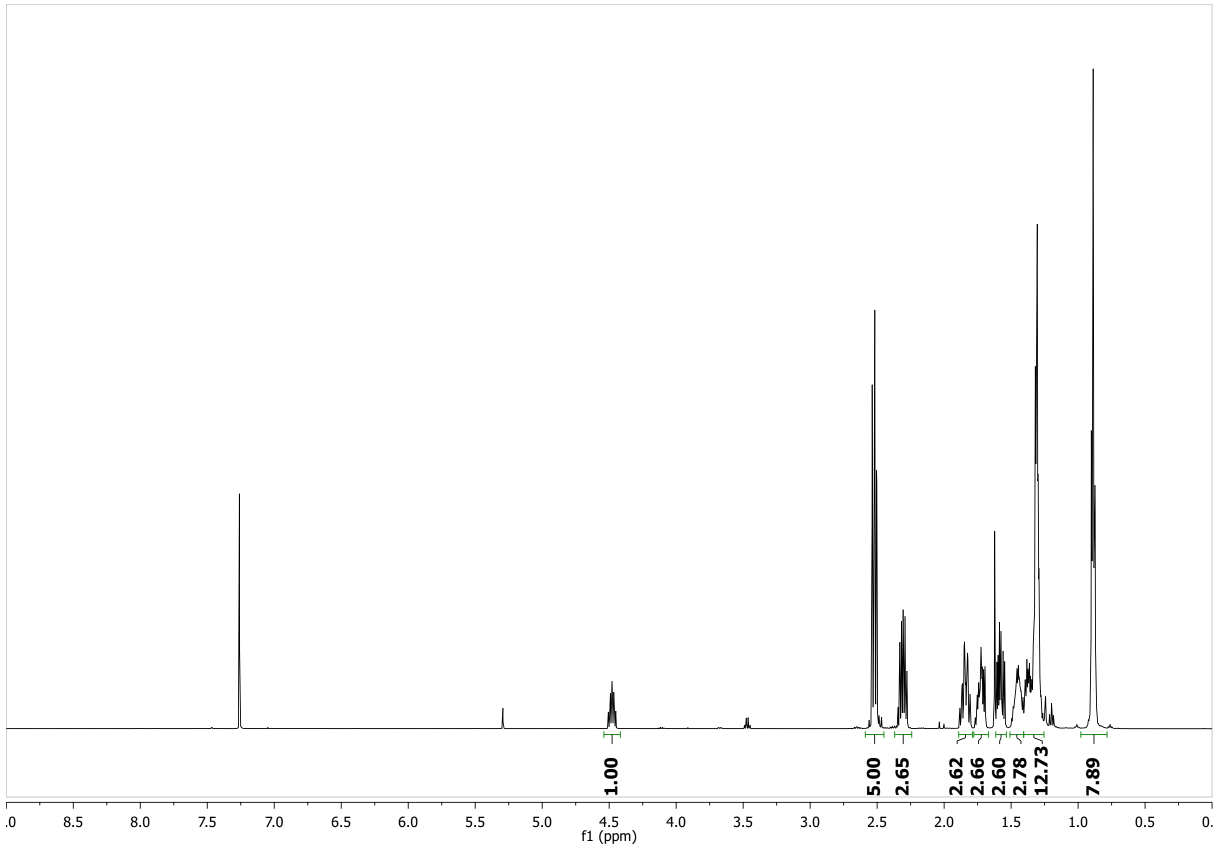
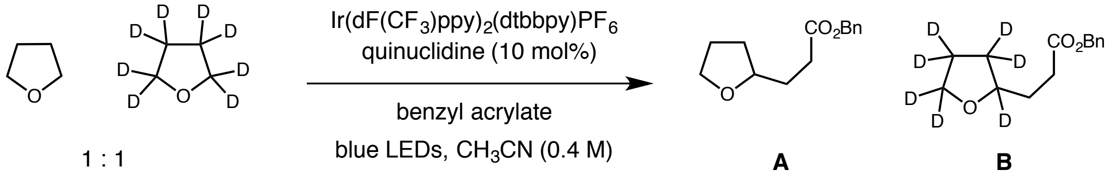
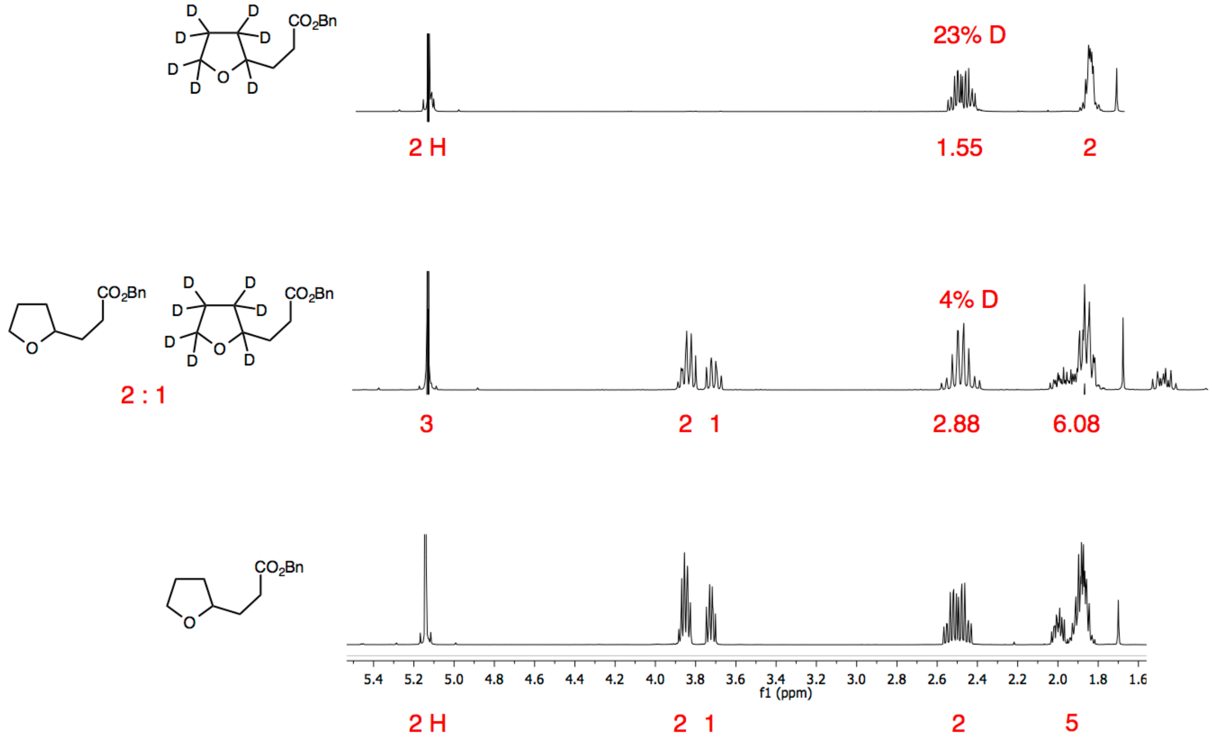




A **B**

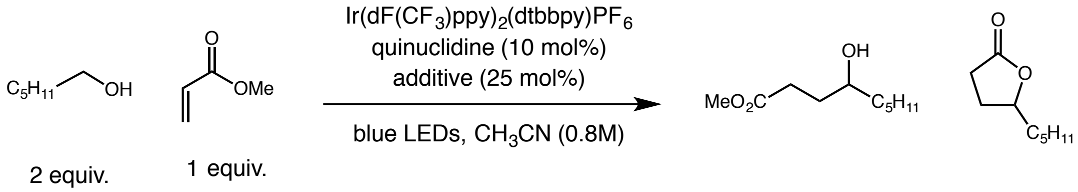
60% yield (2:1 A:B)

Procedure: According to the General α-Alkylation Procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.80 mg, 25.0 µmol, 10 mol%), tetrahydrofuran (61.0 µL, 0.75 mmol, 3.0 equiv), *d*$_8$-tetrahydrofuran (61.0 µL, 0.75 mmol, 3.0 equiv), benzyl acrylate (37.5 µL, 0.25 mmol, 1.0 equiv) and CH$_3$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$_3$)ppy]$_2$(dtbbpy)PF$_6$ (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$_3$CN (0.63 mL, 0.8 M). The resulting solution was then sparged with N$_2$ for 2 minutes. The vial was sealed and placed approximately 3 inches away from a Kessil® 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 ^{1}H NMR and/or GC. The reaction mixture was then degassed by N$_2$ bubbling for 2 minutes prior to resuming irradiation. Each data point represents an average value determined from at least three separate experiments.



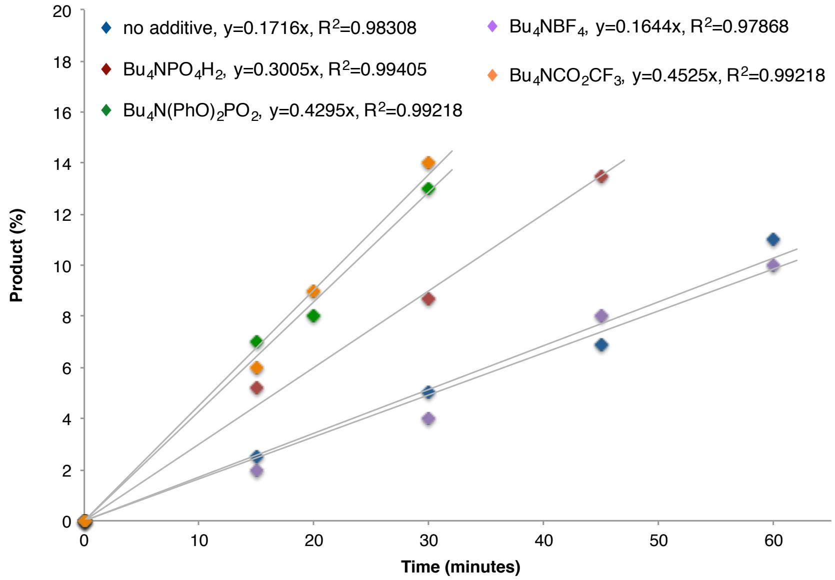
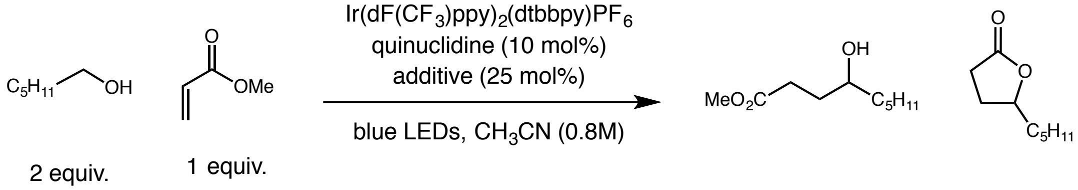


Figure S1. Initial rate of alkylation of 1-hexanol with methyl acrylate in the presence of additives.



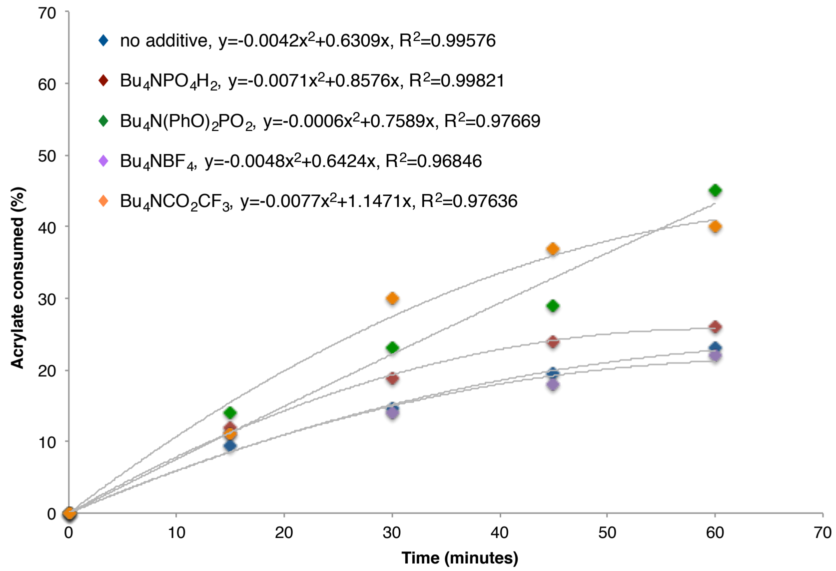


Figure S2. Initial rate of acrylate consumption in the reaction of 1-hexanol with methyl acrylate in the presence of additives.

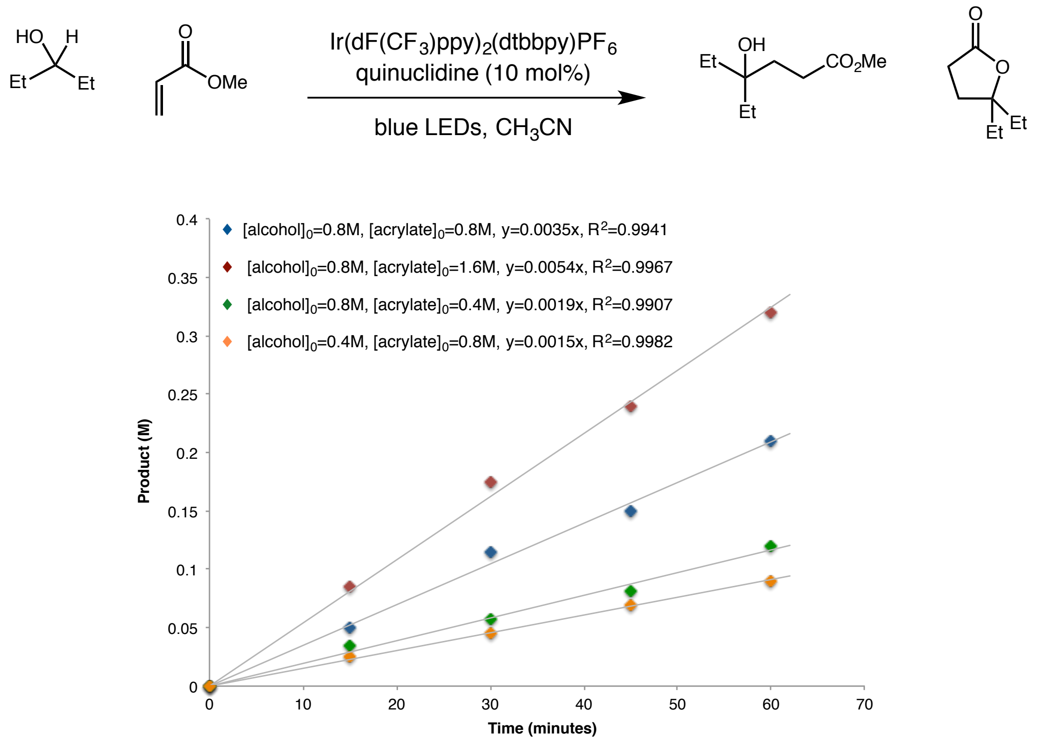


Figure S3. Initial rate of alkylation of 3-pentanol as a function of initial conditions. rate = k[alcohol][acrylate], k = 0.0051 ± 0.0007$M^{-1}s^{-1}$

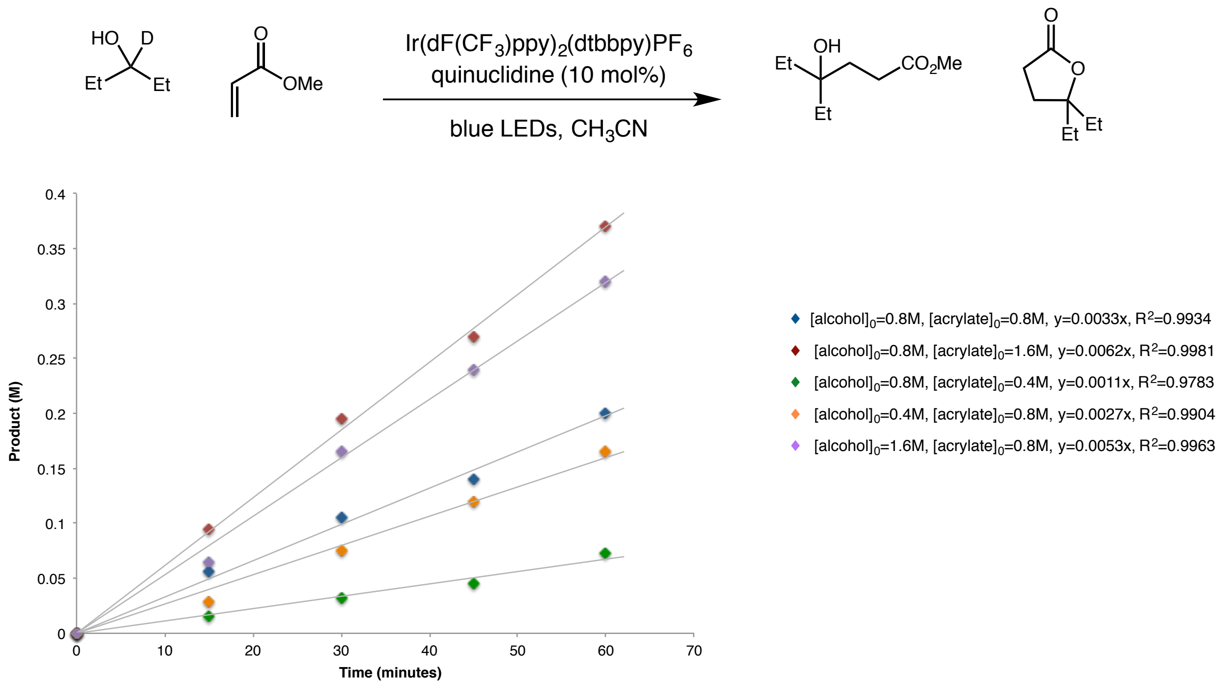


Figure S4. Initial rate of alkylation of D-3-pentanol as a function of initial conditions. rate = k[alcohol][acrylate], k = 0.0044 ± 0.0008$M^{-1}s^{-1}$; KIE = k_H/k_D = 1

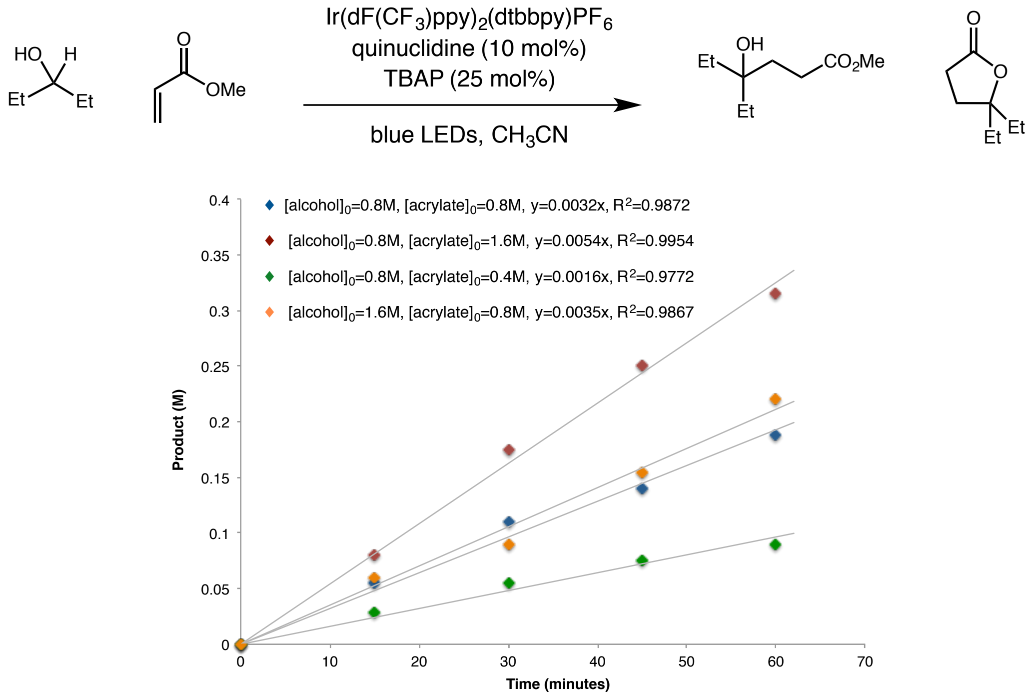


Figure S5. Initial rate of alkylation of 3-pentanol as a function of initial conditions with 25 mol% TBAP. rate = k[alcohol][acrylate], k = 0.004 ± 0.001 $M^{-1}s^{-1}$

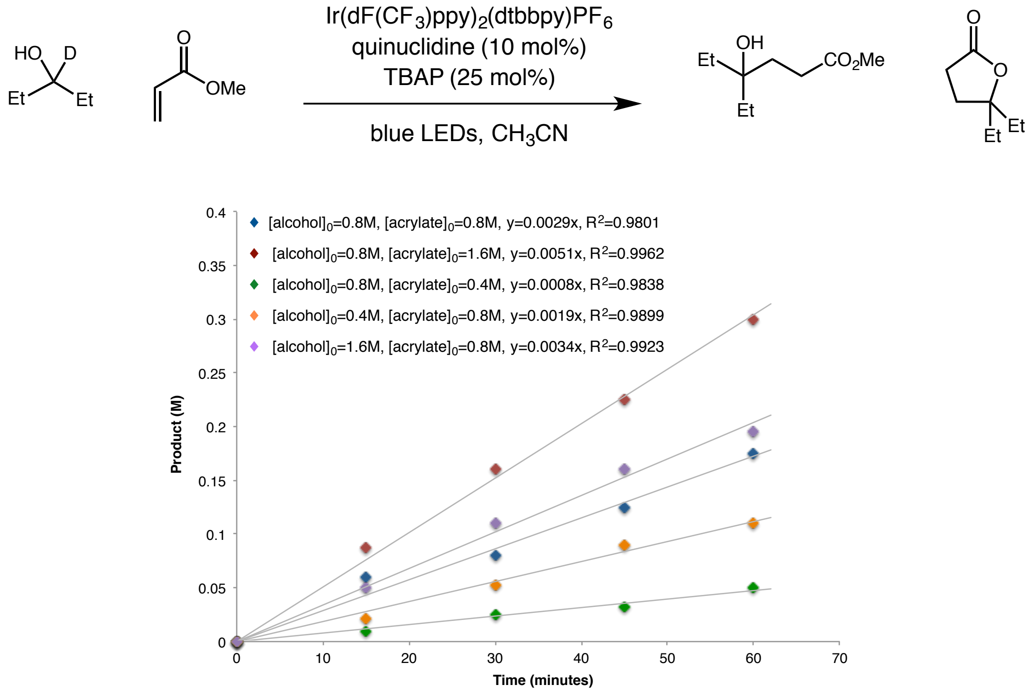


Figure S6. Initial rate of alkylation of D-3-pentanol as a function of initial conditions with 25 mol% TBAP. rate = k[alcohol][acrylate], k = 0.004 ± 0.001 $M^{-1}s^{-1}$, KIE = k_H/k_D = 1

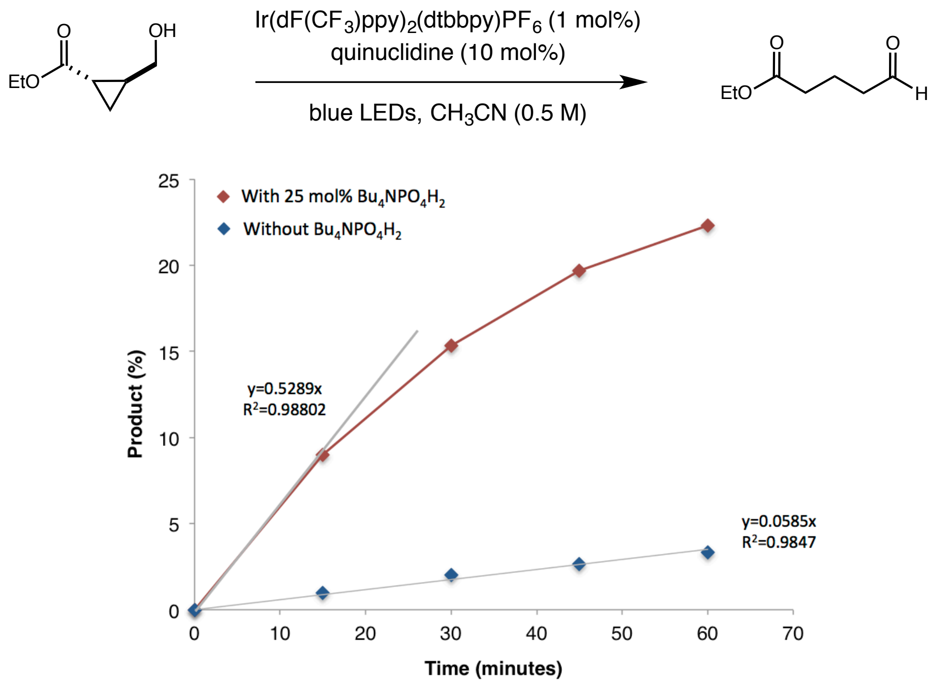
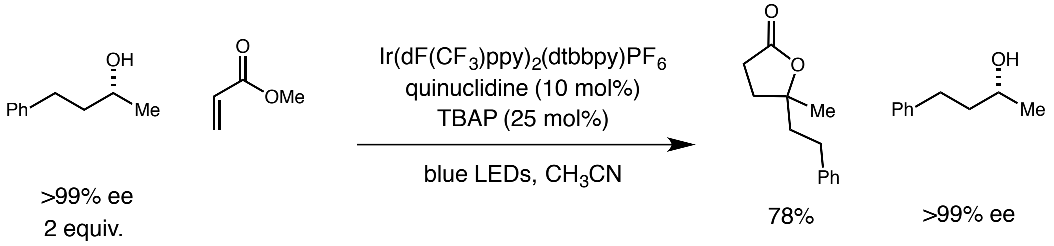


Figure S7. Initial rate of conversion of **36** to **37** in the presence and absence of $Bu_4NPO_4H_2$ (average of three experiments).

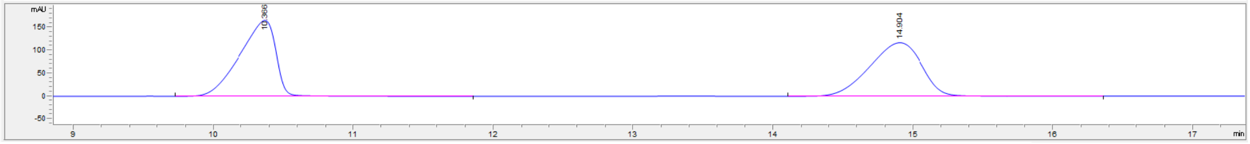
HPLC Data

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



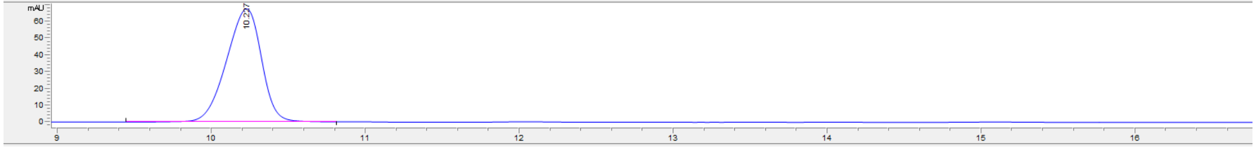
According to the general α-alkylation procedure, Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.80 mg, 25.0 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0 µmol, 25 mol%), (*R*)-4-phenylbutan-2-ol (77.0 µL, 0.50 mmol, 2.0 equiv), methyl acrylate (23.0 µL, 0.25 mmol, 1.0 equiv), and CH$_3$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).

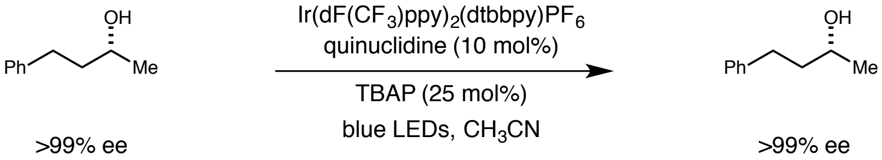
HPLC trace of racemic 4-phenyl-2-butanol:



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.366 BB    0.2727 2963.91431  165.67589  49.6740
   2  14.904 BB    0.4061 3002.81567  116.73311  50.3260

Totals :                  5966.72998  282.40900
```

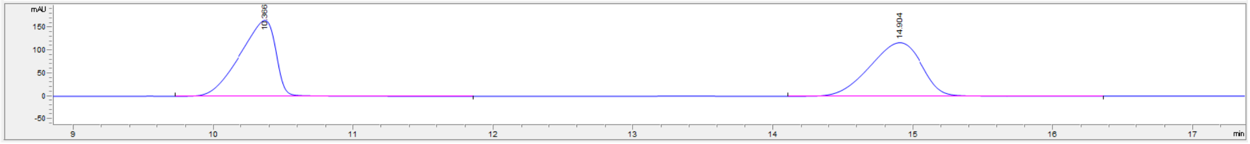
HPLC trace of unreacted 4-phenyl-2-butanol upon completion of the reaction:





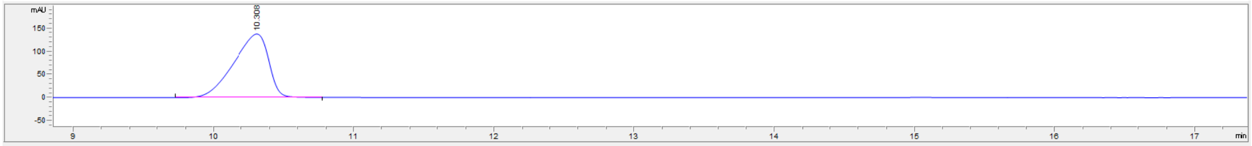
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.80 mg, 2.50 µmol, 1 mol%), quinuclidine (2.50 mg, 25.0 µmol, 10 mol%), tetra-*n*-butylammonium phosphate (21.0 mg, 63.0 µmol, 25 mol%), (*R*)-4-phenylbutan-2-ol (77.0 µL, 0.50 mmol, 2.0 equiv), and CH$_3$CN (0.31 mL, 0.8 M) were subjected to the standard conditions 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_R = 10.2 minutes).

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

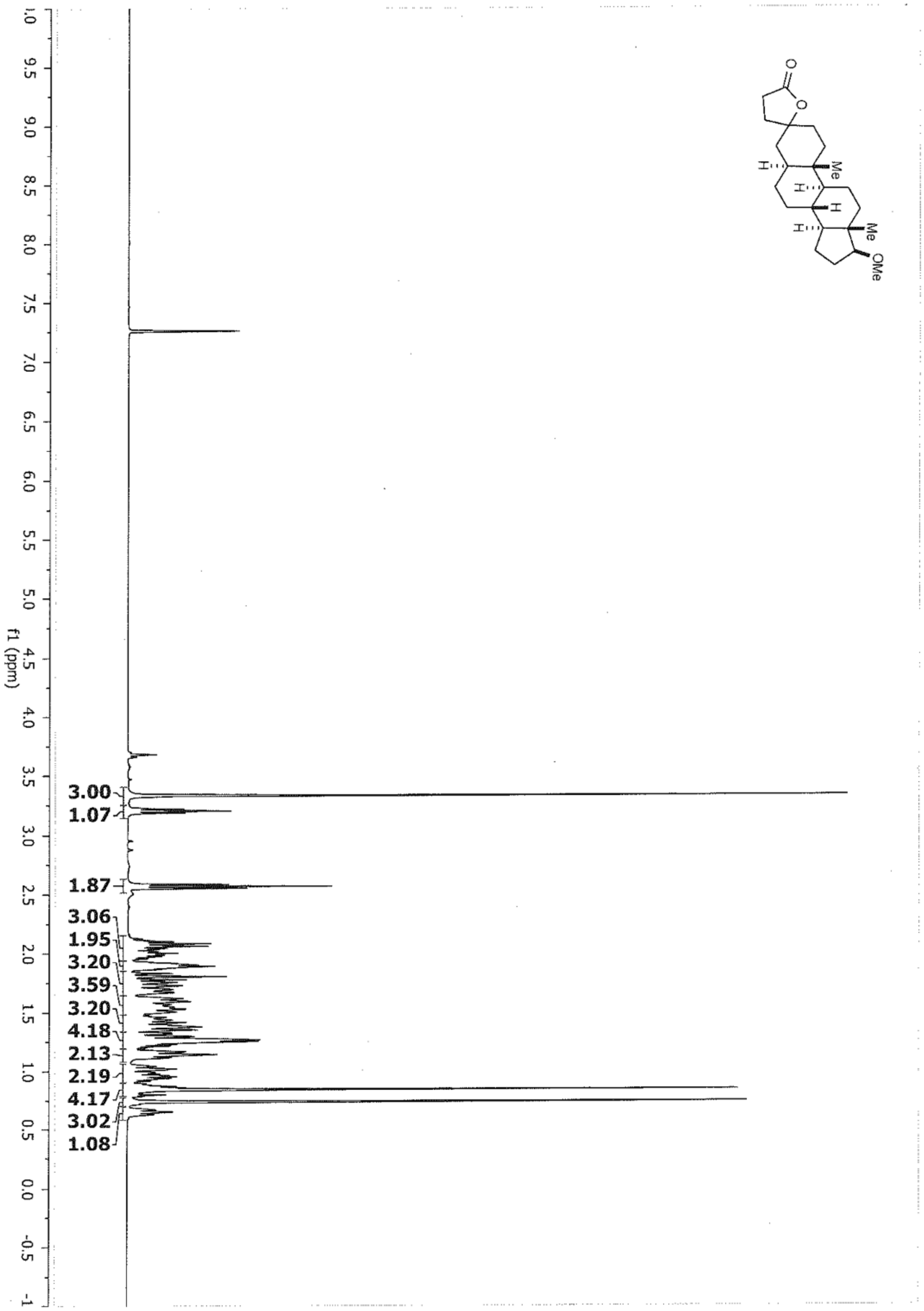


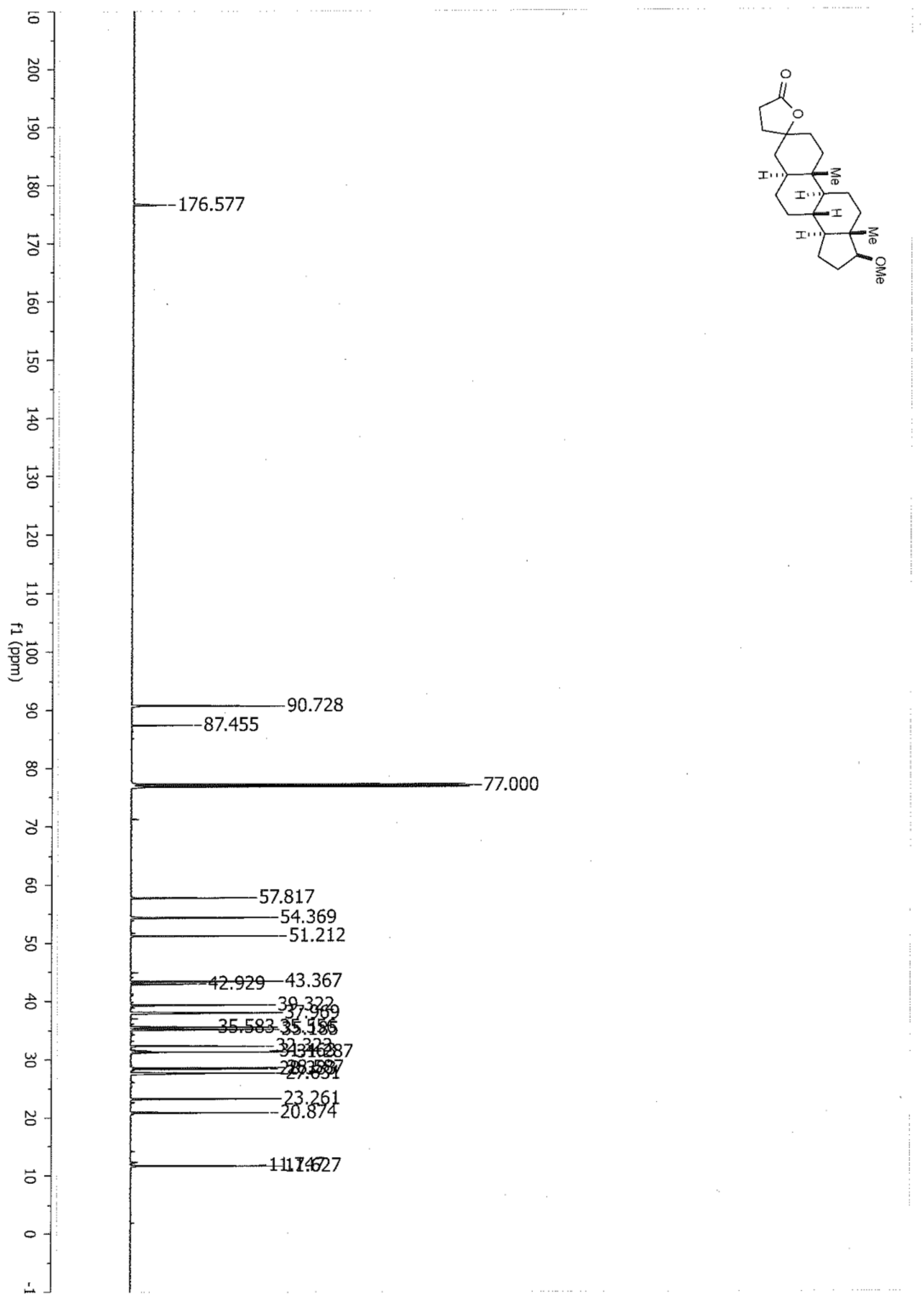
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.366 BB    0.2727 2963.91431  165.67589  49.6740
   2  14.904 BB    0.4061 3002.81567  116.73311  50.3260

Totals :                  5966.72998  282.40900
```

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

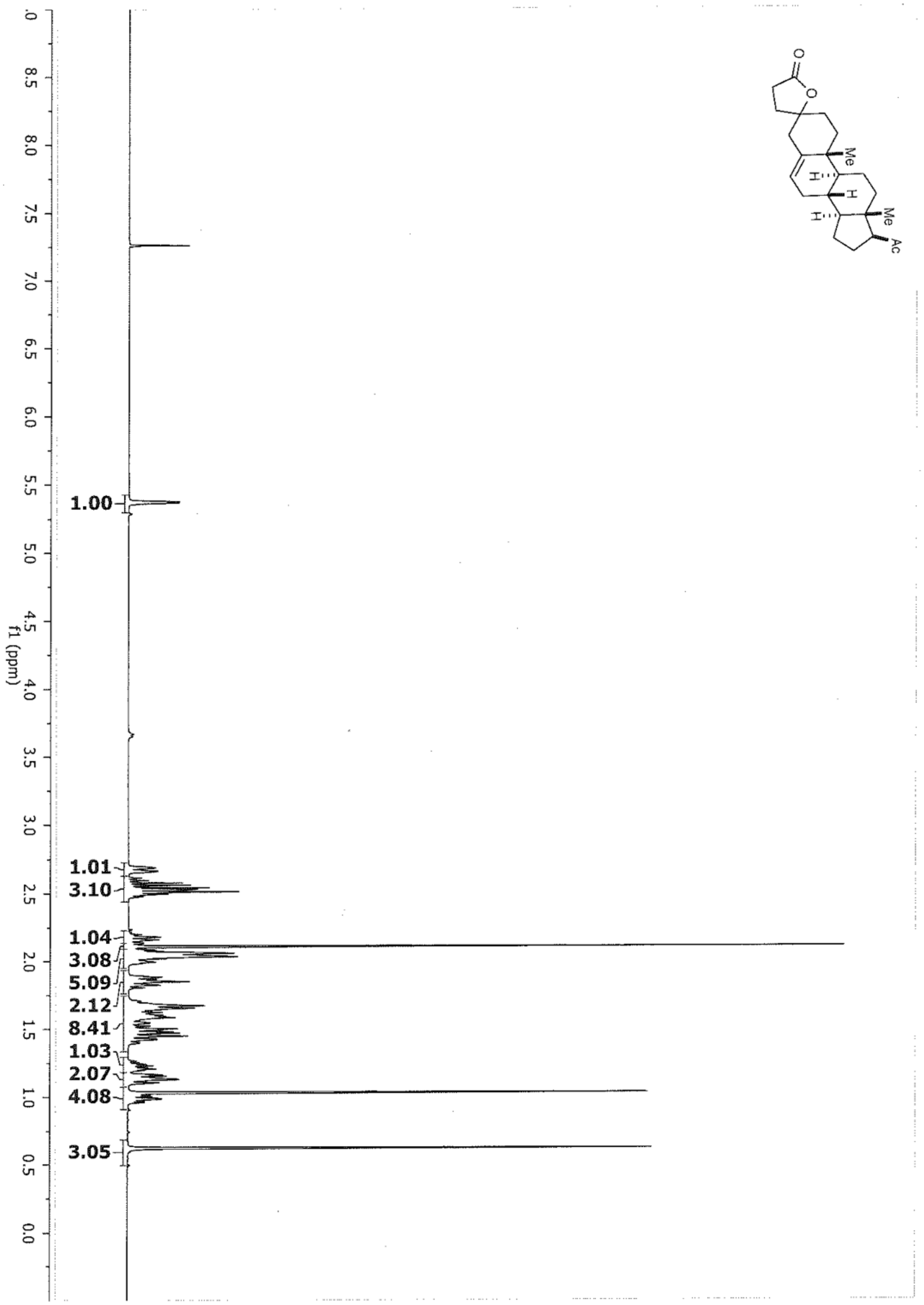


NMR Spectra

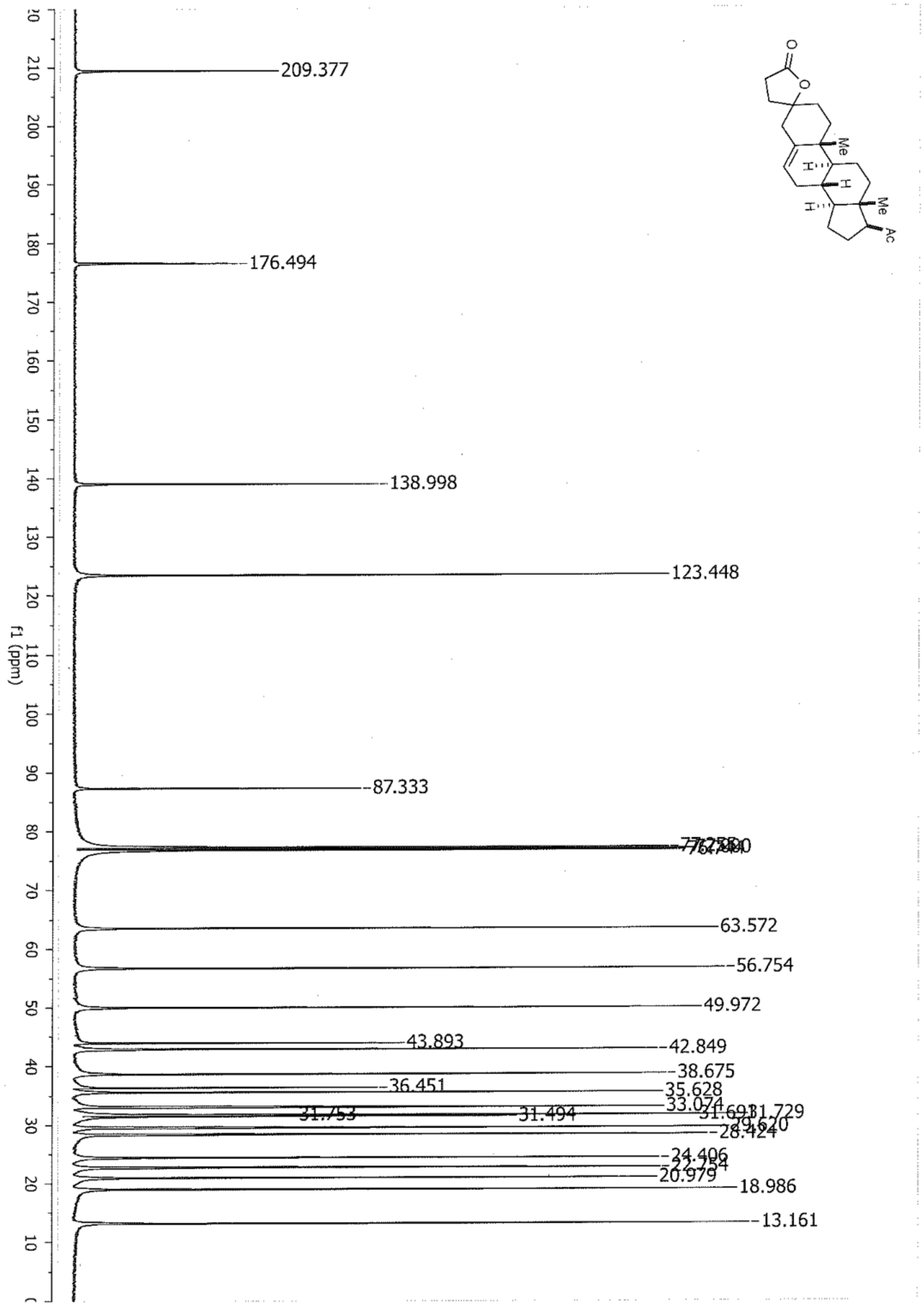

.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
3.00
1.07
1.87
3.06
1.95
3.20
3.59
3.20
4.18
2.13
2.19
4.17
3.02
1.08
O
O
Me
H
H
H
Me
H
OMe

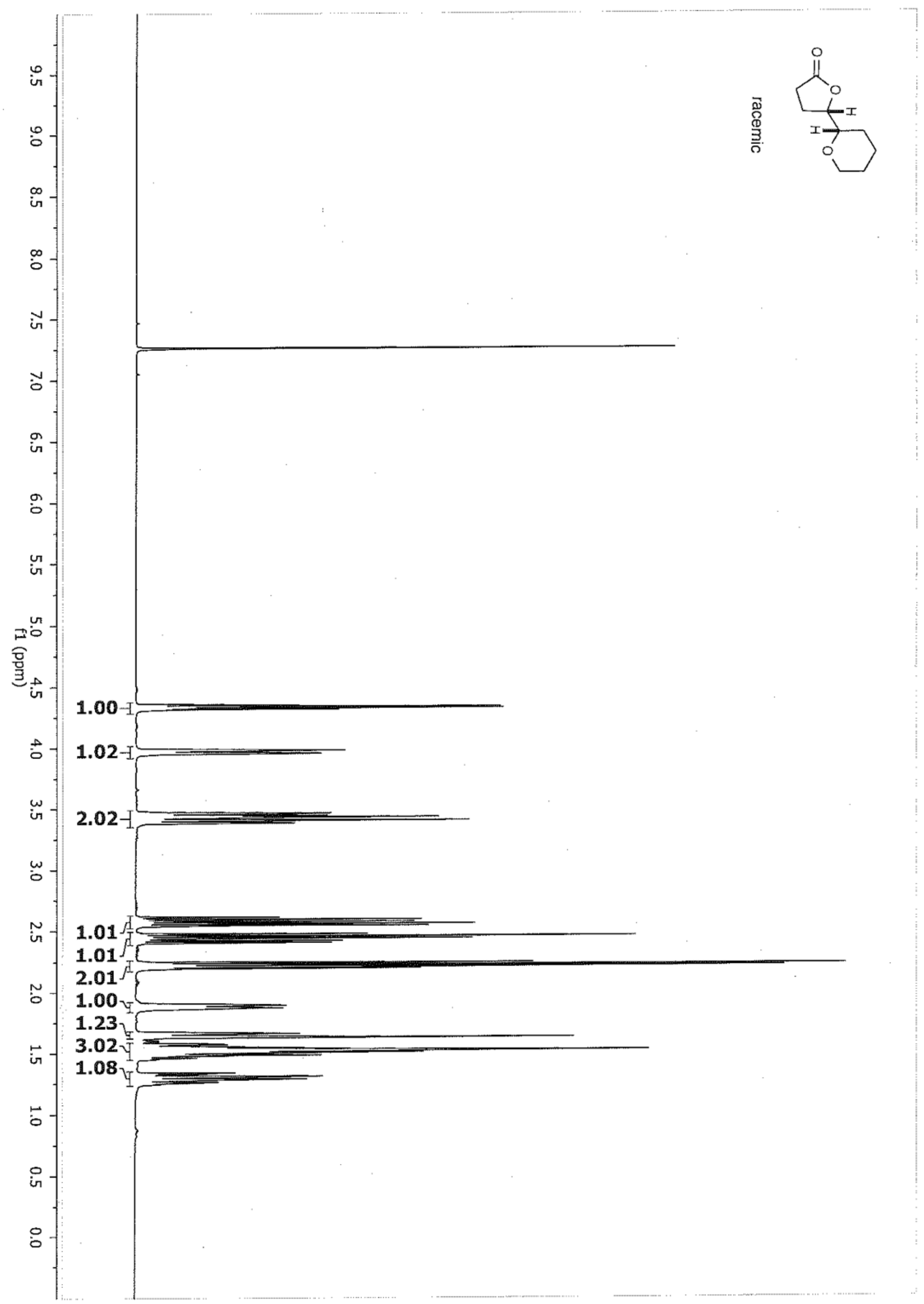


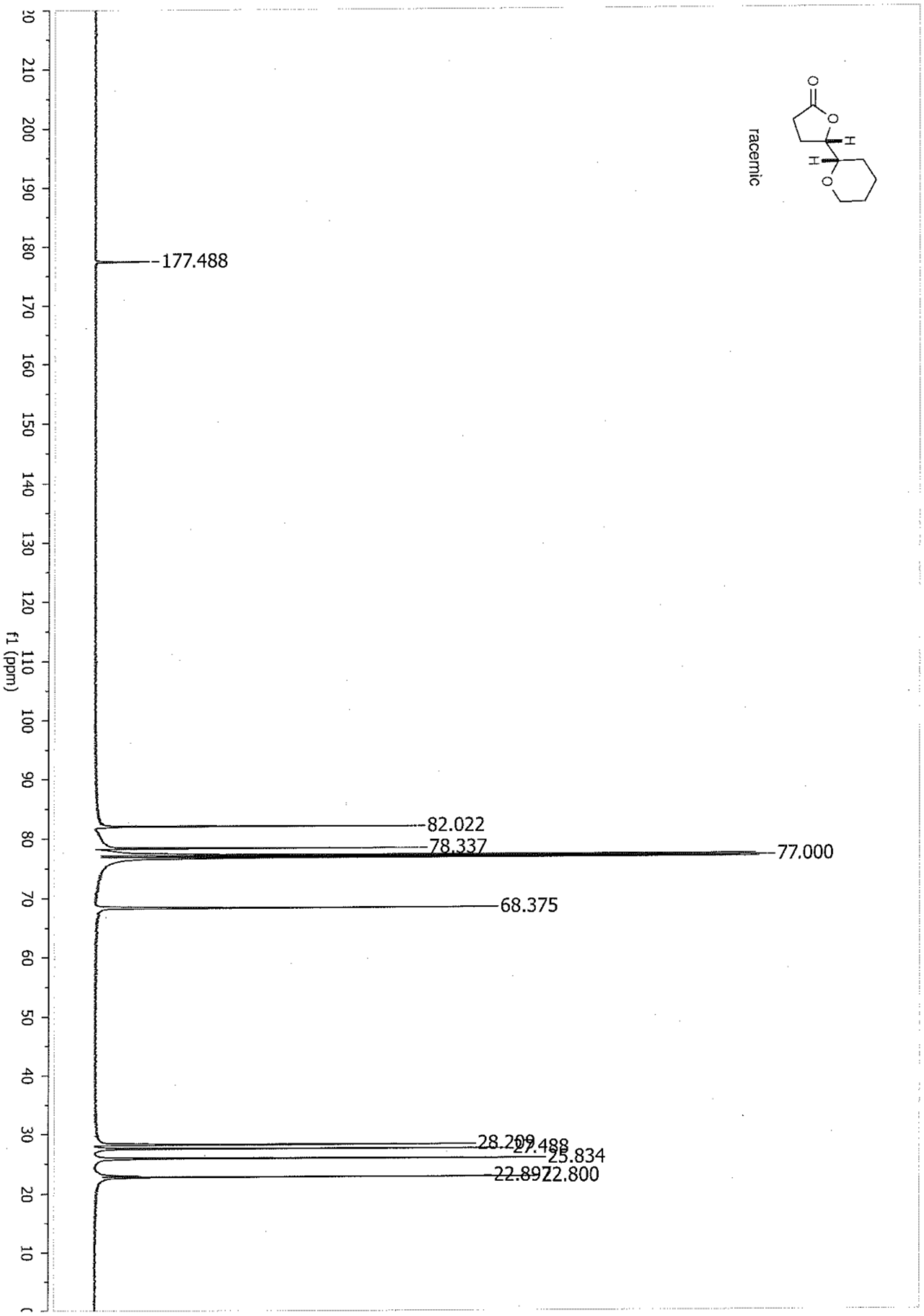
176.577
90.728
87.455
77.000
57.817
54.369
51.212
42.929
43.367
39.322
37.969
35.583
35.156
32.323
31.287
27.651
23.261
20.874
11.627
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
O
O
Me
H
H
H
H
Me
OMe

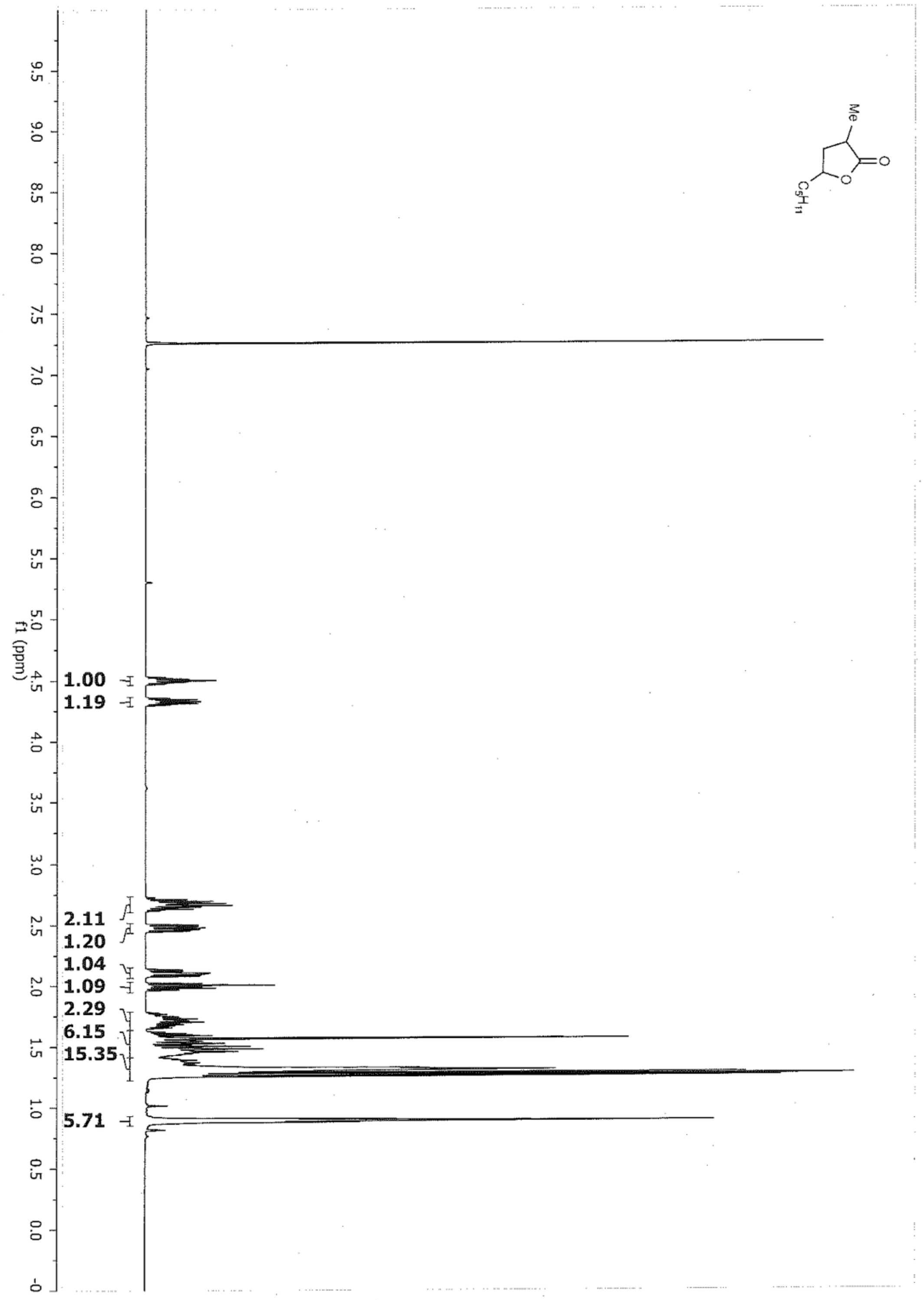


O
O
Me
H
H
H
Me
Ac
1.00
1.01
3.10
1.04
3.08
5.09
2.12
8.41
1.03
2.07
4.08
3.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

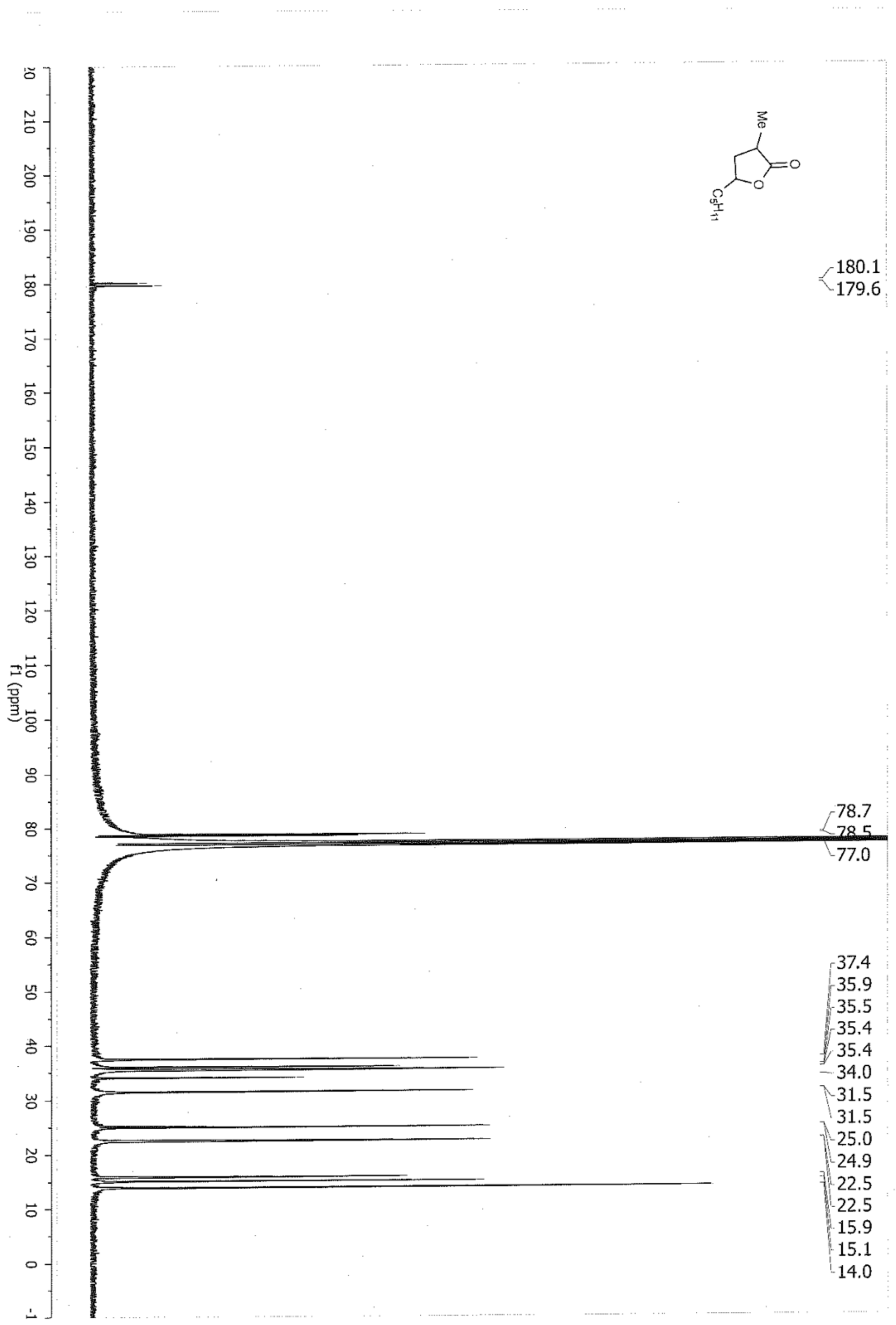

209.377
176.494
138.998
123.448
87.333
63.572
56.754
49.972
43.893
42.849
38.675
36.451
35.628
33.074
31.753
31.494
31.691
31.729
29.620
28.424
24.406
20.979
18.986
13.161
f1 (ppm)
O
Me
H
Ac

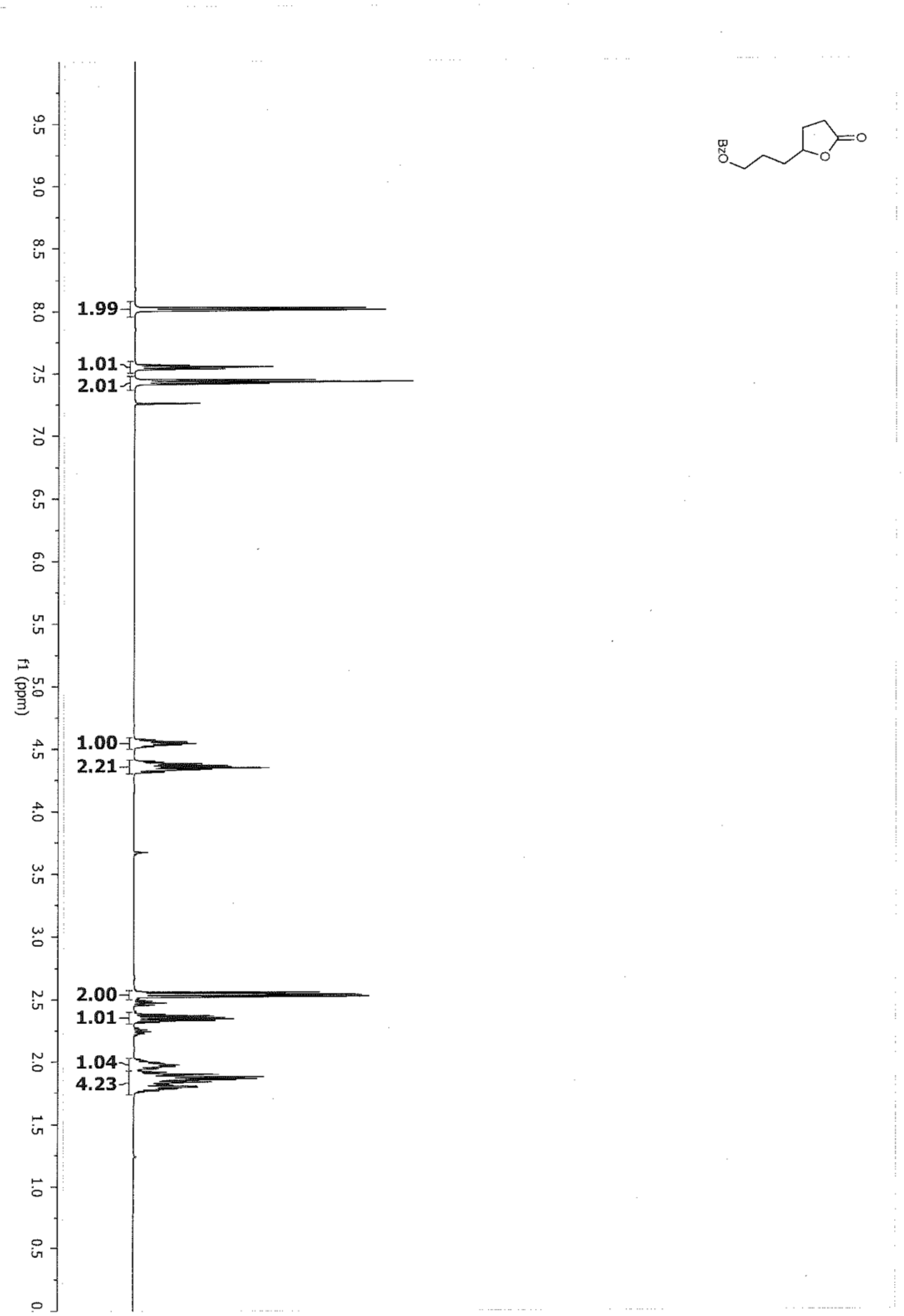

racemic
O
O
H
H
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
1.02
2.02
1.01
1.01
2.01
1.00
1.23
3.02
1.08

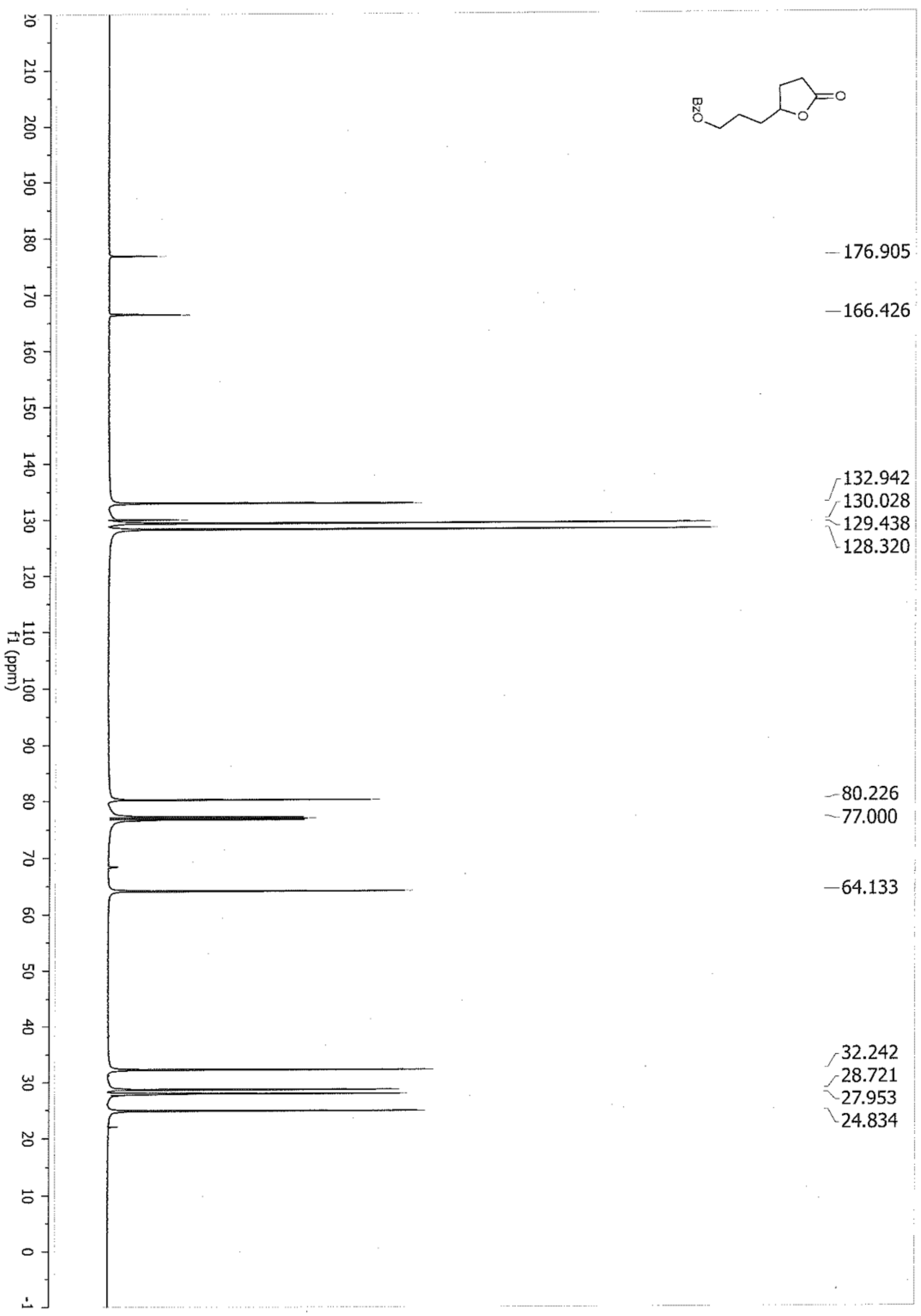

racemic
O
O
H
H
O
177.488
82.022
78.337
77.000
68.375
28.209
27.488
25.834
22.897
22.800
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

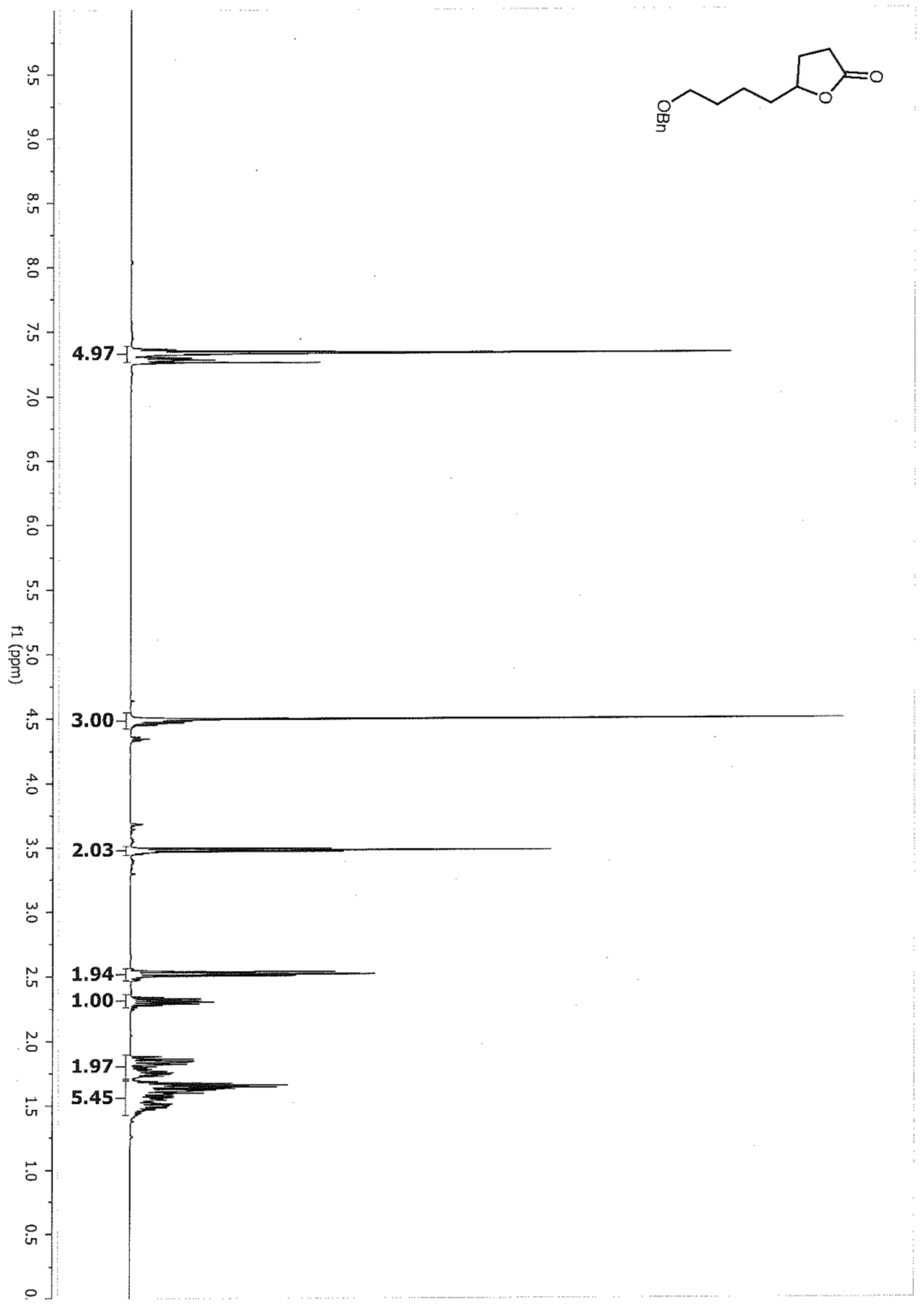


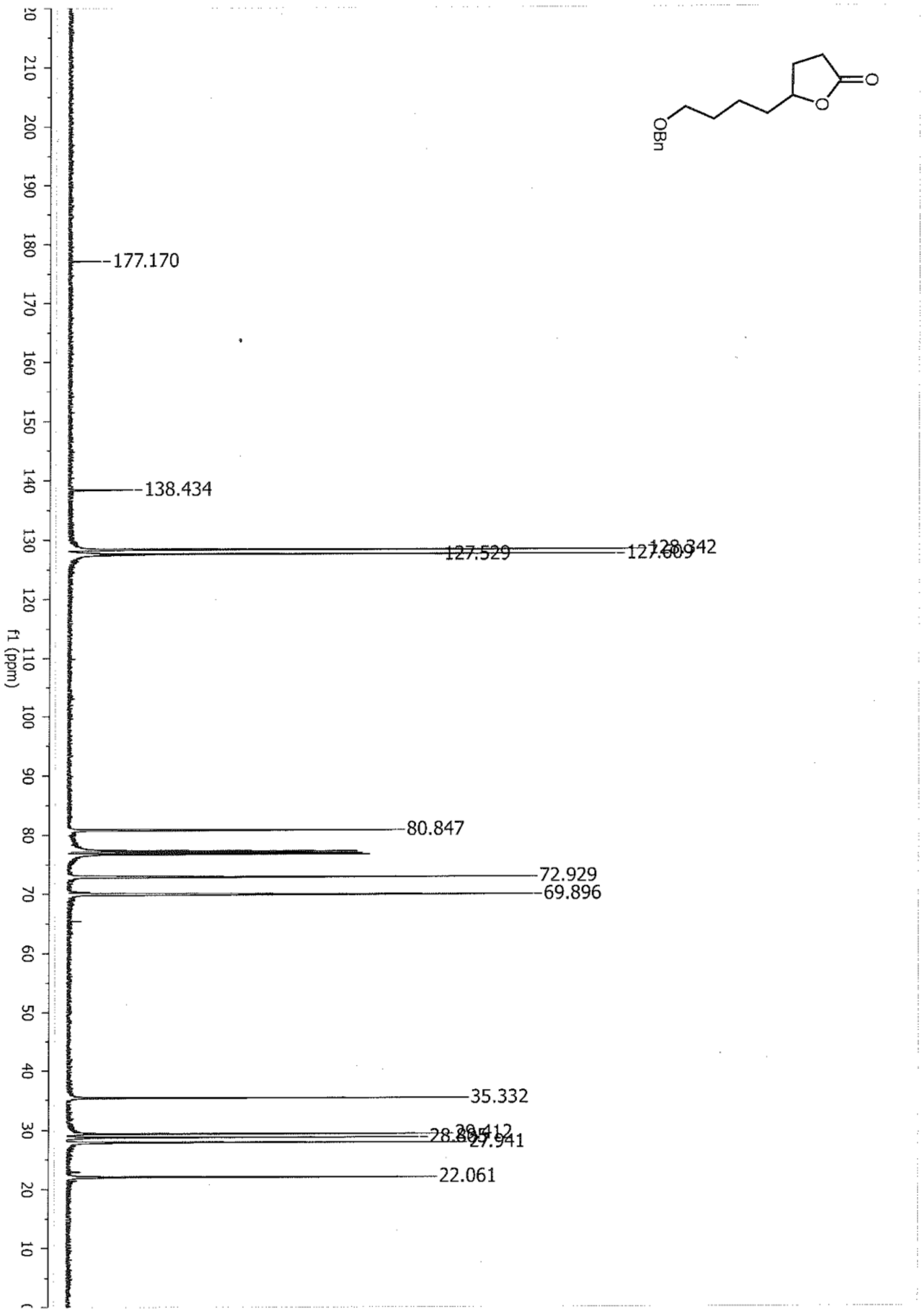
Me
O
O
C5H11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
1.00
1.19
2.11
1.20
1.04
1.09
2.29
6.15
15.35
5.71

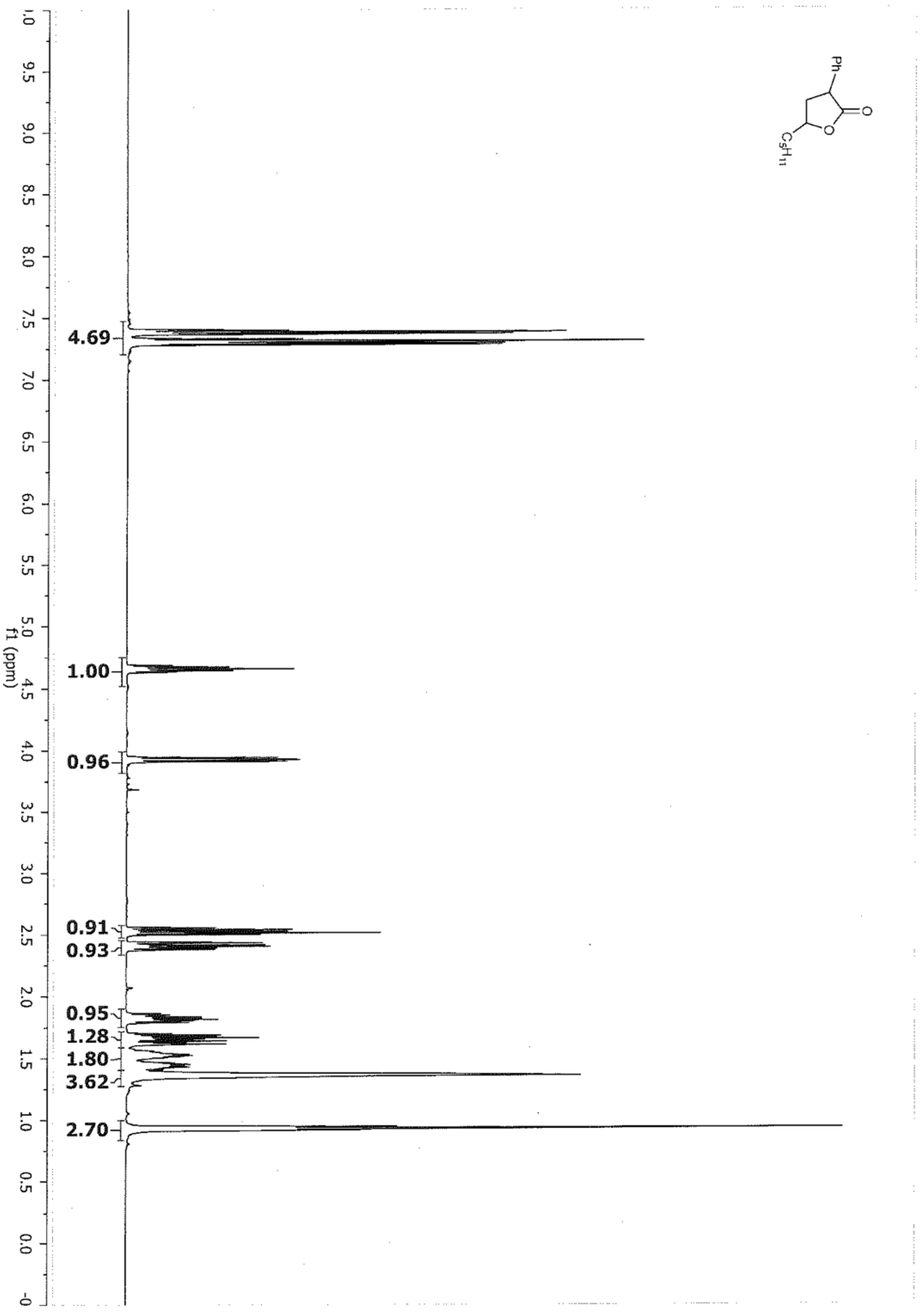

Me
O
O
C5H11
180.1
179.6
78.7
78.5
77.0
37.4
35.9
35.5
35.4
35.4
34.0
31.5
31.5
25.0
24.9
22.5
22.5
15.9
15.1
14.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

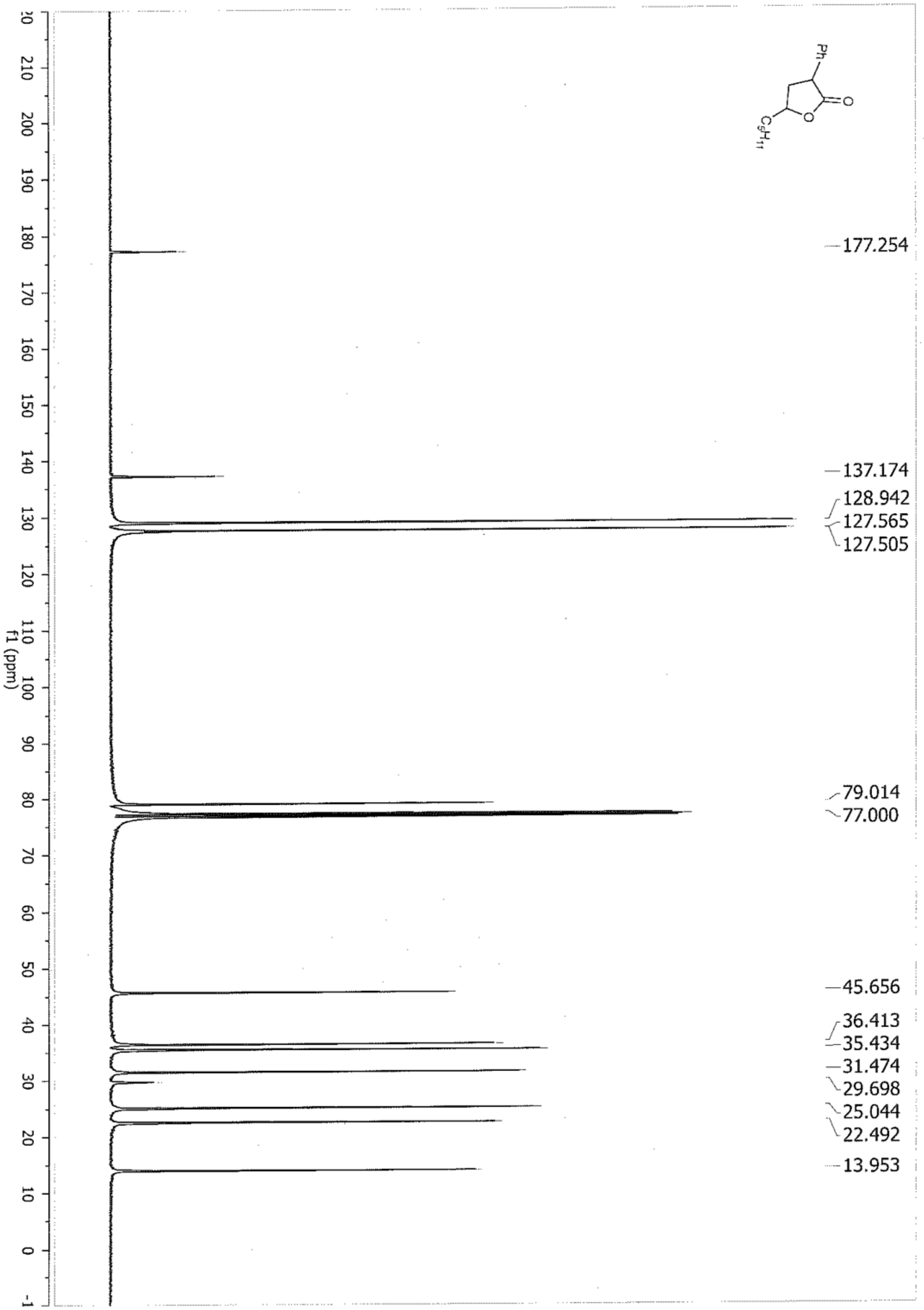

BzO
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
1.99
1.01
2.01
1.00
2.21
2.00
1.01
1.04
4.23

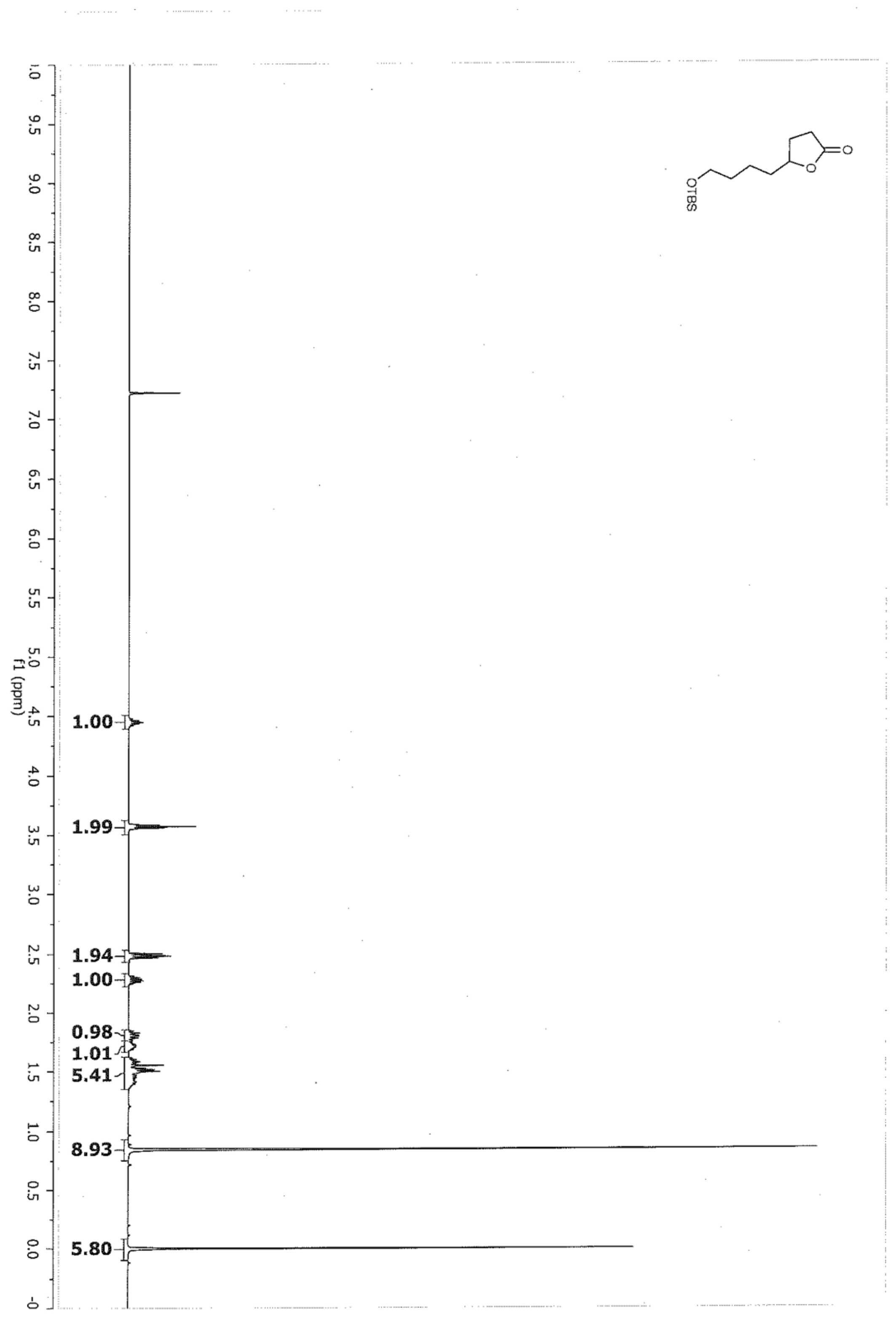

BzO
O
O
176.905
166.426
132.942
130.028
129.438
128.320
80.226
77.000
64.133
32.242
28.721
27.953
24.834
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

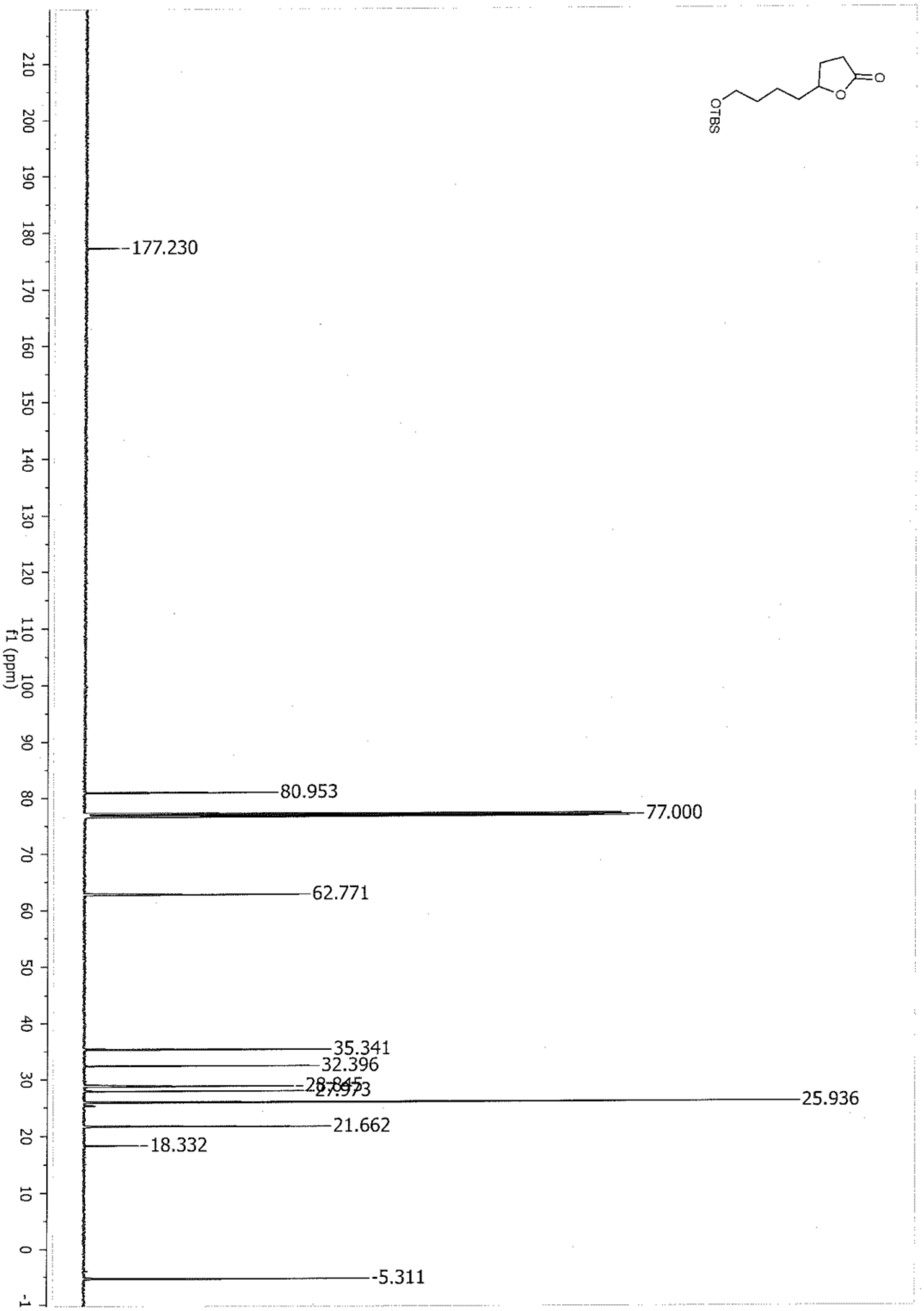

OBn
O
O
4.97
3.00
2.03
1.94
1.00
1.97
5.45
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

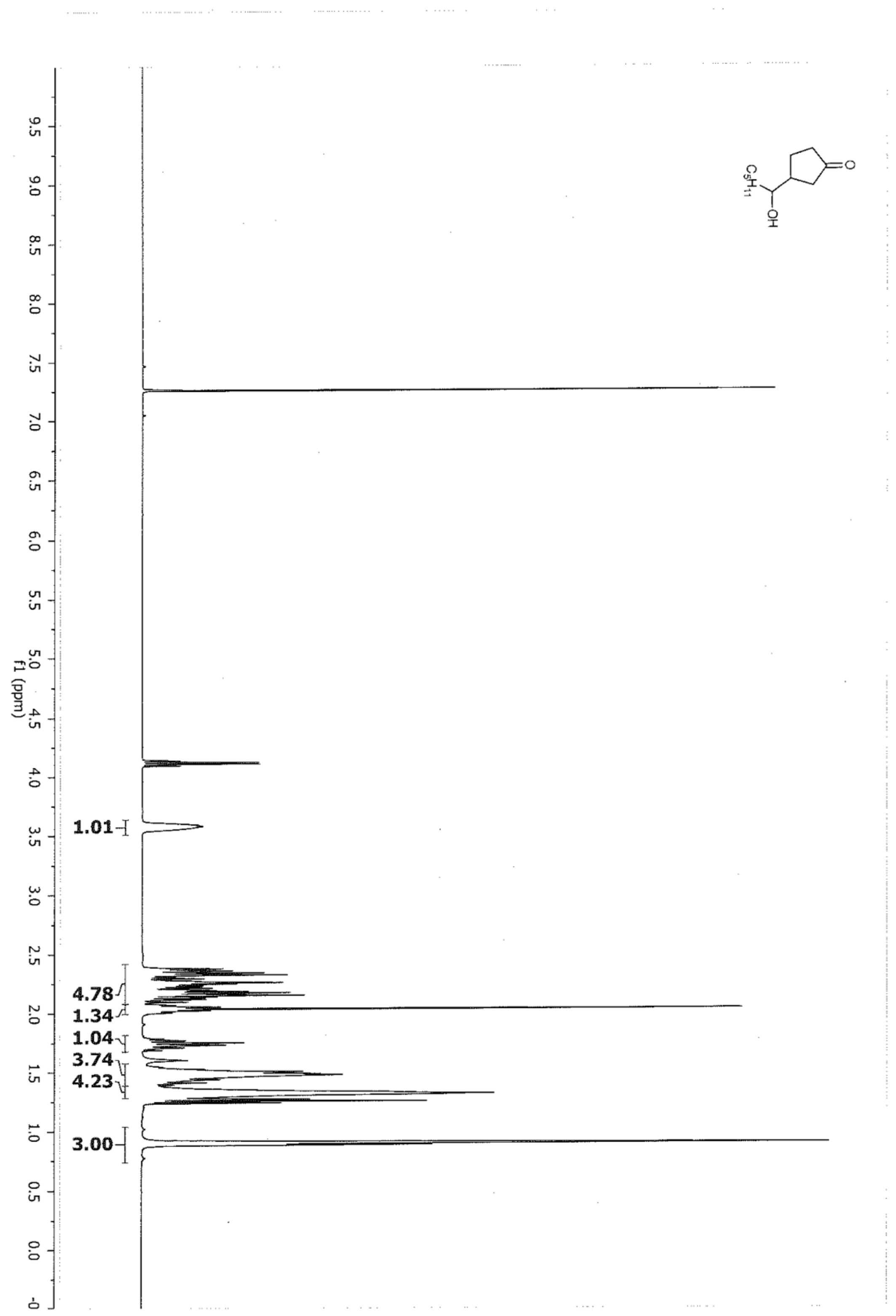

OBn
O
O
177.170
138.434
128.342
127.609
127.529
80.847
72.929
69.896
35.332
29.412
28.805
27.941
22.061
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

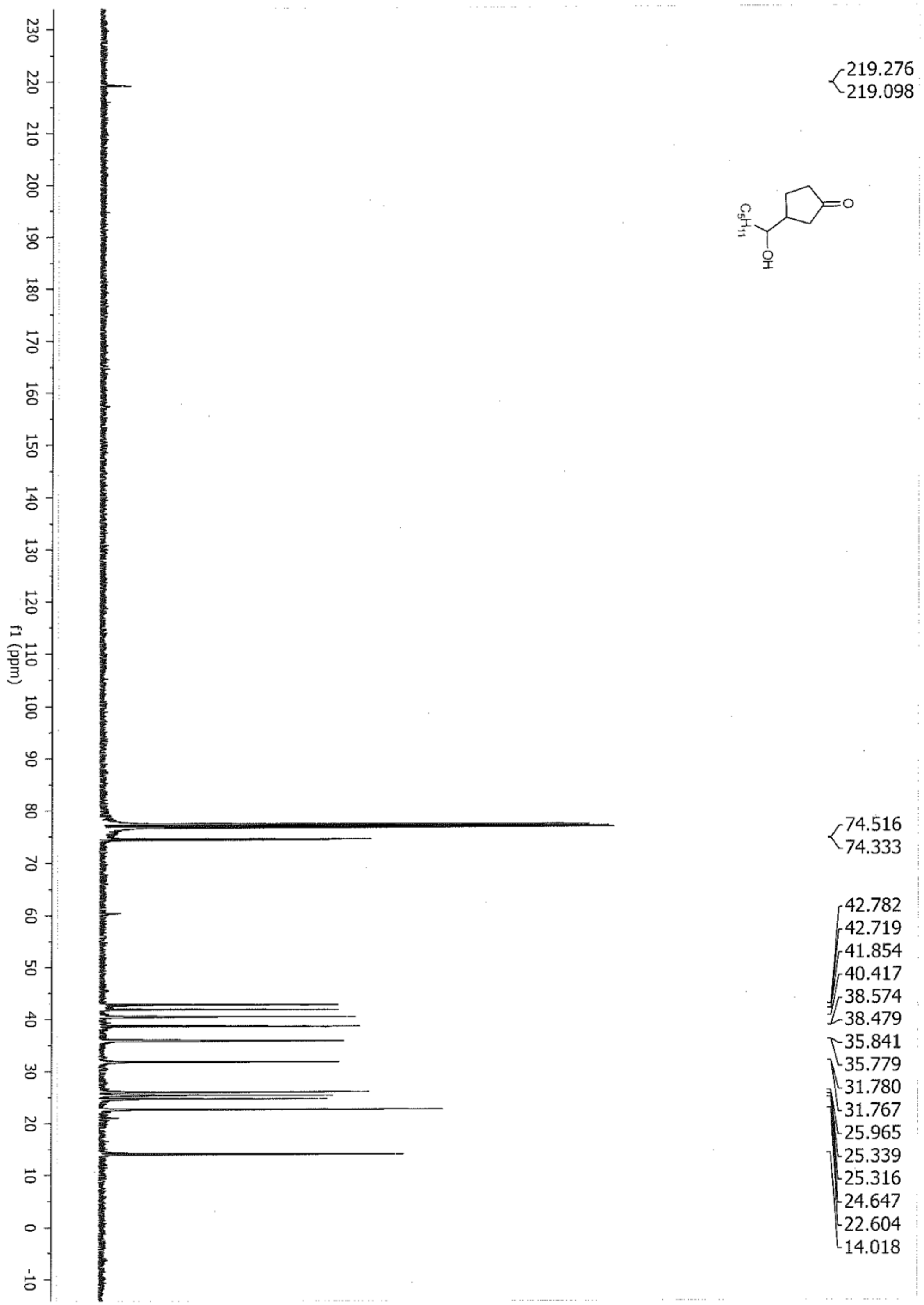

Ph
O
O
C_5H_{11}
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.69
1.00
0.96
0.91
0.93
0.95
1.28
1.80
3.62
2.70

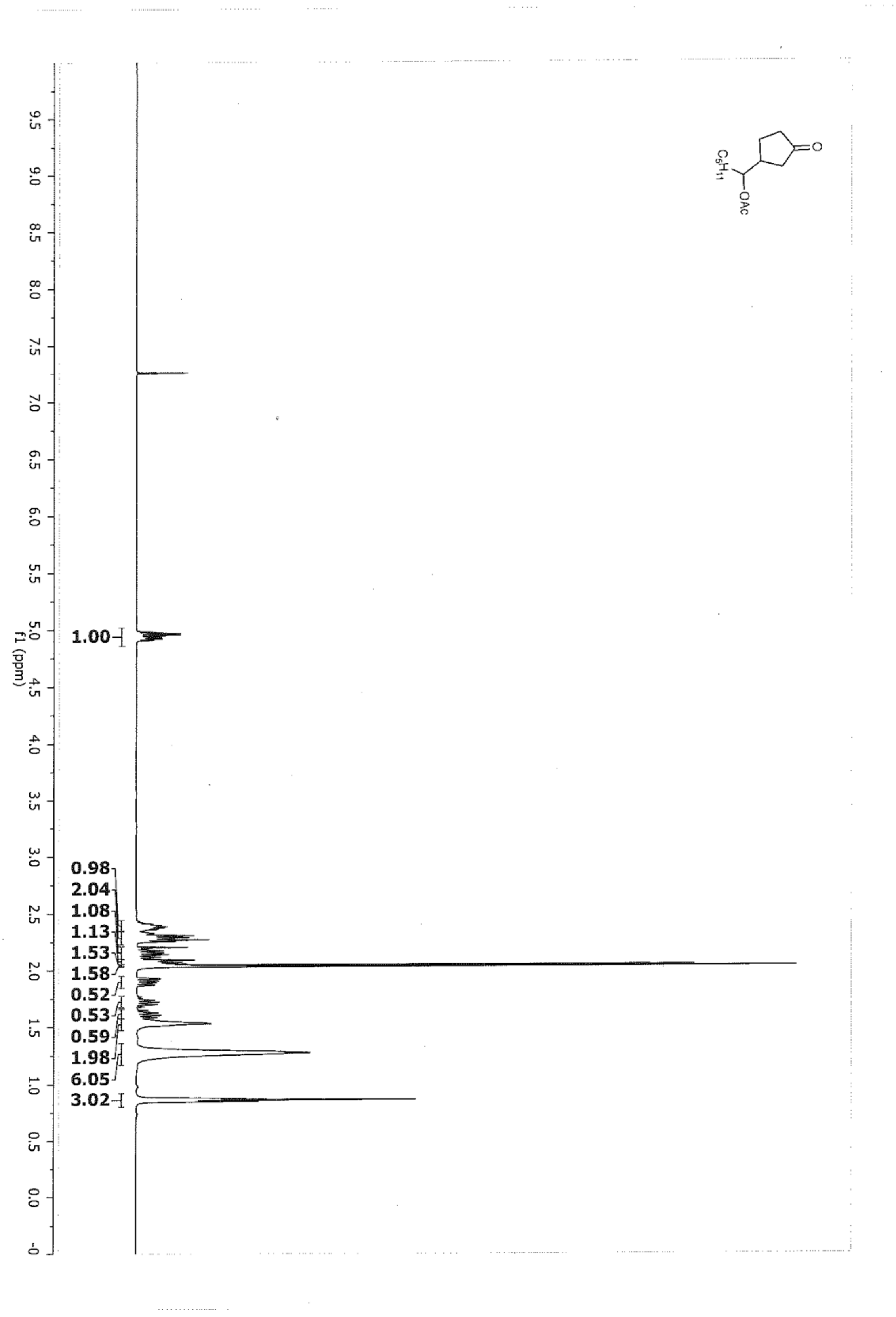

Ph
O
O
C5H11
177.254
137.174
128.942
127.565
127.505
79.014
77.000
45.656
36.413
35.434
31.474
29.698
25.044
22.492
13.953
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

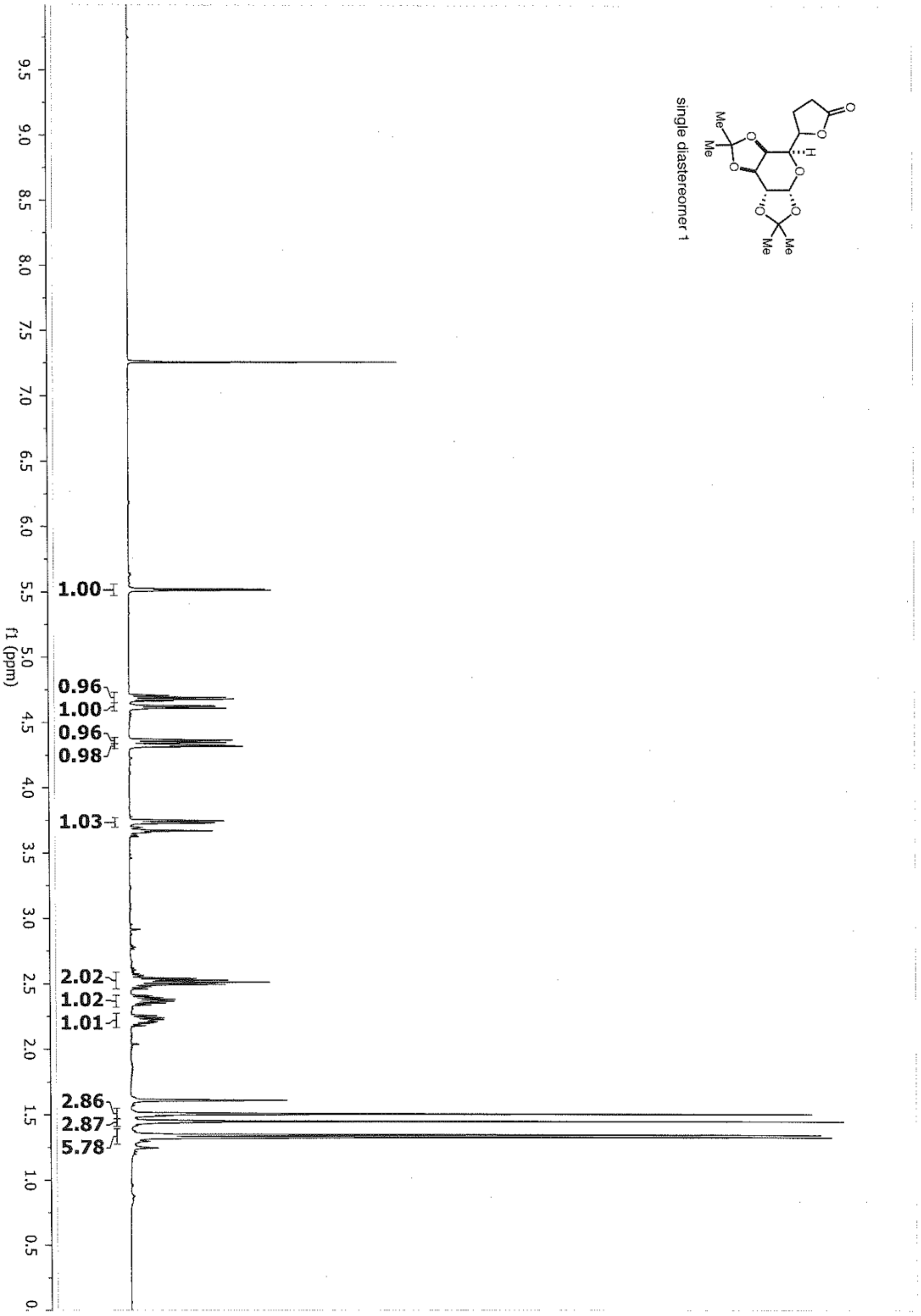

OTBS
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.00
1.99
1.94
1.00
0.98
1.01
5.41
8.93
5.80

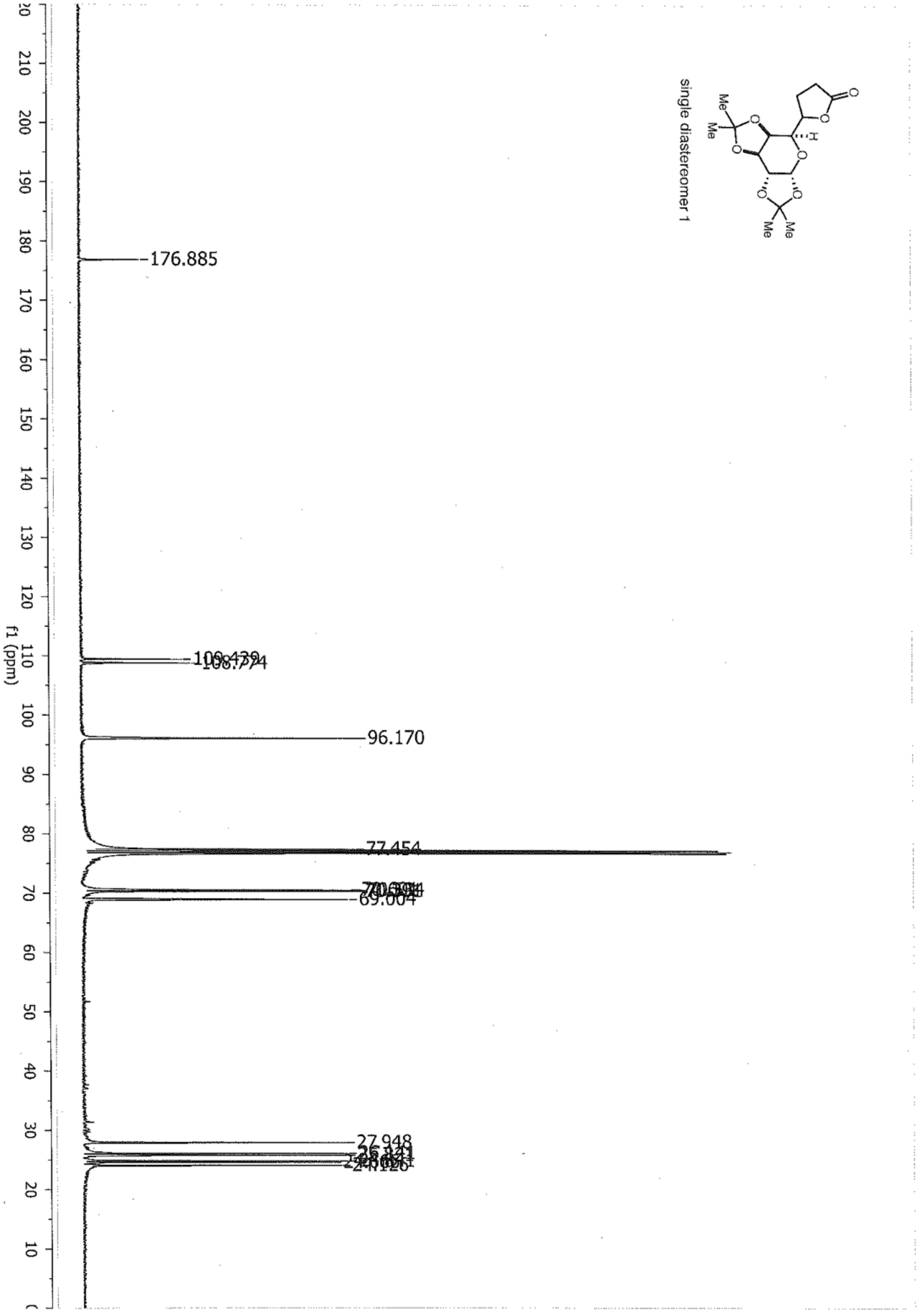

OTBS
O
O
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
177.230
80.953
77.000
62.771
35.341
32.396
28.845
27.973
25.936
21.662
18.332
-5.311

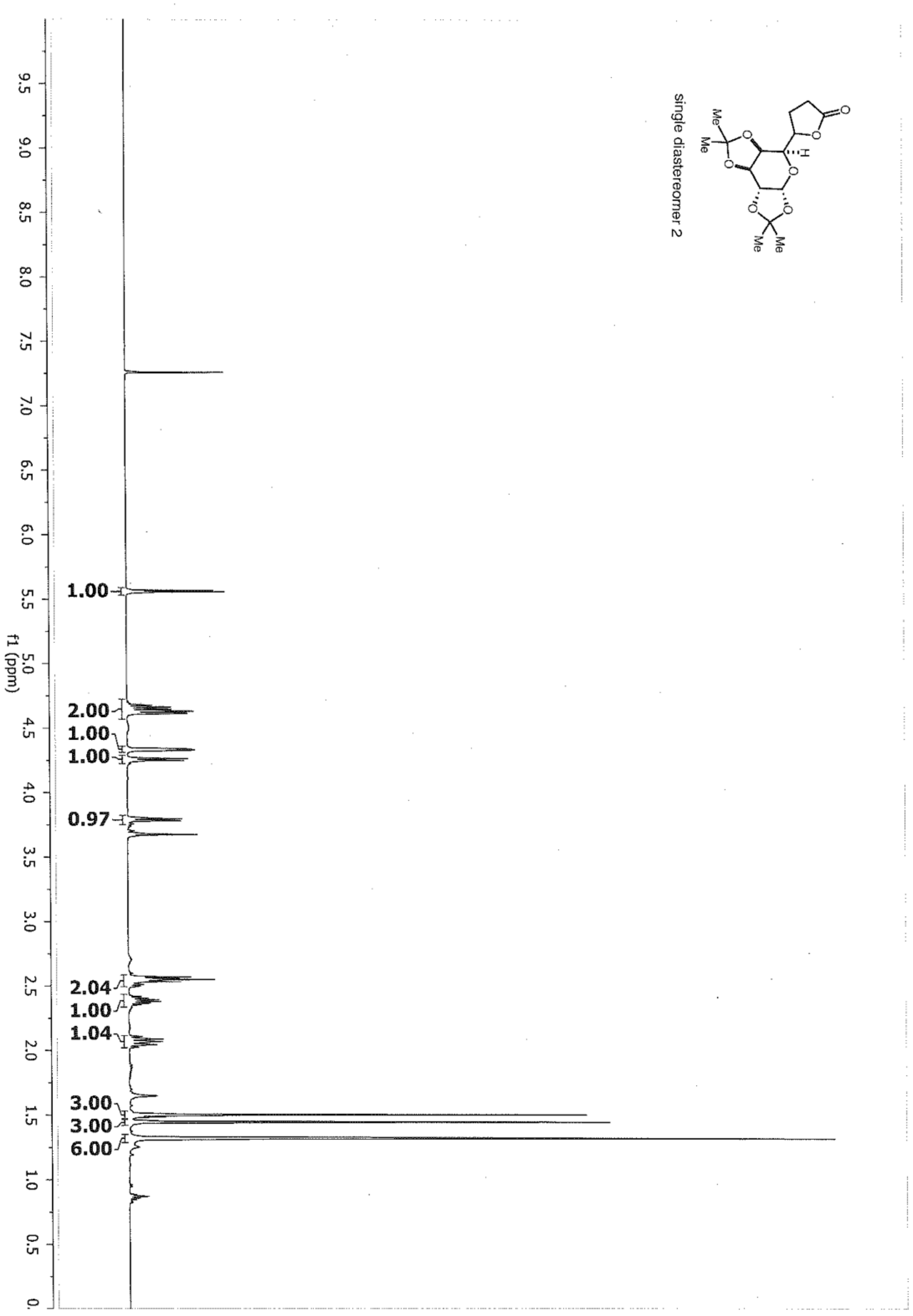

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
1.01
4.78
1.34
1.04
3.74
4.23
3.00
O
OH
C_5H_{11}

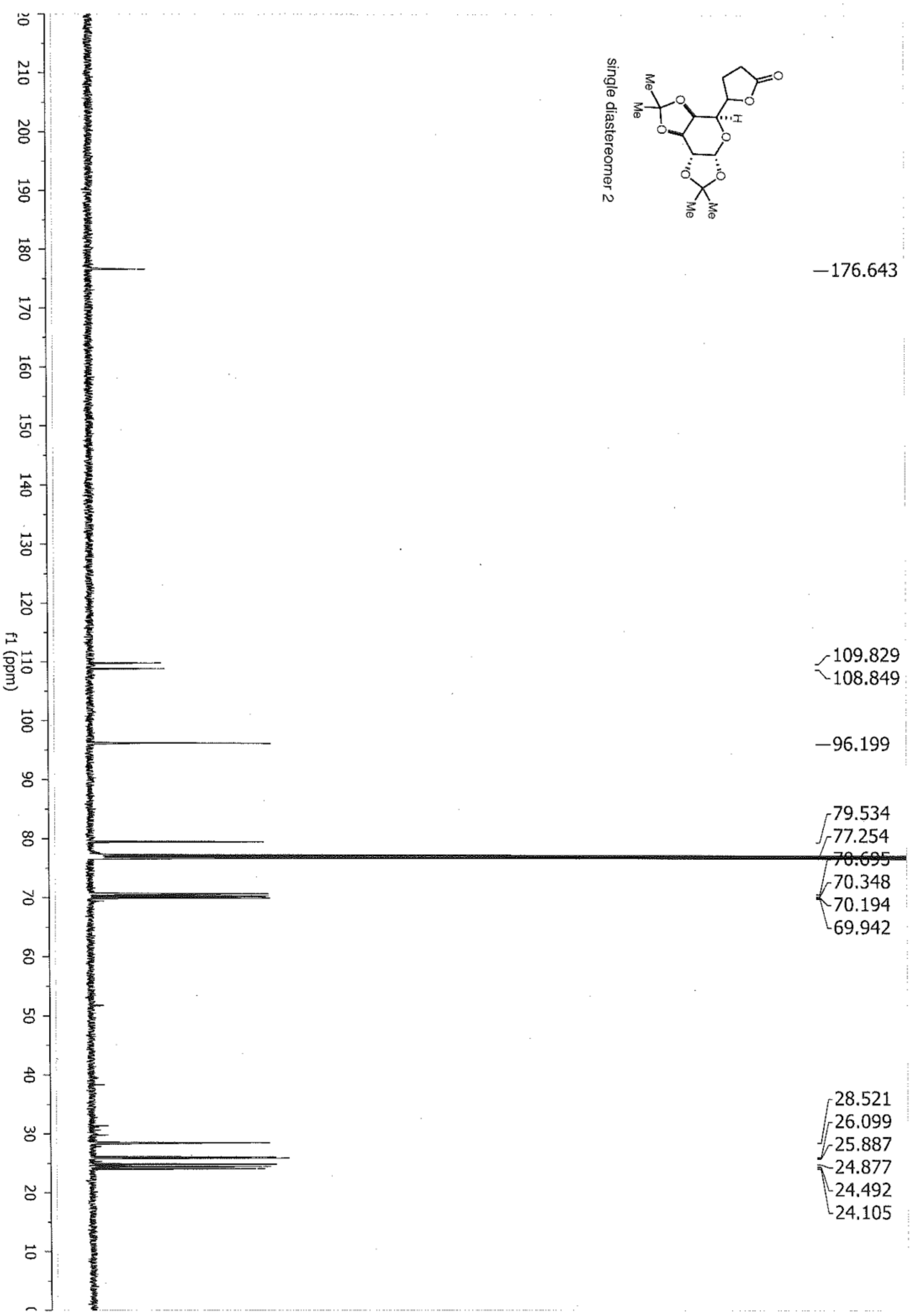

219.276
219.098
74.516
74.333
42.782
42.719
41.854
40.417
38.574
38.479
35.841
35.779
31.780
31.767
25.965
25.339
25.316
24.647
22.604
14.018
O
OH
C5H11
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

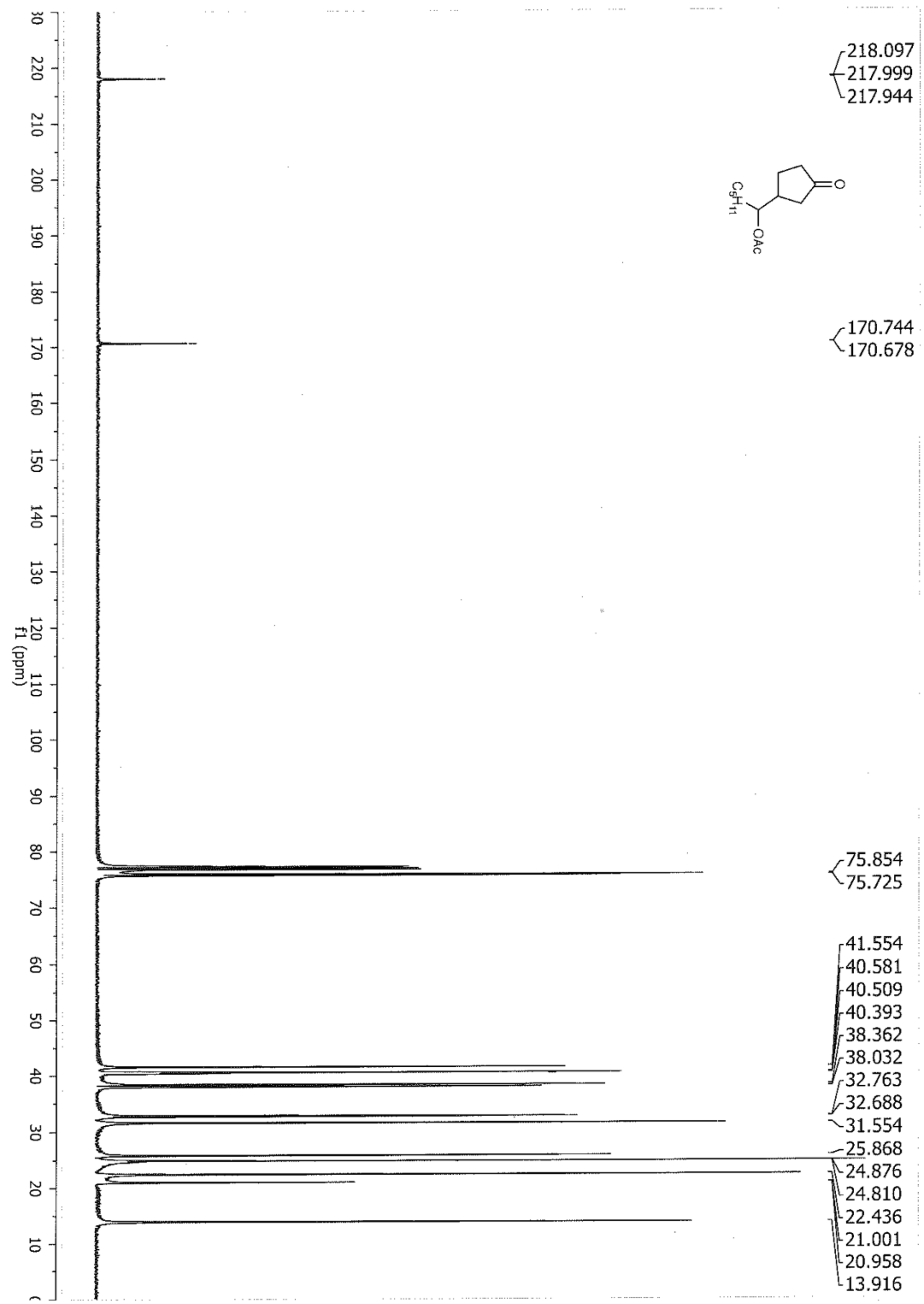

O
C_5H_{11}
OAc
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
1.00
0.98
2.04
1.08
1.13
1.53
1.58
0.52
0.53
0.59
1.98
6.05
3.02

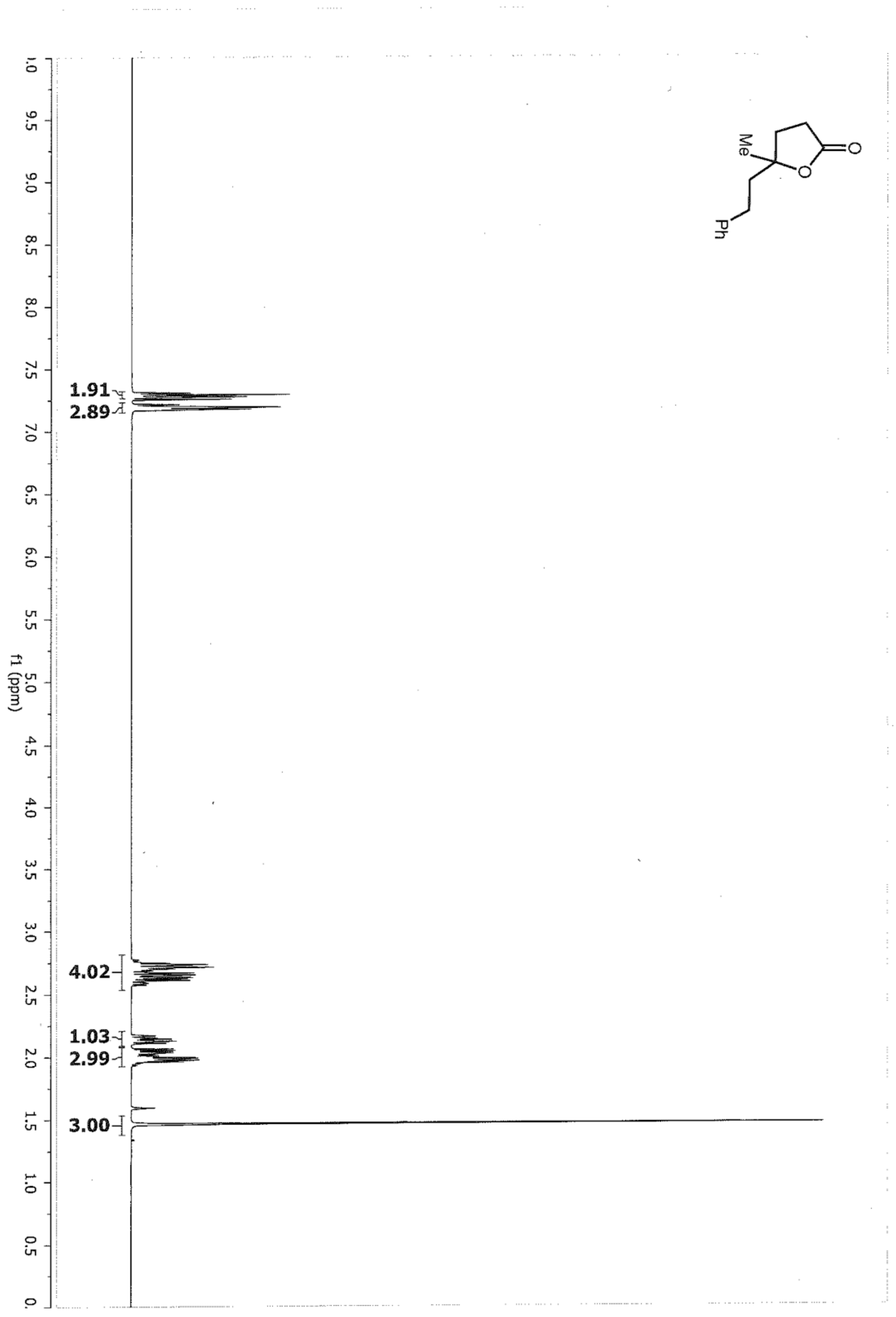

single diastereomer 1
Me
Me
Me
Me
O
H
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)
1.00
0.96
1.00
0.96
0.98
1.03
2.02
1.02
1.01
2.86
2.87
5.78


single diastereomer 1
O
H
Me
Me
Me
Me
176.885
109.439
108.774
96.170
77.454
69.004
27.948
24.126
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

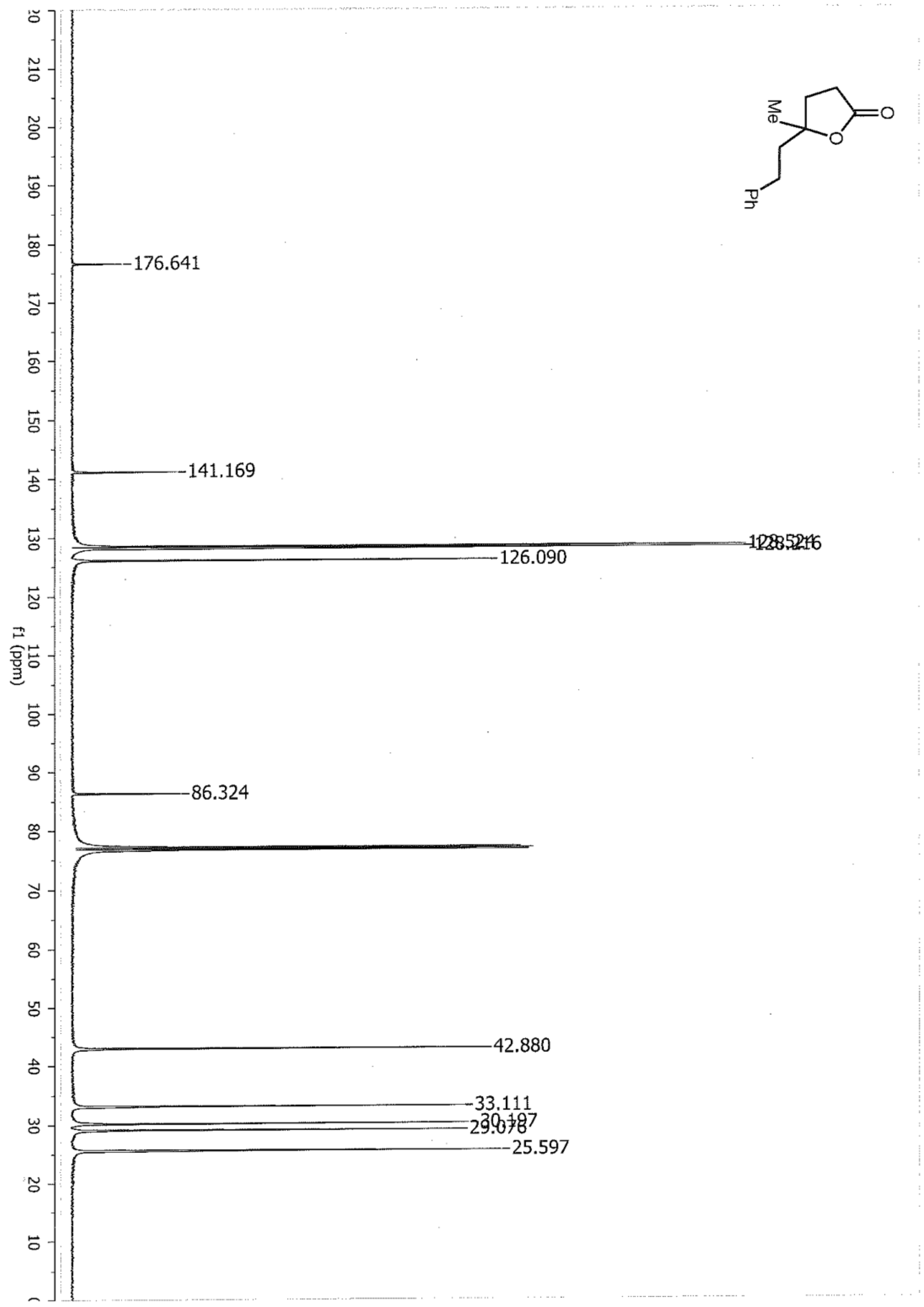

single diastereomer 2


single diastereomer 2
Me
Me
Me
Me
H
O
—176.643
109.829
108.849
—96.199
79.534
77.254
76.695
70.348
70.194
69.942
28.521
26.099
25.887
24.877
24.492
24.105
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


218.097
217.999
217.944
C5H11
OAc
O
170.744
170.678
75.854
75.725
41.554
40.581
40.509
40.393
38.362
38.032
32.763
32.688
31.554
25.868
24.876
24.810
22.436
21.001
20.958
13.916
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



Me
O
O
Ph
1.91
2.89
4.02
1.03
2.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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O
O
Ph
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128.521
128.216
126.090
86.324
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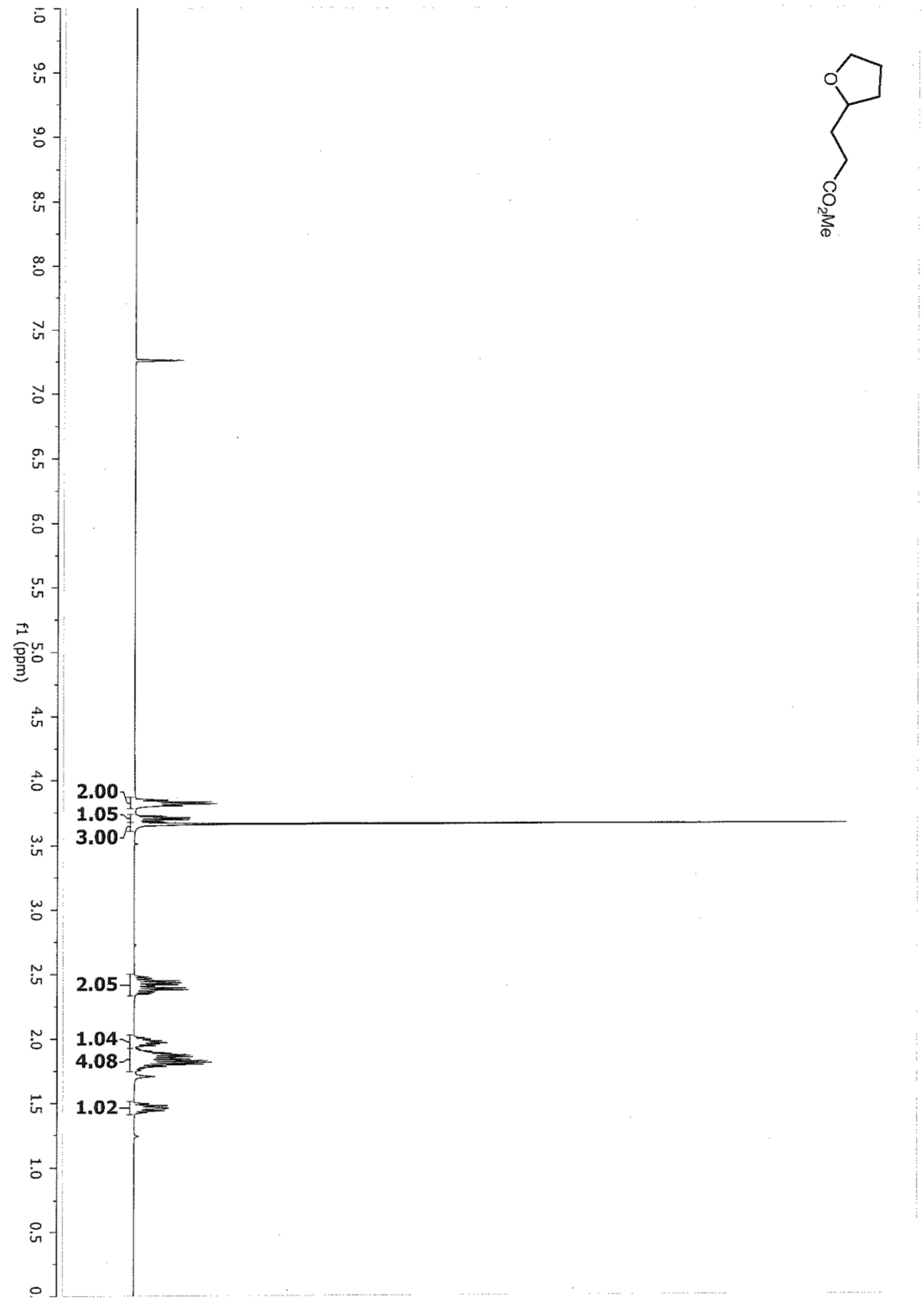
33.111
30.107
29.076
25.597
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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CO2Me
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1.05
3.00
2.05
1.04
4.08
1.02
9.5
9.0
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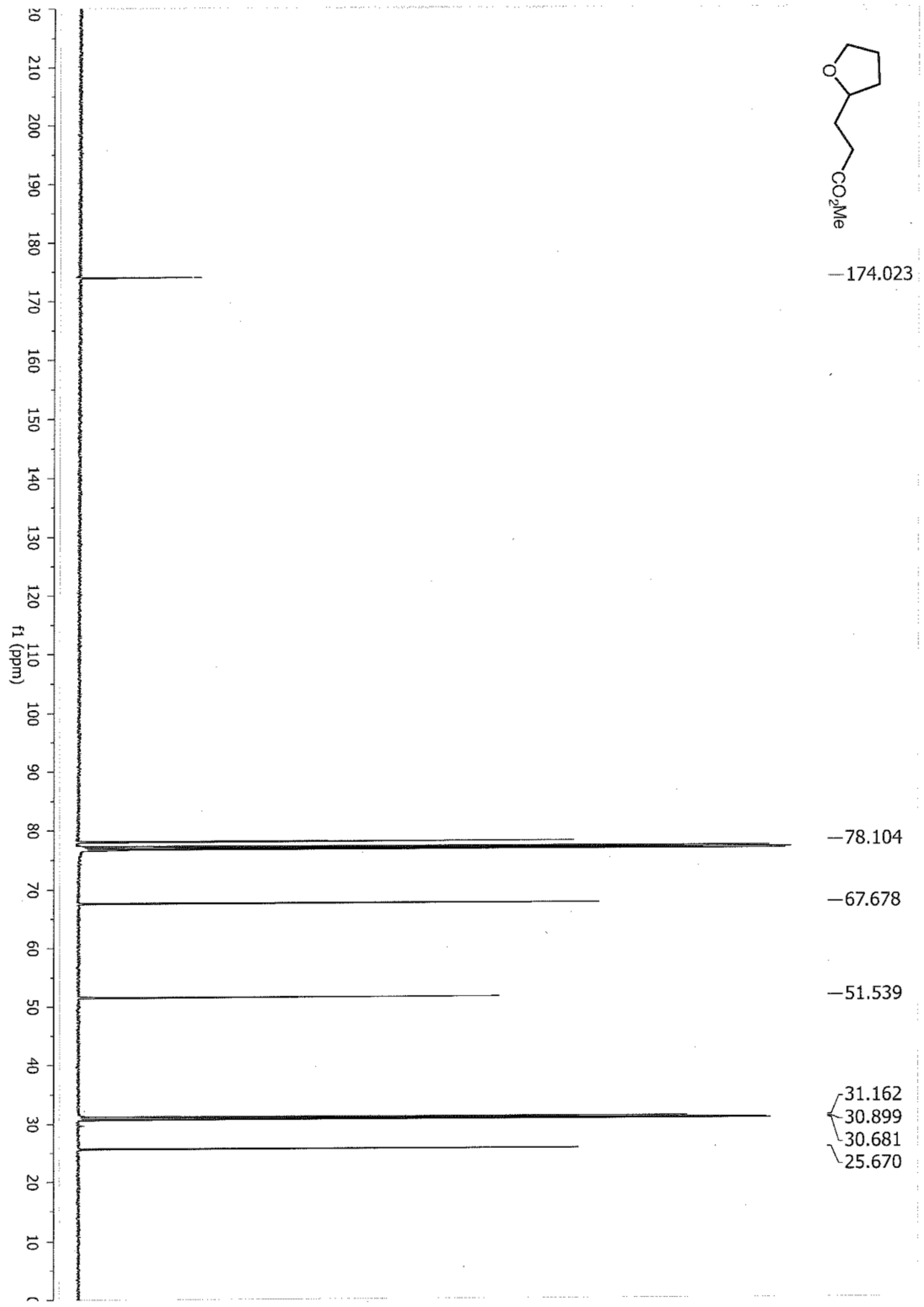
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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CO2Me
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—78.104
—67.678
—51.539
31.162
30.899
30.681
25.670
20
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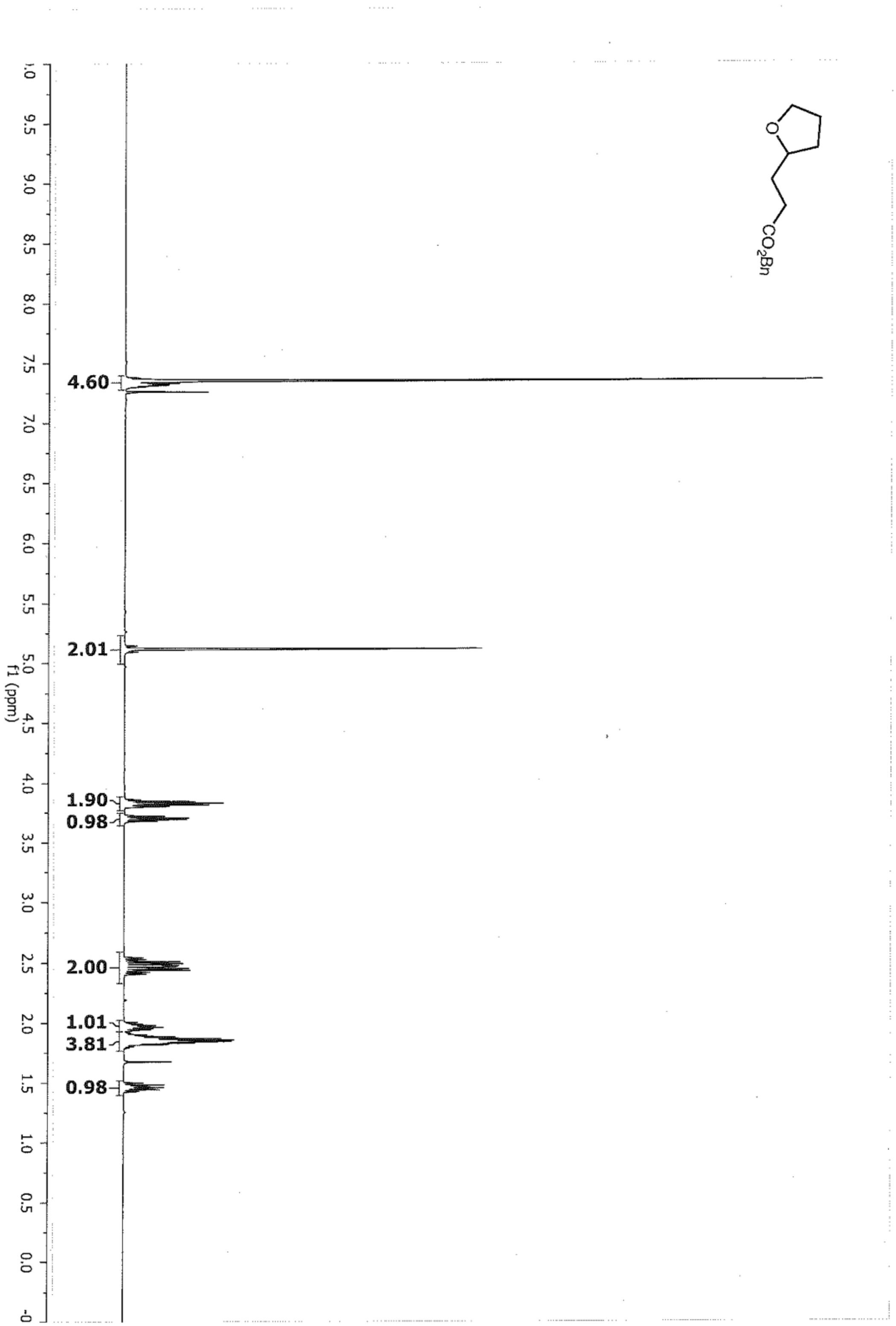
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CO2Bn
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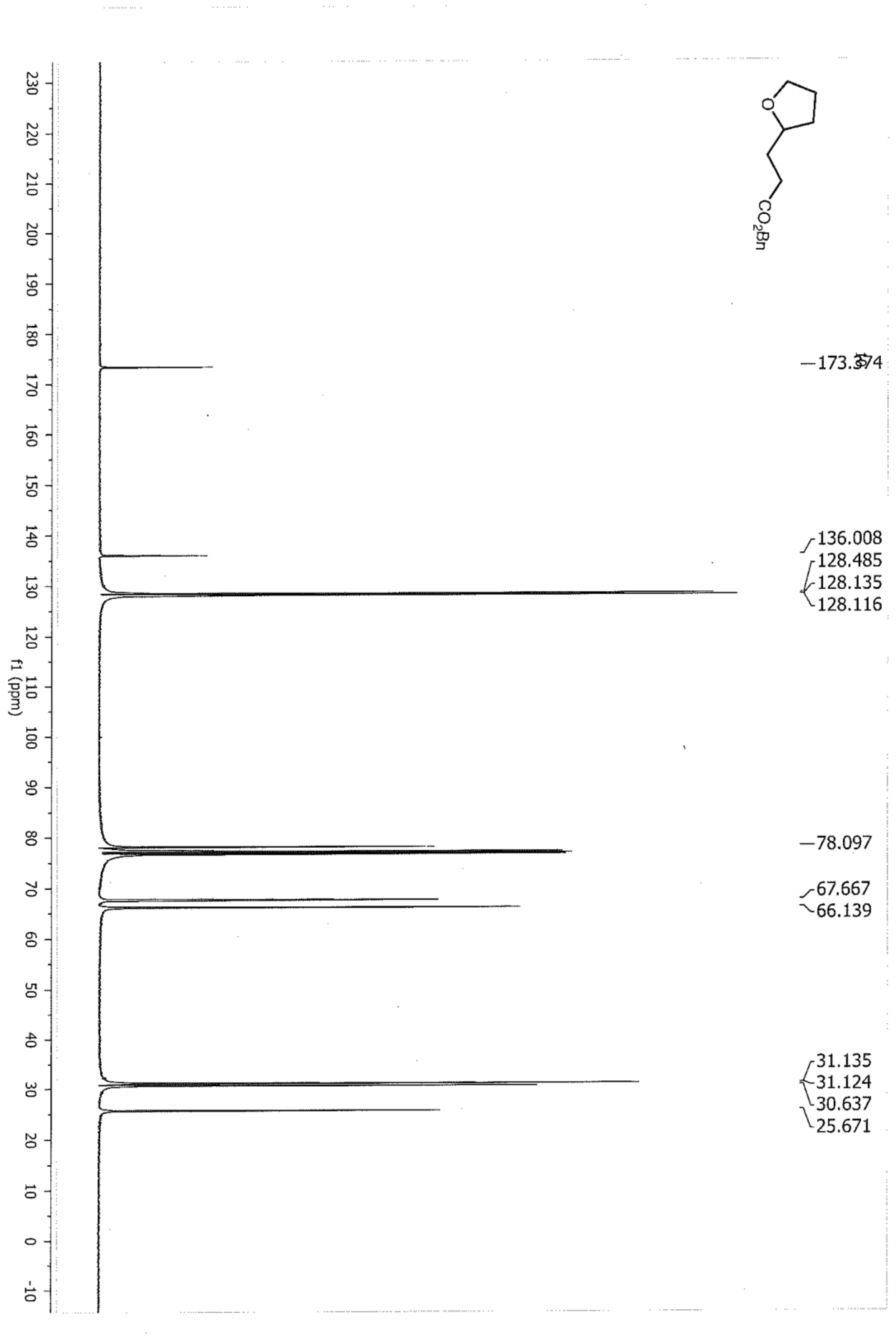
1.90
0.98
2.00
1.01
3.81
0.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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CO$_2$Bn
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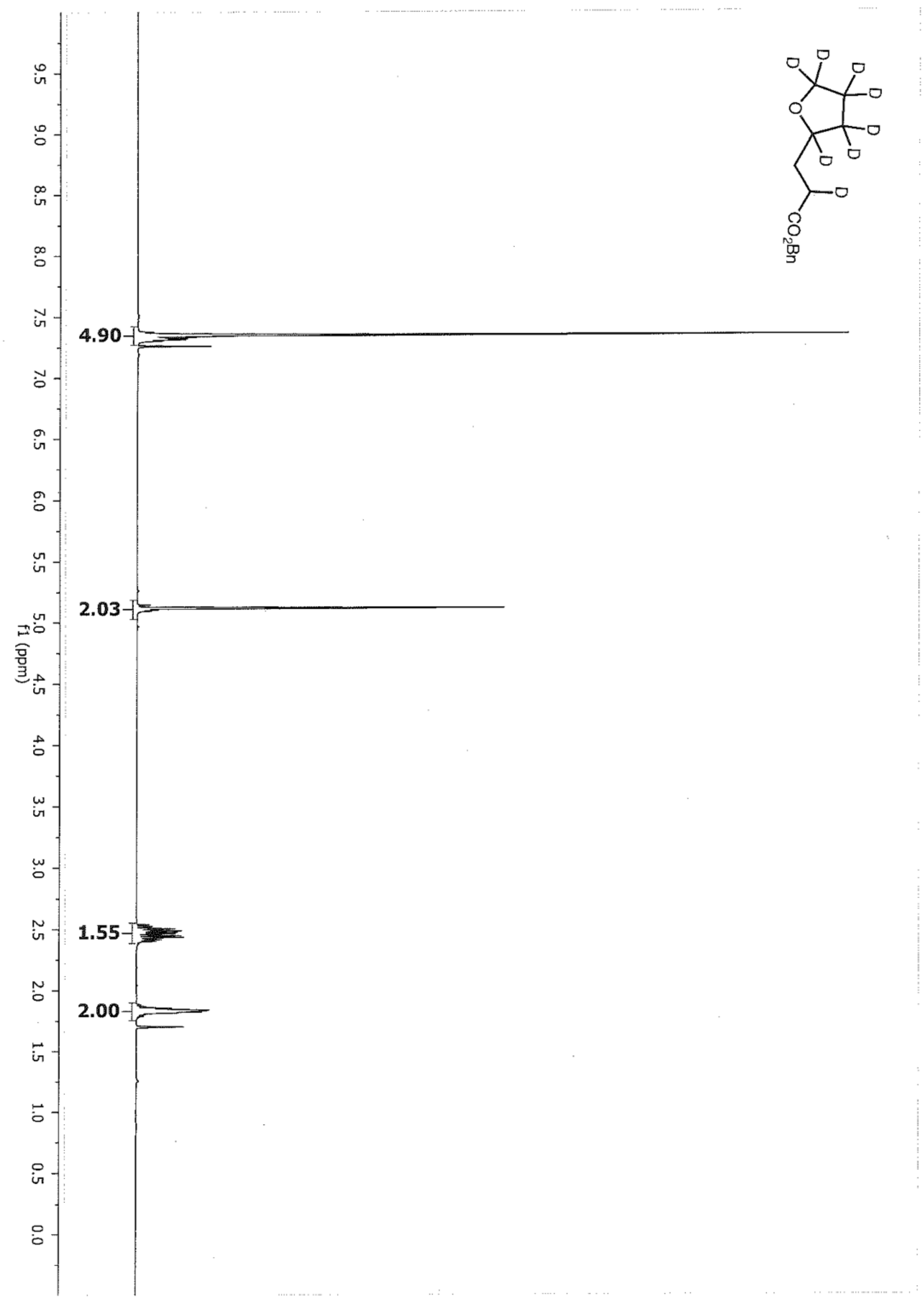
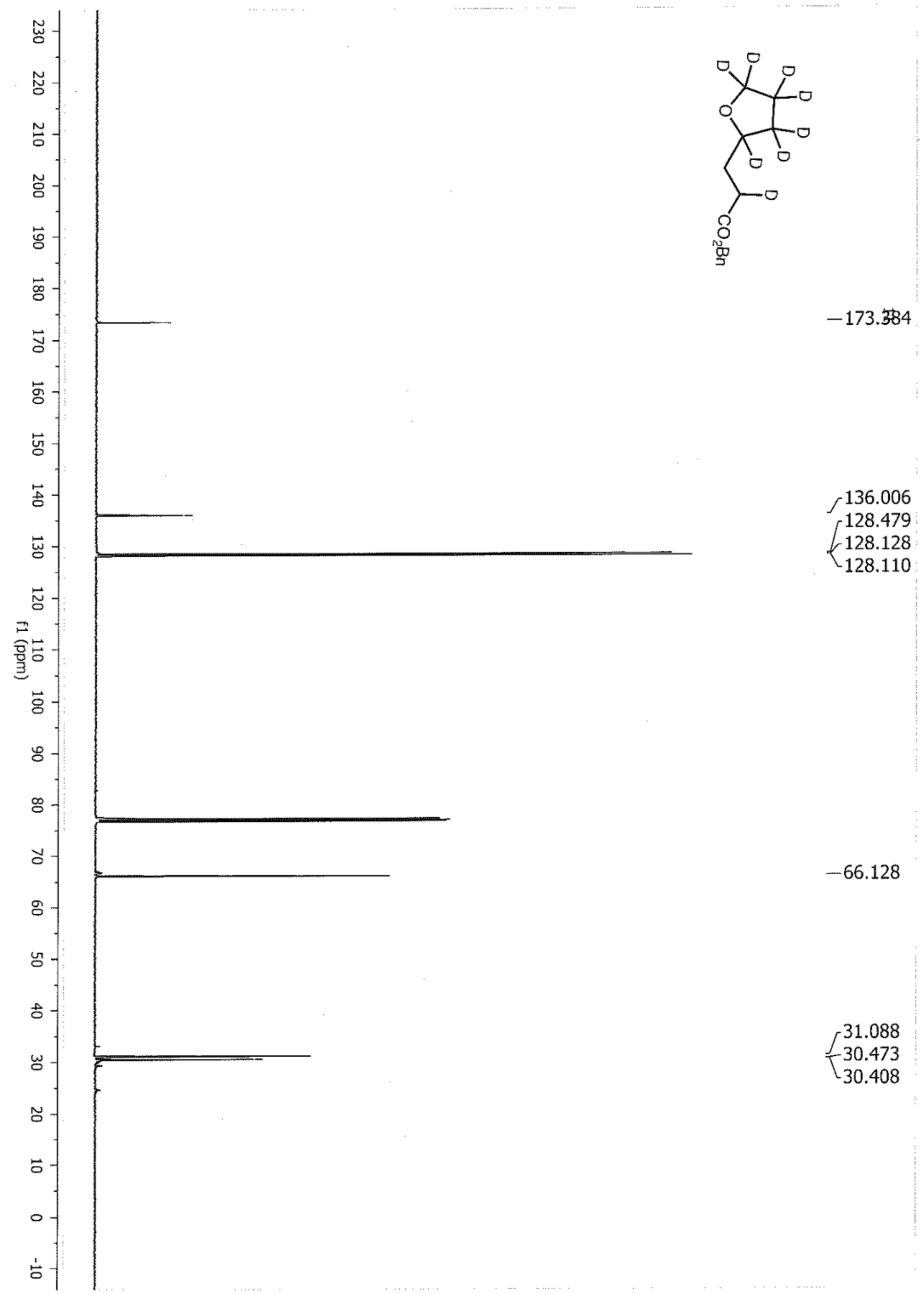
136.008
128.485
128.135
128.116
78.097
67.667
66.139
31.135
31.124
30.637
25.671
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



D
D
O
D
D
D
D
D
D
CO2Bn
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.90
2.03
1.55
2.00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D
D
D
D
D
D
D
O
D
CO2Bn
—173.384
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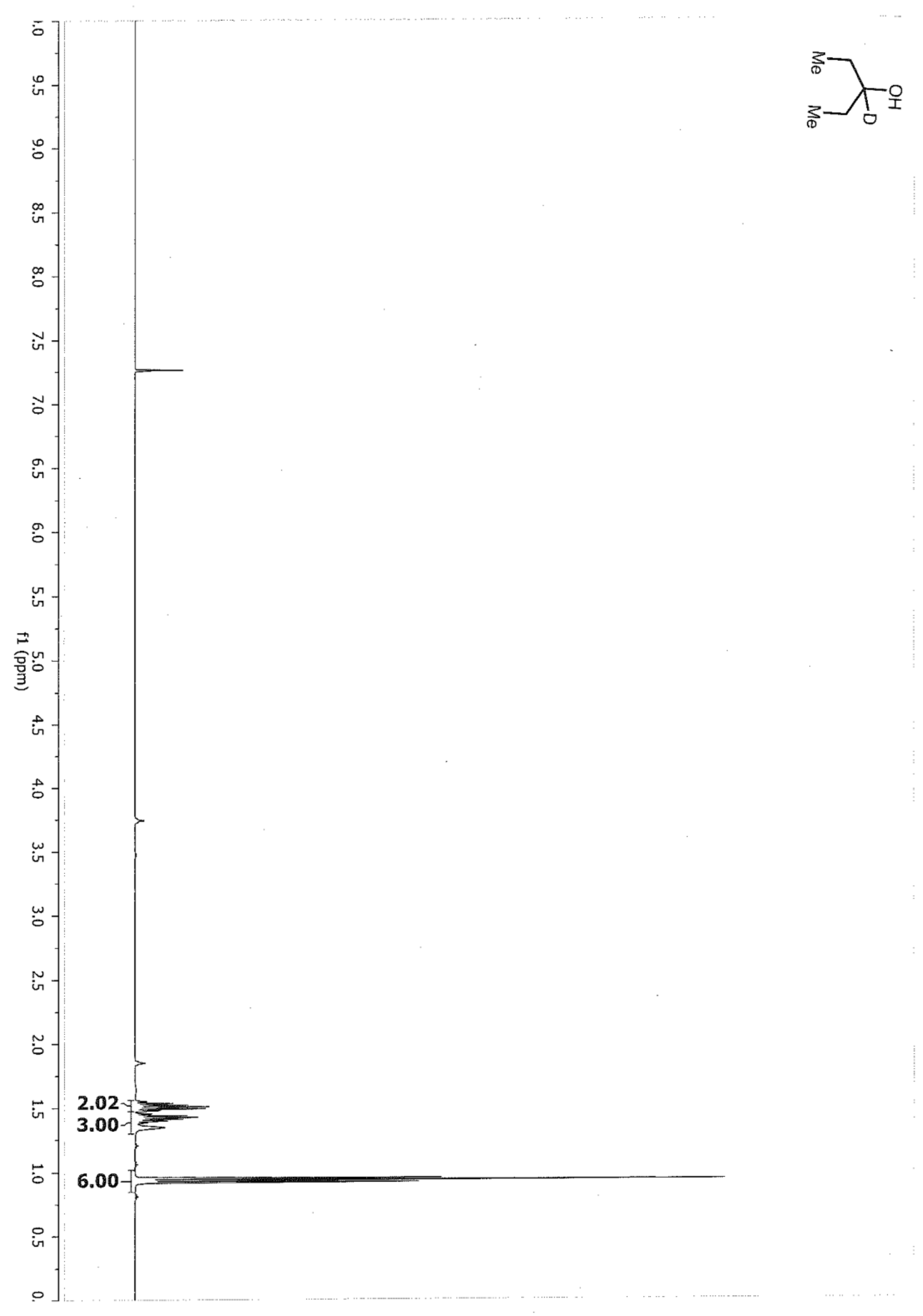
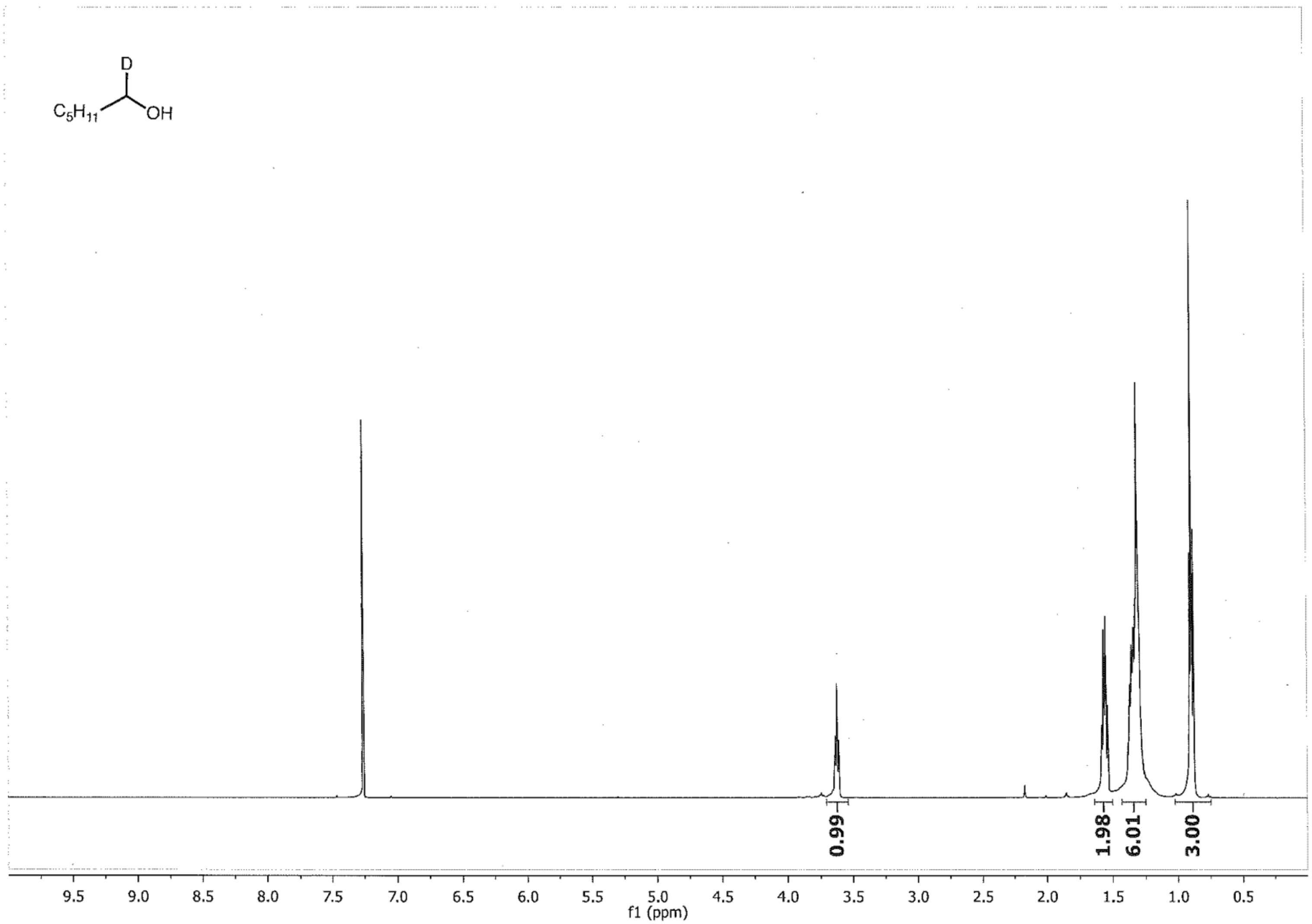
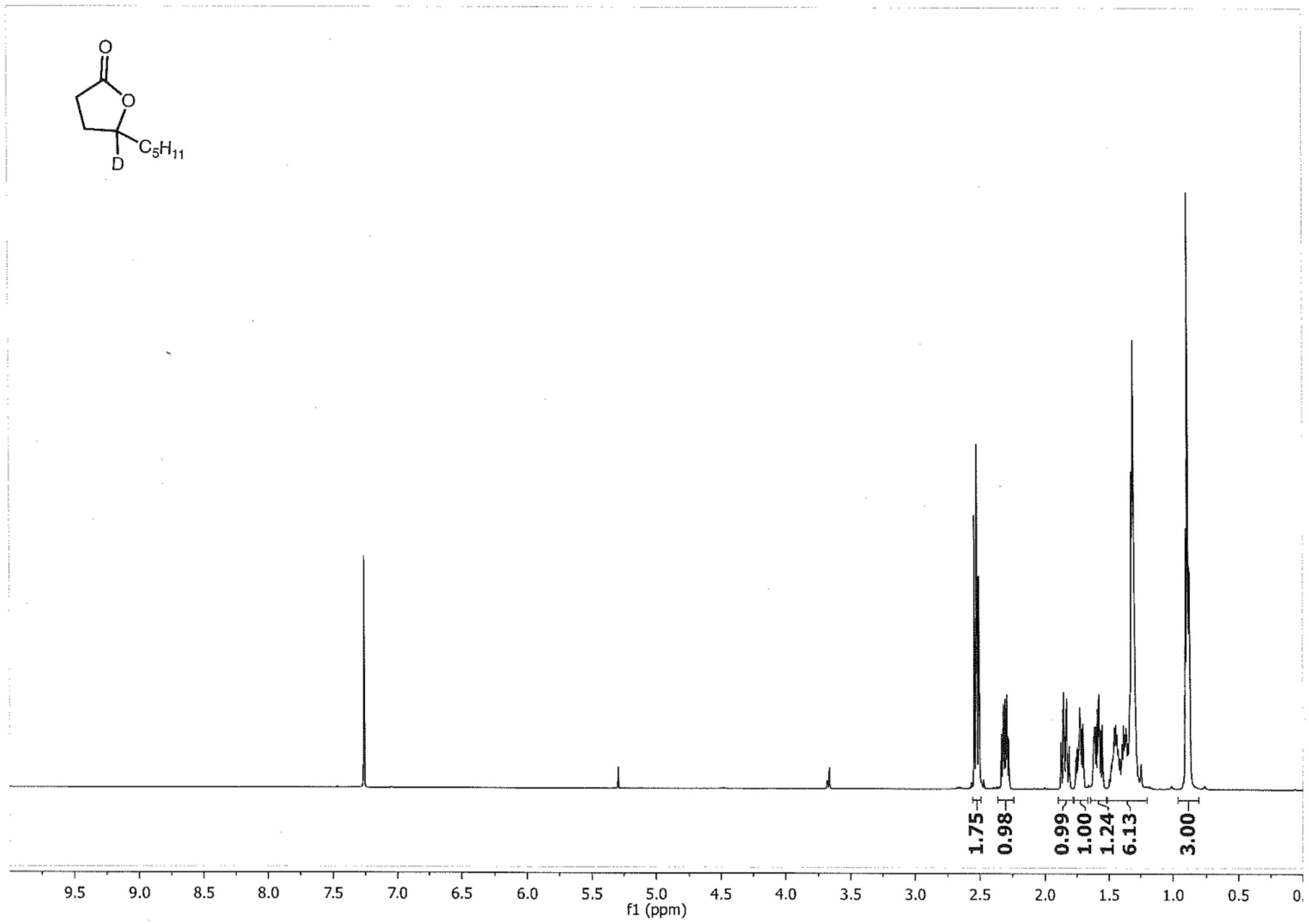
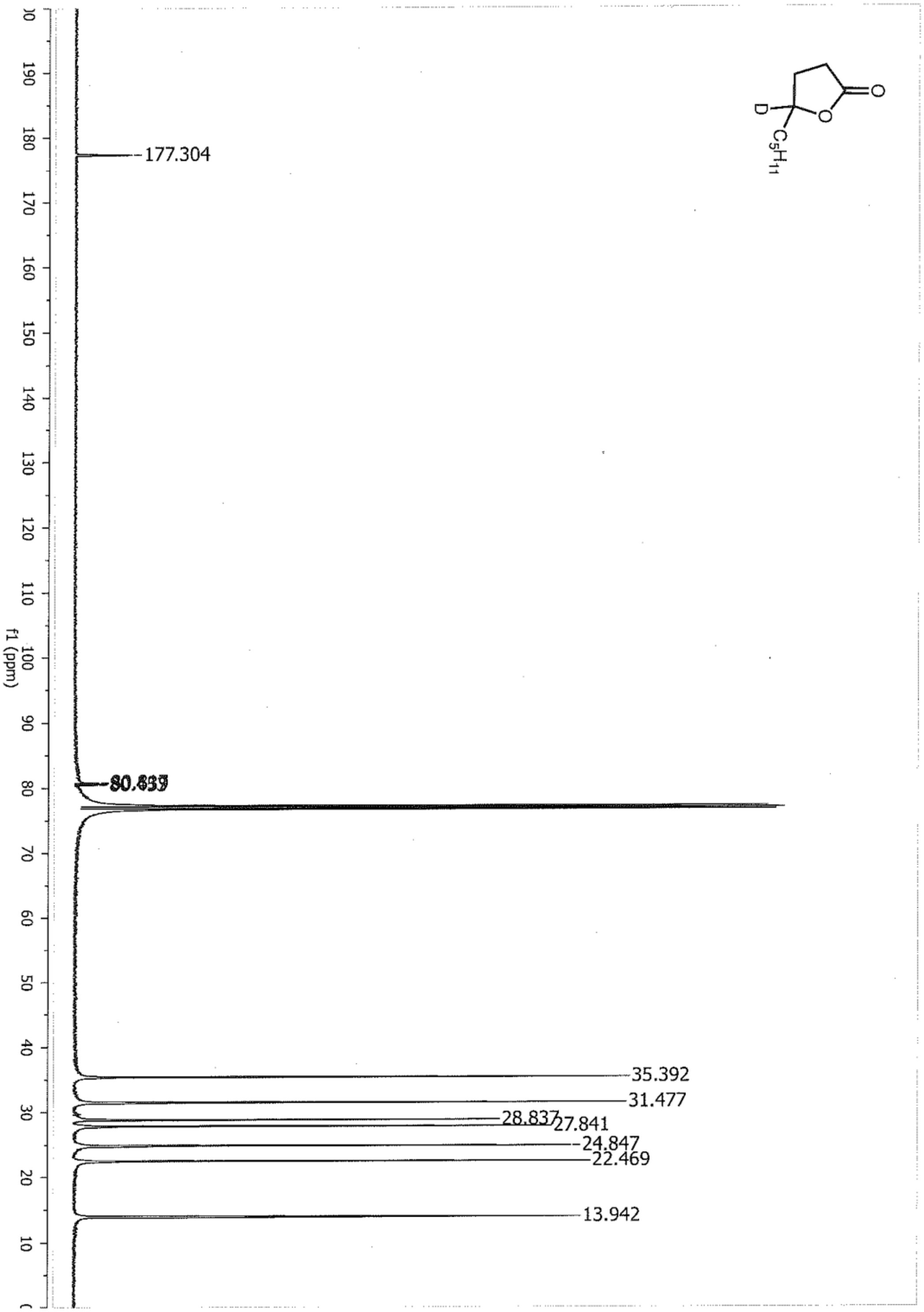
128.479
128.128
128.110
—66.128
31.088
30.473
30.408
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
D
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.02
3.00
6.00


D
C_5H_{11}
OH
0.99
1.98
6.01
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
O
D
C5H11
1.75
0.98
0.99
1.00
1.24
6.13
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



O
O
D
C_5H_{11}
177.304
80.659
35.392
31.477
28.837
27.841
24.847
22.469
13.942
f1 (ppm)
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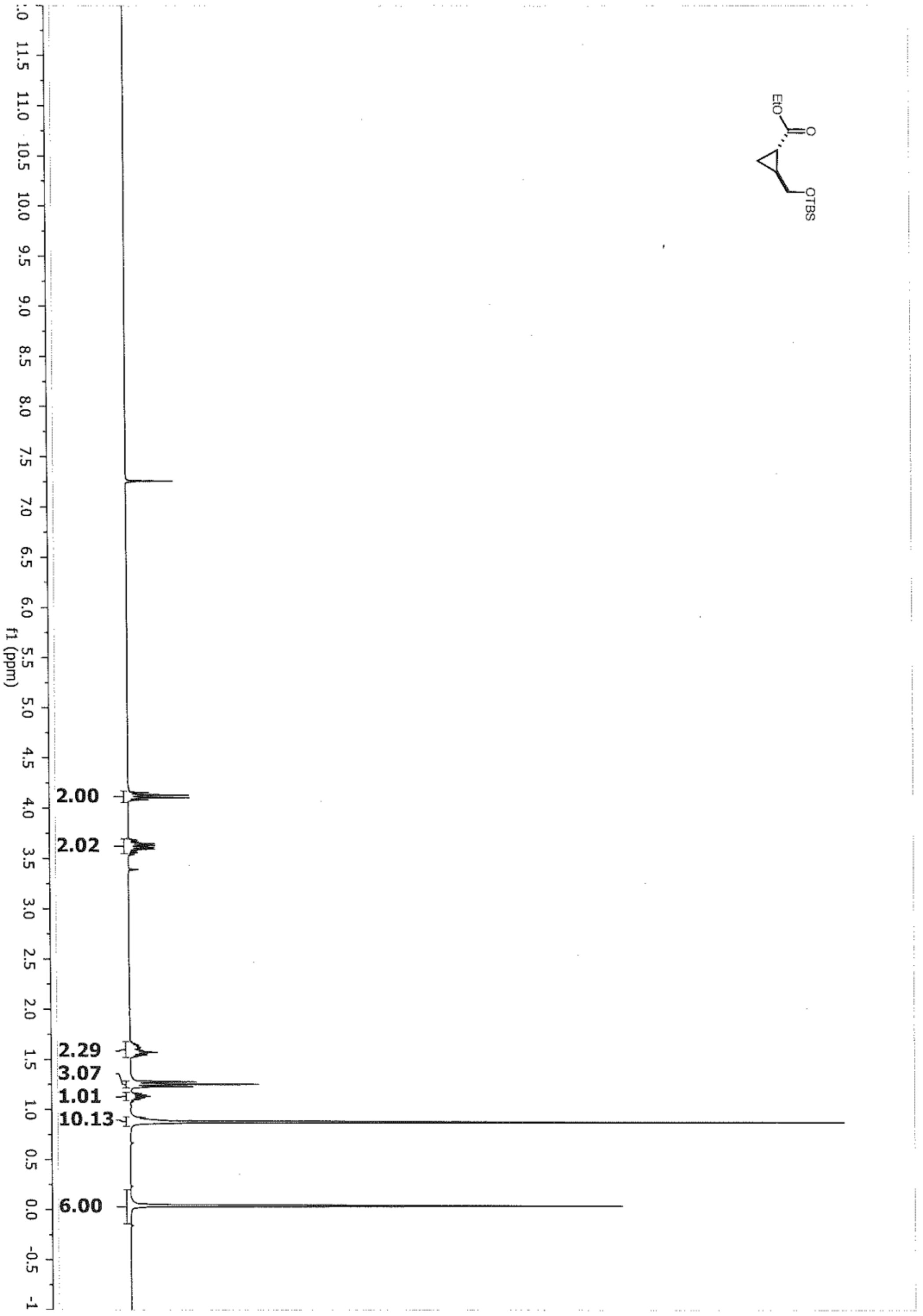
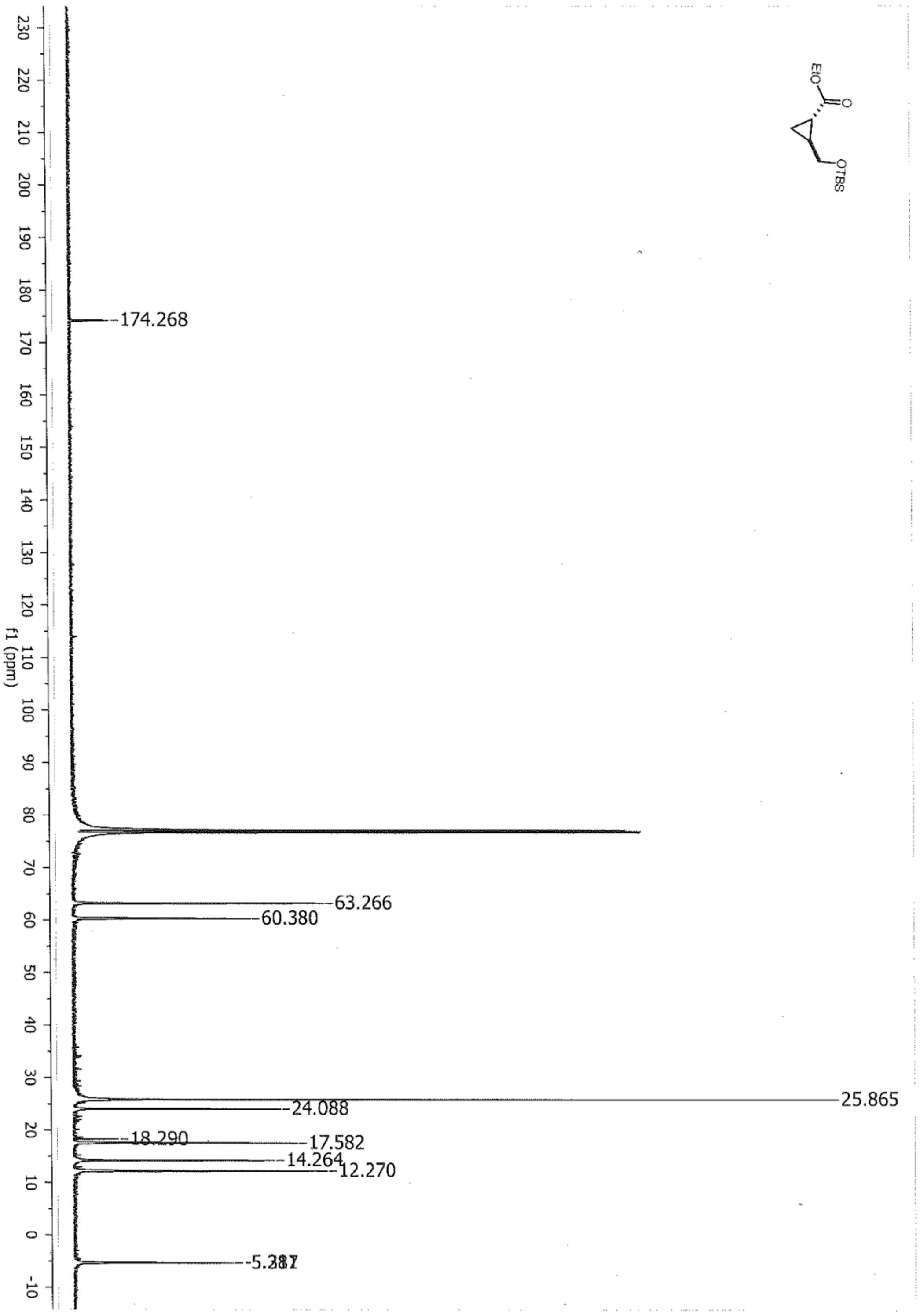
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


O
EtO
OTBS
.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
2.00
2.02
2.29
3.07
1.01
10.13
6.00


EtO
O
OTBS
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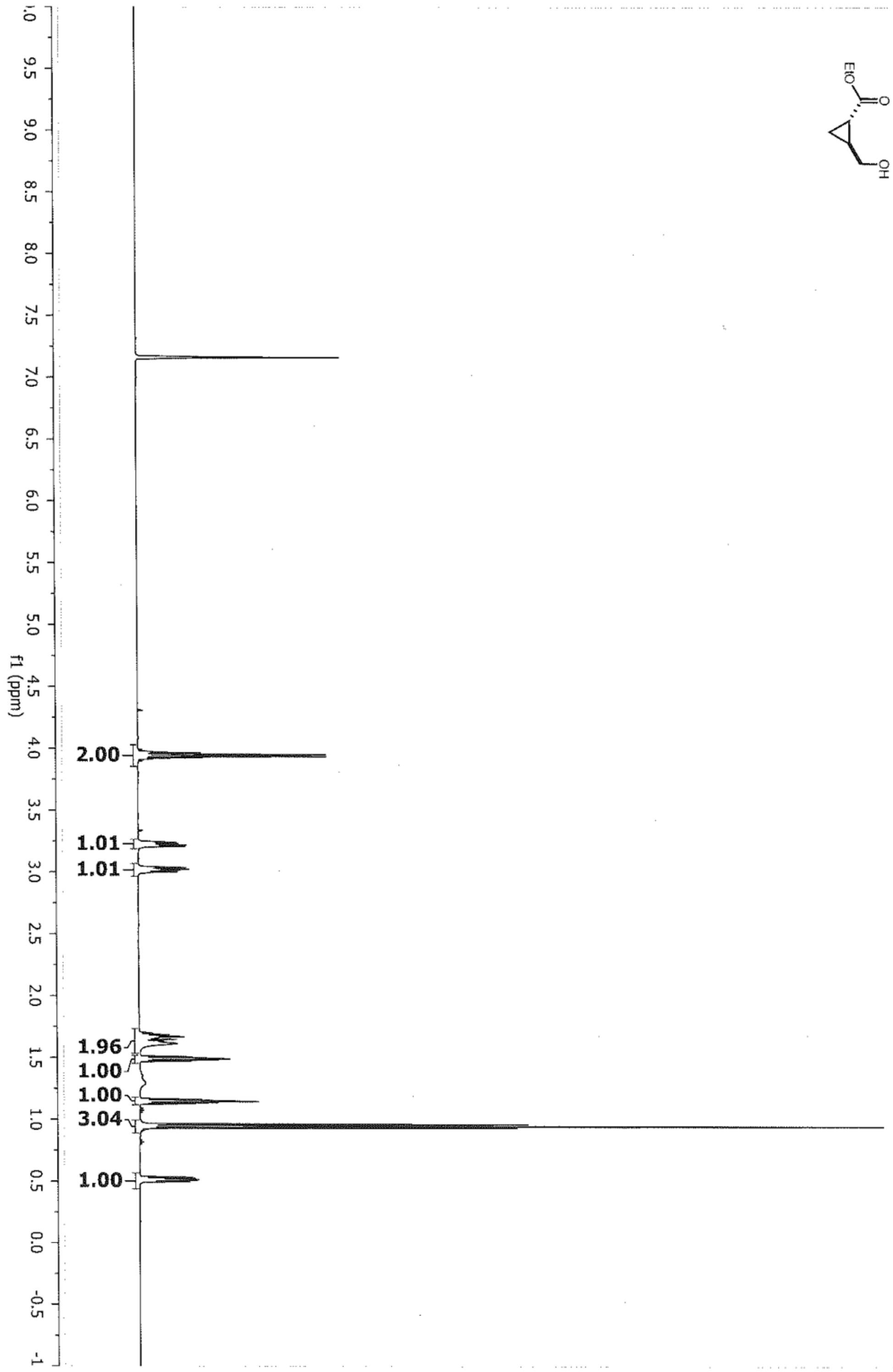
60.380
25.865
24.088
18.290
17.582
14.264
12.270
-5.381
-5.287
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


EtO
O
OH
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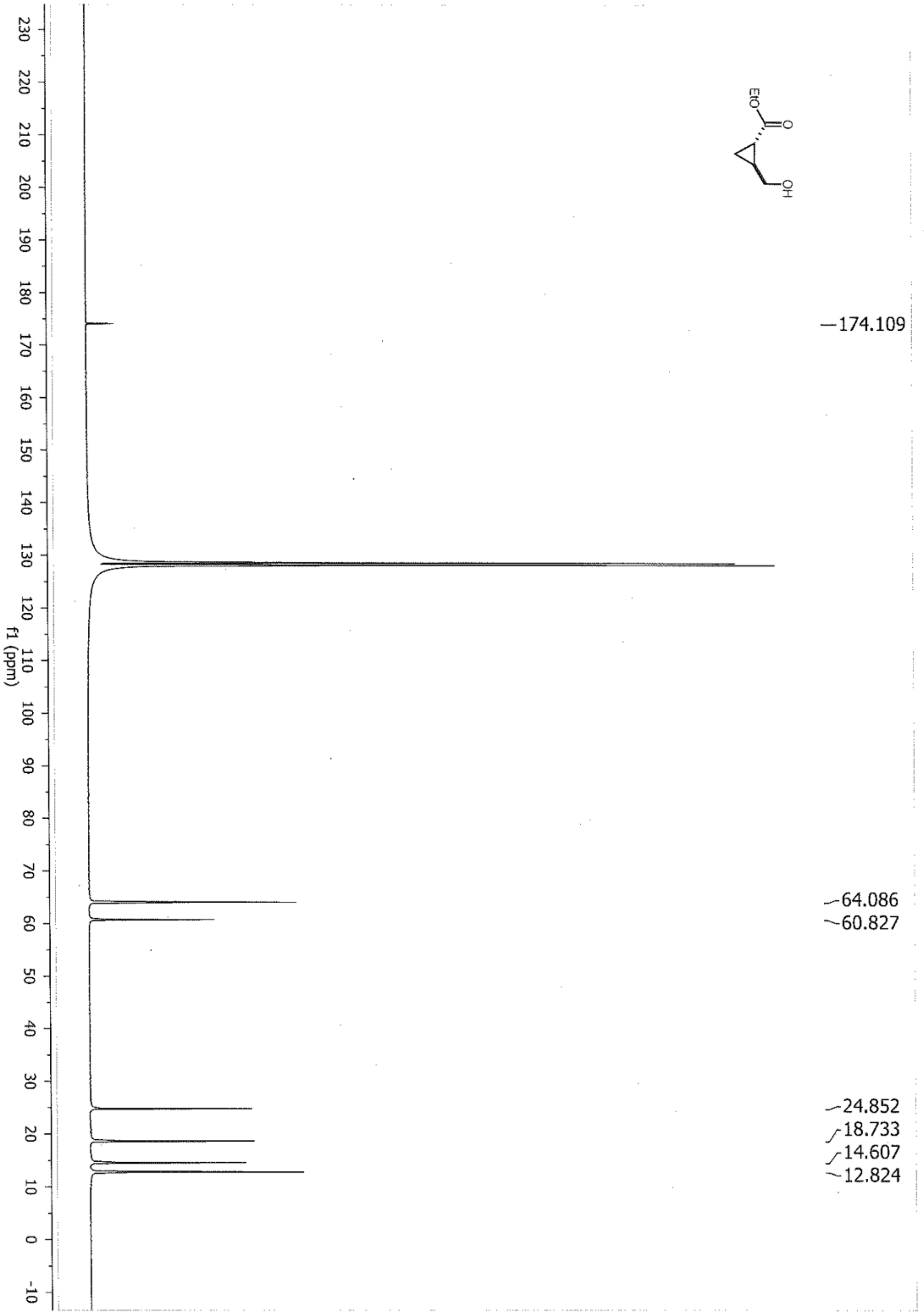
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
2.00
1.01
1.01
1.96
1.00
1.00
3.04
1.00


EtO
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OH
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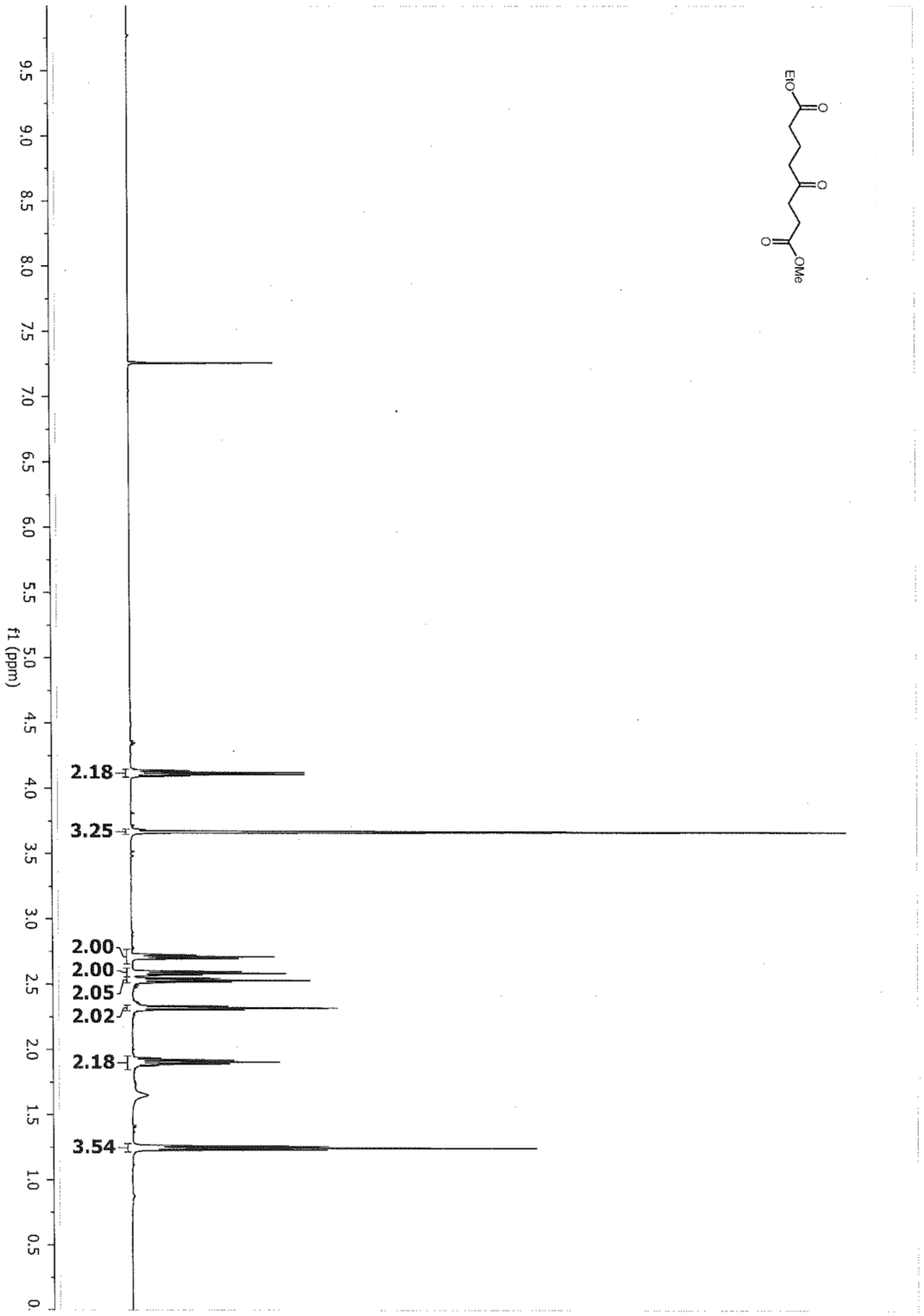
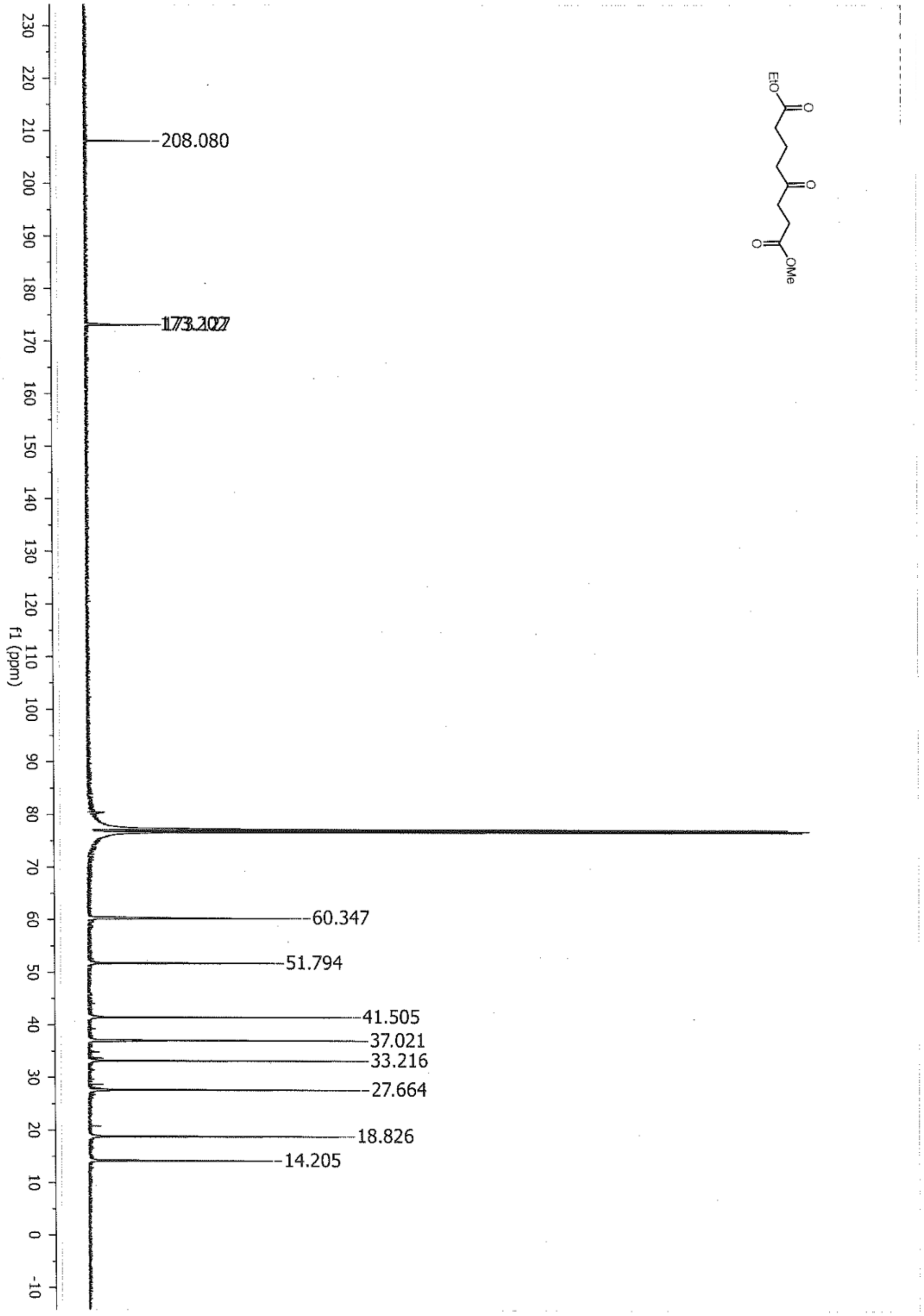
64.086
60.827
24.852
18.733
14.607
12.824
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

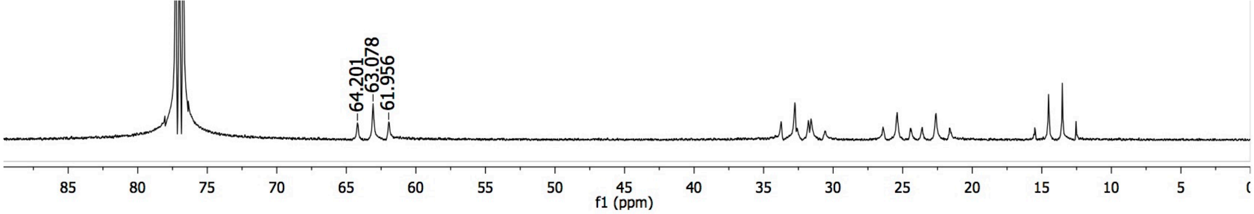

EtO
O
O
O
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)
2.18
3.25
2.00
2.00
2.05
2.02
2.18
3.54


EtO
O
O
O
OMe
208.080
173.2027
60.347
51.794
41.505
37.021
33.216
27.664
18.826
14.205
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

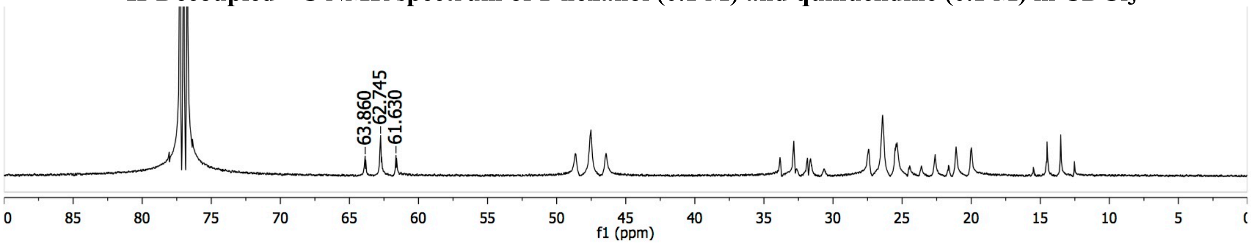
Determination of ${}^{1}J_{CH}$

Solutions of 1-hexanol (10 µL) 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.

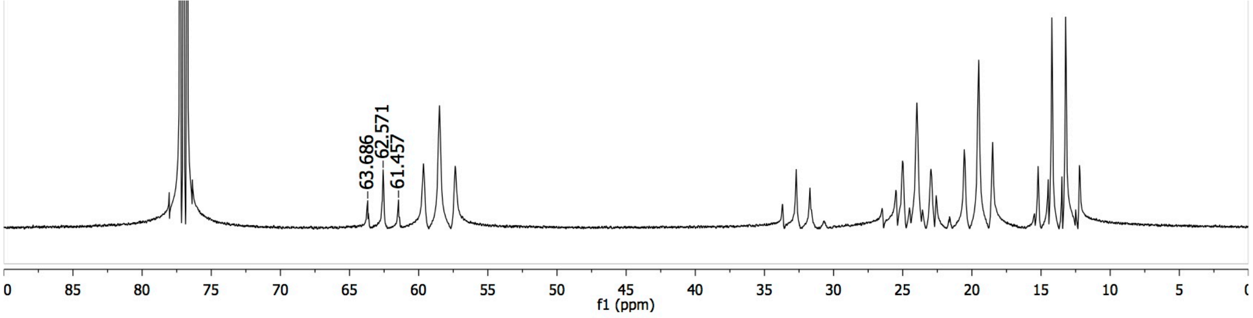
${}^{1}H$-Decoupled ${}^{13}C$ NMR spectrum of 1-hexanol (0.1 M) in $CDCl_3$



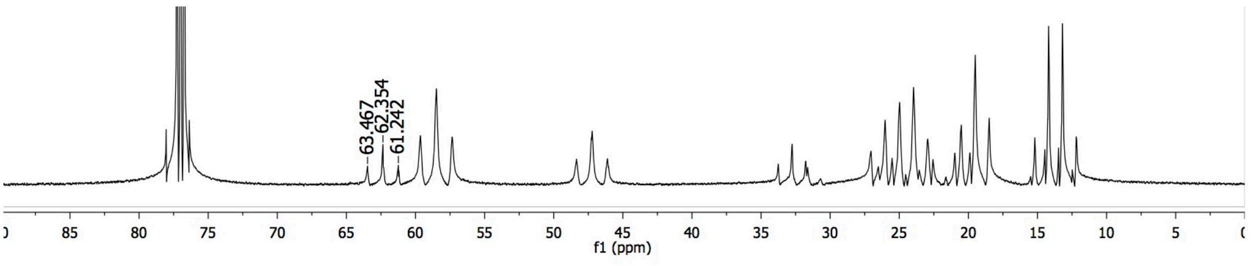
${}^{1}H$-Decoupled ${}^{13}C$ NMR spectrum of 1-hexanol (0.1 M) and quinuclidine (0.1 M) in $CDCl_3$



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



${}^{1}H$-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

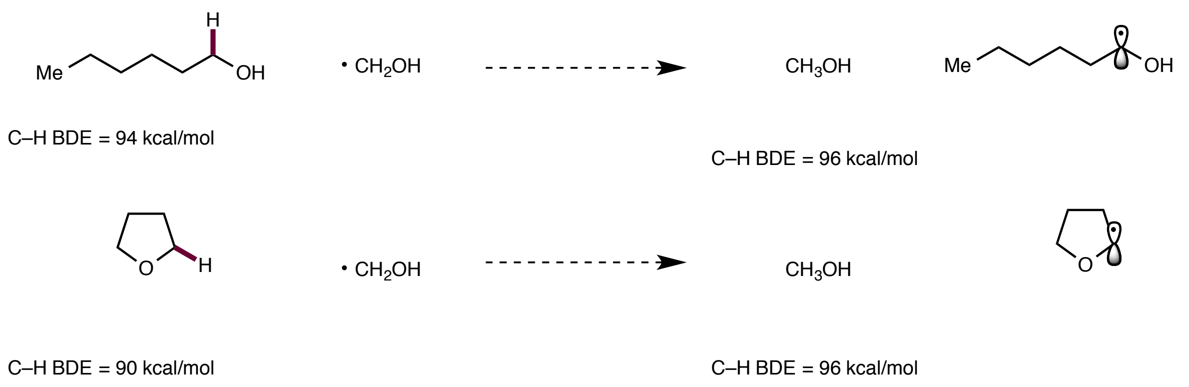
All calculations used DFT methodology as implemented in the Gaussian 09 series of computer programs (*72*, *73*). We employed the unrestricted B3LYP functional (*74–78*). All-electron, split-valence double-ζ plus polarization function 6-31G(d,p) basis sets were used (*79–82*). Calculations were performed 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^{-1}.

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

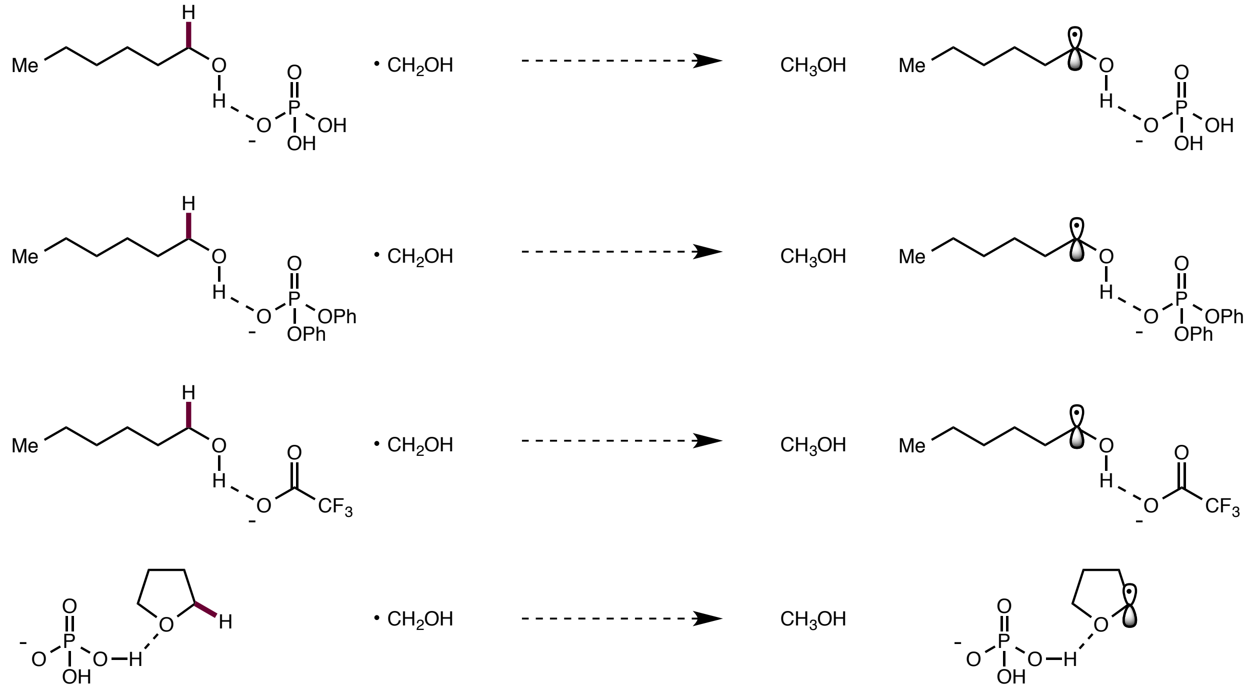


Table S2. Analysis of the isodesmic reactions above. Energies are provided in kcal mol^{-1} using the conversion factor 627.509 kcal mol^{-1} per hartree and are rounded off after the third decimal place. Entropies are provided in e.u. and are rounded off after the third decimal place.

Rxn	Entries for Δ	ΔE+ZPE	ΔG	ΔH	ΔS
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 ΔΔ of the Reactions A and B above; the results are shown below:

Quantity	ΔΔE+ZPE	ΔΔG	ΔΔH	ΔΔS
Hexanol				
Dihydrogen phosphate Bond Weakening	–2.533	0.379	**–3.116**	–11.720
Diphenyl phosphate Bond Weakening	–2.442	–3.043	**–2.419**	2.092
Trifluoroacetate Bond Weakening	–2.497	–0.732	**–3.086**	–7.896
Tetrahydrofuran				
Dihydrogen phosphate Bond Strengthening	4.212	6.585	**2.935**	–12.242

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

The α-oxy C–H bond of tetrahydrofuran is calculated to have a BDE of ~90.3 kcal mol^{-1}. Conversely, when hydrogen-bound to dihydrogen phosphate, the tabulated ΔH values at 6-31G(d,p) predict a tetrahydrofuran α-C–H BDE bond-strengthening of 2.9 kcal mol^{-1}. This increase in BDE corresponds to an α-C–H BDE of 93.2 kcal mol^{-1}.

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

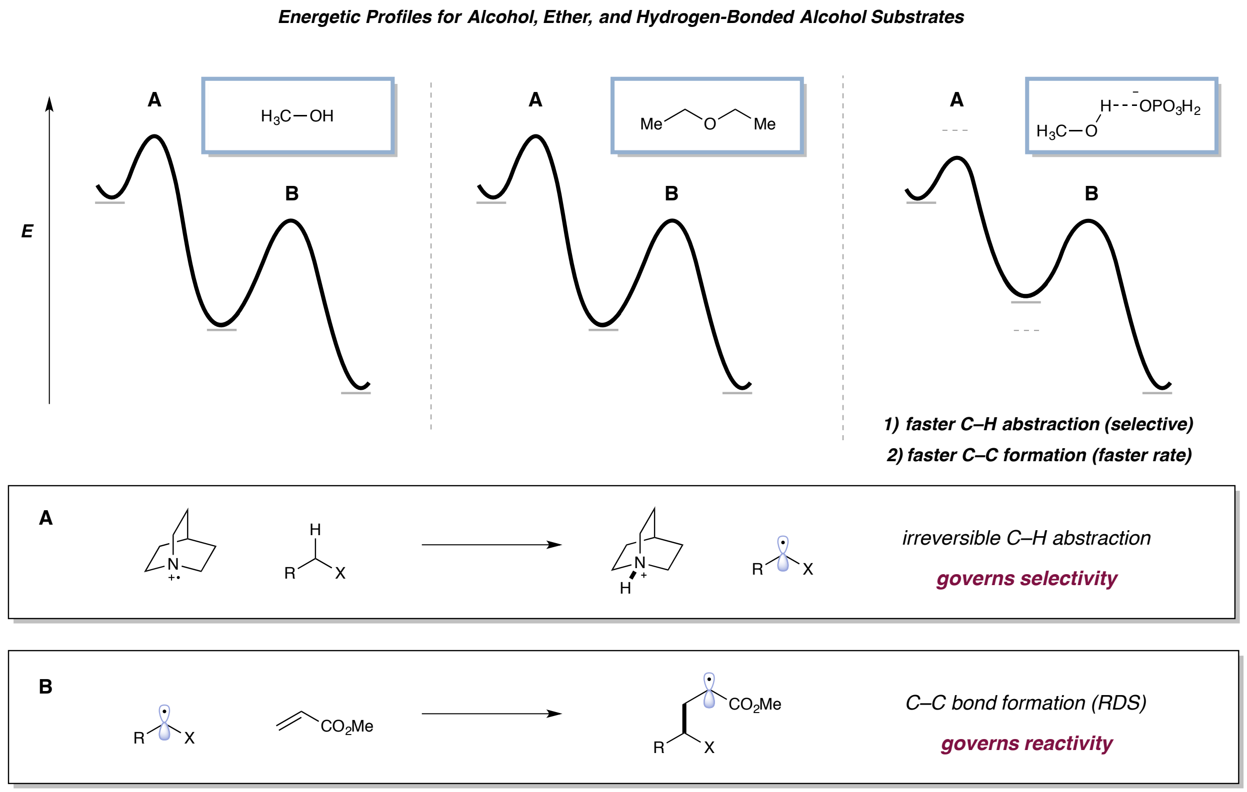


Figure S9. Reaction coordinate diagram showing the proposed effect of TBAP on C–H abstraction and C–C bond formation.