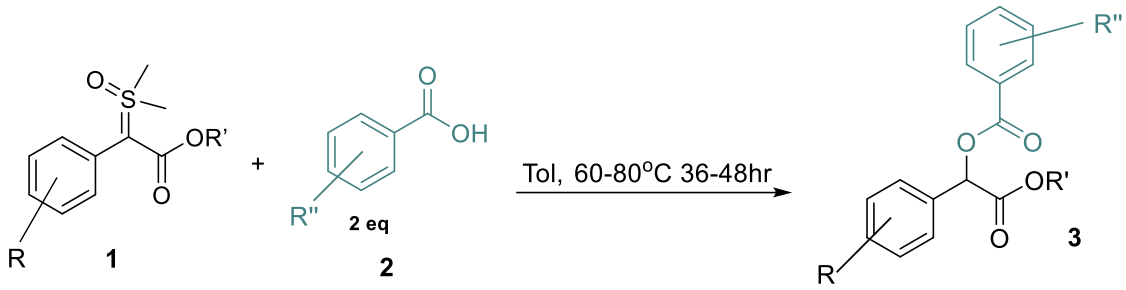
Unique Reactions of Sulfoxonium Ylides

Supporting Information

Marissa Allegrezza

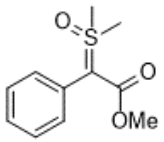
General procedure for racemic O-H insertion of sulfoxonium ylides:



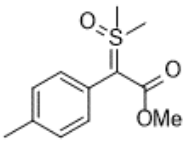
To a 2mL flame dried glass vial with a stir bar, fitted with a screw cap that has a Teflon coated septum for injections, was added 0.1 mmol of the respective sulfoxonium ylide (1 equiv.), 0.02mmol of the respective benzoic acid (2 equiv.), and 0.2mL of toluene (0.5M). The reaction was left to stir at 60-80°C for 48-72hrs. The product was purified by column chromatography using EtOAc: Hexanes (dependent for each product).

Table of ylides for references:

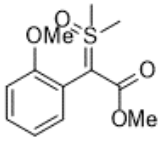
1a



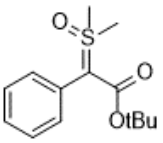
1b



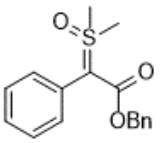
1c



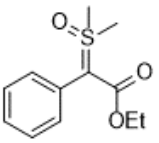
1d



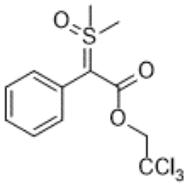
1e



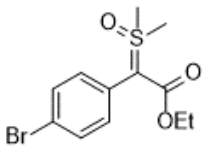
1f



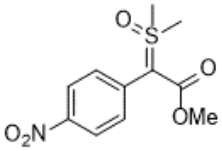
1g



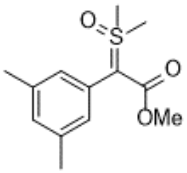
1h



1i

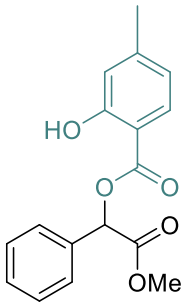


1j



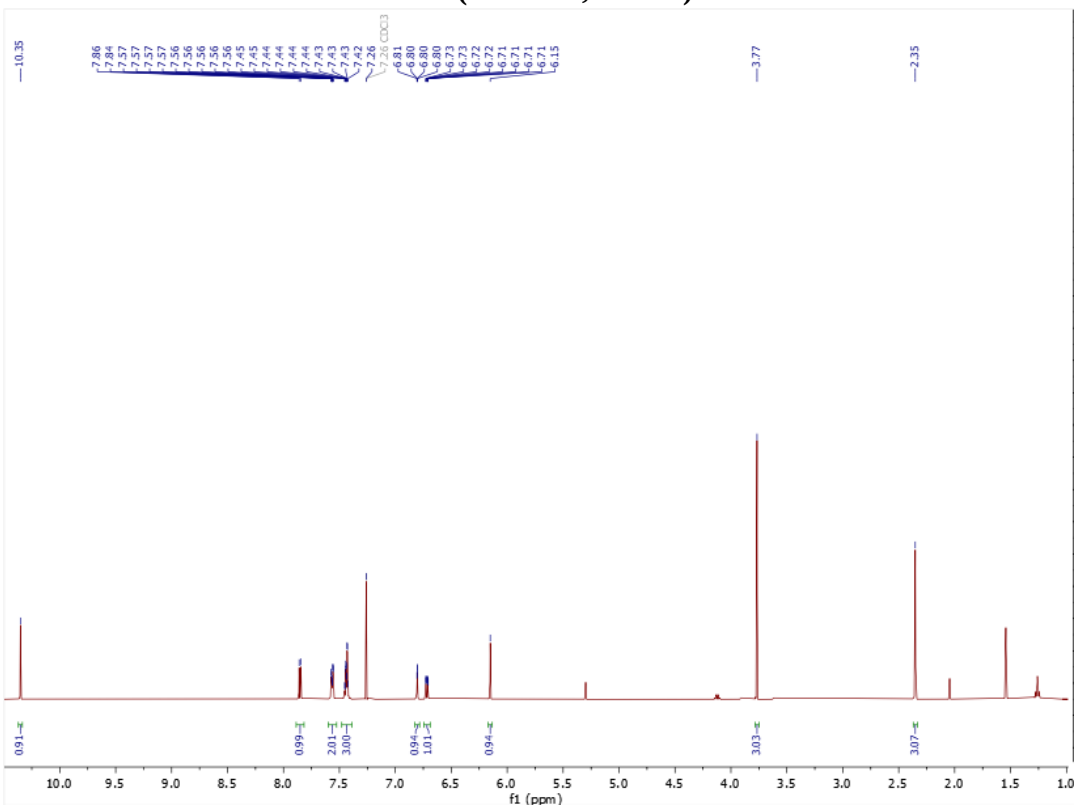
Only spectra for new compounds are provided. For spectra of sulfoxonium ylides and the literature known compounds, please see: Angew. Chem. Int. Ed.2020,59, 15554–15559; Audrey Chan and Karl A. Scheidt. *Journal of the American Chemical Society* **2006** *128* (14), 4558-4559.

3a. 2-methoxy-2-oxo-1-phenylethyl 2-hydroxy-4-methylbenzoate

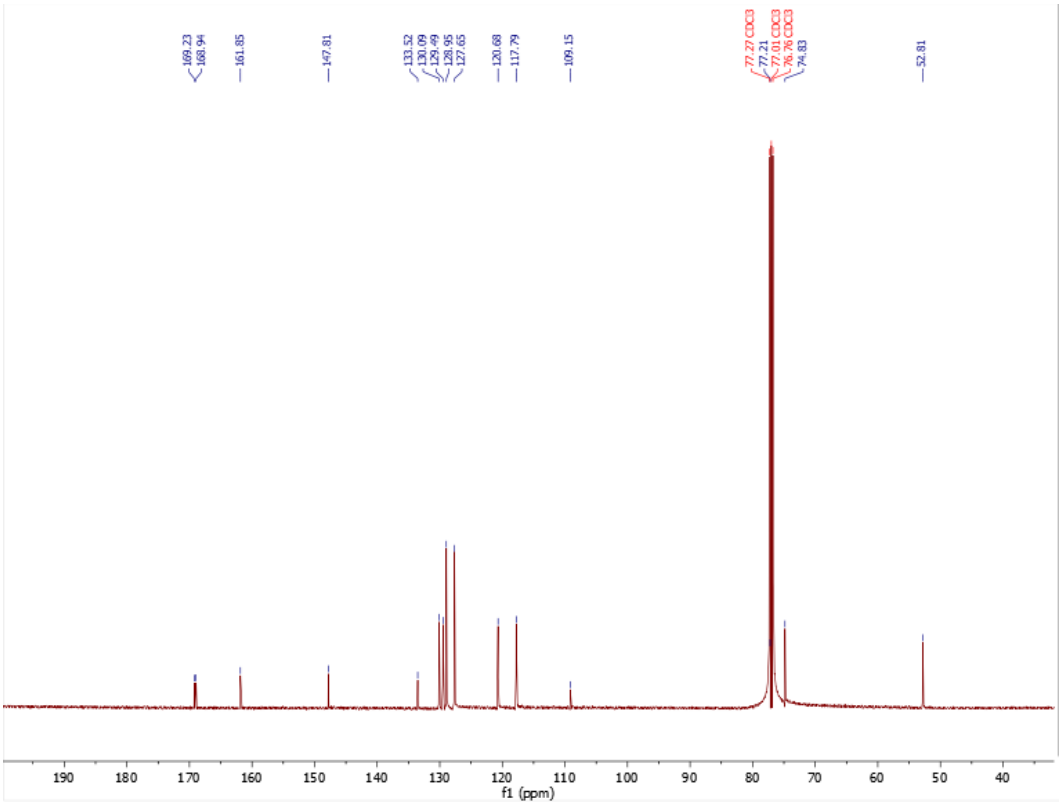


Prepared from **1a** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3a** as a white solid (14% y). **Rf =** 0.47 (1:9 EtOAc/Hex); **m.p=** 104^{o}C; **^{1}H NMR** (500 MHz, CDCl3) δ 10.35 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.48 – 7.39 (m, 3H), 6.80 (dd, J = 1.7, 0.9 Hz, 1H) ppm, 6.72 (ddd, J = 8.3, 1.6, 0.7 Hz, 1H), 6.15 (s, 1H), 3.77 (s, 3H), 2.35 (s, 3H), 1.30 – 1.23 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.38, 169.08, 162.00, 147.96, 133.67, 130.24, 129.63, 129.10, 127.80, 120.83, 117.93, 109.30, 77.36, 74.98, 52.96, 29.85, 22.10 ppm; **IR (neat): ν (cm-1) =** 3238, 3035, 2922, 1760, 1685, 1620, 1578, 1501, 1456, 1433, 1351, 1334, 1292, 1268, 1246, 1221, 1195, 1143, 1088, 1032, 1004, 964, 948, 897, 867, 823, 775, 752, 734, 690, 618, 607.

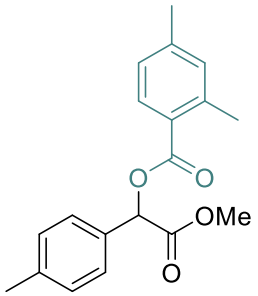
^{1}H NMR (500 MHz, CDCl3): 3a



^{13}C NMR (126 MHz, CDCl$_3$): 3a

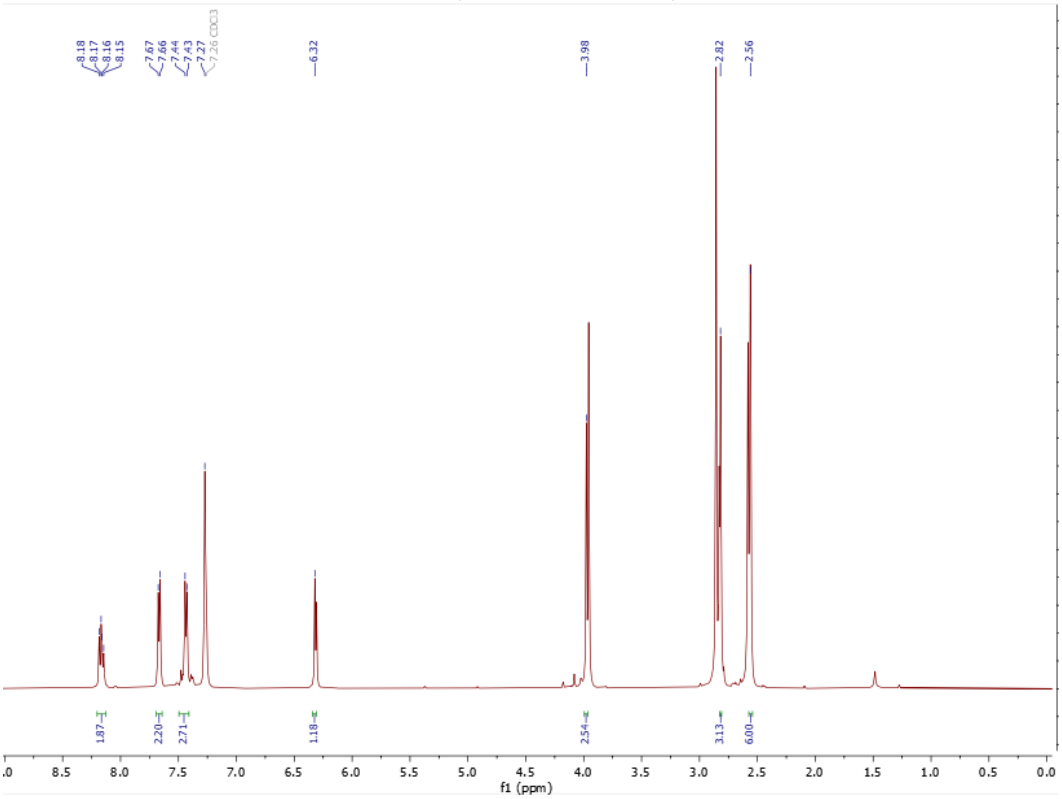


3b. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2,4-dimethylbenzoate

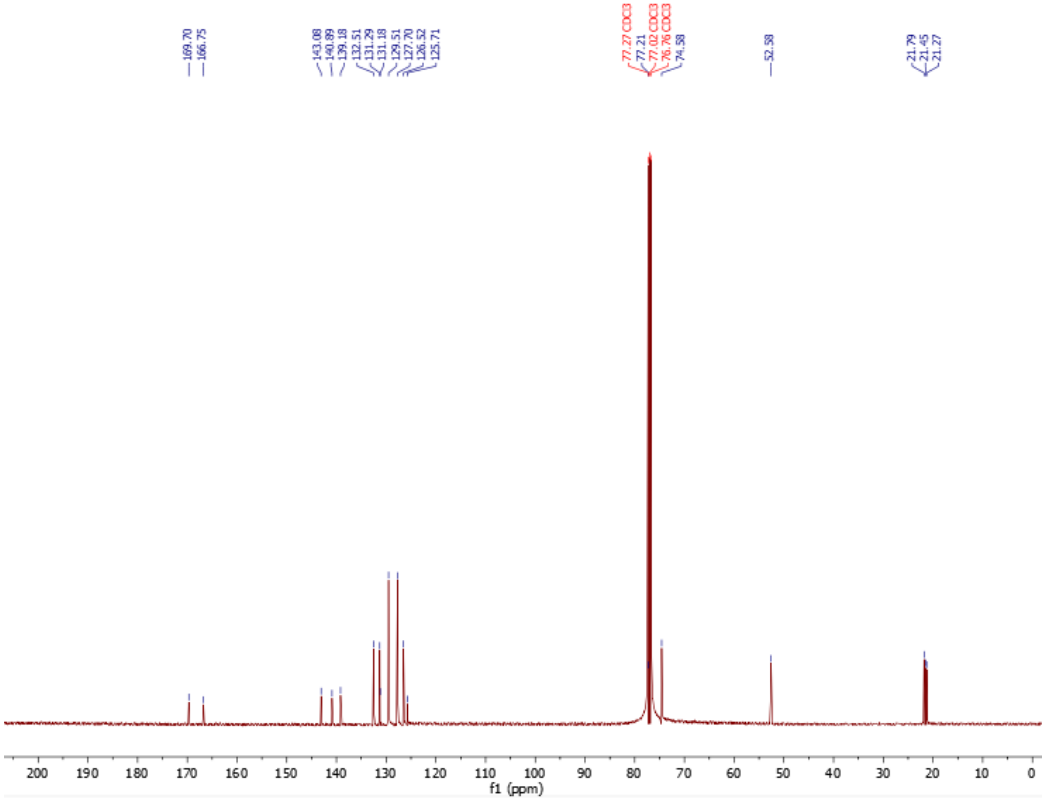


Prepared from **1b** and 2,4-dimethylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3b** as a white solid (53% y). **Rf =** 0.50 (1:9 EtOAc/Hex); **m.p=** 56ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 11.2, 8.1 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 3H), 6.32 (s, 1H), 3.98 (s, 2H), 2.82 (s, 3H), 2.56 (d, *J* = 2.7 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.70, 166.75, 143.08, 140.89, 139.18, 132.51, 131.29, 131.18, 129.51, 127.70, 126.52, 125.71, 77.27, 77.21, 77.02, 76.76, 74.58, 52.58, 21.79, 21.45, 21.27 ppm; **IR (neat): ν (cm-1) =** 2958, 2923, 1752, 1720, 1614, 1571, 1499, 1432, 1387, 1345, 1307, 1274, 1249, 1233, 1214, 1169, 1150, 1073, 1032, 968, 935, 887, 841, 811, 789, 772, 744, 728, 699.

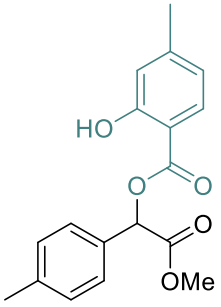
^{1}H NMR (500 MHz, $CDCl_3$): 3b



^{13}C NMR (126 MHz, $CDCl_3$): 3b

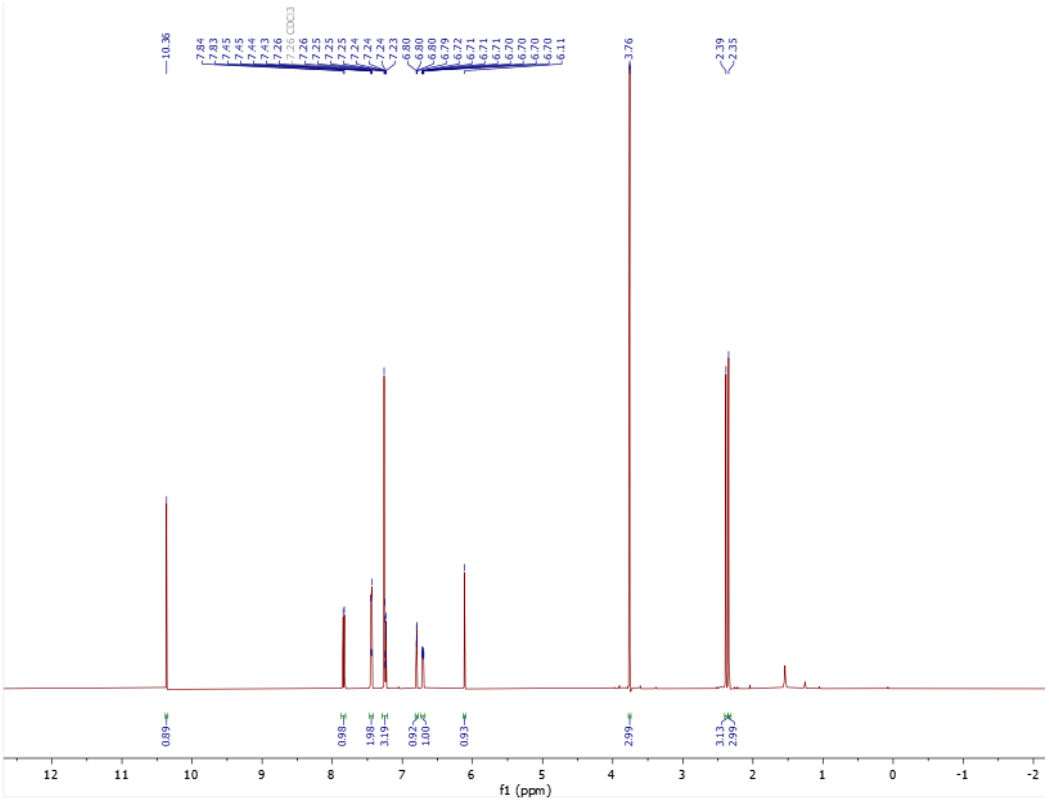


3c: 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2-hydroxy-4-methylbenzoate

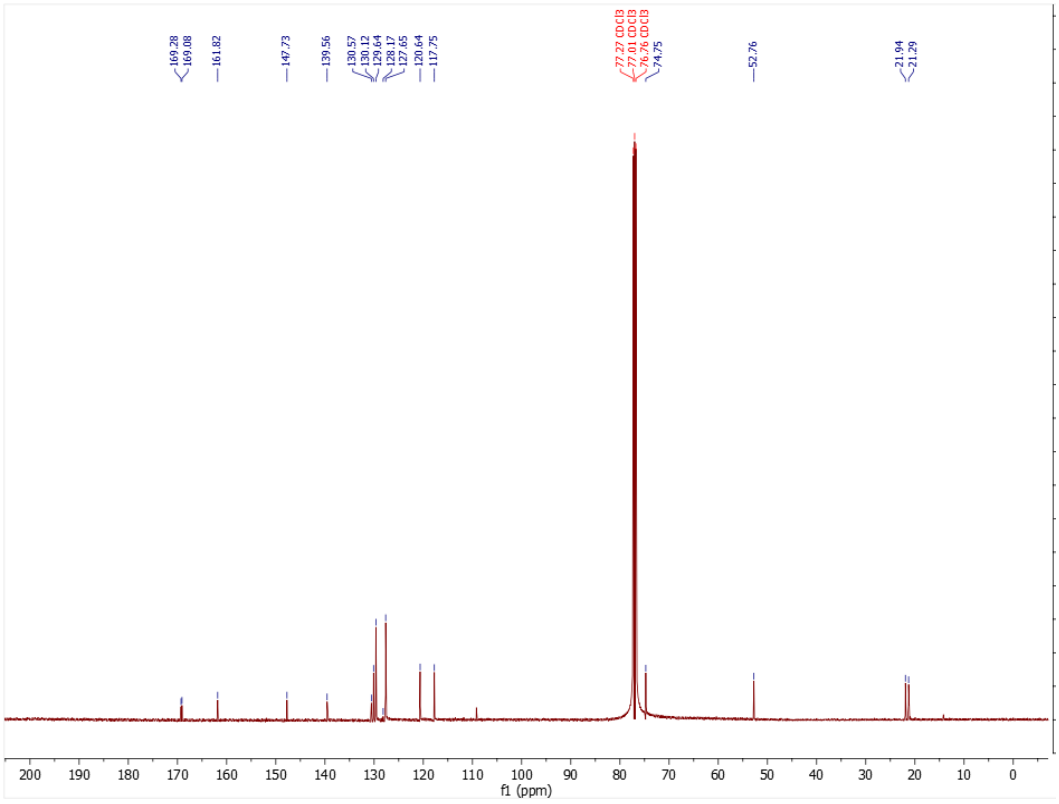


Prepared from **1b** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3c** as a clear foggy oil (35% y). **Rf =** 0.50 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.29 – 7.21 (m, 2H), 6.80 (dd, *J* = 1.7, 0.9 Hz, 1H), 6.71 (ddd, *J* = 8.2, 1.7, 0.7 Hz, 1H), 6.11 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.35 (d, *J* = 0.7 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.43, 169.22, 161.97, 147.87, 139.71, 130.71, 130.26, 129.78, 128.50, 128.32, 127.80, 120.79, 117.90, 109.36, 77.36, 74.90, 60.54, 52.90, 52.21, 22.09, 21.43, 21.20, 14.35 ppm; **IR (neat): ν (cm-1) =** 3221, 2954, 2924, 2856, 1758, 1672, 1623, 1579, 1503, 1437, 1357, 1292, 1246, 1209, 1150, 1090, 1031, 949, 868, 819, 776, 748, 734, 699.

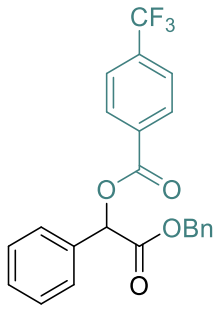
^{1}H NMR (500 MHz, $CDCl_3$): 3c



^{13}C NMR (126 MHz, $CDCl_3$): 3c

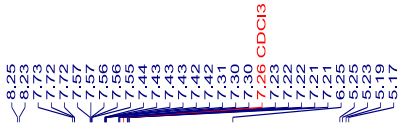


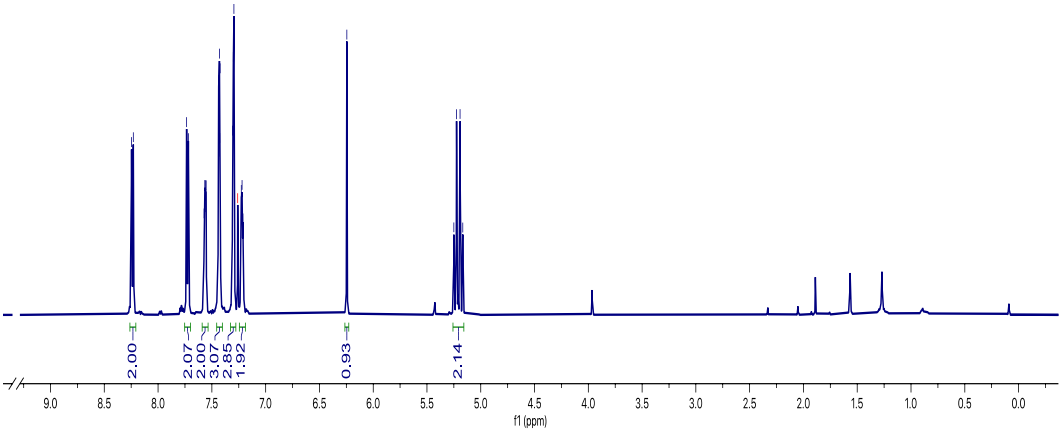
3d. 2-(benzyloxy)-2-oxo-1-phenylethyl 4-(trifluoromethyl)benzoate



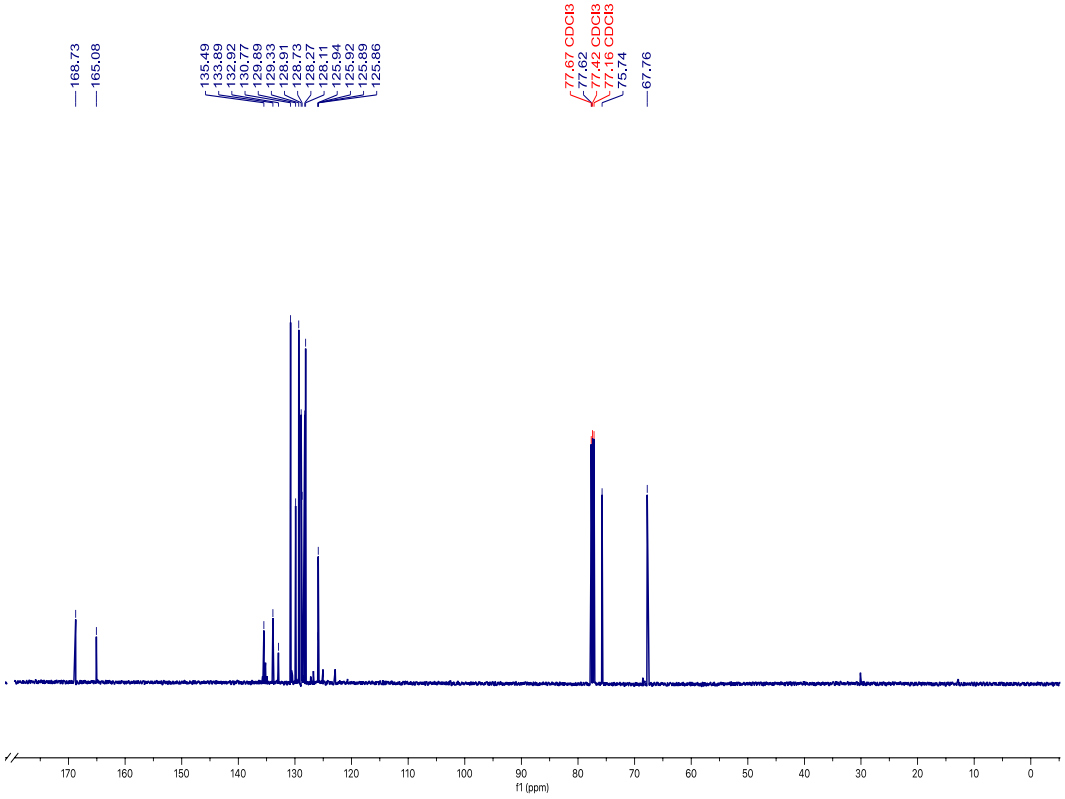
Prepared from **1e** and 4-(trifluoromethyl)benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3d** as a clear oil (74% y). **Rf =** 0.72 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.43 (dt, J = 4.4, 1.7 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.22 (dd, J = 6.9, 2.8 Hz, 1H), 6.25 (s, 1H), 5.24 (d, J = 12.4 Hz, 1H), 5.18 (d, J = 12.4 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.73, 165.08, 135.49, 133.89, 132.92, 130.77, 129.89, 129.33, 128.91, 128.73, 128.27, 128.11, 125.94, 125.92, 125.89, 125.86, 77.67, 77.62, 77.42, 77.16, 75.74, 67.76 ppm; **IR** (neat): ν (cm^{-1}) = 1751, 1729, 1585, 1496, 1454, 1413, 1476, 1323, 1294, 1259, 1204, 1159, 1110, 1065, 1036, 1015, 943, 909, 859, 836, 768, 756, 725, 697, 689, 614.

^{1}H NMR (500 MHz, $CDCl_3$): 3d

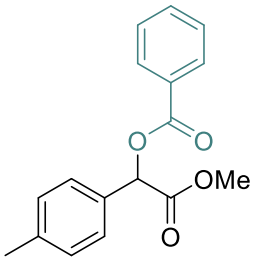




^{13}C NMR (126 MHz, $CDCl_3$): 3d

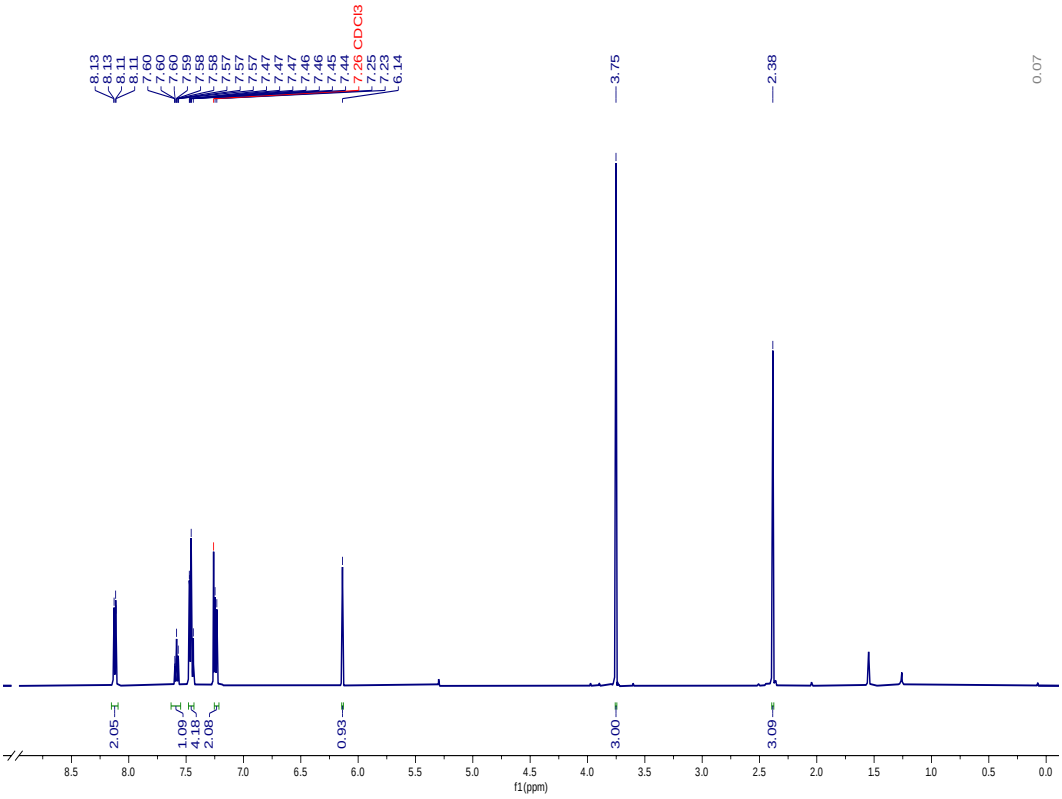


3e. 2-methoxy-2-oxo-1-(p-tolyl)ethyl benzoate

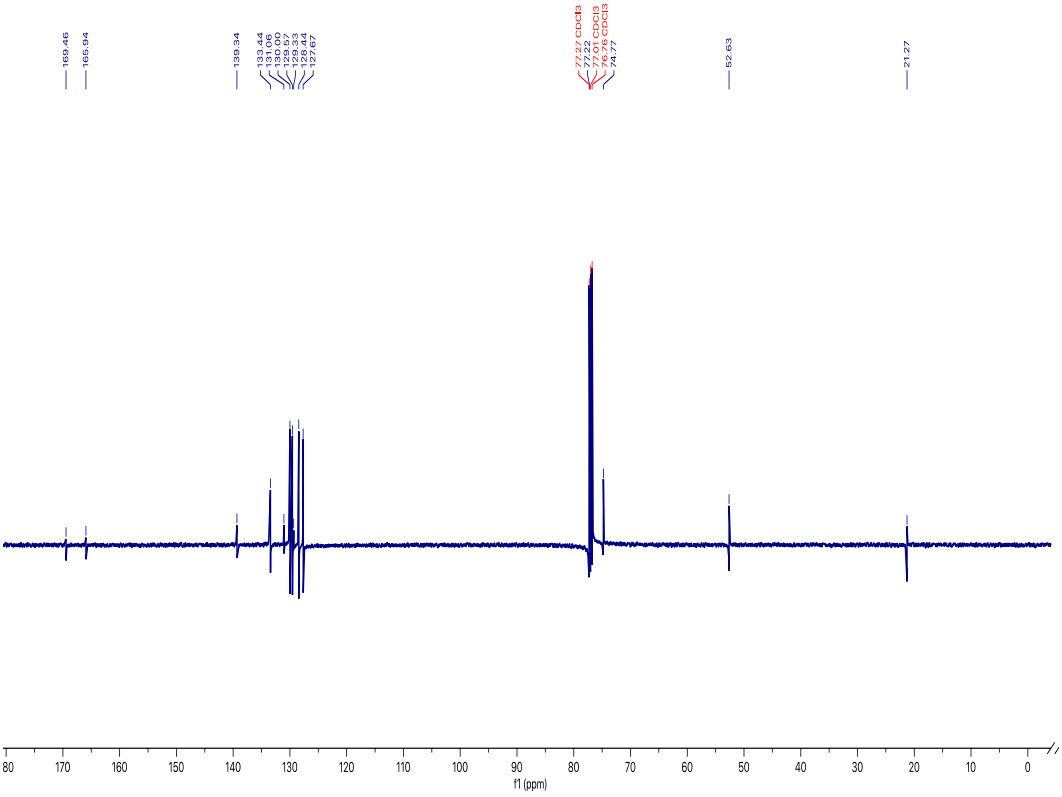


Prepared from **1b** and benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3e** as a white solid (51% y) **Rf =** 0.25 (1:9 EtOAc/Hex); **m.p=** 94°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 2H), 7.63 – 7.55 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 3H), 6.14 (s, 1H), 3.75 (s, 3H), 2.38 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.46, 165.94, 139.34, 133.44, 131.06, 130.00, 129.57, 129.33, 128.44, 127.67, 77.27, 77.22, 77.01, 76.76, 74.77, 52.63, 21.27 ppm; **IR (neat): ν (cm-1) =** 2955, 1755, 1602, 1516, 1456, 1434, 1351, 1316, 1283, 1255, 1210, 1176, 1110, 1070, 1036, 964, 925, 908,845, 819, 791, 753, 708, 635.

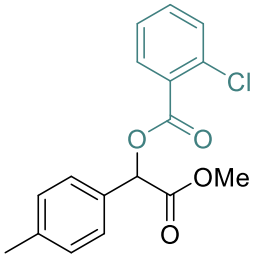
^{1}H NMR (500 MHz, $CDCl_3$): 3e



^{13}C NMR (126 MHz, $CDCl_3$): 3e

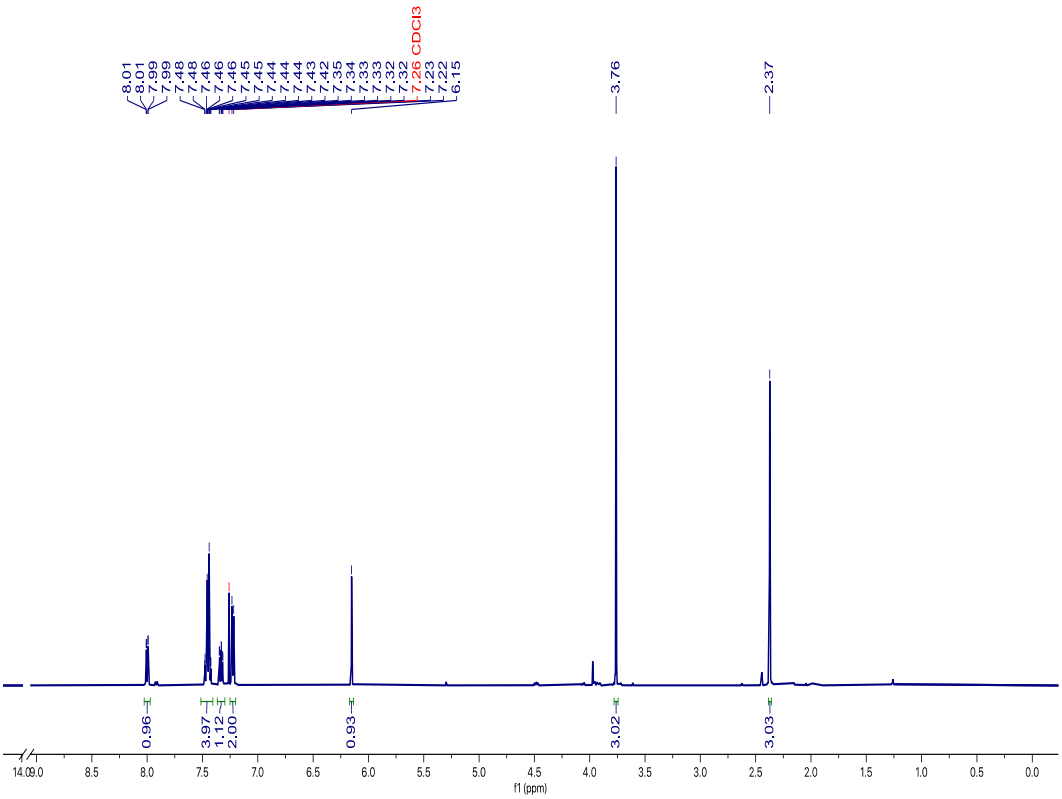


3f. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2-chlorobenzoate

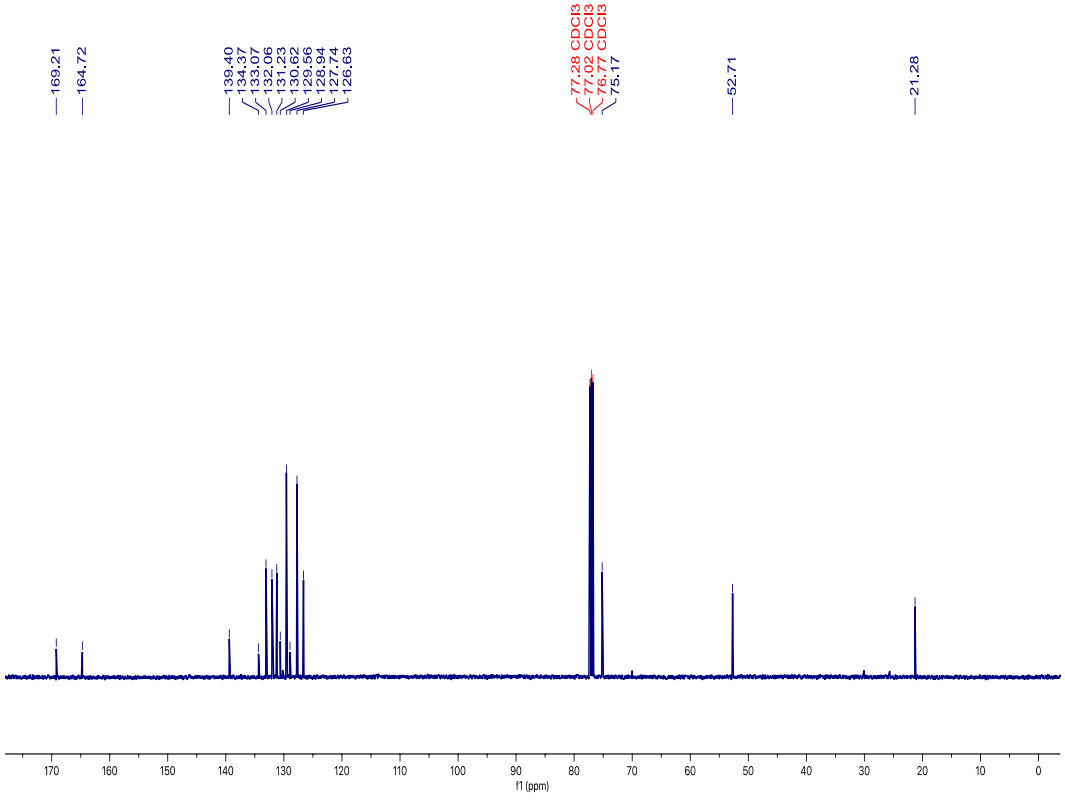


Prepared from **1b** and 2-chlorobenzoic acid. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3f** as clear, colorless oil (48% y). **Rf** = 0.34 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.7, 1.6 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.37 – 7.30 (m, 1H), 7.23 (d, J = 7.8 Hz, 2H), 6.15 (s, 1H), 3.76 (s, 4H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.21, 164.72, 139.40, 134.37, 133.07, 132.06, 131.23, 130.62, 129.56, 128.94, 127.74, 126.63, 77.28, 77.02, 76.77, 75.17, 52.71, 21.28 ppm; **IR (neat): ν (cm^{-1}) =** 2955, 1735, 1591, 1516, 1469, 1436, 1342, 1291, 1242, 1218, 1174, 1110, 1050, 966, 909, 788, 756, 699, 650.

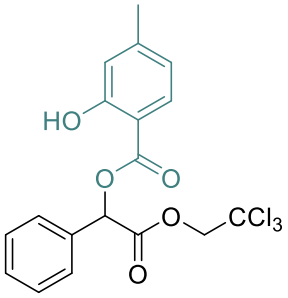
^{1}H NMR (500 MHz, $CDCl_3$): 3f



^{13}C NMR (126 MHz, CDCl$_3$): 3f

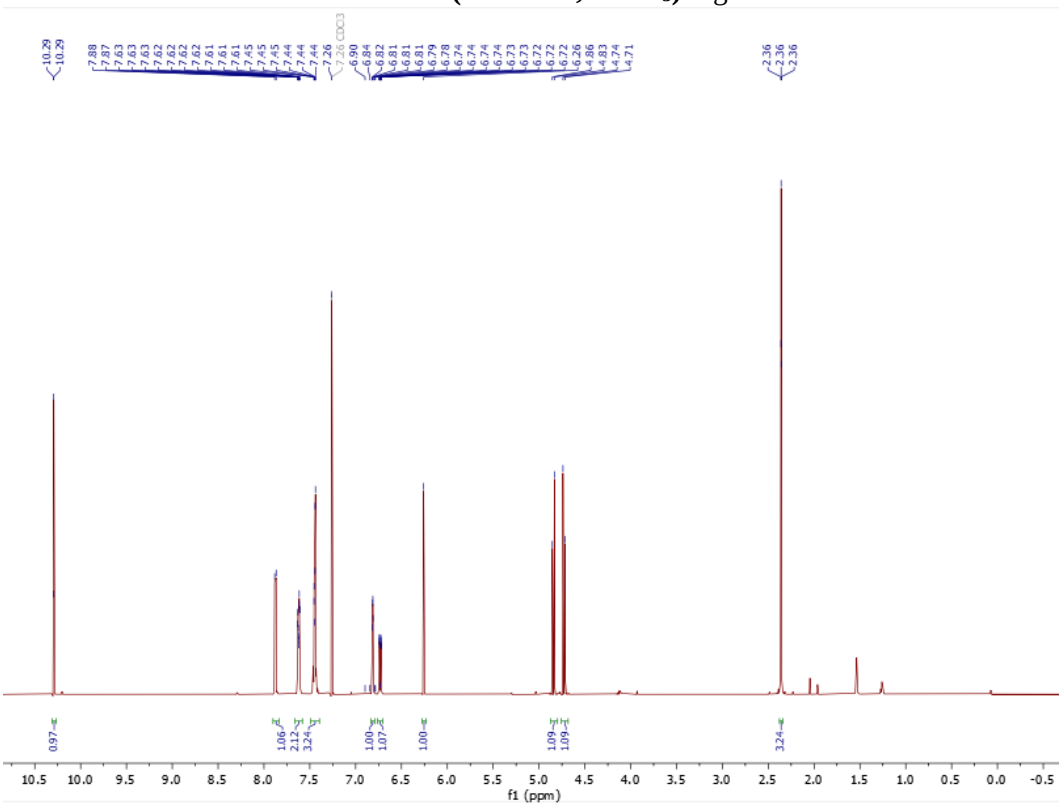


3g. 2-oxo-1-phenyl-2-(2,2,2-trichloroethoxy)ethyl 2-hydroxy-4-methylbenzoate

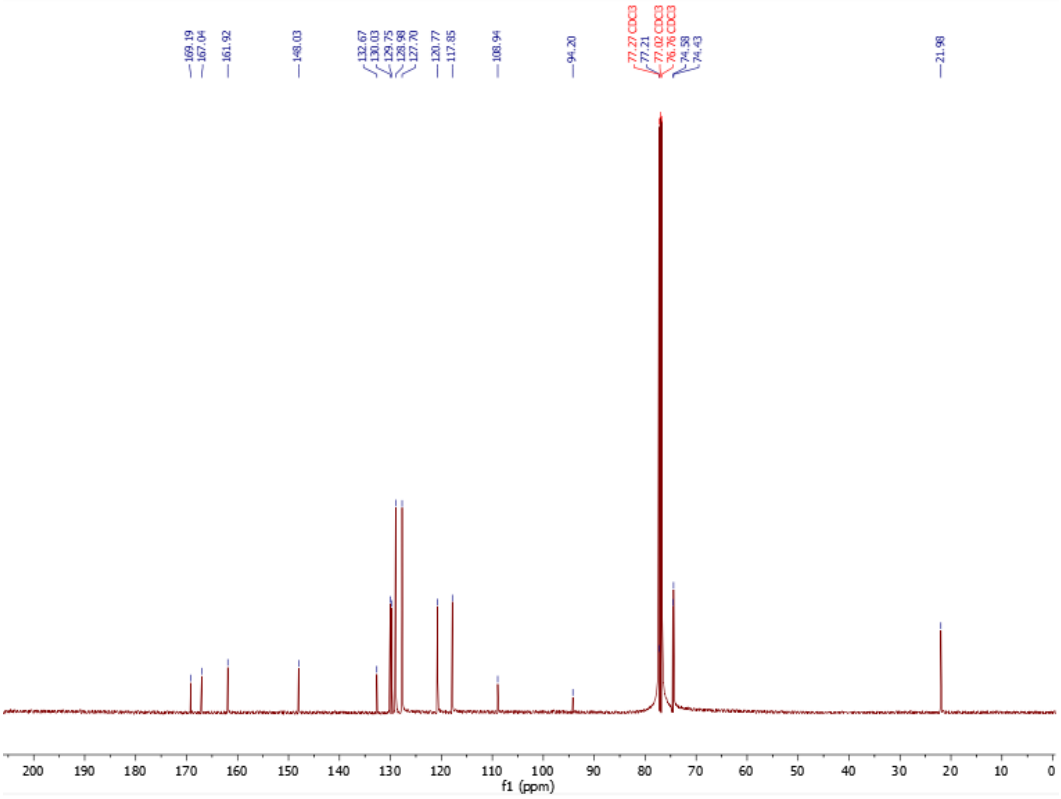


Prepared from **1g** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3g** as a white solid (33% y). **Rf =** 0.57 (1:9 EtOAc/Hex); **m.p=** 105^{o}C; **^{1}H NMR** (500 MHz, CDCl3) δ 10.29 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.49 – 7.40 (m, 3H), 6.81 (dd, J = 1.7, 0.9 Hz, 1H), 6.73 (ddd, J = 8.1, 1.6, 0.7 Hz, 1H), 6.26 (s, 1H), 4.84 (d, J = 11.9 Hz, 1H), 4.73 (d, J = 11.9 Hz, 1H), 2.36 (d, J = 0.7 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.34, 167.18, 162.06, 148.17, 132.81, 130.17, 129.90, 129.12, 127.85, 120.92, 117.99, 109.09, 94.35, 77.36, 74.73, 74.58, 22.12 ppm; **IR (neat): ν (cm-1) =** 1747, 1727, 1675, 1622, 1579, 1522, 1501, 1449, 1371, 1336, 1304, 1265, 1237, 1208, 1175, 1151, 1123, 1094, 1038, 951, 907, 872, 817, 780, 759, 717, 694, 650, 614.

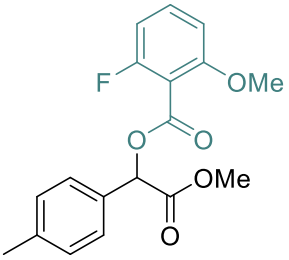
^{1}H NMR (500 MHz, $CDCl_3$): 3g



^{13}C NMR (126 MHz, $CDCl_3$): 3g

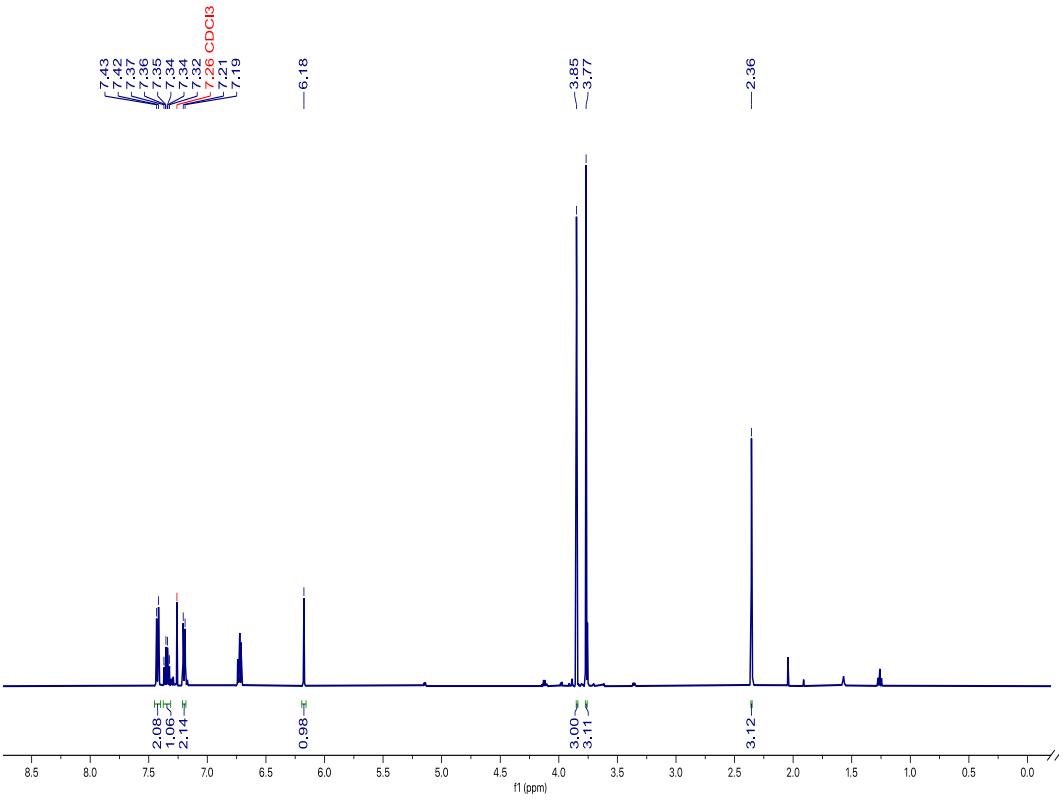


3h. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2-fluoro-6-methoxybenzoate

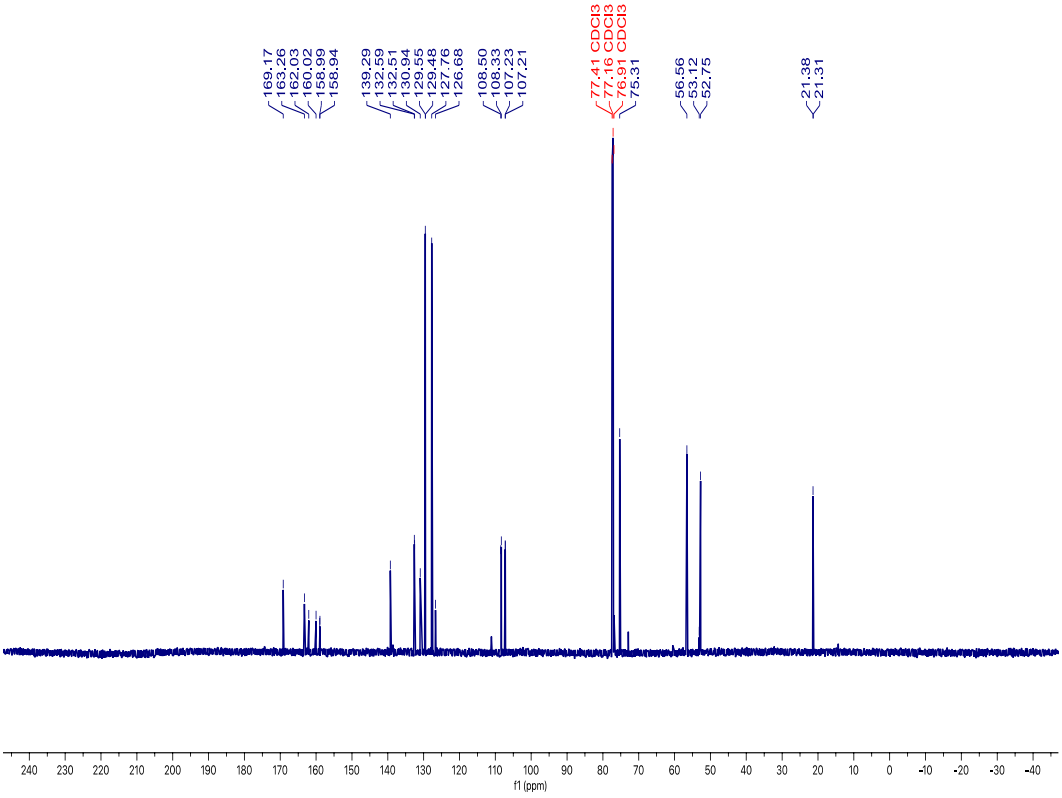


Prepared from **1b** and 2-fluoro-6-methoxybenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 4:6 EtOAc/Hex afforded **3h** as a white solid (53% y). **Rf =** 0.71 (4:6 EtOAc/Hex); **m.p** = 98˚C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.35 (td, J = 8.4, 6.4 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 6.18 (s, 1H), 3.85 (s, 4H), 3.77 (s, 4H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.17, 163.26, 162.03, 160.02, 158.99, 158.94, 139.29, 132.59, 132.51, 130.94, 129.55, 129.48, 127.76, 126.68, 108.50, 108.33, 107.23, 107.21, 77.41, 77.16, 76.91, 75.31, 56.56, 53.12, 52.75, 21.38, 21.31 ppm; **IR** (neat): ν (cm^{-1}) = 2944, 1760, 1736, 1618, 1514, 1472, 1437, 1351, 1304, 1289, 1243, 1216, 1185, 1170, 1084, 1060, 1030, 944, 909, 812, 787, 757, 727, 710, 629.

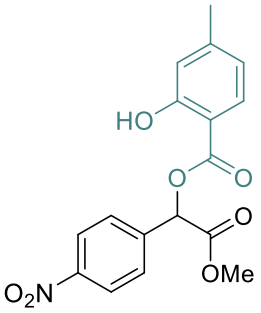
^{1}H NMR (500 MHz, $CDCl_3$): 3h



^{13}C NMR (126 MHz, $CDCl_3$): 3h

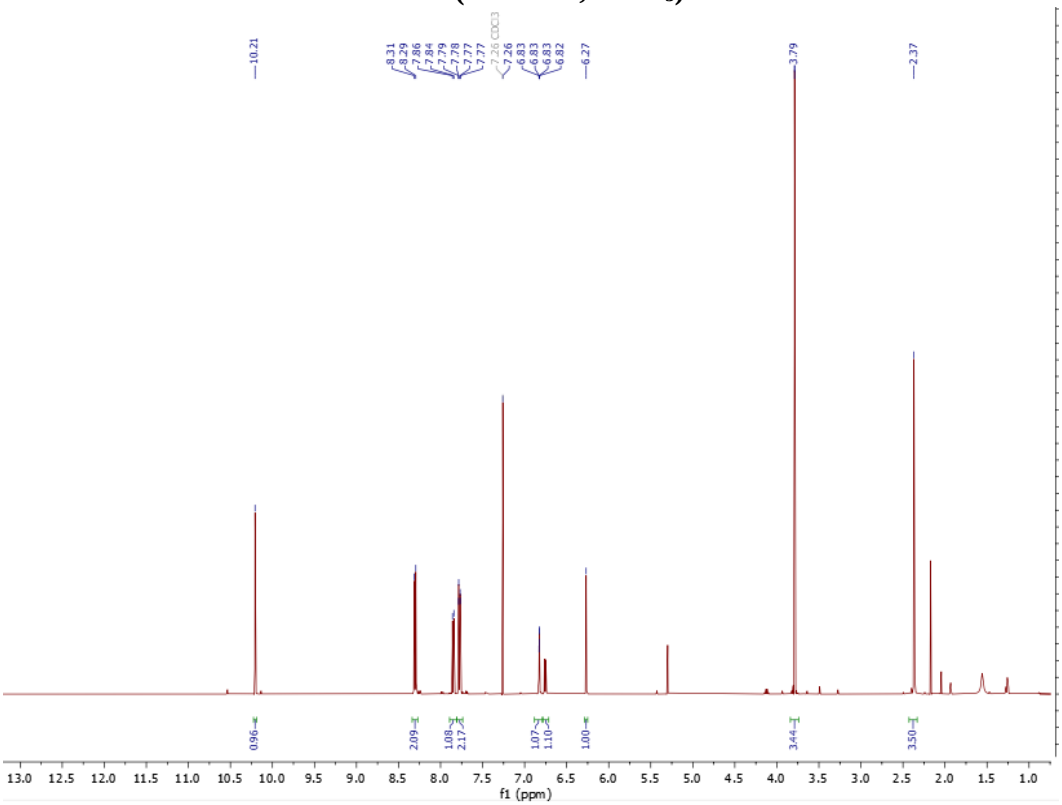


3i. 2-methoxy-1-(4-nitrophenyl)-2-oxoethyl 2-hydroxy-4-methylbenzoate

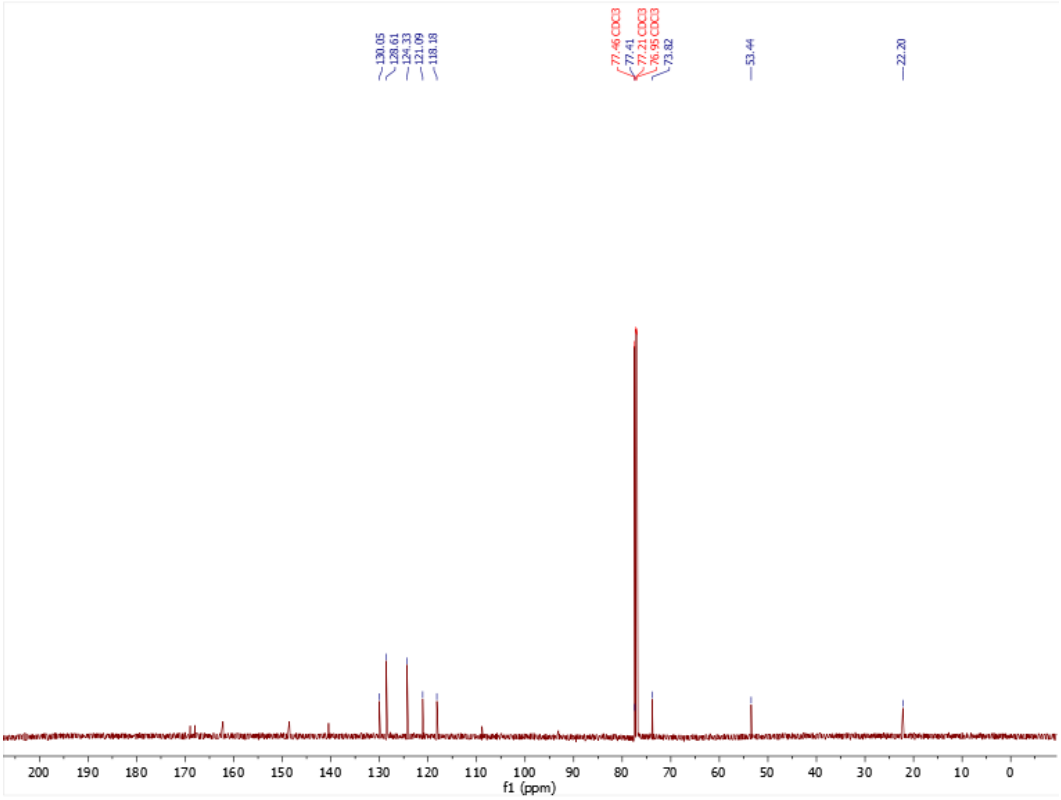


Prepared from **1i** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 6 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3i** as a yellow oil (20% y). **Rf =** 0.40 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, CDCl3) δ 10.21 (s, 1H), 8.34 – 8.27 (m, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.81 – 7.74 (m, 2H), 6.83 (dd, J = 1.7, 0.9 Hz, 1H), 6.76 (ddd, J = 8.2, 1.7, 0.7 Hz, 1H), 6.27 (s, 1H), 3.79 (s, 3H), 2.37 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 130.05, 128.61, 124.33, 121.09, 118.18, 77.46, 77.41, 77.21, 76.95, 73.82, 53.44, 22.20 ppm.

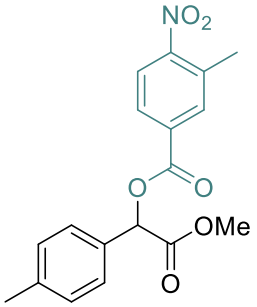
^{1}H NMR (500 MHz, $CDCl_3$): 3i



^{13}C NMR (126 MHz, $CDCl_3$): 3i

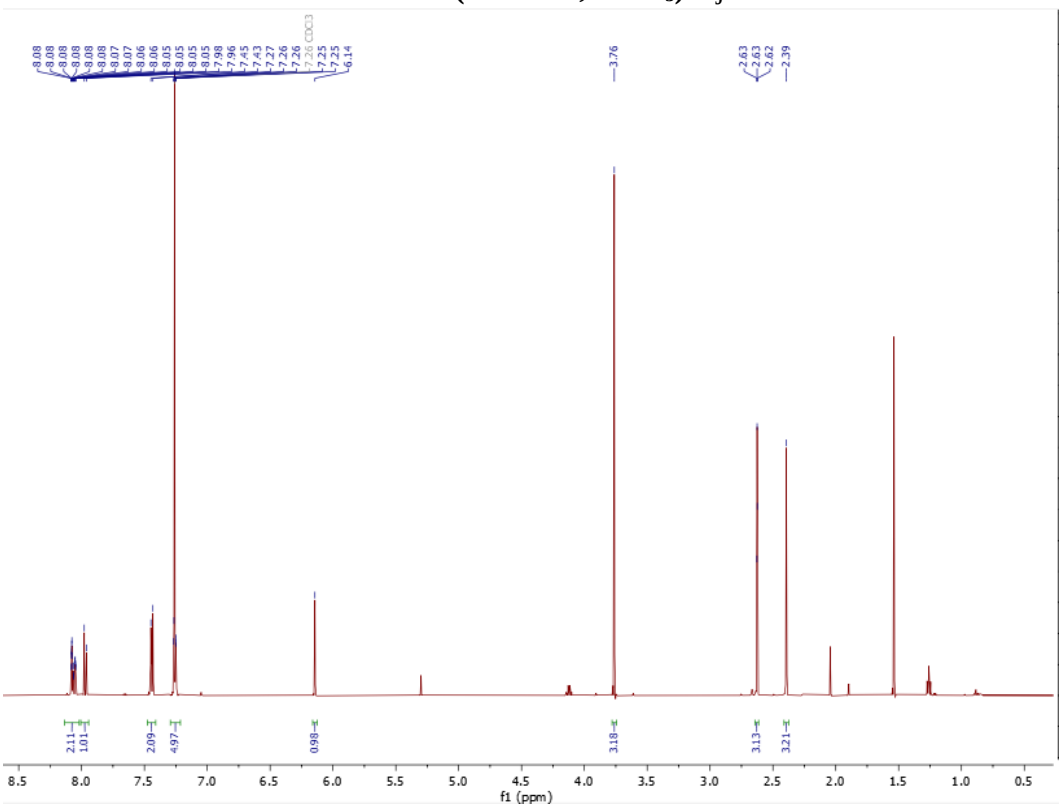


3j. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 3-methyl-4-nitrobenzoate

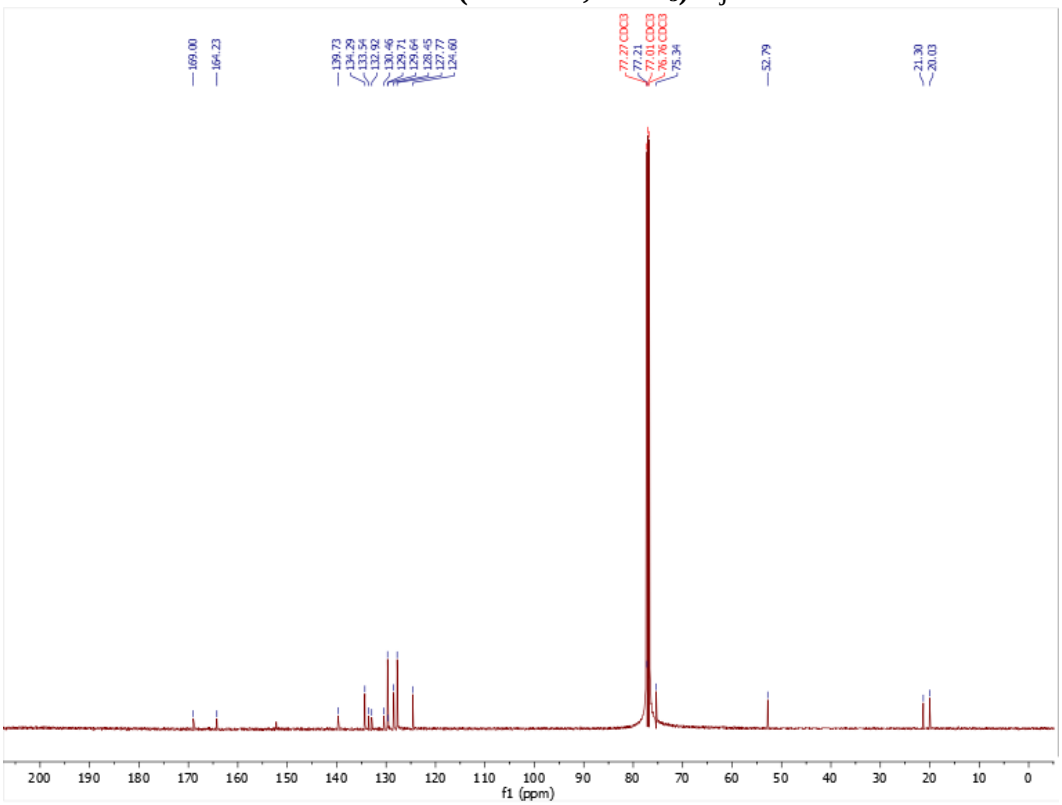


Prepared from **1b** and 3-methyl-4-nitrobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3j** as a white solid (90% y). **Rf =** 0.46 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.29 – 7.21 (m, 2H), 6.14 (s, 1H), 3.76 (s, 3H), 2.63 (s, 2H), 2.62 (s, 1H), 2.39 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.41, 164.64, 152.60, 140.14, 134.70, 133.95, 133.32, 130.86, 130.12, 130.04, 128.86, 128.17, 125.00, 77.61, 75.75, 53.19, 21.70, 20.43 ppm.

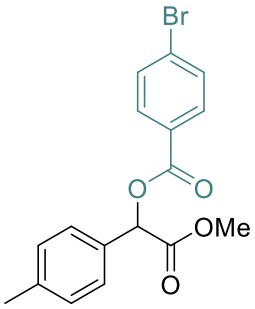
^{1}H NMR (500 MHz, $CDCl_3$): 3j



^{13}C NMR (126 MHz, CDCl$_3$): 3j

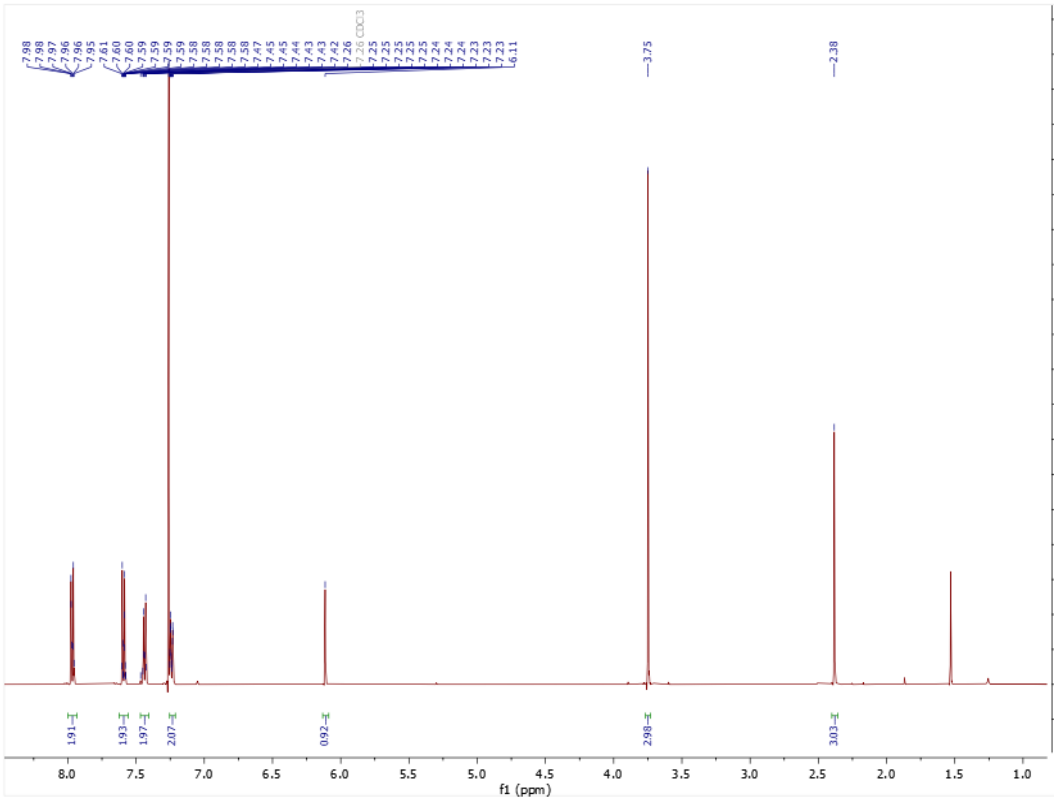


3k. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-bromobenzoate

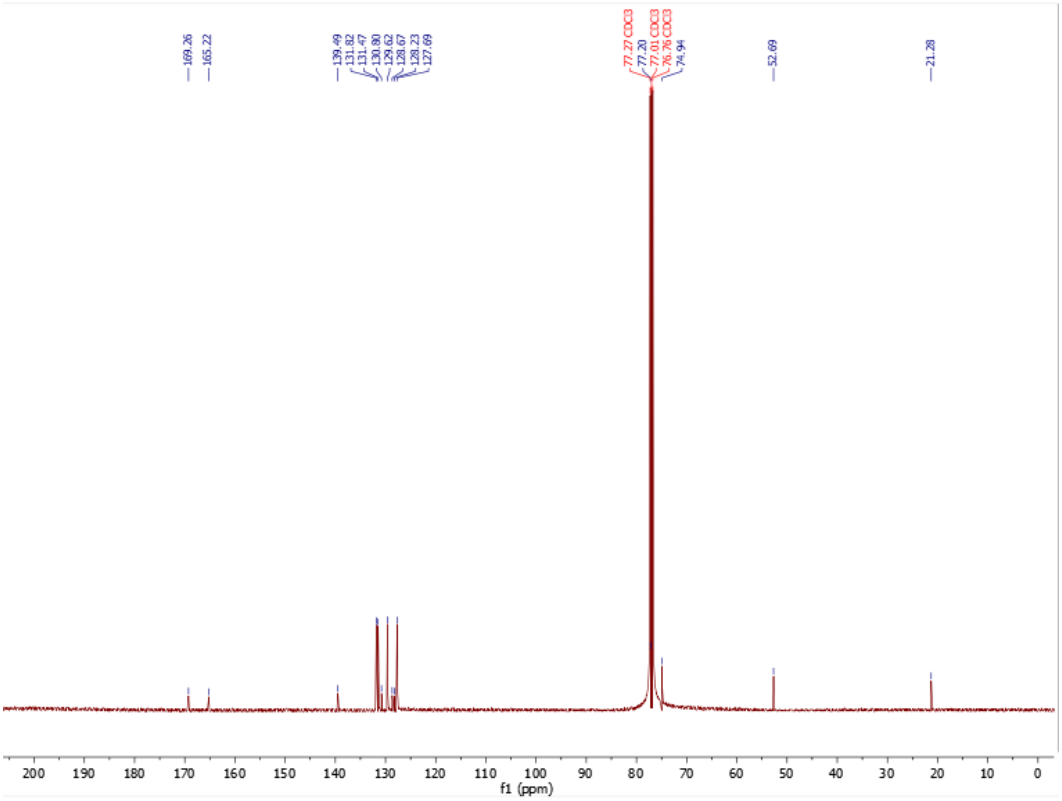


Prepared from **1b** and 4-bromobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3k** as a white solid (67% y). **Rf =** 0.50(1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, CDCl3) δ 8.00 – 7.93 (m, 2H), 7.62 – 7.56 (m, 2H), 7.47 – 7.41 (m, 2H), 7.27 – 7.21 (m, 2H), 6.11 (s, 1H), 3.75 (s, 3H), 2.38 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.26, 165.22, 139.49, 131.82, 131.47, 130.80, 129.62, 128.67, 128.23, 127.69, 77.27, 77.20, 77.01, 76.76, 74.94, 52.69, 21.28 ppm.

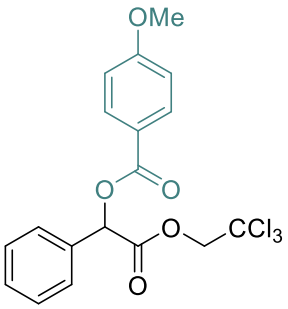
^{1}H NMR (500 MHz, $CDCl_3$): 3k



^{13}C NMR (126 MHz, $CDCl_3$): 3k

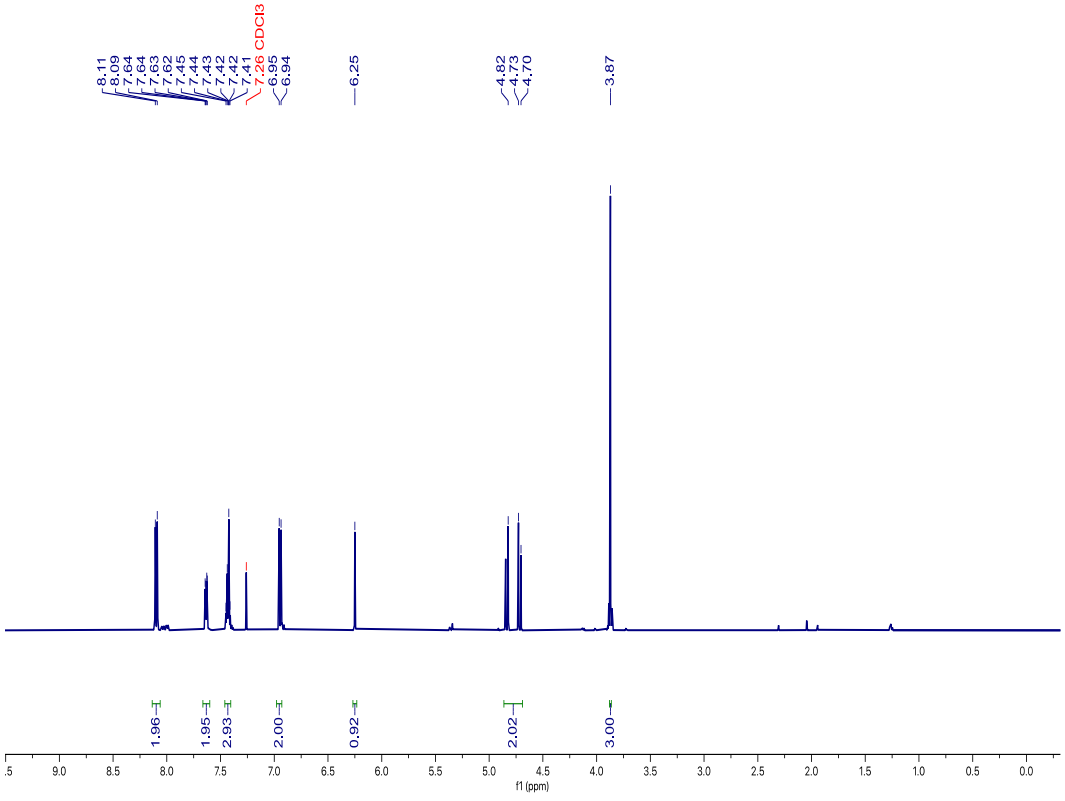


3l. 2-oxo-1-phenyl-2-(2,2,2-trichloroethoxy)ethyl 4-methoxybenzoate

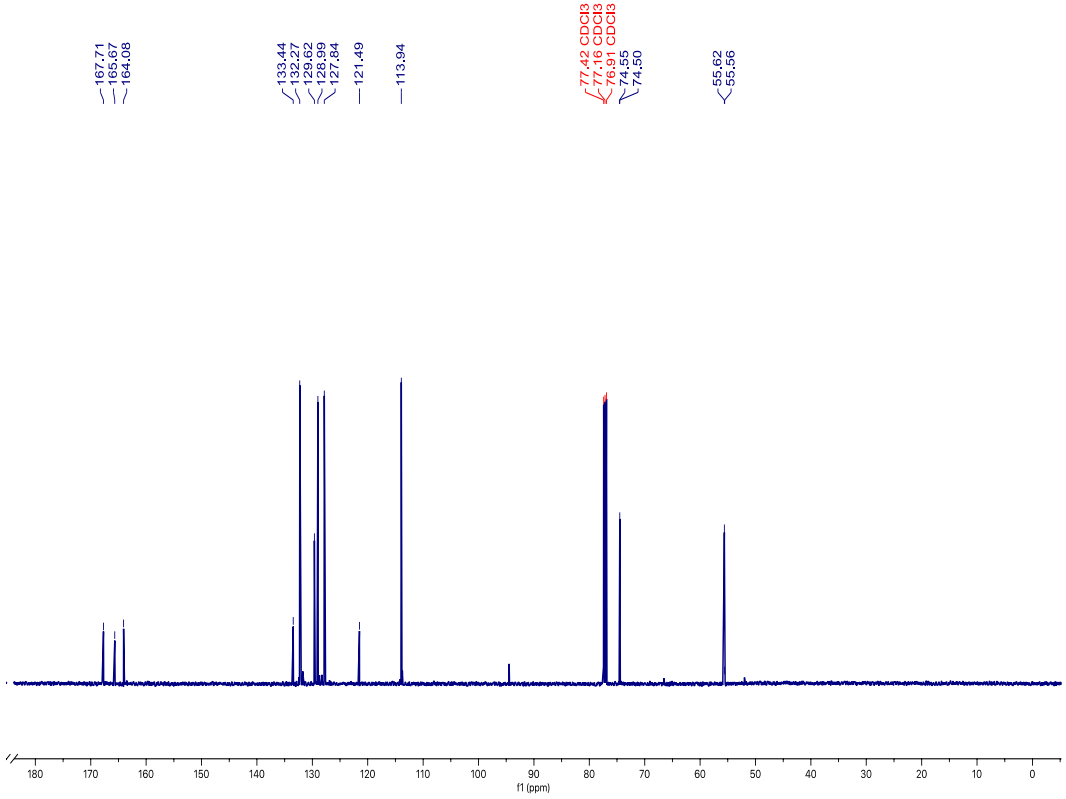


Prepared from **1g** and 4-methoxybenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3l** as a clear colorless oil (48% y). **Rf** = 0.26 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 2H), 6.95 (d, J = 9.0 Hz, 1H), 6.25 (s, 1H), 4.82 (s, 1H), 4.72 (d, J = 11.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.71, 165.67, 164.08, 133.44, 132.27, 129.62, 128.99, 127.84, 121.49, 113.94, 77.42, 77.16, 76.91, 74.55, 74.50, 55.62, 55.56 ppm; **IR (neat): ν (cm^{-1}) =** 2965, 1770, 1719, 1606, 1512, 1465, 1252, 1164, 1096, 1027, 909, 847, 769, 718, 696.

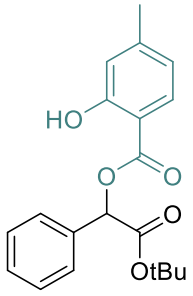
^{1}H NMR (500 MHz, $CDCl_3$): 3l



^{13}C NMR (126 MHz, $CDCl_3$): 3l

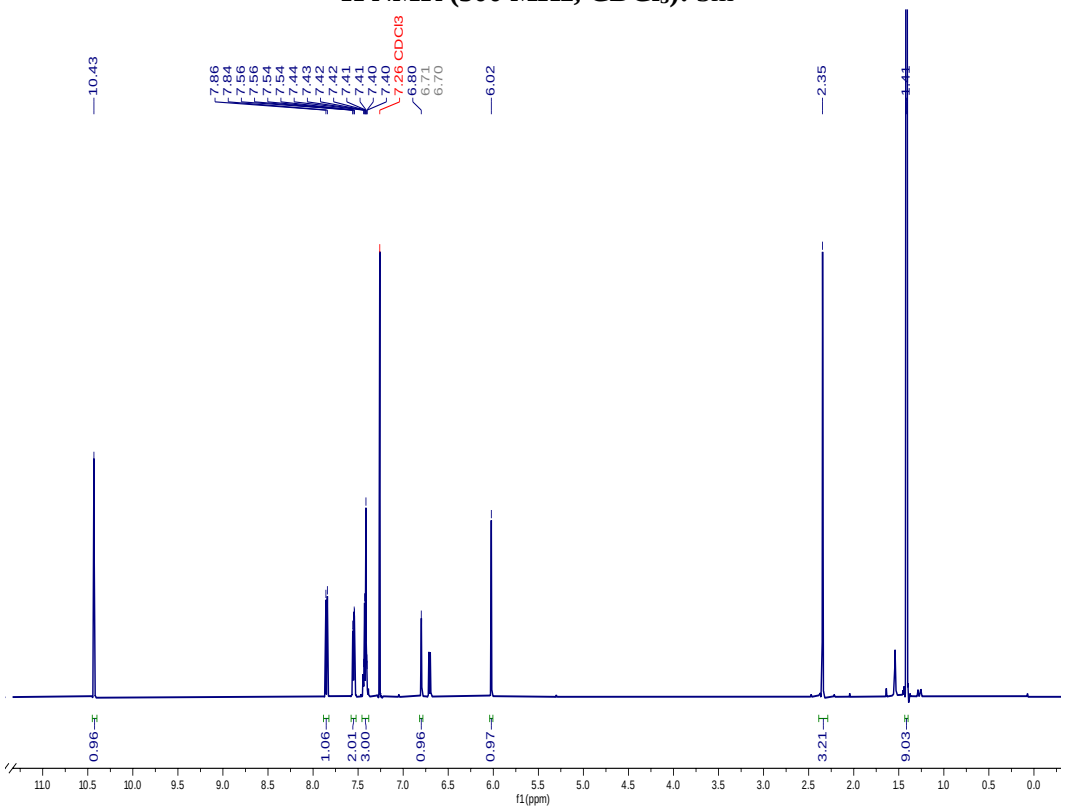


3m. 2-(tert-butoxy)-2-oxo-1-phenylethyl 2-hydroxy-4-methylbenzoate

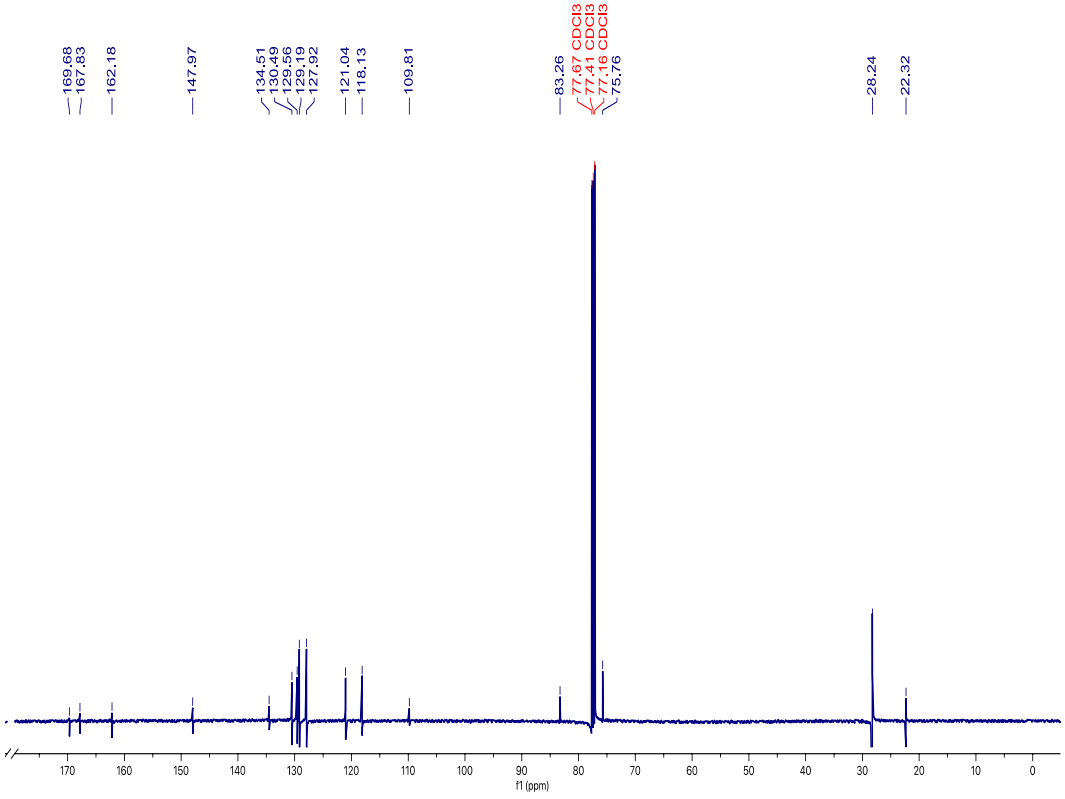


Prepared from **1d** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3m** as a colorless foggy oil (15% y). **Rf =** 0.34 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.55 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.46 – 7.38 (m, 2H), 6.80 (s, 0H), 6.02 (s, 1H), 1.41 (s, 7H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.68, 167.83, 162.18, 147.97, 134.51, 130.49, 129.56, 129.19, 127.92, 121.04, 118.13, 109.81, 83.26, 77.67, 77.41, 77.16, 75.76, 28.24, 22.32 ppm.

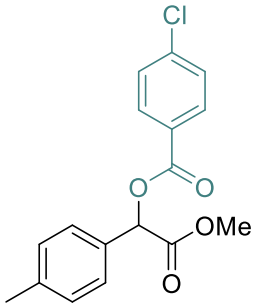
^{1}H NMR (500 MHz, $CDCl_3$): 3m



^{13}C NMR (126 MHz, $CDCl_3$): 3m

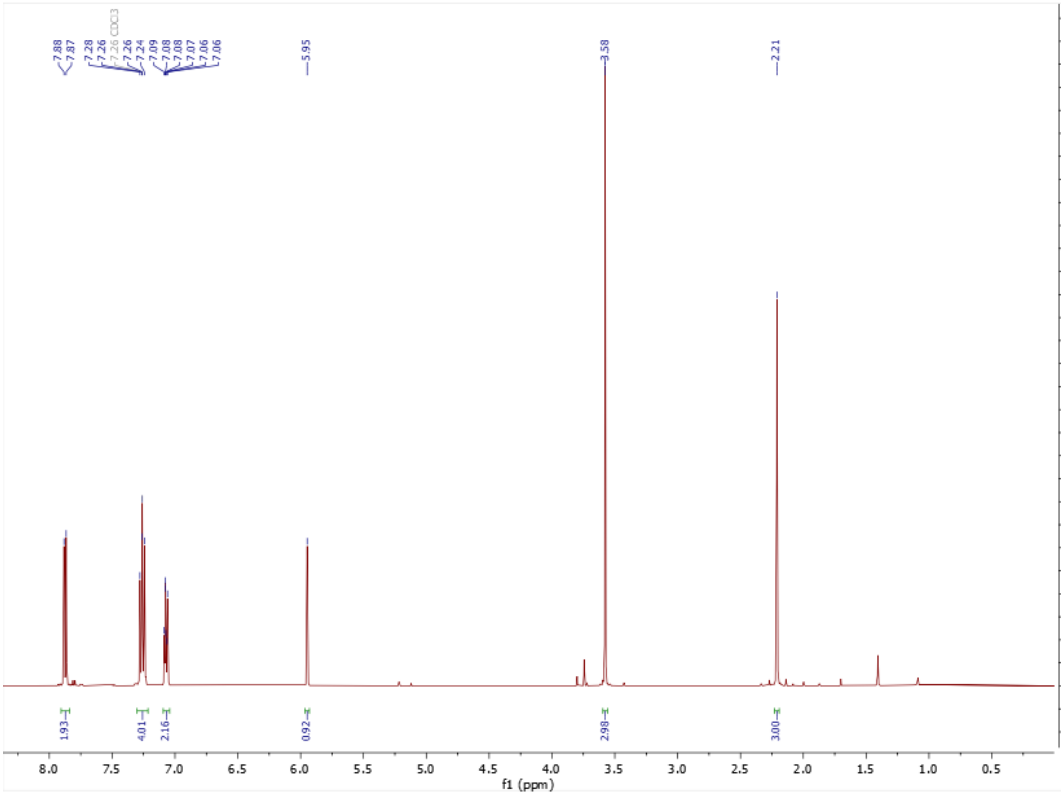


3n. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-chlorobenzoate

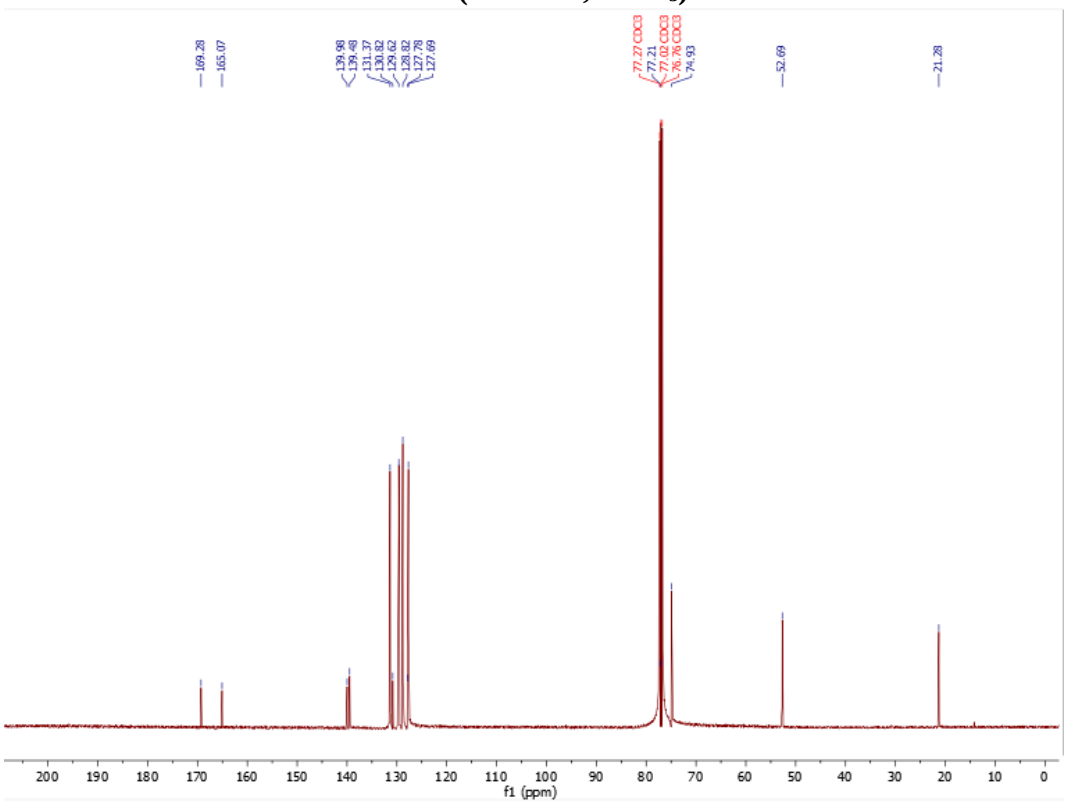


Prepared from **1b** and 4-chlorobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3n** as a white solid (85% y). **Rf =** 0.48 (1:9 EtOAc/Hex); **m.p=** 82°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.26 (tt, *J* = 9.1, 2.1 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.95 (s, 1H), 3.58 (s, 3H), 2.21 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.28, 165.07, 139.98, 139.48, 131.37, 130.82, 129.62, 128.82, 127.78, 127.69, 77.27, 77.21, 77.02, 76.76, 74.93, 52.69, 21.28 ppm; **IR (neat): ν (cm-1) =** 2954, 1753, 1719, 1593, 1515, 1486, 1435, 1400, 1349, 1304, 1284, 1261, 1219, 1168, 1111, 1097, 1037, 1013, 967, 928, 907, 847, 824, 789, 764, 719, 683, 628.

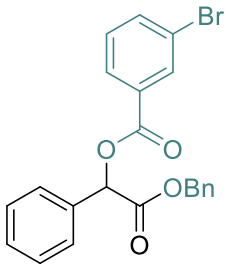
^{1}H NMR (500 MHz, $CDCl_3$): 3n



^{13}C NMR (126 MHz, $CDCl_3$): 3n

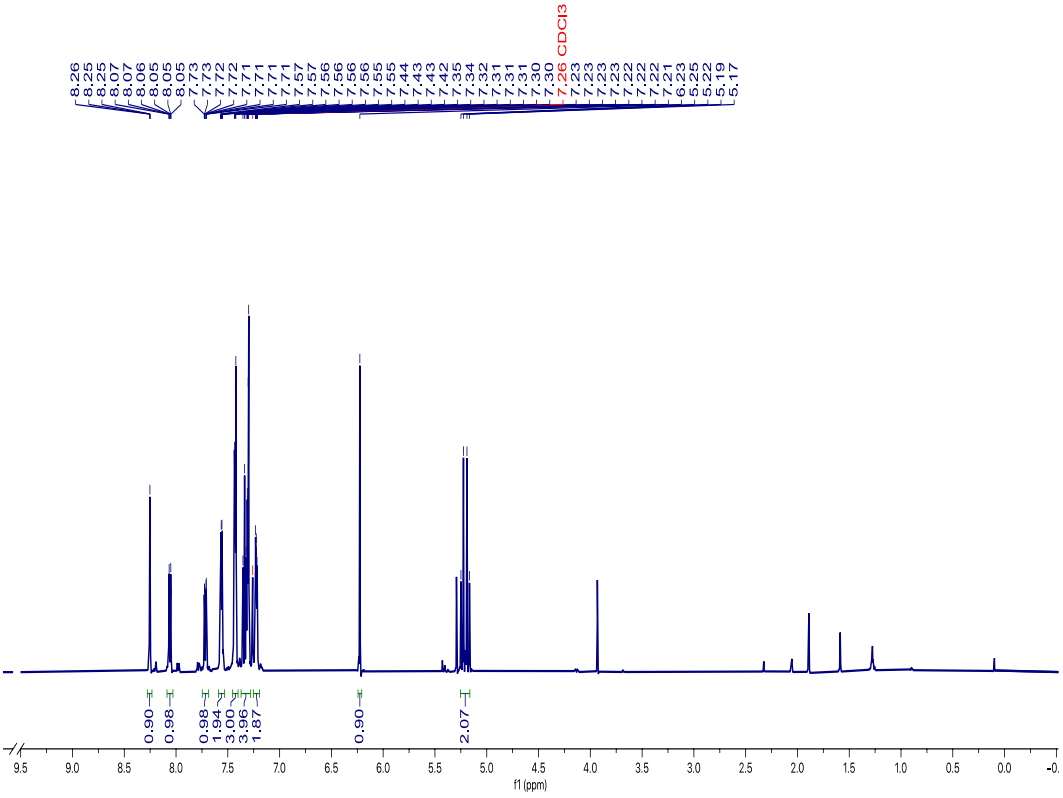


3o. 2-(benzyloxy)-2-oxo-1-phenylethyl 3-bromobenzoate

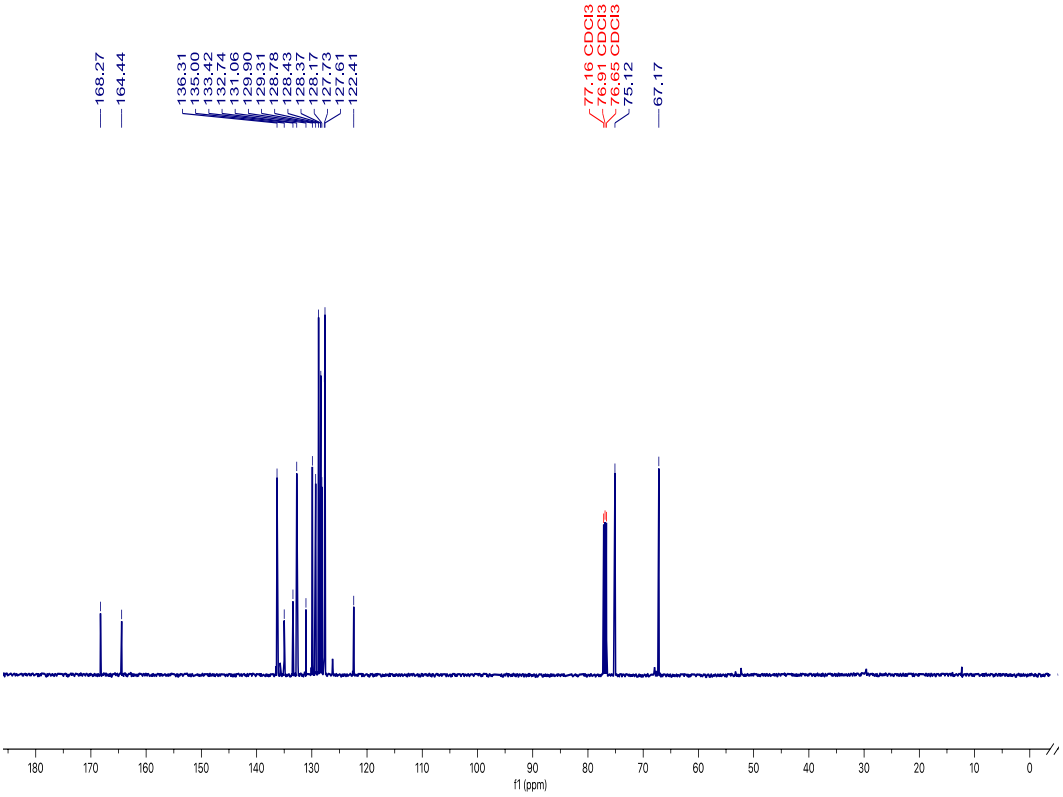


Prepared from **1e** and 3-bromobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3o** as a clear, colorless oil (49%). **Rf** = 0.43 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 (t, J = 1.8 Hz, 1H), 8.06 (dt, J = 7.8, 1.3 Hz, 1H), 7.72 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.45 – 7.40 (m, 3H), 7.37 – 7.28 (m, 4H), 7.25 – 7.19 (m, 2H), 6.23 (s, 1H), 5.27 – 5.15 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.27, 164.44, 136.31, 135.00, 133.42, 132.74, 131.06, 129.90, 129.31, 128.78, 128.43, 128.37, 128.17, 127.73, 127.61, 122.41, 77.16, 76.91, 76.65, 75.12, 67.17 ppm; **IR** (neat): ν (cm^{-1}) = 1756, 1724, 1632, 1591, 1499, 1455, 1425, 1381, 1349, 1246, 1205, 1174, 1115, 1080, 1067, 1026, 909, 836, 809, 745, 694, 672, 651.

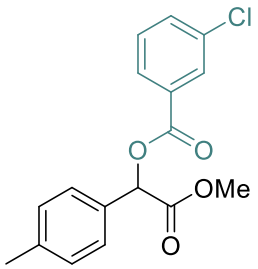
^{1}H NMR (500 MHz, $CDCl_3$): 3o



^{13}C NMR (126 MHz, $CDCl_3$): 3o

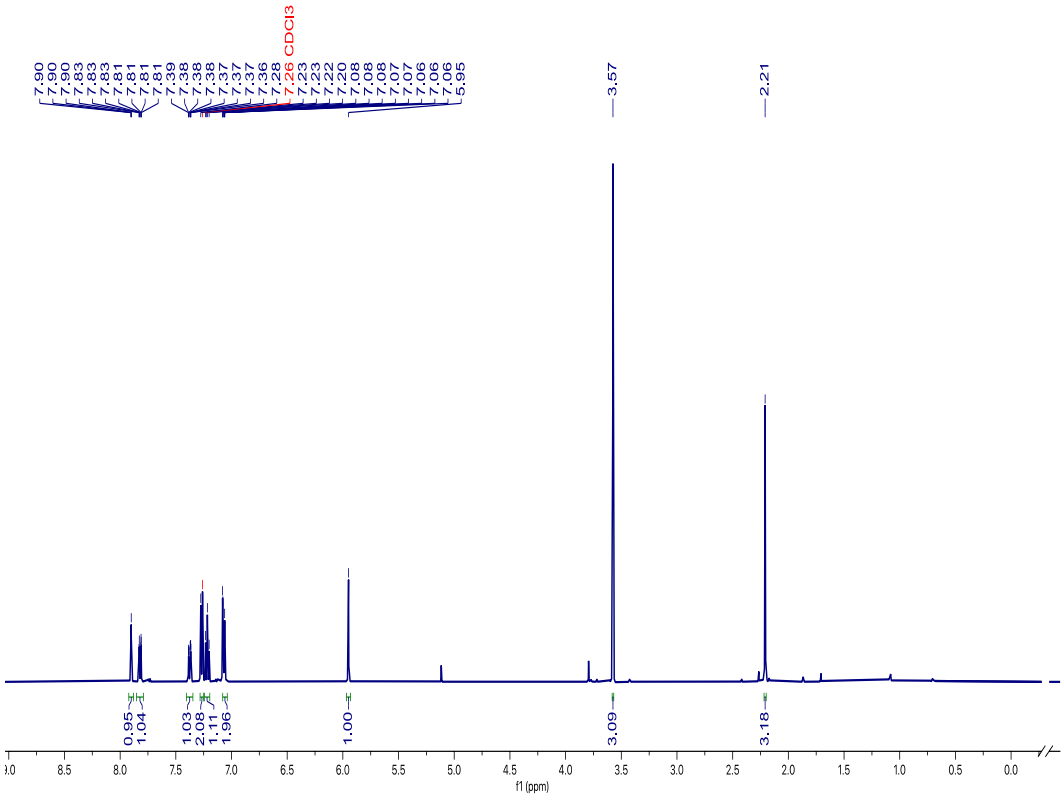


3p. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 3-chlorobenzoate

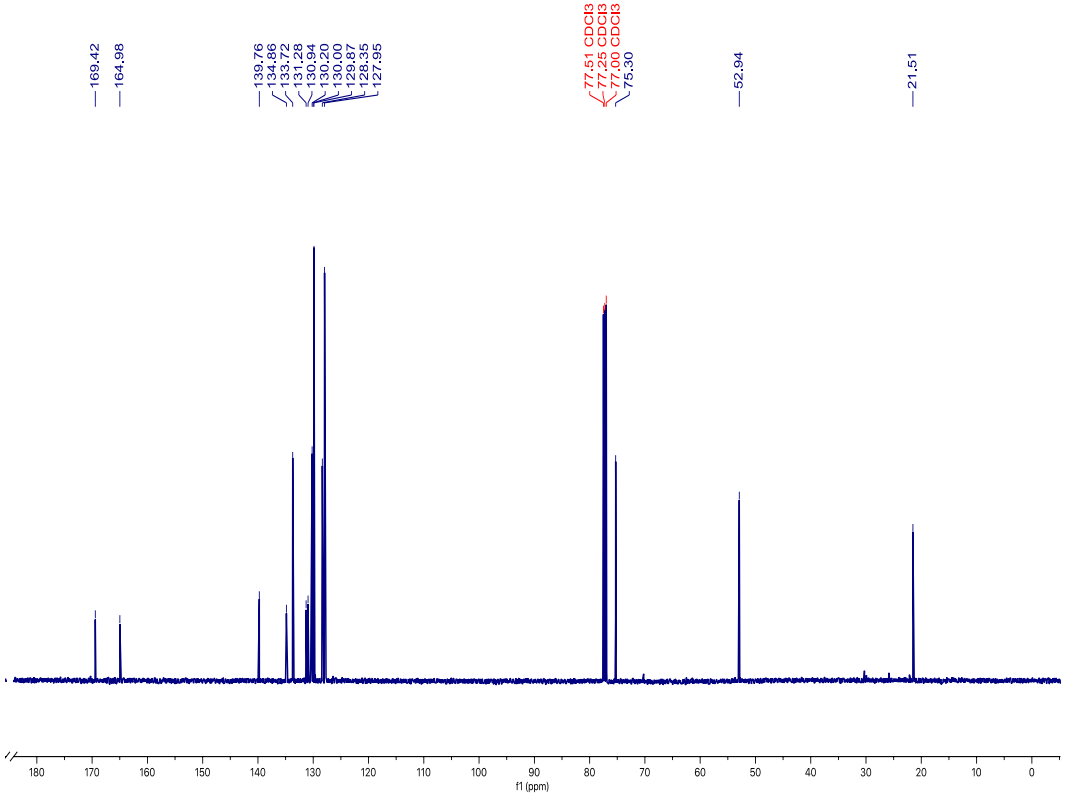


Prepared from **1b** and 3-chlorobenzoic acid. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3p** as clear, colorless oil (74% y). **Rf** = 0.40 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (t, J = 1.9 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.38 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.28 (s, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.10 – 7.04 (m, 3H), 5.95 (s, 1H), 3.57 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.42, 164.98, 139.76, 134.86, 133.72, 131.28, 130.94, 130.20, 130.00, 129.87, 128.35, 127.95, 77.51, 77.25, 77.00, 75.30, 52.94, 21.51 ppm; **IR (neat): ν (cm^{-1}) =** 2955, 1754, 1725, 1626, 1574, 1516, 1470, 1428, 1345, 1286, 1246, 1217, 1176, 1124, 1073, 1037, 969, 909, 854, 812, 763, 745, 729, 701, 673.

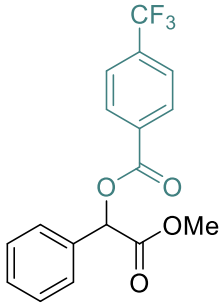
^{1}H NMR (500 MHz, $CDCl_3$): 3p



^{13}C NMR (126 MHz, $CDCl_3$): 3p

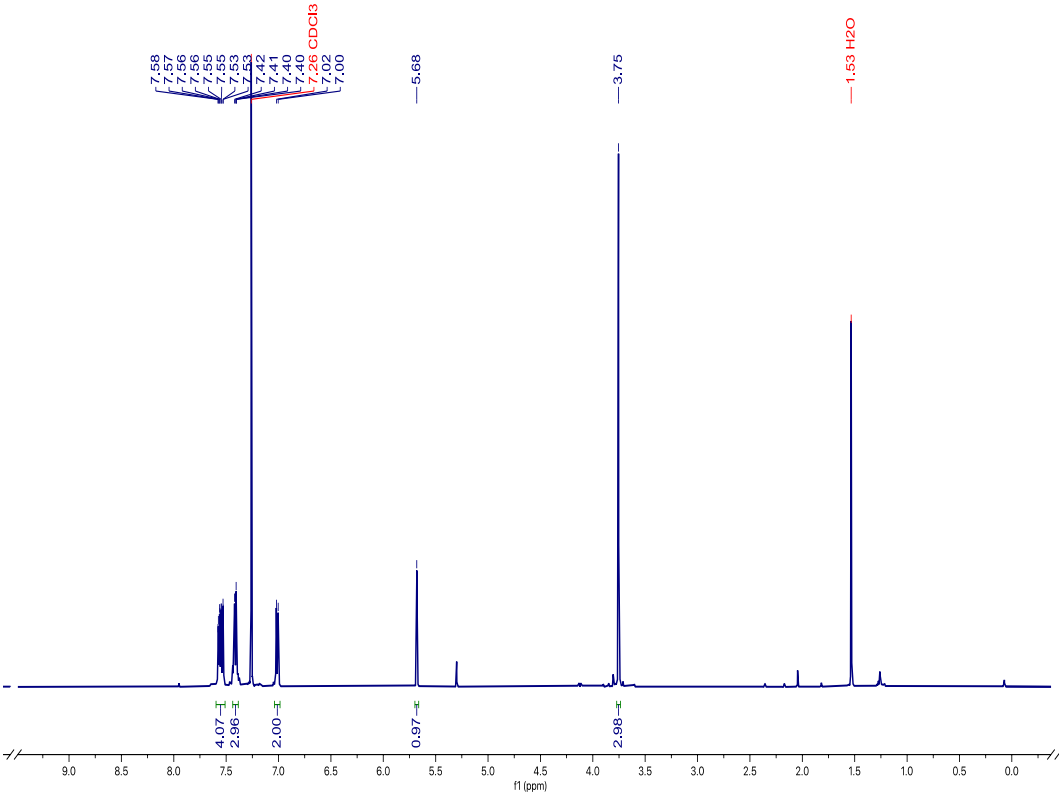


3q. 2-methoxy-2-oxo-1-phenylethyl 4-(trifluoromethyl)benzoate

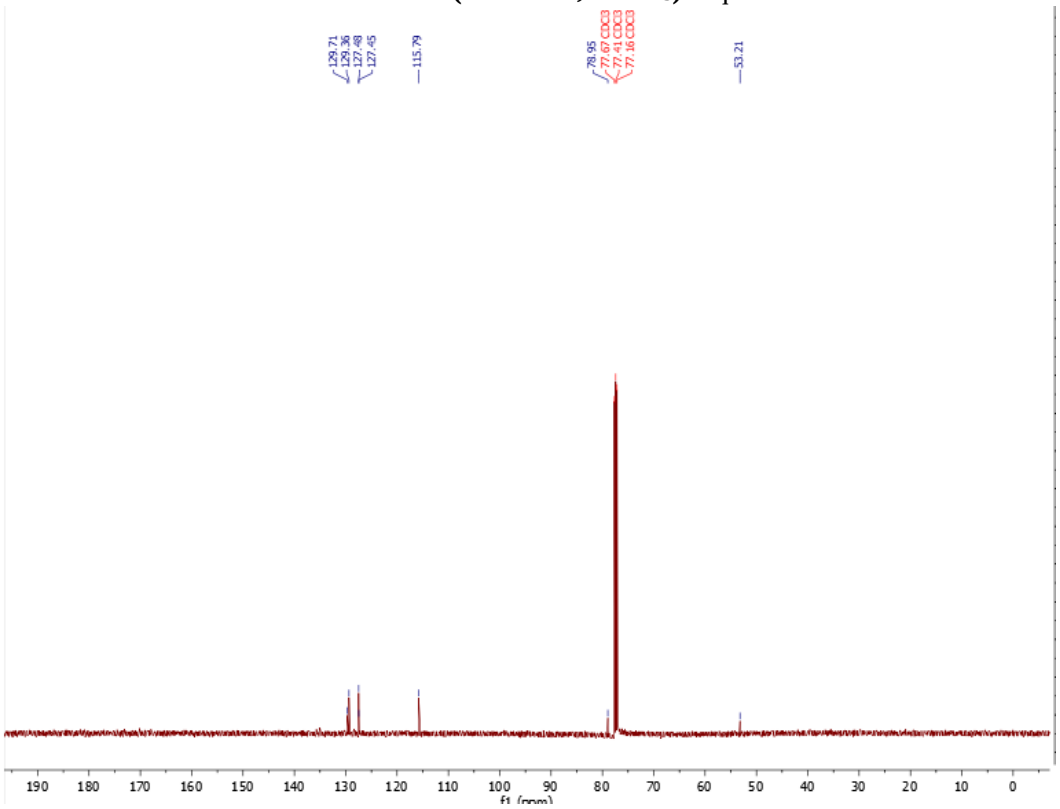


Prepared from **1a** and 4-(trifluoromethyl)benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3q** as a white crystalline solid (57% y). **Rf =** 0.50 (1:9 EtOAc/Hex); **m.p=** 95°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 15.4, 8.4, 1.4 Hz, 6H), 7.44 – 7.38 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 2H), 5.68 (s, 2H), 3.75 (s, 5H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 129.71, 129.36, 127.48, 127.45, 115.79, 78.95, 53.21 ppm; **IR (neat): ν (cm-1) =** 2923, 2850, 1763, 1612, 1516, 1437, 1358, 1325, 1247, 1214, 1179, 1153, 1112, 1053, 1010, 918, 835, 789, 762, 732, 697, 627.

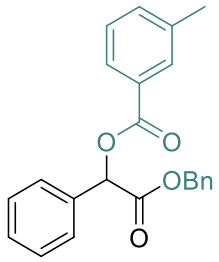
^{1}H NMR (500 MHz, $CDCl_3$): 3q



^{13}C NMR (126 MHz, $CDCl_3$): 3q

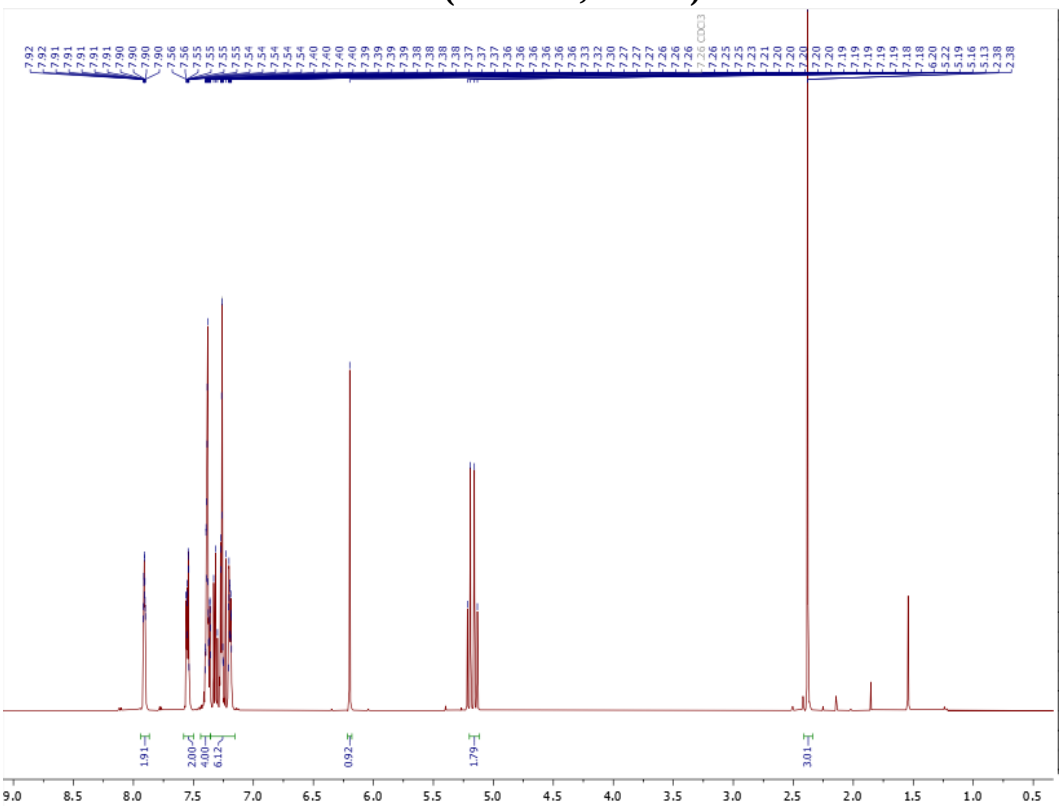


3r. 2-(benzyloxy)-2-oxo-1-phenylethyl 3-methylbenzoate

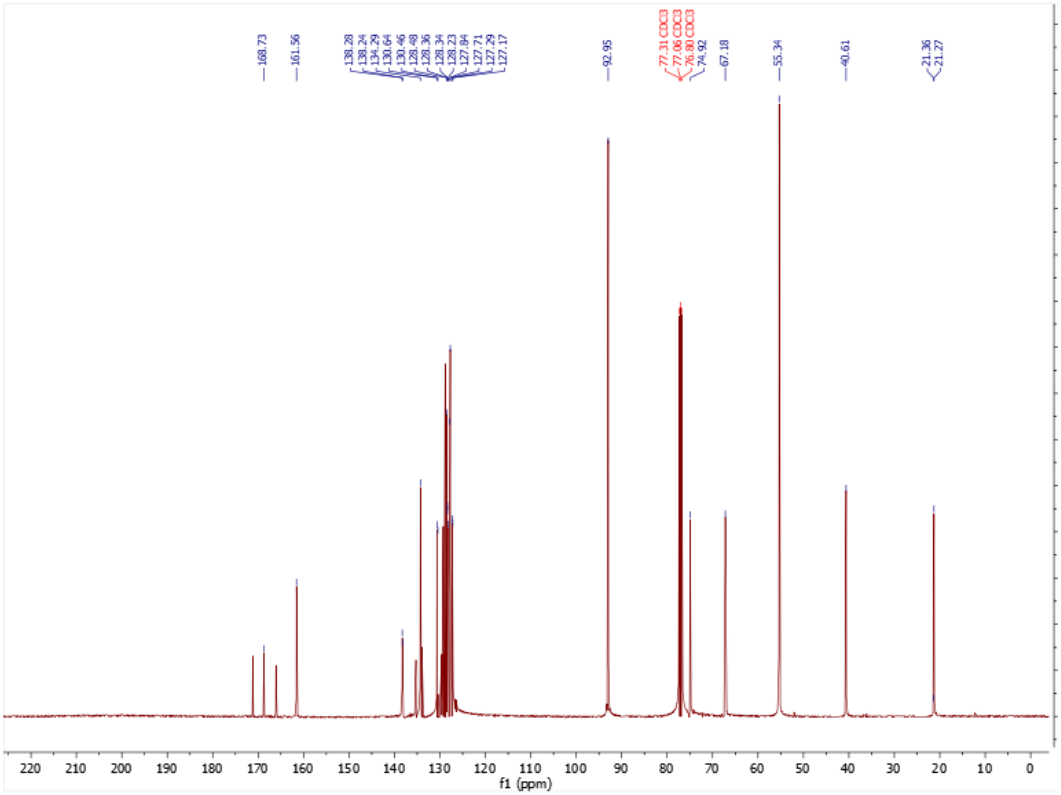


Prepared from **1e** and 3-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3r** as a clear colorless oil (88% y). **Rf =** 0.53 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (dddd, *J* = 5.4, 2.8, 1.7, 1.1 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.44 – 7.34 (m, 4H), 7.38 – 7.16 (m, 6H), 6.20 (s, 1H), 5.20 (d, *J* = 12.5 Hz, 1H), 5.15 (d, *J* = 12.5 Hz, 1H), 2.38 (d, *J* = 0.8 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.73, 161.56, 138.28, 138.24, 134.29, 130.64, 130.46, 128.48, 128.36, 128.34, 128.23, 127.84, 127.71, 127.29, 127.17, 92.95, 77.31, 77.06, 76.80, 74.92, 67.18, 55.34, 40.61, 21.36, 21.27 ppm; **IR (neat): ν (cm-1) =** 3034, 1754, 1721, 1609, 1589, 1497, 1455, 1379, 1347, 1262, 1195, 1170, 1103, 1079, 1029, 1003, 771, 744, 605.

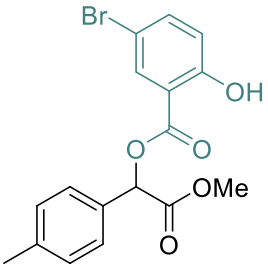
^{1}H NMR (500 MHz, CDCl3): 3r



^{13}C NMR (126 MHz, CDCl3): 3r

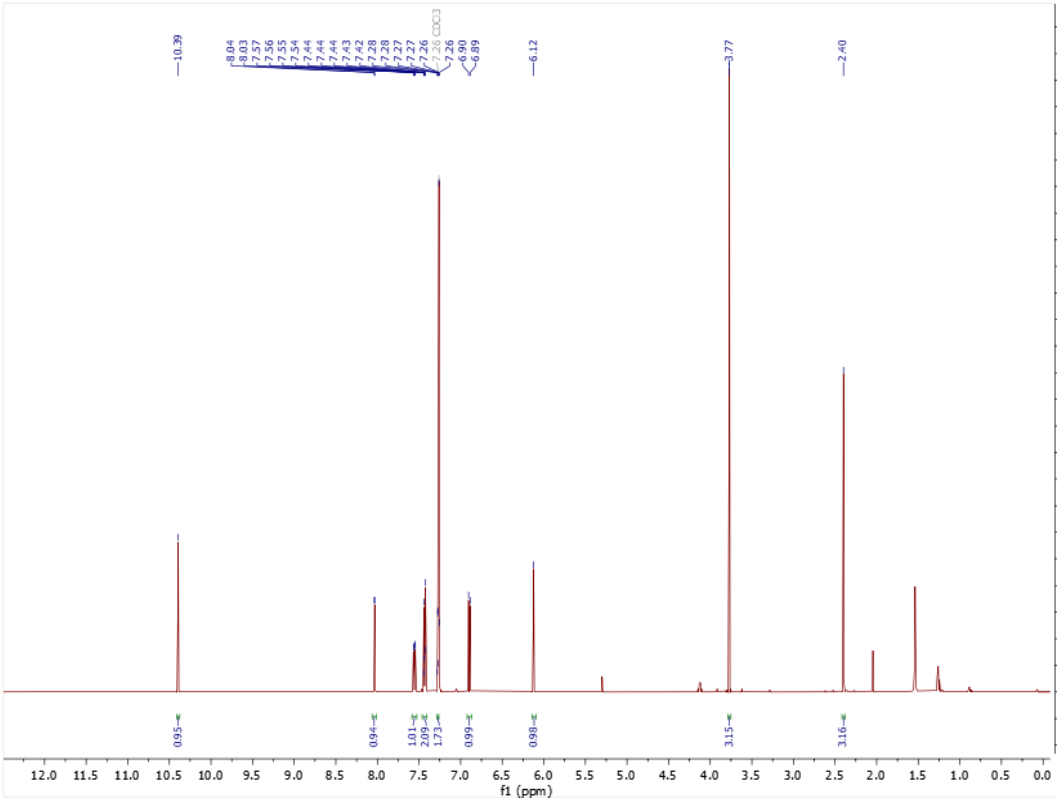


3s. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 5-bromo-2-hydroxybenzoate

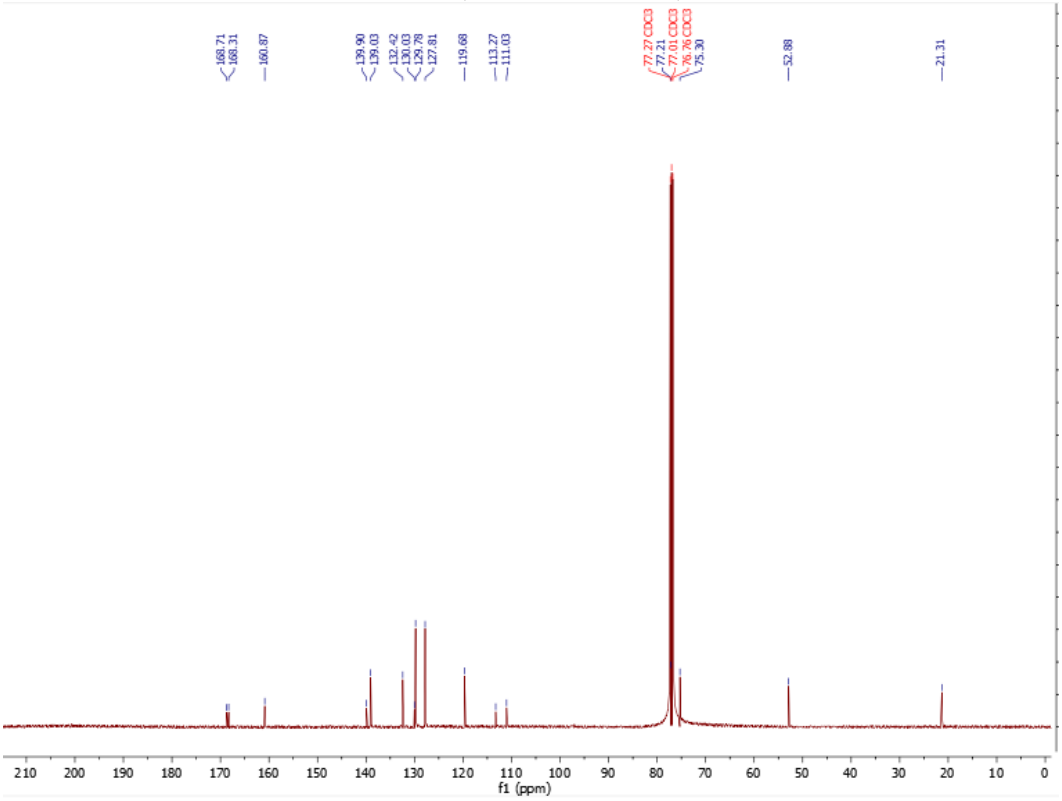


Prepared from **1b** and 5-bromo-2-hydroxybenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3s** as a white solid (30% y). **Rf =** 0.66 (2:8 EtOAc/Hex); **m.p=** 115°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.56 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.28 – 7.26 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.12 (s, 1H), 3.77 (s, 3H), 2.40 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.11, 168.71, 161.28, 140.30, 139.44, 132.82, 130.43, 130.18, 128.21, 120.09, 113.67, 111.43, 77.61, 75.70, 53.28, 21.71 ppm; **IR (neat): ν (cm-1) =** 3251, 1753, 1692, 1606, 1573, 1516, 1472, 1437, 1353, 1324, 1290, 1268, 1223, 1186, 1173, 1140, 1096, 1078, 1028, 964, 894, 835, 791, 752, 702, 629.

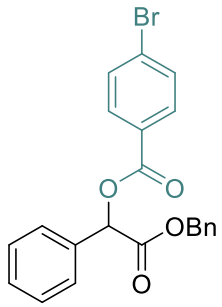
^{1}H NMR (500 MHz, $CDCl_3$): 3s



^{13}C NMR (126 MHz, $CDCl_3$): 3s

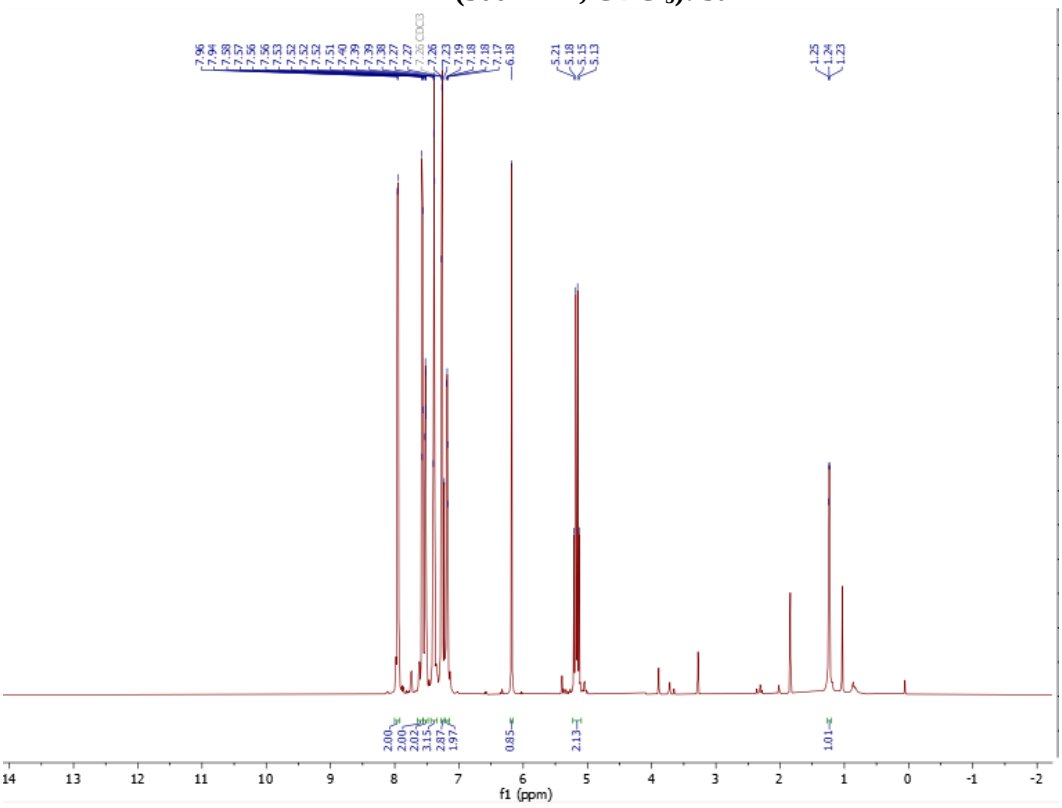


3t. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-methoxybenzoate

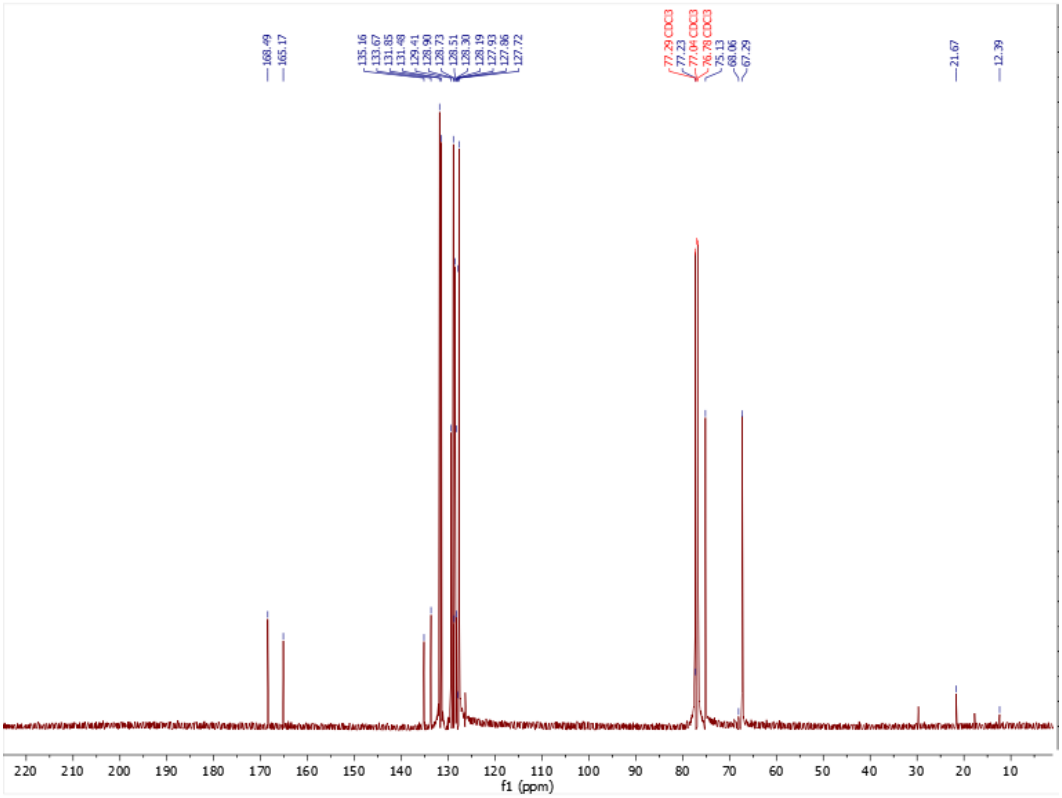


Prepared from **1e** and 4-bromobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3t** as a clear colorless oil (% y). **Rf =** 0.19 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.65 – 7.54 (m, 2H), 7.57 – 7.48 (m, 2H), 7.39 (q, *J* = 3.3 Hz, 4H), 7.28 – 7.21 (m, 2H), 7.24 – 7.15 (m, 2H), 6.18 (s, 1H), 5.23 – 5.10 (m, 3H), 1.26 – 1.20 (m, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.49, 165.17, 135.16, 133.67, 131.85, 131.48, 129.41, 128.90, 128.73, 128.51, 128.30, 128.19, 127.93, 127.86, 127.72, 77.29, 77.23, 77.04, 76.78, 75.13, 68.06, 67.29, 21.67, 12.39 ppm; **IR** (neat): ν (cm^{-1}) = 1747, 1712, 1591, 1485, 1456, 1398, 1340, 1286, 1250, 1207, 1170, 1112, 1100, 1068, 1011, 942, 913, 845, 828, 776, 751, 695, 628.

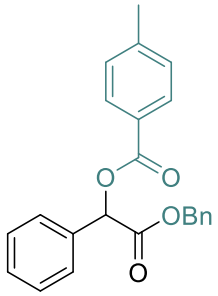
^{1}H NMR (500 MHz, $CDCl_3$): 3t



^{13}C NMR (126 MHz, $CDCl_3$): 3t

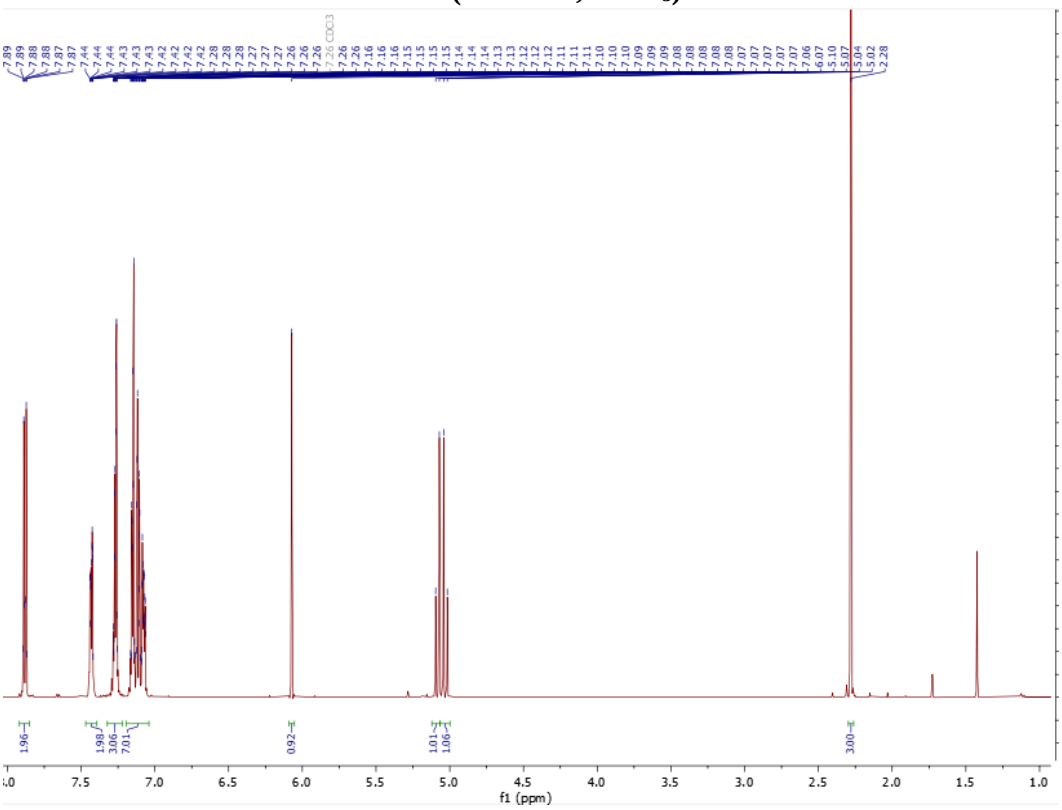


3u. 2-(benzyloxy)-2-oxo-1-phenylethyl 4-methylbenzoate

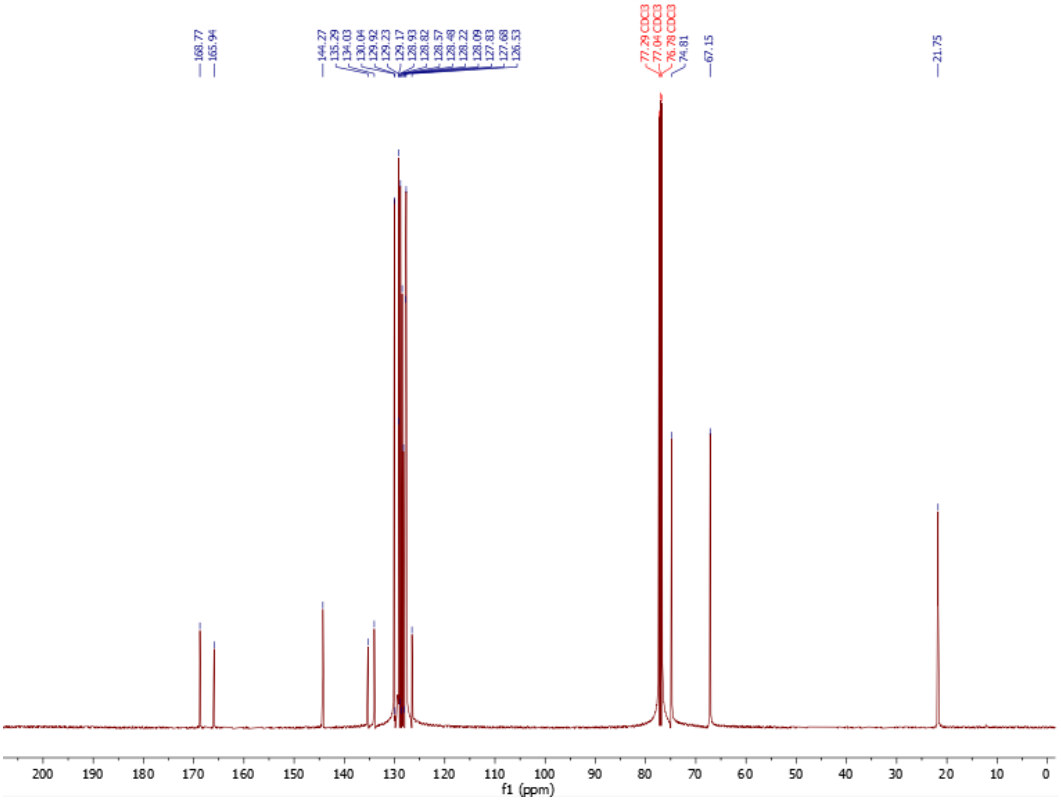


Prepared from **1e** and 4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **3u** as a white solid (65% y) **Rf =** 0.53 (2:8 EtOAc/Hex); **m.p=** 62ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.45 – 7.39 (m, 2H), 7.30 – 7.22 (m, 3H), 7.18 – 7.04 (m, 7H), 5.10 – 4.99 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.15, 166.32, 144.65, 135.67, 134.41, 130.42, 130.30, 130.19, 129.74, 129.60, 129.55, 129.30, 129.20, 129.00, 128.95, 128.86, 128.74, 128.68, 128.60, 128.47, 128.34, 128.27, 128.21, 128.06, 126.92, 126.80, 75.19, 67.53, 22.13 ppm; **IR (neat): ν (cm-1) =** 3028, 1747, 1708, 1613, 1579, 1498, 1455, 1375, 1350, 1306, 1285, 1251, 1203, 1166, 1100, 1027, 952, 906, 839, 744, 695.

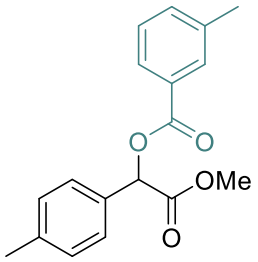
^{1}H NMR (500 MHz, $CDCl_3$): 3u



^{13}C NMR (126 MHz, $CDCl_3$): 3u

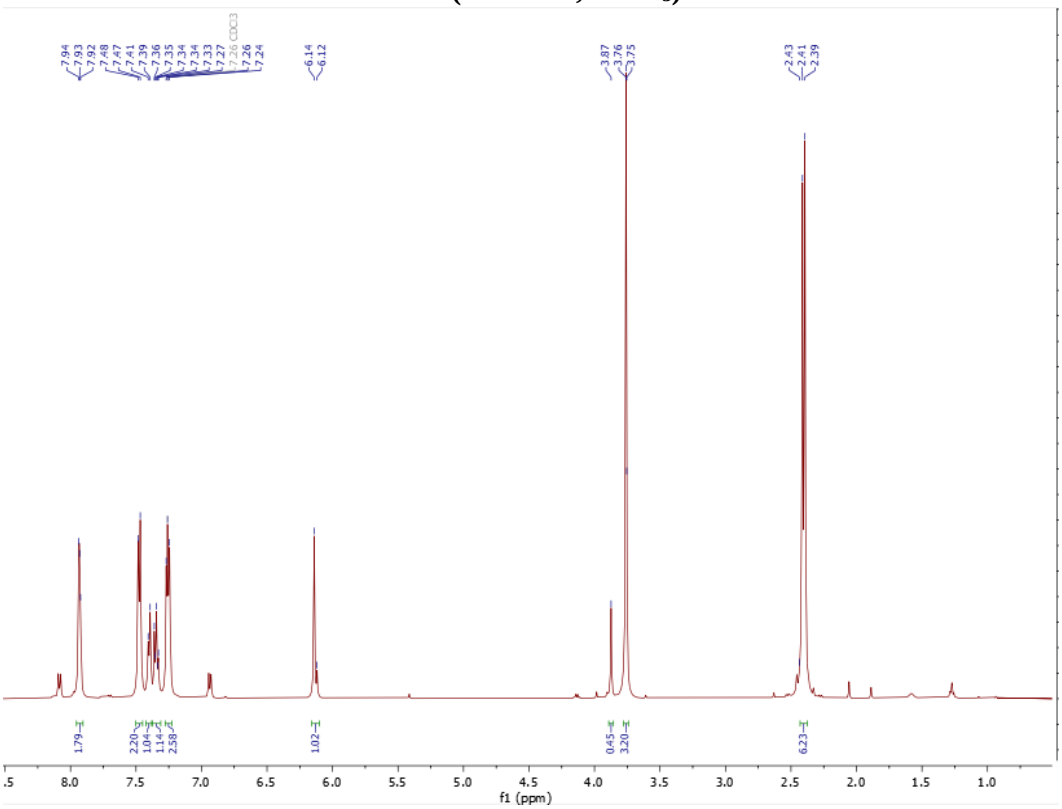


3v. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 3-methylbenzoate

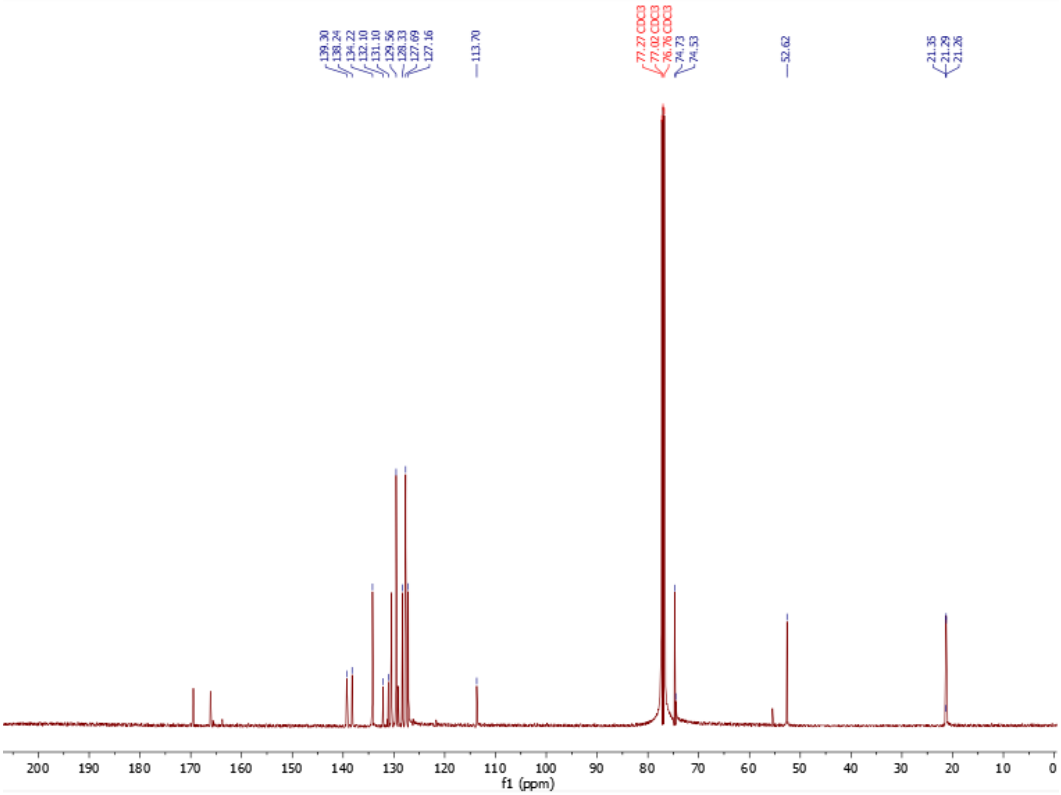


Prepared from **1b** and 3-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3v** as a white solid (85% y) **Rf =** 0.34 (1:9 EtOAc/Hex); **m.p=** 57ºC; **^{1}H NMR** (500 MHz, CDCl3) δ 7.95 – 7.90 (m, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.35 (dd, J = 9.9, 5.8 Hz, 1H), 7.25 (d, J = 7.6 Hz, 2H), 6.13 (d, J = 10.9 Hz, 1H), 3.76 (s, 3H), 2.40 (d, J = 9.1 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 139.30, 138.24, 134.22, 132.10, 131.10, 129.56, 128.33, 127.69, 127.16, 113.70, 77.27, 77.02, 76.76, 74.73, 74.53, 52.62, 21.35, 21.29, 21.26 ppm; **IR (neat): ν (cm-1) =** 2952, 1753, 1716, 1608, 1588, 1513, 1453, 1433, 1347, 1326, 1303, 1282, 1259, 1219, 1189, 1172, 1102, 1045, 970, 930, 914, 847, 825, 783, 748, 679, 635.

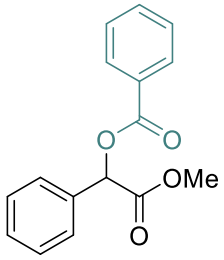
^{1}H NMR (500 MHz, $CDCl_3$): 3v



^{13}C NMR (126 MHz, $CDCl_3$): 3v

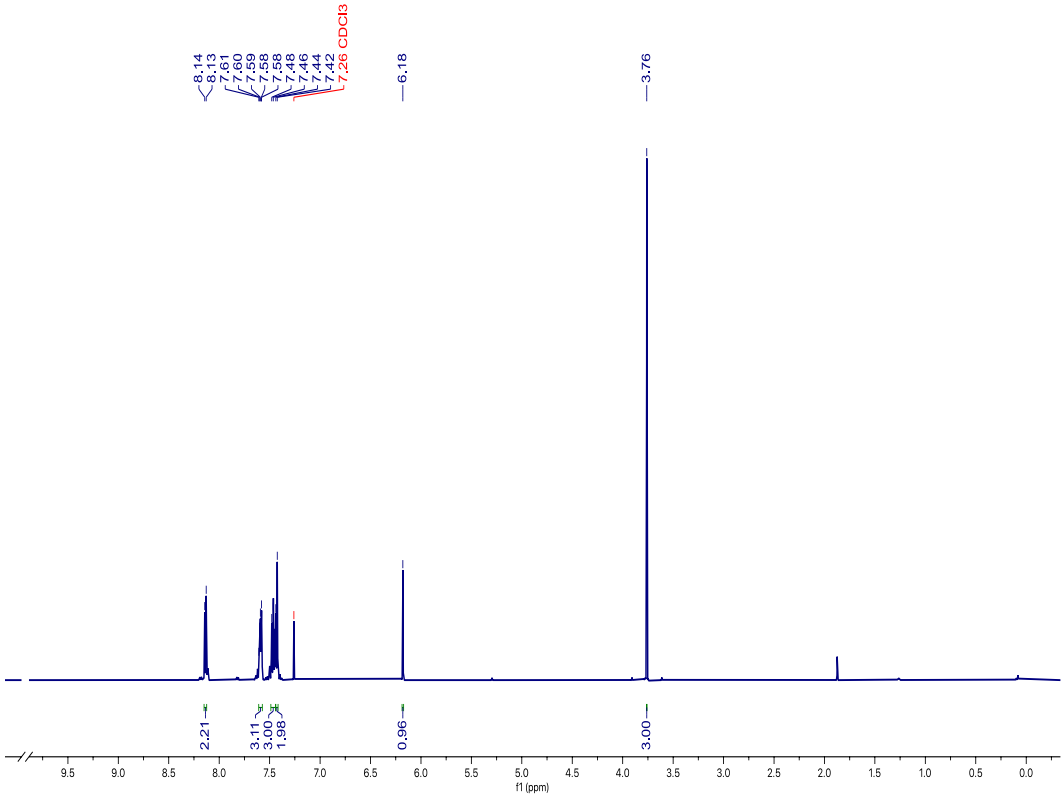


3w. 2-methoxy-2-oxo-1-phenylethyl benzoate

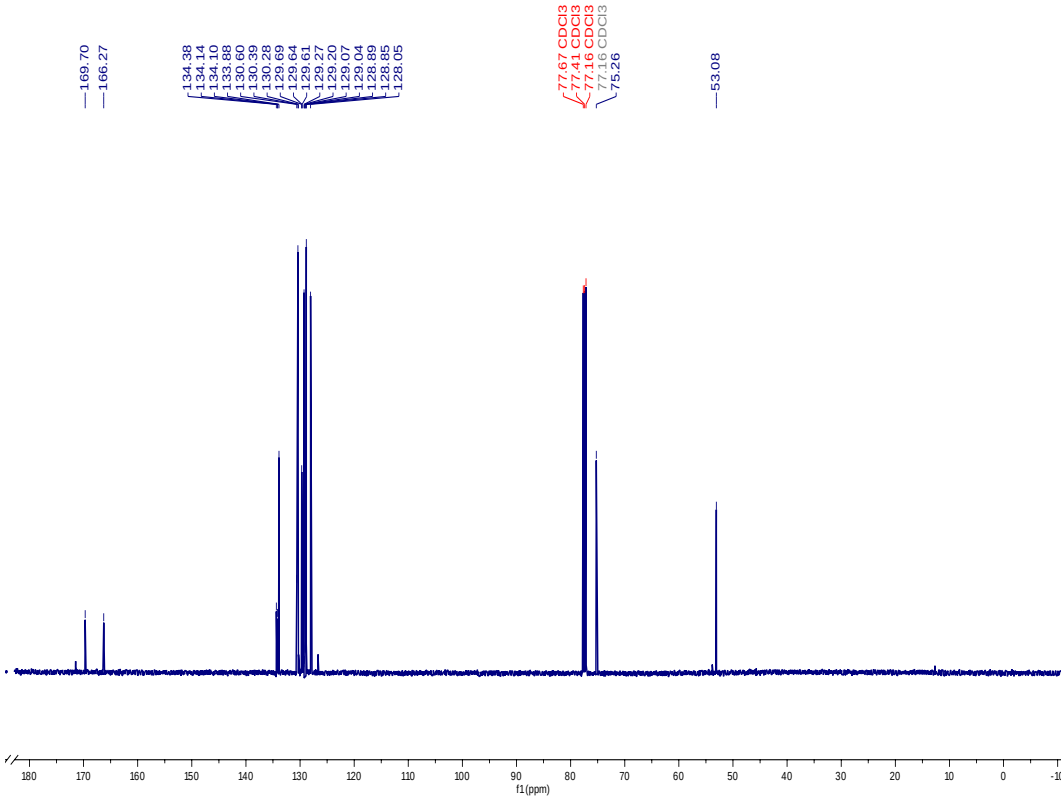


Prepared from **1a** and benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3w** as a white solid (14% y). **Rf =** 0.39 (1:1 CH_2Cl_2/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.1 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.50 – 7.41 (m, 2H), 6.18 (s, 1H), 3.76 (s, 4H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.70, 166.27, 134.38, 134.14, 134.10, 133.88, 130.60, 130.39, 130.28, 129.69, 129.64, 129.61, 129.27, 129.20, 129.07, 129.04, 128.89, 128.85, 128.05, 77.67, 77.41, 77.16, 75.26, 53.08 ppm.

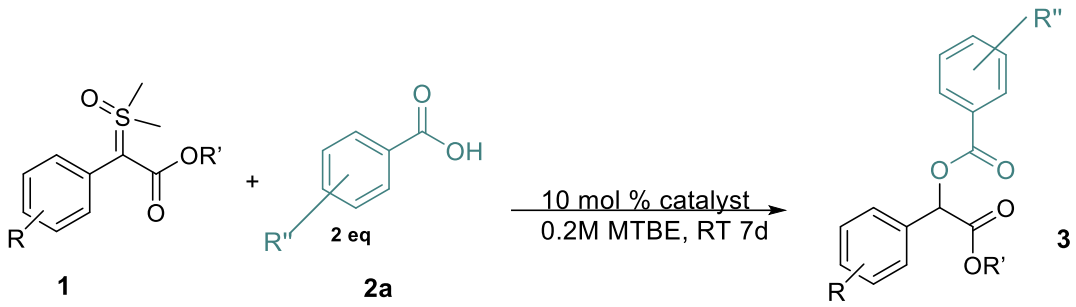
^{1}H NMR (500 MHz, $CDCl_3$): 3w



^{13}C NMR (126 MHz, $CDCl_3$): 3w

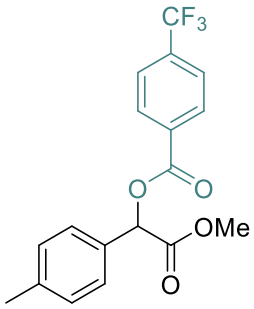


General Procedure for Enantioselective O-H Insertion of Sulfoxonium Ylides:



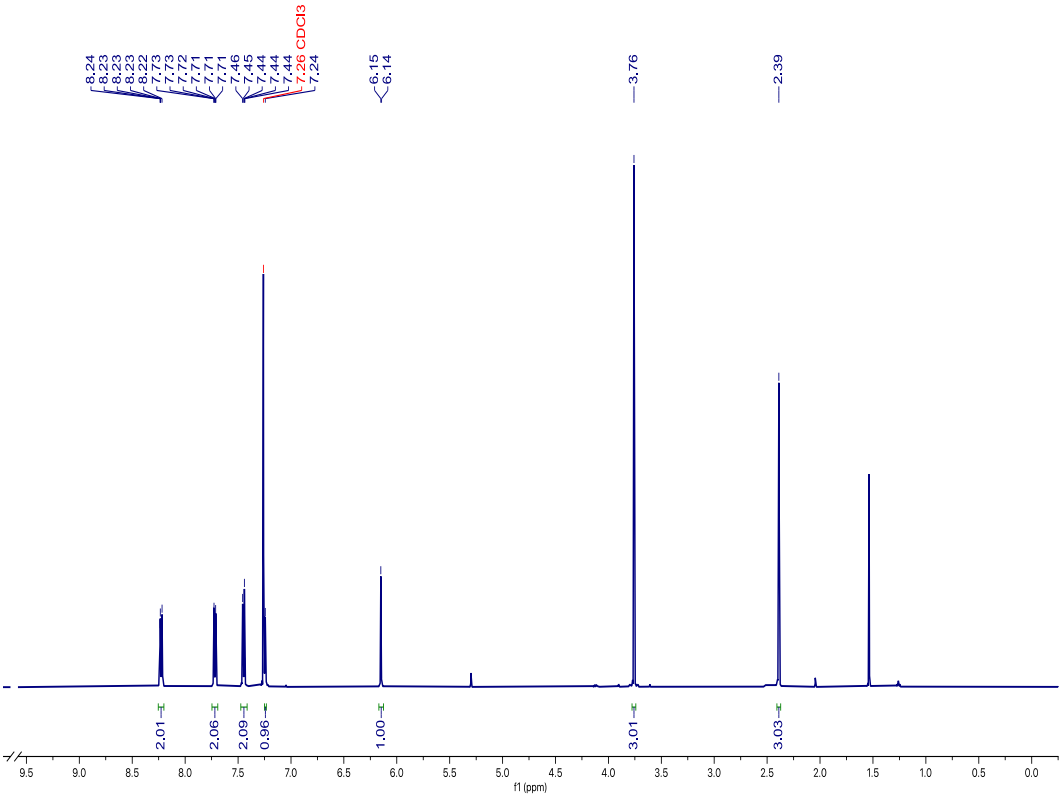
To a 2mL flame dried glass vial with a stir bar, fitted with a screw cap that has a Teflon coated septum for injections, was added 0.1 mmol of the respective sulfoxonium ylide (1 equiv.), 0.1 mmol of the pyrene thiourea catalyst (~6.5 mg), and 0.5mL of MTBE (0.2M). The reaction was left to stir at room temperature for ~15 minutes before 0.02mmol of a benzoic acid was added to the reaction vial. At this point, the reaction was left to react at room temperature until TLC indicated that enough starting material had been consumed (between 1-7 days). The product was purified by column chromatography using 10 EtOAc: 90 Hexanes. The *ee* of the purified product was determined by chiral HPLC depending on the method determined for each product.

3x. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-(trifluoromethyl)benzoate

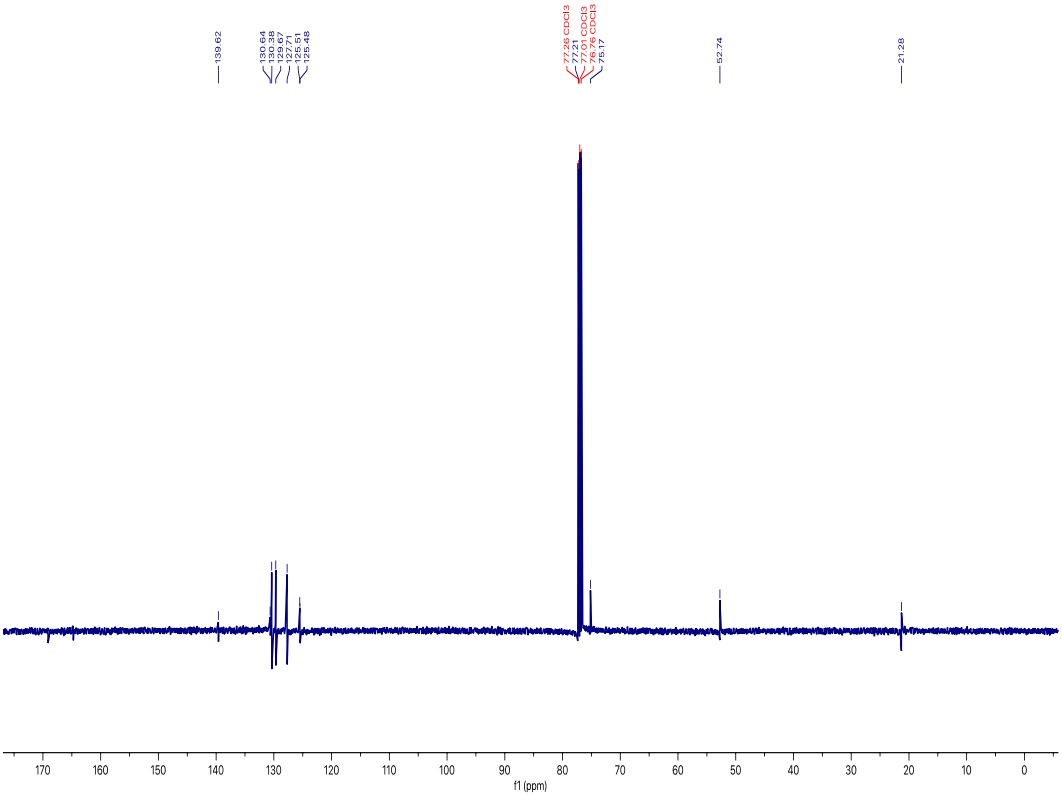


Prepared from **1b** and 4-(trifluoromethyl)benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3x** as a white solid (29% y). **Rf =** 0.37 (1:9 EtOAc/Hex); **m.p=** 105°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 2H), 7.75 – 7.69 (m, 2H), 7.47 – 7.41 (m, 2H), 7.24 (s, 1H), 6.15 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.62, 130.64, 130.38, 129.67, 127.71, 125.51, 125.48, 77.26, 77.21, 77.01, 76.76, 75.17, 52.74, 21.28 ppm; **IR (neat): ν (cm-1) =** 2958, 1756, 1723, 1436, 1413, 1324, 1285, 1262, 1220, 1167, 1098, 1065, 1033, 1016, 964, 860, 823, 791, 771, 744, 699.

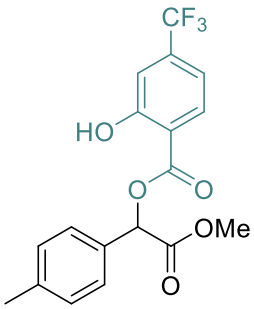
^{1}H NMR (500 MHz, $CDCl_3$): 3x



^{13}C NMR (126 MHz, $CDCl_3$): 3x

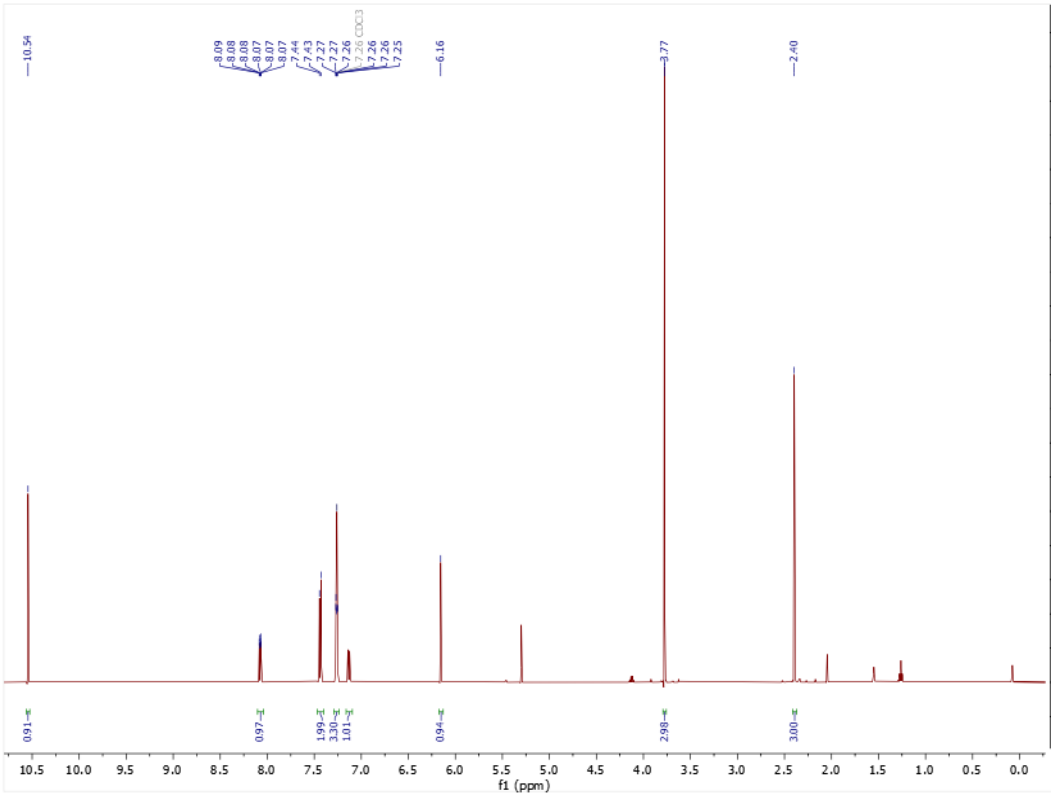


3y. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2-hydroxy-4-(trifluoromethyl)benzoate

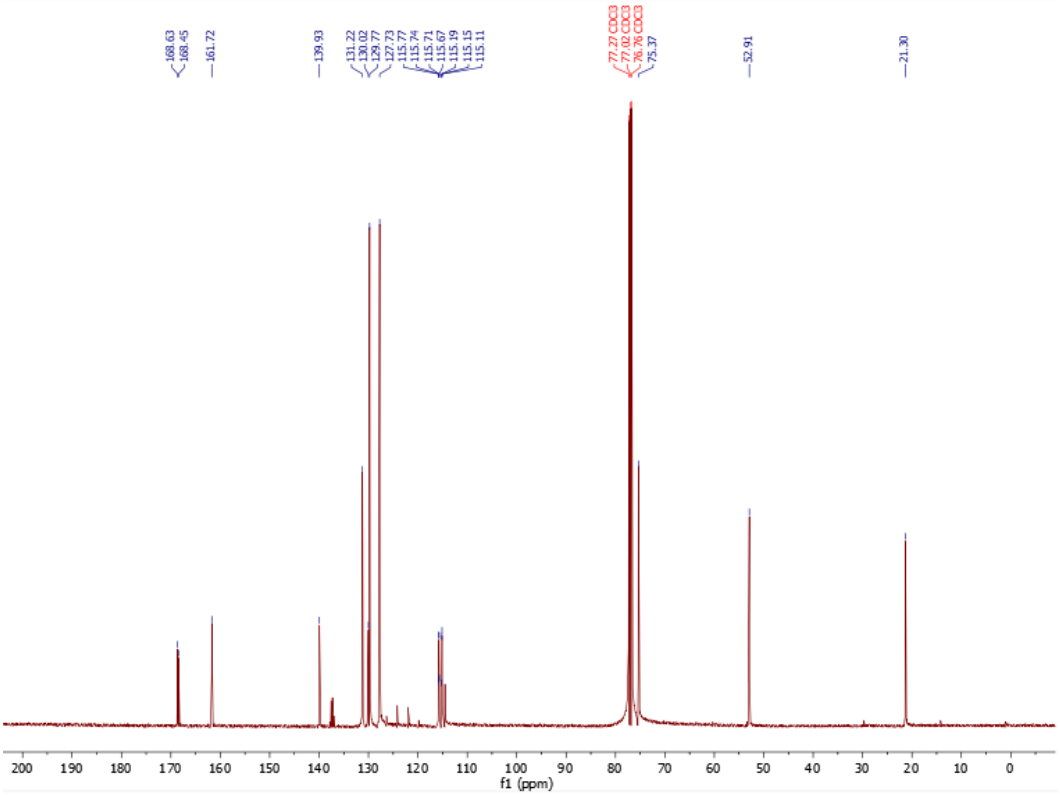


Prepared from **1b** and 2-hydroxy-4-(trifluoromethyl)benzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3y** as a white solid (32% y). **Rf =** 0.51 (1:9 EtOAc/Hex); **m.p=** 62°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.07 (ddd, *J* = 8.2, 1.3, 0.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.29 – 7.23 (m, 3H), 7.13 (ddd, *J* = 8.3, 1.8, 0.7 Hz, 1H), 6.16 (s, 1H), 3.77 (s, 3H), 2.40 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 168.63, 168.45, 161.72, 139.93, 131.22, 130.02, 129.77, 127.73, 115.77, 115.74, 115.71, 115.67, 115.19, 115.15, 115.11, 77.27, 77.02, 76.76, 75.37, 52.91, 21.30 ppm; **IR (neat): ν (cm-1) =** 3273, 2961, 2925, 1755, 1698, 1631, 1584, 1505, 1435, 1367, 1329, 1297, 1280, 1267, 1227, 1170, 1135, 1098, 1067, 1039, 974, 930, 898, 877, 812, 788, 780, 748, 698, 655, 636, 614.

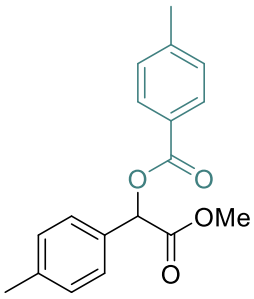
^{1}H NMR (500 MHz, $CDCl_3$): 3y



^{13}C NMR (126 MHz, $CDCl_3$): 3y

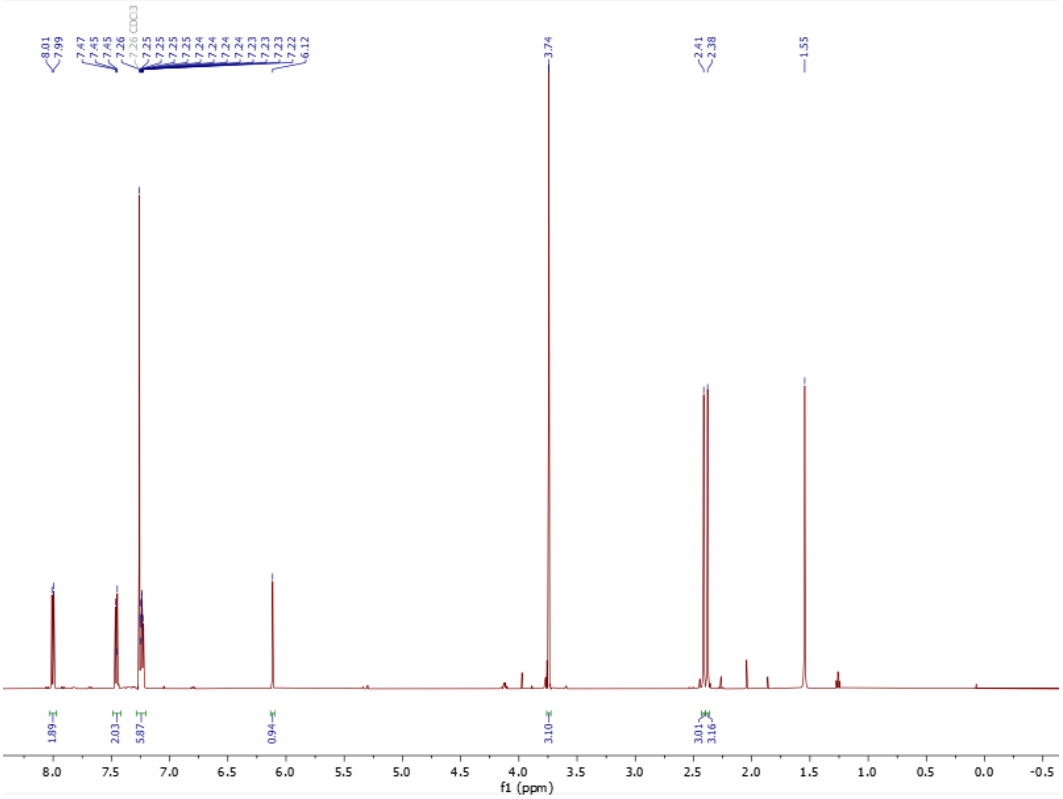


3z. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-methylbenzoate

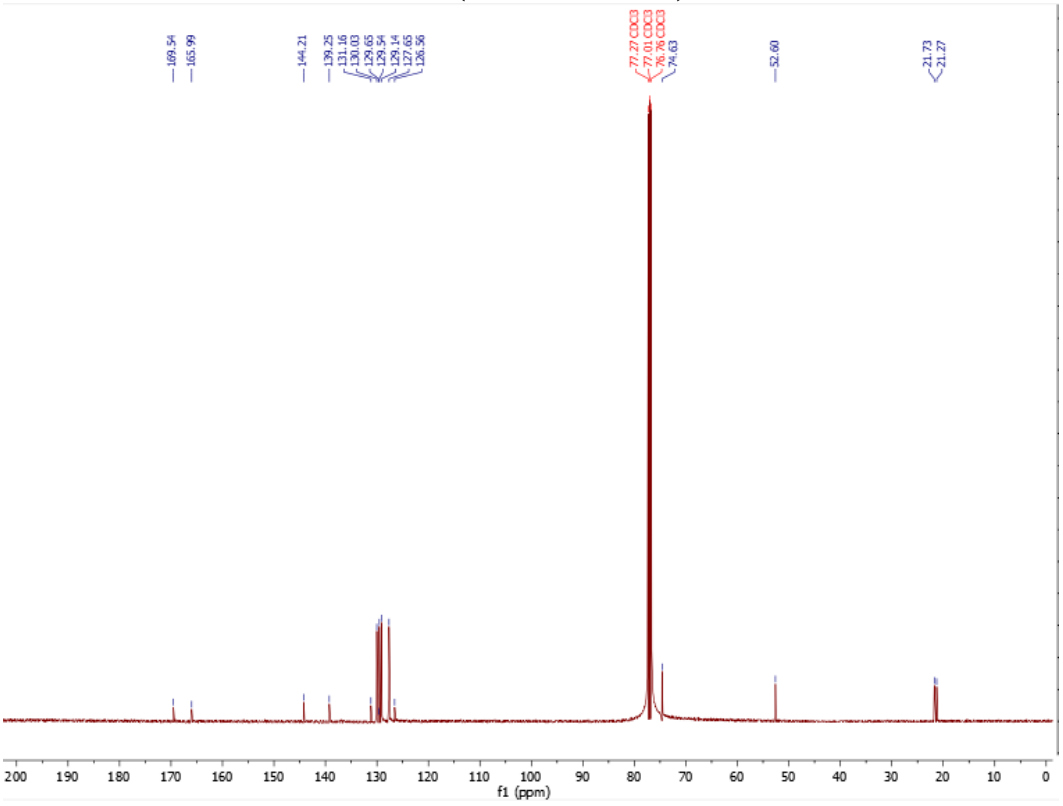


Prepared from **1b** and 4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3z** as a white solid (40% y). **Rf =** 0.23 (1:9 EtOAc/Hex); **m.p=** 62^{o}C; **^{1}H NMR** (500 MHz, CDCl3) δ 8.03 – 7.97 (m, 2H), 7.49 – 7.42 (m, 2H), 7.29 – 7.20 (m, 4H), 6.12 (s, 1H), 3.74 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.54, 165.99, 144.21, 139.25, 131.16, 130.03, 129.65, 129.54, 129.14, 127.65, 126.56, 77.27, 77.01, 76.76, 74.63, 52.60, 21.73, 21.27 ppm; **IR (neat): ν (cm-1) =** 2960, 1756, 1717, 1610, 1514, 1434, 1343, 1305, 1280, 1245, 1216, 1170, 1089, 1034, 1021, 973, 931, 903, 841, 823, 782, 755, 691, 637, 614 .

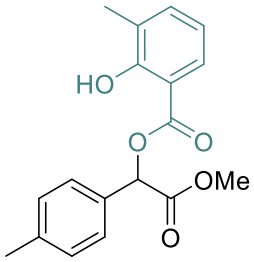
^{1}H NMR (500 MHz, $CDCl_3$): 3z



^{13}C NMR (126 MHz, $CDCl_3$): 3z

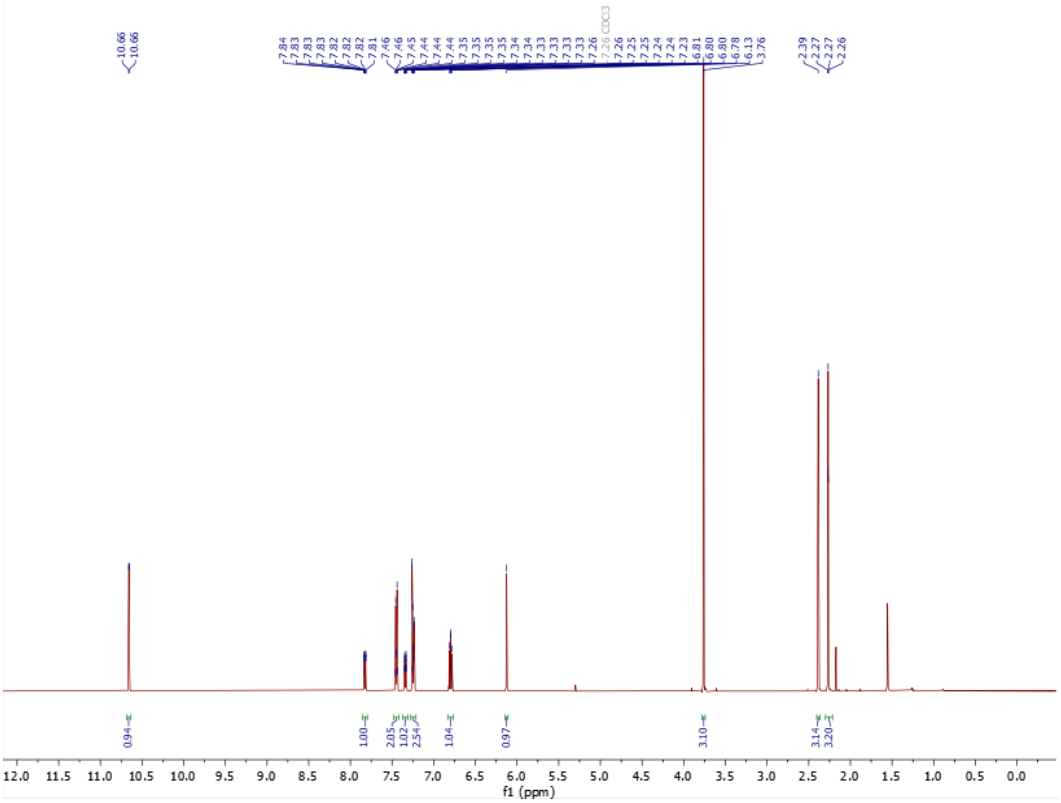


3aa. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 2-hydroxy-3-methylbenzoate

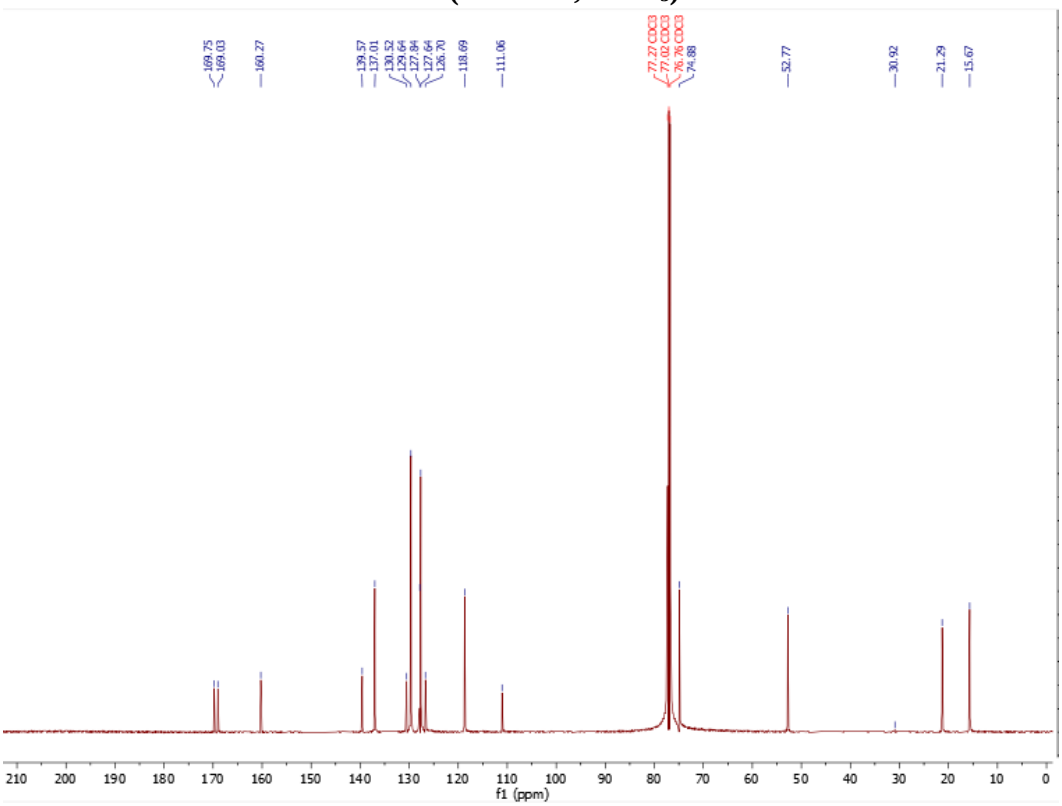


Prepared from **1b** and 2-hydroxy-3-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3aa** as a white solid (53% y). **Rf =** 0.34 (1:9 EtOAc/Hex); **m.p=** 99ºC; **^{1}H NMR** (500 MHz, CDCl3) δ 10.66 (d, J = 0.6 Hz, 1H), 7.82 (ddd, J = 8.0, 1.7, 0.7 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.34 (ddt, J = 7.4, 1.8, 0.9 Hz, 1H), 7.27 – 7.21 (m, 2H), 6.80 (dd, J = 8.0, 7.3 Hz, 1H), 6.13 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.27 (d, J = 0.7 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.64, 168.92, 160.15, 139.46, 136.89, 130.40, 129.53, 127.73, 127.53, 126.59, 118.57, 110.95, 74.77, 52.66, 30.81, 21.17, 15.55 ppm; **IR (neat): ν (cm-1) =** 2952, 1753, 1672, 1614, 1517, 1433, 1357, 1329, 1290, 1267, 1244, 1220, 1172, 1136, 1082, 1043, 971, 936, 87, 825, 812, 782, 755, 681, 635.

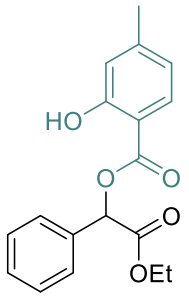
^{1}H NMR (500 MHz, $CDCl_3$): 3aa



^{13}C NMR (126 MHz, $CDCl_3$): 3aa

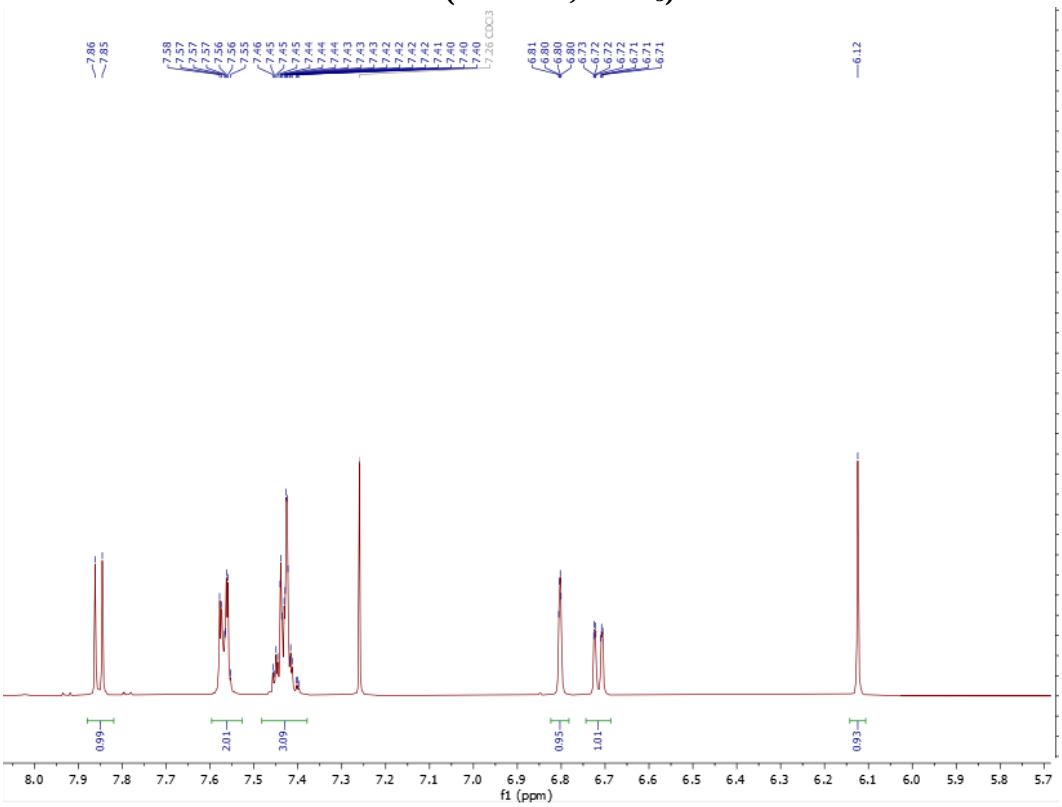


3ab. 2-ethoxy-2-oxo-1-phenylethyl 2-hydroxy-4-methylbenzoate

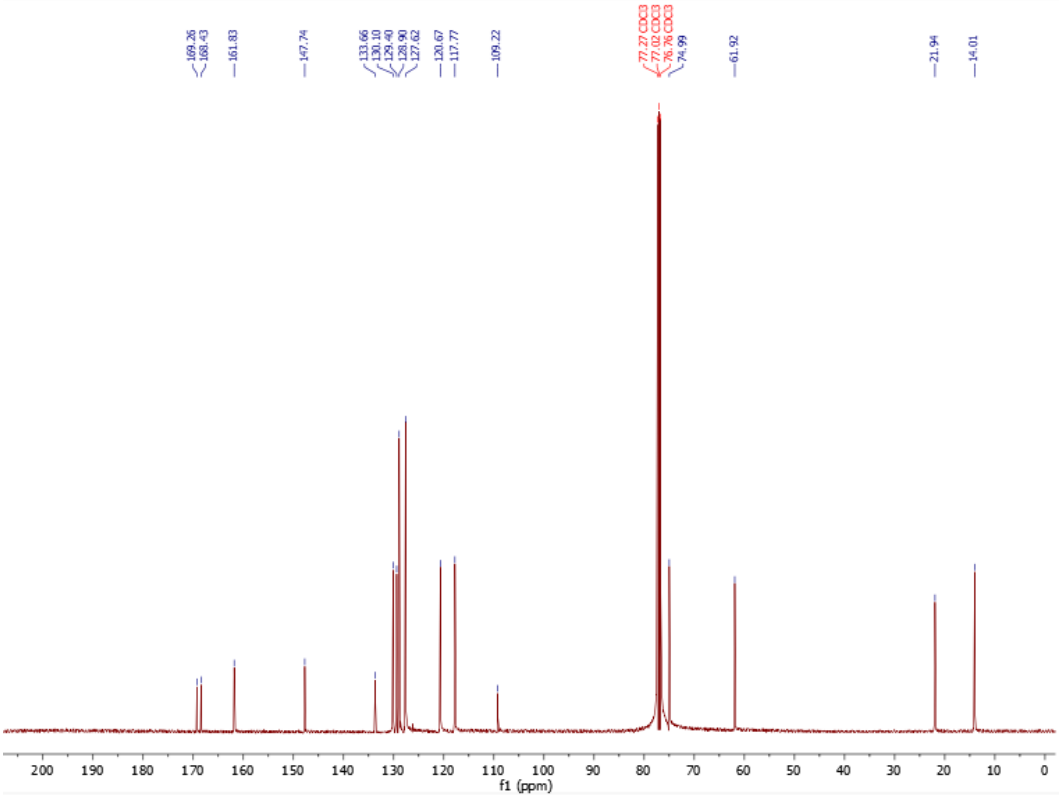


Prepared from **1f** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3ab** as a clear oil (27% y). **Rf =** 0.25 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 6.80 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.74 – 6.69 (m, 1H), 6.12 (s, 1H), 4.31 – 4.14 (m, 2H), 2.35 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.26, 168.43, 161.83, 147.74, 133.66, 130.10, 129.40, 128.90, 127.62, 120.67, 117.77, 109.22, 77.27, 77.02, 76.76, 74.99, 61.92, 21.94, 14.01 ppm; **IR (neat): ν (cm-1) =** 3173, 2988, 2909, 1745, 1672, 1623, 1580, 1505, 1488, 1358, 1300, 1269, 1248, 1211, 1181, 1155, 1095, 1071, 1033, 1008, 952, 907, 864, 805, 772, 735, 694, 618.

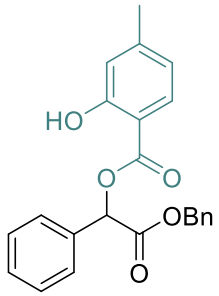
^{1}H NMR (500 MHz, $CDCl_3$): 3ab



^{13}C NMR (126 MHz, $CDCl_3$): 3ab

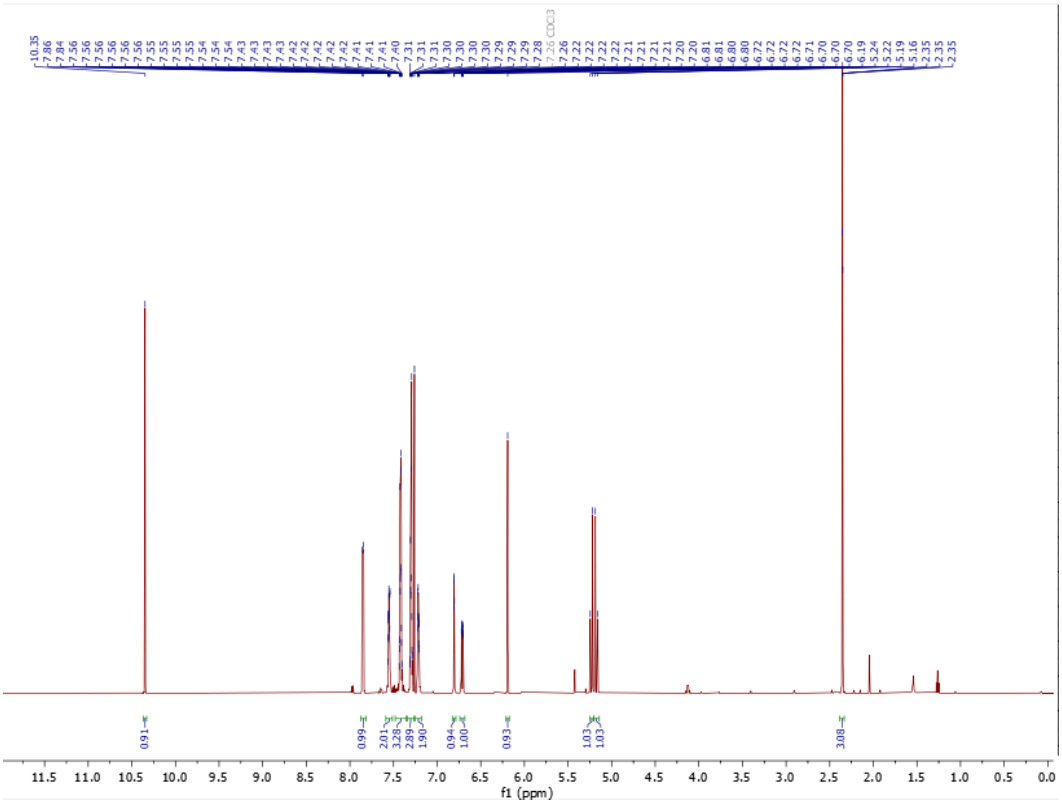


3ac. 2-(benzyloxy)-2-oxo-1-phenylethyl 2-hydroxy-4-methylbenzoate

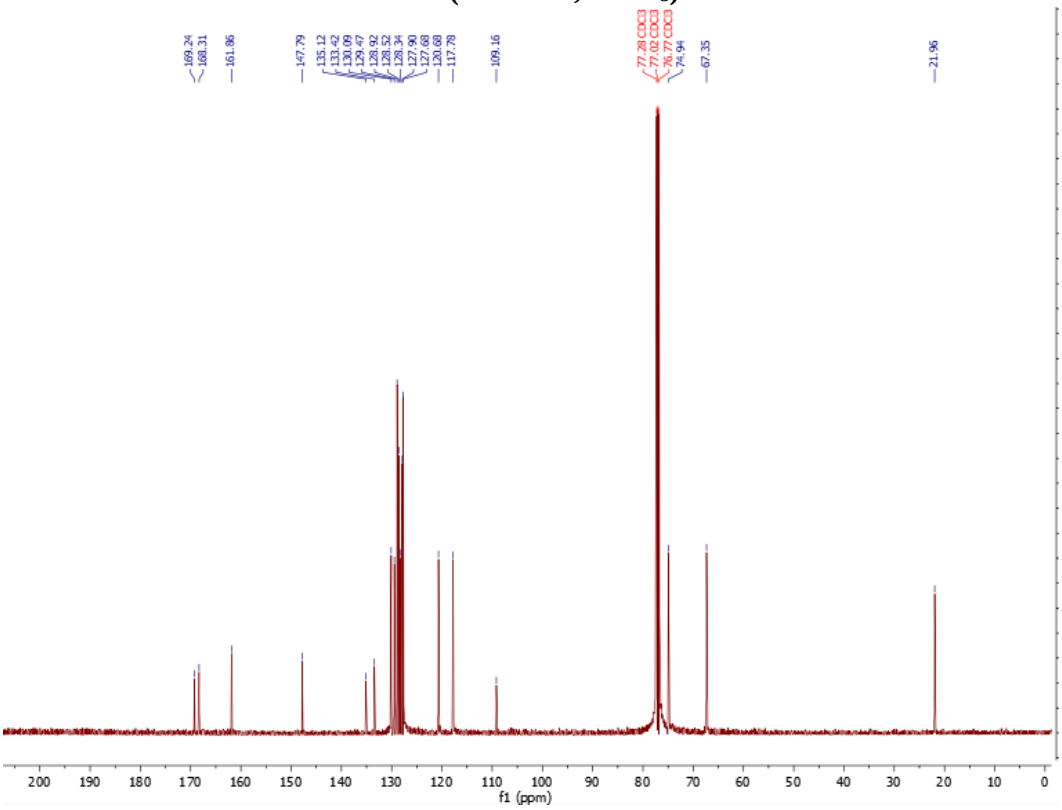


Prepared from **1e** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3ac** as a white solid (12% y). **Rf =** 0.28 (1:9 EtOAc/Hex); **m.p=** 64ºC; **^{1}H NMR** (500 MHz, CDCl3) δ 10.35 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.48 – 7.35 (m, 3H), 7.34 – 7.26 (m, 3H), 7.26 – 7.18 (m, 2H), 6.81 (dd, J = 1.6, 0.9 Hz, 1H), 6.71 (ddd, J = 8.2, 1.6, 0.7 Hz, 1H), 6.19 (s, 1H), 5.23 (d, J = 12.4 Hz, 1H), 5.17 (d, J = 12.4 Hz, 1H), 2.35 (d, J = 0.6 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.24, 168.31, 161.86, 147.79, 135.12, 133.42, 130.09, 129.47, 128.92, 128.52, 128.34, 127.90, 127.68, 120.68, 117.78, 109.16, 77.28, 77.02, 76.77, 74.94, 67.35, 21.96 ppm**; IR (neat): ν (cm-1) =** 3234, 1742, 1671, 1622, 1579, 1503, 1456, 1335, 1324, 1246, 1205, 1184, 1155, 1094, 1023, 950, 911, 870, 826, 776, 748, 734, 695, 609.

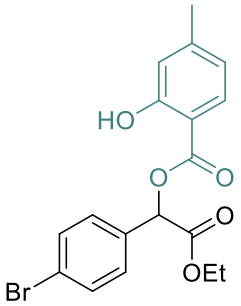
^{1}H NMR (500 MHz, $CDCl_3$): 3ac



^{13}C NMR (126 MHz, $CDCl_3$): 3ac

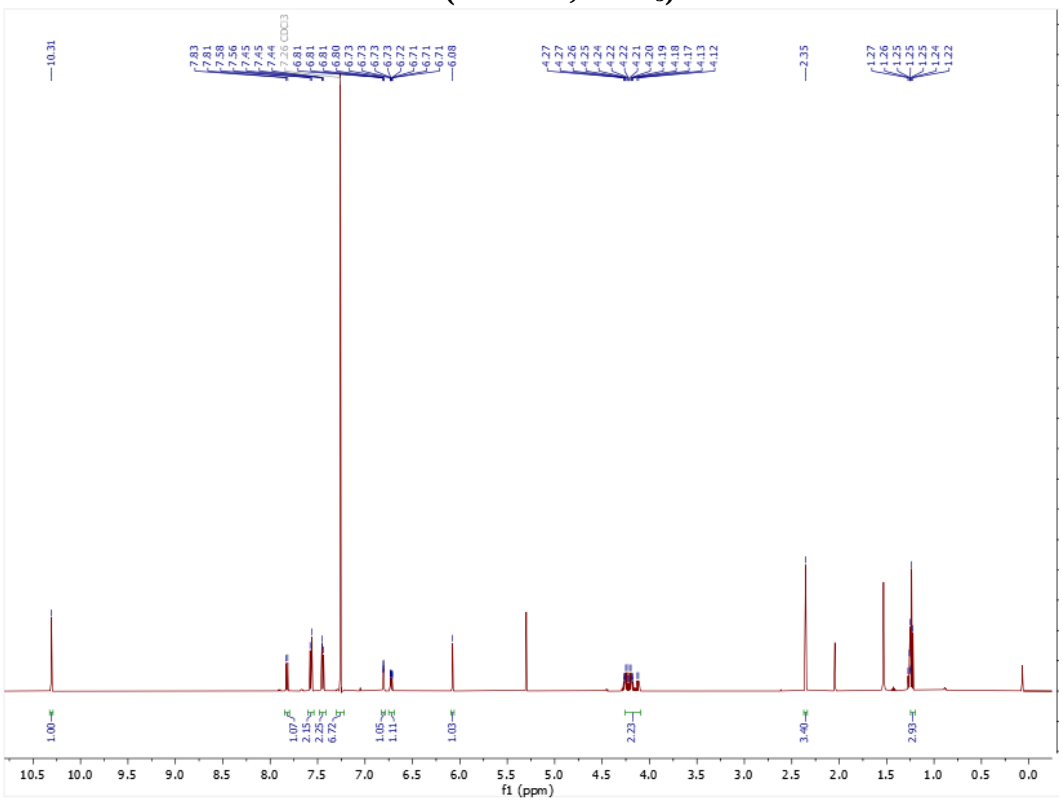


3ad. 1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 2-hydroxy-4-methylbenzoate

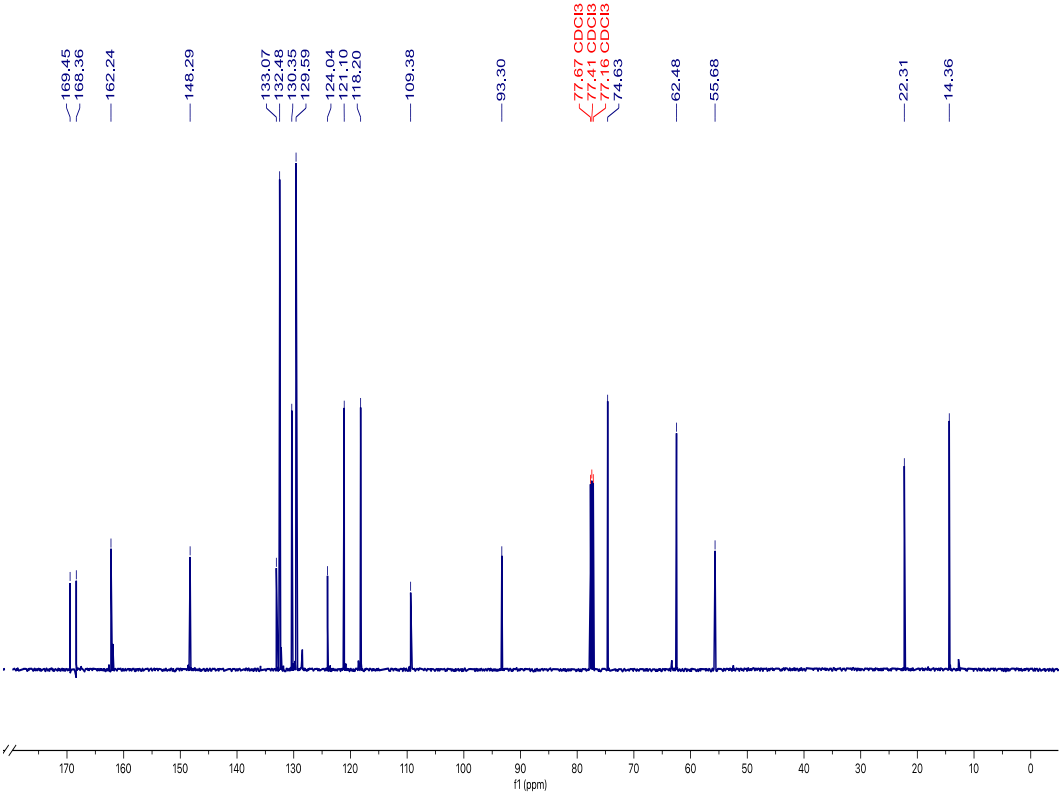


Prepared from **1h** and 2-hydroxy-4-methylbenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3ad** as a white solid (21% y). **Rf =** 0.38 (1:9 EtOAc/Hex); **m.p=** 64°C; **^{1}H NMR** (500 MHz, CDCl3) δ 10.31 (s, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.48 – 7.41 (m, 2H), 6.81 (dd, J = 1.6, 0.9 Hz, 1H), 6.72 (ddd, J = 8.1, 1.6, 0.6 Hz, 1H), 6.08 (s, 1H), 2.35 (s, 3H), 1.23 (d, J = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.45, 168.36, 162.24, 148.29, 133.07, 132.48, 130.35, 129.59, 124.04, 121.10, 118.20, 109.38, 93.30, 77.67, 77.41, 77.16, 74.63, 62.48, 55.68, 22.31, 14.36 ppm; **IR (neat): ν (cm-1) =** 2982, 1752, 1674, 1622, 1595, 1579, 1503, 1489, 1455, 1352, 1287, 1247, 1205, 1150, 1091, 1071, 1033, 1012, 951, 908, 870, 815, 777, 734, 699, 620.

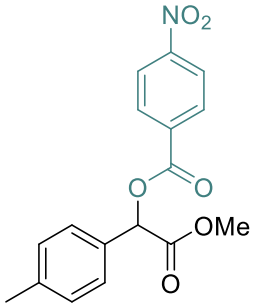
^{1}H NMR (500 MHz, $CDCl_3$): 3ad



^{13}C NMR (126 MHz, $CDCl_3$): 3ad

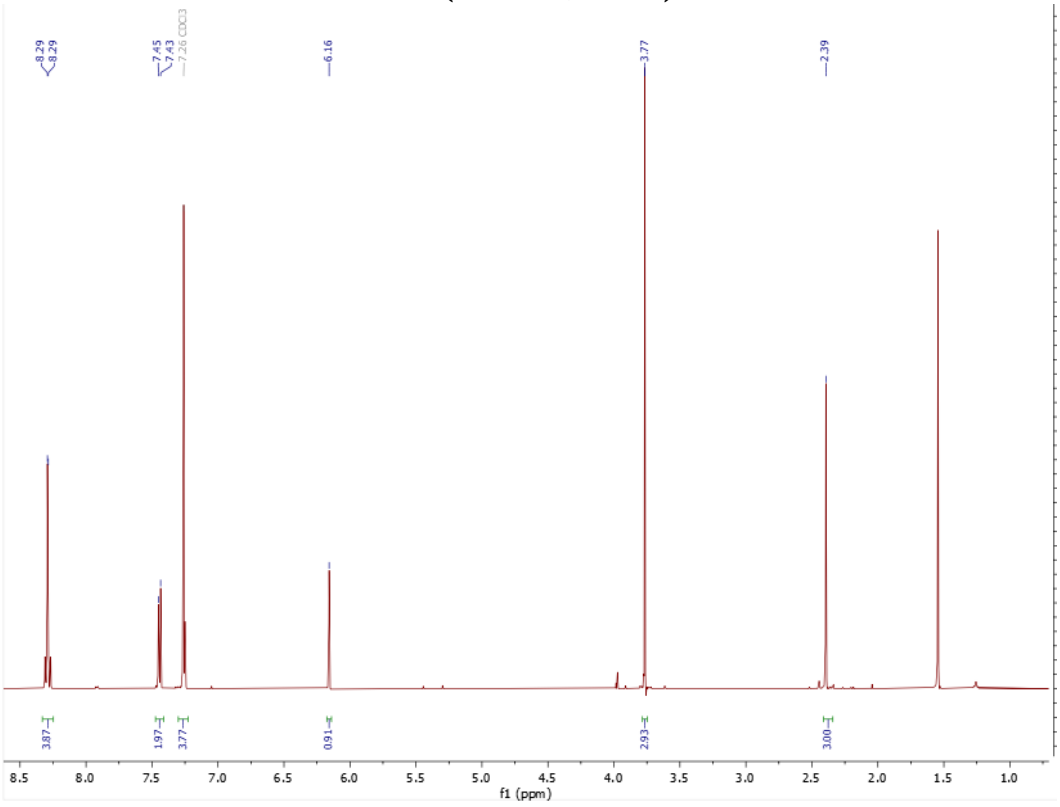


3ae. 2-methoxy-2-oxo-1-(p-tolyl)ethyl 4-nitrobenzoate

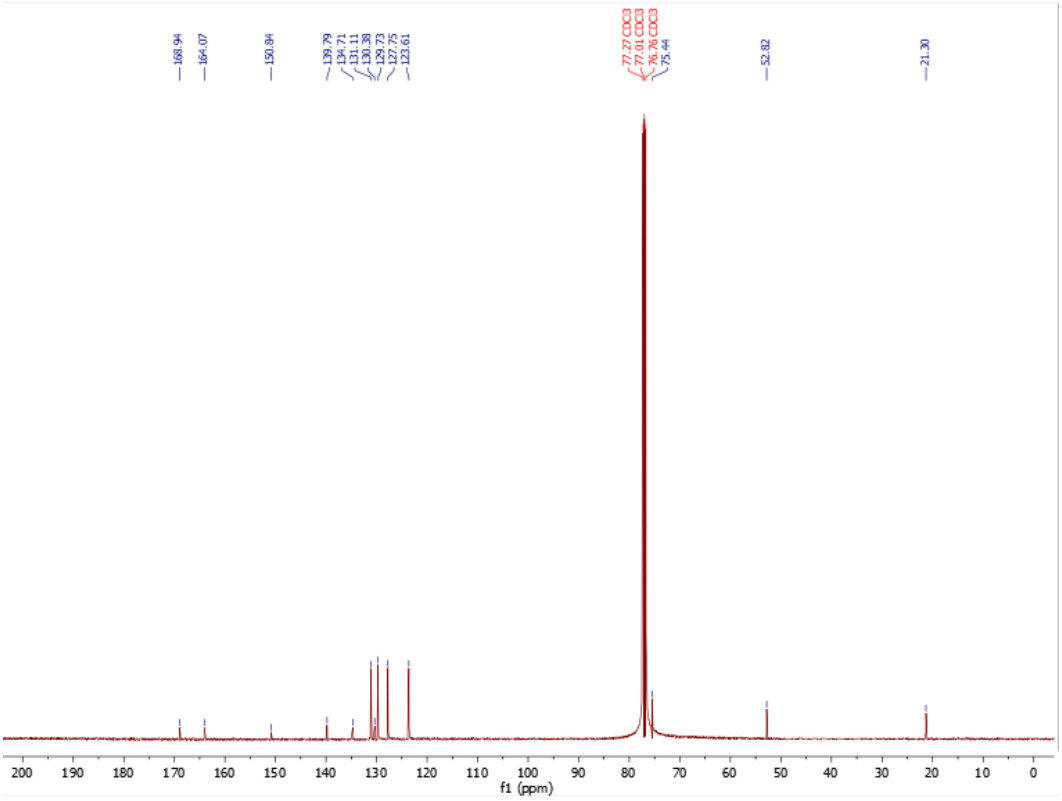


Prepared from **1b** and 4-nitrobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3ae** as a white solid (25% y). **Rf =** 0.19 (1:9 EtOAc/Hex); **m.p=** 81ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 – 8.25 (m, 4H), 7.47 – 7.41 (m, 2H), 7.26 (ddd, *J* = 8.2, 1.9, 0.9 Hz, 2H), 6.16 (s, 1H), 3.77 (s, 3H), 2.39 (s, 3H), 1.26 (d, *J* = 2.3 Hz, 0H) ppm; **^{13}C NMR** (126 MHz, CDCl3) δ 169.35, 164.48, 151.25, 140.19, 135.11, 131.51, 130.78, 130.13, 128.16, 124.01, 75.85, 53.23, 21.70 ppm; **IR (neat): ν (cm-1) =** 3115, 2956, 2926, 2858, 1748, 1724, 1610, 1532, 1434, 1345, 1304, 1287, 1261, 1220, 1171, 1117, 1099, 1036, 1013, 68, 870, 858, 838, 815, 790, 752, 716, 636.

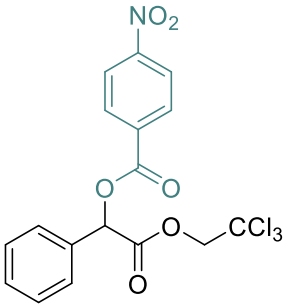
^{1}H NMR (500 MHz, $CDCl_3$): 3ae



^{13}C NMR (126 MHz, $CDCl_3$): 3ae

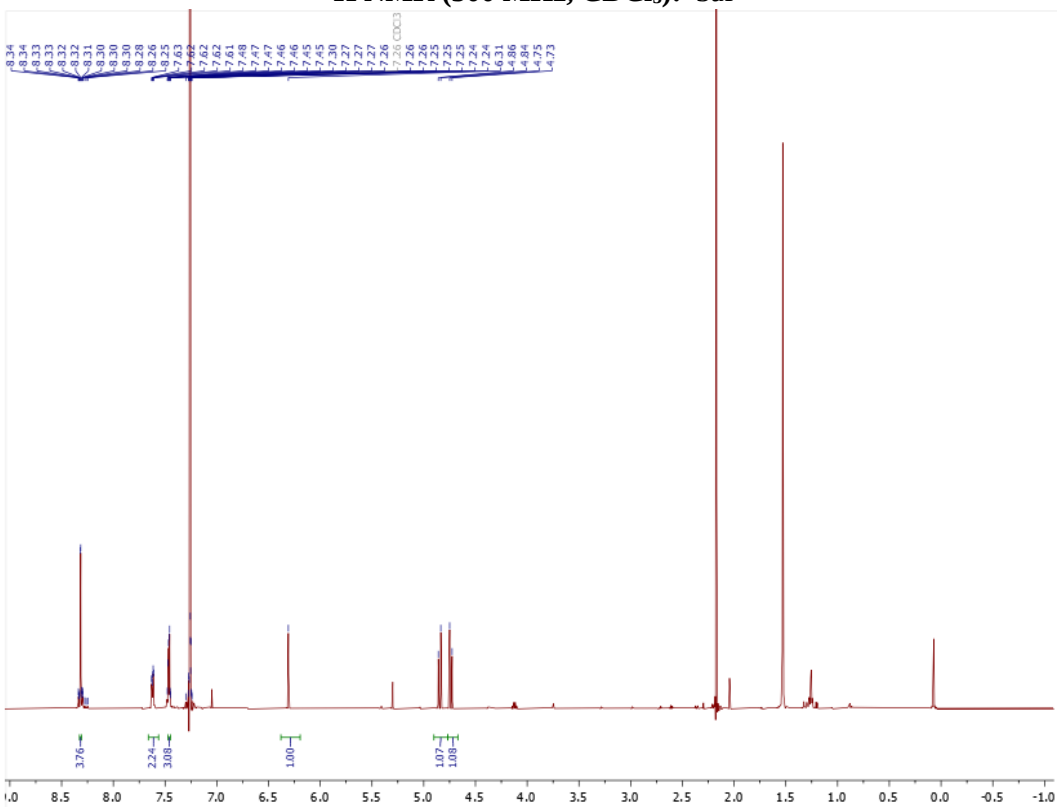


3af. 2-oxo-1-phenyl-2-(2,2,2-trichloroethoxy)ethyl 4-nitrobenzoate

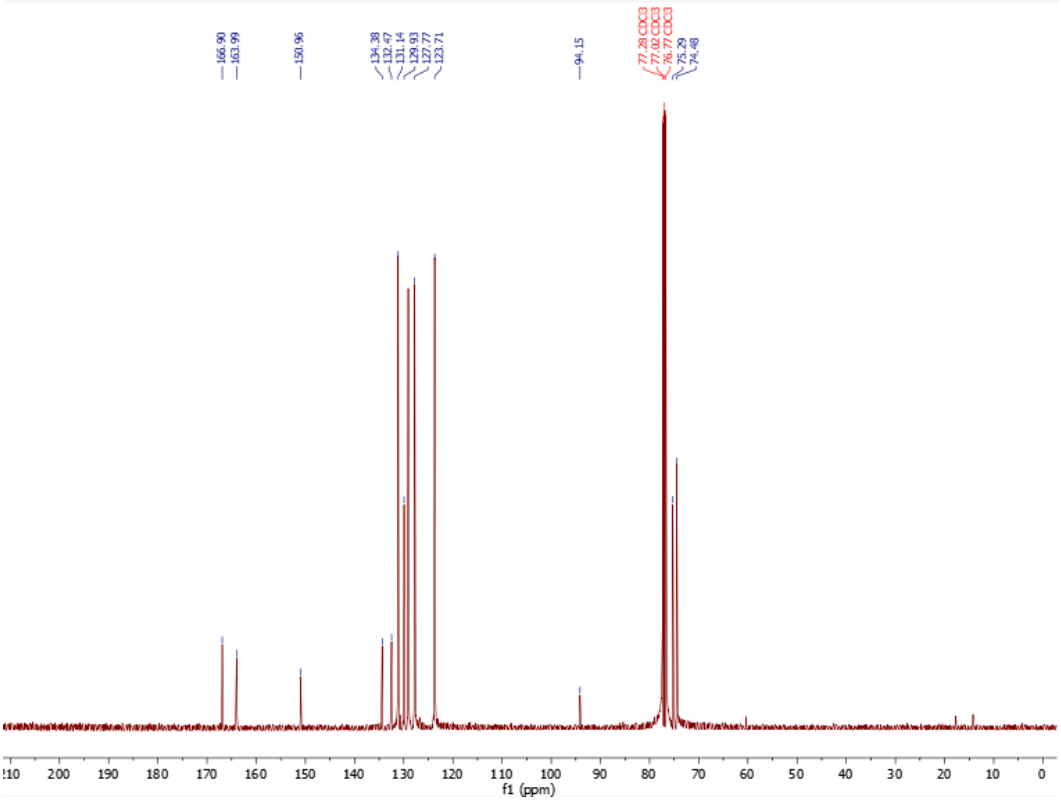


Prepared from **1g** and 4-nitrobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3af** as an off-white solid (38% y). **Rf =** 0.65 (1:9 EtOAc/Hex); **m.p=** 81°C; **^{1}H NMR** (500 MHz, CDCl3) δ 8.36 – 8.28 (m, 4H), 7.65 – 7.59 (m, 2H), 7.51 – 7.43 (m, 3H), 6.31 (s, 1H), 4.85 (d, J = 11.9 Hz, 1H), 4.74 (d, J = 11.9 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.17 (s, 14H), 1.34 – 1.23 (m, 2H), 0.07 (s, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.90, 163.99, 150.96, 134.38, 132.47, 131.14, 129.93, 127.77, 123.71, 94.15, 77.28, 77.02, 76.77, 75.29, 74.4 ppm; **IR (neat): ν (cm-1) =** 3114, 2974, 2865, 1773, 1761, 1728, 1608, 1525, 1496, 1455, 1432, 1411, 1376, 1347, 1323, 1302, 1280, 1257, 1203, 1184, 1152, 1100, 1034, 1014, 938, 909, 874, 857, 817, 783, 737, 713, 698.

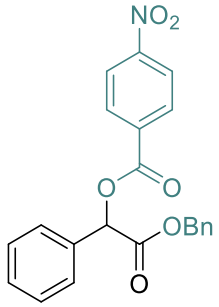
^{1}H NMR (500 MHz, $CDCl_3$): 3af



^{13}C NMR (126 MHz, $CDCl_3$): 3af

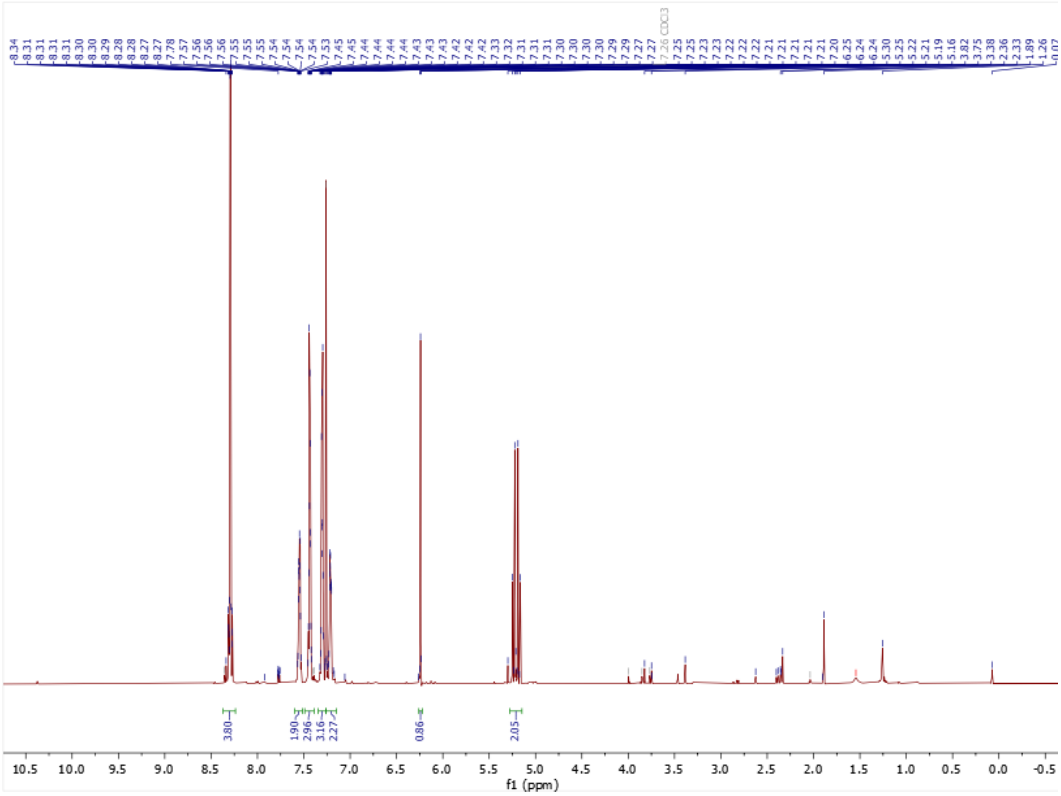


3ag. 2-(benzyloxy)-2-oxo-1-phenylethyl 4-nitrobenzoate

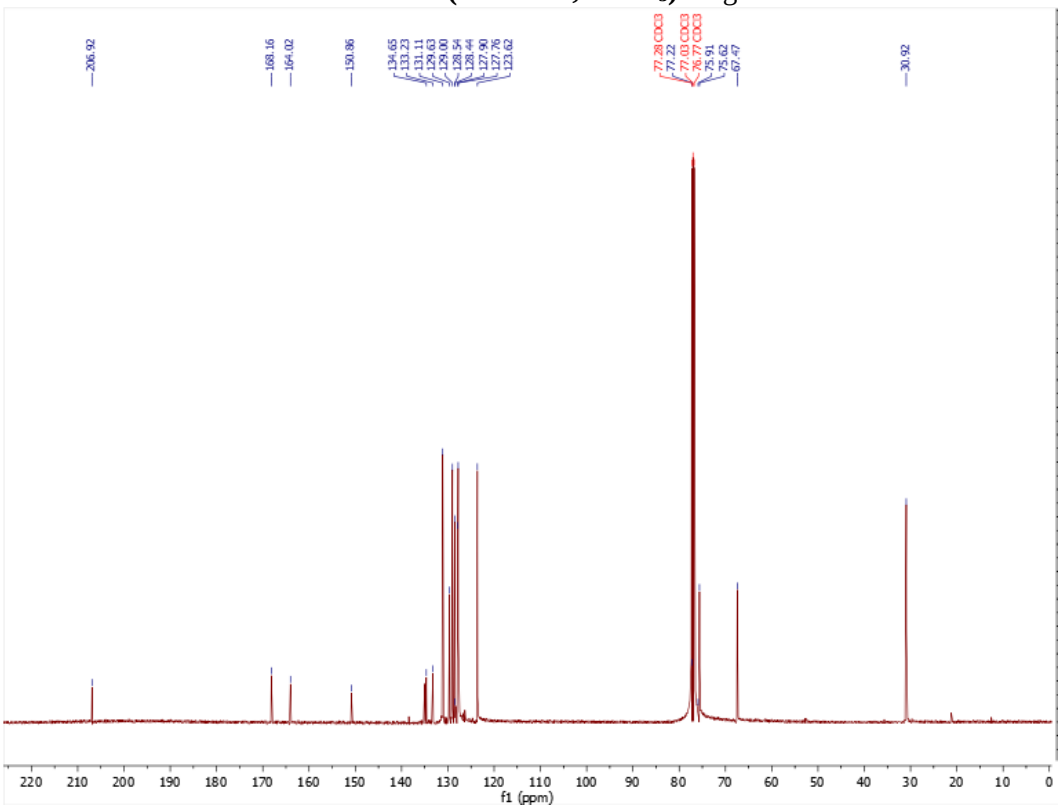


Prepared from **1e** and 4-nitrobenzoic acid. The reaction was allowed to stir for 3 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **3ag** as a white oily solid (10% y). **Rf =** 0.23 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 – 8.24 (m, 4H), 7.55 (ddt, *J* = 4.9, 2.6, 1.3 Hz, 2H), 7.49 – 7.39 (m, 3H), 7.30 (tt, *J* = 3.9, 2.4 Hz, 3H), 7.27 – 7.15 (m, 2H), 6.24 (s, 1H), 5.28 – 5.15 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.05, 168.29, 164.15, 150.99, 138.58, 135.14, 134.78, 133.36, 131.24, 131.05, 130.86, 130.41, 130.28, 129.77, 129.14, 128.89, 128.82, 128.67, 128.57, 128.53, 128.48, 128.45, 128.18, 128.04, 127.89, 127.81, 127.75, 126.82, 126.45, 124.85, 123.95, 123.75, 77.35, 76.04, 75.75, 67.60, 53.00, 52.74, 31.05, 21.33, 12.66 ppm; **IR (neat): ν (cm-1) =** 3035, 2955, 1729, 1690, 1606, 1526, 1497, 1456, 1409, 1380, 1346, 1321, 1258, 1207, 1172, 1099, 1015, 969, 943, 909, 872, 857, 824, 783, 718, 695.

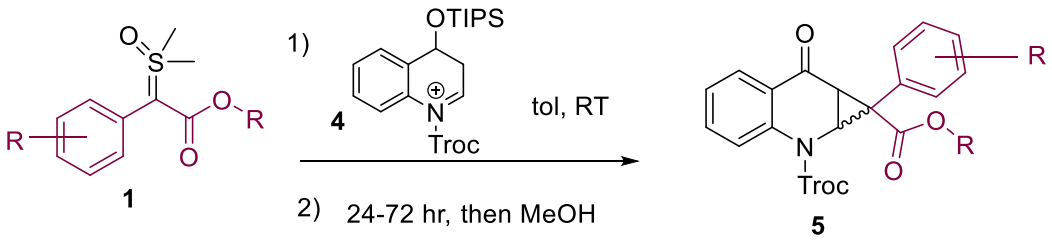
^{1}H NMR (500 MHz, $CDCl_3$): 3ag



^{13}C NMR (126 MHz, $CDCl_3$): 3ag



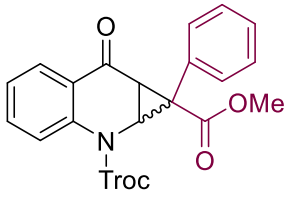
General procedure for racemic cyclopropanation of troc-protected quinolone:



To a 2mL flame dried glass vial with a stir bar, fitted with a screw cap that has a Teflon coated septum for injections, was added 0.1 mmol of the respective quinolone (1 equiv.), 0.80mL of toluene, and 30uL of TIPS-OTF to let react at 70^{o}C for 1hr. After the benzoparylium has formed, 0.1mmol of the respective ylide was added to the reaction vial and was left to react at room temperature until TLC indicated that enough starting material had been consumed (between 1-7 days). 0.3mL of 6.0M HCl was added and the reaction and let stir for atleast 1hr. The product was extracted with water and dichloromethane and then purified by column chromatography using 20 EtOAc: 80 Hexanes.

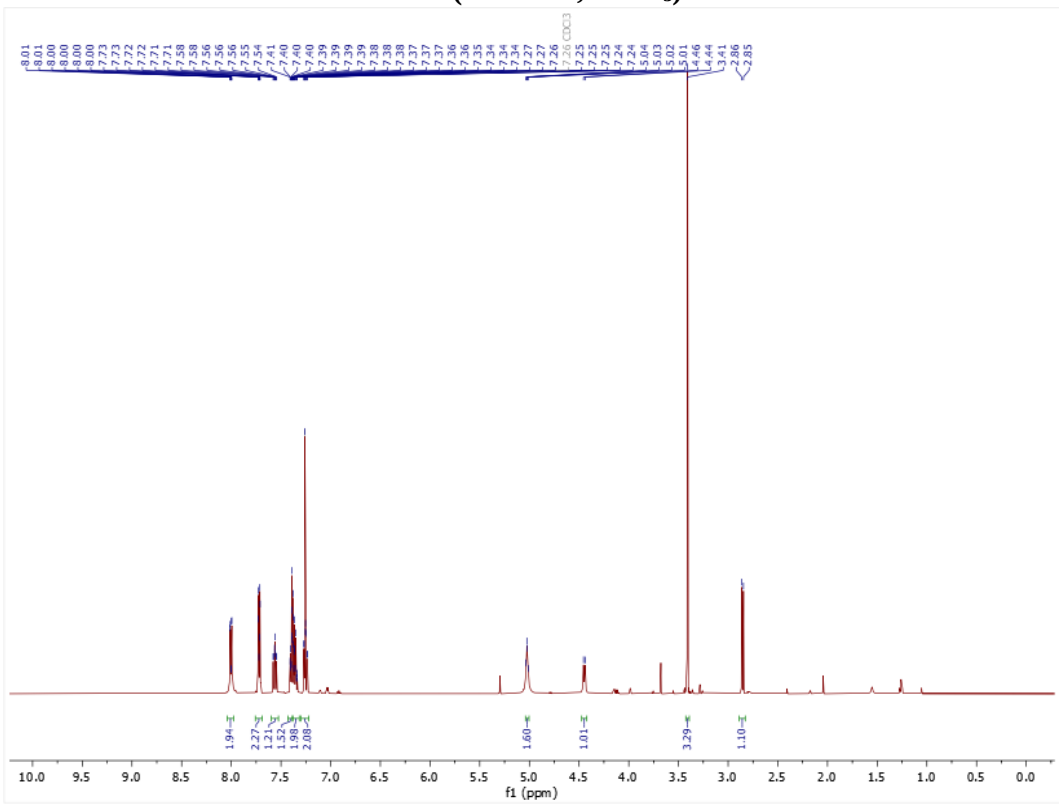
Only spectra for new compounds are provided. The synthesis of the troc protected quinolone follows the same procedure but uses the troc protecting group as opposed to the CBz protecting group: Aitor Maestro, Sebastien Lemaire, and Syuzanna R. Harutyunyan. *Organic Letters* **2022** *24* (5), 1228-1231. DOI: 10.1021/acs.orglett.2c00020.

5a. 1-methyl 2-(2,2,2-trichloroethyl) 7-oxo-1-phenyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate

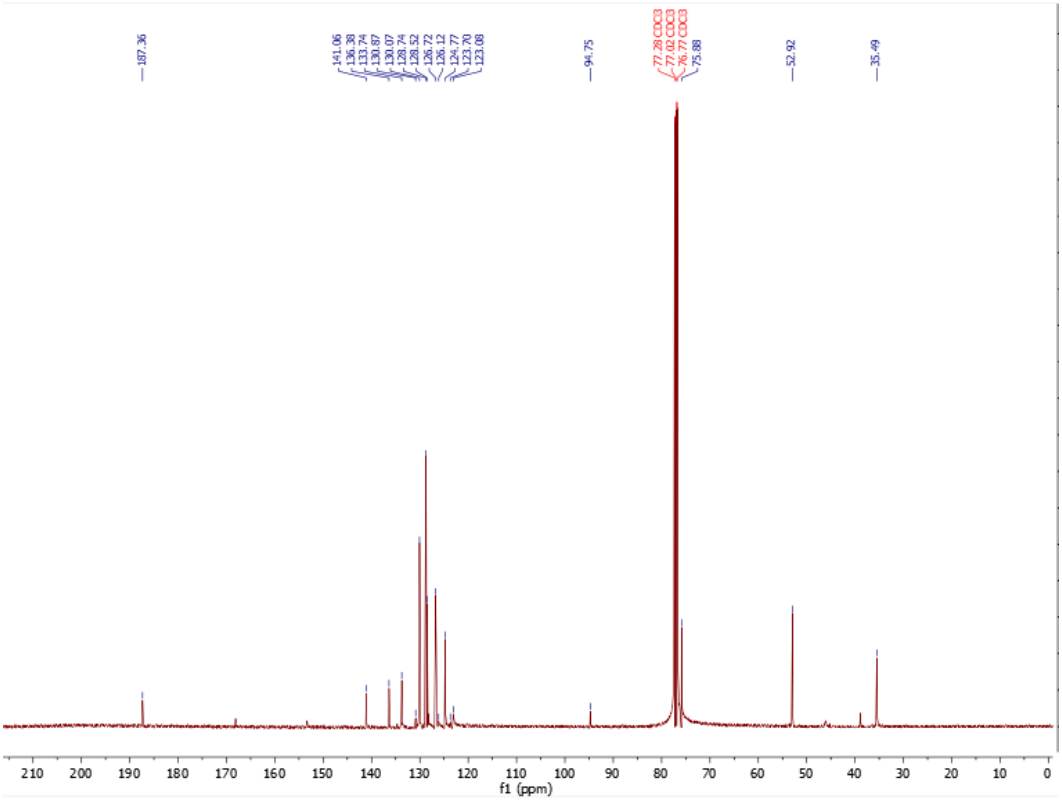


Prepared from **4a** and **1a**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5a** as a beige solid (58% y). **Rf =** 0.50(1:9 EtOAc/Hex); **m.p=** 143ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.00 (s, 1H), 7.76 – 7.69 (m, 2H), 7.56 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.39 – 7.32 (m, 1H), 7.25 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 5.02 (s, 2H), 4.45 (d, *J* = 8.1 Hz, 1H), 3.41 (s, 3H), 2.85 (d, *J* = 8.1 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.36, 141.06, 136.38, 133.74, 130.87, 130.07, 128.74, 128.52, 126.72, 126.12, 124.77, 123.70, 123.08, 94.75, 77.28, 77.02, 76.77, 75.88, 52.92, 35.49 ppm; **IR (neat): ν (cm-1) =** 3027, 2954, 1741, 1715, 1685, 1601, 1483, 1462, 1437, 1390, 1328, 1312, 1237, 1198, 1180, 1151, 1090, 1058, 1032, 941, 919, 885, 808, 794, 757, 713, 700, 683.

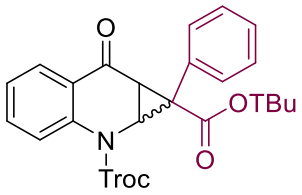
^{1}H NMR (500 MHz, $CDCl_3$): 5a



^{13}C NMR (126 MHz, $CDCl_3$): 5a

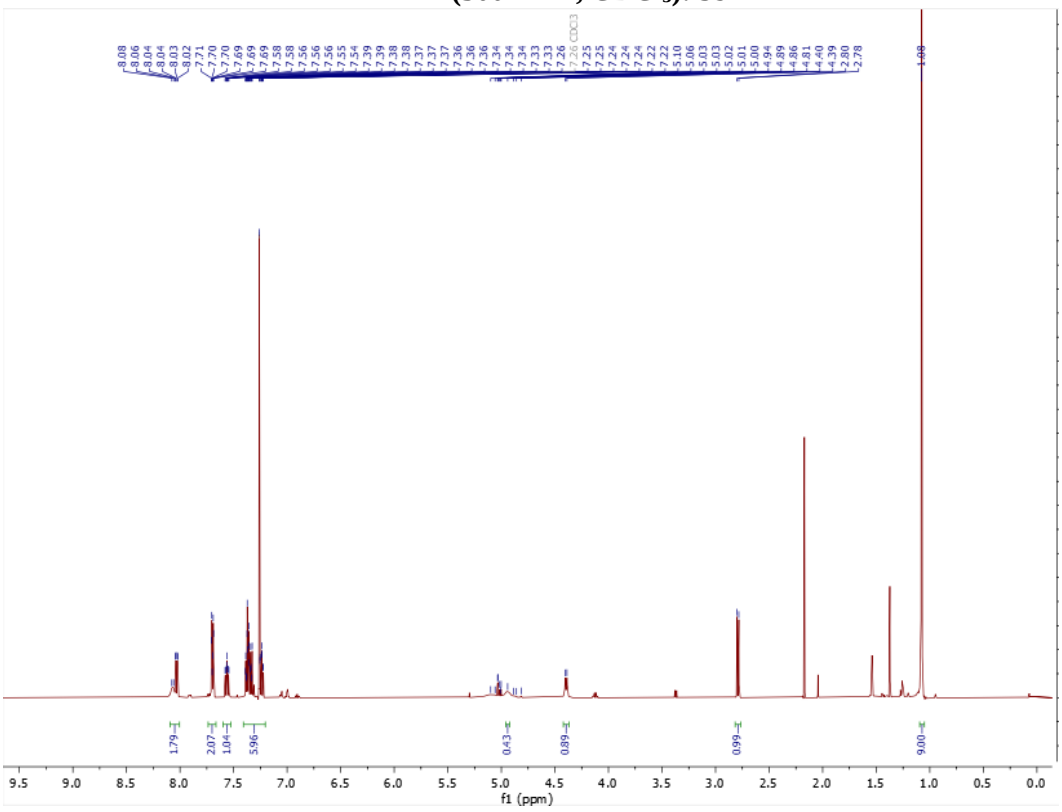


5b. 2,2,2-trichloroethyl 1-(formyl-t)-7-oxo-1-phenyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-2-carboxylate--butyl-l1-oxidane (1/1)

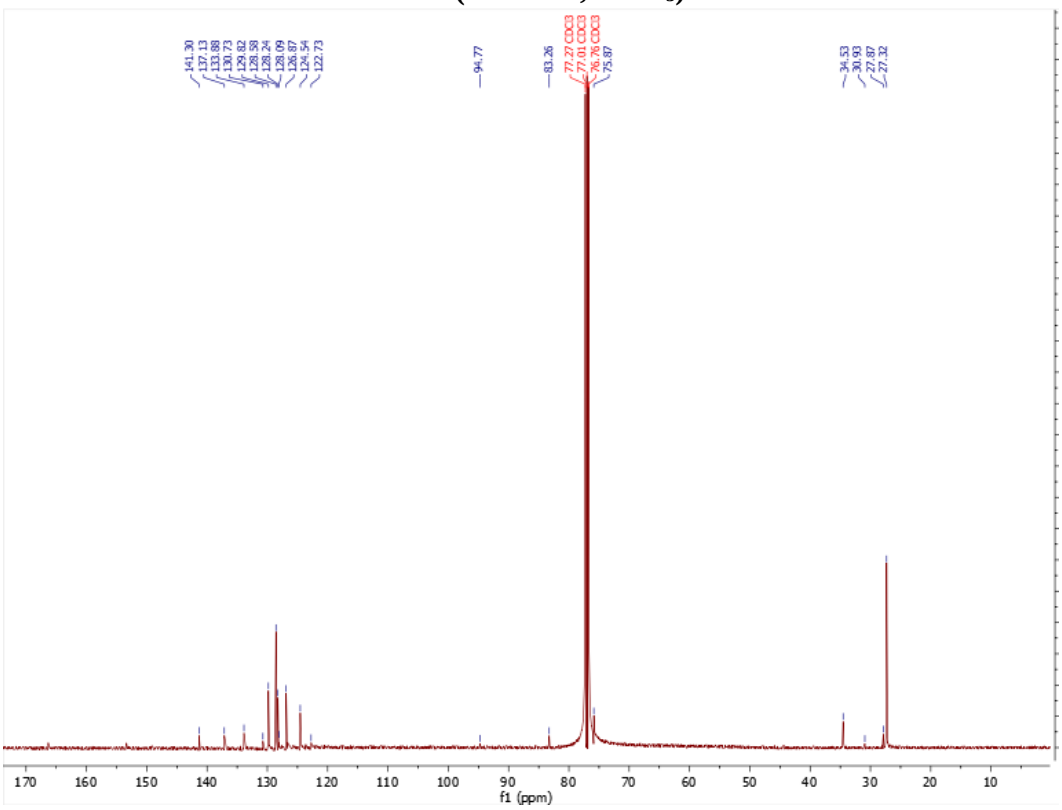


Prepared from **4a** and **1d**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5b** as a clear foggy oil (53% y). **Rf =** 0.50(1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 2H), 7.74 – 7.66 (m, 2H), 7.56 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.41 – 7.20 (m, 4H), 5.02 (d, *J* = 79.3 Hz, 2H), 4.40 (d, *J* = 8.1 Hz, 1H), 2.79 (d, *J* = 8.1 Hz, 1H), 1.08 (s, 9H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.30, 137.13, 133.88, 130.73, 129.82, 128.58, 128.24, 128.09, 126.87, 124.54, 122.73, 94.77, 83.26, 77.27, 77.01, 76.76, 75.87, 34.53, 30.93, 27.87, 27.3 ppm.

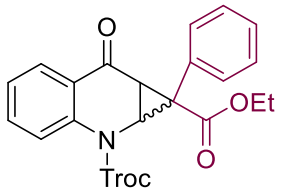
^{1}H NMR (500 MHz, $CDCl_3$): 5b



^{13}C NMR (126 MHz, $CDCl_3$): 5b

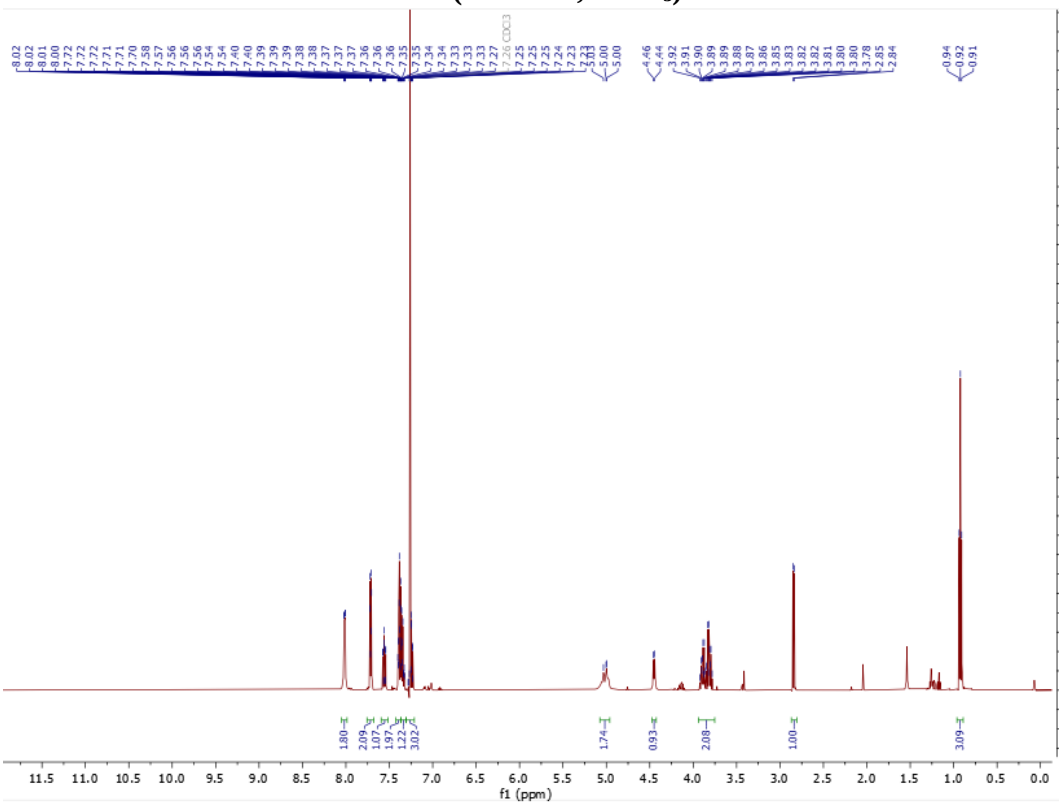


5c. 1-ethyl 2-(2,2,2-trichloroethyl) 7-oxo-1-phenyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate

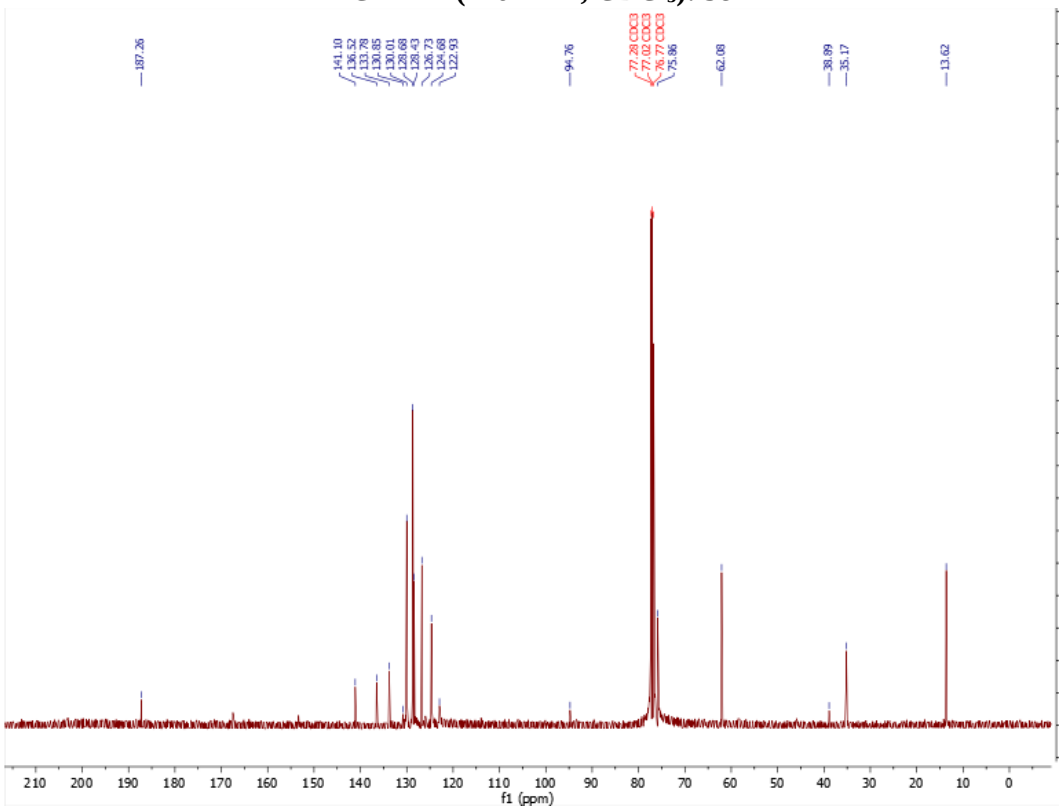


Prepared from **4a** and **1f**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5c** as a white solid (58% y). **Rf =** 0.50 (1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.76 – 7.68 (m, 2H), 7.56 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.31 – 7.21 (m, 3H), 5.08 – 4.96 (m, 2H), 4.45 (d, *J* = 8.1 Hz, 1H), 3.85 (ddq, *J* = 38.4, 10.9, 7.1 Hz, 2H), 2.84 (d, *J* = 8.1 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.66, 167.90, 153.73, 141.50, 136.91, 134.18, 131.24, 130.40, 129.08, 128.83, 128.63, 127.13, 125.08, 123.34, 95.16, 77.61, 76.26, 62.48, 53.82, 39.28, 35.57, 14.02 ppm; **IR (neat): ν (cm-1) =** 3059, 3028, 2970, 1737, 1707, 1687, 1602, 1483, 1460, 1428, 1379, 1329, 1298, 1255, 1233, 1191, 1159, 1122, 1096, 1040, 1010, 944, 862, 820, 794, 862, 820, 794, 751, 714, 698, 684.

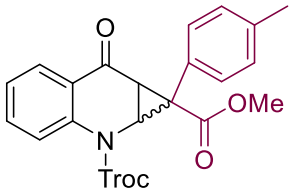
^{1}H NMR (500 MHz, $CDCl_3$): 5c



^{13}C NMR (126 MHz, $CDCl_3$): 5c

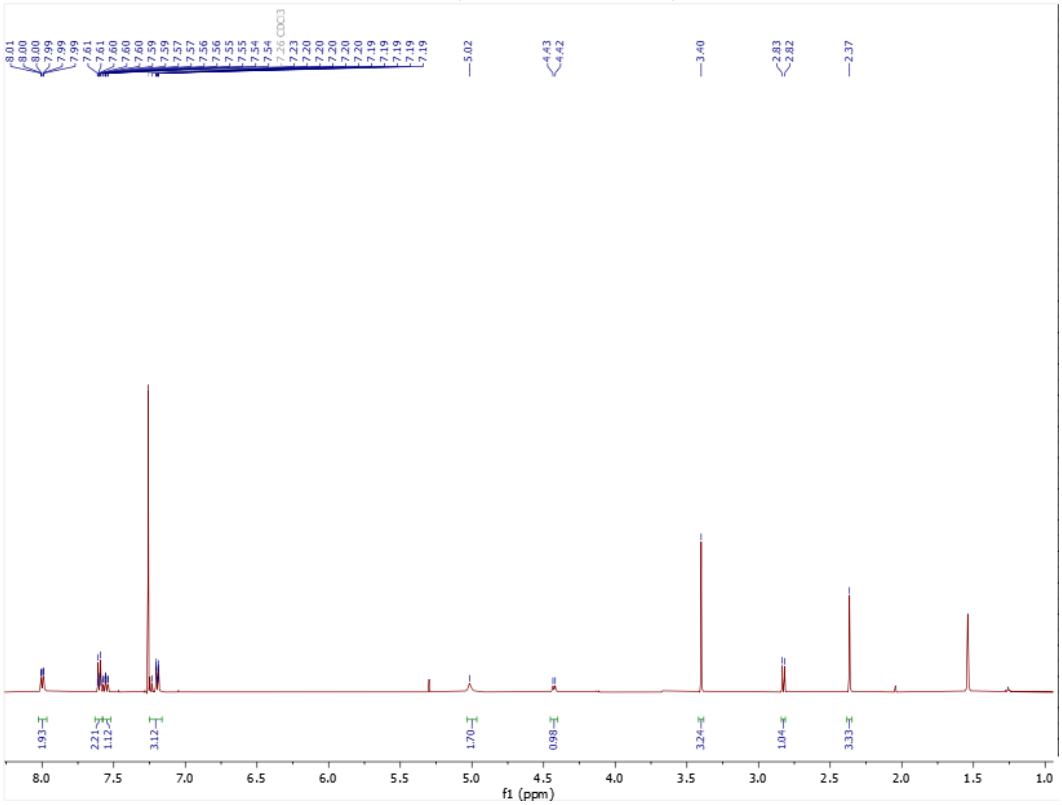


5d. 1-methyl 2-(2,2,2-trichloroethyl) 7-oxo-1-(p-tolyl)-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate

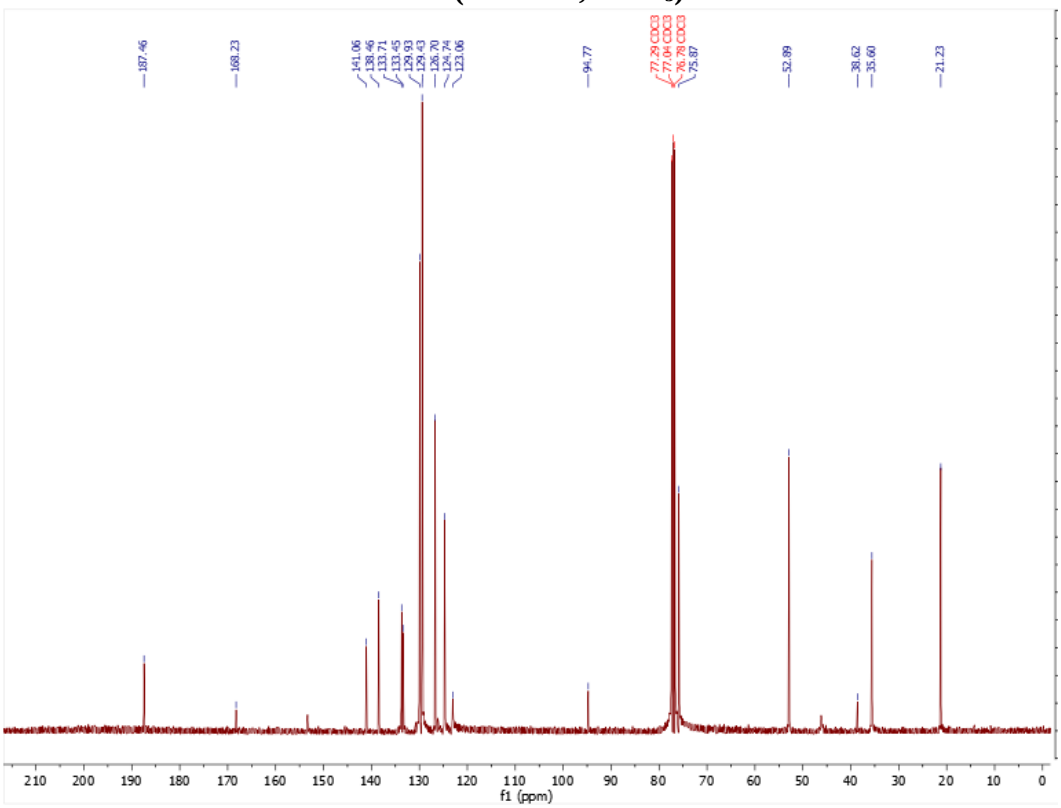


Prepared from **4a** and **1b**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 2:8 EtOAc/Hex afforded **5d** as a white solid (58% y). **Rf =** 0.50 (2:8 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.63 – 7.57 (m, 2H), 7.61 – 7.52 (m, 1H), 7.25 – 7.16 (m, 3H), 5.02 (s, 2H), 4.43 (d, *J* = 8.0 Hz, 1H), 3.40 (s, 3H), 2.83 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.46, 168.23, 141.06, 138.46, 133.71, 133.45, 129.93, 129.43, 126.70, 124.74, 123.06, 94.77, 77.29, 77.04, 76.78, 75.87, 52.89, 38.62, 35.60, 21.23 ppm**; IR (neat): ν (cm-1) =** 3041, 2954, 1721, 1685, 1602, 1516, 1481, 1461, 1437, 1382, 1324, 1292, 1259, 1230, 1199, 1180, 1151, 1096, 1057, 1034, 939, 881, 813, 769, 758, 710, 648.

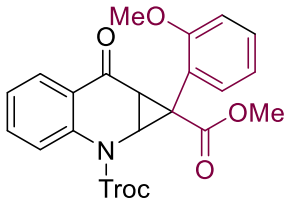
^{1}H NMR (500 MHz, $CDCl_3$): 5d



^{13}C NMR (126 MHz, $CDCl_3$): 5d

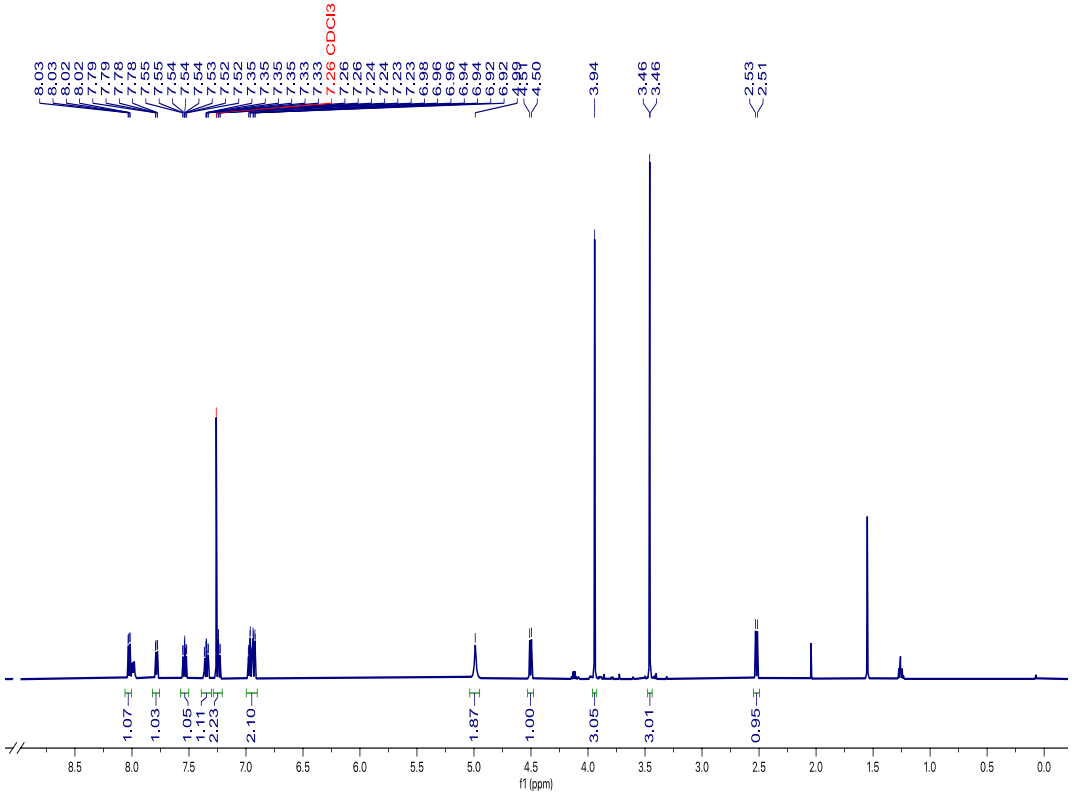


5e. 1-methyl 2-(2,2,2-trichloroethyl) 1-(2-methoxyphenyl)-7-oxo-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate

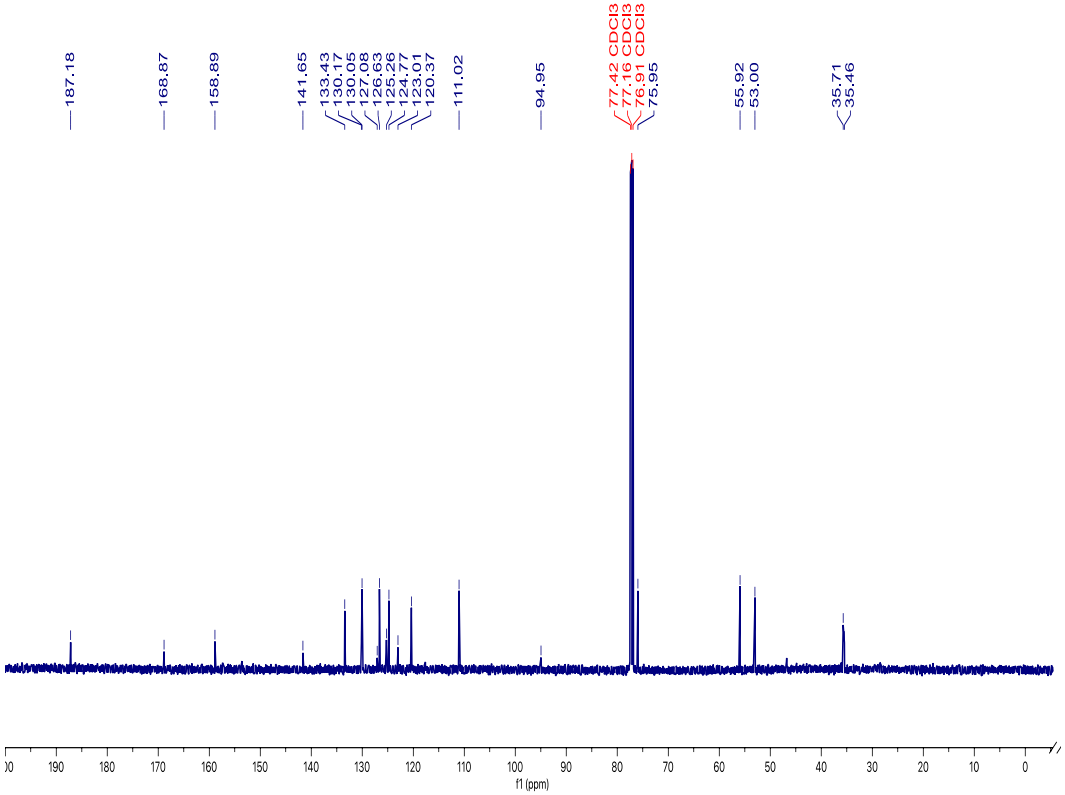


Prepared from **4a** and **1c**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5e** as a clear foggy oil (53% y). **Rf =** 0.50(1:9 EtOAc/Hex); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.78 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 7.24 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00 – 6.90 (m, 2H), 4.99 (s, 2H), 4.50 (d, *J* = 7.9 Hz, 1H), 3.94 (s, 3H), 3.46 (s, 3H), 2.52 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.18, 168.87, 158.89, 141.65, 133.43, 130.17, 130.05, 127.08, 126.63, 125.26, 124.77, 123.01, 120.37, 111.02, 94.95, 77.42, 77.16, 76.91, 75.95, 55.92, 53.00, 35.71, 35.46 ppm.

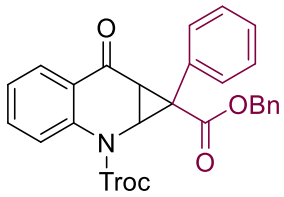
^{1}H NMR (500 MHz, $CDCl_3$): 5e



^{13}C NMR (126 MHz, $CDCl_3$): 5e

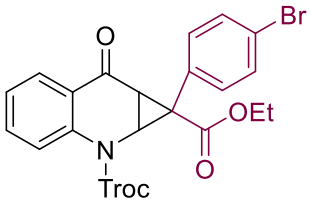


5f. 1-benzyl 2-(2,2,2-trichloroethyl) 7-oxo-1-phenyl-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



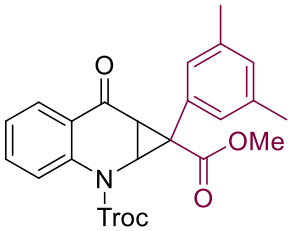
Prepared from **4a** and **1e**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5f** as a white solid (36% y). **Rf** = 0.50(1:9 EtOAc/Hex). Complete characterizations will be in Communication mentioned above.

5g. 1-ethyl 2-(2,2,2-trichloroethyl) 1-(4-bromophenyl)-7-oxo-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



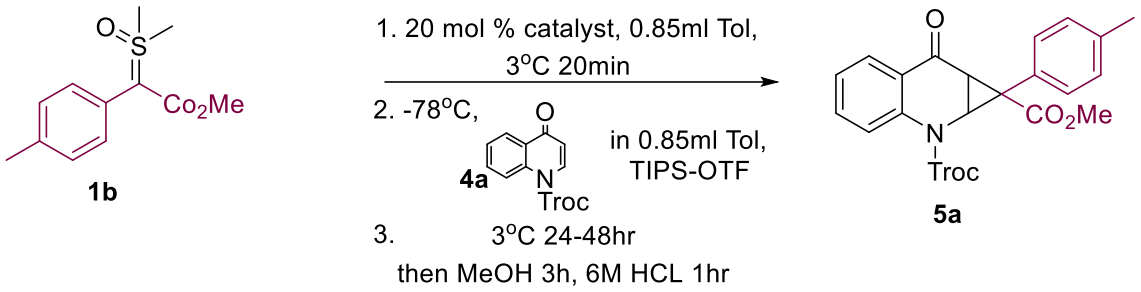
Prepared from **4a** and **1h**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5g** as a clear foggy oil (30% y). **Rf** = 0.50 (1:9 EtOAc/Hex). Complete characterizations will be in Communication mentioned above.

5h. 1-methyl 2-(2,2,2-trichloroethyl) 1-(3,5-dimethylphenyl)-7-oxo-1,1a,7,7a-tetrahydro-2H-cyclopropa[b]quinoline-1,2-dicarboxylate



Prepared from **4a** and **1j**. The reaction was allowed to stir for 6 days. Purification by column chromatography in 1:9 EtOAc/Hex afforded **5h** as a white solid (55% y). **Rf** = 0.50(1:9 EtOAc/Hex). Complete characterizations will be in Communication mentioned above.

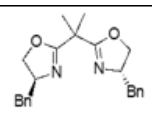
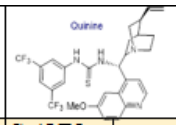
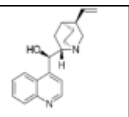
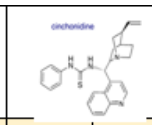
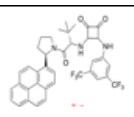
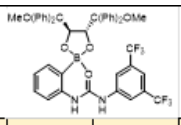
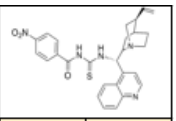
Quinolone Chiral Versions: Catalyst screening



To a 2mL flame dried glass vial with a stir bar, fitted with a screw cap that has a Teflon coated septum for injections, was added 0.1 mmol of the respective quinolone (1 equiv.), 0.80mL of toluene, and 30uL of TIPS-OTF to let react at 70°C for 1hr. After the benzoparylium has formed, the reaction was brought down to -78°C in a dry ice and acetone bath, where 0.1mmol of the respective ylide dissolved in 0.80mL of toluene, was added to the reaction vial. The reaction was left to react at 3°C for 24-48hrs or until TLC indicated that enough starting material had been consumed. 0.3mL of MeOH was added and the reaction and let stir for atleast 1hr .The product was extracted with water and dichloromethane and then purified by column chromatography using 20 EtOAc: 80 Hexanes. The *ee* of the purified product was determined by chiral HPLC depending on the method determined for each product.

Catalyst and lewis acid screen:

method																
A					$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee
															CuI	0% ee
B					$Cu(OTf)_2$	6% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee
															CuI	0% ee
C					Cu(Otf)2	0% ee			Cu(Otf)2	0% ee						
D					Cu(Otf)2	NR			Cu(Otf)2	NR						
E	$Zn(OTf)_2$	0% ee			$Zn(OTf)_2$	0% ee										
F			Cu(Otf)2	0% ee	Cu(Otf)2	0% ee	Cu(Otf)2	0% ee	Cu(Otf)2	NR						

													
$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee										
CuI	0% ee												
$Cu(OTf)_2$	0% ee	$Cu(OTf)_2$	0% ee					$Cu(OTf)_2$	0% ee				
CuI	0% ee												
		$Zn(OTf)_2$	0% ee										
		$Cu(OTf)_2$	0% ee							$Cu(Otf)_2$	0% ee	$Cu(Otf)_2$	0% ee
		$Zn(OTf)_2$	NR										
		CuCl	NR										
		$Zn(OTf)_2$	5% ee							$Cu(Otf)_2$	0% ee	$Cu(Otf)_2$	NR
		CuCl	NR										
		$Zn(OTf)_2$	12% ee	$Zn(OTf)2$	0% ee	$Zn(OTf)_2$	0% ee						
		$Sc(OTf)_2$	0% ee										
		CuI	0% ee										
		CuCl	0% ee										
		$In(Cl)_3$	0% ee										
		tetrakis	0% ee										
		$Cu(Br)_2$	0% ee										
		Cu(Br)	0% ee										
		Fe(Cl)3	0% ee										
		$Co(Oac)_2$	0% ee										
		$Yt(Otf)_3$	0% ee										
		Cu(Otf)	0% ee										
		$Cu(Otf)_2$	0% ee										