A Highly Selective Methodology for the Direct Conversion of Aromatic Aldehydes to Glycol Monoesters

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General Procedure. To a mixture of MeSO_3H 98% (1 mL, 15 mmol) and Al_2O_3 (acidic 1). Then the mixture was poured into water and extracted two times with ethyl acetate (20 mL). The organic layer was washed with a saturated solution of sodium bicarbonate (30 mL). The organic layer was dried (CaCl_2) and evaporated in vacuo to give a residue, which was almost a pure glycol monoester product. Further purification of the products was carried out by silica-gel, short column chromatography.

2-Hydroxyethyl benzoate (5).²² ^1H NMR (CDCl_3 , 250 MHz) δ 3.96 (t, 2H), 4.45 (t, 2H), 7.49-7.58 (m, 3H, Ar-H), 8.1 (d, 2H, Ar-H); IR (neat) 1718 cm^{-1} .

2-Hydroxyethyl 4-methylbenzoate (6).²² ^1H NMR (CDCl_3 , 250 MHz) δ 2.39 (s, 3H), 3.88 (t, 2H), 4.41 (t, 2H), 7.2-7.31 (m, 2H, Ar-H), 7.91 (m, 2H, Ar-H); IR (neat) 1720 cm^{-1} .

2-Hydroxyethyl 4-chlorobenzoate (8).²² ^1H NMR (CDCl_3 , 250 MHz) δ 3.98 (t, 2H), 4.45 (t, 2H), 7.43 (d, 2H, Ar-H), 7.14 (d, 2H, Ar-H); IR (neat) 1712 cm^{-1} .

2-Hydroxypropyl benzoate (14).²² ^1H NMR (CDCl_3 , 250 MHz) δ 1.99 (m, 2H), 3.78 (t, 2H), 4.45 (t, 2H), 7.41-7.58 (m, 3H, Ar-H), 8.05 (d, 2H, Ar-H); IR (neat) 1718 cm^{-1} .

2-Hydroxy-1-methylethyl benzoate (16).²² ^1H NMR (CDCl_3 , 250 MHz) δ 1.27 (m, 3H), 3.76 (d, 1H), 5.21 (m, 1H), 7.42-7.56 (m, 3H, Ar-H), 8.04 (d, 2H, Ar-H); IR (neat) 1722 cm^{-1} .

2-Hydroxy-2-methylethyl benzoate (17).²² ^1H NMR (CDCl_3 , 250 MHz) δ 1.35 (m, 3H), 4.16-4.31 (t, 3H), 7.42-7.56 (m, 3H, Ar-H), 8.04 (d, 2H, Ar-H); IR (neat) 1722 cm^{-1} .

2-Hydroxyethyl 3-methylbenzoate (7). ^1H NMR (CDCl_3 , 250 MHz) δ 2.37 (s, 3H, $-\text{CH}_3$), 3.94 (t, 2H, $-\text{CH}_2\text{OH}$), 4.43 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 7.19-7.37 (m, 2H, Ar-H), 7.83-8.18 (m, 2H, Ar-H); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ 21.49, 61.16, 67.79, 127.14, 128.59, 130.16, 130.49, 134.20, 138.46, 167.46; IR (neat) 3440, 1715, 1610, 1580, 1450, 1370, 1280, 1200, 1115, 1080, 925, 740,

680 cm^{-1} ; MS (m/e) 180 (3.5, M^+), 163 (51.6), 119 (base peak), 91(31.7%). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$: C, 66.65; H, 6.71. Found: C, 66.52; H, 6.50 %.

2-Hydroxyethyl 2,4-dihydroxybenzoate (9). ^1H NMR (DMSO-d_6 , 250 MHz) δ 3.7 (t, 2H, $-\text{CH}_2\text{OH}$), 4.28 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 6.3 (s, 1H, Ar-H), 6.38 (d, 1H, Ar-H) 7.72 (d, 1H, Ar-H); ^{13}C NMR (DMSO-d_6 , 62.9 MHz) δ 59.28, 66.79, 102.75, 104.37, 108.59, 132.18, 163.10, 164.56, 169.62; IR (neat) 3312, 1700, 1625, 1515, 1425, 1390, 1315, 1266, 1210, 1150, 1100, 1066, 999, 900, 834 cm^{-1} ; MS (m/e) 198 (28.6, M^+), 180 (32.9), 137 (74), 136 (base peak), 108 (43.9%). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}_5$: C, 54.55; H, 5.09. Found: C, 54.31; H, 4.97 %.

2-Hydroxyethyl 2-hydroxybenzoate (10). ^1H NMR (DMSO-d_6 , 250 MHz) δ 3.94 (t, 2H, $-\text{CH}_2\text{OH}$), 4.45 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 6.86 (m, 1H, Ar-H), 6.96 (m, 2H, Ar-H), 7.46 (m, 1H, Ar-H) 7.86 (m, 1H, Ar-H); ^{13}C NMR (DMSO-d_6 , 62.9 MHz) δ 61.37, 63.92, 118.04, 119.68, 130.35, 136.21, 162.09, 170.22; IR (neat) 3340, 1720, 1625, 1517, 1430, 1390, 1324, 1268, 1206, 1153, 1100, 1066, 997, 897, 834 cm^{-1} ; MS (m/e) 182 (20, M^+), 160 (35), 121 (65), 120 (base peak), 93 (41). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}_4$: C, 59.34; H, 5.53. Found: C, 59.23; H, 5.26 %.

2-Hydroxyethyl 4-methoxybenzoate (11). ^1H NMR (CDCl_3 , 250 MHz) δ 3.82 (s, 3H, $-\text{OMe}$), 3.88 (t, 2H, $-\text{CH}_2\text{OH}$), 4.20 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 6.99 (d, 2H, Ar-H), 7.92 (d, 2H, Ar-H); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ 55.25, 61.71, 65.90, 113.3, 120.82, 131.50, 162.48, 165.66; IR (neat) 3440, 1720, 1600, 1590, 1455, 1430, 1280, 1230, 1180, 1110, 1080, 1045, 755, 665 cm^{-1} ; MS (m/e) 196 (34, M^+), 151 (62), 135 (43.2), 107 (base peak). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.22; H, 6.16. Found: C, 61.07; H, 5.98 %.

2-Hydroxyethyl nicotinate (12). ^1H -NMR (CCl_4 , TMS, 250 MHz) δ 3.95 (t, 2H, $-\text{CH}_2\text{OH}$), 4.47 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 7.46 (m, 1H, Ar-H), 7.82 (m, 1H, Ar-H), 8.11(m, 1H, Ar-H), 8.69(m, 1H, Ar-H); ^{13}C NMR (CCl_4 , TMS, 62.9 MHz) δ 61.69, 66.32, 122.61, 128.10, 136.01, 147.3, 147.6, 165.01; IR (neat) 3400, 1725, 1590, 1495, 1452, 1310, 1293, 1250, 1124, 1075, 800, 750, 701, 665 cm^{-1} ; MS (m/e) 167 (19.9, M^+), 150 (12.4), 124 (13.5), 106 (40.7), 78 (base peak), 51 (65.6%). Anal. Calcd for $\text{C}_8\text{H}_9\text{NO}_3$: C, 57.48; H, 5.43. Found: C, 57.11; H, 5.24 %.

2-Hydroxyethyl 1-naphthoate (13). $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) δ 3.81 (t, 2H, $-\text{CH}_2\text{OH}$), 4.35 (t, 2H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 7.28-7.48 (m, 3H, Ar-H), 7.7(d, 1H, Ar-H), 7.82(d, 1H, Ar-H), 8.04(d, 1H, Ar-H), 8.75(d, 1H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 62.9 MHz) δ 61.40, 66.86, 124.87-134.18, 168.08; IR (neat) 3500, 1715, 1600, 1520, 1360, 1285, 1250, 1205, 1180, 1140, 1050, 960, 790 cm^{-1} ; MS (m/e) 216 (25.1, M^+), 199 (18.2), 172 (30.2), 155 (base peak), 127 (48.9%). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_3$: C, 72.21; H, 5.59. Found: C, 71.98; H, 5.31%.

Diethylene glycol monobenzoate (15). $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) δ 3.72(m, 4H, $-\text{OCH}_2\text{CH}_2\text{OH}$), 3.85 (t, 2H, $\text{PhCO}_2\text{CH}_2\text{CH}_2\text{O}-$), 4.50 (t, 2H, $\text{PhCO}_2\text{CH}_2\text{CH}_2\text{O}-$), 7.41-7.59 (m, 3H, Ar-H), 8.06 (d, 2H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3) δ 63.20, 64.91, 66.18, 68.65, 130.53, 131.82, 132.07, 135.29, 169.14; IR (neat) 3416, 2916, 1717, 1600, 1449, 1320, 1274, 1200, 1165, 1130, 1066, 1033, 890 cm^{-1} ; MS (m/e) 210 (1.1, M^+), 149 (19.7), 105 (100), 77 (31.6), 45 (32.5%). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C, 62.85; H, 6.71. Found: C, 62.69; H, 6.58%.

2-Aminoethyl benzoate (18). To a mixture of MeSO_3H 98% (1 mL, 15 mmol) and Al_2O_3 (acidic type 540 C, 0.27 g, 3 mmol) were added benzaldehyde (1 mmol) and then 2-aminoethyl-ethanol (1 mmol). The mixture was stirred and heated in an oil bath at 80 $^\circ\text{C}$ for 4.5 hrs. (Table 1, entry 14). The mixture was poured into saturated solution of sodium bicarbonate and extracted two times with ethyl acetate (20 mL). Then organic layer was dried (CaCl_2) and evaporated in vacuo to give 2-aminoethyl benzoate (**18**) (81%). $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) δ 3.53(t, 2H, $-\text{OCH}_2\text{CH}_2\text{NH}_2$), 3.73 (t, 2H, $\text{OCH}_2\text{CH}_2\text{NH}_2$), 4.67 (s, 2H, $-\text{NH}_2$), 7.31 (m, 3H, Ar-H), 7.74 (d, 2H, Ar-H); $^{13}\text{C NMR}$ (CDCl_3 , 62.9 MHz) δ 43.19, 61.98, 127.44, 128.87, 130.09, 133.69, 169.19; IR (neat) 3357, 3074, 2948, 1724, 1652, 1556, 1519, 1388, 1313, 1974, 806, 717 cm^{-1} ; MS (m/e) 165 (10.3, M^+), 149 (48.9), 105 (100), 77 (31.6%). Anal. Calcd for $\text{C}_9\text{H}_{11}\text{NO}_2$: C, 65.44; H, 6.71. Found: C, 65.27; H, 6.52%.