Supporting Information for

**“InBr₃ Catalyzed Friedel-Crafts Addition of Indoles to Chiral
Aromatic Epoxides: a Facile Route to Enantiopure Indolyl
Derivatives.”**

Marco Bandini, Pier Giorgio Cozzi,* Paolo Melchiorre, Achille Umani-Ronchi*

Dipartimento di Chimica “G. Ciamician”, via Selmi 2, 40126 - Bologna, Italy

(R)-2-(1H-3-Indolyl)-2-phenylethanol (3a): white solid. Yield: 70 %; M.W. = 237.30; R_f 0.35 (cyclohexane/AcOEt 75:25); mp 108-109.5 °C; $[\alpha]_D^{25} = +12.8$ (c 1.6, CHCl₃); ee = 99% by HPLC: isocratic 80/20 *n*-hex/IPA, t_s = 20.4 min, t_R = 25.4 min; ¹H NMR (300 MHz, CDCl₃) δ 1.61 (br, 1 H), 4.18-4.23 (m, 2 H), 4.50 (t, J = 6.7 Hz, 1 H), 7.03-7.48 (m, 10 H), 8.11 (br, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 45.59, 66.38, 111.09, 115.82, 119.24, 119.41, 121.81, 122.15, 126.63, 126.87, 128.19 (2), 128.49 (2), 136.32, 141.51; GC-MS m/z (relative intensity) 51 (11), 63 (5), 77 (15), 102 (10), 128 (15), 178 (30), 206 (100), 237(25); IR (nujol) 3500, 3410, 3245, 1615, 1600, 1480, 1340, 1100, 1040, 1015, 700 cm⁻¹; Anal. calcd for (C₁₆H₁₅NO): C, 80.98; H, 6.37; N, 5.90; Found: C, 81.10; H, 6.22; N, 5.73.

(R)-2-(5-Cyano-1H-indol-3-yl)-2-phenyl-ethanol (3b): white solid. Yield: 41%; M.W. = 262.31; R_f 0.35 (cyclohexane/AcOEt 7:3); mp 136-139 °C; $[\alpha]_D^{25} = +39.3$ (c 0.7, CHCl₃); ee = 70% by HPLC: isocratic 87/13 *n*-hex/IPA, t_s = 43.6 min., t_R = 45.4 min; ¹H NMR (300 MHz, CDCl₃) δ 1.93 (br, 1 H), 4.13-4.25 (m, 2 H), 4.45 (t, J = 6.6 Hz, 1 H), 7.20-7.40 (m, 8 H), 7.73 (s, 1H), 8.48 (br, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ 45.27, 66.33, 102.21, 112.04, 117.02, 120.71, 123.96, 124.92, 125.0, 126.82, 127.04, 128.08 (2), 128.71 (2), 137.99, 140.76; GC-MS m/z (relative intensity) 51 (10), 77 (15), 153 (5), 176 (20), 231 (100), 262 (15); IR (nujol) 3500, 3340, 3100, 1580, 1460, 1100, 1043, 720 cm⁻¹; Anal. calcd for (C₁₇H₁₄N₂O): C, 77.84; H, 5.38; N, 10.68; Found: C, 77.90 ; H, 5.39 ; N, 5.26.

(R)-2-(5-Bromo-1H-indol-3-yl)-2-phenyl-ethanol (3c): Yield: 54%; M.W. = 316.19; R_f 0.28 (cyclohexane/AcOEt 75:25); mp 129-130 °C; $[\alpha]_D^{25} = +66.5$ (c 1.2, CHCl₃); ee = 99% by HPLC: isocratic 86/14 *n*-hex/IPA, t_s = 32.0 min, t_R = 35.2 min; ¹H NMR (300 MHz, CDCl₃) δ : 1.77 (br, 1 H), 4.14-4.23 (m, 2 H), 4.42 (t, J = 6.6 Hz, 1 H), 7.16-7.35 (m, 8 H), 7.57 (s, 1H), 8.26 (br, 1 H); ¹³C NMR (50 MHz, CDCl₃) δ : 45.33, 66.35, 112.55, 112.71, 115.66, 121.74, 123.01, 125.02, 126.83, 127.80, 128.09 (2), 128.62 (2), 134.89, 141.01; GC-MS m/z (relative intensity) 51 (9), 77 (10), 88 (15), 102 (19), 129 (10), 151 (15), 176 (25), 204 (80), 284 (95), 286 (100), 315 (20), 317 (15); IR (nujol)

3540, 3409, 3230, 1605, 1470, 1350, 1110, 1000, 760 cm^{-1} ; Anal. calcd for ($\text{C}_{16}\text{H}_{14}\text{NOBr}$): C, 60.78; H, 4.46; N, 4.43; Found: C, 60.81 ; H, 4.39 ; N, 4.38.

(R)-2-(5-Methoxy-1H-indol-3-yl)-2-phenyl-ethanol (3d): white solid. Yield: 54%; M.W. = 267.32; R_f 0.3 (cyclohexane/AcOEt 75:25); mp 98-102.5 $^{\circ}\text{C}$; $[\alpha]_D^{25} = +60.6$ (c 1.7, CHCl_3), ee = 99% by HPLC: isocratic 85/15 n -hex/IPA, $t_S = 20.1$ min., $t_R = 26.3$ min; ^1H NMR (200 MHz, CDCl_3) δ 1.58 (br, 1 H), 3.77 (s, 3H), 4.17-4.25 (m, 2 H), 4.57 (t, $J = 6.9$ Hz, 1 H), 6.87 (s, 1H), 7.11-7.36 (m, 8 H), 7.99 (br, 1 H); ^{13}C NMR (50 MHz, CDCl_3) δ 45.62, 55.85, 66.38, 101.21, 111.79, 112.34, 115.63, 122.57, 126.69, 127.36, 128.22 (2), 128.56 (2), 131.51, 141.42, 153.83; GC-MS m/z (relative intensity) 55 (15), 77 (11), 91 (15), 132 (9), 165 (20), 207 (25), 220 (20), 236 (100), 267 (35); IR (nujol) 3520, 3400, 3260, 1570, 1480, 1210, 1020, 700 cm^{-1} ; Anal. calcd for ($\text{C}_{17}\text{H}_{17}\text{NO}_2$): C, 76.38; H, 6.41; N, 5.24; Found: C, 76.49; H, 6.43; N, 5.41.

(R)-2-(5-Nitro-1H-indol-3-yl)-2-phenyl-ethanol (3e): white solid. Yield: 24%; M.W. = 282.29; R_f 0.31 (cyclohexane/AcOEt 6:4); mp 161-163 $^{\circ}\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ : 1.87 (br, 1 H), 4.20-4.25 (m, 2 H), 4.51 (t, $J = 7.0$ Hz, 1 H), 7.28-7.37 (m, 6 H), 7.40 (s, 1H), 8.09 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.8$ Hz, 1 H), 8.39 (d, $J = 2.2$ Hz, 1 H), 8.51 (br, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ : 45.27, 66.45, 111.06, 116.66, 117.97, 119.00, 124.79, 126.83, 127.16, 128.12, 128.82 (2), 139.21, 140.53, 144.64; IR (nujol) 3461, 3225, 3050, 1619, 1377, 1108, 1029, 737, 697 cm^{-1} ; Anal. calcd for ($\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3$): C, 68.07; H, 5.00; N, 9.92; Found: C, 68.12; H, 4.93; N, 9.83.

(R)-2-(2-Methyl-1H-3-indolyl)-2-phenylethanol (3f): yellow oil. Yield: 78 %; M.W. = 251.32; R_f 0.31 (cyclohexane/AcOEt 75:25); oil; $[\alpha]_D^{25} = -84.1$ (c 0.79, CHCl_3), ee = 99% by $\text{Eu}(\text{hfc})_3$; ^1H NMR (300 MHz, CDCl_3) δ 1.57 (br, 1 H), 2.41 (s, 3 H), 4.33-4.37 (m, 2 H), 4.50 (t, $J = 7.5$ Hz, 1 H), 7.02-7.49 (m, 9 H), 7.91 (br, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.22, 45.05, 65.00, 109.89, 110.42, 119.09, 119.41, 120.99, 126.20, 127.58, 127.84 (2), 128.31 (2), 133.16, 135.34, 141.56; GC-MS m/z (relative intensity) 51 (11), 63 (8), 77 (15), 102 (20), 130 (18), 178 (30), 204 (35), 220 (100), 251 (35); IR (neat) 3544, 3400,

3060, 3030, 2925, 2890, 1620, 1610, 1590, 1460, 1300, 1270, 1030, 740, 700 cm^{-1} ; Anal. calcd for ($\text{C}_{17}\text{H}_{17}\text{NO}$): C, 81.24; H, 6.82; N, 5.57; Found: C, 81.34; H, 6.78; N, 5.66.

(R)-2-(1-Methyl-3-indolyl)-2-phenyl-ethanol (3g): yellow oil. Yield: 68%; M.W.= 251.32; R_f 0.32 (cyclohexane/AcOEt 8:2); $[\alpha]_D^{25} = -0.61$ (c 0.76, CHCl_3); ee = 99% by HPLC: isocratic 85/15 n -hex/IPA, $t_s = 22.3$ min, $t_R = 40.6$ min; ^1H NMR (200 MHz, CDCl_3) δ 1.58 (br, 1 H), 3.78 (s, 3 H), 4.16-4.25 (m, 2 H), 4.50 (t, $J = 6.8$ Hz, 1 H), 6.97 (s, 1 H), 7.01-7.49 (m, 9 H); ^{13}C NMR (50 MHz, CDCl_3) δ 32.80, 45.63, 66.50, 109.22, 114.39, 118.97, 119.38, 121.80, 126.63 (2), 127.37, 128.19 (2), 128.54 (2), 137.24, 141.70; GC-MS m/z (relative intensity) 51 (5), 77 (10), 102 (15), 144 (10), 178 (20), 204 (25), 220 (100), 251 (30); IR (neat) 3549, 3400, 3060, 3030, 1610, 1600, 1470, 1360, 1335, 1020, 910, 735 cm^{-1} ; Anal. calcd for ($\text{C}_{17}\text{H}_{17}\text{NO}$): C, 81.24; H, 6.82; N, 5.57; Found: C, 81.30; H, 6.80; N, 5.50.

(R)-2-(1H-Indol-3-yl)-2-(3-chlorophenyl)-ethanol (3h): yellow oil. Yield: 65%; M.W.= 271.74; R_f 0.31 (cyclohexane/AcOEt 75:25); $[\alpha]_D^{25} = +26.6$ (c 0.73, CHCl_3); ee = 99% by HPLC: isocratic 80/20 n -hex/IPA, $t_s = 23.4$ min., $t_R = 26.8$ min; ^1H NMR (300 MHz, CDCl_3) δ 1.61 (br, 1 H), 4.18 (ddd, $J_1 = 6.6$ Hz, $J_2 = 6.6$ Hz, $J_3 = 10.8$ Hz, 2 H), 4.46 (t, $J = 6.6$ Hz, 1 H), 7.06-7.25 (m, 6 H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 1H), 8.14 (br, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 45.33, 66.17, 110.69, 115.31, 119.11, 119.67, 121.86, 122.42, 126.49, 126.82, 128.26, 128.50, 129.69, 134.31, 136.34, 143.83; GC-MS m/z (relative intensity) 63 (5), 77 (8), 102 (15), 130 (10), 176 (25), 204 (40), 240 (100), 242 (35), 271 (20); IR (neat) 3550, 3405, 3070, 2880, 1605, 1595, 1470, 1455, 1430, 1080, 1050, 1020, 760 cm^{-1} ; Anal. calcd for ($\text{C}_{16}\text{H}_{14}\text{ClNO}$): C, 70.72; H, 5.19; N, 5.15; Found: C, 70.81; H, 5.15; N, 5.11.

(R)-2-(2-Methyl-1H-indol-3-yl)-2-(3-chlorophenyl)-ethanol (3i): yellow oil. Yield: 82%; M.W. = 285.77; R_f 0.28 (cyclohexane/AcOEt 75:25); $[\alpha]_D^{25} = -59.4$ (c 0.63, CHCl_3); ee = 99% by HPLC: isocratic 80/20 n -hex/IPA, $t_s = 25.4$ min, $t_R = 29.5$ min; ^1H NMR (300 MHz, CDCl_3) δ 1.57 (br, 1 H), 2.41 (s, 3H), 4.30-4.35 (m, 2 H), 4.46 (t, $J = 7.5$ Hz, 1 H), 7.01-7.43 (m, 8 H), 7.94 (br, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.29, 44.70, 64.75, 109.46, 110.51, 118.89, 119.63, 121.22, 126.04, 126.44, 128.05, 128.33, 129.55, 133.23, 134.15, 135.35, 143.84; GC-MS m/z (relative intensity) 51 (7), 77 (10), 108 (15), 130 (10), 176 (20), 204 (25), 217 (25),

254 (100), 256 (33), 285 (30); IR (neat) 3535, 3400, 3080, 2925, 1605, 1595, 1570, 1460, 1430, 1300, 1080, 1032, 743 cm^{-1} ; Anal. calcd for ($\text{C}_{17}\text{H}_{16}\text{ClNO}$): C, 71.45; H, 5.64; N, 4.90; Found: C, 71.50; H, 5.61; N, 4.87.

(1R,2S)-trans-1-(2-Methyl-1H-indol-3-yl)-1,2,3,4-tetrahydronaphthalen-2-ol (3j): pale yellow oil. Yield: 84%; M.W. = 277.36; R_f 0.3 (cyclohexane/AcOEt 75:25); $[\alpha]_D^{25} = -30.0$ (c 0.42, CHCl_3); ee = 83% by HPLC: isocratic 80/20 *n*-hex/IPA, $t_{(1R,2S)} = 14.4$

min, $t_{(1S,2R)} = 17.6$ min; ^1H NMR (300 MHz, CDCl_3) δ : δ 1.89 (br, 1 H), 1.96-2.01 (m, 1H), 2.31-2.38 (m, 1H), 2.43 (s, 3H), 3.08-3.15 (m, 2H), 4.14-4.28 (m, 2 H), 6.85 (t, $J = 8.9$ Hz, 1 H), 6.92-7.01 (m, 4 H), 7.09 (t, $J = 7.8$ Hz, 1 H), 7.17 (d, $J = 6$ Hz, 1 H), 7.32 (d, $J = 8.7$ Hz, 1 H), 7.94 (br, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 12.09, 26.90, 28.66, 30.65, 46.28, 71.75, 110.28, 110.77, 119.09, 119.32, 121.02, 125.84, 125.89, 127.08, 128.19, 129.04, 134.09, 135.58, 137.47; GC-MS m/z (relative intensity) 51 (6), 77 (10), 102 (15), 117 (25), 132 (40), 146 (30), 165 (10), 189 (15), 218 (100), 232 (20), 259 (18), 277 (95); IR (nujol) 3535, 3398, 3020, 2970, 1610, 1530, 1300, 1040, 1430, 1300, 1080, 1032, 740 cm^{-1} ; Anal. calcd for ($\text{C}_{19}\text{H}_{19}\text{NO}$): C, 82.28; H, 6.90; N, 5.05; Found: C, 82.32; H, 6.86; N, 4.97.