Supporting information for

Synthesis of 1α- and 1β-(indol-2-yl)deoxyribose derivatives

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I General

Reactions were performed under an atmosphere of dry argon. Catalysts, reagents and solvents were obtained from commercial suppliers (Aldrich or Fluka) and were used without further purification. Tetrahydrofuran (THF) was distilled from benzophenone/Na under Ar. 1α- and 1β-Ethynyl-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (1αa and 1βa) were prepared as an anomeric mixture (2/1) and separated using HPLC according to the previously reported procedure. Pd(PPh3)4, Pd2(dba)3·CHCl3, and (2-biphenyl)di-t-butylphosphine was used as obtained.

NMR spectra were recorded on a Varian UNITY 300 INOVA, Varian UNITY 400 INOVA and Brucker Avance III instrument at 300 MHz, 400 MHz and 600 MHz (1H) and 75 MHz, 100 MHz and 150 MHz (13C) as solutions in C6D6 or in CDCl3 and are referenced to the residual solvent signal or TMS. Chemical shifts are given in δ-scale, coupling constants J are given in Hz. Infrared spectra were recorded on a Bruker IFS 55 instrument with ATR technique in wave numbers (cm⁻¹). HR mass spectra were recorded on a ZAB-SEQ (VG Analytical) spectrometer using EI or FAB. Melting points (uncorrected) were determined using Kofler apparatus. TLC was performed on silica gel 60 F254-coated aluminium sheets (Merck). Column chromatography was performed on a preparative silica gel with 25×250 mm size 63-200 μm (170-230 mesh ASTM). HPLC separations were performed on a Gilson 321 H2 pumps with 25×250 mm preparative silica gel column (Labio, Czech Republic), filled with BIOSPHER PSI 100 sorbent (7μm mesh).
II. Synthesis of compounds 5α and 5β.

General procedure for the Sonogashira reaction of substituted iodoanilines with 1α- and 1β-ethynlydeoxyriboses. To a solution of 1α or 1β (100 mg, 0.26 mmol) and N-trifluoroacyl-2-iodoaniline 4 (0.52 mmol) in acetonitrile (0.6 mL) was added Pd(PPh₃)₄ (15 mg, 0.013 mmol) and Et₃N (0.4 mL) and the reaction mixture was stirred for 4 h at 70 °C. Then the reaction mixture was diluted with water (5 mL), extracted with Et₂O (4 × 3 mL), the combined organic fractions were dried over MgSO₄, and concentrated under the reduced pressure. Gradient column chromatography of the residue on silica gel (hexane → hexane/CH₂Cl₂/Et₂O 10/2/1) yielded the corresponding products.

Bis-(O-toluoyl)-1α-[(2-(N-trifluoroacyl)phenyl]ethynyl]deoxyribose (5αa). The reaction was carried out at 0.26 mmol scale with respect to 1α (100 mg). Column chromatography on silica gel yielded 113 mg (77%) of the title compound as a colourless sirup: 1H NMR (600 MHz, C 6D6) δ 8.53 (s, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 8.1 Hz, 2H), 7.15 – 7.13 (m, 1H), 6.93–6.88 (m, 3H), 6.80 (d, J = 8.0 Hz, 2H), 6.67–6.62 (m, 1H), 5.42–5.38 (m, 1H), 4.77 (dd, J = 8.0, 2.8 Hz, 1H), 4.58–4.54 (m, 1H), 4.37 (d, J = 1.6 Hz, 1H), 8.36 (s, 1H), 8.13 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 7.9 Hz, 2H), 6.64 (dd, J = 8.3, 1.9 Hz, 1H), 5.38 (d, J = 6.4 Hz, 1H), 4.75 (dd, J = 8.0, 2.6 Hz, 1H), 4.56 (bs, 1H), 4.36 (d, J = 17.1, 11.7, 5.0 Hz, 2H), 2.24 – 2.14 (m, 1H), 2.07 (d, J = 14.0 Hz, 1H), 1.97 (s, 3H), 1.92 (s, 3H); 13C NMR (151 MHz, C 6D6) δ 166.41, 166.19, 154.67 (q, J = 37.1 Hz), 144.55, 144.12, 137.36, 132.07, 130.50 (2C), 130.40, 130.35 (2C), 129.79 (2C), 129.69 (2H), 128.31, 127.93, 125.59, 120.14, 116.51 (q, J = 289.2 Hz), 113.37, 98.81, 83.38, 79.85, 76.51, 68.93, 64.61, 39.86, 21.73, 21.68; IR (KBr) 3371, 2953, 1718, 1271, 1177, 1104, 757 cm⁻¹; HRMS calcd for C₃₁H₂₆F₃NO₆ (M-H) 564.1640, found 564.1637.

Bis-(O-toluoyl)-1α-[(2-(N-trifluoroacyl)-4-chlorophenyl]ethynyl]deoxyribose (5αb). The reaction was carried out at 0.26 mmol scale with respect to 1α (100 mg). Column chromatography on silica gel yielded 86 mg (55%) of the title compound as a colourless sirup. 1H NMR (600 MHz, C 6D6) δ 8.49 (d, J = 1.6 Hz, 1H), 8.36 (s, 1H), 8.13 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 7.9 Hz, 2H), 6.64 (dd, J = 8.3, 1.9 Hz, 1H), 5.38 (d, J = 6.4 Hz, 1H), 4.75 (dd, J = 8.0, 2.6 Hz, 1H), 4.56 (bs, 1H), 4.36 (d, J = 17.1, 11.7, 5.0 Hz, 2H), 2.24 – 2.14 (m, 1H), 2.07 (d, J = 14.0 Hz, 1H), 1.97 (s, 3H), 1.92 (s, 3H); 13C NMR (151 MHz, C 6D6) δ 166.40, 166.14, 154.60 (q, J = 37.4 Hz), 144.74, 144.19, 138.07, 136.36, 132.78, 130.48 (2C), 130.27 (2C), 129.80 (2C), 128.31, 127.93, 125.59, 120.14, 116.27 (d, J = 289.3 Hz), 111.69, 99.59, 83.37, 78.96, 76.53, 68.82, 64.54, 39.80, 21.72, 21.66; IR (KBr) 3370, 2925, 1739, 1718, 1577, 1269, 1177, 1104, 753 cm⁻¹; HRMS calcd for C₃₁H₂₅ClF₃NO₆ (M-H) 598.1250, found 598.1245.

Bis-(O-toluoyl)-1α-[(2-(N-trifluoroacyl)-5-chlorophenyl]ethynyl]deoxyribose (5αc). The reaction was carried out at 0.52 mmol scale with respect to 1α (200 mg). Column chromatography on silica gel yielded 124 mg (47%) of the title compound as a colourless sirup. 1H NMR (600 MHz, C 6D6) δ 8.32 (s, 1H), 8.14 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 2.4 Hz, 1H), 6.91 (d, J = 7.9 Hz, 2H), 6.85 (dm, J = 8.5 Hz, 3H), 5.38 (dm, J = 6.4 Hz, 1H), 4.71 (dd, J = 8.1, 2.5 Hz, 1H), 4.58–4.54 (m, 1H), 4.37 (d, J = 17.1, 11.7, 5.0 Hz, 2H), 2.15 (dd, J = 14.3, 8.0, 6.4 Hz, 1H), 2.06 (dm, J = 14.0 Hz, 1H), 1.97 (s, 3H), 1.96 (s, 3H); 13C NMR (151 MHz, C 6D6) δ 166.38, 166.14, 154.60 (q, J = 37.4 Hz), 144.74, 144.19, 138.07, 136.36, 132.78, 130.48 (2C), 130.27 (2C), 129.80 (2C), 128.31, 127.93, 125.59, 120.14, 116.27 (d, J = 289.3 Hz), 111.69, 99.59, 83.37, 78.96, 76.53, 68.82, 64.54, 39.80, 21.72, 21.66; IR (KBr) 3370, 2925, 1739, 1717, 1577, 1269, 1177, 1110, 753 cm⁻¹; HRMS calcd for C₃₁H₂₆ClF₃NO₆ (M-H) 598.1250, found 598.1245.
166.41, 166.14, 154.57 (q, J = 37.3 Hz), 144.75, 144.21, 135.77, 131.83, 130.82, 130.49 (2C), 130.42, 130.35 (2C), 129.81 (2C), 129.79 (2C), 128.32, 127.85, 121.30, 116.38 (q, J = 289.3 Hz), 114.97, 99.82, 83.50, 78.57, 76.56, 68.78, 64.57, 39.75, 21.73, 21.72; IR (KBr) 3374, 2924, 1739, 1718, 1532, 1277, 1177, 1107, 754 cm⁻¹; HRMS calc'd for C₃₁H₂₅ClF₃NO₆ (M-H) 598.1250, found 598.1244.

**Bis-(O-toluoyl)-1α-[[2-(N-trifluoroacyl)-5-(carboxymethyl)phenyl]ethynyl]deoxyribose (5αd).** The reaction was carried out at 0.52 mmol scale with respect to 1α (200 mg). Column chromatography on silica gel yielded 89 mg (28%) of the title compound as a white solid: m.p. 146 °C; ¹H NMR (600 MHz, C₆D₆) δ 8.55 (s, 1H), 8.37 (d, J = 8.7 Hz, 1H), 8.19 (d, J = 1.7 Hz, 1H), 8.15 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H), 7.90 (dd, J = 8.7, 1.7 Hz, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 7.9 Hz, 2H), 5.40 (d, J = 6.4 Hz, 1H), 4.74 (dd, J = 8.1, 2.5 Hz, 1H), 4.58 – 4.51 (m, 1H), 4.38 (dd, J = 17.0, 11.7, 4.9 Hz, 2H), 3.44 (s, 3H), 2.16 (ddd, J = 14.3, 7.9, 6.6 Hz, 1H), 2.06 (dm, J = 14.0 Hz, 1H), 1.97 (s, 3H), 1.95 (s, 3H); ¹³C NMR (151 MHz, C₆D₆) δ 166.40, 166.16, 165.43, 154.75 (q, J = 37.6 Hz), 144.65, 144.17, 140.55, 133.57, 131.81, 130.49 (2C), 130.33 (2C), 129.80 (4C), 128.30, 127.87, 127.82, 119.58, 116.32 (q, J = 289.3 Hz), 113.44, 99.58, 83.49, 78.94, 76.48, 68.83, 64.57, 52.10, 39.72, 21.72, 21.71; IR (KBr) 3367, 2926, 1743, 1721, 1701, 1610, 1588, 1534, 1439, 1274, 1178, 1102, 752 cm⁻¹; HRMS calc'd for C₃₃H₂₈F₃NO₈ (M-H) 622.1694, found 622.1691.

**Bis-(O-toluoyl)-1β-[[2-(N-trifluoroacyl)phenyl]ethynyl]deoxyribose (5βa).** The reaction was carried out at 0.52 mmol scale with respect to 1β (200 mg). Column chromatography on silica gel yielded 227 mg (77%) of the title compound as a yellowish solid: m.p. 106.2 °C; ¹H NMR (600 MHz, C₆D₆) δ 8.53 (s, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.2 Hz, 2H), 7.09 (dd, J = 7.7, 1.3 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H), 6.91 – 6.86 (m, 1H), 6.81 (d, J = 8.3 Hz, 2H), 6.63 (td, J = 7.6, 1.0 Hz, 1H), 5.44 (dm, J = 5.9 Hz, 1H), 4.84 (dd, J = 9.7, 6.0 Hz, 1H), 4.56 (dd, J = 11.8, 4.4 Hz, 1H), 4.35 (dd, J = 11.8, 4.6 Hz, 1H), 4.26 – 4.22 (m, 1H), 2.26 (dd, J = 13.7, 9.7, 6.0 Hz, 1H), 2.14 (dd, J = 13.7, 6.0, 1.4 Hz, 1H), 2.02 (s, 3H), 1.94 (s, 3H); ¹³C NMR (151 MHz, C₆D₆) δ 166.38, 166.05, 154.78 (q, J = 37.1 Hz), 144.54, 144.01, 137.45, 132.09, 130.47 (2C), 130.45, 130.39 (2C), 129.83 (2C), 129.66 (2C), 128.30, 128.01, 125.57, 120.33, 116.64 (q, J = 289.2 Hz), 113.30, 97.19, 83.77, 80.26, 77.17, 69.01, 64.72, 40.29, 21.79, 21.68; IR (KBr) 3373, 2950, 2922, 1739, 1720, 1610, 1541, 1270, 1178, 1105, 752 cm⁻¹; HRMS calc'd for C₃₃H₂₈F₃NO₈ (M+H) 565.1712, found 565.1721.

**Bis-(O-toluoyl)-1β-[[2-(N-trifluoroacyl)-4-chlorophenyl]ethynyl]deoxyribose (5βb).** The reaction was carried out at 0.52 mmol scale with respect to 1β (200 mg). Column chromatography on silica gel yielded 193 mg (62%) of the title compound as a colourless sirup; ¹H NMR (600 MHz, C₆D₆) δ 8.43 (d, J = 1.8 Hz, 1H), 8.37 (s, 1H), 8.07 – 8.02 (m, 4H), 6.96 (d, J = 7.9 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 8.3 Hz, 1H), 6.62 (dd, J = 8.3, 2.0 Hz, 1H), 5.46 (d, J = 5.8 Hz, 1H), 4.82 (dd, J = 9.4, 6.2 Hz, 1H), 4.59 (dd, J = 11.8, 4.2 Hz, 1H), 4.29 (dd, J = 11.8, 4.4 Hz, 1H), 4.25 – 4.21 (m, 1H), 2.26 (dd, J = 13.9, 9.5, 6.0 Hz, 1H), 2.14 (ddd, J = 13.6, 6.1, 1.4 Hz, 1H), 2.02 (s, 3H), 1.94 (s, 3H); ¹³C NMR (151 MHz, C₆D₆) δ 166.33, 166.06, 154.72 (q, J = 37.6 Hz), 144.63, 144.13, 138.18, 136.38, 132.81, 130.46 (2C), 130.34 (2C), 129.85 (2C), 129.64 (2C), 128.31, 127.95, 125.81, 120.59, 116.41 (q, J = 289.2 Hz), 111.59, 98.06, 83.80, 79.35, 77.10, 68.94, 64.58, 40.25, 21.79,
21.67; IR (KBr) 3369, 2951, 1737, 1720, 1576, 1268, 1177, 1104, 917, 753 cm⁻¹; EI-MS m/z (%): 599 (8), 327 (72), 258 (43), 230 (88), 119 (100), 91 (98), 65 (28); HRMS (EI) calcd for C₃₁H₂₅ClF₃NO₆ 599.1323, found 599.1324.

**Bis-(O-toluoyl)-1β-[(2- (N-trifluoroacyl)-5-chlorophenyl)ethynyl]deoxyribose (5βc).** The reaction was carried out at 0.52 mmol scale with respect to 1β (200 mg). Column chromatography on silica gel yielded 176 mg (57%) of the title compound as a colourless sirup; ¹H NMR (600 MHz, C₆D₆) δ 8.37 (bs, 1H), 8.09 – 8.00 (m, 5H), 7.00 – 6.93 (m, 3H), 6.85 – 6.78 (m, 3H), 5.46 (d, J = 5.7 Hz, 1H), 4.80 (dd, J = 9.4, 6.3 Hz, 1H), 4.60 (dd, J = 11.7, 3.8 Hz, 1H), 4.30 – 4.19 (m, 2H), 2.31 – 2.22 (m, 1H), 2.14 (dd, J = 13.7, 6.2 Hz, 1H), 2.02 (s, 3H), 1.95 (s, 3H); ¹³C NMR (151 MHz, C₆D₆) δ 166.34, 166.06, 154.74 (q, J = 37.5 Hz), 144.64, 144.13, 135.89, 131.69, 130.79, 130.47 (2C), 130.42, 130.35 (2C), 129.86 (2C), 129.68 (2C), 128.30, 127.96, 121.55, 116.52 (q, J = 289.2 Hz), 114.92, 98.29, 83.89, 79.99, 77.18, 68.91, 64.57, 40.21, 21.79, 21.70; IR (KBr) 3374, 2951, 1740, 1719, 1532, 1271, 1178, 1103, 753 cm⁻¹; EI-MS m/z (%): 599 (10), 433 (10), 327 (43), 230 (39), 119 (100), 91 (71), 65 (15); HRMS (EI) calcd for C₃₁H₂₅ClF₃NO₆ 599.1323, found 599.1324.

**Bis-(O-toluoyl)-1β-[(2-N-trifluoroacyl)-5-(carboxymethyl)phenyl]ethynyl]deoxyribose (5βd).** The reaction was carried out at 0.52 mmol scale with respect to 1β (200 mg). Column chromatography on silica gel yielded 75 mg (33%) of the title compound as a white solid: m.p. 115 °C. ¹H NMR (600 MHz, C₆D₆) δ 8.58 (s, 1H), 8.33 (d, J = 8.7 Hz, 1H), 8.13 (d, J = 1.9 Hz, 1H), 8.07 (dd, J = 8.1, 1.6 Hz, 4H), 7.88 (dd, J = 8.7, 1.9 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 5.46 (d, J = 5.9 Hz, 1H), 4.82 (dd, J = 9.6, 6.1 Hz, 1H), 4.57 (dd, J = 11.8, 4.3 Hz, 1H), 4.30 (dd, J = 11.8, 4.4 Hz, 1H), 4.23 (dd, J = 13.7, 6.1, 1.5 Hz, 1H), 2.14 (d, J = 13.7, 6.1, 1.5 Hz, 1H), 2.02 (s, 3H), 1.94 (s, 3H); ¹³C NMR (151 MHz, C₆D₆) δ 166.35, 166.05, 165.44, 154.91 (q, J = 37.6 Hz), 144.60, 144.09, 140.69, 133.54, 131.85, 130.47 (2C), 130.36 (2C), 129.85 (2C), 129.68 (2C), 128.30, 128.00, 127.74, 119.76, 113.32, 98.05, 83.87, 79.37, 77.19, 68.95, 64.64, 52.11, 40.23, 21.79, 21.66; IR (KBr) 3282, 2949, 1749, 1722, 1716, 1540, 1439, 1416, 1280, 1180, 1164, 754 cm⁻¹; HRMS calcd for C₃₃H₂₈F₃NO₈ (M-H) 622.1694, found 622.1695.

### III. Synthesis of compounds 6α and 6β.

**General procedure for the palladium complex catalyzed cyclization of 5 to 6.** To a solution of 5α or 5β (0.2 mmol) in MeCN (3 mL) was added Pd₂(dba)₃·CHCl₃ (7.5 mg, 0.007 mmol), (2-biphenyl)di-t-butylphosphine (18 mg, 0.06 mmol) and K₂CO₃ (84 mg) and the reaction mixture was heated to 120 °C for 5h. Then it was stirred at rt (usually 18-20 °C) overnight. Then the solvent was removed under the reduced pressure, water was added (5 mL) followed extraction with Et₂O (3 × 3 mL), the combined organic fractions were dried over MgSO₄, and concentrated under the reduced pressure. Gradient column chromatography of the residue on silica gel (hexane → hexane/CH₂Cl₂/Et₂O 10/2/1) yielded the corresponding products.

**Bis-(O-toluoyl)-1α-(1H-indol-2-yl)deoxyribose (6αa).** The reaction was carried out at 0.12 mmol scale with respect to 5αa (69 mg). Column chromatography on silica gel yielded 46.5 mg (81%) of the title compound as a colourless sirup. ¹H NMR (600 MHz, C₆D₆) δ 8.20 (d, J = 8.1 Hz, 2H), 7.86 (bs, 1H), 7.82 (d, J = 8.1 Hz,
Bis-(O-toluoyl)-1α-(1H-6-chloroindol-2-yl)deoxyribose (6ab). The reaction was carried out at 0.21 mmol scale with respect to 5ab (123 mg). Column chromatography on silica gel yielded 59 mg (57%) of the title compound as a white solid: m.p. 165 °C; 1H NMR (600 MHz, C₆D₆) δ 8.20 (dm, J = 8.2 Hz, 2H), 7.77 (dm, J = 8.2 Hz, 2H), 7.60 (d, J = 1.8 Hz, 1H), 7.18 (dd, J = 4.7, 2.3 Hz, 1H), 6.92 (d, J = 8.3 Hz, 2H), 6.81–6.75 (m, 3H), 6.00 (d, J = 1.1 Hz, 1H), 5.43 (dm, J = 6.4 Hz, 1H), 5.02 (dd, J = 8.0, 4.1 Hz, 1H), 4.44–4.35 (m, 3H), 2.30 (ddd, J = 14.3, 7.7, 6.9 Hz, 1H), 2.08 (ddd, J = 14.0, 3.8, 2.9 Hz, 1H), 1.97 (s, 3H), 1.92 (s, 3H); 13C NMR (151 MHz, C₆D₆) δ 166.58, 166.25, 144.30, 144.24, 141.53, 134.92, 130.54 (2C), 130.33 (2C), 129.85 (2C), 129.76 (2C), 129.19, 128.30, 127.91, 127.88, 121.97, 121.20, 111.73, 99.85, 83.04, 76.81, 75.07, 64.67, 38.53, 21.73, 21.68; IR (KBr) 3427, 2990, 1718, 1610, 1284, 1180, 814, 753 cm⁻¹; HRMS calcd for C₂₉H₂₇NO₅ (M+H) 504.1572, found 504.1571.

Bis-(O-toluoyl)-1α-(1H-5-chloroindol-2-yl)deoxyribose (6ac). The reaction was carried out at 0.17 mmol scale with respect to 5ac (100 mg). Column chromatography on silica gel yielded 40 mg (48%) of the title compound as a white solid: m.p. 163 °C; 1H NMR (600 MHz, C₆D₆) δ 8.19 (d, J = 8.2 Hz, 2H), 7.77 (s, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 1.8 Hz, 1H), 7.18 (dd, J = 4.7, 2.3 Hz, 1H), 6.92 (d, J = 8.3 Hz, 2H), 6.81–6.75 (m, 3H), 6.00 (d, J = 1.1 Hz, 1H), 5.43 (dm, J = 6.4 Hz, 1H), 5.02 (dd, J = 8.0, 4.1 Hz, 1H), 4.44–4.35 (m, 3H), 2.30 (ddd, J = 14.3, 7.7, 6.9 Hz, 1H), 2.08 (ddd, J = 14.0, 3.8, 2.9 Hz, 1H), 1.97 (s, 3H), 1.92 (s, 3H); 13C NMR (151 MHz, C₆D₆) δ 166.58, 166.20, 144.51, 144.24, 141.53, 134.92, 130.54 (2C), 130.33 (2C), 129.86 (2C), 129.74 (2C), 128.80, 128.29, 127.85, 126.23, 122.65, 120.62, 112.59, 99.45, 83.08, 76.78, 75.11, 64.67, 38.51, 21.73, 21.68; IR (KBr) 3427, 2990, 1718, 1610, 1284, 1180, 814, 753 cm⁻¹; HRMS calcd for C₂₉H₂₆ClNO₅ (M+H) 503.1500, found 503.1495.

Bis-(O-toluoyl)-1α-[1H-5(carboxymethyl)indol-2-yl]deoxyribose (6ad). The reaction was carried out at 0.12 mmol scale with respect to 5ad (75 mg). Column chromatography on silica gel yielded 25 mg (40%) of the title compound as a white solid: m.p. 60 °C; 1H NMR (400 MHz, C₆D₆) δ 8.70–8.66 (m, 1H), 8.25 (dd, J = 8.6, 1.6 Hz, 1H), 8.18 (dm, J = 8.2 Hz, 2H), 8.12 (s, 1H), 7.78 (dm, J = 8.2 Hz, 2H), 7.01 (dm, J = 8.6 Hz, 1H), 6.91 (dd, J = 8.5, 0.6 Hz, 2H), 6.77 (dd, J = 8.5, 0.6 Hz, 2H), 6.21–6.18 (m, 1H), 5.46–5.41 (m, 1H), 5.06–5.02 (m, 1H), 4.44–4.36 (m, 3H), 3.63 (s, 3H), 2.32 (ddd, J = 14.4, 8.0, 6.6 Hz, 1H), 2.10 (dd, J = 14.0, 4.2, 2.7 Hz, 1H), 1.97 (s, 3H), 1.89 (s, 3H); 13C NMR (101 MHz, C₆D₆) δ 168.26, 166.62, 166.25, 144.54, 144.26, 141.45, 139.24, 130.53 (2C), 130.32 (2C), 129.86 (2C), 129.77 (2C), 129.00, 128.27, 127.85, 124.22, 124.10, 123.20, 111.36, 101.03, 83.11, 76.82, 75.11, 64.71, 51.80, 38.46, 21.76, 21.68; IR (KBr) 3341, 2949, 1737, 1718, 1312, 1274, 1109, 753 cm⁻¹; HRMS calcd for C₃₁H₂₉NO₇ (M) 527.1944, found 527.1949.
Bis-(O-toluoyl)-1β-(1H-indol-2-yl)deoxyribose (6βa). The reaction was carried out at 0.46 mmol scale with respect to 5βa (262 mg). Column chromatography on silica gel yielded 111 mg (51%) of the title compound as a yellowish sirup: $^1$H NMR (600 MHz, CD$_3$OD) δ 8.57 (s, 1H), 8.08 (dd, J = 30.9, 8.1 Hz, 4H), 7.66 (d, J = 7.6 Hz, 1H), 7.25–7.18 (m, 3H), 6.97 (d, J = 7.9 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.33 (bs, 1H), 5.35 (d, J = 5.7 Hz, 1H), 5.30 (dd, J = 10.4, 5.5 Hz, 1H), 4.54 (dd, J = 11.6, 5.7 Hz, 1H), 4.43–4.34 (m, 2H), 2.19 (dd, J = 13.5, 5.1 Hz, 1H), 2.13–2.05 (m, 1H), 2.02 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (151 MHz, CD$_3$OD) δ 167.27, 166.28, 144.47, 144.27, 138.31, 137.24, 130.50 (2C), 130.45 (2C), 129.84 (2C), 129.82 (2C), 129.40, 128.31, 128.05, 122.63, 121.27, 120.57, 111.88, 100.28, 83.97, 77.58, 76.30, 65.31, 40.44, 21.80, 21.68; IR (KBr) 3352, 2949, 1715, 1610, 1456, 1271, 1178, 1105, 752 cm$^{-1}$; HRMS calcd for C$_{29}$H$_{27}$NO$_5$ (M+H) 470.1962, found 470.1964.

Bis-(O-toluoyl)-1β-(1H-6-chloroindol-2-yl)deoxyribose (6βb). The reaction was carried out at 0.33 mmol scale with respect to 5βb (198 mg). Column chromatography on silica gel yielded 70 mg (42%) of the title compound as a yellowish sirup: $^1$H NMR (600 MHz, CD$_3$OD) δ 8.56 (s, 1H), 8.11 (d, J = 7.6 Hz, 2H), 8.00 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.20 (bs, 1H), 7.14 (bs, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 6.16 (s, 1H), 5.34 (d, J = 5.3 Hz, 1H), 5.22 (dd, J = 10.3, 5.5 Hz, 1H), 4.47 (dd, J = 11.8, 5.7 Hz, 1H), 4.41 (dd, J = 11.7, 3.5 Hz, 1H), 4.36–4.32 (m, 1H), 2.16 (dd, J = 13.9, 5.5 Hz, 1H), 2.07–2.01 (m, 1H), 2.02 (s, 3H), 1.93 (s, 3H); $^{13}$C NMR (101 MHz, CD$_3$OD) δ 167.62, 166.57, 144.87, 144.77, 139.59, 137.73, 130.77 (2C), 130.70 (2C), 130.17 (4C), 128.55, 128.16, 128.09, 122.30, 121.50, 112.22, 100.39, 84.28, 77.73, 77.70, 76.32, 65.46, 40.64, 22.11, 22.00; IR (KBr) 3332, 2950, 1716, 1611, 1270, 1177, 1104, 753 cm$^{-1}$; HRMS calcd for C$_{29}$H$_{26}$ClNO$_5$ (M+H) 504.1572, found 504.1575.

Bis-(O-toluoyl)-1β-(1H-5-chloroindol-2-yl)deoxyribose (6βc). The reaction was carried out at 0.27 mmol scale with respect to 5βc (160 mg). Column chromatography on silica gel yielded 57 mg (43%) of the title compound as a colourless sirup: $^1$H NMR (300 MHz, CD$_3$OD) δ 8.74 (s, 1H), 8.10 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 2.0 Hz, 1H), 7.19–7.16 (m, 1H), 7.01–6.92 (m, 3H), 6.79 (dd, J = 8.5, 0.6 Hz, 2H), 6.09–6.05 (m, 1H), 5.33 (dm, J = 5.6 Hz, 1H), 5.23 (dd, J = 10.3, 5.6 Hz, 1H), 4.53–4.31 (m, 3H), 2.17 (ddd, J = 13.8, 5.7, 1.4 Hz, 1H), 2.08–1.98 (m, 1H), 2.02 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (75 MHz, CD$_3$OD) δ 167.42, 166.32, 144.63, 144.47, 140.01, 135.37, 130.48 (2C), 130.39 (3C), 129.89 (2C), 129.81 (2C), 128.26, 127.86, 126.18, 122.81, 120.68, 112.87, 99.74, 84.05, 77.45, 76.07, 65.23, 40.33, 21.83, 21.72; IR (KBr) 3343, 2950, 1718, 1617, 1311, 1272, 1185, 1120, 1070, 861 cm$^{-1}$; HRMS calcd for C$_{29}$H$_{26}$ClNO$_5$ (M-H) 503.1500, found 503.1494.

Bis-(O-toluoyl)-1β-[1H-5(carboxymethyl)indol-2-yl]deoxyribose (6βd). The reaction was carried out at 0.23 mmol scale with respect to 5αd (146 mg). Column chromatography on silica gel yielded 23 mg (19%) of the title compound as a white solid: m.p. 61 °C; $^1$H NMR (400 MHz, CD$_3$OD) δ 8.86 (s, 1H), 8.68 (d, J = 1.6 Hz, 1H), 8.25 (dd, J = 8.6, 1.6 Hz, 1H), 8.11 (dm, J = 8.2 Hz, 2H), 8.01 (dm, J = 8.2 Hz, 2H), 7.14 (s, 1H), 6.98 (d, J = 7.9 Hz, 2H), 6.79 (d, J = 7.9 Hz, 2H), 6.23 (d, J = 2.0 Hz, 1H), 5.31 (dm, J = 5.7 Hz, 1H), 5.22 (dd, J = 10.5, 5.5 Hz, 1H), 4.49 (dd, J = 11.6, 5.9 Hz, 1H), 4.41–4.31 (m, 2H), 3.63 (s, 3H), 2.14 (ddd, J = 13.8, 5.5, 1.2 Hz, 1H), 2.02 (s, 3H), 2.01–1.94 (m, 1H), 1.91 (s,
3H); $^{13}$C NMR (101 MHz, C$_6$D$_6$) δ 168.23, 167.46, 166.29, 144.62, 144.50, 139.88, 139.61, 130.49 (2C), 130.42 (2C), 129.89 (2C), 129.84 (2C), 128.28, 127.97, 127.87, 124.32, 124.25, 123.21, 111.57, 101.29, 84.10, 77.43, 76.07, 65.21, 51.74, 40.33, 21.83, 21.70; IR (KBr) 3431, 2953, 1710, 1611, 1440, 1313, 1273, 1178, 1108, 1021, 754 cm$^{-1}$; HRMS calcd for C$_{31}$H$_{29}$NO$_7$ (M+H) 528.2017, found 528.2016.

IV. Synthesis of compounds 7α and 7β.

General procedure for the deprotection of 6 to 7. To a solution of 6α or 6β (0.16 mmol) in MeOH (3 mL) was stepwise added MeONa (0.032 mmol, 1.7 mg) then the reaction mixture was stirred at 20 °C for 12h. Then the solvent was removed under the reduced pressure, the residue was dissolved in EtOAc (5 mL), filtered, and concentrated under the reduced pressure. PTLC on silica gel (EtOAc) yielded the corresponding products.

1α-(1H-Indol-2-yl)deoxyribose (7αa). The reaction was carried out at 0.11 mmol scale with respect to 6αa (50 mg). PTLC on silica gel yielded 19 mg (75%) of the title compound as a white solid: m.p. 122 °C; $^1$H NMR (600 MHz, CD$_3$OD) δ 7.46 (d, $J$ = 7.9 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 1H), 7.08–7.04 (m, 1H), 6.96 (dd, $J$ = 7.5 Hz, 1H), 5.27 (t, $J$ = 7.3 Hz, 1H), 4.40 (dd, $J$ = 11.3, 6.2 Hz, 1H), 4.00 (dd, $J$ = 9.0, 4.9 Hz, 1H), 3.70 (dd, $J$ = 11.8, 3.9 Hz, 1H), 3.64 (dd, $J$ = 11.8, 5.3 Hz, 1H), 2.69–2.62 (m, 1H), 2.18 (ddd, $J$ = 13.0, 7.2, 6.0 Hz, 1H); $^{13}$C NMR (151 MHz, CD$_3$OD) δ 140.81, 138.22, 129.50, 122.41, 121.15, 120.07, 111.99, 100.55, 87.34, 75.57, 73.50, 63.32, 41.88; IR (KBr) 3339, 2924, 1457, 1422, 1349, 1321, 1222, 1068, 1008, 933, 798, 749, 699 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{15}$NO$_3$ (M+H) 234.1125, found 234.1124.

1α-(1H-6-Chloroindol-2-yl)deoxyribose (7αb). The reaction was carried out at 0.04 mmol scale with respect to 6αb (20 mg). PTLC on silica gel yielded 4.4 mg (41%) of the title compound as a white solid: m.p. 153 °C; $^1$H NMR (600 MHz, CD$_3$OD) δ 7.42 (d, $J$ = 8.5 Hz, 1H), 7.33 (d, $J$ = 1.8 Hz, 1H), 6.94 (dd, $J$ = 8.4, 1.9 Hz, 1H), 6.37 (s, 1H), 5.27 (t, $J$ = 7.3 Hz, 1H), 4.40 (dd, $J$ = 11.7, 5.8 Hz, 1H), 4.00 (dd, $J$ = 8.9, 5.0 Hz, 1H), 3.67 (ddd, $J$ = 17.0, 11.8, 4.5 Hz, 2H), 2.65 (ddd, $J$ = 12.9, 7.1, 7.1 Hz, 1H), 2.16 (ddd, $J$ = 10.7, 7.3, 5.9 Hz, 1H); $^{13}$C NMR (151 MHz, CD$_3$OD) δ 142.10, 138.81, 138.22, 129.50, 122.41, 121.15, 120.59, 111.99, 100.55, 87.34, 75.57, 73.50, 63.32, 41.88; IR (KBr) 3286, 2926, 1457, 1323, 1227, 1060, 1009, 917, 827, 691, 597 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{14}$ClNO$_3$ (M-H) 266.0589, found 266.0590.

1α-(1H-7-Chloroindol-2-yl)deoxyribose (7αc). The reaction was carried out at 0.036 mmol scale with respect to 6αc (18 mg). PTLC on silica gel yielded 6.1 mg (64%) of the title compound as a white solid: m.p. 120.8 °C; $^1$H NMR (400 MHz, CD$_3$OD) δ 7.44 (dd, $J$ = 2.0, 0.5 Hz, 1H), 7.29 (dm, $J$ = 8.6 Hz, 1H), 7.02 (dd, $J$ = 8.6, 2.1 Hz, 1H), 6.34 (bs, 1H), 5.25 (dd, $J$ = 7.3, 7.3 Hz, 1H), 4.39 (ddd, $J$ = 6.8, 5.8, 4.9 Hz, 1H), 4.03–3.97 (m, 1H), 3.67 (ddd, $J$ = 17.0, 11.8, 4.6 Hz, 2H), 2.66 (ddd, $J$ = 12.8, 7.1, 7.1 Hz, 1H), 2.15 (ddd, $J$ = 12.9, 7.2, 5.8 Hz, 1H); $^{13}$C NMR (101 MHz, CD$_3$OD) δ 142.84, 136.50, 130.62, 125.67, 122.45, 120.37, 113.17, 100.09, 87.42, 75.36, 73.44, 63.29, 41.92; IR (KBr) 3286, 2934, 2875, 1465, 1450, 1310, 1061, 1006, 914, 794, 693 cm$^{-1}$; HRMS calcd for C$_{13}$H$_{14}$ClNO$_3$ (M-H) 267.0662, found 267.0660.
1α-[1H-5-(Carboxymethyl)indol-2-yl]deoxyribose (7αd). The reaction was carried out at 0.028 mmol scale with respect to 6αd (15 mg). PTLC on silica gel yielded 6 mg (72%) of the title compound as a white amorphous solid: m.p. 120.7 °C; 1H NMR (400 MHz, CD3OD) δ 8.24 (dd, J = 1.6, 0.6 Hz, 1H), 7.77 (dd, J = 8.6, 1.7 Hz, 1H), 7.38 (dm, J = 8.6 Hz, 1H), 6.50 (s, 1H), 5.28 (dd, J = 7.3, 7.3 Hz, 1H), 4.58 (bs, 1H), 4.41 (dd, J = 6.7, 5.8, 4.9 Hz, 1H), 4.02 (td, J = 5.0, 4.0 Hz, 1H), 3.89 (s, 3H), 3.68 (ddd, J = 17.1, 11.8, 4.6 Hz, 2H), 3.34 (bs, 1H), 2.68 (ddd, J = 12.9, 7.1, 1.7 Hz, 1H), 2.17 (ddd, J = 12.9, 7.2, 5.8 Hz, 1H); 13C NMR (101 MHz, CD3OD) δ 170.19, 143.11, 140.94, 129.10, 124.25, 123.72, 122.01, 111.83, 101.68, 87.48, 75.31, 73.45, 63.29, 52.27, 41.89; IR (KBr) 3311, 2948, 2926, 1697, 1617, 1436, 1315, 1296, 1090, 1034, 770 cm⁻¹; HRMS calcd for C15H17NO5 (MH) 291.1103, found 291.1107.

1β-(1H-Indol-2-yl)deoxyribose (7βa). The reaction was carried out at 0.16 mmol scale with respect to 6βa (73 mg). PTLC on silica gel yielded 20 mg (55%) of the title compound as a colorless solid: 1H NMR (400 MHz, CD3OD) δ 7.47 (dm, J = 7.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.06 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 6.96 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.37 (bs, 1H), 5.31 (dd, J = 9.9, 5.9 Hz, 1H), 4.41–4.36 (m, 1H), 3.94 (td, J = 4.5, 2.7 Hz, 1H), 3.76–3.65 (m, 2H), 2.31–2.17 (m, 2H); 13C NMR (101 MHz, CD3OD) δ 139.74, 138.12, 129.46, 122.38, 121.09, 120.08, 111.94, 100.33, 89.08, 76.07, 74.12, 63.84, 43.17. The obtained values are in agreement with the published data.2

1β-(1H-6-Chloroindol-2-yl)deoxyribose (7βb). The reaction was carried out at 0.12 mmol scale with respect to 6βb (62 mg). PTLC on silica gel yielded 19 mg (67%) of the title compound as a yellowish syrup. 1H NMR (400 MHz, CD3OD) δ 7.42 (dm, J = 8.4 Hz, 1H), 7.33–7.31 (m, 1H), 6.95 (dd, J = 8.4, 1.9 Hz, 1H), 6.37 (bs, 1H), 5.28 (dd, J = 9.5, 6.4 Hz, 1H), 4.40–4.35 (m, 1H), 3.96–3.92 (m, 1H), 3.75–3.65 (m, 2H), 2.28–2.16 (m, 2H); 13C NMR (101 MHz, CD3OD) δ 141.01, 138.43, 128.11, 122.11, 120.62, 111.74, 100.40, 89.13, 75.85, 74.08, 63.81, 59.62, 43.10; IR (KBr) 3303, 2928, 2878, 1611, 1452, 1332, 1302, 1219, 1060, 921, 814, 691, 596 cm⁻¹; HRMS calcd for C13H14ClNO3 (M+H) 267.0662, found 267.0657.

1β-(1H-7-Chloroindol-2-yl)deoxyribose (7βc). The reaction was carried out at 0.10 mmol scale with respect to 6βc (48 mg). PTLC on silica gel yielded 14 mg (67%) of the title compound as a white solid: m.p. 154 °C; 1H NMR (600 MHz, CD3OD) δ 7.44 (d, J = 2.0 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.03 (dd, J = 8.5, 2.0 Hz, 1H), 6.34 (s, 1H), 5.29 (dd, J = 9.3, 6.5 Hz, 1H), 4.40–4.35 (m, 1H), 3.98–3.90 (m, 1H), 3.75–3.65 (m, 2H), 2.27–2.17 (m, 2H); 13C NMR (151 MHz, CD3OD) δ 141.82, 136.44, 130.61, 125.73, 122.45, 120.35, 113.12, 99.91, 89.15, 75.85, 74.07, 63.81, 43.18; IR (KBr) 3425, 3248, 3193, 2932, 1447, 1323, 1183, 1061, 914, 877, 794, 690, 591 cm⁻¹; HRMS calcd for C13H14ClNO3 (M+H) 267.0662, found 267.0658.

1β-[1H-5-(Carboxymethyl)indol-2-yl]deoxyribose (7βd). The reaction was carried out at 0.028 mmol scale with respect to 6βd (15 mg). PTLC on silica gel yielded 6 mg (72%) of the title compound as a white amorphous solid: 1H NMR (600 MHz, CD3OD) δ 8.25 (d, J = 0.9 Hz, 1H), 7.78 (dd, J = 8.6, 1.6 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 6.51 (s, 1H), 5.32 (dd, J = 9.1, 6.6 Hz, 1H), 4.57 (bs, 2H), 4.41–4.35 (m, 1H), 3.96 (dd, J = 7.0,
4.4 Hz, 1H), 3.89 (s, 3H), 3.76 – 3.66 (m, J = 11.8, 4.5 Hz, 2H), 2.27 – 2.20 (m, 2H); 13C NMR (151 MHz, CD3OD) δ 170.19, 142.09, 140.87, 129.09, 124.23, 123.72, 122.08, 111.77, 101.52, 89.20, 75.79, 74.08, 63.80, 52.27, 43.16; IR (KBr) 3312, 3272, 2943, 1686, 1438, 1324, 1297, 1236, 1099, 1041, 988, 917, 799, 766 cm⁻¹; HRMS calcd for C15H17NO5 (M+H) 291.1107, found 291.1105.

V References
1α-[(2-N-trifluoroacetyl)phenyl]ethynyl]deoxyribose (5α).
Bis-(O-toluyl)-1α-(1′-(N-trifluoracetyl)phenyl)ethynyl]deoxyribose (5α).
Eis-(O-toluoyl)-1α-[(2-[(N-trifluoroacyl)-4-chlorophenyl]ethynyl] deoxyribose (5Ob).
Et₄N (O toluyl) 1α-[[2 (N trifluoracetyl) 4-chlorophenyl]ethynyl] deoxyribose (5ab).
Bis-(O-tolyl)-1α-[[2-(N-trifluoracetyl)-5-(carboxymethyl)phenyl]ethyl]deoxyribose (5αd).
Bis-(O-toluyl)-1β-[(2-[(N-fluorobenzoyl)phenyl]ethenyl)deoxyribose (5βa).
Bis-\((O\text{-tolyl})\)\(\beta\)-\([1\text{-(N\text{-fluoroacetyl)\text{-4-chlorophenyl}}]}\text{ethynyl}\)deoxyribose (5β).
is-(O-toluoyl)-1β-{2-[(N-trifluoroacetyl)-5-chlorophenyl]ethynyl}deoxyribose (5βx).
Bis-(O-toluoyl)-1α-(1H-benzoimidazole-2-yl)deoxyribose (6αβ).
Bis-(O-toluyl)-1α-[LH-5(ε-carboxymethyl)indol-2-yl]deoxyribose (6αl).

Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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[Chemical structure diagram with labels and spectroscopic data]
Etx-(O-tolyl)-1β-(1H-indol-2-yl) deoxyribose (6βa).

\[
\text{TdG} - \text{TolU}
\]
Eis (O toluyl)-1β-(1H-6-chlorindolyl)deoxyribose (6βb).
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Bis-(O-toluyl)-1β-(1H-6-chloromido-2-yl)deoxyribose (δβ).
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Bis-((O-toluyl)-1β-[1H-5(carboxymethyl)indol-2-yl]deoxyribose (6βd).
Bis-(O-toluoyl)-1β-[1H-5(carboxymethyl)indol-2-yl]deoxyribose (6βd).
1α (1H-Indol-2-yl)deoxyribose ("α").
1α (1H-6-Chloroindol-2-yl)deoxyribose (7α).
1α-[1H-5-(Carboxymethyl)indol-2-yl]deoxyribose (7αd).

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1β-(1H-Indol-2-yl)deoxyribose (7βa).
1β-(1H-7-Chloroindol-2-yl)deoxyribose (7βc)
1β-[1H-5-(Carboxymethylindol-2-yl)]deoxyribose (7βd).

![Chemical structure of 1β-[1H-5-(Carboxymethylindol-2-yl)]deoxyribose (7βd).]