Supporting Information

Stereoselective Synthesis of Alkynyl C-2-Deoxy- β -D-ribofuranosides via Intramolecular Nicholas Reaction: A Versatile Building Block for Non-natural C-Nucleosides

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Experimental Section

General Methods.

NMR spectra were recorded on a Varian Gemini 300 or a Varian UNITY Plus 500 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. FAB-MS and ESI-HRMS analyses were carried out on a JEOL-JMS-AX505HAD and a JEOL-JMS-T100LC mass spectrometer, respectively. Optical rotations were determined with a JASCO-DIP-100 polarimeter. Melting points were determined with Yanako MP-500D and not corrected. All reactions were carried out under an argon atmosphere. THF was freshly distilled from sodium benzophenone ketyl before use, and other solvents were purified with standard methods.¹

Nucleophilic Alkynylation of 1 to Alkynyldiol 2. Typical Procedure.

To a THF (3 mL) solution of acetylenic compound (2.5 mmol) was added 2.6 M *n*-butyllithium in hexane (0.77 mL, 2 mmol) at 0 °C. After stirring for 30 min, a THF (3 mL) solution of 3,5-di-*O*-benzyl-2-deoxy-D-ribofructose (1)² (1.0 mmol) was added dropwise at the same temperature. The reaction mixture was stirred at the same temperature for an additional 30 min and allowed to warm to room temperature over a 5 h period. The reaction mixture was then quenched by adding saturated aqueous NH₄Cl solution (1 mL), evaporated, and poured into CH₂Cl₂. The CH₂Cl₂ solution was washed with brine and H₂O subsequently and evaporated. The residue was subjected to column chromatography (silica gel; eluent, hexane : AcOEt) to give diol 2. The separation of diastereomers, 2(*S*) and 2(*R*) is possible by use of silica gel column chromatography, but not necessary for the following Nicholas reaction.

(2*R*, 3*S*, 5*S*)-1,3-Bis(benzyloxy)-7-(trimethylsilyl)hept-6-yne-2,5-diol (2a(*S*)). Colorless oil, yield 32%. $[\alpha]_D^{27} + 8.8$ (c 1.00, CHCl₃); IR (neat) 3420, 2170 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.41–7.26 (m, 10 H), 4.70–4.50 (m, 5 H), 4.05–3.93 (m, 2 H), 3.66–3.52 (m, 2 H), 3.01 (d, *J* = 7.2 Hz, 1 H), 2.57 (d, *J* = 3.3 Hz, 1 H), 2.13–1.99 (m, 1 H), 1.96–1.83 (m, 1 H), 0.19 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.79, 128.65, 128.59, 128.26, 128.12, 127.96, 106.74, 89.55, 77.83, 73.72, 73.09, 71.72, 70.84, 60.62, 37.69,

0.23; HRMS (ESI) calcd for M + Na⁺, C₂₄H₃₂NaO₄Si: 435.1968; found 435.1951.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)-7-(trimethylsilyl)hept-6-yne-2,5-diol (2a(R)). White solid, yield 58%. mp 35–37 °C; [α]_D²⁷ + 32.0 (c 1.00, CHCl₃); IR (KBr) 3427, 2172 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.41–7.24 (m, 10 H), 4.68–4.49 (m, 5 H), 4.02–3.91 (m, 1 H), 3.86–3.74 (m, 1 H), 3.68–3.52 (m, 2 H), 3.29 (br s, 1 H), 2.90 (br s, 1 H), 2.19–2.07 (m, 1 H), 2.05–1.93 (m, 1 H), 0.18 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.91, 137.81, 128.65, 128.54, 128.25, 128.04, 127.92, 106.60, 89.72, 73.66, 72.41, 71.97, 70.94, 60.62, 38.66, 0.20; HRMS (ESI) calcd for M + Na⁺, C₂₄H₃₂NaO₄Si: 435.1968; found 435.1937.

(2R, 3S, 5S)-1,3-Bis(benzyloxy)hept-6-yne-2,5-diol (2b(S)). Colorless oil, yield 26%. [α]_D²⁹ - 19.2 (c 1.02, CHCl₃); IR (neat) 3411, 3290 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.40–7.22 (m, 10 H), 4.69–4.48 (m, 5 H), 4.03–3.91 (m, 1 H), 3.62–3.50 (m, 2 H), 3.19 (br s, 1 H), 2.66 (br s, 1 H), 2.46 (d, *J* = 2.1 Hz, 1 H), 2.12–2.00 (m, 1 H), 1.95–1.84 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.65, 128.62, 128.55, 128.28, 128.10, 127.96, 84.89, 73.67, 73.07, 72.90, 71.59, 70.78, 59.97, 37.53; HRMS (ESI) calcd for M + Na⁺, C₂₁H₂₄NaO₄: 363.1572; found 363.1607.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)hept-6-yne-2,5-diol (2b(R)). Colorless oil, yield 57%. [α]_D²⁷ - 6.4 (c 0.96, CHCl₃); IR (neat) 3397, 3291 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.39–7.24 (m, 10 H), 4.68–4.48 (m, 5 H), 4.00–3.91 (m, 1 H), 3.83–3.74 (m, 1 H), 3.65–3.51 (m, 2 H), 3.39 (br s, 1 H), 2.88 (br s, 1 H), 2.49–2.44 (m, 1 H), 2.20–2.08 (m, 1 H), 2.06–1.95 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.79, 137.74, 128.57, 128.09, 127.97, 84.77, 73.67, 73.30, 72.36, 71.91, 70.91, 59.97, 38.63; HRMS (ESI) calcd for M + Na⁺, C₂₁H₂₄NaO₄: 363.1572; found 363.1566.

(2R, 3S, 5S)-1,3-Bis(benzyloxy)dodec-6-yne-2,5-diol (2c(S)). Colorless oil, yield 38%. [α]_D²⁹ - 12.8 (c 1.04, CHCl₃); IR (neat) 3428, 2209 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.40–7.26 (m, 10 H), 4.71–4.49 (m, 5 H), 4.04–3.92 (m, 2 H), 3.64–3.52 (m, 2 H), 2.87 (d, *J* = 6.6 Hz, 1 H), 2.55 (s, 1 H), 2.27–2.15 (m, 2 H), 2.10–1.97 (m, 1 H), 1.93–1.82 (m, 1 H), 1.55–1.33 (m, 4 H), 0.96–0.87 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.86, 137.81, 128.62, 128.57, 128.23, 128.05, 127.96, 85.73, 81.10, 77.75, 73.71, 72.95, 71.78, 70.91, 60.41, 38.16, 31.01, 22.24, 18.68, 13.89; HRMS (ESI) calcd for M + Na⁺,

$C_{25}H_{32}NaO_4$: 419.2198; found 419.2210.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)dodec-6-yne-2,5-diol (2c(R)). Colorless oil, yield 46%. $[\alpha]_D^{29}$ - 8.7 (c 0.96, $CHCl_3$); IR (neat) 3401, 2221 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.23 (m, 10 H), 4.68–4.48 (m, 5 H), 4.02–3.92 (m, 1 H), 3.85–3.75 (m, 1 H), 3.66–3.52 (m, 2 H), 3.01 (br s, 1 H), 2.82 (br s, 1 H), 2.29–1.87 (m, 4 H), 1.56–1.30 (m, 4 H), 1.00–0.80 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.99, 137.86, 128.54, 128.04, 127.92, 86.00, 80.99, 77.77, 73.67, 72.43, 72.04, 70.99, 60.50, 39.13, 30.96, 22.24, 18.68, 13.87; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{32}NaO_4$: 419.2198; found 419.2181.

(2R, 3S, 5S)-1,3-Bis(benzyloxy)-7-phenylhept-6-yne-2,5-diol (2d(S)). Colorless oil, yield 31%. $[\alpha]_D^{28}$ - 34.7 (c 1.00, $CHCl_3$); IR (neat) 3417, 2204 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.43–7.21 (m, 15 H), 4.85–4.76 (m, 5 H), 4.68 (s, 2 H), 4.56 (s, 2 H), 4.11–3.99 (m, 2 H), 3.67–3.54 (m, 2 H), 3.08 (s, 1 H), 2.52 (s, 1 H), 2.22–2.09 (m, 1 H), 2.05–1.94 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.76, 131.73, 128.65, 128.57, 128.42, 128.36, 128.28, 128.12, 127.96, 122.75, 90.08, 85.06, 77.83, 73.72, 73.04, 71.72, 70.86, 60.73, 37.80; HRMS (ESI) calcd for $M + Na^+$, $C_{27}H_{28}NaO_4$: 439.1885; found 439.1914.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)-7-phenylhept-6-yne-2,5-diol (2d(R)). White solid, yield 59%. mp 64–66 °C; $[\alpha]_D^{28}$ - 37.3 (c 1.03, $CHCl_3$); IR (KBr) 3417, 2214 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.21 (m, 15 H), 4.91–4.82 (m, 1 H), 4.65–4.48 (m, 4 H), 4.04–3.96 (m, 1 H), 3.92–3.84 (m, 1 H), 3.69–3.55 (m, 2 H), 3.20 (br s, 1 H), 2.75 (br s, 1 H), 2.29–2.18 (m, 1 H), 2.15–2.05 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.87, 137.79, 131.76, 128.55, 128.44, 128.33, 128.10, 127.96, 127.92, 122.70, 89.95, 85.26, 73.67, 72.41, 71.99, 70.97, 60.71, 38.85; HRMS (ESI) calcd for $M + Na^+$, $C_{27}H_{28}NaO_4$: 439.1885; found 439.1866.

(2R, 3S, 5S)-1,3-Bis(benzyloxy)-7-(2-pyrenyl)hept-6-yne-2,5-diol (2e(S)). Colorless oil, yield 33%. $[\alpha]_D^{25}$ - 27.9 (c 0.18, $CHCl_3$); IR (neat) 3426, 2216 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 8.49 (d, $J = 9.3$ Hz, 1 H), 8.16–7.90 (m, 8 H), 7.38–7.19 (m, 10 H), 5.09–5.01 (m, 1 H), 4.70 (s, 2 H), 4.54 (s, 2 H), 4.19–4.05 (m, 2 H), 3.70–3.57 (m, 2 H), 3.40 (br s, 1 H), 2.76 (br s, 1 H), 2.38–2.12 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.78, 137.73, 131.94, 131.26, 131.18, 130.98, 129.69, 128.62, 128.54, 128.34, 128.23, 128.17, 128.05, 127.92, 127.16, 126.21, 125.63, 125.56, 125.42, 124.40, 124.23, 117.16, 95.77,

84.04, 77.78, 73.69, 73.04, 71.75, 70.92, 60.97, 38.19; HRMS (ESI) calcd for $M + Na^+$, $C_{37}H_{32}NaO_4$: 563.2198; found 563.2205.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)-7-(2-pyrenyl)hept-6-yne-2,5-diol (2e(R)). Light brown solid, yield 64%. mp 74–75 °C; $[\alpha]_D^{29}$ - 37.0 (c 0.40, $CHCl_3$); IR (KBr) 3316, 2218 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 8.50 (d, J = 9.0 Hz, 1 H), 8.21–7.95 (m, 8 H), 7.37–7.19 (m, 10 H), 5.11 (t, J = 5.7 Hz, 1 H), 4.73–4.50 (m, 4 H), 4.13–3.95 (m, 2 H), 3.73–3.57 (m, 2 H), 3.48 (br s, 1 H), 2.96 (br s, 1 H), 2.46–2.22 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.87, 137.78, 132.03, 131.37, 131.24, 131.05, 129.82, 128.57, 128.54, 128.41, 128.26, 128.10, 127.97, 127.92, 127.24, 126.29, 125.69, 125.64, 125.46, 124.44, 124.32, 117.16, 95.58, 84.30, 77.77, 73.71, 72.49, 72.06, 71.02, 61.13, 39.15; HRMS (ESI) calcd for $M + Na^+$, $C_{37}H_{32}NaO_4$: 563.2198; found 563.2205.

(2R, 3S, 5S)-1,3-Bis(benzyloxy)-7-(2-thienyl)hept-6-yne-2,5-diol (2f(S)). Colorless oil, yield 33%. $[\alpha]_D^{25}$ - 41.5 (c 0.96, $CHCl_3$); IR (neat) 3416, 2219, 742, 701 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.24 (m, 10 H), 7.22 (dd, J = 5.1, 1.1 Hz, 1 H), 7.17 (dd, J = 3.6, 1.1 Hz, 1 H), 6.94 (dd, J = 5.1, 3.6 Hz, 1 H), 4.79 (dd, J = 7.8, 3.3 Hz, 1 H), 4.65 (s, 2 H), 4.54 (s, 2 H), 4.05–3.97 (m, 2 H), 3.64–3.52 (m, 2 H), 2.72 (br s, 2 H), 2.21–2.07 (m, 1 H), 2.05–1.91 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.73, 132.16, 128.64, 128.57, 128.28, 128.10, 127.96, 127.21, 127.00, 122.68, 93.96, 78.37, 77.77, 73.71, 73.06, 71.68, 70.83, 60.79, 37.67; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{26}NaO_4S$: 445.1450; found 445.1475.

(2R, 3S, 5R)-1,3-Bis(benzyloxy)-7-(2-thienyl)hept-6-yne-2,5-diol (2f(R)). White solid, yield 57%. mp 71–72 °C; $[\alpha]_D^{25}$ - 38.8 (c 1.01, $CHCl_3$); IR (KBr) 3453, 3325, 2224, 742, 701 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.37–7.26 (m, 10 H), 7.23 (dd, J = 5.1, 1.2 Hz, 1 H), 7.16 (dd, J = 3.6, 1.2 Hz, 1 H), 6.95 (dd, J = 5.1, 3.6 Hz, 1 H), 4.86 (t, J = 5.7 Hz, 1 H), 4.64–4.48 (m, 4 H), 4.01–3.94 (m, 1 H), 3.84 (dd, J = 11.1, 6.0 Hz, 1 H), 3.66–3.54 (m, 2 H), 3.32 (br s, 1 H), 2.85 (br s, 1 H), 2.28–2.03 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.87, 137.81, 132.28, 128.57, 128.13, 127.96, 127.28, 127.02, 122.67, 93.82, 78.58, 73.71, 72.43, 72.01, 70.97, 60.84, 38.73; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{26}NaO_4S$: 445.1450; found 445.1462.

(2R, 3S, 5S)-8-Allyloxy-1,3-bis(benzyloxy)oct-6-yne-2,5-diol (2g(S)). Colorless oil,

yield 35%. $[\alpha]_D^{28}$ - 19.4 (*c* 1.03, CHCl₃); IR (neat) 3430 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.41–7.21 (m, 10 H), 5.96–5.81 (m, 1 H), 5.29 (ddd, *J* = 17.4, 3.3, 1.5 Hz, 1 H), 5.20 (ddd, *J* = 10.5, 3.8, 1.5 Hz, 1 H), 4.69–4.49 (m, 5 H), 4.17 (d, *J* = 1.5 Hz, 2 H), 4.06–3.90 (m, 4 H), 3.63–3.52 (m, 2 H), 2.80 (br s, 2 H), 2.11–2.00 (m, 1 H), 1.97–1.86 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.74, 133.99, 128.64, 128.59, 128.25, 128.10, 127.97, 117.94, 87.35, 80.89, 73.72, 72.93, 71.70, 70.86, 70.83, 60.16, 57.62, 37.82; HRMS (ESI) calcd for M + Na⁺, C₂₅H₃₀NaO₅: 433.1991; found 433.1947.

(2*R*, 3*S*, 5*R*)-8-Allyloxy-1,3-bis(benzyloxy)oct-6-yne-2,5-diol (2*g(R)*). Colorless oil, yield 54%. $[\alpha]_D^{27}$ - 14.4 (*c* 1.05, CHCl₃); IR (neat) 3410 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.39–7.20 (m, 10 H), 5.96–5.81 (m, 1 H), 5.34–5.16 (m, 2 H), 4.72–4.66 (m, 1 H), 4.61–4.48 (m, 4 H), 4.24–4.11 (m, 2 H), 4.05–3.92 (m, 2 H), 3.81–3.73 (m, 1 H), 3.64–3.52 (m, 2 H), 2.87 (br s, 2 H), 2.19–1.94 (m, 2 H); ¹³C NMR (CDCl₃, 75 MHz) δ 137.83, 137.76, 133.97, 128.54, 128.05, 127.94, 117.94, 87.22, 81.04, 73.67, 72.31, 71.93, 70.96, 70.81, 60.13, 57.61, 38.63; HRMS (ESI) calcd for M + Na⁺, C₂₅H₃₀NaO₅: 433.1991; found 433.1947.

Nicholas Reaction of Alkynyldiol 2 to Alkynyl C-2-Deoxy-D-ribofuranoside 3. Typical Procedure.

To a CH₂Cl₂ (5 mL) solution of 2 (0.5 mmol) was added Co₂(CO)₈ (0.6 mmol) in one portion at room temperature. The reaction mixture was stirred at this temperature for 1 h, and then TfOH (4 μ L, 0.05 mmol) was added to the solution. After stirring for 5 h, the reaction mixture was quenched by adding Et₃N (0.2 mL). To the mixture was added I₂ (5.0 mmol) slowly, and the resulting mixture was stirred at room temperature for 1 h. The solution of the mixture was washed with saturated aqueous Na₂SO₃ solution and brine subsequently and evaporated. The residue was subjected to column chromatography (silica gel; eluent, hexane : AcOEt) to give 3. The separation of diastereomers, 3(α) and 3(β) is also possible by use of silica gel column chromatography.

(2*R*, 3*S*, 5*R*)-3-Benzyloxy-2-benzyloxymethyl-5-(trimethylsilylethynyl)tetrahydrofuran (3*a*(β)). White solid, yield 90%. mp 72–73 °C; $[\alpha]_D^{27}$ + 8.80 (*c* 1.00, CHCl₃); IR (KBr) 2184 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz)

δ 7.40–7.22 (m, 10 H), 4.77–4.69 (m, 1 H), 4.58 (s, 2 H), 4.50 (s, 2 H), 4.16–4.04 (m, 2 H), 3.66–3.58 (m, 1 H), 3.53–3.45 (m, 1 H), 2.34–2.24 (m, 1 H), 2.13–2.01 (m, 1 H), 0.16 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.25, 138.00, 128.49, 128.44, 127.78, 127.73, 127.70, 104.27, 90.29, 83.95, 81.08, 73.71, 71.31, 70.86, 68.38, 39.91, 0.15; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{24}\text{H}_{32}\text{NaO}_4\text{Si}$: 417.1862; found 417.1837.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzyloxymethyl-5-(trimethylsilylethynyl)tetrahydrofuran (3a(α)). Colorless oil, yield 1%. $[\alpha]_{\text{D}}^{27} + 32.0$ (c 1.00, CHCl_3); IR (neat) 2172 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.40–7.22 (m, 10 H), 4.81–4.74 (m, 1 H), 4.61–4.43 (m, 4 H), 4.30–4.23 (m, 1 H), 4.18–4.10 (m, 1 H), 3.64–3.50 (m, 2 H), 2.51–2.38 (m, 1 H), 2.24–2.12 (m, 1 H), 0.17 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.18, 128.42, 127.70, 127.62, 105.08, 89.95, 82.70, 80.02, 73.67, 71.75, 70.49, 68.32, 39.71, 0.19; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{24}\text{H}_{32}\text{NaO}_4\text{Si}$: 417.1862; found 417.1838.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzyloxymethyl-5-ethynyltetrahydrofuran (3b(β)). Colorless oil, yield 42%. $[\alpha]_{\text{D}}^{28} + 29.8$ (c 1.05, CHCl_3); IR (neat) 2121 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.38–7.21 (m, 10 H), 4.78–4.68 (m, 1 H), 4.56 (s, 2 H), 4.49 (s, 2 H), 4.18–4.06 (m, 2 H), 3.64–3.56 (m, 1 H), 3.52–3.44 (m, 1 H), 2.46 (s, 1 H), 2.36–2.24 (m, 1 H), 2.16–2.03 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.17, 137.91, 128.51, 128.42, 127.81, 127.75, 127.70, 89.96, 82.80, 80.94, 73.67, 71.33, 70.84, 67.74, 39.76; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{21}\text{H}_{22}\text{NaO}_3$: 345.1467; found 345.1437.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzyloxymethyl-5-ethynyltetrahydrofuran (3b(α)). Colorless oil, yield 20%. $[\alpha]_{\text{D}}^{28} + 38.9$ (c 0.99, CHCl_3); IR (neat) 2116 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.38–7.23 (m, 10 H), 4.82–4.76 (m, 1 H), 4.59–4.44 (m, 4 H), 4.30–4.24 (m, 1 H), 4.11 (dt, $J = 6.9, 4.2\text{ Hz}$, 1 H), 3.61–3.48 (m, 2 H), 2.50 (d, $J = 1.8\text{ Hz}$, 1 H), 2.48–2.37 (m, 1 H), 2.24–2.13 (m, 1 H), 0.17 (s, 9 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.10, 138.05, 128.42, 127.71, 83.64, 82.96, 79.82, 73.62, 73.46, 71.72, 70.34, 67.77, 39.45; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{21}\text{H}_{22}\text{NaO}_3$: 345.1467; found 345.1466.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzyloxymethyl-5-(1-hexynyl)tetrahydrofuran (3c(β)). Colorless oil, yield 57%. $[\alpha]_{\text{D}}^{28} + 18.4$ (c 0.99, CHCl_3); IR (neat) 2243 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.35–7.26 (m, 10 H), 4.76–4.68 (m, 1 H), 4.57 (s, 2 H), 4.49 (s, 2 H), 4.14–4.04 (m, 2 H), 3.61 (dd, $J = 10.2, 4.5\text{ Hz}$, 1 H), 3.49 (dd, $J = 10.5, 6.0\text{ Hz}$, 1 H),

2.30–2.14 (m, 3 H), 2.07–1.96 (m, 1 H), 1.53–1.31 (m, 4 H), 0.92–0.85 (m, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.28, 138.07, 128.47, 128.41, 127.73, 127.66, 86.37, 83.66, 81.12, 78.79, 73.66, 71.28, 70.96, 68.32, 40.15, 30.86, 22.21, 18.79, 13.89; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{25}\text{H}_{30}\text{NaO}_3$: 401.2093; found 401.2057.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzoyloxymethyl-5-(1-hexynyl)tetrahydrofuran (3c(α)). Colorless oil, yield 5%. $[\alpha]_{\text{D}}^{28} + 33.6$ (c 0.38, CHCl_3); IR (neat) 2244 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.36–7.24 (m, 10 H), 4.81–4.72 (m, 1 H), 4.60–4.43 (m, 4 H), 4.28–4.21 (m, 1 H), 4.16–4.07 (m, 1 H), 3.63–3.50 (m, 2 H), 2.47–2.36 (m, 1 H), 2.28–2.06 (m, 3 H), 1.54–1.30 (m, 4 H), 0.96–0.82 (m, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.26, 128.42, 127.70, 86.20, 82.48, 80.02, 79.72, 73.66, 71.76, 70.52, 68.25, 40.02, 30.93, 22.22, 18.82, 13.91; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{25}\text{H}_{30}\text{NaO}_3$: 401.2093; found 401.2098.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzoyloxymethyl-5-phenylethynyltetrahydrofuran (3d(β)). Colorless oil, yield 87%. $[\alpha]_{\text{D}}^{29} + 10.4$ (c 0.97, CHCl_3); IR (neat) 2233 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.41–7.14 (m, 15 H), 4.74 (dd, $J = 9.9, 5.4\text{ Hz}$, 1 H), 4.59 (s, 2 H), 4.58 (s, 2 H), 4.35 (dt, $J = 2.4, 6.0\text{ Hz}$, 1 H), 4.18–4.11 (m, 1 H), 3.70 (dd, $J = 10.2, 5.7\text{ Hz}$, 1 H), 3.58 (dd, $J = 10.2, 6.3\text{ Hz}$, 1 H), 2.30 (ddd, $J = 13.2, 5.4, 1.5\text{ Hz}$, 1 H), 1.98–1.85 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 147.76, 138.20, 138.00, 128.54, 128.47, 128.42, 128.25, 127.83, 127.75, 127.66, 110.61, 95.56, 87.28, 84.35, 80.74, 73.59, 71.36, 71.05, 37.56; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{27}\text{H}_{26}\text{NaO}_3$: 421.1780; found 421.1783.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzoyloxymethyl-5-phenylethynyltetrahydrofuran (3d(α)). Colorless oil, yield 12%. $[\alpha]_{\text{D}}^{28} + 28.1$ (c 0.27, CHCl_3); IR (neat) 2204 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.44–7.23 (m, 15 H), 5.02 (dd, $J = 7.5, 5.7\text{ Hz}$, 1 H), 4.62–4.46 (m, 4 H), 4.37–4.30 (m, 1 H), 4.21–4.12 (m, 1 H), 3.67–3.52 (m, 2 H), 3.41–2.56 (m, 1 H), 2.32–2.22 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.20, 131.85, 128.52, 128.44, 128.33, 128.25, 127.81, 127.78, 127.73, 127.70, 122.92, 88.95, 82.91, 80.15, 73.71, 71.75, 70.55, 68.53, 39.76; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{27}\text{H}_{26}\text{NaO}_3$: 421.1780; found 421.1772.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzoyloxymethyl-5-(pyren-2-ylethynyl)tetrahydrofuran (3e(β)). Colorless oil, yield 84%. $[\alpha]_{\text{D}}^{28} - 19.9$ (c 1.12, CHCl_3); IR (neat) 2223 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.51 (d, $J = 9.3\text{ Hz}$, 1 H), 8.23–7.96 (m, 8 H), 7.44–7.23 (m,

10 H), 5.21 (dd, $J = 9.3, 5.7$ Hz, 1 H), 4.63 (s, 2 H), 4.58 (s, 2 H), 4.33–4.21 (m, 2 H), 3.77–3.58 (m, 2 H), 2.60–2.32 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.23, 138.00, 132.13, 131.40, 131.26, 131.08, 129.91, 128.55, 128.46, 128.40, 128.28, 127.86, 127.79, 127.76, 127.70, 127.28, 126.29, 125.69, 125.67, 125.56, 124.46, 93.61, 84.51, 84.06, 81.16, 73.77, 71.44, 71.00, 68.88, 40.28; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{37}\text{H}_{30}\text{NaO}_3$: 545.2093; found 545.2123.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzoyloxymethyl-5-(pyren-2-ylethynyl)tetrahydrofuran (3e(α)). Colorless oil, yield 13%. $[\alpha]_{\text{D}}^{28} + 19.4$ (c 0.46, CHCl_3); IR (neat) 2220 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.57 (d, $J = 9.6$ Hz, 1 H), 8.22–7.93 (m, 8 H), 7.43–7.24 (m, 10 H), 5.31–5.23 (m, 1 H), 4.71–4.47 (m, 5 H), 4.31–4.24 (m, 1 H), 3.73–3.61 (m, 2 H), 2.66–2.44 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.23, 131.27, 131.15, 129.93, 128.51, 128.34, 128.20, 127.81, 127.78, 127.31, 126.24, 125.84, 125.64, 124.43, 94.58, 89.09, 83.24, 80.47, 73.75, 71.93, 70.62, 68.98, 40.10; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{37}\text{H}_{30}\text{NaO}_3$: 545.2093; found 545.2123.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzoyloxymethyl-5-(2-thienylethynyl)tetrahydrofuran (3f(β)). Colorless oil, yield 69%. $[\alpha]_{\text{D}}^{27} - 14.5$ (c 1.01, CHCl_3); IR (neat) 2225, 739, 700 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.37–7.25 (m, 10 H), 7.23 (dd, $J = 5.4, 1.2$ Hz, 1 H), 7.18 (dd, $J = 3.6, 1.2$ Hz, 1 H), 6.94 (dd, $J = 5.4, 3.6$ Hz, 1 H), 4.98 (dd, $J = 9.9, 5.7$ Hz, 1 H), 4.57 (s, 2 H), 4.52 (s, 2 H), 4.21–4.11 (s, 2 H), 3.63 (dd, $J = 10.2, 4.5$ Hz, 1 H), 3.52 (dd, $J = 10.2, 5.4$ Hz, 1 H), 2.42–2.32 (m, 1 H), 2.24–2.12 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.20, 137.95, 132.47, 128.52, 128.44, 127.83, 127.78, 127.70, 127.37, 126.95, 122.67, 91.78, 83.95, 81.04, 78.83, 73.72, 71.39, 70.89, 68.59, 39.79; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{25}\text{H}_{24}\text{NaO}_3\text{S}$: 427.1344; found 427.1327.

(2R, 3S, 5S)-3-Benzoyloxy-2-benzoyloxymethyl-5-(2-thienylethynyl)tetrahydrofuran (3f(α)). Colorless oil, yield 8%. $[\alpha]_{\text{D}}^{27} + 30.1$ (c 1.03, CHCl_3); IR (neat) 2221, 739, 701 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.39–7.25 (m, 10 H), 7.23 (dd, $J = 6.0, 1.2$ Hz, 1 H), 7.17 (dd, $J = 3.0, 1.2$ Hz, 1 H), 6.94 (dd, $J = 6.0, 3.0$ Hz, 1 H), 5.07–5.00 (m, 1 H), 4.62–4.45 (m, 4 H), 4.36–4.29 (m, 1 H), 4.20–4.12 (m, 1 H), 3.66–3.53 (m, 2 H), 2.55–2.42 (m, 1 H), 2.32–2.22 (m, 1 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 138.15, 132.34, 128.46, 127.71, 127.66, 127.23, 126.90, 122.86, 92.77, 82.94, 80.08, 78.66, 73.69, 71.73, 70.49, 68.58,

39.52; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{24}NaO_3S$: 427.1344; found 427.1351.

(**2R**, **3S**, **5R**)-5-(3-Allyloxy-1-propynyl)-3-benzyloxy-2-benzyloxymethyl tetrahydrofuran (**3g(β)**). Colorless oil, yield 72%. $[\alpha]_D^{28} + 25.6$ (c 1.69, $CHCl_3$); IR (neat) 1645 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.26 (m, 10 H), 6.02–5.87 (m, 1 H), 5.35 (dd, $J = 17.4, 3.3\text{ Hz}$, 1 H), 5.23 (dd, $J = 10.5, 3.0\text{ Hz}$, 1 H), 4.97–4.69 (m, 1 H), 4.59 (s, 2 H), 4.55 (s, 2 H), 4.48–4.34 (m, 2 H), 4.34–4.26 (m, 1 H), 4.13–4.06 (m, 1 H), 4.06–3.91 (m, 2 H), 3.69 (dd, $J = 10.2, 5.7\text{ Hz}$, 1 H), 3.57 (dd, $J = 9.9, 6.3\text{ Hz}$, 1 H), 2.26–2.17 (m, 1 H), 1.85–1.73 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.23, 138.00, 134.15, 128.54, 128.46, 127.83, 127.75, 127.71, 118.02, 110.45, 100.42, 86.91, 84.40, 81.59, 80.63, 73.61, 71.38, 70.97, 70.84, 37.03; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{28}NaO_4$: 415.1885; found 415.1885.

(**2R**, **3S**, **5S**)-5-(3-Allyloxy-1-propynyl)-3-benzyloxy-2-benzyloxymethyltetrahydrofuran (**3g(α)**) Colorless oil, yield 3%. $[\alpha]_D^{28} + 11.1$ (c 0.83, $CHCl_3$); IR (neat) 1645 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.26 (m, 10 H), 6.02–5.86 (m, 1 H), 5.39–5.18 (m, 2 H), 4.77–4.65 (m, 1 H), 4.65–4.16 (m, 8 H), 4.06–3.87 (m, 2 H), 3.73–3.52 (m, 2 H), 2.62–2.49 (m, 1 H), 1.88–1.75 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.21, 137.91, 134.12, 128.51, 128.44, 127.87, 127.78, 127.68, 117.97, 112.15, 98.98, 86.52, 83.17, 81.39, 78.69, 73.67, 72.31, 70.71, 70.42, 37.42; HRMS (ESI) calcd for $M + Na^+$, $C_{25}H_{28}NaO_4$: 415.1885; found 415.1922.

Conventional Cyclization of Alkynyldiol **2** to Alkynyl C-2-Deoxy-D-ribofuranoside **3**.³

To a pyridine (6 mL) solution of **2a(S)** (600 mg, 1.45 mmol) was added a $CHCl_3$ (4 mL) solution of *p*-toluenesulfonyl chloride (608 mg, 3.19 mmol) dropwise at 60 °C over a 10 min period. After the reaction mixture was stirred at the same temperature for 6 h, a few chips of ice were added. After stirred for 3 h, the solvent was removed, and the residue was poured into brine and extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated and chromatographed (silica gel; eluent, hexane : AcOEt = 2 : 1) to give **3a(β)** and **4a(α)**: yield 50% (285 mg) for **3a(β)** and 7% (37 mg) for **4a(α)**. The reaction of **2a(R)** (740 mg, 1.79 mmol) in a manner similar to that described for **2a(S)**, led to the formation of **4a(β)** and

3a(α): yield 7% (49 mg) for **4a(β)** and 59% (414 mg) for **3a(α)**.

(2*S*, 3*S*, 5*S*)-3-Benzoyloxy-2-benzoyloxymethyl-5-(trimethylsilylethynyl)tetrahydrofuran **4a(α)**; White solid; $[\alpha]_D^{27} + 19.2$ (*c* 0.98, CHCl₃); mp 72–73 °C; IR (KBr) 2174 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.39–7.22 (m, 10 H), 4.68–4.37 (m, 5 H), 4.18–4.10 (m, 1 H), 4.02–3.94 (m, 1 H), 3.90–3.76 (m, 2 H), 2.46–2.35 (m, 1 H), 2.26–2.16 (m, 1 H), 0.15 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 138.38, 138.26, 128.39, 127.89, 127.60, 127.45, 104.88, 89.87, 81.89, 78.62, 73.72, 71.25, 69.01, 67.41, 39.65, 0.17; HRMS (ESI) calcd for M + Na⁺, C₂₄H₃₂NaO₄Si: 417.1862; found 417.1880.

(2*S*, 3*S*, 5*R*)-3-Benzoyloxy-2-benzoyloxymethyl-5-(trimethylsilylethynyl)tetrahydrofuran **4a(β)**; Colorless oil; $[\alpha]_D^{27} + 43.3$ (*c* 0.97, CHCl₃); IR (neat) 2173 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.40–7.20 (m, 10 H), 4.88–4.80 (m, 1 H), 4.66–4.41 (m, 4 H), 4.33–4.24 (m, 1 H), 4.24–4.19 (m, 1 H), 3.72–3.65 (m, 2 H), 2.45–2.35 (m, 1 H), 2.17–2.05 (m, 1 H), 0.16 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 138.33, 138.15, 128.47, 128.41, 127.86, 127.73, 127.65, 127.52, 105.08, 90.00, 80.86, 78.93, 73.69, 71.72, 68.58, 67.49, 40.07, 0.19; HRMS (ESI) calcd for M + Na⁺, C₂₄H₃₂NaO₄Si: 417.1862; found 417.1860.

Complexation of Alkynyldiol **2a**, **3a**, and **3g(β)** with Dicobalt Octacarbonyl. Typical Procedure.

To a CH₂Cl₂ solution of the respective alkyne was added dicobalt octacarbonyl (1.2 equiv) by portions at room temperature. After stirring for 1 h, the reaction mixture was evaporated. Silica gel column chromatography of the residue gave the corresponding cobalt complex.

Cobalt complex 5a(*S*). Reddish brown oil, yield 96%. $[\alpha]_D^{27} - 126.8$ (*c* 1.00, CHCl₃); IR (neat) 3449, 2087, 2046, 2019 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.42–7.23 (m, 10 H), 5.01–4.91 (m, 1 H), 4.61 (s, 2 H), 4.55 (s, 2 H), 4.02–3.90 (m, 1 H), 3.88–3.76 (m, 1 H), 3.70–3.52 (m, 2 H), 2.90–2.76 (m, 1 H), 2.62–2.50 (m, 1 H), 2.12–1.99 (m, 1 H), 1.94–1.80 (m, 1 H), 0.30 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 200.21, 137.89, 137.73, 128.65, 128.60, 128.34, 128.17, 128.02, 116.08, 73.74, 72.91, 71.70, 71.08, 69.71, 41.10,

1.08; FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 614 (M^+-3CO , 27%), 530 (M^+-6CO , 100%).

Cobalt complex 5a(R). Reddish brown oil, yield 97%. $[\alpha]_D^{27}$ - 108.8 (c 1.03, $CHCl_3$); IR (neat) 3434, 2088, 2047, 2019 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.24 (m, 10 H), 5.11–5.02 (m, 5 H), 4.69–4.49 (m, 4 H), 4.11–4.01 (m, 1 H), 3.90–3.78 (m, 1 H), 3.68–3.56 (m, 2 H), 3.52–3.44 (m, 1 H), 2.92–2.80 (m, 1 H), 2.17–1.95 (m, 2 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.23, 137.78, 137.60, 128.67, 128.65, 128.59, 128.13, 127.99, 116.00, 78.24, 73.74, 72.14, 71.65, 70.99, 70.07, 40.44, 1.11; FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 614 (M^+-3CO , 15%), 530 (M^+-6CO , 100%).

β -Cobalt complex 6a(β). Reddish brown oil, yield 99%. $[\alpha]_D^{27}$ - 130.9 (c 1.03, $CHCl_3$); IR (neat) 2088, 2048, 2020 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.22 (m, 10 H), 5.37–5.21 (m, 1 H), 4.65–4.46 (m, 4 H), 4.38–4.26 (m, 1 H), 4.21–4.10 (m, 1 H), 3.65–3.53 (m, 1 H), 3.51–3.39 (m, 1 H), 2.43–2.28 (m, 1 H), 1.91–1.77 (m, 1 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.20, 138.23, 138.02, 128.55, 128.42, 127.96, 127.86, 127.70, 110.61, 83.95, 81.83, 79.04, 73.53, 71.34, 71.31, 41.64, 0.99; FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 596 (M^+-3CO , 27%), 540 (M^+-5CO , 100%), 512 (M^+-6CO , 68%).

α -Cobalt complex 6a(α). Reddish brown oil, yield 96%. $[\alpha]_D^{27}$ - 134.9 (c 1.03, $CHCl_3$); IR (neat) 2088, 2047, 2018 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.22 (m, 10 H), 5.29–5.18 (m, 1 H), 4.65–4.45 (m, 4 H), 4.30–4.16 (m, 2 H), 3.69–3.53 (m, 2 H), 2.75–2.61 (m, 1 H), 1.95–1.81 (m, 1 H), 0.31 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.20, 138.46, 138.12, 128.46, 127.87, 127.79, 127.63, 127.60, 112.60, 82.52, 80.18, 79.06, 73.53, 72.23, 70.62, 41.67, 1.03; FABMS (in 3-nitrobenzyl alcohol) m/e (rel intensity) 596 (M^+-3CO , 21%), 512 (M^+-6CO , 100%).

Cobalt complex 11. Reddish brown oil, yield 96%. $[\alpha]_D^{28}$ - 116.9 (c 1.03, $CHCl_3$); IR (neat) 2092, 2024, 1617 cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.21 (m, 10 H), 5.99–5.82 (m, 1 H), 5.38–5.14 (m, 3 H), 4.67–4.44 (m, 6 H), 4.34–4.26 (m, 1 H), 4.20–4.07 (m, 3 H), 3.61–3.51 (m, 1 H), 3.47–3.37 (m, 1 H), 2.42–2.32 (m, 1 H), 1.93–1.80 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.44, 138.18, 137.99, 134.49, 128.52, 128.42, 127.87, 127.65, 116.84, 95.58, 93.27, 83.98, 81.63, 78.61, 73.51, 71.83, 71.23, 70.32, 40.91.

Functionalization of Acetylenic Bond of C-2-Deoxy-D-ribofuranoside 3.

(2R, 3S, 5R)-3-Hydroxy-2-hydroxymethyl-5-(trimethylsilylethynyl)tetrahydrofuran (7). Deprotection of the Benzyl Group.

To a CH₂Cl₂ (360 mL) solution of **3a**(β) (4.70 g, 11.9 mmol) was added dropwise 1 M BCl₃ in CH₂Cl₂ (60 mL) at -78 °C over a 20 min period. After the reaction mixture was stirred at the same temperature for 1.5 h, the reaction was quenched by adding MeOH (5 mL) and allowed to warm to room temperature over a 3 h period. The solution was washed with saturated aqueous NaHCO₃ solution and H₂O. The organic layer was evaporated and chromatographed (silica gel; eluent, hexane : AcOEt = 2 : 1) to give **7** as a white solid: yield 93% (2.38 g); mp 64–65 °C; $[\alpha]_D^{27} + 34.0$ (c 1.00, CHCl₃); IR (KBr) 3418, 3385, 2181 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.82–4.75 (m, 1 H), 4.49–4.41 (m, 1 H), 3.90–3.84 (m, 1 H), 3.82–3.73 (m, 1 H), 3.73–3.63 (m, 1 H), 2.24–2.17 (m, 2 H), 2.08–2.01 (m, 1 H), 1.93–1.89 (m, 1 H), 0.18 (s, 9 H); ¹³C NMR (CDCl₃, 75 MHz) δ 104.22, 91.00, 87.07, 73.24, 68.27, 62.87, 43.26, 0.12; HRMS (ESI) calcd for M + Na⁺, C₁₀H₁₈O₃NaSi: 237.0923; found 237.0915.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzoyloxymethyl-5-vinyltetrahydrofuran (8). Partial Hydrogenation of **3b**(β) with Lindlar Catalyst.

To a benzene (2 mL) solution of **3b**(β) (116 mg, 0.36 mmol) was added pyridine (0.1 mL) and Lindlar catalyst (7 mg), then a hydrogen balloon (1 atm) was attached. After stirring at room temperature for 2 h, the mixture was filtered and concentrated to a syrup under reduced pressure. Purification with column chromatography (silica gel; eluent, hexane : AcOEt = 20 : 1) afforded olefin **8** as a colorless oil: yield 87% (101 mg); $[\alpha]_D^{27} + 28.0$ (c 1.23, CHCl₃); IR (neat) 1721 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.36–7.26 (m, 10 H), 5.88–5.81 (m, 1 H), 5.29 (d, *J* = 17.5 Hz, 1 H), 5.13 (d, *J* = 11.8 Hz, 1 H), 4.58–4.55 (m, 3 H), 4.52 (s, 2 H), 4.19–4.16 (m, 1 H), 4.07–4.05 (m, 1 H), 3.59–3.55 (m, 1 H), 3.47–3.43 (m, 1 H), 2.17–2.12 (m, 1 H), 1.78–1.71 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 138.16, 138.11, 138.06, 128.37, 128.32, 127.65, 127.61, 127.58, 116.53, 83.59, 81.39, 79.95, 73.51, 71.11, 71.09, 38.79; HRMS (ESI) calcd for M + Na⁺, C₂₁H₂₄O₃Na: 347.1623; found 347.1595.

(2R, 4S, 5R)-4-Benzoyloxy-5-(benzyloxymethyl)tetrahydrofuran-2-carboxylic acid (9).**Oxidative Acetylene Cleavage of 3b(β).**

To a CCl_4 - CH_3CN - H_2O (1 + 1 + 1.5 mL) mixed solution of **3b(β)** (57 mg, 0.18 mmol) was added sodium periodate (154 mg, 0.72 mmol) and ruthenium(III) chloride hydrate (3 mg, ca. 0.01 mmol) in one portion at room temperature. After stirring at the same temperature for 24 h, the mixture was diluted with saturated aqueous NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 . The CH_2Cl_2 extract was washed with saturated aqueous NH_4Cl solution (10 mL), dried over sodium sulfate, and evaporated. The residue was subjected to reversed-phase column chromatography (Cosmosil 75 C_{18} -OPN; eluent, $\text{MeOH} : \text{H}_2\text{O} = 1 : 1$) to give carboxylic acid **9** as a colorless oil: yield 74% (44 mg); $[\alpha]_D^{27} + 61.6$ (c 0.58, CHCl_3); IR (neat) 1754 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 7.38–7.25 (m, 10 H), 4.70–4.67 (m, 1 H), 4.61 (d, $J = 12.0 \text{ Hz}$, 1 H), 4.54–4.50 (m, 2 H), 4.41 (d, $J = 12.0 \text{ Hz}$, 1 H), 4.20–4.18 (m, 1 H), 4.15–4.12 (m, 1 H), 3.74–3.71 (m, 1 H), 3.54–3.52 (m, 1 H), 2.46–2.40 (m, 1 H), 2.37–2.32 (m, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 174.20, 137.40, 136.45, 128.72, 128.60, 128.40, 128.23, 128.10, 127.81, 83.69, 78.32, 77.07, 73.69, 72.02, 68.33, 36.52; HRMS (ESI) calcd for $\text{M} + \text{Na}^+$, $\text{C}_{20}\text{H}_{22}\text{O}_5\text{Na}$: 365.1365; found 365.1352.

(2R, 3S, 5R)-3-Benzoyloxy-2-benzyloxymethyl-5-(3-(4-methoxyphenyl)isoxazol-5-yl)tetrahydrofuran (10). 1,3-Dipolar Addition of Nitrile Oxide to 3b(β).

To a CH_2Cl_2 (2 mL) solution of 4-methoxybenzohydroximoyl chloride⁴ (32 mg, 0.17 mmol) was added with Et_3N (21 mg, 0.21 mmol), and the reaction mixture was stirred at 0°C for 10 min. To the resulted 4-methoxybenzonitrile *N*-oxide solution was slowly added a CH_2Cl_2 (2 mL) solution of **3b(β)** (55 mg, 0.17 mmol) at the same temperature, and the mixture was allowed to warm to the room temperature over a 24 h period. After addition of saturated aqueous NH_4Cl solution (10 mL), the organic materials were extracted with CH_2Cl_2 , and the combined extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified with column chromatography (silica gel; eluent, hexane : $\text{AcOEt} = 10 : 1$) to give **10** as a colorless oil: yield 85% (69 mg); $[\alpha]_D^{27} - 9.7$ (c 0.27, CHCl_3); IR (neat) $1612, 1431 \text{ cm}^{-1}$; ^1H NMR (CDCl_3 , 500 MHz) δ 7.68 (d, $J = 9.0 \text{ Hz}$, 2 H), 7.35–7.27 (m, 10 H), 6.95 (d, $J = 9.0 \text{ Hz}$, 2 H), 6.47 (s, 1 H), 5.31–5.28 (m, 1

H), 4.57 (s, 4 H), 4.33–4.31 (m, 1 H), 4.24–4.22 (m, 1 H), 3.85 (s, 3 H), 3.65–3.62 (m, 1 H), 3.57–3.54 (m, 1 H), 2.50–2.44 (m, 1 H), 2.30–2.23 (m, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 172.27, 161.78, 160.83, 137.95, 137.73; 128.45, 128.37, 128.16, 127.77, 127.68, 127.65, 127.60, 121.46, 114.23, 99.46, 84.06, 80.66, 73.57, 72.81, 71.32, 70.71, 55.44, 37.67; HRMS (ESI) calcd for M + Na⁺, C₂₉H₂₉NO₅Na: 494.1943; found 494.1968.

3-Benzyloxy-2-benzyloxymethyl-5-(3-oxabicyclo[3.3.0]oct-5-en-7-on-6-yl)tetrahydrofuran (12). Pauson-Khand Reaction of Cobalt Complex 11.

To a CH₂Cl₂–THF (2 + 2 mL) mixed solution of **11** (90 mg, 0.13 mmol) was added *N*-methylmorpholine *N*-oxide (304 mg, 50% water solution) at room temperature. After stirred for 30 min, the solution was evaporated. The residue was poured into CH₂Cl₂ and washed with H₂O. The CH₂Cl₂ extract was concentrated and subjected to column chromatography (silica gel; eluent, CH₂Cl₂ : hexane = 1 : 1) to give a unseparable diastereomeric mixture of **12** as a colorless oil: yield 51% (28 mg); IR (neat) 1709, 1678 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.40–7.19 (m, 10 H), 4.98–4.03 (m, 9 H), 3.59–3.41 (m, 3 H), 3.23–3.04 (m, 2 H), 2.70–2.35 (m, 2 H), 2.22–1.97 (m, 1 H), 1.83–1.54 (m, 1 H); HRMS (ESI) calcd for M + Na⁺, C₂₆H₂₈O₅Na: 443.1834; found 443.1820.

Derivatization of 3a(β) to the Reported Compound S4.

To a THF (38 mL) solution of **3a**(**β**) (739 mg, 1.87 mmol) containing a few drops of water was added dropwise a THF solution of 1.0 M *n*-Bu₄NF (2.8 mL, 2.8 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 30 min. Ether was added to the mixture, and the mixture was washed with brine and evaporated. The residue was subjected to column chromatography (silica gel; eluent, hexane : AcOEt = 15 : 1) to give **3b**(**β**) as a colorless oil: yield 97% (585 mg). This compound was identical to that synthesized from **1** and ethynylmagnesium bromide. To a THF (34 mL) solution of **3b**(**β**) (541 mg, 1.68 mmol) was added dropwise 2.6 M *n*-butyllithium in hexane (0.71 mL, 1.85 mmol) at 0 °C. After stirred for 30 min, iodomethane (0.14 mL, 5.00 mmol) was added to the mixture at the same temperature. The mixture was allowed to warm to room temperature and stirred for an additional 18 h. The reaction mixture was then quenched by adding saturated aqueous NH₄Cl solution (1 mL), and then the residue was poured into ether. The ether solution was washed with H₂O, evaporated, and subjected to column chromatography (silica gel; eluent, hexane : AcOEt = 15 : 1) to give **S1** as a colorless oil: yield 99% (560 mg); ¹H NMR (CDCl₃, 300 MHz) δ7.42–7.18 (m, 10 H), 4.74–4.64 (m, 1 H), 4.56 (s, 2 H), 4.49 (s, 2H), 4.15–4.03 (m, 1 H), 3.64–3.56 (m, 1 H), 3.52–3.43 (m, 1 H), 2.28–2.19 (m, 1 H), 2.08–1.96 (m, 1 H), 1.83 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ134.21, 134.10, 124.44, 124.37, 123.71, 123.63, 79.59, 77.87, 77.05, 73.92, 69.60, 67.24, 66.90, 64.25, 35.95. An AcOEt (20 mL) solution of **S1** (240 mg, 0.71 mmol), Pd/C (10 wt.%, 120 mg), and Pd(OH)₂/C (20 wt.%, 100 mg) was stirred under an H₂ atmosphere (50 atm) at room temperature for 24 h. The slurry was filtrated and evaporated to give **S2** as a colorless oil: yield 98% (112 mg); ¹H NMR (CDCl₃, 300 MHz) δ4.36–4.24 (m, 1 H), 4.24–4.09 (m, 1 H), 3.88–3.54 (m, 3 H), 2.20–1.82 (m, 3 H), 1.80–1.20 (m, 5 H), 1.03–0.82 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ86.78, 78.72, 73.74, 63.48, 41.72, 37.93, 19.55, 14.44. To a CH₂Cl₂ (15 mL) solution of **S2** (100 mg, 0.63 mmol) and DMAP (25 mg, 0.21 mmol) was added Et₃N (0.18 mL) and *t*-BuPh₂SiCl (179 mg, 0.65 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 24 h. The CH₂Cl₂ solution was washed with H₂O, evaporated, and subjected to column chromatography (silica gel; eluent, hexane : AcOEt = 10 : 1) to give **S3** as a colorless oil: yield 58% (146 mg); ¹H NMR (CDCl₃, 300 MHz)

δ 7.72–7.64 (m, 4 H), 7.46–7.34 (m, 6 H), 4.45–4.37 (m, 1 H), 4.19–4.08 (m, 1 H), 3.88–3.74 (m, 2 H), 3.62–3.53 (m, 2 H), 1.98–1.88 (m, 1 H), 1.82–1.24 (m, 5 H), 1.05 (s, 9 H), 0.97–0.86 (m, 3 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.71, 135.64, 133.39, 133.31, 129.85, 129.80, 127.83, 127.79, 86.75, 78.54, 74.85, 65.11, 40.99, 38.11, 27.12, 19.63, 19.52, 14.47. To a CH_2Cl_2 (20 mL) solution of **S3** (95 mg, 0.24 mmol), DMAP (22 mg, 0.18 mmol), and *p*-nitrobenzoyl chloride (57 mg, 0.31 mmol) was added Et_3N (0.10 mL) at room temperature. After stirring for 24 h, the solution was diluted with AcOEt (50 mL) and washed with saturated aqueous sodium potassium tartrate solution (50 mL $\times$ 3) and aqueous 0.1 M HCl solution (50 mL $\times$ 3). The organic layer was evaporated and subjected to column chromatography (silica gel; eluent, hexane : AcOEt = 20 : 1) to give **S4** as a colorless oil: yield 37% (48 mg). ^1H NMR spectrum of **S4** was the same to that reported compound.²

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NOESY Spectra of 3a(β), 4a(β), 3a(α), and 4a(α).

3a(β)

4a(β)

3a(α)

4a(α)

¹H NMR Spectra of 5a(R), 5a(S), 6a(β), 6a(α), and 11.