Supporting Information

Cycloaddition Reactions of Deoxyribofuranosylpropynoates

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I. General

All reagents were commercially available and obtained from Sigma-Aldrich, Acros Organics, and Strem Chemicals companies. Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were performed under argon atmosphere unless otherwise noted. Chromatography was performed on Merck Silica gel 60. Thin layer chromatography was performed on Merck silica gel 60 F₂₅₄ coated aluminum sheets. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE III Spectrometer (¹H at 600 MHz and ¹³C at 150 MHz) and a Varian UNITY 300 (¹H at 300 MHz, ¹³C at 75 MHz) as solutions in CDCl₃, chemical shifts are given in δ-scale (¹H NMR spectra were referenced to residual peak of CDCl₃ at δ 7.26, ¹³C NMR spectra to CDCl₃ at δ 77.00), coupling constants *J* are given in Hz. The IR spectra were recorded on a Bruker IFS 55 spectrometer in KBr tablets and are reported in wave numbers

(cm^{-1}). The MS spectra were recorded on a VG-Analytical ZAB-SEQ device. All melting points are uncorrected and were determined on a Büchi B-545 device and a Kofler apparatus.

II. Synthetic part

1-(*tert*-butyldimethylsilyl)-2-[3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl]ethyne and 1-(*tert*-butyldimethylsilyl)-2-[3,5-di-*O*-(4-toluoyl)-2-deoxy- β -D-ribofuranosyl]ethyne (2 α** and **2 β**).** A solution of the ethynyldeoxyribosides **1 α** and **1 β** (4.24 g, 11.2 mmol) in THF (70 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and lithium diisopropylamide (6.8 mL, 12.3 mmol) was added dropwise. The mixture was stirred for 1.5 hours and then a solution of *tert*-butyldimethylsilyl chloride (1.91 g, 12.3 mmol) in THF (10 mL) was added. The reaction mixture was stirred overnight, while allowed to warm to ambient temperature. Then it was poured to saturated solution of ammonium chloride (60 mL) and extracted with EtOAc ($3 \times 40\text{ mL}$), the combined organic fractions were washed with brine, dried over anhydrous MgSO_4 , filtered and evaporated under reduced pressure. Separation by column chromatography on silica gel (25/1 hexane/EtOAc) afforded 2.09 g of **2 α** (38%) and 1.10 g of **2 β** (20%) as pure anomers. Anomer **2 β** was then recrystallized from EtOH.

2 α : α colourless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.97-7.95 (m, 2H), 7.92-7.90 (m, 2H), 7.24-7.21 (m, 4H), 5.49 (ddd, $J = 7.2, 3.2, 2.5\text{ Hz}$, 1H), 5.00 (dd, $J = 8.0, 3.2\text{ Hz}$, 1H), 4.62-4.60 (m, 1H), 4.56 (dd, $J = 11.8, 3.8\text{ Hz}$, 1H), 4.52 (dd, $J = 11.8, 4.7\text{ Hz}$, 1H), 2.71 (ddd, $J = 13.8, 8.0, 7.4\text{ Hz}$, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.37 (ddd, $J = 13.8, 3.3, 2.6\text{ Hz}$, 1H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.28, 166.23, 144.00, 143.79, 129.84, 129.68, 129.09, 129.05, 127.01, 126.87, 105.07, 88.63, 81.93, 75.69, 68.65, 64.25, 39.82, 26.02, 21.68, 21.64, 16.44, -4.70; IR (KBr) ν_{max} 3034, 2956, 2926, 2890, 2854, 2166, 1771, 1610, 1470, 1368, 1311, 1272, 1180, 1105, 1018, 842, 776, 749 cm^{-1} ; HRMS (m/z) for $\text{C}_{29}\text{H}_{36}\text{O}_5\text{NaSi}$ ($M + \text{Na}$) calcd 515.2223, found: 515.2222; R_f (5/1 hexane/EtOAc) = 0.52 (silica gel plate).

2 β : colorless, needle-like crystals: mp $82\text{--}85\text{ }^{\circ}\text{C}$ (dec.); ^1H NMR (600 MHz, CDCl_3) δ 7.97-7.95 (m, 2H), 7.92-7.90 (m, 2H), 7.24-7.21 (m, 4H), 5.52-5.51 (m, 1H), 4.90-4.87 (m, 1H), 4.56 (dd, $J = 11.8, 4.6\text{ Hz}$, 1H), 4.52 (dd, $J = 11.8, 4.7\text{ Hz}$, 1H), 2.51-2.42 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 0.92 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.24, 165.89, 144.11, 143.68, 129.72, 129.65, 129.13, 129.06, 127.08, 126.76, 103.78,

89.22, 82.57, 76.56, 68.64, 64.42, 40.12, 25.98, 21.64, 21.62, 16.41, -4.83; IR (KBr) ν_{max} 3037, 2956, 2926, 2884, 2854, 2178, 1718, 1613, 1464, 1362, 1266, 1180, 1099, 1024, 839, 755 cm^{-1} ; HRMS (m/z) for $\text{C}_{29}\text{H}_{36}\text{O}_5\text{NaSi}$ ($M + \text{Na}$) calcd 515.2223, found: 515.2222; R_f (5/1 hexan/EtOAc) = 0.59 (silica gel plate).

3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl-ethyne (1 α**).** The starting compound **2 α**

(2.30 g, 4.67 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. A solution of tetrabutylammonium fluoride (1.76 g, 5.60 mmol) in THF (10 mL) was added and the reaction was stirred for 45 minutes while allowed to warm to laboratory temperature. Then it was poured into a saturated solution of ammonium chloride (50 mL) and extracted by EtOAc (3× 30 mL). Combined organic fractions were washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated on vacuum evaporator. The residue was purified by column chromatography on silica gel (5/1 hexane/EtOAc) to yield **1 α** (1.65 g, 93%). The spectral data were in accordance with previously published results.¹

3,5-di-*O*-(4-toluoyl)-2-deoxy- β -D-ribofuranosyl-ethyne (1 β**).** The reaction was done in the

same way as for **1 α** , but from **2 β** (0.86 g, 1.74 mmol) as a starting compound, furnishing **1 β** (0.57 g, 87%). Its spectral data were in accordance with previously published results.¹

Methyl 3-[3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl]propynoate (3 α**).** The solution

of ethynyl deoxyribose **1 α** (0.78 g, 2.06 mmol) in THF (15 mL) was cooled to -78 °C and lithium diisopropylamide 1.8M (1.26 mL, 2.26 mmol) was added dropwise. The mixture was stirred for 1.5 hours at the same temperature and then methyl chloroformate (0.175 mL, 2.26 mmol) was added. The reaction was stirred overnight, while it was allowed to warm to ambient temperature. The reaction was poured into water (15 mL) and then extracted with EtOAc (3× altogether with 30 mL). The combined organic fractions were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (5/1 hexane/EtOAc) furnished **3 α** (0.65 g, 72%) as a colourless oil, which solidified when left standing to a white solid. Its recrystallization from EtOH gave colorless, needle-like crystals: mp 102-104 °C (dec.); ^1H NMR (600 MHz,

CDCl₃) δ 7.99-7.98 (m, 2H), 7.92-7.90 (m, 2H), 7.24-7.23 (m, 4H), 5.56-5.55 (m, 1H), 5.11 (dd, J = 8.2, 1.8 Hz, 1H), 4.63-4.61 (m, 1H), 4.55 (dd, J = 11.9, 3.8 Hz, 1H), 4.50 (dd, J = 11.9, 4.6 Hz, 1H), 3.78 (s, 3H), 2.69 (ddd, J = 14.3, 7.8, 6.9, 1H), 2.46-2.44 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 166.15, 166.07, 153.58, 144.16, 143.94, 129.96, 129.66, 129.16, 129.11, 126.86, 126.66, 86.14, 82.94, 76.85, 74.39, 67.97, 64.07, 52.76, 39.00, 21.69, 21.65; IR (KBr) ν_{max} 3069, 3037, 3009, 2954, 2923, 2858, 2238, 1709, 1610, 1431, 1368, 1272, 1255, 1178, 1106, 1080, 978, 840, 753 cm⁻¹; HRMS (m/z) for C₂₅H₂₄O₇Na (M + Na) calcd 459.1420, found: 459.1414; R_f (5/1 hexane/EtOAc) = 0.25 (silica gel plate).

Methyl 3-[3,5-di-*O*-(4-toluoyl)-2-deoxy- β -D-ribofuranosyl]propynoate (3 β). The same

approach as for **3 α** . The reaction from the starting compound **1 β** (0.66 g, 1.75 mmol) furnished after workup and recrystallization colorless crystals of **3 β** (0.61 g, 79%): mp

102-104 °C (dec.); ¹H NMR (600 MHz, CDCl₃) δ 7.96-7.95 (m, 2H), 7.91-7.89 (m, 2H), 7.25-7.23 (m, 4H), 5.56-5.54 (m, 1H), 4.99 (apt t, J = 7.8 Hz, 1H), 4.55 (dd, J = 11.8, 4.3 Hz, 1H), 4.50 (dd, J = 11.8, 4.5 Hz, 1H), 4.46-4.45 (m, 1H), 3.77 (s, 3H), 2.56-2.54 (m, 2H), 2.42 (s, 3H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 166.23, 165.83, 153.44, 144.33, 143.85, 129.78, 129.71, 129.21, 129.14, 126.93, 126.55, 84.82, 83.10, 77.08, 76.11, 67.74, 64.19, 52.80, 39.18, 21.68, 21.66; IR (KBr) ν_{max} 3067, 3036, 2953, 2877, 2244, 1719, 1611, 1435, 1270, 1178, 1106, 970, 840, 752 cm⁻¹; HRMS (m/z) for C₂₅H₂₄O₇Na (M + Na) calcd 459.1420, found: 459.1413 (for C₂₅H₂₄O₇Na); R_f (5/1 hexane/EtOAc) = 0.29 (silica gel plate).

Methyl 3-[3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl]-1,4,5,6-tetramethylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (4 α). 2-butyne (0.25 mL, 3.15 mmol) was added to a

stirred suspension of powdered anhydrous aluminum chloride (0.21 g, 1.58 mmol) in dry CH₂Cl₂ (10 mL) at -15 °C. After 15 min propynoate **3 α** (0.65g, 1.50 mmol) was added to the resulting complex at -15 °C and the mixture was stirred for 1.5 hours at -15 °C. DMSO (2 mL) was added and the reaction mixture was stirred for another 0.5 hour, while allowed to warm up to room

temperature. The mixture was poured onto crushed ice and extracted with CH₂Cl₂ (3 $\times$ altogether with 20 mL). The combined organic layers were dried over anhydrous MgSO₄,

filtered, and concentrated under vacuum. Column chromatography on silica gel (5/1 hexane/EtOAc) afforded an inseparable mixture of diastereomers (**DS1**: **DS2** 3:2 ratio) of Dewar benzene deoxyribosides (**4α**) as a colourless oil (0.31g, 38%): ¹H NMR (600 MHz, CDCl₃) **DS1**: δ 7.94-7.92 (m, 2H), 7.91-7.86 (m, 2H), 7.24-7.21 (m, 4H), 5.51-5.47 (m, 1H), 5.30 (apt t, *J* = 7.5 Hz, 1H), 4.58-4.49 (m, 3H), 3.62 (s, 3H), 2.81 (apt dt, *J* = 13.6, 7.6 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.30 (ddd, *J* = 13.0, 7.3, 4.9 Hz, 1H), 1.62-1.60 (m, 6H), 1.30 (s, 3H), 1.24 (s, 3H), **DS2**: δ 7.94-7.92 (m, 2H), 7.91-7.86 (m, 2H), 7.24-7.21 (m, 4H), 5.51-5.47 (m, 1H), 5.33 (apt t, *J* = 7.8 Hz, 1H), 4.58-4.49 (m, 3H), 3.67 (s, 3H), 2.87 (apt dt, *J* = 13.6, 7.6 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.23 (ddd, *J* = 13.3, 7.8, 5.0 Hz, 1H), 1.62-1.60 (m, 6H), 1.31 (s, 3H), 1.25 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) **DS1**: δ 168.15, 166.32, 163.88, 144.65, 143.93, 143.74, 142.04, 138.97, 130.12-129.06 (multiple peaks, 10C), 127.06, 126.88, 80.97, 76.21, 75.62, 64.80, 56.06, 54.24, 50.85, 36.72, 21.63, 21.62, 11.26, 11.18, 10.74, 10.43, **DS2**: δ 168.97, 166.17, 163.96, 144.31, 144.00, 143.73, 143.00, 139.16, 130.12-129.06 (multiple peaks, 10C), 127.06, 126.83, 81.29, 76.14, 75.42, 64.94, 56.43, 54.50, 50.91, 37.22, 21.63, 21.62, 11.43, 11.16, 11.15, 10.51; IR (KBr) *v*_{max} 2954, 2924, 2861, 1719, 1611, 1435, 1374, 1272, 1177, 1106, 1019, 841, 755 cm⁻¹; HRMS (*m/z*) for C₃₃H₃₆O₇Na (*M* + Na) calcd 567.2359, found: 567.2361; *R*_f (5/1 hexane/EtOAc) = 0.45 (silica gel plate).

Methyl 3-[3,5-di-*O*-(4-toluoyl)-2-deoxy-β-*D*-ribofuranosyl]-1,4,5,6-tetramethylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylate (4β**)** Prepared in the same manner as **4α**, from **3β**

(0.76g, 1.74 mmol) as the starting compound, the reaction afforded an inseparable mixture of diastereomers (**DS1**: **DS2** 1:1 ratio) of Dewar benzene deoxyribosides (**4β**) as a colourless oil (0.40 g, 42%): ¹H NMR (600 MHz, CDCl₃)

(because the diastereomeric ratio was 1:1 it was impossible to distinguish the signals for each diastereomer separately, corresponding signals are therefore only marked **DS1/DS2**) δ 7.95-7.93 (m, 4H), 7.25-7.24 (m, 2H), 7.23-7.21 (m, 2H), 5.54-5.53 (m, 1H), 5.33 (dd, *J* = 11.6, 5.3 Hz, 1H **DS1**), 5.31 (dd, *J* = 11.6, 5.3 Hz, 1H **DS2**), 4.61 (dd, *J* = 11.6, 4.2 Hz, 1H **DS1**), 4.57 (dd, *J* = 11.7, 4.3 Hz, 1H **DS2**), 4.52 (dd, *J* = 11.6, 3.7 Hz, 1H **DS1**), 4.51 (dd, *J* = 11.6, 3.3 Hz, 1H **DS2**), 4.40-4.38 (m, 1H), 3.72 (s, 3H **DS1**), 3.71 (s, 3H **DS2**), 2.45-2.40 (m, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.22 (ddd, *J* = 13.8, 11.3, 6.6 Hz, 1H **DS1**), 2.10 (ddd, *J* = 13.8, 11.3, 6.5, 1H **DS2**), 1.59 (q, *J* = 1.3 Hz, 3H **DS1**), 1.58 (q, *J* = 1.3 Hz, 3H **DS2**), 1.54 (q, *J* = 1.3 Hz, 3H **DS1**), 1.53 (q, *J* = 1.3 Hz, 3H **DS2**), 1.24 (s, 3H **DS1**), 1.23 (s, 3H **DS2**), 1.21 (s, 3H

DS1), 1.19 (s, 3H **DS2**); ^{13}C NMR (150 MHz, CDCl_3) δ 167.23, 166.30, 166.14, 166.11, 164.02, 163.98, 144.42, 144.09, 144.03, 143.77, 143.75, 143.07, 142.08, 140.44, 140.17, 130.14-129.05 (multiple peaks, 10C), 127.08, 127.04, 126.91, 82.64, 82.42, 76.51, 76.47, 75.50, 75.43, 64.71, 64.52, 56.50, 56.21, 54.69, 54.55, 50.95, 37.55, 37.47, 21.64, 21.61, 11.24, 11.18, 11.13, 11.10, 11.02, 10.87, 10.47; IR (KBr) ν_{max} 3069, 3037, 2950, 2920, 1724, 1610, 1431, 1371, 1272, 1177, 1102, 1018, 755 cm^{-1} ; HRMS (m/z) for $\text{C}_{33}\text{H}_{36}\text{O}_7\text{Na}$ ($M + \text{Na}$) calcd 567.2359, found: 567.2354; R_f (5/1 hexane/EtOAc) = 0.48 (silica gel plate).

General procedure for thermal rearrangement of DB-deoxyribosides 4. Starting compound **4** was dissolved in THF (to 0.05 M) and was heated to 150 °C in a microwave reactor. The reaction proceeded for 2 hours after which the **4** could not be detected, however because of the sugar moiety decomposition, the reaction led to a complex mixture of products, from which the desired product **5** could not be isolated.

General procedure for UV rearrangement of DB-deoxyribosides 4. Starting compound **4** was dissolved in CDCl_3 (to 0.05 M) in a quartz tube. The reaction vessel was irradiated by UV lamp (254 nm) and stirred for 17 hours. The progress of the rearrangement was frequently checked by NMR or TLC, after 22 hours the process was completed. The solvent was evaporated under reduced pressure, column chromatography of the residue on silica gel (5/1 hexane/EtOAc) furnished the rearranged product **5**.

In the reaction done from **4 α** (29 mg, 0.05 mmol), isolated yield of **5 α** was 20 mg (69%).

In the reaction done from **4 β** (117 mg, 0.22 mmol), isolated yield of **5 β** was 41 mg (35%).

Methyl 2-[3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl]-3,4,5,6-tetramethyl-benzoate (5 α). To a solution of zirconocene dichloride (0.33 g, 1.1 mmol) in THF (6 mL), *n*-BuLi 1.6M

(1.38 mL, 2.2 mmol) was added drop wise at -78 °C. After 1 hour of stirring, 2-butyne (0.32 mL, 4.0 mmol) was added and the reaction mixture was stirred for another hour, while allowed to warm up to ambient temperature. Then, propynoate **3 α** (0.44 g, 1.0 mmol) and CuCl (0.20 g, 2.0 mmol) were added and the reaction was stirred for 96 hours. Afterwards 1M HCl (8 mL) was

poured to the reaction and the mixture was extracted with ether (3×8 mL). The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. Column

chromatography of the residue on silica gel (5/1 hexane/EtOAc) furnished **5 α** (0.18 g, 33%) as a colourless oil: ^1H NMR (600 MHz, CDCl_3) δ 7.94-7.89 (m, 4H) 7.21-7.20 (m, 2H), 7.12-7.19 (m, 2H), 5.60-5.55 (m, 2H) 4.57-4.56 (m, 2H), 4.55-4.54 (m, 1H), 3.82 (s, 3H), 2.98 (ddd, $J = 13.0, 6.6, 6.6$ Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 2.33 (ddd, $J = 12.7, 10.3, 7.9$ Hz, 1H), 2.21 (s, 6H), 2.20 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.78, 166.31, 166.28, 143.88, 143.69, 136.35, 134.56, 133.04, 130.39, 130.18, 129.79, 129.65, 129.56, 129.02, 129.01, 127.10, 126.80, 80.37, 78.35, 75.38, 64.91, 51.42, 39.33, 21.63, 21.61, 17.04, 16.49, 16.32, 15.98; IR (KBr) ν_{max} 3037, 2989, 2947, 2920, 1724, 1613, 1449, 1429, 1305, 1371, 1275, 1198, 1180, 1108, 1021, 991, 749 cm^{-1} ; HRMS (m/z) for $\text{C}_{33}\text{H}_{36}\text{O}_7\text{Na}$ ($M + \text{Na}$) calcd 567.2359, found: 567.2349; R_f (5/1 hexane/EtOAc) = 0.34 (silica gel plate).

Methyl 2-[3,5-di-*O*-(4-toluoyl)-2-deoxy- β -D-ribofuranosyl]-3,4,5,6-tetramethyl-benzoate (5 β). The compound was prepared in the same manner as **5 α** . From starting material **3 β** (0.22

g, 0.51 mmol) the reaction yielded **5 β** (0.07 g, 25%) as a colourless oil: ^1H NMR (600 MHz, CDCl_3) δ 7.98-7.94 (m, 4H), 7.27-7.25 (m, 2H), 7.21-7.20 (m, 2H), 5.50 (ddd, $J = 7.1, 3.8, 1.3$ Hz, 1H), 5.38 (dd, $J = 10.9, 5.3$ Hz, 1H), 4.70 (dd, $J = 11.6, 4.2$ Hz, 1H), 4.61 (dd, $J = 11.6, 6.3$ Hz, 1H), 4.40 (apt dt,

$J = 6.3, 4.1$ Hz, 1H), 2.52 (ddd, $J = 13.9, 10.9, 7.2$ Hz, 1H), 2.45-2.41 (m, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.71, 166.45, 466.00, 144.01, 143.69, 136.62, 134.98, 131.07, 130.59, 130.48, 130.45, 129.82, 129.68, 129.15, 129.05, 127.09, 127.02, 82.51, 78.78, 76.19, 64.20, 51.43, 39.73, 21.68, 21.64, 17.20, 16.62, 16.40, 16.04; IR (KBr) ν_{max} 3064, 3032, 2988, 2948, 2923, 1723, 1614, 1448, 1430, 1372, 1305, 1276, 1202, 1177, 1101, 1023, 833, 752 cm^{-1} ; HRMS (m/z) for $\text{C}_{33}\text{H}_{36}\text{O}_7\text{Na}$ ($M + \text{Na}$) calcd 567.2359, found: 567.2353; R_f (5/1 hexane/EtOAc) = 0.48 (silica gel plate).

Methyl 6-[3,5-di-*O*-(4-toluoyl)-2-deoxy- α -D-ribofuranosyl]-2,3-dihydro-1*H*-indene-5-carboxylate (6 α). Chloro-pentamethylcyclopentadienyl-cyclooctadienyl ruthenium complex

(6 mg, 0.015 mmol) was added to a mixture of 1,6-heptadiyne (0.04 mL, 0.33 mmol) and propynoate **3 α** (0.13g, 0.30 mmol) in toluene (7 mL). The reaction was heated to 80 $^{\circ}\text{C}$ and stirred for

72 hours. After cooling down to room temperature the mixture was evaporated and the residue was purified by column chromatography on silica gel (5/1 hexane/EtOAc) to yield indane **6α** (38 mg, 24%) as a colourless solid, which was recrystallized (hexane/ether) to obtain colourless crystals: mp 113-116 °C (dec.); ¹H NMR (600 MHz, CDCl₃) δ 8.02-8.00 (m, 2H), 7.83 (s, 1H), 7.74 (s, 1H), 7.66-7.64 (m, 2H), 7.26-7.25 (m, 2H), 7.15-7.13 (m, 2H), 6.11 (dd, *J* = 8.2, 4.7 Hz, 1H), 5.59 (apt dt, *J* = 6.1, 2.4 Hz, 1H), 4.80 (ddd, *J* = 4.7, 4.7, 1.7 Hz, 1H), 4.60 (dd, *J* = 11.6, 4.9 Hz, 1H), 4.52 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.17 (ddd, *J* = 14.6, 8.3, 6.4 Hz, 1H), 2.99-2.93 (m, 3H), 2.90-2.85 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.15-2.06 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.50, 166.45, 165.88, 149.52, 144.41, 143.78, 143.76, 142.84, 129.83, 129.60, 129.13, 128.89, 127.08, 127.05, 126.43, 125.00, 121.90, 82.90, 79.05, 76.78, 64.99, 51.81, 41.00, 33.18, 32.32, 25.46, 21.67, 21.64; IR (KBr) *v*_{max} 3063, 3037, 2956, 2884, 2842, 1718, 1610, 1440, 1371, 1326, 1266, 1224, 1180, 1111, 1021, 839, 752 cm⁻¹; HRMS (*m/z*) for C₃₂H₂₂O₇Na (M + Na) calcd 551.2046, found: 551.2041; *R*_f (5/1 hexane/EtOAc) = 0.39 (silica gel plate).

The reaction catalyzed by RhCl(PPh₃)₃ (5 mol%) was done under the same conditions as above. From **3α** (0.1 g, 0.23 mmol), the isolated yield of the product **6α** was 22 mg (18%).

Methyl 6-[3,5-di-*O*-(4-toluoyl)-2-deoxy-β-*D*-ribofuranosyl]-2,3-dihydro-1*H*-indene-5-carboxylate (6β). Prepared in the same way as **6α** from **3β** (0.15 g, 0.34 mmol) yielding **6β**

(50 mg, 28%) as colourless crystals after recrystallization: mp 128-131 °C (dec.); ¹H NMR (600 MHz, CDCl₃) δ 8.10-8.00 (m, 2H), 7.96-7.95 (m, 2H), 7.77 (s, 1H), 7.69 (s, 1H), 7.28-7.27 (m, 2H), 7.21-7.20 (m, 2H), 5.97 (dd, *J* = 10.1, 5.4 Hz, 1H), 5.59 (apt dt, *J* = 6.4, 2.1 Hz, 1H), 4.77 (dd, *J* = 11.8, 3.8 Hz, 1H), 4.68 (dd, *J* = 11.8, 3.8 Hz, 1H), 4.52 (apt dt, *J* = 3.7, 2.9 Hz, 1H), 3.86 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.87-2.83 (m, 2H), 2.78-2.69 (m, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 2.09-2.01 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.59, 166.43, 166.29, 149.87, 143.96, 143.75, 143.27, 141.75, 129.77, 129.69, 129.13, 129.09, 127.15, 127.10, 126.09, 125.77, 121.68, 82.50, 78.28, 77.13, 64.68, 51.83, 41.58, 32.99, 32.30, 25.34, 21.68, 21.63; IR (KBr) *v*_{max} 3028, 3007, 2950, 2890, 2857, 1718, 1613, 1445, 1443, 1383, 1329, 1278, 1248, 1186, 1123, 1099, 1078, 755 cm⁻¹; HRMS (*m/z*) for C₃₂H₂₂O₇Na (M + Na) calcd 551.2046, found: 551.2041; *R*_f (5/1 hexane/EtOAc) = 0.45 (silica gel plate).

The reaction catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ (5 mol%) was done under the same conditions as above. From **3β** (0.15 g, 0.34 mmol), isolated yield of the product **6β** was 25 mg (14%).

III. X-ray data

Single-crystal X-ray diffraction were obtained from a Bruker ApexII-CCD diffractometer by monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2)K. The structure was elucidated by direct methods (SHELXS, Sheldrick, 2008) and refined by full-matrix least squares based on F^2 (SHELXL97).² The hydrogen atoms were found on difference electron density map and were fixed into idealized positions (riding model) and assigned temperature factors either $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$, or $1.5 U_{\text{eq}}$ for methyl moiety.

The assignment of absolute configuration was based on known configuration on chiral centre preserved during synthesis of titled compounds.

Crystal data for **2 β** : $\text{C}_{29}\text{H}_{36}\text{O}_5\text{Si}$, $M = 492.67$, Orthorhombic, $P2_12_12_1$ (No 19), $a = 6.1691(2) \text{ \AA}$, $b = 12.1597(4) \text{ \AA}$, $c = 36.7001(10) \text{ \AA}$, $V = 2753.04(15) \text{ \AA}^3$, $Z = 4$, $D_x = 1.189 \text{ Mg m}^{-3}$, colourless crystal of dimensions $0.37 \times 0.25 \times 0.20 \text{ mm}$, multi-scan absorption correction ($\mu = 0.12 \text{ mm}^{-1}$), $T_{\text{min}} = 0.957$, $T_{\text{max}} = 0.976$; a total of 24548 measured reflections ($\theta_{\text{max}} = 27.5^\circ$), from which 6310 were unique ($R_{\text{int}} = 0.025$) and 5692 observed according to the $I > 2\sigma(I)$ criterion. The refinement converged ($\Delta/\sigma_{\text{max}} < 0.002$) to $R = 0.035$ for observed reflections and $wR(F^2) = 0.085$, $GOF = 1.06$ for 323 parameters and all 6310 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{\text{max}} = 0.24$, $\Delta\rho_{\text{min}} = -0.20 \text{ \AA}^{-3}$).

Crystal data for **6α**: C₃₂H₃₂O₇, M = 528.58, Monoclinic, *P*2₁ (No 4), *a* = 5.8134 (2) Å, *b* = 25.5207 (7) Å, *c* = 9.0045 (3) Å, *β* = 94.1370 (10) °, *V* = 1332.44 (7) Å³, *Z* = 2, *D_x* = 1.317 Mg m⁻³, colourless crystal of dimensions 0.61 × 0.43 × 0.23 mm, multi-scan absorption correction (*μ* = 0.09 mm⁻¹), *T_{min}* = 0.946, *T_{max}* = 0.979; a total of 16668 measured reflections (*θ_{max}* = 27.5°), from which 6149 were unique (*R_{int}* = 0.016) and 5751 observed according to the *I* > 2σ(*I*) criterion. The refinement converged (*Δ*/σ_{max} < 0.001) to *R* = 0.033 for observed reflections and *wR*(*F*²) = 0.084, *GOF* = 1.03 for 359 parameters and all 6149 reflections. The final difference map displayed no peaks of chemical significance (*Δρ_{max}* = 0.16 *Δρ_{min}* -0.17 e.Å⁻³).

Crystal data for **6β**: C₃₂H₃₂O₇, M = 528.58, Orthorhombic, *P*2₁2₁2₁ (No 19), *a* = 8.4750 (2) Å, *b* = 10.6790 (2) Å, *c* = 30.1075 (5) Å, *V* = 2724.86 (9) Å³, *Z* = 4, *D_x* = 1.288 Mg m⁻³, colourless crystal of dimensions 0.78 × 0.52 × 0.18 mm, multi-scan absorption correction (*μ* = 0.09 mm⁻¹), *T_{min}* = 0.933, *T_{max}* = 0.984; a total of 19284 measured reflections (*θ_{max}* = 27.5°), from which 6226 were unique (*R_{int}* = 0.018) and 5607 observed according to the *I* > 2σ(*I*) criterion. The refinement converged (*Δ*/σ_{max} < 0.001) to *R* = 0.036 for observed reflections and *wR*(*F*²) = 0.087, *GOF* = 1.02 for 363 parameters and all 6226 reflections. The

final difference map displayed no peaks of chemical significance ($\Delta\rho_{\max} = 0.29$, $\Delta\rho_{\min} -0.18\text{\AA}^{-3}$).

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre with CCDC numbers 948198, 948199, and 948200 for **2 β** , **6 α** , and **6 β** , respectively. Copies of the data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

IV. References

1. Novák, P.; Pohl, R.; Katora, M.; Hocek, M. *Org. Lett.* **2006**, 8, 2051–2054.
2. Sheldrick, G.M. (2008). *Acta Cryst. A* **64**, 112-122.

IV. Copies of ^1H and ^{13}C NMR spectra**2 α**

2 β

3 α

3β

4 α

4β

5 α

5β

6 α

6β