Tetrahedron 64 (2008) 5200–5207

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Co- and homocyclotrimerization reactions of protected 1-alkynyl-2-deoxyribofuranose. Synthesis of *C*-nucleosides, *C*-di- and *C*-trisaccharide analogues

Petr Novák [a], Sylva Číhalová [a], Miroslav Otmar [b], Michal Hocek [b,*], Martin Kotora [a,b,*]

[a] Department of Organic and Nuclear Chemistry and Centre for New Antivirals and Antineoplastics, Faculty of Science, Charles University, Hlavova 8, 128 43 Praha 2, Czech Republic
[b] Institute of Organic Chemistry and Biochemistry, v.v.i., Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic

ARTICLE INFO

Article history:
Received 14 December 2007
Received in revised form 1 March 2008
Accepted 13 March 2008
Available online 15 March 2008

ABSTRACT

Cyclotrimerization of β- or α-ethynyl-3,5-di-*O*-toluoyl-2-deoxy-D-ribofuranose with α,ω-diynes proceeded smoothly under Rh-catalysis to afford the corresponding β- or α-benzene *C*-nucleoside derivatives. Analogous co-cyclotrimerization of α- or β-propynyl- and -phenylethynyl-3,5-di-*O*-toluoyl-2-deoxy-D-ribofuranose with α,ω-diynes gave the corresponding arene derivatives only under microwave irradiation in the presence of a Rh-catalyst in moderate yields. Attempted homocyclotrimerization of β- or α-ethynyl-3,5-di-*O*-toluoyl-2-deoxy-D-ribofuranose under Rh-catalysis led only to enynes while the use of Ru-catalyst gave the desired 1,2,4- and 1,3,5-tri-(2-deoxyribofuranose-1-yl)benzene.

1. Introduction

The cyclotrimerization of alkynes to benzene derivatives is a highly efficient and atom economical method for the synthesis of complex organic molecules. Its popularity stems from the fact that it can be usually carried out under neutral reaction conditions and the reaction has a high tolerance for various polar functional groups. Although cyclotrimerization has been used in the syntheses of many natural compounds or potentially biologically active substances,[1] its role in carbohydrate chemistry has been mainly restricted to the synthesis of benzene rings from alkynes attached to the sugar moiety through ether or amide linker.[2,3] Another example is the seminal work of McDonald who has shown that cyclotrimerization of alkynes can be used for the synthesis of *C*-arylglycosides.[4] This class of compounds is of considerable interest for pharmaceutical reasons, because of their stability toward enzymatic and chemical hydrolysis. Although still in its infancy, the synthesis of *C*-arylglycosides by cyclotrimerization is beginning to attract attention. Thus, Yamamoto et al. have reported Ru-catalyzed synthesis of various *C*-arylribosides[5] and *C*-arylspiroribosides[6] starting from protected 1-ethynylriboses. Moreover, recently a protected 1-ethynyl-2-deoxyribose was used for the Sonogashira cross-couplings and oxidative dimerizations.[7]

C-Nucleosides (characterized by the replacement of the C–N nucleosidic bond by a more stable C–C bond) are of particular interest due to their applications in chemical biology (extension of the genetic alphabet[8] or model compounds for studying enzyme mechanisms[9]). They are usually prepared by *C*-glycosidic C–C bond forming reactions of organometallics with sugar derivatives very often giving low yields and/or selectivities.[10] Therefore, we are working on the development of modular strategies enabling the preparation of series of derivatives from one common easily available intermediate (e.g., cross-coupling reactions of haloaryl-*C*-nucleosides[11]). Based on our experiences in the use of transition metal catalyzed cyclotrimerization reactions for the synthesis of modified purine nucleosides,[12] we have recently reported a preliminary communication[13] on an alternative approach to *C*-nucleosides based on cyclotrimerization of 1-ethynyl-2-deoxyribofuranose with α,ω-diynes. Herein, we present a full report on these results and describe further outcomes pertaining to cyclotrimerizations and homocyclotrimerizations of other (2-deoxy-D-ribofuranosyl)alkynes.

2. Results and discussion

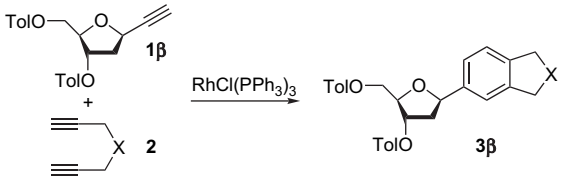
2.1. Co-cyclotrimerization of 1β

According to the preliminary results, the cyclotrimerization of an anomeric mixture with various diynes **2** gave the highest yields of the corresponding benzene derivatives in the presence of a catalytic amount of $Rh(PPh_3)_3Cl$ (Wilkinson's catalyst).[13] The same results were obtained also for the cyclotrimerization of pure

* Corresponding authors. Tel.: +420 221 951 334; fax: +420 221 951 326 (M.K.); tel.: +420 220 183 324; fax: +420 220 183 559 (M.H.).
E-mail addresses: hocek@uochb.cas.cz (M. Hocek), kotora@natur.cuni.cz (M. Kotora).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.03.046

Table 1
Rh-catalyzed cyclotrimerization of **1β** with diynes **2** to **3β**



3β: a, X = C(COOEt)$_2$; **b**, X = C(COMe)$_2$; **c**, X = (COOEt)COMe; **d**, X = C(COOEt)CN; **e**, X = NTs; **f**, X = O

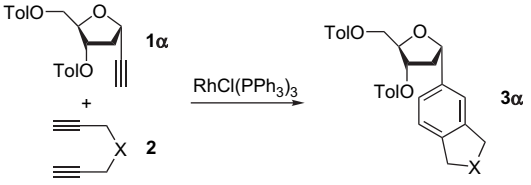
Entry	Diyne **2**	Product **3βx**	Yield (%)
1	**2a**	**3βa**	95
2	**2b**	**3βb**	81
3	**2c**	**3βc**	62
4	**2d**	**3βd**	52
5	**2e**	**3βe**	12
6	**2f**	**3βf**	32

1β-ethynyl-2-deoxy-D-ribofuranose **1β**. The results are displayed in Table 1. The reactions with diynes **2a**–**2d** (entries 1–4) gave rise to the corresponding 1β-aryl-2-deoxy-D-ribofuranoses **3βa**–**3βd** in good yields (52–95%). Nonetheless, in cases where the heterocyclic ring was formed, such as in **3βe** and **3βf** (entries 5 and 6), the yields were rather low. Other transition metal complexes such as Ni(cod)$_2$/2PPh$_3$, Cp*RuCl(cod), or Co(PPh$_3$)$_3$Br could also catalyze cyclotrimerization but their generality with respect to structural variation of diynes did not match with that of Rh(PPh$_3$)$_3$Cl.[13]

2.2. Co-cyclotrimerization of 1α

Because the cyclotrimerizations of protected 1β-ethynyl-2-deoxy-D-ribofuranose with various diynes proceeded with the best results under Rh-catalysis, the reactions of **1α** were carried out in the same manner. The results are presented in Table 2. The cyclotrimerization with diynes bearing carbonyl group functionality(ies) **2a**–**d** proceeded uneventfully as expected. The corresponding 1α-aryl-2-deoxy-D-ribofuranoses **3αa**–**3αd** were obtained from good to excellent isolated yields (53–95%) (entries 1–4). Once again the cyclotrimerization with diynes **2e** and **2f** possessing a heteroatom in the linker connecting both triple bonds gave the corresponding products **3αe** and **3αf** in low yields of 18% and 39%, respectively (entries 5 and 6). The reaction with simple 1,6-heptadiyne **2g** gave **3αg** in surprisingly high yield of 83% (entry 7).

Table 2
Rh-catalyzed cyclotrimerization of **1α** with diynes **2** to **3α**

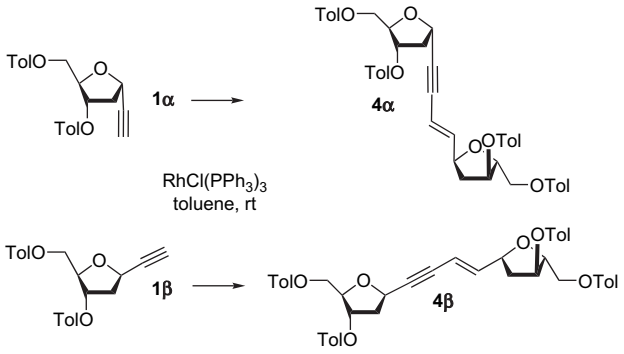


3α: a, X = C(COOEt)$_2$; **b**, X = C(COMe)$_2$; **c**, X = (COOEt)COMe; **d**, X = C(COOEt)CN; **e**, X = NTs; **f**, X = O; **g** = CH$_2$

Entry	Diyne **2**	Product **3αx**	Yield (%)
1	**2a**	**3αa**	95
2	**2b**	**3αb**	63
3	**2c**	**3αc**	83
4	**2d**	**3αd**	53
5	**2e**	**3αe**	18
6	**2f**	**3αf**	39
7	**2g**	**3αg**	83

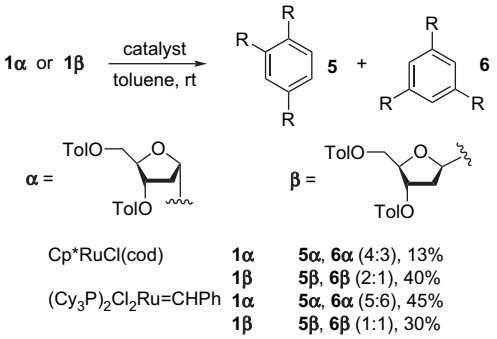
2.3. Homocyclotrimerization of 1α and 1β

Although the cyclotrimerizations of **1α** proceeded generally in good yields, we observed in many cases the formation of a side product in various quantities. The side product was the result of the addition of the terminal triple bond of **1α** onto the terminal triple bond of another molecule of **1α** yielding enyne **4α**. It is important to note that the formation of enyne **4β** was not observed in the case of the cyclotrimerization of **1β**. In order to get further information on the formation of enynes **4**, both alkynes **1β** and **1α** were subjected to cyclotrimerization conditions (cat. RhCl(PPh$_3$)$_3$) in the absence of diyne **2** (Scheme 1). Surprisingly, the formation of homocyclotrimerization products was not observed in any case. Instead, **1α** underwent reaction to afford enyne **4α** in 31% isolated yield. On the other hand, in the case of alkyne **1β** the formation of **4β** was observed in only <5% yield and most of the starting material remained unreacted. It was shown previously that terminal alkynes possessing propargylic hydroxy group or sterically hindered groups (i.e., Me$_3$Si, etc.) undergo head-to-head dimerization to afford enynes.[14] In view of this, it is not unexpected that **1α**, which is sterically hindered alkyne bearing propargylic ether moiety, is more prone to the head-to-head dimerization.



Scheme 1. Rh-catalyzed dimerization of **1β** and **1α**.

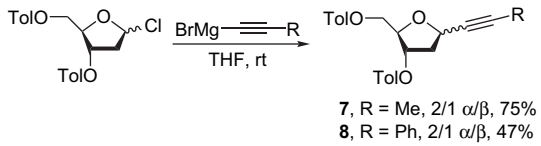
In the next step, we attempted to cyclotrimerize both anomers (**1α** and **1β**) by other transition metal catalysts (Scheme 2). For this purpose, two Ru-catalysts were chosen: Cp*Ru(cod)Cl and Grubbs' first generation carbene complex ((Cy$_3$P)$_2$Cl$_2$Ru=CHPh).[15] The homocyclotrimerization of **1α** in the presence of Cp*Ru(cod)Cl afforded a mixture (4:3 ratio) of 1,2,4- and 1,3,5-tris(2-deoxy-D-ribos-1-yl)benzene **5α** and **6α** in only 13% isolated yield. Under the same conditions, **1β** afforded also an inseparable mixture of 1,2,4- and 1,3,5-tris(2-deoxy-D-ribos-1-yl)benzene **5β** and **6β** (2:1 ratio), but in higher 40% isolated yield. Switching the catalyst for (Cy$_3$P)$_2$Cl$_2$Ru=CHPh did not substantially influence the composition of the regioisomeric mixtures: thus the cyclotrimerization afforded a mixture of **5α** and **6α** in 45% (5:6 ratio) and the reaction of **1β** yielded 1:1 mixture of **5β** and **6β** in 30% isolated yield.



Scheme 2. Ru-catalyzed homocyclotrimerization of **1α** and **1β**.

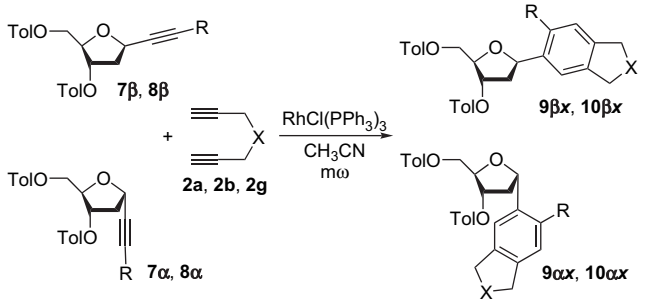
2.4. Synthesis and co-cyclotrimerization of 7 and 8

The successful co-cyclotrimerization of **1α** and **1β** with various diynes raised a question as to whether also internal alkynes attached to the deoxyriboside moiety could undergo the reaction. Thus our effort was directed toward preparation of the corresponding toluoylated 1-propynyl-2-deoxy-D-ribofuranose **7** and 1-phenylethynyl-2-deoxy-D-ribofuranose **8**. The reaction of 1-chlorodeoxyribose with 1-propynyl magnesium bromide or phenylethynyl magnesium bromide afforded in both cases the products as 2:1 mixtures of α and β anomers of **7** and **8** (Scheme 3). The propynyl derivative **7** was obtained in 75% yield, whereas the phenylethynyl one **8** in 47% yield. The obtained anomeric mixtures were resolved into individual anomers by HPLC.



Scheme 3. Synthesis of **7** and **8**.

The first attempts to carry out the co-cyclotrimerization of alkynes **7α**, **7β**, **8α**, and **8β** with various diynes under the previously used conditions (10 mol % $RhCl(PPh_3)_3$, toluene) were not met with success. The alkynes did not react and only oligomerization of diynes was observed. This could probably be attributed to a greater steric hindrance of the internal triple bond. Similar problems were also observed in the cyclotrimerization of diynes with nitriles, and were overcome by us[16] and others[17,18] by carrying out the reaction under microwave irradiation. Thus, the next sets of reactions of individual anomers were executed in acetonitrile under microwave irradiation (Scheme 4). Gratifyingly, in all cases the reaction took place and the desired products were obtained, although in moderate yields (Table 3).



Scheme 4. Microwave-promoted cyclotrimerization of **7** and **8**.

Table 3
Co-cyclotrimerization of **7α** and **8α** with diynes **2a**, **2b**, and **2g**

Entry	Alkyne	Diyne **2**	Product **9αx**	Yield (%)
1	**7α**	**2a**	**9αa**	44
2		**2b**	**9αb**	15
3		**2g**	**9αg**	12
4	**8α**	**2a**	**10αa**	37
5		**2b**	**10αb**	12
6		**2g**	**10αg**	16
7	**7β**	**2a**	**9βa**	41
8		**2b**	**9βb**	36
9		**2g**	**9βg**	47
10	**8β**	**2a**	**10βa**	40
11		**2b**	**10βb**	20
12		**2g**	**10βg**	38

Initially, the co-cyclotrimerizations were performed with α anomers **7α** and **8α** (entries 1–6) The reactions of the methyl derivative **7α** with **2a**, **2b**, and **2g** (entries 1–3) yielded the corresponding products **9αa**, **9αb**, and **9αg** in 44, 15, and 12% isolated yields, respectively. Similar results were also obtained with **8α** (entries 4–6), where products **10αa**, **10αb**, and **10αg** were obtained in 37, 12, and 16% yields, respectively. Then, the co-cyclotrimerizations with β anomers **7β** and **8β** were carried out (entries 7–12). The reactions of the methyl derivative **7β** (entries 7–9) with **2a**, **2b**, and **2g** yielded the corresponding products **9βa**, **9βb**, and **9βg** in 41, 36, and 47% isolated yields, respectively. Similar results were also obtained with **8β** (entries 10–12), where products **10βa**, **10βb**, and **10βg** were isolated in 40, 20, and 38% yields, respectively. In addition, other catalysts such as Cp*RuCl(cod)[19] and $Ni(CO)_2(PPh_3)_2$[20] were also tested in cyclotrimerization of **7** (anomeric mixture) with **2a** under microwave conditions. Regrettably, the first did not catalyze the reaction and the second afforded **9a** (anomeric mixture) in only 18% yield.

It should be emphasized that the data presented in Table 3 do not represent real yields of the desired compounds. Although the reactions in all cases proceeded well, always complex mixtures of compounds were obtained. It took a great deal of work to isolate and purify each target compound **9** or **10** to such degree that it would enable unequivocal spectroscopic confirmation of their structure. Thus, the reported yields represent the amount of a compound isolated in analytical purity. Nonetheless, these results clearly indicate that the protected 1-alkynyl-2-deoxyribofuranoses possess the rather sterically hindered triple bond resulting in lower reactivity. This was also confirmed by attempts to carry out homocyclotrimerization under the above mentioned conditions. Unfortunately, complex reaction mixtures were formed and the desired products were not identified. On the other hand, the obtained results demonstrate the usefulness of microwave irradiation as a tool for forcing substrates, which otherwise do not react under usual conditions, to undergo coupling.

3. Conclusion

In conclusion, we have successfully developed the general protocol for the [2+2+2]-cyclotrimerization of **1α** with various diynes under mild reaction conditions. These results provide a further insight into the scope and versatility of cyclotrimerization of α and β anomers of protected 1-ethynyl-2-deoxyribofuranoses. Moreover, it also showed that both anomers did not undergo homocyclotrimerization under Rh-catalysis and had different reactivity: **1α** underwent head-to-head dimerization, whereas **1β** did not react. Homocyclotrimerization was successfully brought about by Ru-catalysis: carbene complex ($(Cy_3P)_2Cl_2Ru{=}CHPh$) was more efficient for the reaction of **1α**, whereas Cp*Ru(cod)Cl gave better yields with **1β**. To the best of our knowledge, this is the first example of homocyclotrimerization of *C*-ethynylsaccharides. Also successful co-cyclotrimerization of 1-(2-deoxy-D-ribofuranose-1-yl)-alkynes **7** and **8** with diynes to the corresponding benzene derivatives was carried out. The reaction proceeded only under microwave irradiation, probably due to a bigger steric hindrance of the triple bond.

4. Experimental

4.1. General

All solvents were used as-obtained unless otherwise noted. Toluene was distilled from benzophenone/Na, 1,2-dichloroethane, and CH_2Cl_2 from CaH_2 under Ar. Starting diynes **2** were prepared by standard procedures by the reaction of propargyl bromide with the corresponding *C*-acids under basic conditions.[12b] $RhCl(PPh_3)_3$,[21]

and α- and β-[2-deoxy-3,5-bis[*O*-(*p*-toluoyl)]-D-ribofuranosyl]-ethyne[13] were prepared according to previously published procedures. Cp*RuCl(cod) and first generation Grubbs' catalyst were purchased from Strem Ltd. All reactions were carried out under an argon atmosphere using Schlenk-tube technique or in a microwave reactor Biotage Initiator.

4.2. General procedure for $RhCl(PPh_3)_3$ catalyzed cyclotrimerization of 1 with diynes

Into a solution of 1α-ethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose **1α** (0.2 mmol, 76 mg) in dry toluene (3 mL) were added $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg) and diyne **2** (0.24 mmol). The reaction mixture was stirred at 20 °C for 48 h or until the consumption of the starting material (TLC). Then, the volatiles were removed under reduced pressure and column chromatography of the residue on silica gel afforded the title compound.

*4.2.1. 1α-[2,2-Bis(ethoxycarbonyl)-1,3-dihydro-2H-inden-5-yl]-1,2-dideoxy-3,5-di-O-(4-toluoyl)]-D-ribofuranose (**3αa**)*

Compound **2a** (80 μmol, 19 mg), **1α** (67 μmol, 26 mg), $RhCl(PPh_3)_3$ (6.7 μmol, 6 mg). Column chromatography (3:1 hexane/EtOAc) afforded 40 mg (95%) of the title compound as a colorless oil; $[\alpha]_D^{20}$ −1.05 (*c* 0.0285, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 0.87 (3H, t, *J* 7.1 Hz), 0.88 (3H, t, *J* 7.1 Hz), 1.96 (3H, s), 2.00 (3H, s), 1.96–2.00 (1H, m), 2.39–2.46 (1H, m), 3.7–3.81 (4H, m), 3.91 (2H, q, *J* 7.1 Hz), 3.94 (2H, q, *J* 7.1 Hz), 4.45 (1H, dd, *J* 11.6, 5.2 Hz), 4.50 (1H, dd, *J* 11.6, 5.2 Hz), 4.58 (1H, td, *J* 5.2, 2.6 Hz), 5.04 (1H, m), 5.48 (1H, m), 6.88–7.16 (7H, m), 7.88 (2H, m), 8.2 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.6, 14.9, 22.0, 22.1, 41.2, 41.4, 41.6, 61.6, 62.2, 65.3, 77.5, 80.8, 83.2, 122.6, 125.0, 125.6, 128.5, 128.6, 128.8, 128.9, 130.1, 130.8 (2×), 130.9 (2×), 140.0, 141.2, 143.1, 144.2, 144.4, 166.6, 166.9, 172.2, 172.3; IR ν_{max} ($CHCl_3$) 3309, 3029, 2984, 1728, 1612, 1446, 1368, 1271, 1179, 1106, 1067, 1020, 861, 840 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{38}O_9$: 614.2516, found: 614.2507. R_f (3:1 hexane/EtOAc)=0.24.

*4.2.2. 1α-(2,2-Diacetyl-1,3-dihydro-2H-inden-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)]-D-ribofuranose (**3αb**)*

Compound **2b** (70 μmol, 12 mg), **1α** (58 μmol, 22 mg), $RhCl(PPh_3)_3$ (5.8 μmol, 5.4 mg). Column chromatography (3:1 hexane/EtOAc) afforded 20 mg (63%) of the title compound as a colorless oil; $[\alpha]_D^{20}$ −2.8 (*c* 0.0265, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.38 (3H, s), 1.70 (3H, s), 1.96 (3H, s), 2.01 (3H, s), 2.02–2.08 (1H, m), 2.44–2.51 (1H, m), 3.15–3.30 (4H, m), 4.47 (1H, dd, *J* 11.6, 5.2 Hz), 4.52 (1H, dd, *J* 11.6, 5.2 Hz), 4.64 (1H, td, *J* 5.5, 2.7 Hz), 5.08 (1H, m), 5.48 (1H, m), 6.88–6.94 (5H, m), 7.09–7.12 (2H, m), 7.87 (2H, m), 8.21 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 20.0, 22.1, 26.6, 26.7, 38.1, 38.3, 41.2, 65.3, 75.6, 77.6, 80.7, 83.3, 122.7, 123.1, 125.5 (two signals are overlapped by solvent signal), 130.1 (2×), 130.1 (2×), 130.7 (2×), 130.9 (2×), 139.8, 141.0, 143.1, 144.3, 144.5, 166.6, 166.9, 204.3; IR ν_{max} ($CHCl_3$) 3029, 3011, 2926, 1717, 1703, 1612, 1440, 1359, 1272, 1178, 1106, 1020, 839 cm^{-1}; HRMS (EI) calcd for $C_{34}H_{34}O_7$: 472.2614, found: 472.2627. R_f (3:1 hexane/EtOAc)=0.14.

*4.2.3. 1α-[2-Acetyl-2-(ethoxycarbonyl)-1,3-dihydro-2H-inden-5-yl]-1,2-dideoxy-3,5-di-O-(4-toluoyl)]-D-ribofuranose (**3αc**)*

Compound **2c** (0.24 mmol, 43 mg), **1α** (0.2 mmol, 75.6 mg), $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg). Column chromatography (3:1 hexane/EtOAc) afforded 97 mg (83%) of 1:1 mixture of diastereoisomers as a colorless oil; $[\alpha]_D^{20}$ −1.3 (*c* 0.0525, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 0.82 (3H, t, *J* 7.2 Hz), 0.86 (3H, t, *J* 6.8 Hz), 1.83 (1H, m), 1.87 (3H, s), 1.89 (3H, s), 1.90 (3H, s), 1.94 (3H, s), 1.99 (3H, s), 2.01 (1H, m), 2.03 (3H, s), 2.45–2.49 (1H, m), 2.76–2.77 (1H, m), 3.31–3.62 (8H, m), 3.79–3.93 (4H, m), 4.44–4.51 (4H, m), 4.60–4.63 (2H, m), 5.07–5.10 (2H, m), 5.47–5.49 (2H, m), 6.89–7.20 (14, m), 7.87 (4H, m), 8.19 (4H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.5 (2×), 22.1, 22.1 (2×), 22.6, 26.3, 27.1, 37.9, 39.5, 39.6, 39.7, 39.9, 41.2, 62.2, 62.2, 65.0, 65.3, 67.8, 73.4, 77.5, 80.5, 80.8, 83.3, 83.3, 122.6, 125.0, 125.2, 125.5, 125.5, 126.8, 129.1, 129.2, 129.2, 129.6, 130.7, 130.8, 135.8, 139.8, 139.9, 141.1, 141.2, 143.0, 143.1, 144.3, 144.5, 166.6, 166.9, 171.0, 173.0, 202.1, 202.1; IR ν_{max} ($CHCl_3$) 3029, 3011, 2986, 2925, 1715, 1612, 1446, 1272, 1245, 1178, 1106, 1020 cm^{-1}; HRMS (EI) calcd for $C_{35}H_{36}O_8$: 584.2410, found: 584.2393. R_f (2:1 hexane/EtOAc)=0.24.

*4.2.4. 1α-[2-Cyano-2-(ethoxycarbonyl)-1,3-dihydro-2H-inden-5-yl]-1,2-dideoxy-3,5-di-O-(4-toluoyl)]-D-ribofuranose (**3αd**)*

Compound **2d** (80 μmol, 15.2 mg), **1α** (67 μmol, 25.5 mg), $RhCl(PPh_3)_3$ (6.7 μmol, 6.2 mg). Column chromatography (3:1 hexane/EtOAc) afforded 20 mg (53%) as a colorless oil; $[\alpha]_D^{20}$ −2.7 (*c* 0.0055, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 0.82 (3H, t, *J* 7.0 Hz), 1.96 (3H, s), 1.96–2.01 (1H, m), 2.01 (3H, s), 2.41–2.48 (1H, m), 3.15–3.41 (4H, m), 3.78 (2H, q, *J* 7.0 Hz), 4.45 (1H, dd, *J* 11.2, 4.8 Hz), 4.51 (1H, dd, *J* 11.2, 4.8 Hz), 4.62 (1H, td, *J* 5.2, 2.4 Hz), 5.01–5.04 (1H, m), 5.45–5.48 (1H, m), 6.76–7.06 (7H, m), 7.86 (2H, m), 8.21 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.4, 22.0, 22.1, 41.1, 43.6, 43.9, 48.4, 63.5, 65.3, 77.5, 80.6, 83.4, 121.4, 122.6, 125.0, 126.0, 128.3, 130.1 (2×), 130.1 (2×), 130.7 (2×), 130.9 (2×), 138.0, 139.3, 144.0, 144.3, 144.7, 166.6, 166.9, 169.2; IR ν_{max} ($CHCl_3$) 3029, 3011, 1718, 1612, 1442, 1373, 1272, 1244, 1178, 1106, 1020, 840 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{34}N_1O_7$: 567.2257, found: 567.2265. R_f (3:1 hexane/EtOAc)=0.20.

*4.2.5. 1α-(1,3-Dihydro-2-tosyl-2H-indol-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**3αe**)*

Compound **2e** (0.24 mmol, 60 mg), **1α** (0.2 mmol, 76 mg), $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg). Column chromatography (3:1 hexane/EtOAc) afforded 22 mg (18%) of the title compound as a colorless oil; $[\alpha]_D^{20}$ +7.1 (*c* 0.01025, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.85 (3H, s), 1.89–1.93 (1H, m), 1.95 (3H, s), 2.00 (3H, s), 2.39–2.46 (1H, m), 4.38–4.51 (6H, m), 4.58 (1H, td, *J* 5.2, 2.4 Hz), 4.92–4.95 (1H, m), 5.44 (1H, m), 6.59–6.63 (1H, m), 6.73–6.77 (2H, m), 6.85–6.90 (3H, m), 6.97–7.00 (2H, m), 7.36 (1H, s), 7.75–7.80 (2H, m), 7.82–7.86 (2H, m), 8.17–8.21 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 21.7, 22.0, 22.1, 41.2, 54.3, 54.5, 65.2, 77.5, 80.4, 83.3, 120.8, 123.2, 126.0, 128.3, 128.5 (one signal is overlapped by solvent signal), 130.0 (2×), 130.1 (2×), 130.4 (2×), 130.7 (2×), 130.8 (2×), 136.0, 136.2, 138.3, 143.7, 143.9, 144.4, 144.9, 166.5, 166.9; IR ν_{max} ($CHCl_3$) 3275, 2923, 1723, 1708, 1610, 1451, 1347, 1264, 1160, 1093, 1017, 818, 755, 699 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{35}NO_7S$: 626.2213, found: 626.2238. R_f (3:1 hexane/EtOAc)=0.20.

*4.2.6. 1α-(1,3-Dihydroisobenzofuran-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**3αf**)*

Compound **2f** (0.178 mmol, 17 mg, 18.3 μl), **1α** (0.148 mmol, 56 mg), $RhCl(PPh_3)_3$ (14.8 μmol, 13.7 mg). Column chromatography (3:1 hexane/EtOAc) afforded 28 mg (39%) of the title compound as a colorless oil; $[\alpha]_D^{20}$ +4.4 (*c* 0.0045, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.95 (3H, s), 1.96 (3H, s), 2.00–2.05 (1H, m), 2.45–2.52 (1H, m), 4.46 (1H, dd, *J* 11.6, 5.2 Hz), 4.52 (1H, dd, *J* 11.6, 5.2 Hz), 4.62 (1H, td, *J* 5.2, 2.4 Hz), 4.93 (4H, br s), 5.07 (1H, m), 5.50 (1H, m), 6.80–7.10 (7H, m), 7.84–7.86 (2H, m), 8.119–8.22 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0 (2×), 41.4, 65.3, 74.1, 74.2, 77.5, 80.7, 83.3, 119.2, 121.6, 125.7, 128.4 (one signal overlapped by solvent signal), 130.0 (2×), 130.1 (2×), 130.7 (2×), 130.9 (2×), 139.3, 140.7, 143.4, 144.3, 144.5, 166.6, 166.9; IR ν_{max} ($CHCl_3$) 3354, 2946, 2854, 1717, 1609, 1448, 1264, 1176, 1103, 1043, 1017, 903, 840, 751, 691 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{28}O_6$: 472.1886, found: 472.1867. R_f (3:1 hexane/EtOAc)=0.21.

*4.2.7. 1α-(1,3-Dihydro-2H-inden-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**3αg**)*

Compound **2g** (0.24 mmol, 23 mg, 28 μl), **1α** (0.2 mmol, 75.6 mg), $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg). Column chromatography (3:1 hexane/EtOAc) afforded 78 mg (83%) of the title compound as

a colorless oil; $[\alpha]_D^{20}$ +5.1 (*c* 0.01975, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.84 (2H, q, *J* 7.2 Hz), 1.96 (3H, s), 1.97 (3H, s), 2.08–2.14 (1H, m), 2.51–2.55 (1H, m), 2.71 (2H, t, *J* 7.2 Hz), 2.72 (2H, t, *J* 7.2 Hz), 4.78 (1H, dd, *J* 11.6, 5.2 Hz), 4.52 (1H, dd, *J* 11.6, 5.2 Hz), 4.65 (1H, *J* 5.2, 2.4 Hz), 5.11–5.14 (1H, m), 5.50–5.54 (1H, m), 6.86–6.90 (4H, m), 7.09–7.12 (1H, m), 7.17–7.18 (1H, m), 7.31 (1H, s), 7.90–7.93 (2H, m), 8.17–8.20 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0 (2×), 26.6, 33.5, 33.7, 41.5, 65.4, 77.7, 81.0, 83.1, 122.8, 124.8, 125.0, 128.8, 129.2, 129.9 (2×), 130.0 (2×), 130.8 (2×), 130.9 (2×), 142.0, 143.8, 144.2, 144.3, 145.0, 166.6, 166.9; IR ν_{max} ($CHCl_3$) 3381, 2919, 2861, 1713, 1610, 1437, 1263, 1174, 1090, 1014, 831, 747, 689 cm^{-1}; HRMS (EI) calcd for $C_{30}H_{30}O_5$: 470.2093, found: 470.2075. R_f (2:1 hexane/EtOAc)=0.46.

*4.2.8. 3(E)-1,4-Di[1α-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]but-3-en-1-yn (**4α**)*

Into a solution of α-ethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose **1α** (0.2 mmol, 76 mg) in dry toluene (3 mL) was added $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg). The reaction mixture was stirred at 20 °C for 48 h or until consumption of the starting material (TLC). Then, the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (3:1 hexane/EtOAc) that afforded 23 mg (31%) of the title compound as a colorless oil; $[\alpha]_D^{20}$ +34.2 (*c* 0.0095, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.60–1.65 (2H, m), 1.955 (3H, s), 1.959 (3H, s), 1.963 (3H, s), 2.02 (3H, s), 2.04–2.13 (2H, m), 4.33–4.39 (2H, m), 4.39 (2H, dd, *J* 11.6, 4.4 Hz), 4.47 (2H, dd, *J* 11.6, 4.4 Hz), 4.58–4.60 (1H, m), 4.82–4.85 (1H, m), 5.33–5.38 (2H, m), 5.79 (1H, d, *J* 15.9 Hz), 6.13 (1H, dd, *J* 15.9, 5.6 Hz), 6.86–7.00 (8H, m), 8.00–8.02 (2H, m), 8.11–8.16 (6H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0 (2×), 22.1 (2×), 30.9, 38.6, 40.3, 59.2, 65.2, 69.7, 77.0, 77.2, 79.3, 83.2, 83.3, 84.4, 91.2, 110.6, 128.2, 128.3, 128.6, 128.8, 130.0, 130.1, 130.1, 130.8, 130.8, 130.9, 144.2, 144.3, 144.6, 144.7, 145.1, 166.5, 166.7, 166.8, 166.8; IR ν_{max} ($CHCl_3$) 3408, 2914, 1726, 1708, 1606, 1446, 1401, 1370, 1263, 1174, 1094, 1014, 952, 836, 747, 689 cm^{-1}; MS (EI) no molecular peak, 576 (2), 524 (5), 368 (7), 236 (7), 198 (12), 149 (42). R_f (3:1 hexane/EtOAc)=0.26.

*4.2.9. 3(E)-1,4-Di[1β-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]but-3-en-1-yn (**4β**)*

Into a solution of β-ethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose **1α** (0.2 mmol, 76 mg) in dry toluene (3 mL) was added $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg). The reaction mixture was stirred at 20 °C for 48 h or until consumption of the starting material (TLC). Then, the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (3:1 hexane/EtOAc) that afforded 7 mg (9%) of the title compound as a colorless oil; ^1H NMR (400 MHz, C_6D_6) δ 1.55–1.67 (1H, m), 1.79–1.85 (1H, m), 1.97 (3H, s), 1.98 (3H, s), 1.99 (3H, s), 2.08–2.13 (1H, m), 2.23–2.29 (1H, m), 4.21–4.26 (2H, m), 4.37–4.48 (4H, m), 4.82–4.86 (1H, m), 5.33–5.40 (2H, m), 5.81 (1H, dt, *J* 16, 1.6 Hz), 6.05 (1H, dd, *J* 16, 5.8 Hz), 6.88–6.96 (8H, m), 8.00–8.07 (4H, m), 8.13–8.20 (4H, m). R_f (3:1 hexane/EtOAc)=0.26.

4.3. General procedure for homocyclotrimerization of 1α and 1β

Into a solution of 1α- or 1β-ethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose **1α** or **1β** (0.2 mmol, 76 mg) in dry solvent (3 mL) was added the appropriate Ru-catalyst. The reaction mixture was stirred at 20 °C for 48 h or until consumption of the starting material (TLC). Then, the solvent was evaporated under reduced pressure and the residue was subjected to column chromatography.

*4.3.1. Homocyclotrimerization of **1α** to 1,2,4-tri[1α-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]benzene (**5α**) and 1,3,5-tri[1α-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]benzene (**6α**)*

Condition A. Compound **1α** (0.2 mmol, 75.6 mg), Cp*RuCl(cod) (0.02 mmol, 7.6 mg), DCE (3 mL). Column chromatography (3:1 hexane/EtOAc) afforded 10 mg (13%, 4:3 **5α**/**6α**) of a mixture of the title compounds. *Conditions B*. Compound **1α** (0.2 mmol, 75.6 mg), $(PCy_3)_2Cl_2Ru$=CHPh (0.03 mmol, 25 mg), CH_2Cl_2 (3 mL). Column chromatography (3:1 hexane/EtOAc) afforded 34 mg (45%, 5:6 **5α**/**6α**) of a mixture of title compounds. Compounds **5α** and **6α** were separated by HPLC (3:1 hexane/EtOAc). *Unsymmetric product **5α***. A colorless oil; $[\alpha]_D^{20}$ 0 (*c* 0.0035, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6) δ 1.96 (3H, s), 1.99 (3H, s), 2.00 (6H, s), 2.01 (3H, s), 2.03 (3H, s), 2.05–2.16 (3H, m), 2.44–2.50 (1H, m), 2.60–2.70 (2H, m), 4.40–4.61 (9H, m), 5.13–5.16 (1H, m), 5.30–5.33 (1H, m), 5.36–5.39 (1H, m), 5.45–5.51 (3H, m), 6.87–7.00 (12H, m), 7.33–7.36 (1H, m), 7.69–7.71 (1H, m), 7.79–7.82 (1H, m), 7.96–8.25 (12H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.1 (6×), 40.5, 40.95, 41.3, 65.0, 65.2, 65.3, 77.4 (2×), 77.5, 80.8 (2×), 81.5, 83.2 (2×), 83.4, 123.6, 125.6, 126.8, 128.2, 128.5, 130.0, 130.1, 130.2, 130.8, 130.9, 138.9, 141.2, 143.8, 144.2, 144.5, 144.6, 166.7, 166.9; IR ν_{max} (neat) 2956, 2920, 2855, 1718, 1613, 1273, 1180, 1108, 752 cm^{-1}; HRMS (FAB) calcd for $C_{69}H_{66}O_{15}$: 1135.4480, found: 1135.4429. *Symmetric product **6α***. A colorless oil; $[\alpha]_D^{20}$ +12.4 (*c* 0.00465, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.95 (9H, s), 2.00 (9H, s), 2.00–2.05 (3H, m), 2.45–2.49 (3H, m), 4.41–4.45 (6H, m), 4.62–4.63 (3H, m), 5.07–5.10 (3H, m), 5.47–5.49 (3H, m), 6.86–6.88 (6H, m), 6.94–6.96 (6H, m), 7.47 (3H, s), 7.92–7.94 (6H, m), 8.14–8.16 (6H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 21.9, 41.3, 65.1, 77.4, 80.8, 83.2, 122.6, 128.4, 130.0, 130.7, 144.2, 144.4, 144.5, 166.6, 166.8; IR ν_{max} ($CHCl_3$) 2923, 2852, 1726, 1713, 1610, 1450, 1410, 1268, 1179, 1103, 1014, 841, 752, 689 cm^{-1}; HRMS (FAB) calcd for $C_{69}H_{66}O_{15}$: 1135.4480, found: 1135.4468. R_f (3:1 hexane/EtOAc)=0.18.

*4.3.2. Homocyclotrimerization of **1β** to 1,2,4-tri[1β-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]benzene (**5β**) and 1,3,5-tri[1β-(1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranosyl)]-benzene (**6β**)*

Conditions A. Compound **1β** (0.2 mmol, 75.6 mg), Cp*RuCl(cod) (0.02 mmol, 7.6 mg), DCE (3 mL). Column chromatography (3:1 hexane/EtOAc) afforded 30 mg (40%, 2:1 **5β**/**6β**) of a mixture of the title compounds. *Conditions B*. Compound **1β** (0.2 mmol, 75.6 mg), $(PCy_3)_2Cl_2Ru$=CHPh (0.03 mmol, 25 mg), DCM (3 mL). Column chromatography (3:1 hexane/EtOAc) afforded 23 mg (30%, 1:1 **5β**/**6β**) of a mixture of the title compounds. *The unseparable mixture of symmetric **5β** and unsymmetric product **6β***. A colorless oil; $[\alpha]_D^{20}$ −8.2 (*c* 0.01225, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.96 (3H, s), 1.97 (9H, s), 1.98 (9H, s), 1.99 (3H, s), 2.01 (9H, s), 2.02 (3H, s), 1.93–2.05 (6H, m), 2.19–2.24 (3H, m), 2.44–2.51 (3H, m), 4.33–4.40 (6H, m), 4.50–4.68 (12H, m), 5.16–5.20 (3H, m), 5.42–5.47 (3H, m), 5.47–5.55 (6H, m), 6.86–6.98 (24H, m), 7.37 (1H, dd, *J* 8, 1.6 Hz), 7.52 (3H, s), 7.65 (1H, d, *J* 8 Hz), 7.84 (1H, d, *J* 1.6 Hz), 8.08–8.15 (24H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0, 22.1 (2×), 30.9, 41.2, 41.5, 42.7, 65.6, 65.7, 78.2, 78.3 (2×), 78.4 (2×), 78.5, 81.6, 81.7, 84.0, 84.2, 84.3 (2×), 123.7, 124.1, 126.7, 126.9, 128.6, 129.2, 130.1, 130.8 (3×), 138.9, 139.3, 142.3, 143.0, 144.3 (2×), 144.4 (2×), 144.6, 166.6, 166.8, 166.8, 166.9 (2×); IR ν_{max} ($CHCl_3$) 3414, 2920, 1720, 1711, 1689, 1610, 1451, 1407, 1369, 1264, 1176, 1090, 1017, 837, 748, 691 cm^{-1}; HRMS (FAB) calcd for $C_{69}H_{66}O_{15}$: 1135.4480, found: 1135.4458. R_f (3:1 hexane/EtOAc)=0.18.

4.4. 1α-Propynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (7α) and 1β-propynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (7β)

Into a solution of 1-chloro-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (8 mmol, 3 g) in dry THF (45 mL) under argon was slowly added 0.5 M solution of propynyl magnesium bromide (8.5 mmol, 17 mL), the formed reaction mixture was stirred at room temperature for 6 h, and then reduced to 1/3 of its volume in vacuo. Diethyl ether (50 mL) was added and the solution was washed with 10% NH_4Cl (aq) (20 mL), saturated solution of $NaHCO_3$ (20 mL), and

dried ($MgSO_4$). Removal of volatiles in vacuo and column chromatography of the residue on silica gel (3:1 hexane/EtOAc) afforded 2.27 g (75%) of the anomeric mixture of **7α** and **7β** as a pale yellow oil. Further separation of the obtained mixture by a preparative HPLC afforded 0.73 g (24%) of **7α** and 0.35 g (12%) of **7β** as viscous liquids. *Compound* **7α**. ^{1}H NMR (400 MHz, C_6D_6) δ 1.49 (3H, d, *J* 2 Hz), 1.99 (3H, s), 2.00 (3H, s), 2.10–2.19 (1H, m), 2.21–2.28 (1H, m), 4.38 (1H, dd, *J* 11.6, 5.6 Hz), 4.43 (1H, dd, *J* 11.6, 5.6 Hz), 4.56–4.60 (1H, m), 4.72–4.76 (1H, m), 5.35–5.38 (1H, m), 6.89–6.93 (4H, m), 8.08–8.12 (2H, m), 8.12–8.16 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 4.0, 22.0, 22.1, 40.6, 65.3, 69.3, 77.1, 80.4, 82.1, 82.8, 128.9 (2×), 130.0 (2×), 130.8 (2×), 130.9 (2×), 144.2 (2×), 144.4 (2×), 166.4, 166.7; IR ν_{max} (ATR Ge) 1718, 1611, 1270, 1180, 1108, 1021, 752, 692 cm^{-1}; MS (FAB$^+$) no molecular peak, 589 (6), 515 (7), 387 (6), 275 (14), 201 (100). *Compound* **7β**. ^{1}H NMR (400 MHz, C_6D_6) δ 1.41 (1H, d, *J* 2 Hz), 1.95 (3H, s), 1.99 (3H, s), 2.09–2.15 (1H, m), 2.22–2.29 (1H, m), 4.22–4.26 (1H, m), 4.45 (1H, dd, *J* 11.6, 4.9 Hz), 4.52 (1H, dd, *J* 11.6, 4.9 Hz), 4.78–4.83 (1H, m), 5.40–5.43 (1H, m), 6.86 (2H, m), 6.88–6.92 (2H, m), 7.98–8.02 (2H, m), 8.16–8.20 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 3.9, 22.0, 22.1, 40.9, 65.6, 69.6, 77.6, 79.1, 82.6, 83.4, 130.0 (4×), 130.8 (2×), 130.9 (2×), 144.0 (2×), 144.5 (2×), 166.8 (2×); IR ν_{max} (ATR Ge) 1721, 1614, 1273, 1180, 755 cm^{-1}; MS (FAB$^+$) no molecular peak, 589 (7), 515 (6), 387 (6), 275 (10), 201 (100). R_f (3:1 hexane/EtOAc)=0.69.

4.5. 1α-Phenylethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (8α) and 1β-phenylethynyl-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (8β)

Into a solution of 1-chloro-1,2-dideoxy-3,5-di-*O*-(4-toluoyl)-D-ribofuranose (8 mmol, 3 g) in dry THF (45 mL) under argon was slowly added 1 M solution of phenylethynyl magnesium bromide (8.5 mmol, 8.5 mL), the formed reaction mixture was then stirred at room temperature for 6 h, and then reduced to 1/3 of its volume in vacuo. Diethyl ether (50 mL) was added and the solution was washed with 10% NH_4Cl (aq) (20 mL), saturated solution of $NaHCO_3$ (20 mL), and dried ($MgSO_4$). Removal of volatiles in vacuo and column chromatography of the residue on silica gel (3:1 hexane/EtOAc) afforded 1.64 g (47%) of the anomeric mixture of **8α** and **8β** as a pale yellow oil. Further separation of the obtained mixture by a preparative HPLC afforded 0.76 g (22%) of **8α** and 0.34 g (10%) of **8β** as viscous liquids. *Compound* ***8α***. ^{1}H NMR (300 MHz, C_6D_6) δ 1.95 (3H, s), 1.97 (3H, s), 1.96–1.98 (1H, m), 2.18–2.22 (m, 1H), 4.38 (1H, dd, *J* 11.6, 5.4 Hz), 4.45 (1H, dd, *J* 11.6, 5.4 Hz), 4.60–4.63 (1H, m), 4.90–4.94 (1H, m), 5.41–5.45 (1H, m), 6.82–6.89 (4H, m), 6.93–6.97 (3H, m), 7.37–7.44 (2H, m), 8.10–8.17 (4H, m); ^{13}C NMR (75 MHz, C_6D_6) δ 22.0 (2×), 40.4, 65.2, 69.7, 77.0, 83.4, 86.3, 90.4, 124.1, 129.1 (two signals are overlapped by solvent signal), 129.2 (2×), 130.0 (4×), 130.8 (2×), 131.0 (2×), 132.7 (2×), 144.2, 144.4, 166.7, 166.8; IR ν_{max} (ATR Ge) 1718, 1611, 1270, 1177, 1105, 1018, 752 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{35}H_{36}O_7$+H: 455.1859, found: 455.1851. R_f (3:1 hexane/EtOAc)=0.67. *Compound* ***8β***. ^{1}H NMR (300 MHz, C_6D_6) δ 1.94 (3H, s), 2.01 (3H, s), 2.12–2.19 (1H, m), 2.30–2.40 (1H, m), 4.28 (1H, td, *J* 5.1, 2.4 Hz), 4.45–4.55 (2H, m), 4.94–5.00 (1H, m), 5.41–5.45 (1H, m), 6.82–6.85 (2H, m), 6.92–6.95 (5H, m), 7.35–7.38 (2H, m), 8.00–8.03 (2H, m), 8.17–8.20 (2H, m); ^{13}C NMR (75 MHz, C_6D_6) δ 22.0, 22.1, 40.8, 65.5, 69.7, 77.6, 83.7, 86.7, 89.0, 123.8, 128.5 (two signals are overlapped by solvent signal), 129.2 (2×), 130.0 (2×), 130.1 (2×), 130.8 (2×), 130.9 (2×), 132.7 (2×), 144.1, 144.6, 166.4, 166.8; IR ν_{max} (KBr) 1709, 1282, 1270, 1177, 1108, 1081, 752 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{35}H_{36}O_7$+H$^+$: 455.1859, found: 455.1860. R_f (3:1 hexane/EtOAc)=0.67.

4.6. General procedure for cyclotrimerization of 7 with diynes 2

Into a solution of **7α** or **7β** (0.2 mmol, 78 mg) in dry CH_3CN (4.5 ml) were added $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg) and diyne **2** (0.24–30 mmol). The reaction mixture was stirred in a microwave reactor for 1 h (internal temperature reached 180 °C). Then, volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (3:1 hexane/EtOAc) afforded the title compound.

*4.6.1. 1α-(2,2-Bis(ethoxycarbonyl)-6-methylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9αa**)*

Compound **7α** (0.2 mmol, 78 mg), **2a** (0.24 mmol, 57 mg); 56 mg (44%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ 0 (*c* 0.0022, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 0.87 (3H, t, *J* 7.2 Hz), 0.89 (3H, t, *J* 7.2 Hz), 1.84 (1H, ddd, *J* 13.6, 6.4, 3.6 Hz), 1.94 (3H, s), 1.96 (3H, s), 2.02 (3H, s), 2.48 (1H, apparent quint, *J* 7.2 Hz), 3.70–3.87 (4H, m), 3.90–3.98 (4H, m), 4.42 (1H, dd, *J* 11.6, 4.8 Hz), 4.51 (1H, dd, *J* 11.6, 5.6 Hz), 4.65 (1H, td, *J* 5.2, 2.4 Hz), 5.25 (1H, apparent t, *J* 6.8 Hz), 5.51–5.54 (1H, m), 6.74 (1H, s), 6.88–6.90 (2H, m), 6.99–7.03 (2H, m), 7.67 (1H, s), 7.98–8.01 (2H, m), 8.18–8.21 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.6 (2×), 19.7, 22.0, 22.1, 39.8, 41.6, 41.7, 61.7, 62.1, 62.2, 65.4, 77.6, 78.6, 83.3, 122.0, 127.0, 128.2, 128.9, 129.2, 130.1 (2×), 130.1 (2×), 130.8 (2×), 130.7 (2×), 138.8, 139.8, 141.3, 144.2, 144.5, 166.6, 166.9, 172.3, 172.5; IR ν_{max} (acetone) 3468, 2977, 2926, 2872, 1726, 1713, 1444, 1365, 1239, 1178, 1153, 1052, 1014, 903, 859, 827, 707 cm^{-1}; MS (FAB$^+$) M+H 393 (1), 231 (1), 154 (6), 119 (100). R_f (3:1 hexane/EtOAc)=0.40.

*4.6.2. 1β-(2,2-Bis(ethoxycarbonyl)-6-methylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9βa**)*

Compound **7β** (0.2 mmol, 78 mg), **2a** (0.24 mmol, 57 mg); 52 mg (41%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ 0 (*c* 0.00285, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 0.87 (3H, t, *J* 7.2 Hz), 0.89 (3H, t, *J* 7.2 Hz), 1.89 (1H, ddd, *J* 13.2, 10.8, 6.4 Hz), 1.99 (3H, s), 2.01 (3H, s), 2.02 (3H, s), 2.30 (1H, ddd, *J* 13.6, 5.2, 1.2 Hz), 3.61–3.80 (4H, m), 3.87–3.96 (4H, m), 4.37–4.40 (1H, m), 4.63 (1H, dd, *J* 11.6, 4 Hz), 4.66 (1H, dd, *J* 11.6, 4 Hz), 5.35 (1H, dd, *J* 10.8, 5.2 Hz), 5.53 (1H, apparent d, *J* 6.8 Hz), 6.73 (1H, s), 6.91–6.95 (4H, m), 7.67 (1H, s), 8.10–8.14 (2H, m), 8.16–8.20 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.6 (2×), 19.7, 22.1 (2×), 41.1, 41.5, 61.6, 62.1, 65.6, 78.4, 78.8, 83.7, 122.0, 126.9 (two signals are overlapped by solvent signal), 128.9, 130.1 (4×), 130.8 (2×), 130.9 (2×), 134.0, 139.3 (2×), 140.2, 144.6, 166.6, 166.9, 172.2 (2×); IR ν_{max} (acetone) 3468, 2977, 2932, 2901, 2869, 1726, 1713, 1441, 1365, 1239, 1182, 1153, 1052, 1014, 859, 710 cm^{-1}; MS (FAB$^+$) no molecular peak, 369 (1), 181 (7), 119 (100). R_f (3:1 hexane/EtOAc)=0.40.

*4.6.3. 1α-(2,2-Diacetyl-6-methylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9αb**)*

Compound **7α** (0.2 mmol, 78 mg), **2b** (0.3 mmol, 53 mg); 17 mg (15%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −3.9 (*c* 0.0075, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.70 (3H, s), 1.73 (3H, s), 1.88 (1H, ddd, *J* 13.7, 6.1, 3.7 Hz), 1.96 (3H, s), 1.97 (3H, s), 2.03 (3H, s), 2.53 (1H, ddd, *J* 13.9, 7.8, 7.1 Hz), 3.16–3.39 (4H, m), 4.44 (1H, dd, *J* 11.7, 5.2 Hz), 4.54 (1H, dd, *J* 11.9, 5.8 Hz), 4.73 (1H, td, *J* 5.4, 2.4 Hz), 5.28 (1H, apparent t, *J* 7.4 Hz), 5.51 (1H, ddd, *J* 6.4, 3.7, 2.4 Hz), 6.70 (1H, s), 6.88–6.90 (2H, m), 6.97–6.99 (2H, m), 7.60 (1H, s), 7.96–7.98 (2H, m), 8.20–8.22 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 19.9, 22.1 (2×), 26.6, 26.8, 38.2, 38.4, 39.9, 65.3, 75.6, 77.7, 78.6, 83.4, 122.2, 127.1, 127.9, 128.3, 130.1 (2×), 130.8 (2×), 130.9 (2×), 131.3 (2×), 133.6, 138.6, 139.6, 141.3, 144.3, 144.6, 166.6, 167.0, 204.5, 204.6; IR ν_{max} (acetone) 3408, 2949, 2918, 2847, 1708, 1690, 1610, 1441, 1352, 1263, 1174, 1098, 1022, 840, 747, 689 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{35}H_{36}O_7$+Na$^+$: 591.2359, found: 591.2350. R_f (3:1 hexane/EtOAc)=0.35.

*4.6.4. 1β-(2,2-Diacetyl-6-methylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9βb**)*

Compound **7β** (0.2 mmol, 78 mg), **2b** (0.3 mmol, 53 mg); 41 mg (36%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −8.2 (*c* 0.0037,

$CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.66 (3H, s), 1.71 (3H, s), 1.93 (3H, s), 1.94–1.99 (1H, m), 2.00 (3H, s), 2.03 (3H, s), 2.36 (1H, ddd, *J* 14, 5.6, 1.2 Hz), 3.03–3.29 (4H, m), 4.38–4.41 (1H, m), 4.59 (1H, dd, *J* 11.6, 4 Hz), 4.79 (4H, dd, *J* 11.6 Hz), 5.38 (1H, dd, *J* 10.8, 5.2 Hz), 5.57 (1H, apparent d, *J* 6.8 Hz), 6.68 (1H, s), 6.80–6.84 (4H, m), 7.62 (1H, s), 8.11–8.16 (4H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 19.7, 22.1 (2×), 26.6, 26.7, 38.3, 38.9, 41.3, 65.6, 75.6, 78.5, 78.8, 83.8, 122.1, 127.0, 127.9, 128.3, 130.2 (2×), 130.1 (2×), 130.8 (2×), 131.3 (2×), 133.8, 139.0, 139.5, 140.0, 144.4, 144.7, 166.7, 166.9, 204.5, 204.6; IR ν_{max} (acetone) 3069, 3034, 2958, 2920, 2850, 1710, 1609, 1448, 1406, 1359, 1258, 1175, 1093, 1014, 865, 795, 751, 688 cm^{-1}; HRMS (FAB^+) calcd for $C_{35}H_{36}O_7$+Na^+: 591.2359, found: 591.2370. R_f (3:1 hexane/EtOAc)=0.35.

4.6.5. 1α-(6-Methylindanyl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9αg**)

Compound **7α** (0.2 mmol, 78 mg), **2g** (0.3 mmol, 28 mg); 12 mg (12%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ +4.8 (*c* 0.0083, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.85–2.00 (3H, m), 1.958 (3H, s), 1.963 (3H, s), 2.04 (3H, s), 2.53–2.60 (1H, m), 2.73–2.80 (4H, m), 4.45 (1H, dd, *J* 11.6, 5.2 Hz), 4.55 (1H, dd, *J* 11.6, 6 Hz), 4.69 (1H, td, *J* 5.6, 2.8 Hz), 5.31–5.34 (1H, apparent t, *J* 5.8 Hz), 5.55 (1H, m), 6.87–6.90 (5H, m), 7.73 (1H, s), 7.97–8.01 (2H, m), 8.18–8.22 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 20.0, 22.0 (2×), 26.7, 33.6, 33.7, 40.2, 65.4, 77.7, 78.7, 83.2, 122.1, 127.1, 128.8 (two signals are overlapped by solvent signal), 128.9, 129.9 (2×), 130.1 (2×), 130.9 (4×), 132.7, 140.0, 142.5, 143.6, 144.2, 144.4, 166.6, 166.9; IR ν_{max} (acetone) 3404, 3065, 3034, 2923, 2850, 1720, 1710, 1609, 1448, 1406, 1372, 1264, 1178, 1102, 1020, 878, 840, 751, 691 cm^{-1}; HRMS (FAB^+) calcd for $C_{31}H_{32}O_5$+Na^+: 507.2147, found: 507.2157. R_f (3:1 hexane/EtOAc)=0.64.

4.6.6. 1β-(6-Methylindanyl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**9βg**)

Compound **7β** (0.2 mmol, 78 mg), **2g** (0.3 mmol, 28 mg); 45 mg (47%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −21.8 (*c* 0.0055, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.78–1.85 (2H, m), 1.95 (3H, s), 1.95–2.05 (1H, m), 1.995 (3H, s), 2.11 (3H, s), 2.38 (1H, ddd, *J* 13.6, 5.2, 1.2 Hz), 2.66–2.73 (4H, m), 4.41 (1H, td, *J* 5.2, 2.4 Hz), 4.66 (1H, dd, *J* 11.7, 4.4 Hz), 4.67 (1H, dd, *J* 11.7, 4.4 Hz), 5.42 (1H, dd, *J* 10.8, 5.1 Hz), 5.57 (1H, apparent d, *J* 4.9 Hz), 6.84–6.88 (2H, m), 6.87 (1H, s), 6.91–6.95 (2H, m), 7.71 (1H, s), 8.11–8.15 (2H, m), 8.17–8.19 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 19.8, 22.0, 22.1, 26.6, 33.5 (2×), 41.3, 65.7, 78.5, 79.0, 83.6, 122.1, 127.0 (one signal is overlapped by solvent signal), 129.2, 130.0 (2×), 130.1 (2×), 130.8 (2×), 130.9 (2×), 132.9, 138.22, 143.0, 143.9, 144.2, 144.5, 166.7, 166.9; IR ν_{max} (acetone) 3002, 2948, 2920, 2850, 1720, 1609, 1454, 1375, 1267, 1175, 1102, 1020, 868, 751, 688 cm^{-1}; HRMS (FAB^+) calcd for $C_{31}H_{32}O_5$+Na^+: 507.2147, found: 507.2162. R_f (3:1 hexane/EtOAc)=0.64.

4.7. General procedure for cyclotrimerization of 8 with diynes 2

Into a solution of **8α** or **8β** (0.2 mmol, 90 mg) in dry CH_3CN (4.5 mL) were added $RhCl(PPh_3)_3$ (0.02 mmol, 18.5 mg) and diyne **2** (0.30 mmol). The reaction mixture was stirred in a microwave reactor for 1 h (internal temperature reached 180 °C). Then, volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (3:1 hexane/EtOAc) afforded a title compound.

4.7.1. 1α-(2,2-Bis(ethoxycarbonyl)-6-phenylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10αa**)

Compound **8α** (0.2 mmol, 90 mg), **2a** (0.3 mmol, 71 mg); 51 mg (37%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −13.7 (*c* 0.0027, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 0.885 (3H, t, *J* 7.2 Hz), 0.889 (3H, t, *J* 7.5 Hz), 1.91–2.05 (1H, m), 1.98 (3H, s), 2.02 (3H, s), 2.30–2.39 (1H, m), 3.70–3.84 (4H, m), 3.89–3.98 (4H, m), 4.25 (1H, dd, *J* 11.6, 5.1 Hz), 4.37 (1H, dd, *J* 12, 5.7 Hz), 4.64 (1H, td, *J* 5.2, 2.4 Hz), 5.31–5.36 (1H, m), 5.37–5.42 (1H, m), 6.86–6.92 (2H, m), 7.00–7.03 (6H, m), 7.10–7.14 (2H, m), 7.88 (1H, s), 8.04–8.09 (4H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.6 (2×), 22.0, 22.1, 41.5, 41.7, 61.7, 62.3 (2×), 65.6, 77.8, 78.3, 78.6, 83.4, 123.1, 124.9, 126.8, 127.3, 127.6 (2×), 130.0 (2×), 130.1 (2×), 130.4 (2×), 130.8 (4×), 136.6, 140.2, 140.4, 140.7, 140.9, 142.5, 144.0, 144.5, 166.6, 166.8, 172.2, 172.4; IR ν_{max} (acetone) 2985, 2917, 1721, 1709, 1610, 1443, 1365, 1266, 1239, 1176, 1105, 1069, 1018, 907, 841, 755, 701 cm^{-1}; HRMS (EI) calcd for $C_{42}H_{42}O_9$: 690.2618, found: 690.2597. R_f (3:1 hexane/EtOAc)=0.44.

4.7.2. 1β-(2,2-Bis(ethoxycarbonyl)-6-phenylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10βa**)

Compound **8β** (0.2 mmol, 90 mg), **2a** (0.3 mmol, 71 mg); 55 mg (40%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −21.1 (*c* 0.0256, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 0.87 (3H, t, *J* 7 Hz), 0.89 (3H, t, *J* 7 Hz), 1.99 (3H, s), 2.02 (3H, s), 2.00–2.15 (2H, m), 3.60–3.83 (4H, m), 3.89–9.95 (4H, m), 4.19 (1H, td, *J* 5.2, 2.4 Hz), 4.56 (1H, dd, *J* 11.7, 4.2 Hz), 4.67 (1H, dd, *J* 11.7, 4.2 Hz), 5.38–5.43 (1H, m), 5.45–5.52 (1H, m), 6.87–6.98 (7H, m), 7.12–7.18 (3H, m), 7.79 (1H, s), 7.90–7.94 (2H, m), 8.18–8.22 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 14.6 (2×), 22.1 (2×), 30.9, 41.4, 41.5, 42.9, 61.6, 62.2, 65.5, 78.2, 78.8, 83.6, 123.0, 126.5, 127.8, 128.4, 128.6, 129.6 (2×), 130.0 (2×), 130.2 (2×), 130.4 (2×), 130.8 (2×), 130.9 (2×), 132.7, 138.7, 140.5, 141.1, 142.4, 144.3, 166.4, 166.9, 172.1, 172.3; IR ν_{max} (acetone) 3027, 2979, 2956, 2923, 2851, 1727, 1610, 1454, 1365, 1269, 1242, 1179, 1108, 1066, 1018, 868, 800, 752, 701 cm^{-1}; HRMS (EI) calcd for $C_{42}H_{42}O_9$: 690.261754, found: 690.262748. R_f (3:1 hexane/EtOAc)=0.44.

4.7.3. 1α-(2,2-Diacetyl-6-phenylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10αb**)

Compound **8α** (0.2 mmol, 90 mg), **2b** (0.3 mmol, 53 mg); 15 mg (12%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −35.9 (*c* 0.0123, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.69 (3H, s), 1.72 (3H, s), 1.97 (3H, s), 2.03 (3H, s), 2.03–2.09 (1H, m), 2.30–2.44 (1H, m), 3.20–3.46 (4H, m), 4.28 (1H, dd, *J* 11.6, 4.8 Hz), 4.39 (1H, dd, *J* 11.6, 5.6 Hz), 4.71 (1H, td, *J* 5.2, 2.4 Hz), 5.30–5.33 (1H, m), 5.42 (1H, apparent t, *J* 7.2 Hz), 6.85–6.89 (2H, m), 6.90 (1H, s), 6.98–7.01 (2H, m), 7.10–7.20 (5H, m), 7.82 (1H, s), 8.01–8.04 (2H, m), 8.06–8.09 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0, 22.1, 26.6, 26.7, 38.2, 38.3, 41.6, 65.6, 75.7, 77.9, 78.6, 83.5, 123.2, 126.9, 128.0, 128.6 (one signal is overlapped by solvent signal), 128.8 (2×), 129.2 (2×), 130.1 (2×), 130.2 (2×), 130.3 (2×), 130.8 (2×), 140.0, 140.4, 140.5, 140.9, 142.4, 144.1, 144.6, 166.6, 166.8, 204.2, 204.3; IR ν_{max} (acetone) 2926, 2853, 1723, 1710, 1704, 1612, 1441, 1359, 1270, 1207, 1178, 1106, 1017, 754, 703 cm^{-1}; HRMS (FAB^+) calcd for $C_{40}H_{37}O_8$+Na^+: 653.2515, found: 653.2504. R_f (3:1 hexane/EtOAc)=0.35.

4.7.4. 1β-(2,2-Diacetyl-6-phenylindan-5-yl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10βb**)

Compound **8β** (0.2 mmol, 90 mg), **2b** (0.3 mmol, 53 mg); 25 mg (20%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −12.1 (*c* 0.0075, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.65 (3H, s), 1.71 (3H, s), 2.00 (3H, s), 2.02 (3H, s), 2.00–2.15 (2H, m), 3.02–3.32 (4H, m), 4.20 (1H, td, *J* 3.6, 2.4 Hz), 4.52 (1H, dd, *J* 11.6, 4 Hz), 4.77 (1H, dd, *J* 11.6, 4 Hz), 5.41–5.54 (1H, m), 5.50–5.52 (1H, m), 6.90 (1H, s), 6.89–6.92 (2H, m), 6.93–6.96 (2H, m), 7.14–7.24 (5H, m), 7.73 (1H, s), 7.93–7.95 (2H, m), 8.19–8.21 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.1 (2×), 26.6, 26.7, 38.1, 38.2, 43.0, 65.5, 75.6, 78.2, 78.8, 83.7, 123.1, 126.5, 127.9, 128.6 (two signals are overlapped by solvent signal), 128.8 (2×), 130.0 (2×), 130.2 (2×), 130.4 (2×), 130.7 (2×), 130.9 (2×), 138.8, 140.3, 140.9, 141.0, 142.3, 144.4, 166.4, 166.9, 204.2, 204.3; IR ν_{max} (acetone) 2953, 2917, 2851, 1715, 1700, 1610, 1478, 1440, 1356,

1269, 1206, 1108, 1018, 841, 752, 707 cm^{-1}; HRMS (FAB^+) calcd for $C_{40}H_{37}O_8+Na^+$: 653.2515, found: 653.2506. R_f (3:1 hexane/EtOAc)=0.35.

*4.7.5. 1α-(6-Phenylindanyl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10αg**)*

Compound **8α** (0.2 mmol, 90 mg), **2g** (0.3 mmol, 28 mg); 17 mg (16%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −16 (*c* 0.0075, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.80–1.88 (2H, m), 1.98 (6H, s), 2.09–2.14 (1H, m), 2.40–2.44 (1H, m), 2.58–2.82 (4H, m), 4.28 (1H, dd, *J* 11.6, 4.8 Hz), 4.40 (1H, dd, *J* 11.6, 4.8 Hz), 4.66–4.69 (1H, m), 5.34–5.37 (1H, m), 5.44–5.47 (1H, m), 6.86–7.03 (7H, m), 7.10–7.14 (1H, m), 7.26–7.28 (2H, m), 7.92 (1H, s), 8.03–8.07 (4H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.1 (2×), 26.6, 33.4, 33.5, 41.7, 65.7, 78.0, 78.7, 83.3, 123.1, 125.1, 125.5, 126.8, 127.5, 127.7, 130.0 (2×), 130.5 (2×), 130.8 (2×), 130.8 (2×), 139.1, 140.2, 141.2, 142.2, 143.0, 143.9, 144.0, 144.4, 144.4, 145.0, 166.6, 166.8; IR ν_{max} (acetone) 3404, 3065, 3034, 2923, 2850, 1720, 1710, 1609, 1448, 1406, 1372, 1264, 1178, 1102, 1020, 878, 840, 751, 691 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{34}O_5$: 546.2195, found: 546.2205. R_f (3:1 hexane/EtOAc)=0.64.

*4.7.6. 1β-(6-Phenylindanyl)-1,2-dideoxy-3,5-di-O-(4-toluoyl)-D-ribofuranose (**10βg**)*

Compound **8β** (0.2 mmol, 90 mg), **2g** (0.3 mmol, 28 mg); 41 mg (38%) of the title compound as a yellowish oil; $[\alpha]_D^{20}$ −17.5 (*c* 0.0080, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.77–1.87 (2H, m), 1.97 (3H, s), 1.99 (3H, s), 2.07–2.21 (2H, m), 2.66–2.71 (4H, m), 4.19–4.23 (1H, m), 4.64 (1H, dd, *J* 11.6, 4.4 Hz), 4.70 (1H, dd, *J* 11.6, 4.4 Hz), 5.45–5.49 (1H, m), 5.51–5.53 (1H, m), 6.88–6.91 (7H, m), 7.04 (1H, s), 7.29–7.31 (2H, m), 7.81 (1H, s), 7.92–7.96 (2H, m), 8.19–8.23 (2H, m); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0, 22.1, 26.4, 33.5, 33.6, 43.0, 65.6, 78.2, 78.9, 83.5, 123.0, 126.5, 128.0 (two signals are overlapped by solvent signal), 129.2, 130.0 (2×), 130.0 (2×), 130.5 (2×), 130.8 (2×), 130.9 (2×), 137.5, 140.3, 142.9, 144.1, 144.2, 144.3, 144.8, 166.4, 166.8; IR ν_{max} (acetone) 3026, 2952, 2922, 2848, 1719, 1611, 1455, 1373, 1265, 1174, 1100, 1018, 750, 698 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{34}O_5$: 546.2195, found: 546.2205. R_f (3:1 hexane/EtOAc)=0.64.

Acknowledgements

This project was supported by Project No. 1M0508 to the Centre for New Antivirals and Antineoplastics, and projects MSM0021620857 and Z40550506 from Ministry of Education of the Czech Republic.

References and notes

1. For recent review, see: Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741–4767 and references therein.
2. Kaufman, R. J.; Sidhu, R. S. *J. Org. Chem.* **1982**, *47*, 4941–4947.
3. (a) Das, S. K.; Roy, R. *Tetrahedron Lett.* **1999**, *40*, 4015–4018; (b) Dominique, R.; Liu, B.; Das, S.; Roy, D. *Synthesis* **2000**, 862–868.
4. McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605–6606.
5. (a) Yamamoto, Y.; Saigoku, T.; Ohgai, T.; Nishiyama, H.; Itoh, K. *Chem. Commun.* **2004**, 2702–2703; (b) Yamamoto, Y.; Saigoku, T.; Nishiyama, H.; Ohgai, T.; Itoh, K. *Org. Biomol. Chem.* **2005**, *3*, 1768–1775; (c) Yamamoto, Y.; Yamashita, K.; Hotta, T.; Hashimoto, T.; Kuikuchi, M.; Nishiyama, H. *Chem.—Asian J.* **2007**, *2*, 1388–1399.
6. Yamamoto, Y.; Hashimoto, T.; Hattori, K.; Kikuchi, M.; Nishiyama, H. *Org. Lett.* **2006**, *8*, 3565–3568.
7. Adamo, M. F. A.; Pergoli, R. *Org. Lett.* **2007**, *9*, 4443–4446.
8. Recent examples: (a) Kim, Y.; Leconte, A. M.; Hari, Y.; Romesberg, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 7809–7812; (b) Leconte, A. M.; Matsuda, S.; Hwang, G. T.; Romesberg, F. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 4326–4329; (c) Matsuda, S.; Leconte, A. M.; Romesberg, F. E. *J. Am. Chem. Soc.* **2007**, *129*, 5551–5557.
9. Recent examples: (a) Beuck, C.; Singh, I.; Bhattacharya, A.; Hecker, W.; Parmar, V.; Seitz, O.; Weinhold, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3958–3960; (b) Yakovleva, L.; Lal, J.; Kool, E. T.; Shuman, S. *J. Biol. Chem.* **2006**, *281*, 35914–35921; (c) Somoza, A.; Chelliserrykattil, J.; Kool, E. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 4994–4997.
10. Reviews: (a) Wu, Q. P.; Simons, C. *Synthesis* **2004**, 1533–1553; (b) Wellington, W. E.; Benner, S. A. *Nucleosides Nucleotides Nucleic Acids* **2006**, *25*, 1309–1333.
11. (a) Hocek, M.; Pohl, R.; Klepetářová, B. *Eur. J. Org. Chem.* **2005**, 4525–4528; (b) Urban, M.; Pohl, R.; Klepetářová, B.; Hocek, M. *J. Org. Chem.* **2006**, *71*, 7322–7328; (c) Joubert, N.; Pohl, R.; Klepetářová, B.; Hocek, M. *J. Org. Chem.* **2007**, *72*, 6797–6805.
12. (a) Turek, P.; Kotora, M.; Hocek, M.; Cisařová, I. *Tetrahedron Lett.* **2003**, *44*, 785–788; (b) Turek, P.; Kotora, M.; Tišlerová, I.; Hocek, M.; Votruba, I.; Císařová, I. *J. Org. Chem.* **2004**, *69*, 9224–9233; (c) Turek, P.; Novák, P.; Pohl, R.; Hocek, M.; Kotora, M. *J. Org. Chem.* **2006**, *69*, 8978–8981.
13. Novák, P.; Pohl, R.; Hocek, M.; Kotora, M. *Org. Lett.* **2006**, *8*, 2051–2054.
14. For review, see: Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731–1769.
15. For examples on Grubbs first generation carbene complex catalyzed cyclotrimerizations, see: (a) Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983–1984; (b) Witulski, B.; Stengel, T.; Fernández-Hernández, J. M. *Chem. Commun.* **2000**, 1965–1966.
16. (a) Hrdina, R.; Kadlčíková, A.; Valterová, I.; Hodačová, J.; Kotora, M. *Tetrahedron: Asymmetry* **2006**, *17*, 3185–3191; (b) Hrdina, R.; Valterová, I.; Hodačová, J.; Kotora, M. *Adv. Synth. Catal.* **2007**, *349*, 822–826.
17. (a) Zhou, Y.; Porco, J. A.; Snyder, J. K. *Org. Lett.* **2007**, *9*, 393–396; (b) Young, D. D.; Deiters, A. *Angew. Chem., Int. Ed.* **2007**, *47*, 5178–5190.
18. Shanmugasundaram, M.; Aguirre, A. L.; Leyva, M.; Quan, B.; Martinez, L. F. *Tetrahedron Lett.* **2007**, *48*, 7698–7701.
19. Yamamoto, Y.; Okuda, S.; Itoh, K. *Chem. Commun.* **2001**, 1102–1103.
20. (a) Meriwether, L. S.; Colthup, E. C.; Kennerly, G. W.; Reusch, R. N. *J. Org. Chem.* **1961**, *26*, 5155–5163; (b) Colthup, E. C.; Meriwether, L. S. *J. Org. Chem.* **1961**, *26*, 5169–5175; (c) Chalk, A. J.; Jerussi, R. A. *Tetrahedron Lett.* **1972**, 61–62; (d) Müller, E.; Scheller; Winter, W.; Wagner, F.; Meier, H. *Chem.-Ztg.* **1975**, *99*, 155–157; (e) Scheller; Winter, W.; Müller, E. *Liebigs Ann. Chem.* **1976**, 1448–1454.
21. Osborne, J. A.; Jardine, F. H.; Young, F. H.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711–1732.