Synthesis of Carbohydrate-Derived Enynes and Subsequent Metathesis to Yield Polyhydroxylated 1-Vinylcycloalkenes

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In this paper, a new route toward polyhydroxylated 1-vinylcycloalkenes is presented. 1,6- and 1,7-enynes were synthesized in four steps from glyco-ynitols, which are readily available from monosaccharides. These compounds were then cyclized by ring-closing enyne metathesis to afford the title compounds. For example, we converted (2*R*,3*S*,4*R*)-1-*O*-tritylhept-6-yne-1,2,3,4-tetrol (**1**) to the corresponding 1,7-enyne **13** in 53% yield. The ring-closing metathesis of 1,7-enyne **13** with Grubbs catalyst, under Mori's conditions, produced the corresponding polyhydroxylated 1-vinylcyclohexene **19** in 72% yield. The conversion of several glyco-ynitols into polyhydroxylated 1-vinylcycloalkenes was carried out with satisfying yields.

Introduction

Over the last few years, extensive studies have been undertaken regarding the cyclization of enynes. Enyne metathesis leading to 1-vinylcycloalkenes[1−2] has proved itself to be a powerful, and yet simple, method for the construction of useful ring systems. Our laboratory is involved in the synthesis of carbocycles starting from monosaccharides.[3] Such polyhydroxylated carbocyclic rings are widely found in many biologically important molecules and natural products.[4] These polyhydroxylated rings are also interesting scaffolds for the construction of bridged and fused bicyclic systems. In carbohydrate chemistry, the ring-closing metathesis (RCM) of enynes[5−10] is far less documented in comparison to the RCM of dienes.[11−15] An explanation might be that the available methods for the synthesis of carbohydrate-derived enynes do require a significant number of steps for their preparation.

In this paper, we report the efficient preparation of some 1,6- and 1,7-enynes from monosaccharides as well as their cyclization leading to polyhydroxylated 1-vinylcycloalkenes.

Results and Discussion

Our strategy is based on enyne metathesis, using Grubbs catalysts (first and second generation), of acyclic sugar intermediates **II** derived from readily available compounds **I** (Scheme 1). This study was undertaken on four trityl aldohexose derivatives **1**−**4** and two trityl aldopentose derivatives **5**−**6** to yield the corresponding polyhydroxylated 1-vinylcyclohexene and 1-vinylcyclopentene derivatives **III**.

Synthesis of Polyhydroxylated 1,6- and 1,7-Enynes

As shown in Scheme 2, enynes were readily available intermediates obtained in four steps from trityl sugar derivatives.

Recently, we reported the synthesis of 1,1-dibromoalkenes[16] from partially protected and unprotected aldoses and their transformation into glyco-ynitols.[17] The 1,1-dibromo-1-alkenes were obtained by the reaction of (dibromomethyl)triphenylphosphonium bromide with aldoses in the presence of zinc in 1,4-dioxane under reflux. The reaction of these dibromo-olefins with *n*-butyllithium in THF at low temperature afforded the corresponding alkynes. For example, when the reaction is performed on 2-deoxy-6-*O*-trityl-D-glucose, the corresponding 1,1-dibromo-1-olefin is obtained in 63% yield and the reaction of this olefin with *n*BuLi affords the corresponding alkyne **1** in 67% yield. Such glyco-ynitols are obtained from monosaccharides with a one-carbon-atom chain elongation without creating a stereogenic center.

We now report that these glyco-ynitols **1**−**6** can be subjected to a benzylation reaction followed by deprotection of the primary hydroxy group to obtain the corresponding glyco-ynitols **7**−**12**. The benzylated compounds are readily prepared by using benzyl bromide and sodium hydride in DMF at 25 °C. The removal of the trityl group failed when using mild conditions. In concentrated HCl, however, the deprotection takes place quickly to yield the primary alcohol. For example, the benzylation of starting material **1**, followed by acidic treatment with HCl in a mixture of

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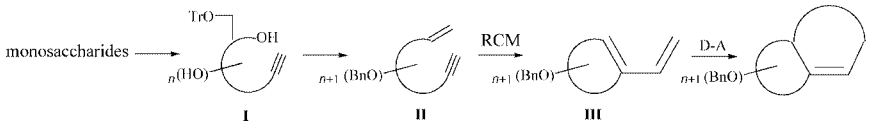
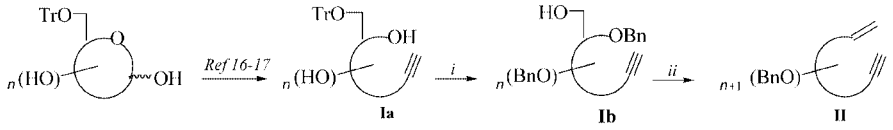


Scheme 1



i : 1/ NaH, BnBr, TBAI, DMF, room temp., 12 h. 2/ HCl, MeOH/$CHCl_3$, room temp., 15 min.

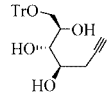
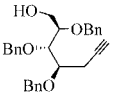
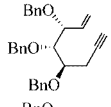
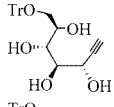
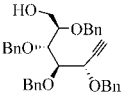
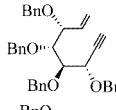
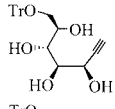
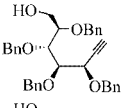
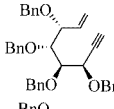
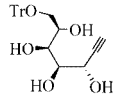
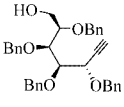
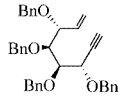
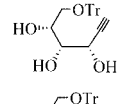
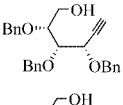
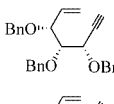
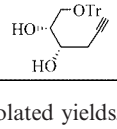
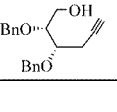
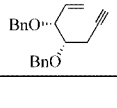
ii : 1/ NMO, TPAP, molecular sieves, CH_2Cl_2, room temp., 20 min. 2/ *t*BuOK, $Ph_3\overset{\oplus}{P}CH_3$, $\overset{\ominus}{Br}$, room temp., 15 min.

Scheme 2

$MeOH/CHCl_3$ at 25 °C, afforded the compound **7** in 76% yield.

The alcohols **7**−**12** were then oxidized with a catalytic amount of tetrapropylammonium perruthenate (TPAP) in the presence of *N*-methylmorpholine N-oxide (NMO) (1.8 equiv.) as co-oxidant. Unfortunately, the carbonyl compounds decomposed during the usual workup on silica gel. The alcohols **7**−**12** were successfully converted, however, into enynes **13**−**18** by a one-pot reaction involving treatment with TPAP and NMO in CH_2Cl_2 at 25 °C followed by addition of preformed methylenetriphenylphosphorane. For example, the compound **7**, treated successively by the oxidation agent and the ylide, led to the 1,7-enyne **13** in 70% yield. The other 1,7-enynes and 1,6-enynes **14**−**18** were synthesized from glyco-ynitols **2**−**6** with satisfying yields (Table 1).

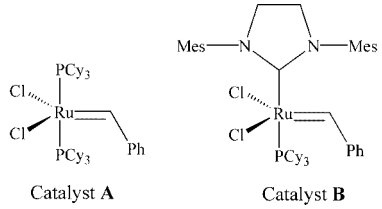
Table 1. Synthesis of polyhydroxylated enynes from glyco-ynitols

Glyco-ynitols **Ia**		Glyco-ynitols **Ib**		Yields [a]	Enynes **II**		Yields [a]
1		**7**		76%	**13**		70%
2		**8**		70%	**14**		80%
3		**9**		60%	**15**		63%
4		**10**		69%	**16**		62%
5		**11**		78%	**17**		69%
6		**12**		81%	**18**		64%

[a] Isolated yields.

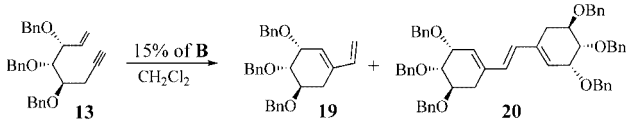
Enyne Metathesis

The 1,6- and 1,7-enynes **13**−**18** prepared above were subjected to ring-closing metathesis catalysts. Ruthenium carbene complexes, Grubbs catalysts (first (**A**) or second generation (**B**); Scheme 3), commonly employed in olefin metathesis also catalyze enyne metathesis.



Scheme 3

Metathesis of compound **13** with Grubbs catalyst **B** (15% mol.) was performed in CH_2Cl_2 at 40 °C under an argon atmosphere to afford a mixture containing the desired 1,3-vinylcyclohexene **19** together with a dimer **20** (Scheme 4), and numerous by-products. The isolated yields of **19** and **20** were 30 and 20%, respectively. The formation of by-products during enyne metathesis with Grubbs catalyst under an argon atmosphere has been observed previously, first by Mori[18] and, more recently, by Madsen.[5]



Conditions :

Argon atmosphere, 40°C, 2h45	30%	20%
Ethylene atmosphere, room temp., 3h	72%	traces

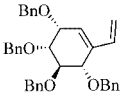
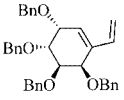
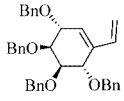
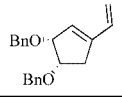
Scheme 4

If the reaction is run, however, under an ethylene atmosphere at room temperature, i.e., Mori's conditions,[18] the desired 1,3-vinylcyclohexene **19** was obtained in 72% yield and only traces of dimer **20** were observed. The structure of **19** was resolved by NMR spectroscopy experiments, with the characteristic resonances observed at δ = 114.2, 139.9, 136.9 and 126.5 ppm attributed to C-2′, C-1′, C-1 and C-

2, respectively, and those at δ = 5.24, 5.12, 6.41 and 5.80 ppm attributed to 2′a-H, 2′b-H, 1′-H, 2-H, respectively. Subsequent 2D-NOESY studies confirmed this structure. The structure of **20** was also confirmed by ^{1}H and ^{13}C NMR spectroscopy and a characteristic ion at *m*/*z* = 849.05 was attributed to $[M + Na]^+$ in its mass spectrum (FAB-MS). This reaction needs a significant loading of Grubbs catalyst to bring it to completion.

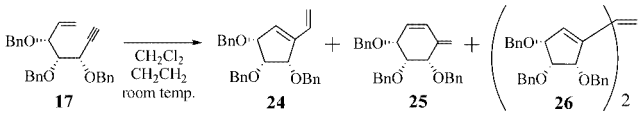
We extended the ruthenium-catalyzed metathesis, using Mori's conditions, to 1,7-enynes (Table 2) with the ruthenium catalyst (15% mol.) in CH_2Cl_2 at room temperature under an ethylene atmosphere. Under these conditions, metathesis of D-*gluco* **14**, D-*manno* **15** and D-*galacto* **16** affords the corresponding 1,3-vinylcyclohexenes **21**, **22** and **23** with yields of 66, 55 and 68%, respectively. When the alkyne is an α-substituted one, we noticed a drop in reactivity (increased reaction time) and a slightly poorer yield. In addition, there is an effect on the yields of the relative configuration at the α-carbon center: in the series of D-*gluco* **21** and D-*galacto* **23**, the yields are better than those in the series of D-*manno* **22**.

Table 2. Ring-closing enyne metathesis with Grubbs catalyst

Enynes **II**	Products **III**	Yields [a]	Conditions
14		**21** : 66%	15% of **B** (24h)
15		**22** : 55%	15% of **B** (46h)
16		**23** : 68%	15% of **B** (24h)
18		**27** : 50% **27** : 55%	15% of **B** (5h) 30% of **A** (48h)

[a] Isolated yields.

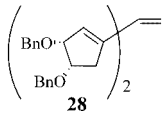
We then extended these conditions to 1,6-enynes **17** and **18**. When **17** was reacted with 15% of **B** at room temperature in CH_2Cl_2 for 30 h under ethylene, however, only a 40% yield of the corresponding 1-vinylcyclopentene **24** was obtained, together with a six-membered by-product **25** and the dimer **26** in 25 and 5% yields, respectively (Scheme 5). In the ^{13}C NMR spectrum of **25**, characteristic resonances are observed at δ = 113.6, 141.6, 129.9 and 127.7 ppm, which are attributed to C-1′, C-1, C-2 and C-3, respectively, and at δ = 5.52 (s), 5.25 (s), 6.32 (dd) and 5.76 ppm (dd), which are attributed to 1′a-H, 1′b-H, 2-H and 3-H, respectively. Subsequent 2D-NOESY studies confirmed its structure. The use of the first-generation catalyst **A** did not afford a better yield in 1,3-vinylcyclopentene **24** (38%; 43% based on recovered **17**), but we did notice the absence of isomer **25**, even after 96 h. A similar observation regarding obtaining this isomer has already been made by Mori et al.,[19−20] who described a possible explanation for the formation of the six-membered ring. It is thought that there are two pathways for the reaction of the alkyne moiety of the enyne with the methylidene ruthenium carbene complex.



Conditions :
15% of **B** (30h) 40% 25% 5%
30% of **A** (96h) 38% - 5%

Scheme 5

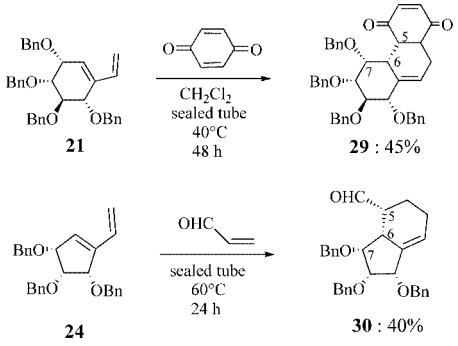
Metathesis of compound **18** afforded a mixture of the desired 1,3-vinylcyclopentene **27**, in 50% yield, together with the dimer **28** (Scheme 6) in 10% yield. We detected only a very small amount of a six-membered by-product. The use of catalyst **A** (30% mol.) afforded 1-vinylcyclopentene **27** in 55% yield after 48 h.



Scheme 6

Diels−Alder Reaction

These polyhydroxylated carbocyclic rings are interesting scaffolds for the construction of bridged and fused bicyclic systems. As an application for these 1-vinylcycloalkenes, compounds **21** and **24** were selected for Diels−Alder reactions (Scheme 7).



Scheme 7

In the first case, the 1-vinylcyclohexene **21** was reacted with 1,4-benzoquinone in CH_2Cl_2 at 40 °C in a sealed tube for 48 h to give mainly the Diels−Alder adduct **29**, which was isolated in 45% yield. Only trace amounts were observed of some other isomers. The structure of **29** was established by analysis of its NMR spectroscopic and mass spectrometric data. In its ^{1}H NMR spectrum, we observe J_{5-6} = 10.1 Hz and J_{6-7} = 2.5 Hz. Subsequent 2D-

NOESY studies confirmed the structure: NOE crosspeaks are observed between 6-H/7-H and 6-H/13a-H.

In the second case, the 1-vinylcyclopentene **24** was treated with an acrolein solution at 60 °C in a sealed tube for 24 h. Only one Diels−Alder adduct **30** was isolated in 40% yield. The structure of product **30** was established by analysis of its NMR and mass spectral data. In its ^{1}H NMR spectrum, we observe J_{5-6} = 3.8 Hz and J_{6-7} = 3.8 Hz. Subsequent 2D-NOESY studies verified the structure: NOE crosspeaks are observed between 5-H/6-H and 6-H/7-H. These two Diels−Alder products were obtained through an endo attack from the same face of the α-substituents.

We are pursuing our studies on further uses of the polyhydroxylated 1-vinylcycloalkenes provided by our methodology.

Conclusion

In summary, several 1,6- and 1,7-enynes were obtained in a versatile manner in five steps from monosaccharides with satisfying yields. The enynes were subjected to ring-closing metathesis reactions mediated by ruthenium carbene complexes to obtain polyhydroxylated 1-vinylcyclohexenes and 1-vinylcyclopentenes, which are useful chiral building blocks.

Experimental Section

General Remarks: Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. THF was distilled from lithium aluminum hydride immediately before use. CH_2Cl_2 was distilled from calcium chloride under argon. Moisture-sensitive reactions were conducted in oven-dried glassware under an argon atmosphere. Flash chromatography was carried out on Kieselgel 60 (230−400 mesh, Merck) and analytical thin-layer chromatography (TLC) was performed on E. Merck glass-backed silica gel sheets (Silica Gel 60 F_{254}). Optical rotations were measured with a Jasco DIP-370 digital polarimeter using a sodium lamp (λ = 589 nm) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WB 300 spectrometer at 300 and 75 MHz, respectively. Spectra were recorded in $CDCl_3$ and chemicals shifts (δ) were expressed in ppm relative to residual $CHCl_3$ or an internal standard. All signals in ^{13}C NMR spectra were assigned through C,H-correlated spectra. IR spectra were recorded as neat films (NaCl cell) and KBr pellets (for solids) with a Nicolet 205 spectrometer. Microanalyses were performed at the Service de Microanalyse de l'Université de Champagne-Ardenne in Reims. Infusion electrospray mass spectra in the positive-ion mode were obtained with an updated (3.6 GHz TDC) Micromass Q-TOF hybrid quadrupole/time-of-flight instrument, equipped with a pneumatically assisted electrospray ion source (Z-spray).

General Procedure 1 for the Synthesis of Compounds 7−12: Tetrabutylammonium iodide (0.2 equiv.) was added to a solution of glyco-1-ynitol **1**−**6** (1.33 mmol) in DMF (18 mL). The mixture was stirred in an ice bath. NaH (1.2 equiv./OH) was added, followed by benzyl bromide (1.2 equiv./OH unit). The mixture was stirred under argon at room temperature for 12 h and was monitored by TLC. After concentration, the crude residue was dissolved by the addition of EtOAc (15 mL). The organic layer was washed with H_2O (15 mL), dried (Na_2SO_4) and concentrated. The crude residue was dissolved by the addition of an MeOH/$CHCl_3$ mixture (20 mL, v/v: 1:1) and then concd. HCl (3 mL) was added. After stirring at room temperature for 15 min, the mixture was concentrated. After extraction with EtOAc/H_2O, the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude residue was purified by flash chromatography to afford the corresponding products **7−11**.

(2*R*,3*S*,4*R*)-2,3,4-Tri-*O*-benzylhept-6-yne-1,2,3,4-tetrol (7): The compound **7** was prepared by general procedure **1** from (2*R*,3*S*,4*R*)-1-*O*-tritylhept-6-yne-1,2,3,4-tetrol (**1**) (537 mg, 1.33 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 9:1, then 8:2) and **7** was obtained as a colorless oil in 76% yield (440 mg). R_f = 0.18 (hexane/EtOAc, 8:2). $[\alpha]_D^{23}$ = −15 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300 and 2100 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 4.84, 4.78, 4.71, 4.57, 4.51, 4.42 (d, PhCH_2), 3.99 (dd, J_{2-3} = 7.0, J_{3-4} = 3.1 Hz, 3-H), 3.94 (dd, J_{1a-2} = 8.0, J_{1a-1b} = 12.0 Hz, 1a-H), 3.89 (m, 4-H), 3.83 (dd, J_{1b-2} = 3.4 Hz, 1b-H), 3.78 (ddd, 2-H), 2.63 (m, J_{5a-7} = J_{5b-7} = 2.7 Hz, J_{5a-5b} = 6.7 Hz, 5a-H, 5b-H), 2.07 (t, 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.5−128.2 (C_6H_5), 81.5 (C-6), 79.4 (C-2), 79.1 (C-3), 77.9 (C-4), 75.6, 72.7, 72.1 (CH_2Ph), 71.2 (C-7), 60.8 (C-1), 20.8 (C-5) ppm. $C_{28}H_{30}O_4$: calcd. C 78.11, H 7.02; found C 78.25, H 6.95; ES-MS: m/z = 453.2 [M + Na]$^+$.

(2*R*,3*R*,4*R*,5*S*)-2,3,4,5-Tetra-*O*-benzylhept-6-yne-1,2,3,4,5-pentol (8): The compound **8** was prepared by general procedure **1** from (2*R*,3*R*,4*R*,5*S*)-1-*O*-tritylhept-6-yne-1,2,3,4,5-pentol (**2**) (196 mg, 0.468 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 8:2) and **8** was obtained as a colorless oil in 70% yield (174 mg). R_f = 0.53 (hexane/EtOAc, 7:3). $[\alpha]_D^{23}$ = +34 (c = 1.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300, 2100 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 5.01, 4.94, 4.86, 4.81, 4.69, 4.64, 4.60 (dd, J_{4-5} = 7.4, J_{5-7} = 2.1 Hz, 5-H), 4.57, 4.41 (d, PhCH_2), 4.26 (dd, J_{2-3} = 6.4, J_{3-4} = 3.3 Hz, 3-H), 4.01 (dd, 4-H), 3.96 (dd, J_{1a-2} = 2.9, J_{1a-1b} = 14.1 Hz, 1a-H), 3.84 (dd, J_{1b-2} = 3.2 Hz, 1b-H), 3.80 (ddd, 2-H), 2.65 (d, 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.9−128.2 (C_6H_5), 81.3 (C-4), 80.9 (C-6), 79.5 (C-3), 79.1 (C-2), 77.2 (C-7), 75.5, 75.3, 71.9, 71.8 (CH_2Ph), 71.8 (C-5), 60.6 (C-1) ppm. $C_{35}H_{36}O_5$: calcd. C 78.33, H 6.76; found C 78.49, H 6.42. ES-MS: m/z = 559.2 [M + Na]$^+$.

(2*R*,3*R*,4*R*,5*R*)-2,3,4,5-Tetra-*O*-benzylhept-6-yne-1,2,3,4,5-pentol (9): The compound **9** was prepared by general procedure **1** from (2*R*,3*R*,4*R*,5*R*)-1-*O*-tritylhept-6-yne-1,2,3,4,5-pentol (**3**) (330 mg, 0.79 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 85:15, then 8:2) and **9** was obtained as a colorless oil in 60% yield (254 mg). R_f = 0.26 (hexane/EtOAc, 8:2). $[\alpha]_D^{25}$ = −35 (c = 0.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300, 2100 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.20 (m, C_6H_5), 5.07, 4.91, 4.78, 4.70, 4.68, 4.63, 4.59, 4.51 (dd, J_{4-5} = 6.8, J_{5-7} = 2.0 Hz, 5-H), 4.43 (d, PhCH_2), 4.10 (dt, J_{1a-2} = J_{1b-2} = 3.3, J_{2-3} = 6.6 Hz, 2-H), 4.00 (dd, J_{3-4} = 3.4 Hz, 4-H), 3.96 (dd, J_{1a-1b} = 11.7 Hz, 1a-H), 3.84 (dd, 1b-H), 3.79 (dd, 3-H), 2.64 (d, 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.7−128.0 (C_6H_5), 81.8 (C-6), 81.0 (C-4), 79.5 (C-3), 78.3 (C-2), 75.1, 74.9, 71.7, 71.0 (CH_2Ph, C-7), 69.4 (C-5), 60.7 (C-1) ppm. $C_{35}H_{36}O_5$: calcd. C 78.33, H 6.76; found C 78.52, H 6.59. ES-MS: m/z = 559.2 [M + Na]$^+$.

(2*R*,3*S*,4*R*,5*S*)-2,3,4,5-Tetra-*O*-benzylhept-6-yne-1,2,3,4,5-pentol (10): The compound **10** was prepared by general procedure **1** from (2*R*,3*S*,4*R*,5*S*)-1-*O*-tritylhept-6-yne-1,2,3,4,5-pentol (**4**) (464 mg, 1.11 mmol). The crude residue was purified by flash chromatogra-

phy (hexane/EtOAc, 85:15) and **10** was obtained as a colorless oil in 69% yield (410 mg). R_f = 0.24 (hexane/EtOAc, 8:2). $[\alpha]_D^{24}$ = +18 (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300, 2100 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.20 (m, C_6H_5), 5.04, 4.94, 4.73, 4.66, 4.68, 4.66 (dd, J_{4-5} = 6.0, J_{5-7} = 2.2 Hz, 5-H), 4.57, 4.55 (d, PhCH_2), 4.07 (dd, J_{3-4} = 5.0 Hz, 4-H), 4.04 (ddd, 2-H), 3.80 (m, 1a-H, 1b-H, 3-H), 2.62 (d, 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.5−128.0 (C_6H_5), 81.8 (C-4), 81.6 (C-6), 79.6 (C-3), 78.7 (C-2), 76.7 (C-7), 75.4, 73.8, 72.9, 71.5 (CH_2Ph), 69.5 (C-5), 62.0 (C-1) ppm. $C_{35}H_{36}O_5$: calcd. C 78.33, H 6.76; found C 78.59, H 6.53. MS: *m*/*z* = 559.7 $[M + Na]^+$.

(2*R*,3*S*,4*S*)-2,3,4-Tri-*O*-benzylhex-5-yne-1,2,3,4-tetrol (11): The compound **11** was prepared by general procedure **1** from (2*R*,3*S*,4*S*)-1-*O*-tritylhex-5-yne-1,2,3,4-tetrol (**5**) (574 mg, 1.05 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 85:15) and **11** was obtained as a colorless oil in 78% yield (343 mg). R_f = 0.20 (hexane/EtOAc, 8:2). $[\alpha]_D^{23}$ = +76 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300, 2100 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.20 (m, C_6H_5), 5.01, 4.98, 4.79, 4.67, 4.64, 4.61 (d, PhCH_2), 4.61 (dd, J_{3-4} = 3.4, J_{4-6} = 2.2 Hz, 4-H), 4.03 (dd, J_{2-3} = 6.9 Hz, 3-H), 3.85 (dd, J_{1a-1b} = 14.8, J_{1a-2} = 7.0 Hz, 1a-H), 3.80 (m, 1b-H, 2-H), 2.63 (d, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ 138.6−128.3 (C_6H_5), 80.2 (C-3, C-5), 79.3 (C-2), 76.6 (C-6), 74.8, 72.8, 71.5 (PhCH_2), 71.0 (C-4), 61.3 (C-1) ppm. $C_{27}H_{28}O_4$: calcd. C 77.86, H 6.79; found C 78.02, H 6.43. ES-MS: *m*/*z* = 439.5 $[M + Na]^+$.

(2*R*,3*S*)-2,3-Di-*O*-benzylhex-5-yne-1,2,3-triol (12): The compound **12** was prepared by general procedure **1** from (2*R*,3*S*)-1-*O*-tritylhex-5-yne-1,2,3-triol (**6**) (873 mg, 2.34 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 8:2) and **12** was obtained as a colorless oil in 81% yield (600 mg). R_f = 0.37 (hexane/EtOAc, 75:25). $[\alpha]_D^{23}$ = +14 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3300, 2100 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.20 (m, C_6H_5), 4.81, 4.65 (d, PhCH_2), 3.85 (m, 1a-H, 1b-H), 3.82 (m, 3-H), 3.76 (m, 2-H), 2.68 (m, 4a-H, 4b-H), 2.11 (t, J_{4a-6} = J_{4b-6} = 2.0 Hz, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.5−128.5 (C_6H_5), 81.4 (C-5), 80.3 (C-2), 76.7 (C-3), 73.0, 72.9 (CH_2Ph), 71.0 (C-6), 61.3 (C-1), 21.2 (C-4) ppm. $C_{20}H_{22}O_3$: calcd. C 77.39, H 7.14; found C 77.68, H 7.01. ES-MS: *m*/*z* = 333.1 $[M + Na]^+$.

General Procedure 2 for Synthesis of Enyne 13−18: Molecular sieves (4 Å, 0.3 g), NMO (1.8 equiv.) and TPAP (0.08 equiv.) were added successively to the glyco-1-ynitol (0.685 mmol) dissolved in freshly distilled CH_2Cl_2 (8 mL). The reaction was stirred under an argon atmosphere for 20 min at room temperature and was monitored by TLC. The flask was then immersed in a bath of water. Methylenetriphenylphosphorane (5 equiv.), prepared from methyltriphenylphosphonium bromide and *t*BuOK in THF (10 mL) at room temperature under an argon atmosphere for 15 min, was then added. The reaction was stirred under argon for 10 min. The reaction mixture was filtered through silica gel (100 mL). The mixture was concentrated and the residue was purified by flash chromatography.

(4*R*,5*S*,6*R*)-4,5,6-Tri-*O*-benzyloct-7-en-1-yne-4,5,6-triol (13): The compound **13** was prepared by general procedure **2** from **7** (295 mg, 0.685 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 98:2) and **13** was obtained as a colorless oil in 70% yield (204 mg). R_f = 0.54 (hexane/EtOAc, 9:1). $[\alpha]_D^{23}$ = −19 (*c* = 0.5, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2223, 1654 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.08 (ddd, J_{7-8a} = 10.2, J_{7-8b} = 17.2 Hz, 7-H), 5.62 (dt, J_{8a-8b} = 1.4 Hz, 8-Ha), 5.53 (dt, 8-Hb), 4.88, 4.75, 4.73, 4.70, 4.61, 4.34 (d, PhCH_2), 4.23 (tt, J_{5-6} = J_{6-7} = 7.0, J_{6-8a} = J_{6-8b} = 1.4 Hz, 6-H), 4.03 (ddd, J_{3a-4} = 7.7, J_{3b-4} = 6.0, J_{4-5} = 3.5 Hz, 4-H), 3.90 (dd, 5-H), 2.64 (m, J_{3a-3b} = 7.7 Hz, 3a-H, 3b-H), 2.09 (t, J_{1-3a} = J_{1-3b} = 2.7 Hz, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.5−128.2 (C_6H_5), 136.8 (C-7), 120.0 (C-8), 82.2 (C-5), 81.9 (C-2), 80.5 (C-4, C-6), 75.4, 73.3, 70.9 (C-1), 70.6 (PhCH_2), 21.2 (C-3) ppm. $C_{29}H_{30}O_3$: calcd. C 81.66, H 7.09; found C 81.77, H 6.98. MS: *m*/*z* = 449.2 $[M + Na]^+$.

(3*S*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-benzyloct-7-en-1-yne-3,4,5,6-tetrol (14): The compound **14** was prepared by general procedure **2** from **8** (162 mg, 0.3 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **14** was obtained as a colorless oil in 80% yield (130 mg). R_f = 0.47 (hexane/EtOAc, 9:1). $[\alpha]_D^{30}$ = +31 (*c* = 0.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2218, 1654 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 5.96 (ddd, J_{6-7} = 6.8, J_{7-8a} = 11.2, J_{7-8b} = 16.4 Hz, 7-H), 5.40 (dd, J_{8a-8b} = 1.7 Hz, 8b-H), 5.33 (dd, 8a-H), 4.94, 4.88, 4.77, 4.65, 4.60, 4.57, 4.56, 4.51 (dd, J_{1-3} = 2.0, J_{3-4} = 7.3 Hz, 3-H), 4.15 (d, PhCH_2), 4.04 (m, 4-H, 5-H), 3.94 (br. t, J_{5-6} = 6.8 Hz, 6-H), 2.58 (d, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.9−127.8 (C_6H_5), 136.6 (C-7), 120.2 (C-8), 81.7, 81.4 (C-4, C-5), 81.1 (C-2), 80.5 (C-6), 76.8 (C-1), 75.7, 75.2, 71.6, 71.6 (C-3), 70.4 (PhCH_2) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.43, H 6.70. MS: *m*/*z* = 555.6 $[M + Na]^+$.

(3*R*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-benzyloct-7-en-1-yne-3,4,5,6-tetrol (15): The compound **15** was prepared by general procedure **2** from **9** (240 mg, 0.43 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **15** was obtained as a colorless oil in 63% yield (145 mg). R_f = 0.26 (hexane/EtOAc, 8:2). $[\alpha]_D^{27}$ = −50 (*c* = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2220, 1656 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.02 (ddd, J_{6-7} = 7.5, J_{7-8a} = 10.2, J_{7-8b} = 17.5 Hz, 7-H), 5.62 (br. dd, J_{8a-8b} = 1.5 Hz, 8a-H), 5.53 (br. dd, 8b-H), 5.07, 4.93, 4.76, 4.68, 4.67, 4.54, 4.54 (dd, J_{1-3} = 2.1, J_{3-4} = 7.9 Hz, 3-H), 4.46, 4.30 (d, PhCH_2), 4.20 (br. t, J_{5-6} = 7.5 Hz, 6-H), 4.14 (dd, J_{4-5} = 3.2 Hz, 4-H), 3.94 (dd, 5-H), 2.61 (d, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.1−128.0 (C_6H_5), 136.8 (C-7), 120.3 (C-8), 82.2 (C-2), 81.0 (C-5), 80.7 (C-4), 80.5 (C-6), 75.9 (C-1), 75.4, 75.0, 71.0, 70.4 (PhCH_2), 69.3 (C-3) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.52, H 6.65. MS: *m*/*z* = 555.6 $[M + Na]^+$.

(3*S*,4*R*,5*S*,6*R*)-3,4,5,6-Tetra-*O*-benzyloct-7-en-1-yne-3,4,5,6-tetrol (16): The compound **16** was prepared by general procedure **2** from **10** (49 mg, 0.09 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **16** was obtained as a colorless oil in 62% yield (30 mg). R_f = 0.5 (hexane/EtOAc, 9:1). $[\alpha]_D^{24}$ = +22 (*c* = 0.3, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2217, 1655 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 5.97 (ddd, J_{6-7} = 7.8, J_{7-8a} = 10.3, J_{7-8b} = 18.0 Hz, 7-H), 5.37 (br. dd, J_{8a-8b} = 1.8 Hz, 8b-H), 5.30 (br. dd, 8a-H), 5.02, 4.97, 4.69, 4.68, 4.68, 4.59, 4.59 (dd, J_{1-3} = 2.1, J_{3-4} = 3.2 Hz, 3-H), 4.46, 4.33 (d, PhCH_2), 4.26 (br. dd, J_{5-6} = 3.3 Hz, 6-H), 4.08 (dd, J_{4-5} = 7.7 Hz, 4-H), 3.83 (dd, 5-H), 2.62 (d, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.0−127.8 (C_6H_5), 136.7 (C-7), 119.2 (C-8), 81.8 (C-2), 81.6 (C-5), 80.5 (C-6), 80.4 (C-4), 76.4 (C-1), 75.0, 71.0, 70.7 (PhCH_2), 68.5 (C-3) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.48, H 6.61. MS: *m*/*z* = 555.6 $[M + Na]^+$.

(3*S*,4*R*,5*R*)-3,4,5-Tri-*O*-benzylhept-6-en-1-yne-3,4,5-triol (17): The compound **17** was prepared by general procedure **2** from **11** (334 mg, 0.8 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **17** was obtained as a colorless oil in 69% yield (230 mg). R_f = 0.46 (hexane/EtOAc, 9:1). $[\alpha]_D^{24}$ = +47 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 2218, 1655 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 5.95 (ddd, J_{5-6} = 7.8, J_{6-7a} =

10.4, J_{6-7b} = 18.1 Hz, 6-H), 5.41 (br. dd, J_{7a-7b} = 1.8 Hz, 7a-H), 5.33 (ddd, J_{5-7b} = 0.8 Hz, 7b-H), 5.00, 4.95, 4.88, 4.69, 4.59, 4.53 (dd, J_{1-3} = 2.1, J_{3-4} = 5.2 Hz, 3-H), 4.46 (d, PhCH_2), 4.15 (br. ddd, 5-H), 3.95 (t, J_{4-5} = 5.2 Hz, 4-H), 2.10 (d, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.0−128.2 (C_6H_5), 135.6 (C-6), 120.1 (C-7), 82.5 (C-4), 81.0 (C-2, C-5), 75.8 (C-1), 75.1, 71.4, 71.5 (PhCH_2), 70.8 (C-3) ppm. $C_{28}H_{28}O_3$: calcd. C 81.52, H 6.84; found C 81.83, H 6.56. MS: *m*/*z* = 435.2 $[M + Na]^+$.

(4*S*,5*R*)-4,5-Di-*O*-benzylhept-6-en-1-yne-4,5-diol (18): The compound **18** was prepared by general procedure **2** from **12** (595 mg, 1.92 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 99:1) and **18** was obtained as a colorless oil in 64% yield (375 mg). R_f = 0.55 (hexane/EtOAc, 9:1). $[\alpha]_D^{25}$ = −34 (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): ṽ = 2223, 1642 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.02 (ddd, J_{5-6} = 5.5, J_{6-7a} = 9.5, J_{6-7b} = 18.0 Hz, 6-H), 5.53 (m, J_{7a-7b} = 0.84 Hz, 7a-H), 5.48 (ddd, 7b-H), 4.84, 4.83, 4.79, 4.54 (d, PhCH_2), 4.13 (tt, J_{4-5} = 5.5, J_{5-7a} = J_{5-7b} = 1.0 Hz, 5-H), 3.82 (q, J_{3a-4} = J_{3b-4} = 5.5 Hz, 4-H), 2.66 (m, 3a-H, 3b-H), 2.11 (t, J_{1-3a} = J_{1-3b} = 2.7 Hz, 1-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.9−128.0 (C_6H_5), 135.8 (C-6), 120.0 (C-7), 82.0 (C-5), 81.8 (C-2), 79.9 (C-4), 73.3, 71.2 (PhCH_2), 70.5 (C-1), 21.7 (C-3) ppm. $C_{21}H_{22}O_2$: calcd. C 83.32, H 7.24; found C 83.49, H 7.02. MS: *m*/*z* = 329.4 $[M + Na]^+$.

General Procedure 3 for Enyne Metathesis 19−25: Freshly distilled CH_2Cl_2 was degassed for 1 h. The enyne (0.5 mmol) was dissolved in CH_2Cl_2 (8 mL) and ethylene gas was passed through the solution for 45 min. Ruthenium catalyst **B** (15% mol) or **A** (30% mol) in CH_2Cl_2 (2 mL) was then added, and the solution was degassed again with ethylene for 20 min. The mixture was stirred under an atmosphere of ethylene at room temperature. The reaction was monitored by TLC. The mixture was then concentrated and the residue was purified by flash chromatography.

(3*R*,4*S*,5*R*)-3,4,5-Tri-*O*-benzyl-1-vinylcyclohexene-3,4,5-triol (19): The compound **19** was prepared by general procedure **3** from **13** (210 mg, 0.49 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 98:2) and **19** was obtained as a colorless oil in 72% yield (200 mg). R_f = 0.36 (hexane/EtOAc, 9:1). $[\alpha]_D^{27}$ = −96 (*c* = 0.57, $CHCl_3$). IR ($CHCl_3$): ṽ = 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.41 (dd, $J_{2'a-1'}$ = 17.4, $J_{2'b-1'}$ = 10.8 Hz, 1-H′), 5.80 (d, J_{2-3} = 4.1 Hz, 2-H), 5.24 (d, 2′a-H), 5.12 (d, 2′b-H), 4.78, 4.74, 4.71 (d, PhCH_2), 4.30 (t, J_{3-4} = 3.9 Hz, 3-H), 4.18 (m, J_{4-5} = 8.2, J_{5-6a} = 5.5, J_{5-6b} = 5.7 Hz, 5-H), 3.80 (dd, 4-H), 2.77 (dd, J_{6a-6b} = 17.4 Hz, 6a-H), 2.28 (dd, 6b-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 138.9 (C-1′), 139.3−128.1 (C_6H_5), 136.9 (C-1), 126.5 (C-2), 114.2 (C-2′), 79.1 (C-4), 74.8 (C-5), 73.3 (C-3), 73.2, 72.9, 72.2 (PhCH_2), 30.0 (C-6) ppm. $C_{29}H_{30}O_3$: calcd. C 81.66, H 7.09; found C 81.89, H 6.91. MS: *m*/*z* = 449.2 $[M + Na]^+$.

1,2-Bis[(3′*R*,4′*S*,5′*R*)-3′,4′,5′-Tris(benzyloxy)cyclohex-1-ene-1yl]-ethene (20): 20 was obtained as a colorless oil in 72% yield (200 mg). R_f = 0.24 (hexane/EtOAc, 9:1). $[\alpha]_D^{26}$ = −123 (*c* = 0.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.28 (s, 1-H), 5.85 (d, $J_{2'-3'}$ = 4.0 Hz, 2′-H), 4.78, 4.74, 4.71 (d, PhCH_2), 4.32 (t, $J_{3'-4'}$ = 3.8 Hz, 3′-H), 4.18 (m, $J_{5'-6a'}$ = 5.5, $J_{5'-6b'}$ = 5.8 Hz, 5′-H), 3.90 (dd, $J_{4'-5'}$ = 9.0 Hz, 4′-H), 2.79 (dd, $J_{6a'-6b'}$ = 17.4 Hz, 6a′-H), 2.31 (dd, 6b′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 136.7 (C-1′), 139.3−128.1 (C_6H_5), 130.7 (C-1), 126.9 (C-2′), 79.2 (C-4′), 74.8 (C-5′), 73.5 (C-3′), 73.2, 72.9, 72.2 (PhCH_2), 30.1 (C-6′) ppm. $C_{56}H_{56}O_6$: calcd. C 81.52, H 6.84; found C 81.90, H 6.95. MS: *m*/*z* = 849.0 $[M + Na]^+$.

(3*R*,4*R*,5*R*,6*S*)-3,4,5,6-Tetra-*O*-benzyl-1-vinylcyclohexene-3,4,5,6-tetrol (21): The compound **21** was prepared by general procedure **3** from **14** (100 mg, 0.2 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **21** was obtained as a colorless oil in 66% yield (66 mg). R_f = 0.30 (hexane/EtOAc, 9:1). $[\alpha]_D^{26}$ = −30 (*c* = 0.63, $CHCl_3$). IR ($CHCl_3$): ṽ = 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.33 (dd, $J_{1'-2'a}$ = 11.1, $J_{1'-2'b}$ = 17.6 Hz, 1′-H), 6.00 (d, J_{2-3} = 5.6 Hz, 2-H), 5.64 (dd, $J_{2'a-2'b}$ = 0.7 Hz, 2′b-H), 5.22 (dd, 2′a-H), 5.02, 4.89, 4.78, 4.57, 4.57 (d, J_{5-6} = 7.1 Hz, 6-H), 4.55 (d, PhCH_2), 4.50 (dd, J_{4-5} = 9.5 Hz, 5-H), 4.18 (dd, J_{3-4} = 3.4 Hz, 3-H), 3.62 (dd, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 140.2 (C-1), 139.3−128.0 (C_6H_5), 135.9 (C-1′), 127.3 (C-2), 117.2 (C-2′), 79.9 (C-6), 79.8 (C-4), 78.7 (C-5), 74.9, 72.9, 72.0, 71.3 (C-3), 69.2 (PhCH_2) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.42, H 6.72. MS: *m*/*z* = 555.2 $[M + Na]^+$.

(3*R*,4*R*,5*R*,6*R*)-3,4,5,6-Tetra-*O*-benzyl-1-vinylcyclohexene-3,4,5,6-tetrol (22): The compound **22** was prepared by general procedure **3** from **15** (130 mg, 0.25 mmol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **22** was obtained as a colorless oil in 55% yield (74 mg). R_f = 0.35 (hexane/EtOAc, 9:1). $[\alpha]_D^{28}$ = −107 (*c* = 0.4, $CHCl_3$). IR ($CHCl_3$): ṽ = 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.32 (dd, $J_{1'-2'a}$ = 11.0, $J_{1'-2'b}$ = 17.6 Hz, 1′-H), 5.83 (d, J_{2-3} = 4.2 Hz, 2-H), 5.33 (d, 2′b-H), 5.17 (d, 2′a-H), 5.11, 5.01, 4.90, 4.86, 4.82, 4.73, 4.70, 4.68 (d, PhCH_2), 4.55 (d, J_{5-6} = 3.2 Hz, 6-H), 4.27 (dd, J_{4-5} = 9.0 Hz, 5-H), 4.26 (t, J_{3-4} = 4.2 Hz, 3-H), 4.17 (dd, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.4−127.0 (C_6H_5), 138.4 (C-1), 137.0 (C-1′), 128.0 (C-2), 115.4 (C-2′), 78.7 (C-4), 76.9 (C-3), 74.7, 74.2 (C-6), 74.1, 73.7, 73.5 (C-5), 73.2 (PhCH_2) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.35, H 6.66. MS: *m*/*z* = 555.2 $[M + Na]^+$.

(3*R*,4*S*,5*R*,6*S*)-3,4,5,6-Tetra-*O*-benzyl-1-vinylcyclohexene-3,4,5,6-tetrol (23): The compound **23** was prepared by general procedure **3** from **16** (25 mg, $4.7 \cdot 10^{-5}$ mol). The crude residue was purified by flash chromatography (hexane/EtOAc, 97:3) and **23** was obtained as a colorless oil in 68% yield (17 mg). R_f = 0.34 (hexane/EtOAc, 9:1). $[\alpha]_D^{23}$ = +10 (*c* = 0.15, $CHCl_3$). IR ($CHCl_3$): ṽ = 1645 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.32 (dd, $J_{1'-2'a}$ = 11.0, $J_{1'-2'b}$ = 17.7 Hz, 1′-H), 5.94 (d, J_{2-3} = 2.6 Hz, 2-H), 5.16 (br. d, 2′b-H), 5.02 (br. d, 2′a-H), 4.81, 4.70, 4.67, 4.55, 4.50 (dd, J_{3-4} = 9.5 Hz, 3-H), 4.47 (d, PhCH_2), 4.17 (d, J_{5-6} = 5.9 Hz, 6-H), 4.00 (m, 4-H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 139.3−128.0 (C_6H_5), 138.5 (C-1), 137.1 (C-1′), 131.3 (C-2), 114.6 (C-2′), 78.9, , 76.9 (C-3), 75.0 (C-4, C-5), 75.0 (C-6), 73.3, 72.9, 72.5 (PhCH_2) ppm. $C_{36}H_{36}O_4$: calcd. C 81.17, H 6.81; found C 81.40, H 6.62. MS: *m*/*z* = 555.2 $[M + Na]^+$.

(3*R*,4*R*,5*S*)-3,4,5-Tri-*O*-benzyl-1-vinylcyclopentene-3,4,5-triol (24): By general procedure **3**, from reaction of **17** (200 mg, 0.485 mmol), two compounds were isolated **24** and **25** by flash chromatography (hexane/EtOAc, 97:3). The compound **24** was obtained as a colorless oil in 40% yield (80 mg). R_f = 0.34 (hexane/EtOAc, 9:1). $[\alpha]_D^{27}$ = −57 (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): ṽ = 1654 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.53 (dd, $J_{1'-2'a}$ = 17.7, $J_{1'-2'b}$ = 10.9 Hz, 1′-H), 6.06 (d, J_{2-3} = 2.4 Hz, 2-H), 5.65 (d, 2′a-H), 5.34 (d, 2′b-H), 4.90, 4.87 (d, J_{4-5} = 5.8 Hz, 5-H), 4.60 (m, PhCH_2), 4.55 (dd, J_{3-4} = 5.8 Hz, 3-H), 4.14 (t, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.3 (C-1), 139.6−127.8 (C_6H_5), 132.0 (C-1′), 131.5 (C-2), 119.1 (C-2′), 78.9 (C-3, C-4), 78.0 (C-5), 72.4, 72.0, 70.5 (PhCH_2) ppm. $C_{28}H_{28}O_3$: calcd. C 81.52, H 6.84; found C 81.49, H 6.94. MS: *m*/*z* = 435.2 $[M + Na]^+$.

(4*R*,5*R*,6*S*)-4,5,6-Tri-*O*-benzyl-1-methylenecyclohex-2-ene-4,5,6-triol (25): The compound **25** was obtained as a colorless oil in 21% yield (43 mg). R_f = 0.30 (hexane/EtOAc, 9:1). $[\alpha]_D^{23}$ = −22 (*c* =

0.4, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.53 (br. d, J_{5-6} = 1.9 Hz, 6-H), 6.32 (dd, J_{2-3} = 10.1, J_{2-4} = 2.4 Hz, 2-H), 5.76 (dd, J_{3-4} = 1.0 Hz, 3-H), 5.52 (s, 1′a-H), 5.25 (s, 1′b-H), 4.98, 4.64 (m, PhCH_2), 4.26 (m, 5-H), 4.22 (m, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 141.6 (C-1), 139.5−127.7 (C_6H_5), 129.9 (C-2), 127.7 (C-3), 113.6 (C-1′), 82.4 (C-6), 79.3 (C-4), 73.1 (C-5), 72.6, 71.9, 71.2 (PhCH_2) ppm. $C_{28}H_{28}O_3$: calcd. C 81.52, H 6.84; found C 81.63, H 6.77. MS: *m*/*z* = 435.2 $[M + Na]^+$.

(3*R*,4*S*)-3,4-Di-*O*-benzyl-1-vinylcyclopentene-3,4-diol (27): The compound **27** was prepared by general procedure **3** from **18** (145 mg, 0.47 mmol) and was obtained as a colorless oil in 50% yield (73 mg). R_f = 0.50 (hexane/EtOAc, 9:1). $[\alpha]_D^{26}$ = −133 (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 1654 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.57 (dd, $J_{1'-2'a}$ = 17.5, $J_{1'-2'b}$ = 10.6 Hz, 1′-H), 5.86 (br. d, J_{2-3} = 2.4 Hz, 2-H), 5.30 (dd, $J_{2'a-2'b}$ = 0.8 Hz, 2a′-H), 5.25 (dd, 2′b-H), 4.75 (m, PhCH_2), 4.58 (dd, J_{3-4} = 6.0 Hz, 3-H), 4.23 (dt, J_{4-5a} = 6.0, J_{4-5b} = 6.6 Hz, 4-H), 2.72 (br. d, 5a-H, 5b-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 145.0 (C-1), 139.4−128.0 (C_6H_5), 133.7 (C-1′), 127.9 (C-2), 117.7 (C-2′), 80.8 (C-3), 78.5 (C-4), 71.3, 71.0 (PhCH_2), 35.5 (C-5) ppm. $C_{21}H_{22}O_2$: calcd. C 82.32, H 7.24; found C 82.55, H 7.02. MS: *m*/*z* = 329.2 $[M + Na]^+$.

(5*R*,6*R*,7*R*,8*R*,9*R*,10*S*)-7,8,9,10-Tetrakis(benzyloxy)tricyclo-[4.2.4.0.0]tetradeca-2,11-diene (29): 1,4-Benzoquinone (36 mg, 4 equiv.) was added to compound **21** (45 mg, 0.084 mmol) dissolved in freshly distilled CH_2Cl_2 (3.5 mL). The mixture was heated at 40 °C in a sealed pressure tube for 48 h and was monitored by TLC. The mixture was then concentrated and the residue was purified by flash chromatography (hexane/EtOAc, 9:1). Compound **29** was obtained as a colorless oil in 45% yield (24 mg). R_f = 0.2 (hexane/EtOAc, 80:20). ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 6.77 (d, J_{2-3} = 10.1 Hz, 2-H), 6.75 (t, J_{12-13a} = 4.2, J_{12-13b} = 4.2 Hz, 12-H), 6.70 (d, 3-H), 4.80, 4.10 (m, PhCH_2), 4.59 (ddd, J_{5-14} = 2.8, J_{13a-14} = 4.2, J_{13b-14} = 5.8 Hz, 14-H), 4.56 (dd, J_{5-6} = 10.1, J_{6-7} = 2.5 Hz, 5-H), 4.00 (m, 8-H, 9-H, 10-H), 3.93 (t, J_{7-8} = 2.5 Hz, 7-H), 3.56 (dd, 6-H), 3.24 (dt, $J_{13a-13b}$ = 24.0 Hz, 13a-H), 2.91 (ddd, 13b-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 187.0 (C-1), 186.3 (C-4), 142.4 (C-11), 138.9−127.9 (C_6H_5), 137.5 (C-2), 135.8 (C-3), 123.3 (C-12), 83.1 (C-6), 81.0, 78.1, 77.0 (C-8, C-9, C-10), 75.8 (C-7), 73.0, 72.9, 72.5, 70.1 (PhCH_2), 32.7 (C-5, C-14), 25.0 (C-13) ppm. $C_{42}H_{40}O_6$: calcd. C 78.73, H 6.29; found C 78.95, H 6.42. MS: *m*/*z* = 663.7 $[M + Na]^+$.

(5*R*,6*R*,7*R*,8*R*,9*S*)-7,8,9-Tris(benzyloxy)-5-formylbicyclo[4.3.0]non-1-ene (30): A solution of **24** (300 mg, 0.72 mmol) in acrolein (3.5 mL) was heated at 60 °C in a sealed pressure tube for 24 h. The reaction was monitored by TLC. The mixture was then concentrated and the residue was purified by flash chromatography (hexane/EtOAc, 85:15). The compound **30** was obtained as a colorless oil in 40% yield (136 mg). R_f = 0.55 (hexane/EtOAc, 75:25). $[\alpha]_D^{25}$ = +15 (*c* = 0.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 7.40−7.30 (m, C_6H_5), 9.42 (d, $J_{5\text{-CHO}}$ = 0.9 Hz, C*H*O), 5.74 (br. dd, J_{2-3a} = 1.1, J_{2-3b} = 2.8 Hz, 2-H), 4.17 (dd, J_{7-8} = 3.9, J_{8-9} = 5.9 Hz, 8-H), 4.03 (d, 9-H), 4.01 (t, J_{6-7} = 3.8 Hz, 7-H), 3.17 (m, J_{5-6} = 3.8 Hz, 6-H), 2.82 (ddt, J_{4a-5} = 3.8, J_{4b-5} = 8.4 Hz, 5-H), 2.20 (m, 3a-H, 3a-H), 2.03 (m, 3b-H), 1.80 (m, 4b-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 200.9 (CHO), 138.9−127.9 (C_6H_5), 137.1 (C-1), 124.6 (C-2), 79.2 (C-7), 78.9 (C-8), 76.8 (C-9), 73.1, 72.8, 71.2 (PhCH_2), 45.7 (C-5), 44.5 (C-6), 22.8 (C-4), 21.9 (C-3) ppm. $C_{31}H_{32}O_4$: calcd. C 79.46, H 6.88; found C 79.55, H 7.02. MS: *m*/*z* = 491.6 $[M + Na]^+$.

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