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Sonogashira Couplings of Halo- and Epoxy-Halo-*exo*-Glycals: Concise Entry to Carbohydrate-Derived Enynes

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Furanose- and pyranose-derived mono- and dihalo-*exo*-glycals undergo Sonogashira coupling reactions in the presence of Pd catalysts to give carbohydrate-derived enynes in a completely stereoselective manner. On the other hand, a furanose-derived 2,3-anhydrohalo-*exo*-glycal, available from D-mannose in five steps, undergoes Pd^0-catalyzed Sonogashira coupling, leading to 2-deoxyenynes.

Introduction

Much of the rich chemistry of carbohydrates emanates from transformations at the anomeric (hemiacetal) center.[1] The advent of unsaturated anomeric derivatives [e.g., *endo*- and *exo*-glycals, **1** (R = H) and **2**, respectively] has added new avenues for additional synthetic transformations.[2] In this context, the less studied *exo*-glycals (2,5- or 2,6-anhydro-1-deoxyhex-1-enitols or -hept-1-enitols, e.g., **2**), are now well-recognized unsaturated carbohydrate derivatives frequently used as intermediates in transformations leading to carbohydrate mimetics or to complex molecules.[3,4] More recently, substituted *exo*-glycals (e.g., **3**)[5] that display additional substituent(s) at the exocyclic carbon atom, while maintaining the enol ether functionality, have also emerged as valuable substrates in synthetic[6] and biological investigations.[7] The olefinic substituent(s) allow(s) easy retrosynthetic correlation with biologically relevant C-glycosides (e.g. **4**),[8] whereas the enol ether moiety permits the incorporation of additional functionality into the carbohydrate entity (Figure 1).[9,10]

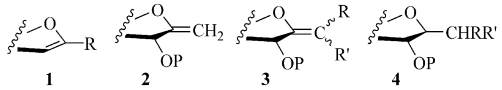
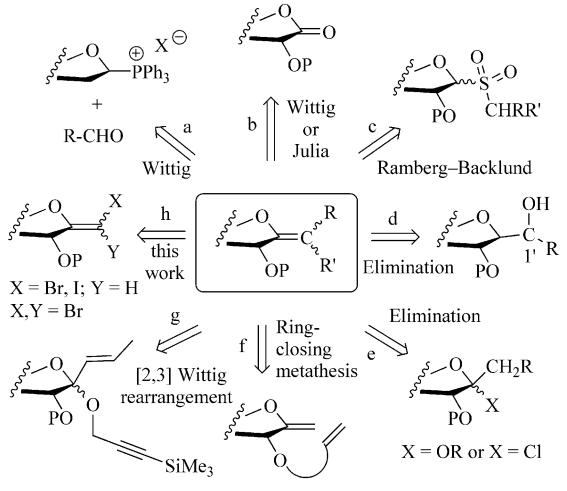


Figure 1. Glycal (**1**), *exo*-glycal (**2**), substituted *exo*-glycal (**3**), and C-glycoside (**4**).

Synthetic strategies to substituted *exo*-glycals **3**[11] have been addressed by Wittig-type olefination of either glycosyl phosphonium salts (Scheme 1a)[12] or sugar lactones (Scheme 1b)[13] and by Julia-type olefination of sugar lactones.[14] More recently, a highly versatile Ramberg–Backlund convergent approach has been described (Scheme 1c).[6a,15] Other strategies also used in the preparation of substituted *exo*-glycals involve elimination of a leaving group located at C-1′ on a C-glycoside (Scheme 1d)[16] or at the anomeric position in ketose-related derivatives (Scheme 1e; X = OR,[17] X = Cl[18]), S_N1' substitution on a vinyl ketose (Scheme 1e; R = CH_2, X = OH),[19] ring-closing olefin metathesis on *exo*-glycals (Scheme 1f),[20] and [2,3] Wittig rearrangement of propargyl ketosides (Scheme 1g).[21]



Scheme 1. Strategies for the synthesis of substituted *exo*-glycals.

Our group has been interested in the synthesis of unsaturated anomeric derivatives (i.e., **1**–**3**), and we have reported novel synthetic entries to glycals (**1**, R = H)[22] and C-1

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glycals (**1**, R = = CR′R′′R′′′).[23] More recently, we have been involved in the design of synthetic routes to substituted *exo*-glycals (**3**)[24] on the basis of cross-coupling reactions of halo-*exo*-glycals (Scheme 1h). In this context, we have explored the Suzuki[25] and Stille[26] cross-coupling reactions of monohalo-*exo*-glycals (Scheme 1h; X = Br, I; Y = H).

In this manuscript, we report in full our studies regarding the Sonogashira cross-coupling reaction[27] of monohalo-,[28] dihalo-, and epoxy-halo-*exo*-glycals aimed at the preparation of carbohydrate-derived enynes,[29] enediynes, and functionalized enynes, respectively.

Results and Discussion

Synthesis of the Precursors

The precursors for these studies were pyranoid iodo-*exo*-glycals **5**–**7** and furanosidic halo-*exo*-glycals **8**–**13** (Figure 2). Pyranoid (*Z*)-iodo-*exo*-glycals **5**–**7** were prepared from the corresponding aldonolactones[30–32] by methylenation (Petasis reagent)[33] followed by stereoselective iodination[25a] with iodonium dicollidinium triflate (IDCT).[34] Furanoid *exo*-glycals **8b** and **8c** were prepared by stereoselective bromination (Br_2, Et_3N, **8b**) or iodination (IDCT, **8c**) of the corresponding epoxy-*exo*-glycal (**8a**, X = H).[25b] Furanoid diacetates **9** were prepared from halo-*exo*-glycals **8b**,**c** by oxirane ring opening [THF/H_2O (3:1), Bu_4NOH, reflux][25b] followed by acetylation (Ac_2O, pyridine). (*Z*)-Halo-*exo*-glycal **10b** was prepared stereoselectively from *exo*-glycal **10a**[17d] (Br_2, Et_3N). On the other hand, bromination of **10** with tetra-*n*-butylammonium tribromide (nBu_4NBr_3)[35] rather than Br_2 resulted in the formation of a 6:1 isomeric mixture of **10b** and **11**, from which (*E*)-bromo-*exo*-glycal **11** could be isolated. Finally, Wittig-type

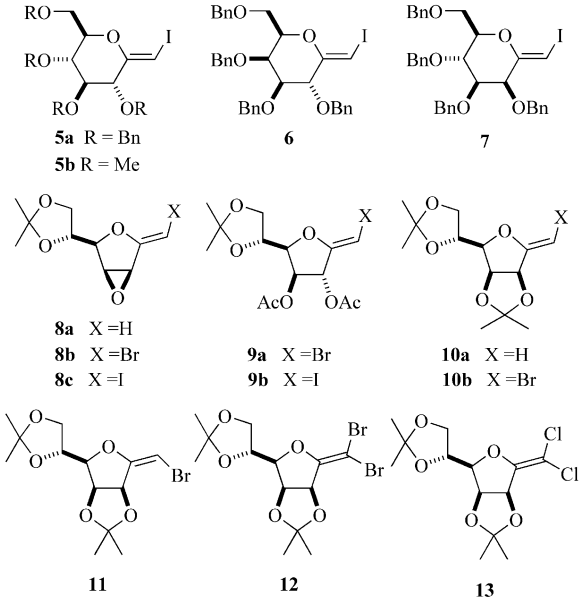


Figure 2. Halogenated *exo*-glycals **5**–**13**.

olefination of 2,3:5,6-di-*O*-isopropylidene-D-mannono-1,4-lactone,[36] according to methodologies developed by the group of Chapleur,[37] led to dihalo-*exo*-glycals **12**[38] and **13**.[39]

These substrates were selected to (1) compare the behavior of pyranoid (**5**–**7**) and furanoid (**8**–**13**) derivatives, (2) study the influence of the halogen (Br vs. I) in the reactivity (e.g., **8b** and **9a** vs. **8c** and **9b**), (3) evaluate the effect of the stereochemistry of the alkenyl halide (**10b** vs. **11**) in the reactivity of these substrates, and (4) assess the reactivity and/or chemoselectivity in dihalogenated derivatives **12** and **13** (Br vs. Cl).

On the other hand, as alkynes we have employed aryl, trimethylsilyl, and alkyl derivatives **14**–**16** (Figure 3).

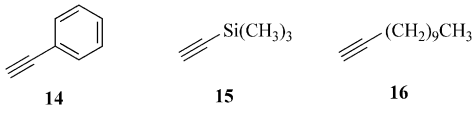


Figure 3. Alkynes employed in the Sonogashira cross-coupling reactions.

Sonogashira Cross-Coupling Reaction of Pyranoid Derivatives

We first explored the reaction of D-glucopyranose-derived alkenyl iodides **5** with alkynes **14**–**16** in the presence of different catalysts and bases (Table 1).

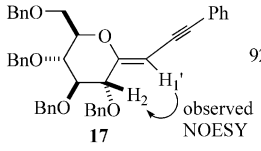
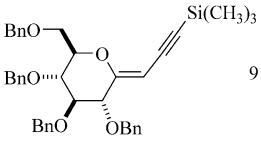
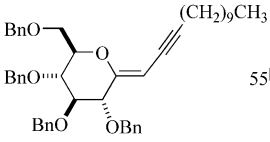
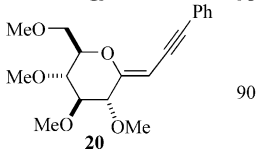
The stereochemistry of the resulting enynes was assigned on the basis of mechanistic grounds, as the cross-coupling takes place with retention of configuration at the alkene[27] and was further proved in the case of compound **17** by an observed NOESY between 1′-H and 2-H (see Table 1, Entry i).

The use of a Pd^{II} catalyst under Sonogashira–Hagihara conditions[40] [$Pd(PPh_3)_2Cl_2$, CuI] in different solvents (Table 1, Entries ii–iv, vii, and viii) did not lead to appreciable amounts of coupled products. Consequently, the use of Pd^0[41,42] was next attempted [$Pd(PPh_3)_4$, CuI, base] and was found to facilitate the formation of the sought enynes (Table 1, Entries i, v, vi, and ix–xi). Concerning the base employed, although piperidine led to good yields of enynes (Table 1, Entries i, v, and ix) a faster reaction was observed when diethylamine was used (Table 1, Entries vi, x, and xi). As expected, methyl- and benzyl-protected derivatives **5a** and **5b** displayed similar behavior in the Sonogashira cross-coupling reaction (Table 1, Entries x and xi).

These optimized reaction conditions were successfully applied to pyranose-derived *galacto*- and *manno*-iodo-*exo*-glycals **6** and **7**, respectively (Table 2). Thus, the Sonogashira cross-coupling reactions were carried out in Et_2NH (10 mL/mmol) in the presence of CuI (0.1 equiv.) and $Pd(PPh_3)_4$ (0.05 equiv.) at room temperature. In all cases, the reaction took place smoothly to afford the desired enynes in good to excellent yields (Table 2, Entries i–vi).

Finally, according to the results outlined in Tables 1 and 2, *gluco*-, *manno*-, and *galacto*-pyranose derivatives all displayed similar behavior, which seems to indicate that there

Table 1. Sonogashira cross-coupling reaction of halo-*exo*-glycals **5a** and **5b** with alkynes **14**–**16**.

Entry	Alkyne (*exo*-Glycal)	Catalyst Base	Reaction time [h]	Product	Yield [%]
i	**14** (**5a**)	$Pd(PPh_3)_4$ Piperidine	12	 **17**	92
ii	**14** (**5a**)	$PdCl_2(PPh_3)_2$ Piperidine	24	**17**	9[a]
iii	**14** (**5a**)	$PdCl_2(PPh_3)_2$ THF/Et_2NH	24	**17**	–
iv	**14** (**5a**)	$PdCl_2(PPh_3)_2$ Et_2NH	24	**17**	–
v	**15** (**5a**)	$Pd(PPh_3)_4$ Piperidine	2	 **18**	91
vi	**15** (**5a**)	$Pd(PPh_3)_4$ Et_2NH	1	**18**	84
vii	**15** (**5a**)	$PdCl_2(PPh_3)_2$ Piperidine	2	**18**	–
viii	**15** (**5a**)	$PdCl_2(PPh_3)_2$ Et_2NH	24	**18**	–
ix	**16** (**5a**)	$Pd(PPh_3)_4$ Piperidine	3	 **19**	55[b]
x	**16** (**5a**)	$Pd(PPh_3)_4$ Et_2NH	1	**19**	98
xi	**14** (**5b**)	$Pd(PPh_3)_4$ Et_2NH	2	 **20**	90

[a] *exo*-Glycal **5a** (90%) was recovered. [b] *exo*-Glycal **5a** (43%) was recovered.

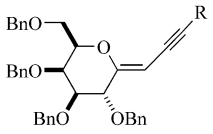
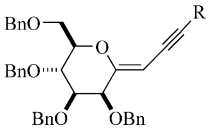
is little or no effect on the reaction rates or yields caused by the stereochemistry of the substituents in the pyranose ring.

Sonogashira Cross-Coupling Reactions of Furanoid Derivatives

Furanoid halo-*exo*-glycals **9a**,**b**, **10b**, and **11** proved to be more reactive than the corresponding pyranosyl derivatives. Thus, the coupling with furanose derivatives could be carried out under standard Sonogashira–Hagihara conditions [$Pd(PPh_3)_2Cl_2$, Et_2NH, CuI, THF],[40] and the results are displayed in Table 3.

On the basis of these results, some conclusions could be drawn: (1) Alkenyl furanosyl iodides gave only slightly better yields than the corresponding alkenyl bromides (Table 3, compare Entries i and ii, iii and iv; v and vi), which is in

Table 2. The $Pd(PPh_3)_4$-catalyzed Sonogashira cross-coupling reaction of iodo-*exo*-glycals **6** and **7** with alkynes **14**–**16** in the presence of CuI in diethylamine as solvent at room temperature.

Entry	Alkyne (Iodo-*exo*-Glycal)	Reaction time [h]	Product	Yield [%]
i	**14** (**6**)	1	 **21a** R = Ph	92
ii	**15** (**6**)	1	**21b** R = $Si(CH_3)_3$	84
iii	**16** (**6**)	2	**21c** R = $(CH_2)_9CH_3$	86
iv	**14** (**7**)	1	 **22a** R = Ph	83
v	**15** (**7**)	1	**22b** R = $Si(CH_3)_3$	92
vi	**16** (**7**)	2	**22c** R = $(CH_2)_9CH_3$	95

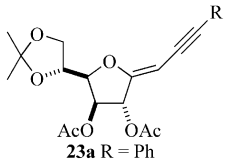
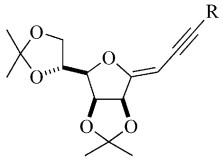
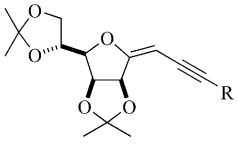
[a] *exo*-Glycal **5a** (90%) was recovered. [b] *exo*-Glycal **5a** (43%) was recovered.

agreement with the higher reactivity of the former to palladium(0) oxidative addition. (2) No appreciable effect due to the orientation and nature of the protecting groups was observed in the outcome of the reaction (Table 3, compare Entries i, iii, and v with Entries vii–ix). (3) *Z* and *E* isomers **10b** and **11** behaved similarly in terms of observed yield and reaction times, although the slightly higher reactivity found for the *Z* isomer could be ascribed to their different steric environments (Table 3, compare Entries vii, viii, and ix with Entries x, xi, and xii). (4) Higher yields and shorter reaction times were observed for alkynes **14** and **15** when compared to less reactive aliphatic alkyne **16**.

Sonogashira Cross-Coupling Reactions on Dihalogenated Substrates

Enediyne derivatives[43] could be easily accessed through Sonogashira coupling[27] from readily available dihalogenated derivatives **12** and **13**.[33,35,36,44] On the other hand, we were also interested in evaluating the reactivity of the two bromine atoms in our substrates. In this context, the Pd-catalyzed highly *trans*-selective monosubstitution of 1,1-dihalo-1-alkenes had attracted considerable attention since the pioneer work of Minato et al.[45] More recently, *trans*-stereoselective cross-coupling reactions have been attained on monosubstituted 1,1-dibromo-1-alkenes in Negishi,[46] Suzuki,[47] Stille,[48] and Sonogashira[49] cross-couplings.

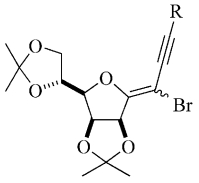
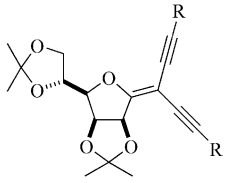
Table 3. The $Pd(PPh_3)_4$-catalyzed Sonogashira cross-coupling reaction of furanoid halo-*exo*-glycals **9a**, **9b**, **10b**, and **11** with alkynes **14**–**16** in the presence of CuI with diethylamine as solvent at room temperature.

Entry	Alkyne (Halo-*exo*-Glycal)	Reaction time [h]	Product	Yield [%]
i	**14** (**9a**)	2	 **23a** R = Ph	88
ii	**14** (**9b**)	1	**23a** R = Ph	91
iii	**15** (**9a**)	1	**23b** R = $Si(CH_3)_3$	87
iv	**15** (**9b**)	1.5	**23b** R = $Si(CH_3)_3$	90
v	**16** (**9a**)	24	**23c** R = $(CH_2)_9CH_3$	93
vi	**16** (**9b**)	24	**23c** R = $(CH_2)_9CH_3$	96
vii	**14** (**10b**)	1	 **24a** R = Ph	76
viii	**15** (**10b**)	1	**24b** R = $Si(CH_3)_3$	74
ix	**16** (**10b**)	12	**24c** R = $(CH_2)_9CH_3$	64[a]
x	**14** (**11**)	2	 **25a** R = Ph	80
xi	**15** (**11**)	1	**25b** R = $Si(CH_3)_3$	71
xii	**16** (**11**)	14	**25c** R = $(CH_2)_9CH_3$	42[b]

[a] *exo*-Glycal **10b** (16%) was recovered. [b] *exo*-Glycal **11** (44%) was recovered.

The reaction of 1′,1′-dibromo-*exo*-glycal **12** with alkynes **14**–**16** (Table 4) took place smoothly under conditions similar to those previously employed with the furanosidic *exo*-glycals (see Table 3). We were pleased to observe that the reaction of **12** with the less reactive aliphatic alkyne **16** could be stopped at the monosubstitution stage to give **26c** as a 1.1:1 unassigned isomeric mixture of *Z*/*E* isomers (Table 4, Entry iii). More reactive alkynes **14** and **15**, however, gave mixtures of enynes and enediynes **26** and **27**, respectively (Table 4, Entries i and ii). Enynes **26a** and **26b** were also obtained as unidentified *Z*/*E* isomeric mixtures. Accordingly, we have been unable to assign a higher reactivity to any of the bromine atoms in dibromo-*exo*-glycal **12**.

Table 4. The $Pd(PPh_3)_4$-catalyzed Sonogashira cross-coupling reaction of dihalo-*exo*-glycals **12** and **13** with alkynes **14**–**16** in the presence of CuI with diethylamine as solvent at room temperature.

Entry	Alkyne (Halo-*exo*-Glycal)	Products (% yield)	
i	**14** (**12**)	 **26a** R = Ph (39%)[a]	 **27a** R = Ph (24%)
ii	**15** (**12**)	**26b** R = $Si(CH_3)_3$[b] (37%)[c]	**27b** R = $Si(CH_3)_3$ (37%)[c]
iii	**16** (**12**)	**26c** R = $(CH_2)_9CH_3$ (35%)[d,e]	———
iv	**14** (**13**)	———	———

[a] Unassigned *Z*/*E* mixture (4:1). [b] Only one major isomer could be identified. [c] *exo*-Glycal **12** (10%) was recovered. [d] Unassigned isomeric *Z*/*E* mixture (1.1:1). [e] *exo*-Glycal **12** (43%) was recovered.

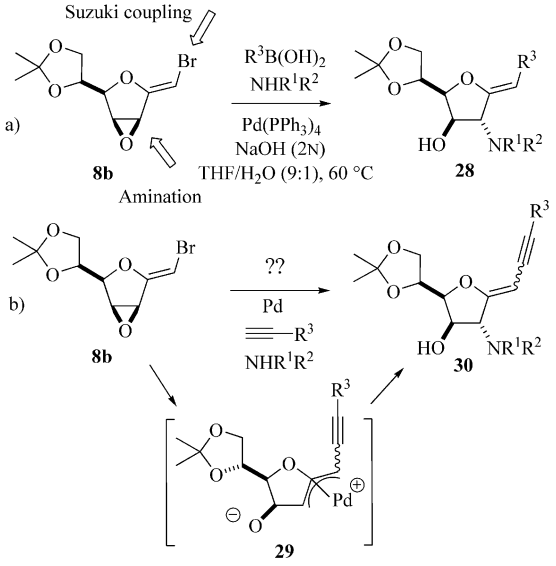
On the other hand, dichloro-*exo*-glycal **13** did not undergo Sonogashira cross-coupling under the various reaction conditions attempted. These results are in agreement with the lower reactivity of alkenyl chlorides when compared to bromides or iodides[50] and to recent results reported by the group of Chapleur.[44]

Sonogashira Cross-Coupling on a Furanose-Derived 2,3-Anhydrohalo-*exo*-glycal

We have recently described a three-component assembly of bromoalkenyl allylic oxirane **8b** with amines and boronic acids to furnish *exo*-glycal derivatives **28** (Scheme 2a).[51] In this context, we speculated about a related transformation of compound **8b** involving a Sonogashira cross-coupling reaction, rather than a Suzuki coupling, which could generate a highly functionalized enyne, that is, **30** (Scheme 2b).

Compound **8b** possesses two reactive sites for palladium-mediated reactions: the allylic oxirane and the alkenyl bromide. The transformation depicted in Scheme 2a supposedly occurs by uncatalyzed, thermal oxirane opening followed by Suzuki cross-coupling of the alkenyl bromide.

Because the Sonogashira cross-coupling reaction takes place at room temperature rather than at 60 °C (and because no appreciable nucleophilic opening of epoxide **8b** with amines had been observed at room temperature) a different reaction course could be anticipated for the transformation proposed in Scheme 1b. Accordingly, we had envisaged that compound **8b** would first undergo Sonogashira cross-coupling at the alkenyl bromide followed by genera-

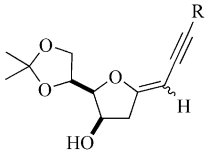
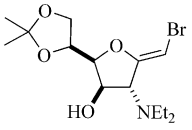
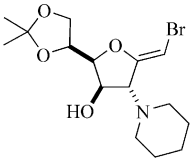


Scheme 2. Three-component reaction of haloalkenyl oxirane **8b**, and the proposed three-component reaction of **8b** involving a Sonogashira coupling.

tion of a π–allyl palladium complex (e.g., **29**),[52] which could then react with the amine (NHR^1R^2) to give functionalized enynes, for example, **30** (Scheme 1b).

However, instead of desired amino alkynes **30**, the reaction of compound **8b** with alkynes **14** and **15** [alkyne (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol-%), CuI (10 mol-%), Et_2NH (4 mL/mmol), room temperature] produced a mixture of 2-deoxyenynes **31a** (1.2:1, unassigned *Z*/*E* mixture) and **31b** (2:1, unassigned *Z*/*E* mixture), respectively (Table 5, Entries i and ii). Likewise, when aliphatic alkyne **16** was employed, a ≈1:1 mixture of enynes **31c** (37%) was obtained, albeit this time accompanied by 2-deoxy-2-amino derivative **32** (17%; Table 5, Entry iii). These results seemed to indicate that the Sonogashira cross-coupling was taking place first and that it was followed by the formation π–allyl palladium complex **29**; the latter will then explain the formation of compounds **31a–c** as geometric enyne mixtures.[53] Furthermore, the addition of hydride from a palladium–hydride species to **29** could be responsible for the formation of the 2-deoxy, rather than the 2-deoxy-2-amino derivatives.[54]

Table 5. Sonogashira cross-coupling reaction of epoxy-bromo-*exo*-glycal **8b** with alkynes **14**–**16** in the presence of amines.

Entry (Alkyne)	Reaction conditions	Products (% yield)
i (**14**)	$Pd(PPh_3)_4$, CuI, Et_2NH, room temp.	 **31a** R = Ph (60%)
ii (**15**)	$Pd(PPh_3)_4$, CuI, Et_2NH, room temp.	**31b** R = $Si(CH_3)_3$ (67%)
iii (**16**)	$Pd(PPh_3)_4$, CuI, Et_2NH, room temp.	 **31c** R = $(CH_2)_9CH_3$ (37%) + **32** (17%)
iv (**14**)	$Pd(PPh_3)_4$, CuI, piperidine, 60 °C	 **33** (60%)

On the other hand, the presence of an unreacted bromine atom in amino alcohol **32** (Table 5, Entry iii) was surprising. Therefore, we carried out several attempts to conduct Sonogashira couplings with **32** and alkyne **14** that were not successful.

When the reaction was carried out in the presence of piperidine at 60 °C (Table 5, Entry iv), only amino alcohol **33** could be isolated. In our hands, all attempts to induce a Sonogashira cross-coupling in compound **33** have met with failure.

Conclusions

Furanose- and pyranose-derived halo-*exo*-glycals are useful synthetic intermediates in the preparation of enyne *exo*-glycals. The reaction can also be applied to dibromo-*exo*-glycals to generate carbohydrate-derived enediynes. Furanose derivatives undergo the cross-coupling reaction under standard Sonogashira–Hagihara conditions, whereas pyranose derivatives required the use of Pd^0 as a catalyst. Alkenyl iodides react with alkynes to give slightly better yields, with shorter reaction times, than the corresponding bromo derivatives. (*E*)-Alkenyl bromides display a slightly higher reactivity than their isomeric (*Z*) counterparts. However, this slight reactivity difference does not allow the preparation of a single monosubstituted enyne from the Suzuki coupling of dihalo-*exo*-glycals. A highly functionalized furanose derivative, containing a bromoalkene and an allylic epoxide, undergoes Sonogashira cross-coupling followed by hydride transfer to a π–allyl palladium complex to furnish 2-deoxyenynes in fair yields. Finally, a series of 2-deoxy-2-amino alkenyl bromides derived from furanoses were reluctant to undergo the Sonogashira coupling under reaction conditions that had proven successful for the transformation of related non-amino derivatives.

Experimental Section

General Remarks: All reactions were performed in dry flasks fitted with glass stoppers or rubber septa under a positive pressure of Ar, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred by syringe or stainless steel cannula. Optical rotations were determined for solutions in chloroform. Flash column chromatography was performed using 230–400 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254 (Merck). Spots were observed first under UV irradiation

(254 nm) then by charring with a solution of 20% aqueous H_2SO_4 (200 mL) in AcOH (800 mL). Anhydrous $MgSO_4$ or Na_2SO_4 was used to dry organic solutions during workup, and evaporation of the solvents was performed under vacuum using a rotary evaporator. Solvents were dried and purified by using standard methods. Unless otherwise noted ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ = 7.25 ppm).

General Procedure for the Sonogashira Coupling Reaction

Method A: To a thoroughly degassed (argon, 10 min) solution of halo-*exo*-glycal in piperidine (10 mL/mmol) was added CuI (5 mol-%) and $Pd(PPh_3)_2Cl_2$ (10 mol-%). The reaction mixture was kept at room temperature with stirring for 5 min. The appropriate terminal alkyne (1 equiv.) dissolved in piperidine (10 mL/mmol) was then added by cannula. The reaction was then stirred at room temperature until complete disappearance of the starting material. The solution was treated with H_2O and extracted with ethyl acetate (EtOAc). The organic layer was then dried and evaporated to furnish a residue, which was purified by flash chromatography (hexane/EtOAc).

Method B: To a thoroughly degassed (argon, 10 min) solution of iodo-*exo*-glycal (0.1 mmol) in piperidine (10 mL/mmol) was added successively $Pd(PPh_3)_4$ (5 mol-%), CuI (0.01 mmol) and the corresponding alkyne (1.1 equiv., 0.11 mmol). The reaction mixture was then stirred at room temperature until complete disappearance of the starting material (1–2 h). The solution was diluted with ethyl acetate and washed successively with saturated NH_4Cl and brine. The organic layer was dried (magnesium sulfate) and evaporated to furnish a residue, which was purified by flash chromatography (hexane/EtOAc).

Method C: To a thoroughly degassed (argon, 10 min) solution of halo-*exo*-glycal in Et_2NH (10 mL/mmol) was added CuI (5 mol-%) and $Pd(PPh_3)_2Cl_2$ (10 mol-%). The reaction mixture was kept at room temperature with stirring for 5 min. The appropriate terminal alkyne (1 equiv.) dissolved in Et_2NH (10 mL/mmol) was then added by cannula. The reaction was then stirred at room temperature until complete disappearance of the starting material. The solution was treated with H_2O and extracted with ethyl acetate (EtOAc). The organic layer was then dried and evaporated to furnish a residue, which was purified by flash chromatography (hexane/EtOAc).

Method D: To a thoroughly degassed (argon, 10 min) solution of iodo-*exo*-glycal (0.1 mmol) in Et_2NH (10 mL/mmol) was added successively $Pd(PPh_3)_4$ (5 mol-%), CuI (0.01 mmol), and the corresponding alkyne (1.1 equiv., 0.11 mmol). The reaction was then stirred at room temperature until complete disappearance of the starting material (1–2 h). The solution was diluted with ethyl acetate and washed successively with saturated NH_4Cl and brine. The organic layer was dried (magnesium sulfate) and evaporated to furnish a residue, which was purified by flash chromatography (hexane/EtOAc).

Compound 17: Iodo-*exo*-glycal **5a** (100 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method B. After purification by flash chromatography (hexane/EtOAc 90:10), compound **17** was obtained as a colorless oil (88 mg, 92%). $[\alpha]_D^{25}$ = +57.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.11 (m, 25 H, Ph), 5.09 (s, 1 H, 1′-H), 4.70–4.47 (m, 8 H, O-CH_2-Ph), 4.09 (ddd, *J* = 10.0, 4.0, 2.0 Hz, 1 H, 5-H), 3.89 (d, *J* = 4.6 Hz, 1 H, 2-H), 3.89–3.72 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.7, 138.3, 138.0, 137.9, 137.4, 131.4 (2 C), 128.5 (2 C), 128.4 (2 C), 128.3 (4 C), 128.1 (2 C), 127.9 (3 C), 127.8 (5 C), 127.7 (4 C), 127.4, 123.9, 93.6, 89.9, 84.2, 83.8, 77.8, 77.7, 77.6, 73.9, 73.6, 73.3, 71.6, 68.5 ppm. MS (API-ES+): *m*/*z* = 637.3 $[M + 1]^+$, 659.3 $[M + Na]^+$. $C_{43}H_{40}O_5$ (636.77): calcd. C 81.11, H 6.33; found C 81.07, H 6.54.

Compound 18: Iodo-*exo*-glycal **5a** (100 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method B. After purification by flash chromatography (hexane/EtOAc, 95:5), compound **18** was obtained as a colorless oil (88 mg, 91%). In a different experiment, glycal **5a** (100 mg, 0.15 mmol) and **15** (22 μL, 0.16 mmol) were treated according to general method D to yield compound **18** (81 mg, 84%). $[\alpha]_D^{25}$ = +33.6 (*c* = 1.2, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.19 (m, 20 H, Ph), 5.00 (s, 1 H, 1′-H), 4.80–4.51 (m, 8 H, O-CH_2-Ph), 4.18 (ddd, *J* = 9.7, 3.1, 2.4 Hz, 1 H, 5-H), 3.91 (d, *J* = 4.1 Hz, 1 H, 2-H), 3.89–3.79 (m, 4 H), 0.18 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 138.3, 138.0, 137.8, 137.4, 128.4 (2 C), 128.3 (2 C), 128.2 (4 C), 127.9 (2 C), 127.8 (7 C), 127.7, 127.6, 127.5, 99.7, 98.7, 89.8, 83.6, 77.6 (2 C), 77.5, 73.8 (2 C), 73.0, 71.4, 68.4, 0.4 (3 C) ppm. MS (API-ES+): *m*/*z* = 633.3 $[M + 1]^+$, 655.3 $[M + Na]^+$. $C_{40}H_{44}O_5Si$ (632.85): calcd. C 75.91, H 7.01; found C 75.79, H 6.94.

Compound 19: Iodo-*exo*-glycal **5a** (100 mg, 0.15 mmol) and 1-dodecyne (**16**; 37 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 90:10), compound **19** was obtained as a colorless oil (103 mg, 98%). $[\alpha]_D^{25}$ = +54.0 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.21 (m, 20 H, Ph), 5.03 (br. s, 1 H, 1′-H), 4.85–4.56 (m, 8 H, O-CH_2-Ph), 4.13 (br. d, *J* = 9.3 Hz, 1 H, 5-H), 3.96 (d, *J* = 6.9 Hz, 1 H, 2-H), 3.92–3.80 (m, 4 H), 2.38 (td, *J* = 10.2, 3.3 Hz, 2 H), 1.67–1.22 (m, 16 H), 0.94 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 138.4, 138.1, 138.0, 137.6, 128.4 (2 C), 128.3 (2 C), 128.2 (4 C), 127.8 (6 C), 127.7 (4 C), 127.6, 127.5, 94.8, 90.6, 84.0, 78.0, 77.7, 77.6, 74.6, 73.9, 73.6, 73.3, 71.6, 68.5, 31.9, 29.6, 29.5, 29.3, 29.2, 28.9 (2 C), 22.6, 19.8, 14.1 ppm. MS (API-ES+): *m*/*z* = 723.5 $[M + Na]^+$. $C_{47}H_{56}O_5$ (700.49): calcd. C 80.53, H 8.05; found C 80.63, H 7.97.

Compound 20: Iodo-*exo*-glycal **5b** (40 mg, 0.07 mmol) and phenylacetylene (**14**; 9 μL, 0.08 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 95:5), compound **20** was obtained as a colorless oil (21 mg, 90%). $[\alpha]_D^{25}$ = +33.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 2 H, Ph), 7.29–7.26 (m, 3 H, Ph), 5.11 (s, 1 H, 1′-H), 3.97 (m, 1 H, 5-H), 3.79–3.67 (m, 3 H), 3.54 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.41 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 130.9 (2 C), 127.9 (2 C), 127.4, 123.7, 93.1, 89.2, 84.3, 84.0, 79.5, 78.6, 76.9, 70.9, 59.4, 58.7, 58.2, 57.2 ppm. MS (API-ES+): *m*/*z* = 333.0 $[M + 1]^+$, 355.0 $[M + Na]^+$. $C_{19}H_{24}O_5$ (332.16): calcd. C 68.66, H 7.28; found C 68.49, H 7.44.

Compound 21a: Iodo-*exo*-glycal **6** (100 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 90:10), compound **21a** was obtained as a colorless oil (88 mg, 92%). $[\alpha]_D^{25}$ = +33.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.23 (m, 25 H, Ph), 5.42 (d, *J* = 1.5 Hz, 1 H, 1′-H), 4.89 (d, *J* = 11.7 Hz, 1 H), 4.71–4.55 (m, 6 H, O-*CH*$_2$-Ph), 4.45 (d, *J* = 11.7 Hz, 1 H), 4.41 (dd, *J* = 9.0, 1.0 Hz, 1 H), 4.07 (t, *J* = 2.0 Hz, 1 H), 3.99 (dt, *J* = 6.0, 2.0 Hz, 1 H), 3.82–3.70 (m, 2 H), 3.68 (dd, *J* = 9.0, 2.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 138.3, 138.1, 138.0, 137.8, 131.4 (2 C), 128.4 (2 C), 128.3 (4 C), 128.1 (2 C), 127.9 (4 C), 127.8 (5 C), 127.7 (3 C), 127.6 (2

C), 127.5, 123.9, 93.6, 90.7, 84.4, 81.6, 78.9, 76.7, 74.3, 74.1, 74.0, 73.5, 72.8, 68.8 ppm. MS (API-ES+): *m*/*z* = 659.3 [M + Na]$^+$. $C_{43}H_{40}O_5$ (636.77): calcd. C 81.11, H 6.33; found C 80.98, H 6.21.

Compound 21b: Iodo-*exo*-glycal **6** (100 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 95:5), compound **21b** was obtained as a colorless oil (79 mg, 84%). $[\alpha]_D^{25}$ = +33.6 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.19 (m, 20 H, Ph), 5.00 (s, 1 H, 1′-H), 4.80–4.51 (m, 8 H, O-CH_2-Ph), 4.18 (ddd, *J* = 9.7, 3.1, 2.4 Hz, 1 H, 5-H), 3.91 (d, *J* = 4.1 Hz, 1 H, 2-H), 3.89–3.79 (m, 4 H), 0.18 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 138.3, 138.0, 137.8, 137.4, 128.4 (2 C), 128.3 (2 C), 128.2 (4 C), 127.9 (2 C), 127.8 (7 C), 127.7, 127.6, 127.5, 99.7, 98.7, 89.8, 83.6, 77.6 (2 C), 77.5, 73.8 (2 C), 73.0, 71.4, 68.4, 0.4 (3 C) ppm. MS (API-ES+): *m*/*z* = 633.3 [M + 1]$^+$, 655.3 [M + Na]$^+$. $C_{40}H_{44}O_5Si$ (632.85): calcd. C 75.91, H 7.01; found C 75.81, H 6.90.

Compound 21c: Iodo-*exo*-glycal **6** (100 mg, 0.15 mmol) and 1-dodecyne (**16**; 36 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 90:10), compound **21c** was obtained as a colorless oil (88 mg, 86%). $[\alpha]_D^{25}$ = +44.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 20 H, Ph), 5.25 (ddd, *J* = 3.9, 2.2, 1.6 Hz, 1 H, 1′-H), 4.93 (d, *J* = 11.5 Hz, 1 H), 4.74–4.60 (m, 6 H, O-CH_2-Ph), 4.50 (d, *J* = 11.7 Hz, 1 H), 4.39 (dd, *J* = 8.8, 1.6 Hz, 1 H, 4-H), 4.12 (t, *J* = 2.4 Hz, 1 H), 4.00 (dt, *J* = 6.0, 2.4 Hz, 1 H), 3.80 (d, *J* = 6.0 Hz, 2 H, 2 6-H), 3.70 (dd, *J* = 8.8, 2.4 Hz, 1 H, 3-H), 2.28 (dt, *J* = 6.9, 2.2 Hz, 2 H), 1.41–1.34 (m, 2 H), 1.25–1.16 (m, 14 H), 0.79 (t, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 138.4, 138.2, 138.1, 137.9, 128.4 (2 C), 128.2 (2 C), 128.1 (3 C), 127.9 (5 C), 127.8 (3 C), 127.7 (2 C), 127.6, 127.5, 127.4, 94.7, 91.3, 81.5, 78.7, 76.7, 74.7, 74.2 (2 C), 73.7, 73.5, 72.7, 68.6, 31.9, 29.6 (2 C), 29.3, 29.2, 28.9 (2 C), 22.7, 19.7, 14.1 ppm. MS (API-ES+): *m*/*z* = 723.5 [M + Na]$^+$. $C_{47}H_{56}O_5$ (700.49): calcd. C 80.53, H 8.05; found C 80.41, H 8.09.

Compound 22a: Iodo-*exo*-glycal **7** (100 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 90:10), compound **22a** was obtained as a colorless oil (79 mg, 83%). $[\alpha]_D^{25}$ = –16.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.24 (m, 25 H, Ph), 5.13 (s, 1 H, 1′-H), 4.91 (d, *J* = 11.0 Hz, 1 H), 4.81–4.58 (m, 6 H, O-CH_2-Ph), 4.46 (d, *J* = 12.7 Hz, 1 H), 4.24 (t, *J* = 8.0 Hz, 1 H, 5-H), 4.11 (d, *J* = 3.0 Hz, 1 H, 2-H), 3.94–3.88 (m, 3 H), 3.74 (dd, *J* = 8.0, 3.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 138.3, 138.1, 138.0, 137.8, 131.4 (2 C), 128.4 (2 C), 128.3 (4 C), 128.1 (2 C), 127.9 (3 C), 127.8 (5 C), 127.7 (4 C), 127.6 (2 C), 127.5, 123.9, 93.6, 90.7, 84.4, 81.6, 78.9, 76.7, 74.3, 74.1, 74.0, 73.5, 72.8, 68.8 ppm. MS (API-ES+): *m*/*z* = 637.1 [M + 1]$^+$, 659.2 [M + Na]$^+$. $C_{43}H_{40}O_5$ (636.77): calcd. C 81.11, H 6.33; found C 81.01, H 6.27.

Compound 22b: Iodo-*exo*-glycal **7** (100 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 95:5), compound **22b** was obtained as a colorless oil (93 mg, 92%). $[\alpha]^{25}$ = –12.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.15 (m, 20 H, Ph), 4.88 (s, 1 H, 1′-H), 4.81–4.35 (m, 8 H, OCH_2Ph), 4.16 (t, *J* = 8.4 Hz, 1 H, 5-H), 3.96 (d, *J* = 3.0 Hz, 1 H, 2-H), 3.84–3.80 (m, 3 H), 3.63 (dd, *J* = 8.4, 3.0 Hz, 1 H, 3-H), 0.14 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 138.3, 138.2, 138.0, 137.6, 128.4 (2 C), 128.3 (2 C), 128.0 (4 C), 127.9 (2 C), 127.8 (7 C), 127.7, 127.6, 127.5, 99.2 (2 C), 93.3, 80.5, 80.0, 74.5, 74.2, 73.6, 73.4, 71.7, 69.8, 69.0, 0.0 (3 C) ppm. MS (API-ES+): *m*/*z* = 633.3 [M + 1]$^+$, 655.3 [M + Na]$^+$. $C_{40}H_{44}O_5Si$ (632.85): calcd. C 75.91, H 7.01; found C 75.83, H 6.88.

Compound 22c: Iodo-*exo*-glycal **6** (100 mg, 0.15 mmol) and 1-dodecyne (**16**; 36 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 90:10), compound **22c** was obtained as a colorless oil (100 mg, 95%). $[\alpha]_D^{25}$ = +14.0 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.21 (m, 20 H, Ph), 4.86 (d, *J* = 10.8 Hz, 1 H), 4.82 (t, *J* = 2.1 Hz, 1 H, 1′-H), 4.72–4.48 (m, 6 H, OCH_2Ph), 4.35 (d, *J* = 12.6 Hz, 1 H), 4.19 (t, *J* = 8.7 Hz, 1 H, 4-H), 3.95 (d, *J* = 3.0 Hz, 1 H, 2-H), 3.83 (d, *J* = 3.6 Hz, 2 H, 2 6-H), 3.74 (td, *J* = 8.7, 3.6 Hz, 1 H, 5-H), 3.62 (dd, *J* = 8.7, 3.0 Hz, 1 H, 3-H), 2.27 (dt, *J* = 6.9, 2.1 Hz, 2 H), 1.64–1.22 (m, 16 H), 0.84 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 138.4, 138.2, 138.1, 137.9, 128.4 (2 C), 128.2 (2 C), 128.1 (3 C), 127.9 (5 C), 127.8 (3 C), 127.7 (2 C), 127.6, 127.5, 127.4, 94.7, 91.3, 81.5, 78.7, 76.7, 74.7, 74.2 (2 C), 73.7, 73.5, 72.7, 68.6, 31.9, 29.6 (2 C), 29.3, 29.2, 28.9 (2 C), 22.7, 19.7, 14.1 ppm. MS (API-ES+): *m*/*z* = 723.5 [M + Na]$^+$. $C_{47}H_{56}O_5$ (700.49): calcd. C 80.53, H 8.05; found C 80.32, H 8.13.

Compound 23a: Bromo-*exo*-glycal **9a** (57 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 60:40), compound **23a** was obtained as a colorless oil (52 mg, 88%). In a different experiment, iodo-*exo*-glycal **9b** (64 mg, 0.15 mmol) and **14** (18 μL, 0.16 mmol) were treated according to general method D to afford **23a** (55 mg, 91%). $[\alpha]_D^{25}$ = +31.5 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 5 H, Ph), 5.54 (s, 1 H, 2-H), 5.37 (d, *J* = 4.0 Hz, 1 H, 3-H), 5.17 (s, 1 H, 1′-H), 4.58 (dd, *J* = 7.9, 4.0 Hz, 1 H, 4-H), 4.37 (ddd, *J* = 7.8, 5.6, 5.3 Hz, 1 H, 5-H), 4.18 (m, 2 H, 2 6-H), 2.14 (s, 3 H, Me), 2.12 (s, 3 H, Me), 1.47 (s, 3 H, Me), 1.37 (s 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3, 169.2, 161.3, 131.4, 128.3 (2 C), 128.1 (2 C), 123.7, 109.8, 94.7, 85.4, 83.6, 83.3, 75.2, 74.2, 72.4, 67.0, 26.9, 25.4, 20.9, 20.8 ppm. MS (API-ES+): *m*/*z* = 423.3 [M + Na]$^+$, 401.2 [M + 1]$^+$. $C_{22}H_{24}O_7$ (400.42): calcd. C 65.99, H 6.04; found C 66.14, H 6.17.

Compound 23b: Bromo-*exo*-glycal **9a** (57 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 70:30), compound **23b** was obtained as a colorless oil (52 mg, 87%). In a different experiment, iodo-*exo*-glycal **9b** (64 mg, 0.15 mmol) and **15** (22 μL, 0.16 mmol) were treated according to general method D to afford **23b** (53.5 mg, 90%). $[\alpha]_D^{25}$ = +21.0 (*c* = 0.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 (d, *J* = 1.1 Hz, 1 H, 2-H), 5.33 (dd, *J* = 3.6, 1.1 Hz, 1 H, 3-H), 4.98 (s, 1 H, 1′-H), 4.57 (dd, *J* = 7.6, 3.6 Hz, 1 H, 4-H), 4.36 (ddd, *J* = 7.6, 5.8, 5.3 Hz, 1 H, 5-H), 4.15 (m, 2 H, 2 6-H), 2.12 (s, 3 H, Me), 2.09 (s, 3 H, Me), 1.46 (s, 3 H, Me), 1.37 (s 3 H, Me), 0.20 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3, 169.1, 162.5, 109.7, 98.9, 85.2, 83.2, 82.2, 75.1, 74.1, 72.3, 66.7, 26.8, 25.5, 20.9 (2 C), 0.2 (3 C) ppm. MS (API-ES+): *m*/*z* = 419.0 [M + Na]$^+$, 397 [M + 1]$^+$. $C_{19}H_{28}O_7Si$ (396.50): calcd. C 57.55, H 7.12; found C 57.71, H 7.17.

Compound 23c: Bromo-*exo*-glycal **9a** (57 mg, 0.15 mmol) and 1-dodecyne (**16**; 36 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 60:40), compound **23c** was obtained as a colorless oil (65 mg, 93%). In a different experiment, iodo-*exo*-glycal **9b** (64 mg, 0.15 mmol) and **16** (22 μL, 0.16 mmol) were converted into **23c** by following general method D. After workup and purification similar

to that above, **23c** was obtained (67 mg, 96%). $[\alpha]_D^{25}$ = +23.4 (*c* = 0.83, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.45 (s, 1 H, 2-H), 5.29 (d, *J* = 3.9 Hz, 1 H, 3-H), 4.90 (s, 1 H, 1′-H), 4.46 (dd, *J* = 7.9,3.9 Hz, 1 H, 4-H), 4.32 (ddd, *J* = 7.9, 6.3, 5.4 Hz, 1 H, 5-H), 4.12 (m, 2 H, 2 6-H), 2.27 (dt, *J* = 6.9, 2.1 Hz, 2 H), 2.09 (s, 3 H, Me), 2.06 (s, 3 H, Me), 1.42 (s, 3 H, Me), 1.33 (s, 3 H, Me), 1.11 (m, 16 H, 8 CH_2), 0.87 (t, *J* = 6.0 Hz, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.5, 169.3, 160.6, 109.8, 96.3, 86.0, 83.0, 75.1, 74.4, 74.3, 72.4, 67.2, 32.1, 29.8 (2 C), 29.5, 29.4, 29.1, 28.9, 27.0, 25.5, 21.9, 21.1, 21.0, 20.0, 14.3 ppm. MS (API-ES+): *m*/*z* = 465.6 $[M+H]^+$. $C_{26}H_{40}O_7$ (464.59): calcd. C 67.22, H 8.68; found C 67.03, H 8.49.

Compound 24a: Bromo-*exo*-glycal **10b** (50 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 80:20), compound **24a** was obtained as a colorless oil (41 mg, 76%). $[\alpha]_D^{25}$ = +109.0 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2 H, Ph), 7.29–7.26 (m, 3 H, Ph), 5.17 (d, *J* = 5.6 Hz, 1 H, 2-H), 4.96 (s, 1 H, 1′-H), 4.81 (dd, *J* = 5.6, 3.7 Hz, 1 H, 3-H), 4.51 (ddd, *J* = 7.7, 6.0, 4.9 Hz, 1 H, 5-H), 4.27 (dd, *J* = 7.7, 3.6 Hz, 1 H, 4-H), 4.20–4.18 (m, 2 H, 2 6-H), 1.49 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.40 (s, 6 H, 2 Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.8, 131.2 (2 C), 128.2 (2 C), 127.7, 123.9, 114.0, 109.5, 93.7, 84.1, 83.2, 82.3, 80.3, 78.2, 73.1, 66.5, 27.0, 26.9, 26.0, 25.4 ppm. MS (API-ES+): *m*/*z* = 357.2 $[M+1]^+$. $C_{21}H_{24}O_5$ (356.41): calcd. C 70.77, H 6.79; found C 70.94, H 6.81.

Compound 24b: Bromo-*exo*-glycal **10b** (50 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 75:25), compound **24b** was obtained as a colorless oil (39 mg, 74%). $[\alpha]_D^{25}$ = +104.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.35 (d, *J* = 0.9 Hz, 1 H, 1′-H), 5.14 (dd, *J* = 5.7, 0.9 Hz, 1 H, 2-H), 4.89 (dd, *J* = 5.7, 3.8 Hz, 1 H, 3-H), 4.50 (m, 1 H, 5-H), 4.23–4.18 (m, 3 H, 4-H and 2 6-H), 1.49 (s, 6 H, 2 Me), 1.43 (s, 3 H, Me), 1.42 (s, 3 H, Me), 0.22 (m, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 114.2, 109.5 (2 C), 99.5, 98.9, 82.8, 79.9, 79.1, 73.0, 66.5, 26.9, 26.8, 25.9, 25.3, 0.1 (3 C) ppm. MS (API-ES+): *m*/*z* = 353.2 $[M+1]^+$. $C_{18}H_{28}O_5Si$ (352.49): calcd. C 61.33, H 8.01; found C 61.51, H 8.12.

Compound 24c: Bromo-*exo*-glycal **10b** (50 mg, 0.15 mmol) and 1-dodecyne (**16**; 36 μL, 0.16 mmol) were treated according to general method D. After stirring for 12 h and purification by flash chromatography (hexane/EtOAc, 80:20), compound **24c** was obtained (38 mg, 60%) followed by recovered starting material **10b** (8 mg, 16%). Data for **24c**: $[\alpha]_D^{25}$ = +107.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.09 (d, *J* = 5.6 Hz, 1 H, 2-H), 4.77 (dd, *J* = 5.6, 3.8 Hz, 1 H, 3-H), 4.73 (m, 1 H, 1′-H), 4.47 (ddd, *J* = 7.8, 5.8, 4.6 Hz, 1 H, 5-H), 4.18–4.14 (m, 3 H, 2 6-H and 4-H), 2.32 (dt, *J* = 6.9, 2.2 Hz, 2 H), 1.55–1.49 (m, 2 H), 1.47 (s, 3 H, Me), 1.46 (s, 3 H, Me), 1.39 (s, 3 H, Me), 1.38 (s, 3 H, Me), 1.26 (m, 14 H), 0.88 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 113.7, 109.4, 94.8, 83.0, 82.9, 80.1, 78.2, 74.4, 73.0, 66.5, 31.8, 29.5, 29.4, 29.3, 29.1, 28.8, 28.7, 26.9 (2 C), 25.9, 25.3, 22.6, 19.7, 14.0 ppm. MS (API-ES+): *m*/*z* = 421.3 $[M+1]^+$, 443.2 $[M+Na]^+$. $C_{25}H_{40}O_5$ (420.58): calcd. C 71.39, H 9.59; found C 71.27, H 9.43.

Compound 25a: Bromo-*exo*-glycal **11** (50 mg, 0.15 mmol) and phenylacetylene (**14**; 18 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 80:20), compound **25b** was obtained as a colorless oil (43 mg, 80%). $[\alpha]_D^{25}$ = +249.7 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H, Ph), 7.28–7.26 (m, 3 H, Ph), 5.41 (d, *J* = 5.8 Hz, 1 H, 2-H), 5.31 (s, 1 H, 1′-H), 4.81 (dd, *J* = 5.8, 4.1 Hz, 1 H, 3-H), 4.45 (m, 1 H, 5-H), 4.15–4.04 (m, 3 H, 2 6-H and 4-H), 1.48 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.41 (s, 3 H, Me), 1.38 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 131.1 (2 C), 128.1 (2 C), 127.5, 123.9, 113.5, 109.3, 92.4, 85.1, 84.7, 83.3, 79.3, 77.9, 72.9, 66.3, 26.8, 26.5, 25.6, 25.0 ppm. MS (API-ES+): *m*/*z* = 357.2 $[M+1]^+$. $C_{21}H_{24}O_5$ (356.41): calcd. C 70.77, H 6.79; found C 57.61, H 6.66.

Compound 25b: Bromo-*exo*-glycal **11** (50 mg, 0.15 mmol) and trimethylsilylacetylene (**15**; 22 μL, 0.16 mmol) were treated according to general method D. After purification by flash chromatography (hexane/EtOAc, 75:25), compound **25b** was obtained as a colorless oil (37 mg, 71%). $[\alpha]_D^{25}$ = +41.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.71 (d, *J* = 1.0 Hz, 1 H, 1′-H), 5.14 (dd, *J* = 5.9, 1.0 Hz, 1 H, 2-H), 4.80 (dd, *J* = 5.9, 3.8 Hz, 1 H, 3-H), 4.43 (m, 1 H, 5-H), 4.14–4.02 (m, 3 H, 4-H and 2 6-H), 1.48 (s, 6 H, Me), 1.44 (s, 3 H, 2 Me), 1.38 (s, 3 H, Me), 0.18 (m, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 113.4, 109.3 (2 C), 99.5, 98.9, 82.8, 79.9, 79.1, 73.0, 66.5, 26.8, 26.5, 25.5, 25.1, 0.0 (3 C) ppm. MS (API-ES+): *m*/*z* = 353.2 $[M+1]^+$. $C_{18}H_{28}O_5Si$ (352.49): calcd. C 61.33, H 8.01; found C 61.22, H 7.94.

Compound 25c: Bromo-*exo*-glycal **11** (50 mg, 0.15 mmol) and 1-dodecyne (**16**; 36 μL, 0.16 mmol) were treated according to general method D. After stirring for 14 h and purification by flash chromatography (hexane/EtOAc, 80:20), compound **25c** was obtained (19 mg, 31%) followed by recovered starting material **11** (22 mg, 44%). Data for **25c**: $[\alpha]_D^{25}$ = +32.7 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.32 (dd, *J* = 6.0, 1.3 Hz, 1 H, 2-H), 5.11 (d, *J* = 1.3 Hz, 1 H, 1′-H), 4.78 (dd, *J* = 6.0, 3.9 Hz, 1 H, 3-H), 4.42 (ddd, *J* = 7.3, 6.1, 4.6 Hz, 1 H, 5-H), 4.11 (dd, *J* = 9.0, 6.1 Hz, 1 H, 6a-H), 4.05 (dd, *J* = 9.0, 4.6 Hz, 1 H, 6b-H), 4.01 (dd, *J* = 7.3, 3.9 Hz, 1 H, 4-H), 2.32 (dt, *J* = 7.1, 2.2 Hz, 2 H), 1.51 (m, 2 H), 1.47 (s, 3 H, Me), 1.44 (s, 3 H, Me), 1.40 (s, 3 H, Me), 1.38 (s, 3 H, Me), 1.25 (m, 14 H), 0.87 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 113.4, 109.3, 93.4, 86.1, 83.1, 79.0, 78.0, 74.9, 73.0, 66.4, 31.9, 29.6 (2 C), 29.3, 29.2, 28.9, 28.8, 26.8, 26.4, 25.5, 25.1, 22.6, 19.7, 14.1 ppm. MS (API-ES+): *m*/*z* = 437.3 $[M+NH_4]^+$. $C_{25}H_{40}O_5$ (420.58): calcd. C 71.39, H 9.59; found C 71.15, H 9.33.

Compounds 26a and 27a: Bromo-*exo*-glycal **12** (100 mg, 0.24 mmol) and phenylacetylene (**14**; 28 μL, 0.26 mmol) were treated according to general method D. Purification by flash chromatography (hexane/EtOAc, 90:10) gave compound **27a** (28 mg, 24%) followed by compound **26a** as an inseparable 4:1 unassigned *Z*/*E* mixture (41 mg, 39%). MS (API-ES+): *m*/*z* = 434.0 $[M]^+$, 436.0 $[M+2].^+$ Data for **26a**, major isomer: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.38 (m, 2 H, Ph), 7.33–7.31 (m, 3 H, Ph), 5.35 (d, *J* = 5.8 Hz, 1 H, 2-H), 4.88 (dd, *J* = 5.8, 3.7 Hz, 1 H, 3-H), 4.51 (m, 1 H, 5-H), 4.24 (dd, *J* = 7.8, 3.7 Hz, 1 H, 4-H), 4.17 (d, *J* = 5.1 Hz, 2 H, 2 6-H), 1.49 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.43 (s, 3 H, Me), 1.41 (s, 3 H, Me) ppm. Selected peaks for **26a**, minor isomer: 5.40 (d, *J* = 5.8 Hz, 1 H, 2-H), 4.93 (dd, *J* = 5.8, 3.7 Hz, 1 H, 3-H), 1.51 (s, 3 H, Me) ppm. Data for **27a**: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 4 H, Ph), 7.34–7.26 (m, 6 H, Ph), 5.52 (d, *J* = 5.9 Hz, 1 H, 2-H), 4.89 (dd, *J* = 5.9, 3.9 Hz, 1 H, 3-H), 4.55 (ddd, *J* = 7.6, 5.9, 4.6 Hz, 1 H, 5-H), 4.32 (dd, *J* = 7.6, 3.9 Hz, 1 H, 4-H), 4.22–4.17 (m, 2 H, 2 6-H), 1.51 (s, 3 H, Me), 1.50 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.42 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.2, 131.4 (2 C), 128.2 (6 C), 128.1, 127.9, 123.5, 123.4, 113.8, 109.6, 93.1, 91.4, 84.3, 83.7, 83.0, 82.5, 80.3, 78.0, 72.9, 66.4, 26.9, 26.8, 25.9, 25.3 ppm. MS (API-ES+): *m*/*z* = 457.2 $[M+1]^+$.

$C_{29}H_{28}O_5$ (456.19): calcd. C 76.30, H 6.18; found C 76.41, H 6.33. Isolated compound **26a** could be converted into compound **27a** in 50% yield by following general method D.

Compounds 26b and 27b: Bromo-*exo*-glycal **12** (100 mg, 0.24 mmol) and trimethylsilylacetylene (**15**; 37 μL, 0.26 mmol) were treated according to general method D. Purification by flash chromatography (hexane/EtOAc, 95:5) gave compounds **27b** (39 mg, 37%) followed by compound **26b** as an inseparable mixture of *Z* and *E* isomers (38 mg, 37%). Data for **26b**, major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (d, *J* = 5.7 Hz, 1 H, 2-H), 4.83 (dd, *J* = 5.7, 3.6 Hz, 1 H, 3-H), 4.47 (m, 1 H, 5-H), 4.23 (dd, *J* = 7.2, 3.6 Hz, 1 H, 4-H), 4.13 (m, 2 H, 2 6-H), 1.48 (s, 3 H, Me), 1.46 (s, 3 H, Me), 1.41 (s, 3 H, Me), 1.39 (s, 3 H, Me), 0.20 (m, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6, 113.8, 109.6, 102.7, 98.4, 83.8, 80.9, 78.2, 72.9, 66.2, 26.9, 26.6, 25.7, 25.4, 0.0 (3 C) ppm. MS (API-ES+): *m*/*z* = 431.1 $[M]^+$, 433.1 $[M + 2]^+$. Data for **27b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (dd, *J* = 5.7, 0.9 Hz, 1 H, 2-H), 4.77 (m, 1 H, 3-H), 4.47 (m, 1 H, 5-H), 4.27 (dd, *J* = 7.5, 3.9 Hz, 1 H, 4-H), 4.15 (d, *J* = 5.4 Hz, 2 H, 2 6-H), 1.47 (s, 6 H, 2 Me), 1.40 (s, 3 H, Me), 1.38 (s, 3 H, Me), 0.18 (m, 18 H, TMS) ppm. MS (API-ES+): *m*/*z* = 449.3 $[M]^+$.

Compound 26c: Bromo-*exo*-glycal **12** (100 mg, 0.24 mmol) and 1-dodecyne (**16**; 58 μL, 0.26 mmol) were treated according to general method D. Purification by flash chromatography (hexane/EtOAc, 80:20) gave compounds **26c** as an inseparable 1:1 mixture of *Z* and *E* isomers (37 mg, 31%) followed by recovered starting material **12** (32 mg, 30%). Data for **26c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.29 (d, *J* = 5.9 Hz, 1 H, 2-H), 4.88 (dd, *J* = 5.9, 3.8 Hz, 0.5 H, 3-H), 4.83 (dd, *J* = 5.9, 3.8 Hz, 0.5 H, 3-H), 4.47 (ddd, *J* = 9.1, 5.4, 4.2 Hz, 1 H, 5-H), 4.18–4.09 (m, 3 H), 2.41 (t, *J* = 6.8 Hz, 2 H), 1.61–1.49 (m, 2 H), 1.48 (s, 3 H, Me), 1.47–1.44 (m, 4 H), 1.42 (s, 3 H), 1.40 (s, 3 H), 1.39 (s, 3 H), 1.26 (br. s, 10 H), 0.88 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4 (2 C), 113.7,113.6, 109.6 (2 C), 99.0, 96.8, 83.7, 83.6, 80.8, 79.9, 79.4, 79.1, 78.5, 77.2, 75.8, 75.5, 72.9, 66.5 (2 C), 31.9 (2 C), 29.6 (4 C), 29.3 (2 C), 29.1 (2 C), 28.8, 28.7, 28.5, 28.4, 26.9 (2 C), 26.6 (2 C), 25.9, 25.8, 25.3 (2 C), 22.7 (2 C), 19.8 (2 C), 14.1 (2 C) ppm. MS (API-ES+): *m*/*z* = 521.1 $[M + Na]^+$, 523.1 $[M + Na + 2]^+$.

General Procedure for the Preparation of 2-Deoxy Derivatives 31: To a thoroughly degassed (argon, 10 min) solution of 2,3-anhydro-bromo-*exo*-glycal **8b** (0.1 mmol) in Et_2NH (10 mL/mmol) was added successively $Pd(PPh_3)_4$ (5 mol-%) and CuI (0.01 equiv.). The reaction was then stirred at room temperature for 5 min, after which time a degassed solution of the corresponding alkyne dissolved in Et_2NH was added. The reaction mixture was stirred until TLC showed complete disappearance of the starting material. The solution was then diluted with ethyl acetate and washed successively with saturated NH_4Cl and brine. The organic layer was dried (magnesium sulfate) and evaporated to furnish a residue, which was purified by flash chromatography (hexane/EtOAc).

Compound 31a: Bromide **8b** (100 mg, 0.36 mmol) and phenylacetylene (**14**; 45 μL, 0.40 mmol) were treated according to the general procedure. After purification by flash chromatography (hexane/EtOAc, 60:40), compound **31a** was obtained as a 1.2:1 separable but unassigned mixture of compounds **31a**: Data for **31a**, major isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (m, 2 H), 7.27 (m, 3 H), 5.14 (br. s, 1 H, 1′-H), 4.59 (t, *J* = 4.3 Hz, 1 H, 3-H), 4.38 (ddd, *J* = 8.6, 6.2, 4.7 Hz, 1 H, 5-H), 4.19 (dd, *J* = 8.6, 5.8 Hz, 1 H, 6a-H), 4.16 (dd, *J* = 8.6, 3.5 Hz, 1 H, 4-H), 4.04 (dd, *J* = 8.6, 4.7 Hz, 1 H, 6b-H), 3.09 (t, *J* = 17.9 Hz, 1 H, 2a-H), 2.98 (dd, *J* = 17.9, 2.7 Hz, 1 H, 2b-H), 1.45 (s, 3 H, Me), 1.37 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.7, 130.8 (2 C), 128.2 (2 C), 127.3 (2 C), 109.6, 91.0, 87.0, 86.6, 80.1, 73.0, 70.1, 67.4, 38.3, 26.9, 25.1 ppm. MS (API-ES+): *m*/*z* = 301.2 $[M + 1]^+$, 323.1 $[M + Na]^+$. Data for **31a**, minor isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (m, 2 H), 7.28 (m, 3 H), 5.31 (s, 1 H, 1′-H), 4.95 (br. s., 1 H, 3-H), 4.38 (ddd, *J* = 8.2, 6.2, 5.1 Hz, 1 H, 5-H), 4.30 (dd, *J* = 8.2, 6.7 Hz, 1 H, 4-H), 4.18 (dd, *J* = 8.6, 6.2 Hz, 1 H, 6a-H), 4.04 (dd, *J* = 8.6, 5.1 Hz, 1 H, 6b-H), 3.30 (d, *J* = 3.3 Hz, 2 H, 2-H), 1.47 (s, 3 H, Me), 1.39 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 131.6 (2 C), 130.9, 128.2 (2 C), 128.1, 109.3, 100.33, 85.9, 83.5, 82.4, 73.6, 72.9, 66.9, 26.9, 25.2, 19.7 ppm. MS (API-ES+): *m*/*z* = 301.0 $[M + 1]^+$, 323.3 $[M + Na]^+$.

Compound 31b: Bromide **8b** (100 mg, 0.36 mmol) and trimethylsilylacetylene (**15**; 54 μL, 0.40 mmol) were treated according to the general procedure. After purification by flash chromatography (hexane/EtOAc, 80:20), compound **31b** was obtained as a 1:1 separable but unassigned mixture of compounds **31b**. Data for **31b**, isomer 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94 (br. s, 1 H, 1′-H), 4.55 (m, 1 H, 3-H), 4.35 (ddd, *J* = 8.5, 6.1, 4.6 Hz, 1 H, 5-H), 4.17 (dd, *J* = 8.8, 6.1 Hz, 1 H, 4-H), 4.12 (dd, *J* = 8.5, 3.4 Hz, 1 H), 4.01 (dd, *J* = 8.8, 4.4 Hz, 1 H), 2.97 (t, *J* = 1.7 Hz, 1 H), 2.94 (dd, *J* = 5.1, 2.4 Hz, 1 H, 2b-H), 1.44 (s, 3 H, Me), 1.37 (s, 3 H, Me), 0.17 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3, 109.9, 102.9, 95.6, 87.3, 80.4, 73.2, 70.3, 67.6, 38.5, 27.1, 25.3, 0.4 (3 C) ppm. MS (API-ES+): *m*/*z* = 297.1 $[M + 1]^+$, 319.0 $[M + Na]^+$. Data for **31b**, isomer 2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.55 (m, 2 H, 3-H, 1′-H), 4.41 (ddd, *J* = 8.3, 6.1, 4.9 Hz, 1 H, 5-H), 4.22 (dd, *J* = 9.0, 6.1 Hz, 1 H, 6a-H), 4.19 (dd, *J* = 8.3, 3.2 Hz, 1 H, 4-H), 4.10 (dd, *J* = 9.0, 4.9 Hz, 1 H, 6b-H), 2.87 (ddd, *J* = 17.0, 5.4, 2.2 Hz, 1 H, 2a-H), 2.65 (d, *J* = 17.3 Hz, 1 H, 2b-H), 1.44 (s, 3 H, Me), 1.38 (s, 3 H, Me), 0.18 (s, 9 H, TMS) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3, 109.9, 102.9, 95.6, 87.3, 80.4, 73.2, 70.3, 67.6, 38.5, 27.1, 25.3, 0.4 (3 C) ppm. MS (API-ES+): *m*/*z* = 297.1 $[M + 1]^+$.

Compound 31c: Bromide **8b** (100 mg, 0.36 mmol) and 1-dodecyne (**16**; 92 μL, 0.40 mmol) were treated according to the general procedure. After purification by flash chromatography (hexane/EtOAc, 60:40), compound **31c** was obtained as a 1:1 inseparable but unassigned mixture of compounds (48 mg, 37%) followed by amino alcohol **32**. Data for **31c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.01 (m, 1 H), 4.59 (m, 1 H), 4.49 (m, 1 H), 4.22 (m, 2 H), 4.17 (dd, *J* = 8.5, 4.6 Hz, 1 H, 2-H), 3.02 (m, 1 H), 2.69 (m, 1 H), 1.39 (m, 16 H), 1.37 (s, 3 H, Me), 0.85 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.2, 109.6, 106.7, 85.4, 80.7, 79.9, 73.5, 66.9, 60.7, 45.1, 31.9 (2 C), 29.6, 27.1 (2 C), 26.3, 25.5, 24.9, 23.0 (2 C), 14.5 (2 C) ppm. MS (API-ES+): *m*/*z* = 365.1 $[M + 1]^+$. Data for **32**: $[\alpha]_D^{25}$ = +45.1 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.16 (d, *J* = 1.2 Hz, 1 H, 1′-H), 4.52 (dd, *J* = 4.6, 2.6 Hz, 1 H, 3-H), 4.34 (m, 2 H), 4.20 (dd, *J* = 8.8, 5.7 Hz, 1 H, 6a-H), 4.10 (dd, *J* = 8.6, 4.4 Hz, 1 H, 6b-H), 3.82 (dd, *J* = 2.6, 1.0 Hz, 1 H, 2-H), 3.60 (q, *J* = 6.9 Hz, 4 H, 2 NEt_2), 1.47 (s, 3 H, Me), 1.38 (s, 3 H, Me), 1.06 (t, *J* = 6.9 Hz, 6 H, 2 NEt_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 109.9, 84.0, 77.1, 73.6, 72.9, 71.0, 67.6, 44.6, 26.9, 25.3, 13.4 ppm. MS (API-ES+): *m*/*z* = 351 $[M + 1]^+$. $C_{14}H_{24}BrNO_4$ (349.2): calcd. C 48.01, H 6.91, N 4.00; found C 48.22, H 6.94, N 3.89.

Compound 33:[51] $[\alpha]_D^{25}$ = +4.5 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.13 (br. s, 1 H, 1′-H), 4.53 (dd, *J* = 4.0, 1.8 Hz, 1 H, 3-H), 4.32 (m, 2 H), 4.19 (dd, *J* = 8.8, 5.7 Hz, 1 H, 6a-H), 4.06 (dd, *J* = 8.8, 4.6 Hz, 1 H, 6b-H), 3.47 (br. s, 1 H, 2-H), 2.48 (m, 4 H), 1.55 (m, 6 H), 1.46 (s, 3 H, Me), 1.37 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.0, 109.7, 85.1, 78.0, 75.3, 73.1, 72.7, 67.7, 51.8 (2 C), 27.2, 26.4 (2 C), 25.6, 24.5 ppm. MS

(API-ES+): *m*/*z* = 362 $[M]^+$, 364 $[M + 2]^+$. $C_{15}H_{24}BrNO_4$ (361.26): calcd. C 49.73, H 6.68, Br 22.06, N 3.87; found C 49.56, H 6.64, Br 21.97, N 3.79.

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