25. Oligosaccharide Analogues of Polysaccharides

Part 6

Orthogonal Protecting/Activating Groups in an Improved Binomial Synthesis of 'Acetyleno-oligosaccharides'

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Bromination of the monosilylated dialkynylated monomer **1a** (*Scheme 1*), dimer **3** and tetramer **5** by *N*-bromosuccinimide (NBS) in the presence of CF_3COOAg gave **2**, **4**, and **6**, respectively, in over 93%. Similar conditions led to bromodesilylation. Either silyl group of the diprotected monomer **1c** was selectively removed by bromolysis. On the one hand, bromodesilylation of **1c** gave **2** in yields varying between 80 and 99%. On the other hand, bromodesilylation of **7**, obtained from **1c** by hydrolytic removal of the tetrahydro-2*H*-pyran-2-yl (Thp) group, yielded 91% of **8**. Mechanistic considerations suggested that the deprotective bromination should be improved by replacing the Me_3Si by a Me_3Ge group. Indeed, bromodegermylation of **1b** was quantitative and *ca.* 60 times faster than bromodesilylation of **1c**. The Me_3Si and Me_3Ge groups can be used for an orthogonal protection/activation of dialkynes. This was shown by desilylating **12** to **11** (*Scheme 2*), while bromination yielded **13**. Both reactions proceeded in high yields; **9** was isolated as a minor by-product of **13**. The reactivity towards bromolysis decreases in the series H-DOPS > $Me_3Ge \approx H > Me_3Si \gg$ Thp-DOPS (DOPS = [*d*imethyl(*o*xy)-*p*ropyl]dimethyl*s*ilyl). Orthogonal bromolysis of DOPS- and Me_3Ge-substituted dialkynes is slightly more selective than the one of Me_3Si- and Me_3Ge-substituted analogues. Coupling of **7** with the bromoalkyne **2** gave the dimer **15** (76%), **14** (2%), and **16** (4%) (*Scheme 3*). The binomial synthesis was optimized so that each cycle, doubling the size of the precursor, requires the minimal number of transformations (*Scheme 4*). The orthogonally protected monomer **1b**, dimer **19**, and tetramer **22** were, on the one hand, hydrolyzed to the alcohols **18** (95%), **21** (91%), and **24** (91%), respectively, and, on the other hand, bromodegermylated to **2** (99%), **4** (97%), and **6** (93%). Cross-coupling of **18** with **2**, **21** with **4**, and **24** with **6** gave the orthogonally protected dimer **19** (73%), tetramer **22** (87%), and octamer **25** (83%), respectively.

Introduction. – The binomial synthesis of 'acetyleno-oligosaccharides' [1–7] requires an orthogonal deprotection of dialkynes and a cross-coupling of haloalkynes with alk-1-ynes [1] [3] [5].

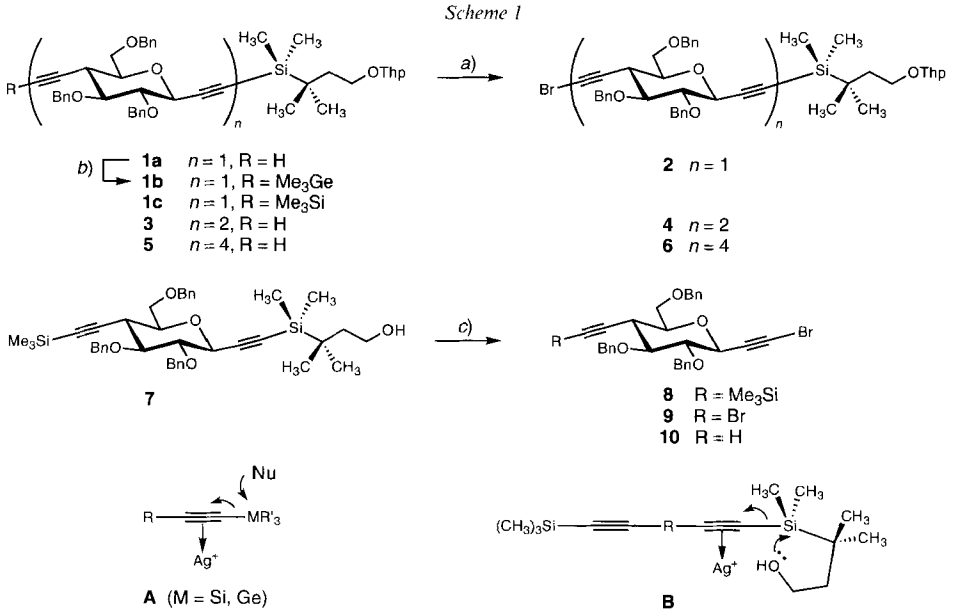
We have described the synthesis and high-yielding orthogonal deprotection of Me_3Si- and [*d*imethyl(*o*xy)*p*ropyl]dimethyl*s*ilyl(DOPS)-protected dialkynes such as **1c** [3]; this constitutes a solution to the first problem. The cross-coupling of saccharide-derived alk-1-ynes and haloalkynes, however, has so far led to mixtures of hetero- and homodimers from which the heterodimers were isolated in yields of only 50–75% [2–4]. Recent studies of a model system [5] led to much improved conditions for the heterocoupling and to a proposal for the mechanism of the hetero- and homocoupling; the value of these conditions for the synthesis of acetyleno-saccharides has yet to be assessed.

The full potential of a binomial synthesis can only be realized by minimizing the number of steps required for doubling the molecular size, and by maximizing the yields.

With this in mind, we have developed new orthogonal protecting groups for dialkynes, and a new procedure for the cross-coupling of saccharide-derived alkynes.

Results and Discussion. – Model studies [5] convinced us of the superiority of bromoalkynes over iodoalkynes for the cross-coupling. The required saccharide-derived bromoalkynes were initially prepared by treating the monomer **1a** [3], the dimer **3** [3], and the tetramer **5** (see below) with *N*-bromosuccinimide (NBS) and catalytic amounts of CF_3COOAg in acetone [8] (*Scheme 1*). The brominations were completed in 25 min, 2 h, and 3 h, respectively, leading to **2**, **4**, and **6** in over 93% yield. However, Me_3Si-protected alkynes can be directly transformed into bromoalkynes under mild conditions using NBS and $AgNO_3$ in acetone [9]. Similar conditions using the more highly soluble CF_3COOAg (*Scheme 1*) led exclusively to bromodesilylation of the Me_3Si–C≡C group of **1c** [3], yielding 80–90% of **2**. Bromodesilylation of the (hydroxypropyl)silyl(H-DOPS)- and Me_3Si-protected **7** [3] proceeded with the opposite regioselectivity and yielded 91% of the bromoalkyne **8** within 15 min in acetone/1,2-dichloroethane 2:5[1]). Thus, dialkynes protected by Me_3Si and DOPS groups can either be orthogonally bromo- or protiodesilylated [3]. However, the bromodesilylation of **1c** was slow (25 h) and the yields were fickle, varying between 80 and 99%.

Scheme 1



a) CF_3COOAg (cat.), NBS, acetone, r.t.; for **1a** and **1b**: 25 min, > 97%; for **1c**: 25 h, 80–99%; for **3**: 2 h, 94%; for **5**: 3 h, 93%. *b*) BuLi, Me_3GeCl, THF, −76° → r.t., 90%. *c*) CF_3COOAg (cat.), NBS, r.t., in acetone, 3 h: **8** (30%), **9** (25%), **10** (37%); in $(CH_2Cl)_2$/acetone 5:2, 15 min: **8** (91%).

[1]) If the reaction was performed in acetone, the yield was only 69% after 15 min; prolonging the reaction time to 3 h led to a mixture of **8** (30%), **9** (25%), and **10** (37%). The bromination was much slower in acetone/CH_2Cl_2 1:10 (14 h) and in $(CH_2Cl)_2$ (22 h) than in acetone, but gave higher yields of **8**, as evidenced by TLC.

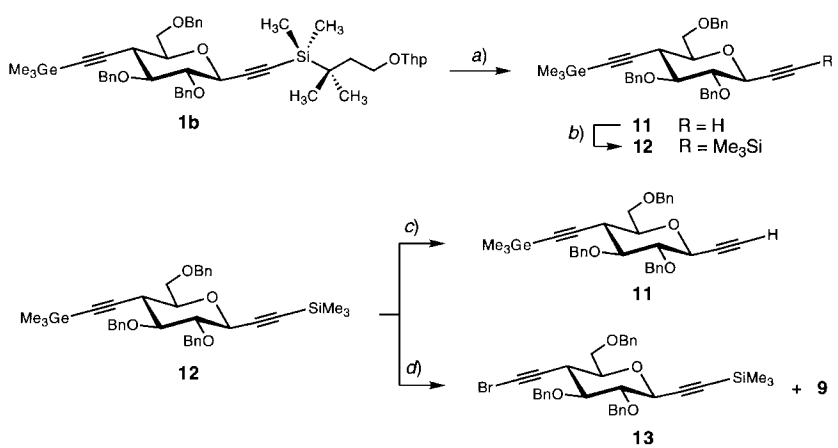
We assume that the crucial step in the bromodesilylation is the formation of an intermediate silver acetylide [9]. Indeed, NBS does not react with alkynes in the absence of a silver salt [8], and silver acetylides are formed by treating (trimethylsilyl)alkynes with $AgNO_3$ in aqueous EtOH [10], probably by nucleophilic cleavage of the Si–C bond in a Ag^I-alkyne complex [11] (see **A** (M = Si) in *Scheme 1*). In such a complex, intramolecular attack on the Si-centre, resulting in cleavage of the C–Si bond and leading to the silver acetylide, as in **B** (*Scheme 1*), is expected to be faster than the intermolecular process illustrated by **A** (M = Si). This explains the regioselectivity of the bromodesilylation of **7**; the preferred cleavage of the C–$SiMe_3$ group in **1c** is due to steric hindrance of the intermolecular attack at the Si-centre of the DOPS group.

This reaction mechanism suggests that a more highly nucleophilic alkyne should lead to higher yields of bromoalkynes. Substitution of the Me_3Si group by a Me_3Ge group should enhance the nucleophilicity, due to the stronger β-effect of Ge [12] [13], and facilitate the formation of the silver(I)-alkyne complexes.

Treatment of the monoprotected dialkyne **1a** with BuLi and then by Me_3GeCl[2]) yielded 90% of **1b**. Bromination of the germyl-alkyne **1b** to **2** in acetone was rapid (25 min *vs.* 25 h for **1c**) and quantitative. In contrast to the even more highly nucleophilic but also more labile R_3Sn–C≡C group, the Me_3Ge–C≡C group was stable under the conditions of cross-coupling[3]).

The C–Ge bond of Me_3Ge–C≡C–Ph is cleaved by alkali 35 times more slowly than the C–Si bond of Me_3Si–C≡C–Ph [15]. Obviously, replacing the DOPS by the Me_3Ge group should give orthogonally protected, activated dialkynes. This was checked on the dialkyne **12** (*Scheme 2*), prepared in a yield of 86% by selective deprotection of **1b** to **11**

Scheme 2



a) HCl, then K_2CO_3, r.t.; **11** (99%). *b*) BuLi, Me_3SiCl, THF, −76 → 0°; **12** (86%). *c*) K_2CO_3/EtOH, r.t.; 99%. *d*) CF_3COOAg (cat.), NBS (1.0 equiv.), r.t.; **13** (94%), **9** (3%), **12** (1%).

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[2]) Me_3GeCl is commercial (*Aldrich*) and easily prepared (see [14] and ref. cit. therein).

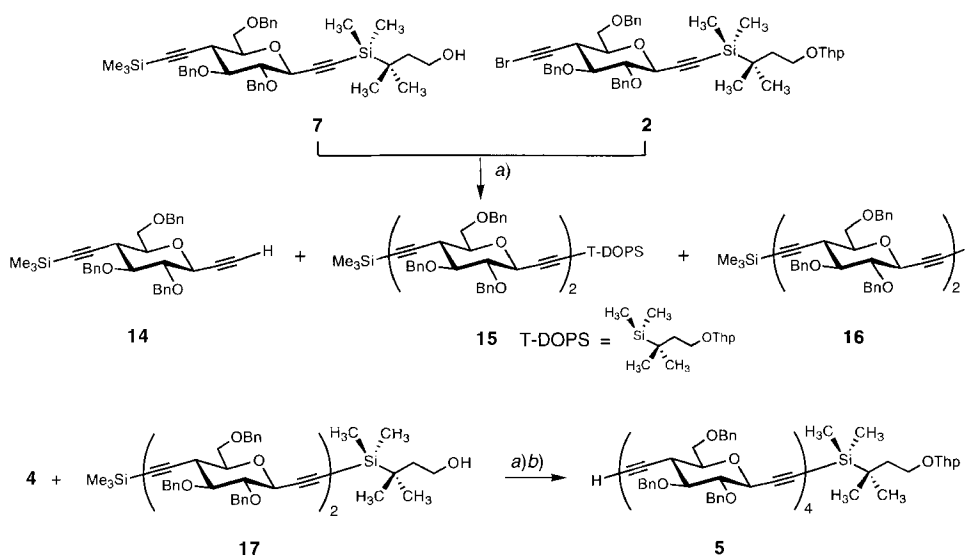
[3]) Treatment of a mixture of **1b**, 2-(3-butynyloxy)tetrahydro-2*H*-pyran and 1-bromo-3-methoxypropyne with $[Pd_2(dba)_3]$/CuI (dba = dibenzylideneacetone) and 1,2,2,6,6-pentamethylpiperidine [5] in benzene for 75 h led to 85% recovery of **1b** (see *Exper. Part*).

(99%) followed by silylation (BuLi, Me_3SiCl). On the one hand, treatment with K_2CO_3/EtOH for 3.5 h led to quantitative desilylation of **12** to **11**; no sign of degermylation was found in the ^{1}H-NMR spectrum of the crude product. On the other hand, bromination of **12** gave **13** in 94% yield, together with 3% of the dibromodialkyne **9** and 1% of starting material **12**.

These results indicate that the reactivity towards bromination decreases in the series H-DOPS > Me_3Ge[4]) ≈ H > Me_3Si ≫ Thp-DOPS. The orthogonal protecting[5])/activating Me_3Si and Me_3Ge groups can be directly introduced into dialkynes, while 'acetylenosaccharides' have to be prepared by the introduction of DOPS-protected ethyne, a building block requiring 6 steps for its preparation [3]. The Me_3Si- and Me_3Ge-protected dialkynes are regioselectively deprotected and brominated, respectively, in high yield.

In spite of the disadvantages associated with the introduction of the DOPS-ethynyl moiety, the DOPS group is expected to prove a better choice for the binomial synthesis of high 'acetyleno-oligomers' than the Me_3Si group, since the combination of the DOPS and Me_3Ge protecting groups ensures a more highly regioselective bromination than the Me_3Si and Me_3Ge couple. This selectivity will be important if the separation of the monobromoalkynes from the dibrominated by-products and the starting material should become increasingly more difficult with each cycle in the binomial synthesis.

Scheme 3



a) $[Pd_2(dba)_3]$/CuI (cat.), 1,2,2,6,6-pentamethylpiperidine (3–5 equiv.), r.t.; **7** + **2** → **15** (76%) + **16** (4%) + **14** (2%). *b*) K_2CO_3; **5** (72% overall).

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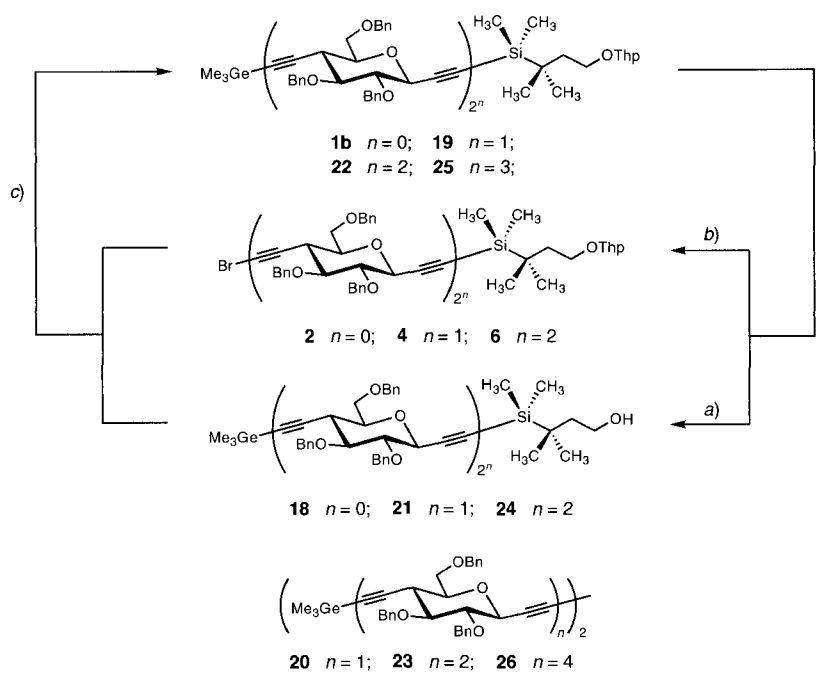
[4]) Bromination of **7** in acetone/CH_2Cl_2 2:5 at room temperature gave **8** within 15 min. Addition of CH_2Cl_2 slowed the reaction. Bromination of **16** in acetone at room temperature gave **2** within 25 min. Bromination of **19** in acetone was much faster than in CH_2Cl_2.

[5]) The Me_3Ge group can be regioselectively removed by protonolysis under mild condition [16].

The selective bromodesilylation of **7** to **8** suggests that the deprotected H-DOPS group does not have to be removed prior to cross-coupling. Indeed, although treatment of **7** with Et_3N (5 equiv.) in benzene at room temperature for 22 h gave less than 10% of the desilylated **14** (*Scheme 3*), addition of CuI (*ca.* 0.03 equiv.) led to complete conversion of **7** into **14** within 1 h. Under cross-coupling conditions ($[Pd_2(dba)_3]$/CuI/1,2,2,6,6-pentamethylpiperidine (PMP), benzene, 13.5 h), **7** and **2** gave the heterodimer **15** in 76% yield, together with 4% of the homodimer **16** and *ca.* 2% of the alk-1-yne **14**. The coupling of **7** and **2** in DMSO, THF, or $(CH_2Cl)_2$ was completed in 48, 40, and 2 h, respectively; yields of **15** were lower than in benzene. The tetramer **5** was obtained in 72% yield by coupling **4** and **17** [3], followed by desilylation.

The number of steps required for each cycle of the binomial synthesis was then reduced to a minimum of three transformations (*Scheme 4*), shortening the earlier procedure by two steps [1] [3]. On the one hand, the orthogonally protected monomeric tetrahydropyranyl acetal **1b** was hydrolyzed in 95% yield to the alcohol **18**, and, on the other hand, bromodegermylated in 99% yield to **2**. The coupling of **18** and **2** in benzene/$(CH_2Cl)_2$ 12:1 with PMP as the base led to the dimer **19** in 73% yield together with 3% of the homodimer **20**, *ca.* 3% of the alk-1-yne **11**, and *ca.* 5% of **2**. No dimerization product derived from **2** was found.

Scheme 4



a) HCl, r.t.; > 91%. *b*) CF_3COOAg (cat.), NBS, r.t.; > 92%. *c*) $[Pd_2(dba)_3]$/CuI (cat.), r.t.; $n = 0$: 1,2,2,6,6-pentamethylpiperidine (2 equiv.), benzene/$(CH_2Cl)_2$ 12:1, **19** (73%), **20** (3%), **2** (*ca.* 5%), **11** (*ca.* 3%); $n = 1$: Et_3N (4 equiv.), benzene, **22** (87%), **23** (1%), **4** (12%); **25** (83%), **26** (*ca.* 1%), **6** (10%).

Hydrolysis of the dimer **19** under mildly acidic conditions yielded 91% of the alcohol **21**. Bromodegermylation of **19**, best performed in acetone, yielded 97% of **4**. Coupling the dimers **4** and **21** (1:1, 0.08M) in benzene, and in the presence of $[Pd_2(dba)_3]$, CuI, and Et_3N led in 87% yield to the tetramer **22**. Less than 1% of the homodimer **23** was formed, and 12% of the bromoalkyne **4** was recovered. The products were readily separated by FC. No dimerization of the bromoalkyne **4** was observed.

Removal of the Thp group of the tetramer **22** afforded the alcohol **24** (91%). For the bromodegermylation, a small portion of $(CH_2Cl)_2$ had to be used to dissolve the suspension of the tetramer **22** in acetone; the bromide **6** was isolated in 92% yield. The coupling conditions described above transformed the tetramers **6** and **24** (1.1:1; 0.075M in benzene) into the octamer **25** in 83–84% yield. About 10% of **6** were recovered, while a mixture of the homodimer **26** and the octamer **25** (1:1; *ca.* 1%) was detected by MALDI-MS. The products were separated by HPLC.

The Me_3Si, Me_2Si, and Me_3Ge groups can be distinguished from each other by a combination of ^1H- and ^{13}C-NMR spectroscopy. The *s*'s of the $(CH_3)_3Si$ and $(CH_3)_2Si$ groups appear at 0.19–0.10 ppm, and those of the $(CH_3)_3$ Ge groups at 0.23–0.30 ppm. The *q*'s of the $(CH_3)_3Si$ and $(CH_3)_3Ge$ groups appear at 0.00 to −0.28 ppm, while the *q*'s the $(CH_3)_2Si$ groups resonate at −4.27 to −4.36 ppm.

For the range of $\delta(^{13}C)$ values of the ethynyl groups at C(3) and C(6) of the monomers, and at $C(3_A)$ (C(3) of ring A) and $C(8_\omega)$ (C(8) of ring ω) of the oligomers, see *Figure*. The assignments of the *s*'s of $C{\equiv}C{-}GeMe_3$, $C{\equiv}C{-}$DOPS, and C≡C–C≡C of the hetero-oligomers are based on a C–H heteronuclear multiple-bond correlation gradient-accelerated spectroscopic experiment (HMBC.GRASP [17] [18]) of **24**. The intensities of the C–H correlation signals, indicating the strength of couplings between H and C, depend on the proximity of a H-atom to a particular C-atom. $C(1_B)$, *e.g.*, is expected to couple strongly to $H{-}C(6_A)$, and $C(4_B)$ to $H{-}C(5_B)$. However, $C(2_B)$

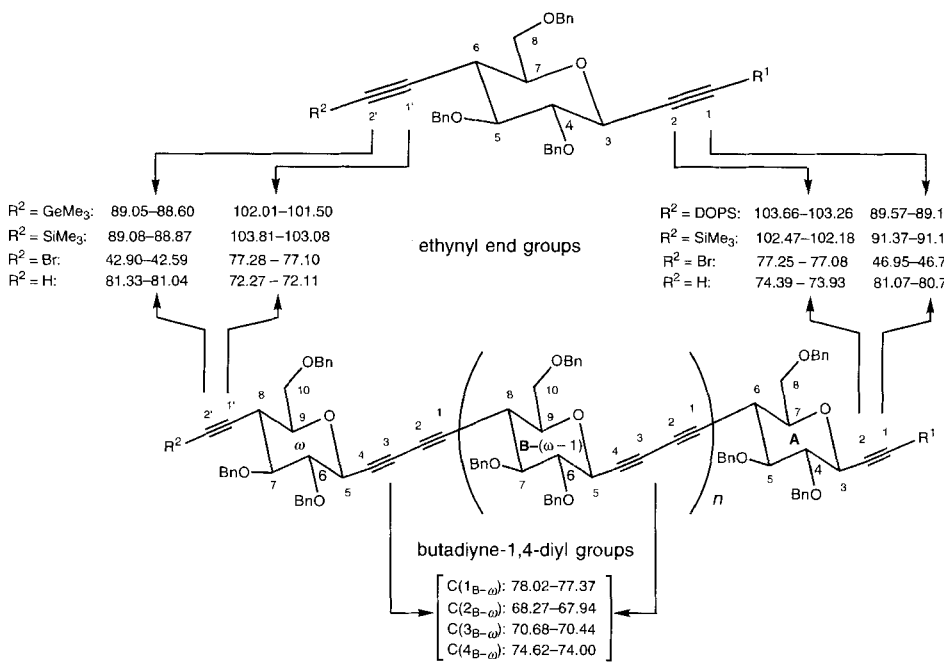


Figure. *^{13}C-NMR Chemical shifts* [ppm] *for the C≡C groups of the 'acetylenomono- and -oligosaccharides'* **1**–**25**. Data from *Exper. Part* and [3]. $n = 0, 2, 6$.

will couple only weakly to H–C(6_A), and C(3_B) weakly to H–C(5_B). Thus, the *s*'s of the tetramer **24** at 103.52, 101.64, 77.91–77.37, and 74.60–74.07 ppm which show the most intense correlation signals in the HMBC.GRASP spectrum are assigned to C(2_A), C($1'_D$), C(1_{B-D}), and C(4_{B-D}), respectively. The weaker signals at 89.57, 89.04, 68.26–68.01, and 70.64–70.46 ppm are assigned to C(1_A), C($2'_D$), C(2_{B-D}), and C(3_{B-D}), respectively. The position of the DOPS and Me_3Ge groups is evidenced by the correlation signals of $(CH_3)_2Si-C(1_A)$ and $(CH_3)_3GeC(2'_D)$.

The IR spectra of **1b**, **8**, **11**, **12**, **19**, **21**, **22**, and **25** show a weak C≡C band for the C≡C–Si and C≡C–Ge groups at 2171–2174 cm^{-1}, while the weak band of C≡C–Br groups of **2**, **8**, **9**, **10**, and **13** appears at 2182–2219 cm^{-1}, and the C≡C–C≡C band of **19**, **22**, and **25** appears at 2259 cm^{-1}, its intensity being proportional to the number of the monomeric units.

The $^4C_1$ conformation of the ethynylated anhydroglucitols is evidenced by the large vicinal coupling constants of the ring H-atoms. *J*(3,4) for ring A and *J*(5,6)'s of the other rings are 9.1–9.7 Hz, while *J*(5,6) of ring A and *J*(7,8) of the other rings are 10.4 Hz, establishing the equatorial position of the ethynyl substituents.

In the MALDI-TOF mass spectra, all 'acetyleno-oligosaccharides' are characterized by their $[M + Na]^+$, and in some cases also the $[M + K]^+$ peaks.

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Experimental Part

General. See [1–4]. DMSO was distilled under vacuum. CuI (*Fluka*) and tris(dibenzylideneacetone)dipalladium(0) ($[Pd_2(dba)_3]$; *Aldrich*) were used without purification. Reactions were run under N_2, and solvents were degassed. After workup, solvents were removed under reduced pressure (rotatory evaporator). HPLC: prepacked HPLC silica-gel column (*J392, Dr. Ing. H. Krauer GmbH*). Gel-permeation chromatography (GPC): *TSK gel® G3000H*, 60 × 2.15 cm, *Tosohaas Co.* FAB-MS: fast-atom-bombardment ionization. The molecular ions of the oligomers with molecular weight higher than 1000 were detected by matrix-assisted laser-desorption ionization mass spectrometry (MALDI-MS): method *A*: the sample was dissolved in DMSO and mixed with the same volume of a soln. of α-cyano-4-hydroxycinnamic acid (CCA, 0.1M) in CF_3COOH/H_2O/MeCN 0.1:33.3:66.6; method *B*: as method *A*, but in toluene, with CCA (0.1M) in MeCN/EtOH/H_2O 50:45:5.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-6-*C*-(bromoethynyl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-*D*-glycero-*D*-gulo-octitol* (**2**). *a*) At r.t., a soln. of 1.35% CF_3COOAg in acetone (0.1 ml, 6.1 μmol) was added to a soln. of **1a** [3] (85 mg, 0.122 mmol) and *N*-bromosuccinimide (NBS; 26 mg, 0.146 mmol) in acetone (1.5 ml). The mixture was protected from light and stirred for 25 min. Usual workup and FC (hexane/AcOEt 95:5) gave **2** (92 mg, 97%).

b) As *a*), but with **1b** (see below) for 25 min: **2** (99%).

c) As *a*), but with **1c** [3] for 25 h: **2** (80–99%). Oil. R_f (hexane/AcOEt 7:3) 0.52. IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*s*, 2945*s*, 2865*m*, 2181*w*, 1497*m*, 1454*m*, 1356*m*, 1324*w*, 1294*w*, 1258*m*, 1132*s*, 1077*s*, 1028*s*, 982*m*, 955*w*, 908*m*, 867*w*, 839*m*, 818*s*, 641*w*, 601*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.26 (*m*, 15 arom. H); 5.01 (*d*, *J* = 10.6, PhC*H*); 4.86 (*d*, *J* = 10.7, PhC*H*); 4.82 (*d*, *J* = 10.7, PhC*H*); 4.80 (*d*, *J* = 10.6, PhC*H*); 4.67 (*d*, *J* = 12.3, PhC*H*); 4.57 (*d*, *J* = 12.3, PhC*H*); 4.55–4.52 (*m*, OCHO); 4.03 (*d*, *J* = 9.3, H–C(3)); 3.88–3.81 (*m*, OCH_2); 3.79 (*dd*, *J* = 11.0, 1.8, H–C(8)); 3.67 (*dd*, *J* = 11.0, 4.8, H–C(8)); 3.53 (*dd*, *J* = 10.1, 8.8, H–C(5)); 3.50–3.41 (*m*, H–C(7), OCH_2, H–C(4)); 2.81 (*t*, *J* = 10.3, H–C(6)); 1.83–1.76 (*m*, 1 H); 1.72–1.47 (*m*, 7 H); 0.99 (*s*, Me); 0.98 (*s*, Me); 0.139 (*s*, MeSi); 0.131 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.13 (*s*); 138.07 (*s*); 138.03 (*s*); 128.38–127.63 (several *d*); 103.41 (*s*); 103.39 (*s*, C(2)); 99.01 (*d*, OCHO); 89.46 (*s*, C(1)); 83.15 (*d*, C(5)); 81.99 (*d*, C(4)); 78.85 (*d*, C(7)); 77.23 (*s*, C(1')); 75.70 (*t*, PhCH_2); 75.45 (*t*, PhCH_2); 73.54 (*t*, PhCH_2); 70.55 (*d*, C(3)); 69.98 (*t*, C(8)); 64.10 (*t*), 64.08 (*t*, OCH_2); 62.42 (*t*); 62.40 (*t*, OCH_2); 42.59 (*s*, C(2')); 38.23 (*d*, C(6)); 37.71 (*t*), 37.68 (*t*); 30.82 (*t*); 25.50 (*t*); 23.17 (*q*, Me); 22.98 (*q*, Me); 19.72 (*s*), 19.70 (*s*); 18.48 (*t*); 0.00 (*q*, Me_2Si); −4.33 (*q*, MeSi); −4.35 (*q*, MeSi). FAB-MS: 773 (0.4, $[M + 1]^+$), 771 (0.4), 692 (3), 689 (3, $[M - Thp + 2]^+$), 91 (100), 85 (38). Anal. calc. for $C_{43}H_{53}BrO_6Si$ (773.88): C 66.74, H 6.90; found: C 66.97, H 7.02.

*3,7-Anhydro-6-*C*-[5,9-anhydro-6,7,10-tri-*O*-benzyl-8-*C*-(bromoethynyl)-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1-yl]-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-*D*-glycero-*D*-gulo-octitol* (**4**). *a*) As described for **2**, with CF_3COOAg (5.9 mg, 0.027 mmol), **3** [3] (623 mg, 0.537 mmol) in acetone (5 ml), and NBS (105 mg, 0.591 mmol); r.t., 2 h). FC (hexane/AcOEt 9:1) gave **4** (585 mg, 94%).

b) As *a*), but with **19** for 2 h; **4** (97%). Oil. R_f (hexane/AcOEt 85:15) 0.13. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.23 (*m*, 30 arom. H); 5.00 (*d*, *J* = 10.5, PhC*H*); 4.91–4.86 (*m*, 4 PhC*H*); 4.82–4.76 (*m*, 3 PhC*H*); 4.69–4.52 (*m*, 4 PhC*H*); 4.57–4.55 (*m*, OCHO); 4.09 (br. *d*, *J* ≈ 9.3, H–C(3)); 4.05 (*d*, *J* = 9.5, H–C(5′)); 3.90–3.77 (*m*, OCH_2, H–C(8), H–C(10′)); 3.72–3.66 (*m*, H–C(8), H–C(10′)); 3.60–3.41 (*m*, OCH_2, H–C(5), H–C(7′), H–C(7), H–C(9′), H–C(4), H–C(6′)); 2.92 (br. *t*, *J* = 10.3, H–C(6)); 2.84 (*t*, *J* = 10.3, H–C(8′)); 1.84–1.51 (*m*, 8 H); 1.002 (*s*, Me); 0.995 (*s*, Me); 0.16 (*s*, MeSi); 0.15 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.00 (2*s*); 137.86 (2*s*); 137.60 (2*s*); 128.47–127.66 (several *d*); 103.26 (*s*, C(2)); 99.03 (*d*, OCHO); 89.56 (*s*, C(1)); 83.07 (*d*, C(5), C(7′)); 81.81 (*d*, C(4)); 81.59 (*d*, C(6′)); 78.88 (*d*, C(9′)); 78.78 (*d*, C(7)); 77.95 (*s*, C(1′)); 77.28 (*s*, C(1″)); 75.90 (*t*, PhCH_2); 75.80 (*t*, PhCH_2); 75.68 (*t*, PhCH_2); 75.52 (*t*, PhCH_2); 74.11 (*s*, C(4′)); 73.65 (*t*, 2 PhCH_2); 70.65 (*s*, C(3′)); 70.55 (*d*, C(3)); 70.49 (*d*, C(5′)); 70.07 (*t*, C(8)); 69.98 (*t*, C(10′)); 67.98 (*s*, C(2′)); 64.09 (*t*, OCH_2); 62.44 (*t*, OCH_2); 42.90 (*s*, C(2″)); 38.14 (*d*), 37.87 (*d*, C(6), C(8′)); 37.69 (*t*); 30.82 (*t*), 25.51 (*t*), 23.17 (*q*, Me); 22.98 (*q*, Me); 19.73 (*t*); 18.48 (*s*); −4.32 (*q*, Me_2Si). FAB-MS: 1155 (1), 1153 (1, $[M - Thp + 2]^+$), 181 (12), 91 (100), 85 (37).

*3,7-Anhydro-6-*C*-*{*5,9-anhydro-8-*C*-*[*5,9-anhydro-6,7,10-tri-*O*-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-*(bromoethynyl)*-*D*-glycero-*D*-gulo-*decitol-1-yl]-6,7,10-tri-*O*-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-*D*-glycero-*D*-gulo-*decitol-1-yl*}*-6,7,10-tri-*O*-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-*D*-glycero-*D*-gulo-*decitol-1-yl*}*-4,5,8-tri-*O*-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-*{*[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl*}-*D*-glycero-*D*-gulo-*octitol* (**6**). *a*) As described for **2**, with CF_3COOAg (1.9 mg, 8.6 μmol; in 0.1 ml of acetone), **5** (see below; 361 mg, 0.173 mmol) in acetone (2 ml) and $(CH_2Cl)_2$ (0.4 ml), and dried NBS (33.9 mg, 0.19 mmol; in 1 ml of acetone; r.t., 3 h). FC (hexane/CH_2Cl_2/AcOEt 60:20:5) gave **6** (342 mg, 93%.).

b) As described in *a*), with **22** (see below) for 4 h: 92% of **6**. Solid. R_f (benzene/THF 97:3) 0.38. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.35–7.21 (*m*, 60 arom. H); 4.98 (*d*, *J* = 10.6, PhC*H*); 4.88–4.81 (*m*, 8 PhC*H*); 4.78–4.71 (*m*, 7 PhC*H*); 4.66–4.51 (*m*, 8 PhC*H*, OCHO); 4.07 (br. *d*, *J* = 9.6, H–$C(5_B)$, H–$C(5_C)$); 4.06 (br. *d*, *J* = 9.7, H–$C(5_D)$); 4.02 (*d*, *J* = 9.6, H–$C(3_A)$); 3.86–3.81 (*m*, OCH_2); 3.80–3.76 (*m*, H–$C(8_A)$, H–$C(10_{B-D})$); 3.69–3.65 (*m*, H–$C(8_A)$, H–$C(10_{B-D})$); 3.57–3.41 (*m*, H–$C(5_A)$, H–$C(7_{B-D})$, H–$C(7_A)$, H–$C(9_{B-D})$, H–$C(4_A)$, H–$C(6_{B-D})$, OCH_2); 2.906 (br. *t*), 2.903 (br. *t*), 2.894 (br. *t*, *J* = 10.3, H–$C(6_A)$, H–$C(8_B)$, H–$C(8_C)$); 2.82 (*t*, *J* = 10.4, H–$C(8_D)$); 1.82–1.47 (*m*, 8 H); 0.98 (*s*, Me); 0.97 (*s*, Me); 0.132 (*s*), 0.131 (*s*), 0.12 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.00 (*s*); 137.96 (*s*); 137.93 (*s*); 137.91 (*s*); 137.86 (*s*); 137.80 (2*s*); 137.73 (2*s*); 137.61 (*s*); 137.55 (2*s*); 128.43–127.63 (several *d*); 103.29 (*s*, $C(2_A)$); 99.01 (*d*), 98.99 (*d*, OCHO); 89.54 (*s*, $C(1_A)$); 83.07 (*d*, $C(5_A)$, $C(7_D)$); 83.01 (*d*), 82.99 (*d* $C(7_B)$, $C(7_C)$); 81.83 (*d*, $C(4_A)$); 81.57 (*d*, $C(6_D)$); 81.43 (*d*), 81.40 (*d*, $C(6_B)$, $C(6_C)$); 78.90 (*d*, $C(9_D)$); 78.85 (*d*), 78.84 (*d*, $C(9_B)$, $C(9_C)$)); 78.78 (*d*, $C(7_A)$); 78.01 (*s*), 77.63 (*s*), 77.54 (*s*, $C(1_{B-D})$); 77.23 (*s*, Br–C≡*C*); 75.87 (2*t*), 75.80 (*t*), 75.75 (*t*), 75.68 (2*t*), 75.64 (*t*), 75.48 (*t*, 8 PhCH_2); 74.31 (*s*), 74.16 (*s*), 74.00 (*s*, $C(4_{B-D})$); 73.77 (*t*), 73.76 (*t*), 73.64 (2*t*, 4 PhCH_2); 70.68 (*s*), 70.58 (*s*), 70.52 (*s*, $C(3_{B-D})$); 70.55 (*d*, $C(3_A)$); 70.49 (*d*, $C(5_{B-D})$); 70.12 (*t*, $C(10_B)$, $C(10_C)$); 70.07 (*t*, $C(8_A)$); 69.98 (*t*, $C(10_D)$); 68.16 (*s*), 68.11 (*s*), 67.95 (*s*, $C(2_{B-D})$); 64.09 (*t*), 64.06 (*t*, OCH_2); 62.41 (*t*), 62.38 (*t*, OCH_2); 42.89 (*s*, $C(1''_D)$); 38.14 (*d*, $C(8_D)$); 37.87 (*d*, $C(6_A)$); 37.80 (*d*, $C(8_B)$, $C(8_C)$); 37.72 (*t*); 37.68 (*t*); 30.81 (*t*); 25.49 (*t*); 23.16 (*q*), 22.98 (*q*), 22.97 (*q*, 2 Me); 19.71 (*t*), 19.69 (*t*); 18.47 (*s*); −4.33 (*q*), −4.34 (*q*), −4.37 (*q*, Me_2Si). MALDI-MS (*A*) for $C_{136}H_{137}BrO_{18}Si$ (2167.56): 2188.7 ($[M + Na]^+$).

Bromination of **7**. *a*) As described for **2**, with 0.68% CF_3COOAg in acetone (0.1 ml, 3.1 μmol), **7** [3] (30 mg, 0.0439 mmol), and NBS (9.4 m, 0.053 mmol) in acetone (0.3 ml; 3 h). Usual workup and FC (hexane/AcOEt 93:7 → 85:15) gave **8** (8 mg, 30%), **9** (6.7 mg, 25%), and **10** (8.7 mg, 37%).

b) As *a*), but in $(CH_2Cl)_2$/acetone 5:2, for 15 min: **8** (91%).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1-*C*-bromo-1,1,2,2-tetrahydro-1,2,6-trideoxy-6-*C*-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**8**): Oil. R_f (hexane/AcOEt 7:3) 0.44. IR ($CHCl_3$): 3067*w*, 3008*m*, 2959*w*, 2910*w*, 2870*w*, 2219*w*, 2174*w*, 1605*w*, 1497*w*, 1454*m*, 1398*w*, 1357*m*, 1295*w*, 1251*s*, 1131*s*, 1085*s*, 1028*s*, 984*w*, 944*w*, 910*w*, 846*s*, 646*w*, 606*w*, 565*w*, 506*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.26 (*m*, 15 arom. H); 4.98 (*d*, *J* = 10.5, PhC*H*); 4.88 (*d*, *J* = 10.6, PhC*H*); 4.84 (*d*, *J* = 10.5, PhC*H*); 4.81 (*d*, *J* = 10.6, PhC*H*); 4.61 (*s*, PhCH_2); 4.05 (*d*, *J* = 9.6, H–C(3)); 3.83 (*dd*, *J* = 10.9, 1.8, H–C(8)); 3.65 (*dd*, *J* = 10.9, 5.5, H–C(8)); 3.57 (*dd*, *J* = 10.4, 8.9, H–C(5)); 3.52 (*ddd*, *J* = 10.4, 5.5, 1.8, H–C(7)); 3.45 (*dd*, *J* = 9.6, 8.9, H–C(4)); 2.78 (*t*, *J* = 10.4, H–C(6)); 0.10 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.28 (*s*); 138.07 (*s*); 137.86 (*s*); 128.45–127.65 (several *d*); 103.15 (*s*, C(1′)); 89.02 (*s*, C(2′)); 83.70 (*d*, C(5)); 81.45 (*d*, C(4)); 79.10 (*d*, C(7)); 77.25 (*s*, C(2)); 75.86 (*t*, PhCH_2); 75.66 (*t*, PhCH_2); 73.70 (*t*, PhCH_2); 70.86 (*d*, C(3)); 70.21 (*t*, C(8)); 46.79 (*s*, C(1)); 38.33 (*d*, C(6)); −0.14 (*q*, Me_3Si). FAB-MS: 663 (1), 617 (1, $[M - 1]^+$), 91 (100), 73 (43).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1-*C*-bromo-6-*C*-(bromoethynyl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D*-glycero-*D*-gulo-octitol* (**9**): Oil. R_f (hexane/AcOEt 7:3) 0.40. IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*m*, 2913*w*, 2870*w*, 2219*w*, 1497*w*, 1454*m*, 1357*w*, 1295*w*, 1260*w*, 1131*s*, 1084*s*, 1028*s*, 911*w*, 833*w*, 602*w*, 563*w*, 524*w*, 512*w*, 504*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.27 (*m*, 15 arom. H); 4.89 (*d*, *J* = 10.6, PhC*H*); 4.88 (*d*, *J* = 10.5, PhC*H*); 4.85 (*d*,

J = 10.7, PhC*H*); 4.81 (*d*, J = 10.5, PhC*H*); 4.65 (*d*, J = 12.3, PhC*H*); 4.55 (*d*, J = 12.3, PhC*H*); 4.03 (*d*, J = 9.6, H–C(3)); 3.77 (*dd*, J = 11.0, 1.8, H–C(8)); 3.66 (*dd*, J = 11.0, 4.8, H–C(8)); 3.54 (*dd*, J = 10.4, 8.8, H–C(5)); 3.49 (*ddd*, J = 10.4, 4.8, 1.8, H–C(7)); 3.46 (*dd*, J = 9.5, 8.9, H–C(4)); 2.81 (*t*, J = 10.4, H–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$): 137.99 (*s*); 137.89 (*s*); 137.72 (*s*); 128.50–127.67 (several *d*); 83.12 (*d*, C(5)); 81.58 (*d*, C(4)); 78.74 (*d*, C(7)); 77.10 (*s*); 77.08 (*s*, C(2), C(1′)); 75.78 (*t*, PhCH_2); 75.68 (*t*, PhCH_2); 73.60 (*t*, PhCH_2); 70.87 (*d*, C(3)); 69.92 (*t*, C(8)); 46.95 (*s*, C(1)); 42.81 (*s*, C(2′)); 38.14 (*d*, C(6)). FAB-MS: 661 (2, $[M + K]^+$), 623 (2, $[M + 1]^+$), 154 (20), 136 (17), 91 (100), 55 (18).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1-*C*-bromo-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-ethynyl-*D*-glycero-*D*-gulo-octitol* (**10**): Oil. R_f (hexane/AcOEt 7:3) 0.38. IR ($CHCl_3$): 3307*m*, 3090*w*, 3067*w*, 3008*m*, 2912*w*, 2870*w*, 2219*w*, 1497*w*, 1454*m*, 1398*w*, 1357*w*, 1295*w*, 1261*w*, 1132*s*, 1076*s*, 1028*m*, 913*w*, 649*m*, 606*w*, 566*w*, 514*w*, 507*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.26 (*m*, 15 arom. H); 4.96 (*d*, J = 10.6, PhC*H*); 4.88 (*d*, J = 10.6, PhC*H*); 4.86 (*d*, J = 10.5, PhC*H*); 4.80 (*d*, J = 10.5, PhC*H*); 4.63 (*d*, J = 12.2, PhC*H*); 4.58 (*d*, J = 12.2, PhC*H*); 4.05 (*d*, J = 9.6, H–C(3)); 3.82 (*dd*, J = 10.9, 1.8, H–C(8)); 3.70 (*dd*, J = 10.9, 5.1, H–C(8)); 3.57 (*dd*, J = 10.4, 9.8, H–C(5)); 3.52 (*ddd*, J = 10.5, 5.1, 1.8, H–C(7)); 3.47 (*dd*, J = 9.5, 8.9, H–C(4)); 2.78 (*td*, J = 10.4, 2.5, H–C(6)); 2.12 (*d*, J = 2.4, H–C(2′)). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.20 (*s*); 138.03 (*s*); 137.77 (*s*); 128.48–127.62 (several *d*); 83.43 (*d*, C(5)); 81.55 (*d*, C(4)); 81.09 (*d*, C(2′)); 79.03 (*d*, C(7)); 77.22 (*s*, C(2)); 75.83 (*t*, PhCH_2); 75.69 (*t*, PhCH_2); 73.67 (*t*, PhCH_2); 72.27 (*s*, C(1′)); 70.87 (*d*, C(3)); 70.06 (*t*, C(8)); 46.86 (*s*, C(1)); 37.04 (*d*, C(6)). FAB-MS: 545 (1, $[M + 1]^+$), 543 (1), 149 (13), 147 (14), 91 (100), 73 (27).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-6-*C*-[(trimethylgermyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**1b**). At −76°, a soln. of **1a** [3] (550 mg, 0.791 mmol) in THF (8 ml) was treated dropwise with BuLi (2.34M in hexane; 0.35 ml, 0.82 mmol), stirred for 70 min at −76°, treated dropwise with a soln. of Me_3GeCl (110 µl, 0.89 mmol) in THF (3 ml), and stirred at −76° for 1.5 h and at −76° → r.t. for 20 min. Usual workup and FC (hexane/AcOEt 93:7) gave **1b** (574 mg, 90%) and **1a** (39 mg, 7%). **1b**: Colourless oil. R_f (benzene/THF 97:3) 0.37. IR ($CHCl_3$): 3090*w*, 3066*w*, 3007*s*, 2945*s*, 2864*s*, 2173*w*, 1497*m*, 1454*m*, 1411*w*, 1355*m*, 1294*m*, 1253*m*, 1132*s*, 1076*s*, 1027*s*, 981*m*, 908*m*, 867*m*, 836*s*, 647*w*, 611*m*, 576*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 4.99 (*d*, J = 10.8, PhC*H*); 4.97 (*d*, J = 10.8, PhC*H*); 4.81 (*d*, J = 10.6, PhC*H*); 4.80 (*d*, J = 10.6, PhC*H*); 4.63 (*s*, PhCH_2); 4.55–4.52 (*m*, OCHO); 4.05 (*d*, J = 9.6, H–C(3)); 3.87 (*dd*, J = 11.0, 1.8, H–C(8)); 3.87–3.81 (*m*, OCH_2); 3.68 (*dd*, J = 11.0, 5.6, H–C(8)); 3.55 (*dd*, J = 10.3, 8.8, H–C(5)); 3.51 (*ddd*, J = 10.6, 5.6, 1.8, H–C(7)); 3.49–3.42 (*m*, OCH_2); 3.45 (*dd*, J = 9.5, 8.9, H–C(4)); 2.76 (*t*, J = 10.4, H–C(6)); 1.82–1.76 (*m*, 1 H); 1.71–1.60 (*m*, 3 H); 1.57–1.48 (*m*, 4 H); 0.985 (*s*, Me); 0.979 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.138 (*s*, MeSi); 0.137 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.49 (*s*); 138.26 (*s*); 138.25 (*s*); 128.35–127.57 (several *d*); 103.68 (*s*), 103.66 (*s*, C(2)); 102.01 (*s*, C(1′)); 98.99 (*d*), 99.01 (*d*, OCHO); 89.15 (*s*, C(1)); 88.71 (*s*, C(2′)); 83.94 (*d*, C(5)); 81.90 (*d*, C(4)); 79.38 (*d*, C(7)); 75.78 (*t*, PhCH_2); 75.43 (*t*, PhCH_2); 73.61 (*t*, PhCH_2); 70.51 (*d*, C(3)); 70.33 (*t*, C(8)); 64.10 (*t*), 64.08 (*t*, OCH_2); 62.41 (*t*), 62.39 (*t*, OCH_2); 38.40 (*d*, C(6)); 37.68 (*t*), 37.65 (*t*); 30.81 (*t*); 25.50 (*t*); 23.17 (*q*), 23.16 (*q*); 22.96 (*q*, 2 Me); 19.72 (*s*), 19.70 (*s*); 18.47 (*t*); −0.27 (*q*, Me_3Ge); −4.31 (*q*), −4.32 (*q*), −4.35 (*q*, 2 MeSi). FAB-MS: 813 (2), 811 (3, $[M - 1]^+$), 809 (2), 731 (4), 730 (5), 729 (12, $[M - Thp + 2]^+$), 728 (6), 727 (8), 725 (6), 181 (28), 137 (19), 136 (22), 121 (21), 119 (66), 118 (19), 117 (63), 115 (45), 92 (58), 91 (100), 86 (13), 85 (91), 83 (16), 75 (32). Anal. calc. for $C_{46}H_{62}GeO_6Si$ (811.69): C 68.07, H 7.70; found: C 68.14, H 7.64.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-[(trimethylgermyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**11**). At r.t., a soln. of **1b** (45 mg, 0.055 mmol) in CH_2Cl_2/MeOH 3:8 (1.1 ml) was treated with 2 drops of 12N HCl, stirred for 50 min, treated with K_2CO_3 (*ca.* 20 mg), and stirred for 10 min. Usual workup and FC (hexane/AcOEt 95:5) gave **11** (32.5 mg, 100%). Oil. R_f (benzene) 0.43. IR ($CHCl_3$): 3307*s*, 3090*w*, 3067*w*, 3008*s*, 2982*m*, 2912*s*, 2870*m*, 2171*w*, 2131*w*, 1497*m*, 1454*s*, 1397*w*, 1359*m*, 1295*m*, 1257*m*, 1136*s*, 1085*s*, 1028*s*, 948*w*, 912*w*, 834*s*, 643*m*, 611*s*, 576*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.43–7.27 (*m*, 15 arom. H); 5.01 (*d*, J = 10.6, PhC*H*); 4.96 (*d*, J = 10.5, PhC*H*); 4.83 (*d*, J = 10.5, PhC*H*); 4.81 (*d*, J = 10.6, PhC*H*); 4.62 (*s*, PhCH_2); 4.05 (*dd*, J = 9.3, 2.1, H–C(3)); 3.88 (*dd*, J = 10.8, 1.7, H–C(8)); 3.68 (*dd*, J = 10.8, 5.5, H–C(8)); 3.58 (*dd*, J = 10.3, 8.9, H–C(5)); 3.58–3.50 (*m*, H–C(7)); 3.48 (*dd*, J = 9.2, 8.8, H–C(4)); 2.78 (*t*, J = 10.2, H–C(6)); 2.52 (*d*, J = 2.1, H–C(1)); 0.29 (*s*, Me_3Ge). ^{13}C-NMR (50 MHz, $CDCl_3$): 138.08 (*s*); 137.88 (*s*); 137.77 (*s*); 128.05–127.30 (several *d*); 101.50 (*s*, C(1′)); 88.60 (*s*, C(2′)); 83.60 (*d*, C(5)); 81.31 (*d*, C(4)); 80.70 (*d*, C(1)); 79.09 (*d*, C(7)); 75.60 (*t*, PhCH_2); 75.32 (*t*, PhCH_2); 73.93 (*s*, C(2)); 73.36 (*t*, PhCH_2); 70.11 (*d*, C(3)); 69.57 (*t*, C(8)); 38.08 (*d*, C(6)); −0.54 (*q*, Me_3Ge). FAB-MS: 585 (4), 583 (5, $[M + 1]^+$), 581 (4), 181 (25), 155 (21), 136 (22), 119 (74), 117 (55), 115 (47), 91 (100).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6-*C*-[(trimethylgermyl)ethynyl]-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**12**). At −76° under Ar, a soln. of **11** (32 mg, 0.055 mmol) in THF (1 ml) was treated with BuLi (1.4M; 47 µl, 0.0065 mmol), stirred for 30 min, treated dropwise with Me_3SiCl (8.3% in THF; 0.1 ml, 0.077 mmol), and stirred at −76° for 30 min and at −76° → r.t. for 20 min. Usual workup and FC

(hexane/AcOEt 96:4) afforded **12** (31 mg, 86%). Oil. R_f (benzene) 0.33. IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*s*, 2962*m*, 2912*s*, 2870*m*, 2173*w*, 1497*m*, 1454*s*, 1411*w*, 1358*s*, 1295*m*, 1252*s*, 1124*s*, 1075*s*, 1028*s*, 912*m*, 846*s*, 647*w*, 611*s*, 578*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.43–7.29 (*m*, 15 arom. H); 4.99 (*d*, *J* = 10.5, PhC*H*); 4.98 (*d*, *J* = 10.6, PhC*H*); 4.88–4.80 (*m*, 2 PhC*H*); 4.64 (*s*, PhCH_2); 4.07 (*d*, *J* = 9.4, H–C(3)); 3.88 (*dd*, *J* = 10.9, 1.7, H–C(8)); 3.70 (*dd*, *J* = 10.9, 5.4, H–C(8)); 3.57 (*dd*, *J* = 10.2, 8.9, H–C(5)); 3.56–3.50 (*m*, H–C(7)); 3.48 (br. *d*, *J* ≈ 9.0, H–C(4)); 2.79 (*t*, *J* = 10.3, H–C(6)); 0.30 (*s*, Me_3Ge); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.48 (*s*); 138.20 (2*s*); 128.37–127.61 (several *d*); 102.47 (*s*, C(2)); 101.95 (*s*, C(1′)); 91.11 (*s*, C(1)); 88.73 (*s*, C(2′)); 83.86 (*d*, C(5)); 81.89 (*d*, C(4)); 79.31 (*d*, (7)); 75.86 (*t*, PhCH_2); 75.56 (*t*, PhCH_2); 73.63 (*t*, PhCH_2); 70.51 (*t*, C(8)); 70.32 (*d*, C(3)); 38.39 (*d*, C(6)); –0.25 (*q*, Me_3Ge, Me_2Si). FAB-MS: 657 (2), 655 (3, $[M + 1]^+$), 653 (2), 181 (25), 119 (85), 117 (71), 115 (53), 91 (100).

Desilylation of **12**. At. r.t., a soln. of **12** (9 mg) was treated with a sat. K_2CO_3 soln. in EtOH (0.5 ml) for 3.5 h. Usual workup gave crude **11**. A ^{1}H-NMR (300 MHz, $CDCl_3$) showed that it was essentially pure (without any traces of the *d* of H–C(2′) at 2.1 ±0.3 ppm).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-6-*C*-(bromoethynyl)-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-(trimethylsilyl)-*D*-glycero-*D*-gulo-octitol* (**13**). As described for **2**, with CF_3COOAg (0.18% in acetone; 100 µl, 8.1 µmol), **12** (18 mg, 0.0275 mmol) in acetone (0.3 ml), and NBS (4.9% in acetone; 100 µl, 0.0275 mmol; r.t., 2.5 h). FC (hexane/AcOEt 96:4) gave **13** (16 mg, 94%), **12** (*ca.* 0.2 mg, 1%), and **9** (0.5 mg, 3%). The ^{1}H-NMR spectra of **9** and **12** were identical to the ones of the authentic samples. **13**: Oil. R_f (benzene) 0.40. IR ($CHCl_3$): 3090*w*, 3066*w*, 3008*s*, 2960*m*, 2909*m*, 2870*m*, 2182*w* (sh), 1497*m*, 1454*s*, 1398*w*, 1358*s*, 1294*m*, 1252*s*, 1130*s*, 1078*s*, 1028*s*, 912*w*, 851*s*, 648*w*, 601*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.27 (*m*, 15 arom. H); 4.99 (*d*, *J* = 10.4, PhC*H*); 4.89 (*d*, *J* = 10.7, PhC*H*); 4.85 (*d*, *J* = 10.7, PhC*H*); 4.81 (*d*, *J* = 10.4, PhC*H*); 4.68 (*d*, *J* = 12.3, PhC*H*); 4.57 (*d*, *J* = 12.3, PhC*H*); 4.04 (*d*, *J* = 9.3, H–C(3)); 3.81 (*dd*, *J* = 11.0, 1.9, H–C(8)); 3.69 (*dd*, *J* = 11.0, 4.7, H–C(8)); 3.54 (*dd*, *J* = 10.5, 8.9, H–C(5)); 3.53–3.48 (*m*, H–C(7)); 3.49 (*dd*, *J* = 9.3, 8.8, H–C(4)); 2.84 (*t*, *J* = 10.3, H–C(6)); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.09 (3*s*); 128.42–127.66 (several *d*); 102.18 (*s*, C(2)); 91.37 (*s*, C(1)); 83.04 (*d*, C(5)); 81.95 (*d*, C(4)); 78.77 (*d*, C(7)); 77.28 (*s*, C(1′)); 75.76 (*t*, PhCH_2); 75.55 (*t*, PhCH_2); 73.54 (*t*, PhCH_2); 70.52 (*d*, C(3)); 69.94 (*t*, C(8)); 42.61 (*s*, C(2′)); 38.20 (*d*, C(6)); –0.28 (*q*, Me_3Si). FAB-MS: 617 (3, $[M + 1]^+$), 615 (2), 181 (33), 136 (23), 91 (100).

General Procedure for the Cross-Coupling of an Alkyne and a Bromoalkyne. At r.t. and under N_2, a mixture of $[Pd_2(dba)_3]$ and CuI was treated with a soln. of an alkyne and a bromoalkyne in a degassed solvent, stirred for 5 min, treated with a base, and stirred until the reaction was completed.

Stability of the Trimethylgermyl Group under the Coupling Conditions. As described above, with $[Pd_2(dba)_3]$ (1.33 mg, 2.9 µmol), CuI (0.46 mg, 2.4 µmol), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (0.10 mmol), 1-bromo-3-methoxypropyne (0.20 mmol), **1b** (14.5 mg, 0.018 mmol) in benzene (1 ml), and 1,2,2,6,6-pentamethylpiperidine (80 µl, 0.44 mmol; 75 h). Usual workup and FC (hexane/AcOEt 95:5) gave **1b** (12.4 mg, 85%).

Cross-Coupling of **7** *and* **2**. As described in the *General Procedure for the Cross-Coupling*, with $[Pd_2(dba)_3]$ (1.36 mg, 2.97 µmol), CuI (0.42 mg, 2.22 µmol), **7** [3] (76.2 mg, 0.111 mmol), **2** [3] (85.8 mg, 0.111 mmol), benzene (1.2 ml), and 1,2,2,6,6-pentamethylpiperidine (55 µl, 0.3 mmol). The mixture was stirred for 13.5 h, diluted with Et_2O, neutralized with cold 0.1N aq. HCl, and processed as usual. FC (hexane/AcOEt 92:8) gave **15** [3] (104 mg, 76%), **16** [3] (5 mg, 4%), **14** [3] (*ca.* 2 mg, 2%) and a polar brown oil (28 mg, not characterized).

*3,7-Anhydro-6-*C*-{5,9-anhydro-8-*C*-[5,9-anhydro-8-*C*-(5,9-anhydro-6,7,10-tri-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-ethynyl-*D*-glycero-*D*-gulo-decitol-1-yl)-6,7,10-tri-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1-yl]-6,7,10-tri-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D*-glycero-*D*-gulo-decitol-1-yl}-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-*D*-glycero-*D*-gulo-octitol* (**5**). As described in the *General Procedure for the Cross-Coupling*, with $[Pd_2(dba)_3]$ (1.57 mg, 3.4 µmol), CuI (0.51 mg, 2.7 µmol), **4** (148 mg, 0.12 mmol), and **17** [3] (138 mg, 0.12 mmol) in DMSO (distilled; 1.2 ml) and 1,2,2,6,6-pentamethylpiperidine (100 µl, 0.55 mmol). After 10 h, the mixture was diluted with Et_2O, treated with cold 0.1N aq. HCl (3 ml), and processed as usual. FC (hexane/AcOEt 9:1 → 8:2) gave a white solid (192 mg). The soln. of the solid in THF (4 ml) was treated with a sat. K_2CO_3 soln. in MeOH (5 ml) for 8 h. Usual workup and FC (hexane/CH_2Cl_2/AcOEt 60:20:6) gave **5** (180 mg, 72%). White solid. R_f (benzene/THF 97:3) 0.31. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.21 (*m*, 60 arom. H); 5.00 (*d*, *J* = 10.8, PhC*H*); 4.95 (*d*, *J* = 10.8, PhC*H*); 4.89–4.72 (*m*, 12 PhC*H*); 4.66–4.51 (*m*, 10 PhC*H*); 4.57–4.55 (*m*, OCHO); 4.12–4.02 (*m*, H–C(3_A), H–C(5_{B-D})); 3.89–3.77 (*m*, OCH_2, H–C(8_A), H–C(10_{B-D})); 3.76–3.66 (*m*, H–C(8_A), H–C(10_{B-D})); 3.62–3.41 (*m*, H–C(4_A), H–C(6_{B-D}), H–C(5_A), H–C(7_{B-D}), H–C(7_A), H–C(9_{B-D}), OCH_2); 2.95–2.87 (*m*, H–C(6_A), H–C(8_{B-C})); 2.80 (*td*, *J* = 10.3, 2.2, H–C(8_D)); 2.14 (*d*, *J* = 2.3, H–C≡C); 1.80–1.47 (*m*, 8 H); 0.99 (*s*, Me); 0.98 (*s*, Me); 0.14 (*s*, MeSi); 0.13 (*s*, MeSi). MALDI-MS (*A*) for $C_{136}H_{138}O_{18}Si$ (2088.66): 2110.4 ($[M + Na]^+$).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-[(3-hydroxy-1,1-dimethylpropyl)-dimethylsilyl]-6-*C*-[(trimethylgermyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**18**). At r.t., a soln. of **1b** (573 mg, 0.706 mmol) in CH_2Cl_2 (2 ml) was treated with 0.12N HCl/EtOH (8.5 ml) and stirred for 2.5 h. Usual workup and FC (hexane/AcOEt 8:2) gave **18** (490 mg, 95%) and **1b** (12 mg, 2%). **18**: Oil. R_f (hexane/AcOEt 8:2) 0.24. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.27 (*m*, 15 arom. H); 4.99 (*d*, *J* = 10.9, 2 PhC*H*); 4.83 (*d*, *J* = 10.7, PhC*H*); 4.82 (*d*, *J* = 10.7, PhC*H*); 4.65 (*s*, PhCH_2); 4.07 (*d*, *J* = 9.6, H–C(3)); 3.89 (*dd*, *J* = 10.9, 1.6, H–C(8)); 3.70 (*t*, *J* = 7.3, CH_2OH); 3.72–3.66 (*m*, H–C(8)); 3.58 (*dd*, *J* = 10.3, 8.9, H–C(5)); 3.56–3.48 (*m*, H–C(7)); 3.46 (br. *t*, *J* = 9.3, H–C(4)); 2.77 (*t*, *J* = 10.3, H–C(6)); 1.59 (*t*, *J* = 7.3, CH_2); 0.97 (*s*, 2 Me); 0.23 (*s*, Me_3Ge); 0.150 (*s*, MeSi); 0.145 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.41 (*s*); 138.25 (*s*); 138.19 (*s*); 128.37–127.63 (several *d*); 103.88 (*s*, C(2)); 101.90 (*s*, C(1′)); 89.23 (*s*, C(1)); 88.82 (*s*, C(2′)); 83.91 (*d*, C(5)); 81.80 (*d* C(4)); 79.35 (*d*, C(7)); 75.81 (*t*, PhCH_2); 75.35 (*t*, PhCH_2); 73.63 (*t*, PhCH_2); 70.46 (*t*, C(8)); 70.29 (*d*, C(3)); 59.58 (*t*, CH_2OH); 41.96 (*t*); 38.39 (*d*, C(6)); 23.49 (*q*, 2 Me); 18.75 (*s*); –0.26 (*q*, Me_3Ge); –4.27 (*q*, Me_2Si). FAB-MS: 730 (2), 729 (4), 728 (2), 727 (3), 725 (2), 181 (13), 119 (33), 116 (27), 115 (21), 92 (24), 91 (100), 75 (32).

Coupling of **18** *with* **2**. As described in the *General Procedure for the Cross-Coupling*, with [Pd_2(dba)$_3$] (5.69 mg, 0.012 mmol), CuI (1.62 mg, 0.0085 mmol), **2** (400 mg, 0.517 mmol) and **18** (376 mg, 0.517 mmol) in degassed benzene/$(CH_2Cl)_2$ 12:1 (6.2 ml), and 1,2,2,6,6-pentamethylpiperidine (200 µl, 1.1 mmol; r.t., 10 h). FC (hexane/AcOEt 94:6 → 9:1) gave **19** (480 mg, 73%), **11**/**2** *ca.* 1:2 (31 mg), **20** (17 mg, 3%), and some unidentified polar by-products (130 mg).

*3,7-Anhydro-6-*C*-{5,9-anhydro-6,7,10-tri-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-[(trimethylgermyl)ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-*D*-glycero-*D*-gulo-octitol* (**19**): Syrup. R_f (hexane/AcOEt 7:3) 0.23. IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*s*, 2945*s*, 2867*s*, 2259*w*, 2173*w*, 1497*m*, 1454*s*, 1356*s*, 1294*m*, 1258*m*, 867*w*, 836*s*, 611*m*, 574*w*, 506*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.21 (*m*, 30 arom. H); 4.98 (*d*, *J* = 10.6, PhC*H*); 4.97 (*d*, *J* = 10.5, PhC*H*); 4.87–4.75 (*m*, 6 PhC*H*); 4.63–4.52 (*m*, 4 PhC*H*); 4.52–4.51 (*m*, OCHO); 4.08 (*dd*, *J* = 9.6, 0.6, H–C(5′)); 4.02 (*d*, *J* = 9.6, H–C(3)); 3.86–3.78 (*m*, OCH_2, H–C(8), H–C(10′)); 3.70–3.65 (*m*, H–C(8), H–C(10′)); 3.58–3.42 (*m*, OCH_2, H–C(4), H–C(6′), H–C(5), H–C(7′), H–C(7), H–C(9′)); 2.89 (br. *t*, *J* = 10.2, H–C(6)); 2.76 (*t*, *J* = 10.4, H–C(8′)); 1.82–1.76 (*m*, 1 H); 1.70–1.59 (*m*, 3 H); 1.55–1.47 (*m*, 4 H); 0.98 (*s*, Me); 0.97 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.134 (*s*), 0.133 (*s*, MeSi); 0.125 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.33 (*s*); 138.13 (*s*); 138.03 (*s*), 137.99 (*s*); 137.93 (*s*); 137.81 (*s*); 128.40–127.62 (several *d*); 103.33 (*s*), 103.30 (*s*, C(2)); 101.68 (*s*, C(1″)); 99.02 (*d*), 98.99 (*d*, OCHO); 89.52 (*s*, C(1)); 89.00 (*s*, C(2″)); 83.86 (*d*, C(7′)); 83.11 (*d*, C(5)); 81.83 (*d*, C(4)); 81.49 (*d*, C(6′)); 79.44 (*d*, C(9′)); 78.82 (*d*, C(7)); 77.80 (*s*, C(1′)); 75.87 (*t*, PhCH_2); 75.76 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 75.48 (*t*, PhCH_2); 74.43 (*s*, C(4′)); 73.70 (*t*, PhCH_2); 73.66 (*t*, PhCH_2); 70.55 (*d*, C(3)); 70.47 (*d*, C(5′)); 70.47 (*s*, C(3′)); 70.36 (*t*, C(10′)); 70.10 (*t*, C(8)); 68.08 (*s*, C(2′)); 64.10 (*t*), 64.07 (*t*, OCH_2); 62.41 (*t*), 62.38 (*t*, OCH_2); 38.34 (*d*, C(8′)); 37.88 (*d*, C(6)); 37.73 (*t*), 37.70 (*t*); 30.81 (*t*); 25.50 (*t*); 23.17 (*q*, Me); 22.98 (*q*, Me); 19.72 (*t*), 19.70 (*t*); 18.48 (*s*); –0.28 (*q*, Me_3Ge); –4.32 (*q*), –4.34 (*q*), –4.36 (*q*, Me_2Si).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-1,5-anhydro-2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-[(trimethylgermyl)ethynyl]-*D*-glucitol}* (**20**): Syrup. R_f (hexane/AcOEt 7:3) 0.28. IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*s*, 2913*s*, 2869*m*, 2170*w*, 1604*w*, 1497*m*, 1454*m*, 1397*w*, 1357*m*, 1292*m*, 1258*w*, 1133*s*, 1076*s*, 1028*s*, 912*w*, 834*s*, 611*s*, 575*w*, 520*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.23 (*m*, 15 arom. H); 4.97 (*d*, *J* = 10.5, PhC*H*); 4.86 (*d*, *J* = 10.5, PhC*H*); 4.83 (*d*, *J* = 10.4, PhC*H*); 4.75 (*d*, *J* = 10.5, PhC*H*); 4.62 (*s*, PhCH_2); 4.11 (*d*, *J* = 9.4, H–C(1)); 3.86 (*dd*, *J* = 10.9, 1.8, H–C(6)); 3.68 (*dd*, *J* = 10.9, 5.5, H–C(6)); 3.57 (*dd*, *J* = 10.2, 8.9, H–C(3)); 3.62–3.49 (*m*, H–C(5)); 3.45 (*dd*, *J* = 9.3, 8.9, H–C(2)); 2.76 (*t*, *J* = 10.2, H–C(4)); 0.29 (*s*, Me_3Ge). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.71 (*s*); 138.51 (*s*); 138.09 (*s*); 128.77–127.94 (several *d*); 102.00 (*s*, C(1′)); 89.26 (*s*, C(2′)); 84.15 (*d*, C(3)); 81.70 (*d*, C(2)); 79.77 (*d*, (5)); 76.90 (*s*); 76.12 (*t*, PHCH_2); 75.94 (*t*, PhCH_2); 73.97 (*t*, PhCH_2); 70.70 (*t*, C(6)); 70.58 (*s*); 70.37 (*d*, C(1)); 38.53 (*d*, C(4)); –0.12 (*q*, Me_3Ge). FAB-MS: 663 (3), 647 (3), 530 (4), 181 (11), 137 (10), 123 (14), 121 (17), 119 (40), 116 (27), 115 (22), 111 (14), 109 (24), 107 (20), 105 (24), 97 (28), 95 (41), 93 (22), 92 (22), 91 (100), 85 (29), 83 (40), 81 (47), 79 (24), 77 (17), 70 (34), 69 (71), 67 (41), 57 (81), 55 (92).

*3,7-Anhydro-6-*C*-{5,9-anhydro-6,7,10-tri-*O*-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C*-[(trimethylgermyl)ethynyl]-*D*-glycero-*D*-gulo-decitol-1-yl}-4,5,8-tri-*O*-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C*-[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]-*D*-glycero-*D*-gulo-octitol* (**21**). As described for **18**, with **19** (460 mg, 0.361 mmol) in CH_2Cl_2 (1.5 ml) and 12N HCl/EtOH 2:98 (6 ml; r.t., 100 min). Usual workup gave **21** (395 mg, 91%). R_f (hexane/AcOEt 7:3) 0.23. IR ($CHCl_3$): 3674*w*, 3606*w* (br.), 3090*w*, 3067*w*, 3007*s*, 2912*m*, 2865*s*, 2259*w*, 2173*w*, 1604*w*, 1497*m*, 1454*s*, 1397*w*, 1357*s*, 1294*m*, 1252*m*, 1127*s*, 1075*s*, 1028*s*, 914*m*, 836*s*, 611*m*, 575*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.21 (*m*, 30 arom. H); 4.97 (*d*, *J* = 10.5, PhC*H*); 4.96 (*d*, *J* = 10.7, PhC*H*); 4.87 (*d*, *J* = 10.5, PhC*H*); 4.85–4.81 (*m*, 2 PhC*H*); 4.79 (*d*, *J* = 10.8, PhC*H*); 4.76 (*d*, *J* = 10.6, PhC*H*); 4.75 (*d*,

J = 10.6, PhC*H*); 4.62 (*d*, J = 12.8, PhC*H*); 4.59 (*d*, J = 12.8, PhC*H*); 4.60 (*d*, J = 12.0, PhC*H*); 4.55 (*d*, J = 12.1, PhC*H*); 4.09 (*dd*, J = 9.6, 0.5, H–C(5′)); 4.03 (*d*, J = 9.6, H–C(3)); 3.85 (*dd*, J = 10.9, 1.7, H–C(10′)); 3.79 (*dd*, J = 11.1, 1.7, H–C(8)); 3.70–3.65 (*m*, CH_2OH, H–C(8), H–C(10′)); 3.58–3.50 (*m*, H–C(5), H–C(7′), H–C(7), H–C(9′)); 3.45 (br. *t*, J = 9.3, H–C(4)); 3.44 (*dd*, J = 9.7, 9.0, H–C(6′)); 2.90 (br. *t*, J = 10.4, H–C(6)); 2.76 (*t*, J = 10.4, H–C(8′)); 1.58 (*t*, J = 7.5, CH_2); 1.55 (*s*, OH); 0.962 (*s*, Me); 0.958 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.134 (*s*, MeSi); 0.129 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.32 (*s*); 138.11 (*s*); 138.05 (*s*); 137.95 (*s*); 137.87 (*s*); 137.81 (*s*); 128.40–127.62 (several *d*); 103.54 (*s*, C(2)); 101.66 (*s*, C(1″)); 89.54 (*s*, C(1)); 89.01 (*s*, C(2″)); 83.86 (*d*, C(7′)); 83.10 (*d*, C(5)); 81.75 (*d*, C(4)); 81.48 (*d*, C(6′)); 79.44 (*d*, C(9′)); 78.81 (*d*, C(7)); 77.69 (*s*, C(1′)); 75.88 (*t*, PhCH_2); 75.77 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 75.39 (*t*, PhCH_2); 74.48 (*s*, C(4′)); 73.70 (*t*, PhCH_2); 73.68 (*t*, PhCH_2); 70.49 (*d*, C(3)); 70.46 (*d*, C(5′)); 70.44 (*s*, C(3′)); 70.35 (*t*, C(10′)); 70.08 (*t*, C(8)); 68.13 (*s*, C(2′)); 59.60 (*t*, CH_2OH); 41.99 (*t*, CH_2); 38.34 (*d*, C(8′)); 37.87 (*d*, C(6)); 23.48 (*q*, 2 Me); 18.74 (*s*); −0.28 (*q*, Me_3Ge); −4.31 (*q*, Me_2Si). MALDI-MS (*A*) for $C_{72}H_{82}GeO_9Si$: (1192.14): 1215 ([*M* + Na]$^+$), 1230 ([*M* + K]$^+$).

Coupling of **4** *with* **21**. As described in the *General Procedure for the Cross-Coupling*, with [Pd(dba)$_3$] (3.02 mg, 6.60 μmol), CuI (0.94 mg, 4.94 μmol), **4** (298 mg, 0.240 mmol) and **21** (287 mg, 0.241 mmol) in degassed benzene (3 ml), and Et_3N (138 μl, 0.99 mmol; r.t., 12 h). FC (AcOEt/CH_2Cl_2/hexane 4:15:600 → 2:5:200) gave **22** (464 mg, 87%), **4** (36 mg, 12%), **23** (18 mg, 1%), and a brown oil (78 mg) which tailed in TLC and was not identified.

*3,7-Anhydro-6-*C-{*5,9-anhydro-8-*C-{*5,9-anhydro-8-*C-{*5,9-anhydro-6,7,10-tri-*O-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C-*[(trimethylgermyl)ethynyl]-*D-glycero-D-gulo-*decitol-1-yl*}-*6,7,10-tri-*O-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl*}-*6,7,10-tri-*O-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-*D-glycero-D-gulo-*decitol-1-yl*}-*4,5,8-tri-*O-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-*C-{*[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl*}-D-glycero-D-gulo-*octitol* (**22**): White solid. R_f (hexane/AcOEt 7:3) 0.32. IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*m*, 2914*m*, 2869*w*, 2259*w*, 2173*w*, 1497*m*, 1454*m*, 1397*w*, 1357*m*, 1294*m*, 1261*m*, 1133*s*, 1076*s*, 1028*s*, 913*w*, 835*m*, 611*w*, 574*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.21 (*m*, 60 arom. H); 4.98 (*d*, J = 10.6, PhC*H*); 4.97 (*d*, J = 10.6 PhC*H*); 4.88–4.81 (*m*, 7 PhC*H*); 4.78–4.71 (*m*, 7 PhC*H*); 4.63–4.51 (*m*, 8 PhC*H*, OCHO); 4.08 (br. *d*, $J \approx 9.6$, H–C(5_D)); 4.06 (br. *d*, J = 9.6), 4.05 (br. *d*, $J \approx 9.6$, H–C(5_B), H–C(5_C)); 4.02 (*d*, J = 9.6, H–C(3_A)); 3.86–3.76 (*m*, H–C(8_A), H–C(10_{B-D}), CH_2O); 3.69–3.65 (*m*, H–C(8_A), H–C(10_{B-D})); 3.58–3.42 (*m*, H–C(5_A), H–C(7_{B-D}), H–C(7_A), H–C(9_{B-D}), OCH_2, H–C(4_A), H–C(6_{B-D})); 2.90 (br. *t*, J = 10.3, H–C(8_B), H–C(8_C)); 2.89 (br. *t*, J = 10.3, H–C(6_A)); 2.76 (*t*, J = 10.4, H–C(8_D)); 1.82–1.42 (*m*, 8 H); 0.98 (*s*, Me); 0.97 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.132 (*s*), 0.131 (*s*), 0.124 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.32 (*s*); 138.11 (*s*); 138.02 (*s*); 137.98 (*s*); 137.92 (*s*); 137.82 (3*s*); 137.75 (2*s*); 137.58 (2*s*); 128.43–127.63 (several *d*); 103.31 (*s*, C(2_A)); 101.66 (*s*, C($1'_D$)); 99.01 (*d*), 98.99 (*d*, OCHO); 89.55 (*s*, C(1_A)); 89.05 (*s*, C($2'_D$)); 83.86 (*d*, C(7_D)); 83.07 (*d*, C(5_A)); 83.05 (*d*); 83.01 (*d*, C(7_B), C(7_C)); 81.84 (*d*, C(4_A)); 81.47 (*d*), 81.41 (*d*, C(6_B), C(6_C)); 81.45 (*d*, C(6_D)); 79.45 (*d*, C(9_D)); 78.85 (*d*), 78.80 (*d*, C(9_B), C(9_C)); 78.80 (*d*, C(7_A)); 78.02 (*s*), 77.62 (*s*), 77.38 (s, C(1_{B-D})); 75.87 (*t*, 3 PhCH_2); 75.75 (*t*, PhCH_2); 75.68 (*t*, 2 PhCH_2); 75.62 (*t*, PhCH_2); 75.48 (*t*, PhCH_2); 74.62 (*s*), 74.20 (*s*), 74.03 (*s*, C(4_{B-D})); 73.77 (*t*, 2 PhCH_2); 73.71 (*t*, PhCH_2); 73.65 (*t*, PhCH_2); 70.68 (*s*), 70.56–70.46 (*s*, C(3_{B-D})); 70.56 (*d*, C(3_A)); 70.50 (*d*, C(5_B), C(5_C)); 70.46 (*d*, C(5_D)); 70.36 (*t*), 70.14 (*t*, C(10_B), C(10_C)); 70.14 (*t*, C(10_D)); 70.08 (*t*, C(8_A)); 68.27 (*s*), 68.13 (*s*), 67.96 (*s*, C(2_{B-D})); 64.10 (*t*), 64.07 (*t*, OCH_2); 62.41 (*t*), 62.38 (*t*, OCH_2); 38.35 (*d*, C(8_D)); 37.88 (*d*, C(6_A)); 37.81 (*d*, C(8_B), C(8_C)); 37.74 (*t*), 37.71 (*t*); 30.81 (*t*); 25.50 (*t*); 23.17 (*q*, Me); 22.99 (*q*, Me); 19.72 (*t*), 19.70 (*t*); 18.48 (*s*); −0.28 (*q*, Me_3Ge); −4.33 (*q*, MeSi); −4.36 (*q*, MeSi). MALDI-MS (*A*) for $C_{139}H_{146}GeO_{18}Si$ (2205.37): 2227 ([*M* + Na]$^+$).

1,1′-(Buta-1,3-diyne-1,4-diyl)bis{(1*S*)-*1,5-anhydro-4-*{*5,9-anhydro-6,7,10-tri-*O-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C-*[(trimethylgermyl)ethynyl]-*D-glycero-D-gulo-*decitol-1-yl*}-*2,3,6-tri-*O-*benzyl-4-deoxy-*D-glucitol*} (**23**): White solid. R_f (hexane/AcOEt 7:3) 0.38. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.21 (*m*, 30 arom. H); 4.97 (*d*, J = 10.6, PhC*H*); 4.87–4.70 (*m*, 7 PhC*H*); 4.61–4.51 (*m*, 4 PhC*H*); 4.08 (br. *d*, J = 9.7, H–C(5′)); 4.07 (*d*, J = 9.6, H–C(1)); 3.85 (*dd*, J = 10.9, 1.6, H–C(10′)); 3.77 (*dd*, J = 10.9, 1.6, H–C(6)); 3.67 (*dd*, J = 10.9, 5.6, H–C(10′)); 3.66 (*dd*, J = 11.1, 4.7, H–C(6)); 3.58–3.49 (*m*, H–C(3), H–C(7′), H–C(5), H–C(9′)); 3.44 (*dd*, J = 9.4, 9.0), 3.43 (*dd*, J = 9.5, 9.0, H–C(2), H–C(6′)); 2.89 (br. *t*, J = 10.3, H–C(4)); 2.76 (*t*, J = 10.4, H–C(8′)); 0.28 (s, Me_3Ge). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.31 (*s*); 138.10 (*s*); 137.83 (*s*); 137.79 (*s*); 137.75 (*s*); 137.48 (*s*); 128.45–127.63 (several *d*); 101.65 (*s*, C(1″)); 89.02 (*s*, C(2″)); 83.85 (*d*, C(7′)); 83.03 (*d*, C(3)); 81.46 (*d*), 81.31 (*d*, C(2), C(6′)); 79.44 (*d*, C(9′)); 78.92 (*d*, C(5)); 77.23 (*s*, C(1′)); 76.41 (*s*); 75.88 (*t*, PhCH_2); 75.85 (*t*, PhCH_2); 75.73 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 74.56 (*s*, C(4′)); 73.76 (*t*, PhCH_2); 73.70 (*t*, PhCH_2); 70.45 (2*d*, C(1), C(5′)); 70.37 (*t*), 70.08 (*t*, C(6), C(10′)); 70.37 (*s*); 70.15 (*s*, C(3′)); 68.23 (*s*, C(2′)); 38.33 (*d*), 37.77 (*d*, C(4), C(8′)); −0.28 (*q*, Me_3Ge). MALDI-MS (*A*) for $C_{130}H_{130}O_{16}Ge_2$ (2093.96): 2118.5 ([*M* + Na]$^+$).

*3,7-Anhydro-6-*C-{*5,9-anhydro-8-*C-{*5,9-anhydro-8-*C-{*5,9-anhydro-6,7,10-tri-*O-*benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-*C-*[(trimethylgermyl)ethynyl]-*D-glycero-D-gulo-*decitol-1-yl*}-*6,7,10-tri-*O-*ben-

zyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-C-[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]*-D-glycero-D-gulo-*octitol* (**24**). As described for **18**, with **22** (382 mg, 0.173 mmol) in CH_2Cl_2 (2.9 ml) and 12N HCl/EtOH 2:98 (4 ml; r.t., 5 h, and diluted with CH_2Cl_2). FC (hexane/CH_2Cl_2/AcOEt 6:2:1 → 6:3:2) gave **24** (334 mg, 91%). White solid. R_f (benzene/THF 97:3) 0.12. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.21 (*m*, 60 arom. H); 4.97 (*d*, J = 10.7, PhC*H*); 4.96 (*d*, J = 10.7, PhC*H*); 4.88–4.80 (*m*, 7 PhC*H*); 4.78–4.72 (*m*, 7 PhC*H*); 4.63–4.52 (*m*, 8 PhCH_2); 4.08 (br. *d*, $J \approx$ 9.6, H–C(5_D)); 4.06 (br. *d*, $J \approx$ 9.6, H–C(5_B), H–C(5_C)); 4.03 (*d*, J = 9.6, H–C(3_A)); 3.85 (*dd*, J = 10.9, 1.6, H–C(8_A)); 3.80–3.77 (*m*, H–C(10_{B-D})); 3.70–3.65 (*m*, H–C(8_A), H–C(10_{B-D}), CH_2OH); 3.58–3.49 (*m*, H–C(5_A), H–C(7_{B-D}), H–C(7_A), H–C(9_{B-D})); 3.47–3.42 (*m*, H–C(4_A), H–C(6_{B-D})); 2.903 (br. *t*, J = 10.4, H–C(8_B), H–C(8_C)); 2.896 (br. *t*, J = 10.3, H–C(6_A)); 2.76 (*t*, J = 10.4, H–C(8_D)); 1.62–1.58 (*m*, OH); 0.960 (*s*, Me); 0.956 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.132 (*s*, MeSi); 0.128 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$, HMBC.GRASP [17] [18]): 138.31 (*s*); 138.09 (*s*); 138.03 (*s*); 137.93 (*s*); 137.85 (*s*); 137.80 (3*s*); 137.73 (2*s*); 137.57 (2*s*); 128.43–127.63 (several *d*); 103.52 (*s*, C(2_A)); 101.64 (*s*, C($1'_D$)); 89.57 (*s*, C(1_A)); 89.04 (*s*, C($2'_D$)); 83.85 (*d*, C(7_D)); 83.04 (*d*); 83.00 (*d*, C(7_B), C(7_C)); 83.05 (*d*, C(5_A)); 81.76 (*d*, C(4_A)); 81.46 (*d*, C(6_D)); 81.43 (*d*), 81.40 (*d*, C(6_B), C(6_C)); 79.44 (*d*, C(9_D)); 78.87 (*d*), 78.84 (*d*, C(9_B), C(9_C)); 78.79 (*d*, C(7_A)); 77.91 (*s*), 77.59 (*s*); 77.37 (*s*, C(1_{B-D})); 75.88 (*t*, 3 PhCH_2); 75.76 (*t*, PhCH_2); 75.68 (*t*, 2 PhCH_2); 75.62 (*t*, PhCH_2); 75.39 (*t*, PhCH_2); 74.60 (*s*), 74.19 (*s*), 74.07 (*s*, C(4_{B-D})); 73.77 (*t*, 2 PhCH_2); 73.70 (*t*, PhCH_2); 73.67 (*t*, PhCH_2); 70.64 (*s*), 70.56 (*s*), 70.49 (*s*, C(3_{B-D})); 70.49 (*d*, C(3_A)); 70.49 (*d*, C(5_B), C(5_C)); 70.45 (*d*, C(5_D)); 70.35 (2*t*), 70.12 (*t*, C(10_{B-D})); 70.06 (*t*, C(8_A)); 68.26 (*s*), 68.13 (*s*), 68.01 (*s*, C(2_{B-D})); 59.60 (*t*, CH_2OH); 41.99 (*t*); 38.34 (*d*, C(8_D)); 37.87 (*d*, C(6_A)), 37.80 (2*d*, C(8_B), C(8_C)); 23.47 (*q*, 2 Me); 18.74 (*s*); −0.28 (*q*, Me_3Ge); −4.31 (*q*, Me_2Si). MALDI-MS (*A*) for $C_{134}H_{138}GeO_{17}Si$ (2127.25): 2143.8 ([M + Na]$^+$).

3,7-Anhydro-6-C-{5,9-anhydro-8-C-{5,9-anhydro-8-C-{5,9-anhydro-8-C-{5,9-anhydro-8-C-{5,9-anhydro-8-C-{5,9-anhydro-8-C-{5,9-anhydro-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy-8-C-[(trimethylgermyl)ethynyl-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-6,7,10-tri-O-benzyl-1,1,2,2,3,3,4,4-octadehydro-1,2,3,4,8-pentadeoxy*-D-glycero-D-gulo-*decitol-1-yl}-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1-C-{[1,1-dimethyl-3-(tetrahydro-2H-pyran-2-yloxy)propyl]dimethylsilyl}*-D-glycero-D-gulo-*octitol* (**25**). As described in the *General Procedure for the Cross-Coupling*, with [Pd_2(dba)$_3$] (1.42 mg, 3.10 µmol), CuI (0.45 mg, 2.36 µmol), **24** (240 mg, 0.113 mmol) and **22** (274 mg, 0.126 mmol) in degassed benzene (1.5 ml), and Et_3N (65 µl, 0.47 mmol; r.t., 15 h, extracted with benzene). HPLC (toluene/THF 98.3:1.7) gave **25** (380 mg, 83%), crude **6** (25 mg, 10%), and **26**/**25** *ca.* 1:1 (7 mg; MALDI-MS: 4086.5 ([**25** + Na]$^+$), 3972.8 ([**26** + Na]$^+$), 3991.2 ([**26** + K]$^+$)). **25**: White solid. R_f (benzene/THF 97:3) 0.28. IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*m*, 2912*m*, 2870*m*, 2259*w*, 2172*w*, 1497*m*, 1454*m*, 1358*m*, 1295*m*, 1262*w*, 1134*s*, 1078*s*, 1028*s*, 915*w*, 834*w*, 611*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.21 (*m*, 120 arom. H); 4.98 (*d*, J = 10.5, PHC*H*); 4.97 (*d*, J = 1.5, PhC*H*); 4.88–4.81 (*m*, 15 PhC*H*); 4.76 (br. *d*, J = 10.6, 8 PhC*H*); 4.72 (br. *d*, J = 10.5, 7 PhC*H*); 4.63–4.51 (*m*, 16 PhC*H*, OCHO); 4.08 (br. *d*, $J \approx$ 9.6, H–C(5_H)); 4.06 (br. *d*, $J \approx$ 9.6, H–C(5_{B-G})); 4.02 (*d*, J = 9.6, H–C(3_A)); 3.86–3.76 (*m*, CH_2O. H–C(8_A), H–C(10_{B-H})); 3.67–3.65 (*m*, H–C(8_A), H–C(10_{B-H})); 3.58–3.50 (*m*, H–C(5_A), H–C(7_{B-H}), H–C(7_A), H–C(9_{B-H}), CH_2O); 3.44 (br. *t*, J = 9.2, H–C(4_A), H–C(6_{B-H})); 2.90 (br. *t*, J = 10.3, H–C(8_{B-G})); 2.89 (br. *t*, J = 10.3, H–C(6_A)); 2.76 (*t*, J = 10.4, H–C(8_H)); 1.81–1.47 (*m*, 8 H); 0.98 (*s*, Me); 0.97 (*s*, Me); 0.28 (*s*, Me_3Ge); 0.13 (*s*, MeSi); 0.12 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.29 (*s*); 138.08 (*s*); 138.00 (*s*); 137.97 (2*s*); 137.90 (*s*); 137.79 (3*s*); 137.77 (4*s*); 137.72 (3*s*); 137.70 (4*s*); 137.54 (4*s*); 128.85–127.63 (several *d*); 103.26 (*s*, C(2_A)); 101.62 (*s*, C($1'_H$)); 99.01 (*d*), 98.99 (*d*, OCHO); 89.54 (*s*, C(1_A)); 89.04 (*s*, C($2'_H$)); 83.84 (*d*, C(7_H)); 83.05 (*d*, C(5_A)); 83.03 (*d*); 82.98 (*d*, C(7_{B-G})); 81.82 (*d*, C(4_A)); 81.45 (*d*, C(6_H)); 81.40 (*d*, C(6_{B-G})); 79.43 (*d*, C(9_H)); 78.83 (*d*, C(9_{B-G})); 78.78 (*d*, C(7_A)); 78.00 (*s*), 77.57 (*s*, C(1_{B-H})); 75.86 (*t*, PhCH_2); 75.74 (*t*, PhCH_2); 75.67 (*t*, 6 PhCH_2); 75.61 (*t*, 2 PhCH_2); 75.48 (*t*, 6 PhCH_2); 75.60 (*s*), 74.18 (5*s*), 74.00 (*s*, C(4_{B-H})); 73.76 (*t*, 6 PhCH_2); 73.69 (*t*, PhCH_2); 73.64 (*t*, PhCH_2); 70.67 (*s*), 70.54 (*s*, C(3_{B-H})); 70.54 (*d*, C(3_A)); 70.48 (*d*, C(5_{B-H})); 70.44 (*d*, C(5_H)); 70.34 (*t*, C(10_H)); 70.10 (*t*, C(8_A)); 70.34 (*t*), 70.10 (*t*, C(10_{B-G})); 68.26 (*s*); 68.13 (5*s*), 67.94 (*s*, C(2_{B-G})); 64.08 (*t*), 64.06 (*t*, OCH_2); 62.41 (*t*), 62.38 (*t*, OCH_2); 38.33 (*d*, C(8_H)); 37.86 (*d*, C(6_A)); 37.79 (*d*, C(8_{B-G})); 37.71 (*t*), 37.68 (*t*); 30.80 (*t*); 25.49 (*t*); 23.16 (*q*, Me); 22.97 (*q*, Me); 19.71 (*t*), 19.69 (*t*); 18.47 (*s*); −0.29 (*q*, Me_3Ge); −4.33 (*q*), −4.35 (*q*), −4.37 (*q*, Me_2Si). MALDI-MS (*B*) for $C_{263}H_{258}GeO_{34}Si$ (4063.62): 4085.0 ([M + Na]$^+$), 4103.0 ([M + K]$^+$).

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