58. Oligosaccharide Analogues of Polysaccharides

Part 3

A New Protecting Group for Alkynes: Orthogonally Protected Dialkynes

by **Chengzhi Cai** and **Andrea Vasella***

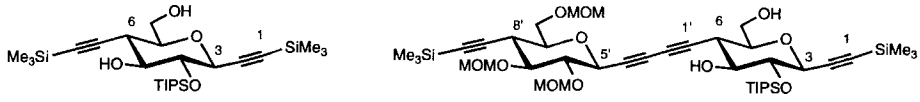
Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

(30. I. 95)

Dialkynes of the type **3** (*Scheme 1*) are regioselectively deprotected by treating them either with base in a protic solvent (→ **4**), or – after exposing the OH group – by catalytic amounts of base in an aprotic solvent (→ **5** and **8**). The Me_3Si-protected **12** (*Scheme 2*) is inert to catalytic BuLi/THF which transformed **11** into **9**, while K_2CO_3/MeOH transformed both **10** into **9**, and **12** into **13**, evidencing the requirement for a more hindered (hydroxypropyl)silyl substituent. *C*-Silylation of the carbanions derived from **17**–**19** (*Scheme 3*) with **15** led to **20**–**22**, but only **22** was obtained in reasonable yields. The key intermediate **27** was, therefore, prepared by a *retro-Brook* rearrangement of **23**, made by silylating the hydroxysulfide **16** with **15**. The OH group of **27** was protected to yield the {[*d*imethyl(*o*xy)*p*ropyl]dimethylsilyl}*a*cetylenes (DOPSA's) **21**, **28**, and **29**. The orthogonally protected acetylenes **20**–**22**, **28**, and **29** were de-trimethylsilylated to the new monoprotected acetylene synthons **30**–**34**. The scope of the orthogonal protection was checked by regioselective deprotection of the dialkynes **39**–**42** (*Scheme 4*), prepared by alkylation of **35** (→ **39**), or by Pd^0/CuI-catalyzed cross-coupling with **36**–**38** (→ **40**–**42**). The cross-coupling depended upon the solvent and proceeded best in *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). Main by-product was the dimer **43**. On the one hand, K_2CO_3/MeOH removed the Me_3Si group and transformed **39**–**42** into the monoprotected **44**–**47**; catalytic BuLi/THF, on the other hand, transformed the alcohols **48**–**51**, obtained by hydrolysis of **39**–**42**, into the monoprotected dialkynes **52**–**55**, all steps proceeding in high yields. Addition of the protected DOPSA groups to the lactones **56** (→ **57**–**59**) and **62** (→ **63**) (*Schemes 5* and *6*) gave the corresponding hemiketals. Reductive dehydroxylation of **57** and **58** failed; but similar treatment of **59** yielded the alcohol **61**. Similarly, **63** was transformed into **64** which was protected as the tetrahydropyranyl (Thp) ether **65**. In an optimized procedure, **62** was treated sequentially with lithiated **31**, BuLi, and Me_3SiCl (→ **66**), followed by desilyloxylation to yield 60% of **67**, which was protected as the Thp ether **68**. Under basic, protic conditions, **68** yielded the monoprotected bisacetylene **69**; under basic, aprotic conditions, **67** led to the monoprotected bisacetylene **70**. These procedures are compatible with the butadiynediyl function. The butadiyne **73** was prepared by cross-coupling the alkyne **69** and the iodoalkyne **71** (obtained from **70**, together with the triiodide **72**) and either transformed to the monosilylated **76** or, *via* **77**, to the monosilylated **78**. Formation of the homodimers **74** and **75** was greatly reduced by optimizing the conditions of cross-coupling of alkynes.

Introduction. – Our projected synthesis of oligosaccharide analogues of polysaccharides [1] requires the regioselective desilylation [2] of protected monosaccharide- or oligosaccharide-derived diacetylenes of the type represented by compounds **1** and **2**. We have already described a reagent-controlled, regioselective desilylation of **1**, based on the different reactivities of the two $Me_3SiC{\equiv}C$ groups [2]. The $Me_3SiC{\equiv}C$ groups attached at C(6) of **1** and the equivalent moiety in **2** (attached at C(8′)) were regioselectively desilylated in 96 and 69% yield, respectively, using the same mild conditions (CN^-/$AgNO_3$ [3] [4]). The conditions for the regioselective desilylation of the propargylic ether moiety of **1** (2 equiv. of BuLi/THF; 90%), however, failed with **2** on account of the labile

butadiynediyl moiety. Although the regioselective desilylation of one of the two $Me_3SiC{\equiv}C$ groups in the presence of the butadiynediyl group may give access to some of the desired oligomers, any binomial synthesis [1] [5] [6] based on the cross-coupling of alkynes requires an orthogonal deprotection of dialkynes. Orthogonally protected dialkynes are thus of interest beyond the limits of our immediate goals. Well-defined alkyne oligomers ([6] and ref. cit. therein) [7] have indeed attracted considerable interest, particularly in the field of organic electronic materials [7–15]. In this context, the butadiynediyl moiety has several advantages, being conjugated, rigid, and linear [7] [16–27]. In principle, the butadiynediyl moiety also allows a binomial assembly of oligomers [1], an advantage that has, however, not yet been used[1]).



1 **2**

MOM = $MeOCH_2$, TIPS = $(i\text{-}Pr)_3Si$

The crucial requirements for an binomial synthesis are a high-yielding regioselective deprotection and cross-coupling. No orthogonally protected, unsymmetrical, 1,(ω – 1)-dialkynes are known. The *Cadiot-Chodkiewicz* reaction and its modifications have been widely used to cross-couple terminal acetylenes [30–33], but yields are often unsatisfactory [34–36], particularly when repetitive cross-coupling is required, and no systematic optimization studies have been published. We now describe a new alkyne protecting group and the synthesis of the first orthogonally protected dialkynes.

Concept, Results, and Discussion. – Terminal alkynes have most often been protected by silylation [37]. Small trialkylsilyl groups (*e.g.* Me_3Si) on alkynes can be selectively removed in the presence of bulky ones (*e.g.* (*tert*-butyl)dimethylsilyl), but the opposite selectivity – required for orthogonal protection – is unknown. A key to orthogonal protection may be found in a kinetically favored intramolecular process, as illustrated in *Scheme 1*. The alkynyl groups of **3** are protected by a small and by a bulky silyl group, respectively. The bulky silyl moiety possesses a masked OH group at the terminal position. In protic solvents and under basic conditions, the less hindered Me_3Si group will be selectively removed. This leads to the monodeprotected **4**. Conversely, the bulkier silyl group should be selectively cleaved off by deprotecting the masked OH group of **3** under mild conditions and treating the resulting alcohol **6** with catalytic amounts of a strong base in an aprotic solvent (→ **7**). Intramolecular attack of the alkoxy group should lead to the oxasilacyclopentane **8** and to an acetylide anion, which is protonated by the alcohol **6**, to generate the regioselectively deprotected **5** and the alkoxy anion derived from **6**. *Eaborn* and *Mahmoud* have indeed shown that the intramolecular cleavage of the Si–C bond in $PhCH_2SiMe_2(CH_2)_3OH$ with NaOMe/MeOH to form toluene is more than 100 times faster than the intermolecular cleavage of $PhCH_2SiMe_3$ [38].

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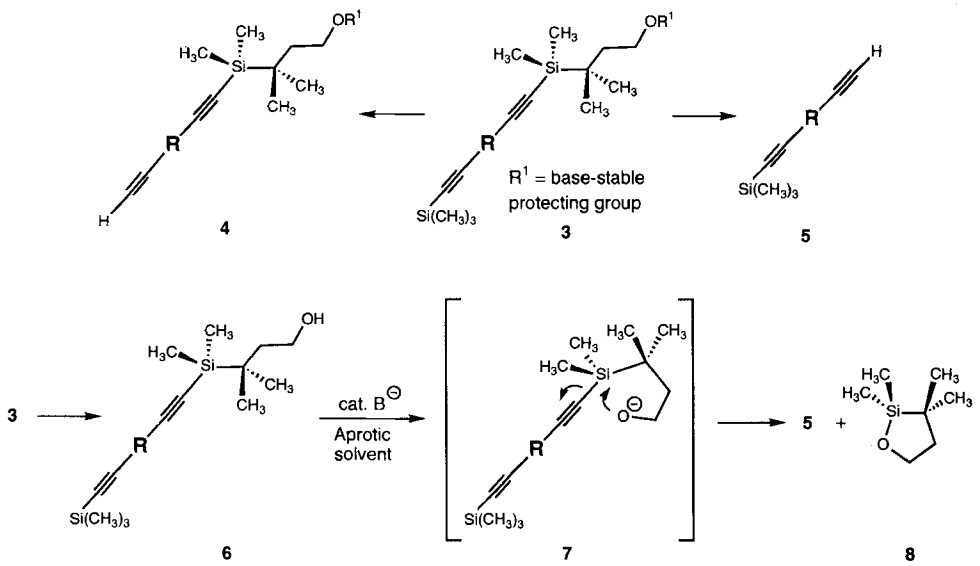
[1]) *Diederich* and coworkers [28] [29] carried out a *Hay* coupling of *trans*-bis(triisopropylsilyl)-protected tetraethynylethene in the presence of a terminal mono-alkyne as a capping reagent. This led to a mixture of products bridged by butadiynediyl moieties (degree of oligomerization $X_n = 22$), the pentamer being the longest isolated oligomer (2% yield).

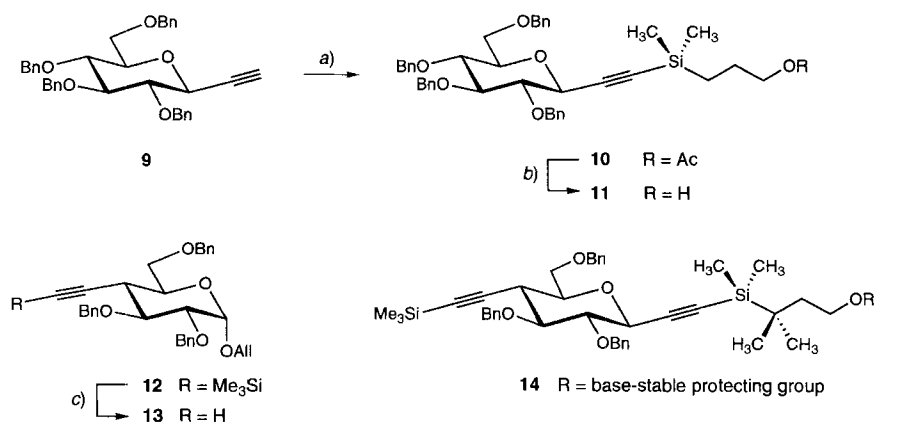
Scheme 1



The base-stable protecting group R^1 in **3** has the function of both protecting **6** during removal of the Me_3Si group, and of facilitating the separation of the cross-coupled products from the homo-coupled ones.

We first tested the selective intramolecular desilylation (*Scheme 2*) on a mixture of the Me_3Si-protected alkyne **12** [1] and the alcohol **11** under basic aprotic conditions. This alcohol was readily available in two steps by treating **9** [2] with BuLi at −76° and then with (3-acetoxypropyl)dimethylsilyl chloride [39] to yield 74% of **10** followed by reduc-

Scheme 2

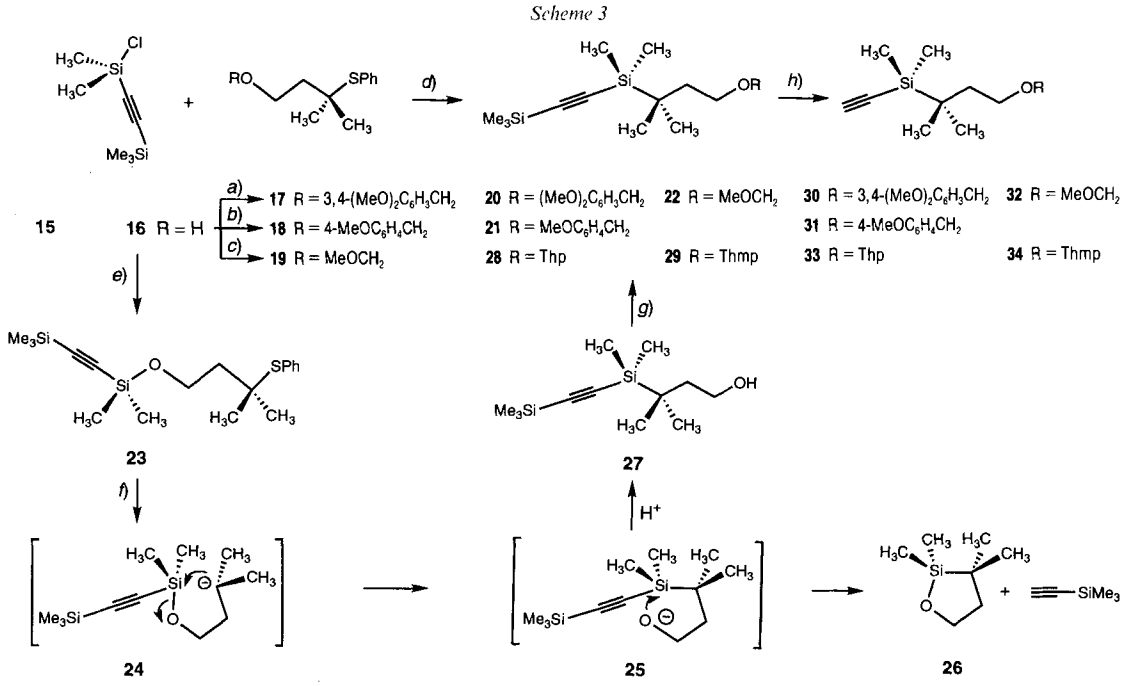


a) BuLi (1 equiv.), $ClSiMe_2(CH_2)_3OAc$, THF, −76°; 74%. *b*) DIBAH, THF, r.t.; 80%. *c*) Bu_4NF, THF, r.t.; quant.

tion of **10** with diisobutylaluminium hydride (DIBAH) to **11** (80%). A 1:1 mixture **11**/**12** in THF was treated with 0.2 equiv. of BuLi at −76 to −20° for 1 h. The ^{1}H-NMR spectrum of the mixture isolated after acidic workup showed the acetylenic *d* of **9** at 2.52 ppm, and no trace of the acetylenic *d* at 2.10 ppm, characteristic of **13**, which was prepared separately by desilylation ($Bu_4NF \cdot 3H_2O$/THF, quant.) of **12**. Both **12** and **10**, however, were desilylated with K_2CO_3 in MeOH, showing that the small steric difference between the silyl groups of these compounds is insufficient for a regioselective detrimethylsilylation. A higher degree of steric hindrance requires a more highly substituted alkyl or 3-oxypropyl moiety, as it is realized in **14**.

Several attempts to obtain compounds of the type **14** by *C*-silylation of alkynes did not lead to satisfactory results. While silylation of the tertiary carbanion derived from **19** (*Scheme 3*), prepared from the readily available **16**[2]), with 2 equiv. of lithium 4,4′-di(*tert*-butyl)biphenyl (LiDBB) [40–45] and the chlorosilane **15** (see [47] and *Exper. Part*) gave

Scheme 3



Thp = tetrahydro-2*H*-pyran-2-yl, Thmp = tetrahydro-4-methoxy-2*H*-pyran-4-yl

a) NaH, 3,4-$(MeO)_2C_6H_3CH_2Cl$, THF/DMF, 5°; 21%. *b*) NaH, 4-$MeOC_6H_4CH_2Cl$, THF/DMF, r.t.; 82%. *c*) $FeCl_3$, 4-Å molecular sieves, $CH_2(OMe)_2$, CH_2Cl_2, −10° to r.t.; 58%. *d*) LiDBB (2 equiv.), **15**, −90°; 30% for **20**; 22% for **21** and 25% for 1-methoxy-4-[(3-methylbutoxy)methyl]benzene; 60% for **22**. *e*) Et_3N, r.t.; 99%. *f*) LiDBB, THF, −90°, 1 h; HCl/EtOH; 50% overall from 3-methylbut-2-enal. *g*) for **21**: 4-methoxybenzyl 2,2,2-trichloroacetimidate, trifluoromethanesulfonic acid (TfOH; cat.), Et_2O, r.t.; 75%; for **28**: 3,4-dihydro-2*H*-pyran, TsOH · Py (cat.), CH_2Cl_2, r.t.; 96%; for **29**: 5,6-dihydro-4-methoxy-2*H*-pyran, TsOH · Py (cat.), CH_2Cl_2, r.t.; 78%. *h*) K_2CO_3, MeOH, r.t.; 89–92%.

[2]) From 3-methylbut-2-enal in nearly quantitative yields (see [46] and *Exper. Part*).

ca. 60% of the bis-silylated ethyne **22**, yields were considerably lower for the *O*-benzyl-protected analogues **20** (30%) and **21** (22%), prepared from the thioethers **17** and **18**, respectively. These low yields are due to a competing protonation of the tertiary carbanion, as evidenced by the isolation of *ca.* 25% of 1-methoxy-4-[(3-methylbutoxy)methyl]-benzene from the reaction **18** → **21**. For this reason, we prepared the silylated acetylenes **31**, **33**, and **34**, derived from **27**, and introduced these synthons into a variety of compounds. We reasoned that the C_{tert}–Si bond should be formed by a *retro-Brook* rearrangement[3]) of the carbanion **24** to **25**, provided that the *Brook* rearrangement of **25** into 2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane (**26**) [53] and $Me_3SiC{\equiv}CH$ (the mechanism for the deprotection) can be suppressed.

The starting material **23** was prepared in a very high yield by silylating the crude alcohol **16** with **15**. Generation of the tertiary carbanion **24** (*Scheme 3*) from **23** with 2 equiv. of LiDBB in THF was rapid even at −100°, as indicated by the almost immediate change of the green color of LiDBB to red. The reaction was monitored by GC, showing that the *retro-Brook* rearrangement of **24** into **25** was relatively slow[4]), and that some of the intermediate **25** was cleaved to **26** and $Me_3SiC{\equiv}CH$. Quenching the reaction after 0.5 h at −78° with aqueous HCl solution yielded only 20% of **27**. To suppress the cleavage of **25**, Li^+ was replaced by Al^{3+}, Ce^{3+}, Zn^{2+}, or Mg^{2+}, either by transmetallation of **24**·Li^+ at temperatures between −78 and −100° or by reductive metallation of the thioether **23** with active Zn or Mg[5]). These experiments did not result in higher yields, nor did the combination of **24**·Li^+ with Et_3Al to form the corresponding 'ate' complex [56]. Fragmentation and other side reactions associated with the highly reactive tertiary carbanion **24** (*cf.* [57]) were, however, suppressed at low temperatures (−90° to −100°), while the rearrangement still took place at a useful rate. The yield was improved by rapid quenching at −90°, using 2M HCl in EtOH instead of aqueous HCl, to ensure a homogeneous solution. In this way, **27** was obtained on a multigram scale in overall yields of 45–52% from 3-methylbut-2-enal. Protection of the OH group of **27** and removal of the Me_3Si groups were straightforward. The doubly silylated acetylene **21** was obtained in 75% by benzylation of **27** with 4-methoxybenzyl 2,2,2-trichloroacetimidate [58]. The tetrahydro-2*H*-pyran-2-yl (Thp) derivative **28** and similarly the tetrahydro-4-methoxy-2*H*-pyran-2-yl (Thmp) derivative **29** were obtained in the usual way in 96 and 78% yield, respectively. The selective desilylation of **20**–**22**, **28**, and **29** with K_2CO_3/MeOH yielded 89–92% of the DOPSA building blocks **30** (R = 3,4-$(MeO)_2C_6H_3CH_2$), **31** (R = 4-$MeOC_6H_4CH_2$), **32** (R = $MeOCH_2$), **33** (R = Thp), and **34** (R = Thmp).

To check the use of these building blocks for the preparation of orthogonally protected dialkynes, we introduced them into a range of aliphatic and aromatic compounds (*Scheme 4*). Alkylation of **33** with the alkynyl bromide **35** [59] gave **39** (59%). The result of the cross-coupling of **33** and **36** [60] (1:1 equiv.) catalyzed by Pd^0/CuI [61–64] depended upon the solvent. Et_3N and $(i\text{-}Pr)_2NH$, which are mostly used for such couplings, were unsatisfactory, and so were piperidine and pyrrolidine [65–67]. The best results were obtained with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA); treating **36** with **33** in

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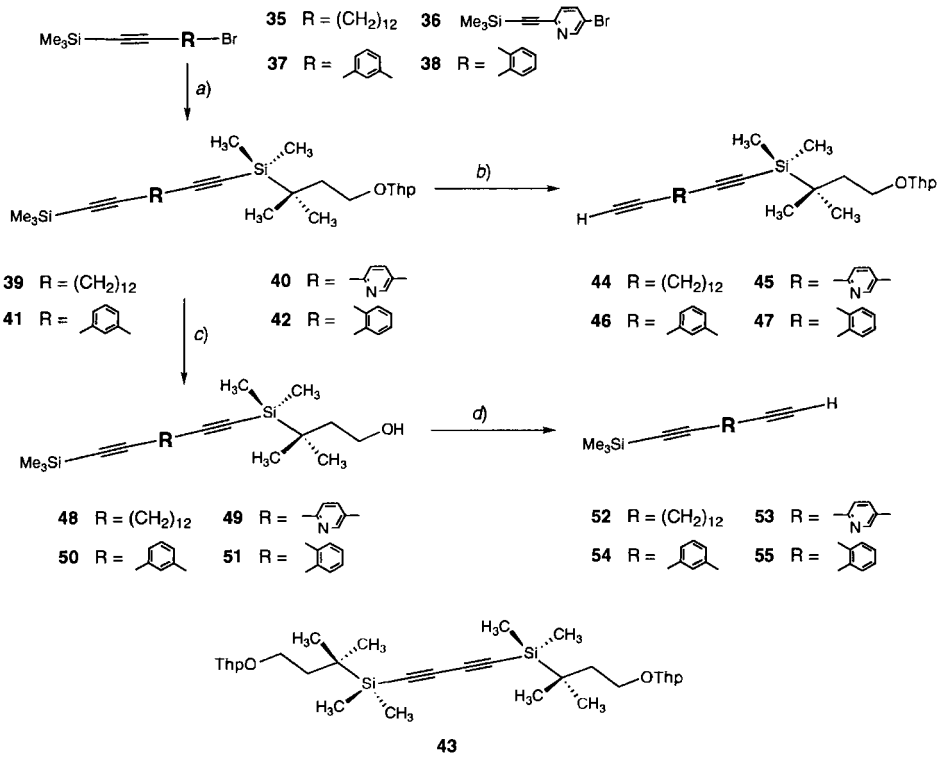
[3]) For the *retro-Brook* rearrangement, see [48–52] and ref. cit. therein.

[4]) As compared to that of primary and secondary carbanions. For the dependence of the rate of the silyl migration on steric and electronic effects of the substituents, see [48–50] [52] [54].

[5]) Generated by treatment of MX_n with LiDBB [55]. Active Zn did not react with **23** while Mg did, but led to many by-products.

Scheme 4



a) For **39**: Thp-DOPSA (**33**), BuLi, THF/DMPU, −76° to r.t.; 59%; for **40**–**42**: **33**/[Pd(PPh$_3$)$_4$]/CuI, TMEDA, 90°, 15 min to 10 h; 49–98%. *b*) K_2CO_3/MeOH, r.t.; quant. *c*) H^+, MeOH or EtOH, r.t.; > 95%. *d*) BuLi (0.1 equiv.), THF; 99% for **53**–**55**; 91% for **52**.

TMEDA for 15 min at 90° in the presence of [Pd(PPh$_3$)$_4$]/CuI yielded **40** in 95–98%. Similarly, **41** and **42** were obtained from **37** [68] and **38** [69] in 62 and 49% yield, respectively. The main by-product **43** resulted from homocoupling of **33** [70].

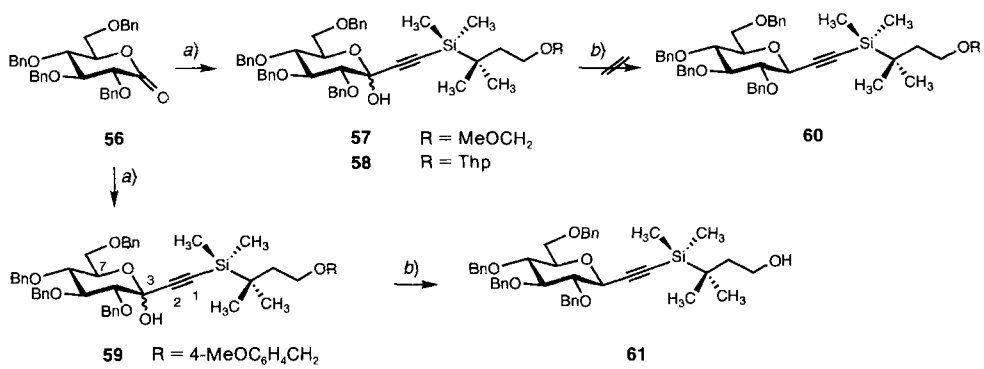
These dialkynylated products were regioselectively deprotected. Treatment of **39**–**42** with K_2CO_3/MeOH at room temperature led quantitatively within 0.5, 1.5, 1.5, and 11 h, respectively, to the mono-deprotected dialkynes **44**–**47**. The Thp group was hydrolyzed by heating an EtOH solution of **39** in the presence of pyridinium toluene-4-sulfonate to give **48** (95%). More conveniently, treatment of **40**–**42** with *Amberlyst 15* (H^+ form) in MeOH [71] afforded the alcohols **49**–**51** in almost quantitative yields. The desilylating *Brook* rearrangement in the presence of 0.1 equiv. of BuLi was completed in 5 to 40 min at −76° for **49** and **50**, in 2 h at −20° for **48**, and in *ca.* 12 h at r.t. for **51**, and the monoprotected dialkynes **52**–**55** were isolated in very high yields. The remarkable sluggishness of the last reactions is most probably due to the increase of steric hindrance in the transition state. The ^{1}H-NMR spectra of the crude **53**–**55** showed only one H–C≡C signal in the range of 2.00–3.79 ppm (at 3.30, 3.07, and 3.30 ppm, resp.), indicating that

the $Me_3SiC{\equiv}C$ group is stable under these conditions. GC analysis of crude **52** showed no trace of hexadeca-1,15-diyne.

The regioselectivity of the deprotection of **39–42** establishes the efficiency of the orthogonal protecting scheme for this type of bis(silylalkynyl) compounds. Remarkably, the rates of the removal of the Me_3Si groups by intermolecular desilylation depend strongly upon the constitution of the substrate (duration of the deprotection between 0.5 h and 11 h at r.t.). An even wider spread of rates is found for the removal of the DOPS group by intramolecular desilylation (duration of the deprotection between 5 min at −76° and 12 h at r.t.), and this may prove useful in the regioselective deprotection of even more highly alkynylated compounds.

To demonstrate the use of these orthogonally protected building blocks in the synthesis of acetylenosaccharides, we introduced the *O*-protected DOPSA's into the lactone **56** [1] (*Scheme 5*). Reaction of the lithium acetylides derived from **32**, **33**, and **31** with **56**

Scheme 5

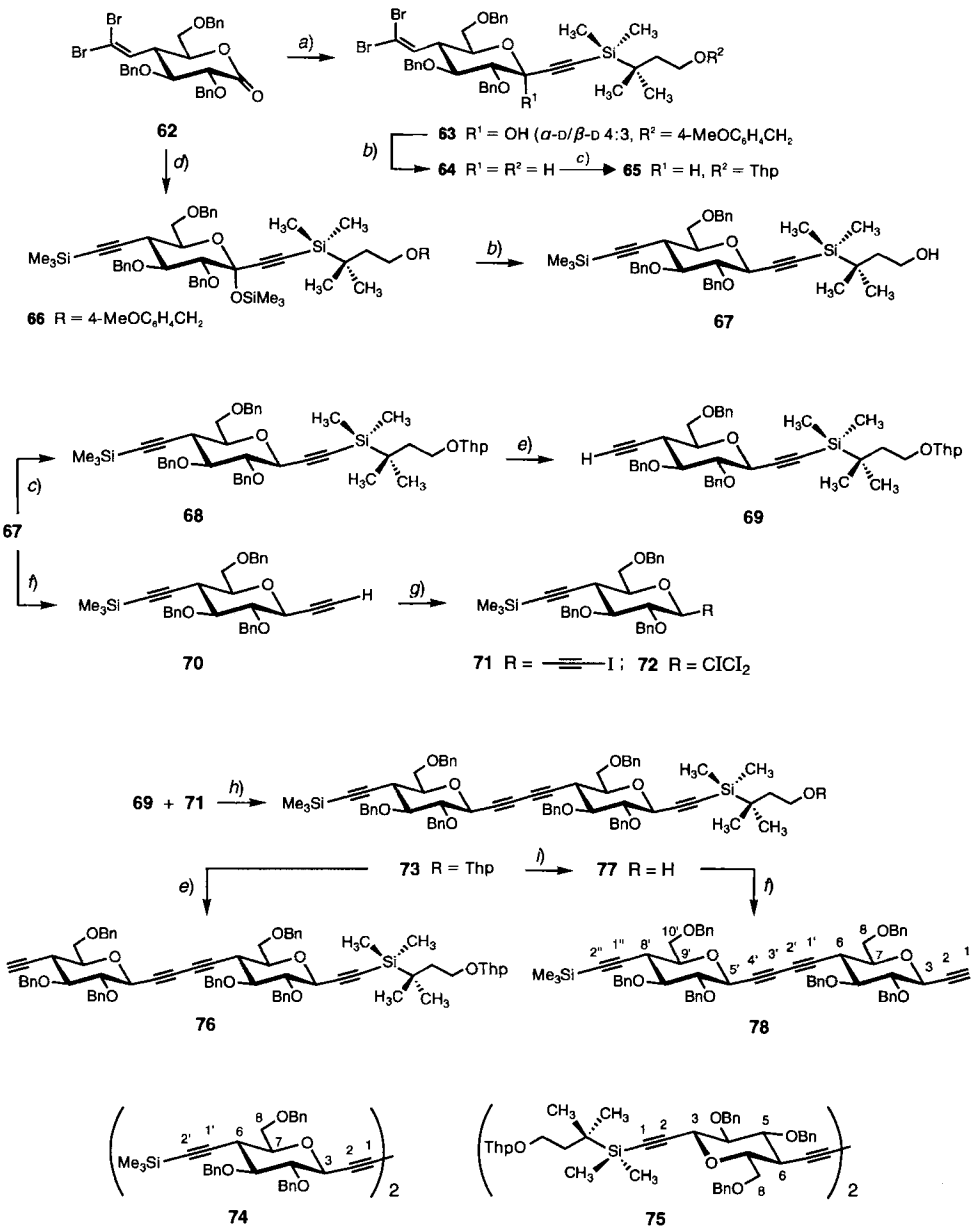


a) $MeOCH_2$-DOPSA (**32**), Thp-DOPSA (**33**), or (4-$MeOC_6H_4CH_2$)-DOPSA (**31**), BuLi, THF, −76°; 72–91%. *b*) $Et_3SiH/BF_3 \cdot Et_2O$ (excess), $MeCN/CH_2Cl_2$, −76 to −10°; 82% for **61**.

yielded 77, 91, and 72%, respectively, of the hemiketals **57–59**. While reductive dehydroxylation ($Et_3SiH/BF_3 \cdot OEt_2$, CH_2Cl_2/MeCN, −20 to 0°) [72] of the hemiketals **57** and **58** did not lead to **60**, but gave complex mixtures, it transformed **59** in high yield into the alcohol **61**, removing both the anomeric OH and the 4-methoxybenzyl group [73], provided that more than 2 equiv. of Et_3SiH and $BF_3 \cdot OEt_2$ were used. The (4-$MeOC_6H_4CH_2$)-DOPSA (**31**) thus appeared to be best suited for our purposes.

The lactone **62** (*Scheme 6*) served as an intermediate for the synthesis of the bis(trimethylsilyl) analogue of **68** [1]. A similar route was used for the transformation of **62** into **65**. Addition of the lithium acetylide derived from (4-$MeOC_6H_4CH_2$)-DOPSA (**31**) to **62** gave a mixture of the anomeric hemiketals **63** (α-D/β-D 4:3; 86%). Reductive dehydroxylation and debenzylation afforded the alcohol **64** (66%) which was protected as the Thp ether **65** (87%). The transformation of **65** into **68**, however, was far from satisfactory. An efficient preparation of the monoprotected dialkynes **69** and **70**, however, proceeded *via* the alcohol **67** which was obtained from the lactone **62**. At low

Scheme 6



a) (4-MeOC$_6$H$_4$CH$_2$)-DOPSA (**31**) BuLi, THF, −76°; 92%. *b*) BF$_3$·OEt$_2$/Et$_3$SiH (excess), MeCN/CH$_2$Cl$_2$; 70% for **64**; 60% overall for **67** from **62**. *c*) 3,4-Dihydro-2*H*-pyran, TsOH·Py (cat.), CH$_2$Cl$_2$, r.t.; 88% for **65**; 99% for **68**. *d*) 1. *a*); 2. BuLi (2.0 equiv.), −76°, 3 h; 3. Me$_3$SiCl. *e*) K$_2$CO$_3$/MeOH, r.t.; > 98%. *f*) BuLi (cat.), THF, −70→8°; > 96%. *g*) I$_2$·morpholine, benzene, 45°; **71** (82%), **72** (11%). *h*) [Pd$_2$(dba)$_3$]/CuI/(fur)$_3$P (cat.), DMSO, r.t.; **73** (76%), **74** (10%), and **75** (9%). *i*) *Amberlyst 15* (H$^+$ form), MeOH, r.t.; quant.

temperature, the dibromovinyl group of **62** was not affected by the lithium acetylide derived from **31**, so we combined its addition to **62** with the transformation of the dibromovinyl into the (trimethylsilyl)ethynyl group. Treatment of **62** with the lithium acetylide from **31** at −76° for 1.5 h, followed by addition of BuLi (2 equiv.) at −76° for 3 h, and finally of Me_3SiCl (2 equiv.) in THF yielded the crude, exclusively α-D-configurated bis-acetylene **66**. Crucial to this reaction is the use of the exact amount of (carefully titrated) BuLi. The transformations were monitored by ^{1}H-NMR spectroscopy. Excess Et_3SiH and $Br_3 \cdot OEt_2$ in CH_2Cl_2/MeCN transformed the crude **66** to the alcohol **67**. The overall yield from the crude lactone **62** [1] was 60%. The orthogonally protected monomer **67** is thus available on a multigram scale from readily accessible allyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside [1] [74] in eight steps, including five FC purifications, and in an overall yield of 35%. The orthogonal deprotection of the monomer **67** was straightforward. On the one hand, protection of **67** gave quantitatively the Thp ether **68** which was deprotected under protic conditions (K_2CO_3/MeOH) to the monoprotected bis-acetylene **69** (99%). On the other hand, intramolecular desilylation with 0.05 equiv. of BuLi under aprotic conditions (THF) at −90° to 8° yielded the monoprotected bis-acetylene **70** (96%).

The conditions of the orthogonal deprotection are compatible with the relatively labile butadiynediyl moiety. For the cross-coupling required for the preparation of the orthogonally protected dimer **73**, we iodinated **70** according to *Southwick* and *Kirchner* [75] to obtain 82% of **71** together with 11% of the triiodoalkene **72**. The formation of triiodoalkenes as by-product of this procedure has apparently not yet been described. Cross-coupling[6]) of the iodoalkyne **71** with **69** gave the heterodimer **73** in 76% yield. The homodimers **75** and **74** were isolated in 9 and 10% yield, respectively, while the usual conditions [77] gave the heterodimer **73** and the homodimers **75** and **74** in 46, 21, and 25% yield, respectively.

The dimer **73** was regioselectively desilylated (K_2CO_3/MeOH) to **76** (98%). Hydrolysis of the ThpO group of **73** gave the alcohol **77** (99%), which was treated with 0.1 equiv. of BuLi at −90 to 10° for 7 h to yield 99% of **78**.

The terminal acetylenes are characterized by a medium and sharp ≡C–H stretching band at 3287–3380, or, for alkynylated saccharides, at 3307–3308 cm^{-1}. Their C≡C stretching band appears at 2020–2117 cm^{-1}. It is, as a rule, weaker than that of disubstituted ethynes. All disubstituted ethynes, with the exception of the disilylated ethynes **20**–**22**, **28**, and **29**, and the hemiketals **57**–**59** and **63**, give a sharp, weak C≡C band at 2110–2180 cm^{-1}, while the butadiyne **43** shows a corresponding band at 2065 cm^{-1}. In the ^{1}H- and ^{13}C-NMR spectra, the Me_3Si groups resonate at 0.27–0.13 and at 0.30 to −0.63 ppm, respectively. The Me_2Si groups of the DOPS moiety resonate at higher fields than the Me_3Si groups (δ 0.24–0.10 and −4.60 to −3.95 ppm, resp.).

The CI-MS of the hemiketals **57** and **58** show the $[M + NH_4]^+$ peak at *m/z* 771 and 810, respectively, while the one of **59** is devoid of a $[M + NH_4]^+$ peak; the base peak at *m/z* 556 corresponding to $[M + NH_4]^+$ of the lactone **56** is generated by fragmentation of **59** under the conditions (NH_3) of measurement. The FAB-MS of **59**, however, shows the $[M - OH]^+$ peak at *m/z* 811. In the IR spectra of **57**–**59** and **63**, OH bands appear at 3560 to 3580 cm^{-1}, but no carbonyl absorption is present, indicating the absence of significant amounts of the corresponding ketones in $CHCl_3$ solution. The anomeric configuration of the hemiketals **59** and **63** is easily deduced from the chemical shifts of H–C(7), as an axial OH group leads to a larger downfield shift than an axial ethynyl group [1]. The α-D/β-D ratio is 1:1 for **59** and 4:3 for **63**. A comparison of the chemical shifts for C(1), C(2), and C(3) of the α-D-anomers to that of the β-D-anomers of **59**, **63**, and similar hemiketals [1] reveals that the C(3) *s* of the α-D-anomers (95.45–95.37 ppm) appears at higher field than that of the β-D-anomers (101.73–100.30 ppm);

[6]) The conditions (see *Exper. Part*) were derived from a systematic study of the mechanism of the alkyne-alkyne coupling [76].

similarly, the *s*'s of C(1) and C(2) of the α-D-isomers (105.3–103.42 and 91.69–91.27, ppm, resp.) resonate at lower field than those of the β-D-isomers (93.90–91.69 and 89.24–87.24 ppm, resp.). This observation is rationalized by the presence of two O-atom lone pairs antiparallel to the ethynyl group in the β-D-isomers and one only in the α-D-isomers. The α-D-configuration of the silylated ketal **66** is deduced from the chemical-shift values of C(3) (96.22 ppm), C(1) (104.16 ppm), C(2) (93.02 ppm), and H–C(7) (4.03 ppm).

The $^4C_1$ conformation of the ethynylated glucitols is evidenced by the large vicinal coupling constants of ring H-atoms. The J(3,4) (9.1–9.7 Hz) and J(5,6) (10.3–10.4 Hz) values establish the equatorial position of the ethynyl substituents. Characteristic long-range couplings of *ca.* 2.3 Hz are observed between H–C(6) or H–C(3) and the acetylenic H. The acetylenic H resonates at *ca.* 2.4 ppm for the C(3)-ethynylated and at *ca.* 2.1 ppm for the C(6)-ethynylated compounds.

The MS of **72** shows the $[M + 1]^+$ peak at m/z 919. The MS of the dibromoethylenes **63–65** display the typical pattern for fragments containing two Br-atoms. The olefinic H's resonate between 6.06 and 5.95 ppm, and the large J_{vic} with H–C(6) indicates an antiperiplanar arrangement of these H-atoms. The olefinic ^{13}C *s*'s appear at 93.34–93.00 ppm and the *d*'s at 135.15–134.65 ppm.

A H,H-COSY experiment leads to the assignment of the H–C(4) and H–C(6′) signals of **78** (*Scheme 6*) by correlation with the *dd* of H–C(3) and the broad *d* of H–C(5′), respectively. Due to extensive overlapping of the H–C(7) and H–C(9′) signals, the H–C(8) and H–C(10′) signals are difficult to assign. The more strongly deshielded $H_{pro\text{-}S}$–C(8)[7]) (J(7,8) = 1.8 Hz) of all 6-*ethynylated* monomers and of the homodimer **74** resonate at 3.85–3.84 ppm, whereas the one of the 6-*butadiynylated* **75** is found at 3.80 ppm. Thus, the signal of **78** at 3.78 ppm is assigned to H–C(8) and the one at 3.83 ppm to H–C(10′). The less strongly deshielded $H_{pro\text{-}R}$–C(8)'s of both the 6-ethynylated monomers and the 6-butadiynylated homodimers resonates at 3.65–3.70 ppm. Their J(7,8) values reflect the population of the rotamers, being 4.9–5.1 Hz when C(6) is linked to a butadiynyl or a terminal ethynyl group (see **75** and compare with **74** and other monomers), and 5.4–5.6 Hz when C(6) is $Me_3SiC{\equiv}C$-substituted. Calculations[8]) agree well with this observation. Thus, the *dd* of **78** at 3.68 ppm with J(8,7) = 5.0 Hz is assigned to H–C(8) and the *dd* at 3.67 ppm with J(10′,9′) = 5.5 Hz to H–C(10′). Both H–C(5) and H–C(7′) of **78** resonate at 3.55 ppm with the typical J(5,6) or J(7′,8′) = 10.2 Hz and J(5,4) = or J(7′,6′) = 8.9 Hz. C,H-COSY Experiments allow to assign the ^{13}C-NMR signals (C(5), C(7′), C(7), and C(9′) are assigned by comparison with the other monomers and homodimers). The ^{13}C signals of the butadiynediyl moiety are assigned as described before [2]. In a ^{13}C-NMR (125 MHz, $CDCl_3$) experiment, two acetylenic C's give rise to one *s* at 74.41 ppm, but to two *s*'s at 75.54 and 74.19 ppm when dissolved in C_6D_6; the *s* overlapping with the $CDCl_3$ signals is then also well resolved, resonating at 78.80 ppm. The long-range coupling of H–C(6) and H–C(5′) through a butadiynediyl moiety results in a *dd*, (J = 9.7, 0.6 Hz) at 4.09 ppm for H–C(5′) and a broad *t* at *ca.* 2.91 ppm for H–C(6), at lower field (*ca.* 0.1 ppm) than for H–C(8′). The H- and C-signals of the heterodimers **73**, **76**, and **77** are assigned by comparison to those of **78**.

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Experimental Part

General. Reactions were run under Ar or N_2. Evaporation: solvents were removed under reduced pressure by a rotatory evaporator. For other general informations, see [1]. The numbering of atoms is based on the systematic name of the compounds. MS: ESI = electron-spray ionization, FAB = fast-atom-bombardment ionization.

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[7]) According to *Bock* and *Duus* [78], the *dd* of the $H_{pro\text{-}R}$–C(6) of D-glucose appears at higher field than that of the $H_{pro\text{-}S}$–C(6).

[8]) Macromodel (MM3* force field, gas phase) calculations of 4-deoxy-4-*C*-ethynyl-6-*O*-benzyl-β-D-glucopyranoside show that the *tg* form is the most stable rotamer due to the π–π interaction between the C(4) ethynyl group and the Ph ring of the O^6-benzyl group. When C(4) is bound to a CH≡C group, the CH≡C group is parallel to the Ph ring (distance between C(1′) and C(1″) = 4.20 Å, and 4.24 Å between C(2′) and C(4″)), when C(4) is, however, bound to a $Me_3SiC{\equiv}C$ group, steric interaction between the Me_3Si and Ph groups increases the distance between the C≡C and the Ph groups which are no longer parallel (distance between C(1′) and C(1″) = 4.44 Å, and between C(2′) and C(4″) = 5.08 Å). This leads to a ΔE between the *tg* and *gt* conformers of 4.1 kJ/mol in the first, and of 1.5 kJ/mol in the second one. We thank Dr. *B. Bernet* for the calculation and for discussions.

*1-C-[(3-Acetoxypropyl)dimethylsilyl]-3,7-anhydro-4,5,6,8-tetra-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-*D*-glycero-*D*-gulo-octitol* (**10**). At −76°, a stirred soln. of **9** (575 mg, 1.05 mmol) in THF (5 ml) was treated dropwise with 0.9M BuLi in hexane (1.2 ml, 1.05 mmol), stirred at −76° for 30 min, treated with $ClSiMe_2(CH_2)_3OAc$ [39] (0.6 ml, 3.1 mmol) in one portion, and stirred at r.t. for 10 min. Usual workup and FC (hexane/AcOEt 92:8) yielded **10** (546 mg, 74%). Oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.11 (*m*, 20 arom. H); 5.02–4.53 (*m*, 4 PhC*H*$_2$); 4.05 (*d*, *J* = 9.3, H–C(3)); 3.95 (*t*, *J* = 7.0, 2 H–C(3′)); 3.68–3.54 (*m*, H–C(4), H–C(5), H–C(6), 2 H–C(8)); 3.42–3.39 (*m*, H–C(7)); 1.98 (*s*, Ac); 1.67–1.57 (*m*, 2 H–C(2′)); 0.74–0.68 (*m*, 2 H–C(1′)); 0.17 (*s*, Me_2Si).

*3,7-Anhydro-4,5,6,8-tetra-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-[(3-hydroxypropyl)dimethylsilyl]-*D*-glycero-*D*-gulo-octitol* (**11**). At −40°, a stirred soln. of **10** (210 mg, 0.297 mmol) in CH_2Cl_2 (2.5 ml) was treated with 1.0M DIBAH in CH_2Cl_2 (2 ml, 2.0 mmol), stirred for 10 h from −40° to r.t., poured into Et_2O, washed with aq. 1N HCl soln. and H_2O, and processed as usual. FC (AcOEt/hexane 10:90→20:80) afforded **11** (157 mg, 80%). Oil. R_f (AcOEt/hexane 3:7) 0.12. IR ($CHCl_3$): 3620*m* (br.), 3000*s*, 2920*s*, 2870*s*, 2180*w*, 1495*w*, 1450*s*, 1360*s*, 1290*w*, 1250*s*, 1090*s*, 1070*s*, 1020*s*, 860*m*, 640*m*, 700*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37–7.11 (*m*, 20 arom. H); 5.02 (*d*, *J* = 10.5, PhC*H*); 4.89 (*d*, *J* = 11.0, PhC*H*); 4.80 (*d*, *J* = 11.0, PhC*H*); 4.80 (*d*, *J* = 10.5, PhC*H*); 4.79 (*d*, *J* = 10.8, PhC*H*); 4.61 (*d*, *J* = 12.2, PhC*H*); 4.54 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 10.8, PhC*H*); 4.05 (*d*, *J* = 9.3, H–C(3)); 3.73 (*dd*, *J* = 10.9, 2.0, H–C(8)); 3.68 (*dd*, *J* = 10.9, 4.4, H–C(8)); 3.64–3.54 (*m*, H–C(4), H–C(5), H–C(6), 2 H–C(3′)); 3.41 (*ddd*, *J* = 9.2, 4.4, 2.0, H–C(7)); 1.67–1.57 (*m*, 2 H–C(2′)); 0.63–0.60 (*m*, 2 H–C(1′)); 0.169 (*s*, MeSi); 0.166 (*s*, MeSi). ^{13}C-NMR (200 MHz, $CDCl_3$; assignment based on C,H-COSY of **61**): 138.47 (*s*); 138.06 (*s*); 137.96 (*s*); 137.93 (*s*); 128.36–127.30 (several *d*): 103.18 (*s*, C(2)); 90.15 (*s*, C(1)); 85.96 (*d*); 82.24 (*d*); 79.09 (*d*, C(7)); 77.57 (*d*); 75.65 (*t*, PhCH_2); 75.28 (*t*, PhCH_2); 75.06 (*t*, PhCH_2); 73.47 (*t*, PhCH_2); 70.18 (*d*, C(3)); 68.66 (*t*, C(8)); 65.22 (*t*, C(3′)); 26.97 (*t*); 11.64 (*t*); −2.0 (*q*, Me_2Si). ESI ($^+$Q3)-MS: 703 (30, $[M + K]^+$), 687 (100, $[M + Na]^+$). Anal. calc. for $C_{41}H_{48}O_6Si$ (664.91): C 74.06, H 7.28; found: C 73.87, H 7.07.

*Allyl 2,3,6-Tri-O-benzyl-4-deoxy-4-C-ethynyl-α-*D*-glucopyranoside* (**13**). At r.t., **12** (41 mg, 0.072 mmol) was treated with a soln. of $Bu_4NF \cdot 3\,H_2O$ (7.6 mg, 0.024 mmol) in THF (1 ml) and stirred for 15 min. Usual workup and filtration through a short pad of silica gel (AcOEt) gave **13** (38 mg, 100%). Syrup. R_f (hexane/AcOEt 7:3) 0.44. $[\alpha]_D^{20} = +26.3$ (*c* = 2.56, $CHCl_3$). IR ($CHCl_3$): 3308*s*, 3089*m*, 3067*m*, 3042*m*, 3007*s*, 2926*s*, 2870*m*, 2120*w*, 1951*w*, 1875*w*, 1811*w*, 1724*w*, 1646*w*, 1604*w*, 1496*m*, 1454*s*, 1352*m*, 1262*m*, 1148*s*, 1090*s*, 1040*s*, 1028*s*, 935*m*, 913*m*, 858*w*, 822*w*, 646*s*, 563*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.44–7.24 (*m*, 15 arom. H); 5.94 (*dddd*, *J* = 17.2, 10.3, 6.5, 5.3, H–C(2′)); 5.34 (*dq*, *J* = 17.2, 1.5, H_a–C(3′)); 5.26 (*dq*, *J* = 10.3, 1.1, H_b–C(3′)); 4.94 (*d*, *J* = 12.4, PhC*H*); 4.91 (*d*, *J* = 12.4, PhC*H*); 4.86 (*d*, *J* = 3.6, H–C(1)); 4.77 (*d*, *J* = 12.1, PhC*H*); 4.63 (*d*, *J* = 13.2, 2 PhC*H*); 4.54 (*d*, *J* = 12.2, PhC*H*); 4.17 (*ddt*, *J* = 12.9, 5.3, 1.4, H_a–C(1′)); 4.02 (*ddt*, *J* = 12.9, 6.6, 1.1, H_b–C(1′)); 3.97 (*dd*, *J* = 10.4, 9.6, H–C(3)); 3.91 (*dt*, *J* = 10.7, 3.1, H–C(5)); 3.73 (br. *d*, *J* = 3.2, 2 H–C(6)); 3.46 (*dd*, *J* = 9.5, 3.6, H–C(2)); 2.82 (*td*, *J* = 10.6, 2.3, H–C(4)); 2.10 (*d*, *J* = 2.3, H–C(2″)). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.65 (*s*); 138.24 (*s*), 138.10 (*s*); 133.76 (*s*, C(2′)); 128.40–127.53 (several *d*); 118.24 (*t*, C(3′)); 96.19 (*d*, C(1)); 81.61 (*d*, C(2″)); 79.65 (*d*); 79.20 (*d*, C(2), C(3)); 75.93 (*t*, PhCH_2); 73.54 (*t*, PhCH_2); 73.18 (*t*, PhCH_2); 71.58 (*s*, C(1″)); 70.33 (*d*, C(5)); 69.81 (*t*, C(6)); 68.34 (*t*, C(1′)); 36.88 (*d*, C(4)). FAB-MS: 497 (9, $[M - 1]^+$), 181 (37), 155 (20), 154 (34), 147 (24), 137 (32), 136 (37), 107 (31), 105 (26), 95 (28), 92 (39), 91 (100), 83 (26), 81 (31), 79 (23), 77 (26), 73 (22), 71 (26), 69 (45), 67 (26), 57 (44), 55 (52). Anal. calc. for $C_{32}H_{34}O_5$ (498.62): C 77.08, H 6.87; found: C 76.91, H 7.10.

Selective Desilylation of **11** *in the Presence of* **12**. At −76°, a soln. of **11** (6.2 mg, 0.011 mmol) and **12** (6.6 mg, 0.010 mmol) in THF (0.3 ml) was treated with one drop uf BuLi (*ca.* 0.0011 mmol in THF) and stirred for 1.5 h at −76 to 0°. TLC (hexane/AcOEt 7:3) indicated complete consumption of **11** (R_f 0.12) and the formation of **9** (R_f 0.40), while **12** (R_f 0.44) was unchanged. Usual workup and drying under h.v. gave an oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.52 (acetylenic *d* of **9**); no signal at 2.10 (acetylenic *d* of **13**).

Desilylation of **10** *and* **12**. At r.t., a soln. of **11** (6.0 mg, 0.011 mmol) and **12** (6.6 mg, 0.010 mmol) in MeOH (0.5 ml) was treated with K_2CO_3 (*ca.* 5 mg) and stirred for 1 h. TLC (CH_2Cl_2) indicated the presence of the two starting and the two desilylated products (slightly more **9** than **13**).

(Chloro)dimethyl[(trimethylsilyl)ethynyl]silane (**15**) [47]. At −15 to −10°, a mechanically stirred soln. of Me_2SiCl_2 (90 ml, 0.74 mol) in THF (50 ml) was treated dropwise for 3.5 h with a soln. of $Me_3SiC{\equiv}CMgBr$ [79] [80] (0.30 mol) in THF (320 ml), stirred at −10° r.t. for 1 h, and evaporated. Dry hexane (500 ml) was added to the residue. The mixture was stirred for 1 h and filtered. Washing of the filter residue with 250 ml of hexane, evaporation of the filtrates, and distillation of the residue (46–48°/15 Torr) gave **15** (39 g, 44% based on $Me_3SiC{\equiv}CH$). Colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.57 (*s*, Me_2Si); 0.20 (*s*, Me_3Si).

3-Methyl-3-(phenylthio)butan-1-ol (**16**) [46]. At 0°, a stirred soln. of 3-methylbut-2-enal (76 g, 0.905 mol) and PhSH (99.69 g, 0.905 mol) in $CHCl_3$ (190 ml) was treated dropwise with NEt_3 (3.2 ml, 23 mmol) over 3 min, stirred at r.t. for 4 h, cooled to 0°, treated dropwise with a soln. of $NaBH_4$ (15 g, 1.6 mol) in H_2O (65 ml), stirred vigorously for 1 h at 5° and for 20 min at r.t., and then treated slowly with aq. 1N HCl. The org. layers were separated, and the

aq. layer was extracted with $CHCl_3$. The combined org. phases were washed with brine, dried (Na_2SO_4) and evaporated. Drying under h.v. gave **16** (177 g, 99.7%) which was used directly for the next steps.

3,4-Dimethoxybenzyl 3-Methyl-3-(phenylthio)butyl Ether (**17**). At r.t., a soln. of **16** (11.18 g, 57.05 mmol) in THF (100 ml) was added dropwise within 20 min to a stirred suspension of NaH (55–65% in mineral oil; 2.41 g, *ca.* 61 mmol, washed 2× with dry hexane) in DMF (60 ml). The mixture was stirred at r.t. for 1 h, treated dropwise with 3,4-dimethoxybenzyl chloride (10.65 g, 57.05 mmol), stirred at r.t. for 2 h and at 5° overnight, treated with cold H_2O, extracted with Et_2O, and processed as usual. FC (hexane/AcOEt 97:3→93:7) afforded **17** (4.2 g, 21%). Solid. M.p. 64–66°. R_f (hexane/AcOEt 9:1) 0.18. IR ($CHCl_3$): 3062*w*, 3007*s*, 2963*s*, 2937*s*, 2865*m*, 2839*m*, 1720*w*, 1608*m*, 1594*m*, 1518*s*, 1514*s*, 1465*s*, 1456*s*,1440*s*, 1421*s*, 1384*m*, 1365*s*, 1332*m*, 1264*s*, 1157*s*, 1140*s*, 1090*s*, 1028*s*, 945*w*, 918*w*, 858*m*, 818*m*, 640*w*, 595*w*, 566*w*, 507*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.51–7.46 (*m*, 2 arom. H); 7.37–7.27 (*m*, 3 arom. H); 6.91 (br. *s*, 1 arom. H); 6.86 (br. *d*, J = 3.1, 2 arom. H); 4.46 (*s*, ArCH_2); 3.89 (*s*, MeO); 3.88 (*s*, MeO); 3.70 (*t*, J = 7.1, CH_2OAr); 1.84 (*t*, J = 7.1, CH_2); 1.27 (*s*, 2 Me). ^{13}C-NMR (200 MHz, $CDCl_3$): 149.42 (*s*); 148.95 (*s*); 137.89 (2*d*); 132.34 (*s*); 131.41 (*s*); 129.12 (2*d*); 128.87 (*d*); 120.56 (*d*); 111.38 (*d*); 111.26 (*d*); 73.22 (*t*); 67.43 (*t*); 56.19 (*q*); 56.09 (*q*); 48.23 (*s*); 41.67 (*t*); 29.37 (2*q*). EI-MS: 346 (1, M^+), 151 (100, $(MeO)_2C_6H_3CH_2^+$).

4-Methoxybenzyl 3-Methyl-3-(phenylthio)butyl Ether (**18**). At −10°, a soln. of **16** (32.0 g, 163 mmol) in THF (150 ml) was added dropwise to a stirred suspension of NaH (55–65% in mineral oil; 8.09 g, *ca.* 185 mmol; washed 2× with dry hexane) in DMF (300 ml). The mixture was stirred at −10° for 1 h and at r.t. for 1 h, treated at 0° dropwise within *ca.* 10 min with 4-methoxybenzyl chloride (24.0 ml, 177 mmol), stirred at r.t. for 6 h, treated with H_2O (1 ml), and stirred at r.t. for 20 min. Usual workup and FC (hexane/AcOEt: 95:5) afforded **18** (42.4 g, 82%). Colorless oil. R_f (hexane/AcOEt 95:5) 0.16. IR ($CDCl_3$): 3050*m*, 3000*s*, 2960*s*, 2950*s*, 2860*s*, 1880*w*, 1720*w*, 1610*s*, 1585*m*, 1465*s*, 1440*s*, 1390*m*, 1365*s*, 1300*s*, 1250*s*, 1170*s*, 1130*m*, 1090*s*, 1030*s*, 920*w*, 820*m*, 690*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.49–7.48 (*m*, 2 arom. H); 7.47–7.19 (*m*, 5 arom. H); 6.91–6.83 (*m*, 2 arom. H); 4.44 (*s*, ArCH_2); 3.86 (*t*, J = 7.1, CH_2OAr); 3.81 (*s*, MeO); 1.82 (*t*, J = 7.1, CH_2); 1.26 (*s*, 2 Me). ^{13}C-NMR (200 MHz, $CDCl_3$): 159.08 (*s*); 137.46 (2*d*); 131.95 (*s*); 130.52 (*s*); 129.20 (2*d*); 128.68 (*d*); 128.45 (2*d*); 113.82 (2*d*); 72.63 (*t*); 67.05 (*t*); 55.20 (*t*); 47.95 (*s*); 41.36 (*t*); 29.11 (2*q*). CI-MS: 334 (4, $[M + NH_4]^+$), 319 (6), 318 (18), 317 (100, $[M + H]^+$). Anal. calc. for $C_{19}H_{24}O_2S$ (316.46): C 72.11, H 7.64, S 10.13; found: C 72.20, H 7.56, S 9.90.

3-(Methoxymethoxy)-1,1-dimethylpropyl Phenyl Sulfide (**19**). At −10°, a suspension of $FeCl_3$ (2.616 g, 16.13 mmol), 4-Å molecular sieves (14 g), and **16** (7.914 g, 40.38 mmol) in CH_2Cl_2 (60 ml) was treated dropwise with $CH_2(OMe)_2$, stirred for 1 h at −10° and for 16 h at r.t., treated with 1M aq. NaOH (7 ml) and $MgSO_4$ (to absorb H_2O), and decanted. The residue was washed with CH_2Cl_2. The combined CH_2Cl_2 solns. were washed with H_2O and processed as usual. MPLC (hexane/AcOEt 94:6) gave **19** (5.65 g, 58%). Colorless oil. R_f (hexane/AcOEt 7:3) 0.62. IR ($CHCl_3$): 3050*w*, 3000*s*, 2950*s*, 2920*s*, 2880*s*, 2820*m*, 2770*w*, 1580*w*, 1570*w*, 1470*s*, 1440*s*, 1380*m*, 1360*m*, 1300*m*, 1240*m*, 1145*s*, 1100*s*, 1060*s*, 1040*s*, 960*m*, 935*m*, 910*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.50 (*m*, 2 arom. H); 7.39–7.29 (*m*, 3 arom. H); 4.63 (*s*, 2 H); 3.77 (*t*, J = 7.3, 2 H); 3.38 (*s*, MeO); 1.81 (*t*, J = 7.3, 2 H); 1.28 (*s*, 2 Me). ^{13}C-NMR (200 MHz, $CDCl_3$): 137.49 (2*d*); 131.93 (*s*); 128.74 (2*d*); 128.49 (*d*); 96.46 (*t*); 64.88 (*t*); 55.20 (*q*); 47.76 (*s*); 41.31 (*t*); 29.07 (2*q*). CI-MS: 258 (100, $[M + NH_4]^+$), 241 (86, $[M + 1]^+$), 209 (36, $[M - OMe]^+$). Anal. calc. for $C_{13}H_{20}O_2S$ (240.36): C 64.96, H 8.39, S 13.34; found: C 65.21, H 8.57, S 13.63.

1-{{3-{Dimethyl[(trimethylsilyl)ethynyl]silyl}-3-methylbutoxy}methyl}-4-methoxybenzene (**21**). a) *By Silylation of* **18**. At −90°, a soln. of **18** (1.266 g, 4 mmol) in THF (12 ml) was treated dropwise with a soln. of LiDBB in THF [41] (freshly prepared by treatment of a soln. of di(*tert*-butyl)biphenyl (DBB; 2.81 g, 10.56 mmol) in THF (14 ml) with Li (61 mg, 8.8 mmol)) until the color of the mixture changed from dark red to green, then treated with **15** (1.68 g, 8.8 mmol), stirred at −90° for 1 h, diluted with Et_2O, neutralized with aq. $NaHCO_3$ soln., and processed as usual. FC (hexane/AcOEt 99.75:0.25→99.5:0.5) afforded the mixture of **21** and 1-methoxy-4-[(3-methylbutoxy)-methyl]benzene. A 2nd FC (benzene) gave **21** (320 mg, 22%) and *1-methoxy-4-[(3-methylbutoxy)methyl]benzene* (210 mg, 25%).

b) *By Benzylation of* **27**. At r.t., a soln. of **27** (see below; 230 mg, 0.948 mmol) and 4-methoxybenzyl 2,2,2-trichloroacetimidate (321.6 mg, 1.14 mmol) in Et_2O (5 ml) was treated with TfOH (0.25% in Et_2O; 0.1 ml, 0.0028 mmol), stirred for 4 h at r.t., and neutralized with $NaHCO_3$. Usual workup and FC (hexane/AcOEt 9:1) gave **21** (256 mg, 75%). Colorless liquid. R_f (hexane/AcOEt 95:5) 0.25. R_f (benzene) 0.39. IR ($CHCl_3$): 3000*m*, 2950*s*, 2760*m*, 1610*m*, 1585*w*, 1510*s*, 1460*m*, 1405*w*, 1360*w*, 1300*w*, 1250*s*, 1170*m*, 1090*m*, 1030*m*, 850*s*, 820*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27–7.25 (*m*, 2 arom. H); 6.88–6.85 (*m*, 2 arom. H); 4.42 (*s*, ArCH_2); 3.79 (s, MeO); 3.57 (*t*, J = 7.4, 2 H–C(1)); 1.66 (*t*, J = 7.4, 2 H–C(2)); 0.96 (*s*, 2 Me); 0.15 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (200 MHz, $CDCl_3$): 159.06 (*s*); 130.75 (*s*); 129.16 (2*d*); 115.02 (*s*, C≡C); 112.21 (*s*, C≡C); 113.71 (2*d*); 72.58 (*t*); 67.12 (*t*); 55.21 (*q*); 38.40 (*t*); 23.27 (2*q*); 18.53 (*s*); −0.10 (3*q*); −4.25 (2*q*). CI-MS: 380 (100, $[M + NH_4]^+$). Anal. calc. for $C_{20}H_{34}O_2Si$ (362.66): C 66.24, H 9.45; found: C 66.34, H 9.35.

1-Methoxy-4-[(3-methylbutoxy)methyl]benzene: Colorless liquid. R_f (hexane/AcOEt 95:5) 0.25. R_f (benzene) 0.23. IR ($CHCl_3$): 3000*m*, 2975*s*, 2920*m*, 2860*m*, 1610*m*, 1585*w*, 1510*s*, 1460*m*, 1440*w*, 1360*m*, 1300*m*, 1250*s*, 1170*m*, 1090*s*, 1040*s*, 820*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.26–7.21 (*m*, 2 arom. H); 6.87–6.82 (*m*, 2 arom. H); 4.41 (*s*, ArCH_2); 3.78 (*s*, MeO); 3.44 (*t*, J = 6.8, 2 H–C(1)); 1.69 (*m*, H–C(3)); 1.47 (*q*, J = 6.8, 2 H–C(2)); 0.86 (*s*, Me); 0.84 (*s*, Me). ^{13}C-NMR (200 MHz, $CDCl_3$): 159.03 (*s*); 130.78 (*s*); 129.09 (2*d*); 113.66 (2*d*); 72.47 (*t*); 68.47 (*t*); 55.14 (*q*); 38.55 (*t*); 25.04 (*d*); 22.57 (2*q*). CI-MS: 226 (100, $[M + NH_4]^+$), 208 (23, M^+). Anal. calc. for $C_{13}H_{20}O_2$ (208.30): C 74.96, H 9.68; found: C 75.04, H 9.74.

1-{[3-{(Dimethyl[(trimethylsilyl)ethynyl]silyl}-3-methylbutoxy]methyl}-3,4-dimethoxybenzene (**20**). As described for **21** from **18**, **20** was obtained from **17** in 30% yield. R_f (hexane/AcOEt 85:15) 0.31. IR ($CHCl_3$): 3007*m*, 2961*m*, 2862*m*, 1608*w*, 1594*w*, 1517*s*, 1465*m*, 1442*w*, 1420*w*, 1364*w*, 1331*w*, 1252*s*, 1157*m*, 1140*m*, 1087*m*, 1029*m*, 944*w*, 843*s*, 824*s*, 566*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.91 (br. *s*, 1 arom. H); 6.86–6.84 (*m*, 2 arom. H); 4.43 (*s*, ArCH_2); 3.89 (*s*, MeO); 3.87 (*s*, MeO); 3.59 (*t*, J = 7.5, 2 H–C(1)); 1.68 (*t*, J = 7.5, 2 H–C(2)); 0.97 (*s*, 2 Me); 0.16 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.67 (*s*); 148.18 (*s*); 130.91 (*s*); 119.86 (*d*); 114.82 (*s*, *C*≡C); 111.94 (*s*, *C*≡C); 110.73 (*d*); 110.59 (*d*); 72.58 (*t*, Ar*C*H$_2$); 66.93 (*t*, C(1)); 55.62 (*q*, MeO); 55.51 (*q*, MeO); 38.14 (*t*, C(2)); 23.12 (2*q*); 18.28 (*s*, C(3)); –0.35 (*q*, Me_3Si); –4.50 (*q*, Me_2Si). EI-MS: 392 (1, M^+), 377 (2, $[M - Me]^+$), 155 (49), 151 (100, $(MeO)_2C_6H_3CH^+$). Anal. calc. for $C_{21}H_{36}O_3Si_2$ (393.69): C 64.23, H 9.24; found: C 64.42, H 9.04.

1-{[3-Methoxymethoxy)-1,1-dimethylpropyl]dimethylsilyl}-2-(trimethylsilyl)ethyne (**22**). Similarly to **18**, **22** was obtained from **19** in 60% yield. Oil. R_f (CH_2Cl_2) 0.39. IR ($CHCl_3$): 3006*s*, 2960*s* (sh), 2900*s* (sh), 1470*m*, 1410*w*, 1390*w*, 1370*w*, 1255*s*, 1150*s*, 1110*s*, 1070*s*, 1040*s*, 940*m*, 915*m*, 845*s* (sh), 700*w*, 670*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.52 (*s*, CH_2O_2); 3.65 (*t*, J = 7.8, 2 H–C(3)); 3.37 (*s*, MeO); 1.65 (*t*, J = 7.8, 2 H–C(2)); 0.98 (*s*, 2 Me); 0.17 (*s*, Me_3Si); 0.13 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 115.17 (*s*, *C*≡C); 112.01 (*s*, *C*≡C); 96.36 (*t*, CH_2O_2); 64.62 (*t*, C(3)); 55.03 (*q*, MeO); 38.37 (*t*, C(2)); 23.26 (2*q*); 18.43 (*s*, C(1)); –0.17 (*q*, Me_3Si); –4.30 (*q*, Me_2Si). CI-MS: 304 (100, $[M + NH_4]^+$). Anal. calc. for $C_{14}H_{30}O_2Si_2$ (286.56): 58.68, H 10.55; found: C 58.95, H 10.76.

1-{Dimethyl[3-methyl-3-(phenylthio)butoxy]silyl}-2-(trimethylsilyl)ethyne (**23**). At r.t., a vigorously stirred soln. of **16** (14.65 g, 74.7 mmol) and **15** (14.95 g, 78.47 mmol) in THF (380 ml) was treated dropwise within 5 min with Et_3N (12.5 ml, 90 mmol), stirred for 30 min at r.t., evaporated, treated with hexane (400 ml), stirred for 10 min, and filtered. The filtrate was concentrated to *ca.* 100 ml, kept at –20° for 1 day, and filtered. The filtrate was brought to dryness by azeotropic-coevaporations with toluene. Drying under h.v. (4d) gave **23** (26.00 g, 99.4%) as an oil which was used directly for the next step. R_f (hexane/AcOEt 95:5) 0.52. IR ($CHCl_3$): 3050*w*, 3000*m*, 2960*s*, 2100*w*, 1950*w*, 1580*w*, 1470*m*, 1440*m*, 1400*w*, 1380*w*, 1360*w*, 1300*w*, 1250*s*, 1130*m*, 1080*s*, 1050*s*, 995*w*, 830*s*, 690*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.50 (*m*, 2 arom. H); 7.35–7.31 (*m*, 3 arom. H); 3.94 (*t*, J = 7.3, 2 H–C(1)); 1.81 (*t*, J = 7.3, 2 H–C(2)); 1.27 (*s*, 2 Me), 0.25 (*s*, Me_2Si): 0.185 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.49 (2*d*); 132.01 (*s*); 128.65 (2*d*); 128.42 (*d*); 114.43 (*s*, *C*≡C); 110.79 (*s*, *C*≡C); 60.42 (*t*, C(1)); 47.77 (*s*, C(3)); 43.91 (*t*, C(2)); 29.08 (*q*, 2 Me); –0.18 (*q*, Me_3Si); –0.22 (*q*, Me_2S). CI-MS: 368 (100, $[M + NH_4]^+$), 351 (99, $[M + 1]^+$), 253 (9). Anal. calc. for $C_{18}H_{30}OSSi_2$ (350.67): C 61.65, H 8.62, S 9.14; found: C 61.38, H 8.86, S 9.37.

3-{Dimethyl[(trimethylsilyl)ethynyl]silyl}-3-methylbutan-1-ol (**27**). At –85 to –95°, LiDBB/THF [41] (freshly pepared from Li (1.01 g, 145.5 mmol) and DBB (42.5 g, 159.5 mmol) in 180 ml of THF) was slowly added to a vigorously stirred soln. of **23** (24.2 g, 69.1 mmol) in THF (520 ml). After addition of the LiDBB soln., the color of the mixture changed from dark red to green. The green soln. was stirred for 65 min at –90°, treated rapidly with 2M HCl in EtOH (90 ml, freshly prepared) for *ca.* 10 min, and poured into Et_2O (1200 ml) and H_2O (250 ml). The Et_2O layer was washed with H_2O (3 × 250 ml), dried ($MgSO_4$), and evaporated. The residue was completely dissolved in hot EtOH (300 ml). The soln. was cooled to r.t.; after 3 h, 30 g of DBB crystallized. The mother liquor was concentrated to *ca.* 170 ml. Crystallization at 4° overnight gave another crop of DBB (6 g). Evaporation of the mother liquor and FC (180 g of silica gel, hexane (700 ml) to remove PhSH and the remaining DBB, then hexane/AcOEt 98:2→95:5) gave **27** (8.589 g, 51% overall from 3-methylbut-2-enal, > 95% pure according to GC). Light yellow oil. R_f (hexane/AcOEt 85:15) 0.20. IR ($CHCl_3$): 3620*m*, 3500*m*, 3000*m*, 2960*s*, 2880*s*, 2860*s*, 1460*s*, 1410*m*, 1385*m*, 1360*w*, 1250*s*, 1060*m*, 1040*m*, 1030*m*, 1010*s*, 990*m*, 960*w*, 830*s*, 700*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.77 (*q*, J = 7.1, CH_2O); 1.63–1.58 (*m*, addn. of D_2O→change of signals, 2 H–C(2), OH); 0.97 (*s*, 2 Me); 0.17 (*s*, Me_3Si); 0.14 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 115.57 (*s*, *C*≡C); 112.24 (*s*, *C*≡C); 59.56 (*t*, C(1)); 42.60 (*t*, C(2)); 23.68 (*q*, 2 Me); 18.71 (*s*, C(3)); –0.18 (*q*, Me_3Si); –4.25 (*q*, Me_2Si). CI-MS: 162 (100, $[M - Me_3SiC{\equiv}CH + NH_4]^+$). EI-MS: 229 (5), 158 (12), 157 (78), 155 (100), 147 (63), 144 (15), 129 (33), 83 (42), 75 (34), 73 (21), 70 (38), 55 (20). Anal. calc. for $C_{12}H_{26}OSi_2$ (242.51): C 59.43, H 10.81; found: C 59.58, H 10.88.

2-{3-{Dimethyl(trimethylsilyl)ethynyl]silyl}-3-methylbutoxy}tetrahydro-2H-pyran (**28**). At r.t., a stirred soln. of **27** (1.00 g, 4.12 mmol) and 3,4-dihydro-2*H*-pyran (0.76 ml, 8.4 mmol) in CH_2Cl_2 (40 ml) was treated with pyridinium toluene-4-sulfonate (56 mg, 0.22 mmol) and stirred for 18 h. Usual workup and FC (hexane/AcOEt

95:5) gave **28** (1.288 g, 96%). Oil. R_f (CH_2Cl_2) 0.30. IR ($CHCl_3$): 3000*m*, 2950*s*, 2860*m*, 1460*m*, 1450*w*, 1440*w*, 1410*w*, 1380*w*, 1360*w*, 1350*w*, 1320*w*, 1250*s*, 1200*w*, 1180*w*, 1130*m*, 1115*m*, 1075*m*, 1020*s*, 980*m*, 900*m*, 840*s*, 820*s*, 700*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.58–4.56 (*m*, H–C(2)); 3.92–3.74 (*m*, CH_2O); 3.53–3.47 (*m*, CH_2O); 1.86–1.51 (*m*, 4 CH_2); 0.97 (*s*, 2 Me); 0.16 (*s*, Me_3Si); 0.11 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 115.09 (*s*, *C*≡C); 112.22 (*s*, *C*≡C); 99.00 (*d*, OCHO); 64.40 (*t*, CH_2O); 62.43 (*t*, CH_2O); 38.32 (*t*); 30.84 (*t*); 22.50 (*t*); 23.37 (*q*); 23.20 (*q*); 19.76 (*t*); 18.47 (*s*); –0.12 (*q*, Me_3Si); –4.24 (*q*, MeSi), –4.30 (*q*, MeSi). CI-MS: 344 (10, $[M + NH_4]^+$), 102 (100), 85 (27). Anal. calc. for $C_{17}H_{34}O_2Si_2$: C 62.51, H 10.49; found: C 62.56, H 10.57.

*4-{3-{Dimethyl[(trimethylsilyl)ethynyl]silanyl}-3-methoxybutoxy}tetrahydro-4-methoxy-2*H*-pyran* (**29**). At r.t., a stirred soln. of **27** (1.00 g, 4.12 mmol) and 5,6-dihydro-4-methoxy-2*H*-pyran (0.15 ml, 1.36 mmol) in CH_2Cl_2 (5 ml) was treated with pyridinium toluene-4-sulfonate (11.4 mg, 0.045 mmol) and stirred for 1 h. Usual workup and FC (hexane/AcOEt 92:8) gave **29** (252 mg, 78%). Oil. R_f (hexane/AcOEt 7:3). 0.34. IR ($CHCl_3$): 3007*m*, 2962*s*, 2865*m*, 1467*m*, 1424*w*, 1410*w*, 1385*w*, 1354*m*, 1305*m*, 1252*s*, 1164*m*, 1144*m*, 1114*s*, 1099*s*, 1054*m*, 1008*m*, 969*w*, 949*w*, 930*w*, 906*w*, 842*s*, 823*s*, 632*w*, 575*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.69 (*t*, *J* = 5.4, 2 CH_2O); 3.52 (*t*, *J* = 8.0, CH_2O); 3.21 (*s*, MeO); 1.79 (*t*, *J* = 5.4, 2 CH_2); 1.62 (*t*, *J* = 8.0, CH_2); 0.98 (*s*, 2 Me); 0.16 (*s*, Me_3Si); 0.13 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 115.05 (*s*, *C*≡C); 112.35 (*s*, *C*≡C); 98.01 (*s*, C(4)); 65.28 (*t*, 2 C(2), C(6)) 56.82 (*t*, C(1′)); 47.72 (*q*, MeO); 39.15 (*t*, C(3); C(5)); 34.40 (*t*, C(2′)); 23.62 (*q*, 2 Me); 18.75 (*s*, C(3′)); 0.07 (*q*, Me_3Si); –4.05 (*q*, Me_2Si). EI-MS: 341 (0.2, $[M - Me]^+$), 157 (16), 156 (20), 155 (100), 115 (97), 85 (12), 73 (21). Anal. calc. for $C_{18}H_{36}O_3Si_2$ (356.65): C 60.62, H 10.17; found: C 61.06, H 9.87.

Selective Desilylation of **20**–**22**, **28**, *and* **29**; *Preparation of* **30**–**34**. At r.t. the title compounds (0.634 mmol) were treated with a sat. K_2CO_3 soln. in MeOH (2 ml). After 1–2.5 h, usual workup and FC gave **30** (92%), **31** (92%), **32** (89%), **33** (89%), and **34** (90%), resp.

4-{{3-[Ethynyl(dimethyl)silyl]-3-methylbutoxy}methyl}-1,2-dimethoxybenzene (**30**): Oil. R_f (hexane/AcOEt 85:15) 0.31. IR ($CHCl_3$): 3287*m*, 3007*s*, 2961*s*, 2939*s*, 2863*s*, 2032*m*, 1608*w*, 1594*m*, 1517*s*, 1465*s*, 1442*m*, 1420*m*, 1386*w*, 1364*m*, 1333*w*, 1263*s*, 1157*s*, 1140*s*, 1087*s*, 1029*s*, 944*w*, 841*s*, 824*s*, 615*w*, 571*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.90 (br. *s*, 1 arom. H); 6.86–6.84 (*m*, 2 arom. H); 4.43 (*s*, Ar*CH*$_2$); 3.89 (*s*, MeO); 3.87 (*s*, MeO); 3.58 (*t*, *J* = 7.5, 2 H–C(1)); 2.36 (*s*, CH≡C); 1.69 (*t*, *J* = 7.5, 2 H–C(2)); 0.99 (*s*, 2 Me); 0.14 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.57 (*s*); 148.18 (*s*); 130.85 (*s*); 119.9 (*d*); 110.77 (*d*); 110.58 (*d*); 93.84 (*d*, *C*H≡C); 88.12 (*s*, CH≡C)); 72.63 (*t*, Ar*C*H$_2$); 66.68 (*t*, C(1)); 55.63 (*q*, MeO); 55.53 (*q*, MeO); 37.84 (*t*, C(2)); 22.91 (*q*, 2 Me); 18.14 (*s*, C(3)); –4.62 (*q*, Me_2Si). EI-MS: 320 (10, M^+), 151 (100, $(MeO)_2C_6H_3CH_2^+$), 83 (21).

1{{3-[Ethynyl(dimethyl)silyl]-3-methylbutoxy}methyl}-4-methoxybenzene (**31**): Oil. R_f (benzene) 0.30. IR ($CHCl_3$): 3380*s*, 3000*s*, 2950*s*, 2860*s*, 2020*m*, 1610*s*, 1590*m*, 1510*s*, 1460*s*, 1450*m*, 1410*m*, 1380*m*, 1360*m*, 1500*m*, 1250*s*, 1170*s*, 1090*s*, 1030*s*, 950*w*, 940*w*, 920*w*, 820*s*, 680*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.28–7.25 (*m*, 2 arom. H); 6.89–6.86 (*m*, 2 arom. H); 4.43 (*s*, Ar*CH*$_2$); 3.81 (*s*, MeO); 3.57 (*t*, *J* = 7.3, 2 H–C(1)); 2.36 (*s*, CH≡C); 1.68 (*t*, *J* = 7.3, 2 H–C(2)); 0.98 (*s*, 2 Me); 0.14 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 159.07 (*s*); 130.68 (*s*); 129.90 (2*d*); 113.71 (2*d*); 94.06 (*s*, CH≡C); 88.42 (*d*, *C*H≡C); 72.62 (*t*, Ar*C*H$_2$); 66.88 (*t*, C(1)); 55.22 (*q*, MeO); 38.10 (*t*, C(2)); 23.16 (*q*, 2 Me); 18.38 (*s*, C(3)); –4.37 (*q*, Me_2Si). CI-MS: 308 (4, $[M + NH_4]^+$), 121 (100). Anal. calc. for $C_{17}H_{26}O_2Si$ (290.48): C 70.29, H 9.02; found: C 70.53, H 9.20.

[3-[(Methoxymethoxy)-1,1-dimethylpropyl]dimethylsilyl]ethyne (**32**): Oil. R_f (CH_2Cl_2) 0.34. IR ($CHCl_3$): 3295*s*, 3000*m*, 2940*s*, 2895*s*, 2860*m*, 2830*m*, 2780*w*, 2040*m*, 1470*m*, 1405*m*, 1390*m*, 1370*m*, 1260*s*, 1150*s*, 1105*s*, 1070*s*, 1040*s*, 940*m*, 915*m*, 840*s*, 820*s*, 690*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.63 (*s*, OCH_2O); 3.65 (*t*, *J* = 7.8, 2 H–C(3)); 3.38 (*s*, MeO); 2.39 (*s*, CH≡C); 1.68 (*t*, *J* = 7.8, 2 H–C(2)); 1.01 (*s*, 2 Me); 0.17 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 96.39 (*t*,OCH_2O); 94.20 (*d*, CH≡C); 88.17 (*s*, CH≡C); 64.41 (*t*, C(3)); 55.10 (*q*, MeO); 38.00 (*t*, C(2)); 23.02 (*q*, 2 Me); 18.24 (*s*, C(1)); –4.43 (*q*, Me_2Si). CI-MS (NH_3): 232 (100, $[M + NH_4]^+$). Anal. calc. for $C_{11}H_{22}O_2Si$ (214.38): C 61.63, H 10.34; found: C 61.67, H 10.50.

*2-{3-[Ethynyl(dimethyl)silyl]-3-methylbutoxy}-tetrahydro-2*H*-pyran* (**33**): Oil. R_f (CH_2Cl_2) 0.26. IR ($CHCl_3$): 3380*m*, 3000*m*, 2940*s*, 2860*s*, 2020*m*, 1460*m*, 1450*m*, 1440*m*, 1410*w*, 1380*m*, 1360*m*, 1350*m*, 1320*w*, 1250*s*, 1200*w*, 1180*w*, 1130*s*, 1110*s*, 1070*s*, 1020*s*, 980*m*, 950*w*, 900*m*, 860*m*, 840*s*, 820*s*, 680*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.59–4.57 (*m*, H–C(2)); 3.92–3.84 (*m*, CH_2O); 3.54–3.44 (*m*, CH_2O); 2.37 (*s*, CH≡C); 1.87–1.49 (*m*, 4 CH_2); 1.01 (*s*, Me); 1.00 (*s*, Me); 0.16 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 98.93 (*d*, C(2)); 94.07 (*s*, CH≡*C*); 88.33 (*d*, *C*H≡C); 64.11 (*t*,CH_2O); 62.35 (*t*, CH_2O); 37.49 (*t*); 30.78 (*t*); 25.47 (*t*); 25.47 (*t*); 23.10 (*q*, Me); 22.93 (*q*, Me); 19.67 (*t*); 18.27 (*s*); –4.38 (*q*, MeSi); –4.41 (*q*, MeSi). CI-MS: 272 (4, $[M + NH_4]^+$), 102 (100). Anal. calc. for $C_{14}H_{26}O_2Si$ (254.44): C 66.09, H 10.30; found: C 66.00, H 10.32.

*4-{3-[Ethynyl(dimethyl)silyl]-3-methylbutoxy}tetrahydro-4-methoxy-2*H*-pyran* (**34**): R_f (hexane/AcOEt/CH_2Cl_2 7:3:1) 0.45. IR ($CHCl_3$): 3287*m*, 3007*s*, 2963*s*, 2943*s*, 2865*s*, 2032*m*, 1467*m*, 1424*w*, 1386*w*, 1354*m*, 1305*m*, 1258*s*, 1164*m*, 1144*s*, 1114*s*, 1099*s*, 1055*s*, 1008*s*, 969*w*, 949*m*, 930*w*, 906*m*, 841*s*, 823*s*, 658*w*, 633*w*, 612*w*, 577*m*, 553*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.69 (*t*, *J* = 5.4, 2 CH_2O); 3.52 (*t*, *J* = 8.0, 2 H–C(1′)); 3.20 (*s*, MeO); 2.38 (*s*,

CH≡C); 1.78 (*t*, *J* = 5.4, 2 CH_2); 1.64 (*t*, *J* = 8.0, 2 H–C(2′)); 1.00 (*s*, 2 Me); 0.16 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 97.45 (*s*, C(4)); 93.99 (*s*, CH≡*C*); 87.99 (*d*, *C*H≡C); 64.72 (*t*, C(2), C(6)); 56.06 (*t*, C(1′)); 47.23 (*q*, MeO); 38.28 (*t*, C(2′)); 33.86 (*t*, C(3), C(5)); 22.93 (*q*, 2 Me); 18.11 (*s*, C(3′)); −4.60 (*q*, Me_2Si). EI-MS: 283 (0.01, $[M-1]^+$), 269 (0.05, $[M-Me]^+$), 153 (11), 116 (12), 115 (100), 114 (15), 86 (30), 84 (10), 83 (85), 73 (10), 55 (16). Anal. calc. for $C_{15}H_{28}O_3Si$ (284.47): C 63.33, H 9.92; found: C 63.47, H 9.77.

*2-{3-{Dimethyl[16-(trimethylsilyl)hexadeca-1,15-diynyl]silyl}-3-methylbutoxy}tetrahydro-2*H*-pyran* (**39**). At −76°, a stirred soln. of **33** (210 mg, 0.825 mmol) in THF (3 ml) was treated with 1.35 M BuLi in hexane (0.61 ml, 0.823 mmol), stirred for 1 h, treated with DMPU (*N,N′*-dimethylpropyleneurea; 1 ml) then with a soln. of **35** [59] (342 mg, 0.99 mmol) in THF (0.5 ml), and stirred for 2.5 h at −76 to −15° and for 6 h at r.t. After dilution with hexane and washing with aq. sat. NH_4Cl soln., usual workup and FC (hexane/AcOEt 99.5:0.5) gave **39** (252 mg, 59%). Oil. R_f (hexane/AcOEt 95:5) 0.31. IR ($CHCl_3$): 3007*w*, 2930*s*, 2856*s*, 2169*m*, 1720*w* (br.), 1465*m*, 1410*w*, 1384*w*, 1365*w*, 1353*w*, 1324*w*, 1252*m*, 1133*m*, 1116*m*, 1077*m*, 1024*s*, 980*m*, 955*w*, 904*w*, 843*s*, 638*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.58–4.57 (*m*, H–C(2)); 3.90–3.85 (*m*, CH_2O); 3.53–3.47 (*m*, CH_2O); 2.21 (*t*, *J* = 7.2, 2 CH_2); 1.86–1.27 (*m*, 14 CH_2); 0.97 (*s*, 2 Me); 0.15 (*s*, Me_3Si); 0.10 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 108.70 (*s*, *C*≡C); 107.80 (*s*, *C*≡C); 99.03 (*d*, C(2)); 84.23 (*s*, *C*≡C); 82.33 (*s*, *C*≡C); 64.43 (*t*), 62.45 (*t*, C(6), C(1′)); 38.05 (*t*); 30.88 (*t*); 29.60 (*t*); 29.59 (*t*); 29.54 (*t*); 29.51 (*t*); 29.10 (*t*); 28.81 (*t*); 28.66 (*t*); 25.54 (*t*); 23.25 (*q*, Me); 23.11 (*q*, Me); 19.87 (*t*); 19.80 (*t*); 18.53 (*s*, C(3′)); 0.20 (*q*, Me_3Si); −4.01 (*q*, MeSi); −4.05 (*q*, MeSi). EI-MS: 503 (0.05, $[M-Me]^+$), 166 (17), 146 (21), 132 (14), 129 (14), 85 (100), 75 (32), 73 (81), 70 (16), 59 (29). Anal. calc. for $C_{31}H_{58}O_2Si_2$ (518.97): C 71.75, H 11.26; found: C 71.60, H 10.98.

*5-{{[1,1-Dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}ethynyl}-2-[(trimethylsilyl)ethynyl]pyridine* (**40**). At r.t., a stirred soln. of **36** [60] (50 mg, 0.197 mmol) in TMEDA (0.3 ml) was treated with $[Pd(PPh_3)_4]$ (2.3 mg, 0.0020 mmol), CuI (1.8 mg, 0.0095 mmol), and $Me_3SiC{\equiv}CH$ (1 mg), heated (at *ca.* 50°) for 10 min, cooled to r.t., treated with a soln. of **33** (38 mg, 0.149 mmol) in TMEDA (0.7 ml), heated to 90°, and stirred for 15 min. After dilution with hexane, washing with brine, usual workup and FC (hexane/AcOEt 97:3) gave **40** (63 mg, 98%). White solid. M.p. 48–49°. R_f (hexane/AcOEt 95:5) 0.10. IR ($CHCl_3$): 3059*w*, 3007*s*, 2958*s*, 2863*s*, 2386*w*, 2349*w*, 2162*m*, 1583*w*, 1545*w*, 1466*s*, 1442*w*, 1410*w*, 1385*w*, 1365*m*, 1324*w*, 1253*s*, 1132*s*, 1116*s*, 1077*s*, 1024*s*, 979*m*, 955*w*, 934*w*, 904*m*, 869*s*, 849*s*, 824*s*, 656*w*, 628*w*, 605*w*, 559*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.61 (*dd*, *J* = 2.1, 0.9, H–C(6)); 7.68 (*dd*, *J* = 8.1, 2.1, H–C(4)); 7.38 (*dd*, *J* = 8.1, 0.9, H–C(3)); 4.58–4.56 (*m*, OCHO); 3.96–3.85 (*m*, CH_2O); 3.55–3.47 (*m*, CH_2O); 1.86–1.48 (*m*, 4 CH_2); 1.045 (*s*, Me); 1.041 (*s*, Me); 0.27 (*s*, Me_3Si); 0.21 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 152.65 (*d*, C(6)); 141.72 (*s*, C(2)); 138.85 (*d*, C(4)); 126.44 (*d*, C(3)); 119.56 (*s*, C(5)); 103.35 (*s*, *C*≡C); 102.24 (*s*, *C*≡C); 99.15 (*d*, OCHO); 98.80 (*s*, *C*≡C); 97.05 (*s*, *C*≡C); 64.30 (*t*, CH_2O); 62.56 (*t*, CH_2O); 38.23 (*t*); 30.83 (*t*); 25.48 (*t*); 23.38 (*q*, Me); 23.26 (*q*, Me); 19.80 (*t*); 18.74 (*s*); −0.32 (*q*, Me_3Si); −4.32 (*q*, MeSi); −4.35 (*q*, MeSi). EI-MS: 412 (2.5, $[M-Me]^+$), 343 (27), 342 (11), 328 (28), 259 (55), 258 (59), 257 (42), 256 (100), 200 (76), 184 (27), 143 (16), 120 (21), 85 (80), 75 (19), 73 (17). Anal. calc. for $C_{24}H_{37}NO_2Si_2$ (427.73): C 67.39, H 8.72, N 3.27; found: C 67.28, H 8.77, N 3.26.

Ethynylation of **37**. As described for **40**, with **37** [68] (266 mg, 1.048 mmol) in TDEDA (1 ml), $[Pd(PPh_3)_4]$ (30 mg, 0.026 mmol), CuI (15 mg, 0.79 mmol), and **33** (228 mg, 0.896 mmol) in TMEDA (4 ml; 90°, 0.5 h). FC (hexane/AcOEt 99:1): **41** (230 mg, 62%) and **43** (82 mg, 32%).

*2-{3-{Dimethyl{{3-[(trimethylsilyl)ethynyl]phenyl}ethynyl}silyl}-3-methylbutoxy}tetrahydro-2*H*-pyran* (**41**): Oil. R_f (hexane/AcOEt 95:5) 0.25. R_f (CH_2Cl_2) 0.50. IR ($CHCl_3$): 3006*m*, 2957*s*, 2862*s*, 2151*s*, 1594*w*, 1569*w*, 1475*s*, 1442*w*, 1406*w*, 1385*w*, 1366*w*, 1354*w*, 1324*w*, 1253*s*, 1163*s*, 980*m*, 944*s*, 901*m*, 858*s*, 842*s*, 823*s*, 648*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57–7.56 (*m*, 1 arom. H); 7.40–7.38 (*m*, 2 arom. H); 7.25–7.21 (*m*, 1 arom. H); 4.59–4.57 (*m*, OCHO); 3.96–3.86 (*m*, CH_2O); 3.56–3.47 (*m*, CH_2O); 1.87–1.48 (*m*, 4 CH_2); 1.038 (*s*, Me); 1.035 (*s*, Me); 0.24 (*s*, Me_3Si); 0.20 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.36 (*d*, C(2)); 131.80 (*d*, C(4), C(6)); 128.18 (*d*, C(5)); 123.41 (*s*, C(3)); 123.34 (*s*, C(1)); 105.07 (*s*, *C*≡C); 104.06 (*s*, *C*≡C); 99.15 (*d*, OCHO); 94.91 (*s*, *C*≡C); 93.31 (*s*, *C*≡C); 64.42 (*t*, CH_2O); 62.56 (*t*, CH_2O); 38.29 (*t*); 30.85 (*t*); 25.50 (*t*); 23.42 (*q*); 23.28 (*q*); 19.83 (*t*); 18.75 (*s*); −0.10 (*q*, Me_3Si); −4.23 (*q*, MeSi); −4.26 (*q*, MeSi). EI-MS: 411 (2, $[M-Me]^+$), 341 (18), 272 (37), 258 (25), 257 (95), 256 (29), 255 (100), 183 (83), 120 (26), 85 (83), 75 (30), 55 (24). Anal. calc. for $C_{25}H_{38}O_2Si_2$ (426.75): C 70.36, H 8.98; found: C 70.37, H 9.02.

*2,2′-[(Buta-1,3-diyne-1,4-diyl)bis(dimethylsilanediyl)bis(3-methylbutane-3-yl-1-yloxy)]bis(tetrahydro-2*H*-pyran)* (**43**). White solid. M.p. 65–66° (EtOH). R_f (hexane/AcOEt 95:5) 0.08. IR (CHCl): 3007*m*, 2946*s*, 2863*m*, 2065*m*, 1465*m*, 1454*w*, 1442*w*, 1411*w*, 1386*w*, 1366*w*, 1354*w*, 1324*w*, 1259*s*, 1132*s*, 1116*s*, 1077*s*, 1024*s*, 980*s*, 955*w*, 933*w*, 905*m*, 867*m*, 840*s*, 823*s*, 638*w*, 604*w*, 582*w*, 556*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.59–4.56 (*m*, OCHO); 3.92–3.80 (*m*, CH_2O); 3.56–3.41 (*m*, CH_2O); 1.82–1.48 (*m*, 4 CH_2); 1.00 (*s*, 2 Me); 0.16 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 99.09 (*d*, OCHO); 89.18 (*s*, *C*≡C); 84.16 (*s*, *C*≡C); 64.10 (*t*, CH_2O); 62.52 (*t*, CH_2O); 37.98 (*t*);

30.82 (*t*); 25.51 (*t*); 23.30 (*q*); 23.09 (*q*); 19.79 (*t*); 18.79 (*s*); −4.43 (*q*, MeSi); −4.47 (*q*, MeSi). EI-MS: 506 (0.01, M^+), 181 (19), 85 (100), 75 (27). Anal. calc. for $C_{28}H_{50}O_4Si_2$ (506.87): C 66.35, H 9.94; found: C 66.48, H 9.92.

*2-{3-{Dimethyl{{2-[(trimethylsilyl)ethynyl]phenyl}ethynyl}silyl}-3-methylbutoxy}tetrahydro-2*H*-pyran* (**42**). As described for **40**, with **38** [69] (130 mg, 0.513 mmol), TMEDA (2 ml), $[Pd(PPh_3)_4]$ (15 mg, 0.013 mmol), CuI (7.3 mg, 0.038 mmol), and **33** (108 mg, 0.424 mmol) in TMEDA (1 ml; 90°, 5 h), then again with $[Pd(PPh_3)_4]$ (7 mg; 90° for 1 h and 60° for 10 h). FC (hexane/AcOEt 99:1): **43** (53 mg, 49%) and **42** (102 mg, 47%). Oil. R_f (CH_2Cl_2) 0.43. IR ($CHCl_3$): 3064*w*, 3007*m*, 2958*s*, 2862*m*, 2398*w*, 2158*m*, 1601*w*, 1475*m*, 1441*m*, 1410*w*, 1385*w*, 1366*w*, 1354*w*, 1324*w*, 1252*s*, 1133*m*, 1116*m*, 1099*w*, 1077*m*, 1025*s*, 980*m*, 954*w*, 932*w*, 904*w*, 871*s*, 846*s*, 822*s*, 644*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.48–7.43 (*m*, 2 arom. H); 7.31–7.21 (*m*, 2 arom. H); 4.59–4.57 (*m*, OCHO); 3.95–3.85 (*m*, CH_2O); 3.56–3.46 (*m*, CH_2O); 1.86–1.40 (*m*, 4 CH_2); 1.08 (*s*, Me); 1.07 (*s*, Me); 0.26 (*s*, Me_3Si); 0.23 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 132.58 (*d*, C(3)); 132.57 (*d*, C(6)); 128.02 (*d*, C(4), C(5)); 125.70 (*s*, C(2)); 125.66 (*s*, C(1)); 104.25 (*s*, *C*≡C); 103.31 (*s*, *C*≡C); 99.10 (*d*, OCHO); 98.37 (*s*, *C*≡C); 96.79 (*s*, *C*≡C); 64.38 (*t*, CH_2O); 62.48 (*t*, CH_2O); 38.08 (*t*); 30.84 (*t*); 25.51 (*t*); 23.52 (*q*); 23.36 (*q*); 19.78 (*t*); 18.73 (*s*); 0.04 (*q*, Me_3Si); −4.06 (*q*, MeSi); −4.10 (*q*, MeSi). EI-MS: 426 (0.05, M^+), 411 (0.2, $[M - Me]^+$), 257 (37), 255 (36), 183 (29), 143 (68), 85 (99), 75 (35), 73 (100). Anal. calc. for $C_{25}H_{38}O_2Si_2$ (426.75): C 70.36, H 8.98; found: C 70.57, H 9.22.

General Procedure for Removal of the Trimethylsilyl Groups in **39**–**42**. At r.t., the title compounds (46–55 mg) were treated with a sat. K_2CO_3 soln. in MeOH (1 ml) for 10.5, 0.5, 1.5, 1.5 h, resp. Usual workup and FC gave **44**–**47**, resp., in quantitative yields.

*2-{3-[(Hexadeca-1,15-diynyl)dimethylsilyl]-3-methylbutoxy}tetrahydro-2*H*-pyran* (**44**): Oil. R_f (hexane/AcOEt 95:5) 0.26. FC (hexane/AcOEt 99:1). IR ($CHCl_3$): 3308*m*, 3007*m*, 2930*s*, 2856*s*, 2169*m*, 2116*w*, 1465*m*, 1442*w*, 1411*w*, 1384*w*, 1365*w*, 1353*w*, 1324*w*, 1253*m*, 1133*m*, 1116*m*, 1077*m*, 1024*s*, 980*w*, 955*w*, 904*w*, 867*w*, 838*m*, 823*m*, 673*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.58–4.57 (*m*, H–C(2)); 3.90–3.85 (*m*, CH_2O); 3.53–3.47 (*m*, CH_2O); 2.21 (*t*, J = 7.0, 2 H–C(3″)); 2.17 (*td*, J = 7.0, 3.8, 2 H–C(14″)); 1.93 (*t*, J = 3.8, H–C(16″)); 1.86–1.27 (*m*, 14 CH_2); 0.978 (*s*, Me); 0.973 (*s*, Me); 0.10 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 108.70 (*s*, *C*≡C); 99.03 (*d*, C(2)); 84.81 (*d*, *C*H≡C); 82.33 (*s*, *C*≡C); 68.04 (*s*, *C*≡C); 64.43 (*t*, CH_2O); 62.45 (*t*, CH_2O); 38.04 (*t*); 30.88 (*t*); 29.58 (*t*); 29.52 (*t*); 29.12 (*t*); 29.08 (*t*); 28.81 (*t*); 28.77 (*t*); 28.66 (*t*); 28.51 (*t*); 23.25 (*q*, Me); 23.11 (*q*, Me); 19.87 (*t*); 19.79 (*t*); 18.53 (*s*, C(3′)); 18.41 (*t*); −4.01 (*q*, MeSi); −4.05 (*q*, MeSi). EI-MS: 446 (0.05, M^+), 431 (0.1, $[M - Me]^+$), 159 (12), 85 (100), 75 (13), 70 (15), 59 (12). Anal. calc. for $C_{28}H_{50}O_2Si$ (446.80): C 75.27, H 11.28; found: C 75.28, H 11.28.

*5-{{[1,1-Dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}ethynyl}-2-ethynylpyridine* (**45**): White solid. M.p. 79–80°. R_f (hexane/AcOEt 9:1) 0.07. IR ($CHCl_3$): 3302*s*, 3007*s*, 2958*s*, 2863*s*, 2360*w*, 2340*w*, 2160*m*, 2117*w*, 1584*w*, 1545*m*, 1466*s*, 1442*m*, 1410*w*, 1385*m*, 1365*m*, 1354*m*, 1324*w*, 1286*m*, 1260*s*, 1131*s*, 1116*s*, 1078*s*, 1024*s*, 980*m*, 955*w*, 934*w*, 904*m*, 850*s*, 823*s*, 652*m*, 558*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.63 (*d*, J = 2.2, H–C(2)); 7.70 (*dd*, J = 8.2, 2.2, H–C(4)); 7.41 (*d*, J = 8.2, H–C(5)); 4.59–4.55 (*m*, OCHO); 3.99–3.82 (*m*, CH_2O); 3.57–3.45 (*m*, CH_2O); 3.24 (*s*, CH≡C); 1.76–1.50 (*m*, 4 CH_2); 1.04 (*s*, 2 Me); 0.22 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.44 (*d*, C(2)); 140.66 (*s*, C(6)); 138.60 (*d*, C(4)); 126.31 (*d*, C(5)); 119.76 (*s*, C(3)); 101.71 (*s*, *C*≡C); 98.84 (*d*, OCHO); 98.75 (*d*, *C*H≡C); 82.18 (*s*, *C*≡C); 78.67 (*s*, *C*≡C); 63.99 (*t*, CHO); 62.56 (*t*, CH_2O); 37.95 (*t*); 30.54 (*t*); 25.18 (*t*); 19.51 (*t*); 23.08 (*q*, Me); 22.97 (*q*, Me); 18.44 (*s*); −4.64 (*q*, Me_2Si). EI-MS: 354 (0.4, $[M - 1]^+$), 340 (0.9, $[M - Me]^+$), 271 (15), 256 (17), 187 (19), 186 (27), 185 (35), 184 (100), 143 (18), 129 (14), 128 (68), 127 (14), 85 (99), 75 (18), 55 (15). Anal. calc. for $C_{21}H_{29}NO_2Si$ (355.55): C 70.94, H 8.22, N 3.94; found: C 71.11, H 8.45, N 3.92.

*2-{3-{[(3-Ethynylphenyl)ethynyl]dimethylsilyl}-3-methylbutoxy}tetrahydro-2*H*-pyran* (**46**): Oil. R_f (hexane/AcOEt 9:1) 0.30. IR ($CHCl_3$): 3305*s*, 3007*m*, 2959*s*, 2861*m*, 2151*m*, 2112*w*, 1593*w*, 1570*w*, 1475*m*, 1466*m*, 1442*m*, 1408*m*, 1385*w*, 1366*w*, 1354*m*, 1324*w*, 1261*s*, 1132*s*, 1078*s*, 1024*s*, 956*m*, 925*s*, 901*m*, 867*m*, 839*s*, 823*s*, 657*m*, 627*m*, 606*w*, 552*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.59 (*t*, J = 1.2, H–C(2)); 7.44 (*dt*, J = 7.5, 1.4), 7.43 (*dt*, J = 7.4, 1.5, H–C(6), H–C(4)); 7.25 (*t*, J = 7.6, H–C(5)); 4.60–4.56 (*m*, OCHO); 3.99–3.83 (*m*, CH_2O); 3.59–3.46 (*m*, CH_2O); 3.07 (*s*, CH≡C); 1.77–1.51 (*m*, 4 CH_2); 1.04 (*s*, 2 Me); 0.20 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 135.84 (*d*, C(2)); 132.51 (*d*, C(4)); 132.35 (*d*, C(6)); 128.65 (*d*, C(5)); 123.90 (*s*, C(3)); 122.69 (*s*, C(1)); 105.22 (*s*, *C*≡C); 99.44 (*d*, OCHO); 93.87 (*d*, *C*H≡C); 82.99 (*s*, *C*≡C); 78.05 (*s*, *C*≡C); 64.64 (*t*, CH_2O); 62.79 (*t*, CH_2O); 38.48 (*t*); 31.06 (*t*); 25.70 (*t*); 23.60 (*q*, Me); 23.46 (*q*, Me); 20.00 (*t*); 18.94 (*s*); −4.08 (*q*, Me_2Si). EI-MS: 339 (2.3, $[M - Me]^+$), 269 (15), 185 (24), 184 (18), 183 (90), 143 (11), 129 (11), 126 (18), 85 (100), 75 (19), 55 (11). Anal. calc. for $C_{22}H_{30}O_2Si$ (354.56): C 74.53, H 8.53; found: C 74.49, H 8.63.

*2-{3-{[(2-Ethynylphenyl)ethynyl]dimethylsilyl}-3-methylbutoxy}tetrahydro-2*H*-pyran* (**47**). Oil. R_f (hexane/AcOEt 9:1) 0.30. IR ($CHCl_3$): 3308*s*, 3065*w*, 3007*s*, 2945*s*, 2862*s*, 2159*m*, 1474*s*, 1442*m*, 1410*w*, 1385*m*, 1366*m*, 1354*m*, 1324*w*, 1253*s*, 1133*s*, 1116*s*, 1095*m*, 1077*s*, 1024*s*, 980*m*, 954*m*, 933*m*, 905*m*, 854*s*, 838*s*, 822*s*, 651*m*, 623*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.50–7.45 (*m*, H–C(3), H–C(6)); 7.31–7.24 (*m*, H–C(4), H–C(5)); 4.60–4.57 (*m*,

OCHO); 3.98–3.82 (*m*, CH_2O); 3.60–3.46 (*m*, CH_2O); 3.34 (*s*, CH≡C); 1.80–1.49 (*m*, 4 CH_2); 1.06 (*s*, 2 Me); 0.22 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 132.76 (*d*, C(3)); 132.57 (*d*, C(6)); 128.69 (*d*, C(4)); 128.44 (*d*, C(5)); 126.64 (*s*, C(2)); 125.40 (*s*, C(1)); 104.30 (*s*, *C*≡C); 99.33 (*d*, OCHO); 97.52 (*d*, *C*H≡C); 82.47 (*s*, *C*≡C); 81.66 (*s*, *C*≡C); 64.65 (*t*, CH_2O); 62.73 (*t*, CH_2O); 38.29 (*t*); 31.06 (*t*); 25.70 (*t*); 23.54 (*q*, Me); 23.36 (*q*, Me); 19.98 (*t*); 18.91 (*s*); –4.04 (*q*, MeSi); –4.09 (*q*, MeSi). EI-MS: 353 (0.05, $[M-1]^+$), 339 (0.3, $[M-Me]^+$), 185 (15), 184 (15), 183 (80), 170 (10), 167 (10), 143 (29), 85 (100), 75 (19), 55 (10). Anal. calc. for $C_{22}H_{30}O_2Si$ (354.56): C 74.53, H 8.53; found: C 74.58, H 8.49.

General Procedure for Cleavage of the Thp Groups in **39**–**42**. a) *For* **39**: A soln. of **39** (105 mg, 0.202 mmol) in EtOH (2 ml) was treated with pyridinium toluene-4-sulfonate (5 mg) and heated to 60° for 3 h. Evaporation and FC (hexane/AcOEt 99:1→95:5) gave **48** (95%).

b) *For* **40**–**42**: At r.t., a stirred soln. of each title compound (100 mg) in MeOH (2 ml) was treated with *Amberlyst 15* (25–35 mg; H^+ form, stirred with 6N HCl, washed with H_2O to pH 7, refluxed with EtOH for 0.5 h, filtered, and dried) for 5, 20, and 20 h, resp., then filtered. The resin was washed with Et_2O. Evaporation of the combined filtrate and washings and FC gave **49**–**51** in quant. yield.

3-{Dimethyl[16-(trimethylsilyl)hexadeca-1,15-diynyl]silyl}-3-methylbutan-1-ol (**48**): Oil. R_f (hexane/AcOEt 9:1) 0.10. IR (CHCl: 3617*w*, 3515*w* (br.), 3007*m*, 2930*s*, 2857*s*, 2169*s*, 1726*w* (br.), 1601*w*, 1464*m*, 1428*w*, 1409*w*, 1385*w*, 1364*w*, 1324*w*, 1252*s*, 1068*w*, 1009*m* (br.), 843*s*, 822*s*, 641*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.77 (*t*, *J* = 7.2, CH_2O); 2.23–2.19 (*m*, 2 H–C(3′), 2 H–C(14′)); 1.61 (*t*, *J* = 7.2, 2 H–C(2)); 1.52 (*d*, exchange with D_2O, OH); 1.51–1.26 (*m*, 10 CH_2); 0.90 (*s*, 2 Me); 0.15 (*s*, MeSi); 0.11 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 109.27 (*s*, *C*≡C); 107.81 (*s*, *C*≡C); 84.24 (*s*, *C*≡C); 82.40 (*s*, *C*≡C); 59.87 (*t*, C(1)); 42.76 (*t*, C(2)); 29.58 (*t*); 29.53 (*t*); 29.50 (*t*); 29.09 (*t*); 29.07 (*t*); 28.81 (*t*); 28.65 (*t*); 28.63 (*t*); 23.75 (*q*, 2 Me); 19.87 (*t*); 18.89 (*s*, C(3)); 0.19 (*q*, Me_3Si); –3.95 (*q*, Me_2Si). EI-MS: 434 (0.04, M^+), 419 (1.4, $[M-Me]^+$), 147 (100), 133 (64), 73 (90), 59 (32). Anal. calc. for $C_{26}H_{50}OSi_2$ (434.85): C 71.81, H 11.59; found: C 71.96, H 10.30.

3-{Dimethyl{{2-[(trimethylsilyl)ethynyl]pyridin-5-yl}ethynyl}silyl}-3-methylbutan-1-ol (**49**): White solid. M.p. 78–79°. R_f (hexane/AcOEt 7:3) 0.26. IR ($CHCl_3$): 3617*w*, 3427*w* (br.), 3007*m*, 2961*s*, 2900*m*, 2862*m*, 2161*m*, 1730*w*, 1583*w*, 1545*w*, 1466*s*, 1410*w*, 1365*m*, 1253*s*, 1024*m*, 1010*m*, 961*w*, 934*w*, 869*s*, 849*s*, 823*s*, 657*w*, 632*w*, 610*w*, 559*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.61 (*dd*, *J* = 2.1, 0.9, H–C(2)); 7.68 (*dd*, *J* = 7.9, 2.2, H–C(4)); 7.38 (*dd*, *J* = 7.9, 0.9, H–C(5)); 3.80 (*m*, after addn. of D_2O *t*, *J* = 7.5, 2 H–C(3′), OH); 1.68 (*t*, *J* = 7.5, 2 H–C(2′)); 1.04 (*s*, 2 Me); 0.27 (*s*, Me_3Si); 0.23 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.32 (*s*, C(2)); 141.50 (*s*, C(6)); 138.57 (*s*, C(4)); 126.16 (*s*, C(5)); 119.08 (*s*, C(3)); 102.98 (*s*, *C*≡C); 102.16 (*s*, *C*≡C); 98.26 (*s*, *C*≡C); 96.89 (*s*, *C*≡C); 59.36 (*t*, C(3′)); 41.74 (*t*, C(2′)); 23.24 (*q*, 2 Me); 18.63 (*s*, C(1)); –0.61 (*q*, Me_3Si); –4.58 (*q*, Me_2Si). EI-MS: 342 (0.2, $[M-1]^+$), 328 (2.6, $[M-Me]^+$), 258 (20), 199 (37), 185 (21), 184 (100), 129 (22), 75 (22). Anal. calc. for $C_{19}H_{29}NOSi_2$ (343.62): C 66.41, H 8.51, N 4.08; found: C 66.60, H 8.21, N 4.03.

3-{Dimethyl{{3-[(trimethylsilyl)ethynyl]phenyl}ethynyl}silyl}-3-methylbutan-1-ol (**50**): Oil. R_f (hexane/AcOEt 9:1) 0.10. IR ($CHCl_3$): 3616*w*, 3532*w* (br.), 3007*m*, 2960*s*, 2896*m*, 2862*m*, 2150*s*, 1594*m*, 1569*w*, 1475*s*, 1406*m*, 1386*w*, 1364*w*, 1252*s*, 1164*m*, 1096*w*, 1064*w*, 1009*m*, 944*s*, 898*m*, 844*s*, 823*s*, 647*m*, 628*w*, 563*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.56 (*dd*, *J* = 1.6, 0.8, H–C(2′)); 7.43–7.37 (*m*, H–C(4′), H–C(6′)); 7.23 (*td*, *J* = 7.9, 0.8, H–C(5′)); 3.84–3.76 (*m*, 2 H–C(1)); 1.67 (*t*, *J* = 7.5, 2 H–C(2)); 1.38 (br. *s*, exchange with D_2O, OH); 1.04 (*s*, 2 Me); 0.24 (*s*, Me_3Si); 0.21 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 135.34 (*d*, C(2′)); 131.95 (*d*, C(4′)); 131.83 (*d*, C(6′)); 128.24 (*d*, C(5′)); 123.42 (*s*, C(3′)); 123.19 (*s*, C(1′)); 105.42 (*s*, *C*≡C); 103.99 (*s*, *C*≡C); 95.05 (*s*, *C*≡C); 93.10 (*s*, *C*≡C); 59.82 (*t*, C(1)); 42.40 (*t*, C(2)); 23.67 (*q*, 2 Me); 19.00 (*s*, C(3)); –0.08 (*q*, Me_3Si); –4.18 (*q*, Me_2Si). EI-MS: 327 (0.5, $[M-Me]^+$), 257 (14), 198 (36), 184 (29), 183 (100), 129 (31), 75 (39). Anal. calc. for $C_{20}H_{30}OSi_2$ (342.63): C 70.11, H 8.83; found: C 70.00, H 8.76.

3-{Dimethyl{{2-[(trimethylsilyl)ethynyl]phenyl}ethynyl}silyl}-3-methylbutan-1-ol (**51**): Oil. R_f (hexane/AcOEt 9:1) 0.10. IR ($CHCl_3$): 3618*w*, 3065*w* (br.), 3007*m*, 2960*s*, 2898*m*, 2861*m*, 2158*s*, 1476*s*, 1441*m*, 1410*w*, 1386*w*, 1364*w*, 1252*s*, 1099*m*, 1038*m*, 1009*m*, 961*w*, 871*s*, 854*s*, 823*s*, 644*w*, 556*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.49–7.43 (*m*, H–C(3′), H–C(6′)); 7.28–7.22 (*m*, H–C(4′), H–C(5′)); 3.81 (*t*, *J* = 7.4, 2 H–C(1)); 1.68 (*t*, *J* = 7.4, 2 H–C(2)); 1.42 (br. *s*, exchange with D_2O, OH); 1.06 (*s*, 2 Me); 0.26 (*s*, Me_3Si); 0.24 (*s*, Me_2Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 132.67 (*d*, C(3′)); 132.60 (*d*, C(6′)); 128.17 (*d*, C(4′)); 128.08 (*d*, C(5′)); 125.68 (*s*, C(2′)); 125.42 (*s*, C(1′)); 104.56 (*s*, *C*≡C); 103.31 (*s*, *C*≡C); 98.49 (*s*, *C*≡C); 96.64 (*s*, *C*≡C); 59.82 (*t*, C(1)); 42.52 (*t*, C(2)); 23.89 (*q*, 2 Me); 19.01 (*s*, C(3)); 0.04 (*s*, Me_3Si); –3.99 (*s*, Me_2Si). EI-MS: 327 (0.15, $[M-Me]^+$), 257 (25), 198 (29), 184 (23), 183 (100), 129 (28), 75 (37), 73 (18). Anal. calc. for $C_{20}H_{30}OSi_2$ (342.63): C 70.11, H 8.83; found: C 70.35, H 9.02.

General Procedure for Removal of the DOPS *Groups in* **48**–**51**. At –78°, a soln. of each alcohol (35–50 mg) in THF (1 ml) was treated with BuLi (0.1 equiv. in hexane). The mixtures were stirred (**48**: at –78° for 2.5 h, then at –20° for 2 h; **49**: at –78° for 18 min; **50**: at –78° for 40 min; **51**: at –78° for 6 h, at –20° for 14 h, and at r.t. for 9 h), diluted with pentane, and processed as usual. FC afforded **52** in 91%, and **53**–**55** [81] in nearly quant. yield.

1-(Trimethylsilyl)hexadeca-1,15-diyne (**52**): Oil. R_f (hexane/AcOEt 95:5) 0.62. IR ($CHCl_3$): 3307*m*, 3007*w*, 2930*s*, 2856*s*, 2169*m*, 2116*w*, 1700*w*, 1684*w*, 1653*w*, 1558*w*, 1540*w*, 1506*w*, 1465*m*, 1430*w*, 1326*w*, 1252*m*, 1033*w*, 942*w*, 844*s*, 638*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.19 (*t*, *J* = 7.2, 2 H–C(3)); 2.18 (*td*, *J* = 7.2, 2.7, 2 H–C(14)); 1.93 (*t*, *J* = 2.7, CH≡C); 1.56–1.48 (*m*, 2 CH_2); 1.40–1.27 (*m*, 8 CH_2); 0.15 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 107.80 (*s*, *C*≡C); 84.81 (*d*, *C*H≡C); 84.24 (*s*, *C*≡C); 63.03 (*s*, *C*≡C); 29.58 (*t*); 29.56 (*t*); 29.50 (*t*); 29.48 (*t*); 29.12 (*t*); 29.08 (*t*); 28.80 (*t*); 28.77 (*t*); 28.64 (*t*); 28.51 (*t*); 19.86 (*t*); 18.41 (*t*); −0.03 (*q*, Me_3Si). EI-MS: 290 (0.03, M^+), 275 (2.3, $[M - Me]^+$), 137 (10), 99 (11), 73 (100), 59 (40). Anal. calc. for $C_{19}H_{34}Si$ (290.56): C 78.54, H 11.79; found: C 78.75, H 11.70.

5-Ethynyl-2-[(trimethylsilyl)ethynyl]pyridine (**53**): White solid. M.p. 45–46°. R_f (hexane/AcOEt 9:1) 0.24. IR ($CHCl_3$): 3300*s*, 2964*m*, 2901*w*, 2165*w*, 1585*m*, 1545*m*, 1492*w*, 1466*s*, 1410*w*, 1363*m*, 1253*s*, 1128*w*, 1092*w*, 1022*m*, 935*w*, 867*s*, 847*s*, 657*m*, 629*m*, 556*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.65 (*dd*, *J* = 2.1, 0.9, H–C(6)); 7.71 (*dd*, *J* = 8.0, 2.1, H–C(4)); 7.42 (*dd*, *J* = 8.0, 1.0, H–C(3)); 3.30 (*s*, CH≡C); 0.27 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 152.54 (*d*, C(6)); 141.93 (*s*, C(2)); 138.77 (*d*, C(4)); 126.17 (*d*, C(3)); 118.19 (*s*, C(5)); 102.85 (*s*, *C*≡C); 96.98 (*d*, *C*H≡C); 81.94 (*s*, *C*≡C); 79.85 (*s*, *C*≡C); −0.63 (*q*, Me_3Si). EI-MS: 199 (48, M^+), 185 (25), 184 (100), 136 (11). Anal. calc. for $C_{12}H_{13}NSi$ (199.33): C 72.31, H 6.57, N 7.03; found: C 72.42, H 6.82, N 6.98.

1-Ethynyl-3-[(trimethylsilyl)ethynyl]benzene (**54**): Oil. R_f (hexane/AcOEt 9:1) 0.55. IR ($CHCl_3$): 3305*s*, 3007*w*, 2962*m*, 2901*w*, 2360*w*, 2151*m*, 2111*w*, 1594*w*, 1570*w*, 1476*m*, 1408*w*, 1252*s*, 1152*w*, 1095*w*, 1013*w*, 925*s*, 899*m*, 846*s*, 654*m*, 626*m*, 606*w*, 562*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.59 (*d*, *J* = 1.6, H–C(2)); 7.45–7.40 (*m*, H–C(4), H–C(6)); 7.25 (*t*, *J* = 7.1, H–C(5)); 3.07 (*s*, CH≡C); 0.26 (*s*, Me_3Si). ^{13}C-NMR (50 MHz, $CDCl_3$): 135.21 (*d*, C(2)); 131.85 (*d*, C(4)); 131.70 (*d*, C(6)); 128.00 (*d*, C(5)); 123.19 (*s*, C(1)); 122.04 (*s*, C(3)); 103.61 (*s*, *C*≡C); 94.84 (*d*, *C*H≡C); 82.42 (*s*, *C*≡C); 77.44 (*s*, *C*≡C); −0.38 (*q*, Me_3Si). EI-MS: 199 (25, $[M + 1]^+$), 184 (22), 183 (100). Anal. calc. for $C_{13}H_{14}Si$ (198.34): C 78.73, H 7.11; found: C 78.71, H 7.30.

General Procedure for Preparation of the Hemiketals **57–59**. At −76°, a soln. of the corresponding DOPSA **32**, **33**, and **31** (0.22 mmol) in THF (1 ml) was treated with 1.5M BuLi in hexane (0.14 ml, 0.21 mmol) for 1 h. At −76°, the soln. was injected into a soln. of **56** (92 mg, 0.17 mmol) in THF (2 ml). The mixture was stirred (**57**: at −76° for 2 h; **58**: at −76° to −35° for 80 min; **59**: at −76° for 45 min and −76° to r.t. within 10 min), quenched with aq. 0.1N HCl, and processed as usual. FC (hexane/AcOEt 92:8→85:15) gave **57**, **58**, and **59** in 77, 91, and 72% yield, resp.

4,5,6,8-Tetra-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-{[3-(methoxymethoxy)-1,1-dimethylpropyl]dimethylsily}-D-gluco-oct-3-ulopyranose (**57**): Syrup. R_f (hexane/AcOEt 7:3) 0.35. IR ($CHCl_3$): 3580*m* (br.), 3080*w*, 3010*m*, 2940*s*, 2900*s*, 2880*s*, 1500*m*, 1460*m*, 1360*m*, 1260*m*, 1150*m*, 1070*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.06 (*m*, 20 arom. H); 5.08–4.60 (*m*, 4 PhCH_2); 4.58 (*s*, OCH_2O); 4.39 (*s*, exchange with D_2O, 0.55 H, OH); 4.23 (*s*, exchange with D_2O, 0.45 H, OH); 4.03–3.92 (*m*, H–C(7)); 3.88 (*t*, *J* = 8.5, 0.55 H); 3.81–3.55 (*m*, 6 H); 3.48 (*d*, *J* = 8.8, 0.55 H, H–C(4)); 3.35 (*s*, 1.35 H, MeO); 3.30 (*s*, 1.65 H, MeO); 1.64 (*t*, *J* = 7.5, CH_2); 0.99 (*s*, 2 Me); 0.15 (*s*, Me_2Si). CI-MS: 771 (100, $[M + NH_4]^+$). Anal. calc. for $C_{45}H_{56}O_8Si$ (753.04): C 71.77, H 7.49; found: C 71.68, H 7.55.

4,5,6,8-Tetra-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-{[1,1-dimethyl-3-(tetrahydro-2H-pyran-2-yloxy)propyl]dimethylsilyl}-D-gluco-oct-3-ulopyranose (**58**): Syrup. R_f (hexane/AcOEt 7:3) 0.12. IR ($CHCl_3$): 3560*w* (br.), 3270*w* (br.), 2998*m*, 2940*s*, 2860*s*, 1495*m*, 1450*m*, 1360*m*, 1250*m*, 1130*s*, 1110*s*, 1070*s*, 1025*s*, 900*w*, 840*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.15 (*m*, 20 arom. H); 5.10–4.48 (*m*, 4 PhCH_2, OCHO); 4.31 (*s*, exchange with D_2O, OH); 4.08–3.93 (*m*, 10 H); 1.90–1.43 (*m*, 8 H); 1.00 (br. *s*, 2 Me); 0.20 (br. *s*, Me_2Si). CI-MS: 810 (87, $[M + NH_4]^+$), 792 (15), 702 (100).

4,5,6,8-Tetra-O-benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1-C-{[1,1-dimethyl-3-(4-methoxybenzyloxy)propyl]dimethylsilyl}-D-gluco-oct-3-ulopyranose (**59**): Colorless oil. R_f (hexane/AcOEt 7:3) 0.39. IR ($CHCl_3$): 3560*w* (br.), 3000*m*, 2920*m* (sh), 2860*m*, 1610*m*, 1510*s*, 1495*w*, 1450*m* (sh), 1360*m*, 1300*w*, 1250*s*, 1080*s* (sh), 840*m*, 695*s*. ^{1}H-NMR (400 MHz, $CDCl_3$, α-D/β-D 1:1): 7.38–7.13 (*m*, 22 arom. H); 6.86–6.79 (*m*, 2 arom. H); 5.04 (*d*, *J* = 10.7, 0.5 H, PhC*H*); 5.03 (*d*, *J* = 11.6, 0.5 H, PhC*H*); 4.96–4.71 (*m*, 4 PhC*H*); 4.63–4.47 (*m*, 3 PhC*H*); 4.38 (*s*, 1 H, 4-$MeOC_6H_4CH_2$); 4.34 (*s*, 1 H, 4-$MeOC_6H_4CH_2$); 3.98 (*ddd*, *J* = 10.1, 3.8, 1.9, 0.5 H, H–C(7)); 3.93–3.89 (*m*, 1 H, H–C(7), OH); 3.86 (*t*, *J* = 9.2, 0.5 H, H–C(5)); 3.77 (*t*, *J* = 9.2, 0.5 H, H–C(5)); 3.76 (*s*, 1.5 H, MeO); 3.74 (*s*, 1.5 H, MeO); 3.73–3.61 (*m*, H–C(6), 2 H–C(8), 0.5 H–C(4)); 3.59 (br. *s*, 0.5 H, OH); 3.54 (*t*, *J* = 7.3, 2 H–C(3′)); 3.48 (*d*, *J* = 9.5, 0.5 H, H–C(4)); 1.70–1.65 (*m*, 2 H–C(2′)); 0.99 (*s*, Me); 0.98 (*s*, Me); 0.154 (*s*); 0.152 (*s*); 0.128 (*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$, α-D/β-D 1:1): 159.06 (*s*); 159.02 (*s*); 138.86 (*s*); 138.64 (*s*); 138.58 (*s*); 138.28 (*s*); 138.24 (*s*); 138.19 (*s*); 138.07 (*s*); 137.91 (*s*); 130.61 (*s*); 130.60 (*s*); 129.25 (*d*); 129.18 (*d*); 128.49–127.26 (several *d*); 113.74 (*d*); 113.70 (*d*); 105.33 (*s*, C(2) of α-D-**59**); 101.73 (*s*, C(3) of β-D-**59**); 95.37 (*s*, C(3) of α-D-**59**); 92.19 (*s*, C(2) of β-D-**59**); 91.27 (*s*, C(1) of α-D-**59**); 87.24 (*s*, C(1) of β-D-**59**); 84.35 (*d*); 84.15 (*d*); 83.69 (*d*); 82.43 (*d*); 77.65 (*d*); 77.25 (*d*); 75.77 (*t*); 75.65 (*t*); 74.92 (*t*); 74.87 (*t*); 74.37 (*t*); 74.22 (*d*); 73.33 (*t*); 73.29 (*t*); 72.56 (*t*); 72.52 (*t*); 71.96 (*d*); 68.61 (*t*); 68.38 (*t*, C(8)); 66.96 (*t*); 66.81 (*t*, 4-$MeOC_6H_4CH_2$); 55.22 (*q*, MeO); 38.27 (*t*); 38.14

(*t*); 23.46 (*q*); 23.40 (*q*); 23.36 (*q*); 18.76 (*s*); 18.67 (*s*); −4.30 (*q*), −4.34 (*q*), −4.43 (*q*, Me_2Si). CI-MS: 739 (22), 738 (42), 557 (37), 556 (100, $[\mathbf{56} + NH_4]^+$), 448 (13), 121 (17, $MeOC_6H_4CH_2^+$). FAB-MS: 811 (4, $[M - OH]^+$), 211 (18), 181 (16), 121 (100), 91 (98), 75 (11). Anal. calc. for $C_{51}H_{60}O_8Si$ (829.12): C 73.88, H 7.29; found: C 73.59, H 7.02.

3,7-Anhydro-4,5,6,8-tetra-O-*benzyl-1,1,2,2-tetradehydro-1,2-dideoxy-1*-C-*[(3-hydroxy-1,1-dimethylpropyl)-dimethylsilyl]*-D-glycero-D-gulo-*octitol* (**61**). a) At −5°, a soln. of **59** (25 mg, 0.030 mmol) in CH_2Cl_2 (0.3 ml) was treated with a soln. of Et_3SiH (0.15 ml of a soln. of 1 ml of Et_3SiH in 12 ml of $MeCN/CH_2Cl_2$ 5:1, 0.066 mmol) and then with a soln. of $BF_3 \cdot OEt_2$ (0.12 ml of a soln. of 0.83 ml of $BF_3 \cdot Et_2O$ in 10 ml of MeCN, 0.066 mmol) and stirred at r.t. for 20 min. Usual workup and FC (hexane/AcOEt 9:1) gave **61** (17 mg, 82%). Syrup. R_f (hexane/AcOEt 7:3) 0.25. IR ($CHCl_3$): 3620*w*, 3060*w*, 3000*m*, 2920*s*, 2860*s*, 2170*w*, 1950*w*, 1495*m*, 1450*s*, 1360*s*, 1290*m*, 1250*s*, 1090*s*, 1060*s*, 1025*s*, 910*w*, 840*m*, 820*s*, 695*s*. ^{1}H-NMR (500 MHz, H,H-COSY, C,H-COSY, $CDCl_3$): 7.38–7.13 (*m*, 20 arom. H); 5.04 (*d*, J = 10.6, PHC*H*); 4.89 (*d*, J = 11.1, PhC*H*); 4.83 (*d*, J = 10.6, PhC*H*); 4.82 (*d*, J = 11.1, PhC*H*); 4.81 (*d*, J = 10.8, PhC*H*); 4.63 (*d*, J = 12.2, PhC*H*); 4.56 (*d*, J = 12.2, PhC*H*); 4.55 (*d*, J = 10.8, PhC*H*); 4.06 (*d*, J = 9.1, H–C(3)); 3.74 (*dd*, J = 10.9, 2.0, H–C(8)); 3.69 (*dd*, J = 10.9, 4.3, H–C(8)); 3.70 (*t*, J = 7.4, 2 H–C(3′)); 3.66–3.60 (*m*, H–C(4), H–C(5), H–C(6)); 3.44–3.41 (*m*, H–C(7)); 1.60 (*t*, J = 7.4, 2 H–C(2′)); 1.60 (*s*, exchange with D_2O, OH); 0.98 (*s*, 2 Me); 0.15 (*s*, Me_2Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.32 (*s*); 137.89 (*s*); 137.83 (2*s*); 128.19–127.54 (several *d*); 103.72 (*s*, C(2)); 89.22 (*s*, C(1)); 85.82 (*d*); 82.09 (*d*); 78.93 (*d*, C(7)); 77.43 (*d*); 75.44 (*t*, Ph*C*H_2); 75.05 (*t*, Ph*C*H_2); 74.86 (*t*, Ph*C*H_2); 73.26 (*t*, Ph*C*H_2); 70.03 (*d*, C(3)); 68.42 (*t*, C(8)); 59.11 (*t*, C(3′)); 41.61 (*t*, C(2′)); 23.32 (*q*, 2 Me); 18.51 (*s*, C(1′)); −4.42 (*q*, Me_2Si). CI-MS: 566 (100, $[\mathbf{9} + NH_4]^+$), 162 (23, [2,2,3,3-tetramethyl-1-oxa-2-silacyclopentane + $NH_4]^+$). ESI-MS: 731.6 (75, $[M + K]^+$), 715.4 (100, $[M + Na]^+$), 693.5 (50, $[M + H]^+$). Anal. calc. for $C_{43}H_{52}O_6Si$ (692.97): C 74.53, H 7.56; found: C 73.50, H 7.80.

4,5,8-Tri-O-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6*-C-*(2,2-dibromoethenyl)-1*-C-{*[1,1-dimethyl-3-(4-methoxybenzyloxy)propyl]dimethylsilyl*}-D-gluco-*oct-3-ulopyranose* (**63**). As described for **57**–**59**, with **31** (48 mg, 0.16 mmol) in THF (3 ml) and 1.22M BuLi in hexane (0.135 ml, 0.164 mmol; at −76° for 20 min, at −76 to −15° for 10 min, and at −15° for 10 min). The soln. was cooled to −76°, treated with a soln. of **62** (92 mg, 0.149 mmol) in THF (1 ml), and stirred for 0.5 h. FC (hexane/AcOEt 97:3): **63** (α-D/β-D 4:3; 124 mg, 92%). Oil. R_f (CH_2Cl_2/THF 98:2) 0.51. IR ($CHCl_3$): 3572*w* (br.), 3272*w*, 3090*w*, 3066*w*, 3007*m*, 2958*m*, 2928*m*, 2864*m*, 1612*w*, 1586*w*, 1514*s*, 1497*m*, 1464*m*, 1454*m*, 1363*m*, 1302*m*, 1252*s*, 1173*m*, 1086*s*, 1028*s*, 912*w*, 844*s*, 608*w*, 573*w*, 556*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, C,H-COSY; α-D/β-D 4:3): α-D-**63**: 7.41–7.19 (*m*, 17 arom. H); 6.86–6.81 (*m*, 2 arom. H); 6.06 (*d*, J = 10.1, H–C(1′)); 5.02 (*d*, J = 10.6, PhC*H*); 4.83 (*d*, J = 10.5, PhC*H*); 4.70 (*d*, J = 11.0, PhC*H*); 4.61–4.54 (*m*, 3 PhC*H*); 4.41–4.36 (*m*, 2 PhC*H*); 3.96 (*ddd*, J = 10.7, 5.0, 3.0, H–C(7)); 3.78 (*s*, MeO); 3.70 (*d*, J = 9.0, H–C(4)); 3.63 (*dd*, J = 10.3, 9.0, H–C(5)); 3.58–3.47 (*m*, signals overlapped by signals of β-D-isomer, 2 H–C(8), 4-$MeOC_6H_4CH_2OCH_2$); 2.89 (*q*, J = 10.3, H–C(6)); 1.69–1.65 (*m*, signals overlapped by signals of the β-D-isomer, CH_2); 0.975 (*s*, Me); 0.973 (*s*, Me); 0.128 (*s*, MeSi); 0.127 (*s*, MeSi); β-D-**63**: 5.95 (*d*, J = 10.1, H–C(1′)); 5.03 (*d*, J = 11.5, PhC*H*); 4.77 (*d*, J = 11.5, PhC*H*); 4.73 (*d*, J = 11.1, PhC*H*); 4.61–4.54 (*m*, 3 PhC*H*); 4.41–4.36 (*m*, 2 PhC*H*); 3.87 (*ddd*, J = 10.6, 5.2, 2.8, H–C(7)); 3.77 (*s*, MeO); 2.85 (*q*, J = 10.3, H–C(6)); 0.992 (*s*, Me); 0.988 (*s*, Me); 0.165 (*s*, MeSi); 0.161 (*s*, MeSi). ^{13}C-NMR (125 MHz, $CDCl_3$, C,H-COSY; α-D/β-D 4:3): α-D-**63**: 159.10 (*s*, C(4) of 4-$MeOC_6H_4CH_2$); 138.09 (*s*); 137.99 (*s*); 137.93 (*s*); 135.05 (*d*, C(1′)); 130.62 (*s*, C(1) of 4-$MeOC_6H_4CH_2$); 129.27–127.35 (several *d*); 113.76 (*d*, C(2), C(5) of 4-$MeOC_6H_4CH_2$); 105.04 (*s*, C(2)); 95.40 (*s*, C(3)); 93.07 (*s*, C(2′)); 91.62 (*s*, C(1)); 84.31 (*d*, C(4)); 78.37 (*d*, C(5)); 75.35 (*t*, Ph*C*H_2); 74.63 (*t*, Ph*C*H_2); 73.49 (*t*, Ph*C*H_2); 72.61 (*t*, Ar*C*H_2); 70.93 (*d*, C(7)); 70.42 (*t*, C(8)); 66.83 (*t*, 4-$MeOC_6H_4CH_2OCH_2$); 55.26 (*q*, MeO); 49.52 (*d*, C(6)); 38.15 (*t*); 23.41 (*q*); 23.37 (*q*); 18.68 (*s*); −4.34 (*q*); −4.42 (*q*); β-D-**63**: 159.10 (*s*, C(4) of 4-$MeOC_6H_4CH_2$); 138.87 (*s*); 137.99 (*s*); 137.95 (*s*); 135.15 (*d*, C(1′)); 130.54 (*s*, C(1) of 4-$MeOC_6H_4CH_2$); 129.27–127.35 (several *d*); 113.76 (*d*, C(2), C(5) of 4-$MeOC_6H_4CH_2$); 101.50 (*s*, C(3)); 93.34 (*s*, C(2′)); 92.44 (*s*, C(2)); 87.45 (*s*, C(1)); 84.81 (*d*, C(4)); 79.56 (*d*, C(5)); 75.97 (*t*, Ph*C*H_2); 75.17 (*t*, Ph*C*H_2); 73.49 (*t*, Ph*C*H_2); 73.46 (*d*, C(7)); 72.61 (*t*, Ar*C*H_2); 70.48 (*t*, C(8)); 66.80 (*t*, 4-$MeOC_6H_4CH_2OCH_2$); 55.26 (*q*, MeO); 48.92 (*d*, C(6)); 38.30 (*t*); 23.45 (*q*, Me); 23.41 (*q*, Me); 18.76 (*s*); −4.28 (*q*, MeSi); −4.42 (*q*, MeSi). FAB-MS: 907 (1), 905 (2), 903 (1, $[M - 1]^+$), 891 (5), 890 (3), 889 (9), 887 (5, $[M - OH]^+$), 211 (37), 181 (24), 154 (29), 136 (29), 122 (41), 121 (88), 107 (23), 91 (100), 83 (21), 77 (22), 75 (25), 69 (24). Anal. calc. for $C_{46}H_{54}Br_2O_7Si$ (906.83): C 60.93, H 6.00; found: C 60.86, H 5.92.

3,7-Anhydro-4,5,8-tri-O-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6*-C-*(2,2-dibromoethenyl)-1*-C-*[(3-hydroxy-1,1-dimethylpropyl)dimethylsilyl]*-D-glycero-D-gulo-*octitol* (**64**). As described for **61**, with **63** (90 mg, 0.99 mmol) and Et_3SiH (0.7 ml, 4.4 mmol) in CH_2Cl_2/MeCN 3:8 (11 ml), and $BF_3 \cdot OEt_2$ (0.36 ml, 2.9 mmol) in MeCN (8 ml; −20°, 1.5 h). FC (hexane/AcOEt 8:2): **64** (53.5 mg, 70%). Oil. R_f (hexane/AcOEt 7:3) 0.47. $[\alpha]_D^{20} = +3.8$ (c = 1.93, $CHCl_3$). IR ($CHCl_3$): 3580*w* (br.), 3090*w*, 3067*w*, 3007*s*, 2958*s*, 2927*s*, 2863*s*, 2179*w*, 1627*w*, 1605*w*, 1497*m*, 1454*s*, 1400*w*, 1357*s*, 1291*m*, 1260*s*, 1086*s*, 1027*s*, 1011*s*, 911*m*, 840*s*, 818*s*, 649*w*, 601*w*, 556*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.41–7.26 (*m*, 15 arom. H); 6.02 (*d*, J = 10.2, H–C(1′)); 5.04 (*d*, J = 10.6, PhC*H*); 4.82 (*d*,

J = 10.6, PhC*H*); 4.75 (*d*, J = 10.9, PhC*H*); 4.63 (*d*, J = 10.9, PhC*H*); 4.58 (*s*, PhCH_2); 4.04 (*d*, J = 9.7, H–C(3)); 3.72 (*t*, J = 7.4, CH_2OH); 3.62 (*dd*, J = 9.7, 8.7, H–C(4)); 3.57 (*dd*, J = 10.9, 3.1, H–C(8)); 3.51 (*dd*, J = 10.9, 5.1, H–C(8)); 3.42 (*ddd*, J = 10.3, 5.1, 3.1, H–C(7)); 3.35 (*dd*, J = 10.2, 8.7, H–C(5)); 2.85 (*q*, J = 10.2, H–C(6)); 1.60 (*t*, J = 7.5, CH_2); 1.60 (br. *s*, OH); 0.986 (*s*, Me); 0.981 (*s*, Me); 0.159 (*s*, MeSi); 0.153 (*s*, MeSi). ^{13}C-NMR (50 MHz, $CDCl_3$): 137.79 (*s*); 137.54 (2*s*); 134.65 (*d*, C(1′)); 128.11–127.42 (several *d*); 103.45 (*s*, C(2)); 93.00 (*s*, C(2′)); 89.17 (*s*, C(1)); 82.14 (*d*, C(5)); 81.63 (*d*, C(4)); 77.80 (*d*, C(7)); 75.08 (*t*, PhCH_2); 74.92 (*t*, PhCH_2); 73.38 (*t*, PhCH_2); 70.42 (*t*, C(8)); 70.10 (*d*, C(3)); 59.32 (*t*, CH_2OH); 49.38 (*d*, C(6)); 41.71 (*t*); 23.22 (*q*, 2 Me); 18.48 (*s*); –4.56 (*q*, Me_2Si). FAB-MS: 773 (6), 771 (10), 769 (5, $[M + 1]^+$), 181 (16), 154 (27), 138 (11), 137 (18), 135 (21), 107 (13), 91 (100).

3,7-Anhydro-4,5,8-tri-O-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-6*-C-*{2,2-dibromoethenyl)-1*-C-*{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}*-D-glycero-D-gulo-*octitol* (**65**). As described for **28**, with **64** (330 mg, 0.428 mmol), 3,4-dihydro-2*H*-pyran (80 µl, 0.882 mmol), CH_2Cl_2 (5 ml), and pyridinium toluene-4-sulfonate (6 mg, 0.02 mmol). FC (hexane/AcOEt 7:3): **65** (319 mg, 87%). Oil. R_f (hexane/AcOEt 17:3) 0.20. $[\alpha]_D^{25}$ = +7.8 (c = 0.82, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*s*, 2946*s*, 2864*s*, 2179*w*, 1723*w*, 1630*w*, 1497*m*, 1454*s*, 1355*s*, 1324*w*, 1290*m*, 1253*s*, 1116*s*, 1077*s*, 1027*s*, 982*m*, 955*m*, 906*m*, 867*m*, 840*s*, 818*s*, 618*w*, 596*w*, 555*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 6.01 (*d*, J = 10.2, C(1′)); 5.04 (*d*, J = 10.5, PhC*H*); 4.79 (*d*, J = 10.5, PhC*H*); 4.74 (*d*, J = 10.9, PhC*H*); 4.61 (*d*, J = 10.9, PhC*H*); 4.57 (*s*, PhCH_2); 4.55–4.52 (*m*, OCHO); 4.03 (*d*, J = 9.7, H–C(3)); 3.88–3.82 (*m*, CH_2OThp); 3.60 (*dd*, J = 9.7, 8.8, H–C(4)); 3.57–3.42 (*m*, CH_2O of Thp); 3.49 (*dd*, J = 10.4, 5.1, H–C(8)); 3.44 (*dd*, J = 10.4, 3.1, H–C(8)); 3.40 (*ddd*, J = 10.4, 5.1, 3.1, H–C(7)); 3.33 (*dd*, J = 10.2, 8.8, H–C(5)); 2.83 (*q*, J = 10.3, H–C(6)); 1.83–1.49 (*m*, 4 CH_2); 0.99 (*s*, Me); 0.98 (*s*, Me); 0.15 (*s*, MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.04 (2*s*); 137.87 (*s*); 135.02 (*d*, C(1′)); 128.42–127.66 (several *d*); 103.49 (*s*, C(2)); 99.02 (*d*); 98.99 (*d*, acetal C); 93.18 (*s*, C(2′)); 89.39 (*s*, C(1)); 82.49 (*d*, C(5)); 81.92 (*d*, C(4)); 78.09 (*d*, C(7)); 75.45 (*t*, PhCH_2); 75.18 (*t*, PhCH_2); 73.63 (*t*, PhCH_2); 70.73 (*t*, C(8)); 70.44 (*d*, C(3)); 64.09 (*t*); 64.06 (*t*, CH_2O); 62.43 (*t*); 62.40 (*t*, CH_2O); 49.71 (*d*, C(6)); 37.67 (*t*); 37.63 (*t*); 30.80 (*t*); 25.49 (*t*); 23.48 (*q*); 23.15 (*q*); 22.95 (*q*, 2 Me); 19.72 (*t*); 19.70 (*t*); 18.75 (*s*); 18.46 (*s*); –4.33 (*q*), –4.37 (*q*, 2 MeSi). FAB-MS: 857 (0.1), 855 (0.2), 853 (0.1, $[M + 1]^+$), 181 (25), 164 (13), 154 (24), 145 (13), 138 (12), 137 (20), 136 (25), 107 (18), 105 (36), 101 (15), 92 (35), 91 (100), 90 (7), 89 (10), 85 (74), 83 (22), 75 (33). Anal. calc. for $C_{43}H_{54}Br_2O_6Si$ (854.80): C 60.42, H 6.37, Br 18.70; found: C 60.56, H 6.37, Br 18.49.

4,5,8-Tri-O-*benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-1*-C-*{[1,1-dimethyl-3-(4-methoxybenzyloxy)propyl]-dimethylsilyl}-3*-O-*(trimethylsilyl)-6*-C-*[2-(trimethylsilyl)ethynyl]-α*-D-gluco-*oct-3-ulopyranose* (**66**). At –76°, 1.30M BuLi in hexane (carefully titrated [82]; 6.84 ml, 8.89 mmol) was added dropwise within *ca.* 2 min, to a stirred soln. of **31** (2.628 g, 9.05 mmol) in THF (110 ml). The mixture was stirred at –76° for 20 min, at –76 to –15° for 10 min, and at –15° for 10 min. The resulting light-orange-yellow soln. was treated in one portion with a soln. of **62** (crude product [1] from a *Swern* oxidation; 4.850 g, *ca.* 7.9 mmol) in THF (30 ml), stirred at –76° for 1.5 h, treated dropwise within 3 min with 1.30M BuLi in hexane (12.1 ml, 15.73 mmol), and stirred at –76° for 3 h. ^{1}H-NMR of an aliquot of the mixture (treated with 0.1M HCl and worked up as usual): complete disappearance of **63**; *d*'s of C≡CH at 2.08 (J = 2.3, 0.5 H) and 2.12 (J = 2.3, 0.5 H). A soln. of Me_3SiCl (*ca.* 3.2 ml) in THF (10 ml) was added dropwise to adjust the pH of the mixture to *ca.* 6. The light-orange soln.was stirred at –76° for 15 min and at –76 to 5° for 35 min. Usual workup gave crude **66** as an oil which was dried by azeotropic coevaporations with anh. benzene, stirred at r.t. under h.v. for 1 h, and used directly for the next step. A sample was purified by FC (hexane/AcOEt 1:9). Oil. R_f (hexane/AcOEt 9:1) 0.4. $[\alpha]_D^{20}$ = +32.1 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): 3066*w*, 3007*m* (sh), 2959*m*, 2862*m*, 2173*w*, 1612*m*, 1513*m*, 1497*w*, 1454*m*, 1409*w*, 1362*w*, 1302*w*, 1284*w*, 1251*s*, 1133*s*, 1087*s*, 1048*s*, 1028*s*, 846*s*, 673*w*, 598*w*, 581*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40–7.22 (*m*, 15 arom. H); 7.20–7.17 (*m*, 2 arom. H); 6.83–6.80 (*m*, 2 arom. H); 4.98 (*d*, J = 11.7, PhC*H*); 4.81 (*s*, PhCH_2); 4.73 (*d*, J = 11.7, PhC*H*); 4.62 (*d*, J = 12.2, PhC*H*); 4.57 (*d*, J = 12.2, PhC*H*); 4.35 (*s*, ArCH_2); 4.03 (*ddd*, J = 10.8, 5.2, 1.9, H–C(7)); 3.79 (*dd*, J = 11.0, 1.9, H–C(8)); 3.77 (*s*, MeO); 3.73 (*dd*, J = 10.4, 9.3, H–C(5)); 3.72 (*dd*, J = 11.0, 5.2, H–C(8)); 3.54 (*t*, J = 7.3, 4-MeOC$_6$H$_4$CH$_2$OCH_2); 3.26 (*d*, J = 9.3, H–C(4)); 2.74 (*t*, J = 10.7, H–C(6)); 1.68 (*t*, J = 7.4, CH_2); 1.02 (*s*, Me); 1.01 (*s*, Me); 0.23 (*s*, Me_3SiO); 0.175 (*s*, MeSi); 0.170 (*s*, MeSi); 0.12 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 159.05 (*s*, C(4) of 4-MeOC$_6$H$_4$CH$_2$); 139.25 (*s*); 138.65 (*s*); 138.50 (*s*); 130.70 (*s*, C(1) of 4-MeOC$_6$H$_4$CH$_2$); 129.17 (*d*, C(3) and C(6) of 4-MeOC$_6$H$_4$CH$_2$); 128.27–127.15 (several *d*); 113.71 (*d*, C(2) and C(5) of 4-MeOC$_6$H$_4$CH$_2$); 104.16 (*s*, C(2)); 102.50 (*s*, C(1′)); 96.22 (*s*, C(3)); 93.02 (*s*, C(1)); 87.76 (*s*, C(2′)); 85.87 (*d*, C(5)); 81.94 (*d*, C(4)); 75.98 (*t*, PhCH_2); 74.44 (*t*, PhCH_2); 74.20 (*d*, C(7)); 73.26 (*t*, PhCH_2); 72.63 (*t*, ArCH_2O); 70.38 (*t*, C(8)); 67.06 (*t*, 4-MeOC$_6$H$_4$CH_2O); 55.25 (*q*, MeO); 38.26 (*t*, CH_2); 37.75 (*d*, C(6)); 23.50 (*q*, 2 Me); 18.77 (*s*); 1.62 (*q*, Me_3SiO); –0.04 (*q*, Me_3Si); –4.35 (*q*, MeSi); –4.43 (*q*, MeSi). FAB-MS: 889 (1.6, $[M - 1]^+$), 240 (14), 212 (29), 181 (19), 179 (12), 155 (14), 149 (11), 147 (37), 143 (20), 138 (12), 137 (11), 135 (10), 133 (13), 123 (35), 121

(85), 117 (11), 107 (12), 105 (15), 92 (41), 91 (100), 77 (12), 75 (28), 73 (80). Anal. calc. for $C_{52}H_{70}O_7Si_3$ (891.38): C 70.07, H 7.92; found: C 70.18, H 7.93.

*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-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**67**). At −15°, a soln. of crude **66** (see above) and Et_3SiH (7.5, ml, 47.1 mmol) in CH_2Cl_2/MeCN 6:4 (100 ml) was treated with a soln. of $BF_3 \cdot OEt_2$ (4.0 ml, 31.8 mmol) in MeCN (10 ml), stirred at −15 to −5° for 80 min, treated again with Et_3SiH (4 ml, stirred for 1 h at −5 to −2° and for 2 h at −5°, treated with $BF_3 \cdot OEt_2$ (2 ml), stirred at −5 to −3° for 2 h, treated again with Et_3SiH (1 ml) and $BF_3 \cdot OEt$ (0.5 ml), and stirred for 6 h at −15 to 8°. The mixture was cooled to −10°, poured into cold (0°) Et_2O/H_2O, washed seven times with cold H_2O (till pH 7), and processed as usual. FC (hexane(AcOEt 83:17→8:2) gave **67** (3.206 g, 60% overall). Oil. R_f (hexane/AcOEt 7:3) 0.35. $[\alpha]_D^{20} = -32.3$ ($c = 0.54$, $CHCl_3$). IR ($CHCl_3$): 3608*w* (br.), 3090*w*, 3067*w*, 3007*s*, 2960*s*, 2864*m*, 2175*m*, 1497*w*, 1454*m*, 1359*w*, 1294*w*, 1252*s*, 1085*s*, 1028*s*, 1010*m*, 914*m*, 844*s*, 818*s*, 628*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 4.98 (*d*, $J = 10.4$, PhC*H*); 4.96 (*d*, $J = 10.4$, PhC*H*); 4.82 (*d*, $J = 10.6$, PhC*H*); 4.81 (*d*, $J = 10.6$, PhC*H*); 4.63 (*s*, PhCH_2); 4.05 (*d*, $J = 9.7$, H–C(3)); 3.85 (*dd*, $J = 11.0$, 1.7, H–C(8)); 3.71–3.67 (*m*, CH_2OH); 3.67 (*dd*, $J = 11.0$, 5.5, H–C(8)); 3.57 (*dd*, $J = 10.4$, 8.8, H–C(5)); 3.52 (*ddd*, $J = 10.4$, 5.4, 1.7, H–C(7)); 3.46 (*dd*, $J = 9.7$, 8.8, H–C(4)); 2.78 (*t*, $J = 10.4$, H–C(6)); 1.63 (*s*, OH); 1.58 (*t*, $J = 7.5$, CH_2); 0.964 (*s*, Me); 0.960 (*s*, Me); 0.137 (*s*, MeSi); 0.132 (*s*, MeSi); 0.11 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.33 (*s*); 138.23 (*s*); 138.15 (*s*); 128.37–127.63 (several *d*); 103.81 (*s*, C(1′)); 103.35 (*s*, C(2)); 89.27 (*s*, C(1)); 88.87 (*s*, C(2′)); 83.72 (*d*, C(5)); 81.78 (*d*, C(4)); 79.19 (*d*, C(7)); 75.79 (*t*, PhCH_2); 75.33 (*t*, PhCH_2); 73.66 (*t*, PhCH_2); 70.47 (*d*, C(3)); 70.23 (*t*, C(8)); 59.59 (*t*, CH_2OH); 41.96 (*t*); 38.37 (*d*, C(6)); 23.473 (*q*, Me); 23.467 (*q*, Me); 18.73 (*s*); −0.13 (*q*, Me_3Si); −4.29 (*q*, Me_2Si). FAB-MS: 684 (1.9), 683 (5.5, $[M + 1]^+$), 181 (16), 92 (25), 91 (100), 75 (35), 73 (31). Anal. calc. for $C_{41}H_{54}O_5Si_2$ (683.05): C 72.10, H 7.97; found: C 71.92, H 8.09.

*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-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-octitol* (**68**). As described for **28**, with **67** (435 mg, 0.637 mmol), 3,4-dihydro-2*H*-pyran (122 µl, 1.3 mmol), CH_2Cl_2 (4.6 ml), pyridinium toluene-4-sulfonate (16 mg, 0.0637 mmol; 24 h): **68** (482 mg, 99%). Oil. R_f (hexane/AcOEt 7:3) 0.51. IR ($CHCl_3$): 3090*w*, 3066*w*, 3007*s*, 2947*s*, 2865*s*, 2175*m*, 1497*m*, 1454*s*, 1442*m*, 1385*m*, 1355*s*, 1324*w*, 1294*m*, 1252*s*, 1130*s*, 1074*s*, 1027*s*, 970*s*, 905*m*, 844*s*, 818*s*, 644*w*, 600*w*, 505*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.26 (*m*, 15 arom. H); 5.01–4.94 (*m*, 2 PhC*H*); 4.82 (*d*, $J = 10.6$, PhC*H*); 4.81 (*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)); 3.91–3.81 (*m*, H–C(8), CH_2O of Thp); 3.68 (*dd*, $J = 11.0$, 5.4, H–C(8)); 3.56 (*dd*, $J = 10.3$, 8.9, H–C(5)); 3.54–3.41 (*m*, H–C(7), ThpOCH_2); 3.46 (*t*, $J \approx 9.3$, H–C(4)); 2.77 (*t*, $J = 10.4$, H–C(6)); 1.89–1.47 (*m*, 4 CH_2)); 0.985 (*s*, Me); 0.978 (*s*, Me); 0.138 (*s*, MeSi); 0.130 (*s*, MeSi); 0.11 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.52 (2*s*); 138.33 (*s*); 128.48–127.762 (several *d*); 103.72 (*s*); 103.70 (*s*, C(2)); 103.57 (*s*, C(1′)); 99.12 (*d*, OCHO); 89.36 (*s*, C(1)); 88.91 (*s*, C(2′)); 83.86 (*d*, C(5)); 81.99 (*d*, C(4)); 79.32 (*d*, C(7)); 75.91 (*t*, PhCH_2); 75.55 (*t*, PhCH_2); 73.77 (*t*, PhCH_2); 70.65 (*d*, C(3)); 70.37 (*t*, C(8)); 64.22 (*t*), 64.20 (*t*); 63.51 (*t*); 63.07 (*t*); 62.53 (*t*); 62.51 (*t*); 38.51 (*d*, C(6)); 37.82 (*t*); 37.78 (*t*); 30.93 (*t*); 30.83 (*t*); 25.62 (*t*); 25.59 (*t*); 25.47 (*t*); 23.28 (*q*); 23.09 (*q*); 19.94 (*t*); 19.89 (*t*); 19.83 (*t*); 1982 (*t*); 18.59 (*s*); 0.003 (*q*, Me_3Si); −4.20 (*q*, MeSi); −4.23 (*q*, MeSi). FAB-MS: 765 (1, $[M - 1]^+$), 683 (5), 181 (15), 92 (28), 91 (100), 85 (72), 75 (24), 73 (41), 67 (11), 57 (15). Anal. calc. for $C_{46}H_{62}O_6Si_2$ (767.16): C 72.02, H 8.15; found: C 71.91, H 8.02.

*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-ethynyl-*D*-glycero-*D*-gulo-octitol* (**69**). As described for **30**–**34** with **68** (509 mg, 0.663 mmol) and sat. K_2CO_3/MeOH soln. (10 ml; 4.5 h). After neutralization with aq. NH_4Cl buffer to pH *ca.* 7 and washing with H_2O, the aq. layers were extracted with Et_2O and the combined org. phases processed as usual. FC (hexane/AcOEt 95:5→93:7): **69** (12 h h.v.; 455 mg, 99%). Oil. R_f (benzene/THF 97:3) 0.30. IR ($CHCl_3$): 3307*s*, 3090*w*, 3067*s*, 3007*s*, 2945*s*, 2865*s*, 2180*w*, 1497*m*, 1454*s*, 1355*s*, 1294*m*, 1253*s*, 1132*s*, 1076*s*, 1028*s*, 906*m*, 867*m*, 839*s*, 818*s*, 649*s*, 570*w*, 534*w*, 524*w*, 514*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.25 (*m*, 15 arom. H); 5.00 (*d*, $J = 10.7$, PhC*H*); 4.93 (*d*, $J = 10.7$, PhC*H*); 4.83 (*d*, $J = 10.7$, PhC*H*); 4.79 (*d*, $J = 10.6$, PhC*H*); 4.65 (*d*, $J = 12.3$, PhC*H*); 4.60 (*d*, $J = 12.3$, PhC*H*); 4.55–4.52 (*m*, OCHO); 4.05 (*d*, $J = 9.6$, H–C(3)); 3.89–3.81 (*m*, CH_2O of Thp); 3.84 (*dd*, $J = 11.0$, 1.9, H–C(8)); 3.71 (*dd*, $J = 11.1$, 5.1, H–C(8)); 3.57 (*dd*, $J = 10.3$, 8.9, H–C(5)); 3.54–3.41 (*m*, H–C(7), CH_2O); 3.48 (br. *t*, $J = 9.0$, H–C(4)); 2.78 (*td*, $J = 10.6$, 2.3, H–C(6)); 2.11 (*d*, $J = 2.3$, H–C(2′)); 1.83–1.47 (*m*, 4 CH_2); 0.99 (*s*, Me); 0.98 (*s*, Me); 0.14 (*s*, MeSi); 0.13 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.31 (*s*); 138.14 (*s*); 138.10 (*s*); 128.34–127.57 (several *d*); 103.51 (*s*); 103.49 (*s*, C(2)); 98.99 (*d*, OCHO); 89.36 (*s*, C(1)); 83.44 (*d*, C(5)); 81.93 (*d*, C(4)); 81.33 (*d*, C(2′)); 79.11 (*d*, C(7)); 75.73 (*t*, PhCH); 75.45 (*t*, PhCH_2); 73.57 (*t*, PhCH_2); 72.11 (*s*, C(1′)); 70.52 (*d*, C(3)); 70.04 (*t*, C(8)); 64.09 (*t*); 64.07 (*t*, CH_2O); 62.40 (*t*), 62.37 (*t*, CH_2O); 37.71 (*t*); 37.68 (*t*); 37.08 (*d*, C(6)); 30.80 (*t*); 25.49 (*t*); 23.17 (*q*); 22.97 (*q*); 19.70 (*t*); 19.69 (*t*); 18.47 (*s*); −4.33 (*q*);

MeSi); −4.36 (*q*, MeSi). FAB-MS: 693 (2, $[M-1]^+$), 611 (11), 181 (20), 91 (100, $PhCH_2^+$), 85 (86, $C_5H_9O^+$), 75 (25), 69 (20), 57 (29), 55 (26). Anal. calc. for $C_{43}H_{54}O_6Si$ (694.99): C 74.31, H 7.83; found: C 74.14, H 7.66.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetrahydro-1,2,6-trideoxy-6-*C*-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**70**). As described for **52**, with **67** (563 mg, 0.824 mmol), THF (10 ml), and 1.6M BuLi in hexane (26 µl, 0.041 mmol; 1 h at −90 to 70°, 9.5 h at −20 to 8°). Then treatment at −76° with 1N HCl/EtOH (3 drops). FC (AcOEt/hexane 7:93): **70** (20 h h.v.; 428 mg, 96%). Oil. R_f (hexane/AcOEt 7:3) 0.45. $[\alpha]_D^{25} = -25.2$ (*c* = 1.73, $CHCl_3$). IR ($CHCl_3$): 3307*m*, 3090*w*, 3066*w*, 3007*m*, 2960*m*, 2909*m*, 2869*m*, 2174*w*, 1497*w*, 1454*m*, 1398*w*, 1359*m*, 1295*w*, 1252*s*, 1085*s*, 1028*s*, 911*w*, 846*s*, 645*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.29–7.13 (*m*, 15 arom. H); 4.87 (*d*, *J* = 10.8, PhC*H*); 4.83 (*d*, *J* = 10.8, PhC*H*); 4.72 (*d*, *J* = 10.5, PhC*H*); 4.70 (*d*, *J* = 10.5, PhC*H*); 4.52 (*d*, *J* = 12.5, PhC*H*); 4.49 (*d*, *J* = 12.5, PhC*H*); 3.93 (*dd*, *J* = 9.6, 2.2, H–C(3)); 3.74 (*dd*, *J* = 10.9, 1.8, H–C(8)); 3.57 (*dd*, *J* = 10.9, 5.5, H–C(8)); 3.47 (*dd*, *J* = 10.3, 8.8, H–C(5)); 3.43 (*ddd*, *J* = 10.5, 5.5, 1.8, H–C(7)); 3.37 (*dd*, *J* = 9.8, 8.9, H–C(4)); 2.68 (*t*, J = 10.4, H–C(6)); 2.40 (*d*, *J* = 2.2, H–C(1)); −0.08 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.45 (*s*); 138.27 (*s*); 138.18 (*s*); 128.51–127.75 (several *d*); 103.38 (*s*, C(1′)); 89.08 (*s*, C(2′)); 83.84 (*d*, C(5)); 81.71 (*d*, C(4)); 81.07 (*d*, C(1)); 79.35 (*d*, C(7)); 76.00 (*t*, $PhCH_2$); 75.73 (*t*, $PhCH_2$); 74.39 (*s*, C(2)); 73.81 (*t*, $PhCH_2$); 70.46 (*t*, C(8)); 70.00 (*d*, C(3)); 38.49 (*d*, C(6)); 0.00 (*q*, Me_3Si). FAB-MS: 540 (2), 539 (6, $[M+1]^+$), 538 (3, M^+), 537 (7, $[M-1]^+$), 181 (25), 136 (11), 107 (11), 105 (12), 92 (37), 91 (100), 77 (12), 75 (11), 73 (54). Anal. calc. for $C_{34}H_{38}O_4Si$ (538.76): C 75.80, H 7.11; found: C 75.62, H 6.88.

Iodination of **70**. At 45°, a vigorously stirred soln. of I_2 (743 mg, 2.93 mmol) in benzene (7 ml) was treated dropwise within 5 min with a soln. of morpholine (383 µl, 4.4 mmol) in benzene (0.7 ml) and stirred for 20 min. The resulting deep red suspension was stirred vigorously, treated with a soln. of **70** (263 mg, 0.488 mmol) in benzene (5 ml), stirred at 45° for 11 h, ultrasonicated for 3.5 h, and filtered. The filter cake was washed with Et_2O. The combined filtrate and washings were washed with brine, aq. 10% NaH_2PO_4 soln., aq. 10% $Na_2S_2O_3$ soln., and brine, and processed as usual. FC (hexane/AcOEt 95:5) gave **71** (265 mg, 82%) and **72** (47.8 mg, 11%).

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,1,2,2-tetrahydro-1,2,6-trideoxy-1-iodo-6-*C*-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**71**): Colorless syrup. R_f (benzene) 0.37. IR ($CHCl_3$): 3090*w*, 3067*m*, 3008*s*, 2960*s*, 2909*s*, 2869*s*, 2174*s*, 1951*w*, 1877*w*, 1810*w*, 1606*w*, 1497*s*, 1454*s*, 1397*w*, 1357*s*, 1295*s*, 1251*s*, 1082*s*, 1028*s*, 945*w*, 912*m*, 846*s*, 638*w*, 628*w*, 606*w*, 562*w*, 512*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41–7.26 (*m*, 15 arom. H); 4.97 (*d*, *J* = 10.5, PhC*H*); 4.87 (*d*, *J* = 10.5, PhC*H*); 4.84 (*d*, *J* = 10.5, PhC*H*); 4.80 (*d*, *J* = 10.5, PhC*H*); 4.61 (*s*, $PhCH_2$); 4.15 (*d*, *J* = 9.6, H–C(3)); 3.82 (*dd*, *J* = 10.9, 1.8, H–C(8)); 3.65 (*dd*, *J* = 10.9, 5.5, H–C(8)); 3.56 (*dd*, *J* = 10.3, 8.9, H–C(5)); 3.51 (*ddd*, *J* = 10.5, 5.4, 1.8, H–C(7)); 3.45 (*dd*, *J* = 9.5, 9.0, H–C(4)); 2.77 (*t*, *J* = 10.4, H–C(6)); 0.10 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.43 (*s*); 138.20 (*s*); 138.01 (*s*); 128.60–127.78 (several *d*); 103.30 (*s*, C(1′)); 91.47 (*s*, C(2)); 89.12 (*s*, C(2′)); 83.83 (*d*, C(5)); 81.82 (*d*, C(4)); 79.21 (*d*, C(7)); 76.00 (*t*, $PhCH_2$); 75.83 (*t*, $PhCH_2$); 73.83 (*t*, $PhCH_2$); 71.44 (*d*, C(3)); 70.34 (*t*, C(8)); 38.45 (*d*, C(6)); 4.31 (*s*, C(1)); 0.00 (*q*, Me_3Si). FAB-MS: 1329 (2, $[2M+1]^+$), 666 (5), 665 (13, $[M+1]^+$), 664 (6), 663 (13), 243 (10), 181 (42), 179 (14), 167 (14), 165 (14), 155 (17), 154 (30), 153 (11), 152 (11), 139 (11), 138 (14), 137 (25), 136 (36), 129 (11), 128 (11), 119 (12), 115 (15), 109 (12), 107 (29), 105 (24), 103 (15), 95 (13), 93 (12), 92 (68), 91 (100), 90 (15), 89 (20), 83 (13), 81 (13), 81 (13), 79 (16), 78 (12), 77 (31), 75 (20), 74 (12), 73 (81). Anal. calc. for $C_{34}H_{27}IO_4Si$ (664.65): C 61.44, H 5.61; found: C 61.60, H 5.67.

*3,7-Anhydro-4,5,8-tri-*O*-benzyl-1,2-didehydro-1,2,6-trideoxy-1,1,2-triiodo-6-*C*-[(trimethylsilyl)ethynyl]-*D*-glycero-*D*-gulo-octitol* (**72**): Light yellow syrup, its $CHCl_3$ soln. turned red on standing. R_f (hexane/AcOEt 85:15) 0.38. IR ($CHCl_3$): 3442*w* (br.), 3090*w*, 3066*w*, 3006*w*, 2978*s*, 2933*s*, 2873*s*, 2811*m*, 2174*w*, 1496*w*, 1455*m*, 1384*s*, 1352*s*, 1298*m*, 1261*s*, 1252*s*, 1111*s*, 1043*s*, 1027*s*, 933*w*, 915*w*, 844*s*, 595*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.40–7.28 (*m*, 15 arom. H); 5.03 (*d*, *J* = 10.3, PhC*H*); 4.83 (*d*, *J* = 10.4, PhC*H*); 4.74 (*d*, *J* = 10.8, PhC*H*); 4.71 (br. *d*, *J* ≈ 12.5, PhC*H*); 4.64 (*d*, *J* = 12.4, PhC*H*); 4.63 (*d*, *J* = 10.7, PhC*H*); 3.86–3.77 (*m*, H–C(8), H–C(7)); 3.83 (*dd*, *J* = 10.4, 8.7, H–C(5)); 3.76 (*dd*, *J* = 11.0, 5.2, H–C(8)); 3.69 (*d*, *J* = 9.1, H–C(3)); 3.57 (*t*, *J* = 8.9, H–C(4)); 2.80 (*t*, *J* = 10.4, H–C(6)); 0.12 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 138.45 (*s*); 138.32 (*s*); 138.03 (*s*); 128.46–127.53 (several *d*); 119.87 (*s*, C(2)); 103.46 (*s*, C(1′)); 88.94 (*s*, C(2′)); 85.85 (*d*, C(3)); 83.78 (*d*, C(5)); 81.99 (*d*, C(4)); 78.91 (*d*, C(7)); 75.93 (*t*, $PhCH_2$); 75.34 (*t*, $PhCH_2$); 73.71 (*t*, $PhCH_2$); 70.21 (*t*, C(8)); 38.43 (*d*, C(6)); 29.71 (*s*, C(1)); 1.02 (*q*, Me_3Si). FAB-MS: 919 (2, $[M+1]^+$), 181 (24), 154 (21), 136 (28), 107 (22), 91 (100), 83 (24), 81 (26), 73 (54), 69 (40), 57 (43), 55 (54).

Cross-coupling of **71** *and* **69**. At r.t., a mixture of $[Pd_2(dba)_3]$ (dba = 'dibenzylideneacetone', 1.38 mg, 3.0 µmol), CuI (0.48 mg, 2.5 µmol), and tri(fur-2-yl)phosphine (P(fur)$_3$; 1.39 mg, 6.0 µmol) was treated with a soln. of **71** (83 mg, 0.125 mmol) and **69** (87 mg, 0.125 mmol) in DMSO (2.5 ml; distilled and degassed). The brown soln. was stirred for 5 min, treated with 1,2,2,6,6-pentamethylpiperidine (64 µl, 0.354 mmol), stirred for 3 h, diluted with Et_2O, treated with 0.1N aq. HCl (3 ml), and processed as usual. FC (hexane/AcOEt 92:8→9:1) gave **73** (117 mg, 76%), **74** (13 mg, 10%), and **75** (15.4 mg, 9%).

*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*-[(trimethylsilyl)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* (**73**): Syrup. R_f (benzene/THF 97:3) 0.34. IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*m*, 2946*m*, 2867*m*, 2175*w*, 1497*w*, 1454*m*, 1356*m*, 1294*w*, 1252*m*, 1132*s*, 1076*s*, 1028*s*, 907*w*, 844*s*, 818*m*, 609*w*, 573*w*, 506*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.21 (*m*, 30 arom. H); 4.98 (*d*, *J* = 10.5, PhC*H*); 4.96 (*d*, *J* = 10.3, PhC*H*); 4.87–4.74 (*m*, 7 PhC*H*); 4.63–4.57 (*m*, 3 PhC*H*); 4.54–4.51 (*m*, OCHO); 4.08 (*dd*, *J* = 9.6, 0.5, H–C(5′)); 4.03 (*d*, *J* = 9.6, H–C(3)); 3.87–3.78 (*m*, CH_2O, H–C(8), H–C(10′)); 3.68 (*dd*, *J* = 11.0, 4.8, H–C(8)); 3.66 (*dd*, *J* = 11.0, 5.4, H–C(10′)); 3.59–3.41 (*m*, H–C(4), H–C(6′), H–C(5), H–C(7′), H–C(7), H–C(9′), CH_2O); 2.90 (br. *t*, *J* = 10.3, H–C(6)); 2.78 (*t*, *J* = 10.4, H–C(8′)); 1.82–1.47 (*m*, 8 H); 0.982 (*s*, Me); 0.975 (*s*, Me); 0.134 (*s*, MeSi); 0.126 (*s*, MeSi); 0.10 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.24 (*s*); 138.05 (*s*); 138.02 (*s*); 137.98 (*s*); 137,92 (*s*); 137.77 (*s*); 128.41–127.64 (several *d*); 103.29 (*s*, C(2)); 103.10 (*s*, C(1″)); 99.00 (*d*, acetal C); 89.53 (*s*, C(1)); 89.05 (*s*, C(2″)); 83.66 (*d*, C(7′)); 83.10 (*d*, C(5)); 81.82 (*d*, C(4)); 81.46 (*d*, C(6′)); 79.26 (*d*, C(9′)); 78.81 (*d*, C(7)); 77.84 (*d*, C(4′)); 77.23 (*s*, C(1′)); 75.89 (*t*, PhCH_2); 75.76 (*t*, PhCH_2); 75.63 (*t*, PhCH_2); 75.48 (*t*, PhCH_2); 74.33 (*s*, C(3′)); 73.73 (*t*, PhCH_2); 73.65 (*t*, PhCH_2); 70.55 (*d*); 70.52 (*d*, C(3)); 70.48 (*d*, C(5′)); 70.27 (*t*, C(10′)); 70.09 (*t*, C(8)); 68.05 (*s*, C(2′)); 64.07 (*t*, CH_2O); 62.39 (*t*, CH_2O); 38.32 (*d*, C(8′)); 37.87 (*d*, C(6)); 37.72 (*t*); 37.69 (*t*); 30.81 (*t*); 25.49 (*t*); 23.17 (*q*); 22.98 (*q*); 19.69 (*t*); 18.47 (*s*); −0.14 (*q*, Me_3Si); −4.34 (*q*, MeSi); −4.37 (*q*, MeSi). FAB-MS: 1229 (0.3, $[M-1]^+$), 1147 (0.5, $[M-\text{Thp}+2]^+$), 115 (11), 107 (13), 105 (19), 92 (56), 91 (100), 85 (72), 83 (14), 77 (18), 75 (30), 73 (56), 67 (16), 57 (23), 55 (21). Anal. calc. for $C_{86}H_{106}O_{12}Si_2$ (1387.95): C 75.09, H 7.36; found: C 75.02, H 7.45.

*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*-[(trimethylsilyl)ethynyl]-*D*-glucitol}* (**74**): Syrup. R_f (benzene/THF 97:3) 0.64. $[\alpha]_D^{25} = -74.6$ (*c* = 0.77, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*s*, 2960*s*, 2912*s*, 2870*m*, 2174*m*, 1605*w*, 1497*m*, 1454*s*, 1398*w*, 1356*s*, 1292*m*, 1252*s*, 1078*s*, 1028*s*, 912*w*, 846*s*, 610*w*, 572*w*, 509*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.25 (*m*, 15 arom. H); 4.95 (*d*, *J* = 10.6, PhC*H*); 4.85 (*d*, *J* = 10.5, PhC*H*); 4.81 (*d*, *J* = 10.6, PhC*H*); 4.73 (*d*, *J* = 10.5, PhC*H*); 4.61 (*s*, PhCH_2); 4.09 (*d*, *J* = 9.6, H–C(1′)); 3.38 (*dd*, *J* = 11.0, 1.7, H–C(6′)); 3.65 (*dd*, *J* = 11.1, 5.6, H–C(6′)); 3.56 (*dd*, *J* = 10.4, 8.8, H–C(3′)); 3.51 (*ddd*, *J* = 10.5, 5.5, 1.7, H–C(5′)); 3.44 (br. *t*, *J* = 9.2, H–C(2′)); 2.77 (*t*, *J* = 10.4, H–C(4′)); 0.10 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.25 (*s*); 138.08 (*s*); 137.70 (*s*); 128.44–127.64 (several *d*); 103.10 (*s*, C(1″)); 89.04 (*s*, C(2″)); 83.67 (*d*, C(3′)); 81.40 (*d*, C(2′)); 79.32 (*d*, C(5′)); 76.58 (*s*, C(1)); 75.88 (*t*, PhCH_2); 75.68 (*t*, PhCH_2); 73.74 (*t*, PhCH_2); 70.45 (*d*, C(1′)); 70.23 (*s*, C(2)); 70.10 (*t*, C(6′)); 38.30 (*d*, C(4′)); −0.14 (*q*, Me_3Si). FAB-MS: 1075 (2, $[M+1]^+$), 181 (43), 105 (27), 91 (100), 77 (21), 75 (20), 73 (75). Anal. calc. for $C_{68}H_{74}O_8Si_2$ (1075.50): C 75.94, H 6.94; found: C 76.54, H 7.79.

*6,6′-(Buta-1,3-diyne-1,4-diyl)bis{3,7-anhydro-1,1,2,2-tetrahydro-4,5,8-tri-*O*-benzyl-1,2,6-trideoxy-1-*C*-{[1,1-dimethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propyl]dimethylsilyl}-*D*-glycero-*D*-gulo-octitol}* (**75**): Syrup. R_f (benzene/THF 97:3) 0.26. IR ($CHCl_3$): 3090*w*, 3067*w*, 3007*s*, 2945*s*, 2865*s*, 2179*w*, 1497*m*, 1454*s*, 1356*s*, 1294*m*, 1253*s*, 1132*s*, 1075*s*, 1028*s*, 982*m*, 956*m*, 906*m*, 883*w*, 867*m*, 840*s*, 818*s*, 606*w*, 566*w*, 528*w*, 517*w*, 505*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.35–7.20 (*m*, 15 arom. H); 4.98 (*d*, *J* = 10.6, PhC*H*); 4.85 (*d*, *J* = 10.7, PhC*H*); 4.77 (*d*, *J* = 10.6, 2 PhC*H*); 4.63 (*d*, *J* = 12.2, PhC*H*); 4.57 (*d*, *J* = 12.2, PhC*H*); 4.54–4.52 (*m*, OCHO); 4.03 (*d*, *J* = 9.5, H–C(3′)); 3.87–3.82 (*m*, CH_2O); 3.80 (*dd*, *J* = 11.1, 1.8, H–C(8′)); 3.67 (*dd*, *J* = 11.2, 4.9, H–C(8′)); 3.54 (*dd*, *J* = 10.2, 8.8, H–C(5′)); 3.53–3.42 (*m*, CH_2O, H–C(7′)); 3.47 (br. *t*, *J* = 9.2, H–C(4′)); 2.87 (*t*, *J* = 10.3, H–C(6′)); 1.82–1.77 (*m*, 1 H); 1.71–1.60 (*m*, 3 H); 1.55–1.43 (*m*, 4 H); 0.985 (*s*, Me); 0.979 (*s*, Me); 0.137 (*s*, MeSi); 0.130 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.03 (*s*); 138.01 (br. *s*); 128.35–127.60 (several *d*); 103.31 (*s*, C(1″)); 99.03, 99.00 (*d*, OCHO); 89.54 (*s*, C(2″)); 83.19 (*d*, C(5′)); 81.85 (*d*, C(4′)); 78.88 (*d*, C(7′)); 75.71 (*t*, PhCH_2); 75.50 (*t*, PhCH_2); 75.39 (*s*, C(1)); 73.62 (*t*, PhCH); 70.54 (*d*, C(3′)); 70.11 (*t*, C(8′)); 68.40 (*s*, C(2)); 64.09, 64.07 (*t*, CH_2O); 62.43, 62.40 (*t*, CH_2O); 37.84 (*d*, C(6′)); 37.70 (*t*); 37.67 (*t*); 30.81 (*t*); 25.49 (*t*); 23.16 (*q*); 22.97 (*q*); 19.72 (*s*), 19.70 (*s*); 18.47 (*t*); −4.33 (*q*, MeSi); −4.34 (*q*, MeSi). FAB-MS: 1386 (1, $[M-1]^+$), 1220 (3), 1219 (3), 181 (22), 154 (38), 136 (36), 107 (20), 91 (100), 85 (85), 78 (21), 75 (33), 69 (24), 67 (22), 57 (29), 55 (30). Anal. calc. for $C_{86}H_{106}O_{12}Si_2$ (1387.95): C 74.42, H 7.70; found: C 74.46, H 7.70.

*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*-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* (**76**). As described for **69**, with **73** (30 mg, 0.0216 mmol), sat K_2CO_3/MeOH soln. (1 ml; 6.5 h). FC (hexane/AcOEt 9:1→85:15): **76** (14 h h.v.; 24.5 mg, 98%). Syrup. R_f (benzene/THF 97:3) 0.31. IR ($CHCl_3$): 3307*m*, 3090*w*, 3067*m*, 3008*s*, 2945*s*, 2867*s*, 2259*w*, 2180*w*, 1497*m*, 1454*s*, 1356*s*, 1294*w*, 1261*s*, 1131*s*, 1076*s*, 1028*s*, 907*m*, 867*m*, 818*s*, 650*m*, 607*w*, 569*w*, 524*w*, 515*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.38–7.21 (*m*, 30 arom. H); 4.98 (*d*, *J* = 10.6, PhC*H*); 4.94 (*d*, *J* = 10.6, PhC*H*); 4.87–4.82 (*m*, 3 PhC*H*); 4.77 (*d*, *J* = 10.6, PhC*H*); 4.76 (*d*, *J* = 10.6, PhC*H*); 4.74 (*d*, *J* = 10.7, PhC*H*); 4.63 (*d*, *J* = 11.2, PhC*H*); 4.61 (*d*, *J* = 11.2, PhC*H*); 4.59–4.56 (*m*, 2 PhC*H*); 4.54–4.51 (*m*, OCHO); 4.08 (br. *d*, *J* = 9.6,

H–C(5′)); 4.03 (*d*, *J* = 9.5, H–C(3)); 3.87–3.78 (*m*, CH_2O, H–C(8), H–C(10′)); 3.70 (*dd*, *J* = 10.9, 5.0), 3.68 (*dd*, *J* = 10.9, 4.9, H–C(8), H–C(10′)); 3.60–3.41 (*m*, H–C(4), H–C(6′), H–C(5), H–C(7′), H–C(7), H–C(9′), CH_2O); 2.90 (br. *t*, *J* = 10.3, H–C(6)); 2.79 (*td*, *J* = 10.5, 2.3, H–C(8′)); 2.12 (*d*, *J* = 2.3, H–C(2″)); 1.82–1.75 (*m*, 1 H); 1.71–1.59 (*m*, 3 H); 1.56–1.47 (*m*, 4 H); 0.982 (*s*, Me); 0.975 (*s*, Me); 0.134 (*s*, MeSi); 0.126 (*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.15 (*s*); 138.01 (br. *s*); 137.97 (*s*); 137.92 (*s*); 137.66 (*s*); 128.43–127.63 (several *d*); 103.27 (*s*, C(2)); 99.00 (*d*, OCHO); 89.54 (*s*, C(1)); 83.38 (*d*, C(5)); 83.08 (*d*, C(7′)); 81.83 (*d*, C(4)); 81.55 (*d*, C(6′)); 81.04 (*d*, C(2″)); 79.18 (*d*, C(9′)); 78.79 (*d*, C(7)); 77.91 (*s*, C(4′)); 77.23 (*s*, C(3′)); 75.85 (*t*, PhCH_2); 75.76 (*t*, PhCH_2); 75.66 (*t*, PhCH_2); 75.48 (*t*, PhCH_2); 74.23 (*s*, C(2′)); 73.69 (*t*, PhCH_2); 73.65 (*t*, PhCH_2); 72.30 (*s*, C(1′)); 70.57 (*d*); 70.55 (*d*, C(3), C(5′)); 70.48 (*t*, C(10′)); 70.11 (*t*, C(8)); 68.00 (*s*, C(1″)); 64.07 (*t*, CH_2O); 62.39 (*t*, CH_2O); 37.87 (*d*, C(6)); 37.72 (*t*); 37.69 (*t*); 37.03 (*d*, C(8′)); 30.81 (*t*); 25.49 (*t*); 23.17 (*q*); 22.97 (*q*); 19.69 (*t*); 18.47 (*s*); –4.43 (*q*, MeSi); –4.37 (*q*, MeSi). FAB-MS: 1157 ([*M* – 1]$^+$), 1075 ([*M* – Thp + 2]$^+$), 181 (15), 154 (14), 136 (15), 91 (100), 85 (59), 77 (18), 75 (16). Anal. calc. for $C_{74}H_{82}O_{10}Si$ (1159.54): C 76.65, H 7.13; found: C 76.48, H 7.09.

*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-[(trimethylsilyl)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* (**77**). As described for **48**–**51**, with **73** (68 mg, 0.049 mmol) in MeOH (0.7 ml), CH_2Cl_2 (0.3 ml), and *Amberlyst 15* (H^+ form, *ca.* 20 mg; after 6.5 h, another 40 mg in 0.5 ml of MeOH; after 30 h, another 10 mg in 0.5 ml of MeOH; 60 h). FC (hexane/AcOEt 8:2): **77** (57 mg, 101%). Syrup. R_f (hexane/AcOEt 7:3) 0.24. IR ($CHCl_3$): 3579*w* (br.), 3090*w*, 3067*w*, 3008*m*, 2960*m*, 2909*m*, 2866*m*, 2259*w*, 2175*w*, 1497*w*, 1454*m*, 1398*w*, 1357*m*, 1294*m*, 1261*s*, 1252*s*, 1084*s*, 1028*s*, 915*w*, 844*s*, 818*s*, 606*w*, 568*w*, 532*w*, 520*w*, 510*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39–7.21 (*m*, 30 arom. H); 4.97 (*d*, *J* = 10.7, PhC*H*); 4.96 (*d*, *J* = 10.5, PhC*H*); 4.86 (*d*, *J* = 10.7, PhC*H*); 4.84 (*d*, *J* = 10.6, PhC*H*); 4.81 (*d*, *J* = 10.5, PhC*H*); 4.79 (*d*, *J* = 11.0, PhC*H*); 4.76 (*d*, *J* = 10.8, PhC*H*); 4.75 (*d*, *J* = 10.6, PhC*H*); 4.62 (*d*, *J* ≈ 12.2, PhC*H*); 4.61 (*s*, PhCH_2); 4.56 (*d*, *J* = 12.2, PhC*H*); 4.08 (br. *d*, *J* = 9.6, H–C(5′)); 4.03 (*d*, *J* = 9.6, H–C(3)); 3.83 (*dd*, *J* = 11.0, 1.7, H–C(10′)); 3.81 (*dd*, *J* = 11.1, 1.7, H–C(8)); 3.71–3.65 (*m*, CH_2OH, H–C(8), H–C(10′)); 3.59–3.49 (*m*, H–C(5), H–C(7′), H–C(9′), H–C(7)); 3.46 (*t*, *J* ≈ 9.1, H–C(4)); 3.44 (*t*, *J* ≈ 9.1, H–C(6′)); 2.90 (br. *t*, *J* = 10.4, H–C(6)); 2.78 (*t*, *J* = 10.4, H–C(8′)); 1.58 (*t*, *J* = 7.5, CH_2OH); 0.961 (*s*, Me); 0.957 (*s*, Me); 0.133 (*s*, MeSi); 0.129 (*s*, MeSi); 0.10 (*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.23 (*s*); 138.04 (br. *s*); 137.94 (*s*); 137.86 (*s*); 137.76 (*s*); 128.41–127.65 (several *d*); 103.52 (*s*, C(2)); 103.08 (*s*, C(1″)); 89.55 (*s*, C(1)); 89.05 (*s*, C(2″); 83.65 (*d*, C(7′)); 83.08 (*d*, C(5)); 81.74 (*d*, C(4)); 81.45 (*d*, C(6′)); 79.25 (*d*, C(9′)); 78.80 (*d*, C(7)); 77.74 (*s*, C(4′)); 77.22 (*s*, C(1′)); 75.89 (*t*, PhCH_2); 75.76 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 75.39 (*t*, PhCH_2); 74.39 (*s*, C(3′)); 73.72 (*t*, PhCH_2); 73.67 (*t*, PhCH_2); 70.48 (br. *d*, C(3), C(5′)); 70.26 (*t*); 70.07 (*t*, C(8), C(10′)); 68.10 (*s*, C(2′)); 59.58 (*t*, CH_2OH); 41.98 (*t*); 38.32 (*d*, C(8′)); 37.86 (*d*, C(6)); 23.47 (*q*, Me_2C); 18.74 (*s*); –0.15 (*q*, Me_3Si); –4.31 (*q*, Me_2Si). FAB-MS: 1147 ([*M* – 1]$^+$), 181 (36), 154 (10), 136 (14), 107 (15), 105 (20), 92 (60), 91 (100), 89 (10), 77 (18), 75 (59), 73 (56), 69 (12), 65 (11).

*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-[2-(trimethylsilyl)ethynyl]-*D-glycero-D-gulo-*decitol-1-yl}-4,5,8-tri-O-benzyl-1,1,2,2-tetradehydro-1,2,6-trideoxy-*D-glycero-D-gulo-*octitol* (**78**). As described for **70**, with **77** (34.7 mg, 0.03 mmol), THF (1 ml), and BuLi (*ca.* 0.003 mmol in THF/hexane; 5 h at –90 to 3° and 3 h at 3 to 10°). Then 3 drops of 0.1M HCl/EtOH. FC (hexane/AcOEt 92:8→9:1): **78** (16 h h.v.; 31.6 mg, quant.). Syrup. R_f (hexane/AcOEt 7:3) 0.50. IR ($CHCl_3$): 3307*m*, 3090*w*, 3067*m*, 3008*s*, 2958*m*, 2910*s*, 2870*s*, 2259*w*, 2174*w*, 1951*w*, 1876*w*, 1811*w*, 1606*w*, 1497*m*, 1454*s*, 1397*m*, 1357*s*, 1295*s*, 1252*s*, 1082*s*, 1028*s*, 910*s*, 840*s*, 645*m*, 615*w*, 574*w*, 520*w*. ^{1}H-NMR (500 MHz, $CDCl_3$; C,H-COSY, H,H-COSY): 7.39–7.21 (*m*, 30 arom. H); 4.96 (*d*, *J* = 11.0, PhC*H*); 4.93 (*d*, *J* = 11.0, PhC*H*); 4.88 (*d*, *J* = 10.6, PhC*H*); 4.85 (*d*, *J* = 10.6, PhC*H*); 4.81 (*d*, *J* = 10.5, PhC*H*); 4.79 (*d*, *J* = 10.5, 2 PhC*H*); 4.76 (*d*, *J* = 10.6, PhC*H*); 4.61 (*s*, PhCH_2); 4.59 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.09 (*dd*, *J* = 9.7, 0.6, H–C(5′)); 4.01 (*dd*, *J* = 9.7, 2.1, H–C(3)); 3.83 (*dd*, *J* = 11.0, 1.7, H–C(10′)); 3.79 (*dd*, *J* = 11.0, 1.8, H–C(8)); 3.68 (*dd*, *J* = 11.05, 5.0, H–C(8)); 3.67 (*dd*, *J* = 11.0, 5.5, H–C(10′)); 3.55 (*dd*, *J* = 10.2, 8.9, H–C(5), H–C(7′)); 3.55–3.52 (*m*, H–C(7), H–C(9′)); 3.48 (*dd*, *J* = 9.5, 8.9, H–C(4)); 3.44 (*dd*, *J* = 9.5, 8.9, H–C(6′)); 2.91 (br. *t*, *J* = 10.3, H–C(6)); 2.78 (*t*, *J* = 10.4, H–C(8′)); 2.51 (*d*, *J* = 2.1, H–C(1)); 0.10 (*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$; C,H-COSY, H,H-COSY): 138.21 (*s*); 138.03 (*s*); 137.89 (*s*); 137.84 (*s*); 137.82 (*s*); 137.75 (*s*); 128.41–127.65 (several *d*); 103.07 (*s*, C(1″); 89.06 (*s*, C(2″)); 83.64 (*d*, C(7′)); 83.08 (*d*, C(5)); 81.52 (*d*, C(4)); 81.43 (*d*, C(6′)); 80.67 (*d*, C(1)); 79.24 (*d*, C(9′)); 78.82 (*d*, C(7)); 77.60 (*s*, C(4′)); 75.89 (*t*, PhCH_2); 75.84 (*t*, PhCH_2); 75.64 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 74.41 (*s*), 74.40 (*s*, C(1′), C(2)); 73.714 (*t*, PhCH_2); 73.707 (*t*, PhCH_2); 70.46 (*d*, C(5′)); 70.24 (*t*, C(10′)); 70.19 (*t*, C(8)); 69.89 (*d*, C(3)); 68.13 (*s*, C(2′)); 38.30 (*d*, C(8′)); 37.82 (*d*, C(6)); –0.15 (*q*, Me_3Si). ^{13}C-NMR (125 MHz, C_6D_6): 139.28 (*s*); 138.96 (*s*); 138.95 (*s*); 138.91 (*s*); 138.85 (*s*); 138.83 (*s*); 128.65–127.72 (several *d*); 104.67 (*s*, C(1″)); 88.55 (*s*, C(2″)); 84.00 (*d*), 83.08 (*d*, C(5), C(7′)); 82.13 (*d*), 81.95 (*d*, C(4), C(6′)); 81.52 (*d*, C(1)); 79.55 (*d*); 78.95 (*d*, C(7), C(9′)); 78.80 (*s*, C(4′)); 75.75 (*t*, PhCH_2); 75.64 (*t*, PhCH_2); 75.62 (*t*, PhCH_2); 75.59 (*t*, PhCH_2);

75.54 (*s*), 74.19 (*s*, C(2), C(1′)); 73.91 (*t*, PhCH_2); 73.78 (*t*, PhCH_2); 70.87 (*d*); 70.20 (*d*, C(3), C(5′)); 70.82 (*t*), 68.44 (*t*, C(8), C(10′)); 70.73 (*s*), 70.52 (*s*, C(2′), C(3′)); 38.66 (*d*, C(8′)); 38.12 (*d*, C(6)); 0.00 (*q*, Me_3Si). FAB-MS: 1003 (0.5, $[M-1]^+$), 181 (20), 136 (12), 91 (100). Anal. calc. for $C_{65}H_{66}O_8Si$ (1003.32): C 77.81, H 6.63; found: C 77.95, H 6.84.

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