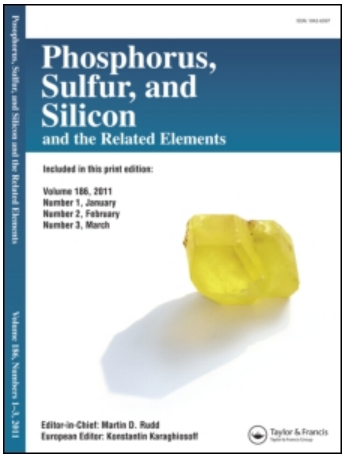

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Formation of Chiral β-Silyl-Vinyl Ethers

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FORMATION OF CHIRAL β-SILYL-VINYL ETHERS

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Chiral formates derived from propane-1,2-diol, 1,2-O-isopropylidene-α-D-xylo- and α-D-gluco-furanoses were subjected to treatment with cyclopentadienyl [tris(trimethylsilylmethyl)] titanium (IV). A mixture of the corresponding (E)- and (Z)-β-silylvinyl ethers were obtained with predominance of the former. It was found that in contrast to (Z)-vinyl ethers, which give β-lactams with chlorosulfonyl isocyanate, the (E)-vinyl ethers gave unstable cycloadducts which undergo rapid elimination reaction leading to (E)-α,β-unsaturated amides.

Keywords: [2+2]cycloaddition; β-lactams; vinyl silanes

INTRODUCTION

Introduction of a silyl substituent to the vinyl ether group should open an access to a variety of silylated cyclic compounds via cycloaddition reactions. A few years ago, we reported that asymmetric [2 + 2]cycloaddition of chlorosulfonyl isocyanate to (*Z*) 1,2-*O*-isopropylidene-3-*O*-(2′-silylvinyl)-5-*O*-trityl-α-D-xylofuranoses proceeded in a high yield and with excellent stereoselectivity to give exclusively the corresponding *cis*-azetidin-2-ones with (*R*)-configuration at the C-4 carbon atom.[1] Although 3-silylated azetidin-2-ones display tendency to facile desilylation under basic conditions, and therefore their use for the β-lactam synthesis is limited, *C*-silyl vinyl ethers could be attractive substrates for organic synthesis.[1,2]

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(*Z*) Silyl vinyl ethers can be obtained by a sequence of reactions involving formation of alkoxyacetylene, introduction of a silyl substituent to the terminal carbon atom, and hydrogenation of the triple bond over Lindlar's catalyst.[3] Attempts to obtain (*E*)-configuration of the double bond via reduction using complex hydrides or sodium in liquid ammonia failed.[1,3] The only successful attempt to synthesize the (*E*) β-silyl vinyl ether has been reported by Denmark and Thorarensen.[3] The authors used addition of lithiodimethylphenylsilane to the triple bond of alkoxyacetylene in the presence of cyanocuprate.

RESULTS AND DISCUSSION

The search for facile and effective preparation of chiral (*E*) β-silyl-vinyl ethers prompted us to investigate the cyclopentadienyl [tris(trimethylsilylmethyl)] titanium (IV) (**1**), Petasis' reagent,[4] for the conversion of carbonyls to alkenyl silanes. We selected as substrates formate **3** derived from compound **2**, 3-*O*- and 5-*O*-formates **6**, **7**, **13–17** obtained from corresponding 1,2-*O*-isopropylidene-α-D-xylo- **4**,[5] **5**[6] and α-D-glucofuranoses **8**,[7] **9**,[8] **10**,[9] **11**,[8] and **12**,[10] respectively. It should be noted that so far a variety of aliphatic and aromatic aldehydes and ketones, lactones and methyl benzoate have been used as substrates for Petasis' reagent,[4] however, to the best of our knowledge, reactions of formates have not been reported yet.

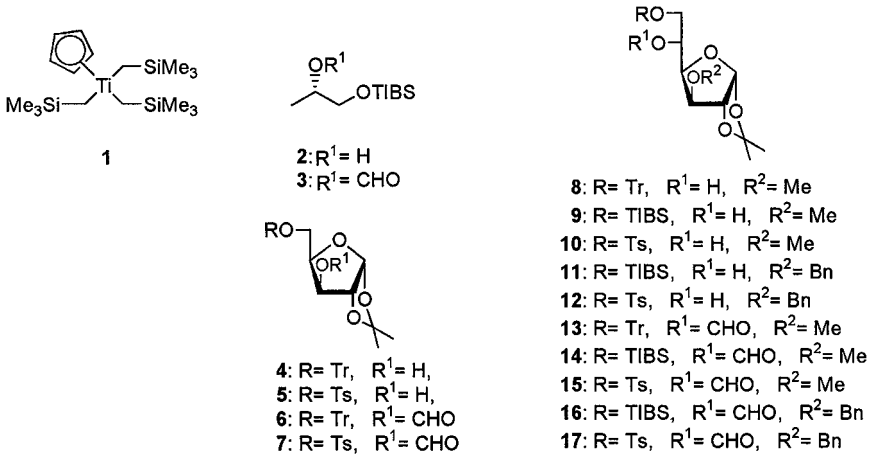
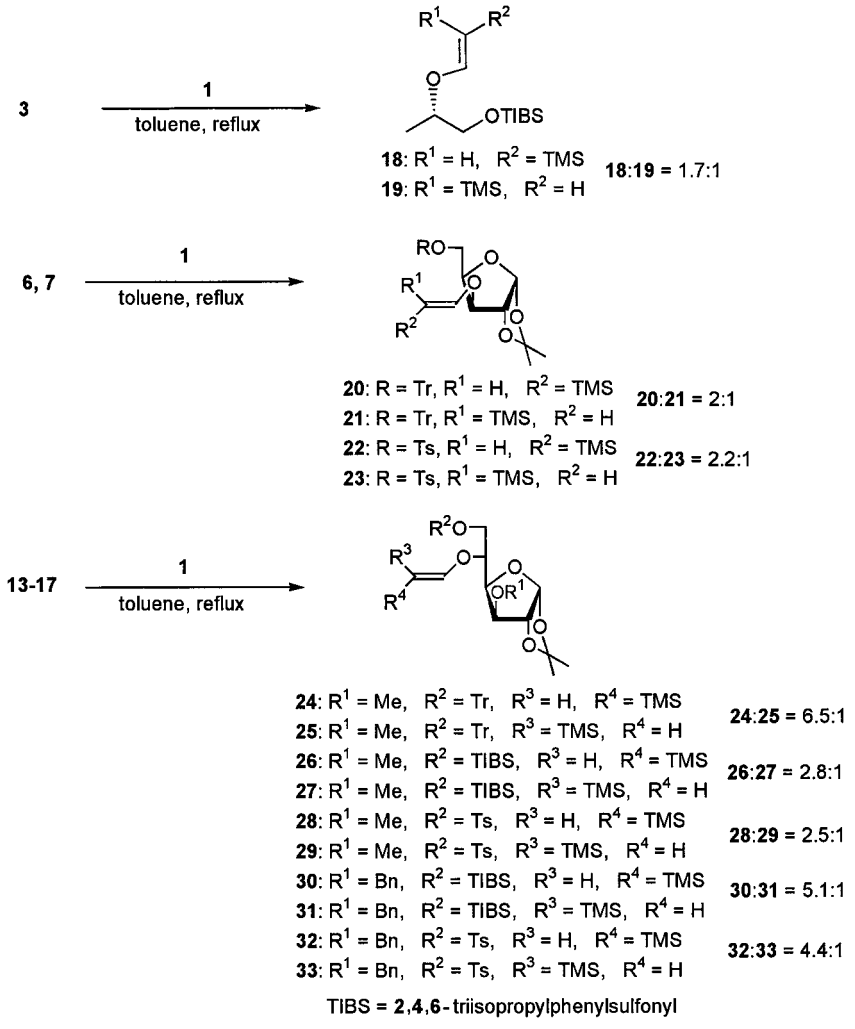


CHART 1

Reactions of formates **3**, **6**, **7**, **13–17** with easy to handle Petasis' reagent **1**[4] were performed under standard conditions. In all cases unseparable mixtures of (*E*) and (*Z*) β-silyl-vinyl ethers **18/19**, **20/21**, **22/23**, **24/25**, **26/27**, **28/29**, **30/31**, and **32/33** were obtained in good yield. The observed values of ratio of geometric isomers produced in these reactions are shown in Scheme 1. In the case of 5-*O*-substituted compounds, one can rationalize results as a function of the size of substituents at O-3 and O-5 oxygen atoms. Bulky substituents at both



SCHEME 1

oxygen atoms promote formation of (*E*)-stereoisomers; compare Tr, TIBS and Ts at O-6, and Bn *versus* Me at O-3 atom (Scheme 1). This phenomenon can be explained in terms of smaller steric requirements of (*E*)-olefins versus respective (*Z*)-isomers.

Reactivity of (*E*) β-silyl-vinyl ethers in comparison to the corresponding (*Z*)-isomers was investigated using [2+2]cycloaddition reaction with chlorosulfonyl isocyanate (CSI). In contrast to (*Z*) olefins, which react readily to provide the corresponding β-lactams,[1] (*E*)-olefins either do not form any β-lactam or it is obtained only in minute amounts. *Trans* substituted cycloadduct, which is probably formed from (*E*)-olefin and CSI, undergoes rapid opening of the four-membered ring to yield (*E*) α,β-unsaturated amide which subsequently is subjected to hydrogenation by Red-Al or to further decomposition. The presence of *trans* α,β-unsaturated amides was detected in substantial amounts in a crude postreaction mixtures by NMR spectra. It should be pointed out, however, that we did not notice any signals corresponding to the respective *cis*-isomer. For example, the mixture **20/21** in reaction with CSI gave *cis*-cycloadducts **34** in 15% yield accompanied by traces of *trans*-compound **35** which was isolated by HPLC and fully characterized. Examination of the crude postreaction mixture by ^{1}H NMR revealed the presence of two doublets at 7.62 and 5.36 with $J = 11.8$ Hz which were assigned to the α,β-unsaturated amide **36**. Similarly, in the case of the mixture

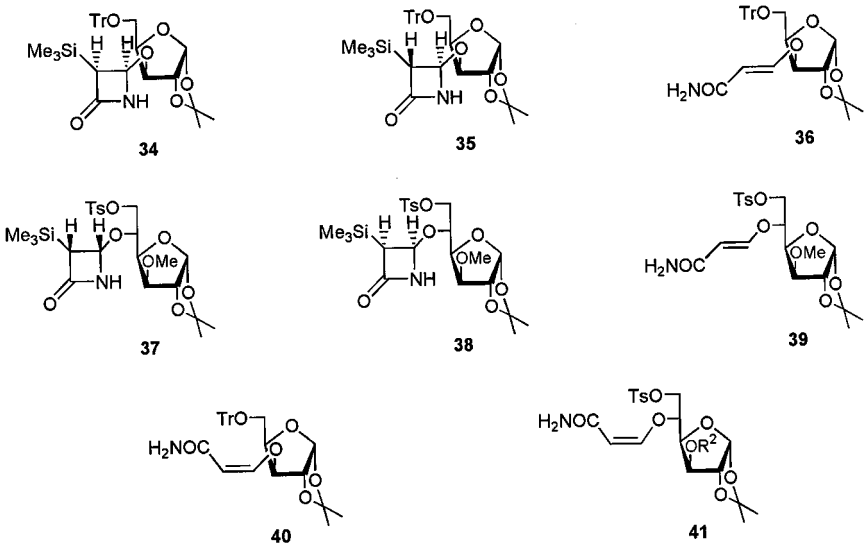
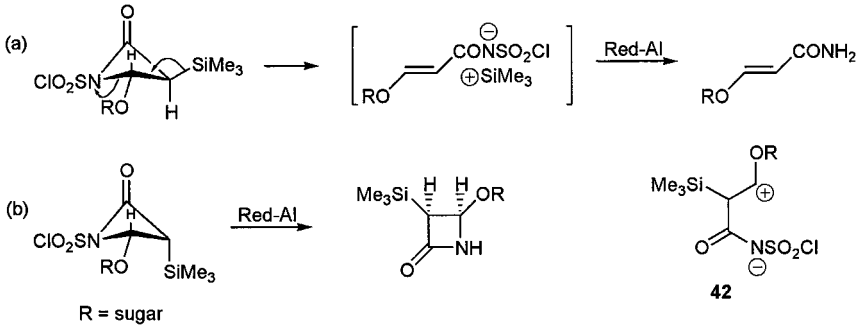


CHART 2

28/29 examination of the postreaction mixture showed the presence of two *cis*-azetidin-2-ones **37** [δ: 5.41 (d, 1H, $J = 4.4$ Hz, H-4′)] and **38** [δ: 5.18 (d, 1H, $J = 4.4$ Hz, H-4′)] and the unsaturated amide **39** [δ: 7.80 and 5.31 (2d, 2H, $J = 11.9$ Hz, H-1′ and H-2′)] in a ratio of about 1:0.16:1.5 respectively. We did not notice any signal that could be assigned to the *trans*-substituted β-lactam. In neither case did we find any signal that could be assigned to the (*Z*) α,β-unsaturated amide **40** and **41**.

It is not clear why only the *trans* 3,4-substituted cycloadducts undergo elimination reaction. The mechanism for the ring opening and elimination of the silyl substituent in the *trans* substituted cycloadducts follows probably the Peterson-like reaction shown in Scheme 2. This can be explained in terms of a bend conformation of the four-membered β-lactam ring, which in the case of *trans*-cycloadduct adopts a geometry suitable for the elimination (Scheme 2a). Heterolytic cleavage of the C—N bond is accelerated by the stabilization of the negative charge at the nitrogen atom by carbonyl and sulfonyl groups. Corresponding *cis*-cycloadduct does not adjust to such arrangement (Scheme 2b). It indicates that the alkoxy substituent prefers a quasi-equatorial position, otherwise both *cis*- and *trans*-adducts should undergo the same elimination leading to the (*Z*)- and (*E*)-olefin respectively. Any other explanation of the reported phenomenon, based on the two-step mechanism of cycloaddition involving formation of the zwitterions **42** does not explain the different reactivity of (*Z*)- and (*E*)-alkoxyvinylsilanes.



SCHEME 2

(*Z*)-Vinylsilanes have been reported to react more rapidly than respective (*E*)-isomers.[11] Stereospecificity of reaction of (*Z*)- and (*E*)-vinylsilanes have also been reported,[12] we did not notice, however, any information concerning the different reactivity of (*Z*)- and (*E*)-isomers with electrophiles.[12a]

CONCLUSION

It was demonstrated that sugar formates readily react with Petasis' reagent to provide mixtures of the corresponding (*E*)- and (*Z*)-alkoxyvinylsilanes with predominance of the former isomer. The ratio of geometric isomers depends on the size of neighboring substituents. More bulky substituents promote larger content of (*E*)-isomers. It was shown that in contrast to the (*Z*)-isomers (which with CSI produce cis β-lactams[1]), the (*E*)-isomers yield unstable adducts which undergo rapid opening of the four-membered ring with elimination of the silyl substituent to give (*E*)-α,β-unsaturated alkoxyamides.

Experimental

M.p.'s were determined on a Kofler hot-stage apparatus with a microscope and are uncorrected. ^{1}H NMR spectra were obtained on Bruker Avance 500 and Varian Gemini AC-200 spectrometers for solution in $CDCl_3$ with tetramethylsilane as an internal standard and are expressed as δ values. Signals for aromatic protons (phenyls) were not characteristic and therefore were not included in the reported spectral data. IR spectra were recorded on a Perkin Elmer FT-IR Spectrum 2000 spectrophotometer. Mass spectra were determined with an AMD 604 Inectra GmbH spectrometer and HPLC-MS system with Mariner and API 356 detectors. Optical rotation were measured using a JASCO P 3010 polarimeter at ambient temperature. The progress of all reactions was checked using thin-layer chromatography (TLC) on Merck silica gel 60-F_{254} plates. Column flash chromatography was performed with Merck silica gel 60 (230–400 mesh). Cyclopentadienyl [tris(trimethylsilylmethyl)] titanium(IV) (**1**), the Petasis' reagent, was obtained according to literature procedure.[4] Compounds **2**, **4**,[5] **5**,[6] **8**,[7] **9**,[8] **10**,[9] **11**,[8] and **12**[10] were synthesized according to the previously reported procedures.

(2S)-1-O-(2,4,6-Triisopropylbenzenesulfonyl)-propane-1,2-diol (2)

Compound **2** was obtained from methyl (*S*)-lactate using a four-step procedure involving formation of acetal, reduction of the methoxycarbonyl function,[13] protection of the primary hydroxymethyl group with 2,4,6-triisopropylbenzenesulfonyl chloride and deprotection of the secondary hydroxy group. M.p. 66–68°C. $[\alpha]_D^{22}$ +5.8 (C 1, CH_2Cl_2). IR: 3600 cm^{-1} (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (d, 3H, $J = 6.5$ Hz, —CH_3), 1.27 (m, 18H, 3 × —CH$\underline{Me}_2$), 2.10 (br s, 1H, —OH),

2.91 (sept., 1H, $J = 6.9$ Hz, *p*-C<u>H</u>Me$_2$), 3.91 (dd, 1H, $J = 7.4$ Hz, $J = 10.2$ Hz, H-1a), 4.03 (dd, 1H, $J = 3.2$ Hz, $J = 10.2$ Hz, H-1b), 4.07–4.16 (m, 3H, H-2, 2 × *o*-C<u>H</u>Me$_2$), 7.19 (s, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.67, 23.51, 24.70, 29.67, 34.26, 65.87, 73.87, 123.85, 129.15, 150.87, 153.94. MS (LSIMS, HR) m/z: $[M + H]^+$ calcd for $C_{18}H_{31}O_4S$: 343.19431. Found: 343.19502.

Anal. Calcd for $C_{18}H_{30}O_4S$ (342.51): C, 63.12; H, 8.83. Found: C, 62.92; H, 8.73.

(2S)-2-O-Formyl-1-O-(2,4,6-triisopropylbenzenesulfonyl)-propane-1,2-diol (3). General Procedure

Compound **2** (1.2 g, 3.5 mmol) was dissolved in dry pyridine (7 mL), the solution was cooled to 0°C and a 1:1 mixture of Ac_2O—HCO_2H (FAM)[14] (7 mL) was added dropwise during 5 min. Stirring was continued for ~3 h (TLC monitoring) while warming up to room temperature. Subsequently, the mixture was poured into a cold saturated aqueous NaCl solution and extracted with toluene (3 × 30 mL). The extract was washed with water, dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate 8.5:1.5 $^v/_v$ as an eluent to give **3** (1.2 g, 92%). M.p. 85–86°C. $[\alpha]_D^{22}$ −17.7 (C 1, CH_2Cl_2). IR: 1727 cm^{-1} (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): 1.26 (d, 18H, $J = 6.9$ Hz, 3 × —CH<u>Me</u>$_2$), 1.33 (d, 3H, $J = 6.5$ Hz, —CH_3), 2.90 (sept., 1H, $J = 6.9$ Hz, *p*-C<u>H</u>Me$_2$), 4.08–4.15 (m, 4H, H-1a, H-1b, 2 × *o*-C<u>H</u>Me$_2$), 5.20–5.27 (m, 1H, H-2), 7.92 (s, 1H, —CHO). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{19}H_{30}O_5SNa$: 393.17117. Found: 393.17140.

Anal. Calcd for $C_{19}H_{30}O_5S$ (370.52): C, 61.64; H, 8.16. Found: C, 61.65; H, 7.98.

3-O-Formyl-1,2-O-isopropylidene-5-O-trityl-α-D-xylofuranose (6)

Compound **6** was obtained from **4** according to the procedure described above (74%). Solid foam. $[\alpha]_D^{22}$ −41.3 (C 1, CH_2Cl_2). IR: 1731 cm^{-1} (film). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.30, 1.54 (2s, 6H, 2 × CH_3), 3.20 (dd, 1H, $J = 9.2$ Hz, $J = 7.4$ Hz, H-5a), 3.46 (dd, 1H, $J = 9.2$ Hz, $J = 5.5$ Hz, H-5b), 4.41–4.50 (m, 1H, H-4), 4.43 (d, 1H, $J = 3.8$ Hz, H-2), 5.40 (d, 1H, $J = 3.0$ Hz, H-3), 5.86 (d, 1H, $J = 3.8$ Hz, H-1), 7.77 (s, 1H, —CHO). MS (EI, HR) m/z: M^+ calcd for $C_{28}H_{28}O_6$: 460.18860. Found: 460.18887.

Anal. Calcd for $C_{28}H_{28}O_6$ (460.54): C, 73.03; H, 6.13. Found: C, 72.93; H, 6.09.

3-O-Formyl-1,2-O-isopropylidene-5-O-tosyl-α-D-xylofuranose (7)

Compound **7** was obtained from **5** according to the procedure described above (77%). Oil. $[\alpha]_D^{22}$ −12.4 (C 1.6, CH_2Cl_2). IR: 1731 cm^{-1} (film). ^1H NMR (400 MHz, $CDCl_3$): δ 1.30, 1.48 (2s, 6H, 2 × CH_3), 2.46 (s, 3H, tosyl), 4.19 (d, 2H, $J = 6.4$ Hz, H-5a, H-5b), 4.45–4.50 (m, 1H, H-4), 4.50 (d, 1H, $J = 3.7$ Hz, H-2), 5.30 (d, 1H, $J = 2.9$ Hz, H-3), 5.87 (d, 1H, $J = 3.7$ Hz, H-1), 7.92 (m, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.65, 26.19, 26.61, 65.67, 75.23, 75.84, 82.99, 104.83, 112.71, 128.05, 129.93, 132.44, 145.18, 159.12. MS (EI, HR) m/z: $[M\text{-}CH_3]^+$ calcd for $C_{15}H_{17}O_8S$: 357.06441. Found: 357.06498.

Anal. Calcd for $C_{16}H_{20}O_8S$ (372.4): C, 52.31; H, 5.85. Found: C, 52.15; H, 5.83.

5-O-Formyl-1,2-O-isopropylidene-3-O-methyl-6-O-trityl-α-D-glucofuranose (13)

Compound **13** was obtained from **8** according to the procedure described above (77%). White solid. M.p. 127–129°C. $[\alpha]_D^{22}$ −35.4 (C 0.57, CH_2Cl_2). IR: 1730 cm^{-1} ($CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.31, 1.49 (2s, 6H, 2 × CH_3), 3.33 (s, 3H, —OMe), 3.39 (dd, 1H, $J = 10.6$ Hz, $J = 6.2$ Hz, H-6a), 3.47 (dd, 1H, $J = 10.6$ Hz, $J = 2.2$ Hz, H-6b), 3.72 (d, 1H, $J = 3.2$ Hz, H-3), 4.45 (dd, 1H, $J = 8.9$ Hz, $J = 3.2$ Hz, H-4), 4.54 (d, 1H, $J = 3.7$ Hz, H-2), 5.23–5.28 (m, 1H, H-5), 5.83 (d, 1H, $J = 3.7$ Hz, H-1), 8.09 (s, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.28, 26.77, 57.74, 63.04, 70.82, 77.62, 81.13, 83.42, 86.68, 105.33, 111.90, 126.98, 127.77, 128.72, 143.77, 160.77. MS (EI, HR) m/z: M^+ calcd for $C_{30}H_{32}O_7$: 504.21480. Found: 504.21795.

Anal. Calcd for $C_{30}H_{32}O_7$ (504.59): C, 71.41; H, 6.39. Found: C, 71.36; H, 6.54.

5-O-Formyl-1,2-O-isopropylidene-3-O-methyl-6-O-(2,4,6-triisopropylbenzenesulfonyl)-α-D-glucofuranose (14)

Compound **14** was obtained from **9** according to the procedure described for compound **3** (88%). White solid. M.p. 77–79°C. $[\alpha]_D^{22}$ −17.2 (C 0.8, CH_2Cl_2). IR: 1733 cm^{-1} (CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, 18H, $J = 6.9$ Hz, 3 × $CH\underline{Me}_2$), 1.30, 1.45 (2s, 6H, 2 × CH_3), 2.90 (sept., 1H, $J = 6.9$ Hz, *p*-$C\underline{H}Me_2$), 3.33 (s, 3H, OMe), 3.74 (d, 1H, $J = 3.3$ Hz, H-3), 4.05–4.15 (m, 2H, *o*-$C\underline{H}Me_2$), 4.26 (dd, 1H, $J = 11.4$ Hz, $J = 6.2$ Hz, H-6a), 4.33 (dd, 1H, $J = 7.3$ Hz, $J = 3.3$ Hz, H-4), 4.48 (dd, 1H, $J = 11.4$ Hz, $J = 2.1$ Hz, H-6b), 4.54 (d, 1H, $J = 3.7$ Hz, H-2), 5.35 (m, 1H, H-5), 5.83 (d, 1H, $J = 3.7$ Hz, H-1), 7.98 (s, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.51, 24.71, 26.22, 26.80, 29.62, 34.24, 57.83,

67.75, 68.79, 77.99, 81.08, 83.41, 105.30, 112.18, 123.74, 129.45, 150.86, 153.72, 159.54. MS (EI, HR) m/z: M^+ calcd for $C_{26}H_{40}O_9S$: 528.23931. Found: 528.23657.

Anal. Calcd for $C_{26}H_{40}O_9S$ (528.68): C, 59.07; H, 7.63. Found: C, 59.32; H, 7.92.

5-O-Formyl-1,2-O-isopropylidene-3-O-methyl-6-O-tosyl-α-D-glucofuranose (15)

Compound **15** was obtained from **10** according to the procedure described for compound **3** (84%). Oil. $[\alpha]_D^{22}$ −21.1 (C 1.17, CH_2Cl_2). IR: 1732 cm^{-1} (film). ^1H NMR (200 MHz, $CDCl_3$): δ 1.31, 1.47 (2s, 6H, 2 × CH_3), 2.45 (s, 3H, tosyl), 3.34 (s, 3H, —OMe), 3.72 (d, 1H, $J = 3.4$ Hz, H-3), 4.21 (ddd, 1H, $J = 11.3$ Hz, $J = 5.7$ Hz, $J = 0.6$ Hz, H-6a), 4.31 (dd, 1H, $J = 7.7$ Hz, $J = 3.4$ Hz, H-4), 4.44 (dd, 1H, $J = 11.3$ Hz, $J = 2.2$ Hz, H-6b), 4.54 (d, 1H, $J = 3.6$ Hz, H-2), 5.29 (dddd, $J = 7.7$ Hz, $J = 5.7$ Hz, $J = 2.2$ Hz, $J = 0.6$ Hz, 1H, H-5), 5.81 (d, 1H, $J = 3.6$ Hz, H-1), 7.95 (s, 1H, —CHO). MS (LSIMS, HR) m/z: $[M + H]^+$ calcd for $C_{18}H_{25}O_9S$: 417.12193. Found: 417.11920.

Anal. Calcd for $C_{18}H_{24}O_9S$ (416.46): C, 51.91; H, 5.80. Found: C, 52.11; H, 6.02.

3-O-Benzyl-5-O-formyl-1,2-O-isopropylidene-6-O-(2,4,6-triisopropylbenzenesulfonyl)-α-D-glucofuranose (16)

Compound **16** was obtained from **9** according to the procedure described for compound **3** (93%). Oil. $[\alpha]_D^{22}$ −37.7 (C 1.35, CH_2Cl_2). IR: 1732 cm^{-1} (film). ^1H NMR (500 MHz, $CDCl_3$): δ 1.24 (m, 18H, 3 × CH$\underline{Me}_2$), 1.30, 1.45 (2s, 6H, 2 × CH_3), 2.89 (sept, 1H, $J = 6.9$ Hz, *p*-C$\underline{H}$Me$_2$), 3.98 (d, 1H, $J = 3.3$ Hz, H-3), 4.11 (m, 2H, *o*-C$\underline{H}$Me$_2$), 4.27 (dd, 1H, $J = 11.4$ Hz, $J = 5.4$ Hz, H-6a), 4.36 (dd, 1H, $J = 7.9$ Hz, $J = 3.3$ Hz, H-4), 4.45, 4.60 (2d, 2H, $J = 11.6$ Hz, benzyl), 4.53 (dd, 1H, $J = 11.4$ Hz, $J = 2.2$ Hz, H-6b), 4.57 (d, 1H, $J = 3.7$ Hz, H-2), 5.35 (m, 1H, H-5), 5.86 (d, 1H, $J = 3.7$ Hz, H-1), 7.78 (s, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.51, 24.71, 24.72, 26.27, 26.81, 29.62, 34.23, 67.49, 68.56, 72.15, 77.60, 80.72, 81.68, 105.28, 112.23, 123.73, 128.21, 128.23, 128.56, 129.53, 136.64, 150.82, 153.70, 159.47. MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{32}H_{44}O_9SNa$: 627.26037. Found: 627.26059.

3-O-Benzyl-5-O-formyl-1,2-O-isopropylidene-6-O-tosyl-α-D-glucofuranose (17)

Compound **17** was obtained from **12** according to the general procedure described earlier (94%). Colorless crystals. M.p. 98–100°C. $[\alpha]_D^{22}$ −36.8 (C 0.47, CH_2Cl_2). IR: 1732 cm^{-1} (film). ^1H NMR (200 MHz,

$CDCl_3$): δ 1.31, 1.47 (2s, 6H, 2 × CH_3), 2.43 (s, 3H, tosyl), 3.96 (d, 1H, $J = 3.3$ Hz, H-3), 4.21 (dd, 1H, $J = 11.4$ Hz, $J = 5.2$ Hz, H-6a), 4.33 (dd, 1H, $J = 8.0$ Hz, $J = 3.3$ Hz, H-4), 4.42, 4.59 (2d, 2H, $J = 11.6$ Hz, benzyl), 4.46 (dd, 1H, $J = 11.4$ Hz, $J = 2.2$ Hz, H-6b), 4.57 (d, 1H, $J = 3.7$ Hz, H-2), 5.30–5.32 (m, 1H, H-5), 5.83 (d, 1H, $J = 3.7$ Hz, H-1), 7.95 (s, 1H, —CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.61, 26.28, 26.85, 68.21, 68.41, 72.14, 77.34, 80.63, 81.66, 105.23, 112.28, 128.01, 128.21, 128.26, 128.57, 129.80, 132.80, 136.61, 144.82, 159.41. MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{24}H_{28}O_9SNa$: 515.13517. Found: 515.13575.

(E) and (Z) (2S)-2-O-(2′-Trimethylsilyl-vinyl)-1-O-(2,4,6-triisopropylbenzenesulfonyl)propane-1,2-diol (18/19)

General procedure. A solution of formate **3** (0.6 g, 1.6 mmol) and titanium complex **1** (0.72 g, 1.9 mmol) in toluene (10 mL) was stirred under reflux (110°C). After 3 h (TLC), the solvent was removed and the residue was purified by column chromatography on silica gel using hexane-ethyl acetate (97:3, v/v) as an eluent to give a mixture of compounds **18** and **19**, in a ratio ca. 1.7:1 (0.3 g, 42%) as an oil. IR: 1605 cm^{-1} (CH_2Cl_2). Compound **18**: ^{1}H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 4.55 (d, 1H, $J = 14.8$ Hz, =CH—), 6.16 (d, 1H, $J = 14.8$ Hz, —OCH=). Compound **19**: ^{1}H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 4.23 (d, 1H, $J = 8.3$ Hz, =CHSi—), 6.52 (d, 1H, $J = 8.3$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + H]^+$ calcd for $C_{23}H_{41}O_4SiS$: 441.24949. Found: 441.25094.

Anal. Calcd for $C_{23}H_{41}O_4SiS$ (440.73): C, 62.68; H, 9.15. Found: C, 62.84; H, 9.26.

(E) and (Z) 1,2-O-Isopropylidene-3-O-(2′-trimethylsilyl-vinyl)-5-O-trityl-α-D-xylofuranose (20/21)

General procedure. A mixture of compounds **20/21**, in a ratio of ca. 2:1, was obtained from **6** according to the procedure described above (68%). IR: 1591, 1611 cm^{-1} (film). Compound **20**: ^{1}H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.32, 1.53 (2s, 6H, 2 × CH_3), 3.33 (dd, 1H, $J = 9.2$ Hz, $J = 7.1$ Hz, H-5a), 3.43 (dd, 1H, $J = 9.2$ Hz, $J = 5.7$ Hz, H-5b), 4.52 (d, 1H, $J = 3.8$ Hz, H-2), 4.66 (d, 1H, $J = 15$ Hz, =CH—), 5.84 (d, 1H, $J = 3.8$ Hz, H-1), 6.21 (d, 1H, $J = 15$ Hz, —OCH=). Compound **21**: ^{1}H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 3.27 (dd, 1H, $J = 9.6$ Hz, $J = 6.8$ Hz, H-5a), 3.47 (dd, 1H, $J = 9.6$ Hz, $J = 6.0$ Hz, H-5b), 4.24 (d, 1H, $J = 8.1$ Hz, =CHSi—), 4.49 (d, 1H, $J = 3.8$ Hz, H-2), 5.88 (d, 1H, $J = 3.8$ Hz, H-1), 6.52 (d, 1H, $J = 8.1$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{32}H_{38}O_5SiNa$: 553.2386. Found: 553.2403.

Anal. Calcd for $C_{32}H_{38}O_5Si$ (530.75): C, 72.42; H, 7.22. Found: C, 72.21; H, 7.34.

(E) and (Z) 1,2-O-Isopropylidene-3-O-(2′-trimethylsilyl-vinyl)-5-O-tosyl-α-D-xylofuranose (22/23)

A mixture of compounds **22/23**, in a ratio of ca. 2.2:1, was obtained from **7** according to the procedure described earlier (60%). IR: 1592, 1611 cm^{-1} (CH_2Cl_2). Compound **22**: ^1H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.32, 1.51 (2s, 6H, 2 × CH_3), 4.53 (d, 1H, $J = 3.7$ Hz, H-2), 4.68 (d, 1H, $J = 15.1$ Hz, =CH—), 5.87 (d, 1H, $J = 3.7$ Hz, H-1), 6.18 (d, 1H, $J = 15.1$ Hz, —OCH=). Compound **23**: ^1H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.49 (2s, 2H, 2 × CH_3), 4.37 (d, 1H, $J = 8.1$ Hz, =CHSi—), 4.50 (d, 1H, $J = 3.6$ Hz, H-2), 5.86 (d, 1H, $J =$ 3.6 Hz, H-1), 6.48 (d, 1H, $J = 8.2$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{20}H_{30}O_7SiSNa$: 465.13792. Found: 465.13829.

Anal. Calcd for $C_{20}H_{30}O_7SiS$ (442.62): C, 54.27; H, 6.83. Found: C, 54.24; H, 6.93.

(E) and (Z) 1,2-O-Isopropylidene-3-O-methyl-5-O-(2′-trimethylsilyl-vinyl)-6-O-trityl-α-D-glucofuranose (24/25)

A mixture of compounds **24/25**, in a ratio of ca. 6.5:1, was obtained from **13** according to the procedure described for compounds **18/19** (84%). IR 1613 cm^{-1} (film). Compound **24**: ^1H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.29, 1.44 (2s, 6H, 2 × CH_3), 3.37 (s, 3H, —OMe), 3.74 (d, 1H, $J = 2.8$ Hz, H-3), 4.51 (d, 1H, $J = 3.8$ Hz, H-2), 4.69 (d, 1H, $J = 14.5$ Hz, =CH—), 5.79 (d, 1H, $J = 3.8$ Hz, H-1), 6.40 (d, 1H, $J = 14.5$ Hz, —OCH=). Compound **25**: ^1H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.32, 1.49 (2s, 6H, 2 × CH_3), 3.38 (s, 3H, —OMe), 3.77 (d, 1H, $J = 2.9$ Hz, H-3), 4.23 (d, 1H, $J = 8.5$ Hz, =CHSi—), 5.90 (d, 1H, $J = 3.8$ Hz, H-1), 6.80 (d, 1H, $J = 8.5$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{34}H_{42}O_6SiNa$: 597.26484. Found: 597.26285.

Anal. Calcd for $C_{34}H_{42}O_6Si$ (574.81): C, 71.05; H, 7.88. Found: C, 70.78; H, 7.30.

(E) and (Z) 1,2-O-Isopropylidene-3-O-methyl-6-O-(2,4,6-triisopropylbenzenesulfonyl)-5-O-(2′-trimethylsilyl-vinyl)-α-D-glucofuranose (26/27)

A mixture of compounds **26/27**, in a ratio of ca. 2.8:1, was obtained from **14** according to the general procedure described for compounds **18/19** (76%). IR: 1602, 1615 cm^{-1} (film). Compound **26**: ^1H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the

mixture: δ 3.37 (s, 3H, —OMe), 4.47 (dd, 1H, $J = 10.8$ Hz, $J = 2.1$ Hz, H-6b), 4.56 (d, 1H, $J = 3.8$ Hz, H-2), 4.65 (d, 1H, $J = 14.5$ Hz, =CH—), 5.85 (d, 1H, $J = 3.8$ Hz, H-1), 6.20 (d, 1H, $J = 14.5$ Hz, —OCH=). Compound **27**: ^{1}H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 3.38 (s, 3H, —OMe), 4.04 (dd, 1H, $J = 9.0$ Hz, $J = 3.2$ Hz, H-4), 4.46 (dd, 1H, $J = 10.9$ Hz, $J = 2.0$ Hz, H-6b), 5.84 (d, 1H, $J = 3.7$ Hz, H-1), 6.59 (d, 1H, J 8.3 Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{30}H_{50}O_8SiSNa$: 621.28934. Found: 621.29272.

Anal. Calcd for $C_{30}H_{50}O_8SiS$ (598.89): C, 60.20; H, 8.41. Found: C, 60.22; H, 8.52.

(E) and (Z) 1,2-O-Isopropylidene-3-O-methyl-6-O-tosyl-5-O-(2′-trimethylsilyl-vinyl)-α-D-glucofuranose (28/29)

A mixture of compounds **28/29**, in a ratio of ca. 2.5:1, was obtained from **15** according to the general procedure described for compounds **18/19** (71%). IR: 1614 cm^{-1} (film). Compound **28**: ^{1}H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.30, 1.46 (2s, 6H, 2 × CH_3), 3.34 (s, 3H, —OMe), 4.53 (d, 1H, $J = 3.8$ Hz, H-2), 4.58 (d, 1H, $J = 14.5$ Hz, =CH—), 5.81 (d, 1H, $J = 3.8$ Hz, H-1), 6.11 (d, 1H, $J = 14.5$ Hz, —OCH=). Compound **29**: ^{1}H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 1.31, 1.47 (2s, 6H, 2 × CH_3), 3.35 (s, 3H, —OMe), 3.77 (d, 1H, $J = 2.9$ Hz, H-3), 4.17 (d, 1H, $J = 8.3$ Hz, =CHSi—), 6.54 (d, 1H, $J = 8.3$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{22}H_{34}O_8SiSNa$: 509.16414. Found: 509.16163.

Anal. Calcd for $C_{22}H_{34}O_8SiS$ (486.67): C, 54.29; H, 7.04. Found: C, 54.40; H, 7.13.

(E) and (Z) 3-O-Benzyl-1,2-O-isopropylidene-6-O-(2,4,6-triisopropylbenzenesulfonyl)-5-O-(2′-trimethylsilyl-vinyl)-α-D-glucofuranose (30/31)

A mixture of compounds **30/31**, in a ratio of ca. 5.1:1, was obtained from **16** according to the general procedure described earlier (48%). IR: 1615, 1601 cm^{-1} (film). Compound **30**: ^{1}H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 3.99 (d, 1H, $J = 3.2$ Hz, H-3), 4.53 (d, 1H, $J = 14.6$ Hz, =CH—), 5.84 (d, 1H, $J =$ 3.7 Hz, H-1), 6.18 (d, 1H, $J = 14.6$ Hz, —OCH=). Compound **31**: ^{1}H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 3.97 (d, 1H, $J = 3.2$ Hz, H-3), 5.83 (d, 1H, $J = 3.7$ Hz, H-1), 6.55 (d, 1H, $J = 8.3$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{36}H_{54}O_8SiSNa$: 697.32064. Found: 697.32241.

Anal. Calcd for $C_{36}H_{54}O_8Si$ (674.96): C, 64.06; H, 8.06. Found: C, 63.51; H, 7.85.

(E) and (Z) 3-O-Benzyl-1,2-O-isopropylidene-6-O-tosyl-5-O-(2′-trimethylsilyl-vinyl)-α-D-glucofuranose (32/33)

A mixture of compounds **32/33**, in a ratio of ca. 4.4:1, was obtained from **17** according to the general procedure described earlier (50%). IR: 1614, 1602 cm^{-1} (film). Compound **32**: ^1H NMR (500 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: 3.98 (d, 1H, $J = 3.2$ Hz, H-3), 5.89 (d, 1H, $J = 3.7$ Hz, H-1), 6.11 (d, 1H, $J =$ 14.6 Hz, —OCH=). Compound **33**: ^1H NMR (200 MHz, $CDCl_3$) selective signals taken from the spectrum of the mixture: δ 3.97 (d, 1H, $J = 3.2$ Hz, H-3), 5.85 (d, 1H, $J = 3.7$ Hz, H-1), 6.50 (d, 1H, $J = 8.3$ Hz, —OCH=). MS (LSIMS, HR) m/z: $[M + Na]^+$ calcd for $C_{28}H_{38}O_8SiSNa$: 585.19544. Found: 585.19513.

[2+2]Cycloadditions of chlorosulfonyl isocyanate to 2′-silylvinyl ethers 20/21, and 28/29 were performed according to the known procedure.[1,15]

(3′S,4′R) and (3′R,4′R) 1,2-O-Isopropylidene-3-O-(3′-trimethylsilyl-azetidin-2′-on-4′-yl)-5-O-trityl-α-D-xylofuranose (34 and 35)

A mixture of stereoisomers **34** and **35**, in a ratio 7.5:1, was obtained from **20/21** in 17% yield. Unsaturated amide **36** was detected in crude post-reaction mixture by ^1H NMR. Compound **34**: $[\alpha]_D^{22}$ −28.0 (C 1, CH_2Cl_2), lit.[1] $[\alpha]_D$ −28.3 (C 1, CH_2Cl_2). Compound **35**: Solid foam; $[\alpha]_D^{22}$ −26.7 (C 0.24, CH_2Cl_2). IR: 1762 cm^{-1} (CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ 0.14 (s, 9H, —$SiMe_3$), 1.37, 1.56 (2s, 6H, 2 × CH_3), 2.70 (d, 1H, $J = 1.5$ Hz, H-3′), 3.24 (dd, 1H, $J = 9.5$ Hz, $J = 3.7$ Hz, H-5a), 3.59 (dd, 1H, $J = 9.5$ Hz, $J = 5.5$ Hz, H-5b), 4.04 (d, 1H, $J = 3.0$ Hz, H-3), 4.31 (m, 1H, H-4), 4.54 (d, 1H, $J = 3.8$ Hz, H-2), 4.94 (d, 1H, $J = 1.5$ Hz, H-4′), 5.93 (d, 1H, $J = 3.8$ Hz, H-1), 6.06 (br s, 1H, NH). MS (EI, HR) *m/z*: M^+ calcd for 573.2547. Found: 573.2522.

Anal. Calcd for $C_{33}H_{39}O_6SiN$: (573.779): C, 69.08; H, 6.85; N, 2.44. Found: C, 68.95; H, 6.77; N, 2.60.

(3′R,4′S) and (3′S,4′R) 1,2-O-Isopropylidene-3-O-methyl-6-O-tosyl-5-O-(3′-trimethylsilyl-azetidin-2′-on-4′-yl)-α-D-glucofuranose (37 and 38)

A mixture of stereoisomers **37** and **38**, in a ratio ca. 7:1, respectively, was obtained from **28/29** in 15% yield. Unsaturated amide **39** was detected in the crude post reaction mixture by ^1H NMR. Spectral data taken for the mixture, IR: 3411, 1778, 1760 cm^{-1} (CH_2Cl_2). Compound **37**: ^1H NMR (500 MHz, $CDCl_3$) selective signals: δ 5.40 (d, 1H, $J = 4.4$ Hz, H-4′), 5.78 (d, 1H, $J = 3.7$ Hz, H-1), 6.14 (br s, 1H, NH). Compound **38**: ^1H NMR (500 MHz, $CDCl_3$) selective signals: δ 5.18

(d, 1H, $J = 4.4$ Hz, H-4′), 5.81 (d, 1H, $J = 3.8$ Hz, H-1), 6.41 (br s, 1H, NH). MS (EI, LSIMS) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{36}O_9SiSN$: 530.18801. Found: 530.18951.

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