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Tributyl[2-(trimethylsilyl)-prop-2-enyl]stannane: A Highly Efficient Reagent for the Allylation of Radicals

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Abstract. Allylation rates of radicals with tributyl[2-(trimethylsilyl)prop-2-enyl]stannane (**2**) have been compared with the ones of the (prop-2-enyl)stannane (**3**) and [2-(methyl)-prop-2-enyl]stannane (**4**). The Me_3Si substituent showed a rate-accelerating effect (4.2:1 to 6.5:1) relative to the H-atom and the Me group for nucleophilic radicals. With electrophilic radicals, the Me group has a better rate accelerating effect than the Me_3Si group. All these results can be understood by postulating a partially polarized transition state. The 1-substituted vinylsilanes which are produced by radical allylation with **2** have been converted by protiodesilylation and ozonolysis to alkenes and α-hydroxy ketones.

Allylstannanes have been introduced by *Keck et al.* [1] for very efficient C–C bond formation *via* radical additions. The fragmentation mechanism involved in these reactions allows to conduct Sn-radical based chains without using Bu_3SnH. Consequently, unwanted direct reduction of the radical intermediates is suppressed. It was recently shown that the efficiency of these reactions is also due to the fact that allylstannanes are more reactive than simple alkenes toward radicals by at least one order of magnitude [2]. In connection with our work on nucleophilic and electrophilic radicals, we have faced situations where radical additions to (prop-2-enyl)stannane were not efficient because of competing radical processes such as dimerization, disproportionation, and H-atom abstraction from the solvent. This prompted us to search for a more reactive synthetic equivalent of (prop-2-enyl)stannane. Recently, *Lee et al.* [3] have reported that radical allylation reactions with [2-(trimethylsilyl)prop-2-enyl]triphenylstannane were apparently faster and higher yielding than reactions with the non-substituted (prop-2-enyl)stannane [4]. To find out the origin of this efficiency, we decided to investigate the allylation reaction of several radicals with the 2-silylated allylstannane **2** and to compare the allylation rates with the non-substituted and the 2-methyl-substituted allylstannanes **3** and **4**, respectively (*Scheme 1*). Moreover, we also report some typical and synthetically useful one-step transformations of the substituted vinylsilanes **5a–e**, which are obtained from the radical allylations with **2**.

The substituted allylstannane **2** was prepared according to *Schlosser*'s procedure [5] in 50% yield by metallation of 2-(trimethylsilyl)prop-1-ene with BuLi/*t*-BuOK and subsequent reaction with Bu_3SnCl. This one-pot procedure was found to be faster and more convenient than the ones of *Lee et al.* [3] and *Overman* and coworkers [6]. The reactivity of **2** toward radicals was then examined by competition experiments with tributyl-(prop-2-enyl)stannane (**3**) and tributyl[(2-methyl)prop-2-enyl]stannane (**4**). In a typical experiment, the radical precursor R–X **1** (0.25 mmol) was irradiated for 12 h in benzene at 10° in the presence of

Scheme 1

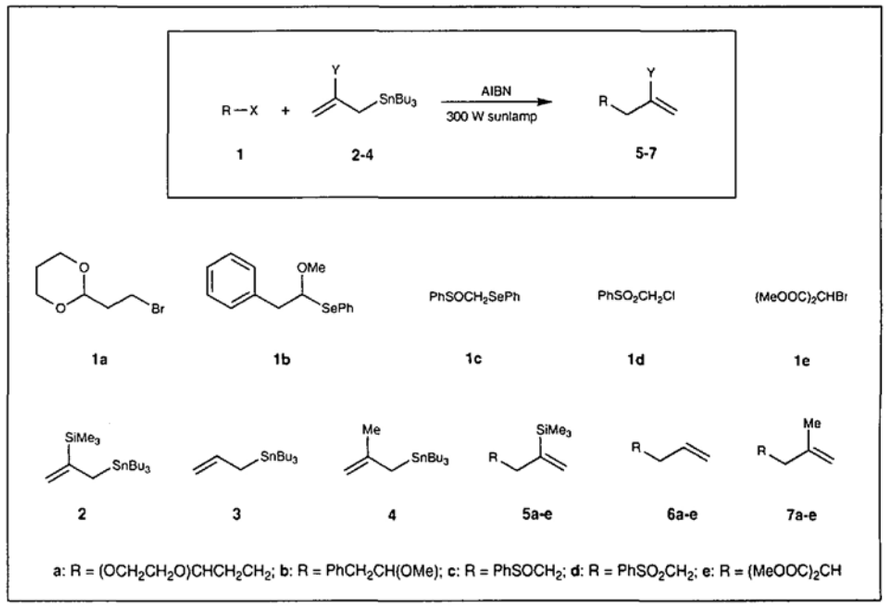

Table. *Competition Experiments for the Allylation of* **1a–e** *with the Allylstannanes* **2–4** *and Allylation Yields with* **2**

Entry	R–X	5/6[a])	5/7[b])	Yield (5) [%][c])
1	**1a**	4.2:1	4.4:1	40
2	**1b**	5:1	6.5:1	63
3	**1c**	2.6:1	1.2:1	75
4	**1d**	3.2:1	1:1.8	63
5	**1e**	3:1	1:2.5	80

[a]) From **1** (0.25 mmol), **2** (1 mmol), **3** (1 mmol) and AIBN (10 mg) in benzene (4 ml). [b]) From **1** (0.25 mmol), **2** (1 mmol), **4** (1 mmol) and AIBN (10 mg) in benzene (4 ml). [c]) From **1** (5 mmol), **2** (6 mmol) and AIBN in benzene (15 ml).

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AIBN and an equimolar mixture of **2/3** or **2/4** (1 mmol of each stannane). The product ratio was then determined by ^{1}H-NMR, and the results are summarized in the *Table*. With the alkyl radical generated from **1a**, the silylated stannane **2** reacted *ca.* four times faster than the H- and the Me-substituted (propenyl)stannanes **3** and **4**. The MeO-substituted alkyl radical derived from the O,Se acetal **1b** showed an even stronger Me_3Si-induced rate enhancement (**5b/6b** 5:1 and **5b/7b** 6.5:1). With the sulfinylated radical **1c**, the rate enhancement was less pronounced relative to the (prop-2-enyl)stannane **3** (**5c/6c** 2.6:1). Almost no rate enhancement was observed relative to the methylated reagent **4** (**5c/7c** 1.2:1). In case of the electrophilic sulfonyl substituted radical **1d**, the Me_3Si group had an activating effect relative to H (**5d/6d** 3.2:1), but the Me-substituted allylstannane **4** was more effective (**5d/7d** 1:1.8). A very similar picture was observed with the malonyl radical **1e** which reacted faster with **2** than with **3** (**5e/6e** 3:1), but the reaction with **4** was even faster (**5e/7e** 1:2.5). We also checked that the rate enhancement led to better yields of isolated products. For example, the allylation of **1b** with **2** gave **5b** in 63% yield (*Entry 2*), although the reaction with **3** gave **6b** in less than 5% yield [7]. Good yields have also been obtained with electrophilic radicals as illustrated by the conversion of **1d** and **1e** to **5d** and **5e** in 63% and 80% yield, respectively (*Entries 4* and *5*).

Our results are neither properly explained by orbital considerations [8] nor by stabilization of the radical adducts **A–C** (*Fig.*) [9]. However, polarization of the transition state offers a satisfactory explanation. The addition of nucleophilic radicals (*Entries 1* and *2*) causes a polarization of the transition state as indicated in the *Figure* (**D–F**). The Me_3Si substitutent stabilizes the partial negative charge in α-position (α-effect) for transition state **D**. Such a stabilization is not present in transition states **E** and **F**. A similar explanation based on the ability of Si to stabilize adjacent electron-rich centers was proposed to account for the reactivity of α-halosilanes during the reduction with Bu_3SnH [10]. With nucleophilic radicals (*Entries 4* and *5*), the polarization is opposite and a partial positive charge appears at C(2) of the prop-2-enyl group (**G–I**). The results are coherent with the order of carbocation stabilizing effect. Indeed, it has been shown that a Me group (**I**) is more stabilizing than a Me_3Si group (**G**), and that a H-atom (**H**) is less stabilizing [11]. The sulfinylated radical derived from **1c** behaves like an ambiphilic radical, and the transition state should not be significantly polarized.

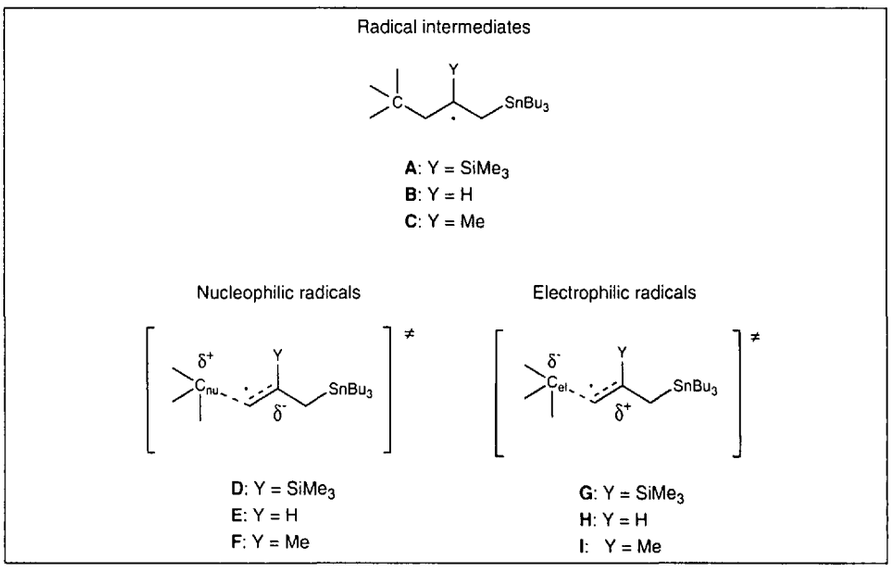
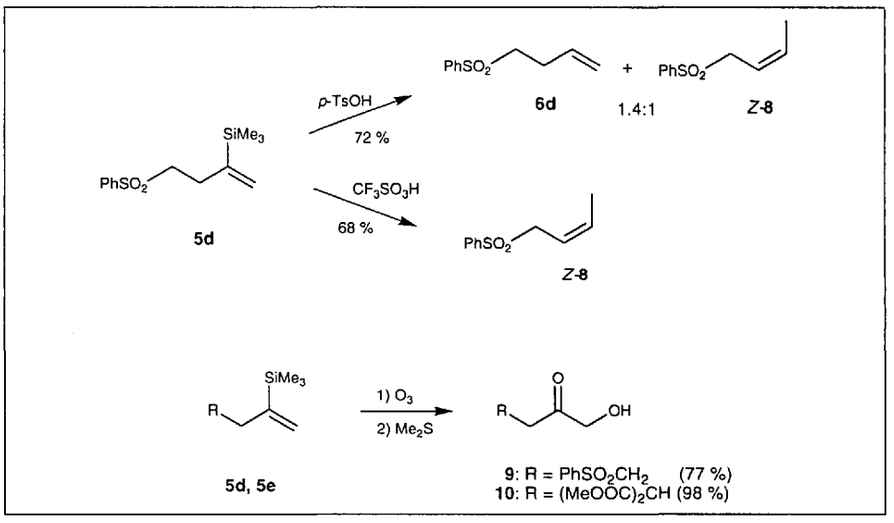


Figure. *Radical intermediates* (**A–C**) *and polarized transition states* (**D–I**)

Scheme 2

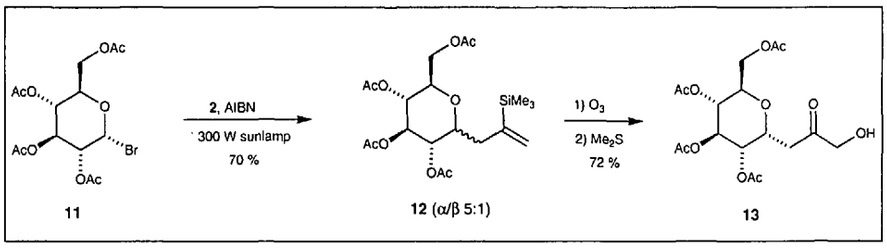


The Me_3Si-substituted olefins produced are very useful building blocks [12]. For instance, they can be converted to alkenyl halides [13], methyl ketones [14], (phenylthio)methyl ketones [15], hydroxymethyl ketones [16] and alkenes [17]. We have decided to examine the protiodesilylation and the ozonolysis with some of our substrates in order to test the compatibility of these transformations with the other functionalities present in the molecule (*Scheme 2*). For instance, **5d** was protiodesilylated to a 1.4:1 mixture of **6d** and (*Z*)-**8** with TsOH in refluxing benzene [17]. By varying the reaction conditions, the formation of the side product (*Z*)-**8** could not be totally avoided. The use of a stronger acid such as triflic acid in CH_2Cl_2 gave exclusively the internal olefin **8** in the (*Z*)-configuration [18]. Ozonolysis of **5d** and **5e** according to *Büchi*'s procedure [16] gave the hydroxymethyl ketone **9** and **10** in nearly quantitative yield.

Since we have demonstrated that **2** is a particularly good allylating agent for alkoxy-substituted radicals, we decided to examine the allylation of glucopyranosyl bromide tetraacetate (**11**; *Scheme 3*) [19]. Irradiation with a 300-W sunlamp of a solution of **11** and **2** in the presence of AIBN yielded **12** in 70% (α/β 5:1). Ozonolysis of **12** (O_3, Me_2S) gave, after chromatography, the diastereoisomerically pure hydroxymethyl ketone **13** in 72% yield. This reaction sequence allows to add three C-atoms containing two oxygenated functionalities and is potentially interesting for chain elongation of carbohydrates [20].

In conclusion, the presence of a Me_3Si group on a C=C bond enhances particular-

Scheme 3



ly well its reactivity toward nucleophilic radicals. This effect, caused by some degree of polarization of the transition state, can probably be used with other types of olefins in order to make them more suitable for radical reactions. Work in that direction is currently underway in our laboratory.

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Experimental Part

General. THF was freshly distilled from K under N_2. CH_2Cl_2 was distilled from P_2O_5. Benzene was distilled from CaH_2 under N_2. For flash column chromatography (FC) and filtration, *Merck* silica gel *60* (70-230 mesh) was used. TLC were run on *Merck* silica gel *60* F_{254} anal. plates; detection either with UV, iodine or by spraying with a soln. of 25 g of phosphomolybdic acid, 10 g of $Ce(SO_4)_2 \cdot 4\ H_2O$, 60 ml of conc. H_2SO_4 and 940 ml of H_2O with subsequent heating. M.p. (not corrected) were determined by using a *Büchi-Totolli* apparatus. Bulb-to-bulb distillations were carried out using a *Büchi GKR-50* apparatus; b. p. refer to air bath temp. The following apparatus were used: NMR: *Bruker AC-250 FT* (^{1}H/250 MHz, ^{13}C/62.9 MHz) and *Varian-Gemini* (^{1}H/200 MHz, ^{13}C/50.3 MHz). Unless otherwise indicated, spectra were recorded in $CDCl_3$ and chemical shifts are given in ppm with TMS signal at 0 ppm or $CHCl_3$ at 7.27 ppm. Elemental analysis: *Ilse Beetz*, Mikroanalytisches Laboratorium. Irradiations were conducted using a sunlamp *Osram Ultra-Vitalux 300 W*. Compounds **1a**, **1d**, **1e**, and **11** are commercially available (*Fluka*). Stannanes **3** and **4** have been prepared according to *Keck*'s procedure [1].

Competition Experiment. A soln. containing the radical precusor **1** (0.25 mmol), AIBN (10 mg), the stannane **2** (403 mg, 1 mmol) and either the stannane **3** (331 mg, 1 mmol) or **4** (345 mg, 1 mmol) in benzene (4 ml) was irradiated at 10° for 12 h with a 300-W sunlamp. The solvent was evaporated and the residue filtered through silica gel (hexane, hexane/AcOEt) to eliminate the tin derivatives. When a halide was used as radical initiator (**1a**, **1d**, and **1e**), MeOH (6 ml) was added after the irradiation period followed by KF (300 mg) and the mixture was stirred for 1 h and filtered. The filtrate was evaporated and the solid residue was extracted with CH_2Cl_2, filtered through cotton, and the filtrate was concentrated before rapid filtration through silica gel as described above. The ratio **5/6** or **5/7** was deduced from ^{1}H-NMR spectra (olefinic protons) and confirmed by GC (packed column, *SE-54*).

General Procedure 1: Radical Allylation with **2**. A soln. containing the radical precusor **1** (5 mmol), the stannane **2** (2.42 g, 6 mmol) and AIBN (15 mg) in C_6H_6 (15 ml) was irradiated at 10° with a 300-W sunlamp. Further portions of AIBN (15 mg) were added every 8 h, and the reaction was followed by TLC. Total disappearence of the starting material took between 12 and 36 h. The solvent was then evaporated and the residue purified by FC (hexane, hexane/AcOEt). When an halide was used as radical initiator (**1a**, **1d**, and **1e**), MeOH (30 ml) was added after the irradiation period followed by KF (1.5 g), and the mixture was stirred for 1 h and filtered. The filtrate was evaporated and the residue treated as above.

General Procedure 2: Ozonolysis of Vinylsilanes [16]. O_3 was passed through a soln. of the vinylsilane (1 mmol) in 10 ml of CH_2Cl_2 at –78° until persistence of a blue color. The soln. was flushed with N_2 until disappearence of the blue color and dimethyl sulfide (0.3 ml, 4 mmol) was added, and the reaction mixture was allowed to warm up to r.t. Evaporation of the solvent gave the crude hydroxymethyl ketone.

Tributyl[2-(trimethylsilyl)prop-2-enyl]stannane (**2**) [5]. A soln. of 2-(trimethylsilyl)prop-1-ene (10.0 g, 175 mmol) in THF (600 ml) was treated at –78° with a 1.6M BuLi soln. in hexane (121 ml, 192 mmol) followed by a 1.56M *t*-BuOK soln. in THF (112 ml, 175 mmol). The mixture was stirred at –40° for 1.5 h, cooled down to –78°, and transferred *via* a *Teflon* cannula (2–3-mm internal diameter) by portion to a soln. of Bu_3SnCl (57.0 g, 175 mmol) in THF (1 l). After 15 min at 15°, the mixture was poured into brine (2 l) and extracted 3 x with petroleum ether (4 l, 2 l, 1 l). The combined org. phases were dried ($MgSO_4$) and the solvent evaporated. The residue was filtered through silica gel (hexane) and distilled under reduced pressure to give **2** (45.9 g, 65%). Colorless liquid. B.p. 130°/10^{-2} Torr. The purity was checked by GC (*SE-54*, 200°). ^{1}H-NMR (250 MHz): 5.36 (*td*, *J* = 3.0, 1.5, C=C*H*H); 5.08 (*d*, *J* = 3.0, C=CH*H*); 1.90 (*d*, *J* = 1.5, CH_2–C=C); 1.65–1.30 (*m*, 12 H); 1.05–0.65 (*m*, 15 H); 0.08 (*s*, MeSi). Anal. calc. for $C_{18}H_{40}SiSn$ (403.29): C 53.61, H 10.00; found: C 53.70, H 9.97.

Methyl 2-Phenyl-1-(phenylselenenyl)ethyl Ether (**1b**). Diphenyl diselenide (1.56 g, 5.0 mmol) in toluene (5 ml) was added to a 1M soln. of DIBAL-H in hexane (10 ml, 10 mmol). The mixture was stirred at r.t. for 30 min, 2-phenylpropionaldehyde dimethyl acetal (0.83 ml, 5.0 mmol) was added and the mixture heated at 50° for 3 h. The cooled reaction mixture was treated with a 5% NaF soln. (17 ml) and extracted with CH_2Cl_2. Drying ($MgSO_4$), evaporation of the solvent, and FC (Et_2O/hexane 1:10) of the residue gave **1b** (1.10 g, 75%). Yellow liquid. ^{1}H-NMR (200 MHz): 7.70–7.60 (*m*, 2 arom. H); 7.40–7.20 (*m*, 3 arom. H); 5.15 (*dd*, *J* = 7.0, 5.9, CH(OMe)(SePh)); 3.50 (*s*, MeO); 3.30 (*d*, *J* = 5.9, CH*H*Ph); 3.29 (*d*, *J* = 7.0, CH*H*Ph). ^{13}C-NMR (50.3 MHz): 138.22; 135.49; 129.27; 128.84; 128.17; 127.60; 126.47; 90.33; 57.28; 44.03. Anal. calc. for $C_{15}H_{16}OSe$ (291.25): C 61.86, H 5.54; found: C 61.55, H 5.46.

Phenyl(phenylselenenyl)methyl Sulfoxide (**1c**). A 0.6M soln. of LiHMDS (108 ml, 65 mmol) in hexane/THF (1.6:1) was added at –78° to a soln. of methyl phenyl sulfoxide (4.50 g, 32 mmol) in THF (30 ml). After 30 min, a soln. of diphenyl diselenide (10.2 g, 32 mmol) in THF (120 ml) was added over 30 min. The reaction mixture was stirred for 30 min at –78°, allowed to warm to r.t., poured into a 10% NH_4Cl soln. and extraced with Et_2O. The combined org. layers were washed with brine, dried ($MgSO_4$) and evaporated. FC (AcOEt/hexane 1:4) of the crude material gave **1c** (7.84 g, 83%). Pale yellow oil. ^{1}H-NMR (200 MHz): 7.75-7.15 (*m*, 10 arom. H); 4.10 (*s*, CH_2SO). Anal. calc. for $C_{13}H_{12}OSSe$ (295.26): C 52.88, H 4.10; found: C 52.59, H 4.30.

2-[4-(Trimethylsilyl)but-5-enyl]-1,3-dioxane (**5a**). From **1a** (500 mg, 2.56 mmol) and **2** (1.34 g, 3.3 mmol) according to *General Procedure 1*. FC (Et_2O/hexane 1:8) of the crude product gave **5a** (232 mg, 40%). Colorless liquid. ^{1}H-NMR (200 MHz): 5.55 (*m*, C*H*H=C); 5.31 (*dm*, *J* = 3.0, CH*H*=C); 4.50 (*t*, *J* = 4.5, O–CH–O); 4.10 (*dd*, *J* = 11.6, 5.1, 2 H, C*H*HO); 3.75 (*td*, *J* = 12.5, 1.4, 2 H, CH*H*O); 2.22–1.90 (*m*, 3 H); 1.70–1.40 (*m*, 4 H); 1.32 (*dm*, *J* = 13, OCH_2CHH). ^{13}C-NMR (50.3 MHz): 151.96 (*s*); 124.06 (*t*); 102.35 (*d*); 66.86 (*t*); 35.70 (*t*); 34.99 (*t*); 25.90 (*t*); 23.35 (*t*); –1.48 (*q*). Anal. calc. for $C_{12}H_{24}O_2Si$ (228.40): C 63.10, H 10.59; found: C 63.19, H 10.54.

1-Phenyl-4-(trimethylsilyl)pent-4-en-2-yl Methyl Ether (**5b**). From **1b** (73 mg, 0.25 mmol) and **2** (403 mg, 1.0 mmol) according to *General Procedure 1*. FC (Et_2O/hexane 1:20) of the crude product gave **5b** (40 mg, 63%). ^{1}H-NMR (200 MHz): 7.35–7.15 (*m*, 5 arom. H); 5.65 (*dt*, *J* = 3.0, 1.4, C=C*H*H); 5.45 (*ddd*, *J* = 3.0, 1.0, 0.8, C=CH*H*); 3.50 (*quint.*, *J* = 6–7, C*H*OMe); 3.30 (*s*, MeO); 2.75 (*d*, *J* = 6.0, PhCH_2); 2.42 (*dddd*, *J* = 14.2, 6.7, 1.3, 1.0, C*H*H–C=C); 2.23 (*dddd*, *J* = 14.2, 6.1, 1.3, 0.8, CH*H*–C=C); 0.1 (*s*, MeSi). ^{13}C-NMR (50.3 MHz): 149.14; 139.32; 129.41; 128.18; 126.94; 126.00; 81.77; 57.03; 40.72; 40.12; –1.28. Anal. calc. for $C_{15}H_{24}OSi$ (248.44): C 72.52, H 9.74; found: C 72.59, H 9.63.

Phenyl 3-(Trimethylsilyl)but-3-enyl Sulfoxide (**5c**). From **1c** (590 mg, 2.0 mmol) and **2** (1.21 g, 3.0 mmol) according to *General Procedure 1*. FC (AcOEt/hexane 1:4) of the crude product gave **5c** (378 mg, 75%). Colorless liquid. ^{1}H-NMR (250 MHz): 7.70–7.40 (*m*, 5 arom. H); 5.58 (*m*, C=C*H*H); 5.39 (*m*, C=CH*H*); 2.87 (*m*, CH_2S); 2.65–2.25 (*m*, CH_2C=C); 0.02 (*s*, MeSi). Anal.

calc. for $C_{13}H_{20}OSSi$ (252.45): C 61.85, H 7.99, S 12.70, Si 11.13; found: C 61.89, H 7.92, S 12.67, Si 11.02.

Phenyl 3-(Trimethylsilyl)but-3-en-1-yl Sulfone (**5d**). From **1d** (381 mg, 2.0 mmol) and **2** (1.0 g, 2.5 mmol) according to *General Procedure 1*. FC (AcOEt/hexane 1:10) gave **5d** (340 mg, 63%). Colorless oil. ^{1}H-NMR (250 MHz): 7.92 (*m*, 2 arom. H); 7.70–7.50 (*m*, 3 arom. H); 5.49 (*m*, C=CH*H*); 5.32 (*m*, C=C*H*H); 3.13 (*m*, CH_2S); 2.49 (*m*, CH_2C=C); 0.02 (*s*, MeSi). Anal. calc. for $C_{13}H_{20}O_2SSi$ (268.45): C 58.16, H 7.51, S 11.94; found: C 58.05, H 7.48, S 11.79.

Dimethyl [2-(Trimethylsilyl)prop-2-en-1-yl]propanedioate (**5e**). From **1e** (1.0 g, 4.7 mmol) and **2** (2.5 g, 6.2 mmol) according to *General Procedure 1*. FC (hexane, AcOEt/hexane 1:10) of the crude product gave **5e** (930 mg, 80%). ^{1}H-NMR (250 MHz): 5.55 (*m*, C=CH*H*); 5.36 (*m*, C=C*H*H); 3.72 (*s*, MeOOC); 3.62 (*t*, *J* = 7.5, CHCOO); 2.72 (*dm*, *J* = 7.5, CH_2C=C); 0.10 (*s*, MeSi). Anal. calc. for $C_{11}H_{20}O_4SSi$ (244.36): C 54.07, H 8.25, Si 11.49; found C 54.20, H 7.91, Si 11.63.

Protiodesilylation of **5d**. *With TsOH*. A soln. of **5d** (75 mg, 0.28 mmol) and TsOH · H_2O (10 mg) in C_6H_6 (1.5 ml) was heated under reflux for 6 h. The mixture was poured into Et_2O and washed with a 1M NaOH soln. and brine. After drying ($MgSO_4$), the solvent was evaporated and FC (AcOEt/hexane 1:4) of the crude product gave an unseparable 1.4:1 mixture of **6d** and (*Z*)-**8** (40 mg, 72%). *With Triflic Acid (TfOH)*. A soln. of **5d** (80 mg, 0.30 mmol) in CH_2Cl_2 (2 ml) was treated with TfOH (90 mg, 0.60 mmol) and the soln. is stirred at r.t. for 6 h. The mixture was then poured into Et_2O and washed with a 1M NaOH soln. and brine. After drying ($MgSO_4$), the solvent was evaporated and FC (AcOEt/hexane 1:4) of the crude product gave (*Z*)-**8** (40 mg, 68%). **6d**: ^{1}H-NMR (200 MHz): 7.95–7.85 (*m*, 2 arom. H); 7.70–7.5 (*m*, 3 arom. H); 5.70 (*ddt*, *J* = 17.3, 9.9, 6.5, C*H*=CH_2); 5.05 (*dq*, *J* = 22.0, 1.5, CH=C*H*H); 5.03 (*dq*, *J* = 11.2, 1.2, CH=CH*H*); 3.15 (*m*, CH_2SO_2); 2.45 (*m*, CH_2CH=CH_2). ^{13}C-NMR (50.3 MHz): 139.04; 133.67; 129.22; 128.02; 117.03; 55.34; 26.77. (*Z*)-**8**: ^{1}H-NMR (200 MHz): 7.92–7.82 (*m*, 2 arom. H); 7.70–7.50 (*m*, 3 arom. H); 5.81 (*dtq*, *J* = 10.6, 1.1, 6.9, MeC*H*=C); 5.40 (*dtq*, *J* = 10.6, 7.9, 1.1, CH_2C*H*=C); 4.88 (*dm*, *J* = 7.9, SO_2CH_2); 1.35 (*dm*, *J* = 6.9, Me). ^{13}C-NMR (50.3 MHz): 138.43 (*s*); 136.18 (*d*); 133.67 (*d*); 128.85 (*d*); 128.25 (*d*); 116.08 (*d*); 54.62 (*t*); 12.50 (*q*). Anal. calc. for $C_{10}H_{12}O_2S$ (196.27): C 61.20, H 6.16; found: C 61.14, H 6.23.

4-Hydroxy-3-oxobutyl Phenyl Sulfone (**9**). From **5d** (92 mg, 0.34 mmol) according to *General Procedure 2*. FC (AcOEt/hexane 1:1) gave **9** (60 mg, 77%). White solid. M.p. 106-108°. ^{1}H-NMR (250 MHz): 7.93 (*m*, 2 arom. H); 7.8–7.55 (*m*, 3 arom. H); 4.30 (*s*, OCH_2CO); 3.49 (*t*, *J* = 7, CH_2SO_2); 2.92 (*t*, *J* = 7.0, CH_2CH_2CO); 3.37 (br., OH). Anal. calc. for $C_{10}H_{12}O_4S$ (228.27): C 52.62, H 5.30, S 14.05; found: C 52.64, H 5.29, S 14.01.

Dimethyl 2-(3-Hydroxy-2-oxopropyl)propanedioate (**10**). From **5e** (168 mg, 0.62 mmol) according to *General Procedure 2*. FC (AcOEt/hexane 1:1, EtOAc) gave **10** (126 mg, 98%). Colorless oil. ^{1}H-NMR (250 MHz): 4.32 (*d*, *J* = 5.0, OCH_2CO); 3.99 (*t*, *J* = 7.0, C*H*CH_2); 3.76 (*s*, MeOOC); 3.02 (*d*, *J* = 7.0, CHCH_2); 2.97 (*t*, *J* = 5.0, OH). Anal. calc. for $C_8H_{12}O_6$ (204.18): C 47.06, H 5.92; found: C 47.00, H 5.86.

3-(α- and β-D-Glucopyranosyl)-2-(trimethylsilyl)prop-1-ene Tetraacetate (**12**). From **11** (3.10 g, 7.5 mmol) and **2** (4.03 g, 10 mmol) according to *General Procedure 1*. FC (AcOEt/hexane 1:4) gave unreacted starting material **11** (1.17 g) and **12** (1.47 g, 70%) as a 5:1 α/β mixture of isomers. Colorless oil. ^{1}H-NMR (250 MHz): 5.63 (*m*, C=CH*H*, α-anomer); 5.60 (*m*, C=CH*H*, β-anomer); 5.40 (*d*, *J* = 2.0, C=C*H*H, α-anomer); 5.39 (*d*, *J* = 2.5, C=C*H*H, β-anomer); 5.30 (*t*, *J* = 9.0, H–C(3), α-anomer); 5.13 (*t*, *J* = 9.0, H–C(3), β-anomer); 5.01 (*dd*, *J* = 10.0, 6.0, H–C(2), α-anomer); 4.93 (*t*, *J* = 9.0, H-C(4), α-anomer); 4.85 (*t*, *J* = 9.0, H–C(4), β-anomer); 4.32 (*ddd*, *J* = 11.0, 6.0, 4.0, H–C(1), α-anomer); 4.18 (*dd*, *J* = 12.0, 5.5, 1 H, H–C(6), α-anomer); 4.17 (*dd*, *J* = 12.0, 5.0, 1 H, H–C(6), β-anomer); 4.02 (*dd*, *J* = 12.0, 2.5, 1 H, H–C(6), β-anomer); 4.00 (*dd*, *J* = 12.0, 2.5, 1 H, H–C(6), α-anomer); 3.86 (*ddd*, *J* = 9.0, 5.5, 2.5, H–C(5), α-anomer); 3.57 (*ddd*, *J* = 10.0, 5.5, 2.5, 1 H, β-anomer); 3.48 (*ddd*, *J* = 10.0, 8.0, 3.5, 1 H, β-anomer); 2.55 (*dd*, *J* = 15.0, 11.0; CH*H*C=C, α-anomer); 2.37 (*dd*, *J* = 15.0, 4.0, C*H*HC=C, α-anomer); 2.03, 2.02, 2.00, 1.99 (*s*, CH_3CO, α-anomer); 0.05 (*s*, MeSi, α-anomer); 0.04 (*s*, MeSi, β-anomer). ^{13}C-NMR (62.5 MHz, α-isomer): 170.50; 170.01; 169.47; 169.36; 146.81; 127.30; 71.06; 70.25; 70.05; 68.79; 68.51; 62.12; 31.68; 20.59; −1.57. Anal. calc. for $C_{20}H_{32}O_9Si$ (444.56): C 54.04, H 7.26, Si 6.32; found: C 54.01, H 7.21, Si 6.25.

1-(α- and β-D-Glucopyranosyl)-3-hydroxypropan-2-one (**13**). From **12** (442 mg, 1.0 mmol) according to *General Procedure 2*. FC (AcOEt/hexane 1:1, AcOEt) gave diastereoisomerically pure **13** (290 mg, 72%). White solid. M.p. 106–107°. ^{1}H-NMR (250 MHz): 5.25 (*t*, *J* = 8.0, H-C(3)); 5.11 (*dd*, *J* = 8.0, 5.0, H–C(2); 4.95 (*t*, *J* = 8.0, H–C(4)); 4.76 (*dt*, *J* = 12.0, 7.0, H–C(1)); 4.33, 4.30 (*AB* system, J_{AB} = 12.0, $COCH_2OH$); 4.24 (*dd*, *J* = 12.0, 6.0, 1 H, H–C(6)); 4.10 (*dd*, *J* = 12.0, 3.0, H–C(6)); 3.89 (*ddd*, *J* = 8.0, 6.0, 3.0, H–C(5)); 3.05 (br., OH); 2.83, 2.77 (*AB* part of an *ABX* system, J_{AB} = 12.0, J_{AX} = 7.0, J_{BX} = 7.0, CH_2–C(1)); 2.06, 2.03, 2.03, 2.01 (4*s*, MeCO). ^{13}C-NMR (62.5 MHz): 206.00; 170.60; 169.89; 169.37; 169.29; 70.53; 69.58; 69.10; 68.79; 68.51; 68.00; 61.79; 36.91; 20.63. Anal. calc. for $C_{17}H_{24}O_{11}$ (404.37): C 50.50, H 5.98; found: C 50.56, H 6.07.

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