Photochemical Deconjugation of Chiral 3-Methyl-2-butenoates Derived from Carbohydrate-Based Alcohols: The Influence of the Sugar Backbone on the Facial Diastereoselectivity

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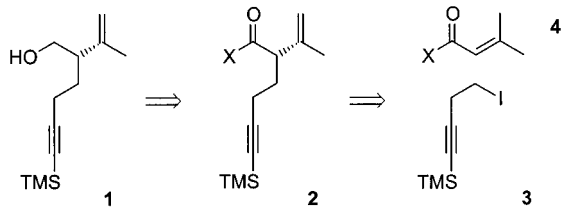
The photodeconjugation of the α-(4-trimethylsilyl-3-butynyl)-substituted senecio acid esters **7** was studied. Chiral alcohols ROH (**9**) were employed as auxiliaries to control the facial diastereoselectivity of the protonation step. The conversion of the four sugar alcohols diacetone-D-glucofuranose, diacetone-D-allofuranose, diacetone-D-gulofuranose, and diacetone-D-fructopyranose (**9a**−**d**) to the esters **7** was achieved in four steps employing 4-iodo-1-trimethylsilylbut-1-yne (**3**) as the alkylating agent (27−45% yield overall). Their photodeconjugation gave the corresponding *β*,*γ*-unsaturated (*R*)-esters **14a**−**d** with moderate to excellent diastereomeric excess. The best results were achieved with diacetone-D-glucofuranose and diacetone-D-fructopyranose as the auxiliary (>95% de). To achieve the synthesis of the target compound **1** which has the (*S*)-configuration, the deconjugation was conducted with the diacetone-L-fructopyranose (*ent*-**9d**) derived ester *ent*-**7d**. L-Fructose (**20**) was prepared from L-sorbose (**15**) in a modified procedure that allowed for the isolation of intermediates. The 2-fold inversion of configuration worked nicely, and the fructofuranose **19** was obtained in 19% yield from L-sorbose. The conversion of L-fructose to the ester *ent*-**7d** was conducted in full analogy to the synthesis of its enantiomer **7d**. Deconjugation of ester *ent*-**7d** yielded the product **2d** (70% yield), which was reduced to the alcohol **1** (85% yield).

Introduction

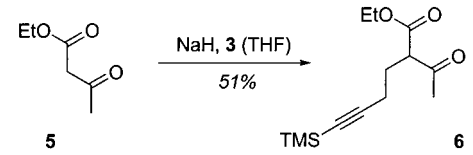
In connection with the synthesis of a heterocyclic sesquiterpene, we required a facile and straightforward access to the enantiomerically pure homoallylic alcohol **1**. A simple consideration regarding possible C−C-bond disconnections led us to employ iodide **3** as a C_4-building block that was to be stereoselectively attached to a C_5-carbon nucleophile (Scheme 1). Reduction of an intermediate carboxylic acid derivative **2** was expected to yield the desired alcohol.

Scheme 1



The synthesis of iodide **3** was easily accomplished from 1-butyn-3-ol following a known procedure.[1] Various enolates generated from chiral senecio acid (3-methyl-2-butenoic acid) derivatives **4** (X = auxiliary), however, failed to give the desired substitution products. Presumably, an elimination of HI occurred that is facilitated by the relatively high acidity of the alkyne at its α-position and by the high basicity of the ester enolates. The elimination product of iodide **3**, 1-trimethylsilylbut-3-en-1-yne, could be detected in the reaction mixture. Contrary to these results, the less basic enolate of ethyl acetoacetate (**5**) yielded the substitution product **6** (eq 1).

(1)



In an attempt to employ this C−C-bond formation reaction for the synthesis of target compound **1** we looked for possible routes to establish the stereogenic center in the intermediate **2** starting from a substitution product related to **6**. Permuting the sequence of events outlined in Scheme 1, one could envisage the deprotonation of a 2-substituted senecio acid ester **7** and its subsequent stereoselective protonation as a viable pathway. The synthesis of the latter compound starting from *β*-keto-esters analogous to **6** appeared feasible. We consequently screened the literature for known procedures that describe the stereoselective protonation[2] of enolates derived from α,*β*-unsaturated esters. Given our interest in photochemical reactions,[3] we found the work of Pete, Muzart, and Piva particularly appealing.[4] In a series of elegant

(1) Molander, G.; Harris, C. R. *J. Am. Chem. Soc.* **1996**, *118*, 4059−4071.

(2) Reviews: (a) Yanagisawa, A.; Yamamoto, H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin 1999; Vol. III, pp 1295−1306. (b) Hünig, S. In *Methoden der Organischen Chemie (Houben-Weyl) 4te Aufl.*; Helmchen, G., Hoffmann, R. W., Mulzer, J., Schaumann, E., Eds.; Thieme, Stuttgart 1996; Vol. E 21, pp 3851−3911. (c) Fehr, C. *Angew. Chem.* **1996**, *108*, 2726−2748; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2566−2587.

(3) Reviews: (a) Bach, T. *Synlett* **2000**, 1699−1707. (b) Bach, T. *Synthesis* **1998**, 683−703. (c) Bach, T. *Liebigs Ann./Recueil* **1997**, 1627−1634.

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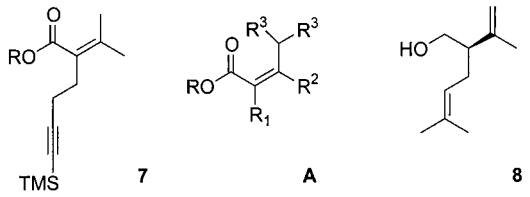
experiments,[5,6] they have shown that esters of the general structure **A** can be photochemically deconjugated to yield β,γ-unsaturated products. The stereoselectivity of the reaction can be either controlled by a chiral alcohol auxiliary R*OH attached to **A** (R = R*) via the ester bond[6] or by a chiral proton source that allows for an enantioselective protonation.[5] As highly enantioselective examples of the latter variant are limited to a few substrates with a certain substitution pattern, we considered the auxiliary-based approach more versatile and more promising. Indeed, the inexpensive, commercially available chiral alcohol 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [diacetone D-glucose, DAGOH (**9a**)][7] has been successfully employed for this purpose. The synthesis of the terpene alcohol (*R*)-(−)-lavandulol (**8**), for example, was achieved via a diastereoselective photodeconjugation.[6d]



For the synthesis of the (*S*)-alcohol **1** and its immediate precursor **2** (X = R*O) from compound **7** an equally effective auxiliary was required that should act as if it was an enantiomer of diacetone D-glucose. Camphor- and menthone-derived auxiliaries that fulfill this requirement have been described,[6a] but they were prepared in multistep syntheses or are very expensive. We therefore decided to study a variety of sugar-based alcohols R*OH in order to evaluate their suitability as chiral auxiliaries[8] in the photodeconjugation of compounds **7** (R = R*). In the following account, we would like to describe the results of this study which finally yielded a reliable method for the photodeconjugation of a senecio acid derivative **7** to the corresponding (*S*)-ester **2** (X = R*O) employing a chiral alcohol readily available from L-fructose.

Results

In an empirical approach we used the alcohols **9** (**9b**, DAAOH = diacetone D-allofuranose;[9] **9c**, DAGuOH = diacetone D-gulofuranose;[9a,10] **9d**, DAFOH = diacetone D-fructopyranose[11]) depicted in Scheme 2 to receive a rough picture of the steric effects exerted by the acetonide

Scheme 2

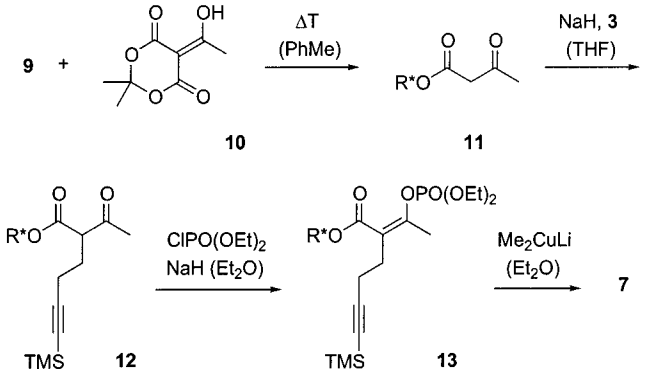
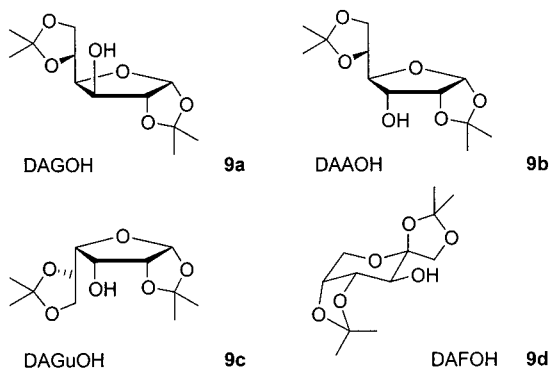


Table 1. Preparation of the Senecio Acid Esters 7a−d

entry	R*	deriv	yield **11**[a] (%)	yield **12**[a] (%)	yield **13**[a] (%)	yield **7**[a] (%)
1	DAG	**a**	quant	46 (58)[b]	77	88
2	DAA	**b**	quant	56 (72)[b]	91	61
3	DAGu	**c**	77	44 (53)[b]	89	73
4	DAF	**d**	96	43 (64)[b]	90	82

[a] Yield of isolated product. [b] Yield based on recovered starting material.

1,2-diol protective groups. In this early stage of the investigation, a rational design appeared less promising to us as the auxiliary-induced diastereoselectivity of carbohydrate-derived and other alkanoates depends strongly on the reaction conditions (vide infra). On the basis of previous results,[6c] we first entertained the notion to vary the proton source of the photodeconjugation reaction and not the auxiliary. We discarded this idea due to the unsatisfactory conversions we achieved in preliminary experiments with DAGOH (**9a**) as the auxiliary and *tert*-butyl alcohol as the proton source.



The reaction sequence selected for the synthesis of the esters **7a−d** followed the route earlier used by Piva in his synthesis of (*R*)-(−)-lavandulol.[6d] To this end, the alcohols **9** were treated with acetyl Meldrum's acid (**10**) to yield the acetoacetates **11**. Subsequent alkylation with iodide **3** as conducted previously with the achiral substrate **5** (vide supra) produced the α-alkylated β-keto esters **12**. After phosphorylation with chloro diethyl phosphate, the enol phosphates **13** were subjected to a substitution reaction by dimethyl cuprate resulting in enantiomerically pure senecio acid esters **7**. The yields of the individual steps are summarized in Table 1.

(4) Review: Pete, J.-P. *Adv. Photochem.* **1996**, *21*, 135−216.
(5) (a) Pete, J.-P.; Henin, F.; Mortezaei, R.; Muzart, J.; Piva, O. *Pure Appl. Chem.* **1986**, *58*, 1257−1262. (b) Piva, O.; Mortezaei, R.; Henin, F.; Muzart, J.; Pete, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 9263−9272.
(6) (a) Mortezaei, R.; Awandi, D.; Henin, F.; Muzart, J.; Pete, J.-P. *J. Am. Chem. Soc.* **1988**, *110*, 4824−4826. (b) Awandi, D.; Henin, F.; Muzart, J.; Pete, J.-P., *Tetrahedron*: *Asymmetry* **1991**, *2*, 1101−1104. (c) Piva, O.; Pete, J.-P. *Tetrahedron*: *Asymmetry* **1992**, *3*, 759−768. (d) Piva, O. *J. Org. Chem.* **1995**, *60*, 7879−7883. (e) Piva, O.; Caramelle, D. *Tetrahedron*: *Asymmetry* **1995**, *6*, 831−832.
(7) Review on chiral pool auxiliaries: Blaser, H. U. *Chem. Rev.* **1992**, *92*, 935−952.
(8) Reviews on carbohydrate-based auxiliaries: (a) Kunz, H.; Rück, K. *Angew. Chem.* **1993**, *105*, 355−377; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 336−358. (b) Reissig, H.-U. *Angew. Chem.* **1992**, *104*, 295−297; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 288−290.
(9) (a) Morris, P. E., Jr.; Kiely, D. E. *J. Org. Chem.* **1987**, *52*, 1149−1152. (b) Baker, D. C.; Horton, D.; Tindall, C. G., Jr. *Carbohydr. Res.* **1972**, *24*, 192−197.
(10) Slessor, K. N.; Tracey, A. S. *Can. J. Chem.* **1970**, *48*, 2900−2906.
(11) Wang, J.-X.; Tu, Y.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224−11235.

Scheme 3

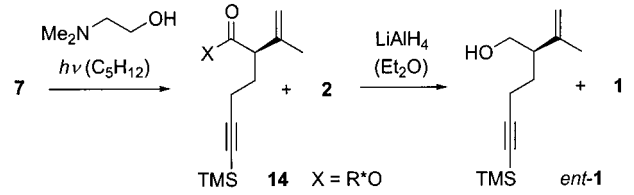


Table 2. Synthesis of the Homoallylic Alcohol *ent*-1 by Photodeconjugation/Reduction

entry	R*	deriv	yield **14**/**2**[a] (%)	de[b] (%)	yield *ent*-**1**/ **1**[a] (%)	ee[c] (%)
1	DAG	**a**	85	>95[d]	88	>95
2	DAA	**b**	73	38	78	36
3	DAGu	**c**	80	66	80	66
4	DAF	**d**	70	>95[d]	85	>95

[a] Yield of isolated product. [b] The diastereomeric excess (de) was determined by integration of appropriate ^{1}H NMR signals. The detection limit for the other diastereoisomer was estimated from previous experience to be <2.5%. [c] The enantiomeric excess (ee) was determined as the optical purity from the mixture of the enantiomeric alcohols **1** and *ent*-**1**. [d] No other diastereoisomer was observed in the ^{1}H and ^{13}C NMR spectra.

Despite the moderate yields achieved in the alkylation step, the overall yields (27−45%) for the conversion **9** → **7** were considered satisfactory and a further optimization was not attempted.

Based on previous results[6] the photochemical deconjugation of compound **7a** was expected to give the levorotatory (*R*)-alcohol *ent*-**1** upon reduction of ester **14a** (Scheme 3, Table 2, entry 1). The reported auxiliary-induced diastereoselectivities for related reactions are high and we aimed at the synthesis of *ent*-**1** as reference material for our further studies. Indeed, the deconjugation of ester **7a** proceeded smoothly and yielded the β,γ-unsaturated product **14a** with >95% de (85% yield). Rayonet lamps RPR-2540 Å ($\lambda = 254$ nm) were employed as light sources, and the reaction was conducted at room temperature in pentane as the solvent with *N*,*N*-dimethylaminoethanol as the proton source. The crude product was directly converted to the homoallylic alcohol *ent*-**1** by reduction with lithium aluminum hydride in diethyl ether. The specific optical rotation of the alcohol *ent*-**1** was determined as $[\alpha]^{20}_D = -27.9$ ($c = 1.1$, MeOH) as compared to the optical rotation of (*R*)-(−)-lavandulol, which was reported as $[\alpha]^{20}_D = -10.1$ ($c = 1.1$, MeOH). The alkyl side chain should not influence the chromophor significantly. A literature search revealed that 2-alkyl-substituted (*R*)-homoallylic alcohols are levorotatory in $CHCl_3$ or MeOH, and the corresponding (*S*)-enantiomers are dextrorotatory.[12] No exception was found. In chloroform, the specific optical rotation of the alcohol *ent*-**1** was $[\alpha]_D = -22.2$ ($c = 1.0$, $CHCl_3$). Based on the known direction of the protonation in DAGO ester derived enols and the optical rotation data, we consider it safe to assume that the products we obtain from the photodeconjugation of substrate **7a** bear a stereogenic center with (*R*)-configuration. The reduction **14a** → *ent*-**1** should proceed racemization-free, and we consequently assigned an optical purity of >95% to the alcohol *ent*-**1**. The optical rotation of this product was taken as reference to determine the optical purity of other mixtures containing the alcohol *ent*-**1** and its enantiomer **1**.

In a sequence similar to the one described above the two furanose-based esters, **7b** and **7c** were converted to the deconjugated products **14b** and **14c** (Scheme 3, Table 2, entries 2 and 3). The diastereomeric excess (de) was low (38% de) for the product **14b** (X = DAAO). Subsequent reduction of the mixture of diastereomeric products yielded a mixture of the homoallylic alcohols **1** and *ent*-**1**. The purified mixture of the two enantiomeric alcohols turned out to be levorotatory, which proved the absolute configuration of the major enantiomer to be *R*. The enantiomeric excess (ee) of this sample was deduced from its optical purity [$[\alpha]_D = -7.9$ ($c = 1.0$, $CHCl_3$), 36% ee] and it correlated well with the value expected due to the diastereomeric excess of the corresponding ester **14b**. Similarly, the products of deconjugation and reduction of the gulose-based ester **7c** were levorotatory. The auxiliary-induced diastereoselectivity determined from ester **14c** (X = DAGuO) was moderate (66% de) which translated into a moderate product enantioselectivity in favor of alcohol *ent*-**1** [$[\alpha]_D = -14.6$ ($c = 1.0$, $CHCl_3$), 66% ee].

In view of the desired diastereoface selection, the D-fructose-based ester **7d** performed equal to the other esters and contrary to our desire (Scheme 3, Table 2, entry 4). Apparently, the differentiation of the diastereotopic faces is more effective than for esters **7b** and **7c** leading to the corresponding (*R*)-products **14d** and *ent*-**1** with high excess. The ester **14d** was obtained in >95% de, and the reduction product *ent*-**1** exhibited an optical purity of >95% [$[\alpha]_D = -22.2$ ($c = 1.0$, $CHCl_3$)].

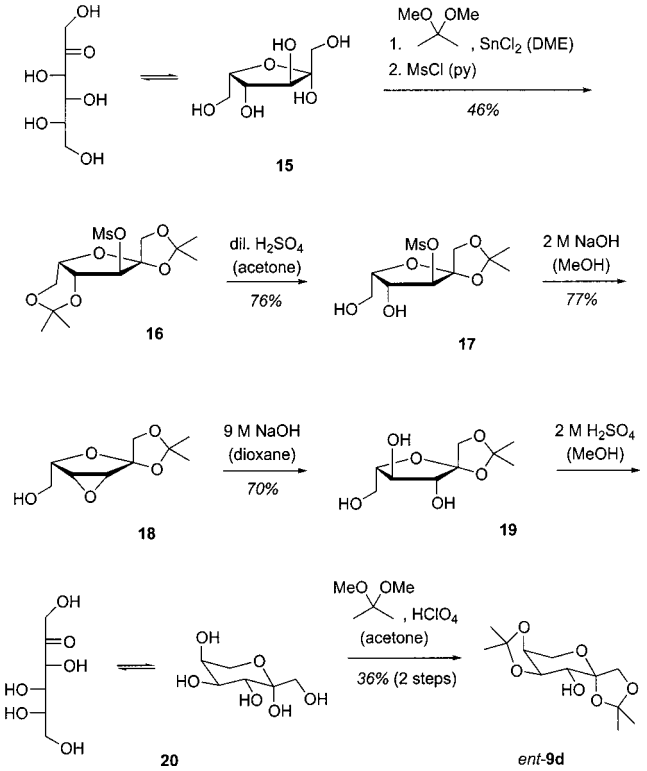
Despite the fact that this result was disappointing with regard to the direction of the face selectivity, we considered the high auxiliary-induced diastereoselectivity beneficial. Whereas the enantiomer of D-glucose is synthetically difficult to access, L-fructose can be prepared from the commercially available, inexpensive starting material L-sorbose. Instead of continuing the tests with D-carbohydrate derivatives we decided at this point in time to possibly shorten our synthetic effort by the preparation of diacetone L-fructopyranose. Its conversion to the ester *ent*-**7d** should yield the desired alcohol **1** upon photodeconjugation and reduction. As precedence for the preparation of L-fructose, we attempted to follow a procedure by Chen and Whistler[13] according to which the transformation is conducted as a one-pot reaction or as a sequence of two one-pot reactions. The second variant includes the isolation of a mesylate (see compound **16** in Scheme 4) as the reaction intermediate. The inversion of two stereogenic centers was achieved via epoxide formation and consecutive ring opening in an intermediate furanose. Unfortunately, we encountered problems in the ring opening of the intermediate epoxide (see compound **18** in Scheme 4), which did not go to completion even after heating the reaction mixture in aqueous acetone for an extended period of time. The alternative procedure[14] we considered reported the isolation of intermediates starting from a protected L-sorbopyranose and appeared easier to follow. The first step of the synthesis, however, requires a 10-fold (w/w) excess of

(12) Recent examples: (a) Takano, S.; Tanaka, M.; Seo, K.; Hirama, M.; Ogasawara, K. *J. Org. Chem.* **1985**, *50*, 931−936. (b) Bandony, R.; Maliverney, C. *Tetrahedron* **1988**, *44*, 471−480. (c) Faure, S. S.; Piva, O. *Synlett* **1998**, 1414−1416.

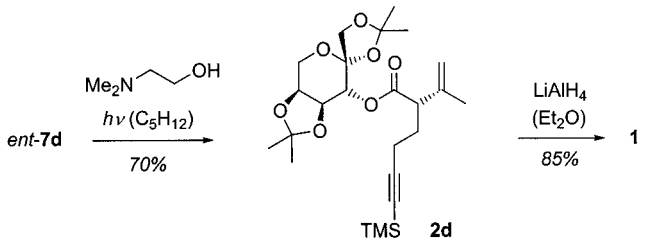
(13) (a) Chen, C.-C.; Whistler, R. L. *Carbohydr. Res.* **1988**, *175*, 265−271. (b) Isopropylidene formation: Morgenlie, S. *Carbohydr. Res.* **1982**, *107*, 137−141.

(14) Gizaw, Y.; BeMiller, J. N. *Carbohydr. Res.* **1995**, *266*, 81−85.

Scheme 4



Scheme 5



$CuSO_4$ relative to the starting material, a fact which shed doubt on its suitability for a potentially necessary scale-up.

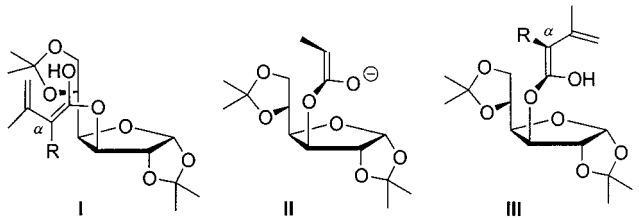
Consequently, we attempted to modify the former procedure[13a] by isolating intermediate products. By this means we were able to control the reaction conditions and to guarantee a complete conversion in each step. As we find this protocol useful it is briefly outlined in Scheme 4 in which all intermediates are depicted. One key modification was the use of NaOH in *dioxane* for the ring opening of epoxide **18** to the triol **19**. Overall, the reaction sequence **15** → **19** proceeded in a yield of 19% and is amenable to scale-up.

Having L-fructose (**20**) in hand, it was converted to the desired diacetone L-fructose *ent*-**9d** (Scheme 4), which was taken through the seqeuence of steps already reported for the D-enantiomer (cf. Scheme 2). The senecio acid ester *ent*-**7d** was obtained in an overall yield of 55% starting from the alcohol *ent*-**9d**. The final conversion to the desired alcohol proceeded as depicted in Scheme 3 for the D-sugars. Deconjugation of the ester *ent*-**7d** gave exclusively the β,γ-unsaturated product **2d**, which was reduced to the enantiomerically pure target compound **1**. The facial diastereoselection was as desired (>95% de) and the reduction proceeded smoothly (Scheme 5).

Discussion

Two facts render any discussion of the conformational behavior of carbohydrates in the course of a stereoselective reaction difficult. First, the number of stereogenic centers is comparably large, and second, multiple Lewis acid/Lewis base interactions due to the presence of several oxygen atoms are possible. Diacetone D-fructopyranose (**9d**) has been previously employed[15,16] as a chiral auxiliary in Diels−Alder reactions and the stereochemical outcome of the reactions has been discussed.[17] These reactions were promoted by aluminum Lewis acids that not only coordinate to the carbonyl oxygen atom of the acrylate dienophile but also to an oxygen atom of the sugar by chelation. Hence, the analogy to the enols we studied is not particularly close.

A possible discussion is further complicated by the known fact that the face discrimination in the protonation of enols depends on the proton source. Piva et al. postulated a conformation **I** to account for the *Si*-face protonation (priority: isopropenyl > R) of DAGO-derived enols by *N*,*N*-dimethylaminoethanol.[6d] Contrary to that, the enolate alkylation of analogous *O*-(*E*)-enolates was suggested to occur via conformation **II** with the enolate oxygen pointing toward the furanose ring due to metal chelation.[18] Although this hypothesis was questioned,[19] it nicely corroborates the outcome of the facial diastereoselectivity in the enolate alkylation of the gulofuranose-(DAGuO)[19] and allofuranose-based (DAAO)[18] esters. The conformation **III** which is related to **II** would equally well explain the stereochemical outcome recorded for the photodeconjugation reaction of DAGO-based senecio acid esters. The consensus is that it is the 5,6-isopropylidene but not the 1,2-isopropylidene acetal which is responsible for the face discrimination in esters of DAGOH and DAGuOH.



If the oxygen atom of DAGO-derived ester enolates is silylated[20] or if α-unsubstituted DAGO enol ethers[21] are

(15) (a) Ferreira, M. L. G.; Pinheiro, S.; Perrone, C. C., Costa, P. R. R.; Ferreira, V. F. *Tetrahedron*: *Asymmetry* **1998**, *9*, 2671−2680. (b) Enholm, E. J., Jiang, S. *J. Org. Chem.* **2000**, *65*, 4756−4758.

(16) Review on auxiliaries employed in cycloaddition reactions: Rück-Braun, K.; Kunz, H. *Chiral Auxiliaries in Cycloadditions*, Wiley-VCH: Weinheim 1999.

(17) Other references to the use of diacetone D-fructopyranose as auxiliary: (a) Heathcock, C. H.; White, C. T.; Morrison, J. J.; VanDerveer, D. *J. Org. Chem.* **1981**, *46*, 1296−1309. (b) Kossmehl, G.; Volkheimer, J. *Liebigs Ann.* **1989**, 1127−1130. (c) Scherer, S., Diploma thesis, TU Darmstadt, 1992. (d) Madsen, J.; Clausen, R. P.; Hazell, R. G.; Jacobsen, H. J.; Bols, M.; Perry, C. C. *Acta Chem. Scand.* **1998**, *52*, 1165−1170. (e) Nouguier, R.; Béraud, V.; Vanelle, P.; Crozet, M. P. *Tetrahedon Lett.* **1999**, *40*, 5013−5014.

(18) Kunz, H.; Mohr, J. *Chem. Commun.* **1988**, 1315−1317.

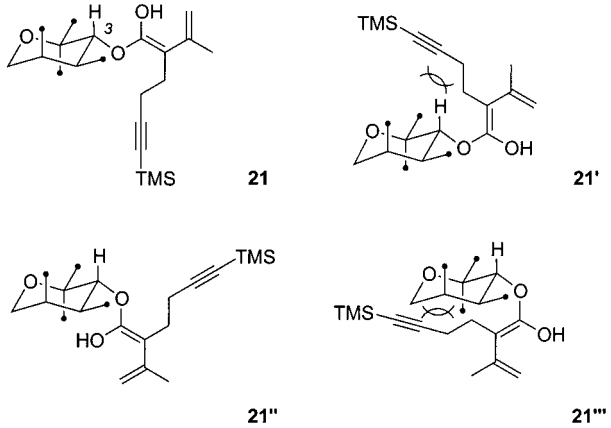
(19) Mulzer, J.; Hiersemann, M.; Buschmann, J.; Luger, P. *Liebigs Ann.* **1996**, 649−654.

(20) Angiborud, P.; Chaumette, J. L.; Desmurs, J. R., Duhamel, L.; Peé, G.; Valnot, J. Y.; Duhamel, P. *Tetrahedron*: *Asymmetry* **1995**, *6*, 1919−1932.

(21) (a) Arnold, T.; Orschel, B.; Reissig, H.-U. *Angew. Chem.* **1992**, *104*, 1084−1086; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1033−1035. (b) Kaluza, Z.; Furman, B.; Patel, M.; Chmielewski, M. *Tetrahedron*: *Asymmetry* **1994**, *5*, 2179−2186.

employed the mode of electrophilic attack is inverted as compared to the enolate alkylation.

Possible conformations accessible for the diacetone L-fructopyranose-based enol **21** which is an intermediate in the transformation *ent*-**7d** → **2d** are depicted schematically below. The black dots represent the cyclic acetals which have been omitted for clarity. Rotation around the unrestricted O−C-bonds gives rise to four conformers. Force field calculations (MM3, Hyperchem 5.1) and molecular models reveal a clear preference of **21** vs **21″** and of **21′** vs **21‴**. This preference is in line with the most stable conformations acrylates of secondary alcohols are known to adopt.[22] The carbonyl oxygen atom and the hydrogen atom are eclipsed as are the enol OH group and the hydrogen atom at C-3 in the enol **21**.



Protonation of the enol in its preferred conformation **21** from the *Re*-face accounts for the observed stereoselectivity. The 1,2-isopropylidene acetal is considered to be responsible for the face discrimination. Possibly, the bulky acid requires the enol to be exposed at the outer sphere of the molecule favoring **21** over **21″**. Hydrogen bridging to the pyranose oxygen atom is impossible for the enol OH group. Contrary to that, hydrogen bridging is possible to a furanose oxygen atom a fact which might explain the enhanced population of conformation **III** in the DAGO-case. Conformation **III** corresponds to conformation **21″** and conformation **I** corresponds to conformation **21′**. The face discrimination observed for the photodeconjugation of esters **7b** and **7c** can be explained based on conformations analogous to **III**. In line with the results of the enolate alkylations (vide supra),[18,19] the enol protonation occurs from the same face, irrespective what alcohol DAGOH, DAAOH, or DAGuOH is used as the auxiliary.

Conclusion and Outlook

In summary, diacetone L-fructopyranose (*ent*-**9d**) was identified as a chiral auxiliary which can be used for the stereoselective photodeconjugation of α-alkylated senecio acid derivatives. A high diastereomeric excess was achieved in the corresponding reaction of ester *ent*-**7d** to the diastereomerically pure *β*,*γ*-unsaturated product **2d**. Reduction yielded the alcohol **1** in high optical purity. It is projected that the reaction is applicable to other related 2-substituted senecio acids and their conversion to homoallylic alcohols. The face discrimination is opposite to the one recorded with the well-established and frequently used diacetone-D-glucose (DAGOH) derived enoates. Diacetone L-fructopyranose might consequently serve as a useful supplement to DAGOH in photodeconjugation reactions giving access to products that are enantiomeric to the products obtained employing DAGOH as the auxiliary.

Experimental Section

General Methods. For general remarks see ref 23. Flash chromatography[24] was carried out using silica gel (Merck, 230−400 mesh) and the reported solvent mixtures of *tert*-butyl methyl ether (TBME)/pentane (P) or ethyl acetate (EtOAc)/hexanes (Hex) as eluents. Solvents used for chromatography (Ac = acetone, Tol = toluene) were distilled prior to use. Elemental analyses were carried out in the Departement of Chemistry, University of Marburg on an Elementar vario EL instrument. Optical rotations were measured on a Perkin-Elmer 241MC polarimeter using sodium low-pressure light in a standard quartz rotation cell.

(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-*O*-yl) 3-Oxobutanoate (11a).[6d] **Typical Procedure A.** (1,2:5,6)-Di-*O*-isopropylidene-D-glucose (**9a**, 15.2 g, 57.6 mmol) was added to a stirred solution of acetyl Meldrum's acid (13.2 g, 60.0 mmol) in toluene (100 mL). The solution was refluxed for 8 h and subsequently concentrated in vacuo. Flash chromatography (TBME/P = 20:80) yielded compound **11a** as a slightly yellow oil (19.8 g, 100%). ^{1}H NMR: δ = 1.31 (s, 6H), 1.40 (s, 3H), 1.52 (s, 3H), 2.28 (s, 3H), 3.47 (d, J = 17.1 Hz, 1H), 3.55 (d, J = 17.1 Hz, 1H), 3.97−4.11 (m, 2H), 4.15−4.25 (m, 2H), 4.57 (d, J = 3.8 Hz, 1H), 5.27−5.33 (m, 1H), 5.87 (d, J = 3.8 Hz, 1H). ^{13}C NMR: δ = 26.4, 26.8, 26.9, 28.2, 30.5, 50.6, 60.8, 71.6, 72.0, 74.1, 75.1, 103.8, 110.1, 112.6, 167.1, 201.9. The NMR data were in agreement with the reference data.[6d]

(1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranos-3-*O*-yl) 3-Oxobutanoate (11b). According to typical procedure A, 6.0 g of (1,2:5,6)-di-*O*-isopropylidene-D-allose[9] (**9b**, 23 mmol) yielded 7.9 g of the ester **11b** (100%). R_f = 0.26 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 1750 cm^{-1} (s, C=O), 1721 (s, C=O). ^{1}H NMR: δ = 1.28 (s, 3H), 1.29 (s, 3H), 1.36 (s, 3H), 1.47 (s, 3H), 2.25 (s, 3H), 3.44 (s, 2H), 3.83 (dd, J = 8.6, 5.7 Hz, 1H), 4.01 (dd, J = 8.6, 6.8 Hz, 1H), 4.08 (dd, J = 4.5, 8.5 Hz, 1H), 4.23 (dt, J = 5.7, 5.8 Hz, 1H), 4.79 (dd, J = 5.1, 3.9 Hz, 1H), 4.84 (dd, J = 5.1, 8.6 Hz, 1H), 5.78 (d, J = 3.9 Hz, 1H). ^{13}C NMR: δ = 24.8, 26.1, 26.5, 26.6, 29.7, 49.8, 65.5, 73.3, 74.9, 77.4, 77.4, 104.0, 109.8, 113.0, 166.0, 199.5. $[\alpha]^{20}_D$ = +76.8 (c = 5.3, $CHCl_3$). Anal. Calcd for $C_{16}H_{24}O_8$ (344.36): C, 55.81; H, 7.02. Found: C, 55.91; H, 6.77.

(1,2:5,6-Di-*O*-isopropylidene-α-D-gulofuranos-3-*O*-yl) 3-Oxobutanoate (11c). According to typical procedure A, 2.0 g of (1,2:5,6)-di-*O*-isopropylidene-D-gulose[9a] (**9c**, 7.7 mmol) yielded 2.03 g of the ester **11c** as a colorless oil (77%). R_f = 0.49 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 1755 cm^{-1} (s, C=O), 1723 (s, C=O). ^{1}H NMR: δ = 1.35 (s, 3H), 1.37 (s, 3H), 1.43 (s, 3H), 1.55 (s, 3H), 2.29 (s, 3H), 3.52 (s, 2H), 3.55 (dd, J = 8.6, 7.2 Hz, 1H), 4.06 (dd, J = 8.6, 6.4 Hz, 1H), 4.09 (dd, J = 8.9, 6.6 Hz, 1H), 4.55 (dt, J = 5.8, 4.0 Hz, 1H), 4.83 (dd, J = 5.8, 4.0 Hz, 1H), 5.09 (dd, J = 5.8, 6.6 Hz, 1H), 5.81 (d, J = 4.0 Hz, 1H). ^{13}C NMR: δ = 25.1, 26.6, 26.6, 26.8, 26.9, 49.6, 66.2, 72.5, 74.9, 78.5, 81.1, 105.0, 109.3, 114.6, 165.8, 182.9. $[\alpha]^{20}_D$ = +58.8 (c = 0.9, $CHCl_3$). Anal. Calcd for $C_{16}H_{24}O_8$ (344.36): C, 55.81; H, 7.02. Found: C, 56.02; H, 6.81.

(1,2:4,5-Di-*O*-isopropylidene-α-D-fructopyranos-3-*O*-yl) 3-Oxobutanoate (11d). According to typical procedure A, 6.5 g (1,2:4,5)-di-*O*-isopropylidene-D-fructose[11] (**9d**, 25 mmol) yielded 8.64 g of the ester **11d** (96%) as a solid. R_f = 0.26 (TBME/P = 20:80). Mp: 63−65 °C. IR (film): $\tilde{\nu}$ = 1749 cm^{-1} (s, C=O); 1720 (s, C=O). ^{1}H NMR: δ = 1.36 (s, 3H), 1.38 (s,

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3H), 1.48 (s, 3H), 1.54 (s, 3H), 2.29 (s, 3H), 3.53 (d, J = 15.5 Hz, 1H), 3.59 (d, J = 15.5 Hz, 1H), 3.94 (d, J = 13.3 Hz, 1H), 3.97 (d, J = 13.3 Hz, 1H), 4.07 (d, J = 13.5 Hz, 1H), 4.13 (dd, J = 13.5, 2.2 Hz, 1H), 4.25 (dd, J = 5.4, 2.2 Hz, 1H), 4.29 (dd, J = 7.7, 5.4 Hz, 1H), 5.14 (d, J = 7.7 Hz, 1H). ^{13}C NMR: δ = 26.4, 26.8, 26.9, 28.2, 30.5, 50.6, 60.8, 71.6, 72.0, 74.1, 75.1, 103.8, 110.1, 112.6, 167.1, 189.9. $[\alpha]^{20}_D = -149.0$ (c = 0.9, $CHCl_3$). Anal. Calcd for $C_{16}H_{24}O_8$ (344.36): C, 55.81; H, 7.02. Found: C, 55.51; H, 7.20.

(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-*O*-yl) 2-Acetyl-6-trimethylsilyl-5-hexynoate (12a). Typical Procedure B. A solution of the acetoacetate **11a** (4.5 g, 13 mmol) in THF (10 mL) was added to a suspension of pentane-washed sodium hydride (60% in mineral oil, 390 mg, 15.1 mmol) in THF (20 mL) at 0 °C. After hydrogen evolution ceased, the solution was kept at 0 °C for 2 h and 1-iodo-4-(trimethylsilyl)-3-butyne[1] (3.3 g, 13 mmol) was added rapidly to the stirred solution. The solution was heated under reflux for 48 h and hydrolyzed with 20 mL of a saturated NH_4Cl solution, and the layers were separated. The aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (TBME/P = 20:80) to yield compound **12a** as a slightly yellow oil (2.81 g, 46%). Mixture of diastereoisomers, dr = 51/49. R_f = 0.34 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 2175 cm^{-1} (s, C≡C); 1749 (s, C=O); 1720 (s, C=O). ^{1}H NMR: δ = 0.13 (s, 9H), 1.29 (s, 3H), 1.31 (s, 3H), 1.390 (s, 1.5H), 1.394 (s, 1.5H), 1.51 (s, 3H), 2.03−2.10 (m, 2H), 2.26 (s, 1.5H), 2.28 (s, 1.5H), 2.27−2.38 (m, 2H), 3.68 (t, J = 7.4 Hz, 0.5H), 3.74 (t, J = 7.1 Hz, 0.5H), 3.98 (dd, J = 8.0, 2.3 Hz, 1H), 4.09 (dd, J = 8.0, 4.3 Hz, 1H), 4.14−4.28 (m, 2H), 4.47 (d, J = 3.5 Hz, 1H), 5.31 (d, J = 2.3 Hz, 0.5H), 5.34 (d, J = 1.5 Hz, 0.5H), 5.85 (d, J = 3.8 Hz, 0.5H), 5.87 (d, J = 4.0 Hz, 0.5H). ^{13}C NMR: δ = 0.0, 17.7, 25.1, 26.2, 26.7, 26.8, 26.9, 29.0, 29.4, 35.3, 49.4, 57.7, 58.4, 67.5, 67.7, 72.3, 76.7, 80.0, 80.1, 83.1, 83.3, 104.8, 104.9, 105.1, 109.5, 112.4, 167.9, 168.0, 201.8, 202.3. HRMS ($C_{22}H_{33}O_8Si$): calcd 453.1945, found 453.1934.

(1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranos-3-*O*-yl) 2-Acetyl-6-trimethylsilyl-5-hexynoate (12b). Following typical procedure B, 7.5 g of compound **11b** (22.5 mmol) was converted to ester **12b** (5.84 g, 56%). Mixture of diastereoisomers, dr = 50/50. R_f = 0.16 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1740 (s, C=O). ^{1}H NMR: δ = 0.12 (s, 9H), 1.30 (s, 3H), 1.31 (s, 3H), 1.40 (s, 3H), 1.49 (s, 3H), 1.98−2.10 (m, 2H), 2.27 (s, 3H), 2.42−2.19 (m, 2H), 3.66 (t, J = 7.5 Hz, 0.5H), 3.68 (t, J = 7.3 Hz, 0.5H), 3.85 (dd, J = 8.6, 5.7 Hz, 1H), 4.03−4.12 (m, 2H), 4.24 (dd, J = 5.4, 11.4 Hz, 1H), 4.78 (dd, J = 5.3, 8.2 Hz, 1H), 4.80−4.87 (m, 1H), 5.83 (d, J = 4.0 Hz, 1H). ^{13}C NMR: δ = 0.0, 17.4, 17.5, 26.2, 26.47, 26.49, 26.50, 26.7, 26.8, 26.9, 29.0, 29.1, 57.7, 58.1, 65.8, 65.9, 73.5, 73.9, 74.86, 74.98, 77.2, 77.6, 77.9, 85.9, 86.0, 98.5, 104.2, 104.3, 109.96, 109.98, 113.0, 168.3, 168.5, 201.3, 201.6. Anal. Calcd for $C_{23}H_{36}O_8Si$ (468.61): C, 61.77; H, 8.21. Found: C, 61.61; H, 8.46.

(1,2:5,6-Di-*O*-isopropylidene-α-D-gulofuranos-3-*O*-yl) 2-Acetyl-6-trimethylsilyl-5-hexynoate (12c). According to typical procedure B, 2.0 g (5.9 mmol) of compound **11c** was converted to ester **12c** in 44% yield (1.22 g). Mixture of diastereoisomers, dr = 53:47. R_f = 0.16 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1750 (s, C=O), 1721 (s, C=O). ^{1}H NMR: δ = 0.13 (s, 9H), 1.32 (s, 1.5H), 1.34 (s, 1.5H), 1.36 (s, 1.5H), 1.37 (s, 1.5H), 1.43 (s, 1.5H), 1.44 (s, 1.5H), 1.55 (s, 1.5H), 1.55 (s, 1.5H), 2.01−2.11 (m, 2H), 2.28 (s, 1.5H), 2.29 (s, 1.5H), 2.20−2.45 (m, 2H), 3.55 (dd, J = 8.7, 6.7 Hz, 0.5H), 3.56 (dd, J = 8.7, 6.7 Hz, 0.5H), 3.71 (t, J = 7.2 Hz, 0.5H), 3.75 (t, J = 7.2 Hz, 0.5H), 4.03 (dd, J = 14.3, 6.7 Hz, 0.5H), 4.06 (dd, J = 14.3, 6.7 Hz, 0.5H), 4.09 (dd, J = 14.3, 6.7 Hz, 0.5H), 4.10 (dd, J = 14.3, 6.7 Hz, 0.5H), 4.49 (dd, J = 9.2, 6.7 Hz, 0.5H), 4.57 (dt, J = 9.2, 6.7 Hz, 0.5H), 4.83 (dd, J = 4.0, 5.5 Hz, 1H), 5.02 (dd, J = 5.5, 6.2 Hz, 0.5H), 5.06 (dd, J = 5.5, 6.2 Hz, 0.5H), 5.80 (d, J = 4.0 Hz, 0.5H), 5.81 (d, J = 4.0 Hz, 0.5H). ^{13}C NMR: δ = 0.0, 17.66, 17.71, 25.1, 26.6, 26.66, 26.67, 26.94, 26.97, 57.6, 58.1, 66.2, 66.4, 72.88, 72.93, 74.90, 74.95, 78.1, 78.6, 81.0, 81.1, 86.5, 104.6, 104.9, 105.0, 109.3, 109.5, 114.4, 114.7, 168.2, 168.3, 200.9, 201.1. Anal. Calcd for $C_{23}H_{36}O_8Si$ (468.61): C, 58.95; H, 7.75. Found: C, 58.47; H, 6.47.

(1,2:4,5-Di-*O*-isopropylidene-α-D-fructopyranos-3-*O*-yl) 2-Acetyl-6-(trimethylsilyl)-5-hexynoate (12d). According to typical procedure B, 5.0 g (14.5 mmol) of compound **11d** yielded 2.9 g of the ester **12d** (43%). Mixture of diastereoisomers, dr 53:47. R_f = 0.36 (TBME/P = 20/80). IR (KBr): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1748 (s, C=O), 1721 (s, C=O). ^{1}H NMR: δ = 0.15 (s, 9H), 1.37 (s, 1.5H), 1.37 (s, 1.5H), 1.40 (s, 1.5H), 1.42 (s, 1.5H), 1.48 (s, 1.5H), 1.49 (s, 1.5H), 1.54 (s, 1.5H), 1.56 (s, 1.5H), 2.06−2.16 (m, 2H), 2.33 (s, 1.5H), 2.35 (s, 1.5H), 2.25−2.39 (m, 2H), 3.73−3.79 (m, 1H), 3.84 (dd, J = 9.3, 6.0 Hz, 1H), 3.95 (dd, J = 9.3, 5.3 Hz, 1H), 4.09−4.15 (m, 2H), 4.20−4.22 (m, 1H), 4.28 (dt, J = 7.5, 5.3 Hz, 1H), 5.15 (d, J = 8.1 Hz, 0.5H), 5.16 (d, J = 7.7 Hz, 0.5H). ^{13}C NMR: δ = 0.00, 26.0, 26.1, 26.1, 26.3, 26.5, 26.6, 26.9, 27.6, 29.0, 29.5, 57.8, 58.2, 60.5, 71.3, 71.6, 71.8, 73.6, 74.5, 74.6, 86.1, 103.3, 103.4, 105.0, 109.6, 109.7, 111.9, 112.0, 169.1, 169.2, 201.7, 202.1. Anal. Calcd for $C_{23}H_{36}O_8Si$ (468.61): C, 58.95; H, 7.74. Found: C, 59.22; H, 7.93.

(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-*O*-yl) 2-[1′-(Diethylphosphoryloxy)-ethylidene]-6-trimethylsilyl-5-hexynoate (13a). Typical Procedure C. Sodium hydride (60% in mineral oil, 210 mg, 7.0 mmol, washed with pentane) was suspended in ether (50 mL) and cooled to 0 °C. A solution of compound **12a** (2.8 g, 6.0 mmol) in ether (17 mL) was added to this mixture dropwise via cannula. The solution was warmed to room temperature over 30 min and cooled again to 0 °C. Diethyl chlorophosphate (1.01 mL, 7.0 mmol) was added dropwise, and the solution was stirred at room temperature for 16 h. The solution was hydrolyzed with NH_4-Cl (saturated aqueous, 50 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (EtOAc/Hex = 40/60) to yield compound **13a** as a yellow oil (2.8 g, 77%). R_f = 0.15 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 2175 cm^{-1} (s, C≡C); 1732 (s, C=O); 1652 (w, C=C). ^{1}H NMR: δ = 0.11 (s, 9H), 1.29 (s, 3H), 1.30 (s, 3H), 1.31−1.39 (m, 6H), 1.38 (s, 3H), 1.51 (s, 3H), 2.18 (d, J = 1.8 Hz, 3H), 2.32−2.38 (m, 2H); 2.45−2.53 (m, 2H); 3.99 (dd, J = 8.5, 4.4 Hz, 1H); 4.09 (dd, J = 8.5, 5.9 Hz, 1H); 4.13−4.25 (m, 6H), 4.62 (dd, J = 1.8, 3.7 Hz, 1H), 5.29 (dd, J = 1.8, 3.7 Hz, 1H), 5.89 (d, J = 3.7 Hz, 1H). ^{13}C NMR: δ = 0.0, 16.1 (d, J = 6.9 Hz), 18.3, 19.3, 25.1, 26.3, 26.8, 27.0, 28.4, 64.6 (d, J = 3.9 Hz), 67.5, 72.5, 76.3, 80.2, 83.2, 85.4, 105.3, 105.6, 109.4, 112.1, 117.0 (d, J = 8.0 Hz), 152.2 (d, J = 8.1 Hz), 164.6. ^{31}P NMR: δ = −6.54 (s). $[\alpha]^{20}_D = -28.4$ (c = 0.85, $CHCl_3$). HRMS ($C_{27}H_{45}O_{11}PSi$): calcd 589.2234, found 589.2229.

(1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranos-3-*O*-yl) 2-[1′-(Diethylphosphoryloxy)ethylidene]-6-trimethylsilyl-5-hexynoate (13b). According to typical procedure C, 5.13 g (10.95 mmol) of compound **12b** yielded phosphoenolate **13b** (6.0 g, 91%). R_f = 0.21 (TBME/P = 50/50). IR (film): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1732 (s, C=O), 1645 (w, C=C). ^{1}H NMR: δ = 0.13 (s, 9H), 1.30 (s, 3H),1 0.31−1.35 (m, 6H), 1.33 (s, 3H), 1.41 (s, 3H), 1.53 (s, 3H), 2.24 (d, J = 1.7 Hz, 3H), 2.35−2.48 (m, 2H), 2.49−2.53 (m, 2H), 3.90 (dd, J = 8.5, 6.2 Hz, 1H), 4.06 (dd, J = 8.5, 6.8 Hz, 1H), 4.17−4.23 (m, 5H), 4.24−4.28 (m, 1H), 4.80 (dd, J = 5.0, 8.6 Hz, 1H), 4.85 (dd, J = 5.0, 3.9 Hz, 1H), 5.82 (d, J = 3.9 Hz, 1H). ^{13}C NMR: δ = 0.0, 16.0 (d, J = 6.9 Hz), 18.6, 19.3, 25.1, 26.2, 26.6, 26.7, 28.3, 64.6 (d, J = 6.6 Hz), 65.7, 72.3, 76.4, 77.7, 81.3, 85.1, 104.3, 106.1, 109.9, 113.0, 115.9 (d, J = 8.2 Hz), 152.6 (d, J = 7.5 Hz), 164.3. ^{31}P NMR: δ = −6.82 (s). $[\alpha]^{20}_D = +68.7$ (c = 1.0, $CHCl_3$). Anal. Calcd for $C_{27}H_{45}O_{11}PSi$ (604.71): C, 53.63; H, 7.50. Found: C, 53.36; H, 7.49.

(1,2:5,6-Di-*O*-isopropylidene-α-D-gulofuranos-3-*O*-yl) 2-[1′-(Diethylphosphoryloxy)ethylidene]-6-trimethylsilyl-5-hexynoate (13c). A 1.14 g (2.43 mmol) portion of compound **12c** was converted into 1.30 g (2.15 mmol) of phosphoenolate **13c** following typical procedure C (89%). R_f = 0.20 (TBME/P = 20:80). IR (film): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1734 (s, C=O), 1649 (w, C=C). ^{1}H NMR: δ = 0.12 (s, 9H),

1.31 (s, 3H), 1.31−1.36 (m, 6H), 1.36 (s, 3H), 1.43 (s, 3H), 1.56 (s, 3H), 2.21 (d, J = 1.8 Hz, 3H), 2.26−2.54 (m, 4H), 3.60 (dd, J = 6.6, 8.8 Hz, 1H), 4.09 (dd, J = 9.5, 7.0 Hz, 1H), 4.18 (dd, J = 6.6, 8.8 Hz, 1H), 4.20 (q, J = 7.2 Hz, 4H), 4.62 (dt, J = 6.5, 9.5 Hz, 1H), 4.84 (dd, J = 4.0, 5.5 Hz, 1H), 5.08 (dd, J = 5.5, 7.0 Hz, 1H), 5.81 (d, J = 4.0 Hz, 1H). ^{13}C NMR: δ = 0.00, 16.0 (d, J = 7.0 Hz), 18.4, 19.2, 25.2, 26.6, 27.0, 27.0, 28.5, 64.6 (d, J = 6.6 Hz), 66.7, 72.4, 75.0, 78.2, 81.3, 85.5, 105.0, 105.5, 109.1, 114.2, 116.2 (d, J = 8.2 Hz), 152.7 (d, J = 7.5 Hz), 164.8. $[\alpha]^{20}_D$ = +24.9 (c = 2.2, $CHCl_3$). Anal. Calcd for $C_{27}H_{45}O_{11}PSi$ (604.71): C, 53.63; H, 7.50. Found: C, 53.15; H, 8.68.

(1,2:4,5-Di-*O*-isopropylidene-α-D-fructopyranos-3-*O*-yl) 2-[1′-(Diethylphosphoryloxy)ethylidene]-6-trimethylsilyl-5-hexynoate (13d). A 2.80 g (5.97 mmol) portion of compound **12d** was converted to 3.25 g of phosphoenolate **13d** (5.4 mmol) following typical procedure C (90%). R_f = 0.28 (TBME/P = 50:50). IR (KBr): $\tilde{\nu}$ = 2173 cm^{-1} (s, C≡C), 1722 (s, C=O), 1655 (m, C=C). ^{1}H NMR: δ = 0.11 (s, 9H), 1.27−1.32 (m, 6H), 1.31 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 1.51 (s, 3H), 2.23 (d, J = 1.8 Hz, 3H), 2.36−2.57 (m, 4H), 3.87 (d, J = 9.4 Hz, 1H), 3.93 (d, J = 9.4 Hz, 1H), 4.06−4.11 (m, 2H), 4.15−4.28 (m, 5H), 4.31 (dd, J = 7.8, 5.3 Hz, 1H), 5.20 (d, J = 7.8 Hz, 1H). ^{13}C NMR: δ = 0.0, 16.0 (d, J = 7.0 Hz), 18.6, 19.7, 26.2, 26.4, 26.4, 27.7, 28.2, 60.6, 64.7 (d, J = 6.5 Hz), 69.9, 71.8, 73.7, 74.7, 85.3, 103.7, 105.9, 109.5, 111.9, 115.8 (d, J = 8.6 Hz), 153.9 (d, J = 7.5 Hz), 164.7. ^{31}P NMR: δ = −7.05. $[\alpha]^{20}_D$ = −84.1 (c = 1.0, $CHCl_3$). Anal. Calcd for $C_{27}H_{45}O_{11}PSi$ (604.71): C, 53.63; H 7.50. Found: C, 53.63; H, 7.51.

(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-*O*-yl) 2-(1′-Methylethylidene)-6-trimethylsilyl-5-hexynoate (7a). Typical Procedure D. A solution of methyllithium (1.4 M in diethyl ether, 7.4 mL, 10.3 mmol) was added to a suspension of copper(I) iodide (0.98 g, 5.15 mmol) in diethyl ether (57 mL) at 0 °C dropwise via syringe. A solution of phosphoenolate **13a** (2.75 g, 4.6 mmol) in ether (15 mL) was added dropwise to the cuprate solution via cannula at −78 °C and stirred for 3 h. The reaction was quenched with a solution of NH_4Cl (saturated aqueous, 25 mL), and the layers were separated. The aqueous layer was extracted with ether (3 × 50 mL), and the combined organic layers were washed with brine (100 mL). The organics were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (EtOAc/Hex = 20:80) to yield conjugated ester **7a** as colorless oil (1.76 g, 83%). R_f = 0.59 (TBME/P = 20:80). IR (film): $\tilde{\nu}$ = 2174 cm^{-1} (s, C≡C); 1721 (s, C=O); 1630 (w, C=C). ^{1}H NMR δ = 0.13 (s, 9H), 1.31 (s, 3H), 1.32 (s, 3H), 1.40 (s, 3H), 1.53 (s, 3H), 1.90 (s, 3H), 2.06 (s, 3H), 2.29 (ddd, J = 17.0, 7.8, 8.5 Hz, 1H), 2.32 (ddd, J = 17.0, 7.8, 7.2 Hz, 1H), 2.55 (t, J = 7.8 Hz, 2H), 4.00 (dd, J = 4.6, 8.5 Hz, 1H), 4.12 (dd, J = 5.9, 8.5 Hz, 1H), 4.20 (dd, J = 2.9, 8.6 Hz, 1H), 4.23 (pseudo dt, J = 8.6, 5.4 Hz, 1H), 4.55 (d, J = 3.7 Hz, 1H), 5.27 (d, J = 2.9 Hz, 1H), 5.87 (d, J = 3.7 Hz, 1H). ^{13}C NMR: δ = 0.0, 19.5, 22.8, 23.3, 25.1, 26.2, 26.6, 26.8, 29.0, 67.7, 72.4, 76.1, 80.3, 83.5, 84.8, 105.1, 106.4, 109.4, 112.2, 125.1, 148.2, 167.1. $[\alpha]^{20}_D$ = −46.6 (c = 1.45, $CHCl_3$). HRMS ($C_{23}H_{35}O_7Si$): calcd 451.2152, found 451.2149.

(1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranos-3-*O*-yl) 2-(1′-Methylethylidene)-6-trimethylsilyl-5-hexynoate (7b). A 5.69 g (9.4 mmol) portion of phosphoenolate **13b** was converted into 2.68 g of compound **7b** following typical procedure D (61%). R_f = 0.30 (TBME/P = 20:80). IR (film): $\tilde{\nu}$ = 2174 cm^{-1} (s, C≡C), 1717 (s. C=O), 1632 (w, C=C). ^{1}H NMR δ = 0.12 (s, 9H), 1.32 (s, 3H), 1.35 (s, 3H), 1.42 (s, 3H), 1.53 (s, 3H), 1.90 (s, 3H), 2.06 (s, 3H), 2.31−2.48 (m, 2H), 2.59 (t, J = 7.6 Hz, 2H), 3.90 (dd, J = 8.5, 6.0 Hz, 1H), 4.07 (dd, J = 8.5, 6.8 Hz, 1H), 4.16 (dd, J = 8.3, 4.7 Hz, 1H), 4.29 (dt, J = 6.3, 4.7 Hz, 1H), 4.83 (dd, J = 8.3, 5.2 Hz, 1H), 4.90 (dd, J = 5.2, 3.8 Hz, 1H), 5.84 (d, J = 3.8 Hz, 1H). ^{13}C NMR: δ = 0.0, 19.3, 22.8, 23.2, 25.0, 26.2, 26.5, 26.6, 29.1, 65.8, 72.9, 75.2, 77.7, 85.1, 104.2, 106.8, 109.9, 112.8, 125.0, 147.5, 167.5. $[\alpha]^{20}_D$ = +85.3 (c = 2.3, $CHCl_3$). Anal. Calcd for $C_{24}H_{38}O_7Si$ (466.64): C, 61.77; H, 8.21. Found: C, 61.48; H, 8.18.

(1,2:5,6-Di-*O*-isopropylidene-α-D-gulofuranos-3-*O*-yl) 2-(1′-Methylethylidene)-6-trimethylsilyl-5-hexynoate (7c). A 1.24 g (2.05 mmol) portion of phosphoenolate **13c** was converted into 683 mg (1.5 mmol) of compound **7c** following typical procedure D (73%). R_f = 0.42 (TBME/P = 50:50). IR (film): $\tilde{\nu}$ = 2176 cm^{-1} (s, C≡C), 1721 (s, C=O), 1632 (w, C=C). ^{1}H NMR: δ = 0.12 (s, 9H), 1.33 (s, 3H), 1.38 (s, 3H), 1.46 (s, 3H), 1.56 (s, 3H), 1.90 (s, 3H), 2.05 (s, 3H), 2.27 (ddd, J = 16.6, 8.8, 7.5 Hz, 1H), 2.40 (ddd, J = 9.0, 16.6, 5.9 Hz, 1H), 2.50−2.60 (m, 2H), 3.58 (dd, J = 8.5, 6.6 Hz, 1H), 4.10 (dd, J = 9.4, 6.9 Hz, 1H), 4.12 (dd, J = 8.5, 6.6 Hz, 1H), 4.63 (dt, J = 9.4, 6.6 Hz, 1H), 4.85 (dd, J = 5.5, 4.0 Hz, 1H), 5.11 (dd, J = 6.9, 5.5 Hz, 1H), 5.83 (d, J = 4.0 Hz, 1H). ^{13}C NMR: δ = 0.0, 19.4, 22.6, 25.1, 26.6, 26.7, 26.8, 26.9, 29.1, 66.5, 72.0, 75.1, 78.4, 81.3, 84.4, 106.2, 109.2, 114.2, 123.3, 125.0, 147.4, 167.5. $[\alpha]^{20}_D$ = +46.3 (c = 1.15, $CHCl_3$). Anal. Calcd for $C_{24}H_{38}O_7Si$ (466.64): C, 61.77; H, 8.21. Found: C, 61.97; H. 7.98.

(1,2:4,5-Di-*O*-isopropylidene-α-D-fructopyranos-3-*O*-yl) 2-(1′-Methylethylidene)-6-trimethylsilyl-5-hexynoate (7d). A 3.11 g (5.13 mmol) portion of phospoenolate **13d** was converted into 1.94 g of compound **7d** following typical procedure D (4.2 mmol, 82%). R_f = 0.65 (TBME/P = 40:60). IR (film) $\tilde{\nu}$ 2176 cm^{-1} (s, C≡C), 1721 (s, C=O), 1632 (m, C=C). ^{1}H NMR: δ = 0.12 (s, 9H), 1.23 (s, 3H), 1.29 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.79 (s, 3H), 1.95 (s, 3H), 2.31−2.40 (m, 2H), 2.57 (t, J = 7.0 Hz, 2H), 3.85 (d, J = 9.3 Hz, 1H), 3.97 (d, J = 9.3 Hz, 1H), 4.10−4.13 (m, 2H), 4.23 (ddd, J = 5.3, 2.2, 0.9 Hz, 1H), 4.32 (dd, J = 8.0, 5.3 Hz, 1H), 5.22 (d, J = 8.0 Hz, 1H). ^{13}C NMR: δ = 0.0, 19.7, 22.9, 23.4, 26.2, 26.2, 26.8, 27.7, 29.1, 60.5, 69.7, 71.9, 73.7, 74.9, 84.6, 103.9, 106.7, 109.5, 111.8, 125.1, 148.0, 167.9. $[\alpha]^{20}_D$ = −121.0 (c = 1.2, $CHCl_3$). HRMS ($C_{23}H_{35}O_7Si$): calcd 451.2152, found 451.2155.

(1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranos-3-*O*-yl) 2-Isopropenyl-6-trimethylsilyl-5-hexynoate (14a). Typical Procedure E. The α,β-unsaturated ester **7a** (2.5 mmol, 1.16 g) was dissolved in pentane (250 mL) and irradiated with a TQ150 high-pressure lamp for 8 h in the presence of 0.25 mL of *N*,*N*-dimethylaminoethanol (2.5 mmol, 223 mg). After evaporation of the solvent and purification by flash chromatography (TBME/P = 20:80), compound **14a** was obtained as a single diastereoisomer (NMR) in 85% yield (980 mg). R_f = 0.61 (TBME/P 20/80). IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (w, =C−H), 2176 (s, C≡C), 1744 (s, C=O), 1647 (C=C). ^{1}H NMR: δ = 0.13 (s, 9H), 1.28 (s, 3H), 1.29 (s, 3H), 1.37 (s, 3H), 1.50 (s, 3H), 1.71 (s, 3H), 1.81 (dt, J = 14.1, 6.8 Hz, 1H), 2.02 (dt, J = 14.1, 6.8 Hz, 1H), 2.22 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 7.8 Hz, 1H), 3.92−3.97 (m, 1H), 4.06−4.18 (m, 3H), 4.90−4.94 (m, 2H), 5.26−5.28 (m, 1H), 5.86 (d, J = 3.5 Hz, 1H). ^{13}C NMR δ = 0.0, 17.5, 19.8, 25.0, 26.1, 26.6, 26.7, 26.8, 51.7, 67.5, 72.0, 75.9, 80.3, 83.3, 85.5, 105.1, 105.7, 109.2, 112.3, 114.9, 140.9, 171.5. $[\alpha]^{20}_D$ = −43.5 (c = 1.0, $CHCl_3$). HRMS ($C_{23}H_{35}O_7Si$): calcd 451.2152, found 451.2143.

(1,2:5,6-Di-*O*-isopropylidene-α-D-allofuranos-3-*O*-yl) 2-Isopropenyl-6-trimethylsilyl-5-hexynoate (14b). Irradiation of the α,β-unsaturated ester **7b** (2.5 g, 5.36 mmol) for 6.5 h according to typical procedure E produced the β,γ-unsaturated ester **14b** (1.82 g) as a 2:1 mixture of diastereoisomers in 73% yield. R_f = 0.31 (TBME/P = 20:80). IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (w, =CH_2), 2176 (s, C≡C), 1740 (s, C=O), 1649 (m, C=C). ^{1}H NMR: δ = 0.13 (s, 9H), 1.31 (s, 2.1H), 1.32 (s, 0.9H), 1.34 (s, 0.9H), 1.34 (s, 2.1H), 1.40 (s, 0.9H), 1.41 (s, 2.1H), 1.51 (s, 2.1H), 1.53 (s, 0.9H), 1.75 (s, 0.9H), 1.77 (s, 2.1H), 1.79−1.86 (m, 1H), 2.02−2.08 (m, 1H), 2.22−2.27 (m, 2H), 3.24 (t, J = 15.2 Hz, 0.7H), 3.26 (t, J = 15.2 Hz, 0.3H), 3.85 (dd, J = 8.6, 6.0 Hz, 0.7H), 3.89 (dd, J = 8.6, 5.7 Hz, 0.3H), 4.05 (dd, J = 8.6, 6.8 Hz, 0.3H), 4.06 (dd, J = 8.6, 6.8 Hz, 0.7H), 4.13 (dd, J = 8.6, 4.5 Hz, 0.3H), 4.14 (dd, J = 8.6, 4.5 Hz, 0.7H), 4.16−4.29 (m, 1H), 4.77 (dd, J = 5.2, 8.6 Hz, 1H), 4.86 (dd, J = 4.0, 5.2 Hz, 1H), 4.92−4.95 (m, 2H), 5.81 (d, J = 4.0 Hz, 0.7H), 5.83 (d, J = 4.0 Hz, 0.3H). ^{13}C NMR: δ = 0.00, 17.5, 17.6, 19.8, 20.0, 24.9, 26.1, 26.2, 26.4, 26.5, 26.7, 26.8, 28.5, 28.6, 51.4, 51.5, 65.4, 65.6, 72.8, 72.9, 74.8, 74.9, 77.4, 77.6, 77.8, 85.2, 104.2, 106.05, 106.10, 109.8, 112.8, 114.5, 114.8, 140.9, 141.0, 172.1, 172.2. $[\alpha]^{20}_D$ = +79.3 (c = 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{38}O_7Si$ (466.64): C, 61.77; H, 8.21. Found: C, 61.61; H, 8.46.

(1,2:5,6-Di-*O*-isopropylidene-α-D-gulofuranos-3-*O*-yl) 2-Isopropenyl-6-trimethylsilyl-5-hexynoate (14c). Irradiation of α,β-unsaturated ester **7c** (470 mg, 1.0 mmol) for 3 h

according to typical procedure E produced β,γ-unsaturated ester **14c** (316 mg) as a 5:1 mixture of diastereomers (NMR) in 80% yield. $R_f = 0.14$ (TBME/P = 20:80). IR (film): $\tilde{\nu} = 3081$ cm^{-1} (w, H−C=), 2176 (s, C≡C), 1744 (s, C=O), 1647 (m, C=C). ^1H NMR (major diastereomer): $\delta = 0.13$ (s, 9H), 1.29 (s, 3H), 1.36 (s, 3H), 1.42 (s, 3H), 1.52 (s, 3H), 1.72 (s, 3H), 1.79 (ddd, $J = 14.1, 7.0, 5.7$ Hz, 1H), 2.03 (ddd, $J = 14.1, 7.0, 6.9$ Hz, 1H), 2.22 (pseudo t, $J = 7.0$ Hz, 1H), 2.23 (pseudo t, $J = 7.0$ Hz, 1H), 3.26 (dd, $J = 7.4, 8.3$ Hz, 1H), 3.53 (dd, $J = 8.5, 7.0$ Hz, 1H), 4.06 (dd, $J = 8.3, 6.0$ Hz, 1H), 4.12 (dd, $J = 8.9, 6.6$ Hz, 1H), 4.57 (dt, $J = 8.5, 6.6$ Hz, 1H), 4.84 (dd, $J = 4.0, 5.4$ Hz, 1H), 4.93−4.99 (m, 3H), 5.81 (d, $J = 4.0$ Hz, 1H). ^{13}C NMR (major diastereomer): $\delta = 0.0, 17.5, 19.6, 25.1, 26.4, 26.6, 26.9, 28.3, 51.5, 66.5, 72.3, 75.1, 77.8, 81.4, 85.7, 105.0, 109.0, 109.3, 113.9, 115.2, 140.7, 172.0$. $[\alpha]^{20}_D = +58.1$ ($c = 1.0$, $CHCl_3$). HRMS ($C_{23}H_{35}O_7Si$): calcd 451.2152, found 453.2154.

(1,2:4,5-Di-*O*-isopropylidene-α-D-fructopyranos-3-*O*-yl) 2-Isopropenyl-6-trimethylsilyl-5-hexynoate (14d). Irradiation of 1.85 g (3.96 mmol) of α,β-unsaturated ester **7d** for 5 h according to typical procedure E produced β,γ-unsaturated ester **14d** as a single diastereomer (NMR) in 70% yield (1.78 g). $R_f = 0.51$ (TBME/P = 20:80). IR (film): $\tilde{\nu} = 3075$ cm^{-1} (w, =CH_2), 2176 (s, C≡C), 1732 (s, C=O), 1645 (C=C). ^1H NMR: $\delta = 0.12$ (s, 9H), 1.33 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 1.51 (s, 3H), 1.75 (s, 3H), 1.78−1.85 (m, 1H), 1.99−2.11 (m, 1H), 2.22 (pseudo t, $J = 7.1$ Hz, 2H), 3.28 (t, $J = 7.4$ Hz, 2H), 3.79 (d, $J = 9.2$ Hz, 1H), 3.94 (d, $J = 9.2$ Hz, 1H), 4.07−4.10 (m, 2H), 4.11−4.19 (m, 1H), 4.24 (dd, $J = 7.7, 5.3$ Hz, 1H), 4.91 (s, 1H), 4.94 (s, 1H), 5.12 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR: $\delta = 0.0, 17.6, 19.9, 26.2, 26.2, 26.3, 27.7, 28.5, 51.7, 60.5, 70.4, 71.8, 73.6, 74.7, 85.3, 103.6, 105.9, 109.5, 111.9, 114.7, 141.0, 172.7$. $[\alpha]^{20}_D = -110.0$ ($c = 1.0$, $CHCl_3$). HRMS ($C_{23}H_{35}O_7Si$): calcd 451.2152, found 453.2149.

(*R*)-2-(1′-Methylethenyl)-6-(trimethylsilyl)hexyn-1-ol (*ent*-1). Typical Procedure F. A solution of the deconjugated ester **14a** (830 mg, 1.78 mmol) in ether (10 mL) was added to a suspension of lithium aluminum hydride (102 mg, 2.7 mmol) in THF (25 mL) at 0 °C dropwise via cannula. After the mixture was stirred for 3 h, the reaction was quenched by careful addition of water (102 μL), addition of a solution of sodium hydroxide (15% w/w, 102 μL), and (after 5 min) addition of more water (306 μL) $MgSO_4$ was added. The precipitate was filtered off and washed with ether. The combined organic layers were concentrated and purified by flash chromatography (EtOAc/Hex = 20:80) to yield alcohol *ent*-**1** as a colorless oil (330 mg, 88%). $R_f = 0.26$ (TBME/P = 20:80). IR (film): $\tilde{\nu} = 3373$ cm^{-1} (s, OH), 3073 (w, =CH), 2174 (s, C≡C), 1646 (w, C=C). ^1H NMR: $\delta = 0.13$ (s, 9H), 1.43 (t, br, $J = 5.1$ Hz, 1H), 1.51−1.62 (m, 2H), 1.68 (s, 3H), 2.14 (ddd, $J = 17.0, 7.8, 7.8$ Hz, 1H), 2.23 (ddd, $J = 17.0, 8.0, 6.0$ Hz, 1H), 2.40 (ddt, $J = 8.8, 8.3, 5.6$ Hz, 1H), 3.50 (dd, $J = 11.0, 3.6$ Hz, 1H), 3.56 (dd, $J = 11.0, 5.7$ Hz, 1H), 4.83 (dq, $J = 1.6, 0.9$ Hz, 1H), 4.94−4.96 (m, 1H). ^{13}C NMR: $\delta = 0.0, 17.6, 18.9, 28.2, 48.7, 63.8, 84.8, 106.8, 114.1, 144.0$. $[\alpha]^{20}_D = -22.2$ ($c = 1.2$, $CHCl_3$), −27.9 ($c = 1.1$, MeOH). HRMS ($C_{11}H_{19}OSi$): calcd 195.1205, found 195.1194.

1,2;4,5-Di-*O*-isopropylidene-3-mesylsorbofuranose (16). L-Sorbose (150 g, 0.83 mol) was suspended in 2,2-dimethoxypropane (450 mL). The mixture was warmed to 70 °C, and a solution of anhydrous $SnCl_2$ (3.9 mmol, 750 mg) in 1,2-dimethoxyethane (15 mL) was added dropwise via cannula. The mixture was refluxed until a clear solution was obtained (4−6 h). This mixture was concentrated in vacuo and dissolved in pyridine (300 mL). The solution was cooled to 0 °C, and methanesulfonyl chloride (100 mL, 99.7 g, 0.87 mol) was added dropwise to the stirred solution. The black solution was stored in a refrigerator for 14 h and at room temperature for 4 h. Water (2 L) was added, and the resulting precipitate was filtered and recrystallized from ethanol to yield compound **16** as colorless needles (131 g, 0.39 mol, 47%). $R_f = 0.40$ (Tol/Ac = 80:20). Mp: 123.5 °C. IR (KBr): $\tilde{\nu} = 1340$ cm^{-1} (s, SO_2−O), 1183 (s, SO_2−O). ^1H NMR: $\delta = 1.37$ (s, 3H), 1.41 (s, 3H), 1.46 (s, 3H), 1.54 (s, 3H), 3.15 (s, 3H), 3.91 (dd, $J = 13.0, 3.1$ Hz, 1H), 4.00 (dd, $J = 13.0, 3.2$ Hz, 1H), 4.20 (d, $J = 9.6$ Hz, 1H), 4.22 (d, $J = 3.1$ Hz, 1H), 4.24 (d, $J = 9.6$ Hz, 1H), 4.45 (dd, $J = 3.2, 1.9$ Hz, 1H), 4.87 (d, $J = 1.9$ Hz, 1H). ^{13}C NMR: $\delta = 20.0, 25.7, 25.9, 28.0, 38.8, 60.3, 72.1, 73.2, 73.2, 84.1, 98.2, 109.7, 111.6$. $[\alpha]^{20}_D = -32.1$ ($c = 1.3$, MeOH). Anal. Calcd for $C_{13}H_{22}O_8S$ (338.37): C, 46.14; H, 6.55. Found: C, 46.04; H, 6.23.

1,2-Isopropylidene-3-mesylsorbofuranose (17). The mesylate **16** (118.6 g, 0.35 mol) was dissolved in acetone (500 mL), and 500 mL of dilute H_2SO_4 (0.25% w/w) was added. A solid formed that dissolved upon stirring for 36 h. The solution was neutralized by adding solid $NaHCO_3$ and filtered. The acetone was removed under reduced pressure. Storage at 4 °C gave compound **17** as a white solid (77.8 g; 77%) that proved to be analytically pure by NMR. $R_f = 0.16$ (Ac/Tol = 20:80). Mp: 104.5 °C. IR (KBr): $\tilde{\nu} = 3440$ cm^{-1} (br, O−H), 1380 (s, SO_2−O), 1175 (s, SO_2−O). ^1H NMR $\delta = 1.32$ (s, 3H), 1.41 (s, 3H), 3.26 (s, 3H), 3.49−3.57 (m, 2H), 4.00 (d, $J = 9.3$ Hz, 1H), 4.03 (dt, $J = 6.2, 4.2$ Hz, 1H), 4.06 (d, $J = 9.3$ Hz, 1H), 4.36 (pseudo dt, $J = 5.5, 6.2$ Hz, 1H), 4.62 (d, $J = 5.7$ Hz, 1H), 4.84 (d, $J = 6.2$ Hz, 1H), 5.69 (d, $J = 5.5$ Hz, 1H). ^{13}C NMR: $\delta = 26.4, 27.1, 39.1, 62.0, 71.4, 74.5, 78.7, 84.7, 107.8, 112.3$. $[\alpha]^{20}_D = -90.5$ ($c = 1.3$, MeOH). Anal. Calcd for $C_{10}H_{18}O_8S$ (298.31): C, 40.26; H, 6.08. Found: C, 39.95; H, 6.22.

3,4-Anhydro-1,2-isopropylidene-α-L-tagatofuranoside (18). The diol **17** (50 g, 0.247 mol) was dissolved in methanol (100 mL), and aqueous NaOH (2 M, 100 mL) was added slowly. The solution was warmed to 50 °C and kept at this temperature for 4 h. TLC analysis showed complete conversion. The product was isolated by extraction with $CHCl_3$ (10 × 25 mL) after neutralization with aqueous H_2SO_4 (2 M) and addition of 0.5 L of water. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give epoxide **18** as a colorless oil (28.2 g, 77%). $R_f = 0.33$ (Ac/Tol = 20:80). IR (film): $\tilde{\nu} = 3462$ cm^{-1} (br, OH), 3061 (w, epoxide CH), 1209 (s, CO). ^1H NMR: $\delta = 1.42$ (s, 3H), 1.45 (s, 3H), 2.30 (s, br, 1H), 3.61 (d, $J = 2.6$ Hz, 1H), 3.78−3.81 (m, 3H), 3.99 (d, $J = 9.5$ Hz, 1H), 4.12 (dt, $J = 5.2, 2.6$ Hz, 1H), 4.26 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR $\delta = 25.7, 26.5, 55.2, 56.7, 61.6, 69.2, 76.9, 108.4, 111.3$. $[\alpha]^{20}_D = -33.4$ ($c = 1.1$, MeOH). Anal. Calcd for $C_9H_{14}O_5$ (202.20): C, 53.46; H, 6.98. Found: C, 53.87; H, 7.05.

1,2-*O*-Isopropylidene-fructofuranoside (19). The epoxide **18** (77 g, 0.38 mol) was dissolved in dioxane (500 mL), and aqueous NaOH (9 M, 100 mL) was added. The reaction mixture was heated at 90 °C for 24 h until TLC indicated complete consumption of the epoxide. Upon cooling to room temperature, the mixture was neutralized (aqueous H_2SO_4, 4.5 M), filtered, and concentrated in vacuo. The solid residue was extracted with MeOH (300 mL). After evaporation of the solvent, compound **19** was precipitated by addition of $CHCl_3$ as a yellow semicrystalline solid (59 g, 70%). $R_f = 0.20$ (Ac/Tol = 40:60). IR (film): $\tilde{\nu} = 3417$ cm^{-1} (s, OH). ^1H NMR: $\delta = 1.44$ (s, 3H), 1.53 (s, 3H), 2.82 (s, br, 3H), 3.67 (dd, $J = 12.5, 5.2$ Hz, 1H), 3.79 (dd, $J = 12.5, 3.1$ Hz, 1H), 3.95 (dd, $J = 5.8, 4.3$ Hz, 1H), 4.02 (ddd, $J = 5.8, 5.2, 3.1$ Hz, 1H), 4.04 (d, $J = 9.9$ Hz, 1H), 4.18 (d, $J = 4.3$ Hz, 1H), 4.31 (d, $J = 9.9$ Hz, 1H). ^{13}C NMR: $\delta = 26.6, 26.7, 61.4, 69.5, 76.2, 81.3, 82.6, 109.7, 112.3$. $[\alpha]_D^{20} = -30.6$ ($c = 1.1$, MeOH). HRMS ($C_8H_{13}O_6$): calcd 205.0712, found 205.0711.

L-Fructose (20). Compound **18** (59.0 g, 0.27 mol) was dissolved in MeOH (200 mL) and pH = 2 was adjusted by dropwise addition of aqueous H_2SO_4 (2 M). The solution was warmed to 40 °C for 2 h, cooled, and neutralized (2 M NaOH). The mixture was subsequently filtered and concentrated in vacuo. L-Fructose was obtained as a light brown oil. (33.0 g, 68%). The analytical data were in agreement with the reference data.[13a] L-Fructose was converted into compound *ent*-**9d** by a known procedure.[13b]

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Supporting Information Available: ^{13}C NMR spectra of compounds **1**, **7a**,**d**, **12a**, **13a**, **14a**,**c**,**d**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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