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Synthesis of vinylcyclopentanes via samarium(II) mediated tandem reactions

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Abstract—In the presence of either visible light or HMPA, SmI_2 reacts with some carbohydrate derived ω-iodoallylic alcohols, and their acetylated derivatives, to give vinylcyclopentanediol and vinylcyclopentanetriol derivatives.

1. Introduction

Samarium(II) iodide is a versatile reducing reagent that has been the subject of a large number of scientific papers over the past two decades.[1] The reduction of organic halides by SmI_2 in THF was first described by Kagan's group[2] and several years later Inanaga and coworkers reported that these reactions are faster when hexamethylphosphoramide (HMPA) is added to the reaction mixtures.[3a] Electrochemical studies on SmI_2/THF/HMPA solutions[3b] and X-ray structures of $SmI_2(hmpa)_4$[3c] and $[Sm(hmpa)_6]I_2$[3d] have since been published. Kinetic studies comparing SmI_2 in THF with SmI_2 in THF/HMPA,[3e] and studies on the mechanism of electron transfer (inner-sphere-type versus outer-sphere-type) between Sm(II) and organic substrates,[3f,g] have been reported. An article describing the structure and energetics of the SmI_2–HMPA complex in THF has also appeared in the literature.[3h] Together these papers have given us an appreciation of the role HMPA plays in changing the redox properties of divalent samarium.

While the addition of HMPA to SmI_2 reaction mixtures is now fairly common, significant efforts have been directed towards finding safer promoters of SmI_2 reductions. Several years ago, the groups of Ogawa,[4a] Scaiano[4b] and Molander[5] reported that irradiation of SmI_2 reaction mixtures of organic halides with visible light results in a significant reactivity enhancement. Literature reports described the efficient reduction of organic chlorides by the photoirradiation of SmI_2 reaction mixtures;[4,5] the absorbance of visible light by SmI_2 in the 560–700 nm range was attributed to a $4f^6$ to $4f^5 5d^1$ electronic transition and the observed reactivity enhancement associated with an efficient electron transfer between photoexcited SmI_2 and the organic halides.[4a] More recently, Hilmersson and collaborators have found that mixtures of SmI_2/H_2O/amine can also be successfully used to reduce alkyl halides.[6]

As well as being a popular reducing reagent for individual transformations, samarium(II) iodide is useful in promoting sequential or tandem reactions.[1d,e] In a preliminary communication from our group we reported that *E* and *Z* ω-iodoallylic acetates **1a** and **1b** react with SmI_2 in a stereodivergent manner to give the vinylcyclopentanetriol derivatives **3a** and **3b** [Fig. 1 and Table 1 (entries g and h)].[7] The vinylcyclopentane derivatives **3a** and **3b** are formed by a sequence of Sm(II) mediated steps and, at the time of our first report, our best results were obtained for reactions run at low temperature with an excess of SmI_2 in the presence of both HMPA and MeOH. In contrast, the Bu_3SnH mediated reactions of **1a** and **1b** gave the reductive cyclization compounds **6a** and **6b** [Table 3, entries a and b]. Reaction of the corresponding ω-iodoallylic alcohol **2b** with SmI_2 in THF–HMPA–MeOH under similar conditions was incomplete (Table 1, entry d); initial attempts to improve the efficiency resulted in the formation of complex mixtures and in a lower overall mass balance[8] but we have since overcome these difficulties. We have expanded our investigation so as to establish the generality of this method and to identity the factors that are important with respect to the efficiency and selectivity of these transformations.

The synthesis of functionalized cyclopentane molecules

Keywords: Alkenyl halides; Cyclisation; Samarium and compounds; Tandem or sequential reactions.
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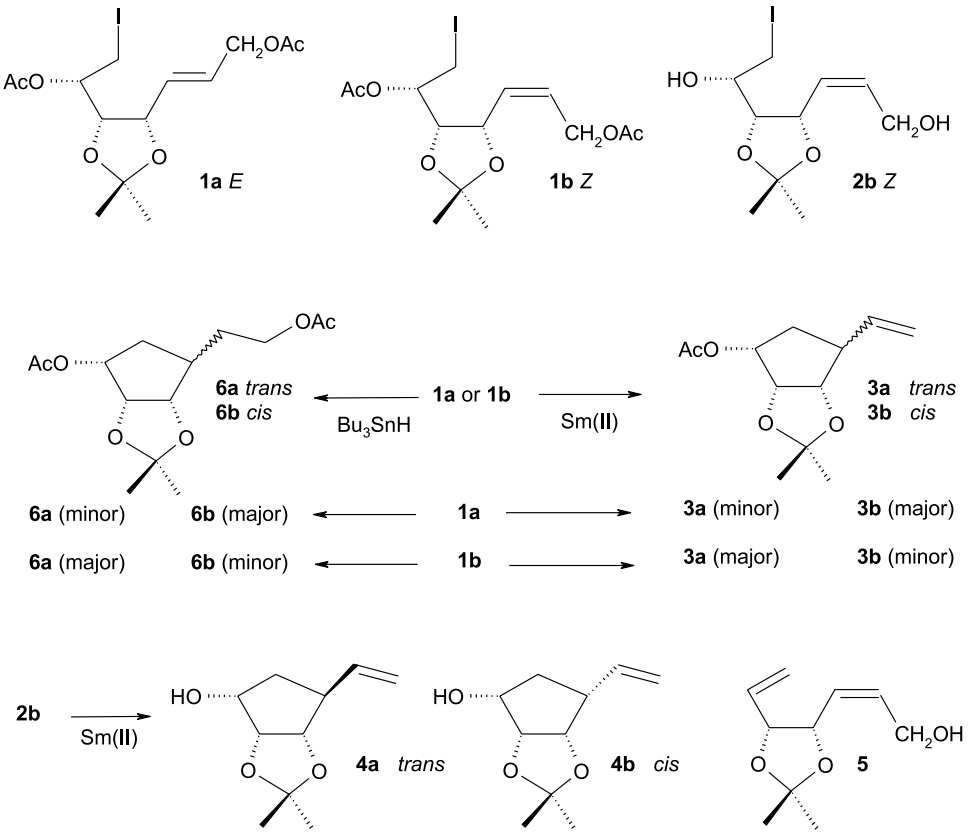


Figure 1. Reaction of **1a**, **1b** and **2b** with SmI_2 and Bu_3SnH.[7]

Table 1. SmI_2 reactions of ω-iodoallylic acetates **1a** and **1b** and ω-iodoallylic alcohols **2a** and **2b**

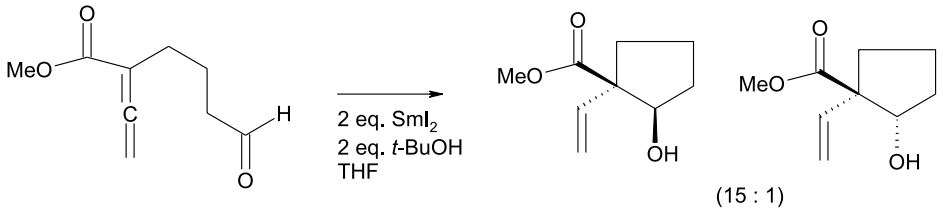
Exp.	S. mat and method[a]		SmI_2/MeOH/HMPA ratio	Isolated yields[b] (%)			
				$Tandem_{trans}$	$Tandem_{cis}$	Diene	S. mat.
a	**2b**	A2 (3 h)	3:0:0	**4a**:11	**4b**:3	**5**:3[c]	50
b	**2b**	A2 (4 h)	3:9:0	**4a**:34	**4b**:13	**5**:19[c]	36[c]
c	**2b**	D (2.5 h)	4:10:0	**4a**+**4b**:57[d] (**4a**/**4b**=89/11)		**5**:14	—[e,f]
d	**2b**	A1	5:11:20	**4a**:51	**4b** —[g]	—[g]	30
e	**2b**	B2	6:10:14.4	**4a**:76	**4b** —[e,f]	—[e,f]	—[e,f]
f	**2a**	B2	6:10:14.6	**4a**+**4b**:62[d] (**4a**/**4b**=53/47)		—[e,f]	—[e,f]
g	**1a**	A1	5:13:21	**3a**:26	**3b**:65	—[g]	—[g]
h	**1b**	A1	5:10:20	**3a**:76	**3b**:6	—[g]	—[g]
i	**1b**	A2 (o.night)	5:0:0	**3a**:34	**3b**:18	—[g]	39

[a] With the exception of entries a and i, reactions were run in THF with 1 equiv of substrate, 9–13 equiv of MeOH, 3–6 equiv of SmI_2 and 0–21 equiv of HMPA; entries a and i were run in the absence of MeOH. See Section 4 for details of Sm(II) methods.
[b] Compounds **4a** and **4b** are somewhat volatile and care must be taken to avoid loss during solvent removal steps.
[c] Isolated as a slightly impure sample as determined by NMR.
[d] In this experiment compounds **4a** and **4b** were isolated as a mixture; the *trans*/*cis* ratio was determined by ^1H NMR.
[e] Compound not detected by TLC analysis of crude products before chromatography.
[f] Not detected by GC–MS analysis of crude products before chromatography.
[g] Not detected by either TLC or NMR analysis of the crude products before chromatography.

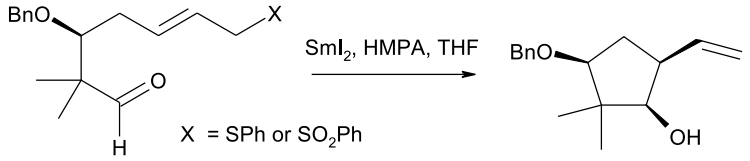
using SmI_2 mediated annulation reactions is a research objective that is shared by many groups. A number of excellent methods have been reported in the literature but only a few of these Sm(II) mediated cyclizations give direct access to vinylcyclopentanes.[1,9] Gillmann[9a] reported that intramolecular reductive coupling of an aldehyde with an allenic ester gives vinylcyclopentanols. The selectivity of the reaction was attributed to chelation with a samarium ion thus favoring formation of the diastereoisomer with the hydroxyl and ester groups *cis* to one another (Scheme 1).

Kan et al.[9b] found that aldehydes tethered to an allyl sulfide or sulfone are also reduced with samarium(II) iodide in the presence of HMPA to give vinylcyclopentanol products in a stereoselective fashion. Unsubstituted 7-(phenylthio)-5-heptenal or 7-(phenylsulfonyl)-5-heptenal substrates give the corresponding *trans* vinylcyclopentanol. Substrates with additional functional groups may react to give *cis* products preferentially as illustrated below (Scheme 2).

Molander and Harris[9c] have described the synthesis of



Scheme 1.



Scheme 2.

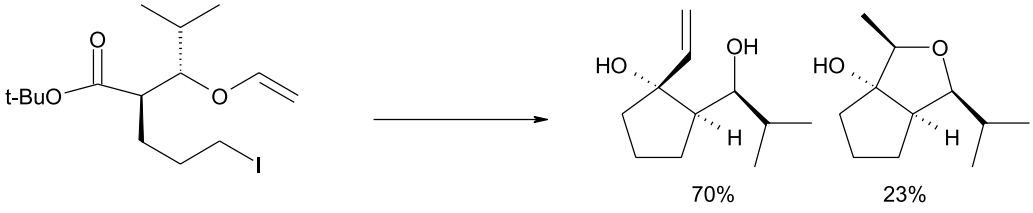
vinylcyclopentanes via a one pot, three step, nucleophilic acyl substitution/ketyl-olefin coupling/β-elimination sequence. Cyclopentanones with a pendant enol ether are generated after the first step. Samarium(II) initiated ketyl-olefin coupling is then either followed by β-elimination or by competitive protonation (Scheme 3).

Aurrecoechea and López[9d] found that ring contraction of 6-enopyranosides to form diastereomeric mixtures of vinylcyclopentanols is possible using SmI_2 and a catalytic amount of Pd(0); the major products are those in which the vinyl and hydroxyl groups of the newly formed stereocenters are *trans* to one another. A representative example is shown below. These reactions are thought to involve Pd(0)-mediated ring opening and formation of an aldehyde tethered to a π-allyl palladium complex. Reduction of the palladium complex with SmI_2 and coupling of the resulting allylsamarium species with the aldehyde function gives the vinylcyclopentanol reaction products (Scheme 4).

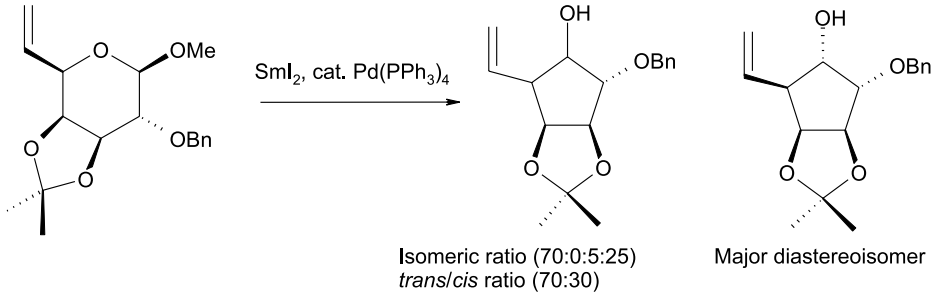
Our approach to vinylcyclopentanes differs from those of other groups (vide supra) in that our annulation reactions do not involve an addition to a carbonyl carbon. Because we have used primary alkyl iodides as substrates, our cyclization reactions result in the formation of only one new stereocenter. The following section describes the synthesis of vinylcyclopentanediol and vinylcyclopentanetriol derivatives from ω-iodoallylic alcohol substrates, or their acetylated derivatives, via a sequence of samarium(II) iodide mediated transformations using either visible light or HMPA as a promoter. The chemoselectivity and the stereoselectivity of these Sm(II) reactions were compared to those with Bu_3SnH. Reactions with Bu_3SnH gave the expected 5-*exo* radical cyclization products whereas vinylcyclopentanes were the major products of the Sm(II) mediated tandem reactions.

2. Results and discussion

The substrates for this present study were prepared by 1,2-reduction of known carbohydrate-derived conjugated *tert*-butyl esters with DIBAL.[10] After workup and chromatography the desired allylic alcohols **2a**, **2b**, **10a**, **10b** and **11**



Scheme 3.



Scheme 4.

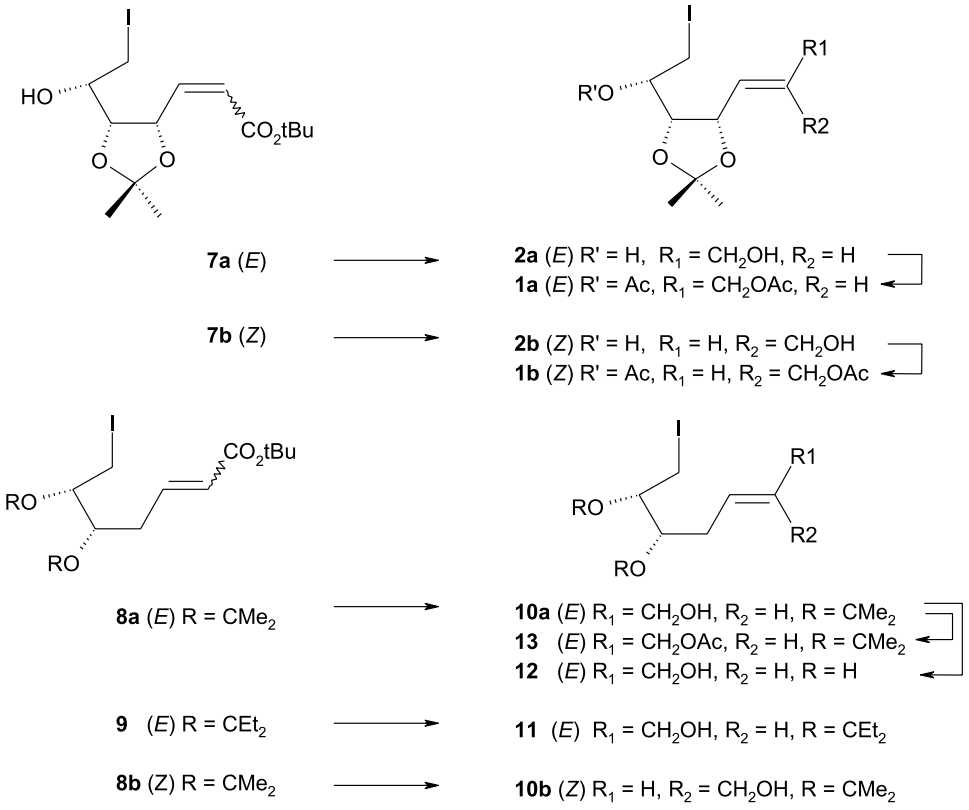


Figure 2. Preparation of ω-iodoallylic alcohols and acetates.

were isolated in moderate to good yields. Acetylation of the free hydroxyl groups of **2a**, **2b** and **10a** under standard conditions gave compounds **1a**, **1b** and **13**. The acetonide group of **10a** was removed by treatment with MeOH and an acidic resin to give the triol **12** in good yield (Fig. 2).

The experimental conditions and results of reactions with Sm(II) for **1a**, **1b**, **2a** and **2b** are shown in Table 1 and those for compounds **10a**, **10b**, **11**, **12** and **13** are summarized in Table 2. We used commercially available solutions of SmI_2 for our experiments. The SmI_2 solution was transferred dropwise, using a cannula, over ca. 10 min to a solution of the ω-iodoallylic alcohol in THF/MeOH or in THF/HMPA/MeOH under an argon atmosphere. The final concentration of the starting material was 0.015 M. It should be noted that, at the time reactions were quenched, the reaction mixtures were still either the deep blue color associated with SmI_2 in THF or the purple color associated with solutions of SmI_2 in THF/HMPA. This was also true for experiments where the reduction was incomplete, as judged by the presence of either unreacted starting material or simple reductive cyclization compounds.

Our initial investigations focused on compound **2b**. Room temperature reactions with an excess of SmI_2 in THF under ambient lighting conditions are incomplete after 3 h and gave complex mixtures of starting material, vinylcyclopentanes (**4a** and **4b**) and non-cyclized β-elimination product **5** (Table 1, entry a). The stereoselectivity of the tandem cyclization-reductive elimination process was poor. One of the reaction condition changes that we considered involved adding a proton source. We also considered either irradiating our reaction mixtures with a visible light source or changing the nature of the Sm(II) reductant by in situ coordination with HMPA ligands. Our mass balance improved when the reaction was run in the presence of MeOH but the reaction was non selective and still incomplete after 4 h at room temperature. There is an marked improvement in stereoselectivity when the Sm(II) reductions were run with either visible light or HMPA as a promoter. Photoirradiation of the reaction mixture, using a xenon lamp, allowed us to push the reduction to completion and to improve the stereoselectivity of the reaction. Unfortunately, an appreciable amount of compound **5** was formed under these conditions. We had more success using HMPA as a promoter for the sequenced reactions of **2b** but light was successfully used with some of the other substrates described in this paper (vide infra).

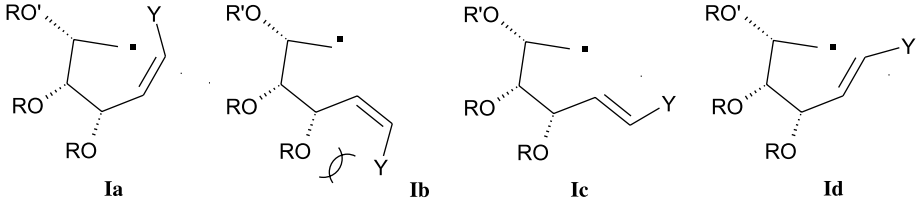
Reaction of **2b** at low temperature with 5 equiv of SmI_2 and 20 equiv of HMPA was stereoselective but incomplete (Table 1, entry d); attempts to push the reduction to completion by simply increasing the quantity of SmI_2 from 5 to 7 equiv, while keeping the SmI_2–HMPA ratio at ca. 1:4, resulted in the formation of some of compound **5**.[8] This loss of chemoselectivity is presumably due to an increase in the rate of the β-elimination reaction due to the increase in the Sm(II) concentration. This pathway, leading to **5**, is competitive with that leading to **4a** (Scheme 5). We have since found that a more successful and convenient approach is to run the reaction at room temperature with a different molar ratio of substrate, SmI_2, and HMPA (vide infra). The selectivity of the reaction was excellent and the isolated yield of **4a** was good (Table 1, entry e).

As one might expect, based on considerations of A-strain,[11]

Table 2. Reactions of 2-deoxy-D-ribose derived substrates with SmI_2–HMPA and SmI_2–hν

Exp.	S.mat.	Method[a] and SmI_2/HMPA ratio		Tandem (T_{trans},T_{cis}) and simple (S_{trans},S_{cis}) reaction product ratios[b]				Yield (%) of vinylcyclo-pentanes
				T_{trans}	T_{cis}	S_{trans}	S_{cis}	
a	**10a**	C	4:19	83	11	6	0	39[c]
b	**10a**	B1	4:19	85	13	2	0	91[d]
c	**10a**	B1	4:19	82	12	6	0	n.d.
d	**10a**	B1	4:9.5	87	2	11	0	72[d]
e	**10a**	C	4:9.5	58	7	32	3	46[d]
f	**10a**	B1	4:4.8	61	8	21	2	44[d,e]
g	**10a**	B1	4:0	16	2	9	0	n.d.[f]
h	**10a**	B2	4:0	28	11	13	3	n.d.[g]
i	**10a**	B2	4:19	90	3	7	0	58[d,h]
j	**10a**	B2	6:14	95	3	2	0	60[d,h]
k	**10a**	D	4:0	91	5	4	0	65[d]
l	**10b**	D	4:0	82	15	3	0	84[d]
m	**10b**	B2	6:14	83	10	7	0	90[d]
n	**10b**	B2	4:19	84	16	0	0	50[c]
o	**10b**	B1	4:19	83	8	9	0	56[d]
p	**13**	D	4:0	80	20	0	0	80[d]
q	**13**	B2	6:14	53	9	31	7	48[d]
r	**13**	B1	4:9.5	82	0	18	0	n.d.
s	**13**	B1	4:19	67	7	20	6	51[d]
t	**11**	D	4:0	78	22	0	0	79[c]
u	**11**	B2	6:14	92	8	0	0	77[c]
v	**11**	B2	4:19	84	14	2	0	74[c]
x	**12**	D	4:0	40	60	0	0	73[c]
y	**12**	B2[i]	6:14	28	51	7	13	56[c,j]

[a] With the exception of entry c, reactions were run in THF with 1 equiv of substrate, 10 equiv of MeOH, 4–6 equiv of SmI_2 and 0–19 equiv of HMPA; entry c was run in the absence of MeOH. See Section 4 for details on Sm(II) methods.
[b] Ratios determined by GC–MS after workup and before concentration of the dried organic phase.
[c] Isolated yield of purified compounds.
[d] GC yields are reported for **14a** and **14b** (volatile compounds); these values were determined after chromatography but before evaporation of solvents. The error associated with these values is less than or equal to 5%.
[e] Incomplete; GC–MS of crude indicated that **10a** accounted for 8% of reaction products.
[f] Incomplete; GC–MS of crude indicated that **10a** accounted for 71% of reaction products. Trace amounts of two unidentified compounds were also detected in the crude products.
[g] Incomplete; GC–MS of crude indicated that **10a** accounted for 45% of reaction products.
[h] The organic phase was washed several times with aq. $CuSO_4$ to remove residual HMPA.
[i] Reaction products for this experiment with **12** were isolated as their acetylated derivatives; product ratios were determined by ^{1}H NMR.
[j] Simple cyclization products **22a**+**22b** were also isolated (14%).



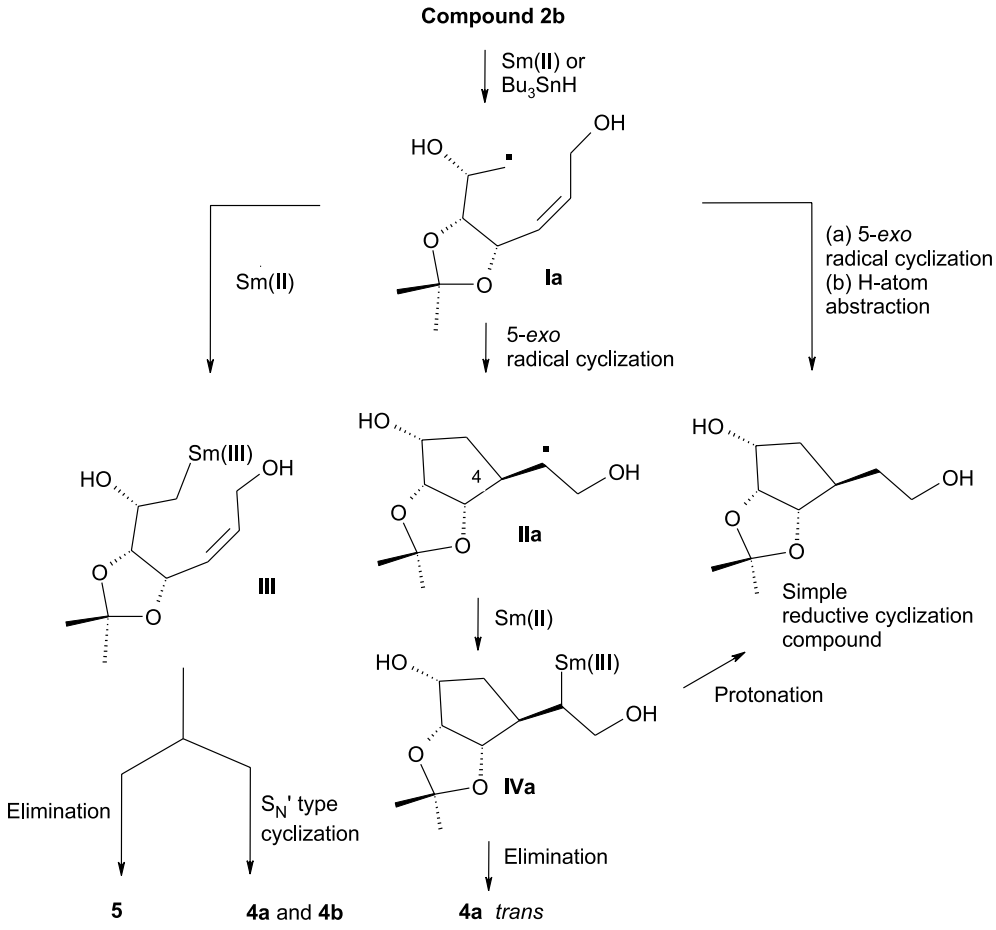
Ia **Ib** **Ic** **Id**

the Sm(II)-mediated cyclization of the *Z* ω-iodoallylic alcohol **2b** is more stereoselective than that of the corresponding *E* isomer **2a**. Cyclization via conformer **Ia** leads to the *trans* product while cyclization via conformer **Ib** is expected to be the minor pathway and leads to formation of the *cis* products. Reaction of **2a**, under the

Table 3. Reductive cyclizations with Bu_3SnH

Entry	S. mat. and method[a]		Simple reductive cyclization products	
			Diastereomeric ratios (*trans*/*cis*)[b]	Isolated yields (%)[c]
a	**1b**	Method E	79/21	**6a**+**6b**:72
b	**1a**	Method E	37/63	**6a**+**6b**:25; **1a**:10
c	**2b**	Method F[d]	93/7	**6a**+**6b**:61
d	**10a**	Method F	82/18	**18a**+**18b**:75
e	**10b**	Method F	90/10	**18a**+**18b**:63
f	**13**	Method F	76/24	**20a**+**20b**:86
g	**11**	Method F	89/11	**19a**+**19b**:73
h	**12**	Method F[d]	42/58	**22a**+**22b**:62

[a] Method E: Bu_3SnH, AIBN, refluxing benzene. Method F: Bu_3SnH, Et_3B, toluene (d–g) or THF (c, h), room temperature.
[b] Ratios determined by ^{1}H NMR and/or GC–MS after workup and chromatography.
[c] Isolated yield of purified compounds.
[d] Products of reactions of **12** and **2b** were isolated as their acetylated derivatives.



Scheme 5. Possible mechanistic pathways.

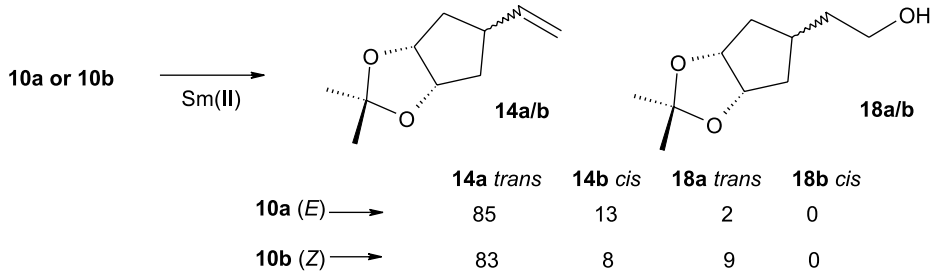
room temperature SmI_2–HMPA conditions, resulted in the formation of both *trans* and *cis*-cyclized products **4a** and **4b** in almost equal proportions (Table 1, entry f).

Reduction of the acetylated derivatives **1a** and **1b** with SmI_2 in the presence of HMPA also results in the formation of vinylcyclopentane products. While the stereoselectivity for the ω-iodoallylic acetate **1b** is slightly less than that observed for the ω-iodoallylic alcohol **2b**, both of these *Z* substrates give predominantly the *trans* tandem products. Once again, as expected, the double bond geometry has a marked effect on the stereoselectivity of these reactions and reduction of the *E* diastereoisomer **1a** gives predominantly the *cis* derivative **3b** (Table 1, entry g).

Two possible mechanisms, that may explain our observations for substrate **2b**, are illustrated in Scheme 5. They involve either a radical or a S_N' type cyclization.[12] It is relevant to note that reduction of **2b** with Bu_3SnH (Table 3, entry c) gives the 5-*exo* radical cyclization products; compounds **5**, **4a** and **4b** were not detected in our Bu_3SnH reaction mixture. This observation together with the requirement of an excess of Sm(II) suggests that organosamarium intermediates are involved at some stage in our reactions and result in the formation of β-elimination products.[13–15] Scheme 5 presents two possible pathways available to compound **2b**.

Sm(II) reduction of **2b** gives a primary radical which may either (1) cyclize in a 5-*exo* fashion to give the cyclic secondary radical **IIa** or (2) be reduced by a second equivalent of Sm(II) to give organosamarium species **III**. Cyclization via conformer **Ia** would eventually give the *trans* product in which the C-4 substituent is on the opposite side as all the other ring substituents. In the Bu_3SnH mediated reaction, H-atom abstraction allows for the transformation of **IIa** to the simple reductive cyclization compound. In the samarium(II) mediated conversion, this is also a possibility if H-atom abstraction from THF is competitive with further reduction. Alternatively, the cyclic secondary radical **IIa** may be reduced by Sm(II) to give an organosamarium intermediate **IVa**; β-elimination results in formation of **4a**. If intermediate **III** is formed, it may then either (1) undergo β-elimination to give diene **5** or (2) cyclize in a S_N' type fashion to give the vinylcyclopentane derivatives **4a** and **4b**. Elimination may be assisted by coordination of the departing hydroxyl groups with Sm(III).

Both the *Z* double bond geometry of **1b** and **2b** and the presence of a substituent at the γ-position are factors that favor formation of *trans* vinylcyclopentanetriol derivatives **3a** and **4a**. Reductions of the *E* isomer **1a** with Sm(II) were less stereoselective than those with **1b** and the major product was the *cis* derivative **3b**. The *E* ω-iodoallylic alcohol **2a** gave almost equal amounts of the *trans* and *cis* compounds **4a** and **4b**. This same tendency for stereodivergence was not, however, seen with the simpler compounds



Scheme 6.

10a and **10b**; these two ω-iodoallylic alcohols lack a substituent at the γ-position. Reduction of either **10a** or **10b** with Sm(II) gives the same *trans* vinylcyclopentane derivative **14a** as the major reaction product (Scheme 6).

Compound **14a** is the major product formed when Sm(II) reacts with either **10a**, **10b** or **13** (see Table 2). It is not the only product however and small quantities of other compounds were detected by GC–MS analysis of our crude reaction products before chromatography; one of these minor components is the expected *cis* isomer **14b**. Based on our results with compound **2b** we considered the possibility that uncyclized β-elimination products (Fig. 3) might be present as minor reaction products. This proved to be incorrect as the minor reaction products were actually the simple reductive cyclization compounds. Reactions run with Bu_3SnH and our substrates (Table 3) allowed us to prepare authentic samples of compounds **18**–**22**; NMR and GC–MS data for these compounds matched those of the minor reaction products of the Sm(II) reactions.

Crude and purified products were analyzed by TLC, GC–MS and by NMR. The product ratios were determined after reaction workup but before chromatography. The vinylcyclopentane derivatives **14a** and **14b** are somewhat volatile and so, with the exception of entries a and n of Table 2, the yields given for these compounds are GC yields determined after chromatography using a calibration curve. Reaction products of substrate **11** are less volatile and yields reported in entries t–v are for the isolated compounds **15a** and **15b**. The isolation of reaction products of substrate **12** with Sm(II)–HMPA was complicated by the solubility of compounds **16a** and **16b** in water and so the yield reported for the last entry of Table 2 corresponds to that of the peracetylated derivatives **17a** and **17b**.

Either visible light or HMPA can be used to facilitate these reactions. Reactions using visible light as a promoter were carried out at room temperature using a xenon lamp with appropriate filters. Reaction conditions involving the photoirradiation of SmI_2 reaction mixtures with a visible light source offered some practical advantages over the HMPA conditions. In addition to the obvious safety consideration of using visible light as a promoter, rather than HMPA, isolated yields of vinylcyclopentanediol derivatives were higher for substrates **11**–**13**. Isolation of the major reaction products was easier due, in part, to a simpler workup procedure and because reactions run under the SmI_2-hν conditions favored the exclusive (Table 2, entries p, t, x) or near exclusive (entries k and l) formation of the vinylcyclopentanediol compounds. The stereochemistry of the SmI_2–hν reactions, of the Figure 3 substrates, was equivalent or slightly less than that observed under our best Sm(II)–HMPA conditions.

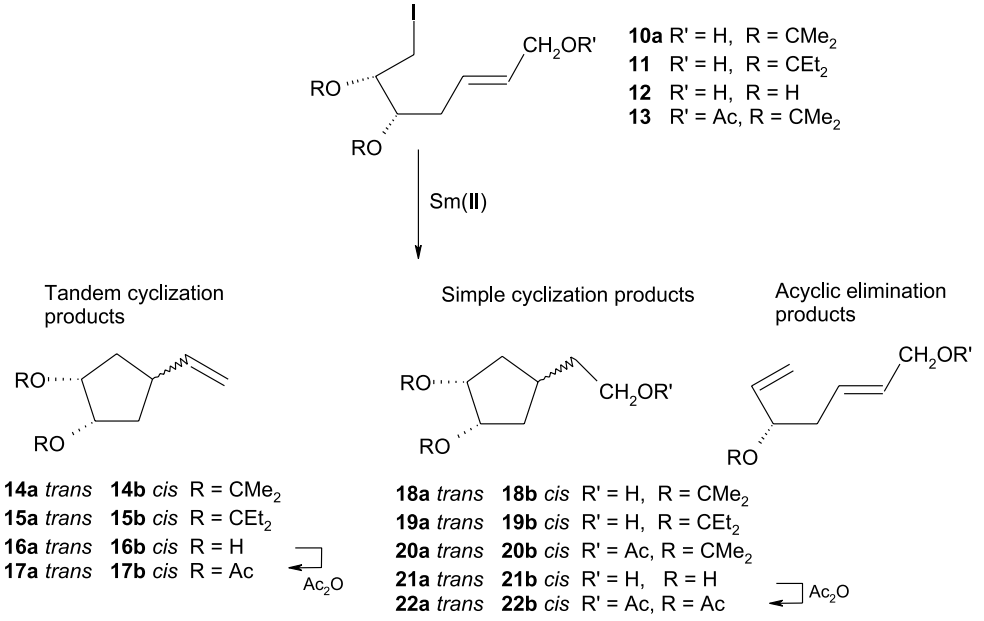


Figure 3. Conversion of ω-iodoallylic alcohols to tandem and simple cyclization products.

The results of the Sm(II)–HMPA mediated reactions of substrates **10**–**13** (Table 2) show that the diastereoselectivity and the product distribution vary with the reaction conditions and the substrate characteristics. Reactions with SmI_2-HMPA were run at either room temperature (Method B2) or at −78 °C (Methods B1 and C) under ambient lighting conditions in the presence of MeOH and with either 4 or 6 equiv of SmI_2 per equivalent of alkenyl iodide. Although the sequenced reactions formally require only 2 equiv of Sm(II), we routinely ran these reactions in the presence of excess reagent. We found that both the quantity of HMPA and its order of addition are key factors in the determining the outcome of these Sm(II)–HMPA mediated reductions. The proportion of unreacted starting material and simple reductive cyclization products increases as the quantity of HMPA is reduced for both the −78 °C and the room temperature reactions. As we decreased the quantity of HMPA (entries b, d, f, g) we observed a drop in the proportion of vinylcyclopentanediol products; in the absence of HMPA at −78 °C (entry g) the major reaction component is unreacted starting material **10a**. Removal of methanol from the reaction mixture does not have an appreciable effect on the ratio of tandem–simple cyclization products (entries b and c).

One might expect a decrease in the ratio of tandem–simple cyclization products under conditions where the Sm(II) reducing reagent is not reactive enough to ensure that reduction of the cyclized radical and β-elimination, to give vinylcyclopentanes, is favored over hydrogen-atom abstraction (Scheme 5). The redox potential of Sm(II)–HMPA complexes varies with the number of coordinated HMPA ligands[3] and so it is not surprising that our results vary with the SmI_2–HMPA ratios. The nature of the Sm(II)–HMPA complexes formed in solution, when SmI_2 in THF is mixed with HMPA, depends on the HMPA–SmI_2 molar ratio. It has been proposed that, in the presence of more than 10 equiv of HMPA, the species formed is $[Sm(HMPA)_6]I_2$. At 4 equiv, the principal species is $[Sm(HMPA)_4(THF)_2]I_2$ and at intermediate concentrations of HMPA (4–10 equiv) both species are present. The exact nature of the Sm(II)–HMPA complexes formed in solution in the presence of less than 4 equiv of HMPA is not well understood.[3f]

With the exception of entries a and e, all of the Sm(II)–HMPA reactions summarized in Table 2 involve the dropwise addition of SmI_2 in THF to solutions of our substrates in THF/MeOH/HMPA (Methods B1 and B2). The order of addition of HMPA had little effect on results of reactions of **10a** with SmI_2 when the **10a**–SmI_2–HMPA ratio was 1:4:19 (entries a and b). This was not true for reactions with a lower HMPA–SmI_2 ratio. If HMPA and the THF solution of SmI_2 were first pre-mixed, before transferring the resulting purple solution to a cooled solution of **10a** in THF–MeOH (Method C), we observed a decrease in the ratio of tandem–simple cyclization products and in the ratio of *trans*:*cis* products (entries d and e). Precomplexation, of Sm(II) with less than 4 equiv of HMPA per equivalent of SmI_2, should result in the formation of Sm(II)–HMPA complexes, with fewer HMPA ligands, that are weaker reducing reagents than the complex or complexes formed when the HMPA–SmI_2 ratio is greater than 4:1 (entry a). Why do we see an increase in the amount of vinylcyclopentanes formed if the THF solution of SmI_2 is added dropwise to a solution of **10a** in THF–MeOH–HMPA? We noticed that, during the initial phase of the transfer process, the deep blue color of the SmI_2/THF solution rapidly dissipates and the deep purple color associated with SmI_2/THF/HMPA solutions persisted only after addition of ca. two molar equivalents of Sm(II). One possible explanation for this observation and for the differences observed for Methods B1 and C (entries d and e) is that during the addition of the first 2 equiv of SmI_2, to the solution of the substrate in THF–MeOH–HMPA, the ratio of HMPA–SmI_2 is actually greater than 4:1 and so the Sm(II)–HMPA species that initially forms and rapidly reacts with **10a** has a greater number of HMPA ligands coordinated to Sm(II) than does the reagent formed under the Method C conditions.

Entry j (Table 2) summarizes a set of convenient reaction parameters for **10a** that allowed us to achieve both a high ratio of tandem–simple reductive cyclization products as well as a high level of diastereoselectivity. The reaction was run at room temperature and does not require premixing of SmI_2 and HMPA. These conditions, as well as the SmI_2–hν conditions, were then used for the reactions of the other substrates of this series. Both the isopropylidene and the isopentylidene substrates **10a** and **11** give excellent ratios of tandem–simple cyclization products under these conditions (entries j and u, Table 2) with a slightly better diastereoselectivity observed for **10a**. Acetylation of the hydroxyl group of **10a** to give **13** had a detrimental effect on the Sm(II)–HMPA sequenced reactions (entry q), however reaction of **13** under the SmI_2–hν conditions exclusively gave compounds **14a** and **14b** in an 80:20 ratio (entry p). Removal of the protecting group of the 1,2-diol group had a bigger impact on product distribution; reductions of **12** with either SmI_2–hν or Sm(II)–HMPA gave slightly more *cis* cyclization products than *trans* cyclization products. We observed a similar level of diastereoselectivity for the Bu_3SnH mediated reaction of **12** (entry h, Table 3). The *trans*/*cis* ratio was 42/58 for the reductive cyclization products of the Bu_3SnH reaction and 40/60 for the tandem products of the SmI_2–hν reaction of **12**.

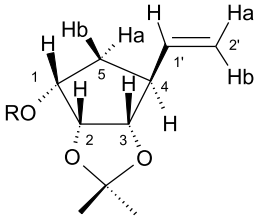
2.1. Structure assignment for tandem and simple cyclization products

The ω-iodoallylic alcohols that we used in this study originate from either D-(+)-ribonic γ-lactone (**1a**, **1b**, **2a**, **2b**) or 2-deoxy-D-ribose (**10**–**13**). The relative configuration of C_4 for compounds **4a** and **4b** was determined using the known configuration of C_1, C_2 and C_3 together with NMR data from NOE and COSY experiments, vicinal coupling constants, and simple ^1H–^1H decoupling experiments. Analysis of the coupling constants associated with the H_3 and H_4 protons is complicated by the fact that, for the ^1H NMR spectrum of **4a** in $CDCl_3$, H_4 appears as a complex multiplet and the H_3 and H_2 signals overlap to give an apparent doublet. ^1H NMR spectra of **4a** were also recorded in acetone-d_6 and benzene-d_6. Although the use of acetone-d_6 did give a better resolution of some signals (i.e. $H_{2a'}$, $H_{2b'}$, H_{5a} and H_{5b}) it did not allow us to resolve the H_2 and

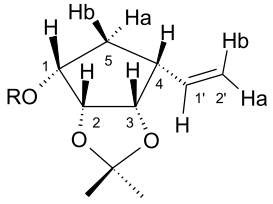
H_3 signals; separation of these signals was achieved, however, using benzene-d_6.

The ^{1}H NMR spectrum of **4b** in $CDCl_3$ was easier to analyze as, unlike **4a**, the H_2 and H_3 protons have different chemical shifts; the signals, of these two protons present as apparent triplets due to similar coupling between H_3 and either H_2 or H_4 as well as between H_2 and either H_3 or H_1. The vicinal coupling constants that we measured ($J_{3,2}$ and $J_{3,4}$ are both ca. 5 Hz) are consistent with the H_3 and H_4 protons *syn* to one another. We therefore assigned structure **4b** to the minor diastereoisomer isolated from the reaction of **2b** with SmI_2 in THF/MeOH (Table 1, entry b).

The NOE experiments that we ran support our structural assignments for compounds **4a** and **4b**. We saw a smaller NOE between the signals of H_4 and of H_2+H_3 in the case of isomer **4a** (where H_4 and H_3 are *anti* and the H_2 and H_3 signals overlap) than we saw in the case of isomer **4b** (where H_4 and H_3 are *syn*). Irradiation of **4a** in acetone-d_6 at 2.60 ppm (H_4) resulted in a total NOE of 1.3% for the overlapping H_2+H_3 signals. Irradiation of **4b** ($CDCl_3+D_2O$) at 2.28 ppm (H_4) resulted in a total NOE of 4.6% for the combined H_2+H_3 signals.



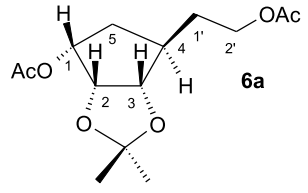
3a R = Ac
4a R = H



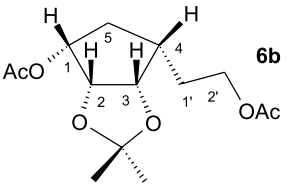
3b R = Ac
4b R = H

We determined the relative configuration of C_4 of compounds **3a** and **3b** in a similar fashion. The $J_{3,4}$ value of **3a** (1.3 Hz) was determined with the help of decoupling experiments and is consistent with H_3 and H_4 *anti* to one another. The COSY spectrum of **3a** showed only a weak correlation between H_4 and H_3. The $J_{3,4}$ coupling constant (4.8 Hz) of **3b** was determined with the help of ^{1}H–^{1}H decoupling and HOM2DJ experiments and was consistent with the H_3 and H_4 protons of **3b** *syn* to one another. Therefore, the relative configurations of compounds **3a** (*trans* isomer) and **3b** (*cis* isomer) are as shown. Our NOE experiments supported this stereochemical assignment. Upon irradiation of the H_3 signal of **3a** we observed a smaller NOE effect for H_4 (2.0%) than we did in the corresponding experiment for **3b** (i.e. 4.3% enhancement for H_4 upon irradiation at H_3). Irradiation of H_4 resulted in a smaller NOE effect for the H_3 proton of **3a** (1.6%) than for the H_3 proton of **3b** (5.7%).

The relative configurations of the simple cyclization products **6a** (*trans* isomer) and **6b** (*cis* isomer) were also determined by using the known configurations of C_1, C_2 and C_3 together with NOE experiments. Upon irradiation of the H_3 signal of compound **6a**, we observed a 8.4% enhancement for the H_2 signal but did not observe an effect for the H_4 signal. A 5.1% effect was also noted for the $H_{1'a}$ multiplet. Upon irradiation of the H_2 signal, we observed enhancements for the H_3 (7.4%) and H_1 (6.3%) signals. In the case of diastereoisomer **6b**, irradiation of the H_3 signal resulted in enhancements for the signals at 4.66 ppm (H_2 and H_1, 8.9%) and 1.78 ppm (H_4 and $H_{1'b}$, 4.8%). We therefore assigned structure **6a** to the major diastereoisomer isolated from the reaction of **1b** with Bu_3SnH and **6b** to the structure of the major isomer from the Bu_3SnH reaction of **1a**.

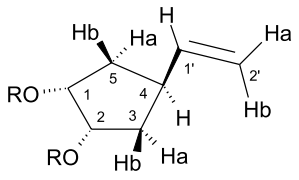


6a

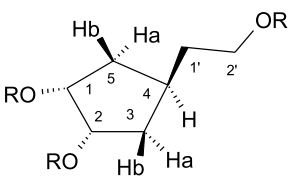


6b

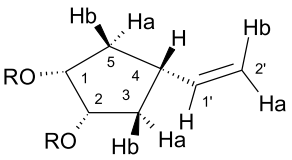
The NMR spectra of the tandem cyclization products **14–17** and the simple cyclization products **18–22** were simpler than those of the previously described compounds but the absence of a stereogenic center at C_3 or C_5 made assignment of the relative configurations at C_4 slightly more complicated. The C_3 and C_5 carbons are equivalent



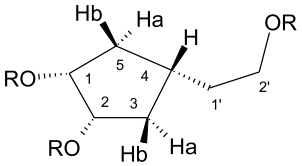
14a-17a



18a-22a



14b-17b



18b-22b

and each have 2 diastereotopic protons with distinct chemical shifts; assignments of the diastereotopic protons were made using the known configuration of C_1 and C_2 together with NMR data and NOE experiments. Once the identity of the Hb and Ha signals of each isomer was established, additional NOE experiments then allowed us to determine the configuration at C_4 for each of the diastereoisomers. Details for the NOE experiments are included in the Supplementary information.

3. Conclusions

The experiments described in this manuscript demonstrate that vinylcyclopentanes can be efficiently and stereoselectively synthesized by the reduction of carbohydrate derived ω-iodoallylic alcohols with an excess of Sm(II). In contrast, reductions of these same ω-iodoallylic alcohols with Bu_3SnH gave (2-hydroxyethyl)cyclopentanediol and -triol derivatives. The sequenced or tandem reactions, leading to vinylcyclopentane formation, are favored when the Sm(II) reaction mixtures are either irradiated with a xenon lamp or when HMPA is added. The quantity of HMPA used and the order of addition of HMPA and SmI_2 are important reaction parameters. Reactions can be run at either −78 °C or at room temperature. In general, the diastereomeric ratios of the *trans–cis* cyclization products for reactions run with HMPA were equal, or slightly higher, than those found for either the SmI_2–hν or Bu_3SnH reactions. The chemoselectivity of the Bu_3SnH reactions is different of course from the Sm(II) mediated reactions and we isolated only the simple reductive cyclization products from these reactions. For the substrates originating from 2-deoxy-D-ribose, reactions run under the SmI_2–hν conditions presented several advantages over those run with Sm(II)–HMPA. In addition to the obvious safety advantage of using visible light as a promoter, rather than HMPA, isolated yields of vinylcyclopentanediol derivatives were higher for substrates **11**–**13** due, in part, to a simpler workup procedure and because reactions run under the SmI_2–hν conditions gave exclusively (**11**–**13**), or nearly exclusively (**10a**, **10b**), the tandem cyclization products.

4. Experimental

4.1. General experimental

Unless otherwise noted, ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ on a Varian Gemini 300 BB instrument. The symbols s′, d′, t′, and q′, used for ^{13}C NMR data, represent carbons having zero, one, two and three attached hydrogens, respectively. HMQC and NOE NMR experiments were run on a Brüker AMX2 500 instrument. FTIR spectra were recorded on either a Bomem MB series instrument or a Perkin–Elmer Series 1600 instrument. Mass spectra were run on a Kratos 25 RFA instrument.[†] Melting points were recorded on a Fisher–Johns apparatus and are uncorrected. GC–MS analysis were run on a Hewlett–Packard GCD Plus instrument (HP-5 column, 30 m length, 0.25 mm diameter, 1 mL/min flow rate; electron ionization detector); oven ramp initial temperature 50 °C, final temperature 275 °C, rate = 22 °C/min. Optical rotations were measured at 589 nm in ethanol (100%) with a JASCO P-1010 Digital or a JASCO DIP-370 polarimeter. The reported concentrations are in g/100 mL. Radial chromatography was carried out with a Harrison Research Chromatotron and silica gel plates.

4.1.1. (2*E*)-2,3,7-Trideoxy-7-iodo-4,5-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol (2a). A solution of **7a** (0.1511 g, 0.3794 mmol) in THF (9.1 mL) was prepared under a nitrogen atmosphere and cooled in a dry ice–acetone bath (−25 to −35 °C). To this solution was added, dropwise over 10 min, a solution of DIBAL (2.30 mL, 1.0 M solution in hexanes, 2.30 mmol).[16] The reaction mixture was stirred under these conditions for 1.5 h and then quenched with a saturated aqueous solution of NH_4Cl (5.0 mL). The mixture was stirred and the white cloudy solution was then filtered through a short pad of silica gel. The heterogeneous filtrate was transferred to a separatory funnel and the layers separated; the aqueous layer was extracted with EtOAc (20 mL × 3) and the combined organic phases were washed with H_2O (30 mL) and brine (30 mL). The organic layer was then dried over $MgSO_4$, filtered and concentrated. The residue was purified by radial chromatography [2 mm silica plate] to give 0.0934 g (75.7%) of **2a** (oil): R_f = 0.20 (1:1 EtOAc–hexanes). $[\alpha]_D$ = −5.4 (*c* 0.91, 15.7 °C). ^{1}H NMR δ: 6.00 (ddt, J = 15.5, 0.8, 4.9 Hz, 1H, H_2), 5.84 (ddt, J = 15.5, 6.9 Hz, 1.4 Hz, 1H, H_3), 4.74 (apparent t, J_{app} = 6.6 Hz, 1H, H_4), 4.20 (apparent d, J = 4.7 Hz, 2H, H_1), 3.98 (dd, J = 6.4, 8.0 Hz, 1H, H_5), 3.41–3.62 [m, 3H; H_6, H_{7a}, and OH. Upon D_2O exchange this region integrates for 2H and simplifies to a dd at 3.55 ppm (J = 2.4, 10.1 Hz, 1H, H_{7a}) and a partially resolved ddd at 3.47 ppm (J = 2.5, 8.7, 7.0 Hz, 1H, H_6), 3.35 (dd, J = 6.5, 10 Hz, 1H, H_{7b}), 2.83 (broad singlet, 1H, OH; D_2O exchangeable), 1.46 (s, 3H, CH_3), 1.37 (s, 3H, CH_3). ^{13}C NMR δ: 132.7 (C_2), 126.4 (C_3), 108.9 ($C(CH_3)_2$), 80.0 (C_5), 77.6 (C_4), 68.9 (C_6), 62.5 (C_1), 27.8 (CH_3), 25.2 (CH_3), 14.2 (C_7). FTIR (cast): 3383 (s, br) cm^{-1}. GC–MS: t_R = 10.75 min; *m/z*: 313 (0.6%, M − CH_3), 157 (8.8%, M − ICH_2CHOH), 128 (9.5%), 125 (4.7%), 99 (24.1%), 59 [100%, $(CH_3)_2COH^+$]. HRMS: found 312.9934; calcd for M − CH_3 = $C_9H_{14}IO_4$: 312.9937.

4.1.2. (2*E*) 2,3,7-Trideoxy-7-iodo-4,5-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol diacetate (1a). A solution of **2a** (0.0935 g, 0.285 mmol) and DMAP (0.0017 g, 0.0139 mmol) in CH_2Cl_2 (1.5 mL) was prepared under anhydrous conditions and cooled at −78 °C. Acetic anhydride (0.12 mL, 1.27 mmol) and NEt_3 (0.17 mL, 1.22 mmol) were then simultaneously added dropwise (over 3 min) to this mixture.[17] The reaction mixture was stirred for 10 min, quenched with a mixture of H_2O–ether (5 mL, 1:1 v/v) and then warmed up to room temperature. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with aqueous citric acid (20 mL, 10%), saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL). The organic phase was then dried over $MgSO_4$, filtered and concentrated. Purification of

[†] Most of our compounds do not give detectable molecular ions in EI mode but they do give an intense M − CH_3 fragment that is a well known characteristic of *O*-isopropylidene molecules;[23] we were able to obtain an accurate mass for these M − 15 fragments.

the residue by radial chromatography [(1 mm silica plate, eluant: 18% EtOAc–hexanes (100 mL) followed by 1:1 EtOAc–hexanes (50 mL)] gave **1a** (0.1094 g, 93.1%). R_f=0.24 (16% EtOAc–hexanes); mp 58–59 °C. $[\alpha]_D=-35$ (*c* 1.12, 25 °C). ^{1}H NMR δ: 5.92 (apparent ddt, J=15.5, 1.0, 5.7 Hz, 1H, H_2), 5.69 (apparent ddt, J=15.5, 6.8, 1.4 Hz, 1H, H_3), 4.70 (apparent t, J_{app}=6.3 Hz, 1H, H_4), 4.60–4.50 [2H, overlapping signals of H_{1a} (4.58 ppm, dd, J=5.5, 13.6 Hz) and H_{1b} (4.52 ppm, dd, J=5.9, 13.6 Hz)], 4.33 (apparent dt, J=8.6, 3.4 Hz, 1H, H_6), 4.25 (dd, J=5.9, 8.6 Hz, 1H, H_5), 3.51 [2H, overlapping signals of H_{7a} (3.54 ppm, dd, J=3.2, 11.1 Hz) and H_{7b} (3.49 ppm, dd, J=3.5, 11.0 Hz)], 2.08 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 1.48 (s, 3H, CH_3), 1.39 (s, 3H, CH_3). ^{13}C NMR δ: 170.5 (C=O), 169.3 (C=O), 127.9 (C_3 and C_2, confirmed by HMQC experiment), 109.3 ($C(CH_3)_2$), 77.8 (C_5), 76.9 (C_4), 68.9 (C_6), 63.6 (C_1), 27.7 ($C(CH_3)_2$), 25.2 ($C(CH_3)_2$), 20.9 (CH_3CO), 20.8 (CH_3CO), 7.5 (C_7). FTIR (solution in CH_2Cl_2) 1741 (s), 1736 (s) cm^{-1}. MS [EI] *m/z*: 397 (23.2%, M−CH_3), 235 (28%), 211 (51.6%), 170 (51.3%), 141 (40.3%), 43 (100%, CH_3CO^+). HRMS: found 397.0152; calcd for M−CH_3=$C_{13}H_{18}IO_6$: 397.0148. MS [CI, NH_3] *m/z*: 430 (20.6%, M+NH_4), 397 (19.7%), 355 (74.1%), 43 (100%).

4.1.3. (2*Z*)-2,3,7-Trideoxy-7-iodo-4,5-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol (2b). A solution of DIBAL (6.2 mL, 1.0 M in hexanes, 6.2 mmol) was added, dropwise over 10 min, to a cooled (−25 to −35 °C) solution of **7b** (0.4097 g, 1.0288 mmol) in THF (23.3 mL) under a nitrogen atmosphere.[16] After an additional 55 min the reaction mixture was quenched with MeOH (8.5 mL). Ether (6.5 mL), NaF (0.18 g, 4.3 mmol) and H_2O (1 mL) were added and the cloudy solution was filtered. The filter cake was washed with EtOAc (3×5 mL) and the combined filtrates were concentrated. Purification by radial chromatography (1:1 EtOAc–hexanes, 4 mm silica plate) allowed for the separation of **7b** (0.0509 g, 12.4% recovery) from **2b** (0.2319 g, 68.7% yield of pure sample and 0.0162 g, 4.8% yield of a slightly impure sample as determined by ^{1}H NMR). Compound **2b**: mp 88–90 °C, R_f=0.27 (silica, 1:1 EtOAc–hexanes). $[\alpha]_D$=30.4 (*c* 1.5, 25 °C). ^{1}H NMR δ: 5.97 (partially resolved dddd, J=11.2, 1.1, 7.4, 6.4 Hz, 1H, H_2), 5.67 (partially resolved ddd, J=1.3, 9.5, 11.1 Hz, 1H, H_3), 5.15 (ddd, J=1.0, 6.1, 9.4 Hz, 1H, H_4), 4.29 (ddd, J=1.5, 7.4, 12.4 Hz, 1H, H_{1a}), 4.13 (dd, J=6.4, 12.3 Hz, 1H, H_{1b}), 4.04 (dd, J=6.2, 8.7 Hz, 1H, H_5), 3.58 (m, 1H, H_{7a}), 3.35–3.50 (m, 3H, H_6, H_{7b}, OH; upon D_2O exchange this region integrates for 2H), 2.40 (broad s, 1H, OH; D_2O exchangeable), 1.49 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C NMR δ: 131.4 (d′), 130.8 (d′), 109.5 (s′), 80.4 (d′), 73.5 (d′), 68.3 (d′), 57.9 (t′), 28.1 (q′), 25.5 (q′), 13.7 (t′). FTIR (film): 3357 (s, br) cm^{-1}. MS [CI] *m/z*: 346 (1.0%, M+NH_4), 329 (2.3%, M+1), 253 (100%, loss of H_2O and CH=$CHCH_2OH$). MS [EI] *m/z*: 313 (4.7%, M−CH_3), 295 [6.7%, M−(CH_3 and H_2O)], 171 (12.4%, ICH_2CHOH^+), 157 (13.2%, M−ICH_2CHOH), 99 (81.0%), 59 [100%, $(CH_3)_2COH^+$]. HRMS: found 312.9934; calcd for M−CH_3=$C_9H_{14}IO_4$: 312.9937.

4.1.4. (2*Z*)-2,3,7-Trideoxy-7-iodo-4,5-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol diacetate (1b). A solution of **2b** (0.1697 g, 0.5173 mmol) and DMAP (0.0061 g, 0.0499 mmol) in CH_2CH_2 (2.7 mL) was prepared under anhydrous conditions and cooled to −78 °C. Ac_2O (0.21 mL, 2.226 mmol) and NEt_3(0.30 mL, 2.2 mmol) were then simultaneously added dropwise (over 3 min).[17] The reaction mixture was stirred for 1.5 h, quenched with a mixture of H_2O–ether (5 mL, 1:1 v/v) and then warmed up to room temperature. The mixture was extracted with EtOAc (3×10 mL) and the combined organic layers were washed with aqueous citric acid (20 mL, 10%), saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL). The organic phase was then dried, filtered and concentrated. Purification by radial chromatography (20% EtOAc–hexanes, 2 mm silica plate) gave pure **1b** (0.2017 g, 95%) as a pale yellow oil. R_f=0.34 (TLC, 20% EtOAc–hexanes). $[\alpha]_D$=15.0 (*c* 1.69, 25 °C). ^{1}H NMR δ: 5.78 (m, 1H, H_2), 5.60 (m, 1H, H_3), 5.02 (ddd, J=1.1, 6.2, 8.6 Hz, 1H, H_4), 4.74 [ddd, J=1.1, 7.1, 13.3 Hz, 1H, H_{1a}), 4.61 (ddd, J=1.6, 6.2, 13.3 Hz, 1H, H_{1b}), 4.43 (m, 1H, H_6), 4.25 (dd, J=6.2, 8.3 Hz, 1H, H_5), 3.46–3.55 [2H, H_{7a}+H_{7b}; overlapping signals at 3.53 ppm (dd, J=3.4, 11.1 Hz) and 3.49 ppm (dd, J=3.9, 11.1 Hz)], 2.09 (s, 3H, CH_3CO), 2.05 (s, 3H, CH_3CO), 1.48 (s, 3H, CH_3), 1.40 (s, 3H, CH_3). ^{13}C NMR δ: 170.5 (s′, C=O), 169.4 (s′, C=O), 128.6 (d′, C_3), 128.1 (d′, C_2), 109.4 (s′, $C(CH_3)_2$), 77.8 (d′, C_5), 73.0 (d′, C_4), 68.8 (d′, C_6), 59.8 (t′, C_1), 27.6 (q′, $C(CH_3)_2$), 25.1 (q′, $C(CH_3)_2$), 20.91 (q′, $COCH_3$), 20.86 (q′, $COCH_3$), 7.3 (t′, C_7). FTIR (film) 1741 (s) cm^{-1}. MS [EI] *m/z*: 397 (6.6%, M−CH_3), 43 (100%, CH_3CO^+). HRMS: found 397.0153; calcd for M−CH_3=$C_{13}H_{18}IO_6$: 397.0148.

4.1.5. (2*E*) 2,3,4,7-Tetradeoxy-7-iodo-5,6-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol (10a). The method used for the reduction of **8a** is based on a procedure described in the literature.[18] A solution of DIBAL (1.0 M in toluene, 1.05 mL, 1.05 mmol) was added dropwise over 10 min to a cooled (0 °C) solution of compound **8a** (0.200 g, 0.523 mmol) in anhydrous toluene (10 mL) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 2 h and then quenched by the addition of *tert*-butanol (1.2 mL). The mixture was stirred for 30 min, water (0.10 mL) was added and stirring continued for another 30 min. To this mixture was added an aqueous solution of NaOH (2 M, 1.5 mL), CH_2Cl_2 (20) mL and H_2O (10 mL). The layers were separated and the aqueous phase was neutralized by the addition of dilute aqueous HCl (0.1 M) and re-extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed successively with saturated aqueous solutions of $NaHCO_3$ (25 mL) and NaCl (25 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Radial chromatography of the crude residue gave 0.007 g (3.5% recovery) of starting material, 0.013 g (8% yield) of the corresponding conjugated aldehyde (GC purity 95%, contaminated with the saturated aldehyde) and 0.097 g (60% yield) of the allylic alcohol **10a** (GC purity 98%) as a colorless oil (R_f=0.35 silica, 4:1:1 CH_2Cl_2–Et_2O–hexanes). $[\alpha]_D$=87.7 (*c* 0.18, CH_2Cl_2, 20.7 °C). ^{1}H NMR δ: 5.77 (m, 2H, H_2 and H_3), 4.37 (partially resolved ddd,* J=5.5, 6, 8 Hz, 1H, H_6), 4.19 (ddd, J=5.5, 6, 7 Hz, 1H, H_5), 4.14 (m which simplifies after resolution enhancement to a partially resolved dd, J=1, 1 Hz, 1H, H_{1a}), 4.13 (m that simplifies to a dd after resolution enhancement, J=1, 2 Hz, 1H, H_{1b}), 3.20 (dd, J=8, 10 Hz, 1H, H_{7a}), 3.15 (dd, J=6, 10 Hz, 1H, H_{7b}), 2.35 (m, 2H, H_{4a} and H_{4b}), 1.63 (s

large, 1H, 1×OH), 1.48 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). $^*J$ values calculated after resolution enhancement. ^{13}C NMR δ: 132.1 (d, C_2/C_3), 127.7 (d, C_2/C_3), 108.7 (s, $C(CH_3)_2$), 78.2 (d′, C_5/C_6), 77.2 (d′, C_5/C_6), 63.5 (t′, C_1), 32.3 (t′, C_4), 28.4 (q′, CH_3), 25.7 (q′, CH_3), 3.4 (t′, C_7). FTIR (film): 3405 (broad, OH), 1675 (w) cm^{-1}. GC–MS: t_R=8.21 min, (EI) *m/z*: 297 (9.1%, M−CH_3), 241 (100%, M−CH_2CH=$CHCH_2OH$), 185 (38.5%, M−I), 183 (58%), 155 (24.6%), 59 (23.6%), 43(60.9%). HRMS (EI) found 296.9985; calcd for M−CH_3=$C_9H_{14}IO_3$: 296.9988.

4.1.6. (2*Z*) 2,3,4,7-Tetradeoxy-7-iodo-5,6-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol (10b). A solution of DIBAL (1.0 M toluene, 1.57 mL, 1.57 mmol) was added dropwise over 15 min to a cooled solution (0 °C) of **8b** (0.272 g, 0.712 mmol) in anhydrous toluene (14 mL) under argon. The mixture was stirred at 0 °C for 5 h and then worked up as per compound **10a**. After radial chromatography we isolated 0.164 g (74%) of allylic alcohol **10b** (GC purity=98%) as a colorless oil. R_f=0.31 (silica, 4:1:1 CH_2Cl_2-Et_2O–hexanes). $[\alpha]_D$=12.9 (*c* 0.26, CH_2Cl_2, 20.7 °C). ^{1}H NMR δ: 5.86 (m, 1H, H_2; decoupling of H_4 protons transformed the signal to an apparent dt with *J*=11, 7 Hz), 5.65 (m, 1H, H_3; decoupling of H_4 protons simplifies this signal to an apparent dt, *J*=11, 1 Hz), 4.40 (apparent dt, *J*=6, 7 Hz, 1H, H_6), 4.29–4.09 [m, 3H, H_{1a}, H_{1b} and H_5; signal is simplified upon decoupling of H_4 protons to a ddd centered at 4.25 ppm (*J*=1, 7, 12.5 Hz, 1H, H_{1a}), a multiplet at 4.17 ppm (1H, H_5) and a ddd centered at 4.12 ppm (*J*=1, 6.5, 12.5 Hz, 1H, H_{1b})], 3.22 (dd, *J*=7,10 Hz, 1H, H_{7a}), 3.17 (dd, *J*=6.5, 10 Hz, 1H, H_{7b}), 2.42 (m, 2H, H_{4a} and H_{4b}), 1.71 (s large, 1H, OH), 1.49 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). ^{13}C NMR δ: 131.4 (d′, C_2/C_3), 128.0 (d′, C_2/C_3), 108.7 (s′, $C(CH_3)_2$), 78.1 (d′, C_5/C_6), 76.8 (d′, C_5/C_6), 58.1 (t′, C_1), 28.1 (q′, CH_3), 27.7 (t′, C_4), 25.5 (q′, CH_3), 3.2 (t′, C_7). FTIR (film): 3410 (s, br), 1650 (w), 1040 (s) cm^{-1}. GC–MS: t_R=8.17 min, (EI) *m/z*: 297 (5.6%, M−CH_3), 241 (100%, M−$CH_2CHCHCH_2OH$), 185 (36.3%, M−I), 183 (71.7%), 155 (30.9%), 85 (20.6%), 59 (27.6%), 43 (61.3%). HRMS (EI) found 296.9990; calcd for M−CH_3=$C_9H_{14}IO_3$: 296.9987.

4.1.7. (2*E*) 2,3,4,7-Tetradeoxy-7-iodo-5,6-*O*-(1-methylethylidene)-D-*ribo*-hept-2-enitol acetate (13). Pyridine (5.5 mmol, 0.44 mL) and Ac_2O (4.6 mmol, 0.43 mL) were added to a cooled (0 °C) solution of **10a** (0.2862 g, 0.9148 mmol) in CH_2Cl_2 (10 mL) under an argon atmosphere. The mixture was stirred 0 °C for 1 h and at room temperature for 12 h. Water (10 mL) was added, the phases separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed successively with aqueous HCl (0.1 M, 10 mL) and saturated aqueous solutions of $NaHCO_3$ (20 mL) and NaCl (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude was purified by radial chromatography to give 0.290 g (89%) of **13** as a colorless oil. R_f=0.91 silica, 4:1:1 CH_2Cl_2–Et_2O–hexanes. $[\alpha]_D$=12.5 (*c* 0.17, CH_2Cl_2, 20.4 °C). ^{1}H NMR δ: 5.76 (m, 2H, H_2 and H_3), 4.54 (apparent dd, 2H, *J*=6, 1 Hz, $2H_1$), 4.36 (partially resolved ddd, 1H, *J*=6, 6, 8 *Hz*, H_6), 4.18 (partially resolved ddd, 1H, *J*=6, 7, 5.5 Hz, H_5), 3.18 (dd, 1H, *J*=10, 8 Hz, H_{7b}), 3.13 (dd, 1H, *J*=10, 6 *Hz*, H_{7a}), 2.35 (m, 2H, H_{4a} and H_{4b}), 2.07 (s, 3H, C=OCH_3), 1.47 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). ^{13}C NMR δ: 170.7 (s′, C=O), 130.9 (d′, C_2/C_3), 126.9 (d′, C_2/C_3), 108.7 (s′, $C(CH_3)_2$), 78.1 (d′, C_5/C_6), 76.98 (d′, C_5/C_6), 64.7 (t′, C_1), 32.4 (t′, C_4), 28.4 (q′, CH_3), 25.7 (q′, CH_3), 20.9 (q′, CH_3), 3.1 (t′, C_7). FTIR (film) 1738 (w), 1673 (w) cm^{-1}. GC–MS: t_R=8.75 min, (EI) *m/z*: 339 (6.1%, M−CH_3), 241 (100%, M−$CH_2CHCHCH_2OAc$), 185 (38.2%), 183 (57.7%, ICH_2CHCHO), 43 (78.8%, CH_3CO). HRMS (EI) found 339.0090; calcd for M−CH_3=$C_{11}H_{16}IO_4$: 339.0093.

4.1.8. (2*E*) 2,3,4,7-Tetradeoxy-7-iodo-5,6-O-(1-ethylpropylidene)-D-*ribo*-hept-2-enoic acid *tert*-butyl ester (9). A mixture of pentan-3-one (5.72 mL, 54.0 mmol), *tert*-butyl (*2E*) 2,3,4,7-tetradeoxy-7-iodo-D-*ribo*-hept-2-enoate[10] (0.500 g, 1.46 mmol), pTSA·H_2O (0.003 g, 0.2 mmol) and molecular sieves were stirred under an argon atmosphere at 70 °C for 24 h. The mixture was filtered and the filtrate diluted with ether (15 mL) and successively washed with saturated aqueous solutions of $NaHCO_3$ (15 mL) and NaCl (15 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by radial chromatography (4 mm silica plate) to give 0.253 g (51%) of starting material and 0.209 g (35%) of **9** (R_f=0.90, 2:2:3 CH_2Cl_2–EtOAc–hexanes) as a white solid, mp 44–45 °C. $[\alpha]_D$=−24 (*c* 0.18, CH_2Cl_2, 20.1 °C). ^{1}H NMR δ: 6.88 (dt, *J*=15.5, 7 Hz, 1H, H_3), 5.86 (dt, *J*=15.5, 1.5 Hz, 1H, H_2), 4.43 (partially resolved ddd, *J*=6, 6, 8 Hz, 1H, H_6), 4.27 (partially resolved ddd, *J*=5.5, 5.5, 8 Hz, 1H, H_5), 3.21 (dd, *J*=7.5, 10 Hz, 1H, H_{7a}), 3.10 (dd, *J*=6.5, 10 Hz, 1H, H_{7b}), 2.45 (m, 2H, H_{4a} and H_{4b}), 1.68 (q, *J*=7.5 Hz, 2H, $C(CH_2CH_3)_2$), 1.64 (q, *J*=7.5 Hz, 2H, $C(CH_2CH_3)_2$), 1.49 (s, 9H, $C(CH_3)_3$), 0.94 (t, *J*=7.5 Hz, 3H, $C(CH_2CH_3)_2$), 0.90 (t, *J*=7.5 Hz, 3H, $C(CH_2CH_3)_2$). ^{13}C NMR δ: 165.5 (s′, C_1), 142.8 (d′, C_3), 125.5 (d′, C_2), 112.8 (s′, $C(CH_2CH_3)_2$), 80.4 (s′, $C(CH_3)_3$), 77.9 (d′, C_5/C_6), 76.0 (d′, C_5/C_6), 32.4 (t′, C_4), 30.1 (t′, CH_2CH_3), 29.1 (t′, CH_2CH_3), 28.1 (q′, $C(CH_3)_3$), 8.6 (q′, CH_2CH_3), 8.0 (q′, CH_2CH_3), 3.1 (t′, C_7). FTIR (KBr) 1700 (s), 1650 (m), 1160 (s) cm^{-1}. GC–MS: t_R=10.04 min, (EI) *m/z*: 381 (24.6%, M−Et), 251 (26.8%), 213 [20.1%, M−(ICH_2 and C_4H_8)], 123 (17.2%), 57 (100%, *t*Bu). HRMS (EI) found 381.0559; mass calcd for M–Et=$C_{14}H_{22}IO_4$: 381.0563.

4.1.9. (2*E*) 2,3,4,7-Tetradeoxy-7-iodo-5,6-*O*-(1-ethylpropylidene)-D-*ribo*-hept-2-enitol (11). A solution of DIBAL (1.0 M toluene, 1.22 mL, 1.22 mmol) was added dropwise over 12 min to a cooled (0 °C) solution of **9** (0.227 g, 0.554 mmol) in anhydrous toluene (12 mL) under an argon atmosphere. The reaction mixture was stirred at 0 °C for 5 h and then worked up as previously described for compound **10a**. Radial chromatography (2 mm silica plate) of the crude products allowed for the separation of 0.118 g (63%) of allylic alcohol **11** from the minor reaction products. Compound **11** was isolated as a colorless oil (GC purity=96%). R_f=0.44 silica, 4:1:1 CH_2Cl_2–ether–hexanes. ^{1}H NMR δ: 5.77 (m, 2H, H_2 and H_3), 4.40 (partially resolved ddd, *J*=6, 6, 8 Hz, 1H, H_6), 4.21 (m, 1H, H_5; signal simplifies to a partially resolved ddd after resolution enhancement, *J*=8, 6, 6 Hz), 4.14 (m, 2H, H_{1a} and H_{1b}), 3.20 (dd, *J*=8, 10 Hz, 1H, H_{7a}), 3.15 (dd, *J*=6, 10 Hz, 1H, H_{7b}), 2.35 (m, 2H, H_{4a} and H_{4b}), 1.68 (m, 4H, 2×CH_2CH_3), 1.56 (s large, OH and H_2O), 0.95 (t, *J*=7.5 Hz, 3H, CH_2CH_3), 0.90 (t, *J*=7.5 Hz, 3H, CH_2CH_3). ^{13}C NMR δ:

131.9 (d′, C_2/C_3), 127.9 (d′, C_2/C_3), 112.5 (s′, $C(CH_2CH_3)_2$), 78.0 (d′, C_5/C_6), 77.0* (d′, C_5/C_6, *This signal is masked by the $CDCl_3$ signal and was detected by a DEPT experiment.), 63.5 (t′, C_1), 32.5 (t′, C_4), 30.2 (t′, CH_2CH_3), 29.1 (t′, CH_2CH_3), 8.6 (q′, CH_2CH_3), 8.0 (q′, CH_2CH_3), 3.8 (t′, C_7). FTIR (film) 3395 (l), 1677 (w) cm^{-1}. GC–MS: $t_R=9.11$ min, (EI) *m/z*: 311 (17.6%, M -Et), 269 (11.1%, M−$CH_2CH{=}CHCH_2OH$), 213 (14.6%, M−I), 81 (27.1%), 57 (100%, $CH{=}CHCH_2OH$). HRMS (EI) found 311.0141; mass calcd for M−Et=$C_{10}H_{16}IO_3$: 311.0144.

4.1.10. (2*E*) 2,3,4,7-Tetradeoxy-7-iodo-D-*ribo*-hept-2-enitol (12). Deprotection was accomplished using the protocol of Hillier et al.[19] A mixture of **10a** (0.151 g, 0.485 mmol), MeOH (1 mL) and an acidic resin (Amberlite IR-120) was stirred at room temperature for 24 h under an argon atmosphere. The mixture was filtered using Celite and the filtrate concentrated. Radial chromatography (2 mm silica plate) gave 0.112 g (85%) of pure **12**: solid, mp 78–79 °C. $R_f=0.30$ (silica, 19:1 CH_2Cl_2-MeOH). $[\alpha]_D=16.1$ (*c* 0.19, 21.4 °C). ^1H NMR (300 MHz, DMSO-d_6) δ: 5.58 (m, 2H, H_2 and H_3), 5.13 (d, 1H, $J=6$ Hz, C_5–OH), 4.69(d, 1H, $J=6$ Hz, C_6-OH), 4.56 (dd, 1H, $J=5$, 5.5 Hz, C_1–OH), 3.87 (apparent t, 2H, H_{1b} and H_{1a} that simplifies to a d with $J=4$ Hz after D_2O exchange), 3.46 (dd, $J=3$, 10 Hz, 1H, H_{7a}), 3.28 (dd, $J=6$, 10 Hz, 1H, H_{7b}), 3.21 (m, 1H, H_5), 3.04 (m, 1H, H_6; simplifies to a ddd after D_2O exchange and resolution enhancement, $J=3$, 6, 7.5 Hz), 2.35 (m, 1H, H_{4a}), 2.04 (m, 1H, H_{4b}). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 132.3 (d′, C_2/C_3), 127.2 (d′, C_2/C_3), 73.3 (d′, C_5/C_6), 72.8 (d′, C_5/C_6), 61.6 (t′, C_1), 36.0 (t′, C_4), 15.7 (t′, C_7). FTIR (KBr) 3304 (br, OH) cm^{-1}. FTIR (solution in CCl_4–MeOH) 1669 (very weak) cm^{-1}. GC–MS: $t_R=8.28$ min, (EI) *m/z*: 254 (1.6%, M−H_2O), 183 (11.2%), 84 [24.5%, M−(ICH_2CHOH and OH)], 83 (60.1%, M−(ICH_2CHOH and H_2O)], 57 (32.3%, $CH{=}CHCH_2OH$), 55 (100%), 54 (50.1%), 44 (19.7%), 43 (26.5%). MS (CI, NH_3) *m/z*: 290 [3.3%, M+18 (M=$C_7H_{13}IO_3$)], 255 [3.3%, (M+1)-H_2O], 254 (16.2%, M−H_2O), 83 [100%, M−(ICH_2CHOH and H_2O)]. HRMS (EI) found 253.9800; calcd for M−$H_2O{=}C_7H_{11}IO_2$: 253.9804.

4.2. General procedures for reactions with samarium(II) iodide

Method A1. A flask containing the substrate (0.15 mmol) and a magnetic stirring bar was closed with a septum and purged with argon using a Firestone valve. Distilled THF (2.5–5.5 mL) was added followed by HMPA and/or MeOH where appropriate; reaction flasks for experiments run at −78 °C were cooled in a dry ice–acetone bath. A commercial solution of SmI_2 in THF (0.1 M, 4.5–7.5 mL, 0.45–0.75 mmol) was transferred via cannula to the reaction mixture. The final concentration of the iodide substrate was 0.015 M. The solution was stirred at −78 °C for 2 h and then at 0 °C for 1.3–2 h under ambient lighting conditions. The reaction was quenched by addition of a dilute aqueous solution of HCl (0.1 M, 5 mL). The mixture was diluted with water (5 mL) and extracted with EtOAc (3×10 mL). The combined organic extracts were washed successively with water (20 mL or 3×20 mL when HMPA was used), saturated aqueous solutions $Na_2S_2O_3$ (20 mL) and NaCl (20 mL), dried over $MgSO_4$, filtered and concentrated. The crude products were purified by radial chromatography (silica gel or Adsorbosil plates, with a mixture of EtOAc and hexanes).

Method A2. As per Method A1, except that reactions were run at room temperature.

Methods B1 and B2. A solution of the substrate (0.348 mmol) in THF (8 mL), HMPA (1.16 mL, 6.67 mmol), and MeOH (0.14 mL, 3.5 mmol) was prepared under an argon atmosphere and either cooled to −78 °C (Method B1) or kept at room temperature (Method B2). To this solution was added, dropwise (ca. 1.2 mL/min), a commercial solution of SmI_2 in THF (0.1 M, 13.9 mL, 1.39 mmol). The reaction was run under ambient lighting conditions and the final concentration of substrate= 0.015 M. The reaction mixture was stirred under an argon atmosphere for 1.75 h and then quenched by the addition of dilute aqueous HCl (0.1 M, 20 mL). The mixture was diluted with ether (20 mL), the phases separated and the aqueous layer re-extracted with ether (3×30 mL). The combined organic phases were washed successively with saturated aqueous solutions of $CuSO_4$ (3×30 mL), $Na_2S_2O_3$ (30 mL) and NaCl (30 mL), dried over $MgSO_4$, filtered. The filtrate was analyzed by GC–MS, concentrated and the crude residue purified by radial chromatography.

Method C. As per Method B1, with the following exceptions: a solution of the substrate (0.385 mmol) in THF (8.8 mL) and MeOH (0.16 mL, 3.9 mmol) was prepared under an argon atmosphere and cooled to −78 °C. In a second flask, a solution of HMPA (1.28 mL, 7.36 mmol) and SmI_2 in THF [0.1 M, 15.4 mL, 1.54 mmol] was stirred at room temperature under an argon atmosphere for 20 min and then transferred dropwise, by cannula (ca. 1.2 mL/min), to the flask containing the iodide substrate.

Method D. A solution of the substrate (0.340 mmol) in THF (8.9 mL) and MeOH (0.14 mL, 3.4 mmol) was prepared under an argon atmosphere in a pyrex flask at room temperature. To this mixture was transferred, via cannula, a solution of SmI_2 in THF [0.1 M, 13.6 mL, 1.36 mmol]. The resulting reaction mixture was irradiated for 4 h in the visible range with a xenon lamp and appropriate filters. A water filter [quartz cylinder dimensions=55 mm (length)× 28 mm (diameter)] and a Schott GG 375 nm filter were placed between the Sciencetech 150 W xenon lamp and the reaction flask at spacing intervals of ca. 0.7, 2.0 and 3.5 cm respectively. Workup as per Method B1 but without the aqueous $CuSO_4$ wash.

4.3. Characterization of the vinylcyclopentanetriol derivatives

Reaction of **2b** *with SmI_2 in THF/MeOH (Method A): preparation of* **4a**, **4b** and **5a**. A THF solution of SmI_2 (6.8 mL, 0.1 M, 0.68 mmol) was added to a solution of **2b** (0.0743 g, 0.2264 mmol), MeOH (0.085 mL, 2.1 mmol) and THF (8.5 mL). After 4 h at room temperature reaction was worked up and the crude residue purified by radial chromatography [using the following series of eluants: 6% EtOAc–CH_2Cl_2 (80 mL), 26% EtOAc–CH_2Cl_2 (100 mL),

50% EtOAc–CH_2Cl_2 (50 mL); 2 mm silica plate] in order to separate **2b** (0.0268 g, 36.1%, slightly impure by ^{1}H NMR) from two other fractions (A and B). Further purification of fraction A (20% EtOAc–hexenes, 1 mm plate) allowed for the separation of **4a** (0.0144 g, 34.5%) and **4b** (0.0055 g, 13.2%). Attempts to further purify fraction B (26% EtOAc–CH_2Cl_2, 1 mm plate) were only partially successful; we isolated **5** (0.0078 g, 18.7% yield) as a slightly impure sample. Although compounds **4a** and **4b** are separable by TLC, they are not separable using our GC method as both compounds have a t_R=6.5 min.

4.3.1. Compound 4a. Oil. R_f=0.26 (TLC, 20% EtOAc–hexanes). $[\alpha]_D$=16.6 (*c* 1.22). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.75 (ddd, J=6.5, 10.5, 17.2 Hz, 1H, $H_{1'}$), 5.09 [2H, overlapping ddd signals; $H_{2b'}$ (5.09 ppm, J=17.3, 1.4, 1.6 Hz) and $H_{2a'}$ (5.07 ppm, J=10.6, 1.4, 1.5 Hz)], 4.49 [2H, apparent d, H_2 and H_3. Upon decoupling at 4.08 ppm (H_1), this signal collapses to an apparent singlet but decoupling at 2.75 ppm (H_4) or at 1.90 (H_{5a} and H_{5b}) had no obvious effect on the H_2+H_3 signal.], 4.08 (broad m, 1H, H_1), 2.75 (m, 1H, H_4), 2.40 (broad, 1H, OH, D_2O exchangeable), 1.90 (m, 2H, $H_{5a}+H_{5b}$), 1.52 (s, 3H, CH_3), 1.36 (s, 3H, CH_3). ^{1}H NMR (benzene-d_6, 300 MHz) δ: 5.42 (ddd, J=10.2, 17.5, 6.7 Hz, 1H, $H_{1'}$), 4.86–4.79 (m, 2H, overlapping signals of $H_{2a'}$ and $H_{2b'}$), 4.13 [dd, 1H, $J_{3,2}$=5.9 Hz, $J_{3,4}$=1.8 Hz, H_3. Upon decoupling at 2.74 ppm (H_4), this H_3 dd collapses to a d (J=6 Hz)], 4.02 [apparent t (J_{app}=ca. 6 Hz) which is a partially resolved dd, 1H, H_2], 3.94 (broad m, 1H, H_1), 2.74 (broad m, 1H, H_4), 2.42 (broad, 1H, OH, D_2O exchangeable), 1.90 [m, 1H, H_5; upon decoupling at 2.74 ppm (H_4), this multiplet collapses to a dd, J=13, 8 Hz], 1.65 [m, 1H, H_5; upon decoupling at 2.74 ppm (H_4), this multiplet collapses to a dd, J=13, 5 Hz], 1.33 (s, 3H, CH_3), 1.12 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 138.0 (*C*H=CH_2), 115.3 (CH=*C*H_2), 111.6 (s′, *C*$(CH_3)_2$), 84.3 (d′, C_2 or C_3), 79.0 (d′, C_2 or C_3), 71.1 (C_1), 44.3 (C_4), 36.0 (C_5), 26.1 (CH_3), 24.3 (CH_3). FTIR (film): 3457 (s) cm^{-1}. MS [EI] *m*/*z*: 184 (0.5%, $M^{+\cdot}$), 169 (100%, M−CH_3). HRMS: found: 169.0862; calcd for M−CH_3=$C_9H_{13}O_3$: 169.0865.

4.3.2. Compound 4b. Oil. R_f=0.18 (TLC, 20% EtOAc–hexanes). ^{1}H NMR δ: 5.91 (m, 1H, $H_{1'}$), 5.08–5.16 (m, 2H, $H_{2a'}+H_{2b'}$), 4.54 [dd that presents as an apparent t, J_{app}=5 Hz, 1H, H_3. Decoupling at 2.28 ppm (H_4) simplifies the H_3 signal to a d ($J_{2,3}$=5 Hz).], 4.47 [dd that presents as an apparent t, J_{app}=5.5 Hz, 1H, H_2. Decoupling at 3.91 ppm (H_1) simplifies the H_2 signal to a d ($J_{2,3}$=5 Hz).], 3.91 (broad m, 1H, H_1), 2.41 (d, J=11 Hz, 1H, OH, D_2O exchangeable), 2.28 (m, 1H, H_4), 1.94 (m, 1H, H_{5b}), 1.63 (m, 1H, H_{5a}), 1.50 (s, 3H, CH_3), 1.35 (s, 3H, CH_3). ^{13}C NMR δ: 135.8 (*C*H=CH_2), 116.2 (CH=*C*H_2), 110.6 (s′, *C*$(CH_3)_2$), 81.6 (C_3), 78.8 (C_2), 72.2 (C_1), 42.8 (C_4), 35.5 (C_5), 25.6 (CH_3), 24.1 (CH_3). MS [EI] *m*/*z*: 183 (11.3%, M−1), 169 (100%, M−CH_3). HRMS: found: 169.0862; calcd for M−CH_3=$C_9H_{13}O_3$: 169.0865.

4.3.3. Compound 5. Compound **5** was isolated as a slightly impure pale yellow oil. R_f=0.39 (TLC, 26% EtOAc–CH_2Cl_2). ^{1}H NMR (acetone-d_6, 300 MHz) δ: 5.81–5.64 (m, 2H, H_2 and H_6), 5.36 (m, 1H, H_3), 5.23 (ddd, J=1, 2, 17 Hz, 1H, H_7), 5.11 (ddd, J=1, 2, 10 Hz, 1H, H_7), 5.03 (partially resolved ddd, J=1, 7, 9 Hz, 1H, H_4), 4.58 (m, 1H, H_5), 4.22 (m, 1H, H_{1a}), 4.05 (m, 1H, H_{1b}), 3.75 (apparent t, J_{app}=5.5 Hz, 1H, OH), 1.42 (s, 3H, CH_3), 1.32 (s, 3H, CH_3]. ^{13}C NMR ($CDCl_3$, 75 MHz): 134.2, 132.4, 128.3, 118.4, 109.0, 80.0, 74.4, 58.8, 28.0, 25.5. FTIR (film): 3421(s) cm^{-1}. GC–MS: t_R=7.09 min; [EI] *m*/*z*: 169 (5.8%, M−15), 109 (26.3%), 98 (100%).

4.3.4. Compound 3a. Compound **3a**: pale yellow oil. R_f=0.29 (TLC, 12% EtOAc–hexanes). $[\alpha]_D$=95.5 (*c* 1.49). ^{1}H NMR δ: 5.77 (ddd, J=6.4, 10.6, 17 Hz, 1H, $H_{1'}$), 5.07–5.16 [2H, overlapping signals for $H_{2b'}$ (δ 5.12, partially resolved ddd, J=17, 1.2, 1.7 Hz) and $H_{2a'}$ (δ 5.10, partially resolved ddd, J=10.6, 1.4, 1.3 Hz)], 4.91 (m, 1H, H_1), 4.67 (apparent t, J_{app}=5.5 Hz ($J_{2,3}\cong J_{2,1}$), 1H, H_2), 4.48 [apparent d ($J_{2,3}$=5.7 Hz), 1H, H_3; this signal is actually more complex. Decoupling at 1.95 ppm (H_{5b}) results in a change of the signal to a dd ($J_{2,3}$=5.7, $J_{3,4}$=1.3 Hz).], 2.77 (broad m, 1H, H_4), 2.09–2.22 (4H, s at δ 2.12 (OCO*C*H_3) and m for H_{5a}], 1.95 (m, 1H, H_{5b}), 1.50 (s, 3H, CH_3), 1.33 (s, 3H, CH_3). ^{13}C NMR δ: 170.7 (C=O); 137.7 (*C*H=CH_2), 115.5 (CH=*C*H_2), 111.4 (*C*$(CH_3)_2$), 84.1 (C_3), 77.9 (C_2), 73.3 (C_1), 43.8 (C_4), 31.7 (C_5), 26.1 (CH_3), 24.5 (CH_3), 20.9 (*C*H_3CO). FTIR (film): 1739 (s), 1637 (w) cm^{-1}. MS [EI] *m*/*z*: 226 (0.6%, $M^{+\cdot}$), 211 (72.3%, M−CH_3), 43 (100%, CH_3CO^+). HRMS: found 211.0973; calcd for M−CH_3=$C_{11}H_{15}O_4$: 211.0970.

4.3.5. Compound 3b. Compound **3b**: pale yellow oil. R_f=0.21 (TLC, 12% EtOAc–hexanes) ^{1}H NMR δ: 5.93 (m, 1H, $H_{1'}$), 5.10–5.17 (m, 2H, overlapping $H_{2a'}$ and $H_{2b'}$ signals), 4.70 [m, 2H, overlapping H_1 and H_2 signals.], 4.53 [1H, H_3. This signal appears to be a dd with line overlap ($J_{3,2}$=5.1, $J_{3,4}$=4.8 Hz) but is actually more complex. Decoupling at δ 2.35 (H_4) collapses the signal to an apparent d, $J_{3,2}$=5.2 Hz. Decoupling at δ 4.70 (H_1+H_2) changes this signal to a m.], 2.35 (m, 1H, H_4), 2.13 (s, 3H, *C*H_3CO), 1.95 (m, 2H, $H_{5a}+H_{5b}$), 1.49 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). ^{13}C NMR δ: 170.9 (C=O); 135.7 (*C*H=CH_2), 116.4 (CH=*C*H_2), 110.8 (*C*$(CH_3)_2$), 81.3 (C_3), 77.8 (C_1 or C_2), 73.7 (C_1 or C_2), 42.5 (C_4), 31.5 (C_5), 25.7 (CH_3), 24.2 (CH_3), 20.9 (*C*H_3CO). FTIR (film): 1738 (s) cm^{-1}. MS [EI] *m*/*z*: 226 (1.1%, $M^{+\cdot}$), 211 (100%, M−CH_3). HRMS: found 211.0968; calcd for M−CH_3=$C_{11}H_{15}O_4$: 211.0970.

4.4. Characterization of the vinylcyclopentanediol derivatives

In most instances *cis* and *trans* vinylcyclopentanediol diastereoisomers were isolated as an inseparable (by radial chromatography) mixture.

4.4.1. NMR and GC–MS analysis of mixtures of 14a (*trans*) and 14b (*cis*) isolated from reactions with 10a, 10b or 13. *Compounds* **14a** and **14b**. Colorless oil (mixture of *cis* and *trans*). R_f=0.91 (silica, 1:2:3 Et_2O–CH_2Cl_2–pentane). GC–MS: t_R=4.2 min, *trans* compound **14a**. [EI] *m*/*z*: 153 (100%, M−CH_3), 111 (19.5%), 93 (86.4%, M−$C_3H_7O_2$), 91 (35.5%), 77 (25%), 59 (16.4%, $(CH_3)_2COH$), 43 (60.4%). t_R=4.4 min, *cis* compound. [EI] *m*/*z*: 153 (98.9%, M−CH_3), 111 (17.6%), 93 (100%, M−$C_3H_7O_2$), 91 (39.5%), 77 (29.2%), 67 (21.2%), 59 (20.8%, $(CH_3)_2COH$), 43 (69.8%). ^{13}C NMR (125 MHz, $CDCl_3$)

chemical shifts assigned to the *trans* isomer **14a**: δ: 140.4 (d′, $C_{1'}$), 113.9 (t′, $C_{2'}$), 108.8 (s′, $C(CH_3)_2$), 80.4 (d′, C_1/C_2), 39.8 (d′, C_4), 39.5 (t′, C_3/C_5), 26.1 (q′, CH_3), 23.7 (q′, CH_3); chemical shifts assigned to the *cis* isomer **10b**: δ: 142.1 (d′, $C_{1'}$), 113.1 (t′, $C_{2'}$), 111.3 (s′, $C(CH_3)_2$), 81.0 (d′, C_1/C_2), 43.0 (d′, C_4), **38.7** (t′, C_3/C_5), 26.9 (q′, CH_3), 24.4 (q′, CH_3). ^{1}H NMR (300 MHz, $CDCl_3$) chemical shifts assigned to the *trans* isomer **14a**: δ 5.74 (partially resolved ddd, 1H, $J_{1'-4}=7$ Hz, $J_{1'-2a'}=10$ Hz and $J_{1'-2b'}=17$ Hz, $H_{1'}$), 5.04 (ddd, 1H, $J_{2b'-4}=1$ Hz, $J_{2b'-2a'}=2$ Hz and $J_{2b'-1'}=17$ Hz, $H_{2b'}$), 4.94 (ddd, 1H, $J_{2a'-4}=1$Hz, $J_{2a'-2b'}=2$ Hz and $J_{2a'-1'}=10$ Hz, $H_{2a'}$), 4.62 (m, 2H, H_1/H_2), 2.80 (m, 1H, H_4), 1.95 (apparent dd, 2H, $J_{4-3a/5a}=6$ Hz and $J_{gem}=14$ Hz, H_{3a}/H_{5a}), 1.44 (s, 3H, CH_3), 1.33 (m, 2H, H_{3b}/H_{5b}), 1.27 (s, 3H, CH_3); chemical shifts assigned to the *cis* isomer **14b**: δ 5.96 (partially resolved ddd, 1H, $J_{1'-4}=$ 8 Hz, $J_{1'-2a'}=10$ Hz and $J_{1'-2b'}=17$ Hz, $H_{1'}$), 4.97 (ddd, 1H, $J_{2b'-4}=1$ Hz, $J_{2b'-2a'}=2$ Hz and $J_{2b'-1'}=17$ Hz, $H_{2b'}$), 4.88 (ddd, 1H, $J_{2a'-4}=1$ Hz, $J_{2a'-2b'}=2$ Hz and $J_{2a'-1'}=$ 10 Hz, $H_{2a'}$), 4,62 (m, 2H, H_1/H_2), 2.59 (m, 1H, H_4), 2.03 (m, 2H, H_{3b}/H_{5b}), 1.69 (m, 2H, H_{3a}/H_{5a}), 1.48 (s, 3H, CH_3), 1.30 (s, 3H, CH_3).

4.4.2. NMR and GC–MS analysis of mixtures of 15a (*trans*) and 15b (*cis*) isolated from reactions with 11. *Compounds* **15a** *and* **15b**. Colorless oil (mixture of *cis* and *trans*). $R_f=0.46$ (silica, 2:5 CH_2Cl_2–pentane). GC–MS: $t_R=5.6$ min, *trans* compound **15a**. [EI] *m/z*: 167 (100%, M−Et), 93 (80.1%, M−$C_5H_{11}O_2$), 91 (33.7%), 77 (22.6%), 57 (76.3%). $t_R=5.7$ min, *cis* compound **15b**. [EI] *m/z*: 167 (76.3%, M−Et), 93 (86.4%, M−$C_5H_{11}O_2$), 91 (37.4%), 77 (26.1%), 57 (100%). ^{13}C NMR chemical shifts assigned to the *trans* isomer **15a**: δ 140.7 (d′, $C_{1'}$), 113.8 (t′, $C_{2'}$), 112.8 (s′, $C(CH_2CH_3)_2$), 80.4 (d′, C_1 and C_2), 40.1 (d′, C_4), 39.5 (t′, C_3 and C_5), 28.2 (t′, CH_2CH_3), 27.8 (t′, CH_2CH_3), 8.8 (q′, CH_2CH_3), 7.6 (q′, CH_2CH_3); chemical shifts assigned to the *cis* isomer **15b**: δ: 141.3 (d′, $C_{1'}$), 113.4 (t′, $C_{2'}$), 116.5 (s′, $C(CH_2CH_3)_2$), 80.8 (d′, C_1 and C_2), 43.0 (d′, C_4), 38.7 (t′, C_3 and C_5), 28.8 (t′, CH_2CH_3), 28.5 (t′, CH_2CH_3), 8.6 (q′, CH_2CH_3), 7.9 (q′, CH_2CH_3); ^{1}H NMR chemical shifts assigned to the *trans* isomer **15a**: δ 5.76 (partially resolved ddd, 1H, $J_{1'-4}=7$ Hz, $J_{1'-2a'}=10$ Hz and $J_{1'-2b'}=17$ Hz, $H_{1'}$), 5.06 (partially resolved ddd, 1H, $J_{2b'-4}=2$ Hz, $J_{2b'-2a'}=2$ Hz and $J_{2b'-1'}=17$ Hz, $H_{2b'}$), 4.96 (partially resolved ddd, 1H, $J_{2a'-4}=1$ Hz, $J_{2a'-2b'}=2$ Hz, $J_{2a'-1'}=10$ Hz, $H_{2a'}$), 4.63 (m, 2H, H_1 and H_2; same chemical shift for both **15a** and **15b**), 2.87 (m, 1H, H_4), 2.01 (partially resolved ddd, 2H, $J_{4-3a/5a}=6$ Hz, $J_{1/2-3a/5a}=$ 1 Hz, $J_{gem}=13$ Hz, H_{3a} and H_{5a}), 1.71 (q, 2H, $J=7$ Hz, CH_2CH_3), 1.58 (q, 2H, $J=7$ Hz, CH_2CH_3), 1.33 (m, 2H, H_{3b} and H_{5b}; this signal overlaps with the H_{3a}/H_{5a} multiplet of the *cis* isomer), 0.97 (t, 3H, CH_2CH_3), 0.88 (t, 3H, CH_2CH_3); the chemical shifts of **15b** overlap with those of **15a** with the exception of the following signals assigned to the *cis* isomer **15b**: δ 5.90 (partially resolved ddd, 1H, $J_{1'-4}=7$ Hz, $J_{1'-2a'}=10$ Hz, $J_{1'-2b'}=17$ Hz, $H_{1'}$), 2.11 (m, 1H, H_4), 1.72 (q, 2H, $J=7$ Hz, CH_2CH_3), 0.96 (t, 3H, CH_2CH_3), 0.87 (t, 3H, CH_2CH_3).

4.4.3. NMR and GC–MS analysis of mixtures of 16a(*trans*) and 16b(*cis*) isolated from reactions with 12. *Compounds* **16a** *and* **16b**. Solid (mixture of *cis* and *trans*). $R_f=0.39$ (silica, 1:19 MeOH–CH_2Cl_2). GC–MS: $t_R=4.62$ min, *trans* isomer **16a**. [EI] *m/z*: 110 (41.9%, M−H_2O), 95 (46.7%), 83 (100%, C_5H_7O), 82 (47.7%), 67 (30.2%), 56 (33.9%), 55 (89.9%), 43 (27.3%), 41 (32.9%), 29 (24.1%), 28 (22.6%), 27 (20.9%); $t_R=4.58$ min, *cis* isomer **16b**. [EI] *m/z*: 110 (37.5%, M−H_2O), 95 (42.4%), 83 (100%, C_5H_7O), 82 (42.4%), 81 (20%), 69 (21%), 67 (31.1%), 56 (37.5%), 55 (93.9%), 43 (28.2%), 41 (33.6%), 39 (27%). ^{13}C NMR chemical shifts assigned to the *trans* isomer **16a**: δ 142.6 (d′, $C_{1'}$), 112.8 (t′, $C_{2'}$), 73.5 (d′, C_1 and C_2), 38.6 (d′, C_4), 38.3* (t′, C_3 and C_5; *both isomers have the same chemical shift for their C_3/C_5 carbons); chemical shifts assigned to the *cis* isomer **16b**: δ 142.8 (d′, $C_{1'}$), 112.9 (t′, $C_{2'}$), 73.2 (d′, C_1 and C_2), 38.3* (t′, C_3 and C_5), 37.9 (d′, C_4). ^{1}H NMR chemical shifts assigned to the *trans* isomer **16a**: δ 5.76 (partially resolved ddd, 1H, $J_{1'-4}=8$ Hz, $J_{1'-2a'}=10$ Hz, $J_{1'-2b'}=17$ Hz, $H_{1'}$), 4.99* (ddd, 1H, $J_{gem}=1$ Hz, $J_{2b'-4}=3$ Hz, $J_{2b'-1'}=17$ Hz, $H_{2b'}$), 4.91* (ddd, 1H, $J_{gem}=1$ Hz, $J_{2a'-4}=2$ Hz, $J_{2a'-1'}=10$ Hz, $H_{2a'}$; *the *cis* and *trans* isomers have the same chemical shifts signals for the $H_{2a'}$ and $H_{2b'}$ protons.), 4.18 (m, 2H, H_1 and H_2), 2.98 (m, 1H, H_4), 2.18 [s large, 2H, 2×OH; the OH signals for the *cis* and *trans* isomers overlap to give a broad singlet centred at 2.18 ppm (exchanges with D_2O) that partially overlaps with the multiplet assigned to the H_{3b} and H_{5b} protons of the *cis* isomer], 1.93 (m, 2H, H_{3a} and H_{5a}), 1.68 (m, 2H, H_{3b} and H_{5b}); chemical shifts assigned to the *cis* isomer **16b**: δ 5.84 (partially resolved ddd, 1H, $J_{1'-4}=$ 7 Hz, $J_{1'-2a'}=17$ Hz, $J_{1'-2'b}=10$ Hz, $H_{1'}$), 4.99* (ddd, 1H, $J_{gem}=1$ Hz, $J_{2b'-4}=3$ Hz, $J_{2b'-1'}=17$ Hz, $H_{2b'}$), 4.91* (ddd, 1H, $J_{gem}=1$ Hz, $J_{2a'-4}=2$ Hz, $J_{2a'-1'}=10$ Hz, $H_{2a'}$; *the *cis* and *trans* isomers have the same chemical shifts signals for the $H_{2a'}$ and $H_{2b'}$ protons.), 4.05 (m, 2H, H_1 and H_2), 2.46 (m, 1H, H_4), 2.18 [broad s, 2H, 2×OH; the OH signals for the *cis* and *trans* isomers overlap to give a broad singlet centred at 2.18 ppm (exchanges with D_2O) that partially overlaps with the multiplet assigned to the H_{2b} and H_{5b} protons of the *cis* isomer], 2.16 (m, 2H, H_{3b} and H_{5b}), 1.55 (m, 2H, H_{3a} and H_{5a}).

4.4.4. NMR and GC–MS analysis of mixtures of 17a (*trans*) and 17b (*cis*) obtained by acetylation of mixtures of 16a and 16b. *Compounds* **17a** *and* **17b**. Oil (mixture of *cis* and *trans*), $R_f=0.87$ (silica, 4:1:1CH_2Cl_2–hexanes–ether). GC–MS: $t_R=6.3$ min, the *cis* and *trans* isomers were not separable using our method; [EI] *m/z*: 212 (2.9%, $M^{\cdot+}$]), 152 [3.5%, M−CH_3COOH (McLafferty)], 127 (10%), 110 (17.7%), 92 [38.8%, M−2×CH_3COOH (McLafferty)], 83 (13.8%), 43 (100%, CH_3CO). ^{13}C NMR chemical shifts assigned to the *trans* isomer: δ: 170.34 (s′, 2×CH_3C=O), 141.7 (d′, $C_{1'}$), 113.6* (t′, $C_{2'}$), 73.8 (d′, C_1 and C_2), 38.0 (d′, C_4), 35.1 (t′, C_3 and C_5), 20.9* (q′, 2×CH_3). *Same chemical shift for CH_3CO and C_2' for both isomers. Chemical shifts assigned to the *cis* isomer: δ 170.29 (s′, 2×CH_3C=O), 142.0 (d′, $C_{1'}$), 113.6* (t′, $C_{2'}$), 73.3 (d′, C_1 and C_2), 37.2 (d′, C_4), 35.2 (t′, C_3 and C_5), 20.9* (q′, 2×CH_3). *Same chemical shift for carbons $C_{2'}$ and CH_3CO for both isomers. ^{1}H NMR chemical shifts assigned to the *trans* isomer **17a**: δ 5.76 (partially resolved ddd, 1H, $J_{1'-4}=7.5$ Hz, $J_{1'-2a'}=10$ Hz and $J_{1'-2b'}=16.5$ Hz, $H_{1'}$], 5.25 (m, 2H, H_1 and H_2), 5.01 (m, 1H, $H_{2b'}$),* 4.94 (m, 1H, $H_{2a'}$),* 2.97 (m, 1H, H_4), 2.05 (s, 2×CH_3 of *trans* and *cis* isomers), 2.02 [m, 2H, H_{3a} and H_{5a} (overlaps with the CH_3 singlet of *cis* and *trans* isomers)], 1.79 (m, 2H, H_{3b} and H_{5b}).

*The signals for protons $H_{2a'}$ and $H_{2b'}$ of the *cis* and *trans* isomers overlap. Chemical shifts assigned to the *cis* isomer **17b**: δ 5.82 (partially resolved ddd, 1H, $J_{1'-4}=8$ Hz, $J_{1'-2a'}=17$ Hz and $J_{1'-2b'}=10$ Hz, $H_{1'}$), 5.13 (m, 2H, H_1 and H_2), 5.01 (m, 1H, $H_{2b'}$),* 4.94 (m, 1H, $H_{2a'}$),* 2.56 (m, 1H, H_4), 2.23 (m, 2H, H_{3b} and H_{5b}), 2.05 (s, $2\times CH_3$ for *trans* and *cis* isomers), 1.65 (m, 2H, H_{3a} and H_{5a}). *The signals of the $H_{2a'}$ and $H_{2b'}$ protons of the *cis* and *trans* isomers overlap.

4.5. Typical procedure for reactions with Bu_3SnH/AIBN (Bu_3SnH Method E)

A solution of **1b** (0.2275 g, 0.5519 mmol) in freshly distilled benzene (9 mL) was prepared under an argon atmosphere at room temperature. Solutions of AIBN (7.5 mg, 0.046 mmol in 2 mL benzene) and Bu_3SnH (0.613 mmol in 2 mL benzene) were then simultaneously added (dropwise over ca. 2 min) to this solution. The reaction mixture was heated at reflux for 4 h, cooled, and concentrated. The residue was diluted with ether (10 mL) and DBU (0.15 mL, 1.0 mmol) was added.[20] The mixture was titrated with a 1 M solution of iodine in ether (2 mL, ca. 2 mmol) and the yellow precipitate that formed was removed by filtration through a short column of silica gel (2×3 cm). The silica was washed with ether (3×10 mL) and the combined filtrates concentrated. The residue was dissolved in ether (10 mL) and the solution stirred with a 30% aqueous solution of KF (10 mL) for 3 h.[21] The heterogeneous mixture was filtered twice, the layers separated and the organic layer was then refiltered through a short pad of silica gel and concentrated. The crude products were purified by radial chromatography [2 mm plate with the following series of eluants: 10% EtOAc–hexanes (50 mL), 20% EtOAc–hexanes (50 mL), 30% EtOAc–hexanes (50 mL)] to give 0.0196 g of **6b** (12.4%), 0.0793 g of **6a** (50.2%) and 0.0150 g of a mixture of **6b** (0.0044 g, 2.8%) and **6a** (0.0106 g, 6.7%).

4.5.1. Compound 6a. Compound **6a** (*trans*): pale yellow oil, $R_f=0.26$ (30% EtOAc–hexanes). $[\alpha]_D=73.5$ (*c* 0.83, 25 °C). ^{1}H NMR δ: 4.92 (m, 1H, H_1), 4.66 [apparent t, $J_{app}=6$ Hz ($J_{1,2}\cong J_{2,3}$), 1H, H_2], 4.34 (d, $J_{2,3}=5.8$ Hz, $J_{4,3}\cong 0$ Hz, 1H, H_3), 4.11 (m, 2H, $H_{2a'}$ and $H_{2b'}$), 2.01–2.22 (m, 8H; H_4, $1\times H_5$, and both OCO*CH*$_3$ singlets at 2.10 and 2.04 ppm.), 1.44–1.81 [m, 6H; CH_3 (s,1.47 ppm) and multiplets for $H_5\times 1$, $H_{1'a}$ and $H_{1'b}$. The multiplets are better separated in the 500 MHz spectrum *i.e.* δ 1.76 ($1\times H_5$), 1.68 (m, $H_{1'a}$) and 1.55 (m, $H_{1'b}$).], 1.30 (s, 3H, CH_3). ^{13}C NMR δ: 170.9 (C=O), 170.7 (C=O), 111.8 ($C(CH_3)_2$), 84.5 (C_3), 78.1 (C_2), 73.1 (C_1), 62.6 ($C_{2'}$), 38.1 (C_4), 32.6 (C_5), 31.2 ($C_{1'}$), 26.1 (CH_3), 24.5 (CH_3), 20.92 (*C*H$_3$C=O), 20.90 (*C*H$_3$C=O). FTIR (film): 1732 (s), 1371 (s), 1238 (s, br), 1071 (s) 1044 (s) cm^{-1}. MS (EI) *m/z*: 271 (100%, M−CH_3), 229 (11.6%), 169 (15.7%), 151 (28.6%), 127 (11.6%), 109 (25.7%), 108 (11.3%), 91 (39.6%). HRMS (EI) found: 271.1180; calcd for M−15=$C_{13}H_{19}O_6$: 271.1182.

4.5.2. Compound 6a. Compound **6b** (*cis*): pale yellow oil. $R_f=0.29$ (30% EtOAc–hexanes). $[\alpha]_D=46.4$ (*c* 0.38, 25 °C). ^{1}H NMR δ: 4.66 (m, 2H, H_1 and H_2), 4.50 [apparent t, $J_{app}=4$ Hz ($J_{2,3}\cong J_{3,4}$), 1H, H_3], 4.05–4.24 (m, 2H, $H_{2'a}$ and $H_{2'b}$), 2.11 [s, 3H, $OCOCH_3$], 2.00 (s, 3H, $OCOCH_3$), 1.93 (m, 2H, $1\times H_5$ and $1\times H_{1'a}$), 1.78 (m, 2H, H_4 and $1\times H_{1'b}$), 1.63–1.70 (m, 1H, $1\times H_5$), 1.47 (s, 3H, CH_3), 1.31 (s, 3H, CH_3). ^{13}C NMR δ: 171.1 (C=O), 170.9 (C=O), 110.6 ($C(CH_3)_2$), 79.8 (C_3), 77.6 (C_2 or C_1), 73.6 (C_2 or C_1), 63.2 ($C_{2'}$), 35.2 (C_4), 31.8 (C_5), 27.6 ($C_{1'}$); 25.7 (CH_3), 24.2 (CH_3), 21.0 (*C*H$_3$CO), 20.9 (*C*H$_3$CO). FTIR (film): 1735 (s, br), 1260 (s), 1094 (s), 1023 (s) cm^{-1}. MS (EI) *m/z*: 271 (100%, M−CH_3), 169 (10.7%), 151 (61.6%), 109 (32.3%), 108 (18.3%), 91 (65.5%). HRMS (EI) *m/z*: found: 271.1183; calcd for M−15=$C_{13}H_{19}O_6$: 271.1182.

4.6. Typical procedure for reactions run with Bu_3SnH/Et_3B (Bu_3SnH Method F)

The method used is an adaptation of a literature procedure.[22] A solution of Et_3B in hexanes (1 M, 0.37 mL, 0.37 mmol, 1.1 equiv) was added to a solution of **10a** (0.106 g, 0.339 mmol) in anhydrous toluene (3 mL) under an argon atmosphere. A solution of Bu_3SnH in toluene was prepared and slowly added to the reaction mixture over 2 h (0.18 mL, 0.67 mmol, 2 equiv of Bu_3SnH in 0.72 mL toluene). After 4 h of stirring at room temperature, the mixture was diluted with hexanes (5 mL) and treated with TBAF (1.0 mL, 1.0 M in THF, 1.0 mmol). Stirring was continued at room temperature for 30 min before filtering the mixture through a short pad of silica gel. The silica was washed with ether (100 mL) and the combined filtrates concentrated. Tin compounds were still present and so the residue was next taken up in ether (10 mL) and treated with DBU (0.67 mmol, 0.10 mL) and an ether solution of I_2 (1 M, 1 mL). The mixture was filtered through a short pad of silica and the silica washed with ether (3×10 mL). The combined filtrates were treated with a 30% aqueous solution of KF (5 mL) and the mixture stirred for 3 h at room temperature. The layers were separated and the organic layer was dried over $MgSO_4$, filtered and concentrated. Radial chromatography of the residue [1 mm plate, Et_2O–hexanes 1:3 gave 0.0475 g (75%) of compounds **18a** and **18b** in a 4.4:1 ratio determined by GC–MS. The mixture of **18a** and **18b** was rechromatographed and the collected fractions were first analyzed by GC–MS before being combined and concentrated. In this way we were able to isolate a pure sample of the *trans* isomer **18a** for characterization purposes; although we were not able to isolate a pure sample of the *cis* isomer **18b** we were able to obtain an enriched sample (*trans–cis*=1:6) for characterization purposes.

4.6.1. Compound 18a. Compound **18a** (*trans*): isolated as an oil; $R_f=0.38$ (silica, 3:1 Et_2O–hexanes). ^{1}H NMR δ: 4.63 (m, 2H, H_1 and H_2), 3.67 (t, 2H, $J_{2',1'}=7$ Hz, $H_{2'}$ protons), 2.24 (m, 1H, H_4), 1.99 (m, 2H, H_{3a} and H_{5a}; in the 500 MHz spectrum this signal appears as a dd with $J=6$ and 14 Hz), 1.61(apparent quadruplet, 2H, $J_{4,1'}=7$ Hz, $J_{2',1'}=7$ Hz, $H_{1'}$ protons), 1.57 (broad s, OH), 1.45 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.14 (m, 2H, H_{3b} and H_{5b}). ^{13}C NMR δ: 108.7 (s′, $C(CH_3)_2$), 80.4 (d′, C_1 and C_2), 62.1 (t′, $C_{2'}$), 39.8 (t′, C_3 and C_5), 37.1 (t′, $C_{1'}$), 32.8 (d′, C_4), 26.0 (q′, CH_3), 23.7 (q′, CH_3). GC–MS: $t_R=6.3$ min, (EI) *m/z*: 171 (79.6%, M−CH_3), 111 (53.5%), 93 (100%), 91 (24.3%), 83 (25.7%), 81 (23.7%), 67 (55.9%), 59 (18.7%), 55 (21.1%), 43 (54.2%).

4.6.2. GC–MS and NMR chemical shifts attributed to

18b (*cis*). R_f=0.38 (silica, 3:1 Et_2O–hexanes). GC–MS: t_R=6.4 min, (EI) *m/z*: 171 (76.3%, M−CH_3), 111 (22.9%), 93 (100%), 91 (21%), 83 (24.3%), 67 (56.8%), 59 (19.5%), 55 (20.7%), 43 (47.5%). Chemical shifts attributed to **18b**: ^{1}H NMR δ: 4.63 (m, 2H, H_1 and H_2), 3.68 (t, 2H, $J_{2',1'}$= 6 Hz, $H_{2'}$ protons), 2.12 (m, 1H, H_4), 1.99 (m, 2H, H_{3b}/H^*_{5b}), 1.79 (partially resolved dt, J=6.5, 7 Hz, 2H, $H_{1'}$ protons), 1.63 (m, 2H, H_{3a}/H^*_{5a}), 1.53 (broad s, OH), 1.50 (s, 3H, CH_3), 1.31 (s, 3H, CH_3). *Tentative assignment of these two signals. ^{13}C NMR δ: 81.1 (d′, C_1 and C_2), 61.9 (t′, $C_{2'}$), 39.8 (t′, C_3 and C_5), 38.0 (t′, $C_{1'}$), 35.5 (d′, C_4), 26.9 (q′, CH_3), 24.2 (q′, CH_3). We were not able to detect a signal for the quaternary carbon ($C(CH_3)_2$) of **18b**.

4.6.3. Compounds 20a and 20b. Reaction of **13** with Bu_3SnH/Et_3B in toluene gave an inseparable mixture of compounds **20a** and **20b** [oil, R_f=0.76 (silica, 4:1:1 CH_2Cl_2–Et_2O–hexanes; 86% yield, **20a** (*trans*): **20b** (*cis*)=3.1:1.0 (GC ratio)]. GC–MS (**20a**) t_R=6.9 min, (EI) *m/z*: 213 (43.5%, M−CH_3), 111 (15.4%), 93 (100%), 43 (46.9%). GC–MS (**20b**): t_R=7.1 min, (EI) *m/z*: 213 (40.5%, M−CH_3), 111 (14%), 93 (100%), 43 (49.1%). NMR chemical shifts attributed to **20a** (*trans*) and **20b** (*cis*). ^{1}H NMR δ: 4.61 (m, 2H, H_1/H_2, *cis* and *trans*), 4.07 (t, 2H, $J_{2',1'}$=7 Hz, $H_{2'}$ protons, *cis* and *trans*), 2.21 (m, 1H, H_4, *trans*), 2.03 (s, 3H, OCOCH_3 of *cis* and *trans*), 1.98 (m, 2H, H_{3a}/H_{5a} signal of *trans* overlaps with the H_{3b}/H_{5b} signal of the *cis*), 1.83 (apparent q, 2H, $J_{4,1'}$=$J_{1',2'}$=6,5 Hz, $H_{1'}$, *cis*), 1.65 (apparent q, 2H, $J_{4,1'}$=$J_{2',1'}$=7 Hz, $H_{1'}$ protons *trans* isomer; partially overlaps with H_{3a}/H_{5a} signal of *cis* isomer), 1.63 (m, 2H, H_{3a} and H_{5a} partial overlap with $H_{1'}$ protons of *trans* isomer), 1.48 (s, 3H, CH_3, *cis*), 1.43 (s, 3H, CH_3, *trans*), 1.275–1.295 (m, 1H, H_4 overlaps with CH_3 singlets of *trans* and *cis* at 1.280 and 1.278 ppm respectively), 1.13 (m, 2H, H_{3b}/H_{5b}, *trans*). ^{13}C NMR (**20b**, *cis*) δ: 171.14 (s′, C=O, Ac), 111.0 (s′, $C(CH_3)_2$), 81.0 (d′, C_1/C_2), 63.6 (t′, $C_{2'}$), 38.0 (t′, C_3/C_5), 35.8 (d′, C_4), 33.9 (t′, $C_{1'}$), 26.9 (q′, CH_3), 24.1 (q′, CH_3), 21.0* (q′, OCOCH_3). ^{13}C NMR (**20a**, *trans*) δ: 171.08 (s′, C=O, Ac), 108.7 (s′, $C(CH_3)_2$), 80.3 (d′, C_1/C_2), 63.8 (t′, $C_{2'}$), 39.7 (t′, C_3/C_5), 33.2 (d′, C_4), 32.8 (t′, $C_{1'}$), 26.0 (q′, CH_3), 23.7 (q′, CH_3), 21.0* (q′, OCOCH_3). *A single signal was observed for both *cis* and *trans* isomers.

4.6.4. Compounds 19a (*trans*) and 19b (*cis*). Reaction of **11** with Bu_3SnH/Et_3B in toluene gave a mixture of compounds **19a** and **19b** [oil, R_f=0.38 (silica, 2:3:2 CH_2Cl_2–hexanes–EtOAc; 73% yield, **19a** (*trans*): **19b** (*cis*)=7.7:1.0 (GC ratio)]. The mixture of **19a** and **19b** was rechromatographed and the collected fractions were first analyzed by GC–MS before being combined and concentrated. In this way, we were able to isolate a pure sample of the *trans* isomer **19a** for characterization purposes; although we were not able to isolate a pure sample of the *cis* isomer **19b** we were able to obtain an enriched sample (*trans*–*cis*=2.8:1.0) for characterization purposes. Compound **19a** (*trans*): isolated as an oil, R_f= 0.38 (silica, 2:3:2 CH_2Cl_2–hexanes–EtOAc). ^{1}H NMR δ: 4.61 (m, 2H, H_1/H_2), 3.67 (t, 2H, $J_{2',1'}$=7 Hz, $H_{2'}$), 2.27 (m, 1H, H_4), 2.02 (apparent ddd, 2H, J=6, 1, 13 Hz, H_{3a}/H_{5a}), 1.69 (q, 2H, J=7.5 Hz, CH_2CH$_3$), 1.60 (apparent q, 2H, $J_{2',1'}$=$J_{4,\ 1'}$=7 Hz, $H_{1'}$), 1.57 (q, 2H, J=7.5 Hz, CH_2CH$_3$), 1.51 (s large, 1H, 1×OH), 1.15 (m, 2H, H_{3b}/H_{5b}), 0.94 (t, 3H, J=7.5 Hz, CH_2CH_3), 0.87 (t, 3H, J=7.5 Hz, CH_2CH_3). ^{13}C NMR δ: 112.8 (s′, $C(CH_2CH_3)_2$), 80.4 (d′, C_1/C_2), 62.2 (t′, $C_{2'}$), 39.9 (t′, C_3/C_5), 37.4 (t′, $C_{1'}$), 33.1 (d′, C_4), 28.2 (t′, CH_2CH_3), 27.7 (t′, CH_2CH_3), 8.8 (q′, CH_2CH_3), 7.6 (q′, CH_2CH_3). GC–MS: t_R=7.3 min, (EI) *m/z*: 185 (64.5%, M−Et), 111 (51.5%), 93 (100%), 91 (23.1%), 81 (26.7%), 67 (67.9%), 57 (90%).

GC–MS and NMR chemical shifts attributed to **19b** (*cis*). GC–MS: t_R=7.5 min, (EI) *m/z*: 185 (50.7%, M− Et), 111 (28.4%), 93 (100%), 91 (20.6%), 67 (65.6%), 57 (87.2%). ^{1}H NMR: The signals of the *cis* isomer **19b** overlap with those of the *trans* isomer **19a** with the following exceptions: δ: 3.66 (t, 2H, $J_{2',1'}$=6.5 Hz, $H_{2'}$), 2.10 (m, 3H, H_{3b}/H_{5b} and H_4), 0.95 (t, 3H, J=7.5 Hz, CH_2CH_3), 0.86 (t, 3H, J=7.5 Hz, CH_2CH_3). ^{13}C NMR δ: 116.2 (s′, $C(CH_2CH_3)_2$), 80.8 (d′, C_1/C_2), 61.8 (t′, $C_{2'}$), 38.4 (t′, C_3/C_5), 38.1 (t′, $C_{1'}$), 35.6 (d′, C_4), 28.8 (t′, CH_2CH_3), 28.23 (t′, CH_2CH_3), 8.6 (q′, CH_2CH_3), 8.0 (q′, CH_2CH_3).

Compounds **22a** and **22b** were prepared by first carrying out a reductive cyclization on compound **12** with Bu_3SnH/Et_3B in THF and by then adding, after 24 h, an excess of Ac_2O (15 equiv) and pyridine (10 equiv) directly to the reaction mixture. The resulting mixture was stirred at room temperature overnight before workup, under our usual conditions, and radial chromatography. Compounds **22a** and **22b** were isolated as a mixture [oil, R_f=0.68 (silica, 4:1:1 CH_2Cl_2–Et_2O–hexanes), 62% yield, NMR ratio of **22a**–**22b**=1.0:1.4]. GC–MS: t_R=8.4 min, the *cis* and *trans* isomers were not separable by our method. (EI) *m/z*: 229 (0.05%), 213 (0.14%), 212 (0.15%), 169 (16%), 152 (4%), 127 (23.1%), 110 (54.2%), 92 (11.6%), 83 (43.2%), 43 (100%). NMR chemical shifts attributed to **22a** (*trans*) and **22b** (*cis*): ^{1}H NMR δ: 5.23 (m, 2H, H_1/H_2, **22a**), 5.12 (m, 2H, H_1/H_2, **22b**), 4.074 (t, 2H, $J_{2',1'}$=7 Hz, $H_{2'}$, **22a**), 4.067 (t, 2H, $J_{2',1'}$=7 Hz, $H_{2'}$, **22b**), 2.39 (m, 1H, H_4, **22a**), 2.22 (m, 2H, H_{3b}/H_{5b}, **22b**), 2.11–1.95 (m, H_{3a}/H_{5a} signal of **22a** overlaps with the H_4 multiplet of **22b** and the CH_3 singlets of both isomers at 2.053 and 2.046 ppm), 1.77 (apparent q, 2H, $J_{4,1'}$=$J_{2',1'}$=7 Hz, $H_{1'}$ protons, **22b**), 1.64 [m, 4H, $H_{1'}$ and H_{3b}/H_{5b} protons, **22a**. After resolution enhancement the signal for the $H_{1'}$ protons appears as a quadruplet at 1.68 ppm ($J_{4,1'}$=$J_{2',1'}$=7 Hz)], 1.50 (m, 2H, H_{3a}/H_{5a}, **22b**). ^{13}C NMR δ: 171.1, 170.4 and 170.3 (s′, C=O, **22a** and **22b**), 73.9 (d′, C_1/C_2, **22a**), 73.3 (d′, C_1/C_2, **22b**), 63.2 (t′, $C_{2'}$, **22a**), 63.1 (t′, $C_{2'}$, **22b**), 35.7 (t′, $C_{1'}$, **22b**), 35.4 (t′, $C_{1'}$, **22a**), 35.1 (t′, C_3/C_5, **22a**), 35.0 (t′, C_3/C_5, **22b**), 31.3 (d′, C_4, **22a**), 30.0 (d′, C_4, **22b**), 20.98 and 20.94 (q′, CH_3 of **22a** and **22b**).

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Supplementary data

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