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Stereochemical control in radical cyclization routes to *N*-glycosides: role of protecting groups and of the configuration (*E* versus *Z*) of the acceptors

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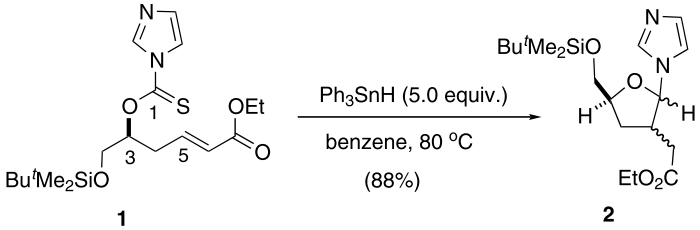
Abstract—The first radical intermediate in the thiourethane-mediated deoxygenation of an alcohol (Barton–McCombie reaction) can participate in an *exo*-hex-5-enyl or *exo*-hept-6-enyl type radical cyclization when a suitable radical acceptor (e.g. α,β-unsaturated ester, oxime ether or hydrazone) is appropriately placed. Carbohydrate-derived imidazolyl and triazolyl thioates with such acceptors, upon addition to excess of a good hydride donor (reverse addition), undergo moderately efficient cyclization reactions to give *N*-heterocyclic furanosides, and, surprisingly even *N*-pyranosides. Depending on the acceptor, glycosides with either C_2-carbon or C_2-amino substituents are formed. In the *exo*-hept-6-enyl cyclizations the (*Z*)-olefin acceptors give excellent stereoselectivity in the generation of the C_2 stereogenic center; only *altro*-isomers are formed. In all cases both α- and β-glycosides are obtained with a moderate preference for the latter.

1. Introduction

Earlier we reported that imidazole thioates derived from a 5- or 6-hydroxy-2,3-enoate (Eqs. (1) and (2)) upon addition to a large excess of an efficient hydrogen donor, undergo cyclization to give surprisingly good yields of imidazolyl glycosides.[1,2] In both cases, not unexpectedly, mixtures of all possible stereoisomers of the products **2** and **4** are formed in this otherwise efficient transformation. Since major applications of this chemistry are likely to be in the area of carbohydrates, we wondered whether the structural features present in this potential class of substrates might offer solutions to this problem. For example, the hydroxyl groups on the tether present opportunities for incorporating cyclic acetal-type protecting groups, which, through the resident conformational features, could influence the stereochemistry of the annulation process.[3] Since both furanosides and pyranosides of *N*-heterocycles appear to be accessible through this unconventional route, which involves the formation of the C_1–C_2 bond, we decided to study in some detail the effect of various structural parameters of the substrate on the course of this reaction. Thus we examined the effects of protecting groups and of *Z*/*E*-configuration of the radical acceptors on hex-5-enyl and hept-6-enyl radical cyclizations. Improvements in selectivity were observed for both reactions. We find that the stereoselectivity in the inherently less selective heptenyl radical cyclization is considerably better when the (*Z*)-isomer of the radical acceptor is employed. These results open new ways of preparing C_2-substituted *N*-heterocyclic pyranosides and furanosides.[4] Full details of these investigations are described herein.



1 **2** (1)

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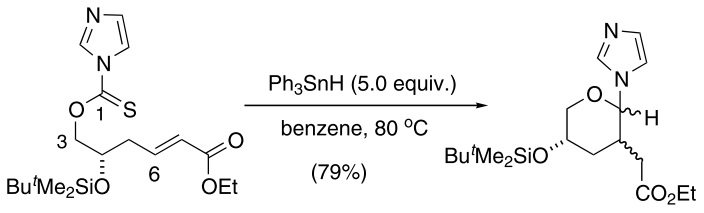
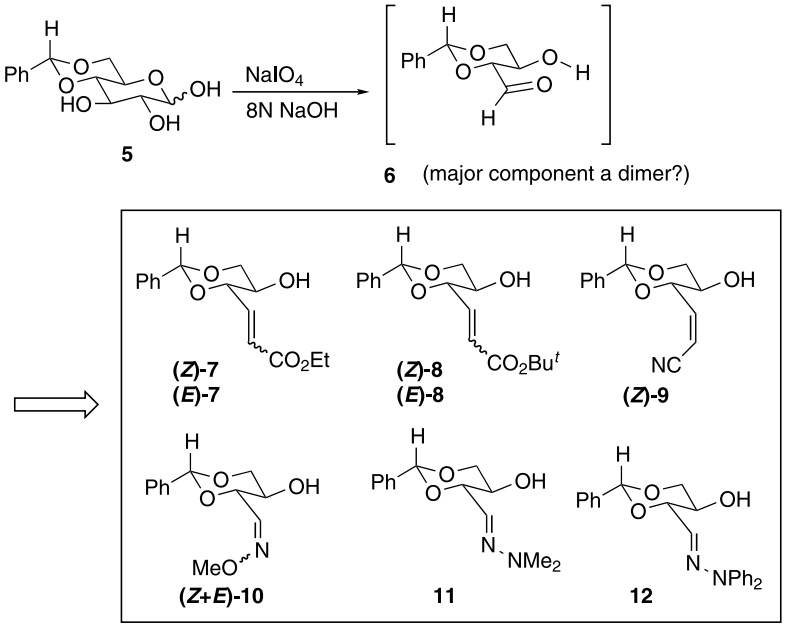


(2)

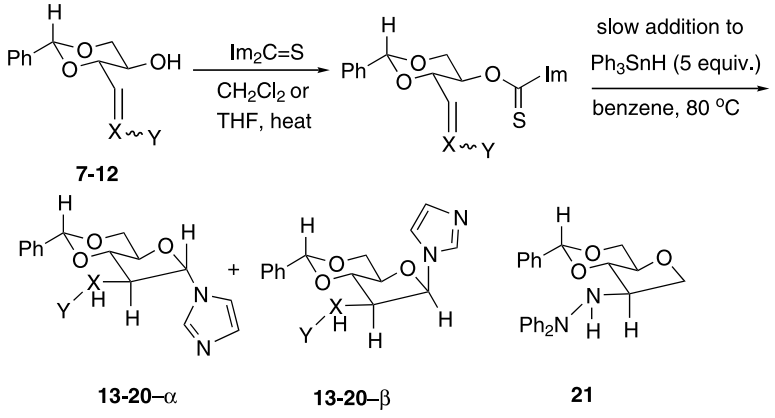
2. Results and discussion

2.1. Hex-5-enyl radical cyclizations. Synthesis of precursors and cyclization studies

Starting materials for the hex-5-enyl type cyclization studies were readily prepared from 4,6-*O*-phenylmethylglucopyranose, **5** (Scheme 1). The aldehyde **6**[5] formed upon periodate cleavage of **5** was not isolated, but was converted directly into the unsaturated precursors **7**–**12** by reaction with the appropriate Wittig reagent, *O*-methylhydroxylamine or *N*,*N*-dimethylhydrazine. In the case of the α,β-unsaturated esters **7** and **8** and the nitrile **9** the major (*Z*)-[6] and minor (*E*)-isomers were separated by column chromatography and subjected to cyclization. The *syn* and *anti* isomers of the oxime[7,8] **10** were not separated and the hydrazones were found to exist as a single geometric isomer by NMR spectroscopy.[9,10] The corresponding imidazole thioates were prepared by heating the alcohols with thiocarbonyl bisimidazole in CH_2Cl_2 or THF (Scheme 2).



Scheme 1. Synthesis of precursors for hex-5-enyl-type cyclyzations.



Scheme 2. Cyclization of substrates **7**–**12** (Tables 1 and 4).

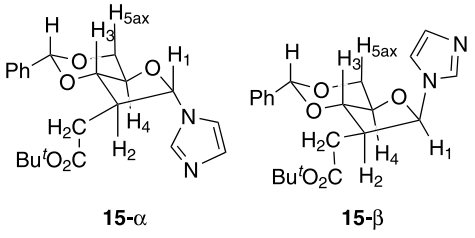
The cyclization reactions were carried out under conditions optimized (see Table 4, experimental) for the formation of the *N*-glycoside.[1] Thus in a typical reaction, 0.16 mmol of (*E*)-**7** and 0.08 mmol of AIBN dissolved in 3.4 mL of benzene was added in ~2 h to 0.80 mmol of Ph_3SnH in 12.5 mL of benzene in an oil bath at 90°C. The reaction was continued for another 30 min at that temperature. The reaction mixture was cooled to room temperature and the solvent was removed. Chromatography of the crude mixture on silica gel using hexane/ethyl acetate solvent gave pure product(s).

The results of cyclization of substrates **7**–**12** (Scheme 2) are shown in Table 1. As we had anticipated, the use of a cyclic acetal as a protecting group indeed results in an improvement in the selectivity of the reaction vis-à-vis the acyclic precursor **1** shown in Eq. (1). The C_2-substituent in the *N*-glycoside is formed exclusively with a β-orientation, irrespective of the geometry of the starting olefin or the [C=N] acceptor (Scheme 2 and entries 1 and 2, 3 and 4, and 6 in Table 1). However, in all cases except for the *N*,*N*-diphenylhydrazone (entry 8) a mixture of α- and β-glycosides is formed. The α- and β-glycosides can be separated in most cases and the structures have been rigorously established by spectroscopic methods. The position of the C_1-hydrogen gives a reliable indication of the anomeric configuration. For the α-anomers the C_1-hydrogen appears consistently 5.80±0.10 ppm and for the β-anomer this proton appears at 6.15±0.15 ppm. In addition, NOE studies further confirm these assignments. For example, the following NOE's are observed for the glycosides **15-α** and **15-β**: **15-α**: $H_1 \rightarrow H_3$; $H_1 \rightarrow CH_2$; $H_2 \rightarrow H_4$; $H_2 \rightarrow$imidazole H; $H_3 \rightarrow CH_2$; $H_3 \rightarrow H_{5axial}$) and **15-β**: ($H_1 \rightarrow H_2$; $H_1 \rightarrow H_4$; $H_2 \rightarrow H_4$; $CH_2 \rightarrow$imidazole H; $H_3 \rightarrow CH_2$; $H_3 \rightarrow H_{5axial}$).

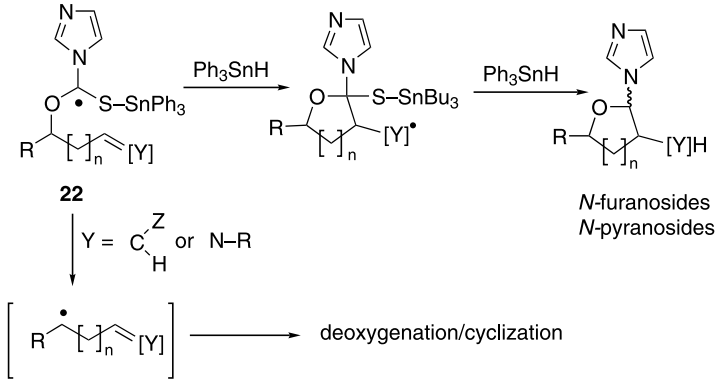
Table 1. Cyclization of imidazole thioates from **7**–**12**[a]

Entry	Alcohol	[Furanoside] X–Y	Yield (%)	α/β
1	***Z*-7**	[**13**] $CHCO_2Et$	44 (32)[b]	1.1/1.0
2	***E*-7**	[**14**] $CHCO_2Et$	54 (28)[b]	0.8/1.0
3	***Z*-8**	[**15**] $CHCO_2Bu^t$	46	0.7/1.0
4	***E*-8**	[**16**] $CHCO_2Bu^t$	40	0.9/1.0
5	***Z*-9**	[**17**] CHCN	81	1.0/0.8
6	**(*Z*+*E*)-10**	[**18**] NOMe	63	1.0/0.8
7	**11**	[**19**] $NNMe_2$	77	1.0/0.3
8	**12**	[**20**] $NNPh_2$	20[c]	α-only

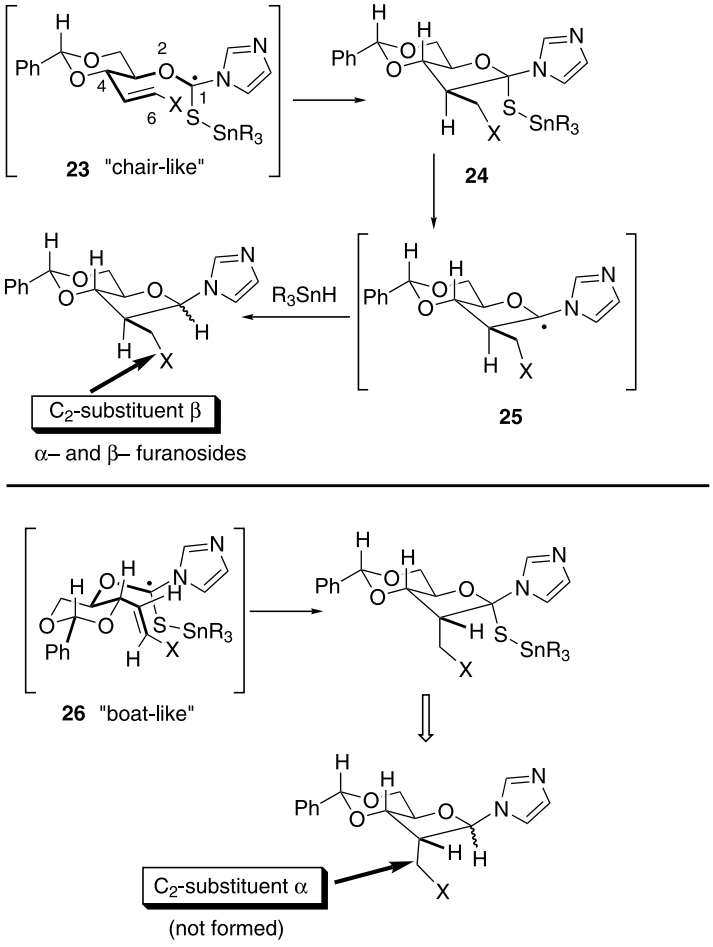
[a] See Scheme 2.
[b] Using Bu_3SnH.
[c] 62% **21** was also formed.



It is known that in the Barton–McCombie reaction the slow step is the collapse of the intermediate **22** (Scheme 3).[11] Since the rate of intramolecular addition to an activated acceptor is likely to be faster than this decomposition, formation of cyclic products, especially in the presence of a sterically demanding, H-atom donor, is not surprising. Analysis of the transition states that lead to the cyclic products provides a satisfactory explanation for the exclusive β-orientation of the C_2-substituent. Of the two possible transition states (Scheme 4), one with the 'chair-like' conformation **23** that leads to the C_2-β product is likely to be favored over the 'boat-like' transition state **26** that results in the C_2-α substituent. In depicting these structures the S–SnR_3 has been arbitrarily chosen to occupy the quasi-axial position at C_1 based on the reasonable assumption that C–S and S–Sn bonds are significantly longer than the C–N bond, and thus the imidazolyl moiety is likely to be sterically more demanding. Homolytic cleavage of the C–S bond in **24** followed by H atom abstraction by the resulting glycosyl radical **25** will result in the two glycosides. Predictably, there is little difference between H-abstraction at either α- or β-face of C_1. The only exception is in the case of the diphenylhydrazone **12**, which gave only the α-glycoside **20-α** in a low (20%) yield. In this case an unusually high yield (62%) of a reduced product **21** was also observed. Even though stereoelectronic effects are known to play an important



Scheme 3. Deoxygenation versus cyclization in the Barton–McCombie reaction.

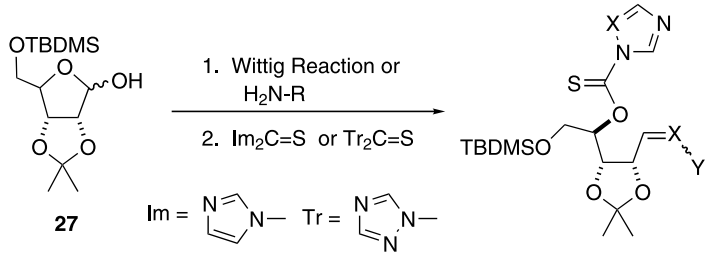


Scheme 4. Origin of stereoselectivity at C_2 of the *N*-furanoside.

role in the capture of anomeric radicals[12] by H-atom donors and electron deficient olefins, the conformation of the strained bicyclo[4.3.0]-system (e.g. **25**) in the present context makes it difficult to achieve any preferential alignment of the suitable orbitals for one conformation to be favored. Simple steric effects might be responsible for the modest selectivity seen for the hydrazones. As we will see later, this becomes an important consideration in the formation of the α/β-anomers of the pyranosides, where the anomeric effect is much more discernable.

2.2. Hept-6-enyl radical cyclizations

Formation of cyclohexane derivatives via *exo*-hept-6-enyl radical cyclization is 20–30 times slower than the *exo*-hex-5-enyl cyclization.[13] Yet we find that several ribose-derived imidazole thioates undergo efficient cyclization to give 1-imidazolyl pyranosides. Prototypical substrates for the cyclization were prepared from the D-ribonolactone-derived hemiacetal **27**[14] by the reactions shown in Scheme 5. The substrates **28**–**38** shown in Figure 1 were prepared using standard reac-



Scheme 5. Synthesis of substrates for hept-6-enyl cyclization studies.

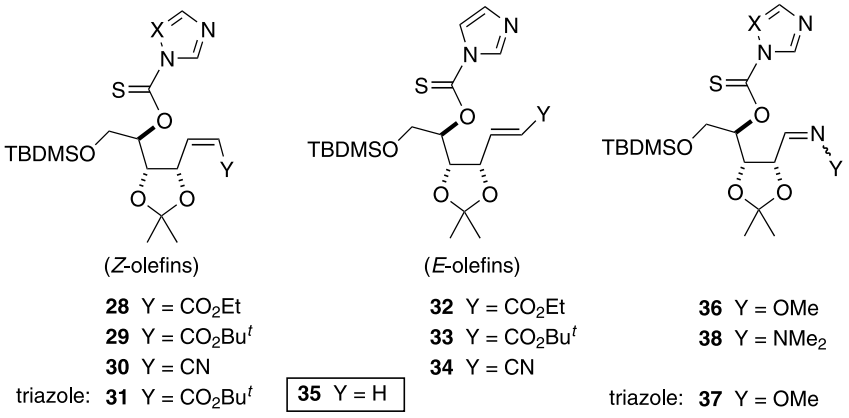


Figure 1. Substrates for hept-6-enyl radical cyclizations (see Scheme 5).

tion conditions. The list also includes two triazole derivatives **31** and **37**, which were prepared to explore the generality of this procedure for the synthesis of other heterocyclic glycosides. The geometrical isomers of the Wittig reaction products were separated, characterized and individually subjected to cyclization reactions. The results of cyclization studies are listed in Tables 2 and 3.

2.3. Configuration of the radical acceptor (olefin or =NR) and stereoselectivity in the cyclization reactions

Both imidazole and triazole thioates carrying activated olefin acceptors **28**–**35** (Fig. 1) undergo *exo*-hept-6-enyl type radical cyclization to give the corresponding *altro* (major) and *allo* (minor) *N*-heterocyclic glycosides. Because of the better stereoselectivity at the C_2-position, cyclization of substrates with the *Z*-enoates (**28**–**31**) are preparatively the most useful (Table 2, entry 1). In a typical experiment, the imidazole thioate **28** (Table 2, entry 1a) mixed with AIBN was slowly added to 5 equiv. of Ph_3SnH dissolved in benzene (0.01 M) in an oil bath at 90°C. Concentration and purification by chromatography gave 68% yield of the corresponding *altro* adducts **39** (α:β = 1:4). The α- and β-anomers were separated and identified by NMR spectroscopy. A similar result, with preponderance of the the β-glycoside, is observed with the analogous *t*-butyl ester **29** and the unsaturated nitrile **30** (entries 1b and 1c). A structurally related triazole thioate **31** also gave exclusively the *altro*-glycosides **42** in 87% yield (entry 1d, Table 2). We did not observe the formation of any of the *allo*-isomers when the pure *Z*-isomers of the substrates were used for the cyclization.

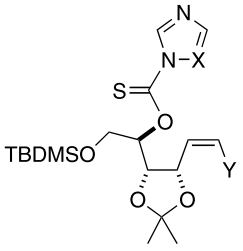
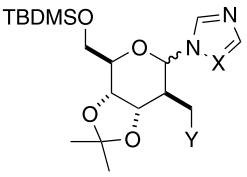
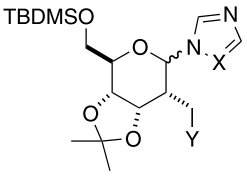
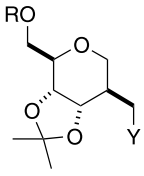
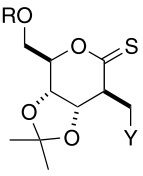
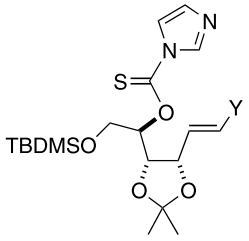
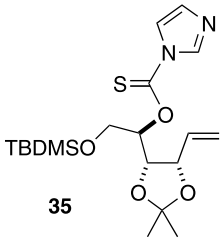
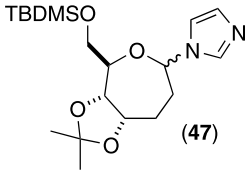
In sharp contrast to the results described in the previous paragraph, use of the *E*-isomers of the Wittig products gave a mixture of pyranosides consisting of both *altro*-**39**–**41** and *allo*-**43**–**45** isomers (entries 2a–c, Table 2), even though the major products still have the *altro*-configuration.[15] An occasional complication is represented by entry 2a, which shows the formation of a byproduct, **46**, in 18% yield. This product is formed especially when the reaction is done at higher temperatures (toluene reflux) (see Section 4, Tables 4 and 5). With low concentration of Bu_3SnH a thionolactone **46*S*** has also been observed in some runs. In the absence of an electron-withdrawing substituent on the olefin **35** (entry 3, Table 2), the reactivity and selectivity erode considerably giving a mixture of products including an *endo*-6-heptenyl cyclization product(s) tentatively identified as **47**. The products of this low yielding reaction were not fully characterized.

Finally the oxime ether substrates **36** and **37** (Table 3), which exist as mixtures of *syn* and *anti* isomers, gave low yields of the *N*-heterocyclic glycosides **48**–**50**. In both cases the *altro* isomers are formed as the major products.

The hydrazone substrate **38** (Scheme 6) upon reaction with triphenyltin hydride gave moderate yields of cyclic products, of which the major isomer (56%) has been tentatively identified as the *allo*-β glycoside **51**. Reaction of **38** with Bu_3SnH leads to no cyclization products, but a deoxygenation product **52** was formed in 41% yield. This further confirms the crucial role of triphenyltin hydride in these relatively slow cyclization reactions.

The difference in the selectivities of the (*Z*)- and (*E*)-olefin acceptors (the former giving exclusively the *altro*-isomer, i.e. the C_2-substituent in the β-configuration) is quite striking. This result (entries 1 and 2, Table 2) can be rationalized on the basis of the conformations of the putative intermediates that lead to the *altro*- and *allo*-products (Scheme 7). Inspection of models suggests that there is an added through-space interaction between the carboethoxy oxygen and the C_5 (radical numbering) acetal oxygen in the transition state **53** for the formation of the *allo* product(s). This is absent in the transition state **54**, which might explain why only *altro* products are obtained from the (*Z*)-acceptors (entry 1, Table 2). There is no such clear distinction between the respective transition states leading from the (*E*)-olefin acceptors and a mixture of *allo*- and *altro*-products are obtained in these cases (entry 2, Table 2).

Table 2. Hept-6-enyl radical cyclization. Effect of olefin geometry[a]

entry	substrates	major products (# in bold) (% yield, α:β ratio)		other products (% yield)	
1.		 (altro)	 (allo)	 **46**[b]	 **46S**[b]
	***Z*-olefins**				
	imidazoles: (a) Y = CO_2Et (**28**)	68 (1.0:4.0) (**39**)	0 (**43**)	0	
	(b) Y = CO_2Bu^t (**29**)	71 (1.0:5.0) (**40**)	0 (**44**)	0	
	(c) Y = CN (**30**)	57 (1.0:3.8) (**41**)	0 (**45**)	0	
	triazole: (d) Y = CO_2Bu^t (**31**)	87 (1.0:3.1) (**42**)	0 (--)	0	
2.		(altro)	(allo)		
	***E*-olefins**				
	imidazoles: (a) Y = CO_2Et (**32**)	52 (1.0:3.2) (**39**)	7 (1.0:3.0) (**43**)	18 (**46**)	
	(b) Y = CO_2Bu^t (**33**)	47 (1.0:4.3) (**40**)	14 (1.0:1.4) (**44**)	0	
	(c) Y = CN (**34**)	73 (1.0:3.7) (**41**)	7 (1.0:2.3) (**45**)	0	
3.	 **35**	21 (1.0: 2.38)[c]	9 (1.0:1.59)[c]	 (**47**) 29% (α:β 1.0:2.56)[c]	

[a] isomer ratios of products were determined by NMR

[b] See also Table 5

[c] tentative

The preponderance of the formation of the β-anomer in the pyranoside formation (Tables 2 and 3 and Scheme 6) is highly suggestive of anomeric stabilization in the radical intermediate involved. Unlike in the *trans*-bicyclic furanoside system **25** (Scheme 4), the α-confirmation of the glycosyl radical **55** (Scheme 8) would be expected to provide some anomeric stabilization[12] to the intermediates from which the β-glycosides are formed. Note that in the *altro* isomers the β-glycoside formation will also be favored by the ease of H delivery from the α-face.

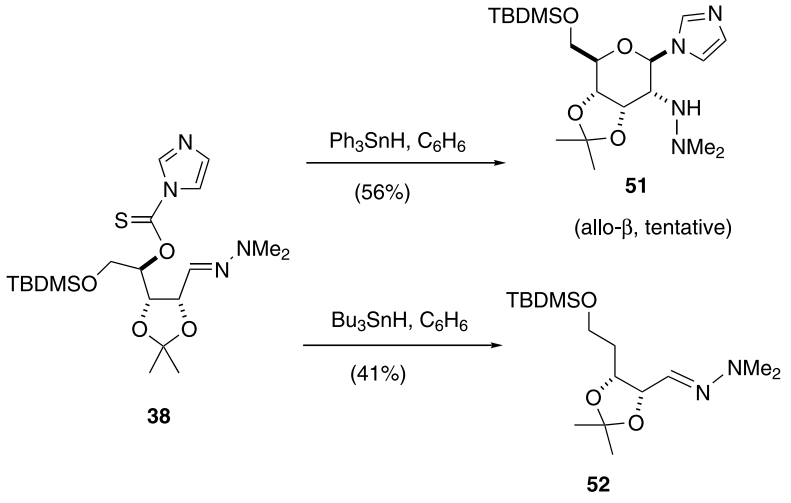
3. Summary

The first radical intermediate in the thiourethane-mediated deoxygenation of an alcohol (Barton–McCombie reaction) can participate in an *exo*-hex-5-enyl or *exo*-

Table 3. Hept-6-enyl radical cyclization. Oxime substrates[a]

entry	substrates	major products (% yield, α:β ratio)	
		(altro)	(allo)
1.	imidazoles: (**36**)	51 (1.0:4.2) (**48**)	32 (1:25)[b] (**49**)
2.	triazole: (**37**)	46 (1.0:1.4) (**50**)	(not determined)[c]

[a] isomer ratios of products were determined by NMR
[b] tentative assignment
[c] trace



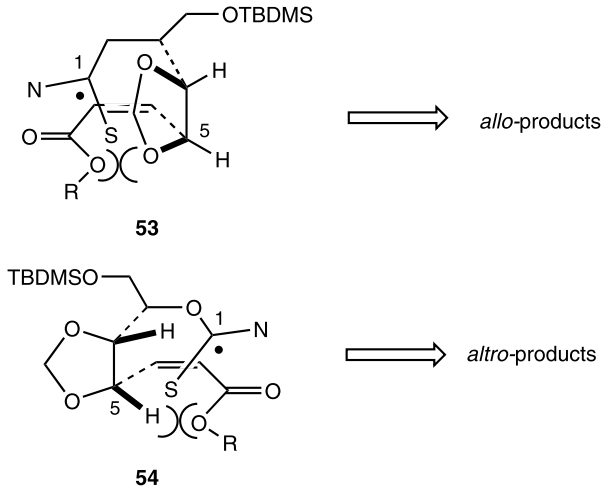
Scheme 6. Effect of the hydride on cyclization versus deoxygenation.

hept-6-enyl type radical cyclization when a suitable radical acceptor (e.g. α,β-unsaturated ester, oxime ether or hydrazone) is appropriately placed. Carbohydrate-derived imidazolyl and triazolyl thiourethanes with such acceptors, upon addition to excess of a good hydride donor (reverse addition), undergo efficient cyclization reactions to give *N*-heterocyclic furanosides, and, surprisingly even *N*-pyranosides. Depending on the acceptor, glycosides with either 2-amino or C_2-carbon substituent are formed. In the *exo*-hept-6-enyl cyclizations, the (*Z*)-olefin acceptors give excellent stereoselectivity in the generation of the C_2 stereogenic center. Only *altro*-isomers are formed. In all cases both α- and β-glycosides are obtained. A moderate preference for the β-anomer in the pyranoside formation may have its origin in the anomeric stabilization of the axial radical. *N*-Heterocyclic glycosides are important class of compounds that represent the structural units of nucleic acids and of several pharmaceutically relevant compounds.[4a–c] We plan to apply these methods for the synthesis of nucleosides, *N*-glycosyl amino acids and unusual *O*- and *C*-glycosides.

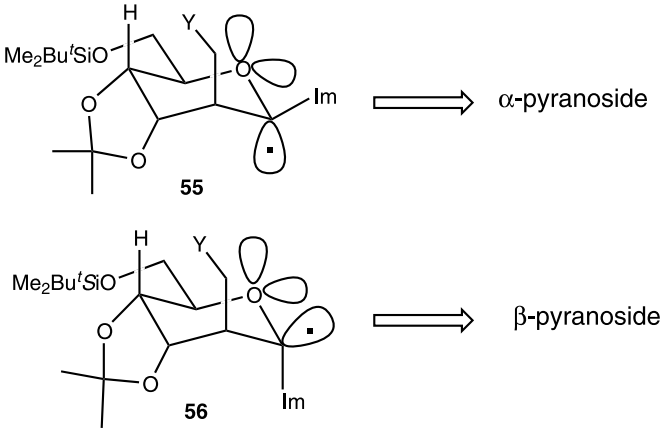
4. Experimental

4.1. General procedures

NMR spectra were recorded on Bruker AM-250, AM-300, DPX-400, or DPX-500 MHz instruments and $CDCl_3$ was used as the solvent unless otherwise mentioned. For ^1H NMR spectra the hydrogen of $CDCl_3$ was used as the standard ($\delta = 7.260$ ppm). The ^{13}C NMR spectra were recorded at 125 MHz, 100 MHz, 75 MHz, or 62.5 MHz and the central line of $CDCl_3$ was used as the standard ($\delta = 77.00$ ppm). Chemical shifts are reported in parts per million on the δ scale, and Hz is used as unit for the coupling constants. Infrared spectra were obtained on Perkin–Elmer 1600 infrared



Scheme 7. Origin of the *altro*-selectivity in the (*Z*)-acceptors (see Table 2).



Scheme 8. Anomeric stabilization in pyranosyl radicals.

spectrometer and are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectra were recorded on the Micromass QTOF electrospray mass spectrometer. Elemental analysis was performed at the Ohio State University. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter with a sodium lamp at 589 nm and 1 mm slit at concentrations expressed as g/dL. All melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. All solvents were purchased from Fisher Co. and freshly distilled. Other chemicals were purchased from Aldrich or Acros and were used as received. Reactions were performed in flame dried glassware under an atmosphere of nitrogen, and monitored by thin layer chromatography (TLC) using EM Science precoated 60 F_{254} plates or gas chromatography (Hewlett–Packard 5890). The GC was equipped with HP-1 column and an FID detector connected to an HP 3396 integrator. Products were isolated by column chromatography using 60–200 mesh silica gel.

Preparation of substrates

4.2. (*E*)- and (*Z*)-(2*R*,4*S*,5*R*)-(5-hydroxy-2-phenyl-[1,3]dioxane-4-yl)-acrylic acid ethyl ester (*Z*)-7 and (*E*)-7

To a 25 mL of flame-dried three-necked round-bottomed flask connected to a condenser were added 78 mg (estimated as 0.310 mmol) of crude [2*R*,4*R*,5*R*]-5-hydroxy-2-phenyl-[1,3]dioxane-4-carbaldehyde **6**[5] and 133 mg (0.384 mmol) of (carboethoxymethylene)-triphenylphosphorane. Freshly dried toluene (10 mL) was added and the mixture was stirred under refluxing condition for 100 min. After the solvent was removed under vacuum, the product as an *E* and *Z* mixture was isolated by flash column chromatography eluting with hexane:EtOAc = 3:1. The *E* and *Z* compounds were isolated as a white solid and a colorless oil respectively in a ratio of 1.0/1.89, and the combined isolated yield was 90%. The same reaction was also performed in dimethoxyethane at rt. The mixture of 78 mg (estimated as 0.310 mmol) of crude 5(*R*)-hydroxy-2(*R*)-phenyl-1, 3-dioxane-4(*R*)-carboxaldehyde **6** and 221 mg (0.634 mmol) of (carboethoxymethylene)triphenylphosphorane in 10 mL of DME was stirred under a nitrogen atmosphere for 26 h, when all starting material disappeared on TLC. After the solvent was removed in a rotary evaporator, the crude mixture was purified by column chromatography eluting with hexane:EtOAc = 2:1. The isolated yield was the same (90%), but the ratio of *Z*:*E* compounds increased to 2.4:1.0.

(*E*)-7: White solid (column chromatography, hexane:EtOAc = 3:1). $R_f = 0.33$ (hexane:EtOAc = 2:1). Mp: 93–95°C. $[\alpha]_D^{20} = -31.7$ (*c* 0.71, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.30 (t, $J = 7.1$ Hz, 3H), 2.71 (br s, 1H), 3.67 (d, $J = 7.5$ Hz, 2H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.21–4.25 (m, 1H), 4.32 (d, $J = 5.6$ Hz, 1H), 5.56 (s, 1H), 6.22 (dd, $J = 15.8$, 1.7 Hz, 1H), 7.18 (dd, $J = 15.8$, 4.5 Hz, 1H), 7.34–7.41 (m, 3H), 7.49–7.51 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 60.7, 65.3, 71.1, 80.4, 100.8, 122.4, 126.1, 128.3, 129.1, 137.2, 143.4, 166.5. IR (NaCl, neat): 3476br s, 2984m, 2924m, 2862m, 1702s, 1656m, 1453m, 1394m, 1370m, 1301s, 1274m, 1224m, 1189m, 1144m, 1082s, 1026s, 979m, 918w, 850w, 757m. Anal. calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.22; H, 6.75.

(*Z*)-7: Colorless oil (column chromatography, hexane:EtOAc = 3:1). $R_f = 0.42$ (hexane:EtOAc = 2:1). $[\alpha]_D^{20} = -66.1$ (*c* 0.61, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.33 (t, $J = 7.1$ Hz, 3H), 3.62–3.73 (m, 1H), 3.83 (d, $J = 6.7$ Hz, 2H), 4.24 (qd, $J = 7.1$, 2.9 Hz, 2H), 4.41 (dd, $J = 10.3$, 4.5 Hz, 1H), 5.19 (apparent td, $J = 9.1$, 1.4 Hz, 1H), 5.55 (s, 1H), 6.09 (dd, $J = 11.8$, 1.2 Hz, 1H), 6.34 (dd, $J = 11.7$, 7.8 Hz, 1H), 7.35–7.37 (m, 3H), 7.47–7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 61.5, 65.6, 72.1, 78.5, 100.7, 122.4, 126.1, 128.3, 129.0, 137.3, 145.2, 168.1. IR (NaCl, neat): 3431br s, 3037w, 2982m, 2930m, 2854m, 1722s, 1694s, 1658m, 1455m, 1422m, 1386s, 1302w, 1209s, 1090s, 1207s, 871w, 827m, 755m, 699s. Anal. calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 63.90; H, 6.70.

4.3. Preparation of (*E*)- and (*Z*)-[2*R*,4*S*,5*R*]-3-(5-hydroxy-2-phenyl-[1,3]dioxane-4-yl)-acrylonitrile (*E*)-9 and (*Z*)-9

To a 100 mL flame-dried three-necked round-bottomed flask connected to a condenser were added 259 mg (estimated as 1.24 mmol) of crude **6** and 412 mg (1.368 mmol) of (cyanomethylene)triphenylphosphorane. Freshly dried toluene (40 mL) was added and the mixture was stirred under refluxing condition for 12 h. Additional 206 mg of (cyanomethylene)triphenylphosphorane was added and the refluxing was continued under a nitrogen atmosphere for 2 h. After the solvent was removed under vacuum, the crude mixture was purified by column chromatography eluting with hexane:EtOAc = 3:1. The isolated (*E*) and (*Z*) compounds were yellowish brown solids, and the *E*/*Z* ratio was 1.0/2.3 (isolated yield 93%).

(*Z*)-9: Yellowish brown solid (column chromatography, hexane:EtOAc = 3:1). $R_f = 0.39$ (hexane:EtOAc = 1:1). Mp: 98–99°C. $[\alpha]_D^{20} = -156.1$ (*c* 0.71, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.68 (br s, 1H), 3.60–3.65 (m, 1H), 3.69 (apparent t, $J = 10.2$ Hz, 1H), 4.31 (dd, $J = 9.9$, 4.2 Hz, 1H), 4.53 (apparent td, $J = 7.9$, 0.8 Hz, 1H), 5.58 (s, 1H), 5.59 (dd, $J = 11.4$, 1.0 Hz, 1H), 6.50 (dd, $J = 11.4$, 7.8 Hz, 1H), 7.36–7.42 (m, 3H), 7.50–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 64.99, 70.81, 80.53, 100.80, 102.62, 115.50, 126.08, 128.26, 129.18, 136.74, 148.88. IR (NaCl, neat): 3458br s, 3068m, 2977m, 2926m, 2860s, 2225s, 1714w, 1634w, 1494w, 1455s, 1402s, 1385s, 1316w, 1295m, 1267m, 1216m, 1134s, 1086s, 1028s, 919m, 872w, 737s, 701s, 675m, 645m. Anal. calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 66.77; H, 5.87; N, 5.85.

4.4. Preparation of [2*R*,4*S*,5*R*]-5-hydroxy-2-phenyl-[1,3]dioxane-4-carbaldehyde *O*-methyl-oxime *syn*- and *anti*-10

To a 100 mL of flame-dried three-necked round-bottomed flask connected to a condenser were added 222 mg (estimated as 1.07 mmol) of crude **6** and 142 mg (1.60 mmol) of *O*-methylhydroxyl amine hydrochloride in 50 mL of methyl alcohol and 1 mL of pyridine. After the mixture was refluxed under a nitrogen atmosphere for 5.5 h, all solvent was removed on a rotary evaporator to get the crude product. The crude mixture was purified by column chromatography eluting with hexane:EtOAc = 4:1. The desired product (0.216 g) was obtained as a white solid (isolated yield 91%). The isolated compound is a *syn*/*anti* mixture in a ratio of 1.0/0.18 based on ^{1}H NMR analysis (C_1 *syn* higher field and C_1-H higher field *anti* isomer; for several carbohydrate examples, see Ref. 7).

***syn*- and *anti*-10**: White solid (*syn*/*anti* = 1.0/0.18) (column chromatography, hexane:EtOAc = 4:1). R_f = 0.60 (hexane:EtOAc = 1:1). Mp: 105–108°C. ^{1}H NMR ($CDCl_3$, 400 MHz): *syn*-**10**: δ 3.70 (apparent t, $J = 10.5$ Hz, 1H), 3.90 (s, 3H), 3.99 (ddd, $J = 10.2$, 9.1, 5.2 Hz, 1H), 4.25 (dd, $J = 8.9$, 3.9 Hz, 1H), 4.38 (dd, $J = 10.9$, 5.2 Hz, 1H), 5.54 (s, 1H), 7.23–7.42 (m, 3H), 7.47–7.52 (m, 3H); *anti*-**10**: δ 3.67 (apparent t, $J = 9.6$ Hz, 1H), 3.80 (apparent td, $J = 9.9$, 5.1 Hz, 1H), 3.96 (s, 3H), 4.38 (dd, $J = 10.8$, 5.0 Hz, 1H), 4.90 (dd, $J = 9.5$, 5.3 Hz, 1H), 5.51 (s, 1H), 6.91 (d, $J = 5.3$ Hz, 1H), 7.33–7.42 (m, 3H), 7.47–7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *syn*-**10**: δ 62.19, 63.99, 70.15, 78.69, 101.35, 126.13, 128.33, 129.21, 137.04, 148.70; *anti*-**10**: δ 62.51, 71.11, 75.62, 77.92, 100.71, 126.10, 128.33, 129.21, 136.94, 149.95. IR (NaCl, neat): 3489br s, 2978w, 3939w, 2252s, 1462m, 1390m, 1221w, 1086m, 1041m, 908s, 733s, 650m. Anal. calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.87; H, 6.62; N, 5.94.

4.5. Prepartion of (*E*)-[2*R*,4*S*,5*R*]-4-(*N*,*N*-dimethylhydrazonomethyl)-2-phenyl-[1,3]dioxane-5-ol 11

To a 100 mL flame-dried three-necked round-bottomed flask connected to a condenser were added 780 mg (estimated as 3.10 mmol) of crude **6** and 932 mg (15.5 mmol, 1.18 mL) of *N*,*N*-dimethylhydrazine with 50 mL of methyl alcohol and small amount of 4 Å MS. After the mixture was refluxed under a nitrogen atmosphere for 17.5 h, and all solvent was removed on a rotary evaporator to get the crude product. The crude mixture was purified by column chromatography eluting with hexane:EtOAc = 6:1 to 4:1 to get 652 mg (84%) of the desired product as the (*E*)-isomer.[9] **(*E*)-11**: Pale yellow solid (column chromatography, hexane:EtOAc = 6:1 to 4:1). $R_f = 0.35$ (hexane:EtOAc = 1:1). Mp: 66-68°C. $[\alpha]_D^{20} = +8.3$ (*c* 0.55, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.83 (s, 6H), 3.64 (br s, 1H), 3.70 (apparent t, $J = 10.6$ Hz, 1H), 3.98 (ddd, $J = 10.2$, 9.1, 5.2 Hz, 1H), 4.24 (dd, $J = 8.9$, 3.2 Hz, 1H), 4.36 (dd, $J = 10.8$, 5.2 Hz, 1H), 5.57 (s, 1H), 6.61 (d, $J = 3.1$ Hz, 1H), 7.31-7.42 (m, 3H), 7.48-7.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 42.41, 65.09, 70.02, 80.54, 101.24, 126.12, 128.21, 128.95, 133.64, 137.46. IR (NaCl, neat): 3392br s, 2966m, 2862s, 2778m, 2358w, 1597m, 1457s, 1396s, 1316w, 1264m, 1220m, 1085s, 1027s, 918m, 823m, 762s, 699s. Anal. calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.17; H, 7.21; N, 11.03.

4.6. Preparation of [2*R*,4*S*,5*R*]-(diphenylhydrazonomethyl)-2-phenyl-[1,3]dioxane-5-ol 12

To a 100 mL of flame-dried one-neck round-bottomed flask were added 780 mg (estimated as 3.10 mmol) of **6** and 1.37 g (6.20 mmol) of *N*,*N*′-dimethyl hydrazine hydrochloride with 50 mL of methyl alcohol, 552 μL of pyridine (6.82 mmol), and small amount of 4 Å MS. The mixture was stirred at rt under a nitrogen atmosphere for 17.5 h. After the solvent was removed in a rotary evaporator, the crude product was purified by column chromatography eluting with hexane:EtOAc = 7:1 to give 993 mg of the desired product as white solid (isolated yield 86%). The isolated compound was assigned as *anti* based on the chemical shift and coupling constant of its characteristic hydrogen (6.63 ppm, d, $J = 3.2$ Hz) on ^{1}H NMR spectrum. **12**: White solid (column chromatography; hexane:EtOAc = 7:1). $R_f = 0.27$ (hexane:EtOAc = 5:1). Mp: 119-120°C. $[\alpha]_D^{20} = +58.8$ (*c* 0.40, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.42 (br s, 1H), 3.75 (apparent t, $J = 10.5$ Hz, 1H), 4.14 (apparent td, $J = 10.0$, 5.3 Hz, 1H), 4.35 (dd, $J = 8.9$, 3.2 Hz, 1H), 4.43 (dd, $J = 10.9$, 5.2 Hz, 1H), 5.56 (s, 1H), 6.63 (d, $J = 3.2$ Hz, 1H), 7.11 (d, $J = 7.4$ Hz, 2H), 7.35–7.43 (m, 7H), 7.47–7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 64.66, 70.20, 80.64, 101.43, 122.35, 124.86, 128.26, 129.91, 135.90, 137.26,

142.95. IR (NaCl, neat): *v* 3453br s, 3062m, 3036m, 2973m, 2927m, 2856m, 2358w, 2248m, 1955w, 1809w, 1703w, 1591s, 1495s, 1455s, 1395s, 1298s, 1215s, 1157s, 1074s, 1027s, 910s, 750s, 733s, 699s, 648s. Anal. calcd for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C, 72.89; H, 6.14; N, 7.42.

4.7. Preparation of (*E*)-[2*R*,4*S*,5*R*]-3-[5-(imidazole-1-carbothioyloxy)-2-phenyl-[1,3]dioxan-4-yl]-acrylic acid ethyl ester (*E*)-7-im

To a flame-dried 50 mL flask were added 51 mg (0.183 mmol) of **(*E*)-7**, 98 mg (0.550 mmol) of 1,1′-thiocarbonyldiimidazole, and 7 mg of DMAP along with 20 mL of fresh distilled THF. The mixture was refluxed under a nitrogen atmosphere for 14 h, and another 200 mg of 1,1′-thiocarbonyldiimidazole was added. Refluxing was continued for 5.5 h, but some starting material was detected on TLC. Finally, 150 mg more of 1,1′-thiocarbonyldiimidazole and 18 h more of refluxing were required to consume all starting material. The solvent was removed under reduced pressure to get deep brown oil. The mixture was purified by flash column chromatography with hexane:EtOAc = 2:1, to get 62.1 mg (89%) of desired product. **(*E*)-7-im**: Pale yellow solid (column chromatography, hexane:EtOAc) = 2:1. R_f = 0.17 (hexane:EtOAc = 2:1). Mp: 100–102°C. $[\alpha]_D^{20} = -106.7$ (*c* 0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (t, J = 7.1 Hz, 3H), 3.84 (apparent t, J = 10.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.71 (dd, J = 10.8, 5.3 Hz, 1H), 4.74–4.69 (m, 1H), 5.54 (apparent td, J = 9.8, 5.2 Hz, 1H), 5.68 (s, 1H), 6.23 (dd, J = 15.7, 1.5 Hz, 1H), 6.96 (dd, J = 15.7, 4.9 Hz, 1H), 7.09 (s, 1H), 7.38–7.42 (m, 3H), 7.50–7.54 (m, 2H), 7.61 (s, 1H), 8.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 60.8, 66.7, 73.4, 76.9, 101.2, 118.0, 124.0, 126.1, 128.4, 129.4, 130.8, 136.3, 136.7, 140.4, 165.6, 181.9. IR (NaCl, neat): 3416br s, 3128m, 3038w, 2979m, 1728s, 1713s, 1666m, 1532m, 1470s, 1392s, 1334s, 1184s, 1139s, 1097s, 1004s, 920m, 852w, 748m, 699m, 653m. Anal. calcd for $C_{19}H_{20}N_2O_5S$: C, 58.75; H, 5.19; N, 7.21. Found: C, 58.61; H, 5.33; N, 7.20.

4.8. Preparation of (*Z*)-[2*R*,4*S*,5*R*]-3-[5-(imidazole-1-carbothioyloxy)-2-phenyl-[1,3]dioxan-4-yl]-acrylic acid ethyl ester (*Z*)-7-im

To a 50 mL of flame-dried flask were added 50 mg (0.180 mmol) of (*Z*)-3-(5(*R*)-hydroxy-2(*R*)-phenyl-[1,3]dioxane-4(*R*)-yl)-acrylic acid ethyl ester, (*Z*)-**7**, 3.0 equiv. of 1,1′-thiocarbonyldiimidazole, and 7 mg of DMAP along with 20 mL of THF. After refluxing the mixture for 5 h, some starting material was detected on TLC. Another 180 mg of 1,1′-thiocarbonyldiimidazole was added and refluxing was continued for 28 h. Additional 100 mg of of 1,1′-thiocarbonyldiimidazole was required to consume all starting material with refluxing for 10 h. After the solvent was removed on a rotary evaporator, the product was isolated by flash column chromatography with hexane:EtOAc = 3:1 to give 66.9 mg of desired product as yellow solid. The isolated yield was 96%. **(*Z*)-7-im**: Yellow solid (column chromatography, hexane:EtOAc = 3:1). R_f = 0.33 (hexane:EtOAc = 2:1). Mp: 101–103°C. $[\alpha]_D^{20} = -51.0$ (*c* 2.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26 (t, J = 7.2 Hz, 3H), 3.92 (apparent t, J = 10.3 Hz, 1H), 4.18 (apparent tt, J = 7.1, 3.8 Hz, 2H), 4.67 (dd, J = 10.6, 5.2 Hz, 1H), 5.58 (apparent td, J = 9.8, 5.2 Hz, 1H), 5.70 (s, 1H), 5.99 (dd, J = 11.7, 0.8 Hz, 1H), 6.02 (apparent t, J = 9.4 Hz, 1H), 6.20 (dd, J = 11.7, 8.8 Hz, 1H), 7.03 (d, J = 0.8 Hz, 1H), 7.36–7.40 (m, 3H), 7.49–7.52 (m, 2H), 7.65 (s, 1H), 8.39 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 60.8, 66.6, 73.0, 74.0, 101.2, 118.4, 124.4, 126.1, 128.3, 129.3, 130.2, 136.5, 136.9, 142.9, 165.4, 182.5. IR (NaCl, neat): 3133m, 3037w, 2982m, 2926m, 1715s, 1659m, 1532m, 1469s, 1392s, 1333s, 1295s, 1279s, 1231s, 1199s, 1126s, 1094s, 1005s, 947w, 919m, 872w, 828m, 752m, 698m. Anal. calcd for $C_{19}H_{20}N_2O_5S$: C, 58.75; H, 5.19; N, 7.21. Found: C, 58.05; H, 5.37; N, 7.13.

4.9. Preparation of (*Z*)-[1*R*,2*R*,4*S*,5*R*]-imidazole-1-carbothioic acid *O*-[4-(2-cyanovinyl)-2-phenyl-[1,3]dioxane-5-yl] ester (*Z*)-9-im

To a flame-dried 25 mL flask were added 94 mg (0.407 mmol) of (*Z*)-**9**, 217 mg (1.220 mmol) of 1,1′-thiocarbonyldiimidazole, and 17 mg of DMAP along with 20 mL of freshly distilled THF. The mixture was refluxed under a nitrogen atmosphere for 7 h, and another 217 mg of 1,1′-thiocarbonyldiimidazole was added. Refluxing was continued for 5 h at which time all starting material was consumed (TLC). The solvent was removed under reduced pressure to give the crude mixture, which was purified by flash column chromatography eluting with hexane:EtOAc = 4:1 to 1:1. The desired product (97 mg) was iolated in an yield of 70%.

(*Z*)-9-im: Pale yellow solid (column chromatography, hexane:EtOAc = 4:1 to 1:1). R_f = 0.55 (hexane:EtOAc = 1:1). Mp: 136-137°C. $[\alpha]_D^{20} = -90.0$ (*c* 0.41, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.91 (apparent t, J = 10.4 Hz, 1H), 4.70 (dd, J = 10.8, 5.3 Hz, 1H), 5.10 (apparent t, J = 9.1 Hz, 1H), 5.58 (dd, J = 11.0, 0.6 Hz, 1H), 5.66 (apparentarent td, J = 9.8, 5.3 Hz, 1H), 5.72 (s, 1H), 6.52 (dd, J = 11.1, 8.7 Hz, 1H), 7.07 (d, J = 0.9 Hz, 1H), 7.38-7.42 (m, 3H), 7.50-7.54 (m, 2H), 7.68 (apparent t, J = 1.3 Hz, 1H), 8.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.52, 71.92, 77.38, 101.42, 104.42, 114.85, 117.77, 126.07, 128.37, 129.53, 131.31, 135.94, 137.55, 147.03, 182.43. IR (NaCl, neat): 3143br s, 3110m, 3082m, 3039m, 2948m, 2872s, 2253m, 2223s, 1767w, 1713w, 1644w, 1534s, 1480s, 1467s, 1392s, 1330s, 1297s, 1276s, 1216s, 1131s, 1097s, 1069m, 1053m, 1006s, 971s, 910s, 871m, 834s, 759s, 735s, 702s, 653s. Anal. calcd for $C_{17}H_{15}N_3O_3S$: C, 59.81; H, 4.43; N, 12.31. Found: C, 59.86; H, 4.76; N, 11.70.

4.10. Preparation of [2*R*,4*S*,5*R*]-imidazole-1-carbothioic acid *O*-[4-(methoxyiminomethyl)-2-phenyl-[1,3]dioxan-5-yl] ester (*Z*)- and (*E*)-10-im

To a flame-dried 100 mL flask were added 163 mg (0.687 mmol) of *Z*- and *E*-**10**, 367 mg (2.061 mmol) of 1,1′-thiocarbonyldiimidazole, and 20 mg of DMAP along with 50 mL of freshly distilled THF. The mixture

was refluxed under a nitrogen atmosphere for 8.5 h, and another 200 mg of 1,1′-thiocarbonyldiimidazole was added. Refluxing was continued for 11 h at which time all starting material was consumed (TLC). The solvent was removed under reduced pressure to give crude mixture, which was purified by flash column chromatography eluting with hexane:EtOAc = 6:1. The desired product **(*Z*)-** and **(*E*)-10-im** was isolated in 90% (215 mg) yield as an yellow solid. The isolated compound was a *syn*/*anti* mixture with a ratio of 1.0/0.13 based on ^{1}H NMR spectrum. Yellow solid (*syn*/*anti* = 1.0/0.13) (column chromatography, hexane:EtOAc = 6:1). R_f = 0.41 (hexane:EtOAc = 1:1). Mp: 85-88°C. ^{1}H NMR ($CDCl_3$, 400 MHz): ***syn***: δ 3.78 (s, 3H), 3.87 (apparent t, J = 10.5 Hz, 1H), 4.68 (dd, J = 9.7, 6.7 Hz, 1H), 4.75 (dd, J = 10.7, 5.3 Hz, 1H), 5.66 (s, 1H), 5.69 (apparent td, J = 9.9, 5.3 Hz, 1H), 7.05 (d, J = 1.2 Hz, 1H), 7.37-7.41 (m, 4H), 7.49-7.52 (m, 2H), 7.61 (apparent t, J = 1.2 Hz, 1H), 8.31 (s, 1H); ***anti***: δ 3.82 (s, 3H), 3.90 (apparent t, J = 10.2 Hz, 1H), 4.69 (dd, J = 9.5, 5.0 Hz, 1H), 5.39 (dd, J = 11.2, 4.4 Hz, 1H), 5.65 (s, 1H), 5.66 (apparent td, J = 9.9, 5.3 Hz, 1H), 6.82 (d, J = 5.3 Hz, 1H), 7.05 (d, J = 1.2 Hz, 1H), 7.37-7.41 (m, 3H), 7.49-7.52 (m, 2H), 7.63 (apparent t, J = 1.2 Hz, 1H), 8.31 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): ***syn***: δ 62.14, 66.80, 71.49, 76.59, 101.58, 118.14, 126.12, 128.39, 129.49, 131.07, 136.23, 136.79, 145.08, 182.60; ***anti***: δ 62.31, 66.80, 71.01, 76.59, 101.31, 118.14, 126.12, 128.39, 129.49, 130.97, 136.23, 136.79, 145.90, 182.44. IR (NaCl, neat): 3412br s, 3129m, 3037m, 2966m, 2938m, 2870m, 1631w, 1532m, 1469s, 1393s, 1355s, 1294s, 1233s, 1103s, 1039s, 1006s, 920m, 887m, 752m, 699m, 651m. Anal. calcd for $C_{16}H_{17}N_3O_4S$: C, 55.32; H, 4.93; N, 12.10. Found: C, 56.03; H, 5.38; N, 11.65.

4.11. Preparation of [2*R*,4*S*,5*R*]-imidazole-1-carbothioic acid *O*-[4-(dimethylhydrazonomethyl)-2-phenyl-[1,3]dioxan-5-yl] ester 11-im

To a flame-dried 100 mL flask were added 363 mg (1.45 mmol) of **11**, 775 mg (4.35 mmol) of 1,1′-thiocarbonyldiimidazole, and 50 mg of DMAP along with 50 mL of freshly distilled THF. After the mixture was refluxed under a nitrogen atmosphere for 3 h, all starting material was consumed (TLC). The solvent was removed under reduced pressure to give the crude mixture, which was purified by flash column chromatography eluting with hexane:EtOAc = 3:1. The desired product **11-im** was isolated in 90% (215 mg) yield. **11-im**: Pale yellow solid (column chromatography, hexane:EtOAc = 3:1). R_f = 0.28 (hexane:EtOAc = 1:1). Mp: 89-90°C. $[\alpha]_D^{20}$ = −92.7 (*c* 0.94, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.76 (s, 6H), 3.88 (apparent t, J = 10.4 Hz, 1H), 4.64 (dd, J = 9.7, 6.0 Hz, 1H), 4.69 (dd, J = 10.6, 5.3 Hz, 1H), 5.67 (s, 1H), 6.41 (d, J = 5.9 Hz, 1H), 7.03 (d, J = 0.7 Hz, 1H), 7.26 (s, 1H), 7.33-7.41 (m, 3H), 7.51-7.54 (m, 2H), 7.60 (s, 1H), 8.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 42.17, 66.97, 72.85, 79.85, 101.60, 118.14, 126.19, 127.46, 128.28, 128.34, 129.28, 130.80, 136.77, 183.09. IR (NaCl, neat): 3431br s, 3135w, 2958w, 2859m, 2790w, 1594m, 1531w, 1466s, 1392s, 1333s, 1292s, 1279s, 1232s, 1162w, 1101s, 1004s, 919m, 827w, 752m. Anal. calcd for $C_{17}H_{20}N_4O_3S$: C, 56.65; H, 5.59; N, 15.54. Found: C, 56.59; H, 5.79; N, 15.19.

4.12. Preparation of [2*R*,4*S*,5*R*]-imidazole-1-carbothioic acid *O*-[4-(diphenylhydrazonomethyl)-2-phenyl-[1,3]dioxan-5-yl] ester 12-im

To a flame dried 100 mL flask were added 716 mg (2.06 mmol) of **12**, 1.10 g (6.18 mmol) of 1,1′-thiocarbonyldiimidazole, and 80 mg of DMAP along with 60 mL of freshly distilled THF. After the mixture was refluxed under a nitrogen atmosphere for 17.5 h, another 1.10 g of 1,1′-thiocarbonyldiimidazole was added. After 9 h refluxing, all starting material was disappeared on TLC. The solvent was removed under reduced pressure to give crude mixture, which was purified by flash column chromatography eluting with hexane:EtOAc = 6:1 to 4:1. The desired product **12-im** was obtained as yellow solid (833 mg) and 26 mg of the starting material was recovered. The isolated yield is 90% (93% based on the recovered starting material). The isolated compound is assigned as *anti* based on the chemical shift and coupling constant of its characteristic hydrogen (6.46 ppm, d, J = 5.7 Hz) on ^{1}H NMR spectrum. Yellow solid (column chromatography; hexane:EtOAc = 6:1 to 4:1). R_f = 0.29 (hexane:EtOAc = 2:1). Mp: 65–67°C. $[\alpha]_D^{20}$ = +26.0 (*c* 0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.93 (apparent t, J = 10.5 Hz, 1H), 4.68 (dd, J = 10.7, 5.4 Hz, 1H), 4.79 (dd, J = 9.5, 5.7 Hz, 1H), 5.68 (s, 1H), 5.83 (apparent td, J = 9.9, 5.4 Hz, 1H), 6.46 (d, J = 5.7 Hz, 1H), 6.98 (dd, J = 8.6, 1.2 Hz, 4H), 7.03 (d, J = 0.7 Hz, 1H), 7.15 (td, J = 7.4, 1.0 Hz, 2H), 7.30–7.33 (m, 4H), 7.36–7.40 (m, 3H), 7.49–7.52 (m, 2H), 7.64 (s, 1H), 8.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.89, 72.14, 79.33, 101.64, 117.98, 122.21, 124.82, 126.19, 128.35, 129.38, 129.74, 130.92, 131.29, 136.55, 136.80, 142.84, 182.77. IR (NaCl, neat): ν 3129m, 3064m, 3038m, 2967m, 2246w, 1955w, 1767w, 1702w, 1592s, 1532w, 1495s, 1464m, 1392s, 1335s, 1300s, 1279s, 1232s, 1157m, 1098s, 1004s, 911s, 831s, 750s, 733s, 699s, 644m. Anal. calcd for $C_{27}H_{24}N_4O_3S$: C, 66.48; H, 4.99; N, 11.56. Found: C, 66.48; H, 5.30; N, 10.79.

4.13. Preparation of (*Z*)-29

To a 100 mL of flame-dried three-necked round-bottomed flask connected to a condenser were added 2.09 g (6.86 mmol) of **27**[14] and 3.09 g (8.23 mmol) of (carb-*tert*-butoxymethylene)triphenylphosphorane. Dimethoxyethane (35 mL) was added and the mixture was stirred at rt for 4 h and then refluxed for a further 4 h. After the solvent was removed under vacuum, *E* and *Z* mixtures of products were isolated by flash column chromatography eluting first with 100% hexane only and then switching to hexane:EtOAc = 95:5. *E* and *Z* products were isolated as colorless oils in a ratio of 0.24/1.0 in a combined isolated yield of 92%.

The (*Z*)-olefin starting material for 29 and 31: Colorless oil (column chromatography, hexane:EtOAc = 95:5). R_f = 0.38 (hexane:EtOAc = 9:1). $[\alpha]_D^{20}$ = +69.3 (*c* 1.0,

$CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.07 (s, 6H), 0.90 (s, 3H), 1.36 (s, 3H), 1.47 (s, 3H), 1.47 (s, 9H), 2.9 (br s, 1H, disappeared with D_2O), 3.59 (ddd, $J=8.4$, 5.4, 3.0 Hz, 1H), 3.69 (dd, $J=10.2$, 5.4 Hz, 1H), 3.78 (dd, $J=10.2$, 3.0 Hz, 1H), 4.26 (dd, $J=8.4$, 6.3 Hz, 1H), 5.69 (ddd, $J=8.5$, 6.3, 1.0 Hz, 1H), 5.89 (dd, $J=11.6$, 1.0 Hz, 1H), 6.18 (dd, $J=11.6$, 8.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −5.16, −5.12, 18.6, 25.6, 28.2, 28.3, 64.6, 70.3, 74.1, 78.2, 81.4, 109.2, 124.3, 143.5, 165.9. IR (NaCl, neat): 3477m, 2854s, 2933s, 2857s, 1716s, 1652s, 1463m, 1369s, 1254s, 1159s, 1058s, 836s, 779s. Anal. calcd for $C_{20}H_{38}O_6Si$: C, 59.70; H, 9.45. Found: C, 59.79; H, 9.69.

A flame-dried three-necked round-bottomed flask was fitted with a double spaced condenser, and 1.00 g (2.45 mmol) of the alcohol from the previous step, 0.97 g (4.90 mmol) of 1,1-thiocarbonyldiimidazole, and 0.1 g of DMAP were placed under a nitrogen atmosphere. Dichloroethane (dried over 4 Å MS, 20 mL) was added, and the mixture was refluxed for overnight (13 h 30 min.). The reaction mixture was cooled to rt, and the solvent was removed by rotary evaporation under house vacuum. The deep brown oil was purified by flash column chromatography eluting with hexane:EtOAc = 97:3 to 95:1 mixture. Desired product (1.031 g) and starting material (86 mg) were obtained. The yield was 89% based on the recovered starting material.

(*Z*)-29: Pale yellow oil (column chromatography, hexane:EtOAc = 97:3 to 95:5). $[\alpha]_D^{20}=+88.5$ (*c* 3.42, $CHCl_3$). $R_f=0.23$ (hexane:EtOAc = 9:1). ^1H NMR ($CDCl_3$, 250 MHz): δ −0.03 (s, 3H), 0.00 (s, 3H), 0.84 (s, 9H), 1.40 (s, 9H), 1.40 (s, 3H), 1.51 (s, 3H), 3.92–4.04 (m, 2H), 4.85 (dd $J=8.1$, 6.3 Hz, 1H), 5.53 (ddd $J=8.1$, 4.0, 2.8 Hz, 1H), 5.68 (dd, $J=11.6$, 1.6 Hz, 1H), 5.75 (ddd, $J=7.8$, 6.4, 1.5 Hz, 1H), 6.13 (dd $J=11.6$, 7.8 Hz, 1H), 6.98 (s, 1H), 7.53 (s, 1H), 8.25 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −5.3, 18.3, 25.4, 25.9, 27.9, 28.2, 61.2, 74.1, 74.9, 81.3, 109.6, 118.0, 124.6, 130.7, 137.2, 142.3, 164.8, 183.3. IR (NaCl, neat): 3125w, 2980m, 2953m, 2938m, 2884m, 2857m, 1713s, 1658w, 1650m, 1531w, 1463m, 1413m, 1391s, 1371s, 1345m, 1327s, 1282s, 1245s, 1156s, 1109m, 1066s, 1022m, 986m, 957m, 876m, 833s. Anal. calcd for $C_{24}H_{40}N_2O_6SSi$: C, 56.22; H, 7.87; N, 5.47; S, 6.24. Found: C, 56.42; H, 8.02; N, 5.38; S, 6.07.

4.14. The (*E*)-olefin starting material for 33 (see Section 4.13)

Isolated as a side product of the Wittig reaction described earlier. Colorless oil (column chromatography, hexane:EtOAc = 95:5). $R_f=0.24$ (hexane:EtOAc = 4:1). $[\alpha]_D^{20}=-4.62$ (*c* 1.19, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.36 (s, 3H), 1.48 (s, 3H), 1.48 (s, 9H), 3.56 (ddd, $J=9.0$, 5.6, 3.1 Hz, 1H), 3.65 (dd, $J=10.0$, 5.6 Hz, 1H), 3.79 (dd, $J=10.0$, 3.1 Hz, 1H), 4.10 (dd, $J=9.3$, 6.6 Hz, 1H), 4.80 (apparent t, $J=5.1$ Hz, 1H), 6.06 (dd, $J=15.6$, 1.5 Hz, 1H), 7.00 (dd, $J=15.6$, 5.2 Hz, 1 H). IR (NaCl, neat): 3496m, 2979m, 2950m, 2930m, 2885m, 2875m, 1717s, 1658m, 1472m, 1463m, 1368s, 1314m, 1256s, 1217m, 1153s, 1062m, 837s, 779m.

4.15. Preparation of alcohol precursors for 30 and 34

To a 100 mL of flame-dried three-necked round-bottomed flask was added 378 mg (1.241 mmol) of **27**, 411 mg (1.366 mmol) of (cyanomethylene)-triphenylphosphorane, and 52 mg of benzoic acid under a nitrogen atmosphere. Freshly dried toluene (40 mL) was introduced via a syringe, and the mixture was refluxed. Two more 206 mg samples of (cyanomethylene)triphenylphosphorane were added after 8 and 12 h, respectively. After the solvent was removed in vacuo, the mixture was purified by flash column chromatography eluting with hexane:EtOAc = 10:1 to 8:1, to get 146 mg of the expected (*E*)-olefin (white solid), and (*Z*)-olefin 163 mg of product (yellow oil) along with 6 mg of a cyclized product (yellow oil).

(*E*)-Olefin: White solid (column chromatography, hexane:EtOAc = 10:1 to 8:1). $R_f=0.48$ (hexane:EtOAc = 4:1). Mp: 68–70°C. $[\alpha]_D^{20}=-6.0$ (*c* 0.55, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.07 (s, 6H), 0.89 (s, 9H), 1.34 (s, 3H), 1.45 (s, 3H), 2.16 (br s, 1H), 3.45 (ddd, $J=9.4$, 5.1, 3.1 Hz, 1H), 3.64 (dd, $J=10.1$, 5.2 Hz, 1H), 3.78 (dd, $J=10.1$, 3.1 Hz, 1H), 4.13 (dd, $J=9.5$, 6.9 Hz, 1H), 4.80 (ddd, $J=6.7$, 3.8, 2.1 Hz, 1H), 5.72 (dd, $J=16.2$, 2.0 Hz, 1H), 7.00 (dd, $J=16.2$, 3.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.54, −5.41, 18.27, 24.99, 25.81, 27.38, 64.11, 69.77, 76.62, 77.19, 100.30, 109.87, 117.26, 151.19. IR (NaCl, neat): 3498br s, 2989m, 2956s, 2930s, 2850s, 2227s, 1638m, 1432m, 1463m, 1383s, 1382s, 1257s, 1217s, 1165m, 1067s, 972w, 864m, 837s, 779s. Anal. calcd for $C_{16}H_{29}NO_4Si$: C, 58.68; H, 8.93; N, 4.28. Found: C, 58.66; H, 8.92; N, 4.12.

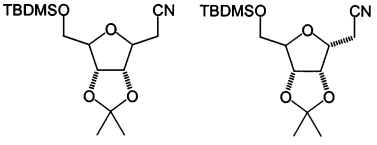
(*Z*)-Olefin: Yellow oil (column chromatography, hexane:EtOAc = 10:1 to 8:1). $R_f=0.35$ (hexane:EtOAc = 4:1). $[\alpha]_D^{20}=-30.4$ (*c* 1.15, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 1.37 (s, 3H), 1.48 (s, 3H), 2.62 (br s, 1H), 3.54 (ddd, $J=9.2$, 4.5, 3.5 Hz, 1H), 3.70 (dd, $J=10.1$, 4.8 Hz, 1H), 4.18 (dd, $J=9.4$, 6.4 Hz, 1H), 5.09 (ddd, $J=8.3$, 6.4, 0.9 Hz, 1H), 5.52 (dd, $J=11.2$, 1.0 Hz, 1H), 6.56 (dd, $J=11.2$, 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.51, −5.41, 18.29, 25.25, 25.82, 27.68, 63.91, 69.37, 76.10, 77.45, 101.76, 110.21, 115.36, 148.94. IR (NaCl, neat): 3498br s, 3070w, 2989m, 2885s, 2857s, 2224m, 1723w, 1631w, 1472s, 1463m, 1383s, 1372s, 1255s, 1219s, 1164s, 1096s, 1063s, 937w, 869m, 837s, 779s, 736m, 670m. HRMS (Electrospray) calcd for $C_{16}H_{29}NNaSO_4$ (M^++Na): 350.1764. Found (M^++Na): 350.1760. Anal. calcd for $C_{16}H_{29}NO_4Si$: C, 58.68; H, 8.93; N, 4.28. Found: C, 58.59; H, 9.32; N, 4.24.

4.16. Preparation of 34

To a flame-dried 100 mL three-necked flask fitted with a condenser were added 133 mg (0.406 mmol) of the

(*E*)-olefin from the previous experiment, 3.0 equiv. of 1,1-thiocarbonyldiimidazole (217 mg, 1.217 mmol), and 15 mg of DMAP. Freshly dried THF (40 mL) was added to the flask, and the mixture was stirred under reflux condition. Another 217 mg of 1,1-thiocarbonyldiimidazole was added after 14 h, and refluxing was continued for 8 h. All solvents were removed under reduced pressure to give a crude brown mixture of products. The mixture was purified by flash column chromatography eluting hexane:EtOAc = 5:1 to 2:1. The desired product **34** was obtained as pale yellow solid (102 mg, 88% based on recovered starting material). In addition a mixture (46 mg) of cyclized byproducts **A** and **B** in a ratio of 0.22/1.0 (*cis*/*trans*) was also obtained. **34**: Pale yellow solid (column chromatography, hexane:EtOAc = 5:1 to 2:1) $R_f = 0.25$ (hexane:EtOAc = 3:1). Mp: 51–53°C. $[\alpha]_D^{20} = -9.5$ (*c* 0.61, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ −0.03 (s, 3H), 0.01 (s, 3H), 0.85 (s, 9H), 1.40 (s, 3H), 1.50 (s, 3H), 3.94 (dd, $J = 12.0$, 3.1 Hz, 1H), 4.03 (dd, $J = 12.0$, 2.4 Hz, 1H), 4.75 (dd, $J = 8.6$, 6.5 Hz, 1H), 4.83 (ddd, $J = 6.4$, 4.7, 1.8 Hz, 1H), 5.39 (apparent dt, $J = 8.5$, 2.8 Hz, 1H), 5.68 (dd, $J = 16.2$, 1.8 Hz, 1H), 6.56 (dd, $J = 16.1$, 4.6 Hz, 1H), 7.05 (d, $J = 0.7$ Hz, 1H), 7.60 (s, 1H), 8.29 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.69, −5.62, 18.14, 25.09, 25.68, 27.47, 60.43, 74.85, 75.86, 80.46, 101.81, 110.22, 116.16, 117.97, 131.19, 136.40, 147.56, 182.24. IR (NaCl, neat): 3412br s, 3131m, 3332m, 2988s, 2954s, 2931s, 2884s, 2857s, 2227s, 1704m, 1639m, 1533m, 1470s, 1392s, 1324s, 1283s, 1165m, 1108s, 1054m, 1023s, 957s, 837s, 813m, 779s, 744m, 673m, 655s. Anal. calcd for $C_{20}H_{31}N_3O_4SSi$: C, 54.89; H, 7.14; N, 9.60. Found: C, 54.93; H, 7.37; N, 9.45.

The isolated side-products were assigned the following structures:



A B

A: ^1H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 6H), 0.90 (s, 3H), 1.35 (s, 3H), 1.53 (s, 3H), 3.73 (d, $J = 4.2$ Hz, 1H), 4.11–4.21 (m, 1H), 4.44 (dd, $J = 6.4$, 4.2 Hz, 1H), 4.70 (dd, $J = 6.4$, 2.7 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.51, −5.37, 18.37, 22.30, 25.04, 25.93, 27.43, 63.84, 80.47, 82.27, 84.22, 85.65, 114.16, 116.85.

B: $R_f = 0.47$ (hexane:EtOAc = 4:1). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.05 (s, 6H), 0.89 (s, 9H), 1.35 (s, 3H), 1.50 (s, 3H), 2.65 (d, $J = 6.7$ Hz, 1H), 3.70 (dd, $J = 11.0$, 2.8 Hz, 1H), 3.78 (dd, $J = 11.0$, 2.9 Hz, 1H), 4.15 (apparent t, $J = 2.8$ Hz, 1H), 4.42 (apparent dt, $J = 6.7$, 4.3 Hz, 1H), 4.71 (dd, $J = 5.9$, 4.3 Hz, 1H), 4.84 (d, $J = 6.1$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.7, −5.6, 18.1, 18.9, 24.6, 25.8, 26.0, 65.4, 78.1, 81.3, 83.3, 84.7, 112.8, 117.6.

4.17. Preparation of starting material for 36 and 37

A dried 100 mL three-necked round-bottomed flask was equipped with a condenser and a magnetic stirring bar. To the flask were added **27** (305 mg, 1.00 mmol) and 133 mg (1.50 mmol) of *O*-methylhydroxyl amine hydrochloride under nitrogen. Methyl alcohol (50 mL) and 1 mL of pyridine were added, and the mixture was refluxed under nitrogen for 5.5 h. The mixture was taken up water, and extracted with dichloromethane. The combined organic phase was washed with brine and dried over $MgSO_4$. After the solid was filtered off, the collected organic phase was concentrated on a rotary evaporator and purified by flash column chromatography eluting with hexane:EtOAc = 6:1. The isolated product (319 mg of colorless oil) was obtained as a *syn*/*anti* mixture in a ratio of 1.0/0.25, and the yield was 96%.

Alcohol precursor for imidazole thioate 36 and triazole thioate 37: Colorless oil (*syn*/*anti* = 1.0/0.25) (column chromatography, hexane:EtOAc = 6:1). $R_f = 0.49$ (hexane:EtOAc = 4:1). ^1H NMR ($CDCl_3$, 250 MHz): major isomer, ***syn***: δ 0.05 (s, 6H), 0.87 (s, 9H), 1.32 (s, 3H), 1.43 (s, 3H), 2.62 (d, $J = 4.8$ Hz, 1H), 3.50–3.70 (m, 3H), 3.83 (s, 3H), 4.09 (dd $J = 8.5$, 6.4 Hz 1H), 4.72 (apparent t, $J = 7.4$ Hz 1H), 7.16 (d, $J = 7.7$ Hz 1 H); minor isomer, ***anti***: δ 0.05 (s, 6H), 0.87 (s, 9H), 1.11 (s, 3H), 1.21 (s, 3H), 2.70 (d, $J = 3.8$ Hz, 1H), 3.71–3.83 (m, 3H), 3.87 (s, 3H), 4.20 (apparent t $J = 6.7$ Hz 1H), 5.26 (apparent t, $J = 6.3$ Hz 1H), 6.83 (d, $J = 6.3$ Hz 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): major isomer, ***syn***: δ −5.3, −5.1, 18.3, 26.0, 27.0, 28.0, 62.0, 64.3, 69.5, 75.4, 78.6, 109.9, 147.2; minor isomer, ***anti***: δ −5.6, −5.5, 18.4, 25.3, 25.7, 27.8, 62.4, 63.1, 70.7, 75.9, 82.4, 113.1, 149.1. IR (NaCl, neat): 3522br, 2987s, 2956s, 2932s, 2884s, 2875s, 2819w, 1795w, 1741w, 1629w, 1471s, 1468s, 1382s, 1255s, 1219s, 1170s, 1154s, 1117s, 1047s.

4.18. Preparation of 36

The reaction was performed with 215 mg (0.65 mmol) of the corresponding alcohol prepared earlier and 345 mg (1.93 mmol) of 1,1-thiocarbonyldiimidazole in 30 mL of freshly dried THF under a nitrogen atmosphere. The mixture was refluxed in an oil bath, and another 200 mg of 1,1-thiocarbonyldiimidazole was added after 9 and 11 h, respectively. Finally, the mixture was refluxed for another 18 h. After the mixture was cooled to rt, all solvent was removed in vaccuo. The crude mixture was purified by flash column chromatography eluting with hexane:EtOAc = 8:1 to 6:1. The desired product was isolated as yellow oil (211 mg, 74%, 97% based on recovered starting material) long with 51 mg of starting material. **36**: Yellow oil (column chromatography, hexane:EtOAc = 8:1 to 6:1). (*syn*:*anti* = 1.0/0.3) $R_f = 0.29$ (hexane:EtOAc = 4:1). ^1H NMR ($CDCl_3$, 400 MHz): major ***syn***: δ 0.00 (s, 3H), 0.04 (s, 3H), 0.88 (s, 9H), 1.39 (s, 3H), 1.51 (s, 3H), 3.57 (s, 3H), 3.99 (dd, $J = 11.7$, 2.9 Hz, 1H), 4.12 (dd, $J = 11.9$, 2.6 Hz, 1H), 4.76–4.81 (m, 2H), 5.49–5.58 (m, 1H), 7.04 (s, 1H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.61 (s, 1H), 8.30 (s, 1 H); minor ***anti***: δ 0.01 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 1.39 (s,

3H), 1.52 (s, 3H), 3.66 (s, 3H), 3.95–4.03 (m, 2H), 4.76–4.81 (m, 1H), 5.31 (apparent t, $J=6.0$ Hz, 1H), 5.49–5.56 (m, 1H), 6.80 (d, $J=5.6$ Hz, 1H), 7.04 (s, 1H), 7.63 (s, 1H), 8.30 (s, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): major ***syn***: δ −5.3, 18.4, 25.3, 25.9, 27.8, 60.7, 61.9, 74.2, 75.1, 80.6, 110.6, 118.1, 131.0, 137.0, 145.9, 182.0. IR (NaCl, neat): 3133w, 2989m, 2953m, 2935m, 2897m, 2856m, 1739w, 1626m, 1531w, 1463m, 1391s, 1344m, 1323s, 1283s, 1246s, 1229s, 1109m, 1076m, 1042s. Anal. calcd for $C_{19}H_{33}N_2O_5SSi$: C, 51.44; H, 7.50; N, 9.42; S, 7.23. Found: C, 51.57; H, 7.61; N, 9.23; S, 7.11.

4.19. Preparation of 31

A flame-dried three-necked round-bottomed flask was fitted with a double spaced condenser, and 192 mg (0.478 mmol) of the requisite (*Z*)-starting alcohol (see Section 4.13), 258 mg (1.43 mmol) of 1,1-thiocarbonylditriazole, and 10 mg of DMAP were placed under a nitrogen atmosphere. Freshly distilled THF (15 mL) was added, and the mixture was refluxed overnight (12 h.). The reaction mixture was cooled to rt, and the solvent was removed by rotary evaporation under house vacuum. The crude product was purified by flash column chromatography eluting with hexane:EtOAc = 10:1 to 8:1 mixture. Desired product (69 mg) and starting material (115 mg) were obtained. The isolated yield of **31** was 28% (70% based on the recovered starting material). **31**: Colorless oil (column chromatography, hexane:EtOAc = 10:1 to 8:1). $R_f=0.31$ (hexane:EtOAc = 6:1). $[\alpha]_D^{20}=+90.6$ (*c* 0.58, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.02 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 1.39 (s, 9H), 1.40 (s, 3H), 1.51 (s, 3H), 4.00 (A of ABX, $J_{AB}=11.8$ Hz, $J_{AX}=5.1$ Hz, 1H), 4.02 (B of ABX, $J_{AB}=11.8$ Hz, $J_{BX}=2.5$ Hz, 1H), 4.88 (dd, $J=7.3$, 6.6 Hz, 1H), 5.63 (ddd, $J=7.5$, 4.5, 3.1 Hz, 1H), 5.72 (dd, $J=11.6$, 1.5 Hz, 1H), 5.78 (ddd, $J=7.9$, 6.7, 1.5 Hz, 1H), 6.19 (dd, $J=11.6$, 7.8 Hz, 1H), 8.02 (s, 1H), 8.85 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.56, 18.15, 25.09, 25.70, 27.56, 27.99, 61.29, 73.97, 75.04, 81.17, 82.38 (two peaks), 109.50, 124.57, 142.38, 153.61, 164.61, 180.69. IR (NaCl, neat): 2985s, 2951s, 2929s, 2860s, 1712s, 1643w, 1516w, 1472w, 1462s, 1388s, 1382s, 1321m, 1279s, 1239s, 1201s, 1157s, 1124s, 1066s, 966w, 943m, 835s, 778m, 666m, 651m. Anal. calcd for $C_{23}H_{39}N_3O_6SSi$: C, 53.77; H, 7.65; N, 8.18; S, 6.24. Found: C, 54.15; H, 7.62; N, 7.33; S, 6.25.

4.20. Preparation of 37

A mixture of the requisite oxime-alcohol (Section 4.17, 131 mg), thiocarbonylditriazole (142 mg), and 10 mg of DMAP were placed in a 50 mL of flame dried three-necked flask, which was connected to a double spaced condenser. Freshly dried THF (20 mL) was added to the flask, and the mixture was refluxed under a nitrogen atmosphere for 6 h. Another 2.0 equiv. of thiocarbonylditriazole was added and refluxing was continued for 16 h. All solvents were removed under reduced pressure, and the dark brown mixture was purified by column chromatography to give 79 mg of **37** as yellow oil along with 50 mg of starting material. The product was a *syn*/*anti* mixture in a ratio of 1.69/1.00 based on ^{1}H NMR spectrum. **37**: Yellow oil (*syn*/*anti* = 1.69/1.0) (column chromatography, hexane:EtOAc = 10:1 to 8:1). $R_f=0.29$ (hexane:EtOAc = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz): ***syn*** (major): δ 0.00 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 1.40 (s, 3H), 1.50 (s, 3H), 3.59 (s, 3H), 4.00 (dd, $J=11.9$, 3.8 Hz, 1H), 4.14 (dd, $J=11.9$, 2.9 Hz, 1H), 4.76–4.83 (m, 2H), 5.61 (ddd, $J=11.0$, 8.1, 4.2 Hz, 1H), 7.34 (d, $J=7.6$ Hz, 1H), 8.05 (s, 1H), 8.92 (s, 1H); ***anti*** (minor): δ 0.00 (s, 3H), 0.01 (s, 3H), 0.84 (s, 9H), 1.38 (s, 3H), 1.50 (s, 3H), 3.70 (s, 3H), 3.98–4.02 (m, 2H), 4.71–4.78 (m, 1H), 5.32 (dd, $J=6.5$, 5.5 Hz, 1H), 5.59–5.63 (m, 1H), 6.88 (d, $J=5.4$ Hz, 1H), 8.05 (s, 1H), 8.93 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): ***syn*** (major): δ −5.60, −5.55, 18.21, 25.19, 25.73, 27.60, 61.05, 62.23, 74.16, 74.87, 81.40, 110.45, 144.43, 146.06, 153.64, 180.54; ***anti*** (minor): δ −5.53, −5.35, 18.16, 24.82, 25.70, 27.21, 61.05, 62.23, 74.16, 74.87, 81.40, 109.76, 144.29, 147.27, 153.61, 180.80. IR (NaCl, neat): 3123w, 2986w, 2952s, 2934s, 2857s, 1797w, 1723w, 1516m, 1466m, 1462m, 1392s, 1378s, 1345m, 1321s, 1279s, 1254s, 1199s, 1124s, 1082s, 1046s, 965s, 942m, 837s, 814m, 779s, 660s. HRMS (Electrospray) calcd for $C_{18}H_{32}N_4NaO_5SSi$ (M^++Na): 467.1755. Found (M^++Na): 467.1716.

5-*exo*-Hex-5-enyl radical cyclizations

4.21. Cyclization of of [(*E*)-7-im] under reverse addition conditions (typical procedure for cyclization)

A flame-dried three-necked 25 mL flask was connected to a condenser, and the flask was charged with 276 mg of Ph_3SnH (0.785 mmol) and 12.5 mL of benzene (dried over CaH_2 and stored over 4 Å MS under a nitrogen atmosphere) under a nitrogen atmosphere. The flask was immersed into an oil bath and the oil bath temperature was adjusted to be 90°C. To the flask was added a solution of 60.9 mg (0.157 mmol) of (*E*)-**7-im**, and 13 mg (0.079 mmol) of AIBN in 3.4 mL of benzene via a syringe pump during 2 h, and the mixture was stirred for another 0.5 h at 90°C (oil bath temperature). The mixture was cooled to rt, and the solvent was removed in vacuo to give crude product. The concentrated mixture was purified by flash column chromatography eluting with hexane only to hexane:EtOAc = 1:2. The cyclized *N*-pyranoside **14** was obtained as white solid (30.5 mg, 54%) in the ratio of $\alpha/\beta=0.8/1.0$. The assignment and configurations were assigned based on comparison of chemical shifts and coupling constants of the corresponding ^{t}Bu esters described in the next experiments. **14-α**: White solid (column chromatography, hexane only to hexane:EtOAc = 1:2). $R_f=0.12$ (hexane:EtOAc = 1:4). $[\alpha]_D^{20}=+25.0$ (*c* 0.62, $CHCl_3$). Mp: 126–129°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, $J=7.2$ Hz, 3H), 2.60 (dd, $J=15.5$, 8.5 Hz, 1H), 2.84 (dd, $J=15.4$, 4.9 Hz, 1H), 3.15 (dddd, $J=8.8$, 8.3, 7.0, 4.9 Hz, 1H), 3.65 (dd, $J=10.6$, 8.8 Hz, 1H), 3.88–4.05 (m, 4H), 4.54 (dd, $J=9.3$, 3.9 Hz, 1H), 5.58 (s, 1H), 5.78 (d, $J=7.0$ Hz, 1H), 7.14 (s, 1H), 7.35–7.41 (m, 4H), 7.49–7.52 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.90, 34.21, 45.28, 61.17, 70.75,

73.10, 82.78, 88.93, 102.61, 117.08, 126.22, 128.40, 129.01, 129.43, 136.16, 136.42, 170.20. IR (NaCl, neat): 3394br m, 3119m, 2982m, 1731s, 1495w, 1455w, 1428w, 1370m, 1282m, 1228m, 1165m, 1094m, 1047s, 1028s, 970s, 913m, 756s, 699s, 661m. HRMS (Electrospray) calcd for $C_{19}H_{22}N_2NaO_5$ (M^++Na): 381.1421. Found (M^++Na): 381.1447. Anal. calcd for $C_{19}H_{22}N_2O_5$: C, 63.67; H, 6.19; N, 7.82. Found: C, 64.45; H, 6.93; N, 6.39.

14-β: White solid (column chromatography, hexane only to hexane:EtOAc = 1:2). $R_f = 0.22$ (hexane:EtOAc = 1:4). $[\alpha]_D^{20} = -84.0$ (*c* 0.77, $CHCl_3$). Mp: 57–60°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.77 (t, $J = 7.1$ Hz, 3H), 1.80 (dd, $J = 17.8$, 11.4 Hz, 1H), 2.69 (dd, $J = 17.8$, 3.5 Hz, 1H), 3.11 (apparent tdd, $J = 11.4$, 7.6, 3.5 Hz, 1H), 3.62 (dd, $J = 11.6$, 9.0 Hz, 1H), 3.75 (ddd, $J = 9.9$, 9.0, 4.0 Hz, 1H), 4.03 (apparent t, $J = 11.0$ Hz, 1H), 4.05 (q, $J = 7.1$ Hz, 2H), 4.63 (dd, $J = 9.8$, 4.3 Hz, 1H), 5.62 (s, 1H), 6.29 (d, $J = 7.5$ Hz, 1H), 6.94 (s, 1H), 7.11 (s, 1H), 7.35–7.41 (m, 3H), 7.48–7.59 (m, 2H), 7.60 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.04, 31.03, 43.25, 61.11, 70.97, 73.05, 81.42, 86.95, 102.84, 117.42, 126.25, 128.42, 128.99, 129.62, 136.15, 136.42, 171.60. IR (NaCl, neat): 3388br m, 3119m, 3061m, 2983m, 2928m, 1729s, 1494m, 1478m, 1428s, 1376s, 1324m, 1228s, 1212s, 1080s, 1027s, 996s, 972s, 914m, 699s, 662m. HRMS (Electrospray) calcd for $C_{19}H_{22}N_2NaO_5$ (M^++Na): 381.1421. Found (M^++Na): 381.1433.

4.22. Optimization of cyclization using 7 and 8

15-α: White solid (column chromatography, hexane only to hexane:EtOAc = 1:2). $R_f = 0.16$ (hexane:EtOAc = 1:2). $[\alpha]_D^{20} = +34.9$ (*c* 0.59, $CHCl_3$). Mp: 125–128°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.33 (s, 9H), 2.54 (dd, $J = 15.1$, 8.5 Hz, 1H), 2.82 (dd, $J = 15.1$, 4.7 Hz, 1H), 3.18 (dddd, $J = 8.8$, 8.5, 6.9, 4.8 Hz, 1H), 3.65 (dd, $J = 10.4$, 8.9 Hz, 1H), 3.94 (apparent t, $J = 10.1$ Hz, 1H), 4.00 (apparent td, $J = 9.8$, 4.1 Hz, 1H), 4.58 (dd, $J = 9.5$, 4.1 Hz, 1H), 5.62 (s, 1H), 5.82 (d, $J = 6.9$ Hz, 1H), 7.20 (s, 1H), 7.21 (s, 1H), 7.41–7.46 (m, 3H), 7.53–7.58 (m, 2H), 7.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.72, 35.87, 45.26, 70.76, 72.92, 81.84, 83.04, 89.05, 102.67, 117.08, 126.25, 128.39, 129.43, 130.29, 136.43, 136.70, 169.43. IR (NaCl, neat): 3393br m, 3119m, 2983m, 2931m, 2872m, 1716m, 1396w, 1369m, 1281m, 1225w, 1150s, 1089s, 1045s, 963s, 934m, 913m, 831w, 760m, 700m. HRMS (Electrospray) calcd for $C_{21}H_{26}N_2NaO_5$ (M^++Na): 387.1915. Found (M^++Na): 387.1944.

15-β: White solid (column chromatography; hexane only to hexane:EtOAc = 1:2). $R_f = 0.29$ (hexane:EtOAc = 1:2). $[\alpha]_D^{20} = -129.6$ (*c* 0.46, $CHCl_3$). Mp: 59–61°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.37 (s, 9H), 1.71 (dd, $J = 17.9$, 11.5 Hz, 1H), 2.64 (dd, $J = 17.8$, 3.3 Hz, 1H), 3.07 (apparent tdd, $J = 11.3$, 7.5, 3.3 Hz, 1H), 3.59 (dd, $J = 11.7$, 9.0 Hz, 1H), 3.74 (apparent td, $J = 9.1$, 4.4 Hz, 1H), 4.03 (apparent t, $J = 10.0$ Hz, 1H), 4.62 (dd, $J = 9.8$, 4.4 Hz, 1H), 5.61 (s, 1H), 6.30 (d, $J = 7.5$ Hz, 1H), 6.94 (s, 1H), 7.11 (s, 1H), 7.37–7.40 (m, 3H), 7.47–7.51 (m, 2H), 7.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.90, 32.17, 43.26, 70.97, 73.07, 81.30, 81.15, 87.14, 102.82, 117.63, 126.25, 128.40, 129.20, 130.14, 136.16, 136.46, 170.92. IR (NaCl, neat): 3388br m, 3119m, 2978m, 2931m, 2872m, 1723s, 1494m, 1455m, 1369s, 1247m, 1227m, 1157s, 1080s, 1046s, 971s, 913m, 755s, 699s. HRMS (Electrospray) calcd for $C_{21}H_{26}N_2NaO_5$ (M^++Na): 387.1915. Found (M^++Na): 387.1902. Anal. calcd for $C_{21}H_{26}N_2O_5$: C, 65.27; H, 6.78; N, 7.25. Found: C, 62.68; H, 6.93; N, 5.64.

Table 4. 5-*exo*-*trig* Radical cyclization with [2*R*,4*R*,5*R*]-5-hydroxy-2-phenyl-[1,3]dioxane-4-carbaldehyde **6** derivatives

Entry	R	Conditions				Yield (%)	(α/β)
		Radical sources (equiv.)	AIBN (equiv.)	Solvent	Temp. (°C)		
1	(*Z*)-**7**	Bu_3SnH (5.0)	0.5	Benzene	90	32	0.84/1.0
2	(*Z*)-**7**	Ph_3SnH (5.0)	0.5	Benzene	90	44	1.13/1.0
3	(*E*)-**7**	Bu_3SnH (5.0)	0.5	Benzene	90	28	0.66/1.0
4	(*E*)-**7**	Ph_3SnH (5.0)	0.5	Benzene	90	54	0.80/1.0
5	(*Z*)-**8**	Ph_3SnH (5.0)	0.5	Benzene	90	46	0.66/1.0
6[a]	(*Z*)-**8**	Ph_3SnH (5.0)	0.5	Benzene	90	23	0.93/1.0
6	(*E*)-**8**	Ph_3SnH (5.0)	0.5	Benzene	90	40	0.89/1.0

[a] Normal addition stirred at 90°C for 3 h.

4.23. Cyclization of (*Z*)-8-im

The typical reverse addition procedure was used under the following conditions: Ph_3SnH (309 mg, 0.880 mmol) in 14 mL of benzene at 90°C, 72.8 mg (0.176 mmol) of **(*Z*)-8-im** and 14.5 mg (0.088 mmol) of AIBN in 3.8 mL of benzene added in 2 h 25 min, the mixture stirred for additional 0.5 h at 90°C (oil bath temperature, column chromatography eluting with hexane only to hexane:EtOAc = 1:2. The cyclized *N*-pyranoside was obtained as white solid (31 mg, 46%) with the ratio of $\alpha/\beta = 0.7/1.0$).

4.24. Cyclization of (*Z*)-9-im

The typical reverse addition procedure was used under the following conditions: Ph_3SnH (295 mg, 0.841 mmol) in 13.3 mL of benzene at 90°C, 52.7 mg (0.168 mmol) of **(*Z*)-9-im** and 14.5 mg (0.088 mmol) of AIBN in 3.6

mL of benzene added in 2 h 20 min, the mixture stirred for additional 0.5 h at 90°C (oil bath temperature), column chromatography eluting with hexane:EtOAc 1:1 to 1:2. The cyclized *N*-pyranoside was obtained as pale yellow solid (38.5 mg, 81%) with the ratio of $\alpha/\beta = 1.0/0.79$). The assignments are based on comparison of chemical shifts and coupling constants (especially of C_1-H) with those of ^{t}Bu esters described in the previous experiments.

α- and β-17: Pale yellow solid (α/β mixture, ratio: 1.0/0.79) (column chromatography, hexane:EtOAc 1:1 to 1:2). $R_f = 0.12$ (EtOAc only). Mp: 126–130°C. ^{1}H NMR ($CDCl_3$, 400 MHz): α-anomer, δ 2.73 (dd, J= 17.5, 4.6 Hz, 1H), 2.88 (dd, J=17.5, 5.2 Hz, 1H), 2.96–3.06 (m, 1H), 3.75–3.81 (m, 1H), 3.95 (apparent t, J=9.7 Hz, 1H), 4.01–4.07 (m, 1H), 4.57 (dd, J= 9.6, 4.2 Hz, 1H), 5.63 (s, 1H), 5.82 (d, J=7.2 Hz, 1H), 7.13 (s, 1H), 7.19 (s, 1H), 7.37–7.42 (m, 3H), 7.49–7.52 (m, 2H), 7.79 (s, 1H); β-anomer, δ 1.91 (dd, J=17.2, 9.9 Hz, 1H), 2.51 (dd, J=17.2, 4.9 Hz, 1H), 2.96–3.06 (m, 1H), 3.68 (d, J=11.2, 9.2 Hz, 1H), 3.75–3.81 (m, 1H), 4.01–4.07 (m, 1H), 4.64 (dd, J=9.9, 4.3 Hz, 1H), 5.64 (s, 1H), 6.17 (d, J=7.5 Hz, 1H), 7.06 (s, 1H), 7.20 (s, 1H), 7.37–7.42 (m, 3H), 7.49–7.52 (m, 2H), 7.76 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): α-anomer, δ 16.15, 44.85, 70.56, 73.43, 81.15, 87.60, 102.75, 116.53, 116.60, 126.22, 128.46, 129.59, 131.13, 136.06, 136.48; β-anomer, δ 14.57, 69.42, 70.07, 73.08, 81.34, 85.90, 102.84, 115.73, 117.38, 126.18, 128.44, 129.55, 130.49, 136.00, 136.21. IR (NaCl, neat): 3115m, 2971s, 2879s, 2251m, 1698s, 1493s, 1455m, 1421m, 1380s, 1314m, 1285m, 1229s, 1168s, 1142m, 1080s, 1048s, 969s, 912s, 823w, 755s, 732s, 701s, 660s. HRMS (Electrospray) calcd for $C_{17}H_{17}N_3NaO_3$ (M^++Na): 334.1162. Found (M^++Na): 334.1180.

4.25. Cyclization of (*syn*+*anti*)-10-im

The typical reverse addition procedure was used under the following conditions: Ph_3SnH (407 mg, 1.16 mmol) in 18.3 mL of benzene at 90°C, 74 mg (0.232 mmol) of **10-im** and 19 mg (0.16 mmol) of AIBN in 5 mL of benzene added in 3 h 15 min, the mixture stirred for additional 0.5 h at 90°C (oil bath temperature), column chromatography eluting with hexane:EtOAc 1:1 to 1:2. The cyclized *N*-pyranoside was obtained as pale yellow solid (42.2 mg, 63%) with the ratio of $\alpha/\beta = 1.0/0.80$).

α- and β-18: Pale yellow oil ($\alpha/\beta = 1.0/0.83$) (column chromatography, hexane:EtOAc=1:1 to 1:2). $R_f = 0.22$ (hexane:EtOAc=1:6). Mp: 96–99°C. ^{1}H NMR ($CDCl_3$, 400 MHz): α-anomer, δ 3.58 (s, 3H), 3.72–3.81 (m, 1H), 3.91–3.97 (m, 2H), 4.00–4.11 (m, 2H), 4.55 (dd, J=9.5, 4.2 Hz, 1H), 5.57 (s, 1H), 5.86 (d, J=5.3 Hz, 1H), 7.14 (s, 2H), 7.36–7.41 (m, 3H), 7.47–7.50 (m, 2H), 7.75 (s, 1H); β-anomer, δ 3.07 (s, 3H), 3.72–3.81 (m, 1H), 3.91–3.97 (m, 2H), 4.00–4.11 (m, 2H), 4.58 (dd, J=9.8, 4.0 Hz, 1H), 5.59 (s, 1H), 6.06 (d, J=6.8 Hz, 1H), 7.06 (s, 1H), 7.12 (s, 1H), 7.36–7.41 (m, 3H), 7.47–7.50 (m, 2H), 7.68 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): α-anomer, δ 61.36, 62.89, 69.00, 70.65, 72.38, 78.92, 87.65, 116.53, 126.24, 129.08, 129.44, 130.41, 136.05, 136.30; β-anomer, δ 53.82, 64.61, 69.41, 70.80, 71.06, 79.44, 85.94, 118.29, 126.25, 129.08, 128.37, 129.45, 136.23, 137.02. IR (NaCl, neat): 3112br m, 2940s, 2893s, 2802w, 2238w, 1701m, 1495s, 1458m, 1425w, 1379s, 1313m, 1283m, 1226s, 1058s, 1078s, 1049s, 1229s, 975s, 911s, 822w, 792w, 733s, 700s, 660s. HRMS (Electrospray) calcd for $C_{16}H_{19}N_3NaO_4$ (M^++Na): 340.1268. Found (M^++Na): 340.1290. Anal. calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.04; N, 13.24. Found: C, 60.17; H, 6.45; N, 11.19.

4.26. Cyclization of 11-im

The typical reverse addition procedure was used under the following conditions: Ph_3SnH (618 mg, 1.760 mmol) in 28 mL of benzene at 90°C, 117 mg (0.352 mmol) of **11-im** and 29 mg (0.176 mmol) of AIBN in 7.6 mL of benzene added in 4 h 35 min, the mixture stirred for additional 0.5 h at 90°C (oil bath temperature). The concentrated mixture was purified by flash column chromatography first eluting with hexane:EtOAc=1:1 and then with EtOAc with 1% Et_3N. The ratio of the crude *N*-pyranosides was α/β=1.0/0.3 measured by ^{1}H NMR. The α-anomer was isolated as a pure component as pale yellow solid (57.6 mg, 54%).

19-α: Pale yellow solid (column chromatography, hexane:EtOAc=1:1 100% EtOAc only with 1% of Et_3N). $R_f = 0.10$ (EtOAc only) or 0.67 (EtOAc:MeOH=9:1). Mp: 120–123°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 6H), 3.80–3.91 (m, 2H), 3.96 (apparent t, J=10.1 Hz, 1H), 4.06 (apparent td, J=9.7, 4.3 Hz, 1H), 4.56 (dd, J=9.6, 4.3 Hz, 1H), 5.55 (s, 1H), 5.75 (d, J=4.9 Hz, 1H), 7.11 (s, 1H), 7.18 (s, 1H), 7.35–7.42 (m, 3H), 7.47–7.50 (m, 2H), 7.75 (s, 1H); NH peak overlaps with 3 Hs between 3.80 and 4.09. The integration of this region becomes smaller as much as 0.4 H with D_2O exchange. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 48.26, 66.19, 70.80, 72.26, 81.71, 90.66, 102.58, 116.44, 126.22, 128.40, 129.44, 130.00, 136.04, 136.42. IR (NaCl, neat): 3209br s, 3116s, 3039m, 2982s, 2948s, 2880s, 2857s, 2778s, 1698w, 1666w, 1494s, 1454s, 1428m, 1379s, 1313s, 1282s, 1224s, 1165s, 1078s, 1049s, 1027s, 991s, 966s, 912s, 813m, 792m, 761s, 735s, 700s, 660s. HRMS (Electrospray) calcd for $C_{17}H_{22}N_4NaO_3$ (M^++Na): 353.1584. Found (M^++Na): 353.1581. Anal. calcd for $C_{17}H_{22}N_4O_3$: C, 61.80; H, 6.71; N, 16.96. Found: C, 61.49; H, 6.77; N, 15.99.

4.27. Cyclization of of 12-im

The typical reverse addition procedure was used under the following conditions: Ph_3SnH (1.06 g, 3.02

mmol) in 24 mL of benzene at 90°C, 138 mg (0.302 mmol) of **12-im** and 50 mg (0.302 mmol) of AIBN in 6.5 mL of benzene added in 4 h 30 min, the mixture stirred for additional 0.5 h at 90°C (oil bath temperature). The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 1:2. Only the α-anomer **20** was formed under these conditions and it was isolated in 20% (25.7 mg) yield. A reduced product **21** was also isolated in 62% (72.4 mg).

20: Pale yellow oil (column chromatography; hexane only to hexane:EtOAc = 2:1). $R_f = 0.34$ (hexane:EtOAc = 1:2). $[\alpha]_D^{20} = -1.9$ (*c* 0.43, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.95 (apparent t, $J = 9.8$ Hz, 1H), 3.98 (apparent t, $J = 9.3$ Hz, 1H), 4.08 (dd, $J = 9.6$, 4.2 Hz, 1H), 4.16 (ddd, $J = 9.0$, 5.4, 1.7 Hz, 1H), 4.53 (s, NH, disappeared with D_2O), 4.55 (dd, $J = 9.7$,.4.4 Hz, 1H), 5.53 (s, 1H), 5.89 (d, $J = 5.4$ Hz, 1H), 6.93 (dd, $J = 8.5$, 0.9 Hz, 4H), 7.00 (s, 1H), 7.05 (apparent td, $J = 7.4$, 0.8 Hz, 2H), 7.12 (s, 1H), 7.24–7.28 (m, 4H), 7.38–7.41 (m, 3H), 7.46–7.49 (m, 2H), 7.51 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.35, 69.49, 70.81, 72.35, 82.85, 89.84, 102.65, 116.78, 120.49, 123.57, 126.23 (two peaks), 128.45, 129.48, 129.99, 136.29, 148.05. IR (NaCl, neat): 3059m, 2966m, 2926m, 2359w, 2320w, 1702m, 1666w, 1589s, 1494s, 1461m, 1379m, 1313m, 1266s, 1224m, 1175m, 1078s, 1049s, 1028s, 969m, 910m, 736s, 698s. HRMS (Electrospray) calcd (M^++Na): 477.1897. Found (M^++Na): 477.1877.

21: Pale yellow solid (column chromatography; hexane only to hexane:EtOAc = 7:1). $R_f = 0.53$ (hexane:EtOAc = 4:1). Mp: 74–77°C. $[\alpha]_D^{20} = -54.6$ (*c* 0.70, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.60 (apparent td, $J = 9.6$, 4.5 Hz, 1H), 3.78 (apparent t, $J = 9.1$ Hz, 1H), 3.92 (apparent t, $J = 9.8$ Hz, 1H), 3.95 (apparent t, $J = 8.0$ Hz, 1H), 4.01 (dd, $J = 9.0$, 6.0 Hz, 1H), 4.16 (dd, $J = 8.9$, 8.1 Hz, 1H), 4.42 (br s, NH), 4.51 (dd, $J = 9.7$, 4.5 Hz, 1H), 5.48 (s, 1H), 7.05 (apparent td, $J = 7.3$, 1.1 Hz, 2H), 7.14–7.18 (m, 4H), 7.29–7.34 (m, 4H), 7.36–7.40 (m, 3H), 7.46–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 59.09, 71.35, 71.75, 72.42, 84.35, 102.23, 102.57, 122.90, 126.25, 128.30, 129.17, 129.24, 136.96, 148.03. IR (NaCl, neat): ν 3271m, 3061s, 3035s, 2982s, 2880s, 2240w, 1952w, 1703w, 1588s, 1495s, 1455s, 1379s, 1311s, 1271s, 1214m, 1169s, 1079s, 1049s, 1028s, 964s, 911m, 885w, 826w, 751s, 697s. HRMS (Electrospray) calcd (M^++Na): 411.1679. Found (M^++Na): 411.1689. Anal. calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21. Found: C, 73.38; H, 6.53; N, 8.14.

exo-Hept-6-enyl radical cyclizations

4.28. The cyclization of 29 by reverse addition (typical procedure for cyclization)

A flame-dried three-necked 25 mL flask was connected to a condenser, and the flask was charged with 02 mg of Ph_3SnH (0.860 mmol) and 13.6 mL of benzene (dried over CaH_2 and stored over 4 Å MS under a nitrogen atmosphere) under a nitrogen atmosphere. The flask was immersed into an oil bath and the oil bath temperature was adjusted to be 90°C. To the flask was added a solution of 88 mg (0.172 mmol) of **29** and 14 mg (0.086 mmol) of AIBN in 3.7 mL of benzene via a syringe pump during 2 h 15 min, and the mixture was stirred for another 0.5 h at 90°C (oil bath temperature). The mixture was cooled to rt, and the solvent was removed in vacuo to give crude product. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 3:1. The cyclized *N*-pyranoside **40** was obtained as a pale yellow oil (59.0 mg, 71%) in a ratio of 0.20:1.0 for the α- and β-anomers. **40-β** (major): Colorless oil (column chromatography, hexane:EtOAc = 24:1), $R_f = 0.63$ (Hexane:EtOAc = 8:1). $[\alpha]_D^{20} = +23.5$ (*c* 3.16, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.07 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.37 (s, 3H), 1.40 (s, 9H), 1.52 (s, 3H), 2.02 (dd, $J = 16.8$, 5.9 Hz, 1H), 2.25 (dd, $J = 16.8$, 8.6 Hz 1H), 2.88 (dddd, $J = 8.6$, 5.9, 3.6, 3.2 Hz, 1H), 3.66–3.69 (ddd, $J = 8.4$, 4.4, 2.1 Hz, 1H), 3.77 (dd, $J = 11.5$, 4.4 Hz, 1H), 3.92 (dd, $J = 11.5$, 2.1 Hz, 1H), 4.24–4.31 (m, 2H), 5.89 (d, $J = 3.2$ Hz, 1H), 6.96 (s, 1H), 7.08 (s, 1H), 7.62 (s, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ −5.1, −5.0, 18.5, 26.0, 28.1, 31.8, 38.5, 62.9, 68.9, 75.4, 79.4, 81.5, 83.2, 109.9, 116.4, 129.7, 135.2, 170.7. The structure was further confirmed by NOE studies. IR (NaCl, neat): 3118br m, 3002s, 2991s, 2980s, 2930s, 2851s, 1728s, 1461m, 1369s, 1254s, 1219s, 1154s, 1064s, 1000m, 941m, 906m, 838s, 779m, 739m, 662m. Anal. calcd for $C_{24}H_{42}N_2O_6Si$: C, 59.72; H, 8.77; N, 5.80. Found C, 59.51; H, 8.61; N, 5.58. Minor product **40-α** was assigned by the characteristic anomeric proton which appears at δ 5.64 (d, $J = 8.5$ Hz, 1H).

In the experiment with the corresponding (*E*)-acrylic acid *tert*-butyl ester **33**, minor amount of *allo* glycosides were also obtained (see Table below). The *allo*-compounds were not fully characterized, but their characteristic anomeric hydrogen peaks were used for the tentative assignments of the configurations.

250 MHz ^1H NMR	*altro*-α	*altro*-β	*allo*-α	*allo*-β
Chemical shift (ppm)	5.67	5.88	5.93	5.28
Coupling constant (Hz)	8.4	3.2	7.1	10.3
Ratio[a]	0.20	1.00	0.08	0.10

[a] The ratio was determined by ^1H NMR after column chromatography.

4.29. Optimization of 6-*exo*-hept-6-enyl radical cyclization

Table 5. 6-*exo*-Hept-6-enyl radical cyclizations using **28**, **32**, **29** and **33**

Expt	R	Conditions				Yield (%)			Comments[a]	
		R_3SnH (equiv.)	AIBN (equiv.)	Solvent	Temp. (°C)	**40**/**44** or **39**/**43**	**46**	**46*S***	*allo* (α/β)	*altro* (α/β)
1	**29**	Bu_3SnH (1.5)	00.2	Toluene	Reflux			33	–	–
2	**29**	Bu_3SnH (1.5)	0.2	Benzene	Reflux	34			–	13/87
3	**29**	Bu_3SnH (1.5)	0.2	Toluene	Reflux		40		–	–
4	**29**	Bu_3SnH (5.0)	0.5	Toluene	90	37				28/72
5	**29**	Bu_3SnH (5.0)	0.5	Benzene	90	57				14/86
6	**29**	Bu_3SnH (10.0)	1.0	Benzene	90	54				15/85
7	**29**	Ph_3SnH (5.0)	0.5	Toluene	Reflux	47	9			25/75
8	**29**	Ph_3SnH (5.0)	0.5	Benzene	Reflux	62				17/83
9	**29**	**Ph_3SnH (5.0)**	**0.5**	**Benzene**	**90**	**71**				**17/83**
10	**29**	Bu_3SnH (5.0)	0.5	Benzene	68	3				–
11[b]	**29**	Ph_3SnH (5.0)	0.5	Benzene	Reflux	15	37			14/86
12	**33**	Ph_3SnH (5.0)	0.5	Benzene	Reflux	61			10/14	14/62
13	**28**	Bu_3SnH (5.0)	0.5	Benzene	90	68				20/80
14	**32**	Bu_3SnH (5.0)	0.5	Benzene	90	59	18		3/9	21/67

[a] The ratio was determined by ^1H NMR before column chromatography.
[b] Normal addition: the mixture of Ph_3SnH (5.0 equiv.) and AIBN (0.5 equiv.) in benzene was added to the solution of substrate in benzene via a syringe pump.

4.30. Cyclization of 29 at high temperature

A flame-dried three-necked 25 mL flask was connected to a condenser, and the flask was charged with 157 mg of Bu_3SnH (0.54 mmol) and 7 mL of toluene (freshly dried over Na) under a nitrogen atmosphere. To the flask was added a solution of 185 mg (0.36 mmol) of **29** and 12 mg (0.072 mmol) of AIBN in 3.5 mL of toluene under reflux conditions via a syringe pump during 2 h 20 min, and the mixture was refluxed for another 3 h. The mixture was cooled to rt, and the solvent was removed in vacuo to give crude product. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 5:1. The isolated product was identified as a thiolactone, **46*S*** (53.7 mg, 33%). **46*S***: (preparative TLC, hexane:EtOAc = 5:1). $R_f = 0.17$ (hexane:EtOAc = 4:1). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.11 (s, 3H), 1.12 (s, 3H), 0.90 (s, 9H), 1.34 (s, 3H), 1.46 (s, 9H), 1.49 (s, 3H), 2.74 (dd, $J = 16.4$, 3.6 Hz, 1H), 2.97 (dd, $J = 16.4$, 8.7 Hz, 1H), 3.08 (ddd, $J = 12.3$, 8.7, 3.7 Hz, 1H), 3.95 (dd, $J = 12.1$, 4.2 Hz, 1H), 4.04 (dd, $J = 8.9$, 6.9 Hz, 1H), 4.11 (dd, $J = 11.9$, 1.6 Hz, 1H), 4.25–4.36 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.2, −5.3, 18.4, 24.7, 25.9, 26.9, 28.0, 37.1, 50.9, 62.0, 71.0, 74.9, 78.8, 82.6, 111.3, 170.7, 218.4. IR (NaCl, neat): 2957m, 2930s, 2857m, 1731s, 1472m, 1368m, 1338m, 1268s, 1212m, 1152s, 1076m, 836m. HRMS (Electrospray) calcd for $C_{21}H_{38}NaO_6SSi$ (M^++Na): 469.2056. Found (M^++Na): 469.2057.

4.31. Cyclization 30 or 34

The reverse addition procedure was used for this cyclization. The amounts of regents used and the time of reaction were as follows: Ph_3SnH (257 mg, 0.732 mmol) in 11.6 mL of benzene; 60 mg (0.146 mmol) of **30** and 12 mg (0.073 mmol) of AIBN in 3.2 mL of benzene added during 2 h 30 min, additional stirring for 0.5 h at 90°C (oil bath temperature). Solvent for column chromatography: hexane:EtOAc = 3:1 to 1:1. The cyclized *N*-pyranoside **41** was obtained as a pale yellow oil (31.9 mg, 57%) with a ratio of *altro*-α/*altro*-β = 0.26/1.0 after column chromatography. **41**: ^1H NMR ($CDCl_3$, 400 MHz): **41-*altro*-β**: δ 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.41 (s, 3H), 1.54 (s, 3H), 2.06 (dd, $J = 17.3$, 5.4 Hz, 1H), 2.38 (dd, $J = 17.3$, 9.7 Hz, 1H), 2.69–2.79 (m, 1H), 3.73 (ddd, $J = 8.9$, 4.3, 2.1 Hz, 1H), 3.82 (dd, $J = 11.6$, 4.4 Hz, 1H), 3.93 (dd, $J = 11.6$, 2.0 Hz, 1H), 4.33 (dd, $J = 8.9$, 5.4 Hz, 1H), 4.52 (dd, $J = 5.4$, 3.4 Hz, 1H), 5.90 (d, $J = 2.9$ Hz, 1H), 6.98 (s, 1H), 7.15 (s, 1H), 7.69 (s, 1H); **41-*altro*-α**: δ 0.00 (s, 6H), 0.89 (s, 9H), 1.39 (s, 3H), 1.50 (s, 3H), 2.10 (dd, $J = 17.3$, 4.5 Hz, 1H), 2.31 (dd, $J = 17.2$, 9.5 Hz, 1H), 2.69–2.76 (m, 1H), 3.82 (dd, $J = 11.6$, 4.4 Hz, 1H), 3.98 (dd, $J = 11.5$, 2.3 Hz, 1H), 4.10 (apparent td, $J = 4.6$, 2.3 Hz, 1H), 4.28–4.35 (m, 2H), 5.74 (d, $J = 10.0$ Hz, 1H), 7.09 (s, 1H), 7.15 (s, 1H), 7.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): **41-*altro*-β**: δ −5.35, −5.33, 14.06, 18.35, 25.80, 25.93, 29.23, 39.24, 65.58, 68.19, 74.43, 80.08, 82.29, 110.31, 115.66, 117.23, 130.18, 136.10; **41-*altro*-α**: δ −5.41, −5.36, 16.36, 18.38, 25.33, 25.83, 27.71, 40.53, 68.20, 72.23, 73.90, 75.51, 80.15, 82.01, 110.18, 116.09, 116.44, 129.06, 136.13. IR (NaCl, neat): 3115 w, 2987m, 2955s, 2991s, 2892s, 2857m, 2253w, 1700w, 1494m, 1472m, 1424w, 1384m, 1370m, 1312w, 1285w, 1253s, 1221s, 1159s, 1077s, 939w, 906w, 838s, 780s, 661m. HRMS (Electrospray) calcd for $C_{20}H_{33}N_3NaO_4Si$ (M^++Na): 430.2133. Found (M^++Na): 430.2116. Anal. calcd for $C_{20}H_{33}N_3O_4Si$: C, 58.94; H, 8.16; N, 10.31. Found: C, 58.35; H, 8.27; N, 9.94.

4.32. Cyclization of 34

The reverse addition procedure was used for this cyclization. The amounts of reagents used and the time of reaction were as follows: Ph_3SnH (296 mg, 0.842 mmol) in 13.3 mL of benzene; 69 mg (0.168 mmol) of the (*E*)-acrylonitrile **34** and 14 mg (0.084 mmol) of AIBN in 3.6 mL of benzene added during 2 h 40 min, additional stirring for 0.5 h at 90°C (oil bath temperature). Solvent for column chromatography: hexane:EtOAc = 3:1 to 1:1. The cyclized *N*-pyranoside was obtained as pale yellow oil **41** and **45** (51.0 mg, 80%) in a ratio of *altro*-α/*altro*-β/*allo*-α/*allo*-β = 0.27/1.0/0.04/0.09 after column chromatography. The assignments of *allo* isomers are based on comparison of chemical shifts and coupling constants with those of related compounds, and should be considered tentative.

400 MHz ^{1}H NMR	*altro*-α	*altro*-β	*allo*-α	*allo*-β
Chemical shift (ppm)	5.74	5.90	5.95	5.34
Coupling constant (Hz)	10.0	2.9	6.9	9.6
Ratio[a]	0.27	1.00	0.04	0.09

[a] The ratio was determined by ^{1}H NMR after column chromatography.

4.33. Cyclization of 36

The reverse addition procedure was used for this cyclization. The amounts of regents used and the time of reaction were as follows: Ph_3SnH (215 mg, 0.613 mmol) in 9.7 mL of benzene; 51 mg (0.123 mmol) of the **36** and 10 mg (0.061 mmol) of AIBN in 2.6 mL of benzene added during 2 h 10 min, additional stirring for 0.5 h at 90°C (oil bath temperature). Solvent for column chromatography: hexane:EtOAc = 2:1 to 1:1. After column chromatography, 39.0 mg (83%) of a mixture of cyclized products was isolated as a yellow oil with a ratio of *altro*-α/*altro*-β/*allo*-α/*allo*-α/*allo*-β = 0.24/1.0/0.03/0.75, only the structure of the major compound (*altro*-β) has been rigorously assigned. The configurations of other diastereomers were assigned by the comparing the chemical shift information and coupling constant with known configuration (vide infra products from **29**/**33** and **30**/**34**). **48**: Colorless oil (column chromatography, hexane:EtOAc = 2:1 to 1:1). R_f = 0.16 (hexane:EtOAc = 1:3). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.05 (s, 3H), 0.06 (s, 3H), 0.89 (s, 9H), 1.24 (br s, 1H), 1.37 (s, 3H), 1.52 (s, 3H), 3.46 (s, 3H), 3.51–3.61 (m, 1H), 3.72 (ddd, *J* = 8.5, 4.3, 1.9 Hz, 1H), 3.78 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.90 (dd, *J* = 11.5, 2.0 Hz, 1H), 4.31 (dd, *J* = 8.5, 6.2 Hz, 1H), 4.46 (dd, *J* = 6.0, 4.4 Hz, 1H), 5.80 (d, *J* = 2.9 Hz, 1H), 7.09 (s, 1H), 7.17 (s, 1H), 7.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.37, −5.33, 18.39, 25.45, 25.83, 29.24, 59.89, 62.17, 63.06, 69.43, 73.05, 78.87, 81.83, 109.78, 117.69, 128.81, 136.19. IR (NaCl, neat): 3168br s, 2981m, 2952s, 2932s, 2893s, 2856s, 2250w, 2211w, 1698w, 1494m, 1472s, 1458s, 1383s, 1251s, 1219s, 1146s, 1064s, 1033s, 1004m, 938w, 911w, 837s, 779s, 733s. HRMS (Electrospray) calcd for $C_{19}H_{35}N_3NaO_5Si$ (M^++Na): 436.2238. Found (M^++Na): 436.2259. Anal. calcd for $C_{19}H_{35}N_3O_5Si$: C, 55.18; H, 8.53; N, 10.16. Found: C, 54.04; H, 8.48; N, 9.28.

250 MHz ^{1}H NMR	*altro*-α	*altro*-β	*allo*-α	*allo*-β
Chemical shift (ppm)	5.86	5.80	6.06	5.62
Coupling constant (Hz)	8.6	2.9	6.4	7.3
Ratio[a]	0.24	1.0	0.03	0.75

[a] The ratio was determined by ^{1}H NMR after column chromatography.

4.34. Cyclization of 31

The reverse addition procedure was used for this cyclization. The amounts of regents used and the time of reaction were as follow: Ph_3SnH (233 mg, 0.663 mmol) in 10.5 mL of benzene; 68 mg (0.113 mmol) of **31** and 11 mg (0.066 mmol) of AIBN in 2.8 mL of benzene added during 3, additional stirring for 0.5 h at 90°C (oil bath temperature). The α/β ratio of the crude product was 0.32/1.0. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 8:1 to 7:1. An α-*altro* and β-*altro* mixture of [4-(*tert*-butyl-dimethylsilanoyloxymethyl)-6-imidazol-1-yl-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*c*]pyran-7-yl]-acetic acid *tert*-butyl ester **42** was isolated in 87% (55.5 mg) yield. **42-α**: Pale yellow oil (column chromatography, hexane:EtOAc = 8:1 to 7:1). R_f = 0.20 (hexane:EtOAc = 4:1). $[\alpha]_D^{20}$ = +20.7 (*c* 0.58, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.02 (s, 3H), 0.04 (s, 3H), 0.86 (s, 9H), 1.36 (s, 3H), 1.39 (s, 9H), 1.48 (s, 3H), 2.32 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.51 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.30 (apparent dq, *J* = 9.6, 5.1 Hz, 1H), 3.75 (dd, *J* = 11.6, 5.4 Hz, 1H), 3.88 (dd, *J* = 11.6, 2.3 Hz, 1H), 4.10 (ddd, *J* = 7.7, 5.3, 2.3 Hz, 1H), 4.28 (apparent t, *J* = 7.3 Hz, 1H), 4.31 (dd, *J* = 9.3, 7.0 Hz, 1H), 5.90 (d, *J* = 9.4 Hz, 1H), 7.97 (s, 1H), 8.33 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −5.41, −5.36, 18.31, 25.29, 25.81, 27.46, 28.02, 35.56, 38.50, 72.05, 74.62, 74.92, 81.25, 84.41, 110.37, 136.13, 152.01, 170.33. The structure was further confirmed by NOE studies. IR (NaCl, neat): 3122w, 2985s, 2954s, 2930s, 2857s, 1725s, 1507m, 1472m, 1401m, 1431m, 1369s, 1272s, 1256s, 1214s, 1152s, 1078s, 999m, 955w, 919w, 837s, 778s, 733m.

42-β: Pale yellow oil (column chromatography, hexane:EtOAc = 8:1 to 7:1). R_f = 0.28 (hexane:EtOAc = 4:1). $[\alpha]_D^{20}$ = −4.3 (*c* 1.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.04 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 1.36 (s, 3H), 1.40 (s, 9H), 1.48 (s, 3H), 1.97 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.38 (dd, *J* = 16.7, 7.0 Hz, 1H), 3.01 (ddd, *J* = 13.7, 7.1, 4.1 Hz, 1H), 3.72 (dd, *J* = 9.1, 4.9, 1.7 Hz, 1H), 3.76 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.91 (dd, *J* = 11.4, 1.7 Hz, 1H), 4.30 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.42 (apparent t, *J* = 6.2 Hz, 1H), 6.41 (d, *J* = 4.0 Hz, 1H), 7.98 (s, 1H), 8.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −5.30, 18.37, 25.43, 25.84, 27.66, 27.98, 32.73, 37.56, 63.06, 69.71, 74.40, 77.83, 81.24, 84.39, 109.47, 143.11, 152.14, 170.55. The structure was further confirmed by NOE experiments. (NaCl, neat): 3122w, 2985s, 2954s,

2931s, 2857s, 1739w, 2236w, 1727s, 1506m, 1472m, 1461m, 1369s, 1272s, 1255s, 1214s, 1157s, 1066s, 1022m, 956m, 939m, 910m, 875m, 837s, 814m, 779s, 734s, 678m. HRMS (Electrospray) calcd for $C_{23}H_{41}N_3NaO_6Si$ (M^++Na): 506.2657. Found (M^++Na): 506.2665.

4.35. The cyclization of triazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethylsilanyloxy)-1(*R*)-[5-(methoxy-iminomethyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} ester 37

The reverse addition procedure was used for this cyclization. The amounts of reagents used and the time of reaction were as follow: Ph_3SnH 162 mg of Ph_3SnH (0. 461 mmol) in 7.3 mL of benzene; 41 mg (0.092 mmol) of **37** and 7.6 mg (0.046 mmol) of AIBN in 2 mL of benzene added during 1 h 20 min, additional stirring for 0.5 h at 90°C (oil bath temperature). The ratio of *altro*-α/*altro*-β of the crude mixture is 0.69/1.0. Solvent for column chromatography: hexane:EtOAc = 6:1. After column chromatography, 17.6 mg (46%) of product was isolated as an yellow oil. The structure of the major product was confirmed by NOE experiments. **50-β**: Pale yellow oil. Column chromatography; hexane:EtOAc = 6:1. R_f = 0.23 (hexane:EtOAc = 2:1). $[\alpha]_D^{20} = -7.4$ (*c* 0.42, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.06 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 1.37 (s, 3H), 1.51 (s, 3H), 3.46 (s, 3H), 3.74 (ddd, J = 8.9, 4.5, 2.0 Hz, 1H), 3.77 (dd, J = 11.4, 4.4 Hz, 1H), 3.81 (dd, J = 5.6, 3.4 Hz, 1H), 3.91 (dd, J = 11.7, 2.0 Hz, 1H), 4.33 (dd, J = 8.7, 6.7 Hz, 1H), 4.44 (apparent t, J = 6.3 Hz, 1H), 6.11 (d, J = 3.4 Hz, 1H), 8.01 (s, 1H), 8.51 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.33, 18.43, 25.23, 25.87, 27.58, 59.76, 62.12, 63.03, 69.82, 72.50, 77.85, 82.81, 109.83, 144.08, 151.83. IR (NaCl, neat): 3263br s, 3118w, 2985m, 2954s, 2931s, 2862s, 1752w, 1508m, 1472m, 1463m, 1382s, 1276s, 1252s, 1218s, 1134s, 1068s, 954m, 914w, 836s, 813m, 780s, 734m, 698w, 677m. HRMS (Electrospray) calcd for $C_{18}H_{34}N_4NaO_5Si$ (M^++Na): 437.2191. Found (M^++Na): 437.2183.

400 MHz ^{1}H NMR	*altro*-α	*altro*-β	*allo*-α	*allo*-β
Chemical shift (ppm)	5.95	6.11	5.87	
Coupling constant (Hz)	8.8	3.4	2.9	
Ratio[a]	0.69	1.0		

[a] The ratio was determined by ^{1}H NMR before column chromatography.

4.36. Cyclization of *O*-4-{[2,3-*O*-(1-methylethyldiene)-5-*O*-[(1,1-dimethyl)ethyl dimethylsilyl]]-D-ribose-*N*,*N*-dimethylhydrazone}-1*H*-imidazole thiocarbamate 38

The reverse addition procedure was used for this cyclization. The amounts of reagents used and the time of reaction were as follow: Ph_3SnH (269 mg, 0. 766 mmol) in 12.1 mL of benzene; 70 mg (0.153 mmol) of **38** and 12 mg (0.077 mmol) of AIBN in 3.3 mL of benzene added during 2 h 20 min, additional stirring for 0.5 h at 90°C (oil bath temperature). After column chromatography (hexane:EtOAc = 2:1 to 1:1), 41.2 mg (63%) of 3-diastereomer mixture was isolated in a ratio of *altro*-α/*altro*-β/*allo*-β = 0.04/0.09/0/1.0. **51**: Pale yellow oil. R_f = 0.17 (hexane:EtOAc = 1:3). Only *allo*-β product was fully characterized. ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.02 (s, 3H), −0.01 (s, 3H), 0.85 (s, 9H), 1.46 (s, 3H), 1.47 (s, 3H), 2.23 (s, 6H), 3.20 (dd, J = 10.4, 8.5 Hz, 1H), 3.55 (apparent t, J = 9.1 Hz, 1H), 3.69 (dd, J = 10.5, 9.1 Hz, 1H), 3.72–3.78 (m, 2H), 3.86–3.91 (m, 1H), 5.18 (d, J = 8.5 Hz, 1H), 7.06 (s, 1H), 7.07 (s, 1H), 7.69 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.35, 18.33, 25.80, 26.50, 26.79, 49.01, 62.89, 63.26, 74.38, 78.11, 78.28, 86.35, 111.86, 117.75, 128.82, 137.03. IR (NaCl, neat): 2985w, 2956s, 2931s, 2856s, 2817m, 2772m, 1716w, 1679w, 4198m, 1472m, 1382m, 1472m, 1382m, 1372m, 1285m, 1248s, 1230s, 1152s, 1080s, 1056s, 963w, 906w, 838s, 780s, 732w, 661m. HRMS (Electrospray) calcd (M^++Na): 449.2555. Found (M^++Na): 449.2558. Anal. calcd for $C_{20}H_{38}N_3O_4Si$: C, 56.31; H, 8.98; N, 13.13. Found: C, 55.66; H, 9.15; N, 11.86. The configuration of the above structure was assigned based on comparing the chemical shift and coupling constant with compounds of known configuration prepared earlier. The others are tentatively assigned based on the following data.

400 MHz ^{1}H NMR	*altro*-α	*altro*-β	*allo*-α	*allo*-β
Chemical shift (ppm)	5.64	5.86	–	5.18
Coupling constant (Hz)	7.4	3.0	–	8.5
Ratio[a]	0.04	0.09		1.0

[a] The ratio was determined by ^{1}H NMR after column chromatography.

4.37. Reaction of 38 with Bu_3SnH

A flame-dried three-necked 50 mL flask was connected to a condenser, and the flask was charged with 384 mg of Bu_3SnH (1.32 mmol) and 16.4 mL of benzene (dried over CaH_2 and stored over 4 Å MS under a nitrogen atmosphere) under a nitrogen atmosphere. The flask was immersed into an oil bath and the oil bath temperature was adjusted to be 90°C. To the flask was added a solution of 120.7 mg (0.264 mmol) of **38** and 21.7 mg (0.132 mmol) of AIBN in 10 mL of benzene via a syringe pump during 4 h, and the mixture was stirred for another 0.5 h at 90°C (oil bath temperature). The mixture was cooled to rt, and the solvent was removed in vacuo to give crude product. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 7:1 to 2:1. After column chromatography, 41.4 mg (41%) deoxygenated product **52** was obtained. **52**: Yellow oil. Column; hexane:EtOAc = 7:1 to 2:1. R_f = 0.56 (hexane:EtOAc = 4:1). $[\alpha]_D^{20} = +20.5$ (*c* 0.64, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.03 (s, 3H), 0.04 (s, 3H), 0.88 (s, 9H), 1.40 (s, 3H), 1.41 (s, 3H), 1.76–1.84 (m, 2H), 2.81 (s, 6H), 3.69–3.78 (m, 2H), 3.98 (ddd, J = 12.3, 8.3, 3.9 Hz, 1H), 4.18 (dd, J = 8.5, 6.7 Hz, 1H), 6.33 (d, J = 6.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.38, −5.35, 18.3,

25.9, 27.0, 27.2, 35.2, 42.5, 59.8, 76.0, 81.9, 108.6, 130.5. IR (NaCl, neat): 2984m, 2953s, 2856m, 2363w, 1802w, 1694w, 1598w, 1472m, 1378m, 1252m, 1167m, 1090s, 1022m, 940s, 883m, 836s, 776m. HRMS (Electrospray) m/z calcd for $C_{16}H_{34}N_2O_3Si$: 353.2236 (M^++Na). Found: 353.2234.

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