A New Reaction Manifold for the Barton Radical Intermediates. Synthesis of *N*-Heterocyclic Furanosides and Pyranosides through the Formation of C₁-C₂ Bond.

Jong Uk Rhee, Brian A. Bliss and T. V. RajanBabu*

Department of Chemistry, 100 W. 18th Avenue, The Ohio State University, Columbus, OH 43210

Supporting Information

1. General Procedures

NMR spectra were recorded on Bruker on AM-250, AM-300, DPX-400, or DPX-500 MHz and CDCl₃ was used as the solvent. For ¹H NMR spectra the hydrogen of CDCl₃ was used as the standard (δ= 7.260 ppm) unless otherwise mentioned. The ¹³C NMR spectrometer was operated at 125MHz, 100 MHz, 75MHz, or 62.5MHz and the central line of CDCl₃ was used as the standard (δ= 77.00 ppm). Chemical shifts are reported in parts per million on the δ scale, and Hz is used for the coupling constants. The multiplicity are expressed as follows: s = singlet, d = doublet, t = triplet, q = quartet. Infrared spectra were obtained on Perkin-Elmer 1600 Infrared Spectrometer and are reported in reciprocal centimeters (cm⁻¹). The relative intensity of IR spectra are reported as follows: br = broad, s = strong, m = medium, w = weak. High resolution mass spectra were measured by The Ohio State University's Shared Analytical Instrumentation Laboratory (SAIL) and recorded on the Micromass QTOF electrospray mass spectrometer. Elemental analysis was performed at the Ohio State University. Optical rotations were measured on 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 by Thomas-Hoover capillary melting point apparatus and are uncorrected.

All solvents were purchased from Fisher Co. and freshly distilled according to the literature before the using. Other chemicals were purchased from Aldrich or Across 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 F₂₅₄ 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.

2. Preparation of Substrates

2. 1. Preparation of 3(*S*)-*O*-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}- γ -butyrolactone

To a flame dried 25 mL one-necked flask were added 2.30 g (22.5 mmol) of 3(*S*)-hydroxy- γ -butyrolactone¹, 4.07 g (27 mmol) of TBSCl, and 3.63 g (56.3 mmol) of imidazole under nitrogen atmosphere. Dried DMF (4 Å MS, 5.0 mL) was slowly added to the flask with stirring in an ice bath. The mixture was stirred at that temperature for 15 min. and at rt for 27 h. After all the starting material was consumed (TLC), the mixture was diluted with dichloromethane. The organic phase was washed with water and brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo. Almost 100% yield of the crude product was obtained as a white solid, and this was used for the next experiment without further purification. If pure compound is needed, it can be purified by recrystallization from petroleum ether or by column chromatography with hexane:EtOAc = 6:1 to 3:1 as eluent.

A

White Solid (column, hexane:EtOAc = 6:1 to 3:1). Mp: 61-62 °C (recrystallization from pet ether). R_f = 0.3 (hexane:EtOAc = 4:1). ¹H NMR (CDCl₃, 400 MHz): δ 0.07 (s, 6 H), 0.87 (s, 9 H), 2.42 (dd, J =17.5, 2.7 Hz, 1 H), 2.68 (dd, J =17.5, 6.1 Hz, 1 H), 4.16 (dd, J =9.7, 2.3 Hz, 1 H), 4.36 (dd, J =9.7, 4.8 Hz, 1 H), 4.57-4.61 (m, 1 H). ¹³C NMR (CDCl₃, 100 MHz): δ -4.93, -4.87, 17.86, 25.57, 38.11, 68.05, 76.06, 175.65. HRMS (Electrospray): Calcd. for C₁₀H₂₀O₃SiNa (M⁺+Na), 239.1079; Found (M⁺+Na), 239.1086.

2. 2. Preparation of 3(*S*)-*O*-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}- γ -butyrolactol

A flame dried 100 mL one-necked flask was charged with 2.35 g (10.9 mmol) of 3(*S*)-*O*-{[(1,1-dimethylethyl) dimethylsilyl]oxy}- γ -butyrolactone under nitrogen atmosphere. Freshly distilled diethyl

ether was added via a syringe to the flask at rt and the temperature was decreased to -78 °C. Dibal-H (1.5 equiv., 1.5M in toluene) was added slowly, and the mixture was stirred at that temperature for 2 h. After all the starting material was consumed (TLC), 20 mL of absolute methyl alcohol was added to quench the excess Dibal-H at -78 °C. The mixture was diluted with diethyl ether and washed with saturated disodium tartarate (0.5 M) and brine. The water phase was extracted 3 or 4 times by diethyl ether, and combined ether was dried over magnesium sulfate. After the solid was filtered off, the organic phase was concentrated in vacuo to give colorless oil as α/β anomeric mixture of the lactols. The crude yield was almost quantitative and it was used for the next experiment without further purification. The mixture could be purified by flash column chromatography with hexane:EtOAc = 6:1.

α/β anomer mixture = 0.22/1.00

B

Colorless liquid (column, hexane:EtOAc = 6:1). R_f = 0.36 (hexane:EtOAc = 3:1). ^1H NMR (CDCl_3 , 400 MHz): major anomer, β , δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.89 (s, 9 H), 1.96 (td, J =17.5, 4.5 Hz, 1 H), 2.05 (d, J =13.3 Hz, 1 H), 3.88 (dd, J =9.5, 3.8 Hz, 1 H), 3.94 (d, J =11.3 Hz, 1 H), 4.06 (d, J =9.5 Hz, 1 H), 4.46-4.49 (m, 1 H), 5.41 (dd, J =10.6, 4.6 Hz, 1 H); minor anomer, α , δ 0.06 (br s, 6 H), 0.88 (s, 9 H), 1.93-1.97 (m, 1 H), 2.03-2.19 (m, 1 H), 3.70 (dd, J =9.1, 2.5 Hz, 1 H), 3.86-3.95 (m, 1 H), 4.10 (dd, J =9.0, 5.0 Hz, 1 H), 4.54-4.62 (m, 1 H), 5.66 (dd, J =4.7, 2.7 Hz, 1 H).

2. 3. Preparation of (*E*) and (*Z*)-ethyl 6-hydroxy-5(*S*)-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-2-hexenoate

To a flame dried 250 mL one-necked flask were added 4.22 g (19.3 mmol) of lactol and 7.40 g (21.2 mmol) of (carbethoxymethylene)triphenylphosphorane under nitrogen. Freshly distilled toluene (100 mL) was added, and the mixture was stirred under refluxing for 2.5. After the solvent was removed in

vacuo, the mixture was purified by flash column chromatography eluting with hexane:EtOAc = 5:1 to give pale yellow oil of the *E/Z* mixture. The isolated yield was 86% and *E/Z* ratio was 4.4/1.0.

C

Pale yellow oil (column, hexane:EtOAc = 9:1 to 5:1). R_f = 0.43 (hexane:EtOAc = 3:1). ^1H NMR (CDCl_3 , 400 MHz): δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.90 (s, 9 H), 1.28 (t, J =7.1 Hz, 3 H), 2.17 (s, 1 H), 2.32-2.44 (m, 2 H), 3.48 (dd, J =11.2, 5.0 Hz, 1 H), 3.57 (dd, J =11.2, 3.9 Hz, 1 H), 3.78-3.89 (m, 1 H), 4.19 (q, J =7.1 Hz, 2 H), 5.86 (ddd, J =15.6, 2.6, 1.3 Hz, 1 H), 6.92 (dt, J =15.6, 7.6 Hz, 1 H). ^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 0.01 (s, 3 H), 0.03 (s, 3 H), 0.83 (s, 9 H), 1.18 (t, J =7.1 Hz, 3 H), 2.21-2.24 (m, 1 H), 2.38-2.48 (m, 1 H), 3.10-3.39 (m, 2 H), 3.71-3.74 (m, 1 H), 4.10 (q, J =7.1 Hz, 2 H), 4.62-4.76 (m, 1 H), 5.86 (d, J =15.6 Hz, 1 H), 6.89 (dt, J =15.6, 7.5 Hz, 1 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ -4.61, 14.25, 18.05, 25.82, 36.88, 53.82, 60.22, 66.10, 123.84, 144.72, 166.65. IR (NaCl, neat): ν 3460s, 3056w, 2927s, 1724s, 1657s, 1471m. HRMS (Electrospray): Calcd. for $\text{C}_{14}\text{H}_{28}\text{O}_4\text{Si Na}$ ($\text{M}^+ + \text{Na}$), 311.1655; Found ($\text{M}^+ + \text{Na}$), 311.1664.

D

Pale yellow oil (column, hexane:EtOAc = 9:1 to 7:1). R_f = 0.52 (hexane:EtOAc = 3:1). $[\alpha]_{\text{D}}^{20} = +58.7$ (c 1.16 in CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 1.27 (t, J = 7.2 Hz, 3 H), 2.57 (br s, 1 H), 2.72 (dddd, J = 14.5, 7.2, 7.2, 1.4 Hz, 1 H), 3.02 (dddd, J = 14.6, 8.7, 4.8, 1.2 Hz, 1 H), 3.38-3.52 (m, 2 H), 3.92 (app dt, J = 10.7, 5.4 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 5.88 (d, J = 11.6 Hz, 1 H), 6.30 (ddd, J = 11.6, 8.7, 7.3 Hz, 1 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ -4.7, 14.2, 18.0, 25.7, 33.1, 60.1, 65.5, 71.9, 121.7, 145.4, 166.8. IR (NaCl, neat): ν 3476s, 2954s, 2929s, 2886s, 2857s, 1721s, 1646m, 1474m, 1464m, 1415m, 1388m, 1362m, 1254s, 1178s, 1111s, 1040s, 837s, 777s.

2. 4. Preparation of (*E*)-ethyl 5(*S*)-hydroxy-6-[[[(1,1-dimethyl)ethyl dimethylsilyl]oxy]-2-hexenoate via TBS migration

To a 250 mL of one-necked flask was added 2.30 g (7.98 mmol) of (*E*)-ethyl 6-hydroxy-5(*S*)-[[[(1,1-dimethyl)ethyl dimethylsilyl]oxy]-2-hexenoate dissolved in 150 mL of absolute methyl alcohol with 1.67 mL (1.5 equivalents) of triethylamine. After stirring for 48 h, the mixture was washed with H₂O and extracted with dichloromethane. The combined organic phase was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. After flash column chromatography with hexane:EtOAc = 7:1 to 4:1, 1.32 g (87% based on recovered starting material) of desired product, (*E*)-ethyl 5(*S*)-hydroxy-6-[[[(1,1-dimethyl)ethyl dimethylsilyl]oxy]-2-hexenoate, was obtained.

E

Pale yellow oil (column, hexane:EtOAc = 7:1 to 4:1). R_f = 0.33 (hexane:EtOAc = 6:1). $[\alpha]_D^{20}$ = -0.48 (*c* 1.45 in CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.90 (s, 9 H), 1.28 (t, *J*=7.1 Hz, 3 H), 2.37 (td, *J*=7.5, 1.2 Hz, 2 H), 3.46 (dd, *J*=9.9, 6.7 Hz, 1 H), 3.63 (dd, *J*=10.0, 3.7 Hz, 1 H), 3.78-3.80 (m, 1 H), 4.19 (q, *J*=7.1 Hz, 2 H), 5.90 (dd, *J*=15.7, 1.3 Hz, 1 H), 6.98 (dt, *J*=15.6, 7.9 Hz, 1 H). ¹H NMR (C₆D₆, 400 MHz): δ 0.05 (s, 6 H), 0.90 (s, 9 H), 0.98 (t, *J*=7.1 Hz, 3 H), 1.91 (d, *J*=4.6 Hz, 1 H), 2.03-2.10 (m, 2 H), 3.17-3.31 (m, 3 H), 3.46-3.56 (m, 1 H), 4.09 (q, *J*=7.1 Hz, 2 H), 5.96 (ddd, *J*=15.6, 2.9, 1.4 Hz, 1 H). ¹H NMR (DMSO-*d*₆, 400 MHz): δ -0.05 (s, 6 H), 0.85 (s, 9 H), 1.21 (t, *J*=7.0 Hz, 3 H), 2.19-2.23 (m, 1 H), 2.37-2.42 (m, 1 H), 3.0-3.39 (m, 1 H), 3.49-3.56 (m, 1 H), 3.56-3.75 (m, 1 H), 4.10 (q, *J*=7.1 Hz, 2 H), 4.80 (d, *J*= 5.1 Hz, 1 H), 5.85 (d, *J*=15.3 Hz, 1 H), 6.91 (dt, *J*=15.6, 7.2 Hz, 1 H). ¹³C NMR (CDCl₃, 100

MHz): δ -5.42, -5.39, 14.25, 18.25, 25.84, 35.98, 60.24, 66.47, 70.52, 123.69, 144.65, 166.28. IR (NaCl, neat): ν 3478 m , 2932 s , 2859 m , 1720 s , 1654 m , 1467 m , 1367 m , 1318 m , 1258 m , 1207 m , 1167 m , 1118 m , 1045 m , 982 w , 839 s , 770 m . HRMS (Electrospray): Calcd. for C₁₄H₂₈O₄SiNa (M⁺+Na), 311.1655; Found (M⁺+Na), 311.1652.

2. 5. Preparation of (*E*)-ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate (6)

To a flame-dried three necked flask were added 1.39 g (4.81 mmol) of (*E*)-ethyl 5(*S*)-hydroxy-6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-2-hexenoate, 1.43 g (7.22 mmol) of 1,1'-thiocarbonyldiimidazole, and 0.2g of DMAP along with 80 mL of dichloromethane (dried over 4 Å MS). The mixture was refluxed under nitrogen atmosphere for 5 h, and another 0.5 equivalent of 1,1'-thiocarbonyldiimidazole was added. Additional refluxing for 1 h consumed all starting material (TLC), and the mixture was concentrated in vacuo to give brown oil. The crude product was purified by flash column chromatography to get 1.72g (90%) of desired product (6) as a yellow oil.

6

Yellow oil (column, hexane:EtOAc = 5:1 to 4:1). R_f = 0.18 (hexane:EtOAc = 4:1). $[\alpha]_D^{20}$ = -18.7 (c 1.4 in CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 0.05 (s, 3 H), 0.04 (s, 3 H), 0.88 (s, 9 H), 1.28 (t, J =7.1 Hz, 3 H), 2.80 (t, J = 6.4 Hz, 2 H), 3.87 (dd, J =9.6, 4.6 Hz, 1 H), 3.90 (dd, J =9.6, 4.6 Hz, 1 H), (q, J =7.1 Hz, 2 H), 5.68 (m, 1 H), 5.95 (ddd, J =15.6, 2.6, 1.3 Hz, 1 H), 6.92 (dt, J =15.6, 7.8 Hz, 1 H), 7.05 (s, 1H), 7.61 (s, 1 H), 8.33 (s, 1 H). ¹³C NMR (CDCl₃, 100 MHz): δ -5.51, 14.21, 18.13, 25.70, 32.69, 60.49, 62.43, 77.21, 82.14, 117.88, 125.05, 130.75, 141.82, 165.83, 183.40. IR (NaCl, neat): ν 3129 w , 2932 s , 2859 m , 2361 w ,

1721s, 1657m, 1531w, 1467s, 1389s, 1322s, 1283s, 1234s, 1173m, 1103s, 1045m, 971s, 839s, 779m.

HRMS (Electrospray): Calcd. for $C_{18}H_{31}O_4N_2Ssi$ ($M^+ + H$), 399.1774; Found ($M^+ + H$), 399.1805.

2. 6. Preparation of 4,6-*O*-benzylidene-D-glucopyranose²

9

A mixture of D-glucose (10.0 g, 55.5 mmol), benzaldehyde dimethyl acetal (9.3 g, 61 mmol), and catalytic amount of *p*-toluensulfonic acid (12 mg) in 40 mL of DMF (dried over 4 Å MS) was heated at 60 °C under house vacuum with nitrogen bubbling to remove methyl alcohol formed during the reaction as a byproduct. The heating was stopped after 3h and 0.3 mL of triethyl amine was added to the reaction mixture at 0 °C, and the excess solvent was removed under high vacuum. The crude mixture was purified by column chromatography eluting with EtOAc (with 1% of Et₃N). The desired product was obtained as a white solid (8.38 g), and the isolated yield was 56%.

2. 7. Preparation of 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde and its dimmer (10/10')

10'

10

Sodium periodate (6.63g) in 65 mL of water and 8N sodium hydroxide solution (1.82 mL) were added slowly to the solution of 4,6-*O*- benzylidene-D-glucopyranose² (4.12 g) in 50 mL of water in an ice-bath (the temperature of reactants should be lower than 10 °C). The mixture was stirred at rt for additional 3 h, and to it was added about 1.8 mL of 8N sodium hydroxide solution to adjust the pH to 7 or little lower than 7. After water was removed in a rotary evaporator, white solid was obtained. The crude product was

dissolved in excess amount of EtOAc, and filtered it under reduced pressure, and the filtrate was washed several times with EtOAc. The combined organic phase was subjected to rotary evaporation to give quantitative amount of **10'**, which is equilibrium with its dimer **10**. This product was used for the next experiment without further purification.

The ^1H NMR spectrum shows that the isolated compound is a mixture of at least three compounds, but the ^{13}C NMR spectrum and subsequent reactions imply that the major compound is the dimer (**10**).

White solid (column chromatography, hexane:EtOAc = 1:3). R_f = 0.43 (hexane:EtOAc = 1:1). Mp: 147-149 °C. ^1H NMR (DMSO- d_6 , 250 MHz) is complex. Three isomers were observed in ^{13}C NMR spectrum, and the major isomer shows δ 57.3, 66.4, 78.9, 84.6, 96.2, 122.5, 124.2, 124.8, 134.1 (*Note*: there is no carbonyl carbon).

2. 8. Preparation of (*E*) and (*Z*) 3-(5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-yl)-acrylic acid ethyl ester (**11a**)

To a 25 mL of flame-dried three-necked round bottom flask connected to a condenser were added 78 mg (estimated as 0.310 mmol) of crude 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde (**10**) and 133 mg (0.384 mmol) of (carbt*tert*-butoxymethylene)triphenylphosphorane. Freshly dried toluene (10 mL) was added and the mixture was stirred under refluxing condition for 1 h 40 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 = 2:1. 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 (**10**) and 221 mg (0.634 mmol) of (carbt*tert*-butoxymethylene)triphenylphosphorane in 10 mL of DME was stirred under nitrogen atmosphere for 26h, and all starting material was 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 proportion of *Z* compound increased to 2.4 to 1.

(E)-11a

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 in 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): ν 3476 *Br s*, 2984*m*, 2924*m*, 2862*m*, 1702*s*, 1656*m*, 1453*m*, 1394*m*, 1370*m*, 1301*s*, 1274*m*, 1224*m*, 1189*m*, 1144*m*, 1082*s*, 1026*s*, 979*m*, 918*w*, 850*w*, 757*m*. Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_5$: C, 64.74; H, 6.52. Found: C, 64.22; H, 6.75.

(Z)-11a

Colorless oil (column chromatography, hexane:EtOAc = 3:1). R_f = 0.42 (hexane:EtOAc = 2:1). $[\alpha]_D^{20}$ = -66.1 (c 0.61 in 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 (app 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): ν 3431 *Br s*, 3037*w*, 2982*m*, 2930*m*, 2854*m*, 1722*s*, 1694*s*, 1658*m*, 1455*m*, 1422*m*, 1386*s*, 1302*w*, 1209*s*, 1090*s*, 1207*s*, 871*w*, 827*m*, 755*m*, 699*s*. Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_5$: C, 64.74; H, 6.52. Found: C, 63.90; H, 6.70.

2. 9. Preparation of (*E*) and (*Z*) 3-(5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-yl)-acrylonitrile (**11b**)

To a 100 mL of flame-dried three neck round bottom flask connected to a condenser were added 259 mg (estimated as 1.24 mmol) of crude 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde (**10**) 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 nitrogen atmosphere for 2h. 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* compound were yellowish brown solids, and the *E/Z* ratio was 1.0/2.3 (isolated yield 93%).

11b

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 in CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 2.68 (Br s, 1H), 3.60-3.65 (m, 1H), 3.69 (app t, J = 10.2 Hz, 1H), 4.31 (dd, J = 9.9, 4.2 Hz, 1H), 4.53 (app 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): ν 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 $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$: C, 67.52; H, 5.67; N, 6.06. Found: C, 66.77; H, 5.87; N, 5.85.

2. 10. Preparation of 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde *O*-methyl-oxime (11c)

To a 100 mL of flame-dried three-necked round bottom flask connected to a condenser were added 222 mg (estimated as 1.07 mmol) of crude 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde (**10**) 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 nitrogen atmosphere for 5.5h, and all solvent was removed in a rotary evaporator to get the crude product. The crude mixture was purified by column chromatography eluting with hexane:EtOAc = 4:1, and 216 mg of the desired product was obtained as a white solid (isolated yield 91%). The isolated compound is a *syn/anti* mixture with a ratio of 1.0/0.18 based on ^1H NMR analysis.

11c

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. ^1H NMR (CDCl_3 , 400 MHz): *syn* δ 3.70 (app 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* δ 3.67 (app t, J = 9.6 Hz, 1H), 3.80 (app 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* δ 62.19, 63.99, 70.15, 78.69, 101.35, 126.13, 128.33, 129.21, 137.04, 148.70, *anti* δ 62.51, 71.11, 75.62, 77.92, 100.71, 126.10, 128.33, 129.21, 136.94, 149.95. IR (NaCl, neat): ν 3489 br s, 2978 w , 3939 w , 2252 s , 1462 m , 1390 m , 1221 w , 1086 m , 1041 m , 908 s , 733 s , 650 m . Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.87; H, 6.62; N, 5.94.

2. 11. Preparation of 4(*R*)-(dimethyl-hydrazonomethyl)-2(*R*)-phenyl-[1, 3]dioxane-5(*R*)-ol (11d)

To a 100 mL flame-dried three-necked round bottom flask connected to a condenser were added 780 mg (estimated as 3.10 mmol) of crude 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde (**10**) and 932 mg (15.5 mmol, 1.18 mL) of *N,N'*-dimethyl hydrazine with 50 mL of methyl alcohol and small amount of 4 Å MS. After the mixture was refluxed under nitrogen atmosphere for 17.5h, and all the 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 give 652 mg of the desired product as pale yellow solid (isolated yield 84%).

11d

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 in CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 2.83 (s, 6H), 3.64 (Br s, 1H), 3.70 (app 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). ¹³C NMR (CDCl₃, 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): ν 3392Br s, 2966m, 2862s, 2778m, 2358w, 1597m, 1457s, 1396s, 1316w, 1264m, 1220m, 1085s, 1027s, 918m, 823m, 762s, 699s. Anal. Calcd. for C₁₃H₁₈O₃N₂: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.17; H, 7.21; N, 11.03.

2. 12. Preparation of (*E*)-3-[5(*R*)-(imidazole-1-carbothioxyloxy)-2(*R*)-phenyl-[1,3]dioxan-4(*R*)-yl]-acrylic acid ethyl ester (12a)

To a flame-dried 50 mL flask were added 51 mg (0.183 mmol) of (*E*)-3-(5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-yl)-acrylic acid ethyl ester, (*E*)-**11a**, 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 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. The mixture was purified by flash column chromatography with hexane:EtOAc = 2:1, and 62.1 mg (89%) of desired product was obtained as a pale yellow solid.

(E)-12a

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 in CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 1.26 (t, J = 7.1 Hz, 3H), 3.84 (app 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 (app 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): ν 3416 Br s, 3128 m , 3038 w , 2979 m , 1728 s , 1713 s , 1666 m , 1532 m , 1470 s , 1392 s , 1334 s , 1184 s , 1139 s , 1097 s , 1004 s , 920 m , 852 w , 748 m , 699 m , 653 m . Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{N}_2\text{S}$: C, 58.75; H, 5.19; N, 7.21. Found: C, 58.61; H, 5.33; N, 7.20.

2. 13. Preparation of (Z)-3-[5(R)-(imidazole-1-carbothioxyloxy)-2(R)-phenyl-[1,3]dioxan-4(R)-yl]-acrylic acid ethyl ester

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)-11a, 3.0 equivalents 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 28h. Additional 100 mg of 1,1'-thiocarbonyldiimidazole was required to

consume all starting material with refluxing for 10h. 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)-12a

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 in CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 1.26 (t, J = 7.2 Hz, 3H), 3.92 (app t, J = 10.3 Hz, 1H), 4.18 (app tt, J = 7.1, 3.8 Hz, 2H), 4.67 (dd, J = 10.6, 5.2 Hz, 1H), 5.58 (app td, J = 9.8, 5.2 Hz, 1H), 5.70 (s, 1H), 5.99 (dd, J = 11.7, 0.8 Hz, 1H), 6.02 (app 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): ν 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 $\text{C}_{19}\text{H}_{20}\text{O}_5\text{N}_2\text{S}$: C, 58.75; H, 5.19; N, 7.21. Found: C, 58.05; H, 5.37; N, 7.13.

2. 14. Preparation of (Z)-imidazole-1(R)-carbothioic acid O-[4(R)-(2-cyano-vinyl)-2(R)-phenyl-[1,3]dioxane-5(R)-yl] ester (12b)

To a flame-dried 25 mL flask were added 94 mg (0.407 mmol) of (Z)-3-(5(R)-hydroxy-2(R)-phenyl-[1, 3]dioxane-4(R)-yl)-acrylonitrile, **11b**, 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 nitrogen atmosphere for 7 h, and another 217 mg of 1,1'-thiocarbonyldiimidazole was added. Refluxing was continued for 5h 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 was obtained as pale yellow solid (97 mg) in an isolated yield of 70%.

12b

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 in CHCl_3). ^1H NMR (CDCl_3 , 400 MHz): δ 3.91 (app t, J = 10.4 Hz, 1H), 4.70 (dd, J = 10.8, 5.3 Hz, 1H), 5.10 (app t, J = 9.1 Hz, 1H), 5.58 (dd, J = 11.0, 0.6 Hz, 1H), 5.66 (app 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 (app 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): ν 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 $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3\text{S}$: C, 59.81; H, 4.43; N, 12.31. Found: C, 59.86; H, 4.76; N, 11.70.

2. 15. Preparation of imidazole-1-carbothioic acid *O*-[4(*R*)-(methoxyimino-methyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] ester (12c)

To a flame-dried 100 mL flask were added 163 mg (0.687 mmol) of 5(*R*)-hydroxy-2(*R*)-phenyl-[1,3]dioxane-4(*R*)-carbaldehyde *O*-methyl-oxime **11c**, 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 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 **12c** was obtained as yellow solid (215 mg) and the isolated

yield is 90%. The isolated compound is *syn/anti* mixture with a ratio of 1.0/0.13 based on ^1H NMR spectrum.

12c

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. ^1H NMR (CDCl_3 , 400 MHz): *syn* δ 3.78 (s, 3H), 3.87 (app 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 (app 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 (app t, J = 1.2 Hz, 1H), 8.31 (s, 1H); *anti* δ 3.82 (s, 3H), 3.90 (app 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 (app 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 (app 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): ν 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 $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_3\text{S}$: C, 55.32; H, 4.93; N, 12.10. Found: C, 56.03; H, 5.38; N, 11.65.

2. 16. Preparation of imidazole-1-carbothioic acid *O*-[4(*R*)-(dimethyl-hydrazonomethyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] ester (12d)

To a flame-dried 100 mL flask were added 363 mg (1.45 mmol) of 4(*R*)-(dimethyl-hydrazonomethyl)-2(*R*)-phenyl-[1, 3]dioxane-5(*R*)-ol **11d**, 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 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 **12d** was obtained as yellow solid (215 mg) and the isolated yield is 90%.

12d

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 in CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 2.76 (s, 6H), 3.88 (app 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). ¹³C NMR (CDCl₃, 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): ν 3431Br s, 3135w, 2958w, 2859m, 2790w, 1594m, 1531w, 1466s, 1392s, 1333s, 1292s, 1279s, 1232s, 1162w, 1101s, 1004s, 919m, 827w, 752m. Anal. Calcd. for C₁₇H₂₀O₃N₄S: C, 56.65; H, 5.59; N, 15.54. Found: C, 56.59; H, 5.79; N, 15.19.

2. 17. Preparation of 3(*Z* and *E*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester

To a 100 mL of flame-dried three necked round bottom flask connected to a condenser were added 2.09 g (6.86 mmol) of 5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-2,3-*O*-(1-methylethyldiene)-D-ribofuranose 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 another 4 h. After the solvent was removed under vacuum, *E* and *Z* mixture products were isolated by flash column chromatography eluting with hexane only to hexane:EtOAc = 95:5. *E* and *Z* mixtures were isolated as colorless oil in a ratio of 0.24/1.0 in a combined isolated yield of 92%.

F

Colorless oil (column chromatography, hexane:EtOAc = 95:5). R_f = 0.38 (hexane:EtOAc = 9:1). $[\alpha]_D^{20}$ = +69.3 (*c* 1.0 in CHCl₃). ¹H NMR (CDCl₃, 300 MHz): δ 0.07 (s, 6H), 0.90 (s, 3H), 1.36 (s, 3 H), 1.47 (s, 3 H), 1.47 (s, 9 H), 2.9 (br s, 1H, disappeared with D₂O), 3.59 (ddd, *J*=8.4, 5.4, 3.0 Hz, 1 H), 3.69 (dd, *J*=10.2, 5.4 Hz, 1 H), 3.78 (dd, *J*=10.2, 3.0 Hz, 1 H), 4.26 (dd, *J*=8.4, 6.3 Hz, 1 H), 5.69 (ddd, *J*=8.5, 6.3, 1.0 Hz, 1 H), 5.89 (dd, *J*=11.6, 1.0 Hz, 1 H), 6.18 (dd, *J*=11.6, 8.6 Hz, 1 H). ¹³C NMR (CDCl₃, 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): ν 3477*m*, 2854*s*, 2933*s*, 2857*s*, 1716*s*, 1652*s*, 1463*m*, 1369*s*, 1254*s*, 1159*s*, 1058 *s*, 836*s*, 779*s*.
 Anal. Calcd. for C₂₁H₃₇O₆Si: C, 59.67; H, 9.52. Found: C, 59.79; H, 9.69.

G

Colorless oil (column chromatography, hexane:EtOAc = 95:5). R_f = 0.24 (hexane:EtOAc = 4:1). $[\alpha]_D^{20}$ = -4.62 (*c* 1.19 in CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.90 (s 9 H), 1.36 (s, 3 H), 1.48 (s, 3 H), 1.48 (s, 9 H), 3.56 (ddd, *J* = 9.0, 5.6, 3.1 Hz, 1 H), 3.65 (dd, *J* = 10.0, 5.6 Hz, 1 H), 3.79 (dd, *J* = 10.0, 3.1 Hz, 1 H), 4.10 (dd, *J* = 9.3, 6.6 Hz, 1 H), 4.80 (app t, *J* = 5.1 Hz, 1 H), 6.06 (dd, *J* = 15.6, 1.5 Hz, 1 H), 7.00 (dd, *J* = 15.6, 5.2 Hz, 1 H). IR (NaCl, neat): ν 3496*m*, 2979*m*, 2950*m*, 2930*m*, 2885*m*, 2875*m*, 1717*s*, 1658*m*, 1472*m*, 1463*m*, 1368*s*, 1314*m*, 1256*s*, 1217*m*, 1153*s*, 1062*m*, 837*s*, 779*m*.

2. 18. Preparation of 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester (14a)

A flame-dried three necked round bottom flask was fitted with a double spaced condenser, and 1.00 g (2.45 mmol) of 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester **F**, 0.97 g (4.90 mmol) of 1,1-thiocarbonyldiimidazole, and 0.1 g of DMAP were placed under nitrogen atmosphere. Dichloromethane (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.

14a

Pale yellow oil (column chromatography, hexane:EtOAc = 97:3 to 95:5). $[\alpha]_D^{20} = +88.5$ (*c* 3.42 in CHCl₃). $R_f = 0.23$ (hexane:EtOAc = 9:1). ¹H NMR (CDCl₃, 250 MHz): δ -0.03 (s, 3 H), 0.00 (s, 3 H), 0.84 (s, 9 H), 1.40 (s, 9 H), 1.40 (s, 3 H), 1.51 (s, 3 H), 3.92-4.04 (m, 2 H), 4.85 (dd *J* = 8.1, 6.3 Hz, 1 H), 5.53 (ddd *J* = 8.1, 4.0, 2.8 Hz, 1 H), 5.68 (dd, *J* = 11.6, 1.6 Hz, 1 H), 5.75 (ddd, *J* = 7.8, 6.4, 1.5 Hz, 1 H), 6.13 (dd *J* = 11.6, 7.8 Hz, 1 H), 6.98 (s, 1 H), 7.53 (s, 1 H), 8.25 (s, 1 H). ¹³C NMR (CDCl₃, 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): ν 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 C₂₄H₄₀O₆N₂SSi: 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.

2. 19. Preparation of 3(*E* or *Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile

To a 100 mL of flame-dried three necked round bottom flask was added 378 mg (1.241 mmol) of D-ribofuranose, 411 mg (1.366 mmol) of (cyanomethylene)triphenylphosphorane, and 52 mg of benzoic acid under 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 8h 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 **H** (white solid), 163 mg of **I** (yellow oil), and 6 mg of cyclized product (yellow oil)

H

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 in CHCl₃). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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): ν 3498br s, 2989m, 2956s, 2930s, 2850s, 2227s, 1638m, 1432m, 1463m, 1383s, 1382s, 1257s, 1217s, 1165m, 1067s, 972w, 864m, 837s, 779s. Anal. Calcd. for C₁₆H₂₉O₄NSi: C, 58.68; H, 8.93; N, 4.28. Found: C, 58.66; H, 8.92; N, 4.12.

I

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 in 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): ν 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 $\text{C}_{16}\text{H}_{29}\text{O}_4\text{NSNa}$ ($\text{M}^+ + \text{Na}$), 350.1764; Found ($\text{M}^+ + \text{Na}$), 350.1760. Anal. Calcd. for $\text{C}_{16}\text{H}_{29}\text{O}_4\text{NSi}$: C, 58.68; H, 8.93; N, 4.28. Found: C, 58.59; H, 9.32; N, 4.24.

2. 20. Preparation of 3(*E*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile (**14b**)

To a flame-dried 100 mL three necked flask fitted with a condenser were added 133 mg (0.406 mmol) of 3(*E*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile **H**, 3.0 equivalents 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 crude brown mixtures. The mixture was isolated by flash column chromatography eluting hexane:EtOAc = 5:1 to 2:1. The desired product **14b** was obtained as pale yellow solid (102 mg, 88% based on recovered starting material) as well as 46 mg of a mixture of **14b** and clized byproducts **J** and **K** in a ratio of 0.22/1.0 (*cis/trans*).

14b

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 in 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 (app 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): ν 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 $\text{C}_{20}\text{H}_{31}\text{O}_4\text{N}_3\text{Si}$: C, 54.89; H, 7.14; N, 9.60. Found: C, 54.93; H, 7.37; N, 9.45.

The Isolated by products were assigned as follows:

J

^1H NMR (CDCl_3 , 400 MHz): δ 0.08 (s, 6 H), 0.90 (s, 3 H), 1.35 (s, 3 H), 1.53 (s, 3 H), 3.73 (d, J = 4.2 Hz, 1 H), 4.11-4.21 (m, 1 H), 4.44 (dd, J = 6.4, 4.2 Hz, 1 H), 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.

K

R_f = 0.47 (hexane:EtOAc = 4:1). ^1H NMR (CDCl_3 , 250 MHz): δ 0.05 (s, 6 H), 0.89 (s, 9 H), 1.35 (s, 3 H), 1.50 (s, 3 H), 2.65 (d, J = 6.7 Hz, 1 H), 3.70 (dd, J = 11.0, 2.8 Hz, 1 H), 3.78 (dd, J = 11.0, 2.9 Hz, 1 H), 4.15 (app t, J = 2.8 Hz, 1 H), 4.42 (app dt, J = 6.7, 4.3 Hz, 1 H), 4.71 (dd, J = 5.9, 4.3 Hz, 1 H), 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.

2. 21. Preparation of 5(*R*)-[2(*R*)-(tert-butyl-dimethyl-silanyloxy)-1-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolane-4(*R*)-carbaldehyde *O*-methyl-oxime

A dried 100 mL three necked round bottom flask was equipped with a condenser and a magnetic stirring bar. To the flask were added 5-*O*-[(1,1-dimethylethyl)dimethylsilyl]-2,3-*O*-(1-methylethyldiene)-D-ribofuranose (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%.

L

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, 6 H), 0.87 (s, 9 H), 1.32 (s, 3 H), 1.43 (s, 3 H), 2.62 (d, J = 4.8 Hz, 1 H), 3.50-3.70 (m, 3 H), 3.83 (s, 3 H), 4.09 (dd J = 8.5, 6.4 Hz 1 H), 4.72 (app t, J = 7.4 Hz 1 H), 7.16 (d, J = 7.7 Hz 1 H); minor isomer, *anti*; δ 0.05 (s, 6 H), 0.87 (s, 9 H), 1.11 (s, 3 H), 1.21 (s, 3 H), 2.70 (d, J = 3.8 Hz, 1 H), 3.71-3.83 (m, 3 H), 3.87 (s, 3 H), 4.20 (app t J = 6.7 Hz 1 H), 5.26 (app t, J = 6.3 Hz 1 H), 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): ν 3522Br, 2987s, 2956s, 2932s, 2884s, 2875s, 2819w, 1795w, 1741w, 1629w, 1471s, 1468s, 1382s, 1255s, 1219s, 1170s, 1154s, 1117s, 1047s.

2. 22. Preparation of imidazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} ester (17)

The reaction was performed with 215 mg (0.65 mmol) of 5(*R*)-[2(*R*)-(tert-butyl-dimethyl-silanyloxy)-1-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolane-4(*R*)-carbaldehyde *O*-methyl-oxime **L** and 345 mg (1.93 mmol) of 1,1-thiocarbonyldiimidazole in 30 mL of freshly dried THF under nitrogen atmosphere. The mixture was refluxed in an oil bath, and another 200 mg of 1,1-thiocarbonyldiimidazole was added after 9 and 11 hr, respectively. Finally, the mixture was refluxed for another 18 h. After the mixture was cooled to rt, all solvent was removed in vacuo. 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.

17

Yellow oil (column chromatography, hexane:EtOAc = 8:1 to 6:1). R_f = 0.29 (hexane:EtOAc = 4:1). ^1H NMR (CDCl_3 , 400 MHz): major *syn*, δ 0.00(s, 3 H), 0.04 (s, 3 H), 0.88 (s 9 H), 1.39 (s, 3 H), 1.51 (s, 3 H), 3.57 (s, 3 H), 3.99 (dd, J = 11.7, 2.9 Hz, 1 H), 4.12 (dd, J = 11.9, 2.6 Hz, 1 H), 4.76-4.81 (m, 2 H), 5.49-5.58(m, 1 H), 7.04 (s, 1 H), 7.27 (d, J = 7.8 Hz, 1 H), 7.61 (s, 1 H), 8.30 (s, 1 H); minor *anti*, δ 0.01 (s, 3 H), 0.03 (s, 3 H), 0.86 (s 9 H), 1.39 (s, 3 H), 1.52 (s, 3 H), 3.66 (s, 3 H), 3.95-4.03 (m, 2 H), 4.76-4.81 (m, 1 H), 5.31 (app t, J = 6.0 Hz, 1 H), 5.49-5.56 (m, 1 H), 6.80 (d, J = 7.8 Hz, 1 H), 7.04 (s, 1 H), 7.63 (s, 1 H), 8.30 (s, 1 H). ^{13}C NMR (CDCl_3 , 75 MHz): major *syn*, δ -5.3, -5.1, 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): ν 3133w, 2989m, 2953m, 2935m, 2897m, 2856m, 1739w, 1626m, 1531w, 1463m, 1391s, 1344m, 1323s, 1283s, 1246s, 1229s, 1109m, 1076m, 1042s. Anal. Calcd. for $\text{C}_{19}\text{H}_{33}\text{O}_5\text{N}_2\text{S}$: 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.

2. 23. Preparation of 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(triazole-1-carbothioyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester (**19a**)

A flame dried three neck round bottom flask was fitted with a double spaced condenser, and 192 mg (0.478 mmol) of 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl F, 258 mg (1.434 mmol) of 1,1-thiocarbonylditriazole, and 10 mg of DMAP were placed under nitrogen atmosphere. Freshly distilled THF (15 mL) was added, and the mixture was refluxed overnight (12h.). 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 = 8:1 solution. Desired product (69 mg) and starting material (115 mg) were obtained. The isolated yield of **19a** is 28%, and 70% based on the recovered starting material.

19a

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 in CHCl_3). ^1H 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): ν 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 $\text{C}_{23}\text{H}_{39}\text{O}_6\text{N}_3\text{Si}$: 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.

2. 24. Preparation of Triazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} ester (**19b**)

A mixture of 5(*R*)-[2(*R*)-(tert-butyl-dimethyl-silanyloxy)-1-hydroxy-ethyl]-2,2-dimethyl-[1,3]dioxolane-4(*R*)-carbaldehyde *O*-methyl-oxime **L** (131mg), thiocarbonyl ditriazole (142 mg), and 10 mg of DMAP were placed in a 50 mL of flame dried three neck 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 nitrogen atmosphere for 6 hr. Another 2.0 equivalent of thiocarbonyl ditriazole 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 **19b** 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 ^1H NMR spectrum.

19b

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). ^1H 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): ν 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 $\text{C}_{18}\text{H}_{32}\text{O}_5\text{N}_4\text{SSiNa}$ ($\text{M}^+ + \text{Na}$), 467.1755; Found ($\text{M}^+ + \text{Na}$), 467.1716.

3. 5-Exo-trig Radical Cyclizations

3. 1. The Reaction of (*E*)-Ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate (6) (*Reverse Addition*)

A flame-dried three-necked 100 mL flask was connected to a condenser, and the flask was charged with 37 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under nitrogen atmosphere. The flask was immersed into an oil bath, and the bath temperature was adjusted to be 90 °C, and Ph_3SnH (2.35 mmol, 825 mg) was added to it. A solution of 0.47 mmol (187 mg) of (*E*)-ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate and 0.235 mmol (38

mg) of AIBN in 10 mL of benzene was added dropwise with stirring via a syringe pump during 3 h 40 min, and the mixture was stirred for another one hour. The mixture was cooled to rt, and the solvent was removed the solvent in vacuo. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 1:1 to 1:3. The isolated yield of the mixture of *N*-furanosides was 88%.

Colorless oil (column; hexane:EtOAc = 1:1 to 1:3). R_f = 0.23 (hexane:EtOAc = 1:3). The stereochemistry of the products was not assigned. First major product; about 2 mg was isolated as a pure form. ^1H NMR (CDCl_3 , 400 MHz): δ 0.08 (s, 6 H), 0.94 (s, 9 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.85 (dd, J = 17.4, 8.7 Hz, 1 H), 1.95 (ddd, J = 12.8, 11.2, 11.2 Hz, 1 H), 2.03 (ddd, J = 12.8, 6.8, 5.4 Hz, 1 H), 2.17 (dd, J = 17.4, 7.5 Hz, 1 H), 3.02 (dddd, J = 13.2, 13.2, 8.6, 6.6, 2.1 Hz, 1 H), 3.79 (dd, J = 11.5, 3.1 Hz, 1 H), 4.02 (dd, J = 11.4, 3.0 Hz, 1 H), 4.09 (qd, J = 7.2, 1.0 Hz, 2 H), 4.17 (app tt, J = 6.9, 3.5 Hz, 1 H), 6.05 (d, J = 6.8 Hz, 1 H), 7.04 (s, 1 H), 7.20 (s, 1 H), 7.68 (s, 1 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ -5.5, -5.3, 14.1, 18.6, 26.0, 30.2, 33.2, 41.2, 60.8, 63.5, 81.0, 88.2, 117.5, 128.5, 136.0, 171.9. IR (NaCl, neat): ν 3116 *Br s*, 2956*s*, 2930*s*, 2859*s*, 1731*s*, 1493*m*, 1469*m*, 1419*m*, 1386*m*, 1343*m*, 1255*s*, 1183*m*, 1077*s*, 1026*m*, 920*m*, 838*s*, 779*s*, 663*m*. HRMS (Electrospray): Calcd for $\text{C}_{18}\text{H}_{33}\text{O}_4\text{N}_2\text{Si}$ ($\text{M}^+ + \text{H}$), 369.2209; Found ($\text{M}^+ + \text{H}$), 369.2210. Second major product; ^1H NMR (CDCl_3 , 400 MHz): δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.91 (s, 9 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.77 (dd, J = 12.8, 8.3 Hz, 1 H), 2.20-2.63 (m, 3 H), 2.85-2.97 (m, 1 H), 3.65 (dd, J = 11.0, 3.6 Hz, 1 H), 3.78 (dd, J = 11.1, 3.7 Hz, 1 H), 4.08 (q, J = 7.2 Hz, 2 H), 4.33 (app tt, J = 7.3, 3.6 Hz, 1 H), 5.53 (d, J = 5.0 Hz, 1 H), 7.07 (s, 1 H), 7.09 (s, 1 H), 7.66 (s, 1 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ -5.40, -5.38, 14.11, 18.37, 25.91, 32.31, 36.71, 42.85, 60.91, 64.69, 79.89, 91.04, 116.49, 129.82, 136.00, 171.32. The other two isomers (**8c** and **8d**) could not be fully characterized because only small amount of the pure product was isolated; but the characteristic anomeric peaks were found at δ 6.10 (d, J = 6.2 Hz) and δ 5.60 (d, J = 5.7 Hz).

400 MHz ¹ H NMR	[8a, 8b, 8c, 8d]			
Chemical shift (ppm)	6.05	5.53	6.10	5.60
Coupling constant (Hz)	6.8	5.0	6.2	5.7

3. 2. The Reaction of (*E*)-Ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate with Bu₃SnH (*Normal Addition*)

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 33.5 mg (0.084 mmol) of (*E*)-ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate and 4 mL of toluene (freshly dried over Na) under nitrogen atmosphere. A solution of 48.9 (0.168 mmol) of Bu₃SnH and 2.8 mg (0.017 mmol) of AIBN in 6 mL of toluene was added dropwise under reflux condition via a syringe pump during 40 min, and the mixture was refluxed for another 1h 20 min. The mixture was cooled to rt, and the solvent was removed the solvent in vacuo. The concentrated mixture was purified by flash column chromatography eluting hexane:EtOAc = 9:1 to 6:1. The isolated compound was the mixture of *cis/trans*-[5-(*tert*-butyl-dimethyl-silanyloxymethyl)-2-thioxo-tetrahydro-furan-3-yl]-acetic acid ethyl ester and yield is 58%.

7

cis/trans = 2.1/1.0 or 1.0/2.1

Yellow oil (column chromatography, hexane:EtOAc = 6:1 to 3:1). *R_f* = 0.13 (hexane:EtOAc = 4:1). ¹H NMR (CDCl₃, 400 MHz): major, δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.89 (s, 9 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.93 (ddd, *J* = 12.6, 11.3, 9.6 Hz, 1 H), 2.43-2.62 (m, 2 H), 3.24 (dd, *J* = 17.0, 3.8 Hz, 1 H), 3.29-3.34 (m, 1 H), 3.79 (dd, *J* = 11.5, 2.6 Hz, 1 H), 3.98 (dd, *J* = 11.5, 2.7 Hz, 1 H), 4.10-4.23 (m, 2 H), 4.83 (app dq, *J* = 6.7, 3.5 Hz, 1 H); minor, δ 0.07 (s, 3 H), 0.09 (s, 3 H), 0.89 (s, 9 H), 1.27 (t *J* = 7.1 Hz, 3 H), 2.07 (app dt, *J* =

8.4, 5.1 Hz, 1 H), 2.43-2.62 (m, 2 H), 3.15 (dd, $J = 16.8, 4.0$ Hz, 1 H), 3.47 (app dq, $J = 9.4, 4.0$ Hz, 1 H), 3.72 (dd, $J = 11.8, 3.7$ Hz, 1 H), 3.97 (dd, $J = 11.7, 3.4$ Hz, 1 H), 4.10-4.23 (m, 2 H), 4.92 (app dq, $J = 8.8, 2.7$ Hz, 1 H). ^{13}C NMR (CDCl_3 , 100MHz): major, δ -.5.42, -5.36, 14.16, 18.32, 25.82, 30.19, 35.13, 37.20, 60.91, 64.02, 78.68, 171.31, 177.41; minor, δ -.5.62, -5.31, 14.15, 18.32, 25.80, 30.14, 35.56, 36.18, 60.86, 65.08, 78.01, 171.31, 178.45. IR (NaCl, neat): ν 2956 s , 2928 s , 2853 m , 2360 m , 1776 w , 1736 s , 1463 m , 1352 m , 1254 s , 1183 m , 1125 m , 1028 m , 839 s , 780 m . HRMS (Electrospray): Calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_4\text{SSiNa}$ ($\text{M}^+ + \text{Na}$), 355.1375; Found ($\text{M}^+ + \text{Na}$), 355.1372.

3. 3. Optimization of 5 -Exo-*trig* Radical Cyclization with (*E*)-Ethyl 6-[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate

(See Table in the Next Page)

Table 1. 5-Exo-*trig* ring closure of (*E*)-ethyl 6-{[(1,1-dimethyl)ethyl dimethylsilyl]oxy}-5(*S*)-[(*N*-imidazolythiocarbonyl) oxy]-2-hexenoate

Entry	Conditions					Yield	
	R ₃ SnH	AIBN	Solvents	Temp. ^m	Cond.	(%)	Comments
1	5.0 Eq.	0.15 Eq.	Toluene	reflux	a	NR	
2	5.0 Eq.	0.25 Eq.	Toluene	reflux	b	NR	
3	10.0 Eq.	1.0 Eq.	Toluene	reflux	c	NR	
4	10.0 Eq.	1.0 Eq.	Toluene	reflux	d	NR	
5	10.0 Eq.	1.1 Eq.	Toluene	reflux	e	NR	
6	2.0 Eq.	0.2 Eq.	Toluene	reflux	f	58 ^k	2.1/1.0 ⁿ
7	3.0 Eq.	0.3 Eq.	Benzene	reflux	g	7 ^k	1.2/1.0 ⁿ
8	5.0 Eq.	0.5 Eq.	Benzene	90 °C	h	76 ^l	51:15:29:5 ^o
9	5.0 Eq.	0.5 Eq.	Benzene	90 °C	i	88^l	^p
10	10.0 Eq.	1.0 Eq.	Benzene	90 °C	j	32 ^l	39:19:37:11 ^q

a. 0.067M substrate in toluene, 0.059M Ph₃SnH in toluene, 100 μL/min via a syringe pump

b. 0.043M substrate in toluene, 0.085M Ph₃SnH in toluene, 50 μL/min via a syringe pump

c. 0.086M substrate in toluene, 0.143M EPHP in toluene, 41 μL/min via a syringe pump

d. 0.061M substrate in toluene, 0.087M EPHP in toluene, 83 μL/min via a syringe pump

e. a mixture of 0.021M substrate and 0.208M EPHP (ethylpiperidine hypophosphite) in toluene, addition of AIBN 333 μL/min via a syringe pumps

f. 0.021M substrate in toluene, addition of 0.028M Bu₃SnH in toluene and AIBN, 150 μL/min via a syringe pump

g. 0.009M substrate in benzene, 0.051M Bu₃SnH in benzene, 62 μL/min via a syringe pump

h. 0.047M substrate in benzene, 0.064M Ph₃SnH in benzene, 45 μL/min via a syringe pump

i. 0.047M substrate in benzene, 0.064M Bu₃SnH in benzene, 26 μL/min via a syringe pump

j. 0.047M substrate in benzene, 0.127M EPHP in benzene, 26 μL/min via a syringe pump

k. Isolated yield of compound **7**

l. Isolated yield of compound **8**

m. Temperature of the oil bath

n. the ratio of *cis/trans* or *trans/cis* based on ¹H NMR

o. the ratio was determined after column chromatography

p. the ratio was not determined

q. the ratio was determined after work-up

3. 4. The Reaction of of 3(*E*)-[5(*R*)-(Imidazole-1-carbothioxyloxy)-2(*R*)-phenyl-[1,3]dioxan-4(*R*)-yl]-acrylic Acid Ethyl Ester

A flame-dried three neck 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 in nitrogen atmosphere) under 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 3-[5(*R*)-(imidazole-1-carbothioxyloxy)-2(*R*)-phenyl-[1,3]dioxan-4(*R*)-yl]-(*E*)acrylic acid ethyl ester (**12a**), 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 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 ^1H esters described in the next experiments.

13a-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 in CHCl_3). Mp: 126-129 °C. ^1H 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): ν 3394 *Br m*, 3119*m*, 2982*m*, 1731*s*, 1495*w*, 1455*w*, 1428*w*, 1370*m*, 1282*m*, 1228*m*, 1165*m*, 1094*m*, 1047*s*, 1028*s*, 970*s*, 913*m*, 756*s*, 699*s*,

661*m*. HRMS (Electrospray) Calcd. for C₁₉H₂₂O₅N₂Na (M⁺+Na), 381.1421; Found (M⁺+Na), 381.1447.

Anal. Calcd. for C₁₉H₂₂O₅N₂: C, 63.67; H, 6.19; N, 7.82. Found: C, 64.45; H, 6.93; N, 6.39.

13a- 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 in CHCl₃). Mp: 57-60 °C. ¹H NMR (CDCl₃, 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 (app 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 (app 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). ¹³C NMR (CDCl₃, 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): ν 3388 *Br m*, 3119*m*, 3061*m*, 2983*m*, 2928*m*, 1729*s*, 1494*m*, 1478*m*, 1428*s*, 1376*s*, 1324*m*, 1228*s*, 1212*s*, 1080*s*, 1027*s*, 996*s*, 972*s*, 914*m*, 699*s*, 662*m*. HRMS (Electrospray): Calcd. for C₁₉H₂₂O₅N₂Na (M⁺+Na), 381.1421; Found (M⁺+Na), 381.1433.

3. 5. Optimization of 5 -Exo-*trig* Radical Cyclization with 3(*E* or *Z*)-[5(*R*)-(Imidazole-1-carbothioxy)-2(*R*)-phenyl-[1,3]dioxan-4(*R*)-yl]-acrylic Acid Ethyl Ester

(See Table in the Next Page)

Table 2. 5-Exo-*trig* Radical Cyclization with 5(*R*)-hydroxy-2(*R*)-phenyl-[1, 3]dioxane-4(*R*)-carbaldehyde Derivatives

Entry	R	Conditions				Yield (%)	(α/β)
		Radical Sources	AIBN	Solvent	Temp		
1	(<i>Z</i>)-Et	Bu ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	32	0.84/1.0
2	(<i>Z</i>)-Et	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	44	1.13/1.0
3	(<i>E</i>)-Et	Bu ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	28	0.66/1.0
4	(<i>E</i>)-Et	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	54	0.80/1.0
5	(<i>Z</i>)- <i>t</i> Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	46	0.66/1.0
6	(<i>Z</i>)- <i>t</i> Bu ^a	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	23	0.93/1.0
7	(<i>Z</i>)- <i>t</i> Bu	EPHP (10.0 Eq) ^b	1.0 Eq	benzene	90 °C	14	^c
8	(<i>E</i>)- <i>t</i> Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	40	0.89/1.0

a. The reaction mixture was added all together and stirred at 90 °C for 3h.

b. Ethylpiperidine hypophosphite (EPHP)

c. The ratio was not determined.

3. 6. The Reaction of (Z)-3-[5(R)-(imidazole-1-carbothioxyloxy)-2(R)-phenyl-[1,3]dioxan-4(R)-yl]-acrylic Acid *tert*-Butyl Ester

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 309 mg of Ph_3SnH (0.880 mmol) and 14 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 72.8 mg (0.176 mmol) of (1,1-dimethylethyl 3-{5(R)-(N-imidazolylthiocarbonyloxy)-2(R)-phenyl-1, 3-dioxane}-4(R)-prop-2(Z)-enoate, and 14.5 mg (0.088 mmol) of AIBN in 3.8 mL of benzene via a syringe pump during 2 h 25 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 only to hexane:EtOAc = 1:2. The cyclized *N*-pyranoside was obtained as white solid (31 mg, 46%) with the ratio of α/β = 0.66/1.0).

M

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 in CHCl_3). Mp: 125-128 °C. ^1H 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 (app t, $J = 10.1$ Hz, 1H), 4.00 (app 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): ν 3393 *Br* *m*, 3119*m*, 2983*m*, 2931*m*, 2872*m*, 1716*m*, 1396*w*, 1369*m*, 1281*m*, 1225*w*, 1150*s*, 1089*s*, 1045*s*, 963*s*, 934*m*, 913*m*, 831*w*, 760*m*, 700*m*. HRMS (Electrospray): Calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_5\text{N}_2\text{Na}$ ($\text{M}^+ + \text{Na}$), 387.1915; Found ($\text{M}^+ + \text{Na}$), 387.1944.

N

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 in CHCl_3). Mp: 59-61 °C. ^1H 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 (app tdd, $J = 11.3, 7.5, 3.3$ Hz, 1H), 3.59 (dd, $J = 11.7, 9.0$ Hz, 1H), 3.74 (app td, $J = 9.1, 4.4$ Hz, 1H), 4.03 (app 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): ν 3388 *Br*

m, 3119*m*, 2978*m*, 2931*m*, 2872*m*, 1723*s*, 1494*m*, 1455*m*, 1369*s*, 1247*m*, 1227*m*, 1157*s*, 1080*s*, 1046*s*, 971*s*, 913*m*, 755*s*, 699*s*. HRMS (Electrospray): Calcd. for C₂₁H₂₆O₅N₂Na (M⁺+Na), 387.1915; Found (M⁺+Na), 387.1902. Anal. Calcd. for C₂₁H₂₆O₅N₂: C, 65.27; H, 6.78; N, 7.25. Found: C, 62.68; H, 6.93; N, 5.64.

3. 7. The Reaction of (*Z*)-Imidazole-1(*R*)-carbothioic acid *O*-[4(*R*)-(2-cyano-vinyl)-2(*R*)-phenyl-[1,3]dioxane-5(*R*)-yl] Ester

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 295 mg of Ph₃SnH (0.841 mmol) and 13.3 mL of benzene (dried over CaH₂ and stored over 4 Å MS in nitrogen atmosphere) under 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 52.7 mg (0.168 mmol) of (2*Z*)-4-{5(*R*)-(N-imidazolythiocarbonyl)oxy-2(*R*)-phenyl-1, 3-dioxanyl}-but-2-enonitrile **12b** and 14.5 mg (0.088 mmol) of AIBN in 3.6 mL of benzene via a syringe pump during 2 h 20 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 = 1:1 to 1:2. The cyclized *N*-pyranoside was obtained as pale yellow solid (38.5 mg, 81%) with the ratio of α/β = 1.0/0.79. The assignment are based on comparison of chemical shifts and coupling constants with those of ^tBu esters described in the previous experiments.

13b

Pale yellow solid (α/β = 1.0/0.79) (column chromatography, hexane:EtOAc 1:1 to 1:2). *R*_f = 0.12 (EtOAc only). Mp: 126-130 °C. ¹H NMR (CDCl₃, 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 (app 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): ν 3115 *m*, 2971*s*, 2879*s*, 2251*m*, 1698*s*, 1493*s*, 1455*m*, 1421*m*, 1380*s*, 1314*m*, 1285*m*, 1229*s*, 1168*s*, 1142*m*, 1080*s*, 1048*s*, 969*s*, 912*s*, 823*w*, 755*s*, 732*s*, 701*s*, 660*s*. HRMS (Electrospray): Calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3\text{Na}$ ($\text{M}^+ + \text{Na}$), 334.1162; Found ($\text{M}^+ + \text{Na}$), 334.1180.

3. 8. The Reaction of Imidazole-1-carbothioic acid *O*-[4(*R*)-(methoxyimino-methyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] Ester

A flame-dried three-necked 50 mL flask was connected to a condenser, and the flask was charged with 407 mg of Ph_3SnH (1.16 mmol) and 18.3 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 74 mg (0.232 mmol) of imidazole-1-carbothioic acid *O*-[4(*R*)-(methoxyimino-methyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] ester **12c** and 19 mg (0.16 mmol) of AIBN in 5.0 mL of benzene via a syringe pump during 3 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 = 1:1 to 1:2. The cyclized *N*-pyranoside was obtained as pale yellow solid (42.2 mg, 63%) with the ratio of $\alpha/\beta = 1.0/0.83$.

13c

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. ^1H 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): ν 3112 *Br m*, 2940*s*, 2893*s*, 2802*w*, 2238*w*, 1701*m*, 1495*s*, 1458*m*, 1425*w*, 1379*s*, 1313*m*, 1283*m*, 1226*s* 1058*s*, 1078*s*, 1049*s*, 1229*s*, 975*s*, 911*s*, 822*w*, 792*w*, 733*s*, 700*s*, 660*s*. HRMS (Electrospray): Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}_3\text{Na}$ ($\text{M}^+ + \text{Na}$), 340.1268; Found ($\text{M}^+ + \text{Na}$), 340.1290. Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}_3$; C, 60.56; H, 6.04; N, 13.24. Found; C, 60.17; H, 6.45; N, 11.19.

3. 9. The Reaction of Imidazole-1-carbothioic acid *O*-[4(*R*)-(dimethyl-hydrazonomethyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] Ester

A flame-dried three neck 50 mL flask was connected to a condenser, and the flask was charged with 618 mg of Ph_3SnH (1.760 mmol) and 28.0 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 117 mg (0.352 mmol) of imidazole-1-carbothioic acid *O*-[4(*R*)-(dimethyl-hydrazonomethyl)-2(*R*)-phenyl-[1,3]dioxan-5(*R*)-yl] ester **12d** and 29 mg (0.176 mmol) of AIBN in 7.6 mL of benzene via a syringe pump during 4 h 35 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 = 1:1 to only EtOAc. The ratio of the crude *N*-pyranosides was $\alpha/\beta = 1.0/0.32$ measured by ^1H NMR. After column chromatography, only α -anomer was isolated as pale yellow solid (57.6 mg, 54%).

13d-α

Pale yellow solid (column chromatography, hexane:EtOAc = 1:1 to EtOAc only with 1% of Et₃N). R_f = 0.10 (EtOAc only) or 0.67 (EtOAc:MeOH = 9:1). Mp: 120-123 °C ¹H NMR (CDCl₃, 400 MHz): δ 2.40 (s, 6H), 3.80-3.91 (m, 2H) 3.96 (app t, J = 10.1 Hz, 1H), 4.06 (app 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 is overlapped with 3 Hs between 3.80-4.09. The integration of this region becomes smaller as much as 0.4 H with D₂O. ¹³C NMR (CDCl₃, 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): ν 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 C₁₇H₂₂O₃N₄Na (M⁺+Na), 353.1584; Found (M⁺+Na), 353.1581. Anal. Calcd. for C₁₇H₂₂O₃N₄: C, 61.80; H, 6.71; N, 16.96. Found: C, 61.49; H, 6.77; N, 15.99.

4. 6-Exo-*trig* Radical Cyclizations

4. 1. The Reaction of 3(*Z*)-{5(*R*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic Acid *tert*-Butyl Ester by Reverse Addition

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 302 mg of Ph₃SnH (0.860 mmol) and 13.6 mL of benzene (dried over CaH₂ and stored over 4 Å MS in nitrogen atmosphere) under 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 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester **14a** 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 was obtained as pale yellow oil (59.0 mg, 71%) with a ratio of $\alpha/\beta = 0.20/1.0$.

15a- α /15a- β = 0.2/1.0

Colorless oil (column chromatography, hexane:EtOAc = 24:1), R_f = 0.63 (Hexane:EtOAc = 8:1). $[\alpha]_D^{20} = +23.5$ (c 3.16 in CHCl_3). Major **15a- β** ; ^1H NMR (CDCl_3 , 300 MHz): δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.91 (s, 9 H), 1.37 (s, 3 H), 1.40 (s, 9 H), 1.52 (s, 3 H), 2.02 (dd, J = 16.8, 5.9 Hz, 1 H), 2.25 (dd, J = 16.8, 8.6 Hz, 1 H), 2.88 (dddd, J = 8.6, 5.9, 3.6, 3.2 Hz, 1 H), 3.66-3.69 (ddd, J = 8.4, 4.4, 2.1 Hz, 1 H), 3.77 (dd, J = 11.5, 4.4 Hz, 1 H), 3.92 (dd, J = 11.5, 2.1 Hz, 1 H), 4.24, -4.31 (m, 2 H), 5.89 (d, J = 3.2 Hz, 1 H), 6.96 (s, 1 H), 7.08 (s, 1 H), 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. IR (NaCl, neat): ν 3118 *Brm*, 3002*s*, 2991*s*, 2980*s*, 2930*s*, 2851*s*, 1728*s*, 1461*m*, 1369*s*, 1254*s*, 1219*s*, 1154*s*, 1064*s*, 1000*m*, 941*m*, 906*m*, 838*s*, 779*m*,

739m, 662m. Anal. Calcd. for C₂₄H₄₂O₆N₂Si: C, 59.72; H, 8.77; N, 5.80. Found: C, 59.51; H, 8.61; N, 5.58.

Minor **15a-α** was assigned by the characteristic peak at δ 5.64 (d, *J* = 8.5 Hz, 1H)

In the experiment with 3(*E*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester, minor amount of glycosides were obtained (see Table 3 in **4. 2.**). The *alllo* compounds were not fully characterized, but their characteristic anomeric hydrogen peaks were used for the tentative assignments of the configurations.

250 MHz ¹ H NMR	<i>altro-α</i>	<i>altro-β</i>	<i>allo-α</i>	<i>allo-β</i>
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. 2. Optimization of 6-exo-*trig* radical cyclization

Table 3. 6-exo-*trig* Radical cyclization

Exp	R	Conditions				Yield (%)			Comments ^a	
		R ₃ SnH	AIBN	Solvent	Temp	15	O	16	<i>allo</i> (α/β)	<i>altro</i> (α/β)
1	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (1.5 Eq)	0.2 Eq	toluene	reflux			33		
2	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (1.5 Eq)	0.2 Eq	benzene	reflux	34				13/87
3	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (1.5 Eq)	0.2 Eq	toluene	reflux		40			
4	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (5.0 Eq)	0.5 Eq	toluene	90 °C	37				28/72
5	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (5.0 Eq)	0.5 eq	benzene	90 °C	57				14/86
6	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (10.0 Eq)	1.0 Eq	benzene	90 °C	54				15/85
7	(<i>Z</i>)- ^{<i>i</i>} Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	toluene	reflux	47	9			25/75
8	(<i>Z</i>)- ^{<i>i</i>} Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	reflux	62				17/83
9	(<i>Z</i>)- ^{<i>i</i>} Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	71				17/83
10	(<i>Z</i>)- ^{<i>i</i>} Bu	Bu ₃ SnH (5.0 Eq)	0.5 Eq	benzene	68 °C	3				
11 ^b	(<i>Z</i>)- ^{<i>i</i>} Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	reflux	15	37			14/86
12	(<i>E</i>)- ^{<i>i</i>} Bu	Ph ₃ SnH (5.0 Eq)	0.5 Eq	benzene	reflux	61			10/14	14/62
13	(<i>Z</i>)-Et	Bu ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	68				20/80
14	(<i>E</i>)-Et	Bu ₃ SnH (5.0 Eq)	0.5 Eq	benzene	90 °C	59	18		3/9	21/67

^a The ratio was determined by ¹H NMR before column chromatography.

^b Normal addition: the mixture of Ph₃SnH (5.0 Eq) and AIBN (0.5 Eq) in benzene was added to the solution of substrate in benzene via a syringe pump.

4. 3. The Reaction of 3(*Z*)-{5(*R*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic Acid *tert*-Butyl Ester by Normal Addition

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 81 mg (0.158 mmol) 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester **14a** and 12.6 mL of benzene (dried over CaH₂ and stored over 4 Å MS in nitrogen atmosphere) under 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 278 mg (0.791 mmol) of Ph₃SnH and 13 mg (0.079 mmol) of AIBN in 3.4 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 isolate products were [4-(*tert*-butyl-dimethyl-silanoyloxymethyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5,*c*]pyran-7-yl]-acetic acid *tert*-butyl ester **O** 24.1 mg, 37%) as well as [4-(*tert*-butyl-dimethyl-silanoyloxymethyl)-6-imidazol-1-yl-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5,*c*]pyran-7-yl]-acetic acid *tert*-butyl ester **15a** (11.1 mg, 15%).

Colorless oil (column chromatography, hexane:EtOAc 20:1 to 15:1). R_f = 0.40 (hexane:EtOAc 8:1). $[\alpha]_D^{20}$ = +24.4 (c 1.23 in CHCl₃). ¹H NMR (CDCl₃, 500 MHz): δ 0.06 (s, 3H), 0.07 (s, 3H), 0.90 (s, 9H), 1.35 (s, 3H), 1.44 (s, 9H), 1.49 (s, 3H), 2.29-2.35 (m, 1H), 2.44-2.50 (m, 2H), 3.32 (ddd, J = 8.4, 5.6, 2.1 Hz, 1H), 3.65 (dd, J = 11.5, 5.6 Hz, 2H), 3.76 (dd, J = 11.6, 2.3 Hz, 1H), 3.82 (dd, J = 11.5, 2.1 Hz, 1H), 3.90 (dd, J = 8.9, 5.1 Hz, 1H), 4.09 (dd, J = 4.9, 1.3 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ -5.23, -5.26, 18.45, 26.00, 26.40, 28.07, 28.25, 33.90, 36.23, 63.81, 65.93, 69.79, 75.38, 79.18, 80.72, 108.84, 171.24. IR

(NaCl, neat): ν 2982 m , 2948 m , 2929 s , 2858 m , 1731 s , 1462 w , 1368 m , 1278 m , 1255 m , 1219 m , 1152 s , 1087 m , 1060 s , 1004 w , 938 w , 861 m , 836 s , 778 m . HRMS (Electrospray): Calcd. for $C_{21}H_{38}O_6SSiNa$ ($M^+ + Na$), 439.2486; Found ($M^+ + Na$), 439.2505. Anal. Calcd. for $C_{21}H_{40}O_6Si$; C, 60.54; H, 9.68. Found; C, 60.27; H, 10.12.

4. 4. Reaction of 3(*Z*)-{5(*R*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl]-acrylic Acid *tert*-Butyl Ester at High temperature

A flame-dried three neck 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 nitrogen atmosphere. To the flask was added a solution of 185 mg (0.36 mmol) 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl]-acrylic acid *tert*-butyl ester **14a** and 12 mg (0.072 mmol) of AIBN in 3.5 mL of toluene under reflux condition 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 4-(*tert*-butyl-dimethyl-silanyloxymethyl)-2,2-dimethyl-6-thioxo-tetrahydro-[1,3]dioxolo[4,5-*c*]pyran-7-carboxylic acid *tert*-butyl ester **16** obtained as pale yellow oil (53.7 mg, 33%).

16

Yellow oil (preparative TLC, hexane:EtOAc = 5:1). R_f = 0.17 (hexane:EtOAc = 4:1). ^1H NMR (CDCl_3 , 400 MHz): δ 0.11(s, 3 H), 1.12(s, 3 H), 0.90 (s, 9 H), 1.34 (s, 3 H), 1.46 (s, 9 H), 1.49 (s, 3 H), 2.74(dd, J = 16.4, 3.6 Hz, 1 H), 2.97 (dd, J = 16.4, 8.7 Hz, 1 H), 3.08 (ddd, J = 12.3, 8.7, 3.7 Hz, 1 H), 3.95 (dd, J = 12.1, 4.2 Hz, 1 H), 4.04 (dd, J = 8.9, 6.9 Hz, 1 H), 4.11 (dd, J = 11.9, 1.6 Hz, 1 H), 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): ν 2957m, 2930s, 2857m, 1731s, 1472m, 1368m, 1338m, 1268s, 1212m, 1152s, 1076m, 836m. HRMS (Electrospray): Calcd. for $\text{C}_{21}\text{H}_{38}\text{O}_6\text{SSiNa}$ ($\text{M}^+ + \text{Na}$), 469.2056; Found ($\text{M}^+ + \text{Na}$), 469.2057.

4. 5. The Reaction of 3(*E* or *Z*)-{5(*R*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile (15b)

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 257 mg of Ph_3SnH (0.732 mmol) and 11.6 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 mg (0.146 mmol) 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile (**Z**)-**14b** and 12 mg (0.073 mmol) of AIBN in 3.2 mL of benzene via a syringe pump during 2 h 30 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 to 1:1. The cyclized *N*-pyranoside was obtained as pale yellow oil (31.9 mg, 57%) with a ratio of *altro*- α /*altro*- β = 0.26/1.0 after column chromatography.

Alternatively, a flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 296 mg of Ph_3SnH (0.842 mmol) and 13.3 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 69 mg (0.168 mmol) 3(*E*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(imidazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylonitrile (**E**)-**14b** and 14 mg (0.084 mmol) of AIBN in 3.6 mL of benzene via a syringe pump during 2 h 40 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 to 1:1. The cyclized *N*-pyranoside was obtained as pale yellow oil (51.0 mg, 80%) with a ratio of *altro*-α/ *altro*-β/*allo*-α/ *allo*-β = 0.27/1.0/0.04/0.09 after column chromatography. The assignments are based on comparison of chemical shifts and coupling constants with those of related compounds, and should be considered tentative.

15b

Yellow oil (column chromatography, hexane:EtOAc = 3:1 to 1:1). R_f = 0.24 (hexane:EtOAc = 1:6).

^1H NMR (CDCl_3 , 400 MHz): **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); **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 (app 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): **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; *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): ν 3115 w, 2987m, 2955s, 2991s, 2892s, 2857m, 2253w, 1700w, 1494m, 1472m, 1424w, 1384m, 1370m, 1312w, 1285w, 1253s, 1221s, 1159s, 1077s, 939w, 906w, 838s, 780i, 661m. HRMS (Electrospray): Calcd. for C₂₀H₃₃O₄N₃SiNa (M⁺+Na), 430.2133; Found (M⁺+Na), 430.2116. Anal. Calcd. for C₂₀H₃₃O₄N₃Si: C, 58.94; H, 8.16; N, 10.31. Found: C, 58.35; H, 8.27; N, 9.94.

400 MHz ¹ H NMR	<i>altro-α</i>	<i>altro-β</i>	<i>allo-α</i>	<i>allo-β</i>
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 ¹H NMR after column chromatography.

4. 6. The Reaction of Imidazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} Ester (**17**)

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 215 mg of Ph₃SnH (0.613 mmol) and 9.7 mL of benzene (dried over CaH₂ and stored over 4 Å MS in nitrogen atmosphere) under 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 51 mg (0.123 mmol) imidazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} ester **17** and 10 mg (0.061 mmol) of AIBN in 2.6 mL of benzene via a syringe pump during 2 h 10 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 = 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* = 0.24/1.0/0.03/0.75, only the major compound (*altro- β*) has been 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 **14a** and **14b**).

18a (altro-β)

Colorless oil (column chromatography, hexane:EtOAc = 2:1 to 1:1). R_f = 0.16 (hexane:EtOAc = 1:3).

^1H 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): ν 3168 *br s*, 2981*m*, 2952*s*, 2932*s*, 2893*s*, 2856*s*, 2250*w*, 2211*w*, 1698*w*, 1494*m*, 1472*s*, 1458*s*, 1383*s*, 1251*s*, 1219*s*, 1146*s*, 1064*s*, 1033*s*, 1004*m*, 938*w*, 911*w*, 837*s*, 779*s*, 733*s*. HRMS (Electrospray): Calcd. for $\text{C}_{19}\text{H}_{35}\text{O}_5\text{N}_3\text{SiNa}$ ($\text{M}^+ + \text{Na}$), 436.2238; Found ($\text{M}^+ + \text{Na}$), 436.2259. Anal. Calcd. for $\text{C}_{19}\text{H}_{35}\text{O}_5\text{N}_3\text{Si}$: C, 55.18; H, 8.53; N, 10.16. Found: C, 54.04; H, 8.48; N, 9.28.

250 MHz ^1H NMR	<i>altro</i> - α	<i>altro</i> - β	<i>allo</i> - α	<i>allo</i> - 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 ^1H NMR after column chromatography.

4. 7. The Reaction of 3(*Z*)-{5(*R*)-[2-(*tert*-Butyl-dimethyl-silanyloxy)-1(*R*)-(triazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic Acid *tert*-Butyl Ester (20a**)**

A flame-dried three neck 50 mL flask was connected to a condenser, and the flask was charged with 233 mg of Ph_3SnH (0.663 mmol) and 10.5 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 68 mg (0.113 mmol) 3(*Z*)-{5(*R*)-[2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-(triazole-1-carbothioxyloxy)-ethyl]-2,2-dimethyl-[1,3]dioxolan-4(*S*)-yl}-acrylic acid *tert*-butyl ester **19a** and 11 mg (0.066 mmol) of AIBN in 2.8 mL of benzene via a syringe pump during 3 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 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-dimethyl-silanoyloxymethyl)-6-imidazol-1-yl-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5,*c*]pyran-7-yl]-acetic acid *tert*-butyl ester (**20a**) was isolated in 87% (55.5 mg) yield.

20a (*altro*- 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 in CHCl_3). ^1H 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 (app 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 (app 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. IR (NaCl,

neat): ν 3122 w , 2985 s , 2954 s , 2930 s , 2857 s , 1725 s , 1507 m , 1472 m , 1401 m , 1431 m , 1369 s , 1272 s , 1256 s , 1214 s , 1152 s , 1078 s , 999 m , 955 w , 919 w , 837 s , 778 s , 733 m .

The structure was confirmed by nOe experiments and the key results are shown below.

20a (altro-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 in CHCl_3). ^1H 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 (app 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. IR (NaCl, neat): ν 3122 w , 2985 s , 2954 s , 2931 s , 2857 s , 1739 w , 2236 w , 1727 s , 1506 m , 1472 m , 1461 m , 1369 s , 1272 s ,

1255s, 1214s, 1157s, 1066s, 1022m, 956m, 939m, 910m, 875m, 837s, 814m, 779s, 734s, 678m. HRMS (Electrospray): Calcd. for $C_{23}H_{41}O_6N_3Si Na$ ($M^+ + Na$) 506.2657; Found ($M^+ + Na$), 506.2665. The structure was confirmed by nOe experiments and the key results are shown below.

4. 8. The Reaction of Triazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} Ester (**20b**)

A flame-dried three neck 25 mL flask was connected to a condenser, and the flask was charged with 162 mg of Ph_3SnH (0.461 mmol) and 7.3 mL of benzene (dried over CaH_2 and stored over 4 Å MS in nitrogen atmosphere) under 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 41 mg (0.092 mmol) triazole-1(*R*)-carbothioic acid *O*-{2-(*tert*-butyl-dimethyl-silanyloxy)-1(*R*)-[5-(methoxyimino-methyl)-2,2-dimethyl-[1,3]dioxolan-4(*R*)-yl]-ethyl} ester **19b** and 7.6 mg (0.046 mmol) of AIBN in 2.0 mL of benzene via a syringe pump during 1 h 20 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 ratio of *altro*- α / *altro*- β of the crude mixture is 0.69/1.0. The concentrated mixture was purified by flash column chromatography eluting with hexane:EtOAc = 6:1. After column chromatography, 17.6 mg (46%) of product was isolated as an yellow oil. The structure of the major products was confirmed by nOe experiments.

20b (altro-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 in CHCl_3). ^1H 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 (app 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): ν 3263 *Br s*, 3118*w*, 2985*m*, 2954*s*, 2931*s*, 2862*s*, 1752*w*, 1508*m*, 1472*m*, 1463*m*, 1382*s*, 1276*s*, 1252*s*, 1218*s*, 1134*s*, 1068*s*, 954*m*, 914*w*, 836*s*, 813*m*, 780*s*, 734*m*, 698*w*, 677*m*. HRMS (Electrospray): Calcd. for $\text{C}_{18}\text{H}_{34}\text{O}_5\text{N}_4\text{Si Na}$ ($\text{M}^+ + \text{Na}$) 437.2191; Found ($\text{M}^+ + \text{Na}$), 437.2183.

400 MHz ^1H NMR	<i>altro-α</i>	<i>altro-β</i>	<i>Allo-α</i>	<i>allo-β</i>
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 ^1H NMR before column chromatography.

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