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Preparation of Carbocyclic *C*-Nucleosides from α-Chlorooxime Precursor

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The syntheses of L-carbocyclic benzothiazolo, benzoxazolo, and benzimidazolo *C*-*nor*-nucleosides are described. The key step is the reaction of the *C*-chlorooxime **7**, obtained by *C*-chlorination with *N*-chlorosuccinimide of [(1*S*,2*R*,3*R*,4*R*)-1-*tert*-butyldimethylsiloxy-2,3-(*O*-isopropylidenedioxy)]cyclopentane-4-carbohydroximic acid (**6**), with different α-amino aromatic compounds. Acidic deprotection gave the benzoxazolo (**11**), benzimidazolo (**12**), and benzothiazolo (**13**) title compounds, in good yields.

Introduction

Nucleoside analogs[1] have received great attention because of their potent biological activities, and therefore, much effort has been focused on their syntheses. One important class of modified nucleosides is the carbocyclic nucleosides[2] in which the furanose ring is replaced by a cylopentane ring; both D- and L-carbocyclic nucleosides are of considerable interest for the development of therapeutic agents, such as D-abacavir[3] (active against HIV), D-entecavir[4] (active against HBV), D-noraristeromycin[5] [lacking the hydroxymethyl substituent, active against human and *Plasmodium falciparum* (*P. falciparum*) recombinant SAH hydrolase], the non-natural isomers L-2′,3′-dideoxy-2′,3′-didehydro-2′-fluoroadenosine[6] (L-2′F-C-d4A, active against HIV), or L-cyclopentenylcytosine[7] (L-CPE-C, active against West Nile virus) (Figure 1).

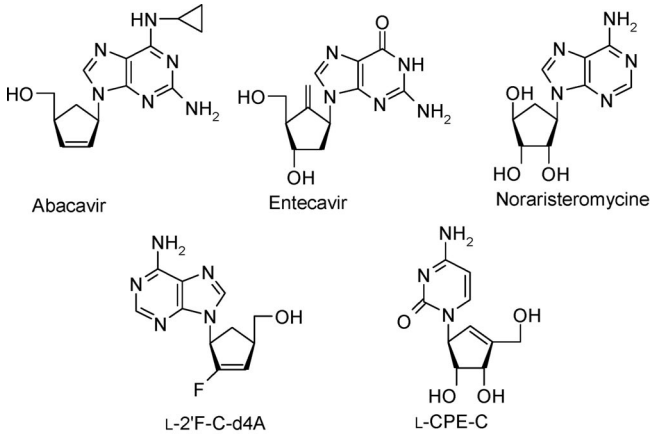

Figure 1. Selected bioactive carbocyclic nucleosides.

Another alteration to the nucleoside structure that has resulted in profound biological effects is the modification of the heterocyclic base, leading to *C*-nucleosides.[3] Among them, naturally occurring pseudouridine,[8] showdomycin,[9] and thiazofurin,[10] have been shown to possess a wide range of medicinal properties, including antibiotic, antiviral, and antitumor activity (Figure 2). Carbocyclic *C*-nucleosides, such as carbocyclic showdomycin[11] and carbocyclic pyrazofurin A[12] possessing the structural features of both carbocyclic nucleosides and *C*-nucleosides, have been given relatively little attention, although they are chemically challenging[13] and may possess interesting biological activity. Also, the chemistry of benzimidazoles and congeneric compounds has been of interest as inhibitors of nucleic acid biosynthesis, as fungicides or insecticides,[14] for characterization and identification of carbohydrates,[15] but also since the discovery that 5,6-dimethyl-1-(α-D-ribofuranosyl)benzimidazole was an integral part of the chemical structure of

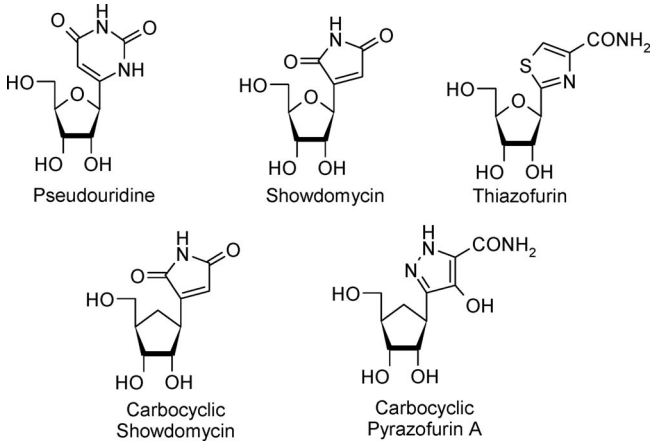

Figure 2. Selected bioactive *C*-nucleosides.

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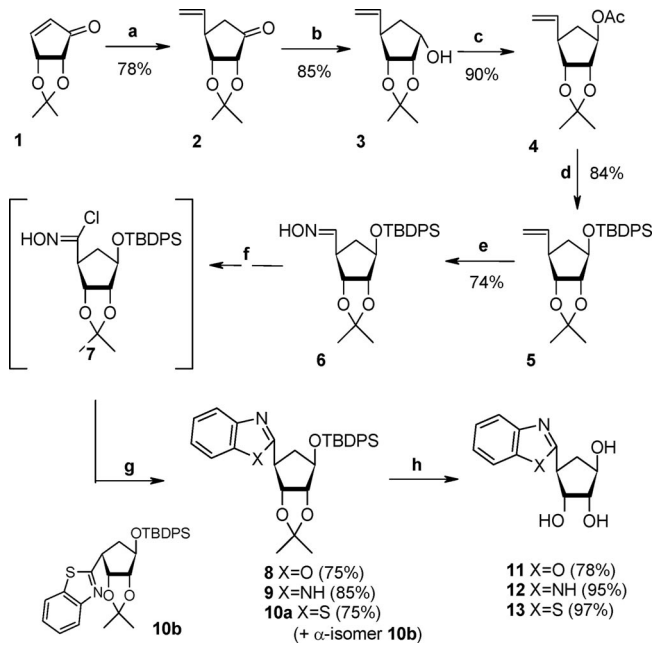
vitamin B2.[16] Recently, Stambasky et al.[37] reported the synthesis of a number of artificial aryl-*C*-nucleosides capable of π-stacking for artificial expanded genetic information systems (AEGIS).

Most of the known carbocyclic *C*-nucleosides have been synthesized as racemic mixtures although a few examples of asymmetric syntheses have been reported, but no L-carbocyclic *C*-nucleosides have been yet described. Therefore, on the basis of the interesting chemical and biological properties of *C*-nucleosides and L-carbocyclic nucleosides, it was of interest to report the preparation of hitherto unknown L-carbocyclic *C*-nucleosides from a *C*-chlorooxime precursor.

Results and Discussion

General methods for the synthesis of *C*-nucleosides include the addition of an organometallic reagent to a ribonolactone derivative followed by hemiacetal deoxygenation,[17] the direct introduction of a preformed heterocyclic base into the anomeric position of a carbohydrate,[18] a Pd^0-mediated coupling reaction,[19] or the construction of the heterocyclic ring from *C*-glycosyl derivatives (e.g., nitrile, thioamide, cyanomethoxyacrylonitrile). Recently, Wamhoff et al. proposed a novel synthetic approach to purine-like *C*-nucleosides from *C*-glycosidic tosyloximino nitrile precursors.[20] Carbocyclic *C*-nucleosides have been obtained from an amide[21] or from a cyanoacetate.[22] A retrosynthetic analysis indicates that L-cyclopentyl carbocyclic *C*-nucleosides can be prepared by direct cyclocondensation of a desired heterocyclic precursor with a functionalized *C*-chlorooxime. It has been reported in the literature that α-chlorooximes[23] are versatile compounds for heterocyclic chemistry. For the synthesis of L-cyclopentyl nucleosides, we selected (–)-cyclopentanol **3** as a chiral intermediate, which was prepared from chiral D-2-cyclopentenone **1**, which is known as a versatile synthon for the syntheses of various D-carbocyclic nucleosides.[24,25] The first practical procedures to obtain **1** were reported by Jeong et al.[26,27] starting from inexpensive D-isoascorbic acid, and then by Chu et al.[28,29] starting from D-ribose. Recently, we reported[30] an optimized synthesis of **1** on the basis of a ring-closing metathesis reaction.[31]

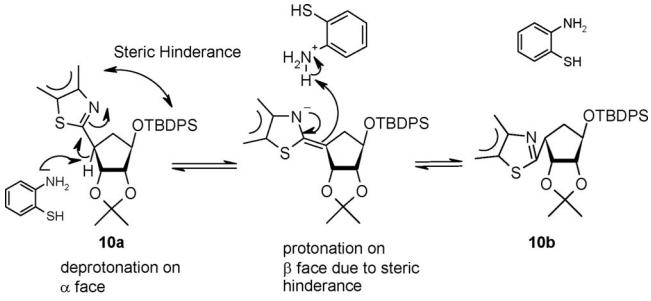
Thus, treatment of **1** with vinyl Grignard in the presence of dimethylsulfur copper, as described by Schneller et al.,[32] gave optically pure cyclopentanone **2** as a single isomer in 78% yield (Scheme 1). The incorporation of a vinyl group onto a cyclopentyl ring by 1,4-enone addition is known to be a high-yielding reaction.[33] This reaction is highly sensitive to temperature, as a slight increase of the temperature by 3 °C induces an important decrease in the yield. Reduction of cyclopentanone **2** with lithium aluminum hydride gave α-alcohol **3** in 85% yield. Mitsunobu[34] acylation of the secondary alcohol of **3** in the presence of diisopropyl azodicarboxylate (DIAD) and triphenylphosphane (TPP) led to **4** (90%) with complete inversion of configuration at the C1′-carbinyl carbon atom, as confirmed by NOESY experiments. Saponification of compound **4** with potassium carbonate in methanol, followed by silylation of the obtained derivative with *tert*-butyldiphenylsilyl chloride (TBDPSCl) gave silylated ether **5** in 84% yield (two steps). *C*-Oxime **6** was readily prepared in two steps through the corresponding aldehyde (obtained by glycol cleavage of **5** with a catalytic amount of OsO_4 in the presence of $NaIO_4$) by addition of hydroxylamine hydrochloride in 74% yield (2 steps). *C*-Chlorooxime **7** was obtained by *C*-chlorination with *N*-chlorosuccinimide (NCS)[35] and a catalytic amount of pyridine in refluxing $CHCl_3$. After evaporation of the volatiles, crude product **7** was directly treated with different α-amino aromatic compounds in EtOH as reported by Shih[36] to afford the benzoxazolo (**8**), benzimidazolo (**9**), and benzothiazolo (**10**) derivatives, respectively, in good yields.



Scheme 1. Reagents and conditions: (a) vinylmagnesium bromide, $CuBrMe_2S$, TMSCl, HMPA, THF, 3 h, –78 °C; (b) $LiAlH_4$, THF, 3 h, room temp.; (c) AcOH, DIAD, PPh_3, THF, 15 h, room temp.; (d) K_2CO_3, MeOH, 1 h, room temp., then TBDPSCl, DMAP, imidazole, CH_3CN, 15 h, room temp.; (e) OsO_4, $NaIO_4$, H_2O, MeOH, acetone, 15 h, room temp., then $NH_2OH{\cdot}HCl$, NaOAc, EtOH, CH_2Cl_2, 2 h, room temp.; (f) NCS, pyridine, $CHCl_3$, 40 °C; (g) 2-aminophenol, EtOH, 60 °C, 2 h (for **8**) or benzene-1,2-diamine, EtOH, 60 °C, 2 h (for **9**) or 2-aminobenzenethiol, EtOH, 60 °C, 2 h (for **10**); (h) 2 M HCl, dioxane.

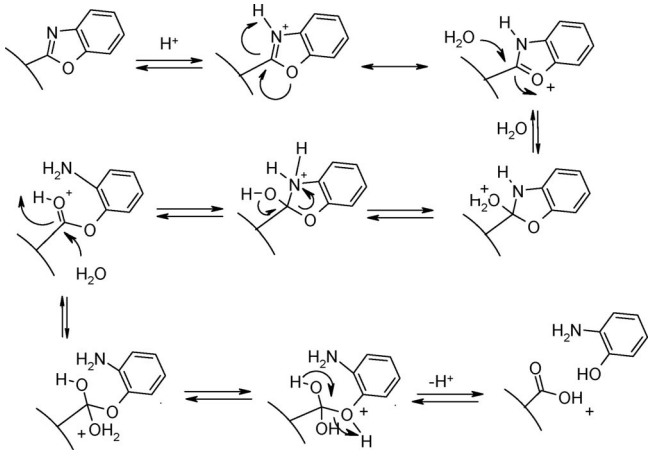
Interestingly, when 2-aminobenzenethiol was treated with *C*-chlorooxime **7**, we observed also the formation of α-isomer **10b**. The mechanism of the isomerization is thought to be as depicted in Scheme 2. Deprotonation of H1′ is followed by an electron push starting from C1′ to give an unsaturated intermediate, which after protonation led to the α-benzothiazolo compound, minimizing thus the interaction with the TBDPS protecting group. Trace amounts of the α-isomer (5%) cannot be avoided during the reaction, but the two diastereomers **10a** and **10b** can be

easily separated by chromatography on silica gel. When the reaction time was increased from 2 to 24 h at 60 °C, α-isomer **10b** was isolated in 52% yield, and the β-isomer was isolated 27%. An increase in the temperature >60 °C or a prolonged reaction time >24 h induced degradation.



Scheme 2.

Treatment of **8**–**10a** with 2 N HCl in dioxane afforded the desired L-carbocyclic *C*-nornucleosides **11**–**13**, respectively. Whereas benzimidazolo **9** and benzothiazolo **10a** compounds were deprotected in good yields (>95%), benzoxazolo compound **11** was only isolated in 78% yield. This is due to an aromatic ring opening acidic degradation of **8**, leading to the formation of the carboxylic acid and the starting α-aminophenol, as depicted in Scheme 3.

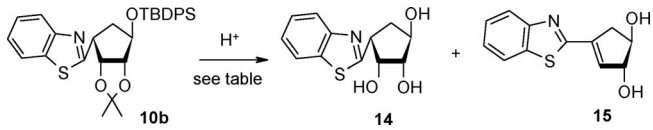


Scheme 3.

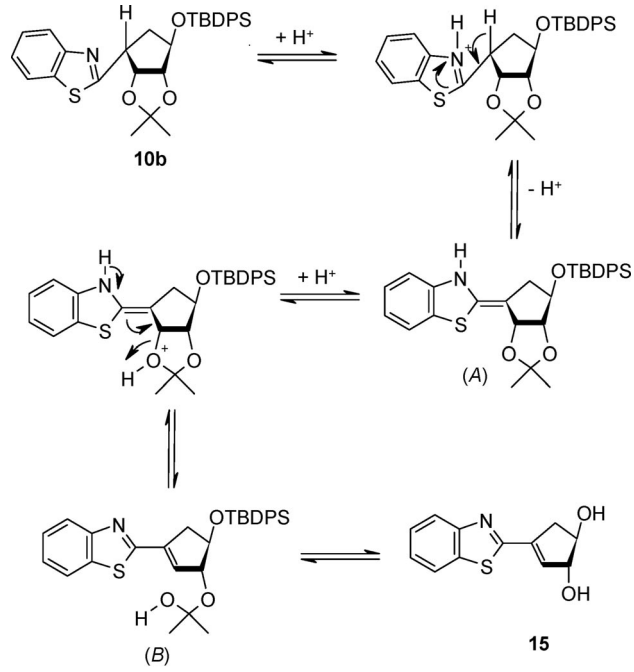
We attempted to deprotect β-benzothiazolo **10a** under a variety of acidic conditions (Table 1), but α-isomer **10b** never gave desired compound **14**; instead unsaturated derivative **15** was obtained (Table 1).

The mechanism of the formation of unsaturated **15** from α-isomer **10b** is thought to be as that depicted in Scheme 4, starting with the protonation of the benzothiazol-2-yl moiety of **10b** followed by its deprotonation, leading to the 3*H*-benzothiazol-2-ylidene analogue (*A*); subsequent protonation of the isopropylidene group followed by deprotonation led to the hemicetal (*B*), which is then converted into **15**.

Table 1. Acidic deprotection of **10b** to **15**.



Entry	Conditions	*T* [°C]	Observation
1	2 N HCl in dioxane	room temp.	partial **15**
2	TFA/H_2O/EtOH (40:10:50)	room temp.	partial **15**
3		50	**15**
4	AcOH/H_2O (70:30)	room temp.	no reaction
5		50	**15**
6	1 M HCl in Et_2O	room temp.	**15**



Scheme 4.

Conclusions

The nucleosides obtained were fully characterized by spectroscopic methods. Nuclear Overhauser enhancement studies confirmed the stereochemistry at C1′. Despite the fact that neither antiviral activities nor toxicities were found, this reaction would potentially be useful to chemists seeking to generate libraries of carbocyclic *C*-nucleosides bearing modified heterocycles (e.g., 5-aminoisoxazoles, 5-alkylisoxazoles) for potential biological activities.

Experimental Section

General Remarks: Commercially available chemicals were used as received. Microwave reactions were carried out with a Biotage Initiator with a maximum power of 300 W and temperatures were measured by an IR sensor. Reactions were monitored by thin-layer chromatography (TLC) analysis using silica gel plates (Kieselgel 60 F_{254}). Compounds were visualized by UV irradiation and/or spraying with ethanol solution 2.5% in phosphomolybdic acid, followed

by charring at 150 °C. Column chromatography was performed on silica gel 60 M (0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance DPX 250 (^{1}H: 249.88 MHz, ^{13}C: 62.84 MHz) and Varian Inova Unity 400 spectrometer (^{1}H: 399.91 MHz, ^{13}C: 100.54 MHz) in [D$_6$]DMSO or a CDCl$_3$/[D$_6$]-DMSO mixture. The NMR spectra were recorded at room temperature. The chemical shifts are given in ppm relative to the residual signal of the solvent, TMS being used as calibration standard with different deuterated solvents. Evidence of purity was confirmed from a proton-decoupled ^{13}C NMR spectrum with a signal-to-noise ratio sufficient to permit seeing peaks with 5% of the intensity of the strongest peak.

(*1R*,2*R*,3*S*,4*R*)-4-Acetyloxy-2,3-(*O*-isopropylidenedioxy)-1-vinylcyclopentane (4): To a solution of alcohol **3** (1.33 g, 7.2 mmol) in THF (30 mL) was dropwise added AcOH (0.82 mL, 14.4 mmol), PPh$_3$ (3.78 g, 14.4 mmol), and DIAD (2.86 mL, 14.4 mmol) at 0 °C under positive pressure of dry argon. After 10 min at 0 °C, the reaction mixture was warmed to room temperature and stirred for 15 h. Then, the reaction mixture was washed with an aqueous saturated solution of NaHCO$_3$ and extracted with AcOEt. The organic layer was dried (MgSO$_4$), filtered, and concentrated. The residue was purified by flash chromatography (petroleum ether/AcOEt, 9:1) to afford **4** (1.47 g, 90%) as an oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 17.3 (*J* = 10.3, 7.9 Hz, 1 H, CH$_2$=C*H*), 5.09 (td, *J* = 17.3, 1.4 Hz, 1 H, C*H*$_2$=CH), 5.06–5.01 (m, 2 H, C*H*$_2$=CH and 4-H), 4.53 (d, *J* = 6.2 Hz, 1 H, 2-H or 3-H), 4.48 (dd, *J* = 6.22, 2.8 Hz, 1 H, 2-H or 3-H), 2.82–2.75 (m, 1 H, 1-H), 2.40 (ddd, *J* = 13.5, 7.2, 6.1 Hz, 1 H, 5-H$_a$), 2.04 (s, 3 H, OAc), 1.69 (td, *J* = 13.9, 4.8 Hz, 1 H, 5-H$_b$), 1.47 (s, 3 H, *i*Pr), 1.29 (s, 3 H, *i*Pr) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 170.1 (C=O), 138.9 (*C*H=CH$_2$), 115.3 (CH=*C*H$_2$), 111.4 (quat., C*i*Pr), 84.9 (2-C or 3-C), 79.5 (4-C), 48.4 (1-C), 35.0 (5-C), 26.7 (*i*Pr), 24.4 (*i*Pr), 21.1 (CH$_3$) ppm. IR: $\tilde{\nu}$ = 2958, 2926, 2856, 1729, 1271, 1072, 702 cm^{-1}. HRMS (ESI): calcd. for C$_{12}$H$_{19}$O$_4$ [M + H]$^+$ 226.2712; found 226.2707.

(*1R*,2*R*,3*R*,4*R*)-4-*tert*-Butyldimethylsiloxy-2,3-(*O*-isopropylidenedioxy)-1-vinylcyclopentane (5): K$_2$CO$_3$ (1.72 g, 12.4 mmol) was added to a solution of **4** (1.4 g, 6.2 mmol) in MeOH (20 mL) at room temperature and stirred for 1 h. Then, the reaction mixture was neutralized with acetic acid, poured in aqueous saturated NaHCO$_3$, and extracted with CH$_2$Cl$_2$. The organic layer was dried with MgSO$_4$, filtered, and concentrated. The residue was dissolved in MeCN (40 mL) and TBDPSCl (1.88 g, 6.8 mmol), DMAP (0.84 g, 6.8 mmol), and imidazole (0.46 g, 6.8 mmol) were added at room temperature under positive pressure of dry argon. After 15 h stirring, the solution was neutralized with aqueous saturated NaHCO$_3$ and extracted with AcOEt. The organic layer was dried with MgSO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/AcOEt, 30:1) to obtain **5** (2.2 g, 84%) as an oil. $[\alpha]_D^{20}$ = +0.9 (*c* = 1.0, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71–7.65 (m, 4 H, H$_{ar}$), 7.45–7.35 (m, 6 H, H$_{ar}$), 6.04 (ddd, *J* = 17.3, 10.2, 8.3 Hz, 1 H, C*H*=CH$_2$), 5.06 (ddd, *J* = 17.2, 1.6, 1.3 Hz, 1 H, CH=C*H*$_2$), 5.01 (ddd, *J* = 10.6, 1.6, 1.1 Hz, 1 H, CH=C*H*$_2$), 4.53 (d, *J* = 6.3 Hz, 1 H, 2-H or 3-H), 4.49 (dd, *J* = 6.3, 2.6 Hz, 1 H, 2-H or 3-H), 4.26 (ddd, *J* = 5.6, 4.0, 1.6 Hz, 1 H, 4-H), 2.69–2.59 (m, 1 H, 1-H), 2.05 (ddd, *J* = 13.0, 7.4, 5.3 Hz, 1 H, 5-H$_a$), 1.61 (td, *J* = 13.4, 5.1 Hz, 1 H, 5-H$_b$), 1.36 (s, 3 H, *i*Pr), 1.25 (s, 3 H, *i*Pr), 1.07 (s, 9 H, *t*Bu) ppm. ^{13}CNMR (100.6 MHz, CDCl$_3$): δ = 140.6 (*C*H=CH$_2$), 135.8 (C$_{ar}$), 133.8 (C$_{ar}$), 133.6 (C$_{ar}$), 129.6 (C$_{ar}$), 127.6 (C$_{ar}$), 114.5 (CH=*C*H$_2$), 110.7 (quat., C*i*Pr), 87.6 (2-C or 3-C), 85.2 (2-C or 3-C), 78.8 (4-C), 49.0 (1-C), 38.2 (5-C), 26.9 (*t*Bu), 26.8 (*i*Pr), 24.5 (*i*Pr), 19.1 (*t*Bu) ppm. IR: $\tilde{\nu}$ = 2931, 2857, 1371, 1064, 700 cm^{-1}. HRMS (ESI): calcd. for C$_{26}$H$_{34}$O$_3$NaSi [M + Na]$^+$ 445.2175; found 445.2174.

(1*R*,2*R*,3*R*,4*R*)-1-Aldoxime-4-*tert*-butyldiphenylsiloxy-2,3-(*O*-isopropylidenedioxy)cyclopentane (6): To a mixture of silyl ether **5** (2.20 g, 5.2 mmol) and NaIO$_4$ (2.23 g, 10.4 mmol) in MeOH was added acetone, H$_2$O (1:1:1, 200 mL), and OsO$_4$ (820 μL, 2.5% in *t*BuOH) at room temperature. After 15 h stirring, the reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. CH$_2$Cl$_2$ was added, and the solution was washed with brine, dried (MgSO$_4$), filtered, and concentrated. Without further purification, hydroxylamine hydrochloride (1.46 g, 20.8 mmol), NaOAc (2.56 g, 21.3 mmol), and EtOH/CH$_2$Cl$_2$ (1:3, 45 mL) was added at room temperature under positive pressure of dry argon, and the mixture was stirred for 2 h. Then the reaction mixture was washed with brine and extracted with CH$_2$Cl$_2$. The organic layer was dried (MgSO$_4$), filtered, and concentrated. The residue was purified by silica gel chromatography (petroleum ether/AcOEt, 3:1) to give **6** (1.69 g, 74%) as an oil as an isomeric mixture of the oxime (*E*/*Z* = 1:1). $[\alpha]_D^{20}$ = +2.7 (*c* = 1.4, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$, *E*/*Z* isomers): δ = 7.70–7.62 (m, 12 H, H$_{ar}$ and C*H*=N-OH), 4.79 (dd, *J* = 19.7, 5.6 Hz, 2 H, 2-H or 3-H), 4.33 (d, *J* = 3.6 Hz, 1 H, 4-H), 2.96–2.90 (m, 1 H, 1-H), 2.18–2.11 (m, 2 H, 5-H), 1.26 (s, 3 H, *i*Pr), 1.25 (s, 3 H, *i*Pr), 1.10 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$, *E*/*Z* isomers): δ = 154.0 (*C*H=N-OH), 135.8 (C$_{ar}$), 135.7 (C$_{ar}$), 133.4 (C$_{ar}$), 133.3 (C$_{ar}$), 129.8 (C$_{ar}$), 129.7 (C$_{ar}$), 110.3 (quat., C*i*Pr), 87.1 (2-C or 3-C), 84.2 (2-C or 3-C), 78.4 (4-C), 45.3 (1-C), 36.4 (5-C), 26.9 (*t*Bu), 26.8 (*i*Pr), 24.2 (*i*Pr), 19.0 (*t*Bu) ppm. IR: $\tilde{\nu}$ = 3404, 2961, 2923, 1259, 1087, 1017, 797 cm^{-1}. HRMS (ESI): calcd. for C$_{25}$H$_{33}$NO$_4$NaSi [M + Na]$^+$ 462.2077; found 462.2073.

(1*S*,2*R*,3*R*,4*R*)-4-*tert*-Butyldiphenylsiloxy-1-(benzoxazol-2-yl)-2,3-(*O*-isopropylidenedioxy)cyclopentane (8): A mixture of **6** (250 mg, 0.566 mmol), *N*-chlorosuccinimide (77 mg, 0.577 mmol), and pyridine (30 μL) in freshly distilled CHCl$_3$ (8 mL) was heated at 40 °C for 40 min under positive pressure of dry argon. The reaction mixture was then concentrated and EtOH (16 mL) and α-aminophenol (127 mg, 1.16 mmol) were added, and the mixture was heated at 60 °C for 2 h under positive pressure of dry argon. The mixture was diluted in CH$_2$Cl$_2$ and washed with brine, dried (MgSO$_4$), filtered, and concentrated under reduced pressure. The crude was purified by flash chromatography (petroleum ether/AcOEt, 7:1) to afford **8** (218 mg, 75%) as an oil. $[\alpha]_D^{20}$ = +30.8 (*c* = 0.8, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.69 (dd, *J* = 6.4, 2.5 Hz, 1 H, H$_{ar}$), 7.54–7.50 (m, 2 H, H$_{ar}$), 7.47–7.43 (m, 3 H, H$_{ar}$), 7.40–7.23 (m, 8 H, H$_{ar}$), 5.60 (dd, *J* = 5.9, 1.1 Hz, 1 H, 2′-H or 3′-H), 4.60 (d, *J* = 5.9 Hz, 1 H, 2′-H or 3′-H), 4.28 (t, *J* = 3.1 Hz, 1 H, 4′-H), 3.56–3.49 (m, 1 H, 1′-H), 2.44–2.34 (m, 2 H, 5′-H), 1.39 (s, 3 H, *i*Pr), 1.30 (s, 3 H, *i*Pr), 0.73 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 167.2 (C=N), 150.8, 141.4, 135.7, 135.6 and 133.3 (C$_{ar}$), 129.6, 127.6, 127.5, 124.5, 124.1, 119.6 and 110.6 (C$_{ar}$), 110.3 (*i*Pr), 86.8 (2′-C or 3′-C), 82.4 (2′-C or 3′-C), 78.2 (4′-C), 44.4 (1′-C), 36.2 (5′-C), 26.4 (*i*Pr and *t*Bu), 24.2 (*i*Pr), 18.7 (*t*Bu) ppm. IR: $\tilde{\nu}$ = 2931, 2857, 2361, 1456, 1044, 702 cm^{-1}. HRMS (ESI): calcd. for C$_{31}$H$_{35}$NO$_4$NaSi [M + Na]$^+$ 536.2233; found 536.2234.

(1*S*,2*R*,3*R*,4*R*)-4-*tert*-Butyldiphenylsiloxy-1-(benzimidazol-2-yl)-2,3-(*O*-isopropylidenedioxy)cyclopentane (9): A mixture of **6** (285 mg, 0.65 mmol), *N*-chlorosuccinimide (90 mg, 0.66 mmol), and pyridine (35 μL) in freshly distilled CHCl$_3$ (6 mL) was heated for 40 min under positive pressure of dry argon. After concentration of the solution under reduced pressure, EtOH (22 mL) and α-phenylenediamine (176 mg, 1.63 mmol) were added, and the mixture was

heated at 60 °C for 2 h under positive pressure of dry argon. The reaction mixture was diluted in CH_2Cl_2 and washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude was purified on silica gel chromatography (petroleum ether/AcOEt, 2:1) to afford **9** (278 mg, 85%) as a foam. $[\alpha]_D^{20}$ = +9.7 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.50 (s, 1 H, NH), 7.77–7.65 (m, 3 H, H_{ar}), 7.62 (dd, *J* = 8.00, 1.32 Hz, 2 H, H_{ar}), 7.50–7.35 (m, 6 H, H_{ar}), 7.24–7.05 (m, 3 H, H_{ar}), 4.91 (d, *J* = 5.6 Hz, 1 H, 2′-H or 3′-H), 4.59 (d, *J* = 5.6 Hz, 1 H, 2′-H or 3′-H), 4.53 (d, *J* = 4.5 Hz, 1 H, 4′-H), 3.75 (d, *J* = 8.7 Hz, 1 H, 1′-H), 2.56 (ddd, *J* = 14.6, 8.7, 5.5 Hz, 1 H, 5′-H_a), 2.09 (d, *J* = 14.6 Hz, 1 H, 5′-H_b), 1.38 (s, 3 H, *i*Pr), 1.19 (s, 3 H, *i*Pr), 1.16 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 155.5 (C=N), 135.8, 135.7, 132.6, 132.4, 130.2 (2 C) and 128.0 (2 C, C_{ar}), 110.8 (*i*Pr), 87.6 (2′-C or 3′-C), 85.6 (2′-C or 3′-C), 80.1 (4′-C), 46.3 (1′-C), 36.0 (5′-C), 27.2 (*t*Bu), 26.6 and 24.2 (*i*Pr), 19.2 (*t*Bu) ppm. IR: ṽ = 2930, 2856, 1737, 1426, 1042, 700 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{37}N_2O_3Si$ [M + H]$^+$ 513.2574; found 513.2560.

(1*S*,2*R*,3*R*,4*R*)-4-*tert*-Butyldiphenylsiloxy-1-(benzothiazol-2-yl)-2,3-(*O*-isopropylidenedioxy)cyclopentane (10a): A mixture of **6** (255 mg, 0.577 mmol), *N*-chlorosuccinimide (78.6 mg, 0.589 mmol), and pyridine (30 μL) in freshly distilled $CHCl_3$ (8 mL) was heated and stirred during 40 min under positive pressure of dry argon. The solvent was evaporated, then EtOH (16 mL) and α-aminothiophenol (148 mg, 1.18 mmol) were added, and the mixture was heated at 60 °C for 2 h under positive pressure of dry argon. The reaction mixture was diluted in CH_2Cl_2 and washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude was purified on silica gel chromatography (petroleum ether/AcOEt, 7:1) to afford **10b** (15 mg, 5%) and **10a** (229 mg, 75%) as a solid. M.p. 107–109 °C. $[\alpha]_D^{20}$ = +25.7 (*c* = 0.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.97 (m, 1 H, H_{ar}), 7.83–7.79 (m, 1 H, H_{ar}), 7.60–7.56 (m, 2 H, H_{ar}), 7.49–7.29 (m, 10 H, H_{ar}), 7.23 (t, *J* = 7.4 Hz, 2 H, H_{ar}), 5.44 (dd, *J* = 6.2, 2.6 Hz, 1 H, 2′-H or 3′-H), 4.63 (d, *J* = 6.19 Hz, 1 H, 2′-H or 3′-H), 4.34–4.31 (m, 1 H, 4′-H), 3.62 (ddd, *J* = 7.9, 5.4, 2.7 Hz, 1 H, 1′-H), 2.45 (ddd, *J* = 13.0, 7.8, 5.0 Hz, 1 H, 5′-H_a), 2.33–2.26 (ddd, *J* = 13.5, 5.1, 7.4 Hz, 1 H, 5′-H_b), 1.42 (s, 3 H, *i*Pr), 1.31 (s, 3 H, *i*Pr), 0.84 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz,$CDCl_3$): δ = 173.0 (C=N), 153.1, 135.7, 135.6, 135.1, 133.5, 133.4, 129.6, 129.5, 127.5, 127.4, 125.8, 124.6, 122.7 and 121.3 (C_{ar}), 111.2 (C*i*Pr), 86.9 (2′-C or 3′-C), 83.8 (2′-C or 3′-C), 78.3 (4′-C), 49.3 (1′-C), 39.4 (5′-C), 26.7 (*i*Pr), 26.5 (*t*Bu), 24.5 (*i*Pr), 18.9 (*t*Bu) ppm. IR: ṽ = 2972, 2925, 1427, 1042 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{36}NO_3SSi$ [M + H]$^+$ 530.2185; found 530.2195.

(1*R*,2*R*,3*R*,4*R*)-4-*tert*-Butyldiphenylsiloxy-1-(benzothiazol-2-yl)-2,3-(*O*-isopropylidenedioxy)cyclopentane (10b): A mixture of **6** (93 mg, 0.210 mmol), *N*-chlorosuccinimide (29 mg, 0.214 mmol), and pyridine (10 μL) in freshly distilled $CHCl_3$ (3 mL) was heated for 40 min under positive pressure of dry argon. After evaporation of all of volatiles, EtOH (6 mL) and α-aminothiophenol (54 mg, 0.43 mmol) were added, and the mixture was heated at 60 °C for 24 h under positive pressure of dry argon. The solvent was evaporated to dryness and the crude was purified by silica gel chromatography (petroleum ether/AcOEt, 7:1) to give **10a** (30 mg, 27%) and **10b** (58 mg, 0.109 mmol, 52%) as an oil. $[\alpha]_D^{20}$ = +39.1 (*c* = 0.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.06 Hz, 1 H, H_{ar}), 7.84 (d, *J* = 7.98 Hz, 1 H, H_{ar}), 7.69–7.62 (m, 4 H, H_{ar}), 7.48–7.31 (m, 8 H, H_{ar}), 5.03 (t, *J* = 5.0 Hz, 1 H, 3′-H), 4.58 (dd, *J* = 5.3, 1.4 Hz, 1 H, 2′-H), 4.30 (d, *J* = 3.4 Hz, 1 H, 1′-H), 4.20 (td, *J* = 13.0, 5.5 Hz 1 H, 4′-H), 2.25 (td, *J* = 13.0, 3.60 Hz, 1 H, 5′-H_a), 2.06 (td, *J* = 13.0, 3.6 Hz, 1 H, 5′-H_b), 1.39 (s, 3 H, *i*Pr), 1.24 (s, 3 H, *i*Pr), 1.09 (d, 9 H, *t*Bu) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.6 (C=N), 152.6, 135.6, 135.4, 133.4 (2 C), 129.8 (2 C), 127.7 (2 C), 125.7, 124.6, 122.6 and 121.3 (C_{ar}), 110.9 (C*i*Pr), 86.8 (2′-C), 80.8 (3′-C), 76.1 (4′-C), 46.4 (1′-C), 37.3 (5′-C), 26.9 (*t*Bu), 25.7 (*i*Pr), 23.9 (*i*Pr), 19.1 (*t*Bu) ppm. IR: ṽ = 2930, 1428, 1162, 1066 cm^{-1}. HRMS (ESI): calcd. for $C_{31}H_{36}NO_3SSi$ [M + H]$^+$ 530.2185; found 530.2195.

(1*S*,2*R*,3*S*,4*R*)-1-Benzoxazol-2-yl-cyclopentane-2,3,4-triol (11): To a 1,4-dioxane (3 mL) solution of **8** (144 mg, 0.28 mmol) was added 2 N HCl (1 mL) at room temperature, and the reaction mixture was stirred for 48 h. Then, $NaHCO_3$ was added, and the solution was evaporated to dryness. The crude was purified by flash chromatography (CH_2Cl_2/MeOH, 5:1) to give **11** (48 mg, 78%) as an amorphous solid. $[\alpha]_D^{20}$ = +31.2 (*c* = 0.2, CH_3OH). ^{1}H NMR (400 MHz, CD_3OD): δ = 7.77 (dd, *J* = 8.0, 1.5 Hz, 1 H, H_{ar}), 7.00–6.93 (m, 1 H, H_{ar}), 6.88–6.75 (m, 2 H, H_{ar}), 4.32 (dd, *J* = 8.0, 4.9 Hz, 1 H, 2′-H), 4.02 (ddd, *J* = 7.2, 4.7, 2.9 Hz, 1 H, 4′-H), 3.83 (dd, *J* = 4.7, 2.9 Hz, 1 H, 3′-H), 2.97 (dd, *J* = 17.8, 8.4 Hz, 1 H, 1′-H), 2.43 (ddd, *J* = 13.9, 9.6, 7.0 Hz, 1 H, 5′-H_a), 1.80 (ddd, *J* = 13.6, 8.5, 4.7 Hz, 1 H, 5′-H_b) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 175.6 (C=N), 149.2, 127.5, 126.3, 123.1, 120.6 and 116.9 (C_{ar}), 79.7 (3′-C), 76.5 and 76.2 (2′-C and 4′-C), 50.0 (1′-C), 34.4 (5′-C) ppm. IR: ṽ = 3331, 2955, 2925, 1658, 1384, 1196 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}NO_4$ [M + H]$^+$ 236.0936; found 236.0944.

(1*S*,2*R*,3*S*,4*R*)-1-Benzimidazol-2-yl-cyclopentane-2,3,4-triol (12): To a 1,4-dioxane (3 mL) solution of **9** (92 mg, 0.179 mmol) was added 2 N HCl (1 mL) at room temperature, and the reaction mixture was stirred for 48 h. Then, $NaHCO_3$ was added, and the solution was evaporated to dryness. The crude was purified by flash chromatography (CH_2Cl_2/MeOH, 5:1) to give **12** (40 mg, 95%) as an amorphous solid. $[\alpha]_D^{20}$ = +72.6 (*c* = 0.6, CH_3OH). ^{1}H NMR (400 MHz, CD_3OD): δ = 7.57–7.46 (m, 2 H, H_{ar}), 7.23–7.13 (m, 2 H, H_{ar}), 4.42 (dd, *J* = 8.1, 5.1 Hz, 1 H, 2′-H), 4.11 (ddd, *J* = 7.2, 5.3, 3.1 Hz, 1 H, 4′-H), 3.92 (dd, *J* = 5.0, 3.1 Hz, 1 H, 3′-H), 3.40 (dd, *J* = 17.6, 9.2 Hz, 1 H, 1′-H), 2.64 (ddd, *J* = 13.8, 9.3, 7.1 Hz, 1 H, 5′-H_a), 1.88 (ddd, *J* = 14.4, 9.4, 5.3 Hz, 1 H, 5′-H_b) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 158.3 (C=N), 139.8, 139.7, 123.3 and 115.5 (2 C, C_{ar}), 79.5 (3′-C), 77.5 (2′-C), 76.8 (4′-C), 44.0 (1′-C), 36.8 (5′-C) ppm. IR: ṽ = 3314, 2920, 1454, 1116, 1053 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{15}N_2O_3$ [M + H]$^+$ 235.1083; found 235.1073.

(1*S*,2*R*,3*S*,4*R*)-1-Benzothiazol-2-yl-cyclopentane-2,3,4-triol (13): To a 1,4-dioxane (3 mL) solution of **10a** (104 mg, 0.196 mmol) was added 2 N HCl (1 mL) at room temperature, and the reaction mixture was stirred for 48 h. Then, the reaction mixture was neutralized with $NaHCO_3$, and the solution was evaporated to dryness. The crude was purified by flash chromatography (CH_2Cl_2/MeOH, 5:1) to give **13** (48 mg, 97%) as an amorphous solid. $[\alpha]_D^{20}$ = +72.5 (*c* = 0.4, CH_3OH). ^{1}H NMR (400 MHz, CD_3OD): δ = 7.99–7.88 (t, *J* = 7.8 Hz, 2 H, H_{ar}), 7.52–7.45 (td, *J* = 7.5, 1.2 Hz, 1 H, H_{ar}), 7.43–7.36 (m, *J* = 7.5, 1.2 Hz, 1 H, H_{ar}), 4.41 (dd, *J* = 8.2, 4.9 Hz, 1 H, 2′-H), 4.12 (ddd, *J* = 7.2, 4.7, 2.8 Hz, 1 H, 4′-H), 3.92 (dd, *J* = 4.7, 2.8 Hz, 1 H, 3′-H), 3.63 (td, *J* = 9.1, 8.4 Hz, 1 H, 1′-H), 2.74 (ddd, *J* = 13.9, 9.5, 7.0 Hz, 1 H, 5′-H_a), 1.95 (ddd, *J* = 13.6, 9.0, 4.5 Hz, 1 H, 5′-H_b) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 176.7 (C=N), 154.1, 136.2, 127.3, 126.2, 123.1 and 122.9 (C_{ar}), 79.6 (3′-C), 79.0 (2′-C), 76.5 (4′-C), 48.7 (1′-C), 38.3 (5′-C) ppm. IR: ṽ = 3316, 2922, 1657, 1113, 1048 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}NO_3S$ [M + H]$^+$ 252.0694; found 252.0687.

(3*R*,4*R*)-1-Benzothiazol-2-yl-cyclopent-1-ene-3,4-diol (15): A solution of protected nucleoside **10b** (30 mg, 0.056 mmol) in 1 M HCl (1 mL) in Et_2O was stirred for 18 h. Then, the reaction mixture was neutralized with $NaHCO_3$, and the organic layer was dried, filtered, and concentrated under reduced pressure. The residue was purified

by flash chromatography (CH_2Cl_2/MeOH, 6:1) to afford **15** (13.0 mg, 97%) as an amorphous solid. $[\alpha]_D^{20}$ = +21.7 (c = 0.4, CH_3OH). ^1H NMR (400 MHz, CD_3OD): δ = 8.00–7.95 (dd, J = 7.8, 4.8 Hz, 2 H, H_{ar}), 7.52 (t, J = 7.8 Hz, 1 H, H_{ar}), 7.44 (t, J = 7.8 Hz, 1 H, H_{ar}), 6.59 (d, J = 1.9 Hz, 1 H, 2′-H), 4.74–4.70 (m, 1 H, 3′-H), 4.59 (s, 2 H, OH), 4.32 (td, J = 6.8, 4.2 Hz, 1 H, 4′-H), 3.36 (tdd, J = 16.5, 7.1, 1.5 Hz, 1 H, 5′-H_a), 2.76 (tdd, J = 16.5, 4.5, 1.5 Hz, 1 H, 5′-H_b) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 166.1 (C=N), 154.6 and 139.1 (C_{ar}), 136.7 (2′-C), 135.9 (1′-C), 127.7 (C_{ar}), 127.1 (C_{ar}), 123.9 (C_{ar}), 123.0 (C_{ar}), 84.5 (4′-C), 80.2 (3′-C), 41.1 (5′-C) ppm. IR: $\tilde{\nu}$ = 3393, 2958, 2927, 1713, 1679, 1640, 1461 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{12}NO_2S$ $[M + H]^+$ 234.0589; found 234.0584.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for described compounds.

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