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A Chiron Approach to Aminocytitols by Petasis-Borono-Mannich Reaction: Formal Synthesis of (+)-Conduramine E and (−)-Conduramine E

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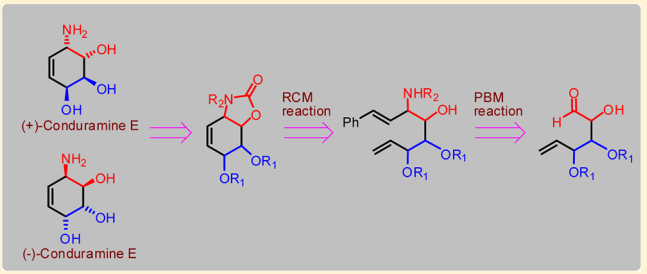
Supporting Information

ABSTRACT: A chiron approach to a stereoselective route for the synthesis of aminocytitols from carbohydrates is described. The formal synthesis of (+)-conduramine E and (−)-conduramine E was achieved by utilizing this strategy. The key features of the synthetic strategy include one-pot three-component Petasis-Borono-Mannich reaction to introduce the *syn*-*β*-amino alcohol functionality of conduramine E and ring-closing metathesis to construct its carbocyclic core. The present synthetic approach paves the way for stereoselective synthesis of several conduramines starting from carbohydrates.



Aminocyclohexenetriols formally called conduramines are the amino derivatives of conduritols, in which an amino functionality is present in place of one of the hydroxyl groups (Figure 1). These densely functionalized aminocyclitols and

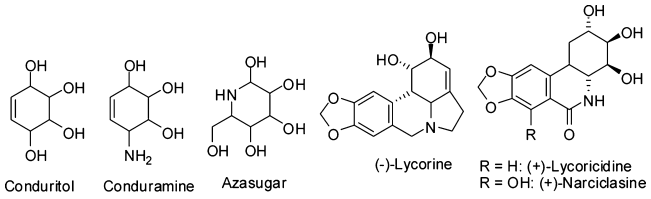


Figure 1. Structure of some important aminocytitols.

structurally related compounds form the basic skeleton of pseudo oligosaccharides and several complex aminoglycoside antibiotics.[1−3] Such units are also the synthetic precursors of pharmacologically important molecules such as Pancratistatin,[4] (+)-lycoricidine,[5] (+)-narciclasine,[6] and (−)-lycorine,[7] with important bioactivities such as antibacterial, antihypertensive, platelet-inhibiting, and cytotoxic (Figure 1). In addition, utilization of aminocyclitols for the syntheses of azasugars,[8] aminosugars,[9] sphingosines,[10] and narcissus alkaloids[11] amplified their importance as synthetic building blocks. Therefore, several elegant approaches to the synthesis of racemic as well as optically pure aminocyclitols and their structural variants have been disclosed to date.[12−27] Very recently Norsikian et al. disclosed a novel approach to conduramines starting from carbohydrate via an unprecedented intramolecular Petasis-Borono-Mannich reaction with an exclusive *anti* stereoselectivity for the newly created *β*-amino alcohol motif.[28]

The interesting structural features associated with biological activities and also as a result of our involvement toward the synthesis of carbohydrate-based chiral building blocks (CBBs)[29] and their exploitation in syntheses of natural products or natural-product-like molecules of significant biological importance[30−36] prompted us to develop an efficient methodology for synthesis of enantiomerically pure aminocyclohexenetriols by a chiron approach. Herein, we wish to disclose a short and efficient formal synthesis of both enantiomers of conduramine E (Figure 2) from carbohydrates involving Petasis-Borono-Mannich (PBM) chemistry[37−41] and ring-closing metathesis.

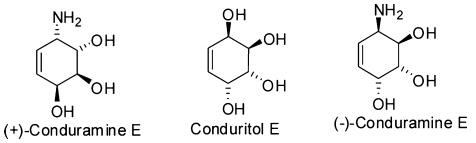


Figure 2. Structures of conduritol E, (+)-conduramine E, and (−)-conduramine E.

The synthesis of (+)-conduramine E was commenced with the selective acetonide protection of hydroxyls at C3 and C4 in methyl-*α*-D-galactopyranoside **1** to give 3,4-*O*-isopropylidine-methyl-*α*-D-galactopyranoside **2** (Scheme 1). Iodination of the primary alcohol was carried out by treating the diol **2** under Garegg and Samuelsson conditions to obtain the iodide **3**, which on treatment with Zn dust in the presence of a catalytic amount cyanocobalamine[42] (vitamin B_{12}) gave the required hydroxy aldehyde **4**, but unfortunately the *α*-hydroxy aldehyde **4** was unstable (Scheme 1).

At this stage, we modified our synthetic strategy by protecting the remaining hydroxyl group at C2 in **3** as its

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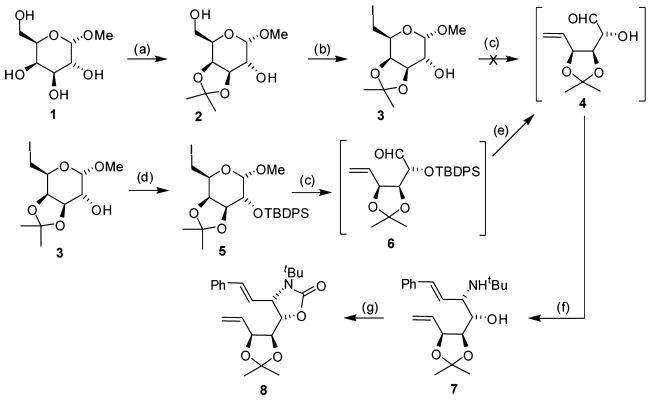
Scheme 1. Synthesis of Oxazolidinone 8[a]



[a]Reagent and conditions: (a) I_2, acetone, 4 h, 70%; (b) I_2, PPh_3, imidazole, toluene, 80 °C, 3 h, 82%; (c) Zn, NH_4Cl, vit. B_{12}, MeOH, 5 min; (d) TBDPSCl, imidazole, DCM, 6 h, 85%; (e) TBAF, EtOH, 30 min; (f) *trans*-2-phenylvinyl boronic acid, $^tBuNH_2$, 80 °C, 24 h; (g) $(Boc)_2O$, Et_3N, DMAP, THF, rt, 12 h, 15% over three steps.

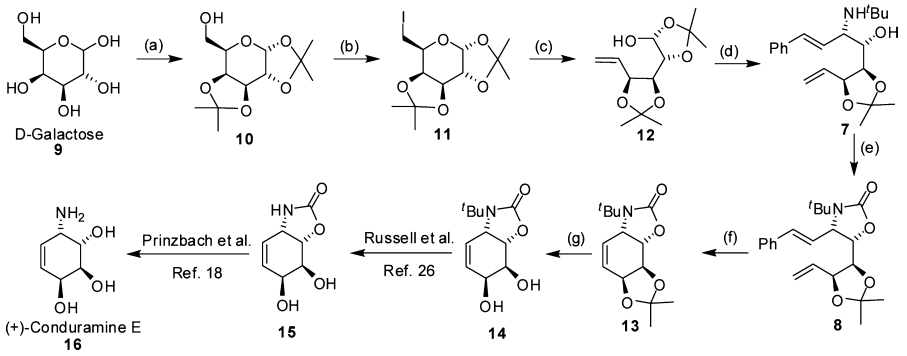
silyl ether. Thus, the iodide **3** was protected as its silyl ether **5**, which on Zn-dust-mediated ring opening in the presence of catalytic amount cyanocobalamine afforded the stereochemically pure silyl protected hydroxy aldehyde **6**. It was then subjected to one-pot desilylation by TBAF followed by PBM reaction of the resulting aldehyde **4** with *trans*-2-phenylvinyl boronic acid and *tert*-butylamine under refluxing condition to obtain the unsaturated amino alcohol **7** (Scheme 1). Since it is well documented in the literature that the chiral α-hydroxy aldehyde furnishes the corresponding *erythro*-1,2 amino alcohol as a single diastereomer,[41] herein the *erythro*-1,2 amino alcohol **7** was also obtained exclusively as a single diastereoismer from the aldehyde **6**. Unfortunately, we could not isolate **7** in its pure form by column chromatographic purification of the crude reaction product (TLC). At this stage, the amino group in **7** was protected by treating it with $(Boc)_2O$ in THF in the presence of Et_3N and DMAP. Here, the Boc protection of the amine **7** with simultaneous oxazolidinone ring formation furnished the oxazolidinone **8** with low yield (15%) in three steps (Scheme 1).

The low yield of **8** was presumably attributed to the instability of the α-hydroxy aldehyde intermediate **4**, and therefore to evade this problem we decided to start our synthetic strategy from D-galactose **9**. Thus, the 1,2;3,4-di-*O*-isopropylidine-α-D-galactopyranoside[43] **10** prepared from **9** on iodination furnished iodide **11** in 86% yield. Its reaction with Zn dust in the presence of a catalytic amount of cyanocobalamine smoothly afforded the hemiacetal **12**, which was then subjected to PBM reaction with *trans*-2-phenylvinyl boronic acid and *tert*-butylamine to afford exclusively the *erythro*-1,2 amino alcohol **7**. Its treatment with $(Boc)_2O$ in THF in the presence of Et_3N/DMAP furnished the oxazolidinone **8** in 40% yield over two steps (Scheme 2). The cyclization of **8** was achieved by using ring-closing metathesis reaction in the presence of Grubbs second generation catalyst to afford conduramine core **13**. Cleavage of the acetonide protection in **13** was done by treating it with TFA to obtain diol **14**, a known intermediate reported by Russell et al. during (±)-conduramine E synthesis.[26] Its spectral data was in close agreement with the data reported by Russell et al. Now, the synthesis of (+)-conduramine E **16** could be completed by TFA-mediated ^tBu deprotection[26] of **14** followed by basic hydrolysis of the oxazolidinone ring[18] in **15** by adopting the procedure reported by Prinzbach et al. (Scheme 2).

We were also interested in synthesis of (−)-conduramine E (**29**), the enantiomer of (+)-conduramine E, involving the PBM reaction on masked α-hydroxy aldehyde of the type **22**. We achieved our goal by adopting the synthetic strategy shown in Scheme 3. Thus, the 2,3;5,6-di-*O*-isopropylidine-α-D-mannofuranose hemiacetal **18** prepared from D-mannose **17** by the standard literature procedure (I_2/acetone)[44] was subjected to undergo Wittig methylenation on anomeric carbon to furnish the alkene **19**. The free hydroxyl group in **19** was protected with TBDPSCl to afford silyl ether **20**. The selective deprotection of terminal acetonide in **20** was done by treating it with 80% aqueous AcOH to obtain the diol **21** (Scheme 3). Its oxidative cleavage with $NaIO_4$ afforded an aldehyde **22**, which was desilylated with TBAF followed by PBM reaction of the resulting α-hydroxy aldehyde **23** with *trans*-2-phenylvinyl boronic acid and *tert*-butylamine under refluxing condition to afford the desired amine **24** in a one-pot fashion. Its protection with $(Boc)_2O$ in THF in the presence of Et_3N/DMAP furnished the oxazolidinone **25** (Scheme 3).

The diene **25** was the enantiomer of diene **8**. The NMR spectra of these two enantiomers (**8** and **25**) were identical, and their optical rotation values were close in magnitude but opposite in sign {$[\alpha]^{28}_D$ = −55.3 (*c* 0.77, $CHCl_3$) for **8**; $[\alpha]^{26}_D$

Scheme 2. Formal Synthesis of (+)-Conduramine E 16[a]



[a]Reagent and conditions: (a) I_2, acetone, 24 h, 80%; (b) I_2, PPh_3, imidazole, toluene, 80 °C, 3 h, 86%; (c) Zn, NH_4Cl, Vit. B_{12}, MeOH, 15 min, 90%; (d) *trans*-2-phenylvinyl boronic acid, $^tBuNH_2$, EtOH, rt, 24 h; (e) $(Boc)_2O$, Et_3N, DMAP, THF, rt, 12 h, 40% over two steps; (f) Grubbs second generation catalyst (10 mol %), DCM, reflux, 24 h, 51%; (g) TFA, DCM, 2 h then H_2O, 1 h, 85%.

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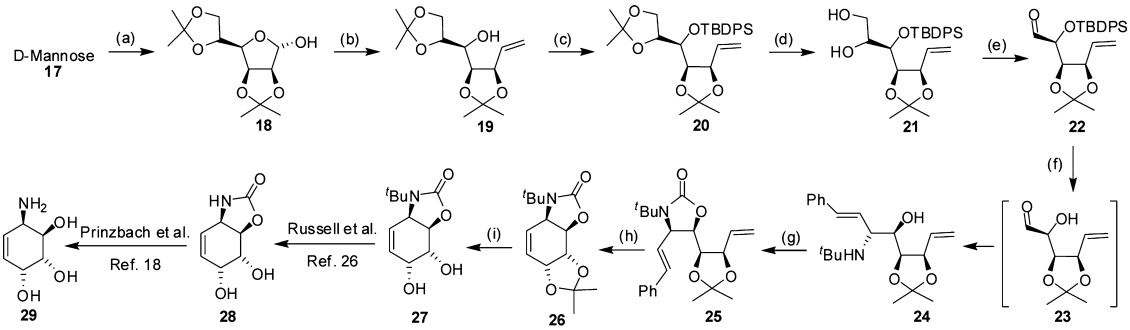
Scheme 3. Formal Synthesis of (−)-Conduramine E 29[a]



[a]Reagent and conditions: (a) I_2, acetone, rt, 24 h, 80% ; (b) Ph_3PCH_3Br, ^tBuOK, THF, −20 °C, 4 h, 85%; (c) TBDPSCl, imidazole, DMF, rt, 24 h, 87%; (d) 80% AcOH, rt, 6 h, 75%; (e) $NaIO_4$, THF/H_2O (9:1), 0 °C to rt, 1.5 h; (f) TBAF, EtOH, 30 min then *trans*-2-phenylvinyl boronic acid, $^tBuNH_2$, 80 °C, 24 h; (g) $(Boc)_2O$, Et_3N/DMAP (3:1), 0 °C to rt, 12 h, 21% from **21**; (h) Grubbs second generation catalyst (10 mol %), DCM, reflux, 24 h, 48%; (i) TFA, DCM, 2 h then H_2O, 91%.

= +66.0 (*c* 0.24, $CHCl_3$) for **25**}. Ring-closing metathesis of diene **25** in the presence of Grubbs second generation catalyst under refluxing condition furnished the required carbocyclic core of (−)-conduramine E **26** (Scheme 3). Finally, the isopropylidene protection in **26** was easily cleaved by treating it with TFA to furnish the diol **27** in 91% yield, from which the (−)-conduramine E **29** could be obtained via **28** by following the procedure reported by Russell et al.[26] Here, it was worth mentioning that **26** and **27** were the enantiomers of **13** and **14**, respectively. The values for their optical rotations were close in magnitude but opposite in sign {$[\alpha]^{28}_D$ = +124.2 (*c* 0.125, $CHCl_3$) for **13** and $[\alpha]^{26}_D$ = −134.0 (*c* 0.112, $CHCl_3$) for **26**}{$[\alpha]^{28}_D$ = +78.5 (*c* 0.23, $CHCl_3$) for **14** and $[\alpha]^{26}_D$ = −73.7 (*c* 0.16, $CHCl_3$) for **27**}.

Here, it is worth mentioning that in our present approach the *syn*-*β*-amino alcohol motif of conduramine E was installed via an intermolecular Petasis-Borono-Mannich reaction, whereas Norsikian et al. disclosed a novel approach to synthesize *anti*-*β*-amino alcohol motif of conduramine C-4 and *ent*-conduramine A-1 by utilizing intramolecular Petasis-Borono-Mannich reaction.[28] Carbohydrates were utilized as a starting material in both the cases.

In summary, we developed a convenient chiron approach to the formal synthesis of both the enantiomers of conduramine E. The commercially available monosaccharides were utilized as starting material to complete the synthesis of key oxazolidinone fused carbocyclic intermediates (**13** and **26**) involving highly diastereoselective Petasis-Borono-Mannich (PBM) and ring-closing metathesis (RCM) reactions. Several aminocytitols could also be synthesized by using this flexible approach starting from carbohydrates.

EXPERIMENTAL SECTION

Compound 2. To a stirred suspension of methyl-*α*-D-galactopyranoside **1** (500 mg, 2.57 mmol) in dry acetone (10 mL) was added I_2 (130 mg, 0.5 mmol) at room temperature, and the reaction was allowed to stir at same temperature for 4 h. After completion of the reaction, excess iodine was quenched with saturated aqueous solution of $Na_2S_2O_3$ and the resulting mixture was concentrated. The reaction mixture was then extracted with EtOAc (3 × 20 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to a residue that on purification by column chromatography gave 2,3-*O*-isopropylidine-methyl-*α*-D-galactopyranoside **2** (420 mg, 1.8 mmol, 70%).

Eluent for column chromatography: EtOAc/hexane (2/1, v/v); $[\alpha]^{27}_D$ = +156.7 (*c* 0.8, $CHCl_3$); R_f = 0.25 (2/1, EtOAc/hexane); IR (neat, cm^{-1}) 3336, 2864, 1639, 1222, 1076, 770; ^1H NMR (300 MHz, $CDCl_3$) *δ* 1.28 (s, 3H), 1.44 (s, 3H), 2.83 (s, 1H, OH), 3.11 (m, 1H, OH), 3.39 (s, 3H), 3.72−3.76 (m, 2H), 3.82−3.89 (m, 1H), 3.97−3.99 (m, 3H), 4.17−4.18 (m, 2H), 4.71 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) *δ* 26.2, 28.0, 55.8, 62.7, 68.4, 69.9, 74.1, 76.6, 99.1, 110.0; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{19}O_6$ 235.1182, found 235.1174.

Compound 3. 2,3-*O*-Isopropylidine-methyl-*α*-D-galactopyranoside **2** (500 mg, 2.14 mmol), PPh_3 (840 mg, 3.2 mmol) and imidazole (435 mg, 6.4 mmol) were taken in a round-bottom flask in dry toluene (15 mL). The reaction mixture was stirred at room temperature with I_2 (815 mg, 3.2 mmol). The dark brown reaction mixture was heated at 80 °C for 3 h. After completion of the reaction, the reaction mixture was quenched with MeOH (2 mL), and the whole mixture was then concentrated to a residue. Saturated aqueous solution of $Na_2S_2O_3$ was added to it. The entire solution was stirred until the reaction mixture became colorless. Afterward, it was extracted with DCM (2 × 20 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to a residue which on column chromatographic purification afforded iodide **3** (600 mg, 1.75 mmol, 82%).

Eluent for column chromatography: EtOAc/hexane (2/5, v/v); $[\alpha]^{28}_D$ = +130.3 (*c* 0.74, $CHCl_3$); R_f = 0.32 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3133, 3077, 2542, 1384, 1215, 1021, 781; ^1H NMR (300 MHz, $CDCl_3$ + CD_3OD) *δ* 1.35 (s, 3H), 1.50 (s, 3H), 3.33−3.38 (m, 2H), 3.48−3.49 (m, 3H), 3.73−3.74 (m, 1H), 4.127−4.134 (m, 1H), 4.19−4.23 (m, 1H), 4.33−4.40 (m, 3H), 4.71 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$ + CD_3OD) *δ* 6.1, 29.7, 31.5, 59.4, 72.6, 73.3, 77.7, 80.2, 103.5, 113.3; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{18}IO_5$ 345.0199, found 345.0191.

General Procedure for Preparation of Aldehyde 4. To a magnetically stirred suspension of Zn dust (680 mg, 10.4 mmol) and NH_4Cl (560 mg, 10.38 mmol) in dry methanol (20 mL) was added cyanocobalamine (7 mg, 0.005 mmol), and the resulting mixture was allowed to stir for 15 min. Afterward, a solution of **3** (150 mg, 0.44 mmol) in dry methanol (5 mL) was added to it, and the resulting solution was further stirred for 5 min. The reaction mixture was filtered through a Celite bed, and the filtrate was evaporated under reduced pressure. The residue obtained was dissolved in ethyl acetate (25 mL) and washed with a mixture of brine and water (1:1 v/v, 10 mL each). The organic layer was dried over Na_2SO_4 and concentrated to give the crude aldehyde **4**, which unfortunately decomposed rapidly.

Compound 5. To a stirred solution of compound **3** (345 mg, 1 mmol) in dry DCM (5 mL) were added imidazole (135 mg, 2 mmol) and TBDPSCl (412 mg, 0.39 mL, 1.5 mmol), and the reaction mixture was allowed to stir for another 6 h. Water (10 mL) was added to the reaction mixture and extracted with DCM (2 × 10 mL). The combined organic layer was evaporated under reduced pressure to give a residue that on purification by column chromatography gave **5** as clear oil (495 mg, 0.85 mmol, 85%).

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Eluent for column chromatography: EtOAc/hexane (1/19, v/v); $[\alpha]^{28}_{D}$ = +84.2 (*c* 1.23, $CHCl_3$); R_f = 0.54 (1/6, EtOAc/hexane); IR (neat, cm^{-1}) 3017, 2361, 1372, 1215, 763; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (s, 9H), 1.24 (s, 3H), 1.33 (s, 3H), 3.23−3.34 (m, 5H), 3.73−3.77 (m, 1H), 4.08−4.13 (m, 1H), 4.26−4.37 (m, 3H), 7.36−7.44 (m, 6H), 7.71−7.77 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 3.2, 19.6, 26.7, 27.3, 28.2, 55.6, 86.4, 72.2, 74.3, 77.4, 128.0, 130.1, 133.1, 134.7, 136.1, 136.5; HRMS (ESI TOF (+)) calcd for $C_{26}H_{35}IO_5SiNa$ $[M + Na]^+$ 605.1196, measured 605.1208.

Compound 8. To a magnetically stirred suspension of Zn dust (1.56 mg, 23.9 mmol) and NH_4Cl (1.3 g, 23.9 mmol) in dry methanol (30 mL) was added cyanocobalamine (16 mg, 0.012 mmol), and stirring was continued for another 15 min. After that, a solution of **5** (580 mg, 0.1 mmol) in dry methanol (5 mL) was added, and the resulting solution was further stirred for 5 min. The reaction mixture was filtered through a Celite bed. The filtrate was evaporated under reduced pressure. The residue obtained was dissolved in ethyl acetate (25 mL) and washed with a mixture of brine and water (1:1 v/v, 10 mL each). The organic layer was dried over Na_2SO_4 and concentrated to give the crude aldehyde **6** (430 mg), which was used immediately for the next step.

To a stirred solution of aldehyde **6** in EtOH (10 mL) was added TBAF (1 mL, 1 M solution in THF), and the reaction mixture was left stirring at room temperature. After 30 min, *trans*-2-phenylvinyl boronic acid (149 mg, 1 mmol) and $^tBuNH_2$ (0.5 mL) were added, and the reaction mixture was left stirring under refluxing condition. After completion of the reaction (24 h, TLC control), the reaction mixture was concentrated to a residue that on column chromatographic purification afforded amine **7** with some unidentified impurities. The impure amine **7** was used directly for the next step.

To a stirred solution of amine **7** in dry THF (5 mL) were added Et_3N (0.42 mL, 3 mmol) and DMAP (170 mg, 1 mmol) at room temperature. The resulting reaction mixture was cooled to 0 °C. $(Boc)_2O$ (1.5 mmol) was then added to it. The stirring was continued for overnight without further cooling. After completion of the reaction, the reaction mixture was concentrated to a residue that on column chromatographic purification furnished the oxazolidinone **8** (59 mg, 0.15 mmol, 15% from **5**) with simultaneous Boc protection followed by oxazolidinone ring formation.

Eluent for column chromatography: EtOAc/hexane (1/2, v/v); $[\alpha]^{26}_{D}$ = −80.0 (*c* 0.28, $CHCl_3$); R_f = 0.33 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3342, 1740, 1219, 769; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.40 (s, 9H), 1.53 (s, 3H), 4.25−4.30 (m, 1H), 4.36−4.50 (m, 3H), 5.37−5.43 (m, 2H), 5.89−6.01 (m, 1H), 6.25 (dd, *J* = 9.0, 15.9 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.32−7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 28.1, 28.6, 54.8, 60.9, 76.5, 76.8, 78.3, 110.1, 120.4, 126.0, 127.0, 129.1, 129.3, 134.5, 135.0, 135.7, 155.8; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{30}NO_4$ 372.2175, measured 372.2169.

Compound 10. To a stirred suspension of D-galactose **9** (5 g, 27.75 mmol) in dry acetone (200 mL) was added I_2 (1.5 g, 5.9 mmol) at room temperature, and the reaction was allowed to stir at same temperature. After 24 h, excess iodine was quenched with aqueous saturated solution of $Na_2S_2O_3$, and the resulting mixture was concentrated. The reaction mixture was then extracted with EtOAc (3 × 100 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to a residue that on purification by column chromatography gave 1,2;3,4-di-*O*-isopropylidine-α-D-galactopyranoside **10** (5.77 g, 22.2 mmol, 80%).

Eluent for column chromatography: EtOAc/hexane (1/4, v/v); $[\alpha]^{28}_{D}$ = −55.3 (*c* 0.77, $CHCl_3$); R_f = 0.29 (1/2, EtOAc/hexane); IR (neat, cm^{-1}) 3532, 3462, 2989, 2930, 1380, 1170; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 6H), 1.41 (s, 3H), 1.49 (s, 3H), 2.61 (s, 1H, OH), 3.69−3.82 (m, 3H), 4.22−4.31 (m, 2H), 4.56−4.59 (m, 1H), 5.52 (d, *J* = 4.95 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.6, 25.2, 26.2, 26.3, 62.4, 68.6, 70.9, 71.0, 71.7, 96.6, 109.0, 109.7; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{21}O_6$ 261.1338, measured 261.1328.

Compound 11. 1,2;3,4-di-*O*-isopropylidine-α-D-galactopyranoside **10** (1.0 g, 3.84 mmol), PPh_3 (1.51 g, 5.76 mmol), and imidazole (785 mg, 11.52 mmol) were taken in a round-bottom flask, and dry toluene (20 mL) was added to it. The reaction mixture was stirred at room temperature with I_2 (1.46 g, 5.76 mmol). The dark brown reaction mixture was then heated at 80 °C for 3 h. After completion of the reaction (TLC control), the reaction mixture was quenched with MeOH (2 mL), and the resulting solution was concentrated to a residue. A saturated aqueous solution of $Na_2S_2O_3$ was added to it. The stirring of the solution was continued until it became colorless. Afterward, it was extracted with DCM (2 × 25 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to a residue that on column chromatographic purification afforded the iodide **11** (1.22 g, 3.3 mmol, 86%).

Eluent for column chromatography: EtOAc/hexane (1/4, v/v); $[\alpha]^{28}_{D}$ = −56.8 (*c* 0.71, $CHCl_3$); R_f = 0.66 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3333, 2979, 2906, 1380, 1258, 1069; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26−1.27 (m, 6H), 1.36 (s, 3H), 1.46 (s, 3H), 3.10−3.14 (m, 1H), 3.21−3.26 (m, 1H), 3.86−3.89 (m, 1H), 4.22−4.23 (m, 1H), 4.31−4.34 (m, 1H), 4.53−4.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.6, 30.8, 31.2, 32.25, 32.3, 75.2, 82.9, 83.4, 83.8, 103.0, 115.1, 115.8; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{20}IO_5$ 371.0355, measured 371.0345.

General Procedure for Preparation of Compound 12. To a magnetically stirred suspension of Zn dust (680 mg, 10.4 mmol) and NH_4Cl (560 g, 10.38 mmol) in dry methanol (20 mL) was added cyanocobalamine (7 mg, 0.005 mmol). The stirring was allowed to continue for another 10 min. After that, a solution of **11** (370 mg, 1 mmol) in dry methanol (5 mL) was added, and the resulting solution was further stirred for 15 min. The reaction mixture was filtered through a Celite bed. The filtrate was evaporated under reduced pressure. The residue obtained was dissolved in ethyl acetate (30 mL) and washed with a mixture of brine and water (1:1 v/v, 10 mL each). The organic layer was dried over Na_2SO_4 and concentrated to give the hemiacetal **12** as a mixture of α and β anomer (220 mg, 0.9 mmol, 90%), which was directly used for the next step.

Compound 8 from Compound 12. To a stirred solution of hemiacetal **12** (245 mg, 1 mmol) in EtOH (6 mL) were added *trans*-2-phenylvinyl boronic acid (149 mg, 1 mmol) and $^tBuNH_2$ (0.5 mL), and the reaction mixture was left stirring. After completion of the reaction (24 h, TLC control), the reaction mixture was concentrated to a residue that on column chromatographic purification afforded amine **7** with some unidentified impurities.

To a stirred solution of amine **7** in THF (5 mL) were added Et_3N (0.42 mL, 3 mmol) and DMAP (170 mg, 1 mmol), and the resulting solution was cooled to 0 °C. $(Boc)_2O$ (1.5 mmol) was added to it ,and the stirring was continued for 12 h. Afterward, the reaction mixture was concentrated under reduced pressure to a residue that on column chromatographic purification furnished the oxazolidinone **8** (155 mg, 0.4 mmol, 40% from **12**).

Compound 13. To a 100 mL two necked oven-dried round-bottom flask fitted with a reflux condenser and septum was added Grubbs second generation catalyst (22 mg, 0.026 mmol) under argon atmosphere. Dry degassed CH_2Cl_2 (25 mL) was added to it through a syringe, and the resulting solution was left stirring. Compound **8** (100 mg, 0.26 mmol) in DCM (5 mL) was added through a syringe to the stirring solution. The septum was replaced with a glass stopper while the stirring was continued. The solution was refluxed for 24 h. The temperature of the mixture was cooled slowly to room temperature. The organic solvent was evaporated under reduced pressure to give a black residue that on column chromatographic purification gave **13** as a semisolid compound (37 mg, 0.133 mmol, 51%).

Eluent for column chromatography: EtOAc/hexane (1/9, v/v); $[\alpha]^{28}_{D}$ = +124.2 (*c* 0.125, $CHCl_3$); R_f = 0.29 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3026, 2791, 1745, 1216, 766; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36−1.37 (m, 6H), 1.46 (s, 9H), 4.23 (d, *J* = 5.9 Hz, 1H), 4.57 (brm, 2H), 4.74 (d, *J* = 6.6 Hz, 1H), 5.72−5.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 28.3, 28.9, 51.7, 54.2, 69.7, 70.9, 71.4, 110.3, 123.3, 129.0, 155.4; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{22}NO_4$ 268.1549, measured 268.1544.

Compound 14. To a 50 mL round-bottom flask compound **13** (30 mg, 0.11 mmol) was taken in DCM (4 mL), and TFA (1 mL) was

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added to it at 0 °C. The mixture was allowed to stir without further cooling. After 2 h, it was cooled to 0 °C, and water (1 mL) was added to it. The resulting solution was further left stirring for 1 h. After that, the reaction mixture was concentrated and coevaporated with toluene under reduced pressure to get a residue that on column chromatographic purification gave the diol **14** (22 mg, 0.095 mmol, 85%).

Eluent for column chromatography: EtOAc/hexane (2/1, v/v); $[\alpha]^{28}_{D}$ = +78.5 (*c* 0.23, $CHCl_3$); R_f = 0.30 (4/1, EtOAc/hexane); IR (neat, cm^{-1}) 3211, 3140, 1740, 1654, 1261, 804; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 9H), 4.24–4.29 (m, 2H), 4.37 (brm, 1H), 4.57–4.60 (m, 1H), 5.75 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.7, 52.6, 54.4, 64.2, 67.5, 73.5, 124.8, 131.7, 156.6; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{18}NO_4$ 228.1236, measured 228.1224.

Compound 19. To a stirred suspension of D-mannose **17** (5 g, 27.75 mmol) in dry acetone (200 mL) was added I_2 (1.5 g, 5.9 mmol), and the reaction was allowed to stir at room temperature. After 24 h, excess iodine was quenched with an aqueous saturated solution of $Na_2S_2O_3$, and the resulting mixture was concentrated under vacuum. The aqueous portion was extracted with EtOAc (3 × 100 mL), and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to a residue that on purification by column chromatography gave 1,2;5,6-di-*O*-isopropylidine-α-D-mannofuranoside **18** (5.78 g, 22.2 mmol, 80%).

To a 250 mL two necked dry round-bottom flask were added methyltriphenylphosphonium bromide (Ph_3PCH_3Br) (39.6 g, 111 mmol) and ^{t}BuOK (9.95 g, 88.8 mmol) under nitrogen atmosphere. Dry THF (100 mL) was added at 0 °C, and the stirring was continued without further cooling. After 1 h, the reaction mixture was again cooled to 0 °C, and the compound **18** (5.78 g, 22.2 mmol) in THF (25 mL) was added to it through a syringe. The solution was stirred until the reaction was completed (TLC control, 4 h). Afterward, the reaction mixture was quenched with an aqueous solution of NH_4Cl (25 mL). It was extracted with EtOAc (3 × 50 mL), and the combined organic layer was evaporated under reduced pressure to give a residue that on column chromatographic purification afforded the olefin **19** as a clear oil (4.87 g, 18.87 mmol, 85%).

Eluent for column chromatography: EtOAc/hexane (1/13, v/v); $[\alpha]^{28}_{D}$ = −35.7 (*c* 1.0, $CHCl_3$); R_f = 0.54 (1/4, EtOAc/hexane); IR (neat, cm^{-1}) 3235, 1634, 1217, 764; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.33 (s, 3H), 1.35 (s, 3H), 1.48 (s, 3H), 2.21 (d, *J* = 8.0 Hz, 1H), 3.41 (dd, *J* = 6.7, 7.7 Hz, 1H), 3.91–4.05 (m, 3H), 4.33 (dd, *J* = 1.09, 7.44 Hz, 1H), 4.64 (t, *J* = 7.5 Hz, 1H), 5.25–5.37 (m, 2H), 5.99–6.10 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.8, 25.6, 26.9, 27.0, 67.4, 70.8, 76.3, 77.0, 79.4, 108.9, 109.5, 119.7, 134.6; HRMS (DART TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{23}O_5$ 259.1545, measured 259.1542.

Compound 20. To a stirred solution of compound **19** (260 mg, 1 mmol) in DMF (2 mL) were added imidazole (275 mg, 4 mmol) and TBDPSCl (412 mg, 0.39 mL, 1.5 mmol), and the reaction mixture was allowed to stir for 24 h. Water (10 mL) was added to it, and the entire solution was extracted with EtOAc (2 × 10 mL). The combined organic layer was evaporated under reduced pressure to give a residue that on purification by column chromatography afforded the silyl ether **20** as clear oil (432 mg, 0.87 mmol, 87%).

Eluent for column chromatography: EtOAc/hexane (1/30, v/v); $[\alpha]^{28}_{D}$ = +37.2 (*c* 1.47, $CHCl_3$); R_f = 0.5 (1/6, EtOAc/hexane); IR (neat, cm^{-1}) 2938, 2796, 1374, 1217, 765; ^1H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.11 (s, 3H), 1.14 (s, 3H), 1.31 (s, 3H), 1.32 (s, 3H), 3.82 (t, *J* = 7.2 Hz, 1H), 3.97–4.10 (m, 4H), 4.40–4.44 (m, 1H), 5.02–5.16 (m, 2H), 5.42–5.54 (m, 1H), 7.35–7.42 (m, 6H), 7.71–7.76 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.1, 25.3, 25.5, 26.4, 27.4, 28.0, 67.5, 72.8, 77.2, 79.1, 79.9, 108.1, 109.4, 118.5, 127.3, 127.6, 129.4, 129.7, 134.1, 134.8, 135.1, 136.4, 136.6; HRMS (ESI TOF (+)) *m*/*z* $[M + Na]^+$ calcd for $C_{29}H_{40}O_5SiNa$ 519.2537, measured 519.2543.

Compound 21. To a 100 mL round-bottom flask was added compound **20** (500 mg, 1 mmol) dissolved in 80% AcOH (10 mL), and the solution was allowed to stir at room temperature. After 6 h, the reaction mixture was concentrated and coevaporated with toluene under reduced pressure to obtain an oily residue that on column chromatographic purification furnished diol **21** (342 mg, 0.75 mmol, 75%).

Eluent for column chromatography: EtOAc/hexane (1/2, v/v); $[\alpha]^{28}_{D}$ = +19.4 (*c* 0.88, $CHCl_3$); R_f = 0.56 (2/5, EtOAc/hexane); IR (neat, cm^{-1}) 3033, 2961, 1641, 1216, 762; ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.15 (s, 3H), 1.25 (s, 3H), 2.36 (s, 1H, OH), 2.71 (s, 1H, OH), 3.67–3.78 (m, 3H), 3.93 (dd, *J* = 3.3, 7.9 Hz, 1H), 4.17–4.22 (m, 1H), 4.35–4.39 (m, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 16.9 Hz, 1H), 5.47–5.59 (m, 1H), 7.36–7.44 (m, 6H), 7.70–7.75 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.0, 25.5, 27.5, 27.9, 63.7, 72.8, 74.3, 78.9, 79.3, 108.8, 119.6, 127.5, 127.9, 129.8, 130.1, 133.7, 134.0, 134.5, 136.5; HRMS (ESI TOF (+)) *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{36}O_5SiNa$ 479.2224, measured 479.2231.

Compound 25. To the diol **21** (500 mg, 1.1 mmol) dissolved in THF/H_2O (9:1, 15 mL) was added $NaIO_4$ (320 mg, 1.5 mmol) at 0 °C, and the mixture was stirred for 1.5 h without further cooling. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (5 mL) at 0 °C and extracted with EtOAc (2 × 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the crude aldehyde **22**, which was immediately used for the next step.

To a stirred solution of aldehyde **22** in EtOH (10 mL) was added TBAF (1.3 mL, 1 M solution in THF), and the reaction mixture was left stirring at room temperature. After 30 min, *trans*-2-phenylvinyl boronic acid (165 mg, 1.1 mmol) and ^{t}BuNH$_2$ (0.5 mL) were added to the reaction mixture, and it was refluxed for 24 h. Solvent was removed under reduced pressure, and the resulting oil was purified by flash chromatography to yield amino alcohol **24** with some unidentified impurities (TLC).

To the stirring solution of amine **24** in dry THF (5 mL) were added Et_3N (0.42 mL, 3 mmol) and DMAP (170 mg, 1 mmol) at room temperature. The resulting mixture was cooled to 0 °C. $(Boc)_2O$ (1.5 mmol) was added to it, and the mixture was stirred overnight without further cooling. After 12 h, the reaction mixture was concentrated to a residue that on column chromatographic purification furnished the oxazolidinone **25** (89 mg, 0.23 mmol, 21% from **21**).

Eluent for column chromatography: EtOAc/hexane (1/9, v/v); $[\alpha]^{26}_{D}$ = +66.0 (*c* 0.24, $CHCl_3$); R_f = 0.3 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3026, 2761, 1745, 1216, 770; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 3H), 1.40 (s, 9H), 1.53 (s, 3H), 4.25–4.30 (m, 1H), 4.35–4.49 (m, 3H), 5.37–5.43 (m, 2H), 5.89–6.01 (m, 1H), 6.25 (dd, *J* = 9.1, 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.8, 28.1, 28.6, 54.8, 60.9, 76.6, 76.8, 78.4, 110.1, 120.4, 126.0, 127.0, 129.1, 129.3, 134.5, 135.0, 135.7, 155.8; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{30}NO_4$ 372.2175, measured 372.2167.

Compound 26. To a 50 mL two necked oven-dried round-bottom flask fitted with a reflux condenser and septum was added Grubbs second generation catalyst (11 mg, 0.013 mmol, 10 mol %) under argon atmosphere. Dry degassed CH_2Cl_2 (15 mL) was added to it, and the reaction mixture was left stirring. Compound **25** (50 mg, 0.13 mmol) in DCM (5 mL) was added through a syringe to the stirring solution. The septum was replaced with a glass stopper, and the solution was refluxed with stirring for 24 h. The temperature of the mixture was cooled slowly to room temperature. The organic solvent was evaporated under reduced pressure to give a black residue that on column chromatographic purification afforded **26** as a semisolid compound (17 mg, 0.062 mmol, 48%).

Eluent for column chromatography: EtOAc/hexane (1/9, v/v); $[\alpha]^{28}_{D}$ = −134.0 (*c* 0.112, $CHCl_3$); R_f = 0.3 (1/3, EtOAc/hexane); IR (neat, cm^{-1}) 3069, 1745, 1217, 765; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36–1.38 (m, 6H), 1.46 (s, 9H), 4.24 (d, *J* = 5.4 Hz, 1H), 4.57 (brm, 2H), 4.75 (d, *J* = 6.3 Hz, 1H), 5.72–5.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 28.3, 28.9, 51.7, 54.2, 69.7, 70.8, 71.4, 110.3, 123.3, 129.0, 155.4; HRMS (ESI TOF (+)) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{22}NO_4$ 268.1549, measured 268.1545.

Compound 27. To a solution of compound **26** (30 mg, 0.11 mmol) in DCM (4 mL) was added TFA (1 mL) at 0 °C, and the reaction was allowed to stir without further cooling. After 2 h, the reaction mixture was again cooled to 0 °C, and water (1 mL) was

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added. The resulting solution was left stirring for another 1 h. After that, the reaction mixture was concentrated and coevaporated with toluene under reduced pressure to obtain a residue that on column chromatographic purification afforded the diol **27** (23 mg, 0.1 mmol, 91%).

Eluent for column chromatography: EtOAc/hexane (2/1, v/v); $[\alpha]^{28}_{D} = -73.7$ (*c* 0.16, $CHCl_3$); $R_f = 0.29$ (4/1, EtOAc/hexane); IR (neat, cm^{-1}) 3420, 2926, 1723, 1219, 768; ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.65 (brs, 1H), 4.08 (brs, 1H), 4.29−4.32 (m, 2H), 4.40 (brm, 1H), 4.63 (dd, J = 4.2, 5.8 Hz, 1H), 5.79 (brm, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.7, 52.6, 54.3, 64.2, 67.3, 73.6, 124.6, 131.8, 156.6; HRMS (ESI TOF (+)) m/z $[M + H]^+$ calcd for $C_{11}H_{18}NO_4$ 228.1236, measured 228.1231.

■ ASSOCIATED CONTENT

Supporting Information

General experimental details, full characterization and copies of ^{1}HNMR and ^{13}CNMR spectra of compounds **2**, **3**, **5**, **8**, **10**, **11**, **13**, **14**, **19**, **20**, **21**, **25**, **26**, and **27** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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