

Supporting Information

Photo Amidoglycosylation of an Allal Azidoformate. Synthesis of β -2-Amido Allopyranosides

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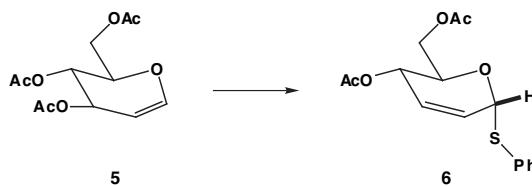
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General: NMR spectra were recorded on a Varian Gemini 200 or Bruker Avance 300 spectrometer at 200 MHz or 300 MHz for ^1H spectra and 50 MHz or 75 MHz for ^{13}C spectra. ^1H chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS, δ 0.00), using as a reference either added TMS or an appropriate signal for residual solvent protons. ^{13}C NMR chemical shifts are reported in parts per million, using the center peak of the solvent signal as a reference. ^{13}C NMR peak multiplicities, where reported, were inferred using DEPT pulse sequences. Infrared spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer. Melting points were obtained using a Thomas Hoover capillary melting point apparatus and are uncorrected. High resolution mass spectra were measured at the Columbia University Mass Spectroscopy Laboratory. Elemental analyses were performed by Galbraith Laboratories, Inc., 2323 Sycamore Dr., Knoxville, TN 37921.

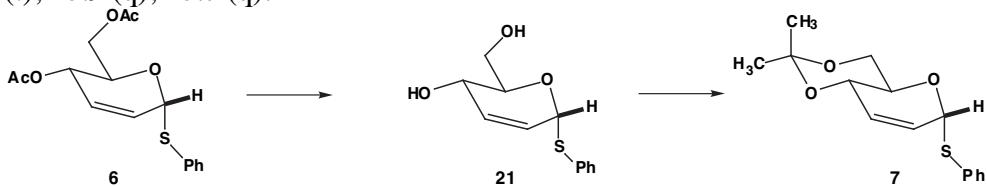
Dichloromethane, dimethylformamide (DMF), piperidine, and triethylamine were distilled from CaH_2 . Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Unless noted, other reagents were obtained commercially and were used as received. Reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon or nitrogen.

CAUTION! Azidoformates are potentially explosive. While we have encountered no difficulties with the preparation and use of azidoformate 2, appropriate safety precautions are strongly recommended.¹

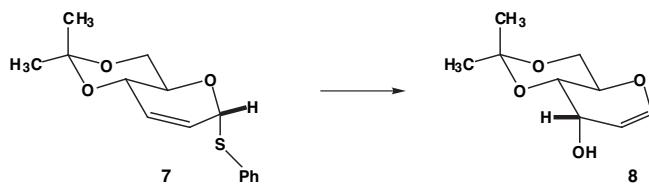


α -Phenylthiopseudoglycal 6.² Tri-*O*-acetyl-D-glucal 5 (2.0 g, 7.4 mmol) was dissolved in CH_2Cl_2 (25 mL) and thiophenol (0.89 g, 0.81 mL, 8.1 mmol) was added. The solution was cooled to $-20\text{ }^\circ\text{C}$ and SnCl_4 (0.4 mL of a 1.0 M solution in CH_2Cl_2 , 0.4 mmol) was added by drops over 5 min. After 25 min, satd aq NaHCO_3 (10 mL) was added and the reaction mixture was allowed to warm to $23\text{ }^\circ\text{C}$. The mixture

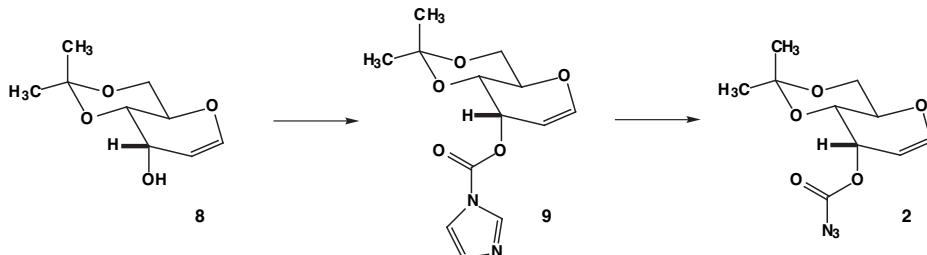
was diluted with CH_2Cl_2 and washed twice with satd aq NaHCO_3 and finally with brine. The organic phase was dried (MgSO_4), filtered, and concentrated to an oil. The crude product was chromatographed ($10 \rightarrow 15 \rightarrow 20\%$ EtOAc/hexanes, 200 g SiO_2), affording α -phenylthio glycoside **6** (1.75 g, 74%) as an oil which crystallized on standing at $-20\text{ }^\circ\text{C}$. $R_f = 0.6$ (30% EtOAc/hexanes); mp 63–65 $^\circ\text{C}$; IR (thin film) 3056, 1742, 1582 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.61–7.50 (m, 2H), 7.38–7.26 (m, 3H), 6.08 (ddd, $J = 10.1, 3.1, 1.9$ Hz, 1H), 5.86 (ddd, $J = 10.1, 1.7, 1.7$ Hz, 1H), 5.76 (ddd, $J = 3.0, 1.6, 1.6$ Hz, 1H), 5.38 (dddd, $J = 9.4, 1.9, 1.9, 1.9$ Hz, 1H), 4.48 (ddd, $J = 9.4, 5.5, 2.9$ Hz, 1H), 4.26 (AB of ABX, $J_{\text{AB}} = 12.1$ Hz, $J_{\text{AX}} = 5.9$ Hz, $J_{\text{BX}} = 2.5$ Hz, $\Delta\nu_{\text{AB}} = 13.5$ Hz, 2H), 2.11 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.6 (s), 170.2 (s), 134.7 (s), 131.7 (d), 128.9 (d), 128.5 (d), 127.6 (d), 127.5 (d), 83.6 (d), 67.2 (d), 65.0 (d), 63.0 (t), 20.9 (q), 20.7 (q).



4,6-O-Isopropylidene phenylthiopseudoglycal **7.**² The diacetate **6** (8.0 g, 24 mmol) was dissolved in 5/1 MeOH/ CH_2Cl_2 (85 mL). The solution was cooled to 0 $^\circ\text{C}$ and stirred with potassium carbonate (10.3 g, 74.5 mmol) during 75 min. The reaction mixture was poured into satd aq NH_4Cl (300 mL) and extracted with CH_2Cl_2 (150 mL). The aqueous phase was further extracted with EtOAc (2 x 100 mL) and the combined organic layers were dried (MgSO_4), filtered, and concentrated. The resulting thick oil was chromatographed ($60 \rightarrow 70 \rightarrow 80\%$ EtOAc/hexanes, 150 g SiO_2), affording diol **21** (5.8 g, 98%). Data for diol **21**: $R_f = 0.2$ (40% EtOAc/hexanes); ^1H NMR (200 MHz, CDCl_3) δ 7.56–7.44 (m, 2H), 7.38–7.20 (m, 3H), 6.03–5.86 (m, 2H), 5.73 (m, 1H), 4.31 (br d, $J = 9.2$ Hz, 1H), 4.10–3.97 (m, 1H), 3.95–3.82 (m, 2H), 2.65 (br s, 1H), 2.32 (br s, 1H). Diol **21** (1.91 g, 8.0 mmol) was concentrated from benzene solution (2 x 10 mL), dissolved in CH_2Cl_2 (20 mL) at 23 $^\circ\text{C}$ and treated with 2-methoxypropene (1.7 g, 2.3 mL, 24 mmol), followed by pyridinium-p-toluenesulfonate (0.40 g, 1.6 mmol). After 3 h satd aq NaHCO_3 (50 mL) was added and the reaction mixture was extracted with CH_2Cl_2 . The organic phase was washed with satd aq NaHCO_3 (2 x 40 mL), dried (MgSO_4), filtered, and concentrated. The residue was chromatographed ($5 \rightarrow 10\%$ EtOAc/hexanes, 80 g SiO_2), providing acetonide **7** (1.89 g, 85%) as a clear, nearly colorless oil which solidified to a white, crystalline solid upon standing in the freezer at $-20\text{ }^\circ\text{C}$. $R_f = 0.5$ (40% EtOAc/hexanes); mp 56–58 $^\circ\text{C}$; IR (thin film) 3057, 1584 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.54–7.44 (m, 2H), 7.36–7.20 (m, 3H), 6.00–5.84 (m, 2H), 5.75 (m, 1H), 4.36–4.25 (m, 1H), 4.07–3.73 (m, 3H), 1.53 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.3, 131.4, 129.9, 128.9, 127.3, 126.9, 99.9, 84.4, 67.4, 65.4, 62.8, 29.1, 19.0.

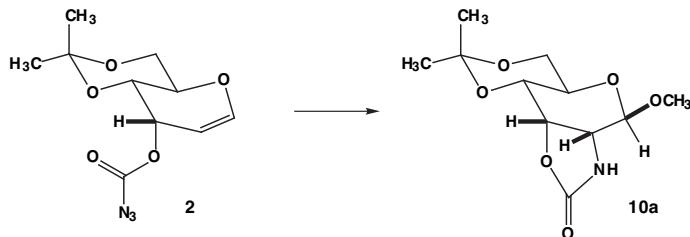


4,6-O-Isopropylidene-D-allal 8. To a 0 °C solution of sulfide **7** (1.5 g, 5.4 mmol) in CH₂Cl₂ (30 mL) was added *m*-chloroperoxybenzoic acid (1.28 g of 80% by weight *m*-CPBA, 5.9 mmol) in one portion with efficient stirring. After 15 min satd aq NaHCO₃ (60 mL) was added to the cold reaction mixture and stirring was continued 3 min until all solids were dissolved. The mixture was transferred to a separatory funnel with CH₂Cl₂ and the layers were separated. The organic layer was washed with satd aq NaHCO₃ (2 x 40 mL), dried (MgSO₄), filtered, and concentrated. The residue was placed under vacuum (0.5 mm Hg) during 30 min, dissolved in THF (15 mL), and treated with piperidine (5 mL) at 23 °C. After stirring 90 min the solution was concentrated and the residue was chromatographed (25→30% EtOAc/hexanes, 55 g SiO₂), yielding allal **8** as a clear, colorless oil (0.87 g, 87%). The product solidified on standing in the freezer at -20 °C. *R*_f = 0.3 (40% EtOAc/hexanes); mp 46–49 °C; IR (thin film) 3468, 1637 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.36 (d, *J* = 5.9 Hz, 1H), 4.94 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.14–3.70 (m, 5H), 2.70 (s, 1H), 1.49 (s, 3H), 1.40 (s, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 145.9, 101.2, 99.7, 70.7, 64.7, 61.6, 60.1, 28.8, 19.2.

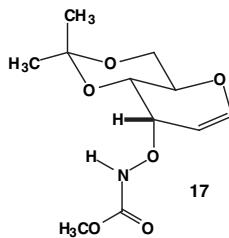


Allal azidoformate 2. CAUTION! Azidoformates are potentially explosive. While we have encountered no difficulties with the preparation and use of azidoformate **2**, appropriate safety precautions are strongly recommended.¹ Carbonyldiimidazole (212 mg, 1.3 mmol) was added to a 23 °C solution of alcohol **8** (162 mg, 0.87 mmol) in CH₂Cl₂ (4 mL). After 75 min satd aq NaHCO₃ (10 mL) was added with vigorous stirring. The mixture was extracted with CH₂Cl₂ and the organic phase was washed twice with satd aq NaHCO₃, dried (Na₂SO₄—the more Lewis-acidic MgSO₄ was avoided), filtered, and concentrated. The crude carbonyl imidazolide **9** (242 mg, 99%) could be checked for purity by ¹H NMR and was used directly in the following reaction. Data for carbonyl imidazolide **9**: *R*_f = 0.2 (40% EtOAc/hexanes); ¹H NMR (200 MHz, CDCl₃) δ 8.16 (m, 1H), 7.44 (dd, *J* = 1.5, 1.5 Hz, 1H), 7.07 (dd, *J* = 1.6, 0.9 Hz, 1H), 6.56 (d, *J* = 5.9 Hz, 1H), 5.40 (dd, *J* = 5.9, 3.7 Hz, 1H), 5.08 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.20–3.80 (m, 4H), 1.53 (s, 3H), 1.35 (s, 3H). The crude carbonyl imidazolide **9** (242 mg, 0.87 mmol) was dissolved in THF (5 mL) at 23 °C and trimethylsilyl azide (175 µL, 150 mg, 1.31 mmol) was added, followed by dibutyltin oxide (43 mg, 0.17 mmol). The initially cloudy mixture cleared over a period of 12 h. Additional portions of trimethylsilyl azide (60 µL, 52 mg, 0.45 mmol each portion) were added at 72 h and 120 h reaction times. After a total reaction time of 190 h the mixture was poured into satd aq NaHCO₃

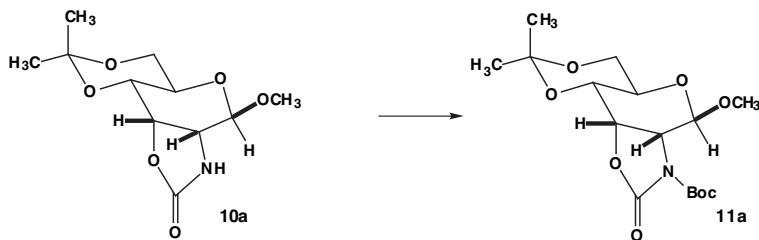
and extracted with CH_2Cl_2 . The organic phase was washed with satd aq NaHCO_3 , dried (Na_2SO_4 —the more Lewis-acidic MgSO_4 was avoided), filtered, and concentrated. The residue was chromatographed rapidly on Davisil® silica (100% hexanes \rightarrow 5% $\text{EtOAc}/\text{hexanes}$, 2 g SiO_2), affording azidoformate **2** (114 mg, 51% from alcohol **8**) as a clear oil that solidified on standing in the freezer at $-20\text{ }^\circ\text{C}$. The azidoformate **2** could be recrystallized from hexanes as colorless needles. Data for azidoformate **2**: $R_f = 0.5$ (40% $\text{EtOAc}/\text{hexanes}$); mp 71–72 $^\circ\text{C}$; IR (thin film) 2185, 2139, 1729, 1635 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.49 (d, $J = 6.2$ Hz, 1H), 5.21 (dd, $J = 5.9, 2.9$ Hz, 1H), 4.98 (dd, $J = 6.0, 6.0$ Hz, 1H), 4.10–3.74 (m, 4H), 1.51 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 156.8, 148.3, 99.9, 97.1, 68.7, 67.0, 65.7, 61.5, 28.6, 18.9. Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_5$: C, 47.06; H, 5.13; N, 16.46. Found: C, 47.10; H, 5.25; N, 16.38.



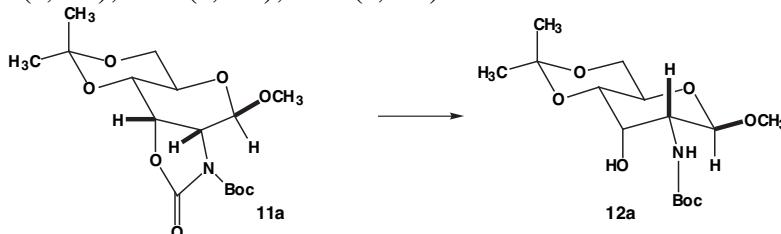
β -Methyl-2-amido-D-allopyranoside 10a. Immediately prior to use, methyl alcohol was stirred with magnesium turnings and a flake of I_2 until all of the magnesium reacted then distilled, followed by a second distillation from NaBH_4 . Azidoformate **2** (28 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (14 mL) containing methyl alcohol (18 mg, 22 μL , 0.55 mmol). The solution was photolyzed in a quartz tube using a Rayonet merry-go-round apparatus (254 nm lamp, Vycor filter) at $23\text{ }^\circ\text{C}$ during 80 min. The reaction mixture was concentrated and the residue chromatographed (60 \rightarrow 70 \rightarrow 80% $\text{EtOAc}/\text{hexanes}$, 5 g SiO_2), providing oxazolidinone **10a** (11 mg, 40%). The product was best visualized by preheating the eluted TLC plate on a hot plate, dipping the plate in a solution of KMnO_4 (1.5 g) in 1.5 M NaOH (150 mL), and then gently heating the TLC plate. $R_f = 0.1$ (60% $\text{EtOAc}/\text{hexanes}$); IR (thin film) 3305, 1763 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.05 (br s, 1H), 4.81 (dd, $J = 7.3, 3.3$ Hz, 1H), 4.47 (d, $J = 4.4$ Hz, 1H), 4.18–4.08 (m, 1H), 4.05–3.94 (m, 1H), 3.92–3.66 (m, 3H), 3.47 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.5, 102.7, 100.3, 74.1, 68.2, 63.7, 62.6, 56.8, 55.6, 28.8, 18.8. A trace (1.3 mg, 5%) of *N*-alkoxyurethane **17** was also isolated.



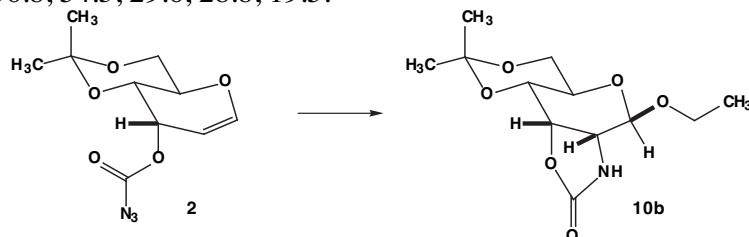
Data for **17**: $R_f = 0.4$ (60% $\text{EtOAc}/\text{hexanes}$); IR (thin film) 3350, 1752, 1636 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.10 (s, 1H), 6.45 (d, $J = 6.2$ Hz, 1H), 5.00 (dd, $J = 6.0, 6.0$ Hz, 1H), 4.21 (m, 1H), 4.13–3.74 (m, 4H), 3.77 (s, 3H), 1.53 (s, 3H), 1.49 (s, 3H).



N-Boc-protected oxazolidinone 11a. Oxazolidinone **10a** (5.5 mg, 0.021 mmol) in THF (2 mL) was treated sequentially with *N,N*-dimethyl-4-amino pyridine (13 mg, 0.11 mmol), triethylamine (11 mg, 15 μ L, 0.11 mmol), and di-*tert*-butyl dicarbonate (23 mg, 24 μ L, 0.11 mmol). After stirring 60 min the reaction mixture was diluted with CH_2Cl_2 and washed once with brine. The aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL) and the combined organic layers were dried (MgSO_4), filtered, and concentrated. The residue was chromatographed (30 \rightarrow 40% EtOAc/hexanes, 2 g SiO_2), providing the Boc-protected derivative **11a** (4.7 mg, 62%) as a clear glass. The product was best visualized on TLC as described for **10a**. R_f = 0.5 (60% EtOAc/hexanes); IR (thin film) 1822, 1726 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 4.79 (d, J = 2.6 Hz, 1H), 4.76 (dd, J = 9.0, 3.1 Hz, 1H), 4.55–4.43 (m, 1H), 4.43 (dd, J = 8.9, 2.2 Hz, 1H), 4.02–3.62 (m, 3H), 3.45 (s, 3H), 1.54 (s, 9H), 1.51 (s, 3H), 1.44 (s, 3H).

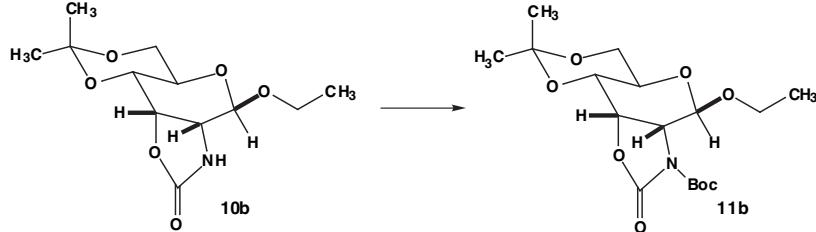


Hydrolysis product 12a. To cyclic carbamate **11a** (4.7 mg, 0.013 mmol) in $\text{THF}/\text{H}_2\text{O}$ (1 mL/0.3 mL) at 23 °C was added $\text{LiOH}\cdot\text{H}_2\text{O}$ (4.5 mg, 0.11 mmol). The mixture was stirred well during 45 min, poured into satd aq NH_4Cl (10 mL), and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried (MgSO_4), filtered, and concentrated. The residue was chromatographed (40% EtOAc/hexanes, 2 g SiO_2), providing alcohol **12a** (2.8 mg, 64%). The product was best visualized on TLC as described for **10a**. R_f = 0.3 (50% EtOAc/hexanes); IR (thin film) 3449, 3362, 1708 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.07 (br d, J = 8.1 Hz, 1H), 4.46 (d, J = 8.4 Hz, 1H), 4.11 (m, 1H), 4.00–3.58 (m, 5H), 3.49 (s, 3H), 2.29 (br, 1H), 1.49 (s, 3H), 1.45 (s, 9H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 155.7, 102.4, 99.9, 79.4, 72.3, 70.0, 64.8, 63.1, 56.8, 54.3, 29.6, 28.8, 19.5.

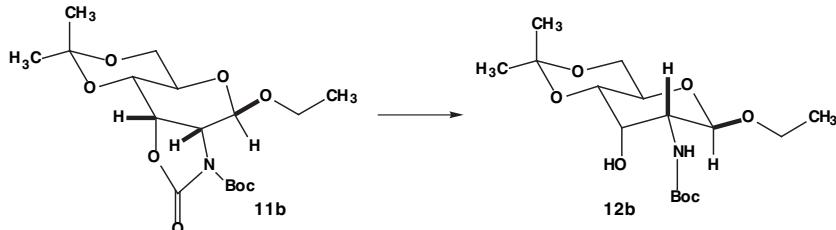


β -Ethyl-2-amido-D-allopyranoside 10b. Immediately prior to use, ethyl alcohol was refluxed 2 h with magnesium turnings and a flake of I_2 then distilled, followed by a second distillation from NaBH_4 . Azidoformate **2** (21 mg, 0.082 mmol) was dissolved in CH_2Cl_2 (11 mL) containing ethyl alcohol (19 mg, 23 μ L, 0.41 mmol). The solution was photolyzed in a quartz tube using a Rayonet merry-go-round

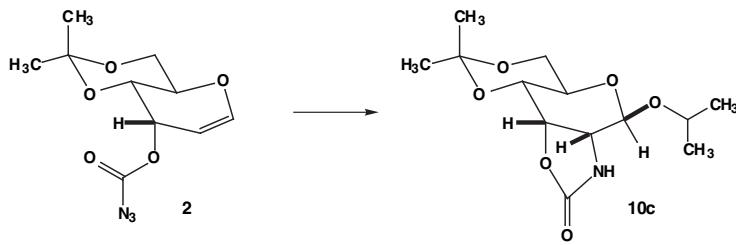
apparatus (254 nm lamp, Vycor filter) at 23 °C during 80 min. The reaction mixture was concentrated and the residue chromatographed (40→50→60→70→80→90→100% EtOAc/hexanes, 5 g SiO₂), providing oxazolidinone **10b** (8.6 mg, 38%) as a clear oil. The product was best visualized on TLC as described for **10a**. R_f = 0.2 (70% EtOAc/hexanes); IR (thin film) 3305, 1765 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.74 (br s, 1H), 4.81 (dd, J = 7.0, 3.3 Hz, 1H), 4.54 (d, J = 5.1 Hz, 1H), 4.15–4.04 (m, 1H), 4.03–3.65 (m, 5H), 3.55 (dq, J = 9.5, 7.1 Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); HRMS (FAB) *m/e* calcd for C₁₂H₂₀NO₆ (M+H)⁺ 274.1291, found 274.1304.



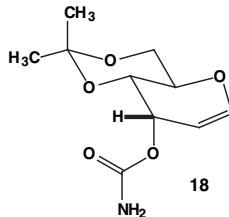
N-Boc-protected oxazolidinone 11b. To a 23 °C solution of oxazolidinone **10b** (6.9 mg, 0.025 mmol) in THF (2 mL) were added sequentially *N,N*-dimethyl-4-amino pyridine (15 mg, 0.13 mmol), triethylamine (13 mg, 17 μ L, 0.13 mmol), and di-*tert*-butyl dicarbonate (27 mg, 29 μ L, 0.13 mmol). After stirring 90 min the reaction mixture was diluted with CH₂Cl₂ and washed once with brine. The aqueous layer was extracted once with CH₂Cl₂ and the combined organic layers were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (30→40% EtOAc/hexanes, 2 g SiO₂), providing the Boc-protected derivative **11b** (7.5 mg, 80%) as a clear oil. The product was best visualized on TLC as described for **10a**. R_f = 0.6 (60% EtOAc/hexanes); IR (thin film) 1822, 1726 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 4.88 (d, J = 2.2 Hz, 1H), 4.77 (dd, J = 8.8, 2.9 Hz, 1H), 4.60–4.48 (m, 1H), 4.43 (dd, J = 8.6, 2.4 Hz, 1H), 4.00–3.61 (m, 4H), 3.53 (dq, J = 9.7, 7.1 Hz, 1H), 1.54 (s, 9H), 1.51 (s, 3H), 1.44 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).



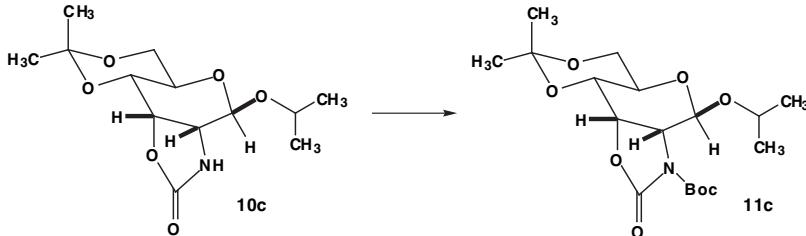
Hydrolysis product 12b. Cyclic carbamate **11b** (7.5 mg, 0.020 mmol) was dissolved in THF (2 mL) at 23 °C and water (0.6 mL) was added, followed by LiOH•H₂O (8.5 mg, 0.20 mmol). The mixture was stirred well during 90 min, poured into satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (40→50% EtOAc/hexanes, 2 g SiO₂), providing alcohol **12b** (5.6 mg, 80%) as a clear oil. The product was best visualized on TLC as described for **10a**. R_f = 0.2 (40% EtOAc/hexanes); IR (thin film) 3451, 3367, 1712 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.04 (br d, J = 7.0 Hz, 1H), 4.55 (d, J = 8.1 Hz, 1H), 4.12 (m, 1H), 3.99–3.59 (m, 6H), 3.54 (dq, J = 9.6, 7.0 Hz, 1H), 2.32 (br, 1H), 1.48 (s, 3H), 1.45 (s, 9H), 1.41 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H).



β -Isopropyl-2-amido-D-allopyranoside 10c. Immediately prior to use, isopropyl alcohol was refluxed 1h with CaO then distilled, followed by a second distillation from NaBH₄. Azidoformate **2** (18 mg, 0.071 mmol) was dissolved in CH₂Cl₂ (9 mL) and isopropyl alcohol (21 mg, 27 μ L, 0.35 mmol) was added. The solution was photolyzed in a quartz tube using a Rayonet merry-go-round apparatus (254 nm lamp, Vycor filter) at 23 °C during 95 min. The reaction mixture was concentrated and the residue chromatographed (50→60% EtOAc/hexanes, 6 g SiO₂), providing oxazolidinone **10c** (6.6 mg, 35%) as a clear oil. The product was best visualized on TLC as described for **10a**. R_f = 0.2 (60% EtOAc/hexanes); IR (thin film) 3306, 1763 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.74 (br s, 1H), 4.81 (dd, J = 6.8, 3.5 Hz, 1H), 4.59 (d, J = 5.1 Hz, 1H), 4.15–3.62 (m, 6H), 1.51 (s, 3H), 1.46 (s, 3H), 1.23 (d, J = 6.2 Hz, 3H), 1.29 (d, J = 5.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 158.7, 100.2, 99.9, 74.4, 71.3, 68.2, 63.8, 62.5, 56.0, 28.8, 23.5, 21.5, 18.8; HRMS (FAB) *m/e* calcd for C₁₃H₂₂NO₆ (M+H)⁺ 288.1447, found 288.1440. In addition, a small amount of carbamate **18** was isolated.

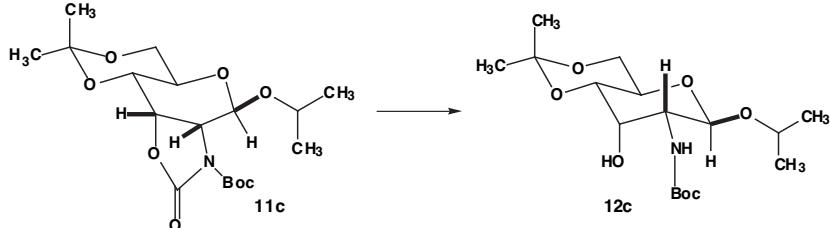


Data for **18**: R_f = 0.1 (40% EtOAc/hexanes); IR (thin film) 3447, 3355, 3266, 3206, 1690, 1631, 1610 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.45 (d, J = 5.9 Hz, 1H), 5.16 (m, 1H), 4.99 (dd, J = 5.9, 5.9 Hz, 1H), 4.65 (br s, 2H), 4.12–3.77 (m, 4H), 1.52 (s, 3H), 1.43 (s, 3H); HRMS (FAB) *m/e* calcd for C₁₀H₁₅NO₅Na (M+Na)⁺ 252.0848, found 252.0859.

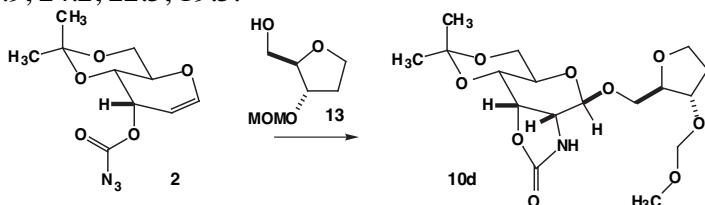


N-Boc-protected oxazolidinone 11c. To a 23 °C solution of oxazolidinone **10c** (7.4 mg, 0.026 mmol) in THF (2 mL) were added sequentially *N,N*-dimethyl-4-amino pyridine (12 mg, 0.10 mmol), triethylamine (10 mg, 14 μ L, 0.10 mmol), and di-*tert*-butyl dicarbonate (23 mg, 24 μ L, 0.10 mmol). After stirring 90 min the reaction mixture was concentrated and the residue was chromatographed (30→40% EtOAc/hexanes, 3 g SiO₂), providing the Boc-protected derivative **11c** (5.5 mg, 55%) as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. R_f = 0.4 (50% EtOAc/hexanes); IR (thin film) 1823, 1725 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 4.97 (d, J = 2.2 Hz, 1H), 4.76 (dd, J = 8.8, 2.9 Hz, 1H), 4.64–

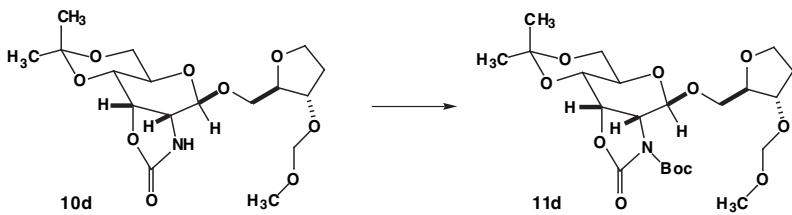
4.51 (m, 1H), 4.38 (dd, $J = 8.8, 2.2$ Hz, 1H), 4.06–3.61 (m, 4H), 1.55 (s, 9H), 1.51 (s, 3H), 1.45 (s, 3H), 1.25 (d, $J = 6.2$ Hz, 3H), 1.16 (d, $J = 6.2$ Hz, 3H).



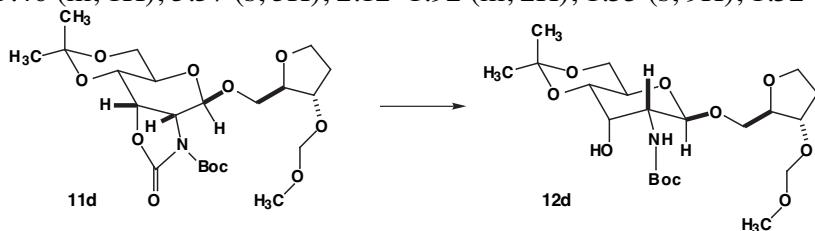
Hydrolysis product **12c.** Cyclic carbamate **11c** (5.5 mg, 0.014 mmol) was dissolved in THF (2.0 mL) at 23 °C and a solution of LiOH•H₂O (2.7 mg, 0.064 mmol) in water (0.6 mL) was added. The mixture was stirred well during 20 min, poured into satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂ (3 x 15 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (45% EtOAc/hexanes, 3 g SiO₂), providing alcohol **12c** (4.8 mg, 94%) as a white film. The product was best visualized on TLC as described for **10a**. $R_f = 0.3$ (45% EtOAc/hexanes); IR (thin film) 3450, 3393 (sh), 1713 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.02 (br, 1H), 4.59 (d, $J = 8.4$ Hz, 1H), 4.12 (m, 1H), 3.98–3.58 (m, 6H), 2.30 (br s, 1H), 1.48 (s, 3H), 1.45 (s, 9H), 1.41 (s, 3H), 1.21 (d, $J = 6.2$ Hz, 3H), 1.14 (d, $J = 6.2$ Hz, 3H); ¹³C NMR (75 MHz, C₆D₆) δ 155.6, 100.7, 99.8, 79.1, 72.5, 72.4, 70.1, 64.7, 63.2, 54.5, 29.6, 28.9, 24.2, 22.5, 19.5.



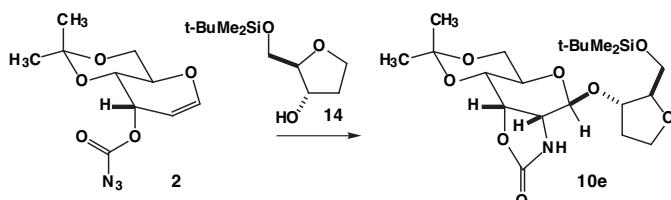
β -2-Amido-D-allopyranoside **10d.** Alcohol **13** was chromatographed (70→90% EtOAc/hexanes, 10 g SiO₂) immediately prior to use in the photolysis reaction. A solution of alcohol **13** (38.0 mg, 0.232 mmol) in CH₂Cl₂ (5.0 mL) was added to azidoformate **2** (19.7 mg, 0.077 mmol) in a quartz reaction tube. The solution was photolyzed using a Rayonet merry-go-round apparatus (254 nm, Vycor filter) at 23 °C during 2 h. The reaction mixture was concentrated and the residue chromatographed (90→100% EtOAc/hexanes, 5 g SiO₂). Oxazolidinone **10d** was isolated, contaminated with some starting alcohol **13** (**10d:13** = 2:1 by ¹H NMR integration, 5.3 mg total, 4.4 mg (15%) of **10d**). An analytical sample of **10d** was obtained by repeated chromatography on silica gel, eluting with EtOAc. Data for **10d**: $R_f = 0.1$ (100% EtOAc); IR (thin film) 3306, 1768 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.03 (br s, 1H), 4.79 (dd, $J = 6.7, 3.4$ Hz, 1H), 4.68 (AB, $J_{AB} = 7.0$ Hz, $\Delta\nu_{AB} = 12.9$ Hz, 2H), 4.58 (d, $J = 5.5$ Hz, 1H), 4.15–3.65 (m, 10H), 3.54 (dd, $J = 11.0, 6.6$ Hz, 1H), 3.40 (s, 3H), 2.15–1.96 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H).



N-Boc-protected oxazolidinone 11d. Oxazolidinone **10d** (2.8 mg, 0.0072 mmol) was dissolved in THF (1.5 mL) at 23 °C and treated sequentially with *N,N*-dimethyl-4-amino pyridine (3.9 mg, 0.036 mmol), triethylamine (4.4 mg, 6.0 μ L, 0.043 mmol), and di-*tert*-butyl dicarbonate (9.5 mg, 10 μ L, 0.044 mmol). After stirring 20 min the reaction mixture was concentrated and the residue was chromatographed (60→70% EtOAc/hexanes, 3 g SiO₂), providing the Boc-protected derivative **11d** (2.1 mg, 60%) as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. R_f = 0.2 (50% EtOAc/hexanes); IR (thin film) 1822, 1726 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.00 (d, *J* = 1.5 Hz, 1H), 4.77 (dd, *J* = 9.2, 3.3 Hz, 1H), 4.71–4.59 (m, 3H), 4.49 (dd, *J* = 9.2, 1.5 Hz, 1H), 4.15–4.05 (m, 1H), 4.03–3.63 (m, 7H), 3.59–3.46 (m, 1H), 3.37 (s, 3H), 2.12–1.92 (m, 2H), 1.55 (s, 9H), 1.52 (s, 3H), 1.44 (s, 3H).

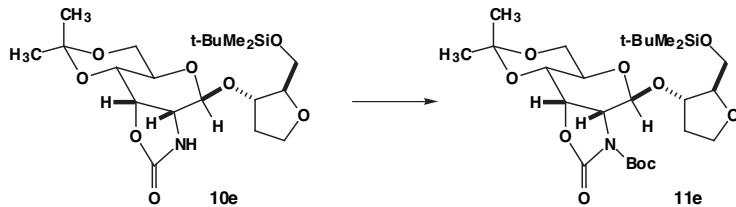


Hydrolysis product 12d. Cyclic carbamate **11d** (1.5 mg, 0.0031 mmol) in THF (1.0 mL) and water (0.3 mL) was treated with LiOH•H₂O (3.5 mg, 0.083 mmol). The reaction mixture was stirred vigorously at 23 °C during 45 min, poured into satd aq NH₄Cl (10 mL), and extracted with three portions of CH₂Cl₂. The combined organic extracts were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (70→80% EtOAc/hexanes, 1 g SiO₂), providing alcohol **12d** (0.8 mg, 57%) as a clear oil. The product was best visualized on TLC as described for **10a**. R_f = 0.3 (70% EtOAc/hexanes); IR (thin film) 3449, 3362, 1714 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.31 (br d, *J* = 8.8 Hz, 1H), 4.66 (AB, *J*_{AB} = 7.0 Hz, $\Delta\nu_{AB}$ = 5.4 Hz, 2H), 4.62 (d, *J* = 8.4 Hz, 1H), 4.22–4.08 (m, 2H), 4.06–3.60 (m, 9H), 3.55 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.37 (s, 3H), 2.25 (br, 1H), 2.22–1.84 (m, 2H), 1.48 (s, 3H), 1.45 (s, 9H), 1.41 (s, 3H).

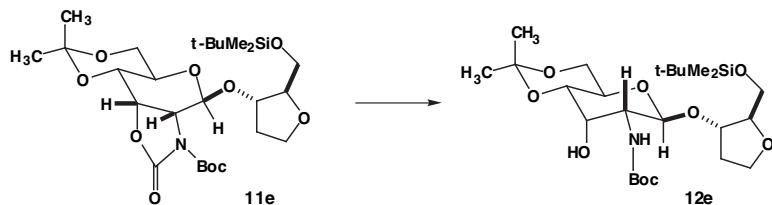


β -2-Amido-D-allopyranoside 10e. Alcohol **14** was chromatographed (30% EtOAc/Hexanes, 10 g SiO₂) immediately prior to use in the photolysis reaction. A solution of secondary alcohol **14** (63 mg, 0.27 mmol) in CH₂Cl₂ (12 mL) was added to azidoformate **2** (20 mg, 0.078 mmol) in a quartz reaction tube. The solution was photolyzed using a Rayonet merry-go-round apparatus (254 nm lamp, Vycor filter) at 23 °C during 1 h 40 min. The reaction mixture was concentrated and the residue chromatographed

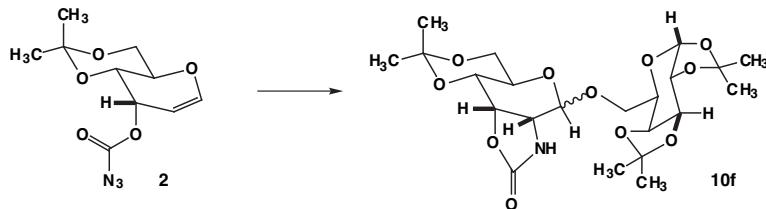
(30→40→50→60→70% EtOAc/hexanes, 5 g SiO₂), providing allopyranoside **10e** (3.7 mg, 10%). The product was best visualized on TLC as described for **10a**. R_f = 0.3 (60% EtOAc/hexanes); IR (thin film) 3305, 1766 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.44 (br s, 1H), 4.80 (dd, J = 6.8, 3.5 Hz, 1H), 4.61 (d, J = 5.5 Hz, 1H), 4.36 (m, 1H), 4.14–3.58 (m, 9H), 3.41 (dd, J = 10.4, 7.1 Hz, 1H), 2.20–1.95 (m, 2H), 1.51 (s, 3H), 1.47 (s, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); HRMS (FAB) *m/e* calcd for C₂₁H₃₈NO₈Si (M+H)⁺ 460.2367, found 460.2363.



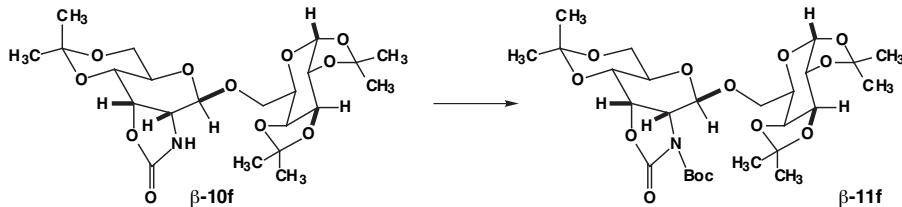
N-Boc-protected oxazolidinone **11e.** To a solution of oxazolidinone **10e** (1.6 mg, 0.0035 mmol) in THF (1.0 mL) at 23 °C was added *N,N*-dimethyl-4-amino pyridine (5.0 mg, 0.041 mmol), followed by triethylamine (4.4 mg, 6.0 μ L, 0.043 mmol), and di-*tert*-butyl dicarbonate (9.5 mg, 10 μ L, 0.044 mmol). After stirring 3 h the reaction mixture was concentrated and the residue was chromatographed (30→40% EtOAc/hexanes, 2 g SiO₂), providing the Boc-protected derivative **11e** (0.9 mg, 47%) as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. R_f = 0.4 (50% EtOAc/hexanes); IR (thin film) 1823, 1806, 1726 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 4.98 (d, J = 2.2 Hz, 1H), 4.76 (dd, J = 8.8, 2.9 Hz, 1H), 4.51 (dd, J = 9.9, 2.9 Hz, 1H), 4.42 (dd, J = 8.6, 2.4 Hz, 1H), 4.37 (ddd, J = 6.7, 2.3, 2.3 Hz, 1H), 4.06–3.80 (m, 5H), 3.79–3.58 (m, 2H), 3.42 (dd, J = 10.6, 6.6 Hz, 1H), 2.24–1.84 (m, 2H), 1.54 (s, 9H), 1.50 (s, 3H), 1.45 (s, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H).



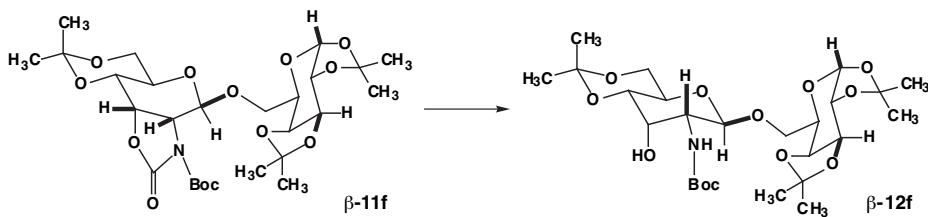
Hydrolysis product **12e.** Cyclic carbamate **11e** (0.9 mg, 0.0016 mmol) in THF (1.0 mL) was treated with a solution of LiOH•H₂O (3.1 mg, 0.074 mmol) in water (0.3 mL). The reaction mixture was stirred vigorously at 23 °C during 2 h, poured into satd aq NH₄Cl (10 mL), and extracted with three portions of CH₂Cl₂. The combined organic extracts were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (30→40% EtOAc/hexanes, 1 g SiO₂), providing alcohol **12e** quantitatively as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. R_f = 0.4 (25% EtOAc/hexanes, 2 elutions); IR (thin film) 3450, 1720 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.09 (br d, J = 9.9 Hz, 1H), 4.63 (d, J = 8.4 Hz, 1H), 4.29 (ddd, J = 5.3, 2.6, 2.6 Hz, 1H), 4.09 (m, 1H), 3.98–3.58 (m, 9H), 3.41 (dd, J = 10.4, 7.1 Hz, 1H), 2.26 (br, 1H), 2.14–1.90 (m, 2H), 1.49 (s, 3H), 1.45 (s, 9H), 1.41 (s, 3H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).



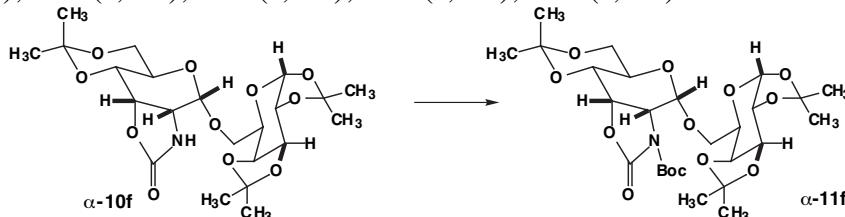
β - and α -2-Amido-D-allopyranosides 10f. Azidoformate **2** (22 mg, 0.086 mmol) was dissolved in CH_2Cl_2 (7 mL) and combined with a CH_2Cl_2 (7 mL) solution of 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose **15** (112 mg, 0.43 mmol). The solution was photolyzed in a quartz tube using a Rayonet merry-go-round apparatus (254 nm lamp, Vycor filter) at 23 °C during 80 min. The reaction mixture was concentrated and the residue chromatographed (40→50→60→70→80→100% EtOAc/hexanes, 5 g SiO_2), providing β -linked allopyranoside β -**10f** (4.7 mg, 11%) and the α -linked diastereomer α -**10f**, containing lower- R_f impurities (3.8 mg total, estimated <75% pure by ^1H NMR, <5% yield). Data for β -**10f**: R_f = 0.3 (80% EtOAc/hexanes); IR (thin film) 3338, 1766 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.13 (br s, 1H), 5.62 (d, J = 5.1 Hz, 1H), 4.74 (dd, J = 5.9, 3.7 Hz, 1H), 4.71 (d, J = 6.6 Hz, 1H), 4.60 (dd, J = 7.9, 2.4 Hz, 1H), 4.34 (dd, J = 4.9, 2.4 Hz, 1H), 4.15 (dd, J = 7.9, 1.7 Hz, 1H), 4.08–3.55 (m, 8H), 1.55 (s, 3H), 1.51 (s, 3H), 1.45 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H). Data for α -**10f**: R_f = 0.1 (80% EtOAc/hexanes); IR (thin film) 3339, 1766 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.50 (d, J = 5.1 Hz, 1H), 5.31 (br s, 1H), 4.84 (d, J = 5.1 Hz, 1H), 4.74 (dd, J = 6.0, 3.5 Hz, 1H), 4.66 (dd, J = 7.9, 2.4 Hz, 1H), 4.42 (dd, J = 8.1, 1.5 Hz, 1H), 4.32 (dd, J = 5.1, 2.6 Hz, 1H), 4.16–3.60 (m, 8H), 1.54 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H).



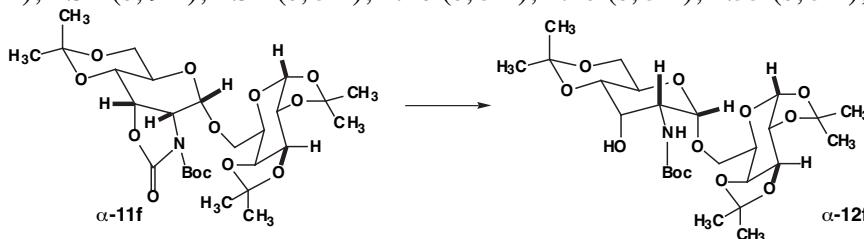
β -N-Boc-protected-2-amido-D-allopyranoside β -11f. Oxazolidinone β -**10f** (4.7 mg, 0.0097 mmol) in THF (2 mL) was treated sequentially with *N,N*-dimethyl-4-amino pyridine (6.0 mg, 0.048 mmol), triethylamine (4.8 mg, 7.0 μL , 0.048 mmol), and di-*tert*-butyl dicarbonate (10 mg, 11 μL , 0.048 mmol). After stirring 60 min the reaction mixture was diluted with CH_2Cl_2 and washed once with brine, dried (MgSO_4), filtered, and concentrated. The residue was chromatographed (40% EtOAc/hexanes, 1 g SiO_2), providing the Boc-protected derivative β -**11f** (4.5 mg, 79%) as a clear oil. R_f = 0.5 (60% EtOAc/hexanes); IR (thin film) 1823, 1802, 1725 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 5.52 (d, J = 5.1 Hz, 1H), 4.98 (d, J = 1.1 Hz, 1H), 4.77 (dd, J = 9.2, 2.9 Hz, 1H), 4.70–4.56 (m, 2H), 4.51 (dd, J = 9.2, 1.5 Hz, 1H), 4.35 (dd, J = 5.1, 2.6 Hz, 1H), 4.27 (dd, J = 7.9, 1.6 Hz, 1H), 4.05–3.73 (m, 5H), 3.60–3.42 (m, 1H), 1.54 (s, 9H), 1.54 (s, 3H), 1.54 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.34 (s, 3H).



β -Linked hydrolysis product $\beta\text{-}12\mathbf{f}$. To a well-stirred mixture of cyclic carbamate $\beta\text{-}11\mathbf{f}$ (4.5 mg, 0.0076 mmol) in THF (1.5 mL) and water (0.5 mL) was added LiOH \bullet H₂O (4.0 mg, 0.095 mmol). After 20 min the reaction mixture was poured into satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂. The organic phase was dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (40% EtOAc/hexanes, 1 g SiO₂), providing alcohol $\beta\text{-}12\mathbf{f}$ (3.3 mg, 77%) as clear oil. R_f = 0.4 (60% EtOAc/hexanes); IR (thin film) 3448, 1713 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.53 (d, J = 5.1 Hz, 1H), 5.17 (br d, J = 7.2 Hz, 1H), 4.79 (d, J = 8.8 Hz, 1H), 4.57 (dd, J = 7.9, 2.4 Hz, 1H), 4.30 (dd, J = 4.9, 2.4 Hz, 1H), 4.23 (m, 1H), 4.21 (dd, J = 7.9, 1.7 Hz, 1H), 4.04–3.56 (m, 8H), 2.25 (br, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.45 (s, 9H), 1.45 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.32 (s, 3H).

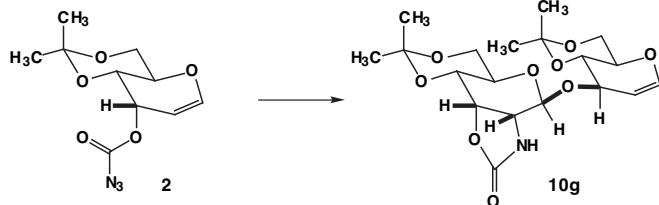


α -N-Boc-protected-2-amido-D-allopyranoside $\alpha\text{-}11\mathbf{f}$. To a solution of (impure) oxazolidinone $\alpha\text{-}10\mathbf{f}$ (3.8 mg, 0.0078 mmol) in THF (2 mL) at 23 °C was added sequentially *N,N*-dimethyl-4-amino pyridine (5.0 mg, 0.039 mmol), triethylamine (4.0 mg, 5.4 μ L, 0.039 mmol), and di-*tert*-butyl dicarbonate (9.0 mg, 9.0 μ L, 0.039 mmol). After stirring 5 h the reaction mixture was concentrated and the residue was chromatographed (40–50% EtOAc/hexanes, 1 g SiO₂), providing the Boc-protected derivative $\alpha\text{-}11\mathbf{f}$ (1.4 mg, 30%). R_f = 0.6 (80% EtOAc/hexanes); IR (thin film) 1820, 1723 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.48 (d, J = 5.1 Hz, 1H), 5.09 (d, J = 4.8 Hz, 1H), 4.59 (dd, J = 7.7, 2.2 Hz, 1H), 4.59 (dd, J = 6.0, 3.8 Hz, 1H), 4.32 (dd, J = 5.9, 5.1 Hz, 1H), 4.28 (dd, J = 4.9, 2.4 Hz, 1H), 4.22 (dd, J = 8.1, 1.8 Hz, 1H), 4.15–3.62 (m, 7H), 1.55 (s, 3H), 1.54 (s, 9H), 1.51 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H).

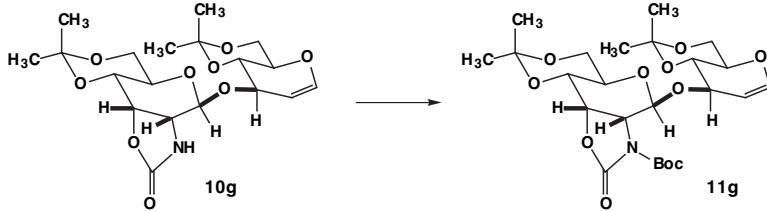


α -Linked hydrolysis product $\alpha\text{-}12\mathbf{f}$. A solution of cyclic carbamate $\alpha\text{-}11\mathbf{f}$ (1.4 mg, 0.0024 mmol) in THF (1 mL) and water (0.3 mL) was treated with LiOH \bullet H₂O (4.0 mg, 0.095 mmol). The reaction mixture was stirred vigorously during 1 h, poured into satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated. The residue was chromatographed (40–50% EtOAc/hexanes, 1 g SiO₂), providing alcohol $\alpha\text{-}12\mathbf{f}$ (0.4 mg, 31%). R_f = 0.4 (40% EtOAc/hexanes, 2 elutions); IR (thin film) 3454, 1712 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.53 (d,

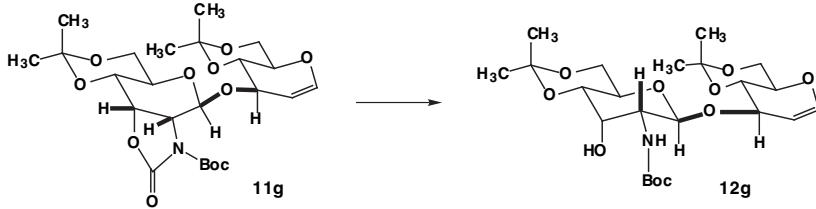
$J = 5.1$ Hz, 1H), 5.49 (br d, $J = 10.3$ Hz, 1H), 4.83 (d, $J = 3.7$ Hz, 1H), 4.62 (dd, $J = 7.9, 2.4$ Hz, 1H), 4.32 (dd, $J = 4.9, 2.4$ Hz, 1H), 4.24 (dd, $J = 7.9, 1.7$ Hz, 1H), 4.12–3.54 (m, 9H), 2.75 (br d, $J = 8.4$ Hz, 1H), 1.54 (s, 3H), 1.50 (s, 3H), 1.45 (s, 9H), 1.45 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H).



β -2-Amido-D-allopyranoside 10g. A solution of 4,6-*O*-isopropylidene-D-glucal **16** (75 mg, 0.40 mmol) in CH_2Cl_2 (11 mL) was added to azidoformate **2** (21 mg, 0.081 mmol) in a quartz reaction tube. The solution was photolyzed using a Rayonet merry-go-round apparatus (254 nm lamp, Vycor filter) at 23 °C during 90 min. The reaction mixture was concentrated and the residue chromatographed (40→50→60→70→80→100% EtOAc/hexanes, 5 g SiO_2), providing allopyranoside **10g** (2.3 mg, 7%). $R_f = 0.1$ (60% EtOAc/hexanes); IR (thin film) 3324, 1763, 1640 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.36 (dd, $J = 6.2, 1.1$ Hz, 1H), 5.58 (br s, 1H), 4.86 (dd, $J = 8.4, 3.3$ Hz, 1H), 4.73 (d, $J = 3.3$ Hz, 1H), 4.71 (dd, $J = 6.2, 1.8$ Hz, 1H), 4.46 (ddd, $J = 7.3, 1.6, 1.6$ Hz, 1H), 4.43–4.33 (m, 1H), 4.12–3.62 (m, 8H), 1.53 (s, 3H), 1.53 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H).

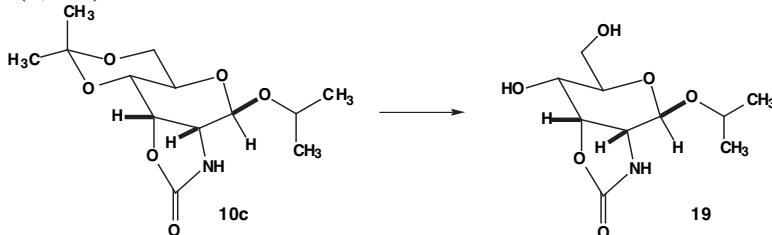


N-Boc-protected oxazolidinone 11g. Oxazolidinone **10g** (2.3 mg, 0.0056 mmol) was dissolved in THF (1.5 mL) at 23 °C and treated sequentially with *N,N*-dimethyl-4-amino pyridine (10 mg, 0.045 mmol), triethylamine (5.0 mg, 6.0 μL , 0.045 mmol), and di-*tert*-butyl dicarbonate (10 mg, 10 μL , 0.045 mmol). After stirring 2 h 45 min the reaction mixture was concentrated and the residue was chromatographed (30% EtOAc/hexanes, 2 g SiO_2), providing the Boc-protected derivative **11g** (1.8 mg, 62%) as a clear oil. $R_f = 0.5$ (50% EtOAc/hexanes); IR (thin film) 1823, 1803, 1724, 1641 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.35 (dd, $J = 6.2, 1.1$ Hz, 1H), 5.12 (d, $J = 1.7$ Hz, 1H), 4.83–4.64 (m, 3H), 4.44 (ddd, $J = 7.5, 1.6, 1.6$ Hz, 1H), 4.42 (dd, $J = 9.2, 1.1$ Hz, 1H), 4.10–3.63 (m, 7H), 1.56 (s, 9H), 1.54 (s, 3H), 1.54 (s, 3H), 1.44 (s, 3H), 1.44 (s, 3H).

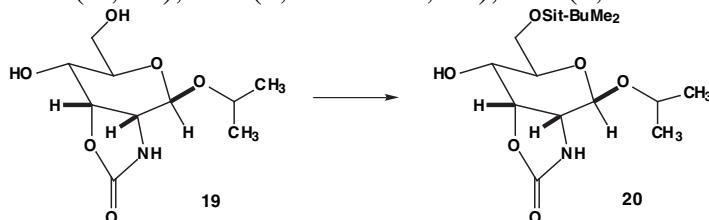


Hydrolysis product 12g. To a solution of cyclic carbamate **11g** (1.8 mg, 0.0035 mmol) in THF (1.0 mL) was added $\text{LiOH}\cdot\text{H}_2\text{O}$ (3.7 mg, 0.088 mmol) in water (0.33 mL). The reaction mixture was stirred vigorously at 23 °C during 1 h, poured into satd aq NH_4Cl (10 mL), and extracted with three portions of

CH_2Cl_2 . The combined organic extracts were dried (MgSO_4), filtered, and concentrated. The residue was chromatographed ($40 \rightarrow 50\%$ EtOAc/hexanes, 2 g SiO_2), providing alcohol **12g** (1.2 mg, 71%) as a clear oil. $R_f = 0.2$ (40% EtOAc/hexanes); IR (thin film) 3443, 1711, 1643 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.31 (dd, $J = 6.2, 1.5$ Hz, 1H), 5.09 (br d, $J = 8.8$ Hz, 1H), 4.74 (d, $J = 8.4$ Hz, 1H), 4.72 (dd, $J = 6.0, 3.5$ Hz, 1H), 4.32 (m, 1H), 4.13 (m, 1H), 4.03–3.58 (m, 9H), 2.34 (br, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.45 (s, 9H), 1.42 (s, 3H), 1.42 (s, 3H).



Diol 19. Acetonide **10c** (6.6 mg, 0.023 mmol) was dissolved in MeOH (2.5 mL) and concentrated HCl (0.13 mL) was added. The solution was stirred at 23 °C during 40 min and solid NaHCO_3 was added with vigorous stirring until the reaction mixture was neutral to litmus paper. The mixture was filtered through celite, rinsing with MeOH , and the filtrate was concentrated. The resulting solids were triturated thoroughly with 10% $\text{MeOH}/\text{CH}_2\text{Cl}_2$, and the washings were filtered through a plug of glass wool and concentrated. The residue was chromatographed ($10 \rightarrow 15 \rightarrow 20\%$ $\text{MeOH}/\text{CH}_2\text{Cl}_2$, 3 g SiO_2), affording diol **19** (2.8 mg, 49%) as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. $R_f = 0.4$ (20% $\text{MeOH}/\text{CH}_2\text{Cl}_2$); IR (thin film) 3338, 1749 cm^{-1} ; ^1H NMR (300 MHz, CD_3OD) δ 4.84 (dd, $J = 7.8, 3.7$ Hz, 1H), 4.64 (d, $J = 4.7$ Hz, 1H), 4.08 (apparent septet, $J = 6.2$ Hz, 1H), 3.99 (dd, $J = 9.2, 3.7$ Hz, 1H), 3.88–3.80 (m, 1H), 3.76–3.62 (m, 3H), 1.21 (d, $J = 6.2$ Hz, 3H), 1.16 (d, $J = 6.1$ Hz, 3H).



Silyl ether 20. Diol **19** (2.8 mg, 0.011 mmol) was dissolved in $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1.5 mL/0.15 mL) at 23 °C and imidazole (6.0 mg, 0.088 mmol) was added, followed by *tert*-butyldimethylsilyl chloride (6.7 mg, 0.044 mmol). After stirring 30 min the reaction mixture was poured into satd aq NaHCO_3 and extracted three times with CH_2Cl_2 . The combined organic extracts were dried (MgSO_4), filtered, and concentrated. The residue was chromatographed ($60 \rightarrow 70 \rightarrow 80\%$ EtOAc/hexanes, 3 g SiO_2), affording monosilylated diol **20** quantitatively as a clear, colorless oil. The product was best visualized on TLC as described for **10a**. $R_f = 0.2$ (60% EtOAc/hexanes); IR (thin film) 3306, 1765 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.46 (br s, 1H), 4.90 (dd, $J = 7.3, 4.0$ Hz, 1H), 4.62 (d, $J = 5.9$ Hz, 1H), 4.04 (dd, $J = 6.1, 4.4$ Hz, 1H), 4.01 (apparent septet, $J = 6.3$ Hz, 1H), 3.92–3.82 (m, 2H), 3.80–3.70 (m, 1H), 3.68–3.58 (m, 1H), 2.90 (d, $J = 6.3$ Hz, 1H), 1.22 (d, $J = 6.2$ Hz, 3H), 1.15 (d, $J = 6.1$ Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 159.0, 99.5, 76.5, 75.4, 70.9, 66.0, 64.4, 56.1, 26.4, 24.0, 21.9, 19.0, -4.9, -5.0.

References for the Supporting Information:

1. For a dramatic report on the instability of a lower molecular weight azidoformate during distillation, see: Feyen, P. *Angew. Chem., Int. Ed. Eng.* **1977**, *16*, 115.
2. Valverde, S.; García-Ochoa, S.; Martín-Lomas, M. *J. Chem. Soc., Chem. Commun.* **1987**, 383. Preparation of phenylthiopseudoglycal **6** and the derived acetonide **7** was reported in the Valverde communication, but experimental details and characterization data were not provided.