Supporting Information

Water-promoted Synthesis of Stereoselective Oxazoline-fused Saccharides and Construction for 1, 2-*cis* Glycosylamines of Multi-modifications of Polyhydroxyl groups

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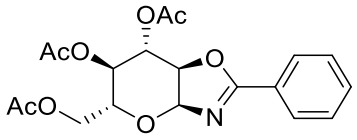
Contents

1. General Information

All starting materials were obtained from commercial suppliers and used without further purification. The ^{1}H NMR and ^{13}C NMR spectra were taken on Bruker Avance-600, 500 or 400, Varian- MERCURY Plus-600 or 400 NMR spectrometer operating at 600 MHz or 400 MHz for ^{1}H NMR, 125 MHz or 100 MHz for ^{13}C NMR, using TMS as internal standard and $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C NMR spectra were recorded with complete proton decoupling. The ESI-MS or EI-MS was recorded on Finnigan LCQ/DECA or Thermo-DFS, respectively. The HRMS were obtained from Micromass Ultra Q-TOF (ESI) or Thermo-DFS (EI) spectrometer. Flash column chromatography was carried out using silica gel (200~400 mesh). Thin layer chromatography (TLC) was used silica gel F254 fluorescent treated silica which were visualised under UV light (254 nm).

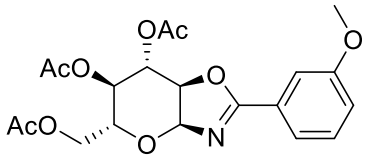
2. Synthetic Procedures and Characterization for oxazolinoses

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-phenyl-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3A)



To a solution of β-D-glucose pentaacetate (195 mg, 0.5 mmol), benzonitrile (50 μL, 0.5 mmol) in dry DCM (dichloromethane), water (10 μL) was added. After the reaction mixture was stirred well, TfOH (90 μL, 1 mmol) was added and stirred for 2 hours at room temperature. Then the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer was combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 2:1) to give product **3A** (144.3 mg, yield 74%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.09 (d, *J* = 7.7 Hz, 1H), 5.33 – 5.29 (m, 1H), 4.98 (ddd, *J* = 8.4, 4.5, 0.9 Hz, 1H), 4.63 (ddd, *J* = 7.7, 3.6, 0.9 Hz, 1H), 4.31 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.75 (ddd, *J* = 8.2, 5.1, 2.9 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 1.94 (s, 3H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.68, 169.54, 169.47, 166.59, 132.68, 128.90, 128.59, 126.21, 93.22, 75.82, 70.55, 68.07, 67.30, 63.28, 20.87, 20.78, 20.61. HRMS (ESI): $C_{19}H_{22}NO_8$ $[M+H]^+$, calculated for: 392.134, found: 392.1351. $[\alpha]_D^{20}$=33.5 (c=0.064, MeOH).

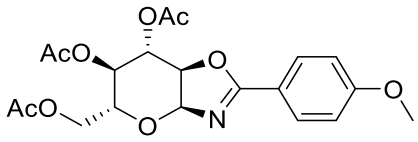
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3B)



3-Methoxybenzonitrile (66.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3B** (123.1 mg, yield 57%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (m, 1H), 7.55 (m, 1H), 7.36 (m, 1H), 7.10 (m, 1H), 6.08 (d,

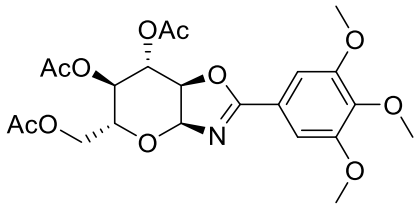
J = 7.7 Hz, 1H), 5.30 (d, *J* = 4.1 Hz, 1H), 4.98 (m, 1H), 4.63 (m, 1H), 4.31 (m, 1H), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.85 (s, 3H), 3.75 (m, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.57, 169.44, 169.35, 166.46, 159.51, 129.56, 127.29,121.20, 119.35, 113.05, 93.07, 75.70, 70.33, 67.93, 67.16, 63.16, 55.40, 20.78, 20.69, 20.54. HRMS (ESI): $C_{20}H_{24}NO_9$ $[M+H]^+$, calculated for: 422.1446, found: 422.1449. $[\alpha]_D^{20}$=40.5 (c=0.074, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3C)



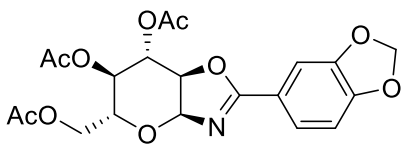
4-Methoxybenzonitrile (66.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3C** (123.1 mg, yield 57%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.05 (d, *J* = 7.6 Hz, 1H), 5.29 (dd, *J* = 5.2, 2.9 Hz, 1H), 5.02 – 4.94 (m, 1H), 4.65 – 4.56 (m, 1H), 4.30 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.17 (m, 2H), 3.85 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.59, 169.45, 169.38, 166.30, 163.05, 130.68, 118.39,113.85, 93.11, 75.61, 70.49, 67.78, 67.23, 63.18, 55.36, 20.79, 20.70, 20.55. HRMS (ESI): $C_{20}H_{24}NO_9$ $[M+H]^+$, calculated for: 422.1446, found: 422.1449. $[\alpha]_D^{20}$=38.7 (c=0.093, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(3,4,5-trimethoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3D)



3,4,5-Methoxybenzonitrile (96.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3D** (161.9 mg, yield 67%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (s, 2H), 6.07 (d, *J* = 7.6 Hz, 1H), 5.34 – 5.29 (m, 1H), 4.99 (m, 1H), 4.62 (m, 1H), 4.32 (dd, *J* = 12.1, 4.9 Hz, 1H), 4.19 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.91 (d, *J* = 2.0 Hz, 9H), 3.79 – 3.71 (m, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.23, 169.06, 165.99, 152.72, 141.51, 120.69, 105.64, 92.71, 75.60, 70.05, 67.43, 66.89, 62.75, 60.54, 55.90, 29.25, 20.45, 20.36, 20.23. HRMS (ESI): $C_{22}H_{28}NO_{11}$ $[M+H]^+$, calculated for: 482.1657, found: 482.1662. $[\alpha]_D^{20}$=35.5 (c=0.093, MeOH).

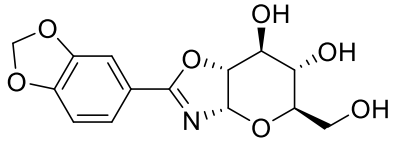
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3E)



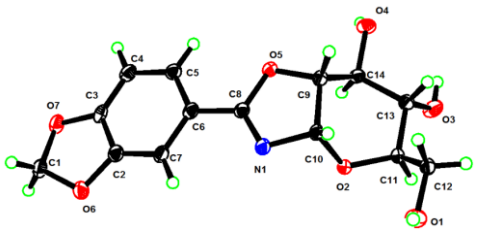
Piperonylonitrile (73.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were

used as described in (**3A**) and give compound **3E** (135.5 mg, yield 62%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.05 (d, *J* = 6.1 Hz, 3H), 5.28 (t, *J* = 4.1 Hz, 1H), 4.97 (ddd, *J* = 8.6, 4.6, 0.9 Hz, 1H), 4.60 (ddd, *J* = 7.7, 3.8, 0.9 Hz, 1H), 4.30 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.22 – 4.16 (m, 1H), 3.74 (ddd, *J* = 8.2, 5.0, 2.8 Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.68, 169.54, 169.46, 166.14, 151.43, 147.88, 124.35, 119.98, 108.80, 108.29, 101.82, 93.16, 75.91, 70.62, 67.98, 67.31, 63.26, 20.85, 20.77, 20.64. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1248. $[\alpha]_D^{20}$=97.5 (c=0.002, MeOH).

Compound **3E** was deprotected with triethylamine in MeOH to give compound **3Y**, the structure of compound **3Y** was identified via X-ray crystallography.

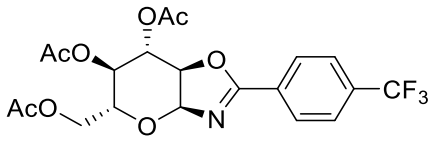


3Y



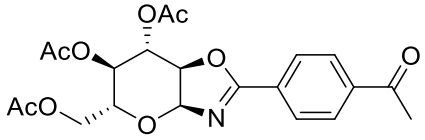
X-ray crastallography of **3Y**

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-(trifluoromethyl)phenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3F)



4-(Trifluoromethyl)benzonitrile(85.5 mg, 0.5 mmol)and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3F** (48.3 mg, yield 21%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 – 8.13 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 5.32 (m, 1H), 5.01 (m, 1H), 4.70 (m, 1H), 4.33 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.21 (dd, *J* = 12.2, 2.9 Hz, 1H), 3.79 – 3.72 (m, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.67, 169.50, 169.48, 165.27, 134.34, 134.12, 129.30, 125.64, 125.61, 93.25, 76.25, 70.51, 68.34, 67.11, 63.14, 20.88, 20.80, 20.64. HRMS (ESI): $C_{20}H_{21}F_3NO_8$ $[M+H]^+$, calculated for: 460.1214, found: 460.1212. $[\alpha]_D^{20}$=42.7 (c=0.075, MeOH).

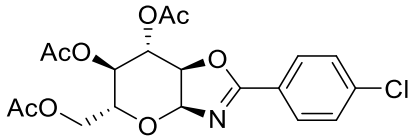
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-acetylphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3G)



4-Acetybenzonitrile (72.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3G** (79.6 mg, yield 35%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 – 8.08 (m, 2H), 8.02 (d, *J* = 8.7 Hz, 2H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.32 – 5.26 (m, 1H), 4.98 (m, 1H), 4.66 (m, 1H), 4.31 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.19 (dd, *J* =

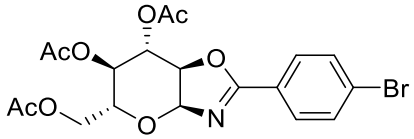
12.1, 2.9 Hz, 1H), 3.74 (m, 1H), 2.64 (s, 3H), 2.16 (s, 3H), 2.08 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.20, 170.54, 169.36, 165.48, 139.90, 130.03, 129.03, 128.30, 128.27, 93.18, 76.03, 70.40, 68.27, 67.00, 63.06, 26.73, 20.76, 20.68, 20.52. HRMS (ESI): $C_{21}H_{24}NO_9$ $[M+H]^+$, calculated for: 434.1446, found: 434.1453. $[\alpha]_D^{20}$=60.3 (c=0.105, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-chlorophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3H)



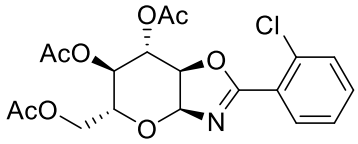
4-Chlorobenzonitrile (68.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3H** (57.5 mg, yield 27%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.39 (m, 2H), 6.07 (d, *J* = 7.7 Hz, 1H), 5.30 – 5.24 (m, 1H), 4.97 (m, 1H), 4.63 (m, 1H), 4.30 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.18 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.76 – 3.67 (m, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.54, 169.36, 165.53, 138.98, 130.09, 128.86, 124.56, 93.15, 75.97, 70.44, 68.11, 67.05, 63.08, 20.76, 20.68, 20.52. HRMS (ESI): $C_{19}H_{21}ClNO_8$ $[M+H]^+$, Calculated for: 426.0950, found: 426.0955. $[\alpha]_D^{20}$=39.2 (c=0.1, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(4-bromophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3I)



4-Bromobenzonitrile (90 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3I** (51.7 mg, yield 22%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 6.07 (d, *J* = 7.7 Hz, 1H), 5.28 (dd, *J* = 9.7, 5.4 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.63 (m, 1H), 4.30 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.18 (dd, *J* = 12.1, 2.8 Hz, 1H), 3.73 (m, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.55, 169.37, 165.65, 131.85, 130.23, 127.56, 125.01, 93.15, 75.97, 70.43, 68.12, 67.05, 63.08, 20.76, 20.68, 20.53. HRMS (ESI): $C_{19}H_{21}BrNO_8$ $[M+H]^+$, calculated for: 470.0445, found: 470.0442. $[\alpha]_D^{20}$=41.7 (c=0.084, MeOH).

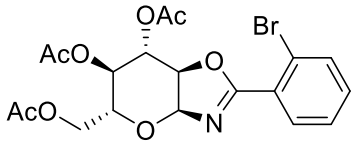
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chlorophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3J)



2- Chlorobenzonitrile (72.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3J** (74.4 mg, yield 35%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.8 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.4 (td, *J* = 7.5,

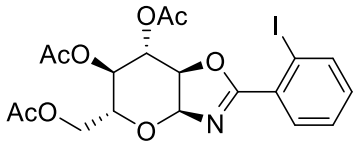
1.4 Hz, 1H), 6.1 (d, *J* = 7.8 Hz, 1H), 5.3 (t, *J* = 4.1 Hz, 1H), 5.0 (ddd, *J* = 8.7, 4.5, 0.9 Hz, 1H), 4.6 (ddd, *J* = 7.8, 3.7, 0.9 Hz, 1H), 4.3 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.2 (dd, *J* = 12.1, 2.8 Hz, 1H), 3.8 (ddd, *J* = 8.4, 5.2, 2.8 Hz, 1H), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 170.2, 169.1, 168.9, 164.7, 133.5, 132.2, 131.2, 130.6, 126.2, 125.4, 93.0, 70.1, 67.6, 66.8, 62.7, 59.9, 20.4, 20.3, 20.2. HRMS (ESI): $C_{19}H_{21}ClNO_8$ $[M+H]^+$, calculated for: 426.095,found: 426.0958. $[\alpha]_D^{20}$=59.1 (c=0.095, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3K)



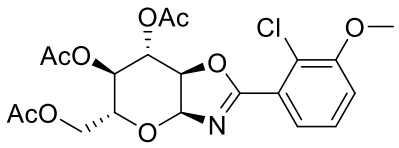
2-Bromobenzonitrile (91.0 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3K** (84.5 mg, yield 38%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.8 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.7 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.4 (dtd, *J* = 22.4, 7.5, 1.6 Hz, 2H), 6.1 (d, *J* = 7.8 Hz, 1H), 5.3 (t, *J* = 4.2 Hz, 1H), 5.0 (ddd, *J* = 8.8, 4.6, 0.8 Hz, 1H), 4.7 (ddd, *J* = 7.9, 3.8, 0.8 Hz, 1H), 4.3 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.2 (dd, *J* = 12.1, 2.8 Hz, 1H), 3.9 (ddd, *J* = 8.3, 5.2, 2.7 Hz, 1H), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.7, 169.6, 169.4, 165.8, 134.3, 132.7, 131.7, 128.0, 127.3, 122.2, 93.4, 75.9, 70.7, 68.1, 67.4, 63.2, 20.9, 20.8, 20.7. HRMS (ESI): $C_{19}H_{21}BrNO_8$ $[M+H]^+$, calculated for: 470.0455, found: 470.0457. $[\alpha]_D^{20}$=19.1 (c=0.115, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-iodophenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3L)



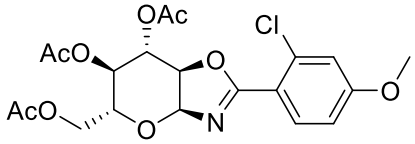
2-Iodobenzonitrile (114.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3L** (142.9 mg, yield 56%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.0 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.8 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.5 (td, *J* = 7.6, 1.2 Hz, 1H), 7.2 (td, *J* = 7.7, 1.7 Hz, 1H), 6.2 (d, *J* = 7.8 Hz, 1H), 5.4 (t, *J* = 4.1 Hz, 1H), 5.0 (ddd, *J* = 8.8, 4.7, 0.9 Hz, 1H), 4.7 (ddd, *J* = 7.8, 3.7, 0.9 Hz, 1H), 4.4 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.3 (dd, *J* = 12.2, 2.8 Hz, 1H), 3.9 (ddd, *J* = 8.4, 5.2, 2.8 Hz, 1H), 2.2 (s, 3H), 2.1 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.7, 169.6, 169.4, 166.5, 141.2, 132.6, 131.6, 131.2, 128.0, 94.7, 93.4, 76.1, 70.7, 68.2, 67.4, 63.1, 20.8, 20.8, 20.7. HRMS (ESI): $C_{19}H_{21}INO_8$ $[M+H]^+$, calculated ford: 518.0306, found: 518.0317. $[\alpha]_D^{20}$=24.7 (c=0.502, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chloro-3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3M)



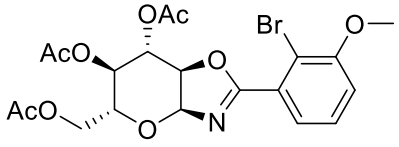
2-Chloro-3methoxybenzonitrile (110.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3M** (54.0 mg, yield 24%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 5.33 (t, *J* = 4.0 Hz, 1H), 4.98 (dd, *J* = 8.8, 4.3 Hz, 1H), 4.63 (dd, *J* = 7.9, 3.7 Hz, 1H), 4.31 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.21 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.69, 169.58, 169.36, 165.45, 127.52, 127.28, 122.99, 122.62, 114.84, 93.29, 75.59, 70.45, 67.95, 67.35, 63.23, 56.53, 20.83, 20.78, 20.68. HRMS (ESI): $C_{20}H_{23}ClNO_9$ $[M+H]^+$, calculated for: 456.1056, found: 456.1060. $[\alpha]_D^{20}$=34.4 (c=0.125, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-chloro-4-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3N)



2-Chloro-4methoxybenzonitrile (110.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3N** (151.2 mg, yield 67%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.8 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.13 (d, *J* = 7.7 Hz, 1H), 5.37 – 5.31 (m, 1H), 5.00 (m, 1H), 4.61 (m, 1H), 4.33 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.23 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.88 (s, 3H), 3.83 (m, 1H), 2.17 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 169.55, 169.41, 164.86, 162.48, 135.50, 133.03, 117.76, 116.40, 112.81, 93.44, 75.29, 70.60, 68.05, 67.33, 63.25, 55.72, 20.84, 20.77, 20.65. HRMS (ESI): $C_{20}H_{23}ClNO_9$ $[M+H]^+$, calculated for: 456.1056, found: 456.1049. $[\alpha]_D^{20}$=62.0 (c=0.079, MeOH).

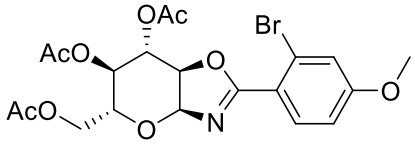
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-3-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3O)



2-Bromo-3methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3O** (116.8 mg, yield 47%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.05 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 5.36 (t, *J* = 4.0 Hz, 1H), 4.99 (m, 1H), 4.65 (m, 1H), 4.32 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.22 (dd, *J* = 12.1, 2.7 Hz, 1H), 3.93 (d, *J* = 7.9 Hz, 4H), 2.15 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.66, 169.56, 169.33, 166.22, 156.62, 130.03, 128.17, 123.22, 114.52, 112.07, 93.28, 75.96, 70.70, 68.00, 67.42, 63.15,

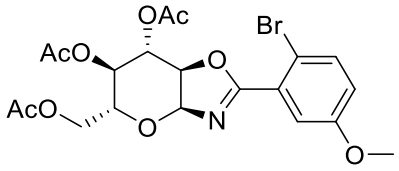
56.61, 20.78, 20.73, 20.66. HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0556. $[\alpha]_D^{20}$=33.5 (c=0.181, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-4-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3P)



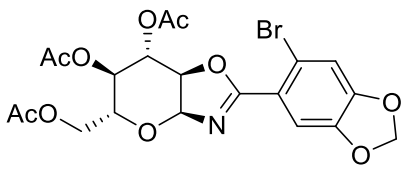
2-Bromo-4methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3P** (151.2mg, yield 67%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.33 (t, *J* = 4.2 Hz, 1H), 4.98 (m, 1H), 4.63 – 4.58 (m, 1H), 4.32 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.21 (dd, *J* = 12.1, 2.7 Hz, 1H), 3.87 – 3.83 (m, 4H), 2.16 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.70, 169.58, 169.43, 162.24, 133.05, 123.34, 121.47, 119.78, 119.76, 113.26, 93.42, 75.52, 70.65, 68.04, 67.37, 63.22, 55.73, 20.86, 20.80, 20.69 HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0558. $[\alpha]_D^{20}$=32.0 (c=0.125, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-5-methoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Q)



2-Bromo-5methoxybenzonitrile (105.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Q** (123.0mg, yield 50%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.9 Hz, 1H), 7.33 (d, *J* = 3.1 Hz, 1H), 6.93 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.14 (d, *J* = 7.8 Hz, 1H), 5.36 (t, *J* = 4.2 Hz, 1H), 5.00 (m, 1H), 4.66 (m, 1H), 4.34 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.23 (dd, *J* = 12.2, 2.8 Hz, 1H), 3.88 (m, 1H), 3.84 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.66, 169.55, 169.37, 158.57, 135.05, 119.21, 116.64, 112.37, 93.40, 77.24, 76.02, 70.72, 68.15, 67.31, 63.13, 60.36, 55.68, 20.82, 20.76, 20.67. HRMS (ESI): $C_{20}H_{23}BrNO_9$ $[M+H]^+$, calculated for: 500.0551, found: 500.0556. $[\alpha]_D^{20}$=32.4 (c=0.074, MeOH).

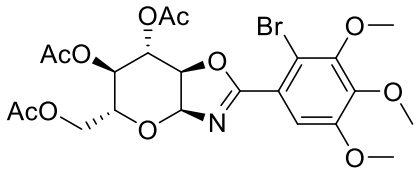
(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(6-bromobenzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3R)



2-Bromopiperonylonitrile (112.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol)

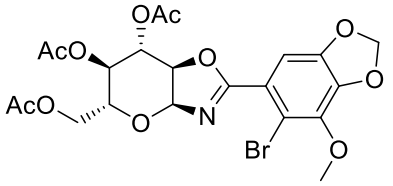
were used as described in (**3A**) and give compound **3R** (139.3mg, yield 54%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (s, 1H), 7.13 (s, 1H), 6.12 (d, *J* = 7.8 Hz, 1H), 6.07 (s, 2H), 5.33 (t, *J* = 4.2 Hz, 1H), 4.99 (m, *J* = 8.7, 4.6, 0.8 Hz, 1H), 4.62 (m, *J* = 7.8, 3.7, 0.9 Hz, 1H), 4.33 (dd, *J* = 12.2, 5.2 Hz, 1H), 4.22 (dd, *J* = 12.2, 2.8 Hz, 1H), 3.84 (m, *J* = 8.3, 5.2, 2.7 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.68, 169.55, 169.38, 165.46, 150.97, 147.25, 133.33, 128.36, 114.32, 110.99, 102.56, 93.29, 75.71, 70.61, 68.08, 67.35, 63.19, 20.81, 20.76, 20.68. HRMS (ESI): $C_{20}H_{21}BrNO_{10}$ $[M+H]^+$, calculated for: 514.0343, found: 514.0354. $[\alpha]_D^{20}$=67.3 (c=0.101, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(2-bromo-3,4,5-trimethoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3S)



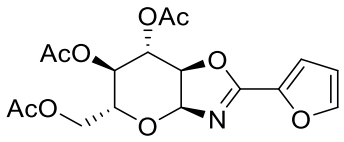
2-Bromo-3,4,5-methoxybenzonitrile (135.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3S** (131.4mg, yield 44%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (s, 1H), 6.10 (d, *J* = 7.7 Hz, 1H), 5.37 – 5.35 (m, 1H), 5.00 (dd, *J* = 9.2, 4.8 Hz, 1H), 4.63 (dd, *J* = 7.8, 4.0 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.23 – 4.19 (m, 1H), 3.94 (s, 3H), 3.90 (s, 6H), 2.15 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.20, 169.07, 168.97, 165.31, 152.08, 151.20, 145.62, 122.64, 110.06, 109.49, 92.96, 75.85, 70.63, 67.62, 66.83, 62.52, 60.72, 60.59, 55.84, 20.36, 20.31, 20.22. HRMS (ESI): $C_{22}H_{27}BrNO_{11}$ $[M+H]^+$, calculated for: 560.0762, found: 560.0761. $[\alpha]_D^{20}$= 45.775 (c=0.142, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(6-bromo-7-methoxybenzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (**3T**)



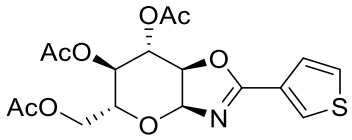
6-Bromo-7-methoxybenzo[d][1,3]dioxole-5-carbonitrile(128 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3T** (147 mg, yield 54%) as a yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.00 (s, 1H), 6.09 (d, J = 7.8 Hz, 1H), 6.06 (s, 2H), 5.32 (t, J = 4.1 Hz, 1H), 5.01 – 4.95 (m, 1H), 4.63 – 4.58 (m, 1H), 4.31 (dd, J = 12.2, 5.2 Hz, 1H), 4.20 (dd, J = 12.2, 2.7 Hz, 1H), 4.04 (s, 3H), 3.84 (ddd, J = 8.2, 5.1, 2.5 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 170.86, 169.73, 169.54, 165.95, 148.70, 141.36, 140.71, 122.17, 109.61, 105.99, 102.64, 93.50, 75.99, 70.87, 68.19, 67.57, 63.35, 60.51, 21.00, 20.96, 20.88. HRMS (ESI): $C_{21}H_{23}BrNO_{11}$ $[M+H]^+$, calculated for: 544.0449, found: 544.0463. $[\alpha]_D^{20}$= 51.061 (c=0.110, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(furan-2-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d] oxazole-6,7-diyl diacetate (3U)



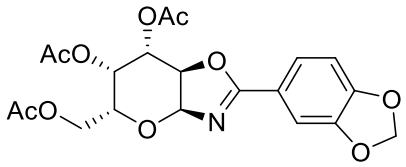
Furan-2-carbonitrile (46.5 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3U** (131.5mg, yield 69%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.12 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 5.27 – 5.23 (m, 1H), 4.98 – 4.95 (m, 1H), 4.59 (ddd, *J* = 7.7, 3.7, 0.9 Hz, 1H), 4.29 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.16 (dd, *J* = 9.7, 2.5 Hz, 1H), 3.75 (ddd, *J* = 8.2, 5.1, 2.8 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 170.55, 169.40, 169.29, 158.24, 146.49, 141.42, 116.92, 111.90, 92.96, 75.69, 70.40, 67.93, 67.05, 63.00, 20.73, 20.66, 20.51.HRMS (ESI): $C_{17}H_{20}NO_9$ $[M+H]^+$, calculated for: 382.1133, found: 382.1143. $[\alpha]^{20}_{D}$=44.4 (c=0.081, MeOH).

(3aS,5R,6R,7S,7aR)-5-(acetoxymethyl)-2-(thiophen-3-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2, 3-d]oxazole-6,7-diyl diacetate (3V)



3-Thiophenecarbonitrile (54 mg, 0.5 mmol) and β-D-glucose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3V** (106.7mg, yield 56%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.38 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 5.30 – 5.27 (m, 1H), 5.00 – 4.95 (m, 1H), 4.59 (m, 1H), 4.31 (dd, *J* = 12.1, 5.0 Hz, 1H), 4.22 – 4.15 (m, 2H), 2.16 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.58, 169.43, 169.37, 162.58, 130.96, 128.40, 127.30, 126.63, 93.09, 75.56, 70.46, 67.88, 67.17, 63.11, 20.78, 20.69, 20.52. HRMS (ESI): $C_{17}H_{20}NO_8S$ $[M+H]^+$, calculated for: 398.0904, found: 398.0917. $[\alpha]^{20}_{D}$=28.2 (c=0.049, MeOH).

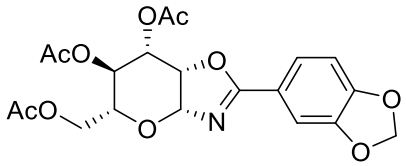
(3aS,5R,6S,7S,7aR)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Ea)



Piperonylonitrile (73.5 mg, 0.5 mmol) and β-D-Galactose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Ea** (98.3 mg, yield 62%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.37 (d, *J* = 1.7 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.03 – 5.93 (m, 3H), 5.41 (s, 1H), 4.98 (dd, *J* = 7.2, 3.1 Hz, 1H), 4.61 (t, *J* = 7.1 Hz, 1H), 4.22 (m, 1H), 4.13 (m, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.98, 169.53, 169.51, 165.17, 150.85, 147.32, 123.75, 119.90, 108.19, 107.72, 101.32,

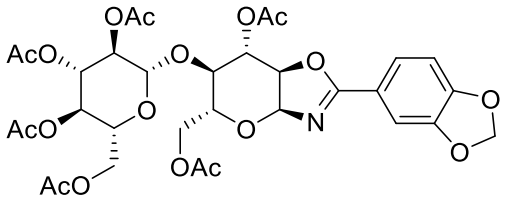
93.63, 76.17, 71.33, 68.80, 65.72, 60.88, 20.29, 20.22, 20.15. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1247. $[\alpha]^{20}_D$=85.3 (c=0.068, MeOH).

(3aR,5R,6R,7S,7aS)-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Eb)



Piperonylonitrile (73.5 mg, 0.5 mmol) and α-D-Mannose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Eb** (96.7 mg, yield 62%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H), 5.74 (d, *J* = 5.5 Hz, 1H), 5.40 (dd, *J* = 8.4, 4.9 Hz, 1H), 5.14 (t, *J* = 8.2 Hz, 1H), 4.81 (t, *J* = 5.2 Hz, 1H), 4.24 (dd, *J* = 12.0, 6.4 Hz, 1H), 4.16 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.83 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.30, 169.76, 168.95, 167.85, 151.03, 147.36, 124.17, 119.55, 108.52, 107.79, 101.35, 93.19, 76.32, 72.86, 68.52, 66.09, 63.27, 20.33, 20.29, 20.27. HRMS (ESI): $C_{20}H_{22}NO_{10}$ $[M+H]^+$, calculated for: 436.1238, found: 436.1238. $[\alpha]^{20}_D$=-76.2 (c=0.042, MeOH).

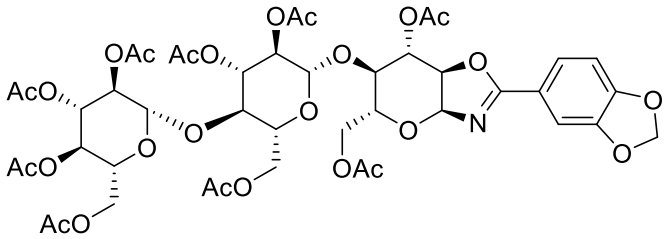
(2S,3R,4S,5R,6R)-2-(((3aS,5R,6R,7S,7aR)-7-acetoxy-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazol-6-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3Ec)



Piperonylonitrile (73.5 mg, 0.5 mmol) and α-D-Cellobiose octaacetate (339 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Ec** (94.5 mg, yield 42%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.05 (s, 2H), 5.97 (d, *J* = 7.4 Hz, 1H), 5.63 (s, 1H), 5.19 – 5.08 (m, 2H), 4.89 (dd, *J* = 9.3, 8.0 Hz, 1H), 4.66 (d, *J* = 8.1 Hz, 1H), 4.54 (ddd, *J* = 7.4, 3.3, 1.1 Hz, 1H), 4.26 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.22 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.6 Hz, 1H), 4.15 – 4.11 (m, 1H), 3.76 – 3.66 (m, 2H), 3.46 (ddd, *J* = 9.0, 5.1, 2.5 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.54, 170.10, 169.28, 169.26, 169.11, 166.80, 151.33, 147.73, 124.45, 119.66, 108.86, 108.22, 101.67, 101.54, 92.45, 76.56, 75.35, 72.84, 71.84, 71.21, 69.76, 67.99, 67.21, 63.48, 61.64, 20.82, 20.77, 20.62, 20.48, 20.45, 20.34. HRMS (ESI): $C_{32}H_{38}NO_{18}$ $[M+H]^+$, calculated for: 724.2083, found: 724.2100. $[\alpha]^{20}_D$ =17.0 (c=0.053, MeOH).

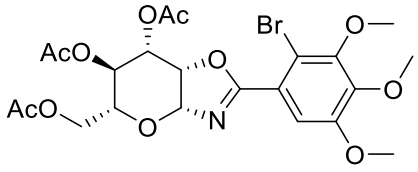
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-6-(((3aS,5R,6R,7S,7aR)-7-acetoxy-5-(acetoxymethyl)-2-(benzo[d][1,3]dioxol-5-yl)-3a,6,7,7a-tetrahydro-5H-pyran

o[2,3-d]oxazol-6-yl)oxy)-2-(acetoxymethyl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3Ed)



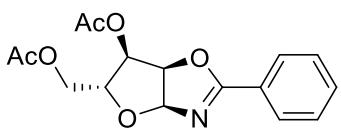
Piperonylonitrile (73.5 mg, 0.5 mmol) and D-Maltotriose pearcetate (483 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Ed** (94.5 mg, yield 18%) as a white powder. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.05 (d, *J* = 1.5 Hz, 2H), 5.39 (d, *J* = 4.0 Hz, 1H), 5.36 – 5.29 (m, 3H), 5.24 (dd, *J* = 3.4, 1.6 Hz, 1H), 5.07 (d, *J* = 9.9 Hz, 1H), 4.85 (ddd, *J* = 15.8, 10.3, 4.0 Hz, 2H), 4.59 – 4.54 (m, 1H), 4.43 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.31 – 4.21 (m, 4H), 4.18 – 4.13 (m, 1H), 4.07 – 4.03 (m, 1H), 3.93 (dd, *J* = 7.1, 2.5 Hz, 3H), 3.72 (dt, *J* = 8.6, 1.7 Hz, 1H), 3.61 (td, *J* = 5.3, 2.6 Hz, 1H), 2.16 (s, 6H), 2.14 (s, 6H), 2.11 (s, 3H), 2.04 (s, 6H), 2.01 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 170.50, 170.48, 170.40, 170.21, 169.83, 169.63, 169.51, 169.42, 167.23, 151.37, 147.88, 124.62, 119.85, 108.99, 108.63, 101.66, 95.77, 95.55, 92.32, 74.82, 73.86, 72.85, 72.05, 70.68, 70.04, 69.42, 68.88, 68.58, 68.52, 67.88, 67.39, 64.02, 62.55, 61.41, 20.96, 20.90, 20.89, 20.73, 20.69, 20.66, 20.57, 20.51.HRMS (ESI): $C_{44}H_{53}NNaO_{26}$ $[M+Na]^+$, calculated for: 1034.2748, found: 1034.2722. $[\alpha]^{20}_{D}$=104.5 (c=0.089, MeOH).

(3aR,5R,6R,7S,7aS)-5-(acetoxymethyl)-2-(2-bromo-3,4,5-trimethoxyphenyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-6,7-diyl diacetate (3Sa)



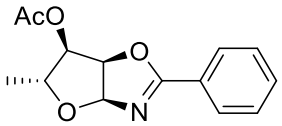
2-Bromo-3,4,5-trimethoxybenzonitrile (135.5 mg, 0.5 mmol) and α-D-Mannose pentaacetate (195 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3Sa** (63.9 mg, yield 23%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.40 (d, *J* = 6.2 Hz, 1H), 5.39 (d, *J* = 1.2 Hz, 1H), 5.01 (d, *J* = 6.2 Hz, 1H), 4.95 (m, 1H), 4.46 (dd, *J* = 12.3, 2.6 Hz, 1H), 4.31 (t, *J* = 6.7 Hz, 1H), 4.25 (dd, *J* = 7.1, 5.1 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.89 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.87, 171.56, 170.92, 167.13, 154.11, 153.03, 147.40, 132.31, 124.44, 111.73, 104.31, 87.02, 83.62, 79.64, 70.71, 64.19, 62.59, 62.47, 57.81, 22.26, 22.16, 20.61. HRMS (ESI): $C_{22}H_{27}BrNO_{11}$ $[M+H]^+$ calculated for: 560.0762, found: 560.0764. $[\alpha]^{20}_{D}$= -9.5 (c=0.084, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-phenyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3a)



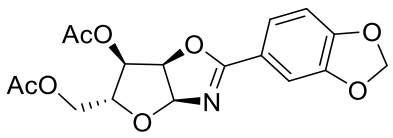
Benzonitrile (51.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3a** (94.5 mg, yield 81%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (m, 4H), 7.57 (m, 2H), 7.47 (m, 4H), 6.33 (d, *J* = 6.1 Hz, 1H), 6.29 (d, *J* = 5.6 Hz, 1H), 5.34 (m, 1H), 5.24 (t, *J* = 5.7 Hz, 1H), 5.06 (dd, *J* = 6.2, 1.0 Hz, 1H), 4.87 (dd, *J* = 9.3, 5.9 Hz, 1H), 4.43 (dd, *J* = 12.4, 2.7 Hz, 1H), 4.33 (m, 1H), 4.23 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.07 (m, 2H), 3.92 (m, 1H), 2.18 (d, *J* = 5.8 Hz, 6H), 2.11 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.66, 170.07, 167.49, 132.54, 128.94, 128.52, 126.08, 100.68, 78.08, 74.03, 73.04, 62.02, 20.75, 20.49. HRMS (ESI): $C_{16}H_{18}NO_6$ $[M+H]^+$, calculated for: 320.1129, found: 320.1128. $[\alpha]_D^{20}$=26.1 (c=0.046, MeOH).

(3aS,5R,6R,6aR)-5-methyl-2-phenyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-6-yl acetate (3b)



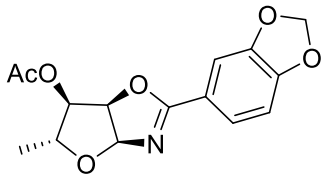
Benzonitrile (51.5 mg, 0.5 mmol) and 1,2,3-Triacetyl-5-deoxy-D-ribose (130 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3b** (94.5 mg, yield 81%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.95 (m, 2H), 7.52 (m, 1H), 7.49 – 7.39 (m, 2H), 6.18 (d, *J* = 5.6 Hz, 1H), 5.17 (t, *J* = 5.6 Hz, 1H), 4.49 (dd, *J* = 9.3, 5.6 Hz, 1H), 3.80 – 3.69 (m, 1H), 2.15 (s, 3H), 1.32 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.34, 167.25, 132.35, 128.85, 128.44, 126.21, 100.00, 78.46, 78.23, 71.61, 20.54, 16.60. HRMS (ESI): $C_{14}H_{16}NO_4$ $[M+H]^+$, calculated for: 262.1074, found: 262.1075. $[\alpha]_D^{20}$=95.0 (c=0.040, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(benzo[d][1,3]dioxol-5-yl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3c)



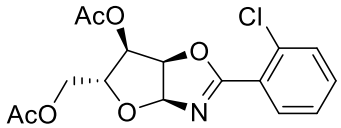
Piperonylonitrile (73.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3c** (130.6 mg, yield 72%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.47 (d, *J* = 1.7 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.24 (d, *J* = 5.6 Hz, 1H), 6.06 (q, *J* = 1.4 Hz, 2H), 5.20 (t, *J* = 5.7 Hz, 1H), 4.85 (dd, *J* = 9.3, 5.8 Hz, 1H), 4.42 (dd, *J* = 12.3, 2.7 Hz, 1H), 4.22 (dd, *J* = 12.3, 5.0 Hz, 1H), 3.91 (ddd, *J* = 9.3, 5.0, 2.7 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.25, 169.63, 166.65, 150.85, 147.37, 123.92, 119.40, 108.45, 107.80, 101.34, 100.19, 77.67, 73.49, 72.56, 61.57, 20.33, 20.07. HRMS (ESI): $C_{17}H_{18}NO_8$ $[M+H]^+$, calculated for: 364.1027, found: 364.1026. $[\alpha]_D^{20}$=940.5 (c=0.007, MeOH)

(3aS,5R,6R,6aR)-2-(benzo[d][1,3]dioxol-5-yl)-5-methyl-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-6-yl acetate (3d)



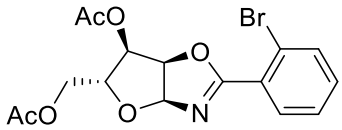
Piperonylonitrile (73.5 mg, 0.5 mmol) and 1,2,3-Triacetyl-5-deoxy-D-ribose (130 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3d** (77.5 mg, yield 51%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.7 (ddd, *J* = 8.2, 3.1, 1.7 Hz, 1H), 7.5 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.1 (s, 2H), 5.6 – 5.4 (m, 1H), 5.4 – 5.3 (m, 1H), 5.3 – 5.1 (m, 1H), 4.5 – 4.3 (m, 1H), 2.1 (d, *J* = 46.9 Hz, 3H), 1.4 (dd, *J* = 35.9, 6.4 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.0, 164.8, 152.1, 147.8, 125.7, 123.2, 109.5, 108.1, 101.9, 100.1, 95.4, 76.4, 75.0, 20.6, 20.3. HRMS (ESI): $C_{15}H_{16}NO_6$ $[M+H]^+$, calculated for: 306.0972, found: 306.0978. $[\alpha]_D^{20}$=465.3 (c=0.120, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-chlorophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl) methyl acetate (3e)



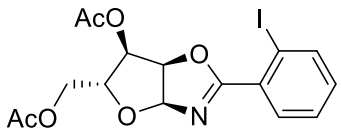
2-Chlorobenzonitrile (72.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3e** (126.0 mg, yield 71%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.45 (td, *J* = 8.1, 7.7, 1.7 Hz, 1H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 6.32 (d, *J* = 5.7 Hz, 1H), 5.26 (t, *J* = 5.8 Hz, 1H), 4.86 (dd, *J* = 9.4, 5.8 Hz, 1H), 4.46 (dd, *J* = 12.3, 2.7 Hz, 1H), 4.26 (dd, *J* = 12.3, 5.1 Hz, 1H), 4.02 (m, 1H), 2.16 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.67, 170.09, 166.60, 133.71, 132.50, 131.73, 130.91, 126.66, 126.15, 100.61, 78.20, 74.00, 73.01, 61.93, 20.76, 20.52. HRMS (ESI): $C_{16}H_{17}ClNO_6$ $[M+H]^+$, calculated for: 354.0739, found: 354.0742. $[\alpha]_D^{20}$=162.3 (c=0.268, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-bromophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl) methyl acetate (3f)



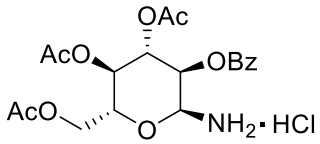
2-Bromobenzonitrile (91.0 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3f** (159.0 mg, yield 79%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 1H), 7.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.37 (m, 2H), 6.30 (d, *J* = 5.7 Hz, 1H), 5.25 (t, *J* = 5.8 Hz, 1H), 4.86 (dd, *J* = 9.5, 5.8 Hz, 1H), 4.45 (dd, *J* = 12.4, 2.7 Hz, 1H), 4.25 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.06 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.65, 170.07, 167.24, 134.10, 132.49, 131.78, 128.44, 127.20, 121.78, 100.57, 78.37, 74.00, 73.03, 61.93, 20.76, 20.57. HRMS (ESI): $C_{16}H_{17}BrNO_6$ $[M+H]^+$, calculated for: 398.0234, found: 398.0229. $[\alpha]_D^{20}$=129.3 (c=0.163, MeOH).

((3aS,5R,6R,6aR)-6-acetoxy-2-(2-iodophenyl)-3a,5,6,6a-tetrahydrofuro[2,3-d]oxazol-5-yl)methyl acetate (3g)



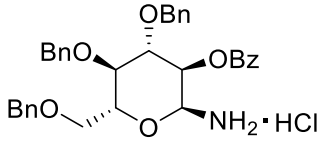
2-Iodobenzonitrile (114.5 mg, 0.5 mmol) and beta-D-Ribofuranose tetraacetate (159 mg, 0.5 mmol) were used as described in (**3A**) and give compound **3g** (142.0 mg, yield 64%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.30 (d, *J* = 5.7 Hz, 1H), 5.25 (t, *J* = 5.7 Hz, 1H), 4.88 (dd, *J* = 9.5, 5.7 Hz, 1H), 4.45 (dd, *J* = 12.3, 2.7 Hz, 1H), 4.25 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.17 – 4.08 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.64, 170.05, 167.93, 140.95, 132.43, 132.17, 131.32, 127.88, 100.57, 94.27, 78.44, 74.06, 73.07, 61.96, 20.77, 20.68. HRMS (ESI): $C_{16}H_{17}INO_6$ $[M+H]^+$, calculated for: 446.0095, found: 446.0094. $[\alpha]_D^{20}$=24.7 (c=0.502, MeOH).

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-amino-5-(benzoyloxy)tetrahydro-2H-pyran-3,4-diyl diacetate (4A)



To a solution of compound **3A** (39 mg, 0.1 mmol) in acetone(5 mL), hydrochloric acid (100 μL, 0.2 mmol, 2.0 M in diethyl ether) and water (25 μL) were added. After stirring for 12h at room temperature, the product formed as a white precipitate. Filtration to give white solid product **4A** (27.5 mg, yield 67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.48 (t, *J* = 9.7 Hz, 1H), 5.13 (m, 2H), 4.36 (d, *J* = 8.7 Hz, 1H), 4.29 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.85 – 3.75 (m, 1H), 2.14 (d, *J* = 1.0 Hz, 3H), 2.07 (d, *J* = 0.9 Hz, 3H), 1.95 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (150 MHz, Methanol-d_4) δ 170.63, 169.87, 169.68, 164.86, 132.16, 129.94, 129.59, 128.14, 79.31, 74.51, 71.91, 71.20, 67.30, 61.22, 19.18, 19.09, 18.96. HRMS (ESI): $C_{19}H_{24}NO_9$ $[M+H]^+$, calculated for: 410.1446, found: 410.1441. $[\alpha]_D^{20}$=38.6(c=0.067 MeOH).

(2S,3R,4S,5R,6R)-2-amino-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-3-yl benzoate (4B)

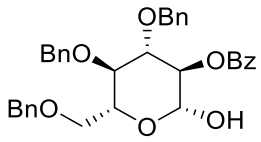


To a solution of compound **3A** (3.0 g, 7.67 mmol) in MeOH, TEA (5.3 mL, 5 eq) was added. The reaction mixture was stirred at room temperature for 2d, then the MeOH and TEA were removed under reduce pressure to give a black oil **5** (2.2 g). The residue was dissolved in dry DMF (30 mL). Then benzyl bromide (4.87 mL, 5eq) and sodium hydride (1.6 g, 5 eq) were added under Nitrogen

atmosphere, stirred at room temperature for 30 min. Then the mixture was poured into water (50 mL) and extracted with ethyl acetate (50 mL) for three times. The organic layerwas combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 5:1) to give the **6** (2.53 g, yield 62%) as a yellow solid. **6**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 2H), 7.38 – 7.34 (m, 5H), 7.33 – 7.29 (m, 5H), 7.29 – 7.24 (m, 5H), 7.18 – 7.16 (m, 1H), 6.09 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 11.8 Hz, 1H), 4.77 – 4.69 (m, 3H), 4.67 (dd, *J* = 7.5, 4.6 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.50 (dd, *J* = 11.7, 7.1 Hz, 2H), 3.89 (dd, *J* = 6.9, 4.7 Hz, 1H), 3.82 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.72 (d, *J* = 2.9 Hz, 1H), 3.63 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 165.9, 138.1, 137.9, 132.3, 128.7, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.9, 127.7, 127.6, 126.9, 94.1, 81.2, 80.2, 74.6, 73.8, 73.5, 72.7, 71.8, 69.4. HRMS (ESI): $C_{34}H_{34}NO_5$ $[M+H]^+$, calculated for: 536.2431, found: 536.2438.

To a solution of **6** (1 g, 1.86 mmol) in acetone (30 mL), hydrochloric acid (1 mL, 0.2 mmol, 2.0 M in diethyl ether) and water (250 μL) were added. After stirring for 12h at room temperature, the product formed as a white precipitate. Filtration to give a white solid product **4B** (0.857 g, yield 83%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.06 (s, 2H), 8.01 – 7.95 (m, 2H), 7.71 – 7.65 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.33 – 7.25 (m, 4H), 7.20 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.17 – 7.06 (m, 3H), 7.04 – 6.95 (m, 2H), 5.13 (t, *J* = 9.2 Hz, 1H), 4.94 (d, *J* = 9.0 Hz, 1H), 4.71 (dd, *J* = 11.0, 6.9 Hz, 2H), 4.61 – 4.48 (m, 4H), 4.04 (t, *J* = 9.2 Hz, 1H), 3.90 (m, 1H), 3.75 – 3.61 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.18, 137.96, 134.04, 130.04, 129.82, 129.05, 128.75, 128.73, 128.65, 128.60, 128.53, 128.34, 128.31, 128.24, 128.20, 128.08, 128.07, 128.01, 81.99, 79.24, 77.59, 76.84, 75.07, 74.61, 72.78, 72.61, 68.38. HRMS (ESI): $C_{34}H_{36}NO_6$ $[M+H]^+$, calculated for: 554.2537, found: 554.2549. $[\alpha]_D^{20}$=59.3 (c=0.054, MeOH).

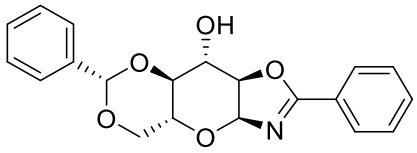
(3R,4S,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-hydroxytetrahydro-2H-pyran-3-yl benzoate (7)



To a solution of **4B** (55.3 mg, 0.1 mmol) in Acetone (5 mL) was added concentrated hydrochloric acid (250 μL) and sodium nitrite (13 mg, 0.2 mmol). After stirring at room temperature for 12h, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer were combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 3:1) to give **7** (45.1 mg, yield 81%) as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 – 8.01 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.29 (m, 11H), 7.21 – 7.17 (m, 4H), 5.58 (t, *J* = 3.3 Hz, 1H), 5.16 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.90 – 4.82 (m, 3H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.59 – 4.55 (m, 2H), 4.27 (t, *J* = 9.5 Hz, 1H), 4.18 (dt, *J* = 10.2, 3.5 Hz, 1H), 3.76 – 3.70 (m, 3H), 3.11 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 165.87, 149.85, 138.13, 138.01, 137.81, 133.25, 129.87, 129.82, 129.68, 128.46, 128.42, 128.41, 128.32, 128.00, 127.95, 127.90, 127.79, 127.76, 127.65, 90.64, 79.69, 78.14, 75.56, 75.12, 74.20, 73.54, 70.43, 68.78. HRMS (ESI): $C_{34}H_{38}NO_7$ $[M+NH_4]^+$, calculated for:

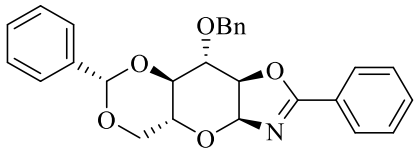
572.2643, found: 572.2628. $[\alpha]_D^{20}$= -68.3 (c=0.112, MeOH).

(3aS,4aR,7S,8aS,9S,9aR)-2,7-diphenyl-3a,4a,5,8a,9,9a-hexahydro-[1,3]dioxino[4',5':5,6]pyrano[2,3-d]oxazol-9-ol (8)



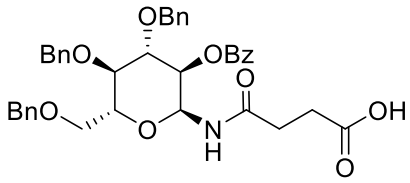
To a solution of compound **3A** (1.5 g, 3.83 mmol) in MeOH, TEA (2.5 mL, 5 eq) was added. The reaction mixture was stirred at room temperature for two days and removed the MeOH and TEA under reduce pressure to give a black oil (2.2 g) which was dissolved in dry Acetonitrile(30 mL), then the benzaldehyde(2 mL, 2eq) and PTSA(3.5 g, 2 eq) were added under Nitrogen atmosphere. After stirring at room temperature for 6 hours, the mixture was poured into water (50 mL) and extracted with ethyl acetate (50 mL) for three times. The organic layer was combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 5:1) to give the **8** (1.06 g, yield 79%) as a yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 7.47 (dd, *J* = 6.7, 3.3 Hz, 4H), 7.42 – 7.35 (m, 4H), 6.05 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 6.7 Hz, 1H), 4.69 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.46 (dd, *J* = 10.4, 4.9 Hz, 1H), 3.94 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.82 – 3.70 (m, 2H), 3.59 (t, *J* = 9.4 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 164.36, 136.47, 131.98, 128.90, 128.18, 128.06, 127.90, 126.31, 125.76, 101.50, 94.87, 80.19, 78.11, 74.32, 68.24, 62.58. HRMS (ESI): $C_{20}H_{20}NO_5$ $[M+H]^+$, calculated for: 354.1336, found: 354.1335.

(3aS,4aR,7S,8aR,9S,9aR)-9-(benzyloxy)-2,7-diphenyl-3a,4a,5,8a,9,9a-hexahydro-[1,3]dioxino[4',5':5,6]pyrano[2,3-d]oxazole (9)



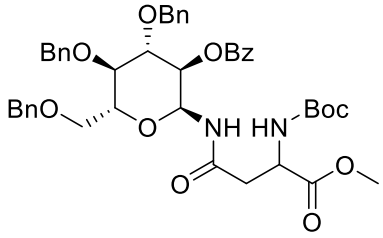
To a solution of compound **8** (45 mg, 1 mmol) in dry DMF was added benzyl bromide(30 μL, 2eq) and sodium hydride(12 mg, 2 eq) under Nitrogen atmosphere. After stirring at room temperature for 30 min, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer was combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 10:1) to give **9** (42.1 mg, yield 95%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.42 (m, 5H), 7.42 – 7.27 (m, 7H), 6.06 (d, *J* = 8.1 Hz, 1H), 5.64 (s, 1H), 4.94 – 4.84 (m, 2H), 4.77 (dd, *J* = 8.1, 4.6 Hz, 1H), 4.44 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.86 – 3.73 (m, 3H), 3.66 (td, *J* = 9.6, 5.1 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 164.83, 137.80, 137.31, 132.39, 128.99, 128.62, 128.47, 128.41, 128.20, 128.03, 127.82, 126.72, 126.07, 101.34, 95.35, 80.74, 80.62, 78.85, 73.20, 68.83, 62.85. HRMS (ESI): $C_{27}H_{26}NO_5$ $[M+H]^+$, calculated for: 444.1805, found: 444.1815.

4-(((2S,3R,4S,5R,6R)-3-(benzoyloxy)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)amino)-4-oxobutanoic acid (10a)



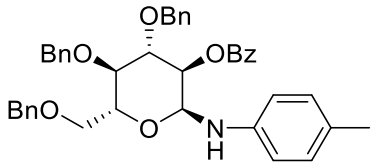
To a solution of **4B** (55.3 mg, 0.1 mmol) in THF (5 mL) was added TEA (3.2 μL,0.3 mmol) and succine anhydride (15 mg, 0.15 mmol). After stirring at room temperature for 3h, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer were combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 1:1) to give **10a** (60.3 mg, yield 92%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.94 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.29 (m, 8H), 7.22 – 7.08 (m, 7H), 6.74 (d, *J* = 9.1 Hz, 1H), 5.29 (t, *J* = 9.3 Hz, 1H), 5.18 (t, *J* = 9.2 Hz, 1H), 4.81 (dd, *J* = 10.9, 8.0 Hz, 2H), 4.77 – 4.63 (m, 2H), 4.52 (dd, *J* = 17.7, 11.4 Hz, 2H), 3.91 (m, 2H), 3.78 (s, 1H), 3.68 – 3.63 (m, 1H), 2.61 – 2.31 (m, 4H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 175.25, 172.24, 166.81, 137.81, 137.63, 137.62, 133.63, 129.81, 128.92, 128.53, 128.38, 128.27, 128.02, 127.86, 127.81, 127.77, 127.71, 82.99, 78.38, 77.51, 76.56, 75.43, 75.06, 73.55, 67.95, 30.71, 29.66. HRMS (ESI): $C_{38}H_{39}NNaO_9$ $[M+Na]^+$, calculated for: 676.2517, found: 676.2520. $[\alpha]^{20}_{D}$=59.8 (c=0.075, MeOH).

(2S,3R,4S,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(3-((tert-butoxycarbonyl)amino)-4-methoxy-4-oxobutanamido)tetrahydro-2H-pyran-3-yl benzoate (10b)



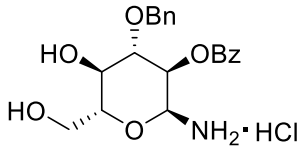
To a solution of **4B** (55.3 mg, 0.1 mmol) in DCM (5 mL) was added TEA (3.2 μL, 0.3 mmol), N-tert-Butoxycarbonyl-L-aspartic acid 1-methyl ester (36 mg, 0.15 mmol) and HATU(76 mg, 0.2 mmol). After stirring at room temperature for 6h, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer were combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 1:1) to give **10b** (57.1 mg, yield 73%) as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.0 – 8.0 (m, 2H), 7.6 (ddt, *J* = 8.7, 7.1, 1.3 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 10H), 7.2 – 7.1 (m, 8H), 6.7 (d, *J* = 9.2 Hz, 1H), 5.7 (d, *J* = 8.9 Hz, 1H), 5.3 (t, *J* = 9.3 Hz, 1H), 5.2 (t, *J* = 9.3 Hz, 1H), 4.9 – 4.8 (m, 2H), 4.7 (d, *J* = 11.1 Hz, 1H), 4.7 (s, 1H), 4.6 (d, *J* = 10.8 Hz, 1H), 4.5 (d, *J* = 12.0 Hz, 1H), 4.5 – 4.4 (m, 1H), 3.9 (dt, *J* = 29.3, 9.1 Hz, 2H), 3.8 – 3.8 (m, 2H), 3.6 – 3.6 (m, 1H), 3.3 (s, 3H), 2.8 – 2.8 (m, 1H), 2.7 (dd, *J* = 16.5, 4.4 Hz, 1H), 1.4 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.4, 170.7, 166.7, 155.6, 137.8, 137.7, 137.7, 133.6, 129.9, 129.1, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 83.0, 80.0, 78.3, 77.5, 76.7, 75.5, 75.1, 73.6, 73.6, 68.0, 52.1, 50.8, 49.8, 37.8, 28.3. HRMS (ESI): $C_{44}H_{51}N_2O_{11}$ $[M+H]^+$, calculated for: 783.3487, found: 783.3499. $[\alpha]^{20}_{D}$=250.0 (c=0.011, MeOH).

(2S,3R,4S,5R,6R)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(p-tolylamino)tetrahydro-2H-pyran-3-yl benzoate (10c)



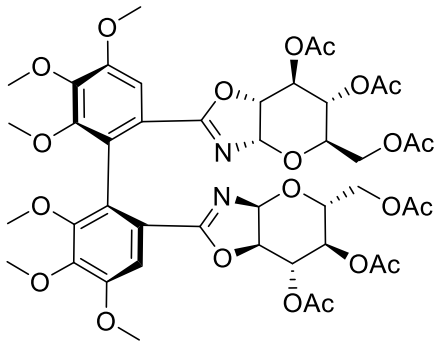
To a solution of **4B** (55.3 mg, 0.1 mmol) in DCM (5 mL) was added TEA (3 drops), Cupric Acetate monohydrate (18.2 mg, 0.1 mmol) and p-Tolylboronic (39 mg, 0.3 mmol). After stirring at room temperature for two days, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer was combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 3:1) to give **10c** (16.8 mg, yield 25%) as a white solid. ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.06 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.50 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.36 – 7.28 (m, 10H), 7.16 (m, 5H), 6.93 – 6.90 (m, 2H), 6.74 – 6.70 (m, 2H), 5.36 (d, *J* = 9.9 Hz, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.07 (dd, *J* = 9.9, 9.0 Hz, 1H), 4.91 – 4.86 (m, 2H), 4.75 (dd, *J* = 27.2, 11.1 Hz, 2H), 4.62 – 4.53 (m, 2H), 4.13 (dd, *J* = 9.3, 8.6 Hz, 1H), 3.84 – 3.78 (m, 3H), 2.16 (s, 3H). ^{13}C NMR (150 MHz, Acetone-d_6) δ 165.32, 143.42, 138.31, 138.27, 138.07, 132.85, 129.10, 128.87, 128.13, 127.77, 127.70, 127.61, 127.39, 127.23, 127.22, 127.05, 126.93, 126.84, 113.94, 83.34, 83.28, 78.17, 75.29, 74.51, 74.07, 73.68, 72.44, 68.65, 19.14. HRMS (ESI): $C_{41}H_{42}NO_6$ $[M+H]^+$, calculated for: 644.3007, found: 644.3010. $[\alpha]_D^{20}$=400.0 (c=0.061, MeOH).

(2S,3R,4S,5R,6R)-2-amino-4-(benzyloxy)-5-hydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-3-yl benzoate (**10d**)



To a solution of **9** (45 mg, 0.1 mmol) in acetone (3 mL) was added 0.25 mL HCl-Et_2O (2M) and water (25 μL). After stirring overnight, the reaction mixture was evaporated under reduced pressure. The residue was washed with dichloromethane for three times and then filtrated to give a yellow solid **10d** (35.2 mg, yield 94%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.97 (s, 2H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.03 (m, 4H), 5.80 (s, 1H), 5.06 (t, *J* = 9.2 Hz, 1H), 4.87 (d, *J* = 9.0 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 3.83 – 3.74 (m, 2H), 3.62 – 3.49 (m, 5H). ^{13}C NMR (125 MHz, DMSO-*d6*) δ 164.98, 138.17, 133.52, 129.61, 129.57, 128.57, 127.93, 127.45, 127.35, 81.75, 79.48, 78.96, 73.98, 71.90, 69.53, 60.01. HRMS (ESI): $C_{20}H_{24}NO_6$ $[M+H]^+$, calculated for: 374.1598, found: 374.1596.

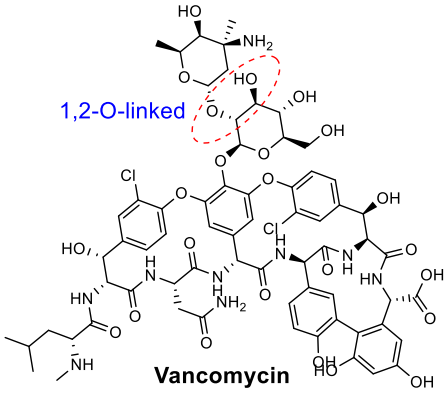
(3aS,3a'S,5R,5'R,6R,6'R,7S,7aR,7'S,7a'R)-((S)-4,4',5,5',6,6'-hexamethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(5-(acetoxymethyl)-3a,6,7,7a-tetrahydro-5H-pyrano[2,3-d]oxazole-2,6,7-triyl) tetraacetate (11)



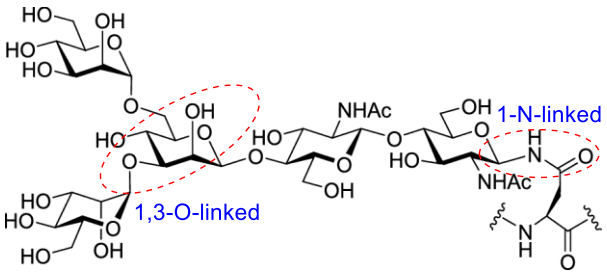
To a solution of compound **3S** (55 mg, 0.1 mmol) in DMF(5 mL) was added copper (64 mg, 1.0 mmol. After stirring at 120℃ for 4 hours, the mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL) for three times. The organic layer were combined and washed with water and brine, dried over anhydrous sodium sulfate, and concentrated in vacuo to give the crude product which was purified by a silica gel column (petroleum ether/ ethyl acetate 2:1) to give **11** (38.0 mg, yield 40%) as a yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 5.79 (d, *J* = 7.6 Hz, 2H), 4.93 – 4.85 (m, 4H), 4.28 (m, 4H), 4.06 (m, 2H), 3.98 (s, 12H), 3.96 (s, 2H), 3.73 (s, 6H), 2.09 (s, 6H), 2.08 (s, 6H), 1.99 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 170.63, 169.52, 169.24, 166.93, 152.88, 151.96, 121.16, 108.46, 92.58, 71.78, 67.53, 67.47, 62.73, 60.88, 60.56, 56.21, 20.74, 20.59. HRMS (ESI): $C_{44}H_{53}N_2O_{22}$ $[M+H]^+$, calculated for: 961.3084, found: 961.3092. $[\alpha]_D^{20}$= -139.4 (c=0.061, MeOH).

3. Supplementary Data

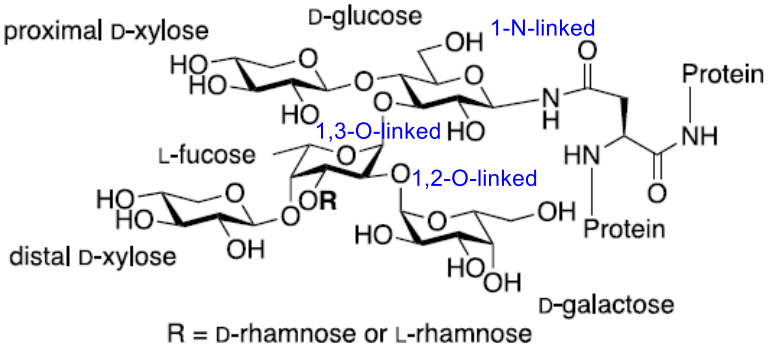
a, Glycopeptides and glycoproteins



Vancomycin

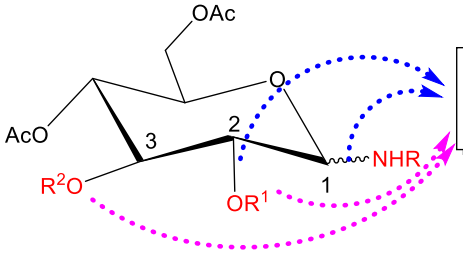


The core pentasaccharides



Conserved pentasaccharide core of chlorovirus N-glycans

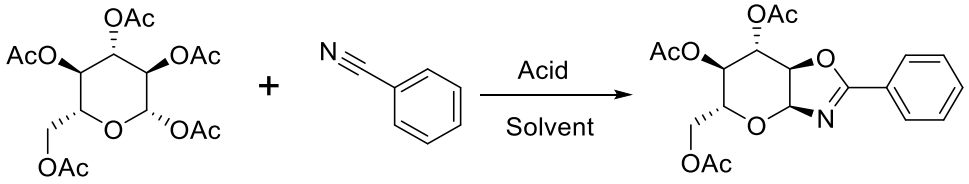
b, Synthetic obstacles in glycochemistry



Main obstacles:
1) 1,2-*cis* glycosidic linkages;
2) Differentiated protection of 2-OH and 3 -OH.

Scheme S1. glycopeptides and glycoproteins

Table S1: optimization of the reaction condition



Entry	Acid	Additive	Solvent	Time	Tem.	Yields [a]
1	TsOH	---	DCM	2h	rt	0
2	HCl	---	DCM	2h	rt	0
3	TFA	---	DCM	2h	rt	0
4	TfOH	---	DCM	2h	rt	0
5	TfOH	$Al(OTf)_3$	DCM	2h	rt	0
6	TfOH	$Fe(OTf)_3$	DCM	2h	rt	0
7	TfOH	$Cu(OTf)_2$ [c]	DCM	2h	rt	30%
8	TfOH	$CuSO_4$	DCM	2h	rt	0
9	TfOH	$CuSO_4$ $5H_2O$	DCM	2h	rt	35%
10	TfOH	H_2O	DCM	2h	rt	40%

[a]: HPLC yield; rt: room temperature; c: Easy to absorb moisture during weighing.

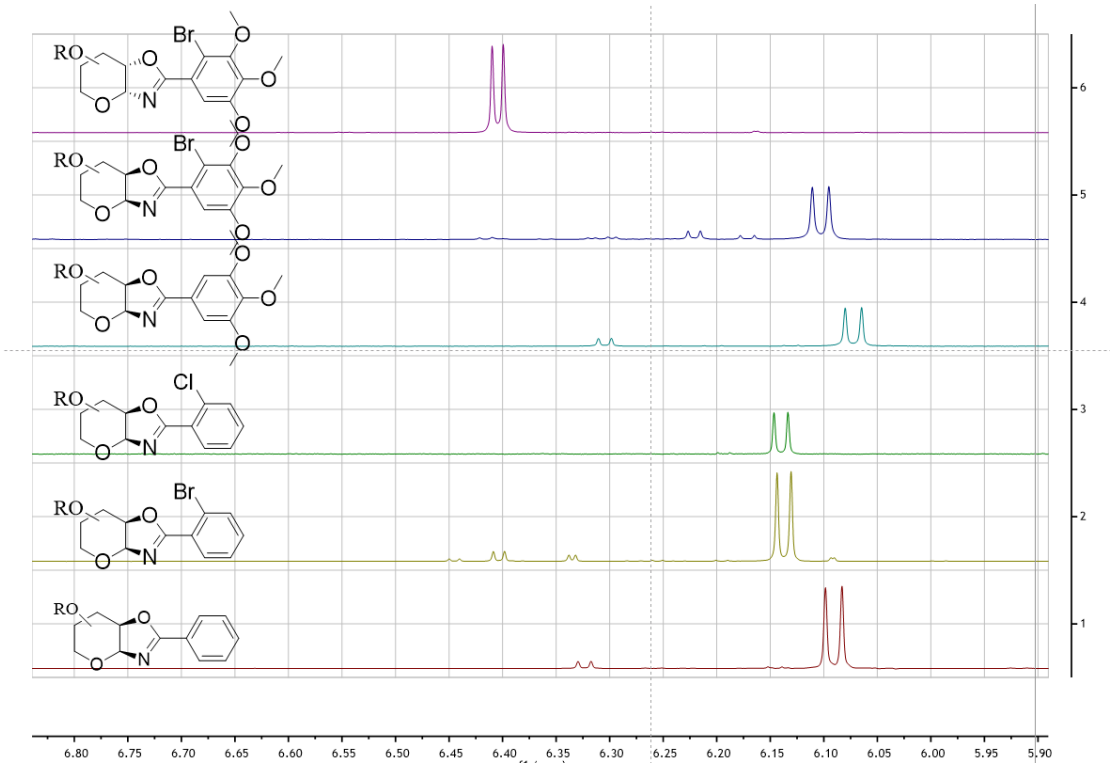
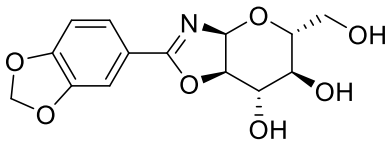


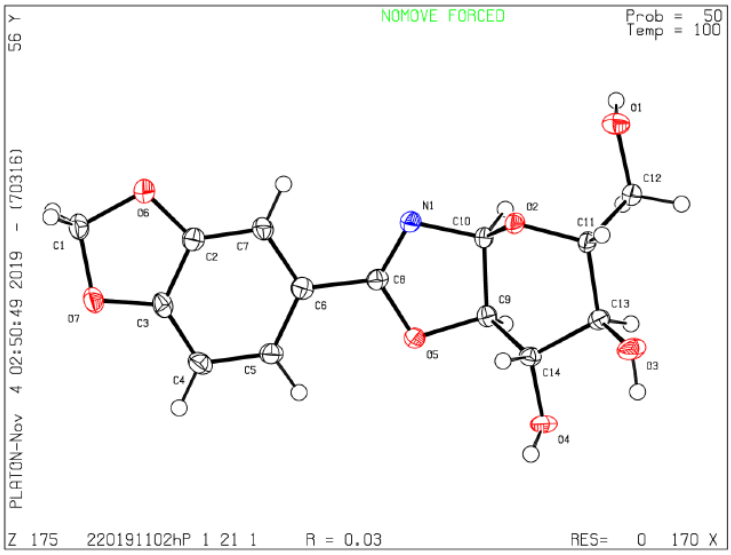
Fig S1. the ^{1}H-NMR spectra of several oxazolinoses

We have compared the ^{1}H-NMR spectra of several oxazolinoses and found visible differences of the hydrogen chemical shift at 1 position between 1-*α* and 1-*β* C-N configurations. The chemical shifts of hydrogen atom on C-1 for 1-*α* oxazolionses are around at 6.10 ppm. Electron-donating or withdrawing substitutes can make the chemical shifts fluctuate slightly. Meanwhile, the chemical shifts of hydrogen atom on C-1 for 1-*β* oxazolinoses are around at 6.40 ppm. Therefore, the difference of two isomers can be recognized *via* ^{1}H-NMR spectra.

4. Crystal Data and Structure Refinement (3Y)



3Y



Bond precision: C-C = 0.0030 A Wavelength=1.54184

Cell: a=4.7659(3) b=12.6787(7) c=11.0168(6)
alpha=90 beta=95.803(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	662.28(7)	662.28(7)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C14 H15 N O7	C14 H15 N O7
Sum formula	C14 H15 N O7	C14 H15 N O7
Mr	309.27	309.27
Dx,g cm-3	1.551	1.551
Z	2	2
Mu (mm-1)	1.078	1.078
F000	324.0	324.0
F000'	325.22	
h,k,lmax	5,15,13	5,15,13
Nref	2344[1230]	2250
Tmin,Tmax	0.937,0.979	0.624,0.754
Tmin'	0.908	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.83/0.96 Theta(max)= 66.583

R(reflections)= 0.0279(2196) wR2(reflections)= 0.0663(2250)

S = 1.042 Npar= 202

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5. DFT Studies

5.1 Computational Methods

All of the DFT calculations were performed with the Gaussian 16 B.01.[1] The geometry optimizations and frequency analysis of the two intramolecular cyclization mechanisms were carried out with the M06-2*X*/6-311G(d) basic set.[2] The frequency analysis was used to confirm the optimized structures as local energy minima or saddle point and acquire Gibbs free energy corrections. The solvent effects of dichloromethane (DCM) were taken into consideration by using solvation model based on density (SMD).[3] The calculated energies are summarized in Table S2. And the computed structures are presented in Figure S2 using CYLview.[4]

Table S2. Summary of the optimized geometries calculated at M06-2*X*/6-311G(d) level.

Geometry	Single-point Energy(a.u.)	Thermal correction of Gibbs Free Energy(a.u.)	Gibbs Free Energy(a.u.)	IF*
A1	-1546.102291	0.374225	-1545.728066	-
TS1	-1546.075232	0.377057	-1545.698175	-268.05
B1	-1546.095596	0.375021	-1545.720575	-
C1	-1393.087355	0.331425	-1392.755930	-
A2	-1546.098542	0.378431	-1545.720111	-
TS2	-1546.060748	0.377981	-1545.682767	-311.18
B2	-1546.078531	0.375146	-1545.703385	-
C2	-1393.067373	0.333863	-1392.733510	-
S1	-1037.981062	0.015921	-1037.965141	-
S2	-1191.054380	0.061245	-1190.993135	-

* The calculated imaginary frequencies for transition states.

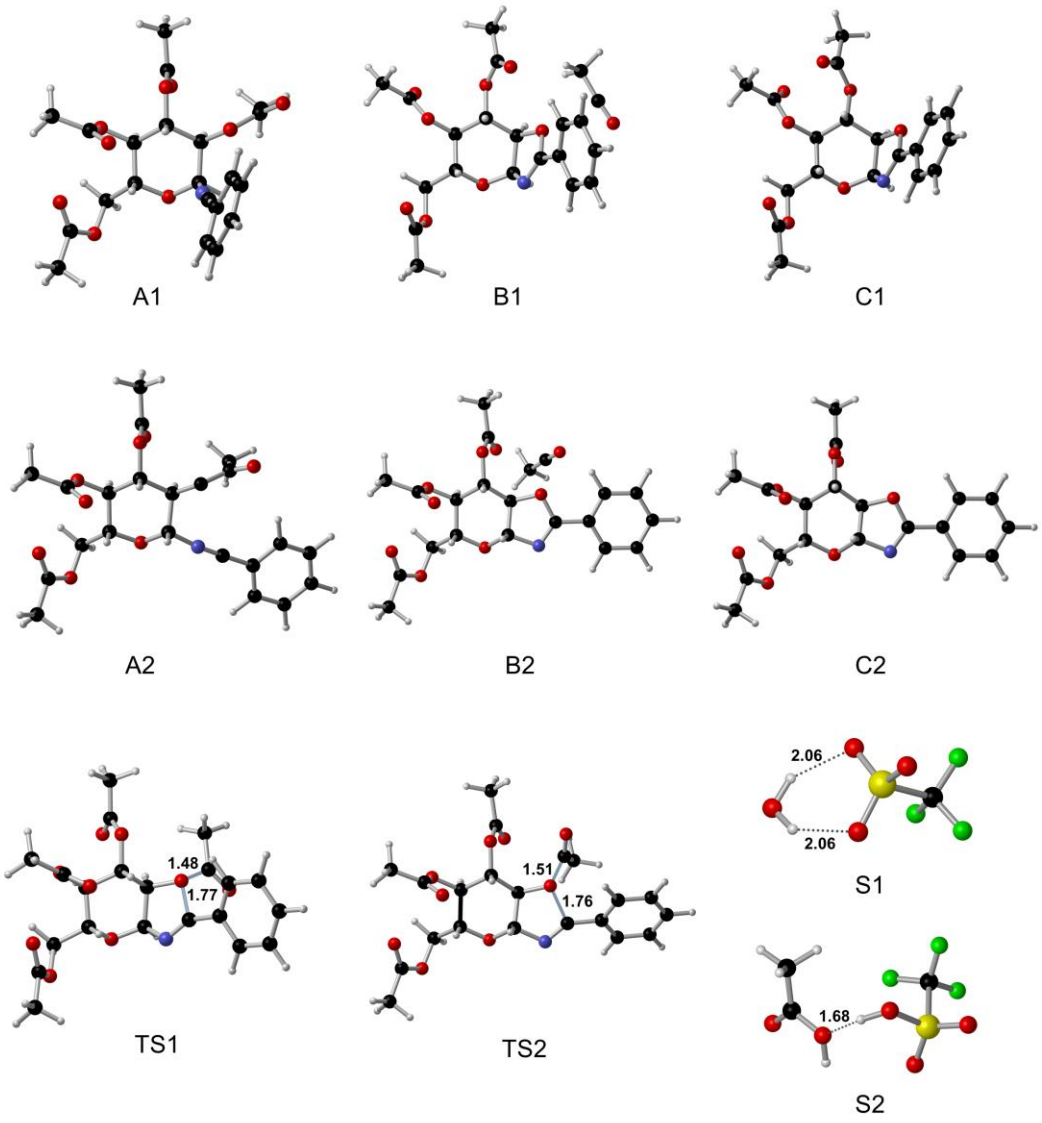

Figure S2. All of the optimized geometries calculated at M06-2*X*/6-311G(d) level. The essential distances are shown in Å.

5.2 M06-2*X* geometries for all the optimized compounds and transition states.

A1							
C	-1.78622700	-0.81825000	-0.10210700	O	-0.43306100	2.62237700	-0.51673100
C	-0.72283900	-1.47590100	-0.98869700	N	1.25941300	0.67548500	-1.17096200
O	-0.44523500	-0.62596500	-2.11837300	C	2.27239200	0.81049500	-0.65521900
C	-0.05663800	0.65696900	-1.83585400	C	3.50383100	1.00118900	0.01037100
C	-1.04024600	1.41553900	-0.92739700	C	3.58124500	2.02191200	0.96990700
C	-1.33047000	0.58114800	0.31640100	C	4.78550100	2.21490900	1.62486400
C	-1.22294100	-2.79500200	-1.55480000	C	5.87970500	1.40437600	1.32590500
O	-0.15080000	-3.70766100	-1.79074300	C	5.78818500	0.39398400	0.36913300
C	0.30114800	-4.35591000	-0.69883800	C	4.59646300	0.18098700	-0.30218800
C	1.39681800	-5.31487500	-1.04539800	C	-0.89240200	3.86312500	-0.87565400
O	-0.14796300	-4.16056700	0.40136900	O	-0.29619200	4.80065200	-0.43843200
				C	-2.08546500	3.94824900	-1.78200200

O	-2.12407900	-1.64828500	1.00605700	O	-4.20525700	-1.62939900	0.76366600
C	-1.18844600	-1.94836600	1.94291400	O	1.94816500	0.66136400	-0.54286100
O	-0.08450800	-1.47543900	1.94804300	N	0.91144300	-1.38366000	-1.20027800
C	-1.73838800	-2.91976100	2.93695900	C	1.88230400	-1.10904800	-0.53786200
O	-2.22820700	1.21719600	1.22261100	C	2.97113400	-1.62759400	0.24317500
C	-3.49289900	1.50030100	0.84140400	C	3.47174100	-0.92610900	1.34533400
O	-3.90567900	1.29213100	-0.26987700	C	4.49470000	-1.49226000	2.08920800
C	-4.26642300	2.10314100	1.97025900	C	5.01125400	-2.73685100	1.73289000
H	-2.71377400	-0.74542900	-0.67204700	C	4.50770300	-3.42807000	0.63344800
H	0.19982400	-1.62808000	-0.42222400	C	3.48273300	-2.87887000	-0.12147700
H	0.08970200	1.18628600	-2.77765400	C	3.15288700	1.28734200	-1.13259500
H	-1.93993600	1.56964400	-1.51933900	O	3.83131300	0.59557200	-1.79489900
H	-0.41103100	0.50485200	0.89375900	C	3.29823000	2.69183600	-0.68126700
H	-1.94609900	-3.24852300	-0.87830600	O	-2.65053400	1.23077500	0.74792100
H	-1.68746700	-2.62020100	-2.52400600	C	-2.59379600	0.45271500	1.85957800
H	1.75723000	-5.80260400	-0.14328300	O	-1.74360100	-0.37504000	2.04198900
H	1.01951800	-6.06019800	-1.74791800	C	-3.70786000	0.79745600	2.79457900
H	2.21259000	-4.78099900	-1.53577800	O	-0.02854700	2.40663000	0.79053600
H	2.71657600	2.63999200	1.17957800	C	-0.25727000	3.59016100	0.17091500
H	4.87163900	2.99695500	2.36890800	O	-0.59754100	3.66817700	-0.97943800
H	6.81779700	1.56285900	1.84515300	C	-0.02061500	4.73353200	1.10481200
H	6.64756100	-0.22616100	0.14695700	H	-2.02013500	1.76581800	-1.06621100
H	4.50038500	-0.59653700	-1.05001300	H	-1.63439000	-1.16135900	-0.27474700
H	-2.96641100	3.49544600	-1.32168400	H	0.74226900	-0.23008300	-2.91133100
H	-2.28292000	4.99914000	-1.97579100	H	0.72902000	1.85859900	-1.74103500
H	-1.89728300	3.43555300	-2.72833300	H	-0.05087800	0.42414500	0.83188300
H	-1.00387300	-3.09525600	3.71897400	H	-4.03821700	0.04706100	-0.90116000
H	-2.66416700	-2.53318800	3.36577000	H	-3.39134300	-0.28969600	-2.52388600
H	-1.96554700	-3.85563500	2.42385000	H	-5.36271100	-3.93232700	-0.97881900
H	-5.27975300	2.32178300	1.64342200	H	-3.72554800	-4.40610800	-0.52891200
H	-4.28372900	1.40910500	2.81228400	H	-4.93429700	-4.09699800	0.74702500
H	-3.77236200	3.01772500	2.30329900	H	3.05614100	0.03587000	1.62195300
				H	4.88935300	-0.96456400	2.94871400
TS1				H	5.81445500	-3.17093100	2.31695200
C	-1.74422700	1.01202100	-0.32894900	H	4.91657900	-4.39335000	0.36109200
C	-1.91691300	-0.36769700	-0.97340800	H	3.07953000	-3.39788200	-0.98283700
O	-1.07183900	-0.42470900	-2.13265300	H	3.28604600	2.71356000	0.41048300
C	0.27153800	-0.26381700	-1.92828900	H	4.23551300	3.08814400	-1.06429900
C	0.64812000	0.98896100	-1.09260400	H	2.46653700	3.29995600	-1.04540400
C	-0.28422200	1.19006200	0.09305100	H	-3.64045300	0.17678000	3.68448000
C	-3.34154800	-0.56513700	-1.47172300	H	-3.65006300	1.85321800	3.06559700
O	-3.74057600	-1.93374600	-1.40542600	H	-4.66082900	0.62656800	2.29242300
C	-4.16922800	-2.35251400	-0.19845400	H	-0.71637400	4.66408500	1.94322900
C	-4.57810000	-3.79183300	-0.23358800	H	0.99195500	4.67985800	1.50827700

H	-0.16630900	5.67255400	0.57714300	H	2.98565200	0.39483400	1.25025200
				H	4.86558300	-0.34809900	2.69698300
B1				H	5.61590600	-2.70749000	2.62913300
C	-1.93903000	0.87179700	-0.42543600	H	4.49375700	-4.32717700	1.13000200
C	-2.14879600	-0.63473800	-0.55956000	H	2.62497500	-3.57885800	-0.32701900
O	-1.51377500	-1.06207700	-1.75726000	H	3.37921800	2.35312900	-0.00749300
C	-0.13476200	-0.89119700	-1.80242300	H	4.44283300	3.10491700	-1.26542200
C	0.36194700	0.51530500	-1.40089500	H	2.72174100	2.71656500	-1.64841900
C	-0.45370900	1.14218900	-0.27202700	H	-4.46437000	3.71763300	1.97488800
C	-3.61781400	-0.97661000	-0.69263900	H	-4.47648000	1.98685400	2.41497200
O	-3.80908500	-2.38960800	-0.77715400	H	-3.04458200	2.95824500	2.74656600
C	-3.79126800	-3.06951200	0.38461300	H	1.39975900	4.96535700	1.20991200
C	-3.99462600	-4.53597000	0.15225800	H	0.70045600	4.94904200	-0.43630700
O	-3.63137300	-2.53936700	1.45252400	H	-0.36585800	4.88883600	0.96237800
O	1.68022400	0.21794000	-0.89791500				
N	0.62339800	-1.77588800	-0.90472100	C1			
C	1.61429000	-1.10120900	-0.49957200	C	1.77956700	-0.16675200	-0.54040500
C	2.71951200	-1.54566000	0.35852700	C	1.22782400	1.25785900	-0.56840200
C	3.34652100	-0.62819800	1.20628500	O	0.56115100	1.45567300	-1.80355800
C	4.38611300	-1.05140000	2.02603200	C	-0.57864700	0.67481900	-1.98537900
C	4.80151000	-2.38028400	1.99269900	C	-0.38358200	-0.82858400	-1.70775600
C	4.16981000	-3.29326900	1.15075900	C	0.60941300	-1.14346500	-0.58700500
C	3.12468300	-2.88052800	0.33451100	C	2.33759900	2.28636000	-0.49551500
C	4.01685900	1.13702300	-1.52616000	O	1.80258300	3.61216700	-0.48755900
O	4.40698500	0.16531800	-1.89816300	C	1.33655900	4.06533100	0.69000000
C	3.60747000	2.42266200	-1.07658600	C	0.77375900	5.44758500	0.55040800
O	-2.58353600	1.32652100	0.76047400	O	1.37483400	3.42021500	1.70480100
C	-3.31753600	2.46664300	0.69400900	O	-1.69585200	-1.22060700	-1.26704600
O	-3.48810500	3.08288100	-0.31983200	N	-1.70910200	1.02903100	-1.12121700
C	-3.86660200	2.81225600	2.04347300	C	-2.28195500	-0.06812800	-0.83247900
O	-0.27963500	2.56157300	-0.24162500	C	-3.52954700	-0.22873100	-0.07054300
C	0.66297100	3.07274600	0.57409200	C	-3.99307900	-1.50021000	0.27067800
O	1.43553400	2.39099700	1.19807800	C	-5.16972800	-1.63237900	0.99984400
C	0.60616700	4.56809700	0.58210300	C	-5.88123900	-0.50094400	1.38720500
H	-2.34690500	1.38982200	-1.29573200	C	-5.41759000	0.76871200	1.04543300
H	-1.71699000	-1.15177100	0.30560400	C	-4.24509400	0.90729400	0.31667300
H	0.14944100	-1.12280800	-2.83154800	O	2.47770400	-0.30779300	0.69941800
H	0.45144700	1.19186400	-2.24892600	C	3.50266100	-1.18349700	0.76630800
H	-0.12449800	0.72153900	0.68204100	O	3.88155500	-1.82599500	-0.17638100
H	-4.17748300	-0.57367500	0.15095700	C	4.05715900	-1.24387700	2.15482200
H	-4.00739600	-0.57294800	-1.62723400	O	1.05136200	-2.48486000	-0.81751500
H	-3.98744300	-5.06385600	1.10261100	C	1.33348000	-3.26451300	0.24655200
H	-4.94374700	-4.70009400	-0.36086900	O	1.19730300	-2.90411200	1.38536400
H	-3.19893200	-4.91494400	-0.49167600	C	1.85247800	-4.59669700	-0.19667400

H	2.46300700	-0.33123600	-1.37695000
H	0.53169000	1.39905800	0.26745500
H	-0.87223500	0.84109500	-3.02448000
H	-0.13594400	-1.39427900	-2.60328200
H	0.09564400	-1.09326200	0.37661300
H	2.94904500	2.12550600	0.39102000
H	2.95419400	2.22863500	-1.39253300
H	0.47643900	5.82371400	1.52623400
H	1.51435300	6.10964000	0.09960100
H	-0.09246100	5.41607400	-0.11364700
H	-3.43435900	-2.37766600	-0.03153100
H	-5.52966100	-2.61945700	1.26630500
H	-6.79851900	-0.60670300	1.95564600
H	-5.97257200	1.64975800	1.34655400
H	-3.87409700	1.88783200	0.04188500
H	4.96442800	-1.84307900	2.16341500
H	4.25831800	-0.23953700	2.52916100
H	3.30618300	-1.70007100	2.80368200
H	1.91020800	-5.27102700	0.65435300
H	1.21501600	-5.01609200	-0.97526200
H	2.84968100	-4.45074000	-0.61852100

A2

C	1.99379500	-0.45303300	-0.54456600
C	1.70953300	1.03646000	-0.29950700
O	0.29935200	1.26948100	-0.45305700
C	-0.44024900	0.54567500	0.47079300
C	-0.34469400	-0.96258100	0.18793800
C	1.12819100	-1.33110500	0.36794700
C	2.41545900	1.89836700	-1.33252000
O	2.73488800	3.18901700	-0.81364000
C	3.82730200	3.23650200	-0.02518600
C	4.10274200	4.63090400	0.44368000
O	4.47674100	2.25774200	0.24006800
O	-1.11237100	-1.64896100	1.15305800
N	-1.81618400	0.93695500	0.30940900
C	-2.93685100	1.13764400	0.19605200
C	-4.32596800	1.34502400	0.05024100
C	-4.80403700	2.61157000	-0.31449100
C	-6.17080300	2.77735300	-0.45719700
C	-7.03177800	1.70250000	-0.23771000
C	-6.54242300	0.44848900	0.12577800
C	-5.17994200	0.25348400	0.27285700
C	-2.25458600	-2.34040100	0.84859300
O	-2.88483200	-2.77183500	1.76780900
C	-2.62583700	-2.52291100	-0.59635200
O	3.38476500	-0.74394100	-0.43676200
C	4.02905100	-0.56767800	0.74542500
O	3.46854800	-0.26722200	1.76355900
C	5.49495400	-0.81030700	0.58168300
O	1.38558400	-2.72276100	0.20354200
C	1.13092200	-3.32876900	-0.97602200
O	0.64162100	-2.75826100	-1.91649700
C	1.52647000	-4.77028200	-0.92942100
H	1.75750900	-0.67583900	-1.58608800
H	2.00740300	1.31779700	0.71393700
H	-0.16498500	0.77147200	1.50821000
H	-0.68196800	-1.14259400	-0.83092200
H	1.38852700	-1.14691400	1.40922800
H	3.32404700	1.40759300	-1.67982200
H	1.74822600	2.07069000	-2.17585000
H	4.93944600	4.62720600	1.13766600
H	4.33753000	5.26137400	-0.41623100
H	3.21418800	5.04241800	0.92466500
H	-4.11417200	3.43016600	-0.47767500
H	-6.56736500	3.74488800	-0.73817700
H	-8.10026200	1.84497000	-0.35046200
H	-7.22372800	-0.37567400	0.29568400
H	-4.77371900	-0.70894600	0.56173000
H	-1.82260200	-3.01311800	-1.15076300
H	-3.51873800	-3.14143800	-0.63253800
H	-2.83356100	-1.56728600	-1.08458300
H	5.98527800	-0.74191500	1.54954200
H	5.66503700	-1.79247600	0.13823800
H	5.90151900	-0.05610400	-0.09410700
H	1.29925000	-5.24285800	-1.88150200
H	2.59423200	-4.84795900	-0.71699200
H	0.99031900	-5.27162900	-0.12177500

TS2

C	-1.82590200	0.65701600	-0.45611600
C	-2.08248500	-0.87226800	-0.43768900
O	-0.89322200	-1.61080300	-0.76720400
C	0.11281700	-1.23565800	0.10234100
C	0.52657400	0.20033500	-0.21594500
C	-0.57256200	1.08354500	0.34266200
C	-3.14104800	-1.23090100	-1.46560700
O	-3.86028500	-2.40483400	-1.08844400

C	-4.79013800	-2.22604100	-0.13027200	H	-0.97607200	4.93166000	-0.41597800
C	-5.50804000	-3.50185900	0.18052400	H	0.65090100	4.87299500	0.26154500
O	-4.98809200	-1.15650200	0.38816600	H	0.43731700	5.09077900	-1.49925500
O	1.82909100	0.30030900	0.38666300				
N	1.34297800	-2.00024400	-0.02387800	B2			
C	2.35396600	-1.36724600	0.18609100	C	-1.73202600	0.67755700	-0.18951100
C	3.78365800	-1.43847600	0.34042000	C	-2.00684800	-0.83031200	-0.45505700
C	4.42741500	-0.67479600	1.31988900	O	-0.82631700	-1.53141900	-0.85634000
C	5.80627100	-0.76425300	1.43521700	C	0.15496600	-1.32709300	0.11992200
C	6.52537400	-1.59845300	0.58126600	C	0.57247500	0.13220500	0.10351800
C	5.87304200	-2.35846300	-0.38705800	C	-0.53027100	0.92738900	0.74872400
C	4.49385200	-2.28695900	-0.51549800	C	-3.02961900	-0.97660800	-1.56966700
C	2.67597300	1.44277000	-0.13513700	O	-3.79449100	-2.17496900	-1.42336500
O	2.76533600	2.35060100	0.59557300	C	-4.77654000	-2.12380500	-0.50469300
C	3.26034500	1.18627200	-1.47395700	C	-5.52855200	-3.41654300	-0.43525500
O	-2.99856700	1.35311200	-0.05172800	O	-4.99585200	-1.14215700	0.15906500
C	-3.46930700	1.20968800	1.21494100	O	1.86240900	0.07585300	0.71275300
O	-2.88469000	0.59892200	2.06752300	N	1.42469400	-2.00496000	-0.07579800
C	-4.77455600	1.92009400	1.37114200	C	2.29731000	-1.18366000	0.35909100
O	-0.39561300	2.49609900	0.30951400	C	3.73487700	-1.43483200	0.51897600
C	0.07278600	3.12309900	-0.78990700	C	4.57660800	-0.44142100	1.02364100
O	0.47700700	2.53079800	-1.75806100	C	5.93632100	-0.69621000	1.16356700
C	0.04750500	4.60555400	-0.60829800	C	6.45453700	-1.93532100	0.79967700
H	-1.67986800	0.96925800	-1.49434700	C	5.61260500	-2.92742100	0.29853200
H	-2.40378800	-1.16508300	0.56486700	C	4.25420900	-2.68220900	0.16091900
H	-0.20780000	-1.34413500	1.14689900	C	2.80179200	2.08456000	-1.89649200
H	0.63877900	0.28828000	-1.29530600	O	3.33603000	2.12025200	-0.92281400
H	-0.69804300	0.86579600	1.40141400	C	2.21518000	2.01488900	-3.19140500
H	-3.83742400	-0.40350200	-1.59895000	O	-2.92485800	1.32883700	0.23897900
H	-2.66228800	-1.46537400	-2.41507500	C	-3.48972400	1.00083200	1.42808700
H	-6.00767700	-3.86827200	-0.71804200	O	-2.98044200	0.25244600	2.21654600
H	-4.78839400	-4.26058200	0.49293100	C	-4.79213700	1.71517800	1.60107500
H	-6.23682600	-3.33106300	0.96874500	O	-0.33365600	2.32941700	0.98260400
H	3.85730600	-0.03935000	1.98884200	C	0.18025600	3.13933400	0.05747400
H	6.31924900	-0.18494600	2.19297000	O	0.55558300	2.75900600	-1.03137400
H	7.60355200	-1.65826500	0.67321200	C	0.23349500	4.55326100	0.53949300
H	6.43928100	-3.00529600	-1.04600500	H	-1.50914800	1.15706500	-1.14662900
H	3.96885000	-2.86549900	-1.26656600	H	-2.38731500	-1.27835100	0.46739000
H	2.71921800	0.42597300	-2.03401900	H	-0.24191600	-1.62695300	1.10228800
H	3.27260400	2.12746400	-2.02134500	H	0.70602400	0.41249300	-0.94437200
H	4.29255500	0.85488000	-1.32469000	H	-0.72861800	0.53729500	1.74406100
H	-5.10044000	1.85728200	2.40637800	H	-3.70155200	-0.11932300	-1.59415500
H	-4.67188300	2.96317500	1.06830600	H	-2.51508100	-1.06943100	-2.52500800
H	-5.51090000	1.44591000	0.72054100	H	-5.97296700	-3.63353500	-1.40830000

H	-4.84032300	-4.22909000	-0.19625500
H	-6.30507600	-3.34957400	0.32255900
H	4.16825800	0.51908500	1.31395900
H	6.59006800	0.07215000	1.55978800
H	7.51510600	-2.13172600	0.91004600
H	6.01685900	-3.89365300	0.01997400
H	3.58762400	-3.44684500	-0.22075000
H	2.98393500	1.63469200	-3.87127800
H	1.35505700	1.34260800	-3.13490100
H	1.90074800	3.02651600	-3.46347500
H	-5.21986300	1.46209600	2.56800900
H	-4.63639200	2.79296400	1.52885900
H	-5.47045200	1.41298300	0.80229100
H	-0.78076100	4.89936300	0.74774200
H	0.79788600	4.60210700	1.47195800
H	0.69429700	5.18504800	-0.21534800

C2

C	-1.51782400	0.72803900	-0.43932100
C	-1.66400300	-0.81846000	-0.47933800
O	-0.45262600	-1.45925700	-0.88728900
C	0.56631500	-1.02943600	-0.03127300
C	0.85621700	0.43976500	-0.27780900
C	-0.27220100	1.22736500	0.33072700
C	-2.74545200	-1.19913800	-1.47650200
O	-3.37960200	-2.43028100	-1.11735100
C	-4.29249000	-2.34446600	-0.13434200
C	-4.89391700	-3.68173500	0.17130500
O	-4.56600700	-1.30673700	0.41446500
O	2.17159700	0.55892800	0.27660700
N	1.87488000	-1.63595400	-0.20104400
C	2.69174800	-0.69498900	0.07267300
C	4.15050000	-0.81775700	0.19636100
C	4.94290900	0.31424400	0.39377400
C	6.32265100	0.17943400	0.50148100
C	6.90992000	-1.07885200	0.41061500
C	6.11748500	-2.20888000	0.21309600
C	4.73991900	-2.08177500	0.10861200
O	-2.72952800	1.32831800	0.02089200
C	-3.15611800	1.11231300	1.28714700
O	-2.52026600	0.50984400	2.10929600
C	-4.49832800	1.73898900	1.50057900
O	-0.16340000	2.65393500	0.32471800
C	0.03074000	3.33092300	-0.82412800
O	0.12602500	2.80596700	-1.90188400
C	0.11240500	4.80365700	-0.55926400
H	-1.43284600	1.08036300	-1.46810200
H	-1.93166100	-1.17174000	0.52059600
H	0.25178300	-1.19942400	1.01193100
H	0.93016800	0.60817900	-1.35479600
H	-0.35562200	0.98667400	1.38826100
H	-3.49729900	-0.41417900	-1.55137300
H	-2.29423000	-1.37217900	-2.45226900
H	-5.31942600	-4.11309200	-0.73597300
H	-4.11245500	-4.35724300	0.52484300
H	-5.66235100	-3.57418600	0.93278500
H	4.48063000	1.29156200	0.46034000
H	6.93866400	1.05793100	0.65517900
H	7.98610800	-1.18134300	0.49453700
H	6.57538600	-3.18883200	0.14356300
H	4.11123200	-2.95185800	-0.04059700
H	-4.79960900	1.61080400	2.53741900
H	-4.46029600	2.79950300	1.24686500
H	-5.22063100	1.25563300	0.84128900
H	-0.80138700	5.13906900	-0.06600300
H	0.94739100	5.00796600	0.11340800
H	0.24988800	5.33689400	-1.49657700

S1

S	0.26480300	0.68415300	0.00000000
O	0.97317600	0.32002100	-1.23161900
O	-0.35622700	2.00266500	-0.00000400
O	0.97317100	0.32002700	1.23162300
C	-1.17025000	-0.47094500	0.00000000
F	-1.93028800	-0.28372300	-1.07869400
F	-1.93029200	-0.28371900	1.07869100
F	-0.75688000	-1.73763600	0.00000300
H	2.73660600	-0.62136000	0.75169300
O	3.26845200	-0.90925800	0.00000000
H	2.73661300	-0.62135800	-0.75169600

S2

O	-3.71520000	0.12093100	-1.02831000
C	-3.00487200	0.62224800	1.22829500
H	-3.86108400	1.28908300	1.28266600
H	-3.06376600	-0.12840500	2.01863000
H	-2.08446500	1.19218700	1.37371800
C	-2.97630800	-0.04893200	-0.10627800

S	1.34512600	-0.82853200	0.03580500	F	1.66131200	1.59161400	0.95796300
O	0.84450600	-1.38534300	-1.19299000	F	0.00947900	1.35698500	-0.41350600
O	2.64243200	-1.14197800	0.55508800	H	-0.62651000	-1.08660100	0.83372100
O	0.29867800	-1.02441700	1.19161400	O	-1.94742700	-0.94781200	-0.18897900
C	1.26110800	1.00840900	-0.15449600	H	-1.93018700	-1.35944300	-1.0700230
F	2.03815500	1.37232200	-1.15646900				

Reference

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. B.01*, Wallingford, CT, 2016.

2. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts* **2007,** *120* (1-3), 215-241.

3. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J Phys Chem B* **2009,** *113* (18), 6378-96.

4. Legault, C. Y. CYLview, 1.0b. http://www.cylview.org.