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Hartmann, Marcel; de Vries, Johannes G.; Minnaard, Adriaan J.; Jäger, Manuel

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Supporting Information

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Catalytic Regioselective Oxidation of Glycosides**
Manuel Jäger, Marcel Hartmann, Johannes G. de Vries,* and Adriaan J. Minnaard*

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EXPERIMENTAL SECTION

General Information

Solvents and Reagents
All solvents used for extraction, filtration and chromatography were of commercial grade, and used without further purification. Reagents were purchased from Sigma-Aldrich, Acros, ABCR, and Carbosynth and were used without further purification. For purification via column chromatography silica gel from either Silicycle (Sila Flash 40-63 µm, 230-400 mesh, abbreviated as SG1) or from Sigma Aldrich (Silica Amorphus, precipitated, Davisil grade 62, pore size 150 Å, 60-200 mesh, abbreviated as SG2) was used. [(Neocuproine)PdOAc]₂OTf₂, methyl-β-maltoside and methyl- β-cellobioside were prepared according to the literature procedures.[25] [26] [27]

Analysis
TLC was performed on Merck silica gel 60, 0.25 mm plates and visualization was done by UV and staining with Seebach’s reagent (a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H₂O (500 mL) and H₂SO₄ (25 mL)) and potassium permanganate stain (a mixture of KMnO₄ (3g), K₂CO₃ (10g), water (300mL)).

¹H-, ¹³C-, APT-, COSY-, HSQC-, NOESY were recorded on a Varian AMX400 (400, 100.59 MHz, respectively) using DMSO-d₆, MeOD-d₄ or D₂O as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (DMSO-d₆: 2.50 for ¹H, δ 39.51 for ¹³C; MeOD-d₄: δ 3.31 for ¹H, δ 49.15 for ¹³C; D₂O: δ 4.80 for ¹H; acetonitrile-d₃: δ 1.94 for ¹H, δ 118 for ¹³C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants J (Hz), and integration. High Resolution Mass measurements were performed using a ThermoScientific LTQ OrbitrapXL spectrometer.
Synthesis of Oxo-glucopyranosides

General Procedure (acetonitrile/water as solvent)
Methyl glycoside (4 mmol, 1.0 eq) and 2,6-dichlorobenzoquinone (12 mmol, 3.0 eq) were suspended in acetonitrile/de-ionized water (10:1, 0.3 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ-OAc)]₂(OTf)₂ (0.1 mmol, 2.5 mol%) was added and the mixture was stirred at rt until the reaction was finished, as indicated by TLC (DCM/MeOH 5:1). Toluene (50 mL) was added and the mixture was extracted twice with water (7 mL). The combined water layers were washed once with ethyl ether (35 mL), filtered and concentrated in vacuo to give the pure keto-sugar.

Methyl-α-D-ribo-hexapyranoside-3-ulose (3)

Methyl-α-glucopyranoside (777 mg, 4.0 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq.) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ-OAc)]₂(OTf)₂ (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 3 h. Methyl-α-D-ribo-hexapyranosid-3-ulose (751 mg, 3.9 mmol) was isolated in 96% yield as a dark brown solid. ¹H NMR [28] (400 MHz, 298 K, DMSO-d₆) : δ = 4.95 (d, J = 4.2 Hz, 1H), 4.29 (dd, J = 4.2, 1.5 Hz, 1H), 4.07 (dd, J = 9.8, 1.4 Hz, 1H), 3.69 (dd, J = 11.9, 1.9 Hz, 1H), 3.59 (dd, J = 11.9, 4.9 Hz, 1H), 3.46 (ddd, J = 9.7, 4.9, 1.8 Hz, 1H), 3.26 (s, 3H).

¹³C NMR (50 MHz, DMSO-d₆): δ = 206.1, 102.2, 75.4, 74.6, 71.9, 60.7, 54.4. HRMS (ESI) calculated for C₇H₁₂O₆Na ([M+Na]+): 215.053, found: 215.052 IR ν max/cm⁻¹: 3436 (OH), 2947 (C-H), 1736 (C=O), 1031 (C-O)

Methyl-β-D-ribo-hexapyranoside-3-ulose (5)

Methyl-β-glucopyranoside (777 mg, 4.0 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ-OAc)]₂(OTf)₂ (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 5 h. Methyl-β-D-ribo-hexapyranosid-3-ulose (686 mg, 3.6 mmol) was isolated in 89% yield as a dark brown solid. ¹H NMR [10,29] (400 MHz, 298 K, DMSO-d₆): δ = 4.20 (d, J = 8.0 Hz, 1H), 4.05
(dd, $J = 10.2, 1.6$ Hz, 1H), 3.97 (dd, $J = 8.0, 1.6$ Hz, 1H), 3.73 (dd, $J = 11.9, 1.7$ Hz, 1H), 3.58 (dd, $J = 12.0, 5.1$ Hz, 1H), 3.45 (s, 3H), 3.21 (ddd, $J = 10.2, 5.1, 1.7$ Hz, 1H).\(^{13}\)C NMR (50 MHz, 298 K, DMSO-\(d_6\)): $\delta = 206.3, 104.8, 76.6, 76.6, 72.2, 60.8, 56.2$. HRMS (ESI) calculated for C\(_{7}\)H\(_{12}\)O\(_6\)Na ([M+Na]+): 215.053, found: 215.052

IR $\nu_{\text{max}}$/cm\(^{-1}\): 3382 (OH), 2953 (C-H), 1738 (C=O), 1036 (C-O)

Methyl-2-(acetylamino)-2-deoxy-\(\alpha\)-D-ribo-hexapyranoside-3-ulose (7)

Methyl-N-acetyl-glucosamine-pyranoside (941 mg, 4 mmol, 1.0 eq) was oxidized according to general procedure using 2,6-dichloro-1,4-benzoquinone (2.12 g, 12.0 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(\(\mu\)-OAc)]\(_2\)(OTf)\(_2\) (105 mg, 2.5 mol%) in acetonitrile/water (13.4 mL, 10 : 1, 0.3 M in substrate) within 4 h. Methyl-2-(acetylamino)-2-deoxy-\(\alpha\)-D-ribo-hexapyranosid-3-ulose (792 mg, 3.4 mmol) was isolated in 85% as a dark brown solid. \(^1\)H NMR (400 MHz, 298 K, DMSO-\(d_6\)) : $\delta = 8.02$ (d, $J = 8.2$ Hz, 1H), 5.49 (d, $J = 6.0$ Hz, 1H), 4.98 (d, $J = 4.0$ Hz, 1H), 4.84 (s, 1H), 4.77 (dd, $J = 7.9, 3.7$ Hz, 1H), 4.17 (dd, $J = 9.5, 5.5$ Hz, 1H), 3.71 (d, $J = 11.7$ Hz, 1H), 3.66 – 3.57 (m, 1H), 3.57 – 3.49 (m, 1H), 3.26 (s, 3H), 1.91 (s, 3H). \(^{13}\)C NMR (50 MHz, DMSO-\(d_6\)) : $\delta = 203.0, 169.7, 100.6, 75.6, 72.2, 58.6, 54.5, 22.2$. HRMS (ESI) calculated for C\(_{9}\)H\(_{15}\)NO\(_6\)H ([M+H]+): 234.0972, found: 234.0972, C\(_{9}\)H\(_{15}\)O\(_6\)Na ([M+Na]+): 256.079, found: 256.079 IR $\nu_{\text{max}}$/cm\(^{-1}\): 3296 (OH), 2878 (C-H), 1734 (C=O), 1035 (C-O)

Methyl-2-deoxy-\(\alpha\)-D-erythro-hexopyranosid-3-ulose (9)

Methyl-2-desoxy-\(\alpha\)-D-glucopyranoside (150 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in 2.5 mL dioxane/DMSO mixture (4:1, 0.3 M) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(\(\mu\)-OAc)]\(_2\)(OTf)\(_2\) (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 30 min. The reaction was quenched by adding water (12 mL) and the resulting precipitate was filtered. The filter was washed with 3 x 2.25 mL of water and the combined water layers were passed over a charcoal column (12 g of charcoal). The charcoal column was washed with 4 column volumes of water and subsequently the product was eluted with
water/acetonitrile 1:1 (2.5 column volumes). Methyl-2-deoxy-α-D-erythro-hexopyranosid-3-ulose (89 mg, 0.50 mmol, 60%) was obtained pure, after freeze drying, as greenish oil. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 5.14 (d, $J = 4.3$ Hz, 1H), 4.18 (dd, $J = 9.9$, 1.1 Hz, 1H), 3.88 (dd, $J = 12.0$, 2.3 Hz, 1H), 3.81 (dd, $J = 12.0$, 4.7 Hz, 1H), 3.69 (ddd, $J = 9.9$, 4.7, 2.3 Hz, 1H), 3.34 (s, 3H), 2.88 (ddd, $J = 14.1$, 4.5, 1.1 Hz, 1H), 2.50 (dd, $J = 14.1$, 1.1 Hz, 1H). $^{13}$C NMR (101 MHz, CD$_3$OD): $\delta$ 207.39 (C$_{\text{quart.}}$), 101.34 (CH), 76.53 (CH), 74.27(CH), 62.79 (CH$_2$), 55.18 (CH$_3$), 46.80 (CH$_2$). HRMS (APCI) calculated for C$_7$H$_{13}$O$_5$ ([M+H]$^+$): 177.076, found: 177.075

**Phenyl-α-D-ribo-hexopyranoside-3-ulose (11)**

Phenyl-α-D-glucopyranoside (108 mg, 0.42 mmol, 1.0 eq) was dissolved in a dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M) and dichlorobenzoquinone (223 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(μ-OAc)]$_2$(OTf)$_2$ (11 mg, 2.5 mol%) were added. The reaction was stirred for 30 min and was quenched by addition of 8 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated using a Genevac (T <40°C), which gave 230 mg of crude product. The crude product was purified by column chromatography (21 g silica gel (SG2), eluent: DCM/MeOH 20/1, DCM was saturated with water), which gave 89 mg (contains about 13% DMSO according to $^1$H-NMR, 0.30 mmol, 73%) of pure phenyl-α-D-ribo-hexapyranoside-3-ulose. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 7.29 (t, $J = 7.9$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 5.83 (d, $J = 4.2$ Hz, 1H), 4.58 (dd, $J = 4.2$, 1.1 Hz, 1H), 4.38 (dd, $J = 9.0$, 1.1 Hz, 1H), 3.85 – 3.74 (m, 3H). $^{13}$C NMR (101 MHz, CD$_3$OD): $\delta$ = 206.9 (C$_{\text{quart.}}$), 158.2 (C$_{\text{quart.}}$), 130.7 (CH), 124.0 (CH), 118.2 (CH), 101.9 (CH), 77.7 (CH), 76.0 (CH), 73.3 (CH), 62.3 (CH$_2$). HRMS (ESI) calculated for C$_{12}$H$_{14}$O$_6$Na ([M+Na]$^+$): 277.068, found: 277.068

**Thiophenyl-β-D-ribo-hexopyranoside-3-ulose (13)**

Phenylthio- β-glucopyranoside (229 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (446 mg, 2.53 mmol, 3.0 eq) were dissolved in 2.8 mL dioxane/DMSO mixture (4:1, 0.3 M)
and [2,9-dimethyl-1,10-phenanthroline]-Pd(µ-OAc)]2(OTf)2 was added portions wise over time (6.5 mol%, 57.2 mg 54.6 µmol in total, 4x1 mol% every 2 h then 2x1.0 mol% every 1 h and 1x0.5 mol% after 1 h). The mixture was stirred at rt for an additional 1 h (12 h in total), no more starting material was observed by NMR-spectroscopy. NMR-spectroscopy of the untreated reaction mixture showed no indication for oxidation, elimination or hydrolyzation of the thiophenyl group. The reaction was quenched by adding water (17 mL) and the resulting precipitate was filtered. The filter was washed with 3 x 2 mL of water and the combined water layers were passed over a charcoal column (10 g charcoal). The charcoal column was washed with 6 column volumes of water and subsequently with acetonitrile/water mixtures (25%, 50%, 75%, 100% acetonitrile, 200 ml each, 50% acetonitrile eluted the product) to elute the product. The fractions containing the product were freeze dried to give 107 mg (0.39 mmol, 47%) of pure product as white fluffy solid. ¹H NMR (400 MHz, CD₃OD): δ = 7.64 – 7.49 (m, 2H), 7.37 – 7.20 (m, 3H), 4.68 (d, J = 10.0, 1H), 4.24 (dd, J = 10.1, 1.4 Hz, 1H), 4.06 (dd, J = 10.0, 1.4 Hz, 1H), 3.93 (dd, J = 12.3, 2.0 Hz, 1H), 3.79 (dd, J = 12.3, 4.9 Hz, 1H), 3.43 (ddd, J = 10.1, 4.9, 2.0 Hz, 1H). ¹³C NMR (101 MHz, CD₃OD): δ = 207.4, 134.0, 133.9, 130.1, 129.1, 91.0, 84.0, 76.1, 73.9, 62.8. HRMS (ESI) calculated for C₁₂H₁₄O₅SNa ([M+Na]+): 293.045, found: 293.045

(6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulse (16)

Methyl-C6-TBDPS-α-glucopyranoside (364 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in DMSO (0.93 mL, 0.9 M) and [2,9-dimethyl-1,10-phenanthroline]-Pd(µ-OAc)]2(OTf)2 (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 30 min. The reaction was quenched by adding water (12 mL) and the resulting precipitate was decanted. The precipitate was dissolved in MeOH/Et₂O to transfer it. Concentration of the dissolved precipitate in vacuo gave 774 mg of crude product, which was purified by silica column chromatography (eluent: gradient of acetone/MeOH 1:1 in DCM 0%-3%). 239 mg of pure (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulse (0.56 mmol, 66%) was isolated as a white foam. ¹H NMR (400 MHz, CD₃OD): δ = 7.82 – 7.64 (m, 4H), 7.54 – 7.28 (m, 6H), 5.08 (d, J = 4.3 Hz, 1H), 4.40 (dd, J = 4.3,
1.4 Hz, 1H), 4.34 (dd, $J = 9.8, 1.4$ Hz, 1H), 4.00 (d, $J = 3.3$ Hz, 2H), 3.74 (dt, $J = 9.7, 3.3$ Hz, 1H), 3.40 (s, 3H), 1.07 (s, 9H). $^{13}$C NMR (101 MHz, CD$_3$OD): $\delta$ = 207.2, 136.9, 136.9, 134.8, 134.7, 131.0, 131.0, 128.9, 103.8, 77.0, 76.3, 73.6, 64.8, 55.8, 27.4, 20.3. HRMS (ESI) calculated for C$_{23}$H$_{30}$O$_6$SiNa ([M+Na]$^+$): 453.170, found: 453.164

(6-O-benzoyl)-methyl-$\alpha$-D-ribo-hexapyranoside-3-ulose (18)

(6-O-benzoyl)-methyl-$\alpha$-D-glucopyranoside (251 mg, 0.84 mmol, 1.0 eq) and 2,6-dichloro-1,4-benzoquinone (447 mg, 2.53 mmol, 3.0 eq) were dissolved in DMSO (0.93 mL, 0.9 M) and [(2,9-dimethyl-1,10-phenanthroline)-Pd($\mu$-OAc)]$_2$(OTf)$_2$ (22 mg, 2.5 mol%) was added. The mixture was stirred at rt for 1 h. The reaction was quenched by adding water (10 mL), the resulting precipitate was filtered and the filter was washed with water (1x10 mL, 1x5 mL). The water layer was passed over a charcoal column (10 g charcoal). The charcoal column was washed with 4.5 column volumes of water, 3 column volumes of water/acetonitrile (3:1) and subsequently the product was eluted with 3 column volumes of DCM/acetone/MeOH/water (56/20/20/4) which gave 409 mg of crude product. The crude product was purified by silica column chromatography (automated, eluent: gradient of DCM/MeOH 0-10%). 113 mg of pure (6-O-benzoyl)-methyl-$\alpha$-D-ribo-hexapyranoside-3-ulose (45%) was isolated as a white foam. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ = 8.09 – 8.03 (m, 2H), 7.65 – 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 5.08 (d, $J = 4.3$ Hz, 1H), 4.72 (dd, $J = 11.9, 2.2$ Hz, 1H), 4.57 (dd, $J = 11.9, 5.7$ Hz, 1H), 4.48 (dd, $J = 4.3, 1.5$ Hz, 1H), 4.34 (dd, $J = 10.0, 1.4$ Hz, 1H), 3.99 (ddd, $J = 9.9, 5.6, 2.1$ Hz, 1H), 3.42 (s, 3H). $^{13}$C NMR (101 MHz, CD$_3$OD): $\delta$ = 206.3, 167.8, 134.6, 131.3, 130.7, 129.8, 103.8, 76.2, 74.2, 74.0, 65.3, 55.9. HRMS (ESI) calculated for C$_{14}$H$_{16}$O$_7$Na ([M+Na]$^+$): 319.079, found: 319.074

Methyl-$\beta$-3-ketomaltoside (20)

Methyl-$\beta$-maltoside (150 mg, 0.42 mmol, 1.0 eq) was dissolved in a dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M), benzoquinone (137 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-
phenanthroline)-Pd(µ-OAc)]2(OTf)2 (2.2 mg, 0.5 mol%) were added. The reaction was stirred for 4.5 h and was quenched by addition of 8 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated by Genevac (T <40°C), which gave 246 mg of crude product. The crude product was purified by column chromatography (10 g silica gel (SG2), eluent: DCM/acetone/MeOH/water 56/20/20/4) which gave 103 mg (0.29 mmol, 69%) of pure methyl- β-3-ketomaltoside.  

\[ {}^1H \text{ NMR (400 MHz, CD}_3\text{OD): } \delta = 5.62 (d, J = 4.5 \text{ Hz, } 1\text{H}), 4.45 (dd, J = 4.5, 1.6 \text{ Hz, } 1\text{H}), 4.25 (dd, J = 9.6, 1.5 \text{ Hz, } 1\text{H}), 4.15 (d, J = 7.8 \text{ Hz, } 1\text{H}), 3.92 - 3.70 (m, 5\text{H}), 3.60 - 3.55 (m, 2\text{H}), 3.51 (s, 3\text{H}), 3.34 - 3.15 (m, 1\text{H}). \]

\[ {}^{13}C \text{ NMR (101 MHz, CD}_3\text{OD): } \delta = 207.2, 105.4, 104.8, 80.6, 78.0, 77.7, 76.6, 76.4, 74.8, 73.4, 62.6, 62.1, 57.5. \]

HRMS (ESI) calculated for C\text{13}H\text{22}O\text{11}Na ([M+Na]+): 377.105, found: 377.105

**Methyl-β-3-ketocellobioside (22)**

Methyl-β-cellobioside (150 mg, 0.42 mmol, 1.0 eq) was in dissolved dioxane/DMSO mixture (4:1, 1.3 mL, 0.32 M) and benzoquinone (137 mg, 1.26 mmol, 3.0 eq) and [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)]2(OTf)2 (2.2 mg, 0.5 mol%) were added. The reaction was stirred for 3 h and was quenched by addition of 6 mL water. The mixture was filtered and the precipitates were washed with water (3 x 2 mL). The water layer was concentrated by Genevac (T <40°C), which gave 275 mg of crude product. The crude product was purified by column chromatography (10 g silica gel (SG2), eluent: DCM/acetone/MeOH/water 56/20/20/4), which gave 79 mg (0.22 mmol, 53%) of pure methyl- β-3-ketomaltoside.  

\[ {}^1H \text{ NMR (400 MHz, CD}_3\text{OD): } \delta = 4.55 (d, J = 7.9 \text{ Hz, } 1\text{H}), 4.25 (dd, J = 10.2, 1.5 \text{ Hz, } 1\text{H}), 4.22 (d, J = 7.8 \text{ Hz, } 1\text{H}), 4.19 (dd, J = 8.0, 1.6 \text{ Hz, } 1\text{H}), 3.95 (dd, J = 12.1, 2.0 \text{ Hz, } 1\text{H}), 3.88 (qd, J = 12.2, 3.1 \text{ Hz, } 3\text{H}), 3.78 (dd, J = 12.1, 5.0 \text{ Hz, } 1\text{H}), 3.66 (t, J = 9.2 \text{ Hz, } 1\text{H}), 3.56 (t, J = 9.0 \text{ Hz, } 1\text{H}), 3.53 (s, 3\text{H}), 3.44 - 3.34 (m, 2\text{H}), 3.24 (dd, J = 9.0, 8.0 \text{ Hz, } 1\text{H}). \]

\[ {}^{13}C \text{ NMR (101 MHz, CD}_3\text{OD): } \delta = 206.8, 105.9, 105.4, 80.5, 78.4, 78.4, 76.6, 76.53, 75.0, 73.6, 62.5, 61.6, 57.5. \]

HRMS (ESI) calculated for C\text{13}H\text{22}O\text{11}Na ([M+Na]+): 377.105, found: 377.100.
Selectivity based on NMR-spectroscopy
The selectivity of the reaction is deduced from the $^1$H-NMR spectra which were taken either during the reaction or from the crude product before any purification or separation.

![Figure 1 Crude reaction mixture of 16](image)

The crude spectrum of 16 shows no additional oxidation products as can be seen from the region from ~3.5 to 5 ppm. Oxidation at C3 is the only product.
Figure 2 Crude reaction mixture of 18

The crude spectrum of 18 shows only minor byproducts as can be seen in the region from 3.2 – 5 ppm, 18 is at least 95% pure with respect to other oxidation products.
Figure 3 Crude reaction mixture of 20

The crude spectrum of 20, shows only minor byproducts in the region from 3 - 5.8 ppm. 20 is more than 90% pure with respective to other oxidation products.
The spectrum of crude 22 shows byproducts at 4.5 - 4.3 ppm, but the byproducts do not exceed 5% per oxidation product.

**Optimization of the catalyst loading**

**Oxidation of methyl-α-glucopyranoside using dichlorobenzoquinone as oxidant**

Methyl-α-glucopyranoside (1 mmol, 1.0 eq) and 2,6-dichlorobenzoquinone (3 mmol, 3.0 eq) were dissolved in DMSO (0.5 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline-Pd(µ-OAc)]₂(OTf)₂ (0.5 mol%, 1 mol% or 1.1 mmol%) was added and the mixture was stirred at rt and followed by NMR.

**Table 1 Catalyst loading using dichlorobenzoquinone as oxidant**

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>Conversion after 30 min[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mol%</td>
<td></td>
</tr>
<tr>
<td>dioxane/DMSO 4:1</td>
<td></td>
</tr>
<tr>
<td>benzoquinone</td>
<td></td>
</tr>
</tbody>
</table>
Oxidation of methyl-α-glucopyranoside using benzoquinone as oxidant

Methyl-α-glucopyranoside (1 mmol, 1.0 eq) and benzoquinone (3 mmol, 3.0 eq) were dissolved in DMSO (0.5 M). The catalyst [(2,9-dimethyl-1,10-phenanthroline)-Pd(µ-OAc)₂]₂(OTf)₂ (0.1 mmol% or 0.5 mmol%) was added and the mixture was stirred at rt and followed by NMR.

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>Conversion after 30 min</th>
<th>Conversion after 60 min</th>
<th>Conversion after 100 min</th>
<th>Conversion after 22 h[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mol%</td>
<td>33%</td>
<td>52%</td>
<td>66%</td>
<td>95%</td>
</tr>
<tr>
<td>0.5 mol%</td>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] no further conversion was observed after prolonged reaction time

Synthesis of methyl allopynanoside and aminoglucoside

Methyl-α-allopyranoside (27)

Methyl-α-D-ribo-hexapyranosid-3-ulose (200 mg, 1.04 mmol, 1.0 eq) was dissolved in MeOH (8.5 mL) and the mixture was cooled to 0 °C. Sodium borohydride (118 mg, 3.12 mmol, 3.0 eq) was added and the mixture stirred for 30 min at rt. Excess borohydride was destroyed by addition of acidic ion exchange resin (Amberlite® 120 H⁺-form), the mixture was filtered over celite and concentrated in vacuo. The residue was co-evaporated with MeOH (3x 10 mL) to give 193 mg (0.99 mmol, 95%) of methyl-α-allopyranoside as
reddish sticky oil. \textsuperscript{1}H NMR\textsuperscript{[3]} (400 MHz, CD\textsubscript{3}OD): \(\delta = 4.69\) (d, \(J = 3.8\) Hz, 1H), 3.98 (appears as t, \(J = 3.2\) Hz, 1H), 3.88 – 3.82 (m, 1H), 3.74 – 3.67 (m, 2H), 3.60 (appears as t, \(J = 3.6\) Hz, 1H), 3.47 (dd, \(J = 9.7, 3.1\) Hz, 1H), 3.43 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CD\textsubscript{3}OD) \(\delta = 101.6, 73.6, 69.6, 69.1, 68.4, 62.8, 56.2\). HRMS (ESI) calculated for C\textsubscript{7}H\textsubscript{14}O\textsubscript{6}Na ([M+Na]\textsuperscript{+}): 217.068, found: 217.068.

\textit{E/Z}-Methyl-3-O-methyloxime-\(\alpha\)-D-ribo-hexapyranoside (28)

\begin{center}
\includegraphics[width=0.2\textwidth]{molecule.png}
\end{center}

Methyl-\(\alpha\)-D-ribo-hexapyranosid-3-ulose (330 mg, 1.70 mmol, 1.0 eq), O-methylhydroxylamine hydrochloride (215 mg, 2.58 mmol, 1.5 eq) and NaHCO\textsubscript{3} (218 mg, 2.58 mmol, 1.5 eq) were heated at reflux for 2 h in methanol (13 mL). After filtration to remove salts, and evaporation of the solvent, the residue was extracted with hot ethyl acetate. The extract was passed over a short silica gel column and was concentrated \textit{in vacuo}, to give methyl-3-O-methyloxime-\(\alpha\)-D-ribo-hexapyranoside (344 mg, 1.55 mmol, 92% as a mixture of \textit{E/Z} isomers) as a sticky yellow solid. HRMS (ESI) exact mass calculated for C\textsubscript{8}H\textsubscript{15}NO\textsubscript{6}H ([M+H]\textsuperscript{+}): 222.097, found: 222.097, C\textsubscript{9}H\textsubscript{15}O\textsubscript{6}Na ([M+Na]\textsuperscript{+}): 244.079, found: 244.079 IR \(\nu_{\text{max}}/\text{cm}^{-1}\): 3454 (OH), 2946 (C-H), 1034 (C-O)

\textit{Methyl-3-amino-\(\alpha\)-D-ribo-hexapyranoside (29a)}

\begin{center}
\includegraphics[width=0.2\textwidth]{molecule.png}
\end{center}

E/Z-Methyl-3-O-methyloxime-\(\alpha\)-D-ribo-hexapyranoside (26; 240 mg, 1.08 mmol, 1.0 eq) in acetic acid (5 mL) was hydrogenated over platinum(IV) oxide (25 mg, 0.11 mmol, 10 mol%) under hydrogen pressure (5 bar) for 24 h. The mixture was passed over a short celite column and concentrated \textit{in vacuo}, to give methyl-3-amino-\(\alpha\)-D-ribo-hexapyranoside (208 mg, 1.08 mmol, 99%) as a sticky slightly yellow solid. The product was directly used in a subsequent per-acetylation reaction. \textsuperscript{1}H NMR (400 MHz, 298 K, DMSO-\textit{d}_6) : \(\delta = 5.21\) (d, \(J = 3.1\) Hz, 1H), 4.31 – 4.26 (m, 2H), 4.23 (dd, \(J = 9.9, 4.1\) Hz, 1H), 4.15 (dd, \(J = 11.0, 4.9\) Hz, 2H), 4.00 (appears as t, \(J = 3.7\) Hz, 1H), 3.90 (s, 3H).
Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-α-D-ribo-hexapyranoside (29b)

Methyl-3-amino-α-D-ribo-hexapyranoside (26a; 208 mg, 1.08 mmol, 1.0 eq) was dissolved in dry pyridine (2.4 mL) and acetic anhydride (1 mL, 9.9 mmol, 8 eq). The reaction mixture was stirred overnight. The mixture was co-evaporated with toluene (1 mL) and purified by automated silicagel column chromatography (GRACE) with a solvent gradient of pentane/EtOAc (1:1 to pure EtOAc) to give methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-α-D-ribo-hexapyranoside (245 mg, 63%, 0.68 mmol) as a white solid.

\[ \text{1H NMR}[^{[3]}] (400 MHz, 298 K, DMSO-\text{d}_6): \delta = 7.11 (d, J = 8.7 Hz, 1H), 4.81 (d, J = 3.2 Hz, 1H), 4.79 – 4.76 (m, 1H), 4.73 (d, J = 9.3 Hz, 2H), 4.15 (d, J = 3.3 Hz, 2H), 4.10 (dd, J = 9.0, 3.4 Hz, 1H), 3.30 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H).

\[ \text{13C NMR} (50 MHz, 298 K, CDCl}_3): \delta = 170.9, 170.8, 169.8, 169.6, 98.1, 66.7, 66.5, 64.1, 62.5, 56.2, 47.9, 23.8, 20.9, 20.9.

Synthesis of methyl-3-acetamido-α-D-ribo-hexapyranoside (29c)

Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-α-D-ribo-hexapyranoside (26b; 141 mg, 0.39 mmol, 1.0 eq) was dissolved in dry methanol (1.4 mL). To this mixture, sodium methanolate (1 M, 0.1 mL) was added and the reaction mixture was stirred overnight at rt upon which the reaction had finished as indicated by TLC (pentane/EtOAc 1:1). The reaction was quenched with acidic ion exchange resin (Amberlite® 120 H⁺-form) and stirred for an additional 10 min. After passing over a short silica gel column, the solvent was removed in vacuo to give methyl-3-amido-α-D-ribo-hexapyranoside (90 mg, 99%, 0.38 mmol) as a sticky slightly red solid.

\[ \text{1H NMR} (400 MHz, 298 K, DMSO-\text{d}_6): \delta = 6.71 (d, J = 8.9 Hz, 1H, NH), 4.52 (d, J = 3.0 Hz, 1H, 1-H), 4.38 – 4.30 (m, 1H, 3-H), 3.63 (dd, J = 11.4, J = 1.6 Hz, 1H, 4-H), 3.56 (dd, J = 5.2, 2.7 Hz, 1H, 2-H), 3.46 (m, 1H, 6'-H), 3.43 (m, 2H, 4-H, 5-H), 3.32 (s, 3H, OCH₃), 1.88 (s, 3H, CH₃). \]

\[ \text{13C NMR} (101 MHz, 298 K, DMSO-\text{d}_6): \delta = 170.9 (\text{NHCOCCH₃}), 99.6 (\text{CH}, C-1), 68.8 (\text{CH}, C-4), 66.3 (\text{CH}, C-2), 66.0 (\text{CH}, 5-C), 60.7 (\text{CH₂}, C-6), 54.8 (\text{OCH₃}), 52.8 (\text{CH}, C-3), 23.6 (\text{NHCOCCH₃}). \]

\[ \text{gCOSY} (400 MHz, 298 K, DMSO-\text{d}_6): \delta (^1\text{H}) / \delta (^1\text{H}) = 6.71 / 4.34 (\text{NH} / 3\text{-H}), 4.52 / 3.56 (1\text{-H} / 2\text{-H}), \]
4.38-4.30 / 6.71, 3.56, 3.43 (3-H / NH, 2-H, 4-H), 3.63 / 3.46, 3.43 (6-H / 6’-H, 5-H),
3.56 / 4.52, 4.34 (2-H / 1-H, 3-H), 3.46 / 3.63, 3.43 (6’-H / 6-H, 5-H), 3.43 / 4.34, 3.43
(4-H / 3-H, 5-H), 3.43 / 3.63, 3.46 (5-H / 6-H, 6’-H). gHSQC (400 MHz, 298 K,
DMSO-\textit{d}_6) : \delta (\text{^1H}) / \delta (\text{^13C}) = 4.52 / 99.63 (1-H / C-1), 4.38 – 4.30 / 52.75 (3-H, C-3),
3.63 / 60.73 (6-H / C-6), 3.56 / 66.34 (2-H / C-2), 3.46 / 60.73 (6’-H / C-6), 3.43 / 68.83
(4-H / C-4), 3.43 / 66.00 (5-H / C-5), 3.32 / 23.58 (OCH\textsubscript{3} / OCH\textsubscript{3}), 1.88 / 54.81 (CH\textsubscript{3} /
CH\textsubscript{3}). NOESY (400 MHz, 298 K, DMSO-\textit{d}_6): \delta (\text{^1H}) / \delta (\text{^1H}) = 3.43 / 3.63, 3.56 (4-H /
6-H, 2-H), 3.43 / 6.71, 1.88 (5-H / NH, CH\textsubscript{3}). HRMS (ESI) calculated for C\textsubscript{9}H\textsubscript{18}NO\textsubscript{6}
([M+H]+): 236.113, found: 236.113, C\textsubscript{9}H\textsubscript{17}NO\textsubscript{6}Na ([M+Na]+): 258.095, found: 258.095

Literature
8145.
Spectroscopic data of keto-sugars 3-22

Methyl-α-D-ribo-hexapyranoside-3-ulose (3)

Figure 5 ¹H-NMR of methyl-α-D-ribo-hexapyranoside-3-ulose in DMSO-d₆
Figure 6 $^{13}$C-NMR of methyl-$\alpha$-D-ribo-hexapyranoside-3-ulose in DMSO-$d_6$
Figure 7 APT-NMR of methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d₄
Figure 8 COSY-NMR of methyl-α-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 9 HSQC-NMR of methyl-α-D-ribo-hexapyranoside-3-ulose in DMSO-d₆
Figure 10 NOESY-NMR of methyl-α-D-ribo-hexapyranoside-3-uloose in DMSO-d6
Figure 11 HR/MS of methyl-α-D-ribo-hexapyranoside-3-uloose
Methyl-β-D-ribo-hexapyranoside-3-ulose (5)

Figure 12 1H-NMR of methyl-β-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 13 COSY-NMR of methyl-β-D-ribo-hexapyranoside-3-uloose in DMSO-d₆
Figure 14 NOESY-NMR of methyl-β-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 15 HSQC-NMR of methyl-β-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 16 $^{13}$C-NMR of methyl-β-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose (7)

Figure 17 1H-NMR of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-d6
Figure 18 $^{13}$C-NMR of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-$d_6$
Figure 19 APT-NMR of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulse in MeOD-d$_4$
Figure 20 COSY-NMR of methyl-2-(acetylamo)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 21 NOESY-NMR of Methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-d6
Figure 22 HSQC-NMR of Methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulose in DMSO-d$_6$
Figure 23 HR/MS of methyl-2-(acetylamino)-2-deoxy-α-D-ribo-hexapyranoside-3-ulos
Methyl-2-deoxy-α-D-erythro-hexopyranoside-3-ulose (9)

Figure 24 $^1$H-NMR of methyl-2-deoxy-α-D-erythro-hexopyranoside-3-ulose in MeOD-d$_4$
Figure 25 $^{13}$C-NMR of methyl-2-deoxy-$\alpha$-D-erythro-hexopyranoside-3-ulse in MeOD-d$_4$
Figure 26 APT-NMR of methyl-2-deoxy-α-D-erythro-hexopyranoside-3-uloose in MeOD-d$_6$
Figure 27 COSY-NMR of methyl-2-deoxy-α-D-erythro-hexopyranoside-3-ulose in MeOD-d$_6$
Figure 28 HSQC-NMR of methyl-2-deoxy-α-D-erythro-hexopyranoside-3-ulose in MeOD-d₆
Figure 29 HR/MS of methyl-2-deoxy-α-D-erythro-hexopyranoside-3-ulos
Phenyl-α-D-ribo-hexapyranoside-3-ulose (11)

Figure 30 $^1$H-NMR of phenyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d$_6$
Figure 31 $^{13}$C-NMR of phenyl-α-D-ribo-hexapyranoside-3-uloze in MeOD-d$_6$
Figure 32 APT-NMR of phenyl-α-D-ribo-hexapyranoside-3-uloce in MeOD-đ₆
Figure 33 COSY-NMR of phenyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d₆
Figure 34 HMQC-NMR of phenyl-α-D-ribo-hexapyranoside-3-ulos in MeOD-d$_6$
Figure 35 pESI-HRMS of phenyl-α-D-ribo-hexapyranoside-3-ulse
Thiophenyl-β-D-ribo-hexopyranoside-3-ulose (13)

Figure 36 1H-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d$_6$
Figure 37 $^{13}$C-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d$_6$
Figure 38 APT-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d₆
Figure 39 COSY-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d6
Figure 40 HMQC-NMR of thiophenyl-β-D-ribo-hexopyranoside-3-ulose in MeOD-d₆
Figure HRMS of thiophenyl-β-D-ribo-hexopyranoside-3-ulose 13
(6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose (16)

Figure 41 $^1$H-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d$_6$
Figure 42 $^{13}$C-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-$d_6$
Figure 43 APT-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-$\alpha$-D-ribo-hexapyranoside-3-uloose in MeOD-$d_6$
Figure 44 COSY-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d$_6$
Figure 45 HSQC-NMR of (6-O-tert-butyl-diphenylsilyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-d$_6$
Figure 46 HR/MS of (6-O-tert-butyl-diphenylsilyl)-methyl-\(\alpha\)-D-ribo-hexapyranoside-3-ulose
(6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose (18)

Figure 47 $^1$H-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-D$_4$
Figure 48 $^{13}$C-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexopyranoside-3-ulose in MeOD-D$_4$
Figure 49 APT-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-D$_4$
Figure 50 HSQC-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-D$_4$
Figure 51 NOESY-NMR of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-ulose in MeOD-D$_4$
Figure 52 HR/MS of (6-O-benzoyl)-methyl-α-D-ribo-hexapyranoside-3-uloose
Methyl-β-3-ketomaltoside (20)

Figure 53 $^1$H-NMR of methyl-β-3-ketomaltoside in MeOD-d$_4$. 
Figure 54 $^{13}$C-NMR of methyl-$\beta$-3-ketomaltoside in MeOD-d$_4$
Figure 55 APT-NMR of methyl-β-3-ketomaltoside in MeOD-d$_4$
Figure 56 COSY-NMR of methyl-β-3-ketomaltoside in MeOD-d₄
Figure 57 HMQC-NMR of methyl-β-3-ketomaltoside in MeOD-d₄
Figure 58 HR/MS of methyl-β-3-ketomaltoside
Methyl-\(\beta\)-3-cellobioside (22)

Figure 59 \(^1\)H-NMR of methyl-\(\beta\)-3-ketocellobioside in MeOD-d₄.
Figure 60 $^{13}$C-NMR of methyl-\(\beta\)-3-ketocellobioside in MeOD-d$_4$
Figure 61 APT-NMR of methyl-β-3-ketocellobioside in MeOD-d$_4$
Figure 62 COSY-NMR of methyl-β-3-ketocellobioside in MeOD-d₄
Figure 63 HMQC-NMR of methyl-β-3-ketocellobioside in MeOD-d$_4$
Figure 64 NOESY-NMR of methyl-β-3-ketocelllobioside in MeOD-d$_4$
Figure 65 HR/MS of methyl-β-3-ketocellulobioside
Spectroscopic data of compound 27, 28 and 29

Methyl-α-allopyranoside (27)

Figure 66 ¹H-NMR of Methyl-α-allopyranoside in MeOD-d₄
Figure 67 $^{13}$C-NMR of Methyl-α-allopyranoside in MeOD-d$_4$
Figure 68 APT-NMR of Methyl-α-allopyranoside in MeOD-d$_4$
Figure 69 COSY-NMR of Methyl-α-allopyranoside in MeOD-d$_4$
Figure 70 HMQC-NMR of Methyl-\(\alpha\)-alloyranoside in MeOD-\(d_4\)
Figure 71 HR/MS of Methyl-α-allopyranoside
Figure 72 ¹H-NMR of E/Z-methyl-3-O-methyloxime-α-D-ribo-hexapyranoside in DMSO-d₆
Figure 73 HR/MS of E/Z-methyl-3-O-methyloxime-α-D-ribo-hexapyranoside
Methyl-3-amino-\(\alpha\)-D-ribo-hexapyranoside (29a)

Figure 74 \(^1\)H-NMR of methyl-3-amino-\(\alpha\)-D-ribo-hexapyranoside in DMSO-d\(_6\)
Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-α-D-ribo-hexapyranoside (29b)

Figure 75 ¹H-NMR Methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-α-D-ribo-hexapyranoside in DMSO-d₆
Figure 76 $^{13}$C-NMR methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-$\alpha$-D-ribo-hexapyranoside in CDCl$_3$
Figure 77 APT-NMR methyl-3-acetamido-2,4,6-tri-O-acetyl-3-deoxy-\(\alpha\)-D-ribo-hexapyranoside in CDCl\(_3\)
Methyl-3-acetamido-α-D-ribo-hexapyranoside (29c)

Figure 78 $^1$H-NMR of methyl-3-acetamido-α-D-ribo-hexapyranoside in DMSO-d$_6$
Figure 79 $^{13}$C-NMR of methyl-3-acetamido-$\alpha$-D-ribo-hexapyranoside in DMSO-d$_6$
Figure 80 APT-NMR of methyl-3-acetamido-α-D-ribo-hexapyranoside in DMSO-d6
Figure 81 COSY-NMR of methyl-3-acetamido-α-D-ribo-hexapyranoside in DMSO-d$_6$
Figure 82 HSQC-NMR of methyl-3-acetamido-α-D-ribo-hexapyranoside in DMSO-d$_6$
Figure 83 NOESY-NMR of methyl-3-acetamido-α-D-ribo-hexapyranoside in DMSO-d$_6$
Figure 84 HR/MS of methyl-3-acetamido-α-D-ribo-hexapyranoside