# Supporting Information

## From D- to L-monosaccharide derivatives via photodecarboxylation-alkylation

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## Table of Contents

| Section                                                                 | Page |
|--------------------------------------------------------------------------|------|
| Experimental details                                                    | 3    |
| General                                                                  | 3    |
| Procedure for the synthesis of NHP-esters of perbenzylated glucoside/mannoside | 4    |
| Procedures for NHP-esters of BDA protected glycosides                    | 11   |
| Procedures of photoalkylation of perbenzylglycosides                    | 18   |
| Procedures for photoalkylation of BDA-glycosides                        | 29   |
| Procedures for synthesis of methyl-L-guloside                            | 35   |
| Addition product with imine as somophile                                 | 38   |
| Scaling up procedure for the synthesis of 18                             | 40   |
| Computational data                                                       | 41   |
| UPLC-MS data                                                             | 49   |
| UPLC method                                                              | 49   |
| Determination of D:L ratio of compound 20                                 | 50   |
| HPLC trace of compound 27                                               | 53   |
| References                                                               | 54   |
| NMR spectra                                                               | 55   |
| NHP Esters, perbenzyl, and synthetic intermediates                       | 56   |
| Photoalkylation products, perbenzyl                                      | 93   |
| Photoalkylation product, with BDA, and their corresponding derivatives   | 148  |
| Synthesis of L-gulosides: intermediate, product and derivative           | 176  |
Addition product with imine as somophile ................................................................. 191
Low temperature NMR study of 25 ........................................................................... 199
Experimental details

General

Solvents and Reagents
Reactions were generally run in normal glass vials (CBN labsuppliers, available in 2 ml, 4 ml or 20 ml) or round bottom flasks. Progress of the reactions was monitored using TLC plates "POLYGRAM SIL G/UV254", visualised using either p-anisaldehyde (PAA) stain (AcOH (300 ml), H$_2$SO$_4$ (6 ml), p-anisaldehyde (1ml)) or phosphomolybdic acid (PMA) stain (phosphomolybdic acid (10 g), EtOH (100 ml)). Compounds were purified by flash chromatography using pentane, diethyl ether (Et$_2$O), ethyl acetate (EtOAc), acetone, toluene and mixtures thereof as the eluent. Anhydrous dichloromethane, and tetrahydrofuran (THF) were obtained from a MBraun solvent purification system (SPS-800), other dry solvents such as methanol and DMF were purchased from Sigma-Aldrich.

Analysis
$^1$H (400 and 600 MHz), $^{13}$C (100 and 150 MHz), $^{31}$P (162 MHz) APT, COSY, (me)HSQC, NOE and NOESY-NMR spectra were measured on "Bruker Avance 600" and "Agilent 400" spectrometers using CDCl$_3$ or CD$_3$OD as the solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: δ 7.26 for $^1$H, δ 77.2 for $^{13}$C, CD$_3$OD: δ 3.31 for $^1$H, δ 49.0 for $^{13}$C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = double double doublet, td = triple doublet, t = triplet, q = quartet, m = multiplet), coupling constants $J$(Hz), and (in case of signals arise from the core sugar structures) H#/C#, where # is the numbering indicated in the structure.

High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer with electron spray ionization (ESI) in positive and negative mode whichever required. (Mass accuracy < 4 ppm)

LED setup

Figure 1 Reaction setup
As shown, the 4 ml reaction vial is secured with a clamp from the back. The blue LED lamp is placed ~5 cm below the vial. The stirring plate is placed ~5 cm to the side of the vial. To cool the
reaction mixture, the small fan is turned on once the blue LED is switched on. The Blue LED source is a Kessil® LED illuminator (model H150 blue, http://www.kessil.com/horticulture/H150.php)

Automated column

Automated column chromatography were performed using Büchi (formerly Grace) Reveleris X2 Flash Chromatography system. All crude mixtures were coated onto celite and loaded onto the system using a solid loader cartridge. Using default settings for the flow rate for the respective sizes of silica columns (40 g silica column: 40 ml / min; 25 g silica column: 32 ml / min; 12 g silica column: 30 ml / min), a linear gradient of increasingly polar solvent in a solvent mixture was set at the beginning before elution had started. The elution was constantly monitored with UV (254 nm, 265 nm, 280 nm) and ELSD, and the composition of the eluent was kept constant manually every time when a signal was observed in either of the detectors (detection limit: UV: 0.05 AU, ELSD: 20 mV). The linear gradient was resumed manually when the signal fell below the detection limit. The fractions collected were then checked by TLC before combining to yield the purified product. Elution time point, if compound could be detected, was indicated with either elution time (min) or column volume (CV)

Ozone generation

Ozone was generated with a Triogen LAB2B Laboratory Ozone Generator. The generator was fed with a steady stream of pure oxygen (2 L / min) from an oxygen cylinder, and the power knob was set to 4. This corresponded to a delivery rate of 3 g / h ozone. The ozone was delivered via a glass Pasteur pipette.

Procedure for the synthesis of NHP-esters of perbenzylated glucoside/mannoside

Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside (32a)

Step 1 (Tritylation): To a stirred solution of methyl α-D-glucopyranoside 29a (10.7 g, 55.0 mmol, 1.5 eq) in DCM (200 ml), trityl chloride (10.0 g, 35.9 mmol, 1.0 eq) and DABCO (4.28 g, 38.2 mmol, 1.06 eq) were added. After overnight stirring, TLC analysis indicated complete consumption of trityl chloride. The solution was stripped of DCM under vacuo. The remaining mixture was redissolved in a 2:1 mixture of EtOAc/water (500 ml). The reaction mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with water (2 × 100 ml) and saturated copper(II) sulfate solution (1 × 50 ml), then brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated in vacuo, during which white solid
appeared. The solid was recrystallized in hot toluene to yield pure trityl glucoside 30a (14.6 g, 93% yield). The analytical data were in full accord with those reported previously.

Step 2 (perbenzylolation): Trityl glucoside 30a (10.5 g, 24.1 mmol, 1 eq) was dissolved in dry DMF (55 ml). The solution was cooled to 0 °C in an ice bath, and 60% w/w sodium hydride in mineral oil (5.78 g, 145 mmol, 6.0 eq) was added. (Caution: depending on the reaction volume and cooling efficiency, it is advised to add sodium hydride portionwise to avoid a runaway reaction.) Benzyl bromide (15.0 ml, 126 mmol, 5.2 eq) was subsequently added slowly. A small exotherm occurred, and the solution became homogeneous. The reaction was left stirring overnight, after which TLC (stained with p-anisaldehyde) indicated complete conversion of starting material with no intermediates. The reaction was subsequently quenched with water (20 ml) and stirred for 10 min. The reaction mixture was then transferred to a separatory funnel and diluted with EtOAc (250 ml) and water (100 ml). The layers were separated and the organic layer was washed with brine (1 × 100 ml), dried over magnesium sulfate and concentrated in vacuo, the crude product 31a was used in the next step without further manipulation.

Step 3 (Detritylation): the crude product 31a (24.1 mmol, 1.0 eq) was dissolved in 10:1 MeOH/DCM (110 ml). Amberlite-H+ (2.01 g) was added, and the mixture was stirred overnight. Complete consumption of the starting material was indicated by TLC. The solution was filtered, and concentrated. The crude product was purified by silica gel column chromatography in 1:4 v/v EtOAc/pentane to afford 32a (7.39 g, 66% yield over 2 steps) as a pale yellow wax. The analytical data were in full accord with those reported previously.

\[
\text{Methyl 2,3,4-Tri-O-benzyl-\(\beta\)-D-glucopyranoside (32b)}
\]

Step 1 (Tritylation): To a stirred solution of methyl \(\beta\)-D-glucopyranoside 29b (5.19 g, 26.7 mmol, 1.0 eq) in DCM (100 ml), trityl chloride (9.20 g, 33.0 mmol, 1.2 eq) and DABCO (3.32 g, 29.6 mmol, 1.1 eq) was added. After overnight stirring, TLC indicated complete consumption of 29b. The solution was stripped of DCM under vacuo. The remaining crude was redissolved in a 2:1 mixture of EtOAc:water (500 ml). The reaction mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with 2 M hydrochloric acid (1 × 100 ml) and brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated in vacuo, during which a voluminous foam formed. The crude product 30b was used in the following step without further purification.

Step 2 (perbenzylolation): Crude trityl glucoside 30b (26.7 mmol, 1.0 eq) was dissolved in dry DMF (60 ml). The solution was cooled to 0 °C in an ice bath, and 60% w/w sodium hydride in mineral oil (5.16 g, 129 mmol, 4.8 eq) was added portionwise. Benzyl bromide (15.4 ml, 134 mmol, 5.0 eq)
was subsequently added SLOWLY. A small exotherm occurred, and the solution became homogeneous. The reaction was left stirring overnight, after which TLC (stained with p-anisaldehyde) indicated complete conversion of the starting material into a more apolar spot with no intermediates remaining. The reaction was subsequently quenched with ethanol (50 ml) and left stirring for 10 min. The reaction mixture was then transferred to a separatory funnel and diluted with EtOAc (200 ml). The organic layer was washed with water (2 × 100 ml) and brine (1 × 100 ml), dried over magnesium sulfate and concentrated in vacuo. The crude product 31b was used in the next step without further manipulation.

Step 3 (Detritylation): The crude product from the previous step 31b (26.7 mmol, 1.0 eq) was dissolved in DCM (130 ml). Iron trichloride hexahydrate (21.1 g, 79.8 mmol, 3.0 eq) and triethylsilane (6.4 ml, 41 mmol, 1.5 eq) were added. After overnight stirring, complete consumption of starting material was indicated by TLC. The reaction was concentrated in vacuo, then redissolved in EtOAc (200 ml), washed with water (2 × 100 ml), then brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated. Crystals (N.B. Triphenylmethane, thus NOT the desired product!) appeared upon standing. The crystals were filtered off and washed with cold EtOH, and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography in 1:9→1:4 EtOAc/pentane to afford 32b (7.61 g, 61% yield over 3 steps) as a wax. The analytical data were in full accord with those reported previously. 3

**Methyl 2,3,4-tri-O-benzyl-α-D-mannopyranoside (32c)**

Step 1 (Tritylation): To a stirred solution of methyl α-D-mannopyranoside 14 (5.31 g, 27.3 mmol, 1.0 eq) in DCM (100 ml), trityl chloride (9.46 g, 33.9 mmol, 1.2 eq) and DABCO (3.50 g, 31.2 mmol, 1.1 eq) were added. After overnight stirring, TLC indicated complete consumption of 14. The solution was stripped of DCM under vacuo. The remaining gruel was redissolved in a 2:1 mixture of EtOAc/water (500 ml). The reaction mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with 2M hydrochloric acid (1 × 100 ml) and brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated in vacuo, during which a large foam formed. The crude product 30c was used in the following step without further purification.

Step 2 (perbenzylation): Crude trityl mannoside 30c (27.3 mmol, 1.0 eq) was dissolved in dry DMF (62 ml). The solution was cooled to 0 °C in an ice bath, and 60% w/w sodium hydride in mineral oil (6.10 g, 129 mmol, 4.8 eq) was added portionwise. Benzyl bromide (16.0 ml, 135 mmol, 4.9 eq) was subsequently added SLOWLY. A small exotherm occurred, and the solution became homogeneous. The reaction was left stirring overnight, after which TLC (stained with p-anisaldehyde) indicated complete conversion of starting material with no intermediates. The
reaction was subsequently quenched with water (30 ml) and left stirring for 10 min. The reaction mixture was then transferred to a separatory funnel and diluted with EtOAc (300 ml) and brine (100 ml). The layers were separated. The water layer was extracted with EtOAc (30 ml) and brine (100 ml). The combined organic layer was washed with brine (2 × 100 ml), dried over magnesium sulfate and concentrated in vacuo. The crude product 31c was used in the next step without further manipulation.

Step 3 (Detritylation): The crude product from the previous step 31c (27.3 mmol, 1.0 eq) was dissolved in DCM (130 ml). Iron trichloride hexahydrate (21.5 g, 81.4 mmol, 3.0 eq) was added. After overnight stirring, triethylsilane (6.4 ml, 40 mmol, 1.5 eq) was added. The reaction was stirred for an additional 6 h, after which TLC indicated that the starting material was consumed completely. The reaction was concentrated in vacuo, then redissolved in EtOAc (300 ml), washed with water (2 × 100 ml), then brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated. Crystals (N.B. NOT the desired product!) appeared upon standing. The crystals were filtered off and washed with cold EtOH, and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography in 1:9 → 1:4 EtOAc/pentane to afford 32c (7.70 g, 61% yield over 3 steps) as a yellow oil. The analytical data were in full accord with those reported previously.4

Step 4 (Oxidation): To a cooled solution of 32a (8.29 g, 17.9 mmol, 1.0 eq) in 5:1 DCM/water (80 ml) at 0 °C, TEMPO (666 mg, 4.26 mmol, 0.24 eq) and (diacetoxy)iodobenzene (BAIB) (14.4 g, 44.6 mmol, 2.5 eq) were added. The solution turned red upon the addition of TEMPO. The solution was warmed to room temperature. After stirring overnight, TLC indicated that the starting material was converted to the acid. Sodium sulfite (2.66 g, 21.0 mmol, 1.2 eq) was subsequently added, and the red color of TEMPO faded away to become a slightly yellow and cloudy solution. The solution was stirred for an additional 10 min and concentrated at 700 mbar, 45 °C to remove excess DCM. The residue was diluted with EtOAc (200 ml) and transferred to a separatory funnel. The organic layer was washed with 2M hydrochloric acid (1 × 30 ml), water (1 × 200 ml) and brine (1 × 200 ml). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The crude product 33a was used in the next step without further purification.

Step 5 (EDC coupling): The crude product from the previous step 33a (17.9 mmol, 1.0 eq) was dissolved in DCM (60 ml), to which N-(3-dimethylaminopropyl)-N-ethylcarbodiimide (EDC) hydrochloride (5.49 g, 28.6 mmol, 1.6 eq) and N-hydroxyphthalimide (4.65 g, 28.5 mmol, 1.6 eq)
were added. The solution was stirred at room temperature overnight. The completion of reaction was indicated by TLC. The reaction mixture was coated onto celite and purified by silica gel column chromatography with 20% EtOAc/pentane as eluent to afford 1 (8.275 g, 72% yield).

\[ ^1H \text{NMR} (400 \text{ MHz, chloroform-}d) \delta 7.90 (dd, J = 5.5, 3.1 \text{ Hz, } 2H), 7.79 (dd, J = 5.5, 3.1 \text{ Hz, } 2H), 7.40 - 7.26 (m, 15H), 4.99 (d, J = 10.9 \text{ Hz, } 1H), 4.93 (d, J = 10.1 \text{ Hz, } 1H), 4.90 - 4.80 (m, 3H), 4.72 (d, J = 3.5 \text{ Hz, } 1H, H1), 4.67 (d, J = 12.1 \text{ Hz, } 1H), 4.58 (d, J = 10.0 \text{ Hz, } 1H, H5), 4.07 (dd, J = 9.7, 8.8 \text{ Hz, } 1H, H3), 3.93 (dd, J = 10.0, 8.9 \text{ Hz, } 1H, H4), 3.63 (dd, J = 9.6, 3.5 \text{ Hz, } 1H, H2), 3.49 (s, 3H). \]

\[ ^{13}C \text{NMR} (101 \text{ MHz, chloroform-}d) \delta 166.3, 161.5, 138.6, 137.9, 135.0, 129.0, 128.7, 128.6, 128.44, 128.36, 128.3, 128.0, 127.9, 127.8, 124.2, 99.0 (C1), 81.4 (C3), 79.2 (C4), 79.1 (C2), 76.1, 75.6, 73.8, 69.0 (C5), 56.2. \]

HRMS (ESI+) Calcd. for C_{36}H_{33}NO_{9}Na ([M + Na]^{+}): 646.2048, found: 646.2036.

1,3-dioxisoindolin-2-yl (2S,3S,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (34)

Step 4 (Oxidation): To a cooled solution of 32b (7.61 g, 16.4 mmol, 1.0 eq) in 5:1 DCM/water (100 ml) at 0 °C, TEMPO (584 mg, 3.74 mmol, 0.23 eq) and BAIB (13.2 g, 40.9 mmol, 2.5 eq) were added. The solution turned red upon the addition of TEMPO. The solution was warmed to room temperature with stirring overnight, after which full conversion was indicated by TLC. Sodium sulfite (4.68 g, 37.1 mmol, 2.3 eq) was subsequently added, and the red color of TEMPO faded away to become a slightly yellow and cloudy solution. The solution was stirred for an additional 10 min and concentrated at 700 mbar, 45°C to remove excess DCM. The residue was diluted with EtOAc (200 ml) and transferred to a separatory funnel. The organic layer was washed with 2M hydrochloric acid (1 × 30 ml), water (1 × 200 ml) and brine (1 × 100 ml). The organic layer was dried over magnesium sulfate and concentrated in vacuo. The crude product was purified by silica gel column chromatography with pure EtOAc as eluent to afford 33b (7.19 g, 92% yield) as an off-white amorphous solid.

\[ ^1H \text{NMR} (400 \text{ MHz, chloroform-}d) \delta 7.35 - 7.23 (m, 15H, excess integration due to overlapping CDCl₃ signal), 4.86 (m, 2H), 4.81 - 4.72 (m, 2H), 4.67 (m, 2H), 4.45 (d, J = 7.4 \text{ Hz, } 1H, H1), 4.01 (d, J = 8.9 \text{ Hz, } 1H, H5), 3.82 (t, J = 8.7 \text{ Hz, } 1H, H4), 3.69 (t, J = 8.4 \text{ Hz, } 1H, H3), 3.58 (s, 3H), 3.49 (dd, J = 8.3, 7.5 \text{ Hz, } 1H, H2). \]

Note: Signal for the OH is not observed. \[ ^{13}C \text{NMR} (101 \text{ MHz, chloroform-}d) \delta 138.3, 137.5, 128.6, 128.5, 128.3, 128.24, 128.15 128.0, 127.92, 127.90, 104.9 (C1), 83.5 (C3), 81.7 (C2), 78.8 (C4), 75.7, 75.2, 74.8, 74.1 (C5), 57.6. \]

Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for C_{38}H_{33}NO_{9}Na ([M + Na]^{+}): 501.1884, found: 501.1868.

Step 5 (EDC coupling): 33b (4.52 g, 9.44 mmol, 1.0 eq) was dissolved in DCM (25 ml), to which EDC hydrochloride (2.82 g, 14.7 mmol, 1.55 eq) and N-hydroxyphthalimide (2.45 g, 15.0 mmol,
1.6 eq) were added. The solution was stirred at room temperature overnight. The completion of the reaction was indicated by TLC. The reaction mixture was coated onto celite and purified by silica gel column chromatography with 20% EtOAc/pentane as eluent to afford 34 (4.03 g, 67% yield).

\[ ^1H \text{NMR} \ (400 \text{ MHz, chloroform-}d) \delta 7.91 \text{ (dd, } J = 5.5, 3.1 \text{ Hz, 2H), } 7.80 \text{ (dd, } J = 5.5, 3.1 \text{ Hz, 2H), } 7.31 \text{ (m, 15H), } 4.98 \text{ – 4.89 (m, 3H), } 4.83 \text{ (m, 2H), } 4.73 \text{ (d, } J = 11.1 \text{ Hz, 1H), } 4.48 \text{ (d, } J = 7.4 \text{ Hz, 1H, H1), } 4.34 \text{ (d, } J = 9.7 \text{ Hz, 1H, H5), } 4.02 \text{ (t, } J = 9.4 \text{ Hz, 1H, H4), } 3.74 \text{ (s, 3H), } 3.60 \text{ – 3.54 (m, 1H, H2).} \]

\[ ^{13}C \text{NMR} \ (101 \text{ MHz, Chloroform}-d) \delta 165.6, 161.5, 138.4, 138.3, 137.8, 129.0, 128.52, 128.51, 128.50, 128.46, 128.3, 128.0, 127.96, 127.93, 127.8, 124.2, 105.0 (C1), 83.8 (C3), 81.6 (C2), 79.0 (C4), 75.9, 75.5, 74.8, 72.9 (C5), 57.7. \]

HRMS (ESI+) Calcd. for C_{36}H_{33}NO_9Na ([M + Na]^+)

1,3-dioxoisindolin-2-yl (2S,3S,4S,5S,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (35)

Step 4 (Oxidation): To a cooled solution of 32c (7.72 g, 16.6 mmol, 1.0 eq) in a 4:1 DCM/water mixture (50 ml) at 0 °C, TEMPO (601 mg, 3.85 mmol, 0.23 eq) and BAIB (13.4 g, 41.6 mmol, 2.5 eq) were added. The solution turned red upon the addition of TEMPO. The solution was warmed to room temperature with stirring overnight, after which full conversion was indicated by TLC. Sodium sulfite (2.47 g, 19.6 mmol, 1.2 eq) was subsequently added, and the red color of TEMPO faded away to become a slightly yellow and cloudy solution. The solution was stirred for an additional 10 min and concentrated at 700 mbar, 45°C to remove excess DCM. The residue was diluted with EtOAc (200 ml) and transferred to a separatory funnel. The organic layer was washed with 2M hydrochloric acid (1 × 30 ml), water (1 × 200 ml) and brine (1 × 200 ml). The organic layer was dried on magnesium sulfate and concentrated in vacuo. The crude product 33c was used in the next step without further purification.

Step 5 (EDC coupling): The crude product from the previous step 33c (16.6 mmol, 1.0 eq) was dissolved in DCM (40 ml), to which EDC hydrochloride (5.09 g, 26.6 mmol, 1.6 eq) and N-hydroxyphthalimide (4.29 g, 26.3 mmol, 1.6 eq) were added. The solution was stirred at room temperature for 1 h. The completion of reaction was indicated by TLC. The reaction mixture was concentrated, then redissolved in 2:1 v/v EtOAc/water mixture (300 ml) and stirred for 10 min until no precipitate could be seen. The mixture was transferred to a separatory funnel, and the two layers were separated. The organic layer was then washed with brine (100 ml), dried on magnesium sulfate and concentrated. The reaction mixture was coated onto celite and purified by silica gel column chromatography with 20% EtOAc/pentane as eluent to afford 35 (6.59 g, 62% yield) as a hard wax.

\[ ^1H \text{NMR} \ (400 \text{ MHz, chloroform-}d) \delta 7.90 \text{ (dd, } J = 5.5, 3.1 \text{ Hz, 2H), } 7.78 \text{ (dd, } J = 5.4, 3.2 \text{ Hz, 2H), } 7.44 \text{ – 7.24 (m, 15H), } 5.00 \text{ (d, } J = 2.8 \text{ Hz, 1H, H1), } 4.92 \text{ (d, } J = 10.4 \text{ Hz, 1H), } 4.87 \text{ – 4.66 (m, 5H),} \]
4.63 (d, $J = 8.9$ Hz, 1H, H5), 4.38 (t, $J = 8.5$ Hz, 1H, H4), 3.97 (dd, $J = 8.5$, 2.8 Hz, 1H, H3), 3.82 (t, $J = 2.8$ Hz, 1H, H2), 3.48 (s, 3H). $^{13}$C NMR (101 MHz, chloroform-$d$) δ 166.2, 161.5, 138.19, 138.17, 138.0, 134.9, 128.9, 128.43, 128.40, 128.37, 128.31, 127.92, 127.85, 127.77, 127.76, 127.74, 124.1, 99.9 (C1), 78.5 (C3), 75.7 (C4), 74.9, 74.4 (C2), 72.9, 72.5, 70.5 (C5), 55.9. HRMS (ESI+) Calcd. for C$_{36}$H$_{33}$NO$_9$Na ([M + Na]$^+$): 646.2048, found: 646.2038.
Procedures for NHP-esters of BDA protected glycosides

1,3-dioxoisindolin-2-yl (2S,3S,4aS,5S,8S,8aR)-8-hydroxy-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyran-3,4-b[1,4]dioxine-5-carboxylate (17)

Step 1 (BDA protection): A dry round bottom flask equipped with a magnetic stirring bar and a reflux condenser was charged with methyl α-D-mannopyranoside 14 (3.10 g, 16.0 mmol, 1.0 eq), dry MeOH (65 ml), butadione (1.7 ml, 19 mmol, 1.2 eq), camphorsulfonic acid (234 mg, 1.00 mmol, 0.06 eq) and trimethyl orthoformate (6.78 g, 63.9 mmol, 4.0 eq). The solution was heated to reflux overnight. Full consumption of the starting material was indicated by TLC. The reaction was subsequently quenched with triethylamine (0.25 ml, 1.8 mmol, 0.11 eq) and concentrated in vacuo. The crude product was used in the next step without further purification.

Step 2 (oxidation): a round bottom flask equipped with a magnetic stirring bar was charged with the product from the previous step (16.0 mmol, 1 eq) and dissolved in a 10:1 MeCN/H₂O mixture (130 ml). The reaction mixture was cooled to 0 °C with an ice bath. TEMPO (820 mg, 5.25 mmol, 0.33 eq) and BAIB (5.54 g, 49.9 mmol, 3.1 eq) was subsequently added. The reaction mixture was warmed to room temperature. Complete consumption of the starting material was indicated by TLC after 2 h, and the mixture was quenched with MeOH (7 ml) and stirred for 5 min. The color of the solution changed from red to faint yellow, indicating that the oxidizing agent was completely quenched. The reaction mixture was then concentrated in vacuo. The remaining residue was co-evaporated with toluene (5x) to remove residual acetic acid. The crude product was used in the next step without further purification.

Step 3 (EDC coupling): The crude from the previous step (16.0 mmol, 1 eq) was dissolved in DCM (61 ml) in a round bottom flask equipped with a stirring bar, to which EDC hydrochloride (5.74 g, 29.9 mmol, 1.9 eq) and N-hydroxyphthalimide (5.59 g, 34.3 mmol, 2.1 eq) were added. The solution was stirred overnight at room temperature. Full consumption of the starting material was observed on TLC. The solution was then concentrated in vacuo and the crude was purified by silica gel column chromatography using 1:4 v/v EtOAc/toluene as eluent to afford product 17 (3.73 g, 50% yield over 3 steps) as a white foam.
$^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.89 (dd, $J = 5.5$, 3.1 Hz, 2H), 7.79 (dd, $J = 5.5$, 3.1 Hz, 2H), 5.01 – 4.68 (m, 1H, H1), 4.62 (d, $J = 10.3$ Hz, 1H, H5), 4.39 (t, $J = 10.2$ Hz, 1H, H4), 4.08 (dd, $J = 10.1$, 3.1 Hz, 1H, H3), 3.97 (dd, $J = 3.2$, 1.5 Hz, 1H, H2), 3.49 (s, 3H), 3.34 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H). Note: Signal for the OH is not observed.

$^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 165.5, 161.3, 134.9, 129.0, 124.1, 102.1 (C1), 100.8, 100.5, 69.3 (C2), 68.5 (C5), 67.9 (C3), 64.6 (C4), 56.0, 48.5, 48.3, 17.8, 17.7. HRMS (ESI+) Calcd. for C$_{21}$H$_{25}$N$_1$O$_{11}$NH$_4$ ([M + NH$_4$]$^+$): 485.1766, found: 485.1766.

1,3-dioxoissoindolin-2-yl (2S,3S,4aS,5S,7S,8aR)-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxine-5-carboxylate (37)

Step 1 (Fischer glycosylation and BDA protection): A dry round bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with 2-deoxy-$d$-glucose 36 (2.06 g, 12.6 mmol, 1.0 eq), dry MeOH (65 ml) and camphorsulfonic acid (214 mg, 0.921 mmol, 0.07 eq) under nitrogen. After refluxing overnight, full consumption of the starting material was shown on TLC. In the same pot, butadiene (1.2 ml, 14 mmol, 1.1 eq) and trimethyl orthoformate (5.5 ml, 50 mmol, 4.0 eq) were added under nitrogen, and the solution was heated to reflux. After reflux overnight, full consumption of the intermediate methyl glucoside was indicated by TLC. The reaction was subsequently quenched with triethylamine (0.13 ml, 0.94 mmol, 0.07 eq) and concentrated in vacuo. The crude product was used in the next step without further purification. Alternatively, the product could be purified by silica gel column chromatography with 1:4 EtOAc/pentane. Starting with methyl 2-deoxy-$d$-glucose 36 (4.79 g, 29.2 mmol), BDA-methyl glycoside product 36BDA (6.98 g, 82% yield) could be obtained. The analytical data were in full accord with those reported previously.$^5$

Step 2 (oxidation): a round bottom flask equipped with a magnetic stirring bar was charged with the product from the previous step (12.6 mmol, 1.0 eq) and dissolved in a 10:1 v/v DCM/H$_2$O mixture (50 ml). The reaction mixture was cooled to 0 °C with an ice bath. TEMPO (494 mg, 3.16 mmol, 0.25 eq) and BAIB (10.3 g, 31.9 mmol, 2.5 eq) were subsequently added. The reaction mixture was warmed to room temperature. TLC indicated complete consumption of the starting material after 5 h, and the mixture was quenched with MeOH (5 ml) and stirred for 5 min. The color of the solution changed from red to faint yellow, indicating that the oxidizing agent was completely quenched. The reaction mixture was then concentrated at 600 mbar, 55 °C until no evaporation was visible. Toluene (40 ml) was added, and the reaction mixture was concentrated at 300 mbar, 55 °C until no evaporation was visible. The reaction mixture was then concentrated in vacuo. The remaining residue was co-evaporated with toluene (5x) to removal residual acetic acid. The crude product was used in the next step without further purification.
Step 3 (EDC coupling): The crude from the previous step (16.0 mmol, 1 eq) was dissolved in DCM (63 ml) in a round bottom flask equipped with a stirring bar, to which N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (2.92 g, 15.2 mmol, 1.2 eq) and N-hydroxyphthalimide (2.28 g, 14.0 mmol, 1.1 eq) were added. The solution was stirred for 6h at room temperature. Full consumption of the starting material was observed on TLC. The solution was then concentrated in vacuo and the crude was purified by silica gel column chromatography eluted with pure toluene → 1:4 v/v Et2O/toluene to afford product 37 (1.88 g, 33% yield over 3 steps).

$^1$H NMR (400 MHz, chloroform-d) δ 7.89 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.79 (dd, $J = 5.5, 3.1$ Hz, 2H), 5.00 (d, $J = 3.4$ Hz, 1H, H1), 4.62 (d, $J = 10.1$ Hz, 1H, H5), 4.21 (ddd, $J = 12.1, 9.7, 4.7$ Hz, 1H, H3), 3.93 (t, $J = 9.9$ Hz, 1H, H4), 3.44 (s, 3H), 3.34 (s, 3H), 3.30 (s, 3H), 2.09 (dd, $J = 12.5, 7.3$ Hz, 1H, H2eq), 1.91 (td, $J = 12.5, 3.6$ Hz, 1H, H2ax), 1.38 (s, 3H), 1.32 (s, 3H). $^{13}$C NMR (101 MHz, chloroform-d) δ 166.1, 134.9, 129.0, 124.2, 100.5, 100.3, 99.9 (C1), 70.1 (C4), 68.3 (C5), 64.5 (C3), 55.7, 48.4, 48.3, 33.4 (C2), 18.0, 17.7. HRMS (ESI+) Calcd. for C$_{21}$H$_{25}$NO$_{10}$Na ([M + Na$^+$]): 474.1371, found: 474.1367.

To synthesize N-tetrachlorohydroxyphthalimide 26 variant, step 3 was modified as follows:

4,5,6,7-tetrachloro-1,3-dioxoisindolin-2-yl [2S,3S,4aS,5S,7S,8aR]-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyran-3,4-b[1,4]dioxine-5-carboxylate (26)

Step 3 (DCC coupling): The crude from the oxidation step (2.89 mmol, 1 eq) was dissolved in DCM (16 ml) in a round bottom flask equipped with a stirring bar, to which N,N'-dicyclohexylcarbodiimide (680 mg, 3.30 mmol, 1.1 eq) and 3,4,5,6-tetrachloro-N-hydroxyphthalimide (977 mg, 3.25 mmol, 1.1 eq) were added. The solution was stirred for 1 h at room temperature. Full consumption of the starting material was observed on TLC. The reaction mixture was filtered through celite. The filtrate was then concentrated in vacuo and the crude was purified by silica gel column chromatography eluted with 1:4 Et$_2$O/pentane to afford product 26 (1.88 g, 79% yield over 2 steps).

$^1$H NMR (400 MHz, chloroform-d) δ 4.99 (d, $J = 3.4$ Hz, 1H, H1), 4.61 (d, $J = 10.2$ Hz, 1H, H5), 4.20 (ddd, $J = 13.4, 9.7, 4.7$ Hz, 1H, H3), 3.92 (t, $J = 10.0$ Hz, 1H, H4), 3.42 (s, 3H), 3.33 (s, 3H), 3.29 (s, 3H), 2.04 (dd, $J = 12.8, 4.8$ Hz, 1H, H2eq), 1.90 (td, $J = 12.5, 3.6$ Hz, 1H, H2ax), 1.37 (s, 3H), 1.31 (s, 3H). $^{13}$C NMR (101 MHz, chloroform-d) δ 165.7, 157.0, 141.2, 130.7, 124.8, 100.6, 100.3, 100.0, 70.0, 68.2, 64.5, 55.6, 48.5, 48.3, 33.4 (C2), 17.9, 17.8. HRMS (ESI+) Calcd. for C$_{21}$H$_{25}$Cl$_{3}$NO$_{10}$Na ([M + Na$^+$]): 609.9812, found: 609.9808. Isotope pattern matches theoretical prediction.
1,3-dioxoisooindolin-2-yl (2S,3S,4aS,5S,7S,8R,8aR)-8-acetamido-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxine-5-carboxylate (41)

Step 1 (Fischer glycosylation): A round bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with N-acetylglucosamine 39 (3.05 g, 13.8 mmol, 1.0 eq) in MeOH (70 ml) and Amberlite-H+ (5.00 g). The reaction mixture was heated to reflux overnight. Complete consumption of starting material was indicated by TLC. The Amberlite was subsequently filtered off, and the filtrate was concentrated to give the crude product which was used in the next step without further purification.

Step 2 (BDA protection): A dry round bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with the crude product from the previous step (13.8 mmol, 1.0 eq), dry MeOH (60 ml), butadiene (1.4 ml, 16.0 mmol, 1.2 eq), camphorsulfonic acid (220 mg, 0.947 mmol, 0.07 eq) and trimethyl orthoformate (5.8 ml, 53.0 mmol, 3.8 eq). The solution was heated to reflux overnight. Full consumption of the starting material was indicated by TLC. The reaction was subsequently quenched with triethylamine (0.30 ml, 2.1 mmol, 0.16 eq) and concentrated in vacuo. The crude product was purified by silica gel column chromatography in pure EtOAc to afford 40 (2.85 g, 59% yield over 2 steps).

1H NMR (400 MHz, methanol-d4) δ 4.64 (d, J = 3.6 Hz, 1H, H1), 4.13 (dd, J = 11.2, 3.6 Hz, 1H, H2), 3.91 (dd, J = 11.2, 8.7 Hz, 1H, H3), 3.82 – 3.74 (m, 1H, H6a), 3.70 – 3.60 (m, 3H, H4, H5 and H6b), 3.40 (s, 3H), 3.25 (s, 3H), 3.24 (s, 3H), 1.97 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H). Note: Signal for the OH and NH are not observed. 13C NMR (101 MHz, methanol-d4) δ 173.5, 101.1, 101.0, 100.2 (C1), 71.8 (C4/5), 68.7 (C3), 68.4 (C4/5), 61.5 (C6), 55.6, 52.4 (C2), 48.3, 22.4, 18.1, 18.0. HRMS (ESI+) Calcd. for C15H27NO8Na ([M + Na]+): 372.1629, found: 372.1632.

Step 3 (oxidation): a round bottom flask equipped with a magnetic stirring bar was charged with 40 (1.15 g, 3.30 mmol, 1.0 eq) and dissolved in a 5:1 v/v MeCN/H2O mixture (24 ml). The reaction mixture was cooled to 0 °C with an ice bath. TEMPO (167 mg, 1.07 mmol, 0.32 eq) and BAIB (3.31 g, 10.3 mmol, 3.1 eq) were subsequently added. The reaction mixture was warmed to room temperature. TLC indicated complete consumption of the starting material after 6h, and the mixture was quenched with MeOH (4 ml) and stirred for 5 min. The color of the solution changed from red to faint yellow, indicating that the oxidizing agent was completely quenched. The reaction mixture was then concentrated at 300 mbar, 55°C until no evaporation was visible. Toluene (5 ml) was added, and the reaction mixture was concentrated at 200 mbar, 55°C until no evaporation was visible. The reaction mixture was then concentrated in vacuo. The remaining residue was co-
evaporated with toluene (3x) to remove residual traces of acetic acid. The crude product was used in the next step without further purification.

Step 4 (EDC coupling): The crude from the previous step (3.30 mmol, 1 eq) was dissolved in DCM (20 ml) in a round bottom flask equipped with a stirring bar, to which EDC hydrochloride (1.02 g, 5.30 mmol, 1.6 eq) and N-hydroxyphthalimide (616 mg, 3.78 mmol, 1.1 eq) were added. The solution was stirred overnight at room temperature. Full consumption of the starting material was observed on TLC. The solution was then concentrated in vacuo and the crude was purified by silica gel column chromatography eluted with 1:1 EtOAc/toluene to afford product 41 (796 mg, 47% yield over 2 steps) as a hard wax. The major rotamer is reported here.

\[ \text{H NMR (400 MHz, chloroform-}d\text{)} \delta 7.89 (dd, J = 5.5, 3.1 Hz, 2H), 7.79 (dd, J = 5.5, 3.1 Hz, 2H), 5.46 (d, J = 8.7 Hz, 1H, NH), 4.93 (d, J = 3.6 Hz, 1H, H1), 4.61 (d, J = 10.1 Hz, 1H, H5), 4.36 (ddd, J = 11.0, 8.7 Hz, 1H, H2), 4.08 (t, J = 9.9 Hz, 1H, H4), 3.94 (dd, J = 11.1, 9.6 Hz, 1H, H3), 3.47 (s, 3H), 3.32 (s, 3H), 3.26 (s, 3H), 2.03 (s, 3H), 1.35 (s, 3H), 1.30 (s, 3H). 13C NMR (101 MHz, chloroform-\text{d}) \delta 169.8, 165.4, 161.2, 134.8, 128.8, 124.0, 100.3, 100.1, 99.4 (C1), 68.5 (C4), 67.7 (C5), 56.1, 50.4, 48.3, 47.9, 23.4, 17.7, 17.5. HRMS (ESI+) Calcd. for C23H29N2O11 ([M + H]+): 509.1761, found: 509.1761. 1H 1d-NOE: irradiation at the region 4.99–4.92 ppm (i.e. around the signal at 4.93 ppm) led to the transfer saturation of spin of the doublet at 4.88 ppm, confirming the additional signals in the 1H NMR were due to rotamers.8

1,3-dioxoisoinolin-2-yl (2R,3R,4aR,5S,7S,8R,8aS)-8-hydroxy-2,3,5-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxine-7-carboxylate (44)

Step 1 (BDA protection): A dry round bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with methyl α-D-galactopyranoside 42 (2.05 g, 10.5 mmol, 1.0 eq) in dry MeOH (70 ml), butadione (2.4 ml, 27 mmol, 2.5 eq), camphorsulfonic acid (170 mg, 0.732 mmol, 0.07 eq) and trimethyl orthoformate (9.5 ml, 87 mmol, 8.2 eq). The solution was heated to reflux overnight. Full consumption of starting material was indicated by TLC. The reaction was subsequently quenched with triethylamine (0.20 ml, 1.4 mmol, 0.14 eq) and concentrated in vacuo. The crude product was purified by silica gel column chromatography in 7:3 EtOAc/pent to afford 43 (1.50 g, 46% yield) as a hard wax.

\[ \text{H NMR (400 MHz, chloroform-}d\text{)} \delta 4.85 (d, J = 3.5 Hz, 1H, H1), 4.20 (dd, J = 10.4, 3.5 Hz, 1H, H2), 4.08 (dd, J = 10.5, 3.2 Hz, 1H, H3), 4.05–4.01 (m, 1H, H4), 3.96 (dq, J = 9.3, 5.0 Hz, 1H, H6a), 3.88–3.79 (m, 2H, H5 and H6b), 3.43 (s, 3H), 3.26 (s, 3H), 3.25 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H). Note: Signal for the OH is not observed. 13C NMR (101 MHz, chloroform-\text{d}) \delta 100.3, 100.3,
Step 2 (oxidation): To a round bottom flask equipped with a magnetic stirring bar charged with 43 (843 mg, 2.73 mmol, 1.0 eq) was added a 5:1 v/v MeCN/H₂O mixture (24 ml). The reaction mixture was cooled to 0 °C with an ice bath. TEMPO (140 mg, 0.896 mmol, 0.33 eq) and BAIB (2.64 g, 8.2 mmol, 3.0 eq) were subsequently added. The reaction mixture was warmed to room temperature. TLC analysis indicated complete consumption of the starting material after 6h, and the mixture was quenched with MeOH (7 ml) and stirred for 5 min. The color of the solution changed from red to faint yellow, indicating that the oxidizing agent was completely quenched. The reaction mixture was then concentrated at 300 mbar, 55°C until no evaporation was visible. Toluene (20 ml) was added, and the reaction mixture was concentrated at 200 mbar, 55°C until no evaporation was visible. The reaction mixture was then concentrated in vacuo. The remaining residue was co-evaporated with toluene (3x) to remove residual traces of acetic acid. The crude product was used in the next step without further purification.

Step 3 (EDC coupling): The crude from the previous step (2.73 mmol, 1.0 eq) was dissolved in DCM (13 ml) in a round bottom flask equipped with a stirring bar, to which EDC hydrochloride (843 mg, 4.40 mmol, 1.6 eq) and N-hydroxyphthalimide (513 mg, 3.15 mmol, 1.2 eq) were added. The solution was stirred overnight at room temperature. Full consumption of the starting material was observed on TLC. The solution was then concentrated in vacuo and purified by silica gel column chromatography eluted with pure toluene→1:4 Et₂O/toluene to afford product 44 (612 mg, 48% yield over 2 steps) as a hard wax.

1H NMR (400 MHz, chloroform-d) δ 7.91 (dd, J = 5.5, 3.1 Hz, 2H), 7.81 (dd, J = 5.5, 3.1 Hz, 2H), 4.99 (d, J = 3.5 Hz, 1H, H1), 4.88 (d, J = 1.7 Hz, 1H, H5), 4.62 – 4.53 (m, 1H, H4), 4.34 (dd, J = 10.6, 3.5 Hz, 1H, H2), 4.22 (dd, J = 10.6, 3.2 Hz, 1H, H3), 3.52 (s, 3H), 3.30 (s, 3H), 3.26 (s, 3H), 2.94 (d, J = 2.7 Hz, 1H, OH), 1.35 (s, 3H), 1.34 (s, 3H). 13C NMR (101 MHz, chloroform-d) δ 165.3, 161.7, 135.1, 128.9, 124.4, 100.5, 100.3, 99.3 (C1), 70.3 (C5), 69.5 (C4), 65.3 (C3), 64.5 (C2), 56.5, 48.2, 48.2, 17.9, 17.9. HRMS (ESI+) Calcd. for C₂₁H₂₆NO₁₁NH₄ ([M + NH₄]⁺): 485.1766, found: 485.1767.

1,3-dioxoisoinodinyl-2-yl (2S,3S,4aS,5S,7R,8S,8aR)-8-hydroxy-2,3-dimethoxy-2,3-dimethyl-7-(p-tolythio)hexahydro-5H-pyrano[3,4-b][1,4]dioxide-5-carboxylate (46)

45 was synthesized according to a literature procedure.⁷

Step 1 (Deacetylation of thioglycoside 45): a round bottom flask equipped with a magnetic stirring bar was charged with peracetylated mannoside 45 (2.24 g, 4.94 mmol, 1.0 eq) and MeOH (30 ml).
Sodium methoxide (388 mg, 7.18 mmol, 1.5 eq) was subsequently added, and the solution was stirred overnight, after which a white precipitate was observed in the solution. TLC indicated complete conversion of the starting material into a polar product. Then the mixture was quenched with amberlite-H+ until pH=7. The white precipitate disappeared after 5 min of stirring with amberlite-H+. The reaction mixture was then concentrated in vacuo. The crude product was used in the next step without further purification.

Step 2 (BDA protection): a round bottom flask equipped with a magnetic stirring bar was charged with the crude product from the previous step (4.94 mmol, 1.0 eq), dry MeOH (27 ml), butadione (0.50 ml, 5.7 mmol, 1.2 eq), camphorsulfonic acid (80 mg, 0.35 mmol, 0.07 eq) and trimethyl orthoformate (1.6 ml, 15 mmol, 3.0 eq). The solution was heated to reflux overnight, after which TLC indicated full consumption of the starting material. The reaction was subsequently quenched with triethylamine (0.20 ml, 3.5 mmol, 0.71 eq) and concentrated in vacuo. The crude product was used in the next step without further purification.

Step 3 (oxidation): a round bottom flask equipped with a magnetic stirring bar was charged with the crude product from the previous step (4.94 mmol, 1.0 eq) in a 5:1 v/v MeCN/H2O mixture (30 ml). The reaction mixture was cooled to 0 °C with ice bath. TEMPO (268 mg, 1.71 mmol, 0.35 eq) and BAIB (5.63 g, 3.54 mmol, 3.5 eq) were subsequently added. The reaction mixture was warmed to room temperature. After overnight stirring, TLC analysis indicated complete consumption of the starting material, and the mixture was quenched with MeOH (5 ml) and stirred for 5 min. The color of the solution changed from red to faint yellow, indicating that the oxidizing agent was completely quenched. The reaction mixture was then concentrated in vacuo. The remaining residue was co-evaporated with toluene (3x) to remove residual traces of acetic acid. The crude product was used in the next step without further purification.

Step 4 (EDC coupling): The crude from the previous step (2.73 mmol, 1.0 eq) was dissolved in DCM (13 ml) in a round bottom flask equipped with a stirring bar, to EDC hydrochloride (843 mg, 4.40 mmol, 1.6 eq) and N-Hydroxyphthalimide (513 mg, 3.15 mmol, 1.2 eq) were added. The solution was stirred overnight at room temperature. Full consumption of the starting material was observed on TLC. The solution was then concentrated in vacuo and purified by silica gel column chromatography eluted with pure toluene→1:4 Et2O/toluene to afford product 46 (612 mg, 48% yield over 3 steps) as a hard wax.

\[^1H\text{NMR}\] (400 MHz, chloroform-\(d\)) \(\delta\) 7.88 (dd, \(J = 5.6, 3.0\ Hz, 2H\)), 7.78 (dd, \(J = 5.5, 3.1\ Hz, 2H\)), 7.40 (d, \(J = 8.1\ Hz, 2H\)), 7.15 (d, \(J = 7.9\ Hz, 2H\)), 5.55 (d, \(J = 1.4\ Hz, 1H, H1\)), 5.20 (d, \(J = 10.3\ Hz, 1H, H5\)), 4.47 (t, \(J = 10.1\ Hz, 1H, H4\)), 4.24 (dd, \(J = 3.2, 1.3\ Hz, 1H, H2\)), 4.07 (dd, \(J = 10.1, 3.1\ Hz, 1H, H3\)), 3.34 (s, 3H), 3.33 (s, 3H), 2.66 (s, 1H, OH), 2.33 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). \[^13C\text{NMR}\] (101 MHz, chloroform-\(d\)) \(\delta\) 165.2, 161.3, 138.6, 134.9, 132.8, 130.2, 129.1, 124.1, 101.0, 100.5, 89.7 (C1), 70.9 (C2), 69.0 (C5), 68.6 (C3), 64.9 (C4), 48.5, 48.4, 21.3, 17.8. \[\text{HRMS (ESI+)}\] Calcd. for \(C_{27}H_{29}NO_{10}SNH_4\) ([M + NH4]+): 577.1850, found: 577.1851.
Procedures of photoalkylation of perbenzylglycosides

General procedure A/B/C:

A 4 mL vial equipped with a septum and magnetic stir bar was charged with a NHP ester of a monosaccharide (0.30 mmol, 1.0 eq), tris(2,2'-bipyridine)ruthenium(II) (0.01 mmol, 0.03 eq, see below), Hantzsch ester (0.33 mmol, 1.1 eq), and solvent (1 ml, see below). The reaction vessel was then sealed with a cap with a silicone/Teflon insert for glass vials, or with a rubber septum for round bottom flasks. The reaction mixture was purged with nitrogen for 2 min, and somophile was subsequently added (see below). The reaction was irradiated for 15 h at room temperature.

| Ru(bpy) source | General procedure A | General procedure B | General procedure C |
|----------------|---------------------|---------------------|---------------------|
| somophile eq   | 1.2                 | 1.2                 | 5                   |
| solvent        | 7:3 v/v THF:water   | Dry THF             | 7:3 v/v THF:PBS buffer (pH=7) |

Following general procedure A, a 4 ml vial was charged with 1 (206 mg, 0.323 mmol, 1 eq), Ru(bpy)$_3$Cl$_2$.6H$_2$O (6.2 mg, 8.3 μmol, 0.026 eq), Hantzsch ester (86.0 mg, 0.340 mmol, 1.05 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, methyl acrylate (32 μL, 0.36 mmol, 1.1 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with 30 ml EtOAc and washed with 10 ml brine. The water layer was back extracted with 10 ml EtOAc. The combined organic layer was dried over MgSO$_4$ and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (linear gradient: 5% to 10% EtOAc in 25 min). The fractions were checked by TLC, and those with the same R$_f$ were combined (2a has a slightly higher R$_f$ value than 2b) to afford 2a (40.5 mg, 24 % yield, adjusted for 8.0 mg phthalimide) and 2b (75.4 mg, 45% yield), both as hard waxes.

2a:

$^1$H NMR ($400$ MHz, chloroform-$d$) δ 7.39 – 7.23 (m, 15H), 4.98 (d, $J = 10.8$ Hz, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.83 – 4.80 (m, 1H), 4.80 – 4.76 (m, 1H), 4.66 (d, $J = 12.2$ Hz, 1H), 4.62 (d, $J = 11.0$ Hz, 1H), 4.52 (d, $J = 3.6$ Hz, 1H, H1), 3.96 (t, $J = 9.2$ Hz, 1H, H3), 3.65 (s, 3H), 3.59 (td, $J = 9.7$, 2.6 Hz, 1H, H5), 3.50 (dd, $J = 9.7$, 3.6 Hz, 1H, H2), 3.34 (s, 3H), 3.19 (t, $J = 9.3$ Hz, 1H, H4), 2.53 – 2.26 (m, 2H, H7), 2.26 – 2.11 (m, 1H, H6a), 1.69 (ddt, $J = 14.6$, 9.1, 5.8 Hz, 1H, H6b).

$^{13}$C NMR (101 MHz, chloroform-$d$) δ 173.9, 138.8, 138.28, 138.26, 128.59, 128.55, 128.54, 128.2, 128.15, 128.07, 128.04, 127.9, 127.8, 98.0 (C1), 82.1 (C3), 81.9 (C4), 80.2 (C2), 75.9, 75.3, 73.5,
69.5 (C5), 55.2, 30.4 (C7), 27.1 (C6). **HRMS (ESI+)** Calcd. for C_{31}H_{36}O_7N_4 ([M + NH_4]^+): 538.2799, found: 538.2798.

**2b:**

\(^1\)H NMR \((400 \text{ MHz, chloroform-}d)\) \(7.38 – 7.25\) (m, 13H), \(7.21\) (dd, \(J = 7.2, 2.3\) Hz, 2H), 4.79 (d, \(J = 12.6\) Hz, 1H), 4.66 (d, \(J = 10.3\) Hz, 1H), 4.63 (d, \(J = 9.8\) Hz, 1H), 4.57 (d, \(J = 2.3\) Hz, 1H, H1), 4.53 (d, \(J = 11.7\) Hz, 1H), 4.45 (m, 2H), 3.85 – 3.77 (m, 2H, H3 and H5), 3.67 (s, 3H), 3.52 (s, 3H), 3.50 (d, \(J = 2.3\) Hz, 1H, H2 overlapped), 3.31 (dd, \(J = 4.8, 3.3\) Hz, 1H, H4), 2.59 – 2.38 (m, 2H, H7), 2.30 (dddd, \(J = 14.0, 10.5, 7.7, 5.8\) Hz, 1H, H6a), 1.97 – 1.83 (m, 1H, H6b). \(^{13}\)C NMR \((101 \text{ MHz, chloroform-}d)\) \(\delta 174.1, 138.8, 138.2, 138.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.7, 127.66, 101.3\) (C1), 76.0 (C4), 75.5 (C2), 74.7 (C3), 73.9 (C5), 73.9, 73.3, 72.3, 56.8, 51.6, 30.6 (C7), 25.7 (C6). **HRMS (ESI+)** Calcd. for C_{31}H_{36}O_7N_4 ([M + NH_4]^+): 538.2799, found: 538.2800.

\((2S,3R,4S,5R,6R)-3,4,5\)-tris(benzyloxy)-2-methoxy-6-(2-(phenylsulfonyl)ethyl)tetrahydro-2H-pyran \((3a)\) and \((2S,3R,4S,5R,6S)-3,4,5\)-tris(benzyloxy)-2-methoxy-6-(2-(phenylsulfonyl)ethyl)tetrahydro-2H-pyran \((3b)\):

Following general procedure A, a 4 ml vial was charged with 1 (164 mg, 0.257 mmol, 1 eq), Ru(bpy)_3Cl_2.6H_2O (5.1 mg, 6.8 \(\mu\)mol, 0.026 eq), Hantzsch ester (67.8 mg, 0.268 mmol, 1.04 eq), phenyl vinyl sulfone (49.1 mg, 0.292 mmol, 1.14 eq), and 7:3 v/v water/THF mixture (1 ml). The solution was purged with nitrogen. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with brine (10 ml). The organic layer was dried over MgSO_4 and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/toluene (linear gradient: 0% to 25% EtOAc in 25 min). The fractions were checked by TLC, and those with the same R_f were combined \((3a)\) has a slightly higher R_f value than \((3b)\) to afford \((3a)\) (35.1 mg, 23% yield, adjusted for 4.8 mg phthalamide) and \((3b)\) (86.0 mg, 55% yield, containing a minor amount of unidentified aromatic impurity), both as hard waxes.

\(3a:\)

\(^1\)H NMR \((400 \text{ MHz, chloroform-}d)\) \(\delta 7.90 – 7.81\) (m, 2H, Ph), 7.68 – 7.61 (m, 1H, Ph), 7.52 (t, \(J = 7.7\) Hz, 2H, Ph), 7.36 – 7.24 (m, 13H), 7.17 (dd, \(J = 6.7, 2.9\) Hz, 2H), 4.97 (d, \(J = 10.9\) Hz, 1H), 4.84 (d, \(J = 10.8\) Hz, 1H), 4.82 – 4.74 (m, 2H), 4.63 (d, \(J = 12.1\) Hz, 1H), 4.50 (d, \(J = 10.8\) Hz, 1H), 4.47 (d, \(J = 3.6\) Hz, 1H, H1), 3.92 (t, \(J = 9.2\) Hz, 1H, H3), 3.59 (td, \(J = 9.6, 3.1\) Hz, 1H, H5), 3.45 (dd, \(J = 9.7, 3.6\) Hz, 1H, H2), 3.30 (s, 3H), 3.24 (dd, \(J = 14.0, 11.4\), 4.7 Hz, 1H, H7a), 3.16 – 3.09 (t, \(J = 9.2\) Hz, 1H, H4 overlap), 3.11 – 3.03 (m, 1H, H7b overlap), 2.23 – 2.11 (m, 1H, H6a), 1.72 (dddd, \(J = 13.9, 11.0, 9.3, 4.6\) Hz, 1H, H6b). \(^{13}\)C NMR \((101 \text{ MHz, chloroform-}d)\) \(\delta 138.9, 138.7, 138.1, 137.8, 133.8, 129.4, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 98.0\) (C1), 81.9 (C3), 81.2 (C4), 80.1 (C2), 75.8, 75.3, 73.5, 68.4 (C5), 55.4, 52.7, 25.4. Note: Some aromatic carbon
signals overlap, causing the apparent loss of signals in the aromatic region. **HRMS (ESI+)** Calcd. for C_{35}H_{38}O_{7}Na ([M + Na]^+): 625.2231, found: 625.2209.

3b:

**1H NMR** (400 MHz, chloroform-\(d_2\)) \(\delta\) 7.88 – 7.82 (m, 2H), 7.59 – 7.47 (m, 3H), 7.38 – 7.27 (m, 11H), 7.22 – 7.15 (m, 4H), 4.76 (d, \(J = 12.6\) Hz, 1H), 4.64 – 4.61 (m, 1H), 4.60 – 4.57 (m, 1H), 4.51 (d, \(J = 2.2\) Hz, 1H, H1), 7.59 – 7.48 (1H, overlapped with impurities), 4.38 (d, \(J = 11.7\) Hz, 1H), 4.31 (d, \(J = 11.9\) Hz, 1H), 3.83 (dt, \(J = 9.8, 3.4\) Hz, 1H, H5), 3.74 (t, \(J = 4.7\) Hz, 1H, H3), 3.47 (dd, \(J = 4.9, 2.2\) Hz, 1H, H2), 3.43 (s, 3H), 3.37 (ddt, \(J = 14.2, 11.4, 10.9, 5.1\) Hz, 1H, H7a), 3.22 (dd, \(J = 4.6, 3.2\) Hz, 1H, H4), 3.20 – 3.10 (m, 1H, H7b), 2.40 – 2.22 (m, 1H, H6a), 2.05 – 1.91 (m, 2H, H6b)

Note: Products peaks were selected based on meHSQC and COSY. **13C NMR** (101 MHz, chloroform-\(d_2\)) \(\delta\) 139.0, 138.6, 137.9, 137.8, 133.7, 129.33, 129.32, 128.5, 128.39, 128.37, 128.2, 128.18, 128.1, 128.07, 128.0, 127.94, 127.87, 127.7, 101.3 (C1), 75.4 (C4), 75.0 (C2), 74.1 (C3), 74.0, 73.2, 73.0 (C5), 72.2, 56.9, 53.5 (C7), 24.5 (C6). Note: Reported peaks >120ppm might belong to unknown impurity and are therefore not diagnostic. Peak selected based on meHSQC and COSY. **HRMS (ESI+)** Calcd. for C_{35}H_{38}O_{7}Na ([M + Na]^+): 625.2231, found: 625.2209

Subsequent hydrogenation of 3b:

To a round bottom flask charged with 3b (86.0 mg, 0.143 mmol, 1 eq.) in degassed MeOH (1.4 ml), 10% w/w palladium of carbon (86 mg, 0.081 mmol, 0.6 eq) was added. The flask was then put under a hydrogen atmosphere with a hydrogen-filled balloon. After overnight stirring, TLC indicated the formation of one polar product. The mixture was filtered over celite, concentrated, and purified by silica gel column chromatography with pure EtOAc as eluent to afford the compound 3b' with the following structure (39.0 mg, 82% yield).

(2S,3R,4S,5S,6S)-2-methoxy-6-(2-(phenylsulfonyl)ethyl)tetrahydro-2H-pyran-3,4,5-triol (3b‘)

**1H NMR** (400 MHz, methanol-\(d_4\)) \(\delta\) 7.97 – 7.89 (m, 2H), 7.76 – 7.70 (m, 1H), 7.65 (ddt, \(J = 8.3, 6.6, 1.4\) Hz, 2H), 4.56 (d, \(J = 1.3\) Hz, 1H, H1), 3.92 (t, \(J = 3.7\) Hz, 1H, H3), 3.91 – 3.86 (m, 1H, H5), 3.55 (dt, \(J = 3.8, 1.2\) Hz, 1H, H2), 3.48 (s, 3H), 3.39 (dddt, \(J = 8.6, 6.4, 1.8\) Hz, 2H, H7), 3.33 – 3.29 (m, 1H, H4 overlapping with CD_{3}OD peak), 2.25 – 2.13 (m, 1H, H6a), 1.91 – 1.80 (m, 1H, H6b).**13C NMR** (101 MHz, chloroform-\(d_2\)) \(\delta\) 140.4, 135.0, 130.6, 129.1, 101.6 (C1), 73.4 (C5), 71.7 (C4), 71.4 (C2), 71.1 (C3), 57.1, 53.7 (C7), 25.7 (C6). **HRMS (ESI+)** Calcd. for C_{14}H_{20}O_{7}Na ([M + Na]^+): 355.0822, found: 355.0819. **NOESY** shows through-space correlation of H1 and H5.
3-((2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)propanenitrile (4a) and 3-((2S,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)propanenitrile (4b):

Following general procedure A, a 4 ml vial was charged with 1 (187.8 mg, 0.294 mmol, 1 eq), Ru(bpy)$_3$Cl$_2$.6H$_2$O (6.3 mg, 0.029 eq), Hantzsch ester (87.0 mg, 0.343 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, acrylonitrile (25 μL, 0.38 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with brine (10 ml). The organic layer was dried over MgSO$_4$ and concentrated. To remove phthalimide, the resulting solid was suspended in cold toluene and the suspension was filtered over celite. The solids and the celite was washed with cold toluene until all product was transferred. (Check by TLC) The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with Et$_2$O/pentane (linear gradient: 10% to 60% Et$_2$O in 25 min, with 4a started to eluted at 46% Et$_2$O and 4b started to elute at 56% Et$_2$O) to afford 4a (25.0 mg, 17% yield) and 4b (89.4 mg, 60% yield), both as hard waxes.

4a:

$^1$H NMR (400 MHz, chloroform-$d$) δ 7.53 – 7.12 (m, 15H), 5.00 (d, $J = 10.8$ Hz, 1H), 4.92 (d, $J = 11.1$ Hz, 1H), 4.85 – 4.77 (m, 2H), 4.66 (d, $J = 12.1$ Hz, 1H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.53 (d, $J = 3.6$ Hz, 1H, H1), 3.98 (t, $J = 9.2$ Hz, 1H, H3), 3.67 (td, $J = 9.7$, 2.8 Hz, 1H, H5), 3.49 (dd, $J = 9.6$, 3.6 Hz, 1H, H2), 3.39 (s, 3H), 3.17 (t, $J = 9.2$ Hz, 1H, H4), 2.47 – 2.30 (m, 2H, H7), 2.13 (dtd, $J = 14.0$, 8.1, 2.8 Hz, 1H, H6a), 1.61 (dddd, $J = 13.6$, 9.7, 7.4, 5.7 Hz, 1H, H6b). $^{13}$C NMR (101 MHz, chloroform-$d$) δ 138.7, 138.2, 138.0, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.8, 119.5 (CN), 98.1 (C1), 82.0 (C3), 81.1 (C4), 80.2 (C2), 75.9, 75.2, 73.5, 68.4 (C5), 55.6, 27.7 (C6), 13.4 (C7). HRMS (ESI+) Calcd. for C$_{30}$H$_{33}$N$_2$O$_5$Na ([M + Na]$^+$): 510.2251, found: 510.2236.

4b:

$^1$H NMR (400 MHz, chloroform-$d$) δ 7.40 – 7.27 (m, 11H), 7.27 – 7.23 (m, 2H), 7.24 – 7.17 (m, 2H), 4.82 (d, $J = 12.6$ Hz, 1H), 4.69 – 4.64 (m, 1H), 4.63 (t, $J = 2.6$ Hz, 2H, hidden H1), 4.52 (d, $J = 11.8$ Hz, 1H), 4.39 (d, $J = 11.9$ Hz, 1H), 4.35 (d, $J = 12.0$ Hz, 1H), 3.91 (dt, $J = 10.4$, 3.3 Hz, 1H, H5), 3.79 (t, $J = 4.4$ Hz, 1H, H3), 3.57 – 3.51 (m, 4H, hidden H2), 3.25 (dd, $J = 4.2$, 3.0 Hz, 1H, H4), 2.59 – 2.40 (m, 2H, H7), 2.36 (dddd, $J = 14.0$, 10.4, 7.0, 5.0 Hz, 1H, H6a), 1.76 (dddd, $J = 14.0$, 9.0, 7.2, 3.6 Hz, 1H, H6b). $^{13}$C NMR (101 MHz, chloroform-$d$) δ 138.7, 138.3, 138.0, 128.7, 128.6, 128.43, 128.39, 128.2, 128.1, 128.03, 127.96, 127.92, 127.7, 119.7 (CN), 101.5 (C1), 75.0 (C4), 74.8 (C2), 74.1, 74.0 (C3), 73.0, 72.6 (C5), 72.1, 57.0, 26.4 (C6), 13.9 (C7). HRMS (ESI+) Calcd. for C$_{30}$H$_{33}$N$_2$O$_5$Na ([M + Na]$^+$): 510.2251, found: 510.2235.
4-((2R,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)butan-2-one (5a) and 4-((2S,3R,4S,5R,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)butan-2-one (5b):

Following general procedure A, a 4 ml vial was charged with 1 (212 mg, 0.33 mmol, 1 eq), Ru(bpy)$_3$Cl$_2$.6H$_2$O (6.7 mg, 0.027 eq), Hantzsch ester (5a) (93.3 mg, 0.368 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, methyl vinyl ketone (32 μL, 0.40 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with water (10 ml), then brine (10 ml). The organic layer was dried over MgSO$_4$ and concentrated. The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (linear gradient: 10% to 20% EtOAc in 25 min, with 5a started to elute at 12% EtOAc and 5b started to elute at 18% EtOAc), to afford contaminated 5a, and pure 5b (89.4 mg, 58% yield) as hard wax. Contaminated 5a was dissolved in Et$_2$O and washed with water, dried over MgSO$_4$ to afford pure 5a (40.2 mg, 24% yield) as hard wax.

**5a:**

$^1$H NMR (400 MHz, chloroform-$d$) δ 7.33 (m, 15H), 4.99 (d, $J = 10.8$ Hz, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 4.85 – 4.77 (m, 2H), 4.65 (m, 2H), 4.52 (d, $J = 3.6$ Hz, 1H, H1), 3.96 (t, $J = 9.2$ Hz, 1H, H3), 3.92 (m, 2H), 3.87 (d, $J = 3.6$ Hz, 1H, H5), 3.75 (td, $J = 9.7$, 2.8 Hz, 1H, H4), 2.52 (dd, $J = 17.2$, 9.6, 5.7 Hz, 1H, H7a), 2.49 (ddd, $J = 17.2$, 9.6, 6.0 Hz, 1H, H7b), 2.10 (m, 4H, H6a overlap), 1.70 – 1.59 (m, 1H, H6b).

$^{13}$C NMR (101 MHz, chloroform-$d$) δ 208.4, 138.8, 138.3, 128.5, 128.2, 128.1, 128.0, 127.9, 127.7, 101.4 (C1), 75.8, 75.3, 73.4, 69.5 (C5), 55.2, 39.8 (C7), 29.8, 25.8 (C6). HRMS (ESI+) Calcd. for C$_{31}$H$_{36}$O$_6$Na ($[M + Na]^+$): 527.2404, found: 527.2398.

**5b:**

$^1$H NMR (400 MHz, chloroform-$d$) δ 7.36 – 7.27 (m, 13H), 7.20 (dd, $J = 6.7$, 1.9 Hz, 2H), 4.79 (d, $J = 12.6$ Hz, 1H), 4.63 (m, 2H), 4.55 (d, $J = 2.3$ Hz, 1H, H1), 4.51 (d, $J = 11.7$ Hz, 1H), 4.43 (m, 2H), 3.81 – 3.73 (m, 2H, H3 and H5), 3.50 (t, $J = 1.8$ Hz, 4H, H2 and OMe), 2.66 – 2.45 (m, 2H, H7), 2.30 – 2.15 (m, 1H, H6a), 2.13 (s, 3H), 1.85 (dtd, $J = 14.8$, 7.6, 3.7 Hz, 1H, H6b). $^{13}$C NMR (101 MHz, chloroform-$d$) δ 209.1, 138.9, 138.3, 138.1, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 101.4 (C1), 75.9 (C4), 75.3 (C2), 74.6 (C3), 74.0 (C5), 73.9, 73.2, 72.3, 56.8, 40.2 (C7), 30.0, 24.7 (C6). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for C$_{31}$H$_{36}$O$_6$Na ($[M + Na]^+$): 527.2404, found: 527.2401.
3-((2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)cyclopentan-1-one (6a) and 3-((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)cyclopentan-1-one (6b):

Following general procedure A, a 4 ml vial was charged with 1 (221 mg, 0.345 mmol, 1 eq), Ru(bpy)$_2$Cl$_2$.6H$_2$O (6.3 mg, 8.4 µmol, 0.024 eq), Hantzsch ester (97.3 mg, 0.384 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, 2-cyclopeniten-1-one (35 µL, 0.41 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with water (10 ml), then brine (10 ml). The organic layer was dried over MgSO$_4$ and concentrated. The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 40 g silica cartridge with EtOAc/pentane (isocratic elution with 10% EtOAc for 10 min, then linear gradient elution to 20% EtOAc for 10 min) to afford 6a (53.4 mg, adjusted for 3.3 mg phthalimide, 30% yield combined) and 6b (50.2 mg, 29%) as hard wax. 6a was isolated as a mixture of diastereomers, which was slightly separable during chromatography. Analytical samples were taken to obtain the for analysis, and the following spectral data were obtained.

6a (diastereomer 1):

$^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.37 – 7.27 (m, 15H), 5.00 (d, $J = 10.8$ Hz, 1H), 4.91 (d, $J = 11.2$ Hz, 1H), 4.86 – 4.74 (m, 2H), 4.66 (d, $J = 12.1$ Hz, 1H), 4.59 (d, $J = 11.2$ Hz, 1H), 4.56 (d, $J = 3.7$ Hz, 1H, H1), 3.98 (t, $J = 9.2$ Hz, 1H, H3), 3.68 (dd, $J = 10.0, 2.2$ Hz, 1H, H5), 3.47 (dd, $J = 9.6, 3.5$ Hz, 1H, H2), 3.35 (s, 3H), 3.19 (t, $J = 9.4$ Hz, 1H, H4), 2.70 – 2.57 (m, 1H, H6), 2.40 – 2.25 (m, 1H, H8a), 2.20 – 2.05 (m, 2H, H8a and H7’a), 2.00 (tdd, $J = 11.6, 7.3, 3.8$ Hz, 1H, H7a), 1.95 – 1.86 (m, 1H, H7b), 1.80 (dd, $J = 18.2, 8.2$ Hz, 1H, H7b). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 219.3, 138.7, 138.2, 138.0, 128.63, 128.57, 128.3, 128.19, 128.15, 128.13, 128.10, 127.8, 98.0 (C1), 82.4 (C3), 80.3 (C2), 79.5 (C4), 75.9, 75.0, 73.5, 71.1 (C5), 55.2, 38.4 (C8), 38.1 (C7’), 36.3 (C6), 26.2 (C7). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for $C_{32}H_{36}O_8$Na ([M + Na$^+$]): 539.2404, found: 539.2395.

6a (diastereomer 2):

$^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.40 – 7.27 (m, 15H), 5.02 (d, $J = 10.8$ Hz, 1H), 4.94 (d, $J = 11.3$ Hz, 1H), 4.86 – 4.75 (m, 2H), 4.66 (m, 2H), 4.56 (d, $J = 3.7$ Hz, 1H, H1), 4.00 (t, $J = 9.2$ Hz, 1H, H3), 3.67 (dd, $J = 10.0, 2.8$ Hz, 1H, H5), 3.50 (dd, $J = 9.6, 3.6$ Hz, 1H, H2), 3.37 (dd, $J = 9.9, 8.6$ Hz, 1H, H4), 3.32 (s, 3H), 2.66 – 2.55 (m, 1H, H6), 2.32 – 2.14 (m, 3H, H7 and H8a), 1.99 (dt, $J = 18.8, 9.6$ Hz, 1H, H8b), 1.74 (dq, $J = 12.6, 9.1$ Hz, 1H, H7a), 1.66 – 1.54 (m, 1H, H7b). $^{13}$C NMR (101 MHz, chloroform-$d$) $\delta$ 219.3, 138.7, 138.22, 138.19, 128.63, 128.61, 128.59, 128.3, 128.2, 128.10, 128.06, 127.8, 97.9 (C1), 82.6 (C3), 80.4 (C2), 78.5 (C4), 75.9, 74.9, 73.4, 70.5 (C5), 55.3, 41.8 (C7’), 38.4 (C8), 36.2 (C6), 22.2 (C7). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for $C_{32}H_{36}O_8$Na ([M + Na$^+$]): 539.2404, found: 539.2396.

6b:

$^1$H NMR (400 MHz, chloroform-$d$) $\delta$ 7.41 – 7.24 (m, 11H), 7.23 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 4.88 (d, $J = 12.8$ Hz, 1H), 4.65 – 4.54 (m, 3H, CH$_2$ and H1), 4.43 (d, $J = 12.1$ Hz, 1H), 4.22 (m, 2H), 3.77 (t, $J = 2.9$ Hz, 1H, H3), 3.55 (m, 4H, OMe and H2), 3.48 (dd, $J = 9.7, 1.8$ Hz, 1H,
H5), 3.06 (t, J = 2.4 Hz, 1H, H4), 2.87 (ddd, J = 17.4, 9.7, 5.2 Hz, 1H, H6), 2.41 (dt, J = 12.9, 6.5, 2.1 Hz, 1H, H7a), 2.34 – 2.20 (m, 1H, H8a), 2.20 – 2.03 (m, 1H, H8b), 1.85 (dd, J = 18.1, 7.8 Hz, 1H, H7'a), 1.76 – 1.64 (m, 1H, H7b), 1.64 – 1.52 (m, 1H, H7'b). 13C NMR (101 MHz, chloroform-d) δ 219.1, 139.0, 137.8, 137.6, 128.7, 128.48, 128.46, 128.39, 128.2, 128.0, 101.6 (C1), 78.8 (C5), 74.3, 73.4 (C2), 73.1 (C3), 73.0 (C4), 72.4, 71.5, 56.6, 41.1 (C7'), 38.4 (C8), 36.8 (C6), 27.2 (C7). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for C32H36O6Na ([M + Na]+): 539.2404, found: 539.2393. Only the major diastereomers can be properly assigned.

Following general procedure B, a 4 ml vial was charged with 1 (208 mg, 0.326 mmol, 1.0 eq), Ru(bpy)3(PF6)2 (8.6 mg, 10 μmol, 0.030 eq), Hantzsch ester (89.5 mg, 0.353 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, diethyl vinylphosphonate (55 μL, 0.36 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was directly coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with acetone/toluene (linear gradient: 0% to 20% acetone in 15 CV, 7a started to elute at the 9th CV and 7b started to elute at the 13th CV) to afford 7a (34.2 mg, impure and thus not reported) and 7b (56.7 mg, 29% yield) as hard wax.

7b:

1H NMR (400 MHz, chloroform-d) δ 7.36 – 7.25 (m, 12H), 7.21 – 7.14 (m, 2H), 4.78 (d, J = 12.6 Hz, 1H), 4.63 (dd, J = 12.3, 1.8 Hz, 2H), 4.56 (d, J = 2.2 Hz, 1H, H1), 4.48 (d, J = 11.7 Hz, 1H), 4.39 (m, 2H), 4.14 – 3.99 (m, 4H), 3.81 – 3.72 (m, 2H, H3 and H5), 3.51 (s, 3H), 3.49 (dd, J = 4.8, 2.2 Hz, 1H, H2), 3.26 (dd, J = 4.5, 3.1 Hz, 1H, H4), 2.33 – 2.14 (m, 1H, H6a), 2.09 – 1.90 (m, 1H, H7a), 1.86 – 1.75 (m, 1H, H6b), 1.75 – 1.64 (m, 1H, H7b), 1.29 (td, J = 7.0, 3.7 Hz, 6H, contains grease). 13C NMR (101 MHz, chloroform-d) δ 138.6, 138.0, 137.9, 128.5, 128.43, 128.40, 128.3, 128.2, 127.99, 127.96, 127.85, 127.79, 101.4 (C1), 75.5 (C4), 75.2 (C2), 74.8 (C5, J = 16.5 Hz), 74.4 (C3), 74.0, 73.2, 72.4, 61.61 (d, J = 6.3 Hz), 61.60 (d, J = 6.3 Hz), 56.9, 23.6 (d, J = 4.2 Hz), 22.37 (d, J = 142.2 Hz), 16.6, 16.5. 31P NMR (162 MHz, chloroform-d) δ 32.5. HRMS (ESI+) Calcd. for C35H42O8PNa ([M + Na]+): 621.2588, found: 621.2593.
4-((2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)butan-2-one (11a) and 4-((2S,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)butan-2-one (11b):

Following general procedure A, a 4 ml vial was charged with 33 (196 mg, 0.306 mmol, 1 eq), Ru(bpy)$_3$Cl$_2$.6H$_2$O (6.4 mg, 8.5 μmol, 0.27 eq), Hantzsch ester (85.5 mg, 0.338 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, methyl vinyl ketone (30 μL, 0.37 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with water (10 ml), then brine (10 ml). The organic layer was dried over MgSO$_4$ and concentrated. The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (linear gradient: 10% to 20% EtOAc in 24 min, 11a started to elute at 14% EtOAc and 11b started to elute at 16% EtOAc) to afford 11a (19.8 mg, 13% yield) and 11b (70.8 mg, 46% yield) as hard wax.

11a:

$^1$H NMR (400 MHz, chloroform-d) δ 7.39 – 7.24 (m, 15H), 4.98 – 4.86 (m, 3H), 4.79 (d, $J$ = 10.9 Hz, 1H), 4.70 (d, $J$ = 11.1 Hz, 1H), 4.64 (d, $J$ = 10.9 Hz, 1H), 4.26 (d, $J$ = 7.8 Hz, 1H, H1), 3.67 – 3.60 (m, 1H, H3), 3.55 (s, 3H), 3.39 (dd, $J$ = 9.2, 7.8 Hz, 1H, H2), 2.57 – 2.47 (m, 2H, H7), 2.19 (dddd, $J$ = 14.0, 8.8, 6.4, 2.0 Hz, 1H, H6a), 2.12 (s, 3H), 1.73 (ddt, $J$ = 14.5, 8.5, 6.1 Hz, 1H, H6b).

$^{13}$C NMR (101 MHz, chloroform-d) δ 208.4, 138.65, 138.36, 138.12, 128.52, 128.50, 128.3, 128.12, 128.04, 128.01, 127.78, 127.77, 104.8 (C1), 84.7 (C3), 82.6 (C2), 81.5 (C4/C5), 75.8, 75.3, 74.9, 73.9 (C4/C5), 75.2, 39.7 (C7), 29.9, 26.0 (C6). HRMS (ESI+) Calcd. for C$_{31}$H$_{36}$O$_6$Na ([M + Na]$^+$): 527.2404, found: 527.2401.

11b:

$^1$H NMR (400 MHz, chloroform-d) δ 7.37 – 7.23 (m, 15H), 4.77 – 4.59 (m, 6H, H1 overlap), 4.52 (d, $J$ = 11.8 Hz, 1H), 3.94 (dt, $J$ = 10.4, 3.9 Hz, 1H, H5), 3.75 (dd, $J$ = 6.9, 5.8 Hz, 1H, H3), 3.51 (dd, $J$ = 5.8, 3.9 Hz, 1H, H4), 3.46 (m, $J$ = 4.7 Hz, 1H, H2 overlap), 3.44 (s, 3H), 2.58 (ddd, $J$ = 17.4, 8.5, 5.6 Hz, 1H, H7a), 2.46 (ddd, $J$ = 17.4, 8.2, 6.9 Hz, 1H, H7b), 2.14 (s, 3H), 2.02 (ddd, $J$ = 14.0, 10.4, 8.2, 5.6 Hz, 1H, H6a), 1.88 (ddddd, $J$ = 14.8, 8.5, 6.9, 3.9 Hz, 1H, H6b). $^{13}$C NMR (101 MHz, chloroform-d) δ 208.3, 138.42, 138.36, 138.2, 128.5, 128.4, 128.2, 128.0, 127.84, 127.81, 127.76, 101.2 (C1), 79.0 (C2), 78.0 (C4), 77.6 (C3), 74.0, 73.6, 72.8, 69.5 (C5), 55.9, 39.8 (C7), 30.0, 22.8 (C6). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for C$_{31}$H$_{36}$O$_6$Na ([M + Na]$^+$): 527.2404, found: 527.2399.
Following general procedure A, a 4 ml vial was charged with 33 (217 mg, 0.339 mmol, 1 eq), Ru(bpy)$_3$Cl$_2$·6H$_2$O (6.5 mg, 8.7 μmol, 0.026 eq), Hantzsch ester (94.4 mg, 0.373 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, acrylonitrile (27 μL, 0.41 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with water (10 ml), then brine (10 ml). The organic layer was dried over MgSO$_4$ and concentrated. The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (linear gradient: 5% to 16% EtOAc in 20 min, with 12a started to elute at 14%, and 12b eluted right after), to afford 12a (35.5 mg, adjusted for 4.5 mg phthalimide, 22% yield) and 12b (85.1 mg, 52% yield) as hard wax.

12a:

$^1$H NMR (400 MHz, chloroform-$_d$) δ 7.44 – 7.21 (m, 15H), 4.99 – 4.87 (m, 3H), 4.79 (d, $J = 10.8$ Hz, 1H), 4.71 (d, $J = 11.0$ Hz, 1H), 4.60 (d, $J = 11.1$ Hz, 1H), 4.33 (d, $J = 7.8$ Hz, 1H, H1), 3.66 (t, $J = 9.0$ Hz, 1H, H3), 3.58 (s, 3H), 3.47 – 3.40 (m, 1H, H2), 3.35 (dd, $J = 9.5$, 2.8 Hz, 1H, H5), 3.26 (t, $J = 9.1$ Hz, 1H, H4), 2.55 – 2.33 (m, 2H, H7), 2.18 (ddt, $J = 13.9$, 8.0, 2.8 Hz, 1H, H6a), 1.81 – 1.61 (m, 1H, H6b).

$^{13}$C NMR (101 MHz, chloroform-$_d$) δ 138.49, 138.46, 137.8, 128.7, 128.53, 128.50, 128.25, 128.18, 128.0, 127.83, 127.82, 119.3, 104.9 (C1), 84.6 (C3), 82.5 (C2), 80.8 (C4), 75.9, 75.2, 74.9, 72.8 (C5), 57.3, 27.6 (C6), 13.5 (C7). Note: Some aromatic carbon signals overlap, causing the apparent loss of signals in the aromatic region. HRMS (ESI+) Calcd. for C$_{30}$H$_{33}$NO$_5$Na ([M + Na]$^+$): 510.2251, found: 510.2245.

12b:

$^1$H NMR (400 MHz, chloroform-$_d$) δ 7.43 – 7.18 (m, 15H), 4.76 – 4.66 (m, 4H, hidden H1), 4.64 – 4.52 (m, 2H), 4.42 (d, $J = 11.9$ Hz, 1H), 4.07 (dt, $J = 10.5$, 3.4 Hz, 1H, H5), 3.75 (t, $J = 5.2$ Hz, 1H, H3), 3.52 (dd, $J = 5.8$, 3.5 Hz, 1H, H2), 3.46 (s, 3H), 3.43 (dd, $J = 4.7$, 3.3 Hz, 1H, H4), 2.52 – 2.33 (m, 2H, H7), 2.19 (dddd, $J = 14.1$, 10.4, 7.2, 5.6 Hz, 1H, H6a), 1.76 (ddt, $J = 14.2$, 8.1, 3.5 Hz, 1H, H6b). $^{13}$C NMR (101 MHz, chloroform-$_d$) δ 138.1, 138.0, 137.8, 128.52, 128.50, 128.46, 128.2, 128.04, 128.01, 128.0, 127.91, 127.85, 119.5, 101.4 (C1), 77.2 (C2), 76.5 (C4), 75.7 (C3), 73.3, 73.2, 72.6, 67.2 (C5), 55.9, 25.7 (C6), 13.7 (C7). HRMS (ESI+) Calcd. for C$_{30}$H$_{33}$NO$_5$Na ([M + Na]$^+$): 510.2251, found: 510.2249.
3-((2R,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-methoxypentahydro-2H-pyran-2-yl)propanenitrile (13a) and 3-((2S,3R,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-methoxypentahydro-2H-pyran-2-yl)propanenitrile (13b):

Following general procedure A, a 4 ml vial was charged with 34 (203 mg, 0.317 mmol, 1 eq), Ru(bpy)₃Cl₂.6H₂O (6.5 mg, 8.7 μmol, 0.027 eq), Hantzsch ester (91.1 mg, 0.360 mmol, 1.1 eq), and 7:3 v/v water/THF mixture (1 ml). After purging with nitrogen, acrylonitrile (25 μL, 0.38 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with water (10 ml), then brine (10 ml). The organic layer was dried over MgSO₄ and concentrated. The product was then coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (linear gradient: 5% to 15% EtOAc in 20 min, with 13a and 13b both started to elute at 10% EtOAc) to afford 13a and 13b mixture (116.0 mg, adjusted for 6 mg phthalimide, 75% yield) as hard wax.

Data of the mixture:

**¹H NMR** (400 MHz, chloroform-d) δ 7.41 – 7.27 (m, 22H), 7.09 (dd, J = 6.6, 3.0 Hz, 1H), 5.03 – 4.70 (m, 5H), 4.69 (d, J = 1.8 Hz, 1H), 4.66 – 4.53 (m, 4.4H), 4.37 (d, J = 12.0 Hz, 1H), 3.89 – 3.79 (m, 1H), 3.90 (dd, J = 8.7, 3.0 Hz, 1H), 3.67 – 3.66 (m, 1H), 3.64 (dd, J = 9.4, 2.7 Hz, 0.7H), 3.59 – 3.54 (m, 4H), 3.34 (s, 3H), 3.18 (dd, J = 3.7, 1.4 Hz, 0.6H), 2.56 – 2.41 (m, 2H), 2.41 – 2.37 (m, 1H), 2.22 (ddt, J = 13.6, 8.2, 2.7 Hz, 1H), 2.17 – 2.09 (m, 0.5H), 1.88 – 1.76 (m, 1H), 1.58 (ddt, J = 13.6, 8.0, 3.6 Hz, 0.5H). **¹³C NMR** (101 MHz, chloroform-d) δ 138.8, 138.4, 138.32, 138.29, 138.21, 137.4, 128.53, 128.49, 128.48, 128.4, 128.3, 128.2, 128.14, 128.11, 128.03, 127.98, 127.94, 127.90, 127.8, 127.73, 127.72, 127.66, 119.63, 119.61, 102.2, 99.3, 80.3, 77.9, 76.3, 76.2, 75.2, 74.6, 74.5, 73.7, 73.6, 73.1, 72.2, 72.2, 70.7, 69.5, 56.7, 55.1, 27.7, 26.5, 13.8, 13.4. **HRMS (ESI⁺)** Calcd. for C₃₀H₃₃NO₅Na ([M + Na⁺]): 510.2251, found: 510.2237.

Diagnostic peaks for 13a:

**¹H NMR** (400 MHz, chloroform-d) δ 4.69 (d, J = 1.8 Hz, 1H, H1), 3.90 (dd, J = 8.7, 3.0 Hz, 1H, H3), 3.81 (t, J = 2.7 Hz, 1H, H2), 3.73 – 3.66 (m, 1H, H4), 3.64 (dd, J = 9.4, 2.7 Hz, 1H, H5), 3.34 (s, 3H), 2.56 – 2.41 (m, 2H, H7), 2.22 (ddt, J = 13.6, 8.2, 2.7 Hz, 1H, H6a), 1.88 – 1.76 (m, 1H, H6b). **¹³C NMR** (101 MHz, chloroform-d) δ 99.3 (C1), 80.3 (C3), 77.9 (C4), 75.2, 74.6 (C2), 73.1, 72.2, 69.5 (C5), 55.1, 27.7 (C6), 13.4 (C7).

Diagnostic peaks for 13b:

**¹H NMR** (400 MHz, chloroform-d) δ 4.77 (s, 1H, H1), 3.97 – 3.92 (m, 1H, H5), 3.81 (m, 1H, H3 overlapped with benzyl peaks), 3.59 – 3.54 (m, 4H, H2 and methoxy), 3.18 (dd, J = 3.7, 1.4 Hz, 1H, H4), 2.41 – 2.37 (m, 2H, H7), 2.17 – 2.09 (m, 1H, H6a), 1.58 (ddt, J = 14.0, 8.0, 3.6 Hz, 1H, H6b). **¹³C NMR** (101 MHz, chloroform-d) δ 102.2 (C1), 76.3 (C2), 76.2 (C4), 74.5 (C3), 73.7, 73.6, 72.3, 70.7 (C5), 56.7, 26.5 (C6), 13.8 (C7).
Deduction:

1. $^1$H NMR and $^{13}$C NMR suggest that there is a mixture of exactly 2 products. From 1H integration, the ratio of major : minor is 1.7:1
2. H6a/b could be located via meHSQC, since the chemical shifts are < 3.0 ppm and thus cannot be alcohols or ethers. Furthermore, chemical shifts difference between H6a and H6b are the greatest in the molecule due to the proximity at with stereogenic C5. meHSQC confirms that one single CH$_2$ carbon is linked to both H6a and H6b.
3. From the COSY, we can locate both H5s of the major and the minor diastereomers.
4. From the COSY, we can locate the C4 of the minor diastereomers, which is isolated. The coupling constant $J = 3.7$ Hz and 1.4 Hz, which are both < 8 Hz. This is a strong indication that this isomer is in a distorted chair with no H$_{ax}$-H$_{ax}$ coupling. This peak therefore cannot be the C4 of a mannoside, which has strong H$_{ax}$-H$_{ax}$ couplings.
Procedures for photoalkylation of BDA-glycosides

3-((2S,3S,4aR,5S,7S,8S,8aR)-8-hydroxy-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxin-5-yl)propanenitrile (18)

Following general procedure A, a 4 ml vial was charged with 17 (146 mg, 0.313 mmol, 1.0 eq), Ru(bpy)$_3$Cl$_2$ (6.3 mg, 8.4 μmol, 0.026 eq), Hantzsch ester (86.1 mg, 0.340 mmol, 1.1 eq), 7:3 water/THF mixture (1 ml). After purging with nitrogen, acrylonitrile (25 μL, 0.38 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with brine (10 ml). The water layer was back extracted with EtOAc (20 ml). The combined organic layer was dried over MgSO$_4$ and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/pentane (linear gradient: 0% to 50% EtOAc in 13 CV, with 18 started to elute at the 13th CV) to afford product 18 (80.1 mg, 77% yield) as a hard wax, which is a 11:1 mixture of diastereomers. The D:L ratio corresponds to the integration of the peak at 3.45 ppm and the peak at 3.37 ppm. These signals arise from the anomeric –OC$_3$H$_3$ on the L and the D isomer, respectively. Only the spectral data of the major diastereomer is reported here.

$^1$H NMR (400 MHz, chloroform-d) δ 4.68 (d, $J = 1.5$ Hz, 1H, H1), 4.40 (dd, $J = 10.9$, 6.5 Hz, 1H, H4), 4.05 – 3.96 (m, 2H, H3 and H5), 3.92 (dd, $J = 3.3$, 1.5 Hz, 1H, H2), 3.45 (s, 3H), 3.25 (s, 3H), 3.22 (s, 3H), 2.66 – 2.44 (m, 2H, H7), 2.28 – 2.07 (m, 2H, H6), 1.29 (s, 3H), 1.24 (s, 3H). Note: Signal for the OH is not observed. $^{13}$C NMR (101 MHz, chloroform-d) δ 119.9, 103.5 (C1), 100.3, 99.9, 74.1 (C3/5), 70.2 (C2), 63.7 (C3/4/5), 56.9, 48.2, 48.1, 26.8 (C6), 17.8, 17.8, 14.8 (C7). HRMS (ESI+) Calcd. for C$_{15}$H$_{25}$NO$_7$Na ([M + Na$^+$]: 354.1523, found: 354.1522.

Alternative procedure:

Following general procedure B, a 4 ml vial was charged with 17 (141 mg, 0.302 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (8.3 mg, 9.6 μmol, 0.030 eq), Hantzsch ester (115 mg, 0.45 mmol, 1.5 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.38 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was directly coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 50% EtOAc in 13 CV, with 18 started to elute at the 13th CV) to afford product 18 (80.8 mg, 81% yield) as a hard wax, which is a 11:1 mixture of diastereomers. Double addition of acrylonitrile was also found in this mixture (9.6 mg, 8% yield) and the spectral data are reported below.

2-((2S,3S,4aR,5S,7S,8S,8aR)-8-hydroxy-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxin-5-yl)methyl)pentanedinitrile (18s)
**1H NMR** (400 MHz, chloroform-\(d\)) \(\delta\) 4.70 (d, \(J = 1.5\) Hz, 1H, H1), 4.44 (dd, \(J = 10.9, 6.5\) Hz, 1H, H4), 4.13 (q, \(J = 6.9\) Hz, 1H, H5), 4.01 (dd, \(J = 10.9, 3.1\) Hz, 1H, H3), 3.94 (dd, \(J = 3.1, 1.5\) Hz, 1H, H2), 3.47 (s, 3H), 3.26 (s, 3H), 3.24 (s, 3H), 3.17 – 3.10 (m, 1H, H7), 2.72 – 2.49 (m, 2H, H9), 2.26 – 2.12 (m, 2H, H6), 2.05 (ddt, \(J = 13.2, 8.2, 5.3\) Hz, 1H, H8a), 1.93 (dddd, \(J = 13.7, 9.8, 7.8, 5.6\) Hz, 1H, H8b), 1.30 (s, 3H), 1.26 (s, 3H). Note: Signal for the OH is not observed.

**13C NMR** (101 MHz, chloroform-\(d\)) \(\delta\) 120.6, 117.9, 103.3 (C1), 100.2, 99.9, 71.9 (C5), 70.0 (C2), 63.8 (C4), 63.5 (C3), 56.8, 48.2, 48.1, 33.3 (C6), 28.2 (C7), 28.0 (C8), 17.7, 17.6, 15.3 (C9).

**HRMS (ESI+)** Calcd. for C\(_{18}\)H\(_{28}\)N\(_2\)O\(_7\)Na ([M + Na]+): 407.1789, found: 407.1792.

3-((2S,3S,4S,5S,6S)-3,4,5-trihydroxy-6-methoxytetrahydro-2H-pyran-2-yl)propanenitrile (25)

A 20 ml glass vial was charged with 18 (69.6 mg, 0.210 mmol, 1.0 eq). A 9:1 v/v mixture of TFA/water (1 ml) was added and the solution was stirred for 2 min, at which TLC showed complete consumption of the starting material, and a strong odor of 2,3-butanadiol leaked from the vial. The solution was concentrated and co-evaporated with toluene (3x) to remove residual TFA. The crude mixture was purified by silica gel column chromatography in pure EtOAc to afford 25 (44.5 mg, 98% yield) as hard wax. Multiple peaks of the minor diastereomer (D-) are visible on 1H-NMR. The diastereomeric ratio was confirmed to be 11:1, which corresponds to the diastereomeric ratio obtained in 18.

**Major: 1H NMR** (400 MHz, chloroform-\(d\)) \(\delta\) 4.49 (d, \(J = 8.2\) Hz, 1H, H1), 3.95 (t, \(J = 3.4\) Hz, 1H, H3 overlap), 3.92 (dd, \(J = 3.7, 1.3\) Hz, 1H, H5 overlap), 3.57 (dd, \(J = 3.8, 3.4\) Hz, 1H, H2), 3.54 (dd, \(J = 3.8, 1.2\) Hz, 1H, H4), 3.51 (s, 3H), 2.59 (dd, \(J = 7.8, 6.5\) Hz, 2H, H7), 2.08 (ddt, \(J = 13.9, 10.2, 6.5\) Hz, 1H, H6a), 1.78 (dtb, \(J = 14.1, 7.9, 3.7\) Hz, 1H, H6b). Note: Signal for the OH is not observed.

**13C NMR** (101 MHz, chloroform-\(d\)) \(\delta\) 121.0, 103.4 (C1), 73.2 (C3), 72.6 (C4/5), 69.6 (C2), 57.0, 27.5 (C6), 14.4 (C7). **HRMS (ESI+)** Calcd. for C\(_{9}\)H\(_{15}\)NO\(_5\)Na ([M + Na]+): 240.0842, found: 240.0843.

**Minor: 1H NMR** (400 MHz, chloroform-\(d\)) \(\delta\) 4.61 (d, \(J = 1.7\) Hz, 1H, H1), 3.78 (dd, \(J = 3.5, 1.7\) Hz, 1H, H2), 3.63 (dd, \(J = 9.3, 3.4\) Hz, 1H, H3), 3.43 (t, \(J = 9.4\) Hz, 1H, H4), 2.21 (ddt, \(J = 13.9, 8.1, 2.6\) Hz, 1H, H6a). No full characterization is possible for the minor product in the mixture.

**Optimization of the synthesis of 18**

General procedure B was followed, and the reactions were carried out at 0.3 mmol scale (see the reported synthesis of 18 above.) The equivalence of all components and the resulting isolated yield were shown below.

| NHP-ester (eq.) | Ru(bpy)\(_3\)(PF\(_6\))\(_2\) (eq.) | Acrylonitrile (eq.) | Hantzsch ester (eq.) | Yield (%) |
|-----------------|-----------------------------|-----------------|-----------------|----------|
| 1.0             | 0.3                         | 1.4             | 1.1             | 78       |
|                 |                             | 1.2             | 1.5             | 81       |
Since all of the yields were comparable, the experiment with the least amount of material was set as the benchmark.

methyl 3-((2S,3S,4aR,5S,7S,8S,8aR)-8-hydroxy-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxin-5-yl)propanoate (19)

Following general procedure B, a 4 ml vial was charged with 17 (139 mg, 0.297 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (7.3 mg, 8.5 μmol, 0.029 eq), Hantzsch ester (83.1 mg, 0.328 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, methyl acrylate (32 μL, 0.36 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 25% EtOAc in 20 min, with 19 started to elute at 23% EtOAc) to afford product 19 (80.8 mg, 74% yield, adjusted for 1.8 mg phthali mum) as hard wax, which is a 5.5:1 mixture of diastereomers. Only the spectral data of the major diastereomer are reported here.

$^1$H NMR (400 MHz, chloroform-d) δ 4.67 (d, $J = 1.4$ Hz, 1H, H1), 4.35 (dd, $J = 10.9$, 6.6 Hz, 1H, H4), 4.02 (dd, $J = 10.9$, 3.1 Hz, 1H, H3), 3.96 – 3.86 (m, 2H, H2 and H5), 3.66 (s, 3H), 3.44 (s, 3H), 3.23 (s, 3H), 2.58 (ddd, $J = 15.7$, 9.5, 6.1 Hz, 1H, H6a), 2.42 (ddd, $J = 16.0$, 9.4, 6.9 Hz, 1H, H6b), 2.11 (ddt, $J = 11.2$, 9.1, 4.2 Hz, 2H, H7), 1.28 (s, 3H), 1.23 (s, 3H). Note: Signal for the OH is not observed. $^{13}$C NMR (101 MHz, chloroform-d) δ 174.2, 103.4 (C1), 100.2, 99.8, 75.3 (C2/5), 70.4 (C2/5), 63.9 (C3 and C4 overlap), 56.7, 51.6, 48.1, 47.9, 31.8 (C6), 25.7 (C7), 17.8, 17.8. HRMS (ESI+) Calcd. for C$_{16}$H$_{28}$O$_9$Na ([M + Na]$^+$): 387.1626, found: 387.1625.

3-((2S,3S,4aR,5S,7R,8S,8aR)-8-hydroxy-2,3-dimethoxy-2,3-dimethyl-7-(p-tolylthio)hexahydro-5H-pyrano[3,4-b][1,4]dioxin-5-yl)propanenitrile (20)

Following general procedure B, a 4 ml vial was charged with 46 (170 mg, 0.304 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (7.7 mg, 9.0 μmol, 0.031 eq), Hantzsch ester (84.0 mg, 0.332 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.37 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was coated onto celite. Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 20% EtOAc in 15 CV, then isocratic elution at 20% EtOAc, with 20 started to elute at the 17th CV). The pure fractions were combined to afford L-configured product 20 (62.1 mg, 48% yield) as hard wax. The D-configured isomer could not be isolated in a pure form. The diastereomeric ratio was determined by UPLC-MS (vide infra) to be 4.7 : 1 (L to D ratio).
**1H NMR** (400 MHz, chloroform-\(d\)) \(\delta\) 7.33 (dd, \(J = 8.2, 1.6\) Hz, 2H), 7.14 (d, \(J = 7.4\) Hz, 2H), 5.38 (d, \(J = 2.0\) Hz, 1H, H1), 4.43 (dd, \(J = 10.9, 7.0\) Hz, 1H, H4), 4.20 (t, \(J = 1.9\) Hz, 1H, H2), 4.18 – 4.11 (m, 1H, H5), 4.05 (dd, \(J = 10.9, 2.2\) Hz, 1H, H3), 3.29 (s, 3H), 3.22 (s, 3H), 2.84 (s, 1H, OH), 2.57 – 2.33 (m, 3H, H6a and H7), 2.33 (s, 3H), 2.22 – 2.05 (m, 1H, H6b), 1.32 (s, 3H), 1.26 (s, 3H).

**HRMS (ESI+)** Calcd. for \(\text{C}_{21}\text{H}_{29}\text{NO}_{6}\text{Na}^+\): 446.1608, found: 446.1608.

Following general procedure B, a 4 ml vial was charged with 17 (141 mg, 0.301 mmol, 1.0 eq), Ru(bpy)\(_3\)(PF\(_6\))\(_2\) (8.0 mg, 9.3 \(\mu\)mol, 0.031 eq), Hantzsch ester (84.2 mg, 0.332 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, diethyl vinylphosphonate (55 \(\mu\)L, 0.36 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with acetone/heptane, (linear gradient: 0% to 50% acetone in 15 CV, then isocratic elution at 50% acetone, with 21 started to elute at the 16\(^{th}\) CV). The pure fractions were combined to afford product 21 (78.3 mg, 59% yield), contaminated with a small amount of a coeluting phosphorus containing compound, as a hard wax, which is a 4:1 mixture of diastereomers. Only the spectral data of the major diastereomer are reported here.

**13C NMR** (101 MHz, chloroform-\(d\)) \(\delta\) 137.5, 130.3, 130.2, 119.8, 100.3, 99.9, 87.0 (C1), 75.2 (C5), 71.6 (C2), 64.6 (C3), 48.2, 48.1, 25.7 (C6), 17.8, 17.7, 14.1 (C7).

Following general procedure A, a 4 ml vial was charged with 37 (139 mg, 0.307 mmol, 1.0 eq), Ru(bpy)\(_3\)Cl\(_2\) (6.1 mg, 8.2 \(\mu\)mol, 0.031 eq), Hantzsch ester (87.1 mg, 0.344 mmol, 1.1 eq), and 7:3 water/THF mixture (1 ml). After purging with nitrogen, acrylonitrile (24 \(\mu\)L, 0.37 mmol, 1.2 eq) was
added. After irradiation for 15 h, the mixture was transferred to a separatory funnel, diluted with EtOAc (20 ml) and washed with brine (10 ml). The organic layer was dried over MgSO$_4$ and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with Et$_2$O/heptane (linear gradient: 0% to 40% EtOAc in 15 CV, with 22 started to elute at 35% EtOAc) to afford product 22 (81.9 mg, 85% yield, adjusted for 5.8 mg phthali-mide) as hard wax, which is a 5.5:1 mixture of diastereomers. Only the major diastereomer is reported here.

Alternative procedure

Following general procedure B, a 4 ml vial was charged with 37 (137 mg, 0.304 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (8.4 mg, 9.8 μmol, 0.029 eq), Hantzsch ester (118 mg, 0.465 mmol, 1.5 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.37 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was concentrated in vacuo and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 40% EtOAc in 15 CV, with 22 started to elute at 35% EtOAc) to afford product 22 (85.6 mg, 89% yield, adjusted for 4.4 mg phthali-mide) as hard wax, which is a 5.5:1 mixture of diastereomers. Only the spectral data of the major diastereomer is reported here.

OR

Following general procedure B, a 4 ml vial was charged with 26 (181 mg, 0.307 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (8.4 mg, 9.7 μmol, 0.032 eq), Hantzsch ester (85.2 mg, 0.336 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.37 mmol, 1.2 eq) was added. After irradiation for 15 h, the reaction mixture was filtered through a small pad of celite. the filtrate was concentrated in vacuo and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 40% EtOAc in 15 CV, with 22 started to elute at 35% EtOAc) to afford product 22 (85.6 mg, 78% yield) as hard wax, which is a 5.5:1 mixture of diastereomers. Only the spectral data of the major diastereomer is reported here.

$^1$H NMR (400 MHz, chloroform-d) δ 4.80 (dd, $J = 4.3, 1.2$ Hz, 1H, H1), 4.09 (dddd, $J = 12.1, 10.4, 4.7$ Hz, 1H, H3), 3.95 (dddd, $J = 9.2, 6.3, 4.9$ Hz, 1H, H5), 3.85 (dd, $J = 10.3, 6.3$ Hz, 1H, H4), 3.40 (s, 3H), 3.25 (s, 3H), 3.24 (s, 3H), 2.65 – 2.44 (m, 2H, H7), 2.29 – 2.08 (m, 2H, H6), 2.01 (dddd, $J = 12.7, 4.7, 1.2$ Hz, 1H, H2eq), 1.80 (td, $J = 12.5, 4.3$ Hz, 1H, H2ax), 1.28 (s, 3H), 1.26 (s, 3H).

$^{13}$C NMR (101 MHz, chloroform-d) δ 119.9, 101.0 (C1), 100.0, 99.7, 73.9 (C5), 70.2 (C4), 60.4 (C3), 56.5, 48.2, 48.1, 35.4 (C2), 26.8 (C6), 18.0, 17.8, 14.9 (C7). HRMS (ESI+) Calcd. for C$_{15}$H$_{28}$N$_3$O$_6$Na ([M + Na$^+$]): 338.1574, found: 338.1575.

3-((2R,3R,4aR,5S,7S,8S,8aS)-8-hydroxy-2,3,5-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxin-7-yl)propanenitrile (23)
Following general procedure B, a 4 ml vial was charged with 44 (143 mg, 0.305 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (8.0 mg, 9.3 μmol, 0.03 eq), Hantzsch ester (84.0 mg, 0.332 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.37 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 50% EtOAc in 9 CV, then isocratic elution at 50% EtOAc, with 23 started to elute at the 10th CV) to afford product 23 (82.7 mg, 82% yield) as hard wax.

$^1$H NMR (400 MHz, Chloroform-d) δ 4.78 (d, $J = 3.9$ Hz, 1H, H1), 4.24 (dd, $J = 10.8, 3.9$ Hz, 1H, H2), 4.12 (dd, $J = 10.8, 3.1$ Hz, 1H, H3), 3.98 (dd, $J = 10.2, 4.9$ Hz, 1H, H5), 3.90 (d, $J = 3.1$ Hz, 1H, H4), 3.48 (s, 3H), 3.27 (s, 3H), 3.24 (s, 3H), 2.74 (s, 1H, OH), 2.58 (dd, $J = 17.0, 8.3, 5.4$ Hz, 1H, H7a), 2.46 (dt, $J = 16.7, 8.0$ Hz, 1H, H7b), 2.34 – 2.19 (m, 1H, H6a), 1.87 (dtd, $J = 13.4, 8.0, 4.9$ Hz, 1H, H6b), 1.32 (s, 3H), 1.31 (s, 3H). $^{13}$C NMR (101 MHz, chloroform-d) δ 119.3, 100.9 (C1), 100.4, 100.2, 77.5 (C5), 70.7 (C4), 64.6 (C2), 63.3 (C3), 57.2, 48.2, 48.1, 30.1 (C6), 17.8, 17.8, 14.9 (C7). HRMS (ESI+) Calcd. for C$_{15}$H$_{25}$NO$_7$Na ([M + Na]$^+$): 354.1523, found: 354.1522.

N-((2S,3S,4aR,5S,7S,8R,8aR)-5-(2-cyanoethyl)-2,3,7-trimethoxy-2,3-dimethylhexahydro-5H-pyrano[3,4-b][1,4]dioxin-8-yl)acetamide (24)

Following general procedure B, a 4 ml vial was charged with 41 (153 mg, 0.301 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (7.8 mg, 9.1 μmol, 0.03 eq), Hantzsch ester (85.2 mg, 0.337 mmol, 1.1 eq), and dry THF (1 ml). After purging with nitrogen, acrylonitrile (24 μL, 0.36 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with acetone/toluene (linear gradient: 0% to 20% acetone in 5 CV, then isocratic elution at 20% acetone, with 23 started to elute at the 10th CV) to afford product 24 (84.7 mg, 76% yield) as hard wax, which is a 5.5:1 mixture of diastereomers. Only the spectral data of the major diastereomer is reported here.

$^1$H NMR (400 MHz, chloroform-d) δ 5.46 (d, $J = 8.7$ Hz, 1H, NH), 4.78 (d, $J = 4.0$ Hz, 1H, H1), 4.21 (ddd, $J = 12.2, 8.6, 4.0$ Hz, 1H, H2), 4.00 (dd, $J = 10.0, 6.4$ Hz, 1H, H4), 3.94 (dt, $J = 9.0, 5.5$ Hz, 1H, H5), 3.83 (t, $J = 10.6$ Hz, 1H, H3), 3.45 (s, 3H), 3.23 (s, 3H), 3.22 (s, 3H), 2.66 – 2.41 (m, 2H, H7), 2.29 – 2.18 (m, 1H, H6a), 2.18 – 2.09 (m, 1H, H6b), 2.01 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). $^{13}$C NMR (101 MHz, chloroform-d) δ 170.1, 119.8, 100.9 (C1), 99.9, 99.6, 73.6 (C5), 68.5 (C4), 63.4 (C3), 57.4, 51.5 (C2), 48.0, 48.0, 27.0 (C6), 23.5, 17.9, 17.7, 14.8 (C7). HRMS (ESI+) Calcd. for C$_{17}$H$_{28}$N$_2$O$_7$Na ([M + Na]$^+$): 395.1789, found: 395.1789.
Procedures for synthesis of methyl-L-guloside

Following general procedure C, a 4 ml vial was charged with 17 (187 mg, 0.399 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (8.0 mg, 11 μmol, 0.028 eq), Hantzsch ester (114 mg, 0.448 mmol, 1.1 eq), and 7:3 THF/PBS buffer (pH=7.4, 0.1 M) (1.3 ml). After purging with nitrogen, ethyl cis-3-bromoacrylate (0.24 ml, 2.0 mmol, 5.0 eq) was added. After irradiation for 15 h, the mixture was diluted with EtOAc (20 ml) and water (15 ml) and transferred to a separatory funnel. The layers were separated, and the organic layer was washed with saturated sodium bicarbonate solution (1 ml) and brine (5 ml). Subsequent purification was performed by automated flash chromatography on a 25 g silica cartridge with EtOAc/pentane (isocratic elution at 20% EtOAc for 10 CV, then linear gradient to 55% EtOAc for 10 CV, with 28 started to elute at 37% EtOAc) to afford product 28 as hard wax. Product 28 was obtained as a mixture of the D- and L-diastereomers, as well as E and Z double bond isomers. The E and Z diastereomers were partially separable. Analytical samples containing majorly the E-configured isomer (42.2 mg, 28%) and the Z-configured isomer (33.5 mg, 22%), as well as a mixed fraction containing the E- and Z- (29.6 mg, 20%) were obtained. The combined yield of all the isolated fractions is 70%. Spectral data of the analytical samples are reported below.

**28,E:**

$^1$H NMR (400 MHz, chloroform-$d$) δ 7.19 (dd, $J = 15.7, 8.3$ Hz, 1H, H6), 6.13 (d, $J = 15.7, 1.0$ Hz, 1H, H7), 4.71 (d, $J = 1.4$ Hz, 1H, H1), 4.48 (dd, $J = 8.3, 6.4$ Hz, 1H, H5), 4.40 (dd, $J = 10.8, 6.3$ Hz, 1H, H4), 4.25 – 4.14 (m, 2H, Et), 4.13 (dd, $J = 10.9, 3.3$ Hz, 1H, H3), 3.95 (dd, $J = 3.2, 1.5$ Hz, 1H, H2), 3.33 (s, 3H), 3.25 (s, 3H), 3.22 (s, 3H), 1.32 – 1.26 (m, 6H), 1.23 (s, 3H). Note: Signal for the OH is not observed. $^{13}$C NMR (101 MHz, chloroform-$d$) δ 166.4, 144.4 (C6), 125.3 (C7), 102.5 (C1), 100.3, 100.1, 73.8 (C5), 70.1 (C2), 69.7, 64.1 (C3), 63.9 (C4), 60.5, 55.7, 48.2, 48.0, 17.8, 17.8, 14.4. HRMS (ESI+) Calcd. for C$_{17}$H$_{25}$O$_9$Na ([M + Na]$^+$): 399.1625, found: 399.1623.

**28,Z:**

$^1$H NMR (400 MHz, chloroform-$d$) δ 6.63 (dd, $J = 11.7, 9.4$ Hz, 1H, H6), 5.95 (dd, $J = 11.7, 1.2$ Hz, 1H, H7), 5.66 (dd, $J = 9.2, 6.9$ Hz, 1H, H5), 4.72 (d, $J = 1.5$ Hz, 1H, H1), 4.41 (dd, $J = 10.9, 6.5$ Hz, 1H, H4), 4.19 (q, $J = 7.2$ Hz, 2H), 4.13 (dd, $J = 10.8, 3.2$ Hz, 1H, H3), 3.95 (dd, $J = 3.2, 1.5$ Hz, 1H, H2), 3.29 (s, 3H), 3.26 (s, 3H), 3.23 (s, 3H), 1.32 – 1.21 (m, 6H, integral off due to overlapping minor diastereomer and grease), 1.22 (s, 3H). Note: Signal for the OH is not observed. $^{13}$C NMR (101 MHz, chloroform-$d$) δ 165.7, 143.9 (C6), 123.7 (C7), 102.4 (C1), 100.5, 100.0, 70.1 (C2), 68.0 (C5), 63.9 (C3), 63.7 (C4), 60.3, 55.8, 48.2, 48.0, 17.8, 17.8, 14.4. HRMS (ESI+) Calcd. for C$_{17}$H$_{25}$O$_9$Na ([M + Na]$^+$): 399.1626, found: 399.1626.
A 20 ml glass vial was charged with the 28 (80.3 mg, 0.213 mmol, 1.0 eq). A 9:1 mixture of TFA/water (1 ml) was added and the solution was stirred for 2 min, at which TLC showed complete consumption of starting material, and a strong odor of 2,3-butadione leaked from the vial. The solution was concentrated and co-evaporated with toluene (3x) to remove residual TFA. The entire crude product was carried onto the next step without further purification.

The crude product from the previous step (0.213 mmol, 1 eq) was dissolved in DCM (5 ml) and added to a 20 ml glass vial equipped with a magnetic stir bar. The solution was cooled to -78 °C with an acetone/liquid nitrogen bath. A steady stream of oxygen/ozone (amount of ozone delivered: 3 g / h) was bubbled into the solution while stirring. After 5 min, the solution turned cloudy, and TLC showed complete consumption of the starting material. To ensure that residual starting material was entirely consumed, another stream of oxygen/ozone was delivered for another 5 min, after which a stream of nitrogen was delivered for 5 min. Dimethylsulfide (78 μL, 1.1 mmol, 5.0 eq) was subsequently added and the reaction mixtures was allowed to warm to room temperature over 1 h. A freshly prepared solution of sodium borohydride (66 mg, 1.7 mmol, 8.2 eq) in MeOH (2 ml) was added. The solution turned clear after 1 min, and the solution was stirred overnight. The solution was subsequently concentrated in vacuo and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g diol-coated silica cartridge with MeOH/DCM (linear gradient: 0% to 100% MeOH in 30 min, with 29 started to elute at 40% MeOH) to afford product 29 (24.3 mg, 59% yield over 2 steps) as a hard wax, which is a 9:1 mixture of diastereomers. Only the spectral data of the major diastereomer are reported here.

\[ ^1H \text{NMR} (400 \text{MHz}, \text{methanol-}d_4) \delta 4.50 (d, J = 8.1 \text{ Hz}, 1H, H1), 3.94 (t, J = 3.5 \text{ Hz}, 1H, H3), 3.92 - 3.86 (m, 1H, H4), 3.78 - 3.70 (m, 3H, H5 and H6), 3.60 (dd, J = 8.1, 3.4 \text{ Hz}, 1H, H2), 3.52 (s, 3H).
\]

\[ ^13C \text{NMR} (101 \text{MHz}, \text{methanol-}d_4) \delta 102.0 (C1), 73.6 (C4), 71.7 (C3), 69.8 (C5), 68.3 (C2), 61.2 (C6), 55.6.
\]

\[ ^1H \text{NMR} (400 \text{MHz}, \text{deuterium oxide}) \delta 4.47 (d, J = 8.4 \text{ Hz}, 1H, H1), 3.92 (t, J = 3.6 \text{ Hz}, 1H, H3), 3.85 (ddd, J = 7.4, 5.0, 1.3 \text{ Hz}, 1H, H5), 3.69 - 3.66 (m, 1H, H4), 3.63 (dd, J = 6.1, 5.1 \text{ Hz}, 2H, H6), 3.51 (dd, J = 8.4, 3.5 \text{ Hz}, 1H, H2), 3.43 (s, 3H).
\]

\[ ^13C \text{NMR} (101 \text{MHz}, \text{deuterium oxide}) \delta 102.6 (C1), 75.0 (C5), 72.2 (C3), 70.5 (C4), 69.2 (C2), 62.1 (C6), 58.1.
\]

HRMS (ESI+) Calcd. for C_{7}H_{14}O_{6}Na ([M + Na]^+): 217.0683, found: 217.0683.
An analytical sample of 29 was peracetylated to acquire the following spectrum. (29')

$^1$H NMR (600 MHz, chloroform-$d$) $\delta$ 5.33 (t, $J = 3.8$ Hz, 1H, H3), 4.93 (dd, $J = 8.1$, 3.4 Hz, 1H, H2), 4.91 (dd, $J = 4.1$, 1.6 Hz, 1H, H4), 4.63 (d, $J = 8.1$ Hz, 1H, H1), 4.17 (td, $J = 6.5$, 1.7 Hz, 1H, H5), 4.11 (dd, $J = 6.5$, 2.5 Hz, 2H, H6), 3.46 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H).

$^{13}$C NMR (151 MHz, chloroform-$d$) $\delta$ 170.5, 169.6, 169.5, 169.0, 99.4 (C1), 70.4 (C5), 68.4 (C2), 67.8 (C4), 67.6 (C3), 61.9 (C6), 56.7, 20.8, 20.7. Acyl signals are overlapping at $\sim$20 ppm.

HRMS (ESI+) Calcd. for C$_{15}$H$_{22}$O$_{10}$Na ([M + Na]$^+$): 385.1105, found: 385.1100.
Addition product with imine as somophile

The procedure of Wang et al. was used.\(^9\)

To a 4 ml vial equipped with a stir bar with septum, was added 26 (59.4 mg, 0.101 mmol, 1.0 eq), ethyl (E)-2-((4-fluorophenyl)imino)acetate (30.0 mg, 0.154 mmol, 1.5 eq), iPr\(_2\)NEt•HBF\(_4\) (21.9 mg, 0.101 mmol, 1.0 eq), and Hantzsch ester (38.9 mg, 0.154 mmol, 1.5 eq). The vial was evacuated and back-filled with nitrogen (three times). Then, degassed acetonitrile (2 mL, FPT 3 cycles) was added using a syringe under nitrogen. The solution was then stirred at room temperature under the irradiation of two 34 W Kessil Blue LEDs for 12 h using a fan to cool the tube. After completion of the reaction, solids were filtered off through a small pad of celite and the celite was rinsed with DCM. The combined filtrates were concentrated and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 40 g silica cartridge with Et\(_2\)O/heptane (linear gradient: 0% to 20% Et\(_2\)O in 13 CV, then isocratic elution at 20% Et\(_2\)O, with 27a starting to elute at 16\(^{th}\) CV and 27b right after) to afford diastereomers 27a and 27b (19.4 mg and 12.7 mg, 70% yield), with the second diastereomer moderately pure, as hard wax.

Alternative procedure:

To a 4 ml vial equipped with a stir bar with PIFA septum, was added 26 (117 mg, 0.198 mmol, 1.0 eq), Ru(bpy)\(_3\)(PF\(_6\))\(_2\) (5.5 mg, 11 μmol, 0.028 eq), ethyl (E)-2-((4-fluorophenyl)imino)acetate (49.1 mg, 0.252 mmol, 1.3 eq), iPr\(_2\)NEt•HBF\(_4\) (43.6 mg, 0.201 mmol, 1.0 eq), and Hantzsch ester (55.5 mg, 0.219 mmol, 1.1 eq). The vial was evacuated and back-filled with nitrogen (three times). Then, degassed acetonitrile (2 mL, FPT 3 cycles) was added using a syringe under nitrogen. The solution was then stirred at room temperature under the irradiation of two 34 W Kessil Blue LEDs for 12 h using a fan to cool the tube. After completion of the reaction, solids were filtered off through a small pad of celite and the celite was rinsed with DCM. The combined filtrates were concentrated and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 40 g silica cartridge with Et\(_2\)O/heptane (linear gradient: 0% to 20% Et\(_2\)O in 13 CV, then isocratic elution at 20% Et\(_2\)O, with 27a starting to elute at 16\(^{th}\) CV and 27b right after) to afford diastereomers 27a and 27b (26.6 mg and 22.9 mg, 55% yield), with the second diastereomer moderately pure, as hard wax.

Diastereomer 1:

\(^1\)H NMR (400 MHz, chloroform-\(d\)) \(\delta\) 6.94 – 6.73 (m, 2H), 6.63 (dt, \(J = 8.6, 2.8\) Hz, 2H), 4.82 (d, \(J = 3.4\) Hz, 1H, H1), 4.30 (d, \(J = 2.8\) Hz, 1H, H6), 4.28 – 4.18 (m, 2H, 2H, Et), 4.09 (ddd, \(J = 25.2, 10.1, 3.5\) Hz, 2H, H3 and H5), 3.81 (t, \(J = 9.7\) Hz, 1H, H4), 3.32 (s, 3H), 3.32 (s, 3H), 3.26 (s, 3H), 1.95 (dd, \(J = 12.7, 4.7\) Hz, 1H, H2eq), 1.74 (td, \(J = 12.5, 3.4\) Hz, 1H, H2ax), 1.32 (d, \(J = 1.2\) Hz, 3H), 1.30 (d, \(J = 1.1\) Hz, 3H), 1.26 (t, \(J = 7.1\) Hz, 3H). Note: Signal for the NH is not observed. \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 170.8, 157.6, 143.4, 115.8 (d, \(J = 22.4\) Hz), 114.9 (d, \(J = 7.6\) Hz), 100.2, 100.0, 98.9 (C1), 71.5 (C5), 69.6 (C4), 65.1 (C3), 61.6, 58.0 (C6), 55.0, 48.5, 48.2, 34.5 (C2), 18.1, 17.9, 14.5. \(^{19}\)F NMR (376 MHz, chloroform-\(d\)) \(\delta\) -127.01 (tt, \(J = 8.8, 4.4\) Hz). HRMS (ESI+) Calcd. for C\(_{22}\)H\(_{32}\)FNO\(_8\)Na ([M + Na\(^+\)]: 480.2004, found: 480.1994.
Diastereomer 2 (moderately pure):

1H NMR (400 MHz, chloroform-d) δ 6.98 – 6.72 (m, 2H), 6.56 (ddd, J = 8.9, 4.3, 1.4 Hz, 2H), 4.85 (d, J = 3.4 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H, H6), 4.34 – 4.26 (m, 1H, H5), 4.22 – 4.10 (m, 3H, H3 and Et), 3.85 (dd, J = 10.5, 9.2 Hz, 1H, H4), 3.29 (s, 3H), 3.24 (s, 3H), 2.98 (s, 3H), 2.01 (dd, J = 12.8, 5.0 Hz, 1H, H2eq), 1.81 (td, J = 12.6, 3.9 Hz, 1H, H2ax), 1.29 (s, 3H), 1.28 (s, 3H), 1.27 – 1.20 (m, 3H). Note: Signal for the NH is not observed. 13C NMR (101 MHz, chloroform-d) δ 172.2, 155.0, 143.5, 115.7 (d, J = 22.4 Hz), 114.5 (d, J = 7.4 Hz), 100.1, 99.9, 98.9 (C1), 70.6 (C5), 67.9 (C4), 64.8 (C3), 61.3, 55.2 (C6), 54.5, 48.1, 47.9, 34.6 (C2), 17.8, 17.8, 14.2. 19F NMR (376 MHz, chloroform-d) δ -127.07 (tt, J = 8.8, 4.4 Hz). HRMS (ESI+) Calcd. for C22H32FNO8Na ([M + Na]+): 480.2004, found: 480.1998.
Scaling up procedure for the synthesis of 18.

Following general procedure B, a 10 ml round bottom flask equipped with a stirring bar with a septum was charged with 17 (521 mg, 1.12 mmol, 1.0 eq), Ru(bpy)$_3$(PF$_6$)$_2$ (29.3 mg, 0.034 mmol, 0.031 eq), Hantzsch ester (312 mg, 1.23 mmol, 1.1 eq), and dry THF (4 ml). After purging with nitrogen, acrylonitrile (88 μL, 1.3 mmol, 1.2 eq) was added. After irradiation for 15 h, the mixture was concentrated in vacuo and coated onto celite. Subsequent purification was performed by automated flash chromatography on a 12 g silica cartridge with EtOAc/heptane (linear gradient: 0% to 50% EtOAc in 13 CV, with 18 started to elute at the 13$^{th}$ CV) to afford product 18 (297 mg, 80% yield) as hard wax, which is a 11:1 mixture of diastereomers. The analytical data were in full accord with those reported above.
Computational data

Density functional theory (DFT) calculations were carried out with the Amsterdam Density Functional (ADF) program. The functional BLYP in combination with TZ2P basis was employed for all the elements. The TZ2P basis set is a large uncontracted set of Slater-type orbitals (STOs) of triple-z quality and has been augmented with two sets of polarization functions on each atom that is, 2p and 3d on H, and 3d and 4f on C and O. The frozen core approximation was adopted for the core electrons: up to 1s for C and O. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each SCF cycle. Dispersion corrections were included employing the D3 scheme with the Becke–Johnson damping [D3(BJ)] developed by Grimme et al. Scalar relativistic effects were accounted for through the zeroth-order regular approximation (ZORA). This level of theory is referred to as ZORA-BLYP-D3(BJ)/TZ2P. All energies and geometries correspond to the neutral, doublet ground state with unrestricted spin. Frequency calculations were employed to confirm the nature of the stationary points. Each SCF cycle converges within $10^{-8}$ Hartree, and the final geometry converges with a maximum gradient of $10^{-5}$ Hartree/Å.

For the following structures, no imaginary frequencies were found, confirming that they are all local minimums on the potential energy surface.
BDA-mannosyl radical:

1. O  -0.917432 -1.747169  0.234151
2. C  0.860341 -0.281135  1.267979
3. C  -0.690305 -0.519559  0.973186
4. C  0.020206 -2.085513 -0.811969
5. C  1.447724 -1.968603 -0.303445
6. O  1.678258 -0.605499  0.121706
7. O  2.163361 -3.609917 -1.953599
8. O  1.162926 -1.162475  2.361695
9. C  1.174377  1.176926  1.601471
10. O -1.270304  0.613758  0.322537
11. C -1.509791 -0.674176  2.254407
12. H -0.107886 -1.433595 -1.681002
13. C -0.251845 -3.524810 -1.251979
14. C  2.406362 -2.377930 -1.369773
15. H  1.554944 -2.630566  0.572163
16. C  1.193315 -3.642267 -4.659577
17. C  0.785566 -3.920968 -2.321317
18. H  0.809414 -5.011103 -2.452113
19. H -1.246148 -3.589340 -1.717079
20. O -0.143993 -4.453243 -0.162082
21. H  3.466236 -2.149929 -1.299980
22. O  0.410961 -3.260743 -3.508797
23. H  0.739705 -3.137773 -5.515438
24. H  1.155519 -4.731655 -4.808499
25. H  2.236562 -3.326113 -4.547983
|   | Bond Energy       |
|---|------------------|
|   | -5070.43 kcal/mol|

|   |   |   |   |   |
|---|---|---|---|---|
| 26.H | -0.623383 | -4.047090 | 0.584503 |
| 27.C | 2.531520 | -1.161934 | 2.814773 |
| 28.C | -0.920661 | 0.921346 | -1.041860 |
| 29.H | 3.232162 | -1.194813 | 1.972205 |
| 30.H | 2.644144 | -2.065483 | 3.419165 |
| 31.H | 2.747824 | -0.283187 | 3.436224 |
| 32.H | 0.160254 | 0.884768 | -1.216839 |
| 33.H | -1.284997 | 1.938297 | -1.212910 |
| 34.H | -1.429459 | 0.241947 | -1.736712 |
| 35.H | -1.160053 | -1.531459 | 2.828504 |
| 36.H | -2.555503 | -0.813112 | 1.966562 |
| 37.H | -1.429223 | 0.227374 | 2.866966 |
| 38.H | 2.246117 | 1.285201 | 1.787399 |
| 39.H | 0.620926 | 1.484879 | 2.492216 |
| 40.H | 0.901035 | 1.832843 | 0.775084 |
BDA-galactosyl radical

Top view

Side view

1. C  -1.844599  1.233051  0.401876
2. C  -0.667767  3.327757  0.525189
3. O  -1.912578  2.660197  0.222083
4. C  -0.730603  0.632368  -0.442188
5. O   0.528046  1.249883  -0.115521
6. C   0.519117  2.674834  -0.291129
7. H  -1.671065  1.012134  1.465455
8. O  -0.315198  3.123043  1.897418
9. C  -0.903870  4.796340  0.176408
10. H -3.892195  2.951031  -1.316950
11. C -4.394396  2.010133  -1.567327
12. H -0.968251  0.807568  -1.498833
13. C  -0.663015  -0.886223  -0.21104
14. H  -5.308163  1.903958  -0.962667
15. H  -4.659737  1.998815  -2.627194
16. O  0.238711  3.022447  -1.656198
17. C  1.895151  3.150854  0.173577
18. C  -3.194042  0.624358  -0.011809
19. C  -2.033176  -1.464139  -0.353750
20. O  -3.139700  -0.805699  0.168298
21. O  -3.518360  0.883080  -1.365584
22. H  -4.001694  0.965961  0.649808
23. H  0.010280  -1.340617  -0.945629
24. O  -0.043537  -1.246472  1.072748
25. H  -2.184947  -2.538405  -0.370936
|      |       |       |       |
|------|-------|-------|-------|
| 26.H | -0.669280 | -1.021034 | 1.783821 |
| 27.C | -1.241950 | 3.641040 | 2.868406 |
| 28.C | 1.173273  | 2.523036 | -2.630425 |
| 29.H | -0.042593 | 5.398598 | 0.478694 |
| 30.H | -1.794229 | 5.161550 | 0.695689 |
| 31.H | -1.054673 | 4.898134 | -0.898539 |
| 32.H | -0.958431 | 3.187169 | 3.821347 |
| 33.H | -2.275276 | 3.365057 | 2.623564 |
| 34.H | -1.168845 | 4.733417 | 2.954675 |
| 35.H | 2.672776  | 2.606149 | -0.368568 |
| 36.H | 2.010986  | 2.955785 | 1.239957 |
| 37.H | 2.009790  | 4.221959 | -0.015971 |
| 38.H | 2.104138  | 3.105912 | -2.631437 |
| 39.H | 0.680154  | 2.632617 | -3.599712 |
| 40.H | 1.407229  | 1.466187 | -2.455052 |

Bond Energy: -5070.50 kcal/mol
BDA-2-deoxyglucosyl radical

1. O  -0.842864 -1.818068  0.158630
2. C  0.825762 -0.312596  1.306755
3. C  -0.695165 -0.591751  0.908884
4. C  0.158341 -2.111480 -0.838866
5. C  1.552764 -1.958259 -0.254838
6. O  1.727947 -0.602516  0.214126
7. O  2.403881 -3.489558 -1.971394
8. O  1.083665 -1.196733  2.409920
9. C  1.078658  1.150093  1.671278
10. O -1.261243  0.538920  0.231586
11. C -1.589975 -0.770489  2.136381
12. H  0.060400 -1.433337 -1.691390
13. C  0.003772 -3.546393 -1.327491
14. C  2.580646 -2.299333 -1.280870
15. H  1.628633 -2.638041  0.615765
16. C -0.080472 -3.717984 -4.501105
17. C  1.073035 -3.821973 -2.402628
18. H  1.126787 -4.892544 -2.644718
19. H -0.992552 -3.711621 -1.752520
20. H  0.130992 -4.245989 -0.492048
21. H  3.629324 -2.054566 -1.143813
22. O  0.826226 -3.072586 -3.596585
23. H -0.115496 -3.096056 -5.398652
24. H -1.095077 -3.798783 -4.081897
25. H  0.277487 -4.724873 -4.768458
26. H  0.835708  1.806339  0.835793
|     |      |      |      |     |      |
|-----|------|------|------|-----|------|
| 27.C|  2.413248 | -1.148086 |  2.962400 |
| 28.C| -0.833106  |  0.874528  | -1.102175 |
| 29.H|  3.175344  | -1.144291  |  2.173896 |
| 30.H|  2.516949  | -2.053092  |  3.566616 |
| 31.H|  2.549384  | -0.268971  |  3.605984 |
| 32.H|  0.257210  |  0.864223  | -1.210125 |
| 33.H| -1.208224  |  1.886231  | -1.282939 |
| 34.H| -1.280736  |  0.195687  | -1.838960 |
| 35.H| -1.262360  | -1.629106  |  2.721136 |
| 36.H| -2.612946  | -0.924884  |  1.782363 |
| 37.H| -1.563672  |  0.126489  |  2.760420 |
| 38.H|  2.134020  |  1.286993  |  1.921188 |
| 39.H|  0.464781  |  1.433375  |  2.530054 |

Bond Energy: -4923.83 kcal/mol
UPLC-MS data

UPLC method

For compounds of which the diastereomeric (or D:L) ratio could not be determined by NMR, UPLC-MS was used. All UPLC-MS were performed using a Thermo Fischer Vanquish UPLC system in combination with Thermo Fischer LCQ Fleet Mass Spectrometer System. Separation of diastereomers could be achieved using an ACQUITY UPLC BEH C8 1.7 μm column, of the dimension 2.1 × 150 mm, using a gradient as shown in the following graph.

Graph 1. UPLC solvent gradient used in the determination of diastereomeric (or D:L) ratio.

| No | Time | Flow [μL/min] | % A | % B | % C | % D | Curve |
|----|------|---------------|-----|-----|-----|-----|-------|
| 1  | 0.000| Run           |     |     |     |     |       |
| 2  | 0.000| 0.300        | 50  | 0   | 0   | 0   | 5     |
| 3  | 1.000| 0.300        | 50  | 0   | 0   | 0   | 5     |
| 4  | 8.000| 0.300        | 50  | 0   | 0   | 0   | 5     |
| 5  | 10.000| 0.300       | 50  | 0   | 0   | 0   | 5     |
| 6  | 11.000| 0.300       | 50  | 0   | 0   | 0   | 5     |
| 7  | 12.000| 0.300       | 50  | 0   | 0   | 0   | 5     |
| 8  | 17.000| 0.300       | 50  | 0   | 0   | 0   | 5     |
| 9  | Stop Run |           |     |     |     |     |       |
| 10 | 17.000| Stop Run     |     |     |     |     |       |

Solvent base (solvent A): water

Solvent B: acetonitrile with 1% formic acid
Determination of D:L ratio of compound 20

**Graph 2.** Zoomed-in chromatograms related to compound 20. All chromatograms are displayed with UV trace at 254 nm. Top: Crude product mixture. Middle: Purified 20, L-diestereomer. Bottom: Impure fraction containing other glycosides, including D-diastereomer.

**Graph 3.** Top 3 rows: Full chromatogram of related to compound 20, total ion count (TIC) trace. Please note the ~0.12 min delay in retention times between TIC and UV trace is caused by the void volume between the UV detector and the mass spectrometer. Bottom 3 rows: Mass spectrum of selected peaks.
Graph 4. Zoomed in chromatogram of crude product mixture of 20, with integration for calculating D:L ratio. Top: Total ion count (TIC) trace. Bottom: UV trace at 254 nm. Please note the ~0.12 min
delay in retention times between TIC and UV trace is caused by the void volume between the UV detector and the mass spectrometer.

Calculation:

2 peaks centered around 12.99 min and 13.06 min in the UV trace were integrated.

Area of peak around 12.99 min (D-product) = 159731 units
Area of peak around 13.06 min (L-product) = 755730 units

D:L ratio = 1:4.7
HPLC trace of compound 27

Spiking experiment

To minimize the fluctuation in retention time due to the varying pH in each sample, a part of the crude sample was spiked with the major and the minor diastereomer respectively. The results were shown below. In the following runs, the retention time of both the major and the minor diastereomers were consistent.

**Graph 5.** Zoomed-in chromatograms related to compound 27. All chromatograms are displayed with UV trace at 254 nm. Top: Crude product mixture. Middle: Crude product mixture spiked with isolated product 27a. Bottom: Crude product mixture spiked with impure fractions containing 27b.
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NMR spectra
NHP Esters, perbenzyl, and synthetic intermediates
ICW423#13-52 RT: 0.31-1.40 AV: 40 T: FTMS + p ESI Full ms [350.00-750.00]

NL:
6.92E5

646.20358
647.20701
648.21062

645.58148
646.58444
647.47470
648.44897

646.22973
646.94107
647.02611
648.21146

646.16745
646.58444
647.47470
648.02611

NL:
6.59E5

C36H33NO9Na:
C36H33N1O9Na1

pa Chrg 1
ICW034403-23 RT: 0.04-0.59 AV: 21 T: FTMS + p ESI Full ms [350.00-750.00]
NHP esters, with BDA
The image contains a graph with m/z values and relative abundance on the y-axis. The x-axis represents ppm. Various peaks are labeled with their corresponding m/z values and charges (z). The molecule 17 is shown in the inset, with labeled atoms and functional groups. The text provides additional information on the experimental conditions, such as mass spectrometry settings and charges. The graph and molecule diagram are consistent with the data presented in the text.
NL: 1.67E6
ICW532#3-24 RT: 0.04-0.62 AV: 22 T:
FTMS + p ESI Full ms
[350.00-750.00]

$\text{[Cl]ClCl}_4$  $\text{N}_1$  $\text{O}_{10}$  $\text{Na}_1$

pa Chrg 1
1D-NOE
NL: 1.36E7
ICW525#3-24  RT: 0.04-0.62  AV: 22 T: FTMS + p ESI Full ms [350.00-750.00]

NL: 6.85E5
C27H33 N2 O10 S1
pa Chrg 1
Photoalkylation products, perbenzyl
NL: 5.76E6
ICW343B#5-21
RT: 0.10-0.56 AV:
17 T: FTMS + p ESI
Full ms
[350.00-750.00]

NL: 6.99E5
C_{31}H_{36}O_{7}N_{4H}:
C_{31}H_{40}O_{7}N_{1}
pa Chrg 1
NL: 2.77E6
ICW426A#13-53
RT: 0.31-1.42 AV:
41 T: FTMS + p ESI
Full ms
[350.00-750.00]

NL: 7.03E5
C31 H36 O6 Na:
C31 H36 O6 Na1
pa Chrg 1
ICW427A#4-23
RT: 0.06-0.59 AV: 20 T: FTMS + p ESI
Full ms [350.00-750.00]

diastereomer 1

6a

C_{32}H_{36}O_{6}Na:
C_{32}H_{36}O_{6}Na^{+}

pa Chrg 1

NL:
2.58E6

NL:
6.96E5

C_{32} H_{36} O_{6} Na:
C_{32} H_{36} O_{6} Na^{+}

pa Chrg 1

538.5 539.0 539.5 540.0 540.5 541.0 541.5 542.0 ...  AV: 20 T: FTMS + p ESI

Full ms [350.00-750.00]
ICWS16B#5-23
0.09-0.59 AV: 19 T:
FTMS + p ESI Full
ms [350.00-750.00]

NL:
1.41E7

ICWS16B#5-23
0.09-0.59 AV: 19 T:
FTMS + p ESI Full
ms [350.00-750.00]

NL:
6.84E5
NL: 4.21E6
ICW407A#3-19
RT: 0.04-0.48 AV: 
17 T: FTMS + p ESI 
Full ms
[350.00-750.00]

NL: 7.03E5
C31 H36 O6 Na: 
C31 H36 O6 Na1 
pa Chrg 1
NL: 7.50E6
ICW407B#3-17
RT: 0.04-0.43 AV: 15 T: FTMS + p ESI
Full ms [120.00-550.00]

NL: 7.03E5
C_{31} H_{36} O_{6} Na:
C_{31} H_{36} O_{6} Na_{1}
pa Chrg 1
NL: 5.03E6
ICW406A#3-20  RT: 0.04-0.52  AV: 18 T:
FTMS + p ESI Full
ms [120.00-550.00]
NL: 1.11E6
ICW424A#13-52
RT: 0.31-1.40  AV: 40  T: FTMS + p ESI
Full ms
[350.00-750.00]

NL: 7.10E5
C_{30}H_{33}NO_{5}Na :
C_{30}H_{33}N_{1}O_{5}Na_{1}
pa Chrg 1
Photoalkylation product, with BDA, and their corresponding derivatives
ICW49244-22

RT: 0.07-0.57
AV: 19 T:
FTMS + p ESI Full
ms [120.00-550.00]
NL: 3.09E6
ICW466#5-21 RT: 0.09-0.54 AV: 17
T: FTMS + p ESI
Full ms [120.00-550.00]

NL: 8.92E5
C9H15NO5Na:
C9H15N1O5Na1
pa Chrg 1
1.44E7
ICW493#5-22 RT: 0.09-0.57 AV: 18
T: FTMS + p ESI
Full ms [120.00-550.00]
Synthesis of L-gulosides: intermediate, product and derivative.
29

[Chemical Structure Image]

[Chemical Spectrum Image]

183
ICW49543-23 RT: 0.04-0.60 AV: 21
T: FTMS + p ESI
Full ms
[120.00-550.00]

NL: 2.13E6
C, H14O6Na:
C, H14O6Na1
pa Chrg 1
Addition product with imine as somophile
Low temperature NMR study of 25

$^1$H-NMR were taken at -40°C, -20°C and 0°C respectively. No other new peaks could be observed, suggesting that the conformers of 25 does not equilibrate, even at room temperature. Distinct feature of this NMR includes the unchanging coupling constant $J$ observed with H1 (δ 4.52, d, $J=8.2$)
Figure 1. $^3$H-NMR of 25 at -40°C.
Figure 2. $^1$H-NMR of 25 at at -20°C.
Figure 3. $^1$H-NMR of 25 at at 0°C.