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Intramolecular Pd-Catalyzed Arylation of 1-amidosugars: A New Route to N-Glycosyl Quinolin-2-ones

Thi Thanh Huyen Luong, a Jean-Daniel Brion,a Ewen Lescop, b Mouad Alami,a* and Samir Messaoudi,a*

a BioCIS, Univ. Paris-Sud, CNRS, University Paris-Saclay, Châtenay-Malabry, France
b Institut de Chimie des Substances Naturelles ICSN-CNRS

sami.messaoudi@u-psud.fr, mouad.alami@u-psud.fr,
Phone: 33(0)1.46.83.58.28; Fax: 33(0)1.46.83.58.28

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General Experimental Methods
All reactions were conducted under an argon atmosphere. Solvents: cyclohexane, ethyl acetate (EtOAc) for extraction and chromatography were technical grade.

1. General Experimental Methods
These compounds were all identified by the usual physical methods, that is 1H NMR, 13C NMR (J-MOD), IR, HR-MS (ESI or APCI). 1H NMR, 13C NMR spectra were measured in CDCl₃. 1H chemical shift are reported in ppm from an internal standard TMS or of residual chloroform (7.27 ppm). The following abbreviations are used: m (multiplet), s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), q (quadruplet), qui (quintuplet), sex (sextuplet). 13C chemical shift are reported in ppm from central peak of deuteriochloroform (77.14). High resolution mass spectra (HR-MS) were recorded on a MicroTOF spectrometer, using ESI or APCI with methanol as the carrier solvent. Nominal and exact m/z values are reported in Daltons. IR spectra were measured and are reported in wave numbers (cm⁻¹). Analytical TLC was performed on precoated silica gel 60-F254 plates. Silica gel 60 (0.0150 – 0.040 mm) was used for flash chromatography. Melting points was recorded on a B-450 apparatus and are uncorrected.

Aminosaccharides 7a-d were synthesized as according to literature protocols¹. Aminomannose 7c is not enough stable for its characterization and was used immediately after its preparation. All arylboronic acid used are commercially available.

2. General Procedure for the Synthesis of Z-3-(2-iodophenyl)acrylic acids 1a-g and their characterization data

Scheme 1: Synthesis of Z-3-(2-iodophenyl)acrylic acids

A variety of Z-3-(2-iodophenyl)acrylic acid 1a-g was synthesized via a Z-selective olefination of the corresponding 2-iodobenzaldehydes 5a-g with the modification of Horner–Wadsworth–Emmons reaction by Ando’s phosphonate, followed by hydrolysis of the ester as depicted in Scheme 1.

2.1. General procedure for the synthesis of 2-iodobenzaldehyde 5a-f

The 2-iodobenzaldehydes were prepared from the corresponding 2-iodophenyl acids in two steps (Scheme 2): firstly, 2-iodobenzoic acids were reduced by using BH₃·THF (1.5 equiv.) to their corresponding alcohols in almost quantitative yields. Then these alcohols were oxidized in mild condition using pyridinium chlorochromate (PCC) to give 2-iodobenzaldehydes. All compound’s RMN spectra were matched with literature.

Scheme 2: Preparation of 2-iodobenzaldehydes.

To a solution of 2-iodobenzoic acids 9a-f (5 mmol, 1 equiv.) in THF (10 mL) at cooled to 0°C with ice bath and was slowly added borane 1M in THF in 10 – 15 mins (7.5 mL, 1.5 equiv.). The mixture was vigorously stirred at room temperature for 5 hours. Excess hydride was carefully destroyed with mixture of THF/H₂O (1/1) and the aqueous phase was saturated with K₂CO₃. The organic layer was

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extracted with diethyl ether (30ml x 3) and the combined organic layer were dried with MgSO₄ and concentrated under vacuum and the product alcohols 10a-f were used without any purification. Crude of (2-iodophenyl)methanol 10a-f was dissolved in DCM (30 mL) and pyridinium chlorochromate (PCC, 6 mmol, 1.2 equiv.) was added portionwise. The reaction was vigorously stirred at room temperature for 12 hours, then filtered through a pad of celite and evaporated under vacuum. The crude mixture was purified by flash silica-gel chromatography (cyclohexan 100%) to afford the 2-iodobenzaldehyde 5a-f.

2-iodobenzaldehyde (5a)

Following the general procedure, using 2-iodobenzoic acid 9a (1240 mg, 5.0 mmol) to afford the 2-iodobenzaldehyde 5a as white solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 97% (1120 mg, 4.85 mmol). Spectroscopic data were in agreement with those in literature data5.

5-bromo-2-iodobenzaldehyde (5b)

Following the general procedure, using 5-bromo-2-iodobenzoic acid 9b (1630 mg, 5.0 mmol) to afford the benzaldehyde 5b as white solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 97% (1120 mg, 4.85 mmol), m.p.: 89-90°C. Spectroscopic data were in agreement with those in literature data5.

5-flouro-2-iodobenzaldehyde (5c)

Following the general procedure, using 5-flouro-2-iodobenzoic acid 9c (800 mg, 3.0 mmol) to afford the benzaldehyde 5c as yellow solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 90% (675 mg, 2.7 mmol). Spectroscopic data were in agreement with those in literature data5.

4-flouro-2-iodobenzaldehyde (5d)

Following the general procedure, using 5-flouro-2-iodobenzoic acid 9d (800 mg, 3.0 mmol) to afford the benzaldehyde 5d as yellow solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 92% (690 mg, 2.76 mmol). Spectroscopic data were in agreement with those in literature data5.
4-chloro-2-iodobenzaldehyde (5e)

Folloing the general procedure, using 5-chloro-2-iodobenzoic acid 9e (845 mg, 3.0 mmol) to afford the benzaldehyde 5e as white solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 85% (680 mg, 2.55 mmol). Spectroscopic data were in agreement with those in literature data5.

4,5-dimethyl-2-iodobenzaldehyde (5f)

Folloing the general procedure, using 5-chloro-2-iodobenzoic acid 9f (830 mg, 3.0 mmol) to afford the benzaldehyde 5f as white solid (purified by silica-gel column chromatography with cyclohexan 100%), yield: 96% (750 mg, 2.88 mmol). Spectroscopic data were in agreement with those in literature data5.

2.2. General procedure for the synthesis of (Z)-3- (2-iodophenyl)acrylic acid 1a-f

a. General procedure for the synthesis of ethyl (Z)-3- (2-iodophenyl)acrylate 6a-f

To a solution of ethyl (diphenylphosphono)acetate (3.6 mmol, 1.2 equiv.) in anhydrous THF (60 ml) was treated with t-BuOK (3.6 mmol, 1.2 equiv.) at -78°C for 15 min under an argon atmosphere. The 2-iodobenzaldehyde 5a-f (3 mmol, 1 equiv.) was added and the mixture was stirred and was gradually warmed for 45 min. The crude reaction was quenched with brine (30 mL) and extracted with EtOAc (3x30 mL). The organic layer was washed with water and dried by MgSO4 then evaporated in vacuum. The crude product was purified by silica gel flash Chromatography (Cyclohexane/EtOAc 95/5) to afford ester 6a-f. The ratio of two isomers Z/E was determined by 1H NMR analysis of the crude reaction obtained after aqueous work up, based on J-coupling (Hz) of two proton of the double bond: J around 12 Hz for the Z-isomer and around 16 Hz for E-isomer.

b. General procedure for the hydrolysis of 6a-f (synthesis of 1a-f)

A 50 mL round bottom flash was charged with acrylate ester 6a-f (2 equiv.) in ethanol (5 ml). A solution of NaOH 0.52 M (10 mL) was added at 50°C (reflux). The mixture was stirred for 2 h, diluted with H2O (10 mL), and the acidity of the solution was adjusted with 1 M HCl to pH 1.0. The mixture was extracted with EtOAc (3 x 20 mL), washed with brine, dried with MgSO4 and evaporated in vacuum to give acid 1a-f. (The ratio of 2 isomer Z/E was determined by 1H NMR analysis of the crude reaction obtained after aqueous work up, based on J-coupling (Hz) of two proton of double bond: J around 12 Hz for Z-isomer and around 15.5 Hz for E-isomer.

2.3. Characterization data of 6a-f and 1a-f

(Z)-ethyl 3-(2-iodophenyl)acrylate (6a)

The Z-selective olefination of 2-iodobenzaldehyde 5a (3 mmol, 693 mg) was performed using the
general procedure described above to provide 6a as a colorless oil; yield 85% (770 mg); Rf = 0.57 (Cyclohexan/EtOAc: 9/1); Z/E ratio = 93/7 (determined by 1H NMR spectrum).

1H NMR (300 MHz, CDCl3):
- **Assigned to Z-isomer:** δ 7.85 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.02 - 6.95 (m, 2H), 6.02 (d, J = 12.1 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H). 1.16 (t, J = 7.1 Hz, 3H).
- **Assigned to E-isomer:** δ 7.93 - 7.86 (m, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.43 - 7.29 (m, 1H), 7.07 - 6.95 (m, 2H), 6.32 (d, J = 16.3 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

Spectroscopic data were in agreement with those in literature data.

(Z)\-[3-(2-iodophenyl)acrylic acid (1a)]

Hydrolysis of ester 6a (2 mmol, 600 mg) was performed according to the general procedure described above to afford acid 1a as colorless needles; yield 97% (530 mg); Rf = 0.22 (Cyclohexan/EtOAc: 5/5); Z/E ratio 93/7, determined by 1H NMR spectrum.

1H NMR (300 MHz, Acetone-D6):
- **Assigned to Z-isomer:** δ 10.20 (br s, 1H), 7.90 (dd, J = 7.9, 1.0 Hz, 1H), 7.64 – 7.42 (m, 1H), 7.37 (td, J = 7.4, 0.9 Hz, 1H), 7.07 (td, J = 7.6, 1.7 Hz, 1H), 7.00 (d, J = 12.1 Hz, 1H), 6.10 (d, J = 12.1 Hz, 1H).
- **Assigned to E-isomer:** δ 10.20 (br s, 1H), 8.05 – 7.83 (m, 2H), 7.51 – 7.48 (1H), 7.07 – 6.98 (1H), 6.47 (d, J = 15.8 Hz, 1H).

Spectroscopic data were in agreement with those in literature data.

(Z)-ethyl 3-(5-bromo-2-iodophenyl)acrylate (6b)

The Z-selective olefination of 5-bromo-2-iodobenzaldehyde 5b (3.35 mmol, 1038 mg) was performed using the general procedure described above to provide 6b as a white powder; yield 87% (1110 mg); Rf = 0.65 (Cyclohexan/EtOAc: 9/1); Z/E ratio 92/8, determined by 1H NMR spectrum;

IR (neat): 1725, 1709, 1542, 1448, 1278, 1170, 1032 cm⁻¹;

1H NMR (300 MHz, CDCl3):
- **Assigned to Z-isomer:** δ 7.68 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 7.13 (dd, J = 8.4, 2.0 Hz, 1H), 6.87 (d, J = 12.0 Hz, 1H), 6.04 (d, J = 12.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H);
- **Assigned to E-isomer:** δ 7.83 – 7.64 (m, 3H), 7.20 – 7.15 (1H), 6.31 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.1 Hz, 1H), 1.34 (t, J = 7.1 Hz, 1H).

13C NMR (75 MHz, CDCl3):
- **Assigned to Z-isomer:** δ 165.1 (C), 144.8 (CH), 141.6 (C), 139.8 (CH), 132.9 (CH), 132.7 (CH), 122.6 (CH), 121.8 (C), 96.1 (C), 60.7 (CH2), 14.1 (CH3).
- **Assigned to E-isomer:** δ 146.3 (CH), 141.2 (CH), 134.1 (CH), 130.3 (CH), 121.8 (CH), 96.1 (CH), 61.0 (CH2), 14.4 (CH3).

(Z)-3-(5-bromo-2-iodophenyl)acrylic acid (1b)

Hydrolysis of ester 6b (2.63 mmol, 1000 mg) was performed according to the general procedure described above to afford acid 1b as colorless needles; yield 93% (860 mg); Rf = 0.31 (Cyclohexan/EtOAc: 5/5); Z/E ratio 93/7, determinized by 1H NMR spectrum; IR (neat): 2919, 1703, 1628, 1541, 1454, 1397, 1379, 1087, 1010, 975 cm⁻¹;
1H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.69 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 2.3 Hz, 1H), 7.14 (dd, J = 8.4, 2.3 Hz, 1H), 6.98 (d, J = 12.0 Hz, 1H), 6.05 (d, J = 12.0 Hz, 1H).
- Assigned to E-isomer: δ 7.87 (d, J = 16 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.22 – 7.12 (m, 1H), 7.09 – 6.96 (m, 1H), 6.29 (d, J = 16.0 Hz, 1H).
13C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 169.5 (C) 147.6 (CH), 141.2 (C), 140.0 (CH), 133.1 (CH), 132.9 (CH), 122.0 (C), 121.4 (CH), 95.8 (C).
- E-isomer: not identified on 13C NMR.
HR-MS (ESI positive, m/z): found 374.8498/376.8467 ([M+Na]+), calc. for C₉H₆O₂BrINa (M+Na): 374.8494/376.8473.

(Z)-ethyl 3-(5-fluoro-2-iodophenyl)acrylate (6c)

The Z-selective olefination of 5-fluoro-2-iodobenzaldehyde 5c (1.8 mmol, 450 mg) was performed using the general procedure described above to provide 6c as a pale-yellow oil; yield 80% (465 mg); Rf = 0.67 (Cyclohexan/EtOAc: 9/1); Z/E ratio 93/7, determinized by 1H NMR spectrum; IR (neat): 1724, 1638, 1595, 1572, 1416, 1384, 1277, 1183, 1018 cm⁻¹;
1H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.77 (dd, J = 8.7, 5.5 Hz, 1H), 7.17 (dd, J = 9.5, 2.9 Hz, 1H), 6.89 (d, J = 12.1 Hz, 1H), 6.77 (td, J = 8.4, 3.0 Hz, 1H), 6.04 (d, J = 12.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H).
- Assigned to E-isomer: δ 7.86 – 7.81 (m, 2H), 7.29 – 7.24 (m, 1H), 6.80 – 6.74 (m, 1H), 6.30 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).
13C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 165.2 (C), 162.43 (d, J = 247.5 Hz, C), 145.2 (CH), 141.49 (d, J = 8.1 Hz, C), 139.81 (d, J = 7.9 Hz, CH), 122.5 (CH), 117.58 (d, J = 22.2 Hz, CH), 117.58 (d, J = 23.3 Hz, CH), 91.2 (d, J = 3.0 Hz, C), 60.6 (CH₂), 14.1 (CH₃).
- Assigned to E-isomer: δ 160.4 (C), 146.7 (C), 145.2 (CH), 141.3 (d, J = 7.7 Hz, CH), 118.8 (d, J = 22.2 Hz, CH), 114.49 (d, J = 23.3 Hz, CH), 91.2 (CH), 61.0 (CH₂), 14.4 (CH₃).
HR-MS (ESI positive, m/z): found 320.9789 ([M+H]+), calc. for C₁₁H₁₁O₂IF (M+H): 320.9788.
Hydrolysis of ester 6c (0.63 mmol, 200 mg) was performed according to the general procedure described above to afford acid 1c as colorless needles; yield 94% (172 mg); $R_f = 0.46$ (Cyclohexan/EtOAc: 4/6); Z/E ratio 2/8, determined by $^1$H NMR spectrum; IR (neat): 1710, 1631, 1595, 1460, 1404, 1278, 1148, 1020 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$):
- **Assigned to Z-isomer:** δ 7.78 (dd, $J = 8.7, 5.4$ Hz, 1H), 7.17 (dd, $J = 9.3, 2.8$ Hz, 1H), 7.00 (d, $J = 12.1$ Hz, 1H), 6.79 (td, $J = 8.5, 3.0$ Hz, 1H), 6.05 (d, $J = 12.1$ Hz, 1H).
- **Assigned to E-isomer:** δ 7.96 – 7.84 (m, 2H), 7.33 – 7.28 (m, 1H), 6.88 – 6.83 (m, 1H), 6.28 (d, $J = 15.7$ Hz, 1H).
$^{13}$C NMR (75 MHz, CDCl$_3$):
- **Assigned to Z-isomer:** δ 170.5 (C), 164.48 – 160.58 ((d, $J = 246$ Hz, C), 147.9 (CH), 140.92 (d, $J = 246$ Hz, C), 139.87 (d, $J = 7.8$ Hz, CH), 121.3 (CH), 117.8 (CH), 117.67 (d, $J = 21.8$ Hz, CH), 91.0 (C).
- **Assigne to E-isomer:** δ 171.6 (C), 149.2 (CH), 141.4 (d, $J = 7.5$ Hz, 1H), 121.4 (CH), 120.0 (CH), 119.3 (141.38 (d, $J = 22.0$ Hz, CH), 114.7 (d, $J = 7.5$ Hz), 114.7 (d, $J = 22.9$ Hz, CH), 94.2 (C).
HR-MS (ESI positive, m/z): found 314.9302 ([M+Na$^+$]), calc. for C$_9$H$_6$O$_2$FINa (M+Na): 314.9294.

The $Z$-selective olefination of 4-fluoro-2-iodobenzaldehyde 5d (0.7 mmol, 175 mg) was performed using the general procedure described above to provide 6d as a colorless oil; yield 85% (190 mg); $R_f = 0.67$ (Cyclohexan/EtOAc: 9/1); Z/E ratio 93/7, determined by $^1$H NMR spectrum; IR (neat): 1722, 1636, 1590, 1574, 1477, 1385, 1264, 1231, 1187, 1027 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$):
- **Assigned to Z-isomer:** δ 7.58 (dd, $J = 8.0, 2.5$ Hz, 1H), 7.44 (dd, $J = 8.6, 5.9$ Hz, 1H), 7.05 (td, $J = 8.4, 2.5$ Hz, 1H), 6.92 (d, $J = 12.0$ Hz, 1H), 6.01 (d, $J = 12.0$ Hz, 1H), 4.11 (q, $J = 7.1$ Hz, 2H), 1.19 (t, $J = 7.1$ Hz, 3H).
- **Assigned to E-isomer:** δ 7.85 (d, $J = 15.8$ Hz, 1H), 7.67 – 7.51 (m, 2H), 7.08 – 6.90 (m, 1H), 6.25 (d, $J = 15.8$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H).
$^{13}$C NMR (75 MHz, CDCl$_3$):
- **Assigned to Z-isomer:** δ 165.4 (C), 161.8 (d, $J = 253.2$ Hz, C), 145.7 (CH), 135.67 (C), 131.3 (d, $J = 8.2$ Hz, CH), 125.6 (d, $J = 23.9$ Hz, CH), 121.7 (CH), 114.9 (d, $J = 21.2$ Hz, CH), 97.9 (d, $J = 7.9$ Hz, C), 60.5 (CH$_2$), 14.2 9 (CH$_3$).
- **E-isomer:** not identified on $^{13}$C NMR.
HR-MS (ESI positive, m/z): found 342.9612 ([M+Na$^+$]), calc. for C$_{11}$H$_{10}$O$_2$IFNa (M+Na): 342.9607.
Hydrolysis of ester 6d (0.56 mmol, 180 mg) was performed according to the general procedure described above to afford acid 1d as pale yellow powder; yield 92% (150 mg); Rf = 0.46 (Cyclohexan/EtOAc: 4/6); Z/E ratio 93/7, determinized by ¹H NMR spectrum; IR (neat): 2924, 1705, 1677, 1635, 1592, 1381, 1306, 1228 cm⁻¹; ¹H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.58 (dd, J = 8.0, 2.5 Hz, 1H), 7.43 (dd, J = 8.6, 5.9 Hz, 1H), 7.06 – 6.94 (m, 2H), 6.01 (d, J = 12.1 Hz, 1H).
- Assigned to E-isomer: δ 7.93 (d, J = 16 Hz, 1H), 7.64 (dd, J = 8.6, 5.9 Hz, 1H), 7.10 – 6.97 (m, 2H), 6.24 (d, J = 15.6 Hz, 1H).
¹³C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 170.1 (C), 161.97 (d, J = 253.6 Hz, C), 148.2 (CH), 135.1 (d, J = 2.7 Hz, C), 131.5 (d, J = 8.2 Hz, CH), 125.7 (d, J = 24.0 Hz, CH), 120.5 (CH), 115.1 (d, J = 21.3 Hz, CH), 97.9 (d, J = 8.9 Hz, C).
- E-isomer: not identified on ¹³C NMR.
HR-MS (ESI positive, m/z): found 314.9302 ([M+Na]⁺), calc. for C₉H₆O₂FINa (M+Na): 314.9294.

Hydrolysis of ester 6e (0.86 mmol, 290 mg) was performed according to the general procedure described above to provide 6e as colorless oil; yield 87% (440 mg); Rf = 0.52 (Cyclohexan/EtOAc: 9/1); Z/E ratio 92/8, determinized by ¹H NMR spectrum; IR (neat): 1702, 1677, 1633, 1571, 1463, 1306, 1249, 1225, 1031 cm⁻¹; ¹H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.85 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.30 (dd, J = 8.3, 2.0 Hz, 1H), 6.90 (d, J = 12.1 Hz, 1H), 6.03 (d, J = 12.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H).
- Assigned to E-isomer: δ 7.93 – 7.78 (m, 2H), 7.47 (d, J = 8.4 Hz, 1H), 7.39 – 7.36 (d, J = 8.3 Hz, 1H), 6.29 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.1 Hz, 1H), 1.35 (t, J = 7.1 Hz, 1H).
¹³C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 165.3 (C), 145.5 (CH), 138.2 (C), 138.0 (CH), 134.6 (C), 130.9 (CH), 127.9 (CH), 122.1 (CH), 98.3 (C), 60.6 (CH₂), 14.2 (CH₃).
- E-isomer: not identified on ¹³C NMR.
HR-MS (ESI positive, m/z): found 336.9492 ([M+H]⁺), calc. for C₁₁H₁₁O₂ClI (M+H): 336.9492.

Hydrolysis of ester 6f (0.86 mmol, 290 mg) was performed according to the general procedure described
above to afford acid 1e as beige powder; yield 96% (254 mg); R_f = 0.4 (Cyclohexan/EtOAc: 5/5); Z/E ratio 91/9, determined by 1H NMR spectrum; IR (neat): 2784, 1975, 1702, 1574, 1428, 1303, 1207, 1030 cm⁻¹; 1H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.86 (d, J = 1.7 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.01 (d, J = 12.1 Hz, 1H), 6.03 (d, J = 12.1 Hz, 1H).
- Assigned to E-isomer: δ 7.96 – 7.88 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 6.28 (d, J = 16.0 Hz, 1H).

13C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 166.2 (C), 145.7 (CH), 139.7 (C), 138.2 (CH), 134.5 (C), 132.0 (CH), 128.6 (CH), 123.0 (CH), 98.6 (C).
- Assigned to E-isomer: δ 146.9 (CH), 139.7 (CH), 138.2 (CH), 129.8 (CH), 129.3 (CH), 122.8 (CH).

HR-MS (ESI positive, m/z): found 330.8994 ([M+Na]⁺), calc. for C₉H₆O₂IClNa (M+Na): 330.8999.

(Z)-ethyl 3-(2-iodo-4,5-dimethylphenyl)acrylate (6f)

The Z-selective olefination of 4-chloro-2-iodobenzaldehyde 5f (1.54 mmol, 400 mg) was performed using the general procedure described above to provide 6f as a yellow oil; yield 86% (437 mg); R_f = 0.56 (Cyclohexan/EtOAc: 9/1); Z/E ratio 91/9, determined by 1H NMR spectrum; IR (neat): 2979, 1726, 1632, 1594, 1478, 1384, 1313, 1265, 1022, 972 cm⁻¹; 1H NMR (300 MHz, CDCl₃):
- Assigned to Z-isomer: δ 7.62 (s, 1H), 7.23 (s, 1H), 6.92 (d, J = 12.1 Hz, 1H), 5.96 (d, J = 12.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.21 (s, 3H), 2.20 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H).
- Assigned to E-isomer: δ 7.85 (d, J = 15.8 Hz, 1H), 7.66 (s, 1H), 7.34 (s, 1H), 6.29 (d, J = 15.8 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.21 (s, 3H), 2.20 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

13C NMR (75 MHz, CDCl₃):
- Assigned to Z-isomer: δ 165.7 (C), 146.4 (CH), 139.3 (CH), 139.2 (C), 136.8 (C), 136.1 (C), 131.3 (CH), 120.9 (CH), 94.9 (C), 60.3 (CH₂), 19.5 (CH₃), 19.2 (CH₃), 14.1 (CH₃).
- Assigned to E-isomer: δ 166.7 (C), 147.7 (CH), 141.1 (C), 140.7 (CH), 137.4 (C), 135.2 (C), 128.3 (CH), 120.1 (CH), 98.0 (C), 60.7 (CH₂), 19.6 (CH₃), 19.3 (CH₃), 14.4 (CH₃).

HR-MS (ESI positive, m/z): found 353.0017 ([M+H]⁺), calc. for C₁₃H₁₅O₂INa (M+Na): 353.0015.

(Z)-3-(4-chloro-2-iodophenyl)acrylic acid (1f)

Hydrolysis of ester 6f (0.88 mmol, 290 mg) was performed according to the general procedure described above to afford acid 1e as colorless needles; yield 96% (0.84 mmol, 254 mg); R_f = 0.31(Cyclohexan/EtOAc: 9/1); Z/E ratio 91/9, determined by 1H NMR spectrum; IR (neat): 2969, 1690, 1630, 1595, 1479, 1382, 1297, 1177, 1140, 1021 cm⁻¹; 1H NMR (300 MHz, CDCl₃):
- **Assigned to Z-isomer**: δ 7.65 (s, 1H), 7.31 (s, 1H), 6.93 (d, J = 12.2 Hz, 1H), 6.03 (dd, J = 12.1, 3.5 Hz, 1H), 2.23 (s, 2H), 2.19 (s, 3H).

- **Assigned to E-isomer**: δ 7.86 (d, J = 15.7 Hz, 1H), 7.74 (s, 1H), 7.65 (s, 1H), 6.44 (d, J = 15.8 Hz, 1H), 2.27 (s, 3H), 2.27 (s, 3H).

13C NMR (75 MHz, Acetone):
- **Assigned to Z-isomer**: δ 166.8 (C), 146.6 (CH), 140.2 (C), 140.0 (CH), 138.1 (C), 137.2 (C), 132.3 (CH), 122.0 (CH), 95.4 (C), 19.5 (CH3), 19.2 (CH3).

- **Assigned to E-isomer**: δ 148.4 (CH), 141.4 (CH), 129.40 (CH), 121.10 (CH), 19.3 (CH3), 19.2 (CH3).

HR-MS (ESI positive, m/z): found 324.9703 ([M+Na]+), calc. for C11H11O2INa (M+Na): 324.9702.

3. **Procedure for the coupling of 2,3,4,6-tetraacetyl-1-amino-β-glucopyranose with Z-3-(2-iodophenyl)acrylic 1a**

To a solution of 1a (200 mg, 0.73 mmol, 1 equiv.), HOBt (0.88 mmol, 1.2 equiv.), EDC.HCl (0.88 mmol, 1.2 equiv.) in anhydrous DMF (7mL, 0.1M) was stirred at room temperature under argon atmosphere for 15 minutes. The tetraacetylated-1-amino-β-glucopyranose 7a (0.88 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at room temperature overnight. Then the mixture was extracted with solution of NH4Cl saturated (3 x 30 ml), and the organic layer was washed with brine (30 mL) and water (30 mL), dried over anhydrous MgSO4 and concentrated under reduced pressure. Flash chromatography over silica gel afford compound 2a in 75% yield (0.55 mmol, 330 mg), as mixture of three isomers: 2a-Zβ, 2a-Eβ and 2a-Zα in ratio 1/0.06/0.2 (determined by 1H NMR). The three isomers were separated by HPLC preparative (conditions: H2O/MeOH gradient from 50% to 80% in 20 min).

**Characterization data of the three isomer: Zβ-2a, Eβ-2a, Zα-2a**

The major isomer Zβ-2a:

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-((Z)-3-(2-iodophenyl)acrylamido)tetrahydro-2H-pyran-3,4,5-triyl triacetate:

Product Zβ-2a was obtained as white solid (262 mg, yield 60%); m.p.: 79 – 81°C; Rf = 0.53 (Cyclohexan/EtOAc: 5/5); [α]D18 + 12.7 (c, 1.0 in CHCl3); IR (neat): 1746, 1694, 1632, 1537, 1463,
1432, 1366, 1210, 1067, 1033, 981 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.9\) Hz, 1H), 7.47 (d, \(J = 7.5\) Hz, 1H), 7.31 (t, \(J = 7.4\) Hz, 1H), 7.01 (t, \(J = 7.6\) Hz, 1H), 6.87 (d, \(J = 12.2\) Hz, 1H), 6.38 (d, \(J = 9.3\) Hz, 1H), 5.94 (d, \(J = 12.2\) Hz, 1H), 5.33 – 5.17 (m, 2H), 5.02 (t, \(J = 9.7\) Hz, 1H), 4.83 (t, \(J = 9.5\) Hz, 1H), 4.27 (dd, \(J = 12.4, 4.3\) Hz, 1H), 4.07 (dd, \(J = 12.4, 1.6\) Hz, 1H), 3.86 – 3.62 (m, 1H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.7 (C), 170.6 (C), 169.9 (C), 169.6 (C), 165.5 (C), 144.0 (CH), 138.9 (CH), 138.8 (C), 130.2 (CH), 130.1 (CH), 127.8 (CH), 123.4 (CH), 98.6 (C), 78.1 (CH), 73.6 (CH), 72.9 (CH), 70.4 (CH), 68.2 (CH), 61.8 (CH\(_2\)), 20.8 (CH\(_3\)), 20.7 (CH\(_3\)), 20.6 (2CH\(_3\)); HR-MS (ESI positive, m/z): found 626.0502 ([M+Na\(^+\)], calc. for C\(_{23}\)H\(_{26}\)NO\(_{10}\)NaI (M+Na\(^+\)): 626.0499.

The minor isomer \(E\beta\)-2a:

\((2R,3R,4S,5R,6R)\)-2-[(acetoxymethyl)-6-[(E)-3-(2-iodophenyl)acrylamido)]tetrahydro-2H-pyran-3,4,5-triyl triacetate:

![Chemical Structure]

Product \(E\beta\)-2a was obtained as beige solid (16 mg, yield 4%); m.p.: 125 – 127°C; \(R_f = 0.53\) (Cyclohexan/EtOAc: 5/5); \([\alpha]_D^{18} = -57.5\) (c, 1.0 in CHCl\(_3\)); IR (neat): 1747, 1667, 1634, 1545, 1433, 1367, 1203, 1086, 1031, 969 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.1\) Hz, 1H), 7.47 (d, \(J = 7.8\) Hz, 1H), 7.31 (t, \(J = 7.6\) Hz, 1H), 7.01 (t, \(J = 7.6\) Hz, 1H), 6.70 (d, \(J = 9.2\) Hz, 1H), 6.22 (d, \(J = 15.5\) Hz, 1H), 5.39 (t, \(J = 8.3\) Hz, 1H), 5.33 (t, \(J = 9.3\) Hz, 1H), 5.07 (t, \(J = 9.7\) Hz, 1H), 4.98 (t, \(J = 9.5\) Hz, 1H), 4.31 (dd, \(J = 12.5, 4.4\) Hz, 1H), 4.13 – 4.03 (m, 1H), 3.92 – 3.81 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.2 (C), 169.9 (C), 169.7 (C), 165.4 (C), 146.3 (CH), 140.1 (CH), 137.8 (C), 131.2 (CH), 128.6 (CH), 127.3 (CH), 122.7 (CH), 101.2 (C), 78.6 (CH), 73.7 (CH), 72.9 (CH), 70.8 (CH), 68.3 (CH), 61.8 (CH\(_2\)), 20.8 (2CH\(_3\)), 20.6 (2CH\(_3\)); HR-MS (ESI positive, m/z): found 626.0502 ([M+Na\(^+\)], calc. for C\(_{23}\)H\(_{26}\)NO\(_{10}\)NaI (M+Na): 626.0499.

The minor isomer \(Z\alpha\)-2a:

\((2R,3R,4S,5R,6S)\)-2-[(acetoxymethyl)-6-[(Z)-3-(2-iodophenyl)acrylamido)]tetrahydro-2H-pyran-3,4,5-triyl triacetate:

![Chemical Structure]

Product \(Z\alpha\)-2a was obtained as white solid (52 mg, yield 11%); m.p.: 85 – 87°C; \(R_f = 0.53\) (Cyclohexan/EtOAc: 5/5); \([\alpha]_D^{18} = -57.5\) (c, 1.0 in CHCl\(_3\)); IR (neat): 1747, 1667, 1634, 1545, 1433,
1367, 1203, 1086, 1031, 969 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 (d, \(J = 7.9\) Hz, 1H), 7.46 - 7.37 (m, 2H), 7.10 (t, \(J = 7.3\) Hz, 1H), 6.96 (d, \(J = 12.2\) Hz, 1H), 6.15 (d, \(J = 12.1\) Hz, 1H), 6.05 (d, \(J = 6.6\) Hz, 1H), 5.79 – 5.59 (m, 1H), 5.07 – 4.95 (m, 1H), 4.71 (t, \(J = 9.6\) Hz, 1H), 4.71 (t, \(J = 9.6\) Hz, 1H), 4.13 (dd, \(J = 12.4\), 3.9 Hz, 1H), 3.91 (dd, \(J = 12.4\), 2.2 Hz, 1H), 3.18 – 3.15 (m, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 170.8 (C), 170.1 (C), 169.3 (C), 169.0 (C), 166.1 (C), 142.0 (CH), 140.2 (C), 139.6 (CH), 130.6 (CH), 129.5 (CH), 128.9 (CH), 126.2 (CH), 97.8 (C), 74.4 (CH), 70.5 (CH), 68.1 (CH), 68.0 (2CH), 61.6 (CH\(_2\)), 20.8 (CH\(_3\)), 20.7 (3CH\(_3\)); HR-MS (ESI positive, m/z): found 626.0507 ([M+Na]\(^+\)), calc. for C\(_{23}\)H\(_{26}\)NO\(_7\)NaI (M+Na): 626.0499.

4. General procedure for the synthesis of N-glycosyl quinoli-2-ones 3a-n and theirs characterization data

4.1. General procedure for the synthesis of N-glycosyl quinoli-2-ones 3a-n

\[ \text{Step 1: Preparation of intermediate 2a-f:} \]
To a solution of 1a-f (0.35 mmol, 1 equiv.), HOBT (0.42 mmol, 1.2 equiv.), EDC.HCl (0.42 mmol, 1.2 equiv.) in anhydrous DMF (3.5 mL, 1M) was stirred at room temperature under argon atmosphere for 15 minutes. The tetraacetylated-1-amino-\(\beta\)-glucopyranose 7a-d (0.42 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at room temperature overnight. Then the mixture was extracted with solution of NH\(_4\)Cl saturated (3 x 30 mL), and the organic layer was washed with brine and water (30 mL), dried over anhydrous MgSO\(_4\) and concentrated under reduced pressure. The crude reaction was used directly to the next step without any purification.

\[ \text{Step 2: The intramolecular N-arylation of 2a-f} \]
A dried Schlenk tube was charged with the crude reaction of 2a-f above, Pd(OAc)\(_2\) (0.0175 mmol, 5 mol%), Tetrabutylammonium acetate (TBAA - 0.53 mmol, 1.5 equiv.). The tube was capped with a rubber septum, evacuated and backfilled under argon. The procedure was repeated once, and then anhydrous dioxane (3 mL, 0.1 M) was added through the septum under argon. The septum was replaced with a Teflon screw cap. The tube was sealed and the mixture was stirred at 100°C for 1 hours. The resulting suspension was cooled at room temperature and filtered through a pad of celite eluting with ethyl acetate and the organic salts were removed. The filtrate was transferred to a separating funnel and was extracted with aqueous NH\(_4\)Cl (30 mL, twice) and with distilled water (30 mL). The combined organic phases was dried with anhydrous MgSO\(_4\), evaporated to dry and purified by flash chromatography over silica gel or by HPLC preparative to afford the desired product.
4.2. Characterization data of 3a–n

\((2R,3R,4S,5S)-2-(acetoxyethyl)-6-(2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3a):\)

Following the general procedure above, acid 1a (0.55 mmol, 150 mg) and β-aminoglucose 7a (0.66 mmol, 230 mg) was stirred overnight at room temperature to afford a crude mixture of 2a with ratio \(Zβ/Eβ/Zα: 1/0.06/0.2\), determined by \(^1\)H NMR of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3a as mixture of 2 isomer β/α: yield 69% (180 mg); ratio β/α: 1/0.2, determined by \(^1\)H NMR after flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers were separated by silica gel column chromatography (Cyclohexan/EtOAc gradient from 10% to 45%).

- **Assigned to 3β-3a isomer:** pale yellow solid (150 mg, yield 57%); m.p.: 187 – 191°C; \(R_f = 0.47\) (Cyclohexan/EtOAc: 5/5); \([\alpha]_D^{18} + 96.9\) (c, 1.0 in CHCl\(_3\)); IR (neat): 1756, 1739, 1658, 1566, 1494, 1455, 1366, 1310, 1205, 1097, 1076, 1031, 984 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 7.96\) (d, \(J = 8.6\) Hz, 1H), 7.63 (d, \(J = 9.5\) Hz, 1H), 7.59 – 7.44 (m, 2H), 7.26 (t, \(J = 7.4\) Hz, 1H), 6.90 (d, \(J = 9.9\) Hz, 1H), 6.60 (d, \(J = 9.5\) Hz, 1H), 5.93 (t, \(J = 9.4\) Hz, 1H), 5.48 (t, \(J = 9.3\) Hz, 1H), 5.39 (t, \(J = 9.7\) Hz, 1H), 4.32 (dd, \(J = 12.5, 4.1\) Hz, 1H), 4.25 (dd, \(J = 12.4, 2.1\) Hz, 1H), 4.11 – 3.95 (m, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H), 1.80 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 170.5\) (C), 169.9 (C), 169.7 (C), 169.1 (C), 162.5 (C), 141.2 (CH), 137.7 (C), 130.5 (CH), 129.5 (CH), 123.3 (CH), 121.3 (C), 120.5 (CH), 116.8 (CH), 80.7 (CH), 75.1 (CH), 73.9 (CH), 68.0 (CH), 67.7 (CH), 61.8 (CH\(_2\)), 20.8 (CH\(_3\)), 20.7 (CH\(_3\)), 20.2 (CH\(_3\)); HR-MS (ESI positive, m/z): found 498.1366 ([M+Na\(^+\)]), calc. for C\(_{23}\)H\(_{22}\)NO\(_{10}\)Na (M+H): 498.1376.

- **Assigned to 3α-3a isomer:** pale yellow solid (30 mg, yield 12%); m.p.: 62 -56°C; \(R_f = 0.52\) (Cyclohexan/EtOAc: 5/5); \([\alpha]_D^{18} +16\) (c, 1.0 in CHCl\(_3\)); IR (neat): 1747, 1669, 1597, 1566, 1454, 1368, 1302, 1250, 1145, 1109, 1046 cm\(^{-1}\); \(^1\)H NMR (400 MHz, Acetone) \(\delta 7.89\) (d, \(J = 9.3\) Hz, 2H), 7.67 (d, \(J = 7.7\) Hz, 1H), 7.66 – 7.51 (m, 1H), 7.29 (t, \(J = 7.2\) Hz, 1H), 6.78 (d, \(J = 6.3\) Hz, 1H), 6.59 (d, \(J = 9.5\) Hz, 1H), 6.10 (t, \(J = 7.0\) Hz, 1H), 5.37 (t, \(J = 6.6\) Hz, 1H), 5.24 (t, \(J = 7.8\) Hz, 1H), 4.69 (dd, \(J = 8.2, 5.6\), 2.9 Hz, 1H), 4.44 (dd, \(J = 12.4, 5.6\) Hz, 1H), 4.19 (dd, \(J = 12.4, 2.9\) Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H), 1.67 (s, 3H); \(^{13}\)C NMR (101 MHz, Acetone) \(\delta 170.8\) (C), 170.4 (C), 170.3 (C), 170.2 (C), 163.7 (C), 141.9 (CH), 141.2 (C), 131.3 (CH), 129.8 (CH), 123.8 (CH), 122.6 (CH), 122.4 (C), 117.5 (CH), 80.2 (CH), 74.5 (CH), 73.2 (CH), 71.0 (CH), 69.1 (CH), 62.6 (CH\(_2\)), 21.0 (CH\(_3\)), 20.9 (CH\(_3\)), 20.8 (CH\(_3\)), 20.4 (CH\(_3\)); HR-MS (ESI positive, m/z): found 476.1566 ([M+H\(^+\)\(^+\)]), calc. for C\(_{23}\)H\(_{22}\)NO\(_{10}\) (M+H): 476.1557. The \(^3\)J coupling constants, between H\(_1\)-H\(_2\), H\(_2\)-H\(_3\) and H\(_3\)-H\(_4\) \((J_{1,2} = 6.3\) Hz, \(J_{2,3} = 6.6\) and \(J_{1,2} = 7.0\) Hz, respectively), indicated averaged values lying between the two conformers α-4C\(_1\) and α-1C\(_4\). The NOE NMR experiments showed a strong nuclear Overhauser effect (NOe) between H4–H5 and H5–H6, which is in agreement with a dynamic conformational equilibrium \(^4\)C\(_1\)-\(^1\)C\(_4\).
Following the general procedure above, acid $1b$ (0.36 mmol, 130 mg) and β-aminoglucose $7a$ (0.44 mmol, 153 mg) was stirred overnight at room temperature to afford a crude mixture of $2b$ with ratio $Z\beta/E\beta/Z\alpha$: $1/0.08/0.18$, determined by $^1$H NMR of crude reaction. This crude was use directly for the next step without purification, using the general procedure described above to afford compound $3b$ as mixture of 2 isomer β/α; yield 63% (126 mg); ratio β/α: 1/0.15, determined by $^1$H NMR after frist flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers was separated by preparative HPLC (water/ACN gradient from 40% to 70%).

**Assigned to β-3b isomer:** white solid (109 mg, yield 55%); m.p.: 182 – 184°C; $[\alpha]_D^{18} +38$ (c, 1.0 in CHCl$_3$); IR (neat): 1756, 1669, 1566, 1494, 1455, 1366, 1310, 1205, 1076, 1031, 984 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 8.8$ Hz, 1H), 7.69 – 7.58 (m, 2H), 7.53 (d, $J = 9.5$ Hz, 1H), 6.83 (d, $J = 9.7$ Hz, 1H), 6.61 (d, $J = 9.5$ Hz, 1H), 5.83 (t, $J = 9.4$ Hz, 1H), 5.46 (t, $J = 9.3$ Hz, 1H), 5.34 (t, $J = 9.8$ Hz, 1H), 4.31 (dd, $J = 12.5$, 4.2 Hz, 1H), 4.21 (dd, $J = 12.5$, 2.2 Hz, 1H), 4.09 – 3.96 (m, 1H), 2.10 (s, 3H), 2.09 (s, 2H), 2.00 (s, 3H), 1.81 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5 (C), 169.9 (C), 169.7 (C), 169.3 (C), 162.1 (C), 140.0 (CH), 136.7 (C), 133.3 (CH), 131.6 (CH), 122.9 (C), 121.8 (CH), 118.5 (CH), 116.3 (C), 80.8 (CH), 75.30 (CH), 73.8 (CH), 68.0 (CH), 67.8 (CH), 61.7 (CH$_2$), 20.9 (CH$_3$), 20.7 (CH$_3$), 20.7 (CH$_3$), 20.2 (CH$_3$); HR-MS (ESI positive, m/z): found 554.0674/556.0661 ([M+H]+), calc. for C$_{23}$H$_{25}$NO$_{10}$Br (M+H): 556.0662/556.0641.

**Assigned to α-3b isomer:** pale yellow solid (16 mg, yield 8%); m.p.: 71 – 74 °C; $[\alpha]_D^{18} +11$ (c, 1.0 in CHCl$_3$); IR (neat): 1747, 1669, 1589, 1494, 1455, 1485, 1369, 1248, 1223, 1053, 910 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.67 – 7.63 (m, 2H), 7.61 – 7.54 (m, 2H), 6.67 – 6.64 (m, 2H), 6.05 (t, $J = 6.7$ Hz, 1H), 5.34 (t, $J = 6.4$ Hz, 1H), 5.25 (t, $J = 7.8$ Hz, 1H), 4.63 – 4.49 (m, 1H), 4.39 (dd, $J = 12.4$, 4.9 Hz, 1H), 4.15 (dd, $J = 12.4$, 2.9 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (75 MHz, Acetone) $\delta$ 170.8 (C), 170.3 (C), 170.2 (C), 170.0 (C), 163.1 (C), 140.7 (CH), 140.0 (C), 133.5 (CH), 131.8 (CH), 124.2 (C), 123.8 (CH), 120.2 (CH), 115.9 (C), 79.9 (CH), 74.9 (CH), 72.5 (CH), 70.6 (CH), 68.6 (CH), 62.3 (CH$_2$), 21.0 (2CH$_3$), 20.8 (CH$_3$), 20.5 (CH$_3$); HR-MS (ESI positive, m/z): found 576.0477/578.0460 ([M+Na]+), calc. for C$_{23}$H$_{24}$NO$_{10}$Na (M+Na): 576.0481/576.0461.

(2R,3R,4S,5R)-2-(acetoxyethyl)-6-(6-fluoro-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3c):
Following the general procedure above, acid 1c (0.35 mmol, 102 mg) and β-aminoglucose 7a (0.42 mmol, 145 mg) was stirred overnight at room temperature to afford a crude mixture of 2c with ratio \(Z\beta:E\beta:Z\alpha: 1/0.1/0.2\), determined by \(^1\text{H} \text{NMR}\) of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3c as mixture of 2 isomer β/α; yield 65\% (134 mg); ratio β/α: 1/0.1, determined by \(^1\text{H} \text{NMR}\) after first flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers were separated by preparative HPLC (water/ACN gradient from 40\% to 70\%).

- **Assigned to β-3c isomer**: white solid (122 mg, yield 59\%); m.p.: 97 – 99\°C; \(\text{R}_f = 0.4\) (Cyclohexan/EtOAc: 5/5); \([\alpha]^D\) +119 (c, 1.0 in CHCl\(_3\)); \(\text{IR}\) (neat): 1756, 1739, 1690, 1573, 1492, 1366, 1310, 1208, 1167, 1070, 1033, 962 \(\text{cm}^{-1}\); \(^1\text{H} \text{NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 – 7.85 (m, 1H), 7.55 (d, \(J = 9.2 \text{ Hz}, 1\text{H}\)), 7.36 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 6.84 (d, \(J = 9.8 \text{ Hz}, 1\text{H}\)), 6.62 (d, \(J = 9.4 \text{ Hz}, 1\text{H}\)), 5.83 (t, \(J = 9.1 \text{ Hz}, 1\text{H}\)), 5.46 (t, \(J = 9.1 \text{ Hz}, 1\text{H}\)), 5.38 – 5.27 (m, 1H), 4.39 – 4.19 (m, 2H), 4.03 (dd, \(J = 7.4, 1.8 \text{ Hz}, 1\text{H}\)), 2.09 (s, 6H), 1.93 (s, 3H), 1.80 (s, 3H); \(^{13}\text{C} \text{NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) 170.5 (C), 169.9 (C), 169.7 (C), 169.2 (C), 162.2 (C), 158.26 (d, \(J = 244.4 \text{ Hz}, 1\text{C}\)), 140.2 (CH), 134.2 (C), 122.42 (d, \(J = 8.2 \text{ Hz}, 1\text{CH}\)), 121.9 (CH), 118.52 (d, \(J = 9.8 \text{ Hz}, 1\text{CH}\)), 118.30 (d, \(J = 23.7 \text{ Hz}, 1\text{CH}\)), 114.43 (d, \(J = 22.4 \text{ Hz}, 1\text{CH}\)), 80.8 (CH), 75.2 (CH), 73.8 (CH), 68.0 (CH), 67.8 (CH), 61.8 (CH\(_2\)), 20.8 (CH\(_3\)), 20.7 (CH\(_3\)), 20.7 (CH\(_3\)), 20.2 (CH\(_3\)); HR-MS (ESI positive, m/z): found 494.1479 ([M+H]\(^+\)), calc. for C\(_{23}\)H\(_{25}\)NO\(_{10}\)F (M+H): 494.1462.

- **Assigned to α-3c isomer**: pale yellow solid (12 mg, yield 6\%); m.p.: 79 – 82\°C; \(\text{R}_f = 0.4\) (Cyclohexan/EtOAc: 5/5); \([\alpha]^D\) +64 (c, 1.0 in CHCl\(_3\)); \(\text{IR}\) (neat): 1746, 1669, 1572, 1494, 1446, 1368, 1310, 1217, 1052, 1034, \(\text{cm}^{-1}\); \(^1\text{H} \text{NMR}\) (300 MHz, CDCl\(_3\)) \(\delta\) 7.74 (dd, \(J = 9.3, 4.2 \text{ Hz}, 1\text{H}\)), 7.59 (d, \(J = 9.5 \text{ Hz}, 1\text{H}\)), 7.27 – 7.13 (m, 2H), 6.70 – 6.65 (m, 2H), 6.09 (t, \(J = 7.0 \text{ Hz}, 1\text{H}\)), 5.35 (t, \(J = 6.6 \text{ Hz}, 1\text{H}\)), 5.27 (t, \(J = 8.1 \text{ Hz}, 1\text{H}\)), 4.64 – 4.54 (m, 1H), 4.39 (dd, \(J = 12.5, 4.7 \text{ Hz}, 1\text{H}\)), 4.15 (dd, \(J = 12.4, 2.8 \text{ Hz}, 1\text{H}\)), 2.10 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 1.74 (s, 3H); \(^{13}\text{C} \text{NMR}\) (75 MHz, CDCl\(_3\)) \(\delta\) 170.8 (C), 169.9 (C), 169.2 (C), 162.2 (C), 158.26 (d, \(J = 244.4 \text{ Hz}, 1\text{C}\)), 140.2 (CH), 134.2 (C), 122.42 (d, \(J = 8.2 \text{ Hz}, 1\text{CH}\)), 121.9 (CH), 118.52 (d, \(J = 9.8 \text{ Hz}, 1\text{CH}\)), 118.30 (d, \(J = 23.7 \text{ Hz}, 1\text{CH}\)), 114.43 (d, \(J = 22.4 \text{ Hz}, 1\text{CH}\)), 80.8 (CH), 75.2 (CH), 73.8 (CH), 68.0 (CH), 67.8 (CH), 61.8 (CH\(_2\)), 20.8 (CH\(_3\)), 20.7 (CH\(_3\)), 20.7 (CH\(_3\)), 20.2 (CH\(_3\)); HR-MS (ESI positive, m/z): found 494.1479 ([M+H]\(^+\)), calc. for C\(_{23}\)H\(_{25}\)NO\(_{10}\)F (M+H): 494.1462.

(2R,3R,4S,5R)-2-(acetoxyethyl)-6-(7-fluoro-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyll triacetate (3d):
Following the general procedure above, acid 1c (0.35 mmol, 102 mg) and β-aminoglucose 7a (0.42 mmol, 145 mg) was stirred overnight at room temperature to afford a crude mixture of 2d with ratio Zβ/Eβ/Zα: 1/0.1/0.24, determined by $^1$H NMR of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3d as mixture of 2 isomer β/α; yield 62% (128 mg); ratio β/α: 1/0.2, determined by $^1$H NMR after first flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers were separated by preparative HPLC (water/ACN gradient from 40% to 70%).

- **Assigned to β-3d isomer:** white solid (107 mg, yield 52%); m.p.: 187 – 190 °C; Rf = 0.38 (Cyclohexan/EtOAc: 5/5); [α]$_D^{18}$ +104 (c, 1.0 in CHCl$_3$); IR (neat): 1752, 1739, 1668, 1573, 1445, 1380, 1310, 1232, 1133, 1097, 1031, 984 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.71 (d, J = 11.6 Hz, 1H), 7.59 (d, J = 9.5 Hz, 1H), 7.49 (dd, J = 8.6, 6.4 Hz, 1H), 6.99 (td, J = 8.3, 2.2 Hz, 1H), 6.85 (d, J = 9.7 Hz, 1H), 6.53 (d, J = 9.5 Hz, 1H), 5.81 (t, J = 9.4 Hz, 1H), 5.48 (t, J = 9.4 Hz, 1H), 5.40 (t, J = 9.6 Hz, 1H), 4.40 – 4.19 (m, 2H), 4.09 – 3.99 (m, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.82 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.7 (C), 169.9 (C), 169.8 (C), 163.8 (C), 162.5 (d, J = 224.7 Hz, C), 162.0 (C), 140.7 (CH), 139.2 (d, J = 12 Hz, C), 131.2 (d, J = 10.5 Hz, CH), 119.4 (CH), 118.0 (C), 111.5 (d, J = 23.2 Hz, CH), 104.3 (d, J = 29.2 Hz, CH), 80.8 (CH), 75.0 (CH), 73.6 (CH), 67.7 (CH), 61.3 (CH$_2$), 20.7 (3CH$_3$), 20.2 (CH$_3$); HR-MS (ESI positive, m/z): found 494.1479 ([M+H]$^+$), calc. for C$_{23}$H$_{25}$NO$_{10}$F (M+H): 494.1462.

- **Assigned to α-3d isomer:** white solid (21 mg, yield 10%); m.p.: 62 – 64.5°C; Rf = 0.38 (Cyclohexan/EtOAc: 5/5); [α]$_D^{18}$ +66.7 (c, 1.0 in CHCl$_3$); IR (neat): 1745, 1702, 1666, 1599, 1436, 1368, 1221, 1036, 848 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.79 – 7.56 (m, 2H), 7.47 (dd, J = 8.6, 6.3 Hz, 1H), 7.05 – 6.94 (m, 1H), 6.73 (d, J = 5.3 Hz, 1H), 6.58 (d, J = 9.5 Hz, 1H), 5.94 – 5.81 (m, 1H), 5.34 (t, J = 5.6 Hz, 1H), 5.22 (t, J = 6.9 Hz, 1H), 4.64 – 4.54 (m, 1H), 4.44 (dd, J = 12.3, 5.4 Hz, 1H), 4.21 (dd, J = 12.4, 3.3 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (75 MHz, Acetone) δ 170.7 (C), 170.1 (C), 169.9 (C), 169.8 (C), 164.2 (d, J = 246.1 Hz, C), 163.1 (C), 140.9 (CH), 131.7 (d, J = 10.2 Hz, CH), 121.2 (CH), 119.1 (CH), 111.3 (d, J = 23.3 Hz, CH), 105.3 (d, J = 28.9 Hz, CH$_2$), 79.3 (CH), 75.1 (CH), 71.6 (CH), 70.1 (CH), 68.0 (CH), 61.9 (CH$_2$), 20.8 (2CH$_3$), 20.6 (CH$_3$), 20.3 (CH$_3$); HR-MS (ESI positive, m/z): found 494.1479 ([M+H]$^+$), calc. for C$_{23}$H$_{25}$NO$_{10}$F (M+H): 494.1462.

(2R,3R,4S,5R)-2-(acetoxymethyl)-6-(7-chloro-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3e):

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Following the general procedure above, acid 1e (0.33 mmol, 93 mg) and β-aminoglucose 7a (0.36 mmol, 125 mg) was stirred overnight at room temperature to afford a crude mixture of 2e with ratio Zβ/Eβ/Zα: 1/0.05/0.2, determined by $^1$H NMR of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3e as mixture of 2 isomer β/α; yield 60% (91 mg); ratio β/α: 1/0.2, determined by $^1$H NMR after frist flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers was separated by
preparative HPLC (water/ACN gradient from 40% to 70%).

**Assigned to β-3e isomer:** white solid (76 mg, yield 50%); m.p.: 209 – 212°C; Rf = 0.29 (Cyclohexan/EtOAc: 5/5); [α]D18 = +110 (c, 1.0 in CHCl3); IR (neat): 1753, 1666, 1555, 1366, 1212, 11156, 1110, 1079, 1037 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (s, 1H), 7.57 (d, J = 9.5 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.22 (dd, J = 8.3, 1.6 Hz, 1H), 6.83 (d, J = 9.7 Hz, 1H), 6.55 (d, J = 9.5 Hz, 1H), 5.77 (t, J = 9.3 Hz, 1H), 5.47 (t, J = 9.3 Hz, 1H), 5.39 (t, J = 9.6 Hz, 1H), 4.33 (dd, J = 12.5, 2.9 Hz, 1H), 4.21 (dd, J = 12.5, 1.7 Hz, 1H), 4.08 – 3.97 (m, 1H), 2.16 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H), 1.80 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.6 (C), 169.8 (C), 169.4 (C), 169.0 (C), 162.0 (C), 140.5 (CH), 138.5 (C), 136.5 (C), 130.3 (CH), 123.7 (CH), 120.4 (CH), 119.7 (C), 116.9 (CH), 80.7 (CH), 75.0 (CH), 73.5 (CH), 67.7 (CH), 67.5 (CH), 61.0 (CH₂), 20.7 (CH₃), 20.6 (CH₃), 20.1 (CH₃); HR-MS (ESI positive, m/z): found 532.0986/534.0983 ([M+Na]⁺), calc. for C₂₃H₂₄NO₆ClNa (M+Na): 532.0986/534.0983.

**Assigned to α-3e isomer:** white solid (15 mg, yield 10%); m.p.: 93 – 95°C Rf = 0.29 (Cyclohexan/EtOAc: 5/5); [α]D18 = +58 (c, 1.0 in CHCl₃); IR (neat): 1745, 1665, 1591, 1553, 1429, 1369, 1221, 1143, 1051, 1034 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1H), 7.60 (d, J = 9.5 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.19 (dd, J = 8.3, 1.8 Hz, 1H), 6.78 (d, J = 4.8 Hz, 1H), 6.61 (d, J = 9.5 Hz, 1H), 5.80 (br s, 1H), 5.31 (d, J = 5.2 Hz, 1H), 5.18 (t, J = 6.4 Hz, 1H), 4.60 (td, J = 6.1, 3.5 Hz, 1H), 4.48 (dd, J = 12.3, 6.1 Hz, 1H), 4.23 (dd, J = 12.3, 3.5 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 1.73 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.7 (C), 169.8 (C), 169.5 (C), 162.6 (C), 140.2 (C), 140.1 (CH), 136.2 (C), 129.7 (CH), 123.4 (CH), 121.7 (CH), 119.9 (C), 117.7 (CH), 78.6 (CH), 73.9 (CH), 71.3 (CH), 69.6 (CH), 67.3 (CH), 61.3 (CH₂), 21.0 (CH₃), 20.9 (CH₃), 20.8 (CH₃), 20.4 (CH₃); HR-MS (ESI positive, m/z): found 532.0986/534.0983 ([M+Na]⁺), calc. for C₂₃H₂₄NO₆ClNa (M+Na): 532.0986/534.0983.

**(2R,3R,4S,5R)-2-(acetoxyethyl)-6-(6,7-dimethyl-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triy triacetate (3f):**

Following the general procedure above, acid 1f (0.3 mmol, 93 mg) and β-aminoglucose 7a (0.36 mmol, 125 mg) was stirred overnight at room temperature to afford a crude mixture of 2f with ratio Zβ/Eβ/Zα: 1/0.10/0.2, determined by ¹H NMR of crude reaction. This crude was use directly for the next step without purification, using the general procedure described above to afford compound 3f as mixture of 2 isomer β/α: yield 60% (91 mg); ratio β/α: 1/0.15, determined by ¹H NMR after frist flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers was separated by silica gel column chromatography (Cyclohexan/EtOAc 35%).

**Assigned to β-3f isomer:** yellow solid (79 mg, yield 52%); m.p.: 137 – 139 °C; Rf = 0.62 (Cyclohexan/EtOAc: 3/7); [α]D18 = +63 (c, 1.0 in CHCl₃); IR (neat): 1745, 1649, 1593, 1555, 1456, 1424, 1368, 1227, 1153, 1050, 103, 882 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (s, 1H), 7.54 (d, J = 9.4 Hz, 1H), 7.24 (s, 1H), 6.87 (d, J = 9.8 Hz, 1H), 6.50 (d, J = 9.4 Hz, 1H), 5.90 (t, J = 9.4 Hz, 1H), 5.46 (t, J = 9.4 Hz, 1H), 5.38 (t, J = 9.7 Hz, 1H), 4.36 (dd, J = 12.5, 3.6 Hz, 1H), 4.19 (dd, J =
12.5, 1.8 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H), 1.80 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.6 (C), 170.0 (C), 169.7 (C), 169.2 (C), 162.7 (C), 140.9 (CH), 140.2 (C), 136.1 (C), 132.1 (C), 129.7 (CH), 119.6 (C), 119.3 (CH), 117.6 (CH), 80.8 (CH), 75.1 (CH), 74.0 (CH), 67.9 (CH), 61.7 (CH2), 21.5(CH3), 20.8 (CH3), 20.7 (CH3), 20.6 (CH3), 19.7(CH3); HR-MS (ESI positive, m/z): found 526.1691 ([M+Na]+), calc. for C25H20NO10Na (M+Na): 526.1689.

- **Assigned to α-3e isomer:** white solid (12 mg, yield 8%); m.p.: 103 – 107°C; Rf = 0.68 (Cyclohexan/EtOAc: 3/7); [α]D 18 +80 (c, 1.0 in CDCl3); IR (neat): 1751, 1732, 1658, 1566, 1424, 1455, 1366, 1310, 1205, 1097, 1076, 1031 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.57 (d, J = 9.4 Hz, 1H), 7.41 (s, 1H), 7.24 (s, 1H), 6.59 – 6.53 (m, 2H), 6.29 (t, J = 7.5 Hz, 1H), 5.35 (t, J = 7.3 Hz, 1H), 5.31 – 5.24 (m, 1H), 4.72 – 4.63 (m, 1H), 4.40 (dd, J = 12.4, 4.3 Hz, 1H), 4.09 (dd, J = 12.3, 2.5 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H), 2.08 (s, 3H), 2.06 (s, 6H), 1.74 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.8 (C), 170.0 (C), 169.7 (C), 169.2 (C), 162.6 (C), 140.9 (CH), 140.5 (C), 138.7 (C), 132.0 (C), 129.1 (CH), 121.0 (CH), 119.6 (C), 116.5 (CH), 79.9 (CH), 73.4 (CH), 72.8 (CH), 70.8 (CH), 68.6 (CH), 62.0 (CH2), 21.1 (CH3), 20.9 (3CH3), 20.4 (CH3), 19.1 (CH3); HR-MS (ESI positive, m/z): found 526.1691 ([M+Na]+), calc. for C25H20NO10Na (M+Na): 526.1689.

(2R,3S,4R,5R)-2-(acetoxy methyl)-6-(2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3g):

Following the general procedure above, acid 1a (0.4 mmol, 110 mg) and β-aminogalactose 7b (0.48 mmol, 166 mg) was stirred overnight at room temperature to afford a crude mixture of 2g with ratio Zβ/Eβ/Zα: 1/0.04/0.27, determined by 1H NMR of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3g as mixture of 2 isomer β/α; yield 76% (145 mg); ratio β/α: 1/0.27, determined by 1H NMR after frist flash chromatography purification (elution: Cyclohexan/EtOAc 6:4). The two isomers was separated by silica gel column chromatography (Cyclohexan/EtOAc 35%).

- **Assigned to β-3g isomer:** yellow solid (114 mg, yield 60%); m.p.: 91 – 94°C; Rf = 0.29 (Cyclohexan/EtOAc: 5/5); [α]D 18 +62 (c, 1.0 in CHCl3); IR (neat): 1750, 1660, 1596, 1455, 1369, 1213, 1052, 1036, 917 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 8.20 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.26 (t, J = 7.1 Hz, 1H), 6.84 (d, J = 9.7 Hz, 1H), 6.59 (d, J = 9.5 Hz, 1H), 6.05 (t, J = 9.8 Hz, 1H), 5.61 (d, J = 2.8 Hz, 1H), 5.39 – 5.17 (m, 1H), 4.36 – 4.19 (m, 2H), 4.18 – 4.08 (m, 1H), 2.31 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.83 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.6 (C), 170.0 (C), 169.7 (C), 169.5 (C), 162.6 (C), 141.3 (CH), 138.0 (C), 130.3 (CH), 129.4 (CH), 123.2 (CH), 121.3 (C), 120.5 (CH), 116.9 (CH), 80.9 (CH), 73.7 (CH), 72.0 (CH), 67.6 (CH), 65.7 (CH), 61.6 (CH2), 21.0 (CH3), 20.8 (CH3), 20.7 (CH3), 20.4 (CH3); HR-MS (ESI positive, m/z): found 498.1376 ([M+Na]+), calc. for C23H25NO10Na (M+Na): 498.1376.

- **Assigned to α-3g isomer:** white solid (31 mg, yield 16%); m.p.: 61 – 63°C; Rf = 0.37 (Cyclohexan/EtOAc: 5/5); [α]D 18 +52.8 (c, 1.0 in CHCl3); IR (neat): 1745, 1702, 1661, 1565, 1370, 1249, 1211, 1070, 1045, 912 cm⁻¹; 1H NMR (300 MHz, Acetone) δ 7.98 (d, J = 8.4 Hz, 1H), 7.87
(d, J = 9.5 Hz, 1H), 7.65 (dd, J = 7.7, 1.1 Hz, 1H), 7.62 − 7.54 (m, 1H), 7.27 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 5.5 Hz, 1H), 6.57 (d, J = 9.5 Hz, 1H), 5.92 (s, 1H), 5.69 (t, J = 3.5 Hz, 1H), 5.44 (dd, J = 7.4, 5.9 Hz, 1H), 4.95 − 4.78 (m, 1H), 4.50 − 4.30 (m, 1H), 4.23 (dd, J = 11.8, 5.2 Hz, 1H), 2.17 (s, 3H), 2.04 (s, 4H), 1.98 − 1.85 (m, 4H), 1.63 (d, J = 18.7 Hz, 3H); 13C NMR (75 MHz, Acetonitrile) δ 170.8 (C), 170.7 (C), 170.2 (C), 170.2 (C), 163.5 (C), 141.9 (CH), 140.8 (C), 131.1 (CH), 129.8 (CH), 123.6 (CH), 122.4 (CH), 122.3 (C), 117.9 (CH), 79.7 (CH), 73.8 (CH), 73.8 (CH), 69.8 (CH), 67.8 (CH), 61.8 (CH2), 20.9 (CH3), 20.8 (CH3), 20.7 (CH3), 20.3 (CH3); HR-MS (ESI positive, m/z): found 498.1376 ([M+Na]+), calc. for C22H25NO10Na (M+Na): 498.1376.

\((2R,3S,4S,5R)\)-2-(acetoxyethyl)-6-(6-bromo-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3h)

Following the general procedure above, acid 1b (0.28 mmol, 100 mg) and β-aminogalactose 7b (0.42 mmol, 144 mg) was stirred overnight at room temperature to afford a crude mixture of 2h with ratio Zβ/Eβ: 1/0.5, determined by 1H NMR of crude reaction. This crude was used directly for the next step without purification, using the general procedure described above to afford compound 3h as mixture of 2 isomer β/α; yield 55% (0.15 mmol, 85 mg); ratio β/α: 1/0.27, determined by 1H NMR after flash chromatography purification (elution: Cyclohexane/EtOAc 6:4). The two isomers was separated by preparative HPLC (water/ACN gradient from 40 to 70%).

- **Assigned to β-3h isomer**: white solid (67 mg, yield 43%); m.p.: 155 − 158°C; \( \Delta_r \) = 0.4 (Cyclohexane/EtOAc: 5/5); \( [\alpha]_D^{20} \) +55 (c, 1.0 in CHCl3); IR (neat): 1753, 1669, 1586, 1486, 1431, 1368, 1231, 1101, 1060, 1035, cm−1; 1H NMR (300 MHz, CDCl3) δ 8.08 (d, J = 9.2 Hz, 1H), 7.68 − 7.44 (m, 3H), 6.78 (d, J = 9.7 Hz, 1H), 6.59 (d, J = 9.5 Hz, 1H), 5.93 (t, J = 9.7 Hz, 1H), 5.59 (d, J = 3.0 Hz, 1H), 5.27 (dd, J = 9.8, 3.0 Hz, 1H), 4.30 − 4.18 (m, 2H), 4.16 − 4.04 (m, 1H), 2.29 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.82 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.4 (C), 169.9 (C), 169.5 (2C), 162.0 (C), 139.9 (CH), 136.9 (C), 133.0 (CH), 131.4 (CH), 122.8 (C), 121.6 (CH), 118.6 (CH), 116.0 (C), 80.8 (CH), 73.7 (CH), 71.7 (CH), 67.6 (CH), 65.6 (CH), 61.5 (CH2), 20.9 (CH3), 20.7 (CH3), 20.6 (CH3), 20.3 (CH3); HR-MS (ESI positive, m/z): found 576.0475/578.0469 ([M+Na]+), calc. for C23H24BrNO10Na (M+Na): 576.0481/578.0461.

- **Assigned to α-3h isomer**: white solid (18 mg, yield 12%); m.p.: 114 − 116°C; \( \Delta_r \) = 0.4 (Cyclohexane/EtOAc: 5/5); \( [\alpha]_D^{20} \) +47 (c, 1.0 in CHCl3); IR (neat): 1756, 1739, 1658, 1566, 1494, 1455, 1366, 1310, 1205, 1097, 1076, 1031, 984 cm−1; 1H NMR (300 MHz, CDCl3) δ 7.79 (d, J = 7.3 Hz, 1H), 7.69 − 7.49 (m, 3H), 6.93 (d, J = 4.3 Hz, 1H), 6.65 (d, J = 9.5 Hz, 1H), 5.81 (br s, 1H), 5.68 (t, J = 3.7 Hz, 1H), 5.45 (dd, J = 6.9, 5.3 Hz, 1H), 4.86 − 4.69 (m, 1H), 4.38 (dd, J = 11.9, 7.2 Hz, 1H), 4.22 (dd, J = 11.9, 5.4 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.66 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.7 (C), 170.0 (C), 169.7 (2C), 162.5 (C), 139.5 (CH), 138.5 (C), 132.8 (CH), 130.8 (CH), 122.9 (CH), 119.1 (CH), 115.8 (C), 78.7 (CH), 73.1 (CH), 69.8 (CH), 69.3 (CH), 66.6 (CH), 60.6 (CH2), 20.9 (2CH3), 20.8 (CH3), 20.5 (CH3); HR-MS (ESI positive, m/z): found 576.0471/578.0461 ([M+Na]+), calc. for C22H24BrNO10Na (M+Na): 576.0461.
Following the general procedure above, acid 1a (0.4 mmol, 110 mg) and α-aminomannose 7c (0.48 mmol, 166 mg) was stirred overnight at room temperature to afford a crude mixture of 2i, ratio Zβ/Eβ/Zα could not determined by $^1$H NMR of crude reaction. This crude was use directly for the next step without purification, using the general procedure described above to afford compound 3i as mixture of 2 isomer β/α; yield 68% (130 mg); ratio β/α: 0.17/1, determined by $^1$H NMR after frist flash chromatography purification. The two isomers was separated by preparative HPLC (water/ACN gradient from 40 to 70%).

- **Assigned to β-3i isomer (min):** yellow solid (19 mg, yield 10%); m.p.: 69 – 72°C; $R_f$ = 0.23 (Cyclohexan/EtOAc: 5/5); $\alpha$ $^1$D $^18$ -16 (c, 1.0 in CHCl$_3$); IR (neat): 1743, 1702, 1665, 1566, 1455, 1369, 1248, 1137, 1070, 1036 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J$ = 8.2 Hz, 1H), 7.62 (d, $J$ = 9.5 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.28 – 7.18 (m, 1H), 6.96 (br s, 1H), 6.61 (d, $J$ = 9.5 Hz, 1H), 6.13 (dd, $J$ = 8.6, 3.8 Hz, 1H), 5.76 (br s, 1H), 5.18 (dd, $J$ = 4.5, 3.2 Hz, 1H), 4.63 (dd, $J$ = 13.0, 8.7 Hz, 1H), 4.47 – 4.40 (m, 2H), 2.24 (s, 3H), 2.19 (s, 3H), 2.05 (s, 3H), 1.85 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.7 (C), 169.4 (C), 162.8 (C), 140.8 (CH), 138.4 (C), 130.4 (CH), 129 (CH), 123.1 (CH), 121.5 (C), 121.4 (CH), 116.3 (CH), 75.1 (CH), 68.5 (CH), 68.4 (2CH), 64.8 (CH), 61.0 (CH$_2$), 21.1 (CH$_3$), 20.9 (CH$_3$), 20.9(CH$_3$), 20.5(CH$_3$); HR-MS (ESI positive, m/z): found 476.1553 ([M+H]$^+$), calc. for C$_{23}$H$_{25}$NO$_{10}$ (M+H): 476.1557.

- **Assigned to α-3i isomer (maj):** yellow solid (111 mg, yield 58%); m.p.: 70 – 73°C; $R_f$ = 0.32 (Cyclohexan/EtOAc: 5/5); $\alpha$ $^1$D $^18$ -16 (c, 1.0 in CHCl$_3$); IR (neat): 1740, 1655, 1564, 1453, 1367, 1221, 1059 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.38 (d, $J$ = 8.8 Hz, 1H), 7.61 (d, $J$ = 9.5 Hz, 1H), 7.49 – 7.37 (m, 2H), 7.17 (t, $J$ = 7.2 Hz, 1H), 6.81 (d, $J$ = 1.4 Hz, 1H), 6.60 (d, $J$ = 9.5 Hz, 1H), 5.69 (dd, $J$ = 3.3, 1.4 Hz, 1H), 5.54 – 5.45 (m, 1H), 5.42 (dd, $J$ = 10.1, 3.4 Hz, 1H), 4.32 (dd, $J$ = 12.4, 4.6 Hz, 1H), 4.23 (dd, $J$ = 12.4, 2.5 Hz, 1H), 3.94 (dd, $J$ = 9.3, 4.6, 2.5 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 1.96 (s, 3H), 1.70 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5 (C), 169.9 (C), 169.5 (C), 169.4 (C), 162.1 (C), 141.0 (CH), 138.5 (C), 129.1 (CH), 128.7 (CH), 122.8 (CH), 121.4 (C), 120.8 (CH), 119.3 (CH), 82.8 (CH), 76.1 (CH), 70.7 (CH), 69.8 (CH), 65.7 (CH), 62.2 (CH$_2$), 20.8 (CH$_3$), 20.8 (CH$_3$), 20.6 (CH$_3$); HR-MS (ESI positive, m/z): found 476.1561 ([M+H]$^+$), calc. for C$_{23}$H$_{25}$NO$_{10}$ (M+H): 476.1557.


Following the general procedure above, acid 1a (0.37 mmol, 100 mg) and β-aminocellulose 7d (0.44 mmol, 279 mg) was stirred overnight at room temperature to afford a crude mixture of 2j. Ratio Zβ/Eβ/Zα: 1/0.08/0.25 determined by 1H NMR of crude reaction. This crude was use directly for the next step without purification, using the general procedure described above to afford compound 3j as mixture of 2 isomer β/α; yield 64 % (180 mg); ratio β/α: 1.0/0.25, determined by 1H NMR after first flash chromatography purification (elution: Cyclohexan/EtOAc 4:6). The two isomers were separated by silica gel column chromatography (Cyclohexan/EtOAc 35 to 55%).

- **Assigned to β-3j isomer**: brown solid (144 mg, yield 51%); m.p.: 187 - 191°C; Rf = 0.32 (Cyclohexan/EtOAc: 5/5); yield 57%, [α] D 18 +32 (c, 1.0 in CHCl3); IR (neat): 1757, 1738, 1659, 1567, 1435, 1367, 131q, 1208, 1136, 1034, 907 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.84 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 9.5 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.26 – 7.20 (m, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.57 (d, J = 9.5 Hz, 1H), 5.85 (t, J = 9.3 Hz, 1H), 5.40 (t, J = 9.3 Hz, 1H), 5.18 – 4.97 (m, 2H), 4.97 (t, J = 8.4 Hz, 1H), 4.73 – 4.47 (m, 2H), 4.41 (dd, J = 12.5, 4.0 Hz, 1H), 4.21 (dd, J = 12.1, 4.0 Hz, 1H), 4.14 – 4.03 (m, 2H), 3.97 – 3.88 (m, 1H), 3.75 – 3.67 (m, 1H). 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.01 (s, 6H), 1.99 (s, 3H), 1.77 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.6 (C), 170.4 (C), 170.2 (C), 169.6 (C), 169.4 (C), 169.1 (C), 162.4 (C), 141.0 (CH), 137.8 (C), 130.2 (CH), 129.5 (CH), 123.2 (C), 121.4 (C), 120.7 (CH), 116.6 (CH), 100.7 (CH), 80.7 (CH), 76.2 (CH), 75.9 (CH), 73.6 (CH), 73.0 (CH), 72.2 (CH), 71.7 (CH), 67.9 (CH), 61.7 (CH), 20.9 (CH3), 20.8 (CH3), 20.7 (4CH3), 20.3 (CH3); HR-MS (ESI positive, m/z): found 764.2410 ([M+H]+);, calc. for C35H28NO18 (M+H): 764.2402.

- **Assigned to α-3j isomer**: yellow solid (36 mg, yield 13%); m.p.: 71 - 75°C; Rf = 0.21 (Cyclohexan/EtOAc: 5/5); yield 7%; [α] D 18 +14 (c, 1.0 in CHCl3); IR (neat): 1758, 1740, 1658, 1565, 1454, 1367, 1212, 1038, 907 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.96 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.58 – 7.42 (m, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 4.2 Hz, 1H), 6.61 (d, J = 9.4 Hz, 1H), 5.86 (s, 1H), 5.39 – 5.16 (m, 2H), 5.10 – 5.02 (m, 2H), 4.78 (d, J = 7.9 Hz, 1H), 4.51 (dd, J = 9.8, 6.1 Hz, 1H), 4.44 (dd, J = 12.1, 3.6 Hz, 1H), 4.38 – 4.24 (m, 2H), 4.07 (dd, J = 12.3, 1.7 Hz, 1H), 3.94 (t, J = 5.8 Hz, 1H), 3.77 (dd, J = 10.0, 2.5 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.71 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.5 (C), 169.9 (C), 169.5 (C), 169.4 (C), 162.1 (C), 141.0 (CH), 138.5 (C), 129.1 (CH), 128.7 (CH), 122.8 (CH), 121.4 (C), 120.8 (CH), 119.3 (CH), 82.8 (CH), 76.1 (CH), 70.7 (CH), 69.8 (CH), 65.7 (CH), 62.2 (2CH2), 20.8 (CH3), 20.8 (CH3), 20.6 (CH3); HR-MS (ESI positive, m/z): found 764.2410 ([M+H]+), calc. for C35H28NO18 (M+H): 764.2402.

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((2R,3R,4S,5R)-4,5-diacetoxy-2-(acetoxymethyl)-6-(2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3k)
Following the general procedure above, acid 1b (0.2 mmol, 70 mg) and β-aminocellulose 7d (0.24 mmol, 152 mg) was stirred overnight at room temperature to afford a crude mixture of 2k, ratio Zβ/Eβ/Zα: 1/0.08/0.2 determined by $^1$H NMR of crude reaction. This crude was use directly for the next step without purification, using the general procedure described above to afford compound 3k as mixture of 2 isomer β/α; yield 60% (100 mg): ratio β/α: 1/0.2, determined by $^1$H NMR after frist flash chromatography purification (elution: Cyclohexan/EtOAc 4:6). The two isomers were separated by silica gel column chromatography (Cyclohexan/EtOAc 35 to 55%).

- **Assigned to β-3k isomer**: brown solid (83 mg, yield 50%); m.p.: 160 – 162°C; $[\alpha]_D^{18}$ +18 (c, 1.0 in CHCl$_3$); IR (neat): 1757, 1668, 1588, 1430, 1366, 1228, 1208, 1166, 1036, 907 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.8$ Hz, 1H), 7.62 (d, $J = 2.1$ Hz, 1H), 7.59 – 7.44 (m, 2H), 6.77 (d, $J = 9.7$ Hz, 1H), 6.59 (d, $J = 9.5$ Hz, 1H), 5.87 – 5.67 (m, 1H), 5.38 (t, $J = 9.3$ Hz, 1H), 5.17 – 4.96 (m, 2H), 5.04 – 4.91 (m, 1H), 4.69 – 4.52 (m, 2H), 4.41 (dd, $J = 12.5$, 4.0 Hz, 1H), 4.20 (dd, $J = 12.1$, 4.0 Hz, 1H), 4.10 – 4.02 (m, 2H), 3.96 – 3.89 (m, 1H), 3.76 – 3.62 (m, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.01 (s, 6H), 1.76 (s, 3H), 1.79 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.6 (C), 170.4 (C), 170.1 (C), 169.6 (C), 169.5 (C), 169.4 (C), 169.0 (C), 161.9 (C), 139.7 (CH), 136.6 (C), 133.0 (CH), 131.6 (CH), 122.9 (C), 121.9 (C), 118.2 (CH), 116.1 (C), 100.7 (CH), 80.7 (CH), 76.3 (CH), 75.8 (CH), 73.4 (CH), 73.0 (CH), 72.2 (CH), 71.7 (CH), 67.9 (CH), 61.7 (2CH$_2$), 20.9 (CH$_3$), 20.8(CH$_3$), 20.7 (4CH$_3$), 20.2 (CH$_3$); HR-MS (ESI positive, m/z): found 864.1325 ([M+Na]$^+$), calc. for C$_{35}$H$_{40}$BrNO$_{18}$Na (M+Na): 864.1326.

- **Assigned to α-3k isomer**: yellow solid (17 mg, yield 10%); m.p.: 106 – 109°C; $[\alpha]_D^{18}$ +19 (c, 1.0 in CHCl$_3$); IR (neat): 1757, 1739, 1658, 1566, 1494, 1455, 1366, 1310, 1205, 1097, 1076, 1031, 984 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 9.1$ Hz, 1H), 7.74 – 7.48 (m, 3H), 6.89 (d, $J = 3.5$ Hz, 1H), 6.64 (d, $J = 9.4$ Hz, 1H), 5.74 (br s, 1H), 5.33 – 5.15 (m, 2H), 5.11 – 5.02 (m, 2H), 4.73 (d, $J = 7.9$ Hz, 1H), 4.49 – 4.35 (m, 3H), 4.30 (dd, $J = 12.4$, 4.7 Hz, 1H), 4.08 (dd, $J = 12.5$, 1.5 Hz, 1H), 3.87 (t, $J = 4.7$ Hz, 1H), 3.77 (ddd, $J = 9.9$, 4.6, 1.7 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H), 1.76 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.7 (C), 170.6 (C), 170.3 (C), 169.6 (C), 169.5 (C), 169.3 (C), 169.2 (C), 162.3 (C), 139.7 (CH), 138.1 (C), 132.6 (CH), 130.5 (CH), 122.9 (C), 122.4 (CH), 120.8 (CH), 115.8 (C), 101.5 (CH), 77.6 (CH), 75.7 (CH), 74.5 (CH), 72.9 (CH), 72.2 (CH), 71.5 (CH), 69.6 (CH), 69.2 (CH), 68.2 (CH), 61.8 (CH$_2$), 61.3 (CH$_2$), 21.0 (CH$_3$), 20.9 (CH$_3$), 20.9 (CH$_3$), 20.8 (CH$_3$), 20.7 (3CH$_3$); HR-MS (ESI positive, m/z): found 864.1325 ([M+Na]$^+$), calc. for C$_{35}$H$_{40}$BrNO$_{18}$Na (M+Na): 864.1326.

1-((3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)quinolin-2(1H)-one (3I):
Following the general procedure above, acid 1a (0.55 mmol, 150 mg) and β-aminoglucose 7a (0.66 mmol, 230 mg) was stirred overnight at room temperature to afford a crude mixture of 2a, ratio Zβ/Eβ/Zα: 1/0.06/0.2 determined by 1H NMR of crude (as compound 2a). This crude reaction (without purification) was added directly to a freshly prepared solution of NaOMe (1.5 equiv) in MeOH (3 mL). The mixture was stirred at room temperature for 30 mins, then Dowex 50WX4 was added. After 1 hours, the crude reaction was filtered to remove the resin and concentrated under vacuum to obtain mixture of glycosyl acrylamide, ratio Zβ/Eβ/Zα: 1/0.08/0/25. This mixture was used for the intramolecular N-arylation, using the general procedure described above to afford compound 3l after first flash chromatography purification (elution: EtOAc/Acetone 8:2) as mixture of 2 isomer β/α; yield 68 % (115 mg); ratio β/α: 1/0.26, determined by the 1H NMR. The two isomers was separated by preparative HPLC (water/ACN: gradient from 5 to 30%).

- Assigned to β-3l isomer: white solid (92 mg, yield 54%); m.p.: 224 – 225°C; Rf = 0.45 (MeOH/EtOAc: 1/9); [α]D18 +11.7 (c, 1.0 in MeOH); IR (neat): 3367, 1752, 1650, 1587, 1453, 1315, 1243, 1119, 1072, 1020, 975 cm⁻¹; 1H NMR (300 MHz, MeOD) δ 8.11 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 9.4 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 9.4 Hz, 1H), 6.56 (d, J = 9.8 Hz, 1H), 4.29 (t, J = 8.6 Hz, 1H), 3.94 (d, J = 12.0 Hz, 1H), 3.80 (dd, J = 12.1, 4.3 Hz, 1H), 3.67 – 3.48 (m, 3H); 13C NMR (75 MHz, MeOD) δ 165.2 (C), 142.5 (CH), 139.0 (C), 131.2 (CH), 130.3 (CH), 124.2 (CH), 123.2 (C), 121.4 (CH), 119.2 (CH), 84.9 (CH), 81.8 (CH), 79.6 (CH), 71.3 (CH), 70.6 (CH), 62.6 (CH₂); HR-MS (ESI positive, m/z): found 330.0954 ([M+Na]+), calc. for C15H17NO6Na (M+Na): 330.0954.

- Assigned to α-3l isomer: white solid (24 mg, yield 14%); m.p.: 104 – 107°C; Rf = 0.45 (MeOH/EtOAc: 1/9); [α]D18 -3 (c, 1.0 in MeOH); IR (neat): 3359, 1752, 1650, 1591, 1487, 1453, 1381, 1283, 1205, 1067, 1011, 990 cm⁻¹; 1H NMR (300 MHz, MeOD) δ 8.02 (d, J = 8.7 Hz, 1H), 7.92 (d, J = 9.4 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.59 (ddd, J = 8.7, 7.4, 1.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 9.4 Hz, 1H), 6.37 (d, J = 3.8 Hz, 1H), 4.75 (d, J = 3.7 Hz, 1H), 4.24 (d, J = 2.6 Hz, 1H), 4.14 – 3.98 (m, 2H), 3.77 (dd, J = 11.5, 1.9 Hz, 1H), 3.63 (dd, J = 11.5, 5.1 Hz, 1H); 13C NMR (75 MHz, MeOD) δ 164.7 (C), 142.9 (CH), 139.9 (C), 132.0 (CH), 130.3 (CH), 124.6 (CH), 122.8 (C), 122.0 (CH), 117.4 (CH), 93.3 (CH), 81.0 (CH), 80.4 (CH), 79.4 (CH), 70.4 (CH), 65.1 (CH₂); HR-MS (ESI positive, m/z): found 330.0954 ([M+Na]+), calc. for C15H17NO6Na (M+Na): 330.0954.

6-bromo-1-((2S,3S,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)quinolin-2(1H)-one (3m):
mmol, 100 mg) was stirred overnight at room temperature to afford a crude mixture of galactamide, ratio Zβ/Eα/Zα: 0.20/0.10/0.1 determined by 1H NMR of crude. This crude reaction (without purification) was added directly to a freshly prepared solution of NaOMe (1.5 equiv) in MeOH (3 mL). The mixture was stirred at room temperature for 30 mins, then Dowex 50WX4 was added. After 1 hour, the crude reaction was filtered to remove the resin and concentrated under vacuum to obtain mixture of glycosyl acrylamide, ratio Eα/Zα: 0.09/1 determined by 1H NMR of crude. This mixture was used for the intramolecular N-arylation, using the general procedure described above. The final crude was purified by preparative HPLC (H2O/ACN: gradient form 10 to 40%) to afford compound α-3m isomer as single product: white solid, yield 55 % (50 mg); m.p.: 219–221 °C; Rf = 0.45 (MeOH/EtOAc: 1/9); [α]D18 = -18.4 (c, 1.0 in MeOH); IR (neat): 3367, 1750, 1660, 1581, 1315, 1243, 1110, 1072, 1020, 975 cm⁻¹; 1H NMR (300 MHz, MeOH) δ 8.67 (d, J = 9.4 Hz, 1H), 7.87 (d, J = 9.4 Hz, 1H), 7.77 (d, J = 2.2 Hz, 1H), 7.56 (dd, J = 9.5, 2.2 Hz, 1H), 6.68 (d, J = 9.4 Hz, 1H), 6.42 (d, J = 1.0 Hz, 1H), 4.22 (d, J = 2.1 Hz, 1H), 3.98 (dd, J = 12.0, 2.2 Hz, 1H), 3.90 – 3.81 (m, 2H), 3.76 (dd, J = 9.5, 3.4 Hz, 1H), 3.54 – 3.43 (m, 1H); 13C NMR (101 MHz, MeOD) δ 164.7 (C), 141.2 (C), 133.7 (CH), 124.8 (C), 122.6 (CH), 121.7 (CH), 116.7 (C), 86.0 (CH), 79.8 (CH), 76.2 (CH), 70.4 (C), 68.4 (CH), 62.8 (CH2). HR-MS (ESI positive, m/z): found 408.0060 ([M+Na]+), calc. for C15H16NBrO6Na (M+Na): 408.0060.

6-bromo-1-((3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)quinolin-2(1H)-one (3n):

Following the general procedure above, acid 1b (0.26 mmol, 92 mg) and β-aminogalactose 7b (0.31 mmol, 135 mg) was stirred overnight at room temperature to afford a crude mixture of galactamide, ratio Zβ/Eβ/Zα: 1/0.10/0.25 determined by 1H NMR of crude. This crude reaction (without purification) was added directly to a freshly prepared solution of NaOMe (1.5 equiv) in MeOH (3 mL). The mixture was stirred at room temperature for 30 mins, then Dowex 50WX4 was added. After 1 hour, the crude reaction was filtered to remove the resin and concentrated under vacuum to obtain mixture of glycosyl acrylamide, ratio could not determined by 1H NMR of crude. This mixture was used for the intramolecular N-arylation, using the general procedure described above to afford compound 3n after frist flash chromatography purification (elution: EtOAc/MeOH: 95/5) as mixture of 2 isomer β/α; yield 60 % (60 mg); ratio β/α: 1/0.22, determined by the 1H NMR. The two isomers was separated by preparative HPLC (water/ACN: gradient from 10 to 40%).

Assigned to β-3n isomer: white solid (49 mg, yield 49%); m.p.: 151–153 °C; Rf = 0.45 (MeOH/EtOAc: 2/8); [α]D18 = +57 (c, 1.0 in MeOH); IR (neat): 3367, 1750, 1660, 1581, 1315, 1243, 1110, 1072, 1010, 975 cm⁻¹; 1H NMR (400 MHz, MeOD) δ 8.33 (d, J = 9.3 Hz, 1H), 7.79 (d, J = 9.8 Hz, 2H), 7.59 (dd, J = 9.2, 2.2 Hz, 1H), 6.64 (d, J = 9.5 Hz, 1H), 6.47 (d, J = 9.6 Hz, 1H), 4.49 (t, J = 9.3 Hz, 1H), 4.03 (d, J = 2.6 Hz, 1H), 3.86 – 3.73 (m, 3H), 3.66 (dd, J = 9.1, 2.9 Hz, 1H); 13C NMR (101 MHz, MeOD) δ 164.7 (C), 141.2 (C), 138.1 (C), 133.7 (CH), 132.1 (CH), 124.8 (C), 122.6 (CH), 121.7 (CH), 116.7 (C), 86.0 (CH), 79.8 (CH), 76.2 (CH), 70.4 (C), 68.4 (CH), 62.8 (CH2).
- **Assigned to α-3n isomer**: white solid (11 mg, yield 11%); m.p.: 93–95 °C; Rf = 0.45 (MeOH/EtOAc: 1/9); [α]D25 -24 (c, 1.0 in MeOH); IR (neat): 3359, 1752, 1650, 1591, 1487, 1453, 1381, 1283, 1205, 1067, 1011, 990 cm⁻¹; ¹H NMR (300 MHz, MeOD) δ 7.88 (d, J = 1.5 Hz, 1H), 7.85 (d, J = 9.5 Hz, 1H), 7.80 – 7.71 (m, 2H), 6.66 (d, J = 9.5 Hz, 1H), 6.60 (d, J = 7.1 Hz, 1H), 5.11 – 5.00 (m, 1H), 4.47 – 4.34 (m, 2H), 3.84 – 3.76 (m, 1H), 3.74 – 3.60 (m, 2H); ¹³C NMR (75 MHz, MeOD) δ 164.8, 141.1, 139.2, 134.3, 132.5, 124.6, 123.8, 118.7, 116.7, 91.1, 84.0, 77.8, 77.7, 72.4, 64.3.

5. **General procedure for Suzuki coupling of 3b with aryl boronic acids and characterization data of 4a-c**

5.1. **Geneal procedure for Suzuki coupling of β-3b with aryl boronic acids:**

A Schlenk tube was charged with β-3b (45 mg, 0.08 mmol, 1 equiv.), arylboronic acid (1.25 equiv.), S-Phos (5 mol%), cesium carbonate (3 equiv.), Pd₂(dba)₃ (2 mmol %), and a stirring bar. The tube was closed with a rubber septum and was evacuated and flushed with argon. This procedure was repeated once, and then freshly degassed dioxane (1 mL) was added under a stream of argon. The reaction tube was quickly sealed and the contents were stirred at 80°C overnight. The reaction mixture was cooled to rt, diluted with EtOAc (10 mL), washed with satd aq NaHCO₃ (5 mL) and brine (5 mL), and dried over MgSO₄. The solvents were removed in vacuo, and the residue was purified by flash chromatography on silica gel (Cyclohexan/EtOAc, 50%) to give 4a-c as desired product.

5.2. **Characterization data of 4a-c**

![Compound β-4a](image-url)

Compound β-4a was prepared by using β-3b (0.09 mmol, 50 mg) and (3,4-dichlorophenyl)boronic acid (0.11 mmol, 21 mg), following the general procedure. The residue was purified by flash chromatography over silica gel (cyclohexan/EtOAc 40%) to afford the desired products β-4a as white powder, yield: 65% (36 mg); Rf = 0.48 (cyclohexan/EtOAc 4/6); m.p.: 124.2 – 127.2°C; [α]D25 +45 (c, 1.0 in CHCl₃); IR (neat): 1754, 1671, 1571, 1437, 1367, 1229, 1152, 1080, 1037, 906 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.02 (d, J = 8.7 Hz, 1H), 7.76 – 7.65 (m, 4H), 7.54 (d, J = 8.4 Hz, 1H), 7.44 (dd,
J = 8.4, 2.0 Hz, 1H), 6.89 (d, J = 10.0 Hz, 1H), 6.65 (d, J = 9.6 Hz, 1H), 5.93 (t, J = 9.2 Hz, 1H), 5.49 (t, J = 9.4 Hz, 1H), 5.39 (t, J = 9.7 Hz, 1H), 4.34 (dd, J = 12.4, 4.1 Hz, 1H), 4.24 (dd, J = 12.5, 2.2 Hz, 1H), 4.10 – 4.00 (m, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H), 1.83 (s, 3H); ²³C NMR (75 MHz, CDCl₃) δ 170.5 (C), 169.9 (C), 169.8 (C), 169.3 (C), 162.3 (C), 141.1 (CH), 139.6 (C), 137.5 (C), 133.8 (C), 133.3 (C), 132.0 (C), 131.1 (CH), 129.1 (CH), 128.9 (CH), 127.5 (CH), 126.3 (CH), 121.8 (C), 121.3 (C)H, 117.5 (CH), 80.8 (CH), 75.3 (CH), 73.9 (CH), 68.1 (CH), 67.9 (CH), 61.8 (CH₂), 20.9 (CH₃), 20.8 (CH₃), 20.7 (CH₃), 20.3 (CH₂); HR-MS (ESI positive, m/z): found 642.0909 ([M+Na]⁺), calc. for C₂₉H₂₇NCl₂O₁₀Na (M+Na): 642.0910.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(6-(4-fluorophenyl)-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyi triacetate (β-4a): 

Compound β-4b was prepared by using β-3b (0.07 mmol, 40 mg) and (4-fluorophenyl)boronic acid (0.09 mmol, 16 mg), following the general procedure. The residue was purified by flash chromatography over silica gel (cyclohexan/EtOAC 40%) to afford the desired products β-4b as white powder, yield: 76% (31 mg); R₇= 0.46 (cyclohexan/EtOAc 5/5); m.p.: 117 – 119.6 °C; [α]D¹⁸ -11.6 (c, 1.0 in CHCl₃); IR (neat): 1756, 1665, 1602, 1566, 1492, 1367, 1034, 918 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (d, J = 8.8 Hz, 1H), 7.80 – 7.63 (m, 3H), 7.69 – 7.57 (m, 2H), 7.16 (t, J = 8.6 Hz, 2H), 6.90 (d, J = 10.1 Hz, 1H), 6.63 (d, J = 9.5 Hz, 1H), 5.95 (t, J = 9.3 Hz, 1H), 5.49 (t, J = 9.4 Hz, 1H), 5.40 (t, J = 9.7 Hz, 1H), 4.33 (dd, J = 12.3, 4.0 Hz, 1H), 4.24 (dd, J = 12.6, 1.9 Hz, 1H), 4.05 (ddd, J = 9.5, 3.9, 1.9 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H), 1.83 (s, 3H); ²³C NMR (75 MHz, CDCl₃) δ 170.4 (C), 169.8 (C), 169.6 (C), 169.2 (C), 162.61 (d, J = 247.2 Hz, C), 162.23 (C), 141.1 (CH), 136.8 (C), 135.57 (d, J = 2.7 Hz, C), 135.22 (C), 129.1 (CH), 128.52 (d, J = 8.0 Hz, 2CH), 127.2 (CH), 121.5 (C), 120.9 (CH), 117.2 (CH), 115.87 (d, J = 21.5 Hz, CH), 80.6 (CH), 75.1 (CH), 73.8 (CH), 67.9 (CH), 67.8 (CH), 61.7 (CH₂), 20.7 (CH₂), 20.6 (CH₃), 20.6 (CH₃), 20.1 (CH₃); HR-MS (ESI positive, m/z): found 592.1610 ([M+Na]⁺), calc. for C₂₉H₂₈NFO₁₀Na (M+Na): 592.1595.

(2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(6-(4-acetylt phenyl)-2-oxoquinolin-1(2H)-yl)tetrahydro-2H-pyran-3,4,5-triyi triacetate (β-4c):
Compound β-4c was prepared by using β-3b (0.08 mmol, 45 mg) and (4-acetylphenyl)boronic acid (0.1 mmol, 16 mg), following the general procedure. The residue was purified by flash chromatography over silica gel (cyclohexane/EtOAc 40%) to afford the desired products β-4c as white powder, yield: 76% (31 mg); Rf = 0.41 (cyclohexane/EtOAc 3/7); m.p.: 194-196 °C; [α]D18 +20 (c, 1.0 in CHCl3); IR (neat): 17531, 16663, 1573, 1439, 1365, 1211, 1152, 1099, 1034, 959 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 8.05 (d, J = 8.3 Hz, 3H), 7.86 – 7.65 (m, 5H), 6.89 (d, J = 9.9 Hz, 1H), 6.64 (d, J = 9.5 Hz, 1H), 5.94 (t, J = 9.4 Hz, 1H), 5.49 (t, J = 9.3 Hz, 1H), 5.39 (t, J = 9.8 Hz, 1H), 4.33 (dd, J = 12.5, 4.2 Hz, 1H), 4.23 (dd, J = 12.5, 2.0 Hz, 1H), 4.11 – 3.99 (m, 1H), 2.61 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H), 1.82 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 197.6 (C), 170.5 (C), 169.9 (C), 169.7 (C), 169.3 (C), 162.3 (C), 144.0 (C), 141.1 (CH), 137.6 (C), 136.2 (C), 134.8 (C), 129.3 (CH), 129.2 (2CH), 127.8 (CH), 127.1 (2CH), 121.7 (C), 121.2 (CH), 117.5 (CH), 80.8 (CH), 75. (CH), 73.9 (CH), 68.0 (CH), 67.9 (CH), 61.8 (CH2), 26.8 (CH3), 20.9 (CH3), 20.7 (CH3), 20.7 (CH3), 20.2 (CH3); HR-MS (ESI positive, m/z): found 616.1794 ([M+Na]^+), calc. for C31H31NO11Na (M+Na): 616.179
$^1\text{H NMR spectrum of 6a (300 MHz, CDCl}_3\text{)}$
H NMR spectrum of 1a (300 MHz, Acetone –D6)
$^1$H NMR spectrum of 6b (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6b (75 MHz, CDCl$_3$)
H NMR spectrum of 1b (300 MHz, CDCl$_3$)

$^{1}$H NMR spectrum of 1b (300 MHz, CDCl$_3$)
The provided image contains a 13C NMR spectrum of a compound labeled as $1b$. The spectrum is taken at 75 MHz in CDCl$_3$. The peak assignments are indicated on the plot, with chemical shifts ranging from approximately 10 to 200 ppm. The spectrum shows distinct peaks corresponding to different chemical environments within the compound.
$^1$H NMR spectrum of 6c (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6c (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 1c (300 MHz, CDCl$_3$)
The image contains a 12C NMR spectrum of compound 1c, recorded at 75 MHz in CDCl3. The spectrum shows various peaks at different ppm values, indicating the chemical shifts of different carbon atoms in the molecule. The spectrum is typical of a C12 NMR, with peaks ranging from 15 to 180 ppm, highlighting the chemical structure and its functional groups.
$^{1}$H NMR spectrum of 6d (300 MHz, CDCl$_3$)
$^{12}$C NMR spectrum of 6d (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 1d (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1d (75 MHz, CDCl$_3$)
1H NMR spectrum of 6e (300 MHz, CDCl₃)
$^{13}$C NMR spectrum of 6e (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 1e (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 1e (75 MHz, Acetone –D6)
$^{1}$H NMR spectrum of 6f (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 6f (75 MHz, CDCl$_3$)
$^{1}H$ NMR spectrum of 1f (300 MHz, Acetone-D$_6$)
$^{13}$C NMR spectrum of 1f (75 MHz, Acetone-D6)
$^{1}$H NMR spectrum of 2a - Zβ (300 MHz, CDCl$_3$)
$\text{CNMR spectrum of 2a - Z\text{\textbeta} (75 MHz, CDCl}_3\text{)}$
$^{13}$C NMR spectrum of 2a - $E\beta$ (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 2a - Za (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 2a - Zα (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3a – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3a – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3a – $\alpha$ isomer (400 MHz, CDCl₃)
$^{13}$C NMR spectrum of 3a – α isomer (100 MHz, Acetone –D6)
$^{1}$H NMR spectrum of 3b – β isomer (300 MHz, CDCl₃)
$^{13}$C NMR spectrum of 3b – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3b – α isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3b – α isomer (75 MHz, Acetone –D6)
$^1$H NMR spectrum of 3c – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3c – β isomer (75 MHz, CDCl$_3$)
H NMR spectrum of 3c –α isomer (300 MHz, CDCl₃)
$^{13}$C NMR spectrum of 3c – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3d – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3d – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3d – α isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3d – α isomer (75 MHz, Acetone –D6)
$^{1}$H NMR spectrum of 3e – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3e – $\beta$ isomer (75 MHz, CDCl$_3$)
NMR spectrum of 3e – α isomer (300 MHz, CDCl₃)

1H NMR spectrum of 3e – α isomer (300 MHz, CDCl₃)
$^{13}$C NMR spectrum of 3e – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3f – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of $\text{3f} - \beta$ isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3f – $\alpha$ isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3f – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3g – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3g – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3g – α isomer (300 MHz, Acetone-D$_6$)
$^{13}$C NMR spectrum of 3g – α isomer (300 MHz, Acetone –D6)
$^1$H NMR spectrum of 3h – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3h – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3h – α isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3h – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3i – α isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3i – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3i – β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3i – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3j – β isomer (300 MHz, CDCl$_3$)

3j (β - isomer)
$^{13}$C NMR spectrum of 3j – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3j – α isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3j – α isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3k –β isomer (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 3k – β isomer (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 3k – α isomer (300 MHz, CDCl$_3$)
\textbf{13C NMR spectrum of 3k - α isomer (75 MHz, CDCl$_3$)}
\( ^1H \) NMR spectrum of 3I –\( \beta \) isomer (300 MHz, Methanol – D4)
$\text{CNMR spectrum of 3l} \ - \ \beta \text{ isomer} \ (75 \text{ MHz, Methanol – D4})$
$^1$H NMR spectrum of 3l – α isomer (300 MHz, Methanol – D4)
\(^{13}\)C NMR spectrum of 3I – \(\alpha\) isomer (75 MHz, Methanol – D4)
$^1$H NMR spectrum of 3m –α isomer (300 MHz, Methanol – D4)
$^{13}$C NMR spectrum of $\alpha$–3m (75 MHz, Methanol – D4)
$^1$H NMR spectrum of 3n – β isomer (400 MHz, Methanol – D4)
$^{13}$C NMR spectrum of 3n – β isomer (100 MHz, Methanol – D4)
$^1$H NMR spectrum of 3n-α isomer (300 MHz, Methanol – D4)
$^{13}$C NMR spectrum of 3n - $\alpha$ isomer (100 MHz, Methanol – D4)
$^1$H NMR spectrum of 4a (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 4a (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 4b (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 4b (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of 4c (300 MHz, CDCl$_3$)
$^{13}$C NMR spectrum of 4c (75 MHz, CDCl$_3$)