Supporting information

Synthesis of photolabile protecting group (PPG) protected uronic acid building blocks: Applications in carbohydrate synthesis with the assistance of continuous flow photoreactor

Varsha Tiwari, a# Adesh Kumar Singh, a# Priyanka Chaudhary, a Peter H. Seeberger, b Jeyakumar Kandasamy a*  

a Department of Chemistry, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh-221005, India. E-mail: jeyakumar.chy@iitbhu.ac.in  
b Max-Planck-Institute of Colloids and Interfaces, Department of Biomolecular Systems, Am Mühlenberg 1, 14476 Potsdam, Germany  
# These authors contributed equally to this work  

Table of Contents

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Content</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General information</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>(a)- General procedure for synthesis of uronic acid esters with 2-nitrobenzyl bromide (1a-10)</td>
<td>2-5</td>
</tr>
<tr>
<td></td>
<td>(b)- General procedure for synthesis of uronic acid esters (1m-1n)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Analytical data of 2-nitrobenzyl protected uronic acid esters (1a-10 and 4a-4d)</td>
<td>5 - 12</td>
</tr>
<tr>
<td>4</td>
<td>Experimental procedure for deprotection of photolabile 2-nitrobenzyl protecting group by using a continuous flow photoreactor</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>Analytical data for various deprotected uronic acids (2a-2o)</td>
<td>13-18</td>
</tr>
<tr>
<td>6</td>
<td>Procedure for synthesis of D-Glucopyranuronic acid, 2,3,4-tris-O- (phenylmethyl)-, 2-nitrophenylmethylene, 1-(2,2,2-trichloroethanimidate) (1aa)</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>General procedure for glycosylation</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>Analytical data for various deprotected uronic acids (5a-5d)</td>
<td>19-21</td>
</tr>
<tr>
<td>10</td>
<td>Copy of 1H and 13C-NMR spectra of intermediates and final compounds</td>
<td>22</td>
</tr>
</tbody>
</table>
1. General Information
Starting materials were prepared using literature procedures or modified procedures. Solvents and chemicals were purchased from commercial sources and used without further purification. Thin layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV), and then further analyzed by charring in stain solution (5% H$_2$SO$_4$ in MeOH). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate/hexane and methanol/ethyl acetate as an eluent. The Continuous Flow Photoreactor was constructed with the help of M/s Lelesil innovative systems, Mumbai, India. The NMR spectra were recorded on BrukerAvance 500 MHz NMR spectrometer and Mass spectra were measured on Water’s Quattro Micro V 4.1. All given $^{13}$C spectra are proton decoupled. The $^1$H NMR and $^{13}$C NMRs of the monosaccharide primary alcohol and corresponding uronic acids were compared with literature reports.

2 (a)- General procedure for synthesis of uronic acid esters with 2-nitrobenzyl bromide: (1a-1o)

To a stirred solution of appropriate uronic acid (0.5 equiv.) in dry DMF, KHCO$_3$ (4.0 equiv.), Bu$_4$NI (0.2 equiv.) and 2-nitrobenzyl bromide (3 equiv.) were added under argon atmosphere. The resulting mixture was stirred for 16 h at room temperature. After completion, the reaction mixture was filtered on celite. The filtrate was washed with water (2×50 mL) and dried over anhydrous sodium sulfate. The solvent was concentrated under reduced pressure to provide crude product which was purified by column chromatography on silica gel of 100-200 mesh size. Ethyl acetate/hexane was used as an eluent.
(b)- Preparation of uronic acid esters 1m and 1n:

**1m preparation**: The compound AA (3.0 g, 8.0 mmol) was stirred in dry pyridine (20 mL) in the presence of tert-butylidemethylsilyl chloride (1.81 g, 12.0 mmol) for overnight at room temperature. After completion, the reaction mixture was evaporated till dryness and dissolved in ethyl acetate. The resulting solution was washed with 0.1N HCl solution and brine solution. The crude was subjected for the column chromatography on silica (30% EtOAc: Hexane) to afford the primary TBDMS protected compound as a colorless syrup (3.13 g, 80% yield). The TBDMS protected compound (1.0 g, 2.0 mmol) was dissolved in DMF (20 ml) at 0°C to which NaH (98 mg, 2 equiv.) followed by 4-bromobenzylbromide (562 mg, 1.1 eq.) was added. The reaction was stirred until TLC starting material got consumed. The reaction was quenched using water (5 mL) and diluted with ethyl acetate (20 mL). The ethyl acetate layer was washed with cold water and evaporated in vacuo. The crude product was further dried under high vacuum and dissolved in THF (20 ml) to which TBAF (3.0 equiv.) was added and stirred until starting material disappeared. The solvent was evaporated and the residue was dissolved in ethyl acetate and washed with brine. The organic layer was evaporated in vacuo and purified using column chromatography (20% EtOAc: Hexane) to afford the pure compound AB (723 mg, 70%) as yellowish oil.

To a vigorously stirred solution of AB (700 mg, 1.3 mmol) in DCM and H₂O was added TEMPO (0.3 eq) and 1-chloro-1, 2-benziodoxol-3(1H)-one (CBI) (909 mg, 2.5 eq). Stirring was allowed until TLC indicated complete conversion of the starting material to a lower running spot (~ 45 min). The reaction mixture was quenched by the addition of 10 ml Na₂S₂O₃ solution (10% in H₂O). The mixture was then extracted twice with EtOAc (10 ml)
and the combined organic layers were dried (Na₂SO₄), filtered and concentrated. The crude compound was purified by column chromatography using EtOAc/petroleum ether which afforded the pure glucuronic acid (560 mg, 78%). Further the glucuronic acid (279 mg, 0.5 mmol) was converted into corresponding 2-nitrobenzyl ester 1m by using the general procedure (2a) mentioned above. The reaction provided 1m as pale yellow viscous liquid (325 mg, 94%).

**In preparation:** The same procedure was adopted as above described for the preparation of 1m. In the place of 4-bromobenzylbromide, 2-naphthylmethylbromide (497mg, 1.1 eq.) was used. The compound AC was obtained as yellowish oil (736 mg, 75%). Corresponding glucuronic acid was obtained as pale yellow viscous compound (532 mg, 74%). The ester 1n was obtained as pale yellow viscous liquid (309 mg, 93%)

((2R,3R,4S,5R,6R)-4,5-bis(benzyloxy)-3-((4-bromobenzyl)oxy)-6-methoxytetrahydro-2H-pyran-2-yl)methanol (AB):

![Image of AB](image)

Yellowish oil (667 mg, 60%); Rf value =0.4 in 20% EtOAc/Hexane. IR: νmax(neat) 3320, 1099, 652 cm⁻¹,[α]D²⁴ = +45.0 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 7.40 (dd, J = 8.6, 1.9 Hz, 2H), 7.35–7.26 (m, 10H), 7.11 (d, J = 8.4 Hz, 2H), 4.98 (d, J = 11.0 Hz, 1H), 4.83–4.73 (m, 3H), 4.64 (d, J = 12.1 Hz, 1H), 4.57 (dd, J = 7.4, 3.9 Hz, 2H), 3.98 (t, J = 9.3 Hz, 1H), 3.76 (dd, J = 11.7, 2.4 Hz, 1H), 3.69–3.62 (m, 2H), 3.52–3.47 (m, 2H), 3.35 (s, 3H), 1.95 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 138.8, 138.1, 137.3, 131.6, 129.5, 128.6, 128.5, 128.2, 128.0, 127.9, 127.7, 121.7, 98.2, 81.9, 80.1, 77.6, 75.8, 74.2, 73.4, 70.8, 61.8, 55.3. HRMS: Calc. for C₂₈H₃₆BrO₆[M+H]⁺: 543.1382, Observed: 543.1383

((2R,3R,4S,5R,6R)-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)tetrahydro-2H-pyran-2-yl)methanol (AC):

![Image of AC](image)

Yellowish oil (685 mg, 65%); Rf value =0.4 in 20% EtOAc/Hexane. IR: νmax(neat) 3233, 1052, 631 cm⁻¹,[α]D²⁴ = +25.0 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 7.79–7.74 (m, 3H), 7.69 (s, 1H), 7.45–7.41 (m, 2H), 7.39 (dd, J = 8.4, 1.6 Hz, 1H), 7.36–7.24 (m,
10H), 5.01 (dd, J = 11.1, 6.6 Hz, 2H), 4.85 (d, J = 11.0 Hz, 1H), 4.79 (dd, J = 11.7, 7.1 Hz, 2H), 4.65 (d, J = 12.1 Hz, 1H), 4.57 (d, J = 3.6 Hz, 1H), 4.04 (t, J = 9.3 Hz, 1H), 3.78 (dd, J = 11.5, 2.3 Hz, 1H), 3.72–3.66 (m, 2H), 3.58 (t, J = 9.3 Hz, 1H), 3.51 (dd, J = 9.6, 3.6 Hz, 1H), 3.35 (s, 3H), 1.89 (s, 1H). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (dd, J = 5.9, 3.6 Hz, 1H), 7.53 (dd, J = 5.7, 3.5 Hz, 1H), 7.47–7.43 (m, 2H), 7.41–7.32 (m, 11H), 7.27 (dd, J = 4.8, 1.7 Hz, 2H), 7.21–7.19 (m, 2H), 5.60–5.53 (m, 2H), 5.02 (d, J = 10.9 Hz, 1H), 4.90–4.84 (m, 3H), 4.69 (t, J = 7.7 Hz, 2H), 4.60 (d, J = 11.0 Hz, 1H), 4.34 (d, J = 10.0 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.84 (t, J = 9.5 Hz, 1H), 3.64 (dd, J = 9.6, 3.5 Hz, 1H), 3.47 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.1, 147.1, 138.4, 137.9, 133.9, 131.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 125.0, 98.8, 81.5, 79.4, 79.3, 75.9, 75.0, 73.6, 70.3, 63.7, 55.7. HRMS: Calc. for C$_{32}$H$_{34}$O$_6$ [M+H]$^+$: 515.2434, Observed: 515.2436

3. Analytical data of 2-nitrobenzyl protected uronic acid esters:

**α-D-Glucopyranosiduronic acid, methyl-2,3,4-tri-O-(phenylmethyl)-2-nitrophenylmethyl ester (1a)**

Pale yellow viscous liquid (289 mg, 94%), $R_f$ value =0.7 in 30% EtOAc/Hexane. IR: $\nu_{\text{max}}$(neat) 1742, 1425, 1120, 1090 cm$^{-1}$. $[\alpha]_D^{24} = -21.7$ [c 0.1, CHCl$_3$]; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (dd, J = 5.9, 3.6 Hz, 1H), 7.53 (dd, J = 5.7, 3.5 Hz, 1H), 7.47–7.43 (m, 2H), 7.41–7.32 (m, 11H), 7.27 (dd, J = 4.8, 1.7 Hz, 2H), 7.21–7.19 (m, 2H), 5.60–5.53 (m, 2H), 5.02 (d, J = 10.9 Hz, 1H), 4.90–4.84 (m, 3H), 4.69 (t, J = 7.7 Hz, 2H), 4.60 (d, J = 11.0 Hz, 1H), 4.34 (d, J = 10.0 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.84 (t, J = 9.5 Hz, 1H), 3.64 (dd, J = 9.6, 3.5 Hz, 1H), 3.47 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.1, 147.1, 138.4, 137.9, 133.9, 131.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.7, 125.0, 98.8, 81.5, 79.4, 79.3, 75.9, 75.0, 73.6, 70.3, 63.7, 55.7. HRMS: Calc. for C$_{32}$H$_{34}$O$_6$ [M+H]$^+$: 614.2390, Observed: 614.2397.

**α-D-Glucopyranosiduronic acid, methyl-2,3,4-tri-O-benzoyl-2-nitrophenylmethyl ester (1b)**

Pale yellow viscous liquid (304 mg, 91%); $R_f$ value =0.4 in 30% EtOAc/Hexane. IR: $\nu_{\text{max}}$(neat) 1750, 1719, 1420, 1099 cm$^{-1}$. $[\alpha]_D^{24} = +93.0$ [c 0.1, CHCl$_3$]; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16–8.10 (m, 2H), 8.00 (dd, J = 17.6, 9.4 Hz, 3H), 7.77 (d, J = 7.7 Hz, 1H), 7.70 (dd, J= 11.9, 5.7 Hz, 2H), 7.62–7.33 (m, 11H), 5.86 (t, J = 9.6 Hz, 1H), 5.73 (d, J = 6.8 Hz, 1H), 5.51–5.41 (m, 1H), 5.26 (tdd, J = 42.0, 9.9, 3.6 Hz, 2H), 5.00 (s, 1H), 4.60 (d, J = 10.1 Hz, 1H), 4.49 (d, J = 9.8 Hz, 1H), 4.22 (td, J = 9.5, 2.7 Hz, 1H), 3.52 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.0, 167.5, 166.8, 165.9, 147.4, 136.8, 134.1, 134.0, 133.6, 133.5, 133.4, 133.4, 131.3, 129.9, 129.9, 129.8, 129.4, 129.2, 129.0,
129.0, 128.9, 128.9, 128.4, 128.4, 128.4, 127.9, 125.2, 125.0, 97.5, 72.6, 71.0, 70.6, 64.1, 62.5, 56.0. HRMS: Calc. for C_{35}H_{30}NO_{12}[M+H]^+: 656.1768, Obsr. 656.1772.

**α-D-Glucopyranosiduronic acid, methyl 2, 3-di-O-acetyl-4-O-benzyl-2-nitrophenoxyethyl ester (1c)**

Pale yellow viscous liquid (240 mg, 93%); R_f value = 0.36 in 30% EtOAc/Hexane. IR: ν_{max}(neat) 1745, 1735, 1410, 1215, 1090 cm^{-1}, [α]_D^{23} = +44.5 [c 0.1, CHCl_3];^1H NMR (500 MHz, CDCl_3) δ 8.15–8.13 (m, 1H), 7.54–7.48 (m, 3H), 7.29–7.27 (m, 4H), 7.20–7.18 (m, 2H), 5.65–5.56 (m, 3H), 5.00 (d, J = 3.5 Hz, 1H), 4.90 (dd, J = 10.2, 3.6 Hz, 1H), 4.59 (s, 2H), 4.40 (d, J = 9.9 Hz, 1H), 3.96 (t, J = 9.6 Hz, 1H), 3.48 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H). ^13C NMR (125 MHz, CDCl_3) δ 170.3, 169.7, 168.4, 147.2, 137.3, 133.9, 131.4, 128.8, 128.5, 128.4, 127.9, 127.8, 125.1, 97.4, 77.6, 74.7, 71.3, 70.9, 69.9, 63.9, 55.7, 20.8, 20.7. HRMS: Calc. for C_{35}H_{32}NO_{11}[M+H]^+: 518.1662, Obsr. 518.1668

**α-D-Glucopyranosiduronic acid, methyl 2, 3-di-O-benzoyl-4-O-benzyl-2-nitrophenoxyethyl ester (1d)**

Yellow viscous liquid (312 mg, 95%); R_f value = 0.42 in 30% EtOAc/Hexane. IR: ν_{max}(neat) 1736, 1716, 1290, 1088, 1375 cm^{-1}, [α]_D^{24} = +62.9 [c 0.1, CHCl_3];^1H NMR (500 MHz, CDCl_3) δ 8.16 (dd, J = 8.0, 1.2 Hz, 1H), 8.01–7.98 (m, 4H), 7.60–7.48 (m, 5H), 7.40 (ddd, J = 12.9, 7.5, 5.3 Hz, 4H), 7.16–7.08 (m, 5H), 6.11 (t, J = 9.7 Hz, 1H), 5.65 (q, J = 15.2 Hz, 2H), 5.26–5.21 (m, 2H), 4.63–4.58 (m, 2H), 4.55 (d, J = 9.9 Hz, 1H), 4.21 (t, J = 9.5 Hz, 1H), 3.50 (s, 3H). ^13C NMR (125 MHz, CDCl_3) δ 168.4, 165.8, 165.4, 147.0, 136.9, 133.9, 133.3, 133.2, 131.4, 129.8, 129.6, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.8, 125.0, 97.5, 77.4, 74.7, 71.8, 71.7, 70.0, 63.8, 55.8. HRMS: Calc. for C_{35}H_{32}NO_{11}[M+H]^+: 642.1975, Obsr. 642.1970

**α-D-Mannopyranosiduronic acid, methyl-2, 3, 4-tri-O-(phenylmethyl)-2-nitrophenoxyethyl ester (1e)**

Pale yellow viscous liquid (261 mg, 85%); R_f value = 0.5 in 20% EtOAc/Hexane. IR: ν_{max}(neat) 1752, 1445, 1135, 1075 cm^{-1}, [α]_D^{24} = +4.7 [c 0.1, CHCl_3];^1H NMR (500 MHz, CDCl_3) δ 8.11–8.13 (m, 1H), 7.55–7.53 (m, 1H), 7.45–7.22 (m, 18H), 5.54 (q, J = 15.3 Hz, 2H), 4.94 (d, J = 2.9 Hz, 1H), 4.85–4.73 (m, 3H), 4.66–4.60 (m, 3H), 4.36–4.27 (m, 2H), 3.93 (dd, J = 8.1, 3.0 Hz, 1H), 3.80 (t, J = 3.1 Hz, 1H), 3.46 (s, 3H). ^13C NMR (125 MHz, CDCl_3) δ 168.8, 147.1, 138.2, 138.0, 138.0, 133.8, 131.9, 128.5, 128.5, 128.3, 128.3, 127.8, 127.7, 127.6, 127.6, 125.0,
α-D-Mannopyranosiduronic acid, methyl 2, 3, 4-tri-O-benzoyl-2-nitrophenylmethyl ester (1f)

Pale yellow solid (291 mg, 89%); M.P:133-135 °C; Rf value = 0.6 in 30% EtOAc/Hexane. IR: ν max (neat) 1755, 1729, 1414, 1040 cm⁻¹. [α]D⁻²⁵ = -60.2 [c 0.1, CHCl₃].¹H NMR (500 MHz, CDCl₃) δ 8.14–8.08 (m, 4H), 7.99–7.97 (m, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.63–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.46–7.37 (m, 7H), 7.30–7.27 (m, 2H), 6.14 (t, J = 10.1 Hz, 1H), 5.95 (dd, J = 10.1, 3.3 Hz, 1H), 5.74 (dd, J = 3.1, 1.7 Hz, 1H), 5.03 (s, 1H), 4.75 (dd, J = 12.1, 2.4 Hz, 1H), 4.54 (dd, J = 12.1, 4.4 Hz, 1H), 4.47–4.39 (m, 1H), 3.57 (s, 3H).¹³C NMR (125 MHz, CDCl₃) δ 166.2, 165.5, 165.4, 133.4, 133.4, 133.1, 133.0, 129.8, 129.8, 129.7, 129.7, 129.3, 129.1, 129.0, 128.6, 128.47, 128.3, 98.7, 70.4, 70.0, 68.7, 66.9, 62.9, 55.6. HRMS: Calc. for C₃₅H₃₆NO₉ [M+H]⁺: 614.2390, Observed: 614.2386

β-D-Glucopyranosiduronic acid, phenyl 2, 3, 4-tri-O-benzoyl-1-thio-2-nitrophenylmethyl ester (1g)

Yellow viscous liquid (338 mg, 92%); Rf value = 0.48 in 30% EtOAc/Hexane. IR: ν max (neat) 1748, 1718, 1422, 1140 cm⁻¹. [α]D⁻²⁴ = +18.7 [c 0.1, CHCl₃].¹H NMR (500 MHz, CDCl₃) δ 8.07 (dd, J = 8.0, 1.5 Hz, 1H), 8.00–7.98 (m, 2H), 7.86–7.82 (m, 4H), 7.58–7.28 (m, 17H), 5.94 (t, J = 9.4 Hz, 1H), 5.73 (t, J = 9.7 Hz, 1H), 5.65–5.51 (m, 3H), 5.11 (d, J = 9.9 Hz, 1H), 4.51 (d, J = 9.8 Hz, 1H).¹³C NMR (125 MHz, CDCl₃) δ 165.9, 165.6, 165.0, 164.9, 147.2, 133.8, 133.7, 133.4, 133.4, 133.3, 131.0, 130.9, 129.9, 129.8, 129.8, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 125.0, 86.4, 77.2, 76.6, 73.5, 70.0, 69.9, 64.3. HRMS: Calc. for C₄₀H₃₂NO₁₁S [M+H]⁺: 734.1696, Observed: 734.1699

β-D-Glucopyranosiduronic acid, phenyl-2, 3, 4-tris-O-(phenylmethyl)-1-thio-2-nitrophenylmethyl ester (1h)

Pale yellow viscous liquid (311 mg, 90%); Rf value = 0.6 in 30% EtOAc/Hexane. IR: ν max (neat) 1743, 1520, 1145, 1130 cm⁻¹. [α]D⁻²⁴ = -2.9 [c 0.1, CHCl₃].¹H NMR (500 MHz, CDCl₃) δ 8.18–8.10 (m, 1H), 7.56–7.20 (m, 22H), 5.53 (d, J = 5.3 Hz, 2H), 5.28 (d, J = 3.1 Hz, 1H), 4.94 (d, J = 10.8 Hz, 1H), 4.87–4.80 (m, 3H), 4.71 (d, J = 11.8 Hz, 1H), 4.61 (t, J = 10.4 Hz, 2H), 4.04 (t, J = 9.0 Hz, 1H), 3.84 (t, J = 9.2 Hz, 1H), 3.65 (dd, J = 9.1, 3.3 Hz, 3H).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.99–7.97 (m, 2H), 7.84–7.80 (m, 4H), 7.52 (dd, $J = 10.5, 4.2$ Hz, 2H), 7.46–7.38 (m, 8H), 7.32–7.25 (m, 5H), 7.13 (d, $J = 7.9$ Hz, 2H), 5.93 (t, $J = 9.4$ Hz, 1H), 5.69 (t, $J = 9.7$ Hz, 1H), 5.58 (dd, $J = 38.5, 14.8$ Hz, 2H), 5.48 (t, $J = 9.6$ Hz, 1H), 5.04 (d, $J = 9.9$ Hz, 1H), 4.48 (d, $J = 9.8$ Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.9, 165.6, 165.0, 164.9, 147.2, 139.1, 134.4, 133.7, 133.4, 133.4, 133.3, 131.0, 129.8, 129.8, 129.8, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.4, 128.3, 126.8, 125.0, 86.5, 76.6, 73.5, 70.0, 69.9, 64.2, 21.2. HRMS: Calc. for C$_{41}$H$_{34}$NO$_{12}$S $^{[\text{M+H}]^+}$: 748.1853, Obsr. 748.1855
α-D-Glucopyranosiduronic acid, methyl-2-nitrophenylmethyl ester-2, 3-dibenzoate (1k)
Pale yellow viscous liquid (177 mg, 83%); Rf value = 0.5 in 40% EtOAc/Hexane. IR: νmax(neat) 3250, 1756, 1718, 1360, 1180, 1080 cm⁻¹ [α]D²³ = +134.5 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 8.2 Hz, 1H), 8.00–7.95 (m, 4H), 7.73–7.68 (m, 1H), 7.50 (dd, J = 4.5, 2.9 Hz, 3H), 7.36 (t, J = 7.5 Hz, 5H), 5.89–5.85 (m, 1H), 5.71 (q, J = 15.0 Hz, 2H), 5.25 (s, 2H), 4.49 (d, J = 9.9 Hz, 1H), 4.22 (t, J = 9.6 Hz, 1H), 3.49 (s, 3H), 3.47 (d, J = 0.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 168.9, 165.7, 162.5, 147.1, 133.9, 133.3, 133.2, 131.3, 129.7, 129.7, 129.1, 128.9, 128.8, 128.7, 128.3, 128.2, 125.0, 97.4, 72.4, 71.0, 70.6, 70.5, 63.9, 55.8. HRMS: Calc. for C₂₈H₂₆NO₁₁ [M+H]⁺: 552.1506, Obs. 552.1501

(2S)-2-nitrobenzyl-2-((3aR, 6R, 6aR)-1-benzyl-6-(benzoxyl)-2-oxohexahydrofuro[3, 2-d]oxazol-5-yl)-2-hydroxyacetate (1l)
Pale yellow viscous liquid (214 mg, 80%); Rf value = 0.6 in 50% EtOAc/Hexane. IR: νmax(neat) 3355, 1762, 1751, 1290, 1120, 1075 cm⁻¹. [α]D²⁴ = -48.6 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 8.10–8.09 (m, 1H), 7.52–7.45 (m, 3H), 7.41–7.38 (m, 3H), 7.29–7.27 (m, 4H), 7.24–7.22 (m, 2H), 7.12–7.10 (m, 2H), 6.22 (d, J = 5.5 Hz, 1H), 5.61 (dd, J = 80.6, 14.8 Hz, 2H), 4.85 (d, J = 3.6 Hz, 1H), 4.69 (d, J = 15.1 Hz, 1H), 4.32 (s, 2H), 4.20–4.17 (m, 2H), 4.10 (d, J = 5.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 166.0, 156.3, 147.3, 136.2, 134.9, 133.8, 131.1, 129.2, 129.1, 129.0, 128.6, 128.3, 128.2, 127.6, 125.0, 101.0, 80.0, 79.9, 77.2, 72.4, 63.8, 63.7, 47.6. HRMS: Calc. for C₂₈H₂₇N₂O₅ [M+H]⁺: 535.1717, Obs. 535.1723

(2S,3S,4S,5R,6R)-2-nitrobenzyl-4,5-bis(benzyloxy)-3-(4-bromobenzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylate (1m)
Pale yellow viscous liquid (325 mg, 94%); Rf value = 0.52 in 20% EtOAc/Hexane. IR: νmax(neat)1730, 1520, 1250, 1070, 565 cm⁻¹ [α]D²⁴ = -7.8 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 8.17–8.06 (m, 1H), 7.50–7.46 (m, 3H), 7.38–7.28 (m, 12H), 7.02 (d, J = 8.1 Hz, 2H), 5.57 (q, J = 15.0 Hz, 2H), 4.99 (d, J = 10.9 Hz, 1H), 4.83–4.76 (m, 3H), 4.69–4.66 (m, 2H), 4.50 (d, J = 11.3 Hz, 1H), 4.29 (d, J = 10.0 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 3.77 (t, J = 9.5 Hz, 1H), 3.61 (dd, J = 9.6, 3.5 Hz, 1H), 3.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 169.0,
(2S,3S,4S,5R,6R)-2-nitrobenzyl-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)-tetrahydro-2H-pyran-2-carboxylate (1n)

Pale yellow viscous liquid (309 mg, 93%); Rf value = 0.5 in 20% EtOAc/Hexane. IR: \( \nu_{\text{max}} \) (neat) 1735, 1515, 1268, 1077 cm\(^{-1}\). \([\alpha]_D^{25} = -8.9 \ [c \ 0.1, \text{CHCl}_3]\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.03 (d, \( J = 7.9 \) Hz, 1H), 7.79–7.78 (m, 1H), 7.73–7.68 (m, 2H), 7.61 (s, 1H), 7.47–7.25 (m, 17H), 5.50 (dd, \( J = 45.3, 15.2 \) Hz, 2H), 5.03 (dd, \( J = 11.0, 5.5 \) Hz, 2H), 4.87 (dd, \( J = 14.7, 11.6 \) Hz, 2H), 4.71 (dd, \( J = 21.0, 8.6 \) Hz, 3H), 4.36 (d, \( J = 9.9 \) Hz, 1H), 4.10 (t, \( J = 9.2 \) Hz, 1H), 3.88 (t, \( J = 9.5 \) Hz, 1H), 3.66 (dd, \( J = 9.6, 3.4 \) Hz, 1H), 3.47 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 169.0, 147.0, 138.4, 137.9, 135.3, 133.7, 133.1, 132.9, 131.4, 128.5, 128.4, 128.1, 128.0, 128.0, 127.8, 127.6, 126.4, 126.0, 125.9, 125.7, 124.9, 98.8, 81.5, 79.4, 79.3, 75.9, 75.1, 73.6, 70.3, 63.7, 55.7. HRMS: Calc. for C\(_{35}\)H\(_{34}\)BrNO\(_3\)[M+H]\(^{+}\): 691.1417, Obsd. 691.1415

\[\beta-D-\text{Glucopyranosiduronic acid, phenyl-4-0-[6-methyl-2, 3, 4-tris-0-(phenylmethyl)-}\beta-D-\text{mannopyranuronosyl]-2, 3-bis-0-(phenylmethyl)-1-thio-2-nitrophosphorylmethyl ester (1o)}\]

Pale yellow viscous liquid (532 mg, 92%); Rf value = 0.5 in 30% EtOAc/Hexane. IR: \( \nu_{\text{max}} \) (neat) 1755, 1745, 1395, 1285, 1076 cm\(^{-1}\). \([\alpha]_D^{24} = +8.8 \ [c \ 0.1, \text{CHCl}_3]\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.12–7.20 (m, 38H), 5.88 (s, 1H), 5.57 (dd, \( J = 42.3, 15.3 \) Hz, 2H), 4.96–4.47 (m, 15H), 4.06 (t, \( J = 9.3 \) Hz, 1H), 3.91–3.83 (m, 3H), 3.64–3.61 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 169.7, 168.9, 147.1, 138.5, 138.0, 138.0, 137.1, 137.0, 134.1, 131.7, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 125.2, 102.5, 98.9, 81.2, 79.3, 77.4, 75.9, 75.3, 75.3, 74.1, 73.5, 73.0, 73.0, 72.3, 72.2, 71.1, 63.9. HRMS: Calc. for C\(_{67}\)H\(_{63}\)N\(_2\)O\(_{16}\)S [M+H]\(^{+}\): 1183.3898, Obsd. 1183.3900
β-D-Glucopyranosiduronic acid, hexyl, 2, 3, 4-tri-O-benzyl-2-nitrophenylmethyl ester (4a)

Pale yellow solid (304 mg, 89%); M.P: 96-97%; Rf value = 0.7 in 30% EtOAc/Hexane. β:α isomer (>20:1); IR: νmax (neat) 1751, 1517, 1305, 1125 cm⁻¹. [α]D²⁴ = -9.6 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 8.15–8.13 (m, 1H), 7.58–7.56 (m, 1H), 7.49–7.45 (m, 2H), 7.39–7.30 (m, 10H), 7.29–7.25 (m, 3H), 7.19 (dd, J = 6.8, 2.8 Hz, 2H), 5.63 (d, J = 15.3 Hz, 1H), 5.53 (d, J = 15.2 Hz, 1H), 4.97 (dd, J = 10.8, 9.6 Hz, 2H), 4.85 (dd, J = 16.8, 11.0 Hz, 2H), 4.76 (d, J = 10.9 Hz, 1H), 4.61 (d, J = 11.0 Hz, 1H), 4.53 (d, J = 7.7 Hz, 1H), 4.04–3.96 (m, 2H), 3.92 (t, J = 9.4 Hz, 1H), 3.73 (t, J = 9.1 Hz, 1H), 3.61–3.53 (m, 2H), 1.71–1.66 (m, 3H), 1.45–1.29 (m, 7H), 0.92 (dd, J = 9.5, 4.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 167.9, 147.1, 138.3, 138.2, 137.8, 133.8, 131.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 125.0, 104.0, 83.9, 81.7, 78.9, 75.7, 74.9, 74.8, 74.5, 70.5, 63.6, 31.6, 29.6, 25.8, 22.5, 14.0. HRMS: Calc. for C₄₀H₄₆NO₉ [M+H]+: 684.3173, Obs. 684.3168

β-D-Glucopyranosiduronic acid-1, 2, 3, 4-tetra-O-benzyl-2-nitrophenylmethyl ester (4b)

Pale yellow powder (293 mg, 85%); M.P: 124-126°; Rf value = 0.72 in 30% EtOAc/Hexane. β:α isomer (>20:1); IR: νmax (neat) 1775, 1480, 1310, 1095 cm⁻¹. [α]D²⁴ = -22.9 [c 0.1, CHCl₃];¹H NMR (500 MHz, CDCl₃) δ 8.15–8.13 (m, 1H), 7.59–7.57 (m, 1H), 7.48–7.45 (m, 2H), 7.41–7.26 (m, 19H), 7.21–7.18 (m, 2H), 5.59 (dd, J = 49.7, 15.2 Hz, 2H), 5.02–4.93 (m, 3H), 4.84 (dd, J = 21.8, 11.0 Hz, 2H), 4.73 (dd, J = 22.2, 11.3 Hz, 2H), 4.64 (dd, J = 13.2, 9.3 Hz, 2H), 4.05 (d, J = 9.7 Hz, 1H), 3.96–3.93 (m, 1H), 3.74 (t, J = 9.0 Hz, 1H), 3.63 (dd, J = 9.0, 7.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 167.9, 147.2, 138.2, 138.1, 137.8, 137.0, 133.8, 131.6, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 125.0, 102.8, 83.9, 81.8, 78.9, 75.7, 74.9, 74.6, 71.4, 63.7. HRMS: Calc. for C₄₁H₄₀NO₉ [M+H]+: 690.2703, Obs. 690.2702
α-D-Glucopyranoside,methyl-6-O-[6-methyl-2,3,4-tris-O-(phenylmethyl)-D-glucopyranuronosyl]-2, 3, 4-tris-O-(phenylmethyl)-2-nitrophenylmethyl ester (4c)

Yellow solid (408 mg, 78%); M.P: 103-105; Rf value = 0.5 in 30% EtOAc/ Hexane. β:α isomer (3:2); IR: νmax(neat) 1762, 1487, 1254, 1082 cm⁻¹. [α]D²⁴ = +12.1 [c 0.1, CHCl₃]; ¹H NMR (500 MHz, CDCl₃) δ 8.12–8.09 (m, 1H), 7.45–7.39 (m, 2H), 7.38–7.24 (m, 29H), 7.18 (ddd, J = 7.7, 6.7, 1.7 Hz, 3H), 5.62–5.43(m, 2H), 5.03–4.92 (m, 3H), 4.88–4.52 (m, 10H), 4.44 (t, J = 8.8 Hz, 1H), 4.17 (dd, J = 10.8, 1.7 Hz, 1H), 4.04–3.97 (m, 2H), 3.91–3.78 (m, 3H), 3.71–3.46 (m, 4H), 3.37 (d, J = 29.8 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 169.2, 167.7, 147.1, 138.8, 138.4, 138.3, 138.2, 138.1, 138.1, 138.0, 137.8, 133.8, 133.7, 131.6, 131.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 125.0, 124.9, 104.1, 98.0, 98.0, 97.8, 84.0, 82.1, 81.9, 81.5, 81.0, 80.1, 79.8, 79.5, 79.3, 78.8, 77.9, 77.7, 77.2, 75.7, 75.7, 75.6, 75.0, 74.9, 74.9, 74.8, 74.6, 73.3, 72.7, 70.4, 70.3, 69.8, 68.9, 66.7, 66.3, 63.5, 55.2. HRMS: Calc. for C₆₂H₄₆NO₁₄ [M+H]⁺: 1046.4327, Obser. 1046.4329

D-Glucopyranosiduronic acid-1, 2, 3, 4-tetra-O-benzyl-2-nitrophenylmethyl ester (4d)

White solid. (165 mg, 52%); M.P: 123-125; Rf value = 0.5 in 20% EtOAc/Hexane. β:α isomer (3:1); IR: νmax(neat) 1775, 1480, 1310, 1095 cm⁻¹. [α]D²⁴ = -9.9 [c 0.1, CHCl₃]; ¹H NMR (500 MHz, CDCl₃) δ 8.15–8.14 (m, 1H), 7.60–7.20 (m, 24H), 5.66–5.53 (m, 2H), 5.03–4.95 (m, 3H), 4.89–4.71 (m, 4H), 4.65 (dd, J = 12.6, 9.4 Hz, 2H), 4.07 (d, J = 9.7 Hz, 1H), 3.97 (t, J = 9.3 Hz, 1H), 3.75 (t, J = 9.0 Hz, 1H), 3.65–3.62 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 169.1, 168.0, 147.2, 138.5, 138.3, 138.1, 137.9, 137.8, 137.0, 136.7, 133.8, 131.6, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 125.1, 102.8, 96.1, 83.9, 81.8, 81.5, 79.4, 79.4, 78.9, 75.9, 75.7, 75.1, 74.9, 74.6, 73.2, 71.4, 70.6, 69.6, 63.7. Calc. for C₄₁H₄₀NO₉ [M+H]⁺: 690.2703, Obser. 690.2705
4. Experimental procedure for deprotection of photolabile 2-nitrobenzyl protecting group by using a continuous flow photoreactor:

Approximately 0.005M solution of photolabile protected uronic acid building blocks were prepared in methanol and added to the reactor B. The solution was circulated with the help of peristaltic pump to the flexi coil with a flow rate 50 RPM which required approx. 3 minutes for completing one cycle. Total six cycles were repeated after which the solvent was evaporated and purified through column chromatography.

5. Analytical data for various deprotected uronic acids:

**Methyl-2, 3, 4-tri-O-benzyl-α-D-glucopyranosiduronic acid (2a)**

![Diagram of 2a]

Colourless oily syrup (110mg, 92%); Rf value = 0.6 in 50% EtOAc/Hexane.

IR: \(\nu_{\text{max}}\) (neat) 3482, 1712, 1120 cm\(^{-1}\). \([\alpha]_D^{24} = +4.4\) [c 0.1, CHCl\(_3\)]; \(^1\)H NMR (500 MHz, DMSO-D\(_6\)) \(\delta\) 7.40–7.22 (m, 16H), 4.91 (d, \(J = 3.4\) Hz, 1H), 4.84 (d, \(J = 11.3\) Hz, 1H), 4.75–4.66 (m, 4H), 4.58 (d, \(J = 11.0\) Hz, 1H), 3.93 (d, \(J = 9.9\) Hz, 1H), 3.79 (t, \(J = 8.3\) Hz, 1H), 3.66–3.62 (m, 1H), 3.56 (dd, \(J = 9.6, 3.4\) Hz, 1H), 3.34 (s, 3H). \(^{13}\)C NMR (125 MHz, DMSO-D\(_6\)) \(\delta\) 170.9, 139.0, 138.8, 138.6, 128.7, 128.6, 128.6, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 98.0, 80.8, 79.6, 75.0, 74.5, 72.0, 70.4, 55.3. HRMS: Calc. for C\(_{28}\)H\(_{31}\)O\(_7\)[M+H]\(^+\): 749.2070, Obsr. 749.2075.

**Methyl-2, 3, 4-tri-O-benzoyl-α-D-glucopyranosiduronic acid (2b)**

![Diagram of 2b]

Colourless Oily syrup (116 mg, 89%); Rf value = 0.5 in 60% EtOAc/Hexane.

IR: \(\nu_{\text{max}}\) (neat) 3545, 1718, 1710 cm\(^{-1}\). \([\alpha]_D^{24} = +62.2\) [c 0.1, CHCl\(_3\)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.00–7.89 (m, 6H), 7.53 (q, \(J = 7.6\) Hz, 2H), 7.46 (t, \(J = 7.4\) Hz, 1H), 7.41–7.36 (m, 4H), 7.32 (t, \(J = 7.8\) Hz, 2H), 6.20 (t, \(J = 8.9\) Hz, 1H), 5.75 (t, \(J = 9.8\) Hz, 1H), 5.37 (d, \(J = 3.6\) Hz, 1H), 5.33 (dd, \(J = 10.1, 3.6\) Hz, 1H), 4.66 (d, \(J = 10.1\) Hz, 1H), 3.54 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.1, 165.7, 165.6, 165.4, 133.4, 133.4, 133.2, 129.9, 129.9, 129.7, 129.0, 128.8, 128.4, 128.4, 128.3, 97.4, 77.2, 71.4, 69.8, 68.0, 56.3. HRMS: Calc. for C\(_{28}\)H\(_{28}\)O\(_{10}\)[M+H]\(^+\): 521.1448, Obsr. 521.1446

**Methyl-2, 3-di-O-acetyl-4-benzyl-α-D-glucopyranosiduronic acid (2c)**

![Diagram of 2c]

Colourless oily syrup (87mg, 91%); Rf value = 0.5 in 50% EtOAc/Hexane. IR: \(\nu_{\text{max}}\) (neat) 3353, 1735, 1719, 1082 cm\(^{-1}\). \([\alpha]_D^{24} = +53.6\) [c 0.1, CHCl\(_3\)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.29 (m, 7H), 7.26–7.25 (m, 2H), 5.59–5.55 (m, 1H), 4.99 (d, \(J = 3.5\) Hz, 1H), 4.88 (dd, \(J = 10.2, 3.6\) Hz, 1H), 4.65 (dd, \(J = 10.2, 3.6\) Hz, 1H), 4.48 (d, \(J = 3.5\) Hz, 1H), 4.28 (dd, \(J = 10.2, 3.6\) Hz, 1H), 4.15 (dd, \(J = 10.2, 3.6\) Hz, 1H), 3.66 (d, \(J = 8.9\) Hz, 1H), 3.54 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.1, 165.7, 165.6, 165.4, 133.4, 133.4, 133.2, 129.9, 129.9, 129.7, 129.0, 128.8, 128.4, 128.4, 128.3, 97.4, 77.2, 71.4, 69.8, 68.0, 56.3. HRMS: Calc. for C\(_{28}\)H\(_{28}\)O\(_{10}\)[M+H]\(^+\): 521.1448, Obsr. 521.1446
Methyl-2, 3-di-O-benzoyl-4-benzyl-α-D-glucopyranosiduronic acid (2d)

Colourless oily liquid (119 mg, 94%); R_f value =0.6 in 50% EtOAc/Hexane.
IR: \( \nu_{\text{max}} \) (neat) 3260, 1715, 1708, 1124 cm\(^{-1}\). [\( \alpha \)]\(_D^{24} \) = +108.1 [c 0.1, CHCl\(_3\)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.10–8.08 (m, 4H), 7.62 (dd, \( J = 15.5, 7.5 \) Hz, 2H), 7.49 (dt, \( J = 15.8, 7.9 \) Hz, 4H), 7.26 (s, 5H), 6.20 (t, \( J = 9.6 \) Hz, 1H), 5.35 (dt, \( J = 10.0, 3.6 \) Hz, 2H), 4.77 (dd, \( J = 38.0, 10.9 \) Hz, 2H), 4.61 (d, \( J = 9.9 \) Hz, 1H), 4.28 (t, \( J = 9.5 \) Hz, 1H), 3.58 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 173.6, 166.0, 165.6, 136.9, 133.5, 133.3, 129.9, 129.7, 129.4, 128.8, 128.4, 128.3, 128.2, 128.0, 97.5, 77.4, 77.3, 77.1, 76.9, 74.8, 71.9, 71.7, 69.8, 55.9. HRMS: Calc. for C\(_{18}\)H\(_{23}\)O\(_5\)[M+H]+: 383.1342, Observed: 383.1343

Methyl-2, 3, 4-tri-O-benzyl-α-D-mannopyranosiduronic acid (2e)

Colourless oily syrup (105 mg, 88%); R_f value =0.5 in 50% EtOAc/PE;
IR: \( \nu_{\text{max}} \) (neat) 3386, 1725, 1135 cm\(^{-1}\). [\( \alpha \)]\(_D^{24} \) = +15.0 [c 1.2 in CHCl\(_3\)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.39–7.28 (m, 15H), 4.96 (s, 1H), 4.76 (dt, \( J = 24.4, 11.2 \) Hz, 4H), 4.64 (d, \( J = 3.9 \) Hz, 2H), 4.31–4.21 (m, 2H), 3.93–3.91 (m, 1H), 3.80–3.79 (m, 1H), 3.46 (d, \( J = 1.3 \) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 174.1, 138.1, 138.0, 137.7, 128.4, 128.1, 127.9, 127.8, 127.7, 127.6, 99.6, 78.5, 75.6, 74.5, 72.9, 72.4, 71.3, 55.7. HRMS: Calc. for C\(_{28}\)H\(_{30}\)O\(_7\)Na [M+Na]+: 501.1890, Observed: 501.1893.

Methyl-2, 3, 4-tri-O-benzoyl-α-D-mannopyranosiduronic acid (2f)

Colorless oily syrup (121 mg, 93%); R_f value =0.4 in 50% EtOAc/PE; IR: \( \nu_{\text{max}} \) (neat) 3558, 1712, 1708 cm\(^{-1}\). [\( \alpha \)]\(_D^{24} \) = -61.4 [c 0.1, CHCl\(_3\)]; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.10 (dd, \( J = 8.2, 1.2 \) Hz, 2H), 7.98–7.97 (m, 2H), 7.87 (dd, \( J = 8.3, 1.2 \) Hz, 2H), 7.62 (t, \( J = 7.4 \) Hz, 1H), 7.54–7.45 (m, 4H), 7.39 (t, \( J = 7.7 \) Hz, 2H), 7.31 (t, \( J = 7.8 \) Hz, 2H), 6.05 (t, \( J = 9.5 \) Hz, 1H), 5.92 (dd, \( J = 9.6, 3.4 \) Hz, 1H), 5.69 (dd, \( J = 3.2, 2.5 \) Hz, 1H), 5.16 (d, \( J = 2.2 \) Hz, 1H), 4.69 (d, \( J = 9.4 \) Hz, 1H), 3.59 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.4, 165.5, 165.4, 165.3, 133.6, 133.4, 133.3, 129.9, 129.8, 129.7, 129.1, 129.0, 128.9, 128.6,
Phenyl-2, 3, 4-tri-O-benzoyl-1-thio-β-D-glucopyranosyduronic acid (2g)

Colorless oily syrup (133 mg, 89%); R$_f$ value = 0.53 in 50% EtOAc/PE; IR: $\nu_{\text{max}}$ (neat) 3440, 1712, 1705 cm$^{-1}$. [a]$_D^{24} = +23.3$ [c 0.1, CHCl$_3$]; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99–7.97 (m, 2H), 7.92–7.91 (m, 2H), 7.84–7.83 (m, 2H), 7.56–7.28 (m, 14H), 5.92 (t, $J = 9.3$ Hz, 1H), 5.73 (t, $J = 9.6$ Hz, 1H), 5.54 (t, $J = 9.6$ Hz, 1H), 5.11 (d, $J = 9.9$ Hz, 1H), 4.39 (d, $J = 9.8$ Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.4, 165.6, 165.1, 164.9, 133.3, 133.3, 133.2, 131.7, 129.9, 129.8, 129.8, 129.2, 129.0, 129.0, 128.9, 128.8, 128.4, 128.4, 128.3, 128.2, 86.5, 73.8, 70.3, 69.9, 66.2. HRMS: Calc. for C$_{38}$H$_{35}$O$_9$S [M+H]$^+$: 599.1376, Obs. 599.1377

Phenyl-2, 3, 4-tri-O-benzyl-1-thio-β-D-glucopyranosyduronic acid (2h)

Colorless oily syrup (132 mg, 95%); R$_f$ value = 0.56 in 50% EtOAc/PE; IR: $\nu_{\text{max}}$ (neat) 3280, 1730, 1095 cm$^{-1}$. [a]$_D^{24} = -7.5$ [c 0.1, CHCl$_3$]; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60–7.58 (m, 2H), 7.42–7.26 (m, 19H), 4.93 (d, $J = 10.3$ Hz, 1H), 4.88 (t, $J = 7.8$ Hz, 2H), 4.81–4.75 (m, 3H), 4.70 (d, $J = 10.8$ Hz, 1H), 4.01 (d, $J = 9.3$ Hz, 1H), 3.87 (t, $J = 9.0$ Hz, 1H), 3.77 (t, $J = 8.6$ Hz, 1H), 3.58 (dd, $J = 9.6$, 8.4 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 172.3, 138.0, 137.7, 137.3, 133.0, 132.3, 129.1, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 88.1, 85.3, 80.2, 78.7, 77.5, 75.7, 75.4, 75.0. HRMS: Calc. for C$_{38}$H$_{33}$O$_9$S [M+H]$^+$: 557.1998, Obs. 557.2001

1, 2, 3, 4-Di-O-isopropylidene-α-D-galactopyranosiduronic acid (2i)

Colorless viscous liquid (62 mg, 90%); R$_f$ value = 0.6 in 50% EtOAc/Hexane. IR: $\nu_{\text{max}}$ (neat) 3315, 1715 cm$^{-1}$. $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 5.53 (d, $J = 5.0$ Hz, 1H), 4.65 (dd, $J = 7.7$, 2.5 Hz, 1H), 4.51 (dd, $J = 7.7$, 2.3 Hz, 1H), 4.40 (dd, $J = 5.0$, 2.5 Hz, 1H), 4.18 (d, $J = 2.2$ Hz, 1H), 1.43 (s, 3H), 1.32 (s, 3H), 1.28 (d, $J = 3.3$ Hz, 6H). $^{13}$C NMR (125 MHz, DMSO-d$_6$) $\delta$ 169.3, 109.1, 108.5, 96.2, 71.9, 70.5, 69.9, 67.7, 26.2, 26.1, 25.1, 24.8. HRMS: Calc. forC$_{12}$H$_{19}$O$_7$ [M+H]$^+$: 275.1131, Obs. 275.1129
Tolyl-2, 3, 4-tri-O-benzoyl-1-thio-β-D-glucopyranosyuronic acid (2j)

White solid (147 mg, 96%); M.P: 195-197 ̊C; Rf value = 0.5 in 50% EtOAc/Hexane. IR: ʋmax (neat) 3356, 1727, 1702 cm⁻¹ [α]D 24 = +12.6 [c 0.1, CHCl₃]; ¹H NMR (500 MHz, CDCl₃) δ 8.00–7.98 (m, 2H), 7.92 (dd, J = 8.4, 1.2 Hz, 2H), 7.85–7.83 (m, 2H), 7.57–7.53 (m, 1H), 7.52–7.48 (m, 1H), 7.47–7.45 (m, 3H), 7.43–7.40 (m, 2H), 7.35 (dd, J = 10.8, 4.9 Hz, 2H), 7.31–7.28 (m, 2H), 7.16 (d, J = 7.9 Hz, 2H), 5.93 (t, J = 9.3 Hz, 1H), 5.70 (t, J = 9.6 Hz, 1H), 5.51–5.47 (m, 1H), 5.05 (d, J = 9.9 Hz, 1H), 4.42 (d, J = 9.7 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 165.7, 165.2, 164.9, 139.1, 134.3, 133.4, 133.4, 133.3, 129.9, 129.9, 129.8, 129.8, 129.1, 128.7, 128.6, 128.4, 128.4, 128.3, 127.0, 86.5, 75.9, 73.5, 70.0, 69.7, 21.2. HRMS: Calc. for C₃₃H₂₉O₉S [M+H]⁺: 613.1532, Obs. 613.1536

Methyl-2, 3-di-O-benzoyl-α-D-glucopyranosiduronic acid (2k)

Colorless oil (94 mg, 90%); Rf value = 0.55 in 50% EtOAc/PE; [α]D 24 = +4.4 [c 0.1, CHCl₃]; IR: ʋmax (neat) 3520, 3286, 1725, 1718, 1135 cm⁻¹ [α]D 24 = +151.7 [c 0.1, CHCl₃]; ¹H NMR (500 MHz, MeOD-d₄) δ 8.00–7.98 (m, 2H), 7.91 (dd, J = 6.0, 4.7 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.42–7.37 (m, 4H), 5.83–5.78 (m, 1H), 5.20 (dd, J = 8.8, 2.7 Hz, 2H), 4.28 (d, J = 10.0 Hz, 1H), 4.09 (t, J = 9.7 Hz, 1H), 3.49 (s, 3H). ¹³C NMR (125 MHz, MeOD-d₄) δ 170.9, 166.1, 165.6, 133.2, 132.9, 129.6, 129.3, 129.2, 128.9, 128.1, 128.1, 97.5, 72.5, 71.7, 71.1, 69.8, 54.7. HRMS: Calc. for C₂₁H₂₁Oₙ [M+H]⁺: 417.1186, Obs.416.1190

2-(1-benzyl-6-(benzoxoy)-2-oxohexahydropyro[3, 2-d]oxazol-5-yl)-2-hydroxyacetic acid (2l)

Colorless oily syrup (54 mg, 79%); Rf value = 0.43 in 60% EtOAc/PE; IR: ʋmax (neat) 3306, 3120, 1711, 1302, 1135, 1070 cm⁻¹, [α]D 24 = -49.4 [c 0.1, CHCl₃]; ¹H NMR (500 MHz, CDCl₃) δ 7.37–7.27 (m, 8H), 7.17 (t, J = 7.4 Hz, 3H), 6.14 (d, J = 5.0 Hz, 1H), 4.73 (s, 1H), 4.65 (d, J = 15.1 Hz, 1H), 4.40–4.31 (m, 2H), 4.17 (d, J = 3.3 Hz, 1H), 4.10 (s, 1H), 4.06–4.04 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 169.3, 156.8, 136.3, 134.7, 129.2, 128.6, 128.6, 128.3, 128.2, 127.8, 101.2, 79.5, 77.4, 77.1, 76.9, 72.6, 64.2, 47.5. HRMS: Calc. for C₂₁H₂₂NO₇ [M+H]⁺: 400.1396, Obs. 400.1395
(2S,3S,4S,5R,6R)-4,5-bis(benzyloxy)-3-(4-bromobenzyloxy)-6-methoxytetrahydro-2H-pyran-2-carboxylic acid (2m)

Colorless viscous liquid (124 mg, 89%); R_f value = 0.20 in 50% EtOAc/PE. IR:ν_max (neat) 3263, 1727, 1077, 585 cm⁻¹; [α]_D^{24} = -1.9 [c 0.1, CHCl₃]; ^1H NMR (500 MHz, CDCl₃) δ 7.40–7.28 (m, 12H), 7.09 (d, J = 8.3 Hz, 2H), 4.99 (d, J = 11.0 Hz, 1H), 4.83–4.74 (m, 3H), 4.66 (t, J = 7.3 Hz, 2H), 4.58 (d, J = 11.1 Hz, 1H), 4.24 (d, J = 10.0 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 3.70 (t, J = 9.5 Hz, 1H), 3.60–3.58 (m, 1H), 3.44 (s, 3H). ^13C NMR (125 MHz, CDCl₃) δ 173.9, 138.3, 137.7, 136.6, 131.4, 129.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 121.7, 98.6, 81.3, 79.2, 79.1, 75.9, 74.3, 73.6, 69.6, 55.8. HRMS: Calc. for C_{26}H_{25}BrO_7 [M+H]^+ = 556.1097, Obsd. 556.1094

(2S,3S,4S,5R,6R)-4,5-bis(benzyloxy)-6-methoxy-3-(naphthalen-2-ylmethoxy)tetrahydro-2H-pyran-2-carboxylic acid (2n)

Colorless viscous liquid (115 mg, 87%); R_f value = 0.20 in 50% EtOAc/PE; IR:ν_max (neat) 3215, 1712, 1120 cm⁻¹. [α]_D^{25} = -6.2 [c 0.1, CHCl₃]; ^1H NMR (500 MHz, CDCl₃) δ 7.79–7.74 (m, 3H), 7.66 (s, 1H), 7.47–7.44 (m, 2H), 7.39–7.32 (m, 11H), 4.99 (dd, J = 26.3, 10.9 Hz, 2H), 4.86–4.78 (m, 3H), 4.67 (t, J = 7.9 Hz, 2H), 4.29 (d, J = 10.1 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.78 (t, J = 9.5 Hz, 1H), 3.62 (dd, J = 9.6, 3.4 Hz, 1H), 3.44 (s, 3H). ^13C NMR (125 MHz, CDCl₃) δ 173.3, 138.4, 137.8, 134.9, 133.2, 133.0, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 127.6, 126.8, 126.0, 125.9, 125.8, 98.6, 81.4, 79.2, 79.2, 75.9, 75.3, 73.6, 69.6, 55.8. HRMS: Calc. for C_{23}H_{21}O_7 [M+H]^+ = 528.2148, Obsd. 528.2150

β-D-Glucopyranosiduronic acid, phenyl-2, 3-di-0-(benzyl)-1-thio-4-O-[2, 3, 4-tri-O-(benzyl)-β-D-glucopyranosiduronic acid] (2o)

Colorless viscous liquid (207 mg, 91%); R_f value = 0.40 in 60% EtOAc/PE; IR:ν_max (neat) 3540, 3325, 1722, 1710, 1130 cm⁻¹. [α]_D^{24} = +21.0 [c 0.1, CHCl₃]; ^1H NMR (500 MHz, CDCl₃) δ 7.38–7.26 (m, 31H), 5.88 (s, 1H), 4.97–4.72 (m, 8H), 4.64–4.57 (m, 4H), 4.49 (t, J = 11.6 Hz, 2H), 4.06 (t, J = 9.3 Hz, 1H), 3.90 (d, J = 16.9 Hz, 2H), 3.80 (t, J = 9.5 Hz, 1H), 3.62 (dd, J = 10.0, 3.8 Hz, 2H). ^13C NMR (125 MHz, CDCl₃) δ 172.8, 169.6,
6. Procedure for synthesis of D-Glucopyranuronic acid, 2,3,4-tris-O-(phenylmethyl)-2-nitrophenylmethyl ester, 1-(2,2,2-trichloroethanimidate) (1aa):

To a stirred solution of thioglycosides, 1h (4g, 5.78 mmol) in 40 ml acetone-water (9:1; v/v) was added N-bromosuccinamide (3.09 g, 17.35 mmol) and stirred for 1 hour at room temperature. After that, the reaction was quenched with NaHCO₃ and evaporated to dryness. The residue was dissolved in ethyl acetate (150mL) and successively washed with sat.aq.NaHCO₃, water, and brine. Organic layer was separated, dried using anhydrous sodium sulphate, evaporated in vacuo. The resulting residue was purified using silica gel column chromatography (2:1 hexane/EtOAc) to give the corresponding hemiacetal 2.43 g (70%) as viscous oil. The hemiacetals were dissolved in dry CH₂Cl₂ (20mL) and cooled to 0°C under argon atmosphere. DBU (0.2 mL, 1.33 mmol) and trichloroacetonitrile (3.34 mL, 33.35 mmol) were added slowly and allowed to stir for 2h. After complete consumption of starting material, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography (30% EtOAc/Hexane) with 1% added Et₃N to afford 2.23g (90%) as colourless foam; α:β isomer (15.31:1); Rf value = 0.6 in 20% EtOAc/Hexane. ¹H NMR (500 MHz, CDCl₃) δ 8.74 (s, 1H), 8.13 (dd, J = 7.7, 1.7 Hz, 1H), 7.54-7.46 (m, 3H), 7.37-7.33 (m, 10H), 7.30-7.28 (m, 3H), 7.23 (dd, J = 6.6, 3.0 Hz, 2H), 6.61 (d, J = 3.5 Hz, 1H), 5.56 (q, J = 15.3 Hz, 2H), 5.03 (d, J = 10.9 Hz, 1H), 4.91 (t, J = 11.2 Hz, 2H), 4.78 (dd, J = 25.2, 11.7 Hz, 2H), 4.61 (dd, J = 29.5, 10.5 Hz, 2H), 4.16 (t, J = 9.3 Hz, 1H), 3.97-3.87 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 168.1, 161.0, 147.1, 138.2, 137.6, 137.6, 133.9, 131.4, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 125.0, 94.0, 91.0, 80.8, 78.8, 78.5, 75.8, 75.3, 73.1, 72.7, 63.8.
7. General procedure for Glycosylation:

7.a. Glycosylation through Glycosyl Imidate donor: Donor 1aa (0.5 mmol, 1 equiv.) and acceptor (non-sugar 3 equiv. and sugar 1.2 equiv.) were dissolved in freshly dried CH₂Cl₂ (8 ml) and added to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (300 mg) under argon atmosphere. The reaction mixture was then cooled to 0 °C to which the activator B(C₆F₅)₃ (10 mol%) was added. The reaction was slowly allowed to reach 0 °C. Upon completion, the reaction was quenched by adding Et₃N and filtered through Celite. The mixture was concentrated in vacuo and the resulting residue was purified by silica gel column chromatography to afford the desired glycosylated product (78-89%).

7.b. Glycosylation through thioglycoside donor: Typical NIS/TfOH-promoted glycosylation procedure: A mixture of glycosyl donor (1h) (0.5 mmol, 1 equiv.), glycosyl acceptor (3 equiv.), and freshly activated molecular sieves (4 Å, 300 mg) in CH₂Cl₂ (8.0 mL) was stirred under argon for 1 h. The solution was cooled to –78 °C and NIS (1.1 equiv.) and TfOH (10 mol%) were added. The reaction was slowly allowed to reach 0 °C. Upon completion, the reaction was quenched by adding Et₃N. The solid was filtered off and the filtrate was washed with 1 M HCl, sat. NaHCO₃ solution, 10% Na₂S₂O₃ and brine. The organic layer was separated, dried with anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding glycoside with 52% yield.

8. Analytical data for various deprotected uronic acids:

*n*-Hexyl-2, 3, 4-tri-O-benzyl-D-glucopyranosiduronic acid (5a)

White foam (123 mg, 90%); Rᶠ value = 0.5 in 50% EtOAc/Hexane. IR: νmax (neat) 3105, 1716, 1132 cm⁻¹; β:α isomer (>20:1); [α]D²⁴ = -6.4 (c 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.38–7.25 (m, 16H), 4.94 (dd, J = 17.6, 11.0 Hz, 2H), 4.81 (d, J = 10.2 Hz, 2H), 4.75 (d, J = 11.0 Hz, 1H), 4.67 (d, J = 10.7 Hz, 1H), 4.54 (d, J = 7.6 Hz, 1H), 4.01–3.96 (m, 2H), 3.85 (t, J = 9.1 Hz, 1H), 3.72 (t, J = 8.8 Hz, 1H), 3.59–3.52 (m, 2H), 1.70–1.64 (m, 2H), 1.43–1.30 (m, 8H), 0.92–0.89 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 138.2, 138.1, 137.4, 128.4, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 103.7, 83.5,
81.5, 78.8, 75.6, 75.0, 74.7, 74.0, 70.5, 31.6, 29.6, 25.7, 22.5, 14.0.HRMS: Calc. for C\textsubscript{33}H\textsubscript{34}O\textsubscript{7}[M+H]\textsuperscript{+}:549.2852, Obser. 549.2849

(Phenylmethyl)-2,3,4-tri-O-benzyl-D-glucopyranosiduronic acid (5b)

Viscous liquid. (130 mg, 94%); R\textsubscript{f} value =0.6 in 50% EtOAc/ Hexane. IR: \nu\textsubscript{max} (neat) 3215, 1705, 1145 cm\textsuperscript{-1}. \beta:\alpha isomer (>20:1); [\alpha]D\textsuperscript{24} = -19.6 [c 0.1, CHCl\textsubscript{3}]; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta 7.37–7.24 (m, 21H), 4.98 (d, J = 12.1 Hz, 1H), 4.90 (dd, J = 15.9, 10.9 Hz, 2H), 4.79 (t, J = 10.4 Hz, 2H), 4.68 (ddd, J = 18.2, 16.2, 9.2 Hz, 4H), 4.00 (d, J = 9.3 Hz, 1H), 3.88–3.84 (m, 1H), 3.70 (t, J = 8.7 Hz, 1H), 3.59 (t, J = 7.7 Hz, 1H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \delta 172.7, 138.2, 138.0, 137.4, 136.9, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 102.5, 83.5, 81.6, 78.7, 75.6, 75.0, 74.8, 74.0, 71.5. HRMS: Calc. for C\textsubscript{34}H\textsubscript{35}O\textsubscript{7}[M+H]\textsuperscript{+}:555.2383, Obser. 555.2387

(2S,4S,5S,6R)-3,4,5-tris(benzyloxy)-6-(((2R,4S,5S,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methoxy)tetrahydro-2H-pyran-2-carboxylic acid (5c)

White solid (198 mg, 87%); M.P: 93-95 °C; R\textsubscript{f} value =0.5 in 60% EtOAc/ Hexane. IR: \nu\textsubscript{max} (neat) 3345, 1701, 1065 cm\textsuperscript{-1}. \beta:\alpha isomer (3:2); [\alpha]D\textsuperscript{24} = +34.5 [c 0.1, CHCl\textsubscript{3}]; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta 7.38–7.19 (m, 31H), 5.01–4.50 (m, 14H), 4.10–3.44 (m, 10H), 3.36 (d, J = 20.3 Hz, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \delta 172.0, 170.4, 138.8, 138.7, 138.3, 138.2, 138.2, 138.1, 138.1, 138.0, 138.0, 137.5, 137.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 103.5, 98.1, 98.0, 97.5, 96.1, 83.1, 82.0, 81.9, 81.2, 80.9, 80.1, 79.9, 79.3, 79.0, 78.7, 77.8, 77.7, 75.7, 75.7, 75.6, 75.3, 75.1, 75.0, 74.9, 74.8, 74.6, 73.9, 73.3, 72.6, 70.3, 69.9, 69.4, 69.0, 66.7, 55.3, 55.2.HRMS: Calc. for C\textsubscript{55}H\textsubscript{55}O\textsubscript{12}[M+H]\textsuperscript{+}:911.4007, Obser. 911.4012
Viscous liquid. (116 mg, 84%); R_f value = 0.6 in 50% EtOAc/ Hexane. IR:ν_max (neat) 3217, 1708, 1085 cm^{-1}.[α]D^{24}= +8.8 [c 0.1, CHCl_3];^1H NMR (500 MHz, CDCl_3) δ 7.43–7.26 (m, 20H), 4.93–4.85 (m, 2H), 4.83–4.66 (m, 5H), 4.03 (d, J = 9.1 Hz, 1H), 3.87 (t, J = 8.9 Hz, 1H), 3.71 (t, J = 8.6 Hz, 1H), 3.61–3.58 (m, 1H).^13C NMR (125 MHz, CDCl_3) δ 174.0, 173.0, 138.5, 138.2, 138.0, 137.8, 137.5, 136.96, 136.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 102.6, 95.9, 83.6, 81.6, 81.4, 79.3, 79.1, 78.7, 75.9, 75.6, 75.3, 75.0, 74.8, 74.0, 73.2, 71.5, 69.9, 69.7. HRMS: Calc. for C_{34}H_{35}O_{7} [M+H]^+:555.2383, Obser. 555.2381

References:

C-NMR (125 MHz, CDCl$_3$) spectrum of compound AB

$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound AB

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound AB
**1H-NMR (500 MHz, CDCl₃) spectrum of compound AC**

**13C-NMR (125 MHz, CDCl₃) spectrum of compound AC**
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1a

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1a
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1b

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1b
H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1c

C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1c
\[ ^1\text{H-NMR (500 MHz, CDCl}_3) \text{ spectrum of compound 1d} \]

\[ ^{13}\text{C-NMR (125 MHz, CDCl}_3) \text{ spectrum of compound 1d} \]
$^{13}$C-NMR (125 MHz, CDCl₃) spectrum of compound 1e

$^1$H-NMR (500 MHz, CDCl₃) spectrum of compound 1e
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1f

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1f
H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1g

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1g
\[ \text{\(^1H\)-NMR (500 MHz, CDCl\(_3\)) spectrum of compound 1h} \]

\[ \text{\(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) spectrum of compound 1h} \]
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1i

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1i
H-NMR (500 MHz, CDCl₃) spectrum of compound 1j

C-NMR (125 MHz, CDCl₃) spectrum of compound 1j

¹³C-NMR (125 MHz, CDCl₃) spectrum of compound 1j
H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1k

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1k
H-NMR (500 MHz, CDCl\textsubscript{3}) spectrum of compound 11

\[ \text{1H-NMR (500 MHz, CDCl}_3\text{) spectrum of compound 11} \]

\[ \text{13C-NMR (125 MHz, CDCl}_3\text{) spectrum of compound 11} \]
$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1m
H-NMR (500 MHz, CDCl₃) spectrum of compound 1n

\textbf{1}n

\textbf{1}H-NMR (500 MHz, CDCl₃) spectrum of compound 1n

\textbf{1}3C-NMR (125 MHz, CDCl₃) spectrum of compound 1n
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 1o

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 1o
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 4a

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 4a
13C-NMR (125 MHz, CDCl₃) spectrum of compound 4b

1H-NMR (500 MHz, CDCl₃) spectrum of compound 4b
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 4c

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 4c
C-NMR (125 MHz, CDCl₃) spectrum of compound 4d

$^1$H-NMR (500 MHz, CDCl₃) spectrum of compound 4d

$^{13}$C-NMR (125 MHz, CDCl₃) spectrum of compound 4d
\[ \text{H-NMR (500 MHz, CDCl}_3\text{) spectrum of compound 1aa} \]

\[ \text{C-NMR (125 MHz, CDCl}_3\text{) spectrum of compound 1aa} \]
$^1$H-NMR (500 MHz, DMSO-$d_6$) spectrum of compound 2a

$^{13}$C-NMR (125 MHz, DMSO-$d_6$) spectrum of compound 2a
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2b

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2b
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2c

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2c
H-NMR (500 MHz, CDCl₃) spectrum of compound 2d

\[ \text{1H-NMR (500 MHz, CDCl}_3\text{) spectrum of compound 2d} \]

\[ \text{13C-NMR (125 MHz, CDCl}_3\text{) spectrum of compound 2d} \]
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2e

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2e
$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2f

$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2f
$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2g

$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2g
H-NMR (500 MHz, CDCl₃) spectrum of compound 2h

1H-NMR (500 MHz, CDCl₃) spectrum of compound 2h

13C-NMR (125 MHz, CDCl₃) spectrum of compound 2h
$^1$H-NMR (500 MHz, DMSO-d$_6$) spectrum of compound 2i

$^{13}$C-NMR (125 MHz, DMSO-d$_6$) spectrum of compound 2i
$^{1}$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2j

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2j
$^1$H-NMR (500 MHz, Methanol-d$_4$) spectrum of compound 2k

$^{13}$C-NMR (125 MHz, Methanol-d$_4$) spectrum of compound 2k
C-NMR (125 MHz, CDCl₃) spectrum of compound 2l

^1^H-NMR (500 MHz, CDCl₃) spectrum of compound 2l

^1^H-NMR (500 MHz, CDCl₃) spectrum of compound 2l

^1^C-NMR (125 MHz, CDCl₃) spectrum of compound 2l
$^{1}$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2m

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2m
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2n

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2n
$^{1}$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 2o

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 2o
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 5a

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 5a
H-NMR (500 MHz, CDCl$_3$) spectrum of compound 5b

C-NMR (125 MHz, CDCl$_3$) spectrum of compound 5b

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 5b
$^{1}$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 5c

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 5c
$^1$H-NMR (500 MHz, CDCl$_3$) spectrum of compound 5d

$^{13}$C-NMR (125 MHz, CDCl$_3$) spectrum of compound 5d