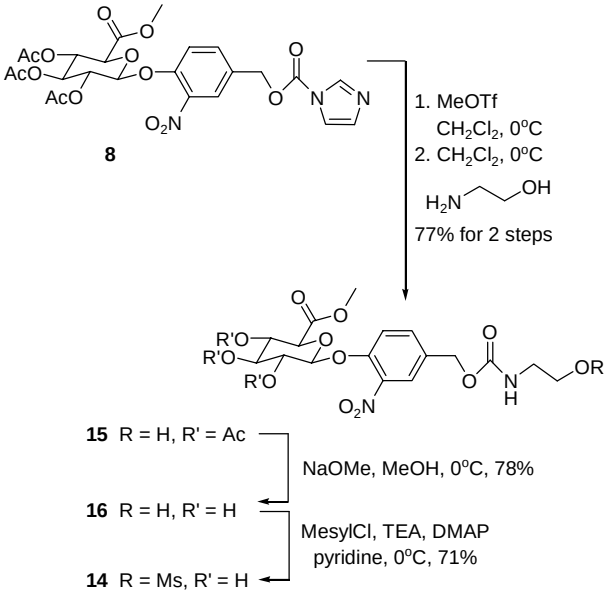
Supporting Information:

Scheme S1



Methyl 1-(4-formyl-2-nitrophenyl)-2,3,4-tri-*O*-acetyl-β-D-**glucopyronuronate (6):**[1] Methyl 1-bromo-2,3,4-tri-*O*-acetyl-α-D-glucopyronuronate[2] (10.75 g, 27.1 mmol) was dissolved in 250 ml anhydrous MeCN. 4-hydroxy-3-nitrobenzaldehyde (7.64 g, 45.7 mmol) was then added followed by 28.5 g (123 mmol) of Ag_2O. The resulting slurry was stirred in the dark under N_2 for 4h. The solution was filtered through Celite to remove solids and the filtrate concentrated *in vacuo*. The residue was brought up in EtOAc (400 ml) and washed with saturated $NaHCO_3$ (6 x 200 ml), water and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The beige solid was triturated with hexanes yielding **6** (12.52 g, 96%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.01, 2.02, 2.03 (3s, 3 x 3H, OAc), 3.64 (s, 3H, $COOCH_3$), 4.80 (d, 1H, H-5, *J*=10 Hz), 5.15 (m, 2H, H-2, H-4), 5.74 (m, 1H, H-3), 5.94 (d, 1H, H-1 *J*=8 Hz), 7.64 (d, 1H, ArH, *J*=9 Hz), 8.22 (dd, 1H, ArH, *J*=9 Hz, *J'*=1.5 Hz), 8.44 (d, 1H, ArH, *J*=1.5 Hz), 9.98 (s, 1H, CHO); ^{13}C NMR (126 MHz, DMSO-d_6) δ 20.17, 20.22, 20.26, 52.65, 68.49, 69.67, 70.43, 71.18, 97.25, 117.58, 126.23, 131.07, 134.74, 140.25, 152.10, 166.85, 168.72, 169.34, 169.49, 190.48; IR (KBr plate) ν 2956, 1756, 1700, 1612, 1538, 1368, 1235, 1074, 1039 cm^{-1}; ESI-MS *m/z* $(M + Na)^+$ 506.1; Anal. Calcd for $C_{20}H_{21}NO_{13}$: C 49.69, H 4.38, N 2.90; Found C 49.92, H 4.55, N 2.80.

Methyl 1-(4-hydroxymethyl-2-nitrophenyl)-2,3,4-tri-*O*-acetyl-β-D-**glucopyronuronate (7):**[1,3] 1.41 g (37.3 mmol) $NaBH_4$ were added to a stirring solution of 12.03 g (24.9 mmol) **6** and 5 g silica gel at 0°C in 300 ml 1:5 IPA:$CHCl_3$. After 45 min, the solution was poured into 300 ml ice water and filtered through Celite. The layers were separated and the organic fraction washed with brine, dried ($MgSO_4$), concentrated *in vacuo*, and triturated with Et_2O, yielding **7** as a white solid (11.65 g, 96 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.99 (s, 3H, OAc), 2.02 (s, 6H, OAc), 3.33 (br

OH), 3.64 (s, 3H, $COOCH_3$), 4.51 (d, 2H, C*H*$_2$OH, *J*=5.5 Hz), 4.73 (d, 1H, H-5, *J*=10 Hz), 5.10 (m, 2H, H-2, H-4), 5.44 (m, 1H, H-3), 5.71 (d, 1H, H-1 *J*=8 Hz), 7.38 (d, 1H, ArH, *J*=8 Hz), 7.62 (d, 1H, ArH, *J*=8 Hz), 7.80 (s, 1H, ArH); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 20.19, 20.22, 20.28, 52.64, 61.32, 68.73, 69.94, 70.75, 71.02, 98.06, 117.70, 122.30, 131.97, 138.54, 140.18, 146.92, 166.92, 168.74, 169.32, 169.51; IR (KBr plate) ν 3527, 1756, 1535, 1367, 1232, 1077, 1039 cm^{-1}; ESI-MS *m/z* $(M + Na)^+$ 508.3; Anal. Calcd for $C_{20}H_{23}NO_{13}$: C 49.49, H 4.78, N 2.89; Found C 49.50, H 4.90, N 3.12.

Methyl 1-(4-(2-bromo-ethylcarbamoyloxymethyl)-2-nitrophenyl)-2,3,4-tri-*O*-acetyl-β-D-glucopyronuronate (9): 3.75 g (7.73 mmol) sugar **7** and 189 mg (1.55 mmol) DMAP in 50 ml dry CH_2Cl_2 under N_2 were subjected to 2.51 g (15.5 mmol) 1,1'-carbonyl-diimidazole. When the reaction was complete by TLC (silica, 5% MeOH/CH_2Cl_2) (2.25 h), the solution was washed with water, 5% NaH_2PO_4, sat. $NaHCO_3$, and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo* to yield 4.19 g of the imidazolyl intermediate **8**. **8** was dissolved in 65 ml anhydrous CH_2Cl_2 under N_2 and cooled to 0°C. 0.90 ml (7.95 mmol) MeOTf was added over 5 min. After 30 min, the reaction was diluted with 30 ml Et_2O and cooled to -20°C to allow all methylated product to precipitate. The white solid was collected by filtration, washed with Et_2O and dried *in vacuo*. The activated compound was suspended in 50 ml anhydrous CH_2Cl_2 under N_2 and 2.22 g (10.85 mmol) 2-bromoethylamine hydrobromide were added. The slurry was brought to 0°C and 1.51 ml (10.85 mmol) TEA added in one portion. The reaction stirred for 2 h and was then washed with water and brine. The organic layer was dried ($MgSO_4$), concentrated *in vacuo* and purified by chromatography (silica, 0-55% EtOAc in hexanes) to give 2.99 g (65 %) **9** as a white solid. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 2.00 (s, 3H, OAc), 2.02 (s, 6H, OAc), 3.39 (t, 2H, *J*=6 Hz), 3.47 (t, 2H, *J*=6 Hz), 3.64 (s, 3H, $COOCH_3$), 4.73 (d, 1H, H-5, *J*=10 Hz), 5.06-5.14 (m, 4H, benzylic C*H*$_2$, H-2, H-4), 5.46 (m, 1H, H-3), 5.74 (d, 1H, H-1 *J*=8 Hz), 7.43 (d, 1H, ArH, *J*=9 Hz), 7.67 (m, 2H, ArH, N*H*), 7.89 (s, 1H, ArH); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 20.22, 20.26, 20.31, 32.44, 42.34, 52.63, 63.81, 68.65, 69.83, 70.66, 71.01, 97.79, 117.72, 123.86, 132.77, 133.51, 139.99, 147.58, 155.70, 166.78, 168.62, 169.21, 169.38; ESI-MS *m/z* $(M + Na)^+$ 657.0, 659.0 (Br isotope pattern); Anal. Calcd for $C_{23}H_{27}BrN_2O_{14}$: C 43.48, H 4.28, N 4.41; Found C 43.74, H 4.20, N 4.34.

Methyl 1-(4-(2-bromo-ethylcarbamoyloxymethyl)-2-nitrophenyl)-β-D-glucopyronuronate (10): 2.84 g (4.47 mmol) **9** were suspended in 90 ml dry MeOH under N_2 at 0°C. 650 µL 30% w/v NaOMe in MeOH were added and the solution stirred for 100 min. The reaction was quenched with 197 µL acetic acid. Removal of solvent was followed by purification on silica (10% MeOH/CH_2Cl_2). The resulting solid was dissolved in acetone and filtered through a 0.2 µm PTFE filter to remove any silica. The solution was concentrated *in vacuo* and triturated (Et_2O) to give 1.80 g (79%) **10**. Data for **10** ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 3.26-3.42 (m, 5H), 3.47 (t, 2H, *J*=6 Hz), 3.65 (s, 3H, $COOCH_3$), 4.13 (d, 1H, H-5, *J*=10 Hz), 5.04 (s, 2H, benzylic C*H*$_2$), 5.31 (m, 2H, H-1, O*H*), 5.49 (d, 1H, O*H* *J*=6 Hz), 5.54 (d, 1H, O*H* *J*=5 Hz), 7.44 (d, 1H, ArH, *J*=9 Hz), 7.63 (m, 2H, ArH, N*H*), 7.86 (s, 1H, ArH); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 32.44, 42.35, 52.02, 63.94, 71.19, 72.71, 75.17, 75.61, 99.76, 116.86, 124.09, 131.27, 133.54, 139.86, 148.58, 155.88, 169.06; ESI-MS *m/z* $(M + Na)^+$ 530.9, 532.9 (Br isotope pattern);

Anal. Calcd for $C_{17}H_{21}BrN_2O_{11}$: C 40.09, H 4.16, N 5.50; Found C 40.32, H 4.46, N 5.39. The major byproduct of this reaction was α,β-unsaturated compound **11**, resulting from base-catalyzed β-acetate elimination. Data for **11** ^{1}H NMR (500 MHz, CD_3OD) δ 3.23 (t, 2H, *J*=5 Hz), 3.45 (t, 2H, *J*=5 Hz), 3.77 (s, 3H, $COOCH_3$), 4.09 (m, 2H), 5.09 (s, 2H, benzylic C*H*$_2$), 5.90 (br. s, 1H, H-4), 6.28 (d, 1H, H-1 *J*=2.5 Hz), 7.57 (d, 1H, ArH, *J*=9 Hz), 7.66 (d, 1H, ArH, *J*=9 Hz), 7.92 (s, 1H, ArH); ^{13}C NMR (126 MHz, CD_3OD) δ 33.67, 44.41, 53.12, 65.83, 66.77, 70.58, 100.08, 114.14, 120.19, 126.04, 134.37, 135.11, 141.05, 142.02, 150.24, 158.73, 163.96.

Methyl 1-(4-(2-hydroxy-ethylcarbamoyloxymethyl)-2-nitrophenyl)-2,3,4-tri-*O*-acetyl-β-D-**glucopyronuronate (15):** 1.05 ml (9.25 mmol) MeOTf were added over 5 min to a solution of 4.87 g (8.41 mmol) **8** in 60 ml anhydrous CH_2Cl_2 under N_2 at 0°C. After 30 min, the reaction was diluted with 30 ml Et_2O and cooled to -20°C to allow all methylated product to precipitate. The white solid was collected by filtration, washed with Et_2O and dried *in vacuo*. The activated compound was suspended in 60 ml anhydrous CH_2Cl_2 under N_2 and brought to 0°C. 761 µl (12.6 mmol) 2-hydroxyethylamine were added and the solution was allowed to warm to room temperature over 2 h and was then washed with water, 5% NaH_2PO_4, sat. bicarbonate and brine. The organic layer was dried ($MgSO_4$), concentrated *in vacuo* and purified by chromatography (silica, 0-5% MeOH in CH_2Cl_2) to give 3.68 g (77 %) **15** as a white solid. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 1.99 (s, 3H, OAc), 2.02 (s, 6H, OAc), 3.05 (q, 2H, *J*=6 Hz), 3.33 (s, 1H, O*H*), 3.38 (q, 2H, *J*=6 Hz), 3.64 (s, 3H, $COOCH_3$), 4.64 (t, 0.5H, N*H*, *J*=6 Hz), 4.74 (d, 1H, H-5, *J*=10 Hz), 5.02 (s, 2H, benzylic C*H*$_2$), 5.10 (m, 2H), 5.46 (t, 1H, *J*=10 Hz), 5.74 (d, 1H, H-1, *J*=8 Hz), 7.27 (t, 0.5H, N*H*, *J*=6 Hz), 7.43 (d, 1H, ArH, *J*=9 Hz), 7.67 (d, 1H, ArH, *J*=9Hz), 7.88 (s, 1H, ArH); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 20.20, 20.23, 20.28, 43.09, 52.64, 59.86, 63.59, 68.69, 69.87, 70.71, 71.05, 97.89, 117.80, 123.89, 133.12, 133.55, 140.11, 147.63, 155.93, 166.90, 168.74, 169.33, 169.51; IR (KBr plate) ν 3394, 2962, 1756, 1708, 1535, 1366, 1235, 1073, 1039 cm^{-1}; ESI-MS *m/z* $(M + Na)^+$ 595.3; Anal. Calcd for $C_{23}H_{28}N_2O_{15}$: C 48.25, H 4.93, N 4.89; Found C 47.96, H 5.14, N 4.91.

Methyl 1-(4-(2-hydroxy-ethylcarbamoyloxymethyl)-2-nitrophenyl)-β-D-**glucopyronuronate (16):** 3.49 g (6.10 mmol) **15** in 100 ml anhydrous MeOH were cooled to 0°C under N_2. 776 µl (4.27 mmol) 30% NaOMe in MeOH were added and the solution allowed to stir for 1 h. 210 µl acetic acid were added and the volatiles removed *in vacuo*. The resulting solid was purified by chromatography (silica, 10-15% MeOH in CH_2Cl_2) and excess silica removed by filtration of an acetone solution through a 0.2 µm PTFE filter. Trituration of the solid with Et_2O yielded 2.15 g (79%) **16** as a white solid. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 3.05 (q, 2H, *J*=6 Hz), 3.25-3.44 (m, 6H), 3.66 (s, 3H, $COOCH_3$), 4.12 (d, 1H, H-5, *J*=10 Hz), 4.63 (t, 0.5H, N*H*, *J*=5.5 Hz), 5.00 (s, 2H, benzylic C*H*$_2$), 5.31 (d, 2H, H-1, OH), 5.49 (d, 1H, OH, *J*= 5.5 Hz), 5.54 (d, 1H, OH, *J*=4.5 Hz), 7.25 (t, 0.5H, N*H*, *J*=6 Hz), 7.44 (d, 1H, ArH, *J*=9 Hz), 7.63 (d, 1H, ArH, *J*=9Hz), 7.85 (s, 1H, ArH); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 43.10, 52.03, 59.88, 63.70, 71.20, 72.72, 75.17, 75.61, 99.80, 116.86, 124.05, 133.51, 133.51, 139.87, 148.53, 155.99, 169.07; IR (KBr plate) ν 3352, 2954, 1737, 1705, 1533, 1354, 1252, 1083, 1060,

1019 cm^{-1}; ESI-MS *m/z* $(M + Na)^+$ 469.2; Anal. Calcd for $C_{17}H_{22}N_2O_{12}$: C 45.74, H 4.97, N 6.28; Found C 47.92, H 5.06, N 5.98.

Methyl 1-(4-(2-methanesulfonyloxy-ethylcarbamoyloxymethyl)-2-nitrophenyl)-β-D-**glucopyronuronate (14):** 950 µl (6.81 mmol) NEt_3, 100mg (0.85 mmol) DMAP and 1.90 g (4.26 mmol) **16** were dissolved in 50 ml anhydrous pyridine and cooled to 0°C. 529 µl (6.81 mmol) methanesulfonyl chloride were added and the reaction checked by TLC (10% MeOH/CH_2Cl_2). After 1 h an additional 0.5 eq (2.13 mmol) of NEt_3 and MsCl were added and the solution was allowed to stir for 1 h more. The volatiles were then removed *in vacuo* and the resulting oil purified by chromatography (silica, 10% MeOH/CH_2Cl_2). The solid was dissolved in acetone, filtered as in **16**, concentrated and triturated with hexanes to give 1.60 g (72%) **14**. The compound decomposes upon prolonged storage at ambient temperature even desiccated under N_2. ^{1}H NMR (500 MHz, CD_3OD) δ 3.03 (s, 3H), 3.44 (m, 2H), 3.48-3.66 (m, 3H, H2-4), 3.76 (s, 3H, $COOCH_3$), 4.09 (d, 1H, H-5, *J*=10 Hz), 4.25 (m, 2H), 5.09 (s, 2H, benzylic CH_2), 5.19 (d, 1H, H-1), 7.37 (d, 1H, ArH, *J*=8 Hz), 7.59 (d, 1H, ArH, *J*=8Hz), 7.83 (s, 1H, ArH); ^{13}C NMR (126 MHz, CD_3OD) δ 37.32, 41.37, 53.11, 66.06, 69.95, 72.77, 74.48, 76.89, 77.25, 102.44, 118.94, 125.64, 133.44, 134.52, 142.24, 150.61, 158.62, 170.81; Anal. Calcd for $C_{18}H_{24}N_2O_{14}S$: C 41.22, H 4.61, N 5.34; Found C 41.52, H 4.55, N 5.24.

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