Supporting information for:

H-Bonding, not Remote Participation, explains the Influence of Remote Substituents on Stereoselectivity in Galactosylations

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Part 1 – Experimental details, Characterisation, Computation details

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1. General Experimental

Reagents and solvents used in the following experiments were bought commercially and used without further purification. $PhCH(OMe)_2$ was purified by distillation prior to use. Ethyl 2,3,6-*O*-benzyl-1-thio-β-D-galactopyranoside was purchased from Biosynth. Anhydrous solvents were obtained using equipment based on Grubb's design[1] and stored in Strauss flasks over 4 Å molecular sieves. Anhydrous DMF and anhydrous pyridine were purchased over 4 Å molecular sieves in Sure/Seal™ bottles packaged under Argon. A Karl Fischer titrator was used to determine the quantity of water in anhydrous solvents. For air- and moisture-sensitive reactions, solvents were added *via* syringes through rubber septa. Air- and moisture-sensitive reactions were carried out under a N_2 atmosphere in oven-dried or flame-dried glassware, which was cooled under reduced pressure prior to use. Molecular sieves were activated by 3 cycles of the following: flame-drying followed by cooling under reduced pressure and 3 vacuum-to-N_2 cycles. Reactions were monitored by thin layer chromatography (TLC) analysis using silica-coated aluminium plates (60 F_{254}) and the eluents outlined. Spots were detected under 254 nm UV light and/or by staining using H_2SO_4 (15%) in EtOH where appropriate. Flash column chromatography was performed using either silica gel [Davisil, 400–230 mesh (63–40 μm)] or a Biotage Isolera™ UV-VIS Flash Purification System (Version 2.3.1) with SNAP KP-Sil (50 μm) or Sfär (20 μm) prepacked silica cartridges. Concentration of products *in vacuo* was carried out using a Büchi rotary evaporator (bath temperatures up to 50 °C) followed by a high vacuum line at room temperature (r.t.).

^{1}H NMR, ^{13}C NMR and 2D NMR spectroscopy was carried out on 400 MHz, 500 MHz or 600 MHz spectrometers using deuterated chloroform ($CDCl_3$). Chemical shifts are reported in parts per million (ppm), referenced to the residual proton of TMS for ^{1}H NMR spectra and to the ^{13}C signal of deuterated chloroform ($CDCl_3$) for ^{13}C NMR spectra. Coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are abbreviated as; s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet) or combinations thereof. For compounds not reported in literature, NMR assignments have been made using COSY, HSQC and HMBC spectroscopy. High-resolution mass spectrometry was carried out by the mass spectrometry service at University College Dublin on a Waters® Micromass GCT system or on an Agilent 6546 QTOF system in electrospray ionization mode (ESI).

Compounds **5b** and **5e** were synthesised by Dr Imlirenla Pongener.

1. Glycosyl Acceptor Synthesis

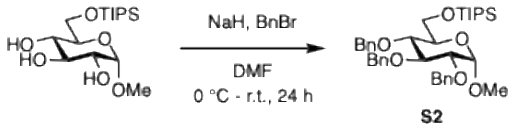
Methyl 6-*O*-triisopropylsilyl-α-D-glucopyranoside (S1)

S1

Following a modified procedure to that reported by Liu and co-workers,[2] methyl α-D-glucopyranoside (10 g, 52 mmol) was dissolved in anhydrous DMF (82 mL) in a flame-dried round bottom flask under a N_2 atmosphere. Imidazole (10.6 g, 156 mmol) and TIPSCl (12.2 mL, 57.2 mmol) were added portion-wise to the flask. The reaction was stirred at room temperature for 24 h to give a clear, colourless solution. The reaction was diluted with water (100 mL) and washed with EtOAc (3 × 100 mL). The combined organic layer was washed with brine (3 × 80 mL) and water (3 × 80 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give silyl ether **S1**. The crude material (18 g) was used in the next step without further purification.

TLC R_f = 0.10 (40% EtOAc in c-Hex).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl-α-D-glucopyranoside (S2)

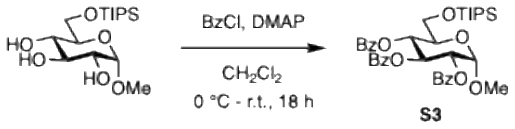


S2

Crude compound **S1** (9.0 g, 26 mmol) in DMF was dissolved in anhydrous DMF (110 mL) in a flame-dried round bottom flask and placed under a N_2 atmosphere. The flask was cooled to 0 °C in an ice bath and NaH (60% dispersion in mineral oil, 3.6 g, 91 mmol) was added to the reaction mixture to give a grey, foamy mixture. The ice bath was removed and the reaction was stirred at room temperature for 30 min. The reaction was then cooled to 0 °C and BnBr (11 mL, 91 mmol) was added dropwise. The ice bath was removed and the reaction mixture was stirred at room temperature for 24 h to give a cloudy, yellow mixture. The reaction mixture was quenched with MeOH (10 mL) and stirred for 10 min. MeOH was then removed *in vacuo* and the solution was diluted with EtOAc (100 mL). The organic layer was washed with HCl (1 M, 3 × 80 mL), satd. aq. $NaHCO_3$ (3 × 80 mL) and brine (3 × 80 mL). The combined aqueous layers were washed with EtOAc (3 × 80 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give benzyl **S2** as a yellow oil. The crude material (11.8 g) was used in the next step without further purification.

TLC R_f = 0.23 (10% EtOAc in c-Hex).

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-triisopropylsilyl-α-D-glucopyranoside (S3)

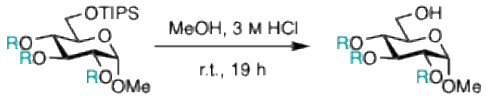


S3

Crude compound **S1** (9.0 g, 26 mmol) was dissolved in anhydrous CH_2Cl_2 (170 mL) and placed under a N_2 atmosphere. The flask was cooled to 0 °C in an ice bath and BzCl (12.1 mL, 104 mmol), pyridine (8.38 mL, 104 mmol) and DMAP (0.64 g, 20 mol%) were added. The ice bath was removed and the reaction was stirred at room temperature for 18 h to give a pale yellow solution. The reaction mixture was then cooled to 0 °C and H_2O (100 mL) was added. The mixture was diluted with CH_2Cl_2 (90 mL). The aqueous layer was washed with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with HCl (1 M, 3 × 90 mL), satd. aq. $NaHCO_3$ (3 × 90 mL) and brine (3 × 90 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give benzoate **QK4** as a yellow oil. The crude material (10.2 g) was used in the next step without further purification.

TLC R_f = 0.39 (20% EtOAc in c-Hex).

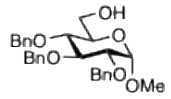
General Procedure A: Cleavage of Triisopropylsilyl Group



5a: R = Bn
5f: R = Bz

Crude silyl ether **S2** or **S3** was dissolved in MeOH (0.1 M) and HCl (3 M, 1.0 equiv.) was added dropwise. The reaction was stirred at room temperature for 19 h to give a yellow solution. The reaction was quenched with satd. aq. $NaHCO_3$ (1.0 equiv.) and stirred for 5 min. The solution was diluted with CH_2Cl_2 (50 mL per 10 mL of MeOH) and the organic layer was washed with satd. aq. $NaHCO_3$ (50 mL per 10 mL of MeOH), H_2O (50 mL per 10 mL of MeOH) and brine (50 mL per 10 mL of MeOH). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give primary alcohol **5a** or **5f**.

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (5a)



Following **General Procedure A**, crude silyl ether **S2** (11.8 g, 19.0 mmol) was used. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give alcohol **5a** as a white foam (7.4 g, 84% over three steps).

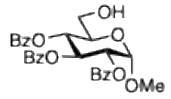
TLC R_f 0.17 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.23 (m, 15H, Ar-H), 4.98 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.87 (d, *J* = 11.0 Hz, 1H, CH*H*Ph), 4.83 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.77 (d, *J* = 12.1 Hz, 1H, CH*H*Ph), 4.66 – 4.61 (m, 2H, 2 × C*H*HPh), 4.57 (d, *J* = 3.6 Hz, 1H, H-1), 4.01 (t, *J* = 9.3 Hz, 1H, H-3), 3.77 – 3.72 (m, 1H, H-6a), 3.71 – 3.60 (m, 2H, H-5 and H-6b), 3.55 – 3.50 (m, 1H, H-4), 3.50 – 3.47 (m, 1H, H-2), 3.34 (s, 3H, OMe), 1.73 – 1.63 (br s, 1H, OH).

^{13}C NMR (101 MHz, Chloroform-d) δ 138.8 (Ar-*C*), 138.2 (Ar-*C*), 138.2 (Ar-*C*), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.6 (Ar-*C*H), 98.2 (C-1), 82.0 (C-3), 80.0 (C-2), 77.4 (C-4), 75.8 (*C*H$_2$Ph), 75.0 (*C*H$_2$Ph), 73.4 (*C*H$_2$Ph), 70.7 (C-5), 61.9 (C-6), 55.2 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[3]

Methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (5f)



Following **General Procedure A**, crude silyl ether **S3** (10.2 g, 15.3 mmol) was used. The crude product was purified by column chromatography, eluting with 20% EtOAc in c-Hex, to give alcohol **5f** as a white foam (6.8 g, 87% over three steps).

TLC R_f 0.40 (20% EtOAc in c-Hex).

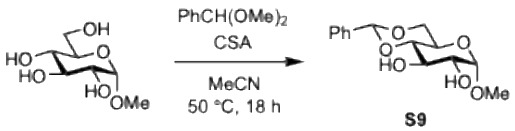
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 4H, Ar-H), 7.88 (dd, *J* = 8.2, 1.1 Hz, 2H, Ar-H), 7.56 – 7.48 (m, 2H, Ar-H), 7.44 – 7.35 (m, 5H, Ar-H), 7.31 – 7.25 (m, 2H, Ar-H), 6.23 (t, *J* = 9.7 Hz, 1H, H-3), 5.51 (t, *J* = 9.9 Hz, 1H, H-4), 5.31 – 5.28 (m, 1H, H-2), 5.27 (d, *J* = 3.7 Hz, 1H, H-1), 4.05 (ddd, *J*

= 10.1, 3.5, 2.4 Hz, 1H, H-5), 3.87 – 3.80 (m, 1H, H-6a), 3.77 – 3.71 (m, 1H, H-6b), 3.47 (s, 1H, OMe), 1.69 (s, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5 (C=O), 165.9 (C=O), 133.8 (Ar-*C*), 133.5 (Ar-*C*), 133.3 (Ar-*C*), 130.1 (Ar-*C*H), 130.0 (Ar-*C*H), 129.8 (Ar-*C*H), 129.3 (Ar-*C*H), 129.2 (Ar-*C*H), 128.7 (Ar-*C*H), 128.7 (Ar-*C*H), 128.6 (Ar-*C*H), 128.4 (Ar-*C*H), 97.3 (C-1), 72.2 (C-2), 70.2 (C-3), 69.9 (C-5), 69.7 (C-4), 61.2 (C-6), 55.8 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[4]

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (S9)



S9

Methyl α-D-galactopyranoside (0.50 g, 2.5 mmol) was suspended in MeCN (25 mL) in a flame-dried crimp top vial and placed under a N_2 atmosphere. Benzylidene dimethyl acetal (0.75 mL, 5.0 mmol) and CSA (0.12 g, 0.50 mmol) were added. The reaction mixture was stirred at 50 °C for 18 h. The reaction was quenched with Et_3N (0.3 mL) and concentrated *in vacuo*. The resulting material was dissolved in CH_2Cl_2 (30 mL) and washed with satd. aq. $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo* to give a white solid. The crude material was purified by recrystallisation from hot EtOAc to give acetal **S9** as a white solid (0.59 g, 84%).

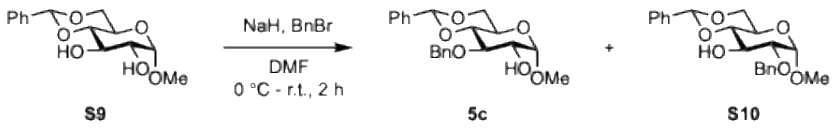
TLC R_f 0.14 (40% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H, Ar-H), 7.41 – 7.33 (m, 3H, Ar-H), 5.54 (s, 1H, PhC*H*), 4.81 (d, *J* = 3.9 Hz, 1H, H-1), 4.30 (dd, *J* = 9.7, 4.3 Hz, 1H, H-6a), 3.94 (td, *J* = 9.2, 1.7 Hz, 1H, H-3), 3.85 – 3.78 (m, 1H, H-5), 3.75 (dd, *J* = 10.4, 9.7 Hz, 1H, H-6b), 3.64 (td, *J* = 9.4, 4.0 Hz, 1H, H-2), 3.50 (t, *J* = 9.3 Hz, 1H, H-4), 3.47 (s, 3H, OMe), 2.65 (app d, *J* = 2.1 Hz, 1H, 3-OH), 2.23 (app d, *J* = 9.6 Hz, 1H, 2-OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2 (Ar-*C*), 129.4 (Ar-*C*H), 128.5 (Ar-*C*H), 126.5 (Ar-*C*H), 102.1 (Ph*C*H), 99.9 (C-1), 81.1 (C-4), 73.1 (C-2), 72.0 (C-3), 69.1 (C-6), 62.5 (C-5), 55.8 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[5]

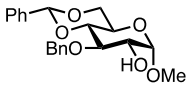
Benzylation of S9 to give 5c and S10



S9 **5c** **S10**

Acetal **S9** (0.59 g, 2.1 mmol) was dissolved in anhydrous DMF (3 mL) in a flame-dried crimp top vial and placed under a N_2 atmosphere. The vial was cooled to 0 °C in an ice bath and NaH (60% dispersion in mineral oil, 84 mg, 2.1 mmol) was added to the reaction mixture to give a grey, foamy mixture. The ice bath was removed and the reaction was stirred at room temperature for 15 min. The reaction was then cooled to 0 °C and BnBr (0.25 mL, 2.1 mmol) was added dropwise. The reaction mixture was stirred for 2 h to give a cloudy, yellow mixture. The reaction mixture was quenched with satd. aq. NH_4Cl (0.3 mL) and stirred for 10 min. The solution was diluted with EtOAc (15 mL). The organic layer was washed with HCl (1 M, 3 × 15 mL), satd. aq. $NaHCO_3$ (3 × 15 mL), H_2O (3 × 15 mL), and brine (3 × 15 mL). The combined aqueous layers were washed with EtOAc (3 × 15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (5c)



Alcohol **5c** was isolated as a white solid (0.38 g, 49%).

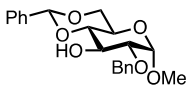
TLC R_f 0.20 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, Ar-H), 7.42 – 7.23 (m, 8H, Ar-H), 5.57 (s, 1H, PhC*H*), 4.96 (d, *J* = 11.5 Hz, 1H, C*H*HPh), 4.83 – 4.74 (m, 2H, C*H*HPh, H-1), 4.30 (dd, *J* = 9.8, 4.3 Hz, 1H, H-6a), 3.87 – 3.75 (m, 3H, H-3, H-5, H-6b), 3.75 – 3.69 (m, 1H, H-2), 3.64 (t, *J* = 9.2 Hz, 1H, H-4), 3.45 (s, 3H, OMe), 2.30 (app d, *J* = 7.4 Hz, 1H, 2-OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6 (Ar-*C*), 137.5 (Ar-*C*), 129.1 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 126.2 (Ar-*C*H), 101.4 (Ph*C*H), 100.0 (C-1), 82.1 (C-4), 79.0 (C-3 or C-5), 75.0 (*C*H_2Ph), 72.6 (C-2), 69.2 (C-6), 62.7 (C-3 or C-5), 55.6 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[6]

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S10)



Alcohol **S10** was isolated as a white solid (0.29 g, 38%).

TLC R_f 0.43 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H, Ar-H), 7.41 – 7.29 (m, 8H, Ar-H), 5.52 (s, 1H, PhC*H*), 4.79 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.71 (d, *J* = 12.2 Hz, 1H, CH*H*Ph), 4.62 (d, *J* = 3.6 Hz, 1H, H-1), 4.26 (dd, *J* = 10.1, 4.7 Hz, 1H, H-6a), 4.15 (td, *J* = 9.3, 2.1 Hz, 1H, H-3), 3.82 (td, *J* = 9.9, 4.7 Hz, 1H, H-5), 3.70 (t, *J* = 10.3 Hz, 1H, H-6b), 3.53 – 3.44 (m, 2H, H-2, H-4), 3.38 (s, 3H, OMe), 2.53 (d, *J* = 2.0 Hz, 1H, 3-OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 (Ar-*C*), 137.2 (Ar-*C*), 129.4 (Ar-*C*H), 128.7 (Ar-*C*H), 128.5 (Ar-*C*H), 128.29 (Ar-*C*H), 128.27 (Ar-*C*H), 126.5 (Ar-*C*H), 102.1 (Ph*C*H), 98.8 (C-1), 81.4 (C-2 or C-4), 79.7 (C-2 or C-4), 73.5 (*C*H_2Ph), 70.4 (C-3), 69.2 (C-6), 62.2 (C-5), 55.5 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[6]

Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (S4)

S4

Methyl α-D-galactopyranoside (0.2 g, 1 mmol) was suspended in MeCN (10 mL) in a flame-dried crimp top vial and placed under a N_2 atmosphere. Benzylidene dimethyl acetal (0.3 mL, 2 mmol) and CSA (46 mg, 0.20 mmol) were added. The reaction mixture was stirred at 50 °C for 18 h. The reaction was quenched with Et_3N (0.1 mL) and concentrated *in vacuo*. The resulting material was dissolved in CH_2Cl_2 (10 mL) and washed with satd. aq. $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a white solid. The crude material was purified by recrystallisation from hot EtOAc to give acetal **S4** as a white solid (0.21 g, 76%).

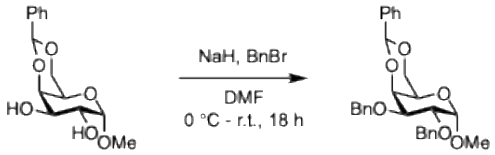
TLC R_f 0.17 (40% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H, Ar-H), 7.40 – 7.33 (m, 3H, Ar-H), 5.54 (s, 1H, PhC*H*), 4.91 (d, *J* = 3.0 Hz, 1H, H-1), 4.29 – 4.21 (m, 2H, H-6a, H-4), 4.06 (dd, *J* = 12.6, 1.9 Hz, 1H, H-6b), 3.93 – 3.85 (m, 2H, H-2, H-3), 3.68 (d, *J* = 1.5 Hz, 1H, H-5), 3.45 (s, 3H, OMe), 2.63 (br s, 1H, OH), 2.40 (br s, 1H, OH).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (Ar-*C*), 129.3 (Ar-*C*H), 128.4 (Ar-*C*H), 126.4 (Ar-*C*H), 101.4 (Ph*C*H), 100.4 (C-1), 76.0 (C-4), 69.94 (C-2 or C-3), 69.85 (C-2 or C-3), 69.4 (C-6), 62.8 (C-5), 55.8 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[7]

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (S5)



S4 **S5**

Acetal **S4** (0.21 g, 0.74 mmol) was dissolved in anhydrous DMF (1.1 mL) in a flame-dried crimp top vial and placed under a N_2 atmosphere. The vial was cooled to 0 °C in an ice bath and NaH (60% dispersion in mineral oil, 76 mg, 1.9 mmol) was added to the reaction mixture to give a grey, foamy mixture. The ice bath was removed and the reaction was stirred at room temperature for 30 min. The reaction was then cooled to 0 °C and BnBr (0.23 mL, 1.9 mmol) was added dropwise. The ice bath was removed and the reaction mixture was stirred at room temperature for 18 h to give a cloudy, yellow mixture. The reaction mixture was quenched with satd. aq. NH_4Cl (3 mL) and stirred for 10 min. The solution was diluted with EtOAc (10 mL). The organic layer was washed with HCl (1 M, 3 × 10 mL), satd. aq. $NaHCO_3$ (3 × 10 mL), H_2O (3 × 10 mL), and brine (3 × 10 mL). The combined aqueous layers were washed with EtOAc (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzyl ether **S5** as a white solid (0.29 g, 84%).

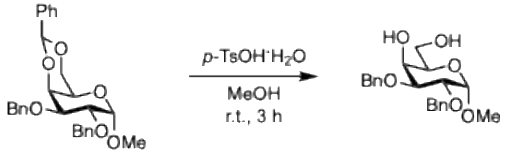
TLC R_f 0.22 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2H, Ar-H), 7.44 – 7.24 (m, 13H, Ar-H), 5.48 (s, 1H, PhC*H*), 4.88 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.83 (d, *J* = 12.4 Hz, 1H, C*H*HPh), 4.78 – 4.72 (m, 2H, C*H*HPh, H-1), 4.68 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.23 – 4.16 (m, 2H, H-4, H-6a), 4.06 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2), 4.02 – 3.95 (m, 2H, H-3, H-6b), 3.57 (d, *J* = 1.7 Hz, 1H, H-5), 3.38 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9 (Ar-*C*), 138.7 (Ar-*C*), 138.0 (Ar-*C*), 129.0 (Ar-*C*H), 128.5 (Ar-*C*H), 128.24 (Ar-*C*H), 128.20 (Ar-*C*H), 127.81 (Ar-*C*H), 127.75 (2 × Ar-*C*H), 127.68 (Ar-*C*H), 126.5 (Ar-*C*H), 101.2 (Ph*C*H), 99.6 (C-1), 76.2 (C-3), 75.6 (C-2), 74.9 (C-4), 74.0 (*C*H_2Ph), 72.3 (*C*H_2Ph), 69.5 (C-6), 62.6 (C-5), 55.7 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[7]

Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (S6)



S5 **S6**

Following a procedure reported by Seeberger and co-workers,[8] benzyl ether **S5** (0.29 g, 0.63 mmol) was dissolved in MeOH (12 mL). *p*-Toluenesulfonic acid monohydrate (0.12 g, 0.63 mmol) was added to the reaction and the solution was stirred at room temperature for 3 h. The reaction mixture was then diluted with EtOAc (20 mL) and washed with satd. aq. $NaHCO_3$ (3 × 20 mL) and brine (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give diol **S6** as a colourless oil (0.23 g, 96%).

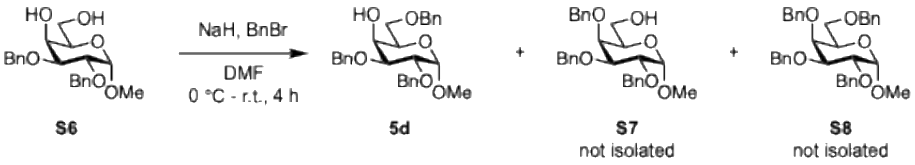
TLC R_f 0.15 (40% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 10H, Ar-H), 4.81 (d, *J* = 11.8 Hz, 2H, 2 × C*H*HPh), 4.71 – 4.64 (m, 3H, 2 × C*H*HPh, H-1), 4.06 (d, *J* = 2.9 Hz, 1H, H-4), 3.95 – 3.82 (m, 3H, H-2, H-3, H-6a), 3.80 – 3.74 (m, 2H, H-5, H-6b), 3.38 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (Ar-*C*), 138.2 (Ar-*C*), 128.69 (Ar-*C*H), 128.66 (Ar-*C*H), 128.57 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 98.8 (C-1), 77.3 (C-2 or C-3), 75.7 (C-2 or C-3), 73.7 (*C*H_2Ph), 73.1 (*C*H_2Ph), 69.3 (C-4), 69.0 (C-5), 63.2 (C-6), 55.5 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[7]

Methyl 2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (5d)



Diol **S6** (0.23 g, 0.61 mmol) was dissolved in anhydrous DMF (1.8 mL) in a flame-dried crimp top vial and placed under a N_2 environment. The vial was cooled to 0 °C in an ice bath and NaH (60% dispersion in mineral oil, 24 mg, 0.61 mmol) was added to the reaction mixture to give a grey, foamy mixture. The ice bath was removed and the reaction was stirred at room temperature for 15 min. The reaction was then cooled to 0 °C and BnBr (72 µL, 0.61 mmol) was added dropwise. The reaction mixture was stirred for 4 h to give a cloudy, yellow mixture. The reaction mixture was quenched with satd. aq. NH_4Cl (0.1 mL) and stirred for 10 min. The solution was diluted with EtOAc (10 mL). The organic layer was washed with HCl (1 M, 3 × 10 mL), satd. aq. $NaHCO_3$ (3 × 10 mL), H_2O (3 × 10 mL), and brine (3 × 10 mL). The combined aqueous layers were washed with EtOAc (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give alcohol **5d** as a white solid (0.15 g, 52%).

TLC R_f 0.31 (20% EtOAc in c-Hex).

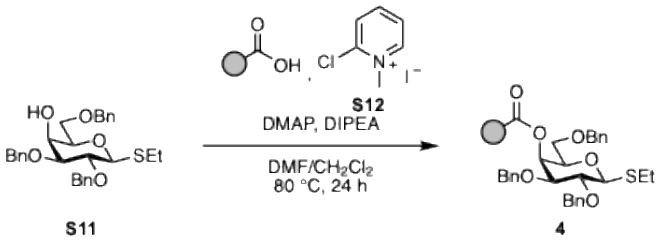
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 15H, Ar-H), 4.80 (t, *J* = 11.9 Hz, 2H, 2 × C*H*HPh), 4.73 – 4.64 (m, 3H, 2 × C*H*HPh, H-1), 4.59 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.54 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.04 (d, *J* = 2.8 Hz, 1H, H-4), 3.89 (t, *J* = 5.9 Hz, 1H, H-5), 3.87 – 3.85 (m, 2H, H-2, H-3), 3.73 (dd, *J* = 10.0, 5.4 Hz, 1H, H-6a), 3.66 (dd, *J* = 10.0, 6.3 Hz, 1H, H-6b), 3.38 (s, 3H, OMe), 2.62 (br s, 1H, OH).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5 (Ar-*C*), 138.3 (Ar-*C*), 138.1 (Ar-*C*), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.14 (Ar-*C*H), 128.12 (Ar-*C*H), 127.94 (Ar-*C*H), 127.91 (Ar-*C*H), 127.88 (Ar-*C*H), 127.77 (Ar-*C*H), 127.75 (Ar-*C*H), 98.7 (C-1), 77.7 (C-2 or C-3), 75.8 (C-2 or C-3), 73.7 (*C*H_2Ph), 73.6 (*C*H_2Ph), 72.9 (*C*H_2Ph), 69.7 (C-6), 68.5 (C-5), 68.2 (C-4), 55.4 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[7]

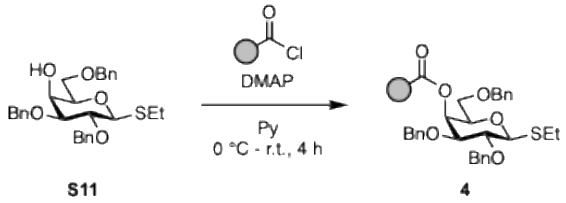
2. Glycosyl Donor Synthesis

General Procedure B: Mukaiyama Esterification



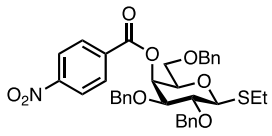
Compound **S11** was dissolved in DMF/CH_2Cl_2 (1:1, 0.11 M) in a flame-dried crimp top vial under a N_2 atmosphere. Benzoic acid (3.0 equiv.), Mukaiyama's salt **S12** (3.0 equiv.) and DMAP (20 mol%) were added. DIPEA (5.0 equiv.) was then added dropwise and the reaction mixture was stirred at 80 °C for 24 h. The reaction was then diluted with CH_2Cl_2 (2 volumes) and quenched with HCl (1 M). After stirring for 30 min, the solution was washed with satd. aq. $NaHCO_3$ (2 volumes), H_2O (2 volumes) and brine (2 volumes). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give benzoate **4**.

General Procedure C: Esterification using Acid Chloride



Compound **S11** was dissolved in anhydrous pyridine (0.11 M) in a flame-dried crimp top vial under a N_2 atmosphere, cooled to 0 °C and stirred for 15 min. Benzoyl chloride (1.5 equiv.) and DMAP (20 mol%) were added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The reaction was then quenched with MeOH and solvents were removed *in vacuo*. The material was dissolved in CH_2Cl_2 (2 volumes) and washed with HCl (1 M, 2 volumes), satd. aq. $NaHCO_3$ (2 volumes), H_2O (2 volumes) and brine (2 volumes). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give benzoate **4**.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-1-thio-β-D-galactopyranoside (4a)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (95 mg, 0.19 mmol) and *p*-nitrobenzoic acid (95 mg, 0.57 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4a** as a brown foam (0.11 g, 89%).

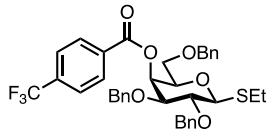
TLC R_f = 0.47 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.18 (m, 2H, *p*-NO_2-ArH), 8.14 – 8.09 (m, 2H, *p*-NO_2-ArH), 7.29 – 7.06 (m, 15H, Ar-H), 5.83 (dd, *J* = 3.4, 1.1 Hz, 1H, H-4), 4.75 (app dd, *J* = 14.2, 10.7 Hz, 2H, 2 × C*H*HPh), 4.66 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.51 – 4.42 (m, 3H, 2 × C*H*HPh, H-1), 4.32 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 3.78 (ddd, *J* = 6.9, 5.8, 1.1 Hz, 1H, H-5), 3.67 (dd, *J* = 9.1, 3.3 Hz, 1H, H-3), 3.58 – 3.51 (m, 2H, H-2, H-6a), 3.45 (dd, *J* = 9.4, 7.4 Hz, 1H, H-6b), 2.78 – 2.65 (m, 2H, S*C*$H_2$$CH_3$), 1.27 (t, *J* = 7.5 Hz, 3H, SCH_2C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (C=O), 150.6 (*p*-NO_2-Ar*C*), 137.9 (Ar-*C*), 137.5 (Ar-*C*), 137.3 (Ar-*C*), 135.2 (Ar-*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 123.7 (Ar-*C*H), 123.5 (*p*-NO_2-Ar*C*H), 85.6 (C-1), 81.0 (C-3), 76.7 (C-2), 75.9 (*C*H_2Ph), 75.7 (C-5), 73.7 (*C*H_2Ph), 72.1 (*C*H_2Ph), 68.6 (C-4), 67.9 (C-6), 25.1 (S*C*$H_2$$CH_3$), 15.1 ($SCH_2$*C*$H_3$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{37}NNaO_8^+$: 666.2132; found: 666.2130.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-trifluoromethylbenzoyl)-1-thio-β-D-galactopyranoside (4b)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (95 mg, 0.19 mmol) and *p*-trifluoromethylbenzoic acid (0.11 g, 0.57 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4b** as a yellow oil (0.11 g, 87%).

TLC R_f = 0.51 (20% EtOAc in c-Hex).

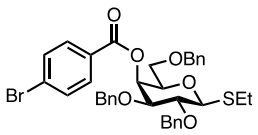
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.11 (m, 2H, *p*-CF_3-ArH), 7.71 (d, *J* = 8.2 Hz, 2H, *p*-CF_3-ArH), 7.38 – 7.13 (m, 15H, Ar-H), 5.90 (dd, *J* = 3.3, 1.1 Hz, 1H, H-4), 4.85 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.73 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.58 – 4.48 (m, 3H, 2 × C*H*HPh, H-1), 4.40 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 3.85 (ddd, *J* = 7.1, 5.7, 1.1 Hz, 1H, H-5), 3.73 (dd, *J* = 9.2, 3.3 Hz, 1H, H-3), 3.65 – 3.59 (m, 2H, H-2, H-6a), 3.53 (dd, *J* = 9.4, 7.3 Hz, 1H, H-6b), 2.85 – 2.71 (m, 2H, S*C*$H_2$$CH_3$), 1.34 (t, *J* = 7.4 Hz, 3H, SCH_2*C*H_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (C=O), 138.1 (Ar-*C*), 137.7 (Ar-*C*), 137.5 (Ar-*C*), 135.2 (Ar-*C*), 134.8 (q, $^2J_{CF}$ = 32.8 Hz, Ar-*C*), 130.4 (Ar-*C*H), 128.51 (Ar-*C*H), 128.49 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 125.6 (q, $^3J_{CF}$ = 3.8 Hz, Ar-*C*H), 123.8 (q, $^1J_{CF}$ = 273.1 Hz, *C*F_3), 85.6 (C-1), 81.2 (C-3), 78.0 (C-2), 76.1 (*C*H_2Ph), 76.0 (C-5), 73.8 (*C*H_2Ph), 72.1 (*C*H_2Ph), 68.3 (C-4), 68.1 (C-6), 25.1 (S*C*$H_2$$CH_3$), 15.2 ($SCH_2$*C*$H_3$).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{37}F_3NaO_6S^+$: 689.2155; found: 689.2154.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-bromobenzoyl)-1-thio-β-D-galactopyranoside (4c)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (89 mg, 0.18 mmol) and *p*-bromobenzoic acid (0.11 g, 0.54 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4c** as a yellow oil (0.10 g, 84%).

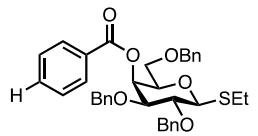
TLC R_f = 0.55 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H, *p*-Br-ArH), 7.63 – 7.55 (m, 2H, *p*-Br-ArH), 7.37 – 7.18 (m, 15H, Ar-H), 5.86 (d, *J* = 3.2 Hz, 1H, H-4), 4.83 (app dd, *J* = 17.0, 10.7 Hz, 2H, C*HH*Ph), 4.73 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.57 – 4.47 (m, 3H, 2 × C*H*HPh, H-1), 4.41 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 3.83 (t, *J* = 6.5 Hz, 1H, H-5), 3.71 (dd, *J* = 9.1, 3.2 Hz, 1H, H-3), 3.65 – 3.59 (m, 2H, H-2, H-6a), 3.52 (dd, *J* = 9.5, 7.2 Hz, 1H, H-6b), 2.86 – 2.70 (m, 2H, SC*H*$_2$CH$_3$), 1.34 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (C=O), 144.7 (*p*-Br-Ar*C*), 138.2 (Ar-*C*), 137.8 (Ar-*C*), 137.6 (Ar-*C*), 131.9 (*p*-Br-Ar*C*H), 131.6 (*p*-Br-Ar*C*H), 128.9 (Ar-*C*), 128.54 (Ar-*C*H), 128.52 (Ar-*C*H), 128.45 (Ar-*C*H), 128.44 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 85.6 (C-1), 81.3 (C-3), 77.9 (C-2), 76.1 (*C*H$_2$Ph), 76.0 (C-5), 73.9 (*C*H$_2$Ph), 72.0 (*C*H$_2$Ph), 68.3 (C-4), 68.0 (C-6), 25.2 (S*C*H$_2$CH$_3$), 15.2 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{37}BrNaO_6S^+$: 699.1386, 701.1366; found: 699.1387, 701.1373.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-benzoyl-1-thio-β-D-galactopyranoside (4d)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (0.11 g, 0.22 mmol) and benzoic acid (81 mg, 0.66 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4d** as a white solid (0.12 g, 93%).

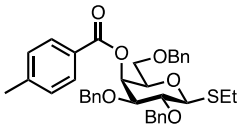
TLC R_f = 0.50 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H, Bz-H), 7.61 – 7.56 (m, 1H, Bz-H), 7.46 (t, *J* = 7.8 Hz, 2H, Bz-H), 7.37 – 7.17 (m, 15H, Ar-H), 5.89 (d, *J* = 3.2 Hz, 1H, H-4), 4.87 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.58 – 4.47 (m, 3H, 2 × C*H*HPh, H-1), 4.42 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 3.84 (t, *J* = 6.4 Hz, 1H, H-5), 3.72 (dd, *J* = 9.2, 3.2 Hz, 1H, H-3), 3.70 – 3.60 (m, 2H, H-2, H-6a), 3.55 (dd, *J* = 9.5, 7.0 Hz, 1H, H-6b), 2.87 – 2.72 (m, 2H, S$CH_2$$CH_3$), 1.34 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C=O), 138.2 (Ar-*C*), 137.8 (Ar-*C*), 137.6 (Ar-*C*), 133.2 (Ar-*C*H), 130.1 (Ar-*C*H), 129.9 (Ar-*C*), 129.9 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 85.5 (C-1), 81.2 (C-3), 77.7 (C-2), 76.2 (C-5), 75.9 (CH_2Ph), 73.8 (CH_2Ph), 71.8 (CH_2Ph), 68.4 (C-6), 67.6 (C-4), 25.0 (SCH_2CH_3), 15.2 (SCH_2CH_3).

NMR spectroscopic data were consistent with those reported in literature.[9]

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-toluoyl-1-thio-β-D-galactopyranoside (4e)



Following **General Procedure C**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (0.10 g, 0.21 mmol) and *p*-methylbenzoyl chloride (42 μL, 0.32 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4e** as a colourless oil (96 mg, 74%).

TLC R_f = 0.51 (20% EtOAc in c-Hex).

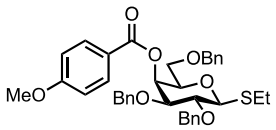
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H, *p*-Tol-ArH), 7.37 – 7.19 (m, 17H, Ar-H), 5.87 (dd, *J* = 3.1, 1.1 Hz, 1H, H-4), 4.86 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.83 – 4.72 (m, 2H, 2 × C*H*HPh), 4.57 – 4.49 (m, 2H, C*H*HPh, H-1), 4.49 – 4.39 (m, 2H, 2 × C*H*HPh), 3.83 (ddd, *J* = 7.0, 5.9, 1.1 Hz, 1H, H-5), 3.74 – 3.61 (m, 3H, H-3, H-2, H-6a), 3.55 (dd, *J* = 9.6, 6.9 Hz, 1H, H-6b), 2.86 – 2.71 (m, 2H, S$CH_2$$CH_3$), 2.43 (s, 3H, CH_3), 1.34 (t, *J* = 7.4 Hz, 1H, SCH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 144.0 (Ar-*C*), 138.3 (Ar-*C*), 137.9 (Ar-*C*), 137.7 (Ar-*C*), 130.2 (Ar-*C*H), 130.2 (Ar-*C*), 129.2 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2

(Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 127.2 (Ar-*C*H), 85.5 (C-1), 81.3 (C-3), 77.9 (C-2), 76.3 (C-5), 76.0 (CH_2Ph), 73.8 (CH_2Ph), 71.8 (CH_2Ph), 68.6 (C-6), 67.4 (C-4), 25.0 (SCH_2CH_3), 21.8 (CH_3), 15.2 (SCH_2CH_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{40}NaO_6S^+$: 635.2438; found: 635.2439.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-anisoyl)-1-thio-β-D-galactopyranoside (4f)



Following **General Procedure C**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (0.10 g, 0.21 mmol) and *p*-methoxybenzoyl chloride (43 μL, 0.32 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4f** as a colourless oil (0.11 g, 85%).

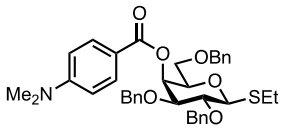
TLC R_f = 0.50 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (app dd, *J* = 9.5, 2.7 Hz, 2H, *p*-OMe-ArH) 7.43 – 7.16 (m, 15H, Ar-H), 6.99 – 6.88 (m, 2H, *p*-OMe-ArH), 5.86 (d, *J* = 3.0 Hz, 1H, H-4), 4.87 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.58 – 4.47 (m, 3H, 2 × C*H*HPh, H-1), 4.42 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 3.85 (s, 3H, OMe), 3.84 – 3.79 (m, 1H, H-5), 3.74 – 3.66 (m, 2H, H-2, H-3), 3.63 (dd, *J* = 9.5, 5.8 Hz, 1H, H-6a), 3.55 (dd, *J* = 9.6, 6.8 Hz, 1H, H-6b), 2.89 – 2.71 (m, 2H, SCH_2CH_3), 1.34 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$ δ 165.5 (C=O), 163.7 (*p*-OMe-Ar*C*), 138.3 (Ar-*C*), 137.9 (Ar-*C*), 137.8 (Ar-*C*), 132.2 (*p*-OMe-Ar*C*H), 128.52 (Ar-*C*H), 128.50 (Ar-*C*H), 128.4 (2 × Ar-*C*H) 128.2 (2 × Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 122.3 (*p*-OMe-Ar*C*), 113.8 (*p*-OMe-Ar*C*H), 85.5 (C-1), 81.3 (C-3), 78.0 (C-2), 76.3 (C-5), 75.9 (CH_2Ph), 73.8 (CH_2Ph), 71.8 (CH_2Ph), 68.6 (C-6), 67.3 (C-4), 55.6 (OMe), 25.0 (SCH_2CH_3), 15.2 (SCH_2CH_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{40}NaO_7S^+$: 651.2387; found: 651.2384.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-dimethylaminobenzoyl)-1-thio-β-D-galactopyranoside (4g)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (94 mg, 0.19 mmol) and *p*-dimethylaminobenzoic acid (94 mg, 0.57 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **4g** as a white foam (0.10 g, 85%).

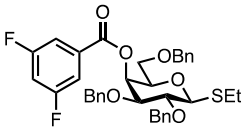
TLC R_f = 0.39 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H, *p*-NMe_2-ArH), 7.31 – 7.13 (m, 15H, Ar-H), 6.65 – 6.60 (m, 2H, *p*-NMe_2-ArH), 5.79 – 5.75 (m, 1H, H-4), 4.80 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.73 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.68 (d, *J* = 10.2 Hz, 1H, CH*H*Ph), 4.49 – 4.43 (m, 2H, C*H*HPh, H-1), 4.43 – 4.33 (m, 2H, 2 × C*H*HPh), 3.74 (td, *J* = 6.3, 1.1 Hz, 1H, H-5), 3.64 – 3.54 (m, 3H, H-2, H-3, H-6a), 3.50 (dd, *J* = 9.7, 6.5 Hz, 1H, H-6b), 2.98 (s, 6H, NMe_2), 2.80 – 2.64 (m, 2H, S*C*H_2CH_3), 1.27 (t, *J* = 7.4 Hz, 3H, SCH_2C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (C=O), 153.5 (*p*-NMe_2-Ar*C*), 138.4 (Ar-*C*), 138.1 (Ar-*C*), 137.9 (Ar-*C*), 131.9 (*p*-NMe_2-Ar*C*H), 128.53 (Ar-*C*H), 128.50 (Ar-*C*H), 128.38 (2 × Ar-*C*H), 128.36 (Ar-*C*H), 128.30 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.6 (Ar-*C*), 111.2 (*p*-NMe_2-Ar*C*H), 85.5 (C-1), 81.4 (C-3), 78.0 (C-2), 76.6 (C-5), 76.0 (*C*H_2Ph), 73.9 (*C*H_2Ph), 71.6 (*C*H_2Ph), 67.0 (C-6), 66.8 (C-4), 40.4 (NMe_2), 25.0 (S*C*H_2CH_3), 15.3 (SCH_2*C*H_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{38}H_{43}NNaO_6S^+$: 664.2703; found: 664.2701.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,5-difluorobenzoyl)-1-thio-β-D-galactopyranoside (10a)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (47 mg, 0.095 mmol) and 3,5-difluorobenzoic acid (43 mg, 0.27 mmol) were used. The crude material was purified

by flash column chromatography, eluting with 20% EtOAc in c-Hex, to form **10a** as a yellow oil (37 mg, 62%).

TLC R_f = 0.49 (20% EtOAc in c-Hex).

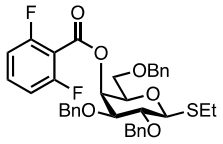
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H, Ar-H), 7.40 – 7.13 (m, 15H, Ar-H), 7.02 (tt, *J* = 8.6, 2.4 Hz, 1H, Ar-H), 5.86 (d, *J* = 3.2 Hz, 1H, H-4), 4.83 (app dd, *J* = 10.7, 3.4 Hz, 2H, 2 × C*H*HPh), 4.74 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.58 – 4.48 (m, 3H, 2 × C*H*HPh, H-1), 4.40 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 3.83 (t, *J* = 6.6 Hz, 1H, H-5), 3.72 (dd, *J* = 9.2, 3.4 Hz, 1H, H-3), 3.65 – 3.57 (m, 2H, H-2, H-6a), 3.51 (dd, *J* = 9.5, 7.3 Hz, 1H, H-6b), 2.86 – 2.70 (m, 2H, SC*H*$_2$CH$_3$), 1.34 (t, *J* = 7.5 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (t, $^4J_{CF}$ = 3.4 Hz, C=O), 162.9 (dd, $^1J_{CF}$ = 250.1 Hz, 11.9 Hz, Ar-*C*), 138.1 (Ar-C), 137.7 (Ar-C), 137.5 (Ar-C), 133.2 (t, $^3J_{CF}$ *J* = 9.1 Hz, Ar-*C*), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 113.1 (d, $^2J_{CF}$ = 26.6 Hz, Ar-*C*H), 108.7 (t, $^2J_{CF}$ = 25.3 Hz, Ar-*C*H), 85.6 (C-1), 81.1 (C-2), 77.8 (C-3), 76.0 (*C*H$_2$Ph), 75.9 (C-5), 73.9 (*C*H$_2$Ph), 72.1 (*C*H$_2$Ph), 68.6 (C-4), 68.0 (C-6), 25.0 (S*C*H$_2$CH$_3$), 15.2 (SCH$_2$*C*H$_3$).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.3 – -108.4 (m).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{36}F_2NaO_6S^+$: 657.2093; found: 657.2094.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-difluorobenzoyl)-1-thio-β-D-galactopyranoside (10b)



Following **General Procedure C**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (80 mg, 0.16 mmol) and 2,6-difluorobenzoyl chloride (30 μL, 0.24 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **10b** as a colourless oil (15 mg, 38%).

TLC R_f = 0.50 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 1H, Ar-H), 7.39 – 7.23 (m, 15H, Ar-H), 6.99 – 6.92 (m, 2H, Ar-H), 5.94 (dt, *J* = 3.0, 1.1 Hz, 1H, H-4), 4.90 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.83 – 4.73 (m, 2H,

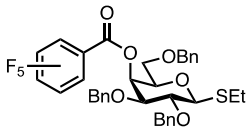
2 × C*H*HPh), 4.57 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.52 – 4.47 (m, 3H, 2 × C*H*HPh, H-1), 3.81 (dd, *J* = 7.5, 5.7 Hz, 1H, H-5), 3.73 – 3.65 (m, 3H, H-2, H-3, H-6a), 3.65 – 3.57 (m, 1H, H-6b), 2.81 – 2.64 (m, 2H, SC*H*$_2$CH$_3$), 1.29 (t, *J* = 7.4, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (dd, $^1J_{CF}$ = 257.2 Hz, 6.1 Hz, Ar-*C*), 160.9 (C=O), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 137.8 (Ar-*C*), 133.0 (t, $^3J_{CF}$ = 10.4 Hz, Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 112.2 (d, $^2J_{CF}$ = 25.3 Hz, Ar-*C*H), 111.1 (t, $^2J_{CF}$ = 18.5 Hz, Ar-*C*), 85.4 (C-1), 81.2 (C-2 or C-3), 77.8 (C-2 or C-3), 76.0 (*C*H$_2$Ph), 75.7 (C-5), 74.0 (*C*H$_2$Ph), 72.1 (*C*H$_2$Ph), 68.8 (C-4), 68.2 (C-6), 24.8 (S*C*H$_2$CH$_3$), 15.2 (SCH$_2$*C*H$_3$).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.2 (dd, *J* = 8.0, 6.3 Hz).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{36}F_2NaO_6S^+$: 657.2093; found: 657.2092.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-pentafluorobenzoyl-1-thio-β-D-galactopyranoside (10c)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (44 mg, 0.09 mmol) and pentafluorobenzoic acid (57 mg, 0.27 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give **10c** as a yellow oil (35 mg, 58%).

TLC R_f = 0.51 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 15H, Ar-H), 5.92 (dd, *J* = 3.3, 1.0 Hz, 1H, H-4), 4.85 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.1 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 10.2 Hz, 1H, CH*H*Ph), 4.57 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.53 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.50 – 4.46 (m, 2H, C*H*HPh, H-1), 3.82 (ddd, *J* = 7.8, 5.6, 1.1 Hz, 1H, H-5), 3.71 (dd, *J* = 9.2, 3.2 Hz, 1H, H-3), 3.68 – 3.61 (m, 1H, H-6a), 3.61 – 3.51 (m, 2H, H-2, H-6b), 2.79 – 2.64 (m, 2H, SC*H*$_2$CH$_3$), 1.29 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

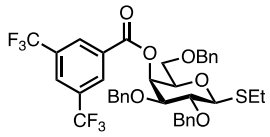
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (C=O), 138.1 (Ar-*C*), 137.7 (Ar-*C*), 137.6 (Ar-*C*), 128.6 (Ar-*C*H), 128.53 (Ar-*C*H), 128.50 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (2 × Ar-*C*H), 128.0 (Ar-*C*H), 127.99 (Ar-

*C*H), 127.98 (Ar-*C*H), 85.5 (C-1), 81.0 (C-3), 77.7 (C-2), 76.0 (*C*H$_2$Ph), 75.3 (*C*H$_2$Ph), 74.0 (C-5), 72.4 (*C*H$_2$Ph), 69.8 (C-4), 67.8 (C-6), 24.9 (S*C*H$_2$CH$_3$), 15.2 (SCH$_2$*C*H$_3$).
Signals for carbons on C_6F_5 were not observed.

^{19}F NMR (376 MHz, $CDCl_3$) δ -137.2 (dp, *J* = 16.4, 5.6 Hz, *p*-F), -148.5 (tt, *J* = 21.1, 4.7 Hz, *o*-F), -160.3 (tt, *J* = 21.0, 6.1 Hz, *m*-F).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{33}F_5NaO_6S^+$: 711.1810; found: 711.1811.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,5-bis(trifluoromethyl)benzoyl)-1-thio-β-D-galactopyranoside (10d)



Following **General Procedure B**, ethyl 2,4,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (69 mg, 0.14 mmol) and 3,5-bis(trifluoromethyl)benzoic acid (0.11 g, 0.42 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to form **10d** as a yellow oil (75 mg, 75%).

TLC R_f = 0.53 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (br s, 2H, Ar-H), 8.07 (br s, 1H, Ar-H), 7.38 – 7.08 (m, 15H, Ar-H), 5.92 (dd, *J* = 3.3, 1.1 Hz, 1H, H-4), 4.84 (app dd, *J* = 10.7, 2.4 Hz, 2H, C*H*HPh, H-1), 4.74 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.60 – 4.48 (m, 3H, 3 × C*H*HPh), 4.38 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 3.86 (ddd, *J* = 7.7, 5.5, 1.1 Hz, 1H, H-5), 3.74 (dd, *J* = 9.1, 3.3 Hz, 1H, H-3), 3.68 – 3.61 (m, 2H, H-2, H-6a), 3.52 (dd, *J* = 9.3, 7.7 Hz, 1H, H-6b), 2.87 – 2.68 (m, 2H, SC*H*$_2$CH$_3$), 1.34 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

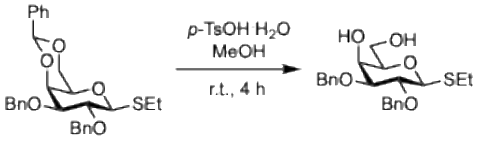
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (C=O), 138.1 (Ar-*C*), 137.5 (Ar-*C*), 137.3 (Ar-*C*), 132.3 (q, $^2J_{CF}$ = 34.1 Hz, Ar-*C*), 132.2 (Ar-*C*), 130.0 (q, $^3J_{CF}$ = 3.9 Hz, Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 126.6 (dq, $^3J_{CF}$ = 7.1, 3.6 Hz, Ar-*C*H), 123.0 (q, $^1J_{CF}$ = 272.9 Hz, *C*F$_3$), 85.2 (C-1), 81.1 (C-3), 77.4 (C-2), 76.0 (*C*H$_2$Ph), 75.6 (C-5), 73.8 (*C*H$_2$Ph), 72.3 (*C*H$_2$Ph), 69.1 (C-4), 67.6 (C-6), 24.3 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$).

^{19}F NMR (376 MHz, CDCl3) δ -62.9.

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{38}H_{40}F_6NO_6S^+$: 752.2475; found: 752.2476.

Synthesis of Donor 15a

Ethyl 2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside (S14)



S13 **S14**

Following a procedure reported by Seeberger and co-workers,[8] benzyl ether **S13** (5.0 g, 10 mmol) and *p*-toluenesulfonic acid monohydrate (1.9 g, 10 mmol) were dissolved in MeOH (200 mL). The reaction mixture was stirred at room temperature for 4 h. The reaction was then diluted with EtOAc (100 mL) and washed with satd. aq. $NaHCO_3$ (3 × 80 mL) and brine (3 × 80 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless oil. Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded diol **S14** as a white solid (3.3 g, 82%).

TLC R_f = 0.1 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H, Ar-H), 7.36 – 7.25 (m, 8H, Ar-H), 4.88 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.76 (d, *J* = 10.3 Hz, 1H, CH*H*Ph), 4.74 – 4.68 (m, 2H, 2 × C*H*HPh), 4.42 (d, *J* = 9.7 Hz, 1H, H-1), 4.05 (dd, *J* = 3.4, 1.1 Hz, 1H, H-4), 3.92 (dd, *J* = 11.7, 6.5 Hz, 1H, H-6a), 3.78 (dd, *J* = 11.7, 4.7 Hz, 1H, H-6b), 3.67 (t, *J* = 9.3 Hz, 1H, H-2), 3.54 (dd, *J* = 8.9, 3.3 Hz, 1H, H-3), 3.46 (ddd, *J* = 6.3, 4.8, 1.1 Hz, 1H, H-5), 2.84 (br s, 1H, OH), 2.82 – 2.67 (m, 2H, SC*H*$_2$CH$_3$), 2.57 (br s, 1H, OH), 1.30 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (Ar-*C*), 137.8 (Ar-*C*), 128.6 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 85.3 (C-1), 82.3 (C-3), 78.0 (C-5), 78.0 (C-2), 75.9 (*C*H$_2$Ph), 72.2 (*C*H$_2$Ph), 67.4 (C-4), 62.6 (C-6), 24.9 (S*C*H$_2$CH$_3$), 15.2 (SCH$_2$*C*H$_3$).

NMR spectroscopic data were consistent with those reported in literature. [10]

Ethyl 2,3-di-*O*-benzyl-6-*O*-triisopropylsilyl-1-thio-β-D-galactopyranoside (S15)

Following a modified procedure to that reported by Liu and co-workers,[2] diol **S14** (0.4 g, 0.1 mmol) was dissolved in CH_2Cl_2 (2 mL). TIPSCl (0.23 mL, 1.1 mmol) and imidazole (75 mg, 1.1 mmol) were added. The reaction was stirred at room temperature for 3 h. The mixture was then diluted with CH_2Cl_2 (5 mL) and washed with HCl (1 M, 3 × 5 mL), satd. aq. $NaHCO_3$ (3 × 5 mL) and brine (3 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless oil. Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded silyl ether **S15** as a colourless oil (0.37 g, 68%).

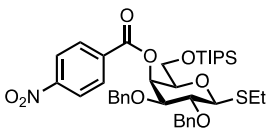
TLC R_f = 0.47 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H, Ar-H), 7.38 – 7.26 (m, 8H, Ar-H), 4.88 (d, *J* = 10.4 Hz, 1H, C*H*HPh), 4.79 (d, *J* = 10.1 Hz, 1H, C*H*HPh), 4.74 (app s, 2H, 2 × C*H*HPh), 4.41 (d, *J* = 9.8 Hz, 1H, H-1), 4.12 (t, *J* = 2.7 Hz, 1H, H-4), 3.98 (dd, *J* = 10.0, 6.6 Hz, 1H, H-6a), 3.89 (dd, *J* = 10.0, 5.3 Hz, 1H, H-6b), 3.74 – 3.68 (m, 1H, H-2), 3.53 (dd, *J* = 8.9, 3.3 Hz, 1H, H-3), 3.40 (t, *J* = 5.7 Hz, 1H, H-5), 2.83 – 2.66 (m, 3H, S*CH*$_2$CH$_3$, OH), 1.29 (t, *J* = 7.5 Hz, 3H, SCH$_2$C*H*$_3$), 1.07 – 1.05 (m, 21H, Si(CH(CH$_3$)$_2$)$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4 (Ar-*C*), 138.1 (Ar-*C*), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5(Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 85.0 (C-1), 82.7 (C-3), 78.3 (C-5), 78.1 (C-2), 75.9 (*C*H$_2$Ph), 72.2 (*C*H$_2$Ph), 66.8 (C-4), 62.9 (C-6), 24.5 (S*C*H$_2$CH$_3$), 18.1 (SiCH(*C*H$_3$)$_2$), 18.0 (SiCH(*C*H$_3$)$_2$), 15.1 (SCH$_2$*C*H$_3$), 12.0 (Si*C*H(CH$_3$)$_2$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{31}H_{48}NaO_5SSi^+$: 583.2884; found: 583.2884.

Ethyl 2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-triisopropylsilyl-1-thio-β-D-galactopyranoside (15a)



Following **General Procedure B**, silyl ether **S15** (0.23 g, 0.41 mmol) and *p*-nitrobenzoic acid (0.20 g, 1.2 mmol) were used. The reaction mixture was stirred at 80 °C for 14 h. Purification by flash column

chromatography, eluting with 20% EtOAc in c-Hex, afforded benzoate **15a** as a yellow foam (90 mg, 31%).

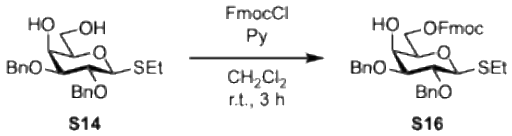
TLC R_f = 0.73 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H, *p*-NO_2-ArH), 8.26 – 8.21 (m, 2H, *p*-NO_2-ArH), 7.39 – 7.21 (m, 10H, Ar-H), 5.94 (d, *J* = 3.2 Hz, 1H, H-4), 4.89 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.83 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.60 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.55 (d, *J* = 9.6 Hz, 1H, H-1), 3.91 – 3.82 (m, 1H, H-6a), 3.79 – 3.71 (m, 3H, H-3, H-5, H-6b), 3.63 (t, *J* = 9.4 Hz, 1H, H-2), 2.89 – 2.72 (m, 2H, SC*H*$_2$CH$_3$), 1.35 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$), 1.05 (s, 3H, Si(C*H*(CH$_3$)$_2$)$_3$), 1.00 – 0.96 (m, 18H, Si(CH(C*H*$_3$)$_2$)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (C=O), 150.7 (*p*-NO_2-Ar*C*), 138.1 (Ar-*C*), 137.7 (Ar-*C*), 135.7 (Ar-*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 123.7 (*p*-NO_2-Ar*C*H), 85.6 (C-1), 81.4 (C-3), 78.0 (C-2), 77.4 (C-5), 76.0 (*C*H$_2$Ph), 72.2 (*C*H$_2$Ph), 68.3 (C-4), 61.4 (C-6), 25.1 (S*C*H$_2$CH$_3$), 18.0 (SiCH(*C*H$_3$)$_2$), 18.0 (SiCH(*C*H$_3$)$_2$), 15.1 (SCH$_2$*C*H$_3$), 11.9 (Si*C*H(CH$_3$)$_2$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{38}H_{51}NNaO_8SSi^+$: 732.2997; found: 732.2995.

Synthesis of Donor 15b
Ethyl 2,3-di-*O*-benzyl-6-*O*-fluorenylmethoxylcarbonyl-1-thio-β-D-galactopyranoside (S16)



S14 **S16**

Following a procedure reported by Seeberger and co-workers,[11] diol **S14** (44 mg, 0.11 mmol) was dissolved in anhydrous CH_2Cl_2 (0.56 mL). FmocCl (28 mg, 0.11 mmol) and pyridine (13 μL, 0.11 mmol) were added and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then quenched with sat. aq. NH_4Cl (1 mL) and diluted with EtOAc (2 mL). The material was then diluted with CH_2Cl_2 (5 mL) and washed with HCl (1 M, 2 × 5 mL), satd. aq. $NaHCO_3$ (2 × 5 mL), H_2O (2 × 5 mL) and brine (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give carbamate **S16** as a white solid (65 mg, 94%).

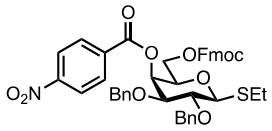
TLC R_f = 0.20 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H, Fmoc-ArH), 7.60 (d, *J* = 7.5 Hz, 2H, Fmoc-ArH), 7.43 – 7.37 (m, 4H, Fmoc-ArH), 7.37 – 7.27 (m, 10H, Ar-H), 4.88 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 10.4 Hz, 1H, CH*H*Ph), 4.72 (app s, 2H, 2 × C*H*HPh), 4.48 – 4.35 (m, 5H, H-1, Fmoc-CH_2, H-6a, H-6b), 4.25 (t, *J* = 7.2 Hz, 1H, Fmoc-C*H*), 4.02 (t, *J* = 2.6 Hz, 1H, H-4), 3.69 – 3.63 (m, 2H, H-2, H-5), 3.56 (dd, *J* = 8.9, 3.2 Hz, 1H, H-3), 2.84 – 2.67 (m, 2H, SC$H_2$$CH_3$), 1.30 (t, *J* = 7.4 Hz, 1H, SCH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (C=O), 143.43 (Ar-*C*), 143.40 (Ar-*C*), 141.4 (Ar-*C*), 138.2 (Ar-*C*), 137.7 (Ar-*C*), 128.7 (Ar-*C*H), 128.51 (Ar-*C*H), 128.50 (Ar-*C*H), 128.48 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.3 (Ar-*C*H), 125.3 (Fmoc-Ar*C*H), 120.2 (Fmoc-Ar*C*H), 85.3 (C-1), 82.2 (C-3), 77.9 (C-2), 76.0 (CH_2Ph), 75.5 (C-5), 72.5 (CH_2Ph), 70.1 (Fmoc-CH_2), 66.81 (C-6), 66.75 (C-4), 46.9 (Fmoc-*C*H), 25.1 (SCH_2CH_3), 15.3 (SCH_2CH_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{38}NaO_7S^+$: 649.2230; found: 649.2232.

Ethyl 2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-fluorenylmethoxylcarbonyl-1-thio-β-D-galactopyranoside (15b)



Following a modified version of **General Procedure C**, carbamate **S16** (65 mg, 0.10 mmol) was dissolved in anhydrous CH_2Cl_2 (0.69 mL) in a flame-dried crimp top vial under a N_2 atmosphere, cooled to 0 °C and stirred for 15 min. *p*-Nitrobenzoyl chloride (19 mg, 0.10 mmol) and pyridine (7 μL, 0.1 mmol) were added slowly. DMAP was not added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzoate **15b** as a colourless oil (19 mg, 24%).

TLC R_f = 0.49 (20% EtOAc in c-Hex).

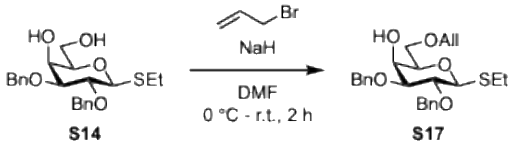
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 2H, *p*-NO_2-ArH), 8.17 – 8.13 (m, 2H, *p*-NO_2-ArH), 7.76 (d, *J* = 7.5 Hz, 2H, Fmoc-ArH), 7.57 (ddt, *J* = 7.6, 4.3, 1.0 Hz, 2H, Fmoc-ArH), 7.44 – 7.38 (m, 2H, Fmoc-ArH), 7.36 – 7.29 (m, 7H, Ar-H), 7.28 – 7.22 (m, 7H, Ar-H), 5.79 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 5.57 (d, *J* = 5.6 Hz, 1H, H-1), 4.79 – 4.69 (m, 4H, 3 × C*H*HPh, H-5), 4.62 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.36 (qd, *J* = 10.4, 7.4 Hz, 2H, Fmoc-CH_2), 4.27 (d, *J* = 6.1 Hz, 2H, H-6a, H-6b), 4.21 (t, *J* =

7.4 Hz, 1H, Fmoc-C*H*), 4.16 – 4.10 (m, 1H, H-2), 3.94 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 2.69 – 2.49 (m, 2H, SC*H*$_2$CH$_3$), 1.30 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (C=O), 155.0 (C=O), 150.8 (Ar-*C*), 143.4 (Ar-*C*), 143.3 (Ar-*C*), 141.4 (Ar-*C*), 137.9 (Ar-*C*), 137.8 (Ar-*C*), 135.2 (Ar-*C*), 131.1 (*p*-NO$_2$-Ar*C*H), 128.53 (Ar-*C*H), 128.46 (Ar-*C*H), 128.17 (Ar-*C*H), 128.11 (Ar-*C*H), 128.03 (Ar-*C*H), 127.96 (Ar-*C*H), 127.9 (Ar-*C*H), 127.3 (Ar-*C*H), 125.28 (Fmoc-Ar*C*H), 125.23 (Fmoc-Ar*C*H), 123.8 (*p*-NO$_2$-Ar*C*H), 120.3 (Fmoc-Ar*C*H), 83.6 (C-1), 77.4 (C-2), 76.5 (C-3), 74.8, 72.8 (*C*H$_2$Ph), 72.7 (*C*H$_2$Ph), 70.3 (Fmoc-*C*H$_2$), 69.9 (C-4), 67.2 (C-5), 66.2 (C-6), 46.8 (Fmoc-*C*H), 23.8 (S*C*H$_2$CH$_3$), 14.8 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{44}H_{45}N_2O_{10}S^+$: 793.2789; found: 793.2788.

Synthesis of Donor 15c
Ethyl 2,3-di-*O*-benzyl-6-*O*-allyl-1-thio-β-D-galactopyranoside (S17)



Following a modified procedure to that reported by Zhao and co-workers,[12] Diol **S14** (50 mg, 0.12 mmol) was dissolved in anhydrous DMF (0.50 mL) and cooled to 0 °C in an ice bath. NaH (60% dispersion in mineral oil, 5 mg, 0.1 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 30 min. The reaction was then cooled to 0 °C and allyl bromide (11 μL, 0.12 mmol) was added slowly over 5 min. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was then poured into ice water (3 mL) and the resulting mixture was washed with CH_2Cl_2 (3 × 5 mL). The combined organic layer was washed with brine (3 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give allyl ether **S17** as a colourless oil (34 mg, 62%).

TLC R_f = 0.26 (20% EtOAc in c-Hex).

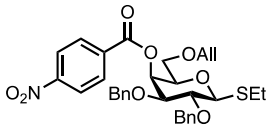
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H, Ar-H), 7.35 – 7.26 (m, 8H, Ar-H), 5.94 – 5.83 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.48 (d, *J* = 5.6 Hz, 1H, H-1), 5.32 – 5.14 (m, 2H, OCH$_2$CH=C*H*$_2$), 4.78 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.74 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.68 (app dd, *J* = 11.7, 7.1 Hz, 2H, 2 × C*H*HPh), 4.31 (t, *J* = 5.9 Hz, 1H, H-5), 4.14 (dd, *J* = 9.7, 5.6 Hz, 1H, H-2), 4.06 (app dq, *J* = 3.7, 1.8

Hz, 1H, H-4), 4.04 – 4.01 (m, 2H, OC*H*$_2$CH=CH$_2$), 3.75 – 3.69 (m, 2H, H-3, H-6a), 3.64 (dd, *J* = 10.2, 6.2 Hz, 1H, H-6b), 2.64 – 2.45 (m, 2H, SC*H*$_2$CH$_3$), 1.28 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.30 (Ar-*C*), 138.26 (Ar-*C*), 134.6 (OCH$_2$*C*H=CH$_2$), 128.7 (Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 117.2 (OCH$_2$CH=*C*H$_2$), 83.2 (C-1), 78.1 (C-3), 75.5 (C-2), 73.0 (O*C*H$_2$CH=CH$_2$), 72.6 (*C*H$_2$Ph), 72.6 (*C*H$_2$Ph), 69.7 (C-6), 68.9 (C-5), 68.3 (C-4), 23.5 (S*C*H$_2$CH$_3$), 14.8 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{38}NaO_7S^+$: 649.2230; found: 649.2232.

Ethyl 2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-allyl-1-thio-β-D-galactopyranoside (15c)



Following **General Procedure B**, alcohol **S17** (18 mg, 0.040 mmol) and *p*-nitrobenzoic acid (20 mg, 0.12 mmol) were used. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzoate **15c** as a yellow oil (14 mg, 58%).

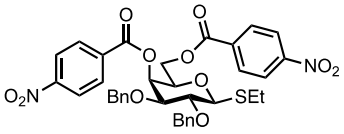
TLC R_f = 0.51 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.25 (m, 2H, *p*-NO$_2$-ArH), 8.18 – 8.12 (m, 2H, *p*-NO$_2$-ArH), 7.37 – 7.22 (m, 10H, Ar-H), 5.84 – 5.72 (m, 2H, OCH$_2$C*H*=CH$_2$, H-4), 5.56 (d, *J* = 5.5 Hz, 1H, H-1), 5.23 – 5.04 (m, 2H, OCH$_2$CH=C*H*$_2$), 4.81 – 4.68 (m, 3H, 3 × C*H*HPh), 4.64 – 4.54 (m, 2H, C*H*HPh, H-5), 4.16 – 4.06 (m, 1H, H-2), 3.98 – 3.85 (m, 3H, H-3, OC*H*$_2$CH=CH$_2$), 3.51 (d, *J* = 5.9 Hz, 2H, H-6a, H-6b), 2.71 – 2.51 (m, 2H, SC*H*$_2$CH$_3$), 1.32 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.7 (*p*-NO$_2$-Ar*C*), 138.1 (Ar-*C*), 138.0 (Ar-*C*), 135.6 (Ar-*C*), 134.2 (OCH$_2$*C*H=CH$_2$), 131.1 (*p*-NO$_2$-Ar*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 123.7 (*p*-NO$_2$-Ar*C*H), 117.5 (OCH$_2$CH=*C*H$_2$), 83.6 (C-1), 76.8 (C-3), 74.9 (C-2), 72.7 (*C*H$_2$Ph), 72.53 (*C*H$_2$Ph), 72.45 (O*C*H$_2$CH=CH$_2$), 70.3 (C-4), 68.7 (C-6), 68.1 (C-5), 23.8 (S*C*H$_2$CH$_3$), 14.8 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{32}H_{35}NO_8S^+$: 616.1976; found: 616.1976.

Ethyl 2,3-di-*O*-benzyl-4,6-*O*-(4-nitrobenzoyl)-1-thio-β-D-galactopyranoside (15d)



Following **General Procedure B**, diol **S14** (22 mg, 0.054 mmol) and *p*-nitrobenzoic acid (27 mg, 0.16 mmol) were used. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give dibenzoate **15d** as an orange solid (27 mg, 71%).

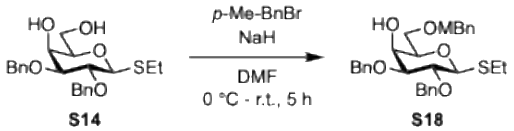
TLC R_f = 0.31 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.28 (m, 4H, *p*-NO_2-ArH), 8.28 – 8.24 (m, 2H, *p*-NO_2-ArH), 8.22 – 8.17 (m, 2H, *p*-NO_2-ArH), 7.39 – 7.30 (m, 5H, Ar-H), 7.29 – 7.23 (m, 5H, Ar-H), 5.87 (d, *J* = 3.3 Hz, 1H, H-4), 4.86 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.80 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.76 (d, *J* = 10.2 Hz, 1H, CH*H*Ph), 4.63 – 4.56 (m, 3H, C*H*HPh, H-1, H-6a), 4.41 (dd, *J* = 11.5, 6.1 Hz, 1H, H-6b), 4.08 (t, *J* = 6.6 Hz, 1H, H-5), 3.80 (dd, *J* = 9.2, 3.3 Hz, 1H, H-3), 3.69 (t, *J* = 9.4 Hz, 1H, H-2), 2.87 – 2.72 (m, 2H, S*H*$_2$CH$_3$), 1.34 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (C=O), 163.5 (C=O), 151.0 (*p*-NO_2-Ar*C*), 150.9 (*p*-NO_2-Ar*C*), 137.9 (Ar-*C*), 137.4 (Ar-*C*), 131.4 (*p*-NO_2-Ar*C*H), 131.2 (*p*-NO_2-Ar*C*H), 131.0 (Ar*C*H), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 128.2 (Ar*C*H), 128.1 (Ar*C*H), 123.9 (*p*-NO_2-Ar*C*H), 123.84 (Ar*C*H), 123.79 (*p*-NO_2-Ar*C*H), 85.9 (C-1), 80.8 (C-3), 77.8 (C-2), 76.1 (*C*H$_2$Ph), 74.3 (C-5), 72.6 (*C*H$_2$Ph), 68.8 (C-4), 63.4 (C-6), 25.4 (S*C*H$_2$CH$_3$), 15.3 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{34}N_2NaO_{11}S^+$: 725.1776; found: 725.1774.

Synthesis of Donor 15e
Ethyl 2,3-di-*O*-benzyl-6-*O*-(*p*-methylbenzyl)-1-thio-β-D-galactopyranoside (S18)



Diol **S14** (50 mg, 0.12 mmol) was dissolved in anhydrous DMF (0.23 mL) and cooled to 0 °C in an ice bath. NaH (60% dispersion in mineral oil, 5.0 mg, 0.12 mmol) was added. The reaction was allowed to warm to room temperature and stirred for 30 min. The reaction was then cooled to 0 °C and *p*-methylbenzyl bromide (17 μL, 0.12 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. The reaction was then quenched with satd. aq. NH_4Cl (1 mL) and diluted with EtOAc (5 mL). The mixture was washed with HCl (1 M, 2 × 5 mL), satd. aq.

$NaHCO_3$ (2 × 5 mL), H_2O (2 × 5 mL) and brine (2 × 5 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzyl ether **S18** as a colourless oil (45 mg, 74%).

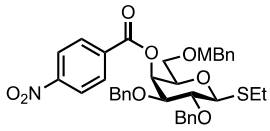
TLC R_f = 0.33 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H, Ar-H), 7.35 – 7.26 (m, 8H, Ar-H), 7.24 – 7.19 (m, 2H, Ar-H), 7.13 (d, *J* = 7.9 Hz, 2H, Ar-H), 5.48 (d, *J* = 5.6 Hz, 1H, H-1), 4.77 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.73 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.67 (app dd, *J* = 11.7, 3.6 Hz, 2H, 2 × C*H*HPh), 4.51 (app s, 2H, 2 × C*H*HPh), 4.31 (t, *J* = 5.7 Hz, 1H, H-5), 4.14 (dd, *J* = 9.7, 5.6 Hz, 1H, H-2), 4.05 (app dt, *J* = 3.0, 1.4 Hz, 1H, H-4), 3.76 – 3.70 (m, 2H, H-3, H-6a), 3.66 (dd, *J* = 10.2, 6.1 Hz, 1H, H-6b), 2.65 (s, 1H, OH), 2.63 – 2.46 (m, 2H, S*CH*$_2$CH$_3$), 2.33 (s, 3H, Ar-CH_3), 1.27 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.3 (Ar-*C*), 138.3 (Ar-*C*), 137.5 (Ar-*C*), 135.1 (Ar-*C*), 129.3 (Ar-*C*H), 129.2 (Ar-*C*H), 128.6 (Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 83.1 (C-1), 78.1 (C-3), 75.5 (C-2), 73.5 (*C*H$_2$Ph), 72.9 (*C*H$_2$Ph), 72.6 (*C*H$_2$Ph), 69.6 (C-6), 68.9 (C-5), 68.3 (C-4), 23.5 (S*C*H$_2$CH$_3$), 21.3 (Ar-CH_3), 14.7 (SCH_2CH_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{30}H_{36}NaO_5S^+$: 531.2176; found: 531.2178.

Ethyl 2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-(*p*-methylbenzyl)-1-thio-β-D-galactopyranoside (15e)



Following **General Procedure B**, alcohol **S18** (45 mg, 0.091 mmol) and *p*-nitrobenzoic acid (45 mg, 0.27 mmol) were used. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzoate **15e** as a yellow oil (34 mg, 58%).

TLC R_f = 0.52 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 2H, *p*-NO_2-ArH), 8.11 – 8.08 (m, 2H, *p*-NO_2-ArH), 7.36 – 7.21 (m, 10H, Ar-H), 7.13 – 7.07 (m, 2H, *p*-Me-ArH), 7.01 (d, *J* = 7.8 Hz, 2H, *p*-Me-ArH), 5.83 (d, *J* = 3.2 Hz, 1H, H-4), 5.54 (d, *J* = 5.5 Hz, 1H, H-1), 4.78 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.75 – 4.68 (m, 2H, 2 × C*H*HPh), 4.62 – 4.57 (m, 2H, C*H*HPh, H-5), 4.45 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.34 (d, *J* =

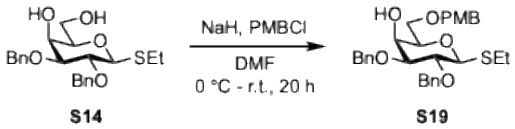
11.7 Hz, 1H, CH*H*Ph), 4.16 – 4.07 (m, 1H, H-2), 3.92 (dd, *J* = 9.9, 3.3 Hz, 1H, H-3), 3.52 (d, *J* = 6.2 Hz, 2H, H6a, H6b), 2.69 – 2.49 (m, 2H, SC*H*$_2$CH$_3$), 2.24 (s, 3H, Ar-CH$_3$), 1.31 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0 (C=O), 150.6 (*p*-NO$_2$-Ar*C*), 138.1 (Ar-*C*), 138.0 (Ar-*C*), 137.6 (Ar-*C*), 135.6 (Ar-*C*), 134.5 (Ar-*C*), 131.0 (*p*-NO$_2$-Ar*C*H), 129.1 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.09 (Ar-*C*H), 128.05 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 123.6 (*p*-NO$_2$-Ar*C*H), 83.6 (C-1), 76.8 (C-3), 74.9 (C-2), 73.6 (*C*H$_2$Ph), 72.7 (*C*H$_2$Ph), 72.4 (*C*H$_2$Ph), 70.0 (C-4), 68.3 (C-6), 68.0 (C-5), 23.8 (S*C*H$_2$CH$_3$), 21.2 (Ar-*C*H$_3$), 14.8 (SCH$_2$*C*H$_3$).

HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calc'd for $C_{37}H_{39}NNaO_8S^+$: 680.2289; found: 680.2287.

Synthesis of Donor 15f

Ethyl 2,3-di-*O*-benzyl-6-*O*-(*p*-methoxybenzyl)-1-thio-β-D-galactopyranoside (S19)



Diol **S14** (0.28 g, 0.69 mmol) was dissolved in DMF (2 mL) and cooled to 0 °C in an ice bath. NaH (60% dispersion in mineral oil, 30 mg, 0.76 mmol) was added portionwise and the reaction mixture was stirred at 0 °C for 30 min. After this time, PMBCl (0.1 mL, 0.8 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction mixture was then quenched with sat. aq. NH_4Cl (2 mL) and diluted with EtOAc (10 mL). The material was then washed with HCl (1 M, 3 × 10 mL), satd. aq. $NaHCO_3$ (3 × 10 mL), H_2O (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give a colourless oil. Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded benzyl ether **S19** as a colourless oil (0.17 g, 46%).

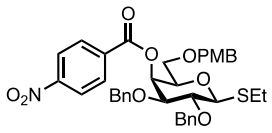
TLC R_f = 0.27 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, Ar-H), 7.36 – 7.23 (m, 10H, Ar-H), 6.92 – 6.85 (m, 2H, Ar-H), 4.87 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.76 (d, *J* = 10.4 Hz, 1H, C*H*HPh), 4.75 – 4.67 (m, 2H, 2 × C*H*HPh), 4.50 (s, 2H, 2 × C*H*HPh), 4.41 (d, *J* = 9.7 Hz, 1H, H-1), 4.08 (d, *J* = 2.7 Hz, 1H, H-4), 3.80 (s, 3H, OMe), 3.79 – 3.64 (m, 3H, H-2, H-6a, H-6b), 3.56 – 3.51 (m, 2H, H-3, H-5), 2.83 – 2.65 (m, 2H, SC*H*$_2$CH$_3$), 2.51 (d, *J* = 2.6 Hz, 1H, OH), 1.31 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (*p*-OMe-Ar*C*), 138.3 (Ar-*C*), 137.9 (Ar-*C*), 130.2 (Ar-*C*), 129.6 (*p*-OMe-Ar*C*H), 128.8 (Ar-*C*H), 128.7 (Ar-*C*H), 128.5 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 114.0 (*p*-OMe-Ar*C*H), 85.2 (C-1), 82.6 (C-3 or C-5), 78.1 (C-2), 77.0 (C-3 or C-5), 76.0 (CH_2Ph), 73.5 (CH_2Ph), 72.2 (CH_2Ph), 69.1 (C-6), 67.0 (C-4), 55.4 (OMe), 24.9 (SCH_2CH$_3$), 15.3 (SCH$_2$$CH_3$).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for: $C_{30}H_{36}NaO_6S^+$ 547.2125; found 547.2123.

Ethyl 2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-(*p*-methoxybenzyl)-1-thio-β-D-galactopyranoside (15f)



Following **General Procedure B**, benzyl ether **S19** (0.17 g, 0.32 mmol) and *p*-nitrobenzoic acid (0.16 g, 0.96 mmol) were used. The crude material was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give benzoate **15f** as an orange oil (0.15 g, 68%).

TLC R_f = 0.39 (20% EtOAc in c-Hex).

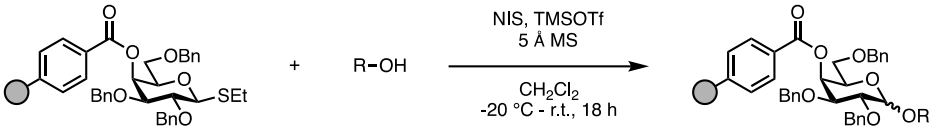
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 2H, *p*-NO_2-ArH), 8.18 – 8.14 (m, 2H, *p*-NO_2-ArH), 7.37 – 7.22 (m, 10H, Ar-H), 7.16 – 7.12 (m, 2H, *p*-OMe-ArH), 6.73 – 6.68 (m, 2H, *p*-OMe-ArH), 5.88 (dd, *J* = 3.4, 1.1 Hz, 1H, H-4), 4.85 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.72 (d, *J* = 10.2 Hz, 1H, C*H*HPh), 4.58 – 4.51 (m, 2H, C*H*HPh, H-1), 4.46 (d, *J* = 11.5 Hz, 1H, C*H*HPh), 4.29 (d, *J* = 11.5 Hz, 1H, C*H*HPh), 3.84 (ddd, *J* = 7.6, 5.5, 1.0 Hz, 1H, H-5), 3.73 (dd, *J* = 9.2, 3.4 Hz, 1H, H-3), 3.69 (s, 3H, OMe), 3.63 – 3.55 (m, 2H, H-2, H-6a), 3.49 (dd, *J* = 9.3, 7.8 Hz, 1H, H-6b), 2.86 – 2.71 (m, 2H, SCH_2CH$_3$), 1.35 (t, *J* = 7.4 Hz, 3H, SCH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (C=O), 159.3 (Ar-*C*), 150.7 (Ar-*C*), 138.0 (Ar-*C*), 137.6 (Ar-*C*), 135.3 (Ar-*C*), 131.3 (Ar-*C*), 131.0 (*p*-NO_2-Ar*C*H), 129.9 (*p*-OMe-Ar*C*H), 129.3 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 123.5 (*p*-NO_2-Ar*C*H), 113.7 (*p*-OMe-Ar*C*H), 85.7 (C-1), 81.1 (C-3), 77.9 (C-2), 76.0 (CH_2Ph), 75.7 (C-5), 73.3 (CH_2Ph), 72.1 (CH_2Ph), 68.6 (C-4), 67.3 (C-6), 55.2 (OMe), 25.2 (SCH_2CH$_3$), 15.2 (SCH$_2$$CH_3$).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for: $C_{37}H_{43}N_2O_9S^+$ 691.2684; found 691.2683.

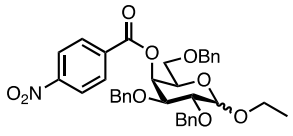
3. Hammett Study

General Procedure D: Galactosylation



An oven-dried crimp top vial was charged with a stir bar and 5 Å molecular sieves. The molecular sieves were activated by flame-drying and then subjected to 3 vacuum-to-N_2 cycles. Glycosyl donor (1.0 equiv.) and alcohol acceptor (0.9 equiv.) were added to the vial and dissolved in anhydrous CH_2Cl_2 (0.02 M) under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min and then cooled to –20 °C in an IMS bath using a chiller. Following stirring at –20 °C for 1 h, NIS (1.5 equiv.) and TMSOTf (0.5 equiv.) were added slowly to give a purple solution. Stirring at –20 °C was continued for 1 h, after which time the reaction mixture was allowed to warm slowly to room temperature over 18 h. The reaction was then quenched with Et_3N (2.0 equiv.) to give an orange solution and diluted with CH_2Cl_2 (2 volumes). The solution was washed with HCl (1 M, 2 volumes), satd. aq. $NaHCO_3$ (2 volumes), H_2O (2 volumes) and brine (2 volumes). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the corresponding glycosylation product. Products were isolated as a mixture of anomers. NMR spectroscopic data of the major α-anomer is reported in each case. Crude α/β-selectivities were recorded from the ^1H NMR spectrum of the reaction mixture prior to purification by column chromatography, using signals corresponding to H-4$^{(')}$.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-D-galactopyranoside (9a)



Glycoside **9a** was prepared *via* **General Procedure D** using donor **4a** (25 mg, 0.039 mmol) and ethanol acceptor (2.0 μL, 0.036 mmol). Purification by flash column chromatography afforded **9a** as a yellow solid (α/β = 74:26, 13 mg, 52%).

TLC R_f = 0.45 (20% EtOAc in c-Hex).

α-9a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H, *p*-NO_2-ArH), 8.10 (d, *J* = 8.8 Hz, 2H, *p*-NO_2-ArH), 7.31 – 7.21 (m, 15H, Ar-H), 5.87 (dd, *J* = 3.6, 1.1 Hz, 1H, H-4), 4.90 (d, *J* = 3.8 Hz, 1H, H-1), 4.83 – 4.79 (m, 2H, 2 × C*H*HPh), 4.65 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.61 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.50 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.39 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.23 (t, *J* = 6.4 Hz, 1H, H-5), 4.14 – 4.08 (m, 1H, H-3), 3.85 – 3.81 (m, 1H, H-2), 3.79 – 3.74 (m, 1H, C*H*HCH$_3$), 3.61 – 3.57 (m, 1H, CH*H*CH$_3$), 3.54 – 3.48 (m, 2H, H-6a, H-6b), 1.29 (t, *J* = 7.09 Hz, 3H, CH_2CH_3).

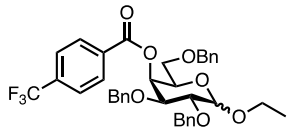
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.7 (*p*-NO_2-Ar*C*), 138.5 (Ar-*C*), 138.2 (Ar-*C*), 137.6 (Ar-*C*), 135.6 (*p*-NO_2-Ar*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 97.6 (C-1), 76.5 (C-3), 75.2 (C-2), 73.8 (*C*H_2Ph), 73.5 (*C*H_2Ph), 72.4 (*C*H_2Ph), 70.2 (C-4), 68.5 (C-6), 67.7 (C-5), 63.9 (*C*H_2CH_3), 15.1 (CH_2*C*H_3).

β-9a

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (d, *J* = 3.3 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{37}NNaO_9^+$: 650.2361; found: 650.2360.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-trifluoromethylbenzoyl)-D-galactopyranoside (9b)



Glycoside **9b** was prepared *via* **General Procedure D** using donor **4b** (25 mg, 0.037 mmol) and ethanol acceptor (2.0 μL, 0.027 mmol). Purification by flash column chromatography afforded **9b** as a colourless oil (α/β = 75:25, 12 mg, 48%).

TLC R_f = 0.44 (20% EtOAc in c-Hex).

α-9b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H, *p*-CF_3-ArH), 7.67 (d, *J* = 7.9 Hz, 2H, *p*-CF_3-ArH), 7.31 – 7.22 (m, 15H, Ar-H), 5.87 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.90 (d, *J* = 3.3 Hz, 1H, H-1), 4.83 – 4.79 (m, 1H, C*H*HPh), 4.72 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.60 (d, *J* = 9.9, 1H, C*H*HPh), 4.57 (d, *J* = 10.3 Hz, 1H, C*H*HPh), 4.39 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.22 (t, *J* = 6.4, 1H, H-5), 4.10 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.87 – 3.82 (m, 1H, H-2), 3.79 – 3.73 (m, 1H, C*H*HCH$_3$), 3.64 – 3.57 (m, 1H, CH*H*CH$_3$), 3.52 (dd, *J* = 6.4, 4.1 Hz, 2H, H-6a, H-6b), 1.28 (t, *J* = 7.2 Hz, 3H, CH$_2$C*H$_3$*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (C=O), 164.7 (*p*-CF_3-Ar*C*), 138.6 (Ar-*C*), 138.3 (Ar-*C*), 137.7 (Ar-*C*), 134.6 (q, $^2J_{CF}$ = 32.4 Hz, Ar-*C*), 130.3 (*p*-CF_3-Ar*C*H), 128.5 (Ar-*C*H), 128.49 (Ar-*C*H), 128.46 (Ar-*C*H), 128.40 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 125.5 (q, $^3J_{CF}$ = 3.8 Hz, Ar-*C*H), 123.8 (q, $^1J_{CF}$ = 272.6 Hz, *C*F_3), 97.7 (C-1), 76.6 (C-3), 75.3 (C-2), 73.8 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 72.3 (*C*H$_2$Ph), 69.7 (C-4), 68.6 (C-6), 67.8 (C-5), 63.9 (*C*H$_2$CH$_3$), 15.1 (CH$_2$*C*H$_3$).

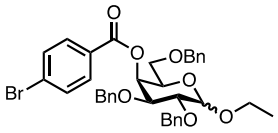
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0.

β-9b

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (d, *J* = 3.2 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calc'd for $C_{37}H_{41}F_3NO_7^+$: 668.2830; found: 668.2830.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-bromobenzoyl)-D-galactopyranoside (9c)



Glycoside **9c** was prepared *via* **General Procedure D** using donor **4c** (25 mg, 0.037 mmol) and ethanol acceptor (2.0 μL, 0.027 mmol). Purification by flash column chromatography afforded **9c** as a yellow oil (α/β = 73:27, 13 mg, 51%).

TLC R_f = 0.47 (20% EtOAc in c-Hex).

α-9c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 1H, *p*-Br-ArH), 7.56 (d, *J* = 8.5 Hz, 1H, *p*-Br-ArH), 7.36 – 7.17 (m, 15H, Ar-H), 5.83 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.88 (d, *J* = 3.7 Hz, 1H, H-1), 4.82 (app dd, *J* = 11.6, 4.5 Hz, 2H, 2 × C*H*HPh), 4.64 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.60 – 4.56 (m, 1H, C*H*HPh), 4.51 – 4.46 (m, 1H, C*H*HPh), 4.45 – 4.40 (m, 1H, C*H*HPh), 4.20 (t, *J* = 6.4 Hz, 1H, H-5), 4.08 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 3.84 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 3.78 – 3.73 (m, 1H, C*H*HCH$_3$), 3.61 – 3.55 (m, 1H, CH*H*CH$_3$), 3.51 (app dd, *J* = 6.4, 3.3 Hz, 2H, H-6a, H-6b), 1.28 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H$_3$*).

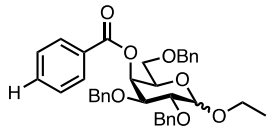
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (C=O), 138.6 (*p*-Br-Ar*C*), 138.3 (*p*-Br-Ar*C*), 132.0 (Ar-*C*), 131.8 (*p*-Br-Ar*C*H), 131.7 (Ar-*C*), 131.5 (*p*-Br-Ar*C*H), 131.4 (Ar-*C*), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 97.7 (C-1), 76.6 (C-3), 75.3 (C-2), 73.8 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 72.2 (*C*H$_2$Ph), 69.4 (C-4), 68.7 (C-6), 67.9 (C-5), 63.8 (*C*H$_2$CH$_3$), 15.1 (CH$_2$*C*H$_3$).

β-9c

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.4 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{37}BrNaO_7^+$: 683.1615, 685.1595; found: 683.1614, 685.1601.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-benzoyl-D-galactopyranoside (9d)



Glycoside **9d** was prepared *via* **General Procedure D** using donor **4d** (25 mg, 0.037 mmol) and ethanol acceptor (2.0 μL, 0.027 mmol). Purification by flash column chromatography afforded **9d** as a white solid (α/β = 64:36, 13 mg, 55%).

TLC R_f = 0.51 (20% EtOAc in c-Hex).

α-9d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H, BzH), 7.60 – 7.53 (m, 1H, BzH), 7.47 – 7.40 (m, 2H, BzH), 7.34 – 7.18 (m, 15H, Ar-H), 5.86 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.89 (d, *J* = 3.6 Hz, 1H, H-1), 4.88 – 4.80 (m, 2H, 2 × C*H*HPh), 4.65 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.61 – 4.56 (m, 1H, C*H*HPh), 4.52 – 4.47 (m, 1H, C*H*HPh), 4.41 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.21 (td, *J* = 6.4, 1.3 Hz, 1H, H-5), 4.09 (dd, *J* = 10.1, 3.4 Hz, 1H, H-3), 3.89 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 3.79 – 3.74 (m, 1H, C*H*HCH$_3$), 3.62 – 3.57 (m, 1H, CH*H*CH$_3$), 3.53 (app dd, *J* = 6.4, 1.0 Hz, 2H, H-6a, H-6b), 1.28 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H$_3$*).

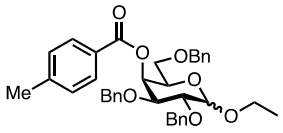
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8 (C=O), 138.5 (Ar-*C*), 138.3 (Ar-*C*), 137.7 (Ar-*C*), 133.1 (Bz-*C*), 133.0 (Bz-*C*H), 129.9 (Bz-*C*H), 128.4 (Bz-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 127.6 (Ar-*C*H), 127.4 (Ar-*C*H), 97.5 (C-1), 76.6 (C-3), 75.2 (C-2), 73.6 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 72.0 (*C*H$_2$Ph), 68.9 (C-4), 68.0 (C-6), 67.5 (C-5), 63.6 (*C*H$_2$CH$_3$), 15.0 (CH$_2$*C*H$_3$).

β-9d

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, *J* = 2.4 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: [M+ Na]$^+$ Calc'd for $C_{36}H_{38}NaO_7^+$: 605.2510; found: 605.2509.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-toluoyl-D-galactopyranoside (9e)



Glycoside **9e** was prepared *via* **General Procedure D** using donor **4e** (25 mg, 0.041 mmol) and ethanol acceptor (2.0 μL, 0.037 mmol). Purification by flash column chromatography afforded **9e** as a yellow oil (α/β = 70:30, 11 mg, 44%).

TLC R_f = 0.41 (20% EtOAc in c-Hex).

α-9e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.20 Hz, 1H, *p*-Me-ArH), 7.34 – 7.18 (m, 17H, Ar-H), 5.84 (d, *J* = 3.3 Hz, 1H, H-4), 4.89 (d, *J* = 3.9 Hz, 1H, H-1), 4.87 – 4.80 (m, 2H, 2 × C*H*HPh), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.61 – 4.53 (m, 1H, C*H*HPh), 4.48 (d, *J* = 12.2, 1H, C*H*HPh), 4.41 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.21 (t, *J* = 6.3 Hz, 1H, H-5), 4.11 – 4.06 (m, 1H, H-2), 3.89 (dd, *J* = 10.1, 3.6 Hz, 1H, H-3), 3.79 – 3.73 (m, 1H, C*H*HCH$_3$), 3.60 – 3.58 (m, 1H, CH*H*CH$_3$), 3.53 (app d, *J* = 6.4 Hz, 2H, H-6a, H-6b), 2.42 (s, 3H, Me), 1.26 (d, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$).

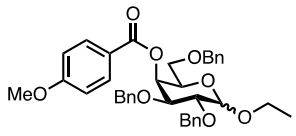
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (C=O), 143.9 (Ar-*C*), 143.8 (Ar-*C*), 138.7 (Ar-*C*), 138.5 (Ar-*C*), 137.9 (Ar-*C*), 130.1 (Ar-*C*H), 129.2 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.34 (Ar-*C*H), 128.32 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.5 (Ar-*C*H), 97.7 (C-1), 76.7 (C-2), 75.4 (C-3), 73.8 (*C*H$_2$Ph), 73.7 (*C*H$_2$Ph), 72.1 (*C*H$_2$Ph), 69.0 (C-6), 68.8 (C-5), 68.2 (C-4), 63.8 (*C*H$_2$CH$_3$), 21.9 (Me), 15.1 (CH$_2$*C*H$_3$).

β-9e

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 2.9 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: [M+ Na]$^+$ Calc'd for $C_{37}H_{40}NaO_7^+$: 619.2666; found: 619.2665.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-anisoyl)-D-galactopyranoside (9f)



Glycoside **9f** was prepared *via* **General Procedure D** using donor **4f** (25 mg, 0.040 mmol) and ethanol acceptor (2.0 μL, 0.036 mmol). Purification by flash column chromatography afforded **9f** as a yellow solid (α/β = 77:23, 10 mg, 41%).

TLC R_f = 0.36 (20% EtOAc in c-Hex).

α-9f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H, *p*-OMe-ArH), 7.37 – 7.18 (m, 15H, Ar-H), 6.93 – 6.88 (m, 2H, *p*-OMe-ArH), 5.83 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.89 (d, *J* = 3.8 Hz, 1H, H-1), 4.87 – 4.80 (m, 2H, 2 × C*H*HPh), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.59 – 4.55 (m, 1H, C*H*HPh), 4.52 – 4.47 (m, 1H, C*H*HPh), 4.44 – 4.39 (m, 1H, C*H*HPh), 4.20 (t, *J* = 6.3 Hz, 1H, H-5), 4.08 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 3.90 – 3.85 (m, 1H, H-2), 3.88 (s, 3H, OMe), 3.82 – 3.73 (m, 1H, C*H*HCH$_3$), 3.60 – 3.56 (m, 1H, CH*H*CH$_3$), 3.53 (app d, *J* = 6.4 Hz, 2H, H-6a, H-6b), 1.27 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H$_3$*).

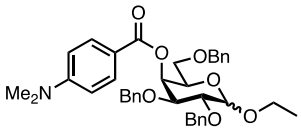
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6 (C=O), 138.7 (Ar-*C*), 138.5 (Ar-*C*), 137.9 (Ar-*C*), 132.3 (*p*-OMe-Ar*C*), 132.1 (*p*-OMe-Ar*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.5 (Ar-*C*H), 122.6 (*p*-OMe-Ar*C*), 113.7 (*p*-OMe-Ar*C*H), 97.7 (C-1), 76.7 (C-3), 75.4 (C-2), 73.7 (*C*H$_2$Ph), 73.6 (*C*H$_2$Ph), 72.0 (*C*H$_2$Ph), 69.0 (C-6), 68.6 (C-4), 68.2 (C-5), 63.7 (*C*H$_2$CH$_3$), 55.6 (OMe), 15.1 (CH$_2$*C*H$_3$).

β-9f

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 2.9 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: [M+ Na]$^+$ Calc'd for $C_{37}H_{40}NaO_8^+$: 635.2615; found: 635.2613.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-dimethylaminobenzoyl)-D-galactopyranoside (9g)



Glycoside **9g** was prepared *via* **General Procedure D** using donor **4g** (25 mg, 0.039 mmol) and ethanol acceptor (2.0 μL, 0.035 mmol). Purification by flash column chromatography afforded **9g** as a white solid (α/β = 88:12, 14 mg, 57%).

TLC R_f = 0.37 (20% EtOAc in c-Hex).

α-9g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H, *p*-NMe_2-ArH), 7.38 – 7.19 (m, 15H, Ar-H), 6.68 – 6.62 (m, 2H, *p*-NMe_2-ArH), 5.81 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.89 (d, *J* = 3.5 Hz, 1H, H-1), 4.88 – 4.80 (m, 2H, 2 × C*H*HPh), 4.64 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.58 – 4.53 (m, 1H, C*H*HPh), 4.51 – 4.46 (m, 1H, C*H*HPh), 4.45 – 4.38 (m, 1H, C*H*HPh), 4.20 (td, *J* = 6.1, 1.2 Hz, 1H, H-5), 4.07 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3), 3.91 (dd, *J* = 10.0, 3.7 Hz, 1H, H-2), 3.81 – 3.74 (m, 1H, C*H*HCH_3), 3.61 – 3.57 (m, 1H, CH*H*CH_3), 3.55 (app d, *J* = 6.2 Hz, 2H, H-6a, H-6b), 3.06 (s, 6H, NMe_2), 1.27 (t, *J* = 6.8 Hz, 3H, CH_2CH_3).

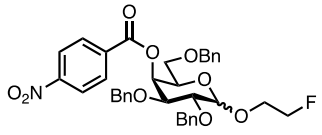
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (C=O), 153.4 (*p*-NMe_2-Ar*C*), 138.7 (Ar-*C*), 138.5 (Ar-*C*), 137.9 (Ar-*C*), 131.8 (*p*-NMe_2-Ar*C*), 131.6 (*p*-NMe_2-Ar*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.6 (Ar-*C*H), 127.5 (Ar-*C*H), 127.2 (Ar-*C*H), 110.7 (*p*-NMe_2-Ar*C*H), 97.6 (C-1), 77.2 (C-3), 75.4 (C-2), 75.8 (CH_2Ph), 73.5 (CH_2Ph), 71.7 (CH_2Ph), 69.2 (C-6), 68.3 (C-5), 67.9 (C-4), 63.5 (CH_2CH_3), 40.1 (NMe_2), 15.0 (CH_2CH_3).

β-9g

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (d, *J* = 3.4 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+ Na]^+$ Calc'd for $C_{38}H_{43}NNaO_7^+$: 648.2932; found: 648.2928.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-D-galactopyranoside (9h)



Glycoside **9h** was prepared *via* **General Procedure D** using donor **4a** (25 mg, 0.039 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.035 mmol). Purification by flash column chromatography afforded **9h** as a yellow solid (α/β = 88:12, 10 mg, 42%).

TLC R_f = 0.33 (20% EtOAc in c-Hex).

α-9h

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H, *p*-NO_2-ArH), 8.12 – 8.08 (m, 2H, *p*-NO_2-ArH), 7.32 – 7.20 (m, 15H, Ar-H), 5.88 (d, *J* = 3.3 Hz, 1H, H-4), 4.96 (d, *J* = 3.7 Hz, 1H, H-1), 4.82 (app dd, *J* = 11.6, 3.7 Hz, 2H, 2 × C*H*HPh), 4.70 – 4.56 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.49 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.40 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.28 (t, *J* = 6.1 Hz, 1H, H-5), 4.12 (dd, *J* = 9.9, 3.4 Hz, 1H, H-3), 3.86 (dd, *J* = 9.8, 3.8 Hz, 1H, H-2), 3.57 – 3.47 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.7 (*p*-NO_2-Ar*C*), 138.4 (Ar-*C*), 138.1 (Ar-*C*), 137.6 (Ar-*C*), 135.6 (*p*-NO_2-Ar*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 98.3 (C-1), 82.6 (d, $^1J_{CF}$ = 170.0 Hz, CH_2CH_2F), 78.7 (d, $^2J_{CF}$ = 33.5 Hz, CH_2CH_2F), 76.3 (C-3), 75.2 (C-2), 73.7 (CH_2Ph), 73.6 (CH_2Ph), 72.5 (CH_2Ph), 70.1 (C-4), 68.5 (C-6), 67.7 (C-5).

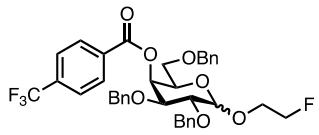
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1.

β-9h

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (d, *J* = 2.9 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+ Na]^+$ Calc'd for $C_{36}H_{36}FNNaO_9^+$: 668.2266; found: 668.2262.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-trifluoromethylbenzoyl)-D-galactopyranoside (9i)



Glycoside **9i** was prepared *via* **General Procedure D** using donor **4b** (25 mg, 0.037 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.034 mmol). Purification by flash column chromatography afforded **9i** as a white solid (α/β = 85:15, 11 mg, 45%).

TLC R_f = 0.46 (20% EtOAc in c-Hex).

α-9i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H, *p*-CF_3-ArH), 7.68 (d, *J* = 8.3 Hz, 2H, *p*-CF_3-ArH), 7.33 – 7.21 (m, 15H, Ar-H), 5.87 (d, *J* = 3.3 Hz, 1H, H-4), 4.95 (d, *J* = 3.7 Hz, 1H, H-1), 4.82 (app dd, *J* = 11.6, 6.6 Hz, 2H, 2 × C*H*HPh), 4.73 – 4.55 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.51 – 4.47 (m, 1H, C*H*HPh), 4.40 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.28 (td, *J* = 6.3, 1.3 Hz, 1H, H-5), 4.11 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.89 – 3.85 (m, 1H, H-2), 3.57 – 3.48 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (C=O), 138.3 (Ar-C), 138.0 (Ar-C), 137.5 (Ar-C), 134.3 (q, $^2J_{CF}$ = 31.0 Hz, Ar-*C*), 133.2 (Ar-C), 130.2 (m, *p*-CF_3-ArH), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 127.9 (Ar-*C*H), 127.7 (Ar-*C*H), 127.7 (Ar-*C*H), 127.5 (Ar-*C*H), 125.4 (d, $^3J_{CF}$ = 3.8 Hz, Ar-*C*H), 122.3 (q, $^1J_{CF}$ = 272.1 Hz, *C*F_3), 98.2 (C-1), 82.6 (d, $^1J_{CF}$ = 169.9 Hz, CH_2CH_2F), 78.9 (d, $^2J_{CF}$ = 29.8 Hz, CH_2CH_2F), 76.2 (C-3), 75.0 (C-2), 73.5 (CH_2Ph), 73.5 (CH_2Ph), 72.2 (CH_2Ph), 69.4 (C-4), 68.4 (C-6), 67.8 (C-5).

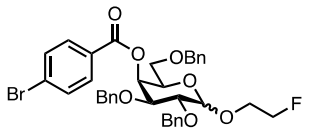
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.11 (CH_2CH_2F), -63.14 (CF_3).

β-9i

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, *J* = 3.5 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+ Na]^+$ Calc'd for $C_{37}H_{36}F_4NaO_7^+$: 691.2289; found: 691.2289.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-bromobenzoyl)-D-galactopyranoside (9j)



Glycoside **9j** was prepared *via* **General Procedure D** using donor **4c** (25 mg, 0.037 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.034 mmol). Purification by flash column chromatography afforded **9j** as a white solid (α/β = 84:16, 8 mg, 30%).

TLC R_f = 0.33 (20% EtOAc in c-Hex).

α-9j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H, *p*-Br-ArH), 7.58 – 7.53 (m, 2H, *p*-Br-ArH), 7.32 – 7.21 (m, 15H, Ar-H), 5.84 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 4.94 (d, *J* = 3.7 Hz, 1H, H-1), 4.82 (app dd, *J* = 11.6 Hz, 4.5 Hz, 2H, 2 × C*H*HPh), 4.73 – 4.54 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.49 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.40 (d, *J* = 11.9 Hz, 1H, CH*H*Ph), 4.26 (td, *J* = 6.3, 1.3 Hz, 1H, H-5), 4.10 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.90 – 3.83 (m, 1H, H-2), 3.56 – 3.46 (m, 2H, H-6a, H-6b).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2 (C=O), 158.0 (*p*-Br-Ar*C*), 138.5 (Ar-*C*), 138.2 (Ar-*C*), 137.8 (Ar-*C*), 131.8 (*p*-Br-Ar*C*H), 131.5 (*p*-Br-Ar*C*H), 129.1 (*p*-Br-Ar*C*), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.6 (Ar-*C*H), 98.3 (C-1), 82.8 (d, $^1J_{CF}$ = 170.2 Hz, CH_2CH_2F), 78.9 (d, $^2J_{CF}$ = 40.5 Hz, CH_2CH_2F), 76.4 (C-3), 75.2 (C-2), 73.7 (CH_2Ph), 73.6 (CH_2Ph), 72.2 (CH_2Ph), 69.2 (C-4), 68.7 (C-6), 68.0 (C-5).

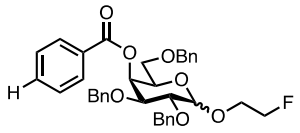
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7.

β-9j

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 3.1 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+ Na]^+$ Calc'd for $C_{36}H_{36}BrFNaO_7^+$: 701.1521, 703.1501; found: 701.1519, 703.1504.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-benzoyl-D-galactopyranoside (9k)



Glycoside **9k** was prepared *via* **General Procedure D** using donor **4d** (25 mg, 0.043 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.039 mmol). Purification by flash column chromatography afforded **9k** as a white solid (α/β = 79:21, 12 mg, 46%).

TLC R_f = 0.28 (20% EtOAc in c-Hex).

α-9k

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H, Bz-H), 7.61 – 7.53 (m, 1H, Bz-H), 7.44 (app q, *J* = 7.4 Hz, 2H, Bz-H), 7.36 – 7.18 (m, 15H, Ar-H), 5.86 (d, *J* = 3.3 Hz, 1H, H-4), 4.95 (d, *J* = 3.7 Hz, 1H, H-1), 4.89 – 4.80 (m, 2H, 2 × C*H*HPh), 4.74 – 4.55 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.51 – 4.40 (m, 2H, 2 × C*H*HPh), 4.27 (t, *J* = 6.3 Hz, 1H, H-5), 4.14 – 4.08 (m, 1H, H-3), 3.92 (dd, *J* = 9.9, 3.7 Hz, 1H, H-2), 3.54 (app dd, *J* = 6.3, 2.3 Hz, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 138.6 (Ar-*C*), 138.3 (Ar-*C*), 137.89 (Ar-*C*), 133.2 (Ar-*C*), 133.2 (Bz-Ar*C*H), 130.0 (Bz-Ar*C*H), 130.2 (Bz-Ar*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.6 (Ar-*C*H), 98.4 (C-1), 82.8 (d, $^1J_{CF}$ = 169.6 Hz, CH_2CH_2F), 79.2 (d, $^2J_{CF}$ = 32.0 Hz, CH_2CH_2F), 76.5 (C-3), 75.3 (C-2), 73.7 (CH_2Ph), 73.7 (CH_2Ph), 72.2 (CH_2Ph), 68.9 (C-4), 68.8 (C-6), 68.2 (C-5).

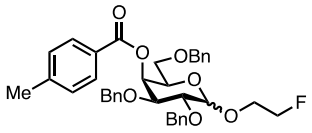
^{19}F NMR (376 MHz, $CDCl_3$) δ -78.4.

β-9k

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, *J* = 3.2 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{36}H_{37}FNaO_7^+$: 623.2416; found: 623.2444.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-toluoyl-D-galactopyranoside (9l)



Glycoside **9l** was prepared *via* **General Procedure D** using donor **4e** (25 mg, 0.041 mmol) and 2-fluoroethanol acceptor (2.1 μL, 0.037 mmol). Purification by flash column chromatography afforded **9l** as a white solid (α/β = 78:22, 10 mg, 39%).

TLC R_f = 0.48 (20% EtOAc in c-Hex).

α-9l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H, *p*-Me-ArH), 7.36 – 7.14 (m, 17H, Ar-H), 5.84 (dd, *J* = 3.4, 1.2 Hz, 1H, H-4), 4.94 (d, *J* = 3.7 Hz, 1H, H-1), 4.87 – 4.79 (m, 2H, 2 × C*H*HPh), 4.72 – 4.53 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.51 – 4.46 (m, 1H, C*H*HPh), 4.42 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.28 – 4.24 (m, 1H, H-5), 4.10 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3), 3.92 (dd, *J* = 10.0, 3.8 Hz, 1H, H-2), 3.54 (app dd, *J* = 6.3, 2.5 Hz, 1H, H-6a, H-6b), 2.42 (s, 3H, Me).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 143.9 (Ar-*C*), 143.8 (Ar-*C*), 138.6 (Ar-*C*), 138.4 (Ar-*C*), 137.9 (Ar-*C*), 129.2 (*p*-Me-Ar*C*H), 128.5 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.6 (Ar-*C*H), 98.4 (C-1), 82.79 (d, $^1J_{CF}$ = 169.4 Hz, CH_2CH_2F), 79.4 (d, $^2J_{CF}$ = 28.0 Hz, CH_2CH_2F), 76.5 (C-3), 75.3 (C-2), 73.7 (CH_2Ph), 73.7 (CH_2Ph), 72.1 (CH_2Ph), 68.9 (C-6), 68.7 (C-4), 68.3 (C-5), 21.8 (Me).

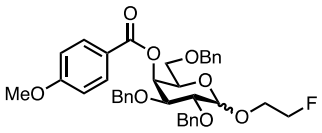
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2.

β-9l

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.4 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{39}FNaO_7^+$: 637.2572; found: 637.2572.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-anisoyl)-D-galactopyranoside (9m)



Glycoside **9m** was prepared *via* **General Procedure D** using donor **4f** (25 mg, 0.040 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.036 mmol). Purification by flash column chromatography afforded **9m** as a white solid (α/β = 86:14, 11 mg, 44%).

TLC R_f = 0.24 (20% EtOAc in c-Hex).

α-9m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H, *p*-OMe-ArH), 7.34 – 7.19 (m, 15H, Ar-H), 6.92 – 6.88 (m, 2H, *p*-OMe-ArH), 5.83 (d, *J* = 2.8 Hz, 1H, H-4), 4.95 (d, *J* = 3.7 Hz, 1H, H-1), 4.89 – 4.80 (m, 2H, 2 × C*H*HPh), 4.74 – 4.54 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.51 – 4.40 (m, 2H, 2 × C*H*HPh), 4.28 – 4.22 (m, 1H, H-5), 4.10 (dd, *J* = 10.1, 3.4 Hz, 1H, H-3), 3.94 – 3.89 (m, 1H, H-2), 3.87 (s, 3H, OMe), 3.54 (app dd, *J* = 6.3, 1.7 Hz, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (C=O), 163.6 (*p*-OMe-Ar*C*), 138.6 (Ar-*C*), 138.4 (Ar-*C*), 137.9 (Ar-*C*), 132.1 (*p*-OMe-Ar*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.5 (Ar-*C*H), 122.5 (*p*-OMe-Ar*C*), 113.8 (*p*-OMe-Ar*C*H), 98.4 (C-1), 82.77 (d, $^1J_{CF}$ = 169.6 Hz, CH_2CH_2F), 79.20 (d, $^2J_{CF}$ = 31.1 Hz, CH_2CH_2F), 76.5 (C-3), 75.3 (C-2), 73.7 (CH_2Ph), 73.6 (CH_2Ph), 72.1 (CH_2Ph), 69.0 (C-6), 68.5 (C-4), 68.3 (C-5), 55.6 (OMe).

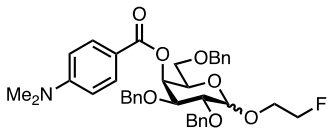
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1.

β-9m

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (d, *J* = 3.2 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{37}H_{39}FNaO_8^+$: 653.2521; found: 653.2540.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(*p*-dimethylaminobenzoyl)-D-galactopyranoside (9n)



Glycoside **9n** was prepared *via* **General Procedure D** using donor **4g** (25 mg, 0.039 mmol) and 2-fluoroethanol acceptor (2.0 μL, 0.035 mmol). Purification by flash column chromatography afforded **9n** as a white solid (α/β = 77:23, 7 mg, 29%).

TLC R_f = 0.24 (20% EtOAc in c-Hex).

α-9n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H, *p*-NMe_2-ArH), 7.36 – 7.18 (m, 15H, Ar-H), 6.68 – 6.63 (m, 2H, *p*-NMe_2-ArH), 5.82 (d, *J* = 3.2 Hz, 1H, H-4), 4.95 (d, *J* = 3.6 Hz, 1H, H-1), 4.91 – 4.80 (m, 2H, 2 × C*H*HPh), 4.74 – 4.62 (m, 3H, C*H*HPh, C$H_2$$CH_2$F), 4.59 – 4.54 (m, 3H, C*H*HPh, CH_2CH_2F), 4.51 – 4.40 (m, 2H, 2 × C*H*HPh), 4.24 (t, *J* = 6.2 Hz, 1H, H-5), 4.09 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.94 (dd, *J* = 9.9, 3.7 Hz, 1H, H-2), 3.58 – 3.52 (m, 2H, H-6a, H-6b), 3.06 (s, 6H, NMe_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (C=O), 153.6 (*p*-NMe_2-Ar*C*), 138.8 (Ar-*C*), 138.5 (Ar-*C*), 138.1 (Ar-*C*), 132.0 (*p*-NMe_2-Ar*C*), 131.8 (*p*-NMe_2-Ar*C*H), 128.45 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.5 (Ar-*C*H), 111.0 (*p*-NMe_2-Ar*C*H), 98.5 (C-1), 82.8 (d, $^1J_{CF}$ = 169.5 Hz, CH_2*C*H_2F), 79.3 (d, $^2J_{CF}$ = 29.0 Hz, *C*$H_2$$CH_2$F), 76.6 (C-3), 75.5 (C-2), 73.8 (*C*H_2Ph), 73.6 (*C*H_2Ph), 71.9 (*C*H_2Ph), 69.3 (C-6), 68.6 (C-5), 67.9 (C-4), 40.3 (NMe_2).

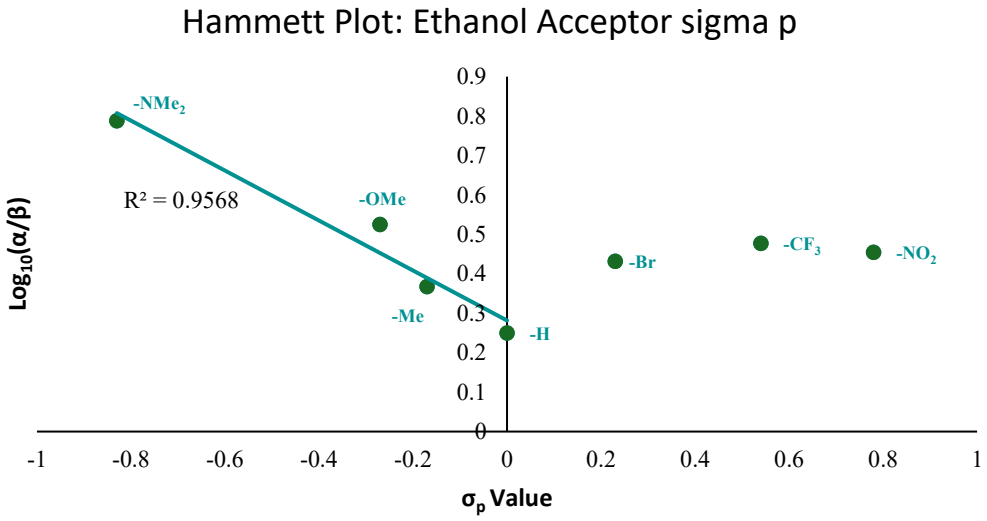
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

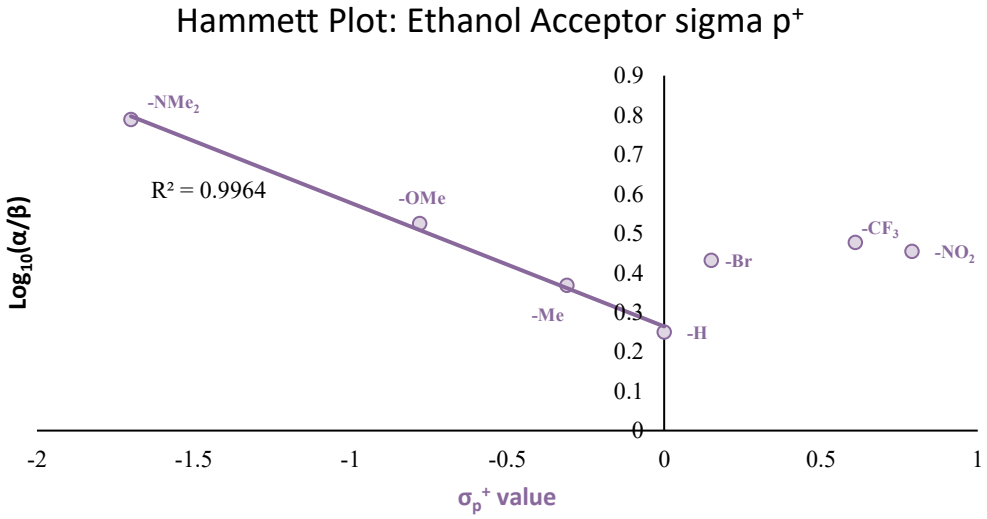
β-9n

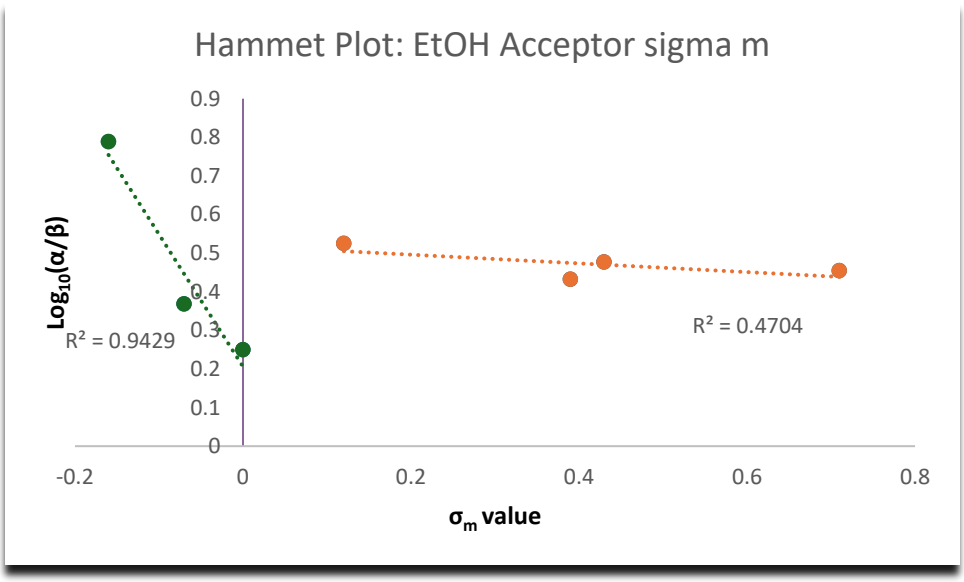
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (d, *J* = 3.4 Hz, 1H, H-4).

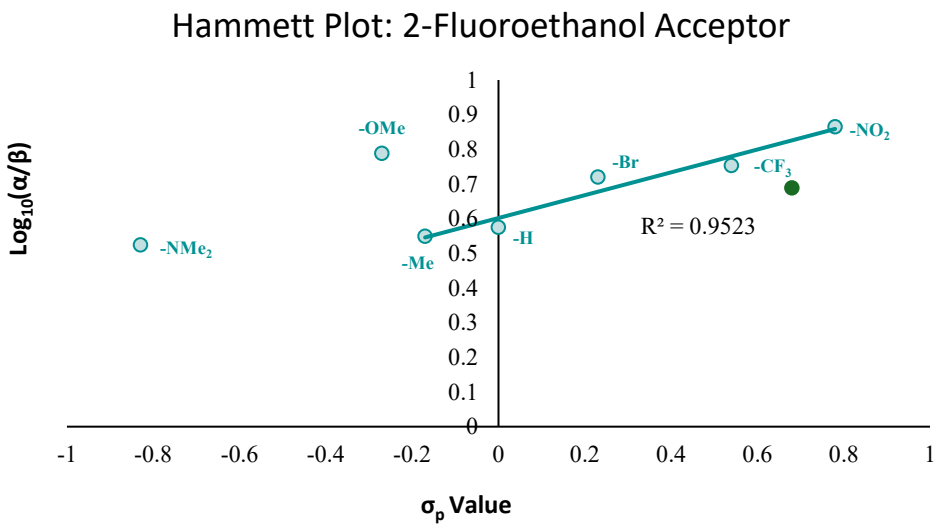
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{38}H_{42}FNaO_7^+$: 666.2838; found: 666.2835.

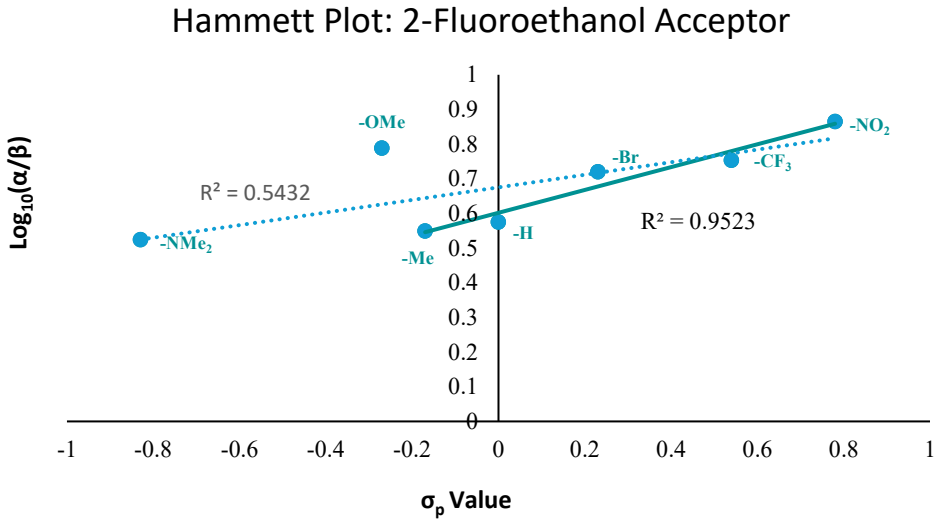
3.2 Alternative Hammett Plots

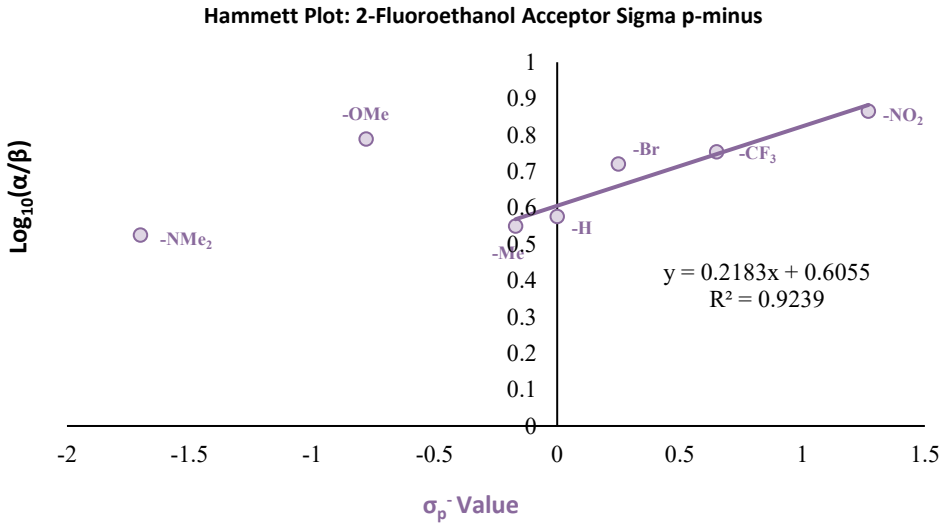


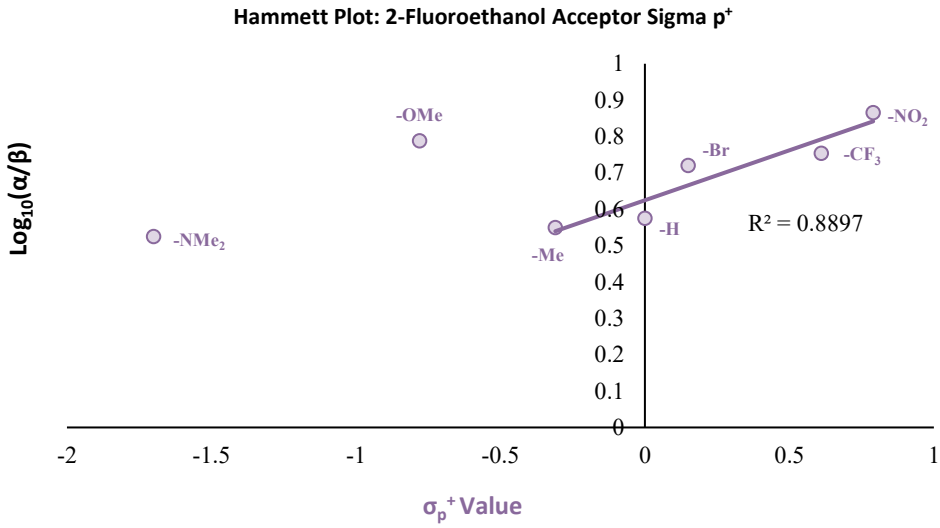


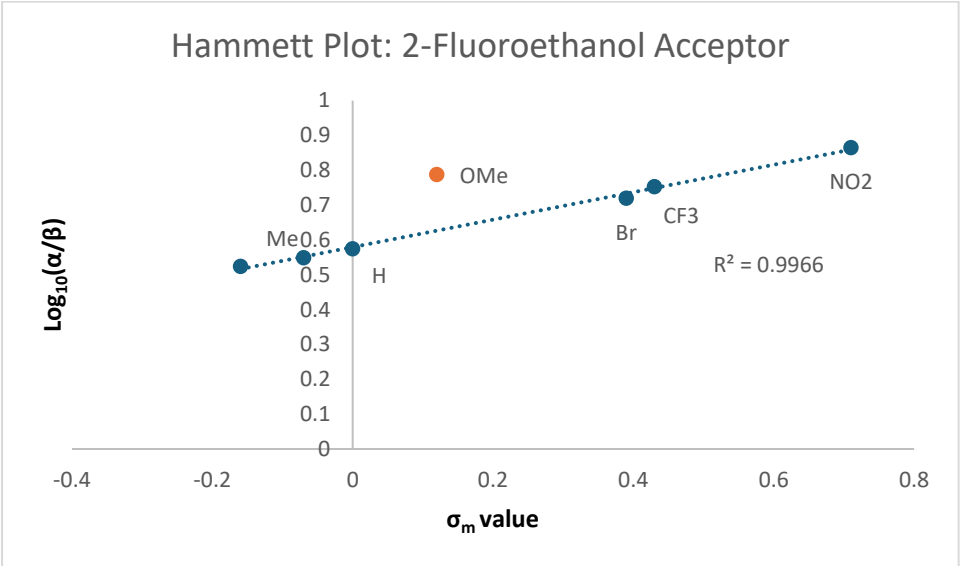



Hammett Plot: 2-Fluoroethanol Acceptor
Log10(α/β)
σp Value
-OMe
-NO2
-Br
-CF3
-NMe2
-H
-Me
R² = 0.9523


Hammett Plot: 2-Fluoroethanol Acceptor
Log10(α/β)
σp Value
-OMe
-NO2
-Br
-CF3
R² = 0.5432
-NMe2
-H
-Me
R² = 0.9523

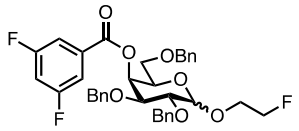

Hammett Plot: 2-Fluoroethanol Acceptor Sigma p-minus
Log10(α/β)
σp- Value
-OMe
-NO2
-Br
-CF3
-NMe2
-H
-Me
y = 0.2183x + 0.6055
R² = 0.9239


Hammett Plot: 2-Fluoroethanol Acceptor Sigma p+
Log10(α/β)
σp+ Value
-OMe
-NMe2
-Me
-H
-Br
-CF3
-NO2
R² = 0.8897
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-2
-1.5
-1
-0.5
0
0.5
1


Hammett Plot: 2-Fluoroethanol Acceptor
Log10(α/β)
σm value
OMe
Me
H
Br
CF3
NO2
R² = 0.9966
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.4
-0.2
0
0.2
0.4
0.6
0.8

4. Fluorine-Substitution Experiments

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,5-difluorobenzoyl)-D-galactopyranoside (11a)



Glycoside **11a** was prepared *via* **General Procedure D** using donor **10a** (50 mg, 0.052 mmol) and 2-fluoroethanol acceptor (3.0 μL, 0.047 mmol). Purification by flash column chromatography afforded **11a** as a colourless oil (α/β = 83:17, 14 mg, 41%).

TLC R_f = 0.43 (20% EtOAc in c-Hex).

α-11a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 2H, Ar-H), 7.37 – 7.17 (m, 15H, Ar-H), 7.05 – 7.00 (m, 1H, Ar-H), 5.83 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4), 4.92 (d, *J* = 3.4 Hz, 1H, H-1), 4.81 (app dt, *J* = 11.6, 3.6 Hz, 2H, 2 × C*H*HPh), 4.74 – 4.54 (m, 6H, 2 × C*H*HPh, CH_2CH_2F), 4.53 – 4.36 (m, 2H, 2 × C*H*HPh), 4.26 (t, *J* = 6.4 Hz, 1H, H-5), 4.10 (dd, *J* = 10.1, 3.2 Hz, 1H, H-3), 3.87 – 3.81 (m, 1H, H-2), 3.55 – 3.46 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (t, $^4J_{CF}$ = 3.7 Hz, C=O), 162.7 (dd, $^1J_{CF}$ = 250.1, 12.0 Hz, Ar-*C*), 137.6 (Ar-*C*), 137.5 (Ar-*C*), 137.4 (Ar-*C*), 133.2 (t, $^3J_{CF}$ = 9.1 Hz, Ar-*C*), 128.4 (Ar-*C*H), 128.29 (Ar-*C*H), 128.26 (Ar-*C*H), 128.20 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.77 (Ar-*C*H), 127.74 (Ar-*C*H), 127.6 (Ar-*C*H), 112.7 (app d, $^2J_{CF}$ = 26.1 Hz, Ar-*C*H), 108.5 (t, $^2J_{CF}$ = 25.2 Hz, Ar-*C*H), 98.1 (C-1), 82.6 (d, $^1J_{CF}$ = 169.6 Hz, CH_2CH_2F), 78.9 (d, $^2J_{CF}$ = 28.4 Hz, CH_2CH_2F), 76.2 (C-3), 74.9 (C-2), 73.7 (CH_2Ph), 73.5 (CH_2Ph), 72.2 (CH_2Ph), 69.7 (C-4), 68.3 (C-6), 67.7 (C-5).

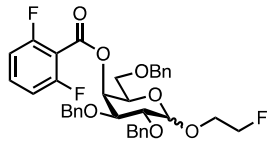
^{19}F NMR δ -63.1 (CH_2CH_2F), -108.1 – -108.2 (m, *m*-F).

β-11a

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (d, *J* = 3.2 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{36}H_{39}F_3NO_7^+$: 654.2673; found: 654.2675.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,6-difluorobenzoyl)-D-galactopyranoside (11b)



Glycoside **11b** was prepared *via* **General Procedure D** using donor **10b** (50 mg, 0.052 mmol) and 2-fluoroethanol acceptor (3.0 μL, 0.047 mmol). Purification by flash column chromatography afforded **11b** as a colourless oil (α/β = 70:30, 13 mg, 38%).

TLC R_f = 0.32 (20% EtOAc in c-Hex).

α-11b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 4.36 (m, 2H, Ar-H), 7.34 – 7.16 (m, 15H, Ar-H), 6.98 – 6.90 (m, 1H, Ar-H), 5.95 – 5.92 (m, 1H, H-4), 4.93 – 4.80 (m, 2H, C*H*HPh, H-1), 4.68 – 4.57 (m, 4H, 2 × C*H*HPh, CH_2CH_2F), 4.57 – 4.50 (m, 4H, 2 × C*H*HPh, CH_2CH_2F), 4.42 – 4.39 (m, 1H, C*H*HPh), 4.26 (t, *J* = 6.6 Hz, 1H, H-5), 4.12 – 4.07 (m, 1H, H-3), 3.85 – 3.77 (m, 1H, H-2), 3.60 (dd, *J* = 6.5, 3.5 Hz, 1H, H-6a), 3.53 – 3.48 (m, 1H, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (C=O), 159.7 (dd, $^1J_{CF}$ = 256.9, 7.2 Hz, Ar-*C*), 138.1 (Ar-*C*), 137.9 (Ar-*C*), 137.8 (Ar-*C*), 132.8 (t, $^3J_{CF}$ = 9.6 Hz, Ar-*C*H), 128.6 (Ar-*C*H), 128.53 (Ar-*C*H), 128.45 (Ar-*C*H), 128.42 (Ar-*C*H), 128.35 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.6 (Ar-*C*H), 112.2 (dd, $^2J_{CF}$ = 23.3, 3.3 Hz, Ar-CH), 111.4 (t, $^2J_{CF}$ = 18.7 Hz, Ar-*C*), 98.4 (C-1), 82.7 (d, $^1J_{CF}$ = 169.6 Hz, CH_2CH_2F), 79.0 (d, $^2J_{CF}$ = 36.3 Hz, CH_2CH_2F), 76.3 (C-3), 75.6 (C-2), 73.9 (CH_2Ph), 73.8 (CH_2Ph), 72.4 (CH_2Ph), 70.0 (C-4), 68.3 (C-6), 67.7 (C-5).

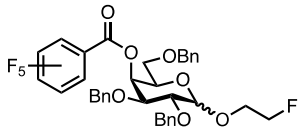
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1 (CH_2CH_2F), -109.1 – -109.3 (m, *o*-F).

β-11b

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (d, *J* = 3.0 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{36}H_{39}F_3NO_7^+$: 654.2673; found: 654.2675.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-pentafluorobenzoyl-D-galactopyranoside (11c)



Glycoside **11c** was prepared *via* **General Procedure D** using donor **10c** (50 mg, 0.073 mmol) and 2-fluoroethanol acceptor (4.0 μL, 0.065 mmol). Purification by flash column chromatography afforded **11c** as a yellow oil (α/β = 68:32, 20 mg, 39%).

TLC R_f = 0.49 (20% EtOAc in c-Hex).

α-11c

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 15H, Ar-H), 5.91 (d, *J* = 3.3 Hz, 1H, H-4), 4.86 (d, *J* = 3.4 Hz, 1H, H-1), 4.85 – 4.79 (m, 2H, 2 × C*H*HPh), 4.66 – 4.59 (m, 4H, 2 × C*H*HPh, CH_2CH_2F), 4.58 – 4.53 (m, 2H, CH_2CH_2F), 4.53 – 4.49 (m, 1H, C*H*HPh), 4.48 – 4.44 (m, 1H, C*H*HPh), 4.25 (t, *J* = 6.5 Hz, 1H, H-5), 4.09 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3), 3.82 – 3.77 (m, 1H, H-2), 3.67 – 3.50 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (C=O), 138.5 (Ar-*C*), 138.1 (Ar-*C*), 137.7 (Ar-*C*), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.47 (Ar-*C*H), 128.44 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 98.3 (C-1), 82.7 (d, $^1J_{CF}$ = 169.7 Hz, CH_2CH_2F), 78.9 (d, $^2J_{CF}$ = 30.5 Hz, CH_2CH_2F), 76.1 (C-3), 75.5 (C-2), 74.0 (CH_2Ph), 73.8 (CH_2Ph), 72.7 (CH_2Ph), 71.1 (C-4), 68.2 (C-6), 67.3 (C-5).
Signals for carbons on C_6F_5 were not observed.

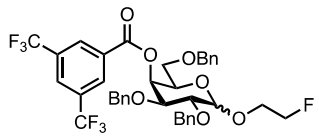
^{19}F NMR (376 MHz, $CDCl_3$) δ -74.8 (CH_2CH_2F), -137.0 – -137.2 (m, *o*-F), -148.6 – -148.7 (m, *p*-F), -160.1 – -160.8 (m, *m*-F).

β-11c

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (d, *J* = 3.2 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{36}H_{36}F_6NO_7^+$: 708.2390; found: 708.2390.

2-Fluoroethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,5-bis(trifluoromethyl)benzoyl)-D-galactopyranoside (11d)



Glycoside **11d** was prepared *via* **General Procedure D** using donor **10d** (38 mg, 0.052 mmol) and 2-fluoroethanol acceptor (3.0 μL, 0.047 mmol). Purification by flash column chromatography afforded **11d** as a colourless oil (α/β = 65:35, 18 mg, 49%).

TLC R_f = 0.50 (20% EtOAc in c-Hex).

α-11d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (app dd, *J* = 21.4, 1.7 Hz, 2H, Ar-H), 8.06 (app d, *J* = 5.2 Hz, 1H, Ar-H), 7.37 – 7.09 (m, 15H, Ar-H), 5.89 (dd, *J* = 3.5, 1.3 Hz, 1H, H-4), 4.92 – 4.89 (m, 2H, C*H*HPh, H-1), 4.84 – 4.77 (m, 2H, 2 × C*H*HPh), 4.71 – 4.67 (m, 3H, C*H*HPh, CH_2CH_2F), 4.64 – 4.49 (m, 3H, C*H*HPh, CH_2CH_2F), 4.41 – 3.35 (m, 1H, C*H*HPh), 4.31 – 4.25 (m, 1H, H-5), 4.13 – 4.08 (m, 1H, H-3), 3.87 – 3.80 (m, 1H, H-2), 3.70 – 3.47 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (C=O), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 137.9 (Ar-*C*), 137.4 (Ar-*C*), 132.3 (q, $^2J_{CF}$ = 34.0 Hz, Ar-*C*), 130.0 (q, $^3J_{CF}$ = 3.7 Hz, Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 127.8 (Ar-*C*H), 126.6 (q, $^1J_{CF}$ = 6.9 Hz, Ar-*C*H), 123.0 (q, $^1J_{CF}$ = 273.1 Hz, *C*F_3), 98.3 (C-1), 82.7 (d, $^1J_{CF}$ = 170.0 Hz, CH_2CH_2F), 79.0 (d, $^2J_{CF}$ = 22.1 Hz, CH_2CH_2F), 76.1 (C-3), 75.5 (C-2), 75.3 (CH_2Ph), 73.7 (CH_2Ph), 72.1 (CH_2Ph), 70.4 (C-4), 68.2 (C-6), 67.7 (C-5).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (CH_2CH_2F), -62.9 (CF_3).

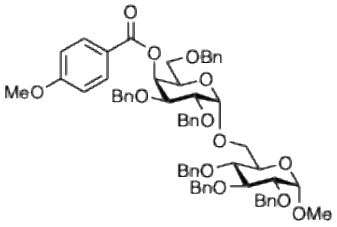
β-11d

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (d, *J* = 3.5 Hz, 1H, H-4).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{38}H_{35}F_7NaO_7^+$: 759.2163; found: 759.2165.

5. Additional Mechanistic Investigations

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-anisoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (12)



Compound **12** was prepared *via* **General Procedure D** using donor **4f** (30 mg, 0.047 mmol) and acceptor **5a** (20 mg, 0.042 mmol). ^{1}H NMR spectroscopic yield and selectivity were recorded from the crude material following work-up (α-only, 52%). Purification by flash column chromatography afforded **12** as a colourless oil (22 mg, 47%).

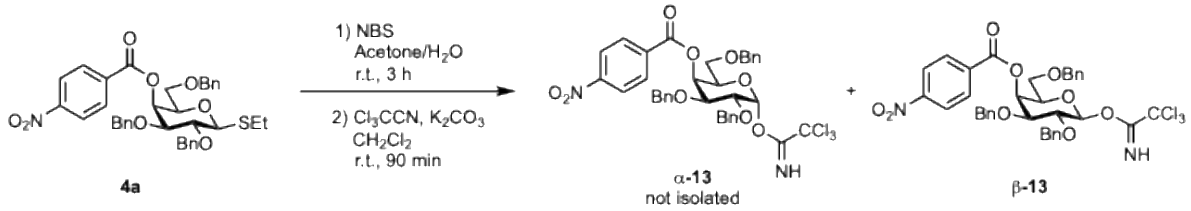
TLC R_f = 0.34 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H, Ar-H), 7.36 – 7.15 (m, 30H, Ar-H), 6.92 – 6.88 (m, 2H, Ar-H), 5.77 (d, *J* = 3.4 Hz, 1H, H-4'), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.87 – 4.75 (m, 3H, 3 × C*H*HPh), 4.74 – 4.62 (m, 3H, 3 × C*H*HPh), 4.58 – 4.55 (m, 3H, 3 × C*H*HPh), 4.54 (d, *J* = 3.7 Hz, 1H, H-1) 4.44 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.37 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.17 (t, *J* = 6.1 Hz, 1H, H-5'), 4.01 (dd, *J* = 9.9, 3.3 Hz, 1H, H-3'), 3.97 (t, *J* = 9.2 Hz, 1H, H-3), 3.90 – 3.88 (m, 1H, H-2)', 3.87 (s, 3H, Ar-OMe), 3.81 – 3.75 (m, 3H, H-5, H-6a, H-6b), 3.63 – 3.54 (m, 1H, H-4), 3.53 – 3.45 (m, 2H, H-6a', H-6b'), 3.42 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.28 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (C=O), 163.6 (*p*-OMe-Ar*C*), 139.0 (Ar-*C*), 138.9 (Ar-*C*), 138.6 (Ar-*C*), 138.4 (Ar-*C*), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 132.1 (*p*-OMe-Ar*C*H), 128.56 (Ar-*C*H), 128.51 (Ar-*C*H), 128.49 (Ar-*C*H), 128.44 (Ar-*C*H), 128.38 (Ar-*C*H), 128.35 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.13 (Ar-*C*H), 128.09 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.72 (Ar-*C*H), 127.68 (Ar-*C*H), 127.54 (Ar-*C*H), 127.50 (Ar-*C*H), 122.6 (Ar-*C*H), 113.8 (*p*-OMe-Ar*C*H), 98.1 (C-1'), 98.0 (C-1), 82.3 (C-3), 80.3 (C-2), 78.1 (C-4), 75.8 (*C*H_2Ph), 75.6 (C-3'), 75.6 (C-2'), 75.1 (*C*H_2Ph), 73.6 (*C*H_2Ph), 73.5 (*C*H_2Ph), 73.0 (*C*H_2Ph), 71.5 (*C*H_2Ph), 70.5 (C-5), 68.9 (C-6'), 68.5 (C-4'), 68.3 (C-5'), 66.4 (C-6), 55.6 (Ar-OMe), 55.2 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{63}H_{66}NaO_{13}^+$: 1053.4396; found: 1053.4395.

2,3,6-Tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-1-thio-D-galactopyranosyl trichloroacetimidate (13)



Thiogalactoside **4a** (0.10 g, 0.16 mmol) was dissolved in a mixture of acetone and H_2O (9:1, 2.2 mL). NBS (32 mg, 0.18 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. The reaction was then quenched with satd. aq. $NaHCO_3$ (0.5 mL) and acetone was removed *in vacuo*. The resulting material was dissolved in CH_2Cl_2 (10 mL) and washed with $Na_2S_2O_3$ (2 × 10 mL) and brine (2 × 10 mL). The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow oil. This oil was dissolved in anhydrous CH_2Cl_2 (0.74 mL), transferred to a flame-dried crimp top vial and placed under a N_2 atmosphere. Trichloroacetonitrile (31 μL, 0.32 mmol) and K_2CO_3 (22 mg, 0.16 mmol) were added and the reaction was stirred vigorously at room temperature for 90 min. After this time, the reaction mixture was subjected to Büchner filtration and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography, eluting with 20% EtOAc in c-Hex, to give trichloroacetimidate **β-13** as a white solid (74 mg, 62% over 2 steps).

TLC R_f 0.23 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H, NH), 8.32 – 8.27 (m, 2H, *p*-NO_2-ArH), 8.22 – 8.14 (m, 2H, *p*-NO_2-ArH), 7.33 – 7.13 (m, 15H, Ar-H), 5.92 (d, *J* = 3.1 Hz, 1H, H-4), 5.86 (d, *J* = 7.8 Hz, 1H, H-1), 4.86 (dd, *J* = 11.0, 6.2 Hz, 2H, 2 × C*H*HPh), 4.76 (d, *J* = 10.6 Hz, 1H, C*H*HPh), 4.59 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.52 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.40 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.06 – 4.00 (m, 1H, H-5), 3.91 – 3.78 (m, 2H, H-2, H-3), 3.65 (dd, *J* = 9.5, 5.5 Hz, 1H, H-6a), 3.56 (dd, *J* = 9.5, 7.7 Hz, 1H, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (C=O), 161.4 (*C*=N), 150.8 (*p*-NO_2-Ar*C*), 138.0 (Ar-*C*), 137.6 (Ar-*C*), 137.5 (Ar-*C*), 135.4 (Ar-*C*), 131.2 (*p*-NO_2-Ar*C*H), 128.5 (2 × Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (2 × Ar-*C*H), 127.9 (Ar-*C*H), 123.7 (*p*-NO_2-Ar*C*H), 98.5 (C-1), 91.0 (Cl_3CCN), 79.6 (C-2 or C-3), 77.7 (C-2 or C-3), 75.5 (CH_2Ph), 73.8 (CH_2Ph), 73.1 (C-5), 72.5 (CH_2Ph), 68.4 (C-4), 67.3 (C-6).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{36}H_{37}Cl_3N_3O_9^+$: 760.1590, 762.1560; found: 762.1567, 760.1589.

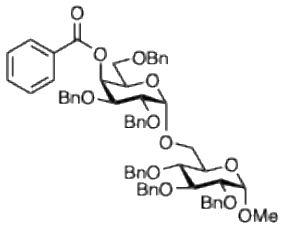
Procedure for Glycosylation using Trichloroacetimidate Donor 13

Following a modified procedure to that reported by Pohl,[13] an oven-dried crimp top vial was charged with a stir bar and 5 Å molecular sieves. The molecular sieves were activated by flame-drying and then subjected to 3 vacuum-to-N_2 cycles. Glycosyl trichloroacetimidate **13** (1.0 equiv.) and alcohol acceptor (0.9 equiv.) were added to the vial and dissolved in anhydrous CH_2Cl_2 (0.02 M) under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min and then cooled to −20 °C in an IMS bath using a chiller. Following stirring at −20 °C for 1 h, TMSOTf (0.5 equiv.) was added dropwise. Stirring at −20 °C was continued for 1 h, after which time the reaction mixture was allowed to warm slowly to room temperature over 18 h. The reaction was then quenched with Et_3N (2.0 equiv.) to give an orange solution and diluted with CH_2Cl_2 (2 volumes). The solution was washed with HCl (1 M, 2 volumes), satd. aq. $NaHCO_3$ (2 volumes), H_2O (2 volumes) and brine (2 volumes). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the corresponding glycosylation product. Crude α/β-selectivities were recorded from the ^{1}H NMR spectrum of the reaction mixture prior to purification by column chromatography, using signals corresponding to H-4'. NMR spectroscopic yields were calculated from the crude reaction mixtures using 1,3,5-trimethoxybenzene (1.0 equiv.) as an internal standard.

Procedure for Competition Experiments

Competition experiments were carried out *via* **General Procedure D**. Equimolar amounts of competing glycosyl donors (1.0 equiv. each) and acceptor **5a** (0.9 equiv.) were used and dissolved in anhydrous CH_2Cl_2 (0.02 M). Product ratios were determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-benzoyl-α-D-galactopyranosyl)-α-D-glucopyranoside (14)



Compound **14** was prepared *via* **General Procedure D** using donor **4d** (28 mg, 0.047 mmol) and acceptor **5a** (20 mg, 0.042 mmol). ^{1}H NMR spectroscopic yield and selectivity were recorded from the crude material following work-up (α-only, 17%). Purification by flash column chromatography afforded **14** as a colourless oil (6 mg, 13%).

TLC R_f = 0.40 (20% EtOAc in c-Hex).

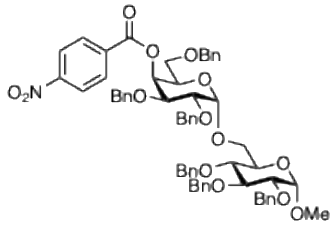
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H, Ar-H), 7.57 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.8 Hz, 2H, Ar-H), 7.35 – 7.15 (m, 30H, Ar-H), 5.80 (d, *J* = 3.4 Hz, 1H, H-4'), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.84 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.80 (app dd, *J* = 11.4, 3.4 Hz, 2H, 2 × C*H*HPh), 4.76 – 4.62 (m, 3H, 3 × C*H*HPh), 4.59 – 4.55 (m, 3H, 3 × C*H*HPh), 4.54 (d, *J* = 3.6, 1H, H-1), 4.45 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.37 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.18 (t, *J* = 6.4 Hz, 1H, H-5'), 4.02 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3'), 3.97 (t, *J* = 9.2 Hz, 1H, H-3), 3.88 (dd, *J* = 10.1, 3.5 Hz, 1H, H-2'), 3.80 – 3.75 (m, 3H, H-6a, H-6b, H-5), 3.61 – 3.56 (m, 1H, H-4), 3.52 – 3.45 (m, 2H, H-6a', H-6b'), 3.42 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2), 3.28 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 165.3 (Bz-*C*), 139.0 (Ar-*C*), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.4 (Ar-*C*), 138.3 (Ar-*C*), 137.9 (Ar-*C*), 133.1 (Ar-*C*H), 130.0 (Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.45 (Ar-*C*H), 128.42 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.6 (Ar-*C*H), 127.5 (Ar-*C*H),127.5 (Ar-*C*H), 98.1 (C-1'), 98.1 (C-1), 82.3 (C-3), 80.3 (C-2), 78.1 (C-4), 75.8 (*C*H_2Ph), 75.6 (C-3'), 75.5 (C-2'), 75.1 (*C*H_2Ph), 73.6 (*C*H_2Ph), 73.5 (*C*H_2Ph), 73.0 (*C*H_2Ph), 71.6 (*C*H_2Ph), 70.5 (C-5), 68.9 (C-4'), 68.8 (C-6'), 68.2 (C-5'), 66.4 (C-6), 55.2 (OMe).

NMR spectroscopic data were consistent with those reported in literature.[14]

6. Glycosyl Acceptor Scope

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (6a)



Disaccharide **6a** was prepared *via* **General Procedure D** using donor **4a** (62 mg, 0.096 mmol) and acceptor **5a** (42 mg, 0.090 mmol). Purification by flash column chromatography afforded **6a** as a yellow foam (α-only, 74 mg, 74%).

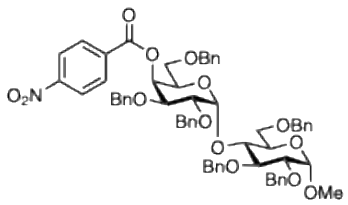
TLC R_f = 0.34 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.21 (m, 2H, *p*-NO_2-ArH), 8.12 – 8.07 (m, 2H, *p*-NO_2-ArH), 7.36 – 7.16 (m, 30H, Ar-H), 5.80 (dd, *J* = 3.3, 1.3 Hz, 1H, H-4'), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'), 4.97 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.87 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.77 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.71 (d, *J* = 12.2 Hz, 2H, 2 × C*H*HPh), 4.65 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.60 – 4.55 (m, 3H, 3 × C*H*HPh), 4.54 (d, *J* = 3.6 Hz, 1H, H-1), 4.45 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.34 (d, *J* = 11.9 Hz, 1H, C*H*HPh), 4.18 (t, *J* = 6.5 Hz, 1H, H-5'), 4.02 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3'), 3.98 (t, *J* = 9.3 Hz, 1H, H-3), 3.83 – 3.76 (m, 4H, H-2', H-4, H-6a, H-6b), 3.62 – 3.57 (m, 1H, H-5), 3.50 – 3.41 (m, 3H, H-2, H-6a', H-6b'), 3.30 (s, 3H, OMe).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (C=O), 150.4 (*p*-NO_2-Ar*C*), 139.4 (Ar-*C*), 138.7 (Ar-*C*), 138.3 (Ar-*C*), 138.1 (Ar-*C*), 137.8 (Ar-*C*), 137.4 (Ar-*C*), 135.4 (Ar-*C*), 130.8 (*p*-NO_2-Ar*C*H), 128.32 (Ar-*C*H), 128.30 (Ar-*C*H), 128.28 (Ar-*C*H), 128.26 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.90 (Ar-*C*H), 127.87 (Ar-*C*H), 127.84 (Ar-*C*H), 127.77 (Ar-*C*H), 127.74 (Ar-*C*H), 127.66 (Ar-*C*H), 127.59 (Ar-*C*H), 127.57 (Ar-*C*H), 127.53 (Ar-*C*H), 127.49 (Ar-*C*H), 127.46 (Ar-*C*H), 123.4 (*p*-NO_2-Ar*C*H), 97.9 (C-1), 97.8 (C-1'), 82.0 (C-3), 80.0 (C-2), 77.8 (C-5), 75.6 (*C*H_2Ph), 75.2 (C-3'), 75.1 (C-2' or C-4), 74.8 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.3 (*C*H_2Ph), 72.6 (*C*H_2Ph), 71.7 (*C*H_2Ph), 70.2 (C-2' or C-4), 69.9 (C-4'), 68.1 (C-6'), 67.5 (C-5'), 66.3 (C-6), 55.0 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{62}H_{63}NNaO_{14}^+$: 1068.4141; found: 1068.4138.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (6b)



Disaccharide **6b** was prepared *via* **General Procedure D** using donor **4a** (37 mg, 0.057 mmol) and acceptor **5b** (24 mg, 0.051 mmol). Purification by flash column chromatography afforded **6b** as a yellow foam (α-only, 22 mg, 36%).

TLC R_f = 0.32 (20% EtOAc in c-Hex).

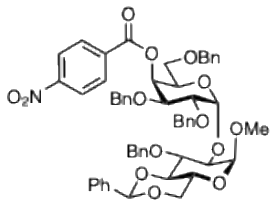
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H, *p*-NO_2-ArH), 8.06 – 8.00 (m, 2H, *p*-NO_2-ArH), 7.38 – 7.06 (m, 30H, Ar-H), 5.81 (dd, *J* = 3.4, 1.4 Hz, 1H, H-4'), 5.78 (d, *J* = 3.8 Hz, 1H, H-1'), 5.02 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.86 (d, *J* = 11.8 Hz, 1H, C*H*HPh), 4.78 – 4.74 (m, 1H, C*H*HPh), 4.68 (d, *J* =

12.2 Hz, 1H, C*H*HPh), 4.65 – 4.43 (m, 7H, 6 × C*H*HPh, H-1), 4.32 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.15 – 4.06 (m, 3H, C*H*HPh, H-3, H-5), 4.03 (t, *J* = 9.6 Hz, 1H, H-4), 3.97 (dd, *J* = 10.2, 3.1 Hz, 1H, H-3'), 3.87 (ddd, *J* = 9.8, 4.1, 2.2 Hz, 1H, H-5'), 3.78 (dd, *J* = 10.6, 4.1 Hz, 1H, H-6a'), 3.73 (dd, *J* = 10.3, 3.9 Hz, 1H, H-2'), 3.67 – 3.64 (m, 1H, H-6b'), 3.58 (dd, *J* = 9.3, 3.5 Hz, 1H, H-2), 3.39 (s, 3H, OMe), 3.37 – 3.30 (m, 2H, H-6a, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.6 (*p*-NO_2-Ar*C*), 139.3 (Ar-*C*), 138.4 (Ar-*C*), 138.1 (Ar-*C*), 138.01 (Ar-*C*), 137.98 (Ar-*C*), 137.6 (Ar-*C*), 135.6 (*p*-NO_2-Ar*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.7 (Ar-*C*H), 128.61 (Ar-*C*H), 128.56 (Ar-*C*H), 128.49 (Ar-*C*H), 128.46 (Ar-*C*H), 128.37 (Ar-*C*H), 128.32 (Ar-*C*H), 128.26 (Ar-*C*H), 128.14 (Ar-*C*H), 128.10 (Ar-*C*H), 128.07 (Ar-*C*H), 128.03 (Ar-*C*H), 128.78 (Ar-*C*H), 127.74 (Ar-*C*H), 127.68 (Ar-*C*H), 127.65 (Ar-*C*H), 127.2 (Ar-*C*H), 126.8 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 97.9 (C-1), 97.6 (C-1'), 82.1 (C-5), 80.3 (C-2), 76.6 (C-3'), 74.5 (*C*H_2Ph), 74.4 (*C*H_2Ph), 74.3 (C-2'), 73.9 (*C*H_2Ph), 73.7 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.0 (C-4), 72.2 (*C*H_2Ph), 69.7 (C-5'), 69.6 (C-4'), 69.4 (C-6'), 68.1 (C-6), 68.0 (C-3), 55.3 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{62}H_{67}N_2O_{14}^+$:1063.4581; found: 1063.4633.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (6c)



Disaccharide **6c** was prepared *via* **General Procedure D** using donor **4a** (41 mg, 0.064 mmol) and acceptor **5c** (22 mg, 0.058 mmol). Purification by flash column chromatography afforded **6c** as a yellow foam (α-only, 37 mg, 62%).

TLC R_f = 0.40 (20% EtOAc in c-Hex).

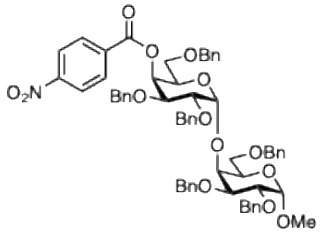
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H, *p*-NO_2-ArCH), 8.08 – 8.04 (m, 2H, *p*-NO_2-ArCH), 7.49 (dd, *J* = 7.6, 1.9 Hz, 2H, Ar-H), 7.40 – 7.34 (m, 3H, Ar-H), 7.33 – 7.12 (m, 20H, Ar-H), 5.57 (d, *J* = 3.4 Hz, 1H, H-4'), 5.56 (s, 1H, PhC*H*), 5.01 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 (d, *J* = 11.1 Hz, 1H, C*H*HPh), 4.91 (d, *J* = 3.5 Hz, 1H, H-1), 4.83 (d, *J* = 12.3 Hz, 1H, C*H*HPh), 4.78 (d, *J* = 11.0 Hz, 1H, C*H*HPh), 4.65 (app dd, *J* = 11.6, 8.8 Hz, 2H, 2 × C*H*HPh), 4.56 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.47 (t,

J = 6.1 Hz, 1H, H-5'), 4.31 (dd, *J* = 10.2, 4.8 Hz, 1H, H-6a), 4.29 – 4.21 (m, 2H, 2 × C*H*HPh), 4.16 – 4.10 (m, 1H, H-3), 4.06 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3'), 3.87 (app dt, *J* = 10.0, 4.2 Hz, 2H, H-2, H-5), 3.82 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2'), 3.74 (t, *J* = 10.3 Hz, 1H, H-6b), 3.59 (t, *J* = 9.4 Hz, 1H, H-4), 3.46 (s, 3H, OMe), 3.34 (dd, *J* = 10.0, 6.0 Hz, 1H, H-6a'), 3.27 (dd, *J* = 10.2, 5.9 Hz, 1H, H-6b').

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.6 (*p*-NO_2-Ar*C*), 138.7 (Ar-*C*), 138.6 (Ar-*C*), 138.1 (Ar-*C*), 137.9 (Ar-*C*), 137.5 (Ar-*C*), 135.7 (Ar-*C*), 130.9 (*p*-NO_2-Ar*C*H), 129.1 (Ar-*C*H), 128.51 (Ar-*C*H), 128.45 (Ar-*C*H), 128.43 (Ar-*C*H), 128.39 (Ar-*C*H), 128.3 (Ar-*C*H), 128.1 (Ar-*C*H), 128.03 (Ar-*C*H), 127.97 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.57 (Ar-*C*H), 127.56 (Ar-*C*H), 126.1 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 101.4 (Ph*C*H), 97.4 (C-1), 95.3 (C-1'), 82.8 (C-4), 77.4 (C-3), 76.2 (C-3'), 75.7 (*C*H_2Ph), 74.9 (C-2'), 74.3 (C-2 or C-5), 73.4 (*C*H_2Ph), 73.2 (*C*H_2Ph), 72.2 (*C*H_2Ph), 70.2 (C-4'), 69.2 (C-6), 68.6 (C-6'), 67.3 (C-5'), 62.4 (C-2 or C-5), 55.3 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{55}H_{59}N_2O_{14}^+$: 971.3955; found: 971.3991.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-galactopyranoside (6d)



Disaccharide **6d** was prepared *via* **General Procedure D** using donor **4a** (50 mg, 0.078 mmol) and acceptor **5d** (33 mg, 0.070 mmol). Purification by flash column chromatography afforded **6d** as a yellow foam (α-only, 40 mg, 49%).

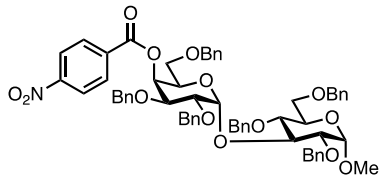
TLC R_f = 0.34 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.17 (m, 2H, *p*-NO_2-ArH), 8.06 – 8.01 (m, 2H, *p*-NO_2-ArH), 7.43 – 7.48 (m, 3H, Ar-H), 7.36 – 7.19 (m, 23H, Ar-H), 7.12 – 7.03 (m, 4H, Ar-H), 5.92 (d, *J* = 3.1 Hz, 1H, H-4'), 5.03 (d, *J* = 3.4 Hz, 1H, H-1'), 4.89 – 4.81 (m, 2H, 2 × C*H*HPh), 4.78 (d, *J* = 2.5 Hz, 3H, 2 × C*H*HPh, H-1), 4.70 (d, *J* = 12.5 Hz, 1H, C*H*HPh), 4.65 – 4.57 (m, 2H, C*H*HPh, H-5), 4.48 (d, *J* = 10.5 Hz, 1H, C*H*HPh), 4.36 – 4.27 (m, 2H, 2 × C*H*HPh), 4.17 – 4.10 (m, 2H, C*H*HPh, H-5'), 4.07 – 3.95 (m, 2H, H-3', H-6a'), 3.94 – 3.82 (m, 5H, C*H*HPh, H-2', H-2, H-3, H-4), 3.51 (dd, *J* = 9.6, 5.9 Hz, 1H, H-6b'), 3.39 (s, 3H, OMe), 3.20 (t, *J* = 8.6 Hz, 1H, H-6a), 3.12 (dd, *J* = 8.7, 4.7 Hz, 1H, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (C=O), 150.5 (*p*-NO_2-Ar*C*), 138.9 (Ar-*C*), 138.4 (Ar-*C*), 138.37 (Ar-*C*), 138.30 (Ar-*C*), 138.1 (Ar-*C*), 137.6 (Ar-*C*), 135.9 (Ar-*C*), 130.9 (*p*-NO_2-Ar*C*H), 128.57 (2 × Ar-*C*H), 128.55 (2 × Ar-*C*H), 128.53 (Ar-*C*H), 128.44 (Ar-*C*H), 128.41 (Ar-*C*H), 128.35 (Ar-*C*H), 128.33 (Ar-*C*H), 128.2 (Ar-*C*H), 128.09 (Ar-*C*H), 128.06 (Ar-*C*H), 128.00 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (2 × Ar-*C*H), 127.6 (2 × Ar-*C*H), 123.5 (*p*-NO_2-Ar*C*H), 100.4 (C-1'), 98.7 (C-1), 77.9 (C-2', C-2, C-3 or C-4), 77.0 (C-3'), 76.7 (C-5'), 75.1 (C-2', C-2, C-3 or C-4), 75.0 (C-2', C-2, C-3 or C-4), 74.2 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.3 (*C*H_2Ph), 73.21 (*C*H_2Ph), 73.16 (*C*H_2Ph), 71.8 (*C*H_2Ph), 69.7 (C-4'), 69.3 (C-2', C-2, C-3 or C-4), 67.8 (C-6'), 67.6 (C-5), 67.4 (C-6), 55.5 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{62}H_{67}N_2O_{14}^+$:1063.4587; found: 1063.4591.

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (6e)



Disaccharide **6e** was prepared *via* **General Procedure D** using donor **4a** (37 mg, 0.057 mmol) and acceptor **5e** (24 mg, 0.051 mmol). Purification by flash column chromatography afforded **6e** as a yellow foam (α-only, 37 mg, 62%).

TLC R_f = 0.40 (20% EtOAc in c-Hex).

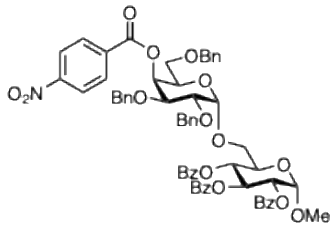
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.18 (m, 2H, *p*-NO_2-ArH), 8.05 – 8.02 (m, 2H, *p*-NO_2-ArH), 7.34 – 7.01 (m, 30H, Ar-H), 5.75 (d, *J* = 3.8 Hz, 1H, H-4'), 5.57 (d, *J* = 3.5 Hz, 1H, H-1'), 4.98 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.75 – 4.69 (m, 2H, C*H*HPh, H-5'), 4.66 (d, *J* = 3.5 Hz, H-1), 4.65 – 4.59 (m, 2H, 2 × C*H*HPh), 4.59 – 4.50 (m, 2H, 2 × C*H*HPh), 4.44 (d, *J* = 12.2 Hz, 1H, C*H*HPh), 4.41 (d, *J* = 11.7, 1H, C*H*HPh), (4.34 – 4.24 (m, 2H, C*H*HPh, H-3), 4.14 – 4.09 (m, 1H, H-3'), 3.85 – 3.77 (m, 2H, H-2', H-4), 3.73 (dt, *J* = 9.9, 2.7 Hz, 1H, H-5), 3.68 (dd, *J* = 10.7, 3.3 Hz, 1H, H-6a), 3.61 (app dd, *J* = 9.7, 3.3 Hz, 2H, H-2, H-6b), 3.46 (dd, *J* = 9.6, 5.4 Hz, 1H, H-6a'), 3.34 (dd, *J* = 9.7, 7.0 Hz, 1H, H-6b'), 3.31 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.5 (*p*-NO_2-Ar*C*), 138.6 (Ar-*C*), 138.1 (Ar-*C*), 138.02 (Ar-*C*), 138.01 (Ar-*C*), 137.96 (Ar-*C*), 137.95 (Ar-*C*), 135.8 (Ar-*C*), 131.0 (*p*-NO_2-Ar*C*H), 128.64 (Ar-*C*H), 128.61 (Ar-*C*H), 128.56 (Ar-*C*H), 128.49 (Ar-*C*H), 128.40 (Ar-*C*H), 128.37 (Ar-*C*H) 128.28 (Ar-

*C*H), 128.23 (Ar-*C*H), 128.17 (Ar-*C*H), 128.12 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.83 (Ar-*C*H), 127.75 (Ar-*C*H), 127.6 (Ar-*C*H), 127.5 (Ar-*C*H), 127.4 (Ar-*C*H), 126.9 (Ar-*C*H), 123.5 (*p*-NO_2-Ar*C*H), 98.1 (C-1'), 97.6 (C-1), 78.9 (C-2' or C-4), 78.9 (C-2), 76.8 (C-3'), 75.9 (C-3), 74.3 (C-2' or C-4), 73.9 (*C*H_2Ph), 73.8 (*C*H_2Ph), 73.7 (*C*H_2Ph), 73.4 (*C*H_2Ph), 73.2 (*C*H_2Ph), 72.0 (*C*H_2Ph), 70.2 (C-4'), 69.9 (C-5), 68.5 (C-6), 68.4 (C-6'), 67.2 (C-5'), 55.2 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{62}H_{67}N_2O_{14}^+$: 1063.4581; found: 1063.4592.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (6f)



Disaccharide **6f** was prepared *via* **General Procedure D** using donor **4a** (98 mg, 0.15 mmol) and acceptor **5f** (70 mg, 0.14 mmol). Purification by flash column chromatography afforded **6f** as a white foam (α-only, 92 mg, 54%).

TLC R_f = 0.33 (20% EtOAc in c-Hex).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H, *p*-NO_2-ArH), 8.08 (d, *J* = 8.5 Hz, 2H, *p*-NO_2-ArH), 8.01 – 7.92 (m, 5H, Bz-H), 7.89 – 7.82 (m, 2H, Bz-H), 7.50 (t, *J* = 7.4 Hz, 2H, Bz-H), 7.44 – 7.12 (m, 21H, Ar-H), 6.15 (td, *J* = 9.9, 5.8 Hz, 1H, H-3), 5.85 (d, *J* = 3.3 Hz, 1H, H-4'), 5.58 (t, *J* = 9.9 Hz, 1H, H-4), 5.26 (dd, *J* = 10.1 Hz, 3.7 Hz, 1H, H-2), 5.21 (d, *J* = 3.7 Hz, 1H, H-1), 4.90 (d, *J* = 3.5 Hz, 1H, H-1'), 4.82 (d, *J* = 11.8 Hz, 2H, 2 × C*H*HPh), 4.65 (app dd, *J* = 13.6, 11.8 Hz, 2H, 2 × C*H*HPh), 4.40 (d, *J* = 12.0 Hz, 1H, C*H*HPh), 4.34 – 4.23 (m, 3H, C*H*HPh, H-5', H-5), 4.14 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3'), 3.88 (app ddt, *J* = 13.5, 10.0, 4.9 Hz, 2H, H-2', H-6a), 3.65 (dd, *J* = 11.0, 2.0 Hz, 1H, H-6b), 3.49 – 3.40 (m, 2H, H-6a', H-6b'), 3.36 (s, 3H, OMe).

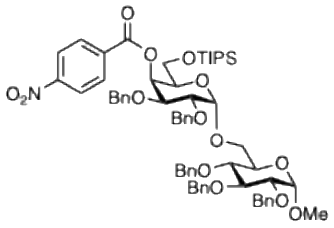
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (C=O), 165.5 (C=O), 165.5 (C=O), 164.1 (C=O), 150.6 (*p*-NO_2-ArC), 138.5 (Bn-Ar*C*), 138.1 (Bn-Ar*C*), 137.6 (Bn-Ar*C*), 135.6 (*p*-NO_2-Ar*C*), 133.6 (Bz-Ar*C*), 133.5 (Bz-Ar*C*), 133.2 (Bz-Ar*C*), 131.0 (*p*-NO_2-Ar*C*H), 130.1 (Ar-*C*H), 130.0 (Ar-*C*H), 129.8 (Ar-*C*H), 129.4 (Ar-*C*H), 129.2 (Ar-*C*H), 129.1 (Ar-*C*H), 128.6 (Ar-*C*H), 128.53 (Ar-*C*H), 128.45 (Ar-*C*H), 128.38 (Ar-*C*H), 128.37 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.90 (Ar-*C*H), 127.85 (Ar-*C*H), 127.8 (Ar-*C*H), 127.72 (Ar-*C*H), 127.69 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 98.1 (C-1'), 97.0 (C-1), 75.7

(C-3'), 75.1 (C-2'), 73.5 (*C*H_2Ph), 73.2 (*C*H_2Ph), 72.2 (C-2), 72.0 (*C*H_2Ph), 70.7 (C-3), 70.1 (C-4'), 69.6 (C-4), 68.5 (C-5' or C-5), 68.3 (C-6'), 67.7 (C-5' or C-5), 66.8 (C-6), 55.6 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{62}H_{57}NNaO_{17}^+$: 1110.3519; found: 1110.3521.

7. Glycosyl Donor Scope

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-triisopropylsilyl-α-D-galactopyranosyl)-α-D-glucopyranoside (16a)



Compound **16a** was prepared *via* **General Procedure D** using donor **15a** (90 mg, 0.13 mmol) and acceptor **5a** (56 mg, 0.12 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **16a** as a yellow oil (α-only, 88 mg, 63%).

TLC R_f = 0.50 (20% EtOAc in c-Hex).

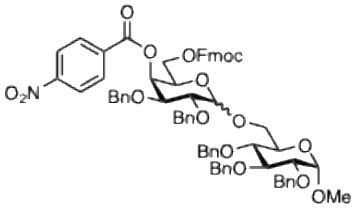
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.21 (m, 2H, *p*-NO_2-ArH), 8.16 – 8.08 (m, 2H, *p*-NO_2-ArH), 7.36 – 7.18 (m, 25H, Ar-H), 5.83 (d, *J* = 3.2 Hz, 1H, H-4'), 5.04 (d, *J* = 3.5 Hz, 1H, H-1'), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.90 – 4.77 (m, 3H, 3 × C*H*HPh), 4.74 – 4.63 (m, 3H, 3 × C*H*HPh), 4.62 – 4.56 (m, 3H, 3 × C*H*HPh), 4.53 (d, *J* = 3.6 Hz, 1H, H-1), 4.10 – 4.05 (m, 1H, H-5'), 4.04 – 3.94 (m, 2H, H-3', H-3), 3.84 – 3.75 (m, 4H, H-2', H-5, H-6a, H-6b), 3.73 – 3.62 (m, 2H, H-6a', H-6b'), 3.55 (t, *J* = 9.4 Hz, 1H, H-4), 3.41 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2), 3.29 (s, 3H, OMe), 1.03 – 0.91 (m, 21H, $Si(CH(CH_3)_2)_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (C=O), 150.6 (*p*-NO_2-Ar*C*), 139.0 (Ar-*C*), 138.61 (Ar-*C*), 138.57 (Ar-*C*), 138.3 (Ar-*C*), 138.1 (Ar-*C*), 135.9 (Ar-*C*), 130.9 (*p*-NO_2-Ar*C*H), 128.7 (Ar-*C*H), 128.6 (Ar-*C*H), 128.52 (Ar-*C*H), 128.45 (Ar-*C*H), 128.4 (Ar-*C*H), 128.3 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.82 (Ar-*C*H), 127.75 (Ar-*C*H), 127.71 (Ar-*C*H), 127.67 (Ar-*C*H), 127.6 (Ar-*C*H), 123.7 (*p*-NO_2-Ar*C*H), 98.1 (C-1), 97.9 (C-1'), 82.3 (C-3), 80.2 (C-2), 78.2 (C-4), 75.9 (*C*H_2Ph), 75.7 (C-3'), 75.5 (C-2' or C-5), 75.1 (*C*H_2Ph), 73.5 (*C*H_2Ph), 72.9 (*C*H_2Ph), 72.0 (*C*H_2Ph),

70.5 (C-2' or C-5), 69.7 (C-4'), 69.5 (C-5'), 66.4 (C-6), 61.7 (C-6'), 55.1 (OMe), 18.0 (SiCH(CH$_3$)$_2$), 11.9 (SiCH(CH$_3$)$_2$).

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ Calc'd for $C_{64}H_{81}N_2O_{14}Si^+$: 1129.5452; found: 1129.5452.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-fluorenylmethoxylcarbonyl-D-galactopyranosyl)-α-D-glucopyranoside (16b)



Disaccharide **16b** was prepared *via* **General Procedure D** using donor **15b** (9 mg, 0.01 mmol) and acceptor **5a** (5 mg, 0.01 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **16b** as a yellow oil (α/β = 85:15, 11 mg, 79%).

TLC R_f = 0.27 (20% EtOAc in c-Hex).

α-16b

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.23 (m, 2H, *p*-NO_2-ArH), 8.16 – 8.10 (m, 2H, *p*-NO_2-ArH), 7.75 (d, *J* = 7.6 Hz, 2H, Fmoc-ArH), 7.55 (dd, *J* = 7.9, 2.1 Hz, 2H, Fmoc-ArH), 7.39 (t, *J* = 7.5 Hz, 2H, Fmoc-ArH), 7.34 (d, *J* = 4.3 Hz, 4H, Ar-H), 7.32 – 7.17 (m, 23H, Ar-H), 5.73 (d, *J* = 3.4 Hz, 1H, H-4'), 5.09 (d, *J* = 3.5 Hz, 1H, H-1'), 4.96 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.87 (d, *J* = 11.3 Hz, 1H, C*H*HPh), 4.80 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.71 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.68 – 4.64 (m, 2H, 2 × C*H*HPh), 4.61 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.58 – 4.51 (m, 3H, 2 × C*H*HPh, H-1), 4.35 (dd, *J* = 10.4, 7.5 Hz, 1H, Fmoc-C*H*H), 4.29 (dd, *J* = 10.4, 7.4 Hz, 1H, Fmoc-CH*H*), 4.24 – 4.17 (m, 4H, Fmoc-C*H*, H-5', H-6a', H-6b'), 4.01 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3'), 3.97 (t, *J* = 9.3 Hz, 1H, H-3), 3.84 (dd, *J* = 9.9, 3.5 Hz, 1H, H-2'), 3.81 – 3.73 (m, 3H, H-5, H-6a, H-6b), 3.55 (t, *J* = 9.3 Hz, 1H, H-4), 3.37 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.29 (s, 3H, OMe).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (C=O), 154.9 (C=O), 150.8 (Ar-*C*), 143.4 (Ar-*C*), 143.3 (Ar-*C*), 141.4 (Ar-*C*), 139.0 (Ar-*C*), 138.6 (Ar-*C*), 138.4 (Ar-*C*), 138.3 (Ar-*C*), 137.9 (Ar-*C*), 135.3 (Ar-*C*), 131.1 (*p*-NO_2-Ar*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.1 (Ar-*C*H), 128.00 (Ar-*C*H), 127.97 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.3 (Ar-*C*H), 125.3 (Ar-*C*H), 125.2 (Fmoc-Ar*C*H), 123.7 (*p*-NO_2-Ar*C*H), 120.3

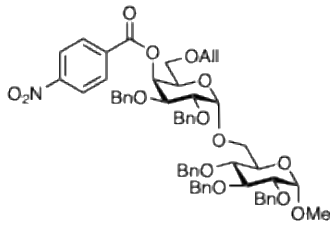
(Fmoc-Ar*C*H), 98.1 (C-1), 97.9 (C-1'), 82.2 (C-3), 80.3 (C-2), 78.0 (C-4), 75.8 (*C*H_2Ph), 75.1 (C-2' and C-3'), 75.1 (*C*H_2Ph), 73.5 (*C*H_2Ph), 72.9 (*C*H_2Ph), 72.2 (*C*H_2Ph), 70.4 (C-5), 70.3 (Fmoc-*C*H_2), 69.9 (C-4'), 66.8 (C-5'), 66.6 (C-6), 66.1 (C-6'), 55.2 (OMe), 46.8 (Fmoc-*C*H).

β-16b

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (d, *J* = 3.0 Hz, 1H, H-4').

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{70}H_{67}NNaO_{16}^+$: 1200.4352; found: 1200.4351.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-allyl-α-D-galactopyranosyl)-α-D-glucopyranoside (16c)



Disaccharide **16c** was prepared *via* **General Procedure D** using donor **15c** (10 mg, 0.017 mmol) and acceptor **5a** (7 mg, 0.01 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **16c** as a yellow oil (α-only, 12 mg, 71%).

TLC R_f = 0.28 (20% EtOAc in c-Hex).

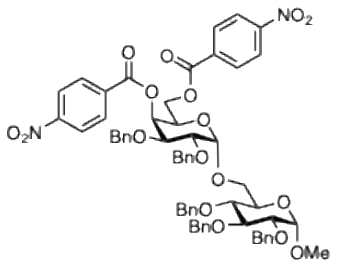
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 8.24 (m, 2H, *p*-NO_2-ArH), 8.16 – 8.11 (m, 2H, *p*-NO_2-ArH), 7.36 – 7.17 (m, 25H, Ar-H), 5.79 – 5.70 (m, 1H, OCH_2CH=CH_2), 5.76 (d, *J* = 2.6 Hz, 1H, H-4'), 5.17 – 5.04 (m, 2H, OCH_2CH=CH_2), 5.08 (d, *J* = 3.6 Hz, 1H, H-1'), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.87 (d, *J* = 11.2 Hz, 1H, C*H*HPh), 4.81 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.79 – 4.69 (m, 3H, 3 × C*H*HPh), 4.66 (d, *J* = 12.1 Hz, 1H, C*H*HPh), 4.61 – 4.56 (m, 3H, 3 × C*H*HPh), 4.54 (d, *J* = 3.5 Hz, 1H, H-1), 4.15 – 4.10 (m, 1H, H-5), 4.04 – 4.01 (m, 1H, H-3'), 3.98 (t, *J* = 9.2 Hz, 1H, H-3), 3.92 – 3.86 (m, 1H, H-6a'), 3.85 – 3.81 (m, 2H, H-2', H-6b'), 3.81 – 3.75 (m, 3H, O*C*H_2CH=CH_2, H-5'), 3.61 (t, *J* = 9.3 Hz, 1H, H-4), 3.48 – 3.39 (m, 3H, H-2, H-6a, H-6b), 3.31 (s, 3H, OMe).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (C=O), 150.7 (*p*-NO_2-Ar*C*), 139.0 (Ar-*C*), 138.6 (Ar-*C*), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 135.7 (Ar-*C*), 134.3 (OCH_2*C*H=CH_2), 131.0 (*p*-NO_2-Ar*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.4 (Ar-*C*H), 128.2 (Ar-*C*H), 128.03 (Ar-*C*H), 127.99 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.80 (Ar-*C*H), 127.75 (Ar-*C*H), 127.72 (Ar-*C*H), 123.69 (*p*-NO_2-

Ar*C*H), 117.6 ($OCH_2CH{=}CH_2$), 98.1 (C-1), 98.0 (C-1'), 82.2 (C-3), 80.2 (C-2), 78.0 (C-4), 75.9 (CH_2Ph), 75.4 (C-3'), 75.3 (C-2'), 75.1 (CH_2Ph), 73.5 (CH_2Ph), 72.8 (CH_2Ph), 72.5 ($OCH_2CH{=}CH_2$), 72.0 (CH_2Ph), 70.5 (C-5'), 70.3 (C-4'), 68.5 (C-6), 67.8 (C-5), 66.5 (C-6'), 55.2 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{58}H_{61}NNaO_{14}^+$: 1018.3984; found: 1018.3983.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-di-*O*-(*p*-nitrobenzoyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (16d)



Disaccharide **16d** was prepared *via* **General Procedure D** using donor **15d** (27 mg, 0.038 mmol) and acceptor **5a** (16 mg, 0.035 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **16d** as a yellow oil (α-only, 19 mg, 45%).

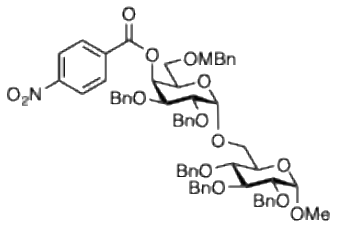
TLC R_f = 0.30 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.25 (m, 2H, *p*-NO_2-ArH), 8.23 – 8.19 (m, 2H, *p*-NO_2-ArH), 8.15 – 8.11 (m, 2H, *p*-NO_2-ArH), 8.10 – 8.07 (m, 2H, *p*-NO_2-ArH), 7.35 – 7.19 (m, 25H, Ar-H), 5.76 (d, *J* = 3.4 Hz, 1H, H-4'), 5.07 (d, *J* = 3.5 Hz, 1H, H-1'), 4.97 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.86 (d, *J* = 11.4 Hz, 1H, C*H*HPh), 4.80 – 4.75 (m, 2H, 2 × C*H*HPh), 4.74 – 4.68 (m, 3H, 3 × C*H*HPh), 4.66 – 4.59 (m, 2H, 2 × C*H*HPh), 4.58 – 4.51 (m, 4H, 3 × C*H*HPh, H-1), 4.40 (dd, *J* = 12.7, 9.2 Hz, 1H, H-6a'), 4.35 – 4.29 (m, 2H, H-5', H-6b'), 4.03 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3'), 3.97 (t, *J* = 9.2 Hz, 1H, H-3), 3.87 (dd, *J* = 10.0, 3.5 Hz, 1H, H-2'), 3.82 – 3.71 (m, 3H, H-5, H-6a, H-6b), 3.46 (t, *J* = 9.3 Hz, 1H, H-4), 3.34 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.30 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (C=O), 164.2 (C=O), 150.9 (*p*-NO_2-Ar*C*), 150.8 (*p*-NO_2-Ar*C*), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.34 (Ar-*C*), 138.26 (Ar-*C*), 137.8 (Ar-*C*), 135.2 (Ar-*C*), 135.0 (Ar-*C*), 131.1 (*p*-NO_2-Ar*C*H), 130.9 (*p*-NO_2-Ar*C*H), 128.62 (Ar-*C*H), 128.61 (Ar-*C*H), 128.60 (Ar-*C*H), 128.56 (Ar-*C*H), 128.55 (Ar-*C*H), 128.53 (Ar-*C*H), 128.52 (Ar-*C*H), 128.51 (Ar-*C*H), 128.47 (Ar-*C*H), 128.46 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 124.2 (*p*-NO_2-Ar*C*H), 123.8 (*p*-NO_2-Ar*C*H), 98.1 (C-1), 97.9 (C-1'), 82.2 (C-3), 80.1 (C-2), 78.0 (C-4), 75.8 (CH_2Ph), 75.2 (CH_2Ph), 75.1 (C-2'), 75.0 (C-3'), 73.4 (CH_2Ph), 73.0 (CH_2Ph), 72.4 (CH_2Ph), 70.2 (C-5), 70.1 (C-4'), 66.73 (C-6), 66.71 (C-5'), 63.7 (C-6'), 55.3 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{62}H_{60}N_2NaO_{17}^+$: 1127.3784; found: 1127.3782.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-6-*O*-(*p*-methylbenzyl)-α-D-galactopyranosyl)-α-D-glucopyranoside (16e)



Disaccharide **16e** was prepared *via* **General Procedure D** using donor **15e** (34 mg, 0.053 mmol) and acceptor **5a** (22 mg, 0.048 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **16e** as a yellow oil (α-only, 47 mg, 84%).

TLC R_f = 0.27 (20% EtOAc in c-Hex).

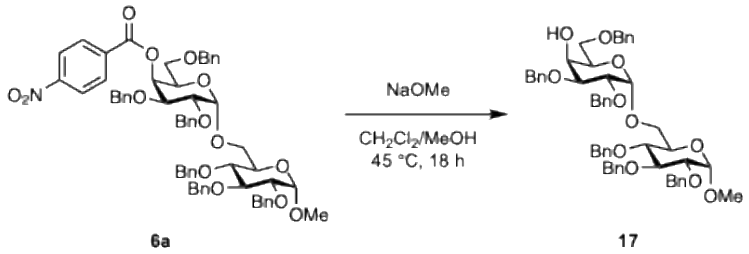
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 2H, *p*-NO_2-ArH), 8.10 – 8.05 (m, 2H, *p*-NO_2-ArH), 7.37 – 7.17 (m, 25H, Ar-H), 7.09 – 7.05 (m, 2H, *p*-Me-ArH), 6.98 (d, *J* = 7.8 Hz, 2H, *p*-Me-ArH), 5.80 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4'), 5.06 (d, *J* = 3.5 Hz, 1H, H-1'), 4.97 (d, *J* = 10.8 Hz, 1H, C*H*HAr), 4.87 (d, *J* = 11.2 Hz, 1H, C*H*HAr), 4.83 – 4.78 (m, 2H, 2 × C*H*HAr), 4.77 – 4.69 (m, 2H, 2 × C*H*HAr), 4.64 (d, *J* = 12.1 Hz, 1H, C*H*HAr), 4.60 – 4.55 (m, 3H, 3 × C*H*HAr), 4.54 (d, *J* = 3.6 Hz, 1H, H-1), 4.41 (d, *J* = 11.9 Hz, 1H, C*H*HAr), 4.28 (d, *J* = 11.7 Hz, 1H, CH*H*Ar), 4.19 – 4.14 (m, 1H, H-5'), 4.01 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3'), 3.97 (t, *J* = 9.3 Hz, 1H, H-3), 3.83 – 3.76 (m, 4H, H-2', H-5, H-6a, H-6b), 3.59 (t, *J* = 9.4 Hz, 1H, H-4), 3.49 – 3.39 (m, 3H, H-2, H-6a', H-6b'), 3.29 (s, 3H, OMe), 2.22 (s, 3H, Ar-CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (C=O), 150.6 (*p*-NO_2-Ar*C*), 138.9 (Ar-*C*), 138.6 (Ar-*C*), 138.5 (Ar-*C*), 138.3 (Ar-*C*), 138.0 (Ar-*C*), 137.6 (Ar-*C*), 135.7 (Ar-*C*), 134.5 (Ar-*C*), 131.0 (*p*-NO_2-Ar*C*H), 129.1 (Ar-*C*H), 128.62 (Ar-*C*H), 128.57 (Ar-*C*H), 128.53 (Ar-*C*H), 128.52 (Ar-*C*H), 128.42 (Ar-*C*H), 128.38 (Ar-*C*H), 128.2 (Ar-*C*H), 128.13 (Ar-*C*H), 128.12 (Ar-*C*H), 128.01 (Ar-*C*H), 127.99 (Ar-*C*H), 127.9 (Ar-*C*H), 127.82 (Ar-*C*H), 127.76 (Ar-*C*H), 127.70 (Ar-*C*H), 127.68 (Ar-*C*H), 123.6 (*p*-NO_2-Ar*C*H), 98.1 (C-1), 98.0 (C-1'), 82.2 (C-3), 80.2 (C-2), 78.0 (C-4), 75.9 (*C*H_2Ar), 75.4 (C-3'), 75.3 (C-2' or C-5), 75.1 (*C*H_2Ar), 73.51 (*C*H_2Ar), 73.48 (*C*H_2Ar), 72.9 (*C*H_2Ar), 71.9 (*C*H_2Ar), 70.4 (C-2' or C-5), 70.0 (C-4'), 68.1 (C-6'), 67.6 (C-5'), 66.5 (C-6), 55.2 (OMe), 21.2 (Ar-CH_3).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{63}H_{65}NNaO_{14}^+$: 1082.4297; found: 1082.4298.

8. Trisaccharide Synthesis

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,6-tri-*O*-benzyl-α-D-galactopyranosyl)-α-D-glucopyranoside (17)



Following a procedure reported by Bundle and co-workers,[15] disaccharide **6a** (70 mg, 0.067 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (4:1, 2.5 mL). A solution of NaOMe in MeOH (1.5 M, 24 μL, 36 μmol) was added dropwise. The reaction mixture was stirred at 45 °C for 18 h. The reaction was then neutralised with Amberlite resin (H^+, IR-120), filtered and concentrated *in vacuo* to give a yellow oil. Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **17** as a colourless oil (32 mg, 53%).

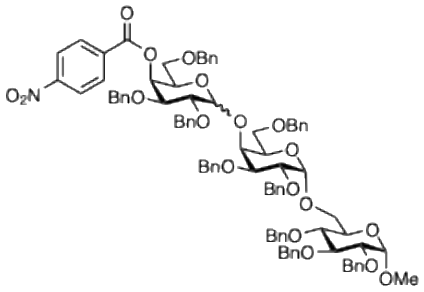
TLC R_f = 0.14 (20% EtOAc in c-Hex).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 30H, Ar-H), 4.99 (d, *J* = 3.2 Hz, 1H, H-1'), 4.96 (d, *J* = 10.8 Hz, 1H, C*H*HPh), 4.86 (d, *J* = 11.0 Hz, 1H, C*H*HPh), 4.80 (d, *J* = 10.7 Hz, 1H, C*H*HPh), 4.75 (d, *J* = 11.6 Hz, 1H, C*H*HPh), 4.72 – 4.65 (m, 4H, 4 × C*H*HPh), 4.61 – 4.56 (m, 2H, 2 × C*H*HPh), 4.54 – 4.51 (m, 3H, 2 × C*H*HPh, H-1), 4.02 (d, *J* = 2.9 Hz, 1H, H-4'), 3.97 (t, *J* = 9.3 Hz, 1H, H-3), 3.92 (t, *J* = 5.8 Hz, 1H, H-5'), 3.83 (app dd, *J* = 6.8, 3.0 Hz, 2H, H-2', H-3'), 3.80 – 3.74 (m, 3H, H-5, H-6a, H-6b), 3.72 – 3.65 (m, 1H, H-6a'), 3.64 – 3.55 (m, 2H, H-4, H-6b'), 3.41 (dd, *J* = 9.7, 3.6 Hz, 1H, H-2), 3.29 (s, 3H, OMe).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0 (Ar-*C*), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.3 (Ar-*C*), 138.3 (Ar-*C*), 138.2 (Ar-*C*), 128.8 (Ar-*C*H), 128.6 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.5 (Ar-*C*H), 128.2 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 128.1 (Ar-*C*H), 128.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.8 (Ar-*C*H), 127.7 (Ar-*C*H), 127.6 (Ar-*C*H), 127.6 (Ar-*C*H), 98.1 (C-1), 97.9 (C-1'), 82.2 (C-3), 80.3 (C-2), 78.1 (C-4), 77.0 (C-2' or C-3'), 75.9 (C-2' or C-3'), 75.8 (*C*H_2Ph), 75.1(*C*H_2Ph), 73.6 (*C*H_2Ph), 73.5 (*C*H_2Ph), 72.7 (*C*H_2Ph), 72.5 (*C*H_2Ph), 70.5 (C-5), 69.7 (C-6'), 68.6 (C-5'), 68.2 (C-4'), 66.4 (C-6), 55.2 (OMe).

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calc'd for $C_{35}H_{60}NaO_{11}^+$: 919.4028; found: 919.4027.

Methyl (2,3,6-tri-*O*-benzyl-4-*O*-(*p*-nitrobenzoyl)-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (18)



Compound **18** was prepared *via* **General Procedure D** using donor **4a** (21 mg, 0.033 mmol) and acceptor **17** (27 mg, 0.030 mmol). Purification by flash column chromatography, eluting with 20% EtOAc in c-Hex, afforded **18** as a colourless oil (α/β = 86:14, 11 mg, 40%).

TLC R_f = 0.32 (20% EtOAc in c-Hex).

α-18

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 2H, *p*-NO_2-ArH), 8.06 – 8.01 (m, 2H, *p*-NO_2-ArH), 7.40 – 7.15 (m, 45H, Ar-H), 5.91 (d, *J* = 3.2 Hz, 1H, H-4''), 5.07 (d, *J* = 3.3 Hz, 1H, H-1'), 5.03 (d, *J* = 3.6 Hz, 1H, H-1''), 4.96 (d, *J* = 10.9 Hz, 1H, C*H*HPh), 4.86 – 4.81 (m, 2H, 2 × C*H*HPh), 4.80 – 4.75 (m, 3H, 3 × C*H*HPh), 4.75 – 4.68 (m, 3H, 3 × C*H*HPh), 4.64 (app dd, *J* = 15.6, 3.4 Hz, 2H, C*H*HPh, H-5''), 4.59 – 4.53 (m, 3H, 3 × C*H*HPh), 4.51 (d, *J* = 3.6 Hz, 1H, H-1), 4.47 (d, *J* = 10.6 Hz, 1H, C*H*HPh), 4.31 – 4.22 (m, 2H, 2 × C*H*HPh), 4.20 – 4.14 (m, 1H, C*H*HPh), 4.09 (d, *J* = 2.6 Hz, 1H, H-4'), 4.05 – 3.95 (m, 4H, C*H*HPh, H-3'', H-3, H-6a'), 3.94 – 3.88 (m, 2H, H-2', H-5'), 3.87 – 3.80 (m, 2H, H-2'', H-3'), 3.74 (app d, *J* = 1.6 Hz, 3H, H-5, H-6a, H-6b), 3.61 – 3.54 (m, 1H, H-4), 3.43 (app tt, *J* = 9.5, 3.4 Hz, 2H, H-2, H-6b'), 3.27 (s, 3H, OMe), 3.24 – 3.13 (m, 2H, H-6a'', H-6b'').

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0 (C=O), 150.5 (*p*-NO_2-Ar*C*), 139.0 (Ar-*C*), 138.9 (Ar-*C*), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.43 (Ar-*C*), 138.37 (Ar-*C*), 138.3 (Ar-*C*), 138.2 (Ar-*C*), 137.6 (Ar-*C*), 135.9 (Ar-*C*), 130.9 (*p*-NO_2-Ar*C*H), 128.7 (Ar-*C*H), 128.6 (Ar-*C*H), 128.52 (Ar-*C*H), 128.51 (Ar-*C*H), 128.50 (Ar-*C*H), 128.48 (Ar-*C*H), 128.46 (Ar-*C*H), 128.40 (Ar-*C*H), 128.38 (Ar-*C*H), 128.35 (Ar-*C*H), 128.30 (Ar-*C*H), 128.25 (Ar-*C*H), 128.18 (Ar-*C*H), 128.16 (Ar-*C*H), 128.12 (Ar-*C*H), 128.06 (Ar-*C*H), 128.0 (Ar-*C*H), 127.9 (Ar-*C*H), 127.8 (Ar-*C*H), 127.81 (Ar-*C*H), 127.77 (Ar-*C*H), 127.75 (Ar-*C*H), 127.70 (Ar-*C*H), 127.64 (Ar-*C*H), 127.61 (Ar-*C*H), 127.60 (Ar-*C*H), 127.5 (Ar-*C*H), 123.5 (*p*-NO_2-Ar*C*H), 100.3 (C-1''), 98.1 (C-1), 97.7 (C-1'), 82.2 (C-3'' or C-3), 80.2 (C-2), 78.1 (C-4), 77.0 (C-3'' or C-3), 76.7 (C-2'' or C-3'), 76.3 (C-4'), 75.9 (*C*H_2Ph), 75.3 (C-2' or C-5'), 75.2 (C-2'' or C-3'), 75.1

(*C*H$_2$Ph), 74.2 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 73.4 (*C*H$_2$Ph), 73.0 (*C*H$_2$Ph), 72.8 (*C*H$_2$Ph), 72.3 (*C*H$_2$Ph), 71.8 (*C*H$_2$Ph), 70.5 (C-5), 69.8 (C-4''), 69.4 (C-2' or C-5'), 67.7 (C-6'), 67.6 (C-6''), 67.6 (C-5''), 66.3 (C-6), 55.2 (OMe).

β-18

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (d, *J* = 3.3 Hz, 1H, H-4'').

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calc'd for $C_{89}H_{91}NNaO_{19}^+$: 1500.6078; found: 1500.6073.

9. General Computational Details

All calculations were run on the Irish Centre for High-End Computing (ICHEC) and the UCD Sonic High Performance Computing clusters.

Initial geometries were preoptimized with the GFN2-xTB[16] extended tight-binding method applying the analytical linearized Poisson-Boltzmann (ALPB)[17] model for CH_2Cl_2 using xTB 6.6.1.[18] The benzyl protecting groups were substituted for methyl groups for computational feasibility. The iMTD-sMTD[19] workflow of CREST (version 2.1.2)[20,21] was used to generate an ensemble of low energy conformers which were sorted within a window of 6 kcal mol^{-1}. This ensemble was reranked using CENSO 1.2.0[22] using the PBE0-D3 functional,[23] def2-TZVP[24] basis set and SMD(CH_2Cl_2) solvation model.[25] The geometries of the lowest lying conformers were reoptimized and vibrational frequencies calculated by DFT using ORCA 5.0.4[26] at the PBE0-D3/def2-TZVP level of theory. Grimme's atom-pairwise dispersion correction (D3)[27] with the Becke-Johnson damping scheme[28] and the resolution of identity (RI)[29] in the split-RJ version[30] with the def2/j auxiliary basis set[31] were used. All vibrational frequencies were calculated numerically, and ground state structures were confirmed by having zero imaginary frequencies.

Transition states (TS) were located either from relaxed potential energy scans or the NEB-TS[32] method using ORCA 5.0.4. These TS guesses were further optimized by DFT at the SMD(CH_2Cl_2)-PBE0-D3/Def2-TZVP level of theory and were confirmed by having only one imaginary frequency and IRC calculations. Constrained conformer searches (constraining the forming/breaking bond distance) of the initial TS guesses using CREST were also performed to identify lower energy TS geometries, before unconstrained re-optimization and calculation of free energies, similar to the work of Bistoni & coworkers.[33]

The stationary point energies have been refined by performing final single point energy calculations with the domain-based local-pair-natural-orbitals coupled cluster method with single, double and perturbative triple excitations (DLPNO-CCSD(T))[34,35] with TightPNO settings and the Dunning correlation-consistent triple-zeta basis set augmented with diffuse functions (aug-cc-pVTZ).[36,37] The corresponding correlation-fitting basis set (aug-cc-pVTZ/C) and SMD(CH_2Cl_2) solvation model were used. In addition, the RIJCOSX[38] approximation to the exchange integrals was used together with the def2/j auxiliary basis set. Final Gibbs free energy values were obtained by adding the electronic energy from the DLPNO-CCSD(T) single-point calculations to the thermochemical correction from the frequency calculations at -20 °C carried out on the PBE0-D3/def2-TZVP level of theory. These values were normalized to the lowest energy α-triflate intermediate.

The local energy decomposition (LED) scheme implemented in the ORCA software was used to decompose the DLPNO-CCSD(T) single point energies into their respective terms to provide a quantitative understanding of the factors determining TS energies during the glycosylation reaction.[39,40] The DLPNO-CCSD(T)/LED scheme has been successfully utilized to decompose the TS energy of various chemical transformations into more meaningful terms.[33,41,42]

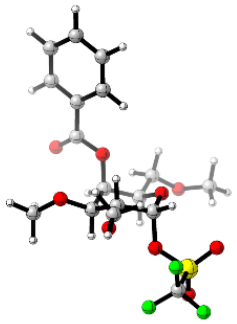
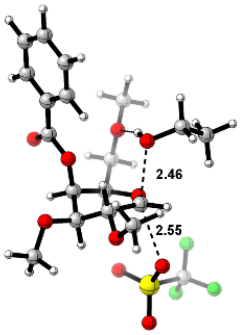
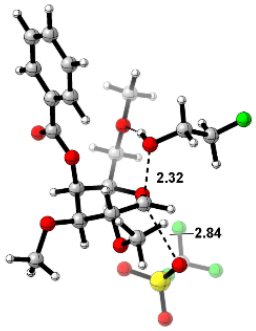
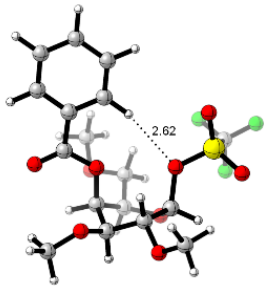
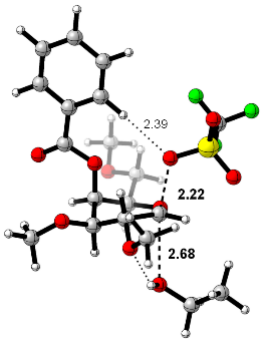
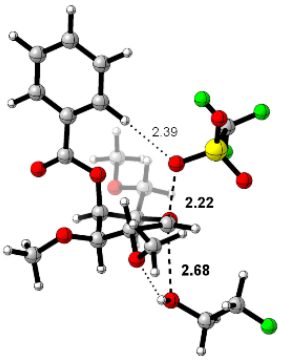
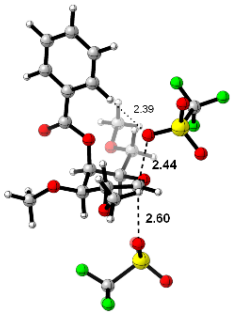
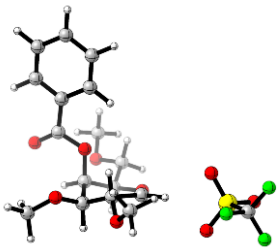
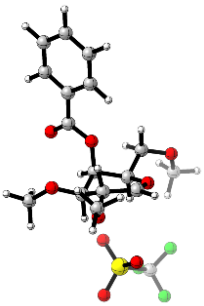
Qualitative non-covalent interactions (NCIs) were visualized with the non-covalent interaction index[43] using the optimised electron density at the PBE0-D3/def2-TZVP level of theory. The wave function files in a ".wfn" file format were obtained from the corresponding .gbw files using Multiwfn program (version 3.8).[44] The following thresholds were applied to generate the NCI isosurface with NCIPLOT4 program;[45] density cutoff = 0.05 a.u. and reduced density gradient (RDG) cutoff = 1.00 au. The surfaces were coloured on a blue-green-red (BGR) scale using VMD program[46] according to values of sign($\lambda 2$)ρ ranging from [–0.05 - 0.05 au] and density isovalue of 0.45 a.u. Thin, delocalized green surface indicates van der Waals interactions. Small, lenticular, bluish surfaces indicate strong interactions such as hydrogen bonding. Steric clashes are shown as red isosurfaces. Dispersion interaction density (DID) plots were generated with the orca_plot module of ORCA 5.0.4 and visualised with ChimeraX 1.8.[47]

Structures were visualised with ChemCraft 1.8[48] and CYLview20.[49]

10. S_N2 Pathways Originating from an α-Triflate Intermediate

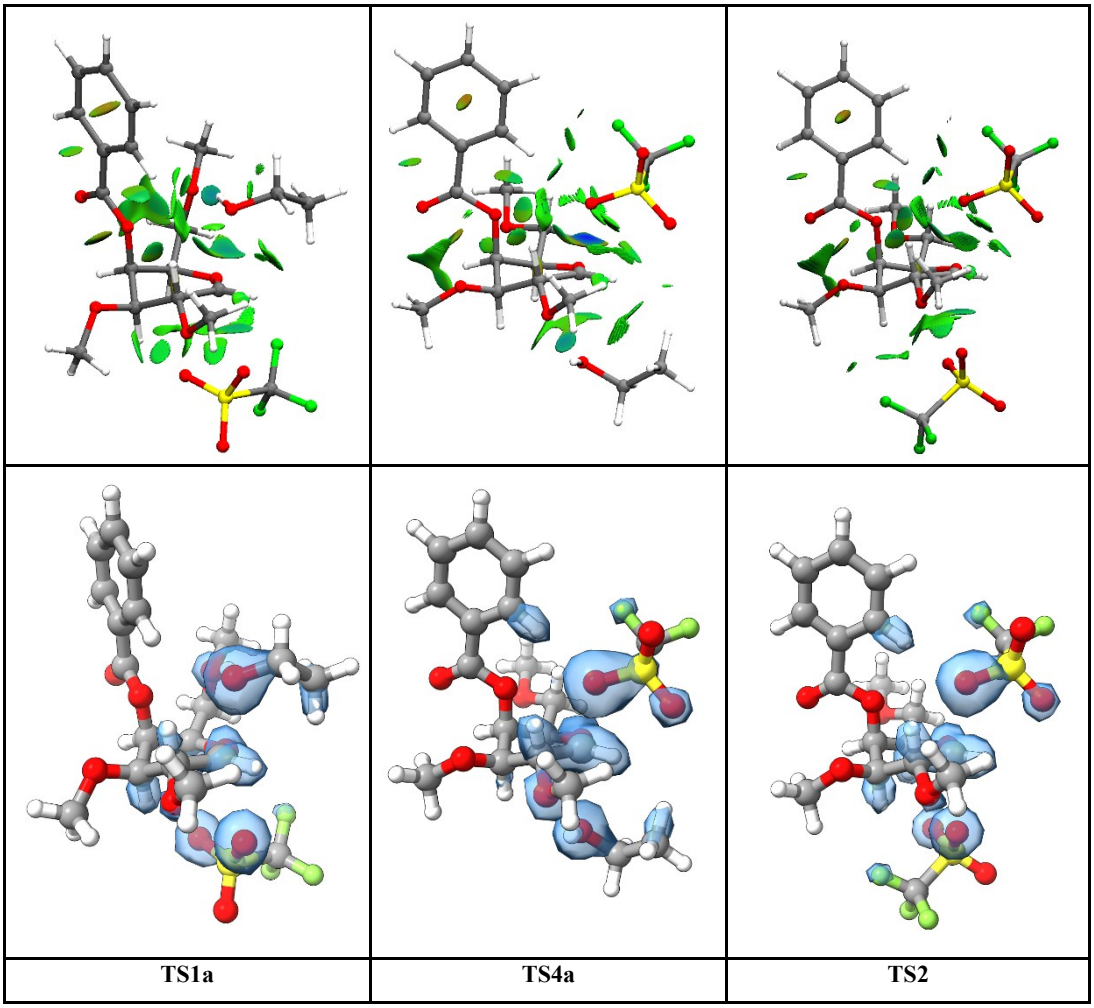
a. Glycosylation using Donor 4d

Supplementary Table 1. Transition state images for the S_N2 glycosylation of ethanol or 2-fluoroethanol with donor **4d** via glycosyl triflate intermediates.

		
α-OTf (0.0)	**TS1$_a$ (14.7)**	**TS1$_b$ (14.5)**
		
β-OTf (2.5)	**TS4$_a$ (12.8)**	**TS4$_b$ (13.7)**
		
TS2 (10.3)	**TS3 (16.5)**	**Ox (16.0)**

i. Non-Covalent Interaction (NCI) Plots:

Supplementary Table 2. Non-covalent interaction images *(top) and dispersion interaction density plots (bottom)* for the S_N2 glycosylation of ethanol with donor **4d** via glycosyl triflate intermediates.



TS1a	TS4a	TS2

ii. Glycosyl Triflate Anomerization (TS3) Details:

Constrained PES scans of the glycosyl triflates using DFT failed to identify suitable transition states of the C_1-O_{OTf} bond breaking step. Barrierless additions of nucleophiles to oxocarbenium ions have been reported using DFT previously in literature.[50] Even the inclusion of explicit CH_2Cl_2 solvent molecules (4 molecules) around the triflate moiety failed to produce a saddle point during the constrained PES scan.[51] Furthermore, conformational searches for stable oxocarbenium ion geometries were troublesome, with most of the conformers generated from CREST using semiempirical tight binding method GFN2-xTB converging to the parent glycosyl triflates when optimizing with DFT. Only several stable conformers were identified, with the lowest energy conformer being approximately ΔG 16.0 kcal mol^{-1}. However, NEB-TS[32] analysis of the reaction coordinates (using *NImages = 20*) between the two glycosyl triflates did successfully converge to a saddle point. Analysis of the absolute imaginary vibrational frequency indicated this TS represented the triflate anion traversing across the planar

anomeric C_1-H of the oxocarbenium intermediate (**TS3**). The free energy of this TS (16.5 kcal mol^{-1}) is only 0.5 kcal mol^{-1} higher than the energy of the oxocarbenium intermediate (**Ox**). This suggests the potential energy surface describing the oxocarbenium intermediates by our DFT method is relatively flat and features only low energy barriers which are difficult to detect with our DFT method.

iii. Extrapolation of DLPNO-CCSD(T) energies to the complete basis set (CBS) limit:

Extrapolation of the DLPNO-CCSD(T) single point energies to the basis set limit were performed to achieve higher accuracy by reducing the error resulting from an incomplete basis set. The extrapolation was performed using the correlation-consistent basis set augmented with diffuse functions (aug-cc-pV*n*Z) and the Karlsruhe def2 basis set (def2-*n*ZVPP) with cardinal numbers (n = 2, 3 and 4) corresponding to double-, triple- and quadruple-zeta basis sets. The implicit solvation was included *via* the SMD model and Tight PNO settings applied.

Basis Set	$TS1_a$	$TS1_b$	α-OTf	TS2	TS3	Ox	β-OTf	$TS4_a$	$TS4_b$
aug-cc-pVTZ (default)	14.7	14.5	0.0	10.3	16.5	16.0	2.5	12.8	13.7
CBS(2/3), aug-cc	15.8	15.6	0.0	11.5	15.4	15.5	2.9	13.6	14.4
CBS(3/4), def2	15.4	15.4	0.0	11.8	14.0	12.5	3.2	13.7	14.5

iv. Local Energy Decomposition (LED) Analysis:

To account for the differences in TS energies between EtOH and FEtOH acceptors, the activation energies from the α- and the β-OTf into the products were decomposed into various terms:

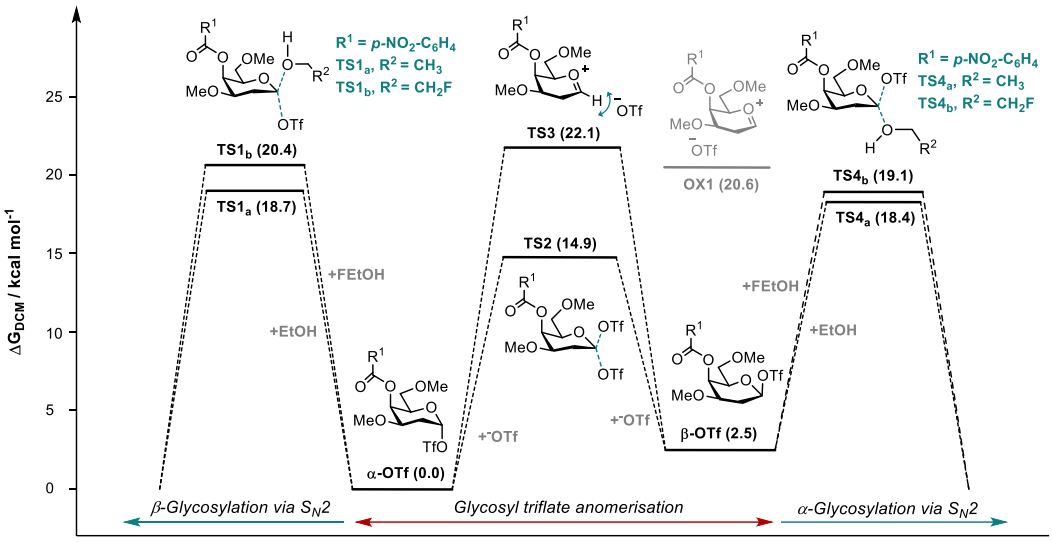
$$\Delta G_{TS} = \Delta E_{geo\text{-}prep} + \Delta E_{disp} + \Delta E_{non\text{-}disp} + \Delta G_{thermo} + \Delta G_{solv}$$

Where $\Delta E_{geo\text{-}prep}$ is the geometric preparation energy, which is the energy needed to distort the reactant's geometries from their equilibrium structure to the one they adopt in the transition state ("strain energy"); ΔE_{disp} is the reactant intermolecular dispersion energy (slightly stabilizing in the TS); $\Delta E_{non\text{-}disp}$ is the non-dispersive term describing all other physical components of the interaction energy (except dispersion) such as electrostatics, orbital interactions, steric repulsion and polarization effects (overall destabilizing in the TS); $\Delta G_{thermo} + \Delta G_{solv}$ are correction terms to account for thermal effects (including entropy) and solvation respectively.

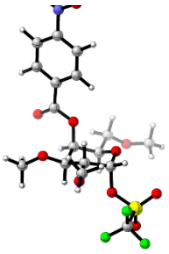
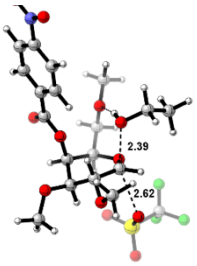
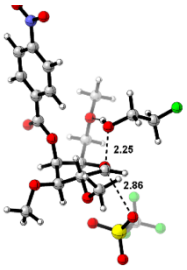
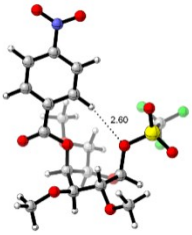
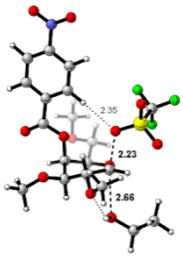
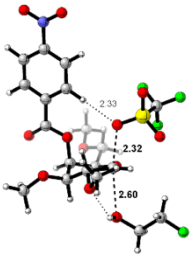
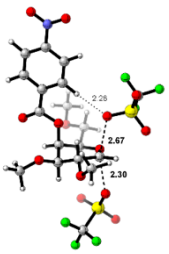
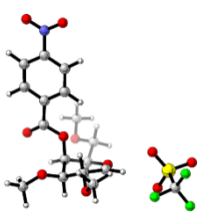
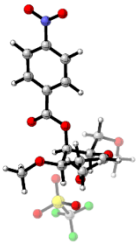
Local Energy Decomposition (LED)						
	TS1 (from α-OTf (ΔG 0.0))			TS4 (from β-OTf (ΔG 2.5))		
	EtOH	FEtOH	FEtOH-EtOH	EtOH	FEtOH	FEtOH-EtOH
ΔG_{TS}	14.7	14.5	-0.2	10.3 (+2.5)	11.1 (+2.5)	0.8
$\Delta G_{thermo} + \Delta G_{solv}$	-23.6	-30.0	-6.5	-19.9	-24.2	-4.3
ΔE_{TS}	38.3	44.5	6.3	30.2	35.3	5.2
$\Delta E_{geo\text{-}prep}$	15.3	16.6	1.3	8.3	8.6	0.3
ΔE_{int}	23.0	28.0	5.0	21.8	26.7	4.9
ΔE_{disp}	-10.6	-11.3	-0.7	-7.2	-7.4	-0.2
$\Delta E_{non\text{-}disp}$	33.6	39.3	5.7	29.0	34.1	5.1

To rationalise some of the energy differences observed between the alcohol acceptors and the benzoate ester donor, local energy decomposition (LED) analysis of the DLPNO-CCSD(T) energies was carried out to determine which chemical interactions differed for pathways involving the two alcohol acceptors. Both glycosylation pathways experience similar differences to the interaction energy term (ΔE_{int}) when it comes to different acceptors, however the $\Delta E_{geo\text{-}prep}$ differs more for the β-glycosylation pathway (1.3 vs 0.3 kcal mol^{-1}). This suggests the α-glycosylation pathway (TS4) is less sensitive to the "strain energy" required to distort the geometry of the β-OTf donor and the acceptors into the TS geometry. This can also be observed from the almost identical C_1-O_{OTf} and C_1-O_{Nu} bond distances of the TS4 geometries, regardless of which alcohol acceptor was used. Also worth noting is the general lower $\Delta E_{geo\text{-}prep}$ for TS4, which is further evidence that the geometries of the reactants distort less in transition states originating from the β-OTf.

b. Glycosylation using Donor 4a



Supplementary Figure 1. Reaction energy diagram for the glycosylation of ethanol or 2-fluoroethanol using donor **4a** via glycosyl triflate intermediates. Relative Gibbs free energy (ΔG) was computed at the SMD(CH_2Cl_2)-(TightPNO)DLPNO-CCSD(T)/aug-cc-pVTZ//SMD(CH_2Cl_2)-PBE0-D3/def2-TZVP level of theory, thermochemical corrections were applied at 253.15 K (-20 °C). The C-2 substituent is omitted from all structures for clarity. R^1 = p-NO_2-C_6H_4

		
α-OTf (0.0)	**TS1$_a$ (18.7)**	**TS1$_b$ (20.4)**
		
β-OTf (2.5)	**TS4$_a$ (18.4)**	**TS4$_b$ (19.1)**
		
TS2 (14.9)	**TS3 (22.1)**	**Ox (20.6)**

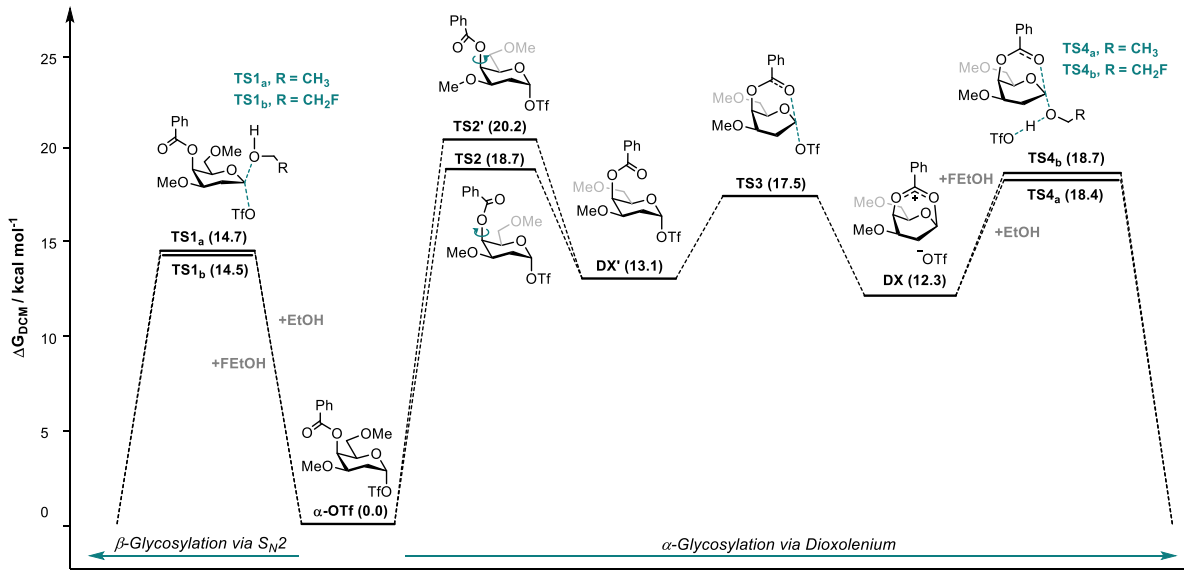
i. Extrapolation of DLPNO-CCSD(T) energies to the complete basis set (CBS) limit:

Basis Set	$TS1_a$	$TS1_b$	α-OTf	TS2	TS3	Ox	β-OTf	$TS4_a$	$TS4_b$
aug-cc-pVTZ (default)	18.7	20.4	0.0	14.9	22.1	20.6	2.5	18.4	19.1
CBS(2/3), aug-cc	20.7	22.6	0.0	16.4	21.1	20.3	2.9	20.1	21.0
CBS(3/4), def2	19.3	21.0	0.0	16.4	19.5	18.9	3.4	19.0	19.6

ii. Local Energy Decomposition (LED) Analysis:

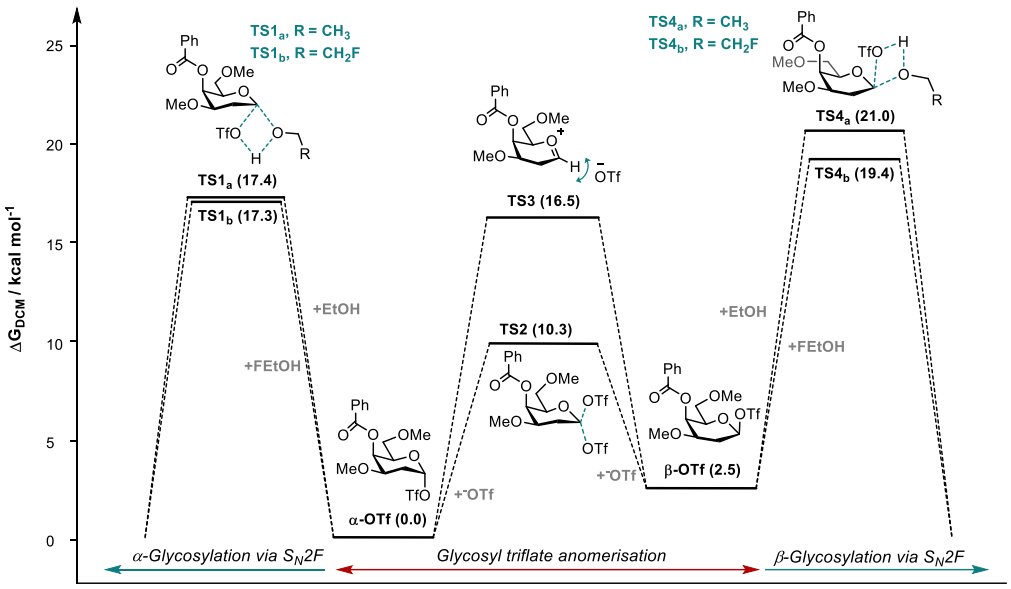
	Local Energy Decomposition (LED)					
	TS1 (from α-OTf (ΔG 0.0))			TS4 (from β-OTf (ΔG 2.5))		
	EtOH	FEtOH	FEtOH-EtOH	EtOH	FEtOH	FEtOH-EtOH
ΔG_{TS}	18.7	20.4	1.6	15.9 (+2.5)	16.6 (+2.5)	0.7
$\Delta G_{thermo} + \Delta G_{solv}$	-24.0	-29.2	-5.2	-17.7	-31.1	-13.4
ΔE_{TS}	42.7	49.6	6.8	33.6	47.7	14.1
$\Delta E_{geo\text{-}prep}$	16.2	17.9	1.7	9.4	9.3	0.0
ΔE_{int}	26.6	31.7	5.1	24.2	38.3	14.1
ΔE_{disp}	-10.9	-11.8	-0.9	-7.2	-11.8	-4.6
$\Delta E_{non\text{-}disp}$	37.5	43.5	6.0	31.5	50.2	18.7

11. Stereoretentive Pathway *via* Dioxolenium Intermediate



Supplementary Figure 2. Reaction energy diagram for the glycosylation of ethanol or 2-fluoroethanol using donor **4d** via a dioxolenium ion intermediate. Relative Gibbs free energy (ΔG) was computed at the SMD(CH_2Cl_2)-(TightPNO)DLPNO-CCSD(T)/aug-cc-pVTZ//SMD(CH_2Cl_2)-PBE0-D3/def2-TZVP level of theory, thermochemical corrections were applied at 253.15 K (-20 °C). The C-2 substituent is omitted from all structures for clarity.

12. Stereoretentive Pathway *via* SN2-Frontside Mechanism



Supplementary Figure 3. Reaction energy diagram for the glycosylation of ethanol or 2-fluoroethanol using donor **4d** via a SN2-frontside mechanism. Relative Gibbs free energy (ΔG) was computed at the SMD(CH_2Cl_2)-(TightPNO)DLPNO-CCSD(T)/aug-cc-pVTZ//SMD(CH_2Cl_2)-PBE0-D3/def2-TZVP level of theory, thermochemical corrections were applied at 253.15 K (-20 °C). The C-2 substituent is omitted from all structures for clarity.

13. Summary of Energies and Coordinates of Computed Structures

Name	$E(el)_{pbe0}$[a]	G_{pbe0}[a]	G_{corr}[b]	$E(el)_{dlpno\text{-}ccsd(t)}$[c]	G_{final}[d]	*imag. freq.* (cm^{-1})
EtOH	-154.931879	-154.872745	0.059134	-154.816275	-154.757141	-
FEtOH	-254.119336	-254.069424	0.049912	-253.954100	-253.904188	-
TfO^-	-961.238450	-961.236620	0.001829	-960.562117	-960.560288	-
S_N2 pathway originating from an α-OTf intermediate (Donor 4d)						
α-OTf	-2033.984787	-2033.641813	0.342973	-2032.418019	-2032.075046	-
β-OTf	-2033.980784	-2033.637631	0.343153	-2032.414147	-2032.070995	-
TS1a	-2188.910194	-2188.489804	0.420391	-2187.229162	-2186.808771	-52.27
TS1b	-2288.096671	-2287.686362	0.410309	-2286.366421	-2285.956112	-36.19
TS2	-2995.219970	-2994.859186	0.360784	-2992.979747	-2992.618963	-18.48
TS3	-2033.955857	-2033.617089	0.338768	-2032.387594	-2032.048827	-20.68
TS4a	-2188.911715	-2188.493666	0.418049	-2187.229813	-2186.811764	-79.81
TS4b	-2288.098810	-2287.688405	0.410405	-2286.367876	-2285.957470	-49.60
Ox	-2033.957688	-2033.619984	0.337704	-2032.387203	-2032.049498	-
S_N2 pathway originating from an α-OTf intermediate (Donor 4a)						
α-OTf(NO_2)	-2238.373423	-2238.038059	0.335364	-2236.665793	-2236.330429	-
β-OTf(NO_2)	-2238.369555	-2238.033298	0.336257	-2236.662766	-2236.326509	-
TS1a(NO_2)	-2393.298429	-2392.879700	0.418729	-2391.476427	-2391.057698	-65.96
TS1b(NO_2)	-2492.484894	-2492.073834	0.411060	-2490.613190	-2490.202130	-36.19
TS2(NO_2)	-3199.609958	-3199.248692	0.361265	-3197.228258	-3196.866993	-7.82
TS3(NO_2)	-2238.343618	-2238.004429	0.339189	-2236.634399	-2236.295210	-34.65
TS4a(NO_2)	-2393.300147	-2392.881497	0.418650	-2391.476900	-2391.058251	-82.71
TS4b(NO_2)	-2492.487257	-2492.076481	0.410776	-2490.615020	-2490.204245	-53.76
Ox(NO_2)	-2238.346678	-2238.006268	0.340410	-2236.637931	-2236.297522	-
Stereorententive pathway via a dioxolenium intermediate (Donor 4d)						
TS2(Dx)	-2033.956126	-2033.612758	0.343367	-2032.388674	-2032.045307	-36.19
TS2'(Dx)	-2033.953293	-2033.610522	0.342770	-2032.385547	-2032.042777	-52.67
Dx	-2033.968064	-2033.624418	0.343646	-2032.399032	-2032.055386	-
Dx'	-2033.963900	-2033.620539	0.343361	-2032.397553	-2032.054192	-
TS3(Dx)	-2033.954236	-2033.613722	0.340514	-2032.387656	-2032.047141	-25.76
TS4a(Dx)	-2188.903146	-2188.485005	0.418142	-2187.220965	-2186.802823	-86.38
TS4b(Dx)	-2288.091396	-2287.680829	0.410567	-2286.359945	-2285.949379	-76.33
Stereoretentive pathway via S_N2 frontside mechanism (Donor 4d)						
TS1a(S_N2F)	-2188.904756	-2188.487533	0.417223	-2187.221655	-2186.804431	-29.62
TS1b(S_N2F)	-2288.092515	-2287.684294	0.408221	-2286.359843	-2285.951621	-18.41
TS4a(S_N2F)	-2188.900319	-2188.483483	0.416835	-2187.215591	-2186.798756	-52.85
TS4b(S_N2F)	-2288.090051	-2287.681750	0.408301	-2286.356653	-2285.948353	-46.30

All energy values are reported in Hartree. [a]SMD(CH_2Cl_2)-PBE0-D3/def2-TZVP level of theory. [b]Calculated as G_{pbe0}-$E(el)_{pbe0}$.[c]SMD(CH_2Cl_2)-(TightPNO)DLPNO-CCSD(T)/aug-cc-pVTZ level of theory. [d]Calculated as $E(el)_{dlpno\text{-}ccsd(t)}$+$G_{corr}$.

EtOH

C	0.708758000	0.489597000	0.009674000
H	1.089634000	-0.534689000	0.008605000
H	1.095419000	0.997890000	0.896797000
H	1.095248000	0.999688000	-0.876488000
C	-0.796840000	0.485268000	0.009873000
H	-1.171758000	-0.046657000	0.894475000
H	-1.172011000	-0.044313000	-0.876026000
O	-1.251151000	1.830562000	0.011721000
H	-2.214098000	1.819953000	0.011668000

FEtOH

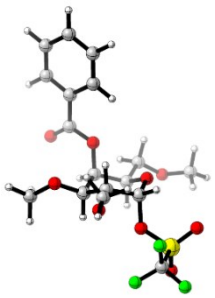
C	0.699495945	0.506979339	0.009751135
H	1.085670686	1.003861822	0.903059989
H	1.085530796	1.005463739	-0.882723403
C	-0.807437800	0.478536544	0.009916857
H	-1.161954194	-0.058918354	0.898471678
H	-1.162274826	-0.056525118	-0.879947486
O	-1.236244464	1.824454637	0.011790972
H	-2.199063420	1.832171720	0.011463209
F	1.172777276	-0.802724328	0.008517051

TfO-

S	-0.910095000	0.000000000	-0.000138000
O	-1.229660000	1.221711000	-0.706192000
O	-1.230642000	-0.000028000	1.410816000
O	-1.229662000	-1.221681000	-0.706241000
C	0.934043000	0.000000000	0.000577000
F	1.422437000	0.000018000	-1.244444000
F	1.422835000	1.078201000	0.622903000
F	1.422836000	-1.078218000	0.622872000

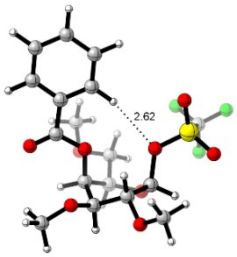
SN2 Pathway – Donor 4a

α-OTf



C	-1.091100000	-3.068474000	-1.237539000
O	-1.146661000	-2.276869000	-0.068780000
C	-0.314419000	-1.155570000	-0.105791000
C	0.314768000	-0.923719000	1.254412000
O	1.162780000	-2.004012000	1.519970000
C	1.393689000	-2.226235000	2.894460000
C	1.073507000	0.405873000	1.251101000
O	2.173744000	0.300612000	0.345837000
C	3.393082000	0.072061000	0.850627000
O	3.640013000	0.052087000	2.031321000
C	0.185581000	1.539152000	0.783318000
C	0.933850000	2.852712000	0.660878000
O	0.111580000	3.988001000	0.705488000
C	-0.559018000	4.290052000	-0.498957000
O	-0.392382000	1.241594000	-0.497534000
C	-1.091265000	0.075901000	-0.565558000
H	-1.823024000	-3.867748000	-1.117510000
H	-1.341751000	-2.494498000	-2.137516000
H	-0.095670000	-3.510685000	-1.364561000
H	0.495384000	-1.288808000	-0.834331000
H	-0.480810000	-0.856753000	2.009918000
H	1.869229000	-1.365047000	3.376245000
H	0.458116000	-2.462298000	3.416978000
H	2.068009000	-3.080173000	2.969305000
H	1.444845000	0.628537000	2.252353000
H	-0.617621000	1.664361000	1.518534000
H	1.540345000	2.839532000	-0.254358000
H	1.610807000	2.931689000	1.516058000
H	0.132038000	4.280136000	-1.352146000
H	-1.377854000	3.593553000	-0.705672000
H	-0.970100000	5.295433000	-0.390409000
H	-1.456166000	-0.037061000	-1.585851000
C	4.403182000	-0.130588000	-0.216207000
C	5.714325000	-0.403876000	0.166915000
C	4.076917000	-0.055775000	-1.569282000
C	6.691315000	-0.602675000	-0.793924000
H	5.953487000	-0.459453000	1.222267000
C	5.057996000	-0.252683000	-2.527971000
H	3.058814000	0.158943000	-1.868124000
C	6.363915000	-0.526824000	-2.142216000
H	7.710429000	-0.817109000	-0.492665000
H	4.803226000	-0.192549000	-3.580079000
H	7.129298000	-0.681706000	-2.894841000
S	-3.650647000	0.653533000	-0.169425000
O	-3.552814000	1.288409000	-1.441030000
O	-2.270247000	0.159125000	0.332835000
O	-4.317427000	1.263216000	0.927459000
C	-4.500037000	-0.964818000	-0.456255000
F	-4.478853000	-1.696658000	0.643047000
F	-5.756647000	-0.721754000	-0.797912000
F	-3.903065000	-1.623721000	-1.436846000

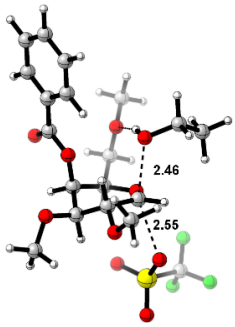
β-OTf



C	1.780288000	3.247500000	-2.534134000
O	1.109892000	3.448396000	-1.307556000
C	0.485567000	2.295439000	-0.813547000
C	-0.678191000	2.731994000	0.054323000
O	-1.717746000	3.115561000	-0.799919000
C	-2.681506000	3.942573000	-0.186930000
C	-1.072227000	1.607500000	0.994638000
O	-1.398467000	0.455394000	0.219167000
C	-2.675996000	0.057698000	0.180813000
O	-3.580212000	0.639876000	0.725966000
C	0.080332000	1.297679000	1.932980000
C	0.003103000	-0.093314000	2.528375000
O	-1.213872000	-0.188159000	3.216270000
C	-1.503014000	-1.508096000	3.605078000
O	1.375029000	1.474962000	1.336825000
C	1.501201000	1.459412000	-0.010931000
H	2.604487000	2.528913000	-2.447462000
H	1.085337000	2.893141000	-3.304808000
H	2.191121000	4.211188000	-2.835572000
H	0.097771000	1.685158000	-1.636194000
H	-0.349274000	3.581312000	0.670714000
H	-2.220411000	4.854846000	0.211489000
H	-3.402880000	4.215838000	-0.957493000
H	-3.212725000	3.428513000	0.621365000
H	-1.938753000	1.883276000	1.592369000
H	0.042619000	2.035128000	2.738369000
H	0.856127000	-0.246826000	3.202690000
H	0.056051000	-0.844425000	1.732120000
H	-0.738375000	-1.902651000	4.287193000
H	-2.464566000	-1.496554000	4.119400000
H	-1.571065000	-2.173141000	2.734166000
C	-2.836563000	-1.188667000	-0.605131000
C	-1.759142000	-1.804901000	-1.238647000
C	-4.107963000	-1.749889000	-0.693889000
C	-1.956540000	-2.974850000	-1.953989000
H	-0.771835000	-1.367625000	-1.171785000
C	-4.300875000	-2.920246000	-1.407907000
H	-4.935972000	-1.259519000	-0.196496000
C	-3.225249000	-3.533608000	-2.038345000
H	-1.117043000	-3.452088000	-2.446395000
H	-5.291023000	-3.356182000	-1.474175000

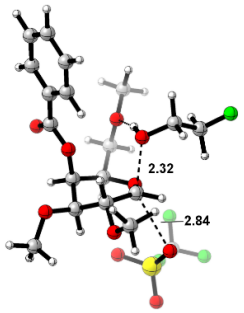
H	-3.376880000	-4.450095000	-2.597576000
O	1.391023000	0.047176000	-0.511032000
S	2.623696000	-0.776310000	-0.955740000
O	2.183807000	-1.719422000	-1.924434000
O	3.758593000	0.056014000	-1.181162000
C	2.998352000	-1.759939000	0.563524000
F	1.964095000	-2.519430000	0.883890000
F	3.286205000	-0.958843000	1.574480000
F	4.043093000	-2.531768000	0.306471000
H	2.514218000	1.783778000	-0.243855000

TS1a



C	-0.391370000	-0.540460000	3.965783000
O	-0.881331000	0.273797000	2.917498000
C	-0.108881000	0.221076000	1.763316000
C	-0.186304000	1.524638000	0.977017000
O	0.381406000	2.576731000	1.694865000
C	-0.562798000	3.415264000	2.334181000
C	0.591177000	1.317854000	-0.312311000
O	1.927685000	1.000893000	0.060172000
C	2.916130000	1.386810000	-0.760958000
O	2.731655000	2.049878000	-1.751215000
C	-0.060079000	0.236199000	-1.153519000
C	0.745382000	-0.370572000	-2.271753000
O	1.860638000	-1.056634000	-1.757161000
C	2.645908000	-1.644661000	-2.772574000
O	-0.524625000	-0.908939000	-0.354515000
C	-0.519085000	-0.927128000	0.898853000
H	-1.048409000	-0.383382000	4.820533000
H	-0.407234000	-1.603283000	3.699293000
H	0.632791000	-0.255628000	4.233720000
H	0.949147000	0.041747000	2.005227000
H	-1.229605000	1.733475000	0.713760000
H	0.003027000	4.202583000	2.832895000
H	-1.241538000	3.871446000	1.604136000
H	-1.149325000	2.867413000	3.077032000
H	0.580945000	2.234913000	-0.903241000
H	-0.982825000	0.646442000	-1.566748000
H	1.053814000	0.438506000	-2.944195000
H	0.102080000	-1.058677000	-2.834094000
H	3.047492000	-0.879258000	-3.446065000
H	3.472096000	-2.162223000	-2.285430000
H	2.060370000	-2.363202000	-3.357625000
H	-0.906231000	-1.835315000	1.344814000
C	4.240294000	0.912863000	-0.303217000
C	5.360083000	1.296265000	-1.037718000
C	4.386653000	0.087714000	0.809932000
C	6.618577000	0.860710000	-0.660535000
H	5.229571000	1.934755000	-1.902961000
C	5.648183000	-0.347792000	1.182241000
H	3.516372000	-0.224441000	1.372031000
C	6.763299000	0.037975000	0.449756000
H	7.488742000	1.160729000	-1.232785000
H	5.761610000	-0.992482000	2.046144000
H	7.748856000	-0.305272000	0.743792000
S	-3.858295000	-0.036961000	0.125901000
O	-3.087805000	0.883133000	-0.686728000
O	-3.063999000	-0.819399000	1.057159000
O	-5.091523000	0.483790000	0.659572000
C	-4.411522000	-1.300307000	-1.096957000
F	-5.169065000	-0.750308000	-2.047139000
F	-3.366351000	-1.879380000	-1.694379000
F	-5.125326000	-2.260668000	-0.507256000
C	1.709299000	-3.472413000	1.056792000
H	1.376724000	-3.701119000	2.072053000
H	2.748599000	-3.812160000	0.968268000
C	0.841598000	-4.174696000	0.039537000
H	-0.206743000	-3.882733000	0.139340000
H	1.168627000	-3.946967000	-0.979086000
H	0.906748000	-5.257162000	0.177786000
O	1.666660000	-2.055687000	0.940958000
H	1.874869000	-1.813202000	0.022010000

TS1b



C	-0.493960872	-0.354278250	4.012776005
O	-0.954264565	0.431891944	2.928068470
C	-0.119892984	0.386986543	1.812929352
C	-0.183175252	1.690987496	1.026716456
O	0.411811452	2.731291097	1.739730658
C	-0.509954113	3.595408997	2.378703118
C	0.566081375	1.477970831	-0.277810889
O	1.906673190	1.145495717	0.063339897
C	2.876465304	1.518634730	-0.787888662
O	2.668352233	2.179512746	-1.774700245
C	-0.114106572	0.405341039	-1.108352072
C	0.657788670	-0.209655178	-2.246027505
O	1.780589491	-0.903956978	-1.757833762
C	2.532840600	-1.507286624	-2.790732893
O	-0.567398006	-0.739845462	-0.298769226
C	-0.523476157	-0.762243496	0.951468566
H	-1.215994706	-0.231998941	4.819445081
H	-0.433316926	-1.416202935	3.749340524
H	0.492725653	-0.012245607	4.345762782
H	0.928023581	0.210940643	2.098088221
H	-1.229515170	1.910602009	0.784577523
H	0.076634960	4.372242825	2.869909578
H	-1.182054728	4.062867375	1.649720665
H	-1.105027122	3.065454614	3.128011795
H	0.551225426	2.396322210	-0.866823127
H	-1.044868023	0.820166419	-1.498772633
H	0.956047091	0.596406884	-2.926241934
H	-0.004699860	-0.893291764	-2.790754709
H	2.919178566	-0.750346149	-3.482078597
H	3.369388855	-2.025344284	-2.322166516
H	1.925090155	-2.227315039	-3.350393345
H	-0.914124144	-1.668053671	1.403049647
C	4.208396738	1.031865775	-0.369764603
C	5.300687579	1.354162944	-1.172134285
C	4.388378688	0.254219559	0.772239800
C	6.565093491	0.903534328	-0.834984385
H	5.143831067	1.956305871	-2.058760593
C	5.656073489	-0.194601320	1.105749593
H	3.538900482	-0.008224660	1.388723807
C	6.743448015	0.128853465	0.304630191
H	7.413509738	1.154725594	-1.460847330
H	5.796216987	-0.800737095	1.993275013
H	7.733693032	-0.225574236	0.568014722
S	-3.936960954	-0.118516598	0.122864746
O	-3.118371978	1.004794238	-0.294843510
O	-3.246437506	-1.086088213	0.953858684
O	-5.277276603	0.211655206	0.538971971
C	-4.189860751	-1.035295863	-1.457697683
F	-4.836039714	-0.283930558	-2.351431315
F	-3.019715336	-1.390972079	-1.998711875
F	-4.902168698	-2.147363008	-1.267027348
C	1.849987129	-3.272194713	1.055746217

H	1.693039502	-3.516905116	2.112306944
H	2.873956329	-3.569627225	0.783582094
C	0.856637990	-4.025927014	0.194736424
H	-0.177731640	-3.817272923	0.493760982
H	0.986047037	-3.788946473	-0.868838746
F	1.080193163	-5.391857482	0.354094226
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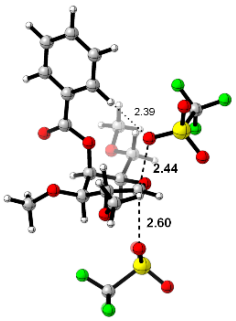
TS2



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C	-0.303229000	1.920113000	-0.159867000
O	-1.383459000	2.322285000	-0.944977000
C	-2.237810000	3.241217000	-0.297400000
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C	-2.451231000	-0.595889000	0.014344000
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C	0.332685000	-0.983257000	2.309051000
O	-0.786014000	-0.850783000	3.136827000
C	-1.128219000	-2.066180000	3.759247000
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C	1.846299000	0.690478000	-0.340036000
H	2.545847000	1.253050000	-3.099380000
H	0.893342000	1.538513000	-3.705676000
H	2.086085000	2.866262000	-3.685710000
H	0.310763000	0.625738000	-1.721433000
H	0.094021000	2.753389000	0.431452000
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H	1.238230000	-1.207270000	2.888104000
H	0.188774000	-1.782678000	1.571499000
H	-0.311525000	-2.433145000	4.393853000
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C	-4.070912000	-2.212257000	-0.903474000
C	-2.078995000	-3.551808000	-2.302140000
H	-0.723918000	-2.109424000	-1.476145000
C	-4.392198000	-3.315720000	-1.675106000
H	-4.835144000	-1.678208000	-0.351728000
C	-3.396026000	-3.986268000	-2.374741000
H	-1.301628000	-4.073407000	-2.848813000
H	-5.419984000	-3.655114000	-1.732366000
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S	2.688816000	-2.194999000	-1.926316000
O	2.583379000	-2.966849000	-3.138427000
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F	1.416448000	-4.117327000	-0.646305000
F	2.682734000	-2.907654000	0.611924000
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O	2.197548000	2.643130000	3.092620000
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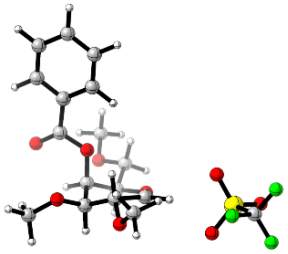
TS3



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O	0.625901000	-2.040610000	2.092049000
C	1.078518000	-2.090085000	3.431476000
C	0.242414000	0.317555000	1.652752000
O	1.130141000	0.280437000	0.545788000
C	2.453044000	0.324548000	0.804363000
O	2.905203000	0.401348000	1.916889000
C	-0.840774000	1.328926000	1.380409000
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C	-1.933272000	-0.362991000	0.084836000
H	-2.726052000	-4.224967000	-0.002719000
H	-2.451359000	-2.910838000	-1.169151000
H	-1.065557000	-3.852088000	-0.549339000
H	-0.345547000	-1.670986000	-0.187910000
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H	-1.424486000	1.497465000	2.286680000
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C	2.676035000	0.190491000	-1.696762000
C	5.444884000	0.268977000	-1.437826000
H	5.085198000	0.377877000	0.679628000
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H	1.599003000	0.159844000	-1.797488000
C	4.861947000	0.185902000	-2.696300000
H	6.523664000	0.299216000	-1.338586000
H	3.026146000	0.081577000	-3.806435000
H	5.487866000	0.151017000	-3.580867000
S	-4.843845000	0.293987000	-1.985982000
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O	-4.951162000	-0.071191000	-0.586038000
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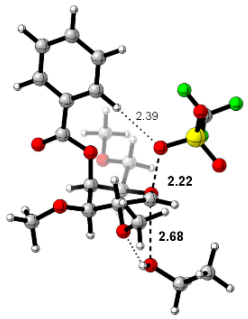
TS4a



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C	2.733829000	1.577265000	0.971074000
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O	1.008743000	-0.740262000	-3.728621000
C	1.382244000	-1.450775000	-4.886371000
O	-0.966683000	-1.454313000	-0.828652000
C	-0.839299000	-1.630027000	0.411306000
H	-1.103921000	-2.333662000	3.188985000
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H	3.057213000	1.658021000	-0.071716000
H	2.027910000	2.386055000	1.193843000
H	1.831154000	0.334085000	-1.446947000
H	-0.506914000	0.252428000	-1.825187000
H	-0.818850000	-1.644092000	-3.366834000
H	0.596863000	-2.470999000	-2.676920000
H	1.919831000	-2.371669000	-4.627488000
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H	2.232385000	-3.928623000	-0.330747000
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O	-0.396930000	-5.985237000	1.149295000
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C	-1.058127000	-5.315818000	-1.268962000
F	-1.550769000	-4.322150000	-2.008268000
F	-1.858804000	-6.370597000	-1.408018000
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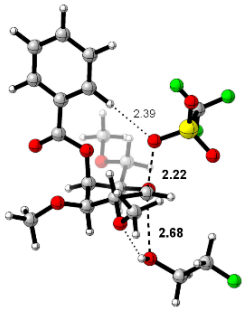
TS4b



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C	1.406026000	-0.415888000	-0.880103000
O	2.166580000	-1.612471000	-0.822606000
C	3.467577000	-1.558518000	-1.159297000
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C	1.447790000	-1.448494000	-4.877583000
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C	-0.704017000	-1.599155000	0.460659000
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H	0.701859000	-2.468939000	-2.656756000
H	1.994281000	-2.365759000	-4.624687000
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C	4.054252000	-5.231373000	-0.528805000
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H	7.142293000	-4.302340000	-1.577200000
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O	-0.346156000	-6.082043000	1.153685000
O	-2.144489000	-4.421622000	0.941100000
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F	-1.452760000	-4.243828000	-1.924259000
F	-1.877137000	-6.287234000	-1.383801000
F	0.157433000	-5.667931000	-1.750089000
H	-1.522163000	-2.120770000	0.946176000
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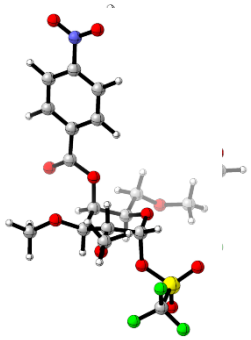
Ox



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H	2.344661000	-4.478892000	-1.639240000
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H	1.215126000	1.853042000	-1.783062000
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C	6.095771000	1.234560000	1.591650000
H	4.281934000	1.102758000	2.739702000
C	6.668265000	1.094650000	0.333489000
H	6.334810000	0.607410000	-1.731585000
H	6.705444000	1.530760000	2.437278000
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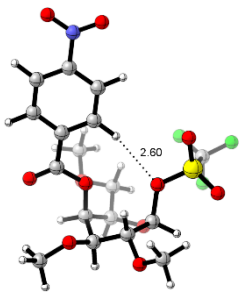
F	-3.097700000	2.230849000	1.064632000
F	-5.176350000	1.751584000	0.745102000
F	-4.239394000	1.285372000	2.630748000

S_N2 Pathway – Donor 4d

α-OTf (NO_2)

C	-1.466971000	-3.172727000	-0.809569000
O	-1.734689000	-2.259947000	0.234549000
C	-0.940078000	-1.112446000	0.195343000
C	-0.540667000	-0.701655000	1.598674000
O	0.285302000	-1.702979000	2.119685000
C	0.283485000	-1.765497000	3.529073000
C	0.172200000	0.649674000	1.552771000
O	1.397718000	0.489470000	0.831201000
C	2.532891000	0.383611000	1.521452000
O	2.622346000	0.504300000	2.716655000
C	-0.663458000	1.683413000	0.830333000
C	0.059241000	3.008066000	0.677837000
O	-0.787787000	4.106637000	0.476844000
C	-1.262335000	4.262255000	-0.841952000
O	-1.024352000	1.221727000	-0.479921000
C	-1.665614000	0.021807000	-0.524152000
H	-2.174318000	-3.995476000	-0.705207000
H	-1.597091000	-2.718486000	-1.798142000
H	-0.446790000	-3.566255000	-0.731599000
H	-0.023372000	-1.291495000	-0.380027000
H	-1.444132000	-0.584989000	2.212802000
H	0.633836000	-0.832884000	3.983870000
H	-0.719457000	-1.994758000	3.909152000
H	0.964320000	-2.568096000	3.813824000
H	0.389971000	0.998628000	2.562478000
H	-1.573446000	1.849596000	1.417572000
H	0.796636000	2.929477000	-0.131435000
H	0.595954000	3.202299000	1.610395000
H	-0.445853000	4.173356000	-1.569836000
H	-2.036635000	3.531161000	-1.094339000
H	-1.689346000	5.264142000	-0.911802000
H	-1.848452000	-0.221795000	-1.569469000
C	3.692546000	0.115968000	0.627337000
C	4.940886000	-0.065234000	1.215450000
C	3.550881000	0.045952000	-0.756406000
C	6.049435000	-0.318245000	0.430697000
H	5.034102000	-0.007740000	2.292319000
C	4.652947000	-0.203731000	-1.552799000
H	2.580787000	0.189343000	-1.212366000
C	5.882671000	-0.382342000	-0.942651000
H	7.026921000	-0.463775000	0.869043000
H	4.564996000	-0.260146000	-2.628854000
S	-4.264182000	0.515268000	-0.641879000
O	-3.961373000	0.969642000	-1.957562000
O	-2.982133000	0.146763000	0.147191000
O	-5.115108000	1.246850000	0.229780000
C	-5.033422000	-1.154099000	-0.830243000
F	-5.177027000	-1.730828000	0.349466000
F	-6.223285000	-1.001655000	-1.391577000
F	-4.282504000	-1.917748000	-1.606326000
N	7.052074000	-0.648899000	-1.782794000
O	6.886487000	-0.704639000	-2.983562000
O	8.123054000	-0.799565000	-1.233176000

β-OTf (NO_2)



C	3.274985000	0.781352000	-3.400453000
O	3.237127000	1.582683000	-2.237892000
C	2.169683000	1.279879000	-1.382801000
C	1.845196000	2.530104000	-0.588609000
O	1.112161000	3.379625000	-1.424059000
C	1.140729000	4.732442000	-1.025917000
C	1.094678000	2.163676000	0.678494000
O	-0.094080000	1.457569000	0.316569000
C	-1.267216000	2.072641000	0.468433000
O	-1.403879000	3.202252000	0.862094000
C	1.969165000	1.291689000	1.560999000
C	1.174670000	0.463913000	2.550878000

O	0.426516000	1.352546000	3.334246000
C	-0.533618000	0.690555000	4.120189000
O	2.846265000	0.422439000	0.828313000
C	2.561307000	0.110963000	-0.458341000
H	3.409026000	-0.282145000	-3.169340000
H	2.355589000	0.900637000	-3.985855000
H	4.125593000	1.117954000	-3.993135000
H	1.283789000	0.992129000	-1.959272000
H	2.792122000	3.001178000	-0.287390000
H	2.168868000	5.114366000	-1.007995000
H	0.564893000	5.293146000	-1.762538000
H	0.687178000	4.882931000	-0.040320000
H	0.814353000	3.053506000	1.238813000
H	2.636014000	1.962661000	2.107647000
H	1.865989000	-0.126865000	3.166513000
H	0.515330000	-0.228689000	2.015587000
H	-0.064426000	-0.014996000	4.818333000
H	-1.071070000	1.448883000	4.690554000
H	-1.248093000	0.140413000	3.493820000
C	-2.399226000	1.181555000	0.095937000
C	-2.190070000	-0.128928000	-0.325918000
C	-3.690050000	1.693749000	0.186446000
C	-3.267437000	-0.929346000	-0.657355000
H	-1.186003000	-0.523393000	-0.396452000
C	-4.775018000	0.904420000	-0.142615000
H	-3.834842000	2.714539000	0.516284000
C	-4.541086000	-0.395778000	-0.558833000
H	-3.125443000	-1.949124000	-0.987290000
H	-5.785408000	1.283737000	-0.080616000
O	1.425847000	-0.871656000	-0.494447000
S	1.629456000	-2.372579000	-0.814285000
O	0.401231000	-2.867675000	-1.331176000
O	2.870108000	-2.606644000	-1.474937000
C	1.800996000	-3.107435000	0.872802000
F	0.718877000	-2.865310000	1.593501000
F	2.859349000	-2.605272000	1.485432000
F	1.952215000	-4.415753000	0.739863000
H	3.428150000	-0.408524000	-0.863877000
N	-5.686284000	-1.237796000	-0.910420000
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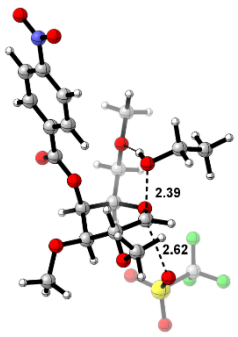
O	-5.464094000	-2.369801000	-1.286342000

TS1a (NO_2)



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O	-0.595848000	1.392482000	3.368837000
C	0.075071000	1.043177000	2.202708000
C	-0.019338000	2.144788000	1.152654000
O	0.657311000	3.291202000	1.566538000
C	-0.186203000	4.304222000	2.083781000
C	0.622582000	1.612768000	-0.117538000
O	1.974162000	1.294166000	0.207497000
C	2.891879000	1.404184000	-0.757813000
O	2.663566000	1.845721000	-1.854608000
C	-0.151496000	0.418002000	-0.642942000
C	0.525902000	-0.486263000	-1.639139000
O	1.640517000	-1.113823000	-1.050991000
C	2.298065000	-1.992794000	-1.940780000
O	-0.617888000	-0.476829000	0.425874000
C	-0.474169000	-0.233339000	1.648083000
H	-0.625698000	1.181001000	5.378025000
H	-0.131356000	-0.290144000	4.513562000
H	1.003114000	1.080091000	4.653565000
H	1.140094000	0.860798000	2.401104000
H	-1.073186000	2.354928000	0.935123000
H	0.456556000	5.145304000	2.344463000
H	-0.914124000	4.630516000	1.332093000
H	-0.718247000	3.966672000	2.977459000
H	0.602359000	2.379780000	-0.893010000
H	-1.079002000	0.791169000	-1.080568000
H	0.822383000	0.119096000	-2.503569000
H	-0.197993000	-1.237128000	-1.978038000
H	2.688416000	-1.447734000	-2.807316000
H	3.128048000	-2.443133000	-1.396695000
H	1.620063000	-2.779957000	-2.289510000
H	-0.903904000	-0.973832000	2.313474000
C	4.225163000	0.919948000	-0.317601000
C	5.284350000	1.037525000	-1.213046000
C	4.419725000	0.336297000	0.931501000
C	6.539587000	0.574795000	-0.869057000
H	5.114475000	1.491012000	-2.181082000
C	5.671368000	-0.131796000	1.286591000
H	3.593733000	0.232321000	1.621532000
C	6.707767000	-0.003720000	0.377928000
H	7.374855000	0.656027000	-1.550564000
H	5.843817000	-0.592317000	2.249397000
S	-3.854389000	0.741614000	0.790528000
O	-3.105780000	1.428674000	-0.243885000
O	-3.042349000	0.243288000	1.885778000
O	-5.094300000	1.365849000	1.179474000
C	-4.399706000	-0.803329000	-0.055980000
F	-5.160560000	-0.527314000	-1.116549000
F	-3.351981000	-1.515502000	-0.481726000
F	-5.109304000	-1.578548000	0.765985000
C	1.571714000	-2.803226000	2.241450000
H	1.318629000	-2.761309000	3.303134000
H	2.587074000	-3.209813000	2.162135000
C	0.595915000	-3.676187000	1.489792000
H	-0.429289000	-3.313234000	1.596750000
H	0.841914000	-3.711203000	0.424541000
H	0.636354000	-4.697675000	1.876797000
O	1.575304000	-1.454390000	1.784817000
H	1.720306000	-1.453889000	0.821385000
N	8.033704000	-0.504316000	0.747814000
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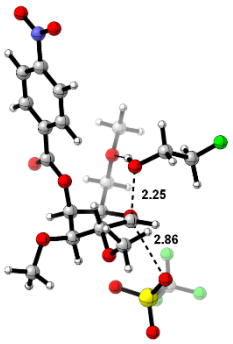
O	8.925993000	-0.400512000	-0.067392000

TS1b (NO_2)



C	-0.586098000	-0.847316000	3.710062000
O	-0.997877000	0.025735000	2.674846000
C	-0.094717000	0.104063000	1.615611000
C	-0.199585000	1.461204000	0.932709000
O	0.331288000	2.466948000	1.741061000
C	-0.645390000	3.251206000	2.401047000
C	0.578140000	1.388093000	-0.367676000
O	1.923627000	1.061833000	-0.023098000
C	2.900486000	1.534292000	-0.803728000
O	2.716824000	2.272777000	-1.736804000
C	-0.056085000	0.372181000	-1.301076000
C	0.768485000	-0.143310000	-2.452680000
O	1.884664000	-0.859109000	-1.974255000
C	2.673045000	-1.396778000	-3.018273000
O	-0.526839000	-0.828969000	-0.601344000
C	-0.419520000	-0.990387000	0.640675000
H	-1.356026000	-0.809061000	4.479757000
H	-0.489840000	-1.880576000	3.358313000

H	0.372363000	-0.522889000	4.131088000
H	0.937666000	-0.038879000	1.956155000
H	-1.250362000	1.649967000	0.685119000
H	-0.107796000	4.008968000	2.971497000
H	-1.304533000	3.748245000	1.679999000
H	-1.250349000	2.648224000	3.084377000
H	0.553740000	2.353938000	-0.873714000
H	-0.972221000	0.812293000	-1.697649000
H	1.082526000	0.712524000	-3.060800000
H	0.138609000	-0.793686000	-3.071009000
H	3.073360000	-0.597452000	-3.650820000
H	3.498816000	-1.936218000	-2.555001000
H	2.087400000	-2.085584000	-3.636910000
H	-0.842617000	-1.918508000	1.009124000
C	4.237137000	1.044500000	-0.381019000
C	5.349716000	1.526919000	-1.064280000
C	4.387673000	0.114625000	0.644388000
C	6.615247000	1.086571000	-0.728605000
H	5.213569000	2.247603000	-1.860393000
C	5.648953000	-0.336992000	0.986158000
H	3.521341000	-0.266394000	1.167425000
C	6.739151000	0.158797000	0.292014000
H	7.492241000	1.449360000	-1.246226000
H	5.789132000	-1.062707000	1.775159000
S	-3.919690000	-0.330850000	-0.160028000
O	-3.092392000	0.828532000	-0.437036000
O	-3.248506000	-1.394001000	0.559787000
O	-5.264121000	-0.038675000	0.273960000
C	-4.160418000	-1.056357000	-1.837751000
F	-4.763491000	-0.191315000	-2.656329000
F	-2.989425000	-1.387322000	-2.392762000
F	-4.909891000	-2.159205000	-1.785417000
C	1.790951000	-3.356354000	0.705731000
H	1.505083000	-3.619578000	1.725616000
H	2.846371000	-3.615202000	0.567170000
C	0.945481000	-4.119182000	-0.289188000
H	-0.122448000	-3.955144000	-0.125931000
H	1.204031000	-3.852340000	-1.318087000
F	1.197120000	-5.477072000	-0.125523000
O	1.616452000	-1.956370000	0.571253000
H	1.850061000	-1.679156000	-0.338298000
N	8.076728000	-0.320918000	0.648114000
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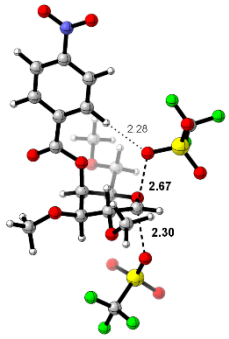
TS2 (NO_2)



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O	1.913697000	1.827396000	-1.004747000
C	1.132939000	0.933634000	-0.290370000
C	-0.059656000	1.607360000	0.358898000
O	-0.878562000	2.094042000	-0.659103000
C	-1.729150000	3.142400000	-0.244664000
C	-0.777514000	0.560083000	1.209610000
O	-1.201544000	-0.503005000	0.362691000
C	-2.496757000	-0.593740000	0.046867000
O	-3.346651000	0.164308000	0.434965000
C	0.131865000	-0.007168000	2.268273000
C	-0.381353000	-1.275069000	2.915170000
O	-1.631696000	-0.970395000	3.461176000
C	-2.266477000	-2.109500000	3.992444000
O	1.454281000	-0.360874000	1.748118000
C	1.926428000	0.150654000	0.700772000
H	3.272073000	0.478505000	-1.841812000
H	1.821461000	0.823930000	-2.820229000
H	3.092137000	2.061585000	-2.626906000
H	0.738700000	0.142775000	-0.953224000
H	0.280801000	2.414355000	1.018210000
H	-1.146773000	3.994316000	0.125527000
H	-2.300288000	3.451698000	-1.120089000
H	-2.428690000	2.821342000	0.534452000
H	-1.641283000	0.998878000	1.708952000
H	0.333906000	0.765763000	3.011896000
H	0.328112000	-1.599285000	3.687614000
H	-0.460091000	-2.071261000	2.164364000
H	-1.674166000	-2.554533000	4.801915000
H	-3.230406000	-1.790511000	4.389431000
H	-2.429973000	-2.868551000	3.216946000
C	-2.754413000	-1.764170000	-0.833381000
C	-1.723463000	-2.602344000	-1.251764000
C	-4.066994000	-2.006693000	-1.228342000
C	-2.004723000	-3.685519000	-2.064639000
H	-0.700811000	-2.412982000	-0.949614000
C	-4.358630000	-3.085390000	-2.040152000
H	-4.854972000	-1.344302000	-0.893370000
C	-3.317858000	-3.906429000	-2.442907000
H	-1.218309000	-4.347481000	-2.400478000
H	-5.370786000	-3.292310000	-2.358347000
O	1.538798000	-2.066014000	-0.729445000
S	2.679780000	-2.969028000	-0.740247000
O	2.782666000	-3.800360000	-1.914212000
O	3.910156000	-2.370020000	-0.272648000
C	2.262106000	-4.169677000	0.595081000
F	1.096994000	-4.776100000	0.350220000
F	2.162669000	-3.562560000	1.779416000
F	3.198946000	-5.113875000	0.699827000
H	2.938699000	-0.159567000	0.464413000
S	2.849152000	2.771349000	2.768570000
O	1.509022000	2.677718000	3.305097000
O	3.917070000	2.831890000	3.732552000
O	3.106286000	1.888268000	1.635811000
C	2.871573000	4.440986000	1.988302000
F	1.920074000	4.553168000	1.060858000
F	2.663799000	5.389161000	2.903631000
F	4.044859000	4.683229000	1.404197000
N	-3.621072000	-5.052728000	-3.302213000
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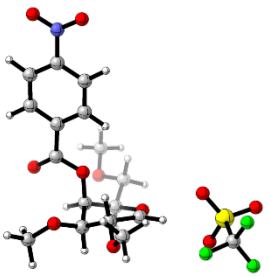
O	-4.776994000	-5.226578000	-3.629389000

TS3 (NO_2)



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O	-2.761243000	0.132177000	0.104014000
C	-1.490952000	0.682606000	0.247452000
C	-0.799749000	0.179773000	1.500750000
O	-0.448583000	-1.146715000	1.279780000
C	-0.262299000	-1.893606000	2.467103000
C	0.415169000	1.069047000	1.758800000
O	1.294286000	0.985067000	0.643764000
C	2.420659000	0.268855000	0.792569000
O	2.720883000	-0.306131000	1.803957000
C	0.010404000	2.507048000	1.953938000
C	1.144324000	3.503524000	1.827419000
O	2.121280000	3.096377000	2.737154000
C	3.339037000	3.785339000	2.558830000
O	-0.993206000	2.952201000	0.964389000
C	-1.637351000	2.157076000	0.250323000
H	-4.130504000	-0.539915000	-1.225041000

H	-3.065683000	0.730953000	-1.872656000
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H	-0.838763000	0.452461000	-0.614874000
H	-1.486329000	0.280015000	2.352705000
H	0.552114000	-1.492946000	3.078803000
H	-1.183713000	-1.915349000	3.059899000
H	-0.006243000	-2.907987000	2.162938000
H	0.935179000	0.749266000	2.662123000
H	-0.504554000	2.615435000	2.909844000
H	0.772322000	4.512011000	2.048623000
H	1.527073000	3.497026000	0.798626000
H	3.744124000	3.613460000	1.553919000
H	3.212743000	4.864061000	2.711207000
H	4.039764000	3.399148000	3.298838000
H	-2.380070000	2.635672000	-0.390565000
C	3.248442000	0.283022000	-0.439776000
C	4.422109000	-0.465666000	-0.436205000
C	2.883621000	1.016227000	-1.566254000
C	5.235057000	-0.487946000	-1.552560000
H	4.690452000	-1.029846000	0.447708000
C	3.691405000	1.004534000	-2.688331000
H	1.972280000	1.598439000	-1.570536000
C	4.852122000	0.251243000	-2.659090000
H	6.149607000	-1.064063000	-1.569914000
H	3.429492000	1.568765000	-3.572606000
S	-3.662261000	4.515124000	-1.697050000
O	-2.575992000	3.738911000	-2.268876000
O	-3.845644000	4.291874000	-0.275039000
O	-3.747319000	5.885844000	-2.133493000
C	-5.161490000	3.734157000	-2.432924000
F	-6.275189000	4.325318000	-1.997204000
F	-5.145982000	3.820735000	-3.764207000
F	-5.235830000	2.439480000	-2.109780000
N	5.712081000	0.238755000	-3.845489000
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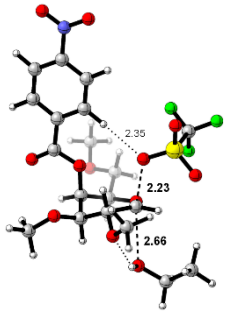
TS4a (NO_2)



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O	3.322163000	0.963370000	1.009149000
C	3.668918000	2.082630000	0.219468000
C	1.610157000	-0.172102000	-0.281845000
O	2.360439000	-1.380346000	-0.273742000
C	3.346902000	-1.526210000	-1.166635000
O	3.679407000	-0.679723000	-1.953470000
C	0.140801000	-0.513186000	-0.299225000
C	-0.222710000	-1.623254000	-1.263793000
O	0.238911000	-1.229643000	-2.522333000
C	0.189526000	-2.280397000	-3.459872000
O	-0.356149000	-0.964969000	0.997810000
C	0.318022000	-0.873445000	2.056493000
H	1.372967000	-0.960441000	4.742436000
H	3.078158000	-0.594235000	4.365450000
H	2.102595000	0.553891000	5.323552000
H	2.407595000	-1.012898000	2.221460000
H	1.340530000	1.540671000	0.970438000
H	4.733497000	2.258788000	0.372404000
H	3.492879000	1.904161000	-0.846376000
H	3.107855000	2.970659000	0.533324000
H	1.832343000	0.392649000	-1.186923000

H	-0.431004000	0.392321000	-0.509652000
H	-1.310234000	-1.772081000	-1.257536000
H	0.252489000	-2.557242000	-0.939377000
H	0.809304000	-3.126381000	-3.137032000
H	-0.838358000	-2.633187000	-3.610752000
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C	3.966277000	-2.873553000	-1.068237000
C	4.984863000	-3.189352000	-1.962904000
C	3.540856000	-3.804695000	-0.123379000
C	5.580208000	-4.435227000	-1.923698000
H	5.303120000	-2.452857000	-2.689628000
C	4.130324000	-5.054811000	-0.075183000
H	2.751579000	-3.556256000	0.574676000
C	5.137919000	-5.346289000	-0.978570000
H	6.371220000	-4.702332000	-2.610516000
H	3.813878000	-5.792494000	0.649359000
O	1.131165000	-2.946343000	2.162943000
S	0.483812000	-3.916353000	3.055103000
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H	-2.149038000	-0.446570000	4.035593000
H	-1.307098000	0.647510000	5.150791000
H	-3.066544000	0.725613000	4.991530000
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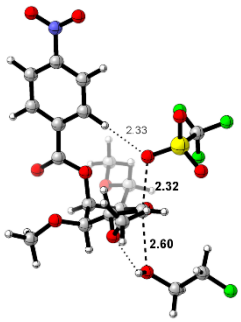
TS4b (NO_2)



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C	0.958233000	-0.751747000	1.734601000
C	1.529373000	0.265701000	0.766878000
O	2.826490000	0.552872000	1.186645000
C	3.323452000	1.784099000	0.701928000
C	1.493735000	-0.346082000	-0.631332000
O	2.249062000	-1.550571000	-0.619072000
C	3.462256000	-1.546963000	-1.186093000
O	3.949263000	-0.594891000	-1.736040000
C	0.079504000	-0.662325000	-1.046146000
C	-0.028196000	-1.586412000	-2.240927000
O	0.672162000	-0.974351000	-3.282924000
C	0.766099000	-1.805879000	-4.417014000
O	-0.687862000	-1.321889000	0.009942000
C	-0.302295000	-1.367822000	1.203908000
H	0.159107000	-1.892827000	4.035257000
H	1.888622000	-1.453628000	4.095506000
H	0.682512000	-0.478324000	4.978667000
H	1.681644000	-1.571961000	1.826093000
H	0.901478000	1.166640000	0.764149000
H	4.323745000	1.905413000	1.116988000
H	3.393431000	1.797735000	-0.390526000
H	2.692061000	2.616701000	1.033240000

H	1.909357000	0.343904000	-1.365766000
H	-0.454975000	0.272052000	-1.227318000
H	-1.086654000	-1.730713000	-2.494177000
H	0.401423000	-2.564732000	-1.990850000
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H	-0.226600000	-2.049217000	-4.815764000
H	1.331409000	-1.261443000	-5.173380000
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C	5.386788000	-3.026496000	-1.615721000
C	3.507887000	-3.930363000	-0.390178000
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H	2.525991000	-3.808442000	0.049502000
C	5.415723000	-5.275142000	-0.849601000
H	7.028453000	-4.378211000	-1.942694000
H	3.699838000	-5.980505000	0.227865000
O	0.525698000	-3.538163000	1.214259000
S	-0.379400000	-4.591060000	1.680871000
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O	-1.500184000	-4.089062000	2.441465000
C	-1.148961000	-5.179768000	0.112833000
F	-1.807560000	-4.191842000	-0.495505000
F	-2.013039000	-6.163743000	0.354611000
F	-0.225260000	-5.637577000	-0.732400000
H	-1.012145000	-1.812983000	1.893715000
C	-2.924305000	0.945564000	2.016071000
H	-3.411450000	1.046083000	1.044146000
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H	-3.320413000	-1.182023000	2.117010000
H	-2.943096000	-0.425055000	3.690901000
F	-4.802957000	-0.117989000	2.972731000
O	-1.535174000	0.844347000	1.772779000
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N	6.111159000	-6.559346000	-0.735162000
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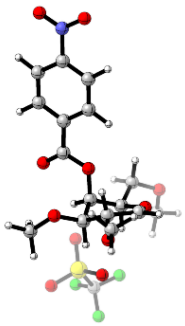
Ox (NO_2)



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O	0.792292000	-2.063318000	-0.219415000
C	0.159370000	-2.597911000	0.930199000
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O	1.853819000	0.565842000	-0.187137000
C	2.599069000	0.338842000	0.906999000
O	2.146120000	0.007632000	1.969312000
C	-0.286900000	1.478651000	-0.724285000
C	0.185098000	2.852372000	-0.305310000
O	-0.586412000	3.890125000	-0.827094000
C	-1.855668000	4.027782000	-0.219671000
O	-0.176098000	1.439824000	-2.216563000
C	0.153602000	0.412653000	-2.834018000
H	1.665910000	-2.923522000	-3.471742000
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H	1.139850000	-1.734432000	-4.696757000
H	1.628957000	-0.927729000	-2.276904000
H	-0.976791000	-1.121295000	-0.722870000
H	0.087775000	-1.861887000	1.736441000
H	-0.843159000	-2.964096000	0.684964000
H	0.776051000	-3.430459000	1.267476000
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H	-1.357591000	1.342966000	-0.557941000
H	1.210300000	3.011140000	-0.645424000
H	0.185537000	2.856078000	0.793905000
H	-1.765775000	4.084448000	0.871233000
H	-2.285407000	4.958230000	-0.591641000
H	-2.530013000	3.205857000	-0.481311000
H	0.128507000	0.507082000	-3.920872000
C	4.043629000	0.563887000	0.646539000
C	4.511416000	1.001102000	-0.590220000
C	4.931801000	0.328802000	1.692393000
C	5.865145000	1.205033000	-0.783532000
H	3.821321000	1.186371000	-1.401985000
C	6.286638000	0.527317000	1.510672000
H	4.551389000	-0.010317000	2.647262000
C	6.726852000	0.963560000	0.272439000
H	6.250184000	1.546171000	-1.734400000
H	6.992684000	0.350094000	2.309949000
S	-3.071696000	0.063798000	1.407231000
O	-3.356919000	-1.196074000	2.050033000
O	-1.960077000	0.810965000	1.960999000
O	-3.106484000	0.041411000	-0.044519000
C	-4.531735000	1.103752000	1.839128000
F	-4.428823000	2.325511000	1.309974000
F	-5.661595000	0.558321000	1.384753000
F	-4.647046000	1.241778000	3.161079000
N	8.162217000	1.178983000	0.072178000
O	8.902779000	0.964491000	1.008361000
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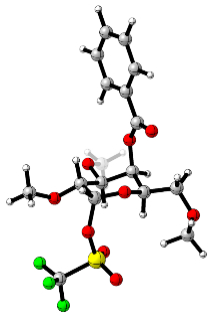
Stereoretentive Dioxolenium Pathway

TS2 (Dx)



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C	0.503388000	-2.273658000	2.693658000
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O	1.630204000	0.035919000	0.673188000
C	2.332803000	0.720041000	-0.227050000
O	2.062115000	1.815151000	-0.647666000
C	-0.474068000	1.509128000	0.753809000
C	0.085521000	2.904737000	1.016331000
O	-0.842623000	3.752762000	1.647706000
C	-1.820480000	4.258166000	0.769708000
O	-0.821131000	1.392657000	-0.633064000
C	-1.431353000	0.262415000	-1.039299000
H	-1.025645000	-2.847915000	-2.280918000
H	-2.609322000	-3.487482000	-1.778982000
H	-2.502050000	-1.874493000	-2.512635000
H	-0.023002000	-1.279797000	-1.008164000
H	-1.374568000	-0.853362000	1.672515000
H	1.271555000	-1.569237000	3.033766000
H	-0.392355000	-2.146239000	3.314545000
H	0.882936000	-3.287623000	2.824203000
H	0.516608000	0.480843000	2.299949000
H	-1.390089000	1.440044000	1.355493000
H	0.432530000	3.337899000	0.076071000
H	0.937102000	2.829739000	1.694279000
H	-1.357823000	4.772246000	-0.083012000

H	-2.483430000	3.474550000	0.385686000
H	-2.424498000	4.972850000	1.330804000
H	-1.352592000	0.219692000	-2.123576000
C	3.529229000	-0.054428000	-0.651296000
C	4.457582000	0.574020000	-1.477262000
C	3.730999000	-1.376462000	-0.259123000
C	5.582489000	-0.111256000	-1.904345000
H	4.286408000	1.601263000	-1.775973000
C	4.855835000	-2.060165000	-0.692287000
H	3.002189000	-1.864927000	0.375448000
C	5.782261000	-1.429135000	-1.512352000
H	6.305190000	0.381308000	-2.544607000
H	5.010252000	-3.089508000	-0.389597000
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O	-4.559015000	1.803492000	0.165186000
O	-2.943371000	0.397114000	-0.964104000
O	-3.456923000	-0.006737000	1.429205000
C	-5.233725000	-0.651274000	-0.428213000
F	-4.801136000	-1.896817000	-0.422206000
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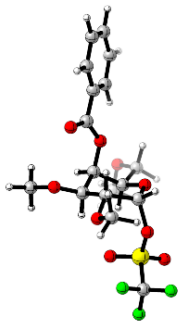
F	-5.593490000	-0.317651000	-1.657541000

TS2′ (Dx)



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C	-0.727428000	-0.759589000	1.113447000
O	-0.223400000	-1.641526000	2.066918000
C	0.106514000	-1.033524000	3.288648000
C	0.165928000	0.407699000	0.683689000
O	1.395358000	0.195752000	-0.023488000
C	2.300510000	-0.775664000	0.128029000
O	2.099303000	-1.857956000	0.610731000
C	-0.671414000	1.253880000	-0.256630000
C	0.028827000	2.495067000	-0.785906000
O	0.504692000	3.321276000	0.239111000
C	-0.509621000	4.037867000	0.908516000
O	-1.011790000	0.498939000	-1.425487000
C	-1.647550000	-0.681319000	-1.261872000
H	-1.402759000	-4.045378000	-0.827646000
H	-3.018074000	-4.250665000	-0.106720000
H	-2.814254000	-3.212049000	-1.531098000
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H	-0.717435000	-0.412765000	3.666491000
H	0.298177000	-1.835452000	4.002648000
H	0.411901000	1.007588000	1.563206000
H	-1.580163000	1.547886000	0.274053000
H	-0.674444000	3.034455000	-1.434178000
H	0.888386000	2.193863000	-1.386024000
H	-1.140067000	4.585936000	0.196869000
H	-1.150732000	3.386887000	1.514455000
H	-0.017562000	4.751532000	1.570396000
H	-1.571424000	-1.225605000	-2.200735000
C	3.616391000	-0.353611000	-0.424447000
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C	3.913216000	0.981797000	-0.687917000
C	5.833503000	-0.981747000	-1.118939000
H	4.342095000	-2.367052000	-0.423458000
C	5.168843000	1.331348000	-1.159261000
H	3.166136000	1.744672000	-0.510550000
C	6.127923000	0.351367000	-1.377848000
H	6.582070000	-1.746915000	-1.289403000
H	5.400254000	2.372136000	-1.354700000
H	7.108788000	0.627029000	-1.748795000
S	-4.060892000	0.430252000	-0.432312000
O	-4.383772000	1.594534000	-1.188630000
O	-3.148603000	-0.509089000	-1.238105000
O	-3.680828000	0.562084000	0.937733000
C	-5.556734000	-0.651788000	-0.457853000
F	-5.313203000	-1.792296000	0.159642000
F	-6.528139000	-0.009586000	0.175301000
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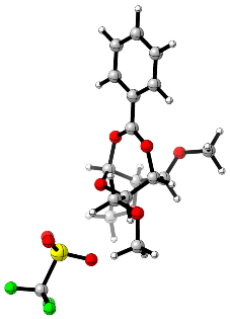
Dx



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C	0.466771000	1.881791000	0.495388000
O	0.365036000	0.816683000	-0.403596000
C	0.035282000	-0.417236000	0.206564000
C	1.682403000	1.756210000	1.423219000
O	2.782412000	1.111735000	0.704038000
C	3.087741000	1.429067000	-0.501248000
O	2.728978000	2.506048000	-1.082809000
C	2.128205000	3.102884000	1.926867000
C	3.279199000	3.041460000	2.917352000
O	2.923819000	2.338204000	4.076916000
C	2.206058000	3.114778000	5.014051000
O	2.592152000	3.887016000	0.819607000
C	2.005991000	3.629900000	-0.365612000
H	-1.133669000	5.928137000	0.189815000
H	0.598617000	5.960327000	-0.171699000
H	-0.555069000	5.264046000	-1.358159000
H	0.202478000	3.000066000	-1.328658000
H	-0.416241000	1.947127000	1.143184000
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H	-0.879103000	-0.323098000	0.802879000
H	-0.129755000	-1.132632000	-0.598248000
H	1.497187000	1.079007000	2.253931000
H	1.269025000	3.608338000	2.375838000
H	3.587485000	4.069006000	3.141666000
H	4.126339000	2.518575000	2.465060000
H	2.763494000	4.019372000	5.283852000
H	1.219410000	3.410504000	4.641354000
H	2.072997000	2.498486000	5.904088000
H	2.196198000	4.456085000	-1.045673000
C	3.930670000	0.508404000	-1.234456000
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C	5.236987000	-0.006494000	-3.180026000
H	4.220074000	1.857729000	-2.889742000
C	5.012817000	-1.626632000	-1.402894000
H	3.814371000	-1.029954000	0.270378000
C	5.520948000	-1.256748000	-2.642716000
H	5.639091000	0.275523000	-4.145351000
H	5.237234000	-2.603154000	-0.991583000
H	6.144979000	-1.949594000	-3.195655000
S	2.224798000	6.941464000	2.522782000
O	3.545367000	6.573268000	2.987431000
O	2.158691000	7.399911000	1.151799000
O	1.156763000	6.055746000	2.933694000
C	1.867438000	8.475746000	3.482531000
F	0.657973000	8.962878000	3.186744000

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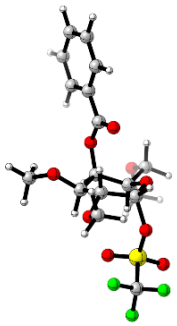
Dx'



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C	0.305400000	-2.195454000	2.446723000
C	-0.022650000	0.280541000	0.784618000
O	1.381397000	0.154047000	0.537042000
C	1.892782000	-0.336228000	-0.591288000
O	1.248975000	-0.642523000	-1.563826000
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C	0.101713000	2.632392000	-0.177389000
O	0.511864000	3.180783000	1.043440000
C	-0.504475000	3.888861000	1.717937000
O	-1.108412000	0.982517000	-1.317207000
C	-1.838690000	-0.139311000	-1.463744000
H	-1.938231000	-3.541932000	-1.947388000
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H	-0.641854000	-1.835916000	-1.235559000
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H	-1.627819000	1.612516000	0.573799000
H	-0.490305000	3.351960000	-0.757310000
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H	-0.928516000	4.673575000	1.078762000
H	-1.317717000	3.236003000	2.056296000
H	-0.047104000	4.352424000	2.592797000
H	-1.840475000	-0.391601000	-2.521431000
C	3.371593000	-0.445571000	-0.516954000
C	4.046682000	-0.921269000	-1.638559000
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C	5.425690000	-1.041699000	-1.620672000
H	3.476923000	-1.193585000	-2.518692000
C	5.468304000	-0.212135000	0.638589000
H	3.564264000	0.279488000	1.495923000
C	6.137813000	-0.686442000	-0.481836000
H	5.947600000	-1.412090000	-2.495449000
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S	-4.146712000	0.668685000	-0.133288000
O	-4.504608000	2.035330000	-0.325379000
O	-3.321782000	0.161934000	-1.326070000
O	-3.642318000	0.243572000	1.131702000
C	-5.682473000	-0.304977000	-0.463505000
F	-5.460937000	-1.600704000	-0.352180000
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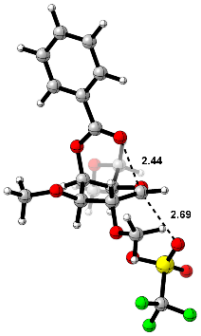
TS3 (Dx)



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O	0.186364000	-2.088710000	1.351312000
C	0.415531000	-2.056545000	2.745297000
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C	2.046406000	-0.184138000	-0.527593000
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C	0.211172000	2.709119000	0.027926000
O	0.593401000	3.243221000	1.259828000
C	-0.452614000	3.904559000	1.943841000
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C	-1.099038000	-0.191499000	-1.447829000
H	-1.775807000	-3.588869000	-1.661871000
H	-3.496746000	-3.364514000	-1.252944000
H	-2.736117000	-2.305806000	-2.455137000
H	-0.282507000	-2.048176000	-0.983983000
H	-1.463485000	-0.855682000	1.473636000
H	1.102739000	-1.252339000	3.029746000
H	-0.524930000	-1.935673000	3.295395000
H	0.867172000	-3.011614000	3.012441000
H	0.210582000	0.644425000	1.991100000
H	-1.497271000	1.566296000	0.730131000
H	-0.424484000	3.402987000	-0.535762000
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H	-1.247558000	3.217534000	2.255241000
H	-0.014567000	4.355861000	2.834236000
H	-1.354794000	-0.350520000	-2.491023000
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C	4.299798000	-0.094589000	0.571725000
C	5.485735000	-0.869973000	-1.823467000
H	3.489834000	-0.897305000	-2.622006000
C	5.674004000	-0.248147000	0.496296000
H	3.835058000	0.206445000	1.501540000
C	6.266854000	-0.635208000	-0.698636000
H	5.949755000	-1.171537000	-2.755180000
H	6.285035000	-0.065974000	1.372536000
H	7.343063000	-0.754510000	-0.753705000
S	-4.360014000	0.982655000	-0.942426000
O	-4.989863000	2.224712000	-1.321751000
O	-3.686645000	0.280228000	-2.019814000
O	-3.625782000	1.016011000	0.306657000
C	-5.792314000	-0.113396000	-0.559605000
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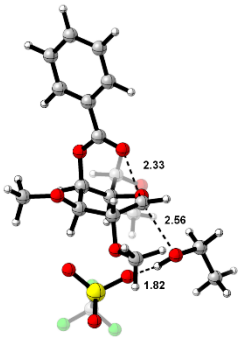
TS4a (Dx)



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C	-0.489635000	-1.655282000	-0.845683000
C	-0.744237000	-0.282022000	-1.449204000
O	-1.671910000	-0.446430000	-2.480944000
C	-1.738714000	0.653065000	-3.367049000
O	-2.581731000	0.843730000	-0.198755000
C	-3.286768000	-0.237981000	0.109109000
O	-2.798003000	-1.310780000	0.409622000
C	-0.326980000	0.696558000	0.812165000
C	-0.739169000	1.646312000	1.916107000
O	0.097762000	1.595021000	3.032294000
C	1.373462000	2.166295000	2.821632000
O	-0.375953000	-0.644768000	1.398633000
C	-0.511713000	-1.653792000	0.663948000
H	0.048463000	-3.916882000	-2.099646000
H	1.804753000	-3.768239000	-1.819550000
H	0.716005000	-4.029581000	-0.443479000
H	-1.299948000	-2.327234000	-1.145632000
H	0.220617000	0.070844000	-1.835834000
H	-2.168174000	1.540198000	-2.888698000
H	-0.745880000	0.902913000	-3.758231000
H	-2.385347000	0.354686000	-4.191983000
H	0.714549000	0.850776000	0.519653000
H	-1.743591000	1.393187000	2.262914000
H	-0.770083000	2.654657000	1.480136000
H	1.286160000	3.185729000	2.425613000
H	1.868798000	2.203402000	3.792286000
H	1.986993000	1.569019000	2.139768000
C	-4.741900000	0.001806000	0.071825000
C	-5.274148000	1.211272000	-0.372398000
C	-5.588780000	-1.023868000	0.487761000
C	-6.647186000	1.388918000	-0.397714000
H	-4.615577000	2.005463000	-0.699058000
C	-6.959833000	-0.839793000	0.462071000
H	-5.161774000	-1.958780000	0.829130000
C	-7.489274000	0.366154000	0.019352000
H	-7.062382000	2.327763000	-0.744803000
H	-7.618206000	-1.636716000	0.787238000
H	-8.563793000	0.509237000	-0.001255000
H	-0.632657000	-2.586810000	1.202224000
C	2.025014000	-2.267101000	2.687187000
H	1.417840000	-3.027214000	3.186659000
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C	3.475263000	-2.404911000	3.090211000
H	3.580318000	-2.278725000	4.171528000
H	3.862712000	-3.390279000	2.819311000
H	4.088560000	-1.644928000	2.599013000
O	1.832589000	-2.454934000	1.295013000
H	2.282483000	-1.720539000	0.837906000
C	-1.168960000	0.786516000	-0.434901000
H	-0.958378000	1.766655000	-0.864268000
S	3.280220000	0.531415000	-0.845004000
O	2.924122000	-0.064327000	0.436894000
O	4.047375000	-0.315773000	-1.721104000
O	2.206554000	1.282907000	-1.458650000
C	4.475592000	1.842798000	-0.345885000
F	4.917845000	2.508505000	-1.413251000
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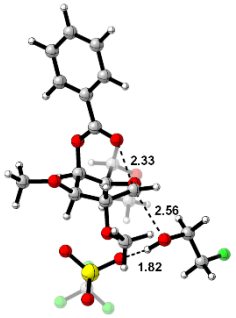
F	5.530324000	1.318347000	0.278719000

TS4b (Dx)



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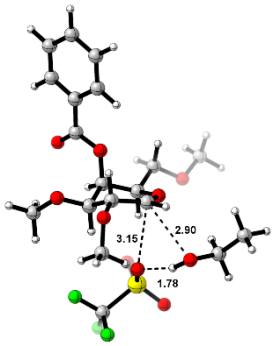
O	0.742260000	-2.131000000	-1.312679000
C	-0.489635000	-1.655282000	-0.845683000
C	-0.744237000	-0.282022000	-1.449204000
O	-1.671910000	-0.446430000	-2.480944000
C	-1.738714000	0.653065000	-3.367049000
O	-2.581731000	0.843730000	-0.198755000
C	-3.286768000	-0.237981000	0.109109000
O	-2.798003000	-1.310780000	0.409622000
C	-0.326980000	0.696558000	0.812165000
C	-0.739169000	1.646312000	1.916107000
O	0.097762000	1.595021000	3.032294000
C	1.373462000	2.166295000	2.821632000
O	-0.375953000	-0.644768000	1.398633000
C	-0.511713000	-1.653792000	0.663948000
H	0.048463000	-3.916882000	-2.099646000
H	1.804753000	-3.768239000	-1.819550000
H	0.716005000	-4.029581000	-0.443479000
H	-1.299948000	-2.327234000	-1.145632000
H	0.220617000	0.070844000	-1.835834000
H	-2.168174000	1.540198000	-2.888698000
H	-0.745880000	0.902913000	-3.758231000
H	-2.385347000	0.354686000	-4.191983000
H	0.714549000	0.850776000	0.519653000
H	-1.743591000	1.393187000	2.262914000
H	-0.770083000	2.654657000	1.480136000
H	1.286160000	3.185729000	2.425613000
H	1.868798000	2.203402000	3.792286000
H	1.986993000	1.569019000	2.139768000
C	-4.741900000	0.001806000	0.071825000
C	-5.274148000	1.211272000	-0.372398000
C	-5.588780000	-1.023868000	0.487761000
C	-6.647186000	1.388918000	-0.397714000
H	-4.615577000	2.005463000	-0.699058000
C	-6.959833000	-0.839793000	0.462071000
H	-5.161774000	-1.958780000	0.829130000
C	-7.489274000	0.366154000	0.019352000
H	-7.062382000	2.327763000	-0.744803000
H	-7.618206000	-1.636716000	0.787238000
H	-8.563793000	0.509237000	-0.001255000
H	-0.632657000	-2.586810000	1.202224000
C	2.025014000	-2.267101000	2.687187000
H	1.417840000	-3.027214000	3.186659000
H	1.641059000	-1.286347000	2.996754000
C	3.475263000	-2.404911000	3.090211000
H	3.862712000	-3.390279000	2.819311000
H	4.088560000	-1.644928000	2.599013000
O	1.832589000	-2.454934000	1.295013000
H	2.282483000	-1.720539000	0.837906000
C	-1.168960000	0.786516000	-0.434901000
H	-0.958378000	1.766655000	-0.864268000
S	3.280220000	0.531415000	-0.845004000
O	2.924122000	-0.064327000	0.436894000
O	4.047375000	-0.315773000	-1.721104000
O	2.206554000	1.282907000	-1.458650000
C	4.475592000	1.842798000	-0.345885000
F	4.917845000	2.508505000	-1.413251000
F	3.907905000	2.724493000	0.480083000
F	5.530324000	1.318347000	0.278719000
F	3.607817000	-2.245695000	4.454572000

Stereoretentive SN2F Pathway

TS1a(SN2F)



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C	0.544448000	0.232559000	1.886242000
C	0.467205000	1.123469000	0.650847000
O	1.217564000	2.264125000	0.911565000
C	0.870799000	3.368048000	0.096263000
C	1.029901000	0.316920000	-0.522423000
O	2.382963000	-0.018308000	-0.241081000
C	3.349717000	0.680004000	-0.871049000
O	3.120891000	1.511475000	-1.710572000
C	0.249363000	-0.946820000	-0.757674000
C	0.928698000	-1.944825000	-1.651274000
O	0.002531000	-2.931139000	-1.997470000
C	0.585168000	-3.954971000	-2.769858000
O	-0.047981000	-1.669085000	0.510235000
C	-0.009502000	-1.116520000	1.626266000
H	-1.933311000	0.508434000	2.869019000
H	-1.365583000	1.607500000	4.144885000
H	-1.309885000	2.125894000	2.447047000
H	1.617400000	-0.012536000	2.024987000
H	-0.576809000	1.367411000	0.422462000
H	1.068380000	3.172031000	-0.962177000
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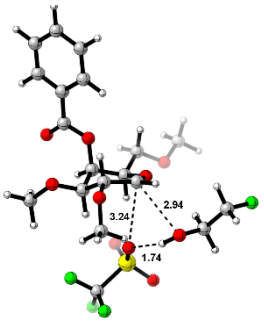
TS1b(SN2F)



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H	-2.894798000	-1.208579000	1.493803000
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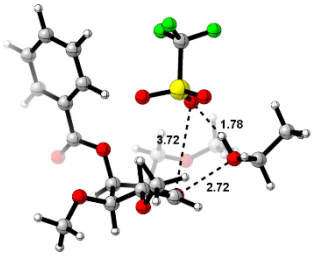
TS4a(SN2F)



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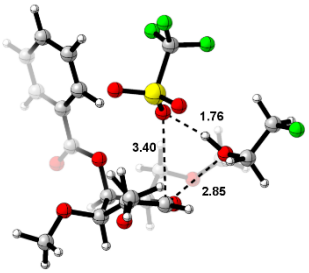
TS4b(SN2F)



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H	-4.177917000	-0.333112000	1.639454000
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