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General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon/nitrogen atmosphere. The solvent (DCM, toluene, DCE, CH₃CN) used in the glycosylation reactions was distilled over CaH₂ and stored on activated 4Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of (NH₄)₆Mo₇O₂₄·4H₂O (25 g/L) and (NH₄)₄Ce(SO₄)₄·2H₂O (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Flash column chromatography was performed on silica gel (300-400 mesh). ¹H and ¹³C spectra were recorded on a Bruker AV 400, Bruker AV 600 in CDCl₃, CD₃OD, CD₃COCD₃ or CD₃SOCD₃. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (¹H NMR in CDCl₃) or the residual signal of the deuterated solvent. Coupling constants (J) are given in Hz. All ¹³C spectra are proton decoupled. Where applicable COSY, HSQC, NOESY, HMBC experiments were used to further elucidate the structure. The anomeric product ratios were analyzed through integration of proton NMR signals or separation.

General procedure for optimization of the hydrogen bond mediated glycosylation

The corresponding donor (1a, 1b or 1c, 1.0 equiv, 0.1 mmol/0.05 mmol), acceptor 2a (2.0 equiv) and organocatalyst C1-C10 (0.1 equiv) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry solvents (83.3 mM for donor) was added to the sealed tube under N₂ atmosphere at room temperature. The reaction mixture was stirred for 16-36 h in the sealed tube under the corresponding condition and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the product.

General procedure A: Glycosyl N-phenyl trifluoroacetimidate donor (1.0-2.0 eq) co-evaporated twice with toluene, acceptor (1.0-1.5 equiv) co-evaporated twice with toluene and Kass catalyst C10 (0.1 equiv-0.2 equiv) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry solvents (83.3 mM for donors) was added to the sealed tube under N₂ atmosphere at room temperature. The reaction mixture was stirred for several hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the product.

General procedure B: Glycosyl N-phenyl trifluoroacetimidate donor (2.0-2.5 equiv) co-evaporated twice with toluene, acceptor (1.0 equiv) co-evaporated twice with toluene, Kass catalyst (0.3 equiv) and activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (5-83.3 mM for acceptors) was added to the sealed tube under N₂ atmosphere at room temperature. The reaction mixture was stirred for several hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the product.
chromatography to deliver the product.

**General procedure C (stereoselective glycosylation with DMF additive):**
Glycosyl N-phenyl trifluoroacetimidate donor (1.5 eq), acceptor (1.0 equiv), Kass catalyst (0.2 equiv) and activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. The dry toluene (0.2 M for acceptors) and super-dry DMF (3.0 equiv) were added to the sealed tube under N₂ atmosphere at room temperature. The reaction mixture was stirred for 24 hours in the sealed tube under the corresponding conditions and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified size exclusion to deliver the product.

**General procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor:**
To a solution of the hemiacetal (1.0 equiv) in acetone (0.16 M hemiacetal in acetone) was added Cs₂CO₃ (1.5 equiv) followed by PTFACl (1.6 equiv). The mixture was stirred for several hours at 0 °C or rt, then the suspension was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate with Et₃N) to give the corresponding N-phenyl trifluoroacetimidates donor.
The structure of catalysts

The catalysts $\text{C1}$, $\text{C2}$, $\text{C3}$ were commercially available.

The catalysts $\text{C4}^{[1]}$, $\text{C5}^{[2]}$, $\text{C6}^{[3]}$, $\text{C7}^{[3]}$, $\text{C8}^{[4]}$, $\text{C9}^{[5]}$, $\text{C10}^{[6]}$ have been reported previously.
The structure of donors

The donors 1a\cite{7}, 1c\cite{8}, 1d\cite{9}, 1f\cite{10}, 1g\cite{11}, 1i\cite{12}, 4a\cite{13}, 4e\cite{14}, 8a\cite{15}, 8b\cite{16}, 8c\cite{17} are known compounds.

Pico: Picoloyl, TMBz: 2,4,6-trimethylbenzoyl
The structure of acceptors
The acceptors 2a, 2b, 2c, 2e, 2f, 2g, 2h, 2l, 2m, 2p, 2q, 2r, 2t, 2u, 6a, 6b, 6c, 6d, 6e, 6f, 6h were commercially available. The acceptors 2d[^18], 2j[^19], 2k[^20], 2l[^21], 2n[^22], 2o[^23], 2s[^24], 6g[^25], 6i[^26] and 6k[^27] have been reported previously.
Synthesis of 2,3,4,6-tetra-O-benzyl-D-glucopyranosyl N-Aryl-2,2,2-trifluoroacetimidate donor (1b)

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal S1 (270 mg, 0.5 mmol) can be converted into the donor 1b after 9 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6:1, with Et3N (TEA)) to yield 1b (299 mg, 0.395 mmol, 79%) as white solid. 1H NMR (400 MHz, Acetone-d6) δ 8.22 – 8.14 (m, 2H), 7.45 – 7.23 (m, 20H), 6.96 (d, J = 8.9 Hz, 1H), 6.47 (brs, 1H), 4.99 (t, J = 8.3 Hz, 1H), 4.93 – 4.84 (m, 4H), 4.66 (d, J = 11.0 Hz, 1H), 4.62 – 4.57 (m, 1H), 4.56 – 4.52 (m, 1H), 4.02 – 3.92 (m, 2H), 3.87 – 3.70 (m, 4H). 13C NMR (100 MHz, Acetone-d6) δ 150.0, 144.3, 139.0, 138.6, 138.5, 138.4, 128.3, 128.23, 128.21, 128.1, 127.9, 127.77, 127.76, 127.70, 127.65, 127.6, 127.5, 127.43, 127.36, 124.6, 120.0, 95.0, 81.4, 79.3, 76.8, 75.2, 74.8, 73.6, 73.0, 72.9, 68.5. HRMS (ESI) Calculated for C34H35O5 [M-[OC(CF3)=NPh]+ 523.2479, found 523.2464.

Synthesis of 2,3,4-tri-O-benzyl-D-Xylopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (1h)

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal S2 (211 mg, 0.5 mmol) can be converted into the donor 1h after 9 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/diethyl ether = 9:1, with TEA) to yield 1h (237 mg, 0.4 mmol, 80%) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.44 – 7.18 (m), 7.09 (dd, J = 13.1, 7.2 Hz), 6.80 (t, J = 8.8 Hz), 6.74 (d, J = 7.5 Hz), 6.38 (s, 1H, H-1α), 5.73 (s, 1, H-1β), 4.95–4.59 (m), 4.01 – 3.87 (m), 3.85 – 3.55 (m). 13C NMR (100 MHz, CDCl3) δ 143.7, 143.5, 138.7, 138.4, 138.0, 137.9, 137.8, 128.9, 128.6, 128.5, 128.44, 128.43, 128.15, 128.04, 128.02, 128.00, 127.9, 127.77, 127.72, 127.66, 120.5, 119.4, 83.1, 81.0, 80.1, 79.0, 77.3, 77.2, 75.9, 75.5, 75.2, 73.8, 73.5, 73.3, 64.4, 62.5. HRMS (ESI) Calculated for C26H27O4 [M-[OC(CF3)=NPh]+ 403.1904, found 403.1890.

Synthesis of 2,3,4,6-tetra-O-methyl-D-glucopyranosyl N-phenyl-2,2,2-trifluoroacetimidate donor (1j)

As the general procedure for preparation of glycosyl trifluoroacetimidate (PTFAI) donor, the corresponding hemiacetal S3 (750 mg, 3.17 mmol) can be converted into the donor 1j after 4 hours at 0 °C, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate
= 40:1, with TEA) to yield 1j (705 mg, 1.73 mmol, 55%) as a colorless oil. 1j-α: 1H NMR (400 MHz, Acetone-d6) δ 7.34 – 7.27 (t, J = 8.2 Hz, 2H), 7.20 – 7.04 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.5 Hz, 2H), 6.42 (brs, 1H), 3.74 – 3.66 (m, 1H), 3.65 – 3.48 (m, 1H), 3.42 (t, J = 9.2 Hz, 1H), 3.34 (brs, 4H), 3.19 (t, J = 9.5 Hz, 1H). 13C NMR (100 MHz, Acetone-d6) δ 145.1, 130.2, 125.7, 120.6, 98.8, 87.5, 84.3, 80.3, 77.0, 72.3, 61.2, 61.0, 60.8, 59.7. 1j-β: 1H NMR (400 MHz, 50 oC, Acetone-d6) δ 7.32 (t, J = 7.3 Hz, 2H), 7.13 (t, J = 7.8 Hz, 1H), 6.95 – 6.78 (d, J = 7.8 Hz, 2H), 5.41 (brs, 1H), 3.62 – 3.49 (m, 8H), 3.47 (s, 3H), 3.34 (s, 3H), 3.23 – 3.09 (m, 4H). 13C NMR (100 MHz, Acetone-d6) δ 144.0, 128.8, 124.2, 119.3, 93.5, 83.2, 81.0, 78.5, 73.3, 70.8, 60.1, 59.8, 58.4, 58.3. HRMS (ESI) Calculated for C18H24F3NO6Na [M+Na]+ 446.1193, found 446.1184.

3,4,6-Tri-O-benzyl-2-O-mesitoyl-D-glucopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4b)

Mesitoyl chloride (1.02 ml, 6 mmol), DMAP (62 mg, 0.5 mmol), and compound S4 [30] (557 mg, 1 mmol) were added to pyridine (5 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H2O and extracted into CH2Cl2. The organic phase was washed with aqueous HCl (1 M), saturated aqueous NaHCO3, and brine and dried over anhydrous Na2SO4. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 12:1) to afford the compound S5 (562 mg, 0.8 mmol, 80%) as a white solid. [α]D25 = 0.7 (c 0.5, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.39 – 7.19 (m, 15H), 7.13 (dd, J = 6.8, 2.6 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.83 (s, 2H), 6.02 (d, J = 5.5 Hz, 1H), 5.27 (dd, J = 10.3, 5.5 Hz, 1H), 4.85 – 4.73 (m, 3H), 4.63 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.47 (d, J = 11.9 Hz, 2H), 4.03 – 3.95 (m, 1H), 3.86 – 3.78 (m, 2H), 3.70 (dd, J = 10.8, 1.7 Hz, 1H), 2.31 (s, 3H), 2.28 (d, J = 3.4 Hz, 9H). 13C NMR (100 MHz, CDCl3) δ 169.8, 139.4, 138.2, 138.1, 138.0, 137.7, 135.1, 132.3, 130.7, 129.9, 128.5, 128.3, 128.0, 127.89, 127.86, 127.7, 127.6, 127.4, 86.3, 80.2, 78.4, 75.4, 75.2, 74.3, 73.5, 71.4, 68.6, 21.20, 21.16, 19.9. HRMS (ESI) Calculated for C46H44F6NO13S Na+ [M+Na]+ 725.2907, found 725.2917.

To a solution of compound S5 (562 mg, 0.8 mmol) in DCM (8 mL), TfOH (18 μl, 0.2 mmol) and NIS (221 mg, 0.96 mmol) were added to the mixture at 0 °C and stirred for 3 hours. The reaction mixture was quenched with Et3N and saturated aqueous Na2S2O3, and the organic phase was washed with saturated aqueous NaHCO3, brine successively. The organic phases was separated and combined, and was then dried over anhydrous Na2SO4. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver hemiacetal S6 as a syrup.
As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S6 can be converted into the donor 4b after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1, with TEA) to yield 4b (504 mg, 0.66 mmol, 82% for 2 steps) as a syrup. $^1$H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.20 (m), 7.17 – 7.01 (m), 6.84 (s), 6.77 (d, $J =$ 7.8 Hz), 5.81 (brs), 5.57 (brs), 4.87 (d, $J =$ 11.5 Hz), 4.73 (d, $J =$ 11.3 Hz), 4.66 (d, $J =$ 12.2 Hz), 4.57 (d, $J =$ 11.5 Hz), 3.93 (t, $J =$ 9.3 Hz), 3.85 – 3.65 (m), 2.28 (s), 2.23 (s). $^{13}$C NMR (100 MHz, Chloroform-d) δ 143.4, 139.9, 138.0, 137.6, 130.1, 128.9, 128.8, 128.7, 128.63, 128.56, 128.55, 128.4, 128.2, 128.1, 128.04, 127.98, 127.93, 127.87, 127.6, 127.5, 127.2, 124.6, 119.4, 95.0, 82.2, 76.0, 75.0, 74.2, 73.6, 71.9, 68.2, 21.3, 20.0. HRMS (ESI) Calculated for C$_{37}$H$_{39}$O$_6$ [M-[OC(CF$_3$)=NPh]]$^+$ 579.2741, found 579.2725.

3,4,6-Tri-O-benzyl-2-O-mesitoxy-2-galactopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4c)

Mesitoyl chloride (1.016 ml, 6 mmol), DMAP (62 mg, 0.5 mmol), and compound S7$^{[3]}$ (543 mg, 1 mmol) were added to pyridine (5 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H$_2$O and extracted into CH$_2$Cl$_2$. The organic phase was washed with aq HCl (1 M), saturated aqueous NaHCO$_3$, and brine and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 12:1) to afford the compound S8 (544 mg, 0.79 mmol, 79%) as a white solid. [α]$_{D}^{25}$ = 6.0 (c 0.7, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.47 (m, 2H), 7.40 – 7.16 (m, 18H), 6.80 (s, 2H), 5.74 (t, $J =$ 9.7 Hz, 1H), 4.92 (d, $J =$ 11.5 Hz, 1H), 4.85 – 4.66 (m, 2H), 4.61 – 4.34 (m, 4H), 4.07 (d, $J =$ 2.6 Hz, 1H), 3.78 – 3.57 (m, 4H), 2.30 (s, 6H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 168.7, 139.4, 138.6, 138.0, 133.8, 131.8, 130.8, 128.9, 128.6, 128.5, 128.4, 128.3, 128.03, 127.97, 127.9, 127.65, 127.63, 127.5, 127.1, 86.6, 82.2, 74.5, 73.7, 72.2, 71.4, 69.9, 68.9, 21.2, 20.3. HRMS (ESI) Calculated for C$_{43}$H$_{44}$NaO$_6$S [M+Na]$^+$ 711.2751, found 711.2756.

To a solution of compound S8 (544 mg, 0.79 mmol) in DCM (8 mL), TfOH (18 μl, 0.2 mmol) and NIS (221 mg, 0.96 mmol) were added to the mixture at 0 °C and stirred for 3 hours. The reaction mixture was quenched with Et$_3$N and saturated aqueous Na$_2$S$_2$O$_3$, and the organic phase was washed with saturated aqueous NaHCO$_3$, brine successively. The organic phases was separated and combined, and then dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation yielded the crude product which was further purified by silica gel column.
chromatography (petroleum ether/ethyl acetate = 5/1) to deliver hemiacetal S9 as a colorless syrup.

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S9 can be converted into the donor 4c after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 20/1, with TEA) to yield 4c (510 mg, 0.664 mmol, 84% for 2 steps) as a syrup. 

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.38 – 7.18 (m), 7.08 (t, J = 7.5 Hz), 6.83 (s), 6.74 (d, J = 7.8 Hz), 5.92 (t, J = 8.9 Hz), 5.80 (s), 4.95 (d, J = 11.5 Hz), 4.74 (d, J = 11.9 Hz), 4.64 – 4.31 (m), 4.06 (d, J = 2.7 Hz), 3.75 – 3.49 (m), 2.27 (s), 2.21 (s).

\[ ^{13}C \text{NMR (100 MHz, Chloroform-}d\text{)} \delta 168.2, 143.5, 139.6, 138.3, 137.8, 137.4, 135.4, 130.8, 129.5, 128.8, 128.6, 128.52, 128.49, 128.4, 128.2, 128.1, 128.04, 128.00, 127.84, 127.77, 127.2, 124.4, 119.4, 95.2, 80.8, 74.8, 74.7, 73.7, 72.0, 71.8, 70.1, 68.3, 21.3, 19.8.

HRMS (ESI) Calculated for C_{37}H_{39}O_{6} [M-[OC(CF_{3})=NPh]]^{+} 579.2741, found 579.2731.

3,4-Di-O-benzyl-2-O-mesityl-O-rhamnopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4d)

Mesitoyl chloride (0.203 ml, 1.2 mmol), DMAP (13 mg, 0.1 mmol), and compound S10 (87 mg, 0.2 mmol) were added to pyridine (1 mL), and the mixture was warmed to 100 °C and stirred for 2 d. The mixture was diluted with H$_2$O and extracted into CH$_2$Cl$_2$. The organic phase was washed with aqueous HCl (1 M), saturated aqueous NaHCO$_3$, and brine and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate = 15:1) to afford the compound S11 (87 mg, 0.15 mmol, 75%). $[\alpha]_D^{25} = -82.3$ (c 0.15, CHCl$_3$);

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.40 (m, 2H), 7.33 – 7.16 (m, 13H), 6.76 (s, 2H), 5.77 (dd, J = 3.2, 1.7 Hz, 1H), 5.46 (d, J = 1.6 Hz, 1H), 4.83 (d, J = 10.8 Hz, 1H), 4.74 (d, J = 11.3 Hz, 1H), 4.57 (d, J = 11.3 Hz, 1H), 4.51 (d, J = 10.8 Hz, 1H), 4.26 – 4.05 (m, 1H), 3.93 (dd, J = 9.4, 3.2 Hz, 1H), 3.46 (t, J = 9.4 Hz, 1H), 2.20 (s, 9H), 1.22 (d, J = 6.2 Hz, 3H).

\[ ^{13}C \text{NMR (101 MHz, Chloroform-}d\text{)} \delta 169.4, 139.6, 138.4, 137.8, 135.7, 134.1, 132.0, 130.6, 129.2, 128.52, 128.50, 128.49, 128.2, 128.1, 127.91, 127.87, 127.8, 86.3, 80.3, 78.5, 75.7, 72.1, 71.4, 69.3, 21.3, 20.1, 17.9.

HRMS (ESI) Calculated for C$_{36}$H$_{39}$O$_5$S [M+H]$^+$ 583.2513, found 583.2516.

To a solution of compound S11 (410 mg, 0.704 mmol) in DCM (7 mL), TFA (52 μl, 0.7 mmol) and NIS (190 mg, 0.85 mmol) were added to the mixture at 0 °C and stirred for 30 min. The reaction mixture was quenched with Et$_3$N and saturated aqueous Na$_2$S$_2$O$_3$, and the organic phase was washed with saturated aqueous NaHCO$_3$, brine successively. The organic phases
was separated and combined, and was then dried over anhydrous Na₂SO₄. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8/1) to deliver hemiacetal S₁₂ (280 mg, 0.571 mmol, 81%) as a syrup.

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S₁₂ (280 mg, 0.571 mmol) can be converted into the donor 4d after 4 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 30/1, with TEA) to yield 4d (267 mg, 0.403 mmol, 71%) as a syrup. 

1H NMR (400 MHz, Acetone-d₆) δ 7.43 (m), 7.40 – 7.26 (m), 7.19 – 7.12 (m), 6.95 (d, J = 7.7 Hz), 6.89 (s), 6.22 (brs), 5.86 (brs), 4.95 (d, J = 11.2 Hz), 4.91 (d, J = 11.2 Hz), 4.75 (d, 11.2 Hz), 4.70 (d, 11.2 Hz), 4.11 (dd, J = 9.5, 3.3 Hz), 3.99 – 3.82 (m), 3.54 (t, J = 9.4 Hz), 2.26 (s), 2.24 (s), 1.35 – 1.24 (m). 13C NMR (100 MHz, Acetone-d₆) δ 169.2, 144.6, 140.5, 139.7, 139.0, 136.2, 131.5, 129.9, 129.3, 129.21, 129.20, 129.15, 128.9, 128.7, 128.5, 125.5, 120.4, 95.9, 80.1, 78.5, 75.9, 72.8, 71.6, 68.9, 21.2, 20.2, 18.4. HRMS (ESI) Calculated for C₃₀H₃₃O₅ [M-[OC(CF₃)=NPh]]⁺ 473.2323, found 473.2287.

2,3,4-Tri-O-benzyl-6-O-picoloyl-D-glucopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4f)

Picolinic acid (176 mg, 1.40 mmol), N,N’-dicyclohexylcarbodiimide (417 mg, 2 mmol), and 4-dimethylaminopyridine (25 mg, 0.20 mmol) were added to a solution of starting material S₁₃[32] (543 mg, 1.00 mmol) in dry CH₂Cl₂ (10 mL), and the resulting mixture was stirred under N₂ for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na₂SO₄, and concentrated in vacuo to afford the crude product which was used without purification in the next step.

The above obtained crude product was dissolved in acetone and H₂O (10 ml, acetone: H₂O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour at rt, and was then quenched with saturated aqueous Na₂S₂O₃. The organic phase was washed with saturated aqueous NaHCO₃ and brine successively, and the organic phases was separated and combined, and was then dried over anhydrous Na₂SO₄. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 1/2) to deliver the hemiacetal S₁₄ (445 mg, 0.8 mmol, 80% for 2 steps).

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S₁₄ (445 mg, 0.8 mmol) can be converted into the donor 4f after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield 4f (535 mg, 0.736 mmol, 92%) as a syrup. 1H NMR (400 MHz, Chloroform-d) δ 8.75 (d, J = 4.5 Hz), 8.01 (d, J = 7.8 Hz), 7.70 (t, J = 7.7 Hz), 7.47 – 7.44 (m), 7.41 – 7.20 (m), 7.08 (t, J = 7.4 Hz), 6.74 (d, J = 7.6 Hz), 5.73 (brs), 4.97 (d, J = 10.8 Hz), 4.94 – 4.75 (m), 4.72 – 4.45 (m), 3.82 – 3.64 (m). 13C NMR (100 MHz, Chloroform-d) δ
164.7, 150.2, 147.7, 143.4, 138.2, 137.2, 137.0, 128.8, 128.68, 128.65, 128.36, 128.33, 128.26, 128.21, 128.01, 127.98, 127.0, 125.4, 124.4, 119.3, 97.1, 84.6, 80.8, 76.0, 75.3, 75.2, 73.9, 64.1. HRMS (ESI) Calculated for C_{33}H_{32}NO_{6} [M-[OC(CF_{3})=NPh]+] 538.2224, found 538.2208.

2,3,6-Tri-O-benzyl-4-O-picoloyl-D-glucopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4g)

Picolinic acid (176 mg, 1.40 mmol), N,N'-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material S15[13] (543 mg, 1.00 mmol) in dry CH_{2}Cl_{2} (10 mL) and the resulting mixture was stirred under N_{2} for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na_{2}SO_{4}, and concentrated in vacuo to afford the crude product which was used for the next step without purification.

The above obtained crude product was dissolved in acetone and H_{2}O (10 ml, acetone: H_{2}O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na_{2}S_{2}O_{3}. The organic phase was washed with saturated aqueous NaHCO_{3}, brine successively, and the organic phase was separated and combined, and was then dried over anhydrous Na_{2}SO_{4}. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to deliver the hemiacetal S16 (440 mg, 0.79 mmol, 79% for 2 steps).

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S16 (440 mg, 0.79 mmol) can be converted into the donor 4g after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield 4g (523 mg, 0.72 mmol, 91%) as a colorless syrup. 4g-β isomer: 1H NMR (400 MHz, Chloroform-d) δ 8.72 (d, J = 8.7 Hz, 1H), 7.98 (dt, J = 7.9 Hz, 1H), 7.78 (td, J = 7.7, 1.8 Hz, 1H), 7.45 (m, 1H), 7.40 – 7.01 (m, 18H), 6.81 (d, J = 7.7 Hz, 2H), 5.70 (s, 1H), 5.47 (t, J = 9.6 Hz, 1H), 4.90 – 4.74 (m, 3H), 4.66 (d, J = 11.4 Hz, 1H), 4.49 (d, J = 12 Hz, 2H), 3.86 (m, 3H), 3.63 (m, 2H). 13C NMR (100 MHz, Chloroform-d) δ 164.1, 149.9, 147.5, 143.4, 137.9, 137.8, 137.7, 137.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.65, 127.58, 127.2, 125.7, 124.5, 119.4, 81.7, 80.96, 75.48, 75.46, 74.2, 73.6, 71.6, 68.8. HRMS (ESI) Calculated for C_{33}H_{32}NO_{6} [M-[OC(CF_{3})=NPh]+] 538.2224, found 538.2217.

2,3,6-Tri-O-benzyl-4-O-picoloyl-D-galactopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4h)

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S16 (440 mg, 0.79 mmol) can be converted into the donor 4h after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield 4h (523 mg, 0.72 mmol, 91%) as a colorless syrup.
Picolinic acid (176 mg, 1.40 mmol), N,N'-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material S17[34] (543 mg, 1.00 mmol) in dry CH2Cl2 (10 mL) and the resulting mixture was stirred under N2 for 2 hours at rt. The solid was filtered off and rinsed successively with DCM, and then the combined filtrate was washed with brine. The organic phase was separated, dried with anhydrous Na2SO4, and concentrated in vacuo to afford the crude product which was used for next step without purification.

The above obtained crude product was dissolved in acetone and H2O (10 ml, acetone: H2O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na2S2O3. The organic phase was washed with saturated aqueous NaHCO3, brine successively, and the organic phases were separated and combined, and was then dried over anhydrous Na2SO4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 1/2) to deliver the hemiacetal S18 (456 mg, 0.82 mmol, 82% for 2 steps).

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, the above corresponding hemiacetal S18 (456 mg, 0.82 mmol) can be converted into the donor 4h after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether /ethyl acetate = 4/1, with TEA) to yield 4h (566 mg, 0.779 mmol, 95%) as a colorless syrup. 4h-β isomer: 1H NMR (400 MHz, Chloroform-d) δ 8.92 – 8.74 (m, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.82 (td, J = 7.7, 1.8 Hz, 1H), 7.48 (ddd, J = 7.6, 4.7, 1.2 Hz, 1H), 7.40 – 7.13 (m, 17H), 7.09 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 7.7 Hz, 2H), 5.93 (d, J = 3.3 Hz, 1H), 5.74 (s, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.85 – 4.71 (m, 2H), 4.59 (d, J = 11.4 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.41 (d, J = 11.7 Hz, 1H), 3.93 (t, J = 8.9 Hz, 1H), 3.85 – 3.70 (m, 1H), 3.63 (t, J = 6.7 Hz, 2H). 13C NMR (100 MHz, Chloroform-d) δ 163.9, 150.3, 147.5, 143.4, 137.8, 137.4, 137.0, 129.3, 128.8, 128.5, 128.41, 128.37, 128.33, 128.29, 128.2, 128.06, 128.0, 127.93, 127.88, 127.83, 127.78, 127.71, 125.5, 124.3, 119.3, 97.1, 79.4, 77.6, 75.7, 73.7, 73.3, 72.3, 68.0, 67.6. HRMS (ESI) Calculated for C33H32NO6 [M-[OC(CF3)=NPh]]+ 538.2224, found 538.2216.

2,4-Di-O-benzyl-3-O-picoloyl-L-rhamnopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4i)

Picolinic acid (176 mg, 1.40 mmol), N,N'-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material S19[35] (437 mg, 1.00 mmol) in dry CH2Cl2 (10 mL) and the resulting mixture was stirred under N2 for 2 hours at rt. The solid was filtered off and rinsed successively with CH2Cl2, and then the combined filtrate was washed with brine. The organic phase was separated, dried over anhydrous Na2SO4, and concentrated in vacuo to afford the crude product which was used for next step without further purification.

The above obtained crude product was dissolved in acetone and H2O (10 ml, acetone: H2O = 9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na2S2O3. The organic phase was washed with saturated aqueous NaHCO3, brine successively, and the organic phases were separated and combined, and was then dried over anhydrous Na2SO4. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 1/2) to deliver the hemiacetal S18 (456 mg, 0.82 mmol, 82% for 2 steps).
9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na$_2$S$_2$O$_3$. The organic phase was washed with saturated aqueous NaHCO$_3$, brine successively, and the organic phases was separated and combined, dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation yielded the crude product which was purified by silica gel chromatography (petroleum ether/ethyl acetate = 1/2) to deliver the hemiacetal 20 (382 mg, 0.85 mmol, 85% for 2 steps).

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, hemiacetal 20 (382 mg, 0.85 mmol) can be converted into the donor 4i after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield 4i (497 mg, 0.8 mmol, 94%) as a colorless syrup. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.93 – 8.70 (m), 8.02 (d, $J = 7.8$ Hz), 7.97 (d, $J = 7.8$ Hz), 7.82 (m), 7.50 (m), 7.37 – 7.16 (m), 7.15 – 7.00 (m), 6.84 (brs), 6.28 (brs), 5.47 (dd, $J = 9.2, 3.4$ Hz), 5.12 (s), 4.92 – 4.88 (m), 4.82 (d, $J = 11.0$ Hz), 4.69 – 4.50 (m), 4.28 (m), 4.05 (brs), 3.94 (t, $J = 9.8$ Hz), 1.43 (d, $J = 6.0$ Hz). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 164.3, 164.2, 150.15, 150.11, 147.8, 147.5, 143.6, 143.4, 143.3, 143.0, 137.90, 137.86, 137.5, 137.1, 137.0, 128.9, 128.8, 128.7, 128.44, 128.41, 128.33, 128.26, 128.01, 127.9, 127.2, 127.1, 125.4, 125.3, 124.6, 119.6, 119.4, 95.4, 78.2, 77.9, 76.6, 75.4, 75.3, 74.7, 74.5, 73.8, 73.4, 72.9, 72.8, 70.9, 18.2, 18.0. HRMS (ESI) Calculated for C$_{26}$H$_{26}$NO$_5$ [M-OC(CF$_3$)=NPh]+ 432.1805, found 432.1790.

2,3-Di-O-benzyl-4-O-picoloyl-L-rhamnopyranosyl N-Phenyl-2,2,2-trifluoroacetimidate donor (4i)

Picolinic acid (176 mg, 1.40 mmol), N,N'-dicyclohexylcarbodiimide (417 mg, 2 mmol), and DMAP (25 mg, 0.20 mmol) were added to a solution of starting material 21[35] (437 mg, 1.00 mmol) in dry CH$_2$Cl$_2$ (10 mL) and the resulting mixture was stirred under N$_2$ for 2 hours at rt. The solid was filtered off and rinsed successively with CH$_2$Cl$_2$, and then the combined filtrate was washed with brine. The organic phase was separated, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo to afford the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the compound 22 (515 mg, 0.95 mmol, 95%) as a syrup. $[\alpha]_D^{25} = -60.0$ (c 1.2, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 4.0$ Hz, 1H), 8.14 (d, $J = 7.8$ Hz, 1H), 7.85 (td, $J = 7.7, 1.5$ Hz, 1H), 7.55 – 7.47 (m, 1H), 7.43 – 7.14 (m, 15H), 5.68 – 5.60 (m, 1H), 5.54 (s, 1H), 4.77 – 4.67 (m, 2H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.51 – 4.41 (m, 2H), 4.07 – 3.99 (m, 2H), 1.30 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 164.6, 149.9, 148.0, 137.94, 137.89, 137.1, 134.4, 131.4, 129.2, 128.5, 128.3, 128.1, 127.84, 127.77, 127.67, 127.5, 127.1, 125.8, 86.2, 77.1, 76.4, 74.7, 72.5, 72.0, 68.2, 17.7. HRMS (ESI) Calculated for C$_{32}$H$_{32}$NO$_5$S [M+H]+ 542.1996, found 542.2006.

The above obtained compound 22 was dissolved in acetone and H$_2$O (10 ml, acetone: H$_2$O =
9:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na₂S₂O₃. The organic phase was washed with saturated aqueous NaHCO₃, brine successively, and the organic phases was separated and combined, dried over anhydrous Na₂SO₄. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to deliver the hemiacetal S₂₃ (372 mg, 0.83 mmol, 87%).

As the general procedure for preparation of glycosyl N-phenyl trifluoroacetimidate (PTFAI) donor, hemiacetal S₂₃ can be converted into the donor 4j after 5 hours at rt, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1, with TEA) to yield 4j (464 mg, 0.747 mmol, 90%) as a syrup.

4j-β isomer: ¹H NMR (400 MHz, Chloroform-d) δ 8.94 – 8.68 (m, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.85 (td, J = 7.7, 1.7 Hz, 1H), 7.51 (m, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 (m, 6H), 7.18 (m, 5H), 5.64 (t, J = 9.4 Hz, 1H), 5.54 (s, 1H), 4.72 (dd, J = 14.8 Hz, J = 12.3 Hz, 2H), 4.56 (d, J = 12.1 Hz, 1H), 4.51 – 4.38 (m, 2H), 4.05 – 4.00 (m, 2H), 1.30 (d, J = 6.2 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 164.6, 149.9, 148.0, 137.94, 137.89, 137.1, 134.4, 131.4, 129.2, 128.5, 128.3, 128.1, 127.84, 127.77, 127.67, 127.5, 127.1, 125.8, 86.2, 76.4, 74.7, 72.5, 72.0, 68.2, 17.7.

Synthesis of donor 8d

To a solution of compound S₂₄ (277 mg, 0.50 mmol) in dry acetone (5 mL), KOH (56 mg, 1.00 mmol) and 2-chlorobenzoxazole (230 μl, 2.00 mmol) were added to the mixture at 0 °C. The reaction mixture was stirred for another 3 hours under N₂ atmosphere. Then, the mixture was filtered off and the combined filtrate was dried over anhydrous Na₂SO₄, concentrated in vacuo to afford the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 12/1, with Et₃N) to afford the donor 8d (278.8 mg, 0.415 mmol, 83%) as colorless oil. 8d-α isomer: ¹H NMR (400 MHz, Acetone-d₆) δ 8.14 – 8.07 (m, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.41 – 7.22 (m, 17H), 6.59 (d, J = 1.5 Hz, 1H), 6.06 (s, 1H), 4.91 (dd, J = 11.2, 7.0 Hz, 2H), 4.74 – 4.65 (m, 3H), 4.57 (d, J = 11.9 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.17 – 4.08 (m, 1H), 3.95 (dd, J = 11.3, 3.7 Hz, 1H), 3.80 (dd, J = 11.3, 1.6 Hz, 1H). ¹³C NMR (100 MHz, Acetone-d₆) δ 164.8, 161.4, 148.5, 133.5, 129.8, 128.7, 128.28, 128.23, 128.18, 128.1, 127.9, 127.4, 118.3, 109.9, 98.9, 77.6, 74.9, 74.6, 73.6, 72.9, 71.5, 68.7, 67.6. HRMS (ESI) Calculated for C₄₁H₃₇NO₆Na [M+Na]⁺ 694.2417, found 694.2413.

Synthesis of acceptor 6j
To a solution of compound S25\textsuperscript{[36]} (253 mg, 0.54 mmol) in dry DMF (10 ml), tetrabutylammonium iodide (41 mg, 0.11 mmol), chloromethyl methyl ether (49 μl, 0.65 mmol) and \(N,N\)-diisopropylethylamine (0.168 ml, 0.65 mmol) were added in sequence at 0 °C under \(N_2\) atmosphere, and then the mixture was warmed up to rt. The reaction mixture was stirred for overnight at this temperature. The resulting mixture was diluted with DCM and washed with HCl (1 M) solution, saturated aqueous NaHCO\textsubscript{3} and brine successively. The organic phase was separated and combined, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to afford the intermediate (198 mg, 0.388 mmol, 72%) as a yellow solid.

The above obtained intermediate (101 mg, 0.198 mmol) was dissolved in dry DMF (1 ml), to which K\textsubscript{2}CO\textsubscript{3} (55 mg, 0.396 mmol), Sodium iodide (6 mg, 0.0396 mmol) and BnBr (48 μl, 0.396 mmol) were added at 0 °C under \(N_2\) atmosphere. The mixture was warmed up to rt and stirred for overnight at this temperature. The resulting mixture was diluted with DCM and washed with HCl (1 M) solution, saturated aqueous NaHCO\textsubscript{3} and brine successively. The organic phase was separated and combined, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to afford the compound S26 (80 mg, 0.133 mmol, 67%) as a solid.

\[^{[36]}\alpha\]D\textsubscript{25} = -1.9 (c 0.45, CHCl\textsubscript{3}); \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.05 – 7.90 (m, 2H), 7.66 – 7.54 (m, 2H), 7.51 – 7.20 (m, 13H), 7.14 – 6.98 (m, 2H), 6.57 (d, \(J = 2.1\) Hz, 1H), 6.46 (d, \(J = 2.1\) Hz, 1H), 5.29 (s, 2H), 5.24 (s, 2H), 5.10 (s, 2H), 5.09 (s, 2H), 3.51 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-d) \(\delta\) 174.0, 162.8, 159.9, 158.9, 158.8, 153.6, 139.8, 137.1, 136.5, 135.8, 130.2, 129.0, 128.9, 128.8, 128.6, 128.3, 128.0, 127.78, 127.76, 127.77, 124.5, 115.9, 110.2, 98.2, 94.3, 94.0, 74.1, 70.9, 70.6, 56.3. HRMS (ESI) Calculated for C\textsubscript{38}H\textsubscript{32}O\textsubscript{7} [M+H]\textsuperscript{+} 601.2221, found 601.2223.

To a solution of compound S26 (51 mg, 0.085 mmol) in mixed solvent (DCM: MeOH = 1:1, 1.7 ml), acetyl chloride (302 μl, 4.25 mmol) was added at 0 °C. The resulting reaction mixture was stirred at the same temperature for several hours, at which time TLC showed the disappearance of all starting material. The reaction mixture was diluted with ethyl acetate, and then washed with saturated aqueous NaHCO\textsubscript{3}, brine successively. The organic phase was separated, combined, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. Filtration and evaporation yielded the crude product which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 7/1) to deliver the acceptor 6\textit{j} (42 mg, 0.0754 mmol, 89%) as a pale yellow solid. \[^{[36]}\alpha\]D\textsubscript{25} = -2.1 (c 0.25, Acetone); \(^1\)H NMR (400 MHz, DMSO-d\textsubscript{6}) \(\delta\) 10.16 (s, 1H), 7.90 (d, \(J = 8.8\) Hz, 2H), 7.64 (d, \(J = 7.4\) Hz, 2H), 7.56 – 7.27 (m, 13H), 6.92 (d, \(J = 2.1\) Hz, 1H), 6.88 (d, \(J = 8.8\) Hz, 2H), 6.70 (d, \(J = 2.2\) Hz, 1H), 5.26 (s, 2H), 5.23 (s, 2H), 5.00 (s, 2H). \(^{13}\)C NMR (100 MHz, DMSO-d\textsubscript{6}) \(\delta\) 172.4, 162.6, 159.6, 159.2, 158.2, 153.1, 138.7, 137.1, 136.9, 136.2, 130.0, 128.6, 128.5, 128.32, 128.27, 128.1, 128.0, 127.6, 127.0, 121.0, 115.4, 109.0, 97.9, 94.2, 72.9, 70.1, 70.0. HRMS (ESI) Calculated for C\textsubscript{36}H\textsubscript{29}O\textsubscript{6} [M+H]\textsuperscript{+} 557.1959, found 557.1962.
Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3a)

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 3a in the sealed tube at 27 °C after 20 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3a (46 mg, 0.0466 mmol, 93%, α/β = 1/1) as a white amorphous solid. Analytical data for 3a was in accordance with that reported previously.38

Methyl 2,3,4-Tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl)-α-D-glucopyranoside (3a, gram-scale synthesis)

As the general procedure A, donor 1c (1158 mg, 1.625 mmol) and acceptor 2a (581 mg, 1.25 mmol) can be converted into the product 3a in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3a (1099 mg, 1.11 mmol, 89%, α/β = 2/1) as a white amorphous solid. Analytical data for 3a was in accordance with that reported previously.38

3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-1,2:5,6-O-diisopropylidene-α-D-galactofuranose (3b)

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2b (13 mg, 0.05 mmol) can be converted into the product 3b in the sealed tube at 30°C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3b (34.4 mg, 0.044 mmol, 88%, α/β = 3/1) as a syrup. Analytical data for 3b was in accordance with that reported previously.39

1-Adamantanyl 2,3,4,6-tetra-O-benzyl-D-glucopyranoside (3c)
As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2c (7.8 mg, 0.05 mmol) can be converted into the product 3c in the sealed tube at 30 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver 3c (31 mg, 0.046 mmol, 92%, α/β = 1.2/1) as a white solid. Analytical data for 3c was in accordance with that reported previously.25

13-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)stevioltert-Butyldiphenylsilyl Ester (3d)

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2d (28 mg, 0.05 mmol) can be converted into the product 3d in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 10/1) to deliver 3d (43.7 mg, 0.0405 mmol, 81%, α/β = 1/1.4) as a white solid. The α and β isomer cannot be separated. 1H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.63 (m), 7.44 – 7.14 (m), 7.12 – 7.05 (m, 2H), 5.21 (d, J = 3.4 Hz, 1H), 5.15 (s, 1.4H), 5.13 (s, 1H), 5.04 – 4.96 (m), 4.93 – 4.53 (m), 4.44 – 4.40 (m, 2.4H), 4.31 (d, J = 12.1 Hz, 1H), 4.07 (t, J = 9.3 Hz, 1H), 3.92 (dt, J = 10.0, 2.3 Hz, 1H), 3.81 (dd, J = 10.4, 2.4 Hz, 1H), 3.76 (t, J = 9.4 Hz, 1H), 3.70 – 3.55 (m), 3.56 – 3.43 (m), 3.34 (m, 1H), 2.29 – 1.30 (m), 1.26 (s), 1.14 (s), 1.12 (s), 1.03 (m), 0.94 (t, J = 8.1 Hz, 2H), 0.75 (s). 13C NMR (100 MHz, Chloroform-d) δ 177.0, 176.7, 153.0, 151.7, 139.2, 138.8, 138.50, 138.52, 138.44, 138.42, 138.2, 138.0, 135.73, 135.70, 135.68, 132.20, 132.17, 130.11, 130.09, 130.06, 128.55, 128.52, 128.47, 128.45, 128.43, 128.3, 128.25, 128.22, 128.17, 128.0, 127.94, 127.90, 127.84, 127.82, 127.76, 127.74, 127.71, 127.65, 127.56, 127.5, 105.2, 104.9, 98.6, 92.5, 86.4, 86.0, 85.3, 82.4, 82.2, 80.4, 78.2, 75.8, 75.6, 75.31, 75.26, 75.0, 74.9, 73.6, 73.5, 70.1, 69.2, 68.3, 57.21, 57.19, 54.0, 53.8, 47.96, 47.91, 45.30, 45.28, 43.9, 43.7, 42.5, 41.8, 41.7, 41.5, 40.8, 40.7, 39.6, 39.5, 39.1, 38.8, 38.7, 37.6, 29.8, 29.43, 29.35, 27.33, 27.28, 22.4, 22.2, 20.4, 20.2, 19.5, 19.42, 19.40, 16.3, 16.2. HRMS (ESI) Calculated for C70H83O8Si [M+H]⁺ 1079.5852, found 1079.5873.

9,10-secoergosta-5,7,10,22-tetraen-3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranoside) (3e)
As the general procedure A, donor 1c (39.2 mg, 0.055 mmol) and acceptor 2e (20.3 mg, 0.05 mmol) can be converted into the product 3e in the sealed tube wrapped in tin foil with freshly activated 4Å MS at 3 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 18/1) to deliver 3e (28 mg, 0.0305 mmol, 61%, α/β = 1.2/1) as a colorless oil. 3e-β: [α]D25 = 47.1 (c 0.45, CHCl 3); 1H NMR (400 MHz, Acetone -d6) δ 7.48–7.20 (m, 20H), 6.28 (d, J = 11.2 Hz, 1H), 6.09 (d, J = 11.2 Hz, 1H), 5.24 (t, J = 5.8 Hz, 2H), 5.08 (brs, 1H), 4.98 (d, J = 11.5 Hz, 1H), 4.93 (d, J = 11.2 Hz, 1H), 4.87 (d, J = 11.1 Hz, 1H), 4.82 – 4.77 (m, 2H), 4.73 – 4.54 (m, 5H), 4.09 – 4.03 (m, 1H), 3.84 – 3.52 (m, 4H), 3.34 (dd, J = 9.0, 7.8 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.54 – 2.42 (m, 2H), 2.24 – 2.11 (m, 1H), 2.03 – 1.96 (m, 2H), 1.94 – 1.22 (m, 16H), 1.04 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.85 (t, J = 6.8 Hz, 6H), 0.58 (s, 3H). 13C NMR (100 MHz, Acetone-d6) δ 146.8, 142.1, 140.21, 140.19, 139.85, 139.8, 136.73, 136.67, 132.8, 129.2, 129.12, 129.06, 129.0, 128.8, 128.7, 128.6, 128.45, 128.36, 128.3, 128.2, 128.1, 122.9, 118.8, 112.6, 102.8, 85.6, 83.3, 79.1, 76.7, 76.0, 75.6, 75.4, 75.0, 73.8, 70.1, 57.3, 57.2, 46.5, 43.8, 43.2, 41.4, 41.3, 34.8, 33.9, 33.0, 28.6, 24.3, 23.0, 21.7, 20.4, 20.1, 18.2, 12.7. HRMS (ESI) Calculated for C62H78NaO6 [M+Na]+ 941.5691, found 941.5689.

(4-Isopropenyl-1-cyclohexen-1-yl)methyl-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranoside) (3f)

As the general procedure A, donor 1d (46.3 mg, 0.065 mmol) and acceptor 2f (7.8 mg, 0.05 mmol) can be converted into the product 3f in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 14/1) to deliver 3f (29 mg, 0.043 mmol, 86%, α/β = 1/1) as a colorless oil. The α and β isomer cannot be separated. 1H NMR (400 MHz, Acetone-d6) δ 7.51–7.04 (m), 5.73 (d), 4.99 – 4.90 (m), 4.89 – 4.85 (m), 4.82 (d), 4.79 – 4.66 (m), 4.66 – 4.52 (m), 4.51 – 4.35 (m), 4.25 (d), 4.09 – 3.78 (m), 3.63 – 3.45 (m), 2.46 – 1.89 (m), 1.85 – 1.55 (m), 1.55 – 1.32 (m). δ 13C NMR (100 MHz, Chloroform-d) δ 150.0, 149.9, 139.0, 138.81, 138.80, 138.75, 138.7, 138.6, 138.1, 138.0, 134.0, 133.5, 128.52, 128.48, 128.45, 128.43, 128.39, 128.36, 128.31, 128.29, 128.27, 128.24, 128.01, 127.98, 127.88, 127.84, 127.80, 127.64, 127.62, 127.60, 127.5, 125.8, 124.9, 108.8, 108.7, 102.6, 95.3, 82.5, 79.7, 79.4, 76.4, 75.4, 75.1, 74.8, 74.6, 73.62, 73.55, 73.52, 73.46, 73.4, 73.2, 73.1, 70.9, 69.4, 69.1, 68.9, 41.09, 41.05, 30.58, 30.56, 27.54, 27.50, 26.6, 26.3, 20.93, 20.89. HRMS (ESI) Calculated for C44H50NaO6 [M+Na]+ 697.3500, found 697.3503.

Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α/β-D-galactotpyranosyl)-α-D-glucopyranoside (3g)
As the general procedure A, donor 1d (46.3 mg, 0.065 mmol) and acceptor 2g (23.3 mg, 0.05 mmol) can be converted into the product 3g in the sealed tube at 30 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3g (42 mg, 0.0425 mmol, 85%, α/β = 2.2/1) as a syrup. Analytical data for 3g was in accordance with that reported previously.40

(3β)-Cholest-5-en-3-yl 2,3,4,6-tetra-O-benzyl-α-D-galactopyranoside (3h)

As the general procedure A, donor 1d (46.3 mg, 0.065 mmol) and acceptor 2h (19.4 mg, 0.05 mmol) can be converted into the product 3h in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver 3h (44 mg, 0.0484 mmol, 97%, α/β = 1/1.5) as a white solid. Analytical data for 3h was in accordance with that reported previously.41

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (3i)

As the general procedure A, donor 1e (46.3 mg, 0.065 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 3i in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3i (45 mg, 0.0456 mmol, 91%, α/β = 1.6/1) as a syrup. Analytical data for 3i was in accordance with that reported previously.41

Methyl 6-O-(2,3,4-tri-O-benzyl-L-rhamnopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3j)

As the general procedure A, donor 1f (45.5 mg, 0.075 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 3j in the sealed tube at 19 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3j (43.6 mg, 0.0494 mmol, 99%, α/β = 1/1) as a white foam. Analytical data for 3j was in accordance with that reported previously.21
**N-[(1,1-Dimethylethoxy)carbonyl]-O-(2,3,4-tri-O-benzyl-L-rhamnopyranosyl)-L-serine methyl ester (3k)**

As the general procedure A, donor 1f (45.5 mg, 0.075 mmol) and acceptor 2i (11 mg, 0.05 mmol) can be converted into the product 3k in the sealed tube at 19 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3k (28 mg, 0.044 mmol, 88%, α/β = 1.5/1) as a syrup. 3k-α isomer: [α]_D^{25} = -7.0 (c 1.1, CHCl₃); 1H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.15 (m, 15H), 5.24 (d, J = 8.8 Hz, 1H), 4.92 (d, J = 11.1 Hz, 1H), 4.81 – 4.52 (m, 6H), 4.47 (m, 1H), 4.03 (dd, J = 9.9, 3.6 Hz, 1H), 3.76 – 3.60 (m, 5H), 3.63 – 3.39 (m, 3H), 1.30 (d, J = 6.1 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 170.7, 155.4, 138.8, 138.5, 138.4, 128.5, 128.4, 128.0, 127.95, 127.92, 127.8, 127.74, 127.66, 98.2, 80.3, 80.2, 79.9, 75.3, 75.0, 72.6, 68.6, 67.6, 53.7, 52.6, 28.5, 18.0. HRMS (ESI) Calculated for C₃₆H₄₅NNaO₉ [M+Na]+ 658.2987, found 658.2986.

3k-β isomer: [α]_D^{25} = 34.1 (c 0.9, CHCl₃); 1H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.38 (m, 2H), 7.36 – 7.24 (m, 13H), 5.72 (d, J = 9.0 Hz, 1H), 4.95 (d, J = 10.8 Hz, 1H), 4.90 (d, J = 12.5 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 4.46 (q, J = 11.9 Hz, 3H), 4.31 (s, 1H), 4.18 – 3.95 (m, 2H), 3.84 (d, J = 3.0 Hz, 1H), 3.73 (3, 3H), 3.61 (t, J = 9.3 Hz, 1H), 3.42 (dd, J = 9.4, 3.0 Hz, 1H), 3.32 (m, 1H), 1.46 (s, 9H), 1.40 (d, J = 6.1 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 171.1, 155.7, 138.7, 138.5, 138.3, 128.2, 128.48, 128.3, 128.2, 127.9, 127.74, 127.69, 127.6, 101.8, 82.1, 80.0, 75.6, 74.1, 74.0, 72.3, 71.6, 71.0, 54.10, 52.6, 28.5, 17.9. HRMS (ESI) Calculated for C₃₆H₄₅NNaO₉ [M+Na]+ 658.2987, found 658.2981.

**Methyl 6-O-(2,3,4-tri-O-benzyl-L-fucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3l)**

As the general procedure A, donor 1g (45.5 mg, 0.075 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 3l in the sealed tube at 25 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3l (34 mg, 0.0386 mmol, 77%, α/β = 1/1.4) as a syrup. Analytical data for 3l was in accordance with that reported previously.40

**Methyl 6-O-(2,3,4-tri-O-benzyl-D-xylopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3m)**
As the general procedure A, donor \(1h\) (38.5 mg, 0.065 mmol) and acceptor \(2a\) (23.3 mg, 0.05 mmol) can be converted into the product \(3m\) in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver \(3m\) (40.3 mg, 0.0465 mmol, 93%, \(\alpha/\beta = 1/1.5\)) as a syrup. Analytical data for \(3m\) was in accordance with that reported previously.42

Methyl 6-O-(2,3,5-tri-O-benzyl-D-ribofuranosyl)-2,3,4-tri-O-benzyl-\(\alpha\)-D-glucopyranoside (3n)

As the general procedure A, donor \(1i\) (38.5 mg, 0.065 mmol) and acceptor \(2a\) (23.3 mg, 0.05 mmol) can be converted into the product \(3n\) in the sealed tube at 27 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver \(3n\) (38 mg, 0.0438 mmol, 88%, \(\alpha/\beta = 1/1\)) as a syrup. Analytical data for \(3n\) was in accordance with that reported previously.43

Synthesis of compound 3o

As the general procedure A, donor \(1c\) (46.3 mg, 0.065 mmol) and acceptor \(2j\) (20.8 mg, 0.05 mmol) can be converted into the product \(3o\) in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver \(3o\) (39.9 mg, 0.0425 mmol, 85%, \(\alpha/\beta = 1/1\)) as a syrup. The \(\alpha\) and \(\beta\) isomer cannot be separated.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.11 – 8.03 (m), 7.62 – 7.51 (m), 7.50 – 7.03 (m), 5.33 – 5.25 (m), 4.97 – 4.92 (m), 4.88 – 4.73 (m), 4.70 – 4.41 (m), 4.37 – 4.25 (m), 4.24 – 4.21 (m), 4.18 – 3.95 (m), 3.78 – 3.58 (m), 3.50 – 3.45 (m), 1.56 (s), 1.32 (s).

\(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 165.51, 165.46, 139.0, 138.7, 138.54, 138.51, 138.3, 138.18, 138.16, 138.1, 133.9, 133.6, 133.3, 132.2, 131.3, 130.1, 130.013, 129.912, 129.1, 128.9, 128.6, 128.52, 128.50, 128.48, 128.46, 128.42, 128.37, 128.35, 128.3, 128.09, 128.05, 128.00, 127.95, 127.9, 127.81, 127.77, 127.75, 127.72, 127.66, 127.6, 127.4, 110.9, 110.8, 104.2, 97.4, 86.3, 85.6, 84.7, 82.4, 82.2, 80.0, 77.8, 76.1, 75.9, 75.8, 75.2, 75.1, 75.0, 74.9, 74.8, 74.1, 74.0, 73.60, 73.56, 73.4, 72.0, 71.9, 70.4, 69.6, 69.0, 68.6, 67.5, 27.77, 27.75, 26.54, 26.51. HRMS (ESI) Calculated for \(C_{56}H_{58}NaO_{13}\) [M+Na]+ 961.3592, found 961.3603.
Synthesis of compound 3p

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2k (33.6 mg, 0.05 mmol) can be converted into the product 3p in the sealed tube at 30 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 3p (50 mg, 0.0419 mmol, 84%, α/β = 2.2/1) as a colorless syrup. 3p-α isomer: [α]$_{D25}$ = 2.4 (c 0.5, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) δ 7.78 (d, $J$ = 8.2 Hz, 2H), 7.49 – 6.98 (m, 38H), 6.81 (d, $J$ = 8.7 Hz, 2H), 6.73 (t, $J$ = 7.4 Hz, 1H), 5.69 (dd, $J$ = 9.4, 7.9 Hz, 1H), 5.20 (d, $J$ = 7.9 Hz, 1H), 5.00 (d, $J$ = 10.8 Hz, 1H), 4.91 (d, $J$ = 11.2 Hz, 1H), 4.87 – 4.62 (m, 8H), 4.55 (d, $J$ = 12.2 Hz, 1H), 4.37 (t, $J$ = 11.9 Hz, 2H), 4.04 – 3.73 (m, 10H), 3.65 – 3.47 (m, 4H). 13C NMR (100 MHz, Chloroform-d) δ 165.1, 159.4, 157.3, 138.9, 138.6, 138.3, 138.05, 138.01, 137.8, 133.4, 133.2, 132.9, 129.9, 129.6, 128.63, 128.61, 128.5, 128.43, 128.38, 128.29, 128.24, 128.18, 128.15, 128.04, 128.02, 127.9, 127.8, 127.7, 127.5, 122.4, 115.8, 115.0, 114.0, 113.7, 99.4, 97.4, 93.9, 83.6, 83.0, 82.0, 80.0, 78.1, 75.8, 75.3, 75.22, 75.16, 74.9, 73.4, 73.2, 70.1, 68.4, 66.6, 55.4. HRMS (ESI) calcd for C$_{76}$H$_{72}$NaO$^{13+}$ [M+Na]$^+$ 1215.4865, found 1215.4849.

3p-β isomer: [α]$_{D25}$ = -1.0 (c 0.5, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) δ 7.79 (d, $J$ = 7.8 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.34 – 7.10 (m, 3H), 7.02 (t, $J$ = 8.2 Hz, 1H), 6.86 – 6.36 (m, 3H), 5.71 (t, $J$ = 9.0 Hz, 1H), 5.19 (d, $J$ = 7.8 Hz, 1H), 4.92 (dd, $J$ = 10.9, 5.7 Hz, 2H), 4.87 – 4.36 (m, 12H), 4.20 (d, $J$ = 11.3 Hz, 1H), 3.91 (q, $J$ = 8.9 Hz, 2H), 3.84 (s, 3H), 3.82 – 3.24 (m, 8H). 13C NMR (100 MHz, Chloroform-d) δ 165.2, 159.4, 157.2, 138.6, 138.5, 138.3, 138.05, 138.01, 137.8, 133.4, 133.1, 133.0, 129.9, 129.8, 129.3, 128.63, 128.55, 128.53, 128.48, 128.43, 128.40, 128.3, 128.22, 128.20, 128.12, 128.07, 127.9, 127.8, 127.7, 122.3, 115.8, 114.8, 114.0, 113.7, 103.9, 98.9, 94.0, 84.7, 83.5, 82.9, 82.5, 78.2, 77.9, 75.9, 75.2, 75.1, 74.8, 73.6, 73.2, 68.9, 55.5. HRMS (ESI) calcd for C$_{76}$H$_{72}$NaO$^{13+}$ [M+Na]$^+$ 1215.4865, found 1215.4853.

Synthesis of compound 3q

As the general procedure A, donor 1e (71.3 mg, 0.1 mmol) and acceptor 2l (11.5 mg, 0.05 mmol) can be converted into the product 3q in the sealed tube at 25 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 3q (28.2 mg, 0.0375 mmol, 75%, α/β = 2.5/1) as a syrup. 3q-α isomer: [α]$_{D25}$ = 9.5 (c 0.88, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.23 (m, 18H), 7.17 – 7.12 (m, 2H), 6.41 (dd, $J$ = 6.2, 1.1 Hz, 1H), 5.14 (d, $J$ = 2.2 Hz, 1H), 5.12 (t, $J$ = 4.2 Hz, 1H), 4.87 – 4.77 (m, 6H), 4.49 (dd, $J$ = 16.3, 11.4 Hz, 2H), 4.08 – 3.96 (m, 2H), 3.88 – 3.63 (m, 5H), 2.03 (s, 3H), 1.99 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 170.6, 170.2, 145.6, 138.4, 138.3, 138.2, 138.1, 138.0, 137.9, 129.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 122.3, 115.9, 114.8, 114.0, 113.7, 103.9, 98.9, 94.0, 84.7, 83.5, 82.9, 82.5, 78.2, 77.9, 75.9, 75.2, 75.1, 74.8, 73.6, 73.2, 68.9, 55.5. HRMS (ESI) calcd for C$_{36}$H$_{27}$NaO$_{13}$ [M+Na]$^+$ 1215.4865, found 1215.4853.
Synthesis the C-glycoside 3r

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2m (8.6 mg, 0.05 mmol) can be converted into the product 3r in the sealed tube with freshly activated 4Å MS at 50 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver 3r (23 mg, 0.033 mmol, 66%, α/β = 1/1.3) as a syrup. Analytical data for 3r was in accordance with that reported previously.

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\text{ESI) calcd for } \text{C}_{44}\text{H}_{48}\text{NaO}_{11} [\text{M+Na}^+] 775.3089, \text{found 775.3071.}
\]

Synthesis the S-glycoside 3s

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2n (12 mg, 0.05 mmol) can be converted into the product 3s in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 3s (25 mg, 0.033 mmol, 66%, α/β = 2/1) as a white solid. The α and β isomer cannot be separated.

\[
\text{H NMR (400 MHz, Chloroform-d)} \delta 7.87 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.46 (m, 1.5H), 7.42 – 7.17 (m, 31H), 7.09 (m, 3H), 5.26 (d, J = 5.4 Hz, 1H), 5.20 (m, 1H), 5.10 (m, 0.5H), 4.93 (d, J = 10.9 Hz, 1H), 4.90 – 4.71 (m, 4.5H), 4.67 (t, J = 12.5 Hz, 1.5H), 4.51 – 4.40 (m, 3.5H), 4.36 (d, J = 12.1 Hz, 0.5H), 4.27 (m, J = 12.0 Hz, 1H), 4.13 (m, 1H), 3.84 (dd, J = 9.4, 5.4 Hz, 1H), 3.76 (s, 4.5H), 3.74 – 3.57 (m, 5H), 3.53 (t, J = 8.8 Hz, 0.5H), 3.44 – 3.32 (m, 3H), 2.97 (dd, J = 14.6, 3.4 Hz, 1H). \text{C NMR (100 MHz, Chloroform-d)} \delta 171.2, 171.1, 138.7, 138.5, 138.1, 138.0, 137.9, 137.8, 137.7, 137.6, 137.7, 133.68, 131.9, 131.8, 128.65, 128.60, 128.56, 128.52, 128.49, 128.48, 128.48, 128.14, 128.08, 128.06, 127.99, 127.95, 127.90, 127.84, 127.81, 127.76, 127.74, 127.51, 127.48, 86.6, 86.1, 86.0, 82.3, 81.6, 79.6, 79.0, 77.7, 77.2, 75.9, 75.8, 75.3, 75.2, 73.5, 73.4, 72.8, 71.7, 68.6, 68.4, 53.0, 52.85, 52.76, 52.69, 35.0, 32.9, 29.8. \text{HRMS (ESI) calcd for C}_{45}\text{H}_{48}\text{NO}_{8} [\text{M+H}^+] 762.3095, \text{found 762.3075.}
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Synthesis the S-glycoside 3t

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2o (20 mg, 0.05 mmol) can be converted into the product 3t in the sealed tube at 50 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 3t (37.3 mg, 0.0404 mmol, 81%, α/β = 2/1) as a syrup. The α and β isomer cannot be separated.
1H NMR (400 MHz, Chloroform-d) δ 7.74 (d, J = 7.6), 7.61 (m), 7.41 – 7.18 (m), 7.12 (m), 6.23 (d, J = 8.6 Hz), 6.15 (d, J = 7.6 Hz), 5.27 (d, J = 5.1 Hz), 4.99 – 4.74 (m), 4.73 – 4.13 (m), 3.84 – 3.61 (m), 3.44 (t, J = 8.9 Hz), 3.35 – 3.20 (m), 3.08 (dd, J = 14.2, 6.5 Hz), 2.89 (dd, J = 14.2, 4.0 Hz), 1.48 (d, J = 5.4 Hz). 13C NMR (100 MHz, Chloroform-d) δ 169.6, 169.5, 156.1, 156.0, 144.1, 144.0, 141.4, 138.7, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 137.9, 137.8, 128.6, 128.5, 128.48, 128.46, 128.4, 128.36, 128.18, 128.13, 128.09, 128.06, 128.01, 127.99, 127.97, 127.94, 127.87, 127.82, 127.80, 127.77, 127.71, 127.71, 127.66, 127.62, 127.2, 125.5, 125.3, 120.05, 120.02, 99.4, 86.7, 85.8, 85.2, 82.62, 82.58, 82.44, 82.3, 81.8, 79.7, 79.2, 77.92, 77.85, 75.9, 75.8, 75.6, 75.2, 75.10 73.6, 72.7, 71.6, 68.9, 68.7, 67.3, 67.1, 55.1, 54.6, 47.3, 47.2, 34.8, 32.8, 29.8, 28.2, 28.1. HRMS (ESI) Calculated for C56H60NO9S [M+H]+ 922.3983, found 922.3990.

**Synthesis the S-glycoside 3u**

As the general procedure A, donor 1c (46.3 mg, 0.065 mmol) and acceptor 2p (6.4 mg, 0.05 mmol) can be converted into the product 3u in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 18/1) to deliver 3u (31.7 mg, 0.049 mmol, 98%, α/β = 1.3/1) as a syrup. Analytical data for 3u was in accordance with that reported previously.44

**Synthesis the N-glycoside 3v**

As the general procedure A, donor 1d (46.3 mg, 0.065 mmol) and acceptor 2q (9.5 mg, 0.05 mmol) can be converted into the product 3v in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver 3v (33.3 mg, 0.047 mmol, 94%, α/β = 1.5/1) as a syrup. 3v-α isomer: [α]D25 = -7.7 (c 1.6, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 – 7.17 (m, 20H), 6.97 (d, J = 8.0 Hz, 2H), 5.87 (d, J = 2.5 Hz, 1H), 4.67 – 4.37 (m, 8H), 4.27 (m, 1H), 4.11 (dd, J = 11.4, 8.6 Hz, 1H), 3.98 (dd, J = 5.9, 2.8 Hz, 1H), 3.85 – 3.68 (m, 3H), 2.88 (s, 3H), 2.22 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 143.2, 138.5, 138.2, 138.1, 137.6, 135.3, 129.5, 128.6, 128.5, 128.4, 128.1, 128.02, 127.99, 127.86, 127.82, 127.77, 127.68, 127.67, 80.0, 76.8, 75.6, 75.2, 73.6, 73.4, 73.0, 72.6, 72.0, 66.7, 31.1, 21.5. HRMS (ESI) Calculated for C42H45NNaO7S [M+Na]+ 730.2809, found 730.2806. 3v-β isomer: [α]D25 = 9.1 (c 1.1, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.0 Hz, 2H), 7.44 – 7.22 (m, 20H), 7.07 (d, J = 8.0 Hz, 2H), 5.17 (d, J = 8.9 Hz, 1H), 4.93 (d, J = 11.6 Hz, 1H), 4.87 – 4.69 (m, 4H), 4.53 (d, J = 11.6 Hz, 1H), 4.37 (s, 2H), 3.94 – 3.86 (m, 2H), 3.66 (dd, J = 9.3, 2.7 Hz, 1H), 3.60 (t, J = 6.4 Hz, 1H), 3.40 (dd, J = 9.2, 2.7 Hz, 1H).
7.1 Hz, 1H), 3.30 (dd, J = 9.2, 5.6 Hz, 1H), 2.63 (s, 3H), 2.30 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 143.2, 138.8, 138.4, 138.2, 136.0, 129.3, 128.59, 128.57, 128.5, 128.3, 128.0, 127.94, 127.88, 127.81, 127.78, 127.73, 127.6, 86.6, 83.5, 74.8, 74.7, 74.6, 73.7, 73.4, 73.1, 68.4, 28.9, 21.6. HRMS (ESI) Calculated for C42H45NNaO7S [M+Na]+ 730.2809, found 730.2801.

**Synthesis the N-glycoside 3w**

As the general procedure A, donor 1c (92.6 mg, 0.13 mmol) and acceptor 2r (12 mg, 0.1 mmol) can be converted into the product 3w in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver 3w (N1: 37.9 mg, 0.059 mmol, 59%, α/β = 1/4.7; N2: 23.7 mg, 0.037 mmol, 37%, α/β = 1/3) as a syrup. Analytical data for 7w-N1 was in accordance with that reported previously.45 3w-N1-β isomer: [α]D25= -21.9 (c 0.65, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 7.88 (dd, J = 6.6, 3.1 Hz, 2H), 7.40 (dd, J = 6.7, 3.1 Hz, 2H), 7.35 – 7.22 (m, 14H), 7.17 (m, 2H), 7.11 – 6.99 (m, 3H), 6.80 – 6.69 (m, 2H), 5.92 (d, J = 9.1 Hz, 1H), 4.99 – 4.89 (m, 2H), 4.87 (d, J = 10.8 Hz, 1H), 4.61 (d, J = 10.8 Hz, 1H), 4.59 – 4.42 (m, 4H), 4.04 (d, J = 10.8 Hz, 1H), 3.97 – 3.84 (m, 2H), 3.78 (dd, J = 12.8, 3.2 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 144.6, 128.58, 128.57, 128.5, 128.2, 128.04, 128.02, 127.88, 127.85, 127.83, 127.78, 127.76, 127.3, 118.8, 92.3, 85.8, 81.0, 78.4, 77.5, 75.9, 75.3, 74.9, 73.7, 68.7. HRMS (ESI) Calculated for C40H40N3O5 [M+H]+ 642.2962, found 642.2968.

**Synthesis the N-glycoside 3x**

As the general procedure A, donor 1i (88.9 mg, 0.15 mmol) and acceptor 2s (33.6 mg, 0.1 mmol) can be converted into the product 3x in the sealed tube with freshly activated 4Å MS at 40 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 3x (45.8 mg, 0.062 mmol, 62%, α/β = 1.5/1) as a syrup. 3x-α isomer: [α]D25= 23.3 (c 0.4, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.84 (s, 1H), 8.41 (s, 1H), 7.35 – 7.22 (m, 15H), 6.35 (d, J = 2.8 Hz, 1H), 4.73 (s, 2H), 4.59 (d, J = 12.2 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.42 (m, 3H), 4.25 (t, J = 5.5 Hz, 1H), 3.85 (dd, J = 10.9, 2.9 Hz, 1H), 3.63 (dd, J = 10.8, 2.8 Hz, 1H), 1.47 (s, 18H). 13C NMR (100 MHz, Chloroform-d) δ 152.8, 152.1, 150.7, 150.3, 143.5, 137.5, 137.0, 129.5, 128.7, 128.61, 128.59, 128.45, 128.38, 128.35, 128.15, 128.12, 128.05, 127.98, 127.8, 87.8, 84.0, 82.0, 79.4, 75.5, 73.7, 72.5, 72.4, 68.5, 28.0. HRMS (ESI) Calculated for C41H48N5O8 [M+H]+ 738.3497, found 738.3491. 3x-β isomer: [α]D25= 26.0 (c 0.8, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 1H NMR (400 MHz, CDCl3) δ 8.82 (s, 1H), 8.79 (s, 1H), 7.39 – 7.24 (m, 10H), 7.21 – 7.15 (m, 3H), 7.00 (dd, J = 7.2, 1.7 Hz, 2H), 6.58 (d, J = 6.0 Hz,
1H), 4.72 (d, J = 11.9 Hz, 1H), 4.63 – 4.44 (m, 6H), 4.32 (d, J = 11.7 Hz, 1H), 4.23 (dd, J = 5.4, 3.2 Hz, 1H), 3.60 (dd, J = 10.6, 3.4 Hz, 1H), 3.53 (dd, J = 10.6, 3.0 Hz, 1H), 1.41 (s, 18H). 13C NMR (100 MHz, Chloroform-d) δ 153.8, 151.8, 150.4, 150.0, 146.4, 137.6, 137.2, 136.5, 128.6, 128.54, 128.49, 128.42, 128.16, 128.13, 128.0, 127.9, 127.8, 127.7, 83.6, 83.0, 82.7, 73.7, 73.4, 73.2, 70.0, 27.8. HRMS (ESI) Calculated for C41H48N5O8 [M+H]+ 738.3497, found 738.3497.
Mechanism studies and proposed catalytic cycle.
In order to gain a deeper understanding of the mechanism of thiourea catalyzed glycosylation, a series of experiments were carried out. Under the new catalysis condition, the pure α conformation donor 1j-α coupled with acceptor 2a producing disaccharide 3y with α/β mixture (α:β = 1:1.2) and the pure β conformation donor 1j-β coupled with acceptor 2a producing disaccharide 3y with α/β mixture (α:β = 1:1) as well, which revealed that the reaction was not Sₙ₂ process. In present of two equivalent hindered base 2,4,6-tri-tert-butylpyrimidine (TTBP), the glycosylation of the donor 1c with acceptor 2a catalyzed by Kass catalyst C10 still works and produce the disaccharide product in 86% yield; exceptionally, the donor 1c was activated by 0.1 equivalent C10 even in present of 0.3 equivalent Et₃N producing disaccharide in 36% yield (donor 1c was recovered in 55%). The results revealed that thiourea C10 not as Brønsted acid/Lewis acid activated glycosyl donor 1c. The interaction of glycosyl donor 1j with C10 was monitored by ¹H NMR and we found the anomer position proton Hₐ of glycosyl donor 1j shift to downfield and the aryl proton Hₜ of glycosyl donor 1j shift to upfield upon addition of thiourea C10 (from 0 equiv to 4 equiv), which support that the hydrogen bond existence on donor 1j and thiourea C10. All together, we brought up a plausible mechanism. Glycosyl imidate donor and thiourea catalyst form the donor-catalyst complex thought hydrogen bond and then generate the glycosyl oxocarbenium species IV and the complex of departing species of leaving group and catalyst species V. Combination with various stereoselective glycosylation strategies, the oxocarbenium species IV can form special intermediate which can be selectively attacked by nucleophiles to produce glycosides VII and H⁺. Protonation of departing species of leaving group can regenerate catalyst II, which can undergo the next catalytic cycle.

As the general procedure A, donor 1j-α (41 mg, 0.1 mmol) was reacted with acceptor 2a (59 mg, 0.12 mmol) catalyzed by Kass catalyst (39 mg, 0.02 mmol) in 1 ml DCM at rt for 30 hours to deliver 3t (33 mg, 0.0483 mmol, 48%, α/β = 1:1.2) as a syrup. Analytical data for 5a was in accordance with that reported previously. As the general procedure A, donor 1j-β (41 mg, 0.1 mmol) was reacted with acceptor 2a (59 mg, 0.12 mmol) catalyzed by Kass catalyst (39 mg, 0.02 mmol) in 1 ml DCM at rt for 30 hours to deliver 3t (46 mg, 0.0673 mmol, 67%, α/β = 1:1) as a syrup. Analytical data for 5a was in accordance with that reported previously.  

The glycosylation of the donor 1c with acceptor 2a catalyzed by Kass catalyst in the presence
of 2,4,6-tri-tert-butylpyrimidine (TTBP)

\[
\begin{align*}
&\text{products} \quad (86\% \text{ yield}) \\
&1c + 2a \rightarrow 3a
\end{align*}
\]

As the general procedure A, donor 1c (35.7 mg, 0.05 mmol), acceptor 2a (46.5 mg, 0.1 mmol), Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol), TTBP (2 equiv, 25 mg, 0.1 mmol) and 0.6 ml DCM can be converted into the product 3a in the sealed tube at rt. after 16 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3a (42.4 mg, 0.043 mmol, 86%, \(\alpha/\beta = 1.6:1\)) as a syrup.

The glycosylation of the donor 1c with acceptor 2a catalyzed by Kass catalyst in the presence of Et\(_3\)N

\[
\begin{align*}
&\text{products} \quad (36\% \text{ yield}) \\
&1c + 2a \rightarrow 3a
\end{align*}
\]

As the general procedure A, donor 1c (35.7 mg, 0.05 mmol), acceptor 2a (46.5 mg, 0.1 mmol), Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol), Et\(_3\)N (0.3 equiv, 2.1 \(\mu\)l, 0.015 mmol) and 0.6 ml DCM can be converted into the product 3a in the sealed tube at rt. after 16 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 3a (42.4 mg, 0.043 mmol, 36%) as a syrup. Note: donor 1c was recovered in 55% yield (19.6 mg, 0.0275 mmol).

\(^1\)H NMR studies for the interaction of Kass catalyst C10 with donor 1j-\(\alpha\)

The interaction of glycosyl donor 1j-\(\alpha\) with C10 was monitored by \(^1\)H NMR at -60 °C in CD\(_2\)Cl\(_2\) and we found the anomeric position proton H\(_a\) of glycosyl donor 1j-\(\alpha\) shift to downfield and the aryl proton H\(_b\) of glycosyl donor 1j-\(\alpha\) shift to upfield upon addition of thiourea C10 (from 0 to 4 equiv), which support that the hydrogen bond existence on donor 1j-\(\alpha\) and thiourea C10.

Neighboring group participation strategy for synthesis of the compound 5a

As the general procedure A, donor 4a (38.4 mg, 0.05 mmol) and acceptor 2a (46.5 mg, 0.1 mmol) can be converted into the product 5a in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 5a (42.7 mg, 0.041 mmol, 82%, \(\alpha/\beta = 1/7.2\)) as a white foam. Analytical data for 5a was in accordance with that reported previously.\(^{25}\)

Neighboring group participation strategy for synthesis of the compound 5b
As the general procedure A, donor 4b (49.9 mg, 0.065 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 5b in the sealed tube at 50 °C after 48 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 5b (44.3 mg, 0.0425 mmol, 85%, β/α > 20/1) as a white foam. 5b-β isomer: [α]D25 = 14.3 (c 1.8, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.19 (m, 26H), 7.13 (dd, J = 7.0, 2.5 Hz, 4H), 6.72 (s, 2H), 5.34 (dd, J = 9.1, 7.9 Hz, 1H), 4.95 (d, J = 10.9 Hz, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.79 – 4.70 (m, 4H), 4.68 (d, J = 7.2 Hz, 1H), 4.62 (dd, J = 11.1, 2.7 Hz, 2H), 4.58 (s, 1H), 4.57 – 4.48 (m, 3H), 4.39 (d, J = 11.3 Hz, 1H), 4.08 (dd, J = 10.7, 1.9 Hz, 1H), 3.95 (t, J = 9.2 Hz, 1H), 3.88 – 3.65 (m, 5H), 3.59 (dd, J = 10.7, 6.0 Hz, 1H), 3.50 (m, 2H), 3.34 (dd, J = 10.0, 9.0 Hz, 1H), 3.26 (s, 3H), 2.23 (s, 6H), 2.20 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 168.2, 139.5, 139.0, 138.5, 138.24, 138.21, 137.9, 136.2, 130.2, 128.7, 128.6, 128.52, 128.49, 128.43, 128.35, 128.2, 128.04, 128.02, 128.00, 127.9, 127.8, 127.72, 127.70, 127.62, 127.61, 127.5, 127.1, 101.2, 97.8, 82.6, 82.1, 79.9, 78.11, 78.08, 75.8, 75.4, 74.9, 74.7, 73.8, 73.6, 73.3, 72.8, 70.0, 68.9, 68.0, 55.2, 21.2, 20.4. HRMS (ESI) Calculated for C65H70NaO12 [M+Na]+ 1065.4759, found 1065.4804.

Neighboring group participation strategy for synthesis of the compound 5c

As the general procedure A, donor 4b (57.6 mg, 0.075 mmol) and acceptor 2c (7.8 mg, 0.05 mmol) can be converted into the product 5c in the sealed tube at 50 °C after 48 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 13/1) to deliver 5c (33.6 mg, 0.046 mmol, 92%, β/α > 20/1) as a syrup. 5c-β isomer: [α]D25 = 14.0 (c 1.4, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.07 (m, 15H), 6.80 (s, 2H), 5.30 (t, J = 8.2 Hz, 1H), 4.93 (d, J = 11.5 Hz, 1H), 4.80 (d, J = 7.8 Hz, 1H), 4.72 (dd, J = 13.2, 11.2 Hz, 2H), 4.60 (dd, J = 11.4, 7.8 Hz, 3H), 3.88 – 3.64 (m, 4H), 3.53 (tt, J = 5.5, 2.1 Hz, 1H), 2.28 (s, 6H), 2.25 (s, 3H), 2.15 – 2.02 (m, 3H), 1.92 – 1.71 (m, 6H), 1.58 (q, J = 12.5 Hz, 6H). 13C NMR (100 MHz, Chloroform-d) δ 168.5, 139.2, 138.32, 138.29, 137.9, 135.7, 130.6, 128.52, 128.49, 128.43, 128.35, 128.2, 128.04, 128.02, 128.00, 127.9, 127.8, 127.72, 127.70, 127.62, 127.61, 127.5, 127.1, 101.2, 97.8, 82.6, 82.1, 79.9, 78.11, 78.08, 75.8, 75.4, 74.9, 74.7, 73.8, 73.6, 73.3, 72.8, 70.0, 68.9, 68.0, 55.2, 21.2, 20.4. HRMS (ESI) Calculated for C47H54NaO7 [M+Na]+ 753.3762, found 753.3795.

Neighboring group participation strategy for synthesis of the compound 5d
As the general procedure A, donor 4c (57.6 mg, 0.075 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 5d in the sealed tube at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 5d (40 mg, 0.0383 mmol, 77%, α/β = 1/10) as a white foam. 5d-β isomer: $[\alpha]_D^{25} = 11.9$ (c 1.2, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.40 – 7.16 (m, 28H), 7.12 – 7.06 (m, 2H), 6.71 (s, 2H), 5.72 (dd, $J = 10.0, 7.9$ Hz, 1H), 4.92 (t, $J = 11.4$ Hz, 2H), 4.80 – 4.69 (m, 3H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 11.2$ Hz, 1H), 4.56 – 4.30 (m, 7H), 4.11 – 4.01 (m, 2H), 3.93 (t, $J = 11.4$ Hz, 2H), 3.81 – 3.69 (m, 2H), 3.60 – 3.48 (m, 2H), 3.44 (t, $J = 9.5$ Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 1.24 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 168.4, 139.2, 139.1, 138.6, 138.5, 138.3, 137.9, 135.8, 130.9, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.3, 127.2, 70.9, 70.8, 68.5, 67.2, 55.2, 21.2, 20.1. HRMS (ESI) Calculated for C$_{65}$H$_{70}$NaO$_{12}$ [M+Na]$^+$ 1065.4759, found 1065.4779.

**Neighboring group participation strategy for synthesis of the compound 5e**

As the general procedure A, donor 4d (99.3 mg, 0.15 mmol) and acceptor 2a (46.5 mg, 0.1 mmol) can be converted into the product 5e in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 5e (76 mg, 0.81 mmol, 81%, α/β = 17/1) as a colorless oil. 5e-α isomer: $[\alpha]_D^{25} = 28.0$ (c 4.5, CHCl$_3$); $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.44 – 7.24 (m, 25H), 6.84 (s, 2H), 5.56 (brs, 1H), 5.00 (d, $J = 10.8$ Hz, 1H), 4.96 – 4.72 (m, 6H), 4.73 – 4.46 (m, 5H), 3.99 (m, 2H), 3.85 (d, $J = 10.9$ Hz, 1H), 3.81 – 3.69 (m, 2H), 3.60 – 3.48 (m, 2H), 3.44 (t, $J = 9.5$ Hz, 2H), 3.35 (s, 3H), 2.28 (s, 3H), 2.26 (s, 6H), 1.24 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 169.4, 139.5, 138.8, 138.5, 138.3, 138.2, 138.1, 135.6, 130.8, 128.61, 128.55, 128.48, 128.45, 128.40, 128.24, 128.15, 128.0, 127.9, 127.83, 127.75, 98.0, 82.2, 80.1, 78.0, 77.8, 76.0, 75.6, 75.2, 73.5, 72.0, 70.2, 69.8, 68.0, 66.4, 55.3, 21.3, 20.0, 17.9. HRMS (ESI) Calculated for C$_{58}$H$_{64}$NaO$_{11}$ [M+Na]$^+$ 959.4341, found 959.4349.

**Neighboring group participation strategy for synthesis of the compound 5f**

As the general procedure A, donor 4d (99.3 mg, 0.15 mmol) and acceptor 2h (38.8 mg, 0.1
mmol) can be converted into the product 5f in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver 5f (83.3 mg, 0.097 mmol, 97%, α/β = 13/1) as a white solid. 5f-α isomer: [α]D25²⁵ = -6.4 (c 0.5, CHCl₃); ¹H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.23 (m, 10H), 6.84 (s, 2H), 5.58 (brs, 1H), 5.36 (brs, 1H), 5.01 (d, J = 1.9 Hz, 1H), 4.89 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 11.2 Hz, 1H), 4.62 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.07 (dd, J = 9.4, 3.3 Hz, 1H), 3.86 (m, 1H), 3.57 – 3.36 (m, 2H), 2.40 – 2.18 (m, 11H), 2.05 – 1.92 (m, 2H), 1.93 – 1.77 (m, 3H), 1.68 – 0.81 (m, 36H), 0.68 (s, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 169.6, 140.4, 139.4, 138.6, 138.3, 135.6, 131.0, 128.48, 128.46, 128.4, 128.2, 128.0, 127.8, 127.6, 122.1, 96.2, 80.4, 78.4, 77.6, 75.6, 71.9, 70.3, 68.0, 56.9, 56.3, 50.3, 42.5, 39.9, 39.7, 38.7, 37.4, 36.8, 36.3, 35.9, 32.1, 32.0, 29.6, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.3, 21.2, 20.1, 19.5, 18.9, 18.0, 12.0. HRMS (ESI) Calculated for C₅₇H₇₈NaO₆ [M+Na]+ 881.5691, found 881.5691.

Conformation-restrained strategy for synthesis of the compound 5g

As the general procedure A, donor 4e (50.4 mg, 0.075 mmol) and acceptor 2t (13.1 mg, 0.05 mmol) can be converted into the product 5g in the sealed tube at 23 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to deliver 5g (30.8 mg, 0.0415 mmol, 83%, α only) as a syrup. [α]D₂⁵ = 23.9 (c 1.1, CHCl₃); ¹H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.22 (m, 10H), 5.48 (d, J = 5.0 Hz, 1H), 4.57 (dd, J = 7.9, 2.4 Hz, 1H), 4.51 (d, J = 3.0 Hz, 1H), 4.28 (dt, J = 7.4, 2.2 Hz, 2H), 4.20 (dd, J = 12.5, 2.1 Hz, 1H), 4.10 (dd, J = 12.5, 1.7 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.83 (dd, J = 10.0, 3.0 Hz, 1H), 3.74 (d, J = 6.4 Hz, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.31 (s, 6H), 1.05 (s, 9H), 0.98 (s, 9H). ¹³C NMR (100 MHz, Chloroform-d) δ 139.2, 138.8, 128.41, 128.37, 128.2, 127.73, 127.66, 127.5, 109.4, 108.6, 98.2, 96.5, 77.7, 74.4, 73.3, 71.3, 71.2, 71.0, 70.8, 70.7, 67.4, 67.3, 67.1, 66.7, 27.8, 27.5, 26.2, 25.1, 24.7, 23.6, 20.8. HRMS (ESI) Calculated for C₄₀H₅₈NaO₁₁Si [M+Na]+ 765.3641, found 765.3643.

Conformation-restrained strategy for synthesis of the compound 5h

As the general procedure A, donor 4e (50.4 mg, 0.075 mmol) and acceptor 2h (19.4 mg, 0.05 mmol) can be converted into the product 5h in the sealed tube at 23 °C after 24 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 15/1) to deliver
5h (35.6 mg, 0.041 mmol, 82%, α only) as a syrup. [α]_D^25 = 36.8 (c 1.0, CHCl₃); ^1H NMR (400 MHz, Chloroform-d) δ 7.48 – 7.20 (m, 10H), 5.30 (brs, 1H), 4.88 (d, J = 3.7 Hz, 1H), 4.85 (d, J = 12.0 Hz, 1H), 4.73 (s, 2H), 4.67 (d, J = 11.9 Hz, 1H), 4.52 (d, J = 3.1 Hz, 1H), 4.22 (d, J = 13.4 Hz, 1H), 4.09 (d, J = 13.4 Hz, 1H), 3.96 (dd, J = 10.0, 3.7 Hz, 1H), 3.83 (dd, J = 10.0, 3.0 Hz, 1H), 3.70 (d, J = 2.1 Hz, 1H), 3.45 (m, 1H), 2.38 (td, J = 12.2, 11.3, 2.9 Hz, 1H), 2.16 (ddd, J = 13.3, 5.0, 2.2 Hz, 1H), 2.06 – 1.74 (m, 5H), 1.60 – 0.81 (m, 51H), 0.67 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 141.0, 139.3, 138.9, 128.4, 128.3, 127.73, 127.71, 127.5, 121.8, 96.0, 78.0, 76.7, 74.4, 73.6, 71.4, 71.2, 67.4, 67.3, 56.9, 56.3, 50.2, 42.4, 40.1, 39.9, 39.7, 37.2, 36.9, 36.3, 35.9, 32.02, 31.6, 30.3, 29.8, 28.4, 28.2, 27.8, 27.5, 24.4, 24.0, 23.6, 23.0, 22.7, 21.2, 20.8, 19.6, 18.9, 12.0. HRMS (ESI) Calculated for C₅₅H₈₄NaO₆Si [M+Na]^+ 891.5929, found 891.5932.

Conformation-restrained strategy for synthesis of the compound 5i

As the general procedure A, donor 4e (50.4 mg, 0.075 mmol) and acceptor 2i (11 mg, 0.05 mmol) can be converted into the product 5i in the sealed tube at 23 °C after 27 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 6/1) to deliver 5i (20.3 mg, 0.029 mmol, 58%, α only) as a colorless syrup. [α]_D^25 = 53.0 (c 1.3, CHCl₃); ^1H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.20 (m, 10H), 5.69 (d, J = 8.6 Hz, 1H), 4.82 (d, J = 11.8 Hz, 1H), 4.78 – 4.58 (m, 4H), 4.52 (d, J = 2.9 Hz, 1H), 4.39 (dd, J = 8.0, 4.0 Hz, 1H), 4.26 – 4.03 (m, 3H), 3.98 (dd, J = 10.1, 3.7 Hz, 1H), 3.77 (m, 2H), 3.64 (d, J = 8.6 Hz, 4H), 1.44 (s, 9H), 1.05 (s, 9H), 0.99 (s, 9H). 13C NMR (100 MHz, Chloroform-d) δ 171.1, 155.6, 139.0, 138.7, 128.4, 128.2, 127.8, 127.7, 127.6, 99.9, 80.1, 74.4, 73.6, 71.04, 71.02, 70.2, 68.0, 67.2, 54.3, 52.6, 29.8, 28.4, 27.8, 27.43, 27.39, 23.5, 20.8. HRMS (ESI) Calculated for C₃₇H₅₅NNaO₁₀Si [M+Na]^+ 724.3487, found 724.3482.

Additives-controlled strategy for synthesis of the compound 5j

As the general procedure C, donor 1c (105 mg, 0.15 mmol), acceptor 2g (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product 5j in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver 5j (69.3 mg, 73%, α/β > 20/1) as a colorless syrup. Analytical data for 9l was in accordance with that reported previously. 47

Additives-controlled strategy for synthesis of the compound 5k
As the general procedure C, donor 1c (105 mg, 0.15 mmol), acceptor 2u (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.3 mmol) and 0.6 mL DCM can be converted into the product 5k in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver 5k (60 mg, 61%, α/β > 20/1) as a colorless syrup. Analytical data for 9l was in accordance with that reported previously.47

**Additives-controlled strategy for synthesis of the compound 3g**

As the general procedure C, donor 1d (105 mg, 0.15 mmol), acceptor 2g (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product 3g in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver 3g (71 mg, 75%, α/β > 20/1) as a colorless syrup. Analytical data for 7g was in accordance with that reported previously.40

**Additives-controlled strategy for synthesis of the compound 5l**

Under the general procedure C, donor 1d (105 mg, 0.15 mmol), acceptor 2u (45 mg, 0.10 mmol), Kass catalyst (40 mg, 0.02 mmol), DMF(30 μL, 0.30 mmol) and 0.5 mL toluene can be converted into the product 5l in the sealed tube with freshly activated 4Å MS at 50 °C after 24 hours, and purified by size exclusion (DCM:MeOH = 1:1) to deliver 5l (76 mg, 80%, α/β = 11/1) as a colorless syrup. Analytical data for 9n was in accordance with that reported previously.48

**Synthesis of the compound 5m**

As the general procedure A, donor 4f (36.4 mg, 0.05 mmol) and acceptor 2a (35 mg, 0.075 mmol) can be converted into the product 5m in the sealed tube at 29 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver
5m (40.5 mg, 0.0404 mmol, 81%, \( \alpha/\beta = 1/7.5 \)) as a colorless syrup. Analytical data for 5m was in accordance with that reported previously.29

**Synthesis of the compound 5n**

As the general procedure A, donor 4h (47.3 mg, 0.065 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 5n in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver 5n (41.6 mg, 0.0415 mmol, 83%, \( \alpha/\beta = 1/11 \)) as a colorless syrup. Analytical data for 5n was in accordance with that reported previously.29

**Synthesis of the compound 5o**

As the general procedure A, donor 4i (40.4 mg, 0.065 mmol) and acceptor 2a (23.3 mg, 0.05 mmol) can be converted into the product 5o in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1.5/1) to deliver 5o (39 mg, 0.0435 mmol, 87%, \( \alpha/\beta = 1/3 \)) as a colorless syrup. Analytical data for 5o was in accordance with that reported previously.29

**Synthesis of the compound 7a**

As the general procedure A, donor 4f (54.6 mg, 0.075 mmol) and acceptor 6a (6.4 mg, 0.05 mmol) can be converted into the product 7a in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver 7a (31 mg, 0.047 mmol, 94%, \( \alpha/\beta = 1/8 \)) as a colorless syrup. Analytical data for 7a was in accordance with that reported previously.49

**TfOH-catalyzed glycosylation for synthesis of the compound 7a**
Donor 4f (43.7 mg, 0.06 mmol), acceptor 6a (6.4 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 μl, 0.025 mmol) was added. The mixture was warmed up to 0 °C and stirred for 5 hours at this temperature, and then quenched with Et3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 3/1) to deliver the product 7a (22.2 mg, 0.0335 mmol, 67%, α/β = 1/3) as a colorless syrup. Analytical data for 7a was in accordance with that reported previously.49

Synthesis of the compound 7b

As the general procedure A, donor 4g (54.6 mg, 0.075 mmol) and acceptor 6a (6.4 mg, 0.05 mmol) can be converted into the product 7b in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver 7b (28.1 mg, 0.0425 mmol, 84%, α/β > 20/1) as a colorless syrup. 7b-α isomer: [α]D25 = 43.1 (c 1.4, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.74 (d, J = 4.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.79 (td, J = 7.7, 1.7 Hz, 1H), 7.46 (m, 1H), 7.40 – 7.03 (m, 18H), 6.88 – 6.70 (m, 2H), 5.54 (dd, J = 10.3, 9.4 Hz, 1H), 5.36 (d, J = 3.5 Hz, 1H), 4.92 (d, J = 11.3 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.73 – 4.68 (m, 2H), 4.55 – 4.21 (m, 4H), 3.81 (dd, J = 9.6, 3.6 Hz, 1H), 3.77 (s, 3H), 3.67 – 3.45 (m, 2H), 13C NMR (100 MHz, Chloroform-d) δ 164.1, 155.3, 150.9, 149.9, 147.8, 138.5, 138.0, 137.8, 137.0, 128.6, 128.2, 128.2, 128.1, 128.0, 127.8, 127.49, 127.46, 127.0, 125.7, 118.5, 114.6, 96.8, 79.7, 79.3, 73.6, 75.6, 73.5, 71.8, 69.3, 68.7, 55.7. HRMS (ESI) Calculated for C40H40NO8 [M+H]+ 662.2748, found 662.2744.

Synthesis of the compound 7c

As the general procedure A, donor 4g (54.6 mg, 0.075 mmol) and acceptor 6b (7.8 mg, 0.05 mmol) can be converted into the product 7c in the sealed tube at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2/1) to deliver 7c (24 mg, 0.0348 mmol, 70%, α/β > 20/1) as a colorless syrup. 7c-α isomer: [α]D25 = 65.5 (c 0.75, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.73 (d, J = 4.6 Hz, 1H), 8.10 – 7.95 (m, 3H), 7.80 (td, J = 7.7, 1.8 Hz, 1H), 7.47 (m, 1H), 7.37 – 7.00 (m, 17H), 5.58 (t, J = 9.9 Hz, 1H), 5.48 (d, J = 3.5 Hz, 1H), 4.93 (d, J = 11.3 Hz, 1H), 4.84 (d, J = 12.1 Hz, 1H), 4.73 (d, J = 11.4 Hz, 1H), 4.66 (d, J = 12.1 Hz, 1H), 4.48 – 4.29 (m, 3H), 4.16 (dt, J = 10.3, 3.5 Hz, 1H), 3.90 (s, 3H), 3.84 (dd, J = 9.6, 3.5 Hz, 1H), 3.52 (m, 2H), 13C NMR (100 MHz, Chloroform-d) δ 166.8, 164.1, 160.3, 149.9, 147.6, 138.3, 137.9, 137.6, 137.0, 131.6, 128.6, 128.24, 128.19, 128.17, 128.0, 127.8, 127.6, 127.5, 127.4, 125.7, 118.5, 114.6, 96.8, 79.7, 79.3, 73.6, 75.6, 73.5, 71.8, 69.3, 68.7, 55.7. HRMS (ESI) Calculated for C40H40NO8 [M+H]+ 662.2748, found 662.2744.
TfOH-catalyzed glycosylation for synthesis of the compound 7c

Donor 4g (43.7 mg, 0.06 mmol) and acceptor 6b (7.8 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N₂ atmosphere at rt. The mixture was stirred for 10 min at -20 °C, and then TfOH (2.3 μl, 0.025 mmol) was added. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et₃N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to deliver the product 7c (17.0 mg, 0.025 mmol, 50%, α/β > 20/1) as a colorless syrup.

Synthesis of the compound 7d

As the general procedure A, donor 4h (54.6 mg, 0.075 mmol) and acceptor 6a (6.4 mg, 0.05 mmol) can be converted into the product 7d in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7d (30.4 mg, 0.046 mmol, 92%, α/β = 1/7) as a colorless syrup. The α and β isomer cannot be separated. 7d-β: 1H NMR (400 MHz, Chloroform-d) δ 8.81 (d, J = 4.6 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.9 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.38 – 7.16 (m, 15H), 7.09 – 7.05 (m, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.93 (d, J = 3.3 Hz, 1H), 4.97 (t, J = 9.2 Hz, 2H), 4.85 (dd, J = 18.5, 11.2 Hz, 2H), 4.61 (d, J = 11.4 Hz, 1H), 4.55 – 4.40 (m, 2H), 3.99 – 3.92 (m, 2H), 3.76 (d, J = 6.3 Hz, 2H). 13C NMR (100 MHz, Chloroform-d) δ 164.0, 155.4, 151.6, 150.2, 147.5, 138.4, 137.7, 137.6, 137.1, 128.42, 128.39, 128.36, 128.32, 128.30, 128.01, 127.98, 127.80, 127.75, 127.1, 125.7, 118.5, 114.64, 114.62, 103.1, 79.4, 78.8, 75.6, 73.8, 72.7, 72.4, 68.38, 68.35, 55.7. HRMS (ESI) Calculated for C₄₀H₄₀NO₈ [M+H]+ 662.2748, found 662.2766.

TfOH-catalyzed glycosylation for synthesis of the compound 7d

Donor 4h (43.7 mg, 0.06 mmol), acceptor 6a (6.4 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N₂ atmosphere at rt.
The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 μl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0 °C and stirred for 5 hours at this temperature, and then quenched with Et₃N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product **7d** (27.1 mg, 0.041 mmol, 82%, α/β = 1/3.5) as a colorless syrup.

**Synthesis of the compound 7e**

As the general procedure A, donor 4h (54.6 mg, 0.075 mmol), acceptor 6b (7.8 mg, 0.05 mmol), Kass catalyst (0.2 equiv, 20 mg, 0.01 mmol) and 2.5 ml DCM can be converted into the product **7e** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver **7e** (27.2 mg, 0.0394 mmol, 79%, α/β = 1/10) as a colorless syrup. **7e-β** isomer: [α]D²⁵ = 1.6 (c 2.3, CHCl₃); ¹H NMR (400 MHz, Chloroform-d) δ 8.71 (brs, 1H), 8.10 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.81 (t, J = 7.6 Hz, 1H), 7.47 (brs, 1H), 7.42 – 7.15 (m, 15H), 7.11 (d, J = 8.6 Hz, 2H), 5.94 (d, J = 3.3 Hz, 1H), 5.14 (d, J = 7.7 Hz, 1H), 5.00 – 4.76 (m, 3H), 4.62 (d, J = 11.4 Hz, 1H), 4.57 – 4.37 (m, 2H), 4.09 – 3.96 (m, 2H), 3.89 (s, 3H), 3.81 (m, 1H), 3.67 (d, J = 6.2 Hz, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 166.7, 164.0, 160.8, 150.3, 147.5, 138.2, 137.54, 137.48, 137.1, 131.7, 128.5, 128.42, 128.38, 128.3, 128.2, 128.0, 127.9, 127.8, 127.1, 125.6, 124.6, 116.2, 101.1, 79.2, 78.5, 75.7, 73.8, 73.1, 72.4, 68.3, 68.2, 52.0. HRMS (ESI) Calculated for C₄₁H₄₀NO₉ [M+H]+ 690.2698, found 690.2721.

**Synthesis of the compound 7f**

As the general procedure A, donor 4i (46.6 mg, 0.075 mmol) and acceptor 6a (6.4 mg, 0.05 mmol) can be converted into the product **7f** in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver **7f** (27.1 mg, 0.049 mmol, 98%, α/β = 1/9.6) as a colorless syrup. **7f-β** isomer: [α]D²⁵ = 54.0 (c 1.4, CHCl₃); ¹H NMR (400 MHz, Chloroform-d) δ 8.80 (brs, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.50 (m, 1H), 7.40 – 7.31 (m, 2H), 7.24 – 7.15 (m, 5H), 7.06 – 7.03 (m, 2H), 6.99 (d, J = 9.1 Hz, 2H), 6.84 (d, J = 9.1 Hz, 2H), 5.17 (dd, J = 9.8, 3.2 Hz, 1H), 5.09 (s, 1H), 5.03 (d, J = 12.3 Hz, 1H), 4.83 (dd, J = 13.9, 11.7 Hz, 2H), 4.70 (d, J = 11.0 Hz, 1H), 4.33 (d, J = 3.2 Hz, 1H), 3.94 (t, J = 9.5 Hz, 1H), 3.77 (s, 3H), 3.58 (m, 1H), 1.47 (d, J = 6.1 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 164.2, 155.3, 151.3, 150.1, 147.6, 138.1, 138.0, 136.9, 128.6, 128.4, 128.1, 128.0, 127.8, 127.6, 127.1, 125.4, 118.2, 114.6, 100.0, 78.4, 77.0, 75.5, 74.5, 75.0, 72.0, 55.7, 18.2. HRMS (ESI) Calculated for C₃₃H₃₄NO₇ [M+H]+ 556.2398, found 556.2320.
Synthesis of the compound 7g

As the general procedure A, donor 4i (46.6 mg, 0.075 mmol) and acceptor 6b (7.8 mg, 0.05 mmol) can be converted into the product 7g in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver 7g (28.3 mg, 0.0485 mmol, 97%, \(\alpha/\beta = 1/15\)) as a colorless syrup. 7g-\(\beta\) isomer: \(\left[\alpha\right]_{D}^{25} = 56.0\) (c 1.3, CHCl₃); \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.82 (d, \(J = 4.2\) Hz, 1H), 8.01 (d, \(J = 8.8\) Hz, 2H), 7.96 (d, \(J = 7.8\) Hz, 1H), 7.81 (t, \(J = 7.7\) Hz, 1H), 7.59 – 7.30 (m, 1H), 7.39 – 7.30 (m, 2H), 7.25 – 7.14 (m, 5H), 7.11 – 7.05 (m, 3H), 7.03 (d, \(J = 8.8\) Hz, 2H), 5.30 (s, 1H), 5.20 (dd, \(J = 9.8, 3.2\) Hz, 1H), 5.02 (d, \(J = 12.2\) Hz, 1H), 4.93 – 4.78 (m, 2H), 4.72 (d, \(J = 11.0\) Hz, 1H), 4.36 (d, \(J = 3.1\) Hz, 1H), 3.97 (t, \(J = 9.5\) Hz, 1H), 3.89 (s, 3H), 3.67 (m, 1H), 1.48 (d, \(J = 6.1\) Hz, 3H). \(^13\)C NMR (100 MHz, Chloroform-d) \(\delta\) 166.8, 164.2, 160.6, 150.2, 147.6, 138.0, 137.9, 137.0, 131.7, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.4, 115.8, 98.1, 78.2, 75.5, 75.2, 72.3, 52.1, 18.2. HRMS (ESI) Calculated for C₃₄H₃₄NO₈ [M+H]+ 584.2279, found 584.2276.

Synthesis of the compound 7h

As the general procedure A, donor 4i (46.6 mg, 0.075 mmol) and acceptor 6c (6.7 mg, 0.05 mmol) can be converted into the product 7h in the sealed tube at 40 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2.5/1) to deliver 7h (23 mg, 0.041 mmol, 82%, \(\alpha/\beta = 1/12\)) as a colorless syrup. 7h-\(\beta\) isomer: \(\left[\alpha\right]_{D}^{25} = 56.4\) (c 1.2, CHCl₃); \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.82 (d, \(J = 4.5\) Hz, 1H), 7.96 (d, \(J = 7.9\) Hz, 1H), 7.81 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.51 (ddd, \(J = 7.6, 4.7, 1.2\) Hz, 1H), 7.38 – 7.28 (m, 2H), 7.24 – 6.97 (m, 8H), 6.94 – 6.73 (m, 2H), 5.15 (dd, \(J = 9.8, 3.3\) Hz, 1H), 5.12 (d, \(J = 0.8\) Hz, 1H), 5.05 (d, \(J = 12.3\) Hz, 1H), 4.92 – 4.79 (m, 2H), 4.70 (d, \(J = 10.9\) Hz, 1H), 4.46 – 4.29 (m, 1H), 3.95 (t, \(J = 9.5\) Hz, 1H), 3.62 – 3.52 (m, 1H), 1.46 (d, \(J = 6.1\) Hz, 3H). \(^13\)C NMR (101 MHz, Chloroform-d) \(\delta\) 164.2, 159.3 (dd, \(J = 243.9, 10.7\) Hz), 154.4 (dd, \(J = 250.2, 11.8\) Hz), 150.1, 147.6 (dd, \(J = 10.7, 3.6\) Hz), 138.0 (d, \(J = 5.2\) Hz), 137.0, 128.8, 128.4, 128.25, 128.16, 128.1, 127.9, 127.7, 127.1, 125.4, 119.5 (dd, \(J = 9.5, 1.9\) Hz), 111.0 (dd, \(J = 22.6, 3.9\) Hz), 105.3 (dd, \(J = 26.9, 22.0\) Hz), 100.5, 78.1, 76.7, 75.4, 75.0, 74.8, 72.3, 18.2. HRMS (ESI) Calculated for C₃₂H₂₉F₂NNaO₆ [M+Na]+ 584.1855, found 584.1854.

Synthesis of the compound 7i
As the general procedure A, donor 4j (62.2 mg, 0.1 mmol) and acceptor 6a (6.4 mg, 0.05 mmol) can be converted into the product 7i in the sealed tube at 30 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7i (27.5 mg, 0.0495 mmol, 99%, α/β > 20/1) as a colorless syrup. 7i-α isomer: [α]D25 = -27.7 (c 1.7, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.78 (d, J = 4.6 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.84 (td, J = 7.8, 1.8 Hz, 1H), 7.49 (ddd, J = 7.6, 4.7, 1.2 Hz, 1H), 7.43 – 7.13 (m, 10H), 6.93 – 6.80 (m, 4H), 5.65 (t, J = 9.8 Hz, 1H), 5.43 (d, J = 1.9 Hz, 1H), 4.87 (d, J = 12.4 Hz, 1H), 4.77 (d, J = 12.4 Hz, 1H), 4.71 – 4.51 (m, 2H), 4.28 (dd, J = 9.8, 3.1 Hz, 1H), 4.15 (m, 1H), 4.00 (t, J = 2.3 Hz, 1H), 3.77 (s, 3H), 1.26 (d, J = 6.2 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 164.7, 155.0, 150.2, 149.9, 149.9, 148.0, 138.2, 138.2, 137.1, 128.5, 128.3, 128.1, 127.8, 127.61, 127.56, 127.0, 125.7, 117.5, 114.7, 97.3, 74.8, 74.6, 73.3, 72.3, 67.5, 55.7, 17.8. HRMS (ESI) Calculated for C33H34NO7 [M+H]+ 556.2330, found 556.2324.

Synthesis of the compound 7j

As the general procedure A, donor 4i (46.6 mg, 0.075 mmol) and acceptor 6d (11 mg, 0.05 mmol) can be converted into the product 7j in the sealed tube with freshly activated 4Å MS at 50 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7j (32 mg, 0.05 mmol, quant, α/β = 1/10) as a colorless syrup. 7j-β isomer: [α]D25 = 61.3 (c 1.1, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.81 (d, J = 4.3 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.51 (m, 1H), 7.33 (m, 2H), 7.25 – 7.16 (m, 6H), 7.15 – 7.03 (m, 4H), 5.29 (s, 1H), 5.19 (dd, J = 9.7, 3.2 Hz, 1H), 5.00 (d, J = 12.2 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.72 (d, J = 11.0 Hz, 1H), 4.36 (d, J = 3.0 Hz, 1H), 3.96 (t, J = 9.5 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.66 (m, 1H), 1.47 (d, J = 6.1 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 168.3, 167.0, 164.2, 159.2, 150.2, 147.5, 138.0, 137.8, 137.0, 135.3, 131.5, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.7, 117.8, 116.6, 98.3, 98.2, 78.1, 76.8, 75.4, 75.2, 72.4, 52.94, 52.90, 52.64, 52.59, 18.2. HRMS (ESI) Calculated for C36H36NO6 [M+H]+ 642.2334, found 642.2333.

TfOH-catalyzed glycosylation for synthesis of the compound 7j

Donor 4i (37.3 mg, 0.06 mmol) and acceptor 6d (11 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N2 atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 μl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et3N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product 7j (26.0 mg, 0.0405 mmol, 81%, α/β = 1/5.5) as a colorless
syrup.

**Synthesis of the compound 7k**

As the general procedure A, donor 4j (62.1 mg, 0.10 mmol) and acceptor 6d (11 mg, 0.05 mmol) can be converted into the product 7k in the sealed tube with freshly activated 4Å MS at 55 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7k (27.2 mg, 0.0425 mmol, 85%, α/β > 20/1) as a brown syrup. 7k-α isomer: [α]_D^25 = -46.3 (c 1.0, CHCl₃); ¹H NMR (400 MHz, Chloroform-d) δ 8.81 (d, J = 4.3 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.51 (m, 1H), 7.33 (m, 2H), 7.25 – 7.16 (m, 6H), 7.15 – 7.03 (m, 4H), 5.29 (s, 1H), 5.19 (dd, J = 9.7, 3.2 Hz, 1H), 5.00 (d, J = 12.2 Hz, 1H), 4.91 – 4.77 (m, 2H), 4.72 (d, J = 11.0 Hz, 1H), 4.36 (d, J = 3.0 Hz, 1H), 3.96 (t, J = 9.5 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.66 (m, 1H), 1.24 (d, J = 6.1 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 168.3, 167.0, 164.6, 158.3, 149.9, 147.7, 138.0, 137.8, 137.2, 135.4, 131.6, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.2, 125.4, 124.7, 117.8, 116.6, 996.4, 76.8, 74.3, 74.1, 73.4, 72.4, 68.0, 53.0, 52.6, 52.59, 17.7. HRMS (ESI) Calculated for C₃₆H₃₆NO₆ [M+H]+ 642.2339, found 642.2344.

**TfOH-catalyzed glycosylation for synthesis of the compound 7k**

Donor 4j (46.6 mg, 0.075 mmol), acceptor 6d (11 mg, 0.05 mmol), freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N₂ atmosphere at rt. The mixture was stirred for 10 min at -20 °C and then TfOH (2.3 μl, 0.025 mmol) was added to the stirred solution. The mixture was warmed up to 0°C and stirred for 5 hours at this temperature, and then quenched with Et₃N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to deliver the product 7k (17.0 mg, 0.0265 mmol, 53%, α/β > 20/1) as a brown syrup.

**Synthesis of the compound 7l**

As the general procedure A, donor 4f (54.6 mg, 0.075 mmol) and acceptor 6e (11.2 mg, 0.05
mmol) can be converted into the product 7l in the sealed tube at 30 °C after 36 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver 7l (28.3 mg, 0.0374 mmol, 75%, α/β = 1/10) as a colorless syrup. 7l-β isomer: [α]D25 = 14.8 (c 0.9, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.77 – 8.73 (m, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.46 (dd, J = 7.6, 4.7, 1.3 Hz, 1H), 7.40 – 7.00 (m, 17H), 6.78 (td, J = 7.6, 1.4 Hz, 1H), 5.57 (t, J = 9.8 Hz, 1H), 5.48 (d, J = 3.4 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 4.83 (d, J = 12.1 Hz, 1H), 4.76 (d, J = 11.5 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.57 – 4.32 (m, 3H), 4.20 (dt, J = 10.3, 3.5 Hz, 1H), 3.83 (dd, J = 9.6, 3.4 Hz, 1H), 3.58 – 4.32 (m, 2H). 13C NMR (100 MHz, Chloroform-d) δ 164.0, 155.8, 150.0, 147.8, 139.6, 138.3, 138.2, 137.7, 137.0, 129.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 126.3, 126.2, 125.6, 124.2, 115.2, 96.8, 87.3, 80.0, 78.4, 75.3, 73.6, 73.4, 71.3, 70.1, 68.5. HRMS (ESI) Calculated for C39H37INO7 [M+H]+ 758.1609, found 758.1617.

**Synthesis of the compound 7m**

As the general procedure A, donor 4h (54.6 mg, 0.075 mmol) and acceptor 6f (13.5 mg, 0.05 mmol) can be converted into the product 7m in the sealed tube at 40°C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver 7m (35.5 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. 7m-β isomer: [α]D25 = 46.2 (c 0.8, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.85 (d, J = 4.4 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.85 (t, J = 7.7 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.56 – 7.12 (m, 24H), 7.06 (t, J = 7.8 Hz, 1H), 6.00 (d, J = 3.1 Hz, 1H), 5.49 (d, J = 7.6 Hz, 1H), 5.14 (d, J = 10.7 Hz, 1H), 5.00 – 4.90 (m, 2H), 4.62 (d, J = 11.1 Hz, 1H), 4.53 (t, J = 8.4 Hz, 1H), 4.44 (d, J = 11.7 Hz, 1H), 4.36 (d, J = 11.6 Hz, 1H), 3.99 (t, J = 6.4 Hz, 1H), 3.89 (dd, J = 9.4, 3.1 Hz, 1H), 3.62 (d, J = 6.3 Hz, 2H). 13C NMR (100 MHz, Chloroform-d) δ 163.8, 151.1, 150.4, 147.5, 141.7, 138.5, 137.5, 137.4, 137.3, 136.4, 129.2, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.2, 127.1, 126.3, 126.0, 125.7, 123.5, 110.3, 100.7, 85.8, 80.4, 77.8, 75.7, 73.8, 72.8, 72.3, 68.2, 67.8. HRMS (ESI) Calculated for C43H39INO7 [M+H]+ 808.1766, found 808.1770.

**Synthesis of the compound 7n**

As the general procedure A, donor 4j (62.2 mg, 0.1 mmol) and acceptor 6e (11.2 mg, 0.05 mmol) can be converted into the product 7n in the sealed tube at 40 °C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3.5/1) to deliver 7n (30 mg, 0.046 mmol, 92%, α/β > 20/1) as a white foam. 7n-α isomer: [α]D25 = -16.0 (c 1.8, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.81 (dd, J = 4.8, 1.6 Hz, 1H), 8.11 (d, J = 7.8 Hz,
1H), 7.86 (td, J = 7.7, 1.6 Hz, 1H), 7.74 (dd, J = 7.9, 1.6 Hz, 1H), 7.51 (ddd, J = 7.7, 4.7, 1.2 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.14 (m, 9H), 7.09 (dd, J = 8.3, 1.4 Hz, 1H), 6.77 (td, J = 7.6, 1.4 Hz, 1H), 5.68 (t, J = 9.9 Hz, 1H), 5.48 (d, J = 2.0 Hz, 1H), 4.89 (d, J = 12.3 Hz, 1H), 4.76 (d, J = 12.2 Hz, 1H), 4.69 (d, J = 12.2 Hz, 1H), 4.61 (d, J = 12.2 Hz, 1H), 4.38 (dd, J = 9.9, 3.0 Hz, 1H), 4.21 – 4.03 (m, 2H), 1.26 (d, J = 6.2 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 164.5, 155.3, 149.9, 147.8, 139.4, 138.10, 138.08, 137.2, 137.1, 129.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.1, 125.7, 124.2, 115.4, 97.9, 87.4, 76.5, 74.9, 74.4, 73.5, 72.3, 68.2, 17.8. HRMS (ESI) Calculated for C32H31INO6 [M+H]+ 652.1191, found 652.1180.

Synthesis of the compound 7o

As the general procedure A, donor 4g (54.6 mg, 0.075 mmol) and acceptor 6g (16.2 mg, 0.05 mmol) can be converted into the product 7o in the sealed tube at 40°C after 40 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7o (37.9 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. 7o-β isomer: [α]D25 = 12.6 (c 0.75, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.83 (d, J = 4.6 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.95 (dd, J = 8.0, 1.2 Hz, 1H), 7.83 (td, J = 7.8, 1.5 Hz, 1H), 7.50 (dd, J = 7.7, 4.5 Hz, 1H), 7.44 – 7.08 (m, 19H), 7.03 (td, J = 7.6, 1.7 Hz, 1H), 6.91 – 6.81 (m, 2H), 5.95 (d, J = 3.3 Hz, 1H), 5.14 (d, J = 7.7 Hz, 1H), 5.01 (d, J = 10.9 Hz, 1H), 4.87 (dd, J = 17.1, 11.2 Hz, 2H), 4.63 (d, J = 11.4 Hz, 1H), 4.54 (d, J = 11.6 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.81 (dd, J = 9.6, 3.4 Hz, 1H), 3.71 (dd, J = 6.3, 4.1 Hz, 2H), 1.91 (s, 3H), 1.90 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 164.0, 156.6, 150.3, 147.6, 145.8, 139.2, 138.9, 138.5, 137.7, 137.65, 137.4, 137.2, 130.0, 128.65, 128.63, 128.49, 128.45, 128.41, 128.39, 128.32, 128.26, 128.2, 128.13, 128.07, 127.95, 127.86, 127.83, 127.77, 127.74, 127.7, 127.2, 125.8, 115.64, 115.60, 101.9, 101.3, 79.4, 79.0, 75.6, 73.9, 73.0, 72.4, 68.6, 68.5, 20.7. HRMS (ESI) Calculated for C47H45INO7 [M+H]+ 862.2235, found 862.2279.

Synthesis of the compound 7p

As the general procedure A, donor 4g (54.6 mg, 0.075 mmol) and acceptor 6h (15 mg, 0.05 mmol) can be converted into the product 7p in the sealed tube at 30 °C after 30 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to deliver 7p (36.6 mg, 0.044 mmol, 88%, α/β = 1/10) as a syrup. 7p-β isomer: [α]D25 = 22.7 (c 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 8.81 (d, J = 4.6 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.3 Hz, 1H), 7.49 (dd, J = 7.7, 4.6 Hz, 1H), 7.38 – 7.16 (m, 15H), 7.08 – 6.99 (m, 4H), 5.94 (d, J = 3.3 Hz, 1H), 5.04 (d, J = 7.7 Hz, 1H), 4.99 – 4.92 (m, 2H), 4.88 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.53 (m, 2H), 4.43 (d, J = 11.7 Hz, 1H), 4.00 – 3.93 (m, 2H), 3.78 (dd, J
Synthesis of the compound 7q

As the general procedure B, donor 4i (62.2 mg, 0.1 mmol) and acceptor 6i (22.6 mg, 0.05 mmol) can be converted into the product 7q in the sealed tube with freshly activated 4Å MS at 60°C after 60 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 1/1) to deliver 7q (40.5 mg, 0.046 mmol, 92%, α/β = 1/13) as a white foam.

7q-β isomer: [α]D25 = -42.8 (c 0.75, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.81 (d, J = 4.5 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 7.86 – 7.80 (m, 3H), 7.60 – 7.30 (m, 13H), 7.29 – 7.11 (m, 8H), 7.06 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.59 (s, 1H), 5.93 (dd, J = 9.4, 3.4 Hz, 1H), 5.61 (d, J = 2.0 Hz, 1H), 5.14 (s, 4H), 4.90 (d, J = 11.1 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.70 (d, J = 11.1 Hz, 1H), 4.61 (dd, J = 3.4, 2.0 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.97 (t, J = 9.4 Hz, 1H).

13C NMR (100 MHz, Chloroform-d) δ 176.9, 164.0, 162.5, 161.3, 161.1, 159.5, 156.7, 149.8, 148.0, 138.4, 138.2, 137.1, 136.3, 135.8, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 126.9, 125.6, 124.1, 115.3, 111.0, 107.6, 104.6, 98.8, 97.5, 78.9, 75.8, 75.0, 74.9, 73.2, 70.6, 70.3, 69.5, 18.2. HRMS (ESI) Calculated for C55H47NNaO10 [M+Na]+ 904.3092, found 904.3128.

Synthesis of the compound 7r

As the general procedure B, donor 4g (90.9 mg, 0.125 mmol) and acceptor 6j (28 mg, 0.05 mmol) can be converted into the product 7r (44.2 mg, 0.0404 mmol, 81%, β/α > 20/1) as a syrup.

7r-β isomer: [α]D25 = -4.4 (c 1.4, CHCl3); 1H NMR (400 MHz, Chloroform-d) δ 8.84 (d, J = 4.4 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.84 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 7.5 Hz, 2H), 7.56 – 7.05 (m, 29H), 6.58 (d, J = 2.2 Hz, 1H), 6.48 (d, J = 2.2 Hz, 1H), 5.97 (d, J = 3.3 Hz, 1H), 5.29 (s, 2H), 5.19 – 5.03 (m, 6H), 4.96 (d, J = 10.8 Hz, 1H), 4.88 (dd, J = 17.2, 11.1 Hz, 2H), 4.63 (d, J = 11.5 Hz, 1H), 4.58 – 4.41 (m, 2H), 4.07 – 3.98 (m, 2H), 3.83 (dd, J = 9.6, 3.4 Hz, 1H), 3.69 (d, J = 6.3 Hz, 2H). 13C NMR (100 MHz, Chloroform-d) δ 174.0, 163.9, 162.8, 159.9, 158.9, 158.7, 153.4, 150.2, 147.3, 139.9, 138.2, 137.6, 137.5, 137.3, 137.0, 136.5, 135.8, 130.3, 129.0, 128.9, 128.7,
128.6, 128.50, 128.47, 128.45, 128.39, 128.26, 128.24, 128.1, 127.92, 127.90, 127.8, 127.7, 127.2, 126.8, 125.7, 125.4, 116.4, 110.2, 101.4, 98.3, 94.0, 79.3, 78.6, 75.8, 74.1, 73.9, 73.0, 72.4, 70.9, 70.6, 68.28, 68.24. HRMS (ESI) Calculated for C_{69}H_{60}NO_{12} [M+H]^+ 1094.4110, found 1094.4154.

**Synthesis of the compound 7s**

As the general procedure B, donor 4j (77.6 mg, 0.125 mmol) and acceptor 6k (23.4 mg, 0.05 mmol) can be converted into the product 7s in the sealed tube with freshly activated 4Å MS at 50 °C after 72 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4/1) to deliver 7s (37.6 mg, 0.042 mmol, 84%, α/β = 8/1) as a yellow syrup. 7s-α isomer: [α]_D{25} = -30.4 (c 0.8, CHCl₃); 1H NMR (400 MHz, Chloroform-d) δ 8.79 (d, J = 4.5 Hz, 1H), 8.13 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 1.7 Hz, 1H), 7.86 (t, J = 7.7 Hz, 1H), 7.78 (d, J = 2.6 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.18 (m, 12H), 7.00 (d, J = 2.7 Hz, 1H), 5.74 – 5.55 (m, 2H), 4.88 (d, J = 12.2 Hz, 1H), 4.77 (d, J = 12.2 Hz, 1H), 4.61 (q, J = 12.1 Hz, 2H), 4.25 (dd, J = 9.7, 3.1 Hz, 1H), 4.08 – 3.94 (m, 2H), 2.74 – 2.69 (m, 4H), 2.49 (s, 3H), 1.89 – 1.78 (m, 3H), 1.51 – 1.34 (m, 8H), 1.32 – 1.20 (m, 7H), 1.01 – 0.93 (m, 6H). 13C NMR (100 MHz, Chloroform-d) δ 182.1, 179.6, 172.3, 172.1, 164.4, 160.2, 152.4, 150.4, 149.9, 147.7, 145.9, 138.0, 137.8, 137.0, 136.1, 134.3, 131.0, 128.6, 128.4, 128.2, 128.1, 127.5, 127.3, 127.2, 126.0, 125.8, 123.5, 120.7, 117.6, 112.4, 96.8, 74.4, 74.2, 73.6, 72.5, 68.4, 34.5, 34.4, 31.6, 24.4, 24.3, 22.6, 21.8, 17.8, 14.1. HRMS (ESI) Calculated for C_{53}H_{56}NO_{12} [M+H]^+ 898.3797, found 898.3819.

**Synthesis of the compound 7t**

As the general procedure B, donor 4j (77.6 mg, 0.125 mmol) and acceptor 6j (28 mg, 0.05 mmol) can be converted into the product 7t in the sealed tube with freshly activated 4Å MS at 55 °C after 72 hours, and purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2/1) to deliver 7t (40.5 mg, 0.041 mmol, 82%, α/β > 20/1) as a syrup. 7t-α isomer: [α]_D{25} = -34.0 (c 1.2, CHCl₃); 1H NMR (400 MHz, Chloroform-d) δ 8.80 (d, J = 4.7 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.9 Hz, 2H), 7.88 (td, J = 7.7, 1.6 Hz, 1H), 7.63 (t, J = 7.3 Hz, 2H), 7.52 (m, 1H), 7.48 – 7.13 (m, 24H), 7.03 (d, J = 9.0 Hz, 2H), 6.59 (d, J = 2.2 Hz, 1H), 6.47 (d, J = 2.2 Hz, 1H), 5.68 (t, J = 9.8 Hz, 1H), 5.60 (d, J = 1.9 Hz, 1H), 5.29 (s, 2H), 5.11 (s, 2H), 5.09 (s, 2H), 4.91 (d, J = 12.4 Hz, 1H), 4.79 (d, J = 12.4 Hz, 1H), 4.75 – 4.53 (m, 2H), 4.33 (dd, J = 9.8, 3.0 Hz, 1H), 4.12 (m, 1H), 4.07 – 3.99 (m, 1H), 1.28 (d, J = 6.2 Hz, 3H). 13C NMR (100 MHz, Chloroform-d) δ 174.0, 164.5, 162.8, 159.88, 158.86, 157.4, 153.4, 149.7, 147.6, 139.8, 138.1, 138.0, 137.5, 137.0, 136.5, 135.7, 130.3, 129.1, 128.9, 128.7, 128.63, 128.57, 128.56, 128.34,
Comparison of the different imidate donors’ reactivity under Kass catalyst-catalyzed conditions

Donor 1a (36.0 mg, 0.05 mmol) and 1c (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst C10 (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.6 ml) was added to the sealed tube under N₂ atmosphere at 0 °C. The reaction mixture was stirred for 10 hours in the sealed tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the donor 1a (29 mg, 0.0405 mmol, 81% recovered) and product 3a (35.5 mg, 0.036 mmol, 72%).

Donor 8a (34.3 mg, 0.05 mmol) and 1c (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.6 ml) was added to the sealed tube under N₂ atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the donor 8a (4.1 mg, 0.006 mmol, 12% recovered), 1c (14.3 mg, 0.02 mmol, 40% recovered) and product 3a (45.4 mg, 0.046 mmol, 92%).

Donor 8b (32.9 mg, 0.05 mmol) and 1c (35.6 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.6 ml) was added to the sealed tube under N₂ atmosphere at -60 °C. The reaction mixture was stirred for 10 hours in the sealed
tube and gradually warmed up to rt. for several hours, and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the donor 8b (16.4 mg, 0.025 mmol, 50% recovered) and product 3a (42.4 mg, 0.043 mmol, 86%).

Donor 8a (34.3 mg, 0.05 mmol) and 4b (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.6 ml) was added to the sealed tube under N₂ atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the donor 4b (32.7 mg, 0.0427 mmol, 85.4% recovered) and product 3a (37.5 mg, 0.038 mmol, 76%).

Donor 8b (32.9 mg, 0.05 mmol) and 4b (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene and Kass catalyst (0.1 equiv, 10 mg, 0.005 mmol) were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.6 ml) was added to the sealed tube under N₂ atmosphere at 0 °C. The reaction mixture was stirred for 12 hours in the sealed tube and gradually warmed up to rt and monitored by TLC analysis. The resulting mixture was transferred into round-bottomed flask and concentrated in vacuo, and then the residue was purified by silica gel column chromatography to deliver the donor 4b (32.3 mg, 0.0422 mmol, 84.4% recovered) and product 3a (37.5 mg, 0.038 mmol, 76%).

Comparison of the different imidate donors’ reactivity under TMSOTf catalyst-catalyzed conditions

Donor 8a (34.3 mg, 0.05 mmol) and 4b (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene, freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N₂ atmosphere at rt. The mixture was stirred for 10 min at 0 °C and then TMSOTf (1.4 μl, 0.0075 mmol) was added to the stirred solution. The mixture was stirred for 1.5 hours at this temperature, and
then quenched with Et$_3$N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography to deliver the product 3a (32.1 mg, 0.0325 mmol, 65%) and 5b (16.7 mg, 0.016 mmol, 32%).

Donor 8b (32.9 mg, 0.05 mmol) and 4b (38.4 mg, 0.05 mmol) co-evaporated twice with toluene, acceptor 2a (23.3 mg, 0.05 mmol) co-evaporated twice with toluene, freshly activated 4Å MS and dry DCM (1 ml) were successively added to the round-bottom flask under N$_2$ atmosphere at rt. The mixture was stirred for 10 min at 0 °C and then TMSOTf (1.4 μl, 0.0075 mmol) was added to the stirred solution. The mixture was stirred for 1.5 hours at this temperature, and then quenched with Et$_3$N. The resulting mixture was evaporated to yield the crude product which was purified by silica gel column chromatography to deliver the product 3a (35.0 mg, 0.0355 mmol, 71%) and 5b (13 mg, 0.0125 mmol, 25%).

**Synthesis of compound 9**

The compound S27$^{[37]}$ (570.7 mg, 1 mmol) was dissolved in acetone and H$_2$O (10 ml, acetone: H$_2$O = 8:1, V/V), to which NBS (635 mg, 3.5 mmol) was added at 0 °C. The resulting mixture was stirred for 1 hour, and was then quenched with saturated aqueous Na$_2$S$_2$O$_3$. The organic phase was washed with saturated aqueous NaHCO$_3$, brine successively, and the organic phases was separated and combined, dried over anhydrous Na$_2$SO$_4$. Filtration and evaporation yielded the crude product which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/1) to deliver the hemiacetal intermediate (354.1 mg, 0.74 mmol, 74%; brsm: 90%). Cs$_2$CO$_3$ (265.2 mg, 0.814 mmol) followed by PTFACl (228 mg, 1.1 mmol) was added to a solution of the above hemiacetal intermediate (354.1 mg, 0.74 mmol) in acetone (7 ml). The mixture was stirred for 4 hours at 0 °C, and then the suspension was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 8/1 to 4/1, with Et$_3$N) to give the compound 9 (270.4 mg, 0.555 mmol, 75%) as a colorless syrup. 9-α isomer: [α]$_D^{25}$ = -23.5 (c 1.0, acetone); $^1$H NMR (400 MHz, Acetone-$_d_6$) δ 8.07 (d, $J$ = 7.7 Hz, 2H), 7.93 (d, $J$ = 7.7 Hz, 2H), 7.70 (t, $J$ = 7.4 Hz, 1H), 7.58 (dt, $J$ = 15.5, 7.5 Hz, 3H), 7.43 (t, $J$ = 7.7 Hz, 2H), 7.36 (t, $J$ = 7.8 Hz, 2H), 7.27 – 7.18 (m, 5H), 7.14 (t, $J$ = 7.4 Hz, 1H), 6.95 (d, $J$ = 7.6 Hz, 2H), 6.48 (s, 1H), 5.89 (s, 1H), 5.75 (dd, $J$ = 9.8, 3.2 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.55 (t, $J$ = 9.7 Hz, 1H), 4.23 (dd, $J$ = 7.1, 5.4 Hz, 1H), 4.06 – 3.92 (m, 3H). $^{13}$C NMR (100 MHz, Acetone-$_d_6$) δ 165.1, 164.9, 143.6, 138.2, 133.7, 129.7, 129.5, 129.4, 128.9, 128.7, 128.1, 128.2, 127.9, 127.6, 124.4, 119.3, 94.7, 75.6,
One-pot synthesis of trisaccharide:

Donor 8c (69.9 mg, 0.1 mmol) co-evaporated twice with toluene, compound 9 (32.5 mg, 0.05 mmol) co-evaporated twice with toluene, Kass catalyst (0.15 equiv, 15 mg, 0.075 mmol) and freshly activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.8 ml) was added to the sealed tube under N₂ atmosphere at 15 °C. The reaction mixture was stirred and gradually warmed up to rt. The reaction was monitored by TLC analysis. When TLC shows that the donor 9c is consumed completely (around 17h), the acceptor 2a (0.1 mmol, 46.5 mg), 0.1 equiv. Kass catalyst were added to the reaction mixture, and the mixture was gradually warmed up to 50 °C and stirred for another several hours (about 2 d.). The resulting mixture was cooled to rt and then transferred into round-bottomed flask and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver the product 10 (26.3 mg, 0.018 mmol, 36%) as a colorless oil. 10: [α]_D25 = 25 (c = 1.0, CHCl₃);

1H NMR (400 MHz, CDCl₃) δ 8.08 (dd, J = 12.5, 4.7 Hz, 4H), 7.93 (d, J = 7.3 Hz, 2H), 7.57 – 7.47 (m, 5H), 7.39 – 7.07 (m, 39H), 5.80 (s, 1H), 5.71 (m, 2H), 5.16 (d, J = 1.6 Hz, 1H), 5.04 – 4.93 (m, 3H), 4.79 (m, 5H), 4.67 – 4.57 (m, 4H), 4.55 – 4.41 (m, 4H), 4.17 – 4.07 (m, 3H), 4.03 – 3.64 (m, 10H), 3.61 – 3.52 (m, 2H), 3.37 (s, 3H). 13C NMR (100 MHz, CDCl₃) δ 165.5, 165.40, 165.37, 138.9, 138.46, 138.42, 138.34, 138.26, 137.9, 130.1, 129.8, 129.7, 128.46, 128.43, 128.39, 128.37, 128.31, 128.29, 128.2, 128.1, 128.0, 127.9, 127.7, 127.66, 127.63, 127.6, 98.1, 98.0, 97.9, 82.2, 80.4, 78.0, 77.8, 75.7, 75.4, 75.1, 74.9, 74.3, 73.51, 73.46, 73.2, 72.8, 72.0, 71.3, 70.7, 70.6, 69.9, 68.9, 68.6, 66.3, 55.2. HRMS (ESI) Calculated for C₈₉H₈₈O₂₉Na [M+Na]⁺ 1483.5818, found 1483.5827.

Donor 8d (67.2 mg, 0.1 mmol) co-evaporated twice with toluene, compound 9 (32.5 mg, 0.05
mmol) co-evaporated twice with toluene, Kass catalyst (0.15 equiv, 15 mg, 0.075 mmol) and freshly activated 4Å MS were added to the sealed tube, and then the sealed tube was evacuated and flushed with N₂ for three times. Dry DCM (0.8 ml) was added to the sealed tube under N₂ atmosphere at 15 °C. The reaction mixture was stirred and gradually warmed up to rt. The reaction was monitored by TLC analysis. When TLC shows that the donor 8d is consumed completely (around 17h), the acceptor 2a (0.1 mmol, 46.5 mg), 0.1 equiv. Kass catalyst were added to the reaction mixture, and the mixture was gradually warmed up to 50 °C and stirred for another several hours (about 2d). The resulting mixture was cooled to rt, transferred into round-bottomed flask and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to deliver the product 10 (32.9 mg, 0.0225 mmol, 45%) as a colorless oil.

References:


$^{1}$H-NMR, $^{13}$C-NMR, of 1b

(400 MHz, Acetone-$d_6$)
(100 MHz, Acetone-\textit{d}_6)
$^1$H-NMR, $^{13}$C-NMR of 1h

400 MHz, CDCl$_3$
$^{1}$H-NMR, $^{13}$C-NMR of 1j-$\alpha$

(400 MHz, Acetone-\textit{d$_6$})
$^{1}$H-NMR, $^{13}$C-NMR of 1j-β

(400 MHz, Acetone-d$_3$)
(100 MHz, Acetone-\text{d}_6)
$\text{(400 MHz, CDCl}_3\text{)}$
$^{1}$H-NMR, $^{13}$C-NMR of 4b

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^{1}$H-NMR, $^{13}$C-NMR of S8

(400 MHz, CDCl$_3$)
S8

(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 4c

4c

(400 MHz, CDCl$_3$)
$4c$

(100 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of S11

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC, NOSY of 4d

(400 MHz, Acetone-$d_6$)
$^{1}H\text{-NMR, }^{13}C\text{-NMR of 4f}$
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR, HSQC of 4g

![Chemical Structure of 4g](image)

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 4h

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^{1}$H-NMR, $^{13}$C-NMR, HSQC of 4i

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of S22

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, HSQC of 4j

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 8d

(400 MHz, Acetone-$d_6$)
\[ \text{8d} \]

(100 MHz, Acetone-\(d_6\))
$^1$H-NMR, $^{13}$C-NMR of S26

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^1\text{H-NMR, } ^{13}\text{C-NMR of 6j}$
(100 MHz, DMSO-d$_6$)
$^1$H-NMR of 3a

3a (known compound)

(400 MHz, CDCl$_3$)
$^1$H-NMR of 3b

3b (known compound)
(400 MHz, CDCl$_3$)
$^1$H-NMR of 3c

3c (known compound)
(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC of 3d
3d
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC, NOSY of $3e$

$3e$

(400 MHz, Acetone-$d_6$)
$^1$H-NMR, $^{13}$C-NMR, HSQC, NOSY of 3f

(400 MHz, CDCl$_3$)
1H-NMR of 3g

3g (known compound)
(400 MHz, CDCl₃)
$^1$H-NMR of 3h

3h (known compound)
(400 MHz, CDCl$_3$)
$^{1}$H-NMR of 3i

3i (known compound)
(400 MHz, CDCl$_3$)
$^1$H-NMR of 3j-α

3j-alfa known compound (400 MHz, CDCl₃)
$^1$H-NMR of 3j-β

3j-β known compound
(400 MHz, CDCl3)
$^1$H-NMR, $^{13}$C-NMR, NOESY of 3k-α

(400 MHz, CDCl$_3$)
{(100MHz, CDCl$_3$)}
$^1$H-NMR, $^{13}$C-NMR, NOESY, HSQC, $^1$H-$^1$H COSY of 3k-β

(400MHz, CDCl$_3$)
$^1$H-NMR of 3I

known compound
(400MHz, CDCl$_3$)
$^1$H-NMR of 3m

known compound
(400 MHz, CDCl$_3$)
\textbf{\textsuperscript{1}H-NMR of 3n-\(\alpha\)}

known compound

(400 MHz, CDCl\textsubscript{3})
$^1$H-NMR of 3n-β

3n-beta
$^1$H-NMR, $^{13}$C-NMR of 3o

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^{1}$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HMBC, HSQC of 3p-β

3p-beta

(400 MHz, CDCl$_3$)
3p-beta
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HMBC, NOESY of 3q-α

3q-alfa

$(400$ MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR, $^{1}$$^{1}$H-$^{1}$H COSY, HMBC, NOESY of 3q-α
$^1$H-NMR of 3r

Known compound
(400 MHz, CDC13)
$^{1}$H-NMR, $^{13}$C-NMR of 3s

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of $3t$

(400 MHz, CDCl$_3$)
$^1$H-NMR of 3u

Known compound
(400 MHz, CDC13)

S148
$^1$H-NMR, $^{13}$C-NMR of 3v-α

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^3$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HMBC of 3v-β

(400 MHz, CDCl$_3$)
$^1$H-NMR of $3w$-N1-$\beta$

(400 MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR of 3w-N2-β

3w-N2-beta

(400 MHz, CDCl$_3$)
3w-N2-beta

(100 MHz, CDCl3)
$^1$H-NMR, $^{13}$C-NMR of $3x$-alfa

$3x$-alfa

$(400$ MHz, CDCl$_3$)
**$^{1}$H-NMR, $^{13}$C-NMR of 3x-$\beta$**

(400 MHz, CDCl$_3$)

![NMR Spectrum](image)
(100 MHz, CDCl₃)
Adding 4 eq C10

Adding 2 eq C10

Adding 1 eq C10

Adding 0 eq C10

S162
$^1$H-NMR of 5a

5a known compound
(400 MHz, acetone-$d_6$)
$^{1}\text{H-NMR, }^{13}\text{C-NMR, }^{1}\text{H-}^{1}\text{H COSY, HSQC of }5\text{b}$

5b

(400 MHz, CDCl$_3$)
$^{1}H$ NMR spectrum of compound 5b

(100 MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR of 5c

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC of 5d

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, HSQC, NOESY of $5e$

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
^1H-NMR, ^13C-NMR of 5f

{(400 MHz, CDCl₃)
(100 MHz, CDCl₃)
\(^{1}\text{H-NMR, }^{13}\text{C-NMR, HSQC of 5g}\)

(400 MHz, CDCl\textsubscript{3})
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC of 5h

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, of 5i

(400 MHz, CDCl$_3$)
\( ^1\text{H-NMR of 5m} \)

Known compound

(400 MHz, CDCl\textsubscript{3})
$^1$H-NMR of 5n

Known compound
(400 MHz, CDCl$_3$)
$^1$H-NMR of 5o

Known compound

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7a

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7b

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 7c

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^{1}$H-NMR, $^{13}$C-NMR of 7d

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^{1}$H-NMR, $^{13}$C-NMR of 7e

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7f

(400 MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR of 7g

(400 MHz, CDCl₃)
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 7h
$^1$H-NMR, $^{13}$C-NMR, NOESY of 7i

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 7j

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7k

(400 MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR of 71

(400 MHz, CDCl$_3$)
S216

71

(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 7m

(400 MHz, CDCl$_3$)
$^{1}$H-NMR, $^{13}$C-NMR of 7n

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7o

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7p

(400 MHz, CDCl$_3$)
$^{1}H$-NMR, $^{13}C$-NMR, NOESY of 7q

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR of 7r
(100 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC, NOESY of 7s

(400 MHz, CDCl$_3$)
$^1$H-NMR, $^{13}$C-NMR, $^1$H-$^1$H COSY, HSQC, NOESY of 7t

(400 MHz, CDCl$_3$)
(100 MHz, CDCl₃)
$^1$H-NMR, $^{13}$C-NMR of 9
(100 MHz, Acetone-$d_6$)
$^1$H-NMR, $^{13}$C-NMR, HSQC, HMBC of 10

(400 MHz, CDCl$_3$)