Supporting Information

β-Stereoselective Kdo *C*-glycosylation by (*p*-Tol)$_2$SO/Tf$_2$O preactivation strategy

Jing-Dong Zhang,[a] Guang-jian Liu[a] and Guo-Wen Xing*[a]

[a] College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China.
E-mail: gwxing@bnu.edu.cn

Contents of Supporting Information

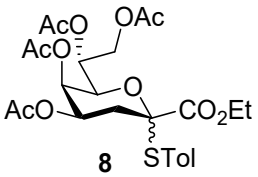
1 Materials and instruments 2
2 Experimental procedures 2
2.1 Preparation of donors 2
2.2 Preparation of acceptors 3
2.3 General procedure (GP) for glycosylation reactions 4
3 Computational methods and data 11
3.1 Computational methods. 11
3.2 Coordinates of all Stationary points for the reaction 12
4 NMR spectra of compounds 22
5 Reference 31

1 Materials and instruments

General experiments and characterizations. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Solvents used were analytical grade. Chemical reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel F254 glass plates and revealed by UV light (254 nm) or heating after dipping in EtOH-H_2SO_4 (7%). Flash column chromatography was performed on silica gel (200-300 mesh). High-resolution mass spectra (HRMS) were obtained in the ESI mode (Bruker micrOTOF-QII mass spectrometer (ESI)). NMR spectra were recorded using $CDCl_3$ as solvents. Chemical shifts (δ) were reported in units per million (ppm) and coupling constants (J) in Hz. ^{1}H NMR spectra, ^{13}C NMR spectra and the selective proton decoupled NMR spectra were recorded on JNM-ECZR spectrometer (400 and 600 MHz) or Bruker Avance III spectrometer (500 MHz).

2 Experimental procedures

2.1 Preparation of donors



8

Ethyl (*p*-tolyl 4,5,7,8-tetra-O-acetyl-3-deoxy-α, β-D-manno-oct-2-ulopyranoside)onate (8)[1]

Compound **8** was prepared according to the literature method.[1]

8α: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.48 – 5.40 (m, 2H), 5.24 (ddd, J = 9.6, 4.3, 2.5 Hz, 1H), 4.72 (dd, J = 9.6, 1.0 Hz, 1H), 4.47 (dd, J = 12.3, 2.5 Hz, 1H), 4.06 – 4.02 (m, 2H), 4.00 (dd, J = 12.2, 4.4 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.34 (s, 3H), 2.30 (t, J = 6.6 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H).

8β: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.7 Hz, 2H), 5.27 (s, 1H), 5.22 (dd, J = 8.4, 6.1 Hz, 1H), 4.93 – 4.82 (m, 1H), 4.57 (d, J = 12.1 Hz, 1H), 4.10 – 3.99 (m, 2H), 3.98 – 3.92 (m, 1H), 3.89 (d, J = 9.5 Hz, 1H), 2.57 (dd, J = 12.6, 4.6 Hz, 1H), 2.35 (s, 3H), 2.19 (t, J = 12.6 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.98 (s, 6H), 1.10 (t, J = 7.1 Hz, 3H).

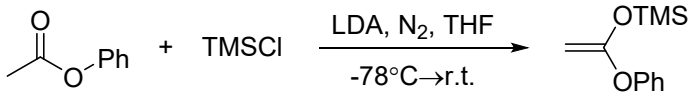
The spectroscopic data coincided with the previous report.[1]

2.2 Preparation of acceptors

9a (1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd.

9b was synthesized according to the previously published procedure.[2]

[[1-[(trimethylsilyl)oxy]ethenyl]oxy]benzene (9b)[2]



The residue was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.28 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 3.48 (d, *J* = 2.4 Hz, 1H), 3.26 (d, *J* = 2.4 Hz, 1H), 0.24 (s, 9H).

The spectroscopic data coincided with the previous report.[2]

9c (1-[(trimethylsilyl)oxy]cyclopentene) was purchased from Bide Pharmatech Ltd.

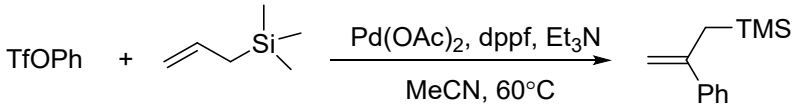
9d (1-phenyl(trimethylsiloxy)ethylene) was purchased from Alfa Aesar of Thermo Fisher Scientific Inc.

9e (allyltributyltin) was purchased from Innochem (Beijing) Technology Co., Ltd.

9f (trimethyl[(1-methylethenyl)oxy]silane) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd.

9g was synthesized according to the previously published procedure.[3]

[1-[(trimethylsilyl)methyl]ethenyl]benzene (9g)[3]



The residue was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 – 7.34 (m, 2H), 7.32 – 7.22 (m, 3H), 5.12 (d, *J* = 1.6 Hz, 1H), 4.90 – 4.78 (m, 1H), 2.08 – 1.94 (m, 2H), -0.11 (s, 9H).

The spectroscopic data coincided with the previous report.[3]

9h (1-(trimethylsiloxy)cyclohexene) was purchased from Alfa Aesar of Thermo Fisher Scientific Inc.

***p*-Tolyl Sulfoxide** was purchased from TCI (Shanghai) Development Co., Ltd.

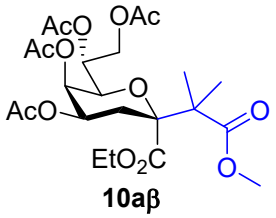
Solvents used for column chromatography were purchased from Bei Jing TongGuang Fine Chemicals Company.

2.3 General procedure (GP) for glycosylation reactions

GP1: To a mixture of thioglycoside donor **8** (1.0 equiv., 0.069 mmol), (*p*-Tol)$_2$SO (3.0 equiv.) and activated 4Å powdered sieves (300mg) in flame-dried glass vessel was added anhydrous CH_2Cl_2 (2.5 mL). The resulting mixture was stirred at preactivation temperature (-60°C) for 10 min, followed by the addition of trifluoromethanesulfonic anhydride (Tf_2O, 13.8 µL, 1.2 equiv.). After activation for 30 min, the solution of **9a-9f** (10.0 equiv.) in anhydrous CH_2Cl_2 (0.5mL) was added. The temperature of reaction mixture was allowed to keep on -60°C for 2h. Subsequently, the temperature was up to -50°C and maintained at this temperature overnight. The reaction mixture was quenched with Et_3N (0.3 mL), diluted with CH_2Cl_2, filtered through diatomite, washed with water, dried and concentrated to leave a residue which was purified by column chromatography on silica gel to afford **10b, 10c, 10d, 10f, 10g, 10h** and glycal.

GP2: To a mixture of thioglycoside donor **8** (1.0 equiv., 0.138 mmol), (*p*-Tol)$_2$SO (3.0 equiv.) and activated 4Å powdered sieves (300mg) in flame-dried glass vessel was added anhydrous CH_2Cl_2 (2.5 mL). The resulting mixture was stirred at preactivation temperature (-60°C) for 10 min, followed by the addition of trifluoromethanesulfonic anhydride (Tf_2O, 27.6 µL, 1.2 equiv.). After activation for 30 min, the solution of **9a-9f** (10.0 equiv.) in anhydrous CH_2Cl_2 (0.5mL) was added. The temperature of reaction mixture was allowed to keep on -60°C for 2h. Subsequently, the temperature was up to -50°C and maintained at this temperature overnight. The reaction mixture was quenched with Et_3N (0.5 mL), diluted with CH_2Cl_2, filtered through diatomite, washed with water, dried and concentrated to leave a residue which was purified by column chromatography on silica gel to afford **10a, 10c, 10d, 10e** and glycal.

Ethyl[2-*C*-(1,1-dimethyl-2-methoxy-2-oxoethyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl]onate (10aβ)



10aβ

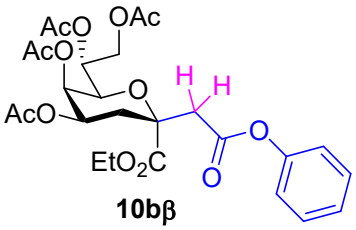
GP2: 39.6 mg, 55% yield from **8**: a colorless syrup. (Petroleum ether/ethyl acetate = 5:1, v/v)

10aβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.25 (s, 1H, H-5), 5.07 (ddd, *J* = 9.4, 5.2, 2.3 Hz, 1H, H-7), 4.81 (ddd, *J* = 12.6, 4.7, 2.8 Hz, 1H, H-4), 4.43 (dd, *J* = 12.2, 2.3 Hz, 1H, H-8), 4.27 – 4.19 (m, 3H, H-8 & $CH_2(CO_2Et)$), 4.10 (d, *J* = 8.4 Hz, 1H, H-6), 3.69 (s, 3H, OMe), 2.42 (t, *J* = 12.7 Hz, 1H, H-3axial), 2.27 (dd, *J* = 12.7, 4.6 Hz, 1H, H-3equatorial), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.32 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$), 1.28 (s, 3H, Me), 1.26 (s, 3H, Me).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.4, 170.8, 170.5, 170.1, 170.0, 170.0 (C1, $^3J_{C\text{-}1/H\text{-}3ax}$ = 6.9 Hz, 151 MHz), 83.9, 71.0, 68.2, 68.2, 64.7, 62.9, 62.0, 52.2, 49.8, 27.8, 21.4, 21.0, 20.8, 20.8, 20.7, 14.3.

HRMS (ESI) m/z Calcd for $C_{23}H_{35}O_{13}$ $[M + H]^+$ 519.2072; found: 519.2078.

Ethyl[2-*C*-(2-phenoxy-2-oxoethyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl]onate (10bβ)



10bβ

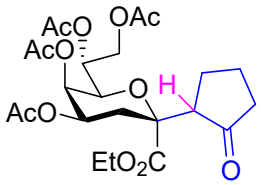
GP1: 16.7 mg, 45% yield from **8**: a colorless syrup. (Petroleum ether/ethyl acetate = 4:1, v/v)

10bβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.35 (m, 2H, aromatic), 7.23 (t, *J* = 7.4 Hz, 1H, aromatic), 7.07 (dd, *J* = 8.5, 1.0 Hz, 2H, aromatic), 5.34 (d, *J* = 1.3 Hz, 1H, H-5), 5.14 (ddd, *J* = 9.5, 5.0, 2.3 Hz, 1H, H-7), 5.03 (ddd, *J* = 12.7, 4.7, 2.9 Hz, 1H, H-4), 4.50 (dd, *J* = 12.2, 2.3 Hz, 1H, H-8), 4.37 (dd, *J* = 9.5, 1.2 Hz, 1H, H-6), 4.27 (q, *J* = 7.1 Hz, 2H, $CH_2(CO_2Et)$), 4.20 (dd, *J* = 12.2, 5.1 Hz, 1H, H-8), 3.11 (d, *J* = 14.2 Hz, 1H, CH_2(glycosidic bond)), 3.00 (d, *J* = 14.2 Hz, 1H, CH_2(glycosidic bond)), 2.39 (dd, *J* = 12.8, 4.3 Hz, 1H, H-3equatorial), 2.17 (t, *J* = 12.7 Hz, 1H, H-3axial), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.31 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.8 (C1, dt, J = 6.7 ($^3J_{C\text{-}1/H\text{-}3ax}$), 5.1 Hz, 151 MHz), 170.7, 170.6, 170.0, 167.0, 167.1, 150.5, 129.7, 126.3, 121.6, 78.6, 71.4, 68.1, 67.2, 64.5, 62.8, 62.3, 45.2, 32.1, 20.9, 20.8, 20.8, 14.3.

HRMS (ESI) m/z Calcd for $C_{26}H_{32}O_{13}Na$ $[M + Na]^+$ 575.1735, found: 575.1741.

Ethyl[2-*C*-(2-oxocyclopentyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl]onate (10cβ)



10cβ

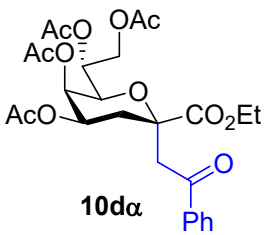
GP2: 63.0 mg, 91% yield from **8** to generate the mixture of **10cα** and **10cβ** (1:10): a pale-yellow syrup. (Petroleum ether/ethyl acetate = 5:1, v/v)

10cβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.30 (dd, J = 3.2, 2.0 Hz, 1H, H-5), 5.08 (ddd, J = 9.5, 5.9, 2.2 Hz, 1H, H-7), 4.88 (ddd, J = 12.8, 4.7, 2.8 Hz, 1H, H-4), 4.52 (dd, J = 9.6, 1.4 Hz, 1H, H-6), 4.43 (dd, J = 12.2, 2.2 Hz, 1H, H-8), 4.28 (q, J = 7.1 Hz, 2H, $CH_2(CO_2Et)$), 4.07 (dd, J = 12.2, 5.9 Hz, 1H, H-8), 2.65 (t, J = 9.1 Hz, 1H, CH(glycosidic bond)), 2.31 – 2.20 (m, 3H, H-3equatorial & acceptor), 2.19 – 2.13 (m, 1H, acceptor), 2.13 – 2.08 (m, 5H, H-3axial & acceptor & OAc), 2.06 (s, 3H, OAc), 2.05 – 2.03 (m, 1H, acceptor), 2.00 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.74 (ddd, J = 16.7, 9.2, 2.5 Hz, 1H, acceptor), 1.33 (t, J = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 215.6, 171.7 (C1, dd, J = 6.5 ($^3J_{C\text{-}1/H\text{-}3ax}$), 1.3 Hz, 151 MHz), 170.8, 170.4, 170.2, 170.0, 80.4, 70.9, 68.3, 67.2, 64.7, 63.0, 61.9, 55.3, 39.4, 31.0, 24.5, 20.9, 20.9, 20.8, 20.8, 20.6, 14.2.

HRMS (ESI) m/z Calcd for $C_{23}H_{33}O_{12}$ $[M + H]^+$ 501.1966, found: 501.1973.

Ethyl[2-*C*-(2-oxo-2-phenylethyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-α-$_D$-manno-oct-2-ulopyranosyl]onate (10dα)[4]



10dα

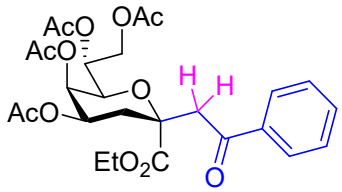
GP2: 59.5 mg, from **8** to generate a mixture of **10dβ** (61% yield) and glycal (1:0.4): a colorless syrup

(Petroleum ether/ethyl acetate = 5:1, v/v); while 8.6 mg, 12% yield from **8** to generate **10dα**: a colorless syrup (Petroleum ether/ethyl acetate = 4:1, v/v).

10dα (α-anomer): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (s, 2H), 7.60 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 2H), 5.34 (s, 1H), 5.28 – 5.22 (m, 1H), 5.20 – 5.15 (m, 1H), 4.47 – 4.34 (m, 1H), 4.21 – 4.14 (m, 2H), 4.11 – 4.05 (m, 1H), 3.99 (d, *J* = 5.9 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.61 – 3.40 (m, 1H), 2.33 (dd, *J* = 9.7, 6.8 Hz, 1H), 2.13 – 2.08 (m, 4H), 2.01 (s, 3H), 1.97 (s, 3H), 1.73 (s, 3H), 1.20 (t, *J* = 6.9 Hz, 3H).

The spectroscopic data coincided with the previous report.[4]

Ethyl[2-*C*-(2-oxo-2-phenylethyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl] onate (10dβ)[4]



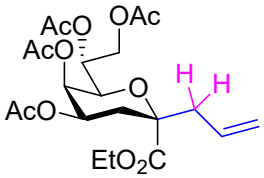
10dβ

GP2: 59.5 mg, from **8** to generate a mixture of **10dβ** (61% yield) and glycal (1:0.4): a colorless syrup (Petroleum ether/ethyl acetate = 5:1, v/v); while 8.6 mg, 12% yield from **8** to generate **10dα**: a colorless syrup (Petroleum ether/ethyl acetate = 4:1, v/v).

The mixture of **10dβ (β-anomer)** and glycal (1:0.3): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (dd, *J* = 8.3, 1.2 Hz, **10dβ**), 7.63 – 7.54 (m, 1H, **10dβ**), 7.47 (t, *J* = 7.8 Hz, 2H, **10dβ**), 5.88 (t, *J* = 2.0 Hz, 0.3H, glycal), 5.71 (ddd, *J* = 4.5, 2.1, 1.3 Hz, 0.3H, glycal), 5.54 – 5.45 (m, 0.3H, glycal), 5.30 – 5.29 (m, 1H, **10dβ**), 5.27 (ddd, *J* = 9.7, 4.1, 2.5 Hz, 0.3H, glycal), 5.14 (ddd, *J* = 12.5, 4.8, 3.0 Hz, 1H, **10dβ**), 4.95 (ddd, *J* = 9.6, 4.9, 2.3 Hz, 1H, **10dβ**), 4.62 (dd, *J* = 12.4, 2.5 Hz, 0.3H, glycal), 4.34 (d, *J* = 9.7 Hz, 0.3H, glycal), 4.31 (dd, *J* = 12.2, 2.3 Hz, 1H, **10dβ**), 4.28 – 4.17 (m, 3.9H), 4.01 (dd, *J* = 12.2, 5.0 Hz, 1H, **10dβ**), 3.53 (d, *J* = 15.3 Hz, 1H, **10dβ**), 3.40 (d, *J* = 15.3 Hz, 1H, **10dβ**), 2.44 – 2.40 (m, 1H, **10dβ**), 2.08 (s, 0.9H, glycal), 2.08 (s, 0.9H, glycal), 2.08 – 2.06 (m, 1H, **10dβ**), 2.06 (s, 3H, **10dβ**), 2.05 (s, 3H, **10dβ**), 2.03 (s, 0.9H, glycal), 2.03 (s, 0.9H, glycal), 1.97 (s, 3H, **10dβ**), 1.97 (s, 3H, **10dβ**), 1.32 (t, *J* = 7.1 Hz, 0.9H, glycal), 1.27 (t, *J* = 7.1 Hz, 3H, **10dβ**).

The spectroscopic data coincided with the previous report.[4]

Ethyl[2-*C*-allyl-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl]onate (10eβ)[4]



10eβ

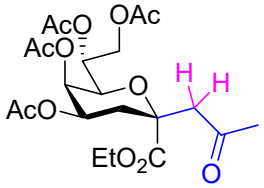
GP2: 45.6 mg, 72% yield from **8**: a colorless syrup. (Petroleum ether/ethyl acetate = 6:1, v/v)

10eβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.76 (dq, *J* = 10.0, 7.3 Hz, 1H, CH(alkene)), 5.28 (s, 1H, H-5), 5.10 (t, *J* = 13.3 Hz, 3H, H-7 & CH(alkene)), 4.92 (ddd, *J* = 12.6, 4.4, 3.0 Hz, 1H, H-4), 4.50 (dd, *J* = 12.2, 2.0 Hz, 1H, H-8), 4.24 (dd, *J* = 8.2, 4.0 Hz, 1H, H-8), 4.21 (q, *J* = 7.1 Hz, 2H, $CH_2(CO_2Et)$), 4.05 (d, *J* = 9.5 Hz, 1H, H-6), 2.50 (d, *J* = 7.2 Hz, 2H, CH_2(glycosidic bond)), 2.25 (dd, *J* = 12.7, 4.3 Hz, 1H, H-3equatorial), 2.09 (s, 6H, OAc*2), 1.99 (s, 3H, OAc), 1.98 (s, 3H, OAc), 1.93 (t, *J* = 12.7 Hz, 1H, H-3axial), 1.30 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.5 (C1, dt, *J* = 7.1 ($^{3}J_{C\text{-}1/H\text{-}3ax}$), 3.0 Hz, 151 MHz), 170.8, 170.6, 170.1, 170.0, 131.2, 119.3, 80.7, 71.1, 68.2, 67.7, 64.7, 62.9, 61.6, 44.5, 31.7, 20.9, 20.9, 20.8, 20.8, 14.4.

The spectroscopic data coincided with the previous report.[4]

Ethyl[2-*C*-(2-oxopropyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-$_D$-manno-oct-2-ulopyranosyl]onate (10fβ)



10fβ

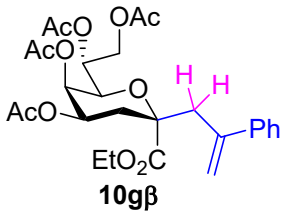
GP1: 28.5 mg, from **8** to obtain a mixture of **10fβ** (84% yield) and EtOAc (1:0.2): a pale-yellow syrup. (Petroleum ether/ethyl acetate = 3:1, v/v)

10fβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.30 (d, *J* = 1.4 Hz, 1H, H-5), 5.09 (ddd, *J* = 9.5, 5.3, 2.2 Hz, 1H, H-7), 5.02 (ddd, *J* = 12.6, 4.8, 3.0 Hz, 1H, H-4), 4.48 (dd, *J* = 12.2, 2.2 Hz, 1H, H-8), 4.27 – 4.21 (m, 3H, H-6 & $CH_2(CO_2Et)$), 4.15 (dd, *J* = 12.2, 5.4 Hz, 1H, H-8), 2.89 (d, *J* = 2.4 Hz, 2H, CH_2(glycosidic bond)), 2.28 (dd, *J* = 12.9, 4.2 Hz, 1H, H-3equatorial), 2.22 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 – 1.99 (m, 4H, H-3axial & OAc), 1.98 (s, 3H, OAc), 1.31 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 204.6, 170.8, 170.8, 170.5 (C1, dt, *J* = 6.4 ($^{3}J_{C\text{-}1/H\text{-}3ax}$), 4.0 Hz, 151 MHz), 170.0, 167.0, 78.8, 71.2, 68.1, 67.1, 64.5, 62.9, 62.1, 52.8, 31.8, 31.7, 20.9, 20.8, 20.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{21}H_{31}O_{12}$ $[M + H]^+$ 475.1810, found: 475.1808.

Ethyl[2-*C*-(2-phenylallyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-D-manno-oct-2-ulopyranosyl]onate (10gβ)



10gβ

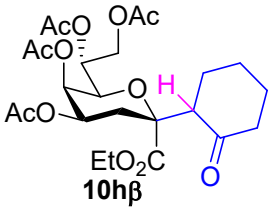
GP1: 16.8 mg, 45% yield from **8**: a pale-yellow syrup. (Petroleum ether/ethyl acetate = 6:1, v/v)

10gβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 – 7.22 (m, 5H, aromatic), 5.34 (d, *J* = 1.1 Hz, 1H, CH_2(alkene)), 5.20 (s, 1H, H-5), 5.16 (s, 1H, CH_2(alkene)), 4.84 (ddd, *J* = 12.7, 4.4, 3.0 Hz, 1H, H-4), 4.80 (ddd, *J* = 9.2, 4.9, 2.1 Hz, 1H, H-7), 4.14 (dd, *J* = 12.1, 2.1 Hz, 1H, H-8), 3.96 – 3.84 (m, 3H, H-6 & $CH_2(CO_2Et)$), 3.81 (dd, *J* = 12.2, 5.1 Hz, 1H, H-8), 2.99 (s, 2H, CH_2(glycosidic bond)), 2.21 (dd, *J* = 12.6, 4.4 Hz, 1H, H-3equatorial), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.00 – 1.97 (m, 1H, H-3axial), 1.96 (s, 3H, OAc), 1.94 (s, 3H, OAc), 1.20 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 171.3 (C1, dt, *J* = 6.6 ($^3J_{C\text{-}1/H\text{-}3ax}$), 2.0 Hz, 151 MHz), 170.8, 170.6, 170.1, 169.9, 143.3, 141.7, 128.1, 127.5, 126.8, 118.6, 81.0, 71.0, 68.1, 67.7, 64.6, 62.7, 61.5, 45.4, 31.9, 21.0, 20.8, 20.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{27}H_{35}O_{11}$ $[M + H]^+$ 535.2173, found: 535.2168.

Ethyl[2-*C*-(2-oxocyclohexyl)-4,5:7,8-tetra-*O*-acetyl-3-deoxy-β-D-manno-oct-2-ulopyranosyl]onate (10hβ)



10hβ

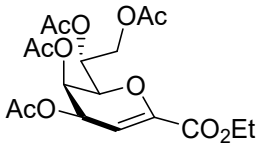
GP1: 31.1 mg, 87% yield from **8**: a pale-yellow syrup. (Petroleum ether/ethyl acetate = 5:1, v/v)

10hβ (β-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.30 (s, 1H, H-5), 5.10 – 5.02 (m, 2H, H-4 & H-7), 4.47 (d, *J* = 2.4 Hz, 1H, H-6), 4.45 (dd, *J* = 4.6, 1.7 Hz, 1H, H-8), 4.26 – 4.17 (m, 2H, $CH_2(CO_2Et)$), 4.15 – 4.11 (m, 1H, H-8), 2.80 (dd, *J* = 11.8, 5.6 Hz, 1H, CH(glycosidic bond)), 2.45 – 2.36 (m, 1H, acceptor), 2.31 – 2.25 (m, 1H, H-3equatorial), 2.24 – 2.18 (m, 1H, acceptor), 2.11 (dd, *J* = 21.1, 8.8 Hz, 2H, acceptor), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 – 2.03 (m, 1H, H-3axial), 2.00 (s, 4H, OAc & acceptor), 1.97 (s, 3H, OAc), 1.89 – 1.80 (m, 1H, acceptor), 1.73 – 1.63 (m, 2H, acceptor), 1.30 (t, *J* = 7.1 Hz, 3H, $CH_3(CO_2Et)$).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 208.2, 172.3 (C1, dd, *J* = 6.4 ($^3J_{C\text{-}1/H\text{-}3ax}$), 1.6 Hz, 151 M Hz), 170.8, 170.4, 170.1, 169.9, 79.2, 71.0, 68.3, 67.3, 64.8, 63.0, 61.5, 58.2, 42.4, 29.8, 27.2, 26.7, 24.7, 20.9, 20.9, 20.8, 20.8, 14.2.

HRMS (ESI) m/z Calcd for $C_{24}H_{34}O_{12}Na$ $[M + Na]^+$ 537.1942, found: 537.1950.

Ethyl (4,5,7,8-tetra-*O*-acetyl-2,3-dideoxy-$_D$-manno-oct-2-enopyranosyl)onate (11)[5]



by-product
11

11 (glycal): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.91 – 5.86 (m, 1H), 5.75 – 5.69 (m, 1H), 5.48 (d, *J* = 3.9 Hz, 1H), 5.28 (ddd, *J* = 9.6, 3.9, 2.5 Hz, 1H), 4.63 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.35 (d, *J* = 9.7 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.24 (dd, *J* = 8.9, 3.6 Hz, 1H), 2.09 (s, 6H), 2.04 (s, 3H), 2.04 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

The spectroscopic data coincided with the previous report.[5]

3 Computational methods and data

3.1 Computational methods.

All calculations were carried out utilizing the Gaussian 16 program package.[6] All geometries of reagents, intermediates and products were optimized by employing the B3LYP-D3(BJ) functional method,[7-9] with the 6-31+g(d,p) basis set[10-14] for all elements. The solvent effect of the dichloromethane (DCM) was considered by the SMD model.[15] The vibrational frequencies of all optimized stationary point structures were calculated at the same level of theory to obtain zero-point energies and Gibbs free energies. The optimized stationary point structures were subsequently characterized by frequency analyses at the same level of theory, in addition to conforming the stationary points to be local minima (no imaginary frequencies). The single-point energies were computed with the B3LYP-D3 functional with the def2-tzvp basis set applying the SMD dichloromethane solvation model. Using SHERMO program to calculate the solutional free energy for all species (sclZPE= 0.9857).[16]

Table S1 The calculated single point energy of optimized structures E_{elec}, total free energies in gas phase G_g and total free energies in solution G_s in a.u. in the DCM solvent (1M) with the temperature of 223.15K at B3LYP-D3/def2-tzvp/SMD(dichloromethane)//B3LYP-D3/6-31+g(d,p)/SMD(dichloromethane) level of theory.

Species	E_{elec}	G_g (223.15K)	Gs (223.15K)
12	-1529.03704799	-1528.6534629	-1528.6514082
8f	-602.05067602	-601.8928248	-601.8907702
13α	-2131.15566744	-2130.5897598	-2130.5877052
13β	-2131.15883077	-2130.5905394	-2130.5884848
10fα	-1721.91717587	-1721.4616971	-1721.4596424
10fβ	-1721.91840380	-1721.4614921	-1721.4594374
$^{-}$OTf	-961.941631836	-961.9373288	-961.9352742
TMSOTf	-1371.19948839	-1371.0901175	-1371.0880628

3.2 Coordinates of all Stationary points for the reaction

12			
1 1			
C	-1.54685900	-1.38355000	-1.11504800
C	-0.64927300	-2.48295500	-0.55994500
C	0.69190900	-2.01528300	-0.20050500
C	0.12744900	0.34321300	-0.47258000
C	-1.31969500	-0.07910400	-0.35061400
H	-1.06492800	-2.90476100	0.37260500
H	-0.55116900	-3.34344600	-1.23251700
H	-1.34347200	-1.21200200	-2.17471700
H	0.37635600	0.59298500	-1.50551900
H	-1.94602600	0.71663600	-0.75476200
O	1.04668500	-0.80766600	-0.15351500
O	-1.61288000	-0.29685600	1.03622400
O	-2.89198900	-1.83790600	-0.94212400
C	-2.78105700	0.22648700	1.52928900
O	-3.53014200	0.89174700	0.84712200
C	-2.96994500	-0.15354900	2.96280400
H	-3.19538600	-1.22461400	3.01822400
H	-2.05361300	0.02757100	3.53014600
H	-3.79723100	0.41509300	3.38675100
C	0.56124200	1.44991700	0.49497900
H	0.39188300	1.13240300	1.52600500
C	2.01191200	1.86357100	0.35223100
H	2.19783700	2.74320000	0.97346400
H	2.67319900	1.05723100	0.67867000
C	-3.84251600	-1.26591600	-1.74364900
O	-0.30399300	2.55320300	0.18063900
O	2.25559100	2.17290300	-1.03278000
C	3.52097300	2.53463000	-1.35852300
C	-1.00736500	3.12734800	1.20633500
O	4.41805500	2.58123400	-0.53785000
O	-0.93197900	2.73441400	2.35188700
O	-3.56283700	-0.44409800	-2.59203700
C	-5.20671000	-1.78350200	-1.41223600
H	-5.20685300	-2.87725300	-1.39984900
H	-5.48699300	-1.43707200	-0.41159100
H	-5.92685700	-1.41245600	-2.14125100
C	-1.84456200	4.26098600	0.70388400
H	-1.20622800	5.00502400	0.21730100
H	-2.55383200	3.89087900	-0.04306300

H	-2.38358100	4.71522100	1.53484300
C	1.77186800	-3.03482600	0.18220300
O	1.53914400	-4.22070900	0.08450100
O	2.86835900	-2.44138300	0.58727100
C	3.99524600	-3.30944200	0.98596000
H	4.25086300	-3.92264000	0.11858800
H	3.63671600	-3.95331800	1.79255100
C	5.12241900	-2.40352700	1.41530400
H	5.97333500	-3.02453900	1.71316900
H	5.44197600	-1.75300400	0.59579100
H	4.83075000	-1.78691800	2.27068000
C	3.63639500	2.87048900	-2.81586900
H	4.68554300	2.99798200	-3.08277600
H	3.18214100	2.08643100	-3.42821600
H	3.09488100	3.80238800	-3.01335200
8f			
0 1			
C	2.74279700	-1.12372500	-0.04303300
H	3.76045200	-0.83112800	0.18985300
H	2.52152200	-2.17881500	-0.17086000
C	1.78385100	-0.19563600	-0.18374200
O	0.51946100	-0.58245900	-0.53879600
Si	-0.99127800	-0.03474700	0.01995200
C	-1.39615700	1.65741700	-0.68875000
H	-2.44623000	1.90184200	-0.48290800
H	-0.77770500	2.44900300	-0.25341600
H	-1.25731300	1.67263500	-1.77630100
C	-2.18517100	-1.32174300	-0.62983700
H	-1.95028800	-2.31504400	-0.23030100
H	-3.21389300	-1.07363400	-0.34146400
H	-2.14607200	-1.37697400	-1.72416600
C	-0.96696000	0.00960900	1.89649300
H	-1.95940200	0.27341400	2.28294300
H	-0.69294900	-0.96801800	2.31000100
H	-0.25441800	0.75104600	2.27547700
C	2.01179100	1.28192600	-0.03011100
H	1.72029200	1.81216000	-0.94402000
H	1.41366300	1.69167600	0.79212500
H	3.06364600	1.49088600	0.17795800
13α			
1 1			
C	0.50219700	-1.63110500	0.00858400

C	-0.90159900	0.28783600	-0.47657900
C	-2.18613400	-0.52383700	-0.33406200
C	-1.89771400	-1.97641200	-0.71059100
C	-0.74624100	-2.54041400	0.11090700
H	-2.96255100	-0.11098400	-0.97673100
H	-1.68949600	-2.01393900	-1.78221200
H	-1.05282100	-2.59393600	1.15883600
H	-0.49823800	-3.54877900	-0.22893700
O	0.17189700	-0.27284400	0.27745400
C	1.45064600	-2.04030500	1.15334100
O	2.18960000	-3.09776300	0.79830000
O	1.47543700	-1.51179700	2.24293900
C	3.10189800	-3.63714900	1.80288500
H	2.50909300	-3.95996400	2.66260100
H	3.76970200	-2.83226100	2.11998300
C	3.85135400	-4.78286800	1.16199400
H	4.54774400	-5.20801200	1.89197200
H	3.16508300	-5.57305200	0.84166200
H	4.42807100	-4.44270300	0.29575500
O	-3.04962700	-2.79822000	-0.43349900
C	-4.01930400	-2.85463400	-1.38185000
O	-3.92100000	-2.30225600	-2.46200600
C	-5.19490100	-3.65718600	-0.91098300
H	-5.78391900	-3.04015600	-0.22297200
H	-4.86906300	-4.54817700	-0.36849400
H	-5.81767400	-3.93304700	-1.76248900
O	-2.61622600	-0.46348000	1.03894500
C	-3.93719600	-0.27214600	1.28343400
O	-4.76445000	-0.12886200	0.40248800
C	-4.21870000	-0.28581200	2.75551100
H	-3.45100300	0.26645000	3.30219000
H	-4.20150000	-1.32442700	3.10580900
H	-5.20432200	0.13980200	2.94530600
C	-1.03346500	1.72535200	0.03690300
H	-1.22743100	1.72020300	1.10979900
O	-2.15265600	2.32102000	-0.65019300
C	-3.16551100	2.84972600	0.08883500
O	-3.18499800	2.83649600	1.30366000
C	-4.22305200	3.43053700	-0.80154300
H	-4.58465700	2.66702500	-1.49686500
H	-3.79684900	4.24690900	-1.39385400
H	-5.04917800	3.80396600	-0.19671800

C	0.21074300	2.52871000	-0.28329500
H	1.08967900	2.05285300	0.15545200
H	0.34839500	2.62005700	-1.36482600
O	0.03450600	3.83902200	0.28999300
C	1.02753000	4.72551200	0.07040200
O	2.02808500	4.44665900	-0.56950600
C	0.72772600	6.05571900	0.69687700
H	0.50368100	5.92913200	1.76036800
H	-0.15759400	6.49227600	0.22242900
H	1.57911700	6.72445600	0.57017700
H	-0.65455300	0.31359200	-1.54740200
C	1.17919200	-1.77071400	-1.36839000
H	1.46721400	-2.81487400	-1.55276000
H	0.49660600	-1.52822000	-2.19031900
C	2.41698700	-0.97069200	-1.55590300
C	2.99640300	-0.80935700	-2.90704900
H	2.66439000	-1.61043500	-3.56935100
H	2.61338800	0.14062600	-3.30875700
H	4.08584900	-0.75008500	-2.87732200
O	2.92661400	-0.44659300	-0.53054000
Si	4.37406800	0.56986600	-0.12812000
C	3.92811600	1.08450100	1.59750300
H	3.85888600	0.22443400	2.27036100
H	4.69258400	1.76728900	1.98745300
H	2.96737900	1.61042000	1.60837000
C	4.40778500	1.97144600	-1.34772500
H	5.19113100	2.67307400	-1.03290200
H	4.64400000	1.64430100	-2.36418000
H	3.46309500	2.52502200	-1.34952800
C	5.77946600	-0.64311200	-0.26270000
H	5.90197500	-1.01336600	-1.28611900
H	6.71388200	-0.14827600	0.02949500
H	5.62814400	-1.49795900	0.40509900
13β			
1 1			
C	0.17675600	-2.03917600	-0.34397400
C	0.85006800	0.10866500	0.50780700
C	2.30472900	-0.10662200	0.10592100
C	2.60849300	-1.60462400	0.12975800
C	1.62316500	-2.38723100	-0.72951300
H	2.96832500	0.42779800	0.78407200
H	2.58290800	-1.94078000	1.16880200

H	1.76906000	-2.12094900	-1.77916900
H	1.79161700	-3.45862700	-0.61108000
O	-0.03262100	-0.63614700	-0.33792500
C	-0.19811800	-2.66202000	1.02545000
O	-1.21668300	-2.01316300	1.59317400
O	0.34275400	-3.64655300	1.48918500
C	-1.67324400	-2.51429400	2.89227000
H	-0.80847500	-2.54363100	3.55955500
H	-2.04174400	-3.53345400	2.74932100
C	-2.74854000	-1.57793800	3.39074800
H	-3.08577900	-1.91993600	4.37467200
H	-2.36744800	-0.55755500	3.49508900
H	-3.60968800	-1.56563100	2.71806800
O	3.92279400	-1.85066600	-0.40993700
C	4.98062300	-1.68840000	0.42605000
O	4.85670000	-1.41404100	1.60493300
C	6.27997900	-1.87091800	-0.29994600
H	6.49516400	-0.95462800	-0.86148600
H	6.21930200	-2.69692700	-1.01272400
H	7.08233100	-2.04259200	0.41828300
O	2.47944400	0.39340300	-1.23513000
C	3.60106800	1.10531100	-1.50892000
O	4.44545700	1.36809900	-0.67320200
C	3.65372200	1.48892300	-2.95724300
H	2.67202500	1.81526100	-3.30777400
H	3.94745900	0.60913000	-3.54176300
H	4.39209700	2.27769800	-3.10273200
C	0.38669400	1.56196300	0.37228200
H	0.37092000	1.83993500	-0.68224900
O	1.33486500	2.39462400	1.07010400
C	1.96206700	3.38784200	0.38329100
O	1.77156200	3.60843800	-0.79668100
C	2.89780500	4.14311500	1.27871400
H	3.62061700	3.45441500	1.72635900
H	2.33288200	4.60942400	2.09233800
H	3.41963100	4.90802800	0.70387300
C	-0.97783900	1.75438000	0.99809200
H	-1.66893300	0.99497400	0.63152700
H	-0.92025900	1.69100100	2.08824400
O	-1.44139500	3.06483000	0.61260300
C	-2.69359000	3.39617200	0.99402000
O	-3.40021900	2.65062800	1.64996100

C	-3.07670000	4.76019400	0.49916400
H	-3.07358400	4.76689000	-0.59589800
H	-2.34612200	5.50167000	0.83644700
H	-4.06933900	5.02060400	0.86656300
H	0.74026500	-0.21942400	1.55118100
C	-0.78278200	-2.60419700	-1.43244800
H	-0.50306500	-2.12860700	-2.37584900
H	-0.63908000	-3.68413600	-1.50021500
C	-2.22196700	-2.29937300	-1.15937300
C	-3.12616600	-3.34655100	-0.64227300
H	-3.46262700	-3.91025600	-1.52782900
H	-2.58600100	-4.05658900	-0.01278300
H	-4.00141700	-2.94902200	-0.13110600
O	-2.61347600	-1.13905100	-1.45513600
Si	-4.17939600	-0.22029200	-1.39252500
C	-4.71070300	-0.18237600	0.38712100
H	-5.55719800	0.51154700	0.46767200
H	-5.04557500	-1.15731100	0.75165500
H	-3.91932500	0.19939300	1.03652600
C	-3.59792500	1.42009600	-2.04154600
H	-4.39367500	2.16710200	-1.93956100
H	-2.72605200	1.77249700	-1.48223900
H	-3.32411200	1.35451700	-3.09999000
C	-5.30110600	-1.17142300	-2.53271500
H	-6.23352800	-0.60976200	-2.66969000
H	-4.84385600	-1.30659400	-3.51900100
H	-5.55857800	-2.15369900	-2.12379100
10fα			
0 1			
C	1.94765000	-0.33631100	0.03188700
C	-0.42048900	-0.10948800	0.46643200
C	-0.38577900	1.41106300	0.32765500
C	1.00254400	1.91143300	0.71960500
C	2.09060800	1.20453700	-0.07588200
H	-1.14757000	1.86565300	0.95919400
H	1.12802800	1.76130600	1.79395500
H	2.00212500	1.49288000	-1.12739000
H	3.07618200	1.50920200	0.28330100
O	0.61266900	-0.73496900	-0.28683300
C	2.82328400	-0.93229600	-1.08339100
O	4.11697100	-0.86965000	-0.73853000
O	2.41738500	-1.30279100	-2.16471700

C	5.08005200	-1.35933600	-1.71305400
H	4.97305700	-0.77279700	-2.62986100
H	4.83823000	-2.40230600	-1.93525900
C	6.45638800	-1.21372100	-1.10238500
H	7.20597100	-1.57882800	-1.81229400
H	6.67915200	-0.16588200	-0.87620200
H	6.54182600	-1.79946100	-0.18144600
O	1.11730300	3.32263300	0.43267000
C	0.62642100	4.18951700	1.35198000
O	0.17564400	3.83530700	2.42625500
C	0.70140800	5.60434500	0.85945500
H	-0.10580400	5.76208100	0.13529900
H	1.65049900	5.79309400	0.35144700
H	0.57075600	6.29364000	1.69422700
O	-0.64381700	1.74668000	-1.05111300
C	-1.46840500	2.78850800	-1.31112100
O	-2.00933200	3.44888100	-0.44248300
C	-1.59568100	3.01752300	-2.78764700
H	-1.67898600	2.06810400	-3.32116500
H	-0.69212100	3.52668200	-3.14299400
H	-2.46299800	3.64678600	-2.98921500
C	-1.72585600	-0.72503600	-0.04845800
H	-1.81596000	-0.55938000	-1.12217500
O	-2.81102100	-0.05587400	0.63174800
C	-3.76984700	0.55782900	-0.10869700
O	-3.76179200	0.59401700	-1.32392300
C	-4.81227500	1.17228800	0.77852700
H	-4.34131100	1.86736600	1.48016600
H	-5.30490900	0.38944900	1.36449300
H	-5.54856100	1.69908900	0.17166200
C	-1.80124400	-2.20184800	0.27891700
H	-0.93883300	-2.72558500	-0.13811000
H	-1.83519300	-2.36159000	1.36020900
O	-3.01326000	-2.70525600	-0.32127900
C	-3.34069600	-3.98438000	-0.04621500
O	-2.66780400	-4.69992100	0.67613800
C	-4.60825400	-4.38711100	-0.74409900
H	-4.44769600	-4.37169100	-1.82739700
H	-5.40747300	-3.67496300	-0.51811800
H	-4.89968300	-5.39014400	-0.43196700
H	-0.31812200	-0.33614900	1.53721500
C	2.35835800	-0.85810500	1.41834900

H	3.37331200	-0.51732000	1.65391400
H	1.71540400	-0.43936700	2.19663200
C	2.36335500	-2.37287800	1.53782800
C	2.23206900	-2.92929200	2.93040900
H	2.88528900	-2.39153900	3.62660600
H	1.20097100	-2.77502700	3.27427300
H	2.45971900	-3.99677500	2.94283500
O	2.48243300	-3.09155500	0.55551800
10fβ			
0 1			
C	0.19477100	-2.11310300	0.68677200
C	-0.04488900	0.10320900	-0.22875200
C	-1.56826100	0.05506400	-0.16380100
C	-2.01676300	-1.39992800	-0.29223000
C	-1.33392900	-2.28914800	0.73772000
H	-2.00116400	0.66000700	-0.95905200
H	-1.79762400	-1.73134000	-1.31027300
H	-1.67192900	-2.01038700	1.73886700
H	-1.59163100	-3.33420400	0.55847300
O	0.54533600	-0.73521900	0.76346700
C	0.77680700	-2.76589300	-0.58918600
O	1.86763900	-2.13109000	-1.01646400
O	0.31442000	-3.76953300	-1.10179600
C	2.55854400	-2.68793200	-2.17481300
H	1.85640600	-2.70714500	-3.01273000
H	2.84865800	-3.71495200	-1.93729600
C	3.75448600	-1.80392300	-2.44743300
H	4.30343200	-2.19827800	-3.30884400
H	3.44479400	-0.77957500	-2.67598500
H	4.43082400	-1.78092900	-1.58743900
O	-3.43975100	-1.50122100	-0.06826900
C	-4.25800100	-1.24578000	-1.11868300
O	-3.84691100	-1.00208200	-2.23842500
C	-5.69996900	-1.29226200	-0.70731600
H	-5.93136900	-0.38581000	-0.13686800
H	-5.89338300	-2.15321100	-0.06221100
H	-6.33517200	-1.32909700	-1.59276200
O	-1.98636100	0.57487700	1.11541600
C	-3.05165800	1.41017700	1.14719600
O	-3.65966100	1.76007400	0.15188000
C	-3.37642000	1.81367000	2.55467400
H	-2.46508500	2.05020000	3.10865900

H	-3.86843500	0.97289700	3.05729500
H	-4.05045500	2.67056000	2.54600700
C	0.53517900	1.49637900	0.02911800
H	0.34134600	1.79257000	1.06046900
O	-0.12927400	2.41594800	-0.86468300
C	-0.77721800	3.48803400	-0.34052200
O	-0.85047400	3.71327700	0.85215000
C	-1.37251200	4.33197500	-1.42884000
H	-2.00764600	3.71851300	-2.07447300
H	-0.57058400	4.74799000	-2.04795500
H	-1.95644000	5.14080900	-0.98983100
C	2.01865000	1.52432600	-0.27352800
H	2.53436500	0.74917100	0.29573100
H	2.20141200	1.37076400	-1.34036700
O	2.50727700	2.82494600	0.11778000
C	3.80484100	3.08579300	-0.14184100
O	4.54565700	2.28350100	-0.68416400
C	4.19038200	4.46211400	0.31999800
H	4.02687500	4.54937700	1.39899100
H	3.56045900	5.21069400	-0.17102600
H	5.23892800	4.64941100	0.08822300
H	0.24889600	-0.22841300	-1.23490200
C	0.83009300	-2.78344500	1.92961600
H	0.42011400	-2.27233700	2.80382200
H	0.51943900	-3.83244700	1.94548400
C	2.35158700	-2.69319600	1.98964600
C	3.14762400	-3.82926900	1.39495400
H	3.22521500	-4.61023300	2.16412000
H	2.65927200	-4.28642000	0.53125900
H	4.15453500	-3.49677600	1.13504900
O	2.90033700	-1.76255200	2.56224300
$^{-}$OTf			
-1 1			
O	1.25138800	-1.44078100	0.12614200
S	0.92442500	-0.00012400	0.00002200
O	1.25031500	0.82988000	1.18457100
O	1.25057000	0.61155500	-1.31063100
C	-0.95504600	-0.00022100	-0.00004100
F	-1.44721500	1.25246700	-0.11726600
F	-1.44746600	-0.52473400	1.14345100
F	-1.44739700	-0.72794600	-1.02627000
TMSOTf			

0 1			
S	0.78685200	-0.87484500	0.05420800
O	1.35800800	-1.83533400	0.99017000
O	0.54110500	-1.24468100	-1.33805900
C	1.96917300	0.58232000	0.01840900
F	3.14138600	0.17411200	-0.48104200
F	2.15769500	1.05710100	1.25371400
F	1.47537400	1.55473600	-0.75596900
O	-0.45262500	-0.17003000	0.70135000
Si	-2.05957800	0.20211100	0.00824100
C	-2.87651500	0.98715200	1.48525800
H	-3.89772700	1.29232200	1.22623100
H	-2.93344800	0.28565900	2.32465600
H	-2.32872800	1.87768200	1.81230500
C	-2.80255200	-1.43152800	-0.49132000
H	-2.26970100	-1.87277600	-1.33958500
H	-2.78430400	-2.14324500	0.34168900
H	-3.84882800	-1.28452300	-0.78661500
C	-1.78827200	1.37491900	-1.41343100
H	-2.76154800	1.65658300	-1.83487900
H	-1.28659300	2.29182300	-1.08676000
H	-1.19767500	0.91408300	-2.21127300

4 NMR spectra of compounds

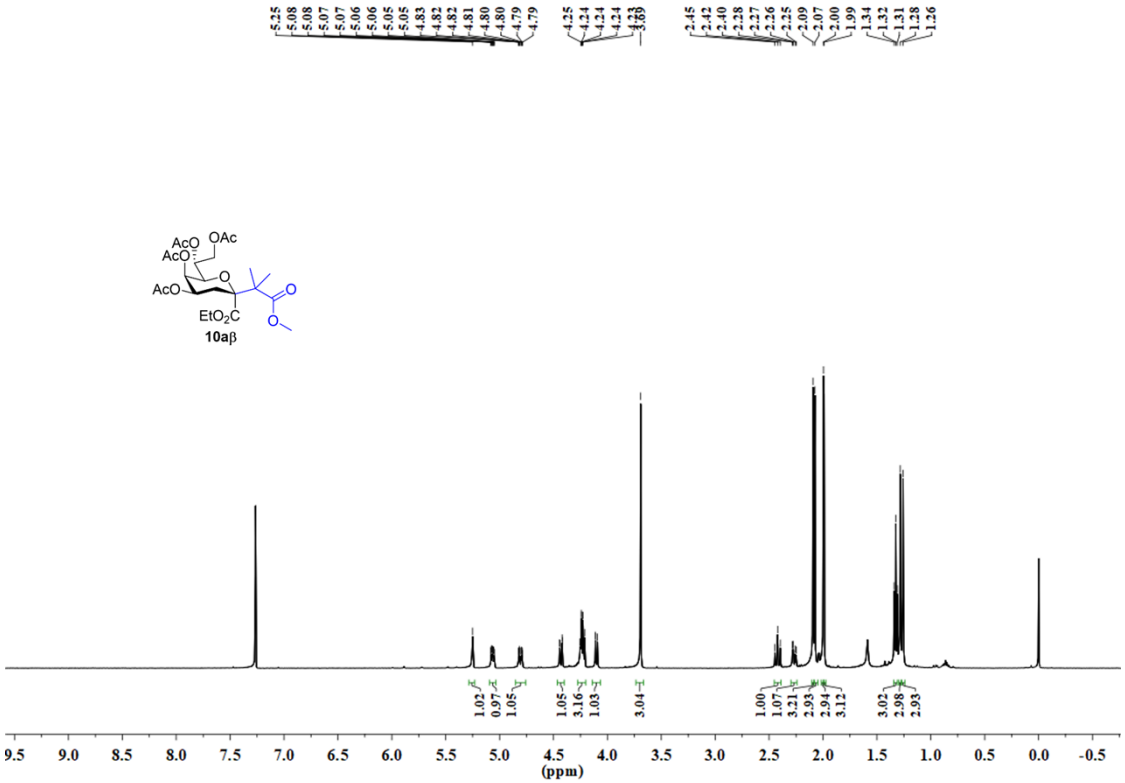


Fig. S1 ^{1}H NMR (500 MHz, $CDCl_3$) of **10aβ**

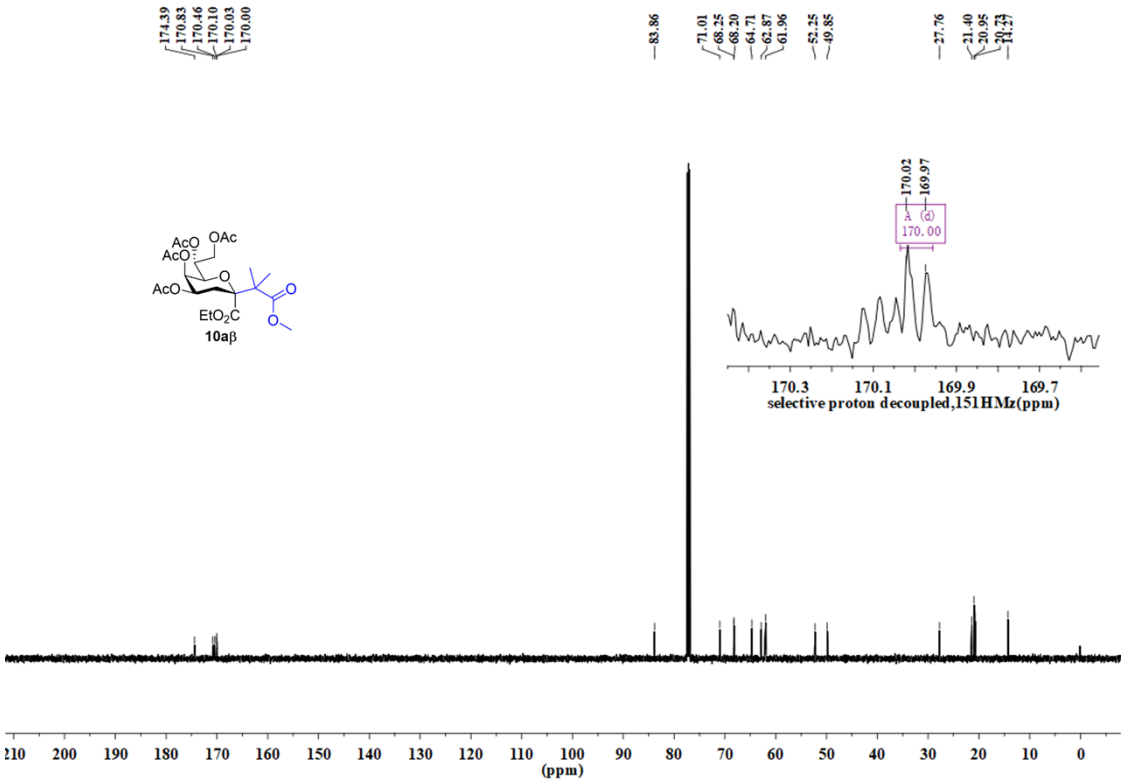


Fig. S2 ^{13}C NMR (151 MHz, $CDCl_3$) and

selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10aβ**

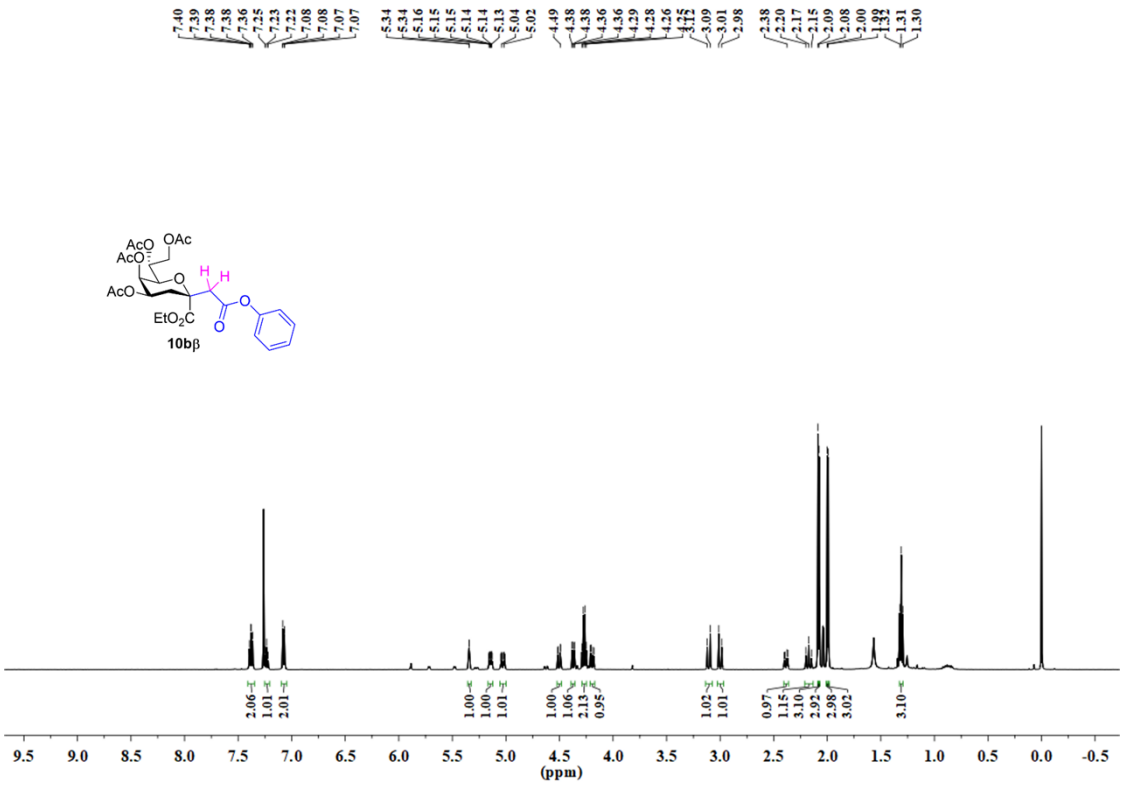


Fig. S3 ^{1}H NMR (500 MHz, $CDCl_3$) of **10bβ**

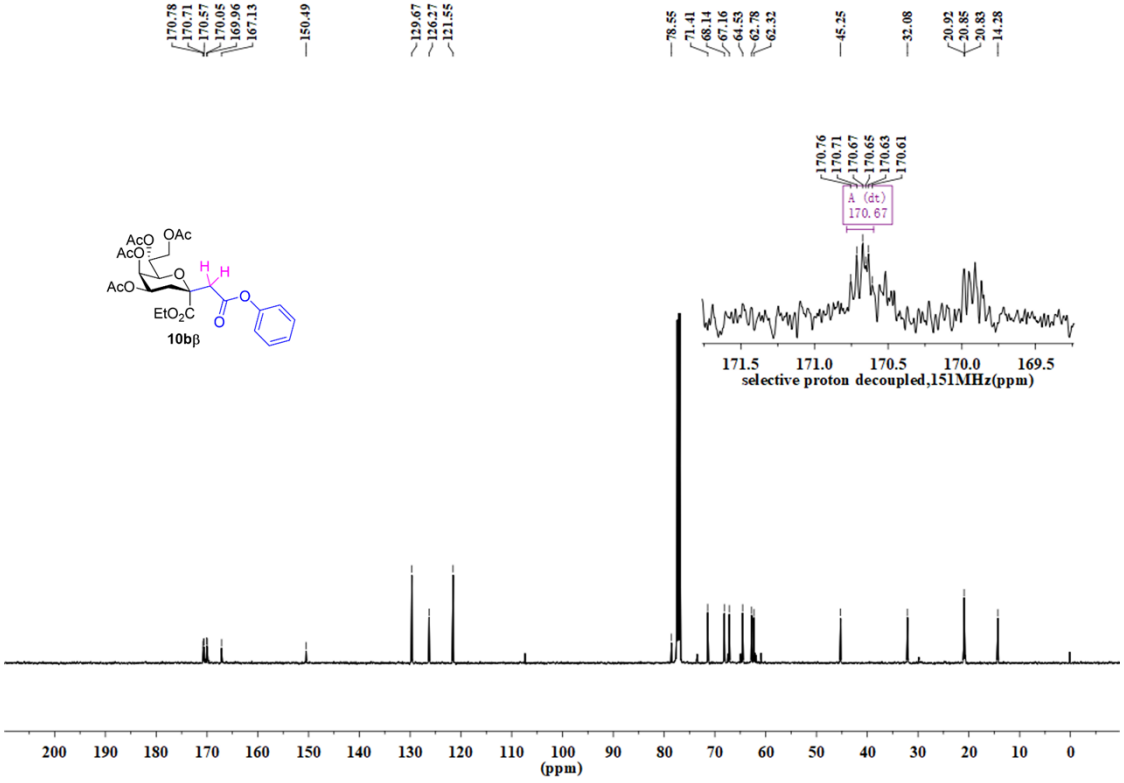


Fig. S4 ^{13}C NMR (126 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10bβ**

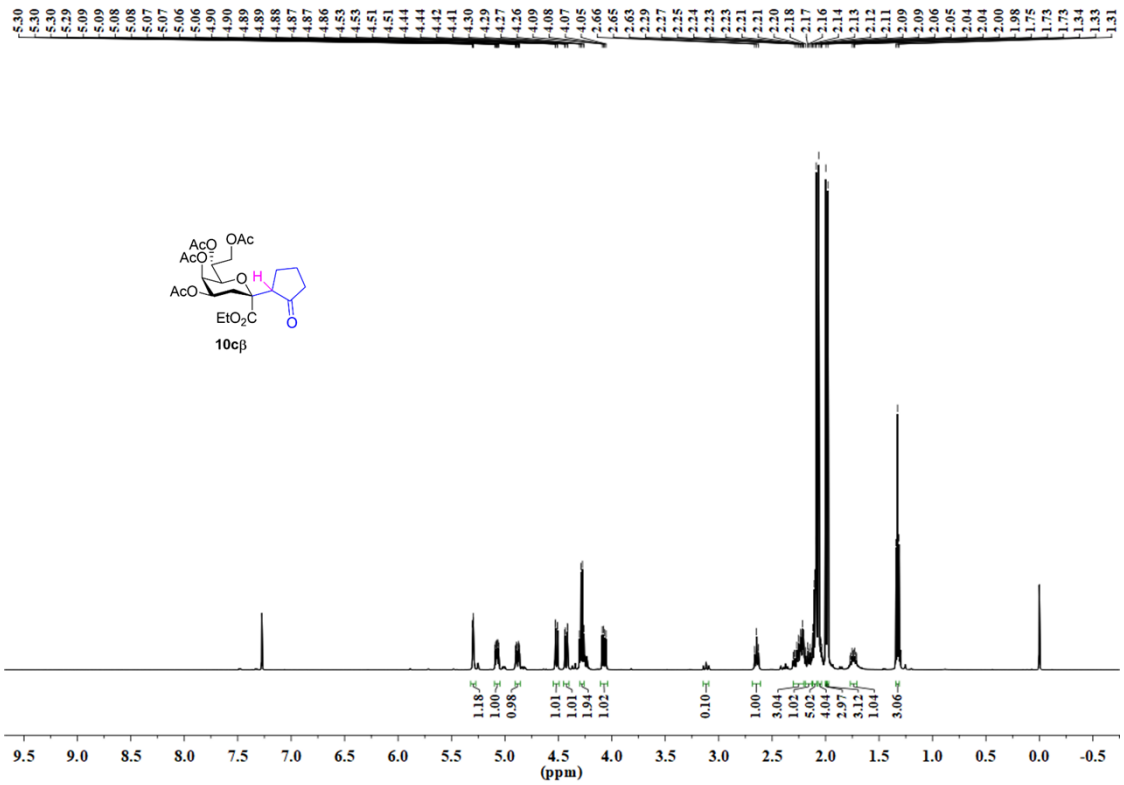


Fig. S5 ^{1}H NMR (500 MHz, $CDCl_3$) of **10cβ**

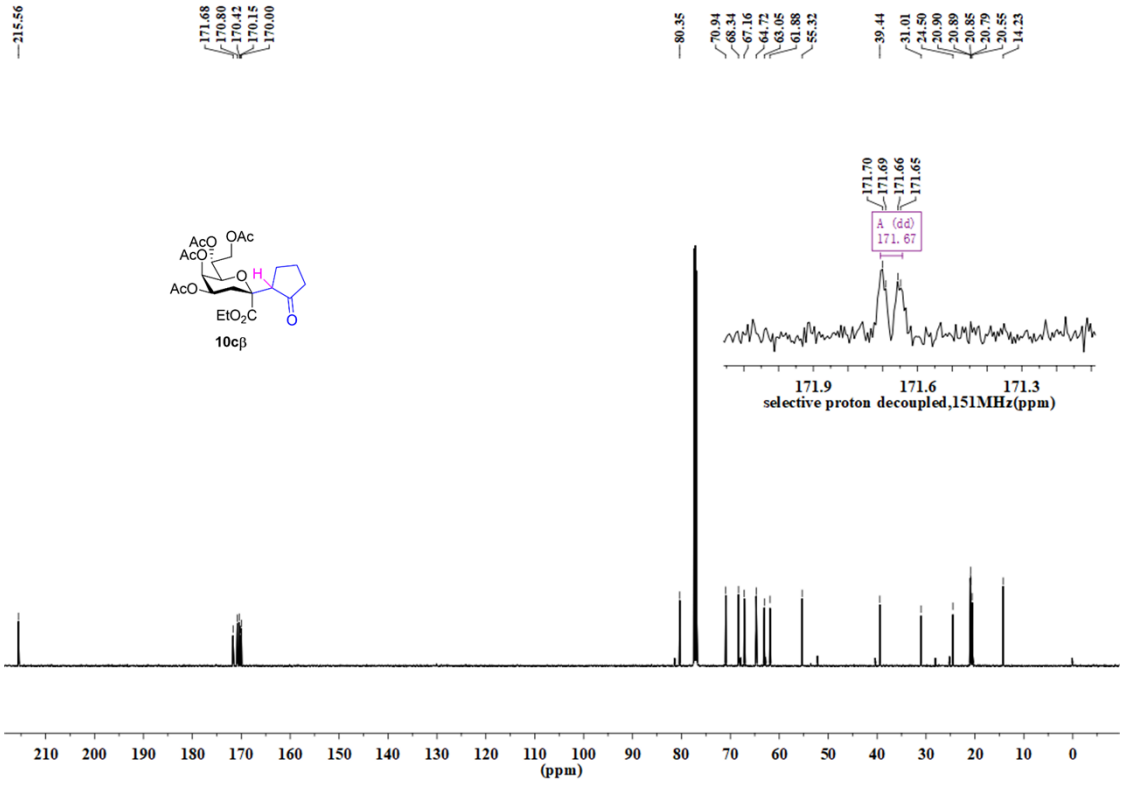


Fig. S6 ^{13}C NMR (126 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10cβ**

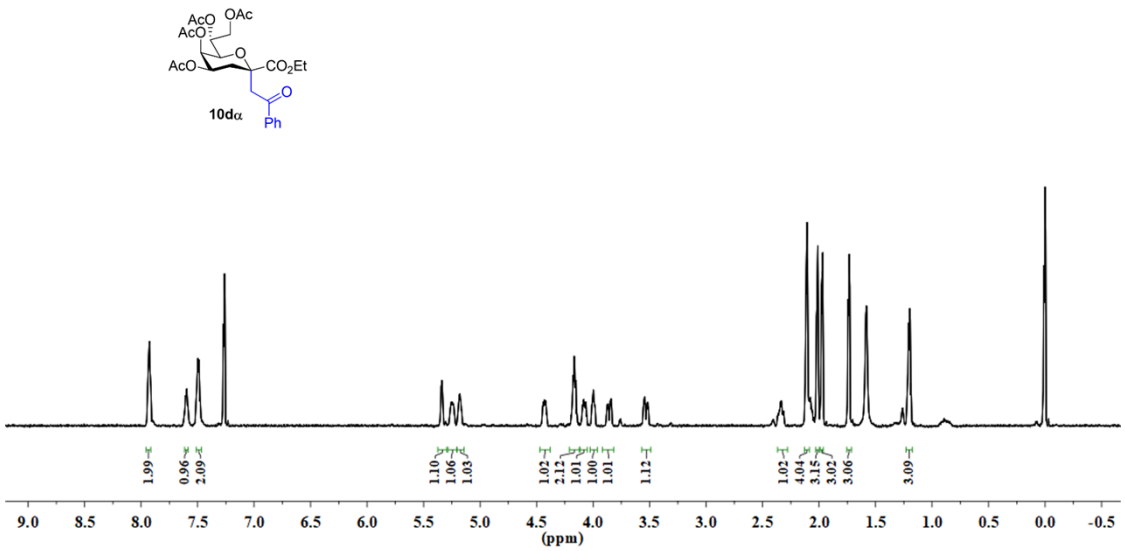


Fig. S7 ^{1}H NMR (600 MHz, $CDCl_3$) of **10dα**

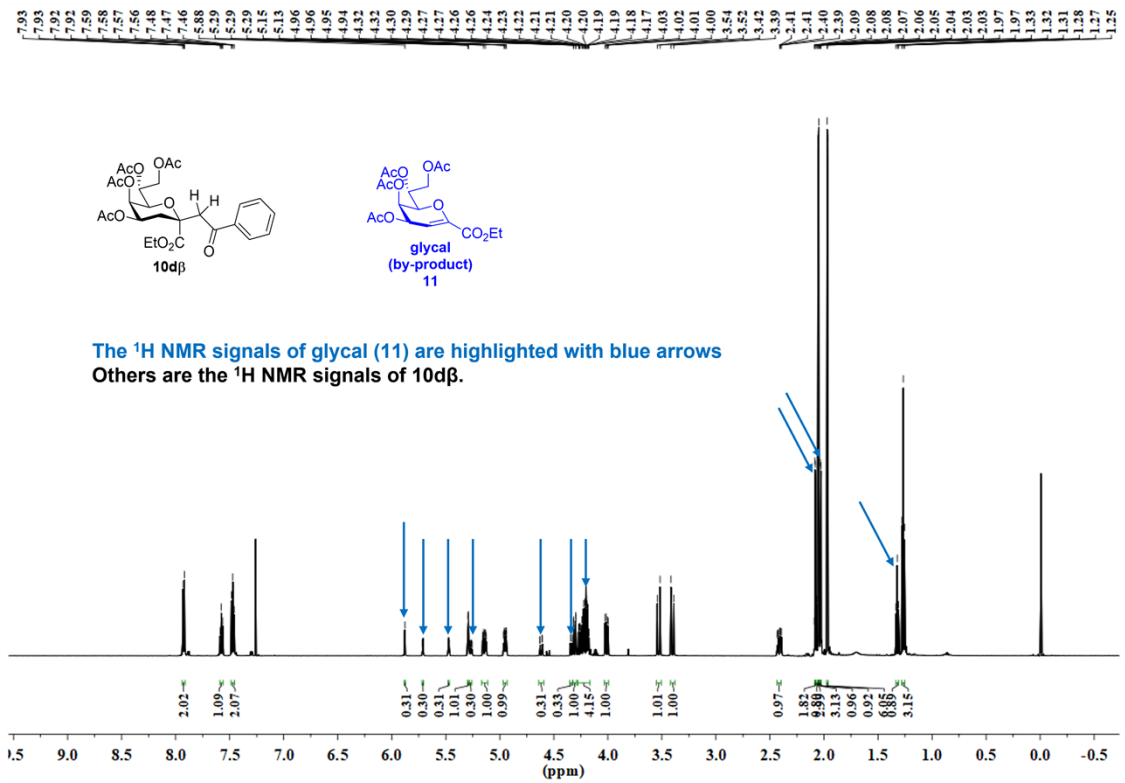


Fig. S8 ^{1}H NMR (600 MHz, $CDCl_3$) of **10dβ**

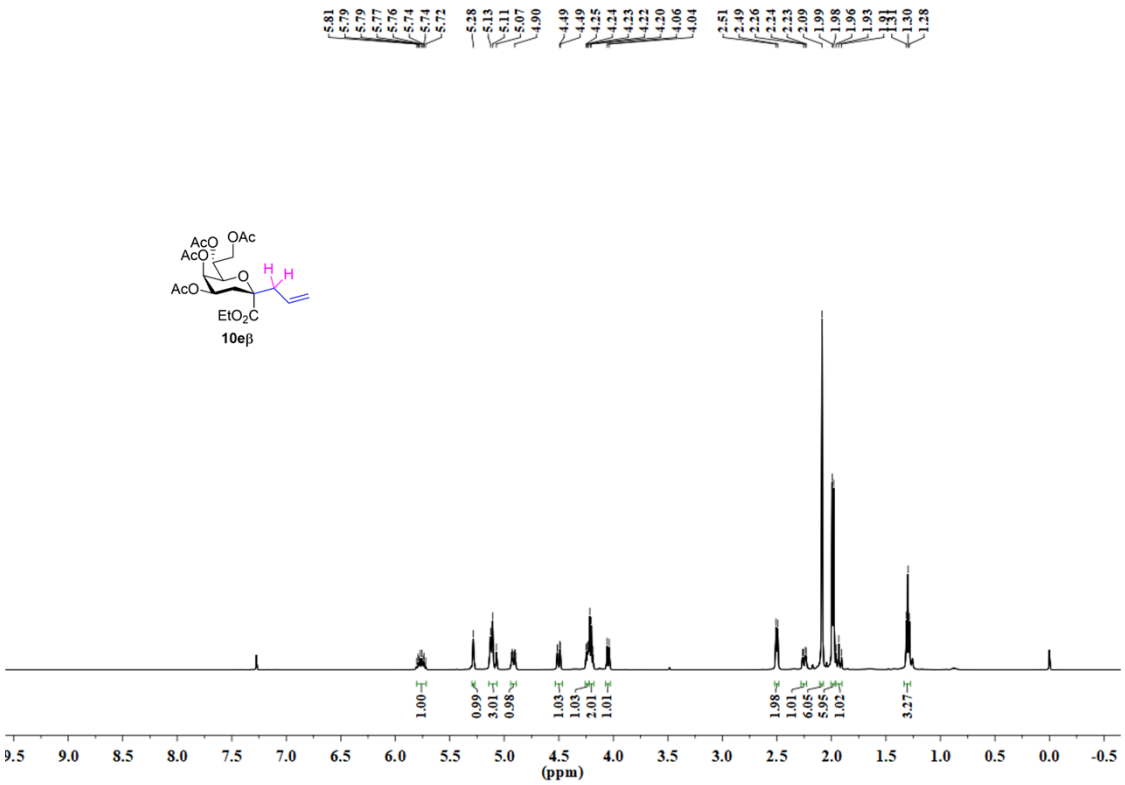


Fig. S9 ^{1}H NMR (500 MHz, $CDCl_3$) of **10eβ**

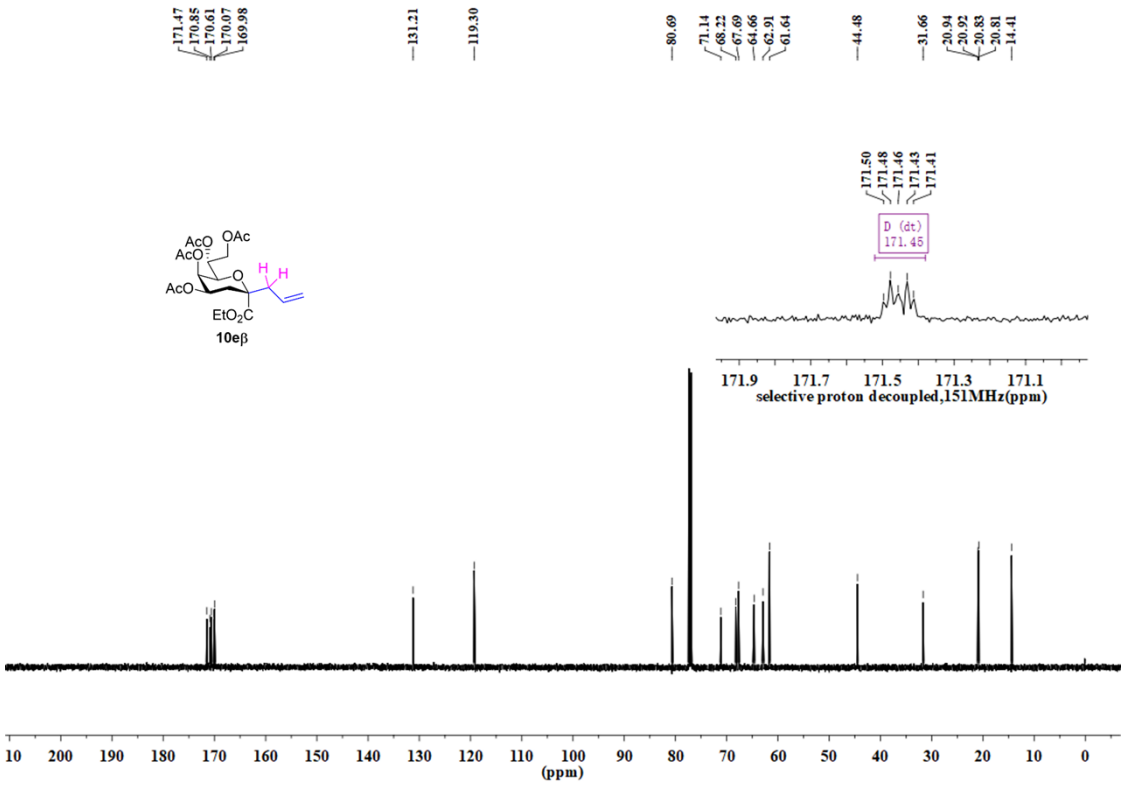


Fig. S10 ^{13}C NMR (151 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10eβ**

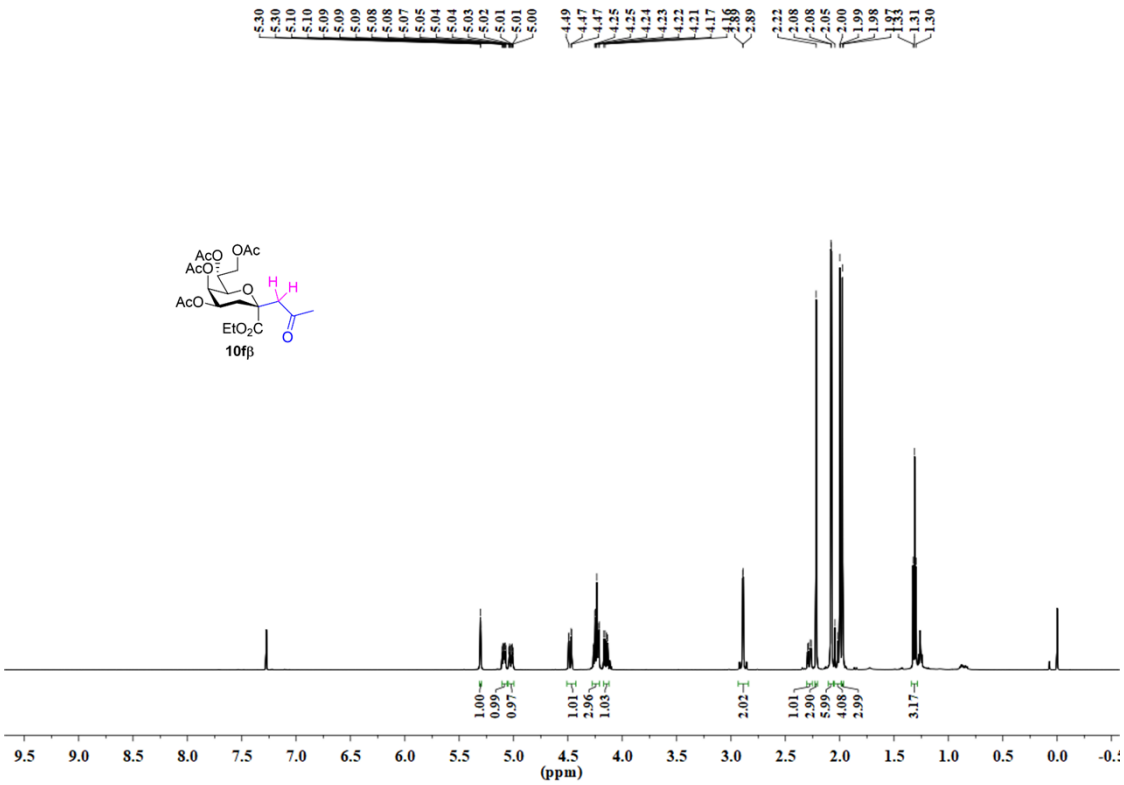


Fig. S11 ^{1}H NMR (500 MHz, $CDCl_3$) of **10fβ**

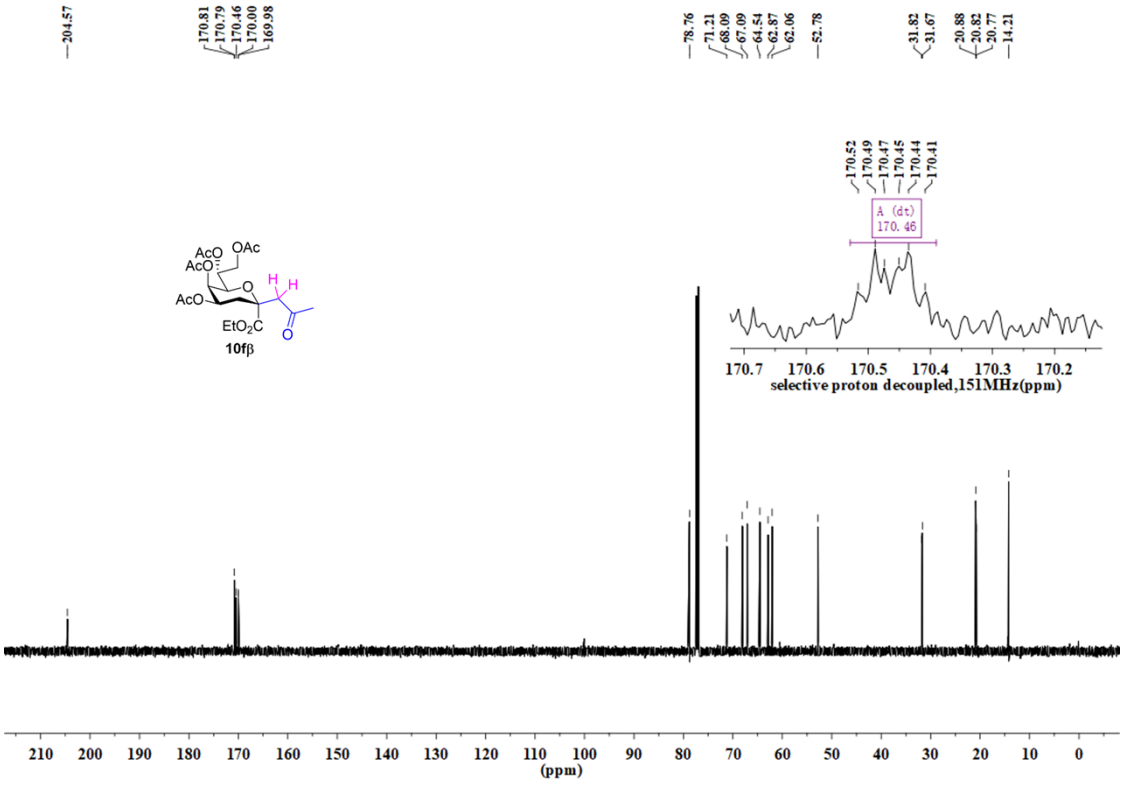


Fig. S12 ^{13}C NMR (151 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10fβ**

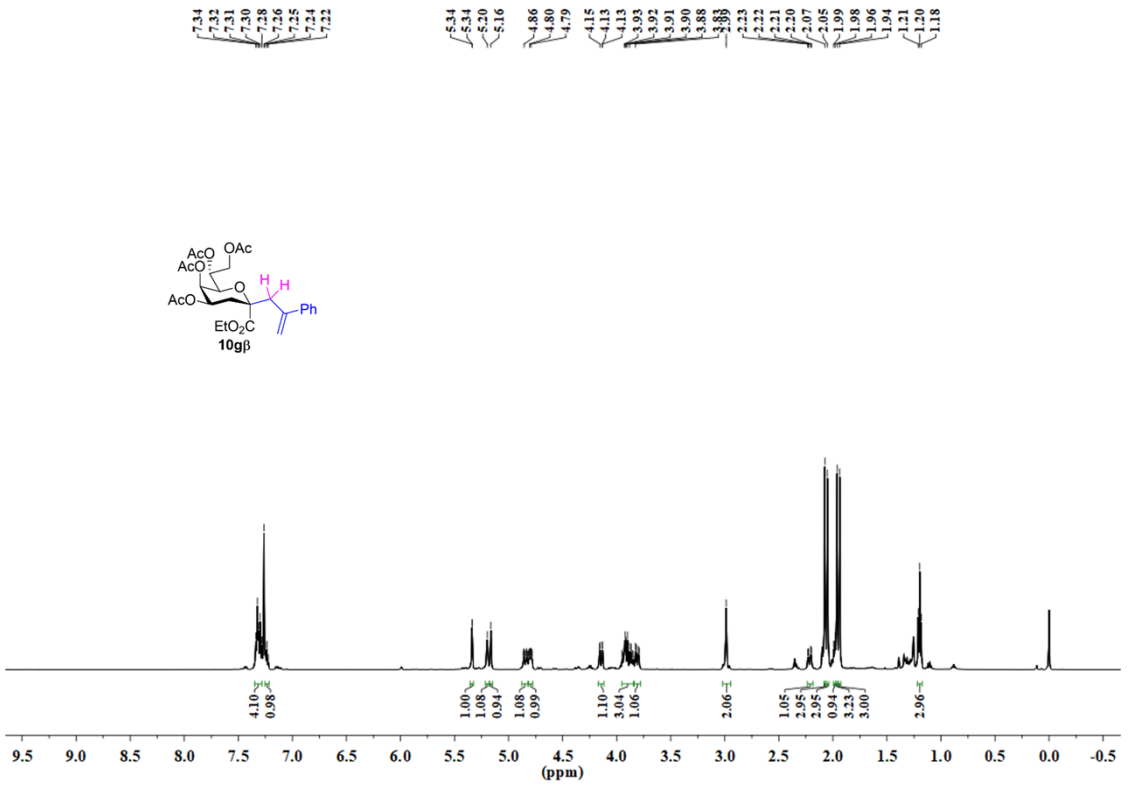


Fig. S13 ^{1}H NMR (500 MHz, $CDCl_3$) of **10gβ**

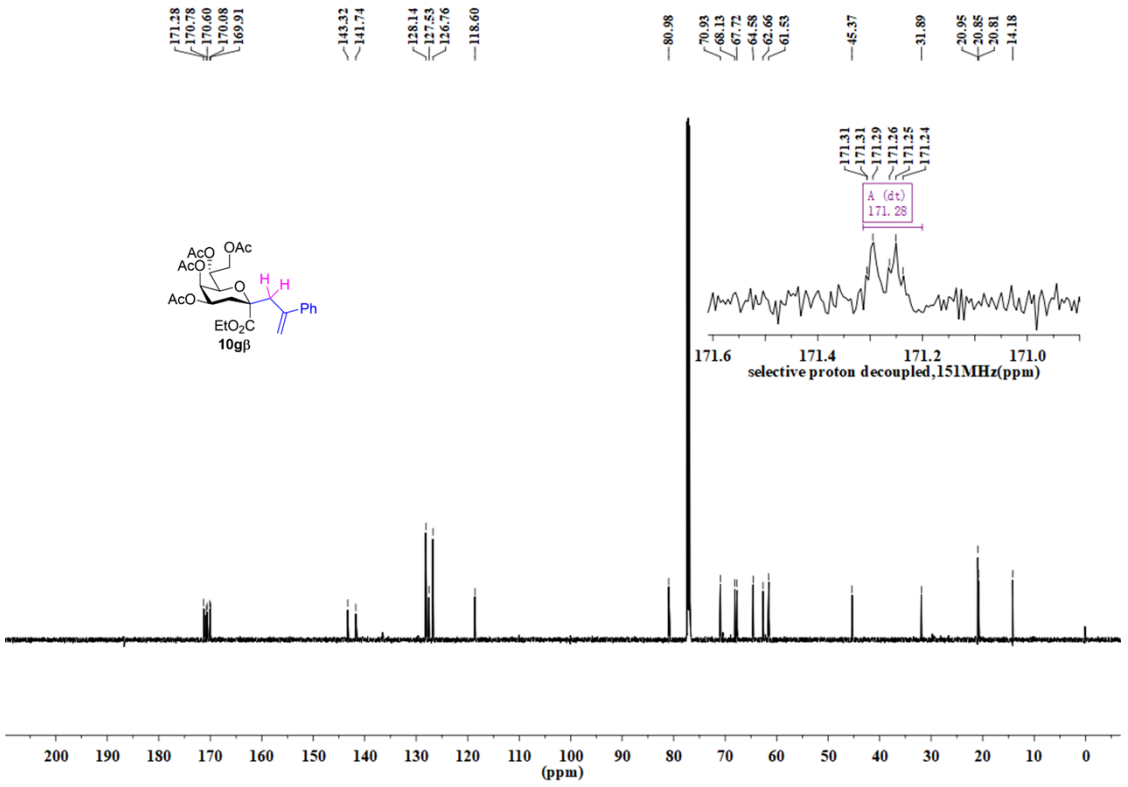


Fig. S14 ^{13}C NMR (151 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10gβ**

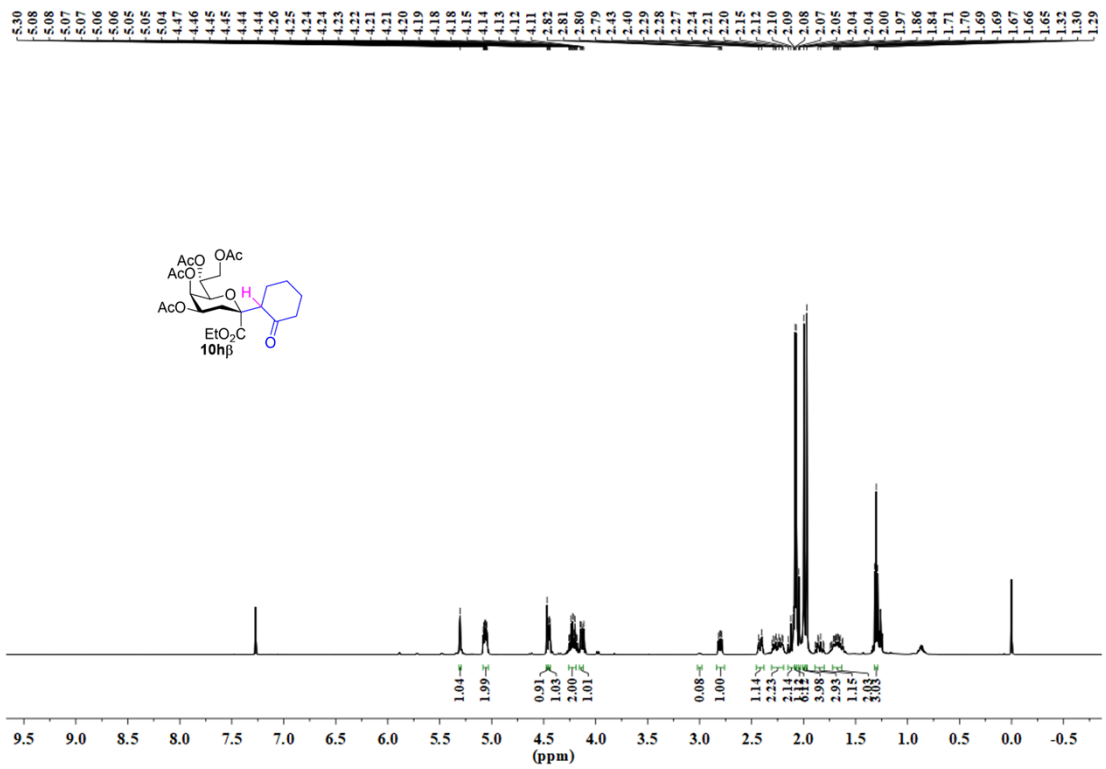


Fig. S15 ^{1}H NMR (500 MHz, $CDCl_3$) of **10hβ**

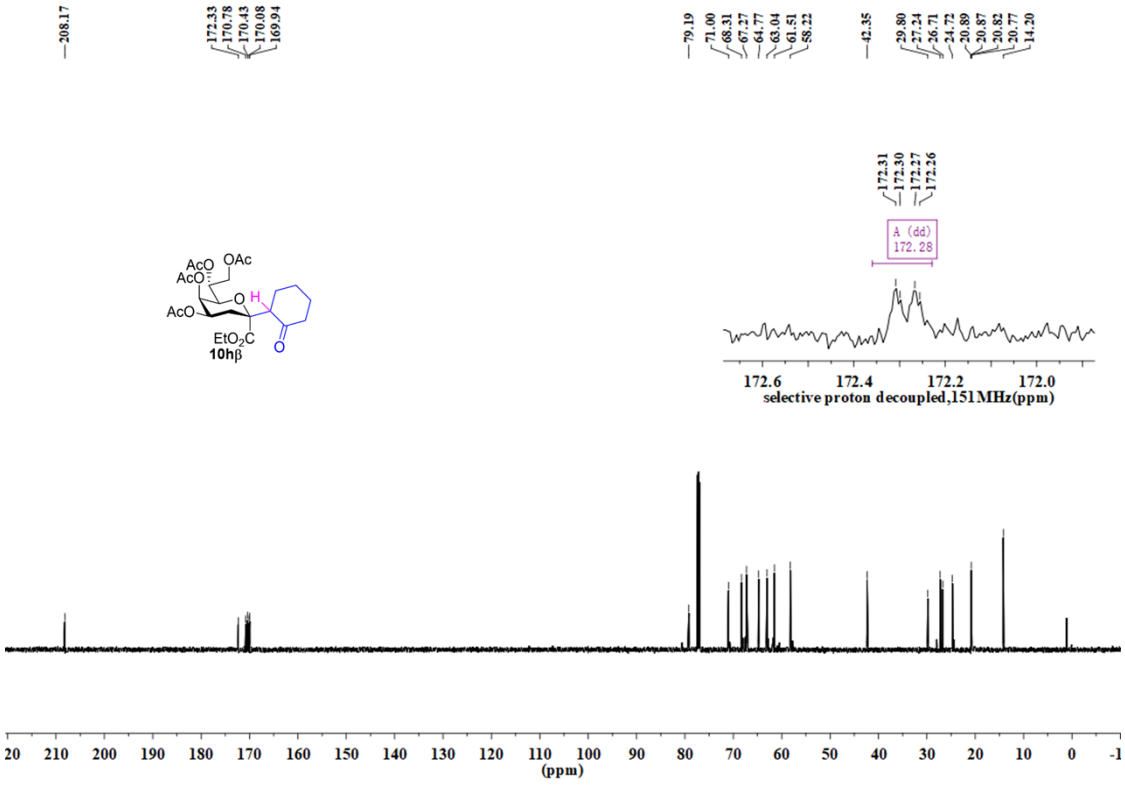


Fig. S16 ^{13}C NMR (151 MHz, $CDCl_3$) and
selective proton decoupled ^{13}C NMR (151 MHz, $CDCl_3$) of **10hβ**

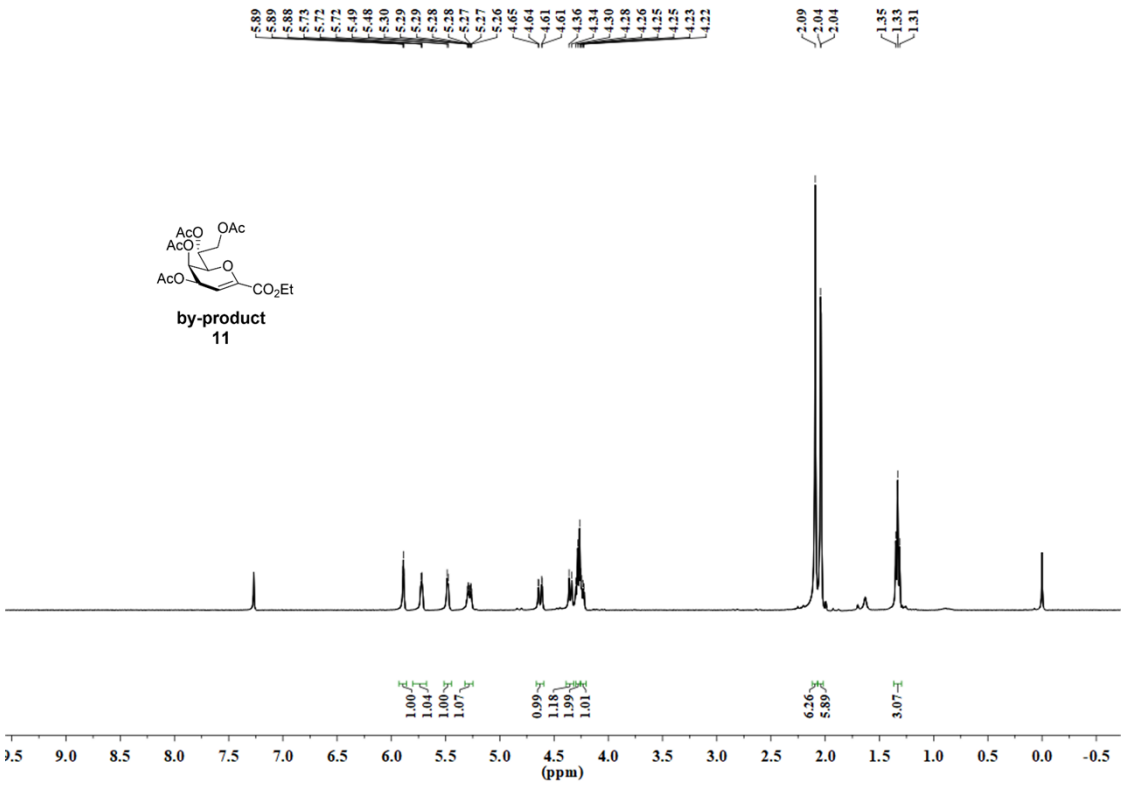


Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) of **glycal**

5 Reference

[1] J. Zhang, X. Gao, S. Liu, Z. Geng, L. Chang, Y. Liu, Q. Ma, G. Xing, G. Liu, D. Fang, *Org. Lett.,* 2023, **25**, 4150-4155.

[2] Q. Wang, J. Shih, K. Y. Tsui, C. J. Laconsay, D. J. Tantillo, J. A. May, *J. Org. Chem.,* 2022, **87**, 8983-9000.

[3] J. Walkowiak, T. M. Del Campo, B. Ameduri, V. Gouverneur, *Synthesis,* 2010, **2010,** 1883-1890.

[4] E. Onobun, D. Crich, *J. Org. Chem.,* 2020, **85**, 16035-16042.

[5] P. Ngoje, D. Crich, *J. Am. Chem. Soc.,* 2020, **142**, 7760-7764.

[6] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[7] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785–789.

[8] A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648–5652.

[9] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.,* 2010, **132**, 154104.

[10] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.,* 1983, **4**, 294–301.

[11] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.,* 1982, **77**, 3654–3665.

[12] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.,* 1980, **72**, 650–654.

[13] A. D. McLean, G. S. Chandler, *J. Chem. Phys.,* 1980, **72**, 5639–5648.

[14] G. W. Spitznagel, T. Clark, P. von Ragué Schleyer, W. J. Hehre, *J. Comput. Chem.,* 1987, **8**, 1109–1116.

[15] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B,* 2009, **113**, 6378–6396.

[16] T. Lu, Q. Chen, *Comput. Theor. Chem.,* 2021, **1200**, 113249.