Supporting Information

Stereoselective Strain-Release Ferrier Rearrangement: The Dual Role of Catalysts

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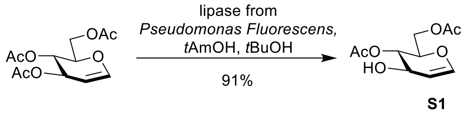
Supplementary Note

All reactions were carried out under a nitrogen atmosphere with magnetic stirring unless otherwise indicated. All commercially obtained reagents were used as received, except where specified otherwise. $Cu(OTf)_2$, $Fe(OTf)_3$, and $Sc(OTf)_3$ were purchased from Alfa and used without further purification. Tetrahydrofuran (THF) and toluene were distilled immediately before use from sodium-benzophenone ketyl. Dichloromethane (CH_2Cl_2), pyridine, and acetonitrile were refluxed over calcium hydride and distilled before use. Anhydrous *N*,*N*-dimethylformamide (DMF), and diethyl ether (Et_2O) were purchased from Sigma-Aldrich and used without further purification. Flash column chromatography was performed on Silica Gel 60 (Merck Co.). Analytical thin-layer chromatography was performed on Silicycle SiliaPlate glass-backed plates coated with silica gel (60 mesh pore size, F-254 indicator) and visualized by exposure to ultraviolet light and/or staining with 5% sulfuric acid in ethanol. Optical rotations were determined with a JASCO P-1020 digital polarimeter. All NMR spectra were recorded with Bruker BBFO-400 (400 MHz) or Bruker AV-500 (500 MHz) NMR spectrometers at ambient temperature using $CDCl_3$ or CD_2Cl_2 as solvents. The NMR spectra were calibrated by using residual undeuterated chloroform (δ_H = 7.26 ppm), $CDCl_3$ (δ_C = 77.16 ppm), residual undeuterated dichloromethane (δ_H = 5.32 ppm), and CD_2Cl_2 (δ_C = 53.84 ppm) as internal references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet.

Supplementary Methods

Section 1. Synthesis of glycal donors.

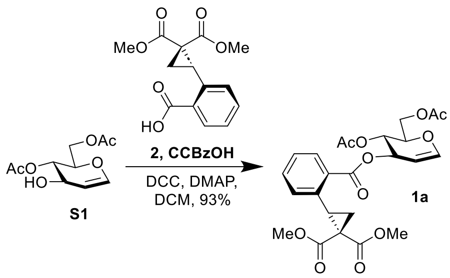
4,6-Di-*O*-acetyl-D-glucal (S1)



Supporting information Fig. 1 │ Synthesis of S1

3,4,6-Tri-*O*-acetyl-D-glucal (1.5 g, 5.6 mmol, 1.0 equiv), lipase from *Pseudomonas fluorescens* (961 mg), 2-methyl-2-butanol (*t*AmOH, 15 mL) and *tert*-Butanol (*t*BuOH, 1.5 mL, 16.2 mmol) were added into a sealed tube. The mixture was stirred for 22 h at 40 °C. After raw material was consumed (determined by thin layer chromatography (TLC), the sealed tube was allowed to cool to room temperature. Then the mixture was filtered through a Büchner funnel and washed with 30 mL of chloroform. Solvents were evaporated under reduced pressure and the crude product was purified by silica gel column chromatography (hexane:EtOAc = 2:1) to obtain **S1** (1.2 g, 5.2 mmol, 91%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (dd, J = 6.1, 1.5 Hz, 1H), 4.97 (dd, J = 8.9, 6.3 Hz, 1H), 4.86 (dd, J = 6.1, 2.8 Hz, 1H), 4.40 (dd, J = 12.3, 5.4 Hz, 1H), 4.33 – 4.31 (m, 1H), 4.24 (dd, J = 12.3, 2.5 Hz, 1H), 4.14 – 4.10 (m, 1H), 2.57 (brs, 1H), 2.13 (s, 3H), 2.09 (s, 3H). The data are identical to the literature.[1]

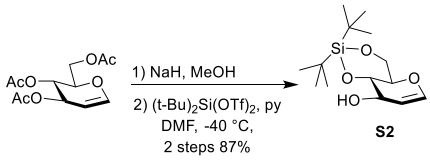
3-*O*-*ortho*-2,2-Dimethoxycarbonylcyclopropylbenzoyl-4,6-di-*O*-acetyl-D-glucal (1a)



Supporting information Fig. 2 │ Synthesis of 1a

To a solution of **S1** (370 mg, 1.6 mmol, 1.0 equiv) and CCBzOH[2] (537 mg, 1.9 mmol, 1.2 equiv) in anhydrous dichloromethane (DCM, 8.0 mL, 0.2 M) were added sequentially *N,N′*-dicyclohexylcarbodiimide (DCC, 497 mg, 2.4 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP, 98 mg, 0.8 mmol, 0.5 equiv). The mixture was stirred for 10 h at room temperature. The resulting mixture was filtered and washed with cold EtOAc, the organic layer was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (toluene:EtOAc = 6:1) to afford **1a** as a colorless syrup (735 mg, 1.49 mmol, 93%, dr = 1:0.85). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.82 (dd, J = 7.8, 1.5 Hz, 0.9H), 7.46 – 7.41 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 (d, J = 7.7 Hz, 2H), 6.51 – 6.47 (m, 2H), 5.60 – 5.57 (m, 1.9H), 5.45 – 5.42 (m, 1.9H), 5.06 – 5.00 (m, 1.9H), 4.49 – 4.43 (m, 2H), 4.31 – 4.21 (m, 4H), 3.88 – 3.83 (m, 2H), 3.80 (s, 2.3H), 3.79 (s, 3H), 3.25 (s, 2.5H), 3.23 (s, 3H), 2.21 – 2.16 (m, 2H), 2.09 (s, 5.4H), 2.08 (s, 2.8H), 2.05 (s, 3H), 1.85 – 1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.6, 170.3, 170.1, 169.6, 169.5, 167.2, 167.1, 166.1, 165.7, 145.5, 145.4, 136.7, 136.4, 132.32, 132.25, 131.0, 130.9, 130.8, 130.3, 129.7, 129.5, 127.8, 127.7, 99.5, 99.3, 74.3, 74.2, 68.9, 68.8, 67.0, 66.7, 61.6, 61.5, 52.71, 52.65, 52.2, 52.0, 36.3, 35.8, 32.7, 32.4, 20.9, 20.8, 20.7, 19.9, 19.7; HRMS (ESI) *m/z* Calcd for $C_{24}H_{26}O_{11}Na$ $[M + Na]^+$ 513.1373, found 513.1390.

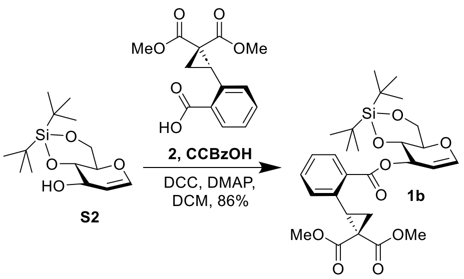
4,6-*O*-Di-(*tert*-butyl)silanediyl-D-glucal (S2)



Supporting information Fig. 3 │ Synthesis of S2

To a solution of 3,4,6-Tri-*O*-acetyl-D-glucal (6.0 g, 22.2 mmol, 1.0 equiv) in MeOH (45 mL, 0.5 M) was added NaH (60% dispersion in mineral oil, 438 mg, 11.1 mmol, 0.5 equiv). The mixture was stirred at 0 °C until all starting material was consumed. The reaction was then quenched with AcOH and pH was adjusted to 7. The mixture was diluted in MeOH, filtered, and concentrated *in vauco*. The crude product without purification was dissolved in anhydrous dimethylformamide (DMF, 75 mL, 0.27 M) under an N_2 atmosphere, and cooled to -45 °C. Then, under constant stirring, di-*tert*-butylsilyl ditriflate ($(t\text{Bu})_2Si(OTf)_2$, 4.7 mL, 14.4 mmol, 0.7 equiv) was added to the reaction mixture dropwise over 15 min. Stirring was continued for 45 min at -45 °C after which pyridine was added and it was allowed to warm to 0 °C. After 30 min at 0 °C, the reaction was quenched by $NaHCO_3$ (sat.) and diluted with EtOAc (300 mL). The organic phase was washed with brine (3 x 150 mL), dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 9:1) to obtain **S2** (5.5 g, 19.2 mmol, 87% for two steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 – 6.23 (m, 1H), 4.76 (dd, *J* = 6.1, 1.9 Hz, 1H), 4.30 (d, *J* = 6.8 Hz, 1H), 4.18 (dd, *J* = 10.3, 5.0 Hz, 1H), 3.96 (t, *J* = 10.2 Hz, 1H), 3.92 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.87 – 3.81 (m, 1H), 2.44 (brs, 1H), 1.07 (s, 9H), 0.99 (s, 9H). The data are identical to the literature.[3]

3-*O*-*ortho*-2,2-Dimethoxycarbonylcyclopropylbenzoyl-4,6-*O*-(di-*tert*-butyl)silanediyl-D-glucal (1b)

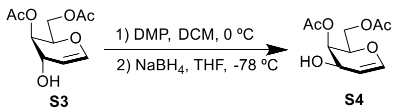


Supporting information Fig. 4 │ Synthesis of 1b

Following the procedure for **1a**, **S2** (1.7 g, 5.9 mmol, 1.0 equiv) was transformed into **1b** (2.8 g, 5.07 mmol, 86%, dr = 1:1) as a colorless oil after purification by silica gel column chromatography (toluene:EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.29 – 7.24 (m, 3H), 6.39 – 6.34 (m, 2H), 5.58 – 5.52 (m, 2H), 5.01 – 4.97 (m, 2H), 4.44 – 4.34 (m, 2H), 4.27 – 4.19 (m, 2H), 4.08 – 3.88 (m, 5H), 3.81 (s, 4H), 3.75 (s, 3H), 3.29 (d, J = 6.4 Hz, 6H), 2.21 – 2.17 (m, 2H), 1.89 – 1.77 (m, 2H), 1.09 (s, 9H), 1.06 (s, 9H), 0.99 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 167.3, 167.2, 167.1, 166.5, 144.8, 144.6, 136.6, 135.9, 132.1, 131.92, 131.2, 130.1, 129.9, 129.5, 127.7, 127.6, 100.60, 100.56, 73.8, 73.5, 73.0, 72.9, 72.9, 65.89, 65.86, 52.7, 52.6, 52.17, 52.15, 36.3, 35.8, 32.8, 32.4, 29.7, 27.4, 26.7, 22.7, 22.6, 20.0, 19.87, 19.85, 19.7; HRMS (ESI) *m/z* Calcd for $C_{28}H_{38}O_9SiNa$ $[M + Na]^+$ 569.2183, found 569.2209.

Tips: *Glucal donors are usually straightforward to separate with toluene and EtOAc eluent. Otherwise, if the product is hard to separate from the unreacted substrate, a tiny quantity of Ac_2O can help acetylate the unreacted glucal. Small adjustments to the typical procedure make silica gel column chromatography with toluene and EtOAc eluent easier to remove anomeric acetate.*

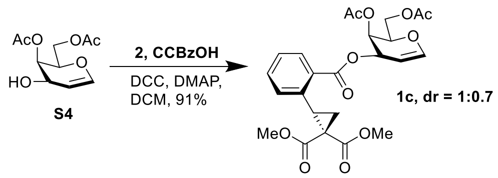
4,6-Di-*O*-acetyl-D-galactal (S4)



Supporting information Fig. 5 │ Synthesis of S4

Compound **S3**[4] (200 mg, 0.9 mmol, 1.0 equiv) was dissolved in distilled DCM (4.4 mL) and then the system was cooled to 0 °C. Then Dess-Martin periodinane (DMP, 444 mg, 1.0 mmol, 1.2 equiv) was added into the system and the reaction was stirred at the same temperature for 1 h. Then sat.$NaHCO_3$ was used to quench the reaction. The system was diluted in DCM, extracted by DCM, and washed with H_2O. The combined organic layers were concentrated *in vacuo* and dried with toluene three times to get the yellow oil without further purification. Then to a solution of oil in distilled THF (4.4 mL) at -78 °C was added $NaBH_4$ (36 mg, 1.0 mmol, 1.1 equiv). The reaction was stirred at -78 °C for 1.5 h. After raw material was consumed (determined by TLC), the system was warmed to 0 °C and sat. NH_4Cl was added to quench the reaction. Extract the system by DCM and the organic layers were concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 2:1) to obtain **S4** (162 mg, 0.73 mmol, 2 steps 81%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) 6.38 (dd, J = 6.2, 1.6 Hz, 1H), 5.50 – 5.48 (m, 1H), 4.90 – 4.88 (m, 1H), 4.60 – 4.58 (m, 2H), 4.30 – 4.12 (m, 2H), 2.12 (s, 3H), 2.04 (s, 3H). The data are identical to the literature.[5]

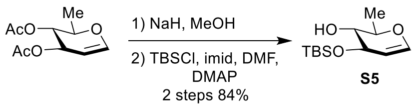
3-*O*-*ortho*-2,2-Dimethoxycarbonylcyclopropylbenzoyl-4,6-di-*O*-acetyl-D-galactal (1c)



Supporting information Fig. 6 │ Synthesis of 1c

Following the procedure for **1a**, **S4** (160 mg, 0.7 mmol, 1.0 equiv) was transformed into **1c** (310 mg, 0.64 mmol, 91%, dr = 1:0.7) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.8, 1.5 Hz, 0.7H), 7.77 (dd, J = 7.9, 1.5 Hz, 1H), 7.46 – 7.42 (m, 1.9H), 7.35 – 7.29 (m, 1.9H), 7.24 – 7.21 (m, 1.9H), 6.51 – 6.47 (m, 1.8H), 5.80 – 5.74 (m, 1.7H), 5.60 – 5.56 (m, 1.9H), 4.95 – 4.90 (m, 1.7H), 4.41 – 4.37 (m, 1.7H), 4.35 – 4.23 (m, 3.7H), 3.90 – 3.80 (m, 1H), 3.80 (s, 3H), 3.79 (s, 2H), 3.73 – 3.67 (m, 1H), 3.29 (s, 2H), 3.27 (s, 3H), 2.21 – 2.15 (m, 2.5H), 2.12 (s, 2H), 2.09 (s, 8H), 1.84 (dd, *J* = 9.0, 5.1 Hz, 1.2H), 1.80 (dd, *J* = 9.0, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.6, 170.2, 170.1, 170.0, 167.2, 167.1, 165.8, 165.4, 145.32, 145.25, 136.8, 136.1, 132.2, 131.0, 130.9, 130.8, 130.0, 129.5, 129.4, 127.7, 127.6, 99.2, 99.1, 73.1, 72.9, 64.70, 64.66, 64.1, 64.0, 62.2, 62.1, 52.7, 52.2, 52.1, 36.5, 36.0, 32.6, 32.3, 20.8, 20.71, 20.65, 19.7; HRMS (ESI) m/z Calcd for $C_{24}H_{26}O_{11}Na$ $[M + Na]^+$ 513.1373, found 513.1390.

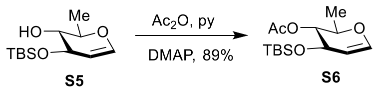
3-*O*-(*tert*-Butyldimethylsilyl)-L-rhamal (S5)



Supporting information Fig. 7 | Synthesis of S5

To a solution of 3,4-Di-*O*-acetyl-L-rhamal (1.0 g, 4.7 mmol, 1.0 equiv) in MeOH (20 mL, 0.2 M) was added NaH (60% dispersion in mineral oil, 93 mg, 2.3 mmol, 0.5 equiv). The mixture was stirred at room temperature until all starting material was consumed (determined by TLC, typically 1.5 h). The reaction was then quenched with AcOH, pH was adjusted to 7. The mixture was filtered and concentrated *in vacuo* to afford white solid without further purification. To a solution of solid in anhydrous DMF (8 mL, 0.6 M) was added imidazole (imid, 478 mg, 7.0 mmol, 1.5 equiv) and DMAP (57.2 mg, 0.5 mmol, 0.1 equiv) under an N_2 atmosphere at 0 °C. Then *tert*-butyldimethylsilyl chloride (777 mg, 5.1 mmol, 1.1 equiv) was added in batches at the same temperature. The resulting mixture was slowly warmed up to room temperature and stirred for 10 h. TLC showed complete consumption of the starting material. The reaction mixture was diluted with water and extracted three times with diethyl ether. The combined organic layers were washed with water and brine, and then dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude silyl ether product was purified by silica gel column chromatography (hexane:EtOAc = 5:1) to obtain **S5** (952 mg, 3.9 mmol, 84% for two steps) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 6.0, 1.3 Hz, 1H), 4.60 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.21 – 4.17 (m, 1H), 3.81–3.98 (m, 1H), 3.53 – 3.63 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 9H), 0.10 (s, 6H). The data are identical to the literature.[6]

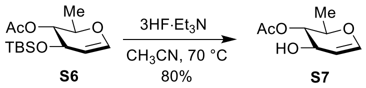
3-*O*-(*tert*-Butyldimethylsilyl)-4-*O*-acetyl-L-rhamal (S6)



Supporting information Fig. 8 | Synthesis of S6

To a solution of **S5** (952 mg, 3.9 mmol, 1.0 equiv) in anhydrous pyridine (19 mL, 0.2 M) was added Ac_2O (0.6 mL, 5.8 mmol, 1.5 equiv) and DMAP (48 mg, 0.4 mmol, 0.1 equiv) at room temperature under N_2 atmosphere, and the solution was kept stirring overnight. TLC (hexane:EtOAc = 8:1) showed complete consumption of the starting material. The solution was evaporated under reduced pressure. The resulting syrup was dissolved in EtOAc, and washed sequentially with water, 1N HCl solution, sat. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 8:1) to provide **S6** (1.0 g, 3.47 mmol, 88%) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (dd, *J* = 6.1, 1.4 Hz, 1H), 4.91 (dd, *J* = 8.1, 6.1 Hz, 1H), 4.67 (dd, J = 6.2, 2.8Hz, 1H), 4.29 – 4.24 (m, 1H), 4.05 – 3.97 (m, 1H), 2.10 (s, 3H), 1.29 (d, J = 6.5 Hz, 3H), 0.87 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). The data are identical to the literature.[7]

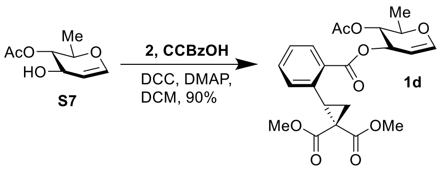
4-*O*-Acetyl-L-rhamal (S7)



Supporting information Fig. 9 │ Synthesis of S7

To a solution of **S6** (1.0 g, 3.5 mmol, 1.0 equiv) in CH_3CN (37 mL, 0.093 M) at 70 °C, 3HF•Et_3N (1.2 mL, 7.0 mmol, 2.0 equiv) was added under an N_2 atmosphere. After stirring at this temperature for 10 h (determined by TLC), the reaction was quenched by adding sat. $NaHCO_3$ and extracted with EtOAc. The combined organic layer was washed with saturated $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc = 4:1) to provide **S7** (480 mg, 2.80 mmol, 80%) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, J = 6.1, 1.6 Hz, 1H), 4.82 – 4.72 (m, 2H), 4.30 – 4.27 (m, 1H), 4.01 – 3.94 (m, 1H), 2.51 (s, 1H), 2.14 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H). The data are identical to the literature.[7]

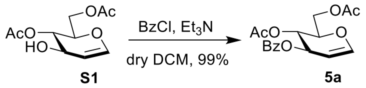
3-*O*-*ortho*-2,2-Dimethoxycarbonylcyclopropylbenzoyl-4-*O*-acetyl-L-rhamal (1d)



Supporting information Fig. 10 │ Synthesis of 1d

Following the procedure for **1a**, **S7** (200 mg, 1.0 mmol, 1.0 equiv) was transformed into **1d** (450 mg, 0.90 mmol, 90%, dr = 1:1) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.8, 1.5 Hz, 1H), 7.83 (dd, J = 7.8, 1.5 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 2H), 6.49 – 6.45 (m, 2H), 5.61 – 5.54 (m, 2H), 5.29 – 5.22 (m, 2H), 5.02 – 4.96 (m, 2H), 4.21 – 4.11 (m, 2H), 3.90 – 3.84 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.27 (s, 6H), 3.26 (s, 3H), 2.22 – 2.18 (m, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 1.87 – 1.76 (m, 3H), 1.36 (dd, J = 6.5, 3.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 169.93, 169.85, 167.2, 167.1, 166.3, 165.9, 145.82, 145.79, 136.6, 136.3, 132.2, 132.11, 131.2, 131.12, 131.06, 130.3, 129.6, 129.5, 127.7, 127.6, 99.1, 72.7, 72.6, 71.7, 71.5, 69.6, 69.3, 52.7, 52.65, 52.2, 52.0, 36.4, 35.7, 32.7, 32.3, 20.93, 20.86, 19.8, 19.7, 16.74, 16.72; HRMS (ESI) m/z Calcd $C_{24}H_{26}O_{11}Na$ $[M+Na]^+$ 455.1318, found 455.1311.

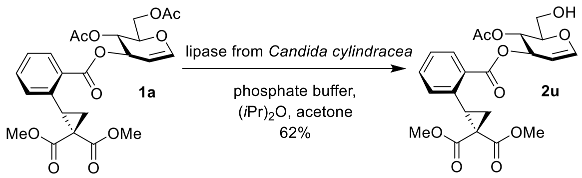
3-*O*-Benzylated-4,6-di-*O*-acetyl-D-glucal (5a)



Supporting information Fig. 11 │ Synthesis of 5a

Compound **S1** (100 mg, 0.4 mmol, 1.0 equiv) and triethylamine (90 uL, 0.7 mmol, 1.5 equiv) were dissolved in anhydrous DCM (1 mL, 0.5 M) at 0 °C. At this temperature, benzoyl chloride (BzCl, 75 μL, 0.7 mmol,1.5 equiv) was added dropwise and the mixture was stirred for 10 h at room temperature. TLC showed complete consumption of the starting material. After dilution with DCM, the solution was washed with water, sat. $NaHCO_3$ and brine. The combined organic phase was dried by Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by silica gel column chromatography (hexane:EtOAc = 3:1) afforded **5a** (142 mg, 0.4 mmol, 99%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.0, 1.4 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 6.50 (dd, J = 6.2, 1.4 Hz, 1H), 5.57 – 5.53 (m, 1H), 5.43 (dd, J = 7.6, 5.8 Hz, 1H), 4.99 (dd, J = 6.2, 3.2 Hz, 1H), 4.49 (dd, J = 12.1, 5.8 Hz, 1H), 4.37 – 4.31 (m, 1H), 4.25 (dd, J = 12.1, 3.2 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H). The data are identical to the literature.[8]

3-*O*-*ortho*-2,2-Dimethoxycarbonylcyclopropylbenzoyl-4-*O*-acetyl-D-glucal (2u)



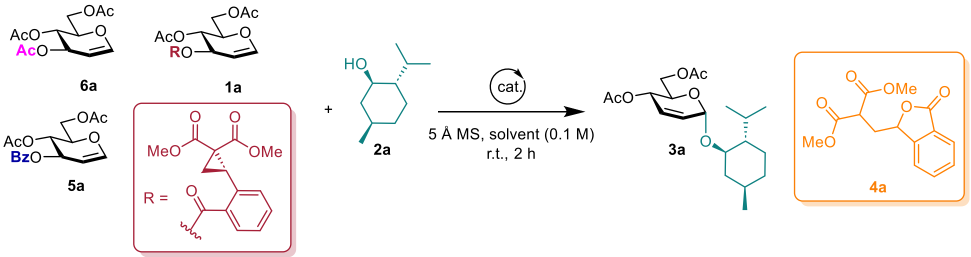
Supporting information Fig. 12 | Synthesis of 2u

To a mixture of **1a** (230 mg, 0.5 mmol) in 0.1 M potassium phosphate buffer (5 mL, pH = 7), diisopropyl ether ((iPr)$_2$O, 1 mL, 0.6 M), acetone (0.6 mL) and lipase from *Candida cylindracea* (lipase CC, 75 mg) was added and this mixture was stirred at room temperature. TLC showed complete consumption of the starting material. After work-up, the mixture was filtered over celite and washed with EtOAc. The filtrate was extracted with EtOAc, and the combined organic layers were washed with brine and dried over Na_2SO_4. The solution was evaporated *in vacuo*. Purification by silica gel column chromatography (hexane:EtOAc = 2:1) obtained **2u** (130 mg, 0.3 mmol, 62%, dr = 10:7) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.81 (dd, J = 7.8, 1.5 Hz, 0.7H), 7.46 – 7.41 (m, 1.9H), 7.34 – 7.29 (m, 1.9H), 7.23 (d, J = 7.7 Hz, 1.7H), 6.51 – 6.49 (m, 1.7H), 5.67 – 5.64 (m, 1.7H), 5.47 – 5.39 (m, 1.7H), 5.01 (dd, J = 6.1, 2.7 Hz, 0.7H), 4.96 (dd, J = 6.1, 2.8 Hz, 1H), 4.10 – 4.05 (m, 1.9H), 3.86 – 3.71 (m, 11H), 3.24 (s, 2H), 3.23 (s, 2.9H), 2.54 (brs, 1.6H), 2.20 – 2.15 (m, 2H), 2.10 (s, 2.1H), 2.07 (s, 3H), 1.84 – 1.77 (m, 1.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.52, 170.47, 170.3, 170.1, 167.2, 167.1, 166.2, 165.9, 145.7, 145.6, 136.6, 136.3, 132.3, 132.2, 131.03, 131.01, 130.3, 129.7, 129.5, 127.8, 127.7, 99.3, 99.1, 76.72, 76.66, 69.3, 69.2, 67.6, 67.3, 60.7, 60.6, 52.77, 52.75, 52.2, 52.0, 36.2, 35.9, 32.7, 32.3, 20.9, 20.86, 19.8, 19.7; HRMS (ESI) *m/z* Calcd $C_{22}H_{24}O_{10}Na$ $[M+Na]^+$ 471.1267, found 471.1266.

Section 2. Optimization of reaction conditions.

Supplementary Table 1 | Condition screening[a]

Table 1. Reaction optimization



Entry	Donor	Lewis acid	Solvent	MS	Yields[b] %	Yield[b] of **4a**%	α:β (selectivity)[c]
1	**1a**	$Sc(OTf)_3$	DCM	5 Å	98	95	4:1
2	**1a**	$Cu(OTf)_2$	DCM	5 Å	98	95	10:1
3	**1a**	$Fe(OTf)_3$	DCM	5 Å	98	95	10:1
4[d]	**1a**	$Fe(OTf)_3$	DCM	5 Å	53	48	10:1
5	**1a**	$Fe(OTf)_2$	DCM	5 Å	N.R.	0	N.D.
6	**1a**	$FeCl_3$	DCM	5 Å	6	trace	-
7	**1a**	$FeCl_2$	DCM	5 Å	N.R.	0	N.D.
8	**1a**	TMSOTf	DCM	5 Å	N.R.	0	N.D.
9	**1a**	TfOH	DCM	5 Å	N.R.	0	N.D.
10	**1a**	$Cu(OTf)_2$	DCE	5 Å	98	95	10:1
11	**1a**	$Fe(OTf)_3$	DCE	5 Å	98	95	10:1
12	**1a**	$Cu(OTf)_2$	Et_2O	5 Å	65	52	10:3
13	**1a**	$Fe(OTf)_3$	Toluene	5 Å	12	trace	10:1
14	**1a**	$Fe(OTf)_3$	CH_3CN	5 Å	N.R.	0	N.D.
15	**5a**	$Cu(OTf)_2$	DCM	5 Å	N.R.	0	N.D.
16	**5a**	$Fe(OTf)_3$	DCM	5 Å	N.R.	0	N.D.
17	**6a**	$Cu(OTf)_2$	DCM	5 Å	74%	-	3:1
18	**6a**	$Fe(OTf)_3$	DCM	5 Å	69%	-	3:1

[a]Unless otherwise noted, all reported yields are isolated and purified products. All reactions were carried out with **1a** or **5a** (0.1 mmol, 1.0 equiv), **2a** (1.2 equiv.), Lewis acid catalyst (0.1 equiv.) and 5 Å MS (50 mg) in corresponding solvent (1.0 ml, 0.1 M) under N_2 atmosphere for 2 h. MS = molecular sieve; DCE = 1,2-dichloroethane; ACN = acetonitrile; N.R. = no reaction; N.D. = no detective.

[b]Isolated yields.

[c]The α/β ratios were determined by ^{1}H NMR analysis.

[d]0.05 equiv of catalyst.

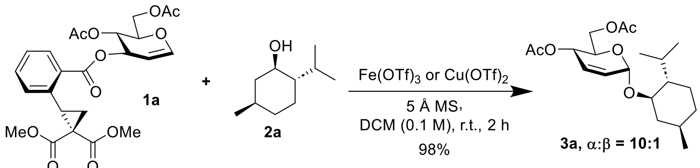
General procedure for the reaction development

A solution of **1a** (50 mg, 0.1 mmol, 1.0 equiv) and L-menthol **2a** (19 mg, 0.12 mmol, 1.2 equiv) in anhydrous solvent (1 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before the catalyst (0.01 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 2 h – 20 h until **2a** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (toluene:EtOAc = 8:1) obtained the **3a** as a colorless oil, followed by changing the eluent system (toluene:EtOAc = 6:1) to afford **4a** as a colorless oil. α anomer of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.81 (m, 2H), 5.26 (dd, *J* = 9.1, 1.4 Hz, 1H), 5.10 (s, 1H), 4.24 – 4.13 (m, 3H), 3.44 – 3.73 (m, 1H), 2.20 – 2.15 (m, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.67 – 1.60 (m, 3H), 1.45 – 1.37 (m, 1H), 1.09 – 0.78 (m, 13H), 0.76 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.4, 128.7, 128.2, 96.3, 81.2, 66.8, 65.5, 63.5, 49.0, 43.5, 34.4, 31.8, 25.7, 23.3, 22.5, 21.3, 21.1, 21.0, 16.3. The data are identical to the literature report.[9] **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.43 (m, 2H), 5.50 (dd, *J* = 9.1, 3.2 Hz, 1H), 3.74 (s, 3H), 3.61 (s, 4H), 2.74 (ddd, *J* = 14.8, 9.4, 3.2 Hz, 1H), 2.14 (ddd, *J* = 14.4, 9.1, 5.0 Hz, 1H). The data are identical to the literature report.[2]

Section 3. Allylic rearrangement with 1a as the donor.

Acceptors **2a–d**, **2f–h**, **2j**, **2m**, **2o**, **2q**, **2s–t** were commercially available. Acceptors **2e**[10], **2i**[11], **2k** and **2l**[12], **2n**[13], **2p**[14], and **2r**[15] were prepared according to the reported literatures.

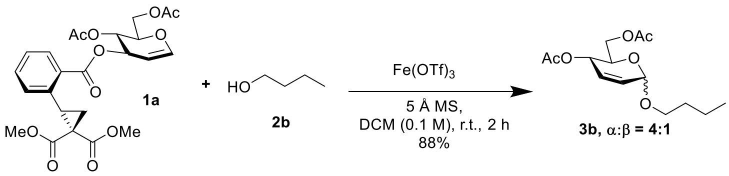
L-Menthyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3a)



Supporting information Fig. 13 | Synthesis of 3a

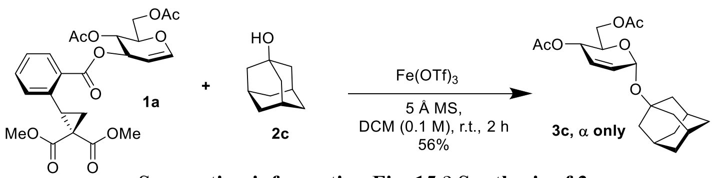
A solution of **1a** (50 mg, 0.1 mmol, 1.0 equiv) and L-menthol **2a** (19 mg, 0.12 mmol, 1.2 equiv) in anhydrous solvent (1 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before $Fe(OTf)_3$ (5.0 mg, 0.01 mmol, 0.1 equiv) or $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 2 h until **2a** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (toluene:EtOAc = 8:1) to give the **3a** as a colorless oil (37 mg, 0.098 mmol, 98%).

n-Butyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3b)



Following the procedure for **3a**, **2b** (11 μL, 0.12 mmol, 1.2 equiv) was transformed into **3b** (29 mg, 0.088 mmol, 88%, α:β = 4:1) as a colorless oil after purification by silica gel column chromatography (hexane:EtOAc = 4:1). α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.80 (m, 2H), 5.31 – 5.28 (m, 1H), 5.03 – 5.00 (m, 1H), 4.26 – 4.21 (m, 1H), 4.17 (dd, *J* = 12.1, 2.5 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.80 – 3.73 (m, 1H), 3.53 – 3.47 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.63 – 1.53 (m, 2H), 1.44 – 1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). The data are identical to the literature report.[16]

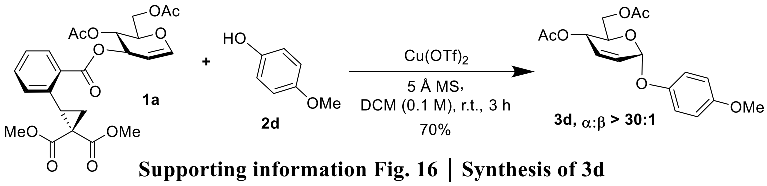
1-Adamantyl 4′,6′-di-*O*-acetyl-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranoside (3c)



Supporting information Fig. 15 ? Synthesis of 3c

Following the procedure for **3a**, **2c** (19 mg, 0.12 mmol, 1.2 equiv) was transformed into **3c** (21 mg, 0.056 mmol, 56%, α only) as a white solid after purification by silica gel column chromatography (hexane:EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (d, *J* = 10.2 Hz, 1H), 5.77 – 5.73 (m, 1H), 5.44 (t, *J* = 2.1 Hz, 1H), 5.27 (d, *J* = 9.2 Hz, 1H), 4.26 – 4.21 (m, 2H), 4.15 (d, *J* = 10.2 Hz, 1H), 2.15 (s, 3H), 2.08 (d, J = 6.0 Hz, 6H), 1.86 (dd, J = 11.5, 7.7 Hz, 6H), 1.68 – 1.57 (m, 6H). The data are identical to the literature report.[9]

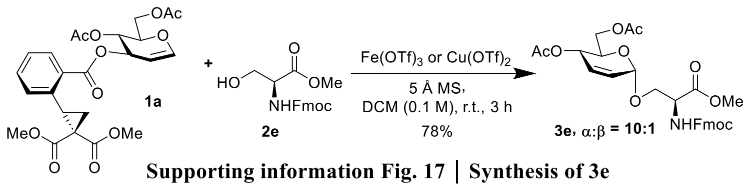
***para*-Methoxyphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3d)**



Supporting information Fig. 16 | Synthesis of 3d

Following the procedure for **3a**, **2d** (15 mg, 0.12 mmol, 1.2 equiv) was transformed into **3d** (24 mg, 0.07 mmol, 70%, α:β > 30:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). When $Fe(OTf)_3$ as catalyst, the yield is 31 %, and α:β > 30:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 7.01 (m, 2H), 6.85 – 6.80 (m, 2H), 6.00 (d, J = 1.8 Hz, 2H), 5.56 (d, J = 1.9 Hz, 1H), 5.40 – 5.34 (m, 1H), 4.30 – 4.23 (m, 2H), 4.19 – 4.13 (m, 1H), 3.77 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H). The data are identical to the literature report.[17]

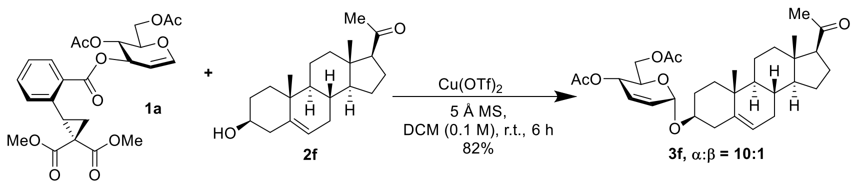
Methyl *N*-(9H-fluorenylmethoxy)carbonyl-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-L-serine (3e)



Supporting information Fig. 17 | Synthesis of 3e

Following the procedure for **3a**, **2e** (42 mg, 0.12 mmol, 1.2 equiv) was transformed into **3e** (44 mg, 0.078 mmol, 78%, α:β = 10:1) as a foamy solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). When $Fe(OTf)_3$ as catalyst, the yield is 74%, and α:β = 10:1. $[\alpha]_D^{24}$ = +53.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 5.91 (t, J = 9.6 Hz, 2H), 5.79 – 5.75 (m, 1H), 5.30 – 5.27 (m, 1H), 4.98 (s, 1H), 4.60 – 4.56 (m, 1H), 4.50 – 4.36 (m, 2H), 4.27 – 4.13 (m, 4H), 4.10 – 3.98 (m, 3H), 3.78 (s, 3H), 2.09 (d, J = 2.0 Hz, 3H), 2.08 (s, 1H), 2.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.5, 170.2, 156.0, 143.9, 143.7, 141.3, 129.6, 127.8, 127.1, 126.4, 125.1, 120.0, 95.3, 69.8, 67.4, 67.2, 65.1, 62.8, 54.5, 52.7, 47.1, 21.0, 20.7; HRMS (ESI) m/z Calcd $C_{29}H_{31}O_{10}NNa$ $[M+Na]^+$ 554.2026, found 554.2056.

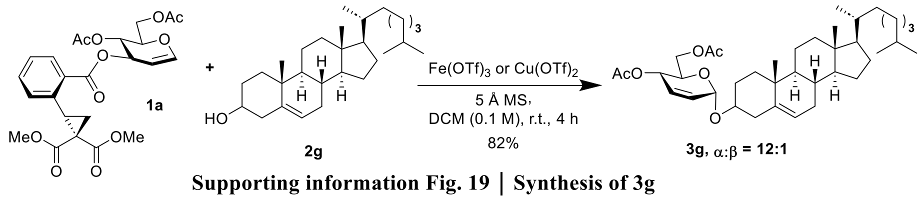
Pregnenolonyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3f)



Supporting information Fig. 18 ? Synthesis of 3f

Following the procedure for **3a**, **2f** (40 mg, 0.12 mmol, 1.2 equiv) was transformed into **3f** (44 mg, 0.082 mmol, 82%, α:β = 10:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.85 (m, 1H), 5.84 – 5.80 (m, 1H), 5.36 (d, J = 3.9 Hz, 1H), 5.32 – 5.27 (m, 1H), 5.17 (s, 1H), 4.28 – 4.13 (m, 3H), 3.60 – 3.52 (m, 1H), 2.54 (d, J = 9.0 Hz, 1H), 2.45 – 2.25 (m, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 – 1.96 (m, 2H), 1.94 – 1.83 (m, 3H), 1.72 – 1.41 (m, 17H), 1.32 – 1.11 (m, 10H), 1.06 – 0.80 (m, 8H), 0.63 (s, 3H). The data are identical to the literature report. [18]

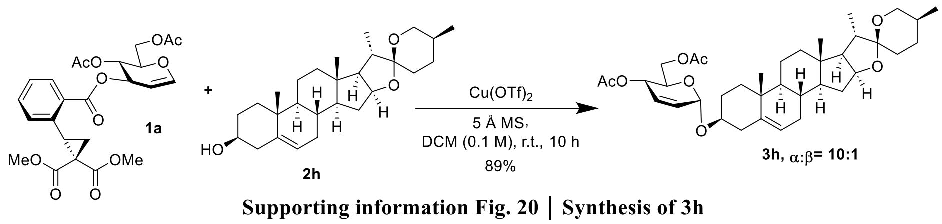
Cholesteryl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3g)



Supporting information Fig. 19 | Synthesis of 3g

Following the procedure for **3a**, **2g** (47 mg, 0.12 mmol, 1.2 equiv) was transformed into **3g** (50 mg, 0.082 mmol, 82%, α:β = 12:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). When $Fe(OTf)_3$ as catalyst, the yield is 78%, and α:β = 12:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (dd, J = 10.2, 1.6 Hz, 1H), 5.83 – 5.79 (m, 1H), 5.36 – 5.34 (m, 1H), 5.30 – 5.29 (m, 1H), 5.18 – 5.15 (m, 1H), 4.26 – 4.14 (m, 3H), 3.59 – 3.51 (m, 1H), 2.45 – 2.28 (m, 2H), 2.08 (d, J = 5.7 Hz, 6H), 2.03 – 1.92 (m, 2H), 1.91 – 1.77 (m, 3H), 1.67 – 1.21 (m, 15H), 1.20 – 0.96 (m, 14H), 0.94 – 0.83 (m, 12H), 0.67 (s, 3H). The data are identical to the literature report.[19]

Diosgeninyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3h)

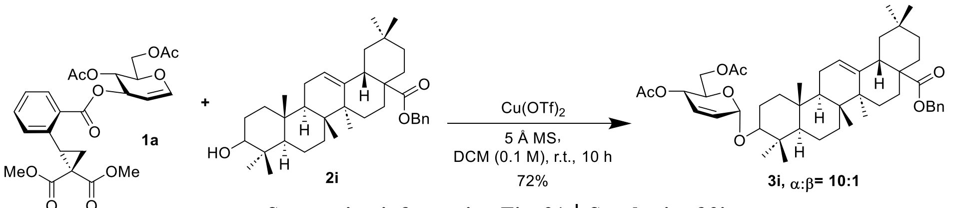


Supporting information Fig. 20 | Synthesis of 3h

Following the procedure for **3a**, **2h** (51 mg, 0.12 mmol, 1.2 equiv) was transformed into **3h** (57 mg, 0.089 mmol, 89%, α:β = 10:1) as a foamy solid after purification by silica gel column chromatography (toluene:EtOAc = 6:1). $[\alpha]^{25}_{D}$ = +0.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (dd, J = 10.3, 1.7 Hz, 1H), 5.81 – 5.78 (m, 1H), 5.35 – 5.32 (m, 1H), 5.30 – 5.24 (m, 1H), 5.17 – 5.12 (m, 1H), 4.42 – 4.36 (m, 1H), 4.27 – 4.13 (m, 3H), 3.59 – 3.50 (m, 1H), 3.47 – 3.43 (m, 1H), 3.35 (t, J = 10.9 Hz, 1H), 2.42 – 2.32 (m, 2H), 2.07 (d, J = 5.7 Hz, 6H), 2.02 – 1.93 (m, 2H), 1.88 – 1.81 (m, 3H), 1.78 – 1.37 (m, 15H), 1.34 – 0.84 (m, 17H), 0.77 – 0.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.3, 140.8, 128.9, 128.4, 121.6, 109.3, 92.8, 80.8, 78.1, 67.1, 66.84, 65.4, 63.2, 62.1, 56.5, 50.1, 41.6, 40.4, 40.3, 39.8, 37.1, 36.8, 32.1, 31.8, 31.4, 31.38, 30.3, 28.8, 28.2, 21.0, 20.9, 20.8, 19.4, 17.1, 16.3, 14.5; HRMS (ESI) m/z Calcd $C_{37}H_{55}O_8$ $[M+H]^+$ 627.3897, found 627.3898.

Gram-scale synthesis: A solution of **1a** (990 mg, 2.0 mmol, 1.0 equiv) in anhydrous DCM (20 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before $Cu(OTf)_2$ (73 mg, 0.2 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 18h until **1a** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (toluene:EtOAc = 15:1) afforded the **3h** as a foamy solid (1.02 g, 1.62 mmol, α:β = 10:1, 81%)

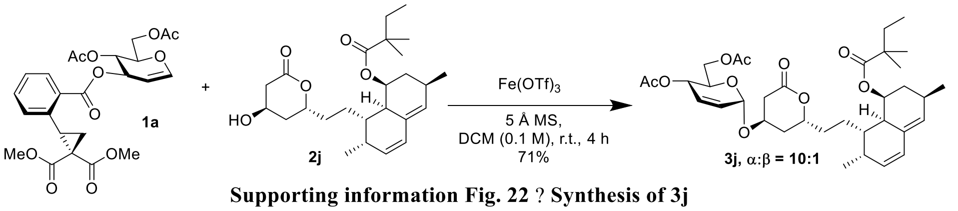
3-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-28-*O*-benzyl oleanolate (3i)



Supporting information Fig. 21 │ Synthesis of 3i

Following the procedure for **3a**, **2i** (67 mg, 0.12 mmol, 1.2 equiv) was transformed into **3i** (56 mg, 0.072 mmol, 72%, α:β = 10:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 6:1). $[\alpha]_D^{25}$ = +78.0 (*c* = 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35 – 7.28 (m, 6H), 5.87 – 5.84 (m, 1H), 5.77 – 5.73 (m, 1H), 5.32 – 5.26 (m, 2H), 5.14 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.09 (d, *J* = 12.6 Hz, 1H), 5.04 (d, *J* = 12.5 Hz, 1H), 4.29 – 4.17 (m, 2H), 4.16 – 4.09 (m, 1H), 3.30 (dd, *J* = 11.6, 4.1 Hz, 1H), 2.90 (dd, *J* = 13.9, 4.5 Hz, 1H), 2.08 – 2.07 (m, 6H), 2.02 – 1.94 (m, 1H), 1.86 – 1.83 (m, 2H), 1.75 – 1.08 (m, 25H), 1.07 – 1.00 (m, 4H), 0.90 (d, *J* = 9.1 Hz, 12H), 0.81 – 0.72 (m, 4H), 0.60 (d, *J* = 3.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 177.5, 170.9, 170.3, 143.7, 136.5, 128.7, 128.4, 128.0, 127.9, 122.5, 91.3, 83.8, 77.3, 67.1, 65.9, 65.3, 63.1, 55.8, 47.6, 46.8, 45.9, 41.7, 41.4, 39.3, 38.3, 38.2, 37.0, 33.9, 33.1, 32.8, 32.4, 30.7, 28.3, 27.6, 25.8, 23.7, 23.4, 23.1, 22.6, 21.0, 20.9, 18.4, 16.9, 16.5, 15.4; HRMS (ESI) *m/z* Calcd $C_{47}H_{66}O_8Na$ $[M+Na]^+$ 781.4655, found 781.4661.

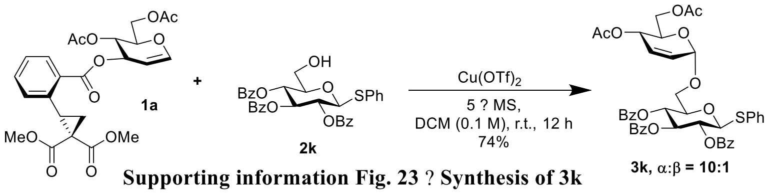
Simvastatinyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3j)



Supporting information Fig. 22 ? Synthesis of 3j

Following the procedure for **3a**, **2j** (51 mg, 0.12 mmol, 1.2 equiv) was transformed into **3j** (46 mg, 0.071 mmol, 71%, α:β = 10:1) as a colorless oil after purification by silica gel column chromatography (toluene:EtOAc = 5:1). $[\alpha]_D^{24}$ = +151.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) *δ* 5.99 (d, *J* = 9.7 Hz, 1H), 5.92 – 5.87 (m, 1H), 5.83 – 5.76 (m, 2H), 5.51 (t, *J* = 3.4 Hz, 1H), 5.34 – 5.31 (m, 2H), 5.29 – 5.22 (m, 1H), 5.14 (s, 1H), 4.58 – 4.52 (m, 1H), 4.36 – 4.29 (m, 1H), 4.26 – 4.07 (m, 3H), 4.03 – 3.97 (m, 1H), 2.74 – 2.62 (m, 2H), 2.48 – 2.26 (m, 4H), 2.07 (s, 3H), 2.05 (s, 3H), 1.97 – 1.94 (m, 2H), 1.84 – 1.24 (m, 17H), 1.13 – 1.04 (m, 10H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) *δ* 177.3, 170.4, 170.1, 169.2, 132.9, 131.7, 129.7, 129.3, 128.3, 127.5, 93.2, 76.7, 73.0, 68.9, 67.9, 67.2, 65.2, 63.0, 42.8, 37.4, 36.7, 35.8, 34.8, 33.1, 33.0, 32.7, 30.7, 27.4, 24.6, 24.5, 24.1, 22.8, 20.8, 20.6, 13.6, 9.1; HRMS (ESI) *m/z* Calcd $C_{35}H_{53}O_{10}$ $[M+H]^+$ 633.3639, found 633.3629.

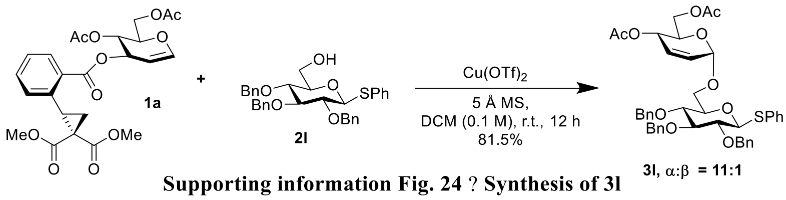
Phenyl 6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (3k)



Supporting information Fig. 23 ? Synthesis of 3k

Following the procedure for **3a**, **2k** (72 mg, 0.12 mmol, 1.2 equiv) was transformed into **3k** (60 mg, 0.074 mmol, 74%, α:β = 10:1) as a white solid after purification by silica gel column chromatography (hexane:EtOAc = 3:1). $[\alpha]^{25}_{D}$ = +22.0 (c = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 4H), 7.81 – 7.77 (m, 2H), 7.54 – 7.50 (m, 4H), 7.43 – 7.35 (m, 5H), 7.33 – 7.23 (m, 5H), 5.92 – 5.85 (m, 2H), 5.77 – 5.73 (m, 1H), 5.61 (t, J = 9.7 Hz, 1H), 5.52 – 5.43 (m, 1H), 5.31 – 5.28 (m, 1H), 5.08 – 5.02 (m, 2H), 4.22 – 4.13 (m, 1H), 4.11 – 4.07 (m, 1H), 4.06 – 3.94 (m, 3H), 3.83 – 3.74 (m, 1H), 2.06 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.3, 165.8, 165.1, 165.0, 133.6, 133.3, 133.2, 132.8, 132.4, 132.1, 129.9, 129.8, 129.8, 129.7, 129.4, 129.2, 129.0, 128.88, 128.82, 128.51, 128.49, 128.4, 128.3, 128.2, 127.3, 94.5, 86.1, 77.3, 74.4, 70.5, 69.4, 66.93, 66.89, 65.1, 62.7, 21.0, 20.7; HRMS (ESI) *m/z* Calcd $C_{43}H_{40}O_{13}SNa$ $[M+Na]^+$ 819.2087, found 819.2103.

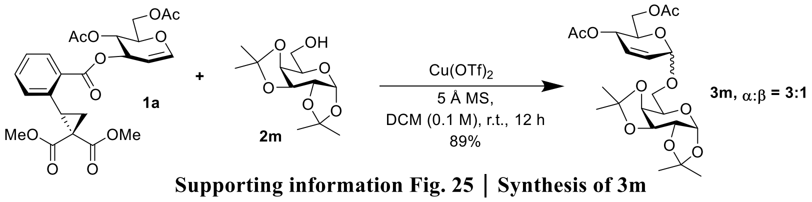
Phenyl 6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-eno-pyranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (3l)



Supporting information Fig. 24 ? Synthesis of 3l

Following the procedure for **3a**, **2l** (66 mg, 0.12 mmol, 1.2 equiv) was transformed into **3l** (60 mg, 0.082 mmol, 82%, α:β = 11:1) as a colorless syrup after purification by silica gel column chromatography (hexane:EtOAc = 4:1). $[\alpha]^{25}_{D}$ = +14.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.41 – 7.22 (m, 20H), 5.93 – 5.81 (m, 2H), 5.34 – 5.31 (m, 1H), 5.16 – 5.11 (m, 1H), 4.92 – 4.87 (m, 3H), 4.84 (d, J = 10.9 Hz, 1H), 4.74 (d, J = 10.3 Hz, 1H), 4.66 (d, J = 10.3 Hz, 2H), 4.25 – 4.15 (m, 1H), 4.12 – 4.04 (m, 2H), 4.01 – 3.94 (m, 1H), 3.84 (dd, J = 11.3, 1.9 Hz, 1H), 3.72 (t, J = 8.8 Hz, 1H), 3.59 (t, J = 9.3 Hz, 1H), 3.54 – 3.45 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.3, 138.3, 138.1, 138.0, 133.8, 131.9, 131.6, 129.1, 128.9, 128.51, 128.49, 128.46, 128.23, 128.0, 127.93, 127.91, 127.81, 127.77, 127.68, 127.5, 94.8, 87.3, 86.7, 80.9, 78.6, 77.9, 75.9, 75.5, 75.1, 67.3, 67.0, 65.2, 62.8, 21.0, 20.8; HRMS (ESI) *m/z* Calcd $C_{43}H_{46}O_{10}SNa$ $[M+Na]^+$ 777.2709, found 777.2704.

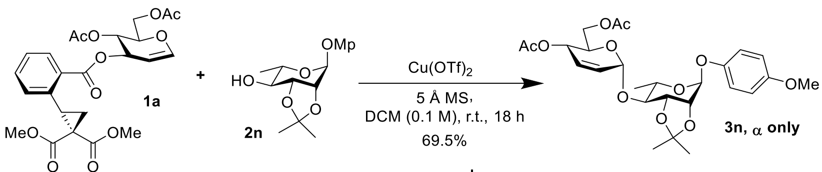
6-*O*-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (3m)



Supporting information Fig. 25 │ Synthesis of 3m

Following the procedure for **3a**, **2m** (32 mg, 0.12 mmol, 1.2 equiv) was transformed into **3m** (43 mg, 0.089 mmol, 89%, α:β = 3:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.80 (m, 2H), 5.51 (d, J = 5.0 Hz, 1H), 5.33 – 5.28 (m, 1H), 5.08 – 5.07 (m, 1H), 4.59 (dd, J = 7.4, 2.4 Hz, 1H), 4.33 – 4.19 (m, 4H), 4.17 – 4.09 (m, 2H), 4.03 – 3.94 (m, 2H), 3.86 (dd, J = 10.2, 6.3 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.52 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H). The data are identical to the literature report.[9]

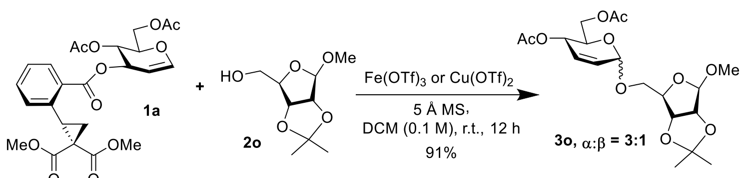
***para*-Methoxyphenyl-4-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (3n)**



Supporting information Fig. 26 │ Synthesis of 3n

Following the procedure for **3a**, **2n** (38 mg, 0.12 mmol, 1.2 equiv) was transformed into **3n** (37 mg, 0.070 mmol, 70%, α only) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 5:1). When $Fe(OTf)_3$ as catalyst, the yield is 23%, and α only. $[\alpha]_{D}^{25}$ = +12.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.95 (m, 2H), 6.84 – 6.79 (m, 2H), 5.92 (dd, J = 10.3, 1.8 Hz, 1H), 5.84 – 5.80 (m, 1H), 5.59 (s, 1H), 5.46 (dd, J = 9.7, 1.6 Hz, 1H), 5.16 (d, J = 2.8 Hz, 1H), 4.38 (dd, J = 12.2, 2.9 Hz, 1H), 4.33 – 4.27 (m, 3H), 4.25 – 4.21 (m, 1H), 3.87 – 3.79 (m, 1H), 3.77 (s, 3H), 3.51 (dd, J = 10.1, 6.7 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H), 1.21 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 155.0, 150.1, 129.7, 127.2, 117.7, 114.6, 109.5, 96.1, 95.0, 80.7, 77.2, 75.9, 66.6, 65.7, 65.0, 62.4, 55.6, 28.1, 26.5, 21.0, 20.9, 17.5; HRMS (ESI) m/z Calcd $C_{26}H_{34}O_{11}Na$ $[M+Na]^+$ 545.1999, found 545.2020.

Methyl 5-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3-*O*-isopropylidene-β-D-ribofuranoside (3o)

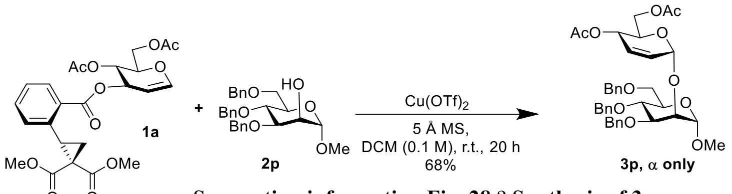


Supporting information Fig. 27│ Synthesis of 3o

Following the procedure for **3a**, **2o** (25 mg, 0.12 mmol, 1.2 equiv) was transformed into **3o** (38 mg, 0.091 mmol, 91%, α:β = 3:1) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 5:1). When $Fe(OTf)_3$ as catalyst, the yield is 87%, and α:β = 3:1. α:β = 3:1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 – 5.92 (m, 1H), 5.90 – 5.78 (m, 2H), 5.29 (dd, J = 9.7, 1.6 Hz, 1H), 5.18 – 5.13

(m, 1H), 5.05 – 5.00 (m, 1H), 4.94 – 4.93 (m, 1.5H), 4.70 – 4.66 (m, 1.5H), 4.57 – 4.55 (m, 1.5H), 4.39 – 4.35 (m, 1H), 4.32 – 4.21 (m, 2.6H), 4.17 (dd, J = 12.1, 2.4 Hz, 1H), 4.10 – 4.02 (m, 1.7H), 3.82 – 3.75 (m, 1.9H), 3.58 (ddd, J = 19.2, 10.2, 7.8 Hz, 1.6H), 3.30 (s, 1H), 3.29 (s, 3H), 2.09 (s, 3H), 2.08 (s, 1H), 2.07 (s, 3H), 2.06 (s, 1H), 1.46 (s, 4H), 1.30 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.2, 129.3, 127.4, 112.3, 109.3, 95.0, 85.12, 85.07, 82.1, 81.9, 72.8, 69.7, 68.7, 67.1, 65.1, 64.2, 63.5, 62.8, 54.9, 54.8, 26.5, 26.4, 25.0 24.9, 21.0, 20.8, 20.75. The data are identical to the literature report.[20]

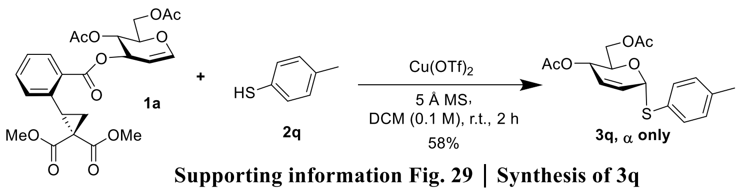
Methoxyl 2-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-3,4,6-*O*-tri-*O*-benzyl-α-D-mannopyranoside (3p)



Supporting information Fig. 28 ? Synthesis of 3p

Following the procedure for **3a**, **2p** (57 mg, 0.12 mmol, 1.2 equiv) was transformed into **3p** (47 mg, 0.068 mmol, 68%, α only) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 4:1). $[\alpha]_D^{25}$ = +27.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 14H), 7.18 – 7.15 (m, 2H), 5.94 – 5.91 (m, 1H), 5.89 – 5.84 (m, 1H), 5.30 – 5.26 (m, 1H), 5.25 – 5.21 (m, 1H), 4.86 – 4.80 (m, 2H), 4.72 – 4.64 (m, 3H), 4.54 (d, J = 12.1 Hz, 1H), 4.50 (d, J = 10.8 Hz, 1H), 4.23 – 4.15 (m, 3H), 4.09 (t, J = 2.4 Hz, 1H), 3.93 – 3.83 (m, 2H), 3.79 – 3.70 (m, 3H), 3.36 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.4, 138.43, 138.38, 128.8, 128.5, 128.33, 128.30, 127.94, 127.88, 127.75, 127.7, 127.6, 127.51, 127.48, 100.3, 95.8, 80.1, 75.1, 74.9, 74.8, 73.4, 72.4, 71.7, 69.3, 67.0, 65.4, 63.2, 54.7, 29.7, 21.0, 20.8; HRMS (ESI) m/z Calcd $C_{38}H_{44}O_{11}Na$ $[M+Na]^+$ 699.2781, found 699.2766.

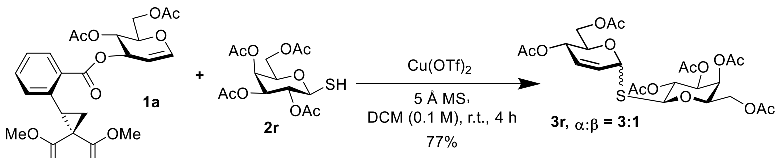
***para*-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-erythro-hex-2-eno-1-thio-α-D-pyranoside (3q)**



Supporting information Fig. 29 | Synthesis of 3q

Following the procedure for **3a**, **2q** (15 mg, 0.12 mmol, 1.2 equiv) was transformed into **3q** (20 mg, 0.058 mmol, 58%, α only) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 6:1). When $Fe(OTf)_3$ as catalyst, there is no reaction. H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.08 – 6.04 (m, 1H), 5.86 – 5.83 (m, 1H), 5.69 – 5.67 (m, 1H), 5.39 – 5.35 (m, 1H), 4.51 – 4.46 (m, 1H), 4.30 – 4.20 (m, 2H), 2.33 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H). The data are identical to the literature report.[21]

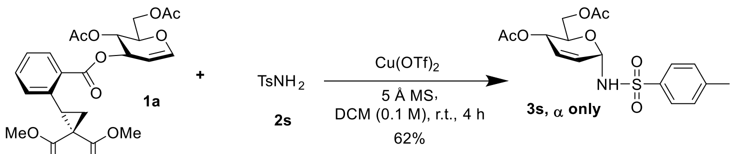
1-Thio-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (3r)



Supporting information Fig. 30 │ Synthesis of 3r

Following the procedure for **3a**, **2r** (45 mg, 0.12 mmol, 1.2 equiv) was transformed into **3r** (45 mg, 0.077 mmol, 77%, α:β = 3:1) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 4:1). When $Fe(OTf)_3$ as catalyst, there is no reaction. α:β = 3:1: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.98 (s, 0.6H), 5.92 – 5.82 (m, 3H), 5.75 (d, *J* = 1.6 Hz, 0.3H), 5.47 – 5.40 (m, 2.4H), 5.31 (t, *J* = 9.9 Hz, 1H), 5.26 – 5.21 (m, 0.7H), 5.09 – 5.06 (dd, *J* = 8.0, 4.0 Hz, 0.3H), 5.01 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 0.3H), 4.63 (d, *J* = 9.9 Hz, 1H), 4.42 – 4.33 (m, 1.3H), 4.28 – 4.07 (m, 6.3H), 4.02 – 3.92 (m, 1.7H), 2.14 (d, *J* = 2.8 Hz, 4H), 2.09 – 2.03 (m, 16H), 1.97 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.7, 170.6, 170.4, 170.34, 170.25, 170.20, 170.18, 170.1, 170.0, 169.7, 169.3, 129.4, 128.2, 127.8, 126.1, 83.5, 81.4, 79.9, 77.3, 75.5, 74.8, 74.5, 74.4, 72.0, 71.8, 68.4, 67.3, 67.2, 64.4, 64.2, 63.1, 62.4, 61.6, 61.4, 21.0, 20.8, 20.81, 20.77, 20.69, 20.66, 20.64, 20.60, 20.58, 20.55; HRMS (ESI) *m/z* Calcd $C_{24}H_{32}O_{14}SNa$ [M+Na]$^+$ 599.1410, found 599.1465.

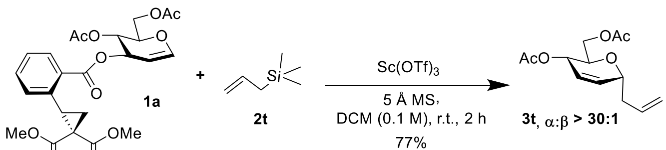
***N*-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-4-methylbenzenesulfonamide (3s)**



Supporting information Fig. 31 │ Synthesis of 3s

Following the procedure for **3a**, **2s** (21 mg, 0.12 mmol, 1.2 equiv) was transformed into **3s** (24 mg, 0.062 mmol, 62%, α only) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). $[\alpha]^{25}_{D}$ = +77.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.84 – 7.78 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.93 – 5.90 (m, 1H), 5.82 – 5.79 (m, 2H), 5.63 – 5.55 (m, 1H), 5.28 – 5.24 (m, 1H), 3.89 (dd, *J* = 12.2, 3.6 Hz, 1H), 3.57 – 3.51 (m, 1H), 3.36 (dd, *J* = 12.2, 2.8 Hz, 1H), 2.43 (s, 3H), 2.02 (s, 6H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.0, 143.9, 138.6, 130.6, 129.6, 127.2, 126.7, 66.8, 64.3, 61.8, 21.5, 20.9, 20.7; HRMS (ESI) *m/z* Calcd $C_{17}H_{21}O_7NS$ [M+H]$^+$ 384.1117, found 384.1111.

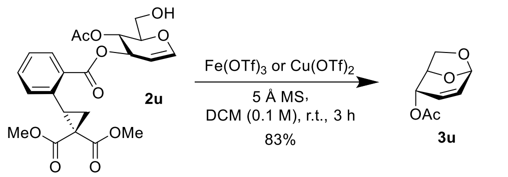
3-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3t)



Supporting information Fig. 32 │ Synthesis of 3t

A solution of **1a** (50 mg, 0.1 mmol, 1.0 equiv) and **2t** (33 μL, 0.12 mmol, 1.2 equiv) in anhydrous DCM (1 mL, 0.1 M) containing freshly activated 5Å molecular sieve was stirred at room temperature for 15 min before $Sc(OTf)_3$ (5.0 mg, 0.01 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 2 h until **2t** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (hexane:EtOAc = 4:1) obtained the **3t** (20 mg, 0.077 mmol, 77%, α:β > 30:1) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.96 – 5.76 (m, 3H), 5.17 – 5.07 (m, 3H), 4.31 – 4.20 (m, 2H), 4.15 (dd, *J* = 11.8, 3.5 Hz, 1H), 3.98 – 3.94 (m, 1H), 2.51 – 2.42 (m, 1H), 2.36 – 2.29 (m, 1H), 2.09 (s, 6H). The data are identical to the literature report. [22]

4-*O*-Acetyl-1,6-anhydro-2,3-dideoxy-β-D-erythro-hex-2-enopyranose (3u)



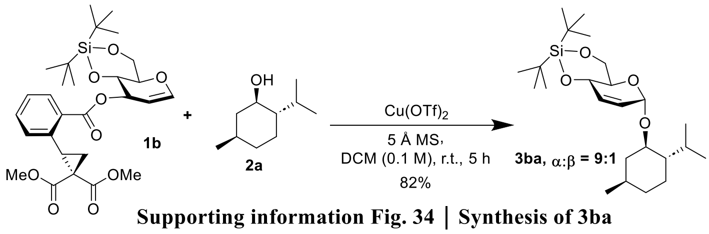
Supporting information Fig. 33 | Synthesis of 3u

A solution of **2u** (60 mg, 0.13 mmol, 1.0 equiv) in anhydrous DCM (1 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before $Cu(OTf)_2$ (4.8 mg, 0.013 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 3 h until **2u** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (hexane:EtOAc = 4:1) afforded the **3u** as a colorless oil (18 mg, 0.083 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.20 – 6.17 (m, 1H), 5.81 – 5.77 (m, 1H), 5.59 (d, *J* = 3.4 Hz, 1H), 4.80 – 4.78 (m, 1H), 4.73 – 4.70 (m, 1H), 3.96 (dd, *J* = 8.0, 6.6 Hz, 1H), 3.53 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.12 (s, 3H). The data are identical to the literature report. [23]

Gram-scale synthesis: A solution of **2u** (2.9 g, 6.5 mmol, 1.0 equiv) in anhydrous DCM (66 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before $Fe(OTf)_3$ (325 mg, 0.65 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 5h until **2u** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (hexane:EtOAc = 4:1) afforded the **3u** as a colorless oil (951 mg, 5.5 mmol, 85%)

Section 4. Allylic rearrangement with 1b–d as donors.

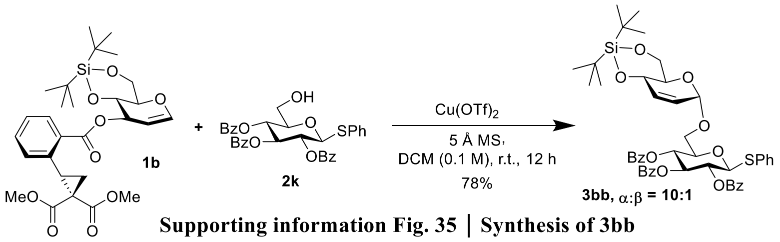
L-Menthyl 4,6-*O*-[bis(1,1-dimethylethyl)silylene]-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3ba)



Supporting information Fig. 34 | Synthesis of 3ba

Following the procedure for **3a**, **2a** (19 mg, 0.12 mmol, 1.2 equiv) was transformed into **3ba** (34 mg, 0.082 mmol, 82%, α:β = 9:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 50:1). $[\alpha]_D^{25}$ = –0.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.01 (d, *J* = 10.4 Hz, 1H), 5.69 – 5.66 (m, 1H), 4.99 (t, J = 1.3 Hz, 1H), 4.39 – 4.31 (m, 1H), 4.13 (dd, J = 3.6, 8.4 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.38 – 3.32 (m, 1H), 2.15 – 1.98 (m, 2H), 1.65 – 1.57 (m, 3H), 1.44 – 1.37 (m, 1H), 1.05 (s, 10H), 0.99 (s, 10H), 0.92 – 0.81 (m, 9H), 0.77 – 0.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 125.2, 96.4, 80.6, 70.6, 67.1, 66.9, 48.7, 43.7, 34.3, 31.8, 27.5, 27.1, 25.6, 23.2, 22.8, 22.3, 21.2, 20.1, 16.2; HRMS (ESI) *m/z* Calcd $C_{24}H_{45}O_4Si$ $[M+H]^+$ 425.3087, found 425.3065.

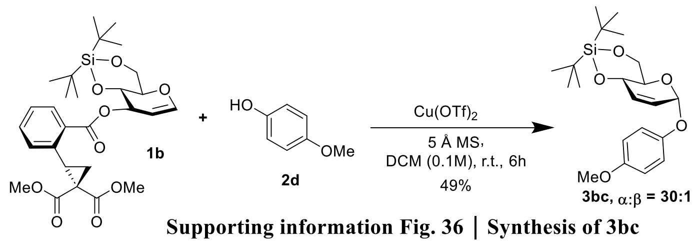
Phenyl 6-*O*-[4,6-*O*-(bis(1,1-dimethylethyl)silylene)-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl]-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (3bb)



Supporting information Fig. 35 │ Synthesis of 3bb

Following the procedure for **3a**, **2k** (70 mg, 0.12 mmol, 1.2 equiv) was transformed into **3bb** (65 mg, 0.078 mmol, 78%, α:β = 10:1) as a foamy solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). $[\alpha]_D^{25}$ = +26.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 4H), 7.82 – 7.78 (m, 2H), 7.56 – 7.50 (m, 4H), 7.43 – 7.23 (m, 12H), 6.02 (d, J = 10.4, 1H), 5.88 (t, J = 9.5 Hz, 1H), 5.60 – 5.51 (m, 2H), 5.46 (t, J = 9.7 Hz, 1H), 5.02 (d, J = 10.0 Hz, 1H), 4.96 – 4.95 (m, 1H), 4.37 – 4.30 (m, 1H), 4.07 – 3.97 (m, 3H), 3.84 – 3.80 (m, 2H), 3.76 – 3.70 (m, 1H), 1.05 (s, 10H), 0.97 (s, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.1, 165.0, 134.5, 133.42, 133.39, 133.3, 133.2, 131.6, 129.9, 129.82, 129.78, 129.3, 129.00, 128.95, 128.9, 128.5, 128.4, 128.29, 128.25, 124.5, 94.9, 85.9, 77.3, 74.4, 70.5, 70.4, 69.7, 67.3, 67.1, 27.51, 27.47, 27.11, 27.06, 22.8, 20.0; HRMS (ESI) *m/z* Calcd $C_{47}H_{52}O_{11}SiSNa$ $[M+Na]^+$ 875.2897, found 875.2835.

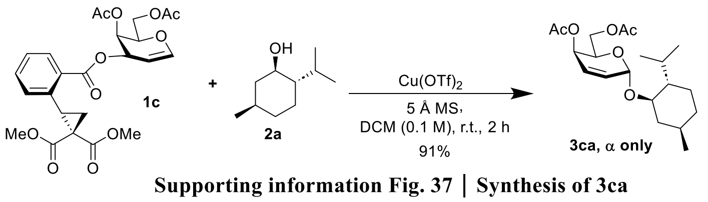
***para*-Methoxyphenyl 4,6-*O*-[bis(1,1-dimethylethyl)silylene]-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3bc)**



Supporting information Fig. 36 │ Synthesis of 3bc

Following the procedure for **3a**, **2d** (15 mg, 0.12 mmol, 1.2 equiv) was transformed into **3bc** (19 mg, 0.049 mmol, 49%, α:β = 30:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 4:1). $[\alpha]_D^{25}$ = +44.2 (c = 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 2H), 6.86 – 6.81 (m, 2H), 6.19 – 6.14 (m, 1H), 5.83 – 5.79 (m, 1H), 5.49 – 5.48 (m, 1H), 4.44 – 4.41 (m, 1H), 4.17 – 4.12 (m, 1H), 3.98 – 3.86 (m, 2H), 3.78 (s, 3H), 1.07 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.4, 135.2, 124.4, 118.4, 114.6, 94.4, 70.2, 68.0, 67.0, 55.7, 27.5, 27.1, 22.8, 20.1; HRMS (ESI) *m/z* Calcd $C_{21}H_{32}O_5SiNa$ $[M+Na]^+$ 415.1917, found 415.1924.

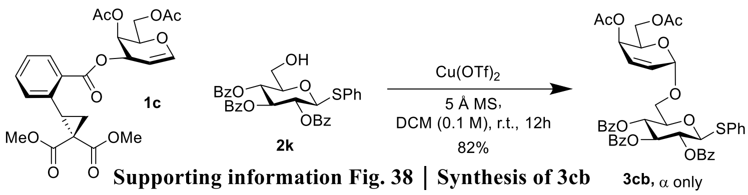
L-Menthyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (3ca)



Supporting information Fig. 37 | Synthesis of 3ca

Following the procedure for **3a**, **2a** (19 mg, 0.12 mmol, 1.2 equiv) was transformed into **3ca** (34 mg, 0.091 mmol, 91%, α only) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.13 – 6.07 (m, 1H), 6.04 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.14 (d, *J* = 2.8 Hz, 1H), 5.01 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.43 – 4.39 (m, 1H), 4.26 – 4.17 (m, 2H), 3.47 – 3.41 (m, 1H), 2.24 – 2.18 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.69 – 1.58 (m, 3H), 1.46 – 1.40 (m, 1H), 1.29 – 1.20 (m, 3H), 1.09 – 0.87 (m, 10H), 0.86 – 0.75 (m, 4H). The data are identical to the literature report.[24]

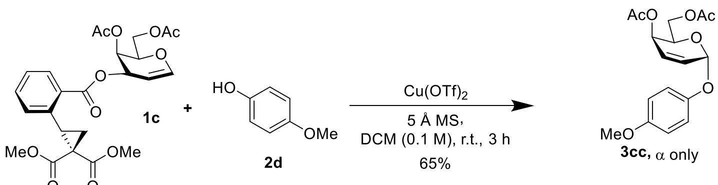
Phenyl 6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (3cb)



Supporting information Fig. 38 | Synthesis of 3cb

Following the procedure for **3a**, **2k** (72 mg, 0.12 mmol, 1.2 equiv) was transformed into **3cb** (66 mg, 0.082 mmol, 82%, α only) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00 – 7.96 (m, 2H), 7.95 – 7.91 (m, 2H), 7.83 – 7.79 (m, 2H), 7.56 – 7.49 (m, 4H), 7.45 – 7.36 (m, 5H), 7.35 – 7.25 (m, 6H), 6.12 – 6.08 (m, 1H), 5.98 – 5.88 (m, 2H), 5.63 (t, *J* = 9.7 Hz, 1H), 5.49 (t, *J* = 9.7 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.97 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.35 – 4.31 (m, 1H), 4.16 – 4.08 (m, 2H), 4.07 – 4.00 (m, 2H), 3.83 – 3.77 (m, 1H), 2.08 (s, 3H), 1.93 (s, 3H). The data are identical to the literature report.[25]

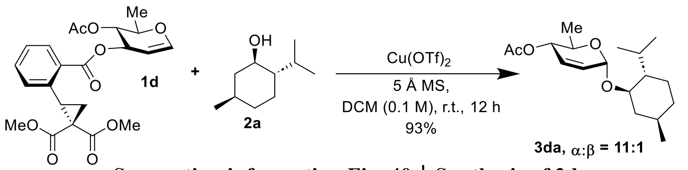
***para*-Methoxyphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranoside (3cc)**



Supporting information Fig. 39 | Synthesis of 3cc

Following the procedure for **3a**, **2d** (15 mg, 0.12 mmol, 1.2 equiv) was transformed into **3cc** (22 mg, 0.065 mmol, 65%, α only) as a colorless oil after purification by silica gel column chromatography (hexane:EtOAc:Et_2O= 5:1:1). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.08 – 7.04 (m, 2H), 6.85 – 6.80 (m, 2H), 6.27 – 6.22 (m, 1H), 6.19 (dd, *J* = 10.0, 3.0 Hz, 1H), 5.62 (d, *J* = 2.9 Hz, 1H), 5.11 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.54 – 4.50 (m, 1H), 4.29 – 4.19 (m, 2H), 3.78 (s, 3H), 2.10 (s, 3H), 1.96 (s, 3H). The data are identical to the literature report.[25]

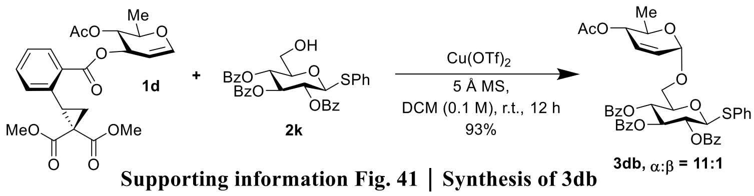
L-Menthyl 4-*O*-acetyl-6-deoxy-2,3-dideoxy-α-L-erythrohex-2-enopyranoside (3da)



Supporting information Fig. 40 | Synthesis of 3da

Following the procedure for **3a**, **2a** (19.5 mg, 0.12 mmol, 1.2 equiv) was transformed into **3da** (28 mg, 0.087 mmol, 87%, α:β = 11:1) as a white solid after purification by silica gel column chromatography (toluene:EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 – 5.82 (m, 1H), 5.73 – 5.70 (m, 1H), 5.15 – 5.11 (m, 1H), 5.04 – 5.01 (m, 1H), 3.98 – 3.91 (m, 1H), 3.56 – 3.49 (m, 1H), 2.28 – 2.22 (m, 1H), 2.08 (s, 3H), 1.68 – 1.61 (m, 2H), 1.42 – 1.17 (m, 6H), 1.09 – 0.73 (m, 14H). The data are identical to the literature report.[26]

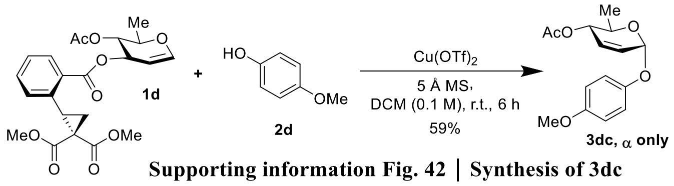
Phenyl 6-*O*-(4-*O*-acetyl-6-deoxy-2,3-dideoxy-α-L-erythrohex-2-enopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (3db)



Supporting information Fig. 41 | Synthesis of 3db

Following the procedure for **3a**, **2k** (73 mg, 0.12 mmol, 1.2 equiv) was transformed into **3db** (72 mg, 0.093 mmol, 93%, α:β = 11:1) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 12:1). $[\alpha]_D^{25}$ = –1.2 (c = 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.93 – 7.89 (m, 2H), 7.81 – 7.77 (m, 2H), 7.54 – 7.48 (m, 4H), 7.43 – 7.22 (m, 12H), 5.92 – 5.80 (m, 2H), 5.76 – 5.72 (m, 1H), 5.56 – 5.47 (m, 2H), 5.07 –5.01 (m, 2H), 4.99 – 4.94 (m, 1H), 4.08 – 3.91 (m, 3H), 3.76 (dd, J = 11.6, 6.3 Hz, 1H), 2.09 (s, 3H), 1.15 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 165.8, 165.3, 165.1, 133.5, 133.3, 133.2, 133.1, 132.8, 132.3, 129.9, 129.8, 129.8, 129.6, 129.2, 129.01, 128.96, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.5, 95.1, 86.3, 78.2, 77.3, 74.3, 70.8, 70.7, 69.5, 67.4, 66.5, 64.9, 36.7, 29.7, 29.4, 24.7, 22.7, 21.1, 18.6, 17.9, 14.2; HRMS (ESI) *m/z* Calcd $C_{41}H_{38}O_{11}SNa$ $[M+Na]^+$ 761.2033, found 761.2054.

***para*-Methoxyphenyl 4-*O*-acetyl-6-deoxy-2,3-dideoxy-α-L-erythrohex-2-enopyranoside (3dc)**

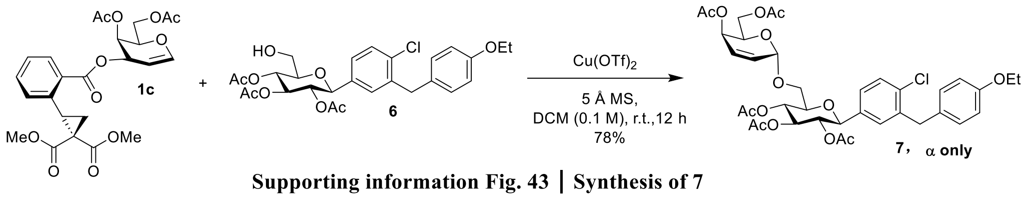


Supporting information Fig. 42 | Synthesis of 3dc

Following the procedure for **3a**, **2d** (73 mg, 0.12 mmol, 1.2 equiv) was transformed into **3dc** (72 mg, 0.078 mmol, 78%, α only) as a colorless syrup after purification by silica gel column chromatography (toluene:EtOAc = 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 7.00 (m, 2H), 6.86 – 6.81 (m, 2H), 6.02 – 5.92 (m, 2H), 5.52 (s, 1H), 5.11 (d, J = 9.1 Hz, 1H), 4.15 – 4.08 (m, 1H), 3.78 (s, 3H), 2.11 (s, 3H), 1.23 (d, J = 6.2 Hz, 3H). The data are identical to the literature report.[27]

Section 5. Application of ferrier rearrangement.

6-*O*-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl) dapagliflozin triacetate (7)



Supporting information Fig. 43 | Synthesis of 7

A solution of **1c** (50 mg, 0.1 mmol, 1.0 equiv) and **6**[28] (65 mg, 0.12 mmol, 1.2 equiv) in anhydrous DCM (1 mL, 0.1 M) containing freshly activated 5 Å molecular sieve was stirred at room temperature for 15 min before $Cu(OTf)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv) was added. The mixture was stirred at room temperature for 12 h until **6** was fully consumed (determined by TLC). The reaction was then quenched with triethylamine and the mixture was directly loaded onto silica gel by concentrating the mixture *in vacuo*. The residue was further purified by silica gel column chromatography (toluene:EtOAc:Et_2O = 4:1:1) to give the **7** as a colorless crystalline solid (59 mg, 0.078 mmol, 78%, only). $[\alpha]_D^{25}$ = –40.7 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 1H), 7.15 (dd, J = 8.3, 2.2 Hz, 1H), 7.06 – 7.01 (m, 3H), 6.83 – 6.77 (m, 2H), 6.13 – 6.09 (m, 1H), 6.00 (dd, J = 10.0, 3.0 Hz, 1H), 5.30 – 5.17 (m, 2H), 5.07 – 4.96 (m, 3H), 4.32 – 4.23 (m, 2H), 4.19 – 4.11 (m, 2H), 4.06 – 3.99 (m, 2H), 3.99 – 3.92 (m, 2H), 3.84 (dd, J = 11.1, 4.6 Hz, 1H), 3.78 – 3.73 (m, 1H), 3.66 (dd, J = 11.1, 2.8 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.69 (s, 3H), 1.39 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.4, 170.3, 169.5, 168.8, 157.5, 139.0, 135.4, 134.5, 131.0, 130.1, 129.80, 129.76, 125.9, 125.4, 114.5, 93.8, 74.3, 72.6, 69.2, 66.6, 66.4, 63.4, 62.5, 62.4, 38.2, 20.81, 20.79, 20.71, 20.65, 20.3, 14.9; HRMS (ESI) *m/z* Calcd $C_{37}H_{41}O_{14}ClNa$ $[M+Na]^+$ 767.2083, found 767.2054.

Section 6. Computational details.

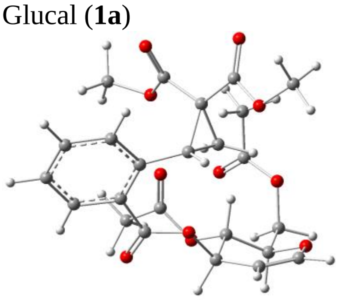
General computational methods

To explore the mechanistic details of the stereoselective Ferrier rearrangement, we performed Density Functional Theory (DFT) simulations of the reaction employing model donor **1a** and model acceptor methanol (MeOH) and *p*-methoxyphenol (*p*-OMePhOH), and $Cu(OTf)_2$ and $Sc(OTf)_3$ as the catalyst, to investigate the mechanisms giving rise to the α-stereoselectivity of the reaction. We proposed that our $Cu(OTf)_2$-catalyzed Ferrier rearrangement with α-selective glycosylation proceeds in three stages: Firstly, the copper(II)-promoted CCBz ring opening resulting in the dissociation of C3-substituent and the migration of the 1,2-double bond, giving rise to an ion pair of the LG anion and glycosyl oxocarbenium. Then another copper(II) species coordinates to the 2,3-position of the glycosyl oxocarbenium, from either α- or β-face, bringing the coordinated alcohol acceptor to the proximity of the glycosyl oxocarbenium. Finally, a directed nucleophilic α-attack by the alcohol at the anomeric position forms the glycosidic bond, and the following dissociation of the copper gives rise to the 2,3-unsaturated product. We assumed that the metal center participating in coordination carries an accompanying triflate anion, which serves as a proton acceptor in the final *O*-glycosylation step. Structures of reagents, products, catalysts, proposed intermediates, and transition states were built with GaussView6.0 and pre-optimized at B3LYP/def2-SV(P) level of theory with Grimme's empirical dispersion D3(BJ), and the pre-optimized structures were subjected to geometry optimization and frequency analysis at MN15-L/def2-TZVP/SMD (solvent = dichloromethane) level of theory. Accurate electronic energy is calculated from the optimized structures at MN15-L/def2-TZVPP/SMD (solvent = dichloromethane) level of theory. MN15-L is a recent Minnesota family functional specifically parameterized for the thermochemistry of organometallic systems containing transition metals. Gibbs free energies of the intermediates were calculated as the sum of thermal corrections derived from frequency analysis at 298K and the accurate electronic energy.

Calculated coordinates and energies of the optimized structures

Charge and spin multiplicity reported as used in DFT computations in the line following the compound name, electronic energies, and thermal corrections reported in atomic units (a.u.):

Reagents
Glucal (**1a**)

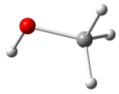


0 1
Electronic energy: -1756.841129
Thermal corrections: 0.412323

O	-2.99064800	-1.12933200	-0.21079700
C	-1.78873400	-0.23684500	-2.16027400
C	-3.71017400	0.96517300	-1.04386300
C	-1.74950100	1.02752000	-2.97108500
H	-2.28321000	-1.08539300	-2.67012100
H	-4.41700500	0.47645000	-1.75125800
C	-2.43151500	2.12966000	-2.62258800
H	-1.07878700	1.06642800	-3.83154700
O	-3.30987000	2.22149000	-1.59356600
C	-4.43201100	1.25924400	0.27089600
H	-4.94747600	0.36009600	0.64028800
H	-5.15445300	2.07701000	0.11341700
H	-2.35064900	3.07862500	-3.16153200
O	-0.40166700	-0.58694000	-1.91872400
O	-3.46963300	1.71408400	1.23015700
C	-2.49028400	0.05929100	-0.82802500
H	-1.77817600	0.57894700	-0.16327400
C	-3.22168200	0.91841400	2.30358000
C	-2.24195600	-1.71134900	0.76059900
O	-1.18675700	-1.26412000	1.15315700
O	-3.87245000	-0.06144400	2.58528200
C	-2.91948700	-2.96084500	1.24667000
H	-3.92579000	-2.70407400	1.61323300
H	-3.02409500	-3.65621200	0.39847300
H	-2.32698000	-3.41881900	2.04712500

C	-2.00703900	1.41508000	3.04704400
H	-2.01406500	1.02819500	4.07352200
H	-1.11468500	1.01619500	2.52861300
H	-1.94969000	2.51254500	3.03347000
C	-0.13592600	-1.85772100	-1.55962400
O	-0.96351700	-2.74704400	-1.59242300
C	1.29767600	-2.07034800	-1.16527000
C	1.66760700	-3.42928300	-1.07128400
C	2.27303100	-1.06634400	-0.93219000
C	2.97735100	-3.81489700	-0.79728200
H	0.88686600	-4.17514200	-1.24033100
C	3.59641600	-1.48176500	-0.68278400
C	3.95591300	-2.82898200	-0.62168300
H	3.23603600	-4.87569200	-0.73441600
H	4.35215900	-0.71040100	-0.49881900
H	4.99533600	-3.10464600	-0.41926900
C	2.05861200	0.42935100	-0.91398200
H	2.43930100	0.94497900	-1.80306100
C	0.98963900	1.13946900	-0.17463600
H	0.59900200	2.05952700	-0.62069200
H	0.29032600	0.53418800	0.40164600
C	2.40509900	1.19573600	0.39655400
C	2.74605900	0.29780300	1.56001900
C	3.14128800	2.49996700	0.33772800
O	3.71453800	3.02198500	1.26362100
O	3.02950900	3.06975800	-0.88571100
O	3.84801800	0.17576100	2.04021100
C	3.63600800	4.36345800	-0.98681400
H	4.71534400	4.30118600	-0.77484800
H	3.46177900	4.69545300	-2.01914400
H	3.17665200	5.06317100	-0.26989900
O	1.68057100	-0.44638300	1.90764100
C	1.96747100	-1.59872600	2.70712800
H	2.42901400	-1.30873800	3.66447700
H	0.99753000	-2.09031500	2.86259900
H	2.65780600	-2.26445000	2.15755400

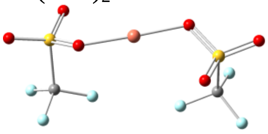
Methanol (MeOH)



0 1
Electronic energy: -115.643892
Thermal corrections: 0.028123

C	0.65915800	-0.01929900	0.00001800
H	1.03571700	-0.54194900	0.90303700
H	1.03438700	-0.55562900	-0.89542800
H	1.08550600	0.99600600	-0.00811400
O	-0.74729800	0.12253600	0.00003700
H	-1.13217600	-0.76292500	0.00010200

$Cu(OTf)_2$

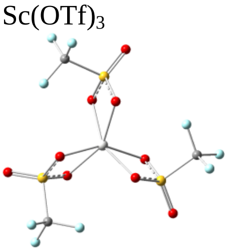


0 2

Electronic energy: -3563.173710
Thermal corrections: 0.005451

S	-2.85303900	0.65045600	-0.18579700
O	-2.56413500	0.75096000	-1.59185800
O	-4.15766500	1.01453000	0.28356300
C	-2.71297600	-1.15881800	0.17345200
F	-2.93997400	-1.41731700	1.46215300
F	-1.49078900	-1.60970700	-0.12780800
F	-3.59681600	-1.85249500	-0.54775900
O	-1.76919100	1.19616900	0.68106900
Cu	-0.00002200	1.15630000	-0.00004500
O	1.76915300	1.19610200	-0.68118700
S	2.85293200	0.65050800	0.18584200
O	4.15759700	1.01472900	-0.28329400
O	2.56378000	0.75095100	1.59185900
C	2.71311100	-1.15877300	-0.17345900
F	2.94038700	-1.41723100	-1.46212000
F	3.59687300	-1.85238300	0.54791400
F	1.49090300	-1.60976800	0.12755400

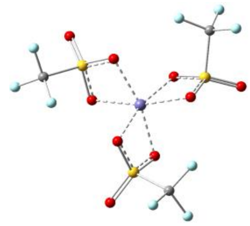
$Sc(OTf)_3$



0 1
Electronic energy: -3644.676415
Thermal corrections: 0.025834

Sc	0.00216400	-0.00144300	-0.32253500
O	-1.77429500	-0.41918300	0.80916300
O	0.52135100	1.74590200	0.80776700
O	1.25165500	-1.33140500	0.80879300
S	-2.44204800	-1.26901700	-0.27014600
S	0.11891400	2.74907900	-0.27224600
S	2.32455000	-1.47993700	-0.26888600
O	-1.40148100	-1.20150100	-1.39056100
O	1.02853300	3.82075900	-0.59157300
O	-0.33739000	1.81403300	-1.39410500
O	1.74597200	-0.61289500	-1.38918200
O	2.79871200	-2.80216600	-0.59225500
C	-1.47575100	3.49788100	0.36617200
C	3.77084700	-0.47219600	0.36731000
C	-2.29887900	-3.02459000	0.36547500
O	-3.82384100	-1.01432200	-0.59216900
F	4.22158900	-1.02556800	1.47946100
F	4.71677200	-0.46623100	-0.55571300
F	3.36203400	0.76409800	0.60743600
F	-1.22175500	4.13429900	1.49618700
F	-1.94072400	4.34186200	-0.53803000
F	-2.35255500	2.52829700	0.57639100
F	-2.99886100	-3.13129100	1.48134800
F	-1.02429400	-3.29510400	0.60037600
F	-2.77544200	-3.84725400	-0.55268900

$Fe(OTf)_3$

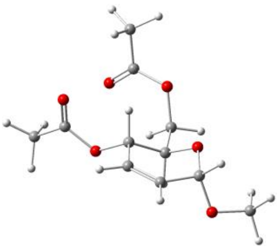


0 6
Electronic energy: -4146.455570
Thermal corrections: 0.028901

O	-1.09299900	1.47982700	0.57610800
O	1.82328800	0.20542000	0.57813200
O	-0.73725900	-1.68410200	0.57459000
S	-2.22049500	1.37035100	-0.42232200
S	2.29508600	1.23340700	-0.42195600
S	-0.07667000	-2.60436700	-0.42379200
O	-1.79653800	0.29172500	-1.38954600
O	3.63814900	1.10092700	-0.96375400
O	1.14857200	1.40879500	-1.38781100
O	0.64717600	-1.69682900	-1.38843900
O	-0.85710100	-3.70461200	-0.96729200
C	2.34904800	2.83130000	0.54523400
C	1.28153400	-3.44464700	0.54665600
C	-3.62734500	0.61293800	0.54686500
O	-2.78234000	2.59794100	-0.96311900
F	0.73519600	-4.25063300	1.46248400
F	2.02518700	-4.18552100	-0.27918200
F	2.06267900	-2.56888800	1.15995500
F	3.31500100	2.75789400	1.46648100
F	2.63003600	3.84152700	-0.28185800
F	1.19829800	3.07839800	1.15110900
F	-4.05075600	1.48669400	1.46568200
F	-3.26007100	-0.50349700	1.15613200
F	-4.64174300	0.34316300	-0.27891200
Fe	-0.00146800	0.00104800	-0.38813000

Products

Glycoside Product α

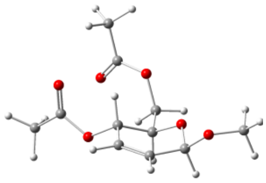


0 1
Electronic energy: -879.685306
Thermal corrections: 0.222459

O	0.93542800	1.29609900	-0.63859700
C	-0.92080600	1.78877000	0.83616900
C	-0.83835900	-0.30529100	-0.48634700
C	-2.22899900	1.56186300	0.98675000
H	-0.45951800	2.74877100	1.09564900
H	-1.30303200	0.18628700	-1.36952700
H	-2.91691900	2.33088400	1.35042200
O	-1.84449300	-0.77003600	0.40661600
C	-0.02554700	-1.50135500	-0.97397500

H	0.62726800	-1.20247700	-1.80870700
H	-0.71264200	-2.30336900	-1.29129300
O	0.76499800	-2.03310600	0.10030400
C	-0.00768600	0.72428400	0.28355900
H	0.54084400	0.22726400	1.10604500
C	2.09048000	-1.75439500	0.08295200
C	2.16040300	1.59486900	-0.13744500
O	2.45036100	1.48567400	1.03234800
O	2.66887900	-1.24531600	-0.85110800
C	3.08695800	2.03334000	-1.24210000
H	3.42896600	1.12268200	-1.76117800
H	2.56123800	2.66488700	-1.97261900
H	3.95208700	2.55652300	-0.81678500
C	2.72585300	-2.11265300	1.40290300
H	3.78638600	-2.35219200	1.25378600
H	2.66287200	-1.21263900	2.04061900
H	2.19361600	-2.93287300	1.90339800
C	-2.82754900	0.21055500	0.66709700
H	-3.39305400	-0.19820500	1.53561200
O	-3.69916300	0.38572200	-0.42159200
C	-4.42885200	-0.79038700	-0.72765000
H	-5.16650700	-0.52159700	-1.49784800
H	-3.76767400	-1.59002700	-1.11255500
H	-4.95738700	-1.17380900	0.16973900

Glycoside Product β

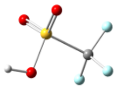


0 1
Electronic energy: -879.682601
Thermal corrections: 0.222125

O	-1.18641800	-1.31740400	-0.59998300
C	0.86009400	-1.87292800	0.57505200
C	0.69540400	0.13257300	-0.88444500
C	2.18620400	-1.77695100	0.43802200
H	0.38164300	-2.74473800	1.03642100
H	0.91050000	-0.45195500	-1.81109600
H	2.87139100	-2.56737500	0.75952900
O	1.90266000	0.52987500	-0.26128300
C	-0.10114000	1.37276500	-1.28832700
H	-0.92639100	1.08887800	-1.95973600
H	0.56955400	2.09202900	-1.78543300
O	-0.62231700	2.02759400	-0.12252300
C	-0.05327000	-0.77301600	0.10115000
H	-0.41209500	-0.18113600	0.96324800
C	-1.94304600	1.86216600	0.13322400
C	-2.31744100	-1.48726900	0.13014500
O	-2.37777000	-1.29895000	1.32391300
O	-2.72766300	1.35325800	-0.63573600
C	-3.46182300	-1.89692500	-0.76074800
H	-3.82110000	-0.98672100	-1.26892200
H	-3.12942500	-2.60815400	-1.53059800
H	-4.27260300	-2.31999800	-0.15524000
C	-2.28049400	2.34372100	1.52156400

H	-3.32576900	2.67620100	1.55723700
H	-2.17419200	1.47318800	2.19361600
H	-1.59437300	3.13192600	1.85961100
O	3.89093100	-0.16518800	0.61468100
C	4.62932700	0.90969100	0.05428800
H	5.53168000	1.03159900	0.67079700
H	4.92617700	0.67758700	-0.98993300
H	4.04674300	1.84771600	0.05991500
C	2.82021900	-0.55041300	-0.17518000
H	3.17867200	-0.77301700	-1.22042600

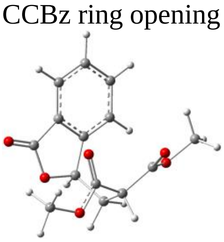
TfOH



0 1
Electronic energy: -961.822763
Thermal corrections: 0.007241

S	-0.85818900	-0.13588100	-0.00000200
O	-1.26619600	-0.69774100	-1.24247100
O	-1.26621800	-0.69765200	1.24250200
C	0.99338600	-0.00560000	0.00000500
F	1.40785900	0.63485500	1.08005600
F	1.40786900	0.63480900	-1.08007000
F	1.47881500	-1.23658500	0.00003300
O	-1.07419000	1.43038000	-0.00005500
H	-2.02734500	1.63009000	0.00002800

CCBz ring opening leaving group



0 1
Electronic energy: -992.824106
Thermal corrections: 0.206330

O	-1.48299100	-1.01260600	1.28943800
C	-1.33554000	-1.91938100	0.26758900
O	-2.26721200	-2.49747100	-0.21742400
C	0.11028400	-1.99123700	-0.04107400
C	0.76757700	-2.75802200	-1.00150900
C	0.79198400	-1.12382600	0.80937700
C	2.15677900	-2.64251400	-1.08371300
H	0.20061100	-3.41946200	-1.66125200
C	2.18033600	-1.02001900	0.74567000
C	2.85320900	-1.78628700	-0.21359700
H	2.71108400	-3.22331200	-1.82637000
H	2.73139000	-0.35769100	1.41609200
H	3.94290600	-1.71838300	-0.28724100
C	-0.22081800	-0.46791200	1.71947500
H	-0.06820700	-0.80673100	2.76078200
C	-0.30983100	1.06229200	1.75701300
H	-1.20313600	1.29996500	2.35672100
H	0.56539200	1.45120400	2.29944500
C	-1.47992300	1.17745500	-0.49352500

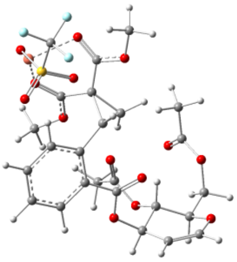
C	0.86749700	2.06432600	-0.35251400
O	0.92278300	2.38997000	-1.50759800
O	1.95283300	1.97392000	0.44200900
O	-1.25199400	0.42578600	-1.40487700
C	3.20672100	2.22275100	-0.19108200
H	3.39240600	1.47246500	-0.97761300
H	3.22047400	3.22643500	-0.64651000
H	3.96671000	2.14722700	0.60020500
O	-2.70743400	1.52111900	-0.08553400
C	-3.79150900	0.82207900	-0.70971000
H	-3.78470100	0.99533100	-1.79811700
H	-3.70657900	-0.25915200	-0.51273000
H	-4.70751100	1.22956100	-0.25877200
C	-0.42815000	1.81553600	0.41215300
H	-0.80041900	2.82535000	0.65992200

Intermediates and Transition States

I. Activation of the glycal donor through CCBz ring opening

I.I Cu-Catalyzed ring opening without coordination

IM1



1 2

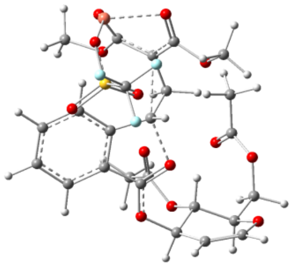
Electronic energy: -4357.809783

Thermal corrections: 0.427682

O	2.52758800	-3.28315200	-0.29945300
C	1.82527000	-1.61786700	-1.86329900
C	0.35202100	-3.58040400	-1.28092900
C	0.60886700	-1.04618600	-2.54216700
H	2.43110600	-2.20840100	-2.57256000
H	0.89634300	-4.29101000	-1.93039400
C	-0.55164300	-1.78469700	-2.60639800
H	0.75933800	-0.21154600	-3.23309900
O	-0.70453600	-3.00168200	-2.05853500
C	-0.36018000	-4.35909200	-0.17693400
H	0.36307900	-4.82890200	0.50262400
H	-1.00787000	-5.12145500	-0.63446800
H	-1.38937200	-1.53395000	-3.26401900
O	2.68610500	-0.50131000	-1.53836000
O	-1.15078300	-3.45820700	0.58244100
C	1.37832300	-2.55853400	-0.73816700
H	0.93774700	-2.00993400	0.10042300
C	-2.50059300	-3.46247500	0.36574600
C	2.70704700	-3.46430100	1.03410200
O	1.83806000	-3.31196100	1.85150800
O	-3.05600200	-4.29078700	-0.30651300
C	4.12666400	-3.86883500	1.32654200
H	4.51225900	-4.55487200	0.55549000
H	4.74785300	-2.95506300	1.30934000
H	4.18748100	-4.32606100	2.32472500
C	-3.15414500	-2.30835900	1.07149000

H	-4.24640000	-2.40429000	1.00072700
H	-2.83954300	-2.27840700	2.12713800
H	-2.83966200	-1.36033200	0.60393200
C	2.97622400	-0.04917900	-0.31085800
O	2.82338600	-0.68205000	0.70893000
C	3.52670000	1.34372800	-0.34878800
C	4.30224000	1.76792900	-1.43451300
C	3.23741100	2.24173100	0.70941500
C	4.82160500	3.06362300	-1.47234600
H	4.49469800	1.07157000	-2.25313000
C	3.74401400	3.54274500	0.64210900
C	4.54089100	3.95168800	-0.43157300
H	5.43615900	3.38140600	-2.31926100
H	3.50537900	4.24602000	1.44382600
H	4.93532200	4.97167600	-0.45727600
C	2.31888100	1.81583700	1.80780200
H	2.64487800	0.92004500	2.33779600
C	1.34819700	2.67796100	2.53516800
H	1.12443700	2.40197500	3.56758000
H	1.28733500	3.74342800	2.30495200
C	0.79967200	1.76284400	1.46357500
C	0.16896500	0.44590700	1.78303900
C	0.43576500	2.37157100	0.14314500
O	0.28885200	1.73209100	-0.89005400
O	0.39018100	3.68637400	0.16259400
O	-0.27533500	-0.33840500	0.96341200
C	0.02434600	4.34380100	-1.06519700
H	-0.99740600	4.03815700	-1.34175900
H	0.07382800	5.41838400	-0.84273800
H	0.73684800	4.07502900	-1.86124800
O	0.23373100	0.16207900	3.07382900
C	-0.20650600	-1.14925100	3.46936600
H	0.32727600	-1.92136600	2.89477700
H	0.02225500	-1.22043400	4.54161900
H	-1.29024200	-1.23679600	3.29933600
Cu	-0.65688600	-0.11638200	-1.20326200
O	-2.58489200	0.40059300	-0.93464300
S	-2.89065200	1.74439100	-0.29800900
O	-2.92457700	2.85643200	-1.25637200
O	-2.16800300	1.97704200	0.96844000
C	-4.66462100	1.49104800	0.21688400
F	-5.13336800	2.61040700	0.76549700
F	-4.75188600	0.50816300	1.11807200
F	-5.41871300	1.17655000	-0.83275400

TS1

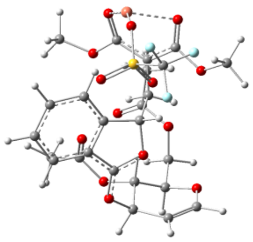


1 2
Electronic energy: -4357.747158
Thermal corrections: 0.427805

O	-5.15958700	-0.21838600	1.06216200
C	-3.88987000	-2.28682600	1.05456400
C	-5.49505700	-1.71558500	-0.78140000
C	-3.52019700	-3.43820000	0.17217000
H	-4.60711300	-2.57374600	1.83925700
H	-6.30673600	-2.24154600	-0.24095000
C	-3.99482700	-3.52344700	-1.07972300
H	-2.84769100	-4.20767700	0.55708100
O	-4.85820500	-2.65468300	-1.64829900
C	-6.12453500	-0.63223000	-1.64172800
H	-6.80655700	-0.01713800	-1.03873100
H	-6.67374000	-1.11053600	-2.46771500
H	-3.72370100	-4.32724700	-1.76989700
O	-2.77538200	-1.80237100	1.86424300
O	-5.11630100	0.19457500	-2.22158700
C	-4.48784700	-1.15454700	0.22398800
H	-3.69059000	-0.65033500	-0.33308200
C	-5.06221200	1.49911400	-1.85271100
C	-4.50087600	0.93321200	1.36604600
O	-3.36182200	1.14075000	1.02749800
O	-5.85541700	2.00785100	-1.09866300
C	-5.38549700	1.88505300	2.11572000
H	-5.98414300	2.43021700	1.36412000
H	-6.07343800	1.34800300	2.78707800
H	-4.76723400	2.60319100	2.67367600
C	-3.87066600	2.18313100	-2.46164900
H	-4.04213800	3.26888200	-2.49250500
H	-2.99718100	1.98446900	-1.81524200
H	-3.64996400	1.78696600	-3.46464800
C	-1.70840500	-1.27833600	1.30895700
O	-1.50569900	-1.24434400	0.08089500
C	-0.68700300	-0.69135700	2.16041200
C	-0.60767000	-0.73753000	3.55577600
C	0.30252800	-0.07882000	1.36836800
C	0.51142800	-0.18052900	4.17074300
H	-1.39894200	-1.22114900	4.13298500
C	1.42500100	0.46013900	1.99686800
C	1.52131000	0.40073500	3.38940400
H	0.61518400	-0.21677400	5.25837600
H	2.23289800	0.89747900	1.41475200
H	2.41971800	0.79786100	3.86890000
C	0.03452300	-0.14675900	-0.09535900
H	0.64190700	-0.86670800	-0.65255600
C	-0.46342900	1.01233900	-0.88141600
H	-0.90738100	0.68017200	-1.82903100
H	-1.16341000	1.63220700	-0.30962100
C	0.88440800	1.67252600	-1.07151300
C	1.31175000	2.69881300	-0.17880100
C	1.78893900	1.16991600	-2.07921200
O	2.92858700	1.57342900	-2.31557600
O	1.27018300	0.13502900	-2.78370300
O	2.46950100	3.15271000	-0.03687600
C	2.19495000	-0.57062200	-3.60995000
H	3.02113400	-0.96093000	-2.99457500
H	1.62312400	-1.39647800	-4.05920500
H	2.60176600	0.08671100	-4.39581500
O	0.33135100	3.17318900	0.62335900

C	0.72008200	4.07077900	1.65366400
H	1.16668500	4.98733200	1.23443000
H	-0.20172200	4.31036000	2.20423900
H	1.45383600	3.59813900	2.32930900
Cu	3.91052800	1.82655200	-0.36007800
O	4.97218100	0.27525200	0.08271900
S	4.18447500	-0.98795400	0.38362400
O	2.91708100	-1.07975800	-0.37562200
O	4.12949400	-1.32731300	1.80655000
C	5.27638000	-2.27275700	-0.40798100
F	5.37311100	-2.05053000	-1.72186400
F	6.49642400	-2.24938600	0.12112100
F	4.75063900	-3.48466100	-0.22198500

IM2

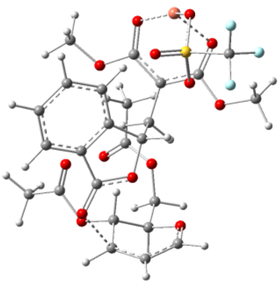


1 2
Electronic energy: -4357.758453
Thermal corrections: 0.426589

O	-5.05001900	-0.53217200	0.82820800
C	-3.94260100	-2.57980100	0.13076600
C	-5.13348400	-1.07557800	-1.49968500
C	-3.58948000	-3.36352400	-1.08931800
H	-4.76358200	-3.03075700	0.70727000
H	-6.08556200	-1.62147300	-1.34897600
C	-3.82365100	-2.86889800	-2.31528300
H	-3.11932600	-4.34225700	-0.97378300
O	-4.43458000	-1.69771000	-2.57889800
C	-5.46623700	0.35070100	-1.90783600
H	-6.17589800	0.78705400	-1.19133900
H	-5.90747600	0.33132500	-2.91691900
H	-3.53825500	-3.38960100	-3.23390100
O	-2.86783600	-2.58985400	1.15357200
O	-4.29291100	1.15914100	-1.97563800
C	-4.30009500	-1.13470500	-0.21947600
H	-3.38521800	-0.55855600	-0.39788500
C	-4.18519500	2.21068500	-1.11815200
C	-4.37667100	0.29192200	1.68067200
O	-3.17866200	0.42130900	1.64355600
O	-5.00959200	2.44678400	-0.26758000
C	-5.31546200	1.01051300	2.60219900
H	-5.67531400	1.90242400	2.05865000
H	-6.18291700	0.38385500	2.86126500
H	-4.77515200	1.33279700	3.50417300
C	-2.93916000	3.01377000	-1.36370200
H	-3.22958300	4.06255100	-1.54725800
H	-2.31011800	2.99902200	-0.45707800
H	-2.35878900	2.62827400	-2.21265200
C	-1.73818400	-1.99906900	0.93600700
O	-1.36761300	-1.68324600	-0.25895700

C	-0.81116000	-1.57431400	1.93663600
C	-0.80336300	-1.74927500	3.32880900
C	0.15696400	-0.80609800	1.25741900
C	0.23428100	-1.15354000	4.03427800
H	-1.57657900	-2.33928600	3.82581200
C	1.17827700	-0.19501800	1.97960700
C	1.21165700	-0.38990000	3.36107200
H	0.30015200	-1.27728300	5.11838500
H	1.93860600	0.40408600	1.48624000
H	2.03148900	0.05559400	3.93062000
C	-0.16879800	-0.78866300	-0.20106900
H	0.60622700	-1.25689300	-0.82384900
C	-0.62110800	0.55445900	-0.81256500
H	-1.02031700	0.32152300	-1.81133100
H	-1.43005300	0.94168200	-0.18252300
C	0.52811100	1.51223500	-0.87698100
C	0.74118600	2.42650900	0.17803700
C	1.54332600	1.31435200	-1.87427700
O	2.59965900	1.93835200	-2.00510500
O	1.25246500	0.28686300	-2.72027300
O	1.78711300	3.06200900	0.46545800
C	2.31232500	-0.11506300	-3.58208900
H	3.18686000	-0.42061600	-2.98619800
H	1.92266900	-0.96865400	-4.15817800
H	2.60264600	0.70321500	-4.26202000
O	-0.33603400	2.57402200	1.00716400
C	-0.12839700	3.27928900	2.21878600
H	0.14691400	4.33068400	2.03124000
H	-1.08398900	3.22254500	2.76210600
H	0.67294700	2.80974100	2.81627600
Cu	3.43720800	2.06441800	0.04089900
O	4.75757400	0.65956900	0.21441000
S	4.20270700	-0.74655400	0.34428600
O	2.97776600	-0.97520000	-0.45459400
O	4.19484800	-1.25667600	1.71839800
C	5.51546400	-1.72073100	-0.54866200
F	5.57978200	-1.35147400	-1.83088000
F	6.70760100	-1.53220900	0.01068300
F	5.21912400	-3.02091300	-0.49777100

TS2



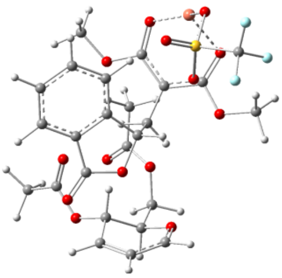
1 2
Electronic energy: -4357.736235
Thermal corrections: 0.426446

O	-5.40307800	-0.46653200	0.43686100
C	-4.32840600	-2.62352300	0.58134500
C	-4.62830700	-1.51254400	-1.59014200
C	-3.73234000	-3.66919200	-0.11576800
H	-4.89682600	-2.77675200	1.49573700

H	-5.56368100	-2.08453600	-1.73967500
C	-3.24950300	-3.42492200	-1.39344500
H	-3.55183900	-4.63862400	0.35180000
O	-3.56200000	-2.36814800	-2.09999600
C	-4.71212200	-0.26590400	-2.44335400
H	-5.66669000	0.23991500	-2.23477400
H	-4.68073100	-0.57058100	-3.50314900
H	-2.59460800	-4.11599300	-1.93492400
O	-2.88667400	-2.11213800	2.27374500
O	-3.63759500	0.62787700	-2.21185700
C	-4.38483000	-1.28907100	-0.09832300
H	-3.40647700	-0.78934800	0.01204200
C	-3.94655300	1.89350800	-1.79158100
C	-4.99367600	0.68539900	1.06545100
O	-3.83378000	0.96317800	1.21083000
O	-5.07842100	2.22660700	-1.53753800
C	-6.17000900	1.52080300	1.47056900
H	-6.45848200	2.12051800	0.58840000
H	-7.02547000	0.89472300	1.76756700
H	-5.87567700	2.20141500	2.28254600
C	-2.72905500	2.75671800	-1.67640400
H	-3.00102100	3.79376200	-1.92746400
H	-2.37202800	2.73873500	-0.63164700
H	-1.90501500	2.39479500	-2.30784700
C	-1.82844500	-1.60831100	1.90622400
O	-1.39892700	-1.73447100	0.64502100
C	-0.86427000	-0.80852100	2.66000500
C	-0.84403500	-0.46970500	4.01601900
C	0.13669200	-0.40521700	1.76842400
C	0.23633600	0.28392700	4.47193200
H	-1.64338100	-0.79897300	4.68457700
C	1.22119100	0.33974400	2.22839900
C	1.25845300	0.67256500	3.58519900
H	0.30192400	0.56355600	5.52715400
H	2.02694400	0.63399000	1.56139300
H	2.11494200	1.23677300	3.96492100
C	-0.22838400	-0.88456200	0.39463100
H	0.54893000	-1.51045800	-0.06462400
C	-0.69259700	0.21445400	-0.58171100
H	-1.11802600	-0.29635800	-1.45779700
H	-1.49834100	0.76435700	-0.07838800
C	0.42411300	1.13149900	-0.98224200
C	0.68784500	2.30361800	-0.23327800
C	1.36482400	0.69045600	-1.96859900
O	2.39409400	1.27365500	-2.34104700
O	1.04983900	-0.51682600	-2.50554700
O	1.73365000	3.00118700	-0.21573000
C	2.05973100	-1.11271700	-3.31236300
H	2.98877500	-1.22705700	-2.73233900
H	1.66598400	-2.09866300	-3.60474300
H	2.26380400	-0.50366500	-4.20923500
O	-0.32609700	2.67067800	0.60131800
C	-0.04618000	3.69413900	1.54332300
H	0.19106500	4.64724500	1.04181200
H	-0.95753200	3.79683800	2.15172900
H	0.80543600	3.41215400	2.18589400
Cu	3.38647400	1.97202600	-0.58412300

O	4.80655000	0.75576600	-0.07399900
S	4.31600500	-0.58176500	0.45642400
O	3.01577200	-0.99090900	-0.11917100
O	4.48415900	-0.74284600	1.90082900
C	5.54626600	-1.73853900	-0.33116600
F	5.45574700	-1.67583100	-1.66379000
F	6.78937700	-1.42647300	0.02551500
F	5.29308100	-2.99208800	0.04929600

IM3

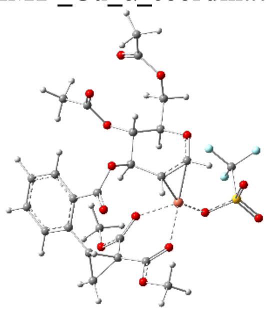


1 2
Electronic energy: -4357.736373
Thermal corrections: 0.426589

O	5.46751800	0.30350700	0.48980500
C	4.39958900	2.17473500	1.58028400
C	4.56391300	2.07708400	-0.86510100
C	3.74815400	3.38215500	1.43063900
H	4.90278900	1.88683100	2.50084200
H	5.48439800	2.68836200	-0.80869700
C	3.17974200	3.68241300	0.19097800
H	3.57447800	4.05148500	2.27508000
O	3.46259400	3.03635600	-0.90911900
C	4.60635900	1.31068100	-2.16814200
H	5.57749300	0.79860800	-2.24157400
H	4.50739400	2.03126000	-2.99763800
H	2.46536900	4.49725400	0.03330200
O	2.90295900	0.81435800	3.11645100
O	3.55935900	0.36328700	-2.28000800
C	4.41604900	1.24732500	0.40965400
H	3.44459200	0.71774600	0.37361800
C	3.91024000	-0.94675400	-2.46107400
C	5.10136300	-1.01772900	0.57734600
O	3.95316500	-1.36783300	0.63301500
O	5.06076000	-1.31103800	-2.45155700
C	6.30400900	-1.91150300	0.53506000
H	6.53236700	-2.09277900	-0.53093500
H	7.17688900	-1.43724700	1.00910500
H	6.06511700	-2.87201600	1.01443800
C	2.71044600	-1.82385500	-2.63699900
H	2.97393600	-2.66633900	-3.29483400
H	2.41890700	-2.23066900	-1.65297500
H	1.84675500	-1.26504900	-3.02590400
C	1.85929700	0.54347700	2.55136000
O	1.43943100	1.24034400	1.47118800
C	0.86524200	-0.49768300	2.84027600
C	0.81603600	-1.41704600	3.89102900
C	-0.13224900	-0.42318000	1.86407500
C	-0.28930400	-2.26585100	3.95198100
H	1.61320200	-1.45024200	4.63809900

C	-1.24537900	-1.25928400	1.93382500
C	-1.31049400	-2.17531400	2.98794200
H	-0.37550400	-2.99448500	4.76309700
H	-2.05263900	-1.18456200	1.21005000
H	-2.18766200	-2.82368300	3.06903900
C	0.26573900	0.62076900	0.86026600
H	-0.49906600	1.39905300	0.72688100
C	0.72451900	0.07166100	-0.50593000
H	1.14541200	0.91867500	-1.06636400
H	1.53426400	-0.64163200	-0.30243800
C	-0.38700600	-0.57554600	-1.27632700
C	-0.65891900	-1.95863300	-1.11146400
C	-1.30934700	0.25013300	-1.99489600
O	-2.32366500	-0.11680600	-2.61296400
O	-1.00064500	1.56887000	-1.94909700
O	-1.70467100	-2.58813900	-1.41050400
C	-2.00029300	2.45407600	-2.44423000
H	-2.94383500	2.30057200	-1.89784100
H	-1.61401400	3.46977500	-2.26712200
H	-2.17321700	2.29534900	-3.52206500
O	0.34376100	-2.65346800	-0.51240500
C	0.05717300	-3.98264800	-0.10384400
H	-0.16845400	-4.62753600	-0.96943300
H	0.96168400	-4.33585400	0.41363700
H	-0.80272000	-4.00005400	0.58676700
Cu	-3.36002300	-1.49378400	-1.41795700
O	-4.83549200	-0.66345700	-0.47171600
S	-4.37835700	0.30843900	0.60682800
O	-3.06010200	0.91244100	0.31142200
O	-4.60255100	-0.17354200	1.96895100
C	-5.58874400	1.70234800	0.35452000
F	-5.45287200	2.22084800	-0.87082100
F	-6.84021200	1.27588900	0.49920900
F	-5.35689000	2.66569400	1.24720200

I.II Cu-Catalyzed ring opening with coordination to 3-CCBz carbonyl groups
IM1'_Cu_α_coordination



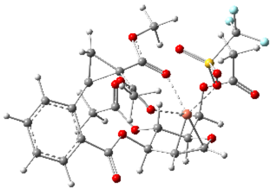
1 2
Electronic energy: -4357.817686
Thermal corrections: 0.433645

O	-0.22162800	2.93135300	0.40825800
C	0.41037200	1.07654600	-0.98910600
C	-1.93251300	1.37024100	-0.19240800
C	-0.18400400	-0.11109300	-1.72306400
H	0.87002500	0.77530800	-0.03571500
H	-1.67914000	0.70321500	0.65474400
C	-1.55082700	-0.25732700	-1.84057300

H	0.46129400	-0.62089700	-2.44412000
O	-2.43998700	0.55108100	-1.24263100
C	-3.04232100	2.29702600	0.26464500
H	-2.78470800	2.75217800	1.23026700
H	-3.96639200	1.70741100	0.36025700
H	-2.03591700	-0.96221300	-2.51891200
O	1.43509600	1.66888500	-1.81108700
O	-3.27136900	3.32435800	-0.70173300
C	-0.66553700	2.09741800	-0.66276700
H	-0.88652700	2.70924500	-1.54750400
C	-3.08531400	4.61116800	-0.32677000
C	0.06354300	4.23351100	0.14691100
O	0.01072000	4.71565400	-0.95551000
O	-2.79254700	4.94310400	0.79713700
C	0.40692800	4.96708600	1.41350100
H	-0.54673400	5.28309700	1.87280700
H	0.94028400	4.31461900	2.12213900
H	0.99975700	5.86223800	1.17365900
C	-3.22989100	5.54419600	-1.49724800
H	-3.54115000	6.53793100	-1.14211100
H	-2.23335800	5.63610900	-1.96672300
H	-3.93617300	5.14977200	-2.24349600
C	2.66682200	1.10636200	-1.64815900
O	3.17673800	0.46110800	-2.52777500
C	3.31478100	1.40290700	-0.32705000
C	3.17224400	2.69354400	0.20154100
C	4.07279000	0.43064600	0.36917400
C	3.78878200	3.04129800	1.40425700
H	2.58783000	3.42829400	-0.35529500
C	4.66909700	0.79228600	1.58278300
C	4.53632900	2.08572900	2.09633700
H	3.68491600	4.05588500	1.79843000
H	5.25317000	0.05234700	2.13360700
H	5.02329400	2.34601900	3.04052500
C	4.16412300	-0.95995600	-0.16664000
H	4.34703800	-1.00593500	-1.24115200
C	4.54349600	-2.16363300	0.61001300
H	5.07349800	-2.95265800	0.07234900
H	4.78502200	-2.06919600	1.67014000
C	3.07110200	-2.00348400	0.27123200
C	2.46156300	-2.77757600	-0.85362600
C	2.13140800	-1.52987200	1.33874100
O	0.98465600	-1.17263700	1.14727300
O	2.69674200	-1.46671300	2.53920000
O	1.27143800	-2.89963800	-1.06617300
C	1.90441100	-0.89434900	3.58978000
H	0.96608900	-1.45804100	3.70851100
H	2.52171500	-0.96236200	4.49570800
H	1.67367200	0.15721700	3.35363400
O	3.38811200	-3.31106000	-1.64746900
C	2.91910700	-3.98527800	-2.82299700
H	2.38403000	-3.27668700	-3.47568500
H	3.81902100	-4.36763500	-3.32344600
H	2.24237200	-4.80912200	-2.54703300
Cu	-0.51503700	-1.67068500	-0.43996400
O	-1.58240200	-2.91772300	0.62233800
S	-2.97785200	-3.25738100	0.11260300

O	-3.21007100	-2.77235400	-1.25809400
O	-3.40795800	-4.60509000	0.46765200
C	-4.01392100	-2.13279400	1.18796100
F	-3.62602900	-0.84841200	1.04732000
F	-5.29949600	-2.21097300	0.85362800
F	-3.88525200	-2.45488200	2.47480700

IM1’_Cu_β_coordination



1 2
Electronic energy: -4357.817686
Thermal corrections: 0.433645

O	-1.58358200	3.66085000	0.22440900
C	-1.42513900	1.91858000	-1.43297200
C	0.40448200	3.63321300	-1.09936500
C	-0.46426700	1.24723800	-2.38165200
H	-2.13331500	2.54792800	-1.99677500
H	-0.09210400	4.40266900	-1.72147100
C	0.79599100	1.77241200	-2.56730200
H	-0.87968900	0.57463800	-3.13620500
O	1.27201300	2.86736400	-1.93867000
C	1.31292400	4.31707600	-0.08118700
H	0.70940400	4.89034400	0.63805400
H	2.02169200	4.98203100	-0.59624200
H	1.45597300	1.46651100	-3.38476600
O	-2.21011100	0.96709200	-0.67808800
O	2.02463600	3.32016200	0.63786200
C	-0.66858000	2.76970600	-0.42505900
H	-0.19626900	2.12379500	0.31986100
C	3.30126700	3.04187600	0.21389500
C	-1.99670000	3.35033500	1.47502100
O	-1.58321800	2.41031600	2.10765200
O	3.91246700	3.76518000	-0.52492000
C	-3.04674900	4.32361300	1.94402800
H	-2.73601000	5.36124500	1.73897600
H	-3.98133000	4.14322100	1.38310200
H	-3.23195800	4.17975200	3.01792700
C	3.78204000	1.73997800	0.78529900
H	4.85048200	1.61116400	0.56364200
H	3.61072600	1.70548600	1.87261700
H	3.21193500	0.90849200	0.33625100
C	-3.13116800	0.29401800	-1.39524000
O	-3.29820600	0.50410100	-2.57616300
C	-3.95775300	-0.68990000	-0.62678200
C	-5.07129700	-1.16113300	-1.34856900
C	-3.72597700	-1.16833400	0.68709800
C	-5.97174500	-2.06663300	-0.79759700
H	-5.20757200	-0.78758700	-2.36459300
C	-4.65093500	-2.08239300	1.22081000
C	-5.76185400	-2.52519200	0.50399800
H	-6.83087600	-2.41083800	-1.38001200
H	-4.49308100	-2.45175200	2.23611200

H	-6.45808800	-3.23274600	0.96381800
C	-2.58240300	-0.77169200	1.57766300
H	-2.61128000	0.26049400	1.94347600
C	-1.95353500	-1.79219600	2.47573000
H	-1.63525400	-1.48409400	3.47226600
H	-2.27978700	-2.82982500	2.38152300
C	-1.14160900	-1.26567900	1.32343100
C	-0.05030800	-0.27932800	1.62076300
C	-0.92687400	-2.11370400	0.10480500
O	-0.57773500	-1.67389700	-0.98277700
O	-1.21950800	-3.38248000	0.28616600
O	0.59786700	0.32737700	0.78864500
C	-0.94566000	-4.26977000	-0.81503000
H	0.13091000	-4.22960100	-1.04825800
H	-1.24150000	-5.26740600	-0.46354200
H	-1.53701700	-3.97233300	-1.69558400
O	0.12281300	-0.09386800	2.91738100
C	1.14872400	0.82821400	3.30013400
H	1.01187100	1.79083100	2.78598300
H	1.05325900	0.94205200	4.38879100
H	2.12898200	0.40019900	3.03717200
Cu	0.73068900	-0.06620700	-1.37032200
O	2.46915600	-1.01949600	-1.06564900
S	2.50322200	-2.33810800	-0.31484600
O	2.39417700	-3.51615200	-1.18191400
O	1.69569700	-2.35136800	0.92349500
C	4.26250300	-2.33159600	0.30343300
F	4.52352300	-3.47883700	0.92636500
F	4.44153000	-1.32853700	1.17351800
F	5.12098600	-2.18025200	-0.70064000

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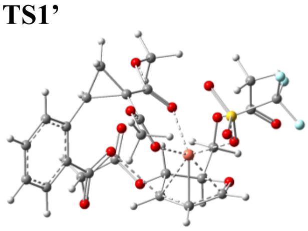

1 2
Electronic energy: -4357.754018
Thermal corrections: 0.430127

O	-1.27841200	3.85657700	-0.76515500
C	-0.69073900	1.86648900	-1.86132800
C	1.07634300	3.51500200	-1.11010100
C	0.28569300	1.22818000	-2.61826800
H	-1.77060400	1.78192000	-2.07409300
H	0.93635800	4.30493500	-1.86808900
C	1.64403400	1.51730200	-2.33810000
H	0.03903200	0.51594000	-3.41067500
O	2.03592800	2.57085000	-1.67987800
C	1.75932600	4.07794000	0.13141100
H	1.04871300	4.72231400	0.67002400
H	2.65957000	4.64334500	-0.15091000
H	2.47576400	0.95673100	-2.77665000
O	-2.23882100	0.93075700	-0.01774400
O	2.10883800	3.00613300	0.99249400
C	-0.27602900	2.85498000	-0.80802200

H	-0.22209700	2.34887300	0.16746800
C	3.40330700	2.55231900	0.93682100
C	-2.01814800	3.93889800	0.38933900
O	-1.55426500	3.67777700	1.46643600
O	4.26425300	3.12205000	0.32230800
C	-3.41411800	4.38353100	0.07976500
H	-3.39964200	5.28337700	-0.55828300
H	-3.88709000	3.57161600	-0.50544400
H	-3.96975500	4.57389400	1.00875300
C	3.56158800	1.28117100	1.72122500
H	4.61983300	0.98808700	1.72733700
H	3.19901100	1.41974000	2.75306300
H	2.95960600	0.47960700	1.26332400
C	-3.24811900	0.66230200	-0.73779300
O	-3.61446100	1.34075100	-1.72185800
C	-4.03724400	-0.60845800	-0.42378800
C	-5.01172800	-0.99593800	-1.35491000
C	-3.81691900	-1.42208900	0.71340200
C	-5.75217300	-2.16671000	-1.19040400
H	-5.16109700	-0.34231700	-2.21652900
C	-4.56919700	-2.59547000	0.87016500
C	-5.52904300	-2.97238300	-0.07072300
H	-6.50368600	-2.45037600	-1.93362500
H	-4.40580100	-3.21903300	1.75274500
H	-6.10413700	-3.89177900	0.07549300
C	-2.81760900	-1.04500700	1.75790100
H	-2.94976600	-0.03730700	2.15690500
C	-2.09391300	-2.00707600	2.62583800
H	-1.84794600	-1.68993700	3.64103700
H	-2.25733000	-3.07783300	2.48952600
C	-1.30113500	-1.33685800	1.51426000
C	-0.43457300	-0.16899100	1.82405600
C	-1.03080300	-2.10385200	0.26547900
O	-0.62583000	-1.61588700	-0.78576000
O	-1.35404400	-3.37472700	0.34675300
O	0.37664200	0.36246200	1.07497100
C	-1.16559600	-4.17401100	-0.83634000
H	-0.10444000	-4.14228700	-1.12919100
H	-1.47531600	-5.18824300	-0.55069700
H	-1.80046900	-3.78722700	-1.64921800
O	-0.64873200	0.29419900	3.04322700
C	0.00053700	1.51987200	3.41799400
H	-0.35536100	2.33865900	2.77631900
H	-0.28585900	1.68856100	4.46520700
H	1.09010700	1.41165300	3.32376000
Cu	0.62045700	-0.01282300	-0.95993600
O	2.39759200	-0.92468100	-1.02570600
S	2.43481400	-2.30822200	-0.36743200
O	2.09451700	-3.39643400	-1.28804600
O	1.82460300	-2.31603400	0.97124600
C	4.27099100	-2.47728600	-0.07866200
F	4.52452200	-3.67101100	0.45003900
F	4.70268900	-1.53603900	0.76365500
F	4.93404100	-2.36106100	-1.22614900

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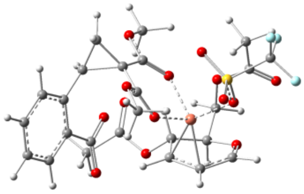

1 2
Electronic energy: -4357.75574852
Thermal corrections: 0.429905

O	-1.11089600	3.76061000	-0.88280700
C	-0.39427700	1.71981600	-1.77615300
C	1.27076400	3.51213300	-1.03195400
C	0.59290900	1.23282700	-2.63435300
H	-1.47844600	1.51089900	-1.91466600
H	1.10645400	4.36220300	-1.71398100
C	1.92797100	1.64101400	-2.41441500
H	0.38294200	0.50730100	-3.42533700
O	2.26793200	2.66391700	-1.70805900
C	1.94880700	3.97079500	0.25075600
H	1.24434500	4.60433800	0.81017700
H	2.87635200	4.51701000	0.02397900
H	2.78355000	1.13458200	-2.87680400
O	-2.44433700	1.19340900	0.30190600
O	2.23156600	2.83724400	1.05746500
C	-0.07145700	2.80220600	-0.78123400
H	-0.08033100	2.37463700	0.23174100
C	3.50331200	2.32467400	1.02196300
C	-1.85402500	3.97694900	0.25534300
O	-1.36775200	3.89341400	1.35201800
O	4.40089900	2.85753700	0.42672100
C	-3.25386000	4.36115100	-0.10772100
H	-3.24523200	5.28182400	-0.71798300
H	-3.66697000	3.54785200	-0.73138900
H	-3.85092500	4.51381600	0.80206000
C	3.58136400	1.04124600	1.79895600
H	4.62431300	0.69895600	1.83198400
H	3.19415100	1.18673500	2.82099400
H	2.95801100	0.27192500	1.31537000
C	-3.20560100	0.78104400	-0.61422700
O	-3.29965300	1.29808800	-1.75602100
C	-4.06518800	-0.46233400	-0.36208400
C	-5.03282400	-0.78472300	-1.32478600
C	-3.90564100	-1.32080200	0.75072600
C	-5.84047400	-1.91539300	-1.19662200
H	-5.11928800	-0.11600000	-2.18342800
C	-4.71069200	-2.46282400	0.86523400
C	-5.67874700	-2.76099100	-0.09520800
H	-6.59298500	-2.14146200	-1.95856500
H	-4.57748200	-3.12413500	1.72585900
H	-6.30250800	-3.65320300	0.01632400
C	-2.88138100	-1.02777800	1.79449900
H	-2.99009900	-0.04542400	2.25504400
C	-2.12222100	-2.03886100	2.56308700
H	-1.82852800	-1.78407800	3.58370900
H	-2.28342900	-3.10060700	2.36499400
C	-1.37390800	-1.29534100	1.46061900
C	-0.50295700	-0.14329100	1.79501500

C	-1.15215100	-1.98577700	0.16058800
O	-0.72430100	-1.44764500	-0.85902600
O	-1.54490200	-3.23837300	0.15407300
O	0.33614100	0.37798000	1.06406700
C	-1.42102600	-3.95913700	-1.08601100
H	-0.36030100	-3.98926000	-1.38014100
H	-1.80875100	-4.96451800	-0.87403500
H	-2.02449700	-3.46453400	-1.86337000
O	-0.72335300	0.31689300	3.01101400
C	-0.11381200	1.56581100	3.37816300
H	-0.55016900	2.37662400	2.77513200
H	-0.34715400	1.69870000	4.44348800
H	0.97203400	1.52260100	3.21465300
Cu	0.68036600	0.05068000	-0.92939900
O	2.38443000	-0.97193900	-0.94836100
S	2.29756200	-2.38510300	-0.35935700
O	1.90676500	-3.39681400	-1.34411300
O	1.64113500	-2.40459600	0.95675400
C	4.10472900	-2.70754600	-0.02420000
F	4.25006900	-3.94266600	0.44572200
F	4.57549200	-1.84665200	0.88056800
F	4.81291600	-2.58200000	-1.14345300

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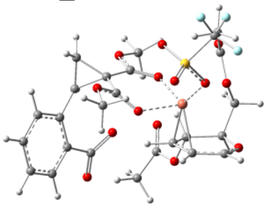

1 2
Electronic energy: -4357.7588431
Thermal corrections: 0.4301042

O	-1.11089600	3.76061000	-0.88280700
C	-0.39427700	1.71981600	-1.77615300
C	1.27076400	3.51213300	-1.03195400
C	0.59290900	1.23282700	-2.63435300
H	-1.47844600	1.51089900	-1.91466600
H	1.10645400	4.36220300	-1.71398100
C	1.92797100	1.64101400	-2.41441500
H	0.38294200	0.50730100	-3.42533700
O	2.26793200	2.66391700	-1.70805900
C	1.94880700	3.97079500	0.25075600
H	1.24434500	4.60433800	0.81017700
H	2.87635200	4.51701000	0.02397900
H	2.78355000	1.13458200	-2.87680400
O	-2.44433700	1.19340900	0.30190600
O	2.23156600	2.83724400	1.05746500
C	-0.07145700	2.80220600	-0.78123400
H	-0.08033100	2.37463700	0.23174100
C	3.50331200	2.32467400	1.02196300
C	-1.85402500	3.97694900	0.25534300
O	-1.36775200	3.89341400	1.35201800
O	4.40089900	2.85753700	0.42672100
C	-3.25386000	4.36115100	-0.10772100
H	-3.24523200	5.28182400	-0.71798300
H	-3.66697000	3.54785200	-0.73138900

H	-3.85092500	4.51381600	0.80206000
C	3.58136400	1.04124600	1.79895600
H	4.62431300	0.69895600	1.83198400
H	3.19415100	1.18673500	2.82099400
H	2.95801100	0.27192500	1.31537000
C	-3.20560100	0.78104400	-0.61422700
O	-3.29965300	1.29808800	-1.75602100
C	-4.06518800	-0.46233400	-0.36208400
C	-5.03282400	-0.78472300	-1.32478600
C	-3.90564100	-1.32080200	0.75072600
C	-5.84047400	-1.91539300	-1.19662200
H	-5.11928800	-0.11600000	-2.18342800
C	-4.71069200	-2.46282400	0.86523400
C	-5.67874700	-2.76099100	-0.09520800
H	-6.59298500	-2.14146200	-1.95856500
H	-4.57748200	-3.12413500	1.72585900
H	-6.30250800	-3.65320300	0.01632400
C	-2.88138100	-1.02777800	1.79449900
H	-2.99009900	-0.04542400	2.25504400
C	-2.12222100	-2.03886100	2.56308700
H	-1.82852800	-1.78407800	3.58370900
H	-2.28342900	-3.10060700	2.36499400
C	-1.37390800	-1.29534100	1.46061900
C	-0.50295700	-0.14329100	1.79501500
C	-1.15215100	-1.98577700	0.16058800
O	-0.72430100	-1.44764500	-0.85902600
O	-1.54490200	-3.23837300	0.15407300
O	0.33614100	0.37798000	1.06406700
C	-1.42102600	-3.95913700	-1.08601100
H	-0.36030100	-3.98926000	-1.38014100
H	-1.80875100	-4.96451800	-0.87403500
H	-2.02449700	-3.46453400	-1.86337000
O	-0.72335300	0.31689300	3.01101400
C	-0.11381200	1.56581100	3.37816300
H	-0.55016900	2.37662400	2.77513200
H	-0.34715400	1.69870000	4.44348800
H	0.97203400	1.52260100	3.21465300
Cu	0.68036600	0.05068000	-0.92939900
O	2.38443000	-0.97193900	-0.94836100
S	2.29756200	-2.38510300	-0.35935700
O	1.90676500	-3.39681400	-1.34411300
O	1.64113500	-2.40459600	0.95675400
C	4.10472900	-2.70754600	-0.02420000
F	4.25006900	-3.94266600	0.44572200
F	4.57549200	-1.84665200	0.88056800
F	4.81291600	-2.58200000	-1.14345300

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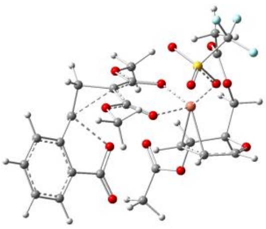


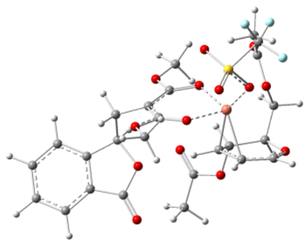
1 2
Electronic energy: -4357.699113

Thermal corrections: 0.424299

O	-1.33563000	3.54932800	-1.11322800
C	-0.37677500	1.46851000	-1.61750600
C	1.08540700	3.53009300	-1.12010600
C	0.56477000	1.09003200	-2.58476400
H	-1.37991600	1.03135200	-1.53639000
H	0.81307300	4.41912100	-1.71015000
C	1.81132400	1.74123700	-2.58604200
H	0.40931400	0.24590700	-3.26034800
O	2.07209000	2.83817900	-1.96084800
C	1.81931000	3.97266800	0.13872200
H	1.16618000	4.68354400	0.66758800
H	2.77445700	4.44714500	-0.13481300
H	2.66568100	1.36669500	-3.16159200
O	-3.64892500	0.60357500	1.81053300
O	2.03662900	2.89669700	1.03460600
C	-0.20260100	2.73155100	-0.82051700
H	-0.22895300	2.47065800	0.24690800
C	3.23405600	2.22915800	0.97361800
C	-2.02577500	4.02143700	-0.02898400
O	-1.53618100	4.08347400	1.06773900
O	4.07726400	2.50336800	0.16109700
C	-3.41729600	4.42018400	-0.41719500
H	-3.86566500	5.04262200	0.37006100
H	-3.42523600	4.94018300	-1.38883100
H	-3.98550500	3.47877300	-0.52267500
C	3.30724400	1.15849600	2.02247300
H	4.35896200	0.88624300	2.18472100
H	2.83251700	1.49420800	2.95732000
H	2.76622300	0.26379400	1.67271200
C	-3.53268200	0.44294900	0.58809500
O	-2.93250800	1.15588400	-0.25244400
C	-4.32494100	-0.71900000	-0.01041600
C	-5.27403300	-0.36094000	-0.97933400
C	-4.24698000	-2.10597800	0.37288600
C	-6.12863100	-1.29572800	-1.55668500
H	-5.31628900	0.68543700	-1.28922500
C	-5.14039100	-3.04421400	-0.24668800
C	-6.06531900	-2.65536000	-1.19073100
H	-6.85169700	-0.97193300	-2.31214100
H	-5.06288100	-4.09687400	0.04010800
H	-6.73397500	-3.38645900	-1.65201000
C	-3.36575500	-2.66257600	1.31883200
H	-3.54033900	-3.72693800	1.51575900
C	-2.29525100	-2.03078700	2.09688000
H	-2.77640600	-1.18936300	2.64690500
H	-1.87677900	-2.74974400	2.82253700
C	-1.25389100	-1.39071100	1.20505100
C	-0.61597100	-0.20978100	1.65024900
C	-0.89948700	-2.02771700	-0.01217300
O	-0.21358800	-1.58184600	-0.95118400
O	-1.41514300	-3.27718200	-0.14335800
O	0.24453900	0.47985700	1.03784600
C	-0.99311000	-4.02391600	-1.28642000
H	0.10768000	-4.04532100	-1.33742700
H	-1.40230100	-5.03582000	-1.14703400
H	-1.39141900	-3.57621400	-2.21292200

O	-0.96915800	0.17812600	2.87737700
C	-0.71696400	1.53121600	3.25576000
H	-1.37824100	2.20175800	2.68400300
H	-0.95900600	1.58751800	4.32701300
H	0.33460300	1.80358400	3.07874400
Cu	0.93780400	0.12617100	-0.76829300
O	2.73157900	-0.69885300	-0.78626800
S	2.78220900	-2.12369900	-0.21766800
O	2.50908600	-3.16304200	-1.21325700
O	2.13712800	-2.22027900	1.09839600
C	4.61483100	-2.25775900	0.10990800
F	4.88770100	-3.46917300	0.59211500
F	5.00785400	-1.34722600	1.00325800
F	5.30558500	-2.07763700	-1.01439000

IM3’

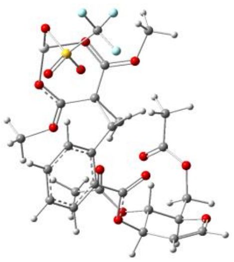


1 2
Electronic energy: -4357.795185
Thermal corrections: 0.430812

O	-1.22349700	2.49387400	-1.82283300
C	-0.30356000	0.44235600	-1.20874500
C	1.12771800	2.56709600	-1.13950500
C	0.68662600	-0.15612400	-1.99511400
H	-1.28279700	-0.02742100	-1.09810200
H	0.99576800	3.51600000	-1.67254900
C	1.83584000	0.58381700	-2.33448500
H	0.61102400	-1.17738700	-2.36957900
O	2.03022600	1.81730900	-2.02639000
C	1.88577100	2.88051900	0.13131200
H	1.27528500	3.57228400	0.73134700
H	2.83991000	3.37301200	-0.12339300
H	2.64417500	0.14145900	-2.92134100
O	-4.20495300	0.45238600	1.50456600
O	2.16275000	1.69401800	0.86199000
C	-0.25545100	1.91957000	-0.93496900
H	-0.57836200	2.11314700	0.09780500
C	2.21488200	1.83022500	2.23171500
C	-1.69066400	3.72102300	-1.44322800
O	-1.16495300	4.35658400	-0.56715000
O	1.91309800	2.86252100	2.77037300
C	-2.89241200	4.12287400	-2.24690100
H	-2.81069900	3.77586000	-3.28923500
H	-3.76803000	3.63720900	-1.78212400
H	-3.02033500	5.21430900	-2.20529300
C	2.68349600	0.58040900	2.91310500
H	2.94732600	0.82550600	3.95207600
H	1.86612600	-0.15804900	2.90140700
H	3.53040000	0.12924600	2.37863500
C	-3.77886500	0.96569300	0.33095200
O	-3.33793100	2.08716400	0.22805000

C	-3.96071500	-0.07693700	-0.70642600
C	-3.73139300	-0.02049100	-2.08322000
C	-4.42946300	-1.22929200	-0.07728800
C	-3.99683200	-1.17076800	-2.82934600
H	-3.34687000	0.89164800	-2.54569200
C	-4.69605400	-2.37768700	-0.81958800
C	-4.47916400	-2.33330900	-2.20143800
H	-3.83391300	-1.17108600	-3.91089200
H	-5.04708300	-3.29462500	-0.34024500
H	-4.68378300	-3.22175000	-2.80623200
C	-4.46399500	-0.96591200	1.40688600
H	-5.45736100	-1.14370300	1.85139200
C	-3.37674100	-1.72590700	2.20460200
H	-3.45138800	-1.39459400	3.25042800
H	-3.62518900	-2.79716600	2.17084900
C	-1.98650500	-1.48466800	1.66173500
C	-1.26620000	-0.34516000	2.09175800
C	-1.44627900	-2.37294600	0.68372000
O	-0.39724200	-2.25333300	0.02006200
O	-2.20989200	-3.47279000	0.46746800
O	-0.16525800	0.10654900	1.65296600
C	-1.77573200	-4.36493000	-0.54841200
H	-0.76154600	-4.74269600	-0.33983600
H	-2.49972600	-5.19368500	-0.54852800
H	-1.77300100	-3.86672000	-1.53357100
O	-1.84237200	0.33214700	3.09646400
C	-1.39654600	1.65784900	3.36891300
H	-1.57468400	2.30733400	2.49451800
H	-2.01184300	2.00496700	4.21150100
H	-0.33022100	1.68707300	3.63995800
Cu	0.87115400	-0.56101300	0.10026300
O	2.64119900	-1.35035900	0.51030600
S	3.65971700	-1.87586500	-0.48273800
O	3.19314300	-1.78053000	-1.88386700
O	4.32320900	-3.09845000	-0.05407200
C	4.96575300	-0.54128500	-0.38430100
F	6.00978000	-0.85481700	-1.14488100
F	5.38622300	-0.36671100	0.86981500
F	4.46473000	0.62933700	-0.82170600

I.III Sc-Catalyzed ring opening without coordination
IM1



2 1
Electronic energy: -3477.56361755
Thermal corrections: 0.4009827

O	5.09132200	0.48771300	0.87759200
C	4.51343800	1.81604500	-1.04619700
C	5.97700100	-0.21437800	-1.23714400
C	4.63408400	1.84858700	-2.53753100

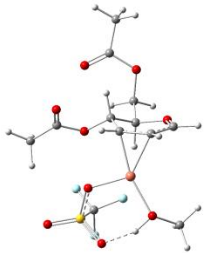
H	5.22180800	2.51853400	-0.57665100
H	6.86938200	0.41801600	-1.07116600
C	5.19647300	0.82401400	-3.21803200
H	4.24463100	2.71108400	-3.08259800
O	5.72784800	-0.25849100	-2.64749600
C	6.31785100	-1.62304800	-0.77975000
H	6.76675100	-1.59718200	0.22257100
H	7.02818700	-2.05815900	-1.49898300
H	5.26516700	0.79216600	-4.30922000
O	3.24575600	2.31244600	-0.55096100
O	5.16307800	-2.46472600	-0.77559500
C	4.78167100	0.41402200	-0.50679400
H	3.89279900	-0.21265300	-0.64998200
C	4.71069300	-2.92871800	0.41373000
C	4.08937100	0.22746000	1.74335000
O	2.94594800	0.05484300	1.37390700
O	5.23616600	-2.68256700	1.46927500
C	4.58311500	0.16620900	3.15740200
H	4.97907900	-0.85298600	3.31571800
H	5.39992600	0.88397400	3.32971300
H	3.75513600	0.33772000	3.86054300
C	3.45401600	-3.74016100	0.23595800
H	3.34204800	-4.43349000	1.08233000
H	2.59797700	-3.04099900	0.23680500
H	3.46061300	-4.28468500	-0.72076100
C	2.11026300	1.70837200	-0.90862700
O	2.04115600	0.70317300	-1.57773400
C	0.89977700	2.38039300	-0.33015100
C	0.93731300	3.72978400	0.05573400
C	-0.32273400	1.68517200	-0.29542100
C	-0.22726300	4.40286600	0.43085300
H	1.89274200	4.25451400	0.03006000
C	-1.49300200	2.38168700	0.04785500
C	-1.45466400	3.73118200	0.40792100
H	-0.17998500	5.45814100	0.71181500
H	-2.45534200	1.86701800	-0.01093300
H	-2.38083800	4.25955700	0.65022100
C	-0.40325200	0.22708300	-0.61858800
H	-0.95640300	-0.02332600	-1.53152100
C	0.52662700	-0.77821500	-0.12140800
H	0.71971600	-1.64664200	-0.75599700
H	1.35179800	-0.45719600	0.52361300
C	-0.85299700	-0.79682700	0.57014800
C	-0.98392200	-0.15650200	1.88583900
C	-1.83417500	-1.85171300	0.22482500
O	-2.81797300	-2.18338200	0.96605200
O	-1.61119300	-2.44704200	-0.88647600
O	-2.11484500	-0.12505400	2.50305300
C	-2.53647200	-3.44721600	-1.41234600
H	-3.52681500	-2.98564700	-1.52191300
H	-2.11746700	-3.73219300	-2.38480900
H	-2.56972300	-4.30663800	-0.72712500
O	0.04775300	0.37822400	2.37996700
C	0.02665100	1.21111300	3.57730900
H	-0.29639400	0.60173600	4.43382700
H	1.06312200	1.54781800	3.69280100
H	-0.65572200	2.05596900	3.40045200

O	-5.69897300	-0.42163700	0.94547600
S	-5.21885200	0.38948900	-0.31892500
O	-3.75458400	0.00851300	-0.26762700
O	-5.52389000	1.79537300	-0.23414500
C	-6.09898100	-0.40281000	-1.79317600
F	-5.76871500	-1.68519100	-1.80906300
F	-7.37979000	-0.24717700	-1.61489200
F	-5.66809900	0.20732900	-2.86611400
Sc	-3.95176000	-0.71078100	1.84703500

II. Nucleophilic attack by the acceptor

II.I Cu-OTf directed attack by MeOH

IM4α



1 2

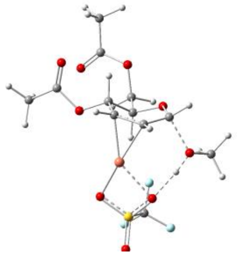
Electronic energy: -3481.153151

Thermal corrections: 0.245176

O	1.08011900	-1.13734200	-0.24607100
C	0.77845200	0.90942700	-1.55357600
C	1.64583800	0.82332600	0.83065700
C	0.66947200	2.30740300	-1.42738800
H	0.62387500	0.41375600	-2.51788300
H	0.69412800	0.63879400	1.35623600
C	1.20562100	2.92678500	-0.26746100
H	0.36600200	2.95459700	-2.25642400
O	1.70916400	2.30124300	0.72201200
C	2.78830300	0.39214500	1.72966000
H	2.65626600	-0.68137100	1.93623200
H	2.74355000	0.96492800	2.66884300
H	1.24565600	4.01956100	-0.15921300
O	4.05603800	0.64637800	1.15073800
C	1.59174500	0.13888100	-0.53872500
H	2.59644300	0.03902200	-0.98881900
C	4.68258500	-0.40845300	0.53093600
C	1.16612100	-2.07191000	-1.26350800
O	1.62972700	-1.76739700	-2.32747900
O	4.11440700	-1.44682900	0.31921100
C	0.57921000	-3.38105800	-0.84475100
H	0.93825900	-3.66632100	0.15691400
H	-0.51967000	-3.27783700	-0.79701100
H	0.84054400	-4.14997800	-1.58506300
C	6.10419900	-0.06969100	0.19225700
H	6.50473600	-0.81443400	-0.50979100
H	6.17573900	0.94607800	-0.22942800
H	6.70673800	-0.08304700	1.11855900
Cu	-1.08707300	1.27289300	-0.87512700
O	-3.08002700	-2.51273400	-0.57662800
S	-2.79158900	-1.13189000	-0.25211100
O	-1.61951200	-0.57024100	-1.07819500
O	-3.89115600	-0.14592100	-0.15495400
C	-2.05462200	-1.11899900	1.47276200

F	-1.08103900	-2.00384500	1.59483000
F	-1.52217800	0.12175600	1.69562700
F	-2.98345700	-1.33454600	2.37682600
O	-2.74822700	2.17866500	-0.34533100
H	-3.41192000	1.42252600	-0.30649000
C	-2.94329800	3.07201100	0.75883200
H	-2.76974900	2.55621800	1.71948600
H	-2.23549100	3.90767200	0.64546300
H	-3.97052100	3.47010500	0.73070900

TS4α

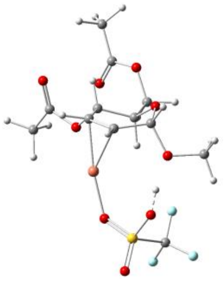


1 2
Electronic energy: -3481.14259729
Thermal corrections: 0.246309

O	1.88277700	-1.25533700	-0.54302200
C	0.85507800	0.27008900	-2.09439200
C	1.13843800	0.82449700	0.32339700
C	-0.00711200	1.35767300	-2.18202000
H	1.09366400	-0.33211900	-2.97946300
H	0.18708800	0.34663800	0.61420400
C	0.09003000	2.40475600	-1.13204700
H	-0.47650700	1.65519900	-3.12613000
O	0.81906600	2.20134400	-0.07704800
C	2.03835300	0.88063300	1.54097100
H	2.04153900	-0.10927400	2.02193200
H	1.64326600	1.63053700	2.24573000
H	0.10119000	3.44901200	-1.46047400
O	3.35898700	1.24903400	1.18564500
C	1.73816100	0.10661800	-0.88552800
H	2.73110300	0.52889800	-1.12649400
C	4.34685500	0.31558700	1.39987000
C	3.13160200	-1.82068900	-0.76921500
O	3.99862600	-1.20430500	-1.32340600
O	4.10982100	-0.77139400	1.85707100
C	3.20658400	-3.20085800	-0.20175000
H	3.50378700	-3.09600600	0.85810300
H	2.23247400	-3.71127400	-0.24542000
H	3.98209600	-3.77524500	-0.72899000
C	5.68080300	0.81647100	0.93673000
H	6.47647700	0.34140100	1.52971900
H	5.80622500	0.50418600	-0.11668100
H	5.74635100	1.91318500	0.99341500
Cu	-1.06729300	-0.25891800	-1.53885800
O	-1.90472900	-1.79405700	-0.50149800
S	-3.14721100	-1.01903300	-0.11249100
O	-2.94479300	0.35050700	-0.78809100
O	-4.44019300	-1.63656500	-0.25660000
C	-2.90044000	-0.61336100	1.69861200
F	-1.72525800	0.03933000	1.83000800

F	-3.86898500	0.18618900	2.10435800
F	-2.86879100	-1.71306500	2.41355300
C	-1.83563100	3.26096900	0.73695200
H	-2.90900900	3.43875400	0.91319600
H	-1.42066700	2.62767600	1.53783200
H	-1.30646900	4.22389300	0.69531800
O	-1.70411800	2.63076300	-0.54899100
H	-2.25829600	1.79136900	-0.59232000

IM5α

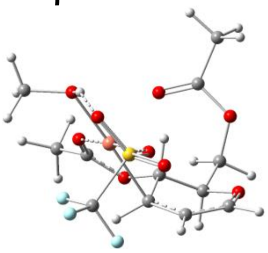


1 2
Electronic energy: -3481.160701
Thermal corrections: 0.245627

O	2.00903200	-1.27890600	-0.05510200
C	1.09672200	-0.28275900	-2.00897000
C	1.33480200	1.00509800	0.12801000
C	0.06582500	0.56797900	-2.31874400
H	1.40541300	-1.08020600	-2.69803500
H	0.43120700	0.58572800	0.61607200
C	-0.08085300	1.88038500	-1.56751200
H	-0.50108500	0.46050500	-3.25111700
O	0.94935800	2.11987200	-0.67816600
C	2.26324900	1.47337200	1.24149300
H	2.26379100	0.72814700	2.04967100
H	1.89613400	2.44013600	1.61968900
H	-0.05385100	2.71269600	-2.29269300
O	3.59225600	1.66895100	0.77940000
C	1.95296800	-0.05524600	-0.78875100
H	2.96551300	0.24035600	-1.10356000
C	4.53441800	0.76807900	1.19304400
C	3.20099500	-1.99072100	-0.12557100
O	4.06618100	-1.66986500	-0.88981700
O	4.26710600	-0.16391000	1.90922400
C	3.22551600	-3.10397400	0.87226600
H	3.58402800	-2.66942600	1.82349300
H	2.22331200	-3.52863800	1.03732100
H	3.93526500	-3.87826900	0.54688000
C	5.87794200	1.05989400	0.59350500
H	6.66691600	0.76430700	1.30160900
H	5.98416800	0.43174500	-0.31051200
H	5.97807000	2.11754000	0.30901100
Cu	-0.59579000	-1.06397000	-1.10065800
O	-2.17426000	-1.53707300	-0.11968700
S	-3.47728800	-0.79387100	-0.06373100
O	-3.41119800	0.43479500	-1.04171900
O	-4.70202500	-1.52024600	-0.23616900
C	-3.42717100	0.02957300	1.62708500
F	-2.28400400	0.71836600	1.70181400
F	-4.44758700	0.85156700	1.73659800

F	-3.45922300	-0.89780800	2.55361600
C	-1.72381100	3.17280000	-0.34997300
H	-2.69884800	3.03308600	0.13716900
H	-0.97097200	3.48544700	0.38888100
H	-1.80914000	3.92616900	-1.15191100
O	-1.35464900	1.89782500	-0.91171900
H	-2.52610600	0.98019700	-1.03667600

IM4β



1 2

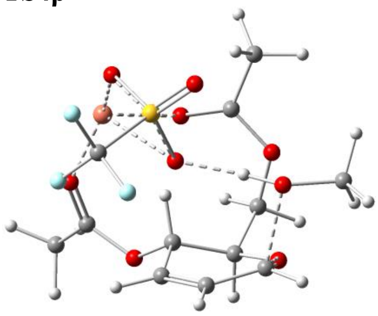
Electronic energy: -3481.158986

Thermal corrections: 0.2504325

O	-2.31271100	-0.54718500	-1.65248400
C	-0.40383800	0.90271500	-1.20147000
C	-2.78559500	1.67254800	-0.94300200
C	-0.01960200	2.19735500	-0.84412700
H	0.12231100	0.37958600	-2.00951200
H	-2.87890300	1.98374600	-1.99981600
C	-0.95415000	3.04871100	-0.27039600
H	1.00457300	2.54576400	-0.97471900
O	-2.24043300	2.80956500	-0.22419500
C	-4.17671100	1.39448500	-0.39069400
H	-4.62157000	0.56499000	-0.96179100
H	-4.78764200	2.30153500	-0.51129000
H	-0.69394400	4.02960400	0.14270600
O	-4.17678700	1.10784000	1.00219000
C	-1.81475800	0.50121200	-0.83352800
H	-1.83747100	0.16416800	0.21626400
C	-4.11188700	-0.18864100	1.40512600
C	-1.81038300	-1.75881300	-1.42845300
O	-0.79323200	-1.92143400	-0.75563800
O	-3.86045800	-1.09084000	0.64052800
C	-2.59916400	-2.86662200	-2.02870100
H	-3.43054900	-3.07657300	-1.32865800
H	-3.03696700	-2.55896100	-2.99119300
H	-1.97924600	-3.76740200	-2.13860200
C	-4.38558600	-0.31767600	2.87451900
H	-4.11833300	-1.32726700	3.21663200
H	-3.83152800	0.44856300	3.44122400
H	-5.46119800	-0.14248200	3.05745100
Cu	0.50468900	-0.68616600	0.09906900
O	3.41960800	-0.61698100	1.70261300
S	3.05119900	0.65358300	1.05141300
O	1.51947400	0.76116900	0.84878600
O	3.61450000	1.90617600	1.50745400
C	3.57769100	0.42500700	-0.73236700
F	2.93006200	-0.65440200	-1.23593500
F	3.21363800	1.48345700	-1.45916000
F	4.87201000	0.23465400	-0.83351400
O	1.34586000	-2.17072000	1.21283200
H	2.14548100	-1.75360600	1.63337100

C	1.70501600	-3.43379900	0.64507600
H	2.00008900	-4.13319000	1.44559300
H	0.81823500	-3.82901000	0.12888900
H	2.53733600	-3.32094200	-0.07327100

TS4β



1 2

Electronic energy: -3481.141687

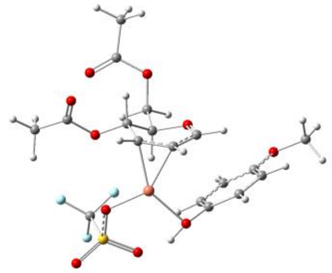
Thermal corrections: 0.2496671

O	-2.38226700	-1.34839200	-1.39291000
C	-0.63503700	0.13156600	-2.29195600
C	-2.59345600	0.94643600	-0.96627500
C	-0.26878300	1.41052700	-2.51895200
H	-0.16586000	-0.70151300	-2.82451000
H	-3.38375300	0.82200100	-1.72732800
C	-0.88618500	2.48359500	-1.75825300
H	0.51142600	1.67734900	-3.23499900
O	-2.03981400	2.26529000	-1.18590400
C	-3.24993600	0.97487600	0.40630700
H	-3.66242100	-0.01969700	0.63281900
H	-4.05915100	1.71858100	0.41366500
H	-0.69476100	3.51174900	-2.05704700
O	-2.33143000	1.39946100	1.41800300
C	-1.58385600	-0.18236500	-1.17788000
H	-0.97090400	-0.35192600	-0.29239200
C	-1.61804200	0.48982000	2.10458300
C	-2.02948700	-2.52035800	-0.82536700
O	-0.98650300	-2.71168200	-0.21878100
O	-1.65146800	-0.69795700	1.82572700
C	-3.05528700	-3.58199300	-1.06399900
H	-3.89380500	-3.42964500	-0.35875400
H	-3.46182700	-3.51249500	-2.08534300
H	-2.61454200	-4.57202500	-0.88068300
C	-0.77450200	1.09775600	3.18067300
H	-0.84980800	0.47965000	4.08998500
H	0.28239400	1.07820400	2.85886200
H	-1.06835200	2.13546400	3.39089100
Cu	0.22207300	-1.79305200	1.06871600
O	2.00318300	-1.04294000	1.45088200
S	2.18867000	0.18536200	0.59113200
O	0.83313400	0.45720900	-0.03061000
O	2.82844300	1.34250500	1.18869200
C	3.26920900	-0.41743500	-0.80616100
F	2.68233700	-1.46773400	-1.38047800
F	3.39805200	0.55475300	-1.70176300
F	4.44753500	-0.76029800	-0.33315200
O	0.29622100	2.94115500	-0.14784400
H	0.29229600	1.94858500	-0.00289700

C	-0.44160700	4.05938300	0.33693000
H	-0.23761400	4.19766800	1.41212900
H	-0.05901400	4.93193000	-0.21540700
H	-1.52863200	3.99032100	0.19274500

II.II Cu-OTf directed attack by *p*-OMePhOH

IM4α'



1 2

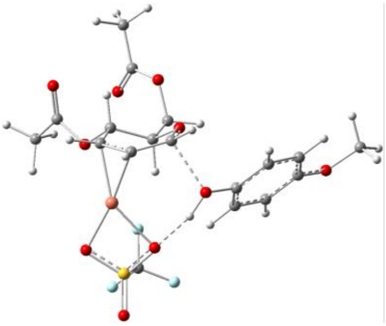
Electronic energy: -3787.227385

Thermal corrections: 0.322812

O	2.02682800	1.17733100	-0.32231600
C	0.56094300	0.71521900	-2.20682700
C	-0.27113300	1.33414700	0.07888400
C	-0.76948700	0.43549900	-2.55735000
H	1.36760400	0.66703500	-2.94701700
H	-0.24622400	0.30089400	0.45923300
C	-1.80995100	0.95430600	-1.71121500
H	-1.05684700	0.11084100	-3.56229700
O	-1.60022400	1.46579100	-0.56170800
C	-0.23432400	2.28287500	1.25758300
H	0.67070600	2.05393800	1.84016500
H	-1.13214300	2.11921900	1.87348000
H	-2.84174800	1.05958200	-2.05783400
O	-0.24453600	3.64012800	0.84844300
C	0.82797800	1.52914000	-0.96300000
H	0.87806300	2.58328800	-1.29683200
C	0.95047500	4.31503200	0.86746800
C	3.16846300	1.75382300	-0.85295000
O	3.11115700	2.38255300	-1.87375000
O	1.99293100	3.76573100	1.10751800
C	4.35956500	1.47143700	0.00226500
H	4.22258000	1.98431900	0.97033100
H	4.43800000	0.39051300	0.19846300
H	5.26564300	1.84376200	-0.49520800
C	0.75049500	5.77250700	0.56964600
H	1.71733400	6.23489200	0.32575100
H	0.03049000	5.91163500	-0.25280800
H	0.32907900	6.26666100	1.46384200
Cu	0.14416500	-1.20043000	-1.64872100
O	2.88387000	-3.80555200	0.18355700
S	1.78509200	-2.87082400	0.26525600
O	1.77308200	-1.83336700	-0.86716900
O	0.40885300	-3.39213100	0.51216400
C	2.09932000	-1.79287100	1.76218100
F	3.24508000	-1.14303100	1.63505300
F	1.10239200	-0.88653400	1.87399900
F	2.11799500	-2.53323800	2.85147200
O	-1.35138300	-2.46392400	-1.07764700
H	-0.80331600	-3.03313800	-0.43165600

C	-2.34200900	-1.75532000	-0.40793300
C	-2.19995300	-1.41244400	0.94357300
C	-3.47481400	-1.35215200	-1.12136300
C	-3.17885100	-0.64091600	1.55896200
H	-1.32959000	-1.76057800	1.50363900
C	-4.46911300	-0.58418500	-0.49607400
H	-3.59466300	-1.68060100	-2.15742600
C	-4.32296200	-0.21051900	0.84896200
H	-3.09548700	-0.36625500	2.61329700
H	-5.35769600	-0.30586700	-1.06418200
O	-5.19965200	0.52996300	1.54243700
C	-6.41179000	0.93964800	0.93287200
H	-6.96508700	1.50166000	1.69849600
H	-6.22060600	1.59743600	0.06372800
H	-7.01206800	0.06812200	0.61260100

TS4α'

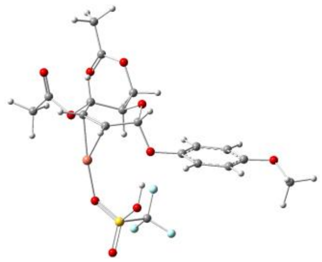


1 2
Electronic energy: -3787.214139
Thermal corrections: 0.323938

O	2.60009400	-0.99859400	-0.10468200
C	1.91566100	-0.35144600	2.10938600
C	0.29796300	-1.21324900	0.40451600
C	0.79658700	0.09376100	2.81594700
H	2.92722700	-0.24353700	2.51759700
H	0.12962400	-0.21663500	-0.03559000
C	-0.49864600	-0.51964800	2.52089600
H	0.88758500	0.59985600	3.78332800
O	-0.64639700	-1.32345200	1.52281100
C	-0.06170600	-2.25451400	-0.63369400
H	0.40363700	-1.97103300	-1.58951100
H	-1.15751000	-2.27548800	-0.74783800
H	-1.21671700	-0.67796900	3.32806000
O	0.37999000	-3.54445000	-0.24460700
C	1.72119200	-1.30671600	0.95931600
H	1.92876200	-2.33099500	1.31950000
C	1.35726500	-4.12849800	-1.01268700
C	3.64639600	-1.88211600	-0.32207800
O	3.84392400	-2.80473100	0.41899500
O	1.82886800	-3.58146200	-1.97517000
C	4.39211600	-1.53126200	-1.56917000
H	3.87085800	-2.03089300	-2.40643200
H	4.38891400	-0.44552800	-1.74965300
H	5.41811000	-1.92250200	-1.50909700
C	1.77092500	-5.45696200	-0.45538000
H	2.10419000	-6.11059800	-1.27541000
H	2.63406300	-5.28248900	0.21360000

H	0.96124000	-5.92769600	0.12158000
Cu	1.36329700	1.50329400	1.44048700
O	2.16052300	2.81207400	0.12086000
S	0.82350200	3.39703100	-0.29182900
O	-0.18106000	2.69021300	0.62980100
O	0.69579600	4.82397500	-0.44724500
C	0.50438300	2.60027800	-1.95756200
F	0.64405200	1.27072100	-1.83091300
F	-0.73516600	2.86161900	-2.34709800
F	1.36844600	3.05101500	-2.83831300
O	-1.80258000	1.02500900	1.95186900
H	-1.31979000	1.77114300	1.50469800
C	-2.74960700	0.49178400	1.09798900
C	-2.65395100	0.65512000	-0.29312600
C	-3.78328300	-0.26616000	1.65301100
C	-3.60215500	0.06872000	-1.11832900
H	-1.86275200	1.27173500	-0.72029400
C	-4.73050800	-0.86645100	0.82604800
H	-3.85320300	-0.37297900	2.73867100
C	-4.64880300	-0.70555000	-0.57240700
H	-3.56596400	0.20121800	-2.20176000
H	-5.53563200	-1.44744100	1.27659200
O	-5.50775900	-1.23754600	-1.44998000
C	-6.60995500	-2.00375000	-0.99108800
H	-7.27236000	-1.40031900	-0.34364900
H	-7.16161600	-2.31229600	-1.89031800
H	-6.27072500	-2.90209300	-0.44273900

IM5α’

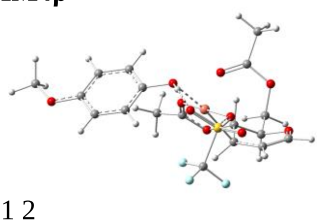


1 2
Electronic energy: -3787.238794
Thermal corrections: 0.3240211

O	3.29112400	-0.57228000	0.03411100
C	2.11524000	-0.35072800	-2.03120500
C	1.52485100	1.02614600	-0.02065000
C	0.82027900	-0.16353600	-2.44035100
H	2.81800500	-0.92477300	-2.64807700
H	0.94431100	0.24334500	0.50887100
C	-0.03577500	0.91239800	-1.80198000
H	0.44836800	-0.60612400	-3.37212600
O	0.65737200	1.71314500	-0.92268900
C	2.03181200	1.99160400	1.04464300
H	2.34875500	1.41494200	1.92577900
H	1.21826000	2.68163400	1.31712400
H	-0.44047700	1.57410300	-2.58191100
O	3.12240000	2.77098800	0.57650700
C	2.65452900	0.37441000	-0.82423300
H	3.38265800	1.13523700	-1.14370900
C	4.36152200	2.47099600	1.07621900

C	4.67909400	-0.54008300	0.07103100
O	5.30366700	0.12897600	-0.70285500
O	4.53862200	1.59015300	1.87975000
C	5.21129800	-1.41470200	1.16045200
H	5.21289900	-0.80376900	2.08192900
H	4.57446400	-2.29757600	1.32557500
H	6.24469000	-1.71022800	0.92840300
C	5.41707100	3.37169300	0.50871000
H	6.20215600	3.53775400	1.26187000
H	5.87570900	2.84397000	-0.34808000
H	4.99663500	4.32577700	0.15826200
Cu	0.96056300	-1.77724600	-1.03557200
O	-0.17539300	-2.92921700	-0.01401900
S	-1.66816600	-2.98496900	0.10725200
O	-2.29959400	-2.08040000	-1.02278800
O	-2.31660700	-4.26262600	0.15680200
C	-2.00560300	-2.00816600	1.68454600
F	-1.41938800	-0.81528100	1.55162700
F	-3.30213200	-1.86014900	1.83742100
F	-1.47740300	-2.65544900	2.69937900
O	-1.16106700	0.25476600	-1.15964300
H	-1.84316800	-1.16274100	-1.13918500
C	-2.21790500	1.09107800	-0.72527400
C	-2.11308400	1.80629400	0.46006700
C	-3.37646900	1.13199000	-1.50502500
C	-3.19967900	2.58222300	0.87242700
H	-1.22190100	1.74402300	1.08471700
C	-4.45614100	1.90964200	-1.09285600
H	-3.42654600	0.57135900	-2.44136100
C	-4.37073000	2.64248600	0.10679600
H	-3.15484500	3.15629300	1.79861100
H	-5.34998700	1.95950500	-1.71471200
O	-5.34303300	3.46890100	0.55057900
C	-6.69956900	3.12782400	0.26919900
H	-7.31383300	3.93477300	0.70480400
H	-6.91370200	3.06884300	-0.81653500
H	-6.96218500	2.16254800	0.74836600

IM4β'

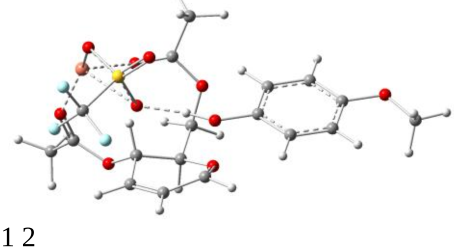


1 2
Electronic energy: -3787.229597
Thermal corrections: 0.329167

O	-1.92749600	-1.44920100	-1.51564600
C	-1.73473800	0.91433600	-0.94712500
C	-3.95568700	-0.23123400	-1.19485300
C	-2.45299500	2.07929300	-0.62837500
H	-0.91662400	0.96292500	-1.67799100
H	-4.01131300	-0.01258100	-2.27751700
C	-3.80100100	1.98741300	-0.32957200
H	-1.96991200	3.05584700	-0.61005900
O	-4.52894400	0.90378900	-0.50466200
C	-4.82833700	-1.44376700	-0.90106400

H	-4.42807400	-2.30987700	-1.44997700
H	-5.85230900	-1.22590200	-1.23943000
H	-4.39691200	2.83749200	0.01863000
O	-4.93289400	-1.73045900	0.48891900
C	-2.49731800	-0.37799300	-0.77086200
H	-2.49937100	-0.65755400	0.29499300
C	-4.08520700	-2.63582800	1.03927200
C	-0.81675200	-1.96943000	-1.00778000
O	-0.17923300	-1.38769300	-0.12923900
O	-3.13147700	-3.07968200	0.44324900
C	-0.44145600	-3.29953000	-1.55431300
H	-1.05396900	-4.04627300	-1.01427200
H	-0.69232300	-3.36669800	-2.62465200
H	0.62531800	-3.49581200	-1.37511200
C	-4.49851300	-2.98736600	2.43905300
H	-3.68921300	-3.53637200	2.94052100
H	-4.76753500	-2.08035900	3.00468900
H	-5.40038900	-3.62464200	2.39855500
Cu	-0.08130100	0.48417100	0.46457800
O	2.25124400	2.59182700	1.49910800
S	1.05261400	3.26241400	0.94546800
O	-0.17271600	2.32804800	0.98881500
O	0.72841900	4.61363600	1.34507900
C	1.36065400	3.28897500	-0.90154600
F	1.53152900	2.01179400	-1.32401600
F	0.29772900	3.78214800	-1.53551400
F	2.43156800	3.98625800	-1.20427100
O	1.63028100	0.06474700	1.57264600
H	2.00502500	0.98546500	1.73276800
C	2.58437900	-0.75703100	0.99781100
C	2.49455800	-2.13360100	1.20855500
C	3.60377900	-0.22287300	0.19445600
C	3.42318000	-2.99333000	0.61958400
H	1.69705900	-2.52377800	1.84405100
C	4.53263500	-1.07435900	-0.38606700
H	3.66813500	0.85680300	0.04256100
C	4.45453800	-2.46875000	-0.18329400
H	3.34911400	-4.06505200	0.80799100
H	5.34598700	-0.68650400	-1.00326800
O	5.40168300	-3.20644400	-0.78715200
C	5.43537700	-4.60689000	-0.59199300
H	4.51531800	-5.08925200	-0.97375700
H	6.30048900	-4.97570900	-1.16170000
H	5.56646800	-4.86030600	0.47667500

TS4β’

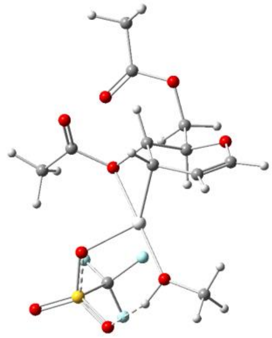


1 2
Electronic energy: -3787.2355482
Thermal corrections: 0.3281563
O -2.38226700 -1.34839200 -1.39291000

C	-0.63503700	0.13156600	-2.29195600
C	-2.59345600	0.94643600	-0.96627500
C	-0.26878300	1.41052700	-2.51895200
H	-0.16586000	-0.70151300	-2.82451000
H	-3.29839264	0.77430604	-1.79855542
C	-0.88618500	2.48359500	-1.75825300
H	0.51142600	1.67734900	-3.23499900
O	-2.03981400	2.26529000	-1.18590400
C	-3.43488162	0.80615734	0.29391585
H	-3.78296218	-0.23364458	0.38490435
H	-4.30132534	1.47994288	0.23674489
H	-0.69476100	3.51174900	-2.05704700
O	-2.70888593	1.21501367	1.45719623
C	-1.58385600	-0.18236500	-1.17788000
H	-0.97090400	-0.35192600	-0.29239200
C	-2.01870221	0.30996011	2.17293764
C	-2.02948700	-2.52035800	-0.82536700
O	-0.98650300	-2.71168200	-0.21878100
O	-1.90496225	-0.84878128	1.80677678
C	-3.05528700	-3.58199300	-1.06399900
H	-3.89380500	-3.42964500	-0.35875400
H	-3.46182700	-3.51249500	-2.08534300
H	-2.61454200	-4.57202500	-0.88068300
C	-1.39225086	0.88951224	3.40208110
H	-1.53729423	0.19250187	4.24333807
H	-0.30342042	0.98131012	3.23777899
H	-1.80550535	1.87903242	3.64176396
Cu	0.22207300	-1.79305200	1.06871600
O	2.00318300	-1.04294000	1.45088200
S	2.18867000	0.18536200	0.59113200
O	0.83313400	0.45720900	-0.03061000
O	2.82844300	1.34250500	1.18869200
C	3.26920900	-0.41743500	-0.80616100
F	2.68233700	-1.46773400	-1.38047800
F	3.39805200	0.55475300	-1.70176300
F	4.44753500	-0.76029800	-0.33315200
O	0.29622100	2.94115500	-0.14784400
H	0.29317219	1.94872876	-0.00189503
C	-0.44434088	4.06352638	0.33872624
C	-1.33674929	3.90368139	1.39916400
C	-0.27446509	5.31809759	-0.24671498
C	-2.05957727	4.99807745	1.87354645
H	-1.47101956	2.91431371	1.85999462
C	-0.99670678	6.41313168	0.22833993
H	0.42898228	5.44429500	-1.08239736
C	-1.88927024	6.25330336	1.28820898
H	-2.76346662	4.87203459	2.70898017
H	-0.86225624	7.40227041	-0.23318131
O	-2.63047317	7.37521425	1.77486510
C	-2.46694239	8.58849666	1.03587696
H	-3.05919510	9.36017032	1.48158594
H	-1.43678254	8.87749520	1.04814619
H	-2.78248740	8.43566475	0.02494979

II.III Sc-OTf directed attack

IM5α_Sc



3 1
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Thermal corrections: 0.2041366

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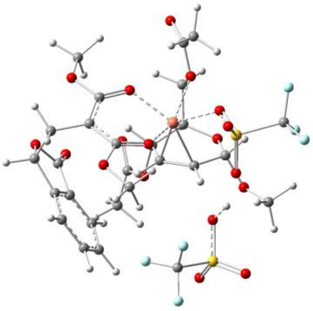
C	1.03557000	0.87373100	-1.11738200
C	2.21092700	0.70102000	1.13377200
C	0.98041200	2.26750000	-0.99832600
H	0.63911400	0.33427800	-1.99553800
H	1.44047100	0.56018300	1.91167300
C	1.73634200	2.85548800	0.07246200
H	0.68622200	2.93081700	-1.82623100
O	2.31440000	2.18375400	0.98122400
C	3.55113400	0.22761300	1.70300100
H	3.52059000	-0.86961700	1.81538800
H	3.67703700	0.68157800	2.69780700
H	1.91710600	3.94169300	0.13281100
O	4.69542200	0.60706100	0.94293700
C	1.77444600	0.03553300	-0.17442200
H	2.79433900	-0.14865700	-0.74495900
C	5.14544800	-0.07237200	-0.13699900
C	1.31382800	-2.31830900	-0.74544600
O	1.52331300	-2.06002000	-1.88799000
O	4.43220500	-0.82460900	-0.79174500
C	1.04503200	-3.64159800	-0.10154100
H	1.65246400	-3.76942600	0.80891000
H	-0.01813100	-3.69585000	0.19547900
H	1.25081700	-4.45328600	-0.81719300
C	6.56893800	0.20212700	-0.47907800
H	6.81327000	-0.15337900	-1.49168100
H	6.78837100	1.27944700	-0.37381100
H	7.20030400	-0.32800500	0.26140500
O	-3.25838900	-2.69348300	-0.74350300
S	-3.31309700	-1.31674600	-0.36519900
O	-2.09486600	-0.41923600	-1.13116500
O	-4.47702800	-0.44778500	-0.31452400
C	-2.46401300	-1.03446300	1.31741900
F	-1.41130900	-1.75958500	1.46651100
F	-2.00692900	0.37228600	1.09122300
F	-3.27799600	-1.03138200	2.29666700
O	-3.26947900	2.48726700	-0.61801500
H	-4.03407700	1.86235300	-0.73014400
C	-3.82074400	3.75028000	-0.00540300
H	-4.08007700	3.52936500	1.04087700
H	-3.04219100	4.52131600	-0.08496200
H	-4.70508900	4.03756300	-0.59508400
Sc	-1.57520900	1.37219100	-0.66451100

II.IV Cu-OTf blocked attack
IM5α_blocked_from_coordinated_route



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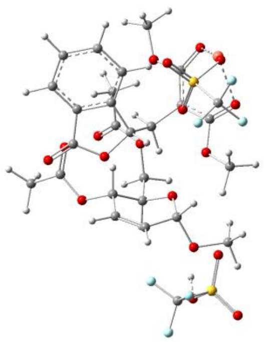
Thermal corrections: 0.495046

O	2.39222600	0.33754700	1.67013900
C	0.43347500	0.11593400	0.43408100
C	0.50316100	-0.74808500	2.81083700
C	0.04010000	-1.13441900	0.03103800
H	0.64791000	0.89414600	-0.30074200
H	1.28458800	-0.80478900	3.58016900
H	-0.12507500	-1.36889300	-1.02268500
O	0.44215300	-2.06341700	2.26670800
C	-0.76268400	-0.41460100	3.59004900
H	-0.68399600	0.59616800	4.01892500
H	-0.86903800	-1.13176200	4.42145200
O	0.52868000	4.87277800	0.18488500
O	-1.92713700	-0.51105200	2.77022200
C	0.94936300	0.33723900	1.81919700
H	0.66359200	1.32365900	2.20876800
C	-3.06486700	0.02230100	3.29002400
C	3.12551400	0.83642500	2.68356200
O	2.65804800	1.17227400	3.74468900
O	-3.08327100	0.55880200	4.37169700
C	4.58365500	0.90052100	2.30233900
H	4.90662400	-0.04938500	1.84658000
H	4.71827500	1.69976200	1.55207300
H	5.18681500	1.13083200	3.19259100
C	-4.24226500	-0.13217600	2.36961700
H	-5.16823000	-0.06234700	2.96036900
H	-4.20964600	0.69772900	1.64285000
H	-4.19259500	-1.06452100	1.78924800
C	1.38013300	3.82815000	0.34086700
O	1.79194500	3.46988400	1.41716600
C	1.66549200	3.28595900	-1.00782500
C	2.51562900	2.24440900	-1.37987200
C	0.90562300	3.99726800	-1.93300400
C	2.58819600	1.92342600	-2.73647700
H	3.07329500	1.68859500	-0.62560900
C	0.97625300	3.68042800	-3.28829700
C	1.82680900	2.63879200	-3.67783600
H	3.23261300	1.10530400	-3.06972900
H	0.36729700	4.20719900	-4.02651700
H	1.89202800	2.36667000	-4.73588300
C	0.05259000	4.98329000	-1.17417300
H	0.23569600	6.02544300	-1.49166500
C	-1.46383400	4.67958800	-1.21492900
H	-1.95414100	5.41501300	-0.55883800

H	-1.80578600	4.86508300	-2.24566400
C	-1.79820400	3.27079700	-0.79276500
C	-1.98032100	2.96502400	0.57979000
C	-1.88829800	2.23113800	-1.76837900
O	-1.99174000	1.01183000	-1.58532200
O	-1.84991400	2.67772900	-3.06274000
O	-2.13326900	1.84182800	1.11848900
C	-1.85424700	1.65901800	-4.05245200
H	-2.69688300	0.96289400	-3.90924000
H	-1.93391200	2.17902100	-5.02076600
H	-0.91900900	1.07173300	-4.01473300
O	-1.99673100	4.05342200	1.39238500
C	-1.85520900	3.81986500	2.78440200
H	-0.86359100	3.38467100	3.00474700
H	-1.93022600	4.80910900	3.26225800
H	-2.63622400	3.14697100	3.17474400
Cu	-1.62923500	0.04043600	0.29941300
O	-2.97342000	-1.47607400	-0.10901600
S	-3.08952600	-2.12143400	-1.46896700
O	-1.79280900	-2.40683100	-2.11618400
O	-4.16404100	-1.59831400	-2.31387500
C	-3.68275300	-3.81423400	-0.94418900
F	-3.91495400	-4.58761200	-2.00889500
F	-4.80959300	-3.73445600	-0.23064400
F	-2.75738000	-4.42914200	-0.18470700
C	0.05784300	-2.31805700	0.95647200
H	-0.90922600	-2.84934100	0.92952800
C	0.66079100	-4.14774200	-0.55260100
H	0.10058900	-3.61840100	-1.34122000
H	1.59013700	-4.57537300	-0.95650000
H	0.01720200	-4.94476200	-0.13794900
O	3.38542000	-2.54525400	1.04486900
O	1.05517200	-3.25556400	0.48940200
H	2.40420400	-2.87115300	0.81634800
S	4.41143000	-2.80653400	-0.10983300
C	4.02717700	-1.38897100	-1.27207100
O	4.07968500	-4.01163600	-0.86348000
O	5.75370700	-2.55822200	0.38839500
F	4.66900100	-1.58055200	-2.42426000
F	2.72141600	-1.32795800	-1.51373500
F	4.43391900	-0.23361300	-0.75075300

IM5α_blocked_from_non_coordinated_route



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Thermal corrections: 0.489944

O	-3.73528800	3.25650500	0.95848300

C	-3.18323600	0.90516800	1.07177000
C	-3.51442900	2.01986900	-1.10834300
C	-3.20787700	-0.25925600	0.41900000
H	-3.21845500	0.96058400	2.16265000
H	-4.60284600	1.81599300	-1.08774600
H	-3.28081600	-1.21363100	0.94290100
O	-2.82762800	0.91181400	-1.68167200
C	-3.28881000	3.22936600	-1.99611500
H	-3.96633500	4.04541000	-1.70653900
H	-3.48157700	2.94341000	-3.04363100
O	-0.44920600	1.21273300	1.85683900
O	-1.94070600	3.68078400	-1.90516700
C	-3.01081000	2.19229300	0.32491400
H	-1.94781000	2.46375000	0.31288300
C	-1.71772000	4.97103600	-1.55930700
C	-3.01198300	4.31065300	1.41233500
O	-1.81144800	4.38038900	1.35330300
O	-2.60406400	5.78112100	-1.41550100
C	-3.91063300	5.40298500	1.92804200
H	-4.09329700	6.09839900	1.08823100
H	-4.87414900	5.00484800	2.28088300
H	-3.39385800	5.95298700	2.72894700
C	-0.25397300	5.22859700	-1.34046600
H	0.38169300	4.53628800	-1.91082100
H	-0.02616800	6.28073900	-1.57242800
H	-0.05854100	5.05431200	-0.26752900
C	-0.10305200	2.04188800	2.87478900
O	-0.90513300	2.45413000	3.67687400
C	1.35860600	2.26143000	2.77665300
C	2.20019400	3.00403400	3.60638000
C	1.84261400	1.53340600	1.68806300
C	3.56711500	2.99286100	3.32182700
H	1.78779500	3.56058700	4.45269300
C	3.21001000	1.50544400	1.41188600
C	4.06213900	2.24175400	2.24013200
H	4.26304700	3.55467400	3.95284300
H	3.60791600	0.90330400	0.59647400
H	5.13928100	2.21216900	2.05018300
C	0.67732900	0.87781200	1.00114500
H	0.77158900	-0.21816200	0.99255200
C	0.38531500	1.38223900	-0.42416600
H	-0.60519500	1.00923100	-0.70944000
H	0.33125300	2.47818400	-0.39464400
C	1.42204200	0.91946800	-1.41226200
C	2.50204500	1.75013700	-1.76438100
C	1.41354300	-0.44739600	-1.84232100
O	2.23668500	-1.02551500	-2.56112700
O	0.34940900	-1.15962100	-1.34696900
O	3.58608600	1.44206700	-2.33496300
C	0.43427500	-2.57168500	-1.50459200
H	1.35347300	-2.94948200	-1.02832900
H	-0.46000800	-2.98729800	-1.01539900
H	0.44584300	-2.85235900	-2.57211200
O	2.35513700	3.06151600	-1.39179100
C	3.51400800	3.86899000	-1.44213600
H	3.91396400	3.94569900	-2.46774600
H	3.20521100	4.86267600	-1.07941000

H	4.30633700	3.46546700	-0.78635400
Cu	4.23503800	-0.33671700	-1.84580800
O	5.04494700	-1.76450100	-0.82781300
S	4.42359200	-1.96895900	0.54425100
O	2.98577500	-1.64457700	0.59872500
O	5.26598300	-1.50115700	1.64704200
C	4.47176800	-3.82943000	0.65241600
F	4.01189000	-4.23182600	1.84104400
F	3.71087000	-4.38215200	-0.29850500
F	5.71842000	-4.28734400	0.50971300
C	-3.01352900	-0.32165500	-1.06641200
H	-2.12416200	-0.91971000	-1.32532200
C	-3.97899200	-1.41345200	-2.98318900
H	-4.94178700	-1.81878300	-3.33187800
H	-3.67976000	-0.55992800	-3.61232900
H	-3.20457700	-2.20044700	-3.01844900
O	-4.17652500	-0.97265700	-1.64066400
O	-5.28152500	-2.87777600	-0.44929100
H	-4.82704900	-2.02308300	-0.86709900
S	-4.25937000	-4.08061400	-0.35700200
O	-4.85553000	-5.29285800	-0.88649500
O	-2.92552000	-3.63973300	-0.75856500
C	-4.21824200	-4.31084300	1.49878000
F	-3.39260600	-5.31125900	1.78162900
F	-5.43354600	-4.60290100	1.94765000
F	-3.78642200	-3.20490300	2.09977600

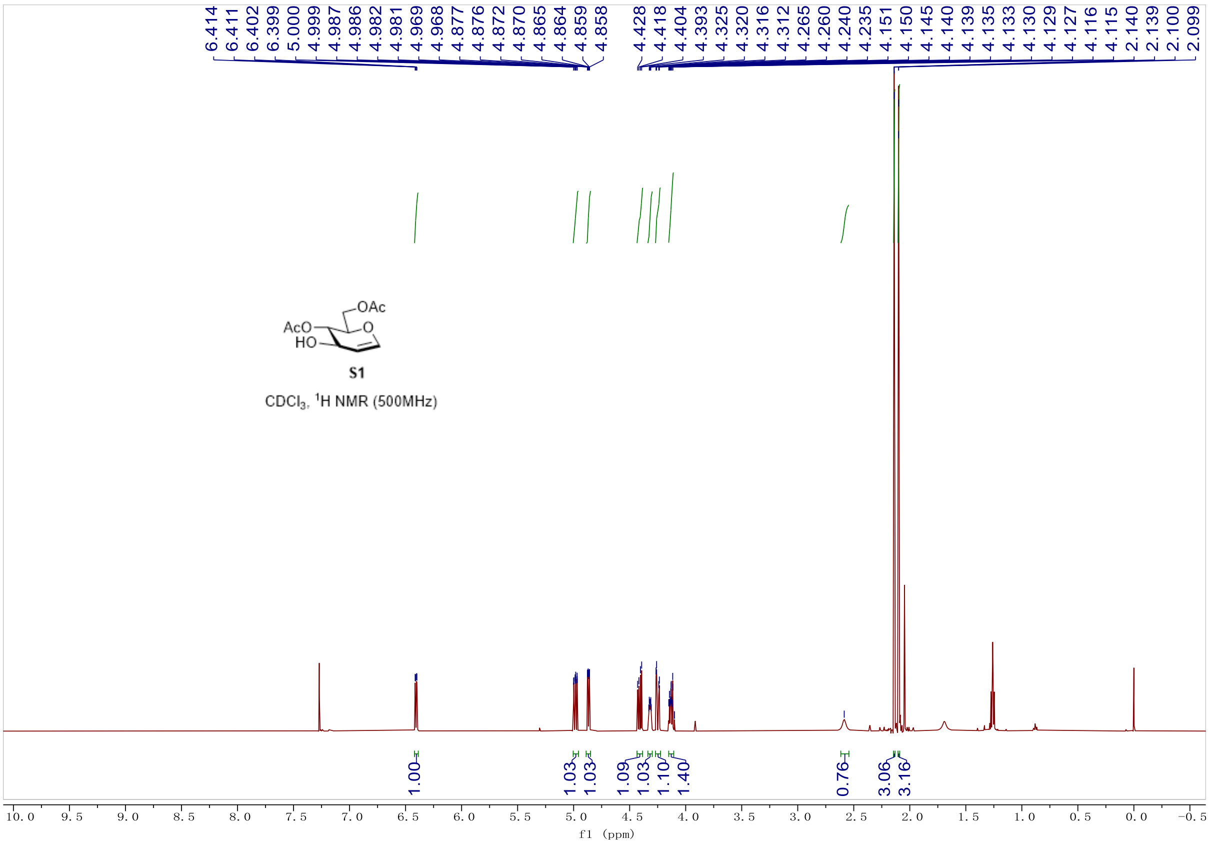
Supplementary References

1. T. Zamysłowski, K. Gorczyca, Y. Zhang, M. Poterała, M. Malinowski, Operationally simple enzymatic deprotection of C-3 position on 3,4,6-tri-*O*-acetyl-D-glucal, *Carbohydr. Res.* 2023, **529**, 108848.
2. H. Ding, J. Lyu, X.-L. Zhang, X. Xiao, X.-W. Liu, Efficient and versatile formation of glycosidic bonds via catalytic strain-release glycosylation with glycosyl *ortho*-2,2-dimethoxycarbonylcyclopropylbenzoate donors, *Nat. Commun.* 2023, **14**, 4010.
3. Y. Mori, H. Hayashi, Practical Synthesis of 1,3-*O*-Di-*tert*-butylsilylene-Protected D- and L-Erythritols as a Four-Carbon Chiral Building Block, *J. Org. Chem.* 2001, **66**, 8666–8668.
4. L. Alberch, G. Cheng, S.-K. Seo, X. Li, F. P. Boulineau, A. Wei, Stereoelectronic Factors in the Stereoselective Epoxidation of Glycals and 4-Deoxypentenosides, *J. Org. Chem.* 2011, **76,** 2532–2547.
5. M. Filice, J. M. Guisan, M. Terreni, J. M. Palomo, Regioselective monodeprotection of peracetylated carbohydrates, *Nat. Protoc.* 2012, **7**, 1783–1796.
6. S. Yalamanchili, T.-A. Nguyen, A. Zsikla, G. Stamper, A. E. DeYong, J. Florek, O. Vasquez, N. L. B. Pohl, C. S. Bennett, Automated, Multistep Continuous-Flow Synthesis of 2,6-Dideoxy and 3-Amino-2,3,6-trideoxy Monosaccharide Building Blocks, *Angew. Chem. Int. Ed.* 2021, **60**, 23171–23175.
7. S. Zhang, Y. Ma, J. Li, J. Ma, B. Yu, X. Xie, Molecular matchmaking between the popular weight-loss herb Hoodia gordonii and GPR119, a potential drug target for metabolic disorder, *Proc. Natl. Acad. Sci. U.S.A.* 2014, **111**, 14571–14576.
8. K. B. Pal, J. Lee, M. Das, X.-W. Liu, Palladium(II)-catalyzed stereoselective synthesis of C-glycosides from glycals with diaryliodonium salts, *Org. Biomol. Chem.* 2020, **18,** 2242–2251.
9. W. Yuan, Y. Liu, C. Li, From the Studies of Hydration and Hydrolysis Reactions to the Discovery of a New Organocatalyst and Its Further Applications in Acetalization and Glycosylation, *Asian J. Org. Chem.* 2017, **6**, 1428–1439.
10. E. I. Balmond, D. Benito-Alifonso, D. M. Coe, R. W. Alder, E. M. McGarrigle, M. C. Galan, A 3,4-trans-Fused Cyclic Protecting Group Facilitates α-Selective Catalytic Synthesis of 2-Deoxyglycosides, *Angew. Chem. Int. Ed.* 2014, **53**, 8190–8194.
11. F. J. Reyes-Zurita, M. Medina-O'Donnell, R. M. Ferrer-Martin, E. E. Rufino-Palomares, S. Martin-Fonseca, F. Rivas, A. Martínez, A. García-Granados, A. Pérez-Jiménez, L. García-Salguero, J. Peragón, K. Mokhtari, P. P. Medina, A. Parra, J. A. Lupiáñez, The oleanolic acid derivative, 3-*O*-succinyl-28-*O*-benzyl oleanolate, induces apoptosis in B16–F10 melanoma cells *via* the mitochondrial apoptotic pathway, *RSC Adv.* 2016, **6**, 93590–93601.
12. E. I. Balmond, D. M.Coe, M. C. Galan, E. M. McGarrigle, α-Selective Organocatalytic Synthesis of 2-Deoxygalactosides, *Angew. Chem. Int. Ed.* 2012, **51,** 9152–9155.
13. D. B. Werz, P. H. Seeberger, Total Synthesis of Antigen *Bacillus Anthracis* Tetrasaccharide—Creation of an Anthrax Vaccine Candidate, *Angew. Chem. Int. Ed.* 2005, **44**, 6315–6318.
14. T. Ogawa, K. Katano, K. Sasajima, M. Matsui, Synthetic studies on cell surface glycans 3: Branching pentasaccharides of glycoprotein, *Tetrahedron* 1981, **37**, 2779-2786
15. N. Floyd, B.Vijayakrishnan, J. R. Koeppe, B. G. Davis, Thiyl Glycosylation of Olefinic Proteins: S-Linked Glycoconjugate Synthesis, *Angew. Chem. Int. Ed.* 2009, **48**, 7798–7802.

16. Y. Liu, T. Song, W. Meng, Y. Xu, P. G.Wang, W. Zhao, Hafnium(IV) triflate as a highly efficient catalyst for Ferrier rearrangement of *O*- and *S*-nucleophiles with glycals, *Tetrahedron Lett.* 2016, **57**, 2758–2762.
17. K. De, J. Legros, B. Crousse, D. Bonnet-Delpon, Synthesis of 2,3-unsaturated glycosides via metal-free Ferrier reaction, *Tetrahedron* 2008, **64**, 10497–10500.
18. B. K. Gorityala, S. Cai, J. Ma, X.-W. Liu, (*S*)-Camphorsulfonic acid catalyzed highly stereoselective synthesis of pseudoglycosides, *Bioorg. Med. Chem. Lett.* 2009, **19**, 3093–3095.
19. G. Narasimha, B. Srinivas, P. R. Krishna, S. Kashyap, $Zn(OTf)_2$-Catalyzed Glycosylation of Glycals: Synthesis of 2,3-Unsaturated Glycosides via a Ferrier Reaction, *Synlett* 2014, **25**, 523–526.
20. B. Srinivas, T. R. Reddy, P. R. Krishna, S. Kashyap, Copper(II) Triflate as a Mild and Efficient Catalyst for Ferrier Glycosylation: Synthesis of 2,3-Unsaturated *O*-Glycosides, *Synlett* 2014, **25**, 1325–1330.
21. P. Chen, S. Li, $Y(OTf)_3$ as a highly efficient catalyst in Ferrier Rearrangement for the synthesis of *O*- and *S*-2,3-unsaturated glycopyranosides, *Tetrahedron Lett.* 2014, **55**, 5813–5816.
22. M. Takumi, H. Sakaue, A. Nagaki, Flash Electrochemical Approach to Carbocations, *Angew. Chem. Int. Ed.* 2022, **61**, e202116177.
23. H. Grugel, F. Albrecht, M. M. K. Boysen, *pseudo* Enantiomeric Carbohydrate Olefin Ligands – Case Study and Application in Kinetic Resolution in Rhodium(I)-Catalysed 1,4-Addition, *Adv. Synth.Catal.* 2014, **356**, 3289–3294.
24. J. Zhou, H. Chen, J. Shan, J. Li, G. Yang, X. Chen, K. Xin, J. Zhang, J. Tang, $FeCl_3$ $6H_2O$/C: An Efficient and Recyclable Catalyst for the Synthesis of 2,3-Unsaturated *O*- and *S*-Glycosides, *J. Carbohydr. Chem.* 2014, **33**, 313–325.
25. A. Sau, C. Palo-Nieto, M. C. Galan, Substrate-Controlled Direct α-Stereoselective Synthesis of Deoxyglycosides from Glycals Using $B(C_6F_5)_3$ as Catalyst, *J. Org. Chem.* 2019, **84**, 2415–2424.
26. J. Wang, C. Deng, Q. Zhang, Y. Chai, Tuning the Chemoselectivity of Silyl Protected Rhamnals by Temperature and Brønsted Acidity: Kinetically Controlled 1,2-Addition vs Thermodynamically Controlled Ferrier Rearrangement, *Org. Lett.* 2019, **21**, 1103–1107.
27. P. Chen, B. Bi, Preparation of 2,3-unsaturated pseudoglycosides with Ferrier Rearrangement promoted by $Tm(OTf)_3$ as a highly efficient catalyst, *Tetrahedron Lett.* 2015, **56**, 4895–4899.
28. M.-C. Yuan, T.-K. Yeh, C.-T. Chen, J.-S. Song, Y.-C. Huang, T.-C. Hsieh, C.-Y. Huang, Y.-L. Huang, M.-H. Wang, S.-H. Wu, C.-H. Yao, Y.-S. Chao, J.-C. Lee, Identification of an oxime-containing C-glucosylarene as a potential inhibitor of sodium-dependent glucose co-transporter 2, Eur. J. Med. Chem. 2018, 143, 611–620.

NMR Spectra

^{1}H spectrum for **S1**



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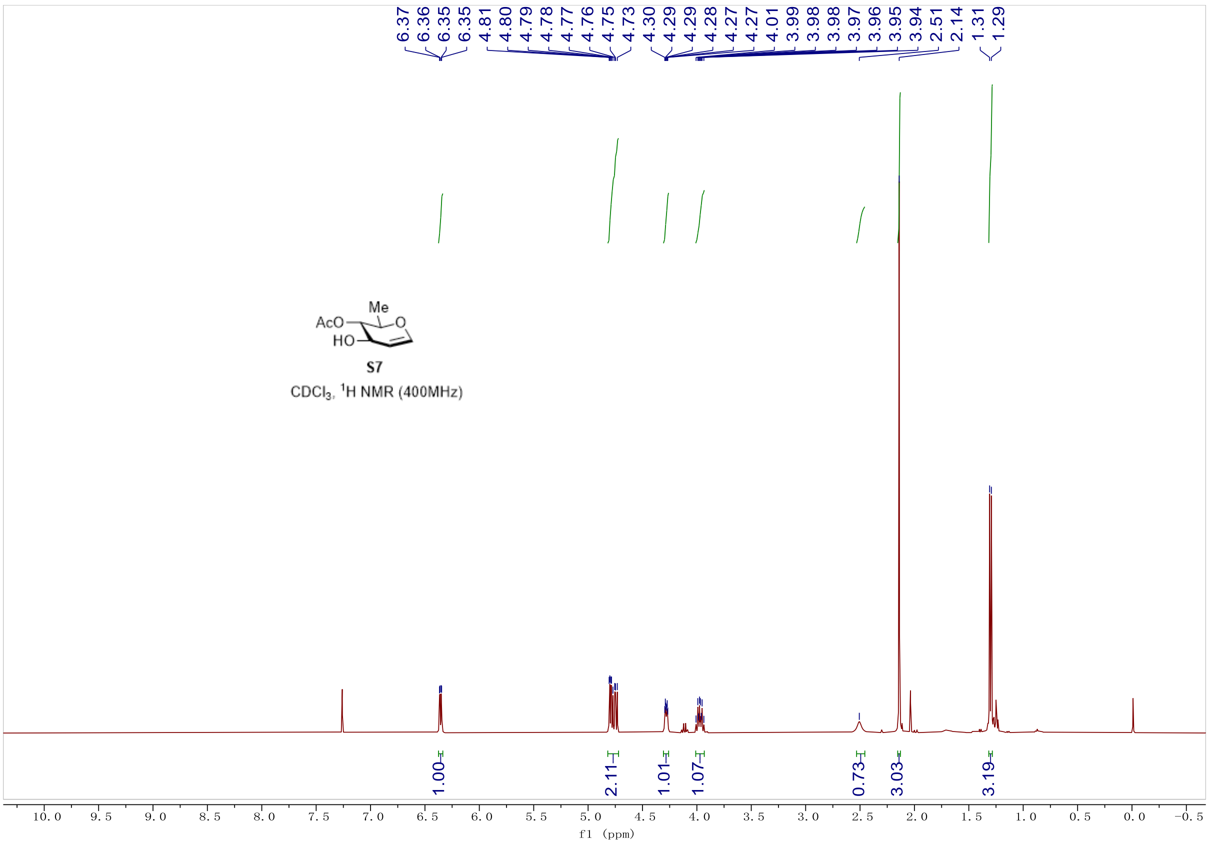
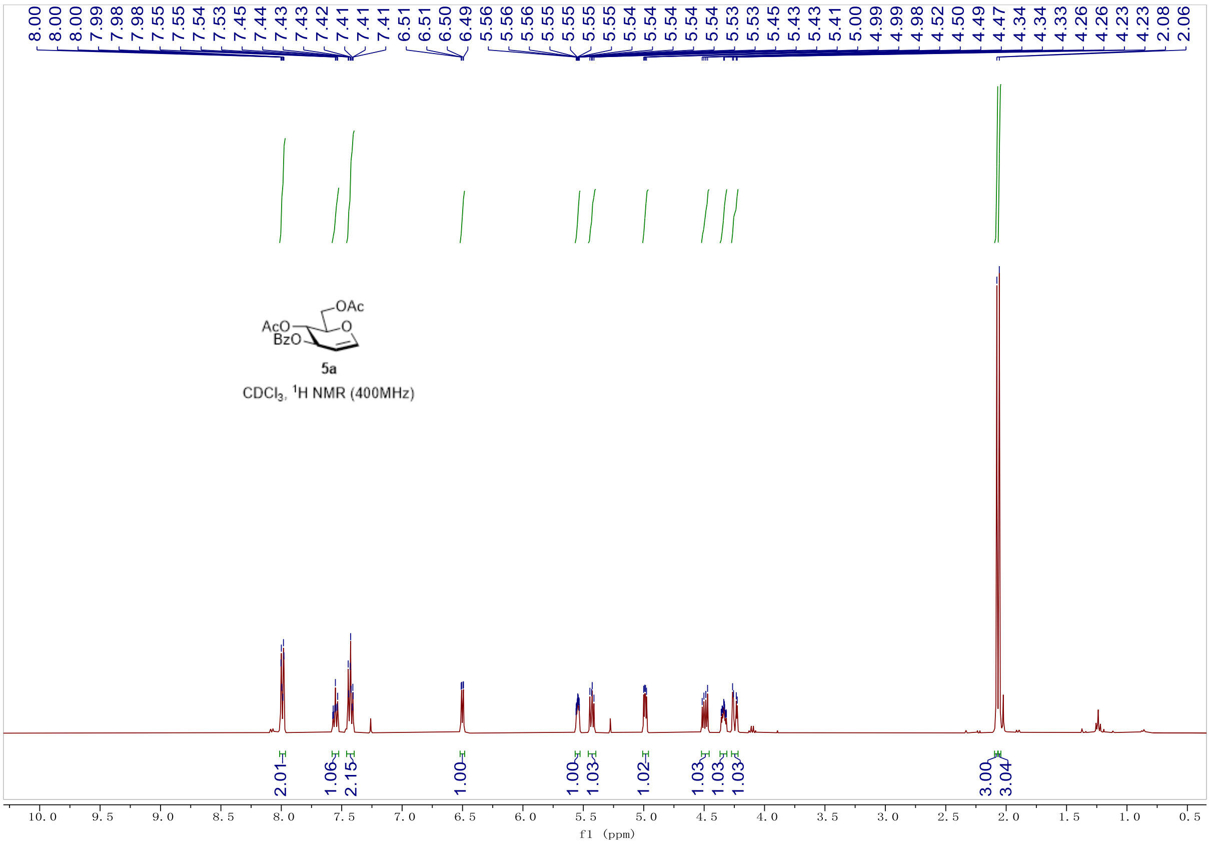
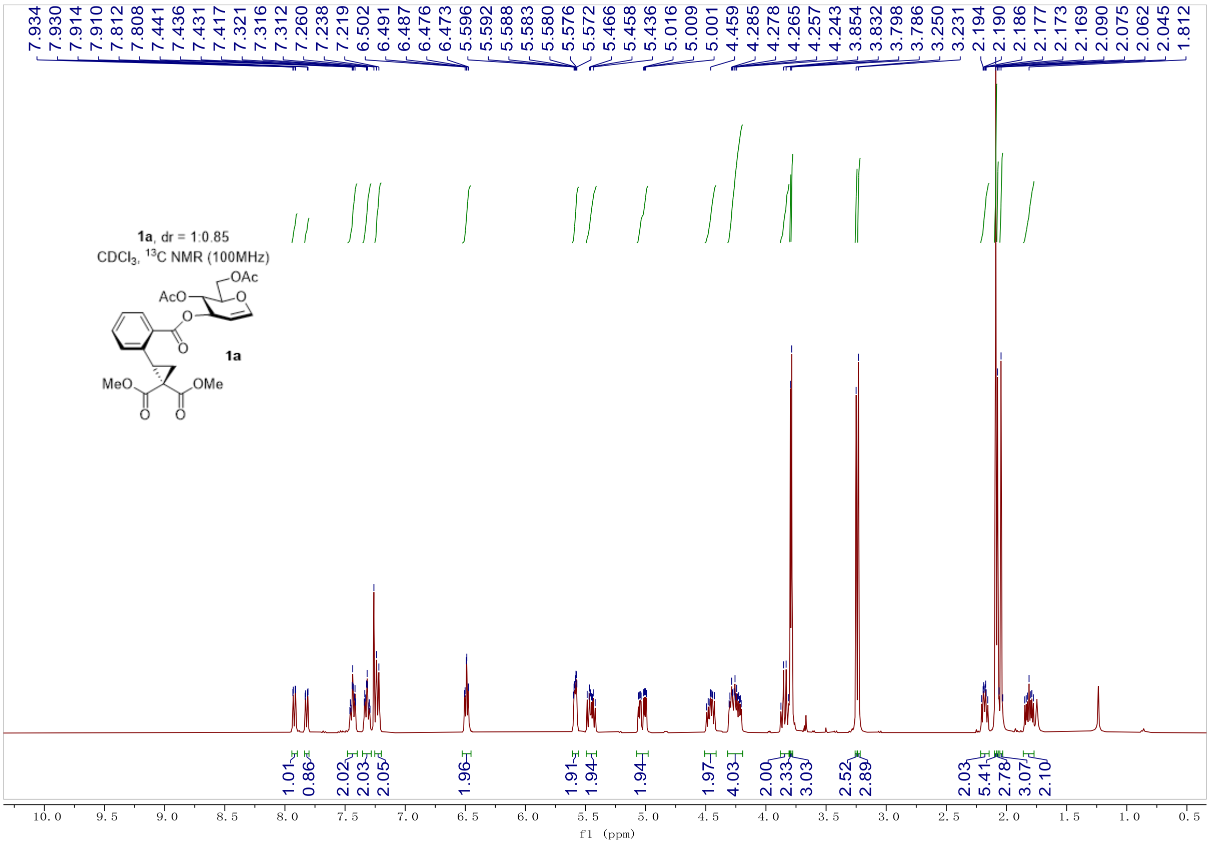
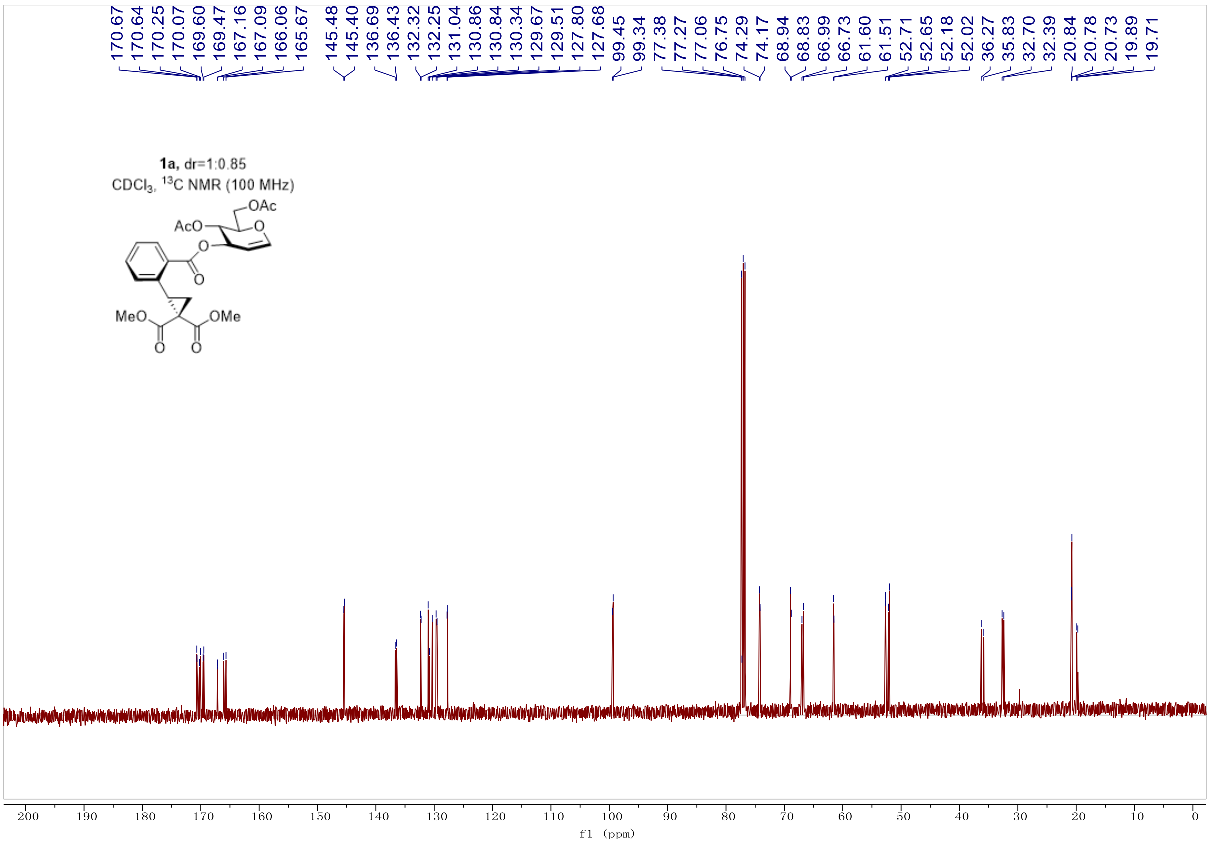


^{1}H spectrum for **5a**



^{1}H and ^{13}C spectra for **1a**





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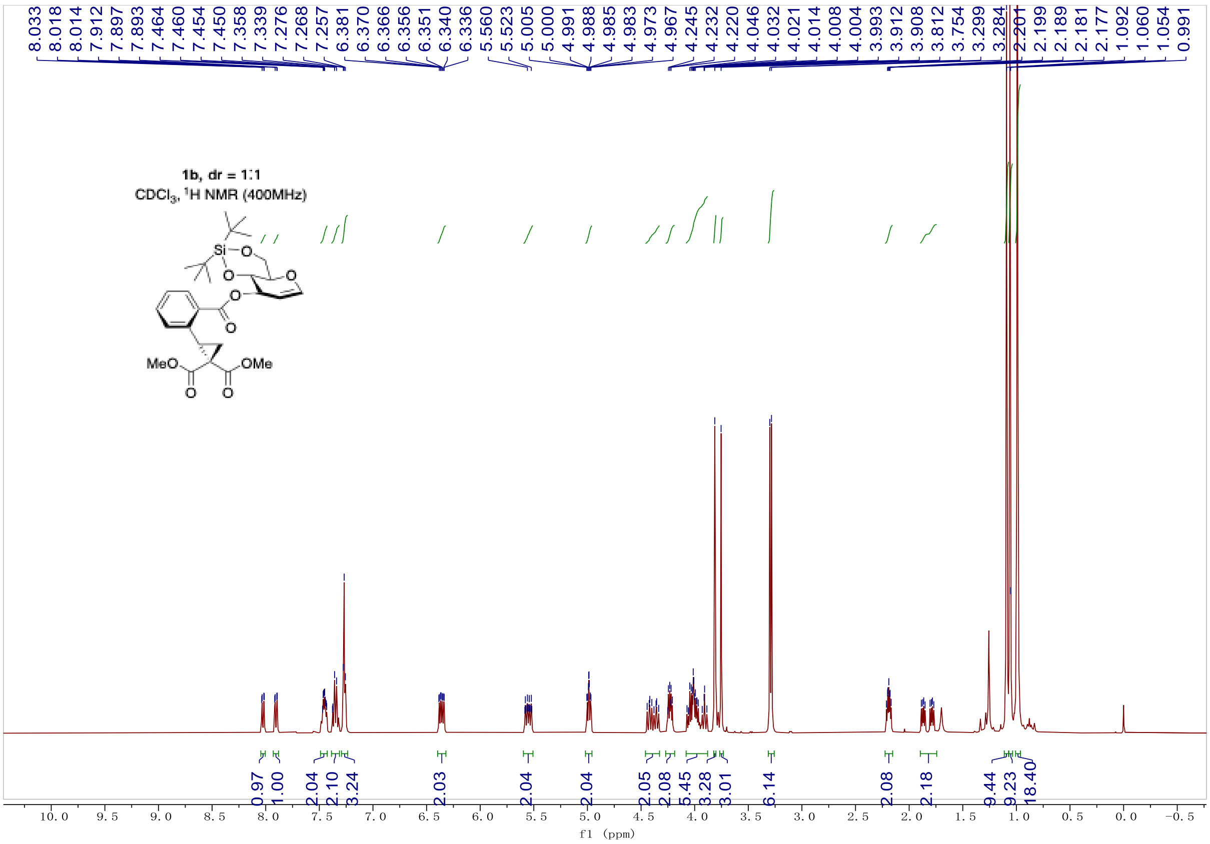

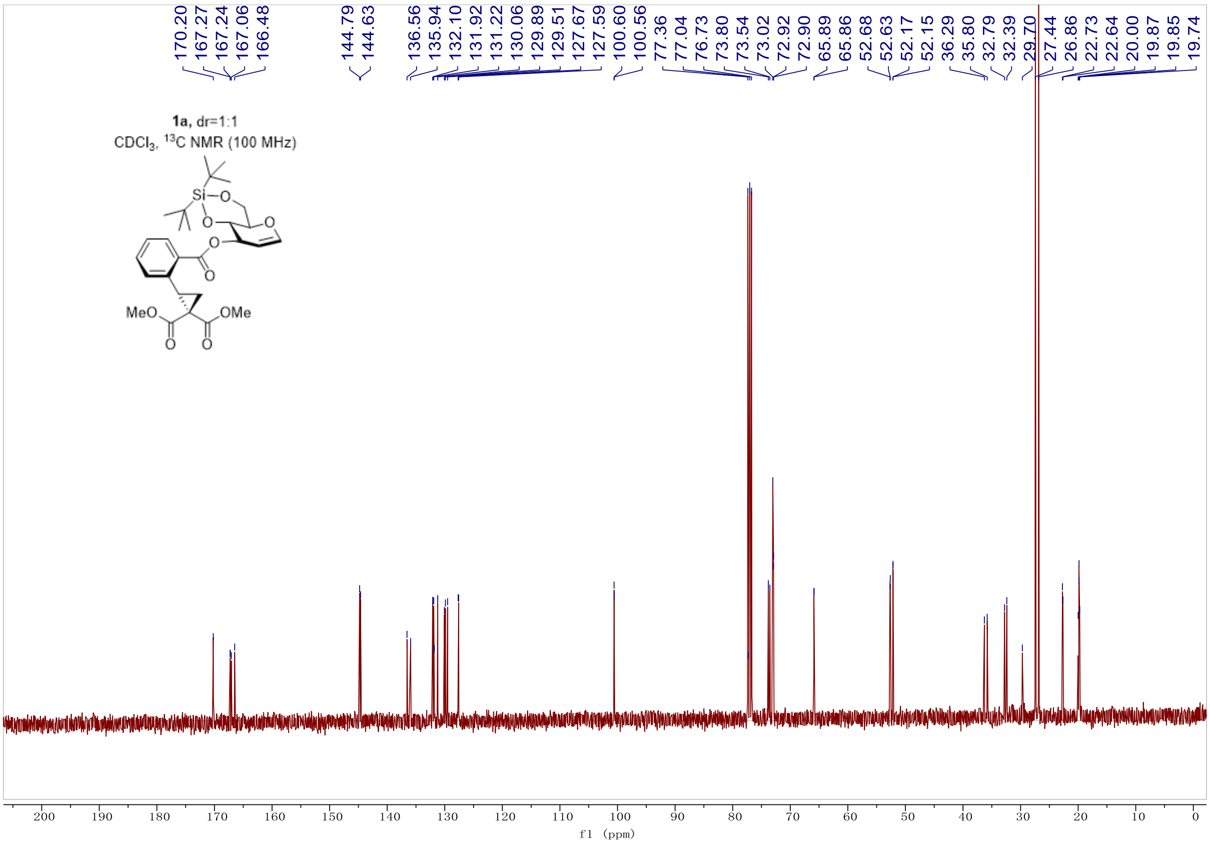

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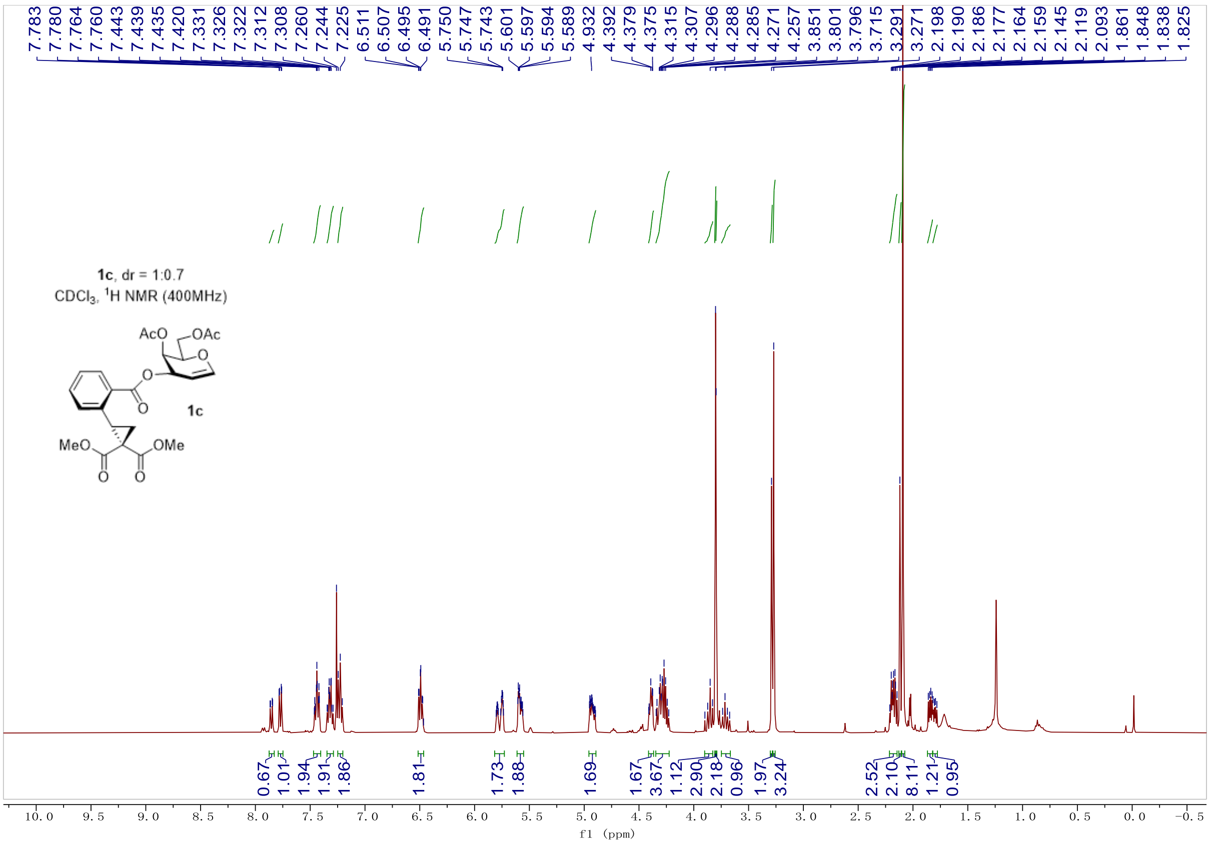

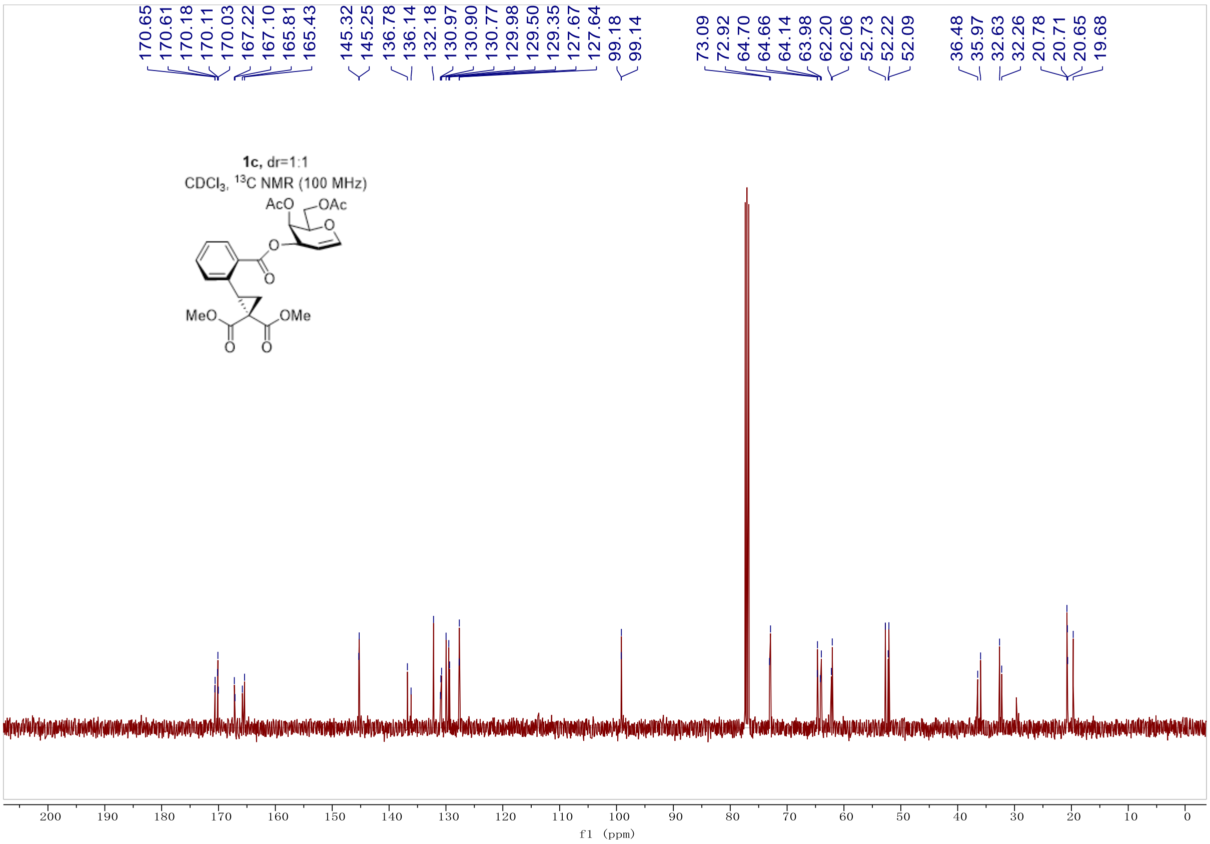

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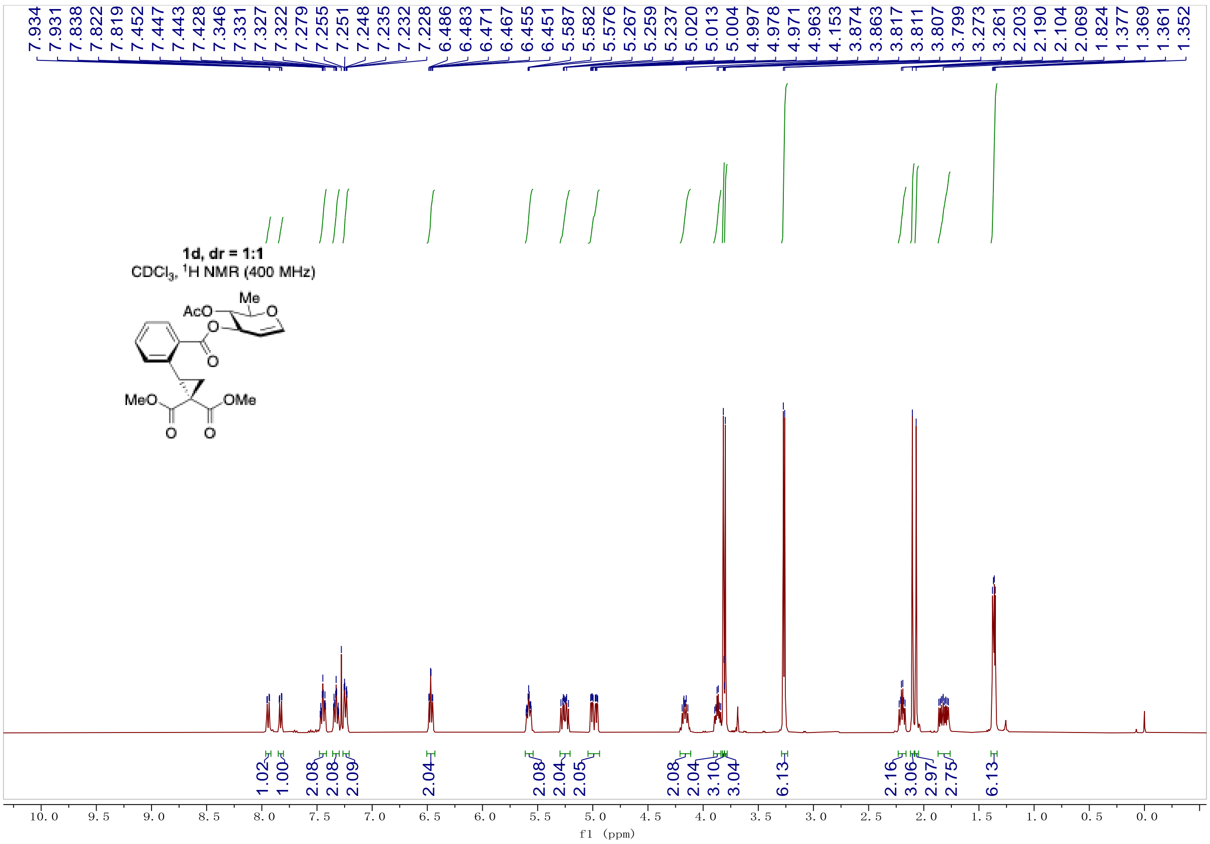
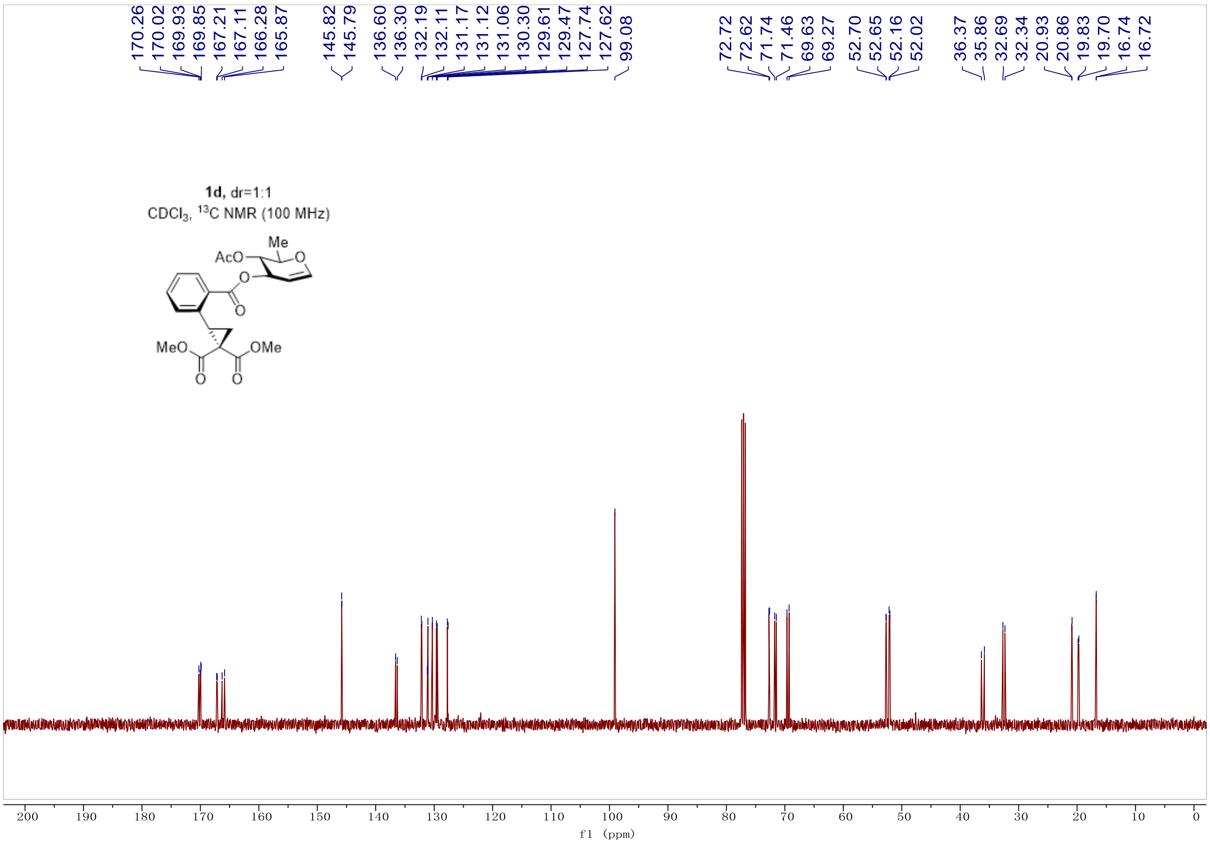
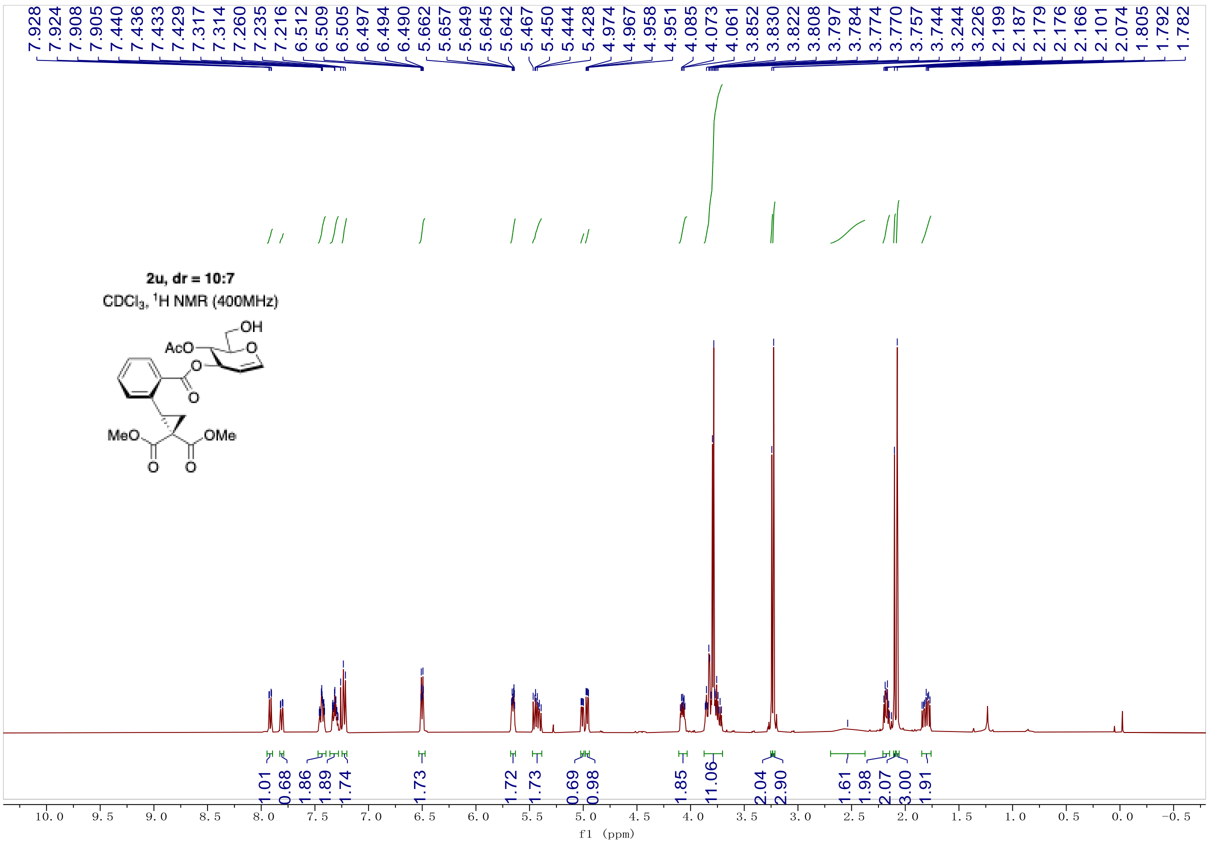
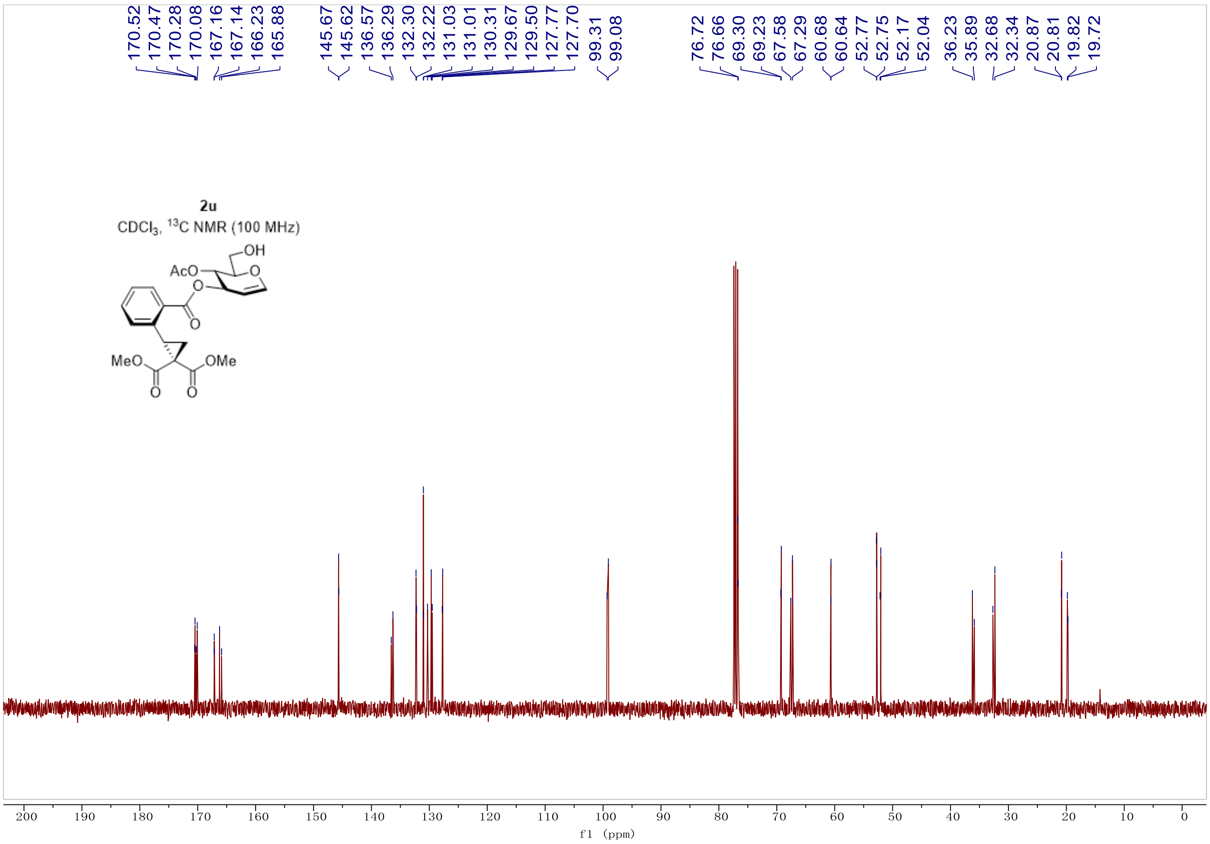




^{1}H and ^{13}C spectra for **2u**





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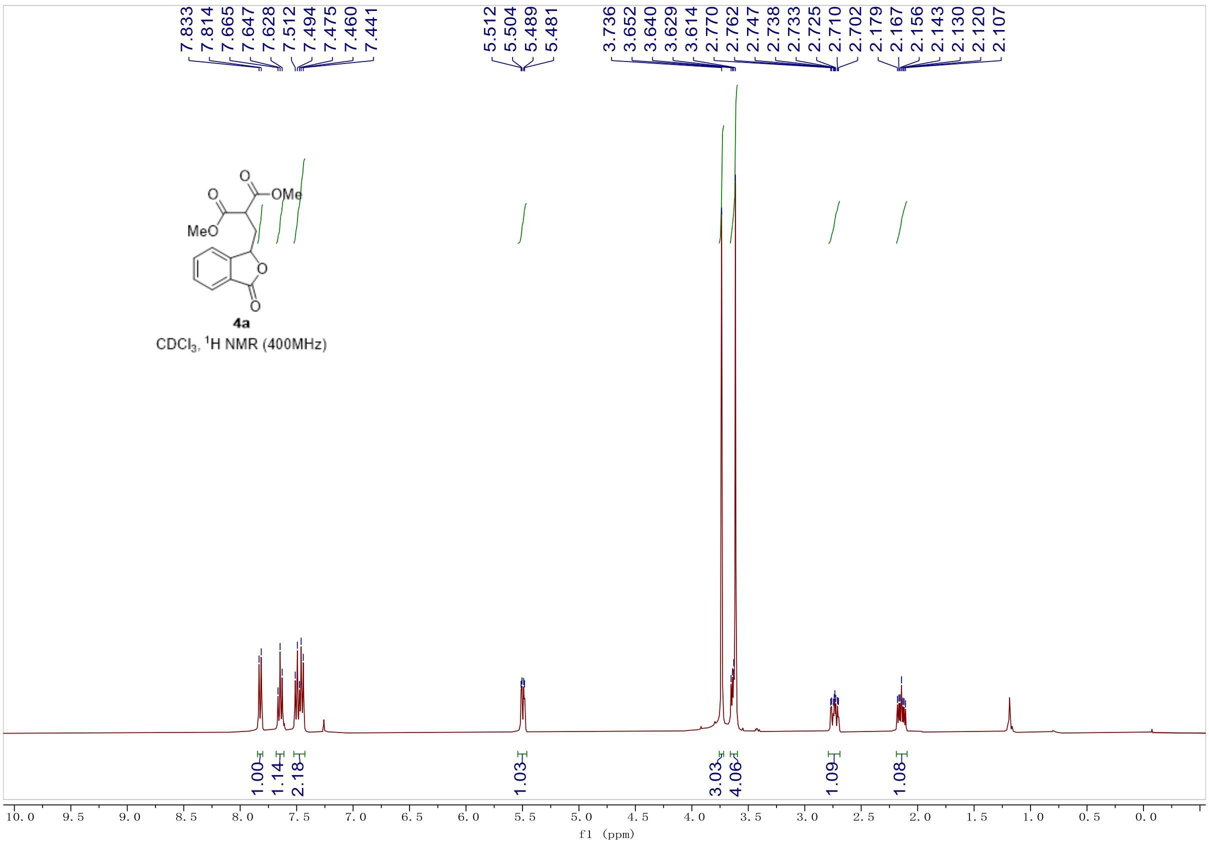
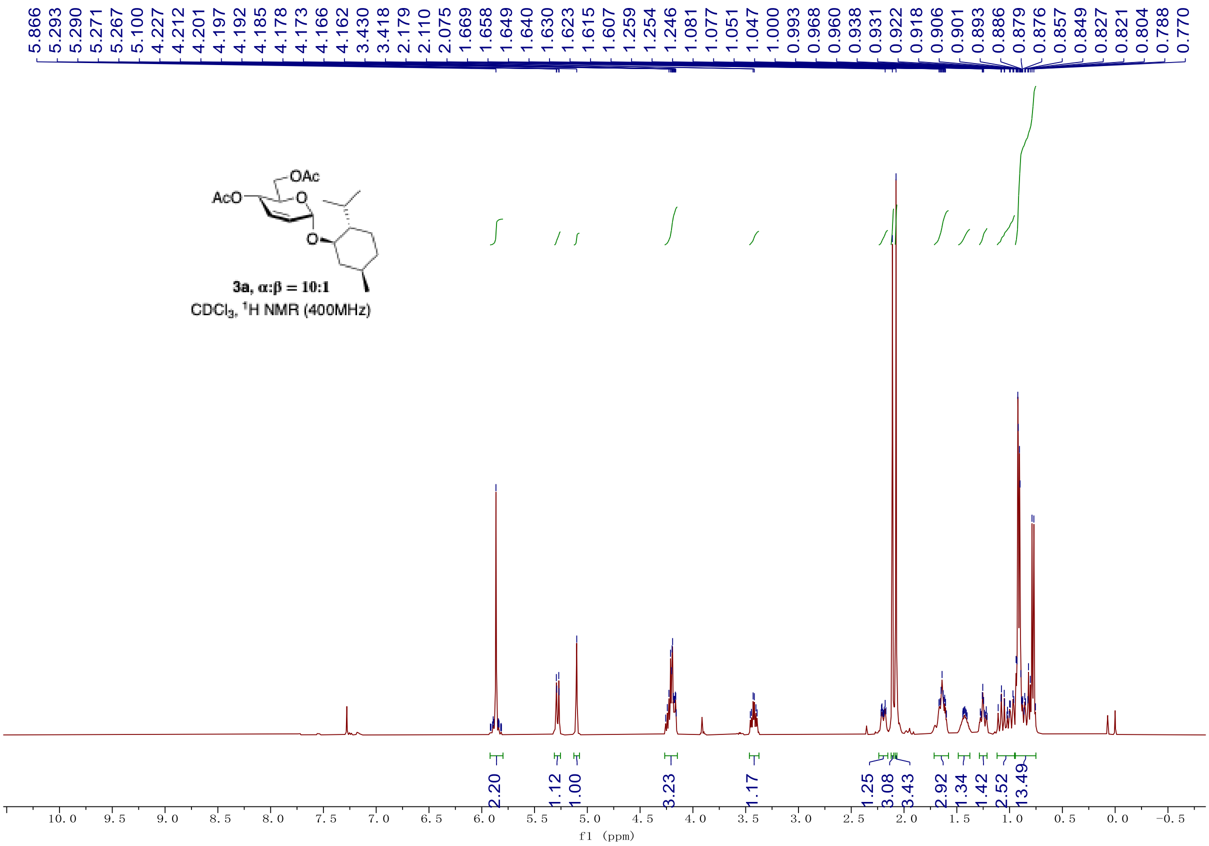


^{1}H spectrum for **3a**



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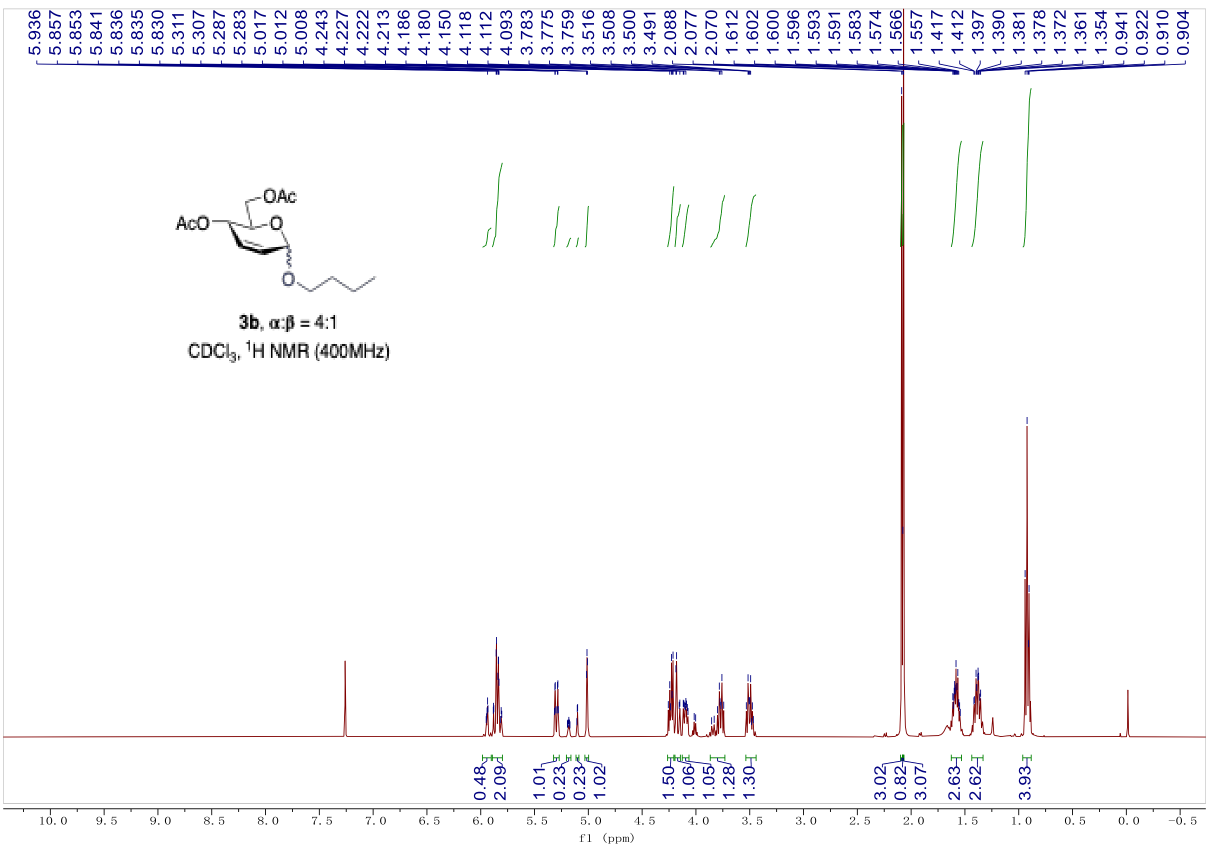

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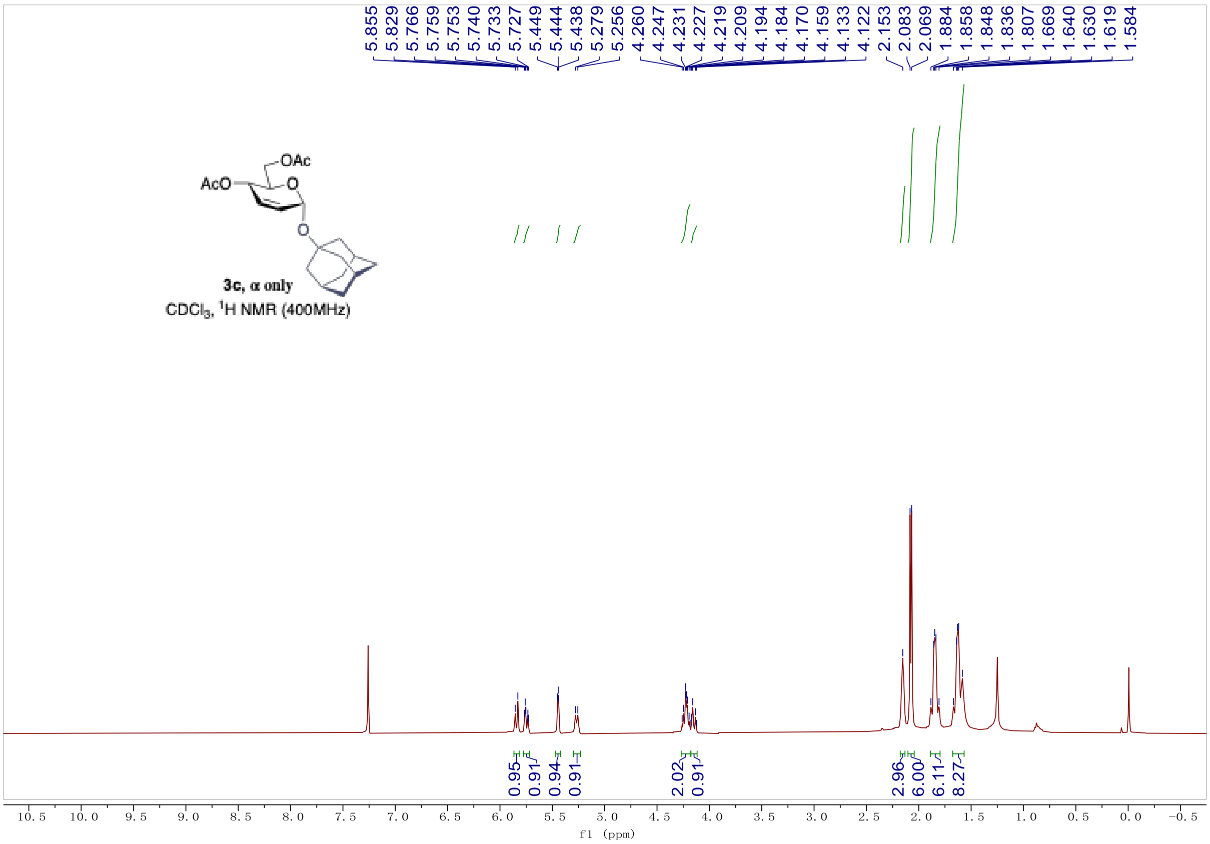
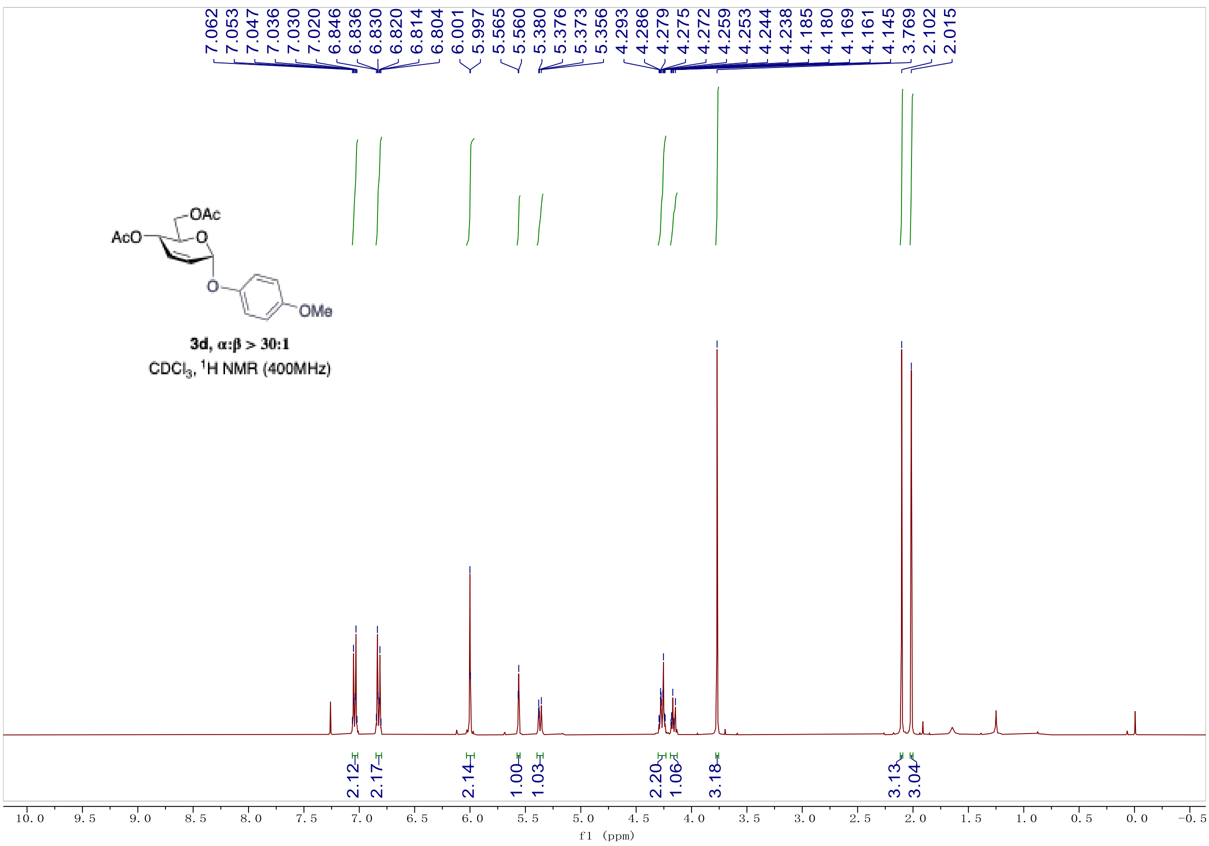
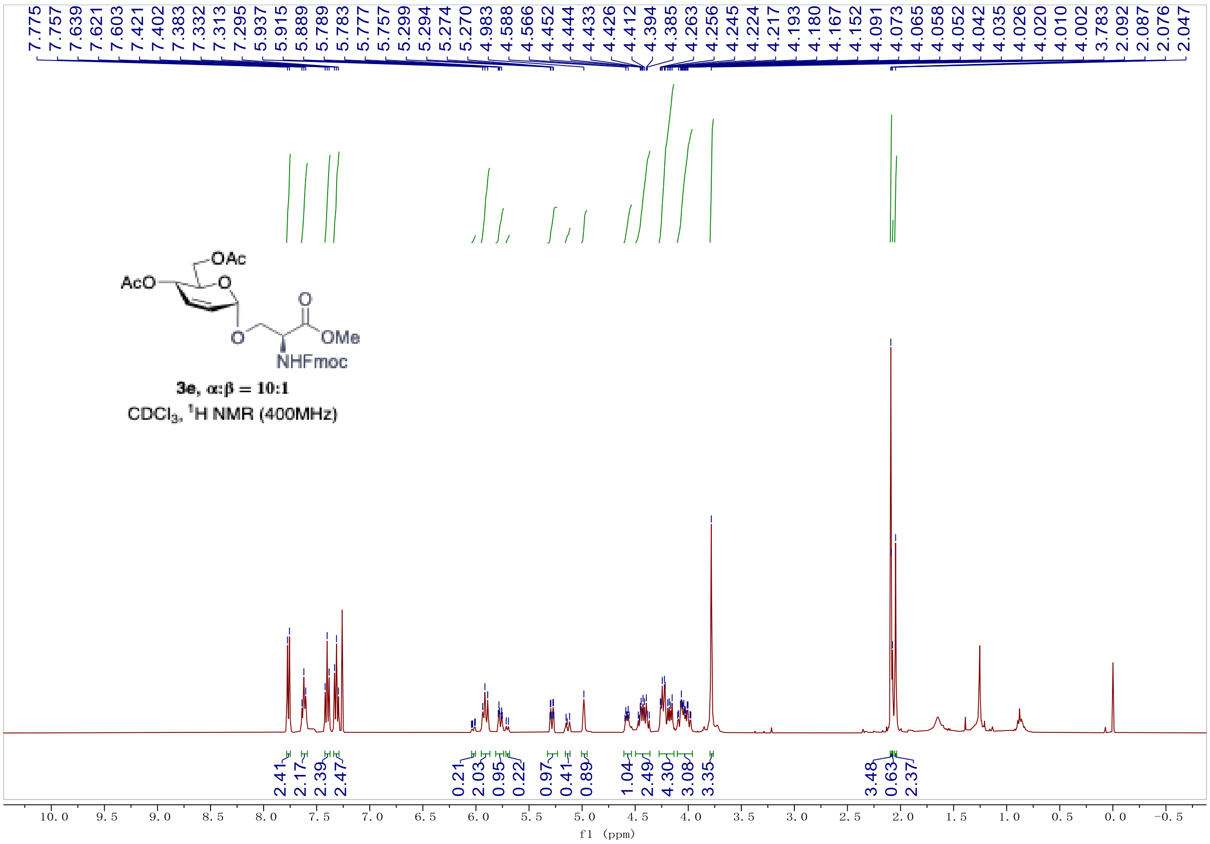
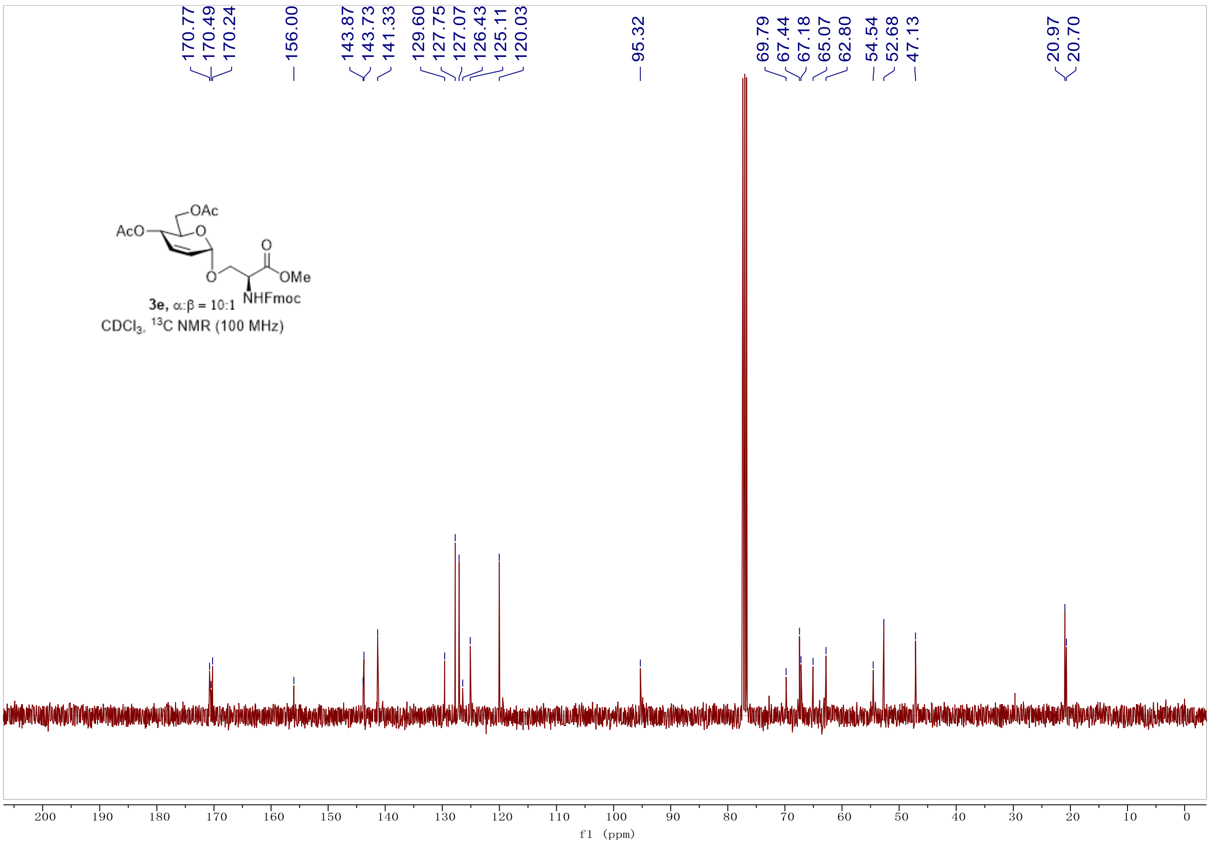


^{1}H spectrum for **3d**

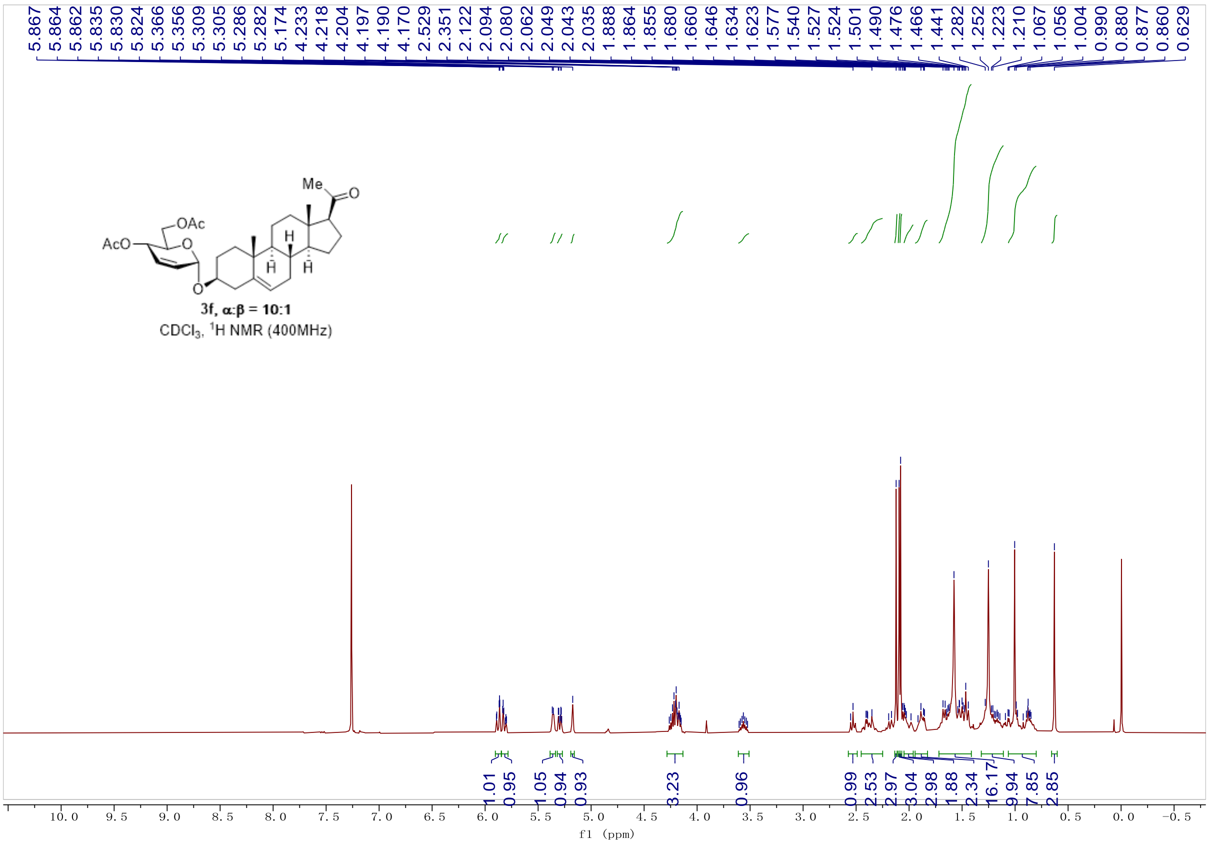


^{1}H and ^{13}C spectra for **3e**

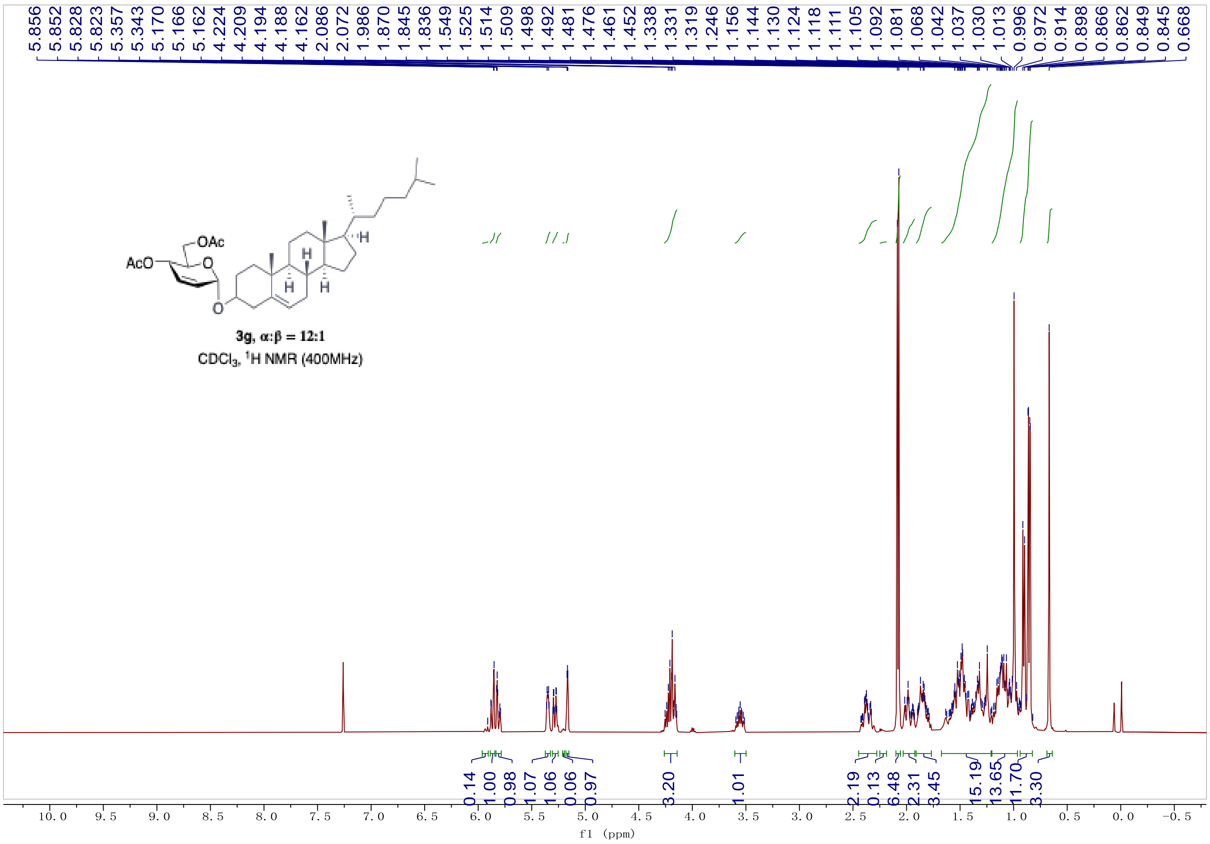




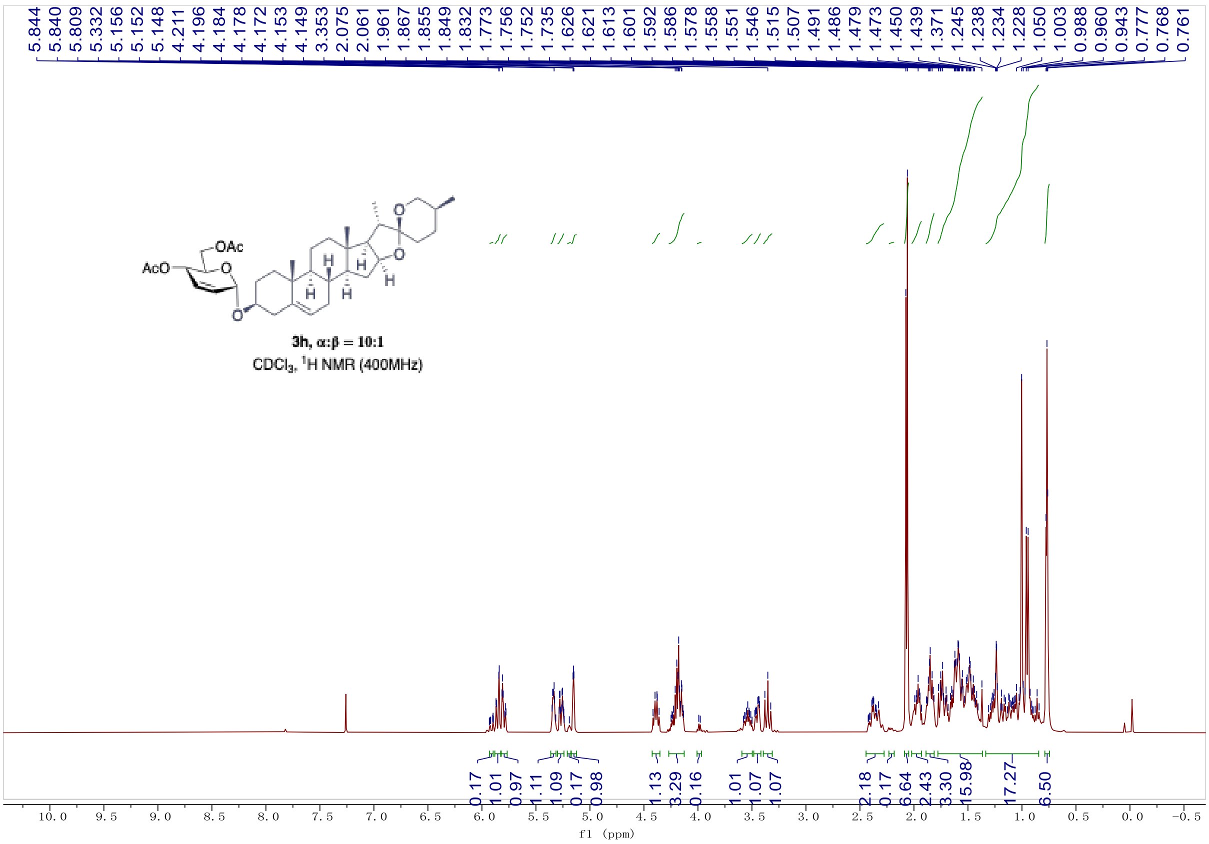
[1]H spectrum for **3f**

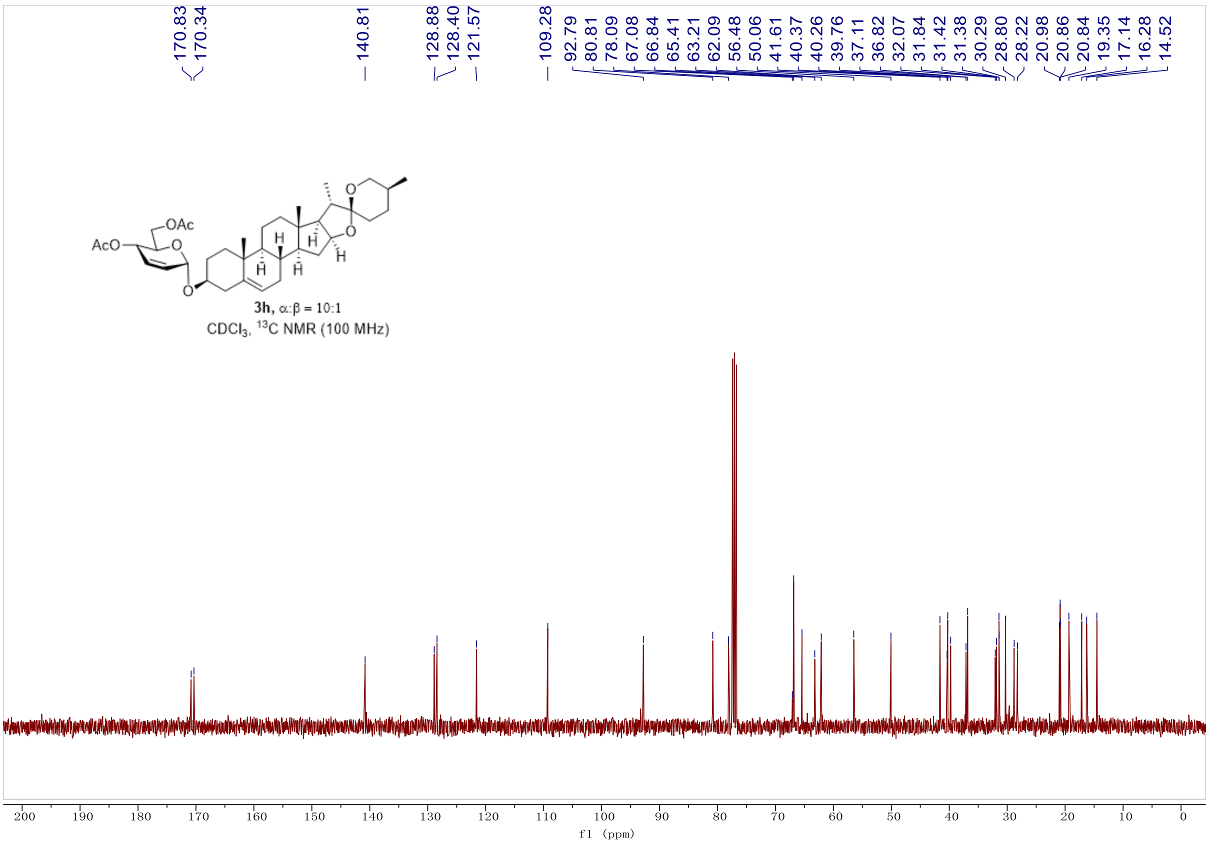


[1]H spectrum for **3g**

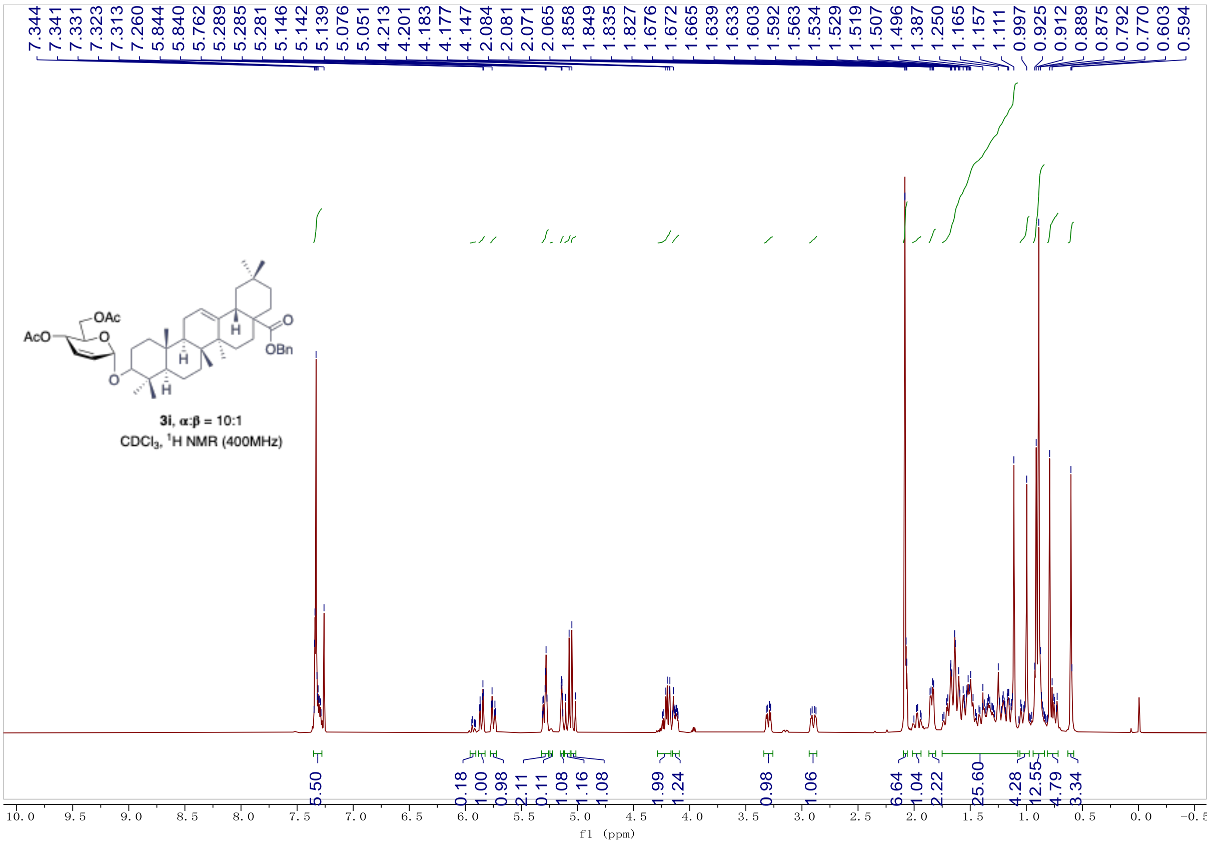


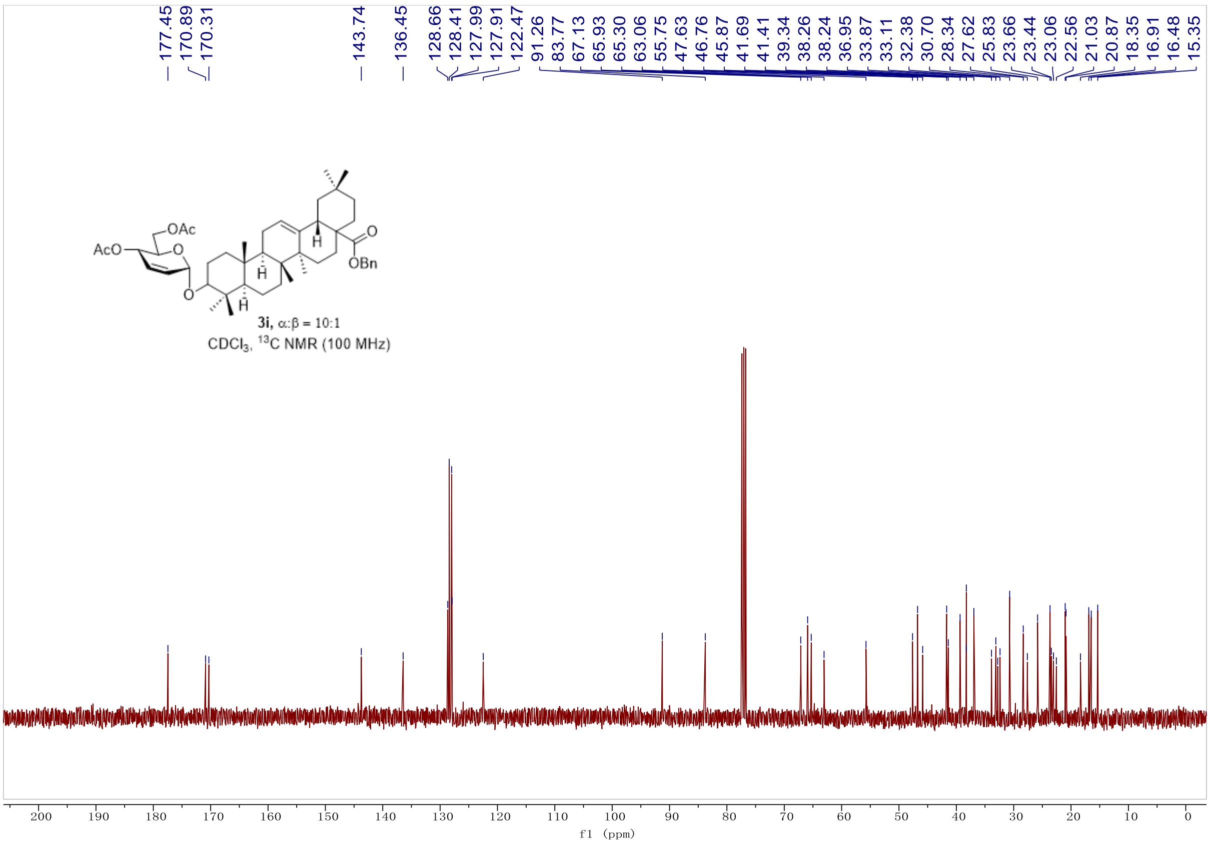
[1]H and [13]C spectra for **3h**





^{1}H and ^{13}C spectra for **3i**





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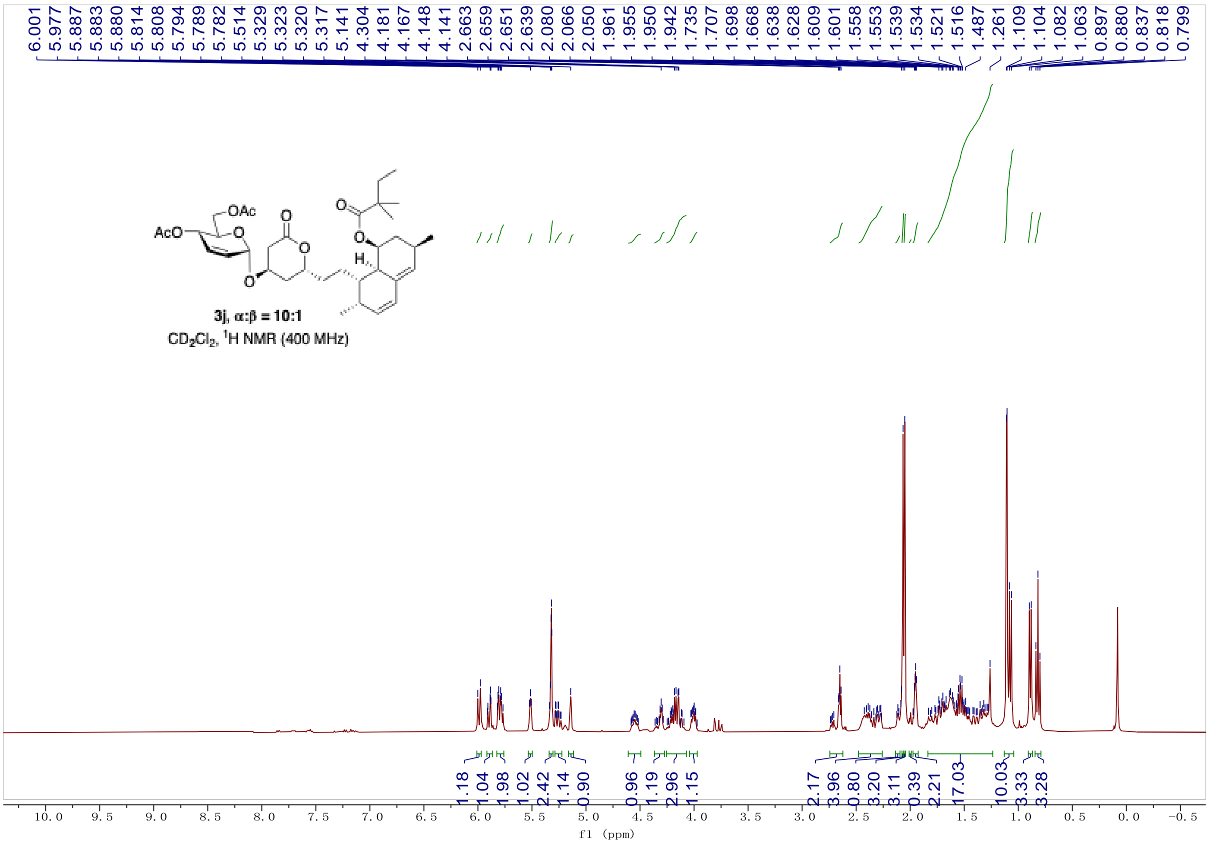

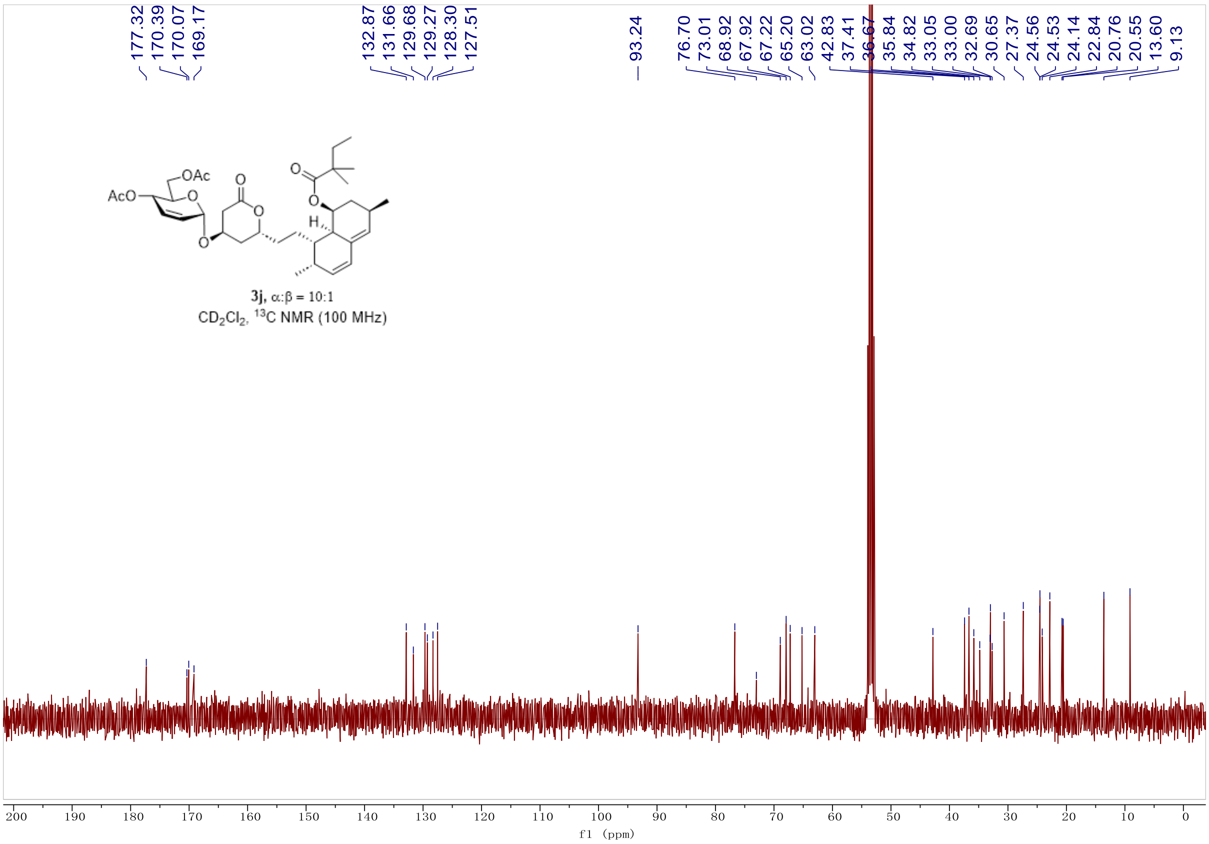

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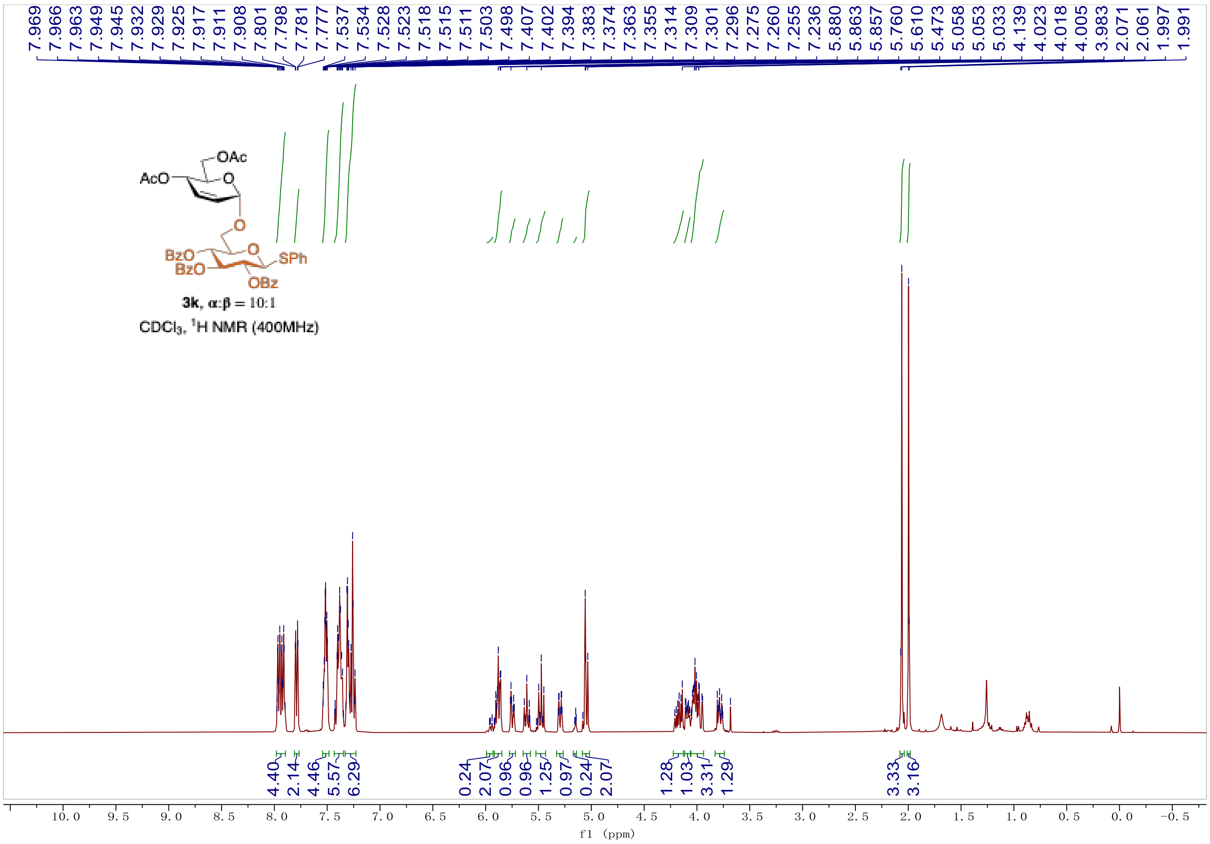
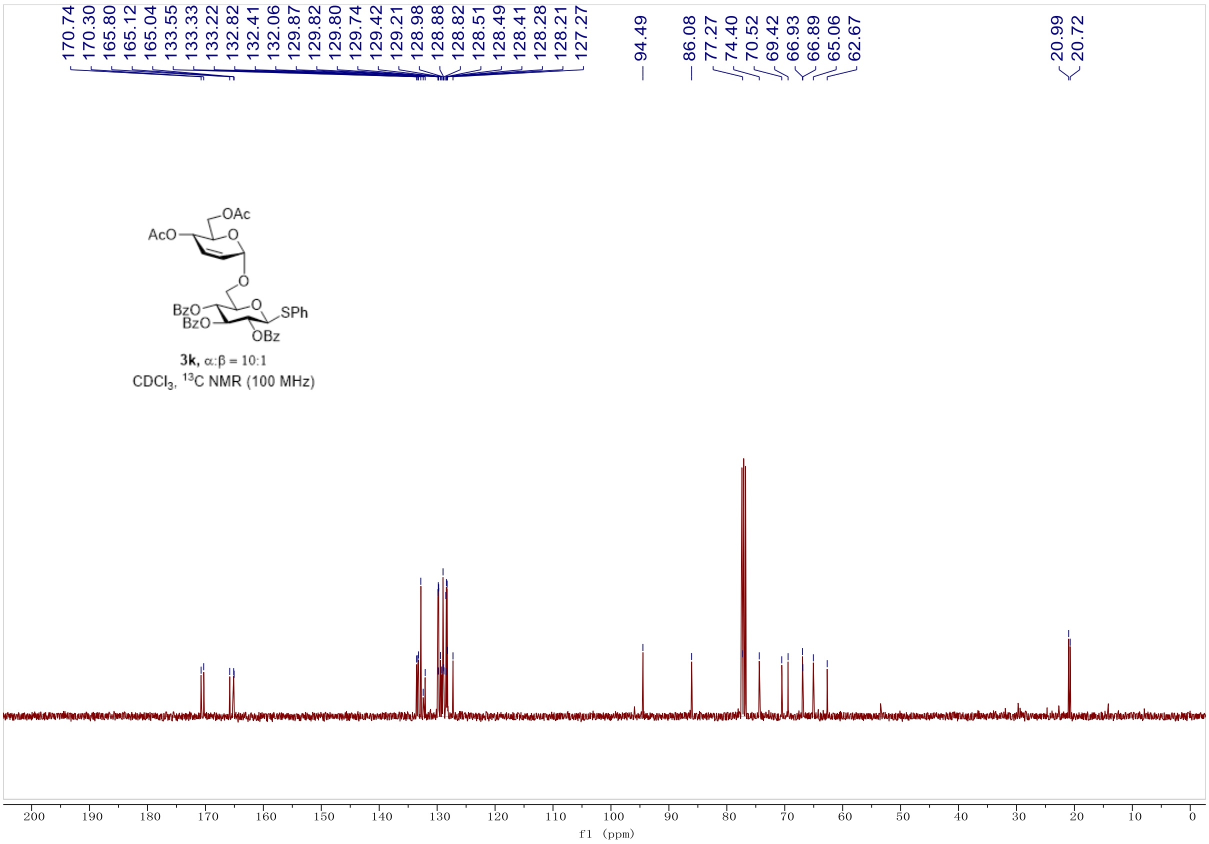
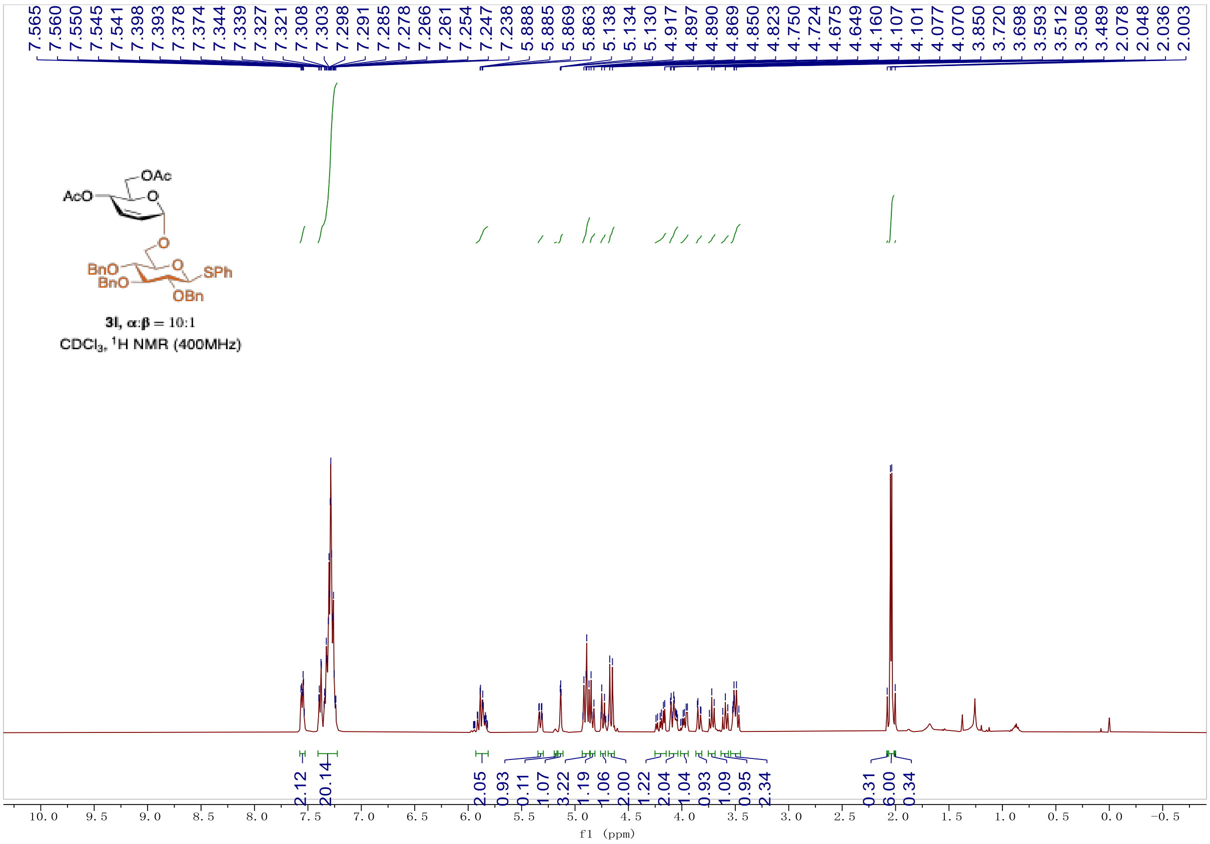
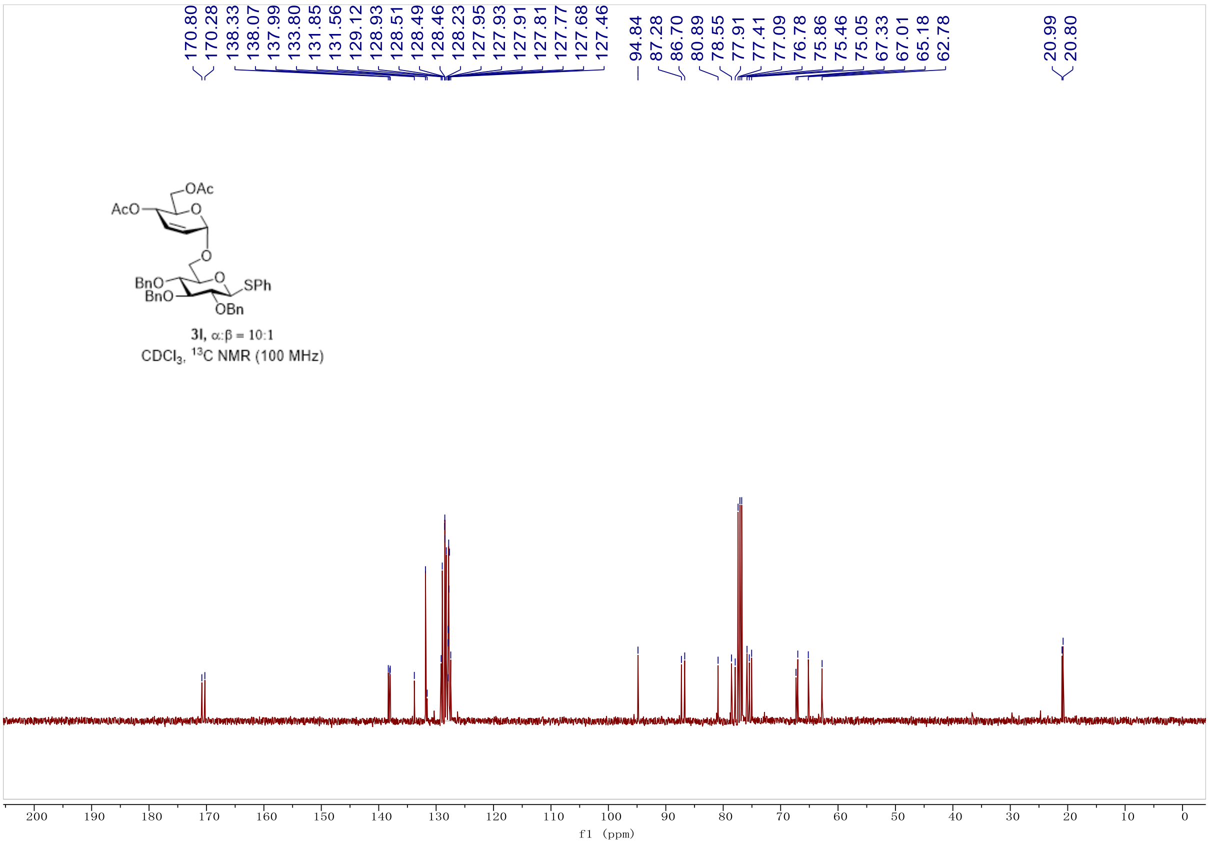




^{1}H and ^{13}C spectra for **3l**





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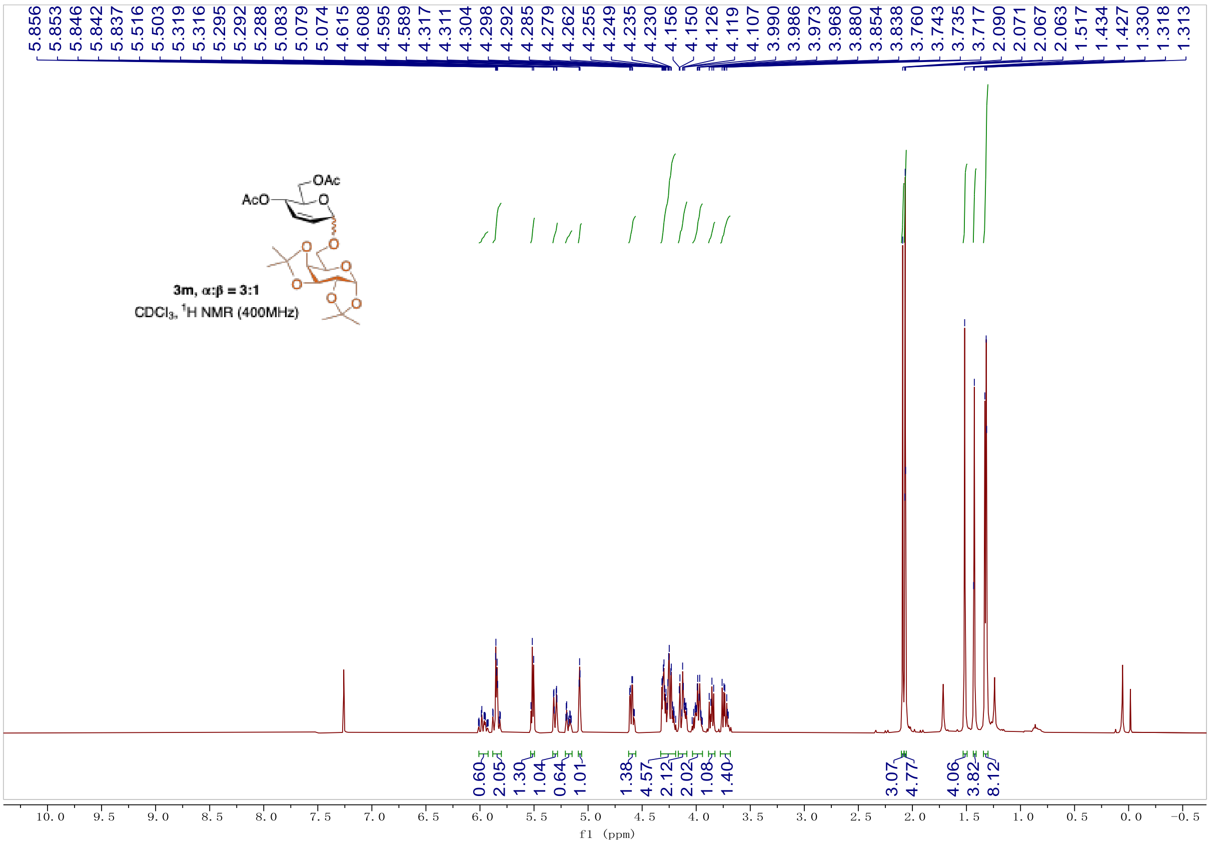

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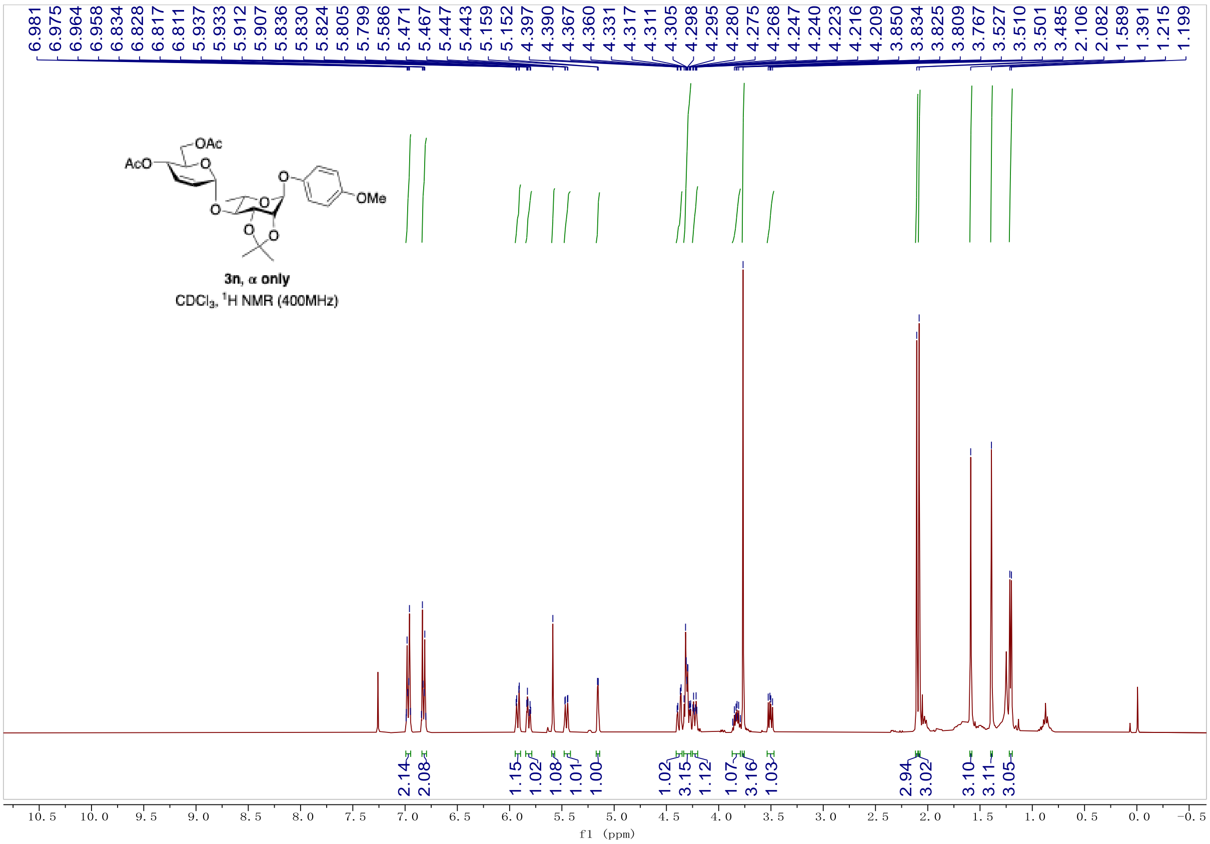

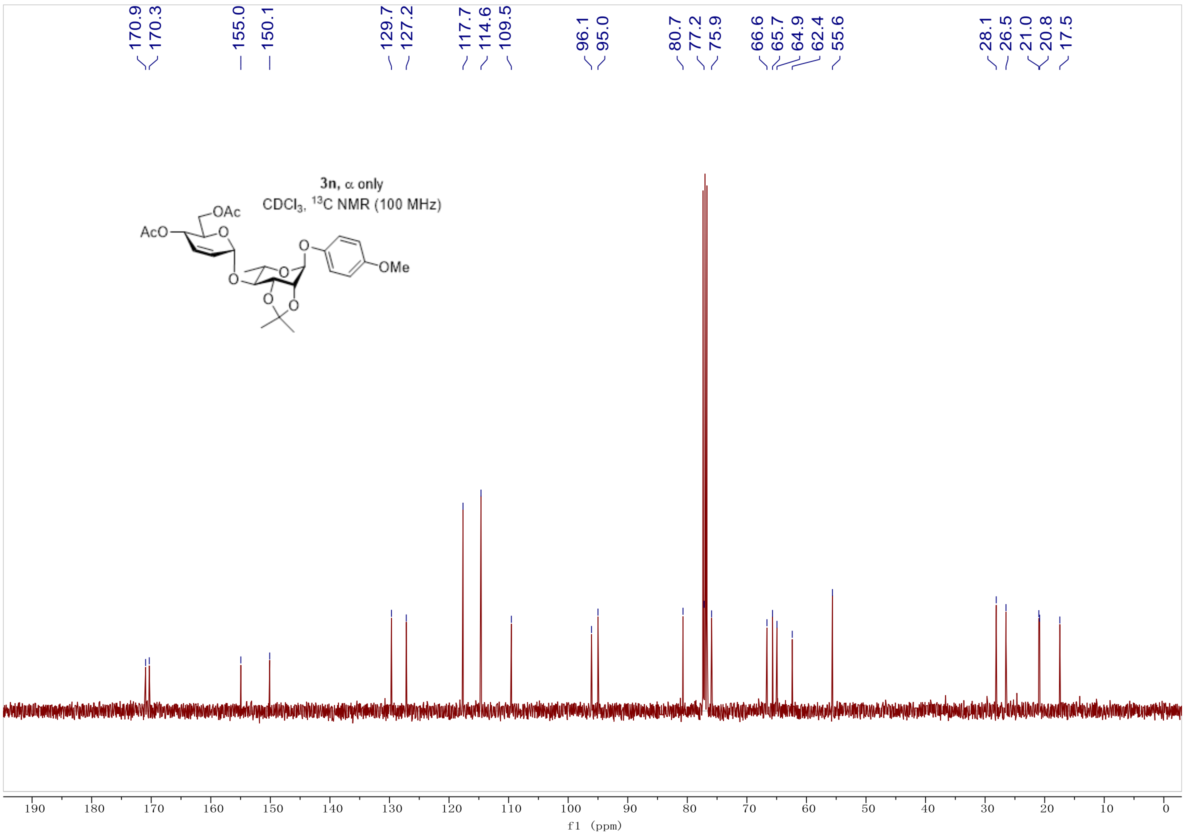

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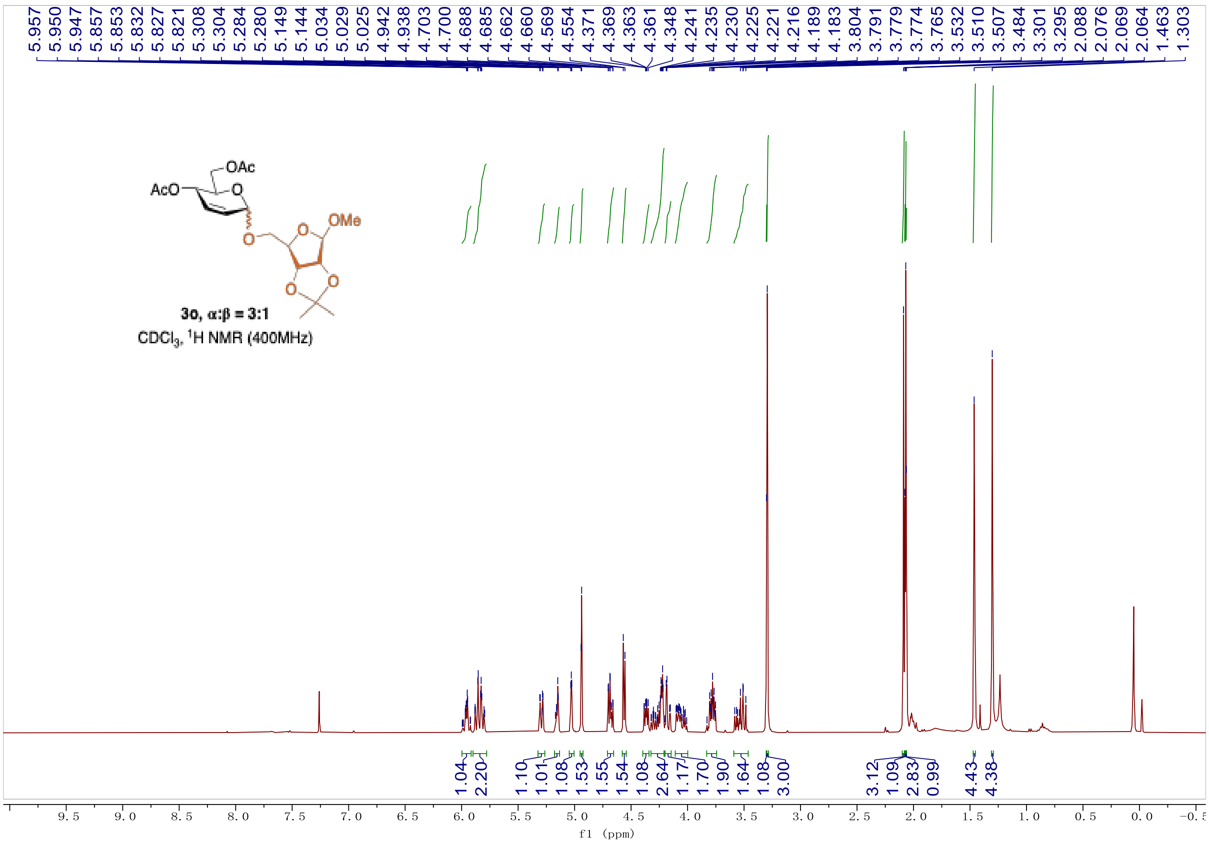

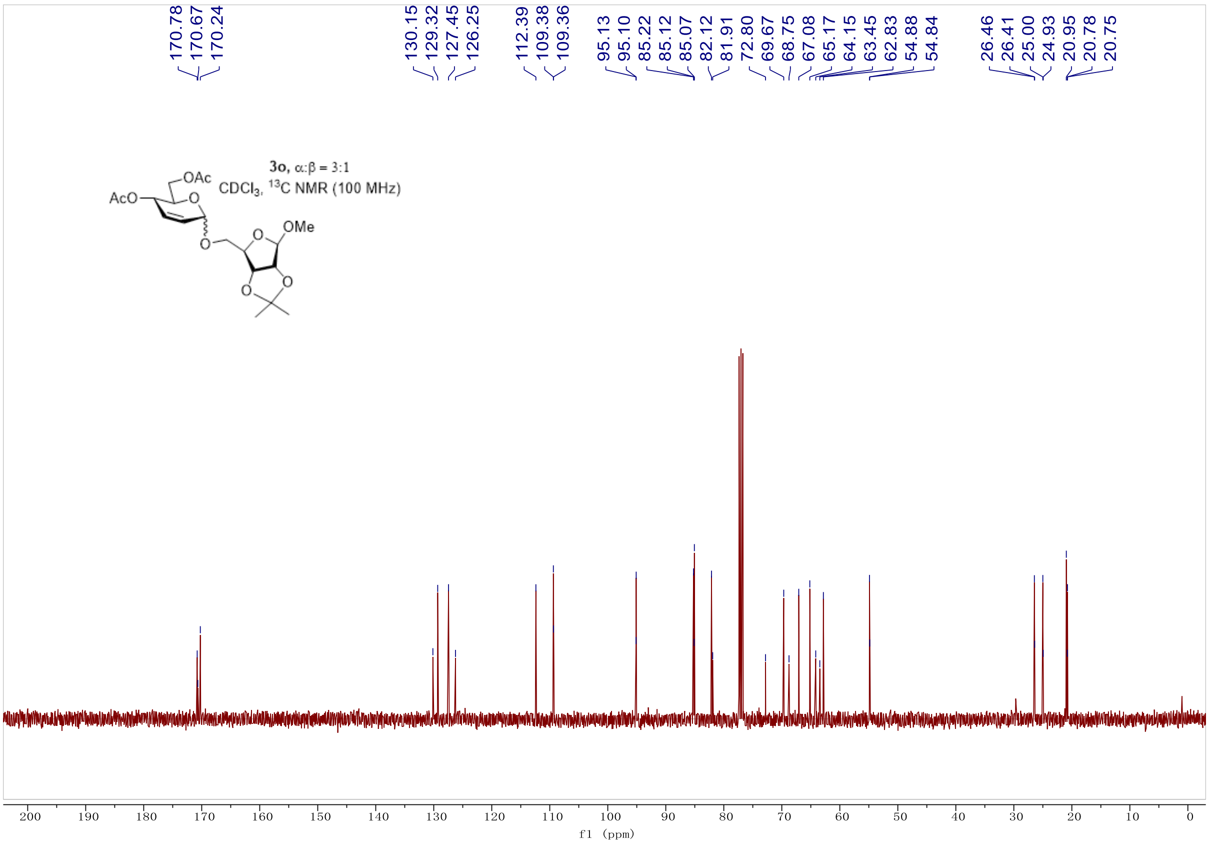

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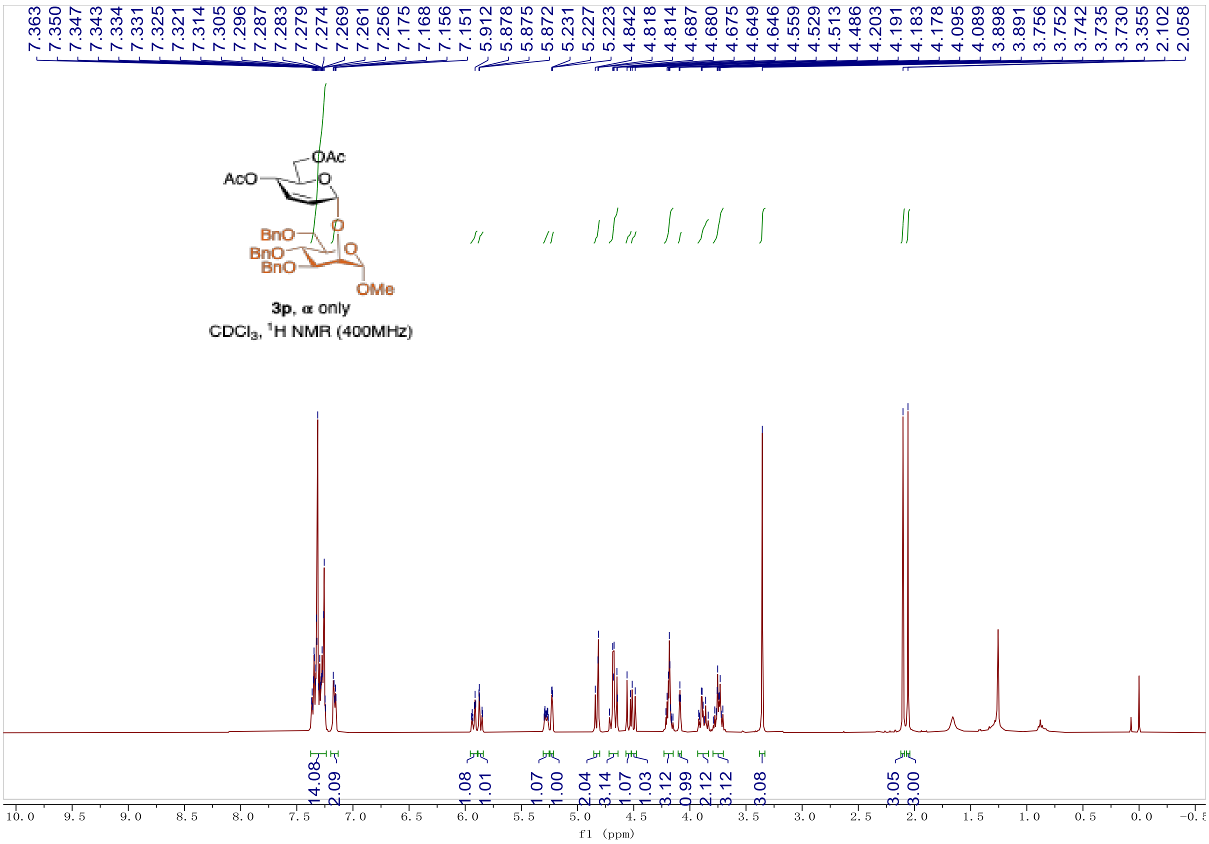

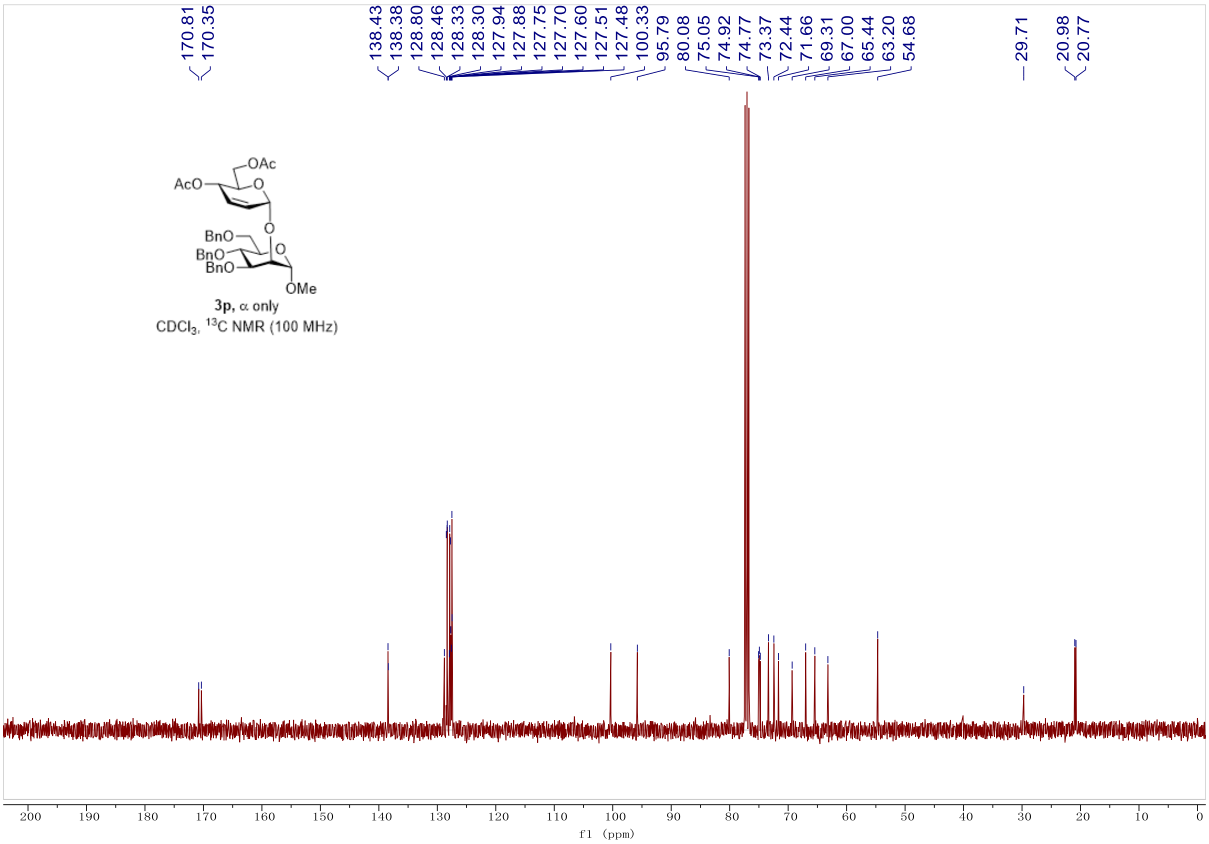

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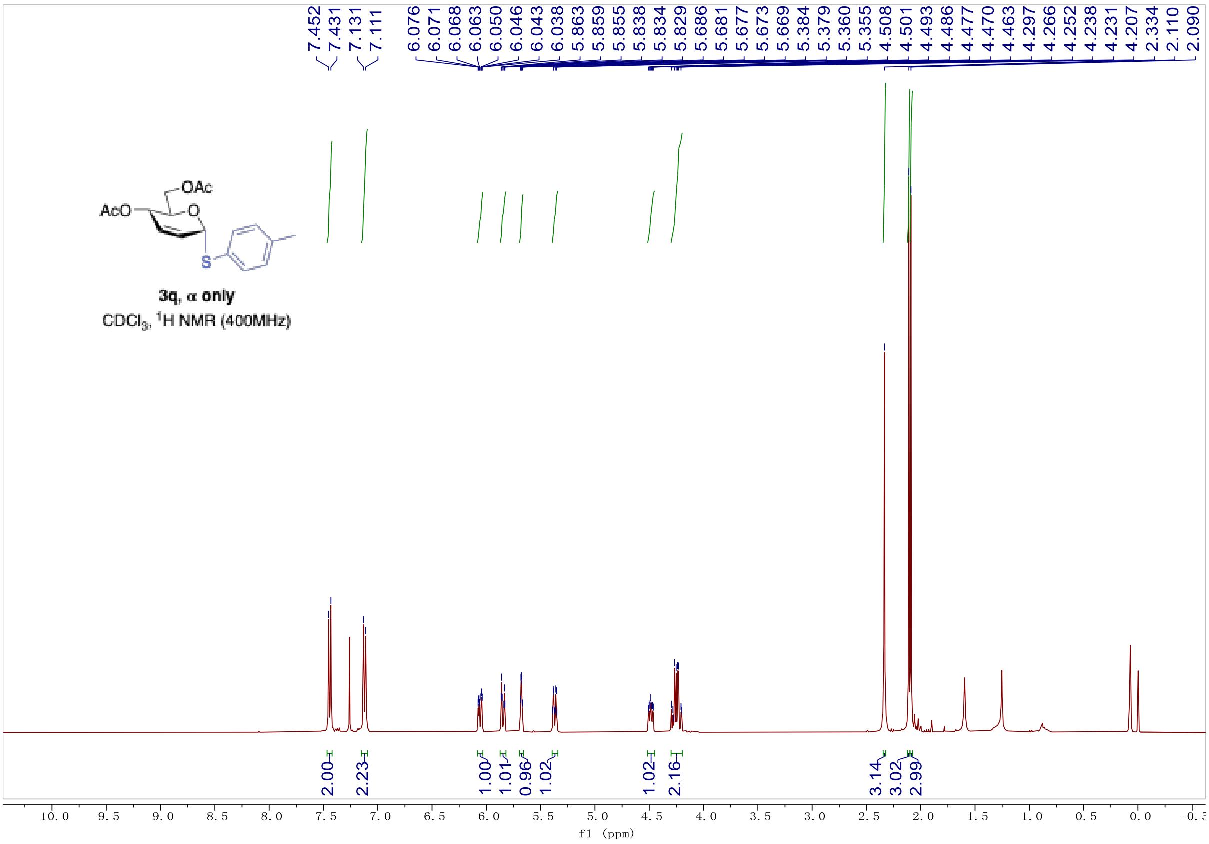
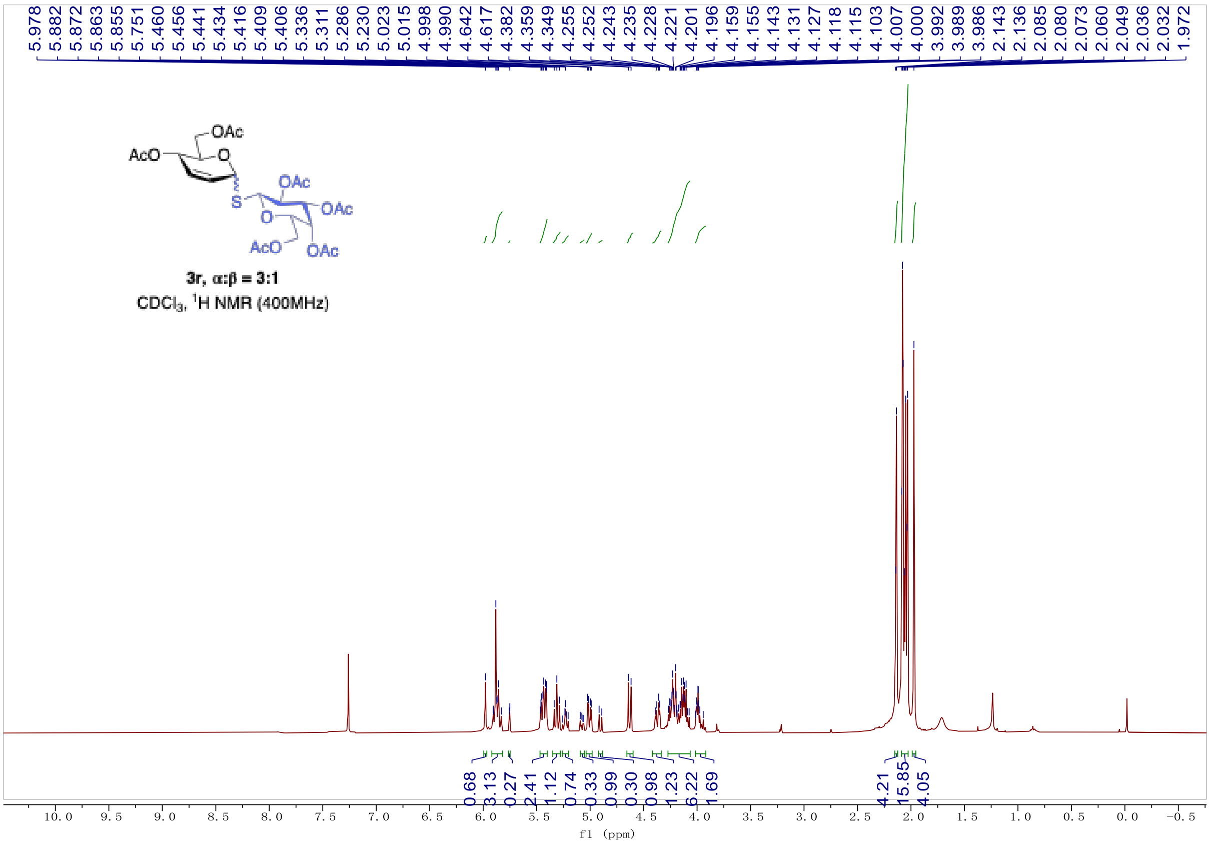
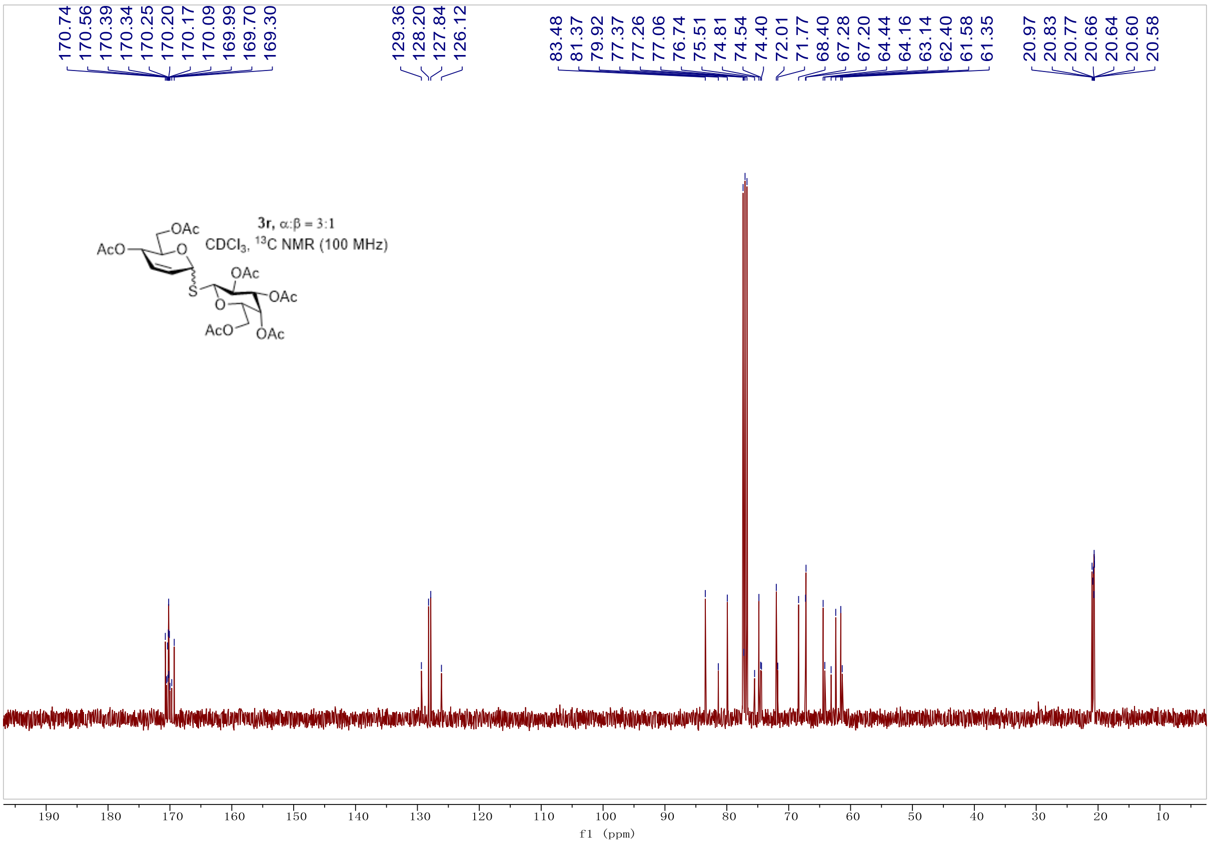


^{1}H and ^{13}C spectra for **3r**





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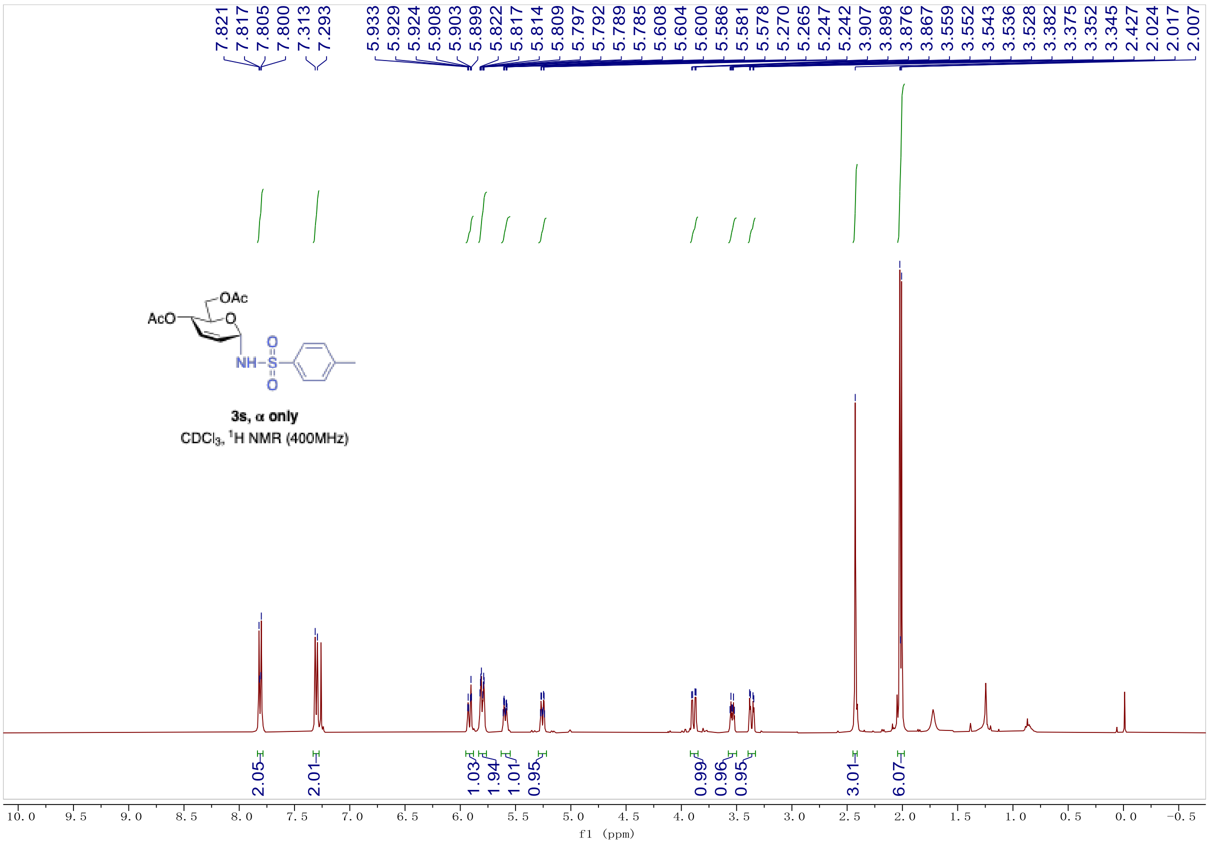

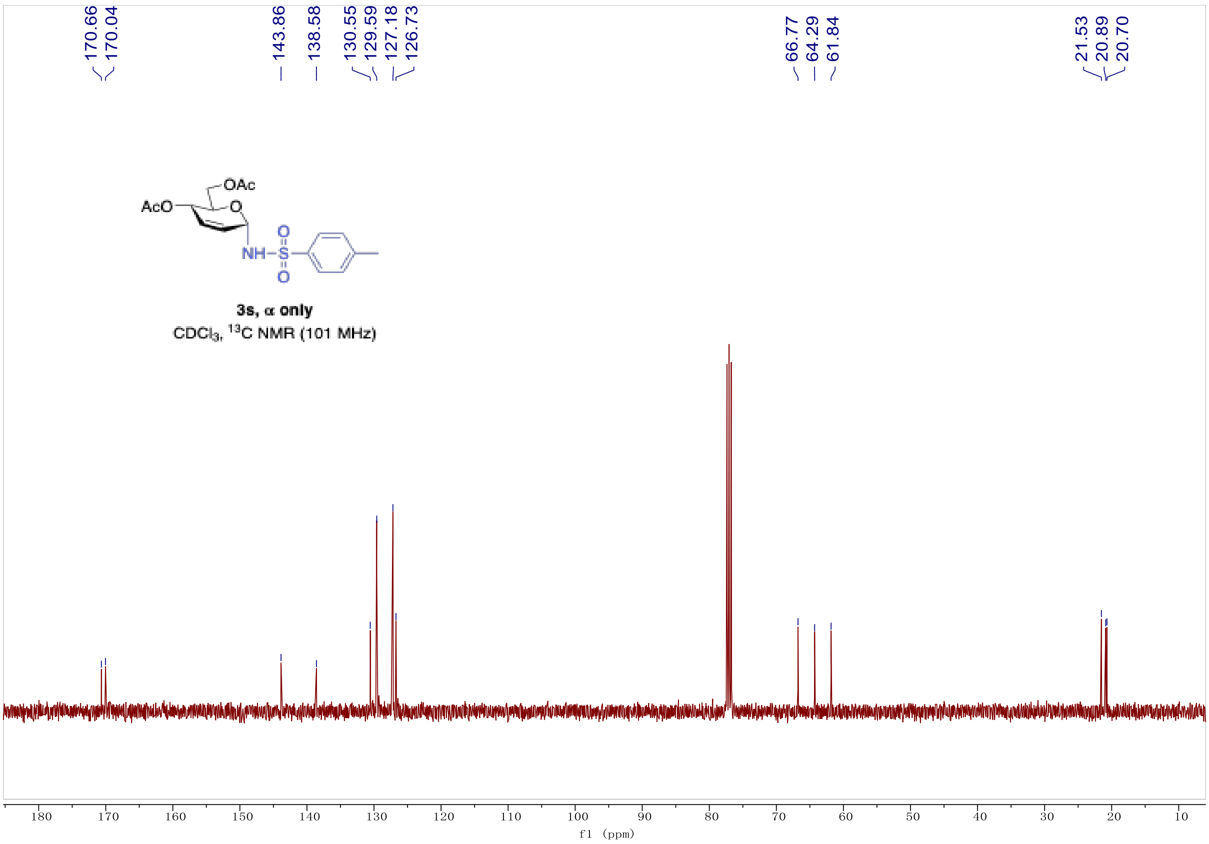

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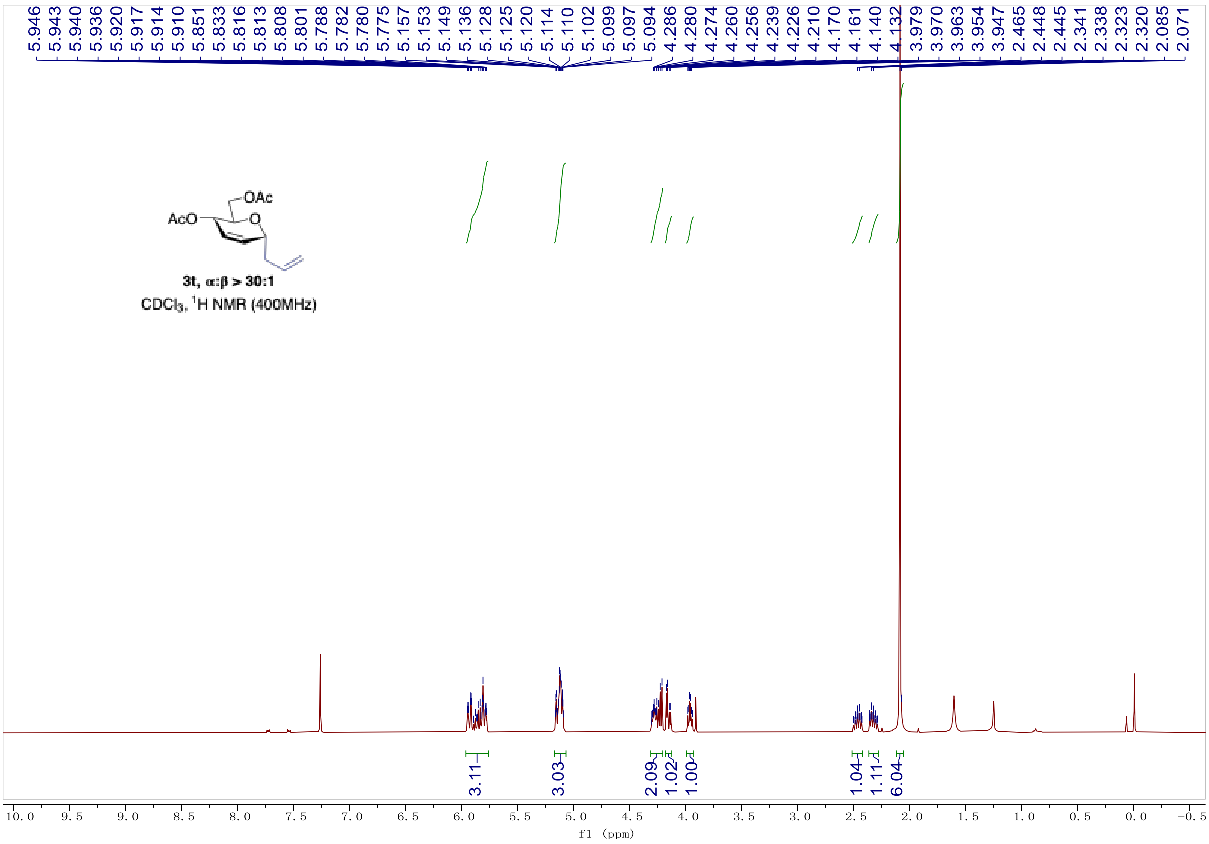

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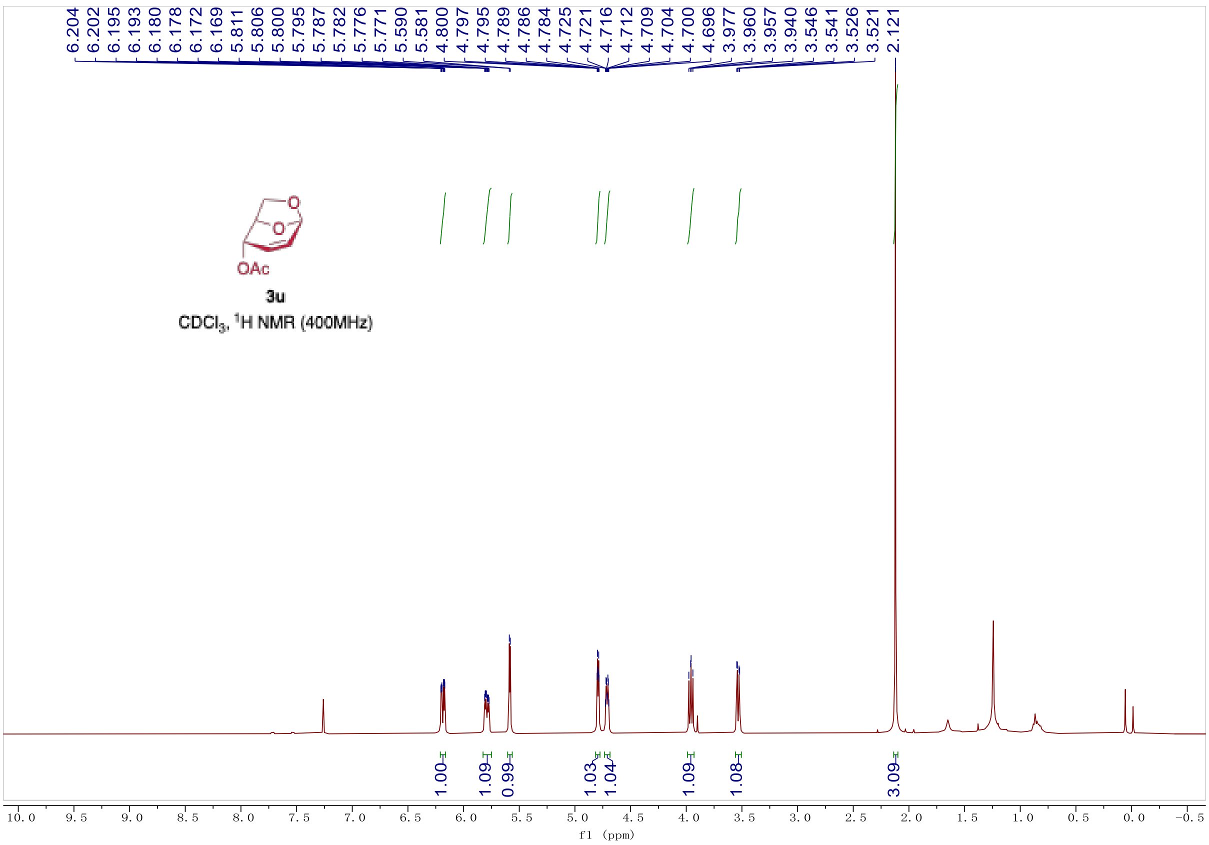
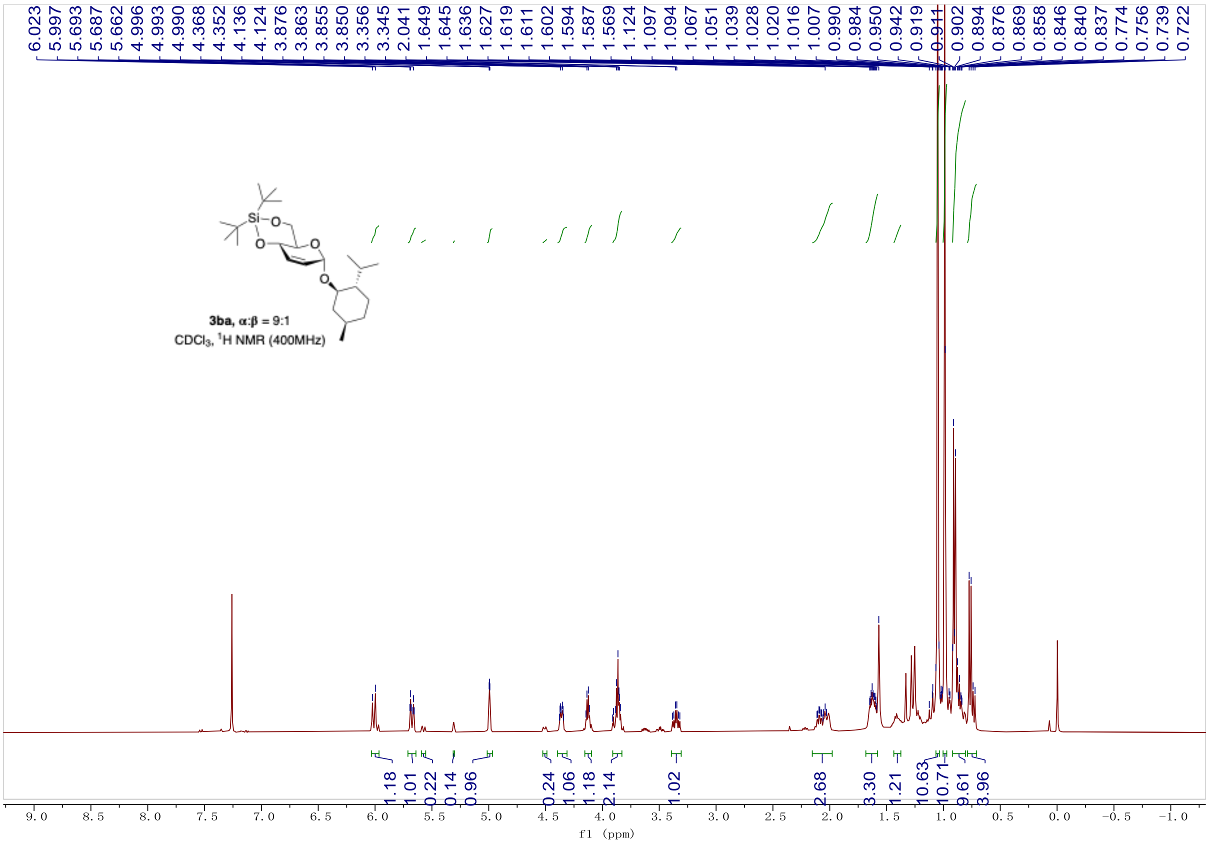
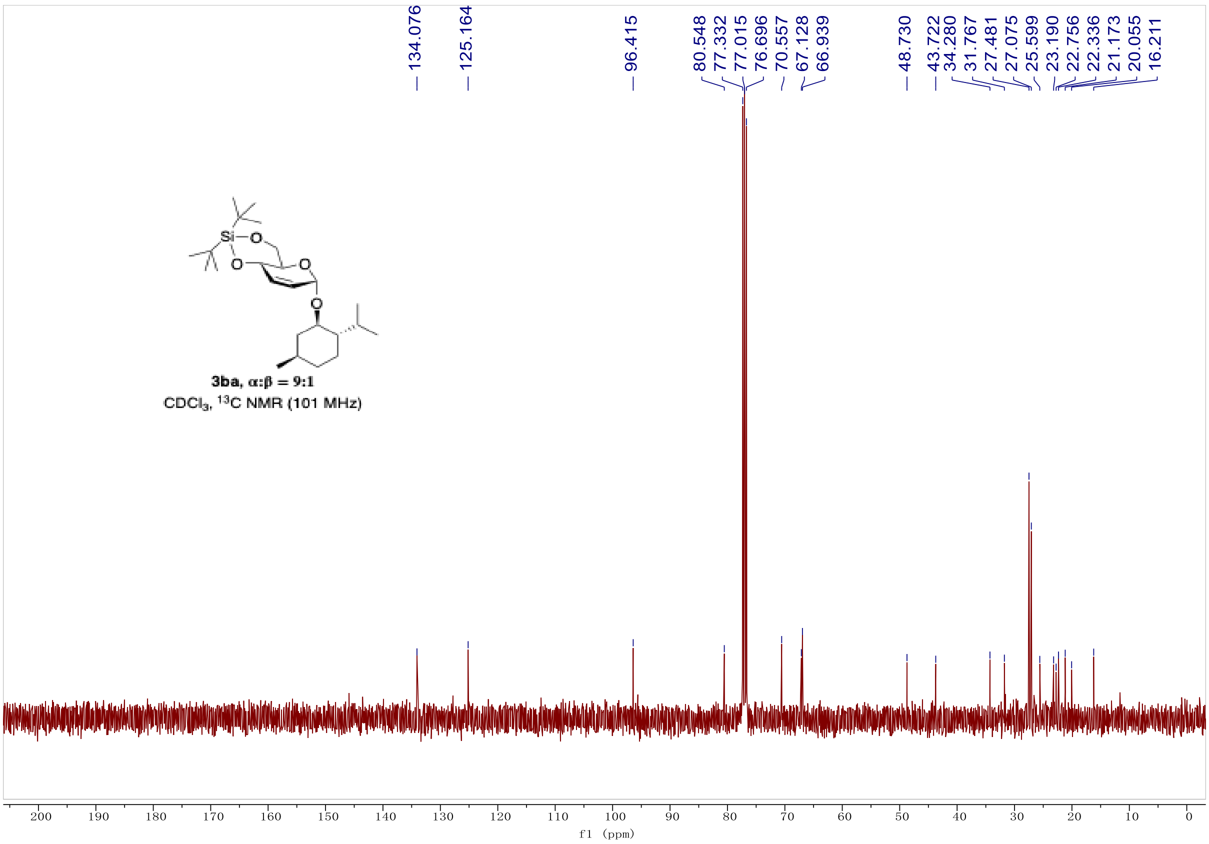


^{1}H and ^{13}C spectra for **3ba**





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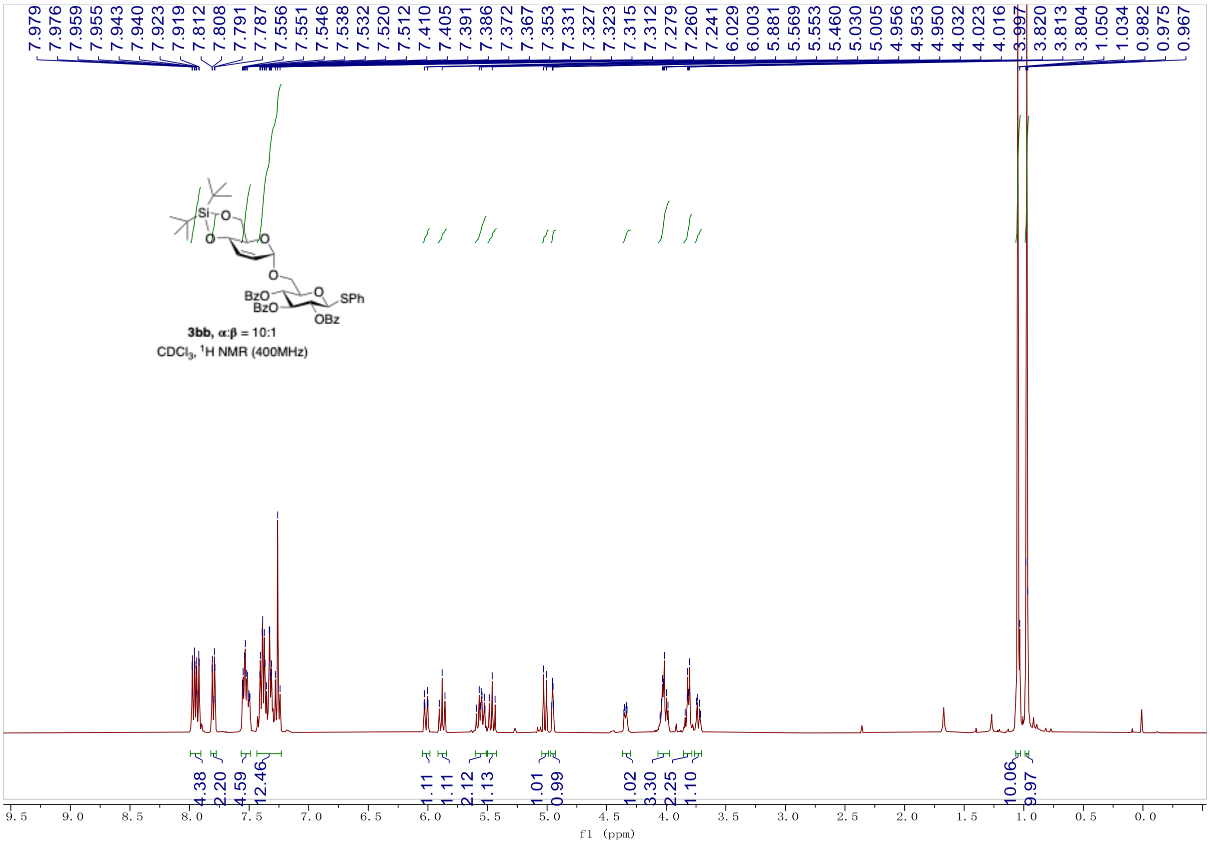

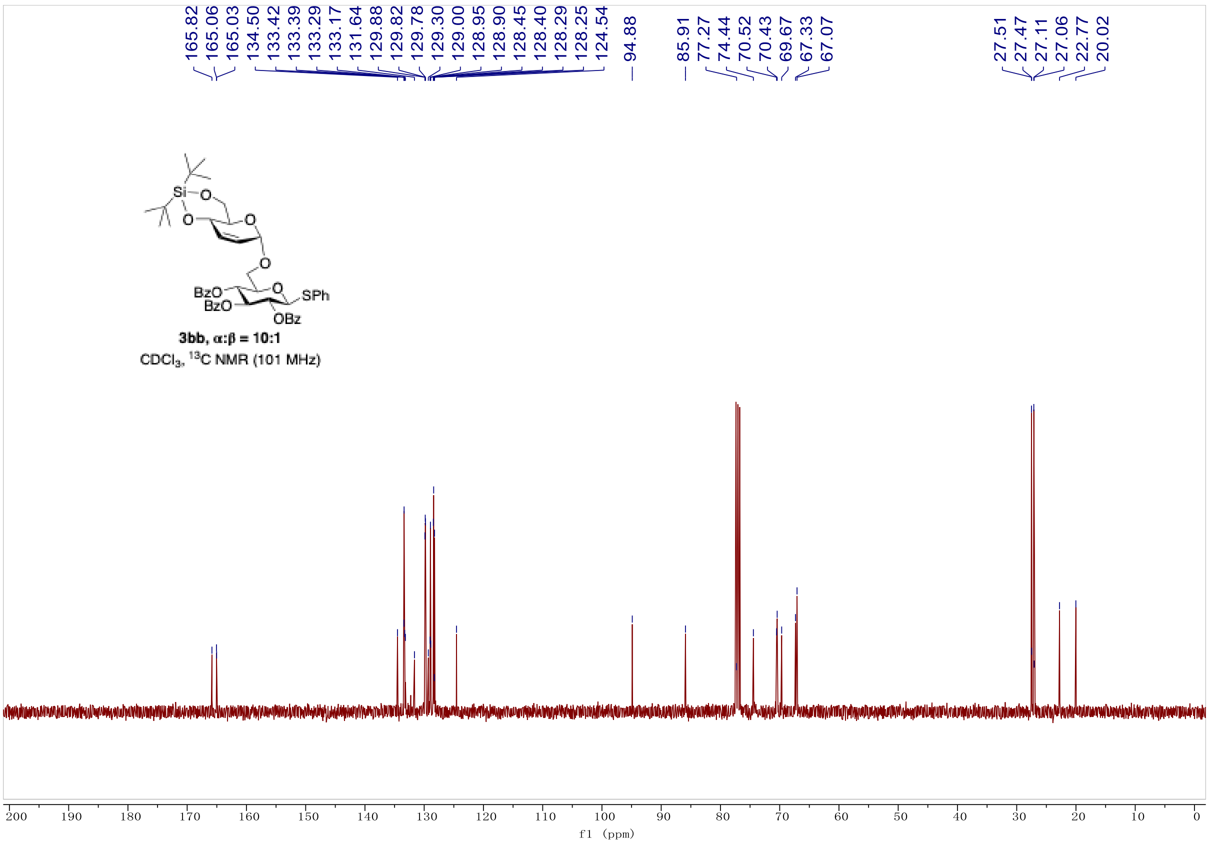

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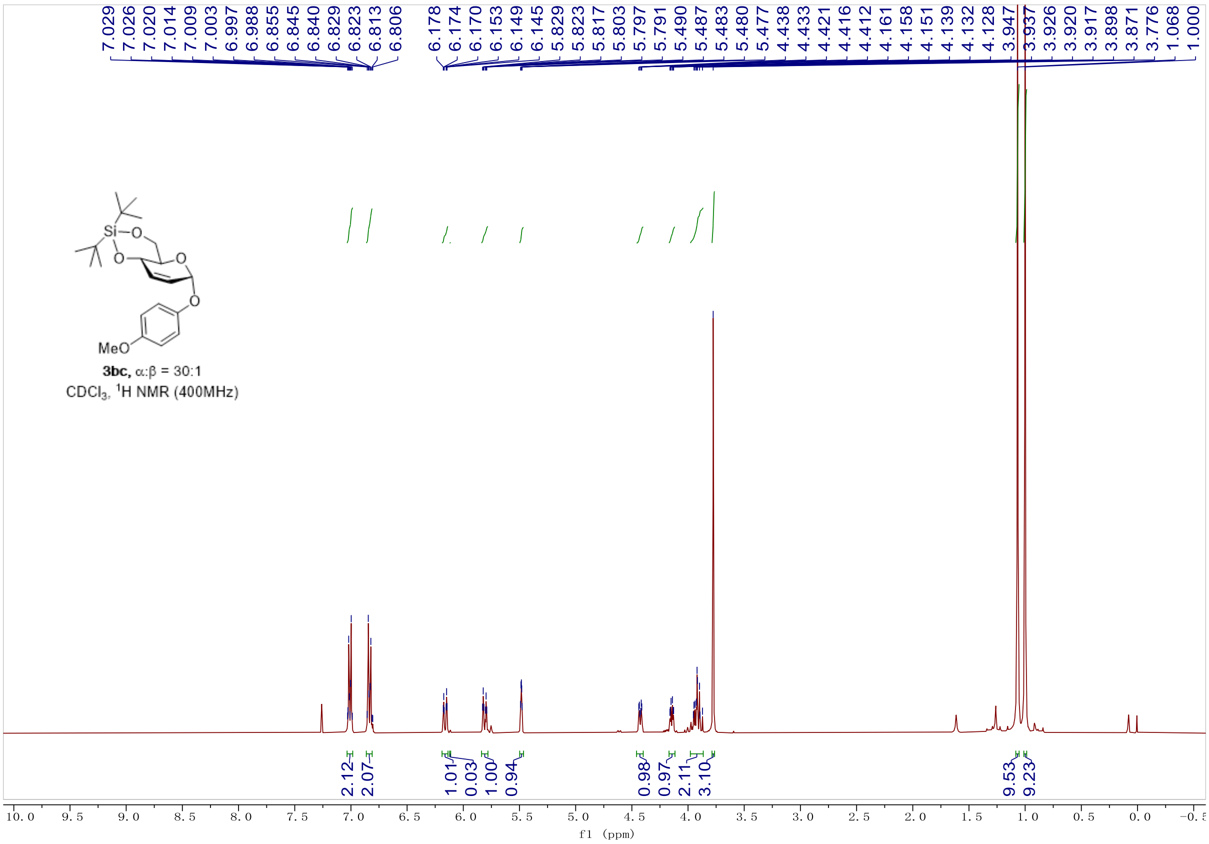

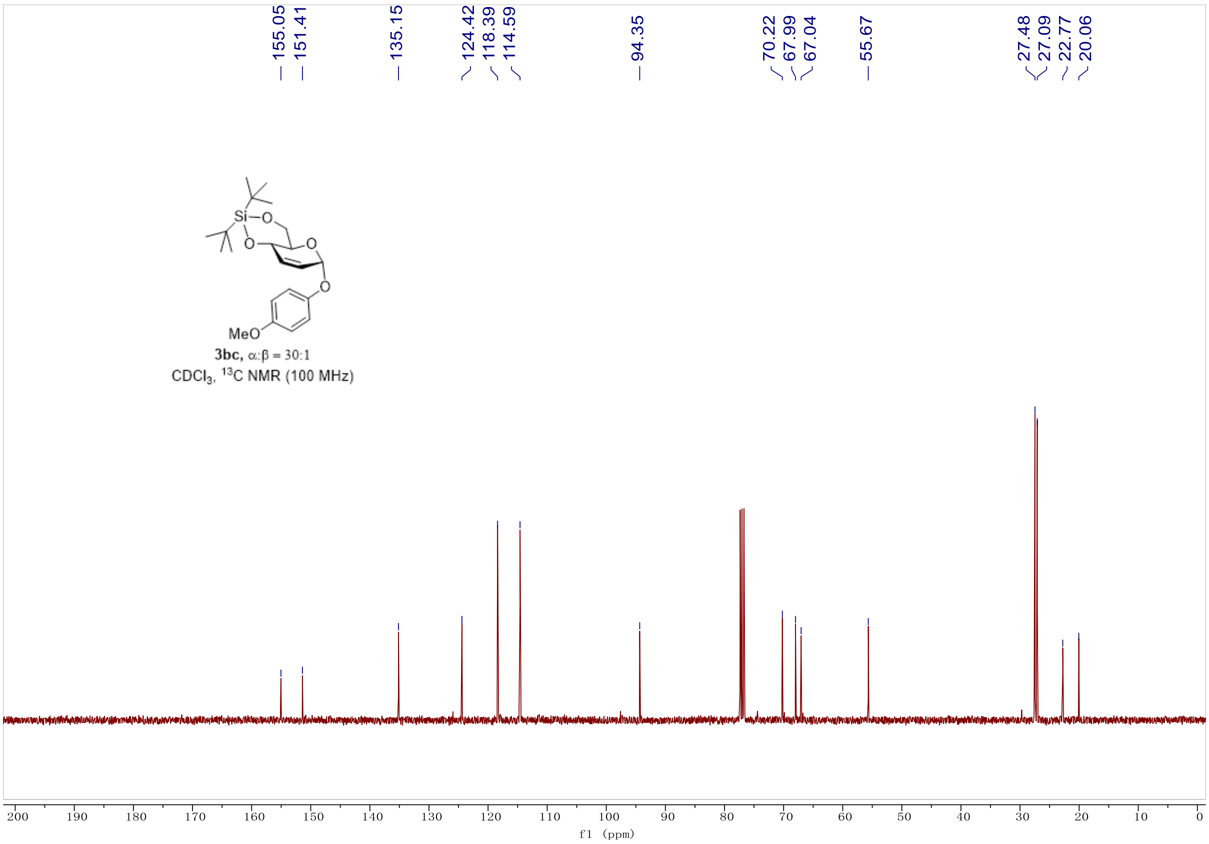

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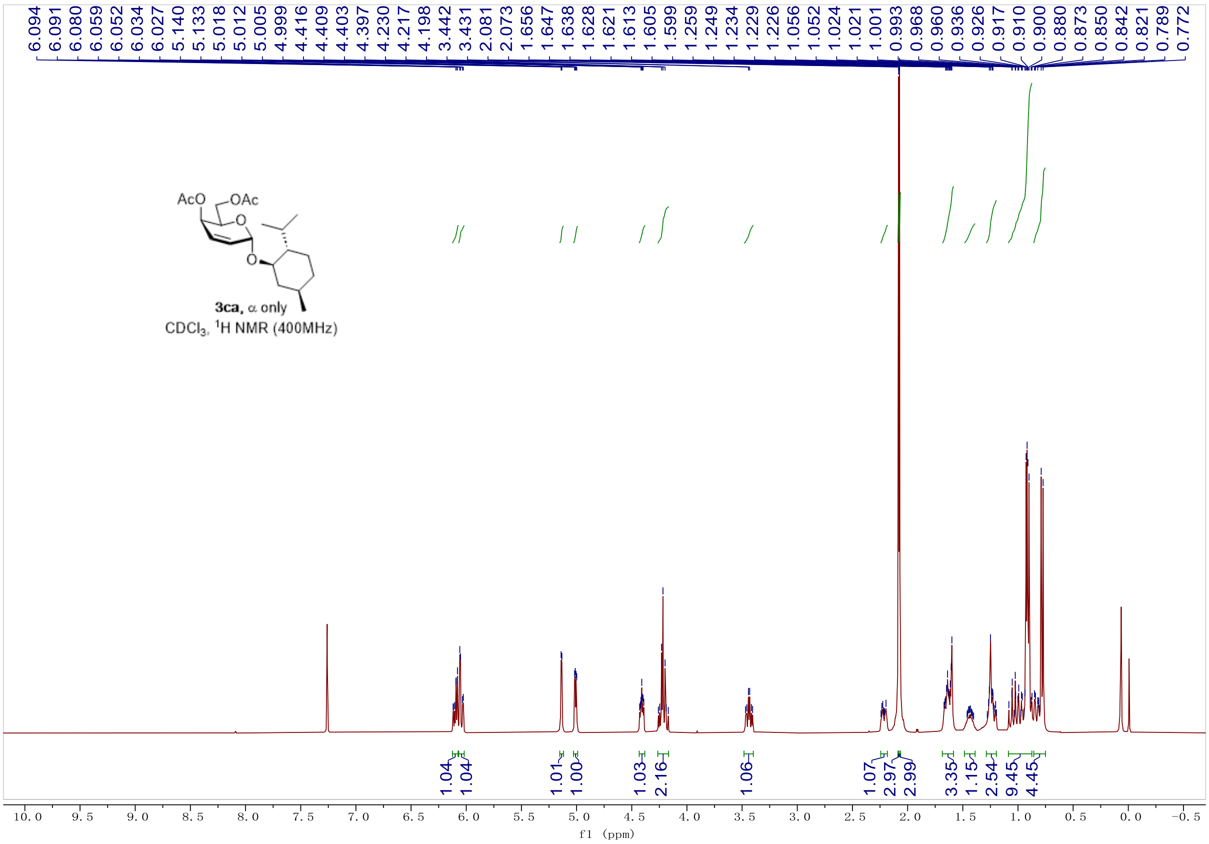

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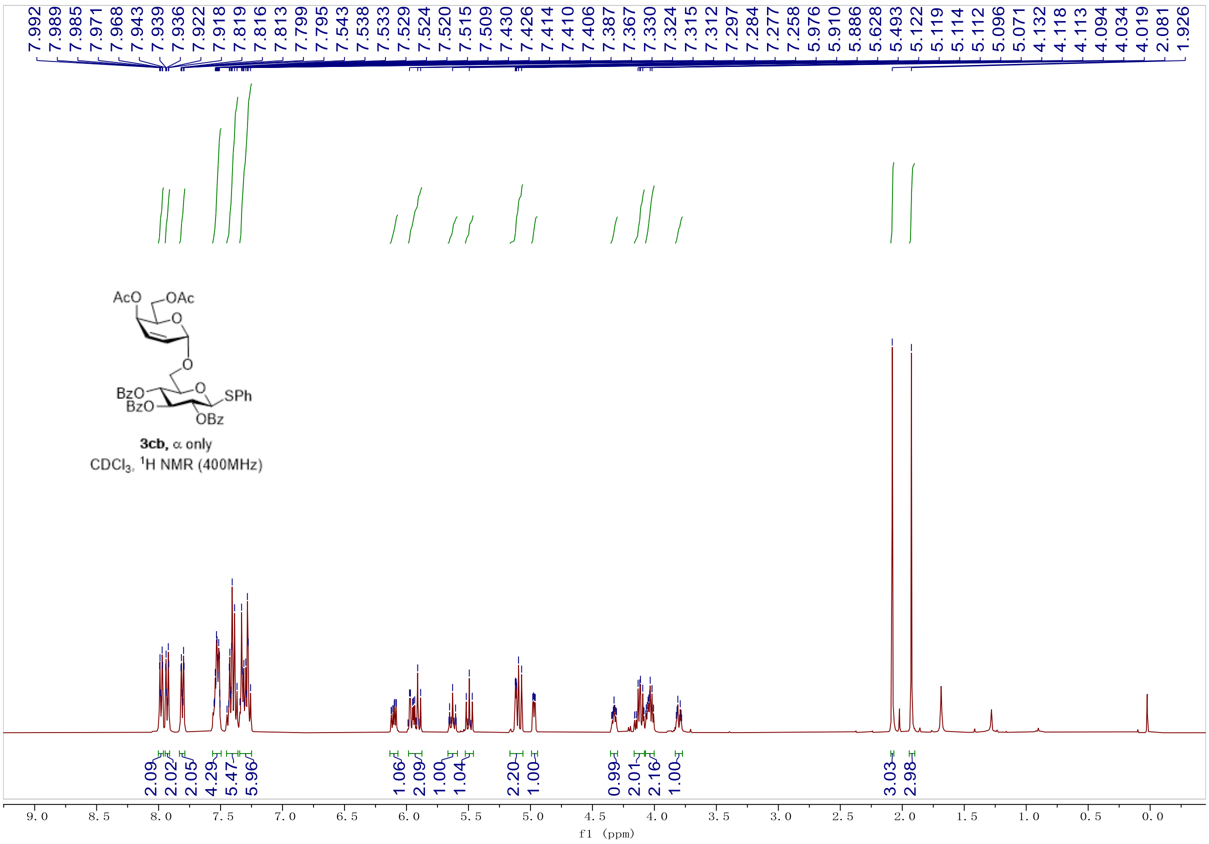

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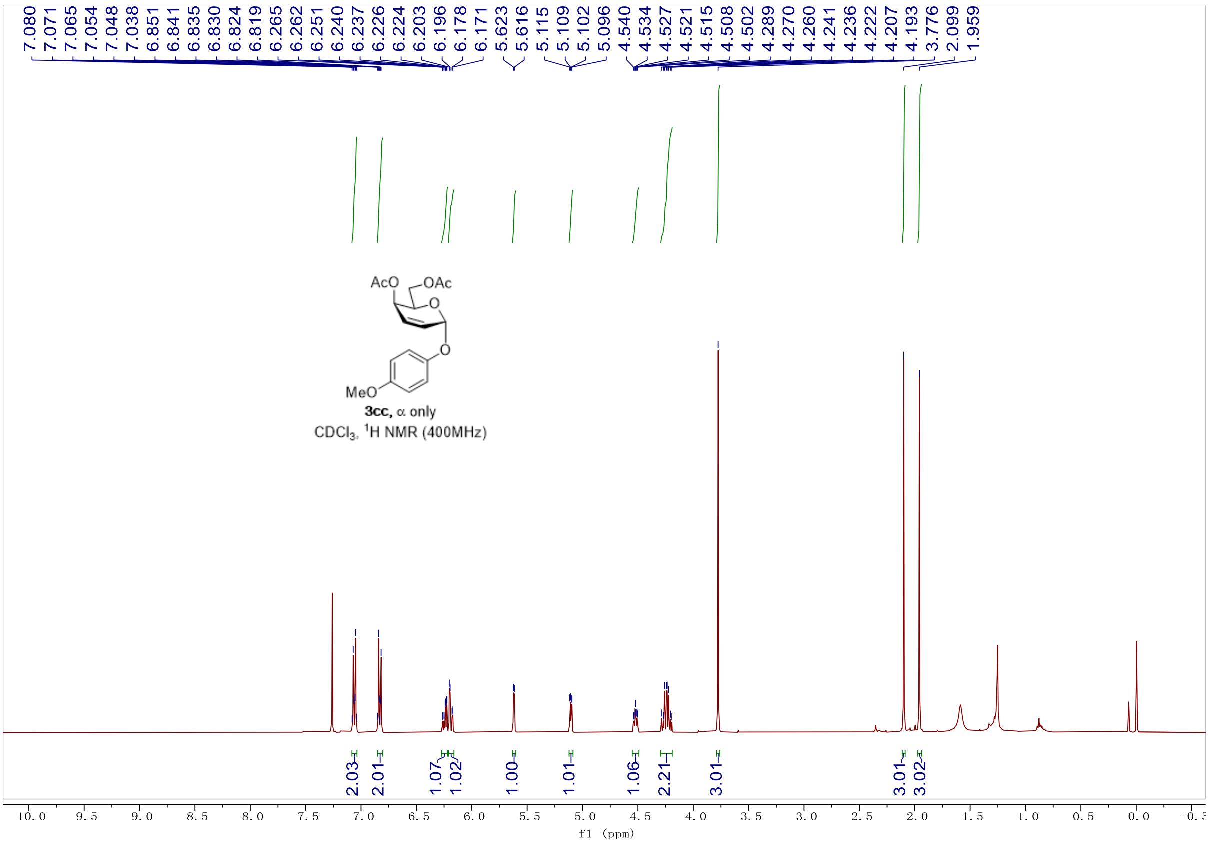

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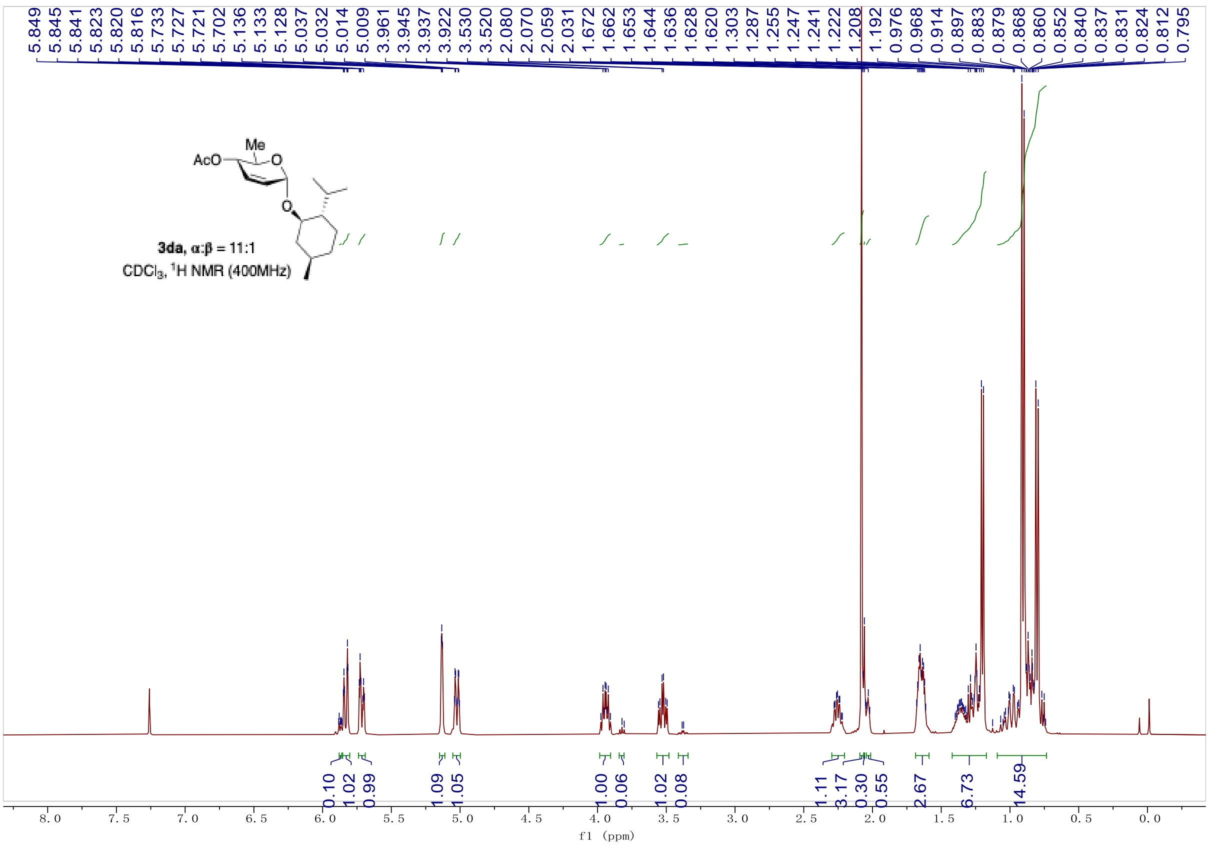
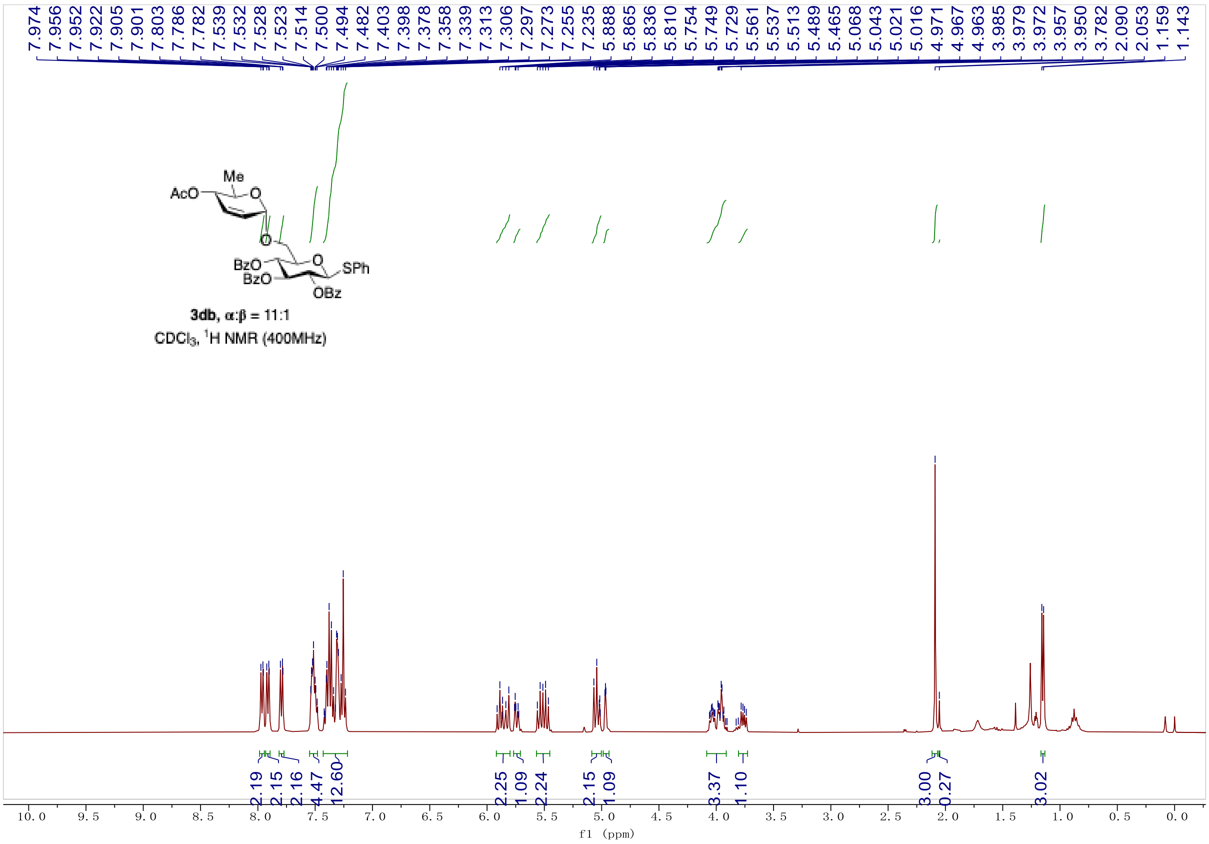
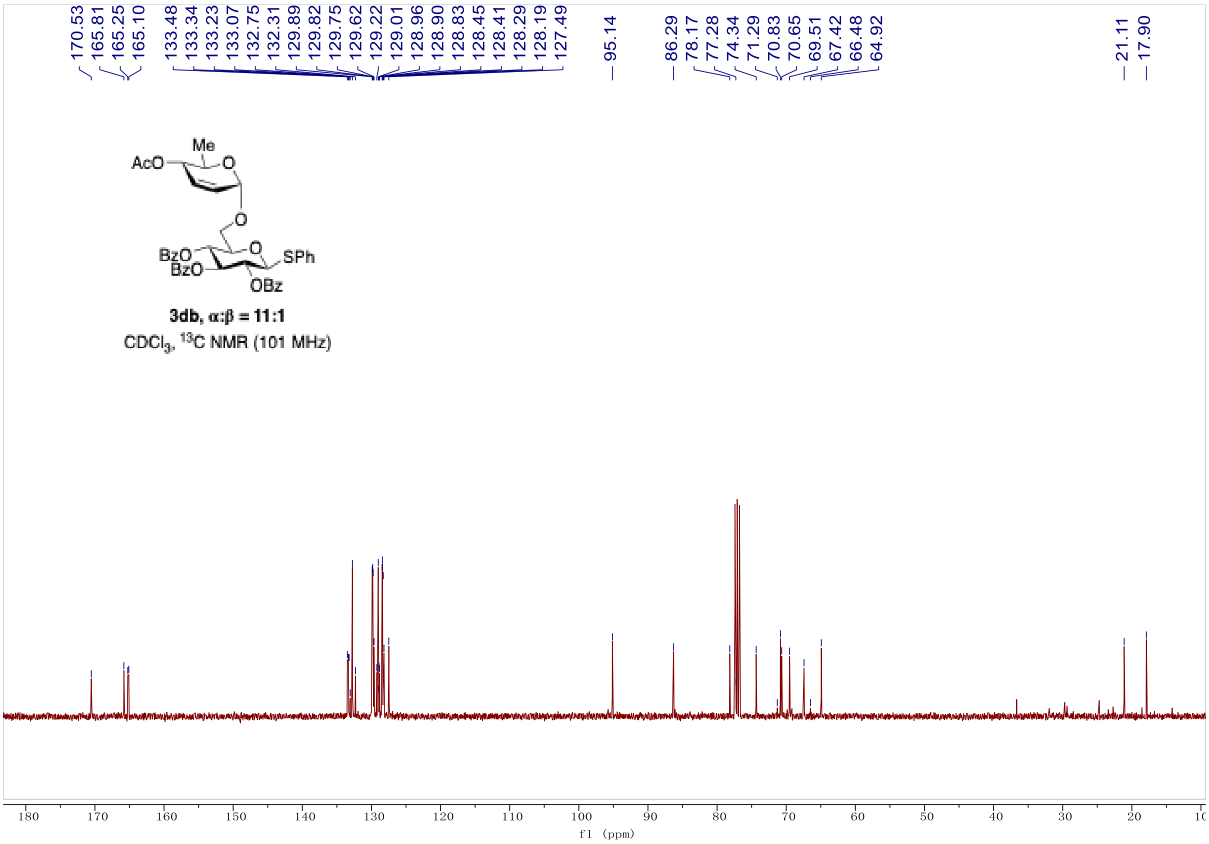


^{1}H and ^{13}C spectra for **3db**





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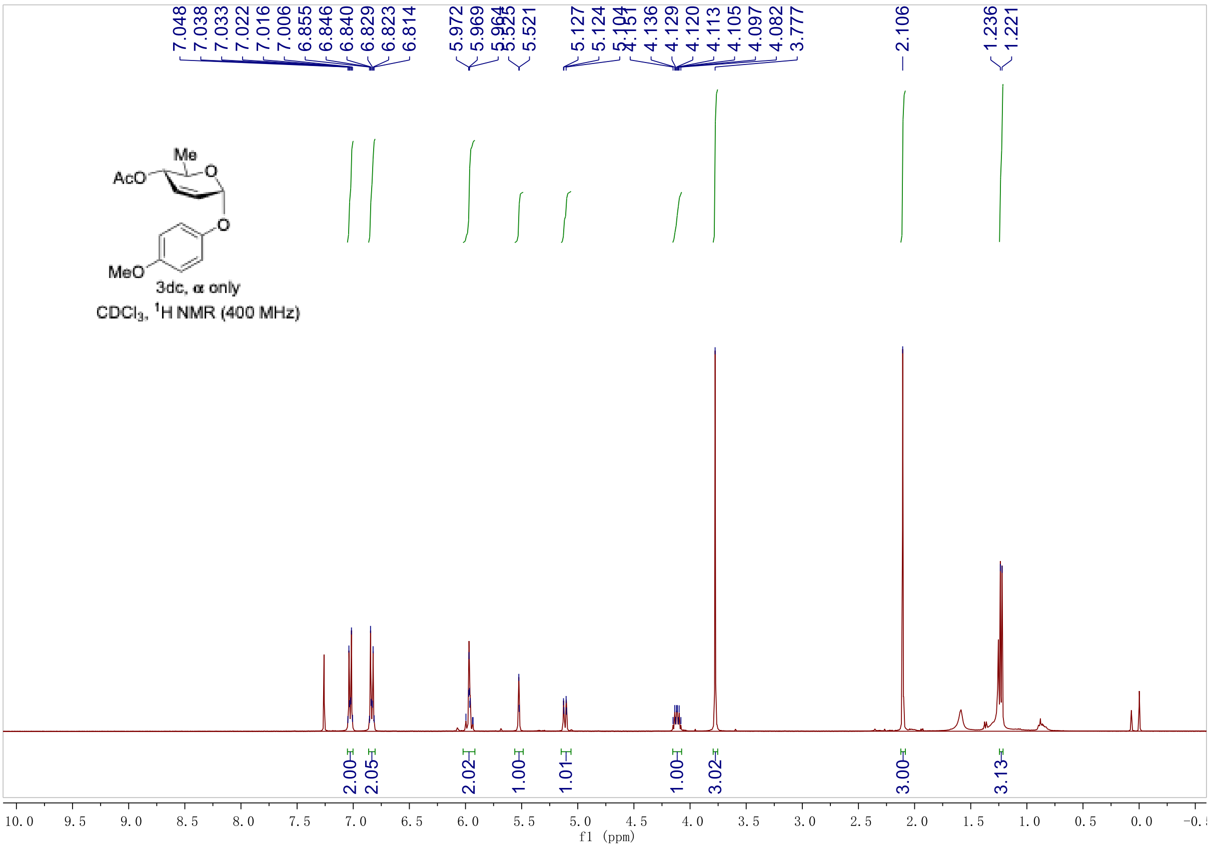
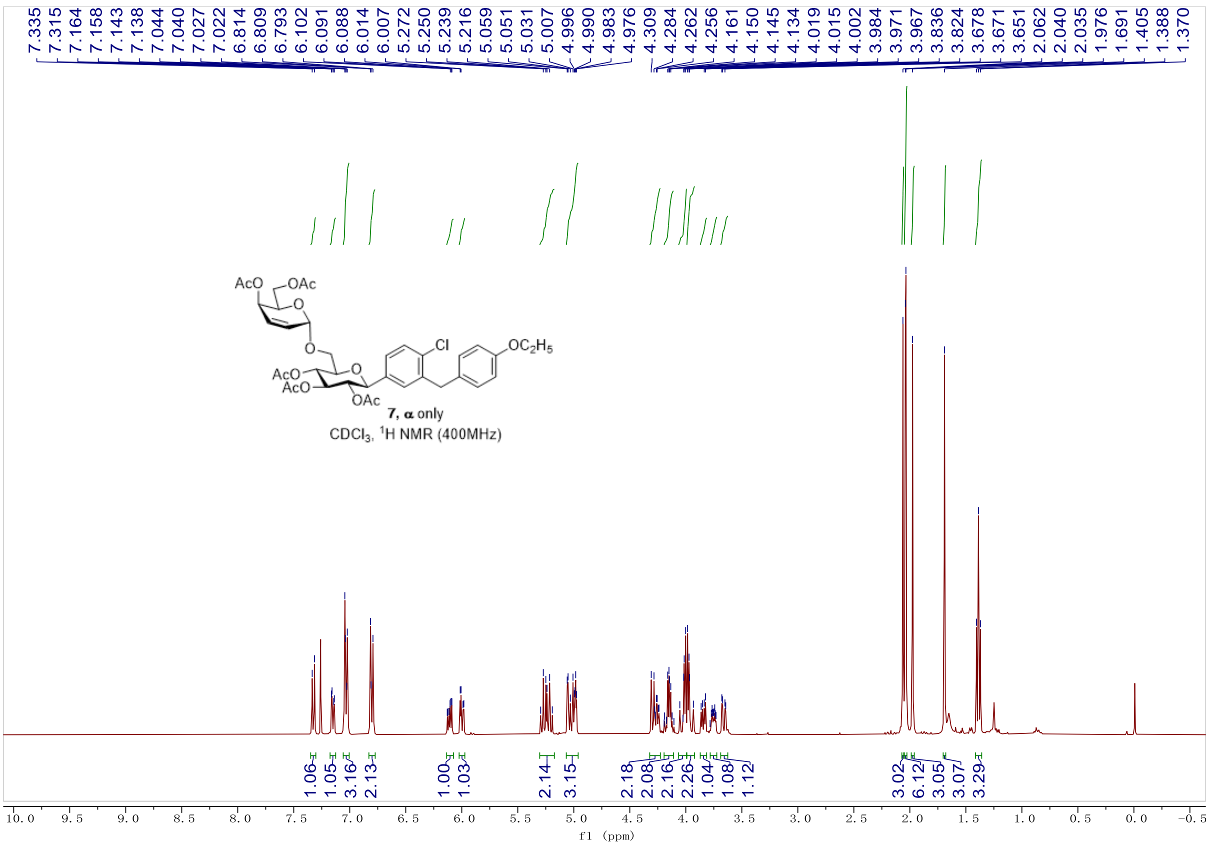
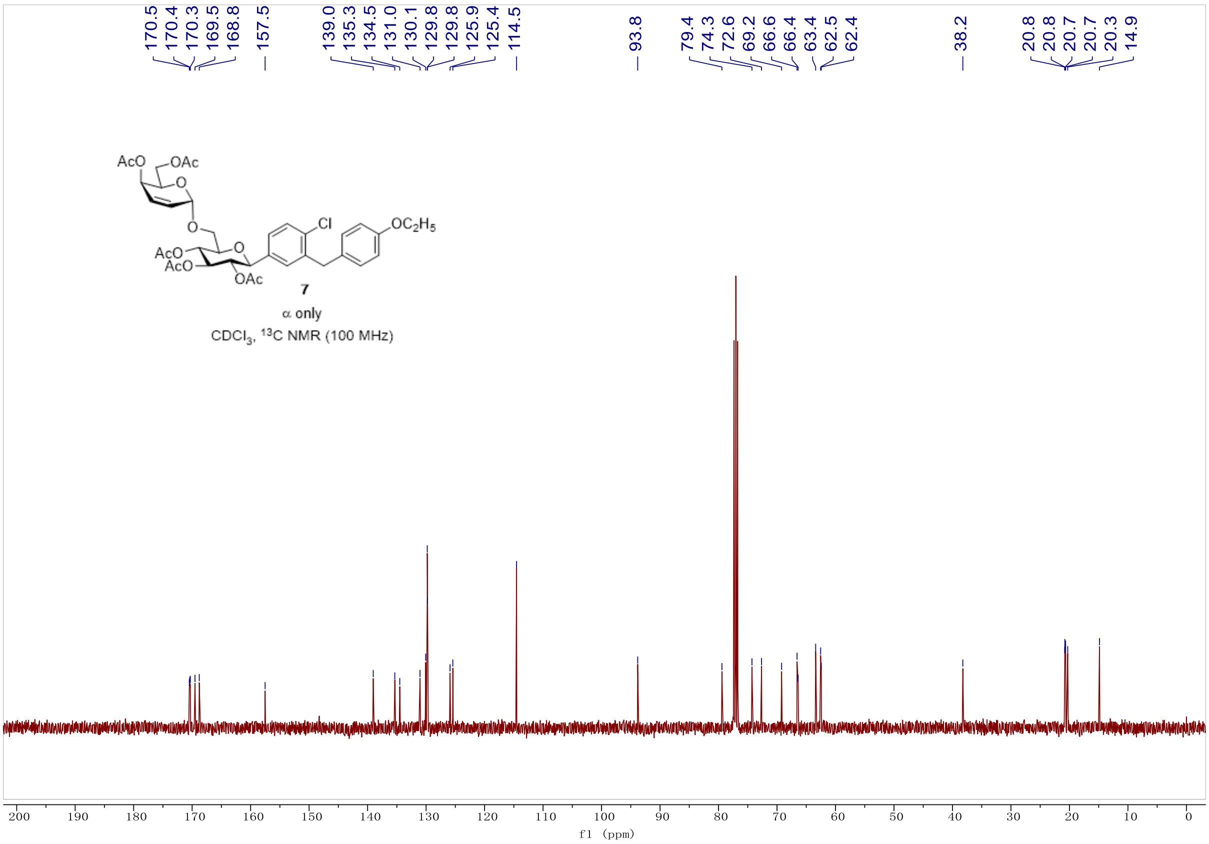


[1]H and[13] C spectra for **7**





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