Supplementary Information

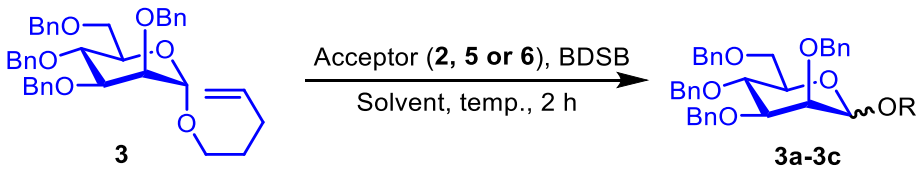
Glycosylation of *n*-Pentenyl Glycosides Using Bromodiethylsulfonium Salt as Activator: Interception of Glycosyl Intermediate by Chloride Ion Transfer

Supanat Buntasana[a] and Panuwat Padungros*[a]

[a]*Green Chemistry for Fine Chemical Production and Environmental Remediation Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand*

*E-mail: panuwat.p@chula.ac.th

I. General procedure for reaction optimization: Investigation of *n*-pentenyl mannoside 3 activated by BDSB (*Table 1*)



In a typical procedure, the *n*-pentenyl mannoside **3** (0.04−0.22 mmol scale), 3 Å molecular sieve, and 0.1 M of solvent (dichloromethane, acetonitrile, nitromethane, or diethyl ether) were added to a round bottom flask and stirred for 30 minutes at room temperature. Then, the flask was moved into the ice bath, followed by the addition of BDSB (1.1 equivalents). After 15 minutes, the reaction was monitored using thin-layer chromatography to confirm complete activation. Next, 5.0 equivalents of glycosyl acceptor **2**, **5**, or 2.0 equivalents of glycosyl acceptor **6** were added and stirred at −60 °C, −40 °C, or 0 °C to room temperature (27–30 °C). The reaction was monitored using thin-layer chromatography until the glycosyl acceptor was consumed. The reaction mixture was quenched by adding saturated aqueous $Na_2S_2O_3$ (1.5 mL) and saturated aqueous $NaHCO_3$ (1.5 mL), extracted with dichloromethane (3 × 10 mL), and washed with brine (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes.

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 1*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (78 mg, 0.13 mmol), BDSB (84 mg, 0.15 mmol), 2,2,2-trifluoroethanol (**2**) (46 µL, 0.64 mmol), and dichloromethane (1.5 mL, [**3**] = 0.09 M) at −60 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (72 mg, 91%, α/β = 2:1).

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 2*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (135 mg, 0.22 mmol), BDSB (146 mg, 0.27 mmol), 2,2,2-trifluoroethanol (**2**) (80 µL, 1.11 mmol), and nitromethane (2.2 mL, [**3**] = 0.10 M) at −60 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (105 mg, 76%, α/β = 2:1).

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 3*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (95 mg, 0.16

mmol), BDSB (103 mg, 0.19 mmol), 2,2,2-trifluoroethanol (**2**) (56 μL, 0.78 mmol), and acetonitrile (1.5 mL, [**3**] = 0.11 M) at −40 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (82 mg, 84%, α/β = 1:1).

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 4*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (113 mg, 0.19 mmol), BDSB (123 mg, 0.22 mmol), 2,2,2-trifluoroethanol (**2**) (60 μL, 0.93 mmol), and diethyl ether (2.0 mL, [**3**] = 0.10 M) at −60 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (53 mg, 45%, α/β = 3:1).

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 5*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (88 mg, 0.14 mmol), BDSB (95 mg, 0.17 mmol), 2,2,2-trifluoroethanol (**2**) (52 μL, 0.72 mmol), and dichloromethane (1.5 mL, [**3**] = 0.10 M) at −40 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (87 mg, 93%, α/β = 2:1).

2,2,2-Trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3a) *Table 1, entry 6*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (78 mg, 0.13 mmol), BDSB (84 mg, 0.15 mmol), 2,2,2-trifluoroethanol (**2**) (46 μL, 0.64 mmol), and dichloromethane (1.3 mL, [**3**] = 0.10 M) at 0 °C to room temperature. After purification, 2,2,2-trifluoroethyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3a**) was obtained as a pale-yellow syrup (72 mg, 91%, α/β = 2:1).

Benzyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (3b) *Table 1, entry 7*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (101 mg, 0.17 mmol), BDSB (110 mg, 0.20 mmol), benzyl alcohol (**5**) (13 μL, 0.13 mmol), and dichloromethane (1.7 mL, [**3**] = 0.10 M) at 0 °C to room temperature. After purification, benzyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranoside (**3b**) was obtained as a colorless syrup (66 mg, 79%, α/β = 1:1) and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**4**) was obtained as a colorless syrup (13 mg, 18%, α).

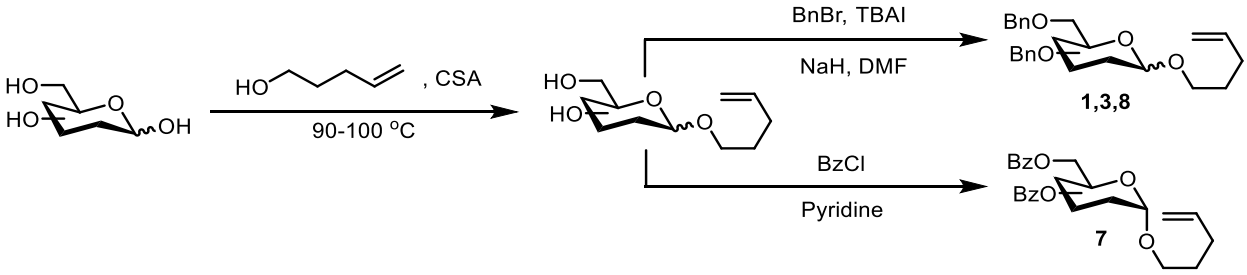
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (3c) *Table 1, entry 8*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (63 mg, 0.12 mmol), BDSB (79 mg, 0.14 mmol), glycosyl acceptor **6** (108 μL, 0.23 mmol), and dichloromethane (1.5 mL, [**3**] = 0.08 M) at 0 °C to room temperature. After purification, methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl)-α-D-glucopyranoside (**3c**) was obtained as a colorless syrup (36 mg, 35%, α/β = 2:1) and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**4**) was obtained as colorless syrup (34 mg, 59%, α).

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl chloride (4) *Table 1, entry 9*

The glycosylation was performed as described in the general procedure. The reaction mixture consisted of *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) (27 mg, 0.04 mmol), BDSB (26 mg, 0.03 mmol), and dichloromethane (1.0 mL, [**3**] = 0.04 M) at 0 °C to room temperature. The reaction mixture was quenched without the addition of a glycosyl acceptor. After purification, 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride (**4**) was obtained as a colorless syrup (18 mg, 75%, α).

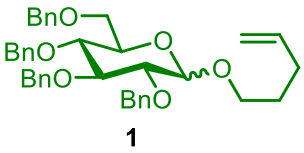
II. Synthesis of *n*-pentenyl glycosides (NPGs)



General procedure: Following the procedure of Fraser-Reid's work,[1] D-camphorsulfonic acid (D-CSA) was added to a mixture of D-sugar and 4-penten-1-ol. The mixture was heated at 90−100 °C for 12 hours under argon. The reaction was extracted with dichloromethane and water. The combined aqueous layer was concentrated to dryness in a rotary evaporator. The crude mixture was purified by column chromatography on silica gel using gradient elution with ethyl acetate and methanol. Then, this material was azeotroped with toluene and dissolved in DMF. BnBr and TBAI were added to the reaction mixture and moved the flask to an ice bath (0 °C). NaH was added at 0 °C to room temperature and stirred for 16 hours. The reaction was monitored using thin-layer chromatography until the starting material was consumed. The reaction mixture was quenched by adding saturated aqueous NH_4Cl, extracted with diethyl ether, and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary

evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes.

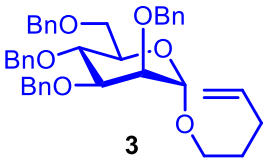
_n_-Pentenyl 2,3,4,6-tetra-_O_-benzyl-α/β-D-glucopyranoside (1)



1

The synthesis was carried out as described in the general procedure. D-(+)-glucose (1.43 g, 7.9 mmol), 4-penten-1-ol (5.0 mL), and D-CSA (18 mg, 0.08 mmol). After purification, the intermediate was obtained as colorless syrup 822 mg (42% yield). Next, this material, TBAI (74 mg, 0.33 mmol), BnBr (1.8 mL, 14.9 mmol), NaH (636 mg, 26.5 mmol), and DMF (0.3 M, 15 mL). After purification, *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (**1**) was provided as a colorless syrup (1.52 g, 75%, α/β = 1: 1). The spectroscopic data of **1** matched that reported in the literature.[2]

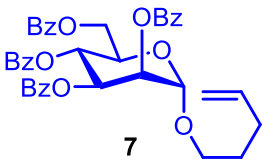
_n_-Pentenyl 2,3,4,6-tetra-_O_-benzyl-α-D-mannopyranoside (3)



3

The synthesis was carried out as described in the general procedure. D-(+)-mannose (1.33 g, 7.4 mmol), 4-penten-1-ol (5 mL), and D-CSA (17 mg, 0.07 mmol). After purification, the intermediate was obtained as colorless syrup 1.14 g (62% yield). Next, this material, TBAI (103 mg, 0.46 mmol), BnBr (2.46 mL, 20.7 mmol), NaH (882 mg, 36.7 mmol), and DMF (0.2 M, 23 mL). After purification, *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (**3**) was provided as a colorless syrup 2.13 g in 76% yield. The spectroscopic data of **3** matched that reported in the literature.[3]

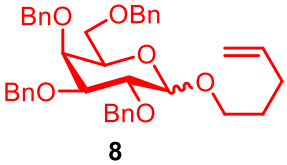
_n_-Pentenyl 2,3,4,6-tetra-_O_-benzoyl-α-D-mannopyranoside (7)



7

The synthesis was carried out as described in the general procedure. D-(+)-mannose (1.75 g, 9.7 mmol), 4-penten-1-ol (5 mL), and D-CSA (23 mg, 0.1 mmol). After workup, the intermediate was obtained as colorless syrup. Next, this material, BzCl (4.9 mL, 48.5 mmol), and DMF (0.3 M, 32 mL). After purification, *n*-pentenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**7**) was provided as colorless syrup 0.95 g in 15% yield (2 steps). The spectroscopic data of **7** matched that reported in the literature.[4]

_n_-Pentenyl 2,3,4,6-tetra-_O_-benzyl-α/β-D-galactopyranoside (8)

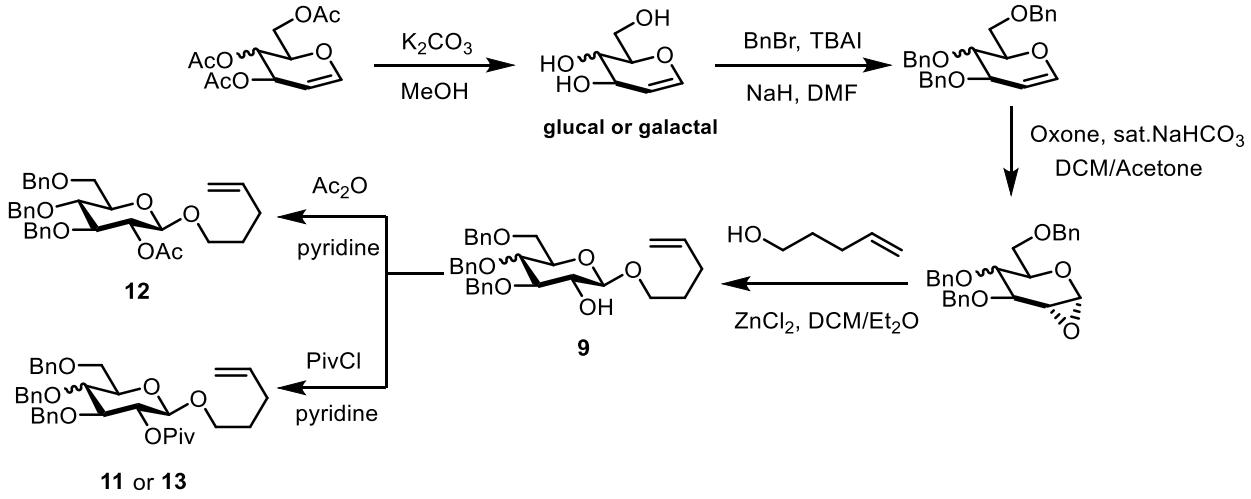


8

The synthesis was carried out as described in the general procedure. D-(+)-galactose (1.66 g, 9.2 mmol), 4-penten-1-ol (6.4 mL), and D-CSA (22 mg, 0.09 mmol). After purification, the intermediate was obtained as colorless syrup 1.24 g (54% yield). Next, this material (756 mg, 3.0 mmol), TBAI (56 mg, 0.15 mmol), BnBr (1.81 mL, 15.2 mmol), NaH (584 mg, 24.3 mmol), and DMF (0.3 M, 10.1 mL). After purification, *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-

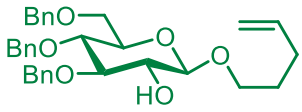
galactopyranoside (**8**) was provided as a colorless syrup 776 g in 42% yield (α/β = 3: 1). The spectroscopic data of **8** matched that reported in the literature.[5]

III. Synthesis of *n*-pentenyl glycosides (NPGs) equipped with 2-*O*-acyl group



General procedure: Following the procedure of Andrade's work,[6] 3,4,6-tri-*O*-acetyl-D-glucal or 3,4,6-tri-*O*-acetyl-D-glalactal was deprotected by using K_2CO_3 in methanol to obtain glucal or galactal. Next, the crude mixture was azeotroped with toluene and then dissolved in DMF. TBAI and BnBr were added to the reaction mixture and moved to an ice bath (0 °C). NaH was added at 0 °C to room temperature for 16 hours. The reaction was monitored using thin-layer chromatography until the starting material was consumed. The reaction mixture was quenched by adding saturated aqueous NH_4Cl, extracted with diethyl ether, and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude mixture was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes. The protected glucal/galactal was followed by an epoxidation reaction by Oxone and acetone in saturated $NaHCO_3$ and CH_2Cl_2.[7] After the starting material was consumed, the solution was extracted with dichloromethane and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude mixture was azeotroped with toluene, then dissolved in dried CH_2Cl_2. 4-Penten-1-ol was added to the reaction mixture, and sublimated $ZnCl_2$ was dissolved in Et_2O, then added into the reaction mixture at 0 °C and stirred for 16 hours. Next, the reaction was workup with sat. $NaHCO_3$, was extracted with dichloromethane and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude mixture was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes.

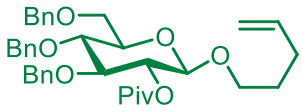
***n*-Pentenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (9)**



9

The synthesis was carried out as described in the general procedure. The crude after epoxidation by Oxone and acetone (3.50 mmol) was dissolved in DCM (0.1 M, 35 mL), then 4-penten-1-ol (0.75 mL, 7.0 mmol) and $ZnCl_2$ (956 mg, 7.0 mmol) were added to the reaction mixture at 0 °C and stirred for 16 hours. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes. *n*-Pentenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**9**) was obtained as a colorless syrup (998 mg, 58% over 2 steps). The spectroscopic data of **9** matched that reported in the literature.[8]

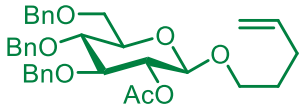
***n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (11)**



11

The synthesis was carried out as described in the general procedure. *n*-Pentenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**9**) (374 mg, 0.72 mmol) was azeotroped with toluene then dissolved in pyridine (0.1 M, 7.2 mL). After that, PivCl (440 µL, 3.60 mmol) was added to the reaction mixture at 0 °C and stirred for 16 hours. The reaction was workup with sat. $NaHCO_3$, extracted with dichloromethane, and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes. *n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**11**) was obtained as a colorless syrup (110 mg, 49%).

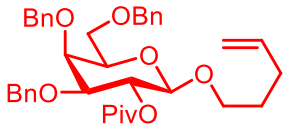
***n*-Pentenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (12)**



12

The synthesis was carried out as described in the general procedure. *n*-Pentenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**9**) (487 mg, 0.94 mmol) was azeotroped with toluene then dissolved in pyridine (0.1 M, 9.5 mL). After that, Ac_2O (440 µL, 4.70 mmol) was added to the reaction mixture at 0 °C and stirred for 16 hours. The reaction was workup with sat. $NaHCO_3$, extracted with dichloromethane, and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes. *n*-Pentenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**12**) was obtained as a colorless syrup (385 mg, 73%).

***n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (13)**

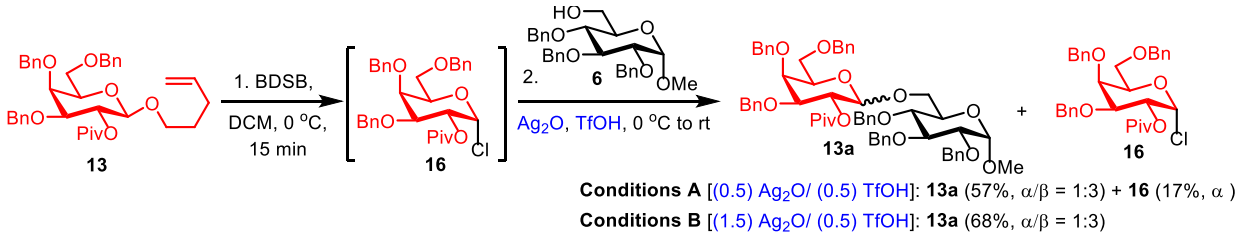


13

The synthesis was carried out as described in the general procedure. *n*-Pentenyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (362 mg, 0.70 mmol) was azeotroped with toluene then dissolved in pyridine (0.3 M, 1.5 mL). After that, PivCl (421 µL, 3.49 mmol) was added to the reaction mixture

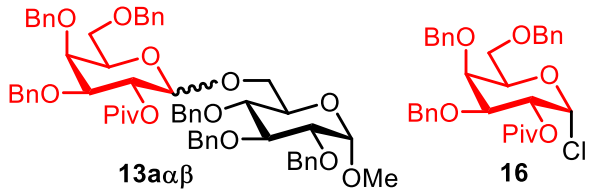
at 0 °C and stirred for 16 hours. The reaction was workup with sat. $NaHCO_3$, extracted with dichloromethane, and washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes. *n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**13**) was obtained as a white solid (303 mg, 72%).

IV. General procedure for Ag_2O/TfOH-mediated glycosylation *(Scheme 3)*



General procedure: Following the reported procedure of Demchenko's work,[9] *n*-pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**13**) (0.06–0.07 mmol), 3 Å molecular sieve, dichloromethane, [c] = 0.1 M were added to a round bottom flask and stirred under argon for 30 minutes at room temperature. Then, the flask was moved into the ice bath, followed by the addition of BDSB (1.1 equivalents). After 15 minutes, the reaction was monitored using thin-layer chromatography (TLC) to confirm complete activation, and the formation of galactosyl chloride **16** was observed on TLC. Next, glycosyl acceptor **6** (0.8 equivalents) and silver oxide (0.5/1.5 equivalents) were added and stirred for 10 minutes at 0 °C. After this time, TfOH (0.5 equivalents) was added, and the mixture was stirred at 0 °C to room temperature. The reaction was monitored using TLC until the glycosyl acceptor was consumed (at 15 min, 30 min, 1 h, 2 h, 3 h, 5 h, and 16 h). The reaction mixture was quenched by adding saturated aqueous $Na_2S_2O_3$ (1.5 mL) and saturated aqueous $NaHCO_3$ (1.5 mL), extracted with dichloromethane (3 × 10 mL) and washed with brine (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. The crude product was purified by column chromatography on silica gel using gradient elution with ethyl acetate and hexanes.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (13a)



Conditions A: the synthesis was carried out as described in the general procedure. *n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**13**) (40 mg, 0.07 mmol), BDSB (40 mg, 0.07 mmol), glycosyl acceptor **6** (22 mg, 0.05 mmol), silver oxide (8 mg, 0.03 mmol, **0.5 equivalents**), TfOH (3 μL, 0.03 mmol), and

dichloromethane (0.7 mL). The reaction was monitored by TLC (20% ethyl acetate in hexanes; *p*-anisaldehyde, R_f = 0.30). The crude mixture was purified by column chromatography using gradient elution with 5–20% ethyl acetate in hexanes as the eluent. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (**13a**) was obtained as a colorless syrup (27 mg, 57%, α/β = 1:3) and 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**16**) (6 mg, 17%, α).

16: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.37 – 7.25 (m, 15H), 6.39 (d, *J* = 3.9 Hz, 1H, **H-1**), 5.36 (m, 1H, **H-2**), 4.94 (d, *J* = 11.3 Hz, 1H), 4.78 – 4.66 (m, 2H), 4.55 (d, *J* = 11.3 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* = 11.8 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.05 – 4.00 (m, 2H), 3.57 (m, 2H), 1.23 (s, 9H).

Conditions B: the synthesis was carried out as described in the general procedure. *n*-Pentenyl 2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**13**) (35 mg, 0.06 mmol), BDSB (35 mg, 0.06 mmol), glycosyl acceptor **6** (23 mg, 0.05 mmol), silver oxide (20 mg, 0.09 mmol, **1.5 equivalents**), TfOH (3 μL, 0.03 mmol), and dichloromethane (0.6 mL). The crude mixture was purified by column chromatography using gradient elution with 5–20% ethyl acetate in hexanes as the eluent. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-*O*-pivaloyl-3,4,6-tri-*O*-benzyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (**13a**) was obtained as a colorless syrup (33 mg, 68%, α/β = 1:3).

V. NMR Spectra of the NPGs and products

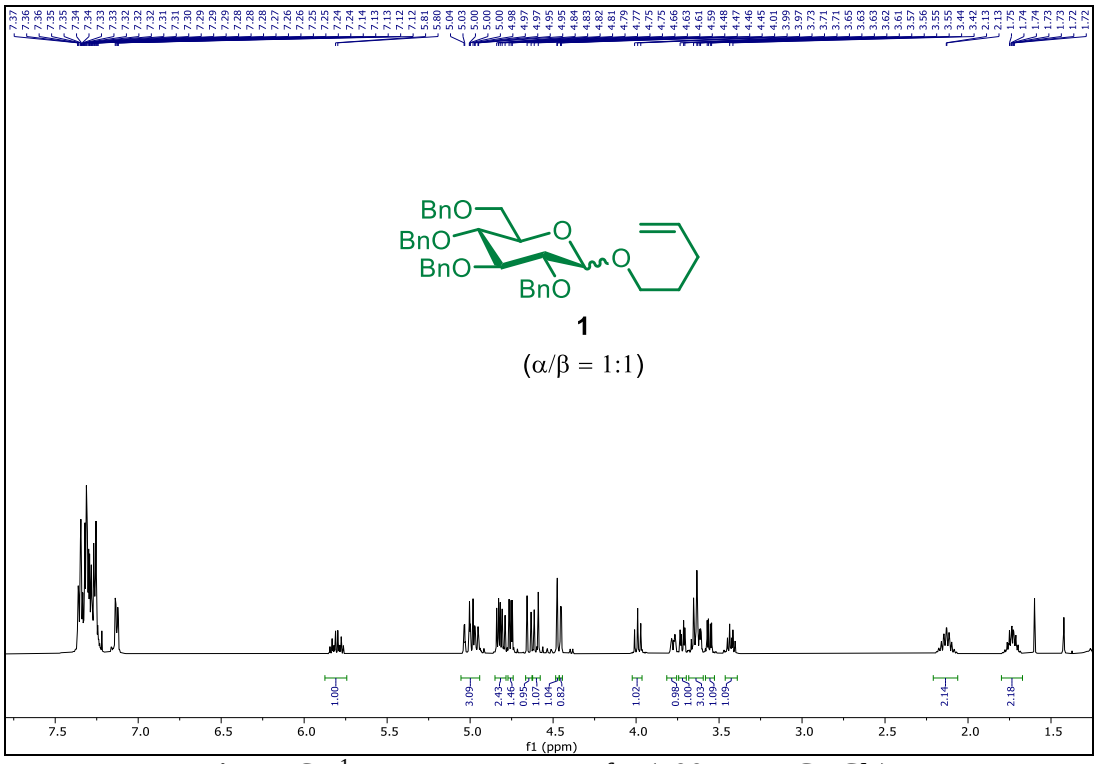


Figure S1 ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$).

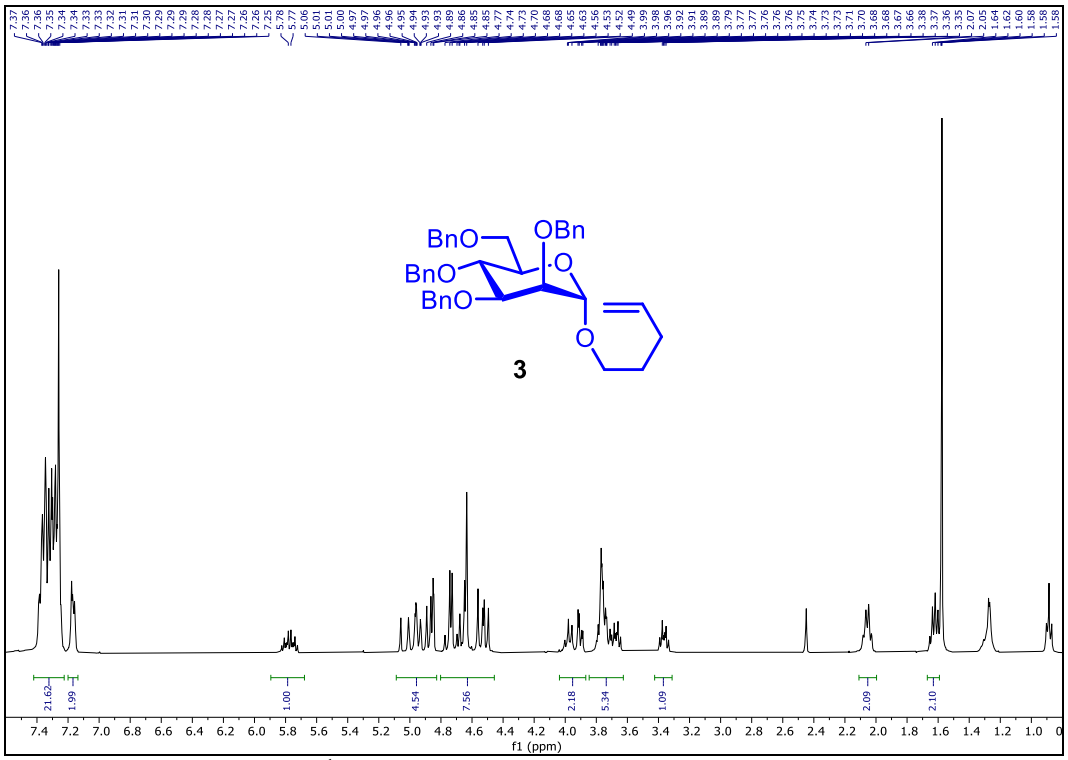


Figure S2 ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

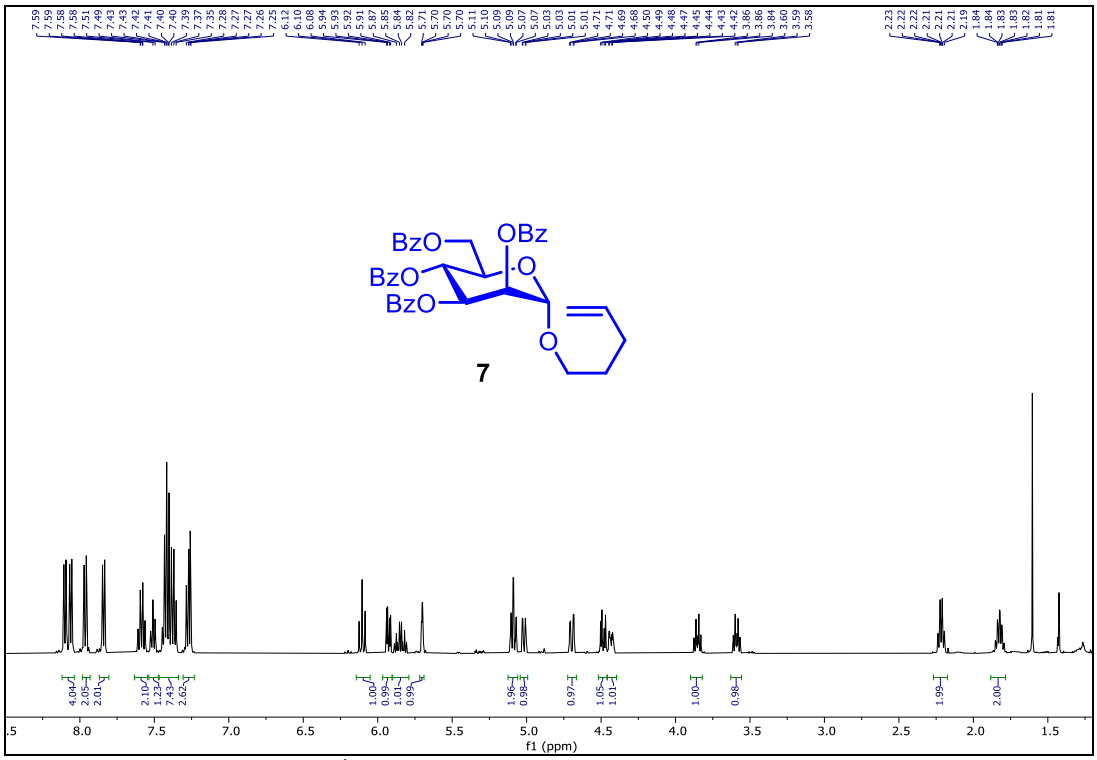


Figure S3 ^{1}H NMR spectrum of **7** (500 MHz, $CDCl_3$).

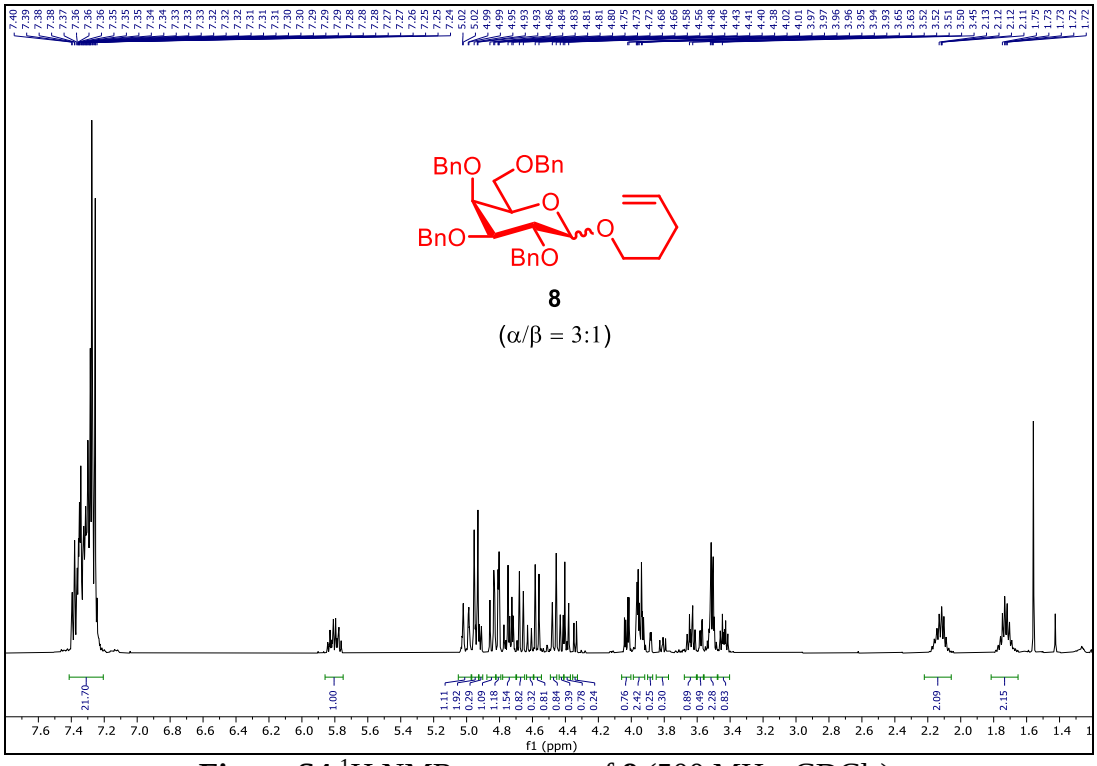


Figure S4 ^{1}H NMR spectrum of **8** (500 MHz, $CDCl_3$).

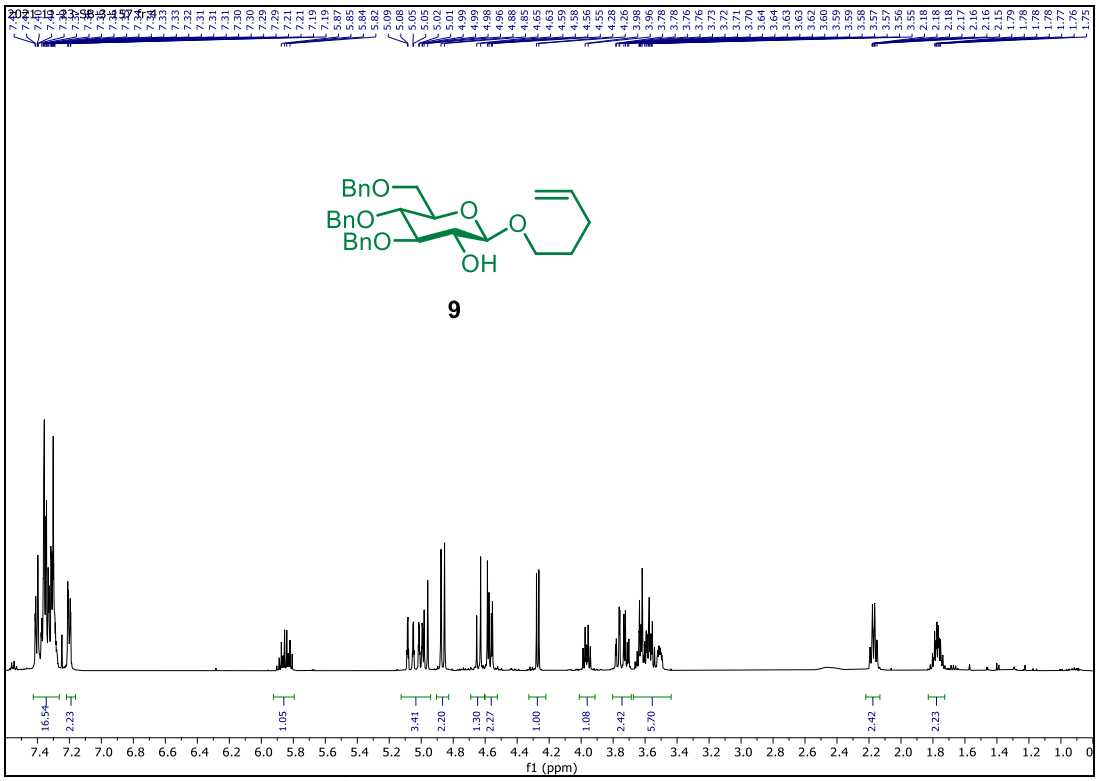


Figure S5 ^{1}H NMR spectrum of **9** (500 MHz, $CDCl_3$).

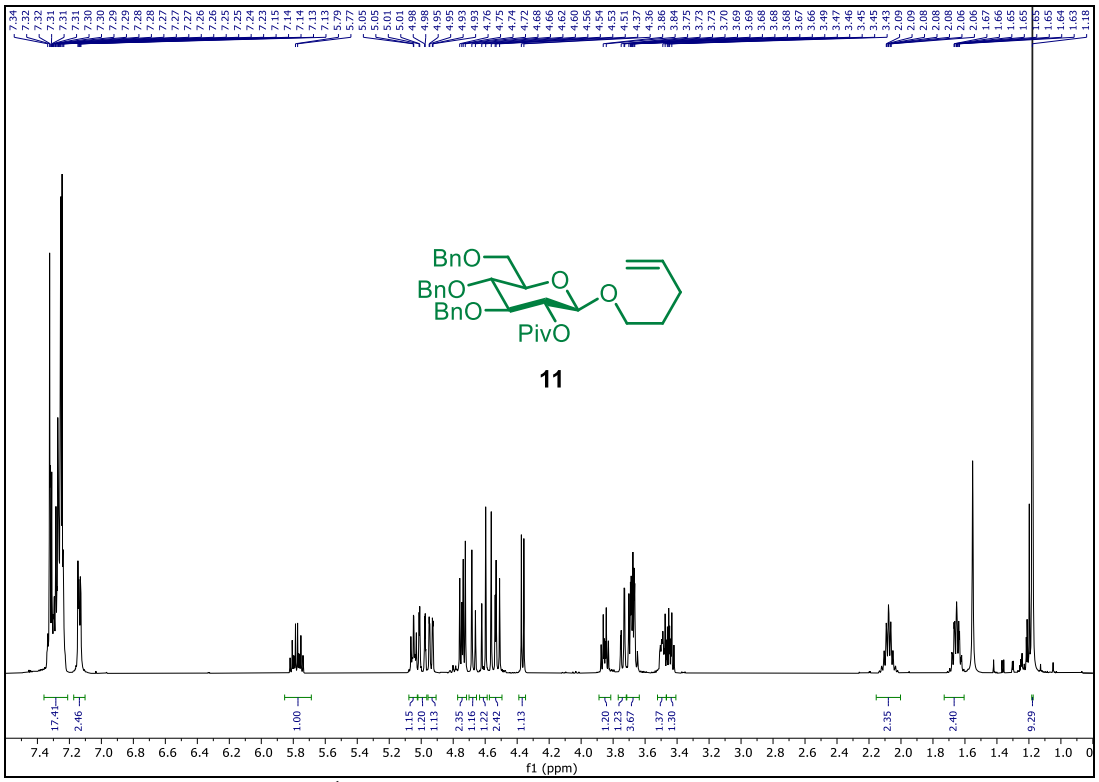


Figure S6 ^{1}H NMR spectrum of **11** (500 MHz, $CDCl_3$).

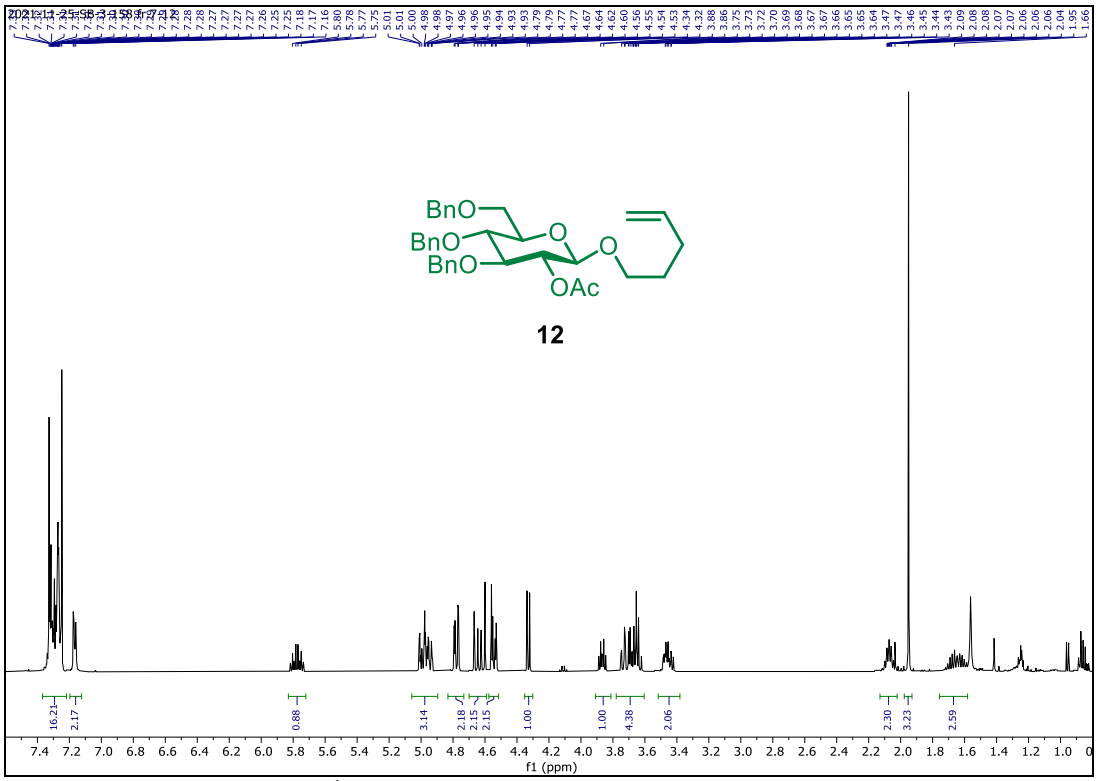


Figure S7 ^{1}H NMR spectrum of **12** (500 MHz, $CDCl_3$).

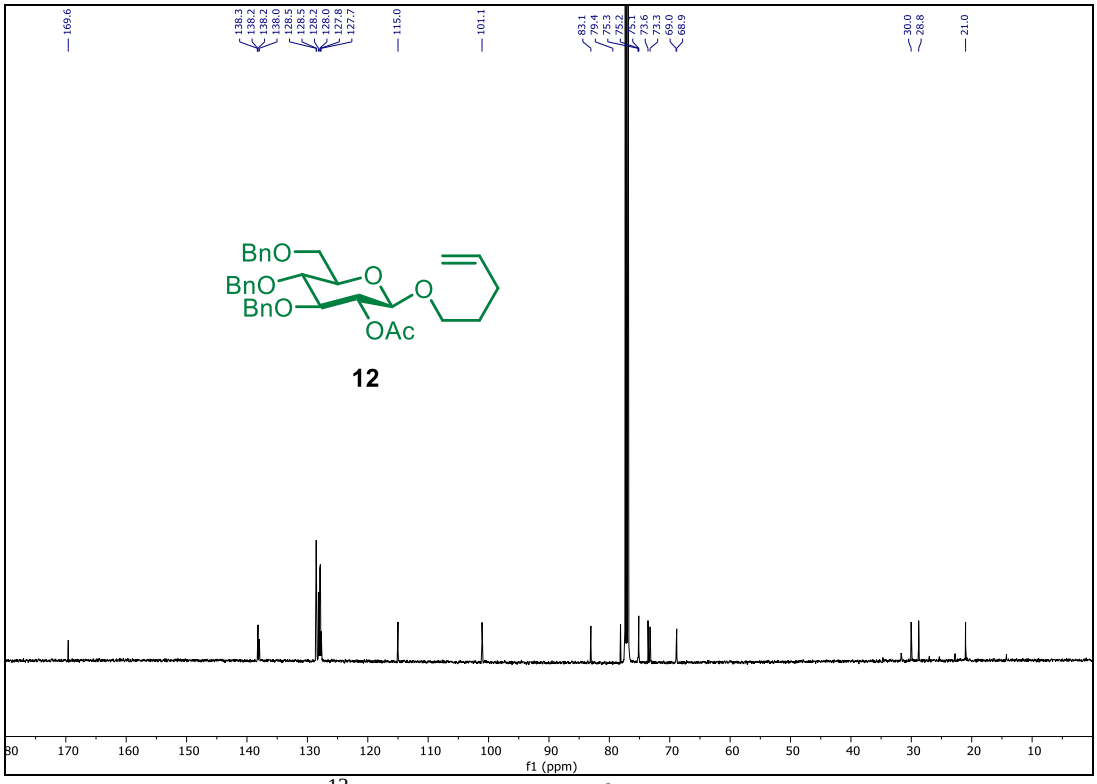


Figure S8 ^{13}C NMR spectrum of **12** (126 MHz, $CDCl_3$).

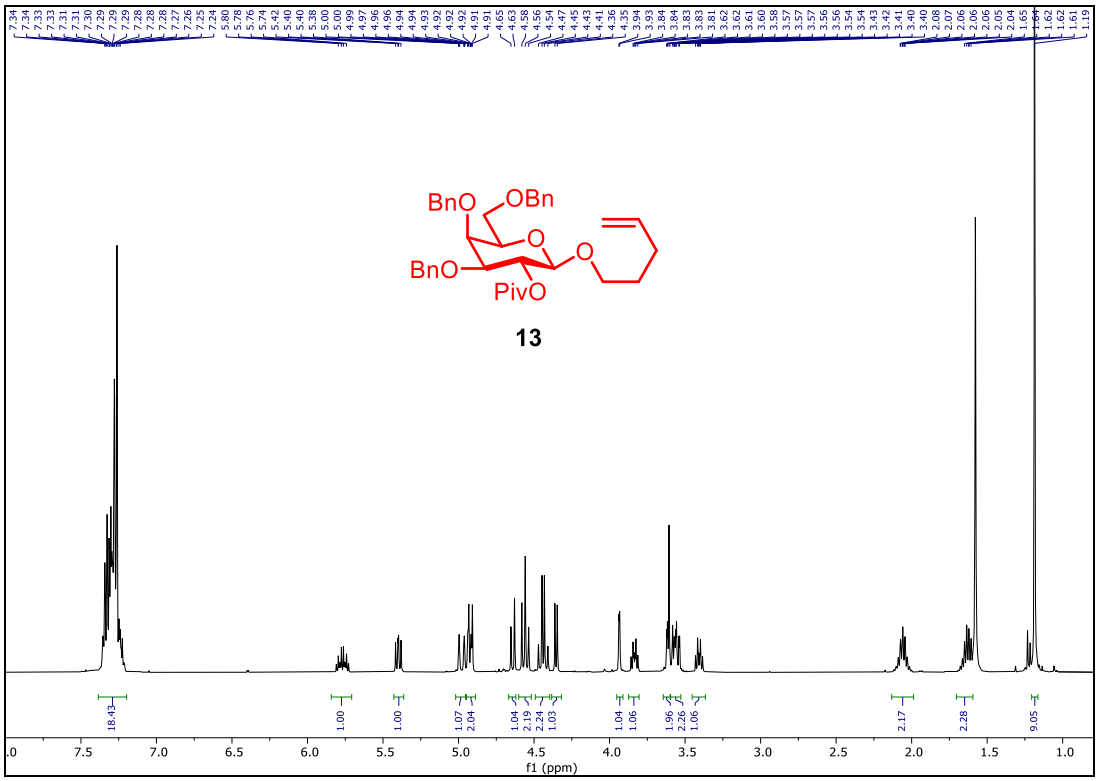


Figure S9 ^{1}H NMR spectrum of **13** (500 MHz, $CDCl_3$).

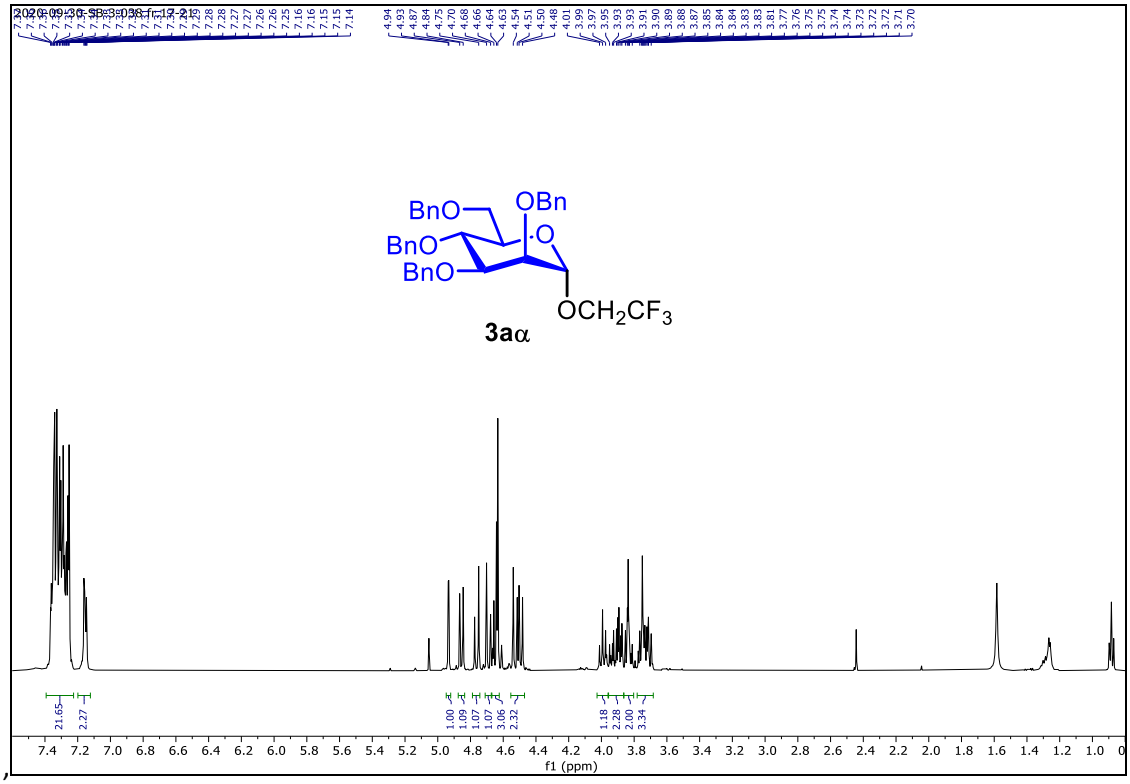


Figure S10 ^{1}H NMR spectrum of **3aα** (500 MHz, $CDCl_3$).

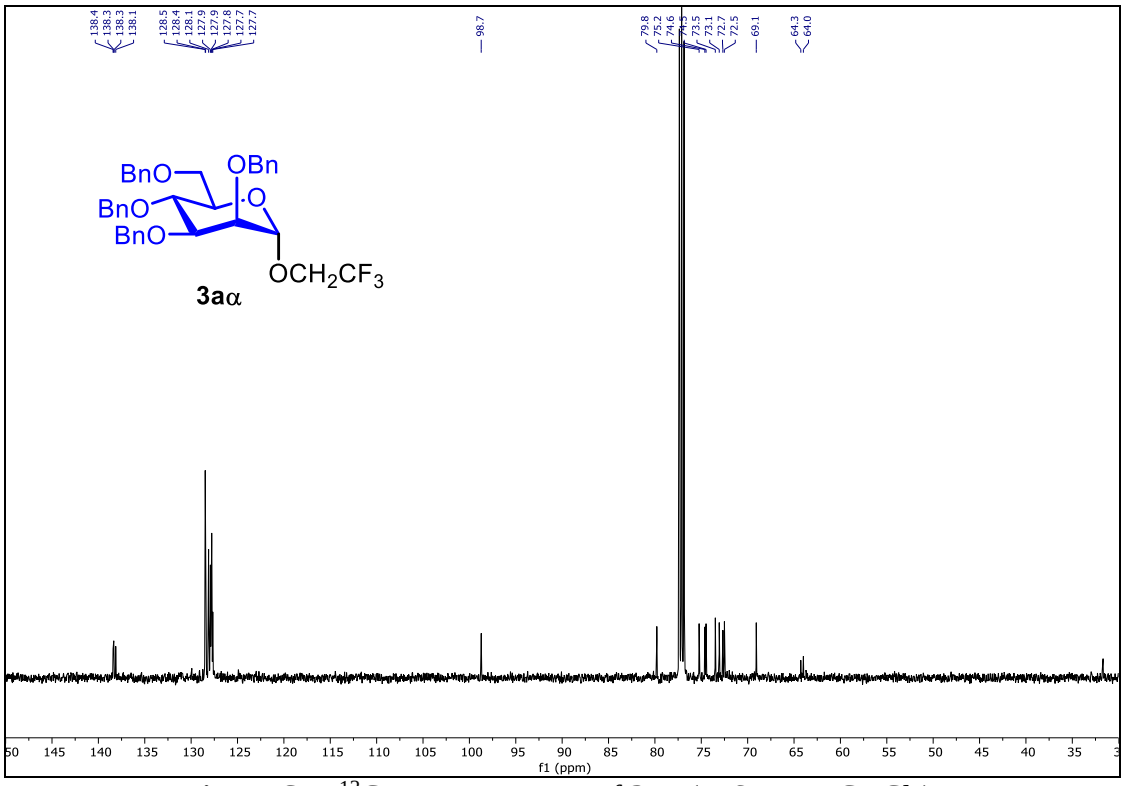


Figure S11 ^{13}C NMR spectrum of **3aα** (126 MHz, $CDCl_3$).

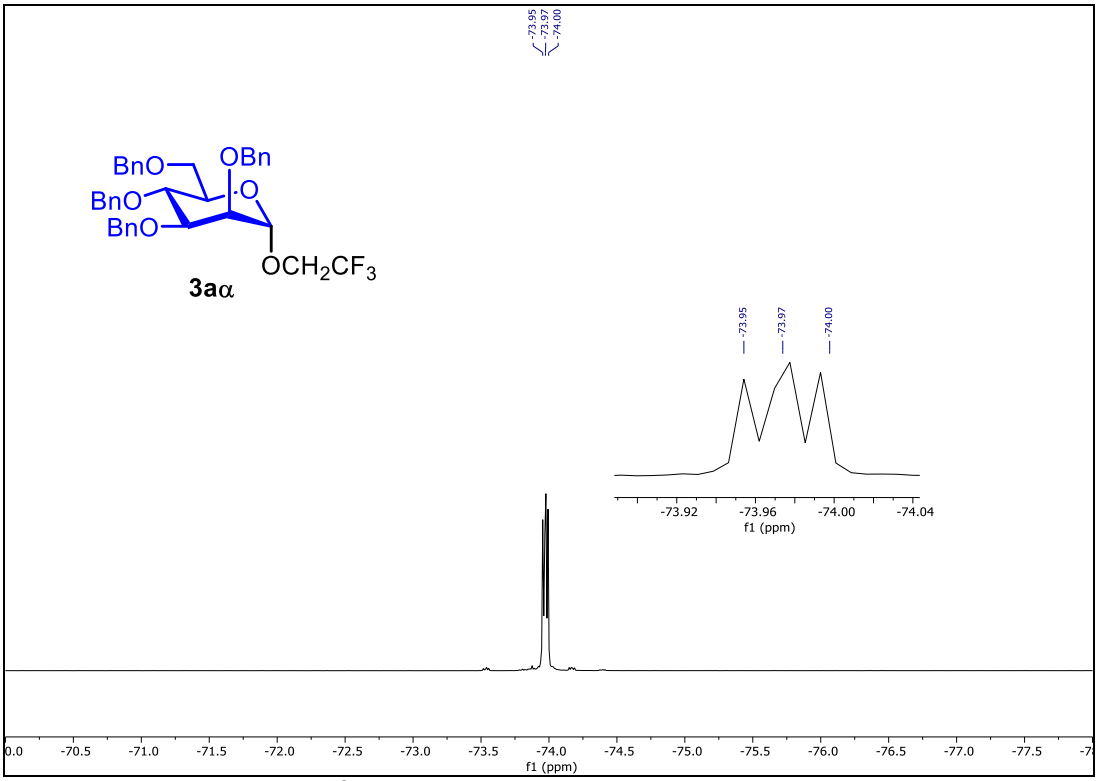


Figure S12 ^{19}F NMR spectrum of **3aα** (471 MHz, $CDCl_3$).

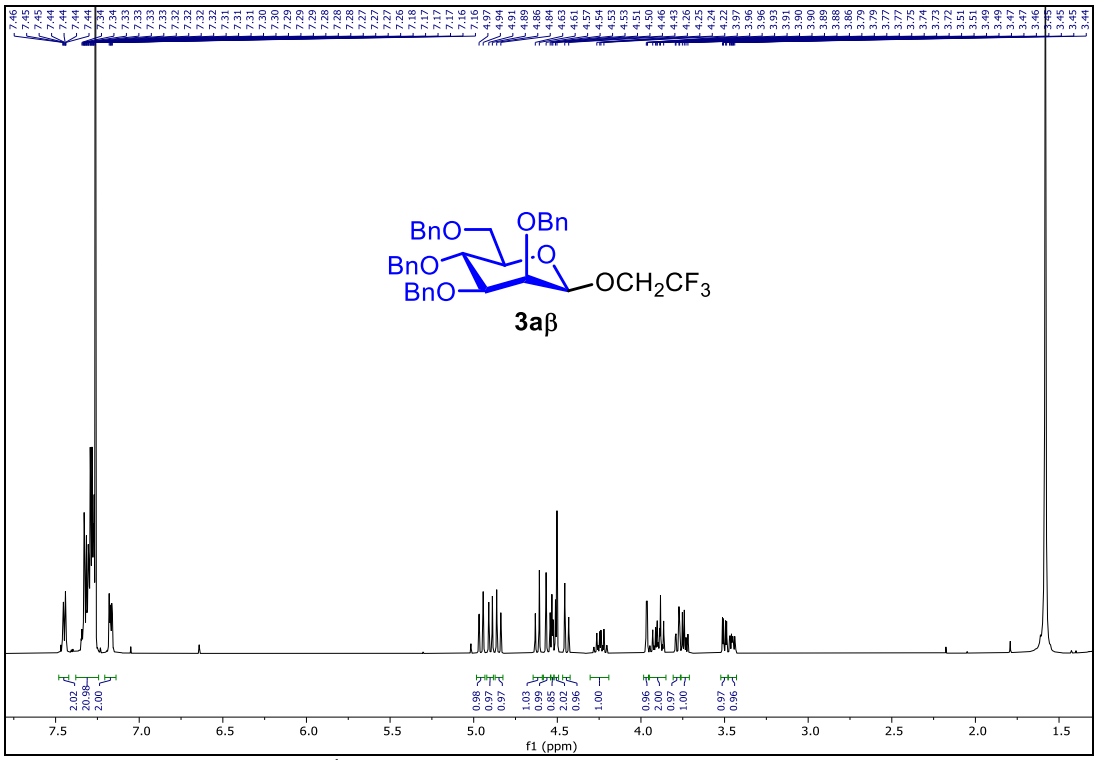


Figure S13 ^{1}H NMR spectrum of **3aβ** (500 MHz, $CDCl_3$).

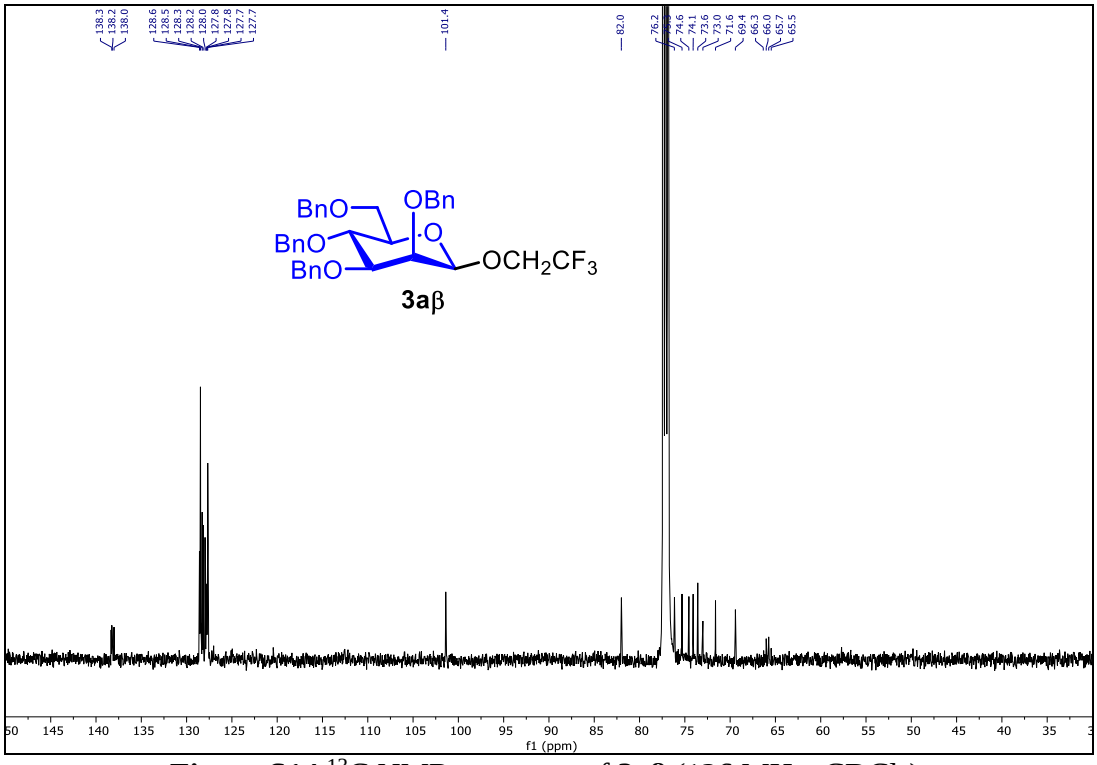


Figure S14 ^{13}C NMR spectrum of **3aβ** (126 MHz, $CDCl_3$).

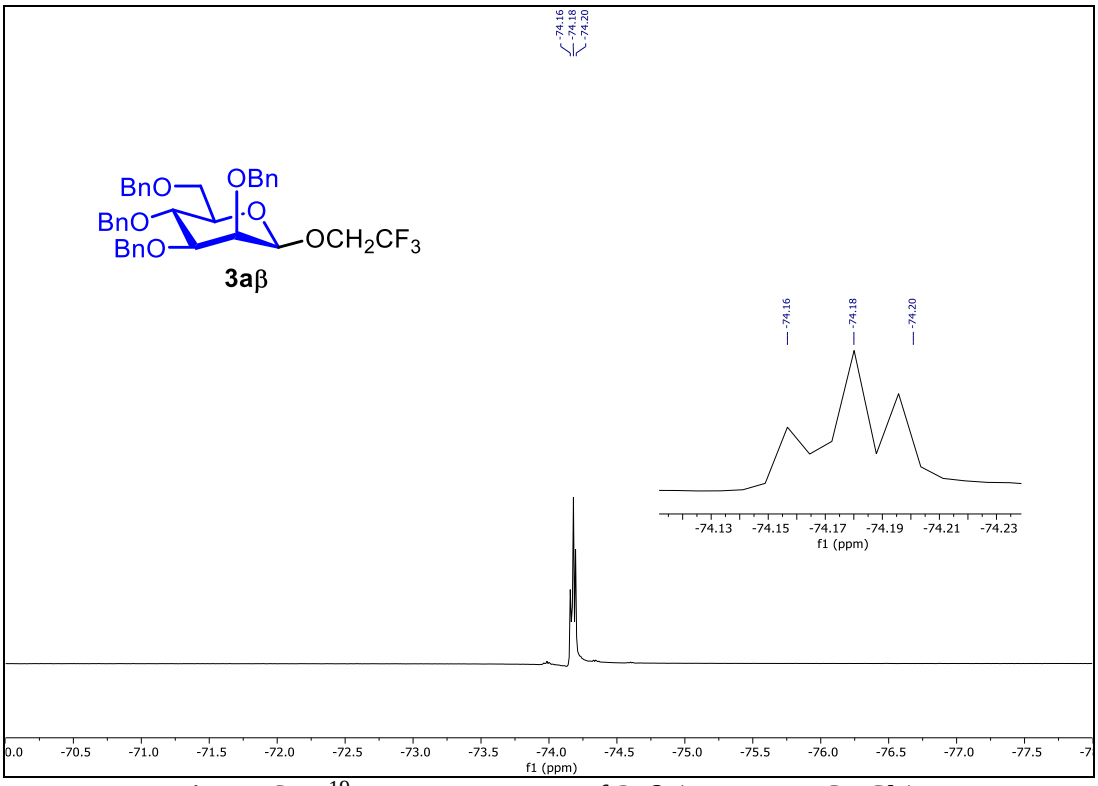


Figure S15 ^{19}F NMR spectrum of **3aβ** (471 MHz, $CDCl_3$).

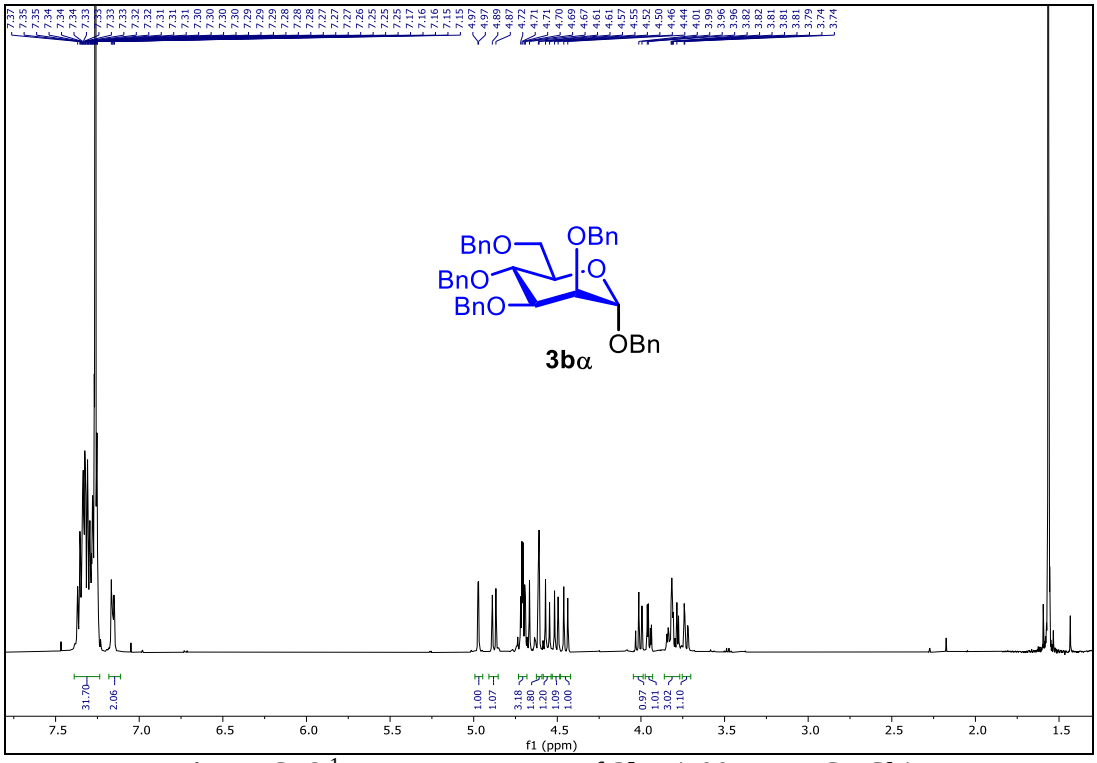


Figure S16 ^{1}H NMR spectrum of **3bα** (500 MHz, $CDCl_3$).

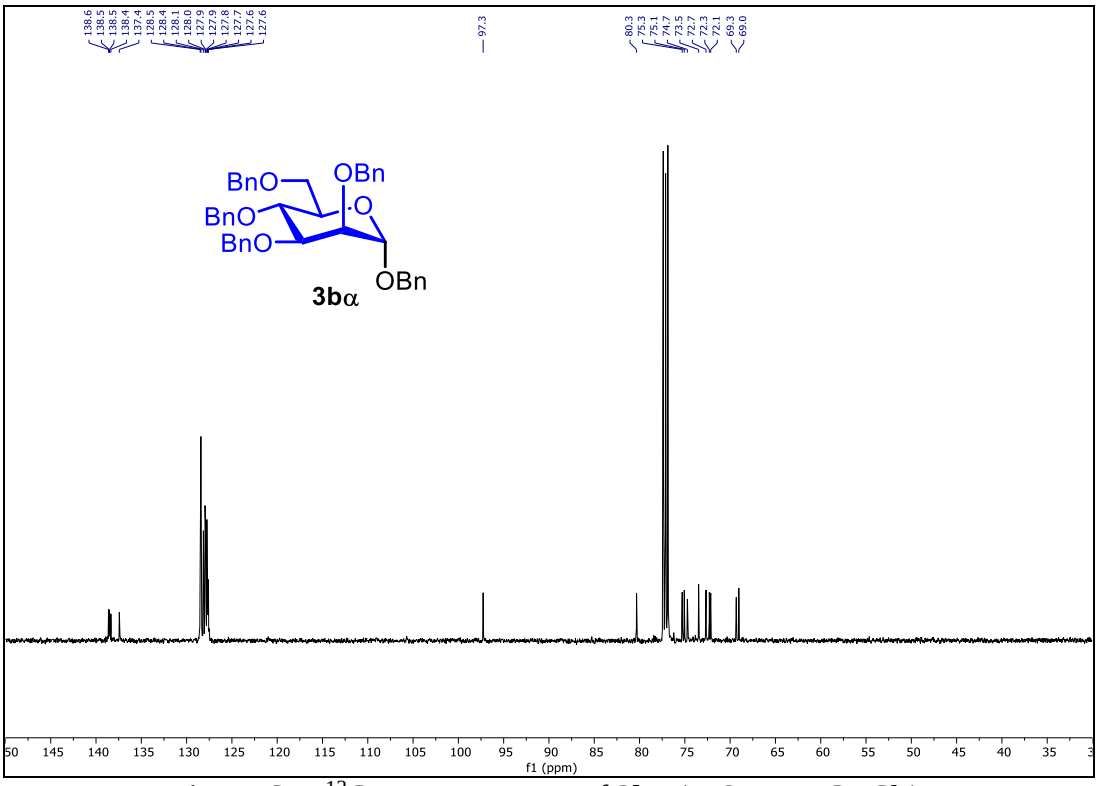


Figure S17 ^{13}C NMR spectrum of **3bα** (126 MHz, $CDCl_3$).

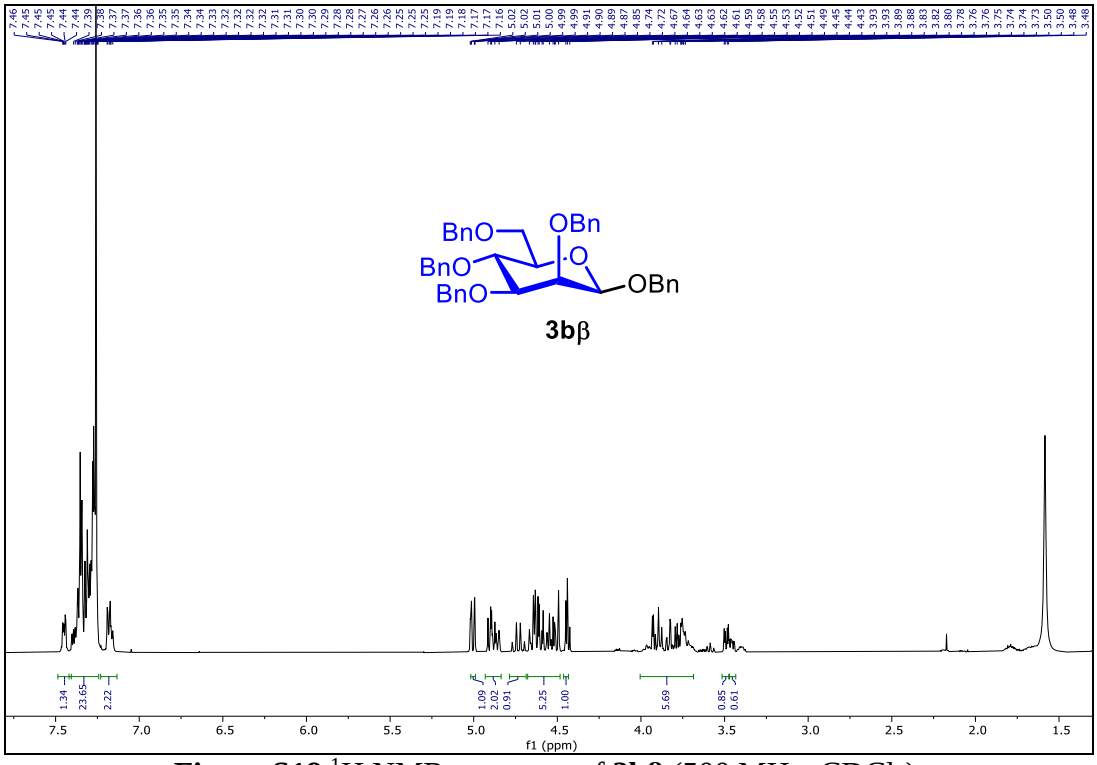


Figure S18 ^{1}H NMR spectrum of **3bβ** (500 MHz, $CDCl_3$).

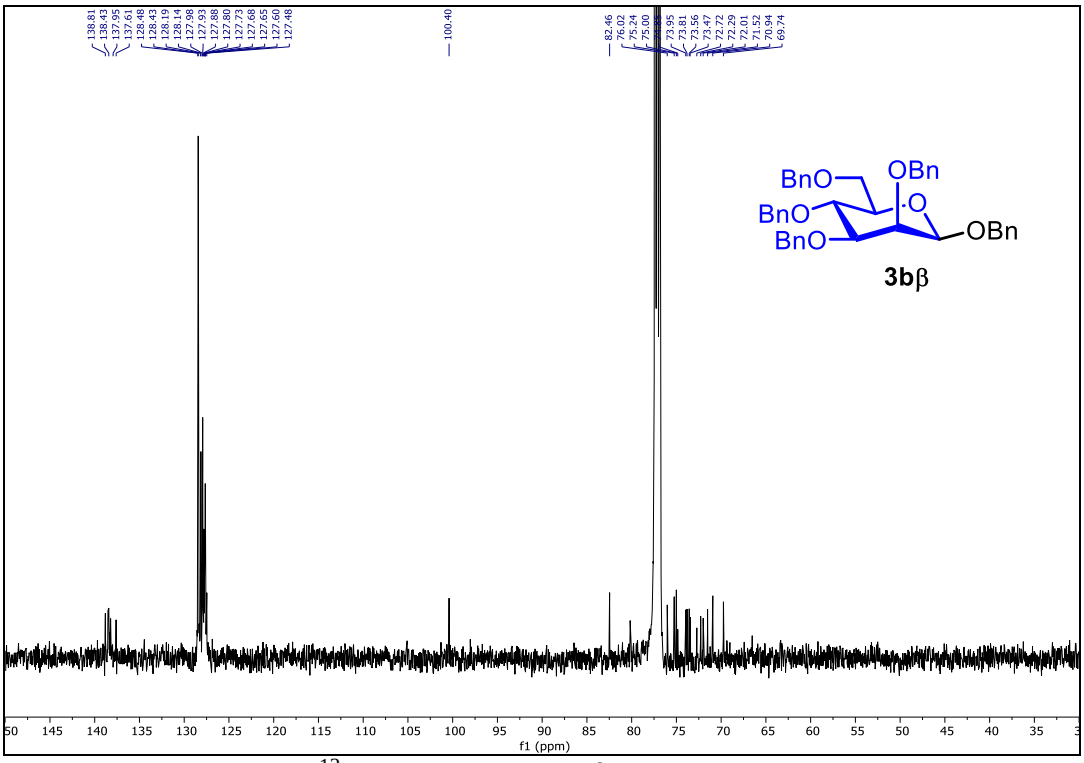


Figure S19 ^{13}C NMR spectrum of **3bβ** (126 MHz, $CDCl_3$).

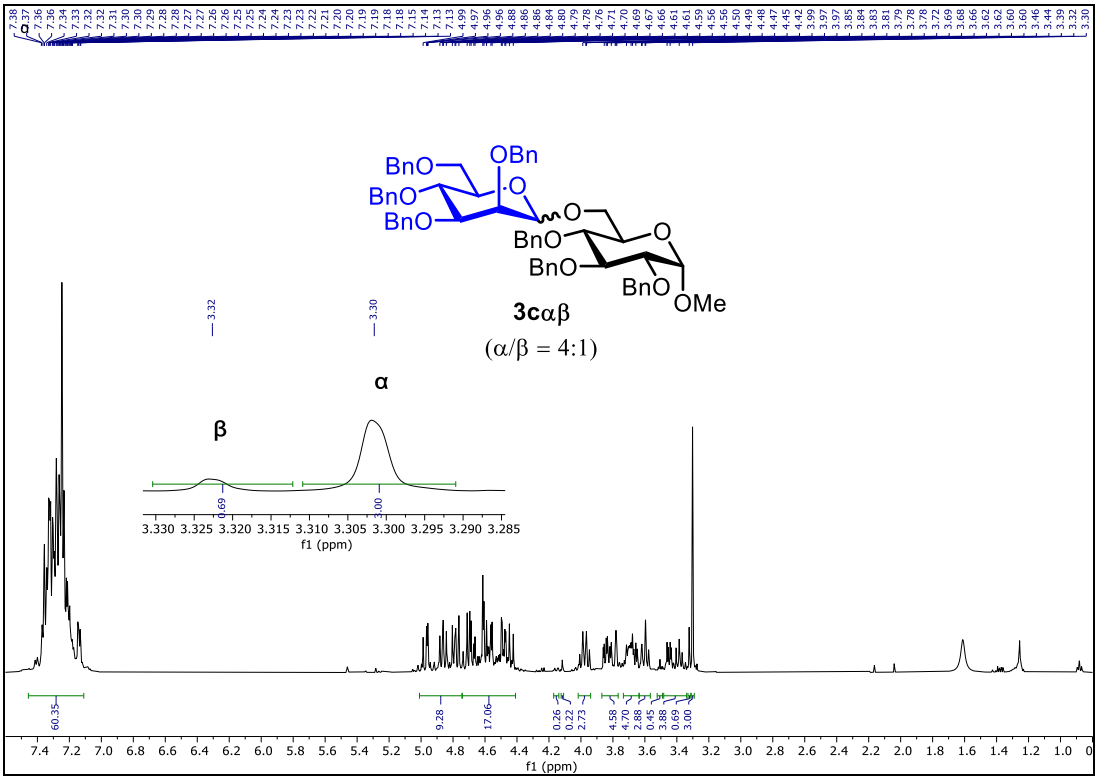


Figure S20 ^{1}H NMR spectrum of **3cαβ** (500 MHz, $CDCl_3$).

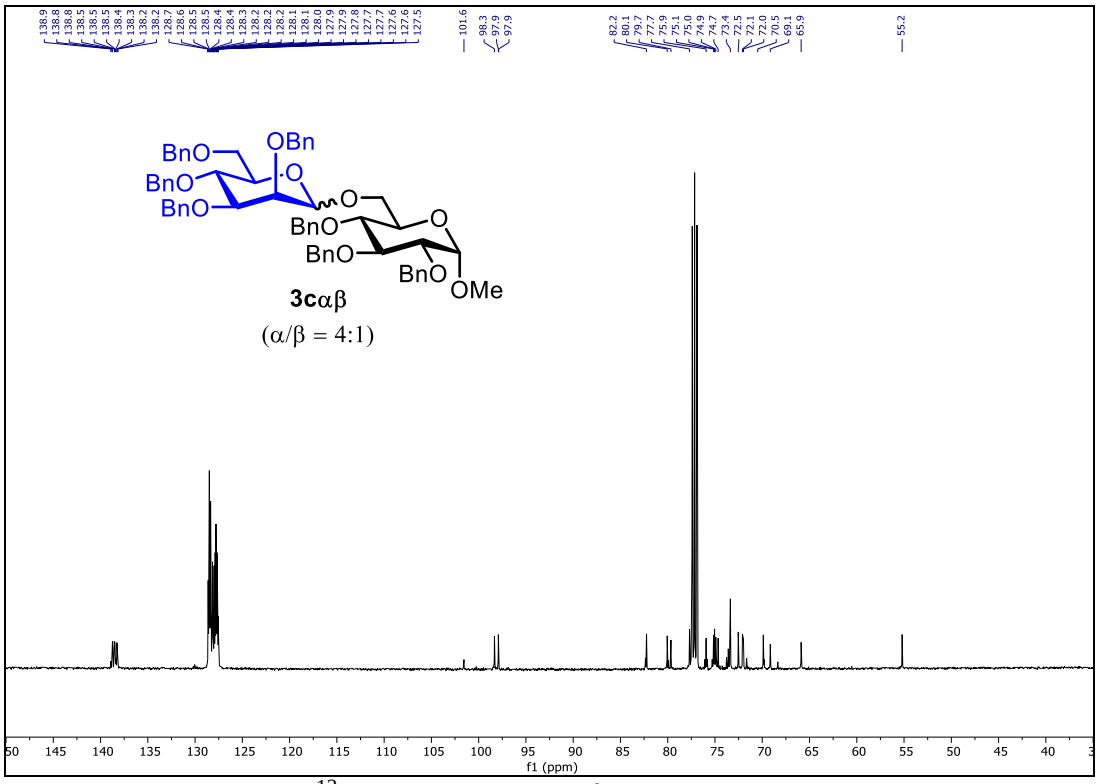


Figure S21 ^{13}C NMR spectrum of **3cαβ** (126 MHz, $CDCl_3$).

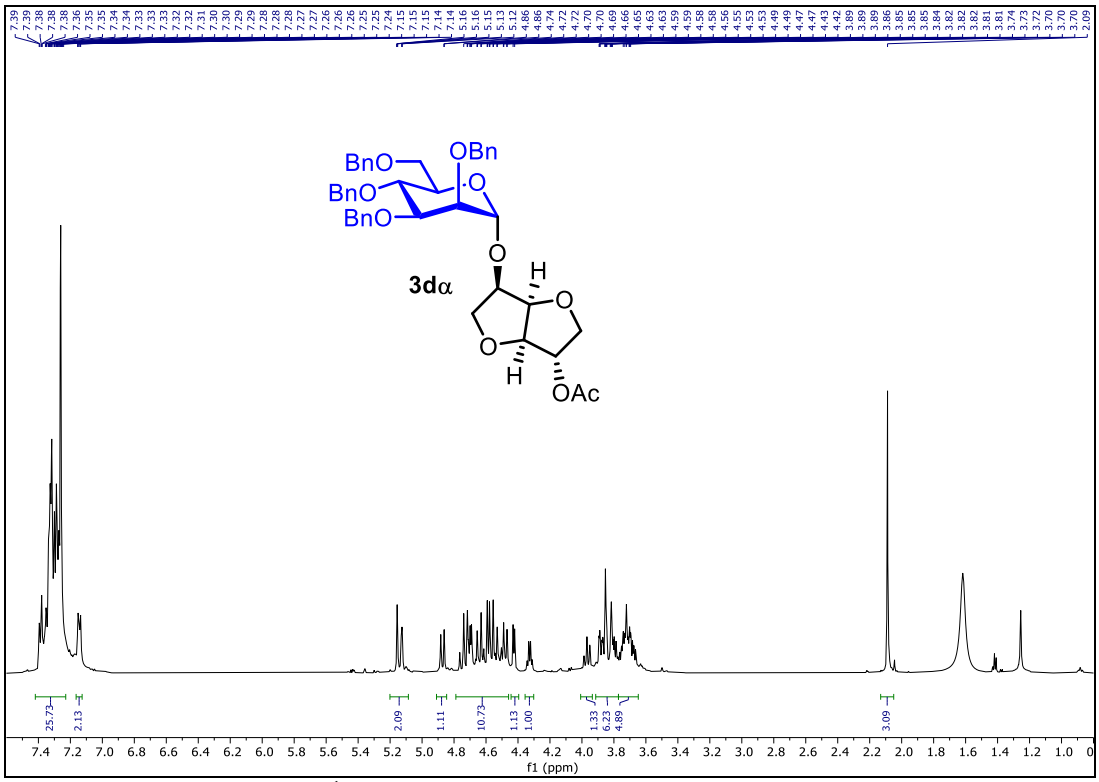


Figure S22 ^{1}H NMR spectrum of **3dα** (500 MHz, $CDCl_3$).

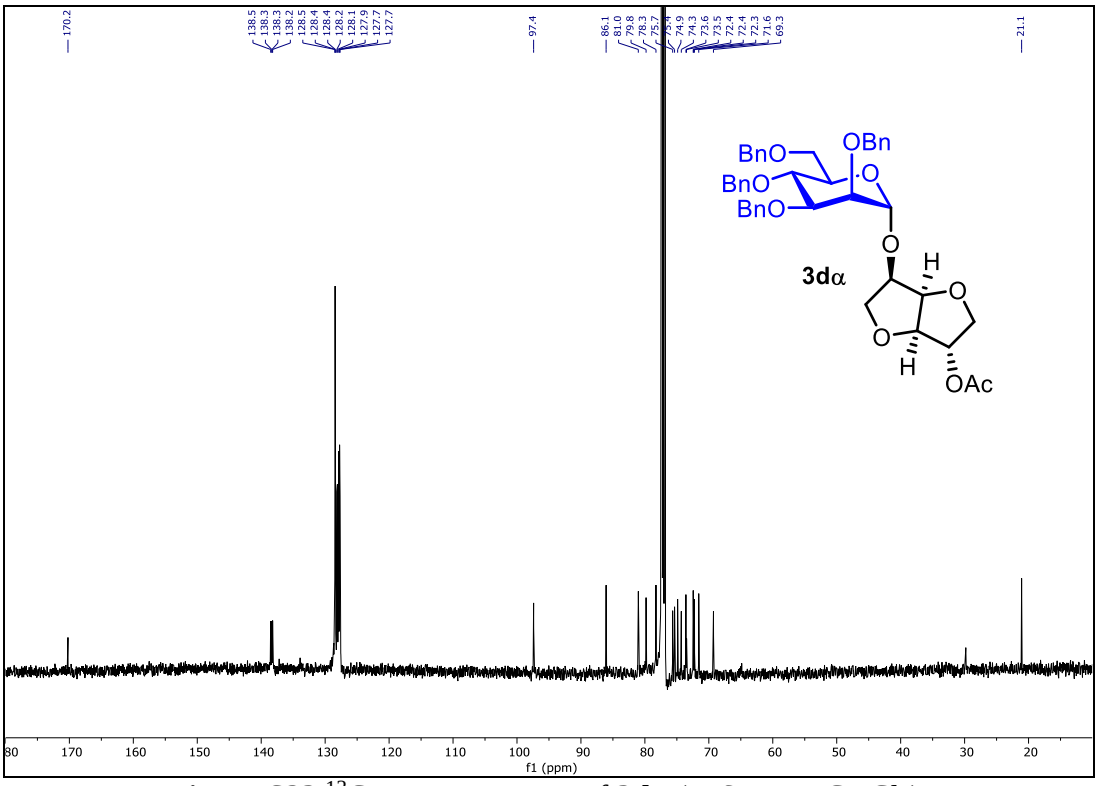


Figure S23 ^{13}C NMR spectrum of **3dα** (126 MHz, $CDCl_3$).

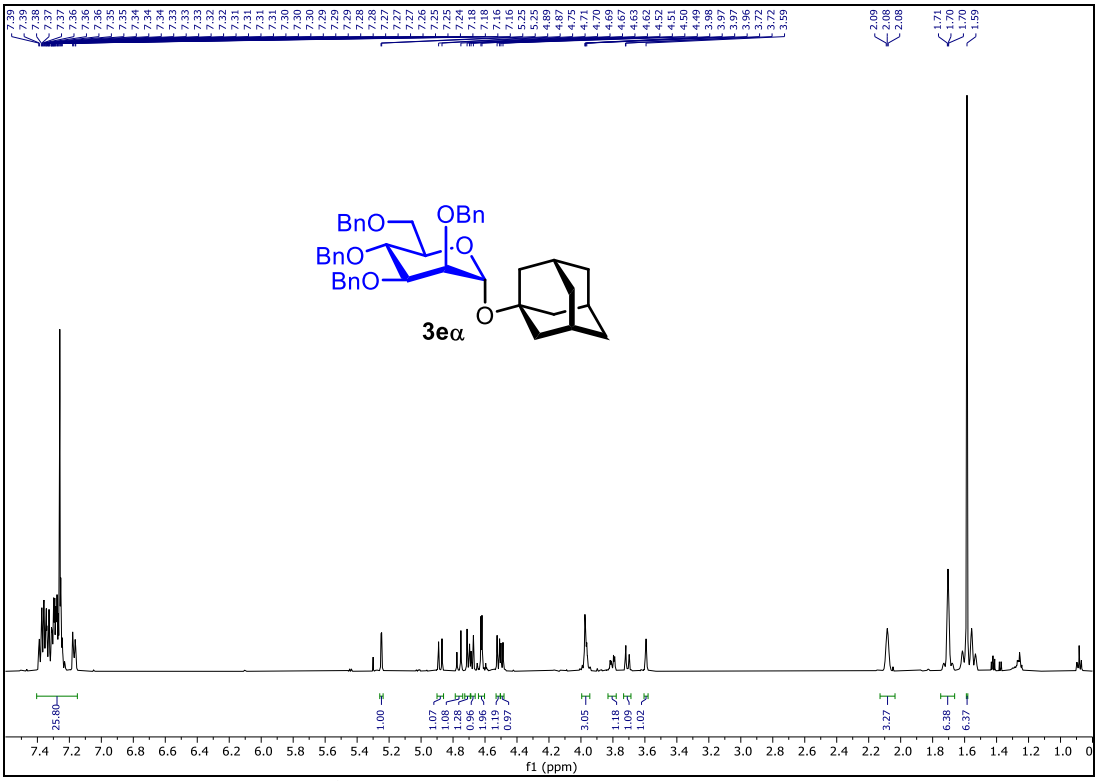


Figure S24 ^{1}H NMR spectrum of **3eα** (500 MHz, $CDCl_3$).

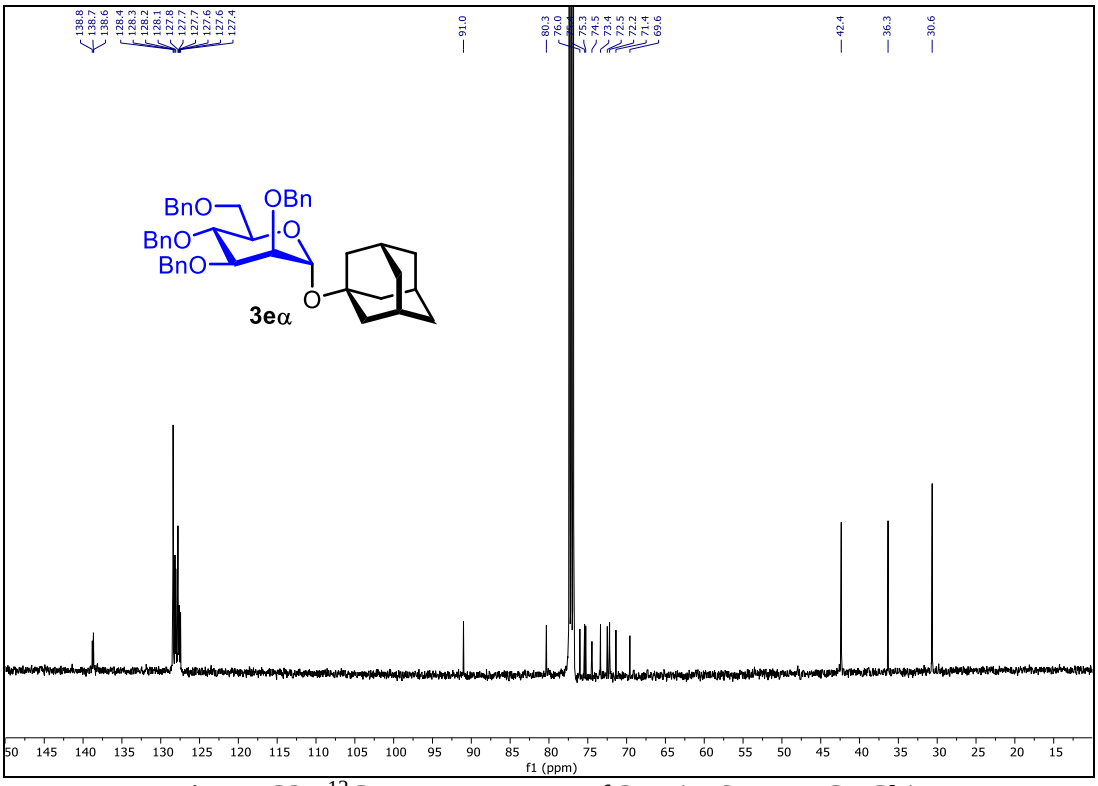


Figure S25 ^{13}C NMR spectrum of **3eα** (126 MHz, $CDCl_3$).

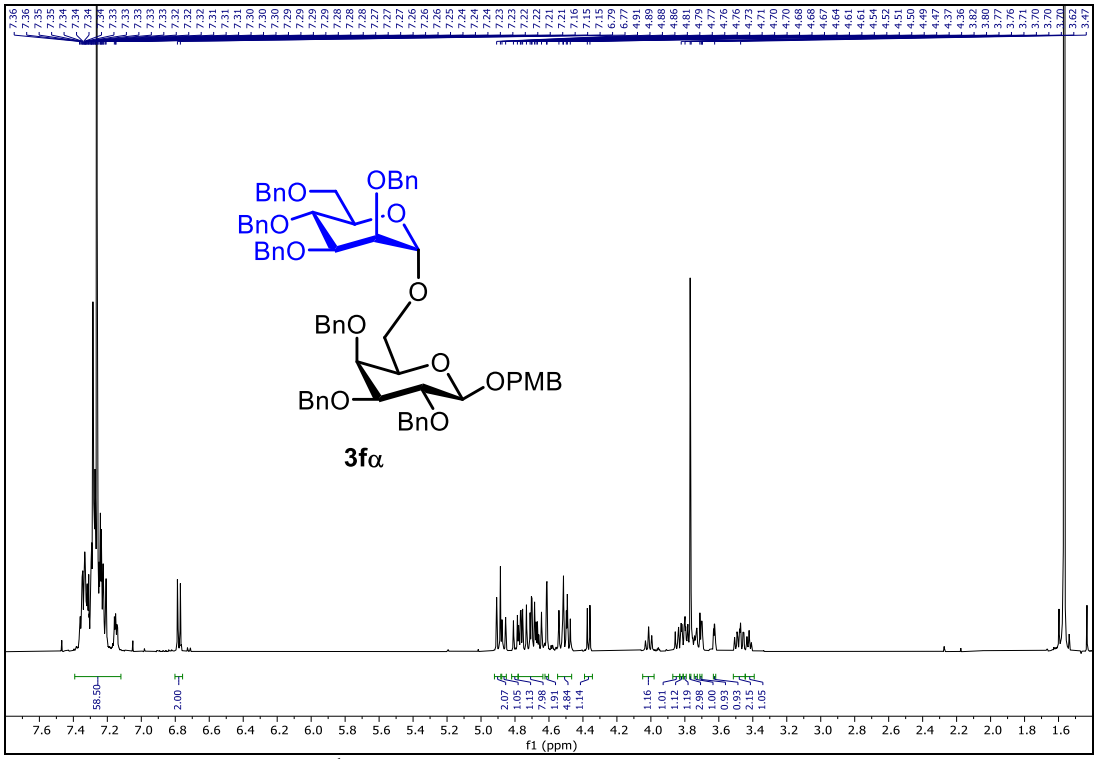


Figure S26 ^{1}H NMR spectrum of **3fα** (500 MHz, $CDCl_3$).

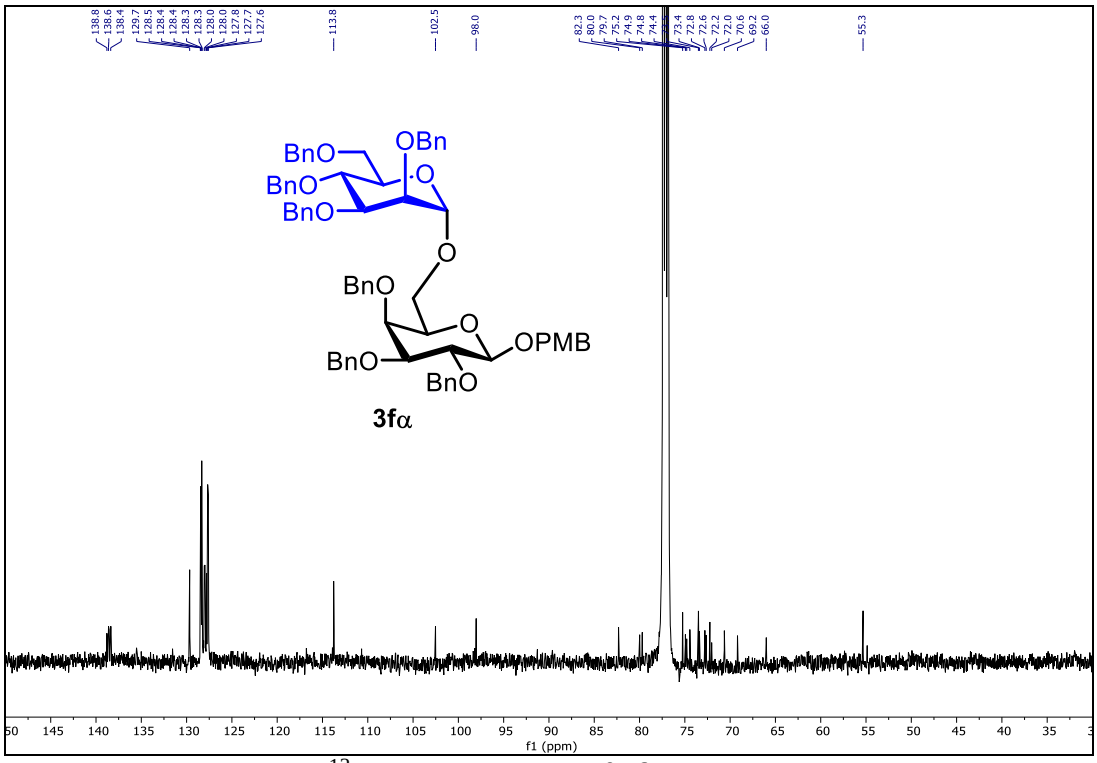


Figure S27 ^{13}C NMR spectrum of **3fα** (126 MHz, $CDCl_3$).

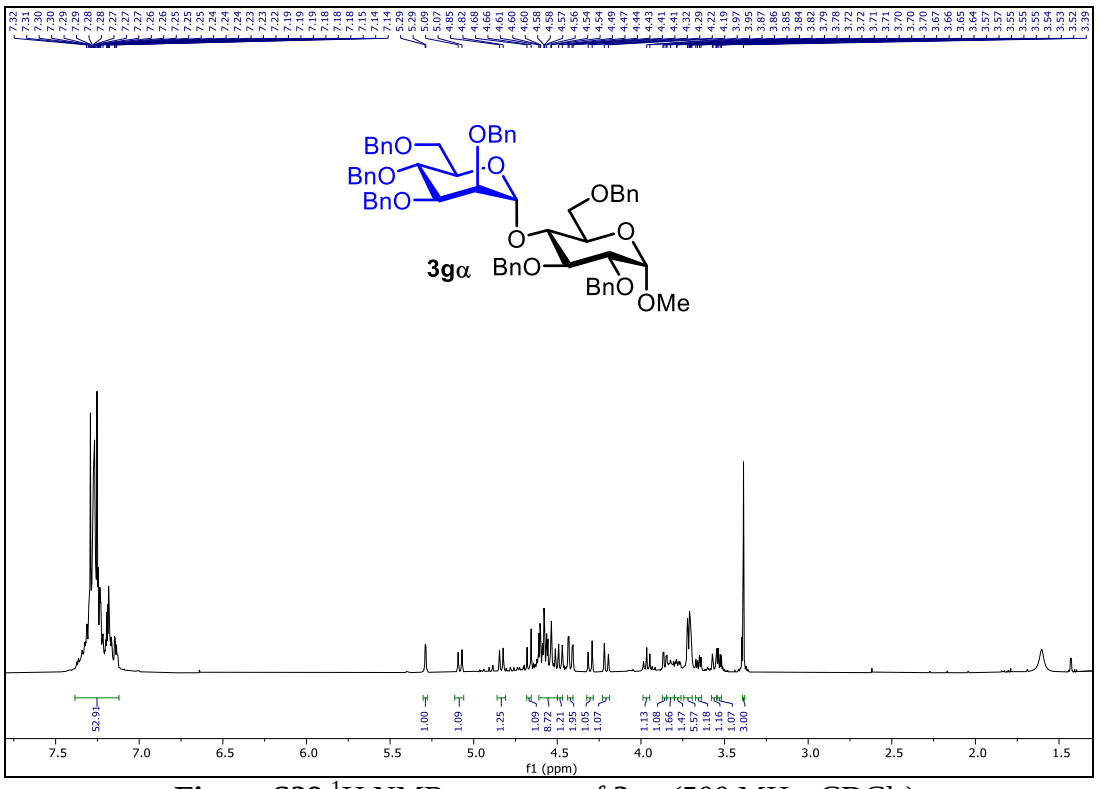


Figure S28 ^{1}H NMR spectrum of **3gα** (500 MHz, $CDCl_3$).

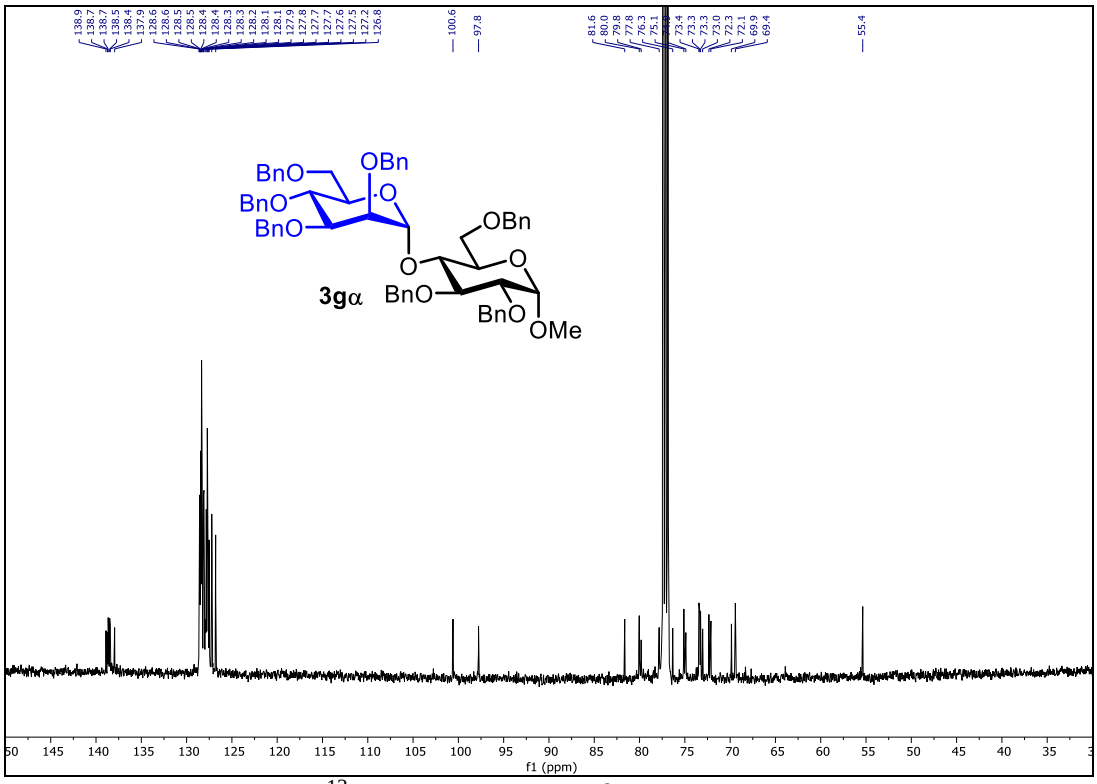


Figure S29 ^{13}C NMR spectrum of **3gα** (126 MHz, $CDCl_3$).

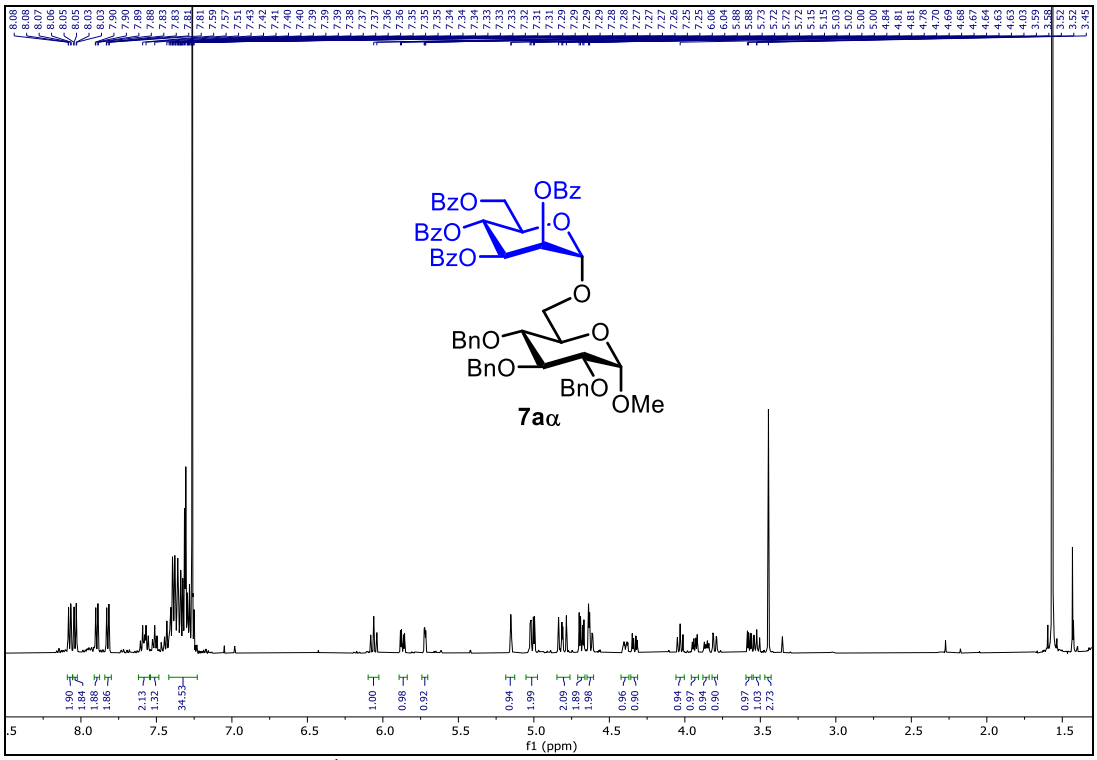


Figure S30 ^{1}H NMR spectrum of **7aα** (500 MHz, $CDCl_3$).

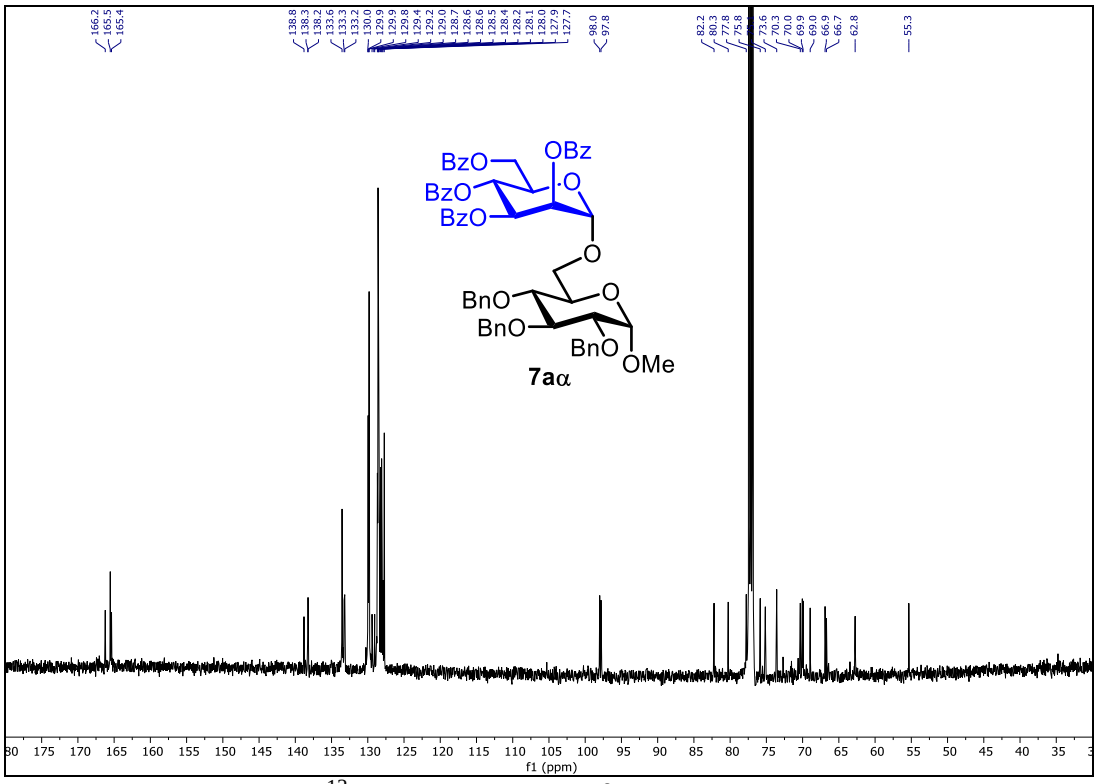


Figure S31 ^{13}C NMR spectrum of **7aα** (126 MHz, $CDCl_3$).

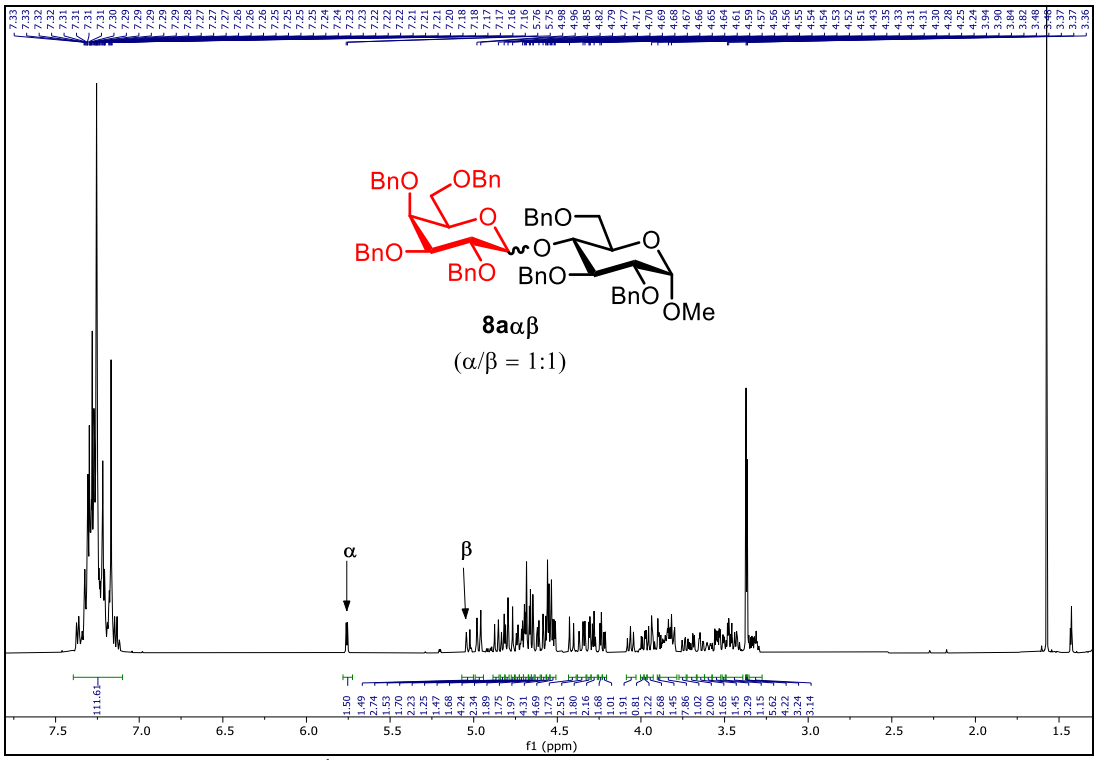


Figure S32 ^{1}H NMR spectrum of **8aαβ** (500 MHz, $CDCl_3$).

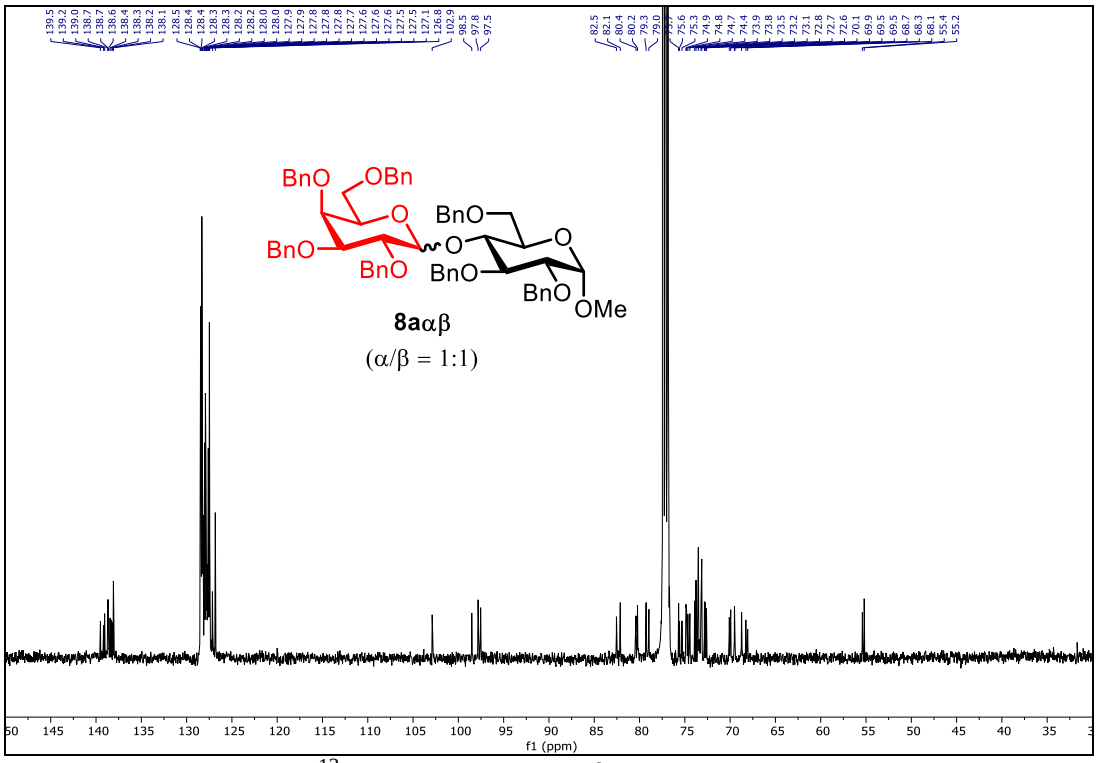


Figure S33 ^{13}C NMR spectrum of **8aαβ** (126 MHz, $CDCl_3$).

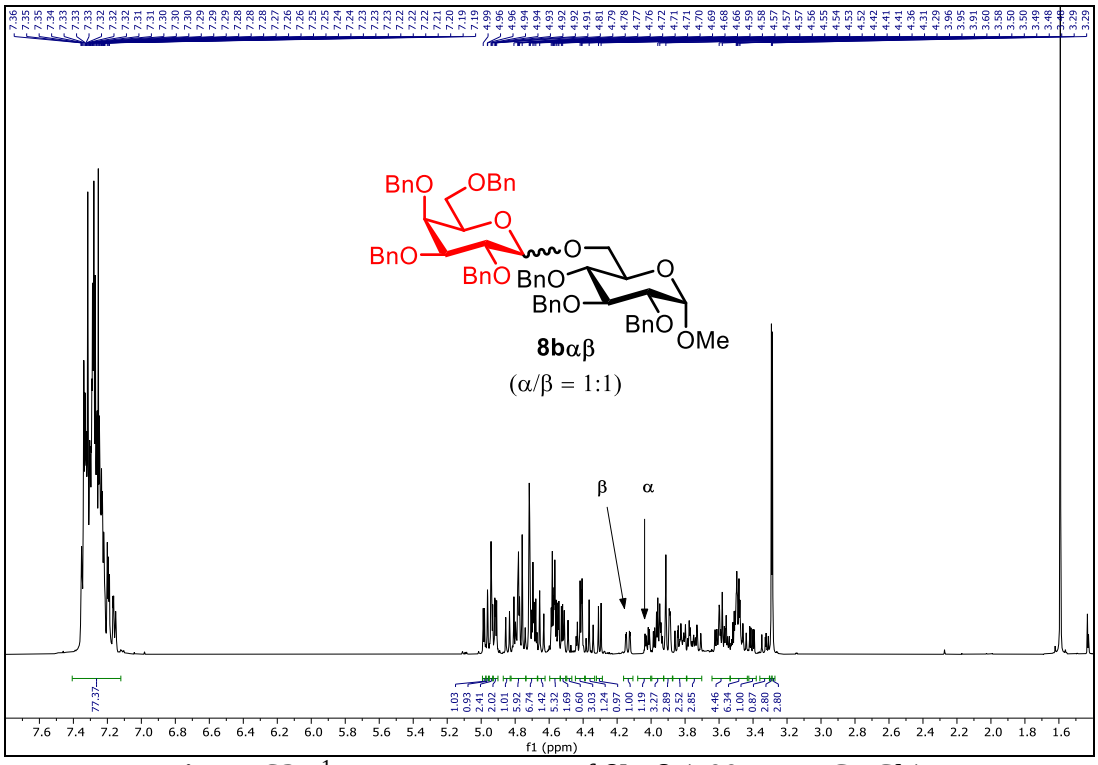


Figure S34 ^{1}H NMR spectrum of **8bαβ** (500 MHz, $CDCl_3$).

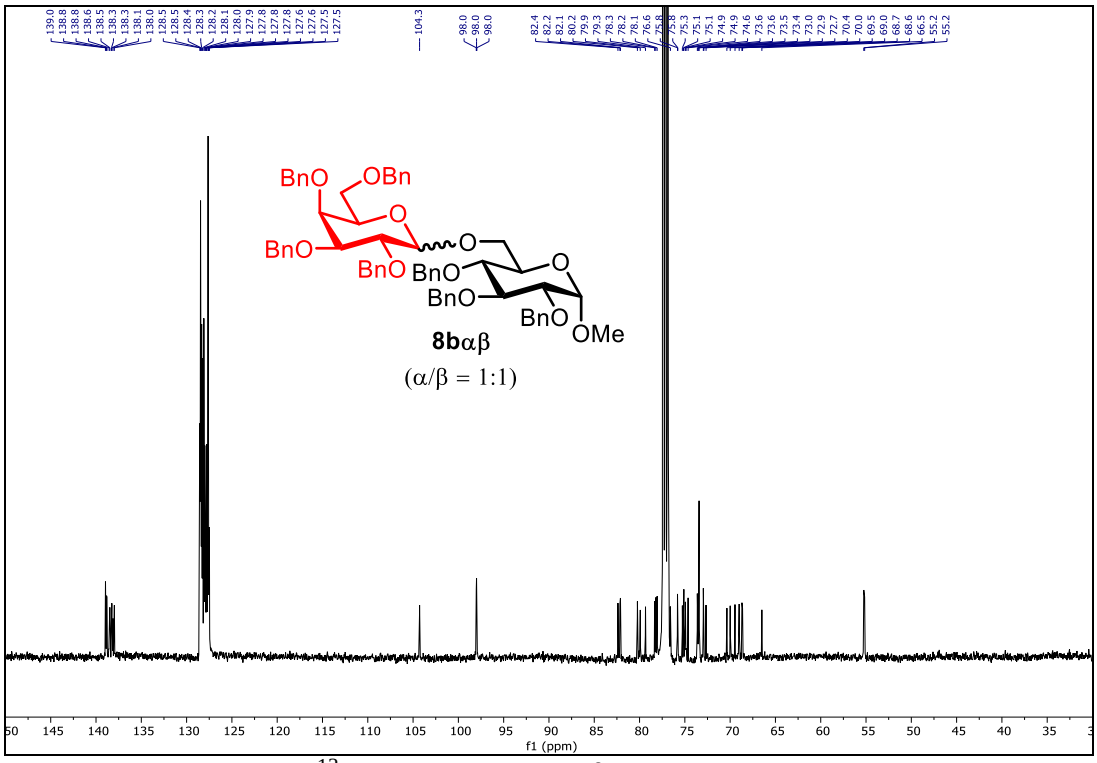


Figure S35 ^{13}C NMR spectrum of **8bαβ** (126 MHz, $CDCl_3$).

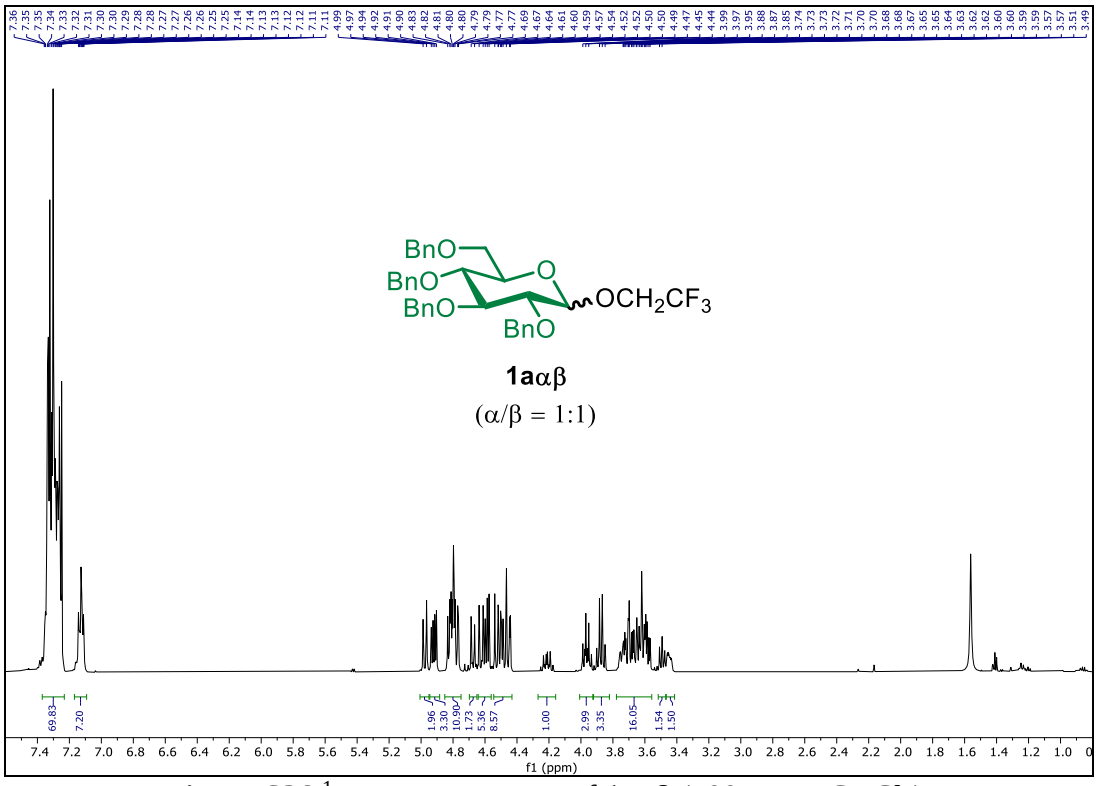


Figure S36 ^{1}H NMR spectrum of **1aαβ** (500 MHz, $CDCl_3$).

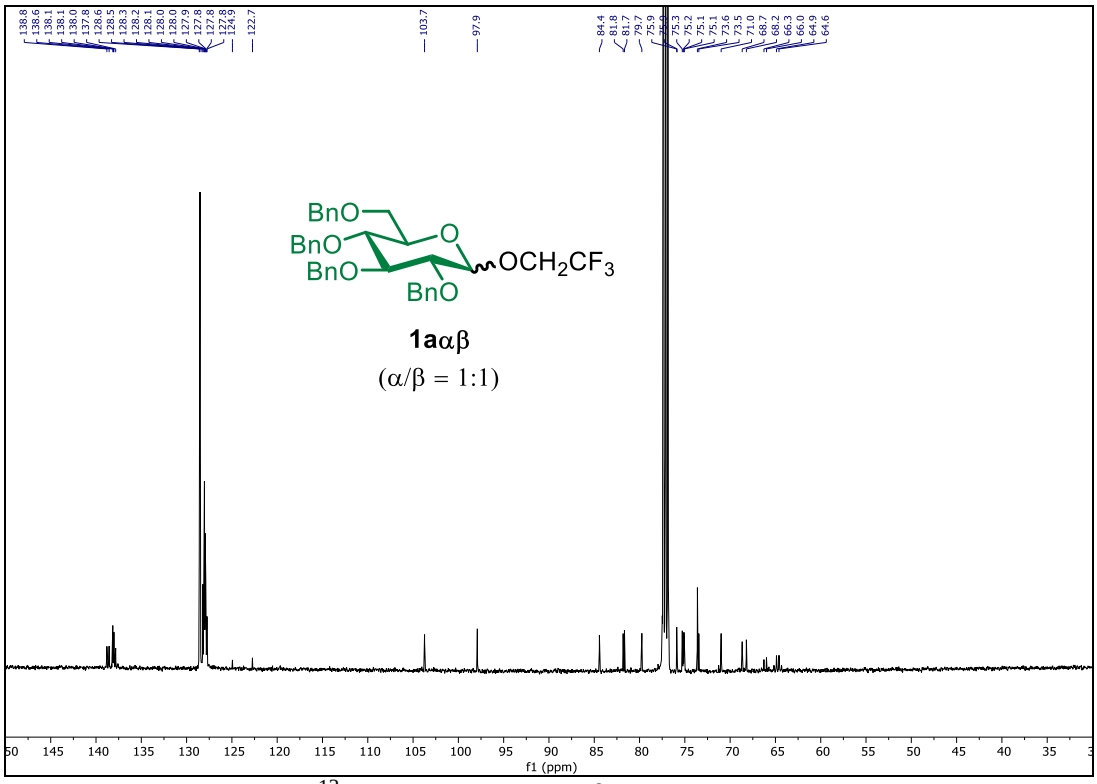


Figure S37 ^{13}C NMR spectrum of **1aαβ** (126 MHz, $CDCl_3$).

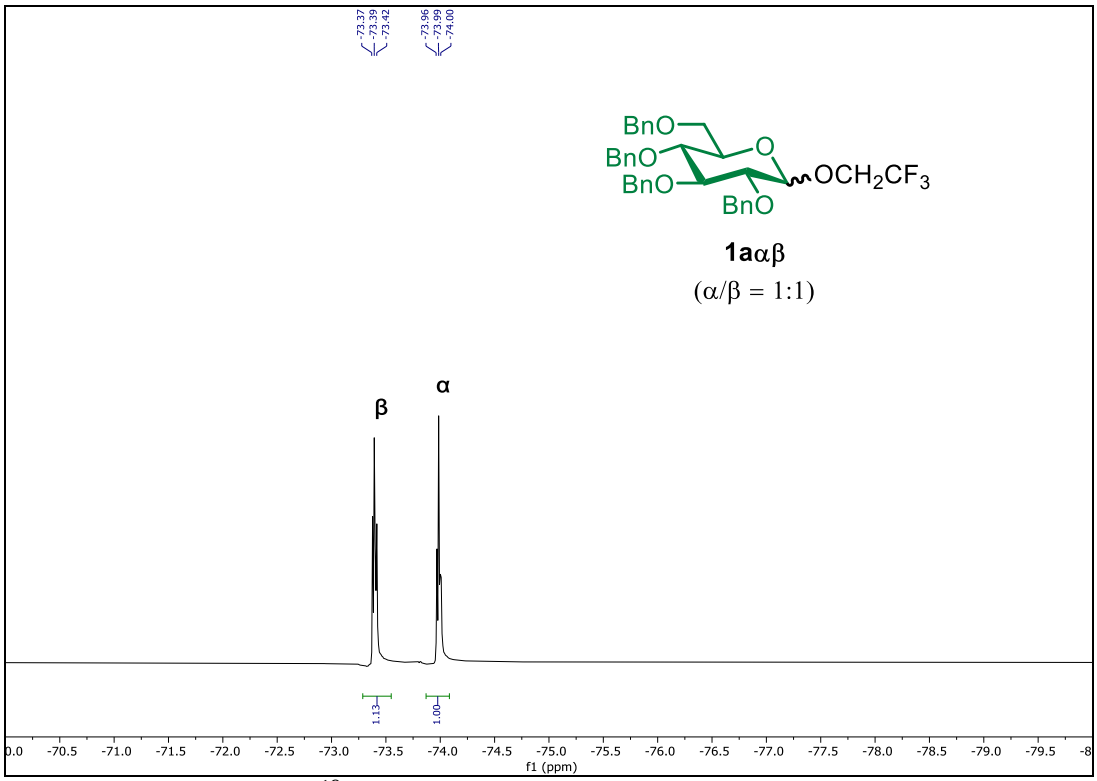


Figure S38 ^{19}F NMR spectrum of **1aαβ** (471 MHz, $CDCl_3$).

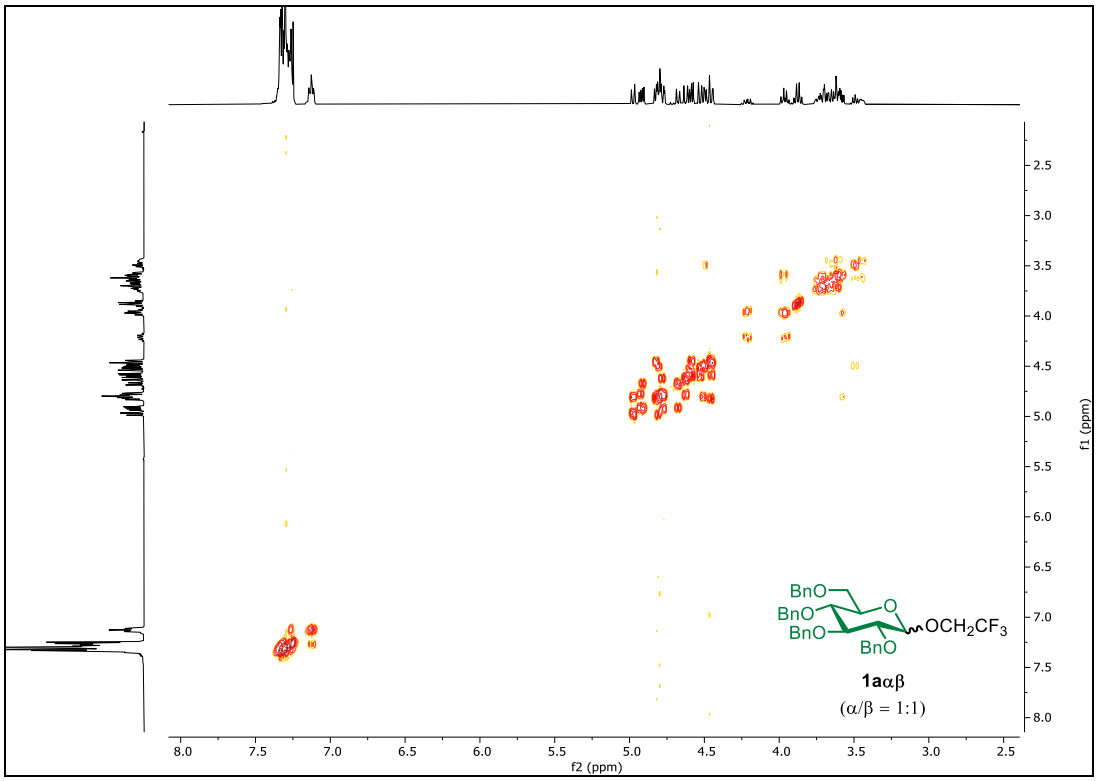


Figure S39 COSY spectrum of **1aαβ** (500 MHz, $CDCl_3$).

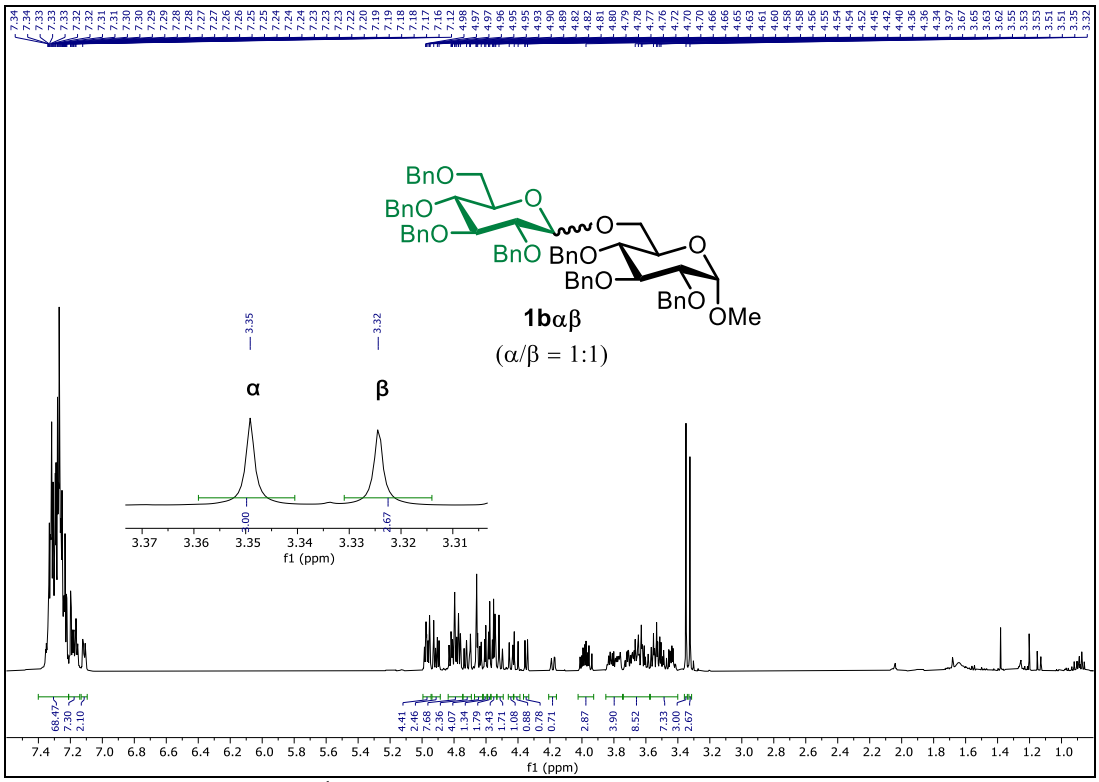


Figure S40 ^{1}H NMR spectrum of **1bαβ** (500 MHz, $CDCl_3$).

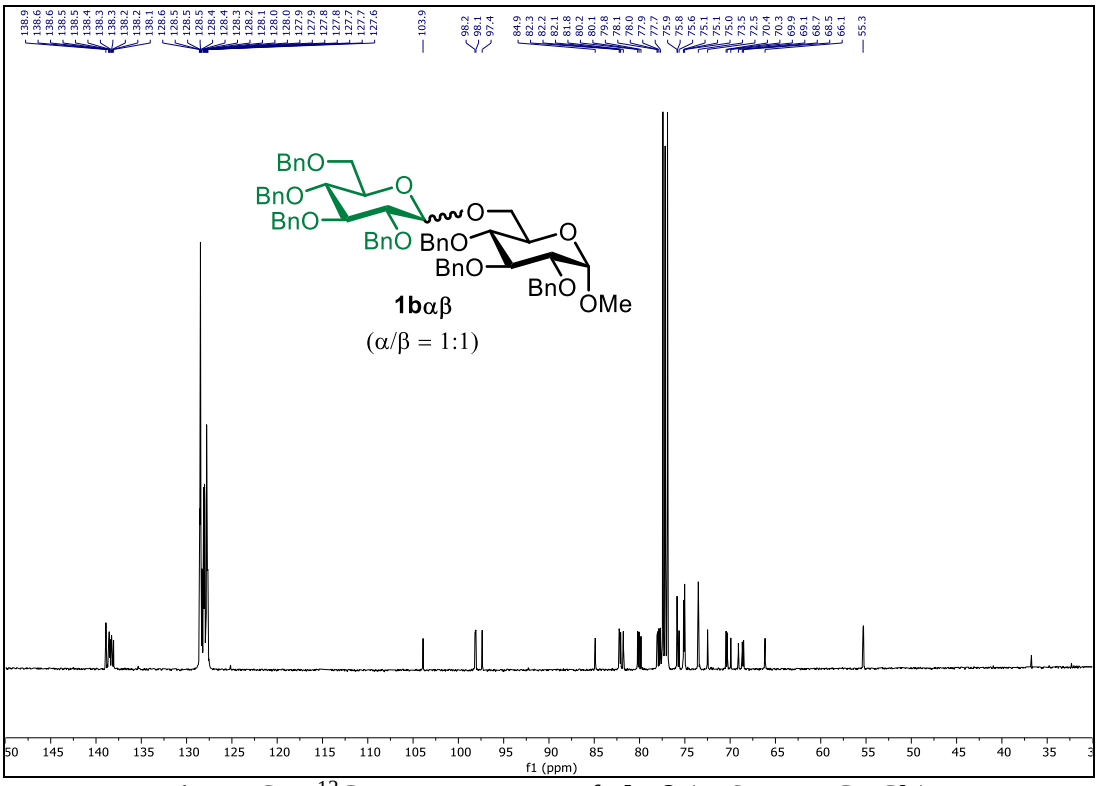


Figure S41 ^{13}C NMR spectrum of **1bαβ** (126 MHz, $CDCl_3$).

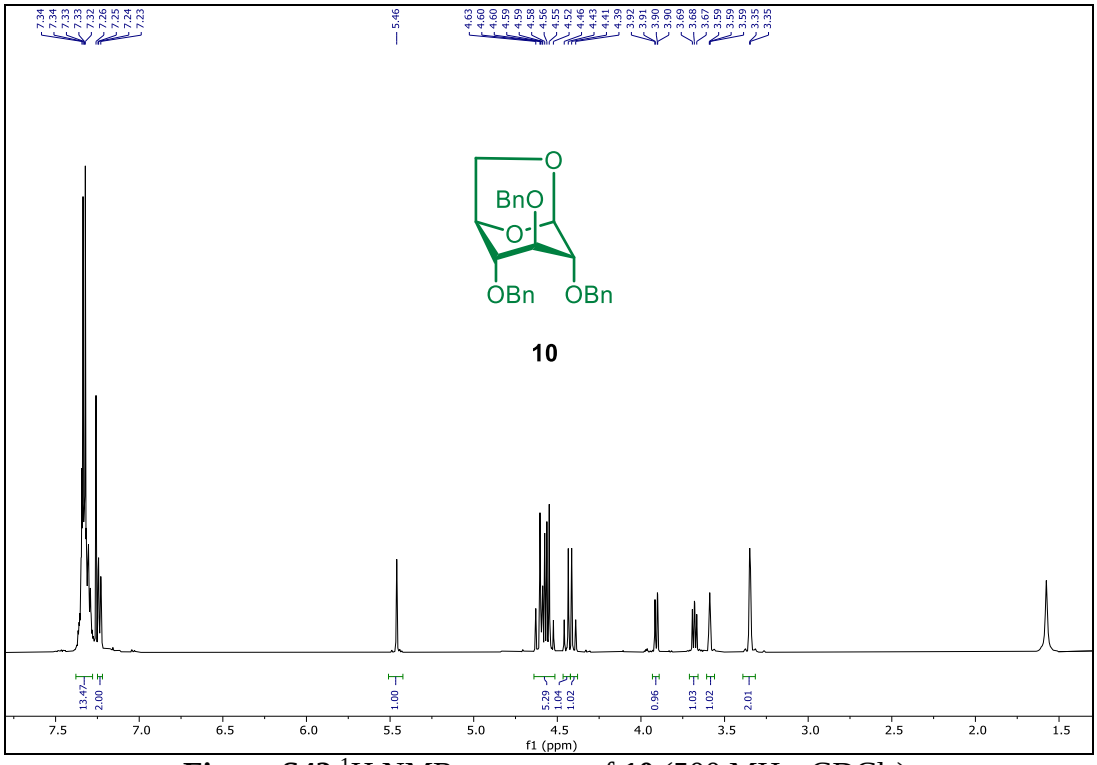


Figure S42 ^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$).

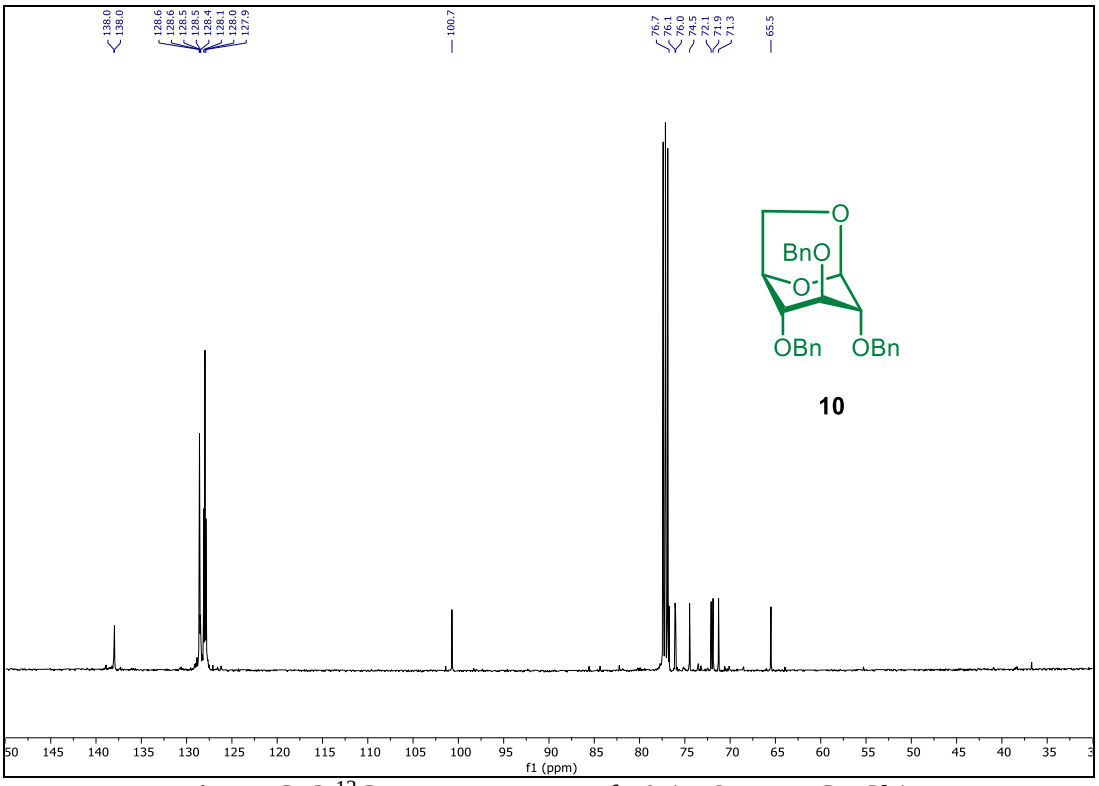


Figure S43 ^{13}C NMR spectrum of **10** (126 MHz, $CDCl_3$).

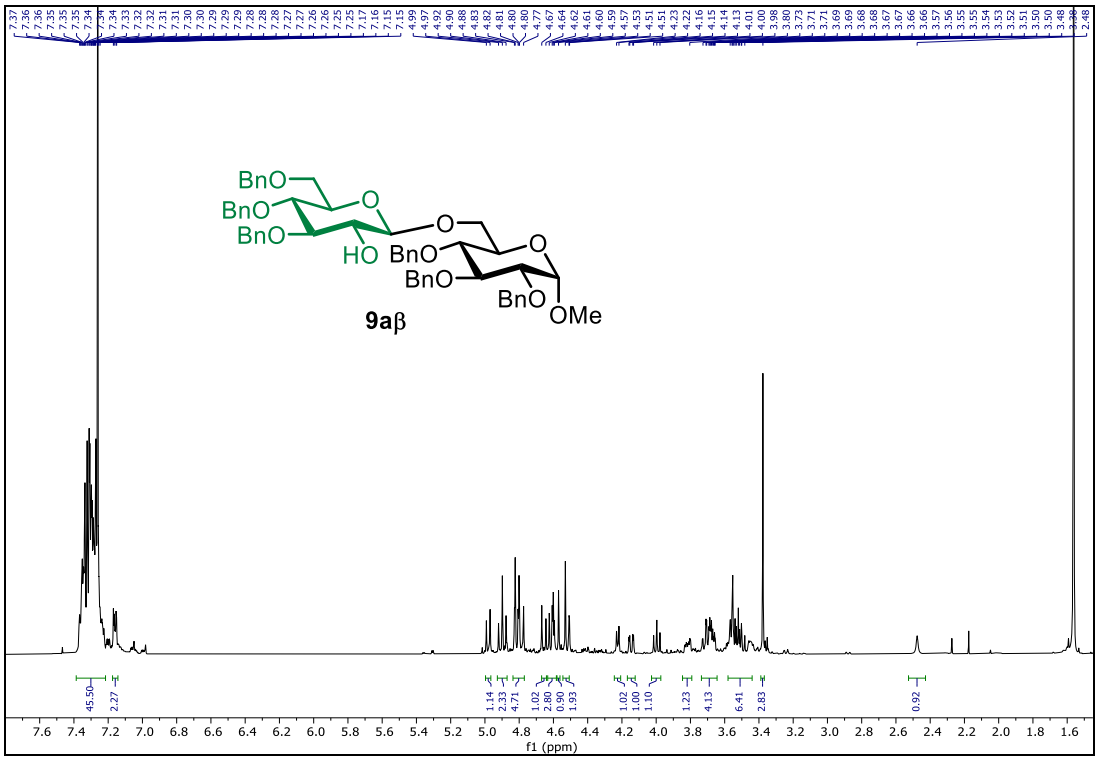


Figure S44 ^{1}H NMR spectrum of **9aβ** (500 MHz, $CDCl_3$).

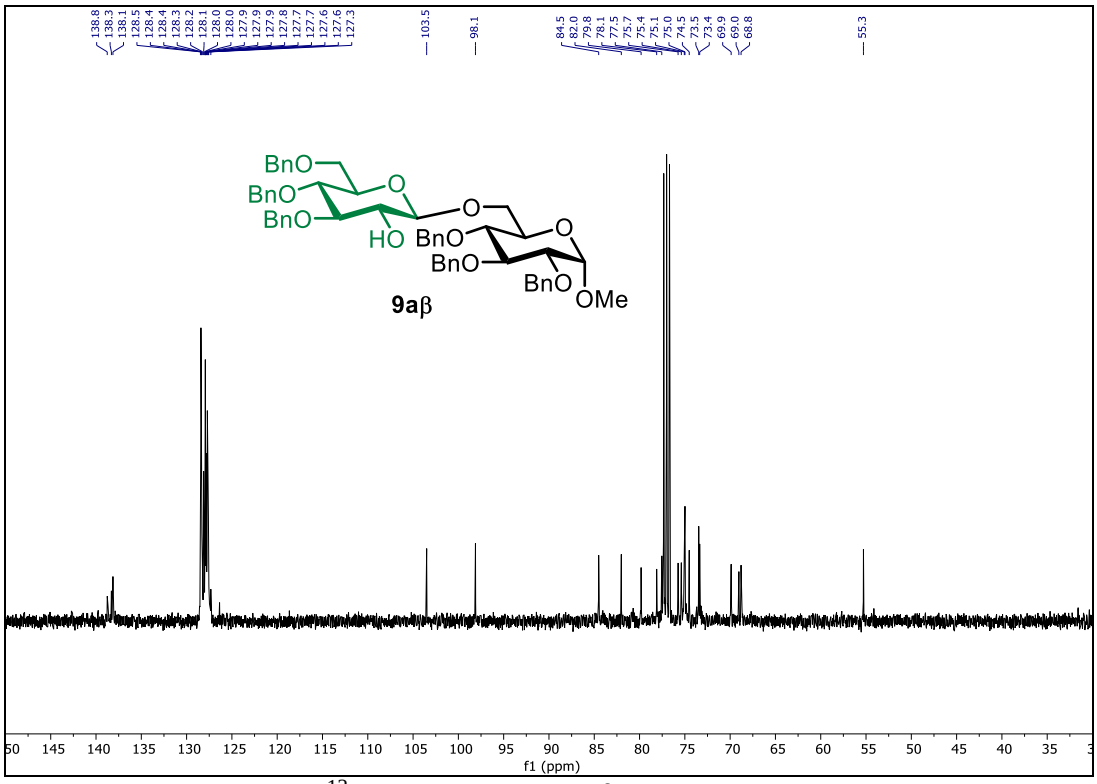


Figure S45 ^{13}C NMR spectrum of **9aβ** (101 MHz, $CDCl_3$).

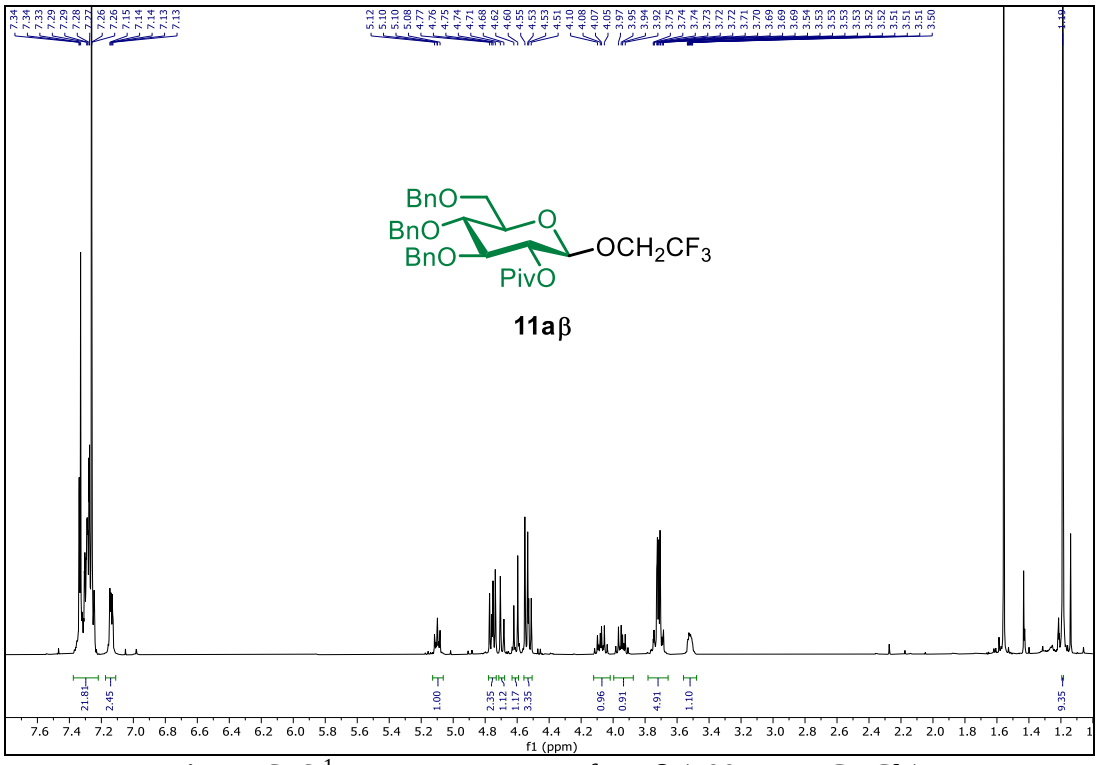


Figure S46 ^{1}H NMR spectrum of **11aβ** (500 MHz, $CDCl_3$).

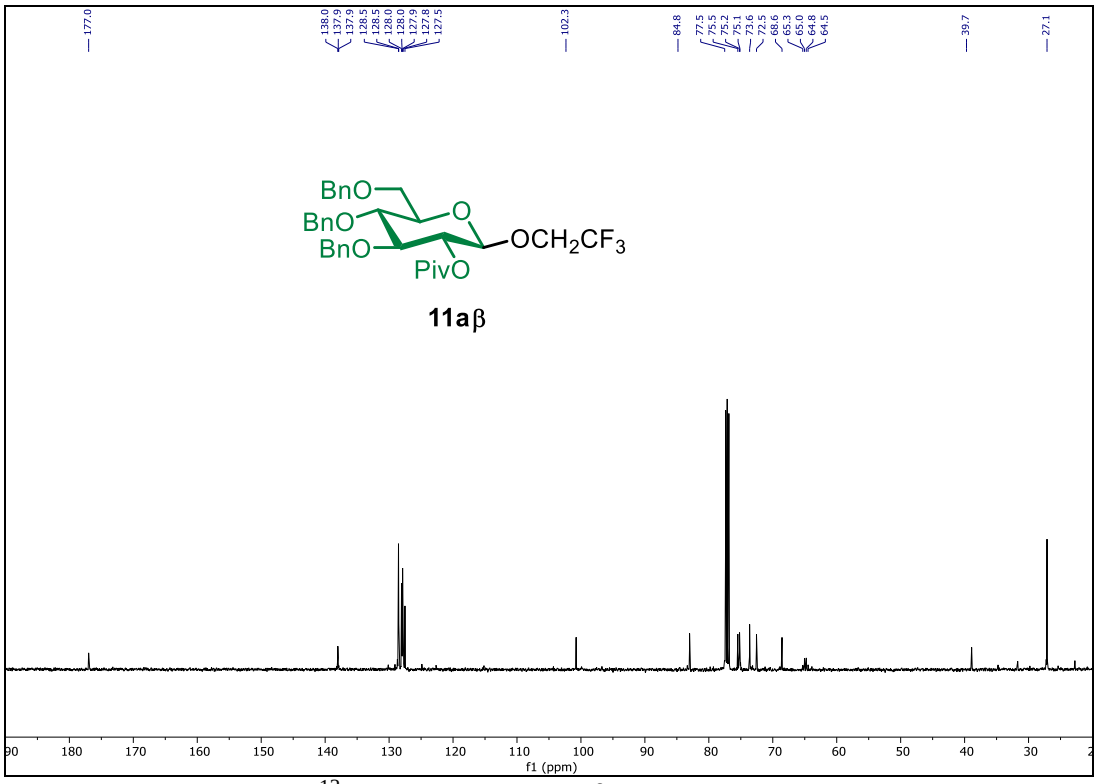


Figure S47 ^{13}C NMR spectrum of **11aβ** (126 MHz, $CDCl_3$).

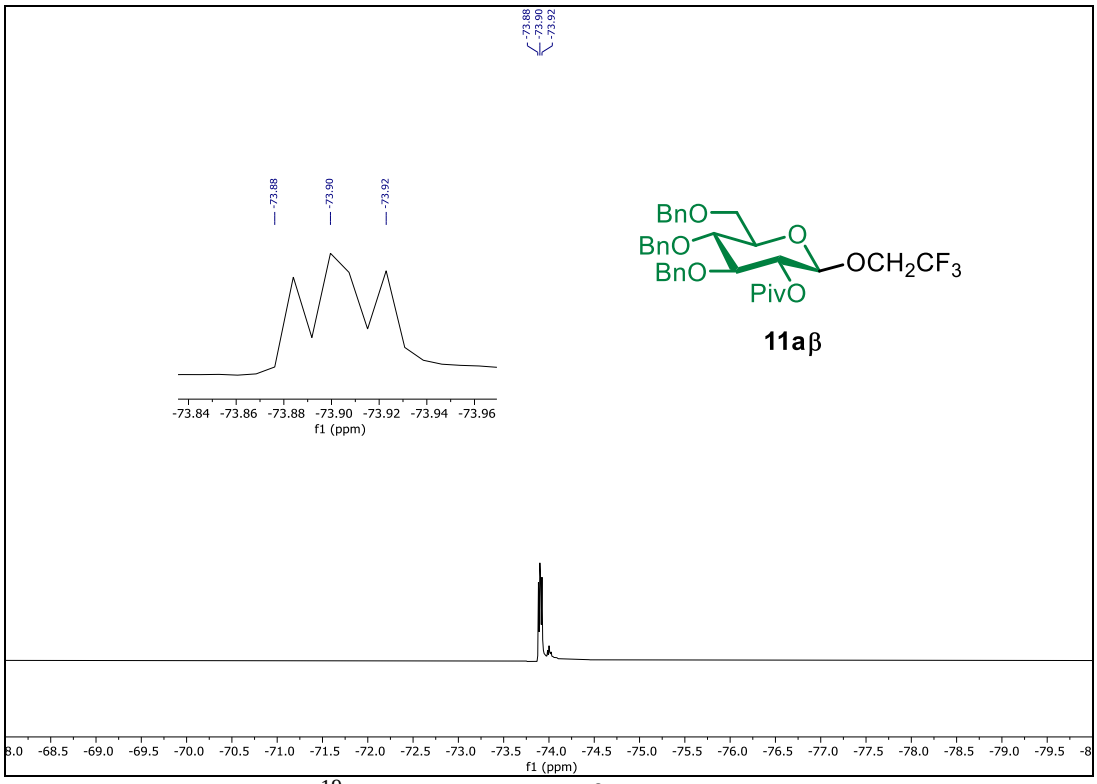


Figure S48 ^{19}F NMR spectrum of **11aβ** (471 MHz, $CDCl_3$).

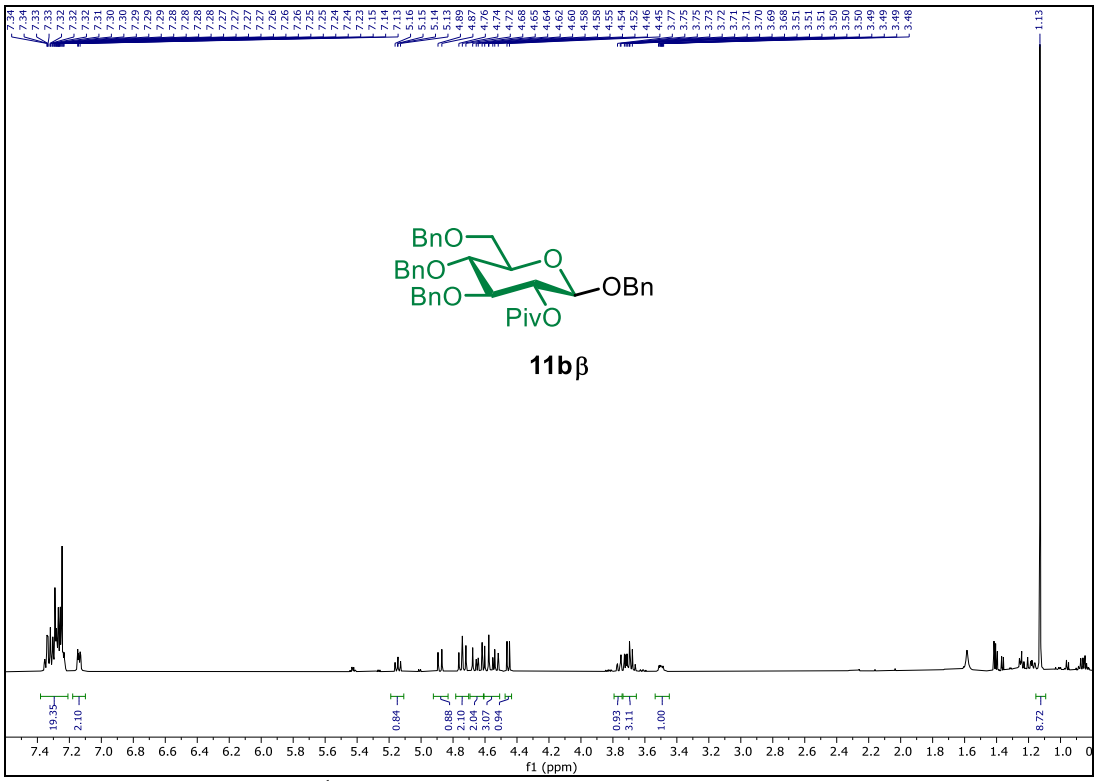


Figure S49 ^{1}H NMR spectrum of **11bβ** (500 MHz, $CDCl_3$).

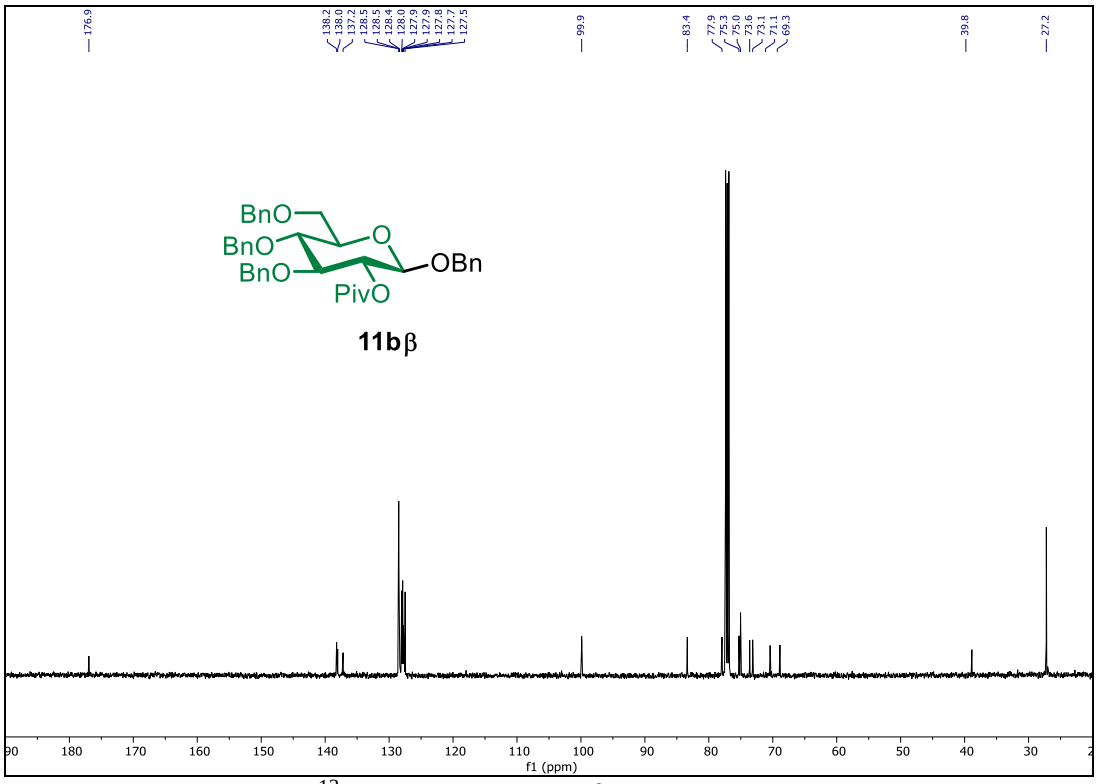


Figure S50 ^{13}C NMR spectrum of **11nβ** (126 MHz, $CDCl_3$).

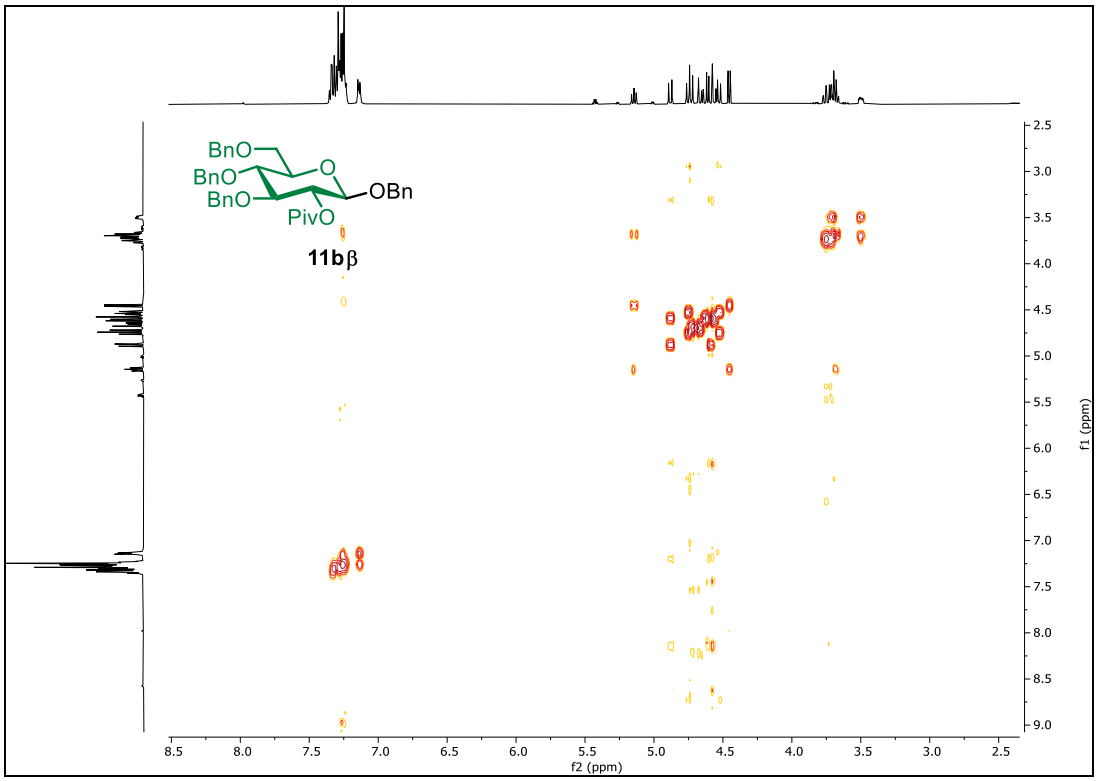


Figure S51 COSY spectrum of **11bβ** (500 MHz, $CDCl_3$).

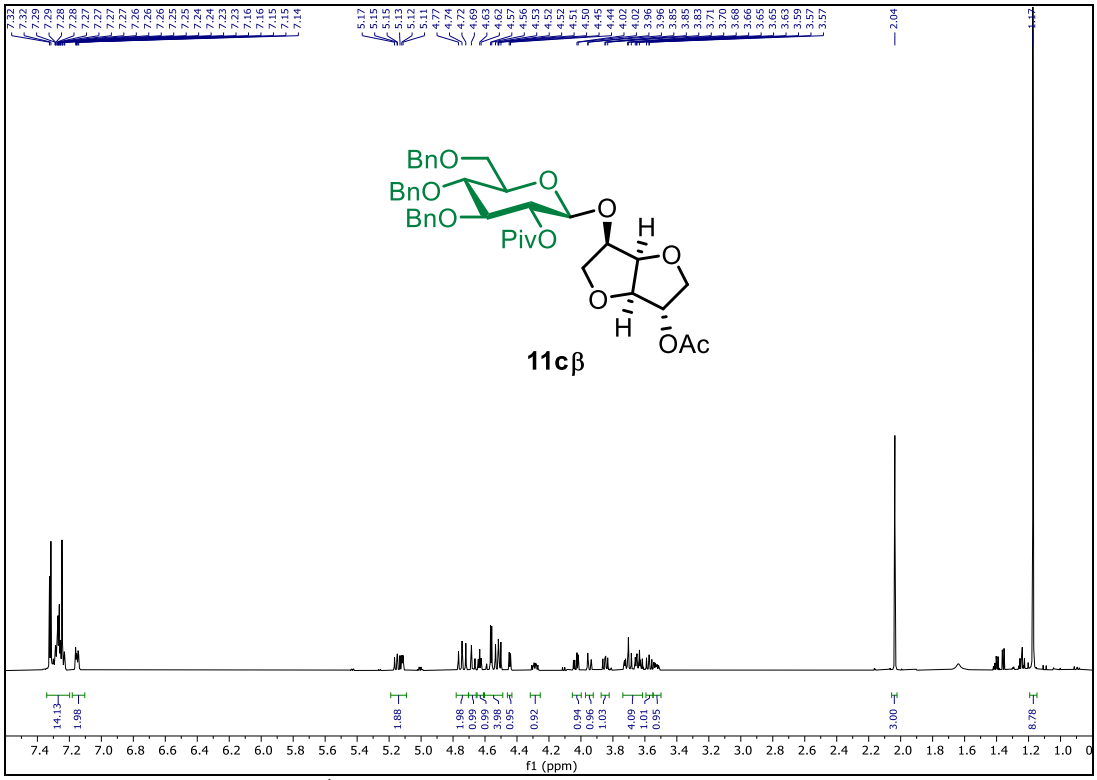


Figure S52 ^{1}H NMR spectrum of **11cβ** (500 MHz, $CDCl_3$).

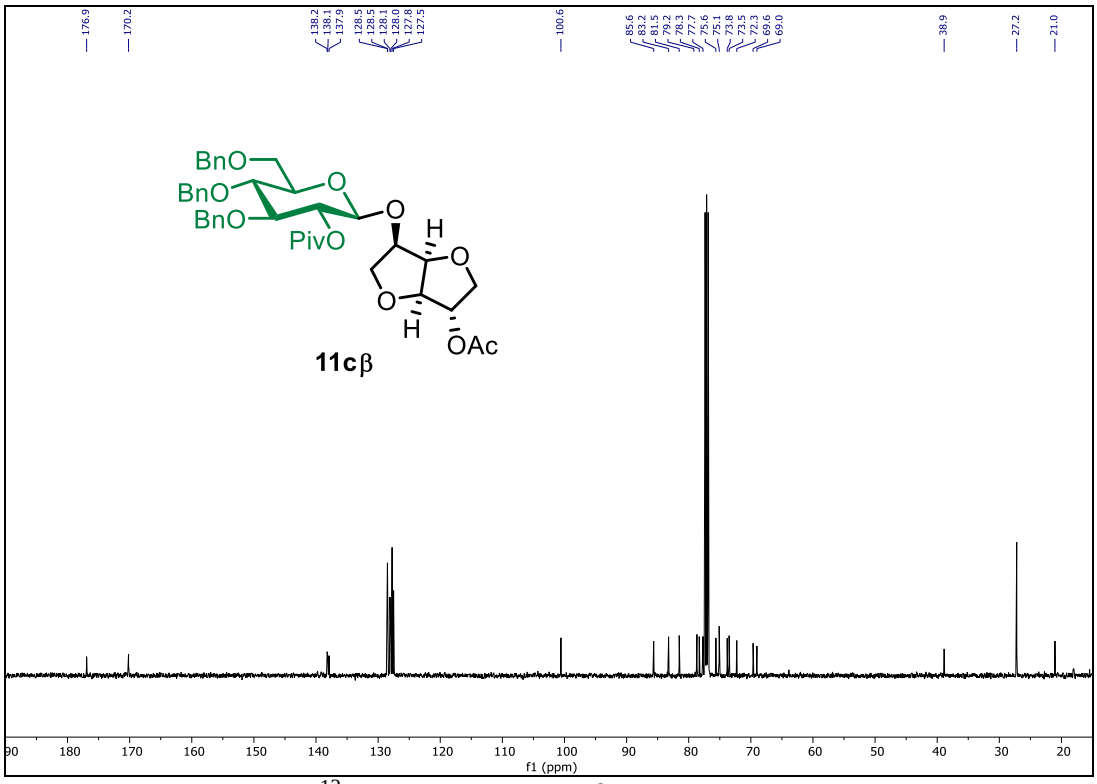


Figure S53 ^{13}C NMR spectrum of **11cβ** (126 MHz, $CDCl_3$).

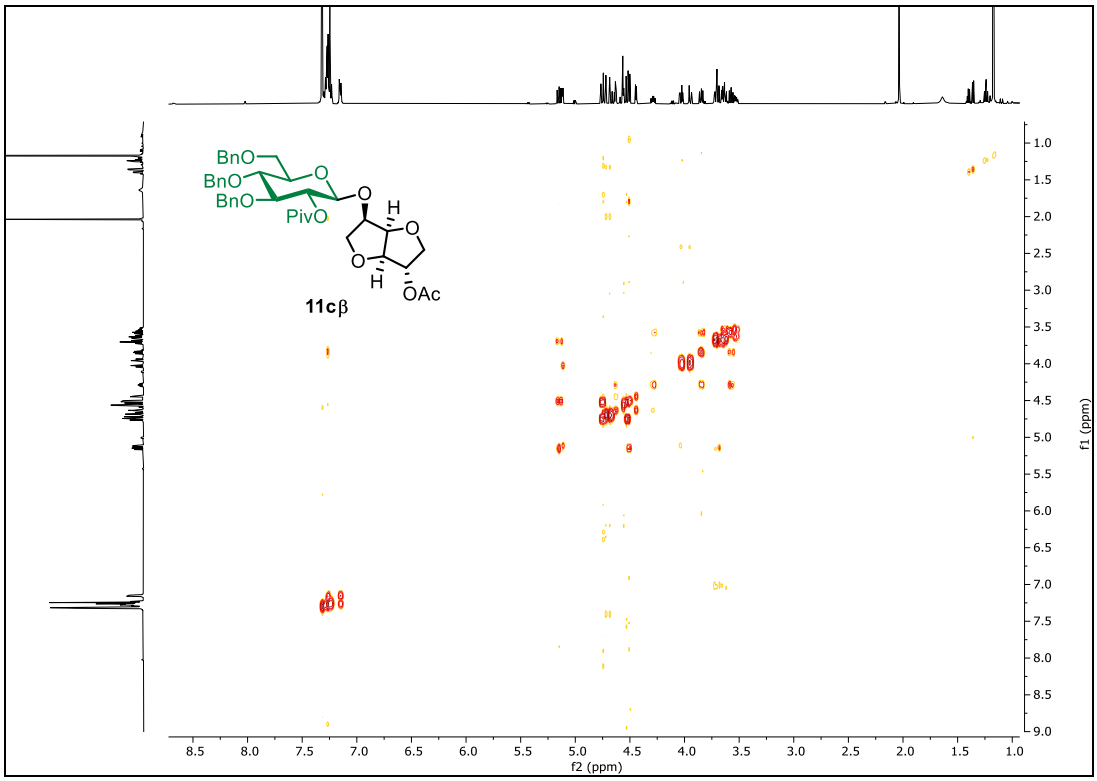


Figure S54 COSY spectrum of **11cβ** (500 MHz, $CDCl_3$).

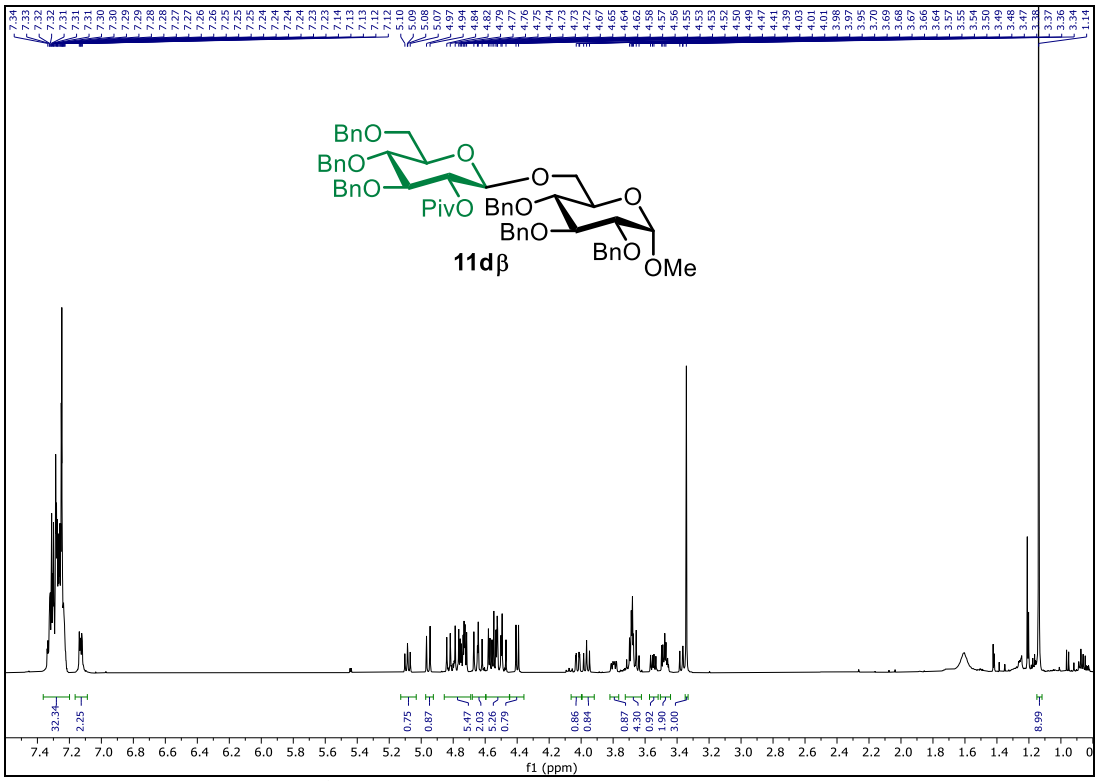


Figure S55 ^{1}H NMR spectrum of **11dβ** (500 MHz, $CDCl_3$).

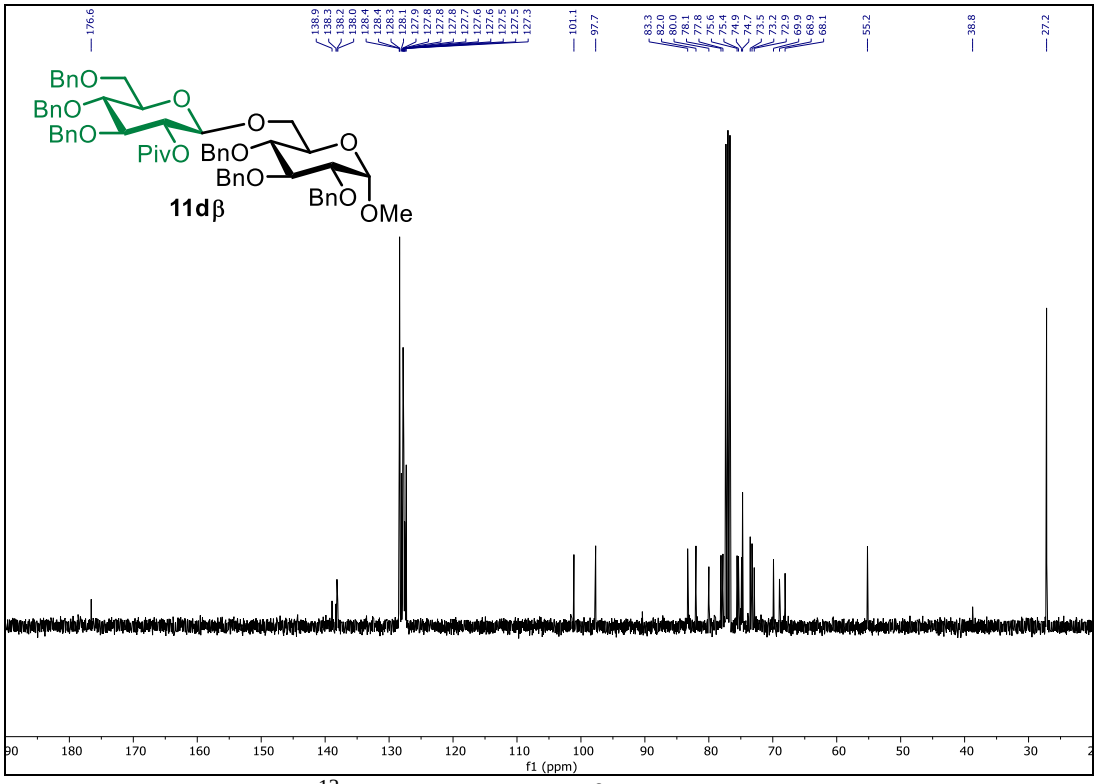


Figure S56 ^{13}C NMR spectrum of **11dβ** (101 MHz, $CDCl_3$).

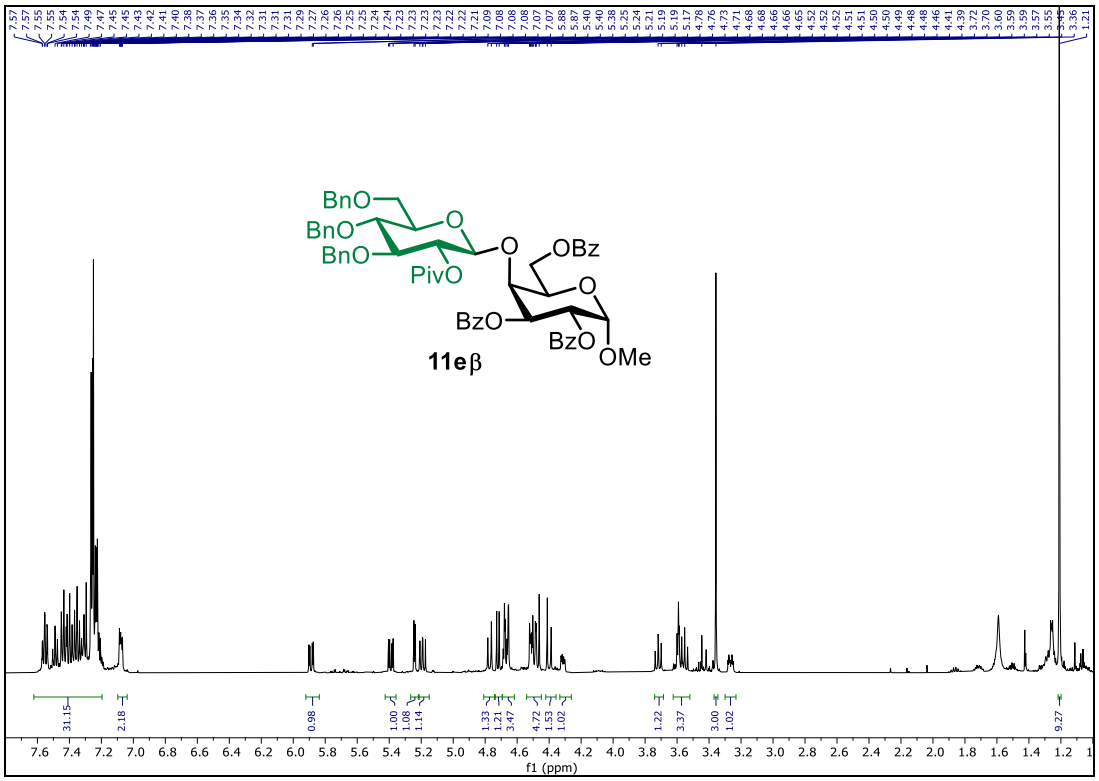


Figure S57 ^{1}H NMR spectrum of **11eβ** (500 MHz, $CDCl_3$).

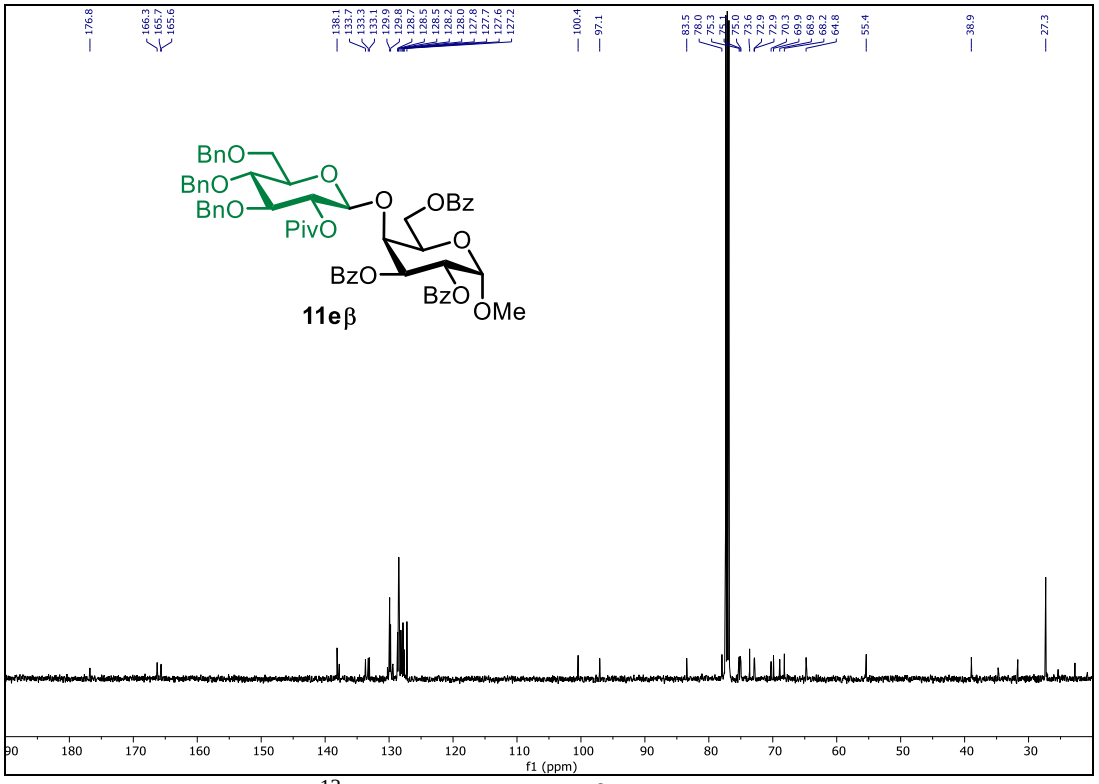


Figure S58 ^{13}C NMR spectrum of **11eβ** (126 MHz, $CDCl_3$).

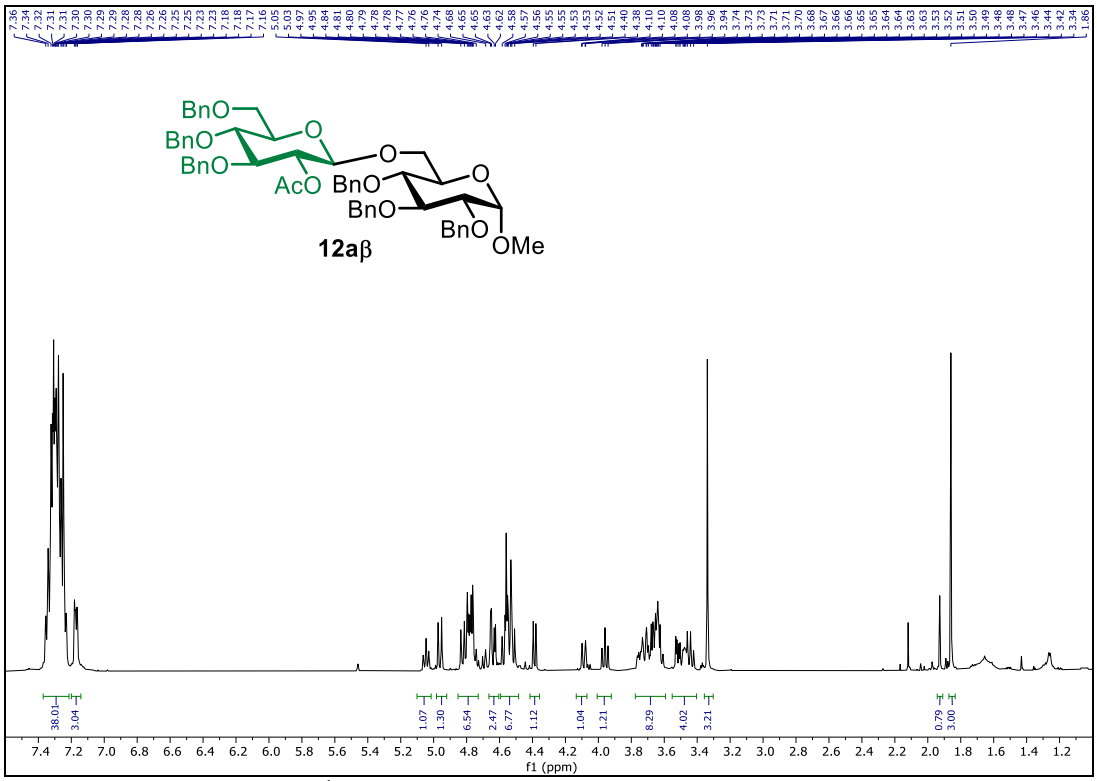


Figure S59 ^{1}H NMR spectrum of **12aβ** (500 MHz, $CDCl_3$).

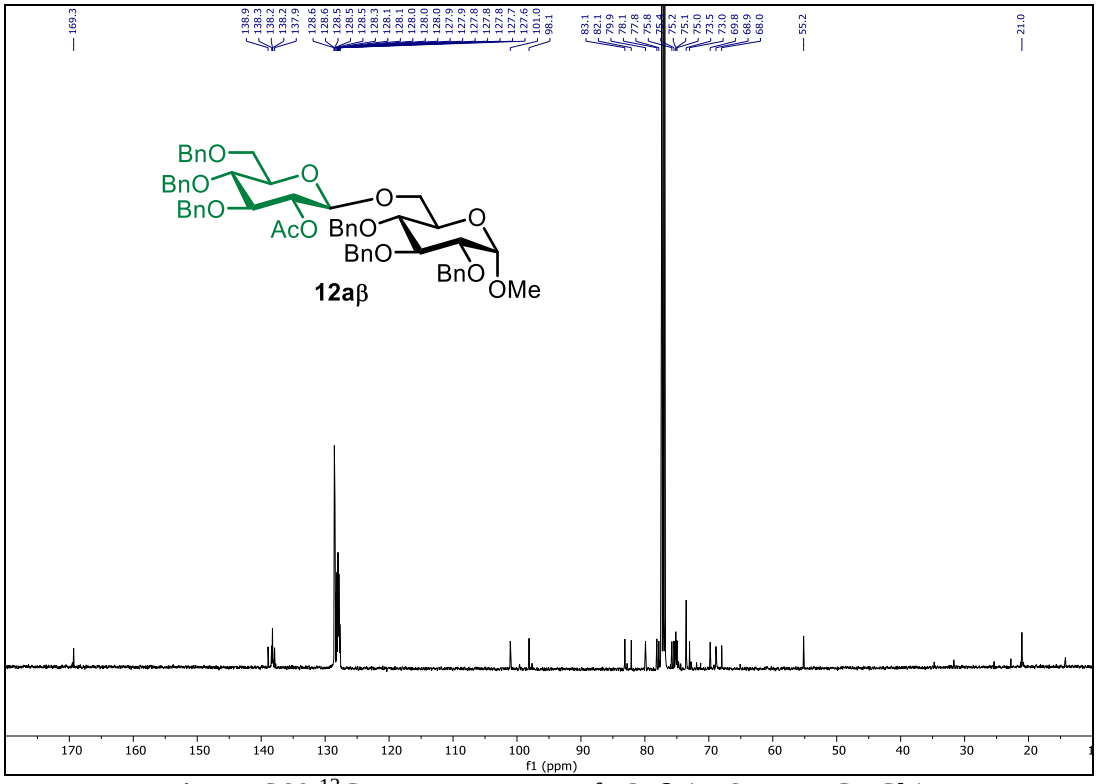


Figure S60 ^{13}C NMR spectrum of **12aβ** (126 MHz, $CDCl_3$).

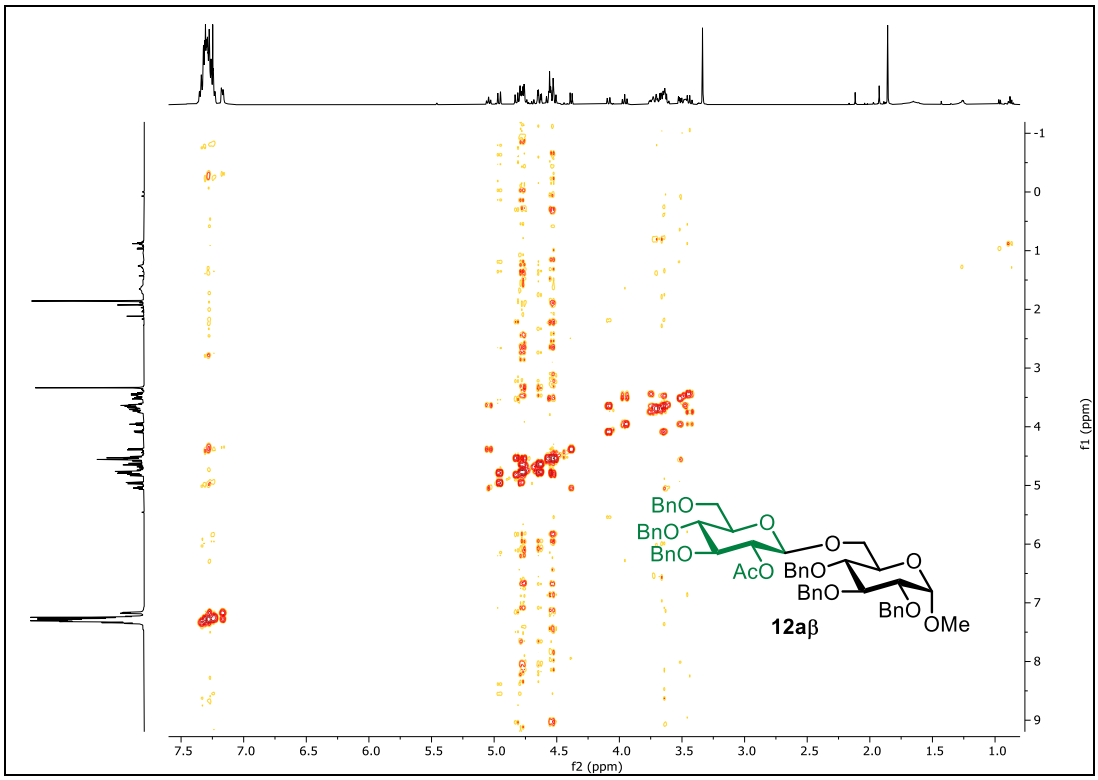


Figure S61 COSY spectrum of **12aβ** (500 MHz, $CDCl_3$).

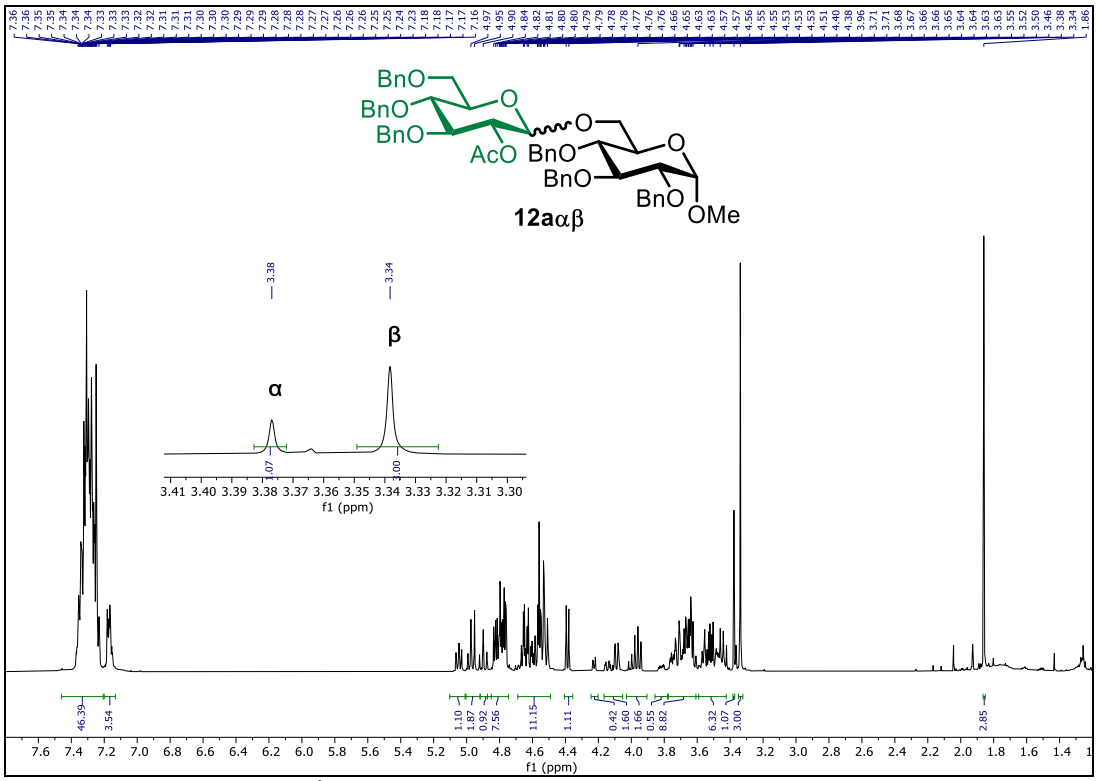


Figure S62 ^{1}H NMR spectrum of **12aαβ** (500 MHz, $CDCl_3$).

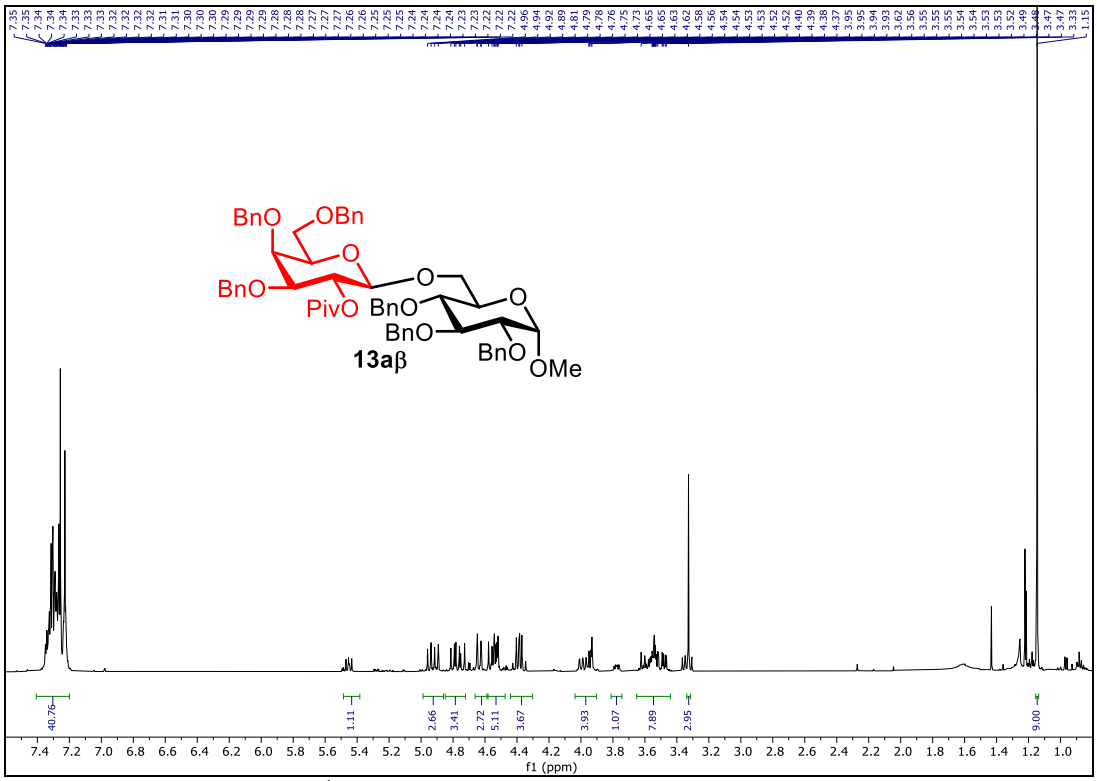


Figure S63 ^{1}H NMR spectrum of **13aβ** (500 MHz, $CDCl_3$).

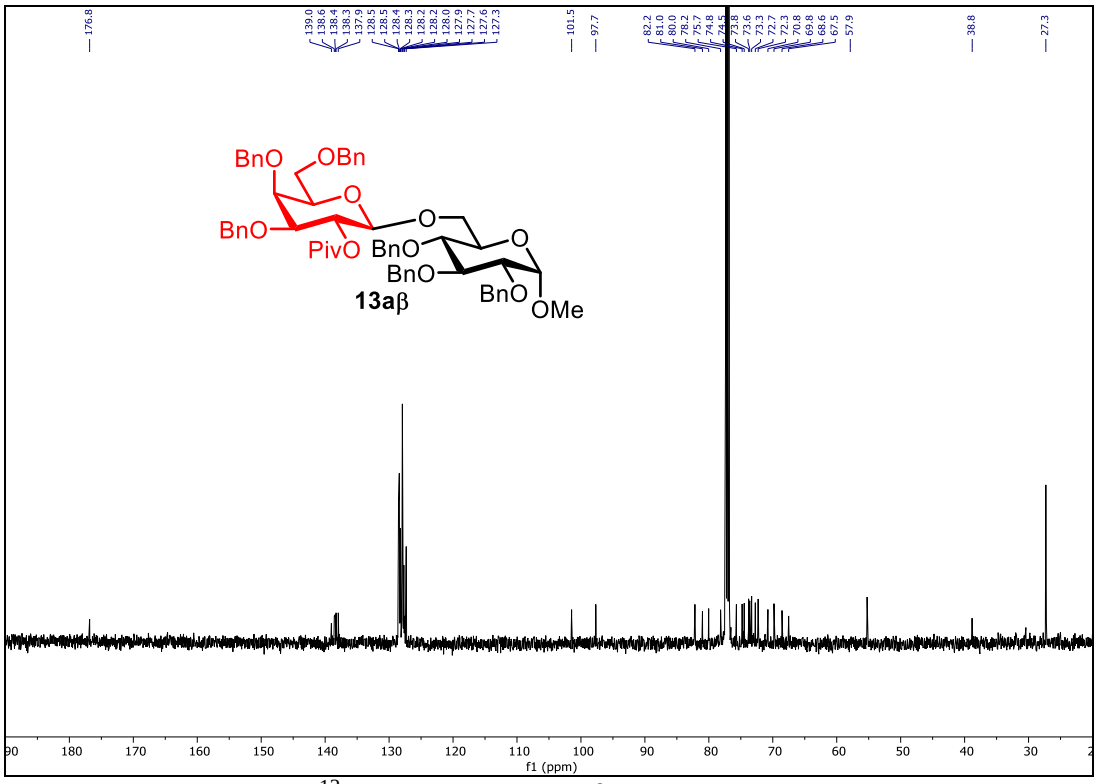


Figure S64 ^{13}C NMR spectrum of **13aβ** (126 MHz, $CDCl_3$).

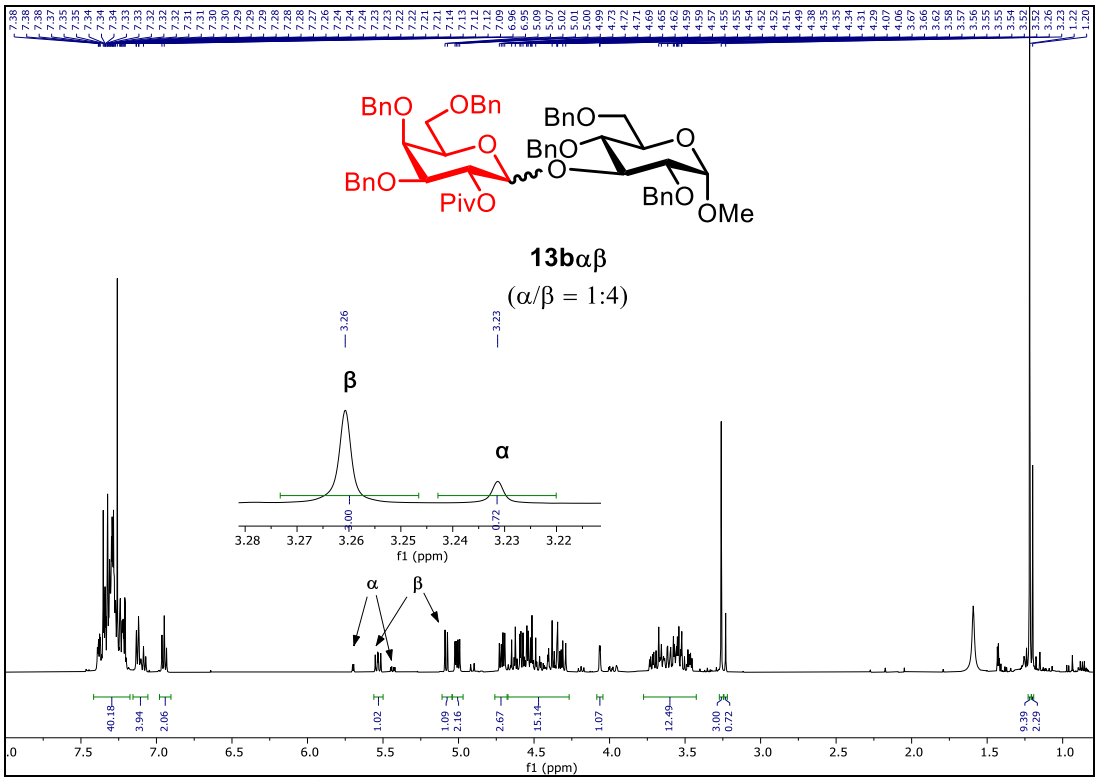


Figure S65 ^{1}H NMR spectrum of **13bαβ** (500 MHz, $CDCl_3$).

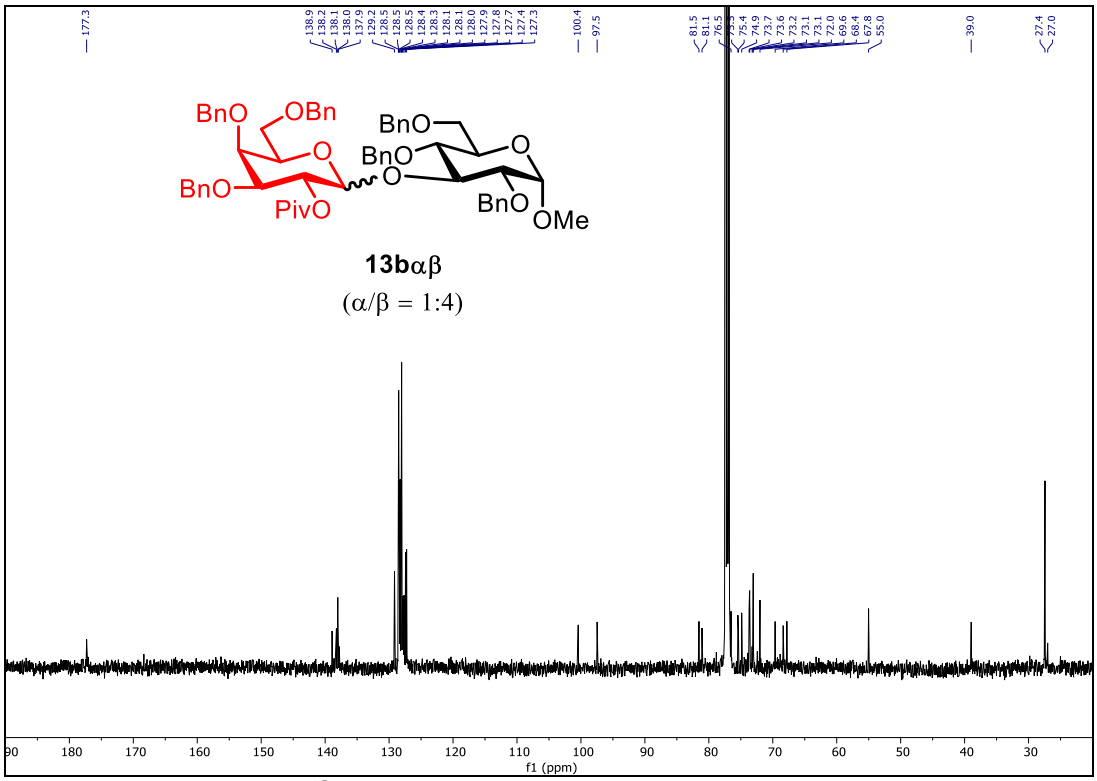


Figure S66 ^{13}C NMR spectrum of **13bαβ** (126 MHz, $CDCl_3$).

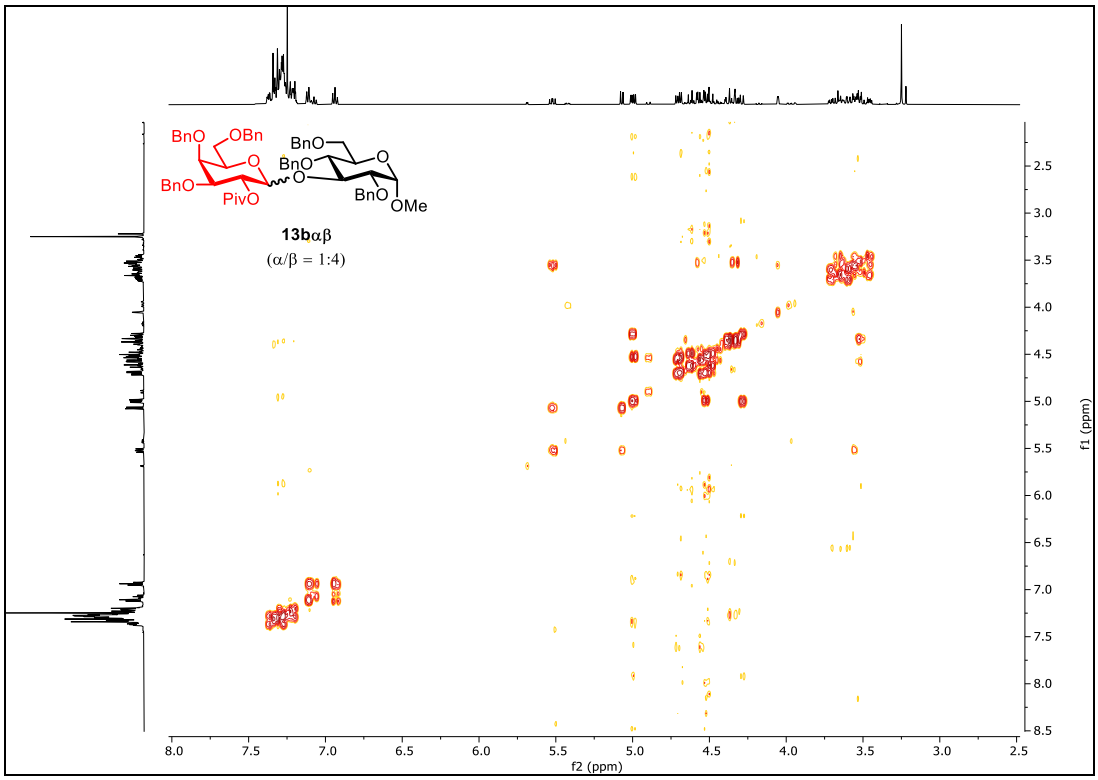


Figure S67 COSY spectrum of **13bαβ** (500 MHz, $CDCl_3$).

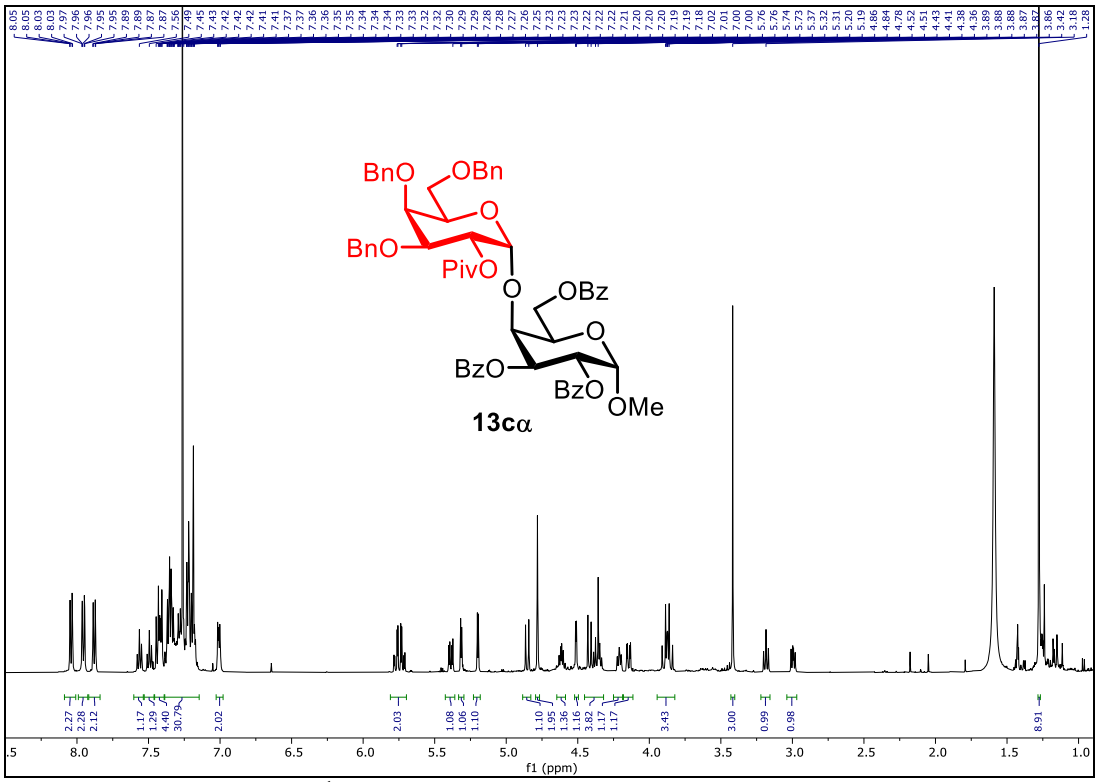


Figure S68 ^{1}H NMR spectrum of **13cα** (500 MHz, $CDCl_3$).

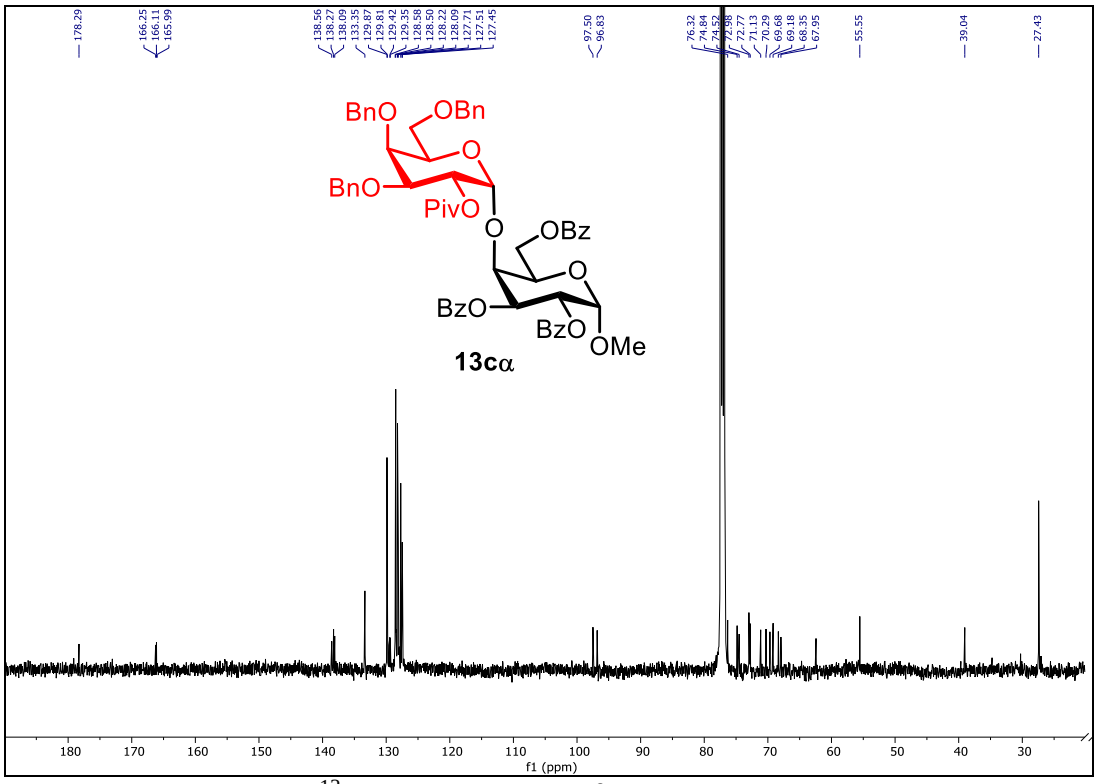


Figure S69 ^{13}C NMR spectrum of **13cα** (126 MHz, $CDCl_3$).

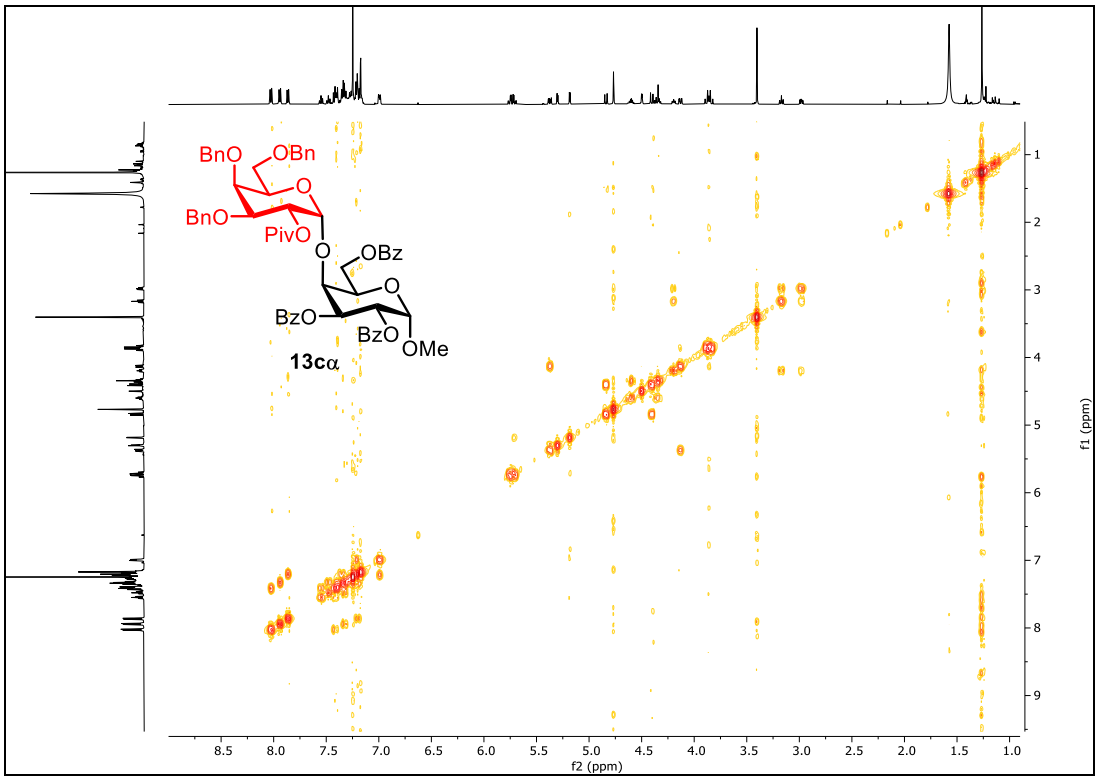


Figure S70 COSY spectrum of **13cα** (500 MHz, $CDCl_3$).

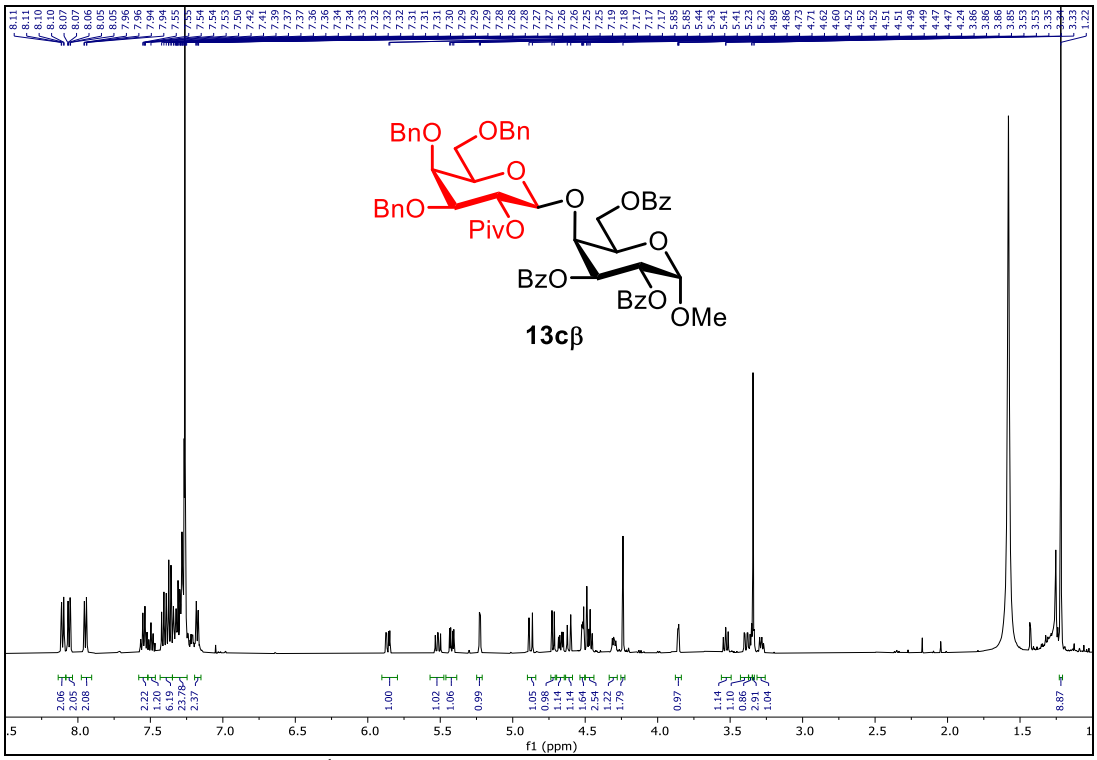


Figure S71 ^{1}H NMR spectrum of **13cβ** (500 MHz, $CDCl_3$).

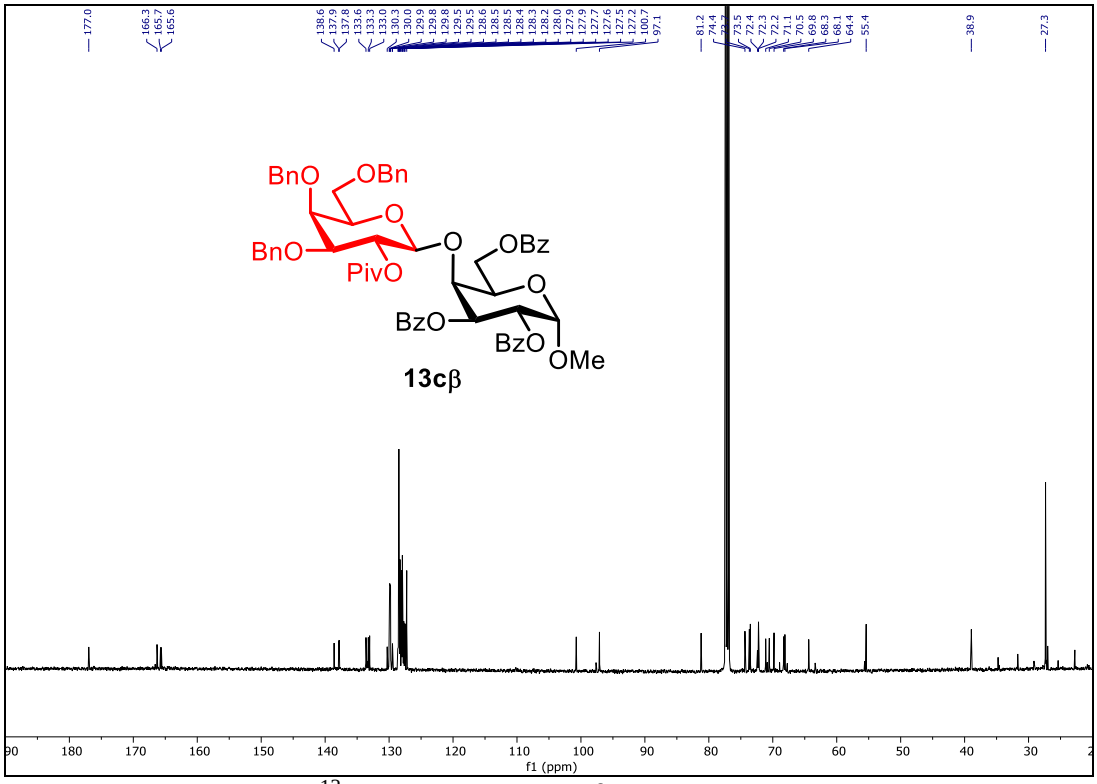


Figure S72 ^{13}C NMR spectrum of **13cβ** (126 MHz, $CDCl_3$).

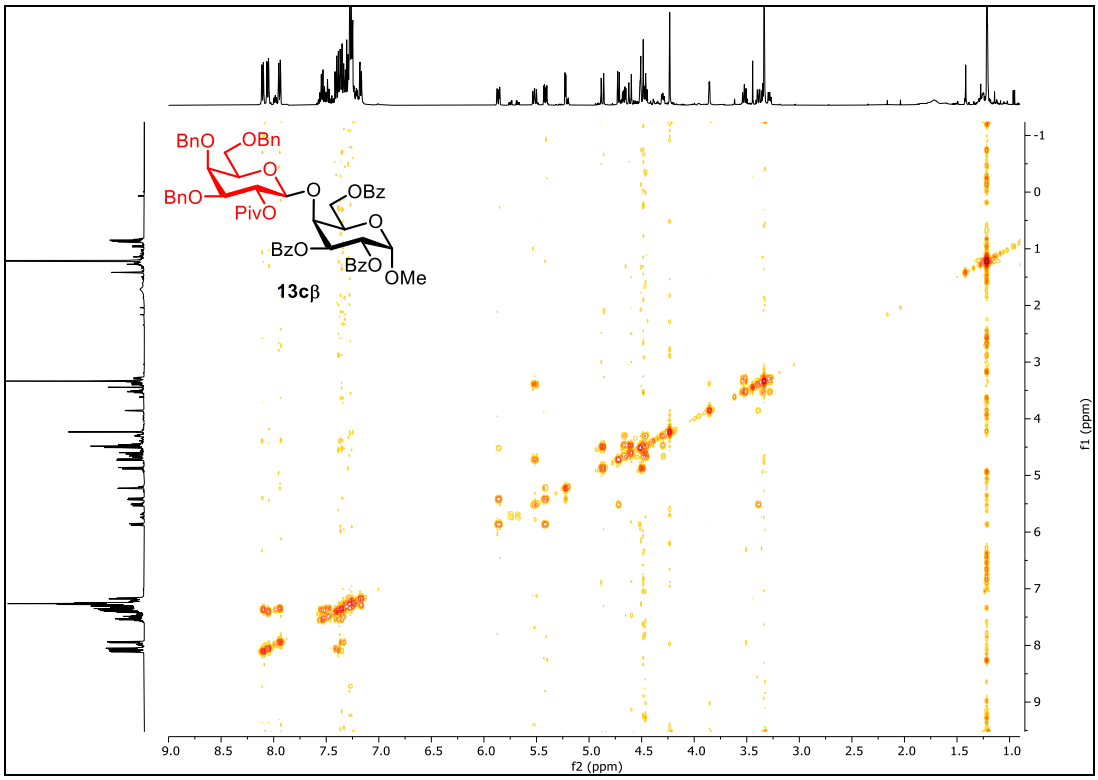


Figure S73 COSY spectrum of **13cβ** (500 MHz, $CDCl_3$).

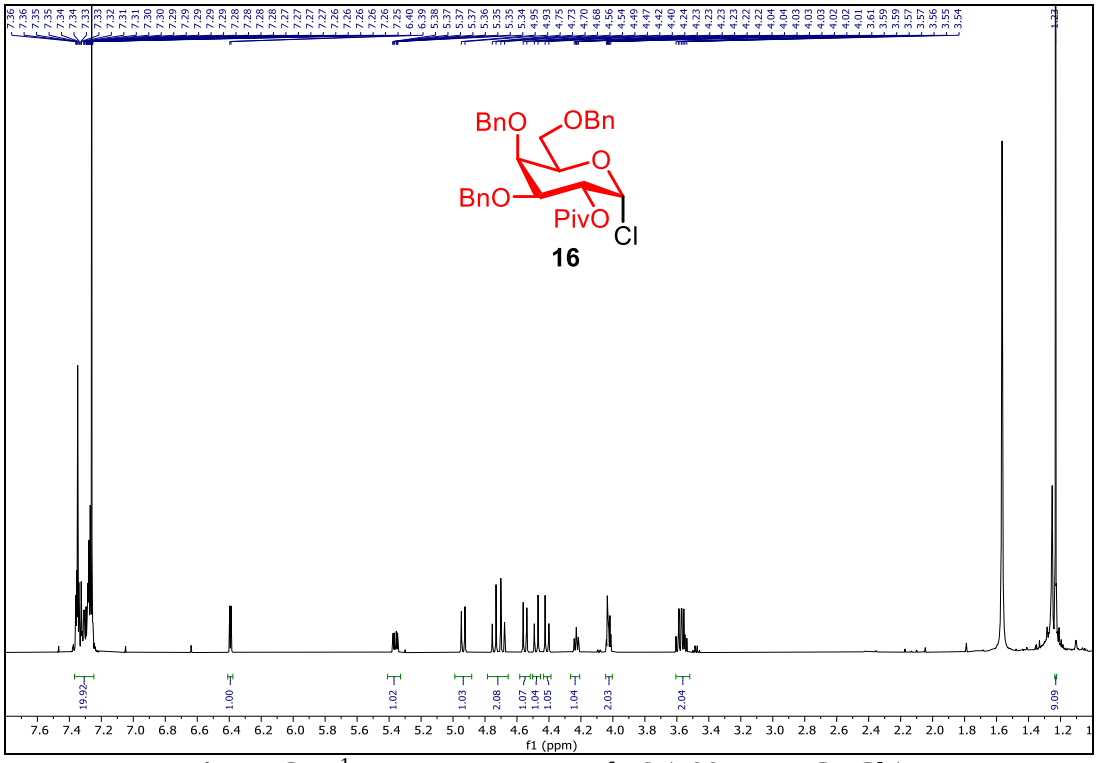


Figure S74 ^{1}H NMR spectrum of **16** (500 MHz, $CDCl_3$).

VI. NMR spectra of the product from the preparative-scale

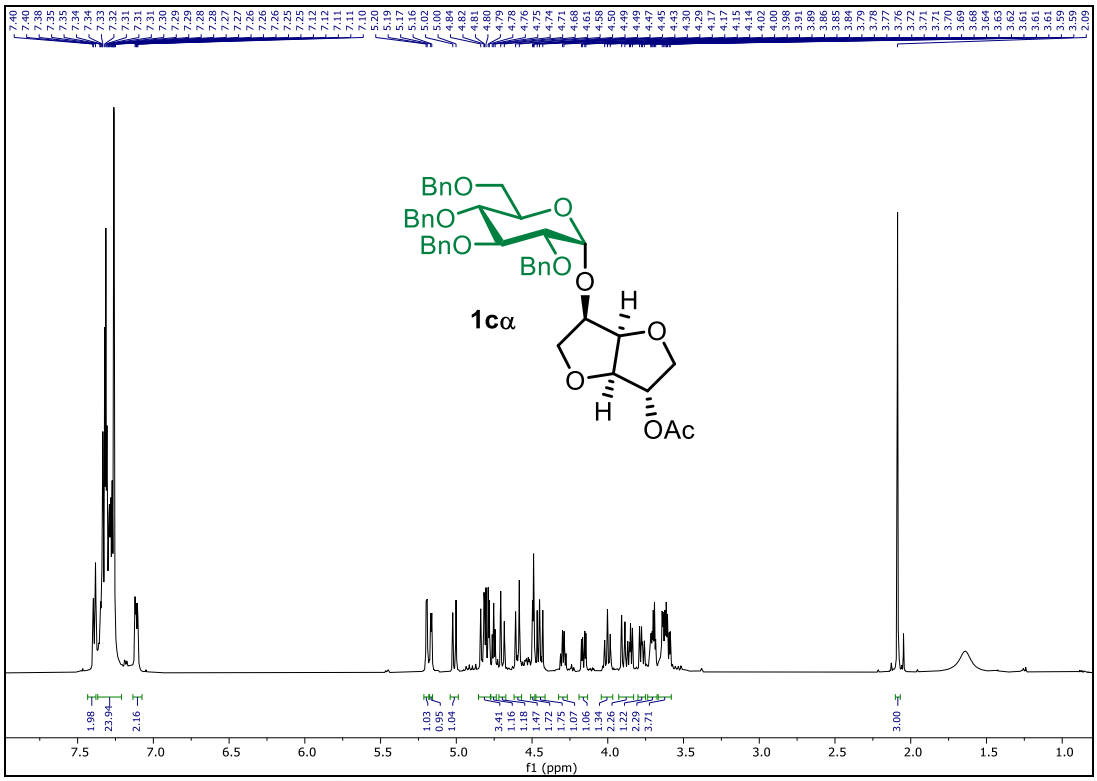


Figure S75 ^{1}H NMR spectrum of **1cα** (500 MHz, $CDCl_3$).

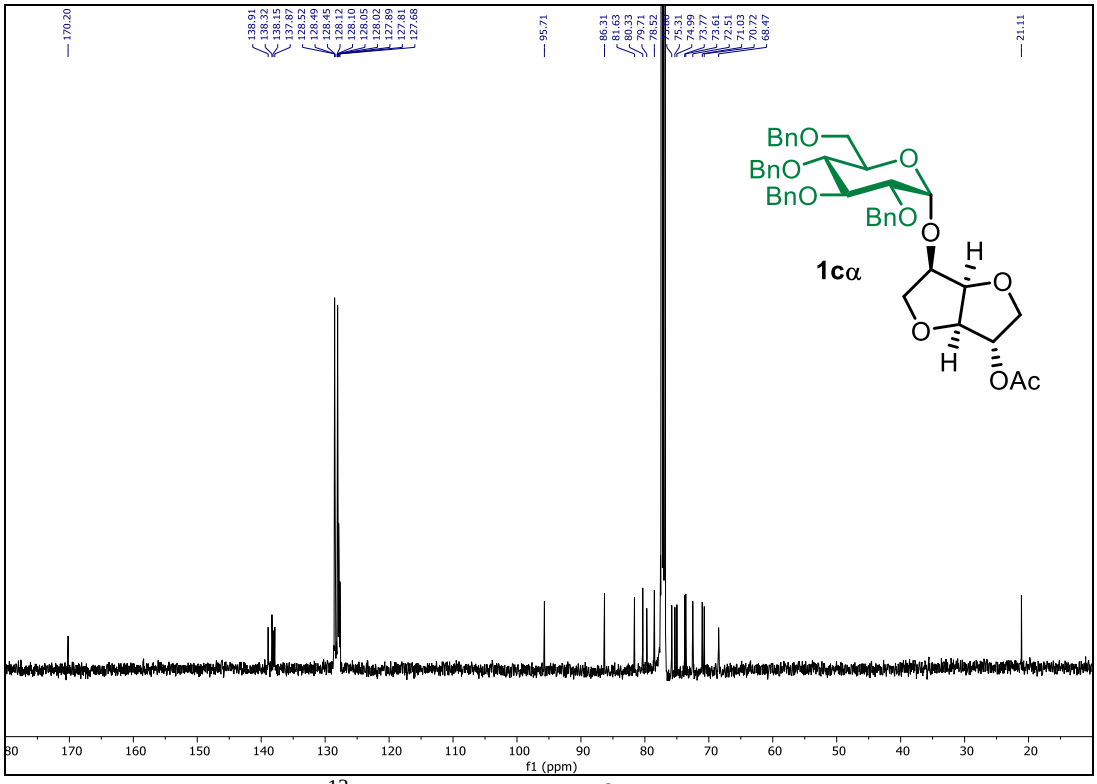


Figure S76 ^{13}C NMR spectrum of **1cα** (126 MHz, $CDCl_3$).

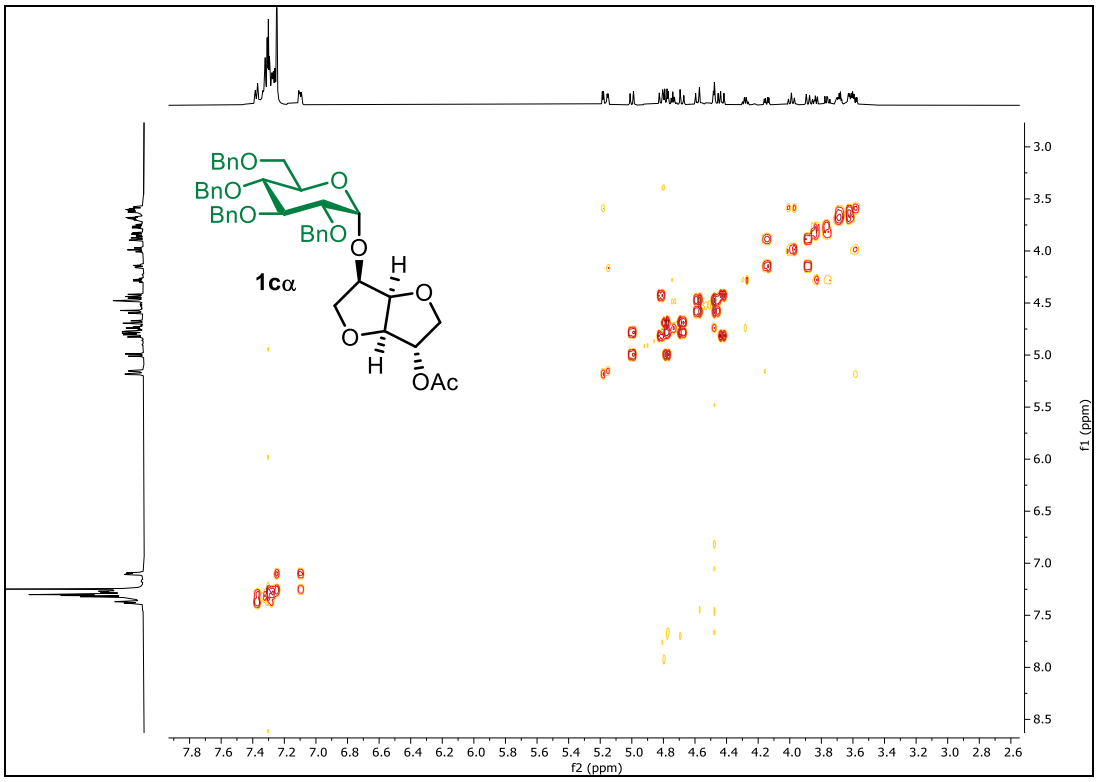


Figure S77 COSY spectrum of **1cα** (500 MHz, $CDCl_3$).

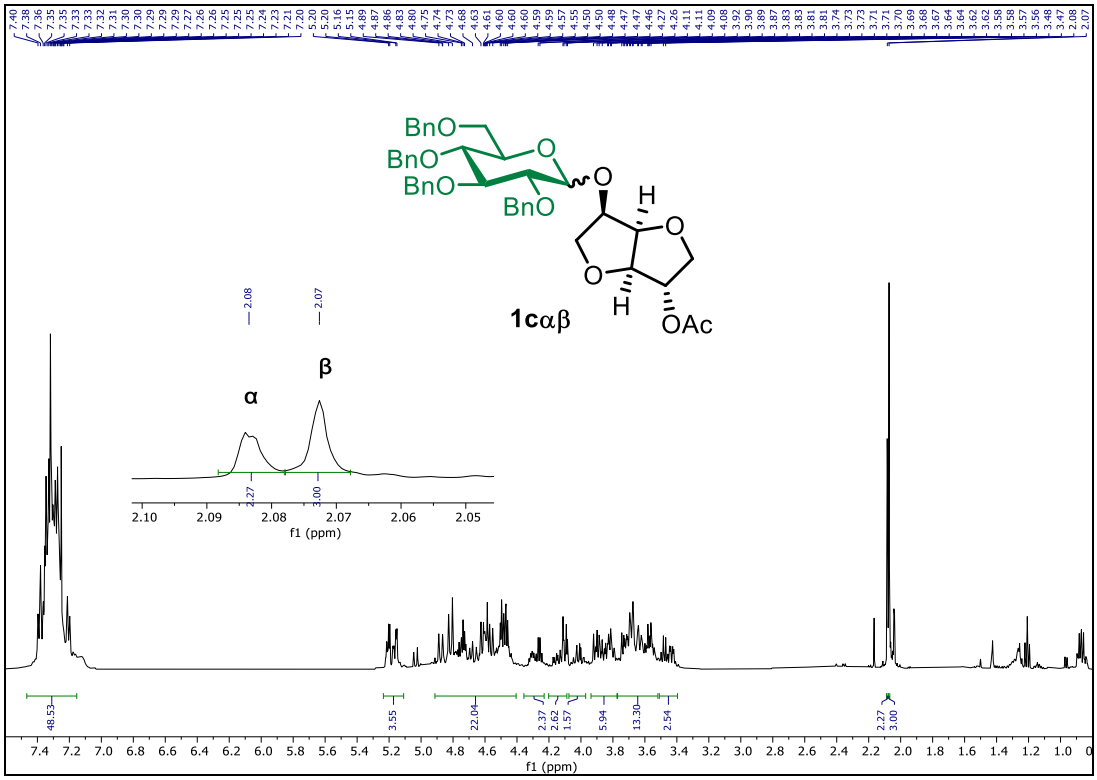


Figure S78 ^{1}H NMR spectrum of **1cαβ** (500 MHz, $CDCl_3$).

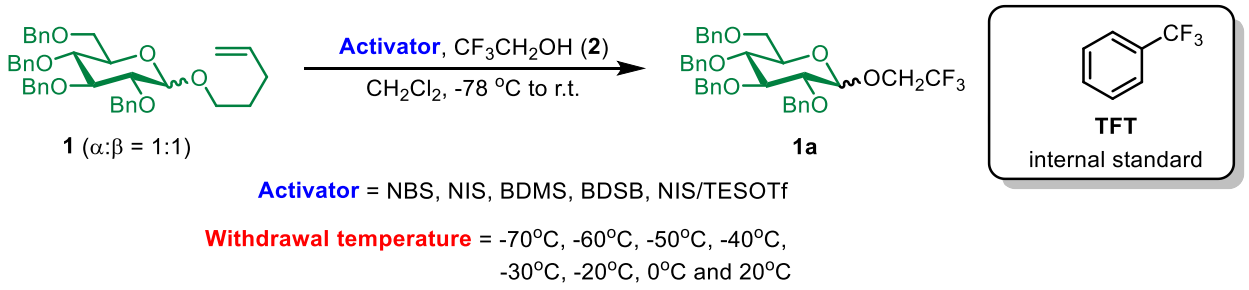
VII. Evaluation of reactivity of halonium activators towards glucosyl donor 1 *(Scheme 1)*

General procedure for glycosylation

In a typical procedure, the *n*-pentenyl glucoside **1** (0.3 mmol scale), 3 Å molecular sieve, and 0.05 M dichloromethane were added to a round bottom flask and stirred for 30 minutes at room temperature. Then, the flask was moved into the −78 °C cooling bath (isopropanol and dry ice), followed by the addition of activator [NBS (1.2 equiv.), NIS (1.2 equiv.), BDMS (1.2 equiv.), BDSB (1.2 equiv.), and NIS (1.2 equiv.)/TESOTf (0.5 equiv.)], 5.0 equiv. of glycosyl acceptor **2** was added. The solution was withdrawn evenly a total of 8 times at

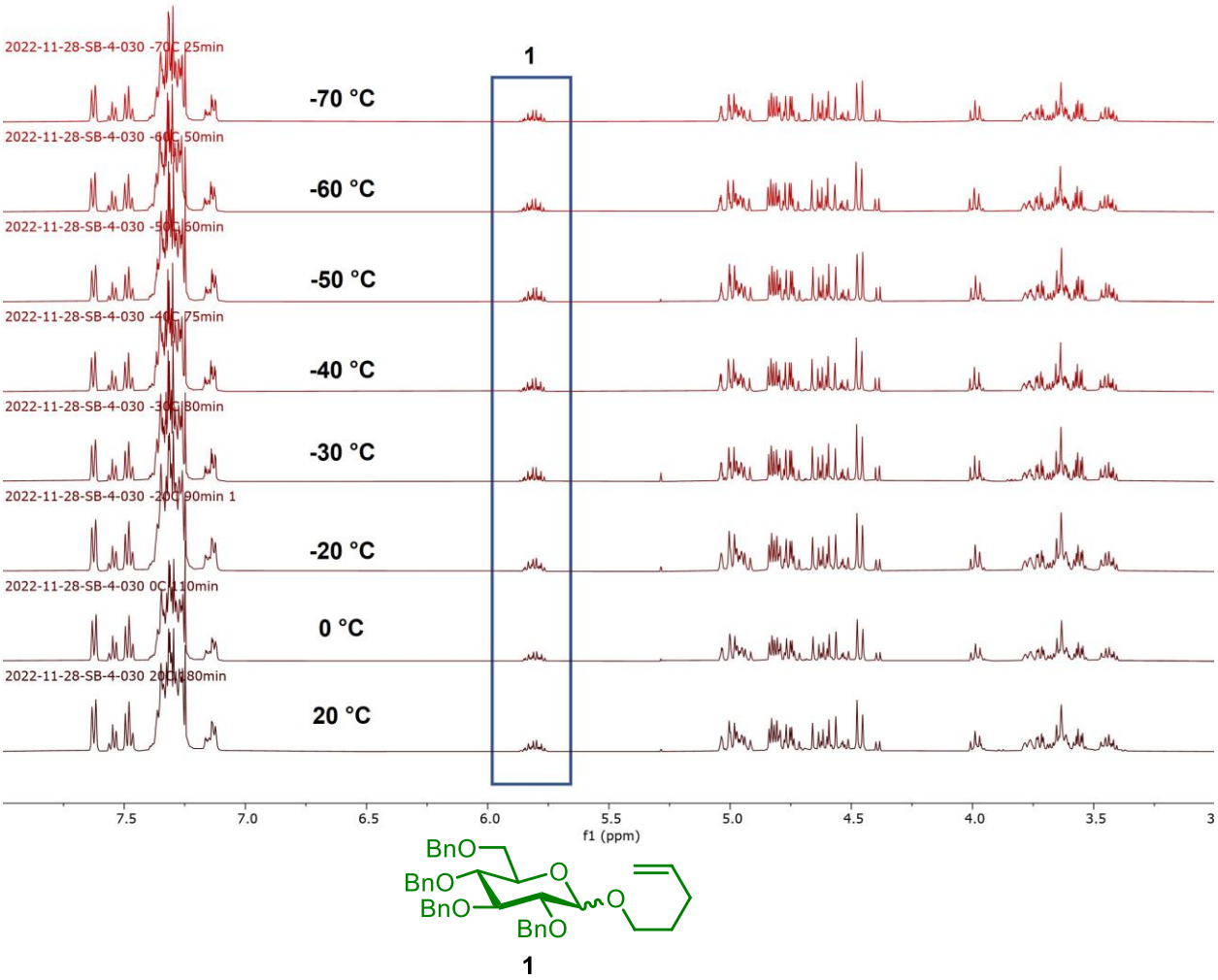
1. −70 °C (approximately 25 minutes after adding glycosyl acceptor **2**)
2. −60 °C (approximately 50 minutes after adding glycosyl acceptor **2**)
3. −50 °C (approximately 60 minutes after adding glycosyl acceptor **2**)
4. −40 °C (approximately 75 minutes after adding glycosyl acceptor **2**)
5. −30 °C (approximately 80 minutes after adding glycosyl acceptor **2**)
6. −20 °C (approximately 90 minutes after adding glycosyl acceptor **2**)
7. 0 °C (approximately 110 minutes after adding glycosyl acceptor **2**)
8. 20 °C (approximately 180 minutes after adding glycosyl acceptor **2**)

For each withdrawal, the solution was quenched by adding saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$, extracted with dichloromethane (2 × 5 mL), and washed with brine (5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness in a rotary evaporator. Then, α,α,α-trifluorotoluene (TFT) was added as an internal standard (mol ratio 1:1 for each sample), and $CDCl_3$ was added into a reaction mixture. This homogeneous solution was withdrawn and added to a 5 mm NMR tube with adjustment of more $CDCl_3$ until the height of the solvent was 4 cm. The conversion of **1** and yield of **1a** was measured by ^1H and ^{19}F NMR, respectively.



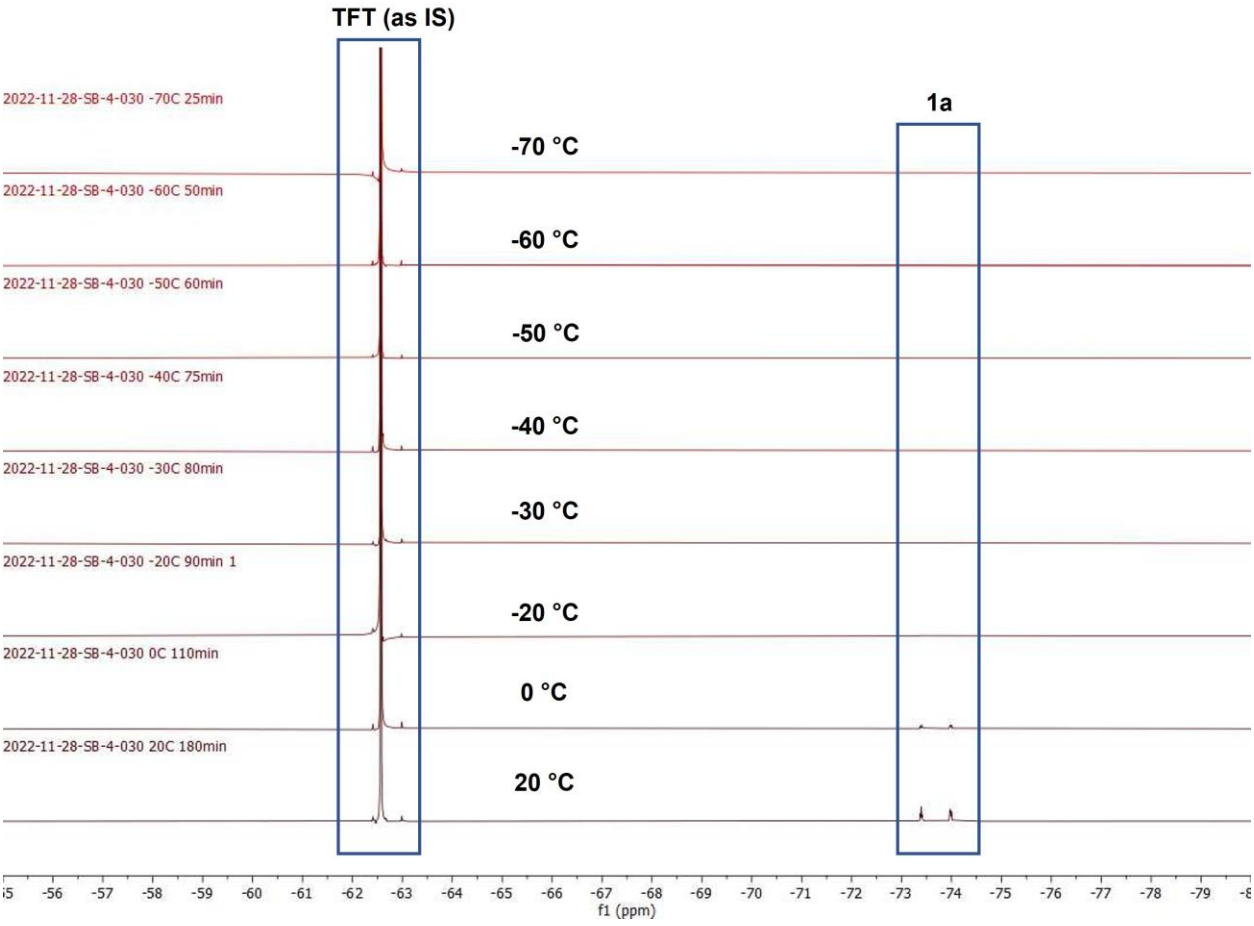
i. NBS as a promoter

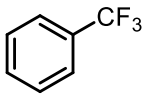
^{1}H NMR monitoring of NPG **1** activated by NBS at –70 °C to 20 °C.



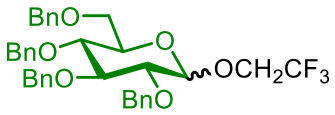
1

^{19}F NMR monitoring of **1a** product generated by NBS at –70 °C to 20 °C.



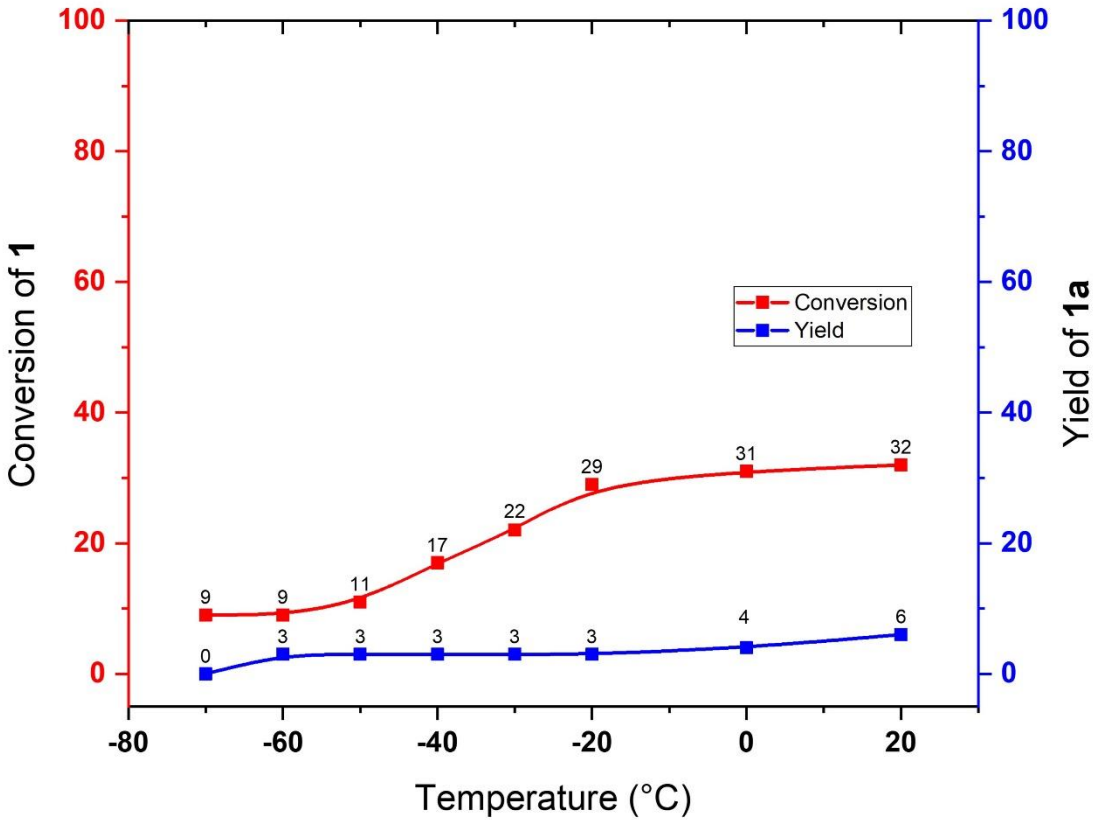


TFT
internal standard



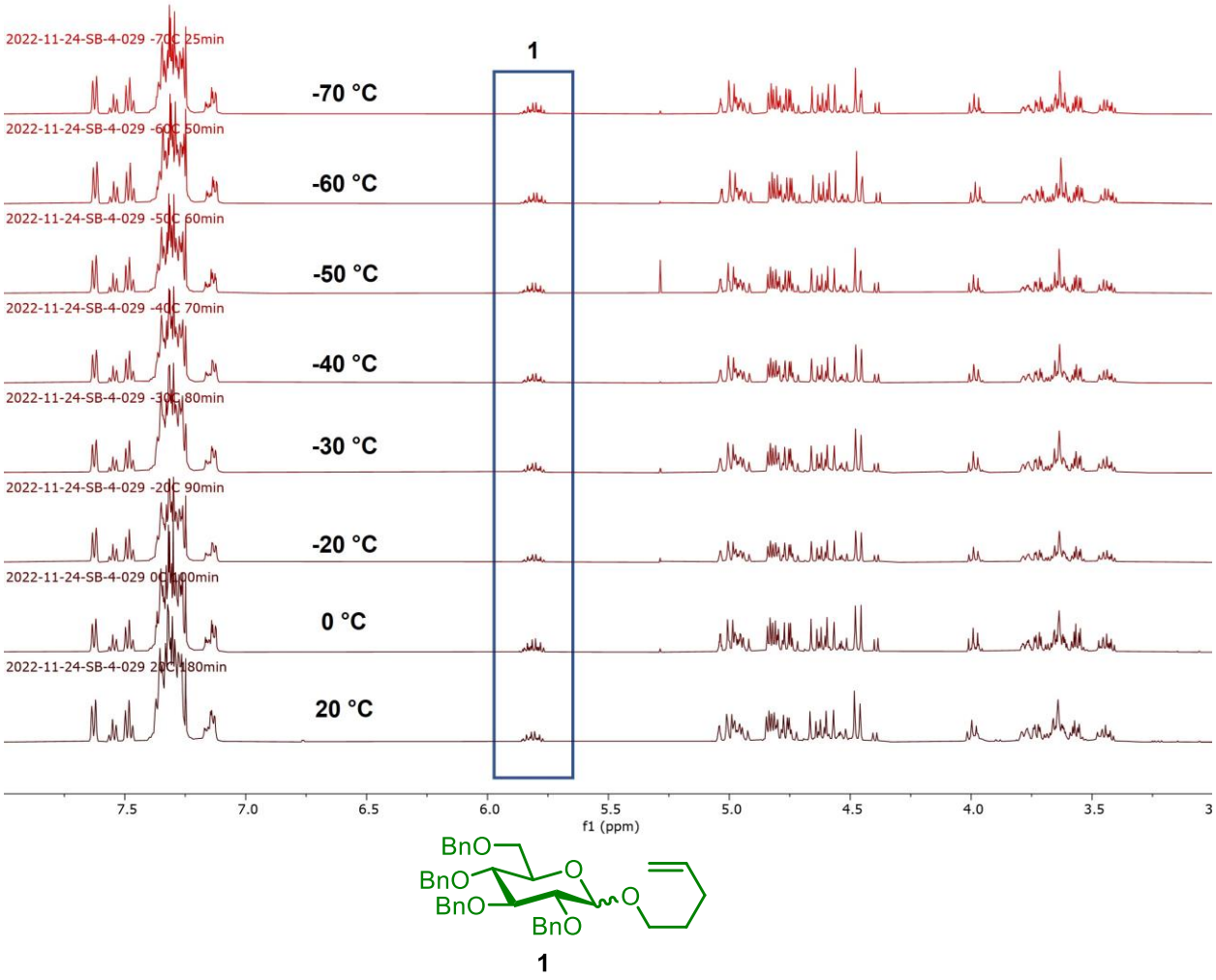
1a

Conversions of **1** and yield of **1a** were evaluated using NBS as an activator at –70 °C to 20 °C.



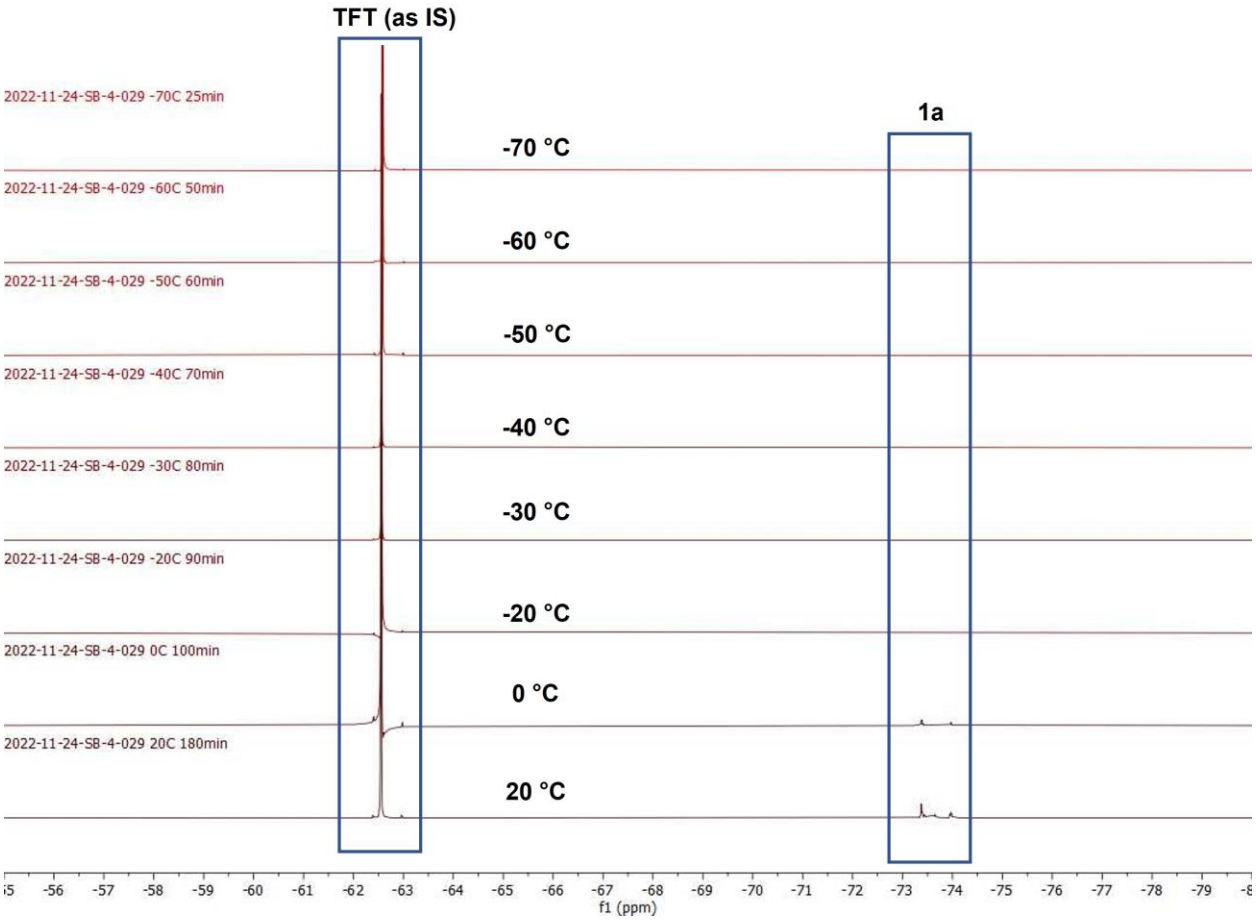
ii. NIS as a promoter

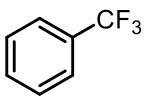
^{1}H NMR monitoring of NPG **1** activated by NIS at –70 °C to 20 °C.



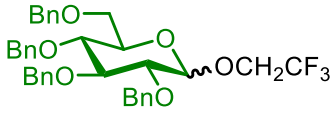
1

^{19}F NMR monitoring of **1a** product generated by NIS at –70 °C to 20 °C.



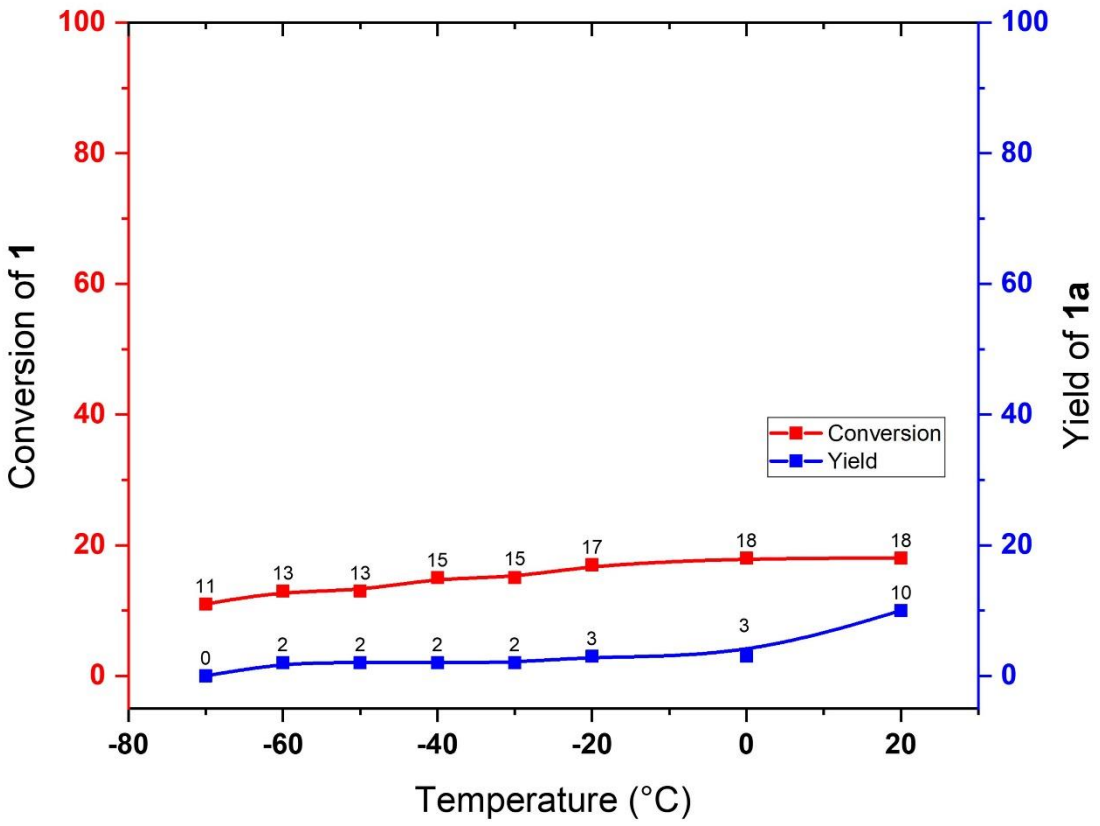


TFT
internal standard



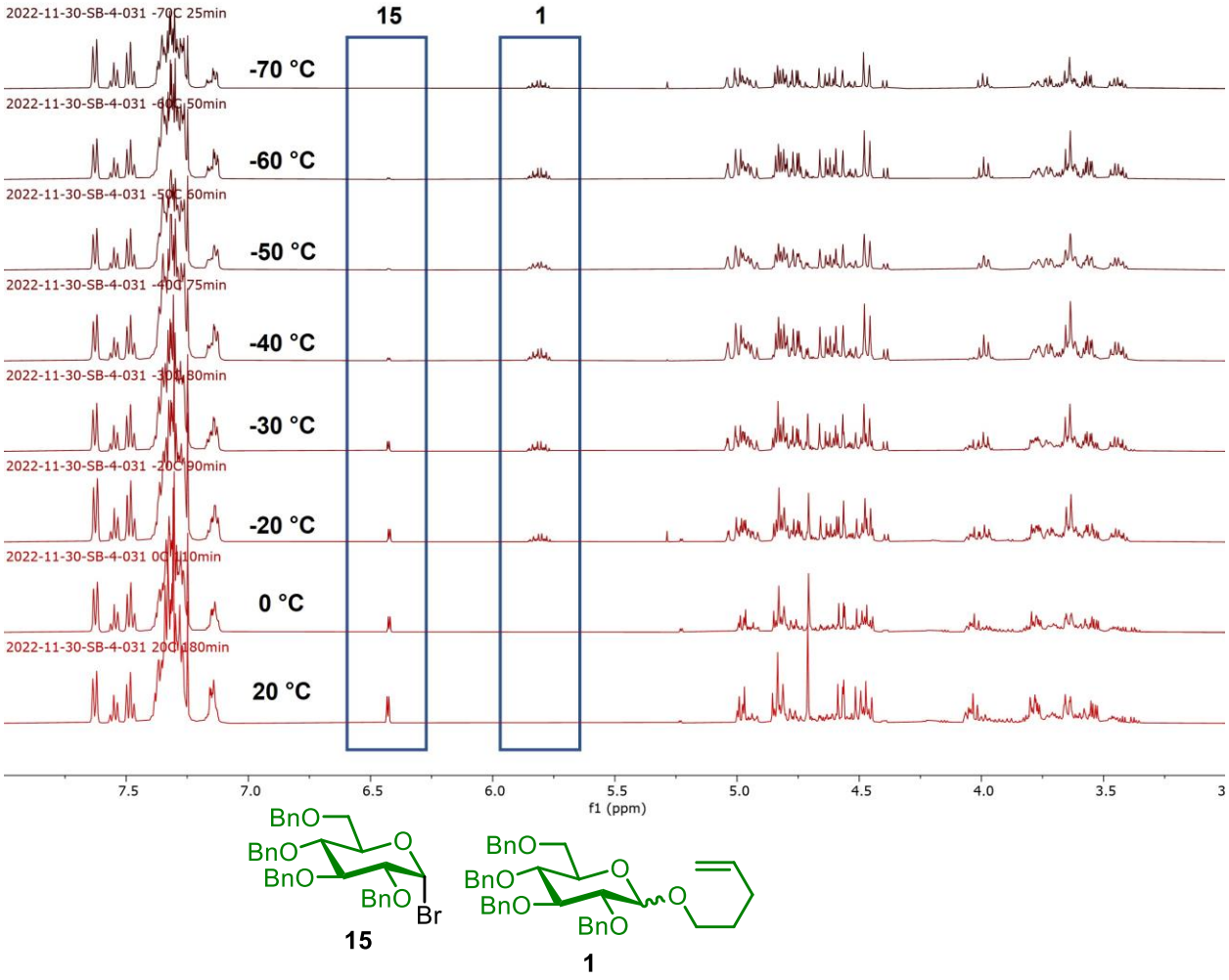
1a

Conversions of **1** and yield of **1a** were evaluated using NIS as an activator at –70 °C to 20 °C.

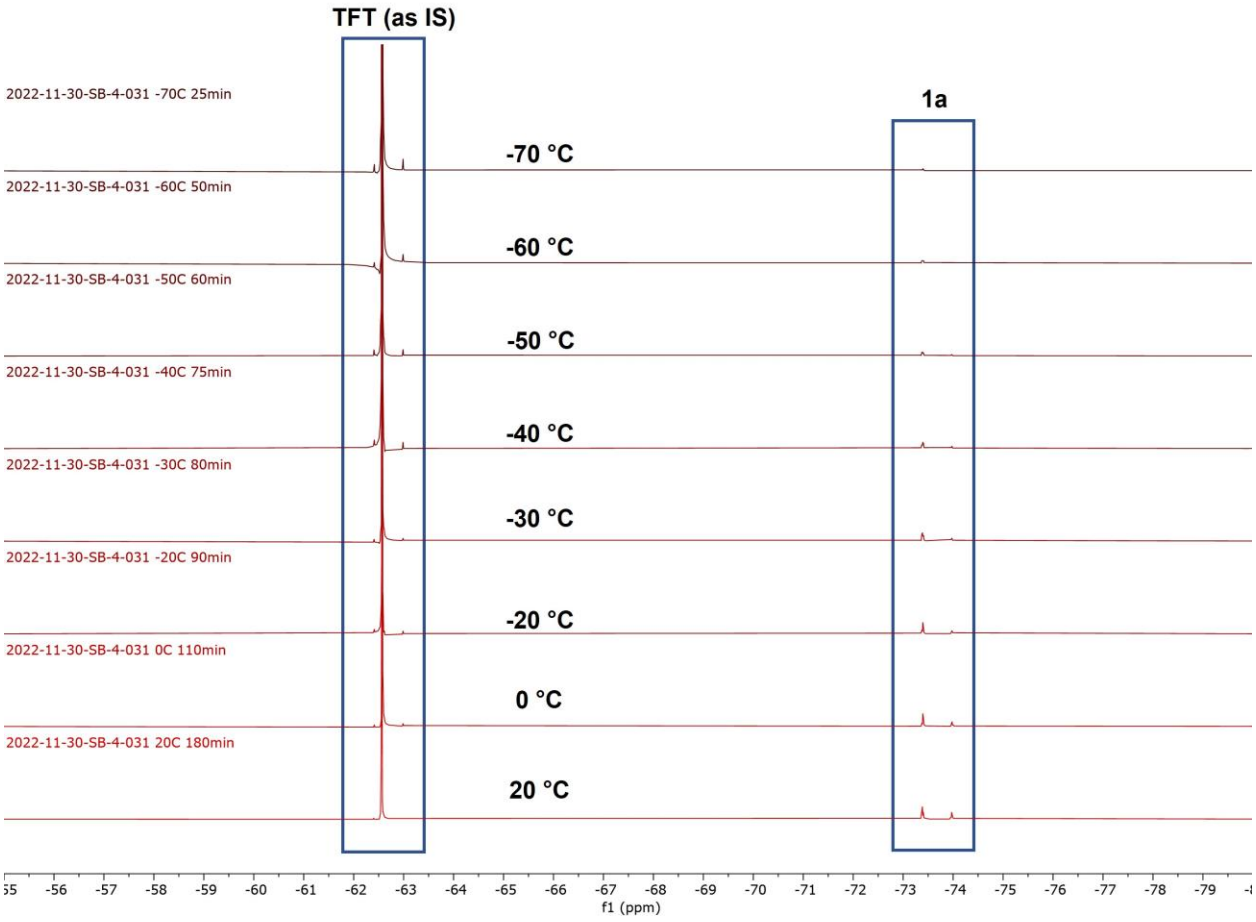


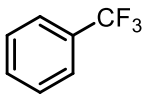
iii. BDMS as a promoter

^{1}H NMR monitoring of NPG **1** activated by BDMS at –70 °C to 20 °C.

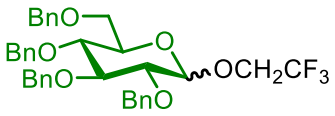


^{19}F NMR monitoring of **1a** product generated by BDMS at –70 °C to 20 °C.



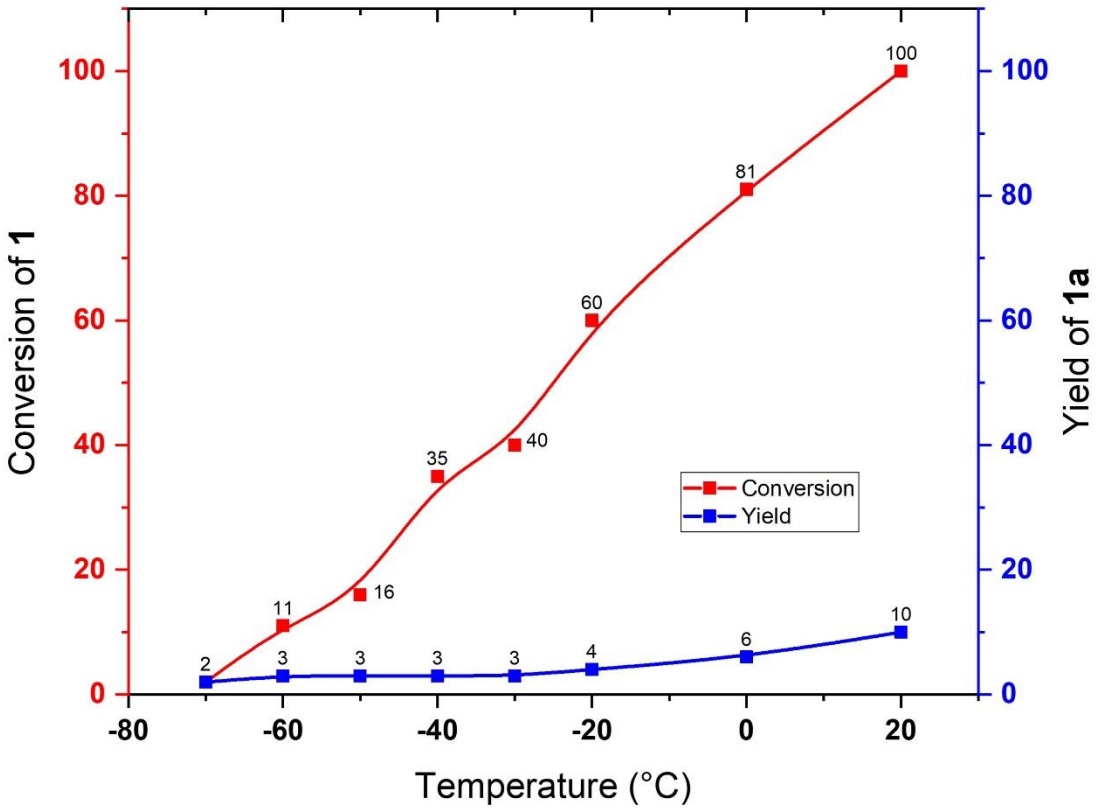


TFT
internal standard



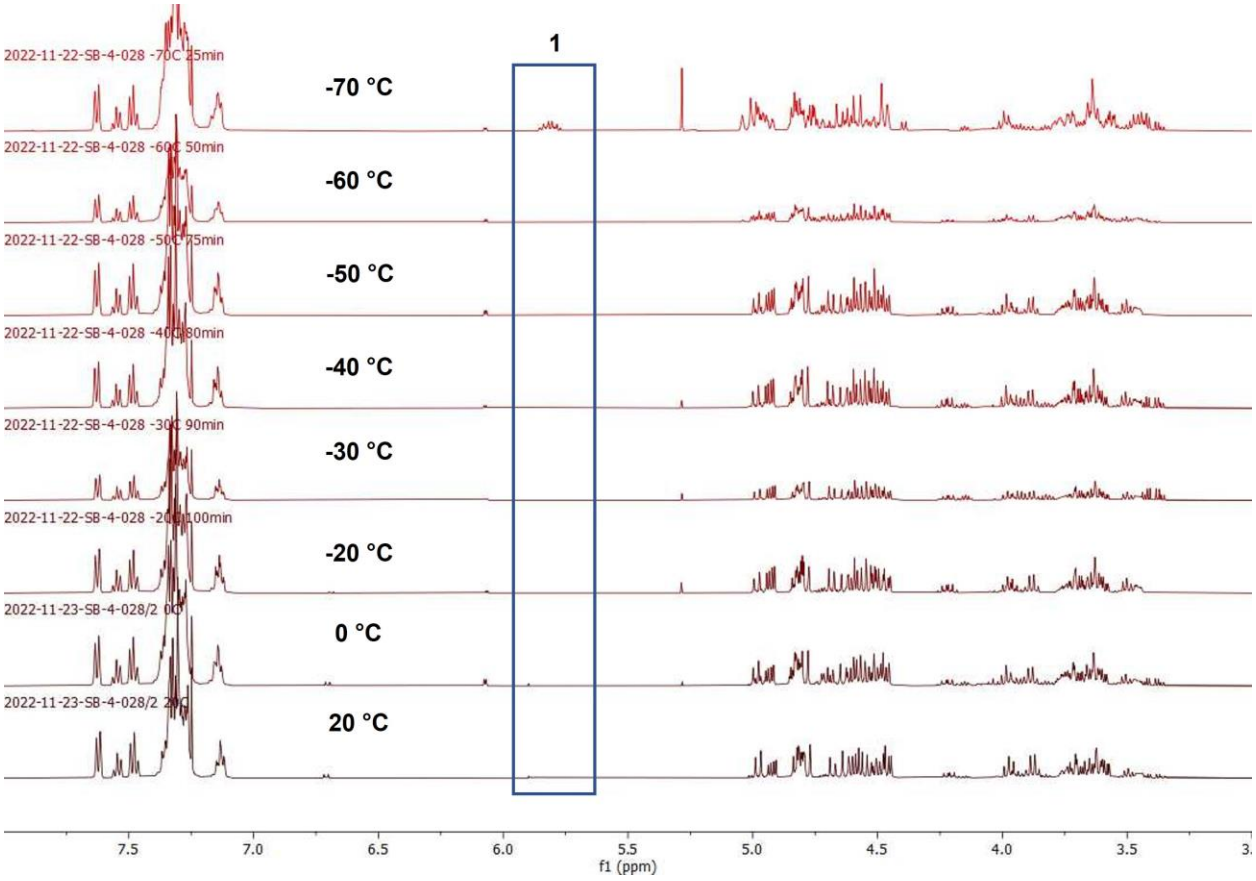
1a

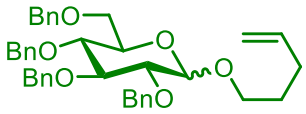
Conversions of **1** and yield of **1a** were evaluated using BDMS as an activator at –70 °C to 20 °C.



iv. BDSB as a promoter

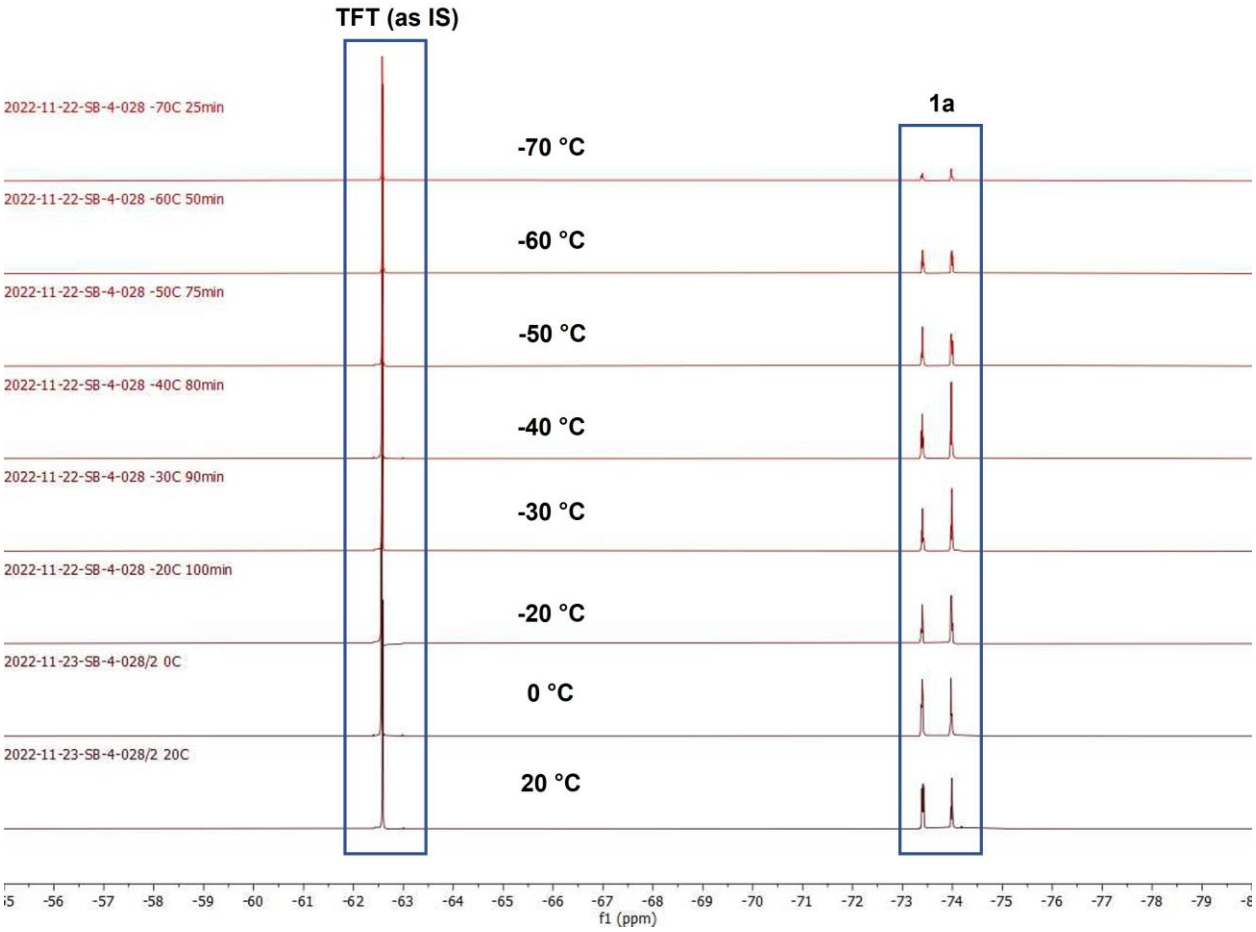
^{1}H NMR monitoring of NPG **1** activated by BDSB at –70 °C to 20 °C.

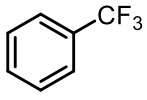




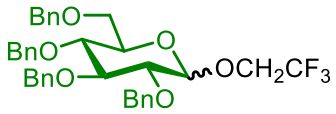
1

^{19}F NMR monitoring of **1a** product generated by BDSB at –70 °C to 20 °C.



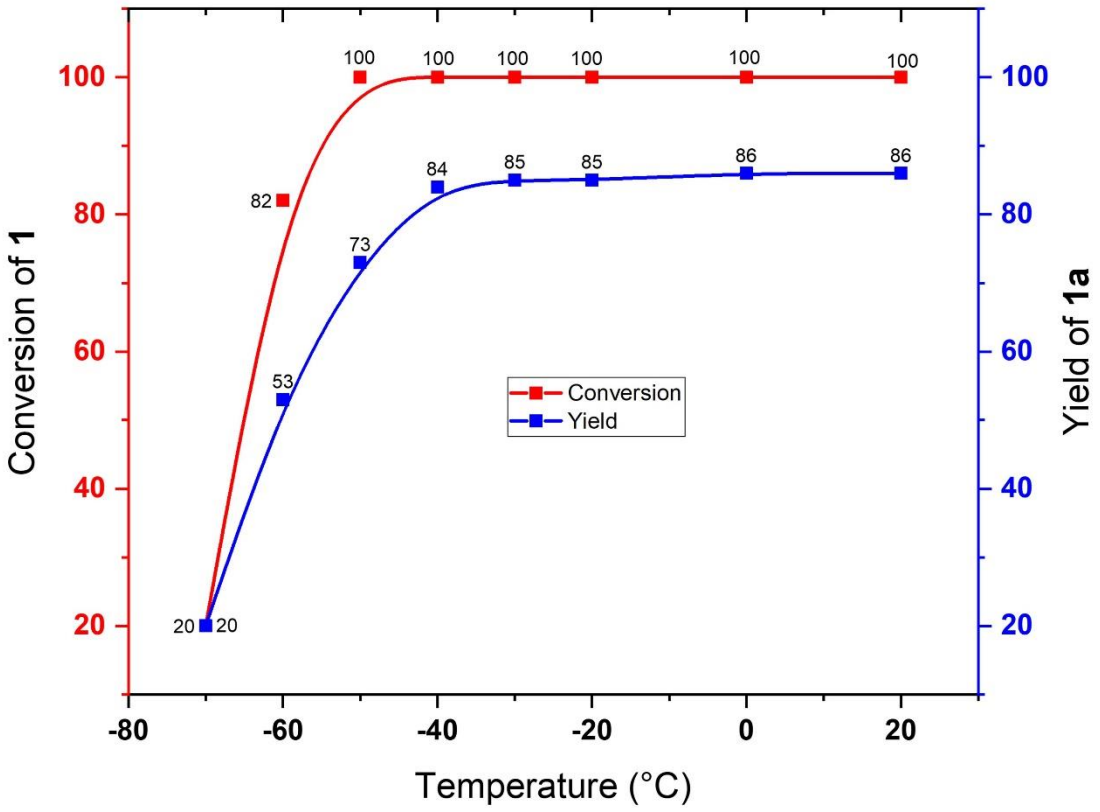


TFT
internal standard



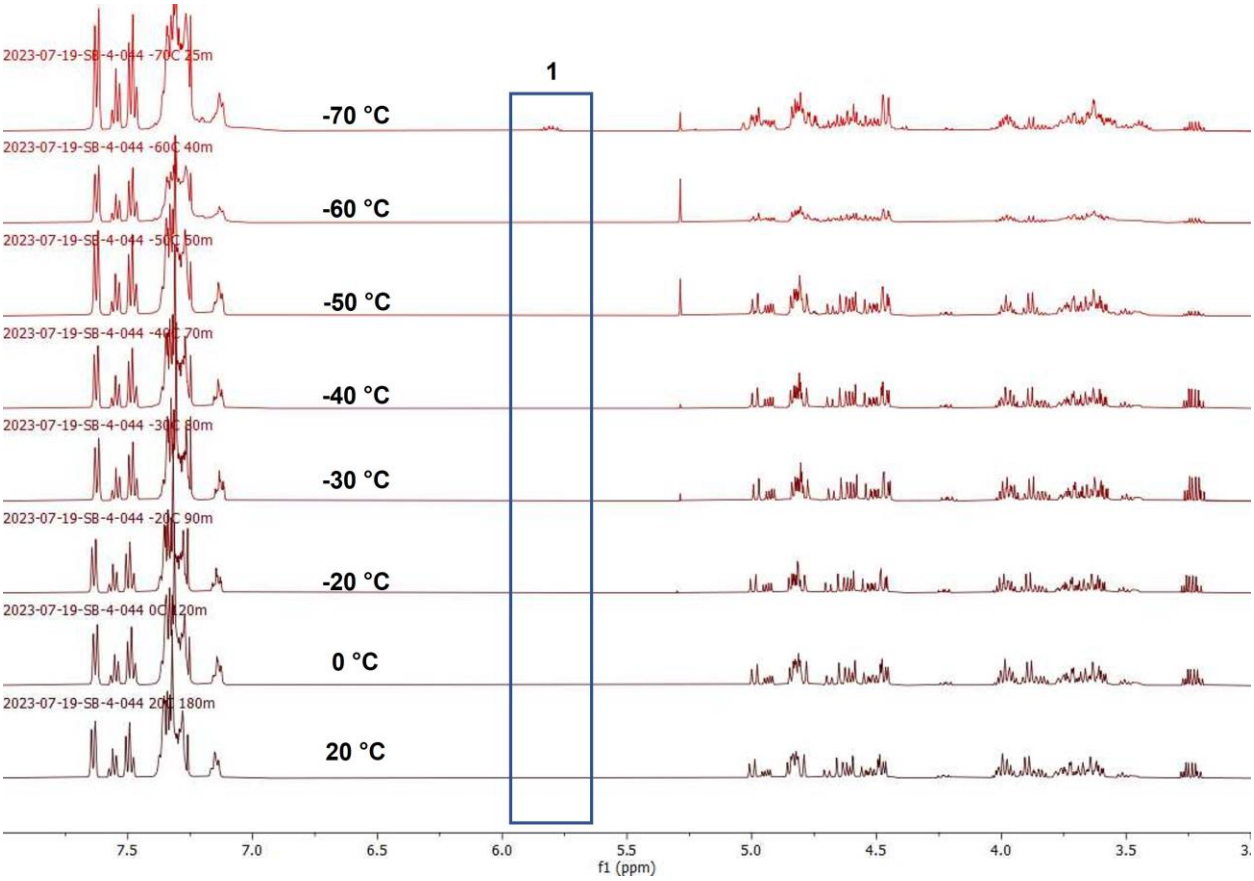
1a

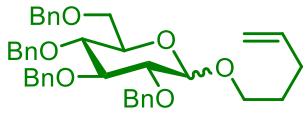
Conversions of **1** and yield of **1a** were evaluated using BDSB as an activator at –70 °C to 20 °C.



v. NIS/TESOTf as a promoter

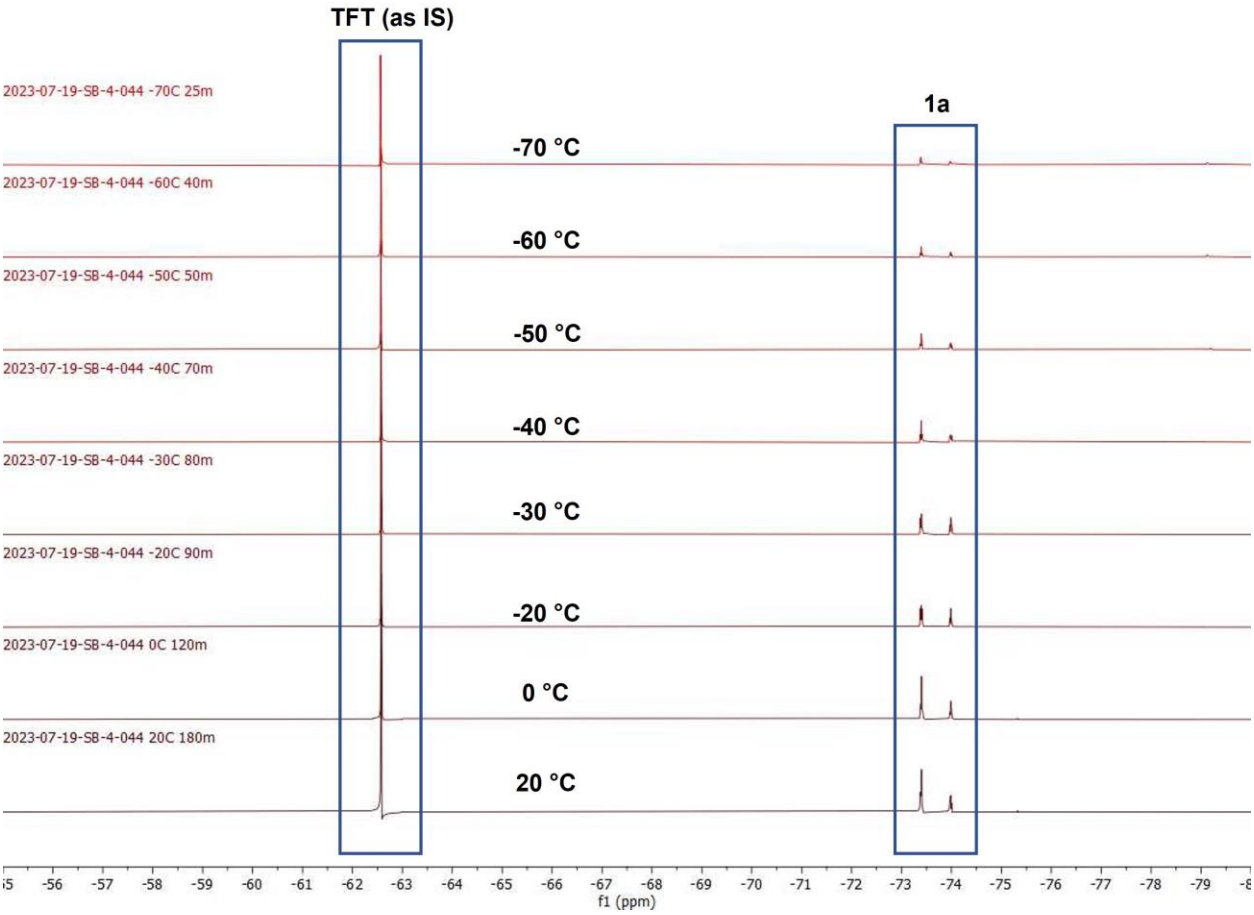
^{1}H NMR monitoring of NPG **1** activated by NIS/TESOTf at –70 °C to 20 °C.



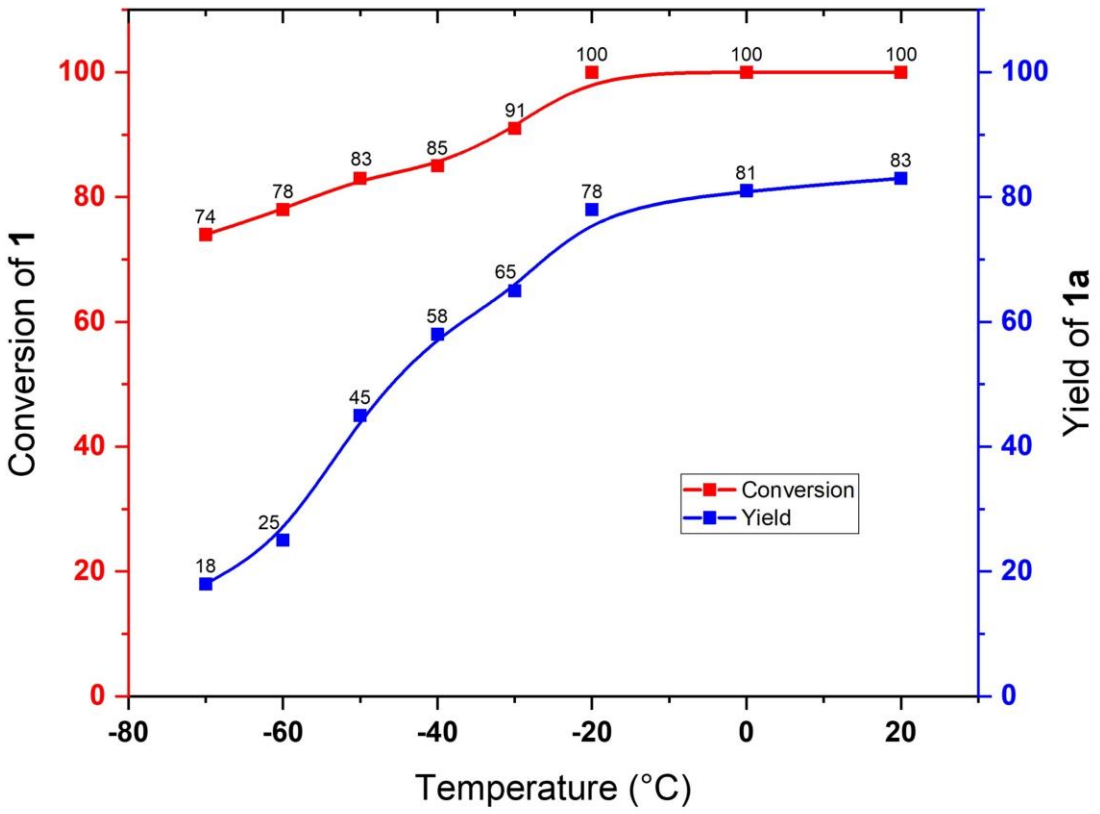


1

^{19}F NMR monitoring of **1a** product generated by NIS/TESOTf at –70 °C to 20 °C.



Conversions of **1** and yield of **1a** were evaluated using NIS/TESOTf as an activator at –70 °C to 20 °C.



VIII. References

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