Electronic Supplementary Information

Stereoselective synthesis of α-D-fructofuranosides using a 4,6-*O*-siloxane-protected donor

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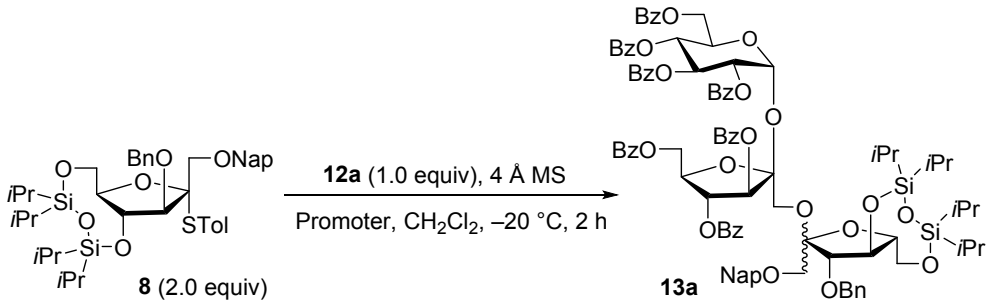
1. General Information

All reactions that require anhydrous conditions were performed in flame-dried glassware under argon atmosphere and all reagents were purchased from commercial suppliers. Solvent purification was conducted according to Purification of Laboratory Chemicals 2nd edn (Perrin, D. D., Armarego, W. L. F. and Perrin, D. R., Pergamon Press: Oxford, 1980). The products were purified by flash column chromatography on silica gel (200 – 300 meshes) from the Anhui Liangchen Silicon Material Company (China). Reactions were monitored by thin layer chromatography (TLC, 0.2 mm, HSGF254) supplied by Yantai Chemicals (China). Visualization was accomplished with UV light, exposure to iodine, stained with ethanolic solution of H_2SO_4/EtOH (1:9, v/v) or basic solution of $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on Varian INOVA-400/54 and Agilent DD2-600/54 spectrometer, in the following solvents (reference peaks include ^1H and ^{13}C NMR): $CDCl_3$ (^1H NMR: 7.26 ppm; ^{13}C NMR: 77.00 ppm), CD_3OD (^1H NMR: 3.31 ppm; ^{13}C NMR: 49.00 ppm), D_2O (^1H NMR: 4.79 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (*J*) were reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer. The specific optical rotation was obtained from Rudolph Research Analytical Autopol VI automatic polarimeter. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS or Thermo Scientific LTQ Orbitrap XL ESI mass spectrometers.

2. Optimization Studies of Glycosylation

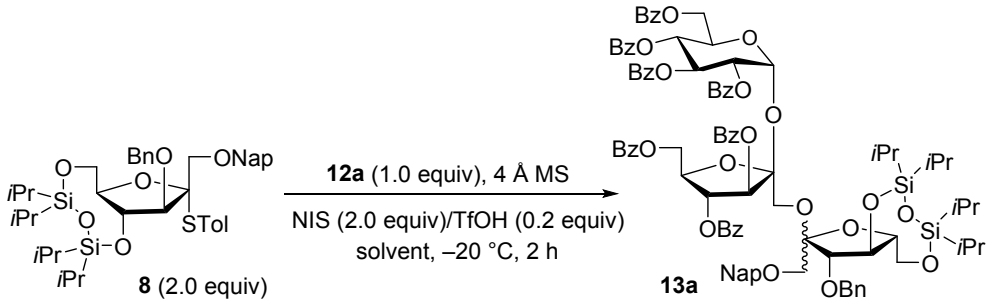
Table S1. Effect of promoter



Entry[a]	Promoter (equiv)	Yield (%)[b]	α/β ratio[c]
1	NBS (2.0)	NR	NR
2	NBS/TfOH (2.0/0.2)	83	12.6/1
3	NBS/TMSOTf (2.0/0.2)	80	14.6/1
4	NBS/AgOTf (2.0/0.2)	91	14.3/1
5	IBr/TfOH (2.0/0.2)	80	13.7/1
6	IBr/TMSOTf (2.0/0.2)	95	11.2/1
7	IBr/AgOTf (2.0/0.2)	94	12.2/1
8	NIS/TfOH (2.0/0.2)	93	15.8/1
9	NIS/TMSOTf (2.0/0.2)	90	11.2/1
10	NIS/AgOTf (2.0/0.2)	93	11.8/1
11	DBDMH (2.0)	91	14.1/1

[a]Reactions were conducted on 0.093 mmol scale and 25 mM concentration of **8** unless otherwise stated. [b]Combined yields of the α and β isomers according to ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the corresponding isomer mixture.

Table S2. Effect of solvent

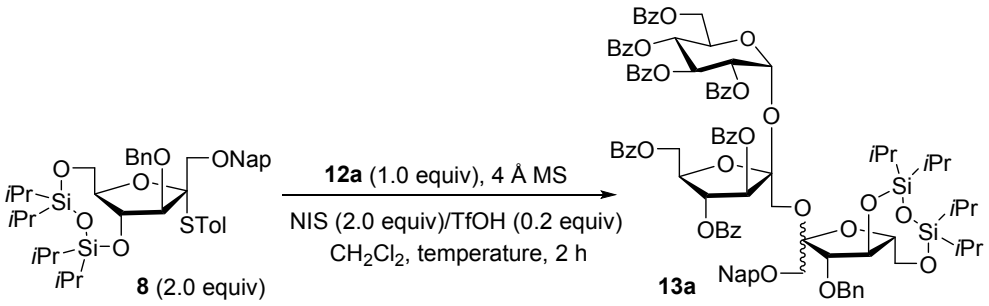


Entry[a]	Solvent	Yield (%)[b]	α/β ratio[c]
1	CH_2Cl_2	93	15.8/1
2	1,2-DCE	90	10.3/1
3	THF	62	6.5/1
4	PhMe	82	8.2/1

5	PhMe/Et_2O	NR	NR
6	PhMe/MeCN	84	8.2/1
7	PhMe/dioxane	NR	NR

[a]Reactions were conducted on 0.093 mmol scale and 25 mM concentration of **8** unless otherwise stated. [b]Combined yields of the α and β isomers according to ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the corresponding isomer mixture.

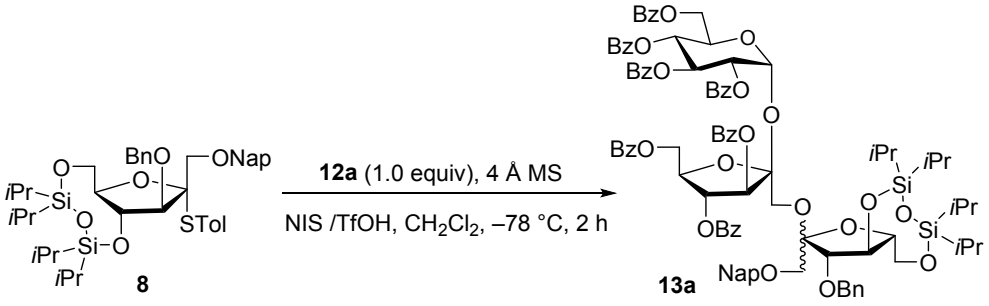
Table S3. Effect of temperature



Entry[a]	Temp. (°C)	Yield (%)[b]	α/β ratio[c]
1	25	86	8.0/1
2	0	90	9.0/1
3	−20	93	15.8/1
4	−40	92	19.0/1
5	−60	93	>20/1
6	−78	95	>20/1

[a]Reactions were conducted on 0.093 mmol scale and 25 mM concentration of **8** unless otherwise stated. [b]Combined yields of the α and β isomers according to ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the corresponding isomer mixture.

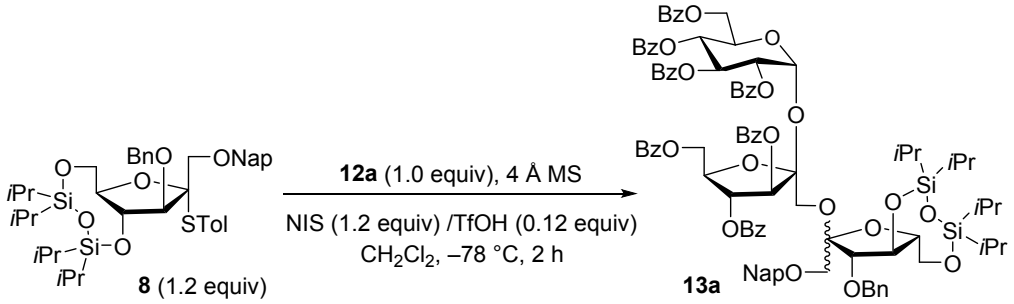
Table S4. Effect of equivalent of the donor 8



Entry[a]	Equiv of 8	Yield (%)[b]	α/β ratio[c]
1	1.1	80	>20/1
2	1.2	93	>20/1
3	1.5	92	>20/1
4	1.8	93	>20/1
5	2.0	95	>20/1

[a]Reactions were conducted on 0.093 mmol scale and 25 mM concentration of **8** unless otherwise stated. [b]Combined yields of the α and β isomers according to ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the corresponding isomer mixture.

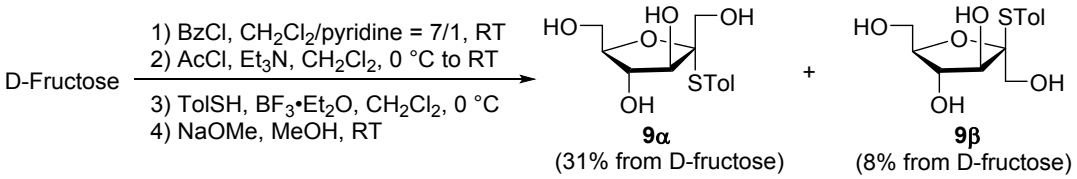
Table S4. Effect of concentration



Entry[a]	Concentration of 8 (mM)	Yield (%)[b]	α/β ratio[c]
1	5	94	>20/1
2	10	94	>20/1
3	25	93	>20/1
4	50	85	>20/1
5	100	83	>20/1

[a]Reactions were conducted on 0.093 mmol scale of **8** unless otherwise stated. [b]Combined yields of the α and β isomers according to ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the corresponding isomer mixture.

3. Synthesis of the Thio-Fructofuranoside Donor



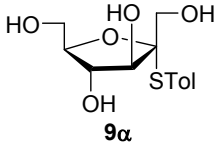
1) To a stirred solution of D-fructose (60.0 g, 333 mmol, 1.0 equiv) in pyridine (100 mL) and CH_2Cl_2 (700 mL) was slowly added benzoyl chloride (BzCl, 193 mL, 1.66 mol, 5.0 equiv) at 0 °C. The reaction was stirred for 2 h at room temperature before

being quenched with saturated aqueous $NaHCO_3$ and extracted three times with CH_2Cl_2. Then the combined organic layers were sequentially washed with 1N HCl aqueous solution, water and brine, and dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by recrystallization from methanol (600 mL).[1]

2) The above pure product (110 g) was dissolved in CH_2Cl_2 (600 mL) at 0 °C, then triethylamine (51.3 mL, 369 mmol, 1.5 equiv) and AcCl (19.7 mL, 276 mmol, 2.0 equiv) were added. After warming to room temperature and stirring for 1 h, the reaction mixture was poured into ice water, stirred for 2 h and extracted with CH_2Cl_2 for three times. The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo* to give a residue.

3) The obtained residue was directly placed in a 2000 mL round-bottom flask, followed by addition of dry CH_2Cl_2 (800 mL). TolSH (25.6 g, 206 mmol, 1.2 equiv) and $BF_3{\cdot}Et_2O$ (21.3 mL, 172 mmol, 1.0 equiv) were successively added under an argon atmosphere at 0 °C. The mixture was stirred for 2 h at this temperature before it was quenched with saturated aqueous $NaHCO_3$, then extracted with CH_2Cl_2. The combined organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was used in the next step without purification.

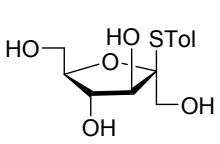
4) To a stirred solution of the above residue in methanol (800 mL) was added sodium methoxide (5 M in methanol, 29.5 mL, 148 mmol, 0.8 equiv), and the resulting mixture was stirred for 30 min at room temperature. It was carefully neutralized with Amberlite IR 120 (H^+) resin, followed by filtration and concentration. The residue was purified through flash column chromatography (CH_2Cl_2/MeOH = 20:1, v/v) to give **9α** (29.8 g, 31% over 4 steps) and **9β** (7.45 g, 8% over 4 steps) as white amorphous powder.



9α

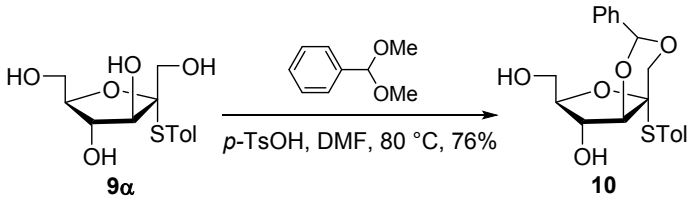
TLC: (CH_2Cl_2/MeOH = 10:1, v/v), R_f = 0.47; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 5.00 (s, 2H), 4.47 (d, J = 56.0 Hz, 2H), 4.09 – 4.13 (m, 2H), 3.94 – 3.70 (m, 4H), 3.53 (d, J = 12.0 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.3, 136.1, 129.7, 126.7, 94.6, 84.1, 79.6, 75.7, 64.5, 59.9, 21.3; **$[\alpha]_D^{25}$** = +179.4 (*c* 0.50, $CHCl_3$); **IR** (neat): ν_{max} = 2923, 1657, 1491, 1400, 1261, 1178, 1035,

945, 809, 733, 703 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{18}NaO_5S$ $[M + Na]^+$ *m/z* 309.0767; found *m/z* 309.0765.



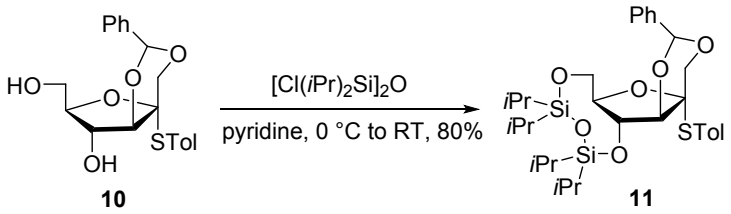
9β

TLC: (CH_2Cl_2/MeOH = 10:1, v/v), R_f = 0.40; **^{1}H NMR** (600 MHz, CD_3OD) δ 7.49 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.45 (d, J = 7.2 Hz, 1H), 4.19 (t, J = 7.6 Hz, 1H), 3.92 – 3.82 (m, 3H), 3.58 (d, J = 12.6 Hz, 1H), 3.47 (d, J = 12.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (150 MHz, CD_3OD) δ 139.5, 137.4, 130.2, 128.8, 97.8, 84.7, 78.2, 77.6, 65.0, 64.8, 21.2; **$[\alpha]_D^{25}$** = −234.0 (*c* 0.40, CH_3OH); **IR** (neat): ν_{max} = 2922, 1491, 1399, 1243, 1025, 921, 840, 809, 701 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{13}H_{18}NaO_5S$ $[M + Na]^+$ *m/z* 309.0767; found *m/z* 309.0764.

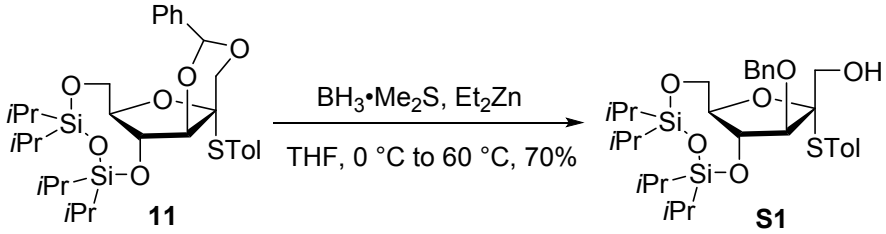


9α **10**

Under argon, to a stirred solution of **9α** (8.10 g, 28.3 mmol, 1.0 equiv) in DMF (100 mL) at room temperature were added benzaldehyde dimethyl acetal (6.40 mL, 42.5 mmol, 1.5 equiv) and catalytic *p*-toluenesulfonic acid monohydrate (270 mg, 1.40 mmol, 0.05 equiv). The mixture was warmed to 80 °C and stirred overnight before it was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. Subsequently, the residue was purified by silical gel column chromatography (petroleum ether/EtOAc = 2.5:1, v/v) to give compound **10** (8.01 g, 76%) as white amorphous powder. **TLC**: (CH_2Cl_2/MeOH = 10:1, v/v), R_f = 0.55; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 7H), 7.18 (d, J = 7.2 Hz, 2H), 5.41 (d, J = 5.6 Hz, 1H), 4.46 – 4.36 (m, 2H), 4.28 – 4.13 (m, 3H), 3.86 (s, 2H), 3.20 – 3.10 (m, 1H), 2.36 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.9, 136.9, 136.2, 129.9, 129.3, 128.3, 126.0, 124.4, 99.7, 89.3, 88.8, 85.3, 78.5, 71.6, 62.7, 21.2; **$[\alpha]_D^{25}$** = +112.4 (*c* 1.68, $CHCl_3$); **IR** (neat): ν_{max} = 3038, 2919, 1491, 1454, 1389, 1210, 1135, 1093, 1020, 875, 810, 733 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{20}H_{22}NaO_5S$ $[M + Na]^+$ *m/z* 397.1080; found *m/z* 397.1079.

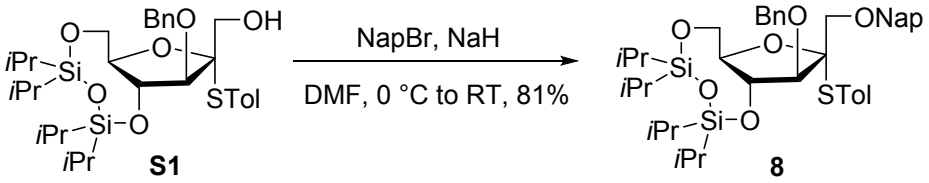


1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (TIPDSCl, 12.7 mL, 39.6 mmol, 2.0 equiv) was added to a solution of **10** (7.40 g, 19.8 mmol, 1.0 equiv) in dry pyridine (70 mL) at 0 °C, then the reaction mixture was stirred at room temperature for 2 h. After disappearance of the starting material as monitored by TLC analysis, the reaction was quenched by water. The aqueous phase was seperated and extracted three times with EtOAc, then the combined organic layers were washed with 0.5% HCl aq. solution, saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered and concentrated in *vacuo* to furnish the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1, v/v) to afford **11** (9.82 g, 80%) as colorless oil. **TLC**: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 7.05 (d, J = 7.6 Hz, 2H), 5.31 (s, 1H), 4.48 – 4.43 (m, 1H), 4.37 (d, J = 3.2 Hz, 1H), 4.34 (s, 1H), 4.16 – 4.10 (m, 2H), 3.93 (d, J = 12.4 Hz, 1H), 3.84 (t, J = 10.8 Hz, 1H), 2.26 (s, 3H), 1.08 – 0.95 (m, 28H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 137.6, 136.2, 129.6, 129.0, 128.2, 126.2, 126.2, 99.5, 89.0, 86.7, 86.6, 80.8, 64.8, 21.2, 17.6, 17.5, 17.5, 17.4, 17.2, 17.0, 17.0, 16.9, 13.6, 13.5, 13.2, 12.6; **$[\alpha]_D^{25}$** = +38.7 (*c* 0.30, $CHCl_3$); **IR** (neat): ν_{max} = 2943, 2866, 1462, 1386, 1247, 1090, 1031, 990, 883, 826, 777 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{32}H_{49}NaO_6SSi_2$ $[M + Na]^+$ *m*/*z* 639.2602; found *m*/*z* 639.2600.



Under an argon atmosphere, diethylzinc (13.3 mL, 1 M in PhMe, 13.3 mmol, 1.0 equiv) was added to a stirred solution of compound **11** (8.20 g, 13.3 mmol, 1.0 equiv) in THF (100 mL) at 0 °C. The reaction was stirred for 1 h at this temperature, before borane-methyl sulfide complex ($BH_3 \cdot Me_2S$, 80.0 mL, 799 mmol, 60.0 equiv) was added. The

reaction mixture was quenched by slowly adding MeOH after it was stirred overnight at 60 °C, then diluted with water and extracted three times with EtOAc. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Flash column chromatography of the residue on silica gel (petroleum ether/EtOAc = 40:1 to 35:1, v/v) gave **S1** (5.71 g, 70%) as colorless syrup. **TLC**: (petroleum ether/EtOAc = 15:1, v/v), R_f = 0.41; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 4.2 Hz, 4H), 7.34 – 7.30 (m, 1H), 7.09 (d, J = 7.8 Hz, 2H), 4.77 (d, J = 3.0 Hz, 2H), 4.42 – 4.39 (m, 1H), 4.12 (d, J = 7.2 Hz, 1H), 4.06 – 4.00 (m, 2H), 3.95 – 3.91 (m, 1H), 3.77 (dd, J = 12.0, 6.6 Hz, 1H), 3.54 (dd, J = 12.0, 7.2 Hz, 1H), 2.50 (t, J = 7.2 Hz, 1H), 2.33 (s, 3H), 1.10 – 1.03 (m, 28H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.9, 137.3, 135.9, 129.4, 128.4, 127.9, 127.9, 127.2, 93.6, 90.5, 78.5, 75.7, 74.0, 64.8, 60.7, 21.2, 17.4, 17.3, 17.2, 17.2, 17.1, 17.1, 17.0, 13.5, 13.1, 12.7, 12.6; **$[\alpha]_D^{25}$** = +79.6 (*c* 0.26, $CHCl_3$); **IR** (neat): ν_{max} = 2926, 2866, 1463, 1385, 1247, 1161, 1107, 1033, 966, 884, 793 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{32}H_{50}NaO_6SSi_2$ $[M + Na]^+$ *m*/*z* 641.2759; found *m*/*z* 641.2760.



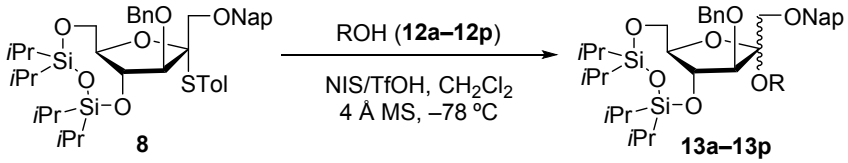
To a stirred solution of **S1** (500 mg, 0.809 mmol, 1.0 equiv) in anhydrous DMF (10.0 mL) was added NaH (60% in mineral oil, 38.8 mg, 0.971 mmol, 1.2 equiv) at 0 °C. After 30 min, 2-naphthylmethyl bromide (215 mg, 0.971 mmol, 1.2 equiv) was added, the reaction was allowed to warm to room temperature. After disappearance of the starting material as monitored by TLC analysis, the reaction was quenched by water and extracted three times with EtOAc. The combined organic layers were washed with saturated aqueous $NaHCO_3$, water, brine and dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by flash column chromatography (petroleum ether/EtOAc = 150:1, v/v) to furnish donor **8** (500 mg, 81%) as colorless oil. **TLC**: (petroleum ether/EtOAc = 20:1, v/v), R_f = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.0, 3.2 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.48 – 7.27 (m, 10H), 7.04 (d, J = 7.6 Hz, 2H), 4.85 (d, J = 11.6 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 4.43 (t, J = 8.0 Hz, 1H), 4.08 (d, J = 7.2 Hz, 1H), 4.01 – 3.86 (m, 3H), 3.56 (s, 2H), 2.32 (s, 3H), 1.11 – 0.95

(m, 21H), 0.92 – 0.82 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.6, 138.2, 135.8, 135.8, 133.2, 132.8, 129.3, 128.2, 127.9, 127.7, 127.7, 127.6, 127.6, 127.4, 126.5, 126.2, 125.8, 125.60, 9.72, 89.9, 78.7, 76.0, 73.7, 73.5, 70.7, 61.8, 21.2, 17.4, 17.3, 17.1, 17.1, 17.0, 17.0, 13.4, 13.0, 12.7, 12.6; **$[\alpha]_D^{25}$** = +9.4 (*c* 0.53, $CHCl_3$); **IR** (neat): ν_{max} = 2942, 2865, 1463, 1248, 1159, 1105, 1032, 884, 853, 810, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{43}H_{58}NaO_6SSi_2$ $[M + Na]^+$ *m*/*z* 781.3385; found *m*/*z* 781.3387.

4. Synthesis of Glycosyl Acceptors

The title compounds **12a**,[2] **12b**,[3] **12c**,[4] **12d**,[5] **12g**–**12n**,[6] and **12k**[7] were synthesized according the reported procedure and their analytical data were identical to those reported in literature. Acceptors **12e**, **12f**, **12j**, **12o**, and **12p** were purchased from commercial suppliers.

5. General Procedure for Glycosylation

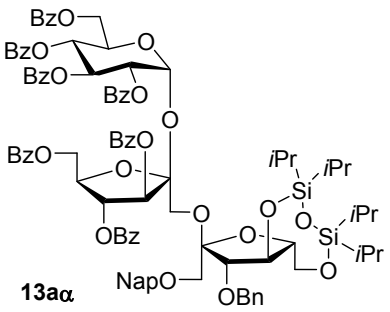


To an oven-dried flask were successively added glycosyl donor (1.2 or 1.5 equiv), glycosyl acceptor (1.0 equiv), and freshly activated 4 Å MS. Then dry CH_2Cl_2 (25 mM concentration of donor **8**) was added under an argon atmosphere, the solution was stirred for 1 h at room temperature and cooled down to −78 °C. NIS (1.2 or 1.5 equiv) and TfOH (0.12 or 0.15 equiv) were added and the resulting mixture was stirred at −78 °C for another 2 h. After the reaction was completed (identified by TLC analysis), it was quenched with Et_3N, followed by filtered through Celite®. The filtration was washed with water and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography using the indicated conditions afforded the corresponding product.

Following the general procedure, the reaction of acceptor **12a** (20.0 mg, 0.019 mmol, 1.0 equiv), donor **8** (16.7 mg, 0.022 mmol, 1.2 equiv) and NIS (5.49 mg, 0.022 mmol, 1.2 equiv)/TfOH (0.198 μL, 0.002 mmol, 0.12 equiv) proceeded in 2 h to afford product **13aα** (30.1 mg, 93%, α/β > 20/1) as white foam, after silica gel column chromatography

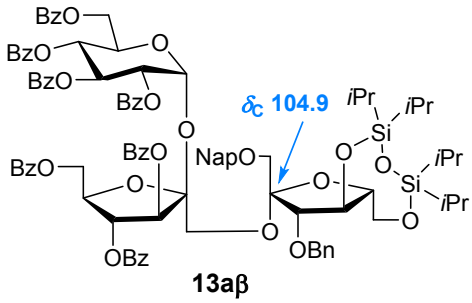
(petroleum ether/ EtOAc = 10:1 to 7:1, v/v).

Note: A gram-scale experiment was performed with **12a** (1.52 g, 1.42 mmol, 1.0 equiv) and **8** (1.29 g, 1.70 mmol, 1.2 equiv) under the standard conditions, yielding **13aα** (2.27 g, 94%, α/β > 20/1).



13aα

TLC: (petroleum ether/EtOAc = 2.5:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 7.97 (t, J = 8.0 Hz, 4H), 7.87 – 7.75 (m, 7H), 7.72 – 7.65 (m, 2H), 7.62 – 7.47 (m, 7H), 7.44 – 7.11 (m, 23H), 6.24 (t, J = 10.0 Hz, 1H), 6.11 (dd, J = 8.4, 3.6 Hz, 2H), 5.92 (t, J = 6.0 Hz, 1H), 5.76 (t, J = 9.6 Hz, 1H), 5.38 (dd, J = 10.4, 3.6 Hz, 1H), 4.79 – 4.61 (m, 4H), 4.56 – 4.39 (m, 3H), 4.39 – 4.22 (m, 4H), 4.12 (d, J = 10.0 Hz, 1H), 4.01 (d, J = 7.6 Hz, 1H), 3.89 – 3.68 (m, 4H), 3.37 (s, 2H), 1.10 – 0.97 (m, 20H), 0.92 – 0.85 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 166.0, 165.5, 165.5, 138.4, 135.5, 133.3, 133.2, 133.2, 133.1, 133.0, 133.0, 132.9, 132.8, 130.2, 129.9, 129.9, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 128.9, 128.8, 128.7, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.8, 127.6, 127.4, 127.2, 126.2, 125.8, 125.8, 125.6, 105.8, 105.5, 90.4, 88.9, 79.5, 78.9, 75.0, 73.3, 73.1, 71.3, 70.1, 69.0, 68.9, 68.8, 64.4, 62.7, 62.4, 61.5, 17.5, 17.3, 17.1, 17.1, 17.0, 13.4, 13.0, 12.6, 12.5; **$[\alpha]_D^{25}$** = +30.9 (*c* 1.08, $CHCl_3$); **IR** (neat): ν_{max} = 2945, 2867, 1725, 1601, 1451, 1263, 1092, 1068, 1025, 885, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{97}H_{100}NaO_{24}Si_2$ $[M + Na]^+$ *m*/*z* 1728.6069; found *m*/*z* 1728.6063.

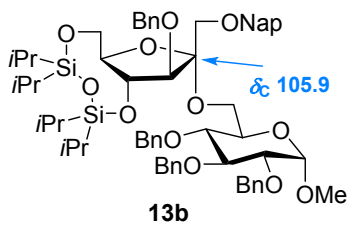


13aβ

Compound **13aβ** was obtained according to conditions of entry 2 in Table S3 using acceptor **12a** (100 mg, 0.095 mmol). **TLC**: (petroleum ether/EtOAc = 2.5:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.2 Hz, 2H), 7.99 (dd, J = 16.4, 8.0 Hz, 7H), 7.82 – 7.76 (m, 7H), 7.55 – 7.44 (m, 11H), 7.41 – 7.35 (m, 9H), 7.31 – 7.26 (m, 6H), 7.26 – 7.19 (m, 5H), 6.14 (t, J = 10.0 Hz, 1H), 6.06 (d, J = 3.6 Hz, 1H), 5.98 (d, J = 6.4 Hz, 1H), 5.88 (t, J = 6.8 Hz, 1H), 5.73 (t, J = 10.0 Hz, 1H), 5.59 (s, 1H), 5.41 (dd, J = 10.4, 3.6 Hz, 1H), 5.00 (d, J = 11.2 Hz, 1H), 4.82 – 4.76 (m, 2H),

4.68 – 4.62 (m, 2H), 4.60 – 4.54 (m, 3H), 4.51 – 4.27 (m, 5H), 3.98 – 3.90 (m, 2H), 3.76 (dd, J = 7.6, 3.6 Hz, 1H), 3.59 (d, J = 9.6 Hz, 2H), 1.04 (d, J = 6.8 Hz, 8H), 1.00 (dd, J = 7.6, 2.0 Hz, 7H), 0.94 (dd, J = 12.8, 7.2 Hz, 8H), 0.83 (d, J = 7.6 Hz, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 166.0, 165.6, 165.5, 165.5, 165.3, 165.1, 138.1, 133.9, 133.5, 133.4, 133.3, 133.2, 133.0, 133.0, 132.9, 130.1, 130.0, 129.9, 129.8, 129.8, 129.7, 129.6, 129.6, 129.2, 129.1, 129.0, 128.9, 128.8, 128.8, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6, 126.8, 126.1, 126.0, 105.8, 104.9, 90.1, 84.9, 83.9, 81.4, 78.4, 78.0, 76.0, 75.7, 73.6, 73.1, 70.9, 70.3, 69.1, 69.0, 65.4, 64.4, 62.4, 62.0, 17.6, 17.4, 17.2, 17.2, 17.1, 17.1, 17.0, 13.2, 13.0, 12.7, 12.4; **$[\alpha]_D^{25}$** = +14.1 (c 0.17, $CHCl_3$); **IR** (neat): ν_{max} = 2924, 2863, 1724, 1454, 1263, 1104, 1026, 799, 735, 708 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{97}H_{100}NaO_{24}Si_2$ $[M + Na]^+$ m/z 1728.6069; found m/z 1728.6066.

According to the general procedure, the acceptor **12b** (50.0 mg, 0.108 mmol, 1.0 equiv), donor **8** (97.9 mg, 0.129 mmol, 1.2 equiv) and NIS (31.6 mg, 0.129 mmol, 1.2 equiv)/TfOH (1.14 μL, 0.013 mmol, 0.12 equiv) were used. The reaction was completed in 2 h to afford **13b** as white foam (110 mg, 93%, α/β > 20/1) after purification by column chromatography (petroleum ether/acetone = 35:1 to 25:1, v/v).

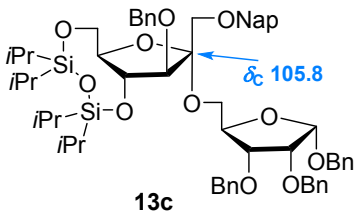


13b

TLC: (petroleum ether/EtOAc = 4:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.74 – 7.67 (m, 3H), 7.49 – 7.41 (m, 3H), 7.40 – 7.22 (m, 20H), 5.00 (d, J = 10.8 Hz, 1H), 4.88 (d, J = 10.8 Hz, 1H), 4.84 – 4.75 (m, 3H), 4.70 – 4.59 (m, 6H), 4.33 (t, J = 7.6 Hz, 1H), 4.07 – 3.98 (m, 2H), 3.85 – 3.73 (m, 6H), 3.62 (s, 2H), 3.56 – 3.50 (m, 2H), 3.36 (s, 3H), 1.08 – 1.04 (m, 8H), 1.02 – 0.97 (m, 13H), 0.95 – 0.90 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 138.4, 138.3, 138.2, 135.6, 133.2, 132.9, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.3, 126.5, 126.0, 125.9, 125.7, 105.9, 97.7, 89.4, 82.2, 79.9, 79.4, 77.9, 76.0, 75.7, 74.7, 73.6, 73.2, 73.1, 69.9, 68.9, 62.1, 61.0, 54.9, 17.6, 17.5, 17.4, 17.4, 17.3, 17.1, 17.1, 17.0, 13.4, 13.0, 12.6, 12.6; **$[\alpha]_D^{25}$** = +3.1 (c 1.17, $CHCl_3$); **IR** (neat): ν_{max} = 2928, 2866, 1454, 1360, 1245, 1028, 884, 855, 816, 733 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{64}H_{82}KO_{12}Si_2$ $[M + K]^+$ m/z 1137.4976; found m/z 1137.4973.

Following the general procedure, the mixture of acceptor **12c** (100 mg, 0.197 mmol,

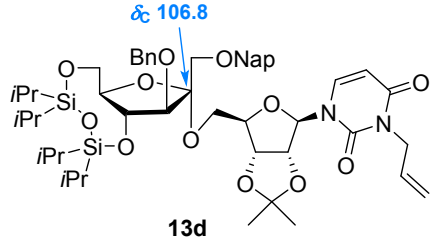
1.0 equiv), donor **8** (216 mg, 0.285 mmol, 1.2 equiv) and NIS (69.9 mg, 0.285 mmol, 1.2 equiv)/TfOH (2.53 μL, 0.029 mmol, 0.12 equiv) was subjected to the glycosylation reaction in 2 h to generate **13c** as colorless syrup (152 mg, 96%, α/β > 20/1) after purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1 to 6:1, v/v).



13c

TLC: (petroleum ether/EtOAc = 3:1, v/v), R_f = 0.40; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.77 – 7.62 (m, 3H), 7.47 (d, J = 3.6 Hz, 4H), 7.41 (d, J = 7.2 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.33 – 7.19 (m, 14H), 5.03 (d, J = 4.8 Hz, 1H), 4.91 (d, J = 12.6 Hz, 1H), 4.79 – 4.59 (m, 6H), 4.57 – 4.53 (m, 3H), 4.31 (t, J = 7.8 Hz, 2H), 3.95 – 3.87 (m, 3H), 3.81 (dd, J = 12.0, 4.8 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.64 – 3.52 (m, 4H), 3.46 (dd, J = 10.2, 4.8 Hz, 1H), 1.13 – 1.02 (m, 21H), 0.986 – 0.962(m, 7H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.5, 138.3, 138.2, 137.9, 135.4, 133.1, 132.9, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 126.5, 125.9, 125.9, 125.8, 105.8, 99.18, 9.53, 82.3, 79.5, 77.7, 76.0, 75.4, 73.5, 73.2, 72.1, 72.0, 68.6, 68.4, 62.1, 62.0, 17.5, 17.4, 17.3, 17.2, 17.1, 17.1, 17.1, 17.0, 13.4, 13.1, 12.6, 12.5; **$[\alpha]_D^{25}$** = +13.6 (*c* 1.00, $CHCl_3$); **IR** (neat): ν_{max} = 2927, 2866, 1454, 1385, 1107, 1027, 884, 815, 787, 732 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{61}H_{74}KO_{11}Si_2$ $[M + K]^+$ *m/z* 1077.4401; found *m/z* 1077.4399.

According to the general procedure, the glycosylation reaction of acceptor **12d** (100 mg, 0.309 mmol, 1.0 equiv) took place with donor **8** (281 mg, 0.370 mmol, 1.2 equiv), and NIS (90.7 mg, 0.370 mmol, 1.2 equiv)/TfOH (3.27 μL, 0.037 mmol, 0.12 equiv) in 2 h to give pure product **13d** (284 mg, 96%, α/β > 20/1), as colorless oil after column chromatography (petroleum ether/EtOAc = 10:1 to 7:1, v/v).

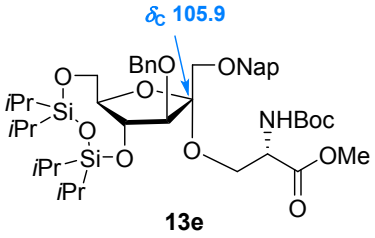


13d

TLC: (petroleum ether/EtOAc = 3:1, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 2H), 7.75 (t, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.46 (dd, J = 6.0, 3.2 Hz, 2H), 7.33 – 7.26 (m, 5H), 5.97 (d, J = 2.8 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.41 (d, J = 8.0 Hz, 1H), 5.19 (dd, J = 37.2, 17.2 Hz, 2H), 4.77 – 4.46 (m, 10H), 4.32 – 4.27 (m, 1H), 3.96 (dd, J = 11.6, 3.2 Hz, 1H), 3.87 – 3.74 (m, 5H), 3.63 (q, J = 10.4 Hz, 2H), 1.60 (s, 4H), 1.34 (s, 3H), 1.06 – 0.98 (m, 28H);

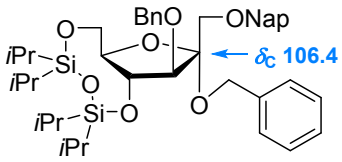
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 150.7, 138.9, 137.8, 134.7, 133.1, 133.0, 131.6, 128.3, 128.3, 128.2, 127.8, 127.7, 127.3, 127.1, 126.2, 126.0, 126.0, 118.0, 113.8, 113.7, 106.8, 101.0, 93.5, 90.0, 86.1, 85.6, 81.5, 81.0, 78.4, 73.8, 73.4, 66.8, 63.2, 61.5, 42.9, 27.4, 25.5, 17.4, 17.3, 17.2, 17.1, 17.1, 17.0, 16.9, 13.4, 13.1, 12.7, 12.5; **$[\alpha]_D^{25}$** = +9.5 (*c* 1.32, $CHCl_3$); **IR** (neat): ν_{max} = 2942, 2866, 1710, 1666, 1453, 1383, 1211, 1085, 1033, 885, 807 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{51}H_{70}N_2NaO_{12}Si_2$ $[M + Na]^+$ *m/z* 981.4359; found *m/z* 981.4356.

Following the general procedure, acceptor **12e** (30 mg, 0.137 mmol, 1.0 equiv), donor **8** (125 mg, 0.164mmol, 1.2 equiv), and NIS (40.2 mg, 0.164 mmol, 1.2 equiv)/TfOH (1.45 μL, 0.037 mmol, 0.12 equiv) were used. The crude product was purified by silica gel column chromatography (petroleum ether/acetone = 35:1 to 25:1, v/v) to afford **13e** (98.0 mg, 84%, α/β > 20/1) as white foam.



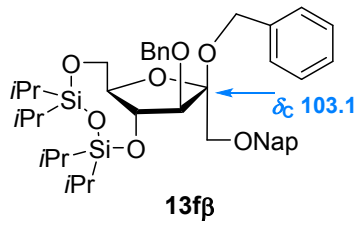
TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.52; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 3H), 7.70 (s, 1H), 7.46 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.27 (s, 5H), 5.52 (d, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.67 – 4.57 (m, 3H), 4.41 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.29 (t, *J* = 7.6 Hz, 1H), 4.02 – 3.94 (m, 2H), 3.93 – 3.77 (m, 4H), 3.66 (s, 3H), 3.58 (s, 2H), 1.44 (s, 9H), 1.09 – 1.01 (m, 21H), 0.98 – 0.94 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 155.5, 138.2, 135.3, 133.2, 133.2, 132.9, 128.2, 128.0, 127.9, 127.6, 127.5, 127.4, 126.6, 125.0, 125.9, 125.8, 105.9, 89.1, 79.9, 79.8, 75.9, 73.6, 73.2, 68.3, 62.4, 62.1, 54.0, 52.3, 28.3, 26.9, 17.4, 17.3, 17.2, 17.1, 17.1, 17.1, 17.0, 13.4, 13.1, 12.7, 12.6; **$[\alpha]_D^{25}$** = +1.1 (*c* 1.03, $CHCl_3$); **IR** (neat): ν_{max} = 2944, 2867, 1715, 1497, 1464, 1366, 1161, 1107, 1030, 884, 784 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{45}H_{67}NKO_{11}Si_2$ $[M + K]^+$ *m/z* 892.3884; found *m/z* 892.3881.

According to the general procedure, the glycosylation reaction of acceptor **12f** (25.0 mg, 0.231 mmol, 1.0 equiv) proceeded with donor **8** (210 mg, 0.277 mmol, 1.2 equiv), and NIS (67.9 mg, 0.277 mmol, 1.2 equiv)/TfOH (2.45 μL, 0.028 mmol, 0.12 equiv) in 2 h to give two isomers **13fα** and **13fβ** (160 mg, 93%, α/β = 6.6/1) as white foam after purification by silica gel column chromatography (petroleum ether/EtOAc = 50:1 to 30:1, v/v).



13fα

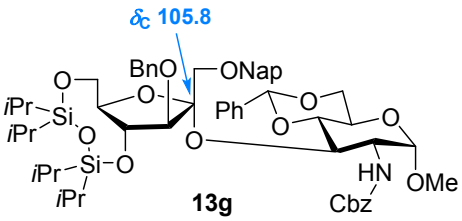
TLC: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.55; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.76 – 7.70 (m, 3H), 7.47 – 7.40 (m, 3H), 7.37 – 7.23 (m, 10H), 4.82 (d, J = 11.6 Hz, 1H), 4.70 (dd, J = 12.0, 5.2 Hz, 2H), 4.66 – 4.59 (m, 3H), 4.36 (t, J = 6.8 Hz, 1H), 4.18 (d, J = 6.0 Hz, 1H), 4.00 – 3.94 (m, 1H), 3.91 – 3.84 (m, 2H), 3.75 – 3.69 (m, 2H), 1.08 – 0.96 (m, 28H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 138.4, 135.5, 133.2, 132.9, 128.2, 128.1, 127.9, 127.9, 127.6, 127.5, 127.4, 127.2, 126.6, 126.0, 125.9, 125.7, 106.4, 89.6, 80.2, 76.7, 73.6, 73.2, 68.5, 63.7, 62.6, 17.5, 17.3, 17.2, 17.2, 17.2, 17.1, 17.0, 17.0, 13.5, 13.1, 12.7, 12.6; **$[\alpha]_D^{25}$** = −0.3 (c 1.11, $CHCl_3$); **IR** (neat): ν_{max} = 2943, 2866, 1463, 1384, 1247, 1106, 1030, 884, 855, 813, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{43}H_{58}NaO_7Si_2$ $[M + Na]^+$ m/z 765.3613; found m/z 765.3614.



13fβ

TLC: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 3H), 7.71 (s, 1H), 7.49 – 7.44 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.34 – 7.22 (m, 10H), 4.78 – 4.68 (m, 5H), 4.64 – 4.58 (m, 2H), 4.36 (d, J = 8.4 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.84 – 3.78 (m, 1H), 3.57 (dd, J = 18.8, 10.4 Hz, 2H), 1.13 – 1.03 (m, 24H), 1.00 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.0, 138.4, 135.4, 133.2, 133.0, 128.1, 128.1, 127.9, 127.8, 127.7, 127.4, 127.4, 127.1, 126.6, 126.1, 125.9, 125.8, 103.1, 84.2, 79.9, 73.6, 72.9, 72.1, 64.2, 63.3, 17.5, 17.4, 17.3, 17.3, 17.1, 17.0, 13.5, 13.1, 12.8, 12.6; **$[\alpha]_D^{25}$** = −17.6 (c 0.37, $CHCl_3$); **IR** (neat): ν_{max} = 2942, 2866, 1463, 1260, 1093, 1034, 885, 800, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{43}H_{58}NaO_7Si_2$ $[M + Na]^+$ m/z 765.3613; found m/z 765.3610.

Following the general procedure, acceptor **12g** (20.0 mg, 0.048 mmol, 1.0 equiv) and donor **8** (54.8 mg, 0.072 mmol, 1.5 equiv) were subjected to glycosylation in the presence of NIS (17.7 mg, 0.072 mmol, 1.5 equiv)/TfOH (0.639 μL, 0.007 mmol, 0.15 equiv) in 2 h to yield **13g** as white foam (45.9 mg, 91%, α/β > 20/1) after purification by silica gel column chromatography (petroleum ether/EtOAc = 10:1 to 3:1, v/v).

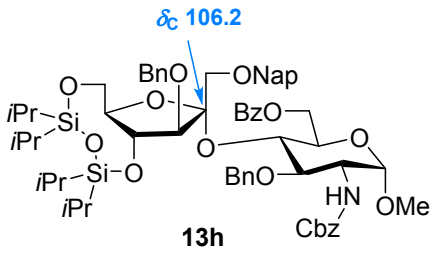


13g

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.68 – 7.64 (m, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 7.46 – 7.42 (m, 2H), 7.39

– 7.19 (m, 10H), 7.17 – 7.11 (m, 6H), 5.75 (d, J = 7.6 Hz, 1H), 5.53 (s, 1H), 5.06 (dd, J = 27.2, 12.0 Hz, 2H), 4.91 (d, J = 3.2 Hz, 1H), 4.60 (dd, J = 24.4, 11.6 Hz, 3H), 4.39 – 4.26 (m, 4H), 4.04 (d, J = 8.8 Hz, 1H), 3.81 – 3.70 (m, 6H), 3.62 – 3.50 (m, 3H), 3.36 (s, 3H), 1.09 – 1.02 (m, 7H), 1.01 – 0.89 (m, 15H), 0.74 (d, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 137.9, 137.2, 136.0, 135.9, 133.2, 132.8, 128.9, 128.6, 128.4, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.8, 127.6, 127.6, 127.4, 126.3, 126.2, 125.9, 125.6, 125.5, 105.8, 101.7, 99.4, 90.6, 80.6, 78.7, 73.6, 73.5, 73.1, 70.4, 70.3, 69.0, 67.0, 63.0, 60.5, 55.4, 55.3, 17.5, 17.3, 17.1, 17.0, 17.0, 17.0, 16.9, 13.3, 13.0, 12.9, 12.6, 12.4; **$[\alpha]_D^{25}$** = −1.6 (c 0.63, $CHCl_3$); **IR** (neat): ν_{max} = 2942, 2865, 1722, 1520, 1463, 1379, 1262,1030, 991, 885, 810, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{58}H_{75}NNaO_{13}Si_2$ $[M + Na]^+$ m/z 1072.4669; found m/z 1072.4671.

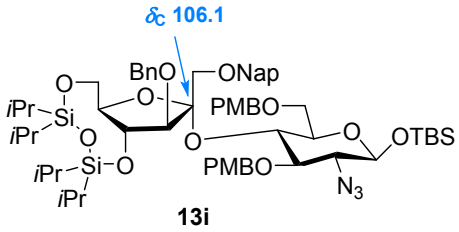
According to the general procedure, the glycosylation reaction of acceptor **12h** (20.0 mg, 0.038 mmol, 1.0 equiv) and donor **8** (43.6 mg, 0.057 mmol, 1.5 equiv) occurred by using NIS (14.1 mg, 0.057 mmol, 1.5 equiv)/TfOH (0.509 μL, 0.006 mmol, 0.15 equiv) in 2 h provided **13h** as white foam (39.4 mg, 90%, α/β > 20/1) after purification by column chromatography (petroleum ether/EtOAc = 8:1 to 5:1, v/v).



13h

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.25; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.81 – 7.75 (m, 1H), 7.72 – 7.61 (m, 2H), 7.55 (t, J = 8.8 Hz, 2H), 7.43 (t, J = 7.6 Hz, 4H), 7.35 – 7.23 (m, 11H), 7.17 – 7.06 (m, 5H), 5.04 (s, 2H), 4.94 (d, J = 10.0 Hz, 1H), 4.80 – 4.61 (m, 5H), 4.52 (t, J = 8.4 Hz, 2H), 4.44 (dd, J = 12.0, 6.8 Hz, 1H), 4.34 (d, J = 11.6 Hz, 1H), 4.19 – 4.00 (m, 3H), 3.98 – 3.88 (m, 3H), 3.82 – 3.69 (m, 3H), 3.58 – 3.47 (m, 2H), 3.36 (s, 3H), 1.02 – 0.83 (m, 23H), 0.65 (t, J = 7.6 Hz, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 155.8, 138.3, 137.7, 136.2, 135.9, 133.2, 132.9, 132.8, 130.2, 129.6, 128.5, 128.3, 128.2, 128.2, 128.1, 127.9, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 126.3, 126.1, 125.7, 125.5, 106.2, 98.4, 91.4, 80.0, 79.7, 76.1, 76.0, 73.3, 73.3, 72.4, 70.1, 67.0, 64.3, 63.0, 55.0, 17.5, 17.3, 17.1, 17.1, 17.0, 17.0, 16.9, 13.3, 13.0, 12.6, 12.5; **$[\alpha]_D^{25}$** = +7.4 (c 0.77, $CHCl_3$); **IR** (neat): ν_{max} = 2924, 2866, 1720, 1509, 1452, 1270, 1104, 1026, 885, 807, 733 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{65}H_{81}NNaO_{14}Si_2$ $[M + Na]^+$ m/z 1178.5088; found m/z 1178.5082.

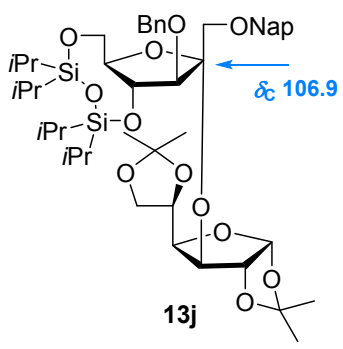
Following the general procedure, acceptor **12i** (20.0 mg, 0.036 mmol, 1.0 equiv), donor **8** (40.6 mg, 0.054 mmol, 1.5 equiv) and NIS (13.1 mg, 0.054 mmol, 1.5 equiv)/TfOH (0.474 μL, 0.005 mmol, 0.15 equiv) were used. The pure product **13i** (41.7 mg, 97%, α/β > 20/1) as white foam was obtained after silica gel column chromatography (petroleum ether/EtOAc = 25:1, v/v).



13i

TLC: (petroleum ether/EtOAc = 3:1, v/v), R_f = 0.60; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 1H), 7.53 – 7.46 (m, 2H), 7.41 (s, 1H), 7.28 – 7.23 (m, 1H), 7.17 – 7.04 (m, 9H), 6.87 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 8.0 Hz, 2H), 4.59 – 4.48 (m, 3H), 4.36 – 4.21 (m, 6H), 4.10 (d, J = 12.0 Hz, 1H), 3.84 (d, J = 8.0 Hz, 1H), 3.59 (s, 3H), 3.57 – 3.51 (m, 3H), 3.49 (s, 3H), 3.48 – 3.40 (m, 2H), 3.40 – 3.13 (m, 4H), 3.10 – 3.04 (m, 1H), 2.95 (t, J = 8.0 Hz, 1H), 0.89 – 0.78 (m, 20H), 0.76 (s, 11H), 0.52 (t, J = 7.8 Hz, 6H), -0.04 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 138.2, 136.0, 133.2, 132.8, 130.5, 129.9, 129.3, 129.1, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 126.1, 126.0, 125.8, 125.6, 113.7, 113.6, 106.1, 97.1, 91.1, 81.6, 79.6, 76.4, 75.8, 75.4, 73.3, 73.2, 73.2, 72.2, 70.2, 69.9, 69.2, 63.2, 55.2, 29.7, 25.6, 18.0, 17.5, 17.3, 17.1, 17.1, 17.0, 16.9, 16.9, 13.3, 13.0, 12.6, 12.5, -4.2, -5.2; **$[\alpha]_D^{25}$** = – 48.6 (*c* 0.43, $CHCl_3$); **IR** (neat): ν_{max} = 2928, 2865, 2109, 1513, 1464, 1248, 1108, 1062, 1034, 839, 734,700 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{64}H_{91}N_3NaO_{13}Si_3$ $[M + Na]^+$ *m/z* 1216.5752; found *m/z* 1216.5749.

According to the general procedure, the glycosylation of acceptor **12j** (25.0 mg, 0.156 mmol, 1.0 equiv) with donor **8** (177 mg, 0.234 mmol, 1.5 equiv) proceeded in the presence of NIS (57.3 mg, 0.234 mmol, 1.5 equiv)/TfOH (2.07 μL, 0.023 mmol, 0.15 equiv) in 2 h, generating **13j** (120 mg, 86%, α/β > 20/1) as colorless syrup after purification by silica gel column chromatography (petroleum ether/EtOAc = 15:1, v/v).

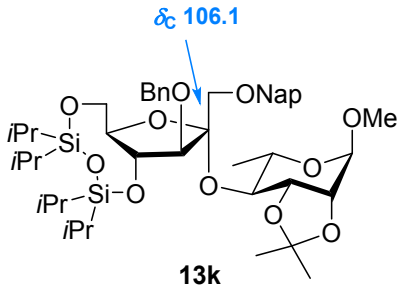


13j

TLC: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.0, 3.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.68 (s, 1H), 7.47 – 7.39 (m, 3H), 7.34 – 7.27 (m, 5H), 5.83 (d, J = 3.6 Hz, 1H), 4.75 (d, J = 11.6 Hz, 1H), 4.71 – 4.62 (m, 3H), 4.59 (d, J = 3.6 Hz, 1H), 4.42 – 4.36 (m, 2H), 4.27 (dd, J = 12.4, 6.0 Hz, 1H), 4.17 (dd, J = 6.8, 3.2 Hz, 1H), 4.06 – 3.96 (m, 4H), 3.91

(dd, J = 12.4, 5.2 Hz, 1H), 3.86 – 3.82 (m, 1H), 3.68 (s, 2H), 1.47 (s, 3H), 1.28 (d, J = 6.4 Hz, 6H), 1.12 – 1.00 (m, 24H), 0.93 (t, J = 6.4 Hz, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.1, 135.5, 133.2, 132.9, 128.2, 127.9, 127.9, 127.6, 127.5, 127.5, 126.5, 126.0, 125.9, 125.7, 111.7, 108.6, 106.9, 105.1, 90.5, 84.4, 80.8, 79.9, 76.3, 75.8, 73.7, 73.2, 72.8, 68.5, 66.9, 62.4, 26.9, 26.5, 26.4, 25.1, 17.5, 17.3, 17.1, 17.1, 17.1, 17.1, 17.0, 13.4, 13.1, 12.7, 12.6; **$[\alpha]_D^{25}$** = −16.2 (c 0.77, $CHCl_3$); **IR** (neat): ν_{max} = 2942, 2867, 1463, 1372, 1275, 1260, 1070, 1028, 884, 851, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{48}H_{70}O_{12}Si_2$ [M + Na]$^+$ m/z 917.4298; found m/z 917.4296.

Following the general procedure, the mixture of acceptor **12k** (50.0 mg, 0.229 mmol, 1.0 equiv), donor **8** (209 mg, 0.275 mmol, 1.2 equiv) and NIS (64.4 mg, 0.275 mmol, 1.2 equiv)/TfOH (2.43 μL, 0.028 mmol, 0.12 equiv) was subjected to glycosylation in 2 h to deliver **13k** as colorless oil (228 mg, 96%, α/β > 20/1) after purification by silica gel column chromatography (petroleum ether/EtOAc = 50:1 to 40:1, v/v).

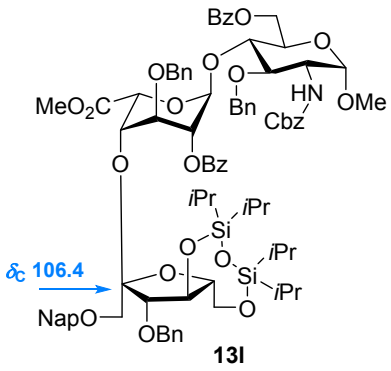


13k

TLC: (petroleum ether/EtOAc = 10:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.0, 3.2 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.48 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 7.33 – 7.26 (m, 3H), 4.83 (d, J = 12.4 Hz, 3H), 4.76 (d, J = 8.4 Hz, 1H), 4.68 (dd, J = 27.6, 11.6 Hz, 2H), 4.47 (t, J = 8.0 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.98 – 3.90 (m, 2H), 3.85 (dd, J = 12.0, 6.8 Hz, 1H), 3.69 (d, J = 10.0 Hz, 1H), 3.65 – 3.57 (m, 2H), 3.44 (d, J = 10.0 Hz, 1H), 3.36 (s, 3H), 1.57 (s, 3H), 1.30 – 1.24 (m, 6H), 1.11 – 0.93 (m, 22H), 0.82 – 0.75 (m, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 139.2, 135.8, 133.2, 132.9, 128.0, 127.9, 127.8, 127.6, 127.3, 127.1, 126.5, 126.2, 125.8, 125.6, 109. 1, 106.1, 97.9, 87.9, 80.9, 77.4, 76.5, 76.1, 74.4, 73.8, 72.7, 71.9, 65.1, 64.0, 54.7, 28.2, 26.3, 18.0, 17.5, 17.3, 17.1, 17.1, 17.0, 16.9, 16.9, 13.3, 13.0, 12.5, 12.5; **$[\alpha]_D^{25}$** = −2.8 (c 1.2, $CHCl_3$); **IR** (neat): ν_{max} = 2928, 2866, 1463, 1384, 1261, 1092, 885, 861, 814, 750 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{46}H_{68}NaO_{11}Si_2$ [M + Na]$^+$ m/z 875.4192; found m/z 875.4189.

According to the general procedure, acceptor **12l** (35.0 mg, 0.039 mmol, 1.0 equiv), donor **8** (43.9 mg, 0.058 mmol, 1.2 equiv) and NIS (14.2 mg, 0.058 mmol, 1.5 equiv)/TfOH (0.512 μL, 0.006 mmol, 0.12 equiv) were used. The reaction was completed in 2 h to provide **13l** as white foam (58.2 mg, 97%, α/β > 20/1) after

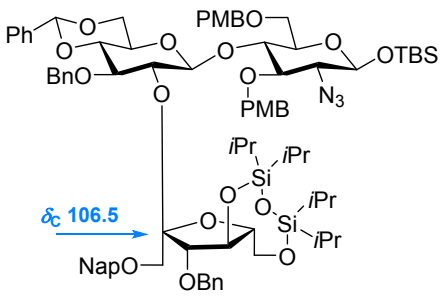
purification by column chromatography (petroleum ether/EtOAc = 10:1 to 7:1, v/v).



13l

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.96 (m, 4H), 7.80 – 7.73 (m, 1H), 7.72 – 7.62 (m, 2H), 7.61 – 7.52 (m, 2H), 7.48 – 7.38 (m, 5H), 7.37 – 7.12 (m, 18H), 7.10 – 6.98 (m, 5H), 5.65 (d, J = 5.6 Hz, 1H), 5.27 – 5.19 (m, 1H), 5.03 (d, J = 5.2 Hz, 1H), 4.89 (d, J = 11.2 Hz, 1H), 4.80 – 4.70 (m, 2H), 4.65 – 4.43 (m, 9H), 4.39 – 4.31 (m, 2H), 4.28 – 4.20 (m, 1H), 4.09 (t, J = 7.2 Hz, 1H), 4.04 – 3.72 (m, 7H), 3.61 – 3.43 (m, 3H), 3.33 (s, 3H), 3.27 (s, 3H), 1.07 – 0.95 (m, 20H), 0.91 – 0.76 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 166.1, 165.2, 155.8, 138.4, 137.9, 137.6, 136.3, 135.5, 133.2, 133.2, 132.9, 129.8, 129.8, 129.3, 128.5, 128.4, 128.2, 128.1, 128.1, 128.1, 127.9, 127.9, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 127.3, 126.4, 126.0, 125.8, 125.6, 106.4, 98.7, 98.4, 90.3, 79.4, 78.4, 78.4, 75.49, 74.83, 74.6, 73.5, 73.1, 72.8, 72.3, 70.8, 69.1, 69.1, 66.9, 62.6, 62.1, 55.2, 54.4, 51.3, 17.5, 17.3, 17.1, 17.1, 17.0, 17.0, 13.4, 13.0, 12.6, 12.5; **$[\alpha]_D^{25}$** = +5.8 (*c* 0.67, $CHCl_3$); **IR** (neat): ν_{max} = 2943, 2866, 1721, 1512, 1452, 1266, 1107, 1026, 885, 812, 734 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{86}H_{101}NNaO_{21}Si_2$ $[M + Na]^+$ *m/z* 1562.6297; found *m/z* 1562.6294.

Following the general procedure, the glycosylation reaction of acceptor **12m** (30.0 mg, 0.033 mmol, 1.0 equiv) and donor **8** (37.9 mg, 0.050 mmol, 1.5 equiv) occurred in the presence of NIS (12.2 mg, 0.050 mmol, 1.5 equiv)/TfOH (0.442 μL, 0.005 mmol, 0.15 equiv) in 2 h to provide **12m** as white foam (49.1 mg, 98%, α/β > 20/1) after purification by column chromatography (petroleum ether/EtOAc = 25:1, v/v).

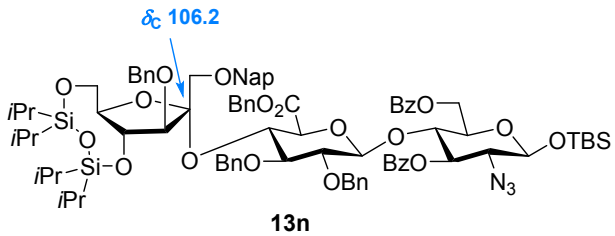


13m

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.69 – 7.54 (m, 3H), 7.47 – 7.35 (m, 4H), 7.34 – 7.23 (m, 10H), 7.23 – 7.14 (m, 6H), 7.14 – 7.09 (m, 2H), 6.90 – 6.70 (m, 4H), 5.44 (s, 1H), 4.91 (d, J = 10.8 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.63 – 4.36 (m, 7H), 4.30 (d, J = 7.6 Hz, 1H), 4.23 (d, J = 12.0 Hz, 1H), 4.15 (q, J = 10.8, 5.4 Hz, 1H), 4.06 (t, J = 8.4 Hz, 2H), 3.83 – 3.75 (m, 2H), 3.74 (s, 3H), 3.66 (s, 3H),3.64 – 3.44 (m, 6H), 3.42 – 3.22 (m, 4H),

3.17 – 3.09 (m, 1H), 3.01 (dd, J = 10.0, 7.6 Hz, 1H), 2.69 (d, J = 9.6 Hz, 1H), 2.48 (t, J = 9.2 Hz, 1H), 1.09 – 0.81 (m, 37H).,0.044 (d, J = 4.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 159.1, 138.5, 138.4, 137.3, 136.4, 133.2, 132.8, 130.5, 129.9, 129.8, 129.4, 128.9, 128.2, 128.2, 128.0, 127.9, 127.8, 127.5, 127.5, 127.2, 126.2, 126.2, 125.9, 125.8, 125.7, 113.9, 113.5, 106.5, 101.1, 101.1, 96.9, 91.3, 82.5, 80.4, 80.3, 78.8, 74.9, 74.8, 74.7, 74.5, 74.0, 73.7, 73.3, 73.1, 70.0, 68.9, 67.6, 67.2, 65.9, 60.3, 55.3, 55.2, 29.7, 25.6, 17.9, 17.5, 17.3, 17.2, 17.2, 17.2, 17.1, 17.0, 13.5, 12.9, 12.7, 12.6, -4.1, -5.1; **$[\alpha]_D^{25}$** = −30.0 (c 0.73, $CHCl_3$); **IR** (neat): ν_{max} = 2930, 2865, 2111, 1513, 1264, 1248, 1035, 839, 7335, 700 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{84}H_{111}N_3NaO_{18}Si_3$ $[M + Na]^+$ m/z 1556.7063; found m/z 1556.7060.

According to the general procedure, the mixture of acceptor **12n** (25.0 mg, 0.026 mmol, 1.0 equiv), donor **8** (29.2 mg, 0.038 mmol, 1.5 equiv), NIS (9.43 mg, 0.038 mmol, 1.5 equiv)/TfOH (0.340 μL, 0.004 mmol, 0.15 equiv) was subjected to the glycosylation reaction in 2 h to give **13n** as white foam (39.0 mg, 97%, α/β > 20/1) after purification by silica gel column chromatography (petroleum ether/EtOAc = 20:1 to 15:1, v/v).

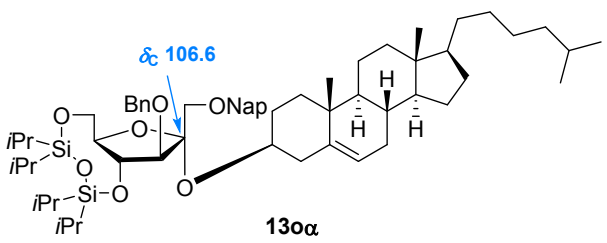


13n

TLC: (petroleum ether/EtOAc = 5:1, v/v), R_f = 0.60; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 7.2 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.27 – 7.20 (m, 5H), 7.14 – 7.10 (m, 3H), 7.10 – 6.90 (m, 15H), 6.90 – 6.81 (m, 4H), 5.09 (t, J = 10.0 Hz, 1H), 4.78 (d, J = 12.4 Hz, 1H), 4.57 – 4.41 (m, 7H), 4.36 (dd, J = 12.4, 8.8 Hz, 3H), 4.29 (dd, J = 12.0, 6.0 Hz, 1H), 4.14 (m, 2H), 4.03 (d, J = 11.6 Hz, 1H), 3.95 (t, J = 8.0 Hz, 1H), 3.83 (t, J = 10.4 Hz, 2H), 3.63 – 3.43 (m, 5H), 3.34 – 3.16 (m, 5H), 0.88 – 0.77 (m, 20H), 0.71 (s, 11H), 0.60 (t, J = 7.2 Hz, 6H), -0.02 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 165.8, 165.6, 138.3, 138.1, 138.0, 135. 8, 135.2, 133.2, 133.1, 132.9, 132.9, 130.1, 129.8, 129.8, 129.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.2, 126.2, 126.0, 125.8, 125.6, 106.2, 102.3, 97.2, 91.0, 82.7, 81.7, 79.6, 75.6, 75.1, 74.9, 73.6, 73.4, 73.2, 72.6, 72.2, 69.2, 66.8, 63.0, 62.7, 29.7, 25.5, 17.9, 17.5, 17.4, 17.1, 17.0, 17.0, 16.9, 13.3, 13.0, 12.6, 12.6, -4.4, -5.3; **$[\alpha]_D^{25}$** = −9.2 (c 0.63, $CHCl_3$); **IR** (neat): ν_{max} = 2929, 2865, 2111,

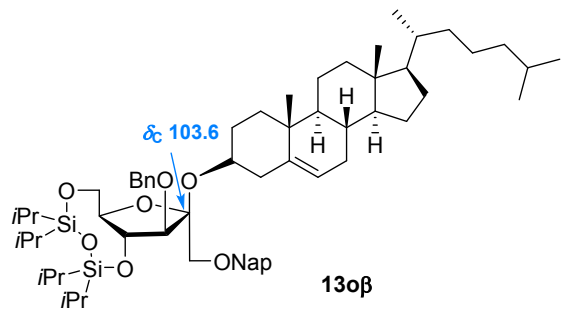
1725, 1453, 1263, 1091, 1065, 1028, 838, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{89}H_{109}N_3NaO_{19}Si_3$ $[M + Na]^+$ *m/z* 1630.6855; found *m/z* 1630.6851.

Following the general procedure, acceptor **12o** (50.0 mg, 0.129 mmol, 1.0 equiv), donor **8** (118 mg, 0.155 mmol, 1.2 equiv), NIS (38.0 mg, 0.155 mmol, 1.2 equiv)/TfOH (1.37 μL, 0.016 mmol, 0.12 equiv) were used. The reaction proceeded in 2 h to provide two isomers **13oα** and **13oβ** (105 mg, 80%, α/β = 12.3/1) as white foam after column chromatography petroleum ether/EtOAc = 100:1 to 90:1, v/v) on silica gel.



13oα

TLC: (petroleum ether/EtOAc = 20:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.0, 3.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.70 (s, 1H), 7.47 – 7.43 (m, 2H), 7.40 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.33 – 7.25 (m, 5H), 5.23 (d, *J* = 5.2 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.68 (t, *J* = 11.6 Hz, 2H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.35 (t, *J* = 6.8 Hz, 1H), 4.05 (d, *J* = 6.4 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.90 – 3.84 (m, 2H), 3.66 – 3.57 (m, 3H), 2.33 – 2.18 (m, 2H), 2.03 – 1.91 (m, 2H), 1.86 – 1.75 (m, 3H), 1.60 – 1.24 (m, 14H), 1.19 – 1.10 (m, 5H), 1.08 – 1.01 (m, 23H), 0.99 (s, 6H), 0.95 – 0.91 (m, 10H), 0.87 (dd, *J* = 6.8, 2.0 Hz, 7H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.3, 138.5, 135.7, 133.2, 132.9, 128.1, 127.9, 127.8, 127.6, 127.4, 127.3, 126.5, 126.0, 125.9, 125.7, 121.4, 106.6, 89.9, 80.0, 73.5, 73.0, 72.3, 69.4, 62.9, 56.8, 56.1, 50.1, 42.3, 41.3, 39.8, 39.5, 37.5, 36.5, 36.2, 35.8, 31.9, 31.9, 30.4, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 17.5, 17.4, 17.2, 17.1, 17.1, 17.1, 13.4, 13.1, 12.7, 12.6, 11.8; **$[\alpha]_D^{25}$** = −20.7 (*c* 0.43, $CHCl_3$); **IR** (neat): ν_{max} = 2936, 2866, 1464, 1381, 1262, 1106, 1032, 885, 813, 737 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{63}H_{96}NaO_7Si_2$ $[M + Na]^+$ *m/z* 1043.6587; found *m/z* 1043.6584.

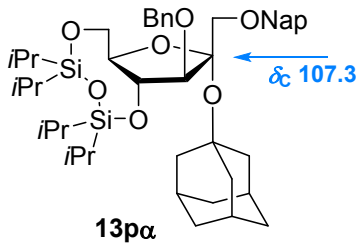


13oβ

TLC: (petroleum ether/EtOAc = 20:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 3H), 7.71 (s, 1H), 7.48 – 7.45 (m, 2H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.29 – 7.24 (m, 5H), 5.25 (d, *J* = 4.8 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 2H), 4.59 – 4.49 (m, 2H), 4.23 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 4.4 Hz, 2H), 3.76 – 3.71 (m, 1H), 3.65 – 3.59 (m, 1H), 3.50 (dd, *J* = 26.0, 10.4 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.22 (dd, *J*

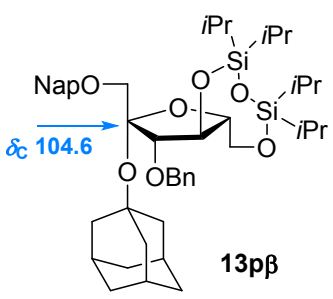
= 13.6, 3.2 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.85 – 1.73 (m, 3H), 1.49 – 1.21 (m, 12H), 1.11 – 1.01 (m, 34H), 0.97 (s, 6H), 0.91 (d, J = 6.4 Hz, 3H), 0.87 (dd, J = 6.4, 1.6 Hz, 7H), 0.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 138.5, 135.5, 133.2, 132.9, 128.1, 128.0, 127.9, 127.8, 127.7, 127.3, 126.4, 126.0, 125.8, 125.8, 121.3, 103.6, 84.2, 79.6, 73.6, 73.0, 72.7, 72.3, 63.8, 56.8, 56.1, 50.1, 42.3, 41.8, 39.8, 39.5, 37.6, 36.5, 36.2, 35.8, 32.0, 31.9, 29.9, 29.7, 28.2, 28.0, 24.3, 23.8, 22.8, 22.7, 22.6, 21.0, 19.3, 18.7, 17.6, 17.5, 17.5, 17.4, 17.2, 17.1, 17.0, 13.5, 13.2, 12.9, 12.6, 11.9; **$[\alpha]_D^{25}$** = −38.0 (c 0.20, $CHCl_3$); **IR** (neat): ν_{max} = 2920, 2867, 1462, 1265, 1096, 1035, 888, 798, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{63}H_{96}NaO_7Si_2$ $[M + Na]^+$ m/z 1043.6587; found m/z 1043.6585.

Following the general procedure, the reaction of acceptor **12p** (25.0 mg, 0.164 mmol, 1.0 equiv) and donor **8** (187 mg, 0.246 mmol, 1.5 equiv) using NIS (60.4 mg, 0.246 mmol, 1.5 equiv)/TfOH (2.18 μL, 0.025 mmol, 0.15 equiv) proceeded in 2 h to afford **13pα** and **13pβ** (113mg, 88%, α/β = 11.2/1) as colorless syrup after silica gel column chromatography (petroleum ether/ EtOAc = 200:1 to 100:1, v/v).



13pα

TLC: (petroleum ether/EtOAc = 20:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.77 – 7.71 (m, 3H), 7.47 – 7.42 (m, 3H), 7.37 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 4.80 (d, J = 12.0 Hz, 1H), 4.68 (t, J = 11.6 Hz, 2H), 4.60 (d, J = 12.0 Hz, 1H), 4.34 (t, J = 7.6 Hz, 1H), 4.07 (d, J = 7.6 Hz, 1H), 3.98 – 3.85 (m, 3H), 3.64 (dd, J = 22.8, 10.4 Hz, 2H), 2.07 (s, 3H), 1.98 – 1.89 (m, 6H), 1.58 (s, 6H), 1.10 – 0.96 (m, 21H), 0.89 (t, J = 6.8 Hz, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 136.0, 133.2, 132.9, 128.0, 127.9, 127.7, 127.6, 127.5, 127.1, 126.5, 126.2, 125.8, 125.6, 107.3, 92.7, 79.2, 76.1, 75.8, 73.4, 72.8, 71.7, 63.1, 44.5, 36.4, 31.0, 17.5, 17.4, 17.2, 17.1, 17.1, 17.1, 13.4, 13.1, 12.6, 12.6; **$[\alpha]_D^{25}$** = −17.0 (c 0.67, $CHCl_3$); **IR** (neat): ν_{max} = 2910, 2865, 1463, 1353, 1249, 1110, 1031, 884, 811, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{46}H_{66}KO_7Si_2$ $[M + K]^+$ m/z 825.3979; found m/z 825.3977.

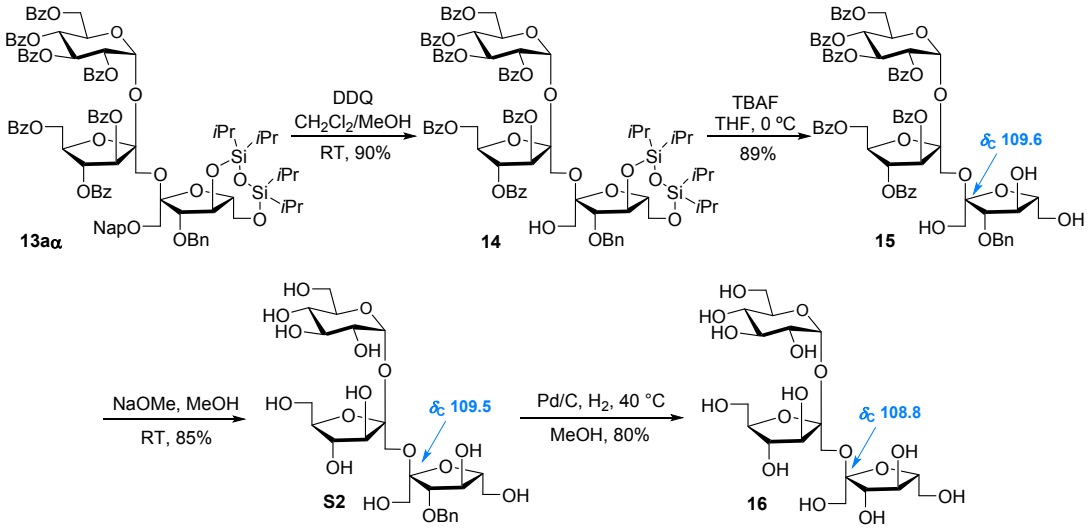


13pβ

TLC: (petroleum ether/EtOAc = 20:1, v/v), R_f = 0.35; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (m, 3H), 7.71 (s, 1H), 7.48 – 7.45 (m, 2H), 7.38 (dd, J = 8.4, 1.6 Hz, 1H), 7.32 – 7.20 (m, 5H), 4.73 – 4.66 (m, 3H), 4.57 – 4.51 (m, 2H), 4.23 (d, J = 8.0 Hz, 1H), 4.03 – 3.97 (m, 2H), 3.84 – 3.78 (m, 2H),

3.52 (d, J = 10.4 Hz, 1H), 2.07 (s, 3H), 1.91 (s, 6H), 1.56 (s, 6H), 1.11 – 1.02 (m, 28H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 135.7, 133.2, 132.9, 128.0, 127.9, 127.9, 127.7, 127.7, 127.2, 126.3, 126.0, 125.8, 104.6, 84.4, 80.5, 75.7, 73.4, 72.7, 72.4, 64.8, 44.7, 36.3, 31.0, 17.7, 17.5, 17.4, 17.1, 17.0, 13.4, 13.2, 13.1, 12.6; **$[\alpha]_D^{25}$** = +20.6 (c 0.17, $CHCl_3$); **IR** (neat): ν_{max} = 2917, 2865, 1463, 1351, 1261, 1156, 1076, 1035, 885, 802, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{46}H_{66}NaO_7Si_2$ $[M + Na]^+$ m/z 809.4239; found m/z 809.4235.

6. Synthesis of Inulin Oligosaccharide Derivatives



To a stirred solution of **13aα** (1.40 g, 0.821 mmol, 1.0 equiv) in a mixture of CH_2Cl_2 (15.0 mL) and MeOH (1.5 mL) at room temperature under argon was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 373 mg, 1.64 mmol, 2.0 equiv). After being stirred for 2 h, the reaction was quench with saturated aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2 for three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated to afford a residue, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1, v/v) to yield **14** (1.15 g, 90%) as white foam. **TLC**: (petroleum ether/EtOAc = 2.5:1, v/v), R_f = 0.40; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.23 (m, 2H), 8.10 – 7.99 (m, 6H), 7.91 – 7.82 (m, 6H), 7.66 – 7.49 (m, 6H), 7.48 – 7.39 (m, 7H), 7.38 – 7.20 (m, 13H), 6.25 (t, J = 10.0 Hz, 1H), 6.12 (d, J = 5.2 Hz, 2H), 5.89 (t, J = 5.6 Hz, 1H), 5.77 (t, J = 10.0 Hz, 1H), 5.39 (dd, J = 10.4, 3.6 Hz, 1H), 4.85 – 4.68 (m, 3H), 4.60 – 4.45 (m, 4H), 4.38 (dd, J = 12.8, 4.0 Hz, 1H), 4.28 (t, J = 8.4 Hz, 1H), 4.09 (d, J = 10.8 Hz, 1H), 4.02 (d, J = 8.0 Hz, 1H), 3.93 – 3.78 (m, 3H), 3.69 (d, J = 10.4 Hz, 1H), 3.55 – 3.40 (m, 2H), 1.14 – 1.00

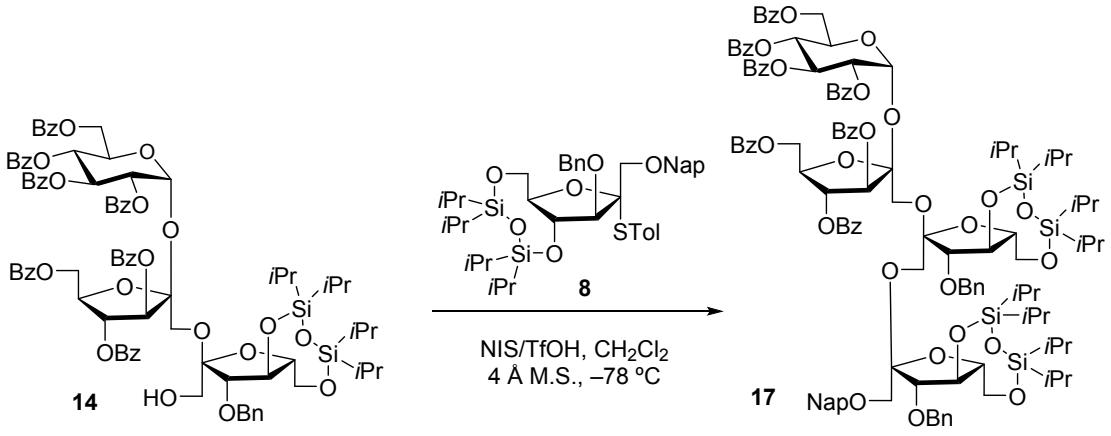
(m, 28H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.6, 165.5, 165.4, 165.2, 165.1, 137.6, 133.5, 133.3, 133.3, 133.0, 133.0, 132.9, 130.2, 129.9, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 129.2, 129.2, 129.0, 128.8, 128.8, 128.7, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 127.7, 127.6, 105.7, 105.3, 90.5, 89.7, 79.5, 79.2, 76.9, 76.6, 74.3, 73.5, 71.4, 70.1, 69.1, 69.0, 64.5, 62.5, 62.1, 61.6, 60.3, 17.4, 17.3, 17.2, 17.2, 17.1, 17.0, 13.6, 13.1, 12.7, 12.6; **$[\alpha]_D^{25}$** = +32.0 (*c* 0.35, $CHCl_3$); **IR** (neat): ν_{max} = 2944, 2867, 1724, 1601, 1451, 1261, 1091, 1204, 884, 801, 735 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{86}H_{92}NaO_{24}Si_2$ $[M + Na]^+$ *m*/*z* 1587.5409; found *m*/*z* 1587.5405.

Tetrabutylammonium fluoride (0.330 g, 1.27 mmol, 2.0 equiv) was added to a solution of compound **14** (1.00 g, 0.639 mmol, 1.0 equiv) in THF (10.0 mL) at 0 °C. The reaction was stirred overnight at this temperature before being quenched with saturated aqueous NH_4Cl and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH = 50:1, v/v) furnished **15** (752 mg, 89%) as colorless syrup. **TLC**: (CH_2Cl_2/MeOH = 30:1, v/v), R_f = 0.48; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 2H), 8.05 – 7.98 (m, 6H), 7.84 (dd, *J* = 15.2, 7.6 Hz, 6H), 7.58 (q, *J* = 7.6 Hz, 2H), 7.51 – 7.38 (m, 10H), 7.37 – 7.23 (m, 14H), 6.14 – 6.03 (m, 3H), 5.99 (d, *J* = 7.2 Hz, 1H), 5.75 (t, *J* = 10.0 Hz, 1H), 5.33 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.80 – 4.53 (m, 8H), 4.46 (dd, *J* = 12.8, 3.6 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 4.01 – 3.95 (m, 2H), 3.79 (d, *J* = 10.8 Hz, 1H), 3.65 – 3.55 (m, 4H), 3.46 (t, *J* = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 166.0, 165.6, 165.6, 165.3, 165.0, 137.2, 133.9, 133.7, 133.6, 133.3, 133.1, 132.9, 130.2, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.0, 128.8, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.7, 109.6, 104.9, 90.3, 87.8, 87.2, 79.0, 76.1, 76.0, 75.2, 72.4, 71.4, 70.0, 69.2, 68.9, 64.4, 62.5, 62.4, 62.0, 58.5; **$[\alpha]_D^{25}$** = +28.3 (*c* 0.63, $CHCl_3$); **IR** (neat): ν_{max} = 2924, 1722, 1601, 1451, 1259, 1091, 1067, 1023, 803, 736, 706 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{74}H_{66}NaO_{23}$ $[M + Na]^+$ *m*/*z* 1345.3887; found *m*/*z* 1345.3884.

A 10 mL round-bottom flask was charged with compound **15** (245 mg, 0.185 mmol, 1.0 equiv) in MeOH (5.0 mL), sodium methoxide (5 M in methanol, 55.0 μL, 0.275 mmol, 1.5 equiv) was dropwise added. After being stirred for 30 min at room temperature, the reaction was carefully neutralized with Amberlite IR 120 (H^+) resin, followed by filtration and concentration. Subjection of the residue to column chromatography on reversed phase silica gel with H_2O/MeOH (5:1 to 2:1, v/v) yielded

S2 (93.5 mg, 85%) as white amorphous powder. **TLC**: (CH_2Cl_2/MeOH = 2:1, v/v), R_f = 0.45; **^{1}H NMR** (400 MHz, CD_3OD) δ 7.40 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 5.46 (d, J = 3.6 Hz, 1H), 4.72 (s, 2H), 4.19 (d, J = 8.4 Hz, 1H), 4.09 (dd, J = 6.4, 4.0 Hz, 1H), 4.04 – 3.94 (m, 3H), 3.86 – 3.79 (m, 3H), 3.77 – 3.62 (m, 10H), 3.42 – 3.34 (m, 2H); **^{13}C NMR** (100 MHz, CD_3OD) δ 139.5, 129.3, 128.8, 128.7, 109.5, 105.0, 94.1, 90.0, 85.0, 83.6, 79.1, 76.8, 75.3, 74.7, 74.3, 73.3, 73.3, 71.5, 63.4, 63.0, 62.9, 62.3, 60.9; **$[\alpha]_D^{25}$** = +70.0 (c 0.20, CH_3OH); **IR** (neat): ν_{max} = 2928, 1406, 1211, 1015, 930, 698 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{25}H_{38}O_{16}$ [M + Na]$^+$ m/z 617.2052; found m/z 617.2050.

A mixture of **S2** (93.5 mg, 0.185 mmol) and 10% Pd/C (28.1 mg, 30% weight of **S3**) in MeOH (1.5 mL) was stirred at 40 °C under a balloon of hydrogen for 5 h. The reaction mixture was then filtered through a short pad of Celite® and the filtrate was concentrated in *vacuo*. Purification of the residue by reversed phase silical gel column chromatography with H_2O gave **16** (63.5 mg, 80%) as white amorphous powder. **TLC**: (CH_2Cl_2/MeOH/H_2O = 22:11:1.4, v/v), R_f = 0.15; **^{1}H NMR** (400 MHz, D_2O, MeOH as internal standard, at 3.34 ppm) δ 5.45 (d, J = 3.6 Hz, 1H), 4.33 (d, J = 8.8 Hz, 1H), 4.17 (d, J = 3.6 Hz, 1H), 4.07 – 3.96 (m, 3H), 3.88 – 3.69 (m, 13H), 3.54 (dd, J = 10.4, 4.0 Hz, 1H), 3.46 (t, J = 9.6 Hz, 1H); **^{13}C NMR** (100 MHz, D_2O) δ 108.8, 104.0, 93.1, 83.7, 82.0, 81.5, 77.6, 76.8, 74.3, 73.2, 73.0, 71.7, 69.8, 62.8, 61.8, 61.1, 60.7, 59.5; **$[\alpha]_D^{25}$** = +53.0 (c 0.47, CH_3OH); **IR** (neat): ν_{max} = 2928, 1726, 1288, 1012, 930, 781 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{18}H_{32}O_{16}$ [M + Na]$^+$ m/z 527.1583; found m/z 527.1581.



According to the general procedure of glycosylation, compound **17** was obtained as white foam (125 mg, 89% yield, α/β > 20/1) from donor **8** (72.7 mg, 0.096 mmol, 1.5 equiv) and acceptor **14** (100 mg, 0.064 mmol, 1.0 equiv). **TLC**: (petroleum ether/EtOAc

= 3:1, v/v), R_f = 0.50; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H), 8.05 – 8.01 (m, 2H), 7.99 – 7.91 (m, 4H), 7.87 – 7.83 (m, 4H), 7.81 – 7.77 (m, 2H), 7.76 – 7.73 (m, 1H), 7.67 – 7.61 (m, 2H), 7.58 – 7.52 (m, 2H), 7.50 – 7.44 (m, 5H), 7.41 – 7.33 (m, 8H), 7.32 – 7.23 (m, 10H), 7.20 (s, 4H), 7.17 – 7.14 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.06 – 7.03 (m, 2H), 6.27 (t, *J* = 10.0 Hz, 1H), 6.14 (d, *J* = 6.8 Hz, 1H), 6.07 (d, *J* = 3.6 Hz, 1H), 5.96 (t, *J* = 6.8 Hz, 1H), 5.77 (t, *J* = 10.0 Hz, 1H), 5.41 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.81 – 4.76 (m, 1H), 4.68 – 4.57 (m, 4H), 4.56 – 4.45 (m, 4H), 4.45 – 4.37 (m, 2H), 4.37 – 4.26 (m, 2H), 4.23 – 4.14 (m, 3H), 4.06 (d, *J* = 8.4 Hz, 1H), 3.93 – 3.84 (m, 3H), 3.81 – 3.69 (m, 4H), 3.60 – 3.47 (m, 4H), 1.06 – 0.95 (m, 51H), 0.81 (d, *J* = 7.2 Hz, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 165.9, 165.7, 165.6, 165.5, 165.2, 165.1, 138.6, 138.4, 135.7, 133.3, 133.2, 132.9, 132.9, 130.3, 120.0, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.6, 127.6, 127.4, 127.1, 126.8, 126.8, 126.4, 126.1, 125.8, 125.6, 105.6, 105.3, 105.0, 90.9, 89.4, 87.5, 79.1, 78.7, 78.1, 75.0, 74.9, 73.6, 72.9, 71.3, 70.3, 69.9, 69.1, 68.9, 64.4, 62.8, 62.5, 62.2, 61.6, 60.2, 17.5, 17.3, 17.3, 17.1, 17.1, 17.1, 17.0, 17.0, 13.5, 13.4, 13.1, 13.0, 12.8, 12.6, 12.5; **$[\alpha]_D^{25}$** = +16.9 (*c* 0.52, $CHCl_3$); **IR** (neat): ν_{max} = 2943, 2866, 1726, 1452, 1262, 1092, 1026, 884, 803, 735, 705 cm^{-1}; **HRMS (ESI)**: calcd. for $C_{122}H_{142}NaO_{30}Si_4$ $[M + Na]^+$ *m*/*z* 2222.8589; found *m*/*z* 2222.8585.

7. References

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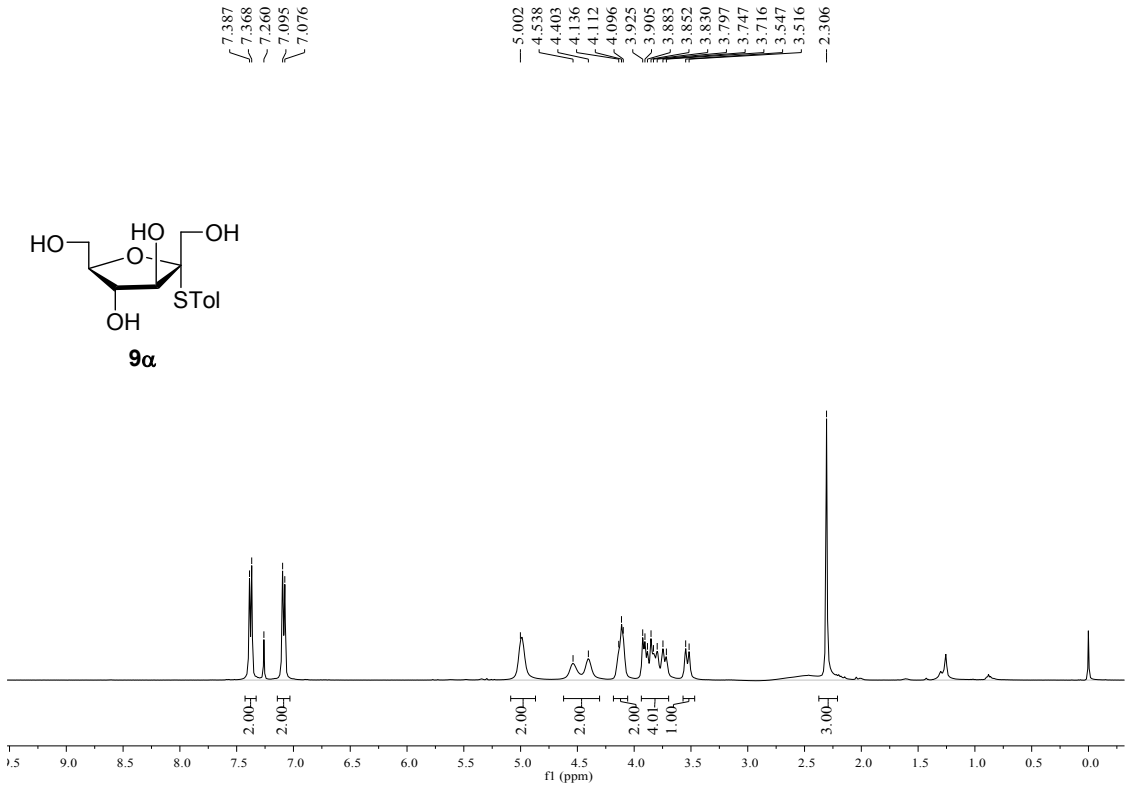
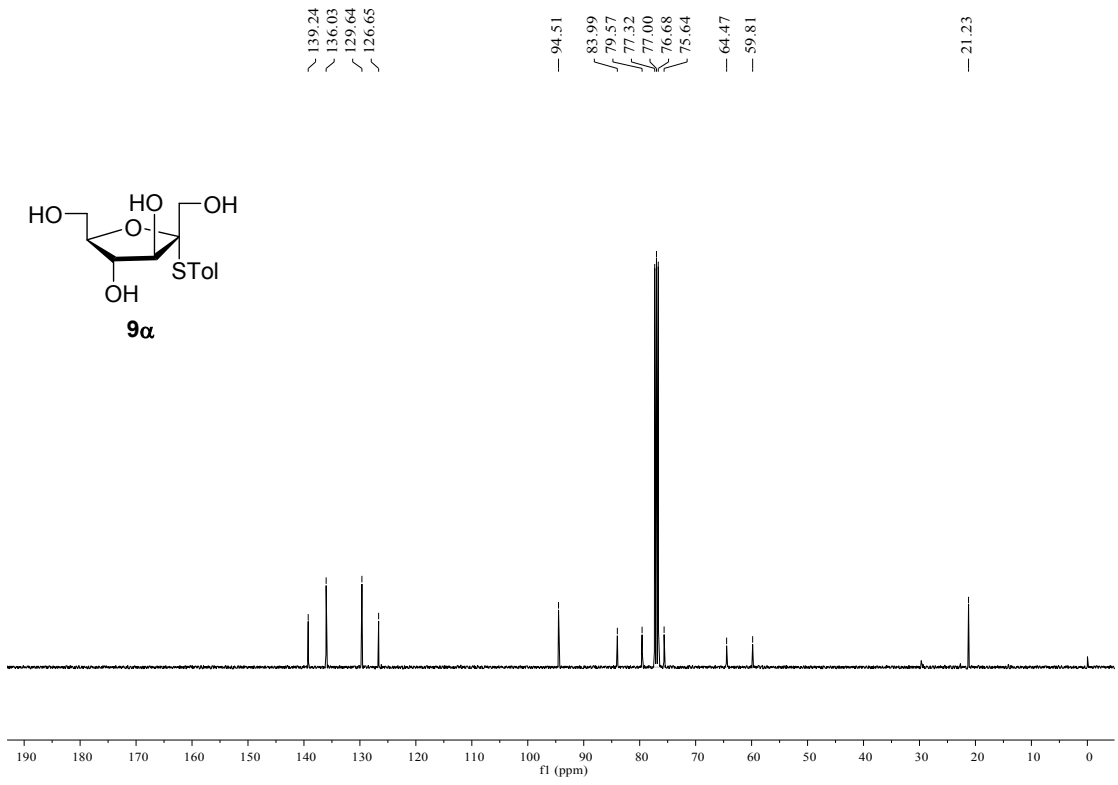
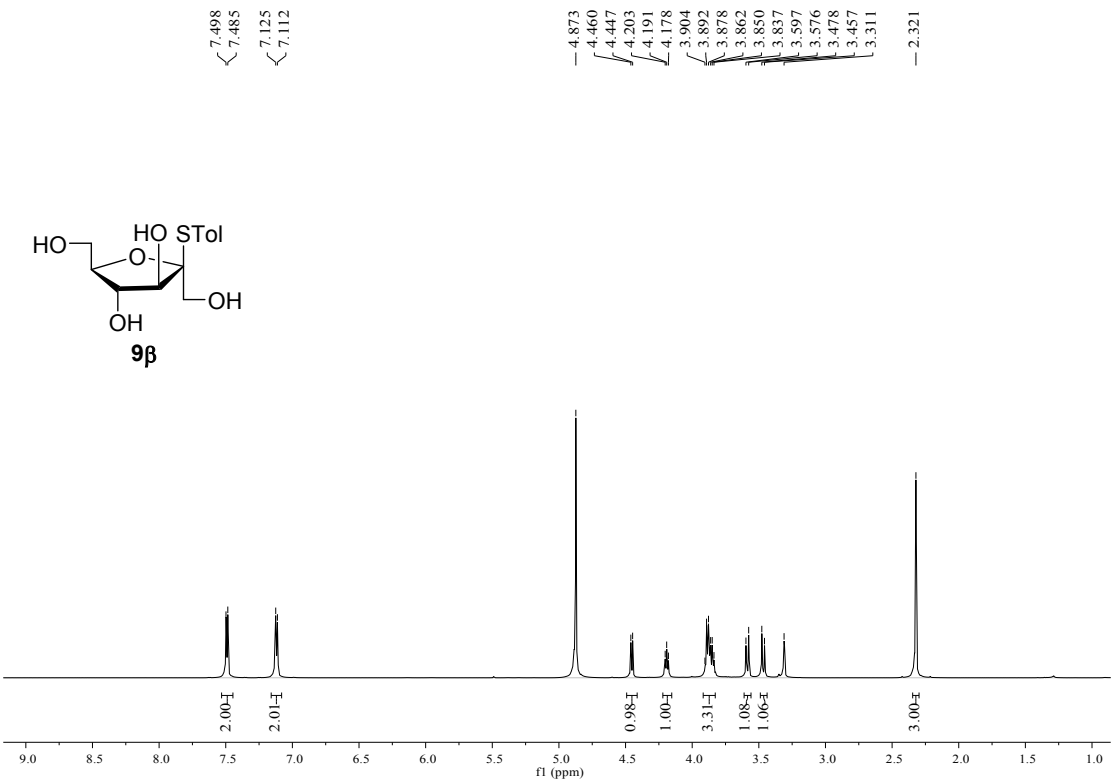
8. NMR Spectra



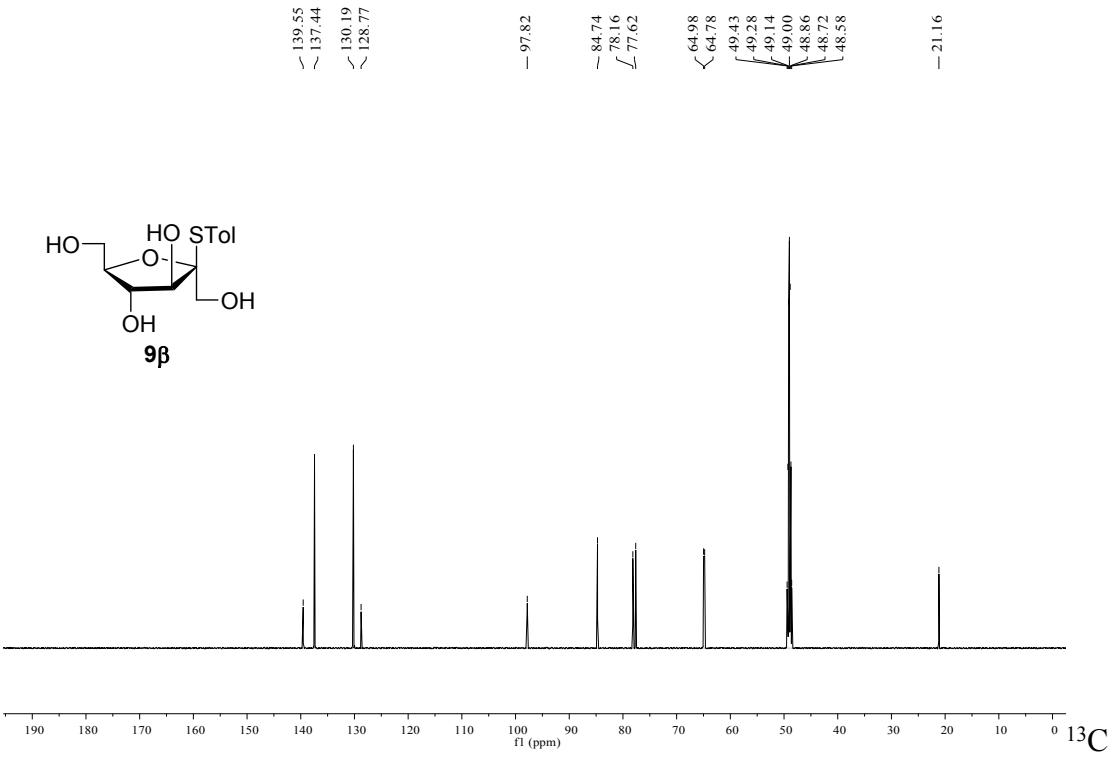
^{1}H NMR spectrum of compound **9α**



^{13}C NMR spectrum of compound **9α**



^{1}H NMR spectrum of compound **9β**



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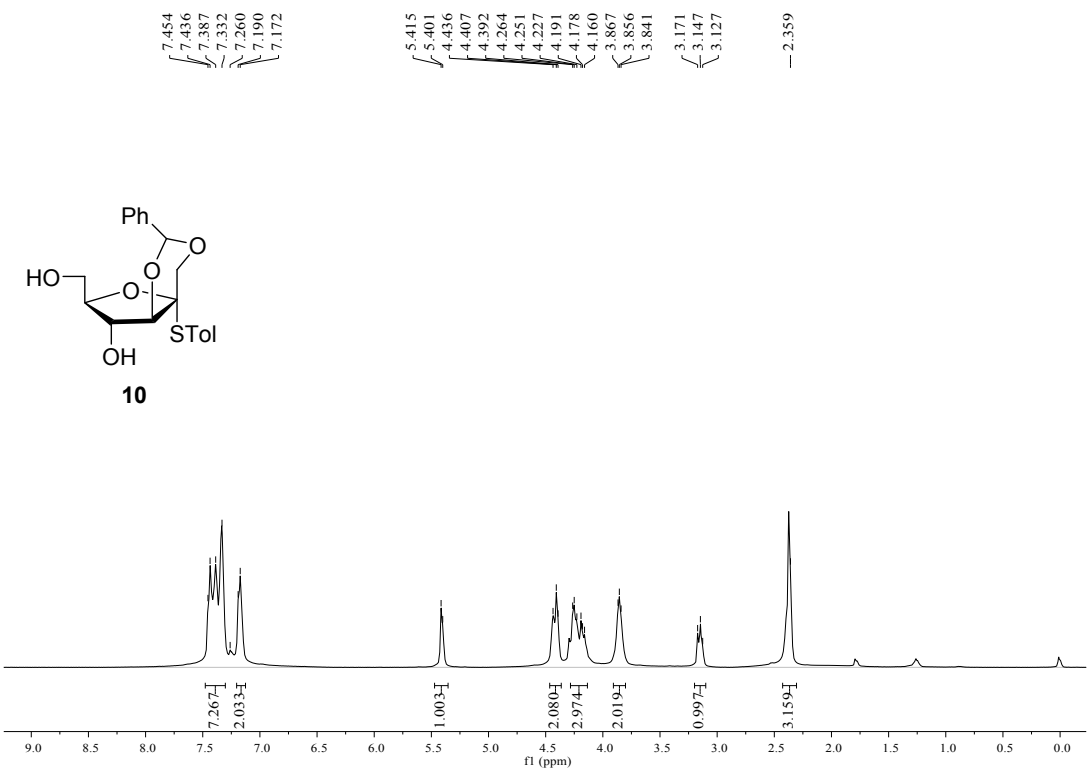

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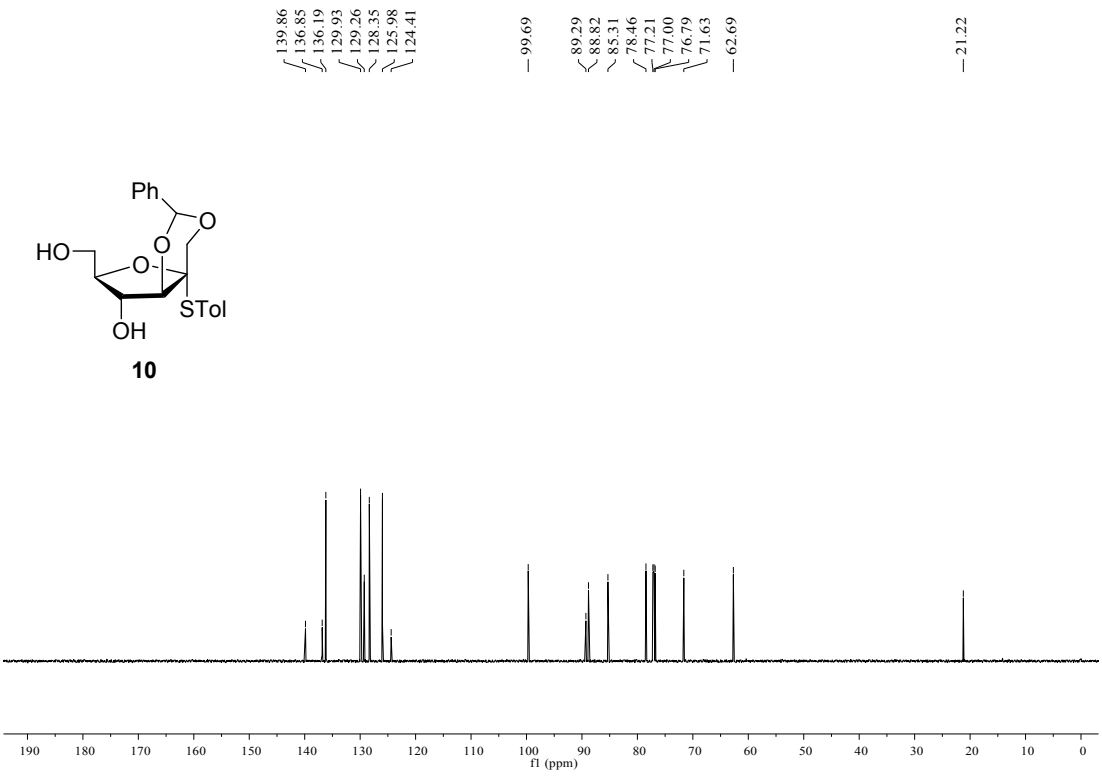

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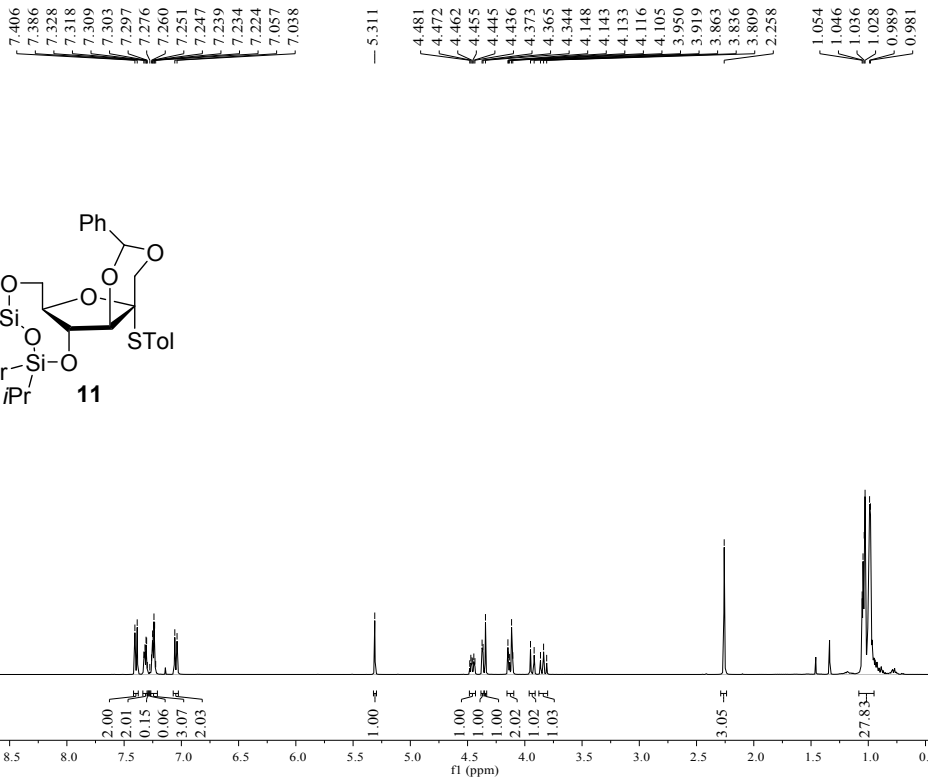

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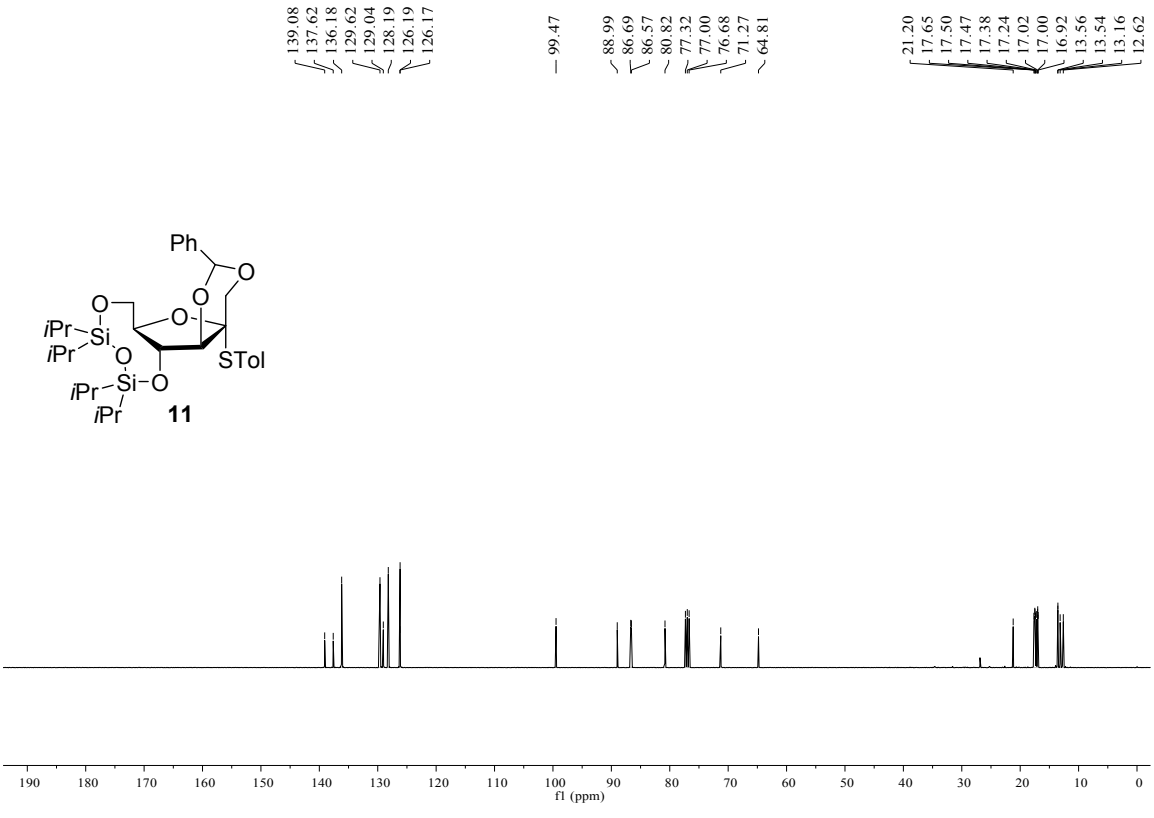
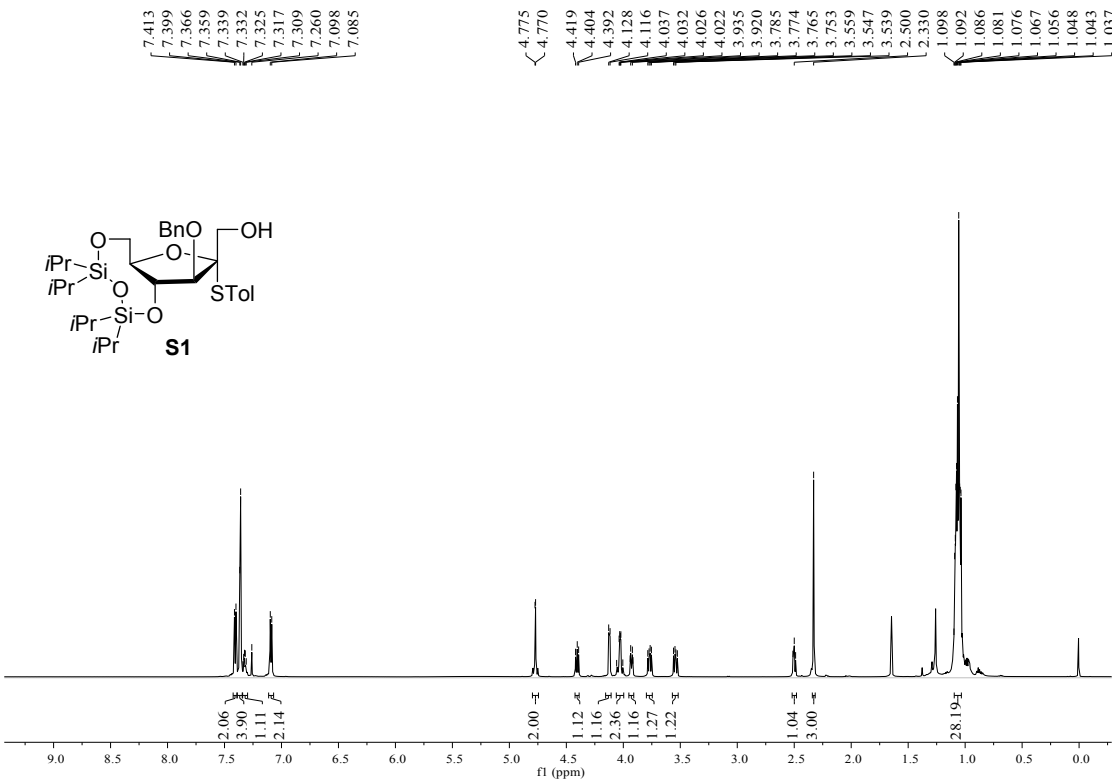
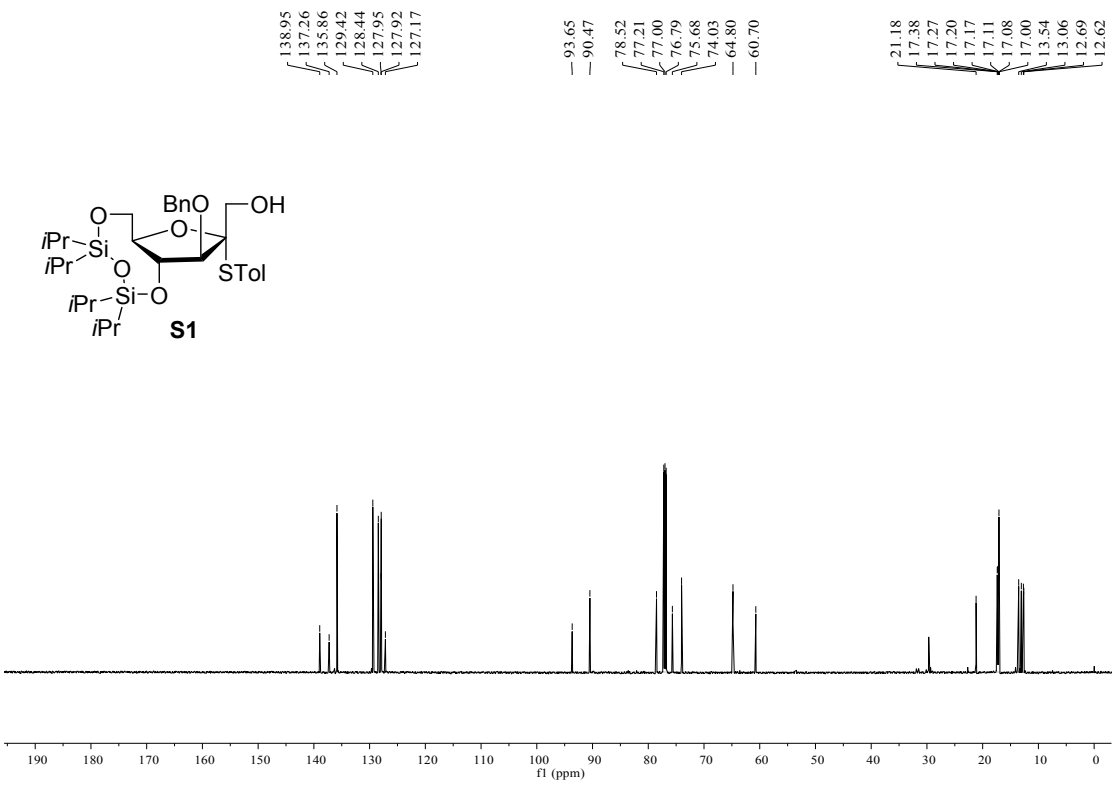


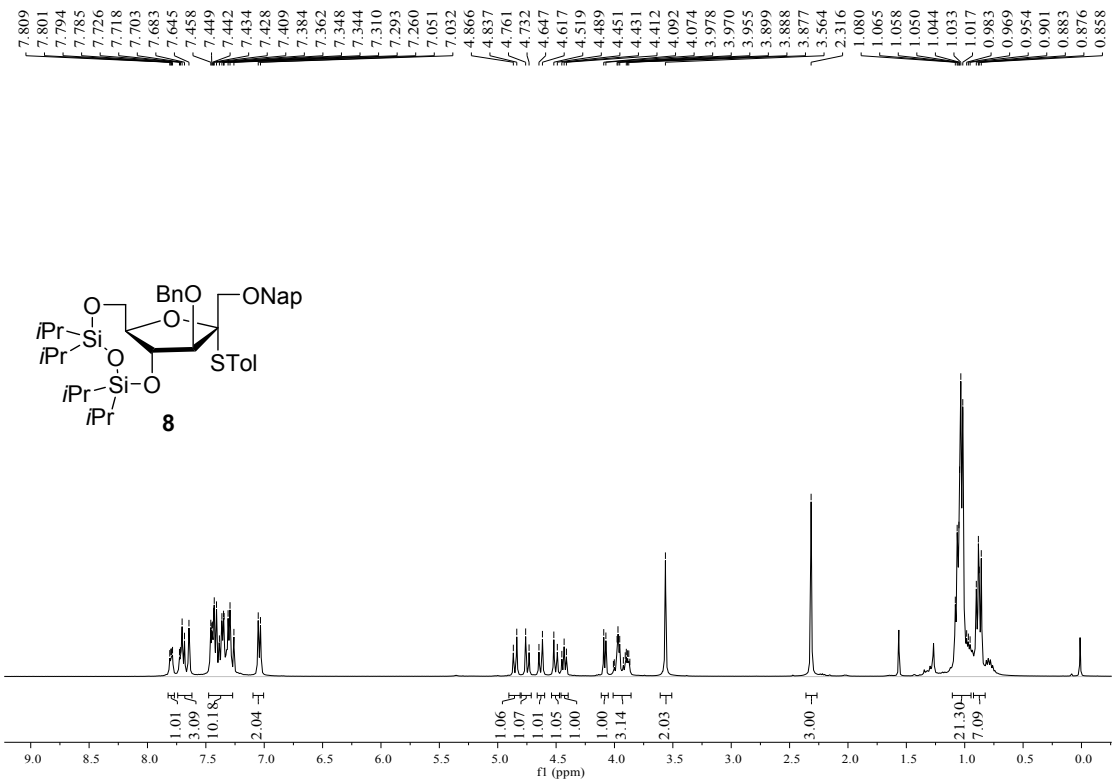
^{13}C NMR spectrum of compound **11**



^{1}H NMR spectrum of compound **S1**



^{13}C NMR spectrum of compound **S1**



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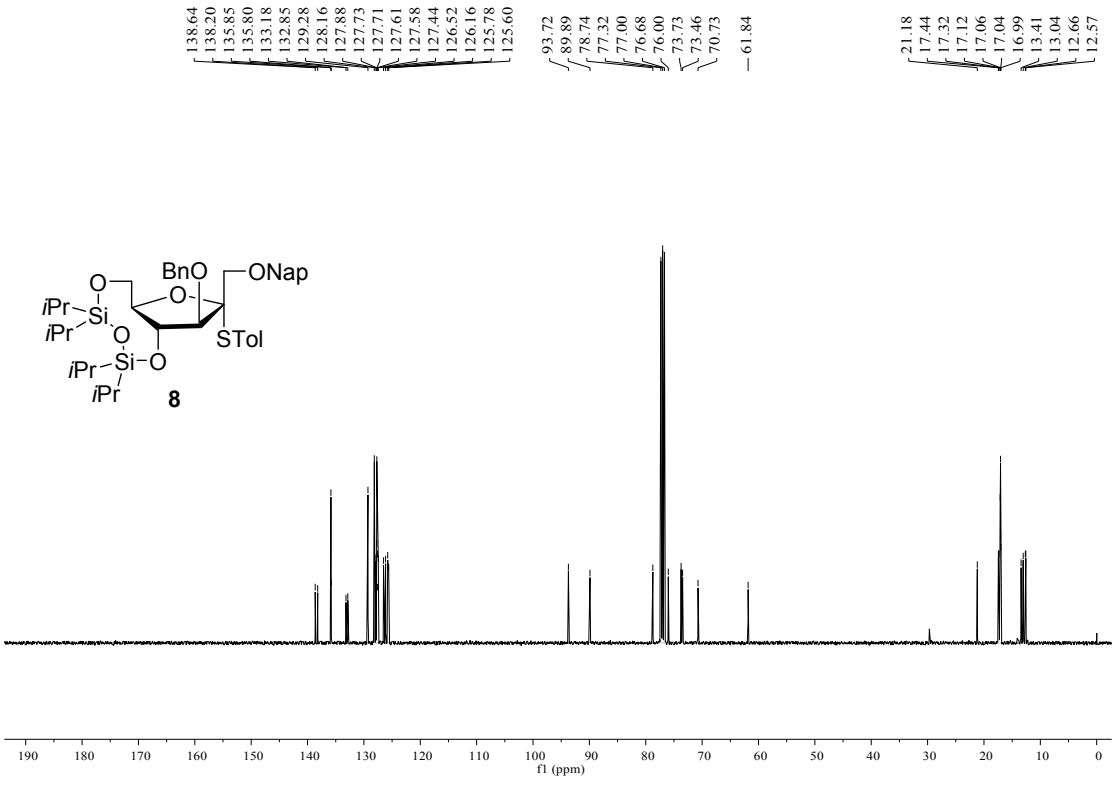

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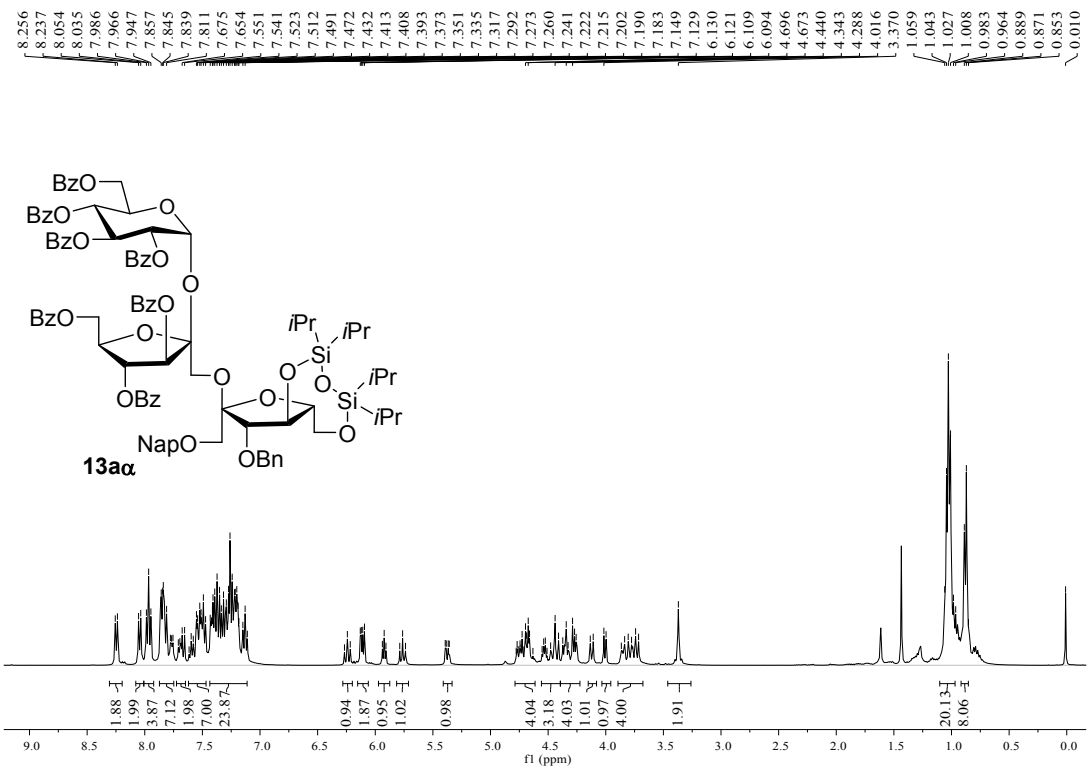
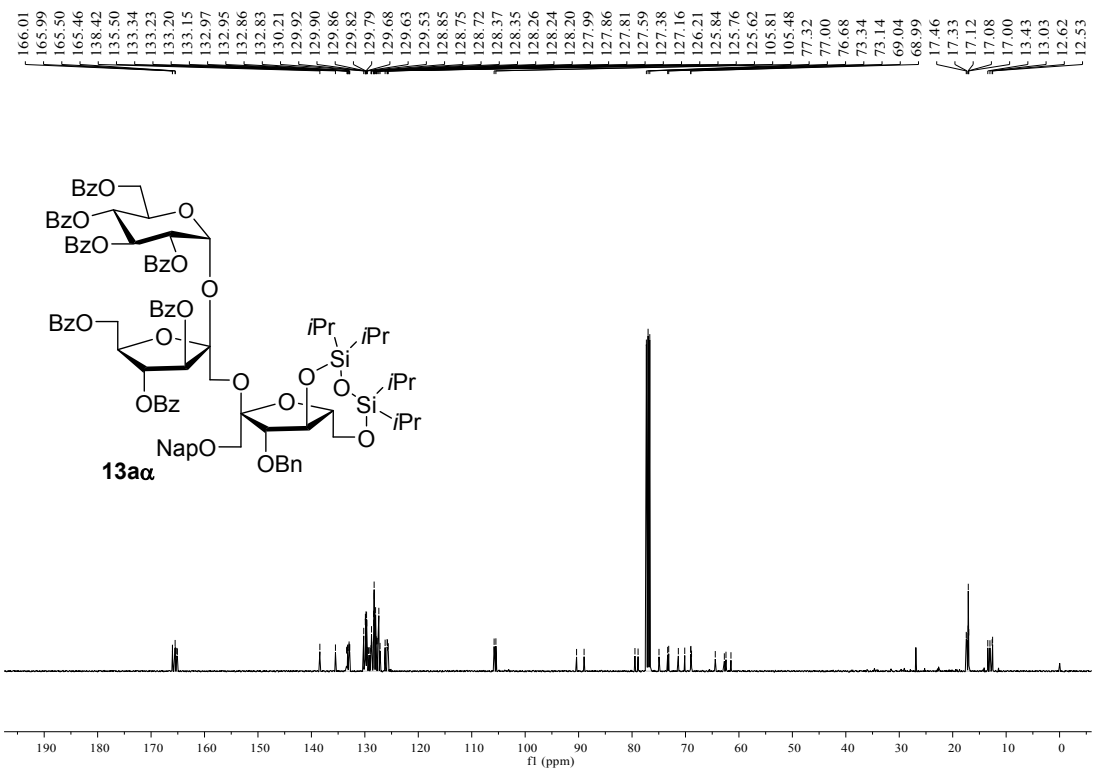
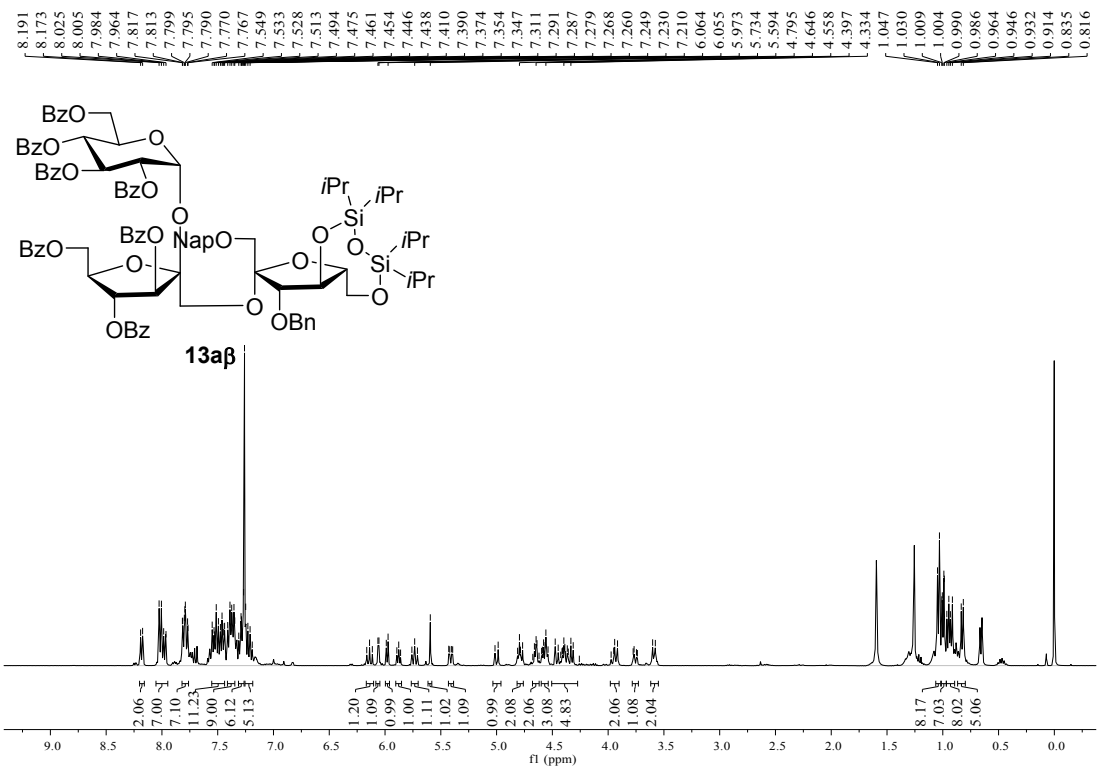


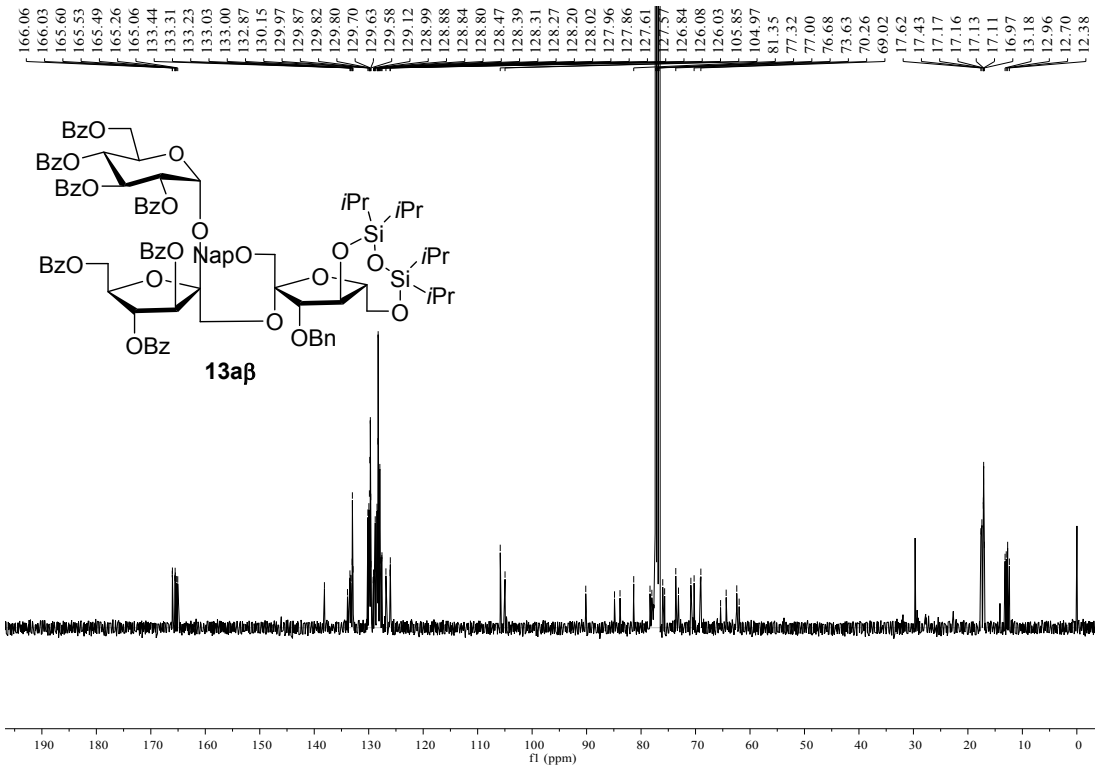
^{1}H NMR spectrum of compound **13aα**



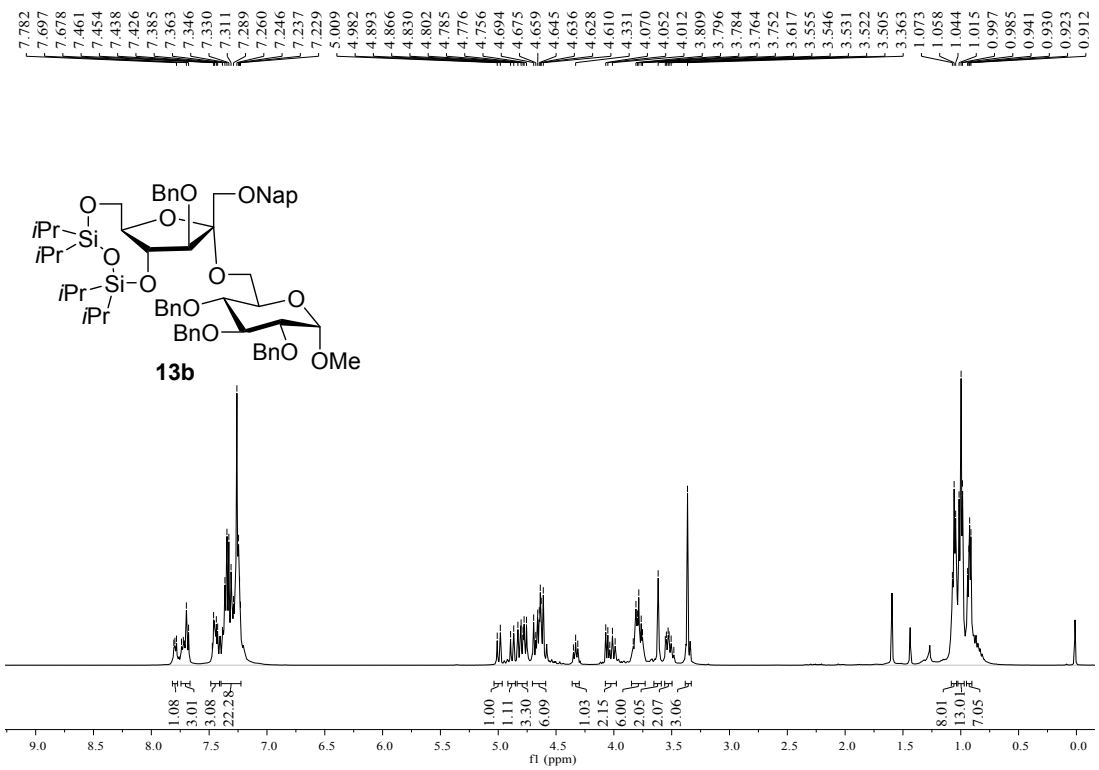
^{13}C NMR spectrum of compound **13aα**



^{1}H NMR spectrum of compound **13aβ**



^{13}C NMR spectrum of compound **13aβ**



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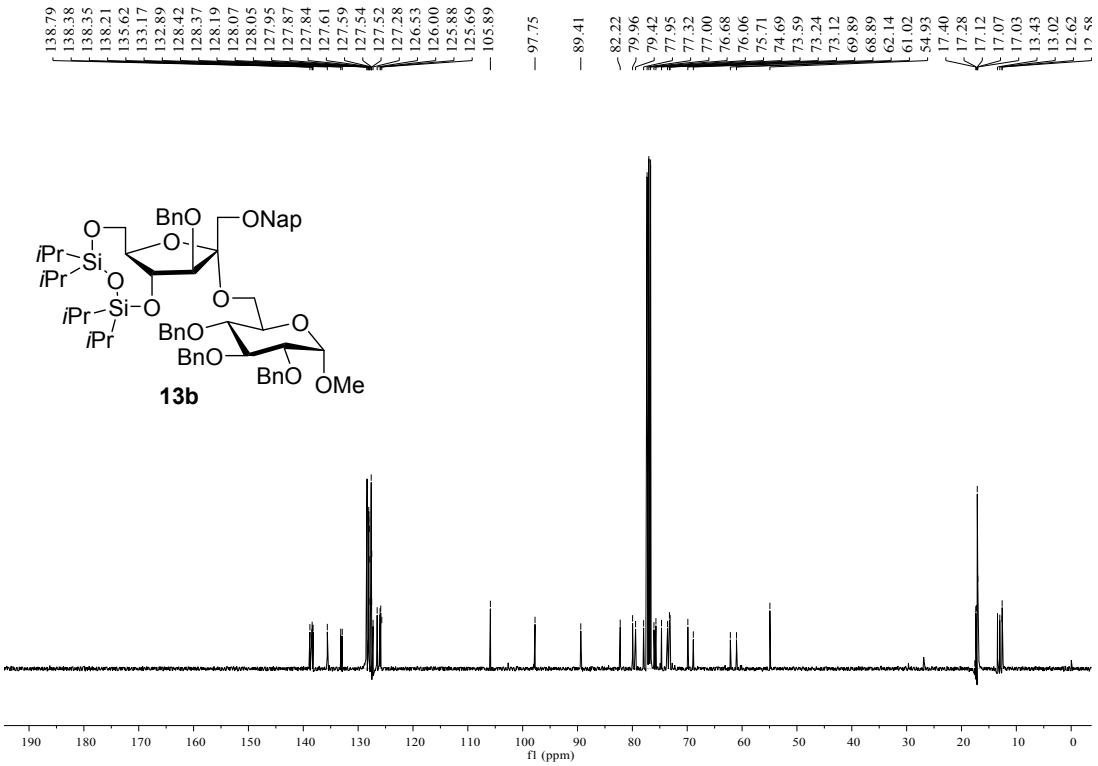
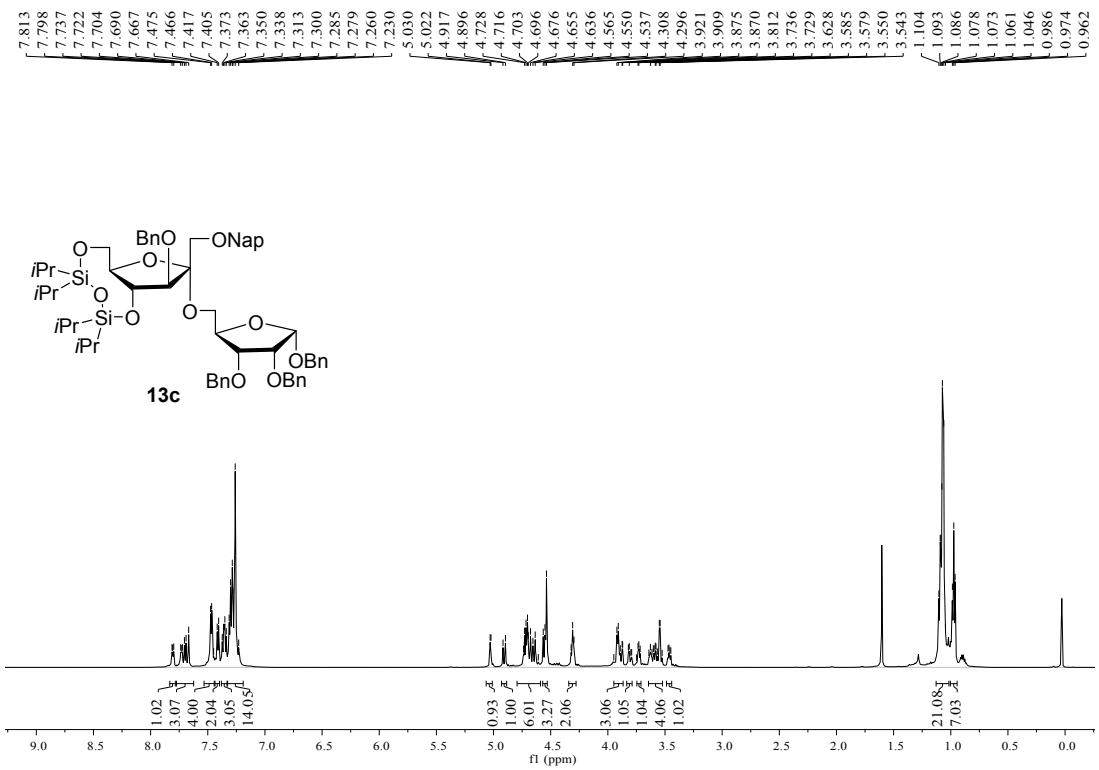


^{13}C NMR spectrum of compound **13b**



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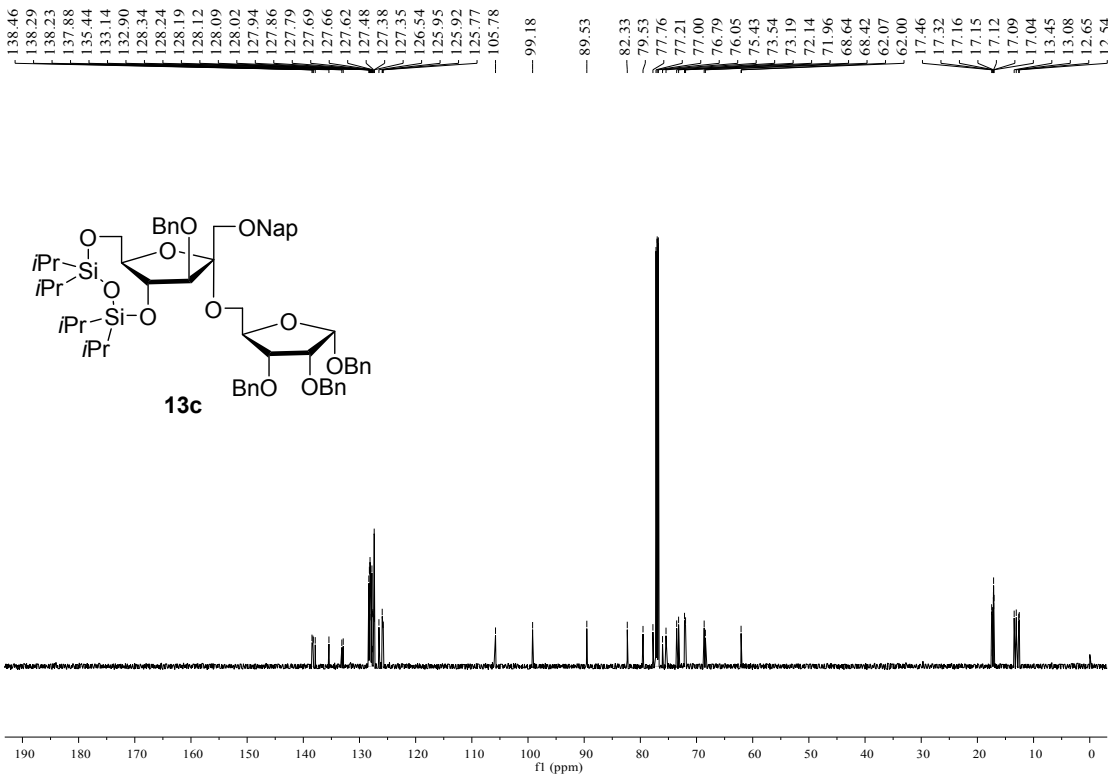
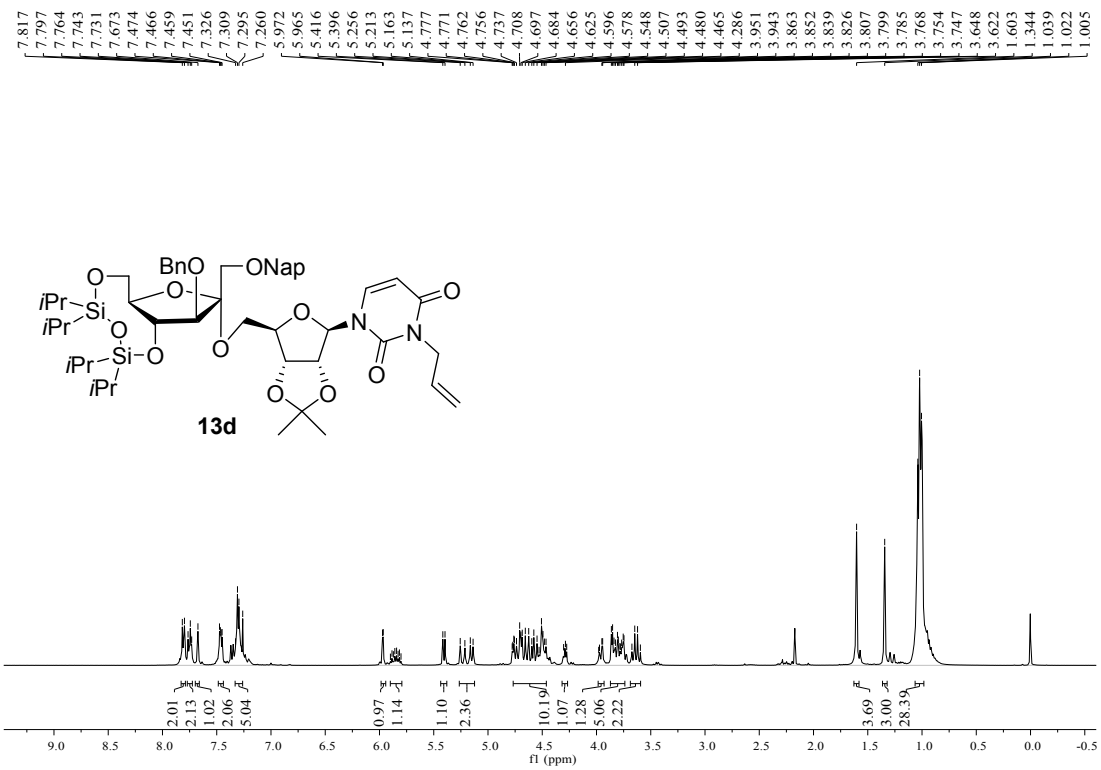


^{13}C NMR spectrum of compound **13c**



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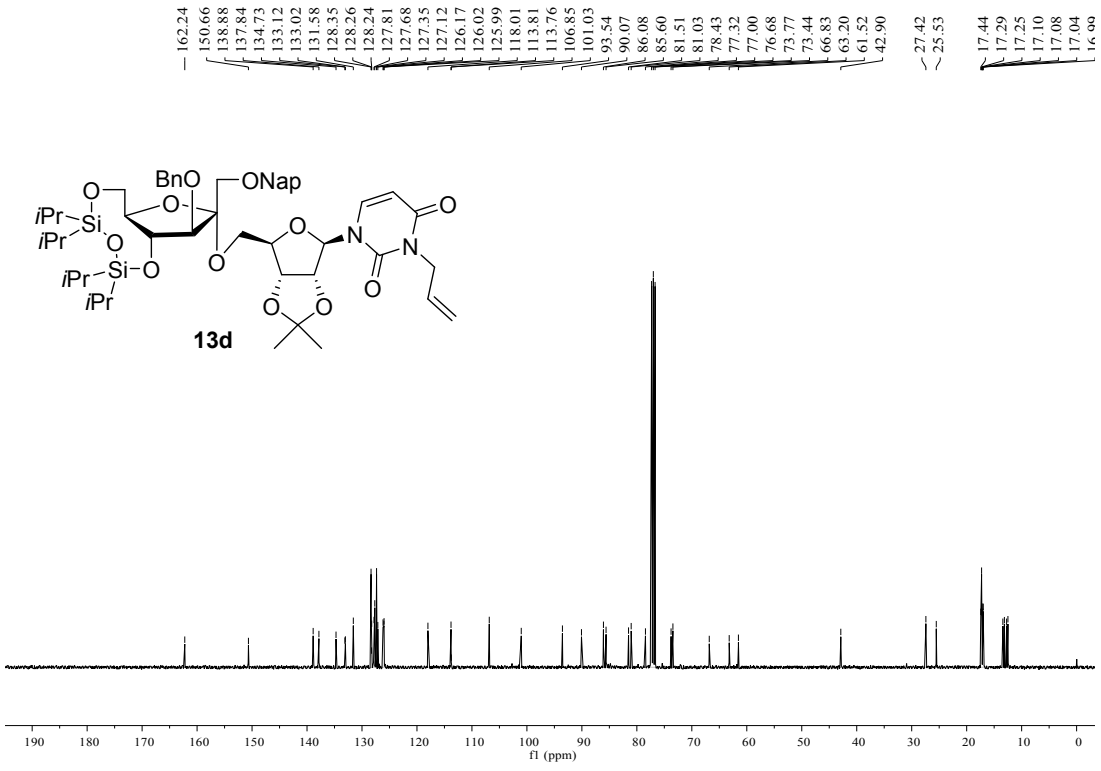

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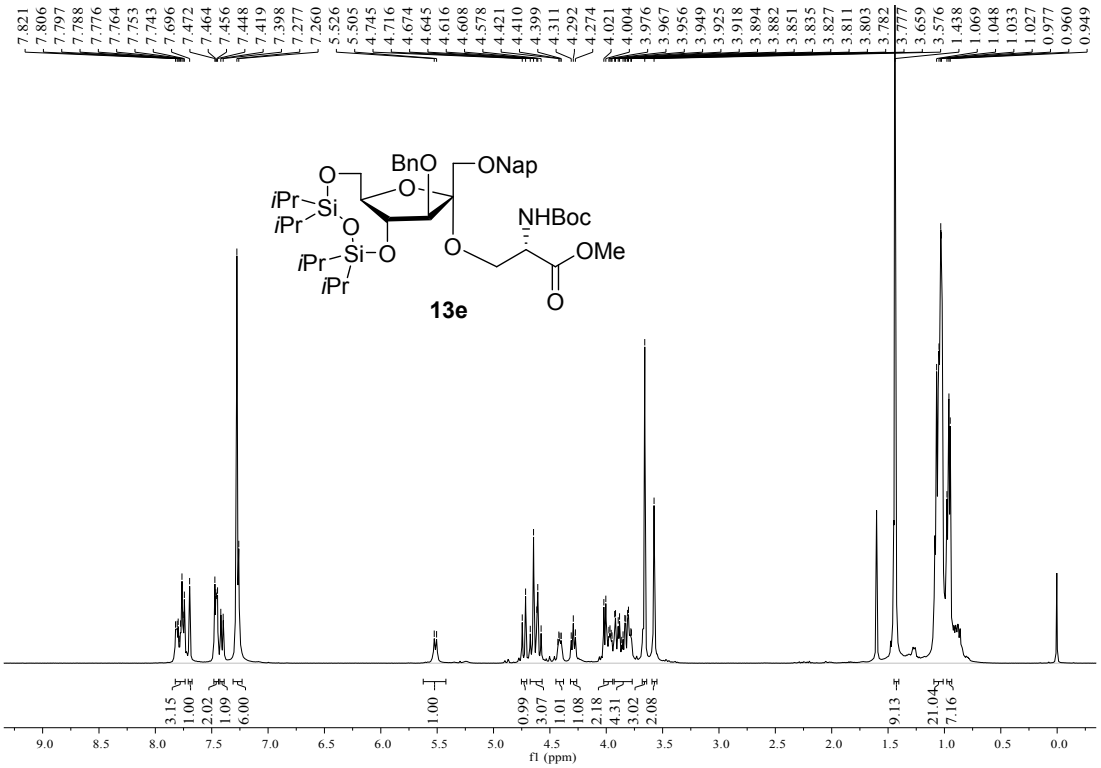

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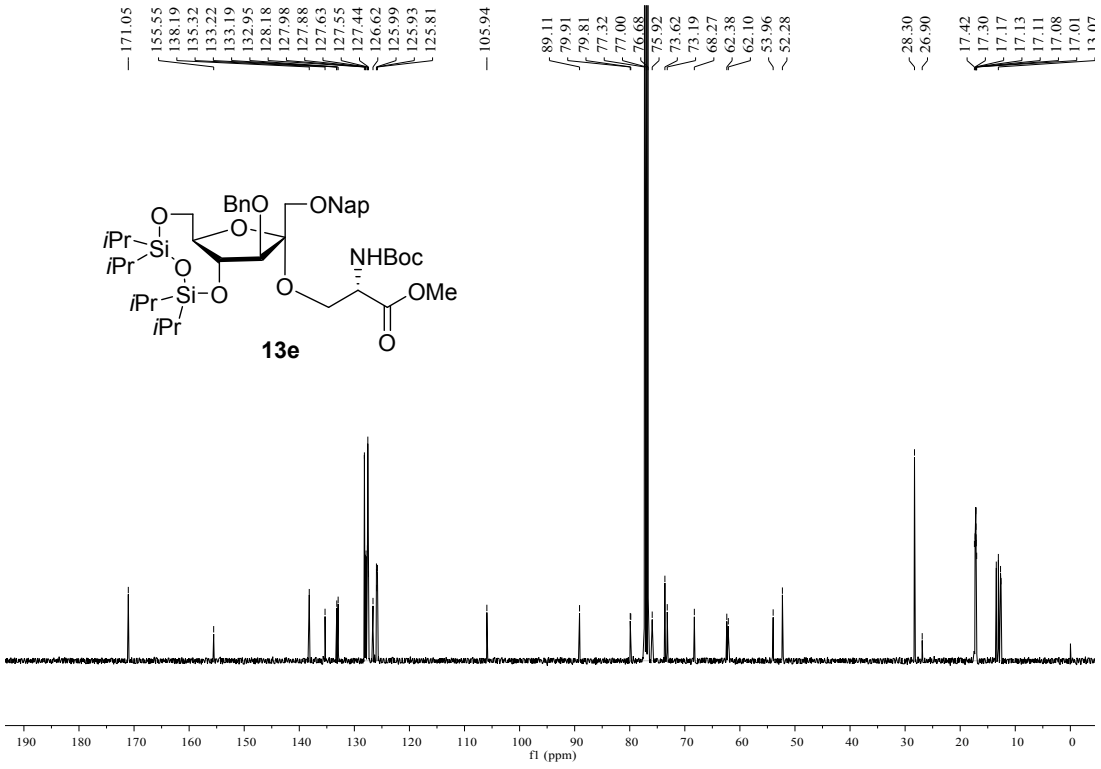
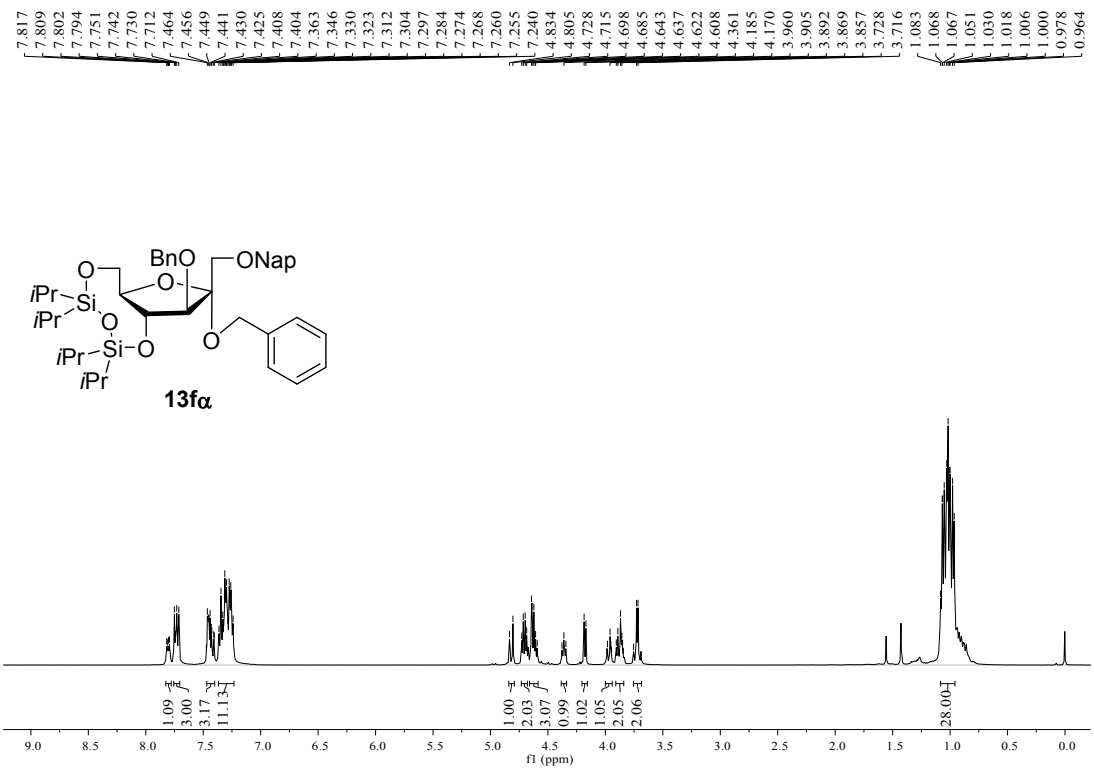
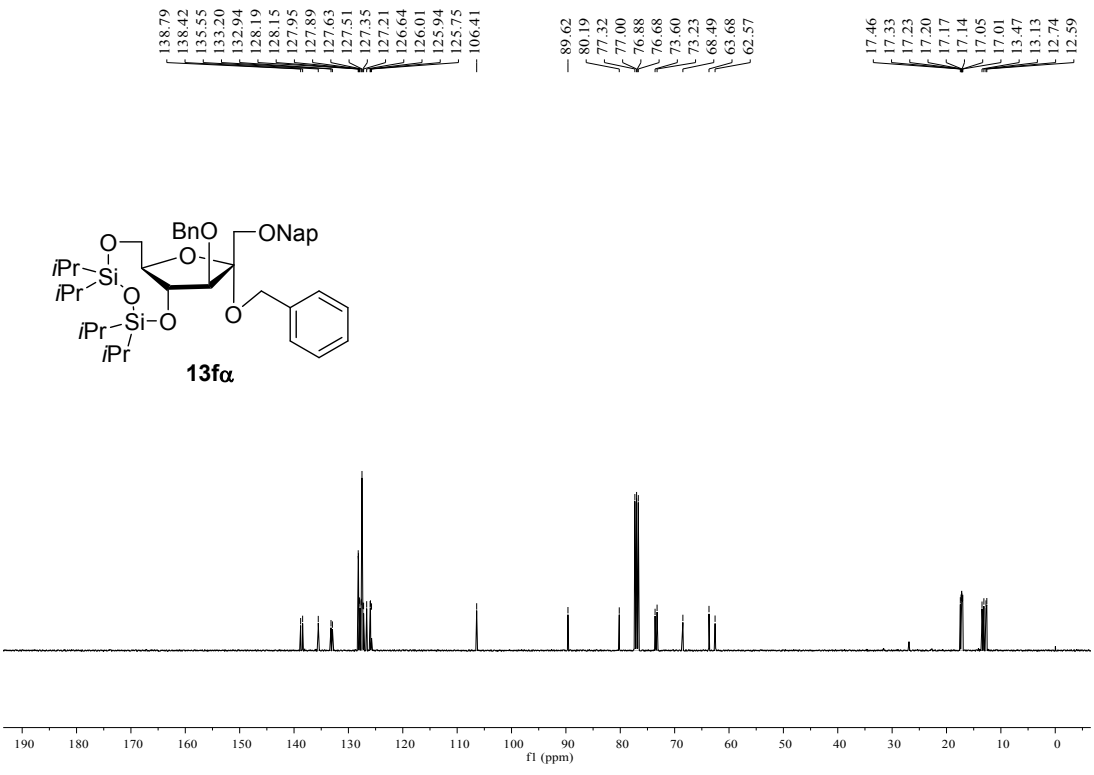


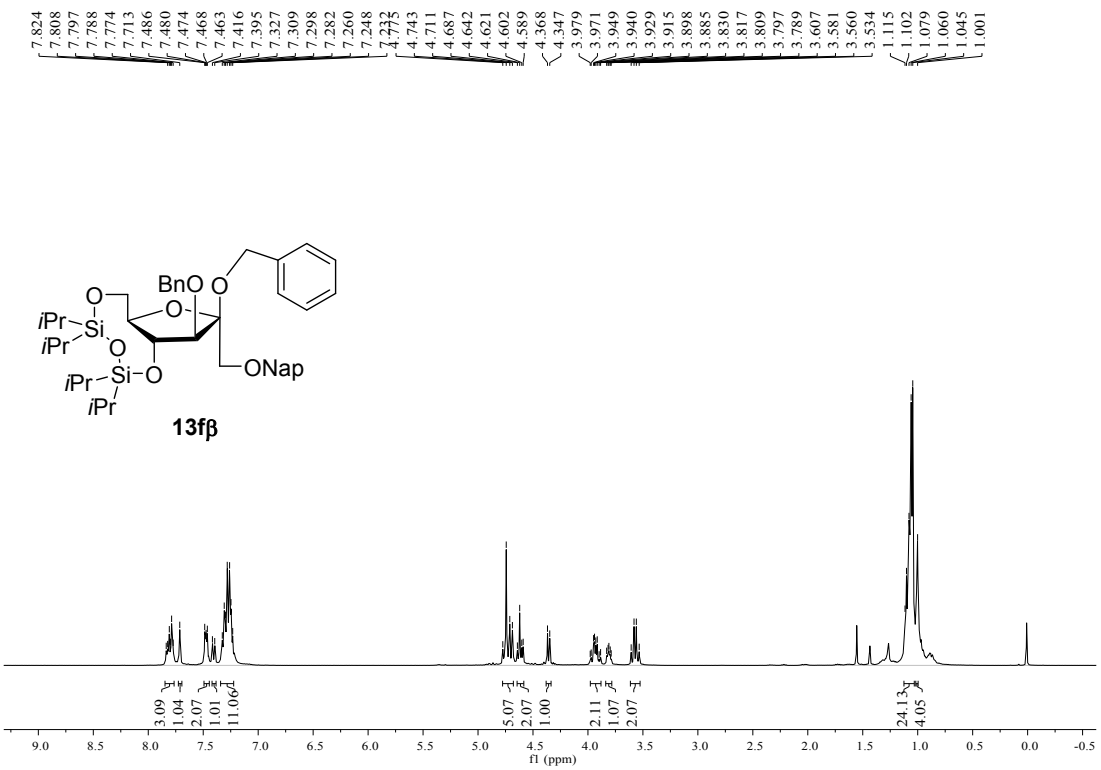
^{13}C NMR spectrum of compound **13e**



^{1}H NMR spectrum of compound **13fα**



^{13}C NMR spectrum of compound **13fα**



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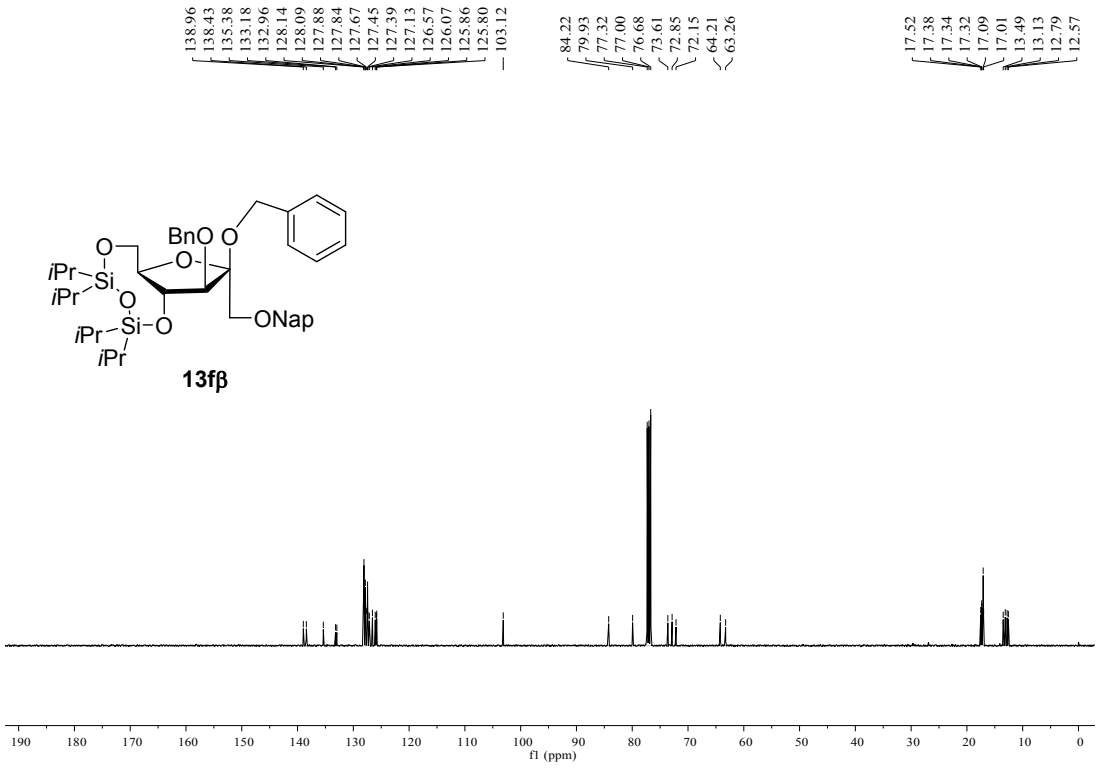

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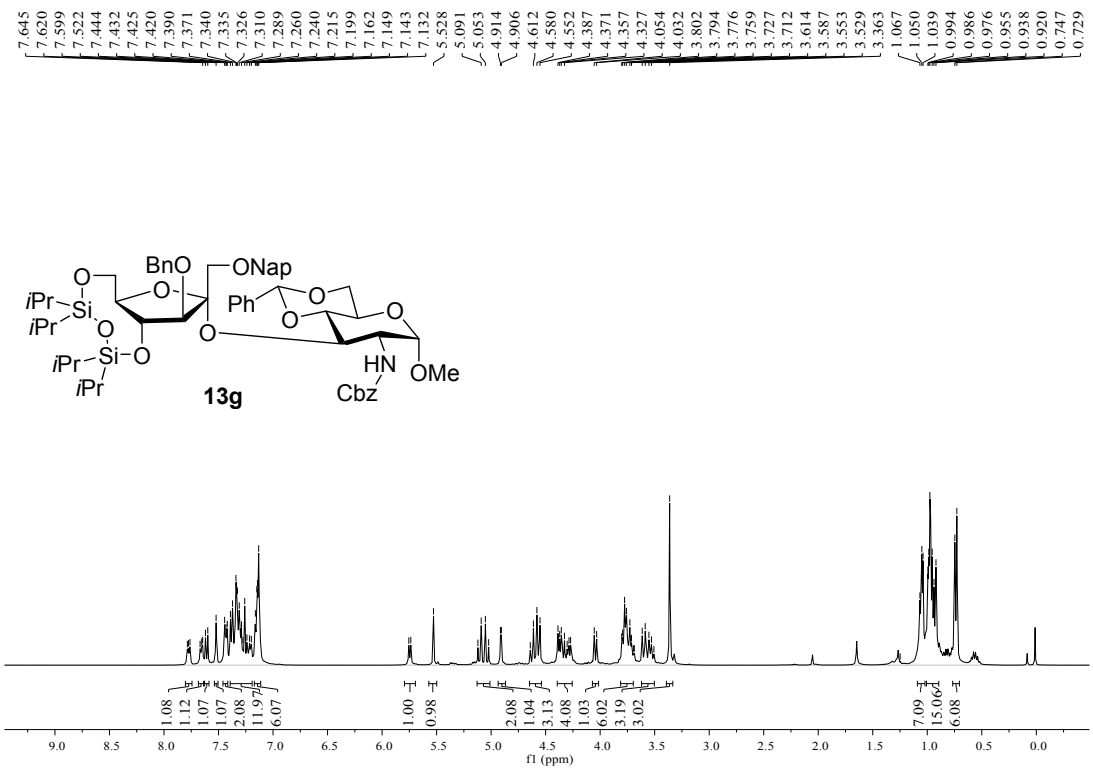

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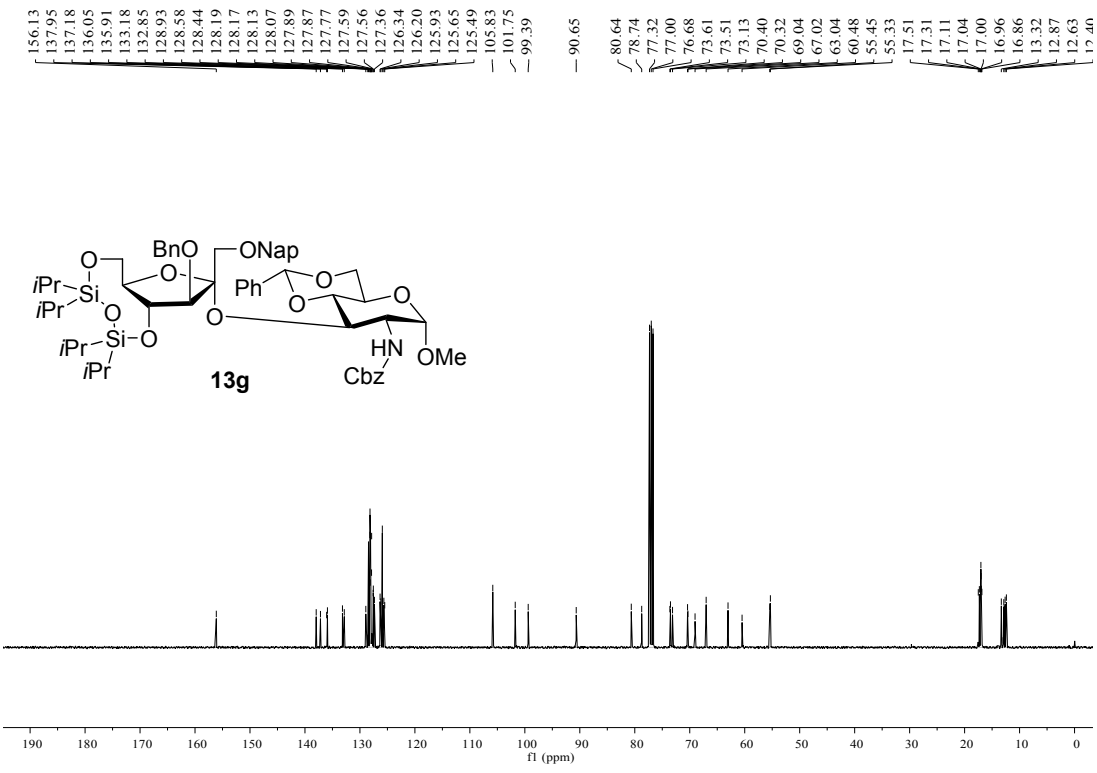
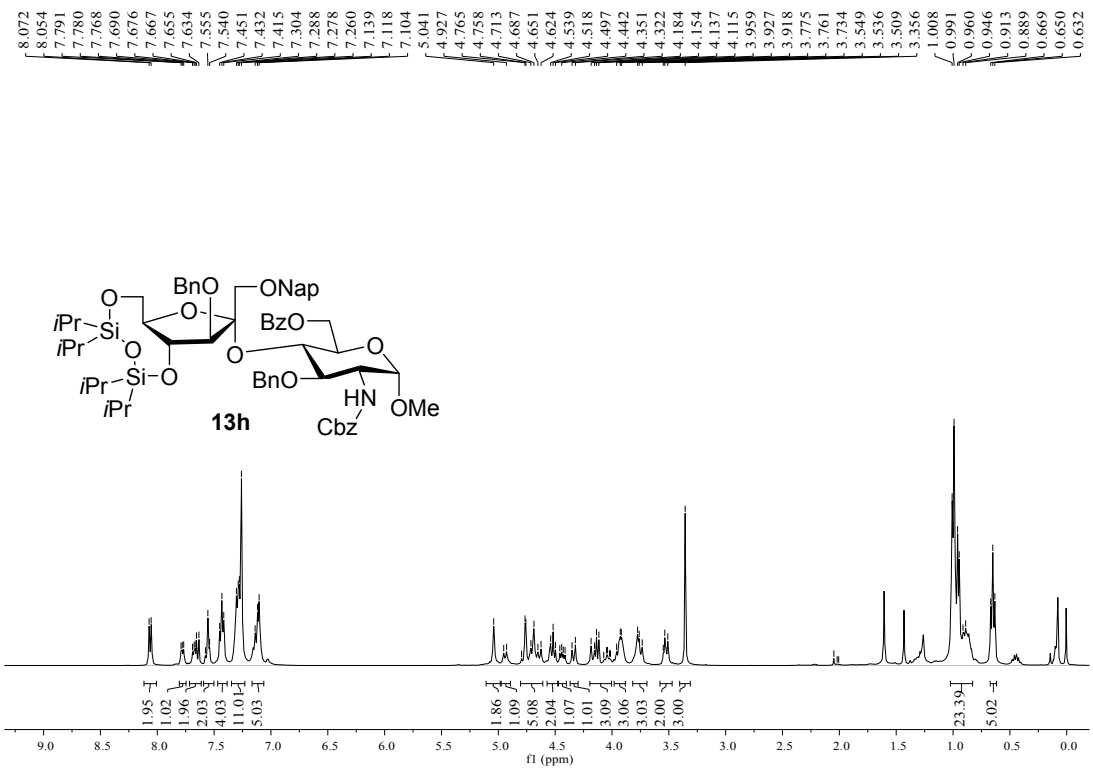
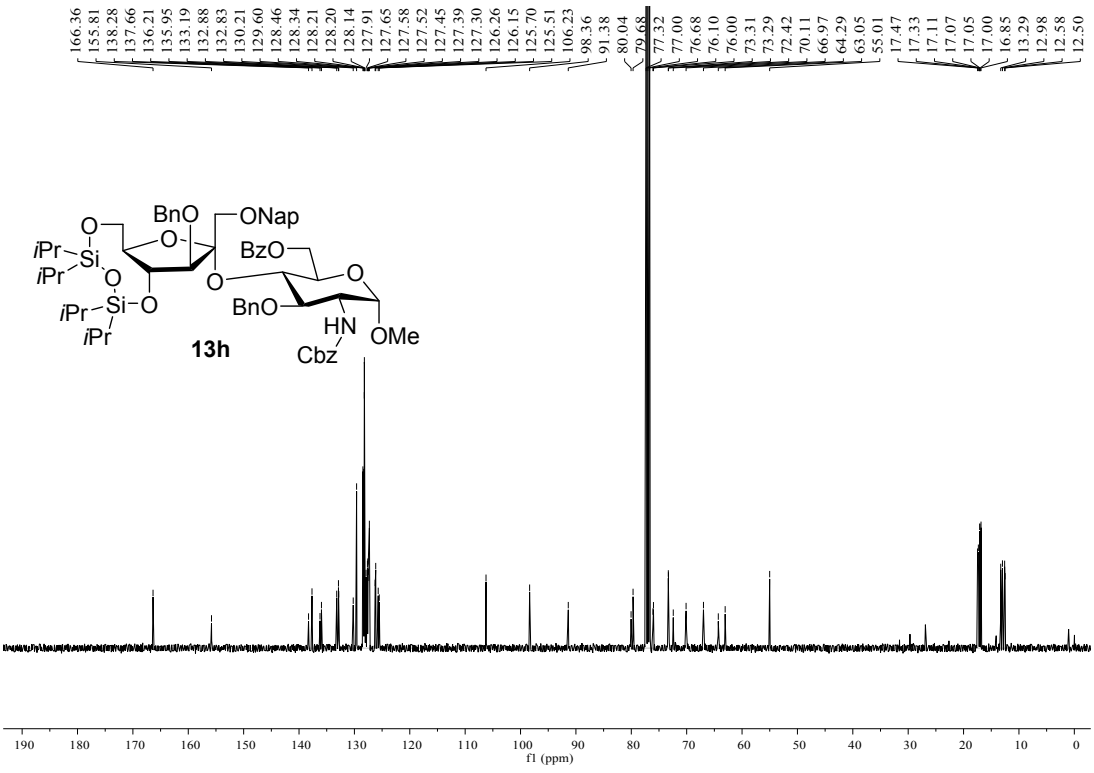


^{13}C NMR spectrum of compound **13g**



^{1}H NMR spectrum of compound **13h**



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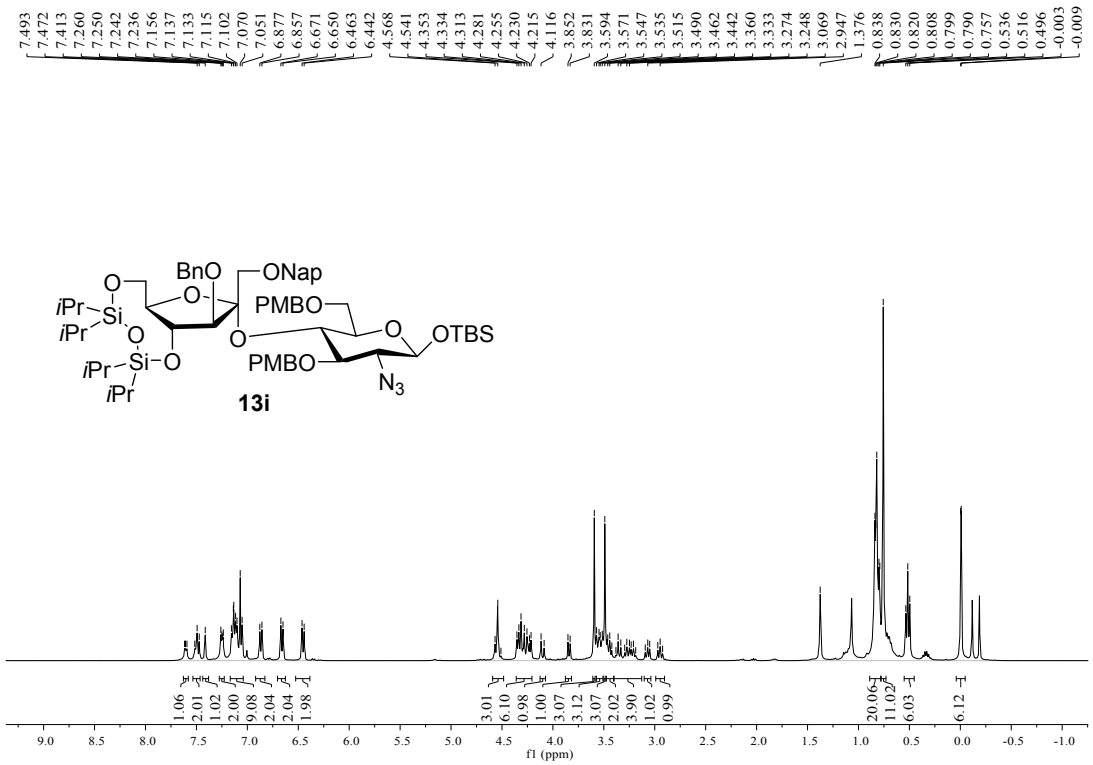
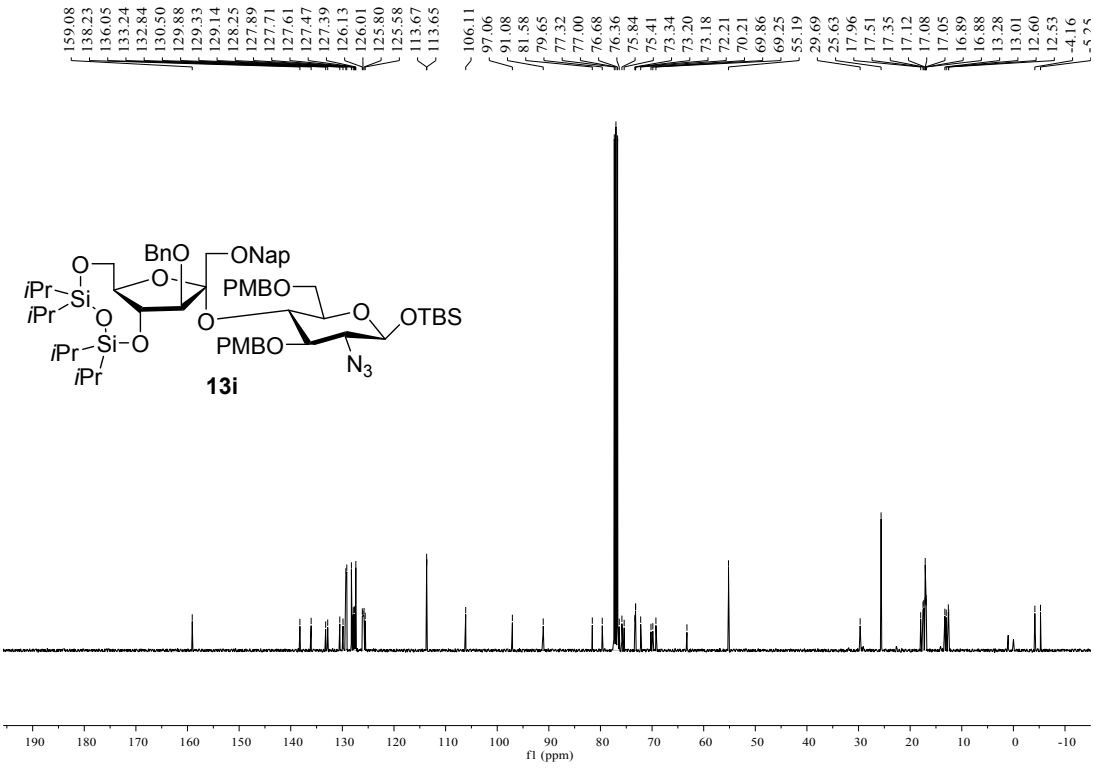
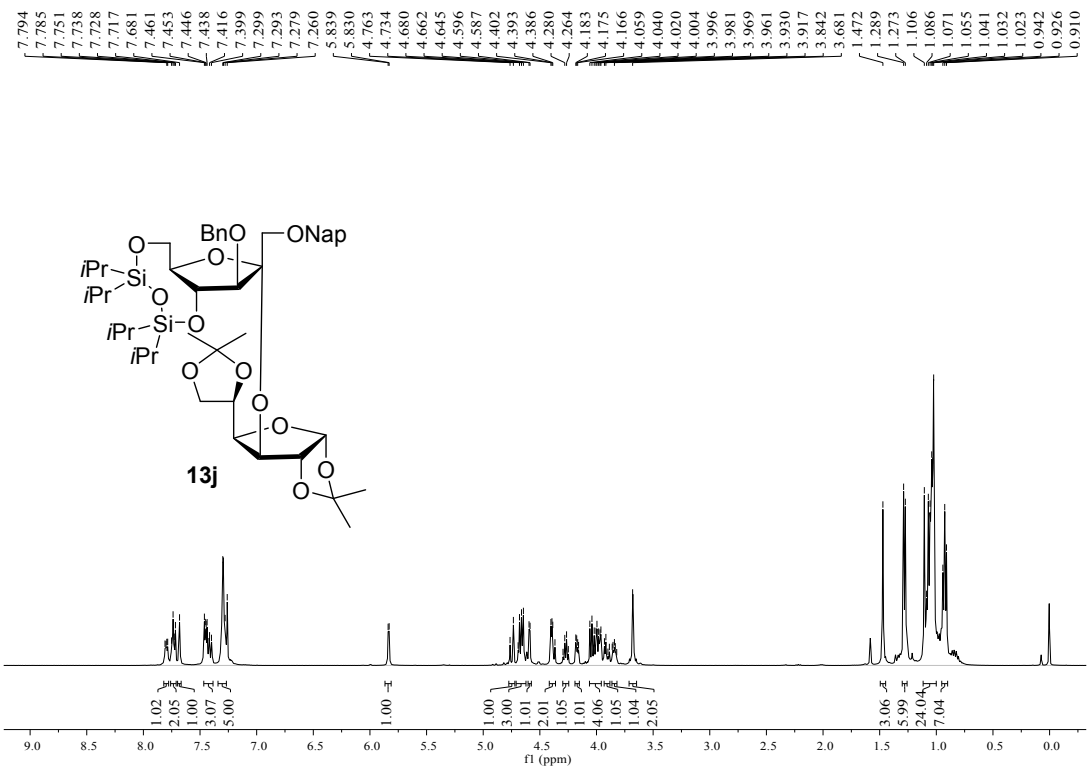


^{1}H NMR spectrum of compound **13i**



^{13}C NMR spectrum of compound **13i**



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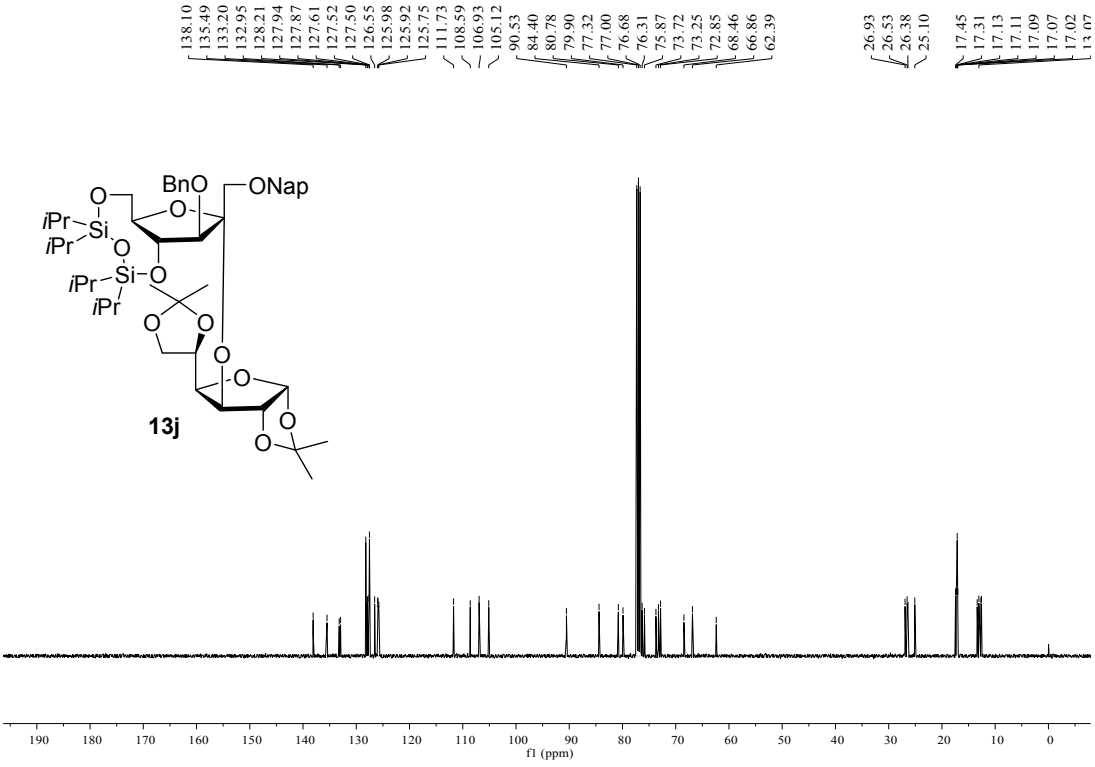

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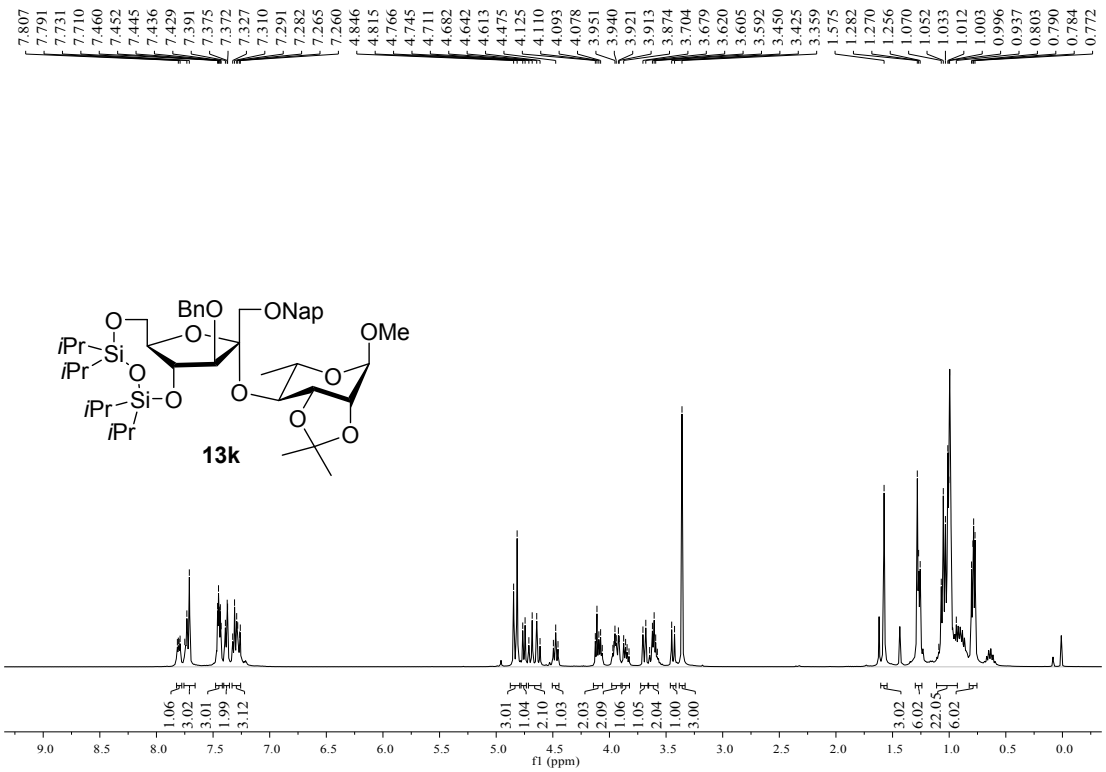

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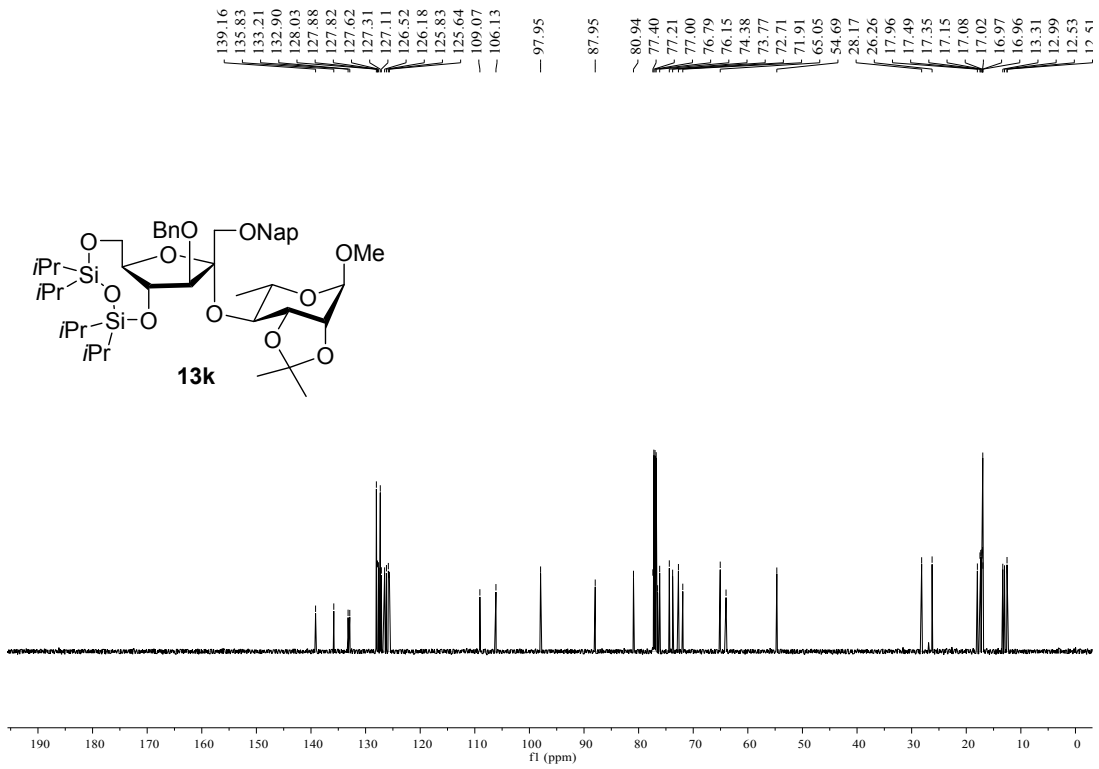

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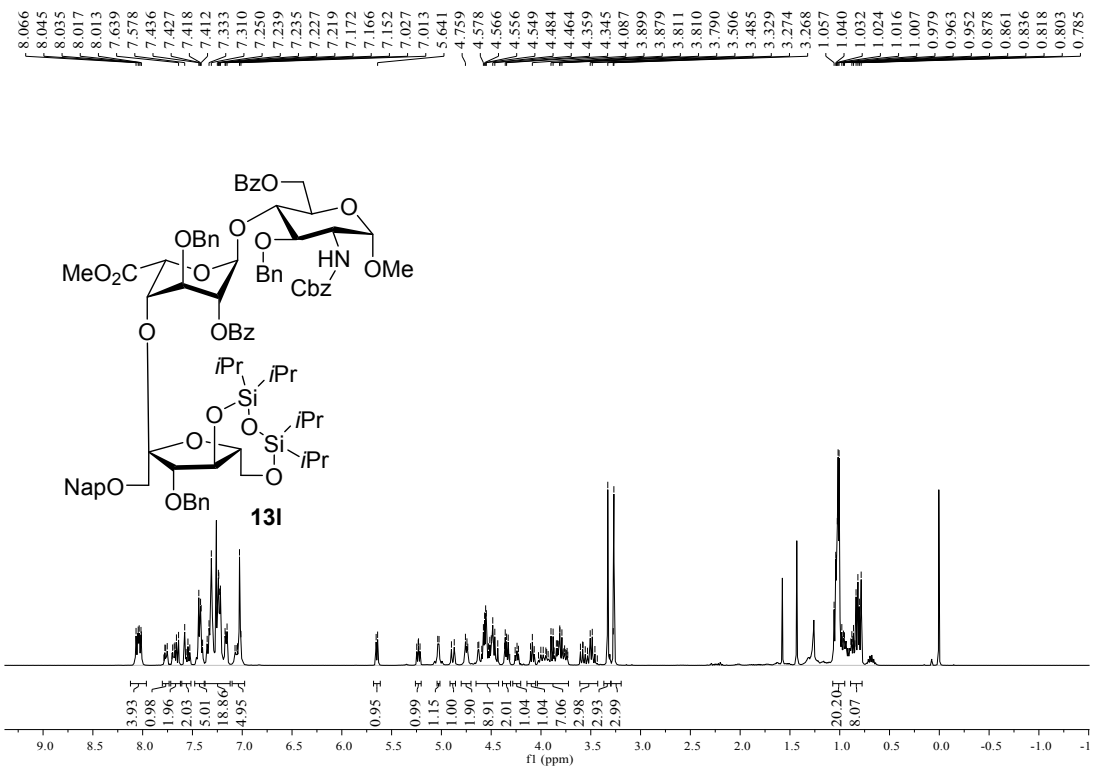

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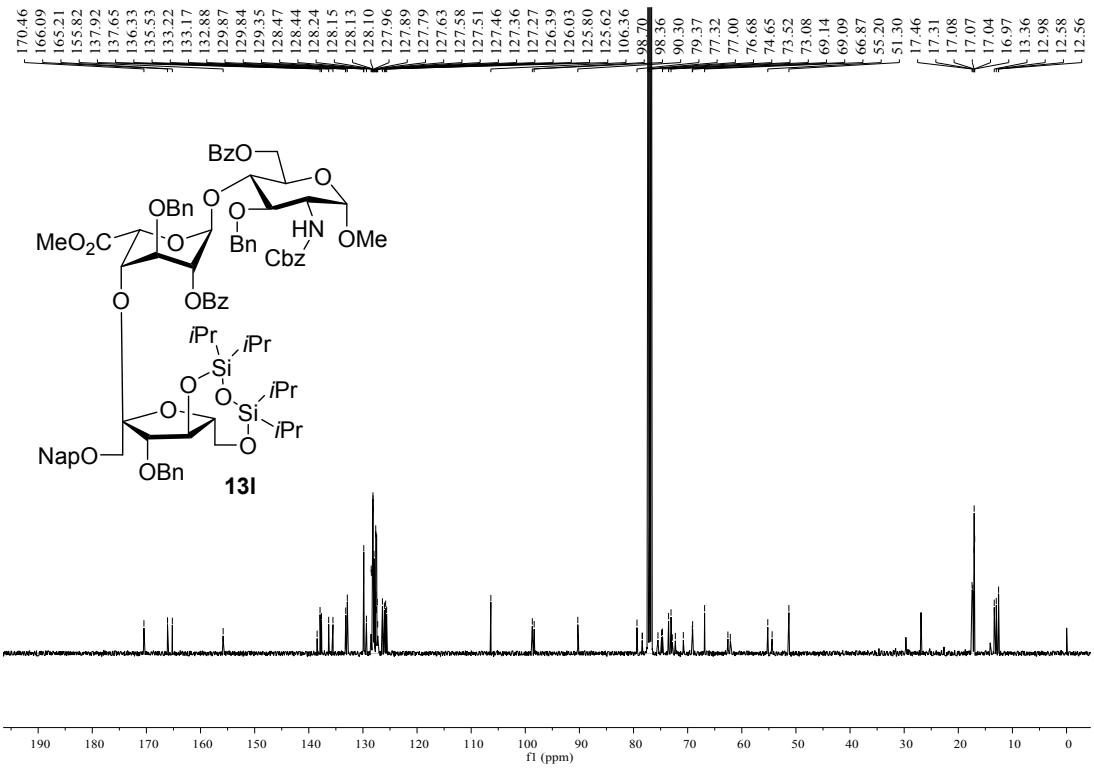

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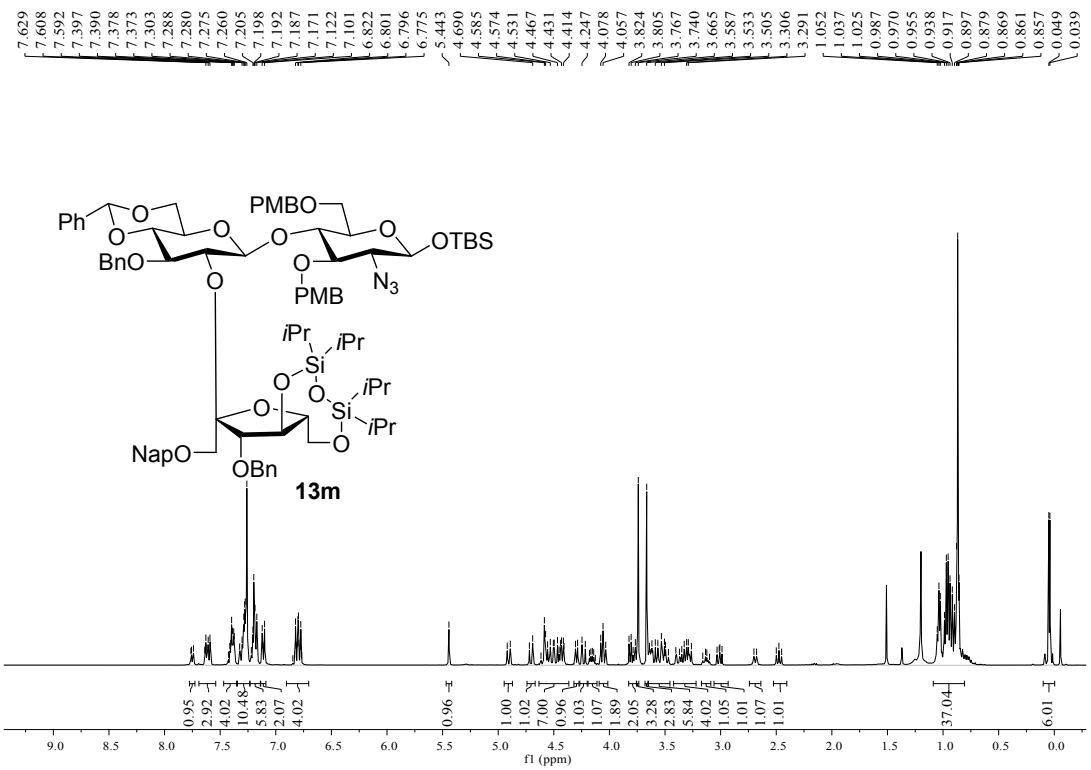

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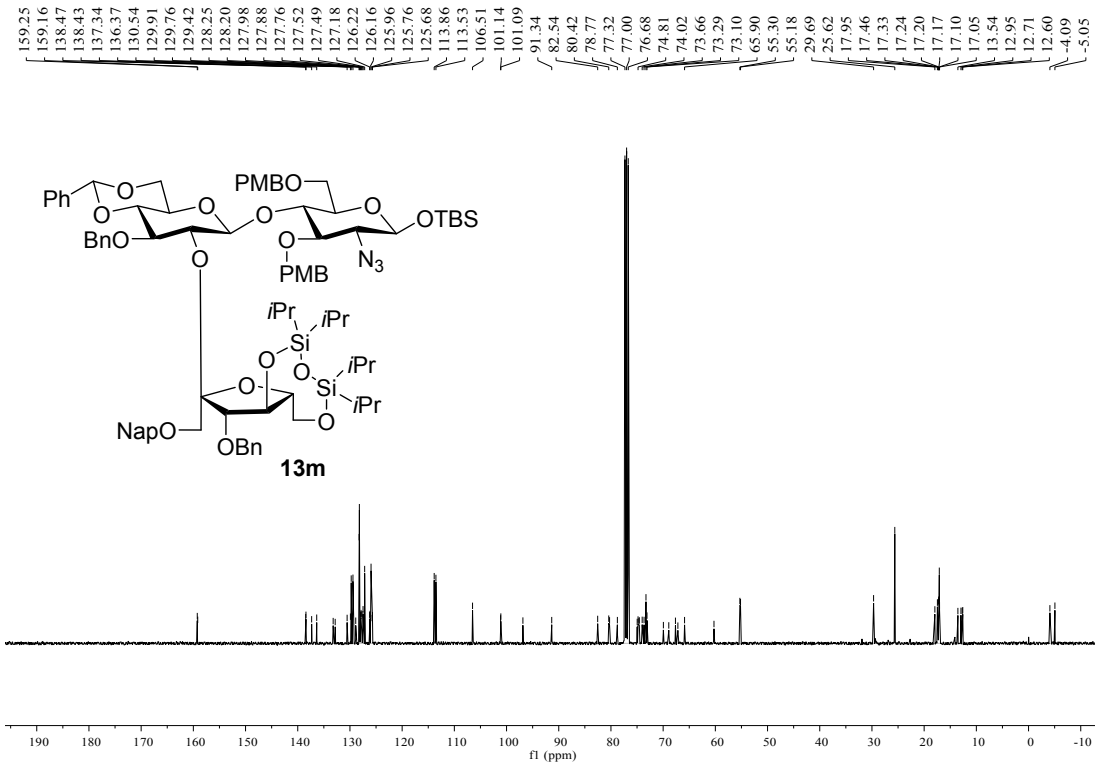

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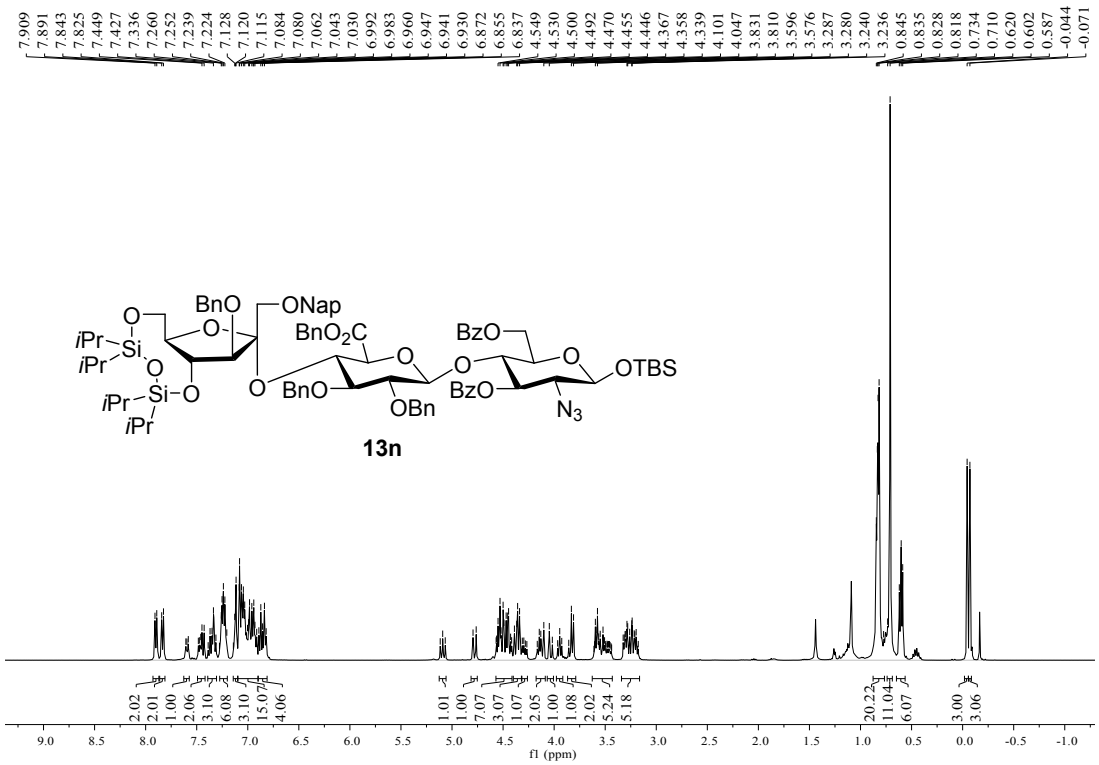

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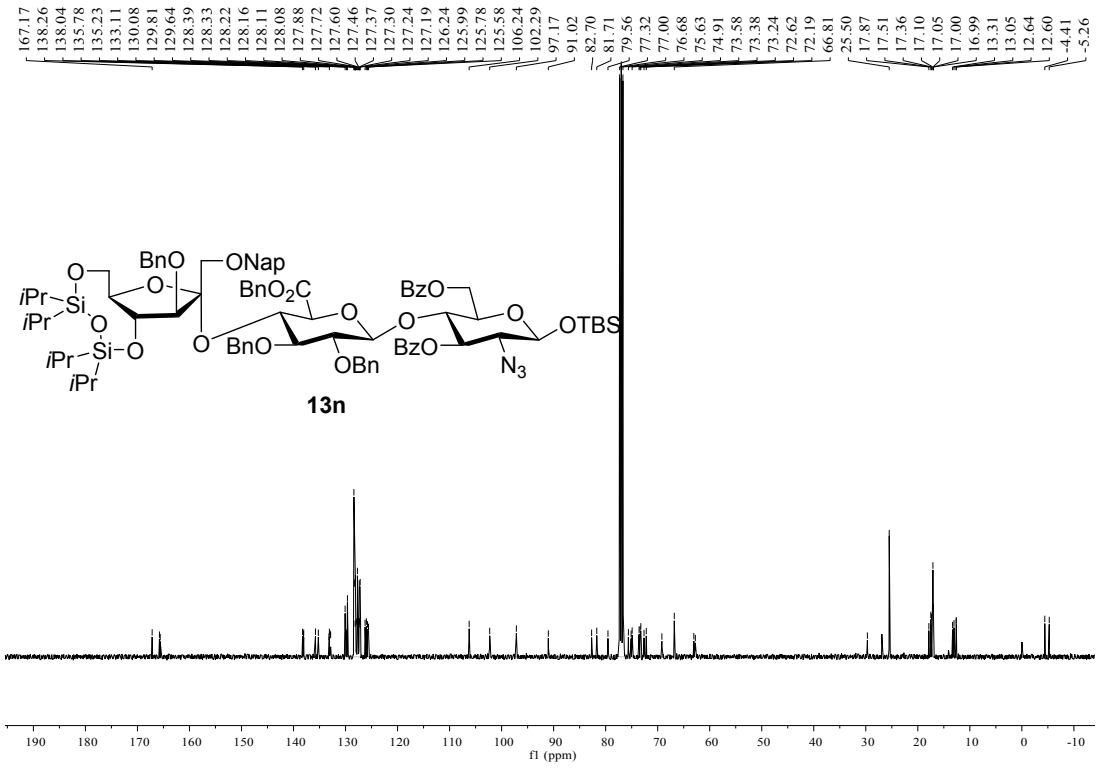

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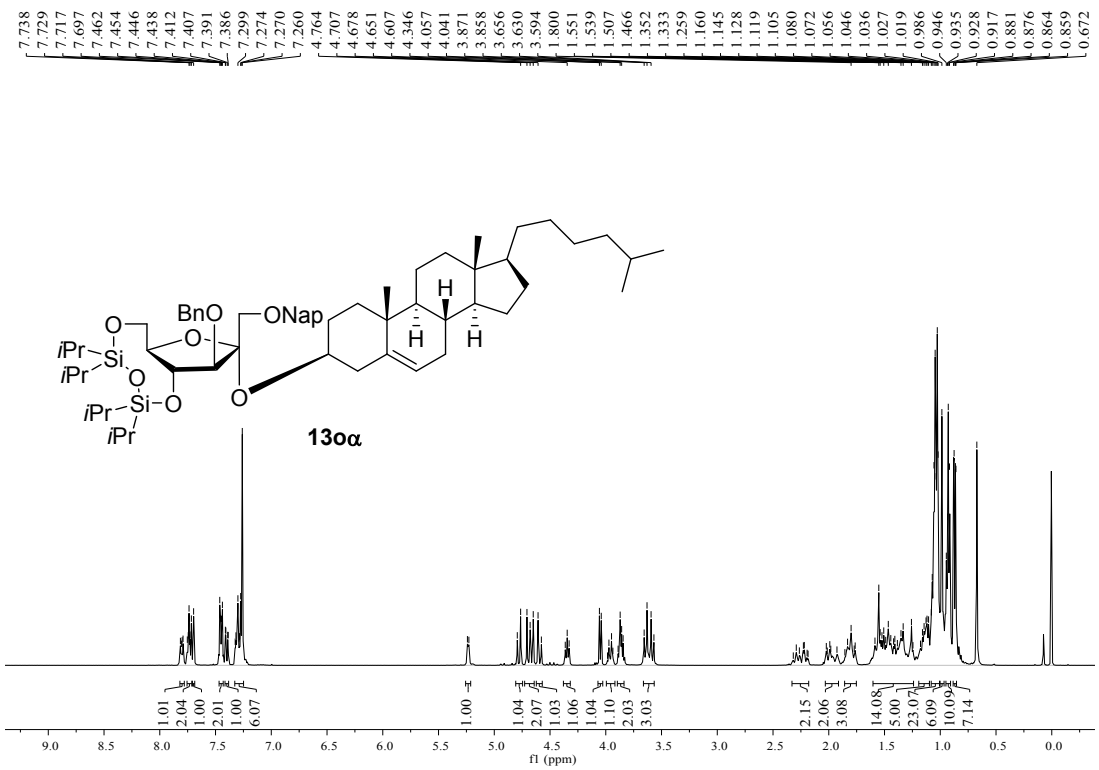
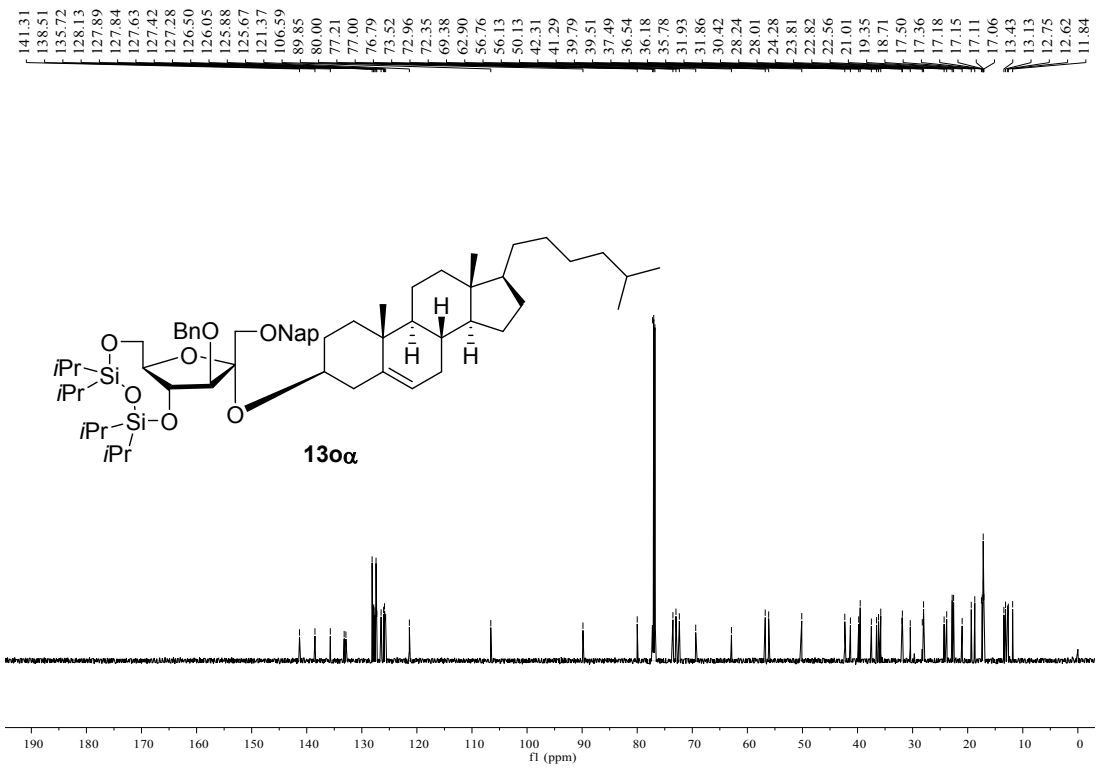
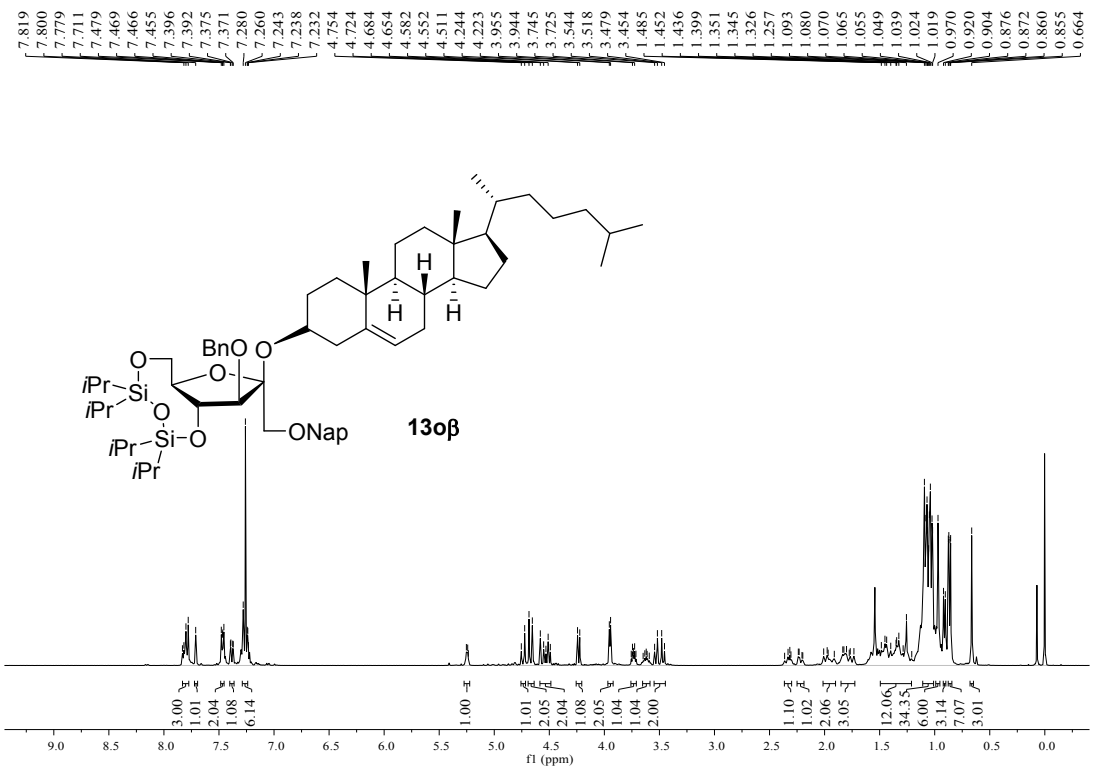


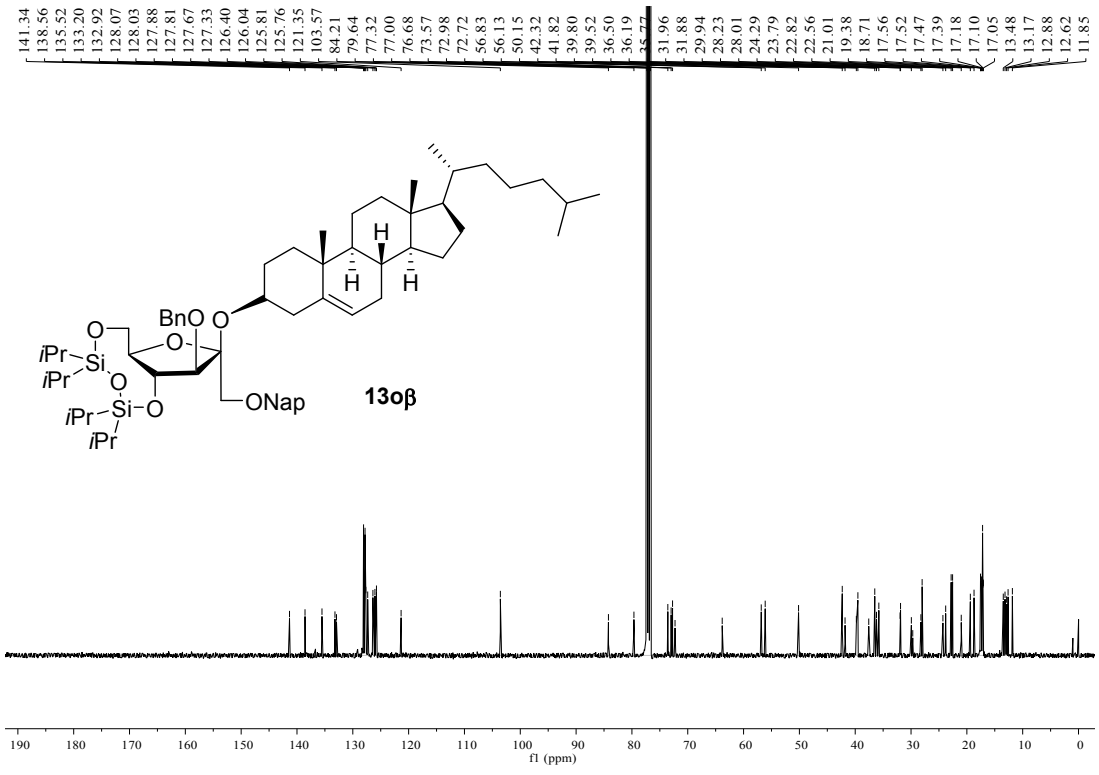
^{1}H NMR spectrum of compound **13oα**



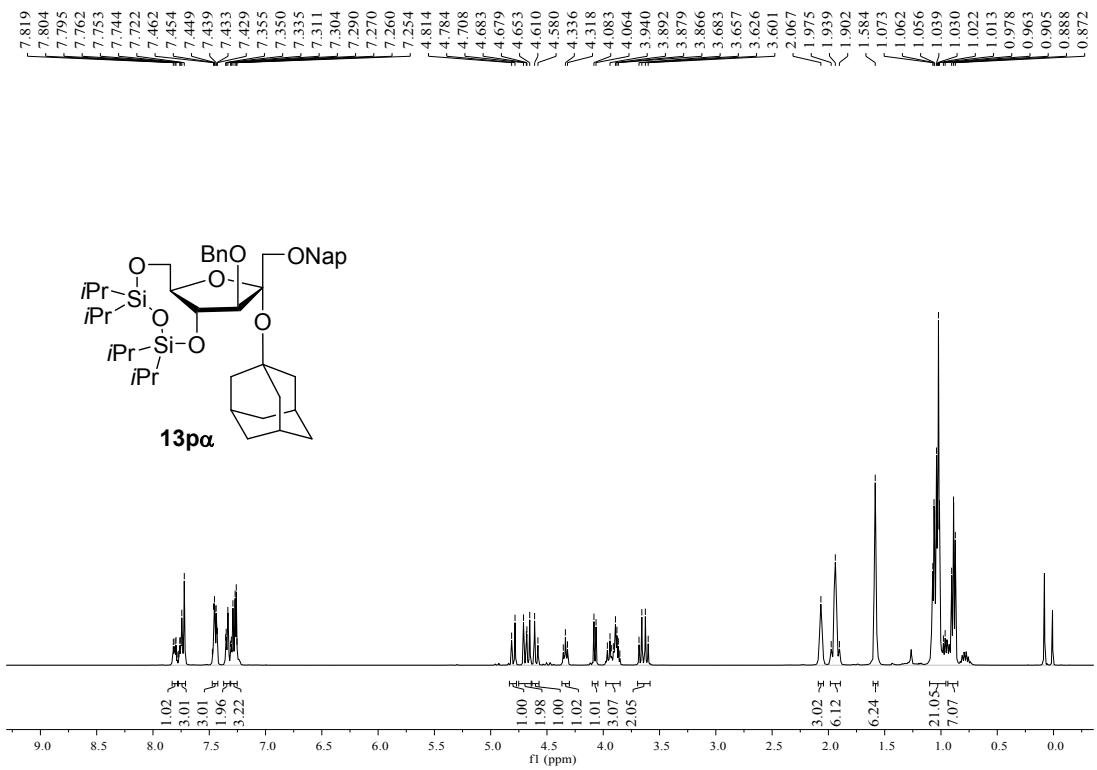
^{13}C NMR spectrum of compound **13oα**



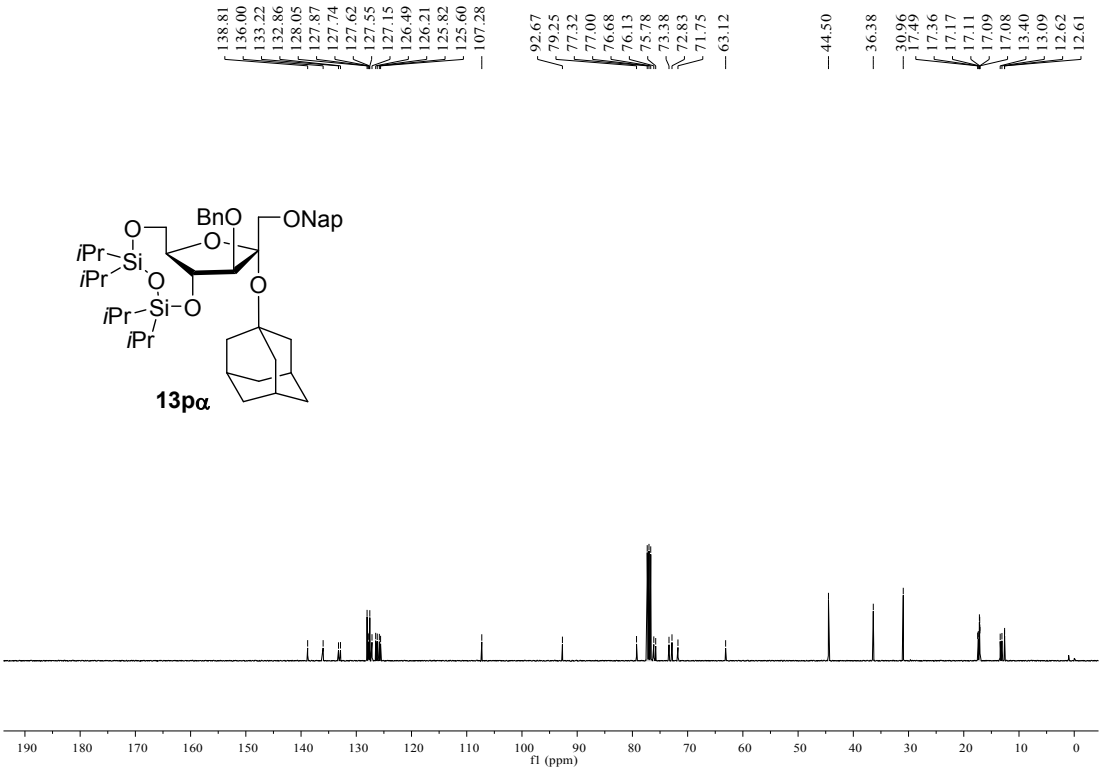
^{1}H NMR spectrum of compound **13oβ**



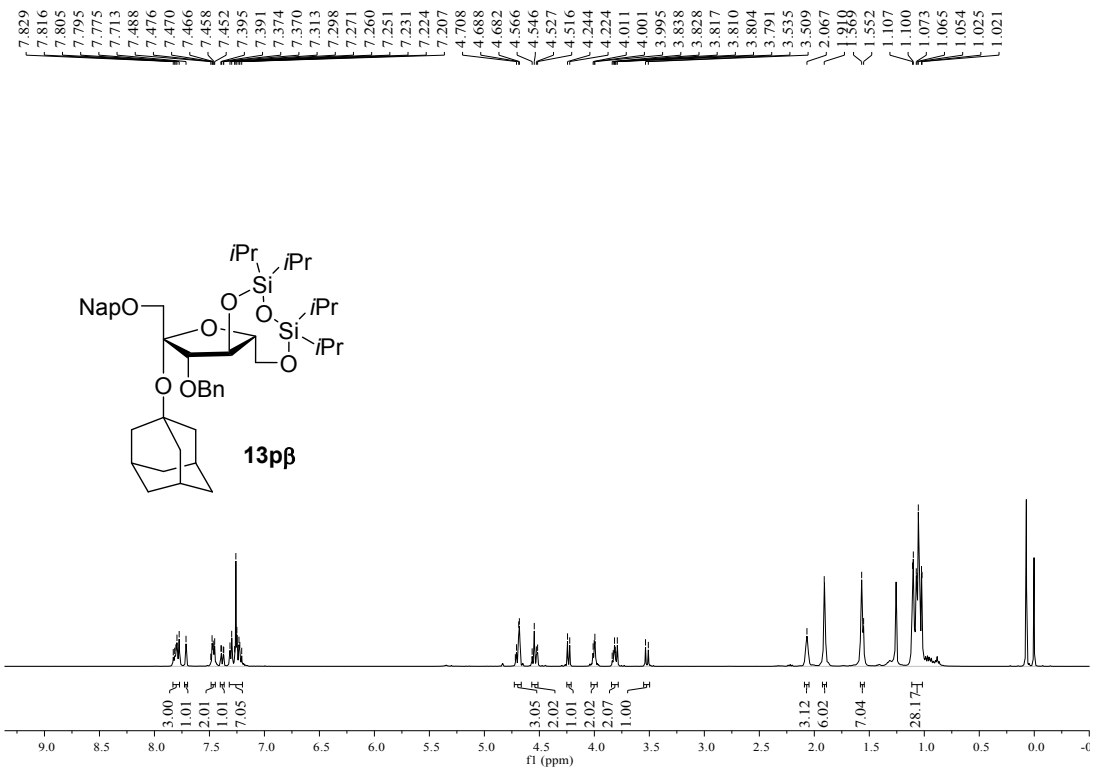
^{13}C NMR spectrum of compound **13oβ**



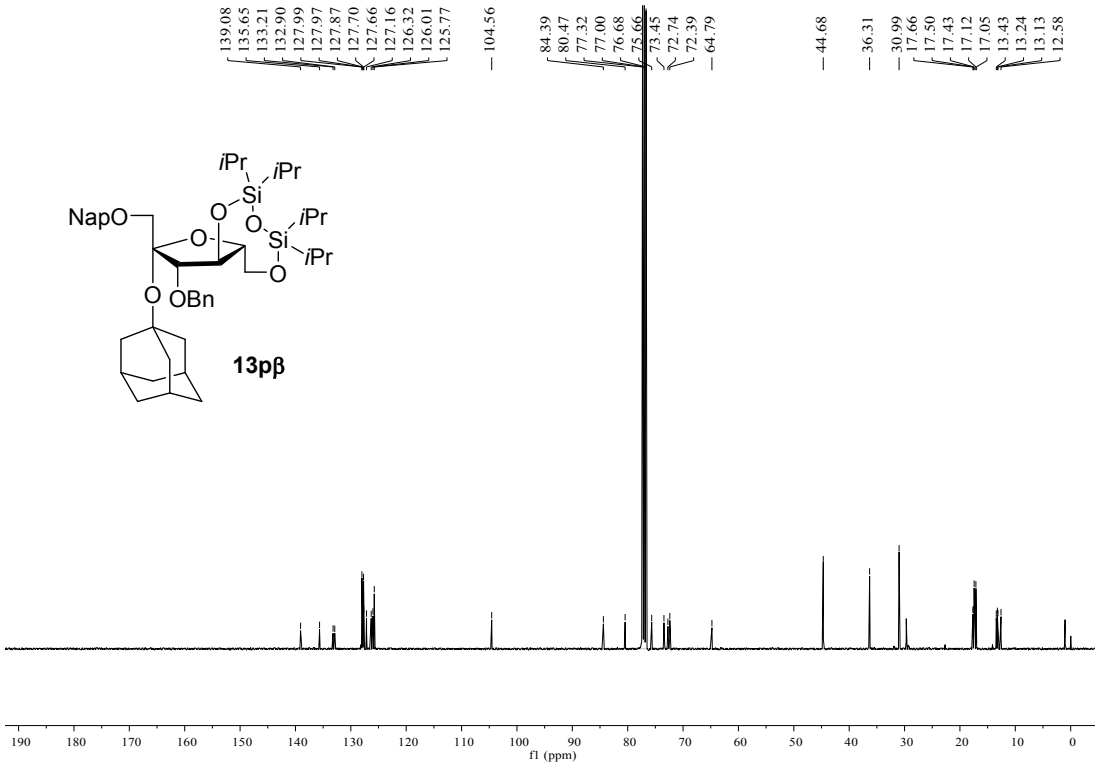
^{1}H NMR spectrum of compound **13pα**



^{13}C NMR spectrum of compound **13pα**



^{1}H NMR spectrum of compound **13pβ**



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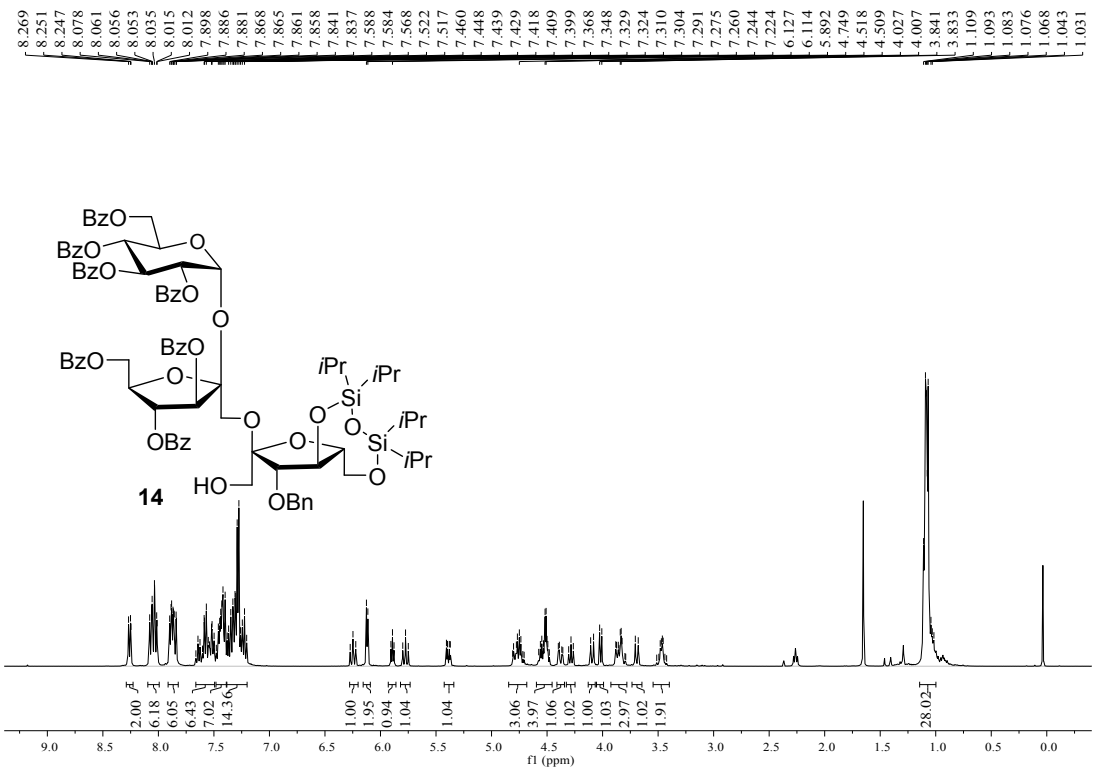
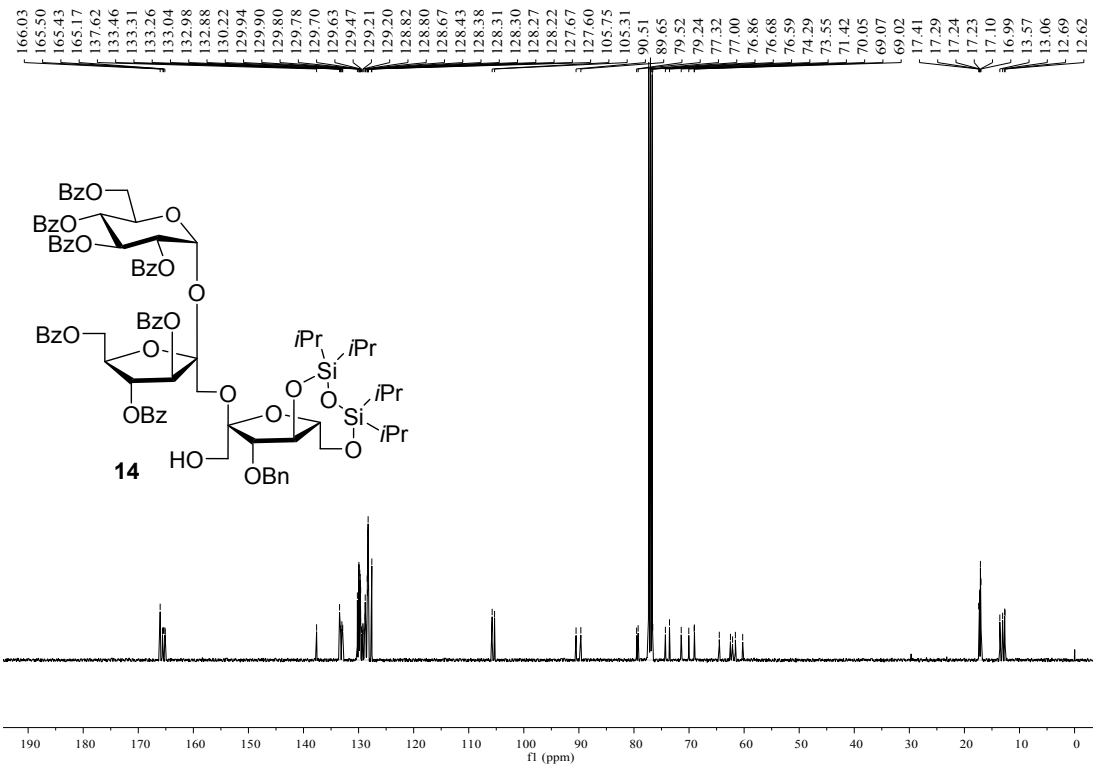
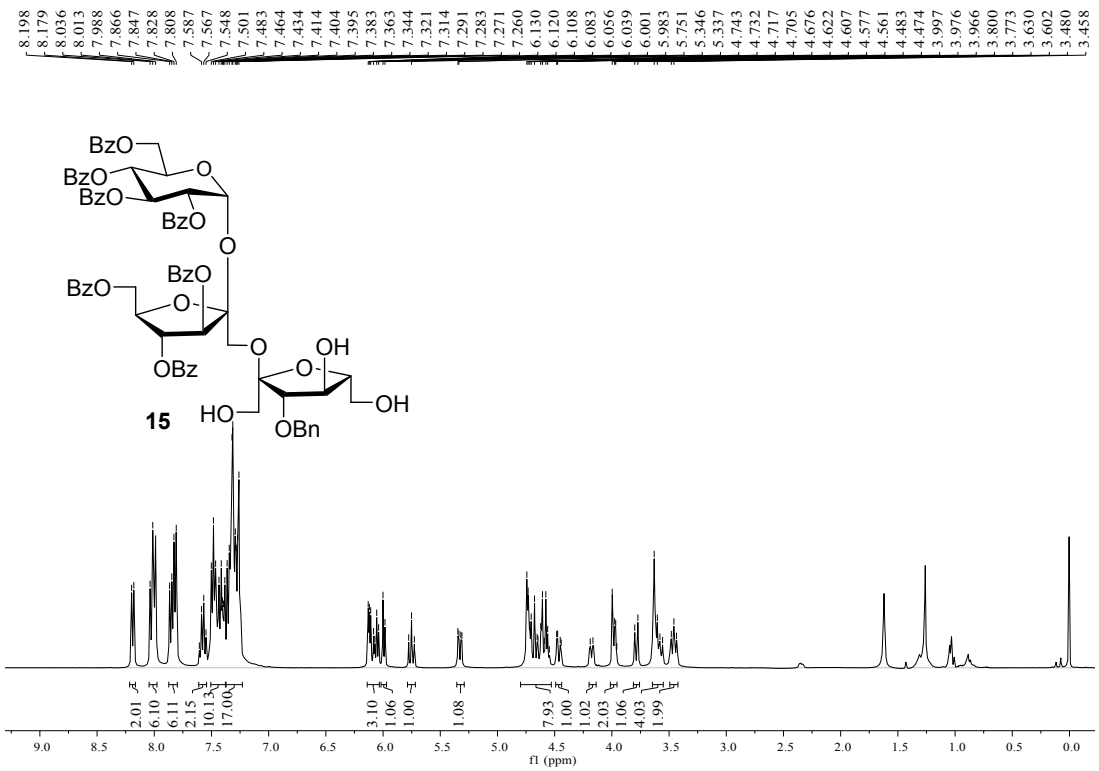


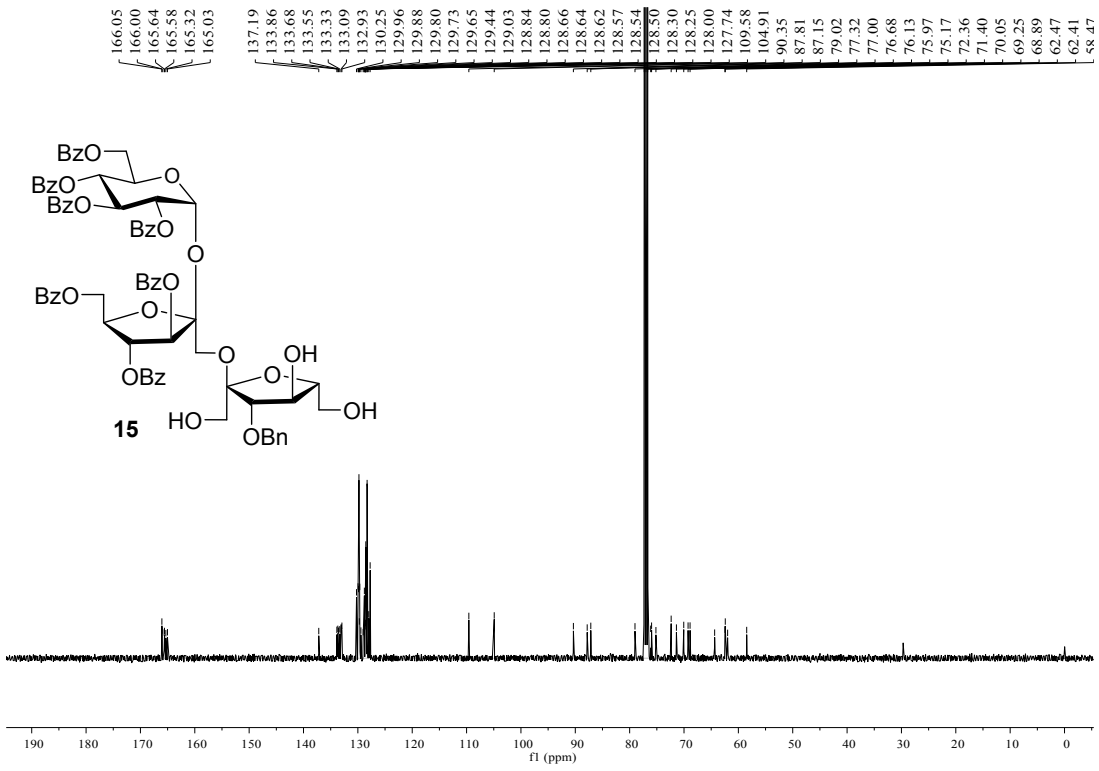
^{1}H NMR spectrum of compound **14**



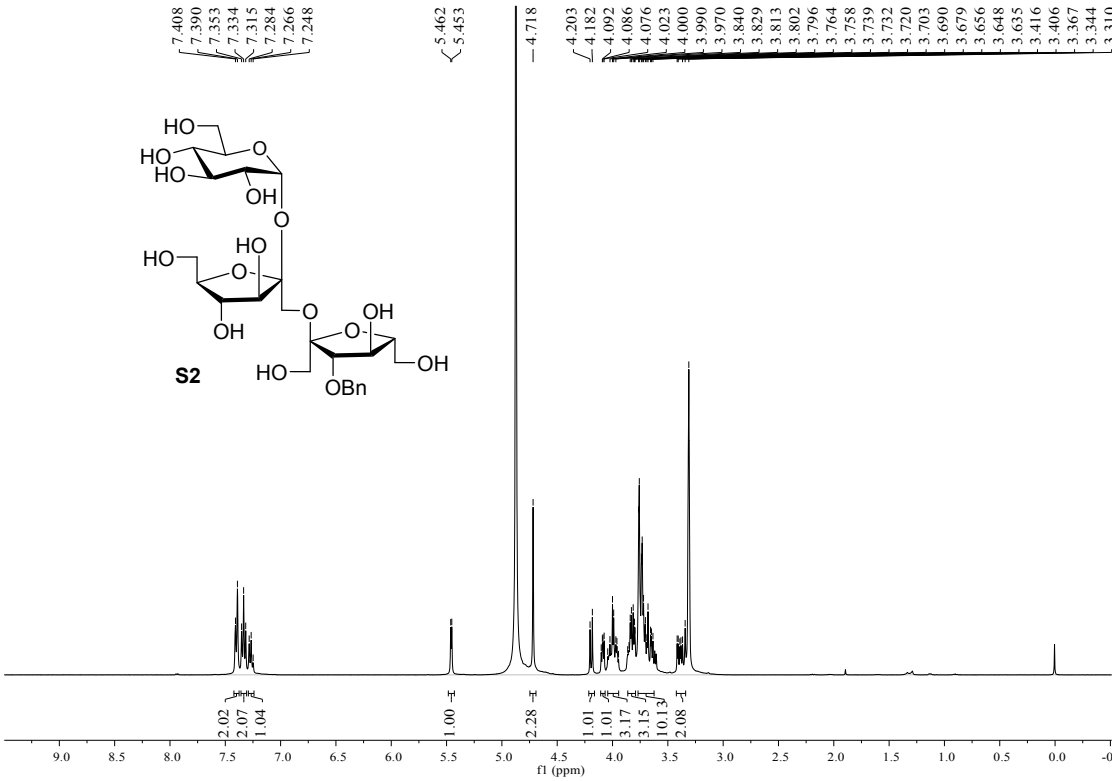
^{13}C NMR spectrum of compound **14**



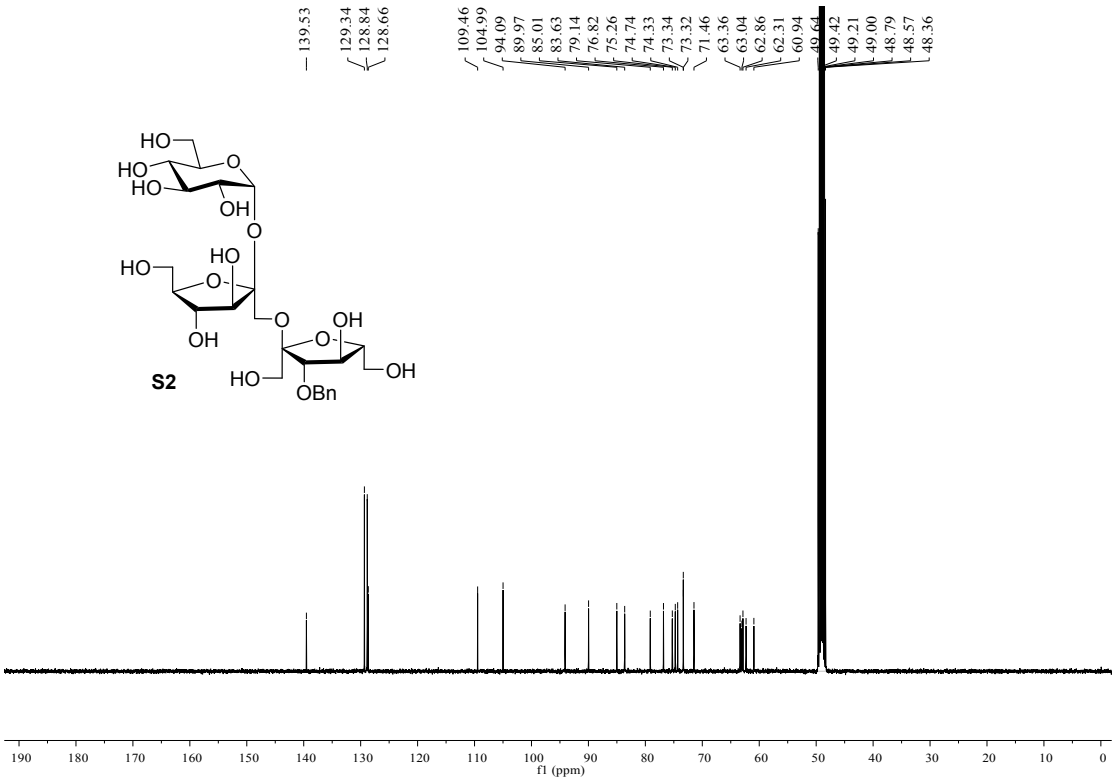
^{1}H NMR spectrum of compound **15**



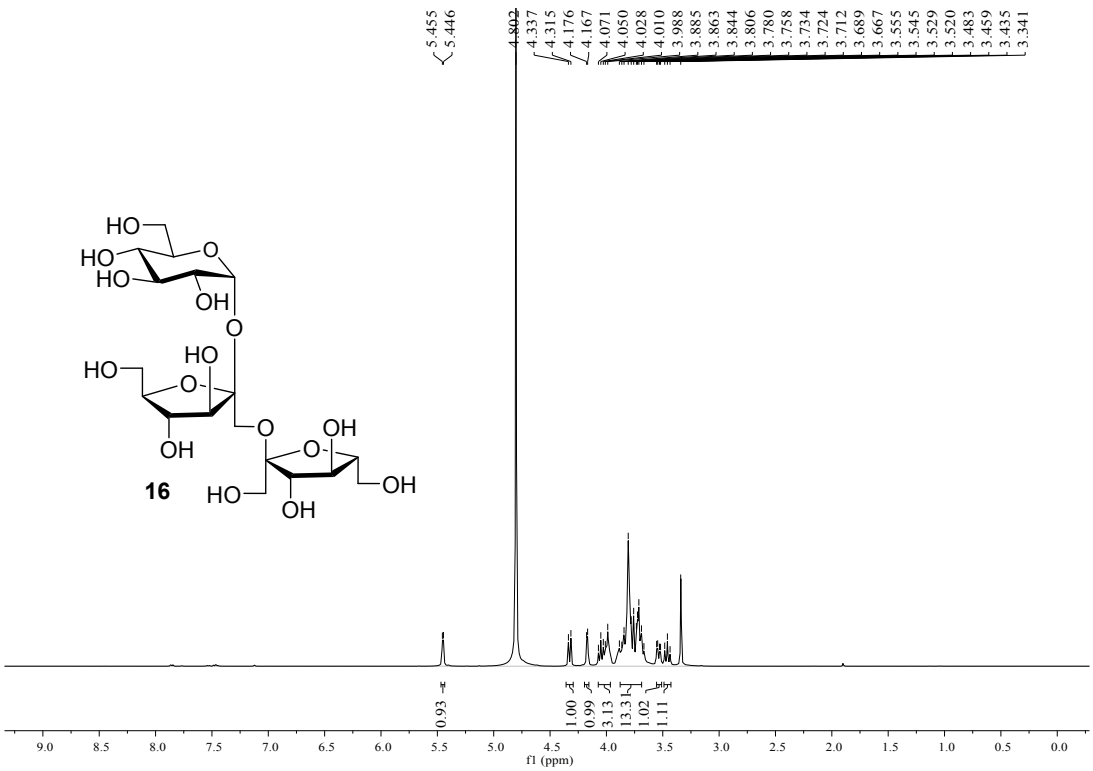
^{13}C NMR spectrum of compound **15**



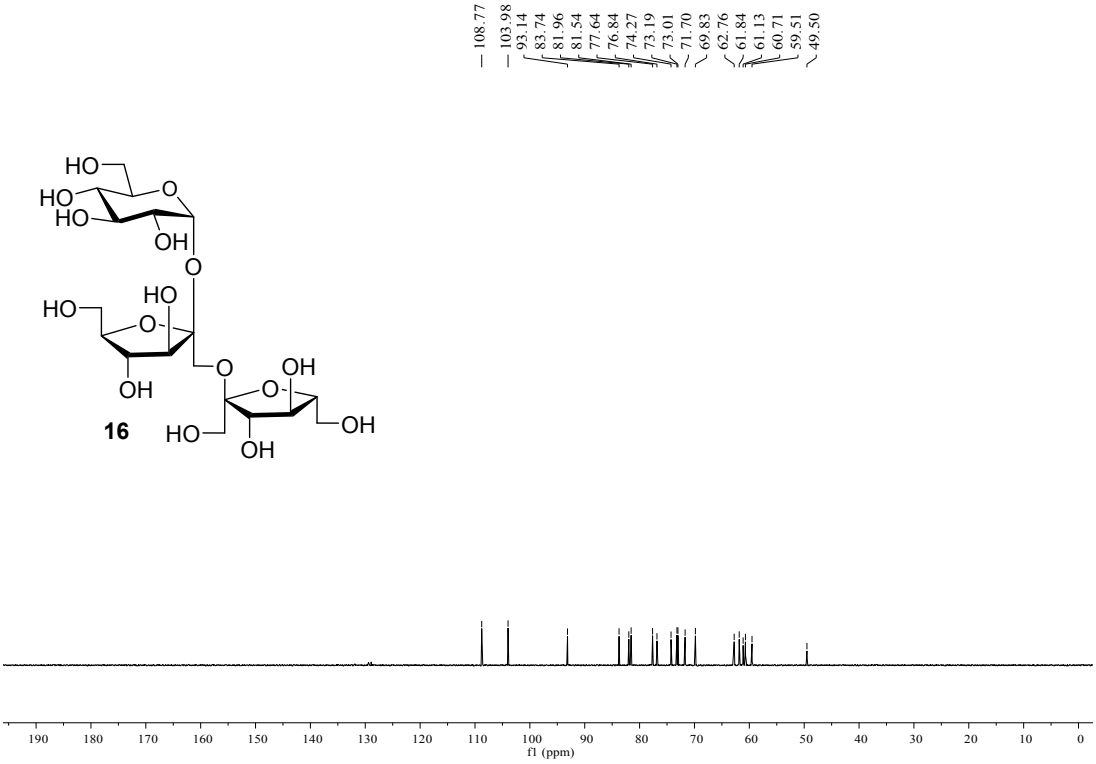
^{1}H NMR spectrum of compound **S2**



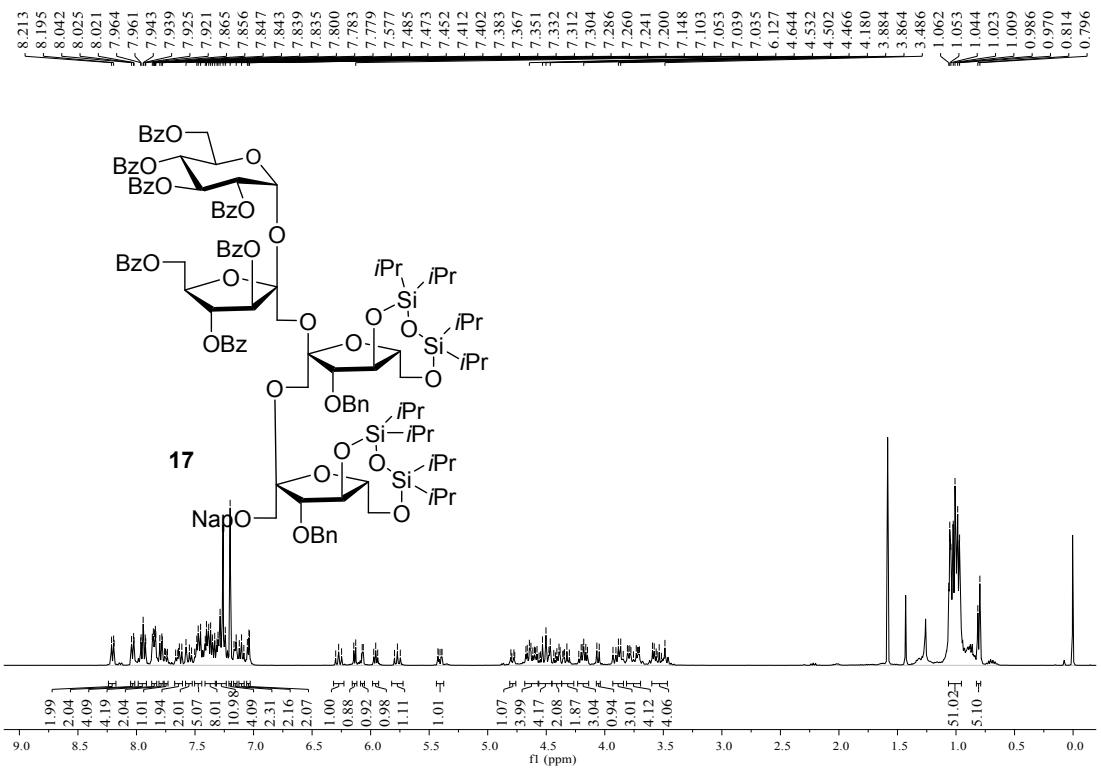
^{13}C NMR spectrum of compound **S2**



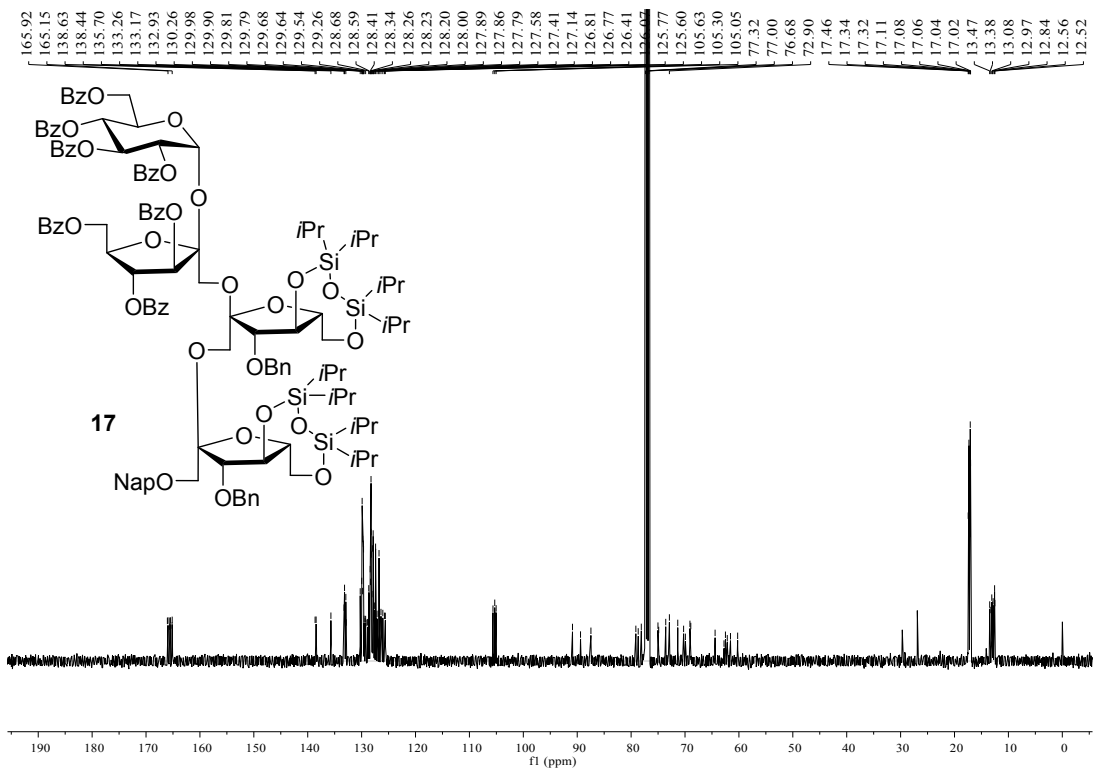
^{1}H NMR spectrum of compound **16**



^{13}C NMR spectrum of compound **16**



^{1}H NMR spectrum of compound **17**



^{13}C NMR spectrum of compound **17**