Supplementary Information

Iron-Catalyzed Iodonium Ion Promoted Activation of Conventional Thioglycosides for Stereoselective 1,2-*Cis* Furanosylations

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Content

1. Materials and methods

Reagents:

Reagents and solvents were obtained from Sigma-Aldrich (www.sigma-aldrich.com), Chem-Impex (www.chemimpex.com) or Acros Organics (www.fishersci.com) and used without further purification unless otherwise indicated. Dry solvents (acetonitrile) were obtained from Acros Organics (www.fishersci.com), and dichloromethane was distilled over CaH_2 under N_2 unless otherwise indicated. THF purchased from Sigma-Aldrich was distilled over Na metal with benzophenone indicator. Toluene was obtained from Sigma-Aldrich.

Reactions:

All reactions were performed in flame-dried glassware under positive N_2 pressure with magnetic stirring unless otherwise noted. Liquid reagents and solutions were transferred through rubber septa via syringes flushed with N_2 prior to use. Cold baths were generated as follows: 0 °C with wet ice/water and −78 °C with dry ice/acetone.

Chromatography:

TLC was performed on 0.25 mm E. Merck silica gel 60 F254 plates and visualized under UV light (254 nm) or by staining with potassium permanganate ($KMnO_4$), cerium ammonium molybdate (CAM), phosphomolybdic acid (PMA), and ninhydrin. Silica flash chromatography was performed on Sorbtech 230–400 mesh silica gel 60.

Analytical Instrumentation:

NMR spectra were recorded on a Varian VNMRS 400 and 500 MHz NMR spectrometer in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in ppm relative to solvent signals: $CDCl_3$ (^1H, 7.26 ppm, ^{13}C, 77.0 ppm); coupling constants are expressed in Hz. NMR spectra were processed using Mnova (www.mestrelab.com/software/mnova-nmr). Mass spectra were obtained at the OU Analytical Core Facility on an Agilent 6538 High-Mass-Resolution QTOF Mass Spectrometer and an Agilent 1290 UPLC.

Nomenclature:

N.B.: Atom numbers shown in chemical structures herein correspond to IUPAC nomenclature, which was used to name each compound.

2. Synthesis of conventional thioglycosides

2.1 Synthesis of ethyl 2,3-bis-*O*-benzyl-5-*O*-tert-butyldiphenylsilyl-1-thio-D-ribofuranoside (2f)

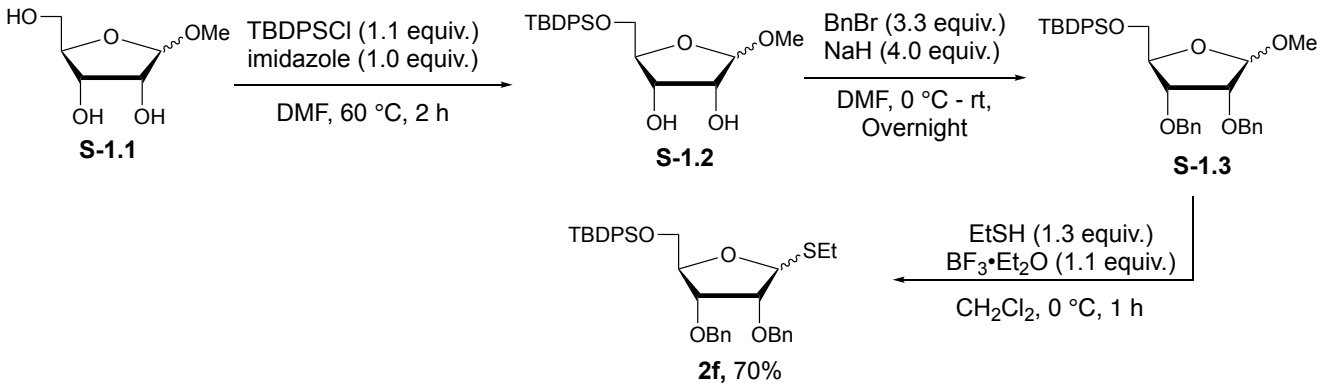
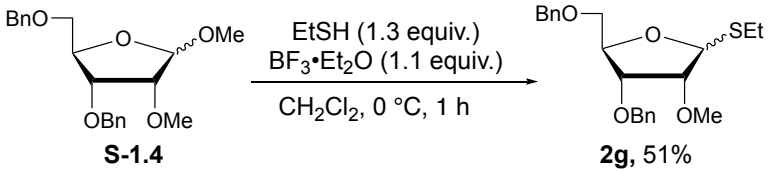


Figure S.1. Scheme for the synthesis of ribofuranoside donor **2f**.

In an oven-dried round bottom flask, methyl ribofuranoside **S-1.1** (1.0 equiv.) was dissolved in dimethylformamide (0.5 M), followed by the addition of imidazole (1.0 equiv.) at room temperature and stirred at the same temperature for the next 15 minutes. Then, TBDPSCl (1.1 equiv.) was added into the stirred suspension, and the resulting mixture was stirred at 60 ℃ for the next 2 hours. Upon complete consumption of the starting material, the reaction mixture was diluted with water (50 mL) and ethyl acetate (50 mL). The layers were separated, and the aqueous layer was washed with ethyl acetate (50x2 mL). Then, the combined organic layers were carefully washed with aq. sat. $NaHCO_3$, brine, and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude viscous oil **S-1.2,** which was then used in the next step without further purification. To the crude **S-1.2,** anhydrous DMF (0.5 M) was added, and the solution was cooled to 0 ℃. To the above-cooled reaction mixture, NaH (4.0 equiv., 60% in mineral oil) was added carefully in one portion, and the reaction was allowed to stir at the same temperature for the next 30 minutes. Then, benzyl bromide (3.3 equiv.) was added to the stirred suspension, and the reaction was allowed to warm up to room temperature and was stirred at the same temperature overnight. The reaction was quenched by the careful addition of methanol (2.0 mL), then the reaction mixture was diluted with water (50 mL) and ethyl acetate (50 mL). The layers were separated, and the aqueous layer was washed with ethyl acetate (50x2 mL). Then, the combined organic layers were carefully washed with aq. sat. $NaHCO_3$, brine, and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude viscous oil **S-1.3.** To the crude **S-1.3,** anhydrous dichloromethane (0.5 M) was added, and the solution was cooled to 0 ℃. To the above-cooled reaction mixture, ethanethiol (1.3 equiv.) was added, followed by the addition of BF_3•Et_2O (1.1 equiv.). The reaction was stirred at 0 ℃ for the next 1 hour, then it was quenched by the careful addition of aq. sat. $NaHCO_3$ followed by the addition of H_2O. The layers were separated, and the organic layer was washed with brine and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude thick syrup. This crude syrup was purified by column chromatography (EtOAc: hexane = 5:95) to afford ribofuranoside donor **2f** (1.61 g, 70%, α:β=1:3). R_f = 0.6 (EtOAc: hexane= 10:90). **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 7H), 7.46 – 7.40 (m, 4H), 7.31 (d, *J* = 5.3 Hz, 11H), 5.26 (d, *J* = 4.5 Hz, 1H), 4.72 – 4.63 (m, 3H), 4.56 (d, *J* = 8.4 Hz, 2H), 4.24 – 4.19 (m, 1H), 4.17 – 4.10 (m, 2H), 3.90 – 3.87 (m, 1H), 3.77 – 3.69 (m, 2H), 2.69 – 2.59 (m, 2H), 1.28 (td, *J* = 7.4, 0.8 Hz, 3H), 1.08 (dd, *J* = 2.3, 0.8 Hz, 3H), 1.03 (d, *J* = 0.9 Hz, 10H), 0.98 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.8, 135.8, 135.8, 135.8, 129.9, 129.8, 128.6, 128.5, 128.5, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 85.9, 83.3, 81.1, 77.7, 72.4, 72.4, 64.0, 27.0, 26.9, 25.2, 19.4, 15.2. **HRMS (ESI):** calc. for $C_{37}H_{44}O_4NaSSi$ (M+Na): 635.2627; found: 635.2624.

2.2 Synthesis of ethyl 2-*O*-methyl,3,5-bis-*O*-benzyl-1-thio-D-ribofuranoside (2g)

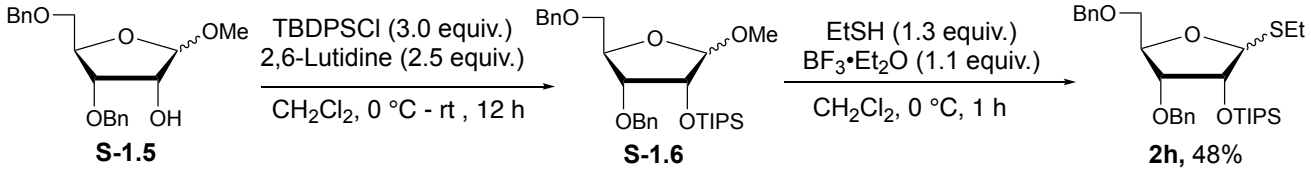


S-1.4 **2g,** 51%

Figure S-2. Scheme for the synthesis of ribofuranoside donor **2g**.

The solution of **S-1.4**[1] (1.0 equiv.) in anhydrous dichloromethane (0.5 M) was cooled to 0 ℃. To the above-cooled reaction mixture, ethanethiol (1.3 equiv.) was added, followed by the addition of BF_3•Et_2O (1.1 equiv.). The reaction was stirred at 0 ℃ for the next 1 hour; then, it was quenched by the careful addition of aq. sat. $NaHCO_3$ followed by the addition of H_2O. The layers were separated, and the organic layer was washed with brine and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude thick syrup. This crude syrup was purified by column chromatography (EtOAc: hexane = 5:95) to afford ribofuranoside donor **2g** (0.221 g, 51%, α:β=1:4). R_f= 0.6 (EtOAc: hexane= 10:90). **^{1}H NMR** (399 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 10H), 5.15 (d, *J* = 4.1 Hz, 1H), 4.52 (dd, *J* = 12.1, 5.3 Hz, 4H), 4.20 – 4.15 (m, 1H), 3.99 (t, *J* = 5.4 Hz, 1H), 3.53 – 3.50 (m, 2H), 3.44 (s, 1H), 3.36 (s, 3H), 2.64 – 2.55 (m, 2H), 1.20 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.3, 137.7, 128.5, 128.5, 128.2, 128.1, 128.0, 127.8, 127.7, 85.5, 83.5, 81.6, 78.1, 73.4, 72.5, 70.9, 58.3, 25.2, 15.1. **HRMS (ESI):** calc. for $C_{22}H_{28}O_4NaS$ (M+Na): 411.1606; found: 411.1608.

2.3 Synthesis of ethyl 2-*O*-triisopropy,3,5-bis-*O*-benzyl-1-thio-D-ribofuranoside (2h)



S-1.5 **S-1.6** **2h,** 48%

Figure S-3. Scheme for the synthesis of ribofuranoside donor **2h**.

To a CH_2Cl_2 solution (0.5 M) of compound **S-1.5**[1] (1.0 equiv.) at 0 ℃ was added 2,6-lutidine (2.5 equiv.) and triisopropylsilyl triflate (3.0 equiv.). The reaction was warmed to room temperature and monitored by TLC. After completion, it was quenched with aq. sat. $NaHCO_3$; the aqueous layer, was separated and extracted with CH_2Cl_2. The organic layers were collected, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude product. The solution of crude **S-1.6** in anhydrous dichloromethane (0.5 M) was cooled to 0 ℃. To the above-cooled reaction mixture, ethanethiol (1.3 equiv.) was added, followed by the addition of BF_3•Et_2O (1.1 equiv.). The reaction was stirred at 0 ℃ for the next 1 hour; then, it was quenched by the careful addition of aq. sat. $NaHCO_3$ followed by the addition of H_2O. The layers were separated, and the organic layer was washed with brine and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude thick syrup. This crude syrup was purified by column chromatography (EtOAc: hexane = 5:95) to afford ribofuranoside donor **2h** (0.350 g, 80%, α:β=1:3). R_f= 0.7 (EtOAc: hexane= 10:90). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 10H), 5.12 (d, *J* = 3.0 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.50 (dd, *J* = 16.7, 11.8 Hz, 2H), 4.34 – 4.26 (m, 2H), 3.99 (dd, *J* = 6.5, 4.5 Hz, 1H), 3.61 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.55 (dd, *J* = 10.6, 5.4 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.61 (dt, *J* = 12.9, 7.5 Hz, 1H), 1.27 (s, 3H), 1.09 – 1.06 (m, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.3, 138.0, 128.4, 128.4, 127.9, 127.8, 127.7, 127.6, 88.8,

80.9, 80.1, 75.9, 73.5, 72.4, 71.4, 25.1, 18.1, 15.1. **HRMS (ESI):** calc. for $C_{30}H_{46}O_4NaSSi$ (M+Na): 553.2784; found: 553.2767.

2.4 Synthesis of ethyl 2-azido-3,5-bis-*O*-benzyl-1-thio-D-ribofuranoside (2i)

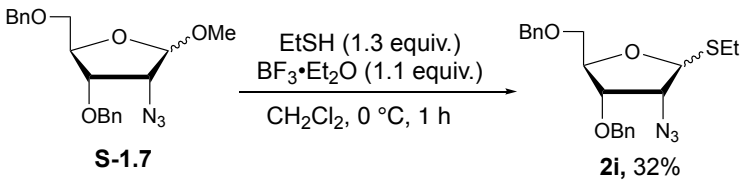


Figure S-4. Scheme for the synthesis of ribofuranoside donor **2i**.

The solution of **S-1.7**[2] **(**1.0 equiv.) in anhydrous dichloromethane (0.5 M) was cooled to 0 ℃. To the above cooled reaction mixture, ethanethiol (1.3 equiv.) was added, followed by the addition of BF_3•Et_2O (1.1 equiv.). The reaction was stirred at 0 ℃ for the next 1 hour, then it was quenched by the careful addition of aq. sat. $NaHCO_3$ followed by the addition of H_2O. The layers were separated, and the organic layer was washed with brine and dried over Na_2SO_4. The solutions were filtered and evaporated under reduced pressure to afford the crude thick syrup. This crude syrup was purified by column chromatography (EtOAc: hexane = 5:95) to afford ribofuranoside donor **2i** (0.180 g, 32%, α:β=1:4). R_f = 0.6 (EtOAc: hexane= 10:90). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 10H), 5.17 (d, *J* = 5.9 Hz, 1H), 4.69 (d, *J* = 11.8 Hz, 1H), 4.63 – 4.54 (m, 2H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.19 (dq, *J* = 9.8, 4.5 Hz, 2H), 3.74 (dd, *J* = 5.8, 5.1 Hz, 1H), 3.56 (dd, *J* = 4.2, 1.3 Hz, 2H), 2.77 – 2.64 (m, 2H), 1.29 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.0, 137.3, 128.7, 128.5, 128.2, 128.1, 127.9, 127.8, 86.0, 82.5, 79.9, 77.5, 76.8, 73.6, 72.9, 70.6, 65.2, 25.2, 15.3. **HRMS (ESI):** calc. for $C_{21}H_{25}O_3N_3NaS$ (M+Na): 422.1514; found: 422.1502.

3. Reaction Development

3.1. General synthetic procedure for the iron-catalyzed iodonium ion promoted 1,2-*cis* furanosylations.

General procedure A: In an oven-dried vial equipped with a stir bar, acceptor **1** (0.025 mmol) was combined with thioglycoside donors **2** (**a-i**) (0.031 mmol, 1.2 equiv.), 4Å molecular sieves (50 mg or 100 wt.%) and dissolved in CH_2Cl_2 (0.05M). The reaction mixture was cooled to 0 ℃ and stirred at the same temperature for the next five minutes, then, to this cold reaction suspension, additive (1.0-1.5 equiv.) and iron salts (0.005 mmol, 0.2 equiv.) were added simultaneously. Upon complete addition, the reaction mixture was stirred at the same temperature while the reaction progress was monitored by TLC and quenched with saturated aqueous $NaHCO_3$ upon completion. The layers were then separated, with the aqueous layer washed with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was dissolved in ethyl acetate and passed through a short silica pad to remove traces of iron (for crude material analysis via ^{1}H-NMR). The filtrate was evaporated, and the resulting crude material was purified by column chromatography.

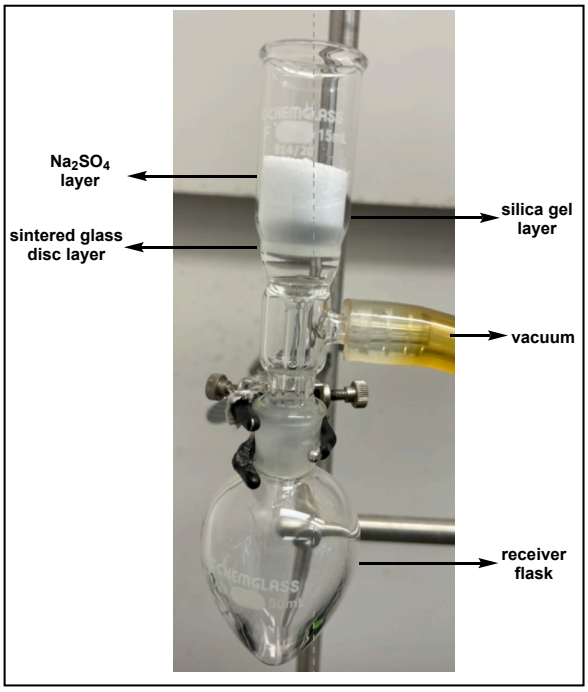
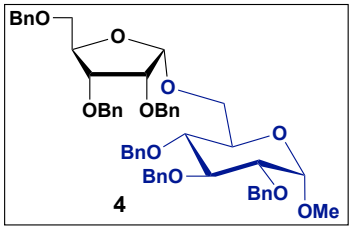


Figure S-5. Image of short silica pad setup for the filtration of crude material to eliminate metal traces

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (4)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 25.0 µmol) was coupled with thiofuranoside donor **2a** (16.0 mg, 31.0 µmol) to afford **4** (21 mg, 24.22 µmol, 91% yield, α:β=6:1) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).



^{1}H NMR (399 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.34 – 7.17 (m, 28H), 5.15 – 5.13 (m, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.77 – 4.72 (m, 3H), 4.70 (d, *J* = 15.9 Hz, 1H), 4.66 – 4.56 (m, 3H), 4.50 (d, *J* = 12.2 Hz, 1H), 4.42 (dd, *J* = 12.0, 5.3 Hz, 2H), 4.23 – 4.12 (m, 2H), 3.97 – 3.92 (m, 1H), 3.90 – 3.85 (m, 2H), 3.78 – 3.72 (m, 2H), 3.66 (dd, *J* = 11.2, 1.6 Hz, 1H), 3.46 (dt, *J* = 9.6, 3.4 Hz, 2H), 3.39 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.33 (s, 3H).

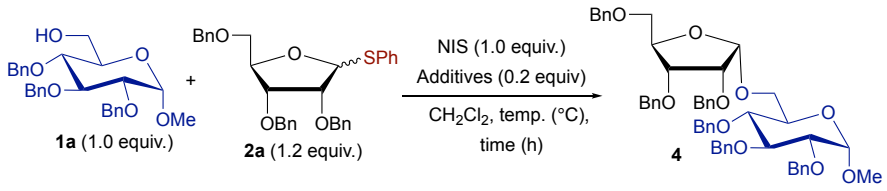
^{1}H NMR (500 MHz, benzene-D_6) δ 7.41 – 7.39 (m, 2H), 7.36 – 7.33 (m, 2H), 7.32 – 7.30 (m, 2H), 7.29 – 7.27 (m, 2H), 7.26 – 7.24 (m, 2H), 7.13 (dt, *J* = 6.3, 3.1 Hz, 9H), 7.07 (s, 2H), 7.03 (td, *J* = 13.3, 6.2 Hz, 9H), **5.17 (d, *J* = 4.2 Hz, 1H),** 4.99 (d, *J* = 11.4 Hz, 1H), 4.95 – 4.91 (m, 2H), 4.81 (d, *J* = 11.3 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), **4.60 (d, *J* = 3.4 Hz, 1H),** 4.40 – 4.36 (m, 4H), 4.34 (dd, *J* = 11.4, 2.8 Hz, 2H), 4.24 – 4.14 (m, 4H), 4.07 (t, *J* = 9.5 Hz, 1H), 3.92 (dd, *J* = 6.2, 3.5 Hz, 1H), 3.82 – 3.77 (m, 2H), 3.63 (dd, *J* = 11.3, 1.7 Hz, 1H), 3.48 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.30 (dd, *J* = 10.5, 3.9 Hz, 1H), 3.26 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.7, 138.4, 138.3, 138.3, 138.1, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 102.2, 98.3, 82.1, 81.5, 80.1, 77.9, 77.9, 76.2, 75.6, 75.1, 73.5, 73.5, 72.5, 72.5, 70.3, 69.8, 66.7, 55.2. The data are identical to the literature report.[3]

3.2. Influence of triflic acid and reduced reaction temperature on reaction efficiency and stereoselectivity.[a]

To understand whether TfOH is playing a crucial role or the triflate (OTf) ion is assisting in the reaction, we perform experiments with TfOH. In the first experiment, we added TfOH in catalytic amount (0.2 equiv, **see Table S-1**), and we observed molecular sieves quenched the TfOH (due to the basicity of sieves), and the reaction outcome was similar as it was with only NIS (no Lewis acid) and the reaction was completed in around 24 hours. We also performed a reaction without molecular sieves, the reaction completion time was relatively less, producing a slightly higher yield, and mixture of anomers, preferring β-selectivity. In the absence of molecular sieves, we observed the decomposition of the donor to unproductive pathways with TfOH as an acid source (entry 1 and 2) (strong Brønsted acid). Hence, these

Table S-1: Table for the Influence of triflic acid and reduced reaction temperature on reaction efficiency and stereoselectivity.



entry	Additive (0.2 equiv.)	M.S.	Temp. (℃)	Time (h)	4, yield[b]	4, (α/β)
1.	TfOH	4Å M.S.	0 ℃	24 h	70%	2/1
2.	TfOH	-	0 ℃	12 h	78%	1/1.1
3.	$Fe(OTf)_3$	4Å M.S.	-80 ℃	6 h	n.r.	n.d.
4.	$Fe(OTf)_3$	4Å M.S.	-60 ℃	6 h	n.r.	n.d.
5.	$Fe(OTf)_3$	4Å M.S.	-40 ℃	14 h	81%	3/1
6.	$Fe(OTf)_3$	4Å M.S.	-20 ℃	6 h	79%	4/1
7.	$Fe(OTf)_3$	4Å M.S.	-10 ℃	2 h	79%	6/1

[a]all the reactions were performed with acceptor (0.025 mmol, 1.0 equiv.), donor (0.03 mmol, 1.2 equiv.), additive (0.025 mmol, 1.0 equiv.), and metal catalyst (0.005 mmol, 0.2 equiv.), molecular sieves MS (100 wt.%) and CH_2Cl_2 (0.05M). [b]yields were calculated after analyzing ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. M.S., molecular sieves; h, hour.

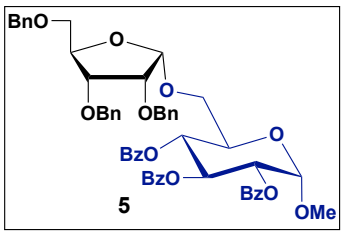
crucial experiments indicated the importance of molecular sieves, mild activating Lewis acid. Additionally, these experiments further suggest the dual role of $Fe(OTf)_3$, 1) A Lewis acid coordinating with the carbonyl group of NIS and assisting the smooth release of iodonium ion, 2) Upon ligand exchange, provides triflate anion which assists in further stabilization of oxocarbenium ion. In conclusion, we believe that Brønsted acid gets quenched in the presence of molecular sieves and shows minimal effect on the reaction outcomes. However, mild Lewis acids remained unaffected by the basic nature of molecular sieves and worked efficiently in catalytic amounts.

We also conducted the experiments at lower temperatures, to understand the effect of temperature on the reactivity and selectivity outcomes. At very low temperatures (-80 ℃, -60 ℃, entries 3 and 4), we observed no reaction. Increasing the temperature to -40 ℃ (entry 5), and -20 ℃ (entry 6), we observed the product formation in good yields. However, our observations indicated that lowering the reaction temperature led to sluggish reactions that required significantly longer reaction times (see **Table S-1**). Interestingly, the selectivity under these lower-temperature conditions was inferior to that observed under our optimized conditions.

4. Substrate scope

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (5)

Following the general procedure, **A**, glycosyl acceptor **1b** (13.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2a** (16.0 mg, 31.0 μmol) to afford **5** (19.0 mg, 20.9 μmol, 81% yield, α:β=5.5:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).

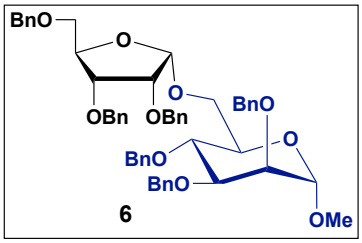


^{1}H NMR (399 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 4H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.35 (td, *J* = 8.1, 5.5 Hz, 8H), 7.31 – 7.26 (m, 12H), 7.21 – 7.17 (m, 2H), 6.11 (t, *J* = 10.0 Hz, 1H), 5.49 (t, *J* = 9.9 Hz, 1H), 5.21 – 5.16 (m, 2H), 4.99 (d, *J* = 4.1 Hz, 1H), 4.66 – 4.59 (m, 4H), 4.54 – 4.45 (m, 3H), 4.41 (s, 1H), 4.31 (t, *J* = 3.9 Hz, 2H), 3.93 (dd, *J* = 11.3, 6.7 Hz, 1H), 3.84 (dd, *J* = 6.6, 3.8 Hz, 1H), 3.80 – 3.72 (m, 2H), 3.40 (t, *J* = 3.3 Hz, 1H), 3.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 138.4, 138.1, 138.0, 133.4, 133.1, 130.0, 129.9, 129.8, 129.4, 129.2, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 127.9, 127.7, 127.7, 127.7, 101.5, 96.7, 81.7, 73.5, 72.6, 72.3, 70.8, 69.9, 69.8, 68.9, 66.8, 55.5. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-mannopyranoside (**6**)

Following the general procedure **A**, glycosyl acceptor **1c** (12.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2a** (16.0 mg, 31.0 μmol) to afford **6** (17.0 mg, 19.6 μmol, 76% yield, α:β=4:1) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).

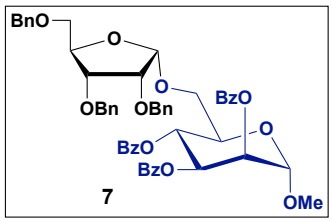


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 6.9, 2.5 Hz, 2H), 7.33 – 7.26 (m, 11H), 7.25 – 7.18 (m, 17H), 5.32 (d, *J* = 3.6 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.72 – 4.68 (m, 2H), 4.67 – 4.60 (m, 5H), 4.55 – 4.51 (m, 2H), 4.45 (d, *J* = 12.2 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.27 (q, *J* = 4.0 Hz, 1H), 3.88 – 3.81 (m, 4H), 3.79 – 3.76 (m, 1H), 3.71 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.54 (dd, *J* = 10.7, 3.3 Hz, 1H), 3.45 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.9, 138.5, 138.2, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 102.2, 99.3, 80.8, 80.3, 73.5, 72.9, 72.7, 72.3, 72.3, 72.0, 69.7, 66.5, 54.8. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-mannopyranoside (7)

Following the general procedure **A**, glycosyl acceptor **1d** (13.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2a** (16.0 mg, 31.0 μmol) to afford **7** (18.5 mg, 20.3 μmol, 79% yield, α:β=5:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



7

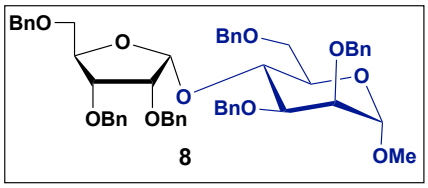
^{1}H NMR (399 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.82 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.58 – 7.48 (m, 2H), 7.45 – 7.38 (m, 4H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.32 – 7.26 (m, 9H), 7.25 – 7.22 (m, 5H), 7.20 (dd, *J* = 7.5, 2.1 Hz, 2H), 5.84 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.77 (t, *J* = 10.1 Hz, 1H), 5.63 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.01 (d, *J* = 4.1 Hz, 1H), 4.93 (d, *J* = 1.8 Hz, 1H), 4.60 (d, *J* = 9.6 Hz, 3H), 4.50 – 4.45 (m, 2H), 4.42 (s, 1H), 4.37 (d, *J* = 11.9 Hz, 1H), 4.32 (q, *J* = 3.8 Hz, 1H), 4.04 – 3.98 (m, 1H), 3.85 (dd, *J* = 6.9, 3.9 Hz, 1H), 3.81 – 3.75 (m, 2H), 3.45 (d, *J* = 11.7 Hz, 1H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.5, 133.5, 133.2, 130.0, 129.9, 129.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 127.7, 127.7, 101.7, 98.3, 73.5, 72.6, 72.3, 70.8, 70.1, 69.9, 67.7, 55.4.

HRMS (ESI): calc. for $C_{54}H_{52}NaO_{13}$ (M+Na): 931.3306; found: 931.3339.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-mannopyranoside (**8**)

Following the general procedure **A**, glycosyl acceptor **1e** (12.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2a** (16.5 mg, 31.0 μmol) to afford **4ae** (16.0 mg, 18.45 μmol, 71% yield, α:β=4:1) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).



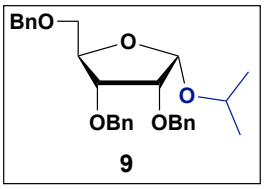
8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.0 Hz, 2H), 7.32 – 7.26 (m, 17H), 7.24 – 7.12 (m, 9H), 7.04 – 7.01 (m, 2H), 5.61 (d, *J* = 4.5 Hz, 1H), 4.82 (d, *J* = 1.8 Hz, 1H), 4.66 (d, *J* = 6.2 Hz, 2H), 4.64 – 4.56 (m, 4H), 4.55 – 4.48 (m, 3H), 4.42 – 4.32 (m, 3H), 4.21 (t, *J* = 9.7 Hz, 1H), 4.08 (dd, *J* = 9.5, 3.1 Hz, 1H), 4.02 (ddd, *J* = 9.4, 5.9, 2.1 Hz, 2H), 3.93 (dd, *J* = 10.6, 2.0 Hz, 1H), 3.83 – 3.79 (m, 2H), 3.72 (dd, *J* = 6.6, 2.4 Hz, 1H), 3.64 (dd, *J* = 6.6, 4.5 Hz, 1H), 3.36 (s, 3H), 3.24 – 3.20 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.8, 138.5, 138.1, 138.0, 137.8, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 127.4, 127.3, 127.0, 101.9, 98.7, 82.3, 80.4, 75.3, 74.1, 73.5, 73.4, 72.5, 71.9, 71.9, 71.4, 71.3, 70.7, 70.4, 70.3, 54.6. The data are identical to the literature report.[1]

Isopropyl 2,3,5-tri-*O*-benzyl-D-ribofuranoside (**9**):

Following the general procedure **A**, isopropanol (5.0 mg, 83.0 μmol) was coupled with thiofuranoside donor **2a** (51.0 mg, 100.0 μmol) to afford **9** (34.0 mg, 73.5 μmol, 88% yield, α:β=4:1) as a colorless viscous oil. R_f = 0.6 (hexane: EtOAc = 80:20).



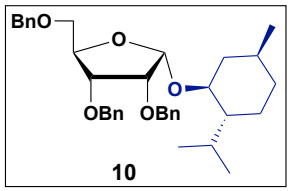
9

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 13H), 7.23 (dq, J = 7.2, 0.7 Hz, 2H), 5.13 (d, J = 4.3 Hz, 1H), 4.76 – 4.68 (m, 2H), 4.64 (d, J = 12.3 Hz, 1H), 4.55 (d, J = 12.7 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 4.44 (d, J = 12.1 Hz, 1H), 4.24 (q, J = 4.0 Hz, 1H), 3.97 (p, J = 6.2 Hz, 1H), 3.84 (dd, J = 6.9, 4.2 Hz, 1H), 3.77 (dd, J = 6.9, 4.2 Hz, 1H), 3.47 (dd, J = 10.5, 3.8 Hz, 1H), 3.38 (dd, J = 10.6, 4.2 Hz, 1H), 1.30 (d, J = 6.3 Hz, 3H), 1.23 (d, J = 6.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 138.2, 128.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 99.8, 81.2, 75.5, 73.5, 72.5, 72.3, 70.1, 23.8, 21.9. The data are identical to the literature report.[1]

***l*-Menthyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside** (**10**):

Following the general procedure **A**, *l*-menthol (5.0 mg, 32.0 μmol) was coupled with thiofuranoside donor **2a** (20.0 mg, 38.5 μmol) to afford **10** (17.2 mg, 30.8 μmol, 96% yield, α:β=6:1) as a colorless viscous oil. R_f = 0.5 (hexane: EtOAc = 80:20).



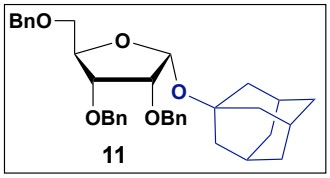
10

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 13H), 7.25 – 7.19 (m, 2H), 5.16 (d, J = 4.3 Hz, 1H), 4.77 – 4.53 (m, 5H), 4.51 – 4.40 (m, 2H), 4.26 (q, J = 4.0 Hz, 1H), 3.84 (dd, J = 6.9, 3.9 Hz, 1H), 3.76 (dd, J = 6.9, 4.3 Hz, 1H), 3.46 (dd, J = 10.5, 3.9 Hz, 1H), 3.38 (ddd, J = 11.0, 6.9, 4.3 Hz, 2H), 2.35 (ddt, J = 14.1, 7.0, 3.6 Hz, 1H), 2.15 (dd, J = 10.0, 5.4 Hz, 1H), 1.62 (dt, J = 12.9, 3.8 Hz, 2H), 1.42 (tdd, J = 9.8, 7.3, 3.1 Hz, 2H), 1.30 – 1.15 (m, 3H), 1.02 – 0.79 (m, 11H), 0.76 (d, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 138.2, 128.5, 128.4, 128.3, 128.2, 127.8, 127.8, 127.7, 127.6, 102.6, 81.2, 80.0, 78.0, 75.5, 73.5, 72.5, 72.2, 70.3, 48.3, 43.4, 34.5, 32.0, 25.1, 23.0, 22.5, 21.4, 16.1. The data are identical to the literature report.[1]

Adamantanyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside (**11**)

Following the general procedure, **A**, 1-adamantanol (5.0 mg, 33.0 μmol) was coupled with thiofuranoside donor **2a** (20.0 mg, 39.5 μmol) to afford **11** (15.0 mg, 27.04 μmol, 82% yield, α:β=8:1) as a colorless viscous oil. R_f = 0.5 (hexane: EtOAc = 80:20).



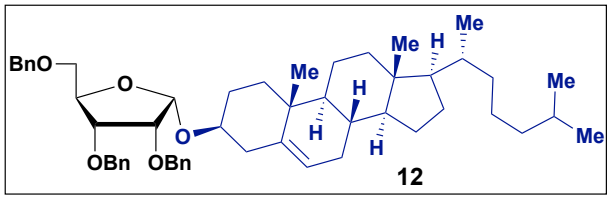
11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 15H), 5.41 (s, 1H), 4.65 (s, 2H), 4.63 – 4.54 (m, 3H), 4.54 – 4.49 (m, 1H), 4.26 (d, *J* = 5.6 Hz, 1H), 3.97 (t, *J* = 5.5 Hz, 1H), 3.77 (q, *J* = 2.0 Hz, 1H), 3.57 (d, *J* = 5.3 Hz, 2H), 2.11 (s, 2H), 1.77 (d, *J* = 11.9 Hz, 3H), 1.70 (d, *J* = 11.9 Hz, 3H), 1.57 (q, *J* = 7.7 Hz, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 138.2, 128.5, 128.4, 128.1, 127.9, 127.8, 127.8, 127.6, 99.1, 81.1, 80.3, 78.7, 74.4, 73.3, 72.3, 72.3, 72.0, 42.8, 36.4, 30.7. The data are identical to the literature report.[1]

Cholesteryl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside (**12**)

Following the general procedure **A**, cholesterol (10.0 mg, 26.0 μmol) was coupled with thiofuranoside donor **2a** (16.0 mg, 31.0 μmol) to afford **12** (13.7 mg, 17.7 μmol, 67% yield, α:β=9:1) as a colorless viscous oil. R_f = 0.5 (hexane: EtOAc = 80:20).



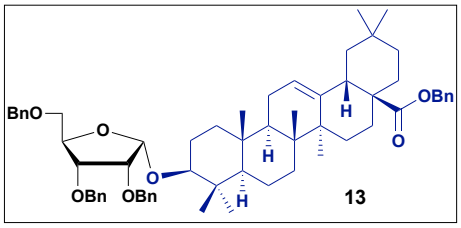
12

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 15H), 5.32 (s, 1H), 5.15 (s, 1H), 4.65 (s, 2H), 4.59 – 4.53 (m, 3H), 4.48 (t, *J* = 11.1 Hz, 1H), 4.30 (dd, *J* = 8.4, 3.3 Hz, 1H), 4.01 (t, *J* = 5.8 Hz, 1H), 3.83 (d, *J* = 4.7 Hz, 1H), 3.62 – 3.42 (m, 3H), 2.35 – 2.24 (m, 1H), 2.09 (s, 1H), 1.98 (t, *J* = 16.1 Hz, 2H), 1.76 (d, *J* = 11.6 Hz, 2H), 1.49 – 1.32 (m, 10H), 1.11 (q, *J* = 10.8 Hz, 6H), 0.98 (d, *J* = 15.6 Hz, 7H), 0.91 (d, *J* = 6.4 Hz, 4H), 0.88 – 0.83 (m, 9H), 0.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 138.4, 138.0, 128.5, 128.4, 128.4, 128.1, 127.9, 127.9, 127.8, 127.8, 127.6, 122.0, 103.5, 80.3, 80.3, 78.7, 73.2, 72.5, 72.4, 71.7, 56.8, 56.2, 50.2, 42.4, 39.8, 39.6, 38.6, 37.3, 36.8, 36.3, 35.9, 32.0, 32.0, 29.8, 29.7, 28.3, 28.1, 24.4, 23.9, 22.9, 22.7, 21.1, 19.4, 18.8, 11.9. The data are identical to the literature report.[1]

Benzyl 3-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl) oleanate (13)

Following the general procedure **A**, benzyl oleanate (14.0 mg, 25.0 μmol) was coupled with thio-furanoside donor **2a** (16.0 mg, 31.0 μmol) to afford **13** (21.2 mg, 22.33 μmol, 87% yield, α:β=10:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 80:20).



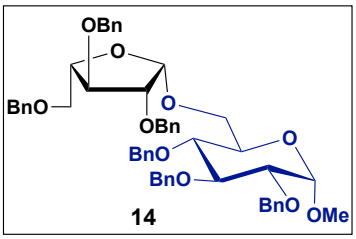
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.6 Hz, 7H), 7.33 – 7.27 (m, 13H), 5.30 – 5.28 (m, 1H), 5.10 (d, *J* = 12.5 Hz, 1H), 5.07 (d, *J* = 1.8 Hz, 1H), 5.04 (d, *J* = 12.6 Hz, 1H), 4.63 (d, *J* = 1.7 Hz, 2H), 4.56 (dd, *J* = 11.9, 6.6 Hz, 3H), 4.52 – 4.48 (m, 1H), 4.30 (td, *J* = 6.2, 4.3 Hz, 1H), 3.93 (dd, *J* = 6.4, 4.8 Hz, 1H), 3.81 (dd, *J* = 4.8, 1.8 Hz, 1H), 3.60 – 3.52 (m, 2H), 2.98 (dd, *J* = 11.7, 4.4 Hz, 1H), 2.90 (dd, *J* = 13.9, 4.5 Hz, 1H), 1.98 (d, *J* = 4.1 Hz, 1H), 1.84 (dd, *J* = 9.0, 3.7 Hz, 2H), 1.78 (d, *J* = 10.1 Hz, 1H), 1.72 – 1.53 (m, 8H), 1.46 (d, *J* = 2.9 Hz, 1H), 1.42 – 1.28 (m, 4H), 1.26 (s, 1H), 1.24 – 1.17 (m, 3H), 1.13 (s, 3H), 1.04 (d, *J* = 14.1 Hz, 2H), 0.92 (s, 3H), 0.90 (s, 4H), 0.87 (s, 4H), 0.83 (s, 3H), 0.69 (s, 4H), 0.59 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 143.8, 138.4, 138.0, 138.0, 136.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 122.6, 107.9, 88.4, 80.3, 80.1, 78.4, 73.3, 72.3, 72.3, 71.9, 66.0, 55.5, 47.6, 46.8, 45.9, 41.8, 41.5, 39.4, 38.8, 38.5, 36.8, 33.9, 33.2, 32.8, 32.5, 30.8, 28.3, 27.7, 26.0, 25.6, 23.7, 23.5, 23.1, 18.4, 17.0, 16.5, 15.4.

HRMS (ESI): calc. for $C_{63}H_{82}O_7$ (M+H): 949.5982; found: 949.5987.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2, 3, 5-tri-*O*-benzyl-β-L-arabinofuranosyl)-α-D-glucopyranoside (14)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 25.0 μmol) was coupled with thio-furanoside donor **2d** (16.0 mg, 32.0 μmol) to afford **14** (18.1 mg, 20.88 μmol, 81% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).

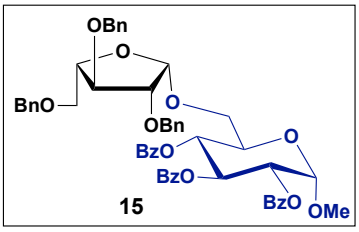


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.3 Hz, 9H), 7.31 – 7.23 (m, 33H), 5.08 (d, *J* = 2.8 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.82 (dd, *J* = 12.6, 10.9 Hz, 3H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.65 (dd, *J* = 12.6, 1.9 Hz, 3H), 4.62 – 4.54 (m, 4H), 4.51 (d, *J* = 2.8 Hz, 2H), 4.43 (d, *J* = 10.6 Hz, 2H), 4.14 – 4.08 (m, 1H), 4.07 – 4.04 (m, 2H), 3.96 (t, *J* = 9.2 Hz, 2H), 3.90 – 3.84 (m, 1H), 3.74 – 3.68 (m, 2H), 3.67 – 3.53 (m, 3H), 3.50 (d, *J* = 6.2 Hz, 2H), 3.38 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.34 (s, 0.65H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.4, 138.3, 138.2, 138.2, 138.1, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 101.6, 98.0, 84.1, 83.3, 82.1, 80.3, 80.1, 77.9, 75.7, 75.1, 73.5, 73.4, 73.2, 72.8, 72.3, 72.0, 72.0, 70.4, 66.4, 55.2. The data are identical to the literature report.[4]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2, 3, 5-tri-*O*-benzyl-β-L-arabinofuranosyl)-α-D-glucopyranoside (15)

Following the general procedure, **A**, glycosyl acceptor **1b** (13.0 mg, 25.0 μmol) was coupled with thio-furanoside donor **2d** (16.0 mg, 31.0 μmol) to afford **15** (16.8 mg, 18.48 μmol, 72% yield, α:β=1:3) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



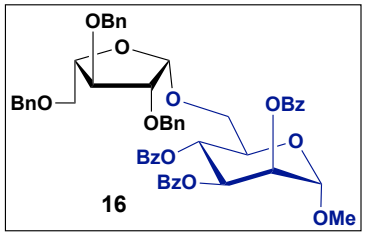
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 5H), 7.89 – 7.85 (m, 2H), 7.55 – 7.49 (m, 3H), 7.41 – 7.27 (m, 24H), 6.15 – 6.09 (m, 1H), 5.55 (t, *J* = 9.9 Hz, 1H), 5.16 (d, *J* = 8.5 Hz, 2H), 4.92 (d, *J* = 3.0 Hz, 1H), 4.68 – 4.59 (m, 4H), 4.59 – 4.52 (m, 2H), 4.41 (d, *J* = 3.2 Hz, 2H), 4.24 – 4.18

(m, 1H), 4.09 (dd, *J* = 10.2, 3.8 Hz, 3H), 3.88 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.54 – 3.49 (m, 3H), 3.43 (s, 0.6H), 3.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.9, 165.2, 138.3, 138.3, 138.0, 133.5, 133.4, 133.2, 130.0, 130.0, 129.8, 129.8, 129.4, 129.2, 129.2, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 101.1, 96.8, 84.3, 83.4, 80.6, 73.2, 72.9, 72.4, 72.4, 72.3, 70.8, 69.5, 68.7, 66.3, 55.6. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-L-arabinofuranosyl)-α-D-mannopyranoside (16)

Following the general procedure **A**, glycosyl acceptor **1d** (13.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2d** (16.0 mg, 31.0 μmol) to afford **16** (16.2 mg, 17.82 μmol, 69% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).

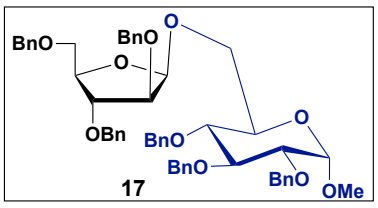


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 2H), 7.97 – 7.94 (m, 2H), 7.83 – 7.80 (m, 2H), 7.55 – 7.52 (m, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.41 (q, *J* = 1.5 Hz, 1H), 7.39 (d, *J* = 3.4 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.33 – 7.26 (m, 10H), 7.24 – 7.16 (m, 7H), 5.86 (s, 1H), 5.85 (t, *J* = 2.2 Hz, 1H), 5.67 – 5.64 (m, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 4.87 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.58 – 4.55 (m, 2H), 4.53 – 4.49 (m, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.25 (s, 1H), 4.08 (dd, *J* = 7.9, 4.4 Hz, 2H), 4.03 (d, *J* = 4.0 Hz, 1H), 3.97 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.57 (d, *J* = 2.2 Hz, 1H), 3.55 – 3.52 (m, 2H), 3.47 (s, 0.7H), 3.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.6, 165.5, 138.3, 138.2, 138.0, 137.9, 133.5, 133.5, 133.5, 133.2, 130.0, 130.0, 129.9, 129.8, 129.4, 129.3, 129.3, 129.2, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 107.2, 101.0, 98.5, 88.5, 84.1, 83.4, 83.4, 80.6, 73.4, 73.3, 73.0, 72.4, 72.2, 72.1, 70.6, 70.5, 70.4, 70.2, 70.1, 69.8, 69.5, 67.4, 66.8, 55.5. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl)-α-D-glucopyranoside (17)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2e** (16.0 mg, 32.0 μmol) to afford **17** (19.5 mg, 22.5 μmol, 87% yield, α:β=1:3) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).

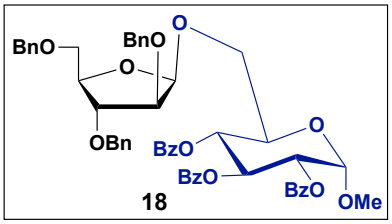


^{1}H NMR (399 MHz, $CDCl_3$) δ 7.43 (tt, *J* = 5.3, 3.1 Hz, 2H), 7.38 – 7.26 (m, 33H), 7.23 – 7.18 (m, 3H), 5.03 – 4.95 (m, 3H), 4.85 – 4.76 (m, 4H), 4.67 (s, 1H), 4.64 (d, *J* = 2.8 Hz, 1H), 4.62 – 4.59 (m, 3H), 4.55 – 4.51 (m, 4H), 4.45 (d, *J* = 12.0 Hz, 2H), 4.13 – 4.06 (m, 4H), 4.00 – 3.92 (m, 2H), 3.71 (d, *J* = 10.1 Hz, 2H), 3.63 – 3.47 (m, 7H), 3.36 (s, 0.6H), 3.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.4, 138.3, 138.3, 138.2, 137.8, 129.1, 128.8, 128.6, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 106.8, 101.1, 98.2, 98.0, 88.0, 84.3, 83.7, 83.4, 82.2, 81.3, 80.8, 80.1, 80.0, 79.0, 78.8, 78.1, 73.5, 73.4, 72.8, 72.3, 72.1, 70.2, 66.5, 55.2, 53.5, 52.9, 52.5. The data are identical to the literature report.[3a]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl)-α-D-glucopyranoside (18)

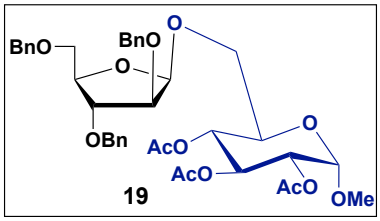
Following the general procedure **A**, glycosyl acceptor **1b** (13.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2e** (16.0 mg, 31.0 μmol) to afford **18** (19.2 mg, 21.2 μmol, 82% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



^{1}H NMR (399 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.93 (d, *J* = 7.1 Hz, 2H), 7.85 – 7.81 (m, 2H), 7.54 – 7.47 (m, 3H), 7.44 – 7.40 (m, 4H), 7.39 – 7.34 (m, 5H), 7.33 (s, 2H), 7.31 – 7.27 (m, 11H), 6.12 (t, *J* = 9.7 Hz, 1H), 5.54 (t, *J* = 9.9 Hz, 1H), 5.24 – 5.17 (m, 2H), 5.06 (t, *J* = 3.7 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.67 – 4.55 (m, 3H), 4.50 – 4.41 (m, 3H), 4.22 – 4.17 (m, 1H), 4.13 – 4.09 (m, 3H), 3.89 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.61 (dd, *J* = 11.7, 5.9 Hz, 1H), 3.52 (d, *J* = 5.4 Hz, 2H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.9, 165.4, 138.3, 138.2, 138.1, 133.5, 133.4, 133.2, 130.0, 130.0, 129.8, 129.8, 129.4, 129.2, 129.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 101.4, 96.8, 84.3, 83.3, 80.6, 73.3, 72.5, 72.3, 72.2, 72.2, 70.7, 69.5, 69.0, 66.0, 55.6. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl)-α-D-glucopyranoside (**19**)
Following the general procedure **A**, glycosyl acceptor **1f** (8.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2d** (16.0 mg, 31.0 μmol) to afford **19** (13.4 mg, 18.6 μmol, 74% yield, α:β=1:3) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



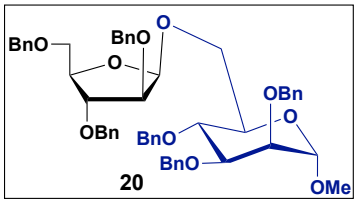
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (tdd, *J* = 12.1, 7.5, 3.2 Hz, 22H), 5.46 (dd, *J* = 10.2, 9.2 Hz, 1H), 5.06 – 4.99 (m, 2H), 4.98 – 4.82 (m, 4H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.61 – 4.51 (m, 7H), 4.13 – 4.05 (m, 4H), 3.95 – 3.87 (m, 2H), 3.73 (dd, *J* = 11.6, 2.6 Hz, 1H), 3.62 – 3.53 (m, 3H), 3.48 (dd, *J* = 11.5, 5.9 Hz, 1H), 3.37 (s, 1H), 3.29 (s, 3H), 2.08 (s, 1H), 2.07 (s, 2H), 2.00 (s, 1H), 1.99 (s, 3H), 1.97 (s, 1H), 1.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 170.3, 170.3, 169.8, 169.6, 138.2, 138.2, 138.0, 138.0, 137.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 106.2, 101.3, 96.9, 96.7, 96.5, 88.4, 84.3, 83.3, 83.1, 82.4, 80.5, 80.5, 73.4, 73.4, 72.4, 72.3, 72.2, 72.1, 71.0, 70.6, 70.4, 69.5, 69.4, 69.1, 68.5, 68.1, 66.0, 55.4, 55.4, 20.9, 20.9, 20.8, 20.8. The data are identical to the literature report.[4a,5]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl)-α-D-mannopyranoside (20)

Following the general procedure **A**, glycosyl acceptor **1c** (12.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2e** (16.0 mg, 32.0 μmol) to afford **20** (18.8 mg, 21.7 μmol, 84% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.4 (hexane: EtOAc = 70:30).

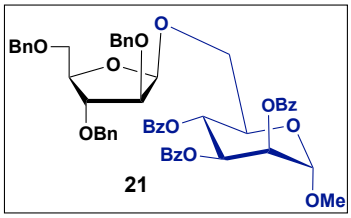
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.33 – 7.26 (m, 26H), 7.25 – 7.21 (m, 8H), 5.13 (d, *J* = 4.0 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 4.74 (s, 1H), 4.70 (d, *J* = 5.9 Hz, 2H), 4.67 (q, *J* = 2.1 Hz, 2H), 4.62 – 4.60 (m, 3H), 4.59 (d, *J* = 1.2 Hz, 2H), 4.56 – 4.54 (m, 2H), 4.52 (d, *J* = 1.4 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 2H), 4.15 – 4.06 (m, 4H), 4.02 (d, *J* = 1.4 Hz, 1H), 3.87 (d, *J* = 3.0 Hz, 1H), 3.84 (d, *J* = 9.2 Hz, 1H), 3.78 (dd, *J* = 3.0, 1.9 Hz, 2H), 3.76 – 3.73 (m, 1H), 3.68 (d, *J* = 10.7 Hz, 1H), 3.62 (s, 1H), 3.60 (s, 2H), 3.28 (s, 0.7H), 3.18 (s, 3H).



^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.6, 138.4, 138.4, 138.3, 138.1, 128.4, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 106.8, 101.2, 99.2, 98.9, 88.0, 84.2, 83.8, 83.7, 80.7, 80.4, 75.3, 75.0, 74.8, 74.6, 73.3, 72.9, 72.8, 72.3, 72.2, 71.9, 71.8, 69.8, 67.3, 54.7. The data are identical to the literature report.[3a]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl)-α-D-mannopyranoside (21)

Following the general procedure **A**, glycosyl acceptor **1d** (13.0 mg, 25.0 μmol) was coupled with thiofuranoside donor **2e** (16.0 mg, 32.0 μmol) to afford **21** (19.5 mg, 21.5 μmol, 83% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



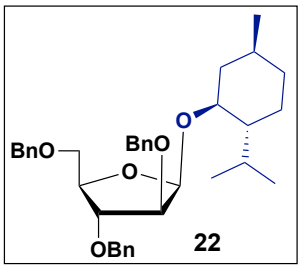
21

^{1}H NMR (399 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.83 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.55 – 7.48 (m, 2H), 7.43 – 7.39 (m, 4H), 7.39 – 7.33 (m, 4H), 7.32 – 7.26 (m, 8H), 7.25 – 7.19 (m, 7H), 5.96 – 5.89 (m, 1H), 5.85 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.12 (d, *J* = 4.0 Hz, 1H), 4.90 (d, *J* = 1.9 Hz, 1H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.62 – 4.57 (m, 2H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.26 – 4.20 (m, 1H), 4.11 – 4.05 (m, 3H), 3.93 (dd, *J* = 11.5, 2.1 Hz, 1H), 3.68 (dd, *J* = 11.3, 6.1 Hz, 1H), 3.50 (dd, *J* = 5.9, 3.1 Hz, 2H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.9, 165.4, 138.3, 138.2, 138.1, 133.5, 133.4, 133.2, 130.0, 130.0, 129.8, 129.8, 129.4, 129.2, 129.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 101.4, 96.8, 84.3, 83.3, 80.6, 73.3, 72.5, 72.3, 72.2, 72.2, 70.7, 69.5, 69.0, 66.0, 55.6. The data are identical to the literature report.[1]

***l*-Menthyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranoside (22)**

Following the general procedure, **A**, *l*-menthol (5.0 mg, 32.0 μmol) was coupled with thiofuranoside donor **2e** (20.0 mg, 38.5 μmol) to afford **22** (16.5 mg, 29.5 μmol, 92% yield, α:β=1:4) as a colorless viscous oil. R_f = 0.5 (hexane: EtOAc = 80:20).

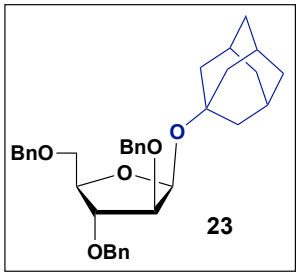


22

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.33 – 7.26 (m, 11H), 5.19 – 5.17 (m, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.08 – 4.05 (m, 3H), 3.58 – 3.55 (m, 2H), 3.46 (td, *J* = 10.6, 4.2 Hz, 1H), 2.23 (td, *J* = 7.0, 2.6 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.63 (dq, *J* = 9.6, 3.5 Hz, 2H), 1.35 – 1.27 (m, 3H), 0.92 (d, *J* = 6.6 Hz, 4H), 0.85 (d, *J* = 7.1 Hz, 6H), 0.73 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.2, 137.9, 128.5, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.7, 97.1, 83.6, 83.4, 79.1, 73.4, 72.7, 72.7, 72.4, 47.6, 40.4, 34.5, 31.5, 25.0, 22.9, 22.5, 21.2, 15.8. The data are identical to the literature report.[1]

Adamantanyl 2,3,5-tri-*O*-benzyl-β-D-arabinofuranoside (23)



23

Following the general procedure, **A**, 1-adamantanol (5.0 mg, 33.0 μmol) was coupled with thiofuranoside donor **2e** (20.0 mg, 39.5 μmol) to afford **23** (15.0 mg, 27.04 μmol, 82% yield, α:β=1:3) as a colorless viscous oil. R_f = 0.5 (hexane: EtOAc = 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 15H), 5.43 (d, *J* = 4.4 Hz, 1H), 4.66 (dd, *J* = 11.8, 9.8 Hz, 2H), 4.59 (d, *J* = 22.2 Hz, 3H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.11 – 4.05 (m, 2H), 4.02 (dd, *J* = 6.6, 4.5 Hz, 1H), 3.69 – 3.64 (m,

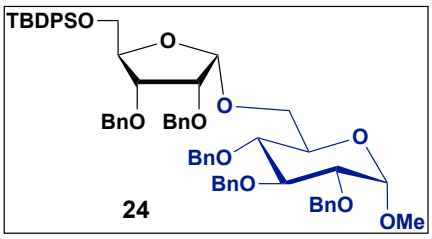
1H), 3.59 (dd, *J* = 9.6, 5.5 Hz, 1H), 2.16 – 2.12 (m, 3H), 1.86 (dq, *J* = 11.2, 2.6 Hz, 3H), 1.78 – 1.73 (m, 3H), 1.66 – 1.58 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.3, 138.0, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 93.9, 84.2, 83.8, 79.9, 74.4, 73.4, 73.3, 72.4, 72.0, 42.9, 36.3, 30.7. The data are identical to the literature report.[1]

5. Iterative synthesis of hexaribosaccharide

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-5-*O*-tertbutyldiphenylsilyl-α-D-ribofuranosyl)-α-D-glucopyranoside (24)

Following the general procedure **A**, glycosyl acceptor **3a** (300.0 mg, 0.646 mmol) was coupled with thiofuranoside donor **2f** (475.0 mg, 0.775 mmol) to afford **24** (550 mg, 0.611 mmol, 84% yield, α:β=17:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.59 – 7.56 (m, 2H), 7.42 – 7.37 (m, 4H), 7.36 – 7.27 (m, 15H), 7.25 (t, *J* = 2.2 Hz, 4H), 7.23 – 7.17 (m, 8H), 5.14 (d, *J* = 4.1 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.78 – 4.71 (m, 4H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 2H), 4.57 (d, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.15 (dt, *J* = 6.6, 3.5 Hz, 2H), 4.05 (dd, *J* = 6.1, 3.6 Hz, 1H), 3.98 – 3.91 (m, 2H), 3.80 – 3.62 (m, 4H), 3.58 (dd, *J* = 11.2, 3.0 Hz, 1H), 3.46 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.34 (s, 3H), 0.96 (s, 9H).

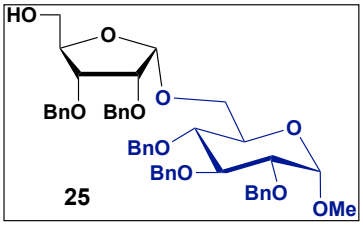
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.8, 138.5, 138.4, 138.4, 135.7, 135.6, 133.4, 133.2, 129.8, 129.8, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 102.2, 98.3, 83.1, 82.1, 80.1, 78.3, 77.9, 75.1, 73.5, 72.6, 72.4, 70.3, 66.7, 63.9, 55.2, 26.9, 19.3.

HRMS (ESI): calc. for $C_{63}H_{70}O_{10}SiNa$ (M+Na): 1037.4636; found: 1037.4616.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-5-hydroxy-α-D-ribofuranosyl)-α-D-glucopyranoside (25)

Silylated furanoside **24** (520 mg, 512 μmol) was dissolved in THF (0.1 M), and TBAF (1 M, 768 μL, 1.5 equiv.) was added to the reaction mixture at room temperature. Reaction progress was monitored by TLC, and upon complete consumption of the starting material, the reaction mixture was condensed and purified by column chromatography to afford **25** (329 mg, 0.425 mmol, 83% yield) as a viscous oil. R_f = 0.2 (hexane: EtOAc = 60:40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.37 – 7.19 (m, 23H), 5.15 (d, *J* = 3.9 Hz, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.83 (d, *J* = 11.0 Hz, 1H), 4.80 – 4.70 (m, 5H), 4.64 – 4.57 (m, 3H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.15 (dq, *J* = 8.8, 3.1 Hz, 2H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.89 (t, *J* = 5.6 Hz, 1H), 3.85 (dd, *J* = 6.3, 3.9 Hz, 1H), 3.78 (dd, *J* = 3.7, 1.6 Hz, 1H), 3.75 – 3.66 (m, 3H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 2H), 3.35 (s, 3H).

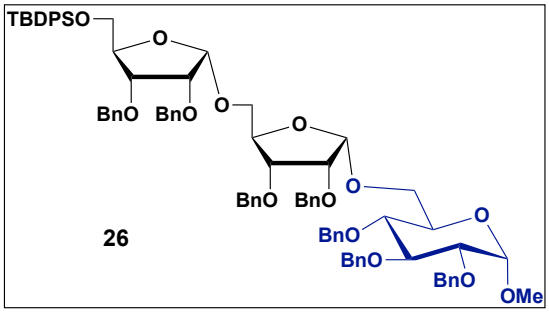


^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.8, 138.4, 138.3, 138.3, 128.5, 128.4, 128.4, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 102.4, 98.3, 82.2, 82.1, 80.1, 78.0, 78.0, 77.4, 77.1, 76.9, 75.9, 75.7, 75.2, 73.5, 72.7, 72.6, 70.3, 66.8, 62.4, 55.2.

HRMS (ESI): calc. for $C_{47}H_{52}O_{10}$ (M+Na): 799.3458; found: 799.3436.

Methyl (2,3-di-*O*-benzyl-5-*O*-tertbutyldiphenylsilyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (26)

Following the general procedure **A**, glycosyl acceptor **25** (283.0 mg, 364.26 µmol) was coupled with thiofuranoside donor **2f** (268.0 mg, 437.0 µmol) to afford **26** (345.0 mg, 259.85 µmol, 71% yield, α:β=12:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



26

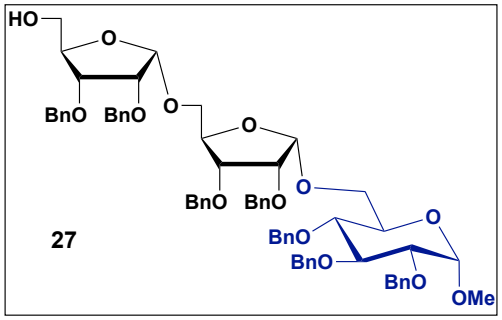
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (ddd, *J* = 15.7, 8.0, 1.6 Hz, 4H), 7.41 (dd, *J* = 7.4, 5.3 Hz, 2H), 7.38 – 7.26 (m, 26H), 7.25 – 7.16 (m, 14H), 7.14 – 7.04 (m, 3H), 5.08 (d, *J* = 4.1 Hz, 1H), 5.04 (d, *J* = 4.2 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.73 (dd, *J* = 11.5, 7.7 Hz, 2H), 4.69 – 4.66 (m, 2H), 4.64 (d, *J* = 2.8 Hz, 1H), 4.61 (d, *J* = 4.3 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.55 (d, *J* = 3.4 Hz, 1H), 4.49 (dd, *J* = 12.0, 6.7 Hz, 2H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.31 (d, *J* = 11.6 Hz, 1H), 4.26 – 4.23 (m, 1H), 4.14 – 4.09 (m, 2H), 4.04 (t, *J* = 3.3 Hz, 1H), 4.01 (dd, *J* = 6.2, 3.0 Hz, 1H), 3.96 – 3.90 (m, 2H), 3.86 (dd, *J* = 6.3, 4.2 Hz, 1H), 3.77 (dd, *J* = 11.2, 2.7 Hz, 1H), 3.71 (d, *J* = 7.3 Hz, 2H), 3.61 (dd, *J* = 11.2, 2.9 Hz, 2H), 3.54 (td, *J* = 11.1, 3.1 Hz, 2H), 3.41 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.32 (s, 3H), 0.96 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ δ 139.2, 138.9, 138.9, 138.7, 138.6, 138.5, 138.2, 135.7, 135.7, 135.6, 133.3, 133.1, 129.9, 129.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 102.2, 101.7, 98.3, 83.6, 82.3, 82.1, 80.1, 78.9, 78.8, 77.9, 77.4, 77.1, 76.9, 75.6, 75.1, 73.5, 72.7, 72.6, 72.3, 72.2, 70.4, 67.5, 66.5, 64.0, 26.9, 19.3.

HRMS (ESI): calc. for $C_{82}H_{90}O_{14}SiNa$ (M+Na): 1349.5998; found: 1349.5951.

Methyl (2,3-di-*O*-benzyl-5-hydroxy-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (27)

Silylated furanoside **26** (315 mg, 237 µmol) was dissolved in THF (0.1 M), and TBAF (1 M, 356 µL, 1.5 equiv.) was added to the reaction mixture at room temperature. Reaction progress was monitored by TLC, and upon complete consumption of the starting material, the reaction mixture was condensed and purified by column chromatography to afford **27** (210 mg, 0.193 mmol, 81% yield) as a viscous oil. R_f = 0.2 (hexane: EtOAc = 60:40).



27

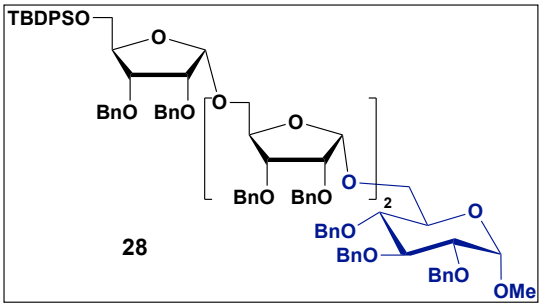
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 23H), 7.25 – 7.22 (m, 8H), 7.21 – 7.18 (m, 3H), 7.17 – 7.13 (m, 2H), 5.08 – 5.06 (m, 1H), 5.02 (d, *J* = 4.1 Hz, 1H), 4.92 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.80 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.72 (ddd, *J* = 16.0, 12.0, 7.5 Hz, 5H), 4.65 – 4.59 (m, 2H), 4.58 – 4.54 (m, 2H), 4.51 (dd, *J* = 11.8, 5.5 Hz, 3H), 4.42 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.25 (d, *J* = 3.3 Hz, 1H), 4.15 – 4.07 (m, 2H), 4.01 (q, *J* = 3.7 Hz, 1H), 3.96 – 3.89 (m, 2H), 3.87 (ddd, *J* = 6.7, 4.1, 1.1 Hz, 1H), 3.78 – 3.71 (m, 5H), 3.62 (td, *J* = 11.6, 2.2 Hz, 2H), 3.54 (dd, *J* = 11.2, 3.5 Hz, 1H), 3.47 – 3.40 (m, 2H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.9, 138.8, 138.6, 138.5, 138.4, 138.1, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 102.2, 101.9, 98.3, 82.8, 82.1, 82.1, 80.1, 78.8, 78.5, 77.9, 77.4, 77.1, 76.9, 76.6, 75.6, 75.5, 75.1, 73.5, 72.7, 72.7, 72.4, 72.3, 70.3, 67.6, 66.6, 62.6, 55.2.

HRMS (ESI): calc. for $C_{66}H_{72}O_{14}Na$ (M+Na): 1111.482; found: 1111.4789.

Methyl (2,3-di-*O*-benzyl-5-*O*-tertbutyldiphenylsilyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (28)

Following the general procedure **A**, glycosyl acceptor **27** (180.0 mg, 165.25 µmol) was coupled with thiofuranoside donor **2f** (122.0 mg, 198.29 µmol) to afford **28** (178.0 mg, 108.53 µmol, 66% yield, α:β=7:1) as a colorless viscous oil. R_f= 0.2 (hexane: EtOAc = 70:30).

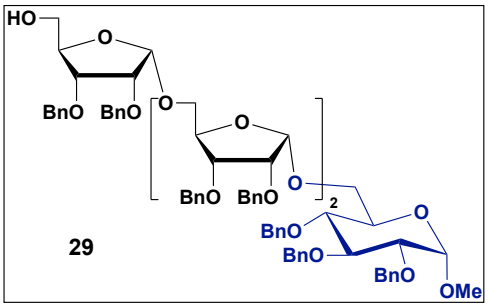


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.44 – 7.40 (m, 2H), 7.36 (tt, *J* = 6.7, 1.1 Hz, 6H), 7.33 – 7.27 (m, 20H), 7.24 – 7.20 (m, 15H), 7.18 – 7.15 (m, 5H), 7.13 – 7.09 (m, 3H), 5.04 (d, *J* = 4.2 Hz, 1H), 5.02 (d, *J* = 4.3 Hz, 1H), 4.98 – 4.96 (m, 1H), 4.91 (dd, *J* = 11.2, 1.1 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.76 – 4.69 (m, 3H), 4.67 (d, *J* = 4.5 Hz, 1H), 4.65 (s, 1H), 4.62 (d, *J* = 11.3 Hz, 3H), 4.58 (d, *J* = 1.8 Hz, 1H), 4.56 – 4.51 (m, 3H), 4.49 (s, 1H), 4.47 (d, *J* = 4.6 Hz, 1H), 4.44 (s, 1H), 4.41 (d, *J* = 11.1 Hz, 1H), 4.35 (dd, *J* = 11.8, 9.6 Hz, 2H), 4.28 – 4.20 (m, 3H), 4.15 – 4.04 (m, 5H), 4.03 – 3.99 (m, 1H), 3.93 – 3.86 (m, 4H), 3.79 – 3.73 (m, 2H), 3.71 (d, *J* = 5.4 Hz, 2H), 3.62 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.59 – 3.55 (m, 2H), 3.51 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.46 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.42 (d, *J* = 1.2 Hz, 1H), 3.32 (d, *J* = 1.1 Hz, 3H), 0.97 (d, *J* = 1.2 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.0, 139.0, 138.9, 138.8, 138.7, 138.6, 138.5, 138.2, 135.7, 135.7, 135.7, 133.3, 133.1, 129.9, 129.9, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.3, 127.3, 102.2, 101.7, 101.7, 101.4, 98.3, 98.0, 83.7, 82.7, 82.4, 82.1, 80.1, 77.4, 77.1, 76.9, 67.7, 67.3, 66.5, 64.1, 55.1, 26.9, 19.3.

HRMS (ESI): calc. for $C_{101}H_{110}O_{18}SiNa$ (M+Na): 1661.7359; found: 1661.7309.

Methyl (2,3-di-*O*-benzyl-5-hydroxy-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (29)



Silylated furanoside **28** (140 mg, 237 µmol) was dissolved in THF (0.1 M), and TBAF (1 M, 128 µL, 1.5 equiv.) was added to the reaction mixture at room temperature. Reaction progress was monitored by TLC, and upon complete consumption of the starting material, the reaction mixture was condensed and purified by column chromatography to afford **29** (90 mg, 0.65 mmol, 75% yield) as a viscous oil. R_f= 0.2 (hexane: EtOAc = 60:40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 23H), 7.26 – 7.20 (m, 19H), 7.18 – 7.16 (m, 3H), 7.15 – 7.11 (m, 2H), 5.02 (dd, *J* = 4.2, 2.4 Hz, 2H), 4.96 (dd, *J* = 4.3, 1.4 Hz, 1H), 4.91 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 11.1 Hz, 1H), 4.75 – 4.70 (m, 4H), 4.67 – 4.63 (m, 3H), 4.60 (s, 1H), 4.58 (d, *J* = 3.8 Hz, 1H), 4.55 (d, *J* = 3.7 Hz, 1H), 4.53 – 4.48 (m, 3H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 4.38 – 4.34 (m, 2H), 4.27 (d, *J* = 11.7 Hz, 1H), 4.25 – 4.21 (m, 2H), 4.13 (ddd, *J* = 7.1, 5.4, 2.4 Hz, 2H), 4.11 – 4.08 (m, 1H), 4.06 (dd, *J* = 6.3, 2.9 Hz, 1H), 4.01 (t, *J* = 3.6 Hz, 1H), 3.93 – 3.85 (m, 4H), 3.78 – 3.70 (m, 6H), 3.66 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.57 (d, *J* = 11.2 Hz, 1H), 3.51 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.48 (d, *J* = 3.1 Hz, 1H), 3.45 (q, *J* = 2.2 Hz, 1H), 3.40 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.32 (s, 3H).

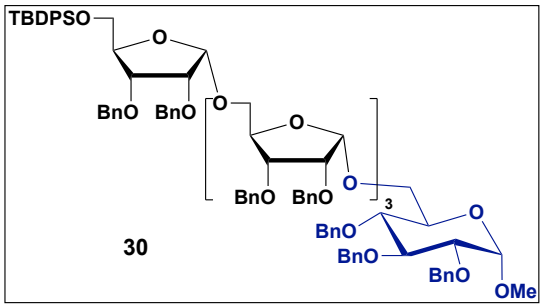
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.0, 138.9, 138.8, 138.6, 138.5, 138.4, 138.1, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3,

102.2, 101.9, 101.8, 98.3, 82.9, 82.4, 82.3, 82.1, 80.1, 79.2, 79.0, 78.6, 77.9, 75.6, 75.6, 75.1, 73.5, 72.7, 72.7, 72.7, 72.4, 72.1, 72.1, 70.3, 67.7, 67.4, 66.5, 62.7, 60.5, 55.2, 55.1.

HRMS (ESI): calc. for $C_{85}H_{92}O_{18}Na$ (M+Na): 1423.6181; found: 1423.6142.

Methyl (2,3-di-*O*-benzyl-5-*O*-tertbutyldiphenylsilyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (30)

Following the general procedure **A**, glycosyl acceptor **29** (85.0 mg, 60.0 μmol) was coupled with thiofuranoside donor **2f** (44.0 mg, 72.0 μmol) to afford **30** (70.0 mg, 35.31 μmol, 59% yield, α:β=5:1) as a colorless viscous oil. R_f = 0.2 (hexane: EtOAc = 70:30).



30

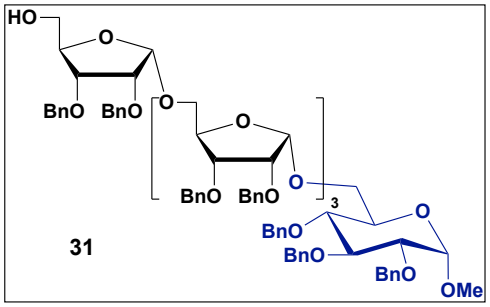
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.59 – 7.57 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 (dd, *J* = 7.3, 1.1 Hz, 4H), 7.35 – 7.27 (m, 24H), 7.25 (d, *J* = 1.8 Hz, 8H), 7.24 – 7.20 (m, 23H), 7.19 – 7.10 (m, 14H), 5.04 (d, *J* = 4.2 Hz, 1H), 5.00 (d, *J* = 4.2 Hz, 1H), 4.96 (d, *J* = 4.2 Hz, 1H), 4.92 – 4.89 (m, 2H), 4.81 – 4.78 (m, 1H), 4.75 – 4.69 (m, 3H), 4.68 – 4.57 (m, 9H), 4.55 (d, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 4.0 Hz, 1H), 4.49 (d, *J* = 4.1 Hz, 1H), 4.47 – 4.43 (m, 3H), 4.40 (d, *J* = 5.2 Hz, 1H), 4.37 (d, *J* = 4.4 Hz, 1H), 4.34 (d, *J* = 6.2 Hz, 1H), 4.31 – 4.27 (m, 1H), 4.25 (d, *J* = 11.5 Hz, 2H), 4.21 – 4.19 (m, 1H), 4.18 (d, *J* = 6.2 Hz, 1H), 4.14 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.07 (ddq, *J* = 14.8, 9.1, 3.1 Hz, 7H), 4.01 (dd, *J* = 6.3, 3.0 Hz, 1H), 3.94 – 3.90 (m, 2H), 3.88 (dd, *J* = 6.3, 4.3 Hz, 2H), 3.85 (dd, *J* = 6.3, 4.4 Hz, 1H), 3.76 (dd, *J* = 4.3, 2.6 Hz, 1H), 3.73 (d, *J* = 2.6 Hz, 1H), 3.71 (d, *J* = 5.9 Hz, 3H), 3.64 – 3.57 (m, 3H), 3.56 – 3.55 (m, 1H), 3.52 (dd, *J* = 11.1, 3.5 Hz, 1H), 3.46 – 3.38 (m, 4H), 3.31 (s, 3H), 0.97 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.1, 139.0, 138.9, 138.8, 138.7, 138.6, 138.5, 138.2, 135.7, 135.7, 135.7, 133.3, 133.1, 129.9, 129.9, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.4, 127.3, 127.3, 102.2, 101.8, 101.7, 98.2, 98.0, 83.7, 82.8, 82.7, 82.4, 82.1, 80.1, 79.4, 79.3, 79.0, 78.9, 77.9, 76.5, 76.5, 76.0, 75.6, 75.1, 73.5, 73.4, 72.7, 72.6, 72.3, 72.1, 72.0, 71.9, 70.4, 67.7, 67.5, 67.2, 66.4, 64.1, 55.1, 26.9, 19.3.

HRMS (ESI): calc. for $C_{120}H_{130}O_{22}SiNa$ (M+Na): 1973.8721; found: 1973.8652.

Methyl (2,3-di-*O*-benzyl-5-hydroxy-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (31)

Silylated furanoside **30** (60 mg, 31.0 μmol) was dissolved in THF (0.1 M), and TBAF (1 M, 45 μL, 1.5 equiv.) was added to the reaction mixture at room temperature. Reaction progress was monitored by TLC, and upon complete consumption of the starting material, the reaction mixture was condensed and purified by column chromatography to afford **31** (40 mg, 0.023 mmol, 75% yield) as a viscous oil. R_f = 0.2 (hexane: EtOAc = 60:40).



31

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 19.7, 7.5, 4.6 Hz, 27H), 7.23 – 7.16 (m, 36H), 7.12 – 7.09 (m, 3H), 5.01 (dd, *J* = 9.9, 4.3 Hz, 2H), 4.95 (d, *J* = 4.5 Hz, 1H), 4.92 – 4.88 (m, 2H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.71 (td, *J* = 11.7, 4.5 Hz, 5H), 4.66 – 4.56 (m, 7H), 4.55 – 4.50 (m, 3H), 4.49 – 4.47 (m, 2H), 4.46 – 4.44 (m, 2H), 4.42 – 4.30 (m, 5H), 4.28 – 4.23 (m, 3H), 4.19 (d, *J* = 10.9 Hz, 2H), 4.16 – 4.12 (m, 2H), 4.08 (ddd, *J* = 16.4, 7.5, 2.9 Hz, 6H), 4.03 – 3.99 (m, 2H), 3.85 (ddd, *J* = 16.4, 6.3, 4.1

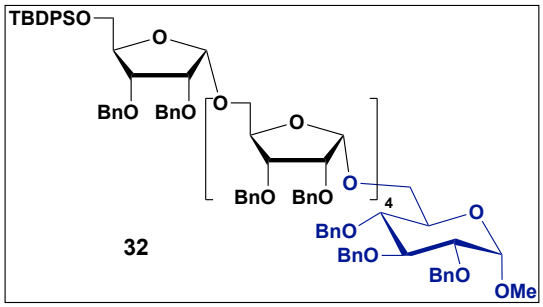
Hz, 5H), 3.78 – 3.68 (m, 8H), 3.67 (d, *J* = 3.4 Hz, 1H), 3.64 (d, *J* = 3.1 Hz, 1H), 3.56 (d, *J* = 11.2 Hz, 1H), 3.51 (dd, *J* = 11.2, 3.3 Hz, 1H), 3.47 (d, *J* = 3.5 Hz, 1H), 3.43 (dt, *J* = 14.1, 4.9 Hz, 4H), 3.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.0, 138.9, 138.9, 138.8, 138.7, 138.5, 138.5, 138.5, 138.4, 138.1, 128.5, 128.5, 128.5, 128.5, 128.3, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.3, 102.2, 101.9, 101.8, 101.7, 98.2, 83.0, 82.6, 82.6, 80.1, 79.3, 79.2, 79.0, 78.6, 77.9, 76.5, 76.4, 75.6, 75.1, 73.5, 72.8, 72.7, 72.7, 72.7, 72.4, 72.1, 72.0, 70.4, 67.7, 67.5, 67.3, 66.5, 62.7, 60.5, 55.1.

HRMS (ESI): calc. for $C_{104}H_{112}O_{22}Na$ (M+Na): 1735.7543; found: 1735.7436

Methyl (2,3-di-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-ribofuranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (32)

Following the general procedure **A**, glycosyl acceptor **31** (28.0 mg, 16.0 μmol) was coupled with thiofuranoside donor **2f** (11.81 mg, 19.27 μmol) to afford **32** (22.0 mg, 9.52 μmol, 59% yield, α:β=5:1) as a colorless viscous oil. R_f = 0.2 (hexane: EtOAc = 70:30).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 5H), 7.42 – 7.39 (m, 3H), 5.03 (d, *J* = 4.3 Hz, 1H), 4.99 (d, *J* = 4.2 Hz, 1H), 4.96 (d, *J* = 4.5 Hz, 1H), 4.91 – 4.86 (m, 4H), 4.80 – 4.76 (m, 2H), 4.72 (d, *J* = 12.0 Hz, 2H), 4.68 (d, *J* = 5.8 Hz, 2H), 4.66 – 4.56 (m, 11H), 4.53 (dd, *J* = 8.1, 4.4 Hz, 2H), 4.49 (d, *J* = 12.2 Hz, 2H), 4.45 (d, *J* = 3.4 Hz, 2H), 4.43 – 4.37 (m, 5H), 4.35 (d, *J* = 5.1 Hz, 1H), 4.33 – 4.28 (m, 2H), 4.26 – 4.17 (m, 6H), 4.14 (q, *J* = 6.1 Hz, 3H), 4.11 – 4.02 (m, 11H), 4.00 (dd, *J* = 6.2, 2.8 Hz, 2H), 3.93 – 3.80 (m, 8H), 3.77 – 3.67 (m, 9H), 3.60 – 3.48 (m, 6H), 3.45 – 3.36 (m, 5H), 3.30 (s, 3H), 3.26 (s, 1H), 0.96 (s, 9H).

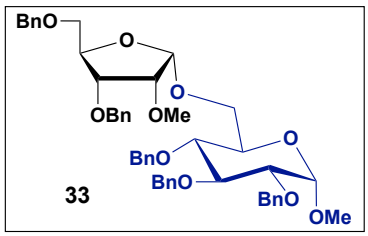
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 139.0, 138.9, 138.8, 138.6, 138.5, 138.2, 135.7, 135.6, 133.3, 133.1, 129.9, 129.9, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 102.2, 101.7, 98.2, 83.7, 82.8, 82.4, 82.1, 80.1, 78.9, 72.7, 72.3, 72.0, 71.9, 70.4, 64.1, 58.3, 55.1, 26.9, 19.3.

HRMS (ESI): calc. for $C_{139}H_{150}O_{26}SiNa$ (M+Na): 2286.0082; found: 2285.9999.

6. Influence of C2-functional group at the selectivity outcomes.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-methoxy-3,5-di-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (33)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 26.0 μmol) was coupled with thiofuranoside donor **2g** (12.0 mg, 31.0 μmol) to afford **33** (19.2 mg, 24.3 μmol, 75% yield, α:β=5:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).

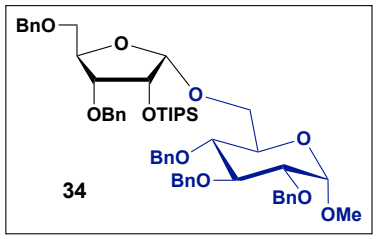


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 18H), 7.25 – 7.19 (m, 7H), **5.16 (d, *J* = 4.2 Hz, 1H)**, 4.95 (d, *J* = 11.0 Hz, 1H), 4.84 – 4.75 (m, 4H), 4.67 – 4.62 (m, 2H), **4.57 (d, *J* = 3.6 Hz, 1H)**, 4.51 – 4.40 (m, 3H), 4.19 – 4.10 (m, 2H), 3.99 – 3.88 (m, 2H), 3.79 – 3.75 (m, 1H), 3.70 – 3.65 (m, 3H), 3.54 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.45 (s, 3H), 3.42 (d, *J* = 3.6 Hz, 1H), 3.37 (d, *J* = 1.4 Hz, 1H), 3.34 (s, 3H).s

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.7, 138.4, 138.2, 138.1, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 101.9, 98.2, 82.2, 81.6, 80.6, 79.9, 77.9, 75.7, 75.1, 73.5, 72.5, 70.1, 69.9, 66.7, 59.0, 55.2. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-*O*-triisopropylsilyl-3,5-di-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (**34**)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 26.0 μmol) was coupled with thiofuranoside donor 2**h** (17.0 mg, 31.0 μmol) to afford **34** (19.7 mg, 21.11 μmol, 82% yield, α:β=6:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).

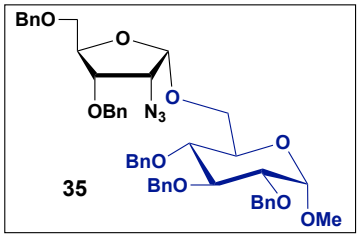


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 13H), 7.25 – 7.09 (m, 11H), **4.99 (d, *J* = 4.4 Hz, 1H),** 4.93 (d, *J* = 11.1 Hz, 1H), 4.86 – 4.79 (m, 3H), **4.76 (d, *J* = 3.2 Hz, 1H),** 4.70 (d, *J* = 18.3 Hz, 1H), 4.66 – 4.60 (m, 2H), 4.54 – 4.49 (m, 2H), 4.44 (dd, *J* = 11.8, 1.6 Hz, 2H), 4.25 (dd, *J* = 6.2, 4.4 Hz, 1H), 4.19 – 4.15 (m, 1H), 4.10 (dd, *J* = 11.0, 3.1 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.81 (dd, *J* = 6.1, 2.5 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.56 (dd, *J* = 11.1, 1.3 Hz, 1H), 3.49 – 3.43 (m, 3H), 3.31 (s, 3H), 1.05 (d, *J* = 4.7 Hz, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.1, 139.0, 138.5, 138.2, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.9, 127.7, 127.7, 127.5, 127.4, 127.3, 102.9, 98.2, 82.5, 82.2, 79.7, 78.1, 78.0, 77.4, 75.6, 75.1, 74.5, 73.5, 73.4, 72.9, 70.7, 70.4, 66.5, 18.2, 18.1, 12.4. The data are identical to the literature report.[1]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-azido-3,5-di-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (**35**)

Following the general procedure **A**, glycosyl acceptor **1a** (12.0 mg, 26.0 μmol) was coupled with thiofuranoside donor **2i** (12.4 mg, 31.0 μmol) to afford **35** (15.3 mg, 19.08 μmol, 74% yield, α:β=6:1) as a colorless viscous oil. R_f = 0.3 (hexane: EtOAc = 70:30).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 17H), 7.22 (tdd, *J* = 9.8, 7.6, 5.9 Hz, 9H), **5.26 (d, *J* = 4.6 Hz, 1H),** 4.94 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 2H), 4.76 (d, *J* = 11.1 Hz, 1H), 4.72 – 4.67 (m, 2H), 4.64 (d, *J* = 12.0 Hz, 1H), **4.57 (d, *J* = 3.5 Hz, 1H)**, 4.51 – 4.45 (m, 2H), 4.39 (d, *J* = 12.1 Hz, 1H), 4.22 (dd, *J* = 10.9, 2.7 Hz, 1H), 4.18 (q, *J* = 3.6 Hz, 1H), 4.01 (dd, *J* = 6.9, 3.3 Hz, 1H), 3.96 (dd, *J* = 9.7, 8.2 Hz, 1H), 3.77 – 3.71 (m, 2H), 3.64 (dd, *J* = 11.0, 1.6 Hz, 1H), 3.53 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.41 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.34 (s, 4H), 3.26 (dd, *J* = 6.9, 4.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.8, 138.3, 137.8, 137.5, 128.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 103.7, 98.4, 82.7, 82.0, 80.0, 78.9, 75.7, 75.1, 73.7, 73.5, 73.1, 70.0, 69.7, 66.7, 61.1, 55.2.

HRMS (ESI): calc. for $C_{47}H_{51}O_9N_3Na$ (M+Na): 824.3523; found: 824.3505.

7. Plausible mechanistic pathway(s) of for the activation of conventional thiofuranosides.

These mechanistic studies provide valuable insight into the reaction pathways involved. Initially, $Fe(OTf)_3$ undergoes ligand exchange with the glycosyl acceptor, while the thioglycoside donor **I** become activated through chelation with NIS, forming complex **II**. This intermediate then dissociates to generate the furanosyl sulfonium ion **IV**, with the concurrent release of succinimide **III**. The sulfonium ion **IV** subsequently transforms into the reactive oxocarbenium ion **VI**, a key intermediate in glycosylation chemistry, along with the formation of phenylsulfenyl iodide **V**. From this point, the oxocarbenium ion **VI** can proceed

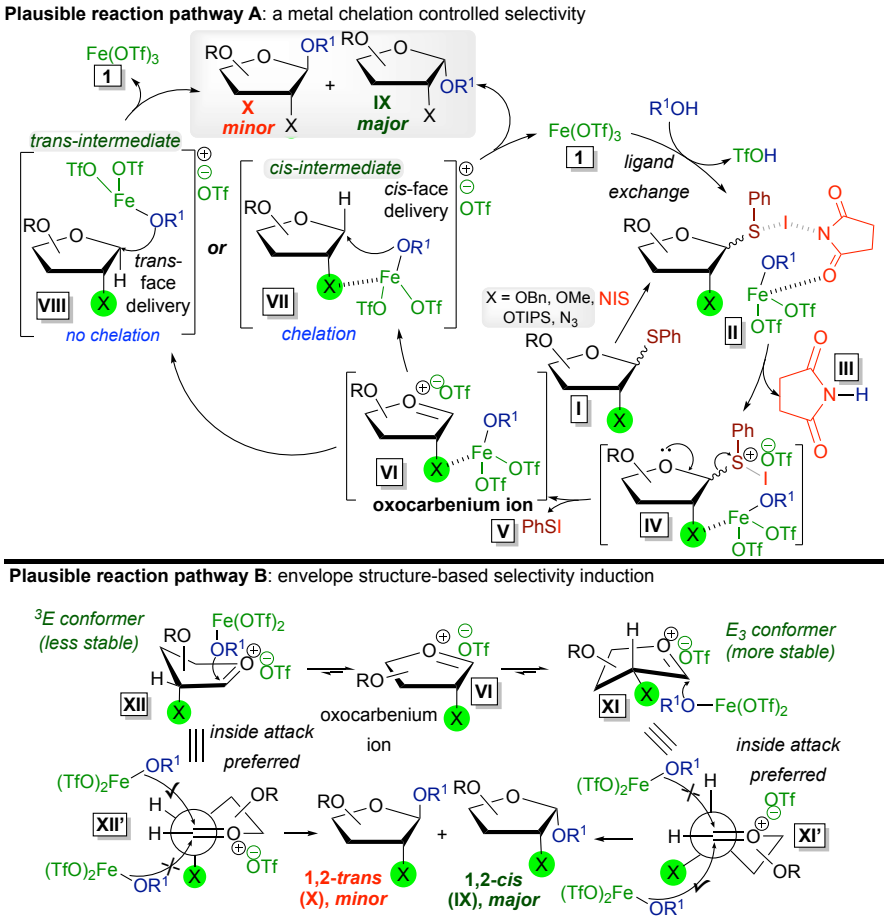


Figure S-6. Plausible mechanistic pathway(s) for the activation of conventional thioglycosides.

along two plausible mechanistic routes. In path **A**, it exists as two intermediates: a more stable Fe-chelated species **VII** and a less stable non-chelated form **VIII**. Intermediate **VII** delivers the acceptor from the *cis* face, leading to the major 1,2-*cis* product **IX**, whereas intermediate **VIII** allows delivery from the trans face, resulting in the minor 1,2-*trans* product **X**. Alternatively, in path **B**, the oxocarbenium ion adopts two envelope conformations: E_3 (**XI**, more stable) and ^3E (**XII**, less stable). The nucleophilic attack occurs from the inner face of each conformer, with the E_3 conformation furnishing the major 1,2-*cis* furanoside **IX** and the ^3E conformation leading to the minor 1,2-*trans* furanoside **X**.

References:

1. B. Ghosh, A. Alber, C. W. Lander, Y. Shao, K. M. Nicholas and I. Sharma, *Org. Lett.*, 2024, **26**, 9436-9441.
2. A. G. Santana, C. G. Francisco, E. Suárez and C. C. González, *J. Org. Chem.*, 2010, **75**, 5371-5374.
3. (a) B. Ghosh, A. Alber, C. W. Lander, Y. Shao, K. M. Nicholas and I. Sharma, *ACS Catal.*, 2024, **14**, 1037-1049; (b) N. Oka, R. Kajino, K. Takeuchi, H. Nagakawa and K. Ando, *J. Org. Chem.*, 2014, **79**, 7656-7664.
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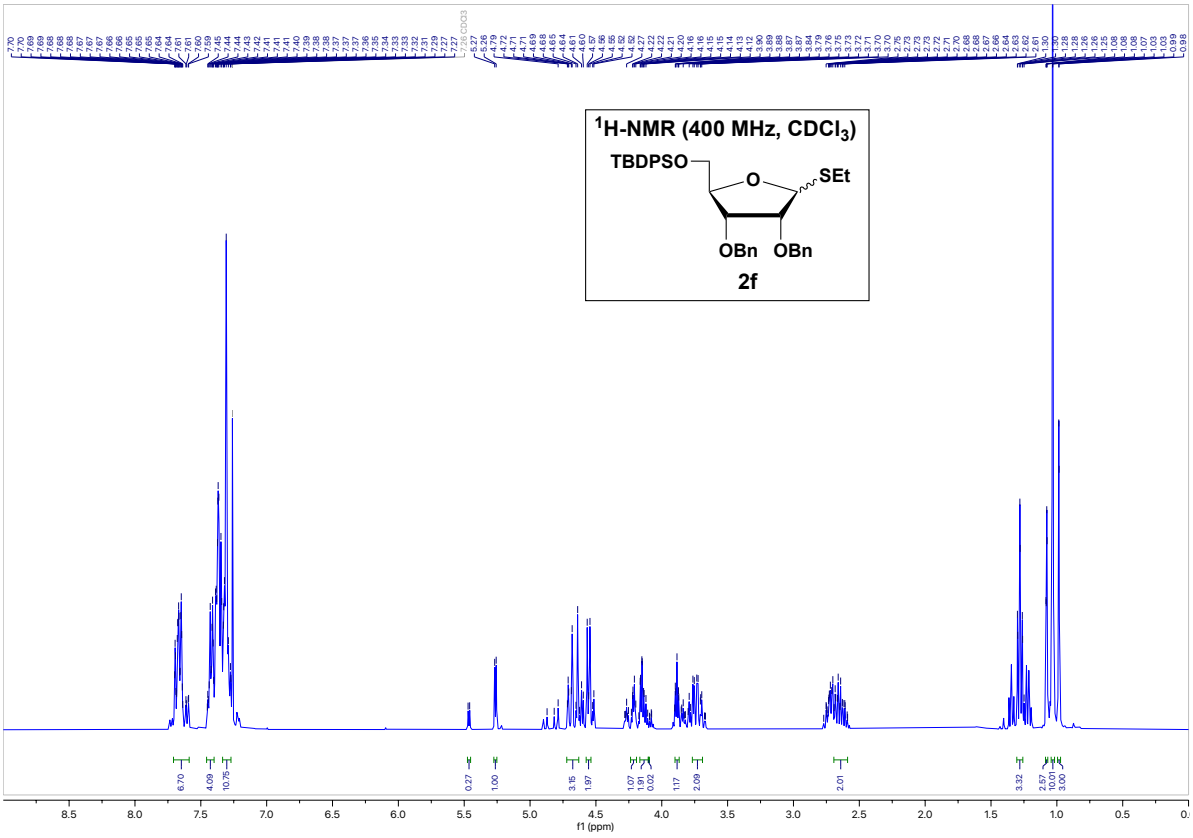
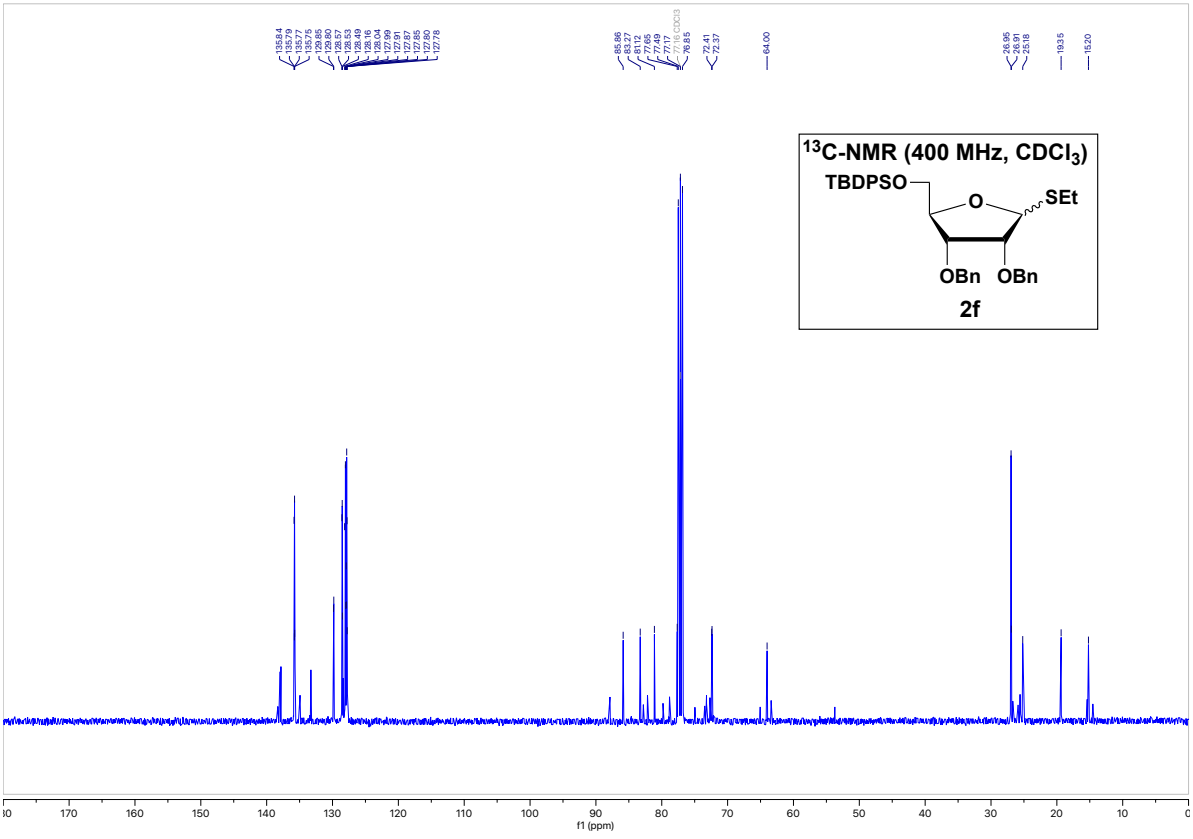
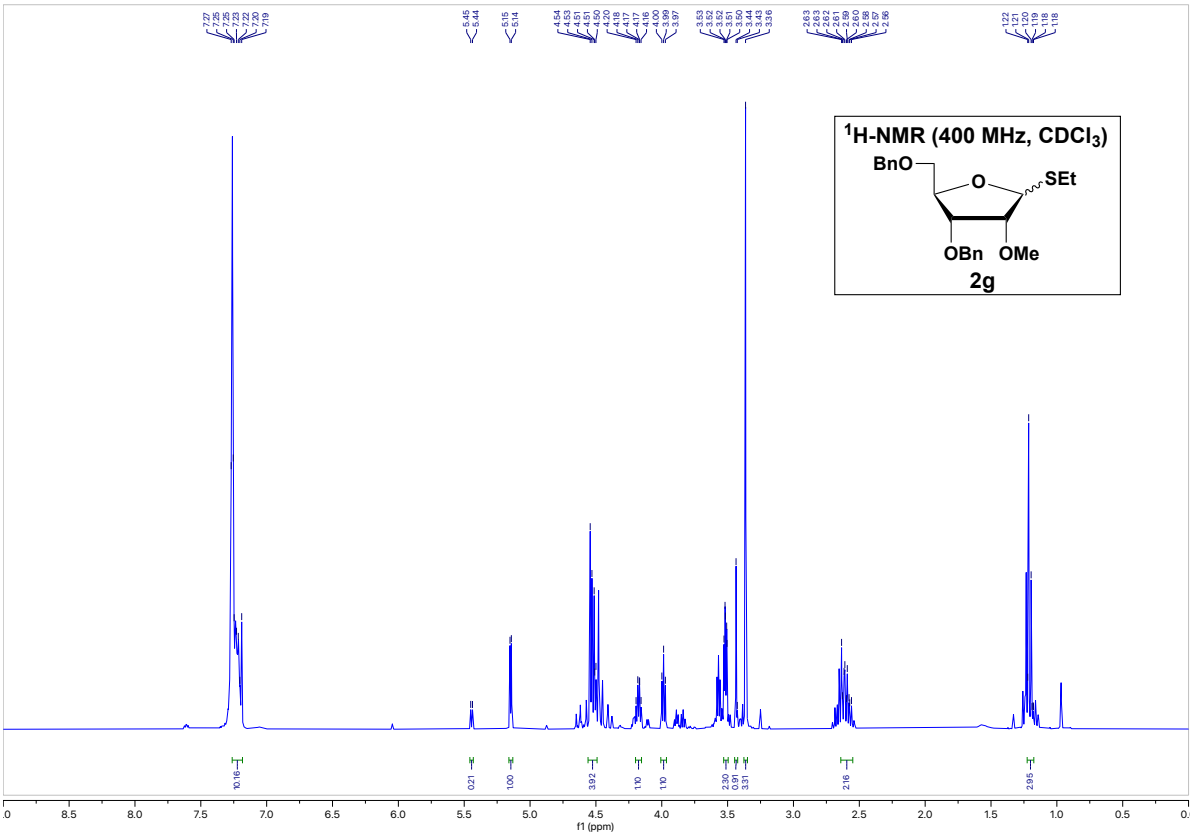
5. Y. J. Lee, K. Lee, E. H. Jung, H. B. Jeon and K. S. Kim, *Org. Lett.*, 2005, **7**, 3263-3266.

NMR Spectrums:



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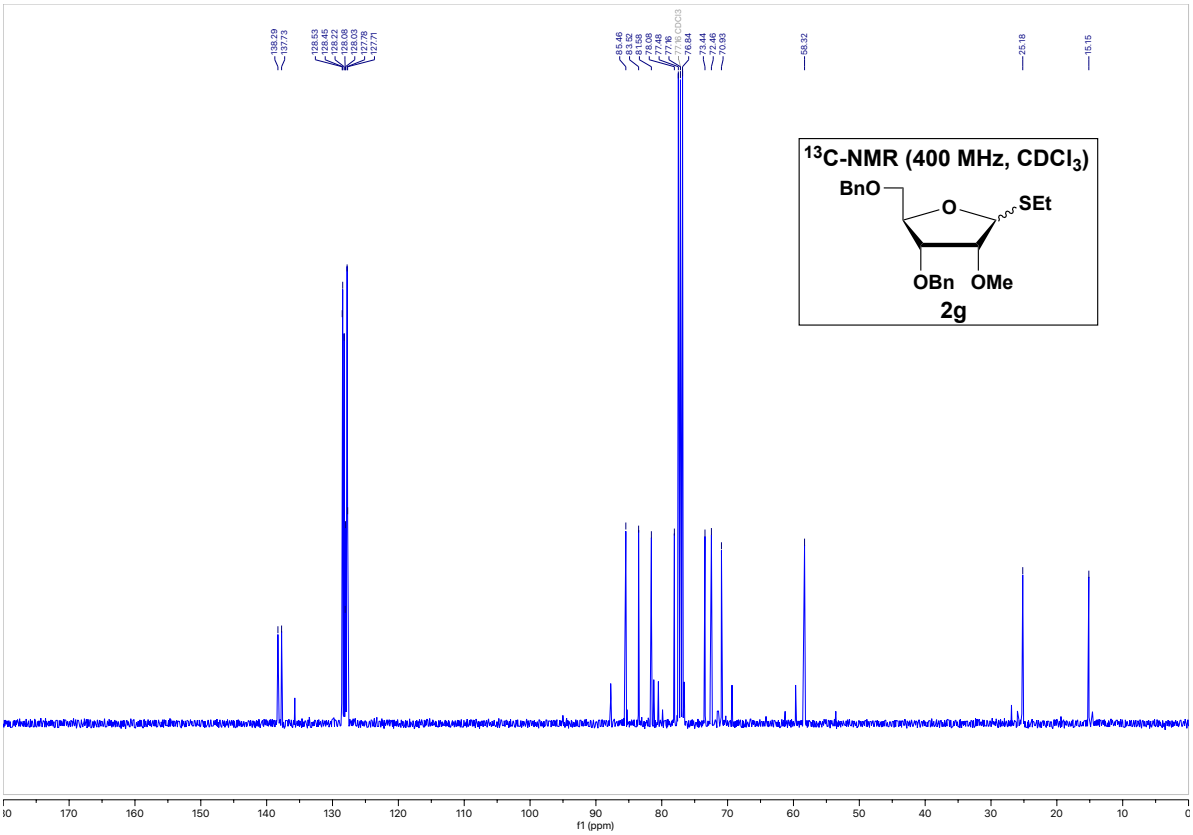
BnO
O
SEt
OBn
OMe
2g
f1 (ppm)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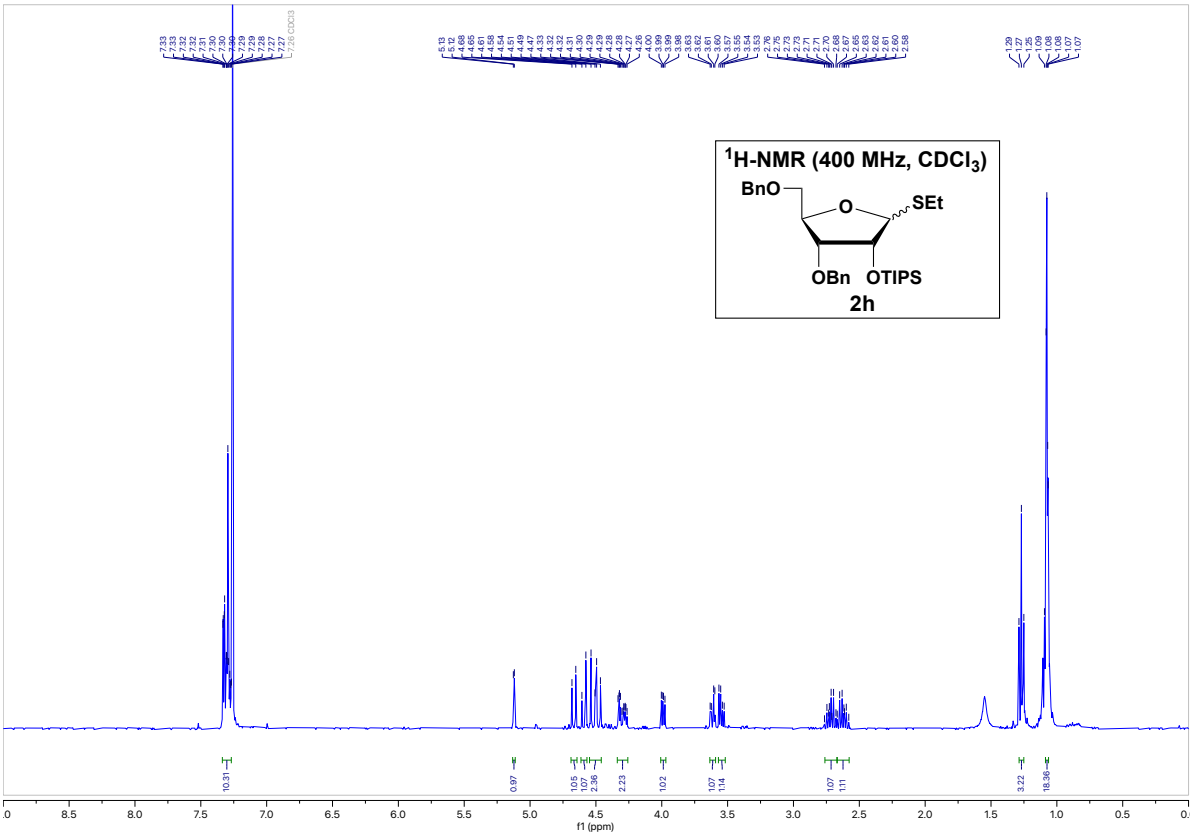
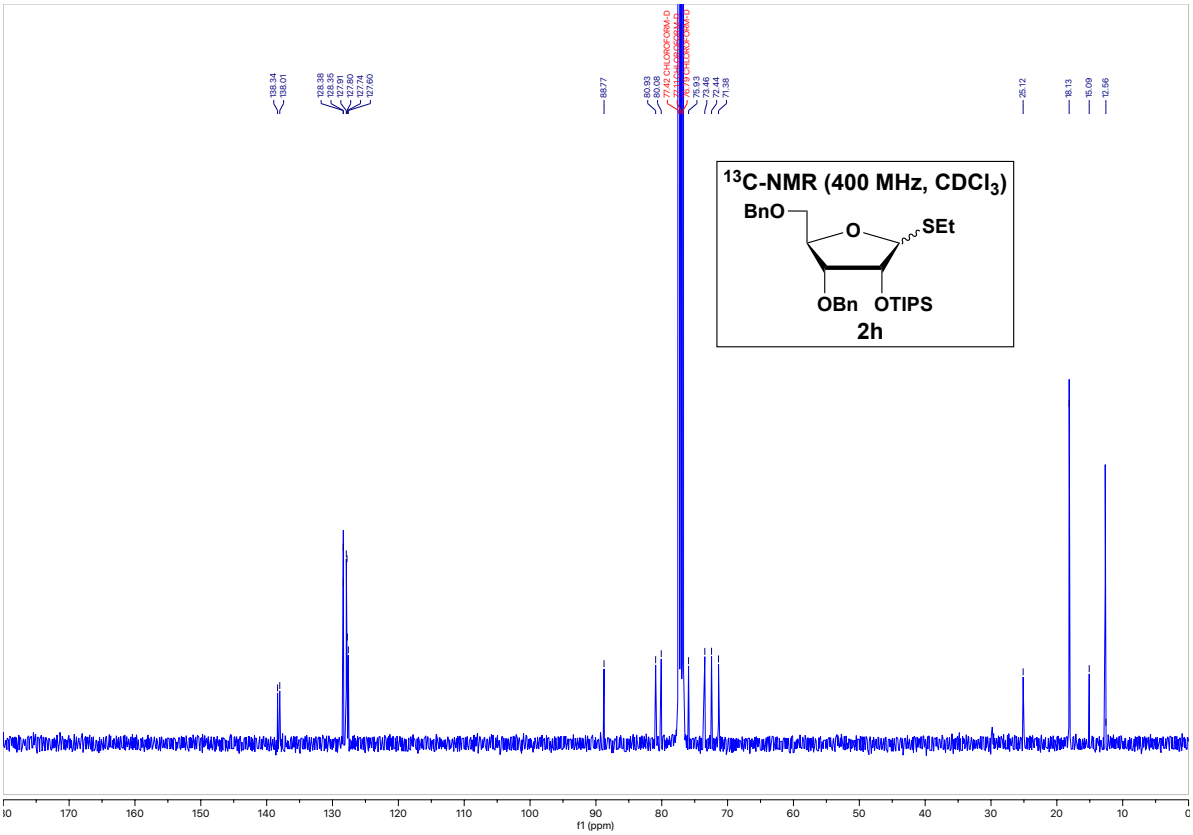
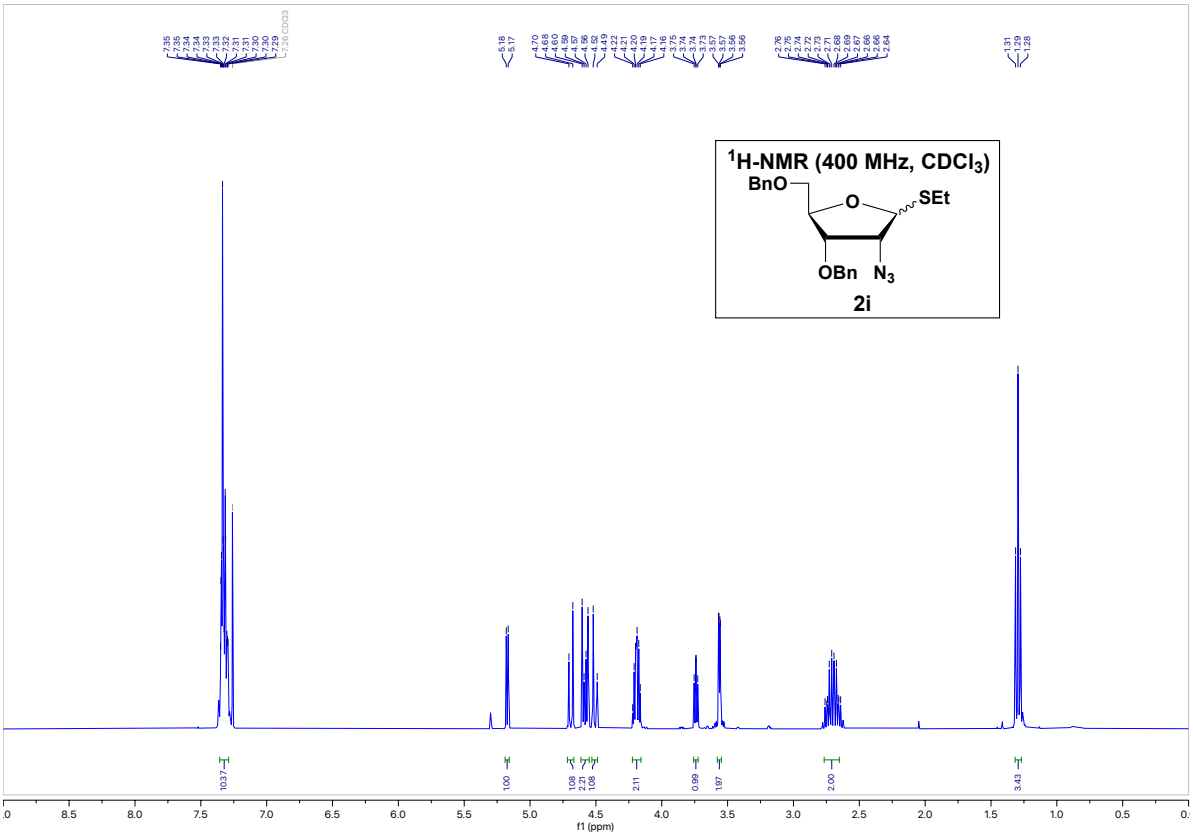
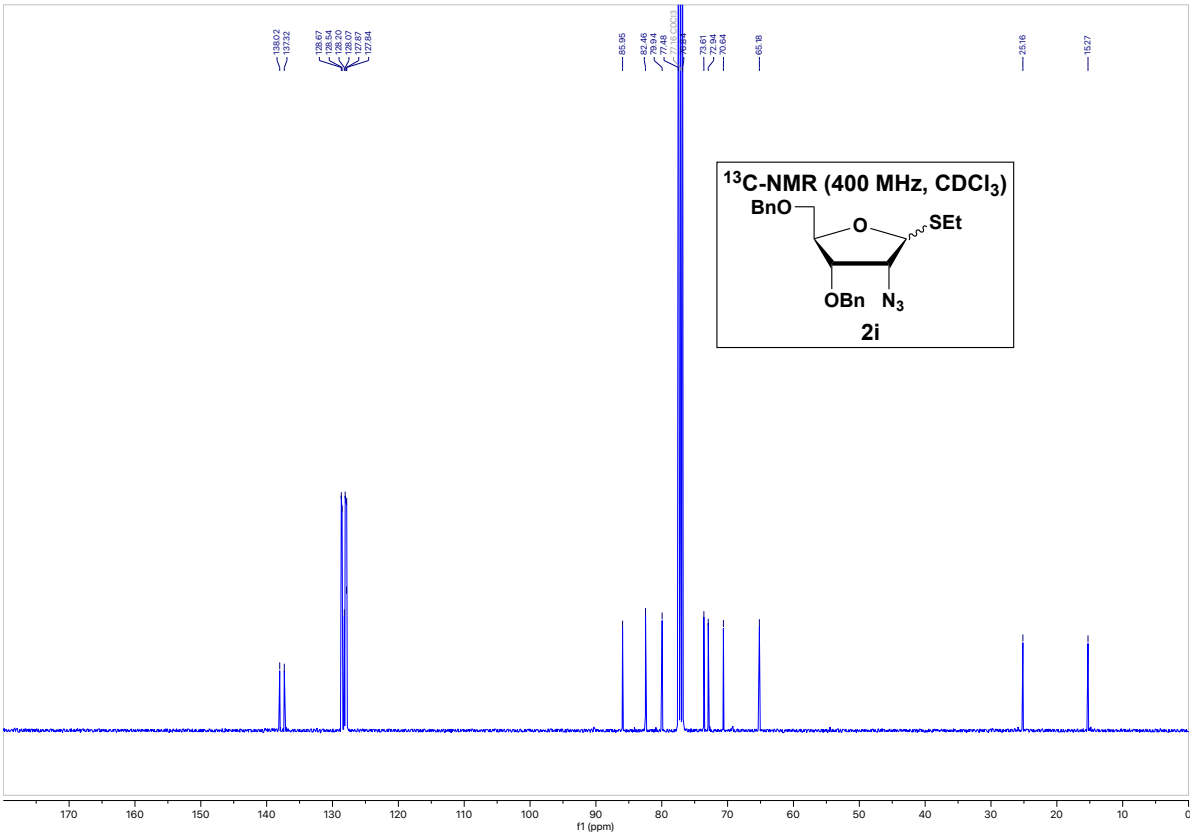
BnO
O
SEt
OBn
OMe
2g
f1 (ppm)


^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
SEt
OBn
OTIPS
2h
f1 (ppm)


^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
SEt
OBn
OTIPS
2h
f1 (ppm)


^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
SEt
OBn
N_3
2i
f1 (ppm)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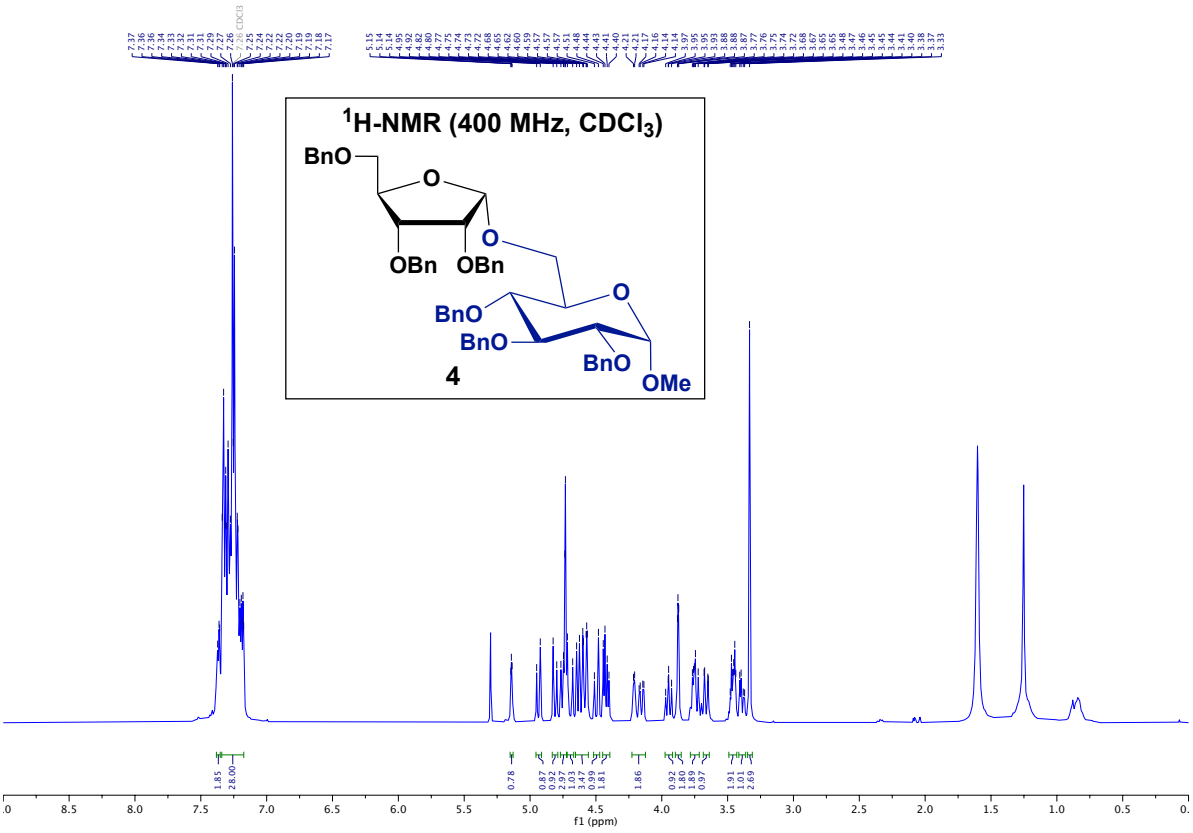
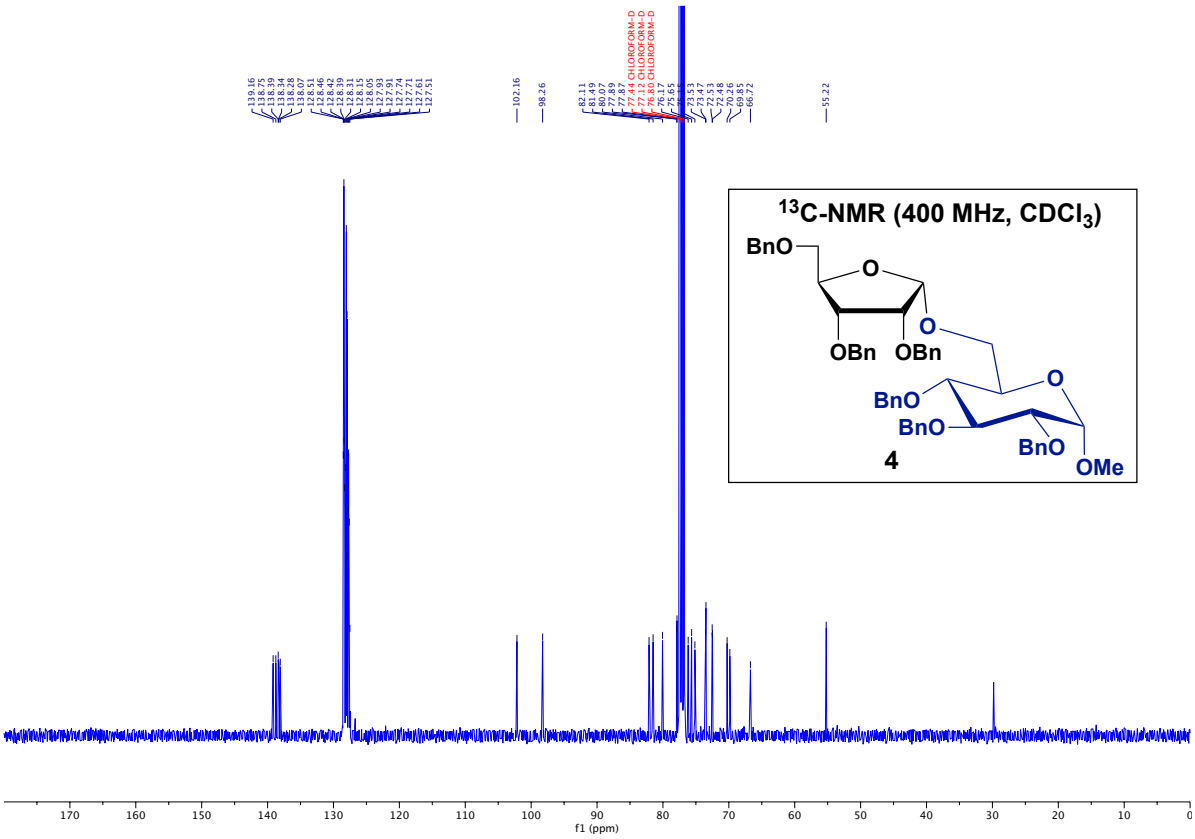
BnO
O
SEt
OBn
N_3
2i
f1 (ppm)


^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
O
BnO
BnO
BnO
OMe
4
f1 (ppm)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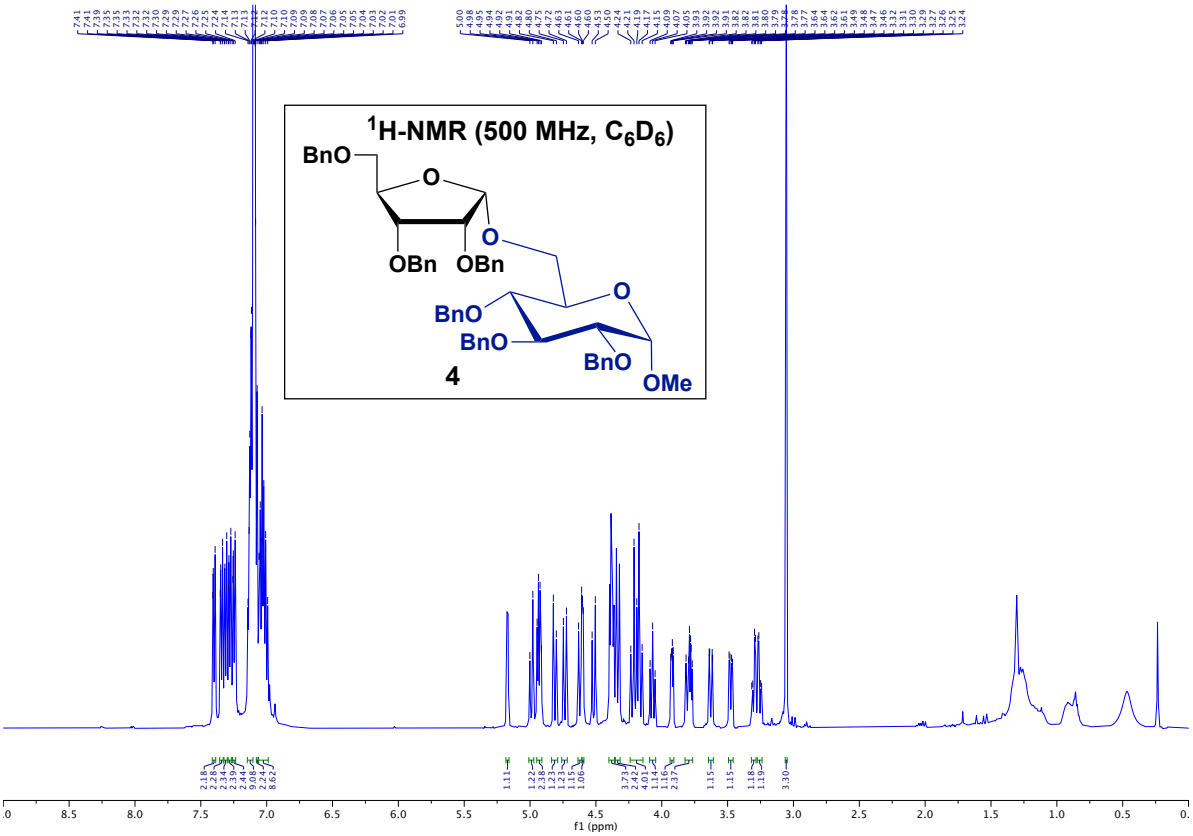
BnO
O
O
OBn OBn
O
BnO
BnO
BnO
OMe
4
f1 (ppm)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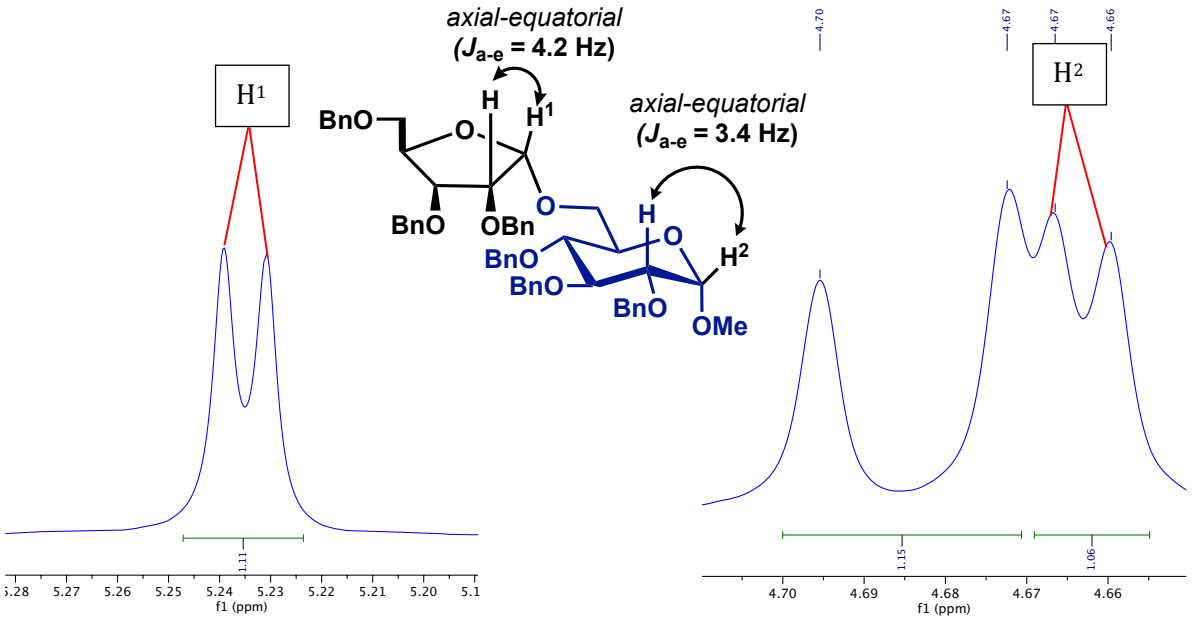
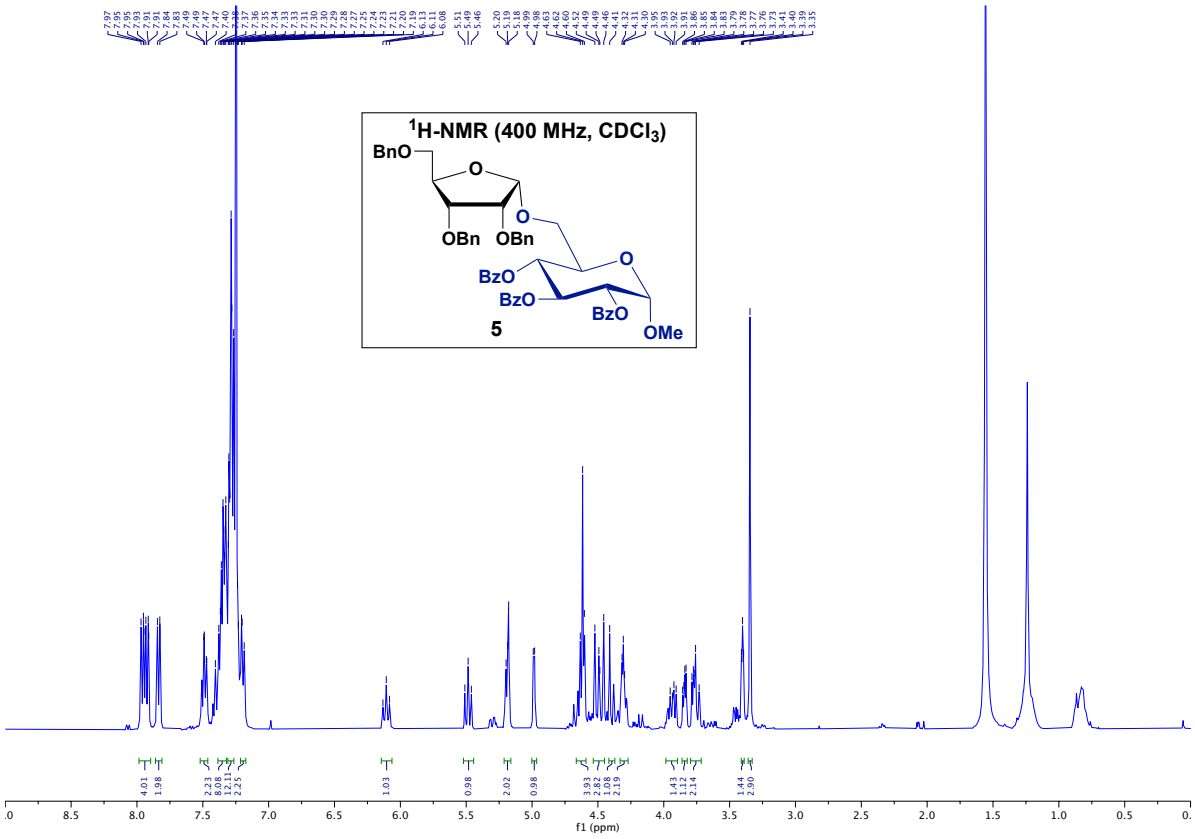
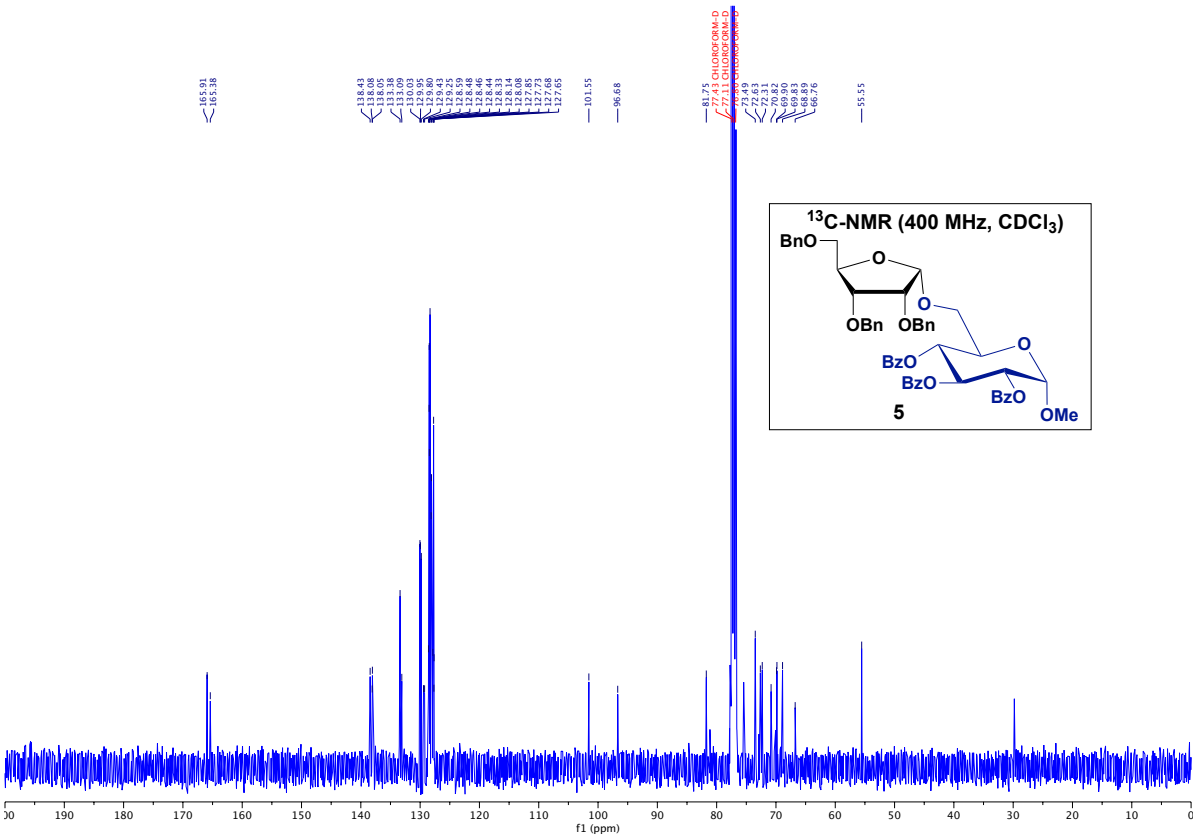
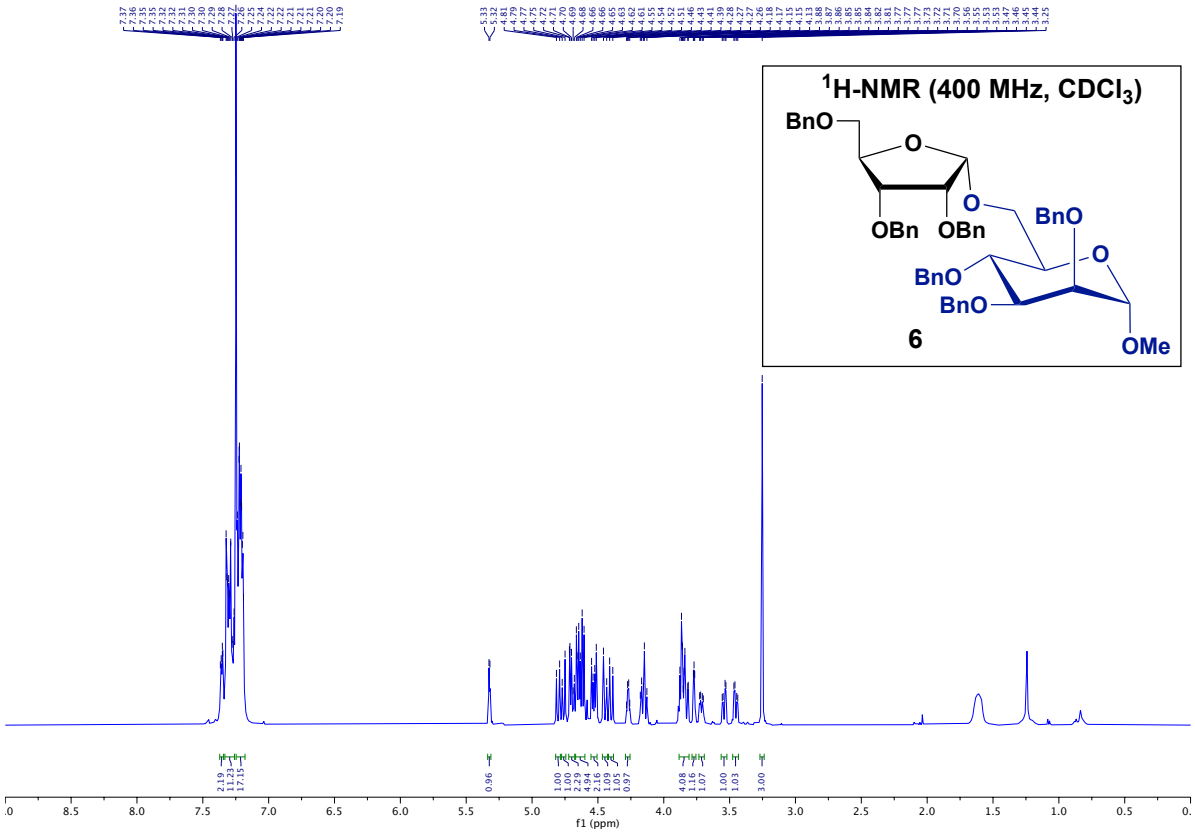
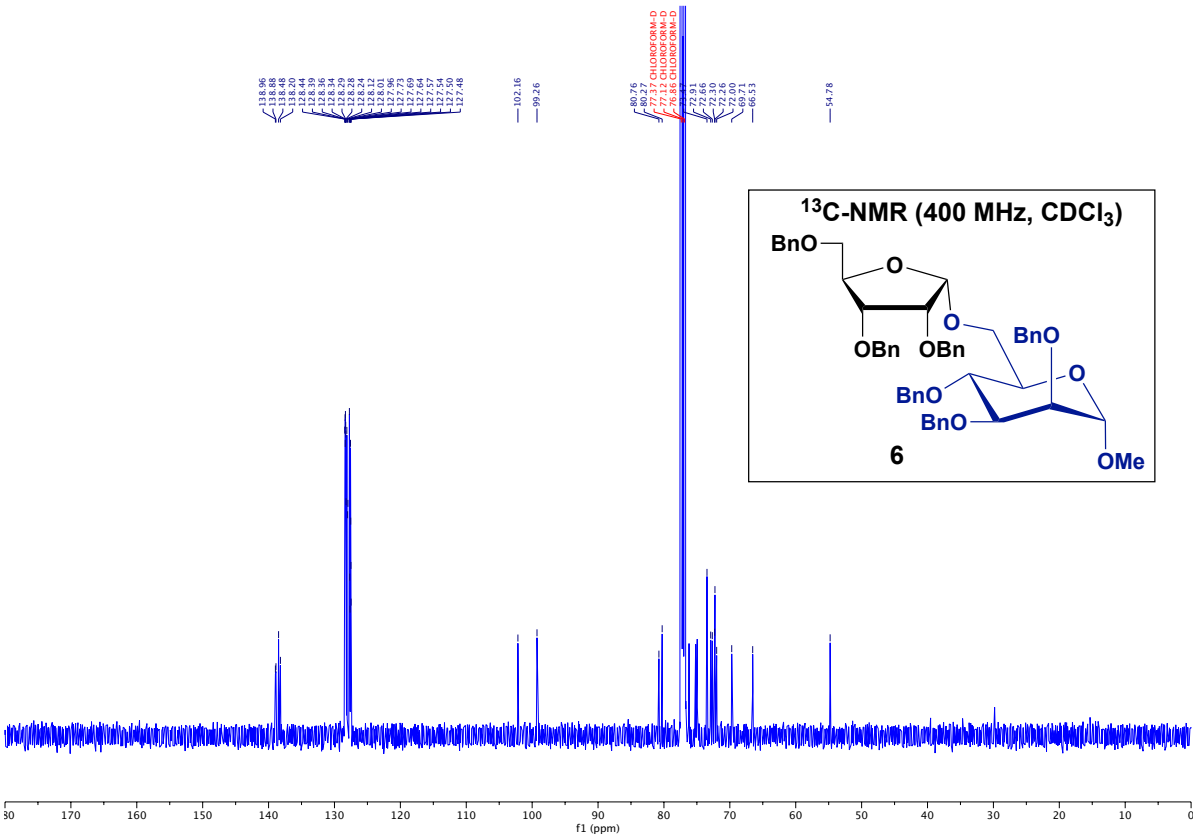
BnO
O
OBn
OBn
O
BnO
BnO
BnO
O
OMe
4
f1 (ppm)

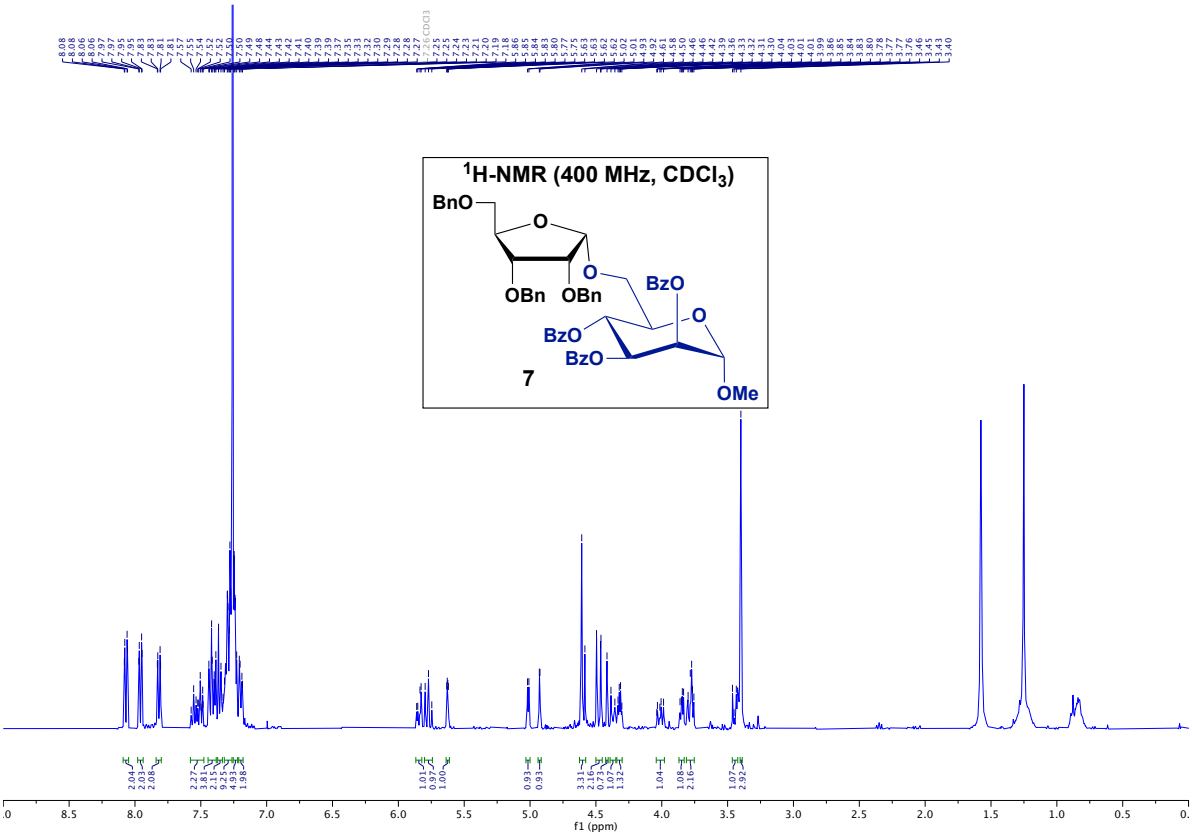

axial-equatorial
(J_{a-e} = 4.2 Hz)
axial-equatorial
(J_{a-e} = 3.4 Hz)
H1
H2
BnO
BnO
OBn
BnO
BnO
BnO
OMe
f1 (ppm)

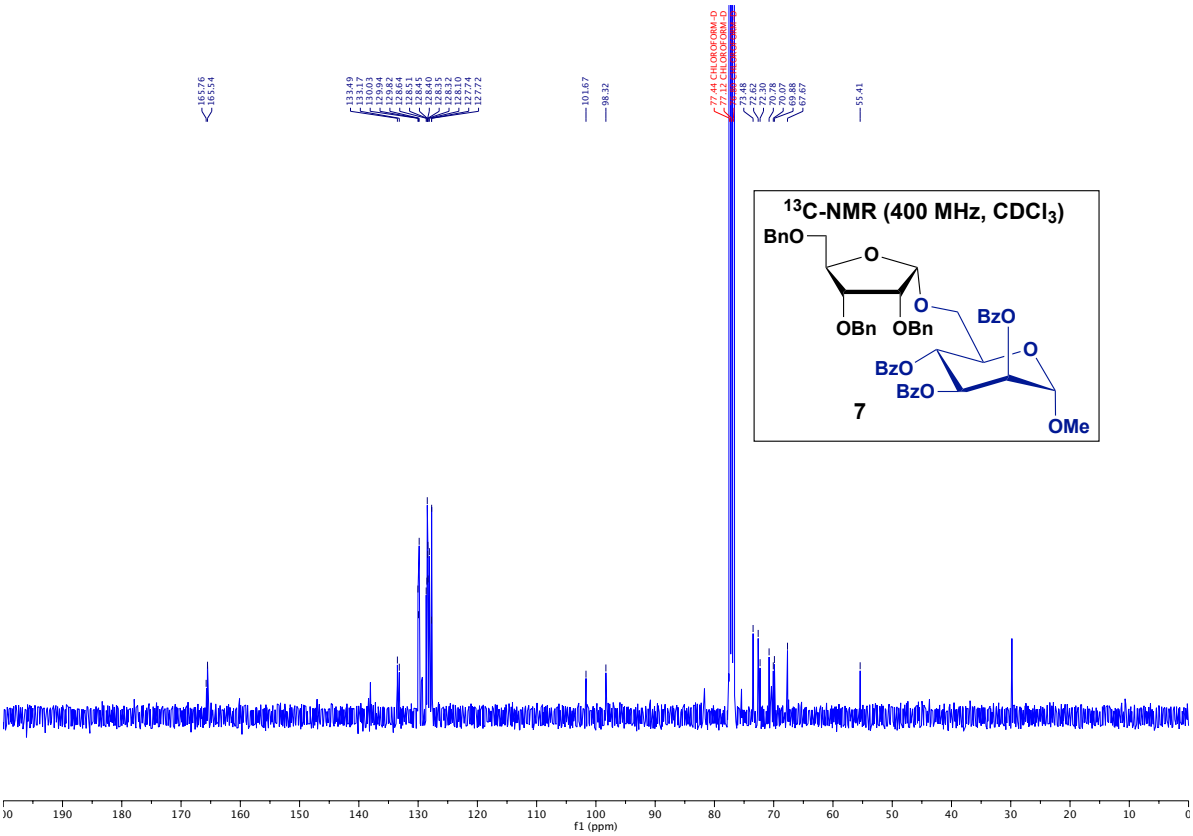

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
O
BzO
BzO
BzO
OMe
5
f1 (ppm)

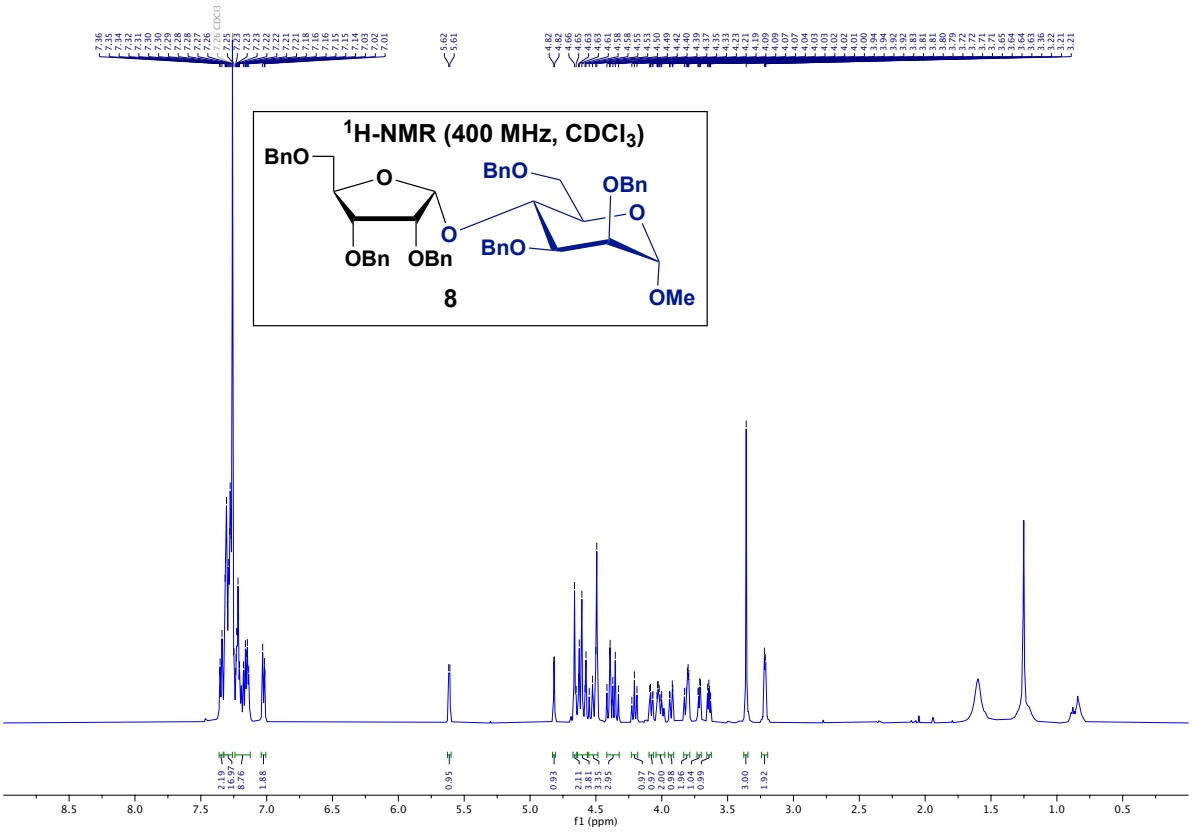

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
O
BzO
BzO
BzO
OMe
5
f1 (ppm)

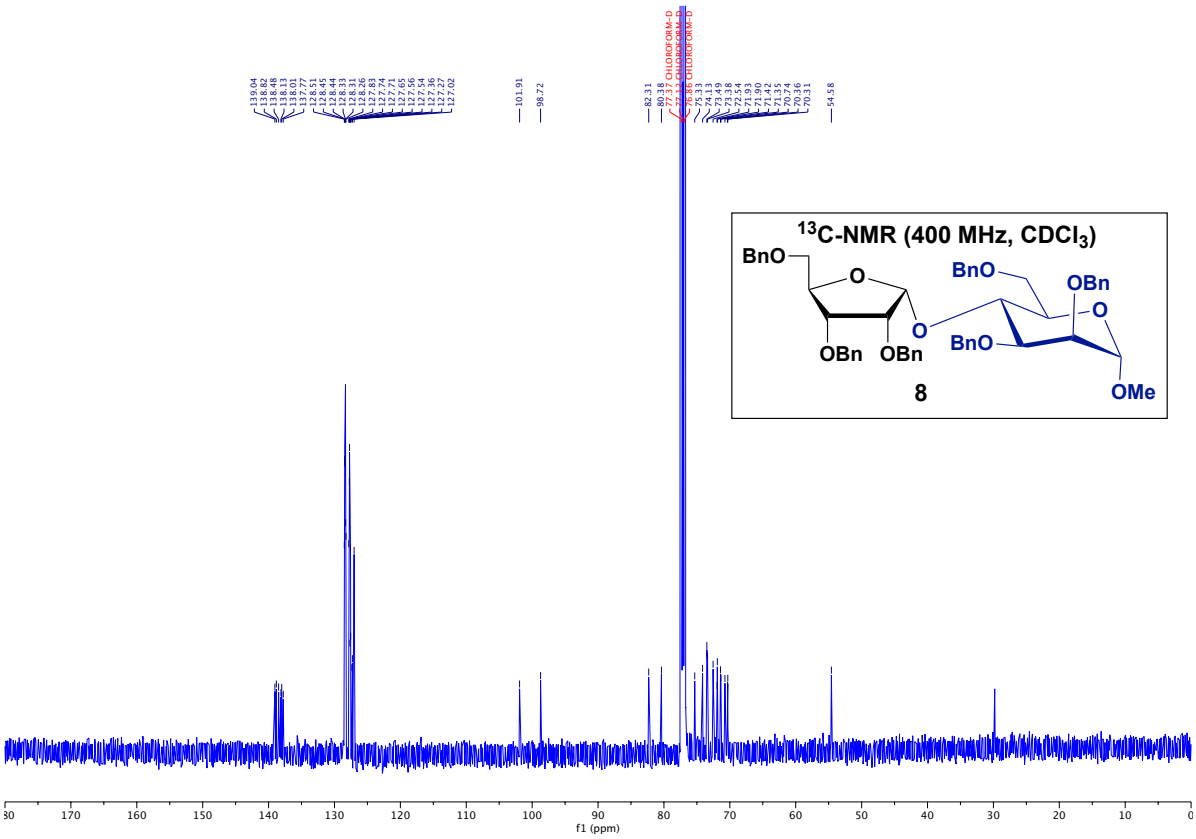

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
OBn OBn
O
BnO
O
BnO
BnO
6
OMe
f1 (ppm)

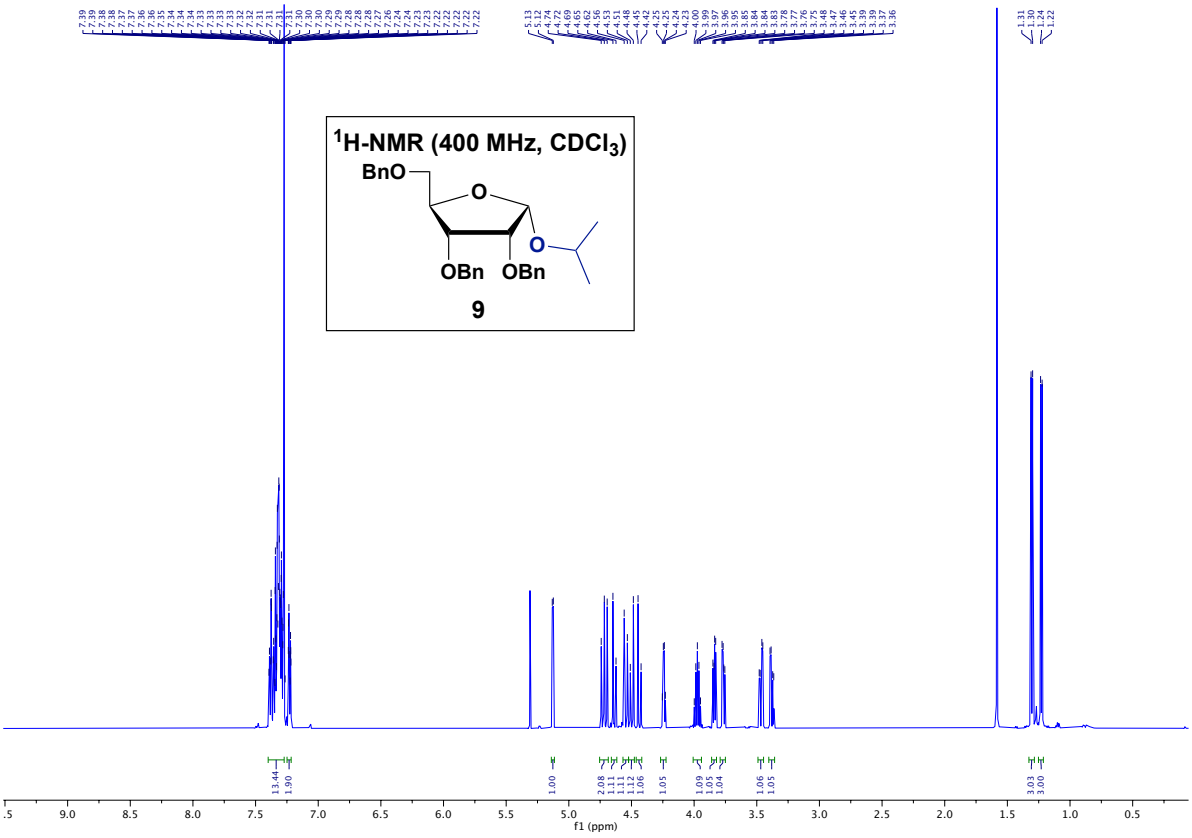

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
OBn OBn
O
BnO
O
BnO
BnO
6
OMe
f1 (ppm)

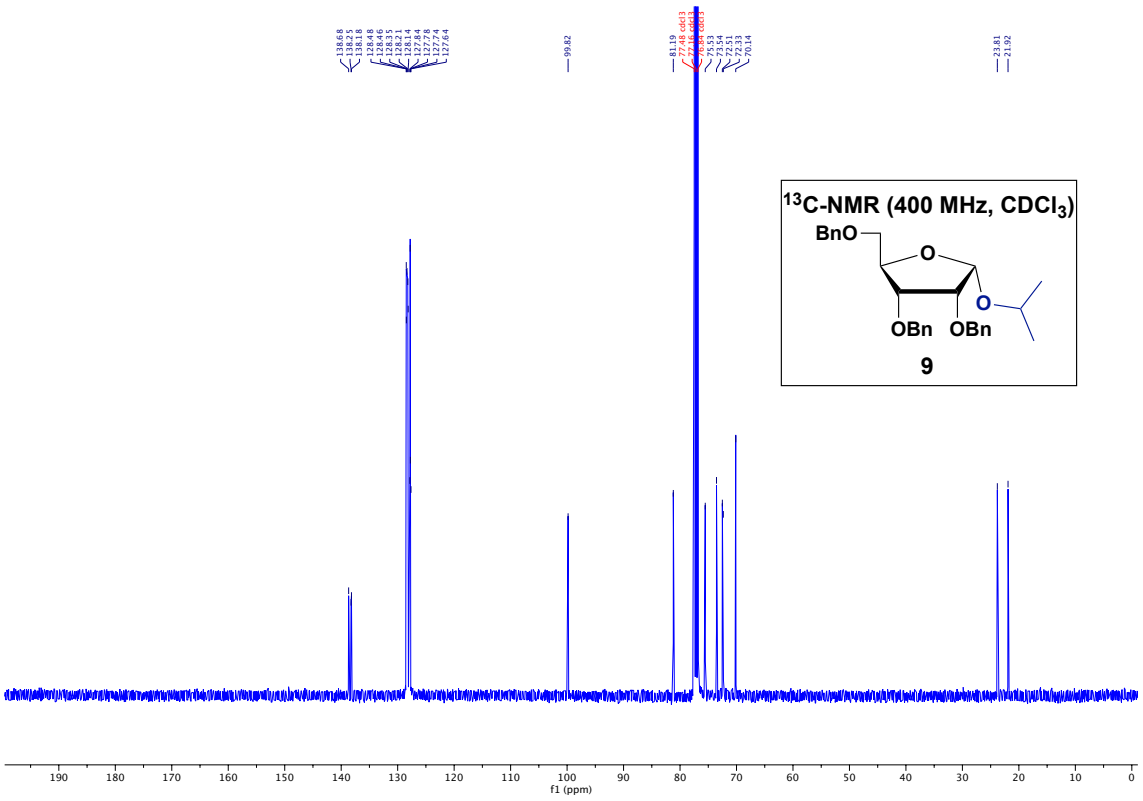

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn
OBn
BzO
O
BzO
BzO
OMe
7
f1 (ppm)

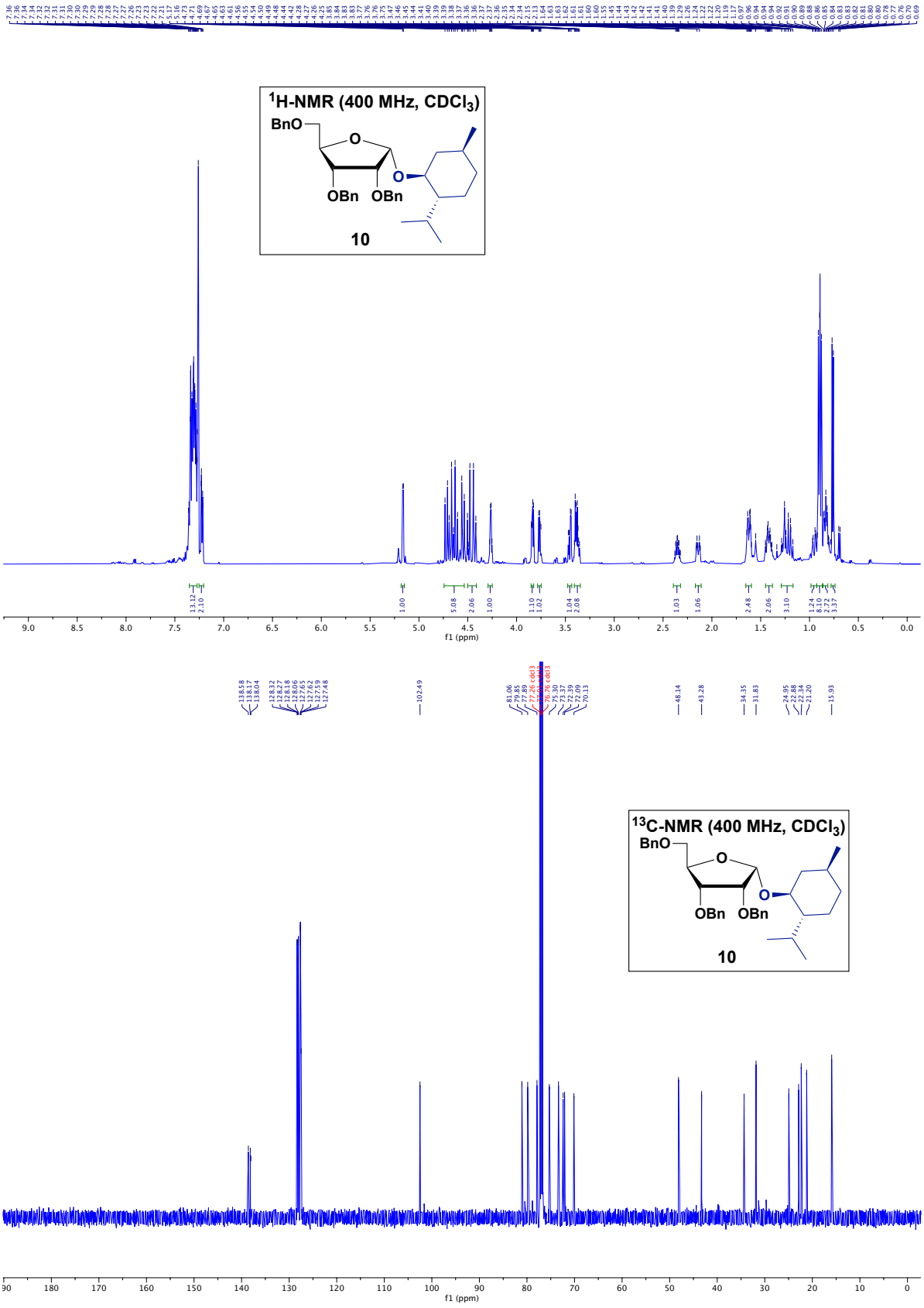

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn
OBn
BzO
O
BzO
BzO
OMe
7
f1 (ppm)

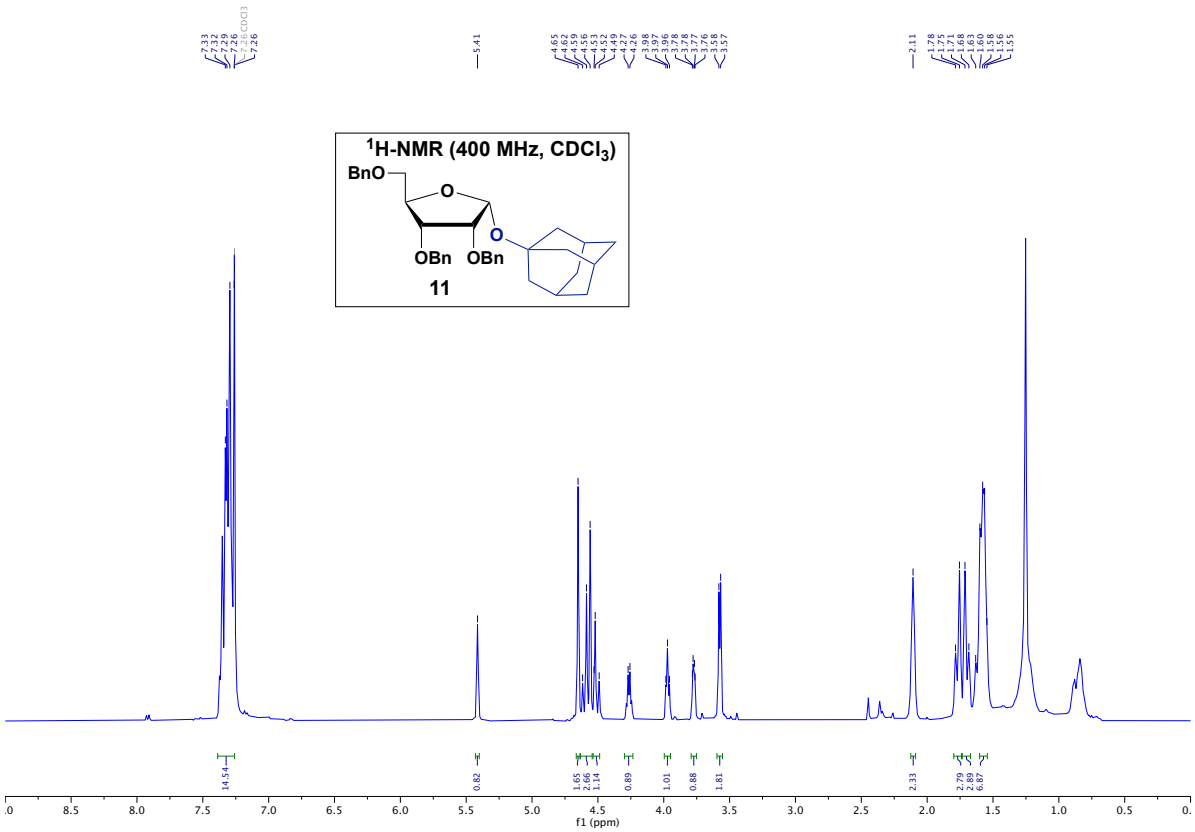

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
OBn
OBn
O
BnO
BnO
OBn
O
BnO
OMe
8
f1 (ppm)

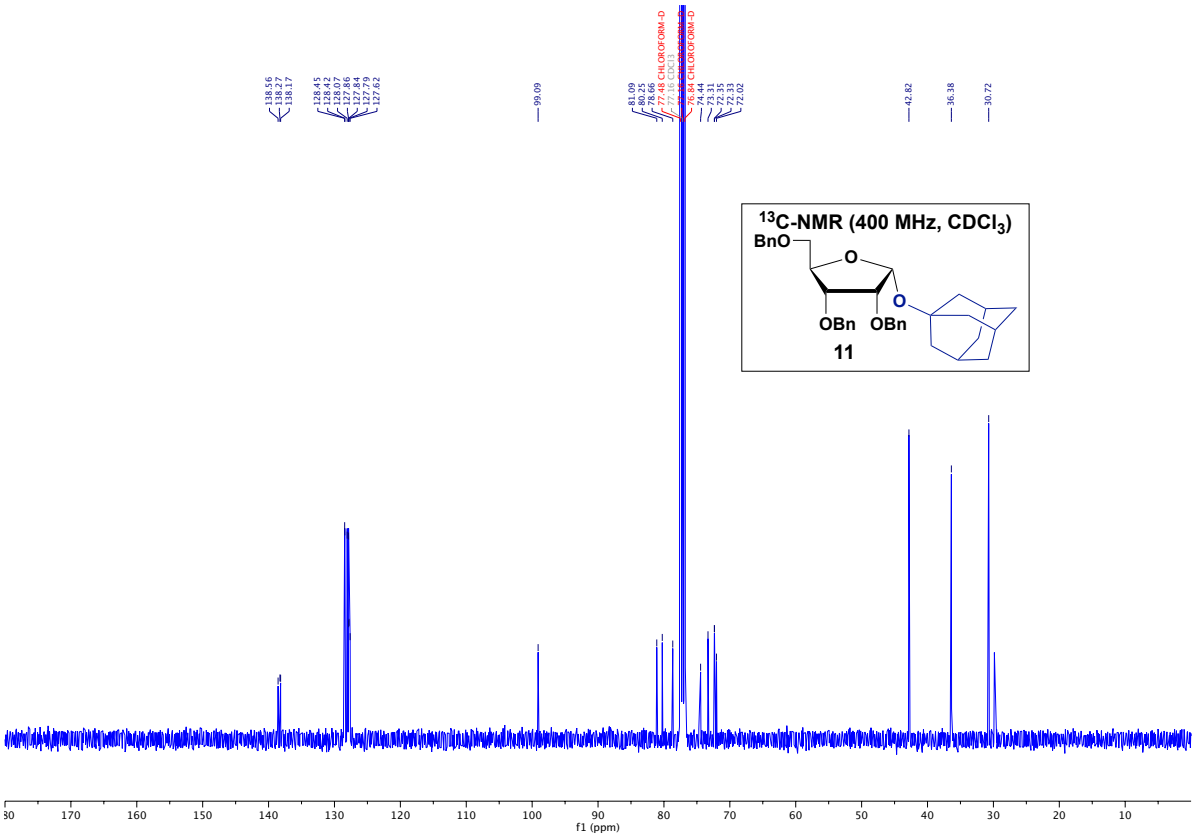

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
OBn
OBn
O
BnO
BnO
OBn
O
BnO
OMe
8
f1 (ppm)

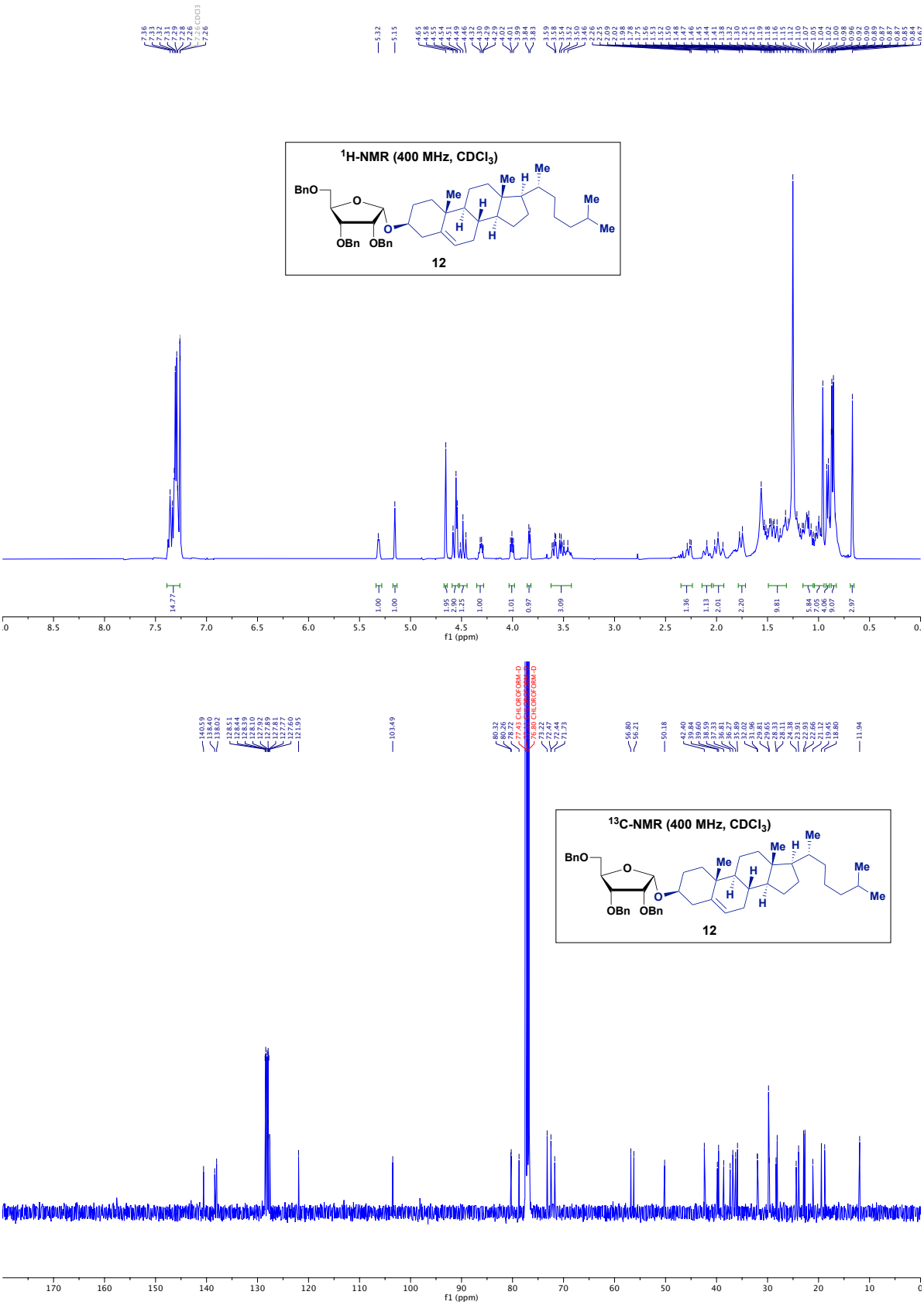

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
9
f1 (ppm)

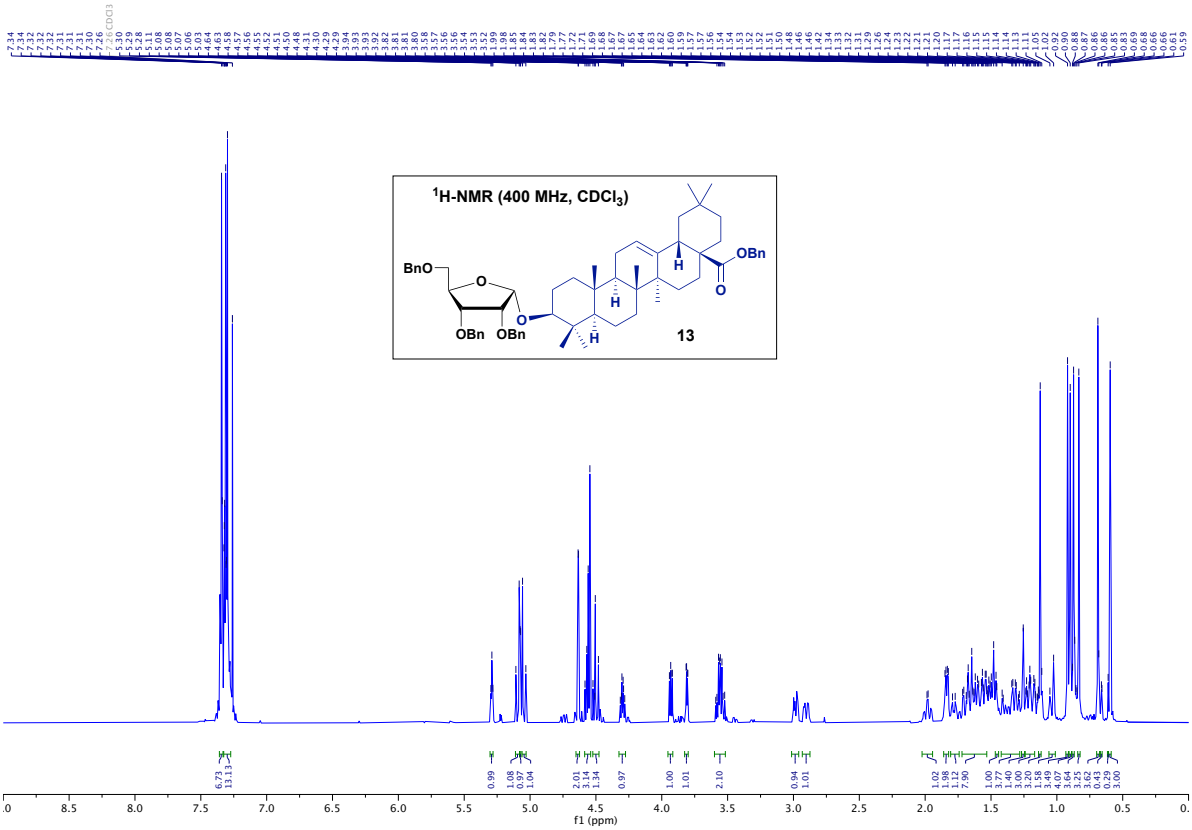

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
9
f1 (ppm)

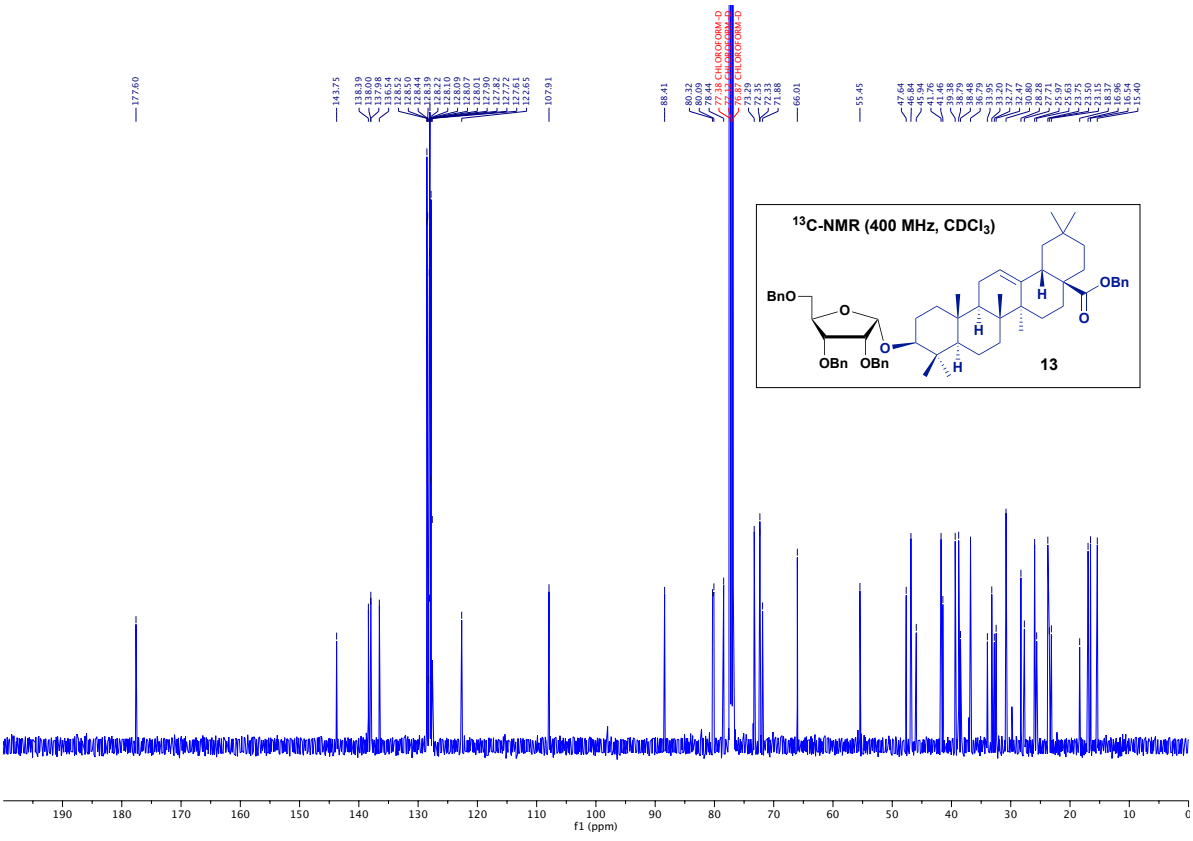

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
10
f1 (ppm)
^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
10
f1 (ppm)

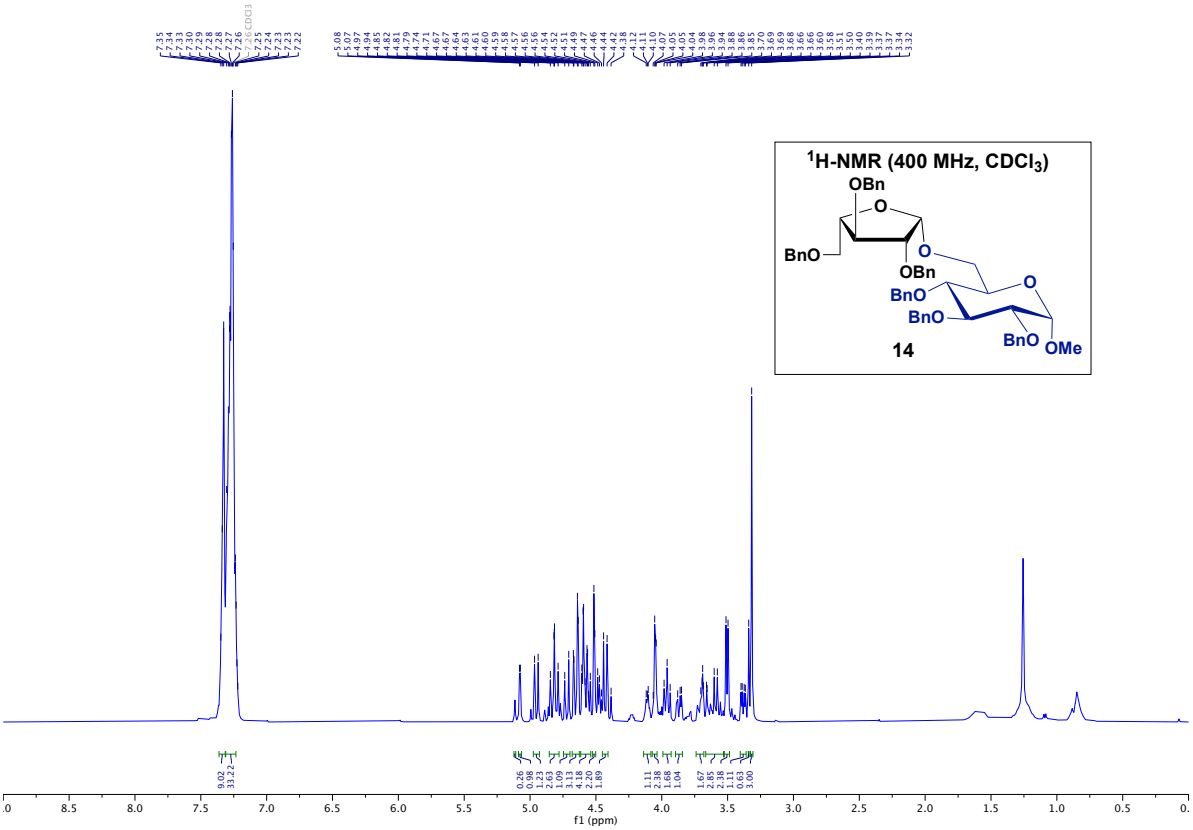

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
11
f1 (ppm)

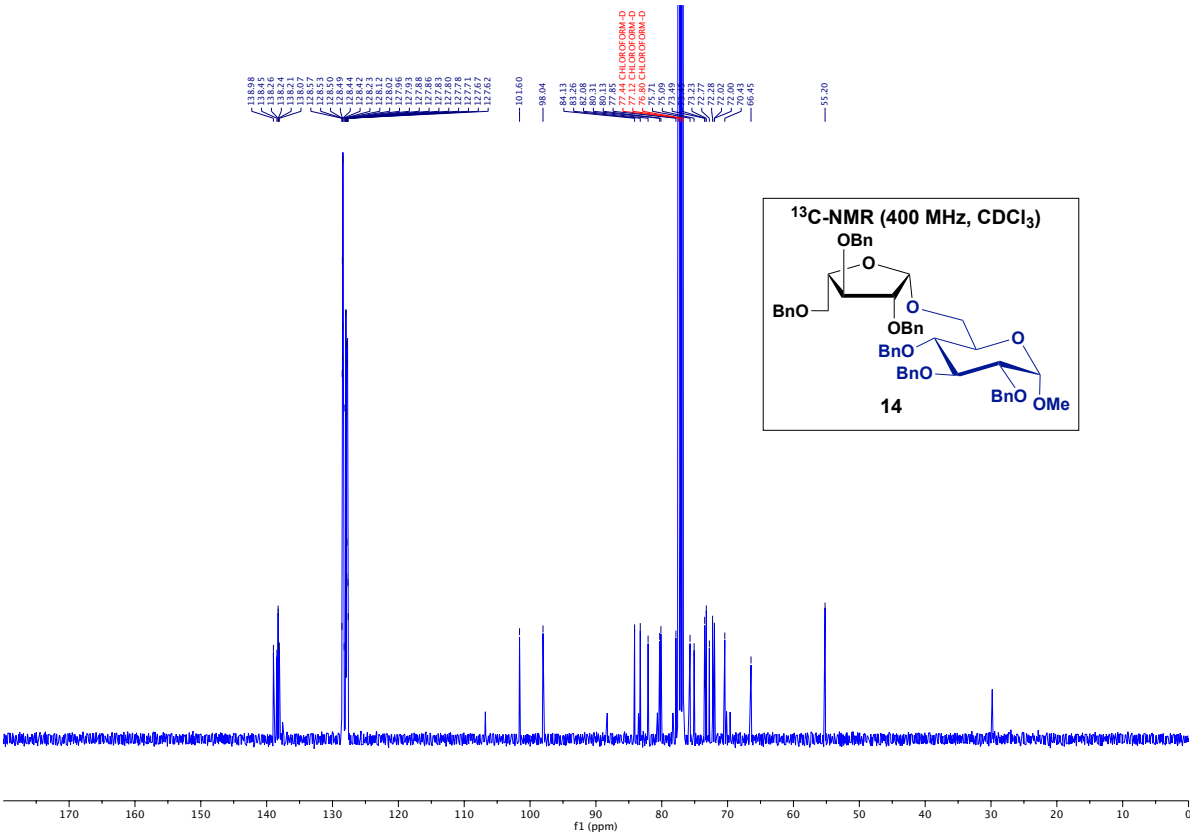

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
O
O
OBn OBn
11
f1 (ppm)

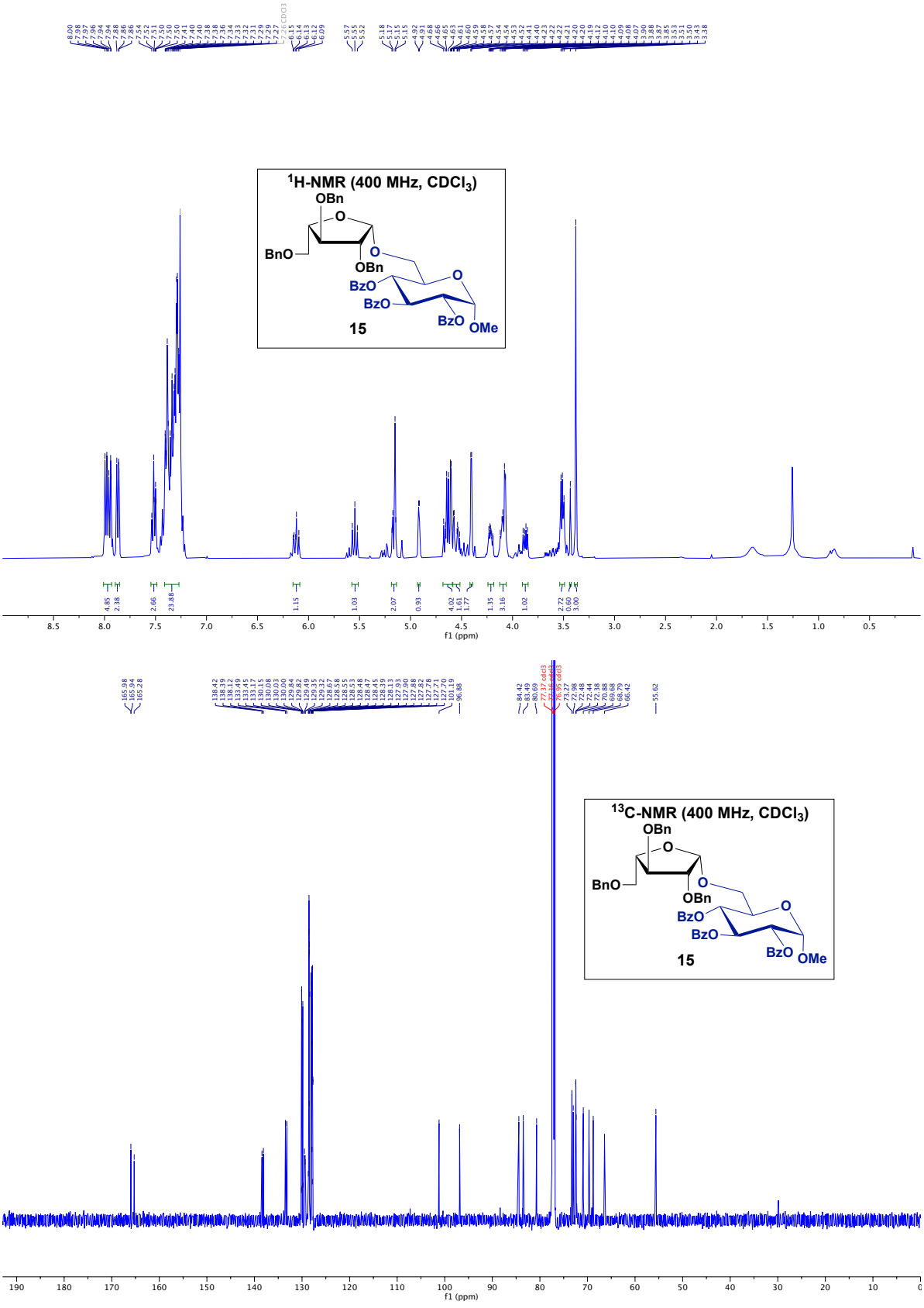

^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
OBn OBn
Me
H
12
f1 (ppm)
^{13}C-NMR (400 MHz, CDCl$_3$)
CHLOROFORM-D
f1 (ppm)

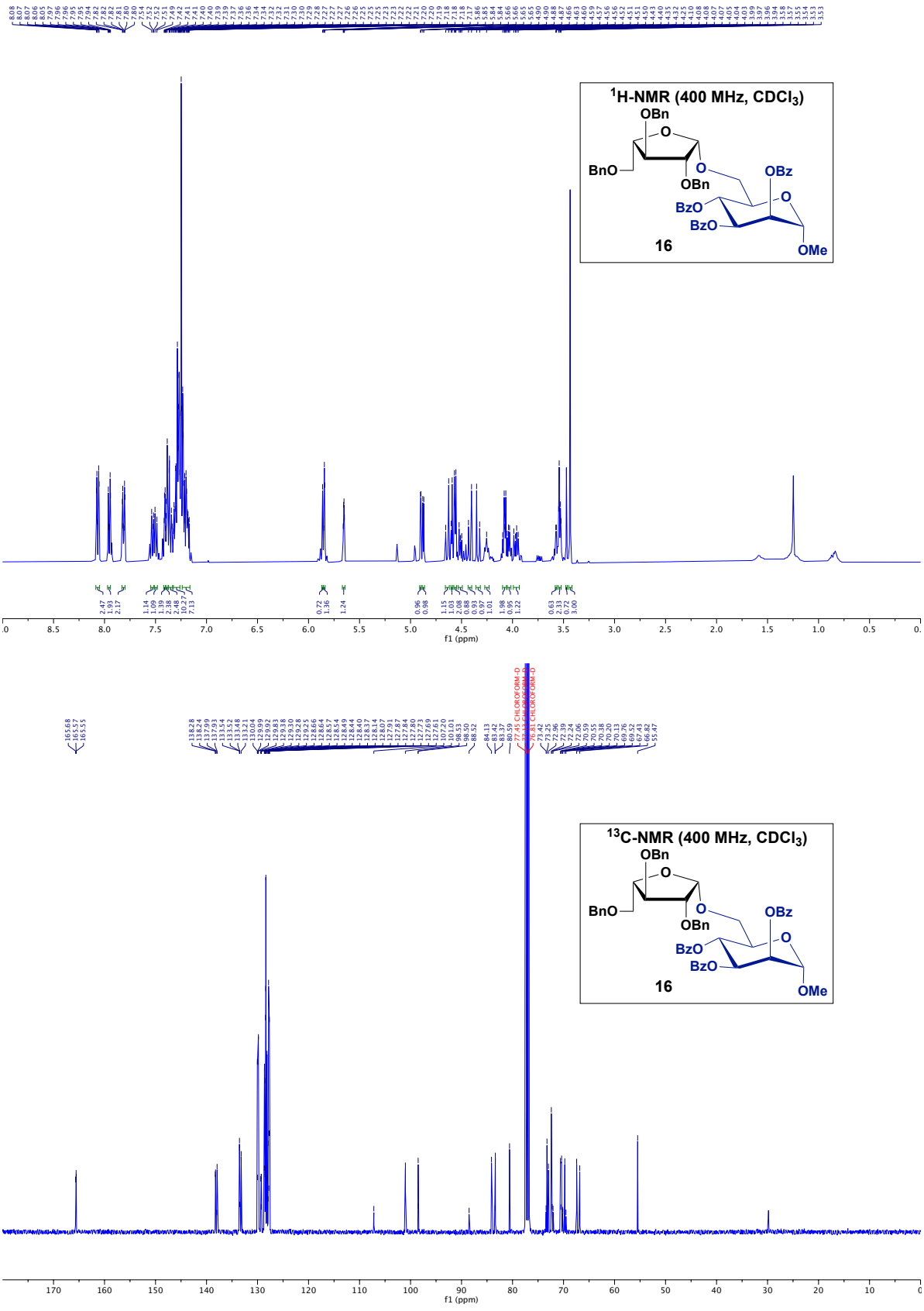

^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
OBn
OBn
OBn
O
H
H
H
O
O
13
f1 (ppm)

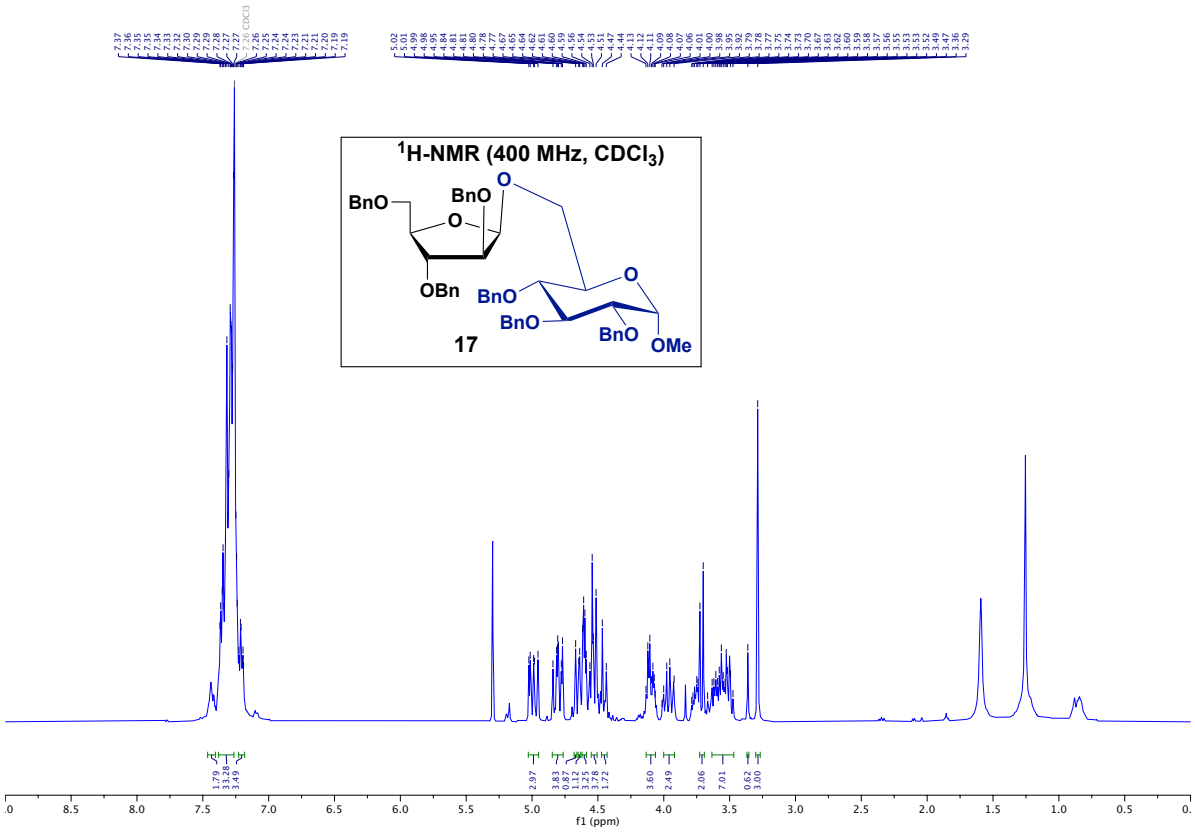

^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
OBn
OBn
OBn
O
H
H
H
O
O
13
f1 (ppm)

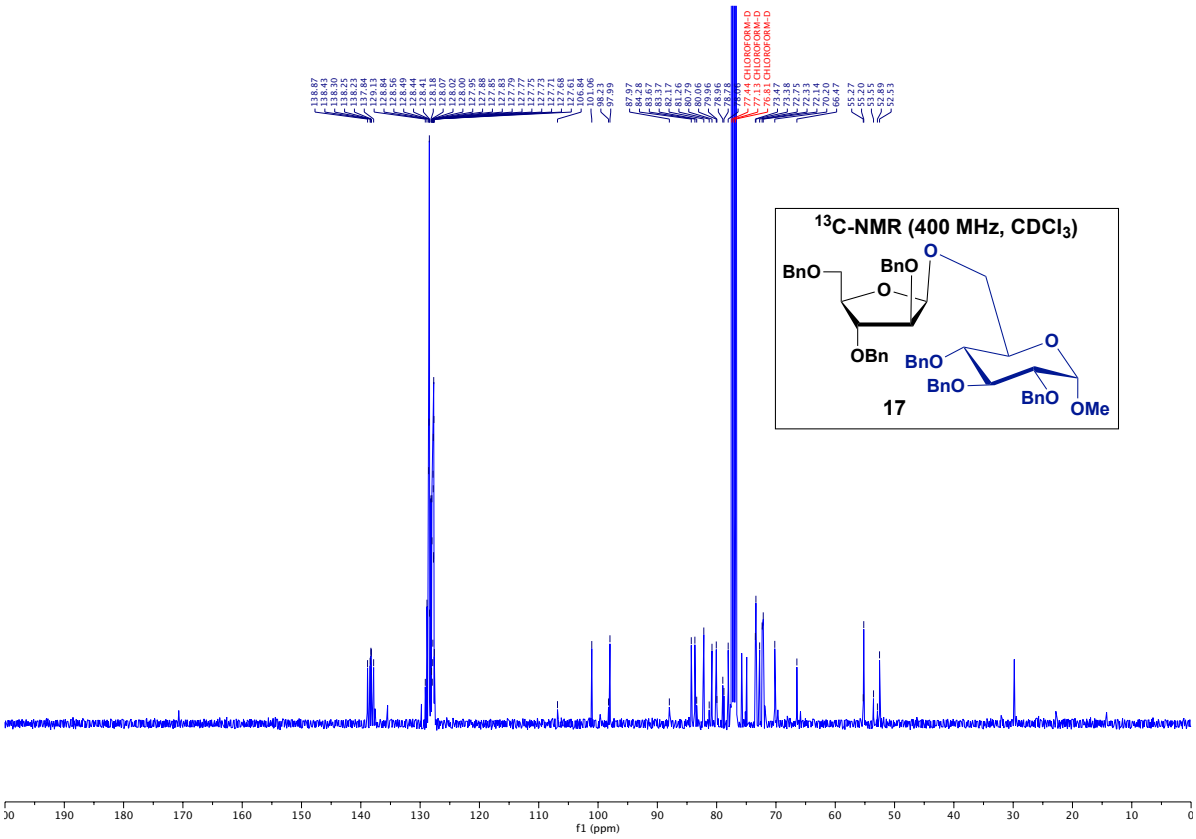

^{1}H-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
BnO
O
BnO
BnO
OMe
14
f1 (ppm)

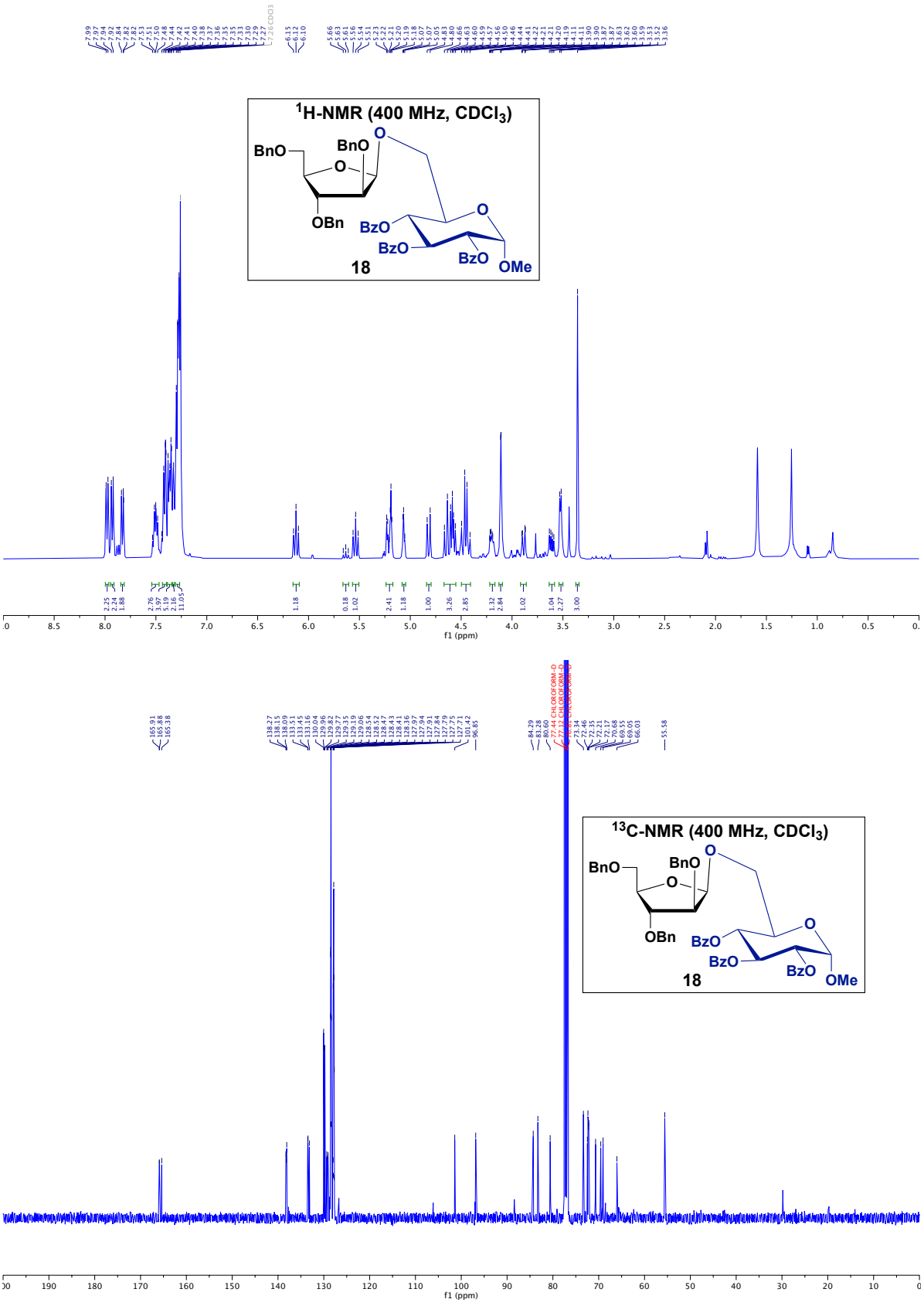

^{13}C-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
BnO
O
BnO
BnO
OMe
14
f1 (ppm)

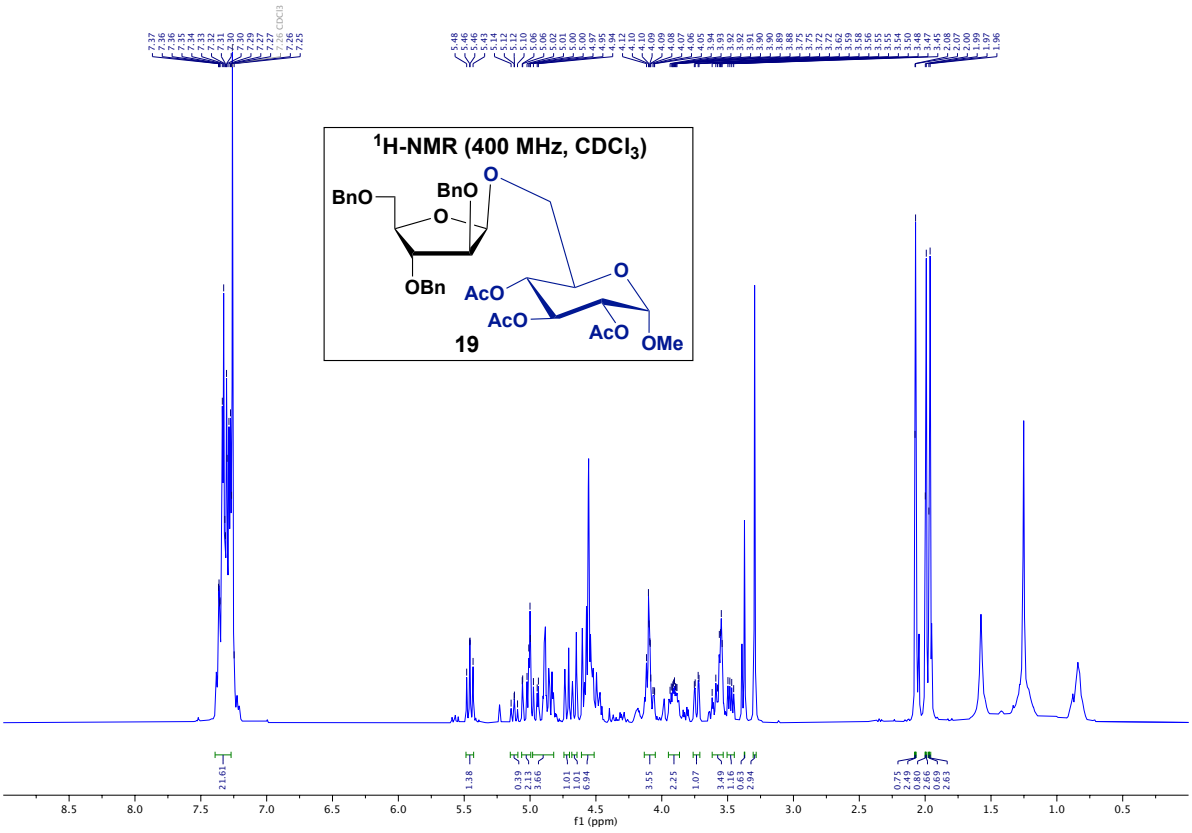

^{1}H-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
O
BzO
BzO
BzO
OMe
15
f1 (ppm)
^{13}C-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
O
BzO
BzO
BzO
OMe
15
f1 (ppm)

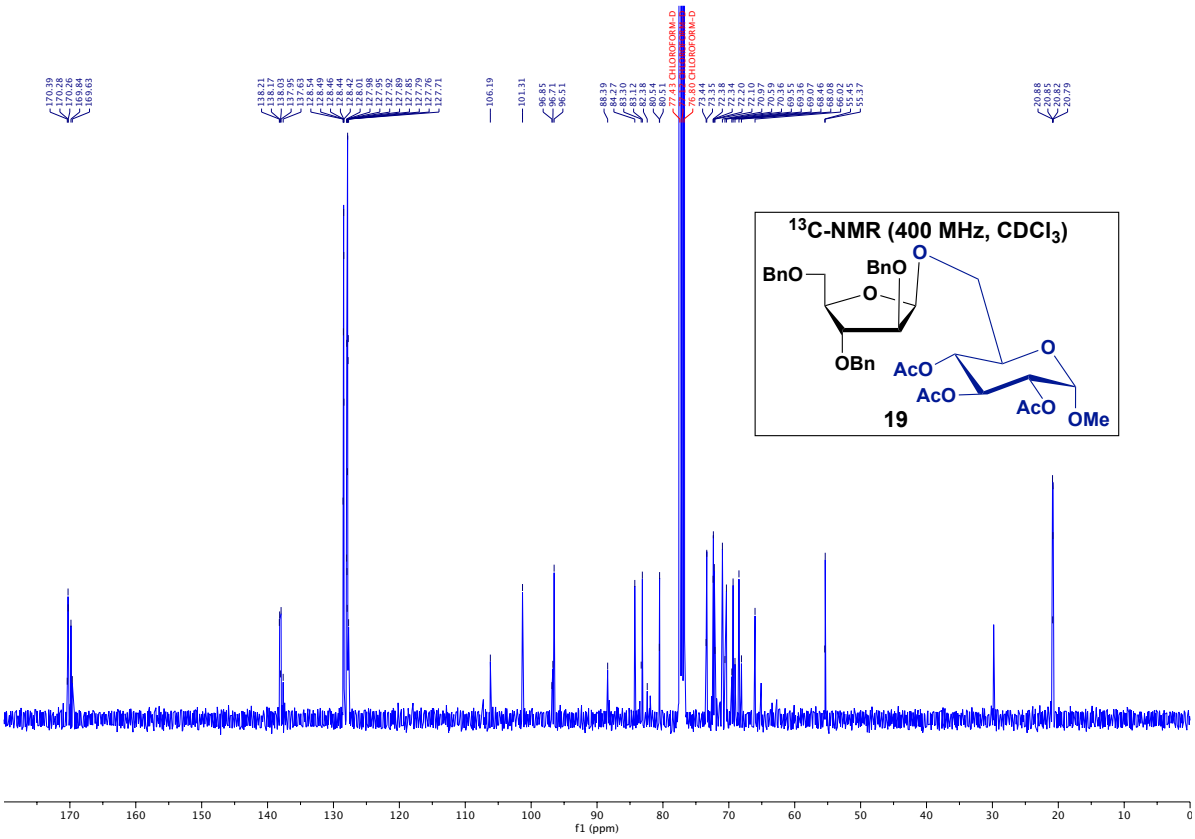

^{1}H-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
OBz
O
BzO
BzO
16
OMe
f1 (ppm)
^{13}C-NMR (400 MHz, $CDCl_3$)
OBn
O
BnO
O
OBn
OBz
O
BzO
BzO
16
OMe
f1 (ppm)

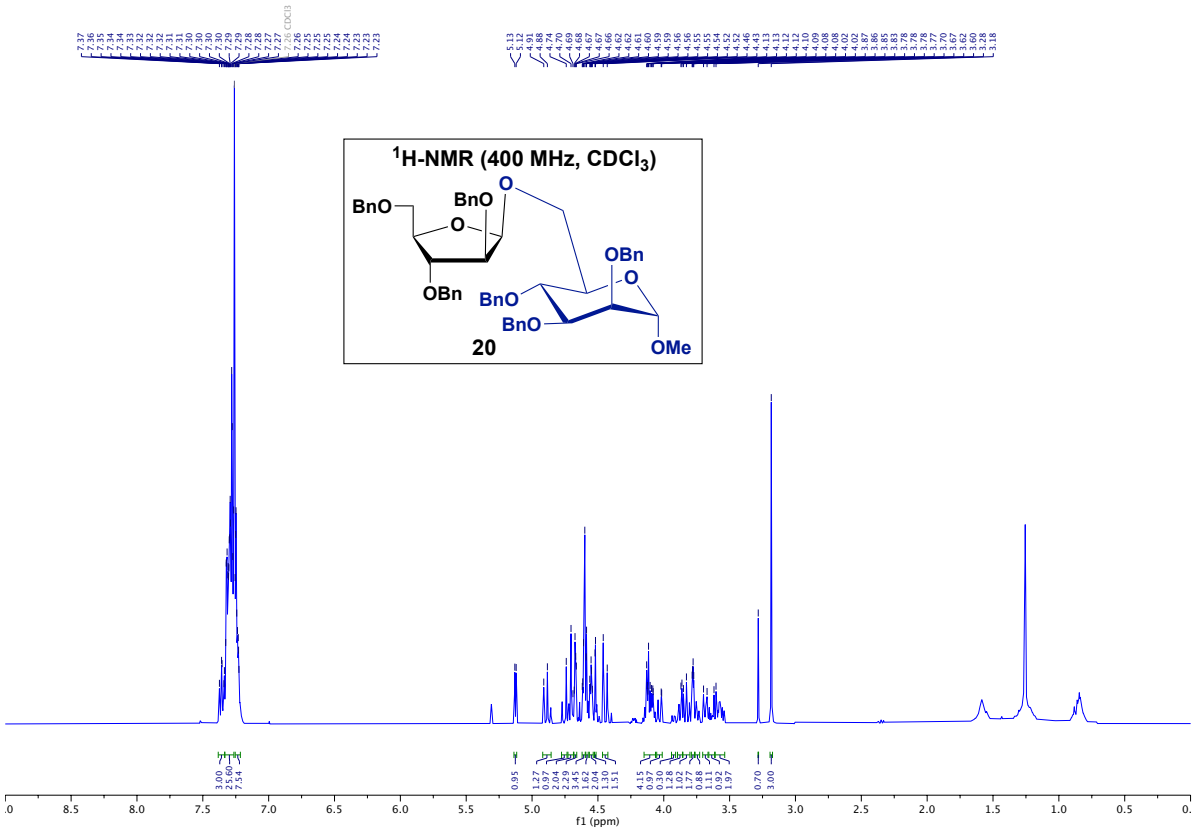

^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
OBn
BnO
BnO
BnO
OMe
17
f1 (ppm)

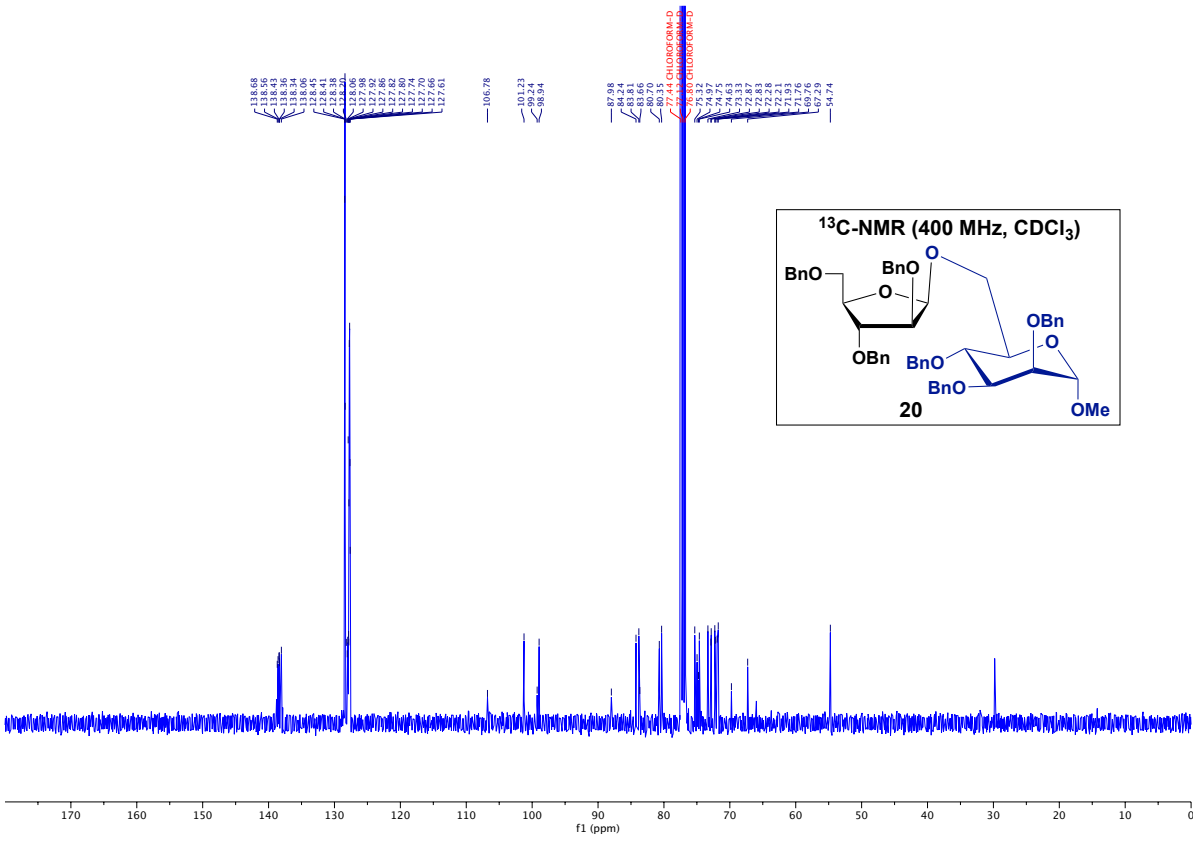

^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
OBn
BnO
BnO
BnO
OMe
17
f1 (ppm)

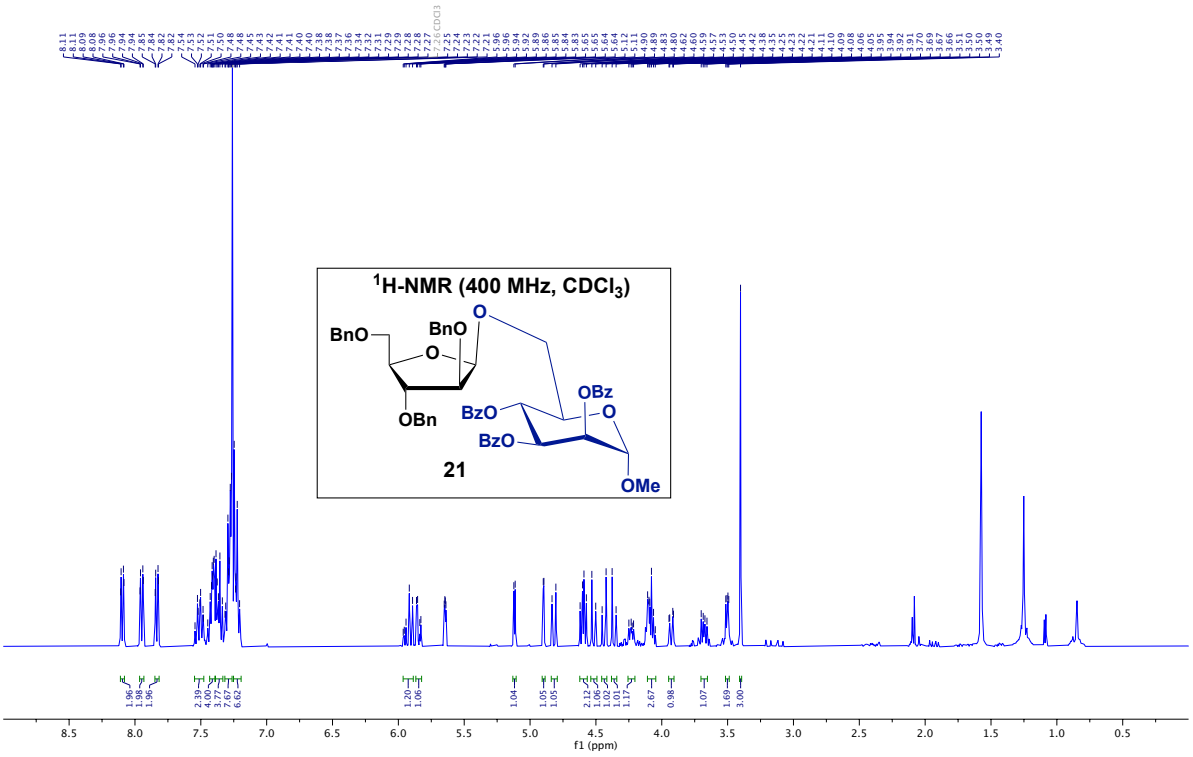

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
BzO
BzO
BzO
OMe
18
f1 (ppm)
^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
BzO
BzO
BzO
OMe
18
f1 (ppm)

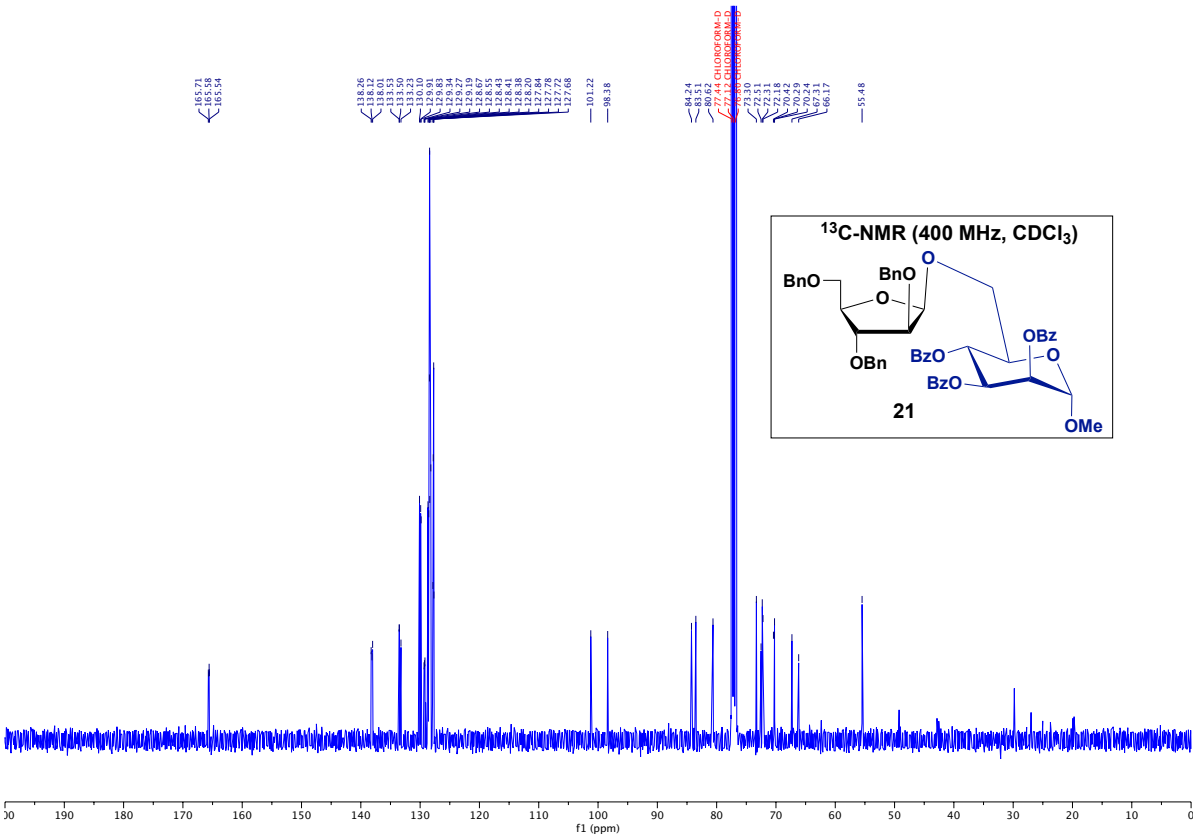

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
AcO
AcO
AcO
O
OMe
19
f1 (ppm)

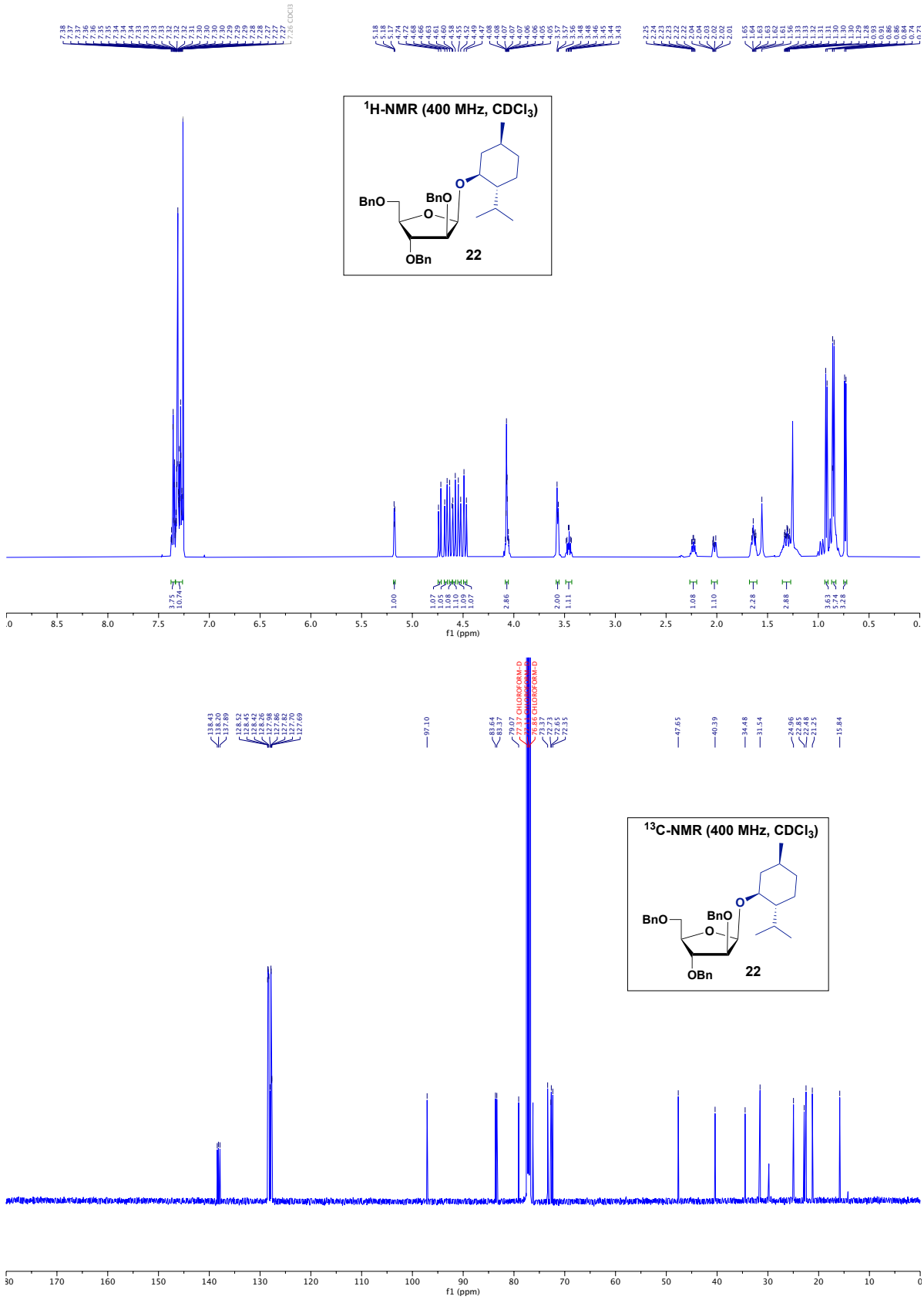

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
AcO
AcO
AcO
O
OMe
19
f1 (ppm)

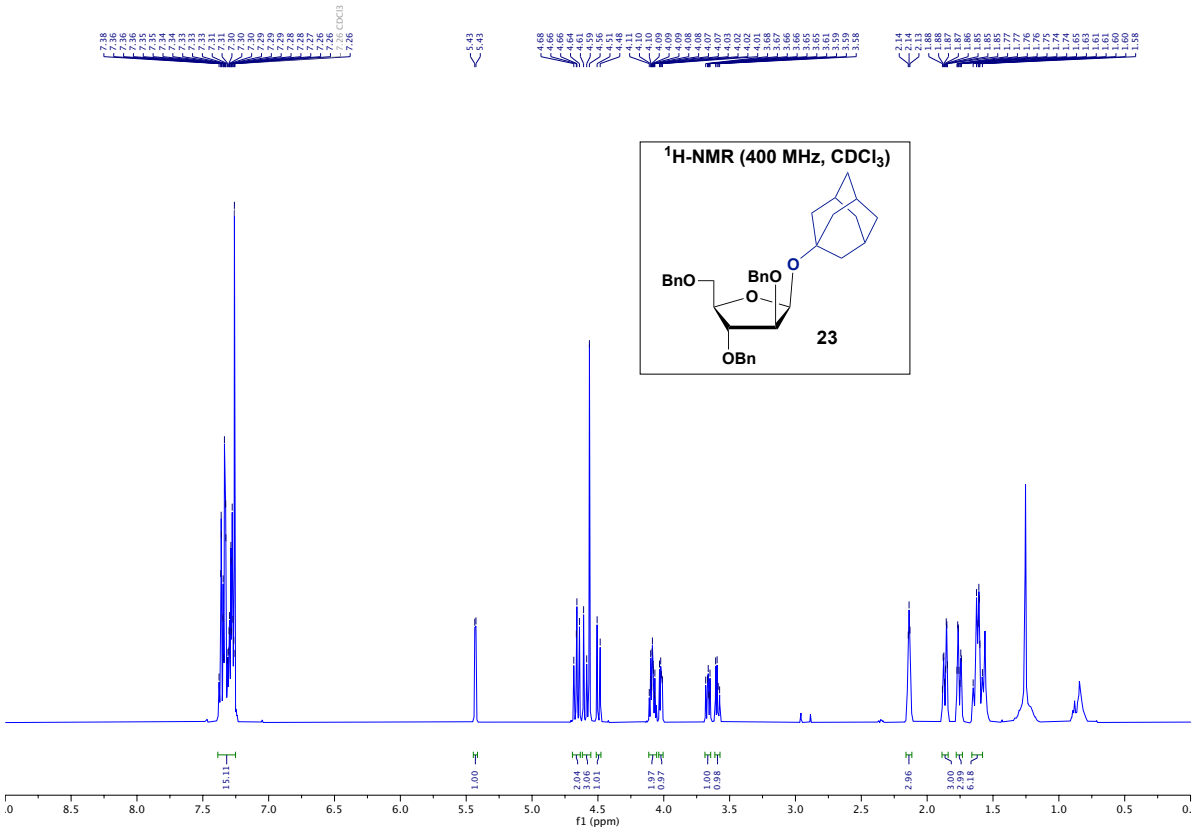

^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
O
OBn
OBn
BnO
BnO
OBn
O
OMe
20
f1 (ppm)

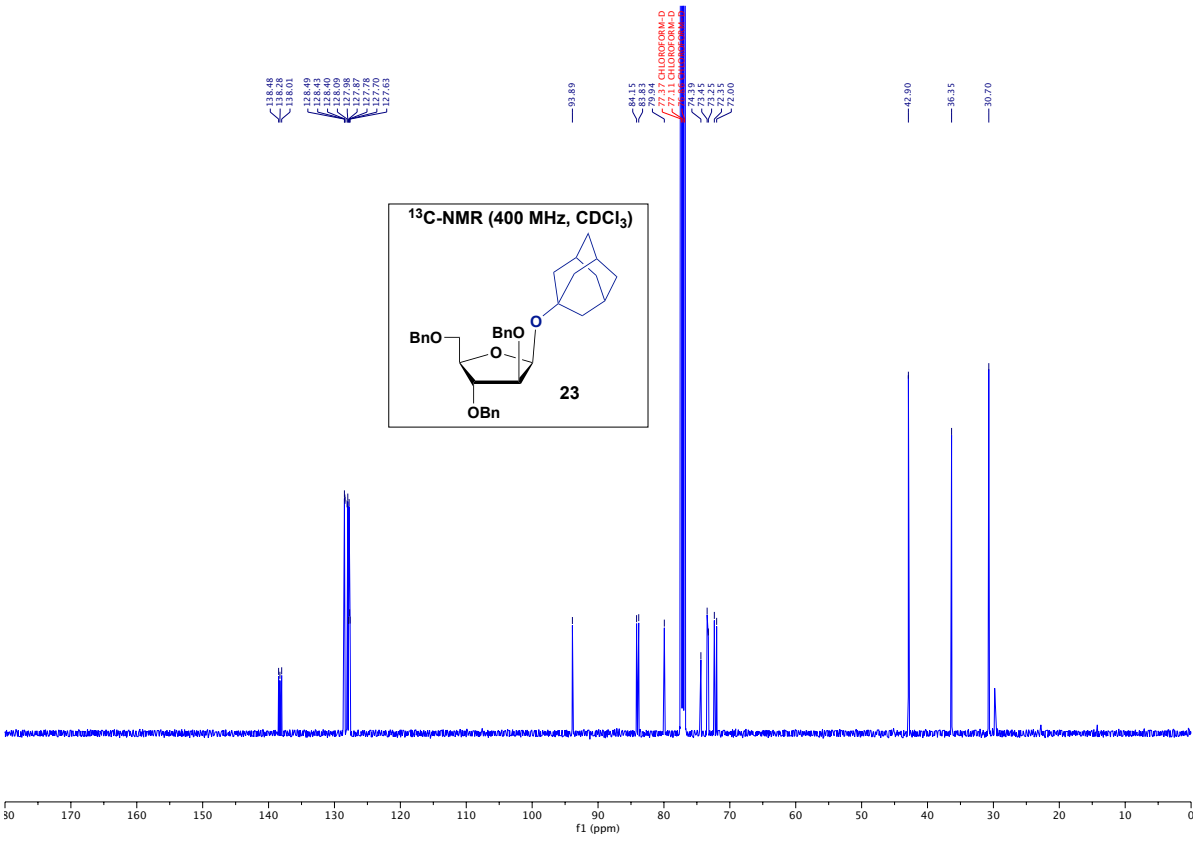

^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
O
OBn
OBn
BnO
BnO
OBn
O
OMe
20
f1 (ppm)

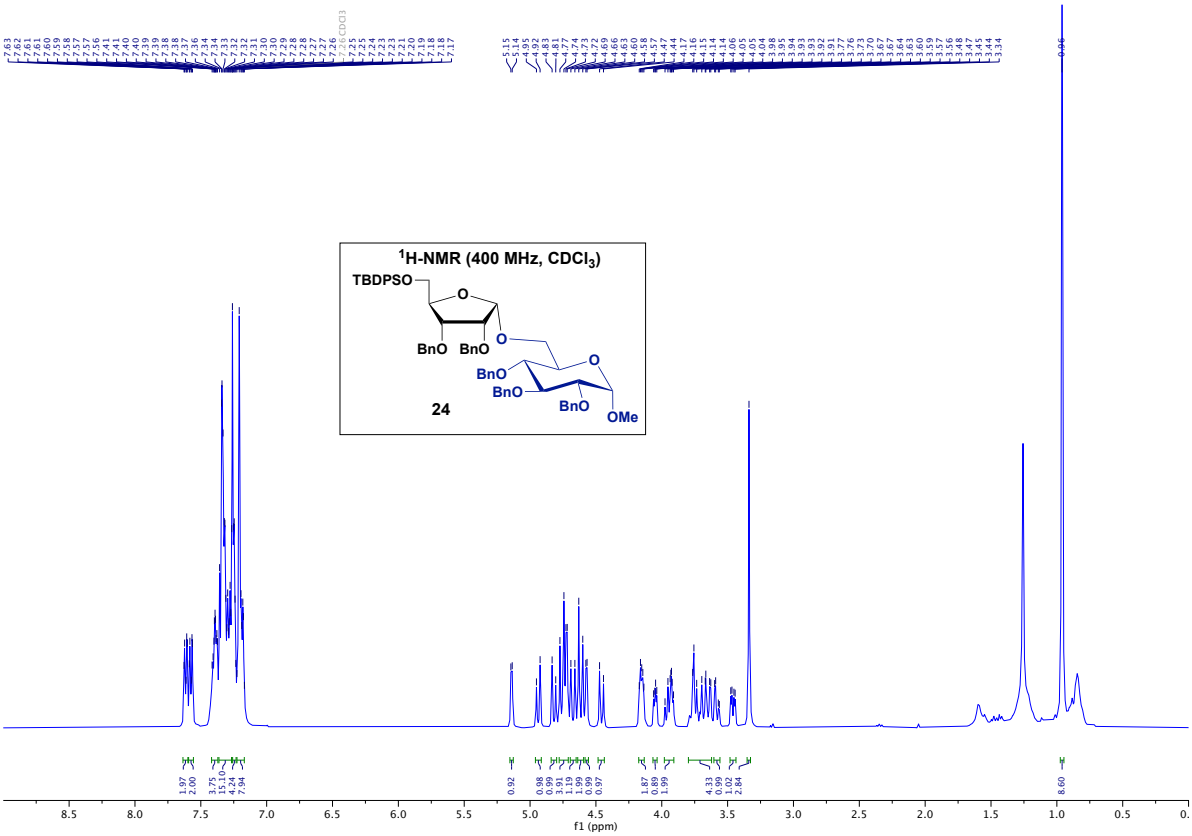

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
BzO
BzO
OBz
O
OMe
21
f1 (ppm)

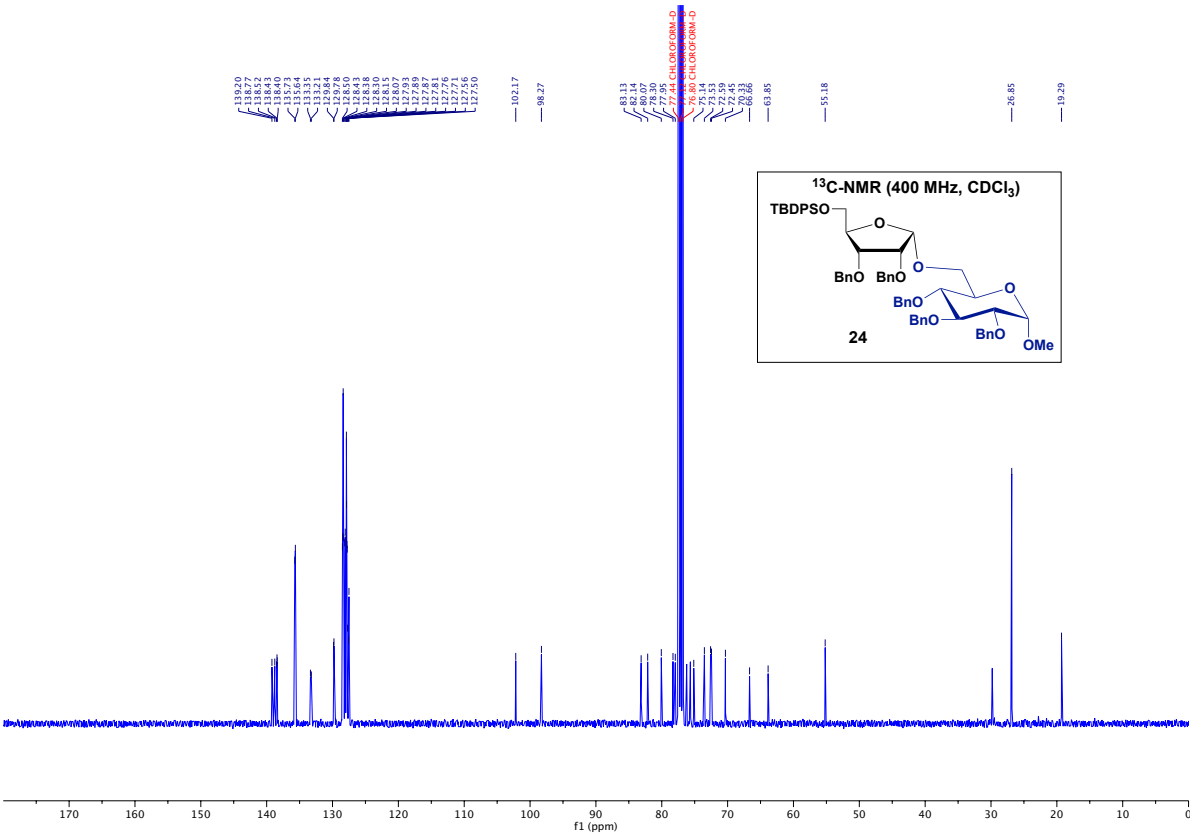

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
BzO
BzO
OBz
O
OMe
21
f1 (ppm)

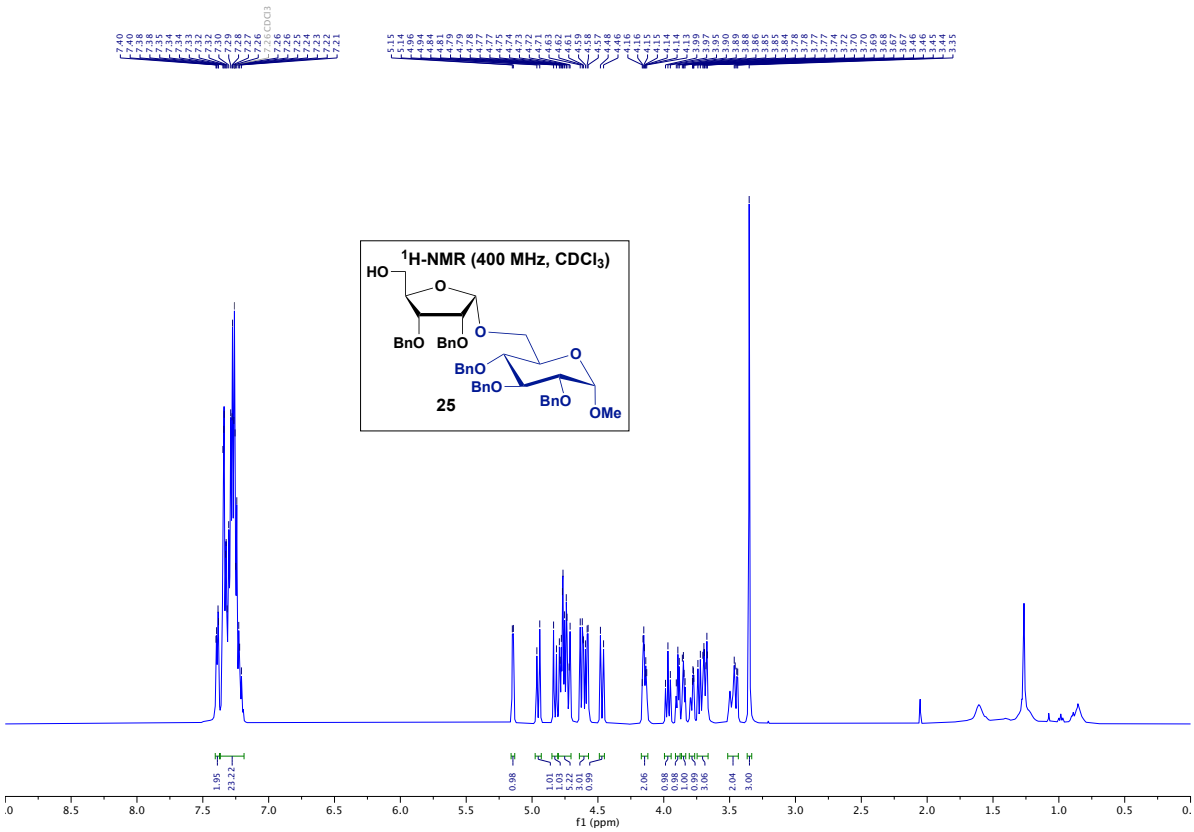

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
22
f1 (ppm)
^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
22
f1 (ppm)

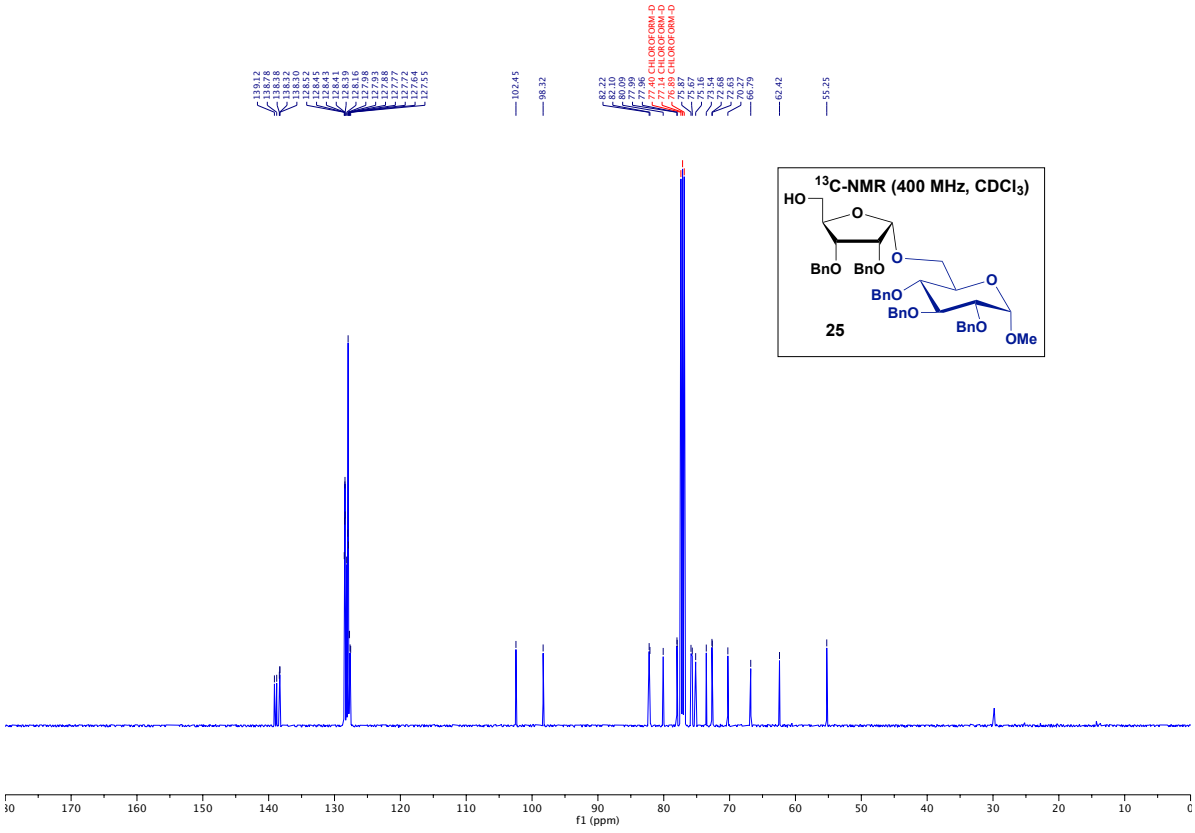

^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
23
f1 (ppm)

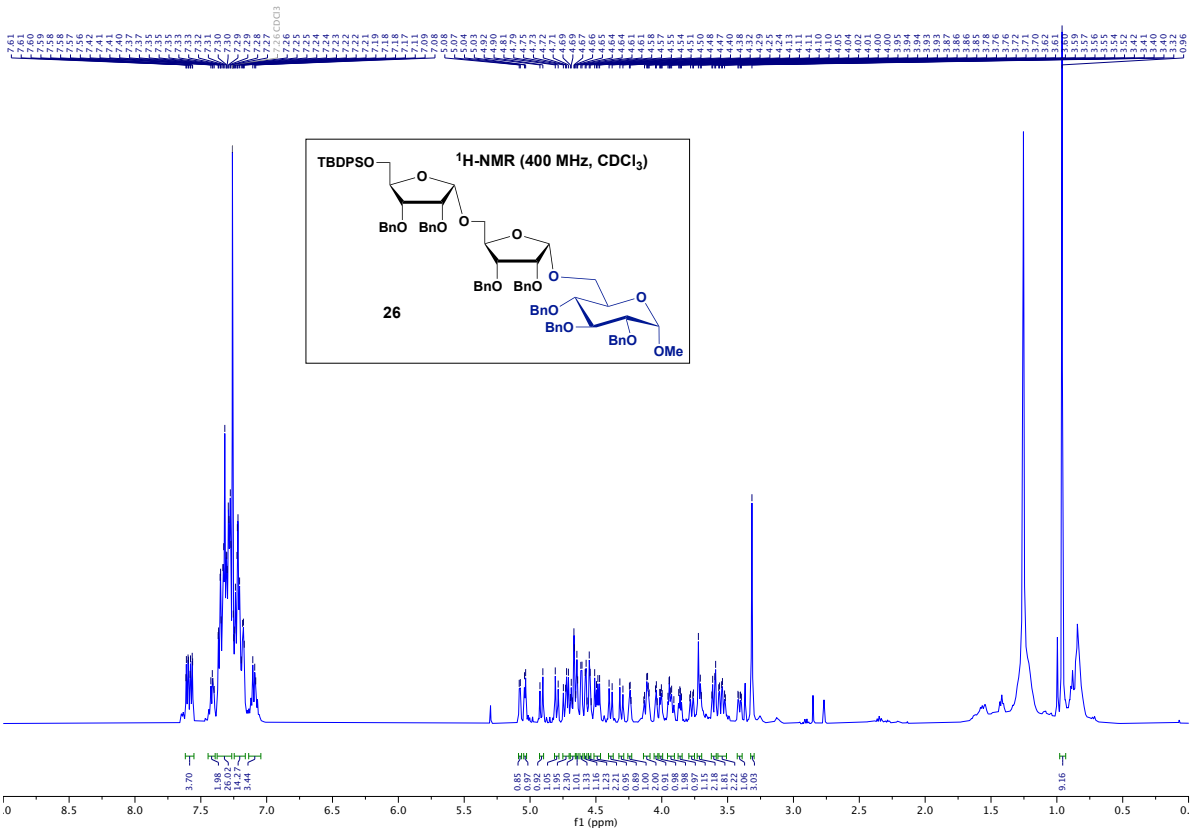

^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
BnO
O
O
OBn
23
f1 (ppm)

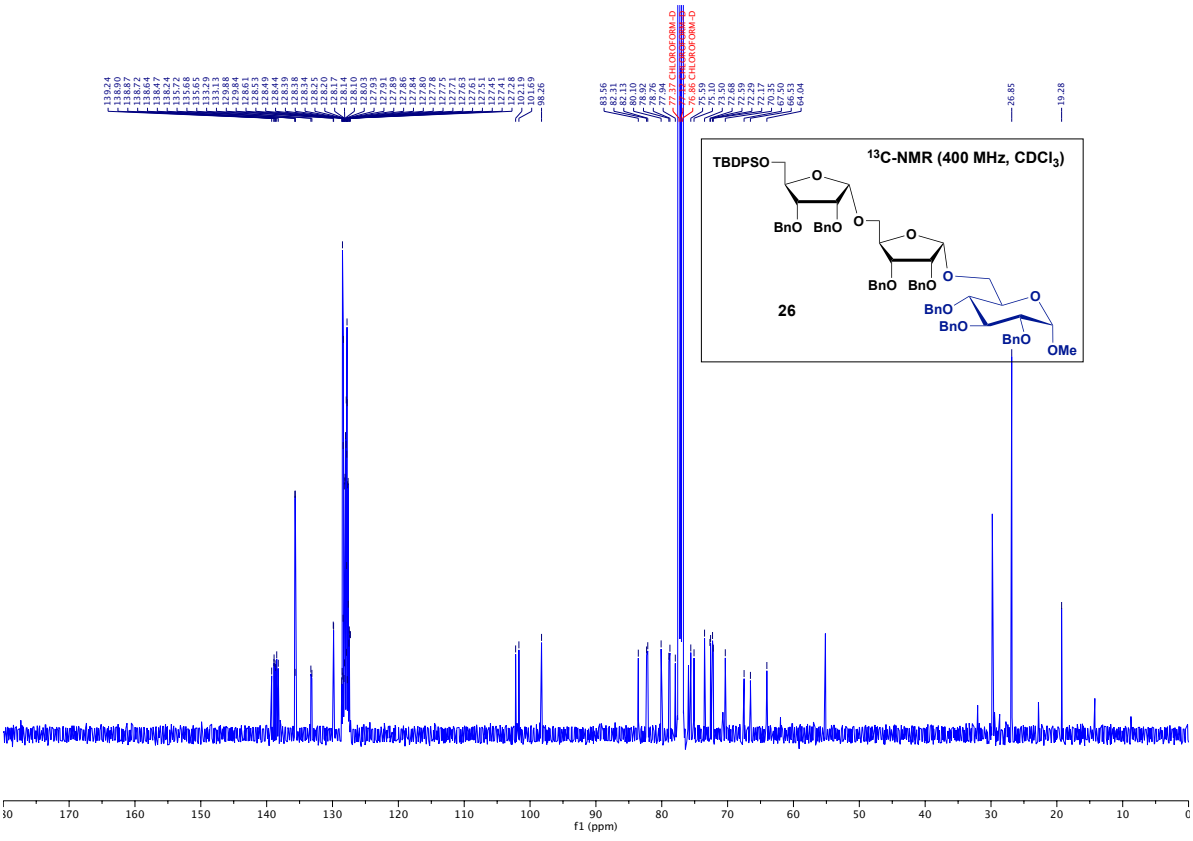

^{1}H-NMR (400 MHz, $CDCl_3$)
TBDPSO
BnO
BnO
BnO
BnO
BnO
OMe
24
f1 (ppm)

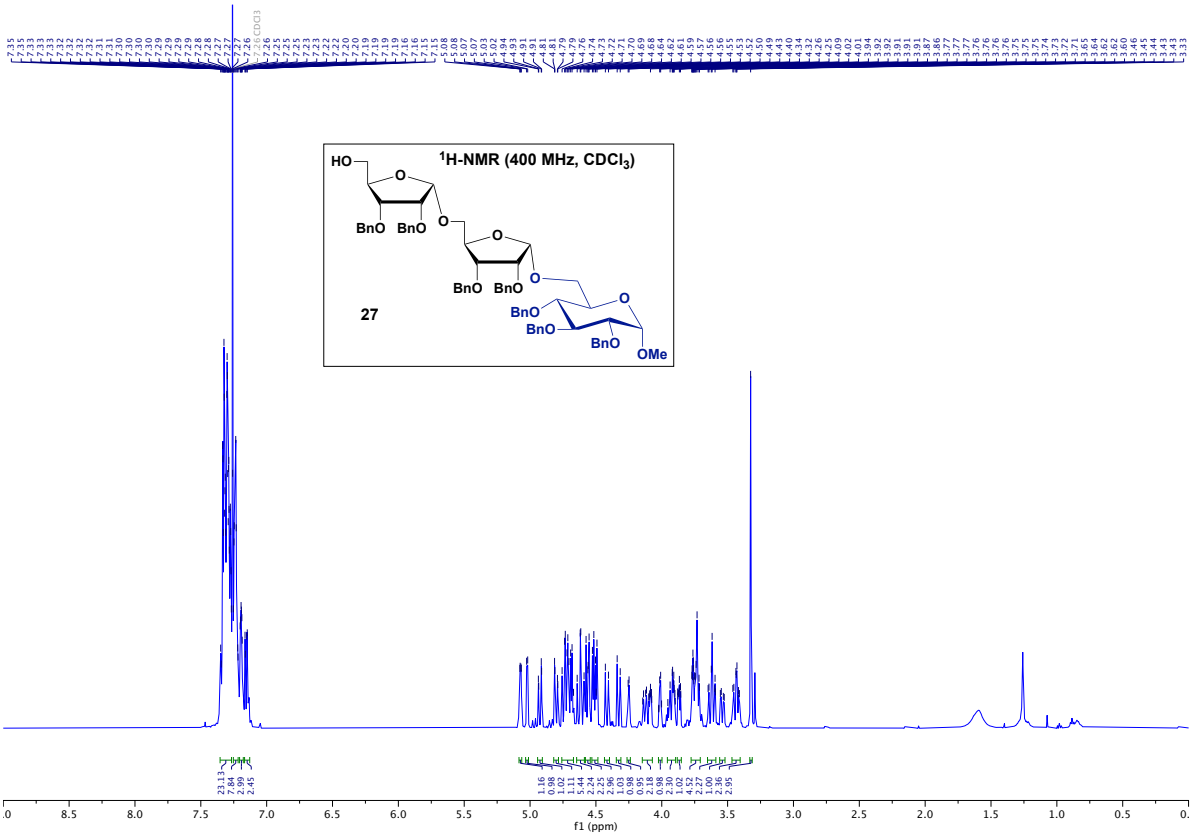

^{13}C-NMR (400 MHz, $CDCl_3$)
TBDPSO
BnO
BnO
BnO
BnO
BnO
OMe
24
f1 (ppm)

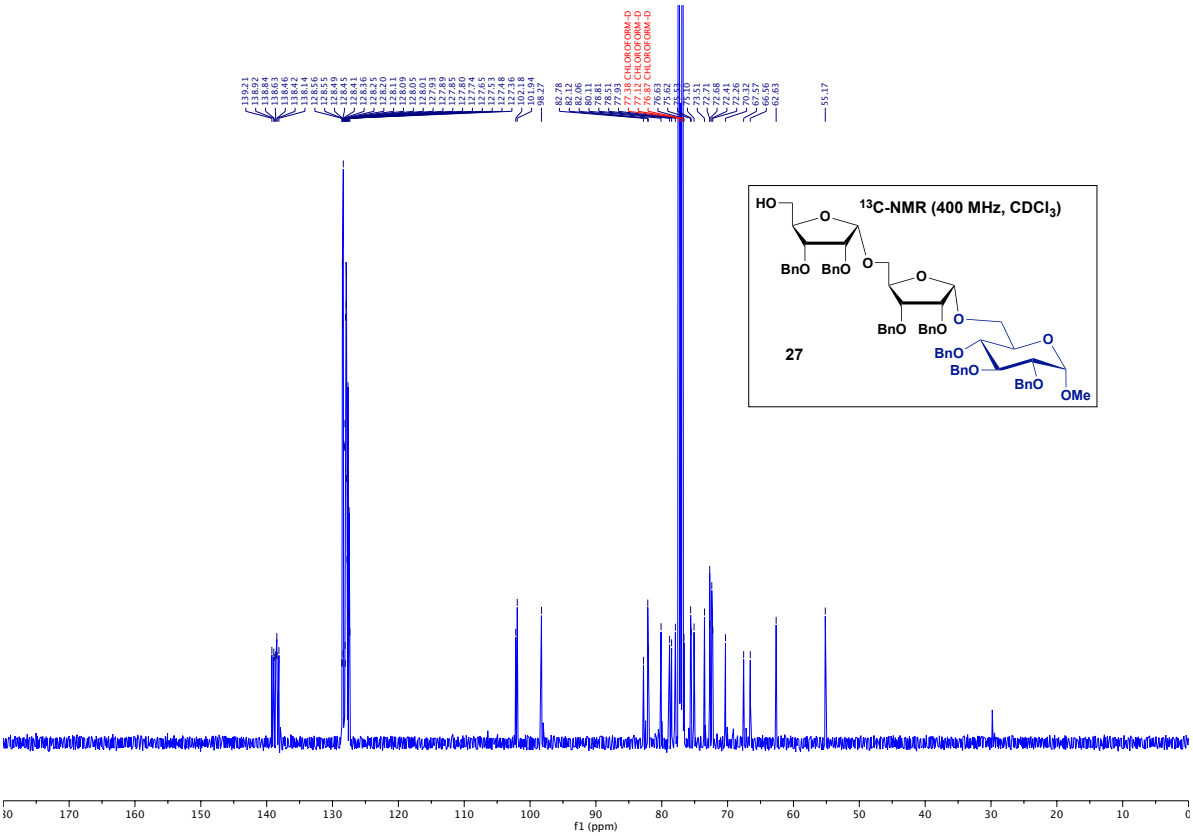

^{1}H-NMR (400 MHz, CDCl$_3$)
HO
BnO
BnO
BnO
BnO
BnO
OMe
25
f1 (ppm)

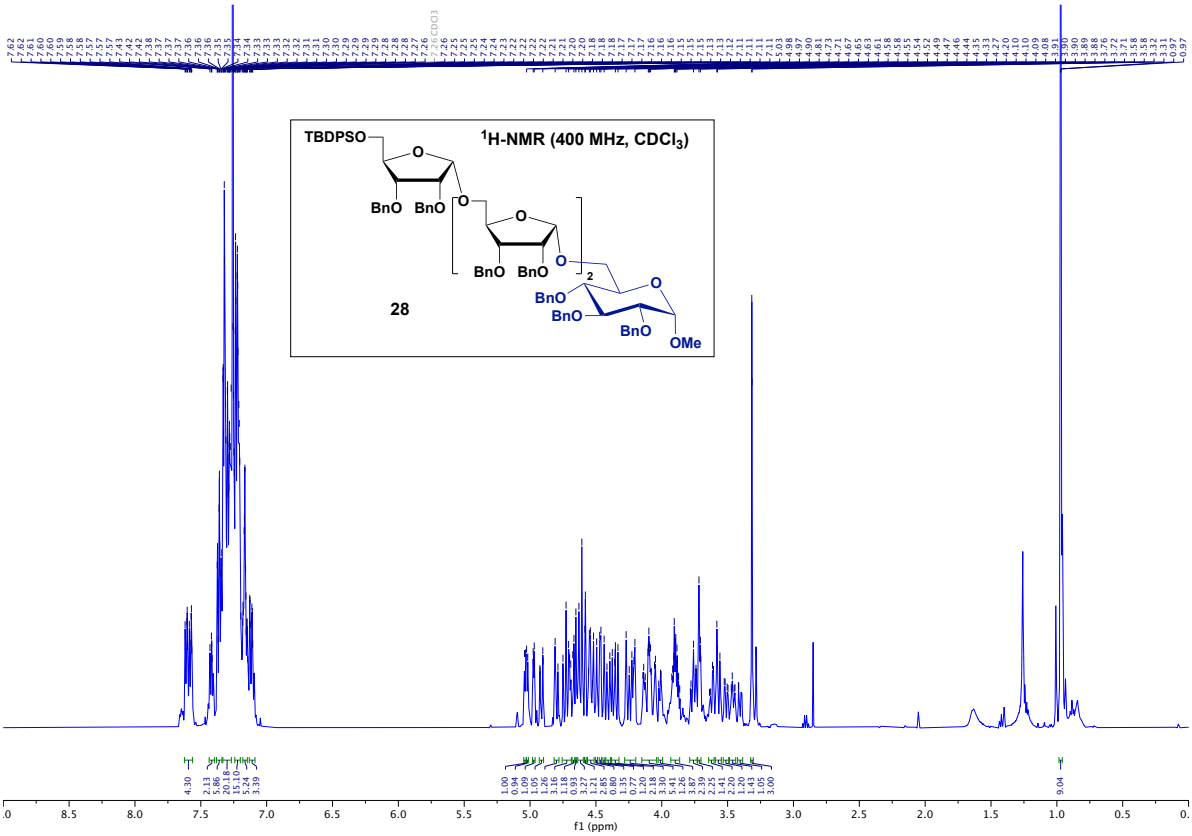

^{13}C-NMR (400 MHz, CDCl$_3$)
HO
BnO
BnO
BnO
BnO
BnO
OMe
25
f1 (ppm)

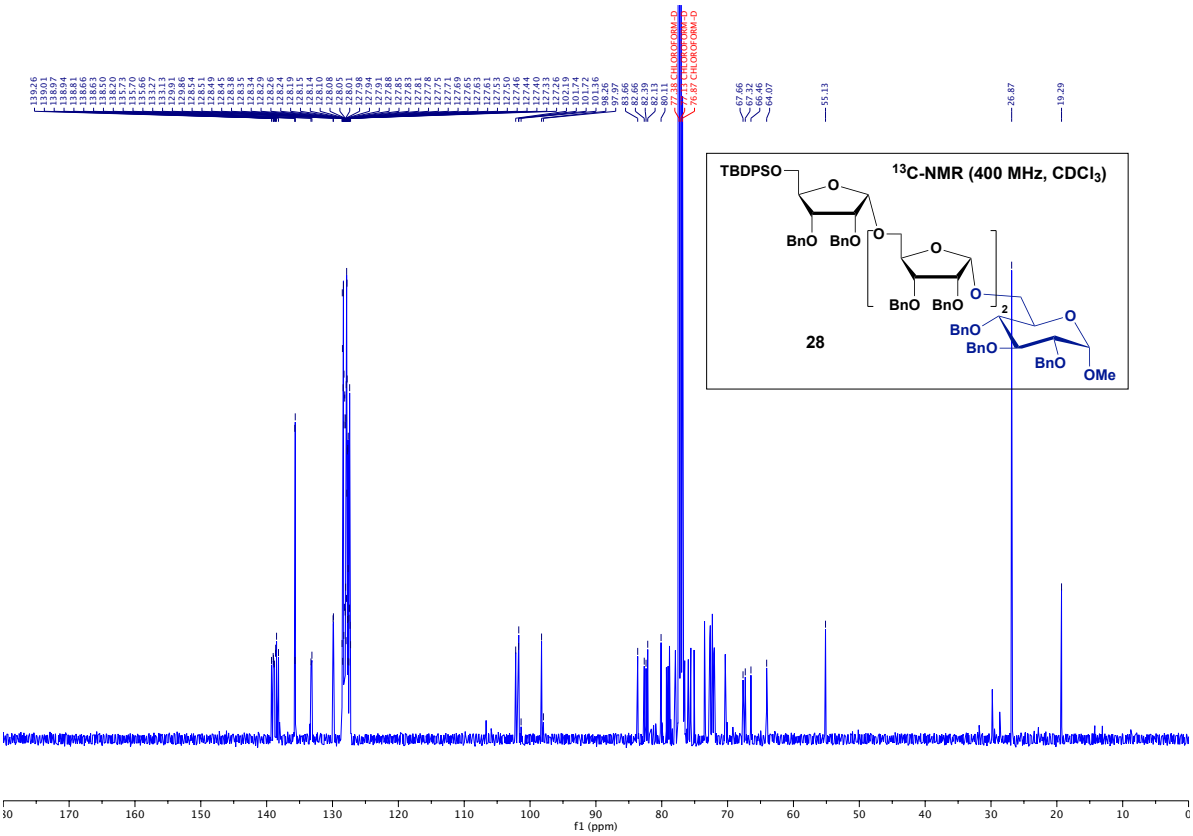

TBDPSO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
OMe
26
^{1}H-NMR (400 MHz, $CDCl_3$)
f1 (ppm)

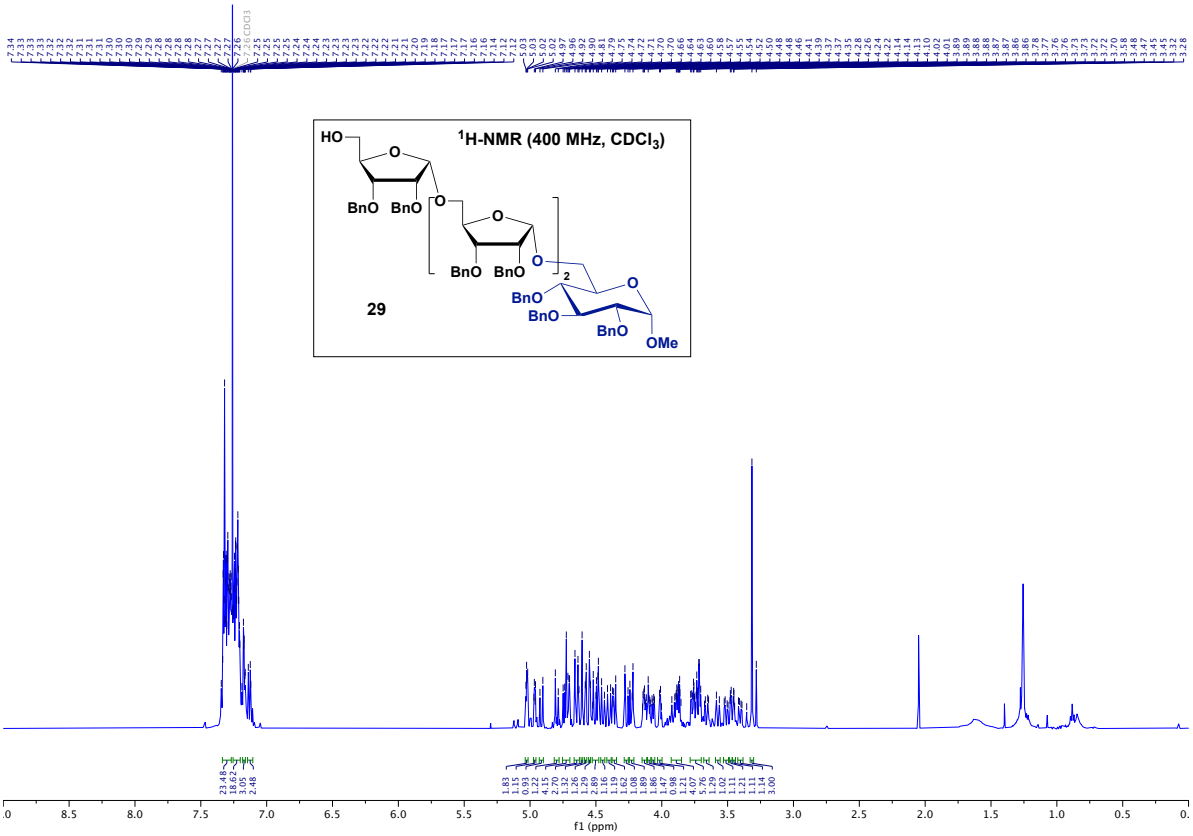

TBDPSO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
OMe
26
^{13}C-NMR (400 MHz, $CDCl_3$)
f1 (ppm)

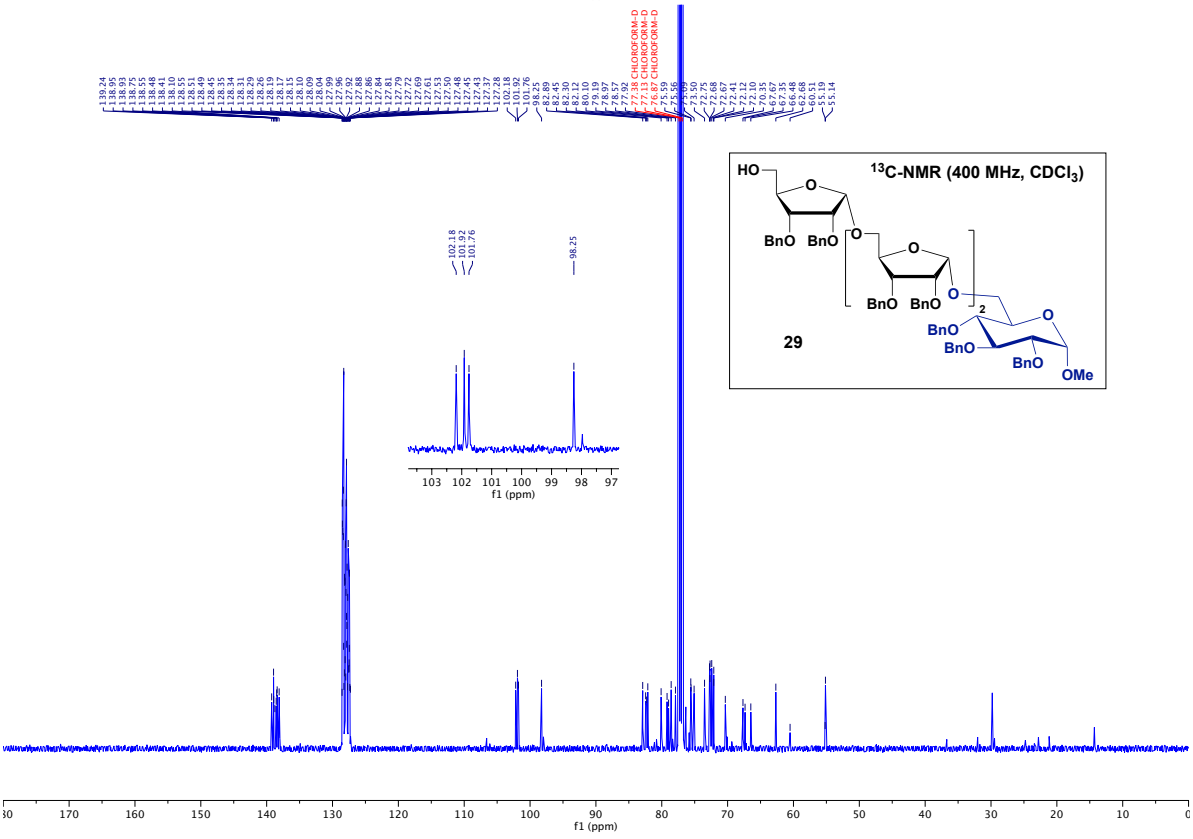

^{1}H-NMR (400 MHz, $CDCl_3$)
HO
BnO BnO
BnO BnO
BnO
BnO
BnO
OMe
27
f1 (ppm)

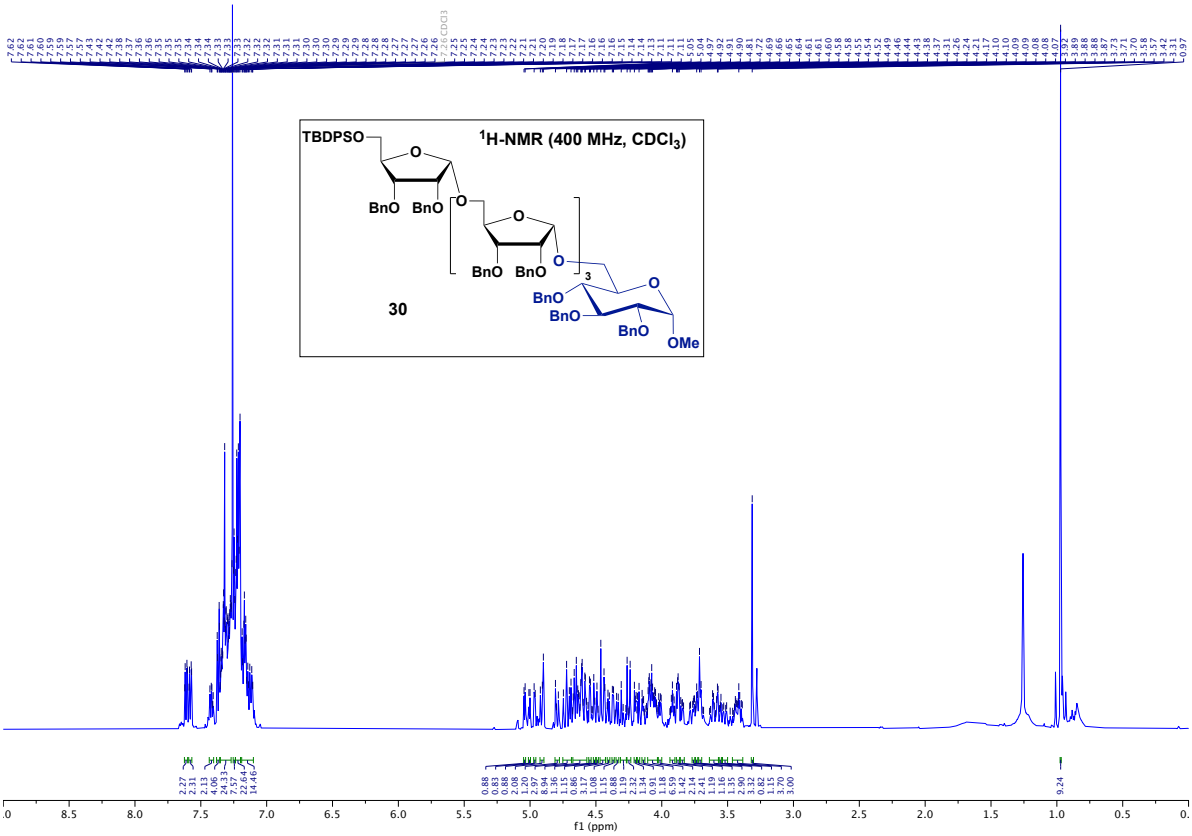

^{13}C-NMR (400 MHz, $CDCl_3$)
HO
BnO BnO
BnO BnO
BnO
BnO
BnO
OMe
27
f1 (ppm)

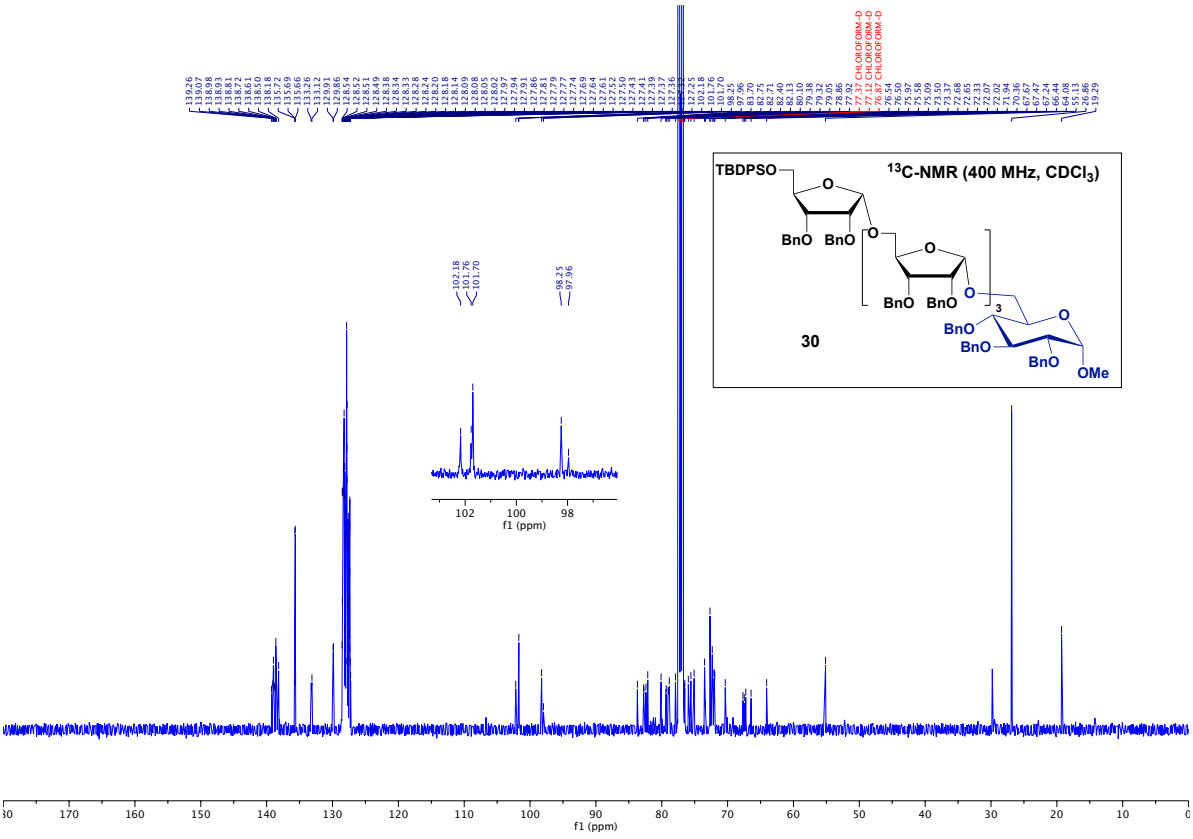

TBDPSO
^{1}H-NMR (400 MHz, $CDCl_3$)
BnO BnO
BnO BnO
BnO BnO
BnO
BnO
BnO
OMe
28
f1 (ppm)

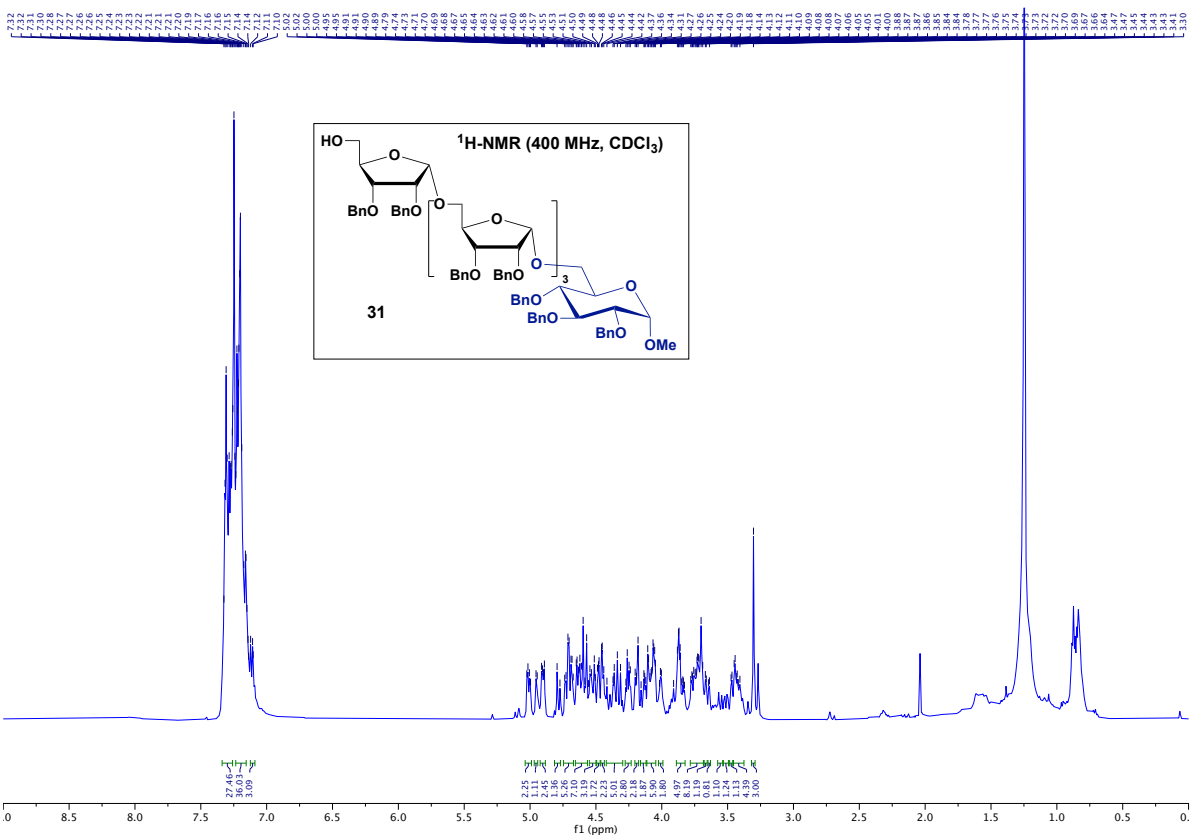

TBDPSO
^{13}C-NMR (400 MHz, $CDCl_3$)
BnO BnO
BnO BnO
BnO BnO
BnO
BnO
BnO
OMe
28
f1 (ppm)

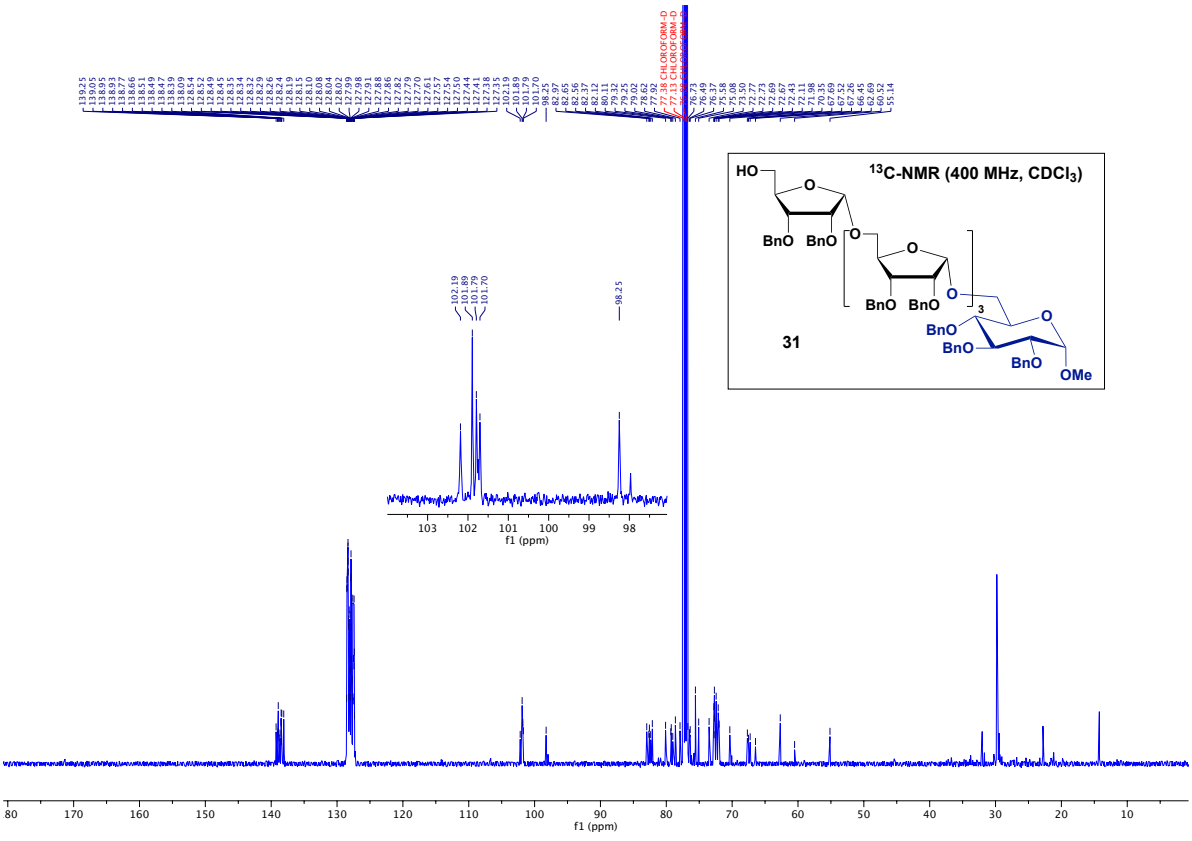

^{1}H-NMR (400 MHz, $CDCl_3$)
HO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
OMe
29
f1 (ppm)

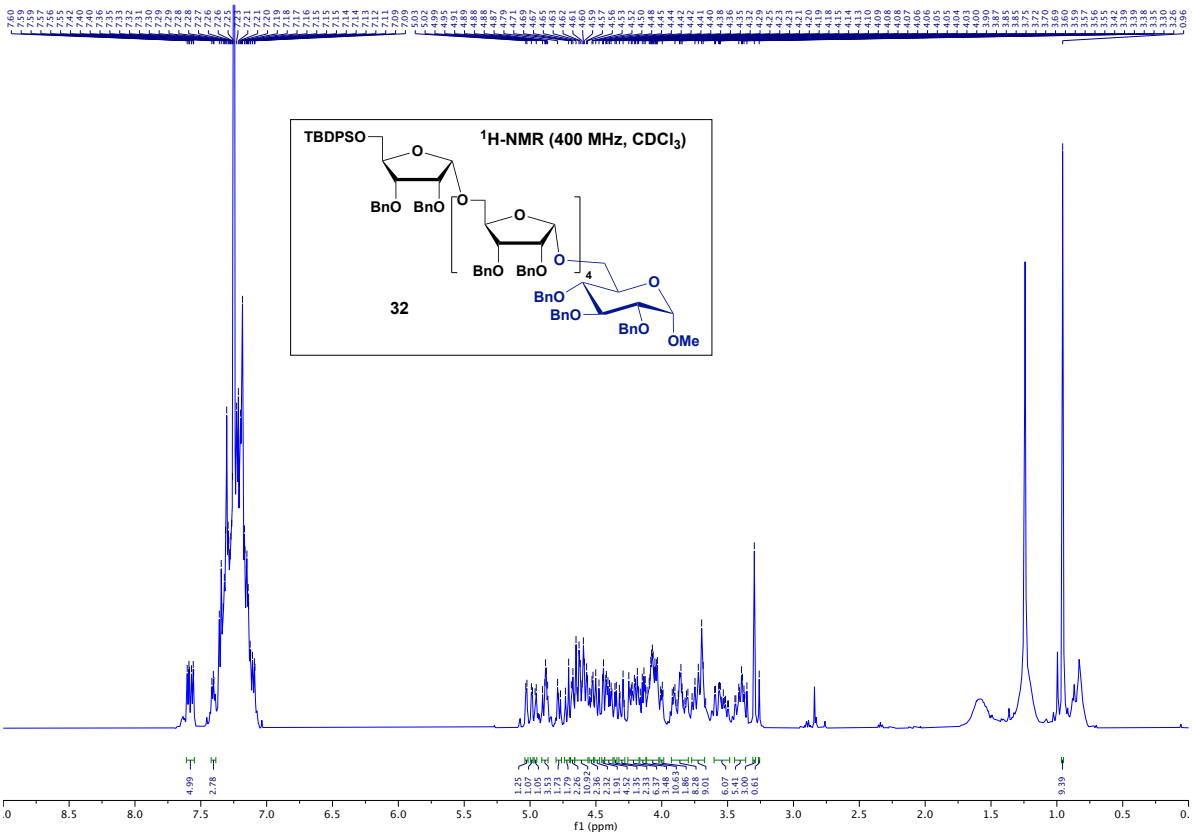

^{13}C-NMR (400 MHz, $CDCl_3$)
HO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
OMe
29
f1 (ppm)

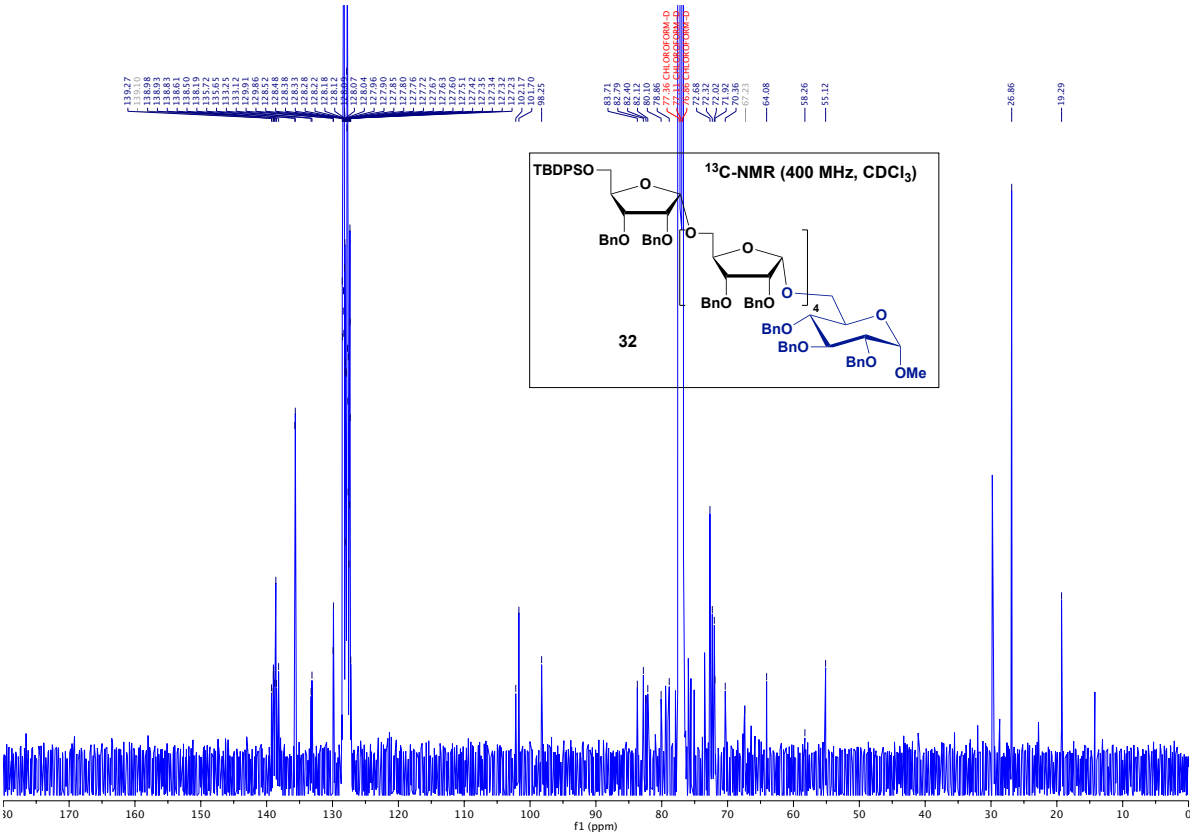

TBDPSO
^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
3
30
OMe
f1 (ppm)

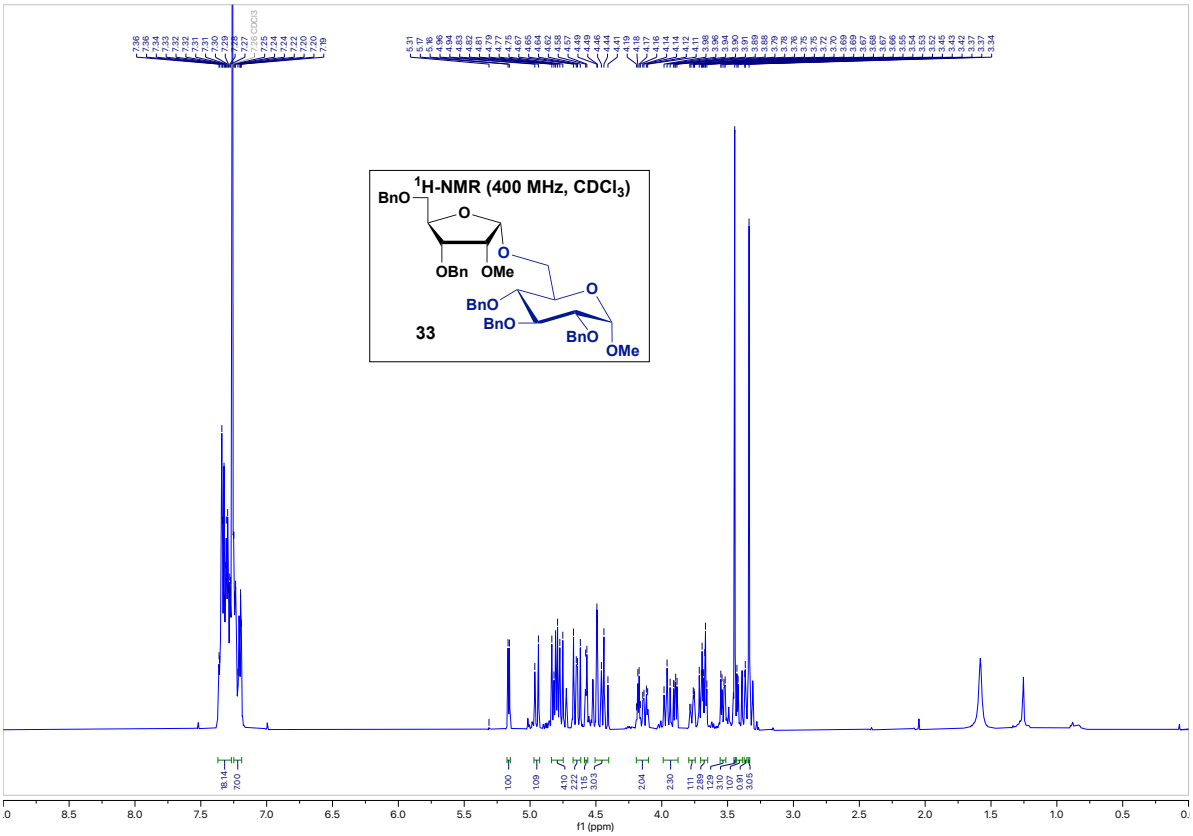

TBDPSO
^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
BnO
O
3
30
OMe
102.18
101.76
101.70
98.25
97.96
f1 (ppm)

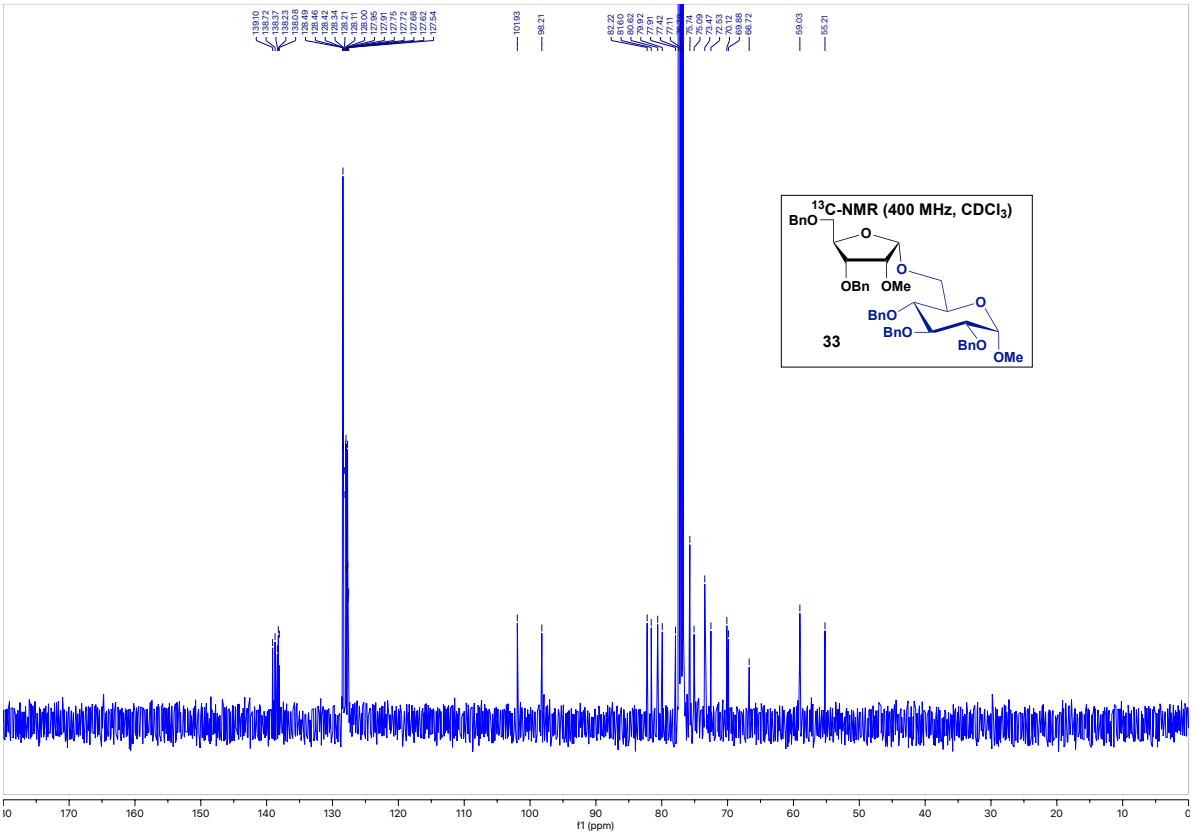

^{1}H-NMR (400 MHz, CDCl$_3$)
31
f1 (ppm)

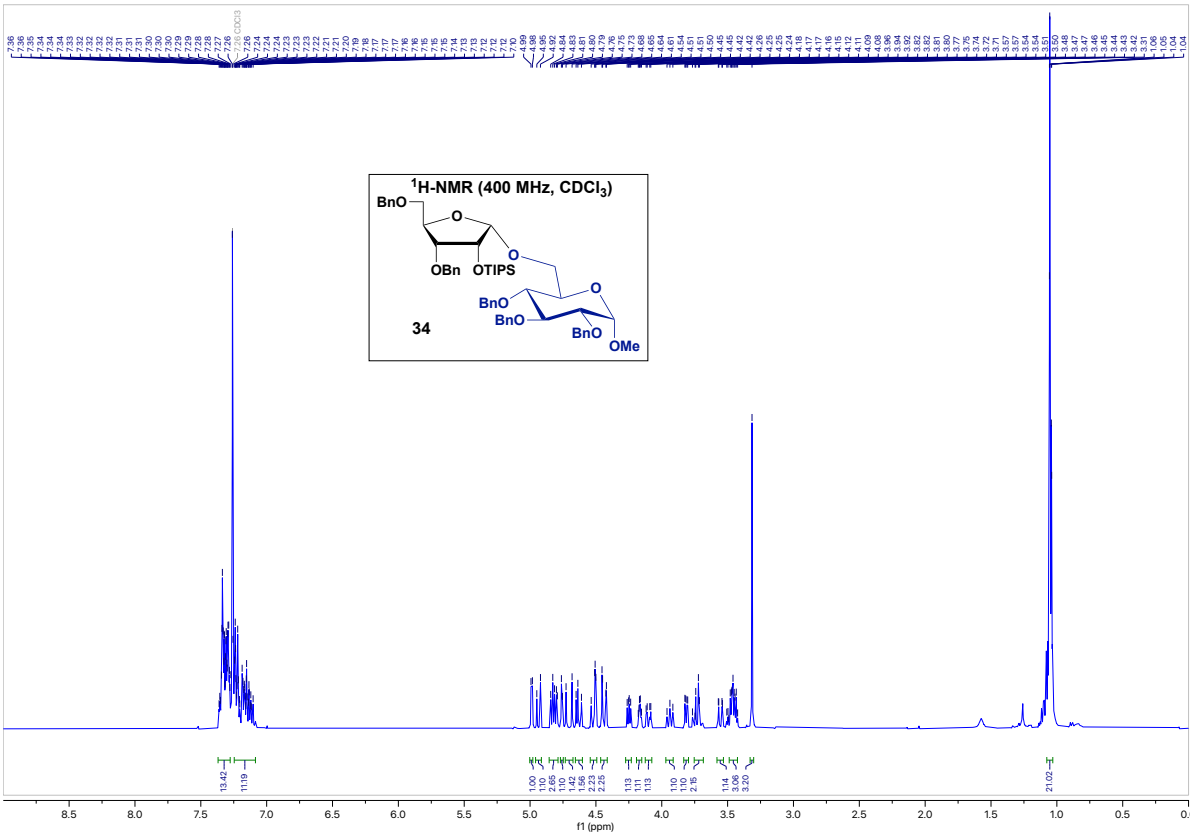

^{13}C-NMR (400 MHz, CDCl$_3$)
31
f1 (ppm)

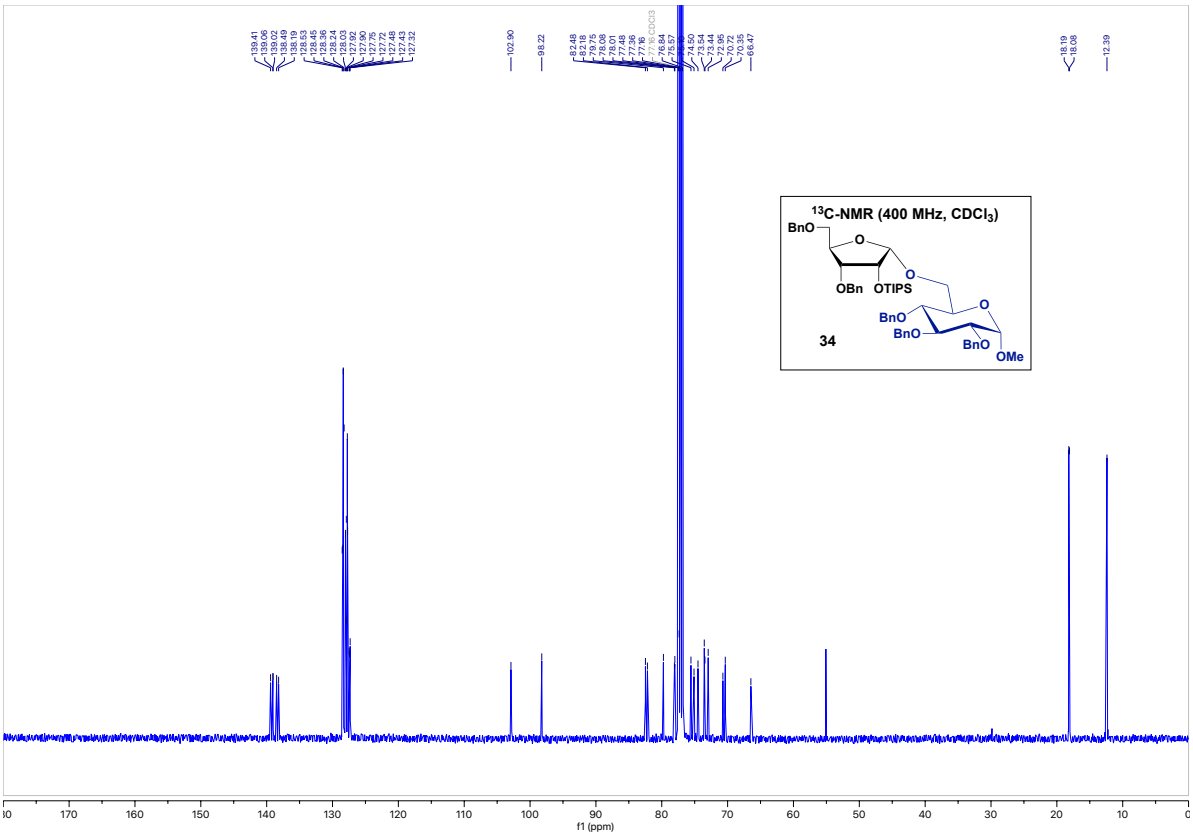

TBDPSO
^{1}H-NMR (400 MHz, $CDCl_3$)
BnO
OMe
32
f1 (ppm)

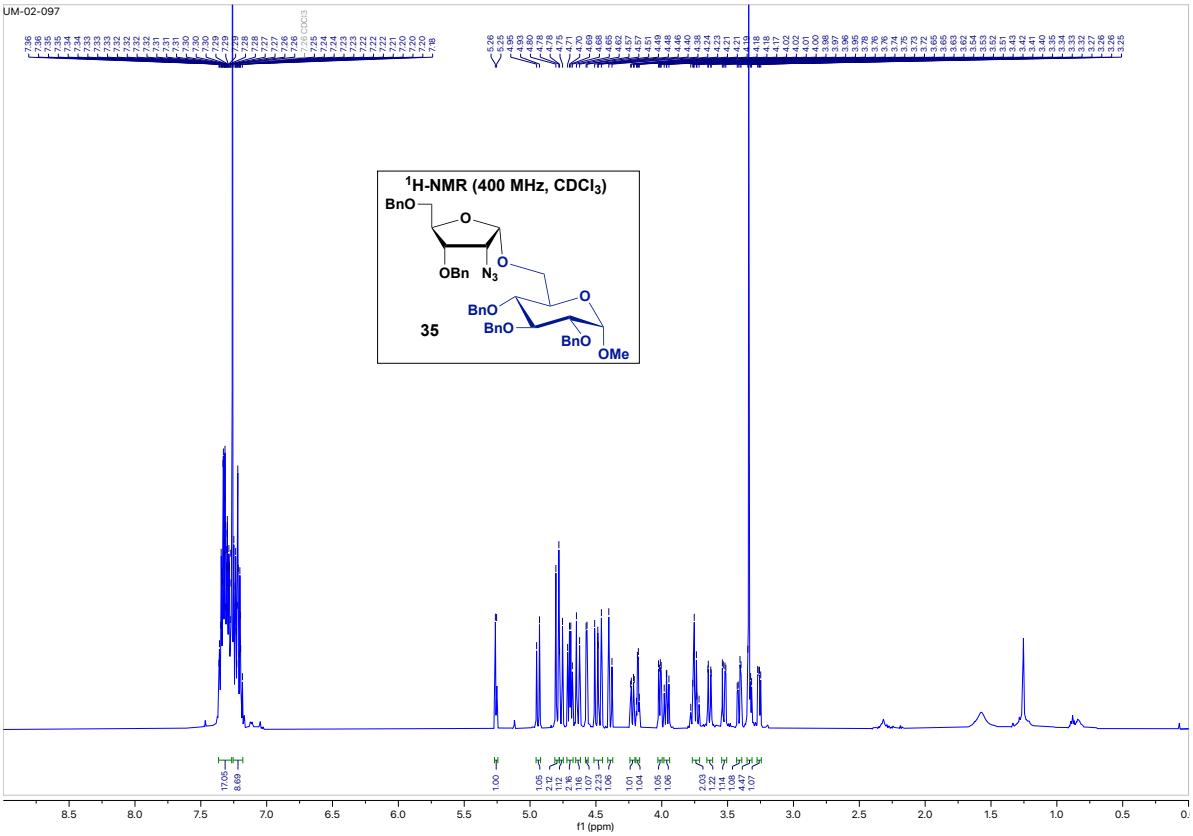

TBDPSO
^{13}C-NMR (400 MHz, $CDCl_3$)
BnO
OMe
32
f1 (ppm)

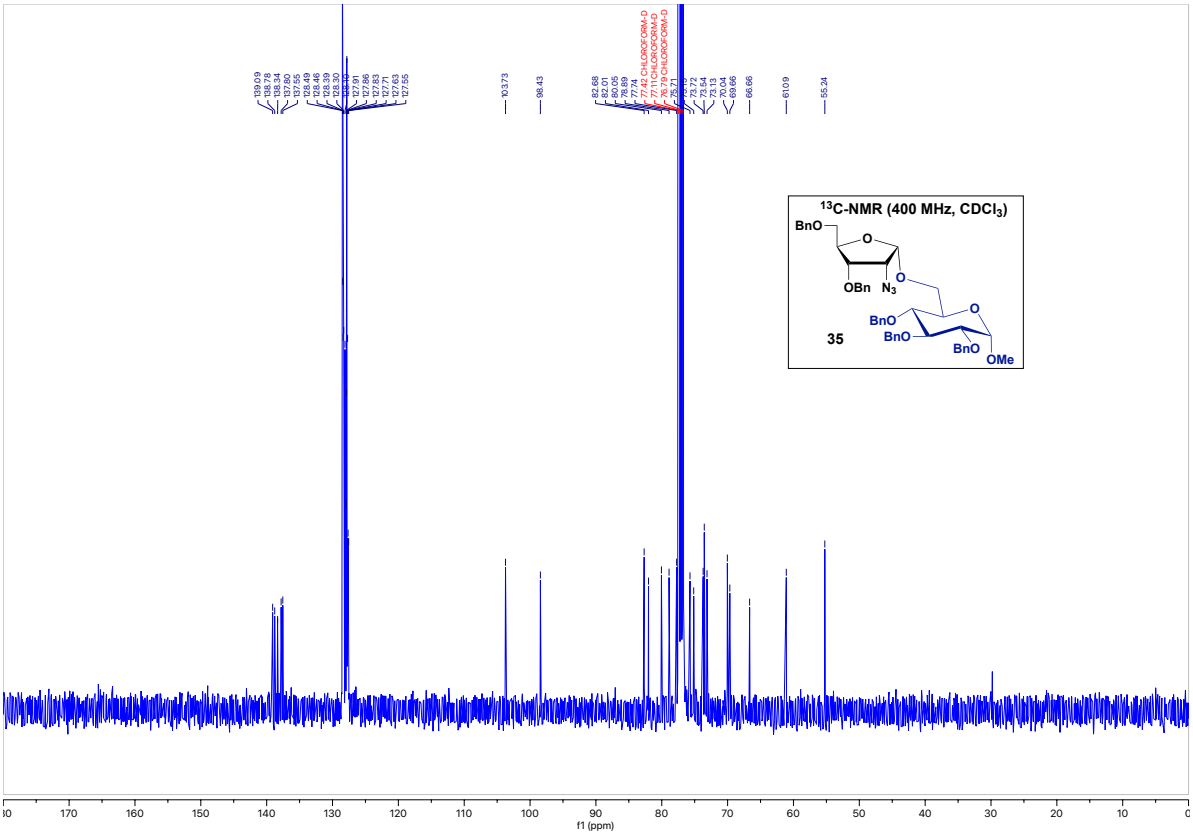

^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
O
OBn
OMe
O
O
BnO
BnO
BnO
O
OMe
33
f1 (ppm)


^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
O
OBn
OMe
O
O
BnO
BnO
BnO
O
OMe
33
f1 (ppm)


^{1}H-NMR (400 MHz, CDCl$_3$)
BnO
O
OBn
OTIPS
O
BnO
BnO
O
BnO
OMe
34
f1 (ppm)


^{13}C-NMR (400 MHz, CDCl$_3$)
BnO
O
OBn
OTIPS
O
BnO
BnO
O
BnO
OMe
34
f1 (ppm)


UM-02-097
^{1}H-NMR (400 MHz, $CDCl_3$)
35


^{13}C-NMR (400 MHz, $CDCl_3$)
35