Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Contents

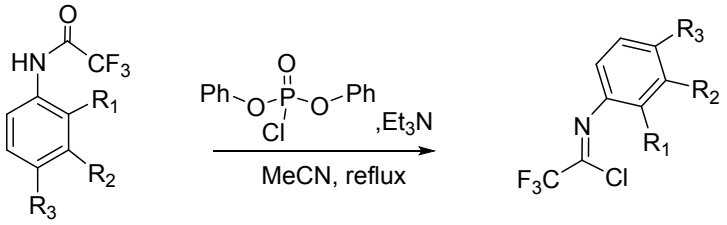
General methods

Chemicals were used as purchased without further purification except 2-methoxyaniline, which was vacuum distilled prior to use. Dry solvents were obtained from a purification solvent system. All reactions of air and moisture sensitive materials were performed under nitrogen atmosphere, with all glassware pre-dried in an oven at 200 °C overnight or flame dried prior to use. Columns were packed with pre-neutralized silica gel LC-60A (40 – 63 μM, pre-neutralized from the manufacturer to a pH of 6.0 to 8.0). TLC analysis was performed on plates (Merck 60, F254), the detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in ethanol. ^{1}H NMR and ^{13}C NMR spectra were acquired using a 500 MHz Avance III HD equipped with a cryogenically cooled 5 mm observe probe optimized for ^{13}C. Chemical shifts are reported in parts per million (ppm) relative to residual solvents signals (δ = 7.26 for ^{1}H NMR and 77.16 for ^{13}C NMR) as the internal standard. ^{19}F NMR spectra were recorded on a 500 MHz instrument using trifluoroacetic acid (δ = -76.55 ppm, $CDCl_3$ solution) in a capillary served as an internal standard. High-resolution mass spectral (HRMS) data were obtained by MALDI – MS using a SolariX XR 7 T ESI/MALDI – FT – ICR MS instrument. Optical rotation data were obtained on an Anton-Paar Polarimeter. All melting points are uncorrected.

Experimental procedures

Synthesis of *N*-substituted imidoyl chlorides

To the solution of a corresponding 2,2,2-trifluoro-*N*-phenylacetamide[1] in MeCN (c = 1.3 M) diphenyl phosphoryl chloride was added (2 equiv) followed by the addition of Et_3N (2 equiv) and the reaction mixture was refluxed (85 °C) overnight. Subsequently, the reaction mixture was cooled down to room temperature, ethyl acetate was added, and the precipitate was filtered off. The filtrate was concentrated in *vacuo* and the crude product was distilled under reduced pressure to afford the desired products. [2]

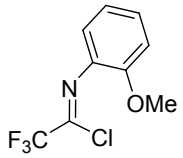


Ia: R_1 = OMe, R_2 = H, R_3 = H
Ib: R_1 = H, R_2 = OMe, R_3 = H
Ic: R_1 = H, R_2 = H, R_3 = OMe

IIa: R_1 = OMe, R_2 = H, R_3 = H, 82%
IIb: R_1 = H, R_2 = OMe, R_3 = H, 79%
IIc: R_1 = H, R_2 = H, R_3 = OMe, 76%

Scheme 1. *N*-substituted imidoyl chloride synthesis.

***N*-(2-methoxyphenyl)-2,2,2- trifluoroacetimidoyl chloride (IIa)**



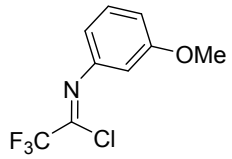
Yield: 82%, 7.10 g

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.02-6.96, (m, 2H), 6.93 (dd, *J* = 7.7, 1.7 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$): δ 149.4, 134.2 (q = 42.7 Hz), 133.3, 128.1, 120.7, 120.4, 116.9 (q = 277.1 Hz), 112.0, 55.8.

The NMR values in accordance with the literature. [1]

***N*-(3-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (IIb)**



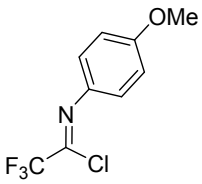
Yield: 79%, 6.85 g

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.14 (m, 2H), 6.98, (ddd, *J* = 7.9, 2.0, 0.7 Hz, 1H), 6.72 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$): δ 160.4, 144.8, 132.3 (q, *J* = 43.1 Hz), 130.1, 128.1, 120.7, 120.4, 117.0 (q, *J* = 277.0 Hz), 113.1, 112.7, 106.4, 79.9, 55.3.

The NMR values in accordance with the literature. [1]

***N*-(4-methoxyphenyl)-2,2,2-trifluoroacetimidoyl chloride (IIc)**



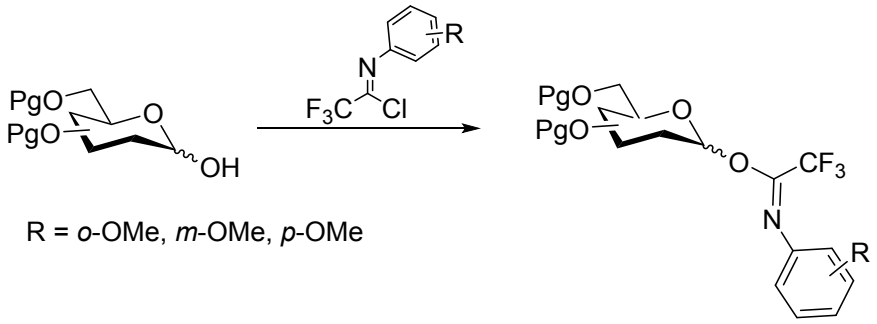
Yield: 76%, 2.32 g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 6.99-6.95 (m, 2H), 3.84 (s, 3H).

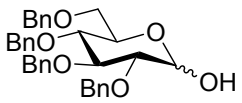
^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 159.7, 135.6, 128.1 (q, J = 42.9 Hz), 124.5, 120.5, 117.2 (q, J = 276.5 Hz), 55.6.

The NMR values in accordance with the literature. [1]

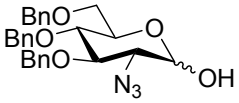
Synthesis of *N*-(methoxyphenyl) trifluoroacetimidate donors



List of hemiacetals used in this study:



3a



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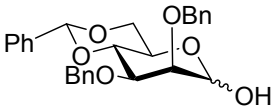

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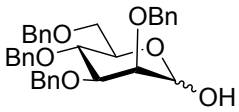
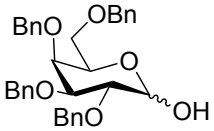


3d



3e

General procedure A

To the solution of hemiacetal (3a-e) in CH_2Cl_2 carbonate (2 equiv) was added (see table) followed by the addition of *N*-phenyl-2,2,2-trifluoroacetimidoyl chloride (2 equiv) (IIa-c) and the reaction mixture was stirred at room temperature overnight unless otherwise stated. The solids were filtered, and the filtrate was concentrated in *vacuo*. The crude products were purified by column chromatography to afford desired PTFA donors.

General procedure B

To the solution of hemiacetal (3a-e) in DMF DABCO (1,4-diazabicyclo[2.2.2]octane) (4 equiv) was added followed by the addition of *N*-phenyl trifluoroacetimidoyl chloride (1.1 equiv). When TLC analysis indicated the full conversion of starting material, the reaction mixture was concentrated in vacuo, diluted with diethyl ether, and washed with $NaHCO_3$ (10% aq. solution) and water (3x), respectively. The organic phase was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude products were purified by column chromatography to afford desired PTFA donors.

General procedure C

To the solution of hemiacetal (3a-e) in CH_2Cl_2 Et_3N (6.7 equiv) was added. The reaction mixture was stirred for 10 min, and then a solution (c = 0.3 M) of *N*-phenyl trifluoroacetimidoyl chloride (2 equiv) was added via syringe pump (1mL/h). When TLC analysis indicated full conversion of starting material, the reaction mixture was washed with $NaHCO_3$ (conc. aq. solution) and brine, respectively. The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude products were purified by column chromatography to afford desired PTFA donors.

General procedure D

To the solution of hemiacetal (3a-e) in pyridine (6.7 equiv) *N*-phenyl trifluoroacetimidoyl chloride (2 equiv) was added. When TLC analysis indicated full conversion of starting material, the reaction mixture was diluted with EtOAc and washed with water. The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude products were purified by column chromatography to afford desired PTFA donors.

General procedure E

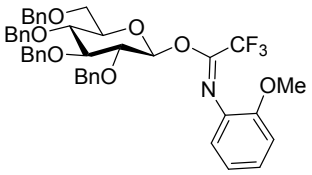
To the solution of hemiacetal (3a-e) in DMF NaH (60% dispersion in mineral oil) (1.1 equiv) was added. The reaction mixture was stirred for 10 min followed by the addition of *N*-phenyl trifluoroacetimidoyl chloride (1.1 equiv). When TLC analysis indicated full conversion of starting material, the reaction mixture was diluted with ethyl acetate and washed with water (3x). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude products were purified by column chromatography to afford desired PTFA donors.

Entry	Hemiacetal	Electrophile (2a-c)	General procedure	Base	Solvent, (concentration) [M]	Time [h]	*α/β*[a] (Yield) [%]
1	3a	2a	B	DABCO	DMF, (c = 0.35)	2	*β* only (91)
2	3a	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only (82)
3	3a	2a	A	Cs_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only (77)
4	3a	2a	C	Et_3N	CH_2Cl_2, (c = 0.1)	2	*β* only (67)
5	3a	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.05)	48	*β* only (74)
6	3a	2a	D	-	pyridine (c = 0.1)	24	Nr
7	3a	2a	C	Et_3N	CH_2Cl_2, (c = 0.1)[b]	2	*β* only (74)
8	3a	2a	C	Et_3N[c]	CH_2Cl_2, (c = 0.1)[b]	1	*β* only (71)
9	3a	2a	C	Et_3N[d]	CH_2Cl_2, (c = 0.1)[b]	24	nr
10	3a	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.15)[b]	8	*β* only (82)
11	3a	2a	A	DBU	CH_2Cl_2, (c = 0.1)[b]	24	nr
12	3a	2a	A	NaH	CH_2Cl_2, (c = 0.1)[a]	24	nr
13	3a	2b	A	K_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only[f]
14	3a	2b	B	DABCO	DMF, (c = 0.35)	2	*β* only[f]
15	3a	2c	A	K_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only[e]
16	3a	2c	B	DABCO	DMF, (c = 0.35)	1.5	*β* only[f]
17	3a	2c	C	Et_3N	CH_2Cl_2, (c = 0.1)[b]	1	*β* only[f]
18	3b	2a	B	DABCO	DMF, (c = 0.35)	4	*β* only (84)
19	3b	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only (76)
20	3c	2a	B	DABCO	CH_2Cl_2, (c = 0.05)	48	1:1 (74)
21	3c	2a	A	K_2CO_3[e]	CH_2Cl_2, (c = 0.05)	48	1:1 (66)
22	3d	2a	A	DBU	CH_2Cl_2, (c = 0.1)[b]	24	nr
23	3d	2a	E	NaH	DMF, (c = 0.1)[b]	24	nr
24	3d	2a	B	DABCO	DMF, (c = 0.35)	2	*β* only (88)
25	3d	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.15)	24	*β* only (73)
26	3d	2a	A	Cs_2CO_3	CH_2Cl_2, (c = 0.15)	6	*β* only (81)
27	3d	2a	C	Et_3N	CH_2Cl_2, (c = 0.1)	24	*β* only (65)
28	3d	2a	A	K_2CO_3	CH_2Cl_2, (c = 0.15)[b]	4 h	*β* only (69)
29	3d	2a	A	DIPEA	CH_2Cl_2, (c = 0.1)	6 h	*β* only (72)
30	3d	2a	B	DABCO	DMF, (c = 0.35)[b]	1	*β* only (66)
31	3e	2a	B	DABCO	DMF, (c = 0.35)	2	*β* only (76)

[a] Anomeric ratio of the crude mixture
[b] Reflux conditions.
[c] TBAI (10% mol) was added.
[d] DMAP (10% mol) was added.
[e] Sonication bath was used.
[f] Product decomposed on the pre-neutralized silica and basic alumina.

Table 1. *N*-substituted trifluoroacetimidate synthesis.

2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D1)



Off-white amorphous solid.

Yield: 91% (4.64 g)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 10H), 7.25 – 7.19 (m, 8H), 7.12 - 7.09 (m, 2H), 6.99 (td, *J* = 8.0, 1.7 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.75 – 6.71 (m, 1H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 2H), 4.71 (d, *J* = 10.8 Hz, 1H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 2H), 3.77 – 3.56 (m, 10H).

^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 149.0, 138.6, 138.1 (C x 2), 138.0, 132.9, 128.7 - 127.5 (C x 22), 125.2, 120.6, 120.5, 111.2, 97.4, 84.6, 81.4, 81.1, 77.3, 75.8, 75.2, 75.0, 73.6, 68.2, 55.6.

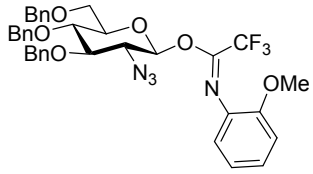
^{19}F NMR{^{1}H NMR} (470 MHz, $CDCl_3$) δ -69.3.

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{43}H_{42}F_3NO_7Na^+$ 764.2806; found 764.2811.

$[\alpha]_D^{25}$ = +45.3 (c = 1.02 $CHCl_3$)

Melting point: 80-82 °C

2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D2)



Yellowish oil.

Yield: 84%, 1.13 g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 13H), 7.20 – 7.14 (m, 3H), 7.08 – 7.03 (m, 1H), 6.88 – 6.84 (m, 2H), 6.79 (dd, *J* = 7.5, 1.3 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.81 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 11.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 4.52 (d, *J* = 12.1 Hz, 1H), 3.85 – 3.25 (m, 10H).

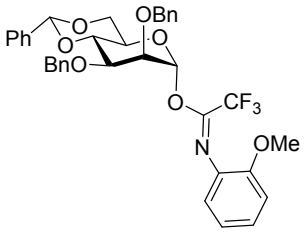
^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 149.0, 138.0, 137.9, 131.6, 129.2, 128.6 - 127.9 (C x 16), 125.4 (x 2), 120.6 (x 2), 111.2, 96.0, 83.1, 77.3, 76.0, 75.8, 75.2, 73.6, 68.0, 65.6, 55.7.

^{19}F NMR{^{1}H NMR} (470 MHz, $CDCl_3$) δ -69.5.

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{43}H_{42}F_3NO_7Na^+$ 699.2401; found 699.2393.

$[\alpha]_D^{25}$ = +33.6 (c = 1.00 $CHCl_3$)

2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-mannopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D3α)



Yellowish oil.

Yield: 74% (*α/β*, 1/1 anomeric mixture), 0.63 g (*α* anomer)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.35 – 7.23 (m, 9H), 7.22 – 7.17 (m, 4H), 7.01 (td, *J* = 8.0, 1.6 Hz, 1H), 6.83 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 5.58 (s, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.67 (bs, 2H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.28 - 4.21 (m, 2H), 3.98 – 3.73 (m, 5H), 3.65 (s, 3H).

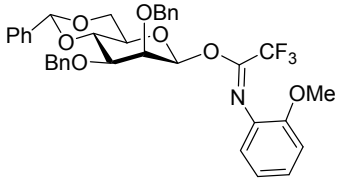
^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 149.0, 138.4, 137.7, 137.6, 132.9, 129.1, 128.5 - 127.8 (x 15), 126.2, 125.4, 120.7, 120.5, 111.2, 101.7, 96.1 ($J_{C\text{-}H}$ = 178.5 Hz), 78.4, 75.7, 74.8, 73.6, 73.5, 68.6, 66.8, 55.6.

^{19}F NMR{^{1}H NMR} (470 MHz, $CDCl_3$) δ -69.8.

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{43}H_{42}F_3NO_7Na^+$ 672.2180; found 672.2175.

$[\alpha]_D^{25}$ = -1.8 (c = 0.82 $CHCl_3$)

2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-mannopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D3β)



Yellowish oil.

Yield: 74% (*α/β*, 1/1 anomeric mixture), 0.63 g (*β* anomer)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 4H), 7.37 – 7.22 (m, 10H), 7.05 (td, *J* = 8.1, 1.6 Hz, 1H),6-89 – 6.72 (m, 2H), 6.70 (d, *J* = 7.5 Hz, 1H), 5.58 (s, 1H), 4.93 (d, *J* = 11.9 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 4.30 – 4.15 (m, 4H), 3.95 – 3.86 (m, 1H), 3.77 – 3.59 (m, 5H).

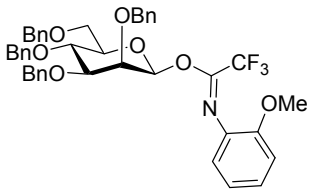
^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 148.9, 138.3, 138.1, 137.5, 132.7, 129.1, 128.7 – 127.7 C (C x 15), 126.2, 125.5, 120.7, 120.5, 111.3, 101.7, 96.5 ($J_{C\text{-}H}$ = 163.2 Hz), 78.4, 78.1, 75.1, 74.8, 72.9, 68.4, 68.3, 55.7.

^{19}F NMR (470 MHz, $CDCl_3$) δ -69.4.

HRMS (MALDI) *m/z*: [M+K^+] Calcd for $C_{43}H_{42}F_3NO_7K^+$ 688.1919; found 688.1913.

$[\alpha]_D^{25}$ = +33.6 (c = 1.00 $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D4)



Colourless oil.

Yield: 88%, 0.94 g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.4 Hz, 2H), 7.29 - 7.27 (m, 5H), 7.25 – 7.19 (m, 11H), 7.16 – 7.11 (m, 2H), 7.01 (td, *J* = 7.9, 1.6 Hz, 1H), 6.82 – 6.78 (m, 2H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 12.2 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.61 – 4.48 (m, 5H), 4.15 (bs, 1H), 3.77 – 3.69 (m, 3H), 3.70 – 3.52 (m, 6H).

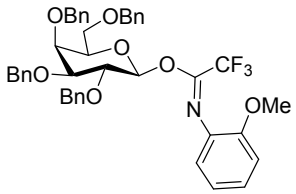
^{13}C NMR{^{1}H NMR} (126 MHz, $CDCl_3$) δ 149.0, 138.5, 138.4, 138.3, 138.1, 133.0, 128.6 - 127.7 (C x 24), 125.2, 120.64, 111.2, 96.4 ($J_{C\text{-}H}$ = 162.6 Hz), 82.0, 75.2, 74.4, 74.1, 73.6, 72.9, 72.1, 69.1, 55.6.

^{19}F NMR{^{1}H NMR} (470 MHz, $CDCl_3$) δ -69.3.

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{43}H_{42}F_3NO_7Na^+$ 764.2806; found 764.2798.

$[\alpha]_D^{25}$ = +17.5 (c = 1.00 $CHCl_3$)

2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl *N*-(2-methoxyphenyl)-2,2,2-trifluoroacetimidate (D5)



Yellowish oil.

Yield: 76%, 0.71 g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 18H), 7.18 – 7.14 (m, 3H), 6.95 (td, *J* = 8.0, 1.6 Hz, 1H), 6.77-6.72 (m, 2H), 6.69 – 6.64 (m, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 10.6 Hz, 1H), 4.81 – 4.75 (m, 1H), 4.73 (d, *J* = 10.7 Hz, 1H), 4.70 – 4.61 (m, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.32 (d, *J* = 11.7 Hz, 1H), 3.98 (bs, 1H), 3.88-3.84 (m, 1H), 3.6 – 3.31 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 138.6, 138.4, 138.3, 138.0, 133.2, 128.6 – 127.7 (C x 23), 125.0, 120.5, 111.2, 97.5, 82.2, 78.3, 75.5, 74.9, 74.5, 73.6, 73.4, 73.2, 68.3, 55.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.0.

HRMS (MALDI) *m/z*: [M+Na^+] Calcd for $C_{43}H_{42}F_3NO_7Na^+$ 764.2806; found 764.2799.

$[\alpha]_D^{25}$ = +42.7 (c = 0.98 $CHCl_3$)

Glycosylations

General procedure A

Under an inert atmosphere, to the solution of the donor (1.2 equiv) and acceptor (1 equiv) in the corresponding solvent (c = 0.05 M) (see table) activator was added (10 mol% with respect to donor). The reaction mixture was monitored with TLC. Upon completion, the reaction was quenched with Et_3N. The solids were filtered over Celite, and the filtrate was concentrated in *vacuo*. The crude NMR was recorded in order to determine the anomers ratio. The crude products were purified by column chromatography to afford the products.

General procedure B

Under an inert atmosphere, to the solution of the donor (1.2 equiv) and acceptor (1 equiv) in the corresponding solvent (c = 0.05 M) (see table) acid scavenger (2,4,6-tri-*tert*-butylpyrimidine) (0.5 equiv), was added followed by the addition of activator (10 mol% with respect to donor). The reaction mixture was monitored with TLC. Upon completion, the reaction was quenched with Et_3N. The solids were filtered over Celite, and the filtrate was concentrated in *vacuo*. The crude NMR was recorded in order to determine the anomers ratio. The crude products were purified by column chromatography to afford the products.

General procedure C

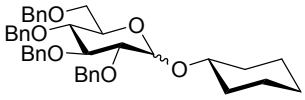
Under an inert atmosphere, to the solution of donor (1.2 equiv) in the corresponding solvent (c = 0.05 M) (see table) activator (10 mol% with respect to donor) was added followed by the addition of acceptor (1 equiv). The reaction mixture was monitored with TLC. Upon completion, the reaction was quenched with Et_3N. The solids were filtered over Celite, and the filtrate was concentrated in *vacuo*. The crude NMR was recorded in order to determine the anomers ratio. The crude products were purified by column chromatography to afford the products.

General procedure D

Under an inert atmosphere, to the solution of acceptor (1.0 equiv) in the corresponding solvent (c = 0.05 M) (see table) activator (10 mol% with respect to donor) was added followed by the slow addition (via syringe pump - 1mL/1h) of donor (1.2 equiv) in 1 mL of solvent. The reaction mixture was monitored with TLC. Upon completion, the reaction was quenched with Et_3N. The solids were filtered over Celite, and the filtrate was concentrated in *vacuo*. The crude NMR was recorded in order to determine the anomers ratio. The crude products were purified by column chromatography to afford the products.

Glycosylation yields provided for the General procedure A: $Fe(OTf)_3$ was used as a catalyst and diethyl ether as a solvent.

Cyclohexyl 2,3,4,6-tetra-*O*- benzyl-D-glucopyranoside (1)



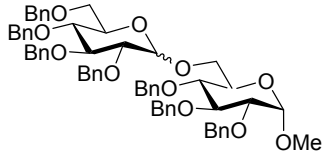
Yield: 95%, 87 mg

1*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 18H), 7.20 – 7.12 (m, 2H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.98 (d, *J* = 3.7 Hz, 1H), 4.86 – 4.80 (m, 2H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.54 – 4.44 (m, 2H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.90-3.88 (m, 1H), 3.77 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.67 – 3.62 (m, 2H), 3.59 – 3.54 (m, 2H), 1.99 – 1.72 (m, 3H), 1.58 – 1.16 (m, 7H).

1*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 18H), 7.21 – 7.14 (m, 2H), 5.00 (d, *J* = 10.9 Hz), 4.93 (d, *J* = 10.8 Hz), 4.84 (d, *J* = 10.9 Hz), 4.76 (d, *J* = 11.1 Hz, 1H), 4.70 (d, *J* = 10.9 Hz, 1H), 4.64 – 4.55 (m, 3H), 4.51 (d, *J* = 7.9 Hz, 1H), 3.80 – 3.71 (m, 2H), 3.69 – 3.61 (m, 2H), 3.56 (t, *J* = 9.3 Hz, 1H), 3.49 – 3.40 (m, 2H), 2.03 – 1.88 (m, 2H), 1.85 – 1.71 (m, 2H), 1.54 – 1.14 (6H).

The NMR values in accordance with literature. [3]

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



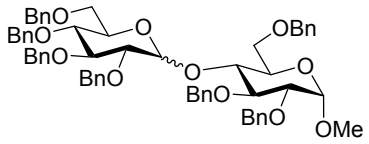
Yield: 96%, 147 mg

2*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 33H), 7.17 – 7.10 (m, 2H), 4.99 (d, *J* = 3.9 Hz, 1H), 4.96 (d, *J* = 11.6 Hz, 1H), 4.92 (d, *J* = 11.3 Hz, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.80 (d, *J* = 10.6 Hz, 1H), 4.77 – 4.71 (m, 2H), 4.66 – 4.55 (m, 5H), 4.54 (d, *J* = 3.6 Hz, 1H), 4.49 – 4.37 (m, 2H), 4.08 – 4.03 (m, 1H), 3.92 – 3.52 (m, 10H), 3.46 - 3.43 (m, 1H), 3.34 (s, 3H).

2*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.15 (m, 35H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.90 (d, *J* = 10.6 Hz, 1H), 4.80 (d, *J* = 10.9 Hz, 1H), 4.82 – 4.75 (m, 3H), 4.70 (d, *J* = 10.9 Hz, 1H), 4.65 – 4.61 (m, 2H), 4.60 – 4.45 (m, 5H), 4.34 (d, *J* = 7.9 Hz, 1H), 4.20 (m, 1H), 3.99 (d, *J* = 9.3 Hz, 1H), 3.84 (dd, *J* = 10.5, 3.0, 1H), 3.77 – 3.41 (m, 9H), 3.31 (s, 3H).

The NMR values in accordance with literature. [4]

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



Yield: 76%, 105

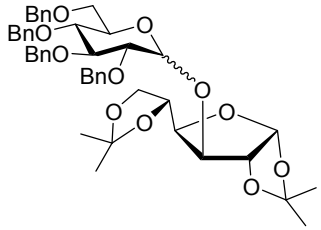
mg

3*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 33H), 7.11 – 7.07 (m, 2H) 5.68 (d, *J* = 3.6 Hz, 1H), 5.02 (d, *J* = 11.5 Hz, 1H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.74 (m, 3H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.61 – 4.46 (m, 7H), 4.40 (d, *J* = 10.8 Hz, 1H), 4.25 (d, *J* = 12.1 Hz, 1H), 4.08 (t, J = 9.1 Hz, 1H), 4.04 (t, J = 9.0 Hz, 1H), 3.92 (t, J = 9.3 Hz, 1H), 3.87 – 3.80 (m, 2H), 3.71 – 3.69 (m, 1H), 3.67 – 3.61 (m, 2H), 3.60 (dd, J = 9.3, 3.6 Hz, 1H), 3.50 – 3.45 (m, 2H), 3.39 – 3.34 (m, 4H)

3*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.33 – 7.15 (m, 33H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.71 (m, 6H), 4.63 – 4.52 (m, 4H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.39 – 4.34 (m, 3H), 3.92 (t, *J* = 9.4 Hz, 1H), 3.86 – 3.80 (m, 2H), 3.71 (dd, *J* = 11.0, 1.9 Hz, 1H), 3.61 – 3.55 (m, 2H), 3.50 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.51 – 3.43 (m, 3H), 3.38 – 3.30 (m, 4H), 3.25 (ddd, J = 10.0, 4.7, 1.9 Hz, 1H)

The NMR values in accordance with literature. [5]

1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-*α*-D-glucofuranose (4)



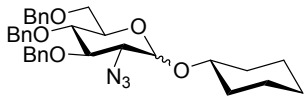
Yield: 76%, 93 mg

4*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 17H), 7.20 – 7.16 (m, 3H), 5.86 (d, *J* = 3.6 Hz, 1H), 5.25 (d, *J* = 3.5 Hz, 1H), 4.99 (d, *J* =11.1 Hz, 1H), 4.87 – 4.81 (m, 3H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.74 (m, 2H), 4.64 – 4.47 (m, 5H), 4.25 (d, *J* = 2.7 Hz, 1H), 4.17 (dd, *J* = 8.0, 2.7 Hz, 1H), 4.08 – 4.07 (m, 1H), 3.96 (t, *J* = 9.3 Hz, 1H), 3.84 – 3.82 (m, 1H), 3.74 (m, 2H), 3.65 – 3.61 (m, 2H), 1.52 (s, 3H), 1.44 (s, 3H), 1.29 (s, 3H), 1.25 (s, 3H).

4*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 20H), 5.97 (d, *J* = 3.3 Hz, 1H), 4.88 (d, *J* = 10.6 Hz, 1H), 4.87 (d, *J* = 10.5 Hz, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 10.0 Hz, 1H), 4.62 (m, 1H), 4.56 (d, *J* = 3.3 Hz, 1H), 4.55-4.53 (m, 2H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.32 – 4.296 (m, 3H), 4.15 (d, *J* = 3.3 Hz, 1H), 4.09 – 4.00 (m, 2H), 3.87 (dd, *J* = 3.3 Hz, 1H), 3.85 – 3.65 (m, 4H), 1.35 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H).

The NMR values in accordance with literature. [6]

Cyclohexyl 2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranoside (5)



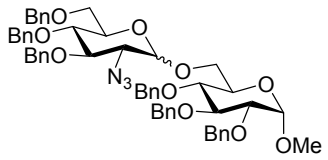
Yield: 80%, 72 mg

5*α* ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 14H), 7.16 – 7.14 (m, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 4.90 – 4.84 (m, 2H), 4.80 (d, *J* = 10.9 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.51 – 4.42 (m, 2H), 4.02 (dd, *J* = 10.3, 8.8 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.76 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.70 (dd, *J* = 10.2, 8.8 Hz, 1H), 3.64 (dd, *J* = 10.7, 2.0 Hz, 1H), 3.62 (dt, *J* = 9.1, 4.0 Hz, 1H), 3.29 (dd, *J* = 10.3, 3.6 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.78 – 1.66 (m, 2H), 1.54 – 1.47 (m, 1H), 1.46 – 1.36 (m, 2H), 1.32 – 1.19 (m, 3H).

***5β*: ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 14H), 7.16 – 7.14 (m, 1H), 5.05 (d, *J* = 3.6 Hz, 1H), 4.90 – 4.84 (m, 2H), 4.81 (d, *J* = 10.7 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.50 (dd, *J* = 10.5 Hz, 1H), 4.48 (dd, *J* = 10.9 Hz, 1H), 4.02 (dd, *J* = 10.3, 8.8 Hz, 1H), 3.92 (dt, *J* = 10.1, 2.8 Hz, 1H), 3.76 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.70 (dd, *J* = 10.1, 8.8 Hz, 1H), 3.64 (dd, *J* = 10.7, 2.1 Hz, 1H), 3.62 (dt, *J* = 9.1, 4.0 Hz, 1H), 3.27 (dd, *J* = 10.2, 3.6 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.78 – 1.66 (m, 2H), 1.54 – 1.47 (m, 1H), 1.46 – 1.36 (m, 2H), 1.32 – 1.19 (m, 3H).

The NMR values in accordance with the literature. [7]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl)-*α*-D-glucopyranoside (6)



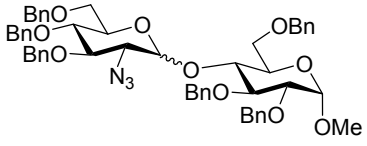
Yield: 83%, 119 mg

6*α* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 28H), 7.17 – 7.14 (m, 1H), 5.00 (d, *J* = 3.6 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.92 (d, *J* = 11.2 Hz), 4.87 – 4.83 (m, 2H), 4.82 – 4.78 (m, 2H), 4.76 (d, *J* = 2.7 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.61 – 4.55 (m, 3H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.05 (t, *J* = 9.4 Hz, 1H,), 3.94 (dd, *J* = 10.2, 8.6 Hz, 1H), 3.85 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.79 – 3.72 (m, 2H), 3.71 – 3.65 (m, 2H), 3.63 (dd, *J* = 10.8, 3.3 Hz, 1H, H-6′), 3.59 – 3.50 (m, 3H), 3.36 (s, 3H), 3.33 (dd, J = 10.3, 3.6 Hz, 1H).

6*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 28H), 7.17 – 7.14 (m, 1H),4.97 (d, *J* = 11.0 Hz, 1H), 4.94 (d, *J* = 11.2 Hz, 1H), 4.88 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.81 – 4.76 (m, 3H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 3.6 Hz, 1H, H-1), 4.57 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 4.18 (d, *J* = 7.8 Hz, 1H), 4.12 (dd, *J* = 10.9, 1.6 Hz, 1H), 4.00 (dd, *J* = 9.6, 8.7 Hz, 1H), 3.81 – 3.79 (m, 1H), 3.70 – 3.62 (m, 3H), 3.57 – 3.53 (m, 1H), 3.52 (dd, *J*=9.6, 8.7 Hz, 1H), 3.51 (dd, J = 9.6, 3.6 Hz, 1H), 3.45 – 3.39 (m, 2H), 3.3 (s, 3H), 3.32 (m, 1H).

The NMR values in accordance with the literature. [8]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl)-*α*-D-glucopyranoside (7)



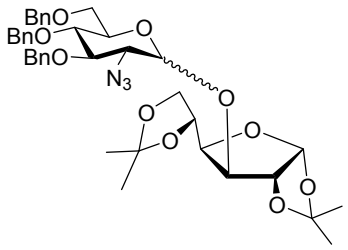
Yield: 84%, 119 mg

7*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.16 (m, 16H), 7.13 – 7.07 (m, 14H), 5.69 (d, *J* = 3.7 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.88 – 4.74 (m, 3H), 4.77 – 4.70 (m, 2H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 1H), 4.52 – 4.46 (m, 3H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.23 (d, *J* = 12.1 Hz, 1H), 4.06 (t, *J* = 9.1 Hz, 1H), 3.87 (t, *J* = 9.3 Hz, 1H), 3.82 (dd, *J* = 10.2, 8.3 Hz, 1H), 3.75 – 3.72 (m, 1H), 3.71 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.65 – 3.60 (m, 3H), 3.54 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.50 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.36 (s, 3H), 3.30 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.25 (dd, *J* = 10.2, 3.9 Hz, 1H).

7*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.16 (m, 15H), 7.14 – 7.17 (m, 15H), 5.00 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.81– 4.72 (m, 4H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.56 (m, 2H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.21 (d, *J* = 8.0 Hz, 1H), 3.95 (t, *J* = 9.3 Hz, 1H), 3.91 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.88 (t, *J* = 9.3 Hz, 1H), 3.75 (dt, *J* = 10.1, 2.5 Hz, 1H), 3.69 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.63 – 3.56 (m, 2H), 3.51 – 3.44 (m, 2H), 3.35 (s, 3H), 3.30 (dd, *J* = 9.9, 8.1 Hz, 1H), 3.22 (t, *J* = 9.4 Hz, 1H), 3.14 (ddd, *J* = 9.9, 4.4, 1.9 Hz, 1H).

The NMR values in accordance with the literature. [9]

1,2:5,6-di-*O*-isopropylidene-3-*O*-(2-azido-2-deoxy-3,4,6-tri-*O*-benzyl-D-glucopyranosyl)-*α*-D-glucopyranoside (8)



Colourless oil

Yield: 72%, 58 mg

8*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 7H), 7.25 – 7.20 (m, 6H), 7.09 – 7.06 (m, 2H), 5.80 (d, *J* = 3.6 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 4.84 – 4.76 (m, 2H), 4.73 (d, *J* = 10.6. Hz, 1H), 4.60 – 4.52 (m, 3H), 4.45 – 4.41 (m, 2H), 4.21 (d, *J* = 2.7 Hz, 1H), 4.10 (dd, *J* = 8.6, 6.2 Hz, 1H), 4.00 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.90 (dd, *J* = 8.6, 5.6 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.73 (ddd, *J* = 9.9, 3.9, 2.0 Hz, 1H), 3.69 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.66 – 3.60 (m, 2H), 3.43 (dd, *J* = 10.3, 3.6 Hz, 1H), 1.41 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H).

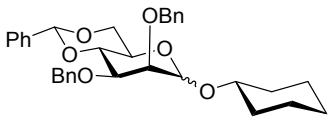
8*α*: ^{13}C NMR {^{1}H NMR} (126 MHz, $CDCl_3$) δ 137.8, 137.7, 137.6, 128.6 -127.9 (C x 15), 112.0, 109.3, 105.2, 98.1, 83.8, 81.9, 81.5, 80.3, 80.1, 78.2, 75.6, 75.3, 73.6, 71.9, 71.6, 68.6, 67.3, 64.0, 26.8, 26.8, 26.2, 25.3.

***8β*: ^{1}H NMR** (500 MHz, CDCl3) δ 7.30 – 7.19 (m, 13H), 7.14 – 7.11 (m, 2H), 5.91 (d, *J* = 3.8 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.77 – 4.69 (m, 3H), 4.56- 4.44 (m, 5H), 4.38 – 4.33 (m, 1H), 4.32 – 4.27 (m, 3H), 3.99 (dd, *J* = 6.3, 4.4 Hz, 2H), 3.71 – 3.55 (m, 4H), 3.38 – 3.27 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H).

***8β*:^{13}C NMR {^{1}H NMR}** δ 137.0, 136.8, 136.7, 127.9 – 126.9 (C x 15), 111.0, 107.6, 104.6, 99.3, 81.9, 81.8, 79.7, 79.3, 76.5, 74.5, 74.0, 74.1, 72.6, 72.3, 71.8, 67.7, 65.2, 65.0, 25.8, 25.5, 25.3, 24.3.

HRMS (MALDI) *m/z*: [M+Na$^+$] Calcd for $C_{39}H_{47}N_3O_{10}Na^+$ 740.3154; found 740.3159.

Cyclohexyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranoside (9)



Yield: 87%, 77 mg (starting from *α* donor)

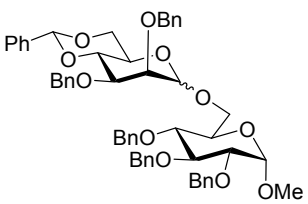
Yield: 83%, 73 mg (starting from *β* donor)

9*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 − 7.49 (m, 2H), 7.43 − 7.25 (m, 13H), 5.59 (s, 1H), 4.90 (d, *J* = 1.2 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.35 - 4.19 (m, 2H), 4.05 – 4.00 (m, 1H), 3.92 − 3.83 (m, 2H), 3.78 (m, 1H), 3.55−3.44 (m, 1H), 1.88 − 1.79 (m, 1H), 1.75−1.68 (m, 3H), 1.54−1.50 (m, 2H), 1.42−1.12 (m, 4H)

9*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 − 7.49 (m, 2H), 7.43 − 7.25 (m, 13H), 5.65 (s, 1H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.89 (d, *J* = 12.5 Hz, 1H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 12.5 Hz, 1H), 4.55 (s, 1H), 4.30 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.22 (t, *J* = 9.6 Hz, 1H), 3.95 (t, *J* = 10.4 Hz, 1H), 3.88 (d, *J* = 3.1 Hz, 1H), 3.72 − 3.66 (m, 1H), 3.58 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.34−3.30 (m, 1H), 1.89 − 1.80 (m, 1H), 1.75−1.68 (m, 3H), 1.54−1.50 (m, 2H), 1.42−1.12 (m, 4H).

The NMR values in accordance with the literature. [10]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranosyl)-*α*-D-glucopyranoside (10)



Yield: 81%, 125 mg (starting from α donor)

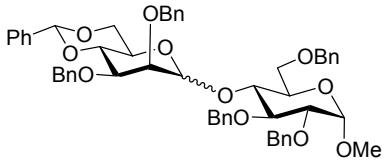
Yield: 79%, 122 mg (starting from β donor)

10*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.45 – 7.15 (m, 28H), 5.52 (s, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.85 (d, *J* = 1.2 Hz, 1H), 4.84 – 4.73 (m, 4H), 4.67 (d, *J* = 12.8 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 3.2 Hz, 1H), 4.50 (d, *J* = 10.1 Hz, 1H), 4.25 – 4.23 (m, 1H), 4.19 – 4.11 (m, 1H), 3.97 – 3.96 (m, 1H), 3.90 (dd, *J* = 9.4, 2.6 Hz, 1H), 3.76 – 3.68 (m, 4H), 3.67 – 3.65 (m, 1H), 3.59 (dd, *J* = 11.0, 1.2 Hz, 1H), 3.44 – 3.34 (m, 2H), 3.30 (s, 3H).

10*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.45 – 7.15 (m, 28H), 5.58 (s, 1H), 5.09 (d, *J* = 10.9 Hz, 1H), 4.96 (d, *J* = 12.1 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.87 – 4.75 (m, 3H), 4.74 - 4.58 (m, 4H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.29 (dd, *J* = 10.4, 4.2 Hz, 1H), 4.20 (t, *J* = 9.5 Hz, 1H), 4.11 - 3.99 (m, 3H), 3.91-3.89 (m, 1H), 3.75 (d, *J* = 3.2 Hz, 1H), 3.69 (d, *J* = 2.9 Hz, 1H), 3.55 – 3.44 (m, 4H), 3.33 (s, 3H), 3.22 – 3.18 (m, 1H).

The NMR values in accordance with the literature. [10]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranosyl)-*α*-D-glucopyranoside (11)



Yield: 73%, 130 mg (starting from α donor)

Yield: 77%, 136 mg (starting from β donor)

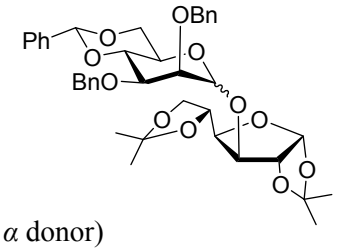
11*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H) 7.49–7.15 (m, 28H), 5.61 (s, 1H), 5.30 (d, J = 1.4 Hz, 1H), 5.11 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.66–4.53 (m, 5H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.30–4.16 (m, 2H), 4.14–4.09 (m, 1H), 3.94 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.91–3.67 (m, 8H), 3.53 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.40 (s, 3H).

11*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H) 7.49–7.15 (m, 28H), 5.54 (s, 1H), 5.08 (d, *J* = 10.9 Hz, 1H), 4.90 – 4.77 (m, 3H), 4.77 (d, *J* = 12.4 Hz, 1H), 4.70 – 4.49 (m, 4H), 4.40 (s, 1H), 4.31 (d,

J= 12.0 Hz, 1H), 4.17 – 4.01 (m, 2H), 3.96 – 3.83 (m, 2H), 3.67 (d, *J* = 3.0 Hz, 1H), 3.65 – 3.61 (m, 1H), 3.60 – 3.44 (m, 3H), 3.43 (s, 3H), 3.36 (dd, *J* = 9.8, 3.0 Hz, 1H), 3.09 (td, *J* = 9.8, 4.9 Hz, 1H).

The NMR values in accordance with literature. [10]

1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranosyl)-*α*-D-glucofuranose



Yield: 69%, 86 mg (starting from *α* donor)

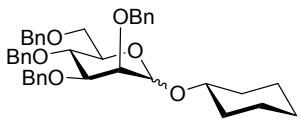
Yield: 67%, 84 mg (starting from *β* donor)

12*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.25 (m, 15H), 5.84 (d, *J* = 3.6 Hz, 1H), 5.67 (s, 1H), 5.21 (d, *J* = 1.5 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 3.6 Hz, 1H), 4.36–4.26 (m, 3H), 4.14–4.00 (m, 4H), 3.99–3.76 (m, 4H), 1.52 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H).

12*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.25 (m, 15H), 5.89 (d, *J* = 3.9 Hz, 1H), 5.63 (s, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.86–3.83 (m, 1H), 3.61 (dd, *J* = 9.7, 3.0 Hz, 1H) 3.35–3.27 (m, 1H), 1.50 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H).

The NMR values in accordance with the literature. [11]

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside (13)



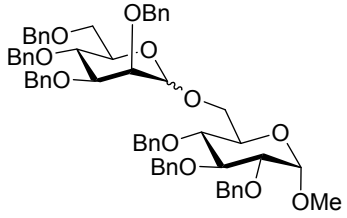
Yield: 88%, 84 mg

13*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.15 (m, 20 H), 5.00 (d, *J* = 1.9 Hz, 1H), 4.88 (d, *J* = 10.7 Hz, 1H), 4.80-4.62 (m, 4H), 4.55-4.43 (m, 2H), 3.98 (dd, J = 9.3, 4,5 Hz, 1H), 3.93 (dd, J = 9.8, 3.0, 1Hz, 1H), 3.88-3.82 (m, 1H,), 3.80-3.77 (m, 2H), 3.73 (dd, *J* = 9.3, 2.2 Hz, 1H), 3.72 – 3.70 (m, 1H), 3.87-3.68 (m, 1H), 1.86 - 1.13 (m, 10H).

13*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.15 (m, 20 H), 4.91 (d, *J* = 12.2 Hz, 1H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 10.5 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.35 (d, *J* = 11.9 Hz, 1H), 4.29 (d, *J* = 10.5 Hz, 1H), 3.82 – 3.64 (m, 5H), 3. – 3.70 (m, 1H), 3.43-3.35 (m, 1H), and 1.86 - 1.13 (m, 10H).

The NMR values in accordance with the literature. [4]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-*α*-D-glucopyranoside (14)



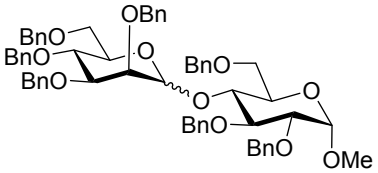
Yield: 83%, 114 mg

14*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.11 (m, 35H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.96 (d, *J* = 1.8 Hz, 1H), 4.86 (dd, *J* = 11.0, 7.3 Hz, 2H), 4.82 (dd, *J* = 11.5, 6.1 Hz, 2H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.65 (d, *J* = 10.9 Hz, 1H), 4.63 - 4.54 (m, 4H), 4.50 (dd, *J* = 11.0, 2.5 Hz, 2H), 4.43 (d, *J* = 12.1 Hz, 1H), 3.99 (t, *J* = 9.5 Hz, 2H), 3.88 – 3.74 (m, 3H), 3.72 – 3.55 (m, 5H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (t, *J* = 9.3 Hz, 1H), 3.30 (s, 3H).

14*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.11 (m, 35H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.83-4.81 (m, 2H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.58 - 4.56 (m, 2H), 4.55 – 4.48 (m, 2H), 4.51 (dd, *J* = 11.0, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.18 (dd, *J* = 10.0, 1.2 Hz, 2H), 4.09 – 4.04 (m, 2H), 3.85 – 3.65 (m, 5H), 3.51 (dd, *J* = 9.3, 2.0 Hz, 1H), 3.49 – 3.35 (m, 4H), 3.33 (s, 3H).

The NMR values in accordance with the literature. [12]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-*α*-D-glucopyranoside (15)



Yield: 76%, 105 mg

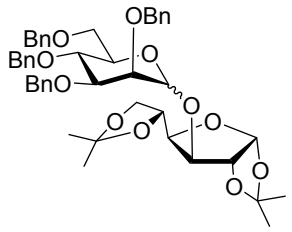
15*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.11 (m, 35H), 5.29 (d, *J* = 1.8 Hz, 1H), 5.11 (d, *J* = 11.9 Hz, 1H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.63 – 4.51 (m, 7H), 4.50 (d, *J* = 10.9

Hz, 1H), 4.44 (dd, *J* = 12.0, 2.3 Hz, 2H), 4.31 (d, *J* = 12.1 Hz, 1H), 4.21 (d, *J* = 12.1 Hz, 1H), 3.96 (t, *J* = 9.4 Hz, 1H), 3.88 – 3.77 (m, 3H), 3.74 – 3.61 (m, 5H), 3.65 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.56 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.54 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.38 (s, 3H).

15*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 35H), 5.15 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.79 (m, 2H), 4.78 – 4.72 (m, 2H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.57 (s, 1H), 4.58 (d, *J* = 9.5 Hz, 1H), 4.51 (d, *J* = 10.9 Hz, 1H), 4.49 – 4.42 (m, 2H), 4.40 (d, *J* = 12.2 Hz, 1H), 4.41 (s, 1H), 4.39 – 4.30 (m, 2H), 3.93 – 3.89 (m, 2H), 3.88 (t, *J* = 9.6 Hz, 1H), 3.74 – 3.70 (m, 1H), 3.69 (d, *J* = 2.9 Hz, 1H), 3.67 (dd, *J* = 11.2, 1.8 Hz, 1H), 3.58 – 3.55 (m, 2H), 3.54 (dd, *J* = 11.3, 5.4 Hz, 1H), 3.47 – 3.40 (m, 1H), 3.37 (s, 3H), 3.30 – 3.25 (m, 2H).

The NMR values in accordance with the literature. [13]

1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-*α*-D-glucofuranose (16)



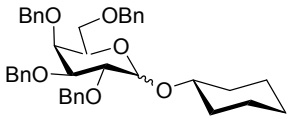
Yield: 71%, 89 mg

16*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.20 (m, 18H), 7.19-7.14 (m, 2H), 5.81 (d, *J* = 3.6 Hz, 1H), 5.25 (s, 1H), 4.92 (d, *J* = 10.6 Hz, 1H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.72-4.60 (m, 3H), 4.60- 4.49 (m, 4H), 4.28-4.26 (m, 1H), 4.07-3.92 (m, 5H), 3.85-3.76 (m, 5H), 1.51 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.25 (s, 3H).

16*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.20 (m, 20H), 5.91 (d, *J* = 3.6 Hz, 1H), 4.90 (d, *J* = 12.1 Hz, 1H), 4.88 (d, *J* = 10.6 Hz, 1H), 4.79 (d, *J* = 11.9 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.60- 4.54 (m, 3H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.49 (s, 1H), 4.48-4.44 (m, 2H), 4.35 (d, *J* = 2.9 Hz, 1H), 4.29 (dd, *J* = 5.1, 3.1 Hz, 1H), 4.13- 4.09 (m, 1H), 4.08-4.04 (m, 1H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.87 (d, *J* = 2.8 Hz, 1H), 3.83-3.76 (m, 2H), 3.53 (dd, *J* = 9.6, 2.9 Hz, 1H), 3.43 – 3.41 (m, 1H), 1.50 (s, 3H), 1.39 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H).

The NMR values in accordance with the literature. [14]

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside (17)



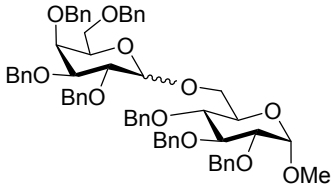
Yield: 86%, 80 mg

17*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 20H), 5.01 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 11.5 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.8 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 1H), 4.04 (dd, *J* = 9.9, 3.6 Hz, 1H), 3.99 – 3.94 (m, 2H), 3.57 – 3.50 (m, 3H), 1.94 – 1.33 (m, 10H).

17*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 20H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.90 (d, *J* = 11.7 Hz, 1H), 4.77 – 4.72 (m, 2H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 7.7 Hz, 1H), 4.44 – 4.37 (m, 2H), 3.87 (d, *J* = 3.0 Hz, 1H), 3.80 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.72 – 3.63 (m, 1H), 3.60 – 3.55 (m, 2H), 3.53 – 3.47 (m, 2H), 1.94 – 1.33 (m, 10H).

The NMR values in accordance with the literature. [7]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-*α*-D-glucopyranoside (18)



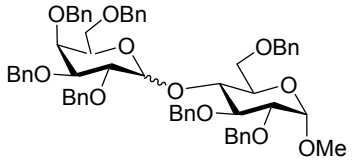
Yield: 81%, 116 mg

18*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 35H), 5.00 (d, *J* = 3.5 Hz, 1H), 4.95 (d, *J* = 11.5 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.81 – 4.78 (m, 2H), 4.73 – 4.66 (m, 4H), 4.65 – 4.54 (m, 2H), 4.54 (d, *J* = 5.3 Hz, 1H), 4.51 (d, *J* = 3.5 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* =11.9 Hz, 1H), 4.04 (dd, *J* = 5.9, 3.5 Hz, 1H), 3.99 – 3.87 (m, 4H), 3.80 – 3.71 (m, 3H), 3.60 (t, *J* = 9.3 Hz, 1H), 3.55 – 3.48 (m, 2H), 3.40 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.32 (s, 3H).

18*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 35H), 4.99 – 4.92 (m, 3H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.72 (m, 5H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.57 (m, 2H), 4.52 (d, J = 11.2 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 4.15 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.99 (t, *J* = 9.2 Hz, 1H), 3.93 – 3.81 (m, 3H), 3.65 – 3.45 (m, 7H), 3.31 (s, 3H).

The NMR values in accordance with the literature. [3]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-*α*-D-glucopyranoside (19)



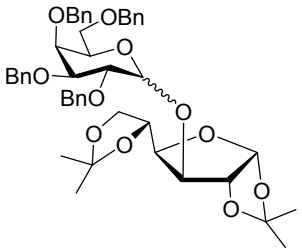
Yield: 77%, 102 mg

19*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 35H), 5.77 (d, *J* = 3.8 Hz, 1H), 4.99 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.74 – 4.63 (m, 4H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 4.56 – 4.51 (m, 3H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 11.6 Hz, 1H), 4.09 (t, *J* = 9.2 Hz, 1H), 4.03 – 3.90 (m, 3H), 3.88 – 3.81 (m, 2H), 3.83 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.70 (dd, *J* = 10.6, 4.7 Hz, 1H), 3.65 (m, 1H), 3.55 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.48 (m, 1H), 3.43 (m, 1H), 3.36 (s, 3H).

19*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 35H), 5.03 (d, *J* = 10.5 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.83 – 4.78 (m, 2H), 4.75 – 4.71 (m, 2H), 4.70 – 4.65 (m, 2H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.55 – 4.54 (m, 1H), 4.54 – 4.51 (m, 2H), 4.36 (d, *J* = 11.9 Hz, 1H), 4.32 (d, *J* = 12.1 Hz, 1H), 4.29 (d, *J* = 7.8 Hz, 1H), 4.22 (d, *J* = 11.8 Hz, 1H), 3.91 – 3.85 (m, 2H), 3.83 – 3.79 (m, 2H), 3.73 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.60 (ddd, *J* = 10.0, 3.4, 2.0 Hz, 1H), 3.53 (t, *J* = 8.7 Hz, 1H), 3.50 – 3.44 (m, 2H), 3.38 – 3.35 (m, 1H), 3.34 (s, 3H), 3.33 – 3.28 (m, 2H).

The NMR values in accordance with the literature. [15]

1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-*α*-D-glucofuranose (20)



Yield: 64%, 78 mg

20*α*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 20H), 5.79 (d, *J* = 3.6 Hz, 1H), 5.12 (d, *J* = 3.7 Hz, 1H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 3.6 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 4.39 – 4.38 (m, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.09 – 3.95 (m, 5H), 3.88 – 3.82 (m, 2H), 3.75 (m, 1H), 3.52 (m, 1H), 3.40 (m, 1H), 1.40 (s, 3H), 1.35 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H).

20*β*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 20H), 5.68 (d, *J* = 3.8 Hz, 1H), 4.95 (d, *J* = 11.9 Hz, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.72 – 4.68 (m, 2H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 10.9 Hz, 1H), 4.46 – 4.44 (m, 2H), 4.43 (d, *J* = 7.9 Hz, 1H), 4.39 – 4.30 (m, 5H), 4.00 – 3.92 (m, 3H), 3.87 – 3.75 (m, 2H), 3.65 (dd, *J* = 9.7, 7.6 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H).

The NMR values in accordance with the literature. [16]

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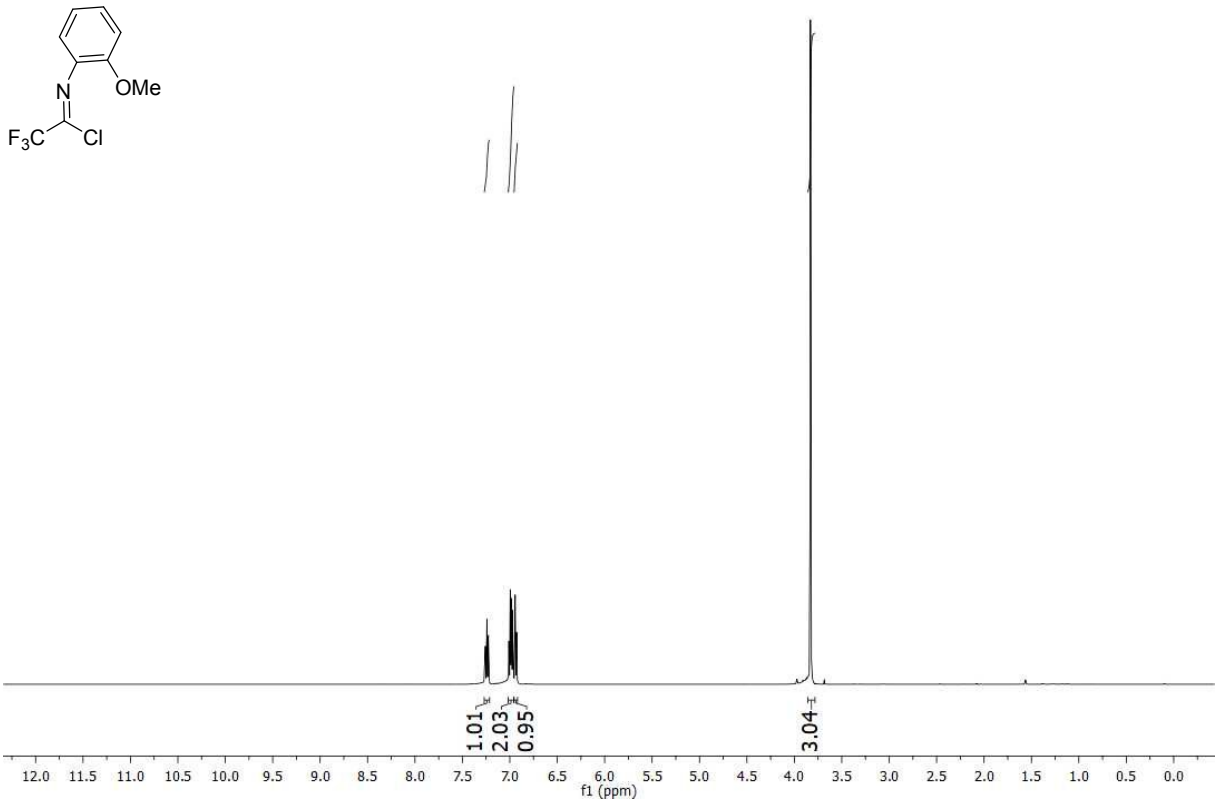
NMR spectra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3.04
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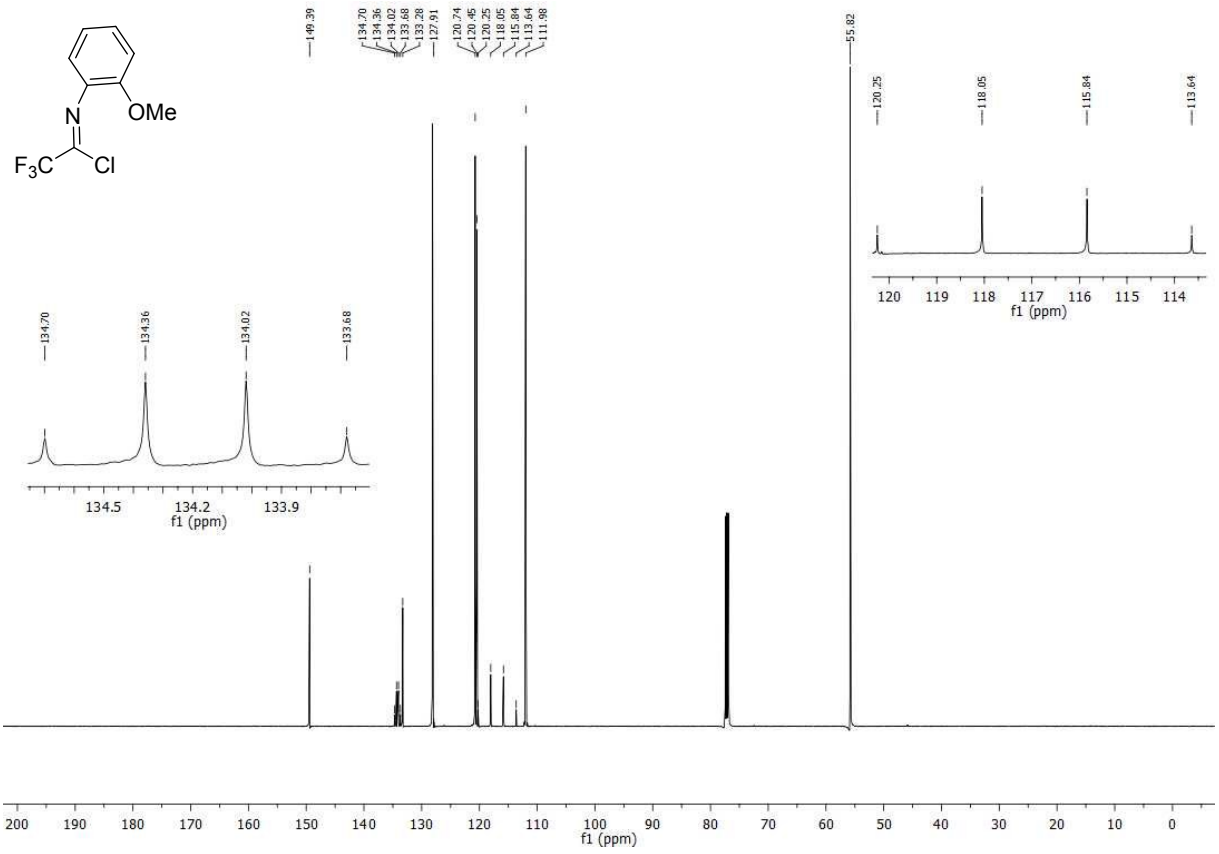
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F3C
Cl
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134.36
134.02
133.68
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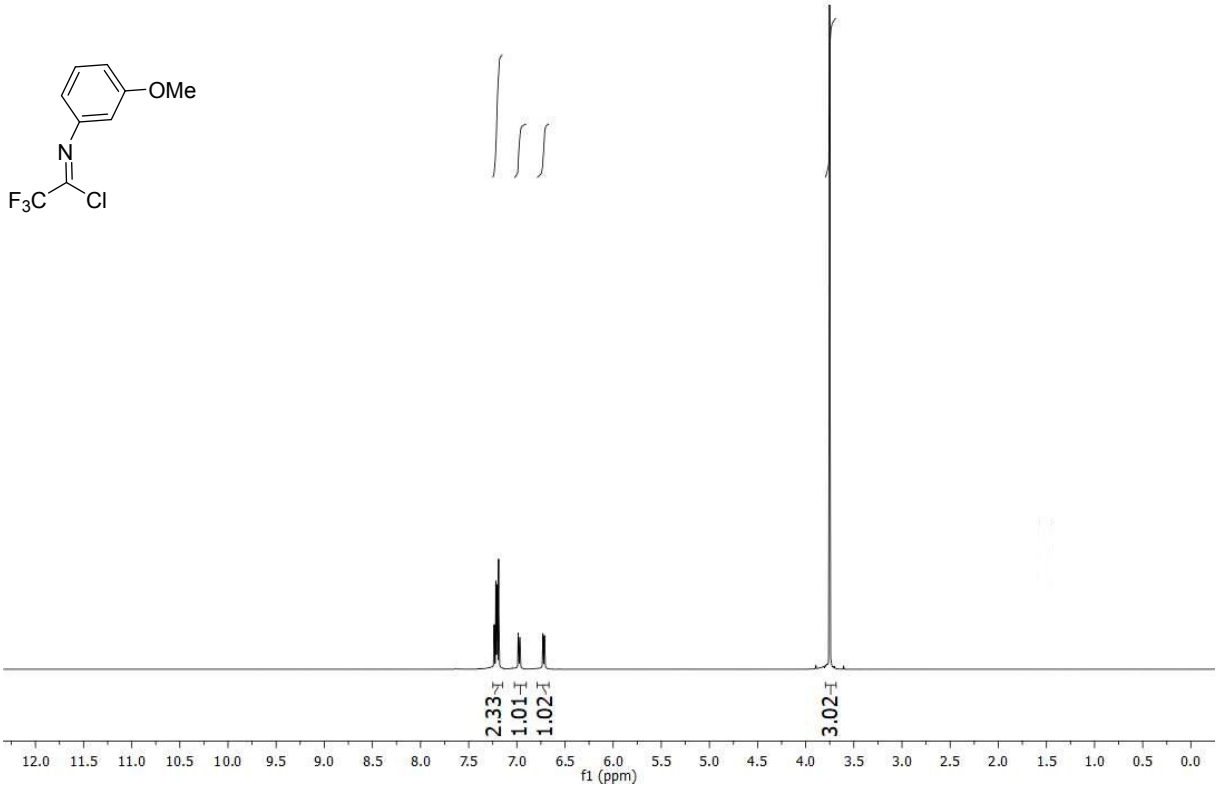
120.74
120.45
120.25
118.05
115.84
113.64
111.98
55.82
f1 (ppm)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Cl
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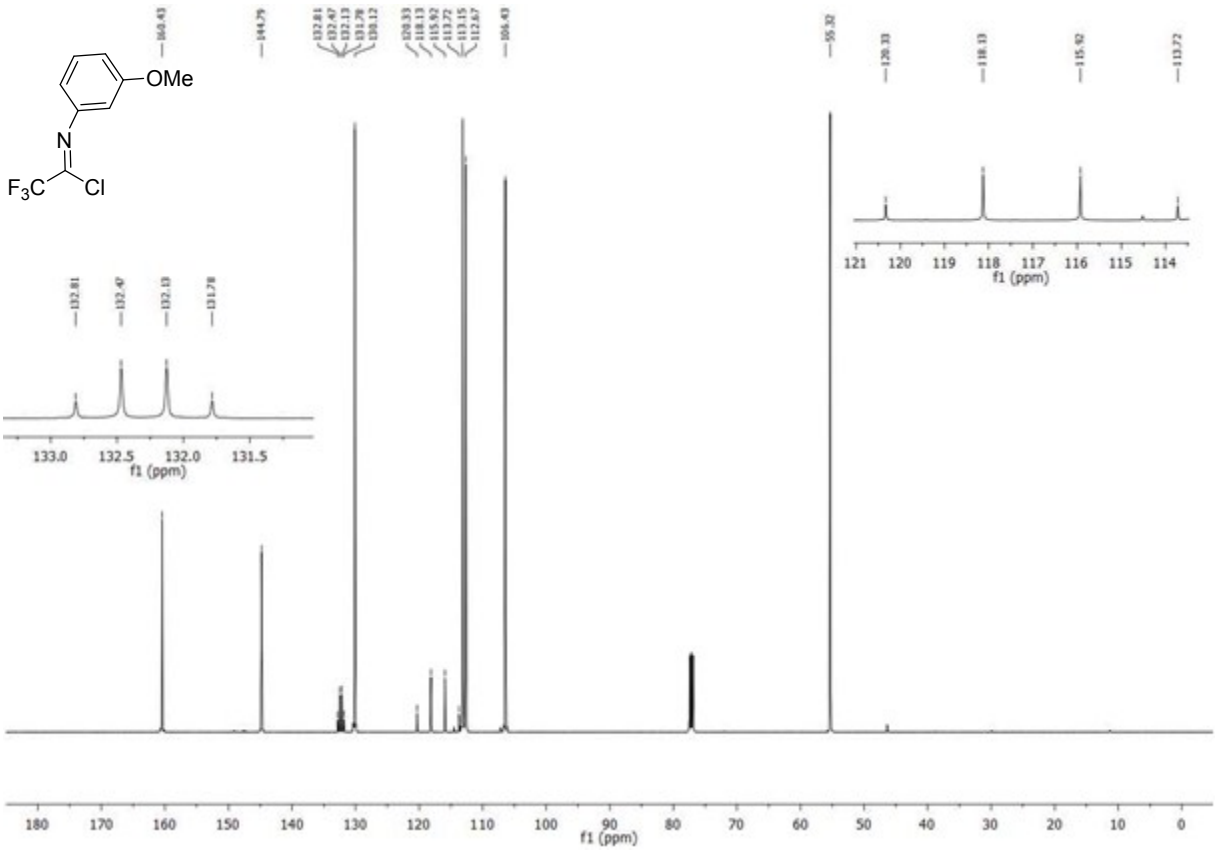
1.02
3.02
f1 (ppm)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Cl
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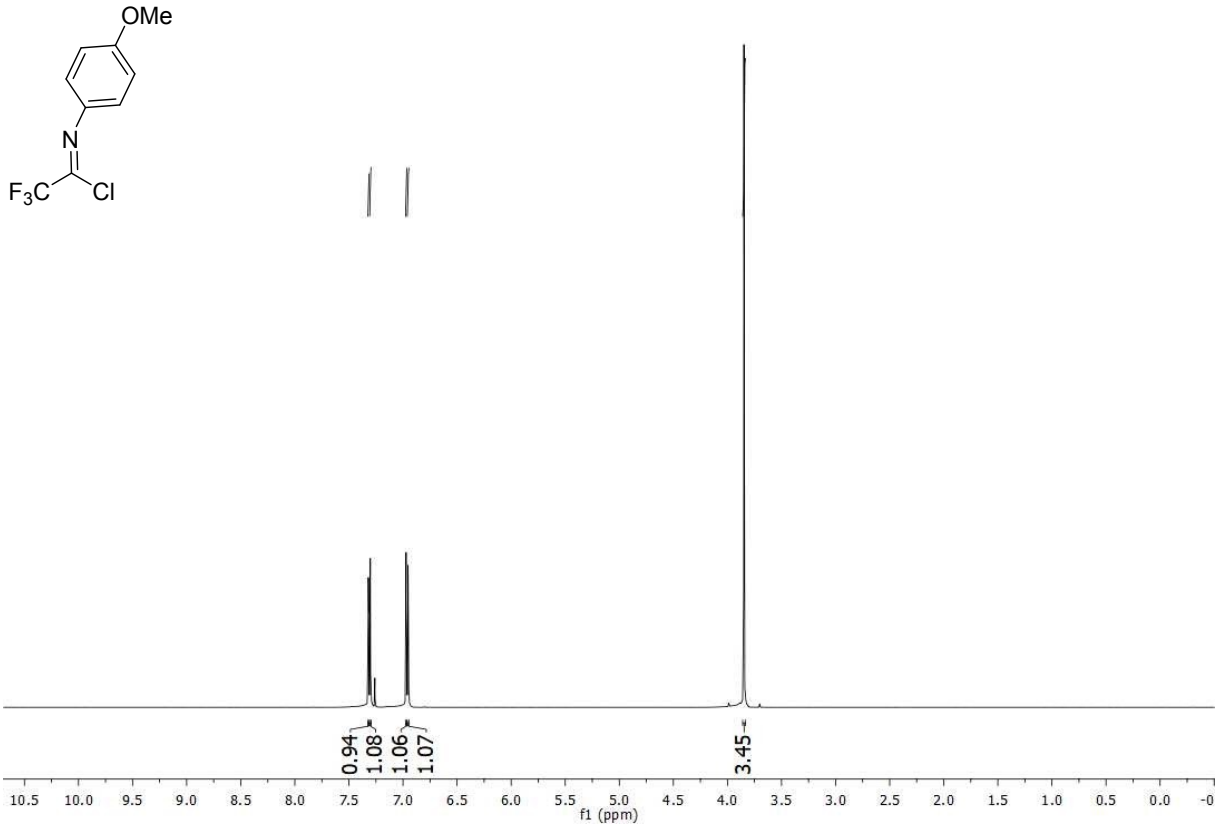
132.81
132.47
132.13
131.78
130.12
120.33
118.13
115.92
113.72
113.15
112.67
106.43
55.32
f1 (ppm)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Cl
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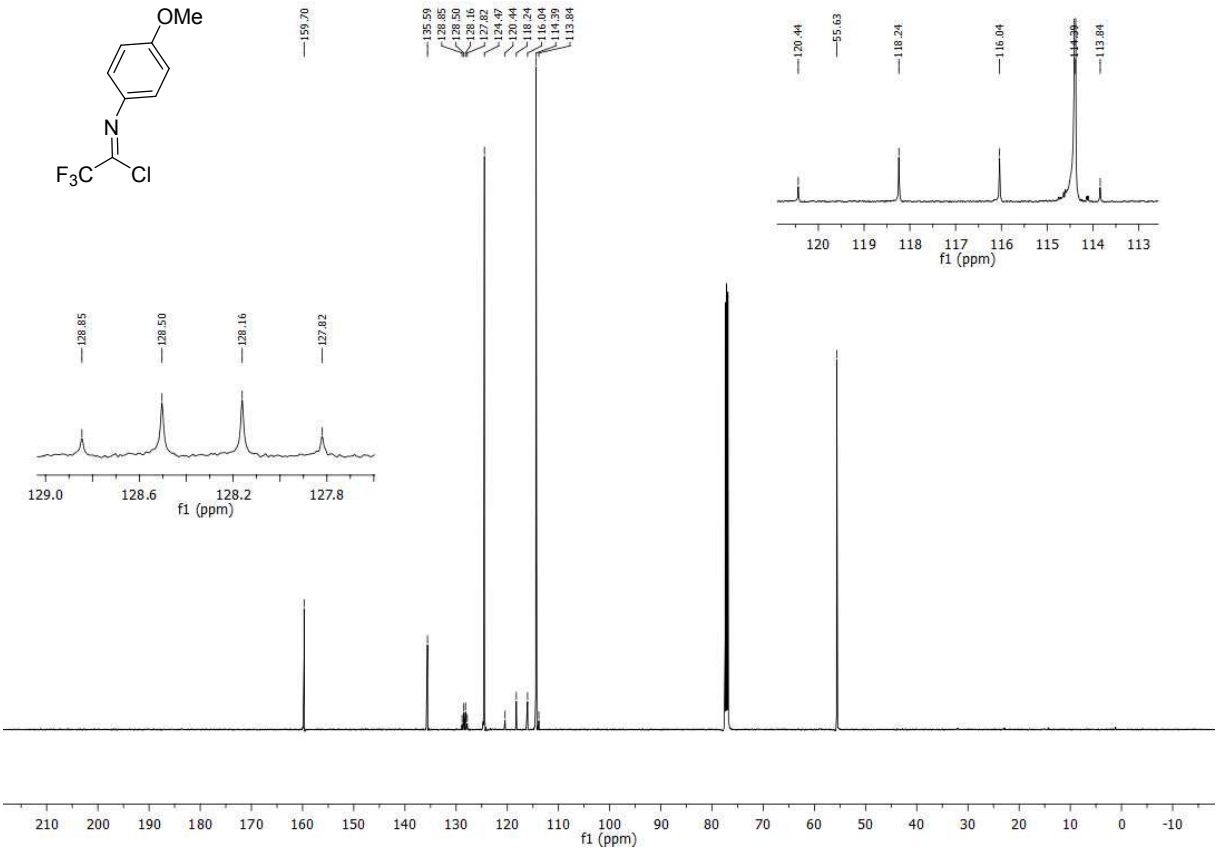
1.08
1.06
1.07
3.45
f1 (ppm)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Cl
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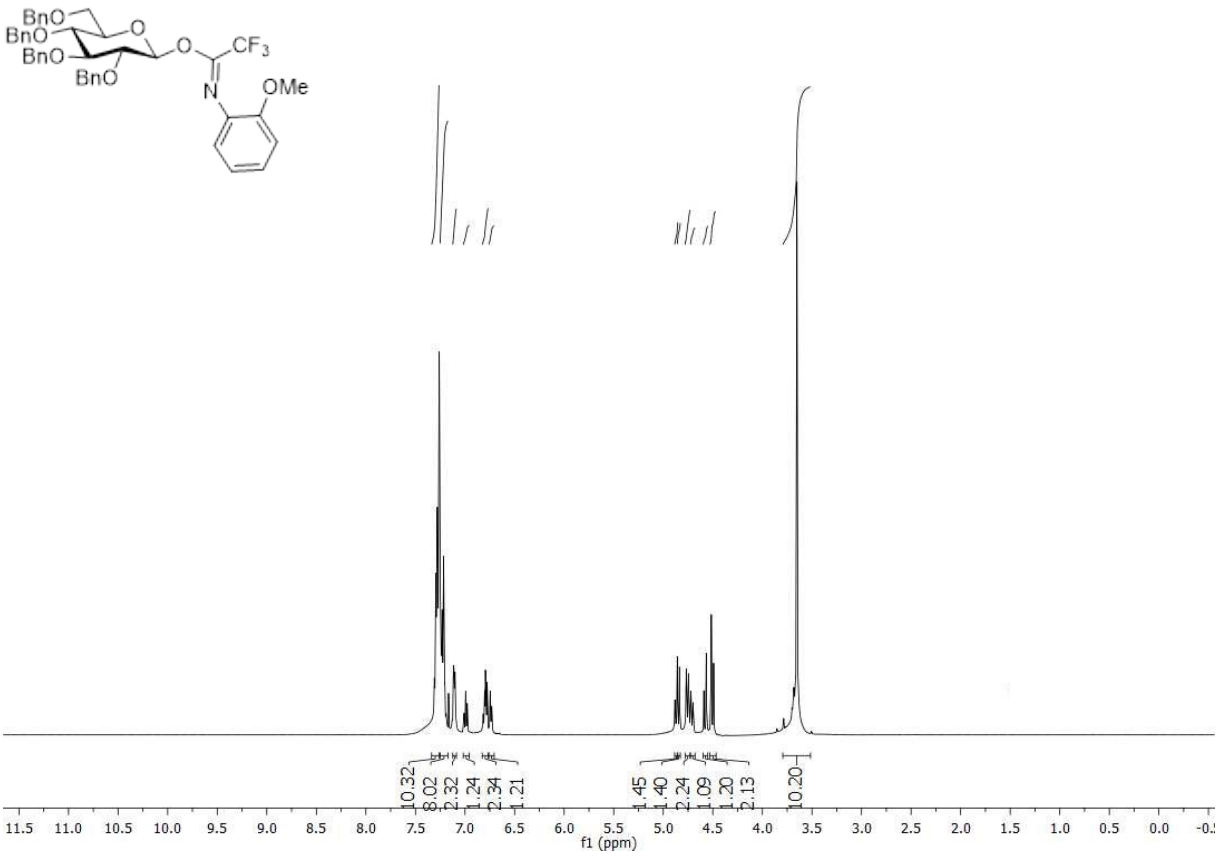
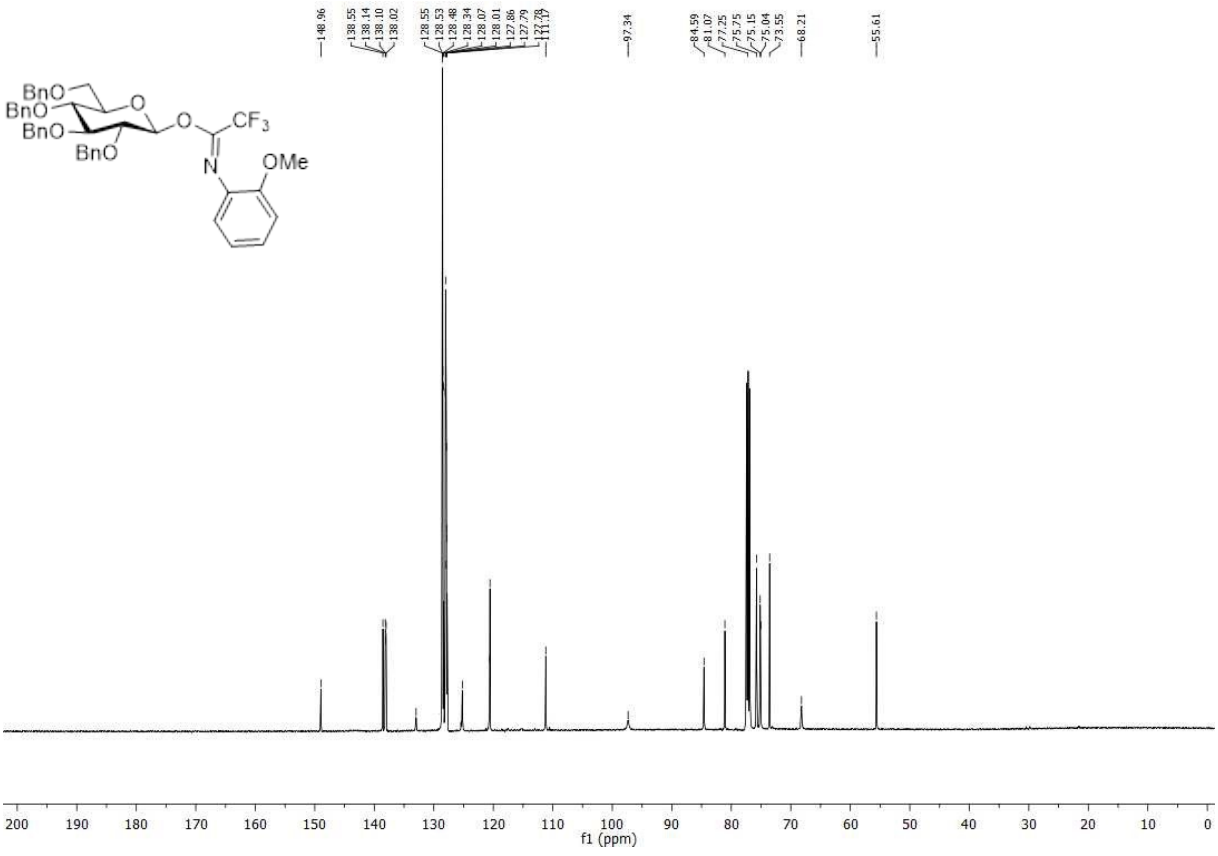
120.44
118.24
116.04
114.39
113.84
55.63
f1 (ppm)


BnO
BnO
BnO
BnO
O
O
CF3
N
OMe
10.32
8.02
2.32
1.24
2.34
1.21
1.45
1.40
2.24
1.09
1.20
2.13
10.20
f1 (ppm)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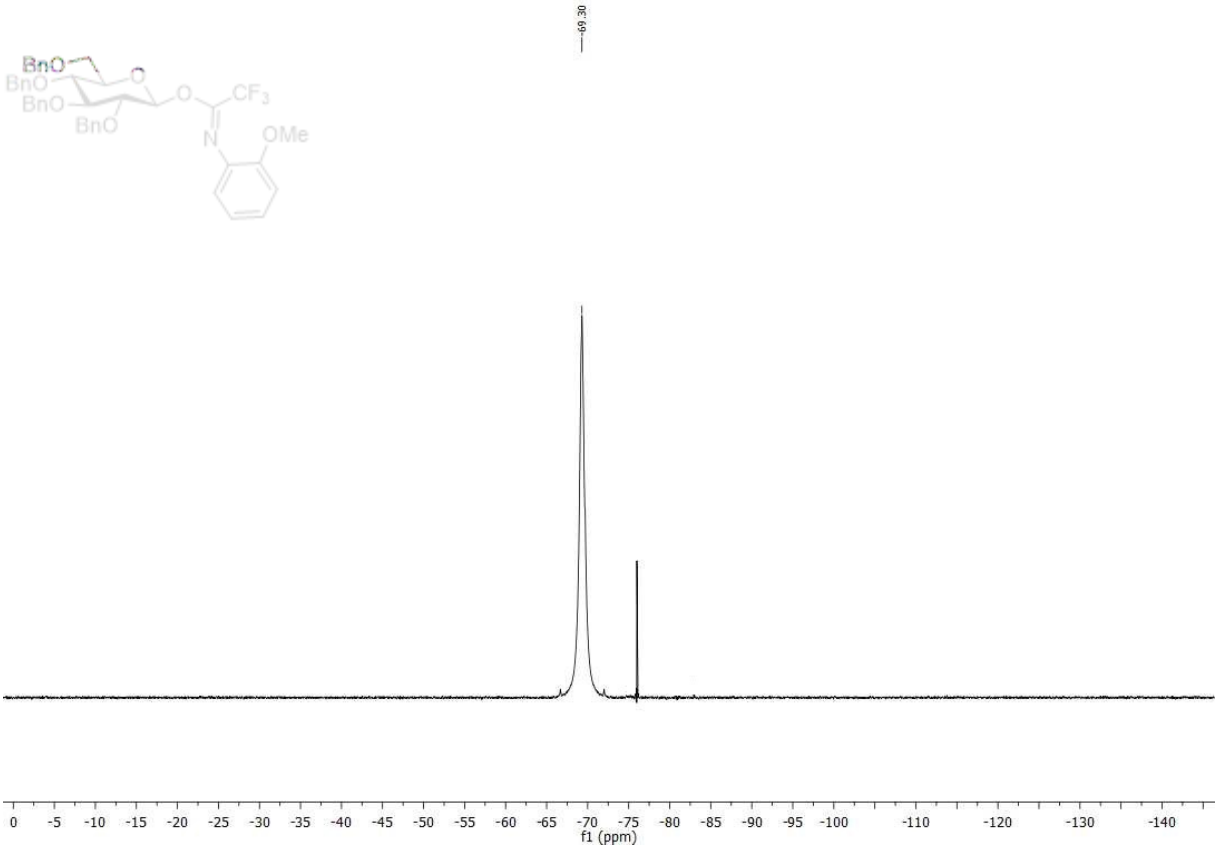
138.55
138.14
138.10
138.02
128.55
128.53
128.48
128.34
128.07
128.01
127.86
127.79
97.34
84.59
81.07
77.25
75.75
75.15
75.04
73.55
68.21
55.61
BnO
BnO
BnO
BnO
O
O
CF3
N
OMe
f1 (ppm)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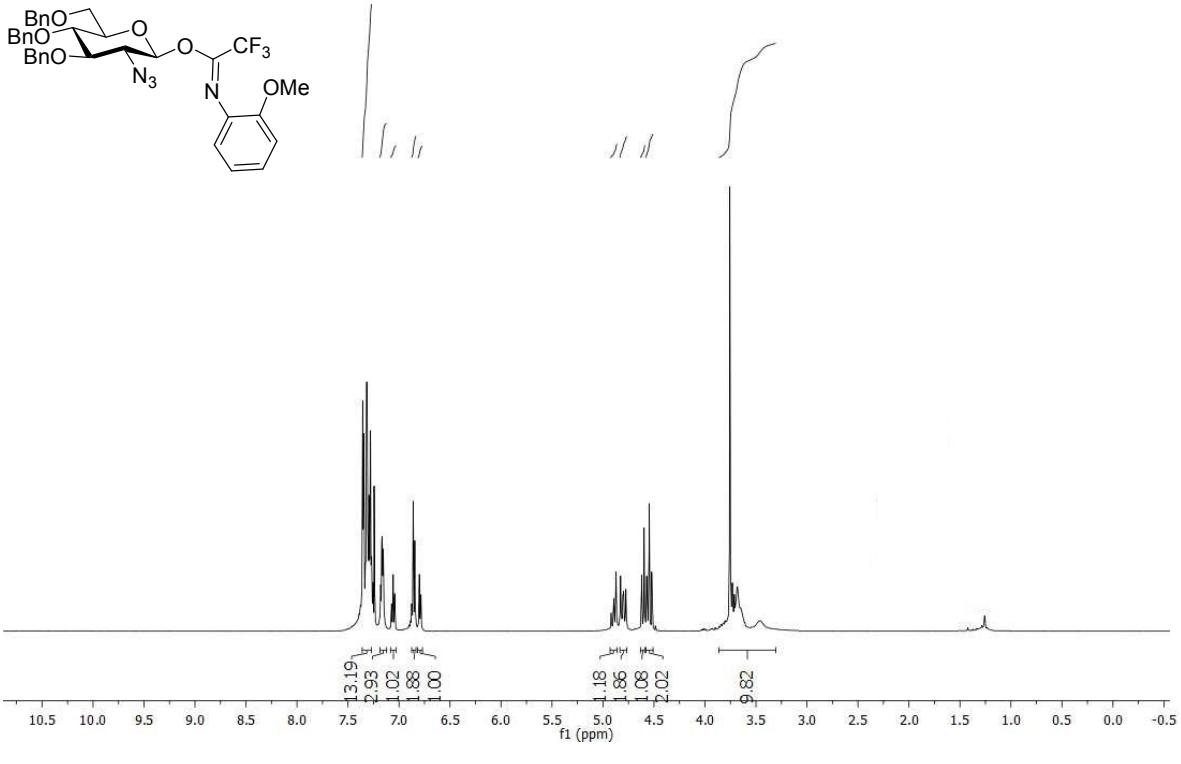
f1 (ppm)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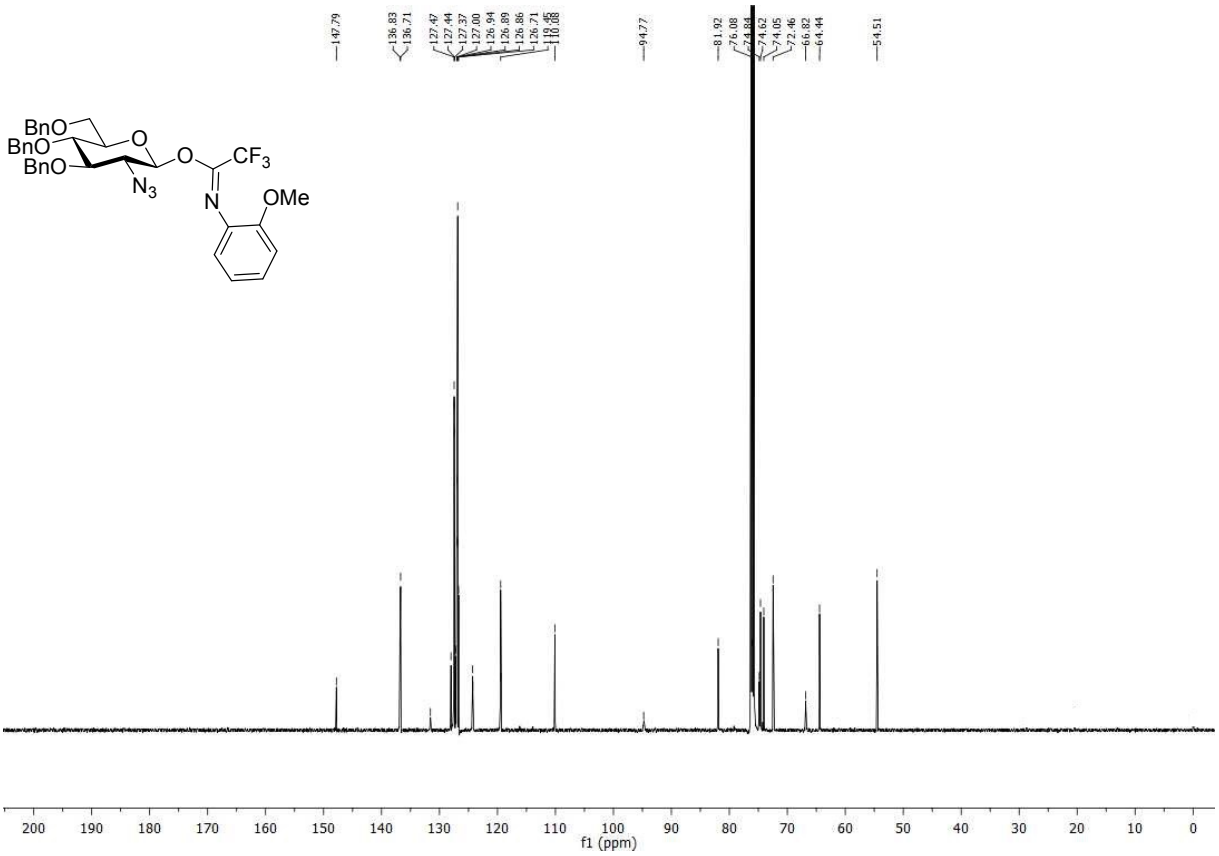
1.18
1.86
1.08
2.02
9.82
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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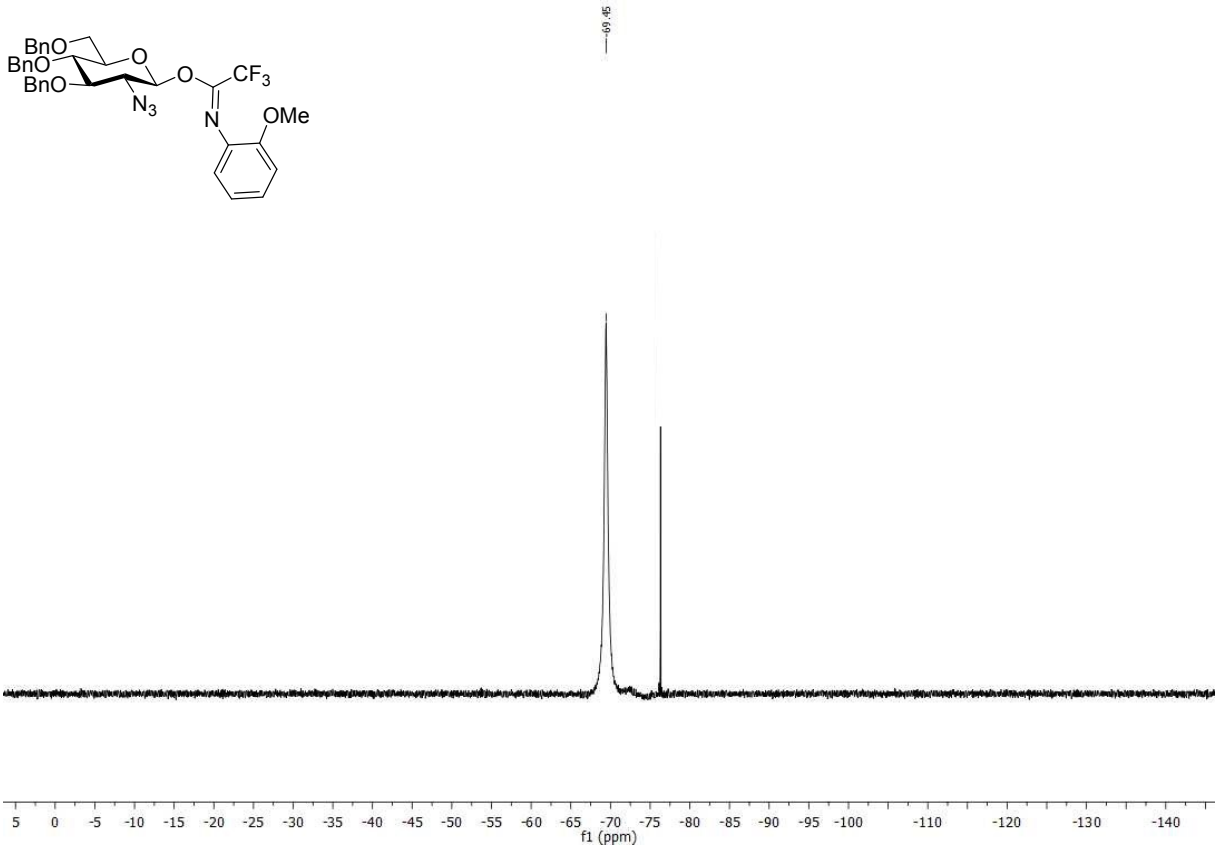
136.71
127.47
127.44
127.37
127.00
126.94
126.89
126.86
126.71
94.77
81.92
76.08
74.84
74.62
74.05
72.46
66.82
64.44
54.51
BnO
BnO
BnO
O
O
CF3
N3
N
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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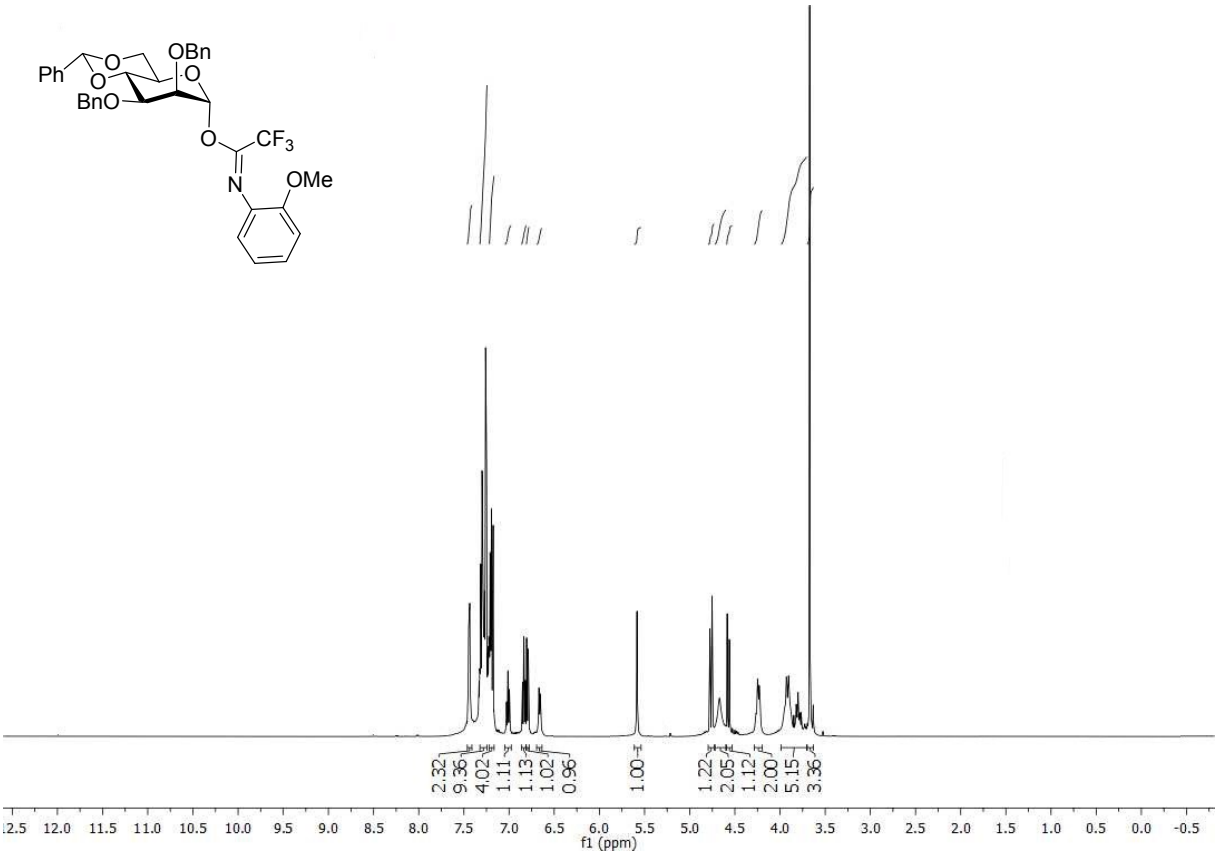
BnO
BnO
O
O
CF3
N3
N
OMe
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140
f1 (ppm)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Ph
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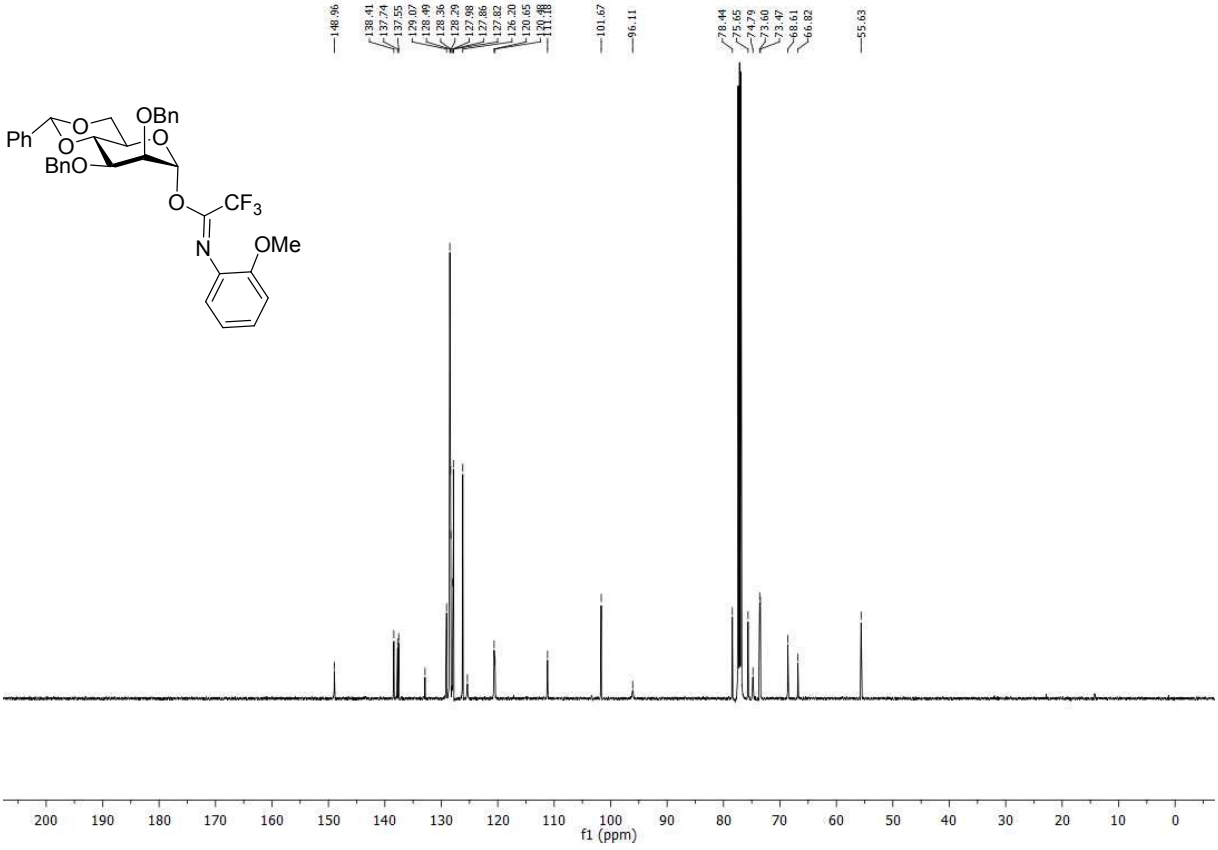
O
O
BnO
O
CF3
N
OMe
2.32
9.36
4.02
1.11
1.13
1.02
0.96
1.00
1.22
2.05
1.12
2.00
5.15
3.36
f1 (ppm)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128.29
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127.86
127.82
126.20
120.65
111.48
101.67
96.11
78.44
75.65
74.79
73.60
73.47
68.61
66.82
55.63
OBn
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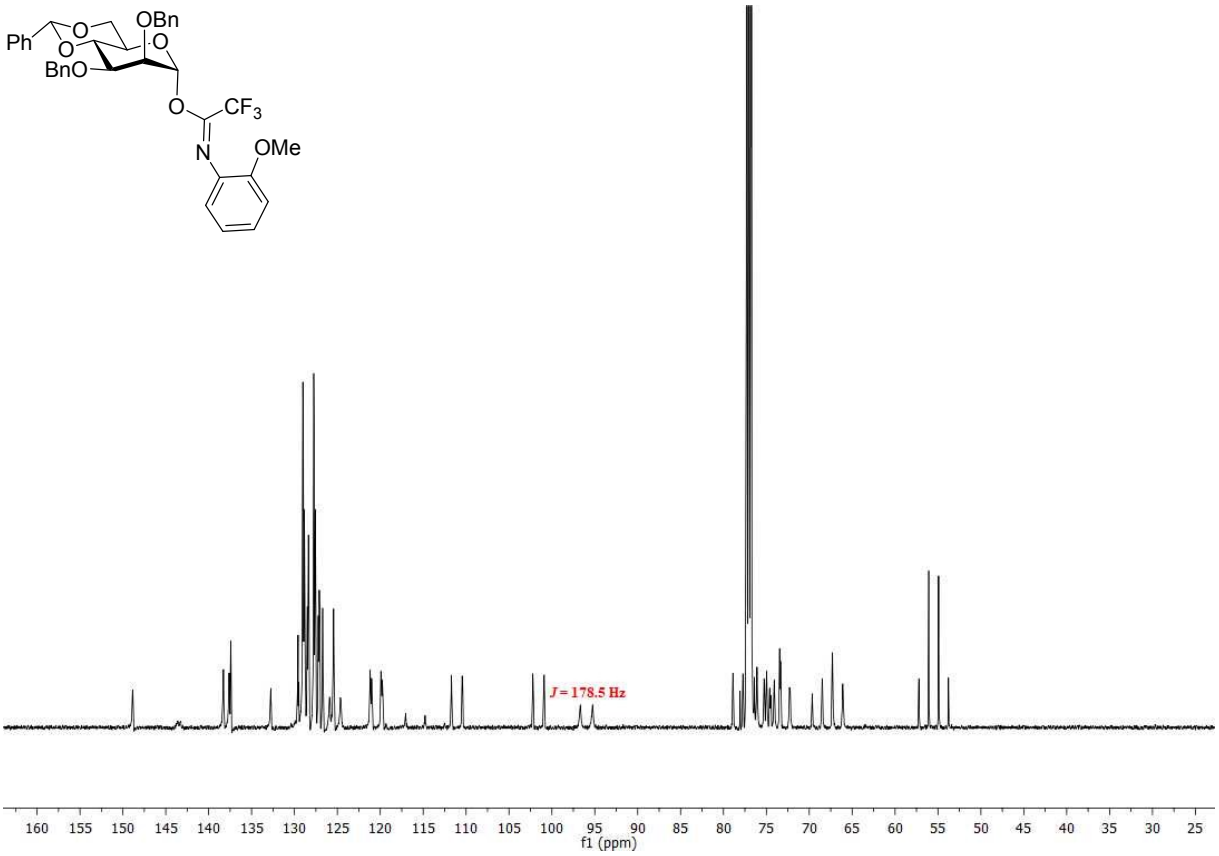
O
BnO
O
CF3
N
OMe
f1 (ppm)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Ph
O
O
O
BnO
O
CF3
N
OMe
J = 178.5 Hz
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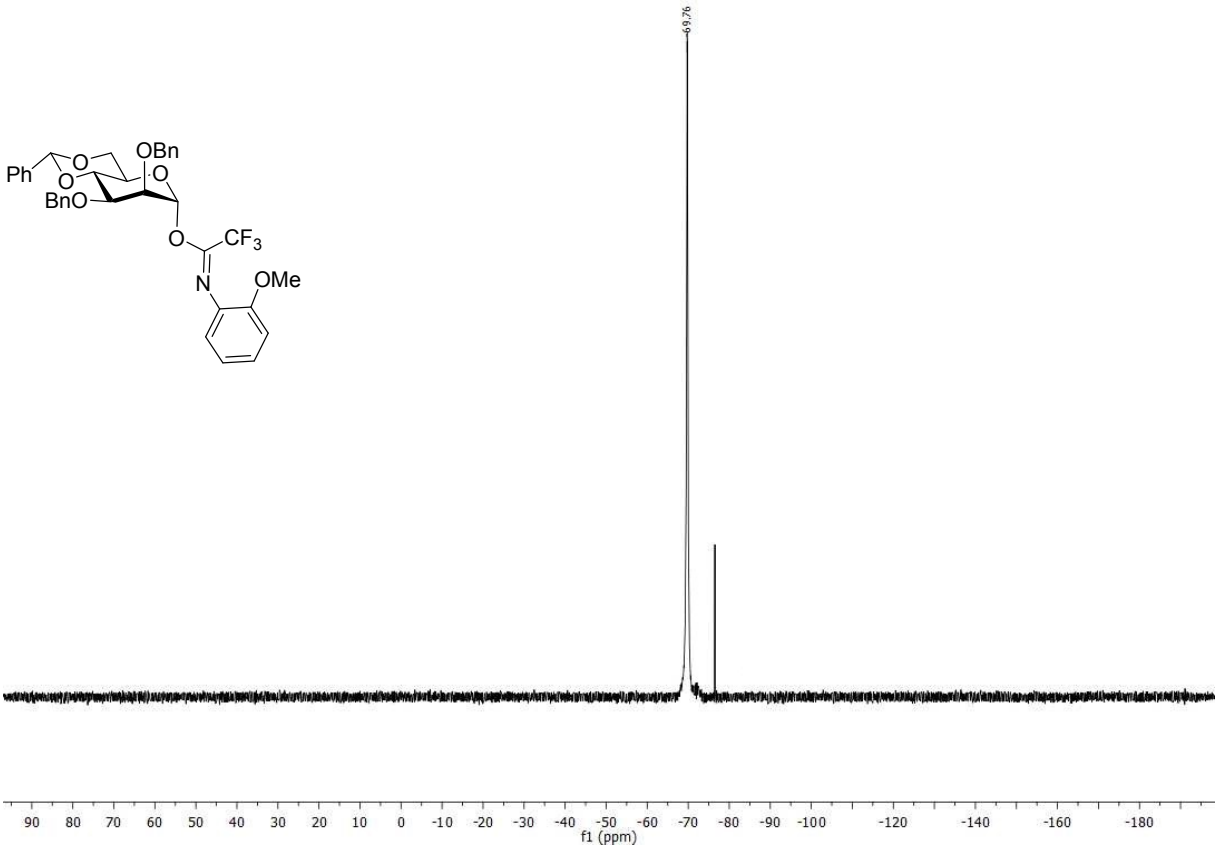
f1 (ppm)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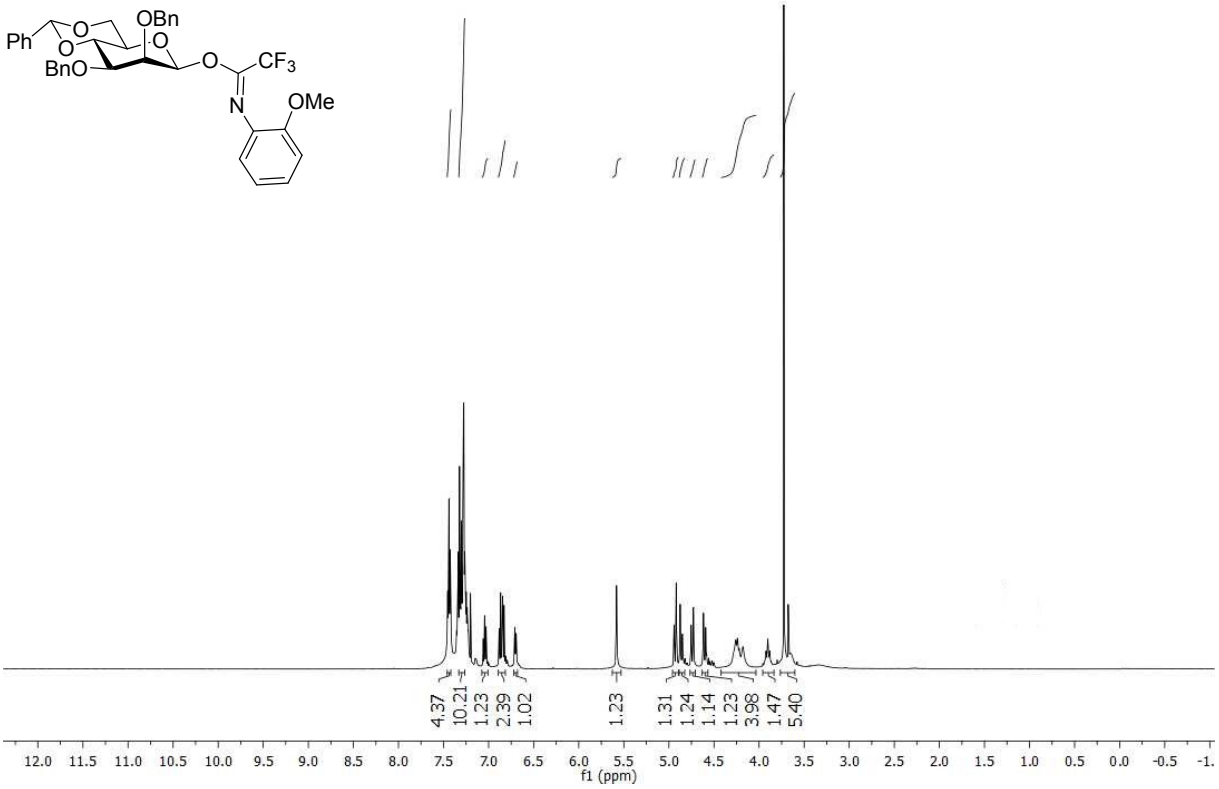
f1 (ppm)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Ph
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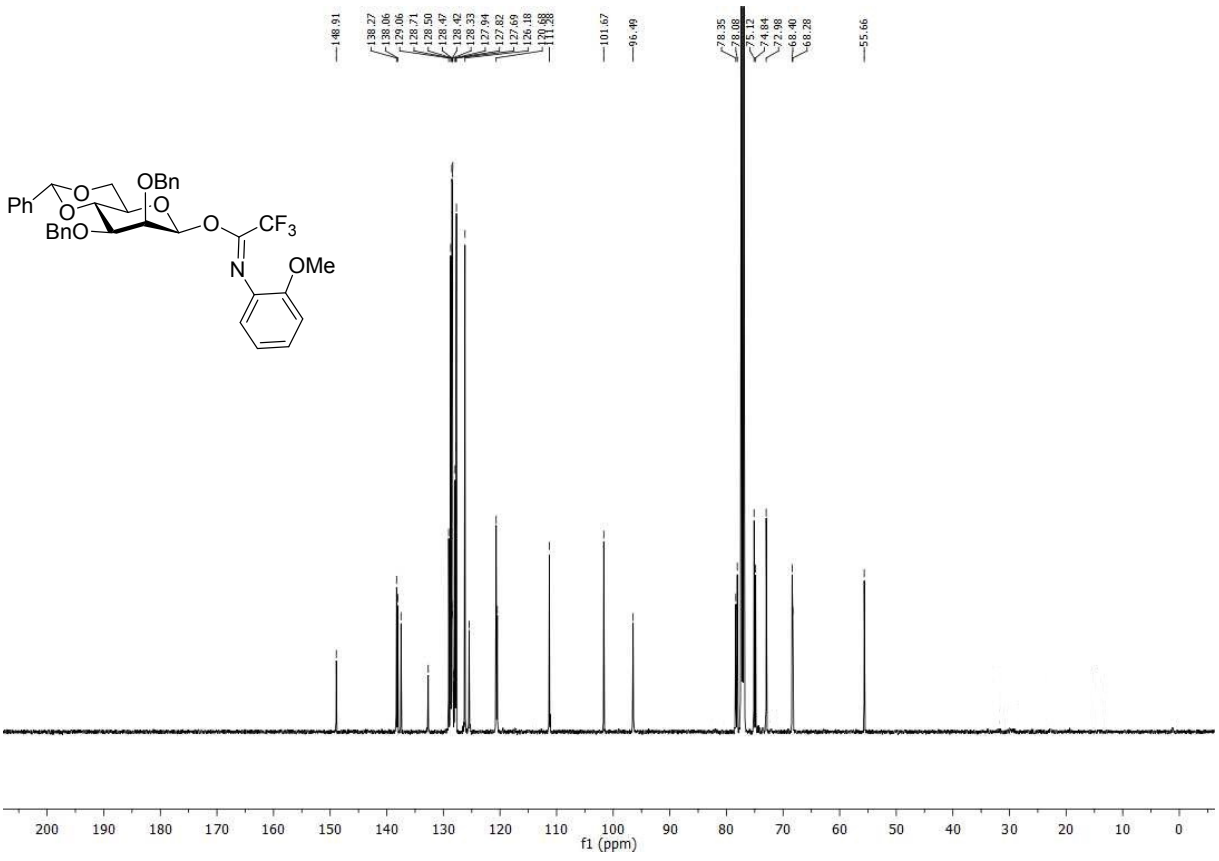
O
O
BnO
CF3
N
OMe
4.37
10.21
1.23
2.39
1.02
1.23
1.31
1.24
1.14
1.23
3.98
1.47
5.40
f1 (ppm)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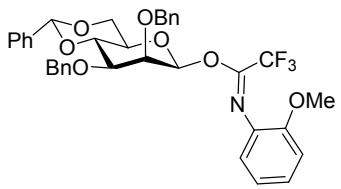
127.94
127.82
127.69
126.18
101.67
96.49
78.35
78.08
75.12
74.84
72.98
68.40
68.28
55.66
OBn
Ph
O
O
O
BnO
CF3
N
OMe
f1 (ppm)


Ph
O
O
OBn
O
BnO
O
CF3
N
OMe

J = 163.2 Hz
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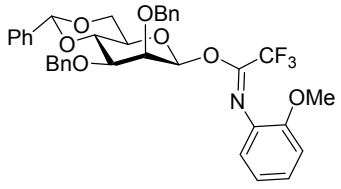
f1 (ppm)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O
CF3
N
OMe

69.35
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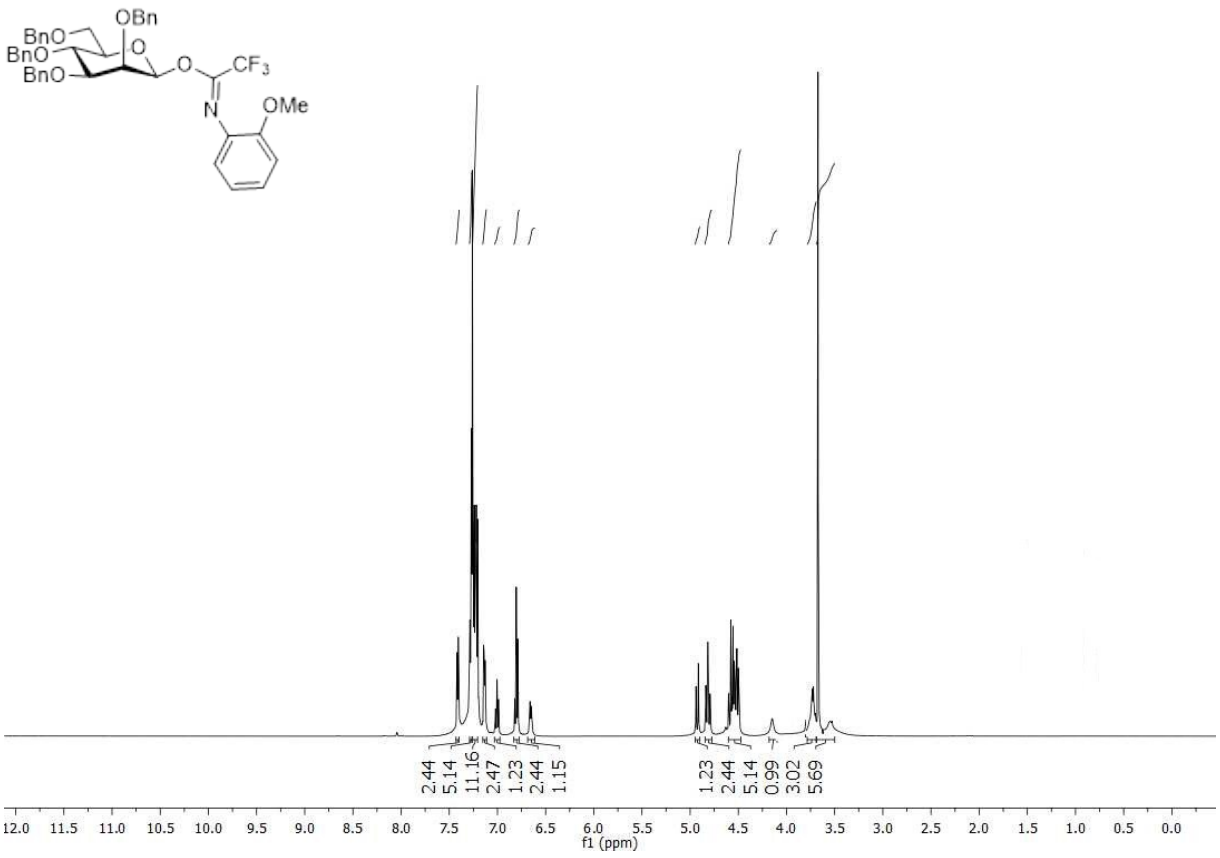
f1 (ppm)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CF3
N
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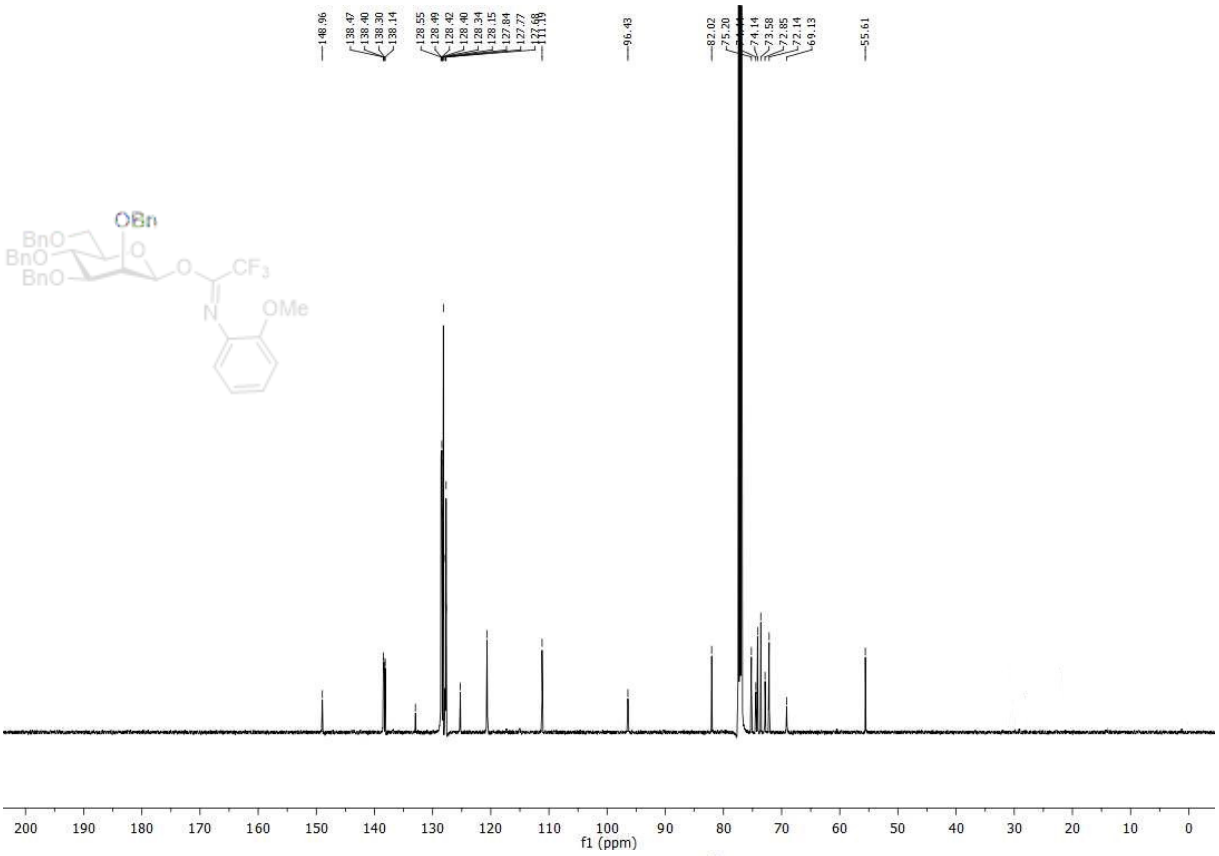
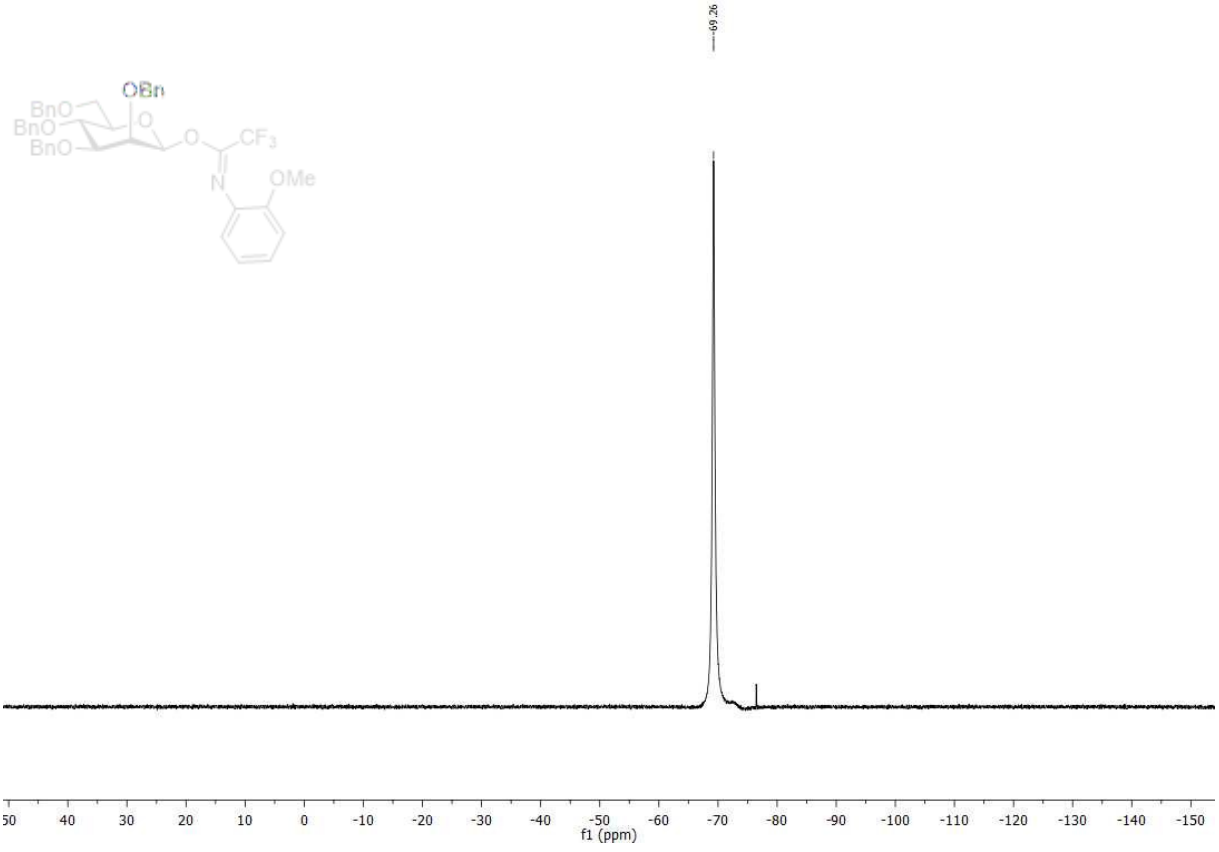
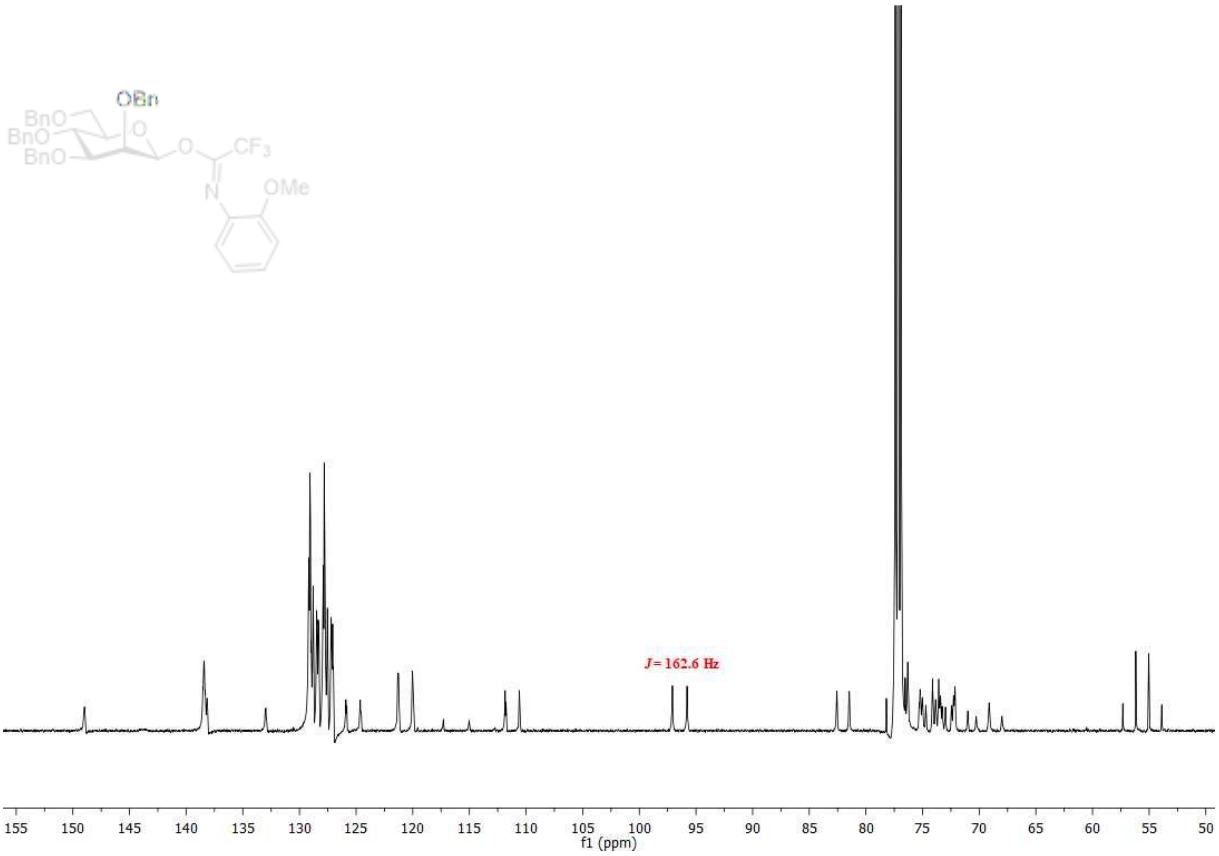
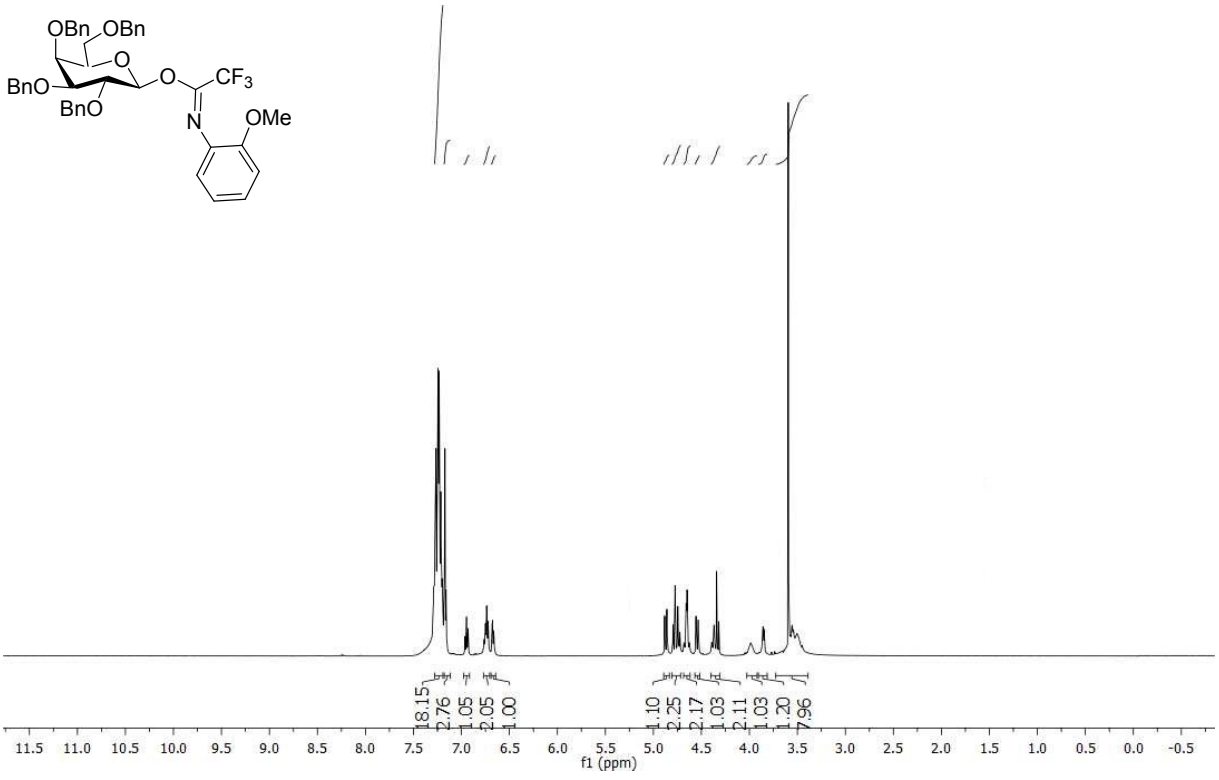
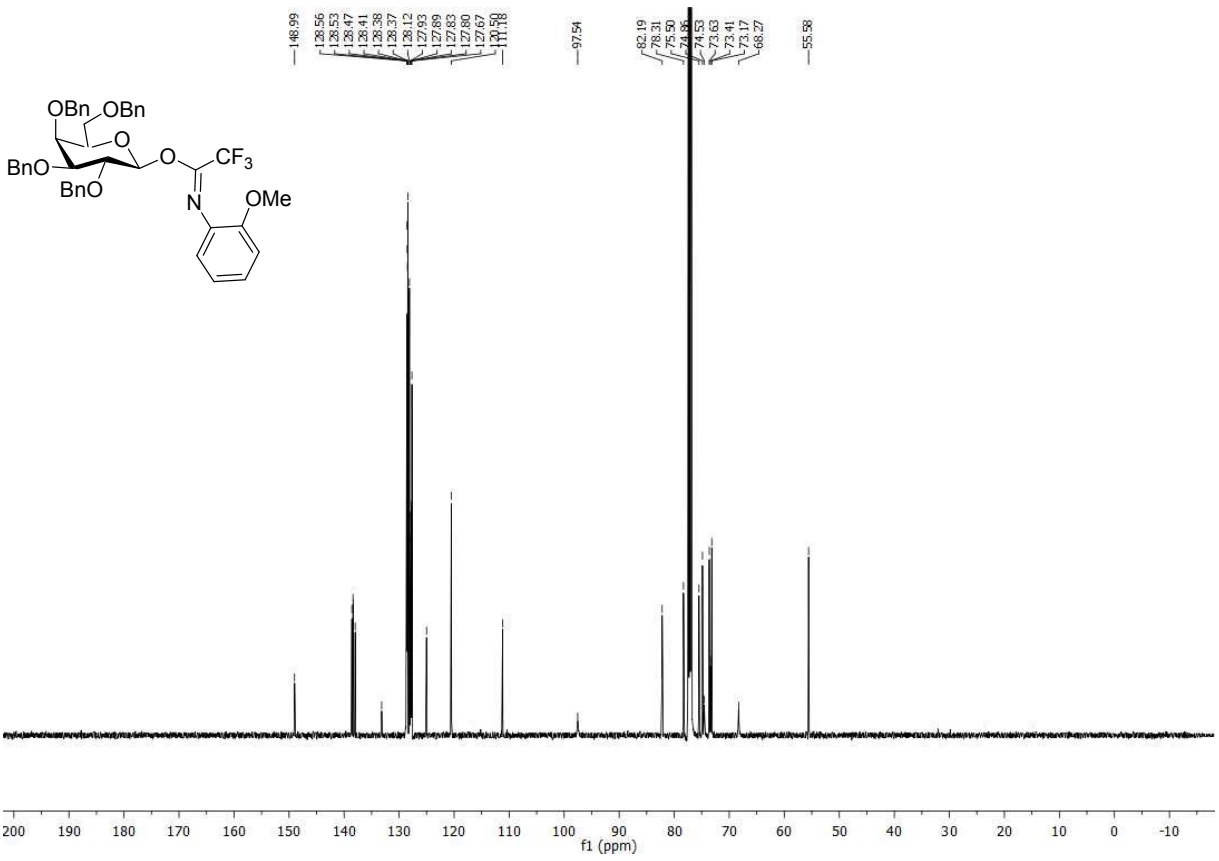
2.44
1.15
1.23
2.44
5.14
0.99
3.02
5.69
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

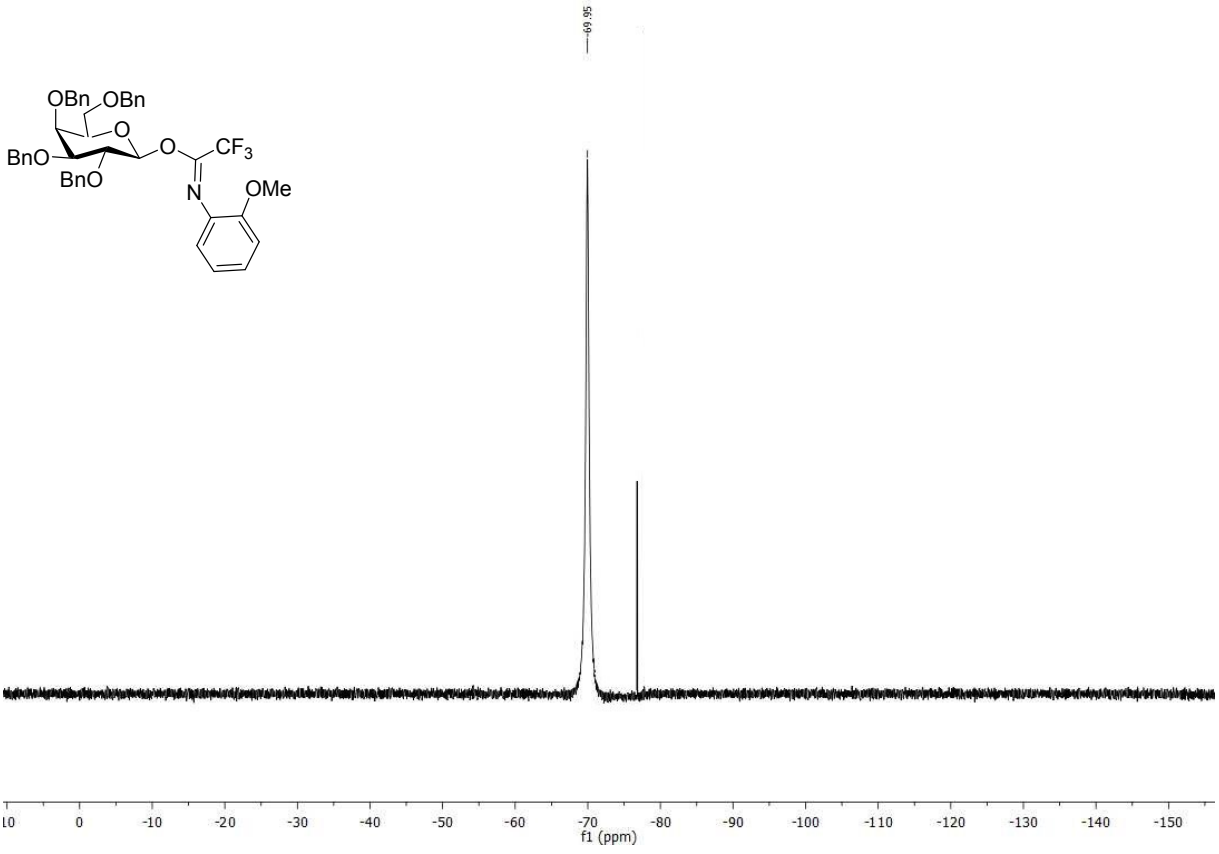

148.96
138.47
138.40
138.30
138.14
128.55
128.49
128.42
128.40
128.34
128.15
127.84
127.77
96.43
82.02
75.20
74.14
73.58
72.85
72.14
69.13
55.61
OBn
BnO
BnO
BnO
O
O
CF3
N
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

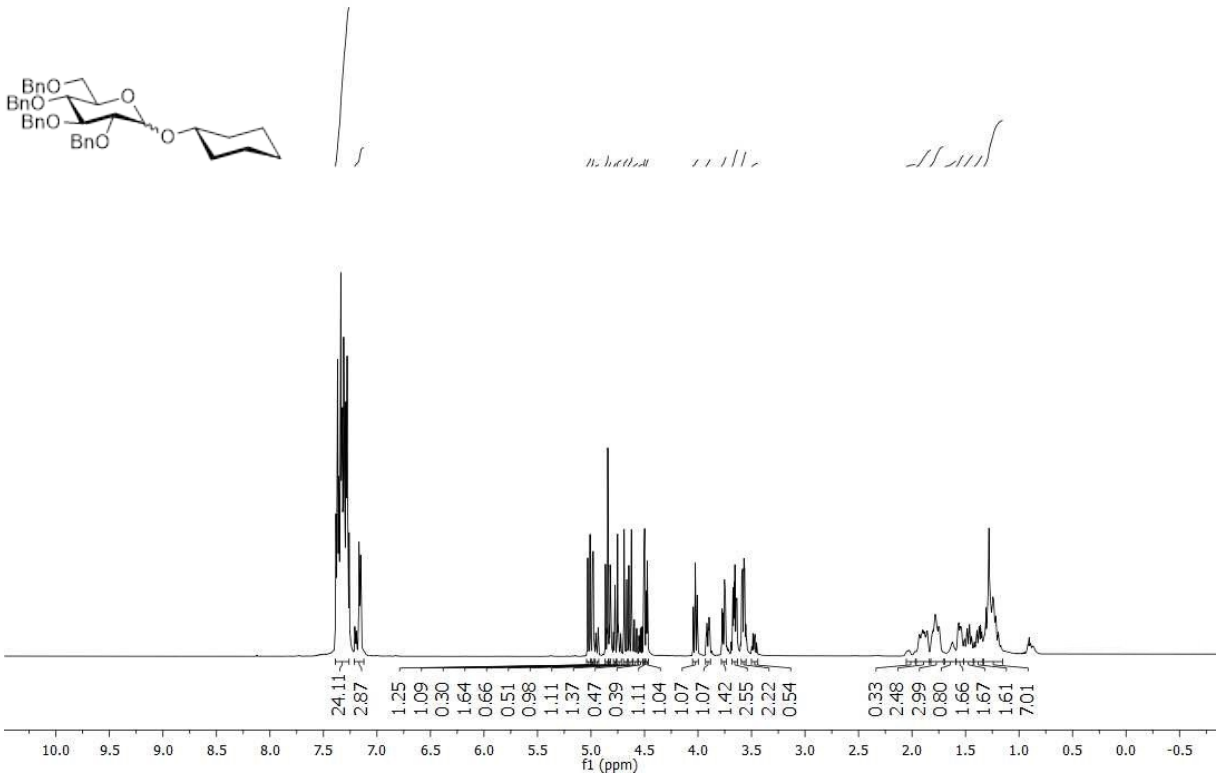

69.26
OBn
BnO
BnO
BnO
O
O
CF3
N
OMe
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

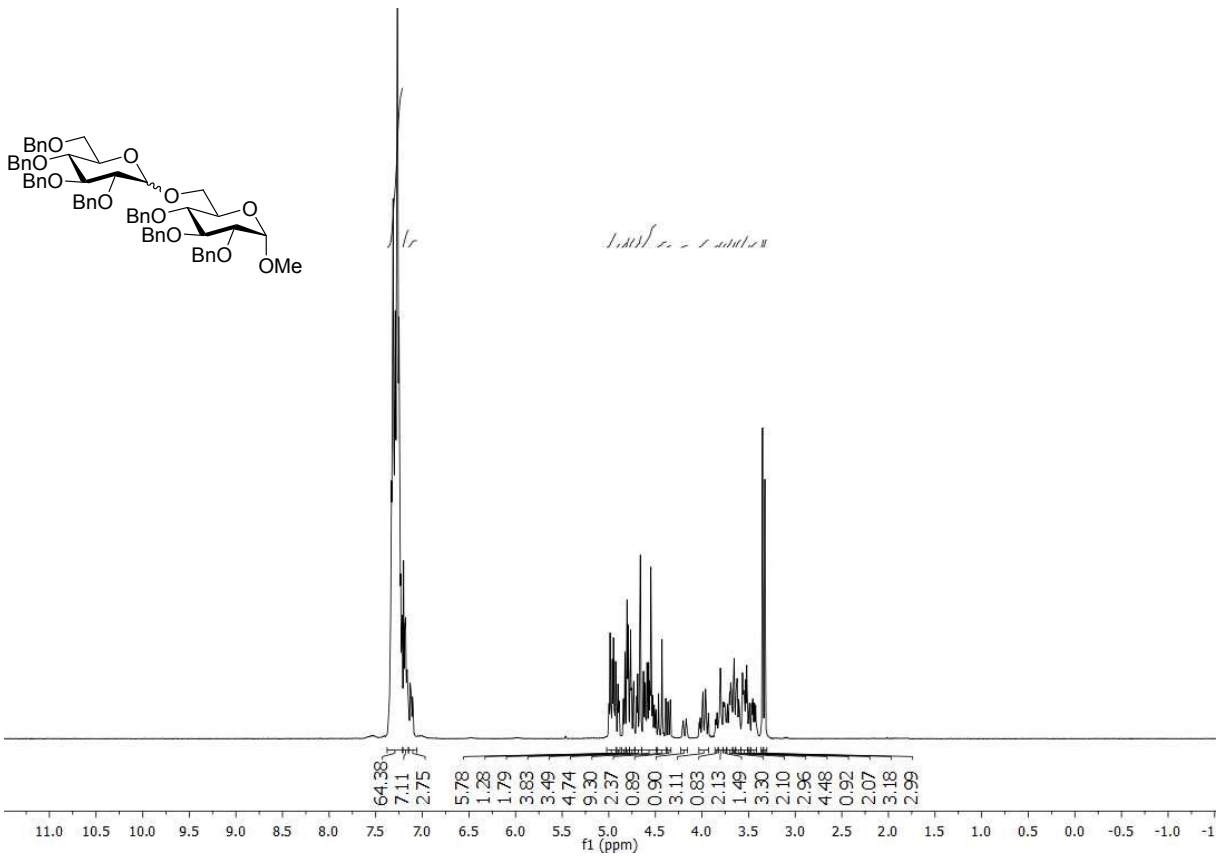

OBn
BnO
BnO
BnO
O
CF3
N
OMe
J= 162.6 Hz
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

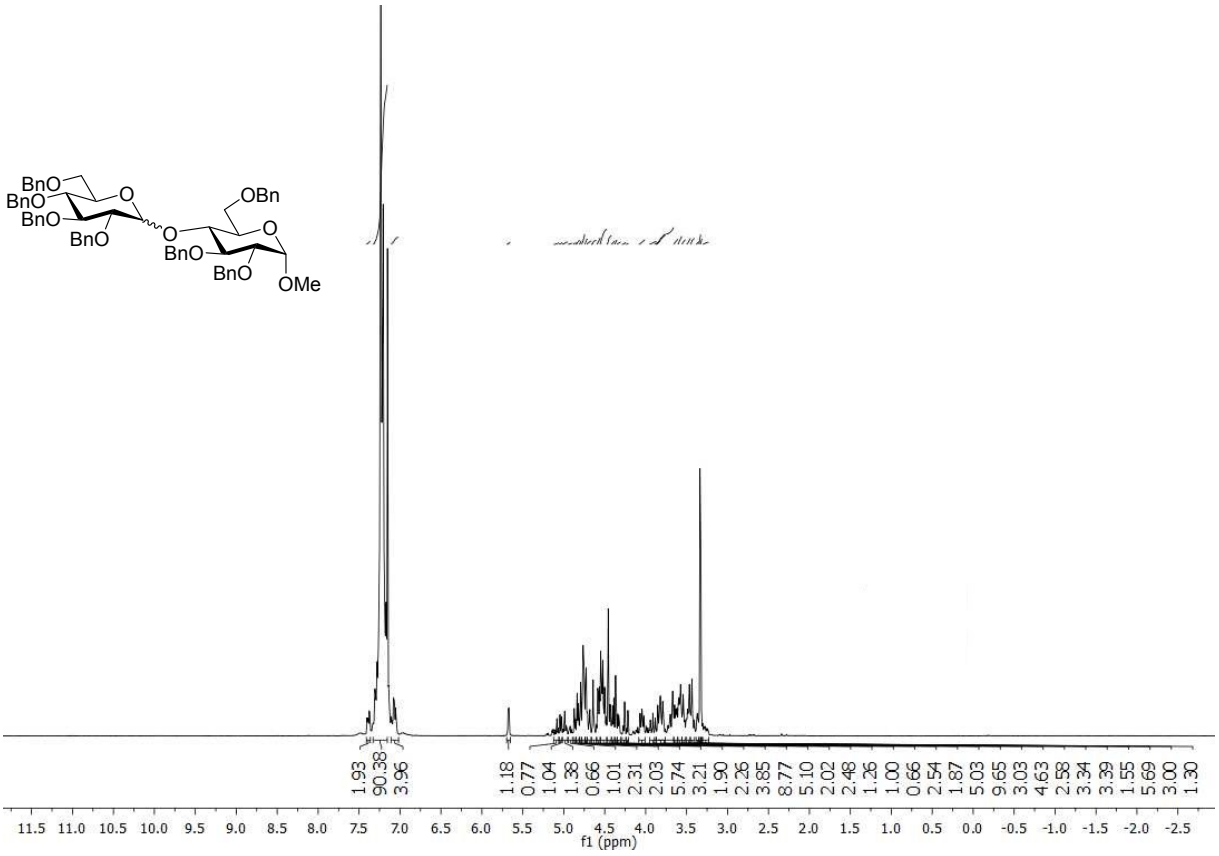

OBn
OBn
O
BnO
O
CF3
BnO
N
OMe
18.15
2.76
1.05
2.05
1.00
1.10
2.25
2.17
1.03
2.11
1.03
1.20
7.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

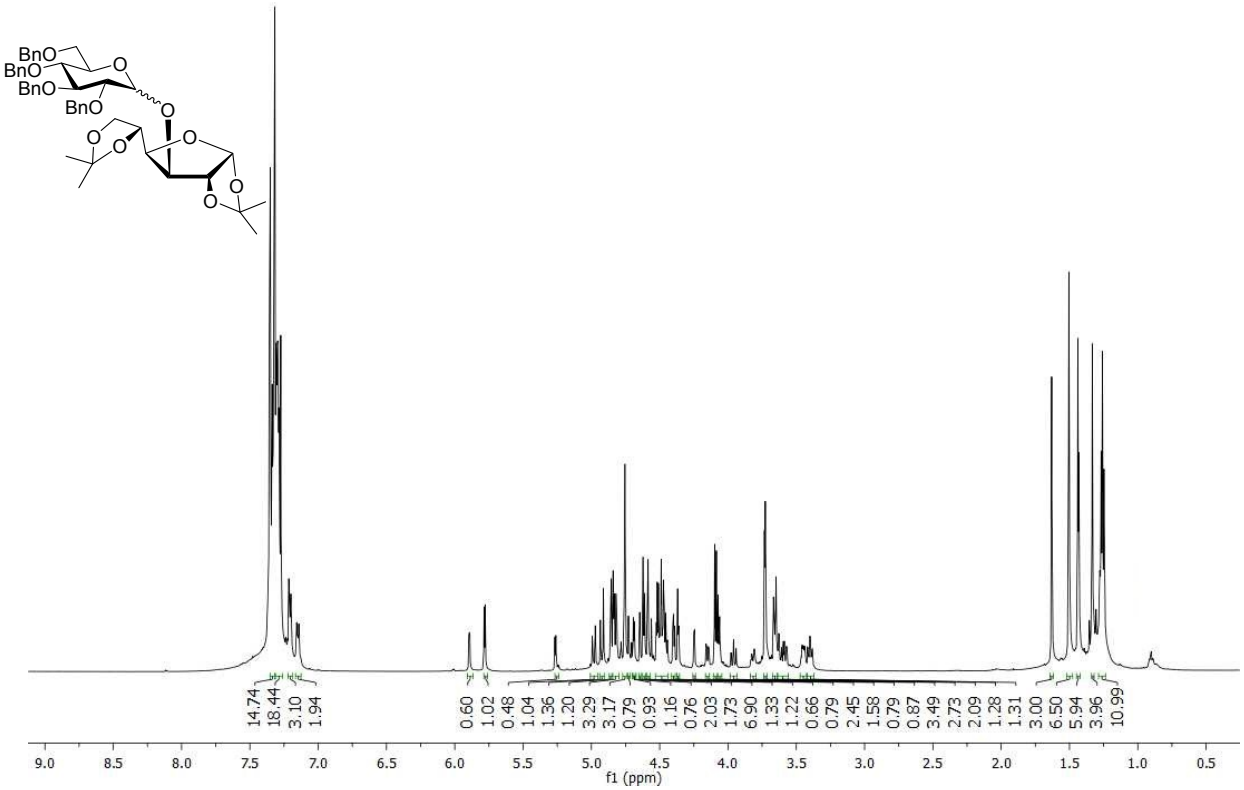

148.99
128.56
128.53
128.47
128.41
128.38
128.37
128.12
127.93
127.89
127.83
127.80
127.67
120.50
111.18
97.54
82.19
78.31
75.90
74.95
74.53
73.63
73.41
73.17
68.27
55.58
OBn
OBn
O
BnO
BnO
O
CF3
N
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

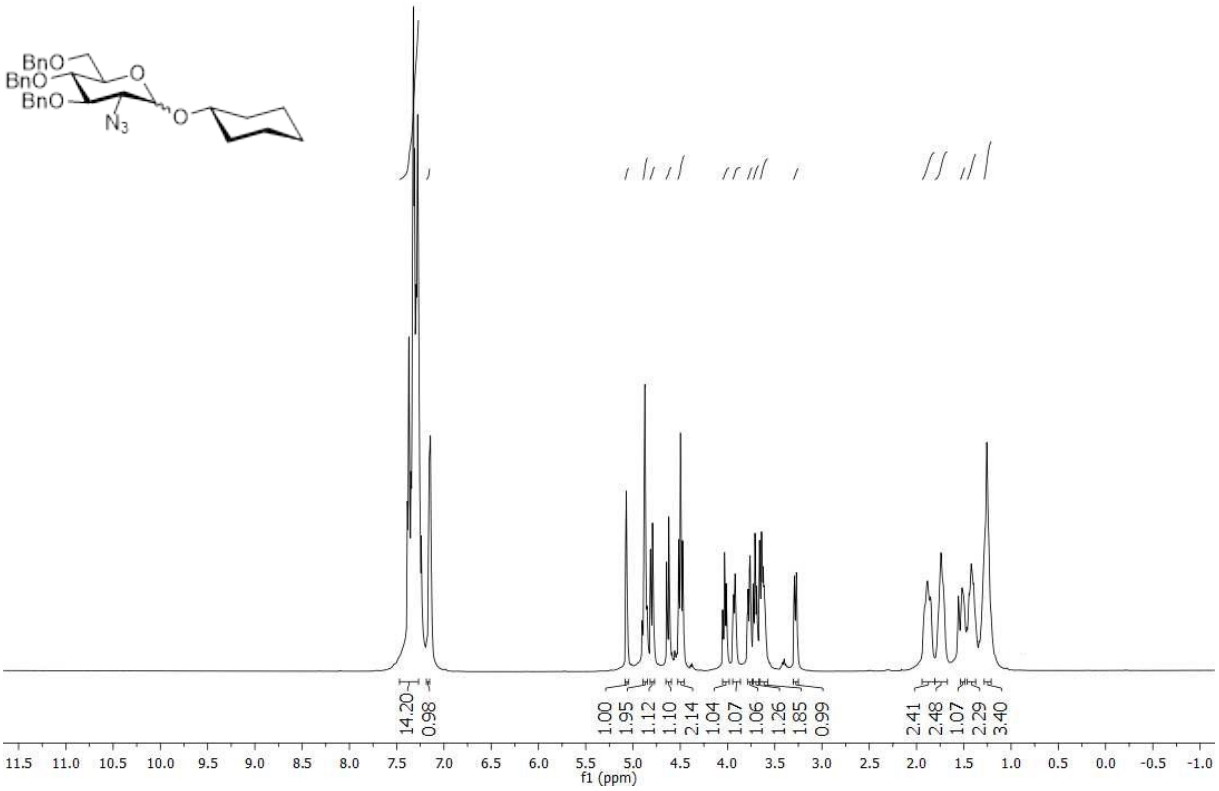

69.95
OBn
OBn
O
BnO
BnO
O
CF3
N
OMe
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

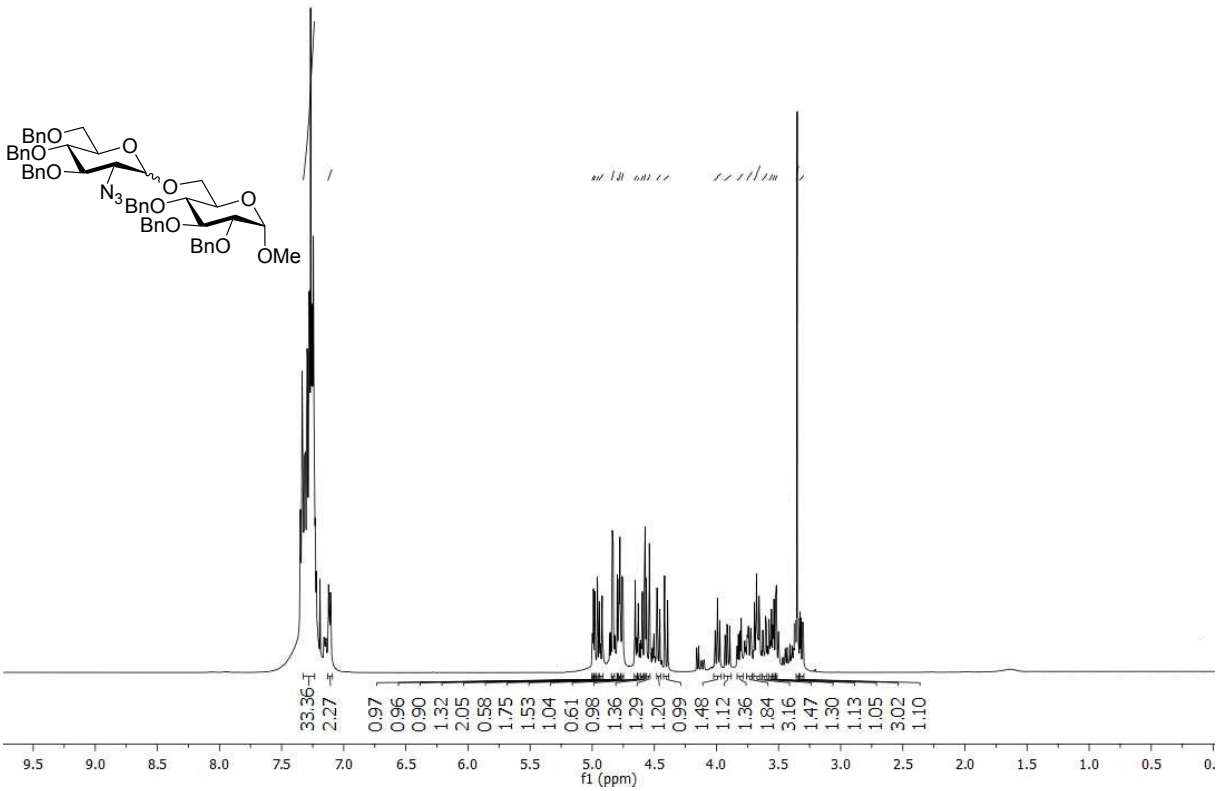

BnO
BnO
BnO
BnO
O
O
24.11
2.87
1.25
1.09
0.30
1.64
0.66
0.51
0.98
1.11
1.37
0.47
0.39
1.11
1.04
1.07
1.07
1.42
2.55
2.22
0.54
0.33
2.48
2.99
0.80
1.66
1.67
1.61
7.01
f1 (ppm)

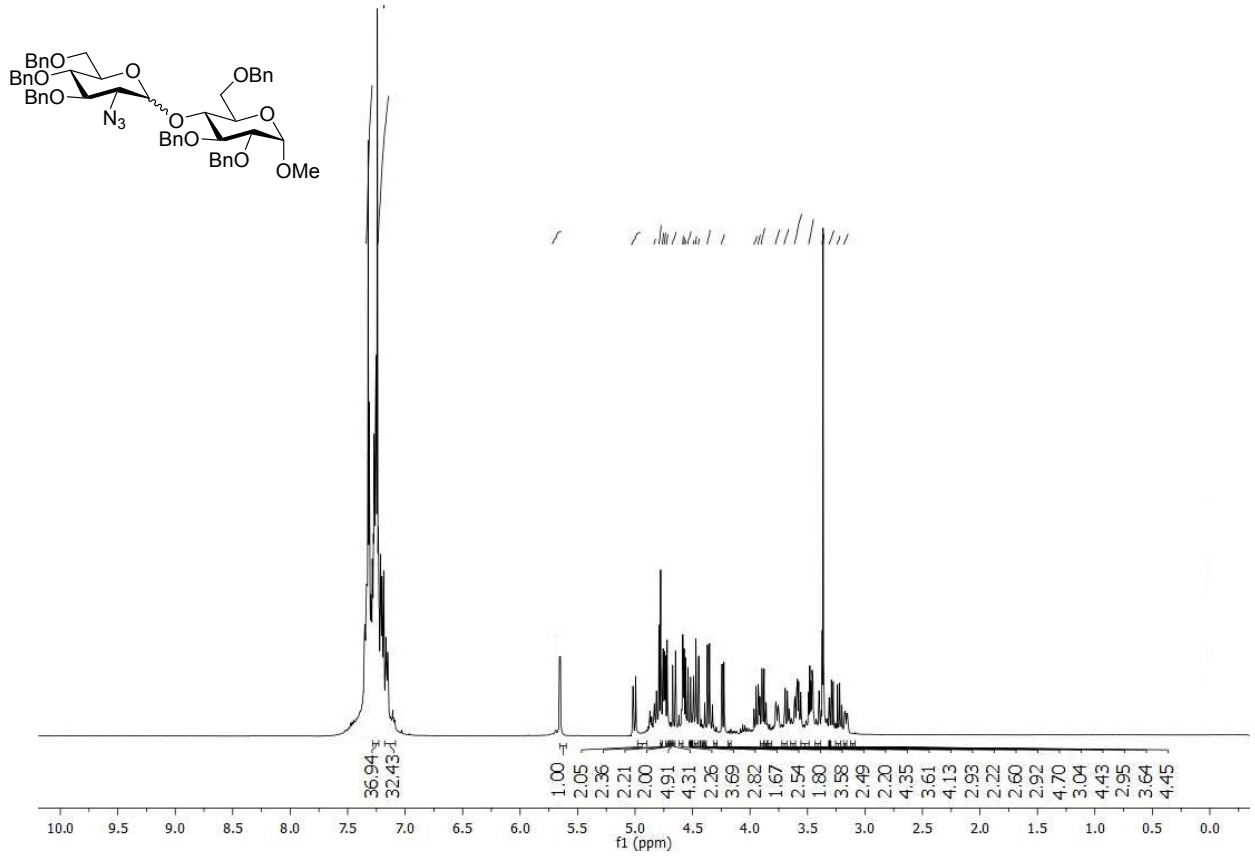

BnO
BnO
BnO
BnO
O
BnO
BnO
BnO
O
O
OMe
64.38
7.11
2.75
5.78
1.28
1.79
3.83
3.49
4.74
9.30
2.37
0.89
0.90
3.11
0.83
2.13
1.49
3.30
2.10
2.96
4.48
0.92
2.07
3.18
2.99
f1 (ppm)

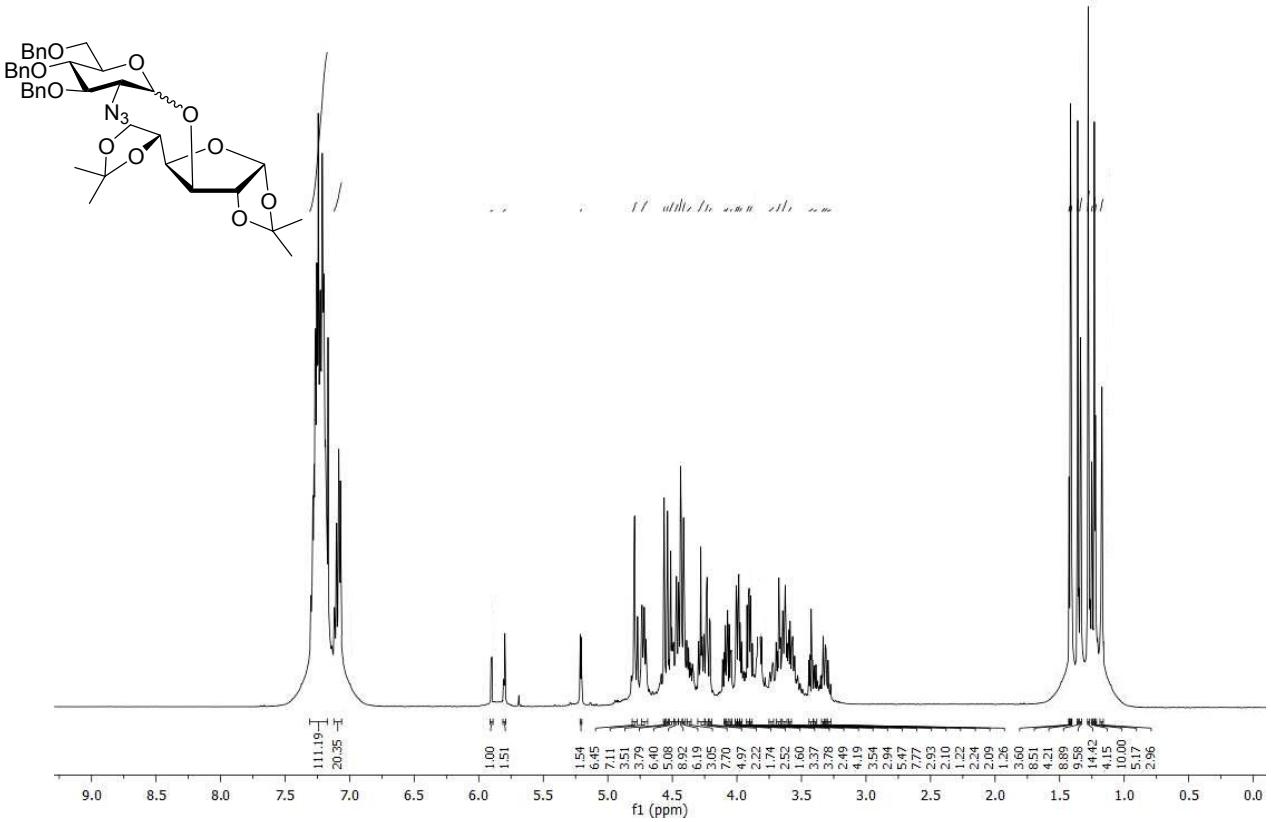

BnO
BnO
BnO
BnO
O
O
OBn
O
BnO
BnO
OMe
1.93
90.38
3.96
1.18
0.77
1.04
1.38
0.66
1.01
2.31
2.03
5.74
3.21
1.90
2.26
3.85
8.77
5.10
2.02
2.48
1.26
1.00
0.66
2.54
1.87
5.03
9.65
3.03
4.63
2.58
3.34
3.39
1.55
5.69
3.00
1.30
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)

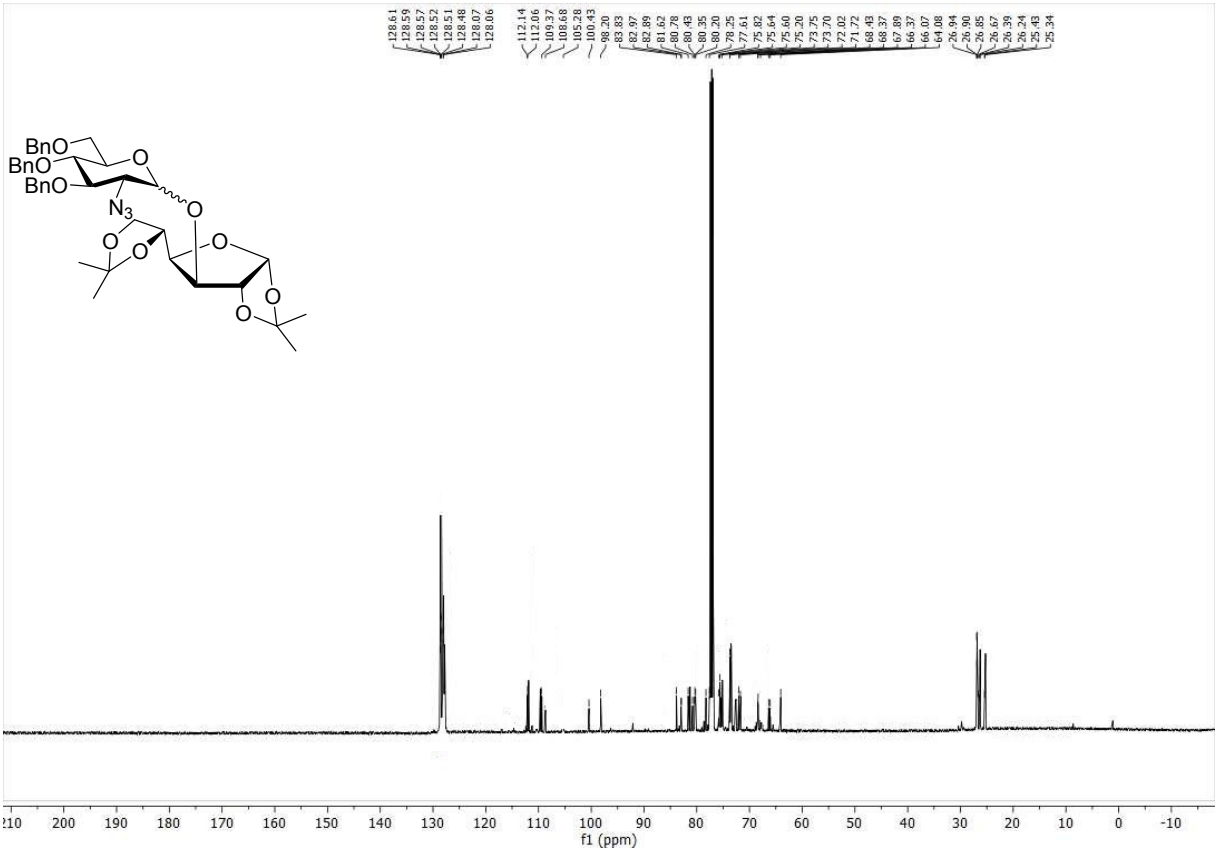

BnO
BnO
BnO
BnO
O
O
O
O
O
O
14.74
18.44
3.10
1.94
0.60
1.02
0.48
1.04
1.36
1.20
3.29
3.17
0.79
0.93
1.16
0.76
2.03
1.73
6.90
1.33
1.22
0.66
0.79
2.45
1.58
0.79
0.87
3.49
2.73
2.09
1.28
1.31
3.00
6.50
5.94
3.96
10.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

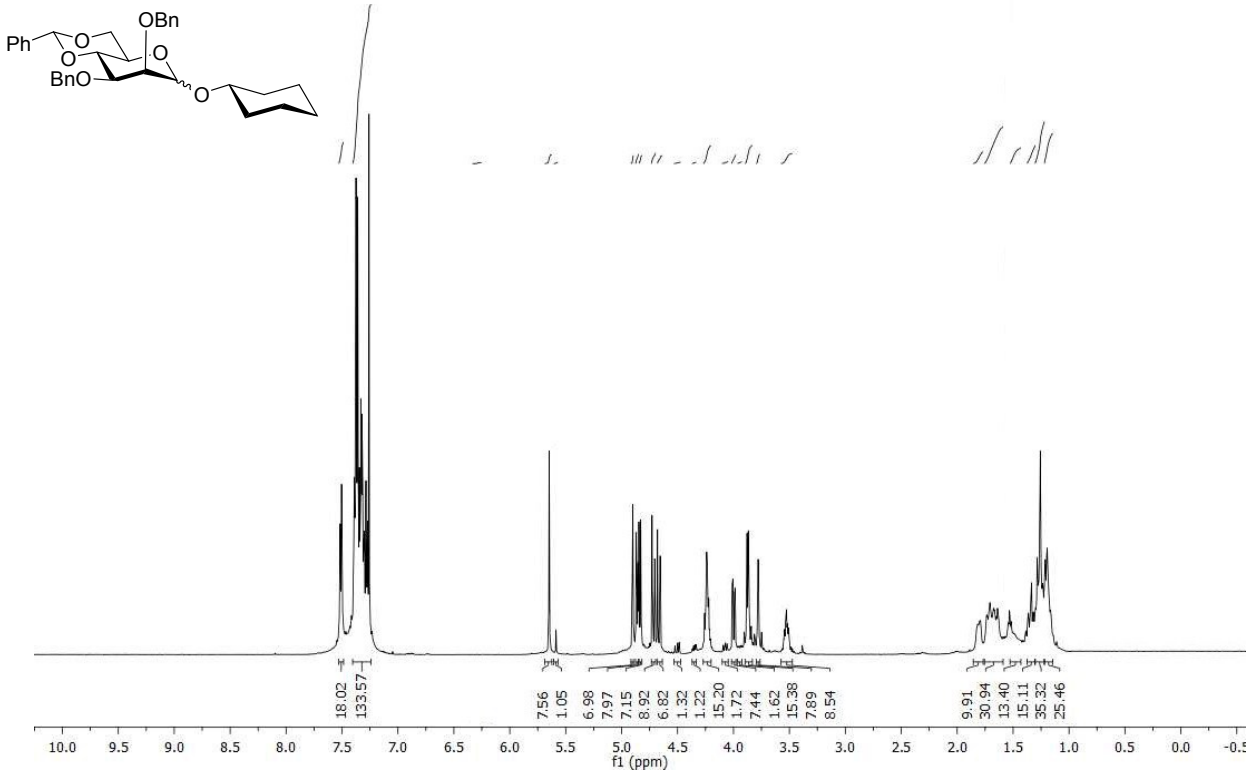

BnO
BnO
BnO
O
N3
O
14.20
0.98
1.00
1.95
1.12
1.10
2.14
1.04
1.07
1.06
1.26
1.85
0.99
2.41
2.48
1.07
2.29
3.40
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

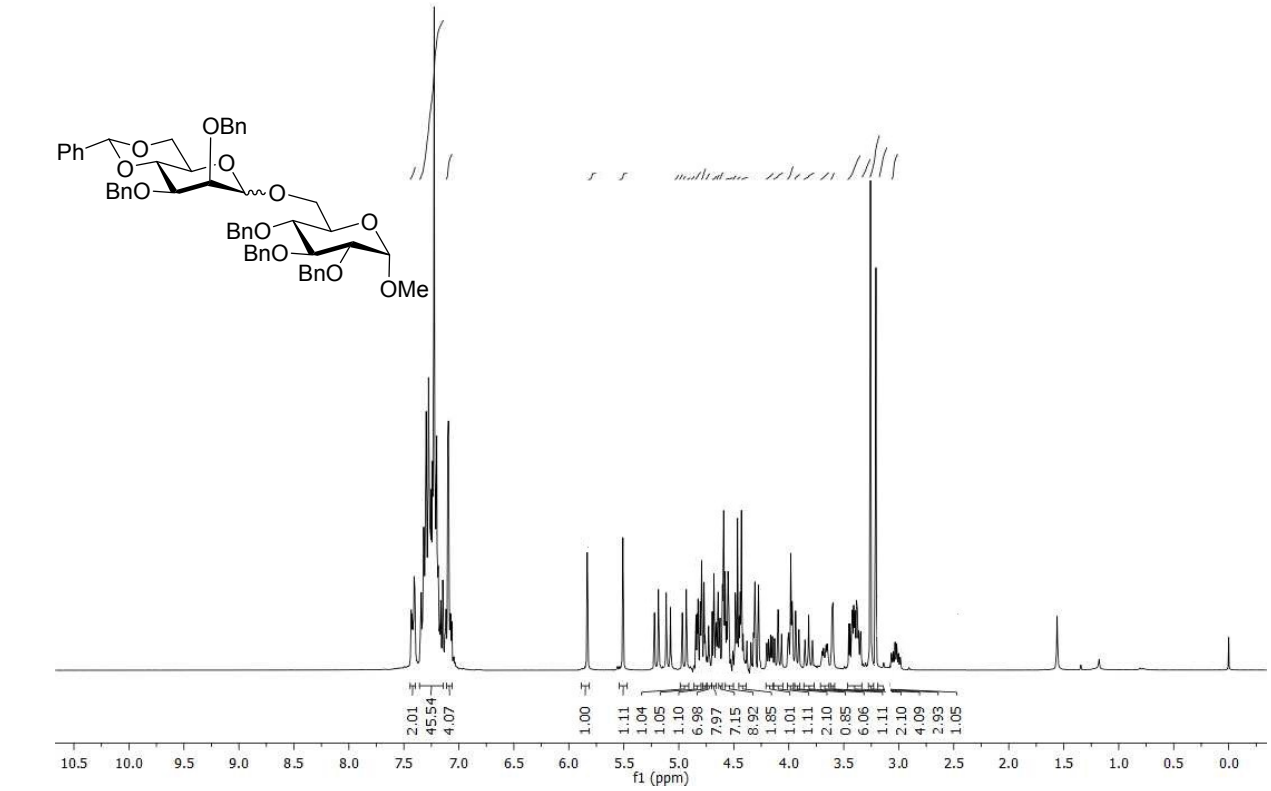

BnO
BnO
BnO
O
N3
O
BnO
BnO
BnO
O
OMe
33.36
2.27
0.97
0.96
0.90
1.32
2.05
0.58
1.75
1.53
1.04
0.61
0.98
1.36
1.29
1.20
0.99
1.48
1.12
1.36
1.84
3.16
1.47
1.30
1.13
1.05
3.02
1.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

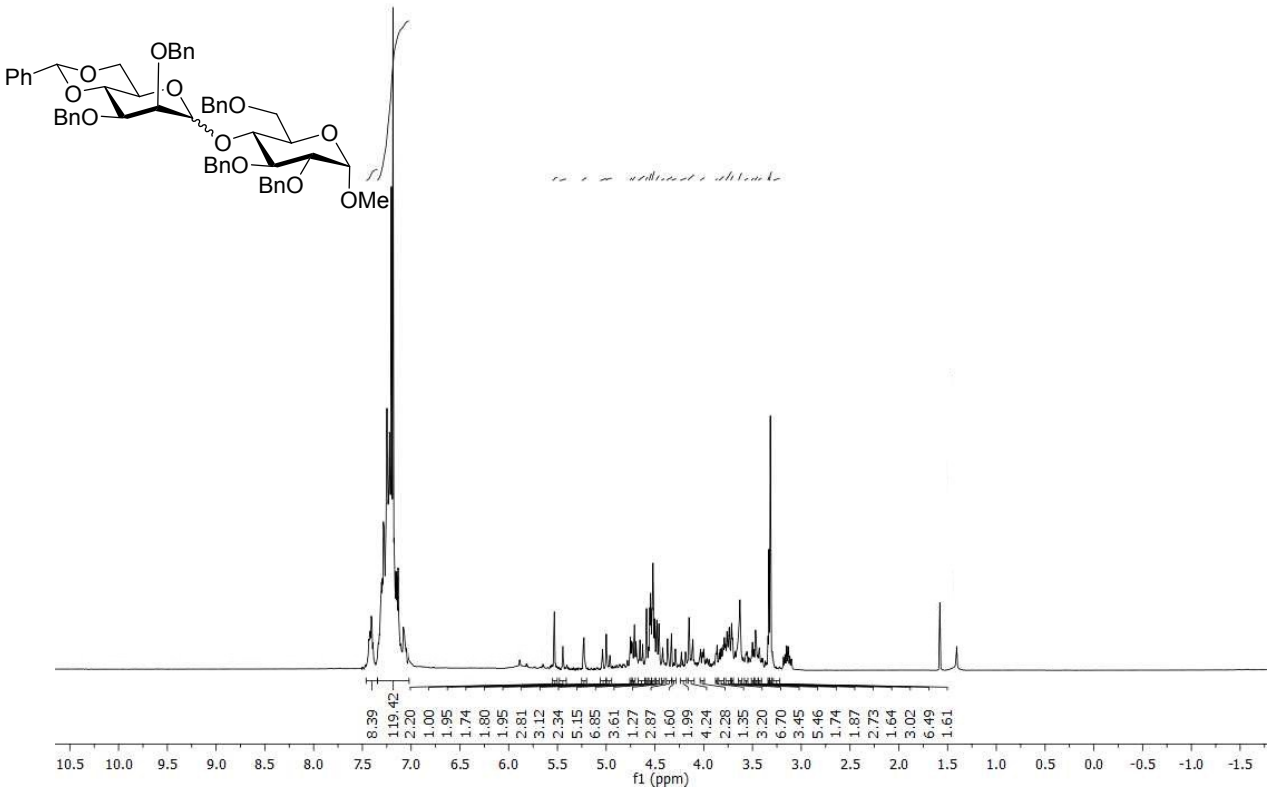

BnO
BnO
BnO
O
N3
O
OBn
O
BnO
BnO
OMe
36.94
32.43
1.00
2.05
2.36
2.21
2.00
4.91
4.31
2.26
3.69
2.82
1.67
2.54
1.80
3.58
2.49
2.20
4.35
3.61
4.13
2.93
2.22
2.60
2.92
4.70
3.04
4.43
2.95
3.64
4.45
f1 (ppm)

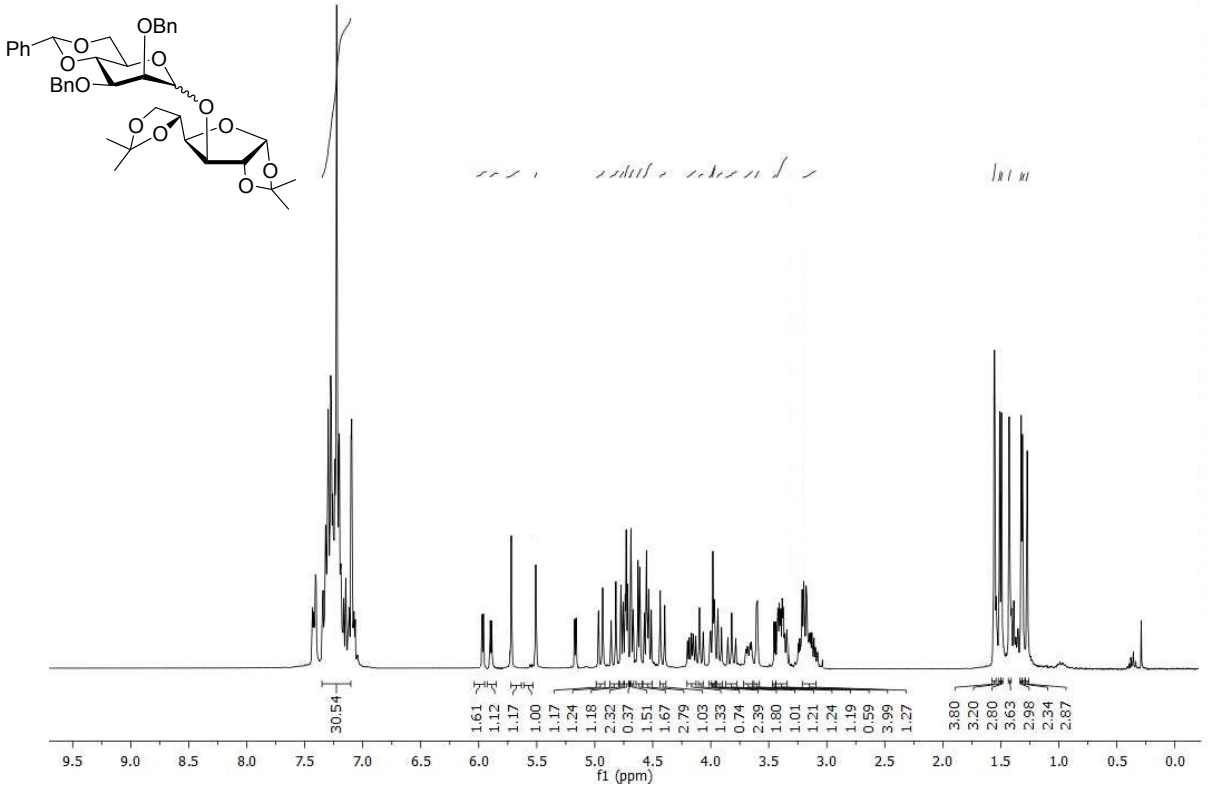

BnO
BnO
BnO
O
N3
O
O
O
O
O
O
111.19
20.35
1.00
1.51
1.54
6.45
7.11
3.51
3.79
6.40
5.08
8.92
6.19
3.05
7.70
4.97
2.22
1.74
2.52
1.60
3.37
3.78
2.49
4.19
3.54
2.94
5.47
7.77
2.93
2.10
1.22
2.24
2.09
1.26
3.60
8.51
4.21
8.89
9.58
14.42
4.15
10.00
5.17
2.96
f1 (ppm)

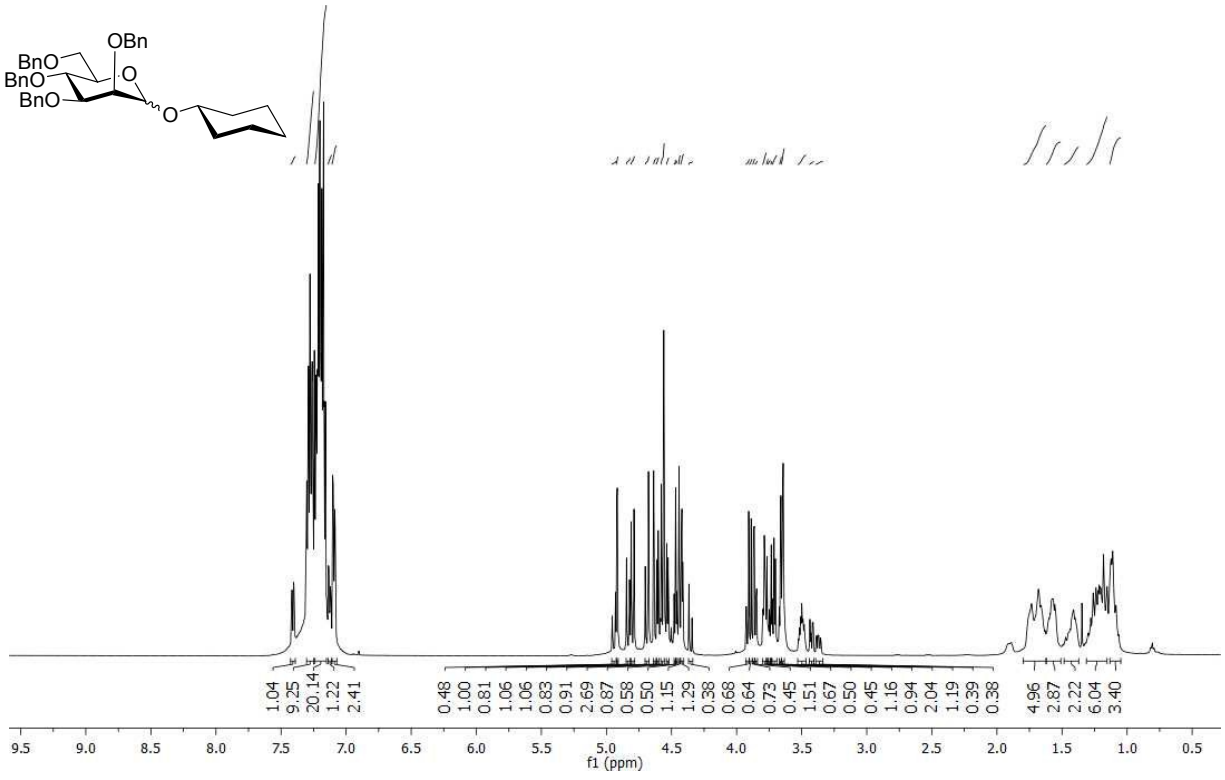

BnO
BnO
BnO
N3
O
f1 (ppm)

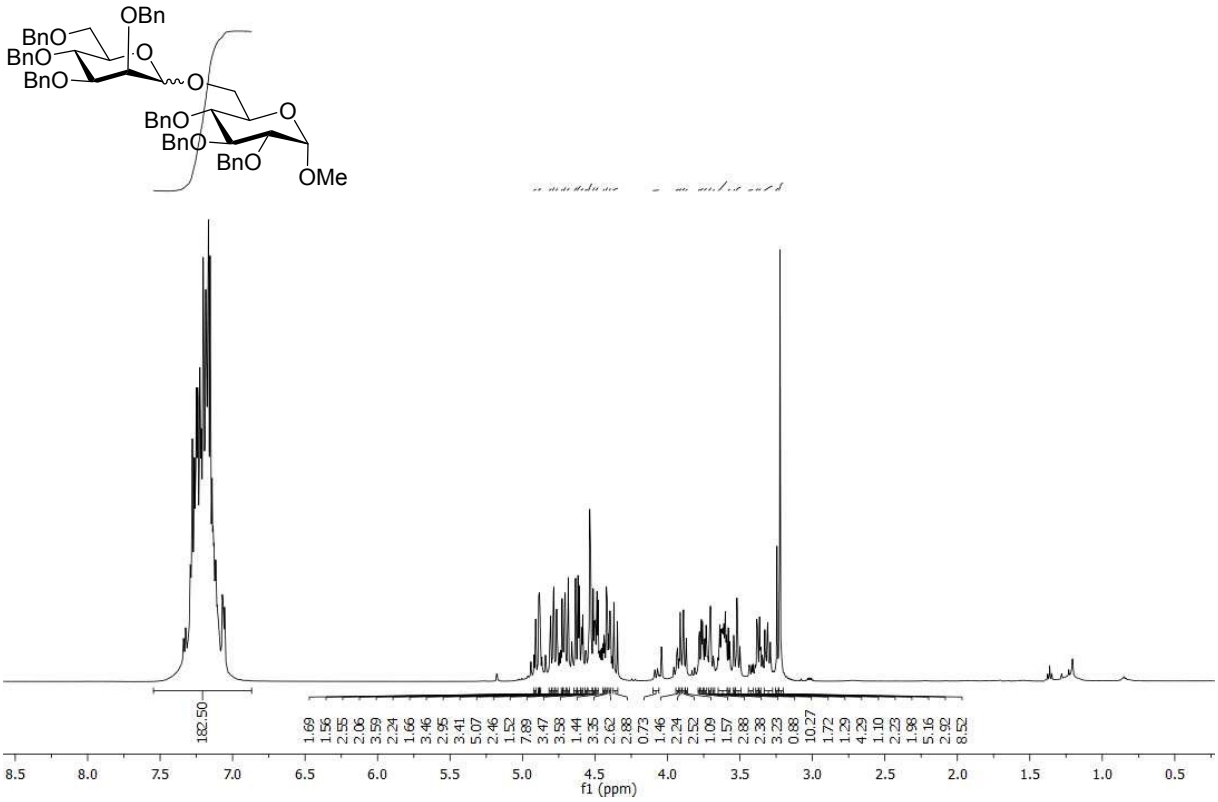

Ph
OBn
BnO
O
f1 (ppm)

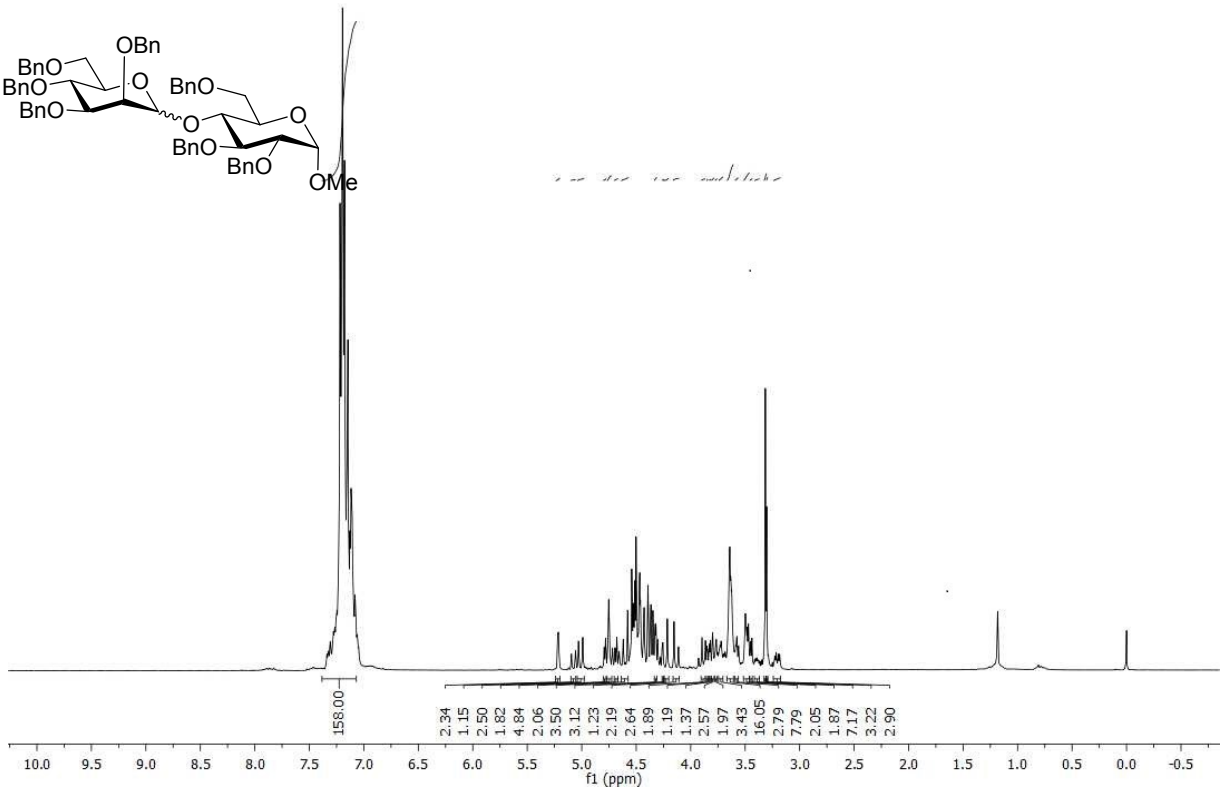

Ph
O
O
OBn
O
BnO
O
BnO
BnO
BnO
O
OMe
2.01
45.54
4.07
1.00
1.11
1.04
1.05
1.10
6.98
7.97
7.15
8.92
1.85
1.01
1.11
2.10
0.85
6.06
1.11
2.10
4.09
2.93
1.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

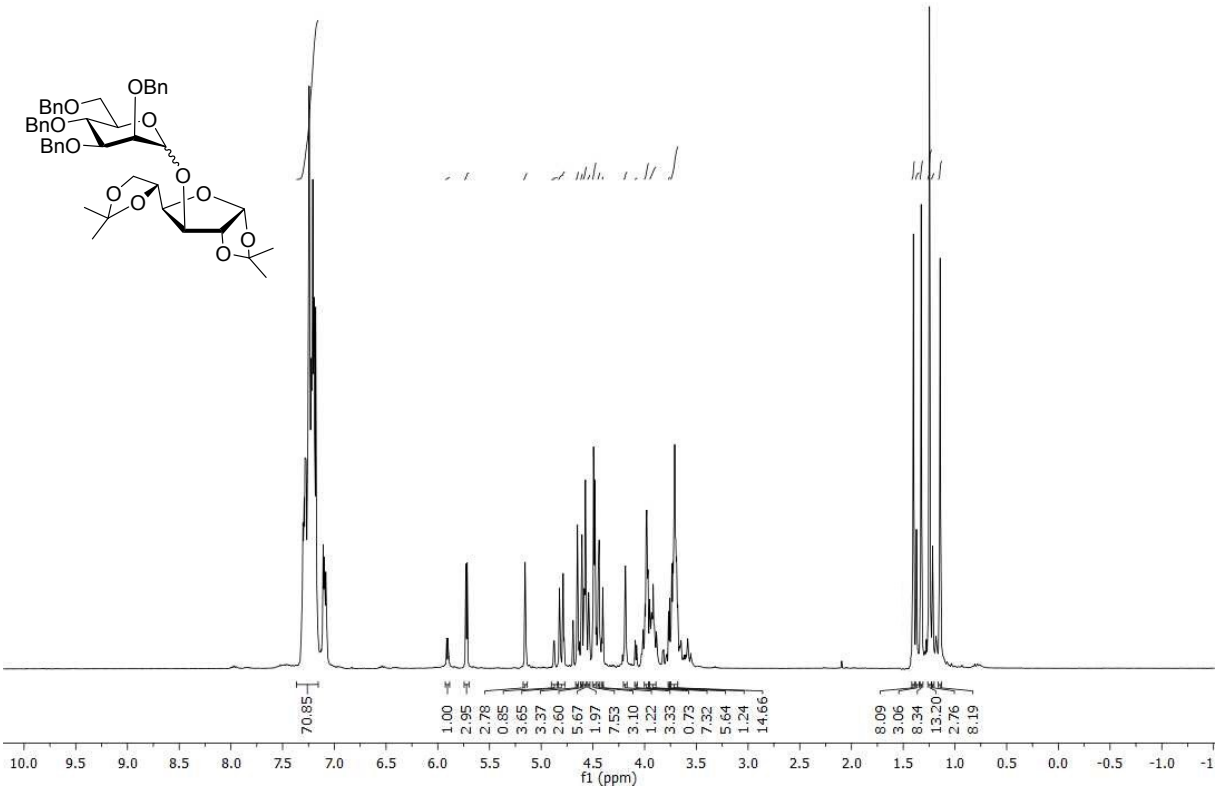

Ph
O
O
OBn
O
BnO
BnO
O
O
BnO
BnO
BnO
OMe
8.39
19.42
2.20
1.00
1.95
1.74
1.80
1.95
2.81
3.12
2.34
5.15
6.85
3.61
1.27
2.87
1.60
1.99
4.24
2.28
1.35
3.20
6.70
3.45
5.46
1.74
1.87
2.73
1.64
3.02
6.49
1.61
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

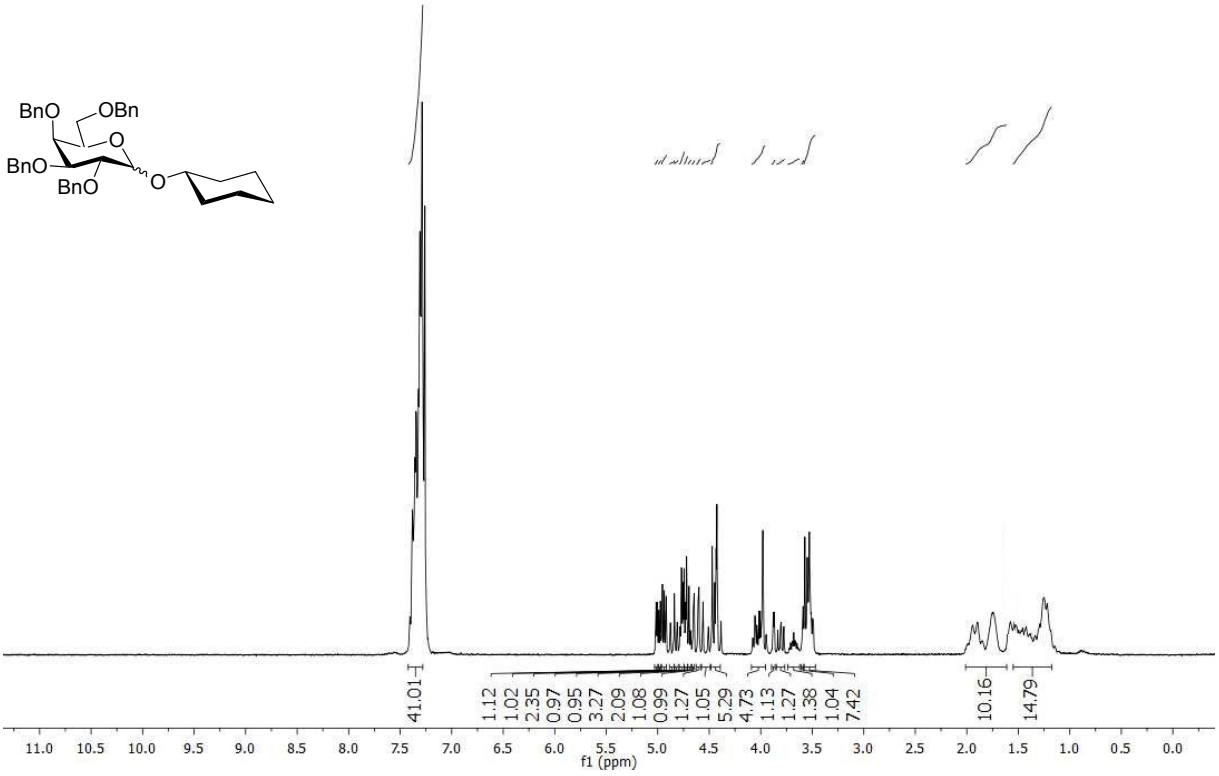

OBn
Ph
BnO
30.54
1.61
1.12
1.17
1.00
1.17
1.24
1.18
2.32
0.37
1.51
1.67
2.79
1.03
1.33
0.74
2.39
1.80
1.01
1.21
1.24
1.19
0.59
3.99
1.27
3.80
3.20
2.80
3.63
2.98
2.34
2.87
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

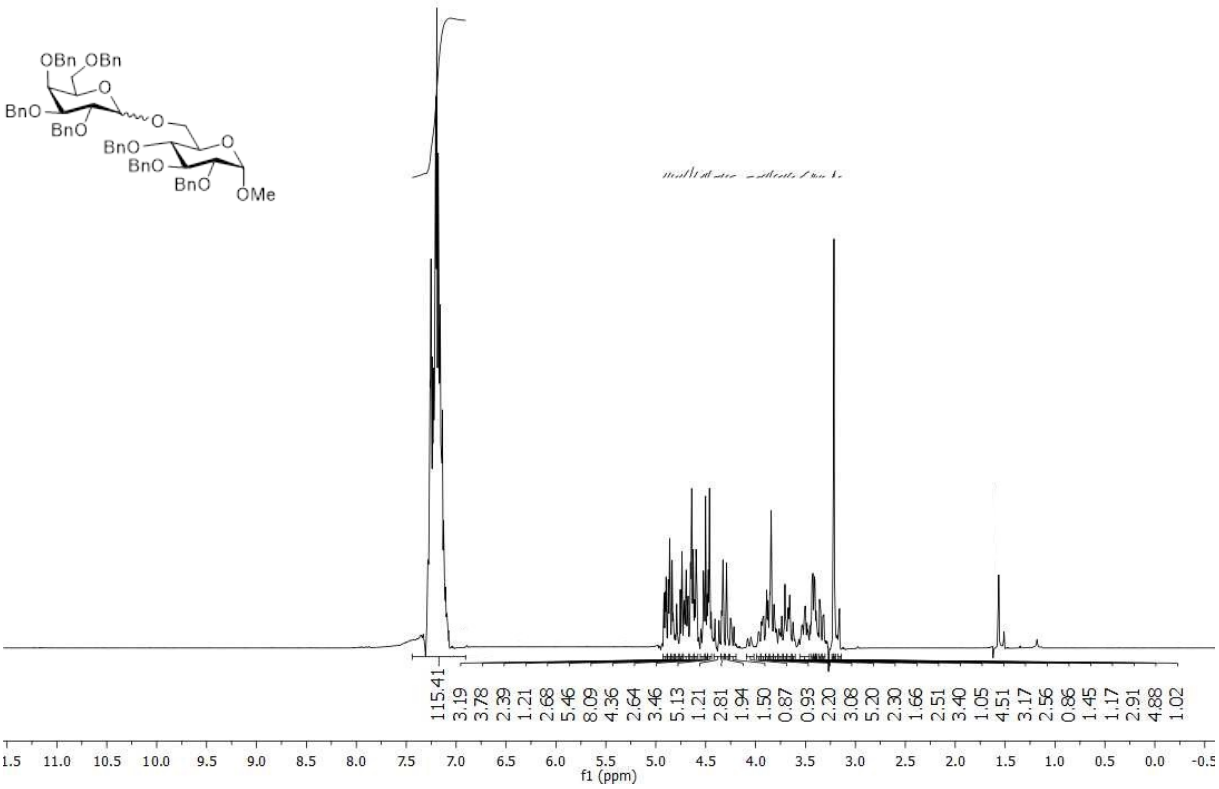

OBn
BnO
BnO
BnO
1.04
9.25
20.14
1.22
2.41
0.48
1.00
0.81
1.06
1.06
0.83
0.91
2.69
0.87
0.58
0.50
1.15
1.29
0.38
0.68
0.64
0.73
0.45
1.51
0.67
0.50
0.45
1.16
0.94
2.04
1.19
0.39
0.38
4.96
2.87
2.22
6.04
3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

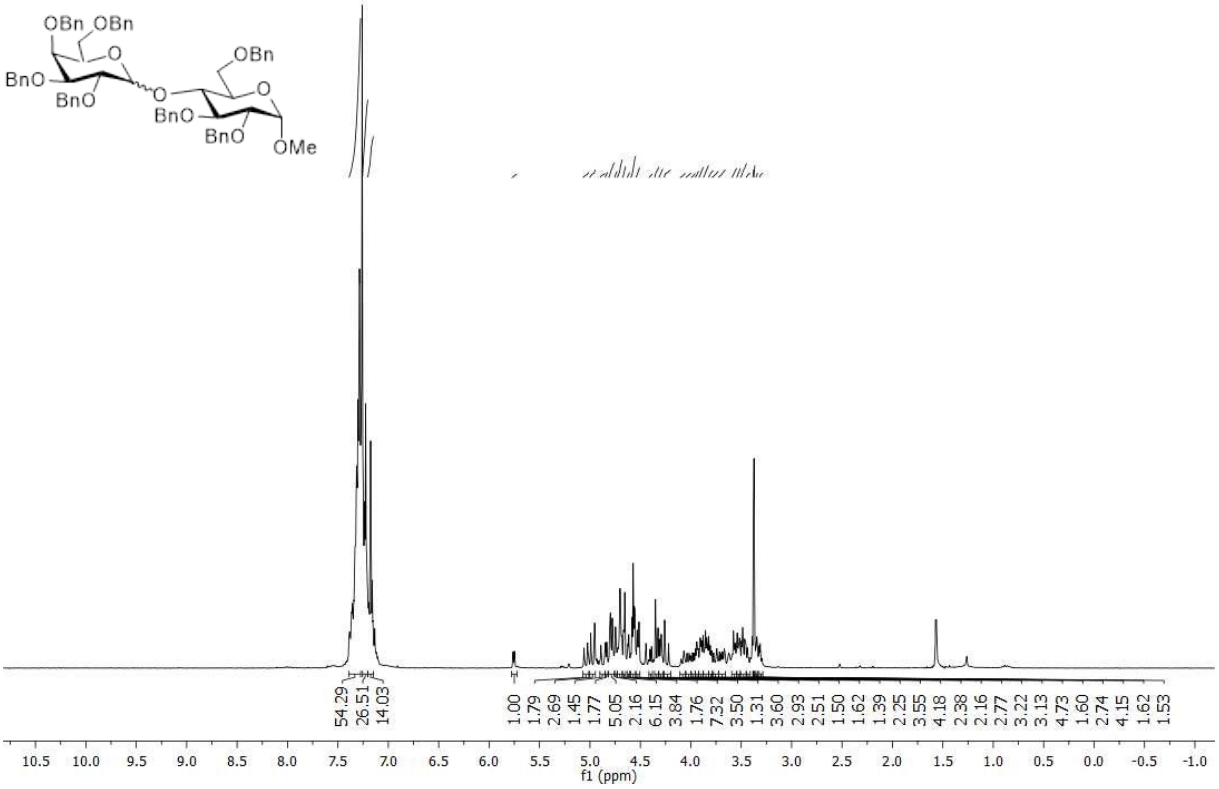

OBn
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
OMe
182.50
f1 (ppm)

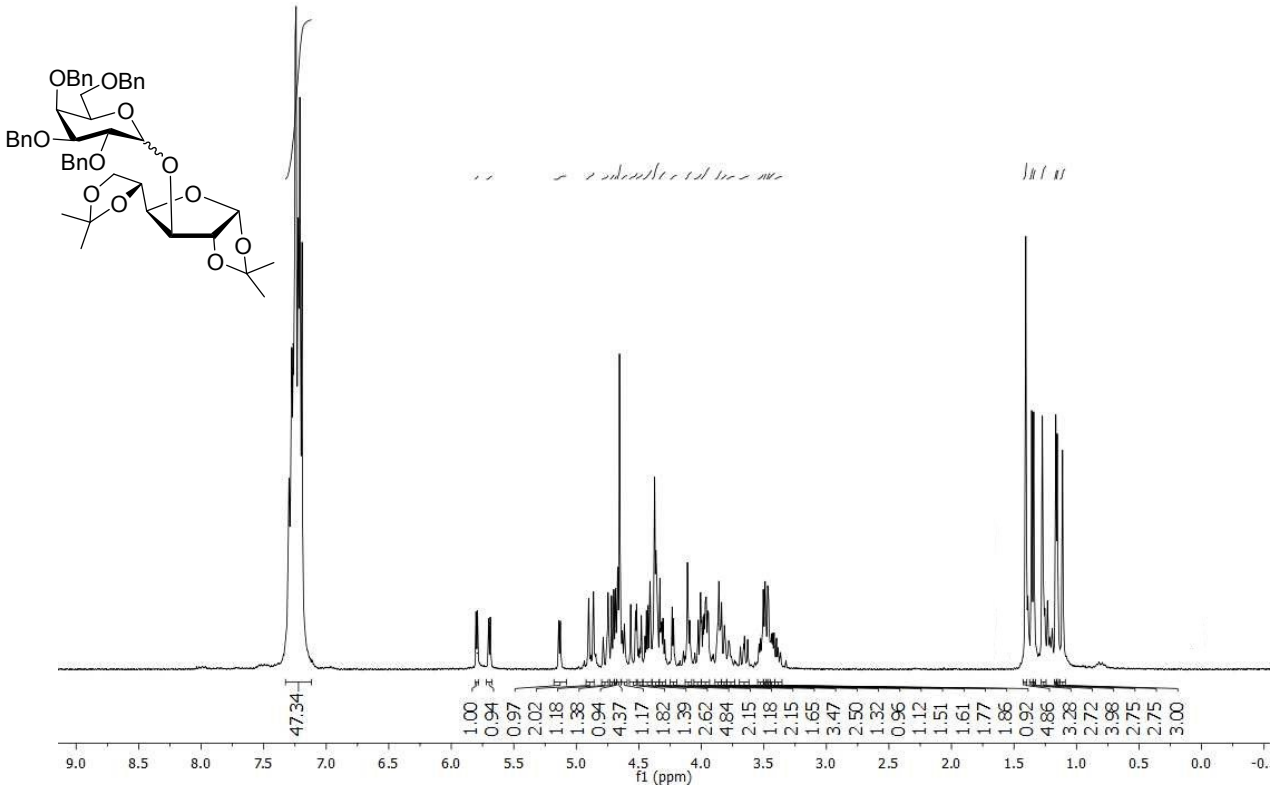

OBn
BnO
BnO
BnO
O
BnO
O
BnO
BnO
OMe
158.00
f1 (ppm)


OBn
BnO
BnO
BnO
O
O
O
O
O
O
O
70.85
1.00
2.95
2.78
0.85
3.65
3.37
2.60
5.67
1.97
7.53
3.10
1.22
3.33
0.73
7.32
5.64
1.24
14.66
8.09
3.06
8.34
13.20
2.76
8.19
f1 (ppm)


BnO
OBn
BnO
BnO
O
O
41.01
1.12
1.02
2.35
0.97
0.95
3.27
2.09
1.08
0.99
1.27
1.05
5.29
4.73
1.13
1.27
1.38
1.04
7.42
10.16
14.79
f1 (ppm)


OBn OBn
BnO
BnO
BnO
BnO
BnO
OMe
115.41
3.19
3.78
2.39
1.21
2.68
5.46
8.09
4.36
2.64
3.46
5.13
1.21
2.81
1.94
1.50
0.87
0.93
2.20
3.08
5.20
2.30
1.66
2.51
3.40
1.05
4.51
3.17
2.56
0.86
1.45
1.17
2.91
4.88
1.02
f1 (ppm)


OBn OBn
OBn
BnO
BnO
BnO
BnO
BnO
OMe
54.29
26.51
14.03
1.00
1.79
2.69
1.45
1.77
5.05
2.16
6.15
3.84
1.76
7.32
3.50
1.31
3.60
2.93
2.51
1.50
1.62
1.39
2.25
3.55
4.18
2.38
2.16
2.77
3.22
3.13
4.73
1.60
2.74
4.15
1.62
1.53
f1 (ppm)


OBn
OBn
BnO
BnO
O
O
O
O
O
O
47.34
1.00
0.94
0.97
2.02
1.18
1.38
0.94
4.37
1.17
1.82
1.39
2.62
4.84
2.15
1.18
2.15
1.65
3.47
2.50
1.32
0.96
1.12
1.51
1.61
1.77
1.86
0.92
4.86
3.28
2.72
3.98
2.75
2.75
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)