Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Exploiting π and Hydrogen Bonding Interactions of Strain-free Pyridinium Tetrafluoroborate Salt for Stereoselective Synthesis of O-Aryl Glycosides

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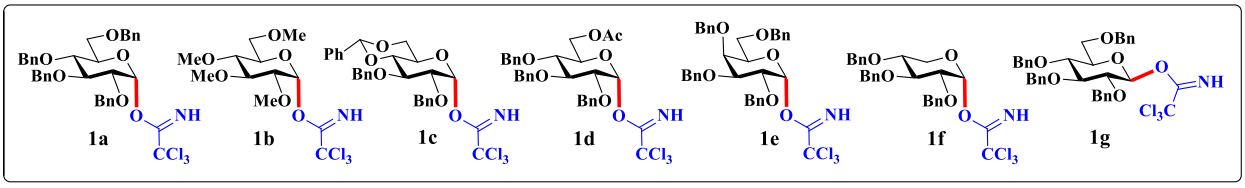
General Information:

All chemicals were purchased as reagent grade and used without further purification unless otherwise mentioned. Solvents were purified by standard procedures. All reactions were carried out under a nitrogen atmosphere with freshly distilled solvents unless otherwise mentioned. Molecular sieves (4Å) were flame-dried before use. Reactions were monitored by analytical thin-layer chromatography 60 F_{254} silica gel, precoated on aluminum plates. TLC plates were visualized by spraying 10% H_2SO_4 in MeOH and heating until spots appeared or under UV light (254 nm). Column chromatography was performed using silica gel (100–200 mesh). ^1H and ^{13}C NMR spectra were recorded at 400, 100 and 500, 125 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane or solvent residual signals (^1H NMR: solvent $CDCl_3$, δ = 7.26 ppm; DMSO-d_6, δ = 2.50 ppm; ^{13}C NMR: solvent $CDCl_3$, δ = 77.00 ppm; DMSO-d_6, δ = 39.52 ppm). The following abbreviations explained multiplicities: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiple), coupling constant (hertz). HRMS spectra were recorded on an ESI-mass spectrometer (Q-TOF, positive ion) and acetonitrile was used to dissolve the sample.

Donors (glycosyl trichloroacetimidates) (**1a** – **1g**) and pyridinium salts (**A**-**H**) were prepared by following the known literature procedure. NMR data of known compounds were consistent with the literature reports.

List of glycosyl trichloroacetimidate donors used in the studies.[1-4]



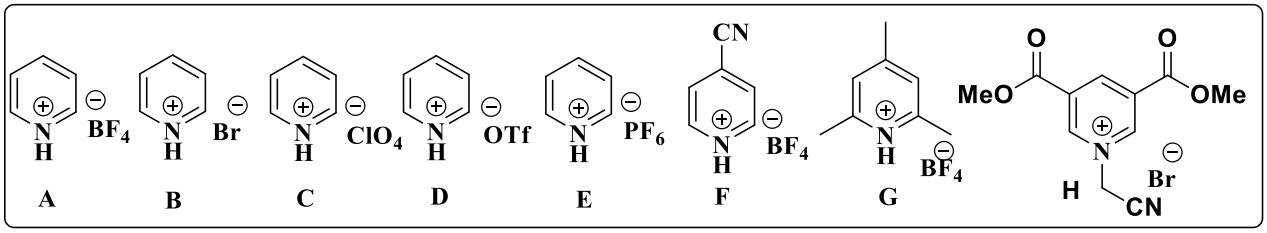
General procedure for the synthesis of glycosyl α-trichloroacetimidates (GP-1):

To a solution of glycosyl hemiacetal (1.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) was added CCl_3CN (10.0 mmol, 10.0 equiv) and a catalytic amount of DBU (0.1 mmol, 0.1 equiv) at 0 °C. After 10 min, the ice bath was removed, and the resulting mixture was allowed to stir at room temperature for 1 h. After completion, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography using ethyl acetate and hexane gradient and 1% of TEA to obtain glycosyl α-trichloroacetimidates (**1a-1f**).

General procedure for the synthesis of glycosyl β-trichloroacetimidates (GP-2):

To a solution of glycosyl hemiacetal (1.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) was added CCl_3CN (10.0 mmol, 10.0 equiv) and K_2CO_3 (5.0 mmol, 5.0 equiv) at room temperature. The reaction mixture was allowed to stir at room temperature for 1 h. After completion, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography using ethyl acetate and hexane gradient and 1% of TEA to obtain glycosyl β-trichloroacetimidates (**1g**).

List of catalysts A-H used in the studies.[5]



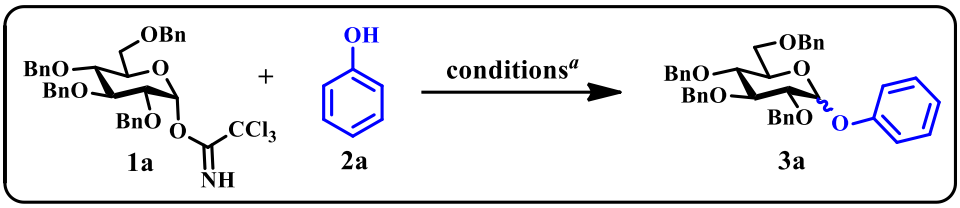
General Procedure for the synthesis of pyridinium salts (GP-3)[5]:

To a round-bottom flask equipped with a stirring bar was added an ethyl ether solution of pyridine, then the corresponding acid was added dropwise. A white precipitation was observed. When the pyridine was consumed completely, the precipitation was filtered, and washed with diethyl ether three times. Afterward, the solid was dried under a vacuum to afford the targeted products (**A**-**H**).

General Procedure for Glycosylation (GP-4):

Under N_2 atmosphere, glycosyl trichloroacetimidate (1.0 equiv.), and phenol acceptor (1.5 equiv.), were weighed into a round bottom flask with a magnetic stir bar. Anhydrous DCM (0.1 M) and activated 4Å MS (molecular sieves) were added followed by the addition of catalyst (10 mol %) and the reaction mixture was stirred at 0 °C for 3 h. After completion, the reaction was diluted with DCM and washed with brine solution. The aqueous phase was extracted with DCM (3X). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give the corresponding *O*-aryl glycosides (**3**-**9**).

Table S1: Optimization Conditions

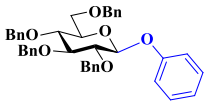
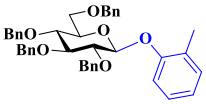
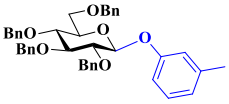
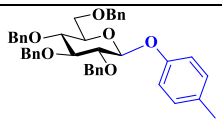
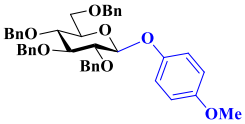
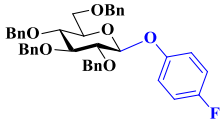
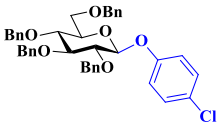
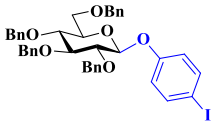


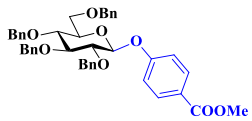
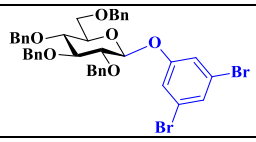
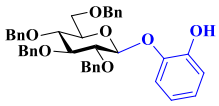
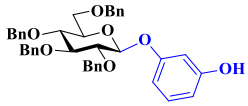
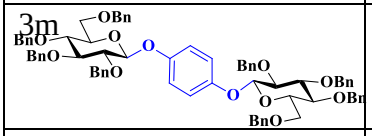
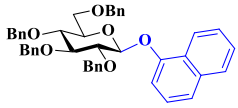
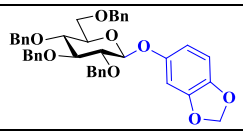
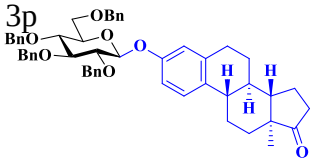
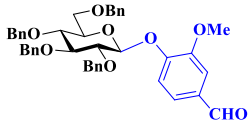
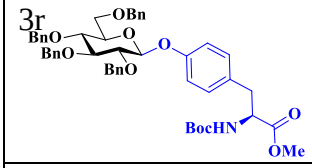
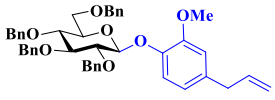
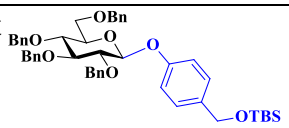
Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)	α:β[c]
1	A	DCM	0	3	74	1:9
2	A	Et_2O	0	3	73	1:4
3	A	ACN	0	3	64	1:1.1
4	A	THF	0	3	52	1:3.5
5	A	Toluene	0	3	68	1:3.5
6	A	DCM	-20	3	75	1:9
7[d]	A	DCM	0	3	78	1:9
8[e]	A	DCM	0-rt	12	58	β only
9[f]	**A**	**DCM**	**0**	**3**	**79**	**β only**
10	B	DCM	0-rt	24	-	-
11	C	DCM	0-rt	24	-	-
12	D	DCM	0	3	76	1:3
13	E	DCM	0	3	68	1:2.1
14	F	DCM	0	3	63	1:2.5
15[g]	HBF_4	DCM	0	3	66	1:3
16	$BF_3{\cdot}OEt_2$	DCM	0	1	69	1:5.5
17	TMSOTf	DCM	0	1	57	3:1
18[h]	A	DCM	0	3	74	1:6.6

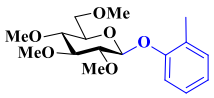
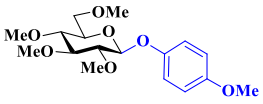
[a]1a (0.1 mmol, 1 equiv.), 2a (0.15 mmol, 1.5 equiv.), catalyst (15 mol %), solvent [0.05 M], 4Å MS (molecular sieves) at 0 °C under nitrogen atmosphere. [b]Yield of isolated product. [c]Anomeric ratios were determined by ^{1}H NMR spectroscopy. [d]10 mol % of catalyst was used. [e]5 mol % of catalyst was used. [f][0.1 M] DCM was used. [g]HBF_4 - 48% wt. in H_2O was used. [h]Inverse addition conditions were used.

Table S2: Compound Characterization List

(+) = yes, (-) = no

Structure	New compounds	Appearance	^{1}H	^{13}C	COSY	HSQC	HRMS
3a 	-(6)	white solid	+	+	-	-	-
3b 	-(6)	white solid	+	+	-	-	-
3c 	-(6)	white solid	+	+	-	-	-
3d 	-(6)	white solid	+	+	-	-	-
3e 	-(6)	white solid	+	+	+	+	-
3f 	-(6)	white solid	+	+	-	- ($+^{19}$F)	-
3g 	-(4)	white solid	+	+	-	-	-
3h 	+	white solid	+	+	-	-	+

3i 	-(6)	white solid	+	+	-	-	-
3j 	+	white solid	+	+	+	+	+
3k 	+	white solid	+	+	-	-	+
3l 	+	Colorless sticky liquid	+	+	+	+	+
3m 	-(8)	Colorless sticky liquid	+	+	-	-	-
3n 	-(4)	Colorless sticky liquid	+	+	-	-	-
3o 	+	Colorless sticky liquid	+	+	-	-	+
3p 	+	Colorless sticky liquid	+	+	-	-	+
3q 	+	Colorless sticky liquid	+	+	-	-	+
3r 	+	Colorless sticky liquid	+	+	-	-	+
3s 	+	Colorless sticky liquid	+	+	-	-	+
3t 	+	Colorless sticky liquid	+	+	-	-	+

4a 	+	Colorless sticky liquid	+	+	+	+	+
4b 	+	White solid	+	+	+	+	+
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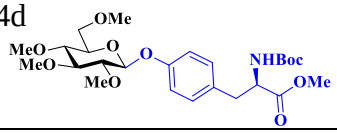
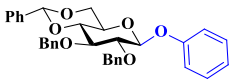
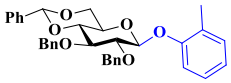
4d 	+	Colorless sticky liquid	+	+	-	-	+
5a 	-[9]	White solid	+	+	-	-	-
5b 	+	White solid	+	+	-	-	+
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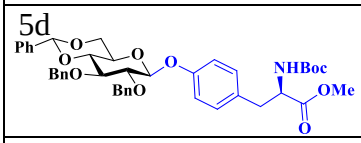
5d 	+	White solid	+	+	+	+	+
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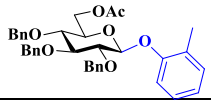
6a 	+	Colorless sticky liquid	+	+	-	-	+
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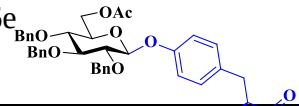
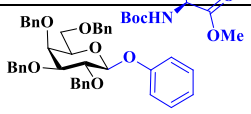
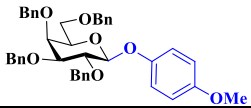
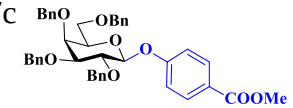
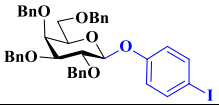
6e 	+	Colorless sticky liquid	+	+	-	-	+
7a 	-[7]	White solid	+	+	-	-	-
7b 	+	White solid	+	+	+	+	+

7c 	-[7]	White solid	+	+	+	+	-
7d 	+	White solid	+	+	+	+	+
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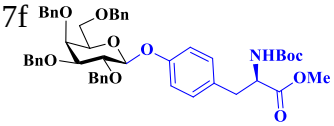
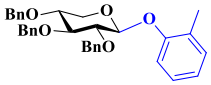
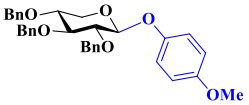
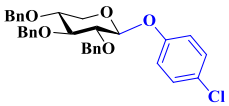
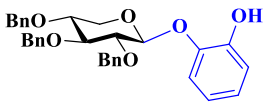
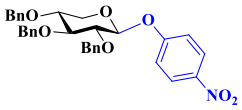
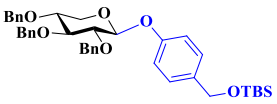
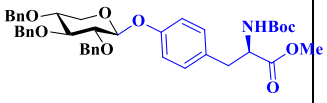
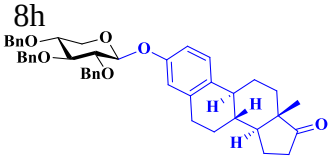
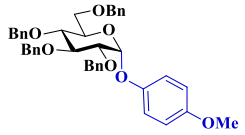
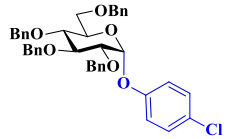
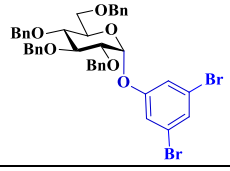
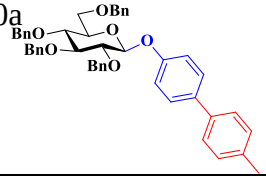
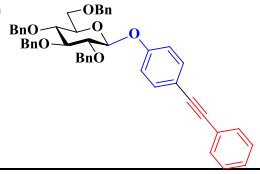
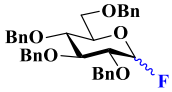
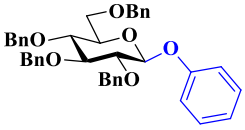
7f 	+	Colorless sticky liquid	+	+	-	-	+
8a 	-[4]	Colorless sticky liquid	+	+	-	-	-
8b 	+	Colorless sticky liquid	+	+	-	-	+
8c 	+	Colorless sticky liquid	+	+	+	+	+
8d 	+	Colorless sticky liquid	+	+	-	-	+
8e 	+	Colorless sticky liquid	+	+	+	+	+
8f 	+	Colorless sticky liquid	+	+	-	-	+
8g 	+	Colorless sticky liquid	+	+	-	-	+
8h 	+	Colorless sticky liquid	+	+	-	-	+

9a 	-(6)	Colorless sticky liquid	+	+	+	+	-
9b 	+	Colorless sticky liquid	+	+	-	-	+
9c 	+	Colorless sticky liquid	+	+	+	+	+
10a 	+	white solid	+	+	-	-	+
10b 	+	White solid	+	+	-	-	+
10c 	-(10)	Colorless sticky liquid	+	+	-	-	-

Characterization Data:

Phenyl 2,3,4,6-tetra-*O*-benzyl–β-D-glucopyranoside (3a)



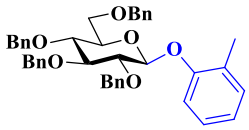
Following **GP-4**, **3a** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **phenol** (0.15 mmol, 14 mg), **catalyst** (1.6 mg, 10 mol%), as a white solid (79%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 20H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.11 – 7.04 (m, 3H), 5.06 (d, *J* = 10.9 Hz, 1H), 5.02 (d, *J* = 6.8 Hz, 1H, H-1β), 4.96 (d, *J* = 10.8 Hz, 1H), 4.84

(dd, *J* = 13.7, 11.0 Hz, 3H), 4.62 – 4.52 (m, 3H), 3.81 – 3.78 (m, 1H), 3.75 (dd, *J* = 6.7, 3.8 Hz, 2H), 3.72 – 3.66 (m, 4H), 3.62 (dd, *J* = 9.6, 4.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.3, 138.4, 138.2, 138.0, 137.9, 129.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 116.8, 101.6 (C1-β), 84.6, 81.9, 77.6, 75.7, 75.1, 75.0, 75.0, 73.4, 68.8, 29.7.

2-Methylphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3b)

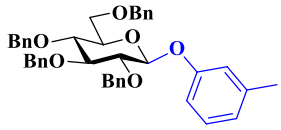


Following **GP-4**, **3b** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **2-methylphenol** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 10 mol%), as a white solid (50 mg, 79%, α:β = 1:25). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 18H), 7.23 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.00 – 6.95 (m, 1H), 5.51 (d, *J* = 3.3 Hz, 0.04H, H-1α), 5.09 (d, *J* = 10.8 Hz, 1H), 5.05 (d, *J* = 7.3 Hz, 1H, H-1β), 4.97 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 3.2 Hz, 1H), 4.86 (d, *J* = 1.9 Hz, 1H), 4.85 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 1.8 Hz, 1H), 4.60 – 4.52 (m, 2H), 3.83 – 3.76 (m, 3H), 3.77 – 3.69 (m, 2H), 3.64 – 3.61 (m, 1H), 2.32 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.4, 138.5, 138.2, 138.1, 137.9, 130.8, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 126.9, 122.3, 114.7, 101.1, 84.8, 82.1, 77.7, 75.7, 75.1, 75.0, 73.5, 68.7, 16.7.

3-Methylphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3c)



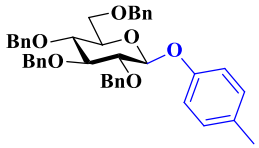
Following **GP-4**, **3c** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **3-methylphenol** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 10 mol%), as a white

solid (50 mg, 75%, α:β = 1:10). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 21H), 7.22 – 7.13 (m, 3H), 6.89 (dd, *J* = 11.1, 7.1 Hz, 3H), 5.49 (d, *J* = 3.5 Hz, 0.11H, H1-α), 5.06 (d, *J* = 10.9 Hz, 1H), 5.01 (d, *J* = 7.5 Hz, 1H, H1-β), 4.96 (d, *J* = 10.9 Hz, 1H), 4.85 (dd, *J* = 13.2, 10.9 Hz, 3.6H), 4.69 (d, *J* = 12.0 Hz, 0.19H), 4.63 – 4.52 (m, 3H), 4.49 (d, *J* = 10.7 Hz, 0.18H), 4.41 (d, *J* = 12.0 Hz, 0.13H), 4.22 (t, *J* = 9.2 Hz, 0.15H), 3.84 – 3.59 (m, 7H), 2.32 (s, 3.3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.3, 139.6, 138.5, 138.2, 138.1, 137.9, 129.2, 128.4, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 123.4, 117.7, 113.8, 101.7 (C1-β), 84.6, 82.0, 77.6, 75.7, 75.1, 75.0, 74.9, 73.4, 68.8, 21.5.

4-Methylphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3d)

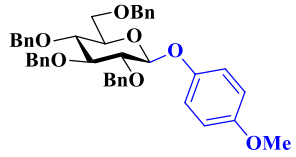


Following **GP-4**, **3d** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **4-methylphenol** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 10 mol%), as a white solid (48 mg, 76%, α:β = 1:16). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 18H), 7.21 – 7.16 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 5.45 (d, *J* = 3.4 Hz, 0.06H, H1-α), 5.06 (d, *J* = 10.9 Hz, 1H), 4.99 – 4.92 (m, 2H, H1-β, OCH_2Ph), 4.83 (t, *J* = 11.7 Hz, 3H), 4.57 (dt, *J* = 15.1, 12.1 Hz, 3H), 3.82 – 3.65 (m, 5H), 3.59 (dd, *J* = 9.2, 3.3 Hz, 1H), 2.31 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.3, 138.5, 138.2, 138.1, 137.9, 132.0, 129.9, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 116.9, 102.0, 84.6, 82.0, 77.6, 77.3, 75.8, 75.0, 75.0, 73.5, 68.7, 20.6.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3e)

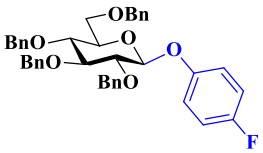


Following **GP-4**, **3e** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **4-Methoxyphenol** (0.15 mmol, 15 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (50 mg, 73%, α:β = 1:11). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 21H), 7.22 – 7.19 (m, 2H), 7.05 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.38 (d, J = 3.5 Hz, 0.09H, H1-α), 5.07 (d, *J* = 10.9 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.90 (d, *J* = 7.5 Hz, 1H, H1-β), 4.86 (d, *J* = 11.6 Hz, 1H), 4.82 (d, *J* = 1.2 Hz, 1.6H), 4.70 (d, *J* = 11.9 Hz, 0.15H), 4.62 – 4.59 (m, 2H), 4.57 – 4.54 (m, 2H), 4.51 (d, *J* = 10.7 Hz, 0.16H), 4.43 (d, *J* = 12.0 Hz, 0.11H), 4.20 (t, *J* = 9.3 Hz, 0.09H).3.82 – 3.79 (m, 0.6H), 3.78 (s, 3H), 3.76 – 3.71 (m, 3H), 3.70 – 3.66 (m, 2H), 3.61 – 3.57 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.2, 151.5, 138.5, 138.2, 138.1, 137.9, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 118.4, 114.5, 102.8 (C-1β), 96.3 (C-1α), 84.6, 82.0, 79.7, 77.7, 75.7, 75.1, 75.0, 73.4, 68.8, 55.6.

4-Fluorophenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3f)



Following **GP-4**, **3f** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **4-Fluorophenol** (0.15 mmol, 17 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (51 mg, 81%, α:β = 1:25). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

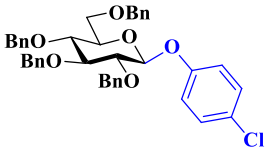
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 18H), 7.20 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.05 (dd, *J* = 9.2, 4.5 Hz, 2H), 6.97 (dd, *J* = 9.1, 8.3 Hz, 2H), 5.36 (d, *J* = 3.5 Hz, 0.04H, 1H, H1-α), 5.04 (d, *J* = 10.9 Hz, 1H), 4.96 (d, *J* = 10.9 Hz, 1H, H1-β),), 4.92 (d, *J* = 7.6 Hz, 1H), 4.87 – 4.83 (m, 3H), 4.68 (d, *J* = 12.0 Hz, 0.04H), 4.61 – 4.53 (m, 3H), 4.50 (d, *J* = 10.8 Hz, 0.06H), 4.42 (d, *J* =

12.0 Hz, 0.04H), 4.19 (t, *J* = 9.3 Hz, 0.03H), 4.14 (d, *J* = 7.2 Hz, 0.01H), 3.80 (dd, *J* = 10.7, 1.9 Hz, 1H), 3.76 – 3.73 (m, 2H), 3.72 – 3.66 (m, 2H), 3.61 – 3.58 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.4, 157.4 (d, $J_{C\text{-}F}$ = 238 Hz), 153.5, 153.4 (d, $J_{C\text{-}F}$ = 2.3 Hz), 138.4, 138.1, 138.0, 137.9, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 118.1 (d, $J_{C\text{-}F}$ = 8.2 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.9 Hz), 102.3 (C-1β), 84.6, 81.9, 77.6, 75.8, 75.1, 75.0, 73.4, 68.7.

HRMS (ESI-TOF): calculated for $C_{40}H_{39}FO_6$ $[M+Na]^+$ 657.2623 found 657.2596.

4-Chlorophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3g)

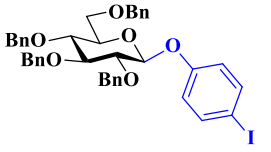


Following **GP-4**, **3g** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.05 mmol, 35 mg), **4-Chlorophenol** (0.075 mmol, 10.4 mg), **catalyst** (0.9 mg, 10 mol%) as a white solid (25 mg, 76%, α:β = 1:25). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 18H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.52 (d, *J* = 1.8 Hz, 0.04H, H1-α), 5.00 (d, *J* = 10.9 Hz, 1H), 4.96 – 4.92 (m, 2H), 4.87 – 4.79 (m, 3H), 4.56 (dt, *J* = 18.4, 11.0 Hz, 3H), 3.81 – 3.72 (m, 3H), 3.70 – 3.64 (m, 2H), 3.63 – 3.57 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 138.4, 138.1, 137.9, 129.4, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 118.2, 101.7 (C1-β), 84.6, 81.9, 77.6, 75.8, 75.1, 75.0, 73.5, 68.7.

4-Iodophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3h)



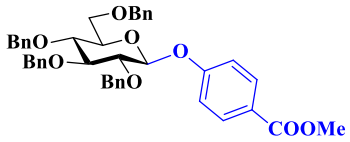
Following **GP-4**, **3h** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **4-Iodophenol** (0.15 mmol, 33 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (60 mg, 82%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2H), 7.30 (dd, *J* = 8.6, 3.8 Hz, 18H), 7.19 (dd, *J* = 7.3, 1.9 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.97 – 4.93 (m, 2H, H1-β), 4.87 – 4.80 (m, 3H), 4.59 – 4.50 (m, 3H), 3.78 (dd, *J* = 10.8, 1.6 Hz, 1H), 3.74 (dd, *J* = 5.4, 2.8 Hz, 2H), 3.67 (dt, *J* = 8.9, 4.3 Hz, 2H), 3.62 – 3.58 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.1, 138.4, 138.0, 137.9, 137.8, 128.4, 128.4, 128.2, 127.9, 127.8, 127.7, 119.1, 101.4 (C1-β), 85.3, 84.6, 81.8, 77.5, 75.7, 75.1, 75.0, 73.4, 68.7.

HRMS (ESI-TOF): calculated for $C_{40}H_{39}IO_6$ $[M+Na]^+$ 765.1684 found 765.1719.

4-Methyl carbonyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3i)

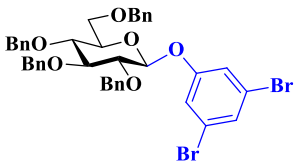


Following **GP-4**, **3i** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **4-Methoxyphenol** (0.15 mmol, 15 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (49 mg, 71%, α:β = 1:2.4). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.26 (m, 26H), 7.20 – 7.17 (m, 2H), 7.14 – 7.04 (m, 4H), 5.47 (d, *J* = 3.5 Hz, 0.42H, H1-α), 5.07 (d, *J* = 7.5 Hz, 1.26H), 5.02 (d, *J* = 12.1 Hz, 1H), 4.97 (d, *J* = 7.5 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.86 (dd, *J* = 12.2, 5.4 Hz, 3H), 4.81 (d, *J* = 3.1 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 0.5H), 4.59 – 4.49 (m, 4H), 4.39 (d, *J* = 12.0 Hz, 0.47H), 3.90 (s, 3H), 3.90 (s, 1.1H), 3.81 – 3.74 (m, 4H), 3.73 – 3.62 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 160.7, 138.3, 137.9, 137.8, 131.5, 131.4, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 124.3, 116.1, 100.8 (C1-β), 95.2 (C1-α), 84.5, 81.8, 79.5, 77.5, 75.8, 75.2, 75.1, 75.0, 73.4, 71.0, 68.6, 51.9.

3,5-Dibromophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3j)



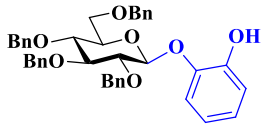
Following **GP-4**, **3j** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **3,5-dibromophenol** (0.15 mmol, 38 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (64 mg, 83%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 1.6 Hz, 1H), 7.33 – 7.27 (m, 18H), 7.18 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.13 (d, *J* = 1.6 Hz, 2H), 4.96 – 4.91 (m, 3H, 2 X OCH_2Ph, H1-β), 4.85 – 4.80 (m, 3H), 4.60 – 4.51 (m, 3H), 3.76 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.73 – 3.70 (m, 2H), 3.67 (dd, *J* = 10.9, 4.9 Hz, 2H), 3.63 – 3.59 (m, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.2, 138.3, 137.9, 137.8, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 123.0, 119.2, 101.4 (C1-β), 84.5, 81.7, 77.3, 75.7, 75.2, 75.1, 75.0, 73.5, 68.5.

HRMS (ESI-TOF): calculated for $C_{40}H_{38}Br_2O_6$ $[M+Na]^+$ 797.0911 found 797.0905.

2-Hydroxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3k)



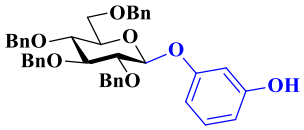
Following **GP-4**, **3k** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-glucopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **catechol** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 15 mol%) as a white solid (44 mg, 70%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 18H), 7.16 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.08 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.97 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.78 – 6.74 (m, 1H), 4.98 (dd, *J* = 7.3, 3.7 Hz, 2H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.86 (dd, *J* = 11.3, 5.6 Hz, 2H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.52 (dd, *J* = 17.4, 11.4 Hz, 2H), 4.21 – 4.14 (m, 2H), 3.83 – 3.66 (m, 4H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.5, 145.1, 138.4, 138.0, 137.7, 136.9, 128.6, 128.4, 128.2, 127.9, 127.8, 127.7, 125.2, 120.3, 119.9, 115.7, 101.1, 81.9, 78.8, 77.4, 77.2, 75.7, 75.0, 74.2, 73.5, 71.4, 68.2.

HRMS (ESI-TOF): calculated for $C_{40}H_{40}O_7$ $[M+Na]^+$ 655.2666 found 655.2642.

3-Hydroxyphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3l)



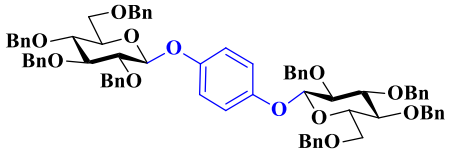
Following **GP-4**, **3l** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **rescorcinol** (0.075 mmol, 8 mg), **catalyst** (1.25 mg, 15 mol%) as a white solid (44 mg, 70%, α:β = 1:4). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 23H), 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 1H), 6.67 – 6.62 (m, 1H), 6.59 (t, *J* = 2.3 Hz, 1H), 6.52 (m, 1H), 5.42 (d, *J* = 3.5 Hz, 0.24H, H1-α), 5.05 – 5.01 (m, 1H), 4.99 – 4.92 (m, 2H), 4.89 – 4.76 (m, 4H), 4.67 (d, *J* = 12.0 Hz, 0.3H), 4.61 – 4.53 (m, 3H), 4.48 (d, *J* = 10.7 Hz, 0.25H), 4.40 (d, *J* = 12.0 Hz, 0.35H), 4.18 (t, *J* = 9.3 Hz, 0.25H), 3.84 – 3.72 (m, 4H), 3.70 – 3.60 (m, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 157.9, 156.8, 138.7, 138.4, 138.1, 137.9, 130.2, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 109.7, 109.4, 109.2, 104.3, 104.1, 101.6 (C1-β), 95.4 (C1-α), 84.6, 81.9, 79.6, 77.7, 75.8, 75.1, 75.0, 74.9, 73.5, 73.4, 73.2, 70.7, 69.1.

HRMS (ESI-TOF): calculated for $C_{40}H_{40}O_7$ $[M+Na]^+$ 655.2666 found 655.2692.

1,4-Bis(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyloxy)benzene (3m)

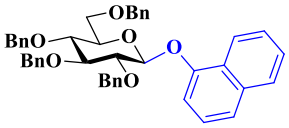


Following **GP-4**, **3m** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **hydroquinone** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (76 mg, 69%, β only). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 18H), 7.20 – 7.16 (m, 2H), 7.00 (s, 2H), 5.04 (d, *J* = 10.9 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 7.5 Hz, 1H, H1-β), 4.83 (t, *J* = 10.2 Hz, 3H), 4.56 (m, 4H), 3.79 – 3.67 (m, 5H), 3.58 (d, *J* = 3.2 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.9, 138.5, 138.2, 138.0, 137.9, 128.4, 128.3, 127.7, 118.0, 102.4 (C1-β), 84.6, 81.9, 77.6, 75.7, 75.0, 75.0, 73.5, 68.7.

1-Naphthyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3n)

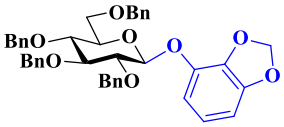


Following **GP-4**, **3n** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **1-Naphthol** (0.15 mmol, 22 mg), **catalyst** (1.6 mg, 10 mol%) as a white solid (51 mg, 77%, α:β = 1:5). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.83 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.39 – 7.27 (m, 21H), 7.21 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.15 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.65 (d, *J* = 3.5 Hz, 0.16H, H1-α), 5.24 (d, *J* = 7.7 Hz, 1H, H1-β), 5.18 (d, *J* = 10.7 Hz, 1H), 5.14 (d, *J* = 10.7 Hz, 0.18H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.95 (d, *J* = 10.6 Hz, 1H), 4.88 (dd, *J* = 10.9, 3.5 Hz, 2H), 4.78 (d, *J* = 11.9 Hz, 0.19H), 4.68 (d, *J* = 12.0 Hz, 0.18H), 4.63 – 4.51 (m, 3H), 4.44 (d, *J* = 12.0 Hz, 0.15H), 4.36 (t, *J* = 9.3 Hz, 0.13H), 3.97 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.86 – 3.62 (m, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.9, 138.4, 138.0, 137.9, 134.5, 128.4, 128.4, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.5, 126.3, 125.8, 125.5, 122.3, 122.0, 109.4, 101.4 (C1-β), 96.2 (C1-α), 84.8, 82.2, 82.0, 80.0, 77.7, 75.8, 75.4, 75.2, 75.0, 73.5, 72.9, 70.9, 68.7, 68.2.

3,4-Methylenedioxyphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3o)



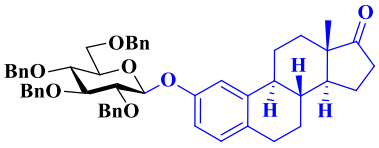
Following **GP-4**, **3o** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **sesamol** (0.15 mmol, 21 mg), **catalyst** (1.6 mg, 10 mol%) as a colorless sticky liquid (47 mg, 72%, α:β = 1:3). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 26H), 7.21 – 7.13 (m, 3H), 6.71 – 6.66 (m, 2.6H), 6.59 – 6.54 (m, 1.4H), 5.95 (s, 2H), 5.93 (s, 0.65H), 5.33 (d, *J* = 3.5 Hz, 0.3H, H1-α), 5.04 (dd, *J* = 10.8, 7.0 Hz, 1.4H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 0.4H), 4.86 (d, *J* = 6.0 Hz, 1H, H1-β), 4.84 (d, *J* = 2.9 Hz, 2.5H), 4.83 – 4.79 (m, 1.5H), 4.69 (d, *J* = 11.9 Hz, 0.4H), 4.63 – 4.52 (m, 4H), 4.50 (d, *J* = 10.7 Hz, 0.3H), 4.43 (d, *J* = 12.0 Hz, 0.3H), 3.80 – 3.75 (m, 1H), 3.75 – 3.65 (m, 5H), 3.63 – 3.54 (m, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.7, 148.0, 143.1, 138.4, 138.2, 138.1, 137.9, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 109.4, 109.2, 108.0, 107.9, 102.8, 101.3, 101.2, 100.4, 100.1 (C1-β), 96.6 (C1-α), 84.6, 81.9, 79.6, 77.6, 77.4, 77.3, 77.2, 75.7, 75.1, 75.0, 73.5, 73.4, 73.3, 70.7, 68.7.

HRMS (ESI-TOF): calculated for $C_{36}H_{38}O_7$ $[M+Na]^+$ 605.2510 found 605.2519.

Estryl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3p)



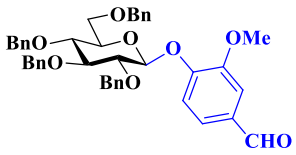
Following **GP-4**, **3p** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **estrone** (0.15 mmol, 40 mg), **catalyst** (1.6 mg, 10 mol%) as a colorless sticky liquid (51 mg, 67%, α:β = 1:10). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 19H), 7.20 (td, *J* = 7.0, 1.4 Hz, 3H), 6.90 (s, 1H), 6.81 (d, *J* = 2.6 Hz, 2H), 5.49 (d, *J* = 3.5 Hz, 0.1H (H1-α), 5.09 – 5.00 (m, 1H), 5.01 – 4.91 (m, 2H), 4.90 – 4.76 (m, 3H), 4.69 (d, *J* = 12.0 Hz, 0.13H), 4.66 – 4.49 (m, 3H), 4.48 (d, *J* = 10.6 Hz, 0.14H), 4.41 (d, *J* = 12.0 Hz, 0.11H), 4.20 (t, *J* = 9.3 Hz, 0.07H), 3.88 (d, *J* = 8.1 Hz, 0.22H), 3.81 – 3.59 (m, 6H), 2.90 – 2.78 (m, 2H), 2.55 – 2.47 (m, 1H), 2.43 – 2.37 (m, 1H), 2.27 (d, *J* = 4.5 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.09 – 1.94 (m, 4H), 1.69 – 1.40 (m, 10H), 1.31 – 1.23 (m, 2H), 0.92 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 221.0, 155.3, 138.4, 138.2, 138.1, 137.7, 137.8, 134.0, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 126.4, 116.9, 114.5, 101.8 (C1-β), 95.2 (C1-α), 84.6, 81.9, 77.6, 75.7, 75.0, 74.9, 73.4, 68.8, 50.4, 47.9, 44.0, 38.2, 35.8, 31.5, 29.5, 26.5, 25.8, 21.5, 13.8.

HRMS (ESI-TOF): calculated for $C_{52}H_{56}O_7$ $[M+Na]^+$ 815.3918 found 815.3905.

2-methoxy-4-formylphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3q)



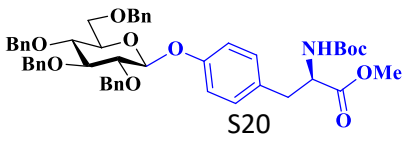
Following **GP-4**, **3q** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **2-methoxy-4-formylphenol** (0.075 mmol, 12 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (18 mg, 53%, α:β = 1:10). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (100 MHz, $CDCl_3$) δ 9.88 (s, 1H), 9.87 (s, 0.12H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.38 – 7.27 (m, 25H), 7.24 – 7.18 (m, 3H), 5.56 (d, *J* = 3.5 Hz, 0.10H), 5.19 (d, *J* = 10.7 Hz, 1H), 5.16 (d, *J* = 3.5 Hz, 0.12H), 5.11 (d, *J* = 11.4 Hz, 0.14H), 5.05 (d, *J* = 7.6 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.91 (dd, *J* = 10.9, 4.1 Hz, 0.3H), 4.85 (dd, *J* = 10.5, 2.6 Hz, 3H), 4.82 (s, 1H), 4.79 (d, *J* = 4.8 Hz, 0.2H), 4.77 (d, *J* = 2.6 Hz, 0.12H), 4.68 – 4.65 (m, 0.41H), 4.60 – 4.51 (m, 3H), 4.48 (d, *J* = 10.8 Hz, 0.5H), 4.45 (d, *J* = 6.8 Hz, 0.2H), 4.41 – 4.38 (m, 0.2H), 4.30 – 4.26 (m, 0.2H), 3.90 (s, 3.3H), 3.84 – 3.78 (m, 2H), 3.75 (td, *J* = 8.3, 3.0 Hz, 1H), 3.71 – 3.58 (m, 4H), 3.53 – 3.49 (m, 0.3H).

^{13}C NMR (125 MHz, **$CDCl_3$**) δ 191.1, 152.1, 150.2, 138.4, 138.2, 137.9, 137.8, 131.5, 128.4, 128.30, 127.9, 127.8, 127.7, 127.6, 127.5, 126.3, 115.5, 109.6, 101.7, 84.3, 81.4, 77.5, 77.2, 75.8, 75.3, 75.1, 74.8, 73.5, 68.7, 55.8.

HRMS (ESI-TOF): calculated for $C_{42}H_{42}O_8$ $[M+Na]^+$ 697.2772 found 697.2790.

2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (3r)



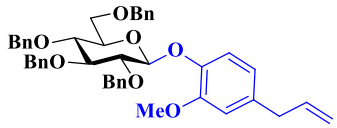
Following **GP-4**, **3r** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-trichloroacetimidate** (0.1 mmol, 69 mg), **Boc-Tyr-OMe** (0.15 mmol, 44 mg), **catalyst** (2.5 mg, 15 mol%) as a colorless sticky liquid (59 mg, 74%, α:β = 1:10). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 20H), 7.19 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.06 – 6.99 (m, 4H), 5.44 (d, *J* = 3.4 Hz, 0.10H, H1-α), 5.04 (d, *J* = 10.9 Hz, 1H), 4.99 – 4.94 (m, 3H, 2 X OCH_2Ph, H1-β), 4.87 – 4.81 (m, 3H), 4.61 – 4.52 (m, 4H), 3.79 (dd, *J* = 10.7, 1.6 Hz, 1H), 3.76 – 3.72 (m, 3H), 3.71 (s, 3H), 3.63 – 3.55 (m, 1H), 3.09 – 3.01 (m, 2H), 1.43 (s, 10H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.4, 156.5, 155.1, 138.4, 138.1, 138.0, 137.9, 130.3, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 116.9, 101.7 (C1-β), 84.6, 81.9, 79.9, 77.6, 75.7, 75.1, 75.0, 73.4, 68.7, 54.4, 52.2, 37.5, 28.3.

HRMS (ESI-TOF): calculated for $C_{49}H_{55}NO_{10}$ $[M+Na]^+$ 840.3718 found 840.3680.

4-A llyl-2-methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (3s)



Following **GP-4**, **3s** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-glucopyranosyl trichloroacetimidate** (0.06 mmol, 40 mg), **4-allyl-2-methoxyphenol** (0.09 mmol, 14 mg), **catalyst** (1.0 mg, 10 mol%) as a colorless sticky liquid (28 mg, 67%, α:β = 1:4). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

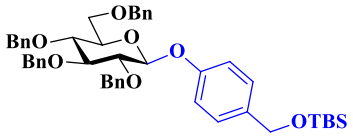
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 23H), 7.20 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.15 (dd, *J* = 14.5, 8.0 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 0.2H), 6.78 – 6.70 (m, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.01 – 5.93 (m, 1H), 5.53 (d, *J* = 3.6 Hz, 0.2H, H1-α), 5.27 (d, *J* = 10.8 Hz, 1H), 5.16 – 5.03 (m, 2H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.98 – 4.86 (m, 1H), 4.90 – 4.77 (m, 4H), 4.71 (d, *J* = 11.8 Hz, 0.17H), 4.65 – 4.51 (m, 3H), 4.49 (dd, *J* = 14.8, 11.4 Hz, 0.5H), 4.42 (d, *J* = 12.0 Hz, 0.2H), 4.26 (t, *J* = 9.4 Hz, 0.2H), 4.18 – 4.15 (m, 0.2H), 3.98 (d, *J* = 9.4 Hz, 0.12H), 3.99 (t, *J* =

9.4 Hz, 0.12H), 3.96 – 3.93 (m, 0.15H), 3.82 (s, 0.71H), 3.80 (s, 3H), 3.79 – 3.70 (m, 4H), 3.69 – 3.56 (m, 2H), 3.38 – 3.33 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 150.8, 149.9, 145.2, 143.8, 138.6, 138.6, 138.2, 138.0, 137.5, 135.2, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 120.6, 120.5, 120.1, 117.8, 115.7, 112.8, 112.4, 102.9, 97.1, 84.5, 81.8, 81.7, 81.4, 79.6, 79.3, 79.1, 77.7, 77.2, 76.7, 75.7, 75.1, 75.0, 74.6, 73.4, 72.7, 71.0, 68.9, 68.3, 67.7, 55.7, 39.9.

HRMS (ESI-TOF): calculated for $C_{44}H_{46}O_7$ $[M+Na]^+$ 709.3136 found 709.3125.

4-(((tert-butyldimethylsilyl)oxy)methyl)phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (3t)



Following **GP-4**, **3t** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **4-(((tert-butyldimethylsilyl)oxy)methyl)phenol** (0.075 mmol, 18 mg), **catalyst** (1.25 mg, 10 mol%) as a colorless sticky liquid (26 mg, 68%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 18H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.19 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.05 (d, *J* = 10.9 Hz, 1H), 4.99 (d, *J* = 7.5 Hz, 1H, H1-β), 4.95 (d, *J* = 10.9 Hz, 1H), 4.83 (t, *J* = 11.8 Hz, 3H), 4.69 (s, 2H), 4.62 – 4.50 (m, 3H), 3.81 – 3.58 (m, 6H), 1.56 (s, 6H), 0.94 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4, 138.4, 138.2, 138.1, 137.9, 135.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 116.6, 101.8 (C1-β), 84.6, 81.9, 77.6, 75.7, 75.0, 75.0, 73.4, 68.7, 64.6, 25.9, -5.2.

HRMS (ESI-TOF): calculated for $C_{47}H_{56}SiO_7$ $[M+Na]^+$ 783.3688 found 783.3658.

2-Methylphenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (4a)

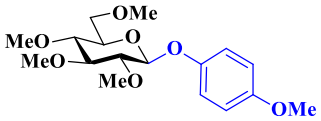
Following **GP-4**, **4a** was prepared from **2,3,4,6-tetra-*O*-methyl–α–D-glucopyranosyl trichloroacetimidate** (0.1 mmol, 40 mg), **2-methylphenol** (0.15 mmol, 16 mg), **catalyst** (1.6 mg, 10 mol%) as colorless sticky liquid (26 mg, 78%, β only). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 6.99 – 6.90 (m, 2H), 4.81 (d, *J* = 7.5 Hz, 1H, H1-β), 3.67 (s, 3H), 3.67 (s, 3H), 3.65 (d, *J* = 2.0 Hz, 1H), 3.62 – 3.57 (m, 1H), 3.56 (s, 3H), 3.42 – 3.40 (m, 1H), 3.39 (s, 3H), 3.34 – 3.30 (m, 1H), 3.27 (d, *J* = 1.6 Hz, 1H), 3.26 (d, *J* = 4.6 Hz, 1H), 2.27 (s, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.6, 130.8, 127.5, 126.8, 122.2, 114.6, 101.1 (C1-β), 86.6, 83.6, 79.2, 74.7, 71.1, 60.9, 60.8, 60.4, 59.4, 16.5.

HRMS (ESI-TOF): calculated for $C_{17}H_{26}O_6$ $[M+Na]^+$ 349.1622 found 349.1661.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (4b)



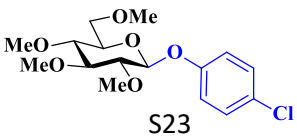
Following **GP-4**, **4b** was prepared from **2,3,4,6-tetra-*O*-methyl–α–D-trichloroacetimidate** (0.1 mmol, 40 mg), **4-methoxyphenol** (0.15 mmol, 20 mg), **catalyst** (1.6 mg, 10 mol%) as white solid (25 mg, 73%, β only). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 9.1 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 4.71 (d, *J* = 7.3 Hz, 1H, H1-β), 3.77 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.64 (d, *J* = 2.0 Hz, 1H), 3.60 – 3.56 (m, 1H), 3.55 (s, 3H), 3.39 (s, 3H), 3.38 – 3.33 (m, 1H), 3.28 – 3.21 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.2, 151.5, 118.3, 102.5, 86.3, 83.5, 79.1, 74.7, 71.2, 60.8, 60.56, 60.4, 59.4, 55.6.

HRMS (ESI-TOF): calculated for $C_{17}H_{26}O_7$ $[M+Na]^+$ 365.1571 found 365.1602.

4-Chlorophenyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside (4c)



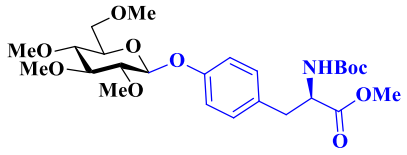
Following **GP-4**, **4c** was prepared from **2,3,4,6-tetra-*O*-methyl–α–D-glucopyranosyl trichloroacetimidate** (0.1 mmol, 40 mg), **4-chlorophenol** (0.15 mmol, 19 mg), **catalyst** (1.6 mg, 10 mol%) as colorless sticky liquid (23 mg, 68%, β only). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.77 (d, *J* = 7.2 Hz, 1H, H1-β), 3.66 (d, *J* = 2.1 Hz, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 3.59 – 3.56 (m, 1H), 3.55 (s, 3H), 3.40 (dd, *J* = 4.8, 2.2 Hz, 1H), 3.38 (s, 3H), 3.29 – 3.21 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 129.3, 127.5, 118.1, 101.5 (C1-β), 86.3, 83.4, 79.0, 74.8, 71.1, 60.9, 60.6, 60.5, 59.4.

HRMS (ESI-TOF): calculated for $C_{16}H_{23}ClO_6$ $[M+Na]^+$ 369.1075 found 369.1086.

2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (4d)



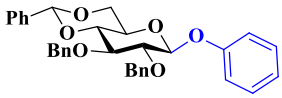
Following **GP-4**, **4d** was prepared from **2,3,4,6-tetra-*O*-methyl–α–D-glucopyranosyl t** (0.1 mmol, 40 mg), **Boc-Tyr-OMe** (0.15 mmol, 44 mg), **catalyst** (1.6 mg, 10 mol%) as colorless sticky liquid (35 mg, 69%, β only). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.94 (d, *J* = 8.2 Hz, 1H), 4.80 (d, *J* = 7.2 Hz, 1H, H1-β), 4.57 – 4.50 (m, 1H), 3.70 (s, 3H), 3.67 – 3.65 (m, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 3.58 – 3.56 (m, 1H), 3.55 (s, 3H), 3.41 – 3.38 (m, 1H), 3.38 (s, 3H), 3.27 – 3.22 (m, 3H), 3.07 – 2.97 (m, 2H), 1.41 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 156.4, 155.1, 130.4, 130.3, 129.8, 129.0, 127.4, 116.7, 115.4, 101.3 (C1-β), 86.3, 83.4, 79.9, 79.0, 74.7, 71.1, 60.9, 60.5, 60.4, 59.3, 54.4, 52.2, 37.4, 28.3.

HRMS (ESI-TOF): calculated for $C_{25}H_{39}NO_{10}$ $[M+Na]^+$ 536.2466 found 536.2455.

Phenyl 2,3,di-*O*-benzyl-4,6-di-O-benzylidene-β-D-glucopyranoside (5a)

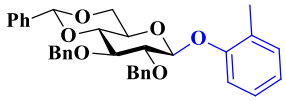


Following **GP-4**, **5a** was prepared from **2,3-di-*O*-benzyl–4,6–*O*-benzylidene-α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **phenol** (0.075 mmol, 7 mg), **catalyst** (0.9 mg, 10 mol%) as white solid (19 mg, 71%, β only) with minor impurity of the byproduct. R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.40 – 7.27 (m, 15H), 7.09 (t, *J* = 8.7 Hz, 3H), 5.62 (s, 1H), 5.16 (d, *J* = 7.4 Hz, 1H, H1-β), 5.00 (d, *J* = 10.9 Hz, 1H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.80 (dd, *J* = 20.7, 9.2 Hz, 2H), 4.44 – 4.35 (m, 1H), 3.90 – 3.76 (m, 5H), 3.58 (dd, *J* = 9.5, 4.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.0, 138.3, 138.0, 137.2, 129.6, 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 125.9, 123.0, 116.8, 101.9 (C1-β), 101.2, 81.7, 81.2, 80.8, 75.5, 75.2, 68.7, 66.2.

2-Methylphenyl 2,3,di-*O*-benzyl-4,6-di-*O*-benzylidene-β-D-glucopyranoside (5b)



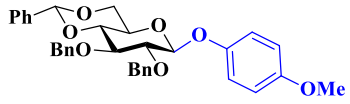
Following **GP-4**, **5b** was prepared from **2,3-di-*O*-benzyl–4,6–*O*-benzylidene-α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **2-Methylphenol** (0.075 mmol, 8 mg), **catalyst** (0.9 mg, 10 mol%) as white solid (20 mg, 74%, β only) with minor impurity of the byproduct. R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.38 – 7.28 (m, 13H), 7.18 (t, *J* = 7.0 Hz, 2H), 7.00 (dd, *J* = 16.0, 8.1 Hz, 2H), 5.62 (s, 1H), 5.17 (d, *J* = 7.5 Hz, 1H, H1-β), 5.01 (d, *J* = 10.8 Hz, 1H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 11.3 Hz, 1H), 4.81 – 4.75 (m, 1H), 4.40 (dd, *J* = 10.6, 5.1 Hz, 1H), 3.92 – 3.83 (m, 3H), 3.61 – 3.54 (m, 1H), 2.31 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.1, 138.4, 138.0, 137.2, 131.0, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 126.9, 125.9, 122.6, 114.7, 101.5 (C1-β), 101.2, 81.9, 81.3, 81.0, 75.6, 75.2, 68.7, 66.1, 16.5.

HRMS (ESI-TOF): calculated for $C_{34}H_{34}O_6$ $[M+Na]^+$ 561.2248 found 561.2271.

4-Methoxyphenyl 2,3,di-*O*-benzyl-4,6-di-*O*-benzylidene-β-D-glucopyranoside (5c)



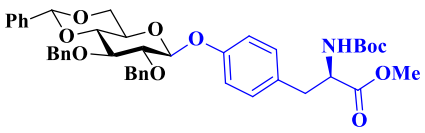
Following **GP-4**, **5c** was prepared from **2,3-di-*O*-benzyl–4,6–*O*-benzylidene-α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-methoxyphenol** (0.075 mmol, 9 mg), **catalyst** (0.9 mg, 10 mol%) as white solid (21 mg, 75%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.41 – 7.29 (m, 14H), 7.02 (d, *J* = 9.1 Hz, 2H), 6.85 (d, *J* = 9.1 Hz, 2H), 5.61 (s, 1H), 5.04 – 4.93 (m, 3H, H1-β), 4.86 (dd, *J* = 14.4, 11.1 Hz, 2H), 4.39 (dd, *J* = 10.5, 5.0 Hz, 1H, H6), 3.87 – 3.81 (m, 2H - H3, H4), 3.79 (s, 3H), 3.79 – 3.71 (m, 2H, H2), 3.54 – 3.48 (m, H5).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 155.5, 151.1, 138.4, 138.1, 137.2, 128.9, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 125.9, 118.5, 114.6, 103.2 (C1-β), 101.1, 81.8, 81.2, 80.8, 75.5, 75.2, 68.7, 66.1, 55.6.

HRMS (ESI-TOF): calculated for $C_{34}H_{34}O_7$ $[M+Na]^+$ 577.2197 found 577.2159.

2,3-di-*O*-benzyl-4,6-benzylidene-β-D-glucopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (5d)



Following **GP-4**, **5d** was prepared from **2,3-di-*O*-benzyl–4,6–*O*-benzylidene-α–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **Boc-Tyr-OMe** (0.075 mmol, 22

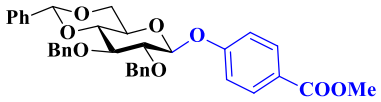
mg), **catalyst** (0.9 mg, 10 mol%) as white solid (26 mg, 74%, β only). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.40 – 7.28 (m, 13H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 5.60 (s, 1H), 5.11 (d, *J* = 7.5 Hz, 1H, H1-β), 4.95 (dd, *J* = 11.1, 6.9 Hz, 3H), 4.84 (t, *J* = 10.8 Hz, 2H), 4.56 (dd, *J* = 13.7, 5.9 Hz, 1H), 4.39 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.87 – 3.74 (m, 4H), 3.72 (s, 3H), 3.57 – 3.51 (m, 1H), 3.11 – 2.99 (m, 2H), 1.42 (s, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.3, 156.1, 138.3, 138.0, 137.2, 130.5, 130.4, 128.9, 128.3, 128.2, 128.0, 127.8, 127.6, 125.9, 116.9, 101.9 (C1-β), 101.2, 81.7, 81.2, 80.8, 79.9, 75.5, 75.2, 68.6, 66.2, 54.4, 52.2, 37.5, 28.3.

HRMS (ESI-TOF): calculated for $C_{42}H_{47}O_{10}N$ $[M+Na]^+$ 748.3092 found 748.3069.

4-Methyl carbonyl Phenyl 2,3,di-*O*-benzyl-4,6-di-O-benzylidene-β-D-glucopyranoside (5e)



Following **GP-4**, **5e** was prepared from **2,3-di-*O*-benzyl–4,6–*O*-benzylidene-α–D-glucopyranosyl trichloroacetimidate** (0.045 mmol, 27 mg), **methyl 4-hydroxybenzoate** (0.068 mmol, 22 mg), **catalyst** (0.9 mg, 10 mol%) as white solid (18 mg, 67%, β only). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.50 (td, *J* = 5.3, 3.0 Hz, 3H), 7.38 (m, 5H), 7.33 – 7.28 (m, 8H), 7.07 – 7.03 (m, 2H), 5.60 (s, 1H), 5.21 (d, *J* = 7.4 Hz, 1H, H1-β), 4.98 – 4.91 (m, 2H), 4.85 (dd, *J* = 13.0, 11.2 Hz, 2H), 4.40 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.90 (s, 3H), 3.89 – 3.75 (m, 4H), 3.62 – 3.56 (m, 1H).

^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 166.5, 160.4, 138.3, 137.8, 137.1, 133.4, 131.6, 129.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 125.9, 124.7, 116.0, 115.8, 115.5, 101.2 (C1-β), 101.1, 81.5, 81.1, 80.7, 75.6, 75.2, 68.6, 66.3, 52.0.

HRMS (ESI-TOF): calculated for $C_{35}H_{34}O_8$ $[M+Na]^+$ 605.2146 found 605.2174.

2-Methylphenyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α/β-D-glucopyranoside (6a)

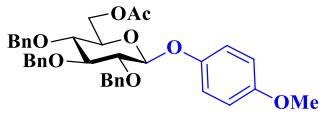
Following **GP-4**, **6a** was prepared from **2,3,4-tri-*O*-benzyl–6–*O*–acetyl-α/β–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **2-methylphenol** (0.07 mmol, 7.6 mg), **catalyst** (1.1 mg, 10 mol%) as colorless sticky liquid (21 mg, 79%, α/β = 1:6). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 19H), 7.20 – 7.10 (m, 2H), 7.03 – 6.92 (m, 2H), 5.45 (d, *J* = 3.4 Hz, 0.16H, H1-α), 5.08 (d, *J* = 10.7 Hz, 1H), 5.02 (d, *J* = 7.7 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.95 – 4.80 (m, 4H), 4.78 (d, *J* = 10.8 Hz, 0.13H), 4.74 (d, *J* = 11.8 Hz, 0.27H), 4.72 – 4.62 (m, 0.27H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.33 (dd, *J* = 11.8, 2.2 Hz, 1H), 4.28 (s, 0.16H), 4.24 (dd, *J* = 11.8, 5.8 Hz, 1H), 3.83 – 3.75 (m, 2H), 3.75 – 3.62 (m, 1H), 3.67 – 3.56 (m, 1H), 2.32 (s, 0.6H), 2.29 (s, 3H), 2. 02 (s, 3H), 1.99 (s, 0.6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.7, 155.3, 138.3, 138.0, 137.5, 130.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 126.8, 122.5, 114.7, 101.1 (C1-β), 95.84 (C1-α), 84.7, 81.9, 81.8, 77.4, 76.7, 75.8, 75.1, 75.0, 72.9, 63.1, 62.8, 20.8, 16.6.

HRMS (ESI-TOF): calculated for $C_{36}H_{38}O_7$ $[M+Na]^+$ 605.2510 found 605.2511.

4-Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α/β-D-glucopyranoside (6b)



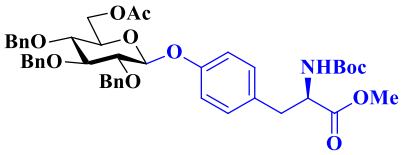
Following **GP-4**, **6b** was prepared from **2,3,4-tri-*O*-benzyl–6–*O*–acetyl-α/β–D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-Methoxyphenol** (0.07 mmol, 7.6 mg), **catalyst** (1.1 mg, 10 mol%) as colorless sticky liquid (21 mg, 77%, α/β = 1:3). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 19H), 7.00 (dd, *J* = 9.2, 2.6 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 5.32 (d, *J* = 3.5 Hz, 0.32H, H1-α), 5.07 (dd, *J* = 10.8, 6.9 Hz, 1.3H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.92 – 4.86 (m, 3H, H1-β), 4.83 (d, *J* = 10.9 Hz, 2H), 4.59 (d, *J* = 10.9 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.78 (s, 3H), 3.78 (s, 0.46H), 3.75 – 3.68 (m, 2H), 3.60 (dd, *J* = 11.4, 6.8 Hz, 2H), 2.04 (s, 1H), 1.98 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.7, 155.4, 138.3, 138.1, 137.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 118.4, 118.2, 114.5, 102.7 (C1-β), 84.6, 81.9, 75.1, 72.9, 63.1, 55.6, 20.8.

HRMS (ESI-TOF): calculated for $C_{36}H_{38}O_8$ $[M+Na]^+$ 621.2459 found 621.2496.

2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α/β-D-glucopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (6c)



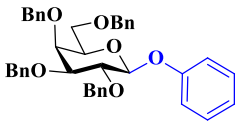
Following **GP-3**, **6c** was prepared from **2,3,4-tetra-*O*-methyl–6–*O*–acetyl-α/β–D-glucopyranosyl trichloroacetimidate** (0.04 mmol, 24 mg), **Boc-Tyr-OMe** (0.05 mmol, 17 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (17 mg, 75%, α/β = 1:5.2). R_f = 0.3 (ethyl acetate/hexane 1:3 (v/v)).

^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 17H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.08 – 6.94 (m, 5H), 5.37 (d, *J* = 3.6 Hz, 0.16H, H1-α), 5.03 (d, *J* = 10.9 Hz, 1H), 5.00 – 4.94 (m, 3H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.82 (dd, *J* = 10.9, 4.4 Hz, 2H), 4.57 (dd, *J* = 12.8, 9.8 Hz, 2H), 4.33 (dd, *J* = 11.8, 1.9 Hz, 1H), 4.24 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.74 (t, *J* = 5.7 Hz, 2H), 3.71 (s, 3H), 3.67 – 3.58 (m, 2H), 3.09 – 2.98 (m, 2.39H), 2.03 (s, 3H), 1.98 (s, 0.57H), 1.41 (s, 10.7H).

^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.0, 138.35, 137.6, 130.3, 128.5, 128.4, 128.2, 128.1, 127.8, 116.9, 101.6, 84.5, 81.8, 75.7, 75.0, 75.0, 73.0, 63.9, 63.1, 61.4, 52.2, 28.3.

HRMS (ESI-TOF): calculated for $C_{44}H_{51}O_{11}N$ $[M+Na]^+$ 792.3354 found 792.3317.

Phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (7a)

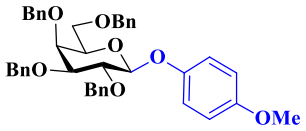


Following **GP-4**, **7a** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **phenol** (0.15 mmol, 19 mg), **catalyst** (0.9 mg, 5 mol%) as white solid (48 mg, 78%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 21H), 7.26 – 7.22 (m, 1H), 7.10 – 7.06 (m, 2H), 7.05 – 7.01 (m, 1H), 5.04 – 4.98 (m, 3H, H1-β, 2XOCH_2Ph), 4.87 (d, *J* = 10.9 Hz, 1H), 4.78 (q, *J* = 11.8 Hz, 2H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.48 – 4.40 (m, 2H), 4.13 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.96 (d, *J* = 2.7 Hz, 1H), 3.72 – 3.67 (m, 1H), 3.66 – 3.60 (m, 3H).

^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 157.4, 138.5, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 122.4, 116.9, 101.9, 82.0, 79.2, 75.4, 74.5, 73.8, 73.6, 73.3, 73.1, 68.8.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside (7b)



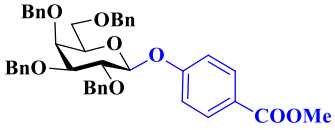
Following **GP-4**, **7b** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **4-methoxyphenol** (0.15 mmol, 19 mg), **catalyst** (0.9 mg, 5 mol%) as white solid (46 mg, 73%, α:β = 1:9). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 22H), 7.03 (d, *J* = 9.1 Hz, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 5.39 (d, *J* = 3.3 Hz, 0.11H, H1-α), 5.01 (dd, *J* = 13.5, 11.3 Hz, 2H), 4.87 – 4.85 (m, 2H, OCH_2Ph, H1-β), 4.80 – 4.74 (m, 2H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.47 – 4.39 (m, 2H), 4.17 (dd, *J* = 7.9, 3.0 Hz, 0.33H), 4.09 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.94 (d, *J* = 2.8 Hz, 1H), 3.77 (s, 3.5H), 3.66 – 3.58 (m, 4H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.1, 151.6, 138.5, 138.4, 137.8, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 118.6, 118.4, 114.4, 103.1 (C1-β), 82.1, 79.3, 75.4, 74.5, 73.7, 73.5, 73.3, 73.1, 68.8, 55.6.

HRMS (ESI-TOF): calculated for $C_{41}H_{42}O_7$ $[M+Na]^+$ 669.2823 found 669.2849.

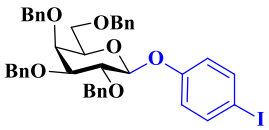
4-Methyl carbonyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (7c)



Following **GP-4**, **7c** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **Methyl 4-hydroxybenzoate** (0.15 mmol, 23 mg), **catalyst** (0.9 mg, 5 mol%) as white solid (49 mg, 74%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.27 (m, 20H), 7.06 (d, *J* = 8.9 Hz, 2H), 5.06 (d, *J* = 7.7 Hz, 1H, H1-β), 4.97 (dd, *J* = 11.2, 8.2 Hz, 2H), 4.87 (d, *J* = 10.8 Hz, 1H), 4.81 – 4.74 (m, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.43 (q, *J* = 11.6 Hz, 2H), 4.14 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.96 (d, *J* = 2.6 Hz, 1H), 3.90 (s, 3H), 3.72 (t, *J* = 6.3 Hz, 1H), 3.67 – 3.55 (m, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 166.7, 160.9, 138.3, 138.2, 137.7, 131.4, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 124.1, 116.1, 101.0 (C1-β), 81.9, 78.9, 77.3, 74.5, 74.0, 73.6, 73.1, 73.0, 68.8, 51.9.

4-Iodophenyl 2,3,4,6-tetra-*O*-benzyl–β-D-galactopyranoside (7d)



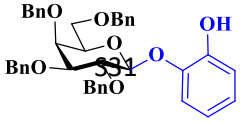
Following **GP-4**, **7d** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **4-Iodophenol** (0.15 mmol, 34 mg), **catalyst** (0.9 mg, 5 mol%) as white solid (51 mg, 82%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.38 – 7.22 (m, 20H), 6.84 – 6.79 (m, 2H), 4.98 – 4.90 (m, 3H, 2 X OCH_2Ph, H1-β), 4.84 (d, *J* = 10.8 Hz, 1H), 4.80 – 4.72 (m, 2H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.41 (q, *J* = 11.6 Hz, 2H), 4.09 (dd, *J* = 9.7, 7.7 Hz, 1H, H2), 3.93 (d, *J* = 2.7 Hz, 1H, H4), 3.68 – 3.54 (m, 4H, H3, H5, H6).

^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 157.3, 138.4, 138.3, 138.2, 137.7, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 119.2, 101.6 (C1-β), 85.0, 82.0 (C3), 79.0 (C2), 75.4, 74.53, 73.9, 73.6, 73.2 (C4), 73.1 (C5), 68.8 (C6).

HRMS (ESI-TOF): calculated for $C_{40}H_{39}IO_6$ $[M+Na]^+$ 765.1684 found 765.1650.

2-Hydroxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (7e)



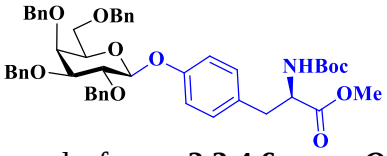
Following **GP-4**, **7f** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **catechol** (0.15 mmol, 16 mg), **catalyst** (0.9 mg, 5 mol%) as colorless sticky liquid (47 mg, 76%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 22H), 7.08 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 5.02 – 4.92 (m, 3H), 4.83 – 4.77 (m, 3H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.57 – 4.45 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 1H), 4.18 – 4.16 (m, 2H), 4.09 (s, 1H), 3.67 – 3.59 (m, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.9, 145.2, 138.4, 138.2, 137.8, 137.2, 128.5, 128.4, 128.3, 128.1, 127.7, 127.5, 125.4, 121.2, 119.8, 115.8, 102.0 (C1-β), 79.2, 75.6, 74.8, 74.5, 74.4, 73.5, 72.6, 70.7, 68.8.

HRMS (ESI-TOF): calculated for $C_{40}H_{40}O_7$ $[M+Na]^+$ 655.2666 found 655.2662.

2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (7f)



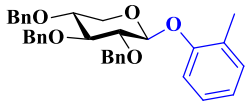
Following **GP-4**, **7e** was prepared from **2,3,4,6-tetra-*O*-benzyl–α–D-galactopyranosyl trichloroacetimidate** (0.1 mmol, 69 mg), **Boc-Tyr-OMe** (0.15 mmol, 23 mg), **catalyst** (0.9 mg, 5 mol%) as colorless sticky liquid (54 mg, 69%, α:β = 1:6.25). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 20H), 7.25 – 7.20 (m, 1H), 7.04 – 6.96 (m, 4H), 5.46 (d, *J* = 3.3 Hz, 0.16H, H1-α), 5.01 – 4.93 (m, 4H, H1), 4.85 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 4.8 Hz, 1H), 4.65 (d, *J* = 11.7 Hz, 1H), 4.55 (dd, *J* = 15.5, 8.0 Hz, 1H), 4.47 – 4.35 (m, 2H), 4.10 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.96 (d, *J* = 2.7 Hz, 1H), 3.71 (s, 0.5H), 3.69 (s, 3H), 3.67 – 3.58 (m, 3H), 3.02 (dd, *J* = 13.1, 6.9 Hz, 2H), 1.42 (s, 10H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 170.0, 156.5, 155.0, 138.3, 137.8, 130.2, 129.8, 128.4, 128.3, 128.2, 127.8, 127.6, 127.5, 117.0, 101.9 (C1-β), 82.0, 79.2, 75.4, 74.5, 73.7, 73.6, 73.3, 73.0, 68.7, 52.2, 28.3.

HRMS (ESI-TOF): calculated for $C_{49}H_{55}NO_{10}$ $[M+Na]^+$ 840.3718 found 840.3707.

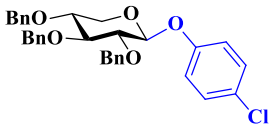
2-Methylphenyl 2,3,4-tri-*O*-benzyl-α/β-D-xylopyranoside (8a)



Following **GP-4**, **8a** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **2-methylphenol** (0.075 mmol, 8.5 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (21 mg, 81%, α:β = 1:12.5). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The NMR data was consistent with the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 16H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.02 – 6.93 (m, 2H), 5.42 (d, *J* = 3.5 Hz, 0.08H, H1-α), 5.03 (dd, *J* = 11.0, 6.9 Hz, 2H, OCH_2Ph, H1-β), 4.91 (s, 2H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.00 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.77 – 3.66 (m, 3H), 3.39 – 3.31 (m, 1H), 2.34 (s, 0.26H), 2.29 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 155.1, 138.5, 138.2, 138.0, 130.9, 128.5, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 126.8, 122.4, 114.6, 101.5 (C1-β), 83.6, 81.6, 77.7, 75.6, 75.2, 73.3, 63.9, 16.5.

4-Chlorophenyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranoside (8b)



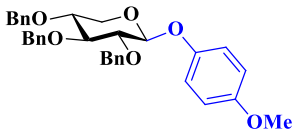
Following **GP-4**, **8b** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-chlorophenol** (0.075 mmol, 10 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (20 mg, 68%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 15H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.96 – 4.91 (m, 2H, OCH_2Ph, H1-β), 4.88 (s, 2H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.64 (d, *J* = 11.6 Hz, 1H), 3.98 (dd, *J* = 11.7, 4.6 Hz, 1H, H5a), 3.71 – 3.62 (m, 3H, H2 – H4), 3.37 – 3.29 (m, 1H, H5b).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 155.7, 138.5, 138.1, 137.9, 129.5, 128.4, 128.1, 118.2, 102.2 (C1-β), 83.4, 81.4, 77.6, 75.6, 75.1, 73.4, 63.9.

HRMS (ESI-TOF): calculated for $C_{32}H_{31}ClO_5$ $[M+Na]^+$ 553.1752 found 553.1766.

4-Methoxyphenyl 2,3,4-tri-*O*-benzyl-α/β-D-xylopyranoside (8c)



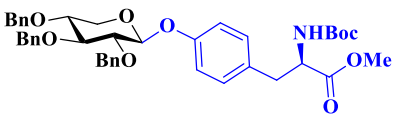
Following **GP-4**, **8c** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-methoxyphenol** (0.075 mmol, 9.8 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (21 mg, 71%, α:β = 1:7.6). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 17H), 7.00 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.27 (d, *J* = 3.6 Hz, 0.14H, H1-α), 5.01 (d, *J* = 10.9 Hz, 1H), 4.96 – 4.86 (m, 3H, 2 x OCH_2Ph, H1-β), 4.82 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 3.99 (dd, *J* = 11.6, 4.8 Hz, 1H, H5a), 3.78 (s, 3.4H), 3.72 – 3.62 (m, 3H, H2-H4), 3.30 (dd, *J* = 11.6, 9.5 Hz, 1H, H5b).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.3, 151.2, 138.6, 138.3, 138.0, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 118.4, 118.2, 114.5, 103.2 (C1-β), 83.6, 81.6, 77.7, 75.6, 75.1, 73.4, 63.9, 55.6.

HRMS (ESI-TOF): calculated for $C_{33}H_{34}O_6$ $[M+Na]^+$ 549.2248 found 549.2232.

2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl-(1→*O*)–N-tert-butoxycarbonyl-L-tyrosine methyl ester (8d)

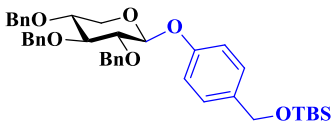


Following **GP-4**, **8d** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **Boc-Tyr-OMe** (0.075 mmol, 22 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (24 mg, 70%, β only). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 16H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.00 – 4.94 (m, 3H, 2 X CH_2Ph, H1-β), 4.89 (s, 2H), 4.78 (dd, *J* = 20.2, 11.3 Hz, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.56 (dd, *J* = 12.8, 5.8 Hz, 1H), 3.99 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.72 (s, 3H), 3.68 (dd, *J* = 10.9, 6.1 Hz, 3H), 3.38 – 3.30 (m, 1H), 3.10 – 2.98 (m, 2H), 1.43 (s, 9H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.3, 156.2, 155.1, 138.5, 138.2, 138.0, 130.4, 130.2, 128.5, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 116.9, 102.1 (C1-β), 83.5, 81.4, 77.6, 75.6, 75.0, 73.4, 63.9, 54.4, 52.2, 37.4, 28.3.

HRMS (ESI-TOF): calculated for $C_{41}H_{47}NO_9$ $[M+Na]^+$ 720.3143. found 720.3148.

4-(((tert-butyldimethylsilyl)oxy)methyl)phenyl 2,3,4,6-tri-*O*-benzyl-β-D-xylopyranoside (8e)



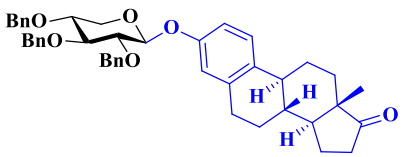
Following **GP-4**, **8e** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-(((tert-butyldimethylsilyl)oxy)methyl)phenol** (0.075 mmol, 19 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (29 mg, 80%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 18H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.92 (dd, *J* = 8.8, 5.5 Hz, 2H, H1-β), 4.82 (d, *J* = 1.3 Hz, 2H), 4.74 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.64 – 4.55 (m, 3H), 3.92 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.66 – 3.55 (m, 3H), 3.26 (dd, *J* = 11.6, 9.3 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 6H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 156.1, 138.5, 138.2, 138.0, 135.7, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 116.6, 102.3 (C1-β), 83.6, 81.5, 77.6, 75.6, 75.1, 73.4, 64.6, 63.9, 25.9, 18.4, -5.2.

HRMS (ESI-TOF): calculated for $C_{39}H_{48}SiO_6$ $[M+Na]^+$ 663.3112 found 663.3127.

Estryl 2,3,4-tri-*O*-benzyl-α/β-D-xylopyranoside (8f)



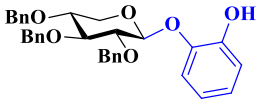
Following **GP-4**, **8f** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **estrone** (0.075 mmol, 22 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (22 mg, 64%, α:β = 1:10). R_f = 0.3 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 18H), 7.22 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.79 (dd, *J* = 12.0, 2.3 Hz, 1H), 5.39 (d, *J* = 3.6 Hz, 0.1H, H1-α), 5.01 – 4.95 (m, 2H, H1-β), 4.89 (d, *J* = 1.4 Hz, 2H), 4.78 (dd, *J* = 18.6, 11.2 Hz, 3H), 4.64 (d, *J* = 11.7 Hz, 1H), 3.98 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.72 – 3.60 (m, 4H), 3.33 (dd, *J* = 11.6, 9.2 Hz, 1H), 2.89 (dd, *J* = 8.7, 3.9 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.40 (d, *J* = 10.2 Hz, 1H), 2.30 – 1.93 (m, 6H), 1.63 – 1.49 (m, 9H), 0.92 (s, 3H).

^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 155.1, 138.6, 138.3, 138.1, 137.9, 134.3, 128.1, 127.9, 127.8, 127.6, 126.4, 117.1, 114.6, 102.3, 83.6, 81.5, 77.7, 75.6, 75.0, 73.3, 63.9, 50.4, 47.9, 44.0, 38.2, 35.8, 31.5, 29.6, 26.4, 25.8, 21.5, 13.8.

HRMS (ESI-TOF): calculated for $C_{45}H_{51}O_6$ $[M+Na]^+$ 710.3578 found 710.3599.

2-Hydroxyphenyl 2,3,4-tri-*O*-benzyl-β-D-xylopyranoside (8g)



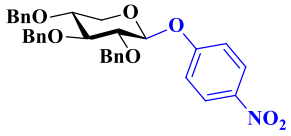
Following **GP-4**, **8g** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **catechol** (0.15 mmol, 9 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (29 mg, 80%, β only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 16H), 7.06 – 6.95 (m, 3H), 6.78 (t, *J* = 7.3 Hz, 1H), 4.96 (m, 2H, OCH_2Ph, H1-β), 4.90 – 4.84 (m, 2H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.12 (t, *J* = 9.3 Hz, 1H), 3.91 (t, *J* = 11.0 Hz, 1H), 3.80 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.59 – 3.54 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 148.7, 145.1, 138.5, 138.1, 137.0, 128.5, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 125.3, 120.6, 119.8, 115.9, 101.4 (C1-β), 81.3, 78.5, 75.7, 74.4, 73.5, 61.0.

HRMS (ESI-TOF): calculated for $C_{32}H_{32}O_6$ $[M+Na]^+$ 631.3036 found 631.3034.

4-Nitrophenyl 2,3,4-tri-*O*-benzyl-α/β-D-xylopyranoside (8h)



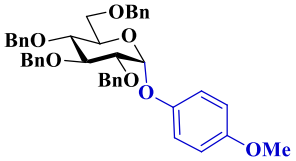
Following **GP-4**, **8h** was prepared from **2,3,4-tri-*O*-benzyl–α/β–D-xylopyranosyl trichloroacetimidate** (0.05 mmol, 30 mg), **4-nitrophenol** (0.075 mmol, 22 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (20 mg, 72%, α:β = 1:14). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 2H), 7.37 – 7.29 (m, 17H), 7.05 (d, *J* = 9.2 Hz, 2H), 5.36 (d, *J* = 3.5 Hz, 0.07H, H1-α), 5.10 (d, *J* = 6.7 Hz, 1H, H1-β), 4.90 – 4.87 (m, 3H), 4.83 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 11.7 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.04 – 3.98 (m, 1H), 3.72 – 3.69 (m, 3H, H2 – H4), 3.45 – 3.38 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 142.7, 138.3, 137.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 125.8, 116.4, 101.1 (C1-β), 83.0, 80.9, 77.4, 75.23, 73.3, 64.0.

HRMS (ESI-TOF): calculated for $C_{32}H_{31}NO_7$ $[M+Na]^+$ 564.1993 found 564.1959.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (9a)

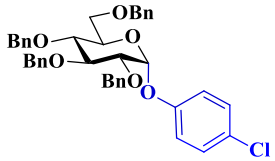


Following **GP-4**, **9a** was prepared from **2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **4-methoxyphenol** (0.075 mmol, 9 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (20 mg, 64%, α:β = 2:1). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 29H), 7.17 (dd, *J* = 19.4, 7.7 Hz, 3H), 7.03 (dd, *J* = 13.3, 5.2 Hz, 3H), 6.81 (dd, *J* = 9.1, 3.1 Hz, 3H), 5.37 (d, *J* = 3.3 Hz, 1H, H1-α), 5.06 (d, *J* = 10.9 Hz, 1H,), 4.96 (d, *J* = 10.9 Hz, 0.6H), 4.91 – 4.79 (m, 5H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.63 – 4.55 (m, 3H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.19 (t, *J* = 9.3 Hz, 1H), 3.93 (d, *J* = 10.1 Hz, 1H), 3.78 (s, 1.5H), 3.78 (s, 3H), 3.75 – 3.69 (m, 4H), 3.62 – 3.57 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.2, 154.9, 151.5, 150.7, 138.7, 138.1, 138.0, 137.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 118.4, 118.1, 114.5, 114.4, 102.7 (C1-β), 96.3 (C1-α), 84.6, 82.0, 81.9, 79.7, 75.7, 75.7, 75.1, 75.0, 75.0, 73.4, 73.2, 70.6, 68.8, 68.3, 55.6, 55.5.

4-Chlorophenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (9b)



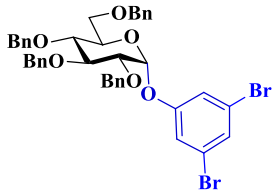
Following **GP-4**, **9b** was prepared from **2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **4-chlorophenol** (0.075 mmol, 11 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (20 mg, 64%, α only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)) along with the minor impurity of the byproduct.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 20H), 7.23 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 5.38 (d, *J* = 3.5 Hz, 1H, H1-α), 5.05 (d, *J* = 10.8 Hz, 1H), 4.89 (d, *J* = 12.7 Hz, 2H), 4.82 (dd, *J* = 16.9, 4.7 Hz, 3H), 4.70 (d, *J* = 19.4 Hz, 1H), 4.60 (dd, *J* = 17.5, 12.9 Hz, 2H), 4.49 (d, *J* = 10.6 Hz, 2H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.18 (t, *J* = 9.1 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.72 (dt, *J* = 11.5, 6.2 Hz, 3H), 3.59 – 3.53 (m, 1H).

^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 155.1, 138.6, 138.0, 137.8, 137.6, 129.3, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 118.0, 95.6 (C1-α), 81.8, 79.6, 75.8, 75.1, 73.5, 73.4, 70.8, 68.1.

HRMS (ESI-TOF): calculated for $C_{40}H_{39}ClO_6$ $[M+Na]^+$ 673.2327 found 673.2352.

3,5-Dibromophenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (9c)

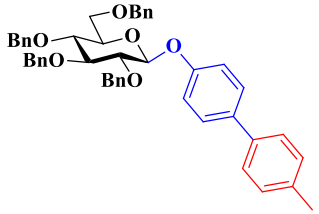


Following **GP-4**, **9c** was prepared from **2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg), **3,5-dibromophenol** (0.075 mmol, 19 mg), **catalyst** (0.9 mg, 10 mol%) as colorless sticky liquid (19 mg, 62%, α only). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 20H), 7.22 (t, *J* = 1.5 Hz, 1H), 7.16 (d, *J* = 1.6 Hz, 2H), 5.32 (d, *J* = 3.5 Hz, 1H, H1-α), 5.02 (d, *J* = 10.8 Hz, 1H), 4.88 – 4.79 (m, 3H), 4.63 – 4.58 (m, 2H), 4.48 – 4.40 (m, 2H), 4.16 – 4.09 (m, 2H), 3.76 (d, *J* = 5.3 Hz, 2H), 3.69 (dd, *J* = 9.6, 3.6 Hz, 2H), 3.58 (d, *J* = 10.6 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 156.8, 138.6, 128.5, 128.4, 128.1, 127.9, 127.8, 126.5, 123.1, 119.0, 117.8, 95.9 (C1-α), 81.7, 79.6, 75.8, 75.1, 73.6, 73.4, 71.4, 68.1.

4-(*p*-tolyl) phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (10a)



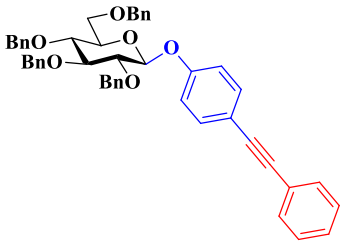
Following literature known procedure[11], the title compound **9a** was prepared from **4-Iodophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside** (0.07 mmol, 54 mg) and ***p*-tolylboronic acid** (0.08 mmol, 12 mg) as white solid (33 mg, 68%). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.27 (m, 18H), 7.25 – 7.19 (m, 3H), 7.14 (dd, *J* = 8.7, 1.0 Hz, 2H), 5.08 – 5.04 (m, 2H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 10.3 Hz, 1H), 4.86 – 4.84 (m, 1H), 4.83 (d, *J* = 3.4 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 3.79 – 3.76 (m, 2H), 3.75 – 3.68 (m, 2H), 3.64 (dd, *J* = 9.6, 4.7 Hz, 1H), 2.40 (s, 3H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.6, 138.4, 138.2, 138.1, 137.9, 137.7, 136.6, 135.6,

129.4, 128.3, 127.9, 127.8, 127.6, 117.1, 101.7, 84.6, 81.9, 77.6, 75.7, 75.1, 75.1, 75.0, 73.5, 68.8, 21.1.

HRMS (ESI-TOF): calculated for $C_{47}H_{46}O_6$ $[M+Na]^+$ 729.3187 found 729.3182.

4-(phenylethynyl) phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (10b)



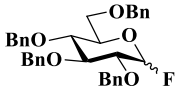
Following literature known procedure[11], the title compound **9b** was prepared from **4-Iodophenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside** (0.07 mmol, 54 mg) and **phenyl acetylene** (0.08 mmol, 12 mg) as white solid (36 mg, 73%). R_f = 0.4 (ethyl acetate/hexane 1:4 (v/v)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.48 – 7.45 (m, 2H), 7.35 – 7.27 (m, 22H), 7.19 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 5.05 – 4.93 (m, 3H), 4.88 – 4.80 (m, 3H), 4.61 – 4.49 (m, 4H), 3.83 – 3.74 (m, 3H), 3.71 – 3.63 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.2, 138.4, 137.9, 133.1, 131.5, 128.5, 128.4, 128.4, 128.3, 128.2, 127.9, 117.4, 116.7, 101.3, 89.1, 88.5, 84.5, 81.9, 77.6, 75.8, 75.2, 75.1, 75.1, 73.5, 68.7.

HRMS (ESI-TOF): calculated for $C_{48}H_{44}O_6$ $[M+Na]^+$ 739.3030 found 739.3025.

2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-fluoro-α/β-D-glucopyranoside (10c)



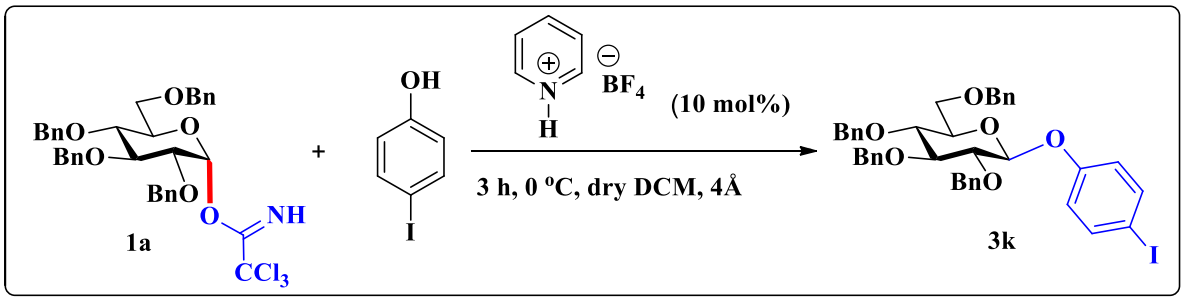
Following **GP-4**, **9c** was prepared from **2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate** (0.05 mmol, 35 mg) and **pyridinium tetrafluoroborate** (8.3 mg, 1 equiv.) as colorless sticky liquid (18 mg, 75%, α:β = 3:1). R_f = 0.5 (ethyl acetate/hexane 1:4 (v/v)). The title compound was also observed as the byproduct in the glycosylation reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 23H), 7.18 – 7.13 (m, 2H), 5.56 (dd, *J* = 53.2, 2.5 Hz, 1H), 5.27 (dd, *J* = 52.9, 6.7 Hz, 0.3H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.91 (d, *J* = 11.1 Hz, 0.3H),

4.87 (d, *J* = 5.5 Hz, 1.2H), 4.85 – 4.82 (m, 1.5H), 4.80 (d, *J* = 3.2 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1.2H), 4.61 (d, *J* = 12.0 Hz, 1.2H), 4.56 (d, *J* = 4.6 Hz, 0.3H), 4.52 (d, *J* = 10.8 Hz, 1.2H), 4.48 (d, *J* = 12.2 Hz, 1H), 3.98 (dd, *J* = 20.1, 10.7 Hz, 2H), 3.78 – 3.71 (m, 3H), 3.70 – 3.65 (m, 1H), 3.61 (dd, *J* = 9.3, 2.6 Hz, 1H), 3.55 (dd, *J* = 9.6, 2.5 Hz, 0.6H).

$^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ 138.4, 137.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 105.5 (d, J_{C-F} = 226.7 Hz), 81.4, 79.3 (d, J_{C-F} = 24.8 Hz), 76.6, 75.8, 75.4, 75.2, 74.9, 73.5, 73.5, 72.6 (d, J_{C-F} = 4 Hz), 67.8.

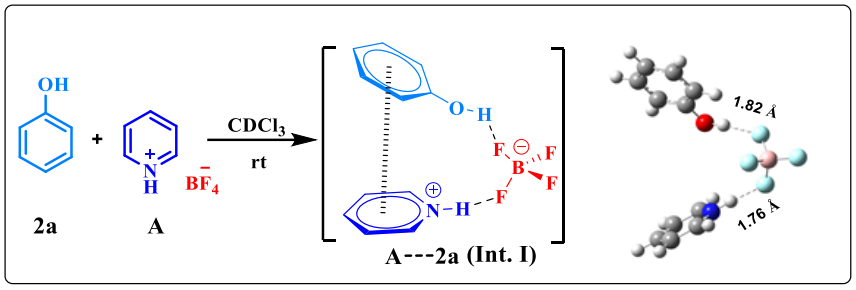
Gram Scale reaction:



Under N_2 atmosphere, glycosyl imidate (685 mg, 1.0 mmol, 1.0 equiv.), 4-iodophenol (328 mg, 1.5 mmol, 1.5 equiv.), were weighed into a round bottom flask with a magnetic stir bar. Anhydrous DCM (0.1 M) and activated 4Å MS (molecular sieves) was added followed by addition of catalyst (10 mol %) and the reaction mixture was stirred at 0 °C for 3 h. After completion, the reaction was diluted with DCM and washed with brine. The aqueous phase was extracted with DCM (3X). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to afford the product (502 mg, 71% yield with α:β = 1:10).

Mechanistic studies:

(a) ^{1}H NMR titration for studying interactions between phenol and catalyst.



Phenol **(2a)** (2.80 mg, 0.03 mmol, 1.0 eq) was dissolved in 0.6 mL of $CDCl_3$. After each ^1H-NMR measurement, 0.99 mg (0.005 mmol) of catalyst **A** was added and the NMR spectrum was remeasured.

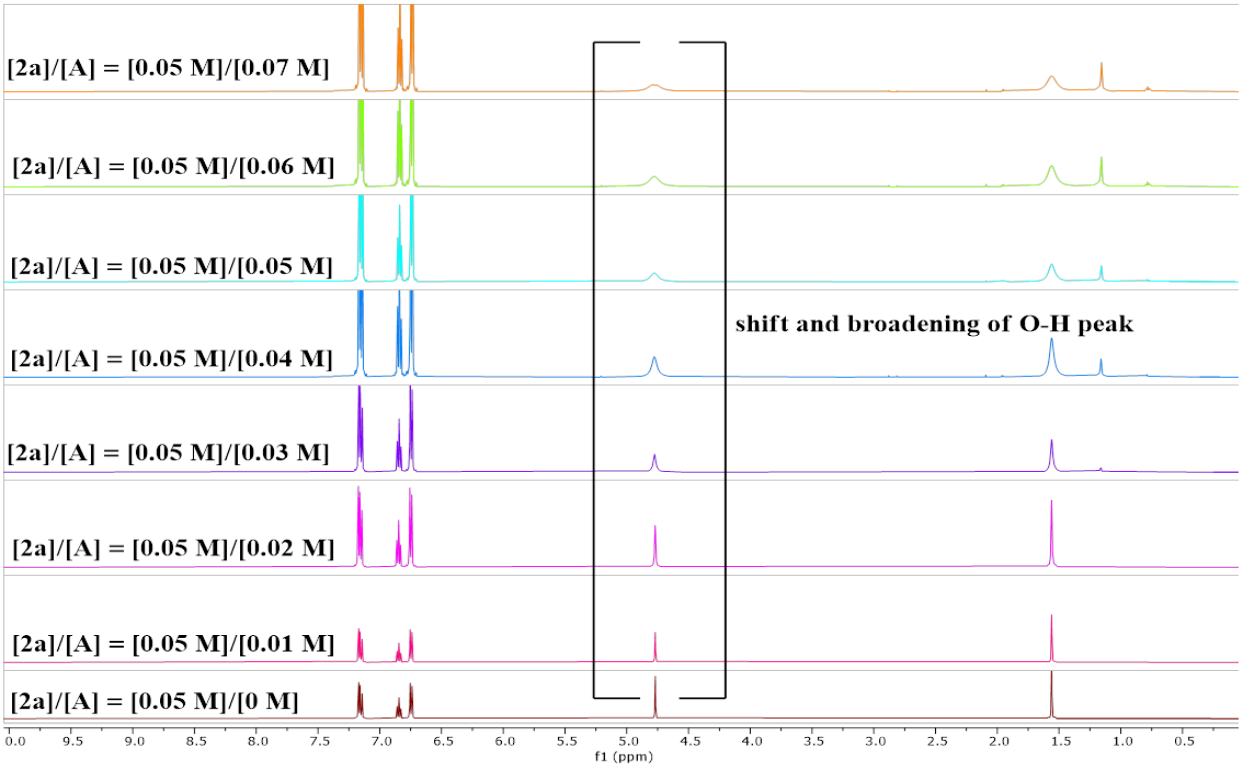


Figure S1a: The full spectra of the NMR titration of the reaction between **2a** and **A.**

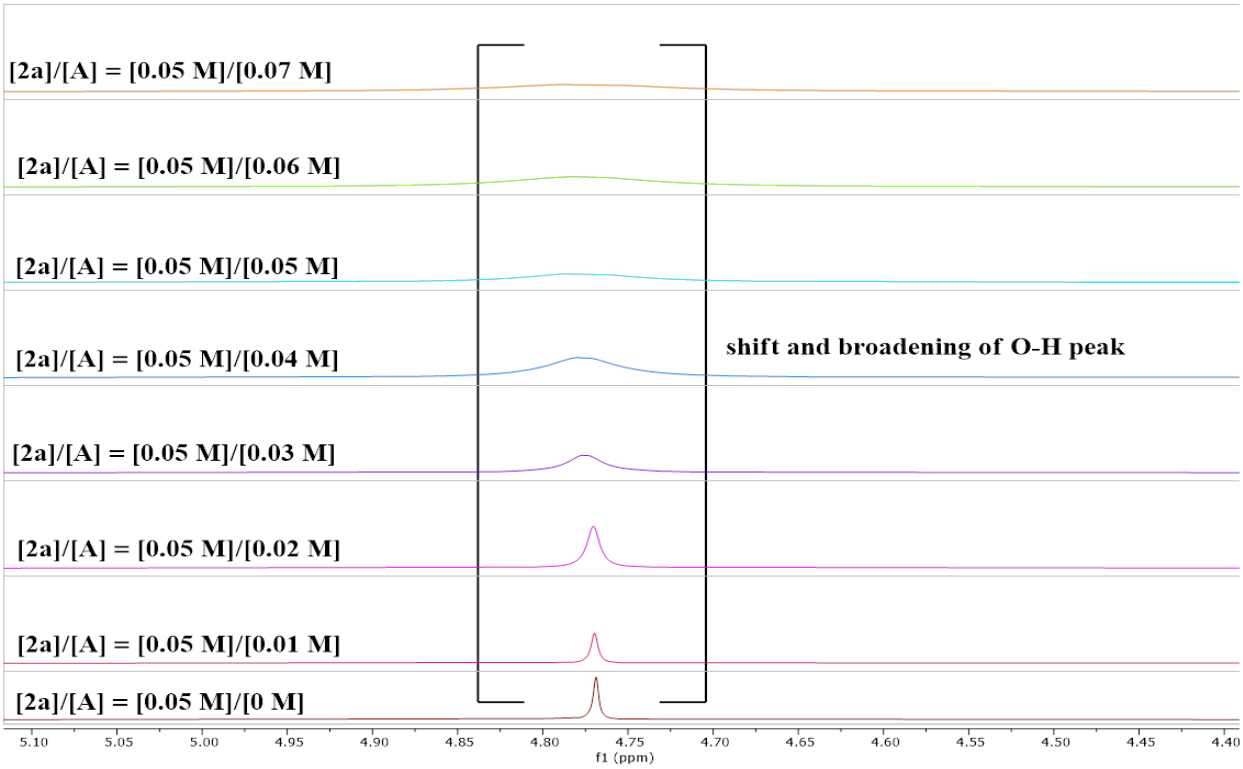


Figure S1b: The zoomed in spectra of the NMR titration of the reaction between phenol **2a** and catalyst **A**

Table S3: Chemical shift and peak width of OH in each NMR titration measurement

Entry	Ratio	Chemical Shift (ppm)	Peak width (Hz)
1.	1/0	4.854	3.20
2.	1/0.4	4.845	18.2
3.	1/0.6	4.861	36.15
4.	1/0.8	4.865	64.45
5.	1/1	4.867	67.30
6.	1/1.2	4.870	92.85
7.	1/1.4	4.868	95.20

From **Figure S1**, the shift and broadening of the O-H peak suggest the close interaction of phenol and catalyst via π-π stacking and H-bonding interactions as shown in the Int. 2a-A.

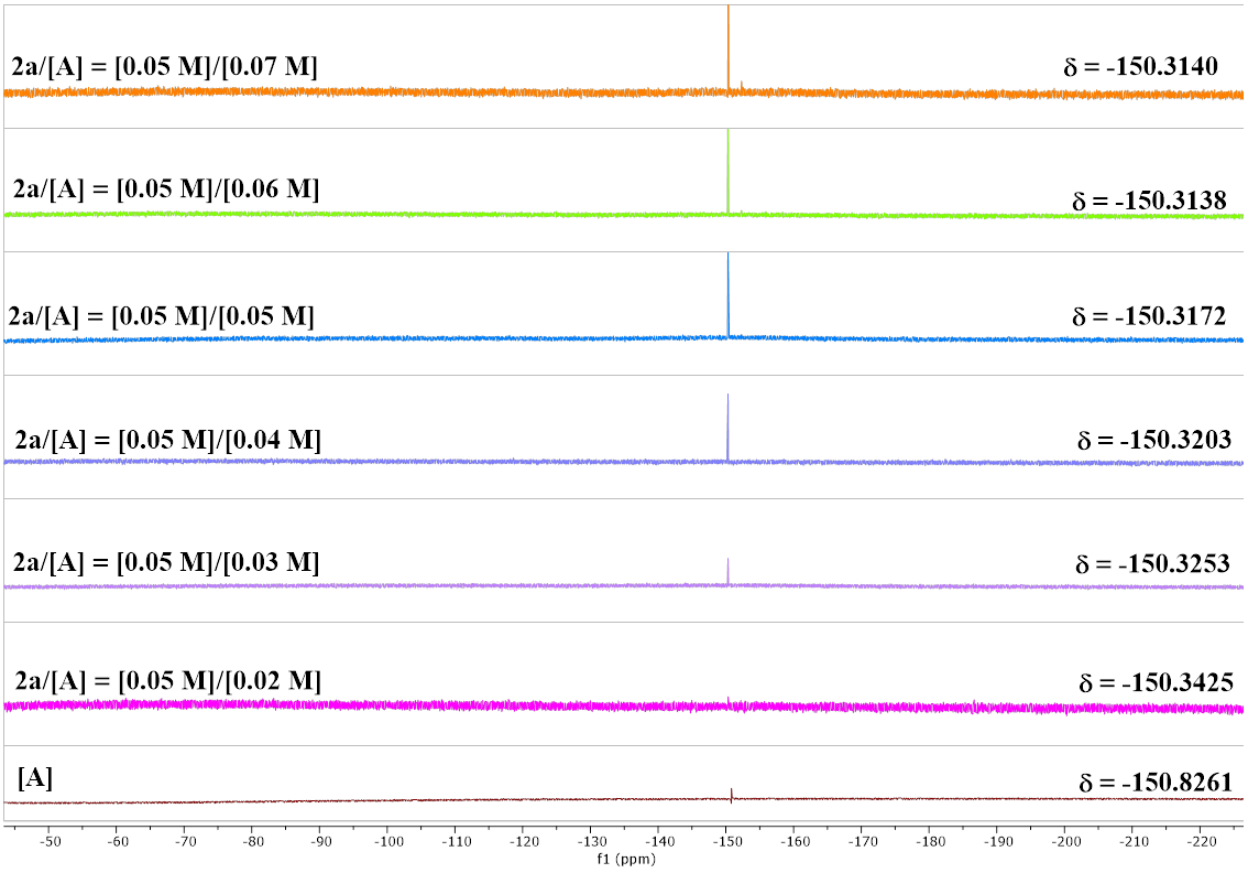
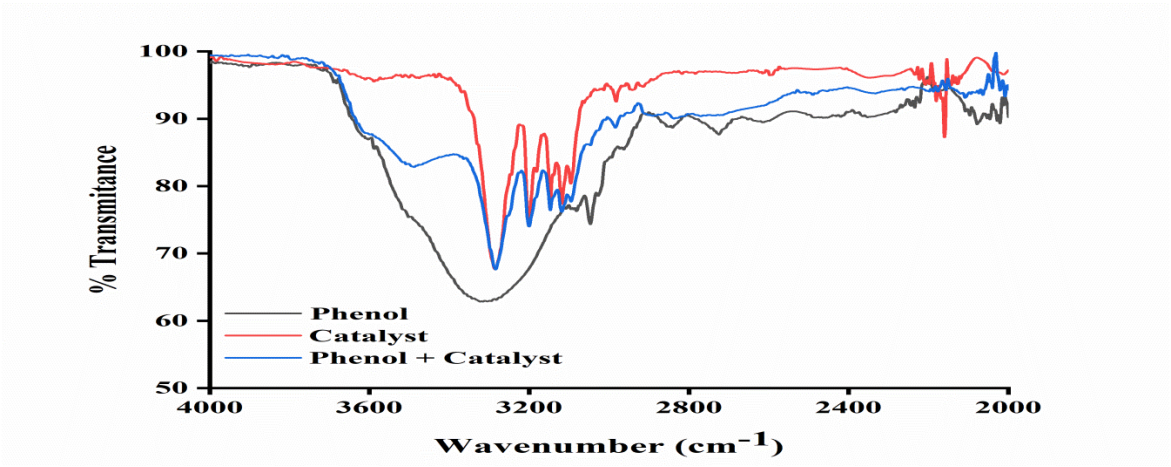


Figure S2: ^{19}F-NMR showing interactions of catalyst B with phenol A in $CDCl_3$ (0.6mL).

There was a slight shift in ^{19}F-NMR, from -150.82 ppm to -150.31 ppm (**Figure 2**). This observation also suggests H-bonding interactions of O-H with the tetrafluoroborate anion of the catalyst.

(b) IR studies:



For further understanding of the interactions of phenol and catalyst, IR studies were performed and we observed a significant shift and broadening of the O-H peak in the spectra. Therefore, it was observed that the catalyst pyridinium tetrafluoroborate in the presence of phenol shows the shift and broadening of O−H stretch due to H-bonding interactions.

ii) ^{1}H NMR study for the interaction between glycosyl trichloroacetimidate and catalyst.

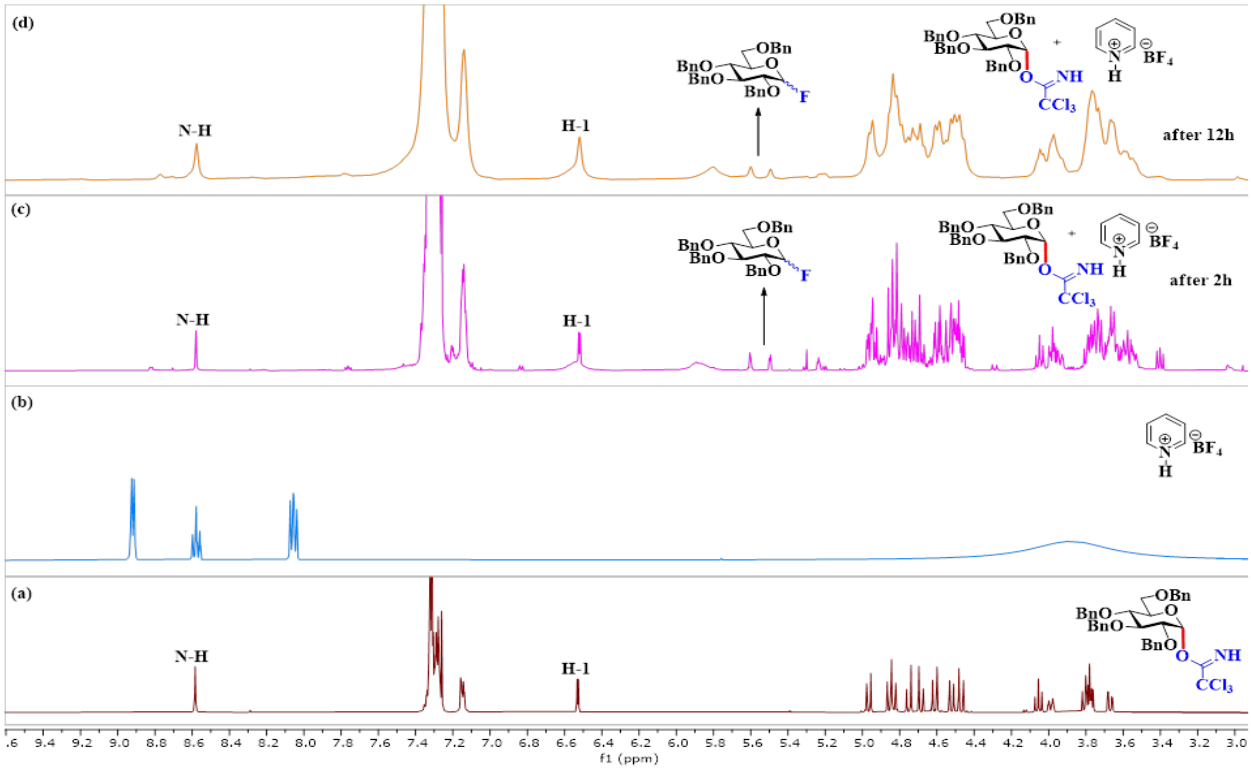


Figure S3: (a) ^{1}H NMR (glycosyl trichloroacetimidate donor **1a**) in $CDCl_3$ **(b)** ^{1}H NMR of pyridinium tetrafluoroborate in DMSO-d_6 **(c)** a mixture of **1a** and catalyst (10 mol %) after 2 h in $CDCl_3$. **(d)** a mixture of **1a** and catalyst (10 mol %) after 12 h in $CDCl_3$.

The ^{1}H NMR study for the interaction between the catalyst and glycosyl trichloroacetimidate was performed. The diminishing of N-H peak suggests slow decomposition of the imidate due to the H-bonding interactions between the imidate N-H and the tetrafluoroborate anion of the catalyst along with the formation of **2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-fluoro-α/β-D-glucopyranoside** as the byproduct in trace amount.

(iii) ^{1}H NMR study for the interaction between glycosyl trichloroacetimidate and phenol.

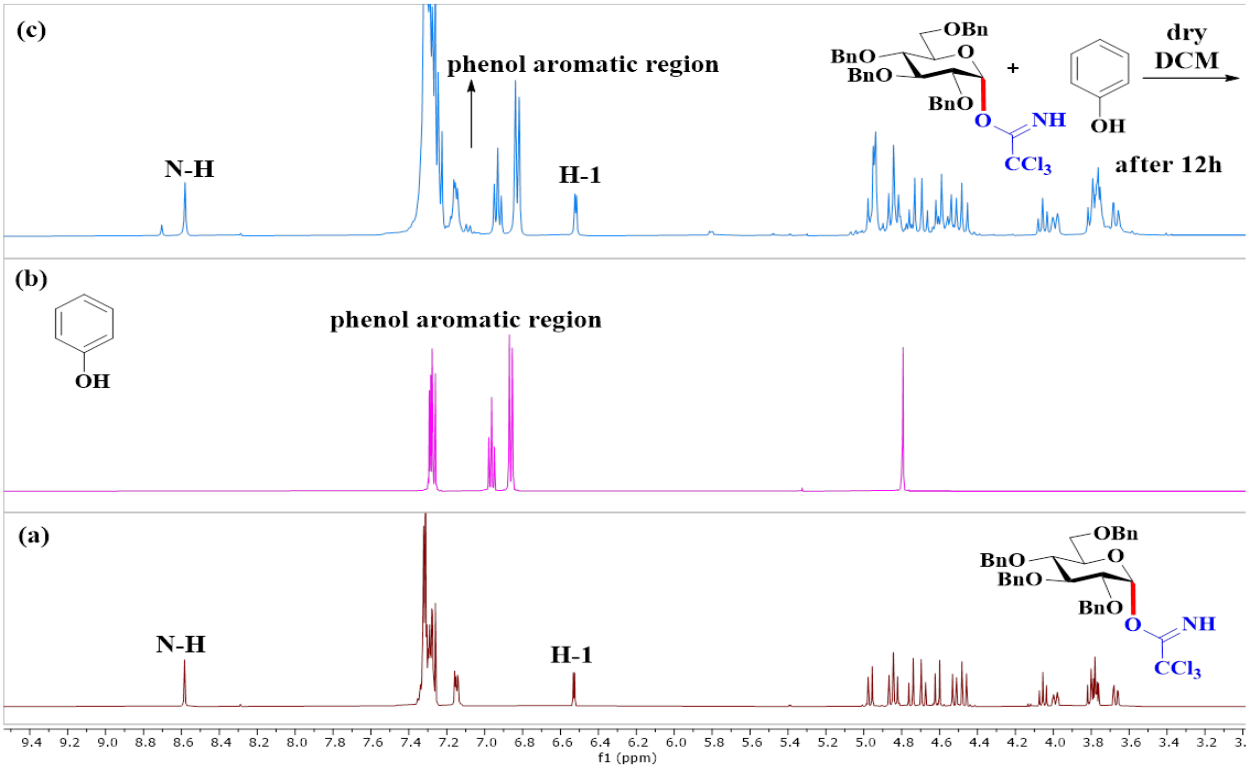


Figure S4: (a) ^{1}H NMR of glycosyl trichloroacetimidate donor **1a** in $CDCl_3$ **(b)** ^{1}H NMR of phenol **A** in $CDCl_3$ **(c)** ^{1}H NMR of glycosyl trichloroacetimidate donor **1a** (1.0 equiv.) and phenol **A** (1.5 equiv.) after 12h in $CDCl_3$.

(c) Hammett Plot:

Table S4: Calculation for Hammett Plot.

Functional group	k_X/k_H	log (k_X/k_H)	σ^-
H	**1**	**0**	**0**
OMe	**1.25**	**0.097**	**-0.26**
Me	**1.05**	**0.022**	**-0.17**
Cl	**0.57**	**-0.244**	**0.19**
COOMe	**0.43**	**-0.366**	**0.75**

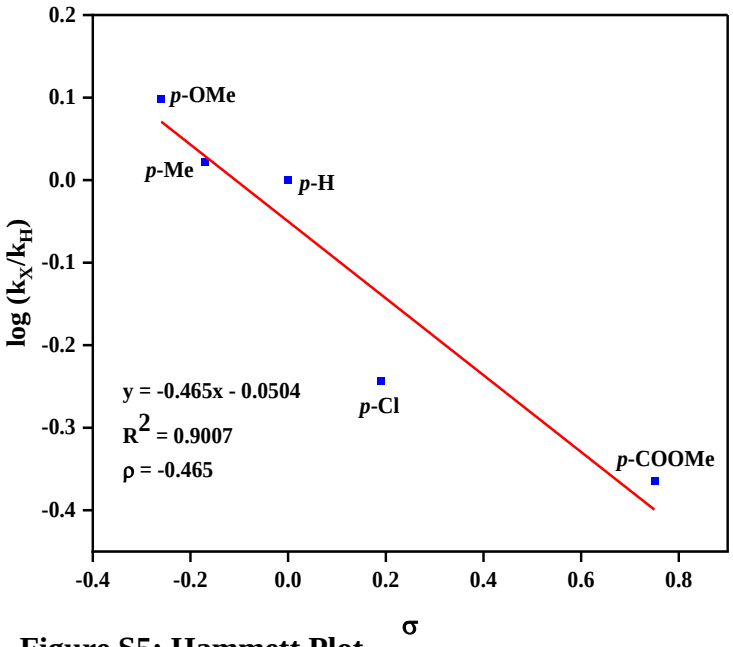


Figure S5: Hammett Plot

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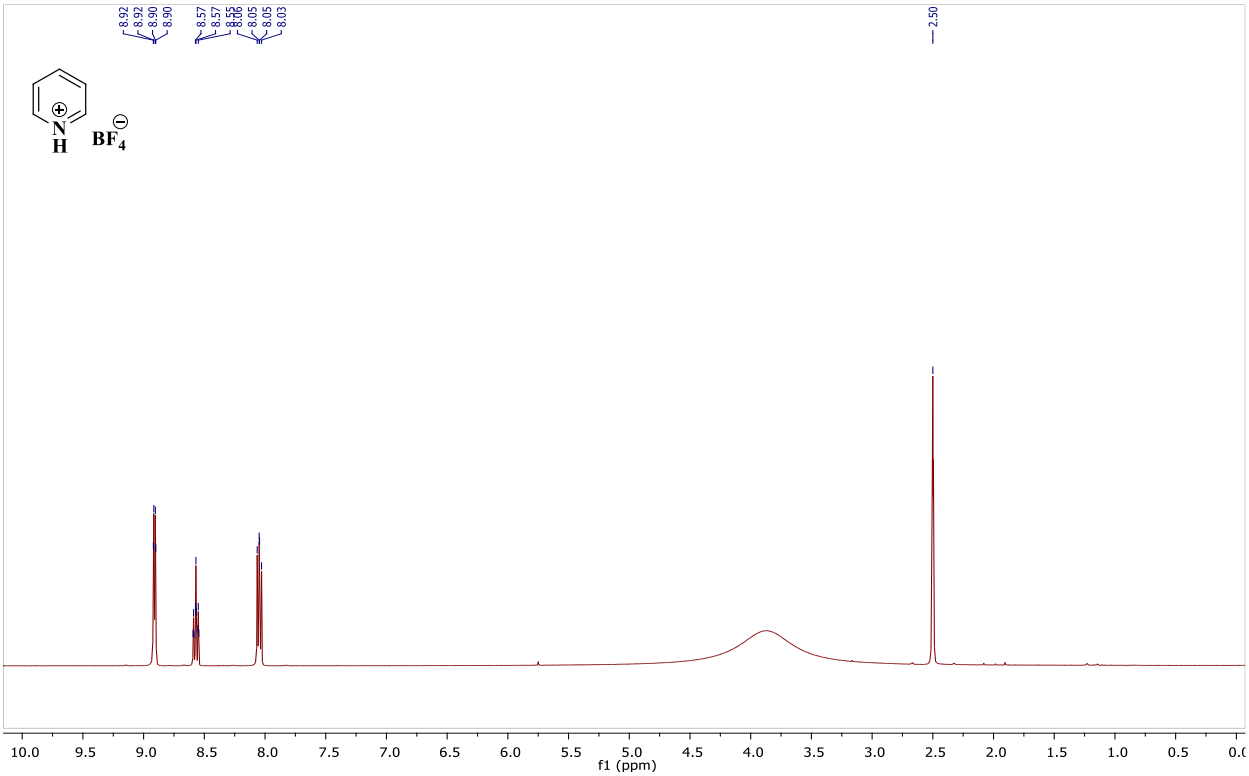
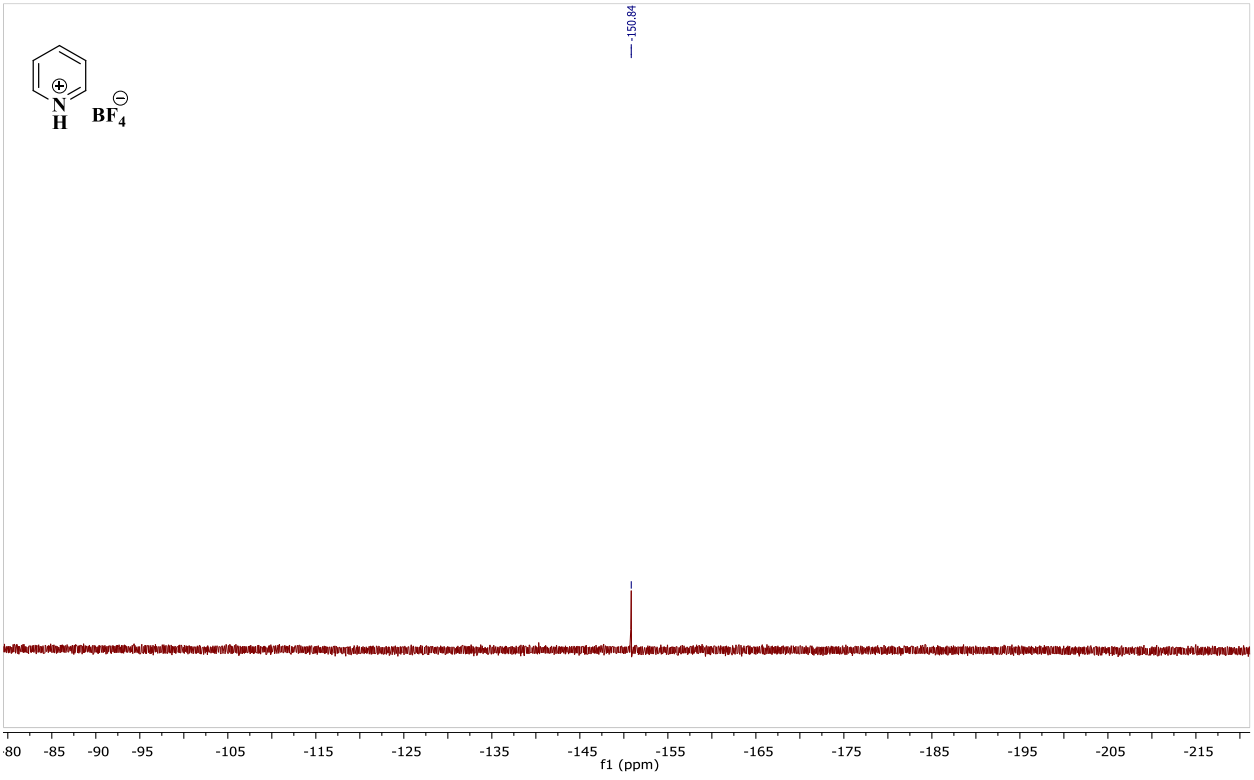
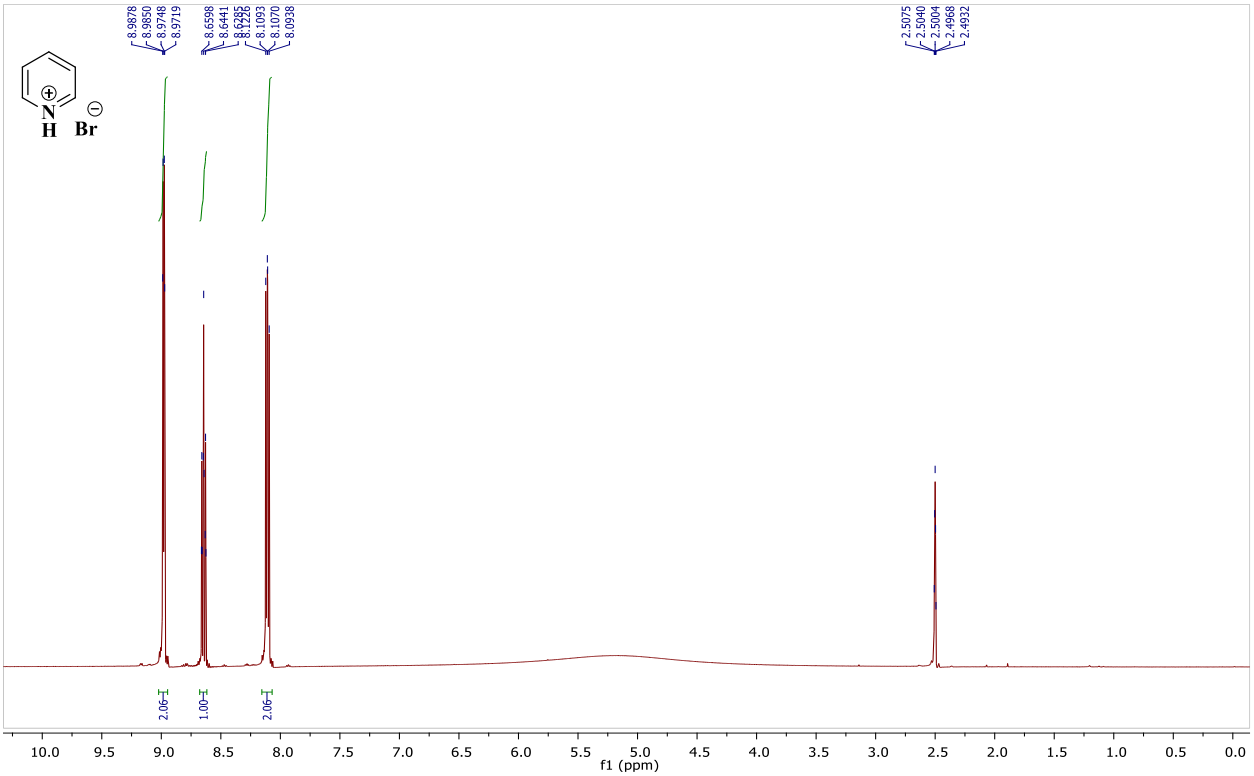
^{1}H NMR spectrum of catalyst A (500 MHz, DMSO-d_6)



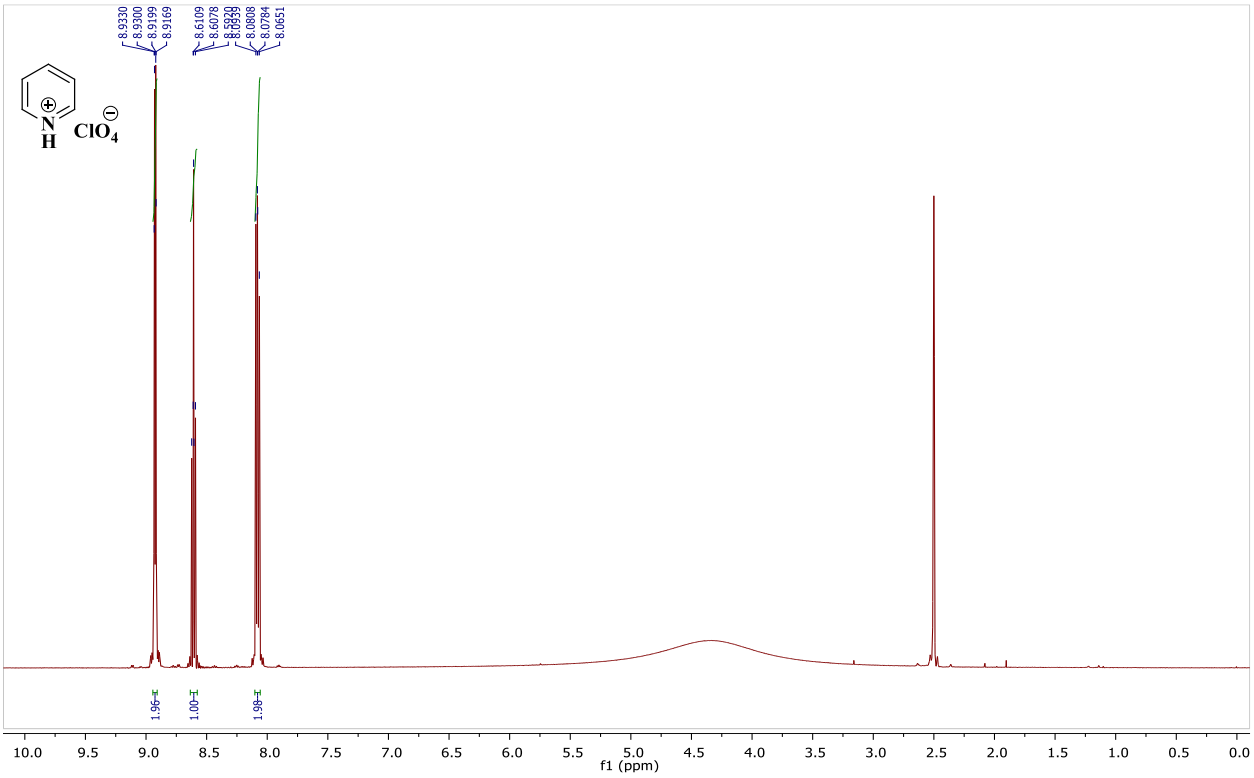
^{19}F NMR spectrum of catalyst A (471 MHz, DMSO-d_6)



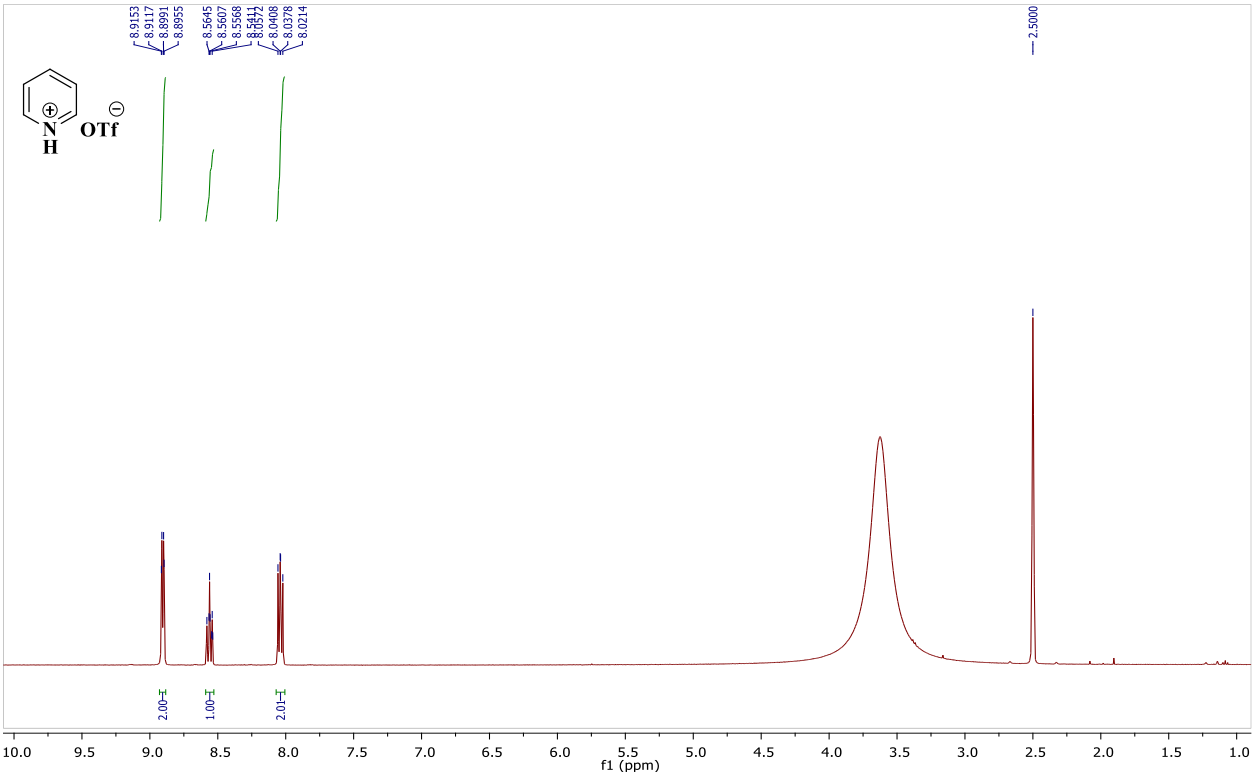
^{1}H NMR spectrum of catalyst B (500 MHz, DMSO-d_6)



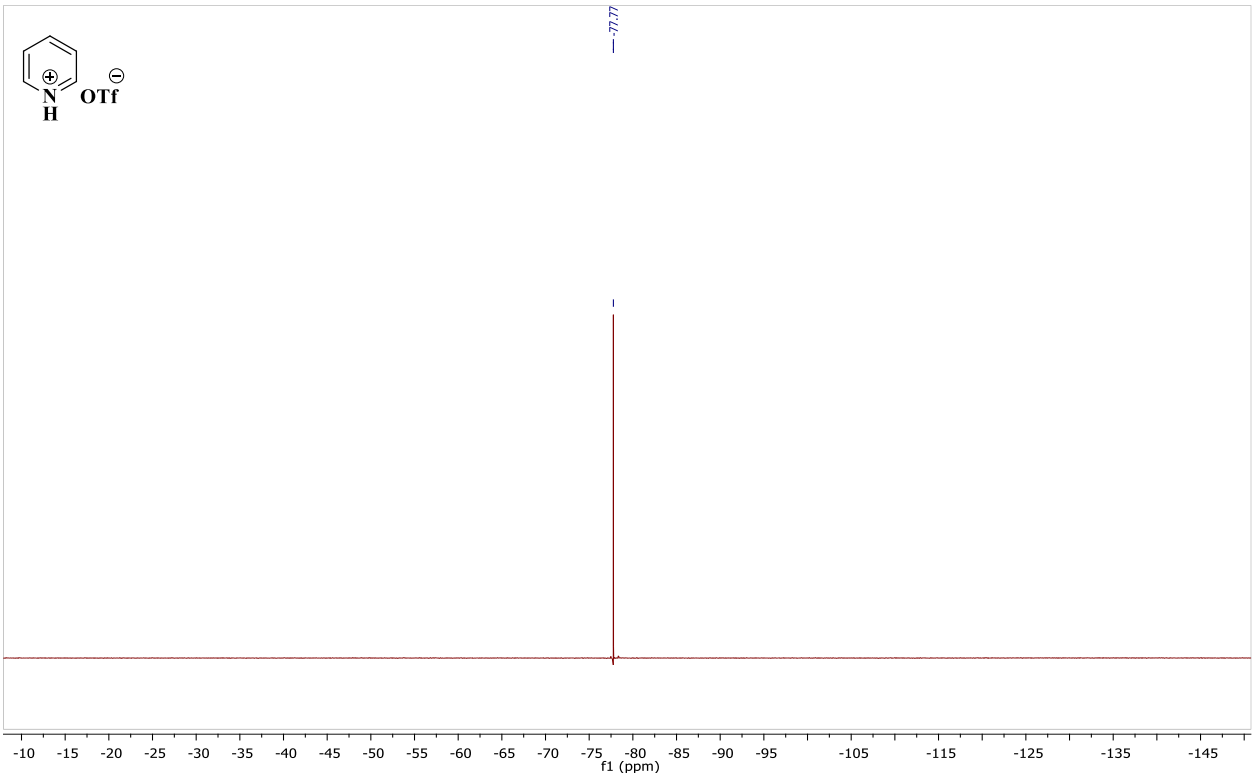
^{1}H NMR spectrum of catalyst C (500 MHz, DMSO-d_6)



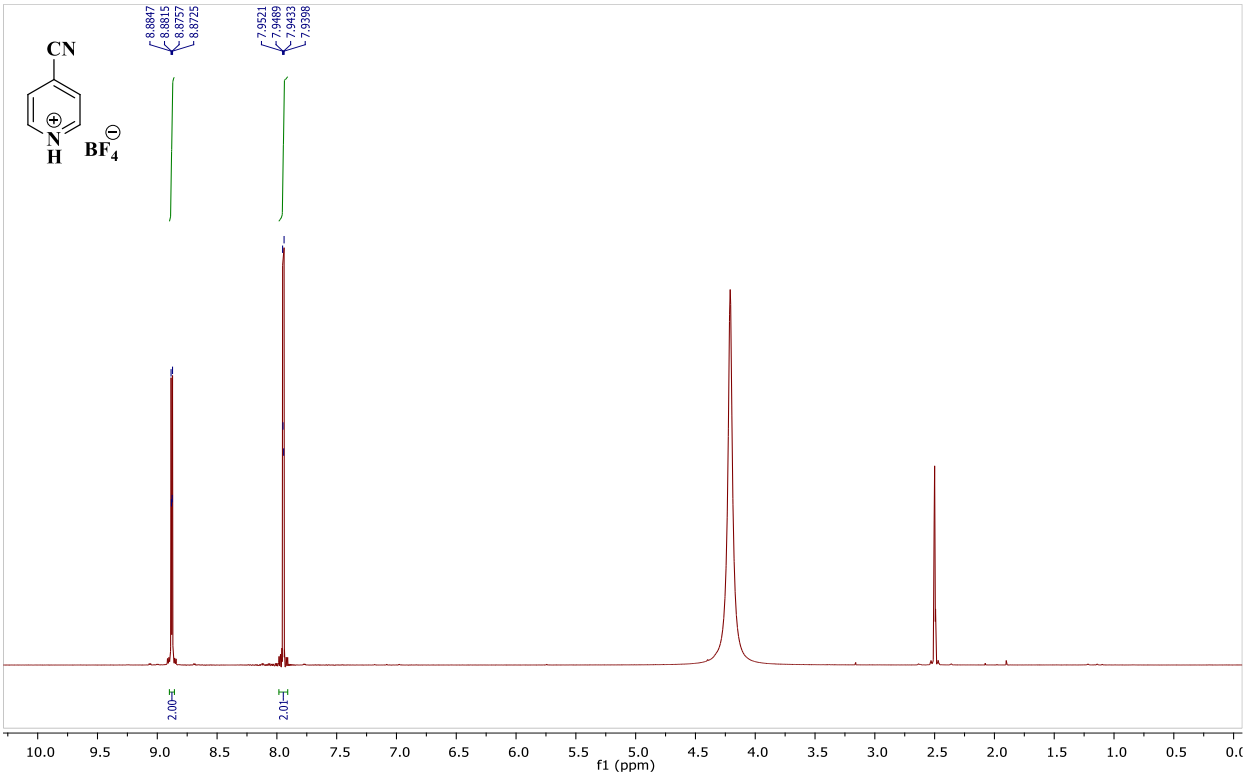
^{1}H NMR spectrum of compound - catalyst D (400 MHz, DMSO-d_6)



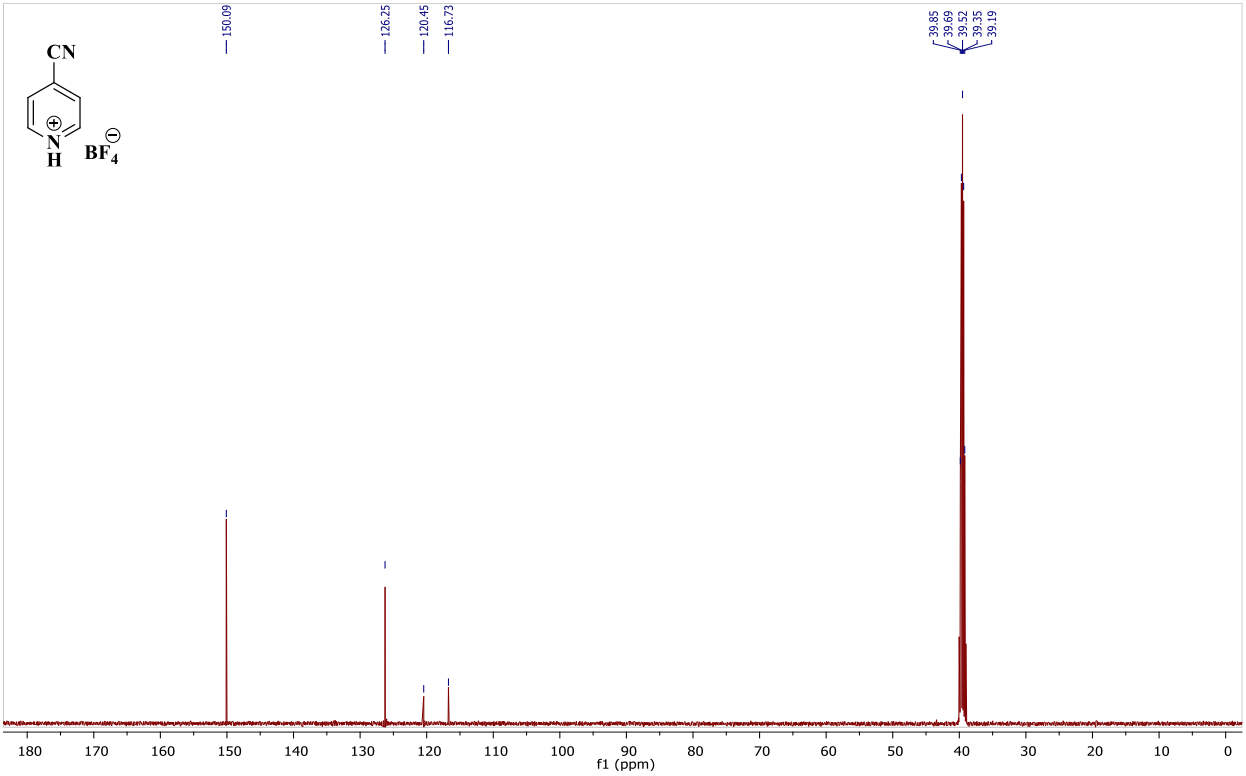
^{19}F NMR spectrum of catalyst D (471 MHz, DMSO-d_6)



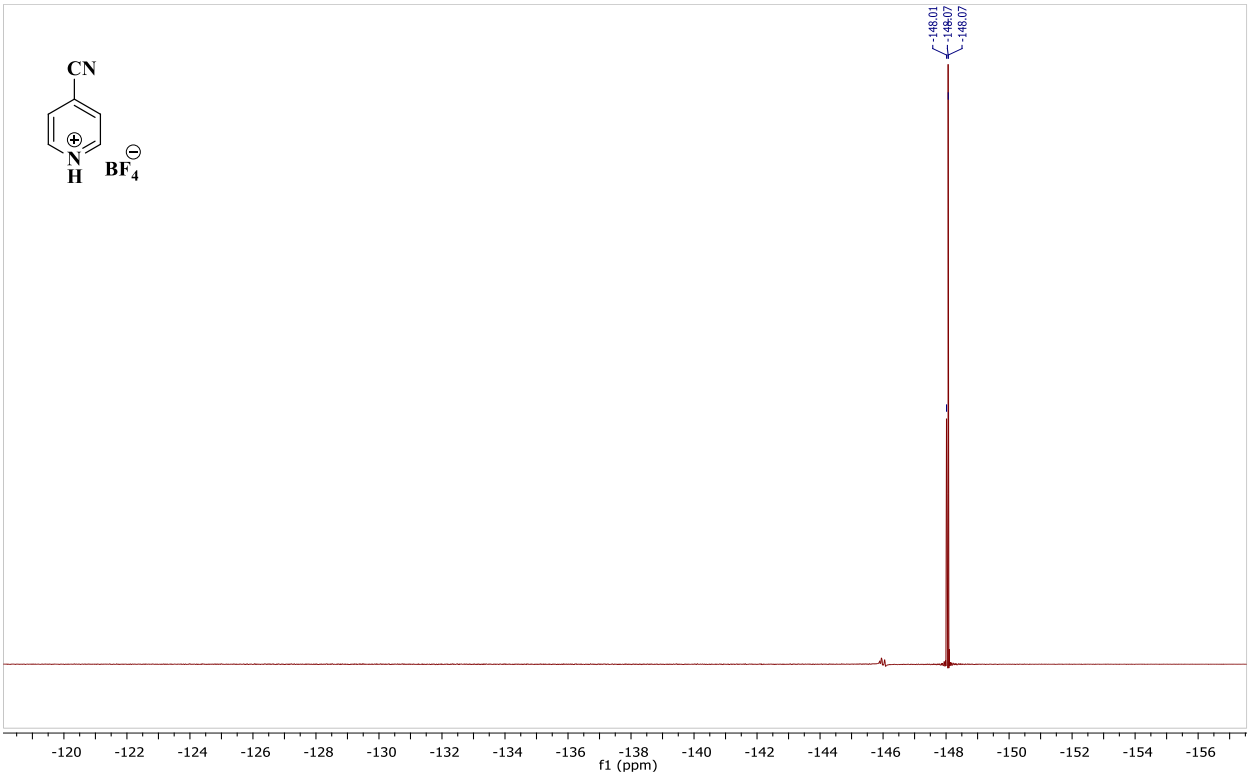
^{1}H NMR spectrum of compound - catalyst E (500 MHz, DMSO-d_6)



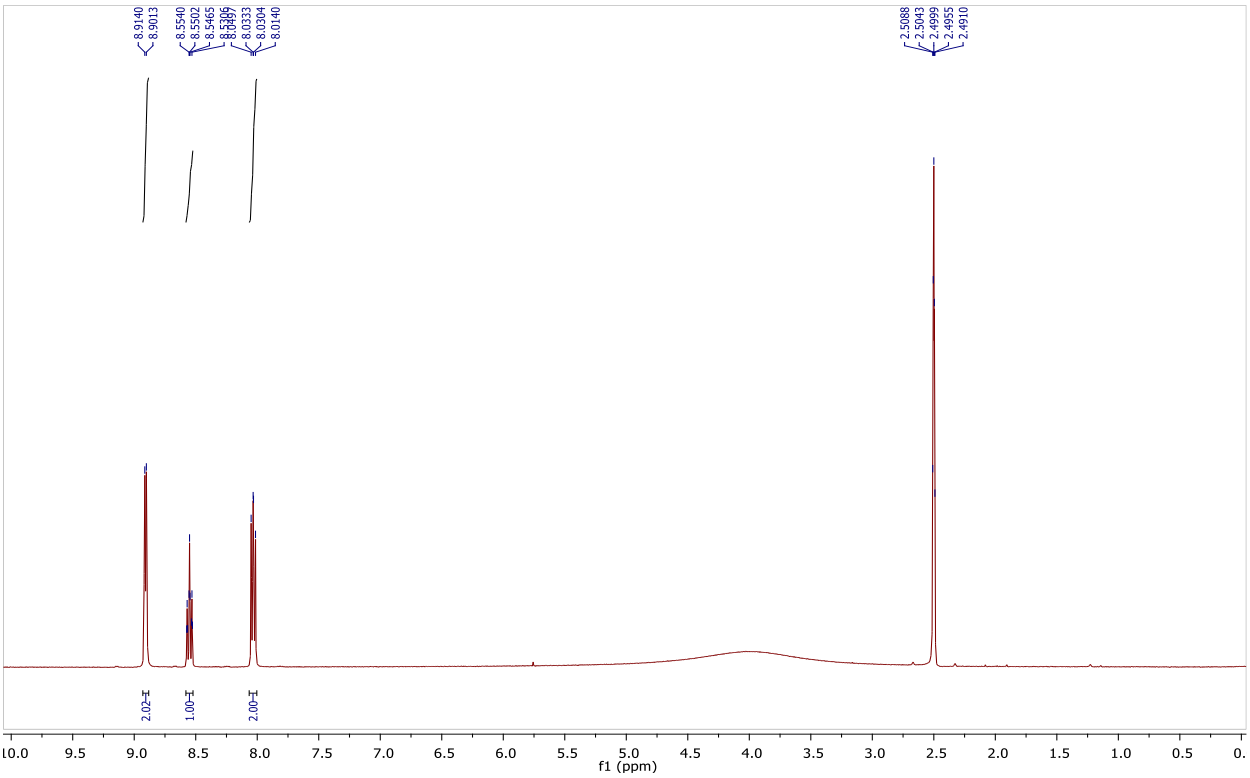
^{13}C {^{1}H} NMR spectrum of compound - catalyst E (125 MHz, DMSO-d_6)



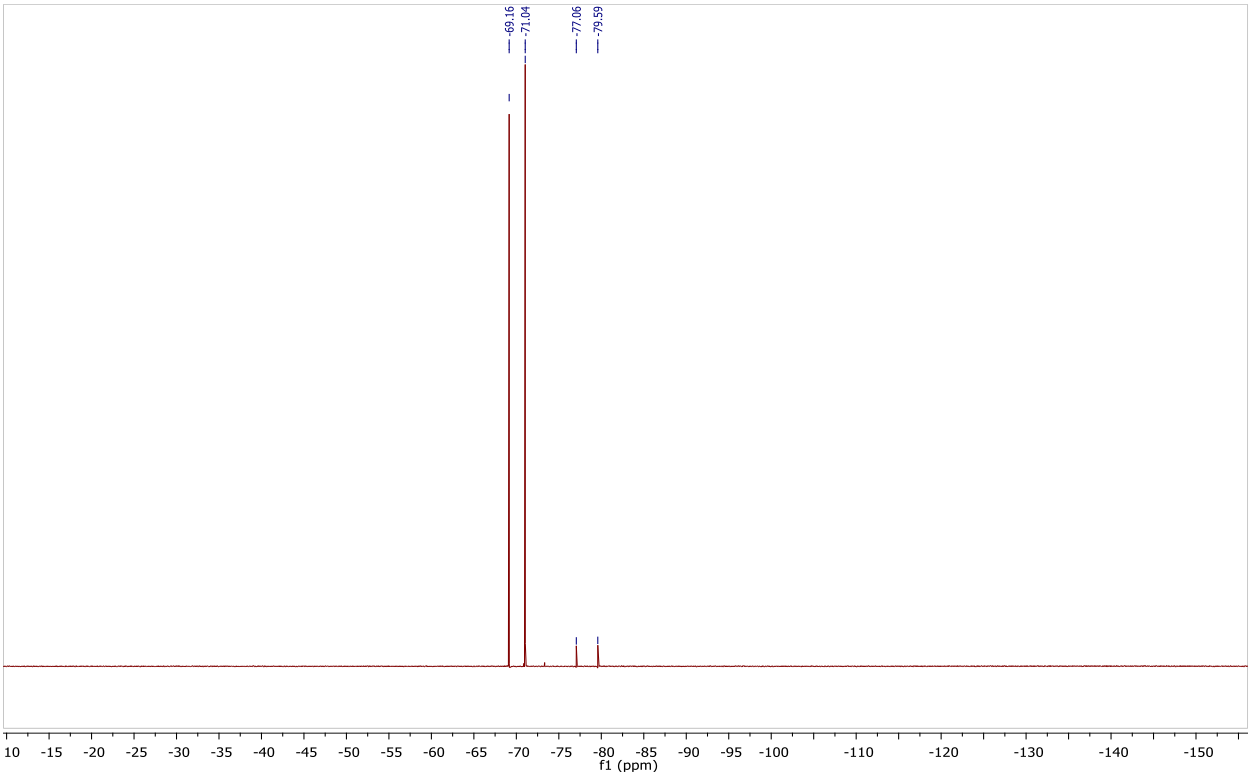
^{19}F {^{1}H} NMR spectrum of compound - catalyst E (471 MHz, DMSO-d_6)



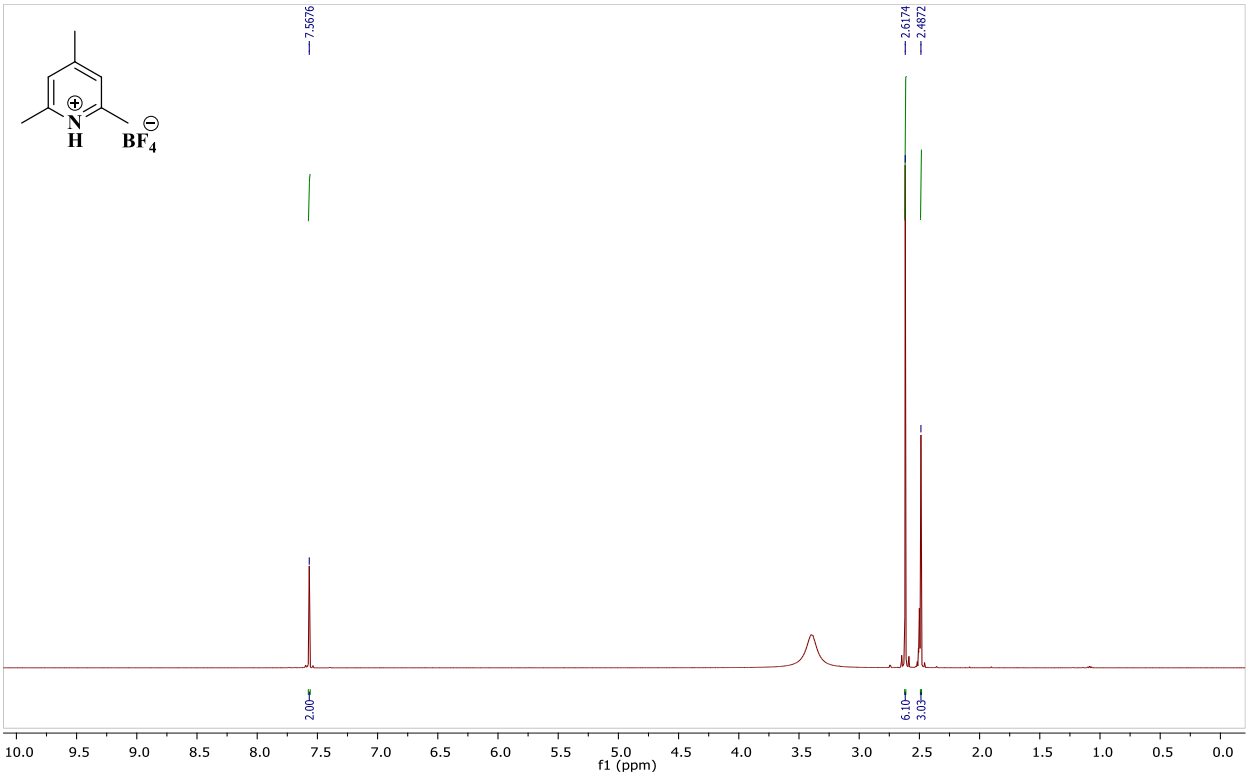
^{1}H NMR spectrum of compound - catalyst F (400 MHz, DMSO-d_6)



^{19}F {^{1}H} NMR spectrum of compound - catalyst F (376 MHz, DMSO-d_6)



^{1}H NMR spectrum of compound - catalyst G (500 MHz, DMSO-d_6)



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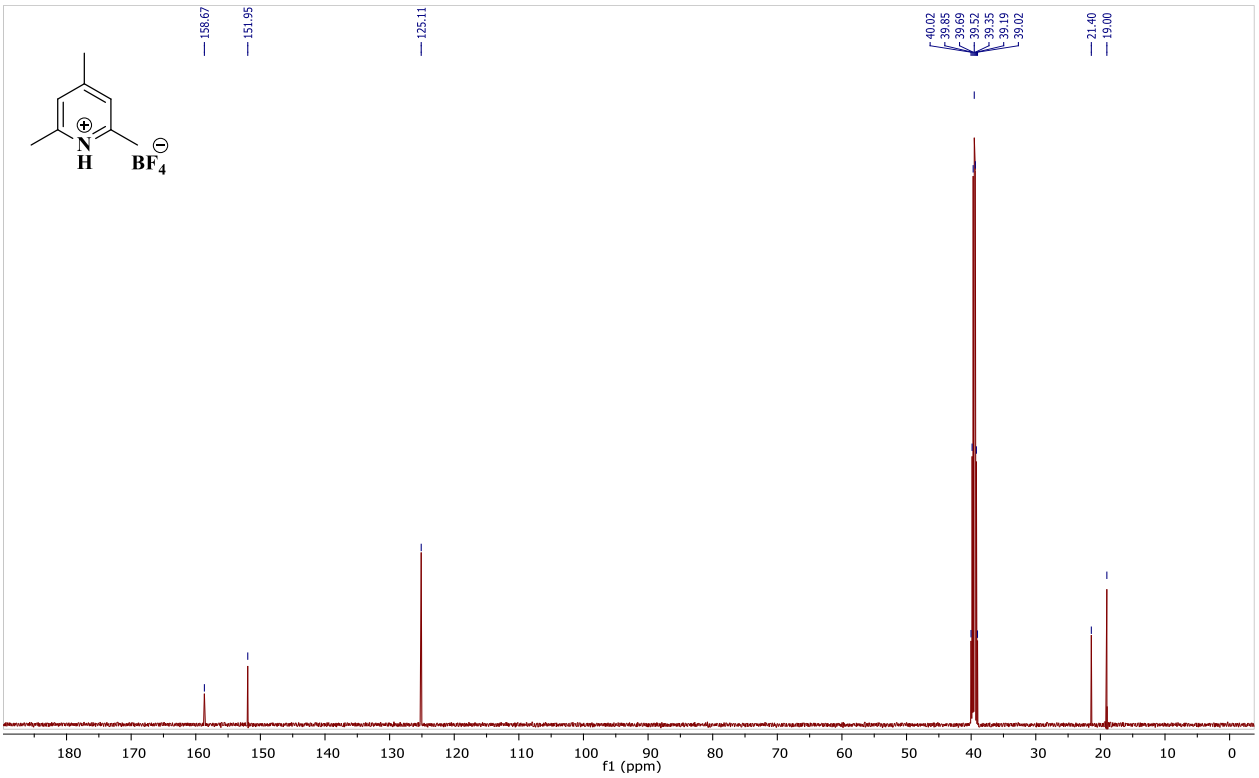
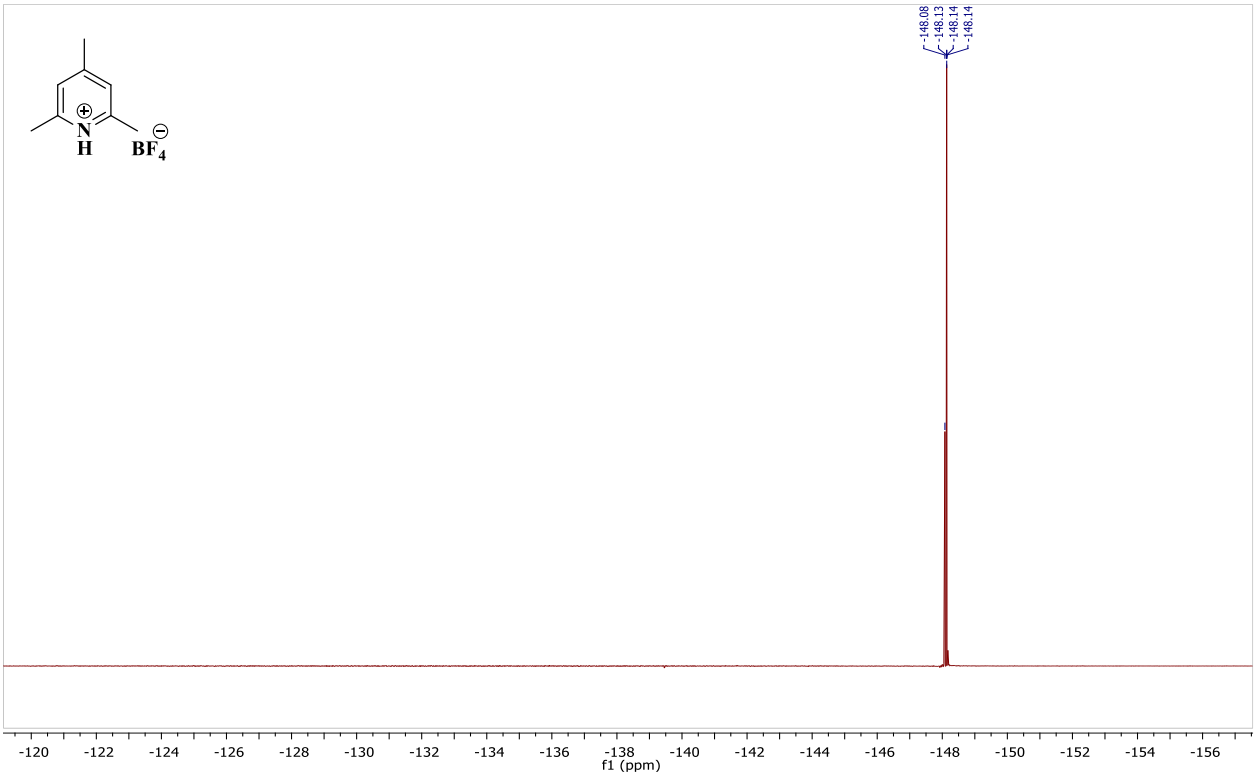
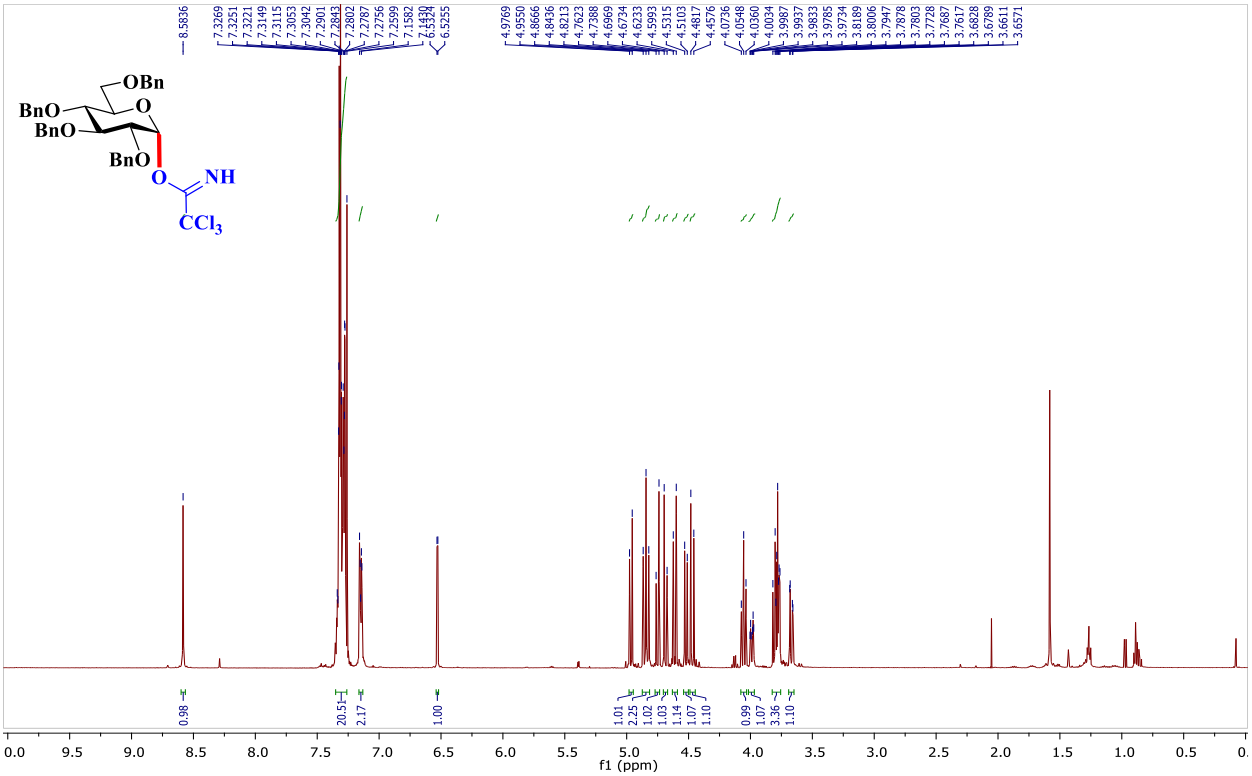


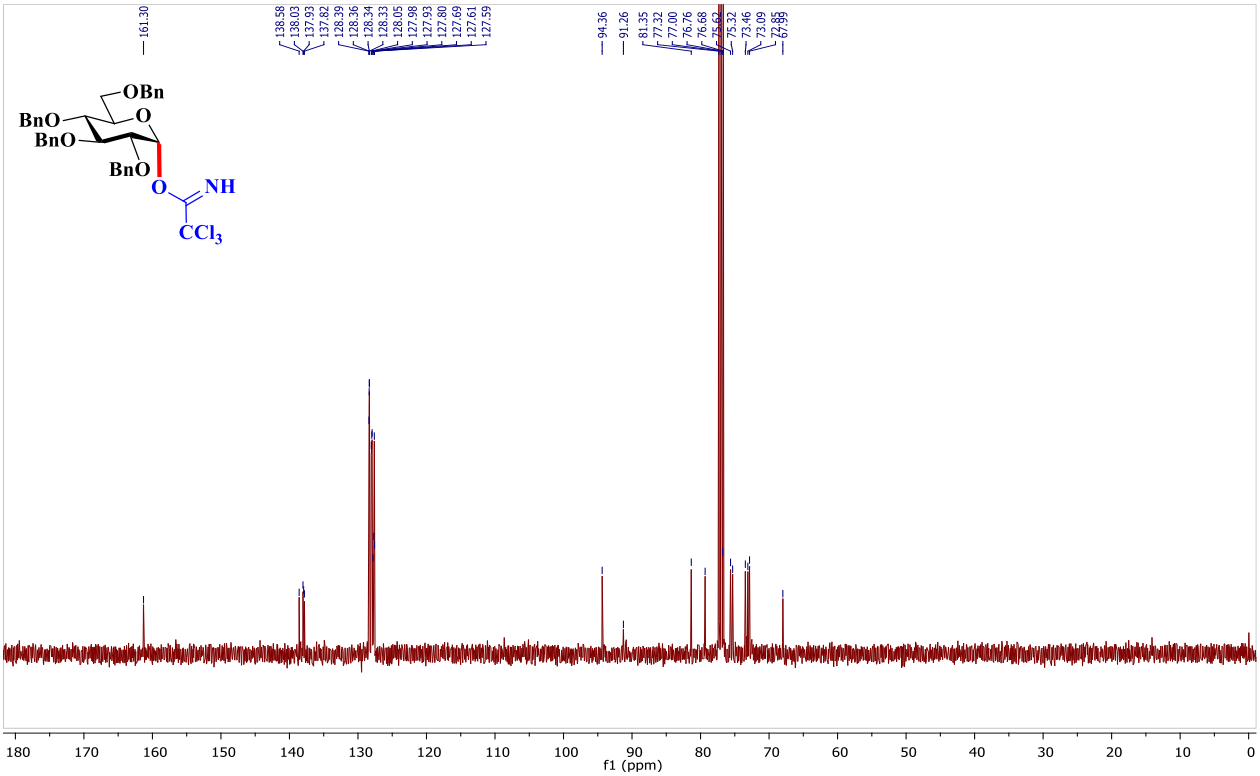
^{19}F {^{1}H} NMR spectrum of compound - catalyst G (471 MHz, DMSO-*d_6*)



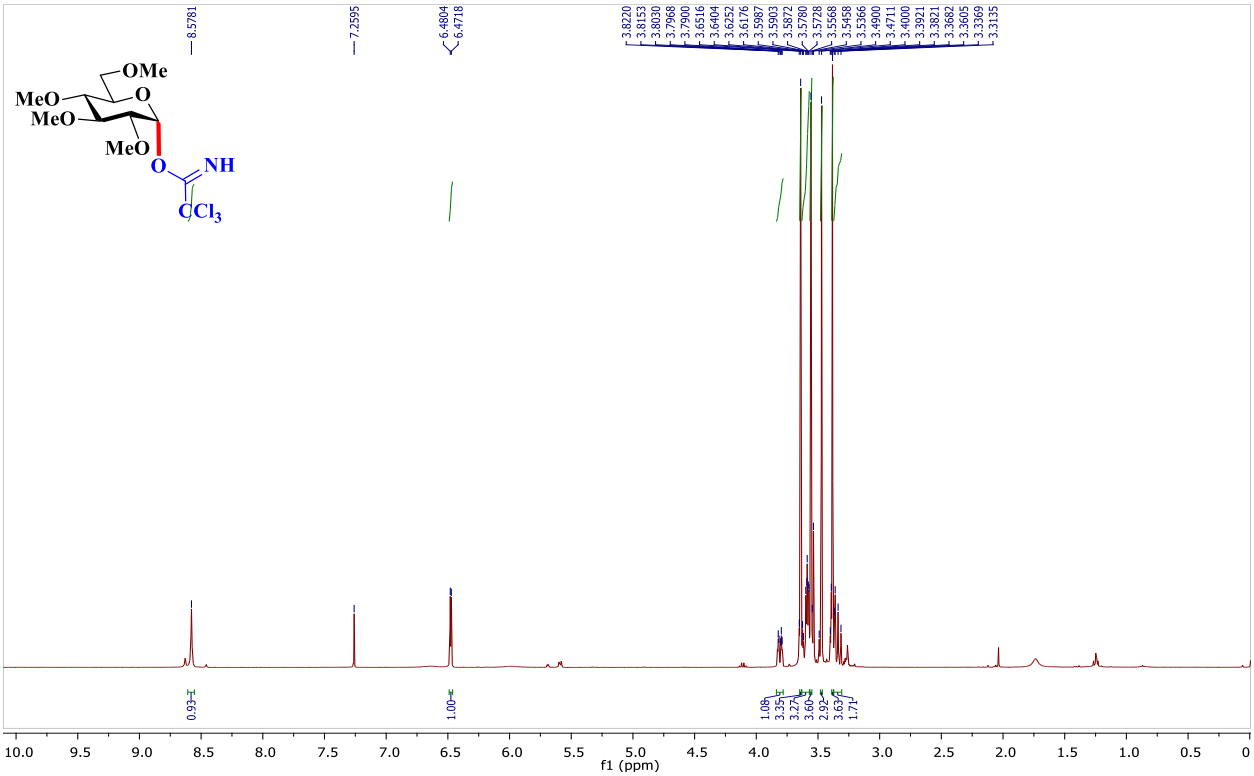
^{1}H NMR spectrum of compound 1a (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR spectrum of compound 1a (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 1b (400 MHz, $CDCl_3$)



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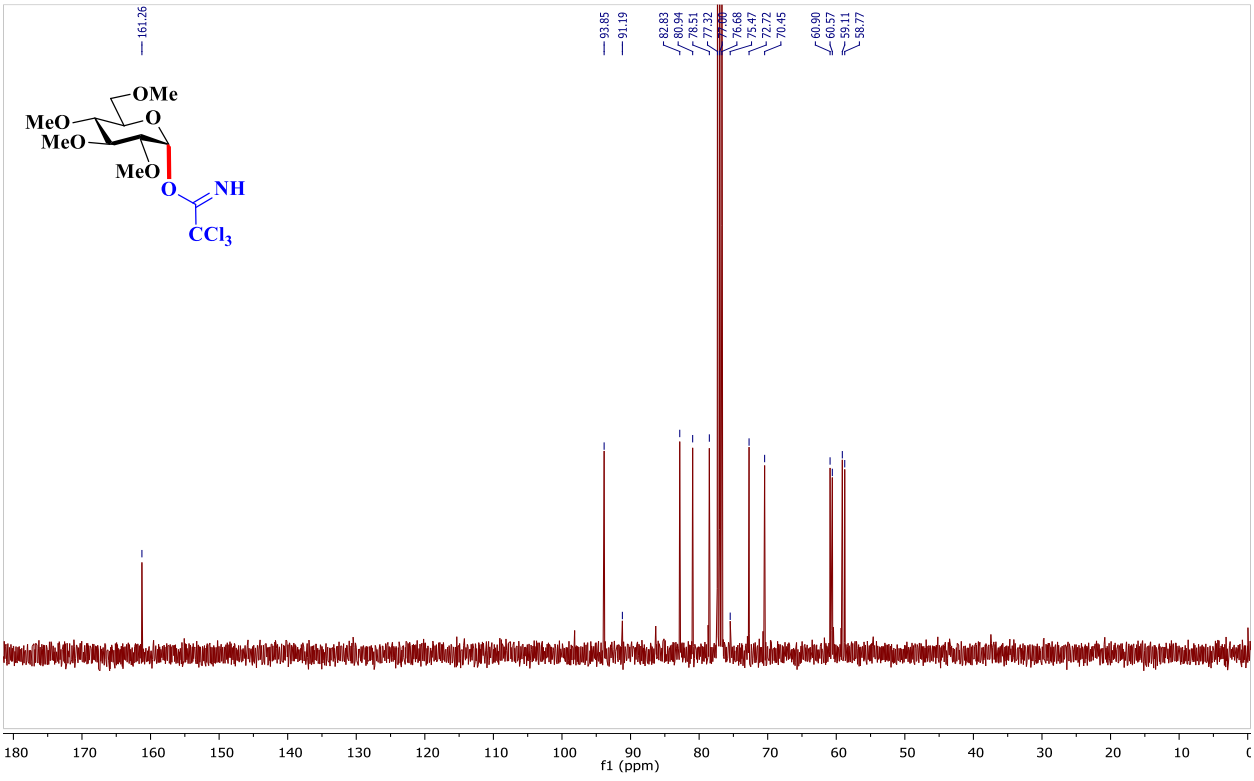
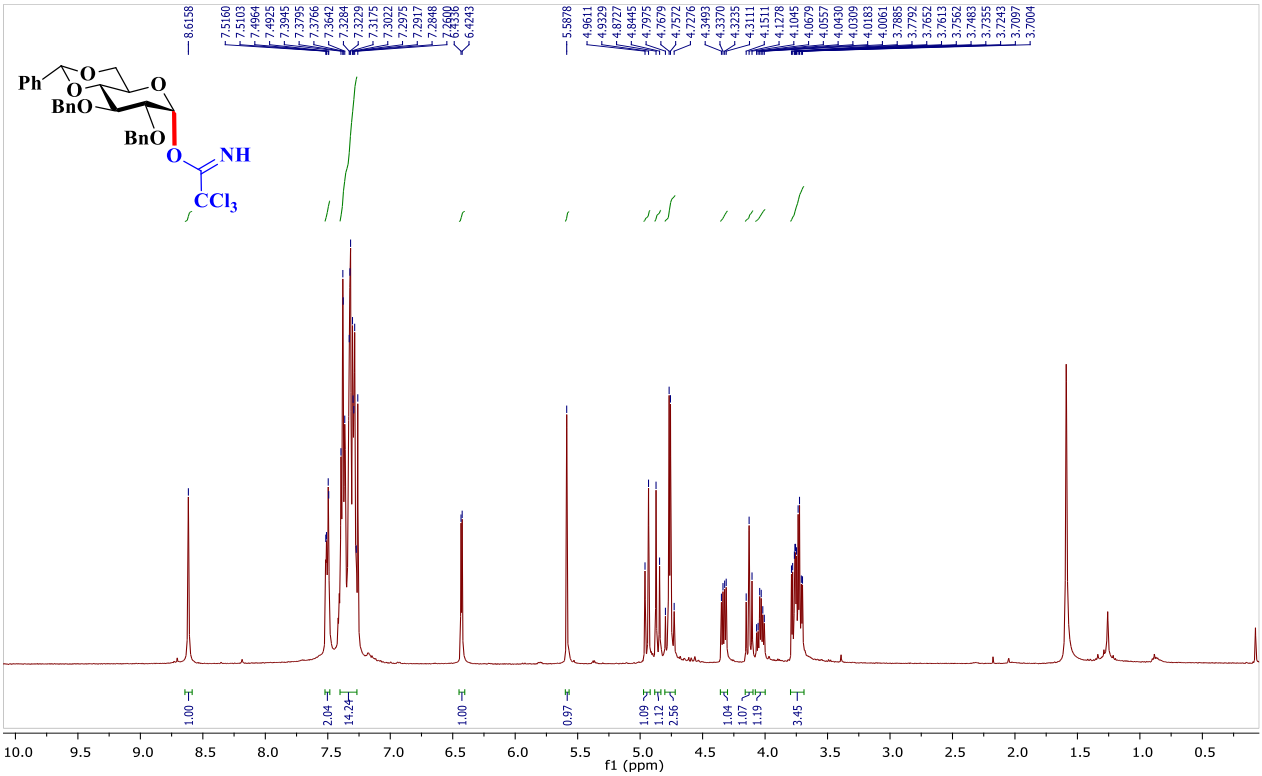


^{1}H NMR spectrum of compound 1c (400 MHz, $CDCl_3$)



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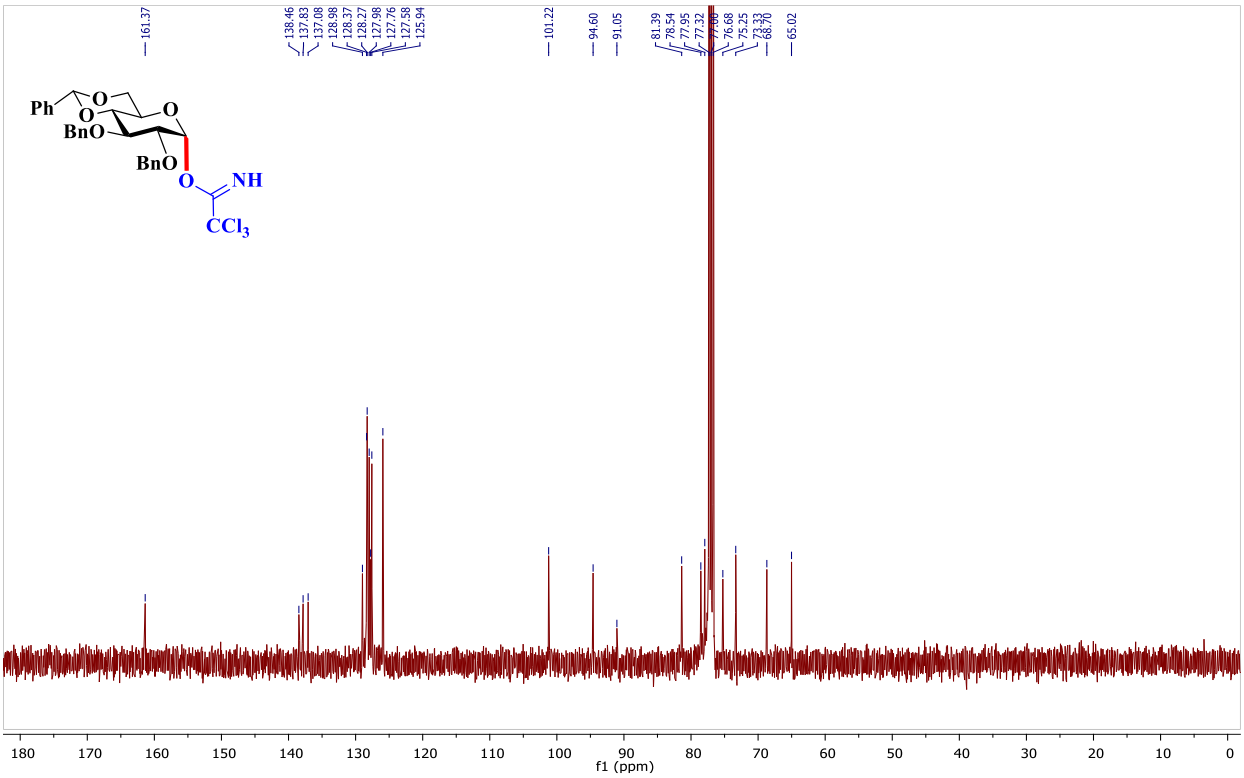

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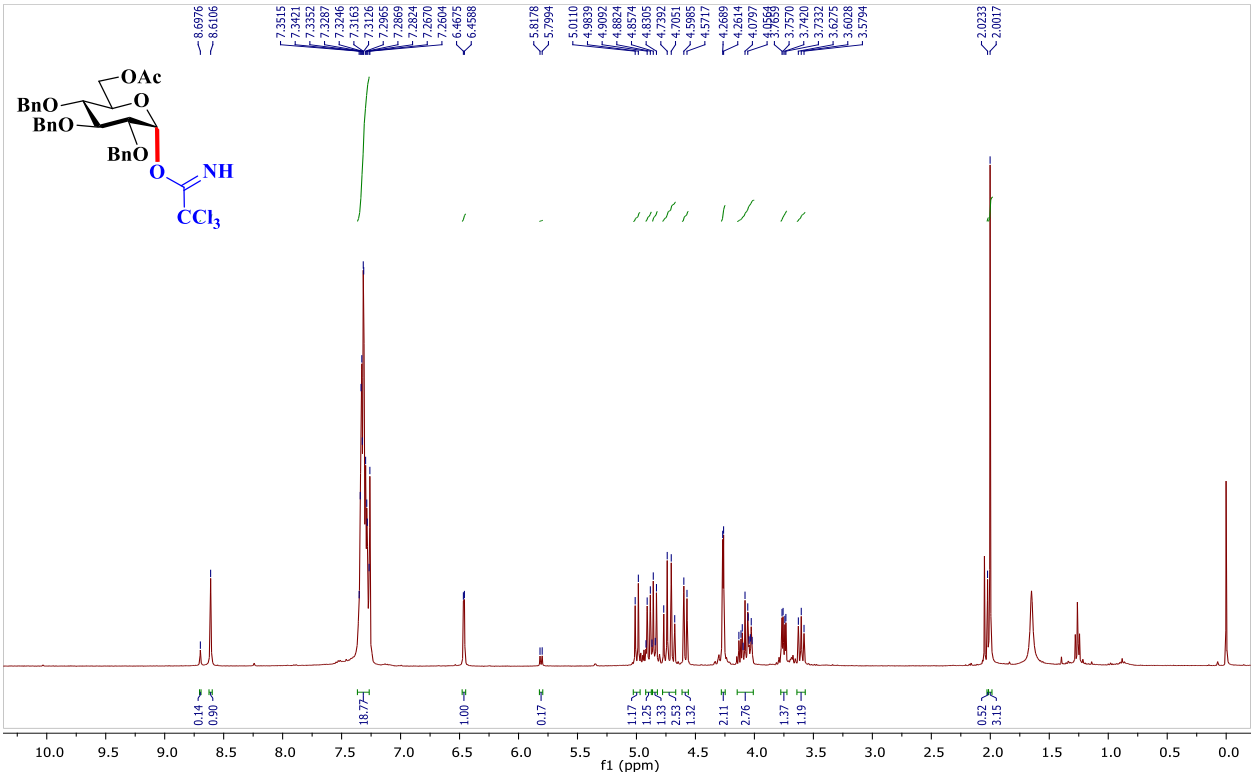
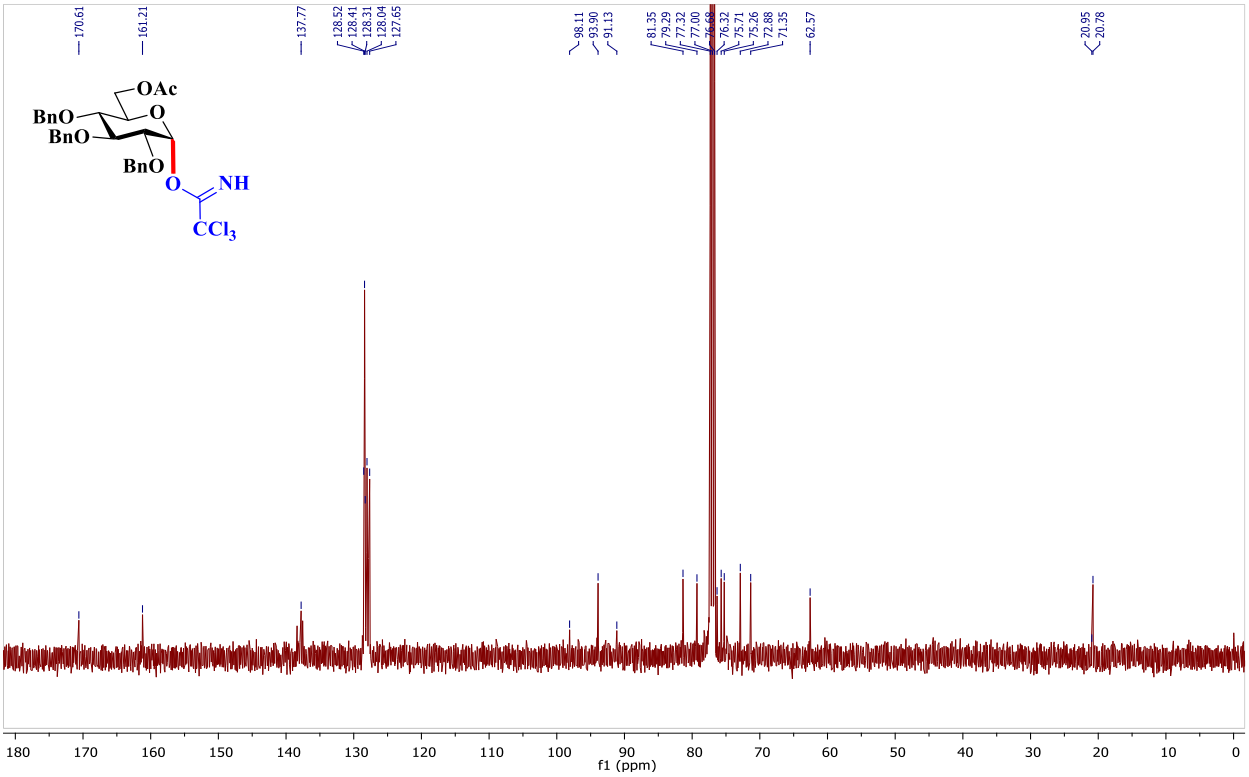
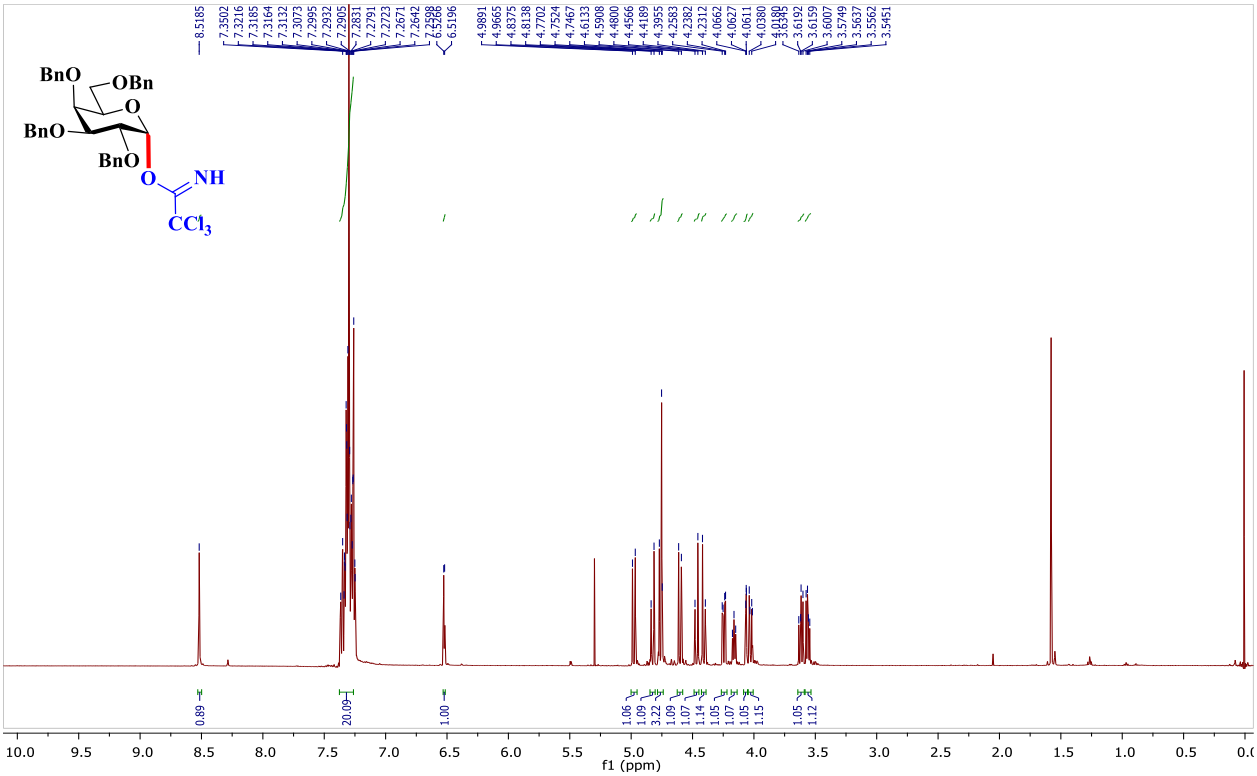


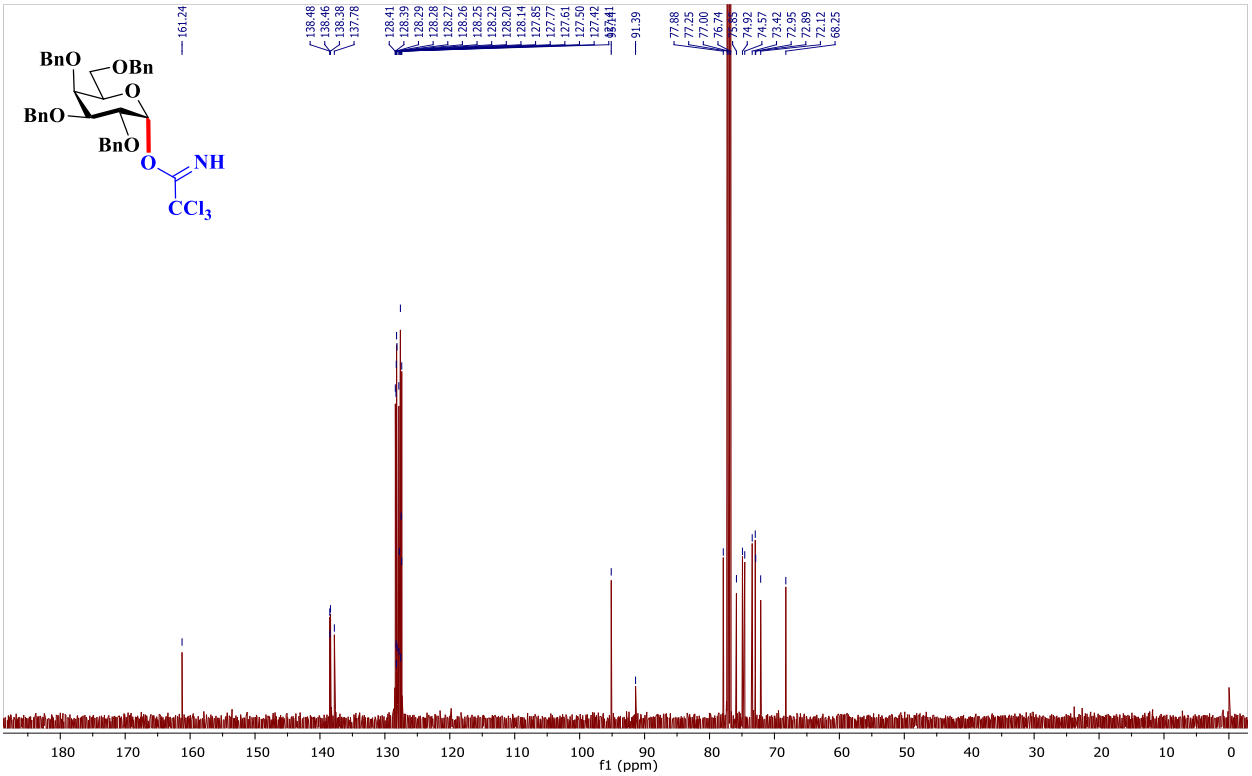
^{13}C {^{1}H}NMR spectrum of compound 1d (100 MHz, $CDCl_3$)



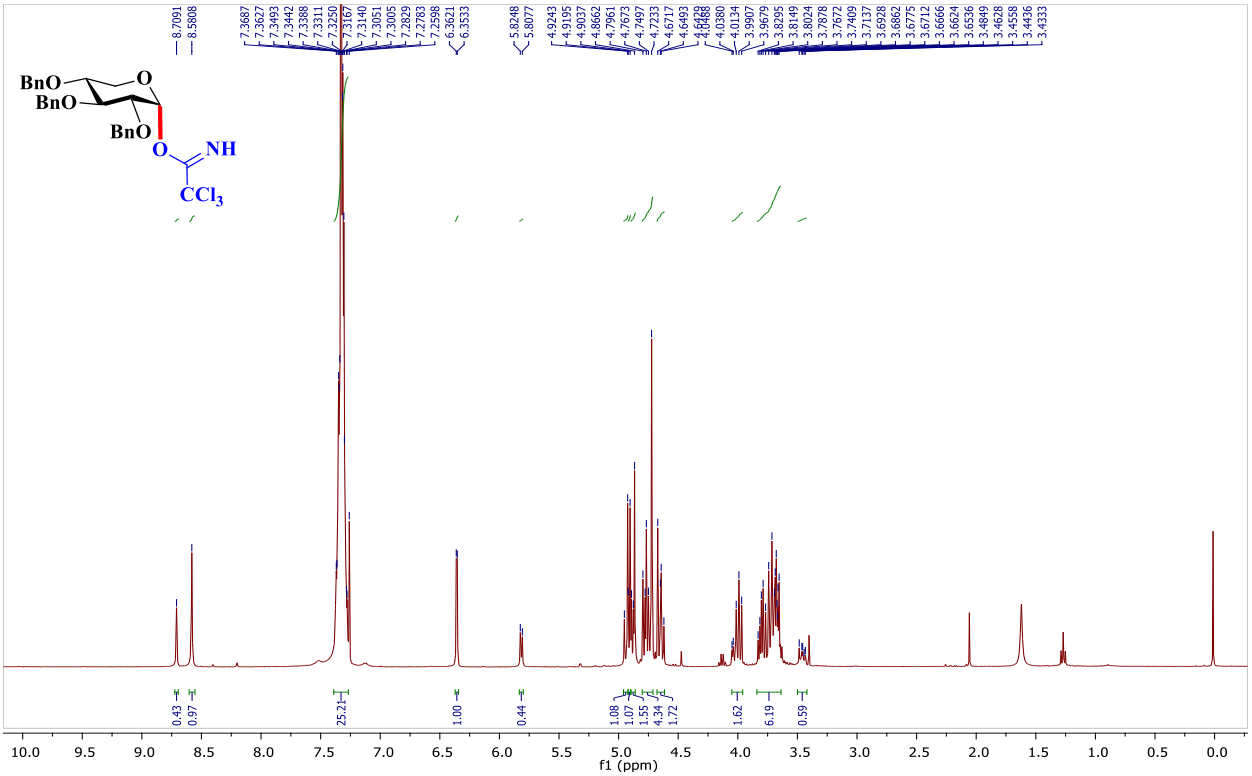
^{1}H NMR spectrum of compound 1e (500 MHz, $CDCl_3$)



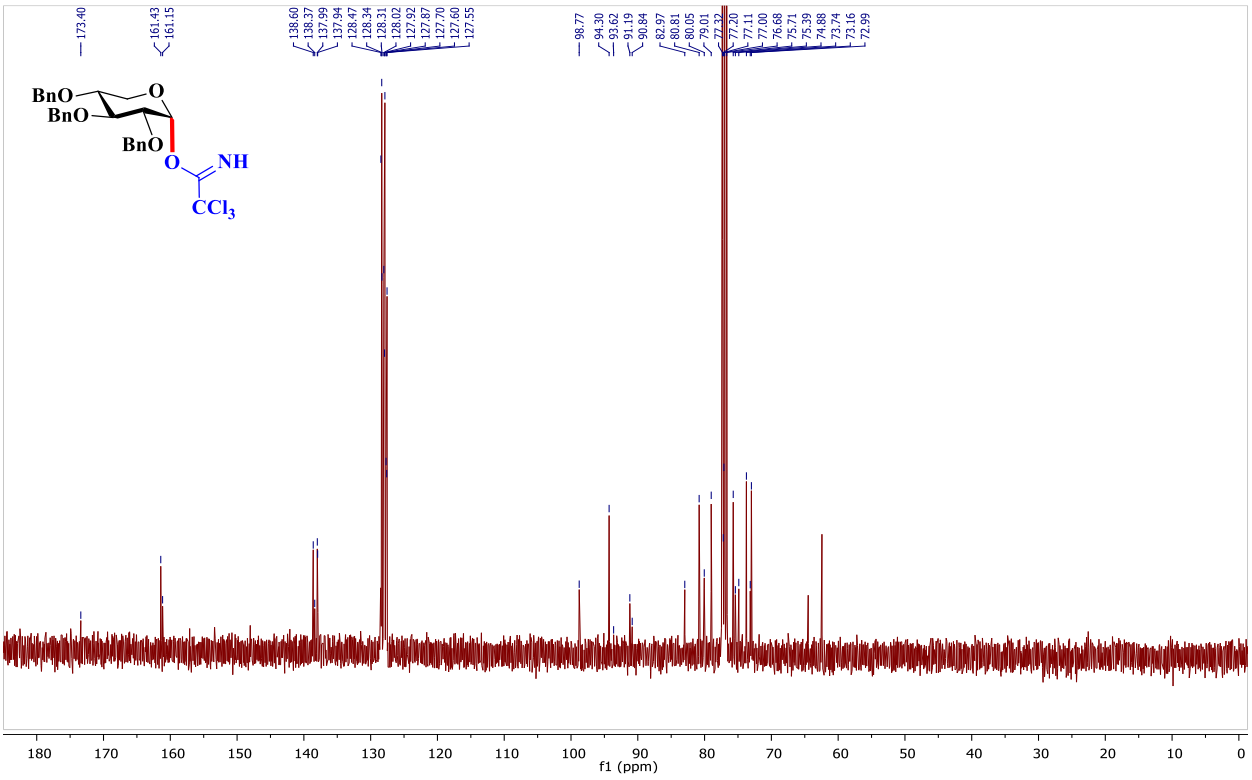
^{13}C NMR spectrum of compound 1e (125 MHz, $CDCl_3$)



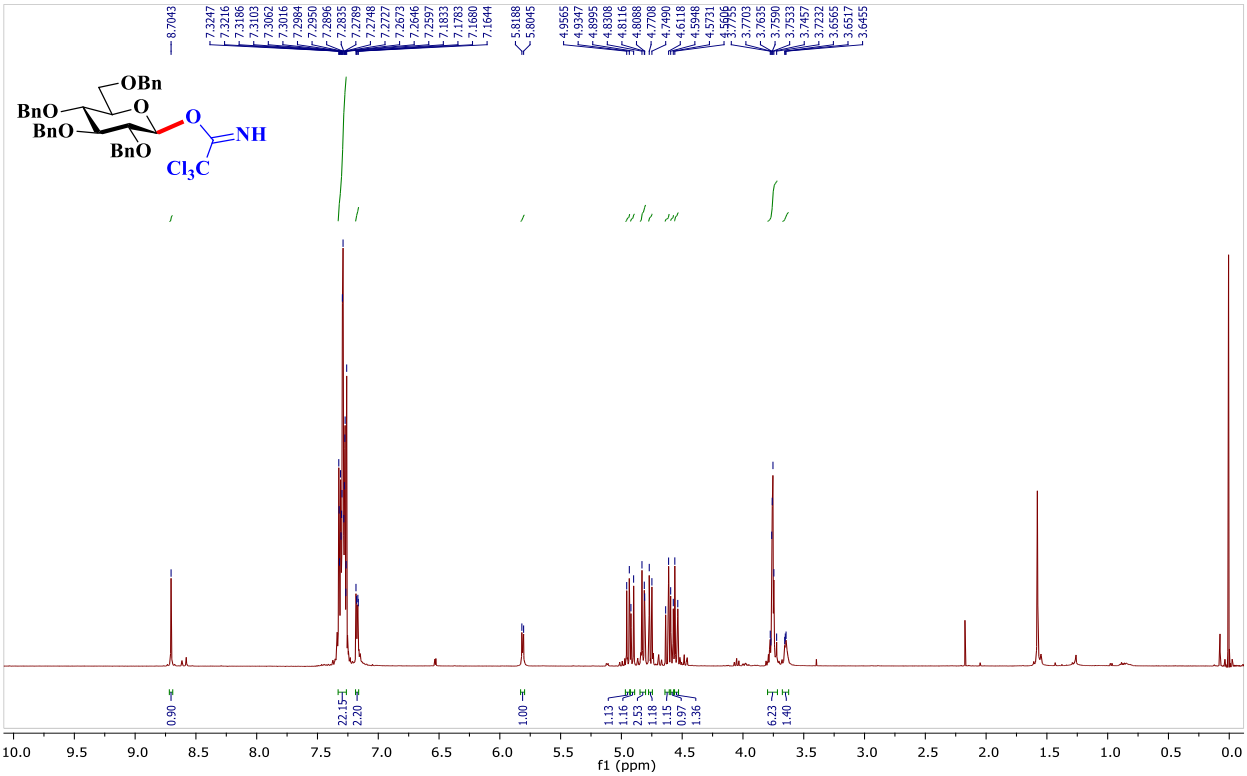
^{1}H NMR spectrum of compound 1f (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound 1f (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 1g (500 MHz, $CDCl_3$)



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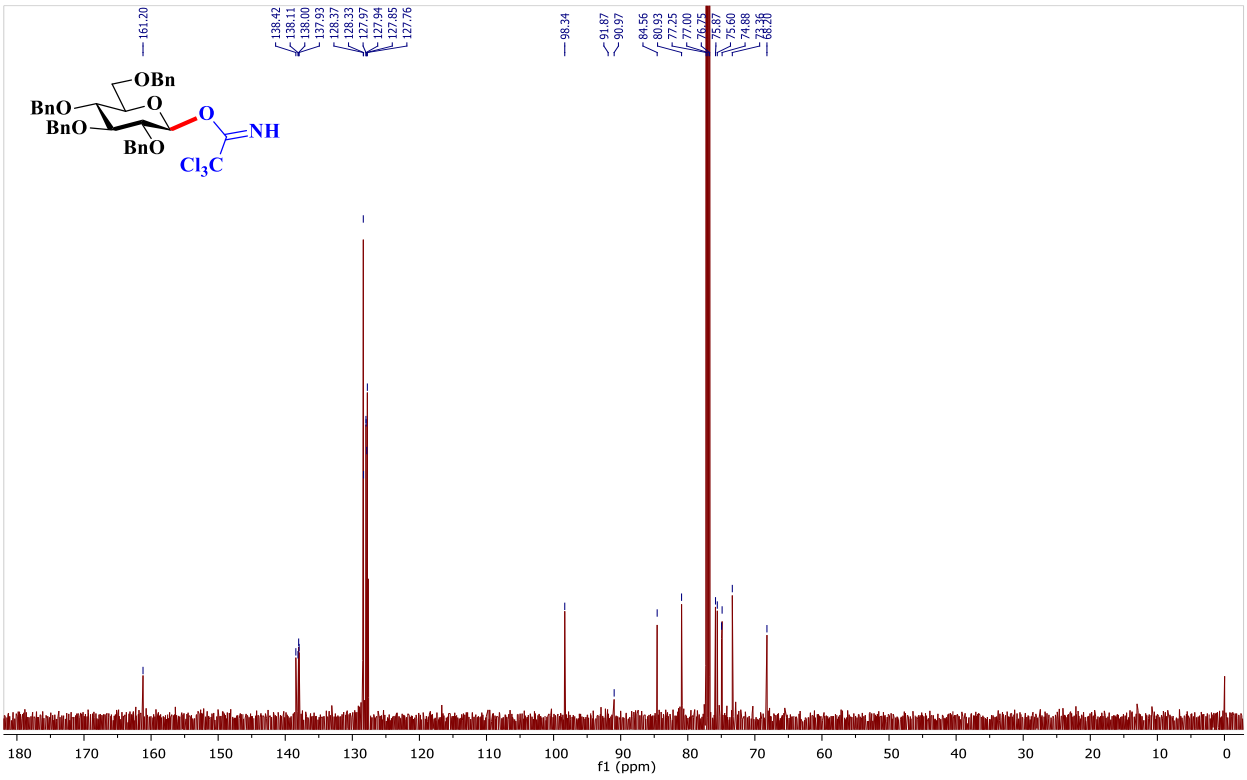
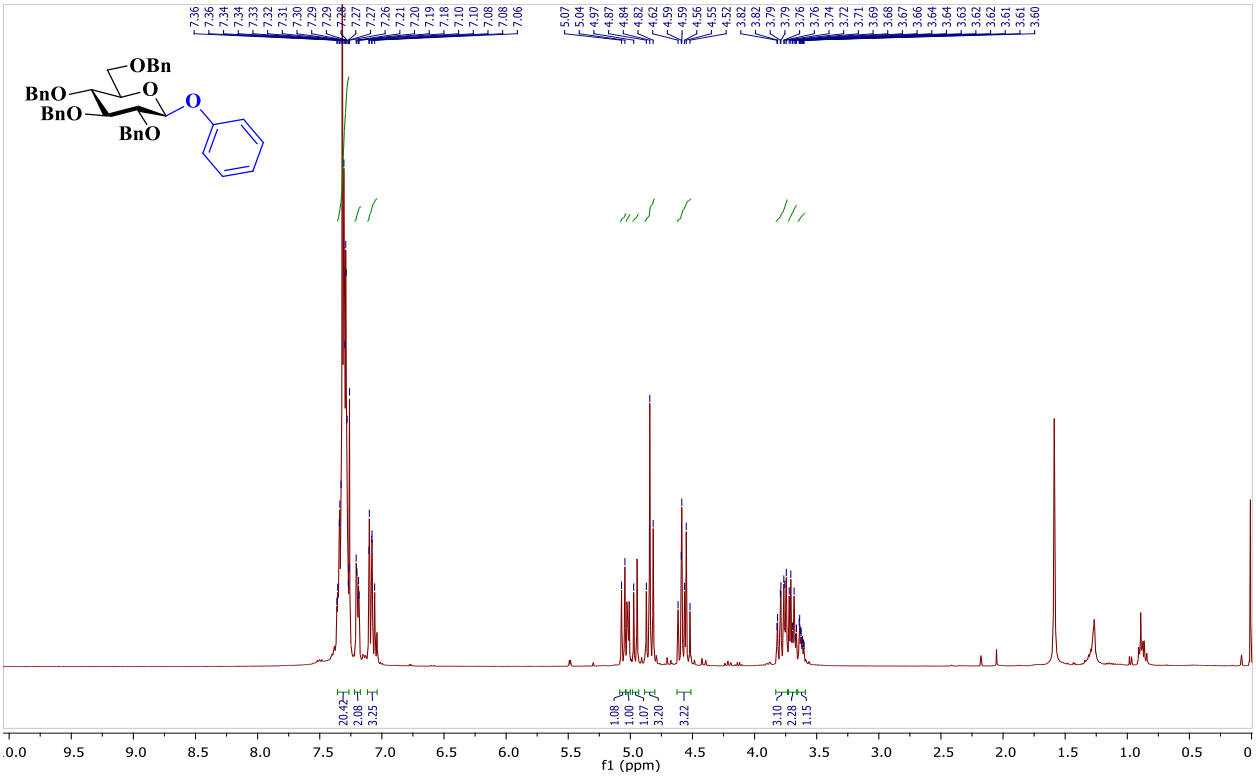
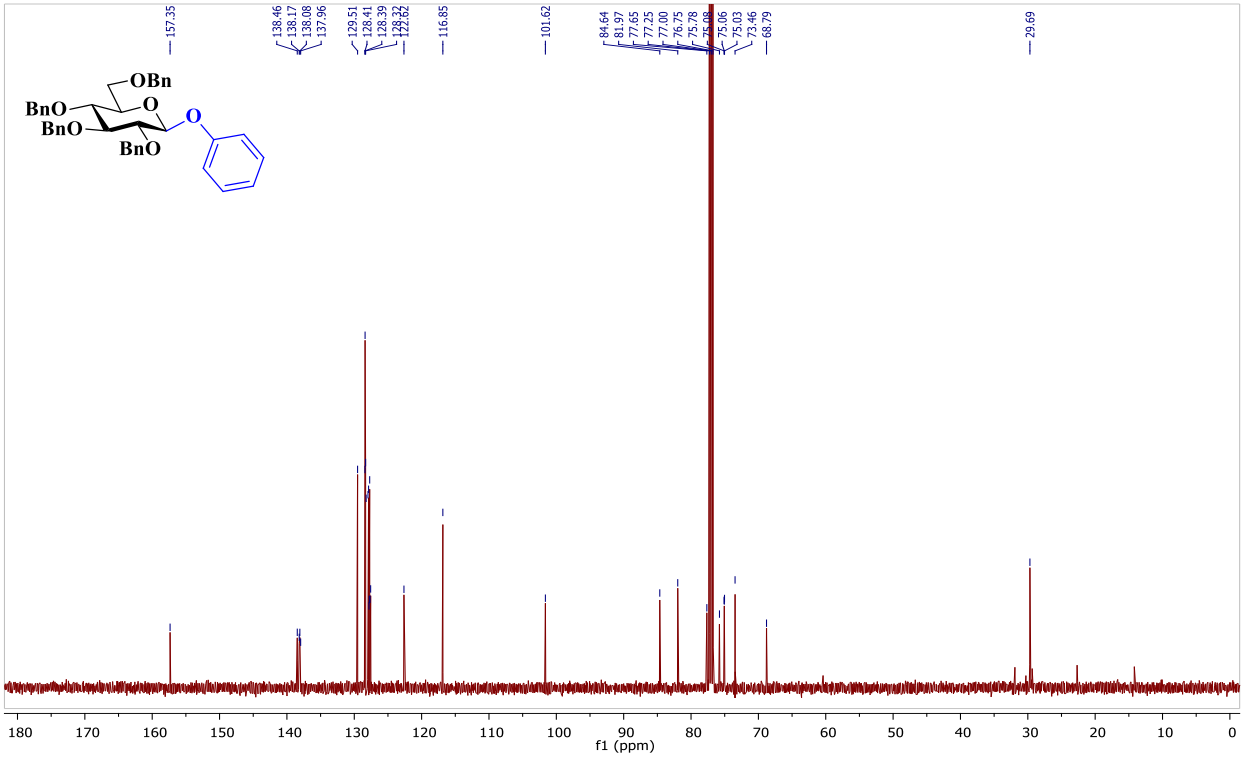


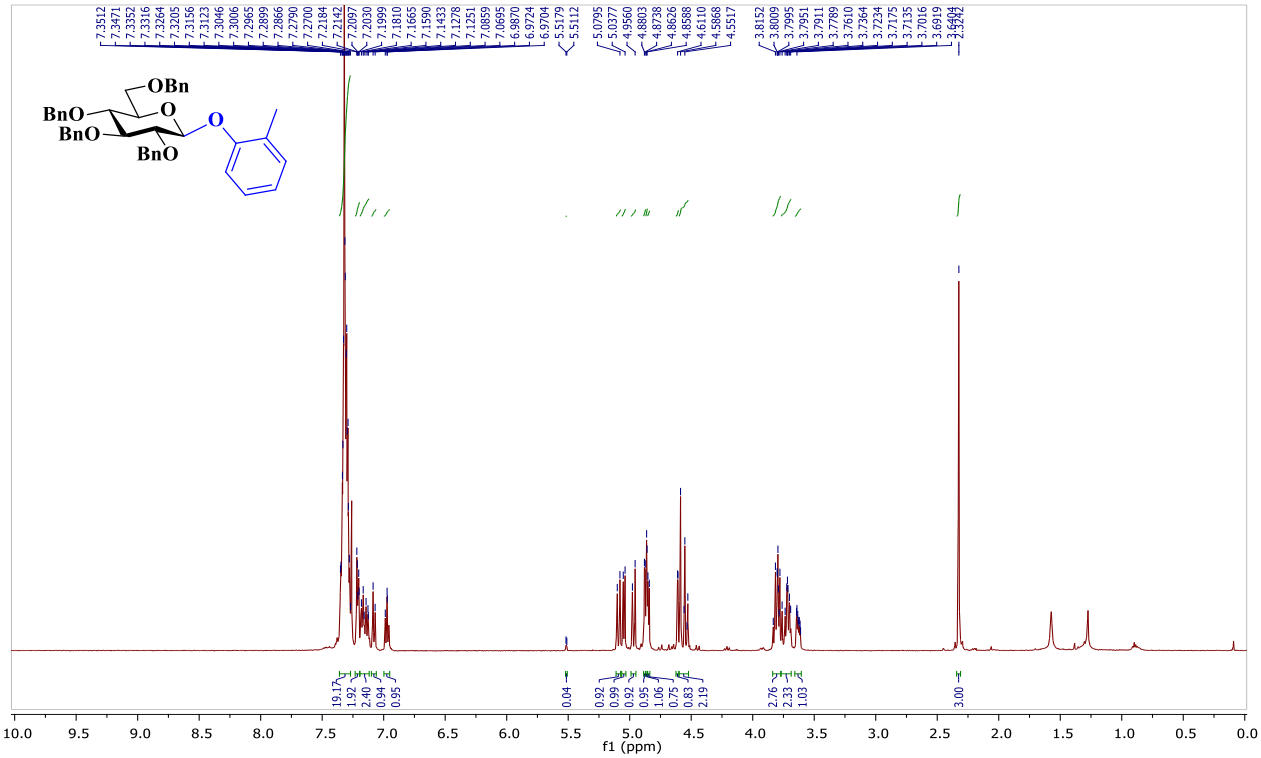
^{1}H NMR spectrum of compound 3a (500 MHz, $CDCl_3$)



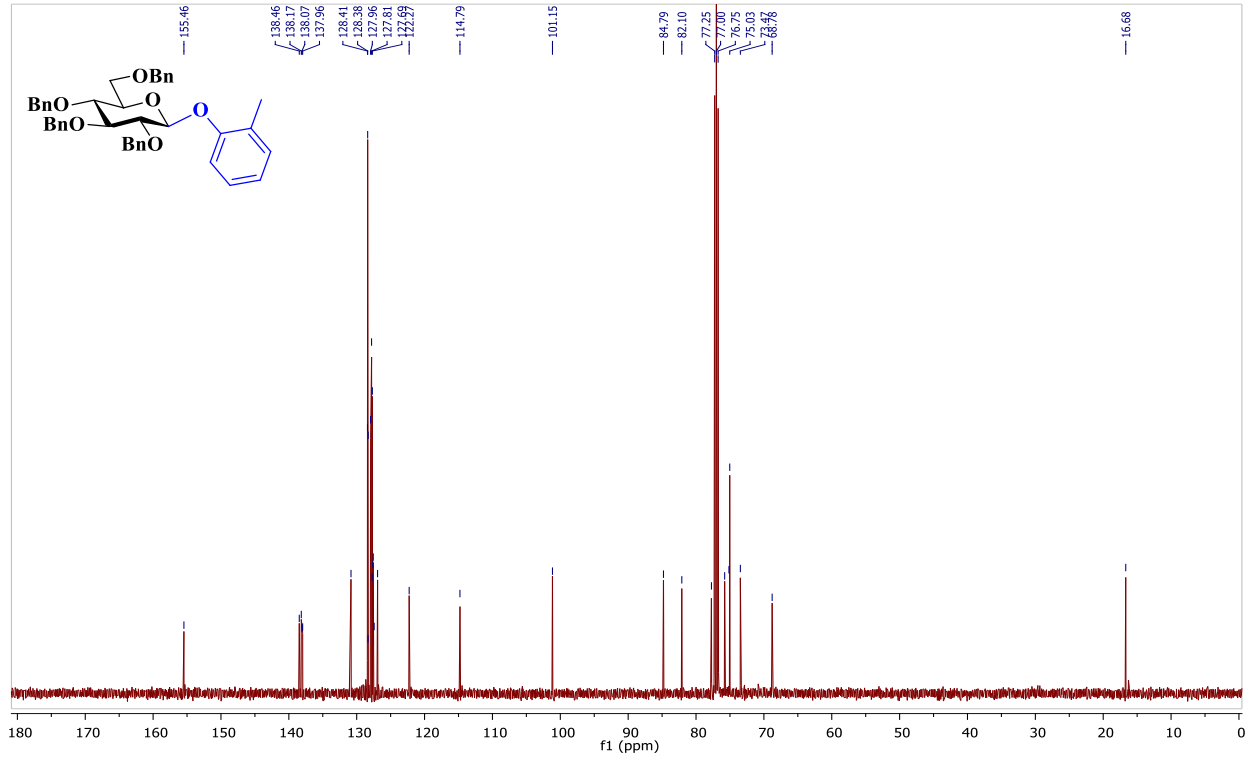
^{13}C {^{1}H} NMR spectrum of compound 3a (125 MHz, $CDCl_3$)



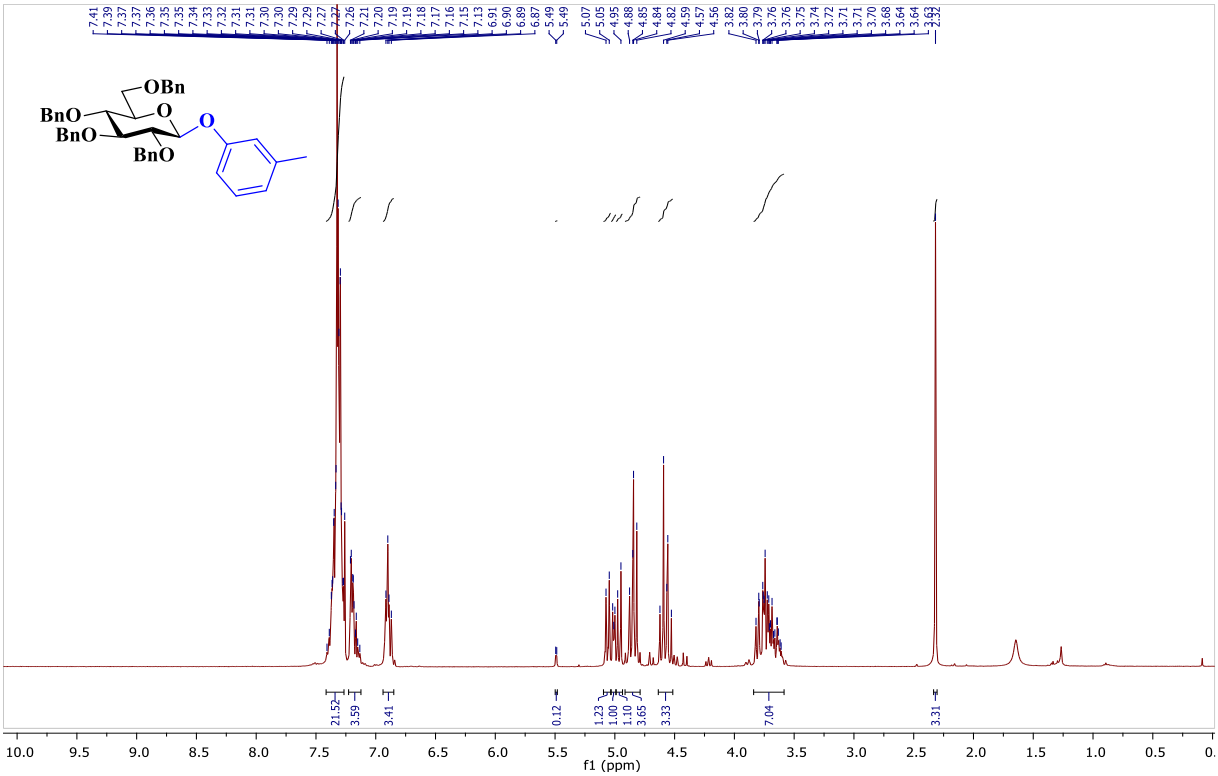
^{1}H NMR spectrum of compound 3b (500 MHz, $CDCl_3$)



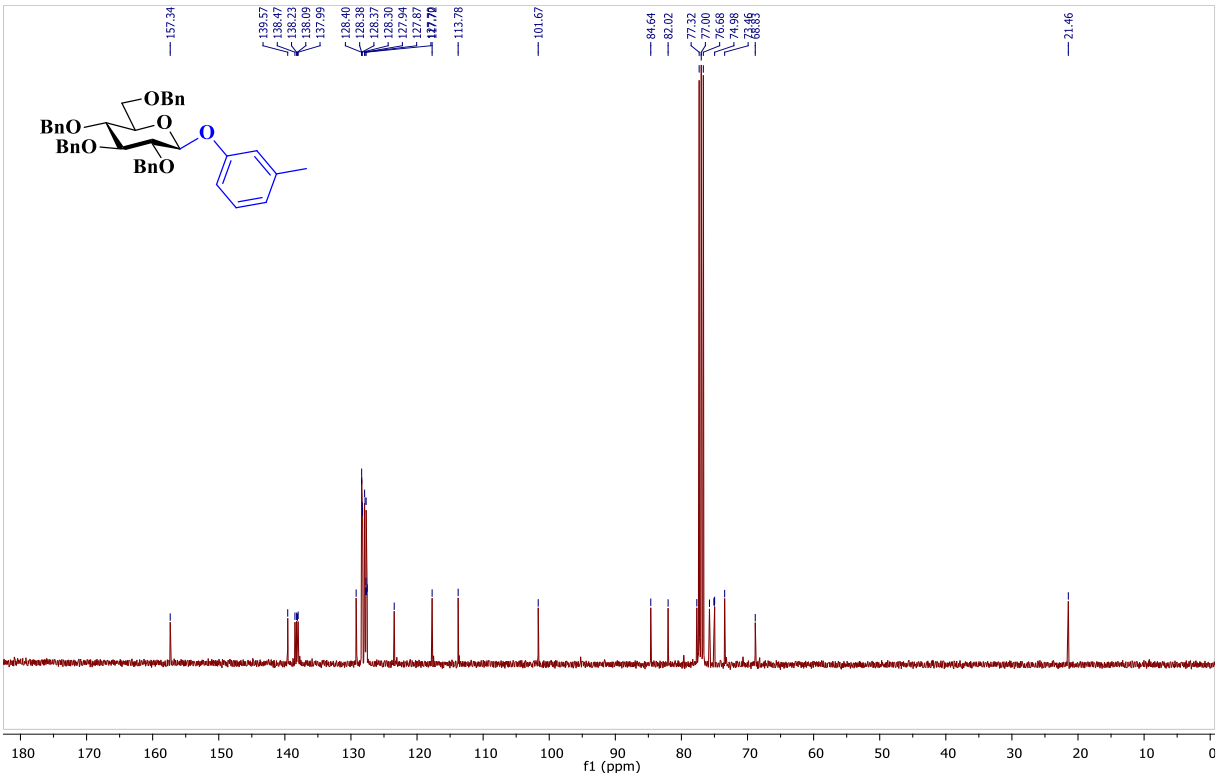
^{13}C {^{1}H} NMR spectrum of compound 3b (125 MHz, $CDCl_3$)



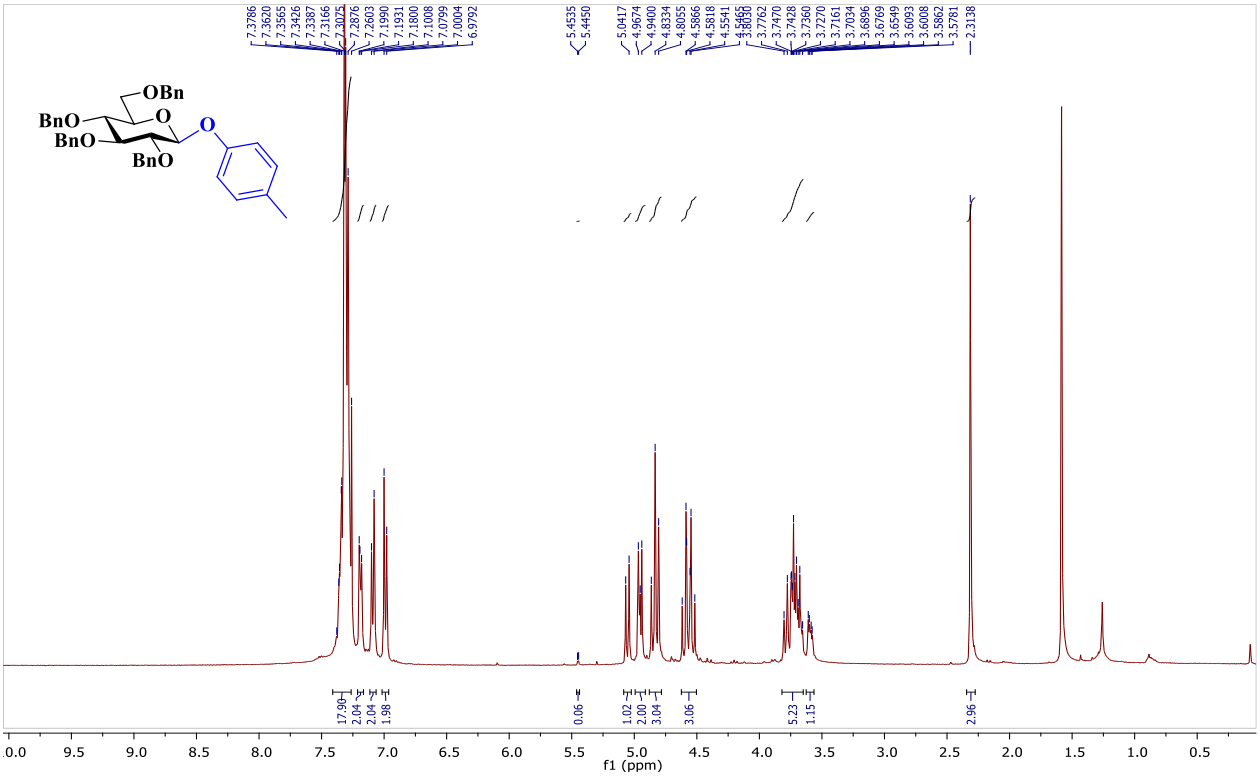
^{1}H NMR spectrum of compound 3c (500 MHz, $CDCl_3$)



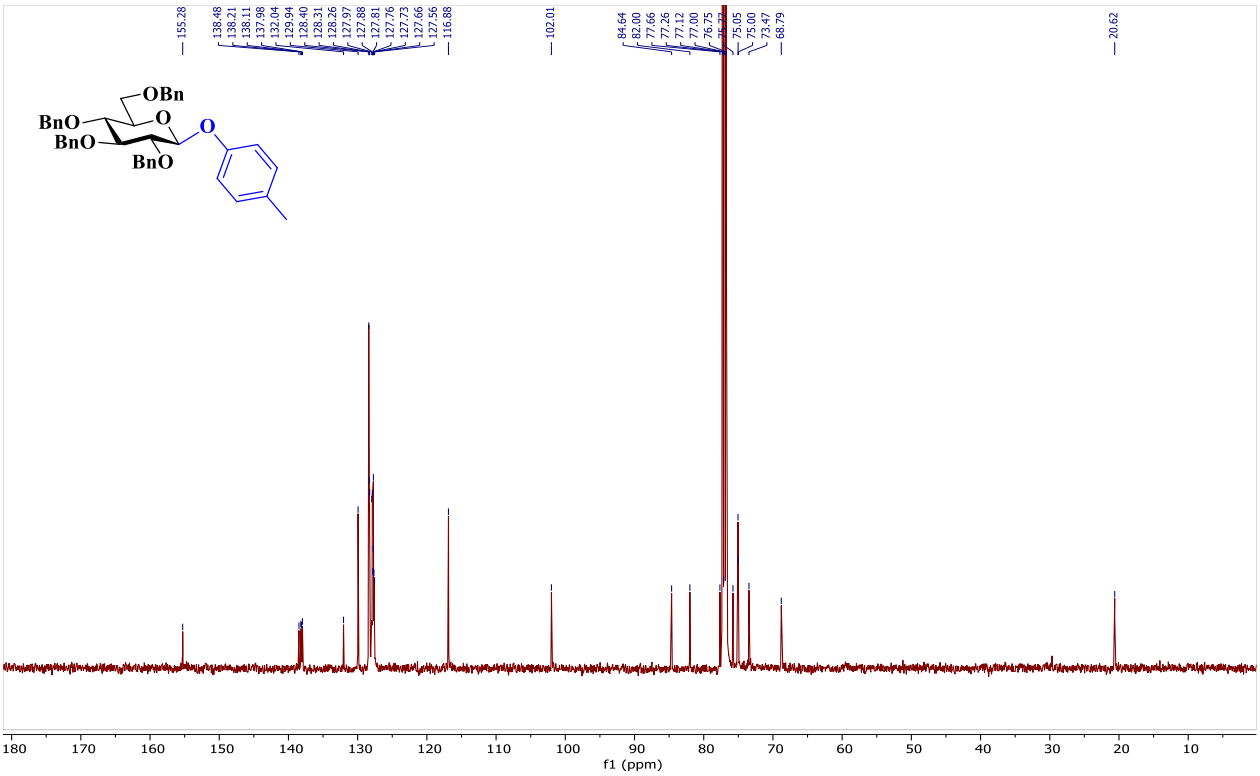
^{13}C {^{1}H} NMR spectrum of compound 3c (125 MHz, $CDCl_3$)



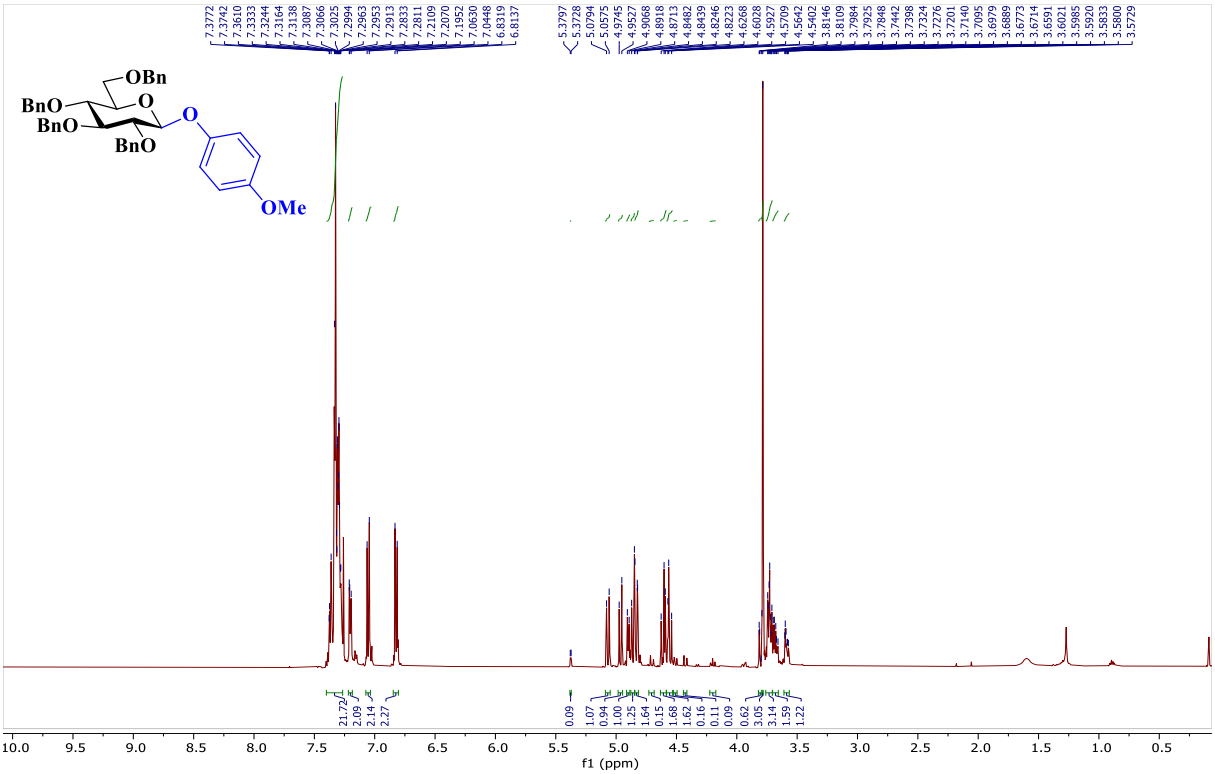
^{1}H NMR spectrum of compound 3d (400 MHz, $CDCl_3$)



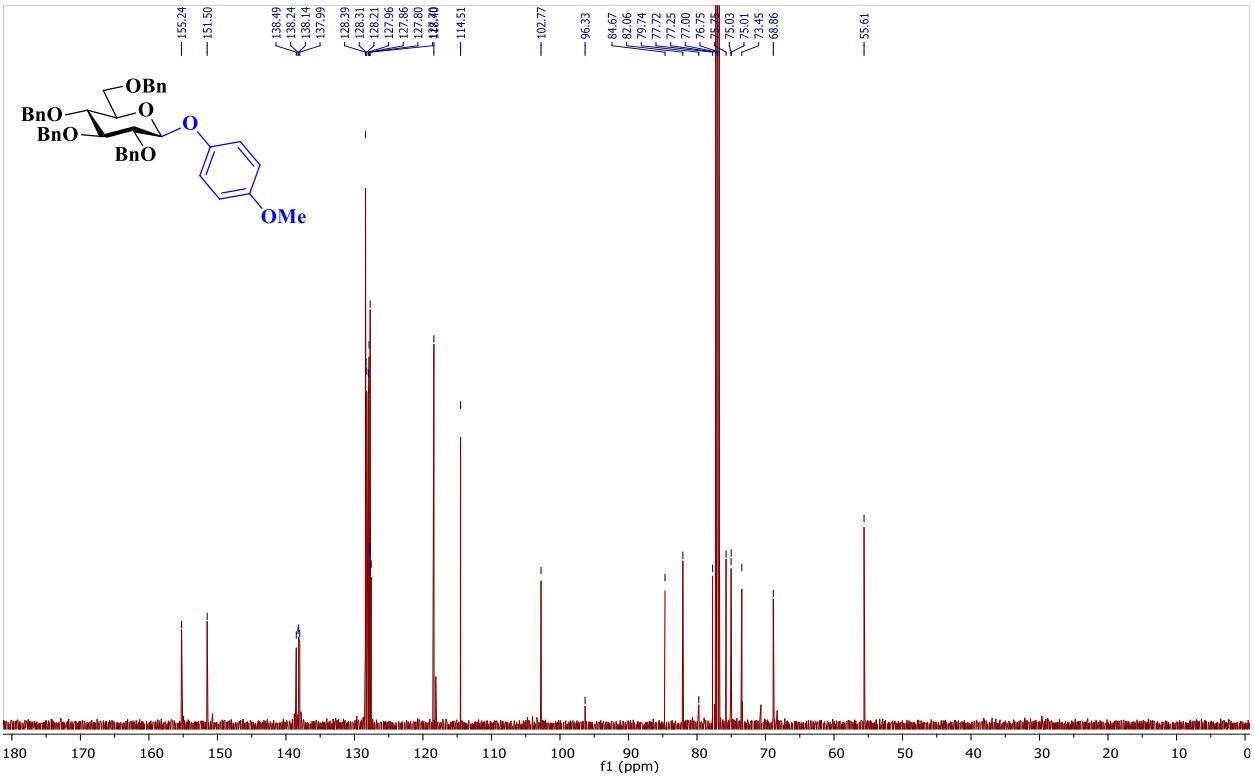
^{13}C {^{1}H} NMR spectrum of compound 3d (100 MHz, $CDCl_3$)



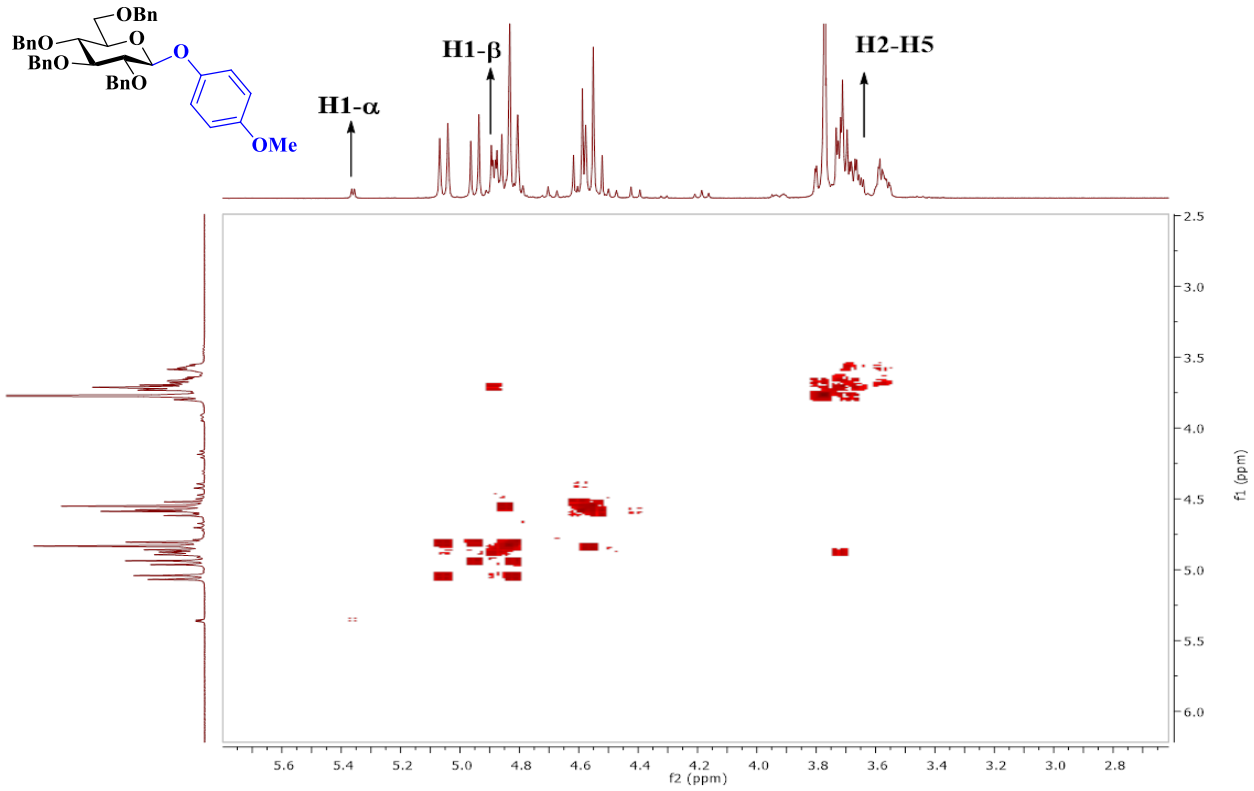
^{1}H NMR spectrum of compound 3e (500 MHz, $CDCl_3$)



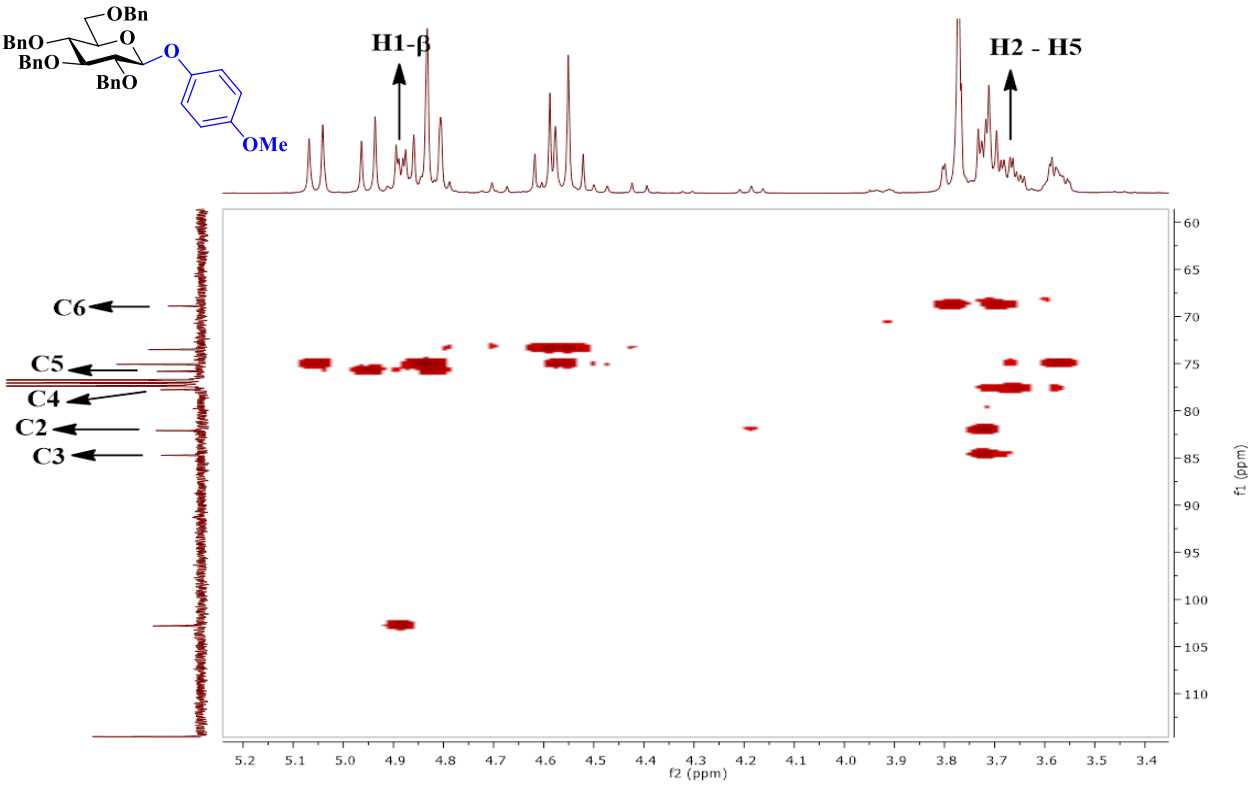
^{13}C {^{1}H} NMR spectrum of compound 3e (125 MHz, $CDCl_3$)



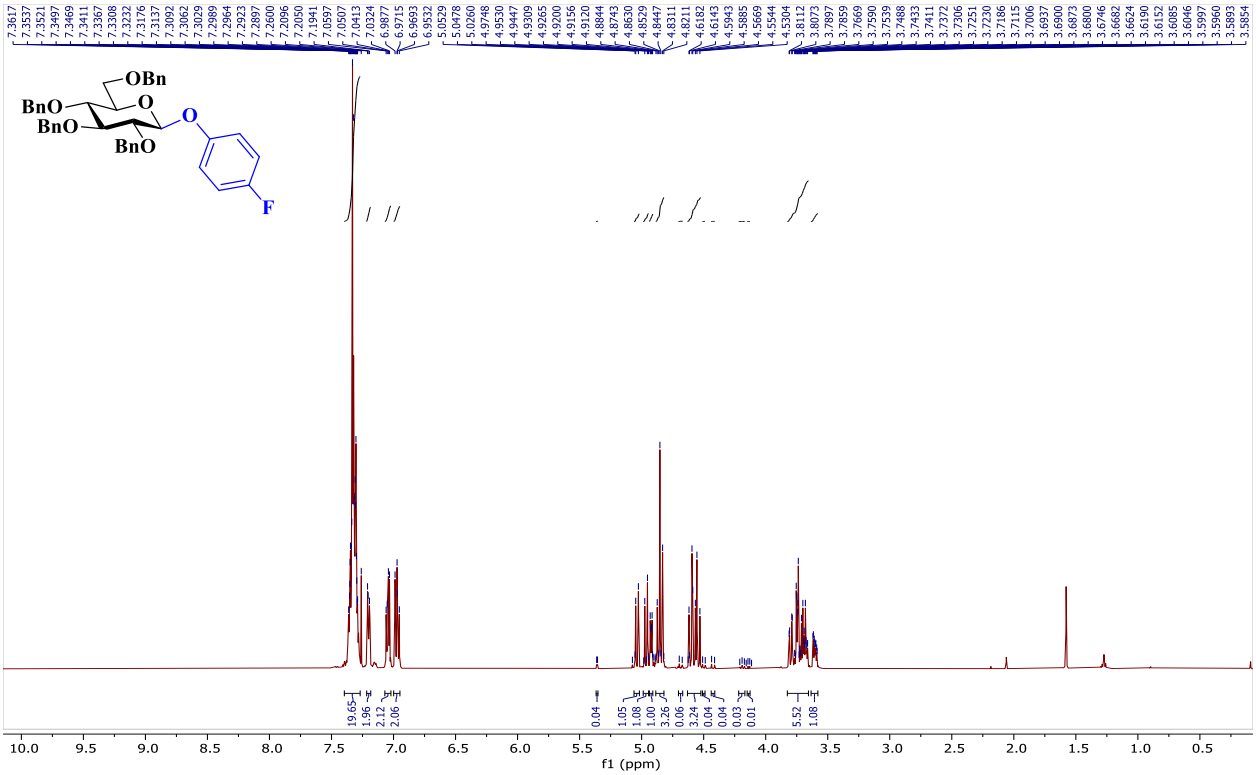
COSY spectrum of compound 3e



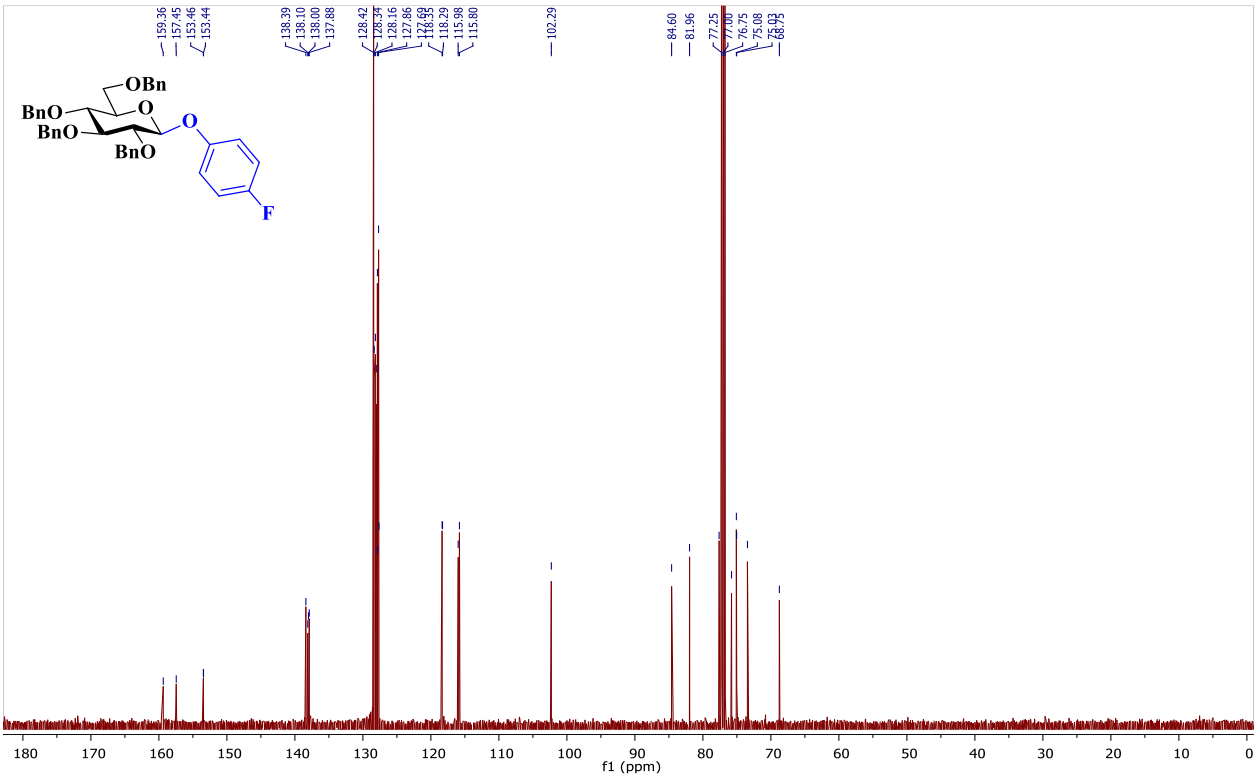
HSQC spectrum of compound 3e



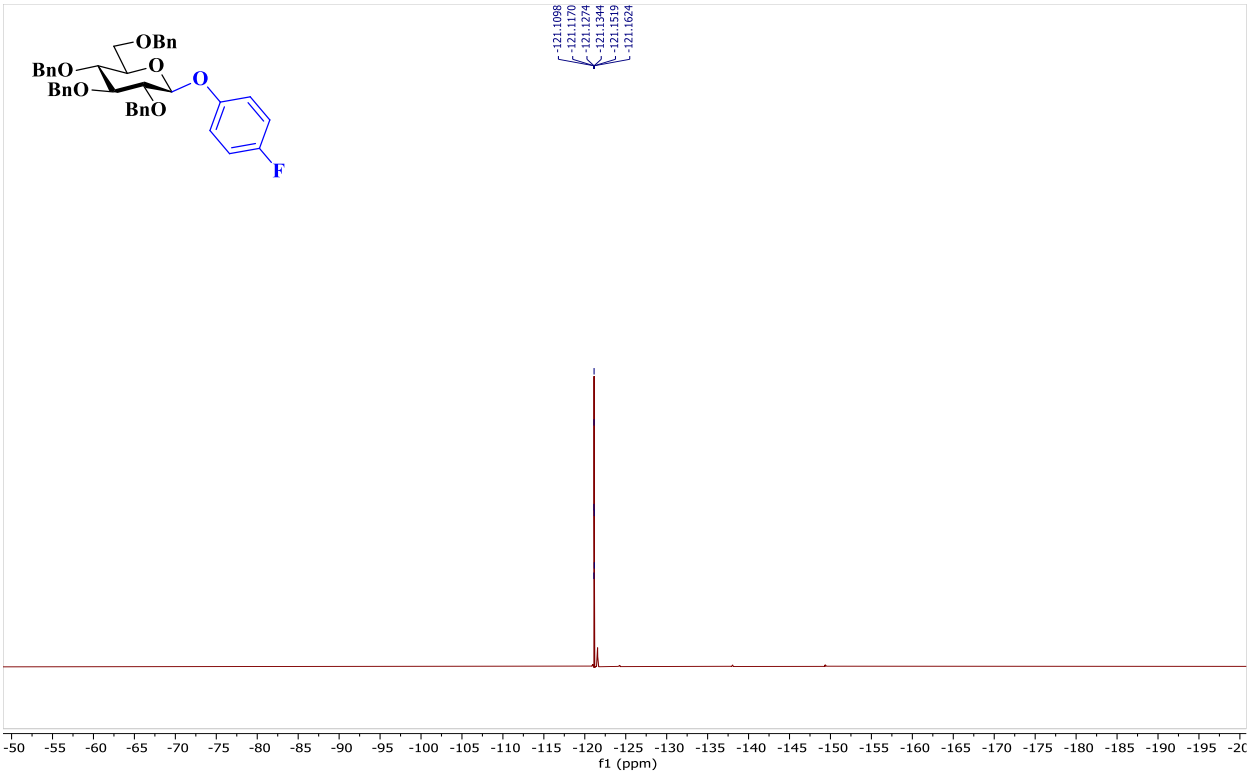
^{1}H NMR spectrum of compound 3f (500 MHz, $CDCl_3$)



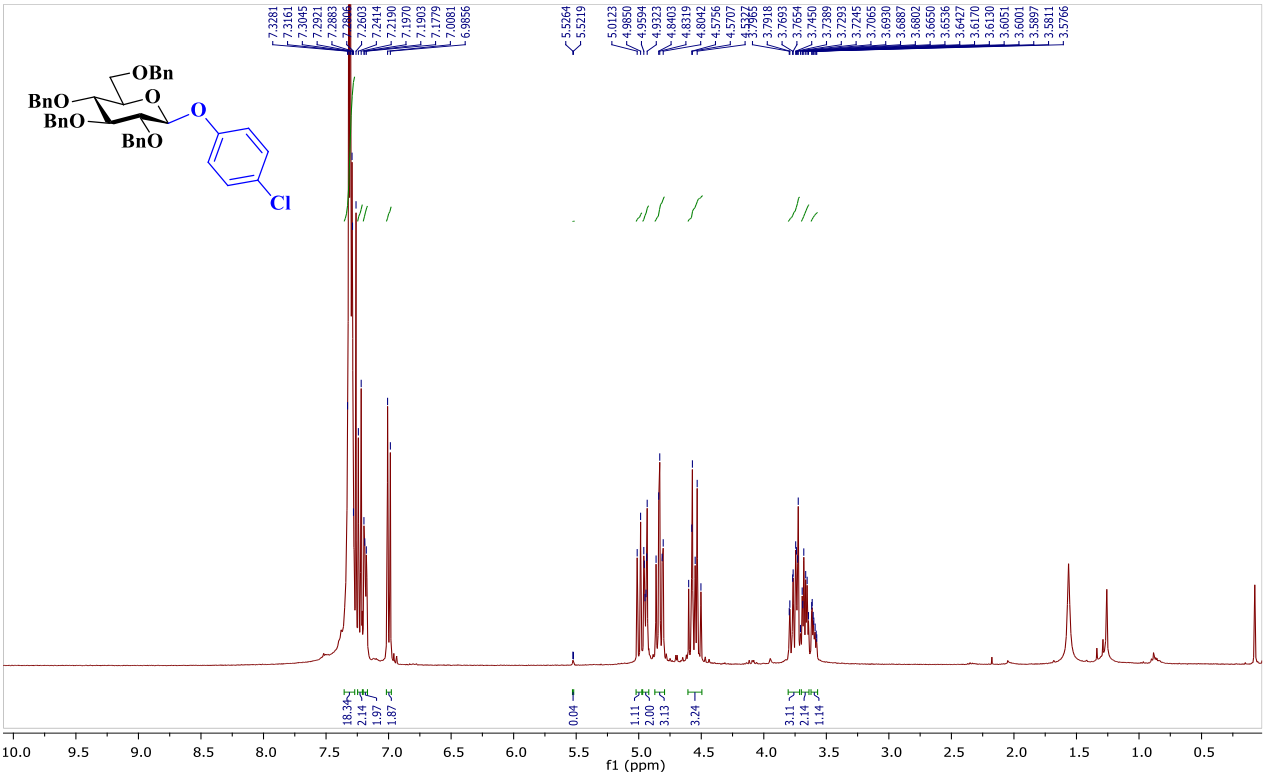
^{13}C {^{1}H} NMR spectrum of compound 3f (125 MHz, $CDCl_3$)



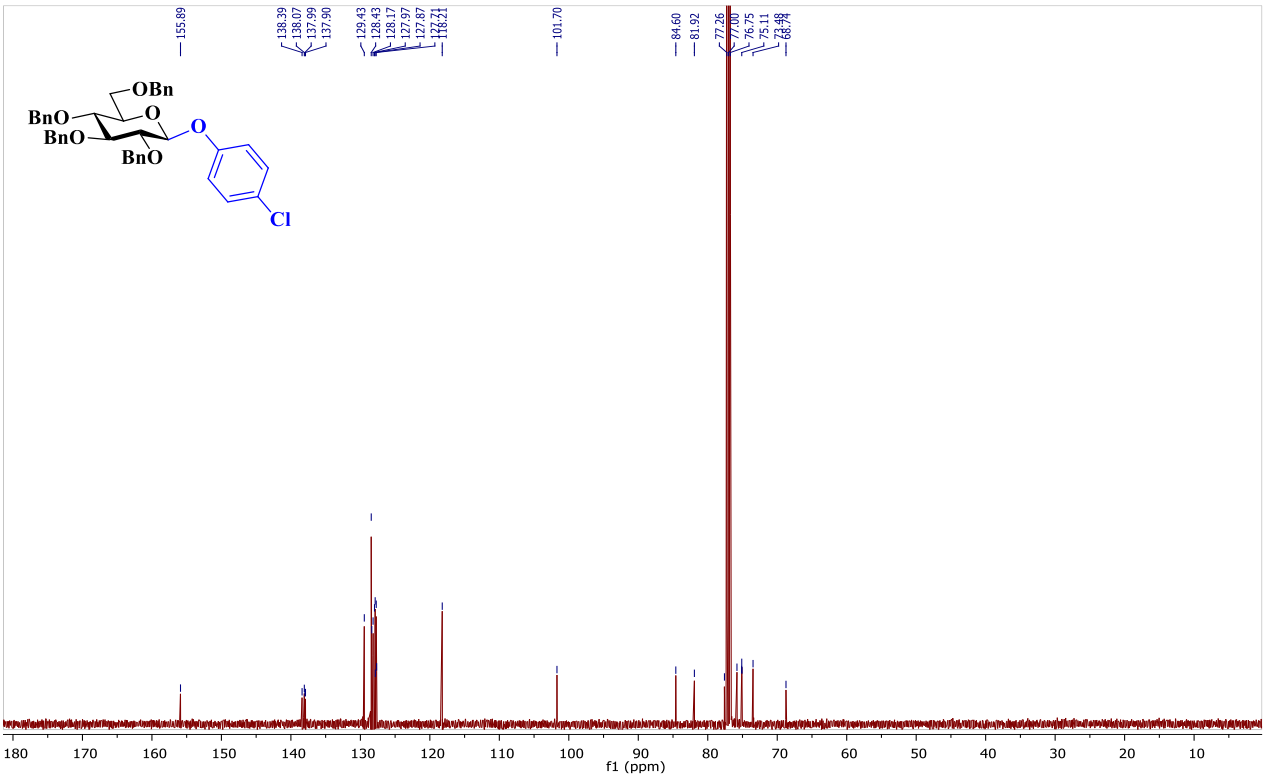
$^{19}F\{1H\}$ (471 MHz) NMR spectra of 3f in $CDCl_3$



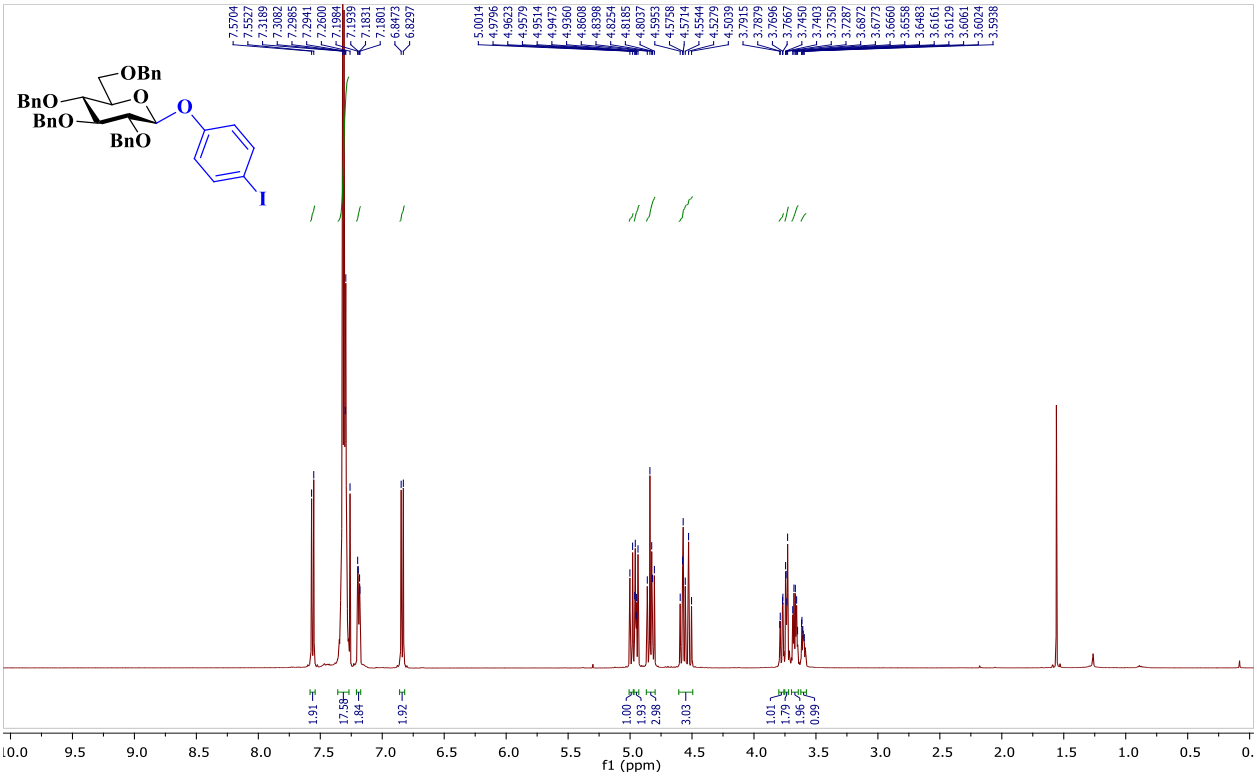
^{1}H NMR spectrum of compound 3g (500 MHz, $CDCl_3$)



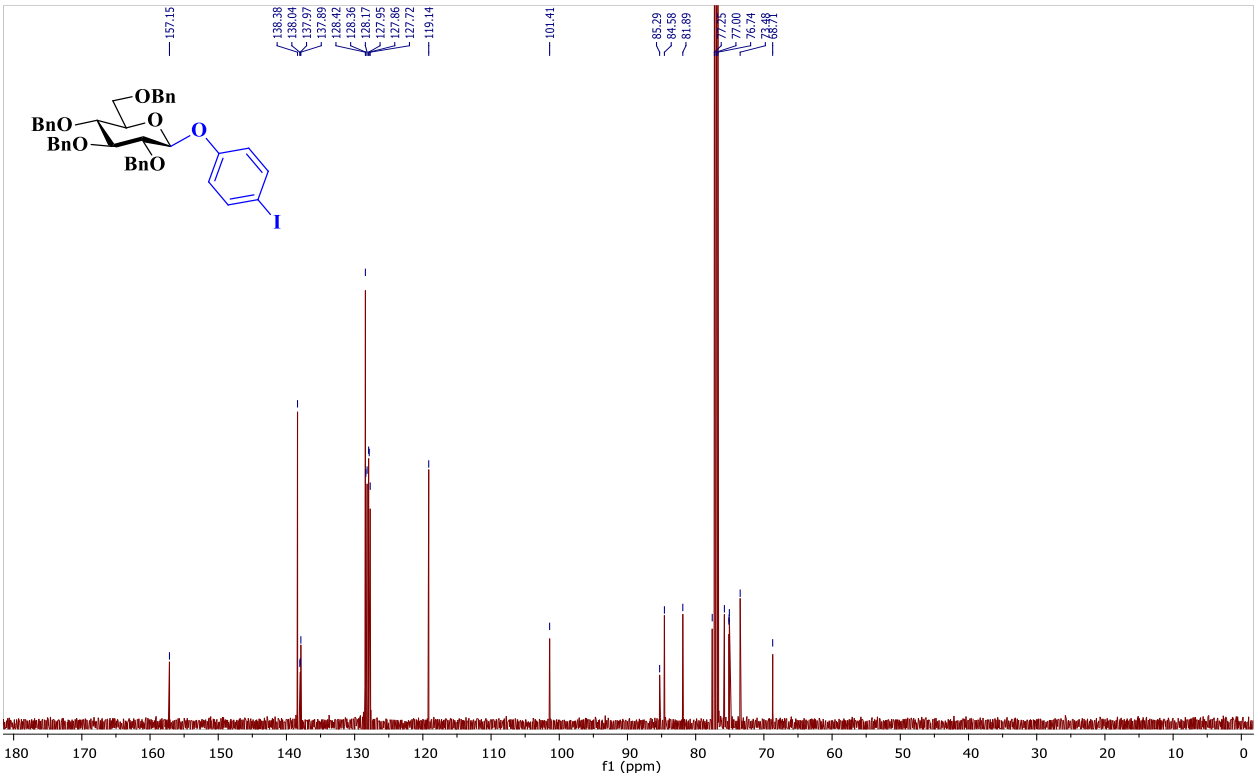
^{13}C {^{1}H} NMR spectrum of compound 3g (125 MHz, $CDCl_3$)



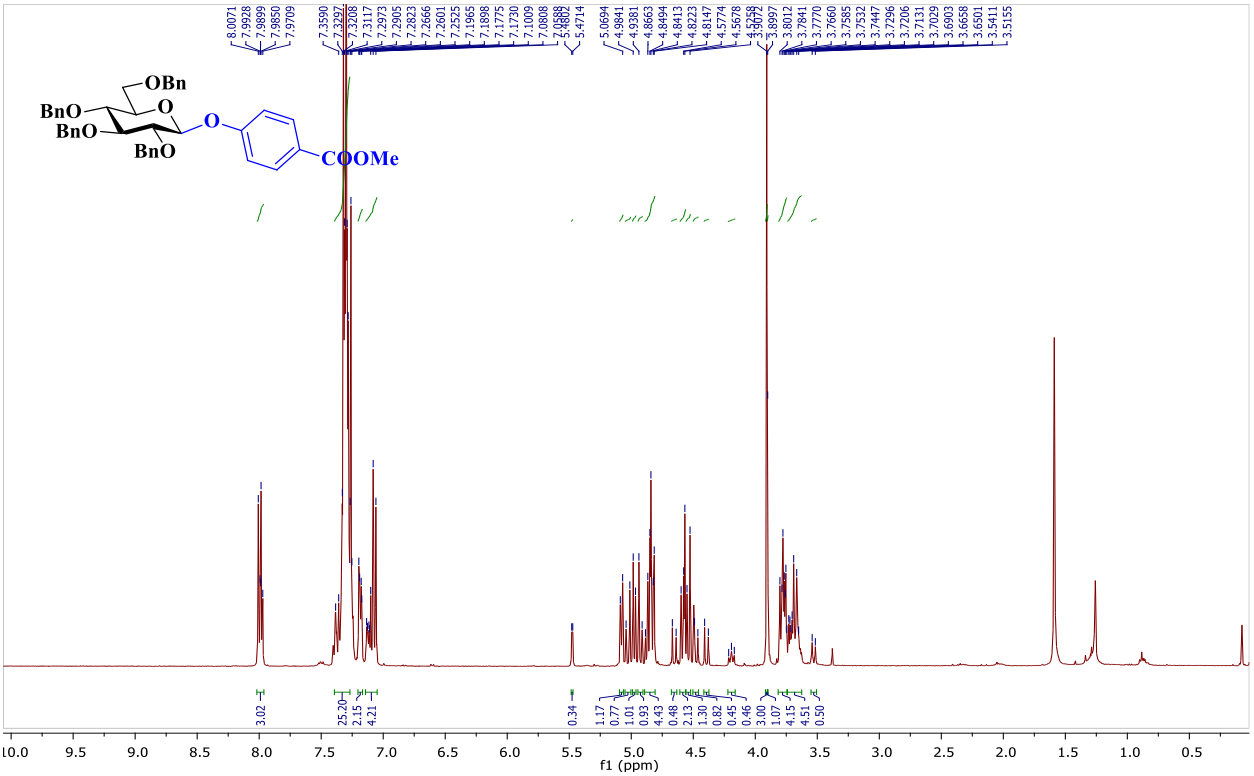
^{1}H NMR spectrum of compound 3h (500 MHz, $CDCl_3$)



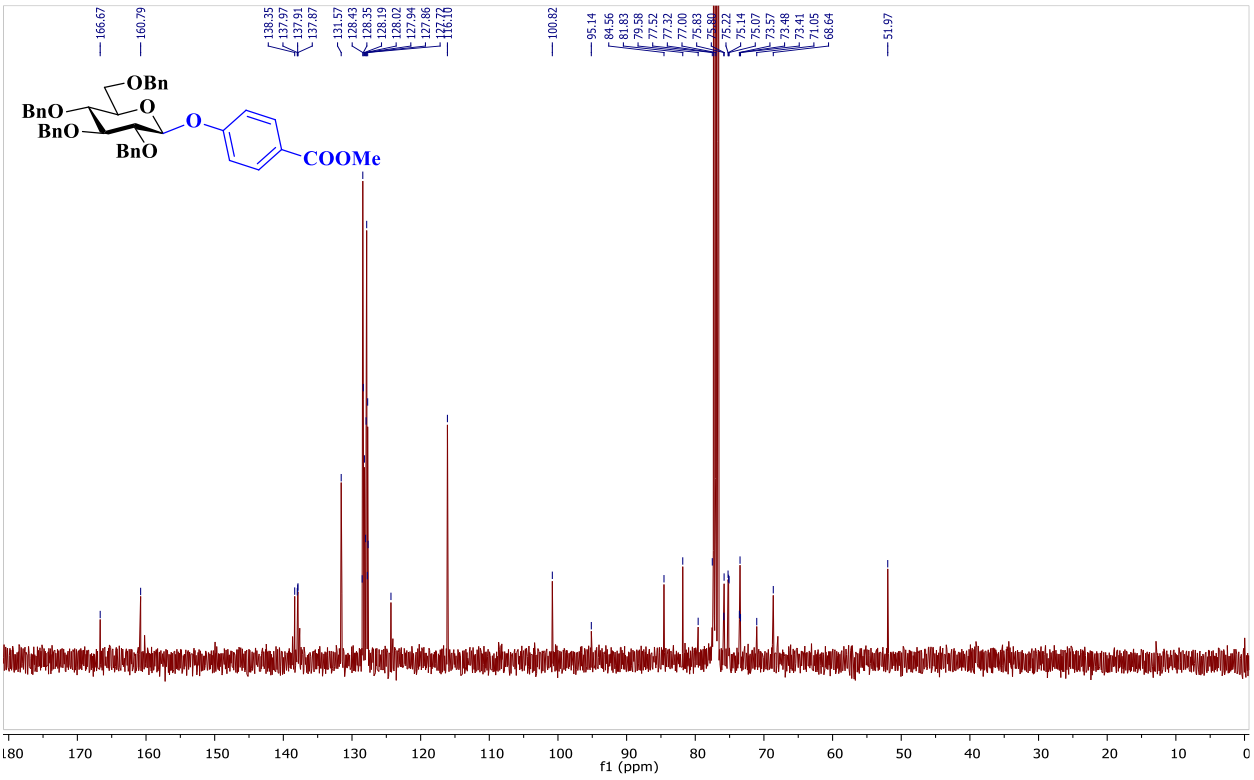
^{13}C {^{1}H} NMR spectrum of compound 3h (125 MHz, $CDCl_3$)



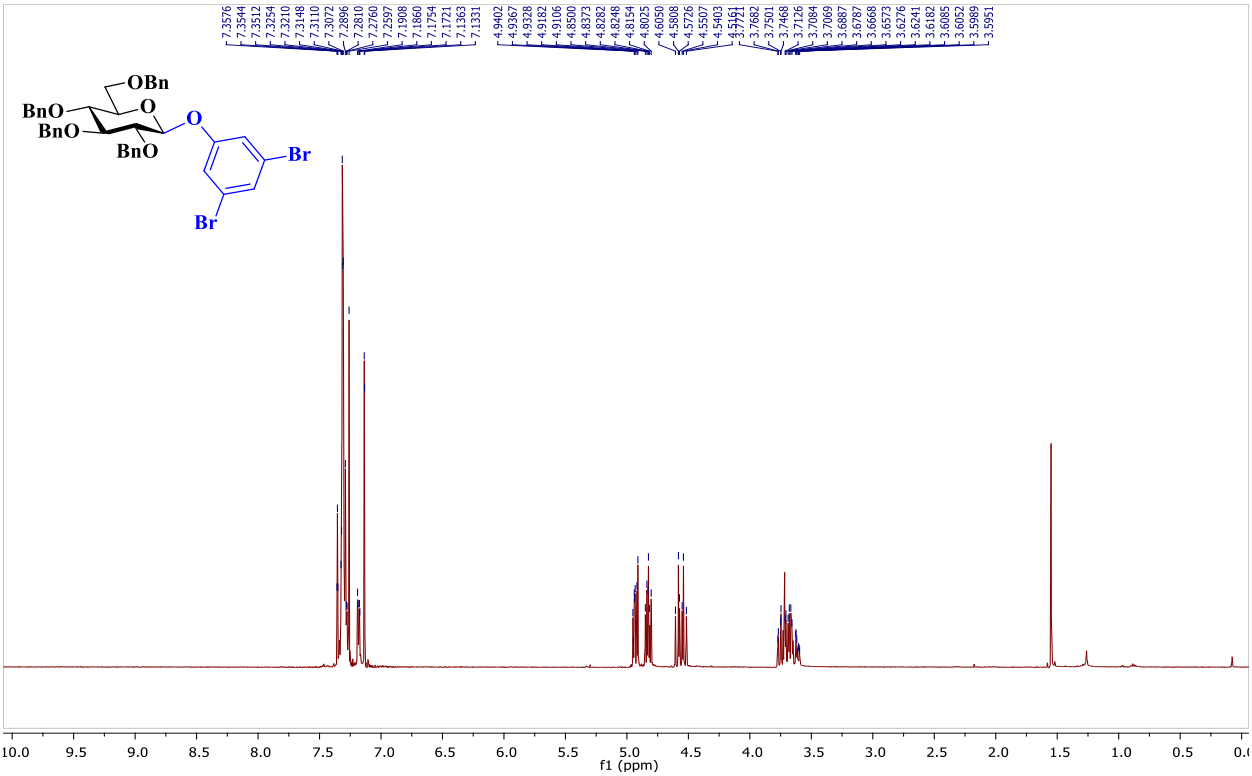
^{1}H NMR spectrum of compound 3i (400 MHz, $CDCl_3$)



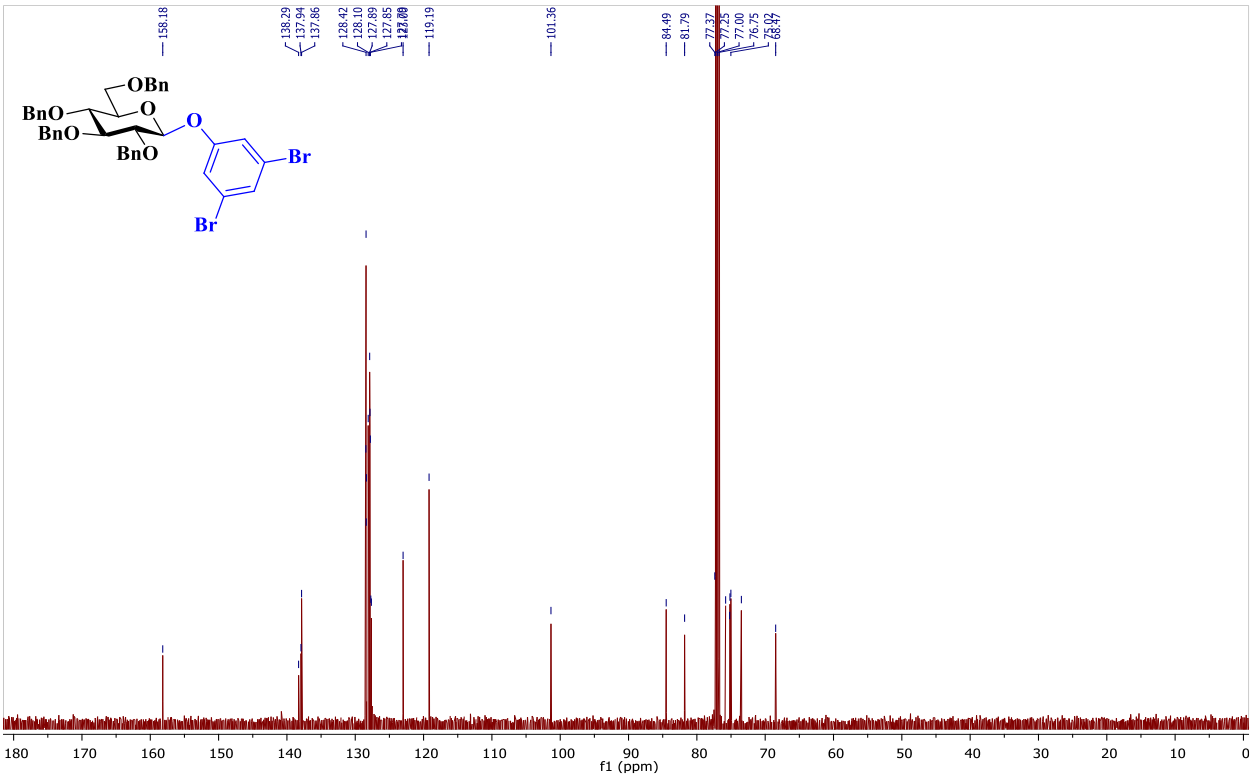
^{13}C {^{1}H} NMR spectrum of compound 3i (100 MHz, $CDCl_3$)



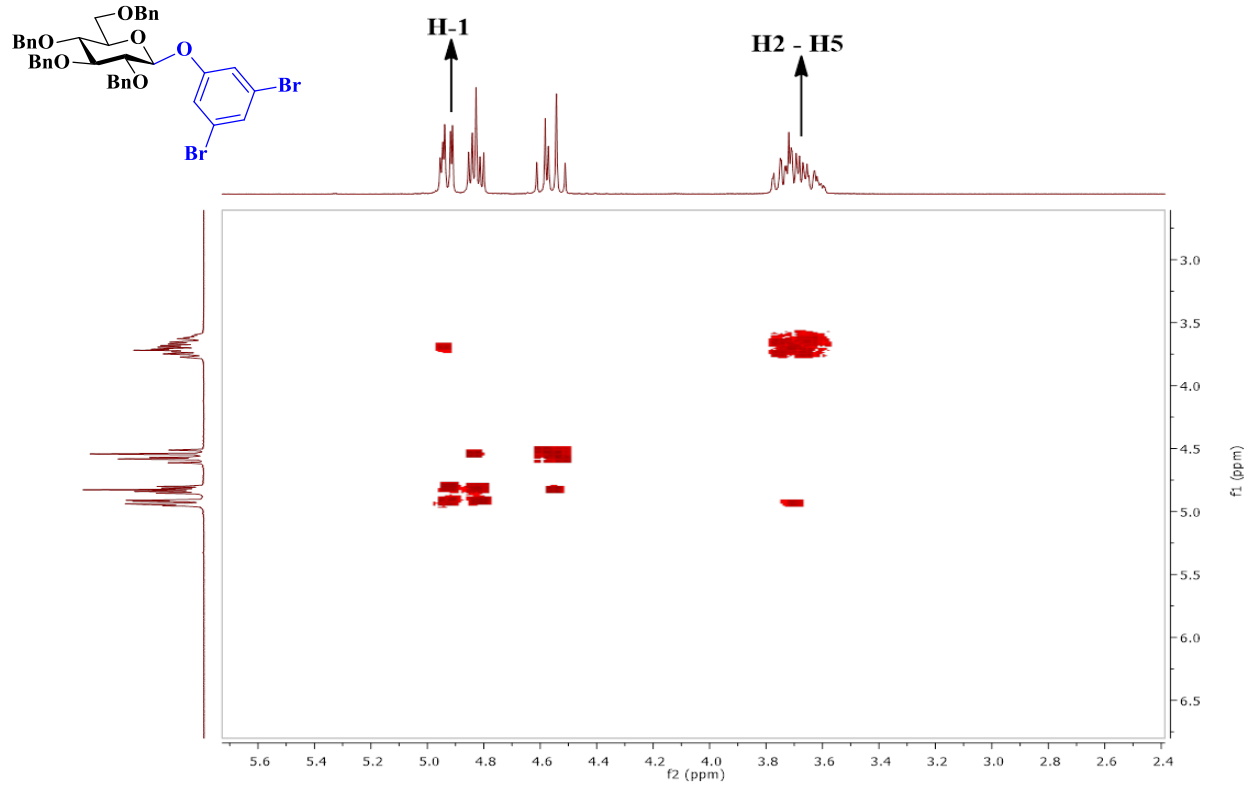
^{1}H NMR spectrum of compound 3j (500 MHz, $CDCl_3$)



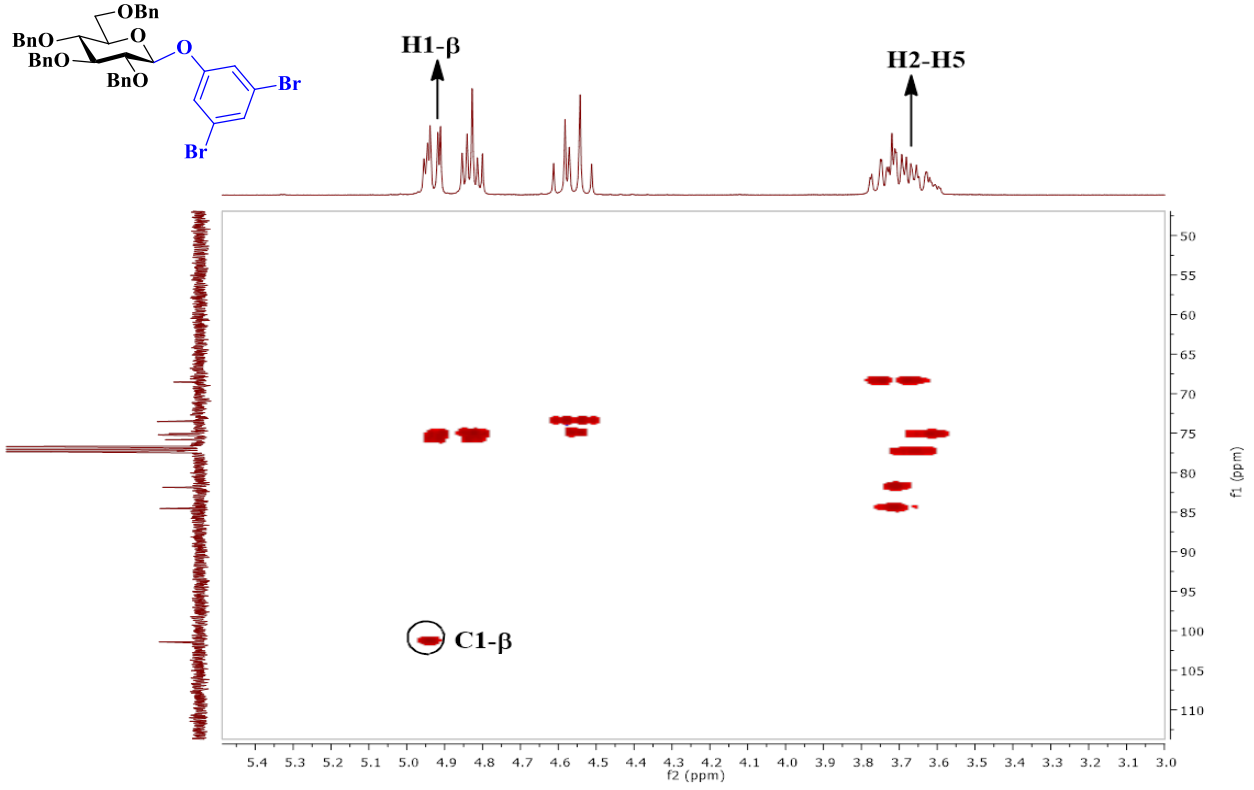
^{13}C {^{1}H} NMR spectrum of compound 3j (125 MHz, $CDCl_3$)



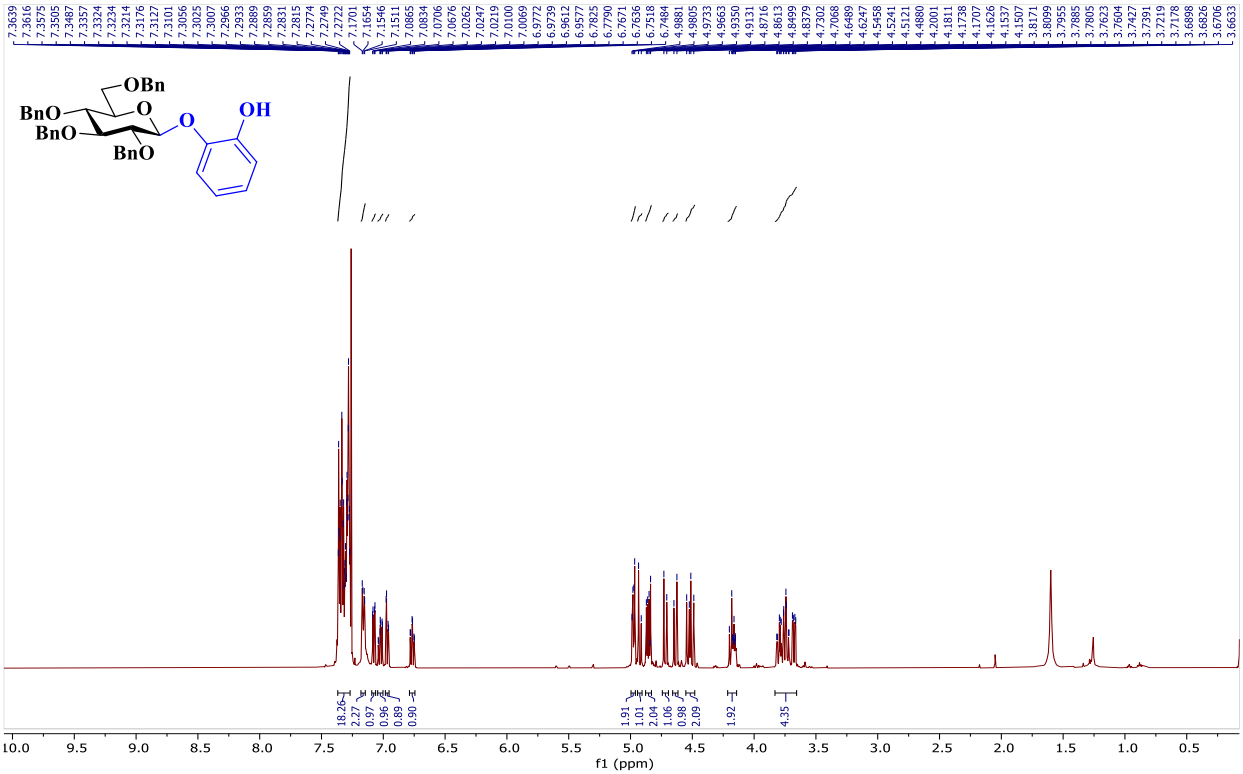
COSY spectrum of compound 3j



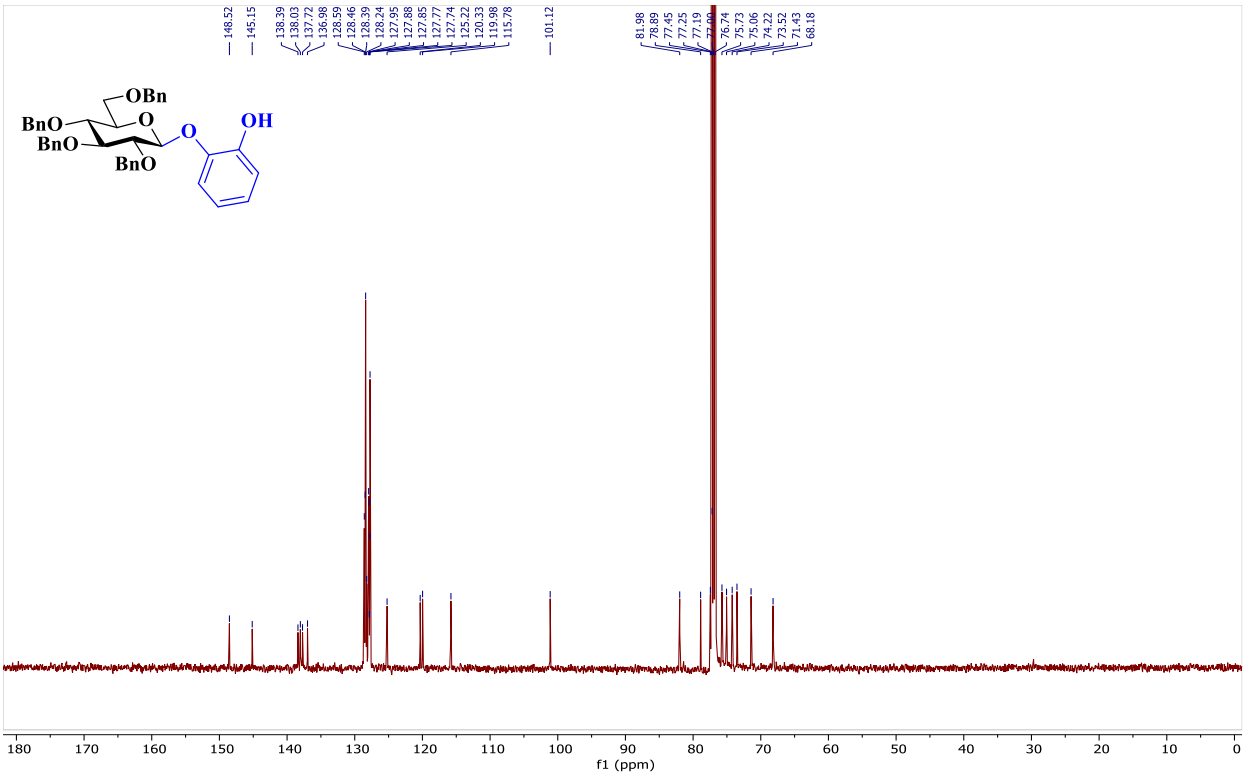
HSQC spectrum of compound 3j



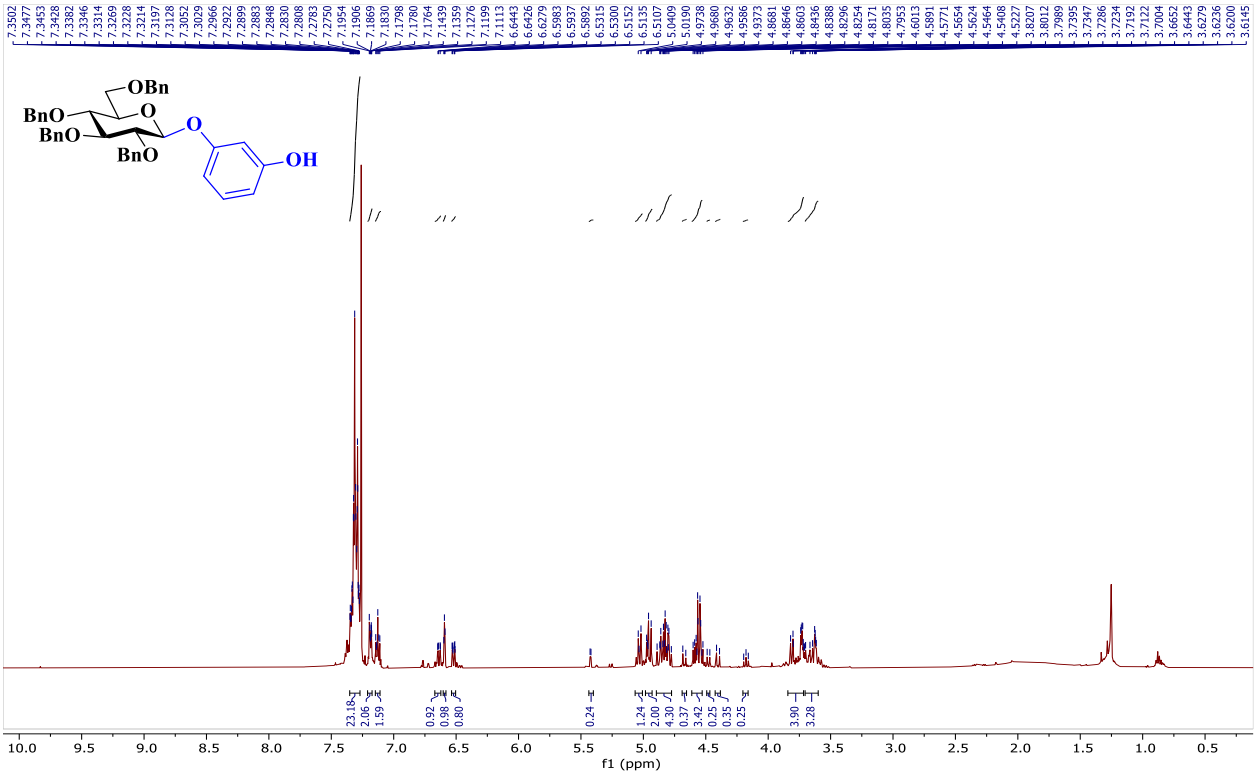
^{1}H NMR spectrum of compound 3k (500 MHz, $CDCl_3$)



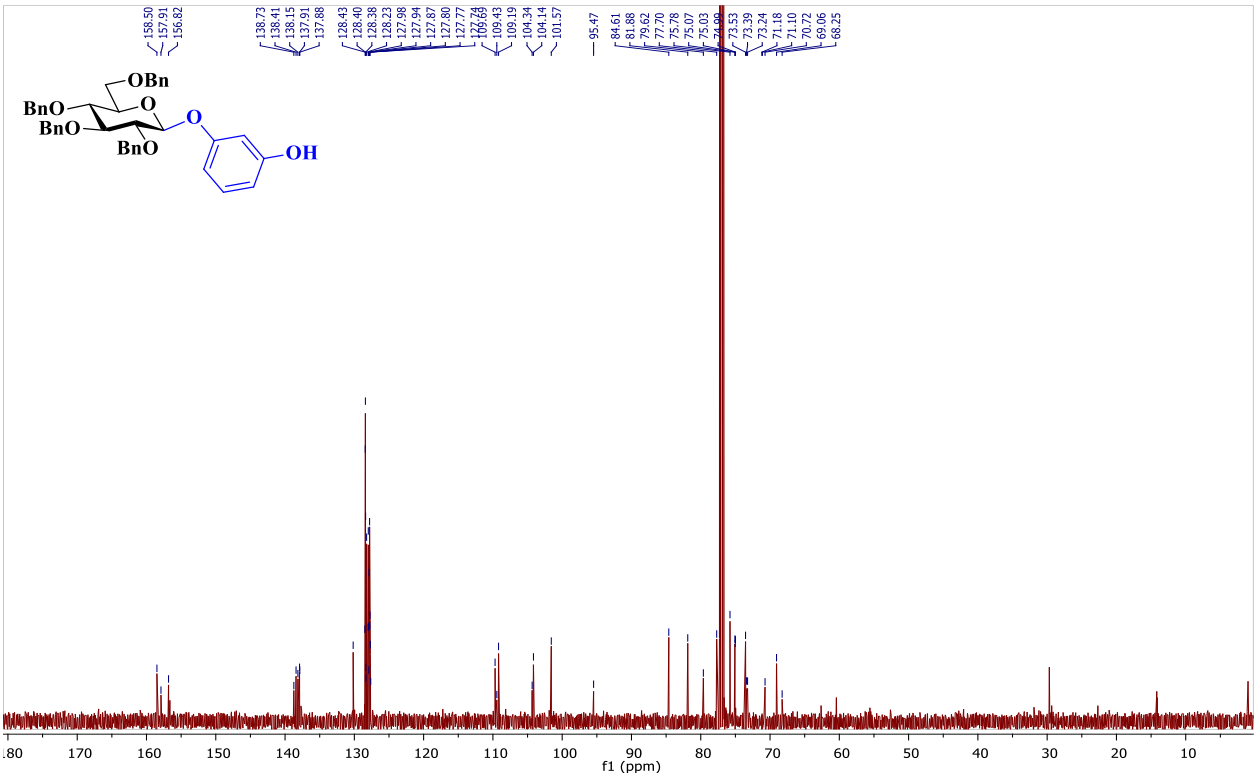
^{13}C {^{1}H} NMR spectrum of compound 3k (125 MHz, $CDCl_3$)



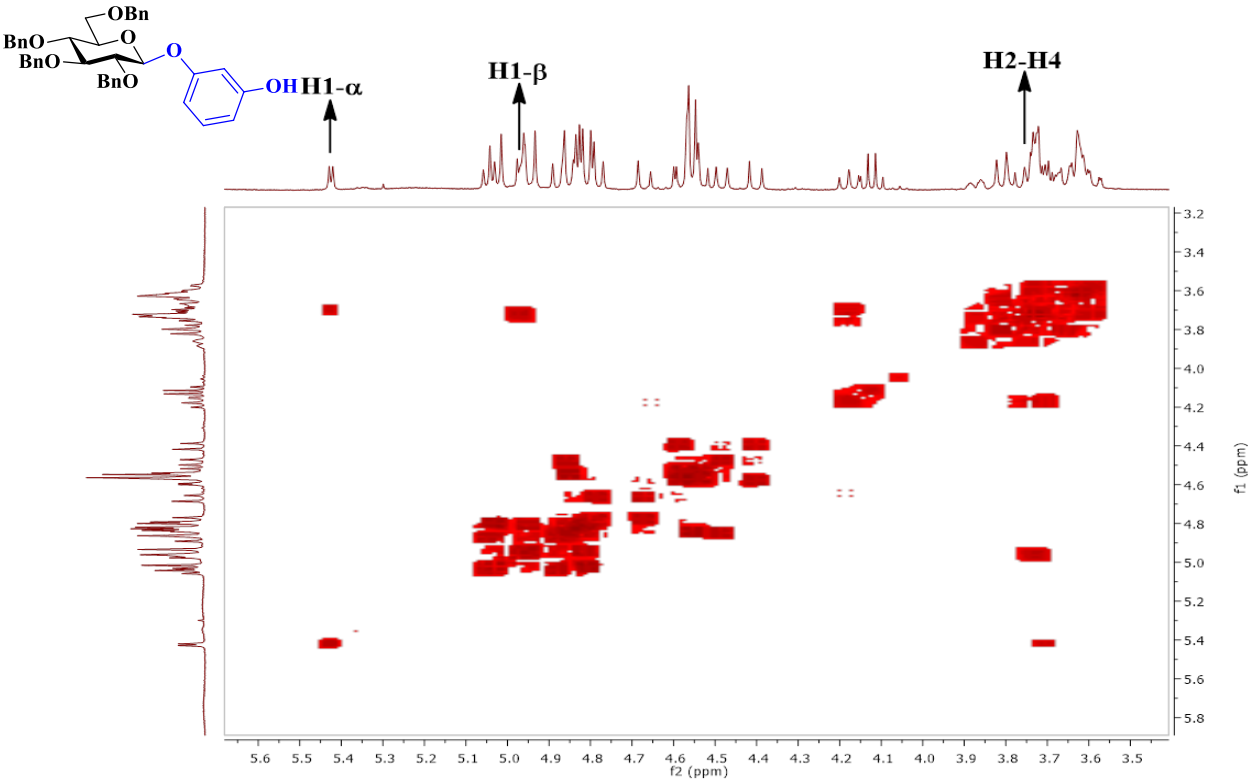
^{1}H NMR spectrum of compound 3l (400 MHz, $CDCl_3$)



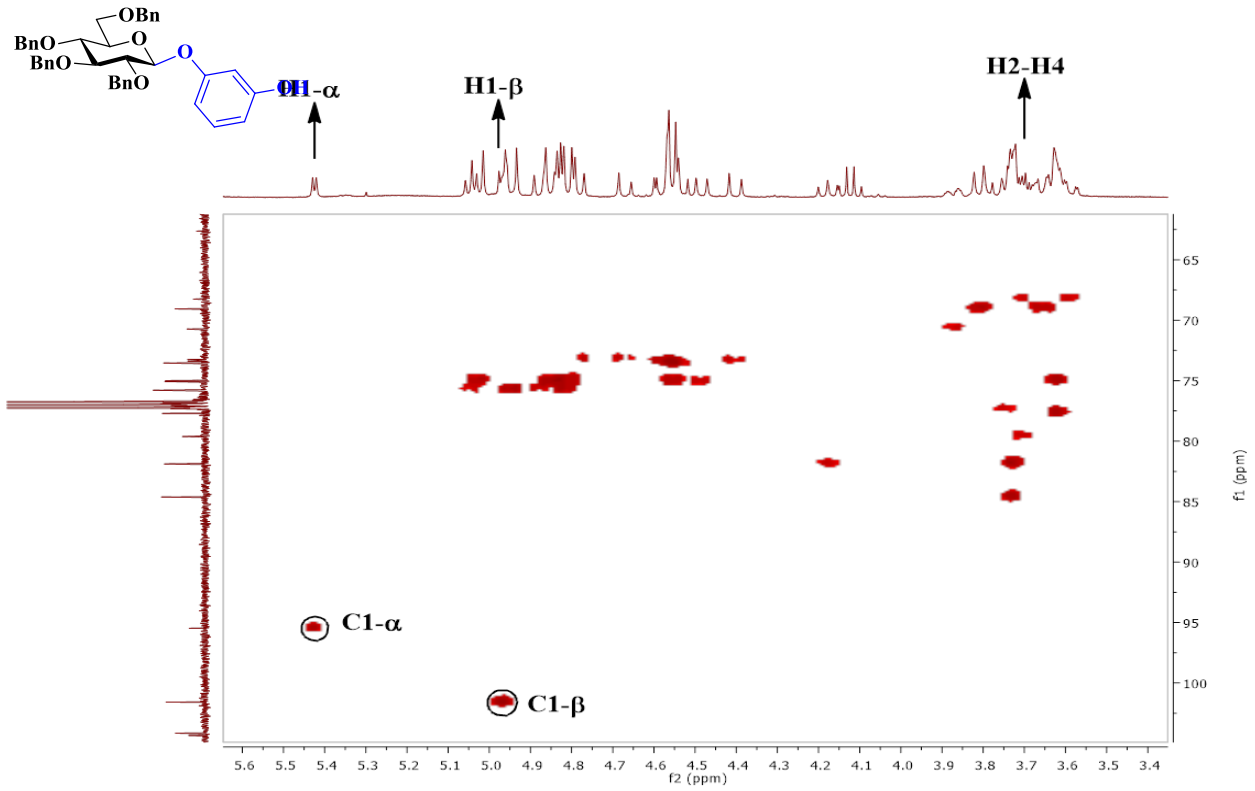
^{13}C {^{1}H} NMR spectrum of compound 3l (100 MHz, $CDCl_3$)



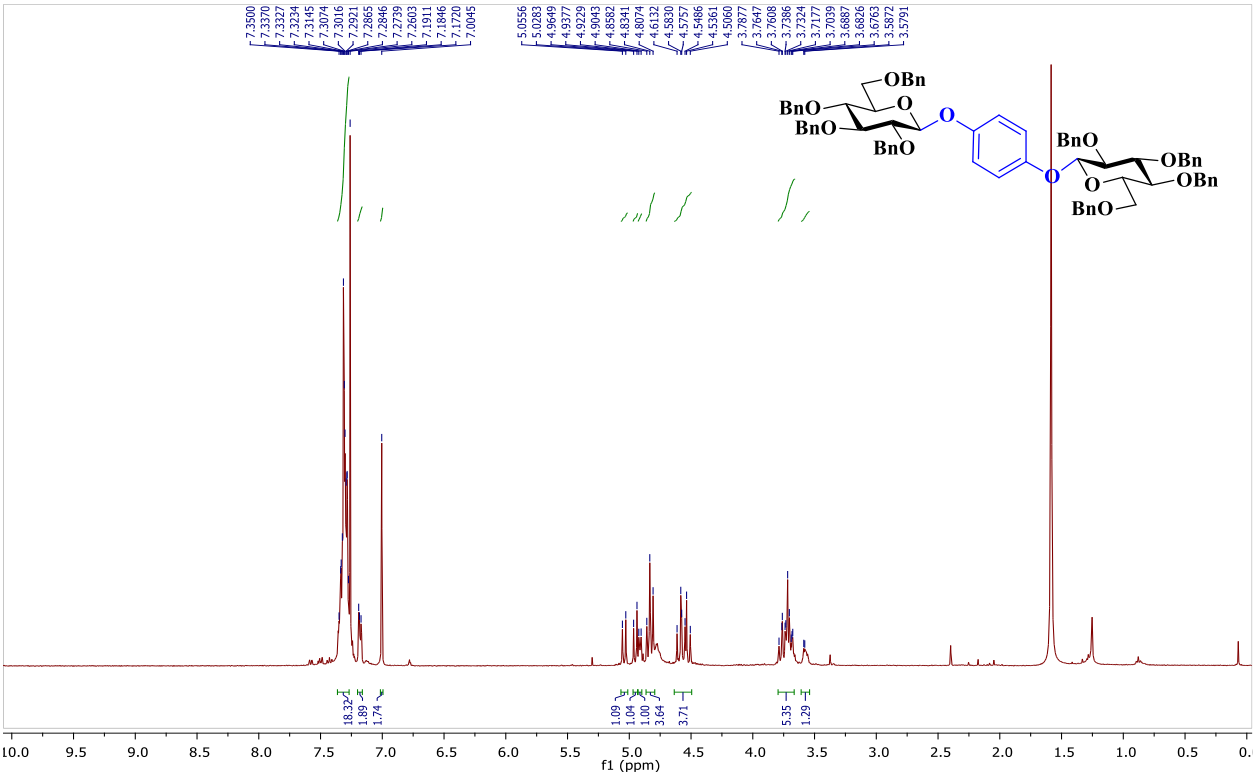
COSY spectrum of compound 3l



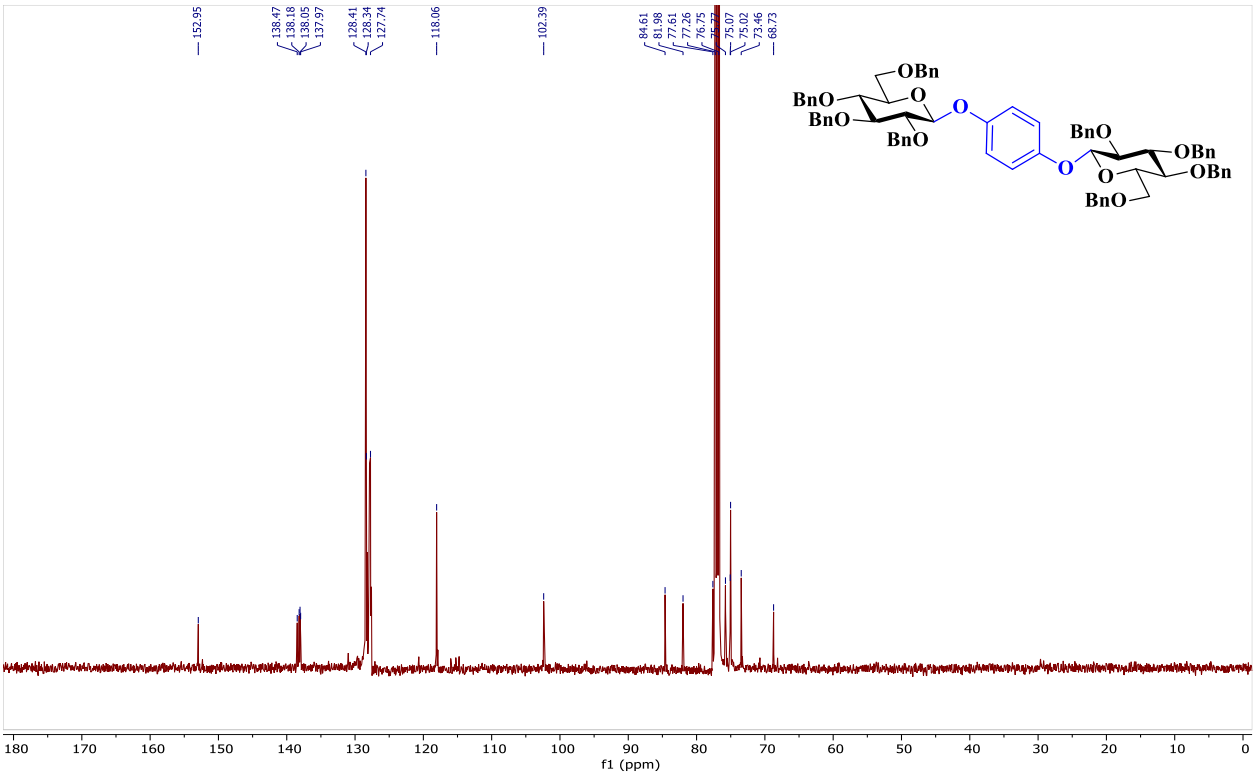
HSQC spectrum of compound 3l



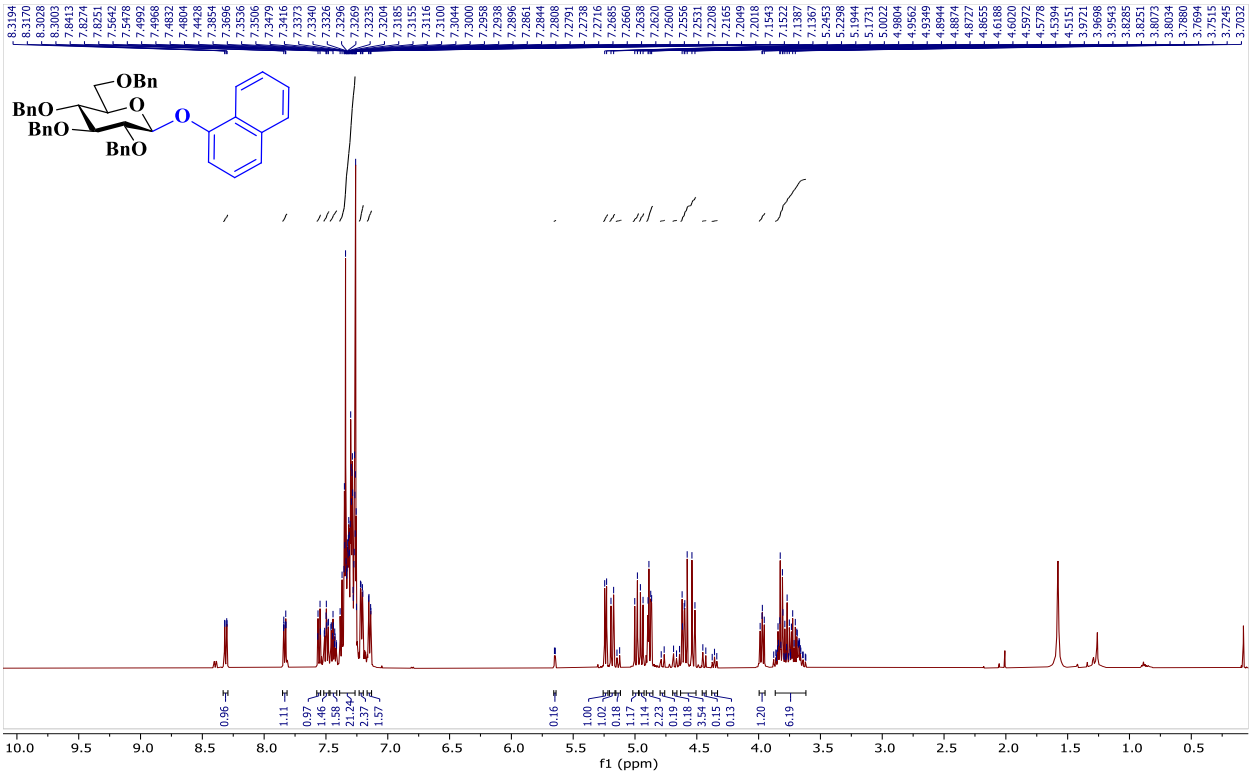
^{1}H NMR spectrum of compound 3m (500 MHz, $CDCl_3$)



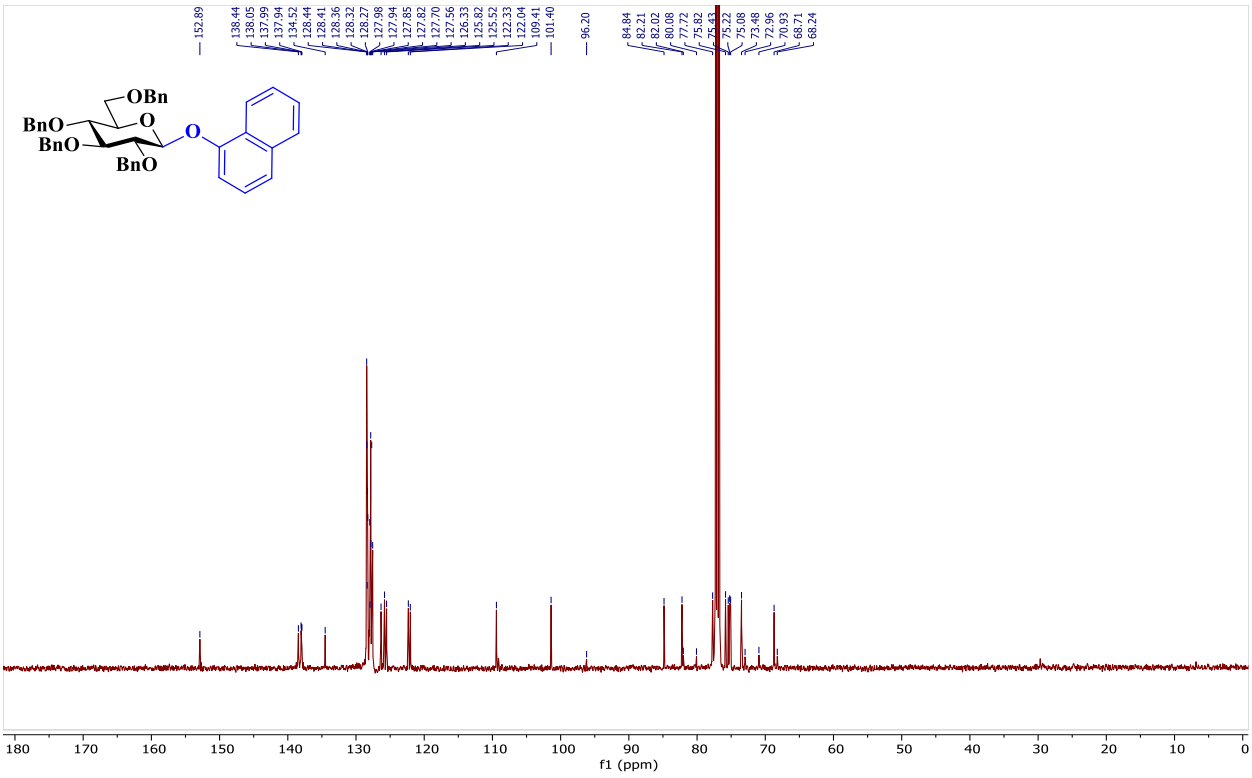
^{13}C {^{1}H} NMR spectrum of compound 3m (125 MHz, $CDCl_3$)



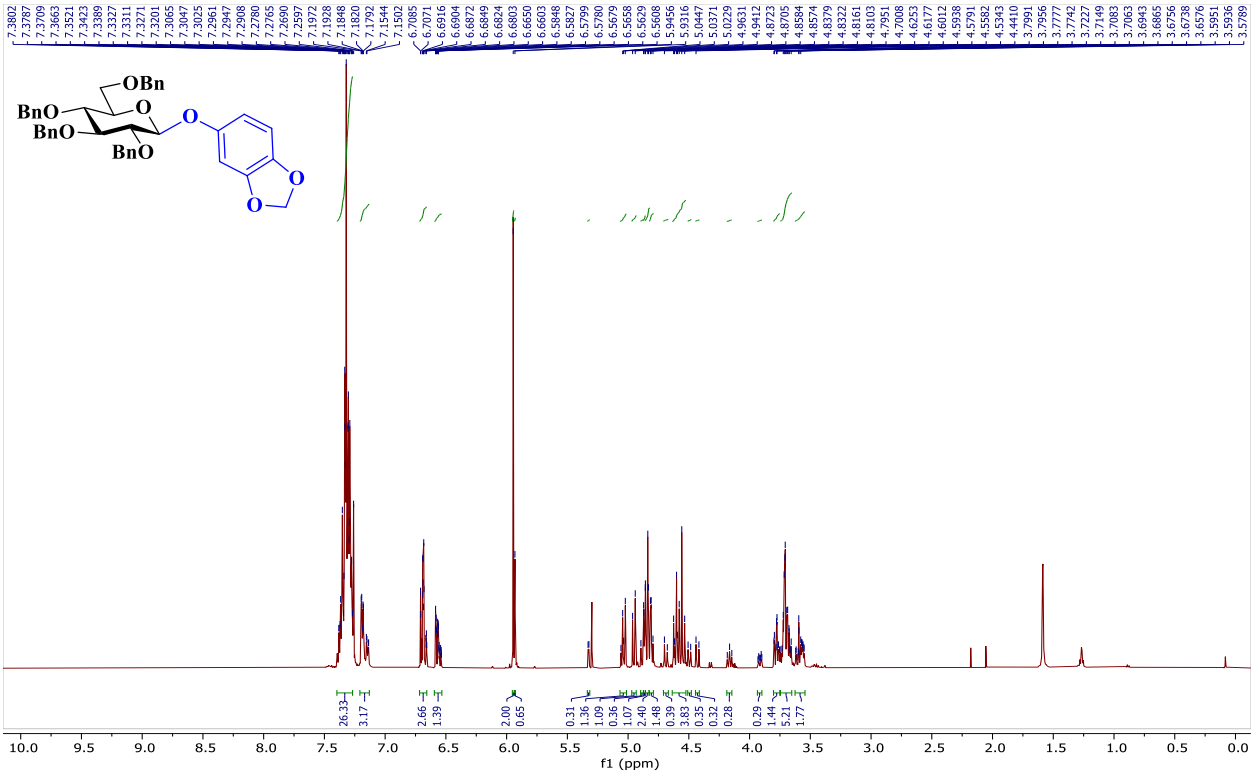
^{1}H NMR spectrum of compound 3n (500 MHz, $CDCl_3$)



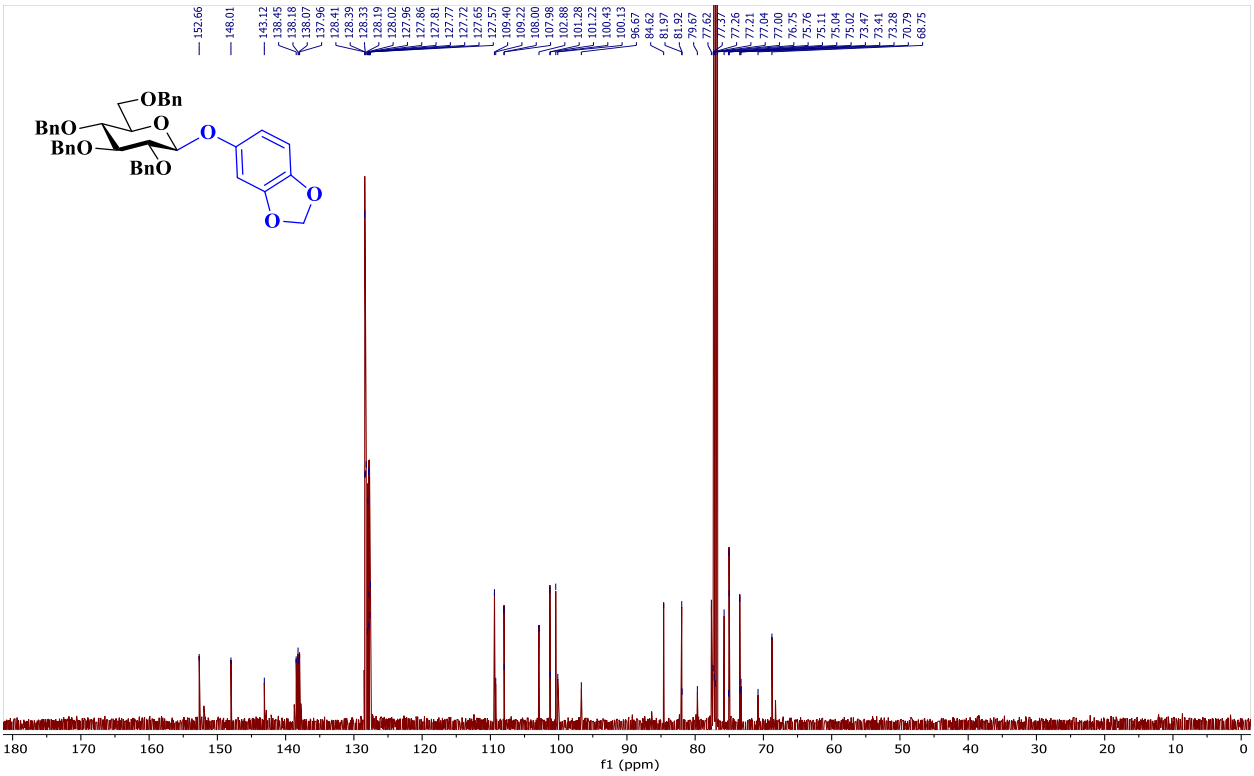
^{13}C {^{1}H} NMR spectrum of compound 3n (125 MHz, $CDCl_3$)



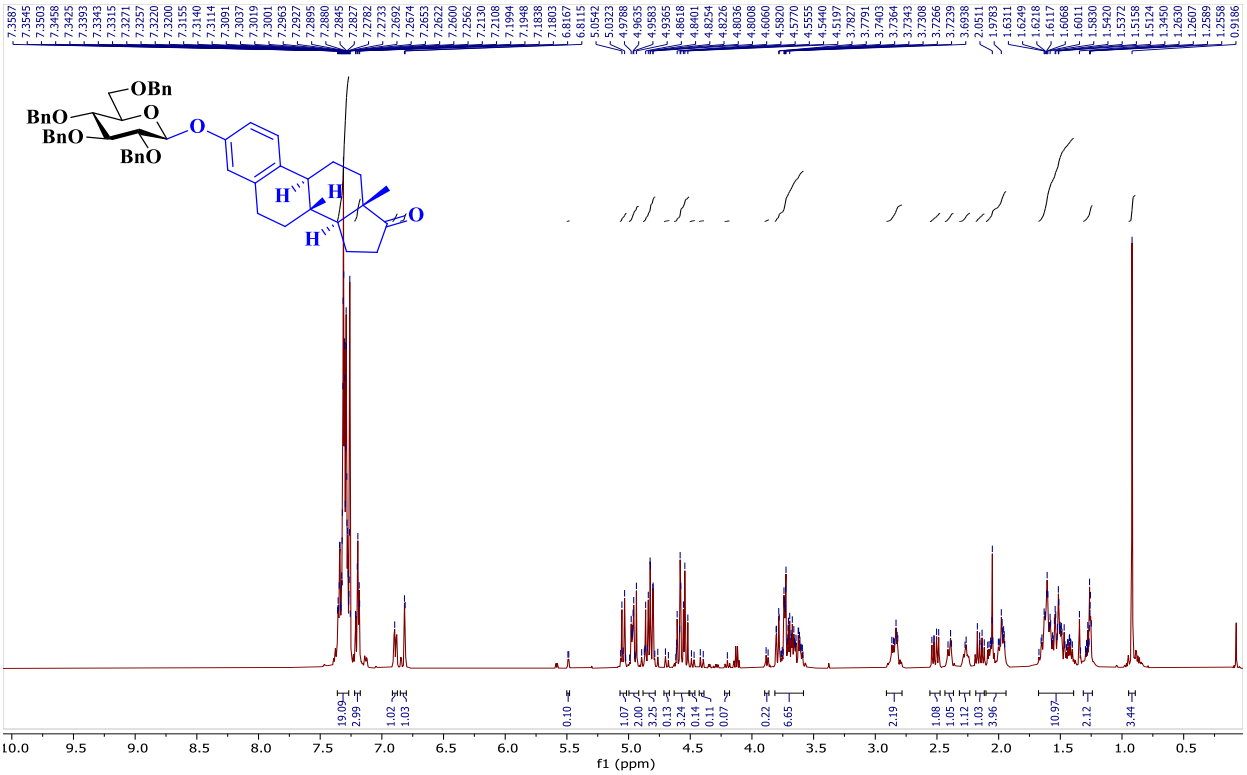
^{1}H NMR spectrum of compound 3o (500 MHz, $CDCl_3$)



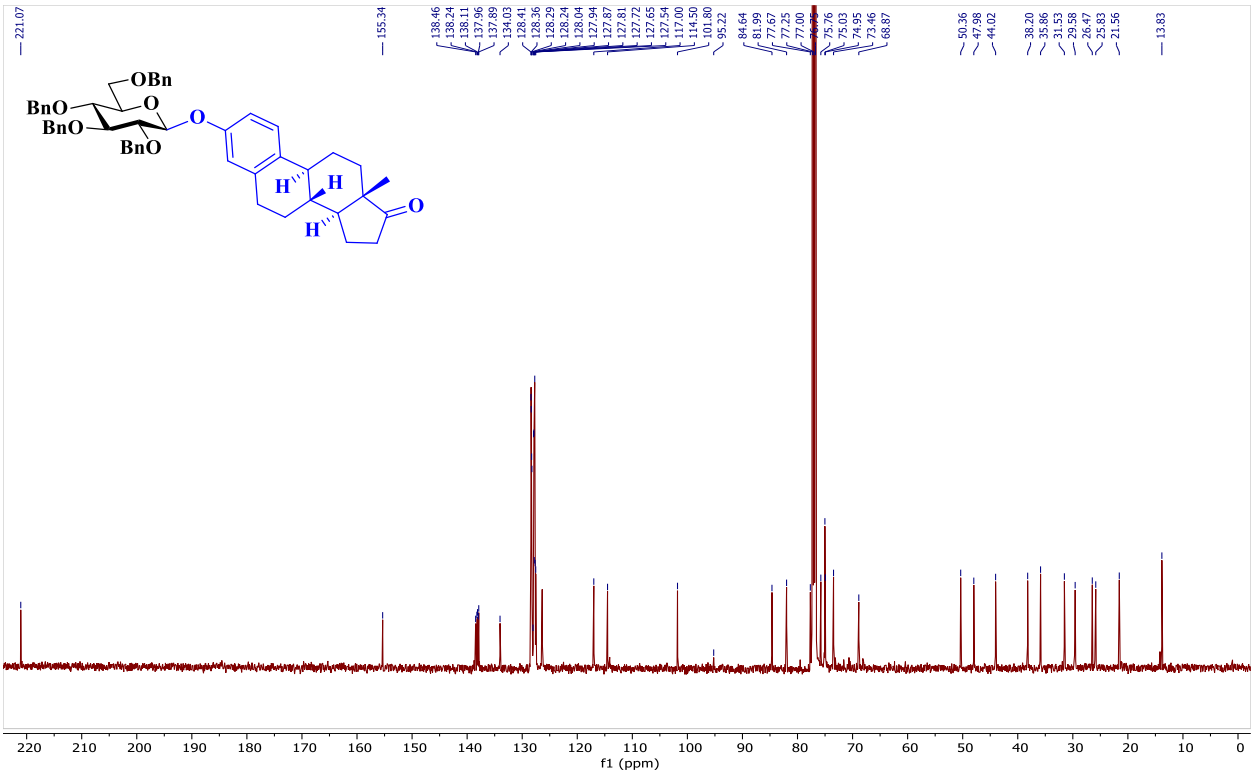
^{13}C {^{1}H} NMR spectrum of compound 3o (125 MHz, $CDCl_3$)



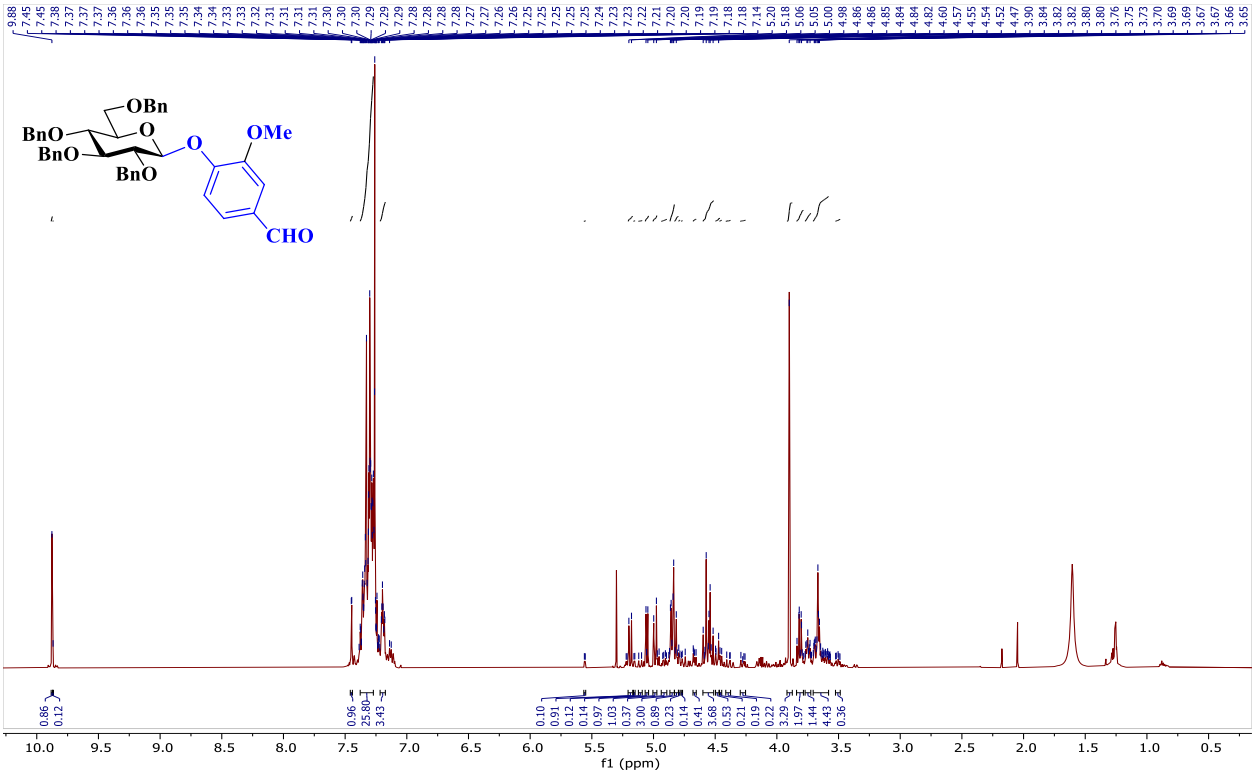
^{1}H NMR spectrum of compound 3p (500 MHz, $CDCl_3$)



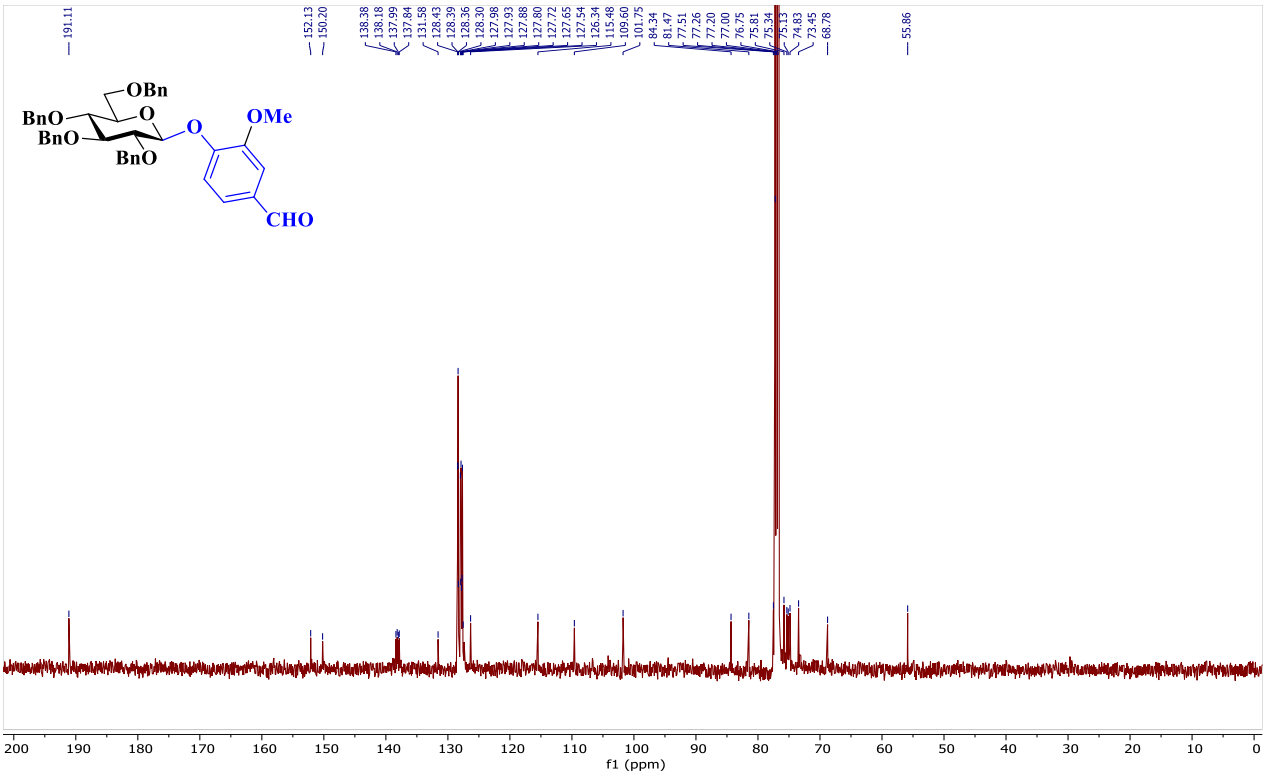
^{13}C {^{1}H} NMR spectrum of compound 3p (125 MHz, $CDCl_3$)



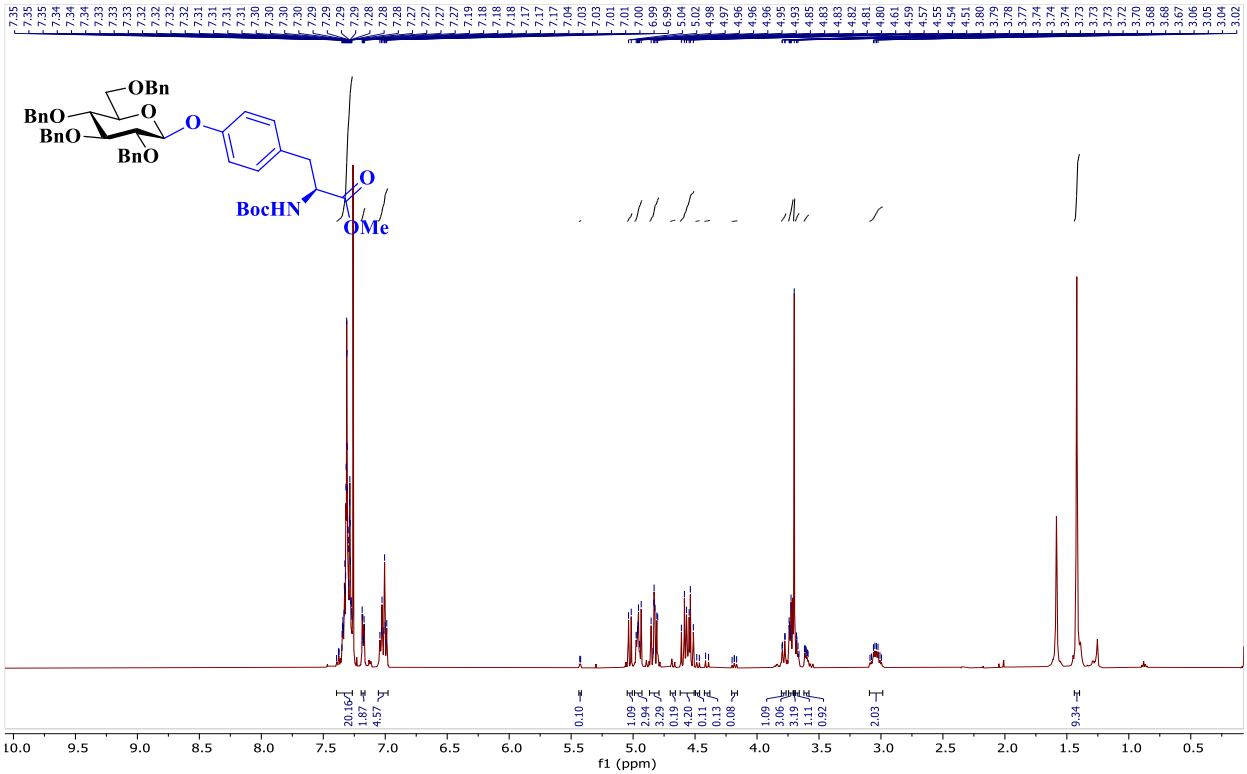
^{1}H NMR spectrum of compound 3q (400 MHz, $CDCl_3$)



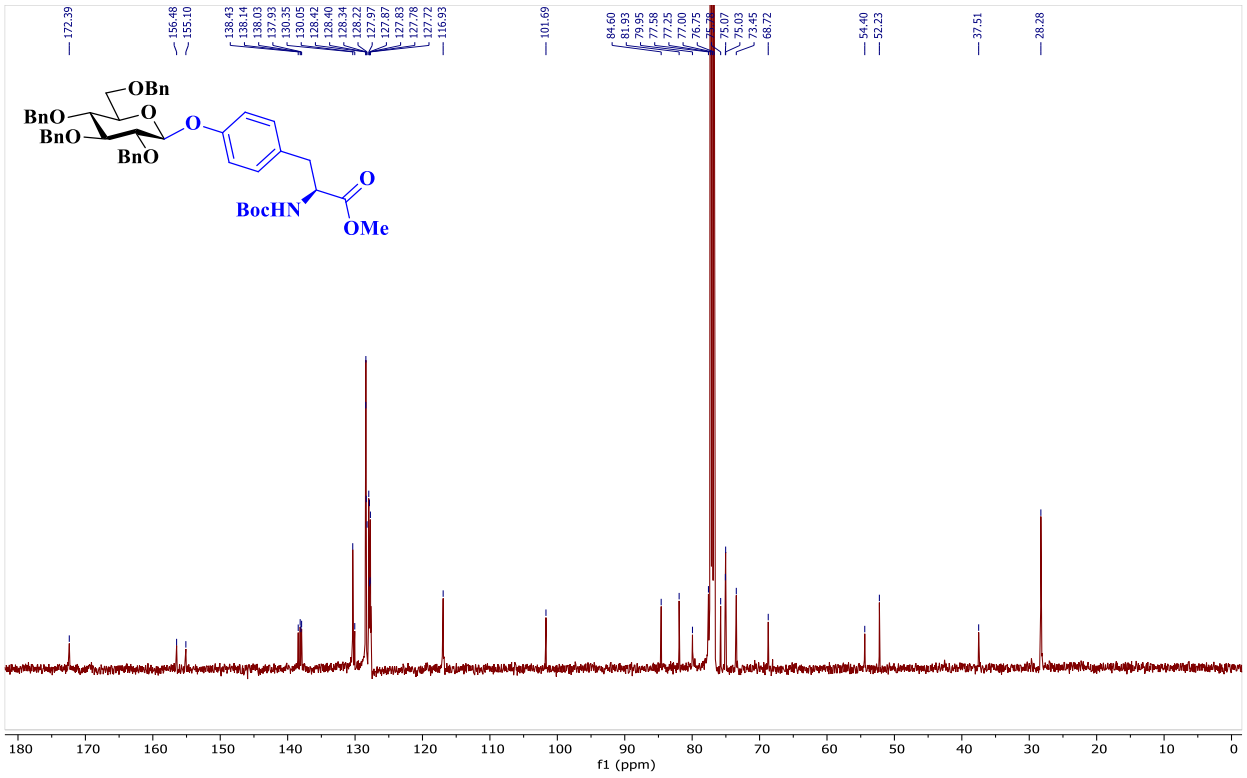
^{13}C {^{1}H} NMR spectrum of compound 3q (100 MHz, $CDCl_3$)



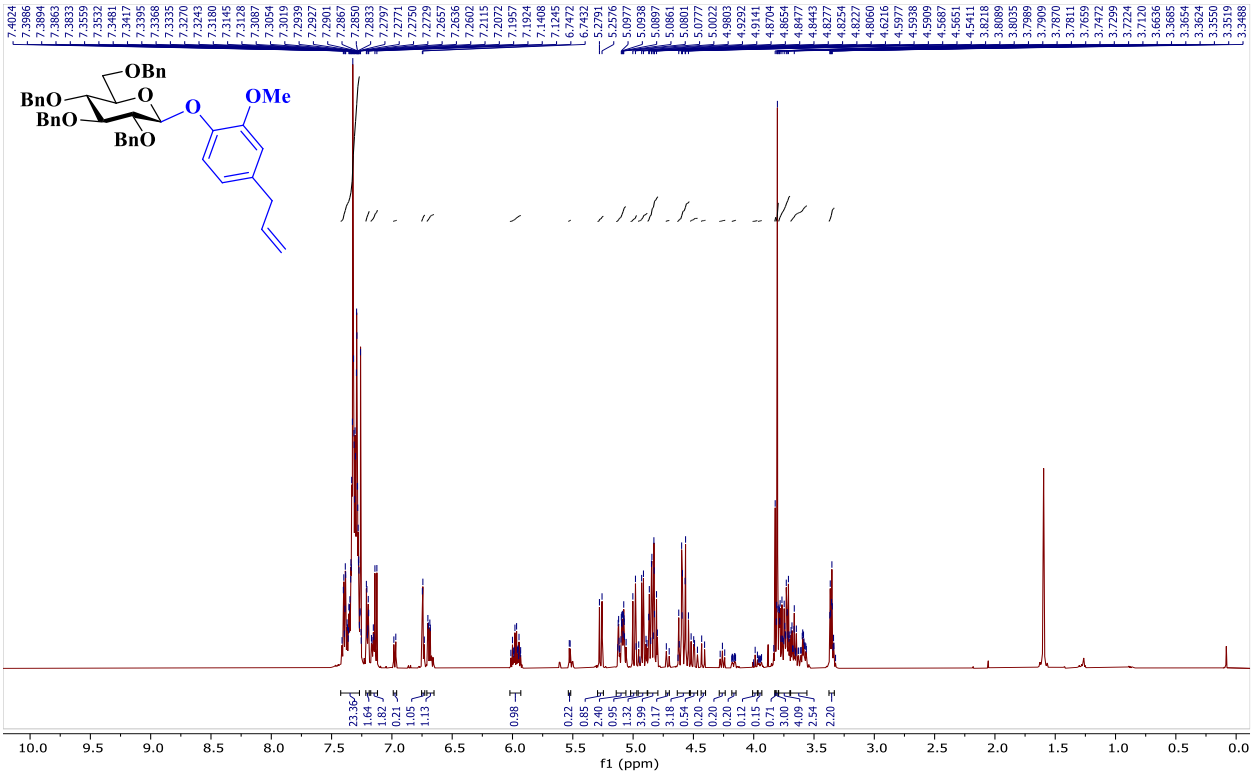
^{1}H NMR spectrum of compound 3r (500 MHz, $CDCl_3$)



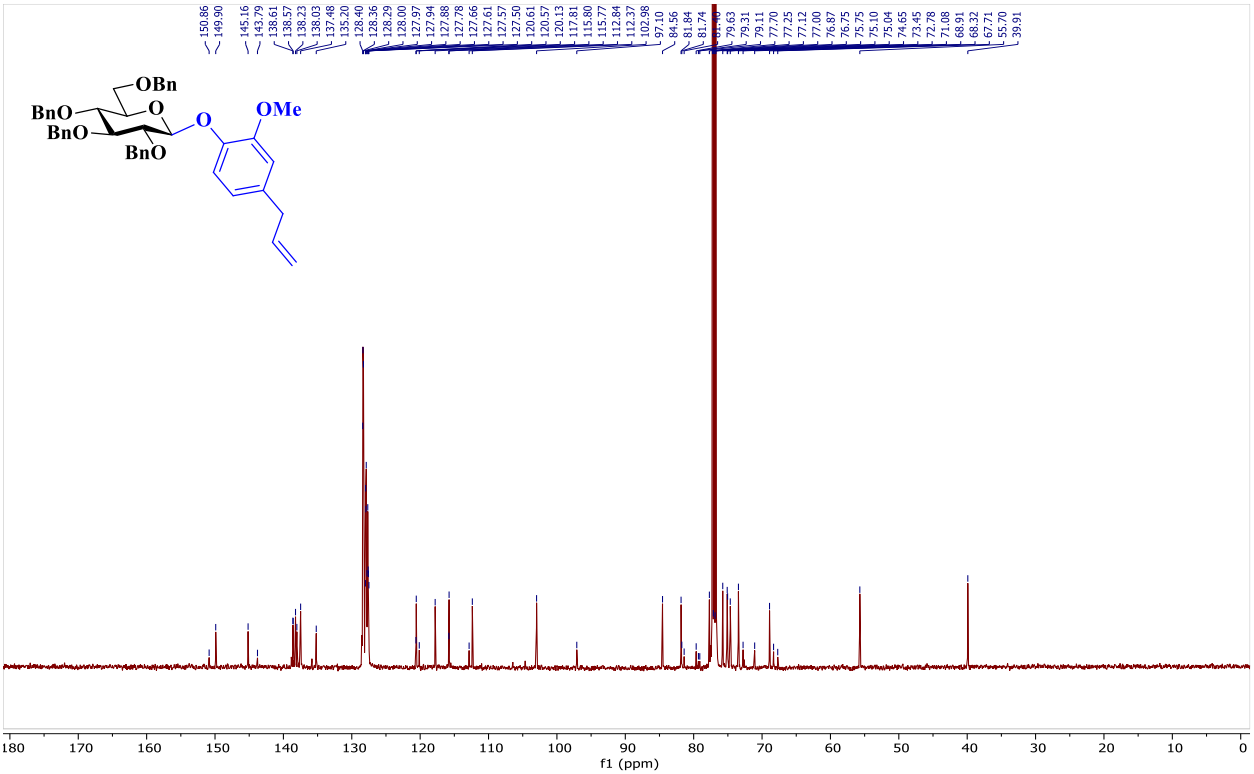
^{13}C {^{1}H} NMR spectrum of compound 3r (125 MHz, $CDCl_3$)



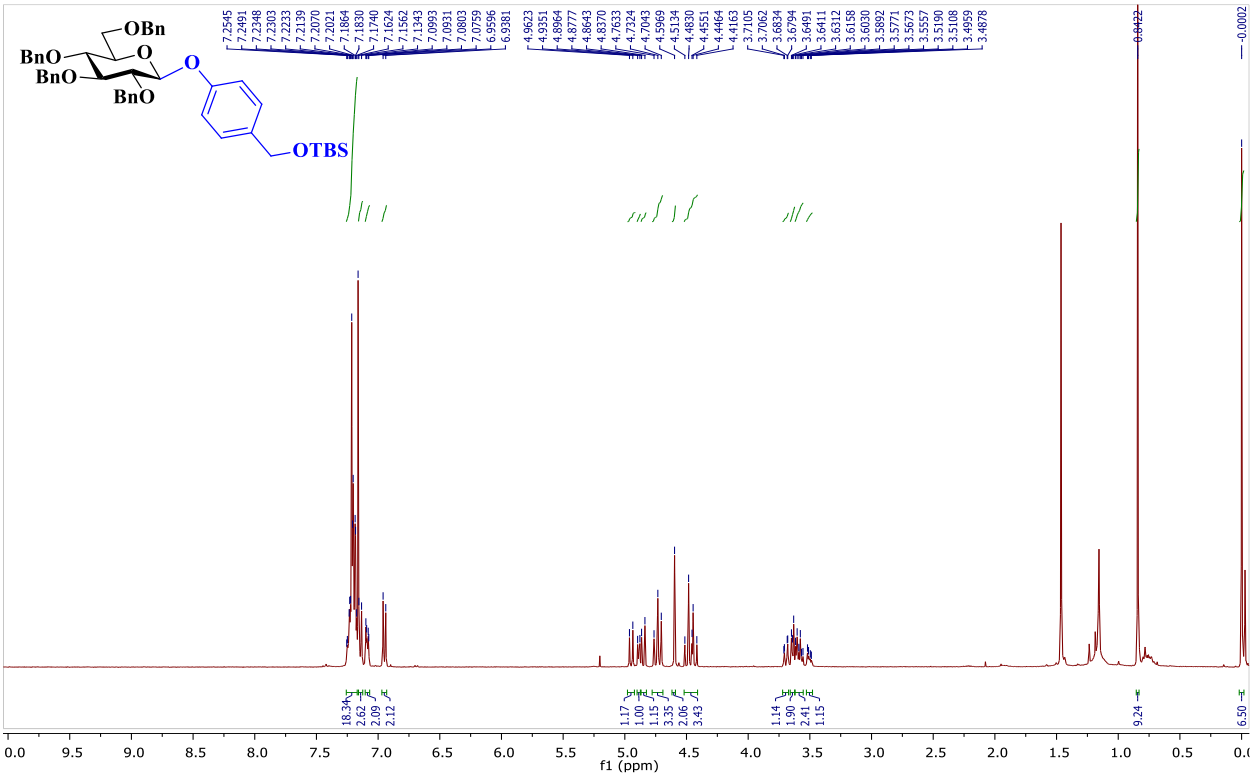
^{1}H NMR spectrum of compound 3s (400 MHz, $CDCl_3$)



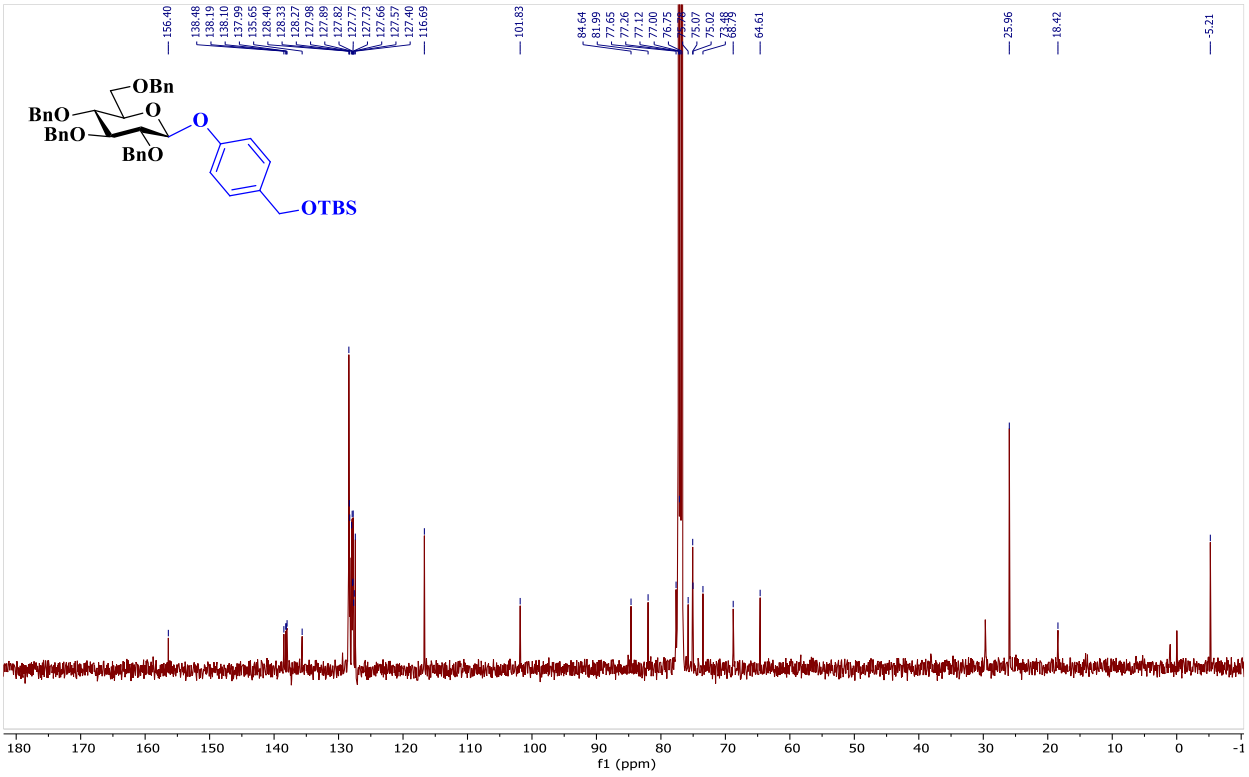
^{13}C {^{1}H} NMR spectrum of compound 3s (100 MHz, $CDCl_3$)



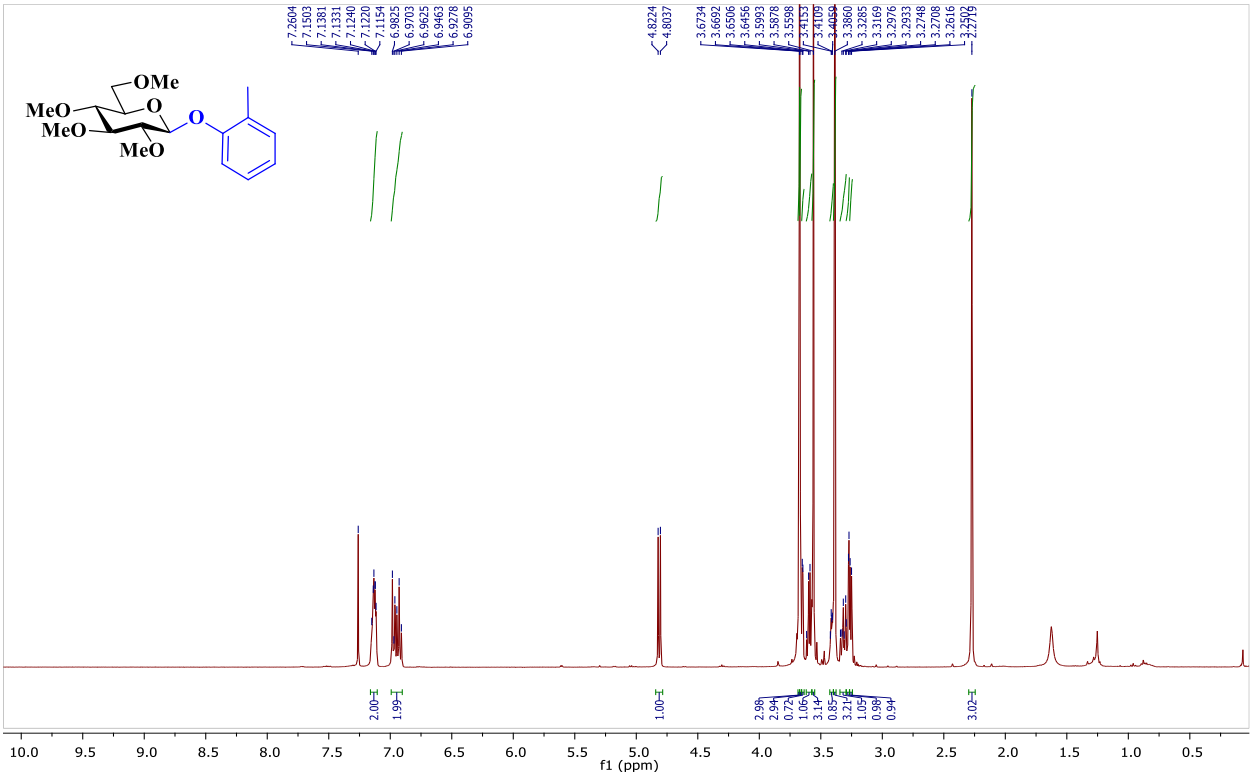
^{1}H NMR spectrum of compound 3t (400 MHz, $CDCl_3$)



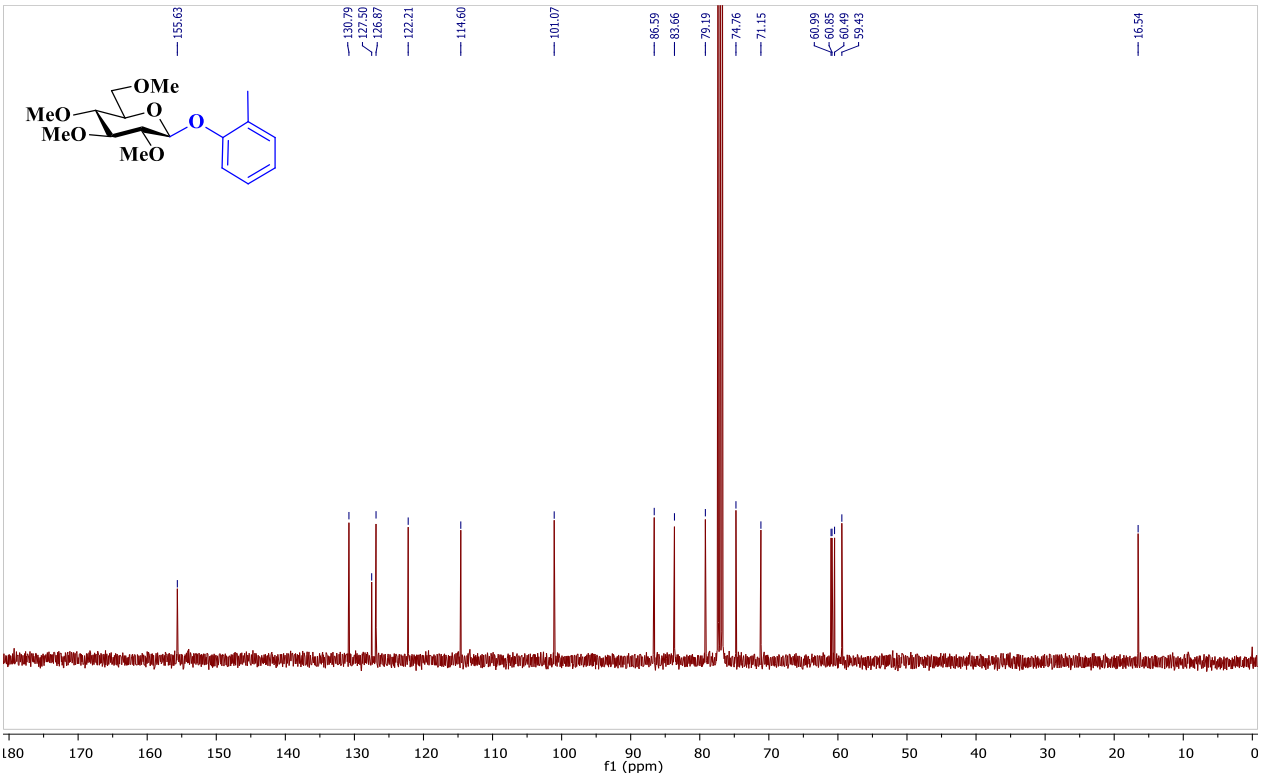
^{13}C {^{1}H} NMR spectrum of compound 3t (100 MHz, $CDCl_3$)



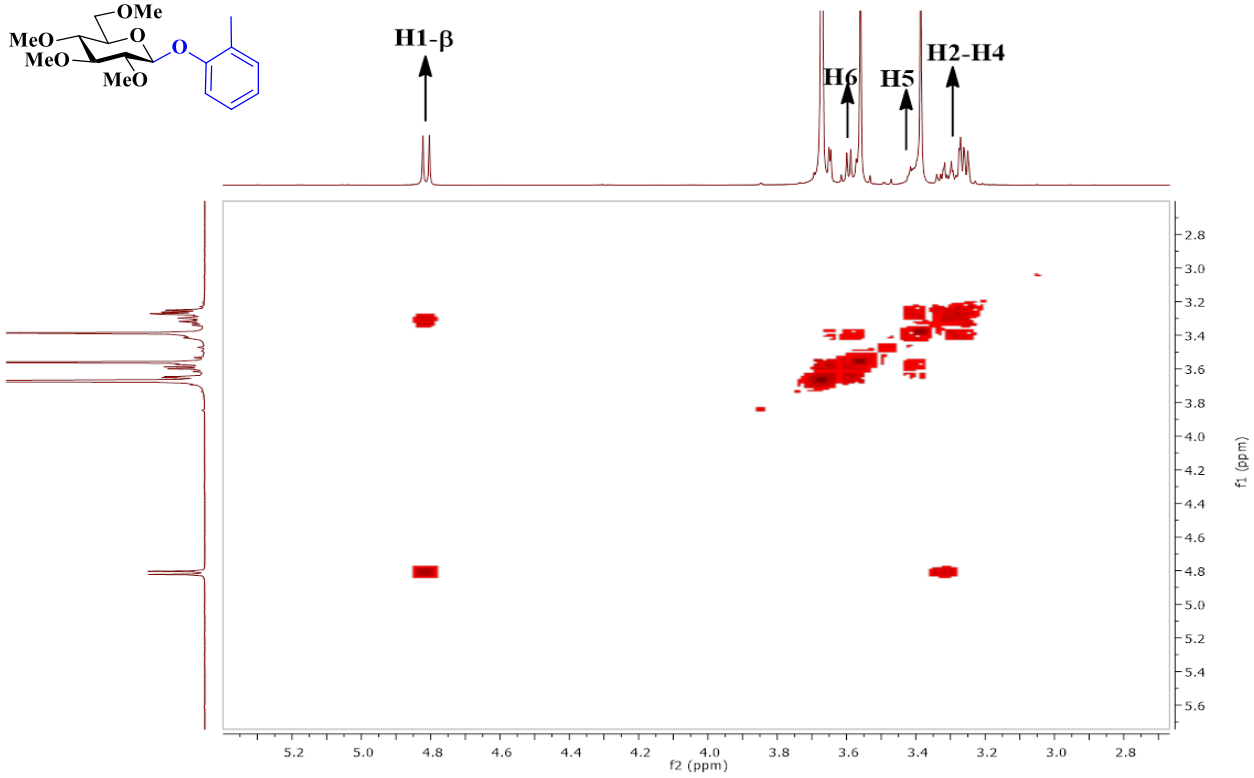
^{1}H NMR spectrum of compound 4a (500 MHz, $CDCl_3$)



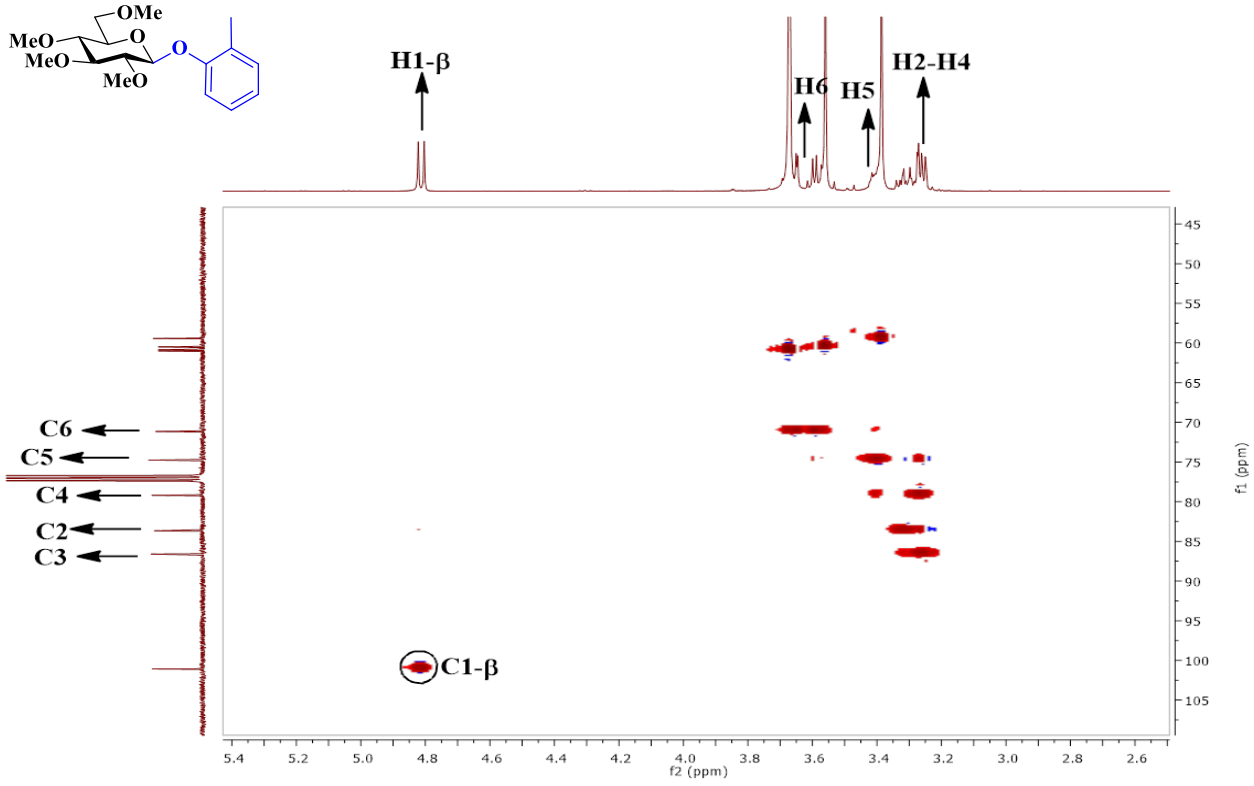
^{13}C {^{1}H} NMR spectrum of compound 4a (125 MHz, $CDCl_3$)



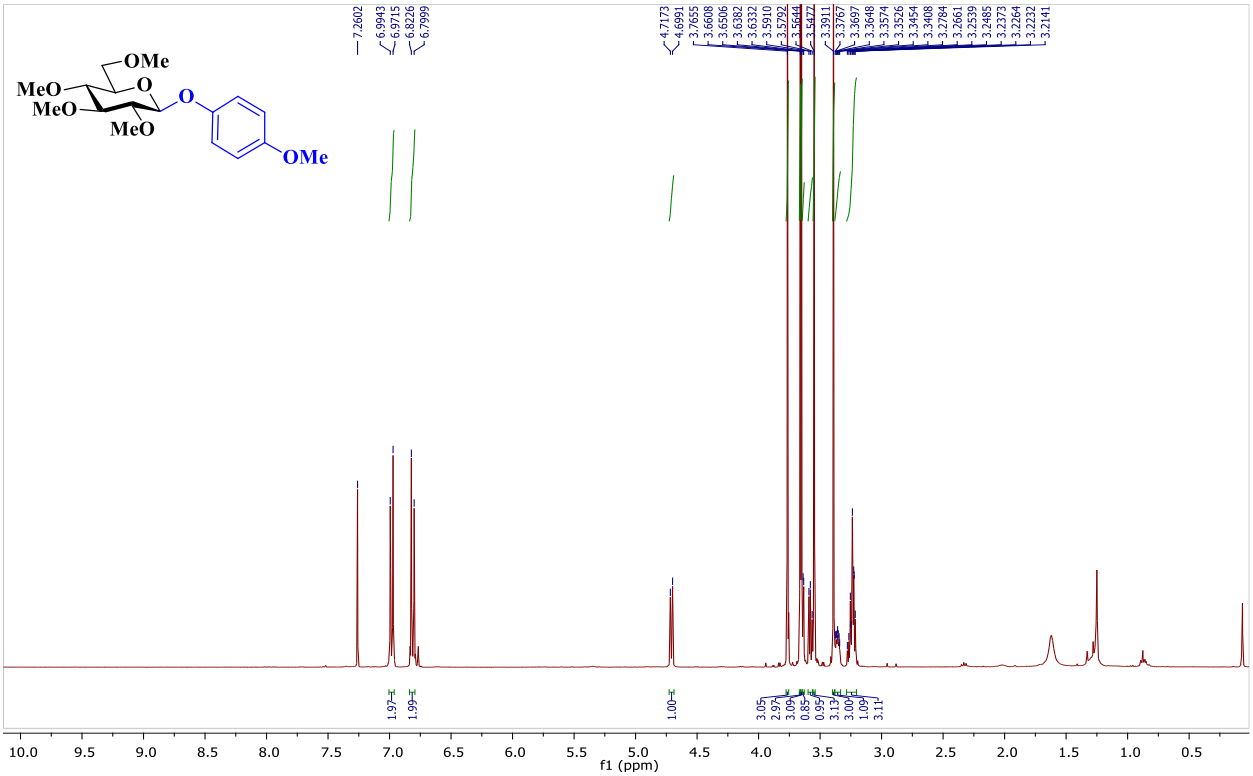
COSY spectrum of compound 4a



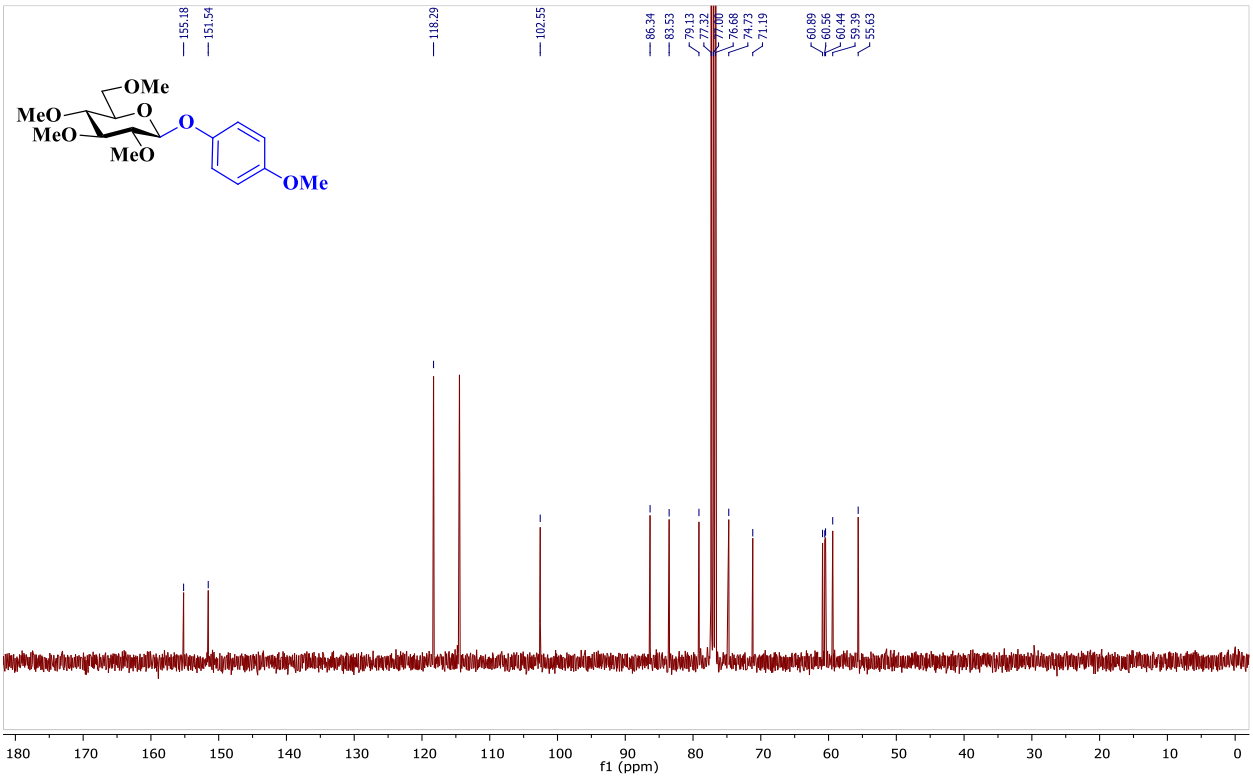
HSQC spectrum of compound 4a



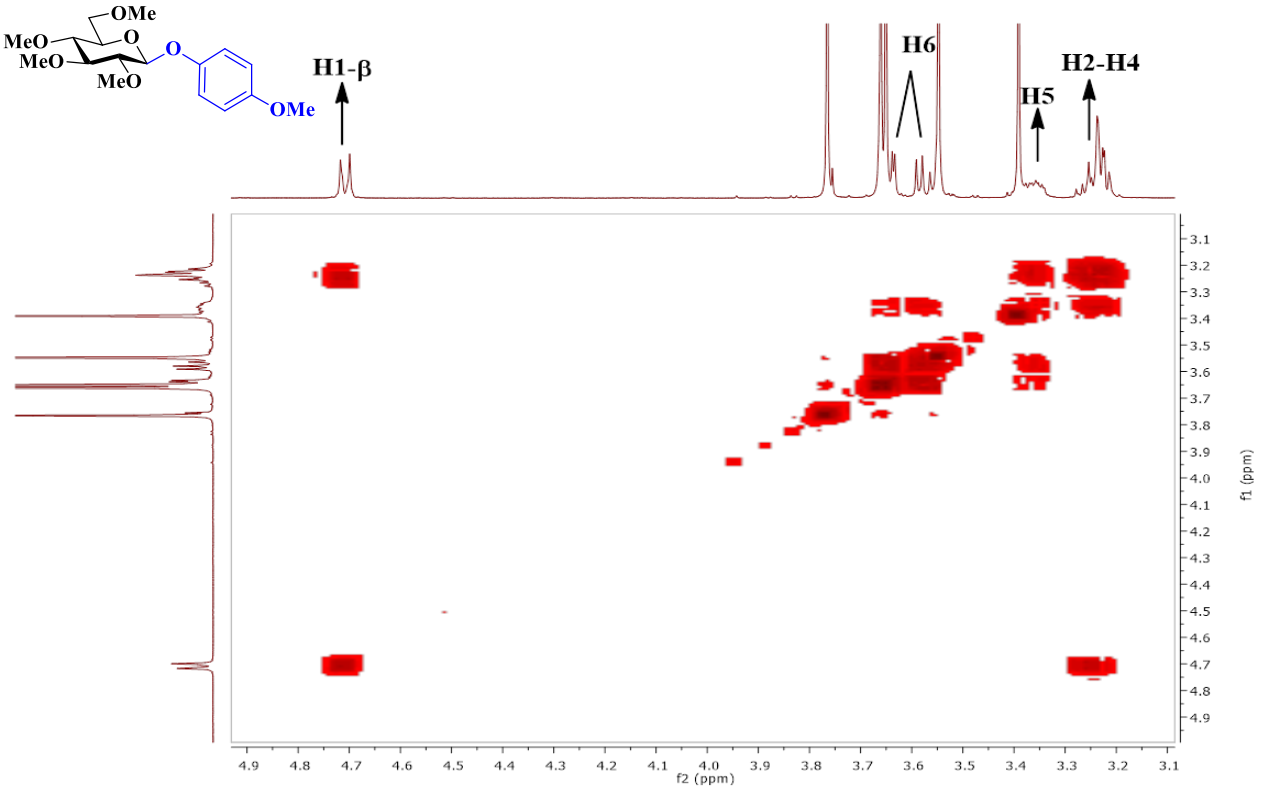
^{1}H NMR spectrum of compound 4b (400 MHz, $CDCl_3$)



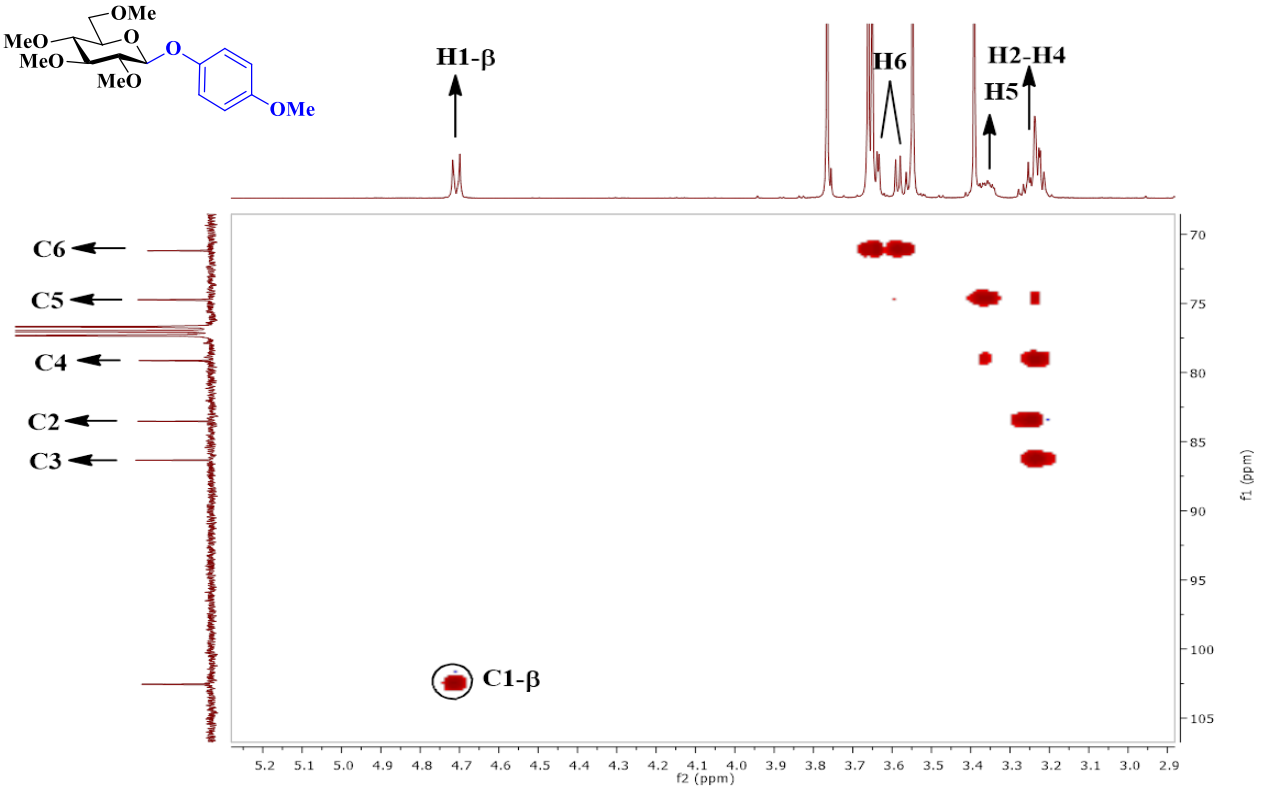
^{13}C {^{1}H} NMR spectrum of compound 4b (100 MHz, $CDCl_3$)



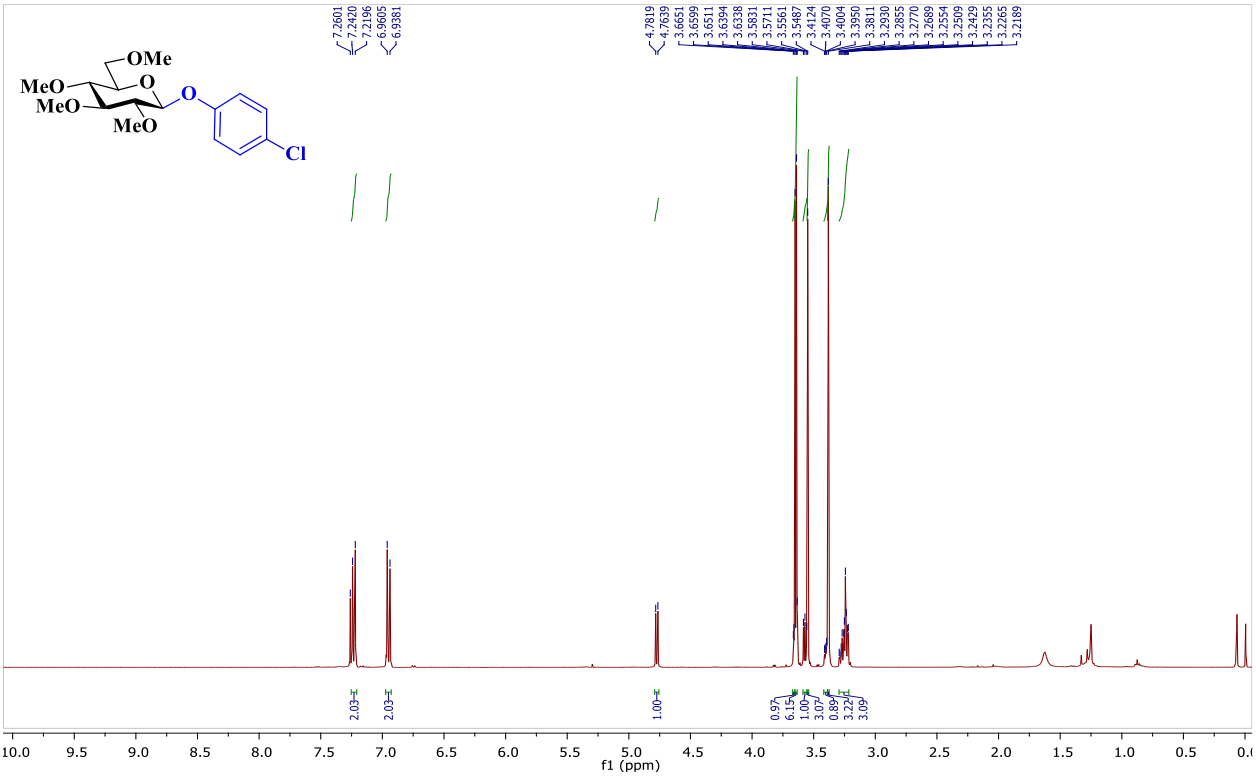
COSY spectrum of 4b



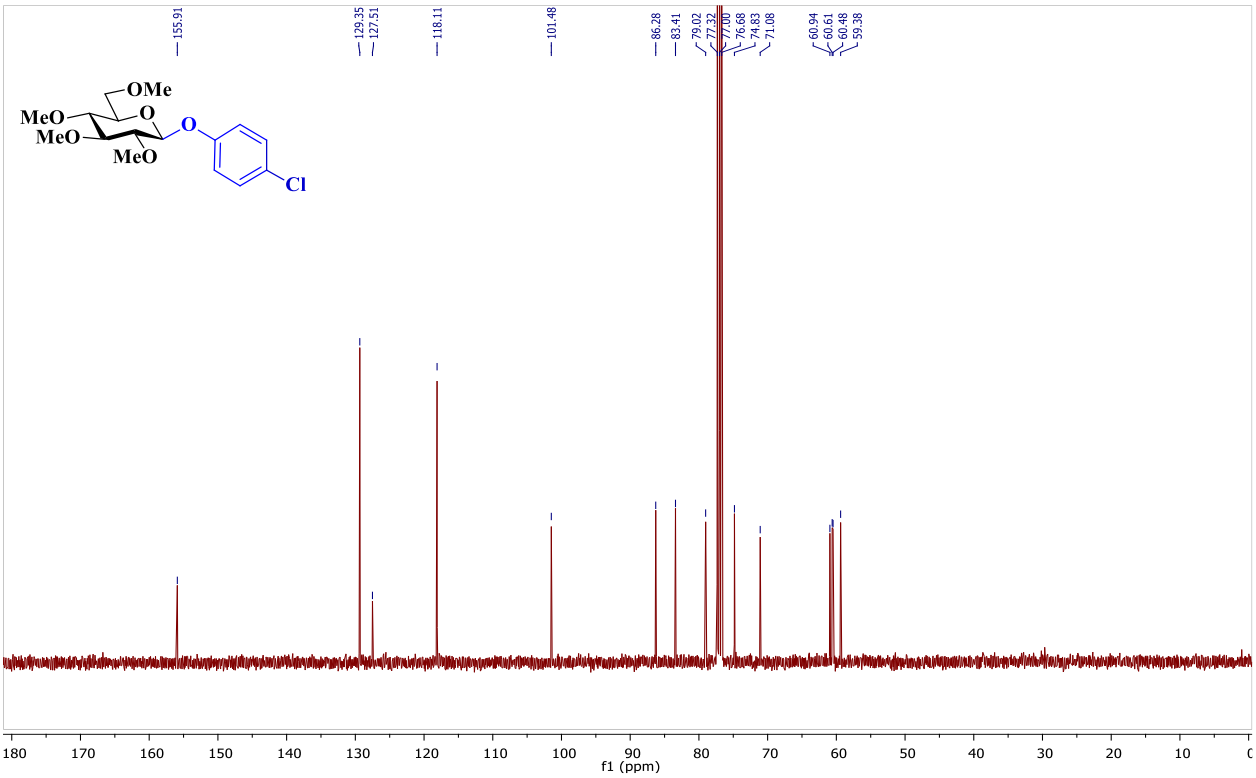
HSQC spectrum of compound 4b



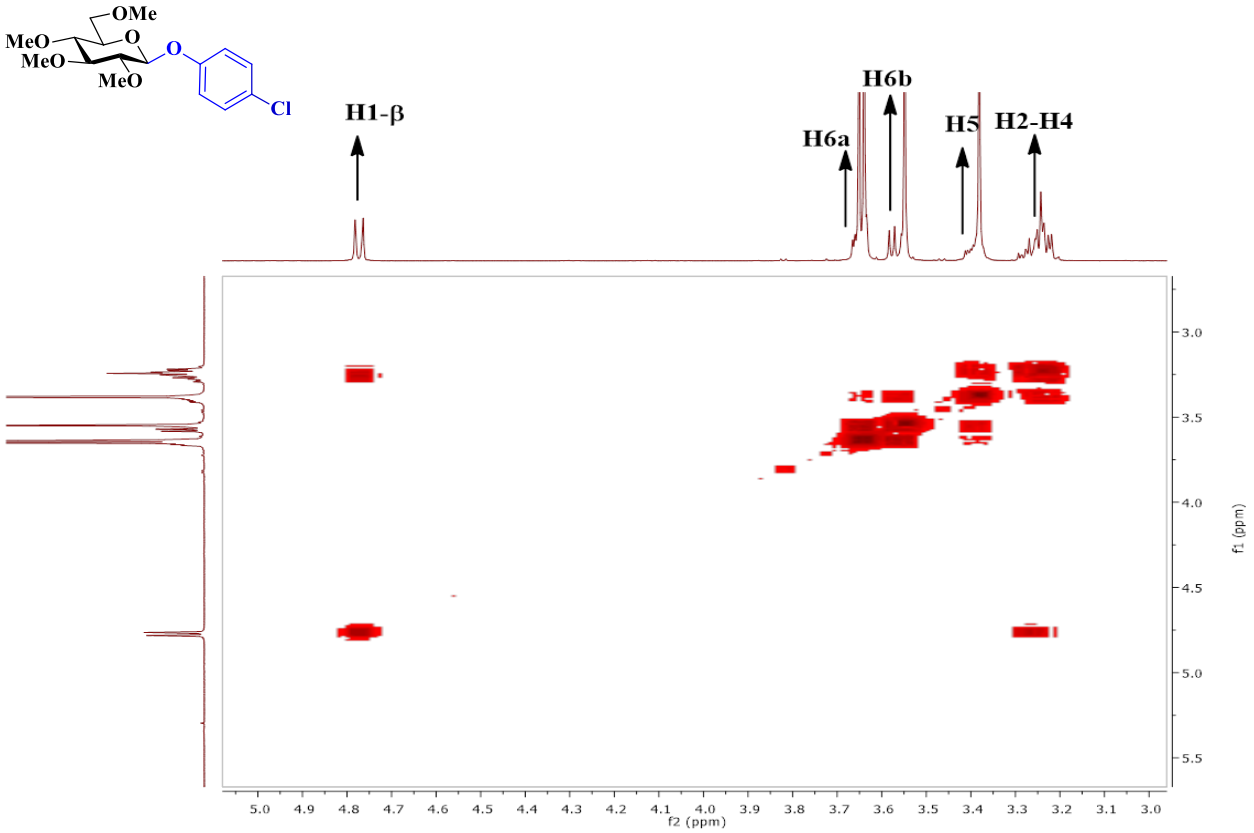
^{1}H NMR spectrum of compound 4c (400 MHz, $CDCl_3$)



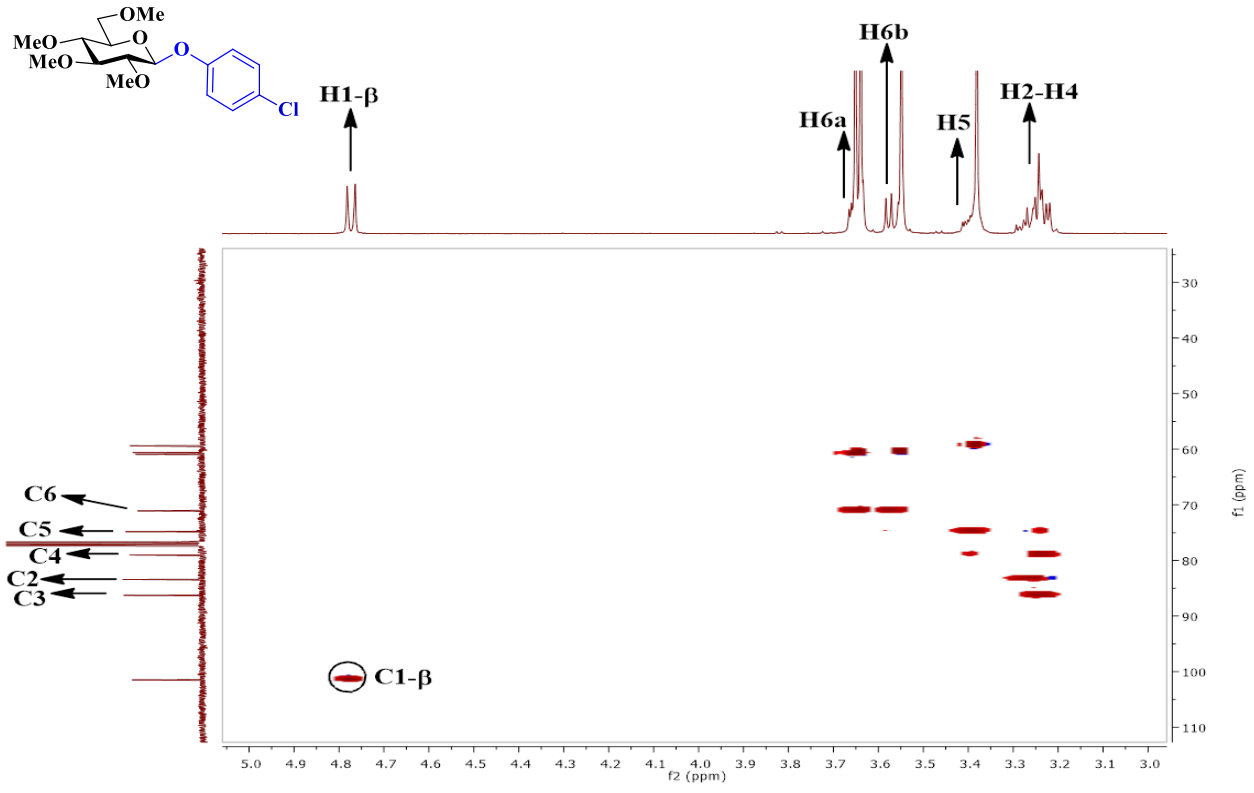
^{13}C {^{1}H} NMR spectrum of compound 4c (100 MHz, $CDCl_3$)



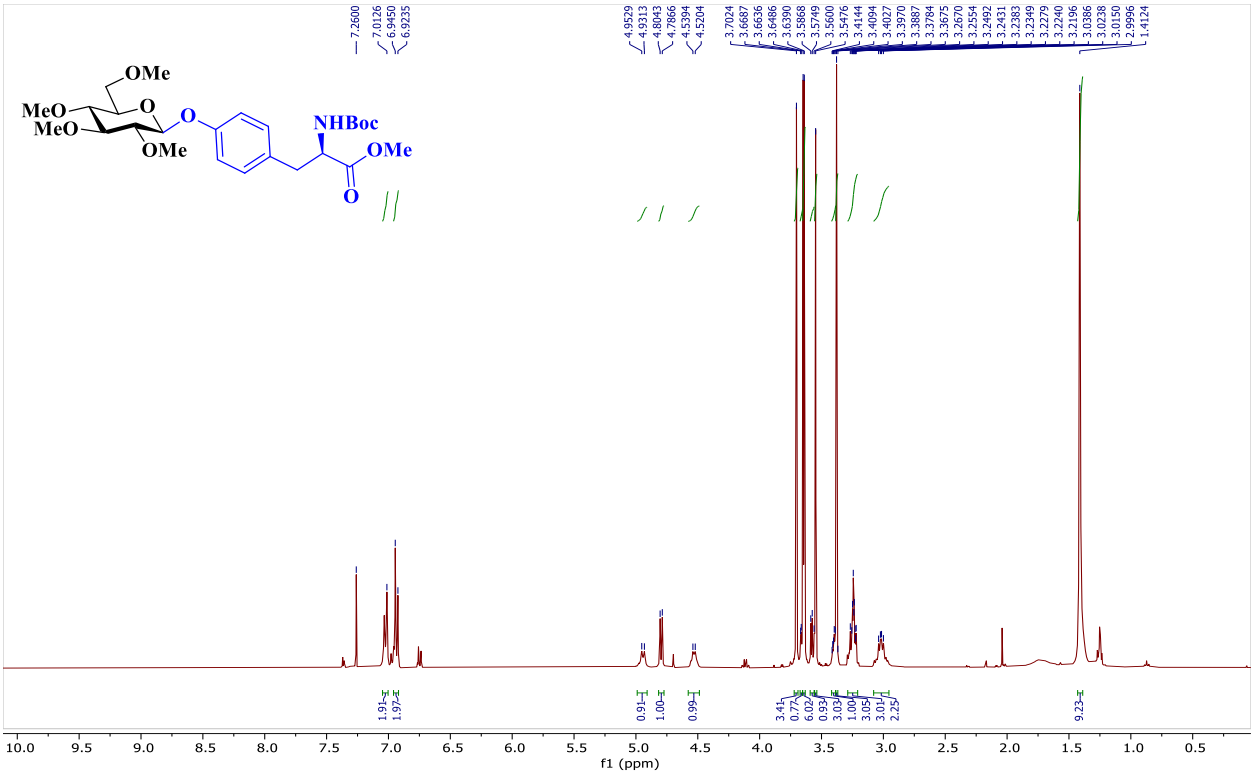
COSY spectrum of compound 4c



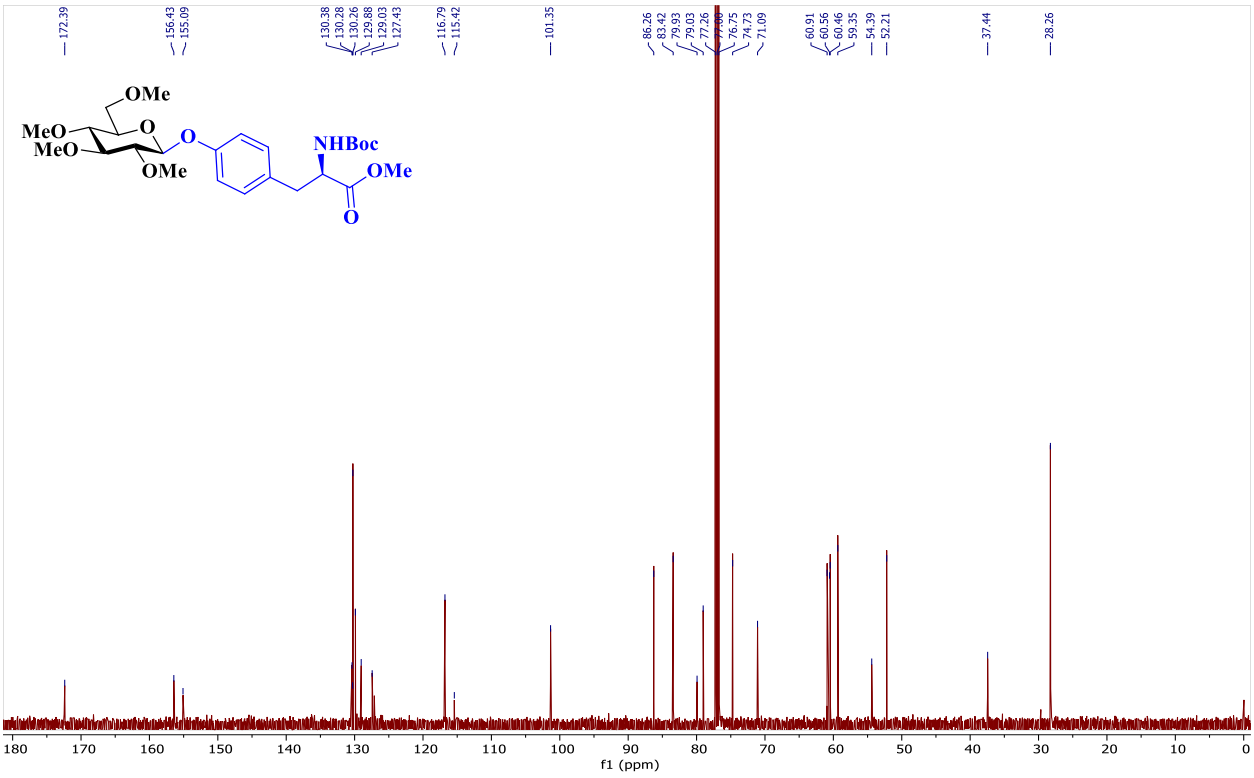
HSQC spectrum of compound 4c



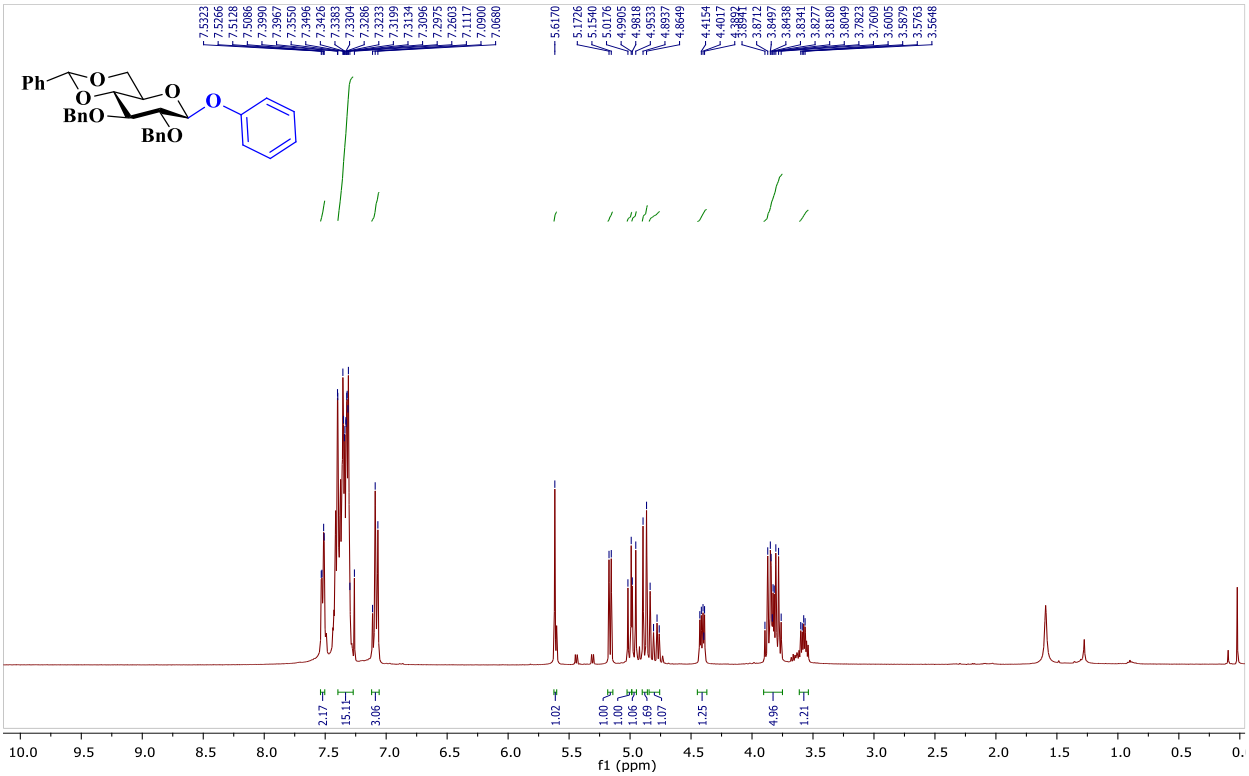
^{1}H NMR spectrum of compound 4d (500 MHz, $CDCl_3$)



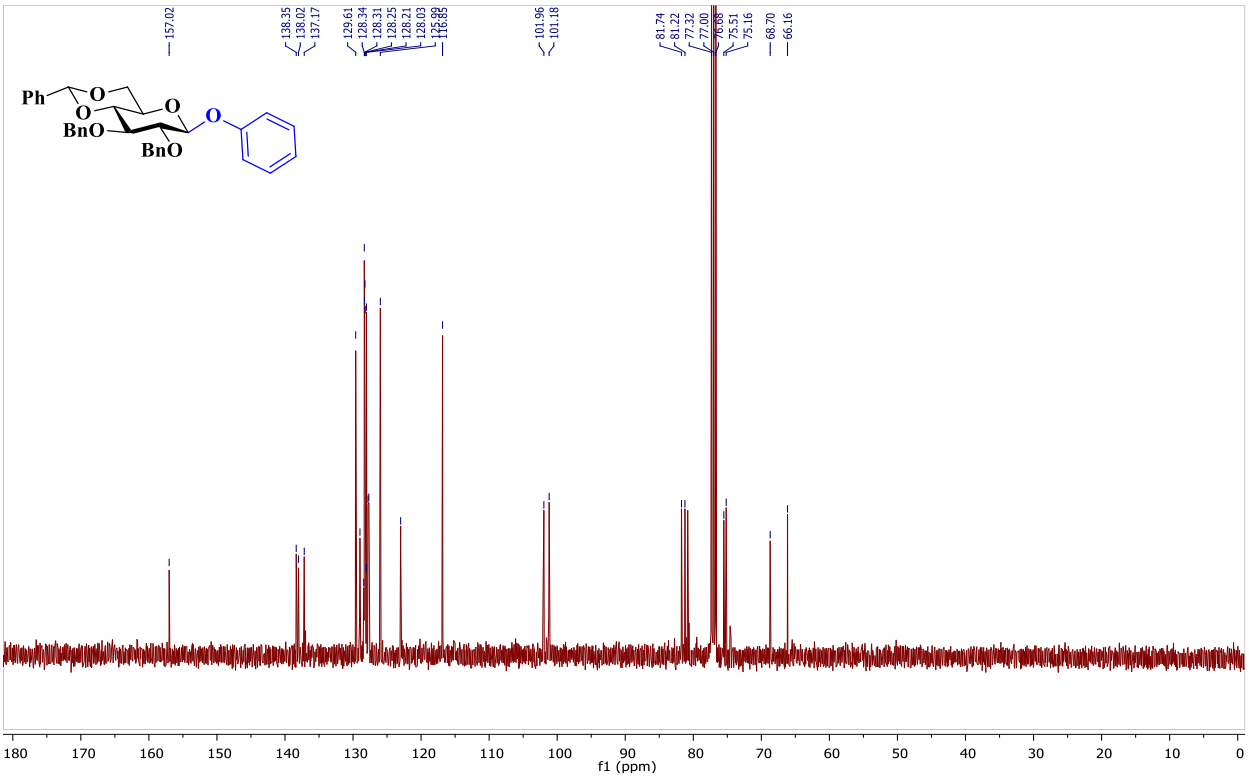
^{13}C {^{1}H} NMR spectrum of compound 4d (125 MHz, $CDCl_3$)



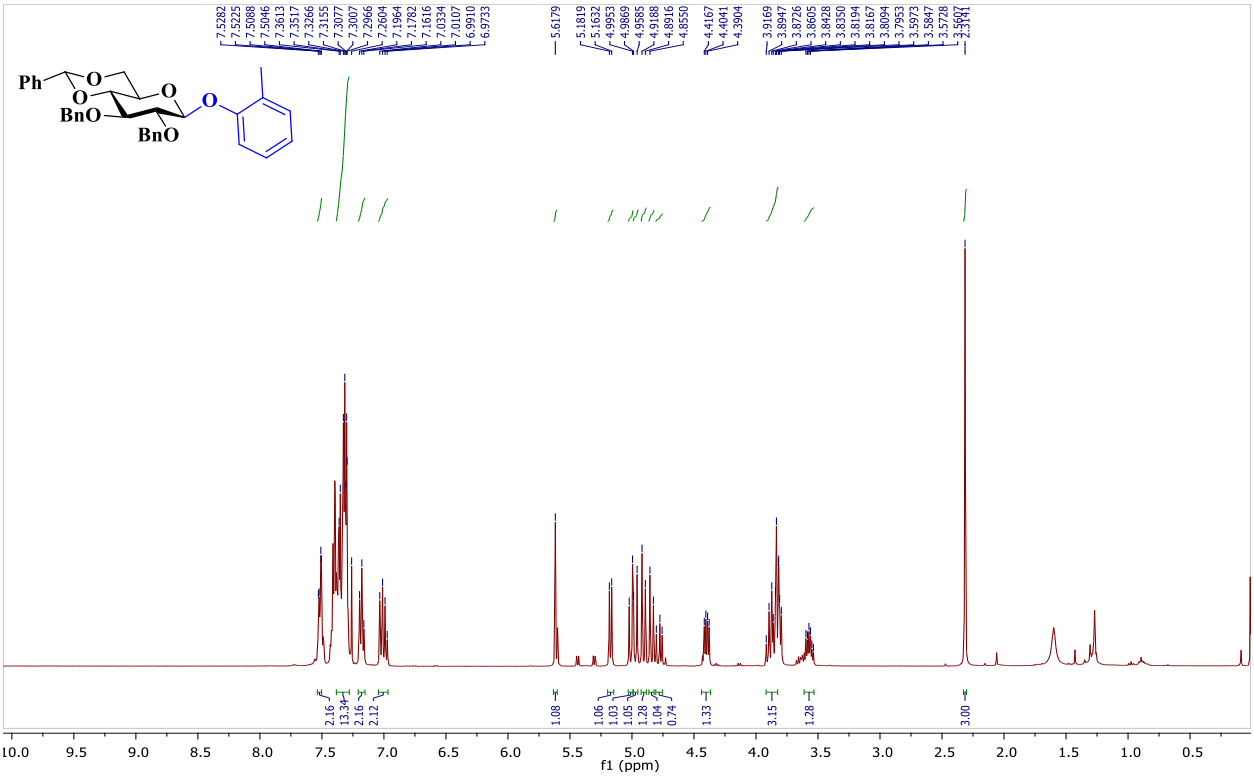
^{1}H NMR spectrum of compound 5a (400 MHz, $CDCl_3$)



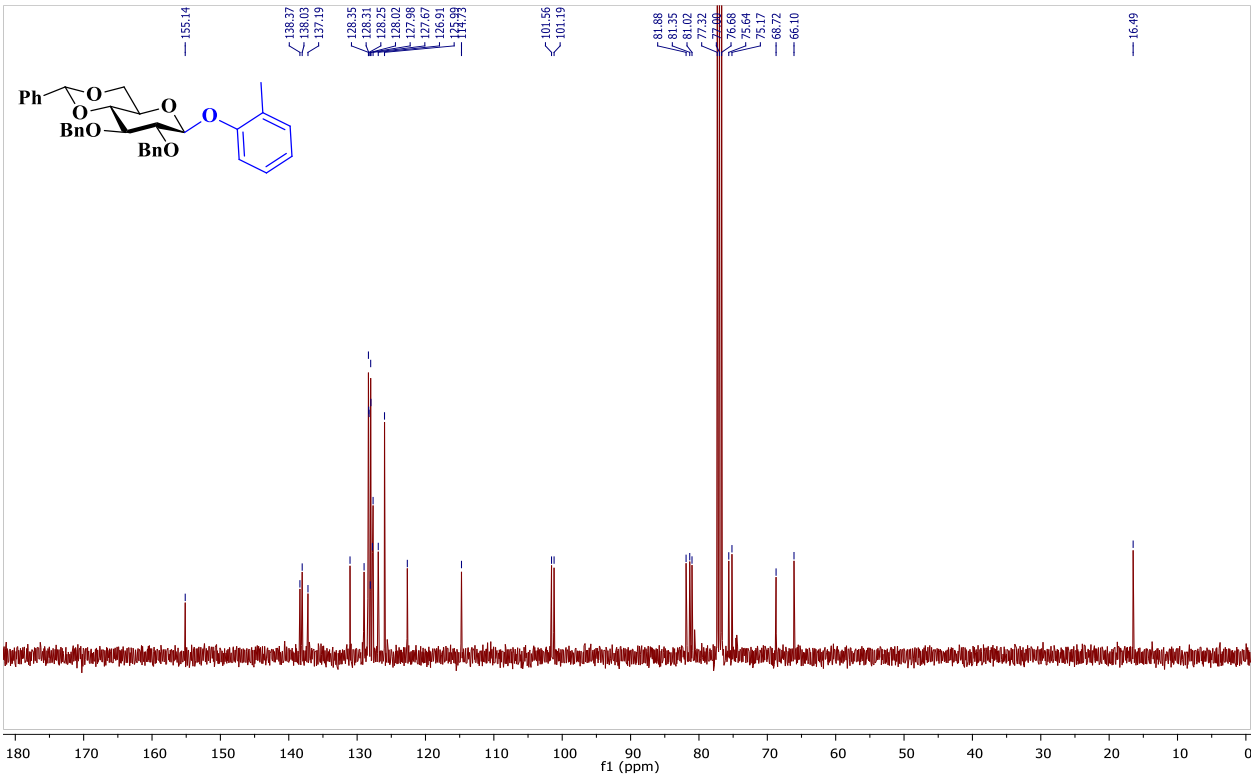
^{13}C {1H} NMR spectrum of compound 5a (100 MHz, $CDCl_3$)



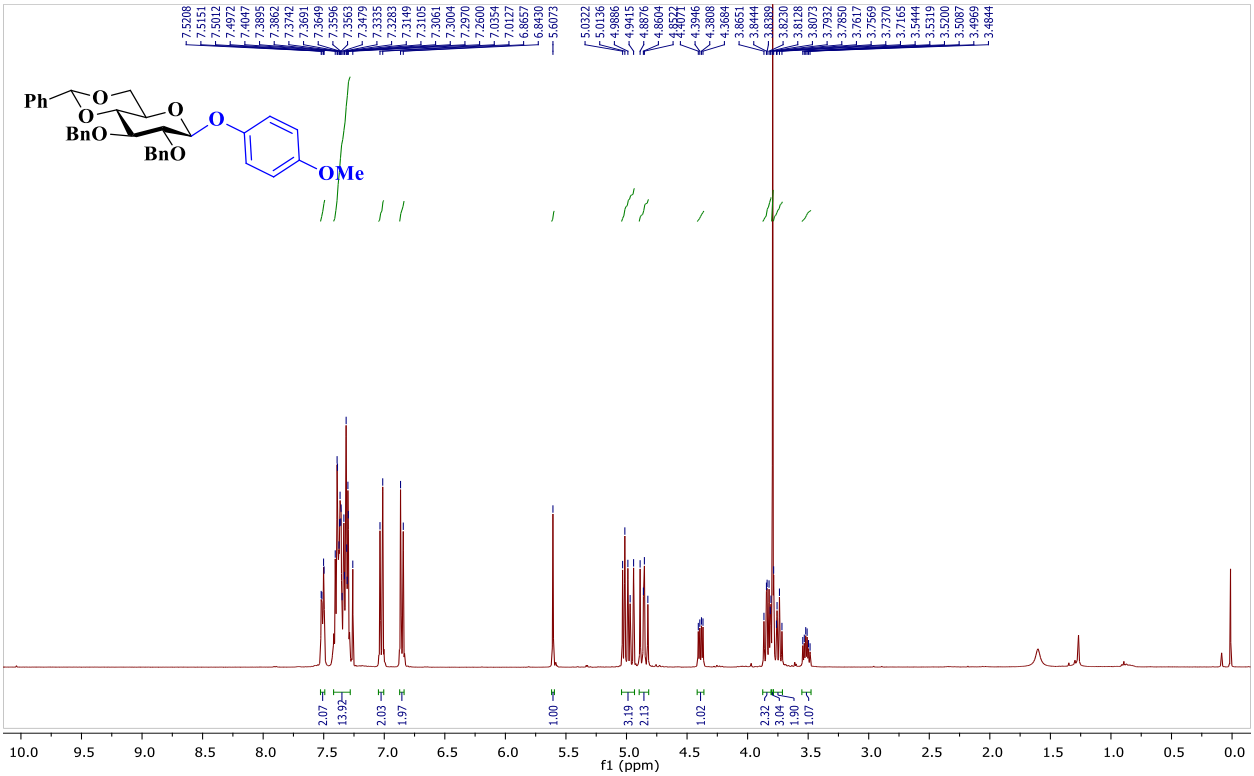
^{1}H NMR spectrum of compound 5b (400 MHz, $CDCl_3$)



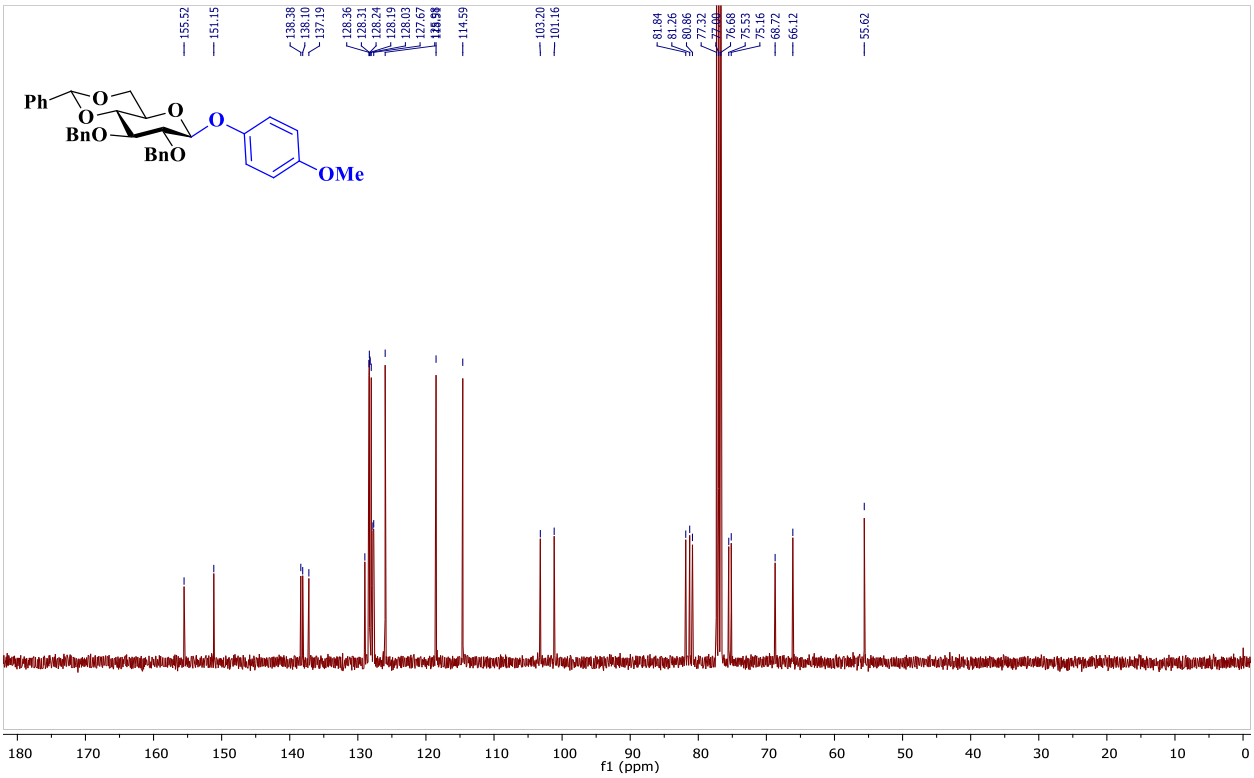
^{13}C NMR spectrum of compound 5b (100 MHz, $CDCl_3$)



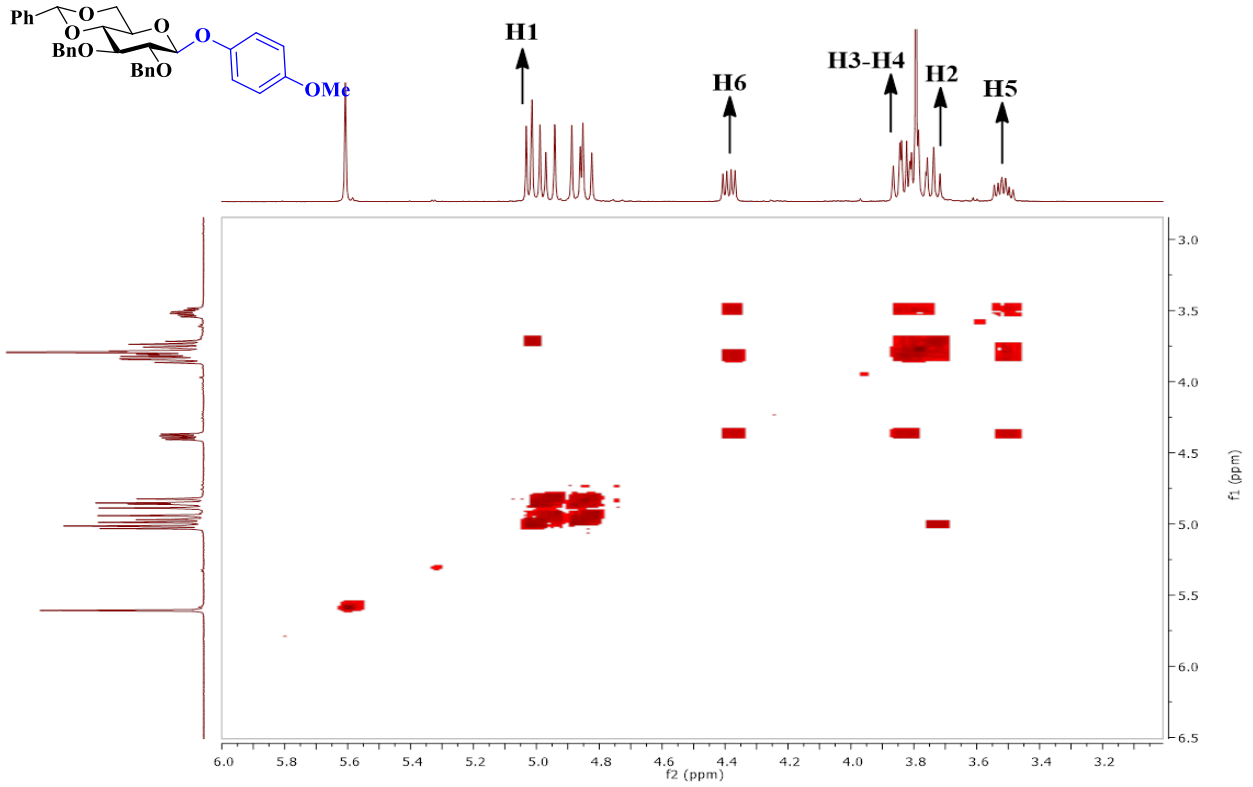
^{1}H NMR spectrum of compound 5c (400 MHz, $CDCl_3$)



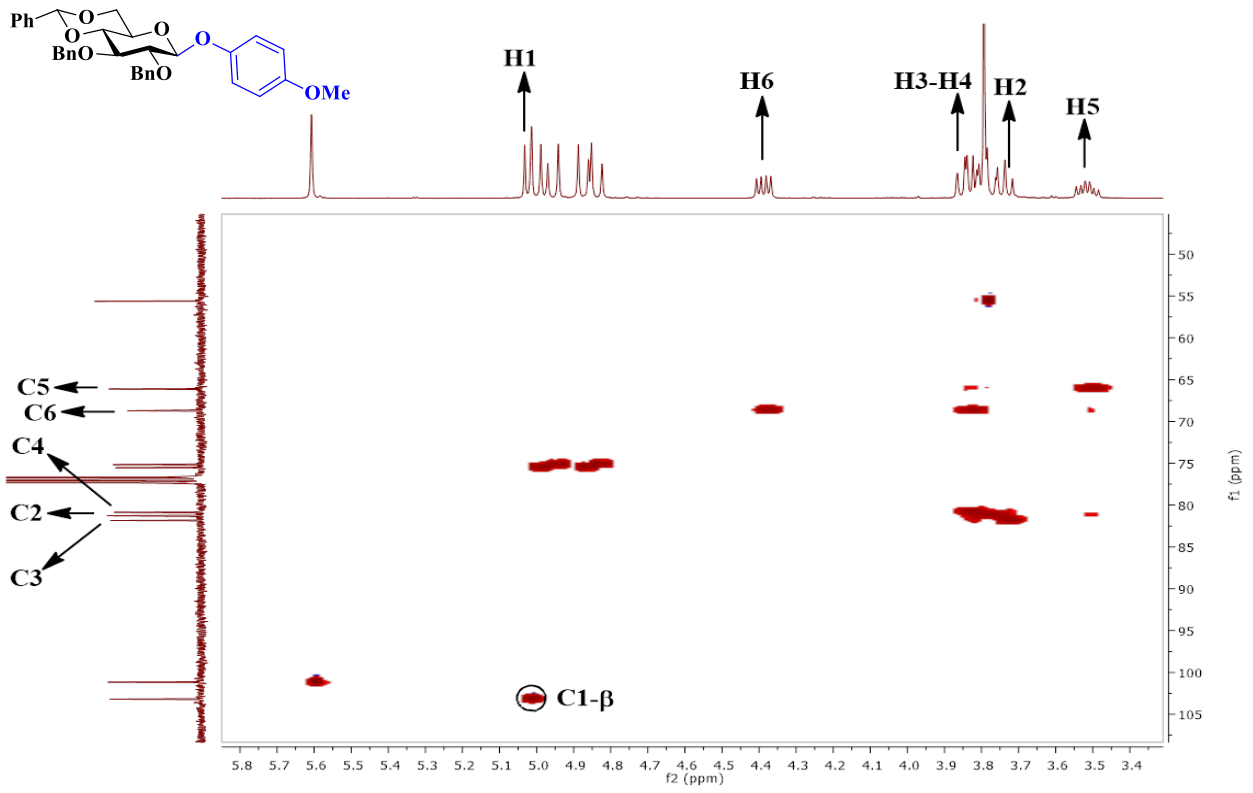
^{13}C {^{1}H} NMR spectrum of compound 5c (100 MHz, $CDCl_3$)



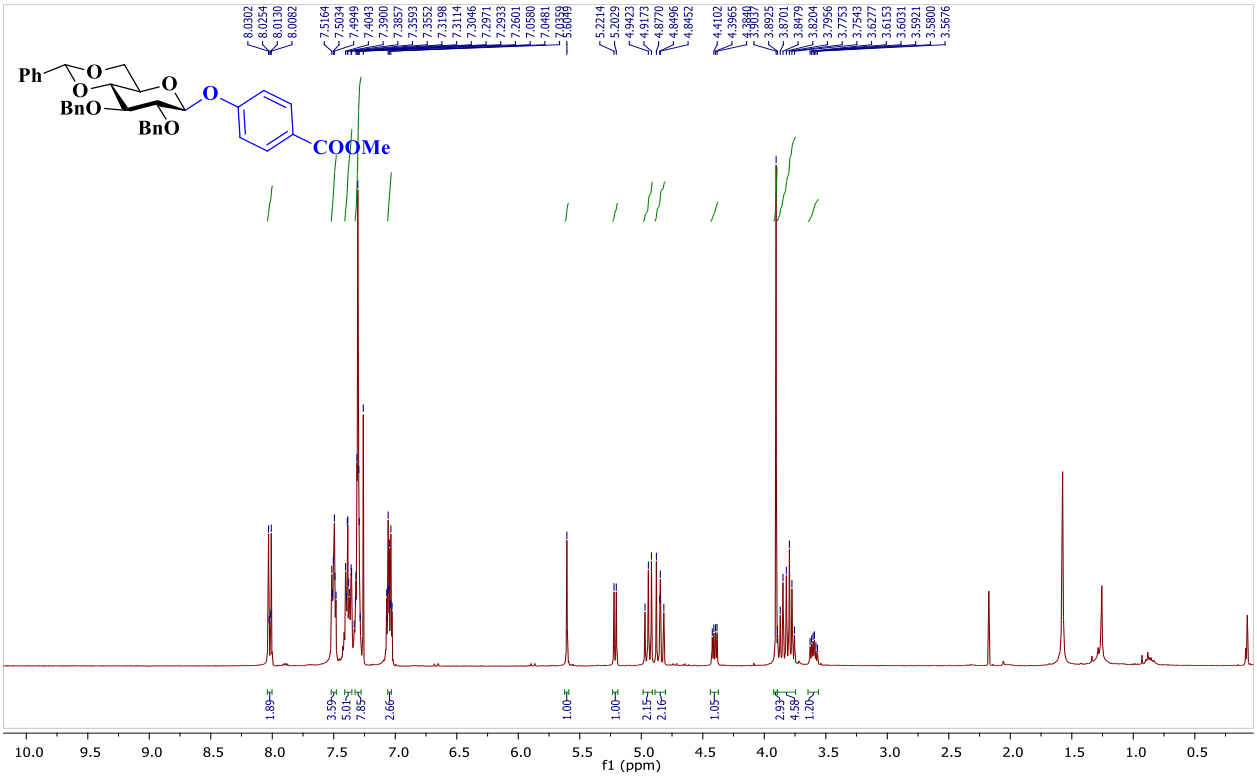
COSY spectrum of compound 5c



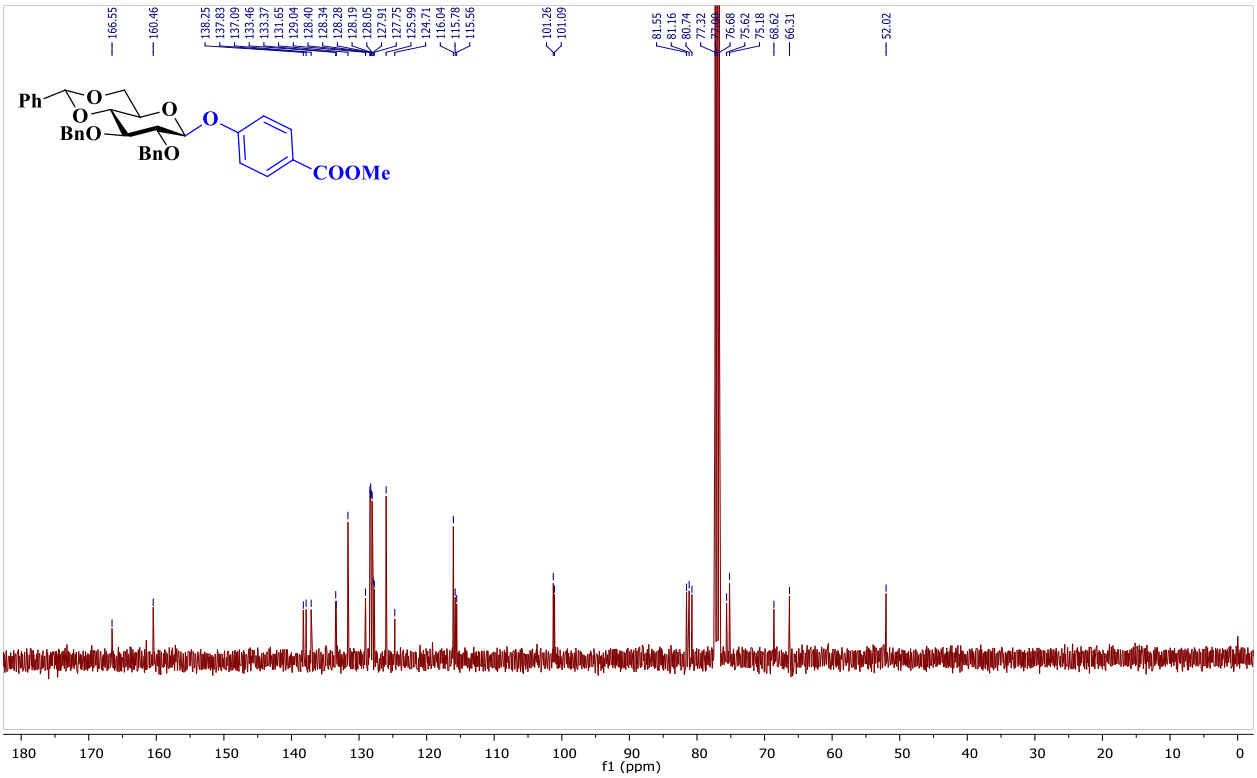
HSQC spectrum of compound 5c



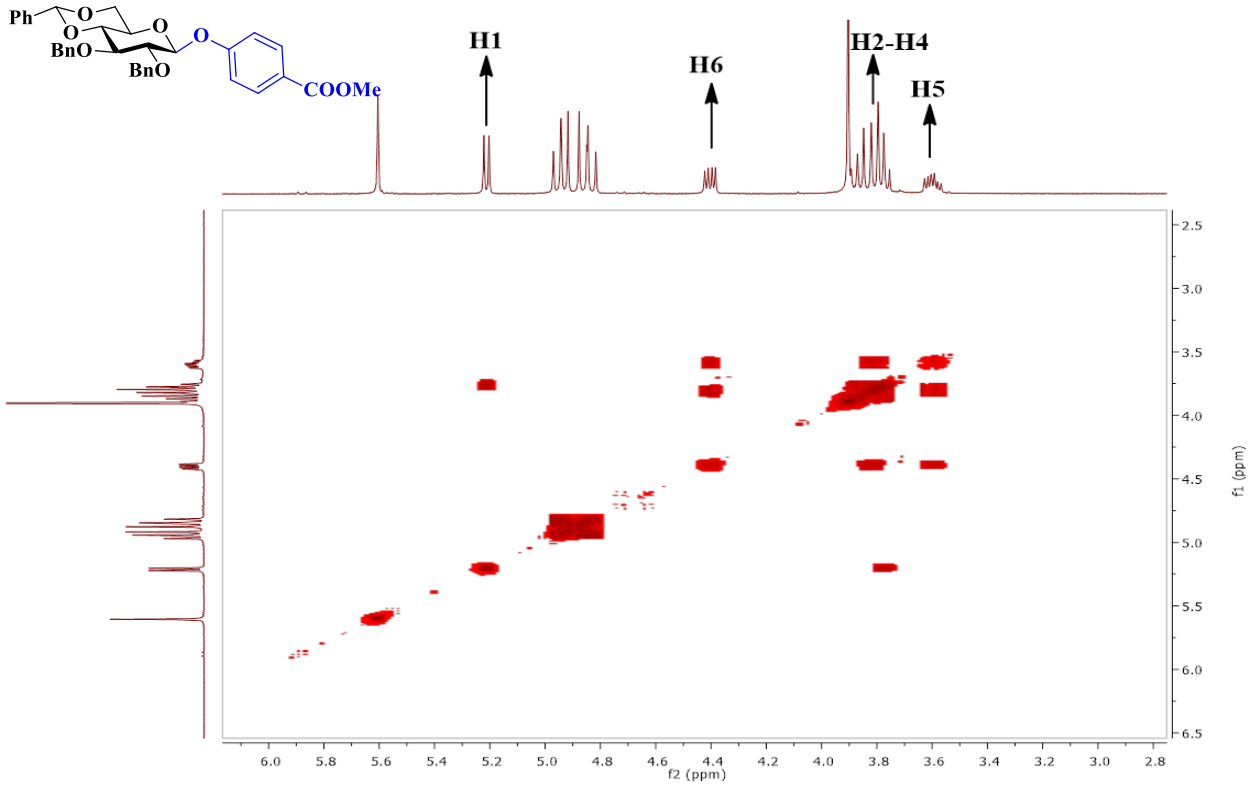
^{1}H NMR spectrum of compound 5d (400 MHz, $CDCl_3$)



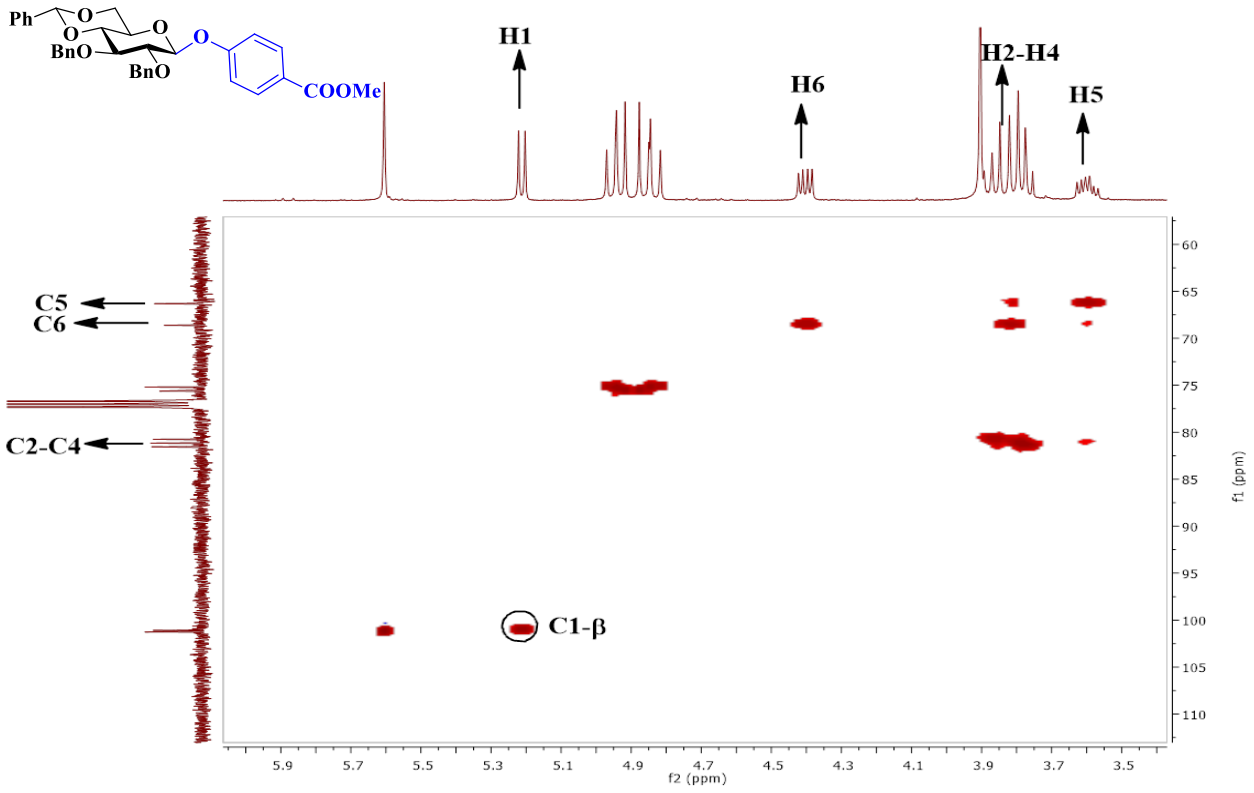
^{13}C {^{1}H} NMR spectrum of compound 5d (100 MHz, $CDCl_3$)



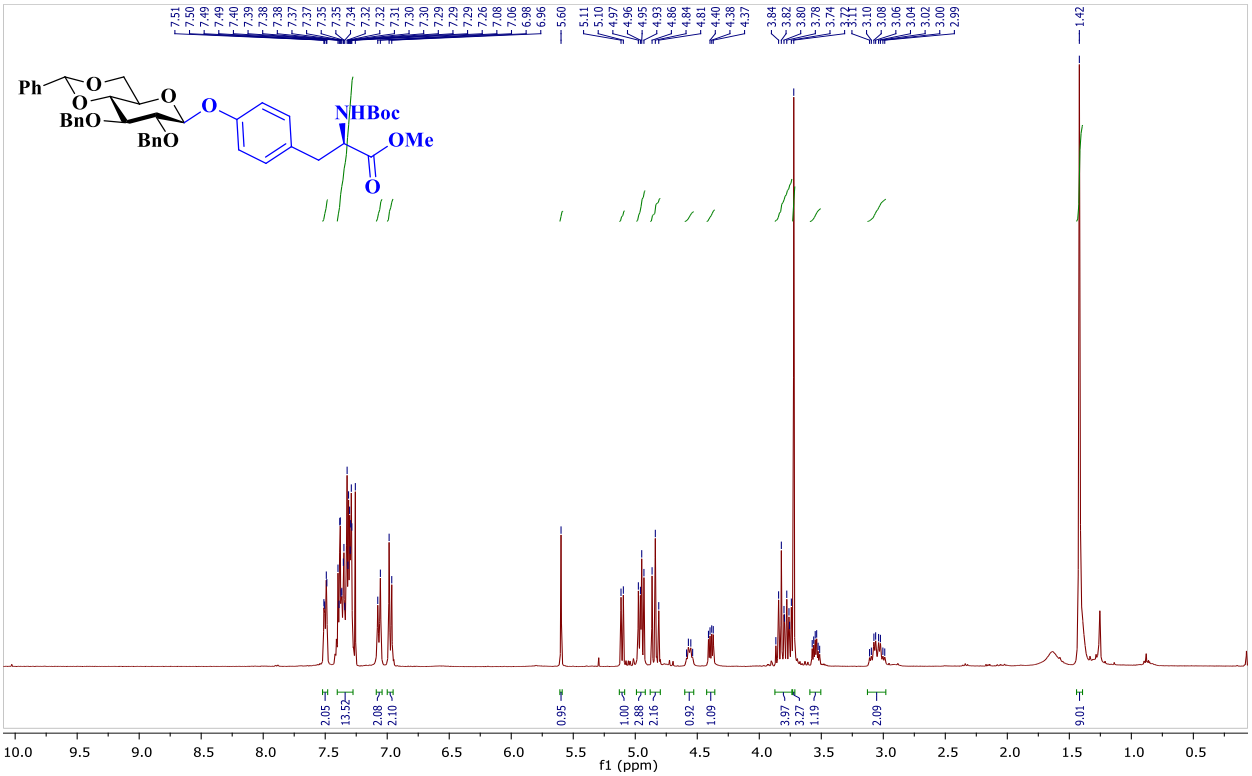
COSY spectrum of compound 5d



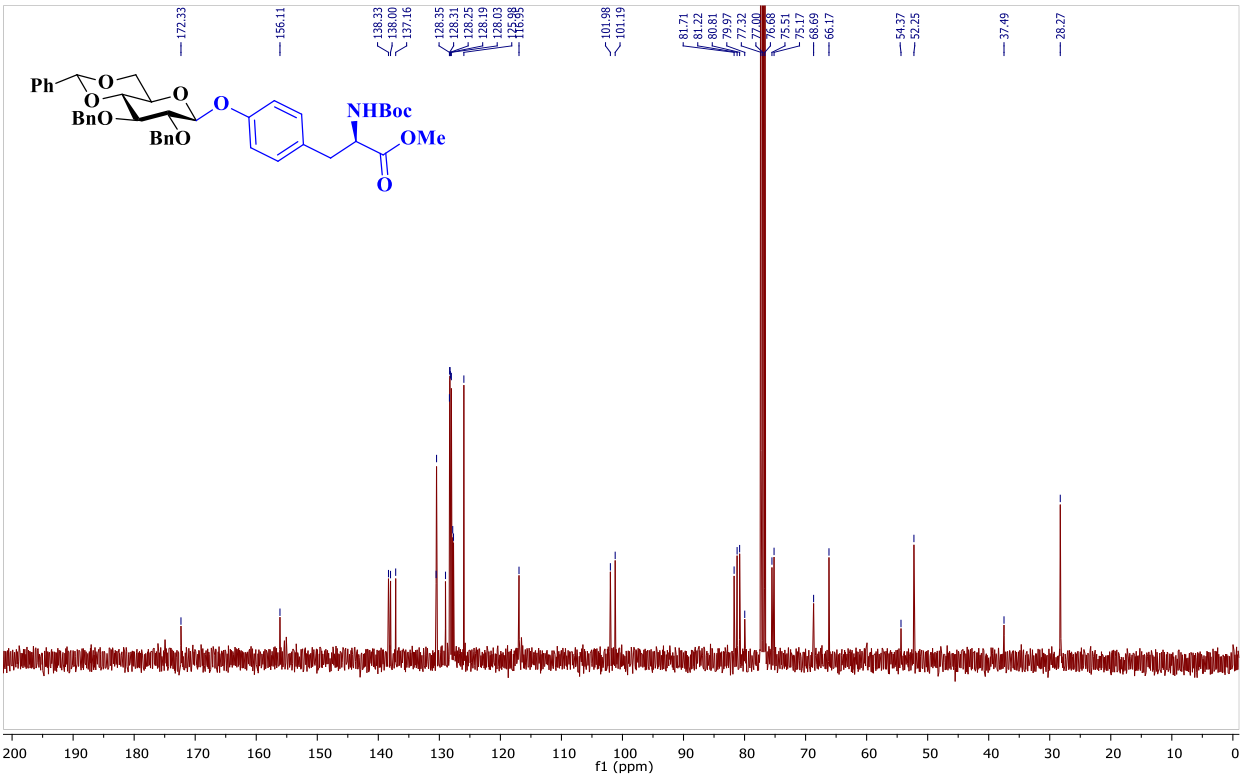
HSQC spectrum of compound 5d



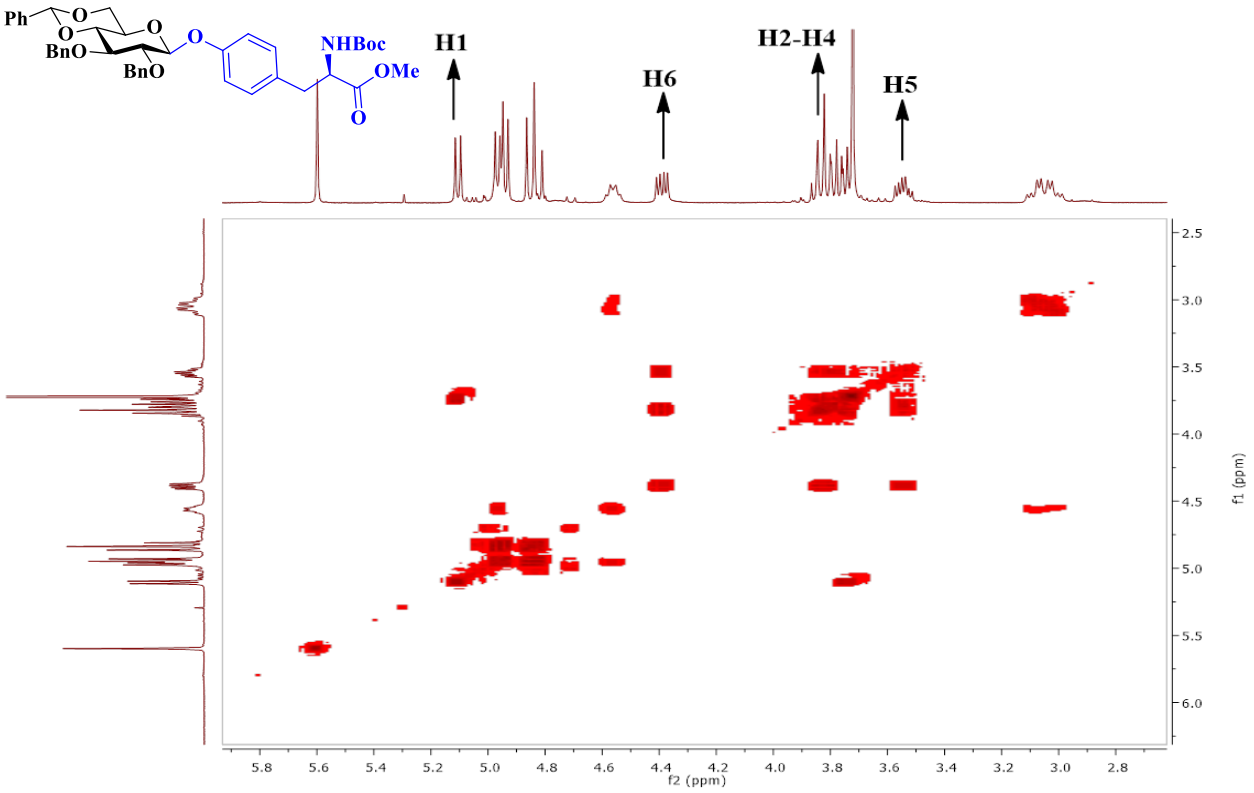
^{1}H NMR spectrum of compound 5e (400 MHz, $CDCl_3$)



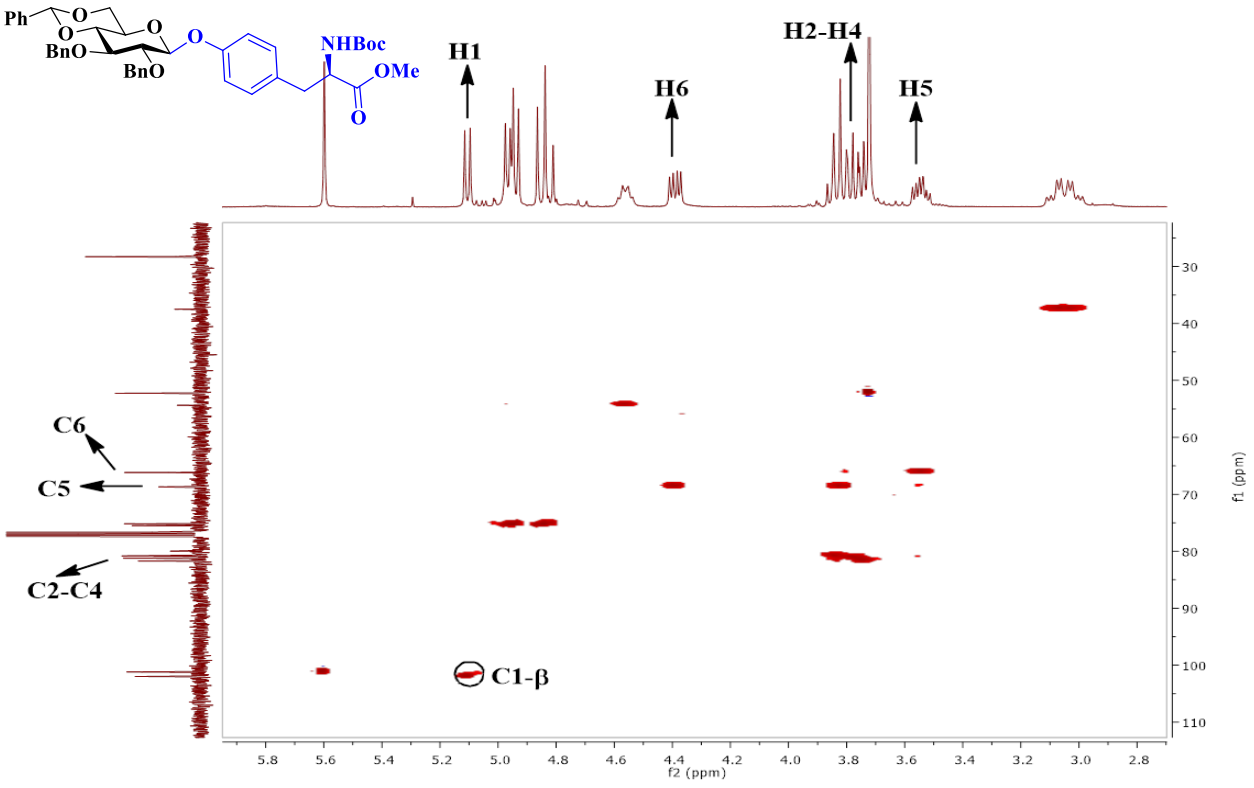
^{13}C {^{1}H} NMR spectrum of compound 5e (100 MHz, $CDCl_3$)



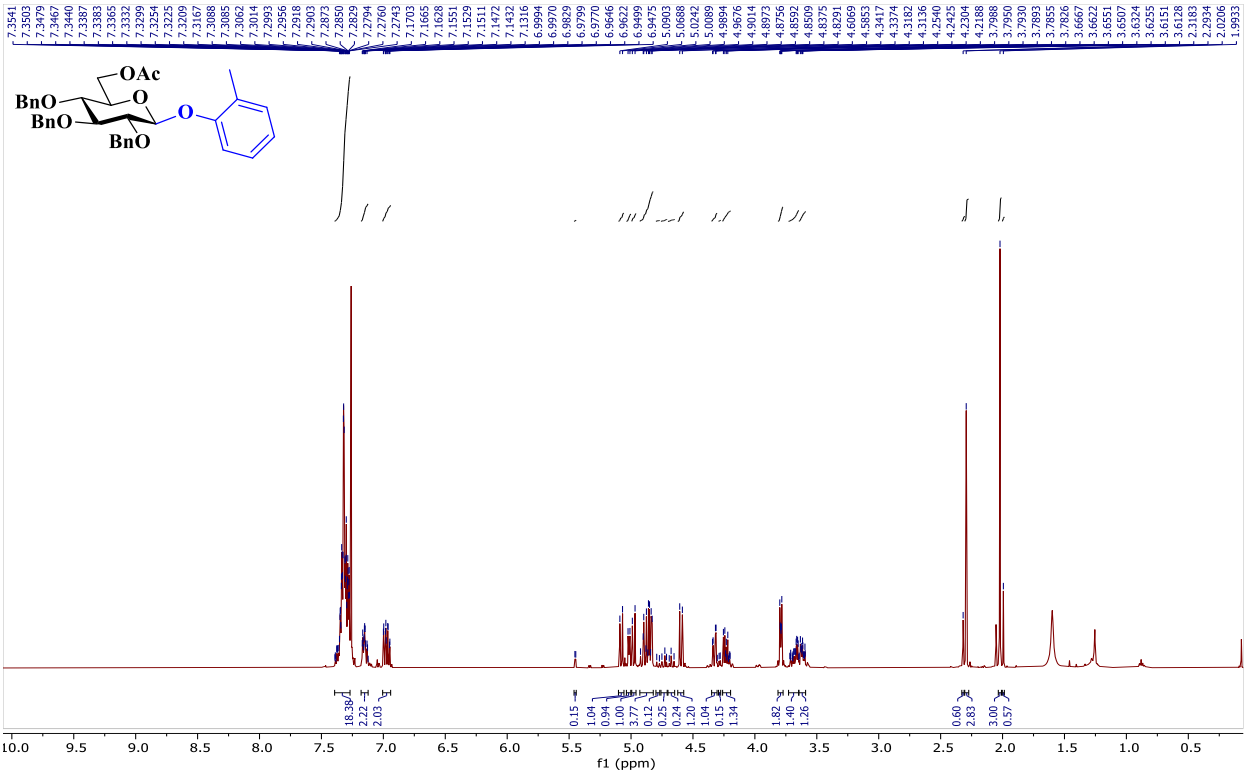
COSY spectrum of compound 5e



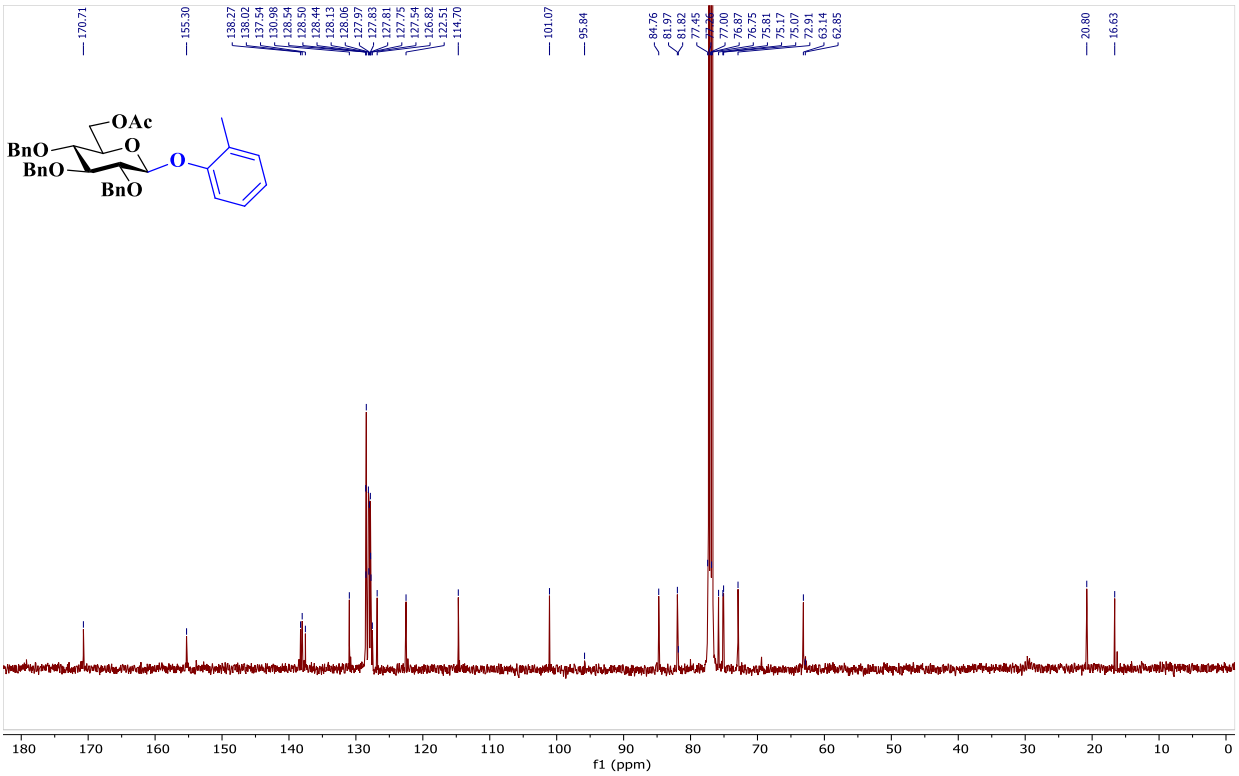
HSQC spectrum of compound 5e



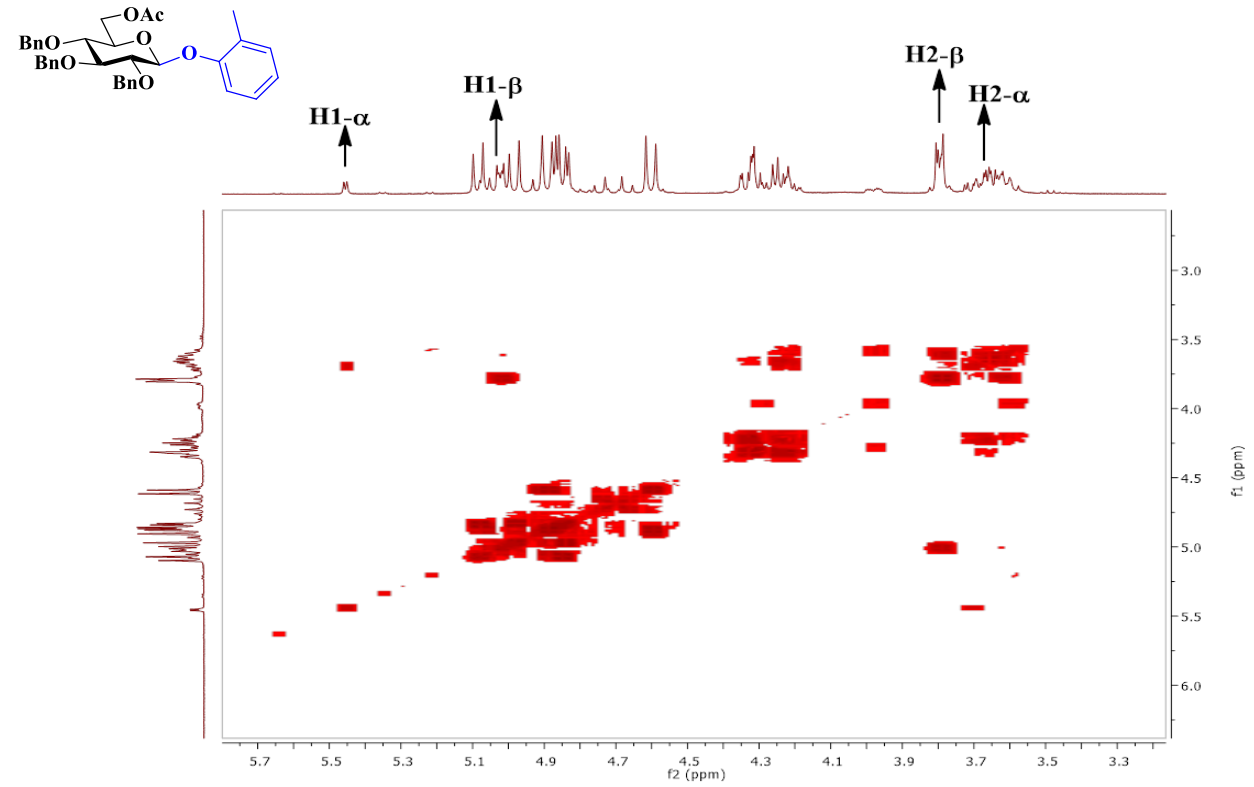
^{1}H NMR spectrum of compound 6a (500 MHz, $CDCl_3$)



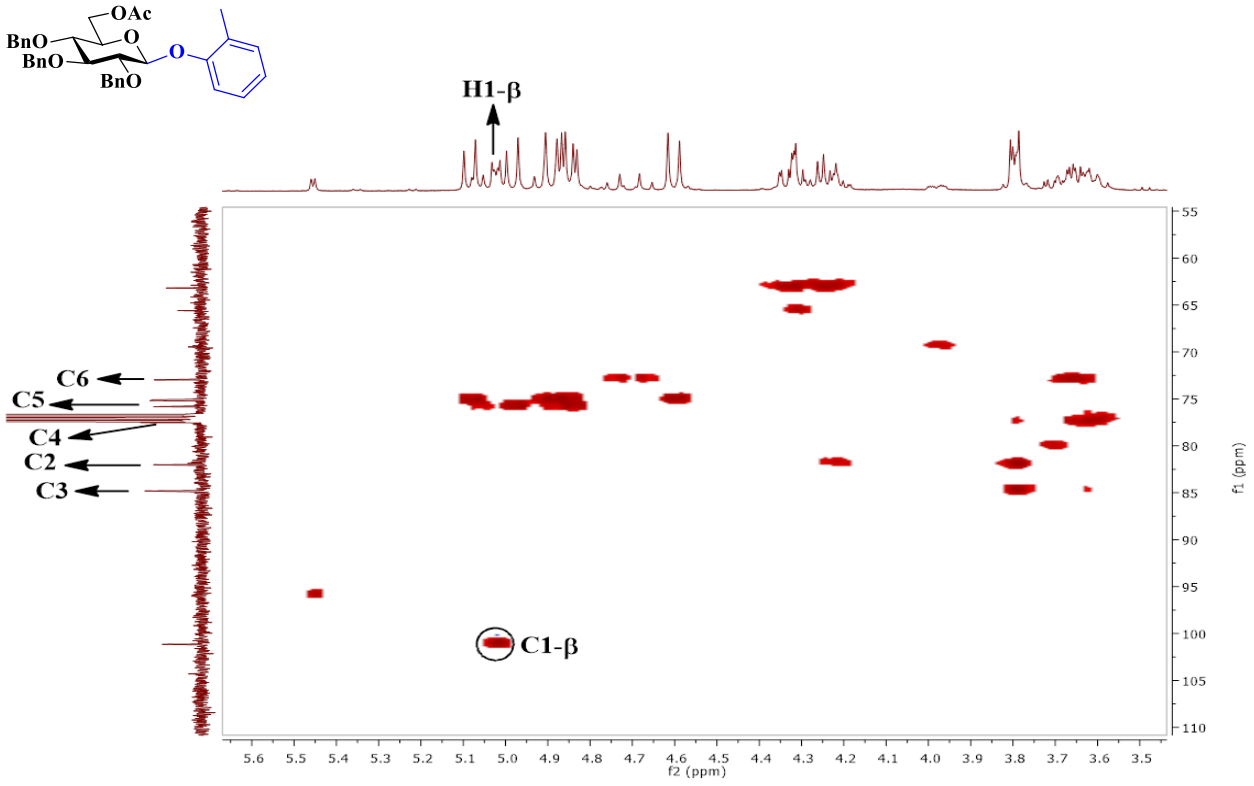
^{13}C {1H} NMR spectrum of compound 6a (125 MHz, $CDCl_3$)



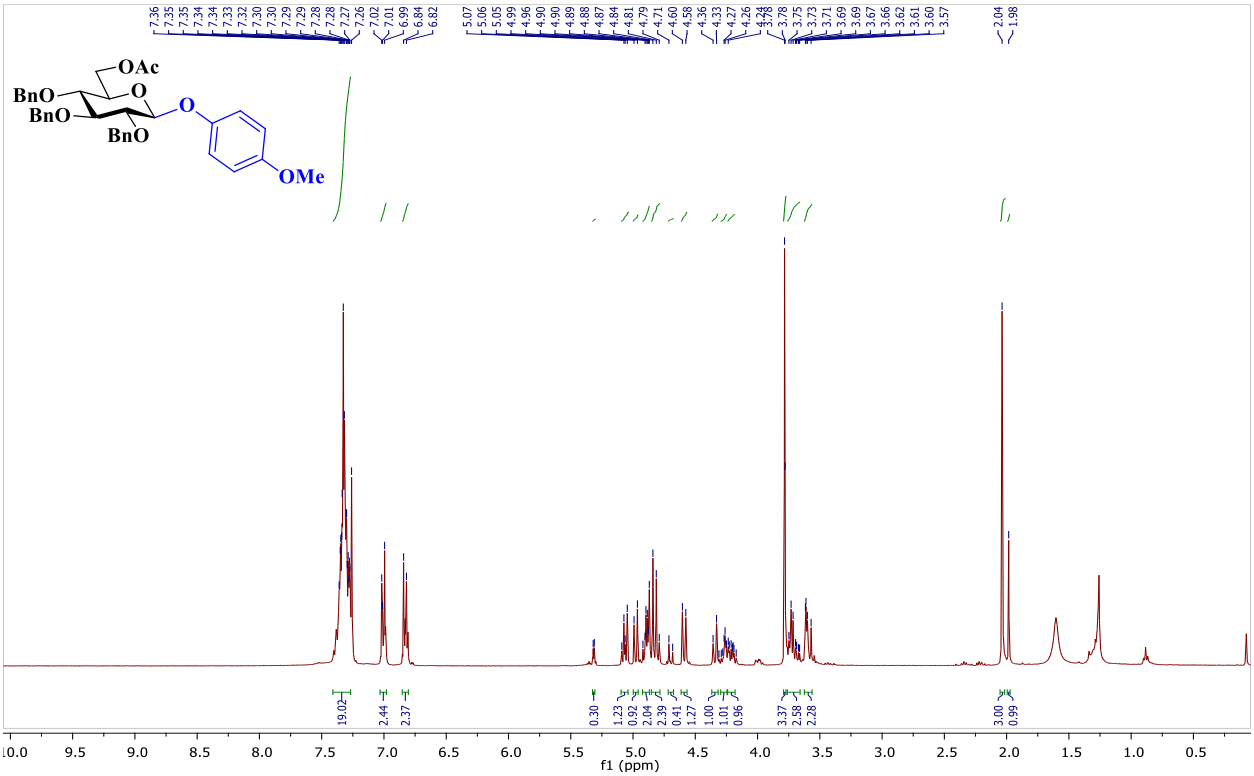
COSY spectrum of compound 6a



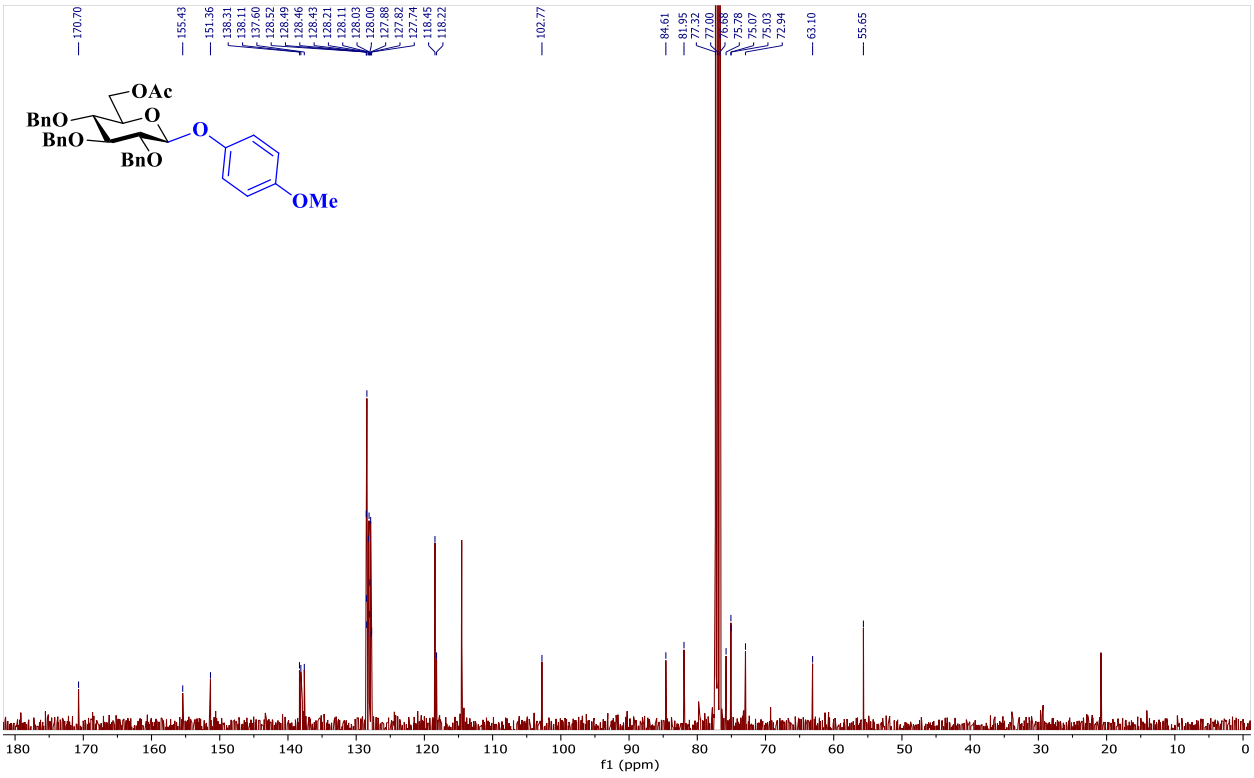
HSQC spectrum of compound 6a



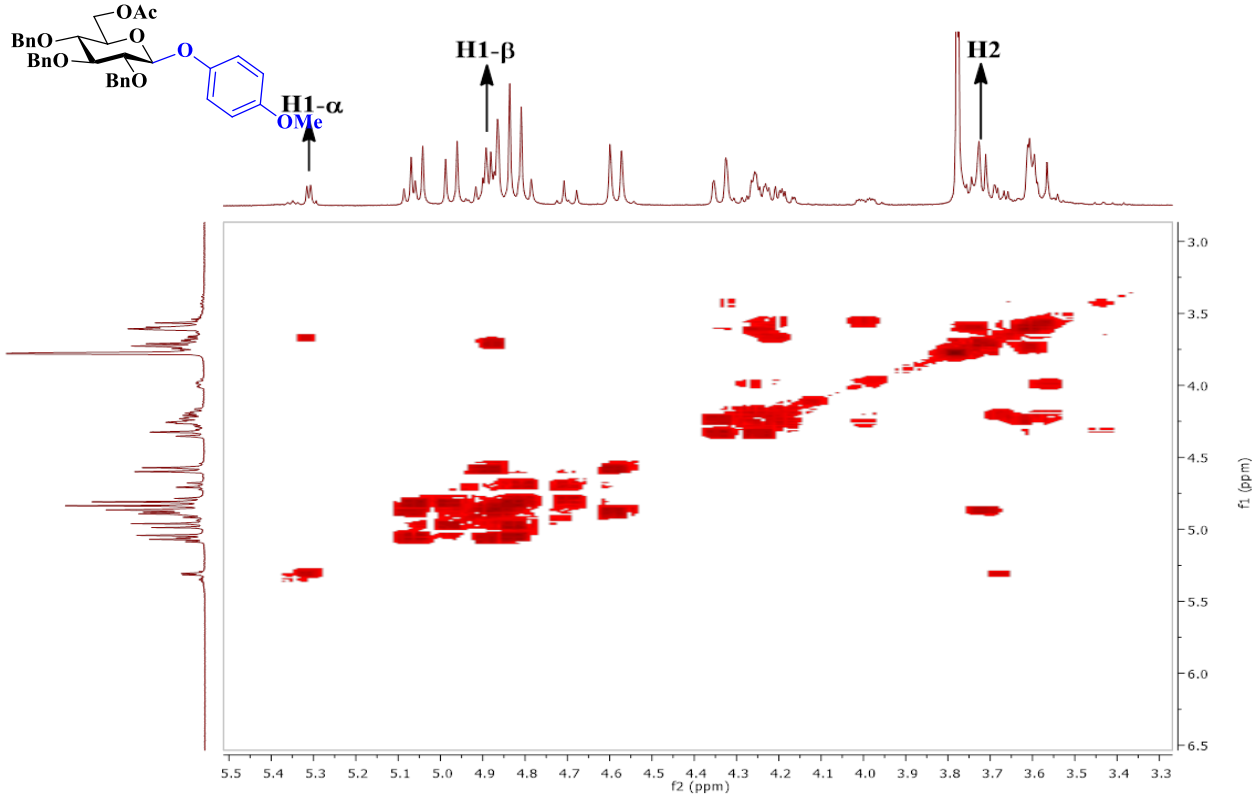
^{1}H NMR spectrum of compound 6b (400 MHz, $CDCl_3$)



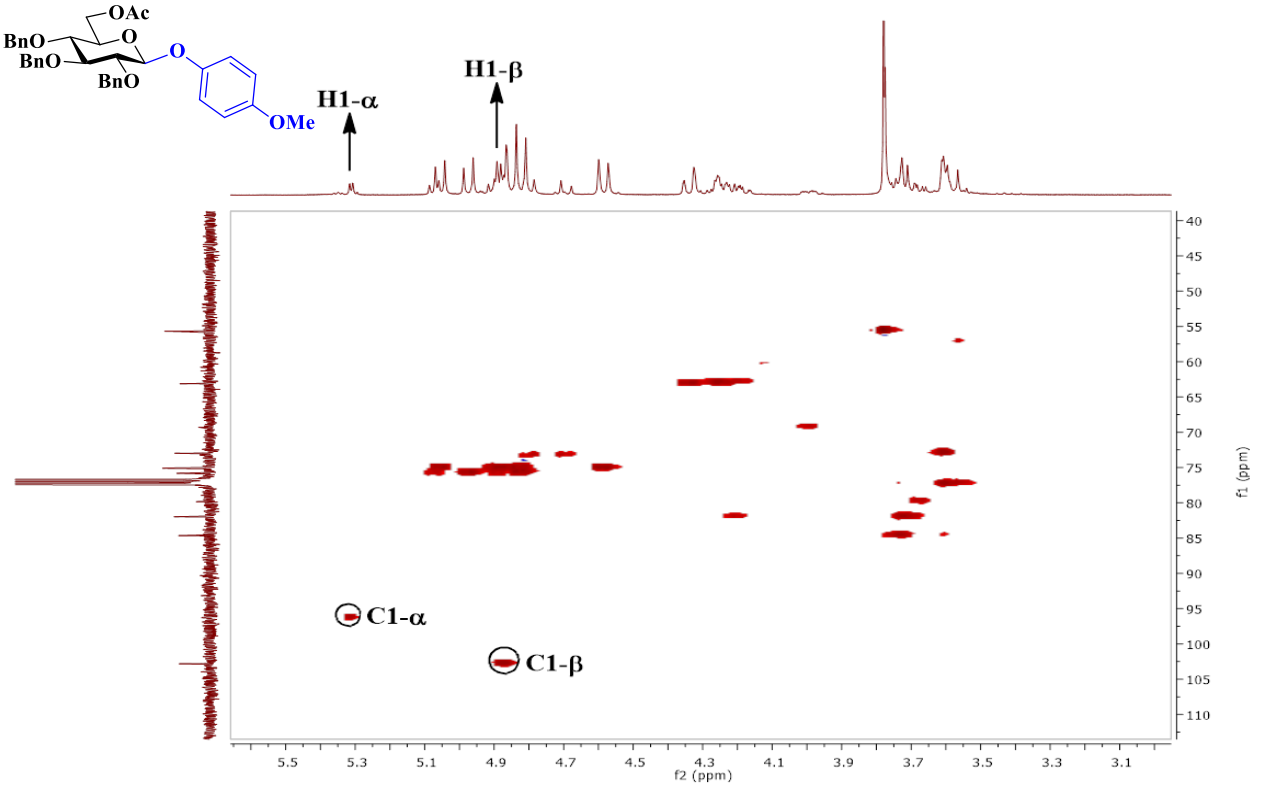
^{13}C {^{1}H} NMR spectrum of compound 6b (100 MHz, $CDCl_3$)



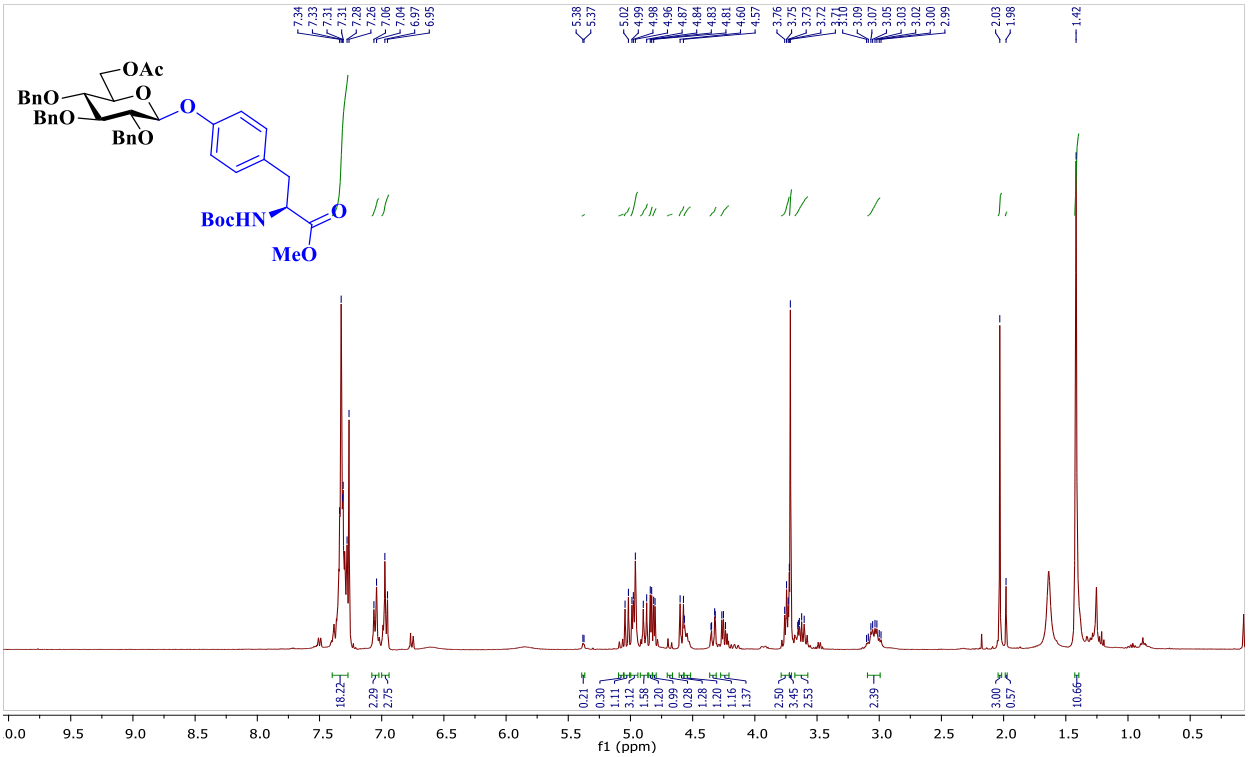
COSY spectrum of compound 6b



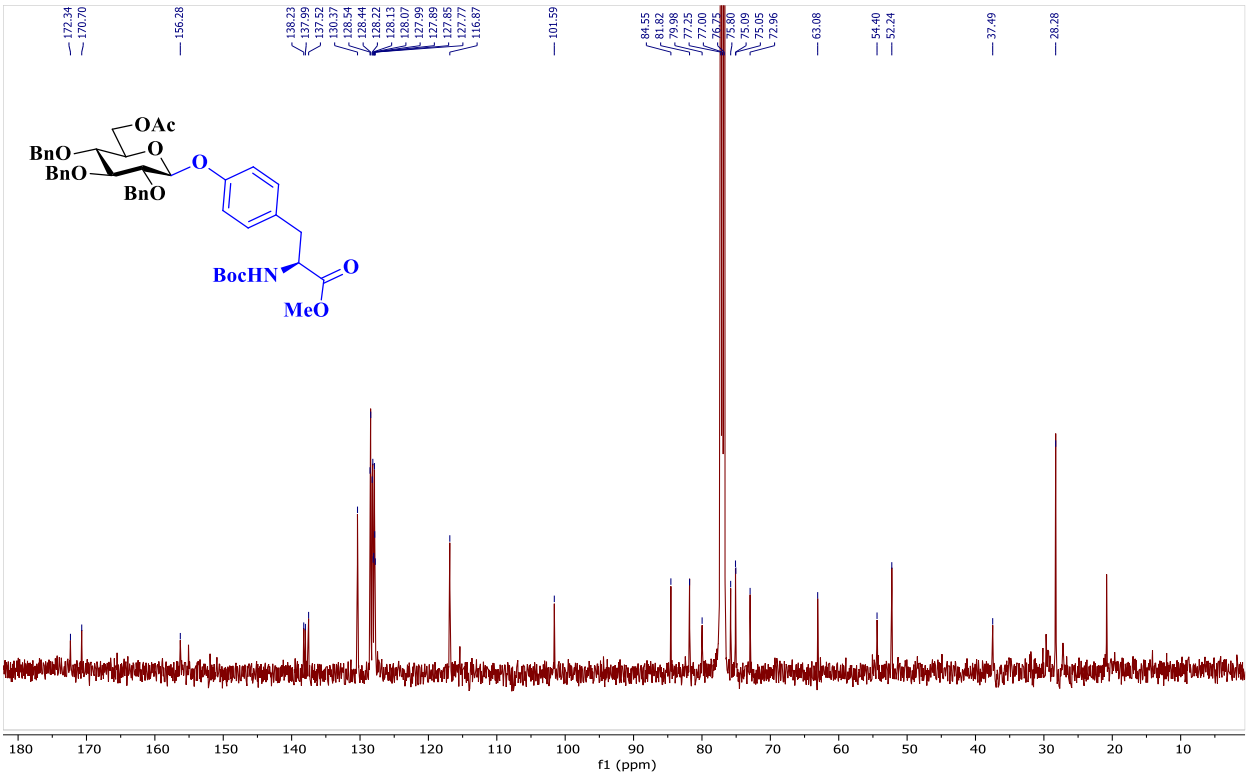
HSQC spectrum of compound 6b



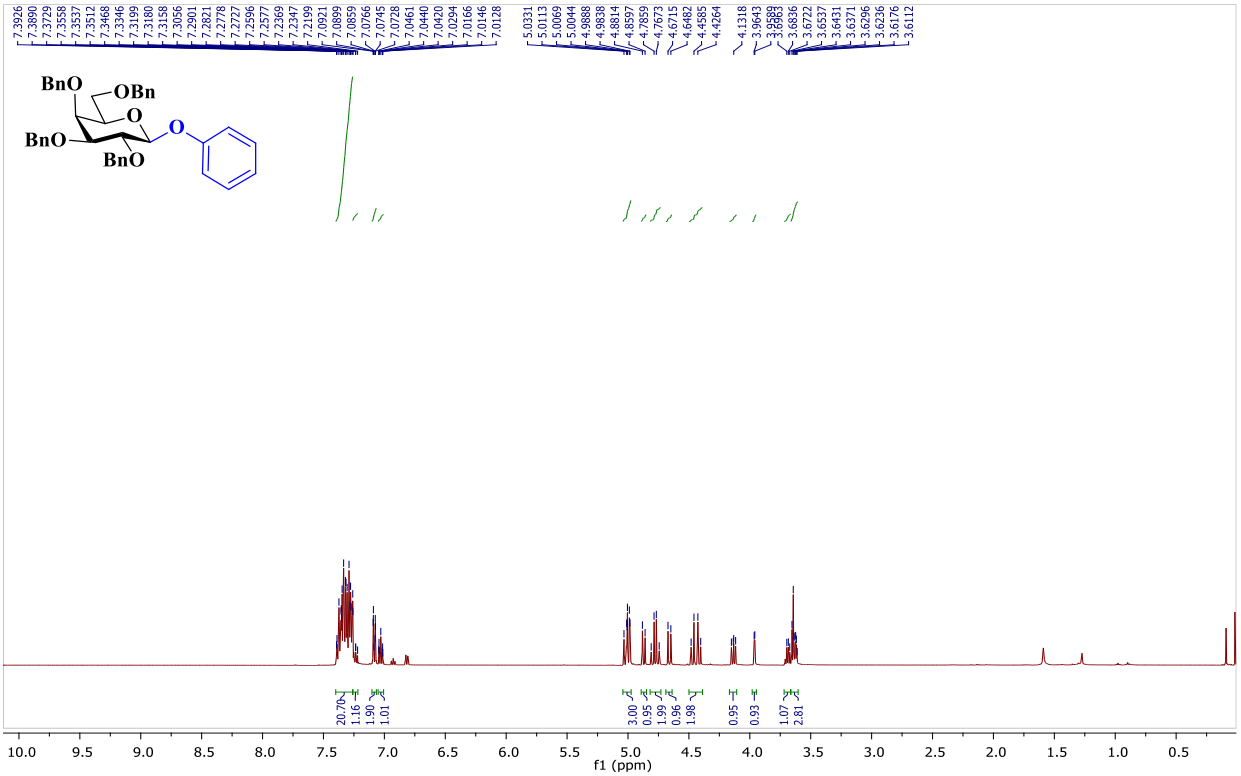
^{1}H NMR spectrum of compound 6c (400 MHz, $CDCl_3$)



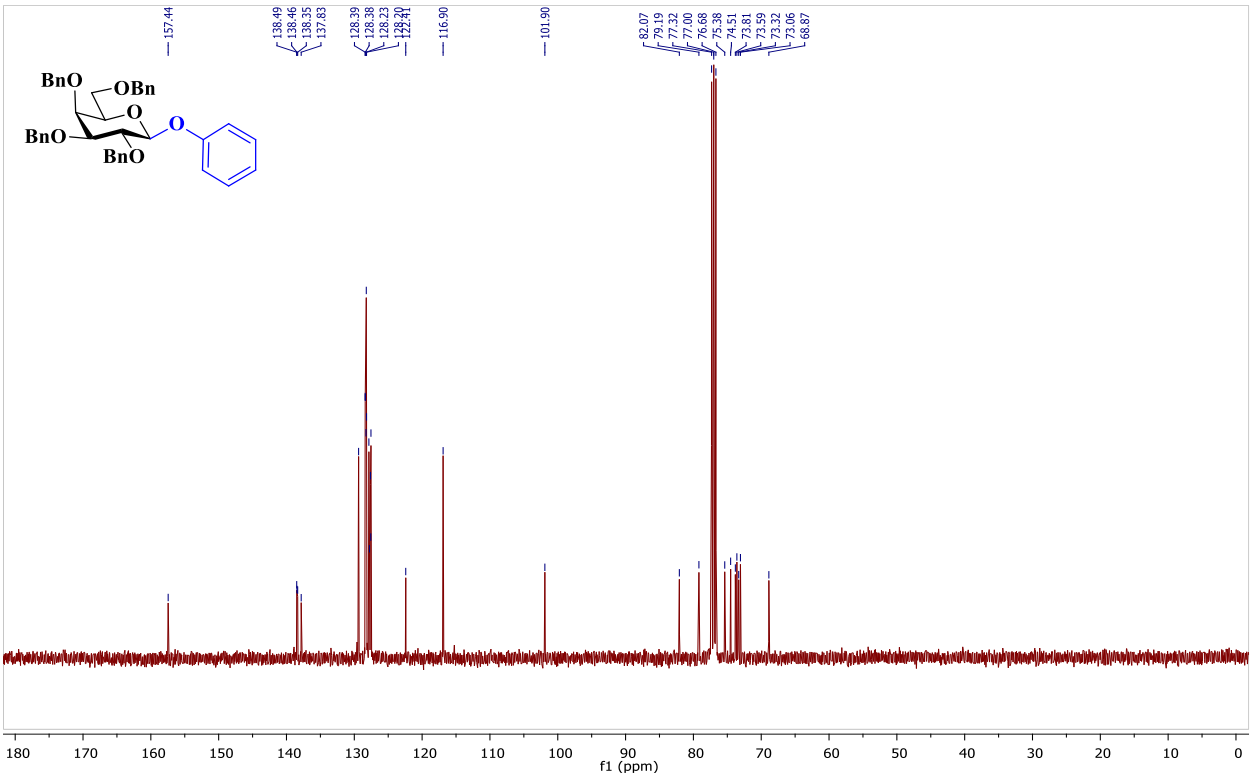
^{13}C {^{1}H} NMR spectrum of compound 6c (100 MHz, $CDCl_3$)



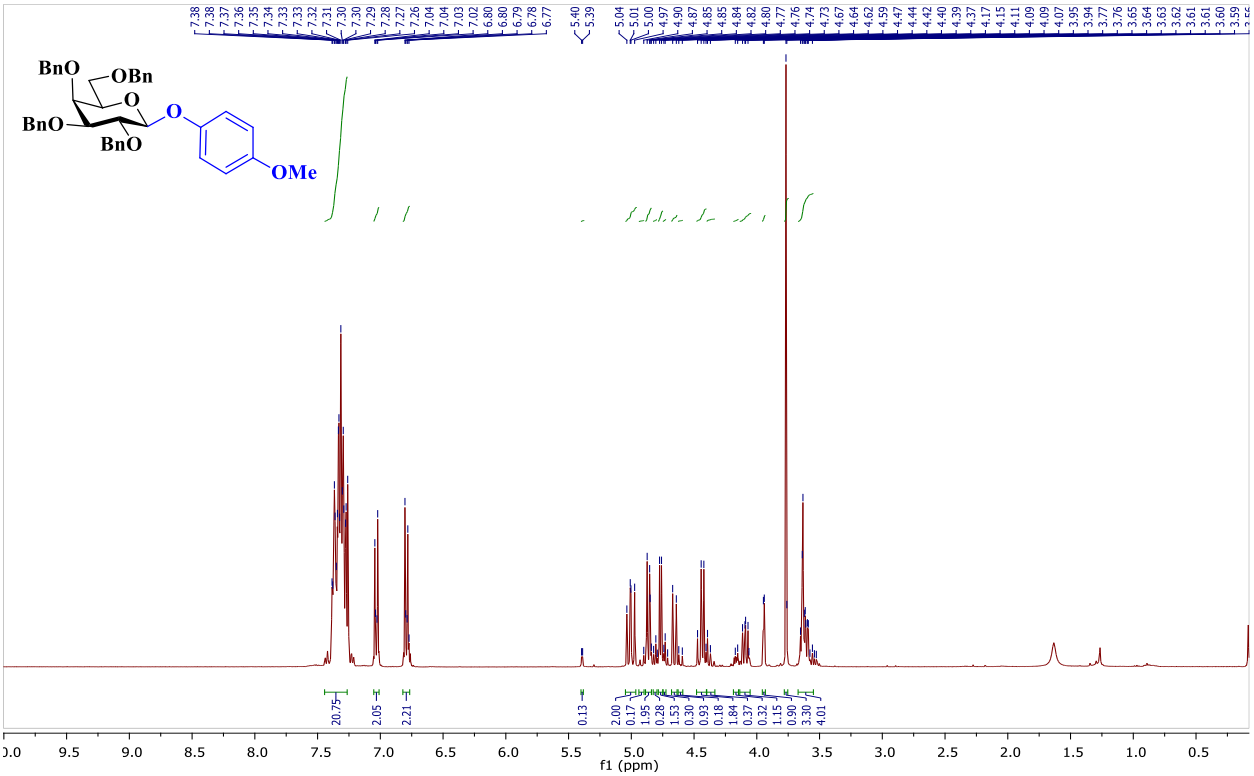
^{1}H NMR spectrum of compound 7a (500 MHz, $CDCl_3$)



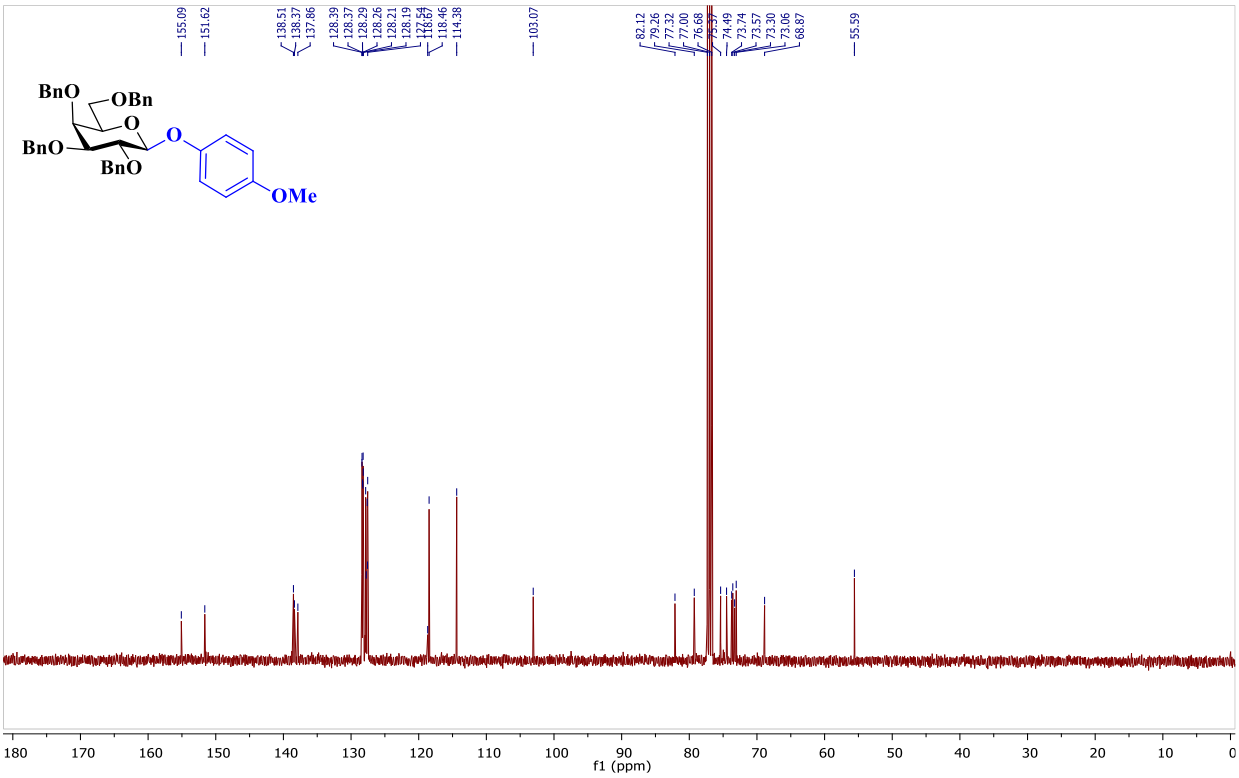
^{13}C {^{1}H} NMR spectrum of compound 7a (125 MHz, $CDCl_3$)



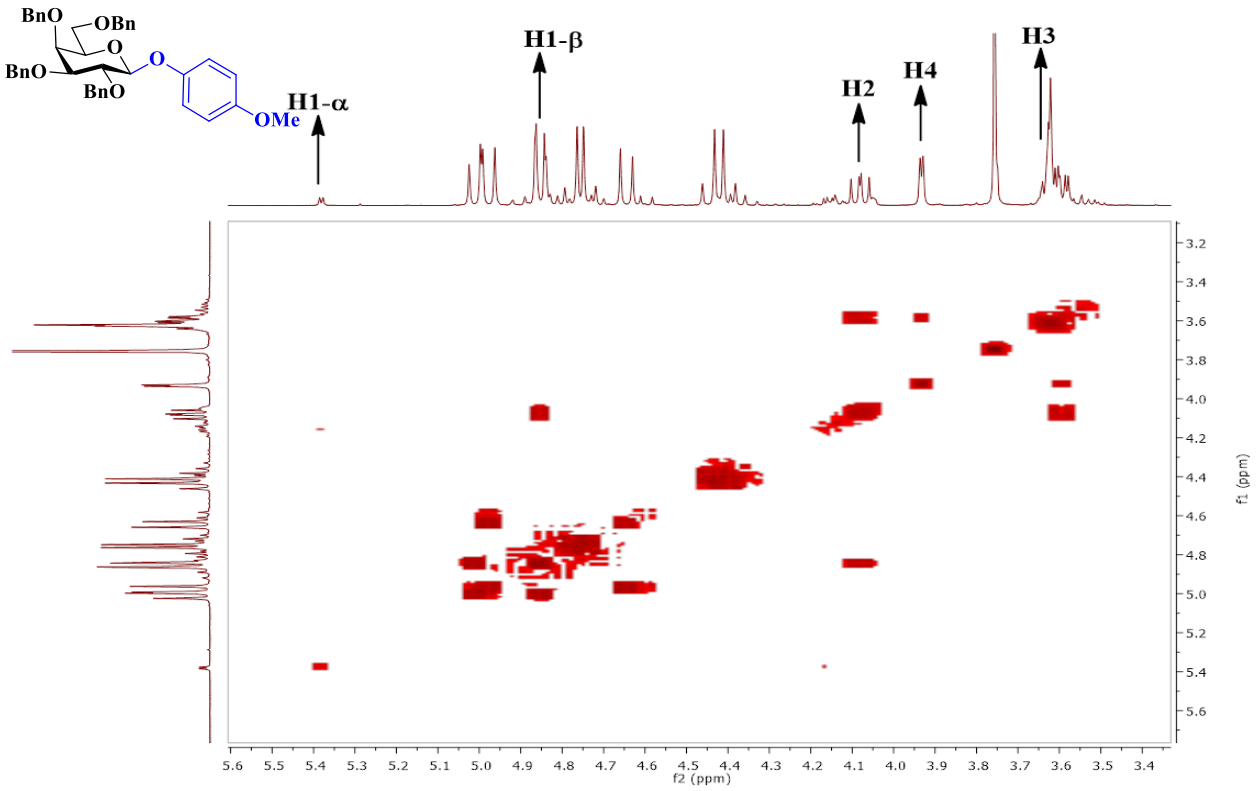
^{1}H NMR spectrum of compound 7b (500 MHz, $CDCl_3$)



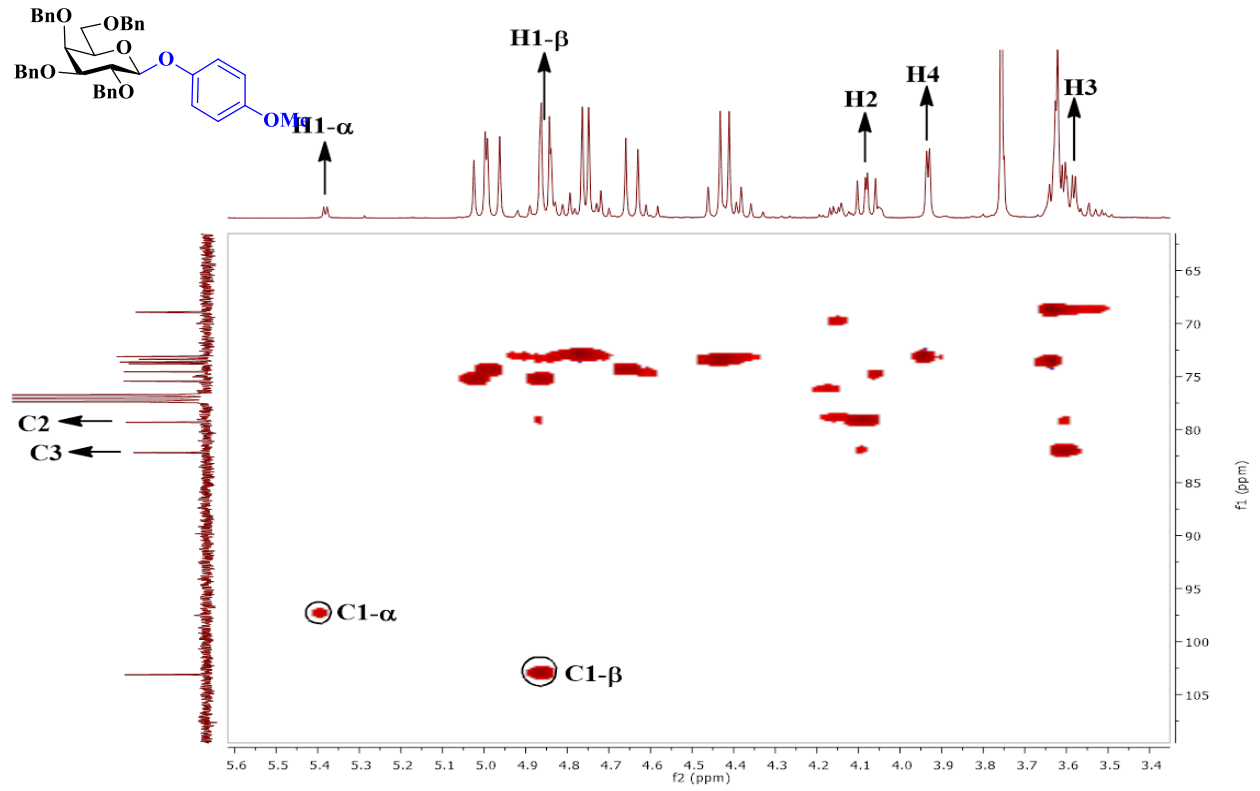
^{13}C {^{1}H}NMR spectrum of compound 7b (125 MHz, $CDCl_3$)



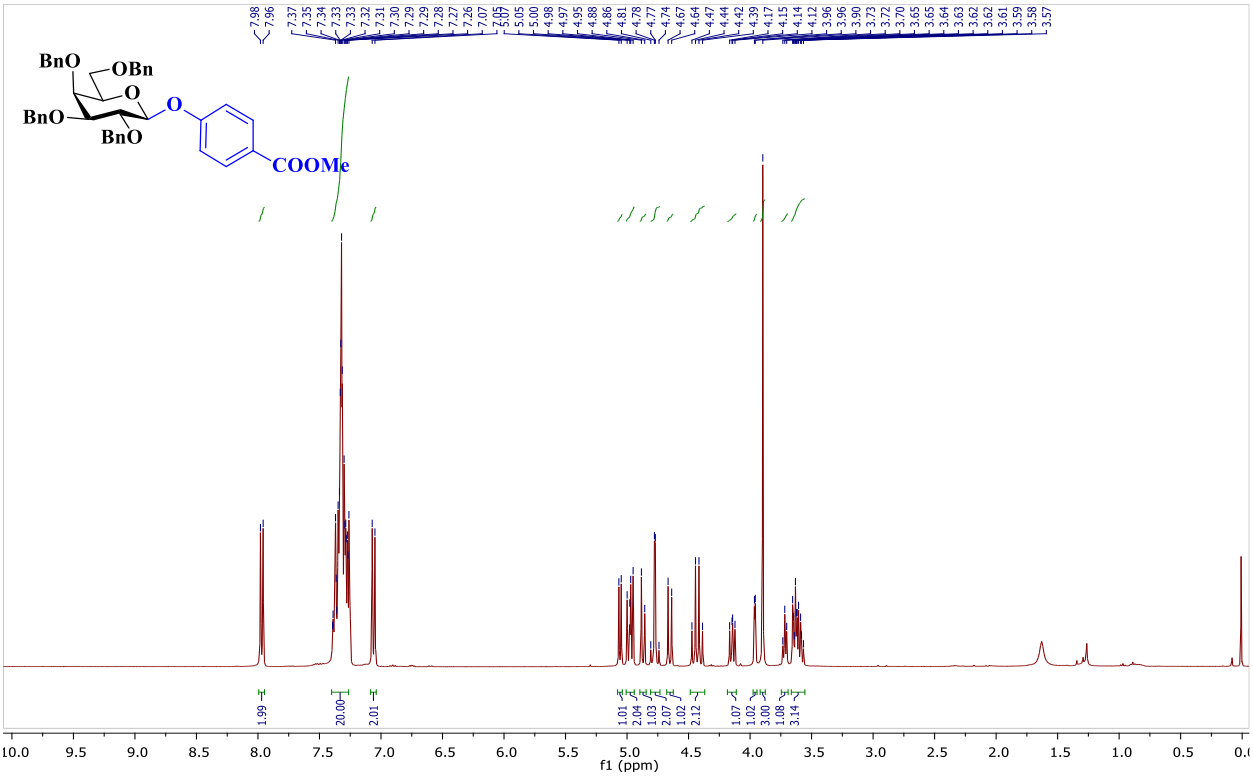
COSY spectrum of compound 7b



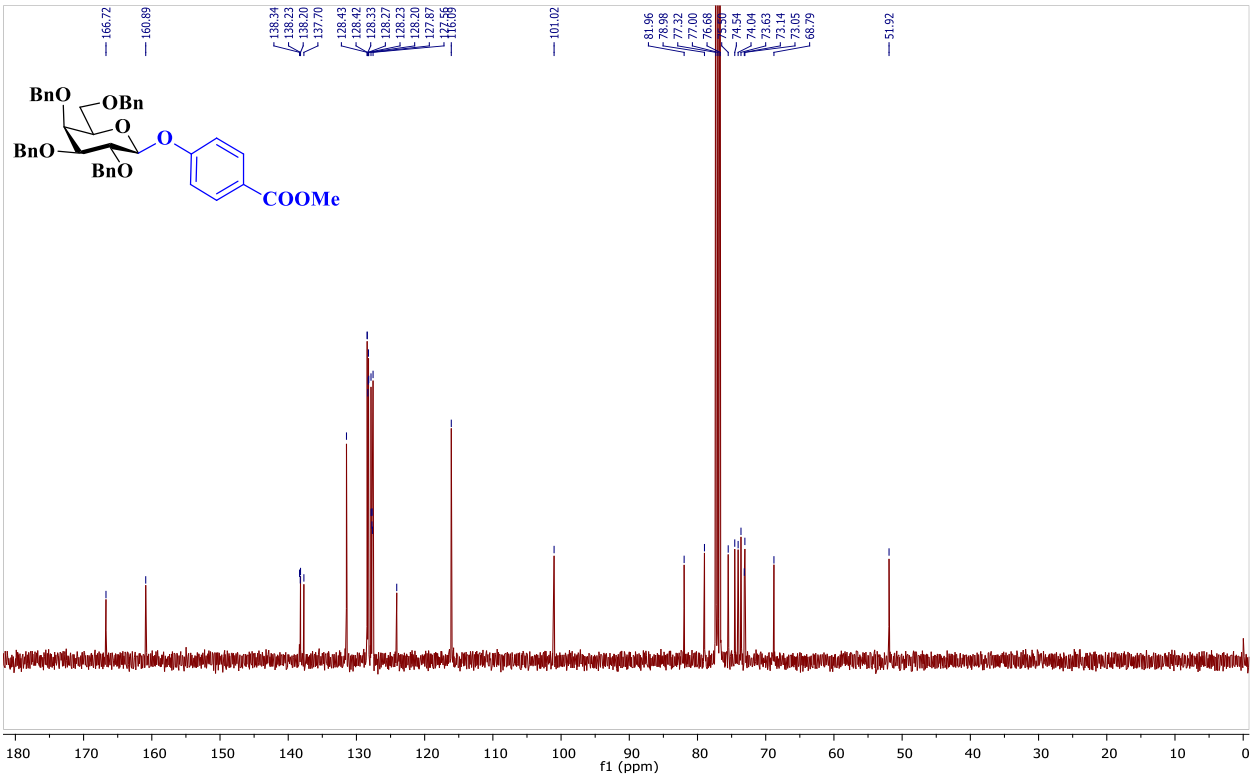
HSQC spectrum of compound 7b



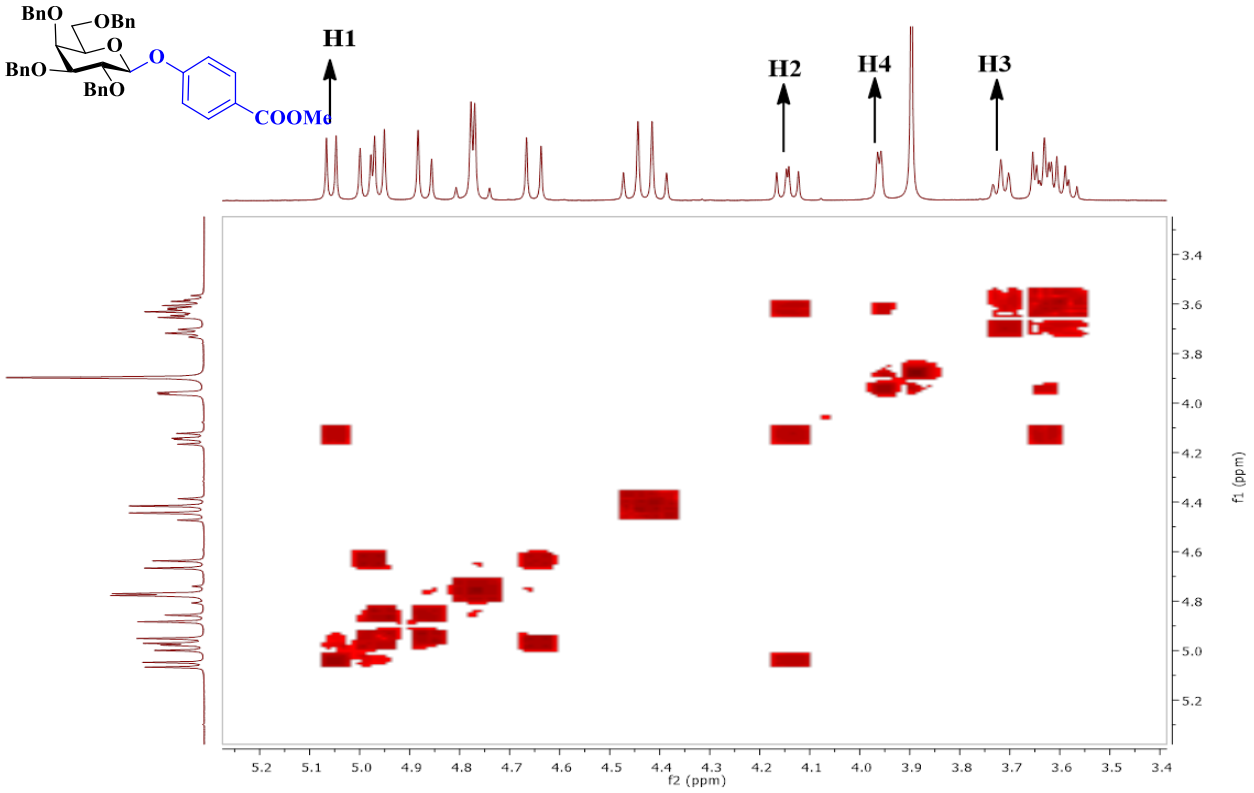
^{1}H NMR spectrum of compound 7c (500 MHz, $CDCl_3$)



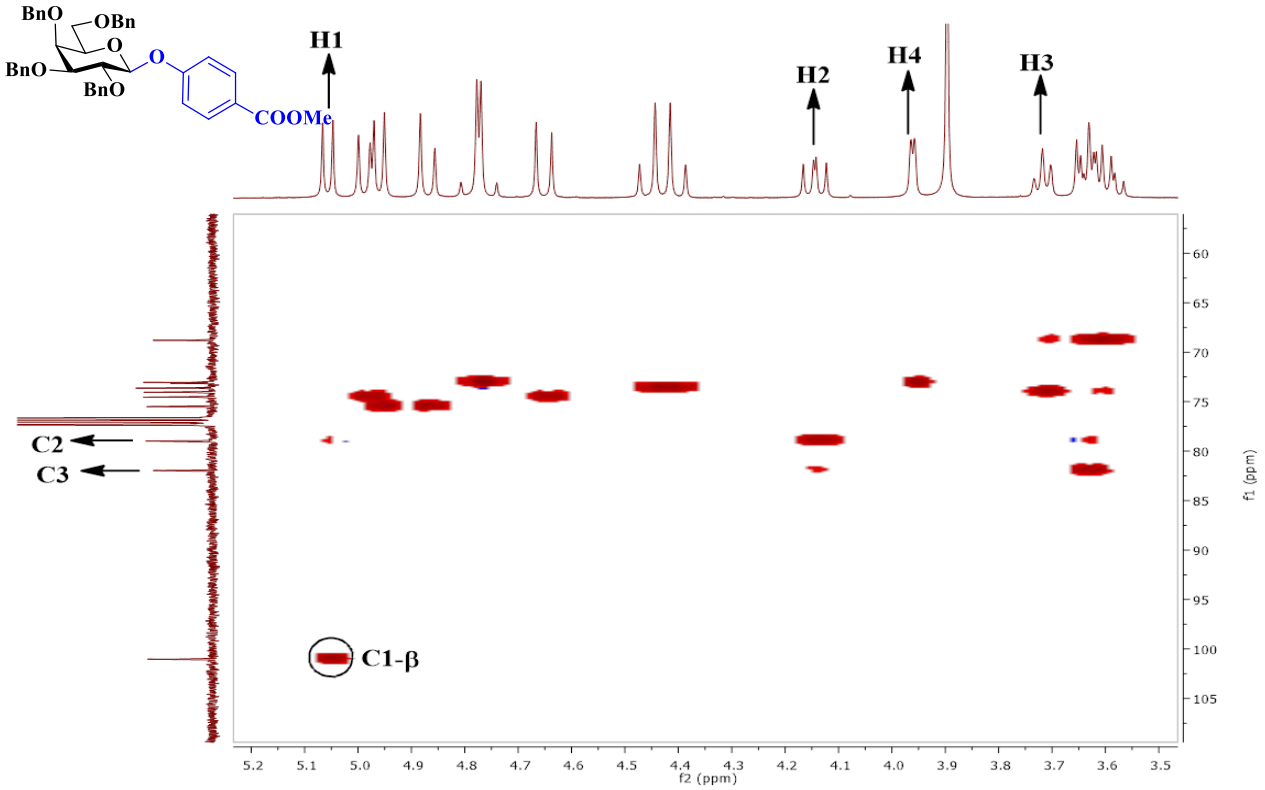
^{13}C {^{1}H} NMR spectrum of compound 7c (125 MHz, $CDCl_3$)



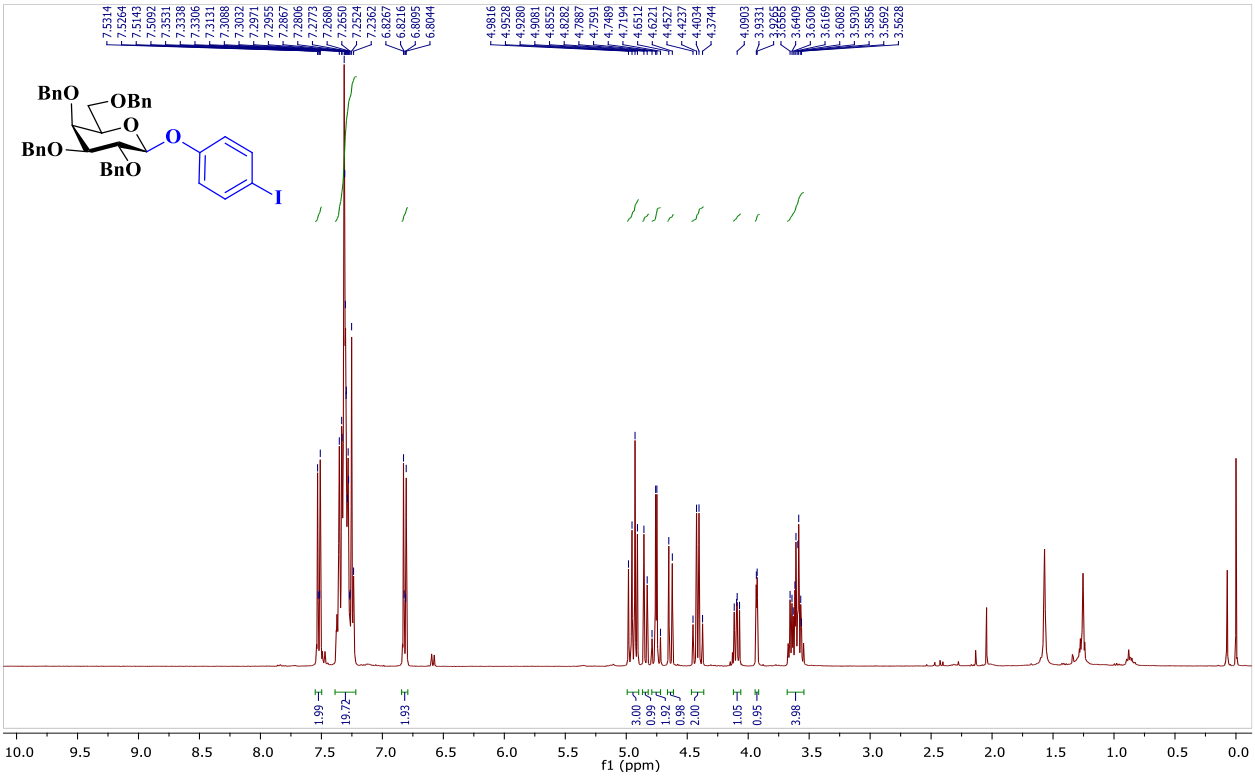
COSY spectrum of compound 7c



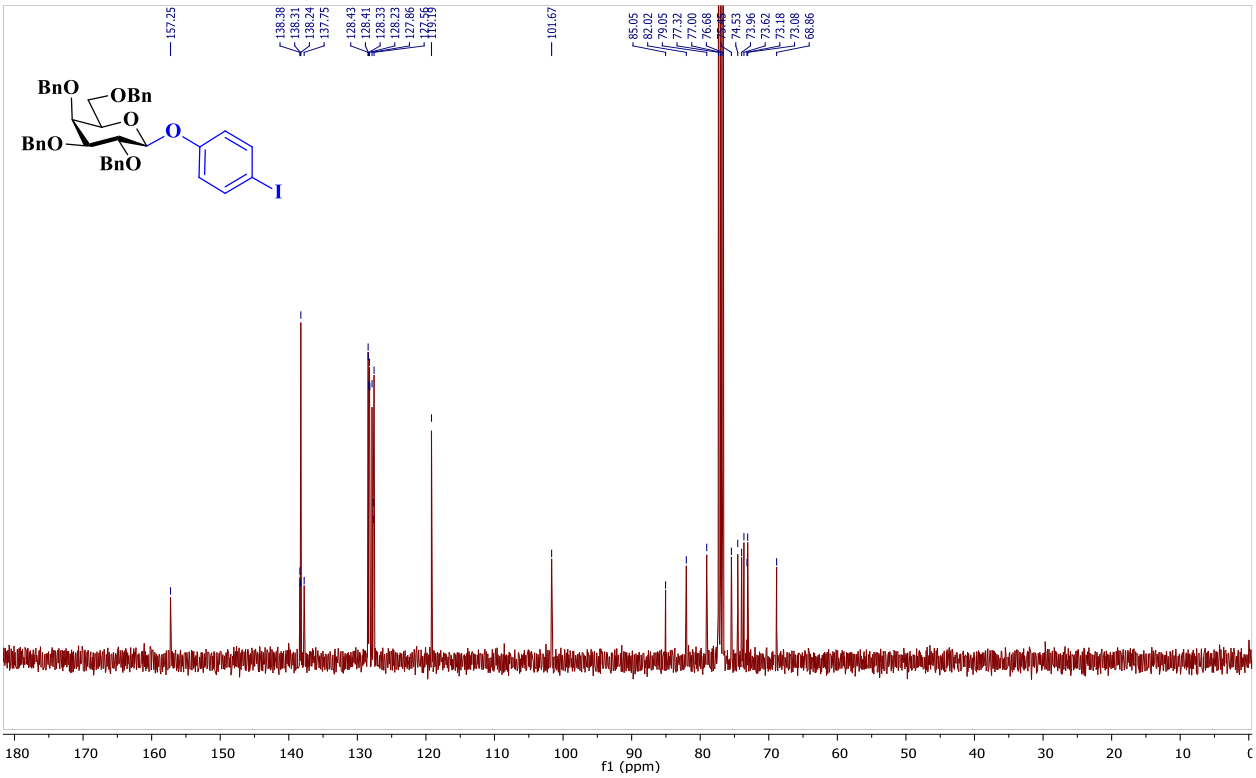
HSQC spectrum of compound 7c



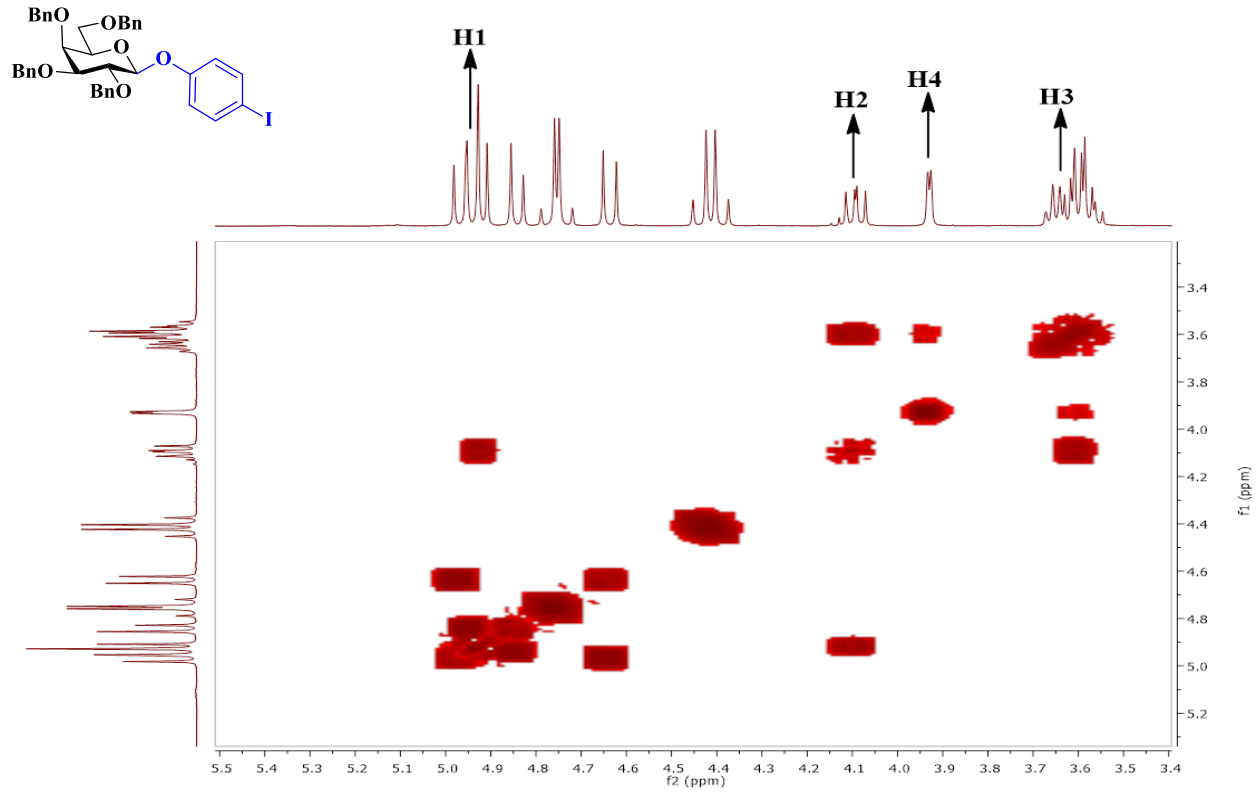
^{1}H NMR spectrum of compound 7d (400 MHz, $CDCl_3$)



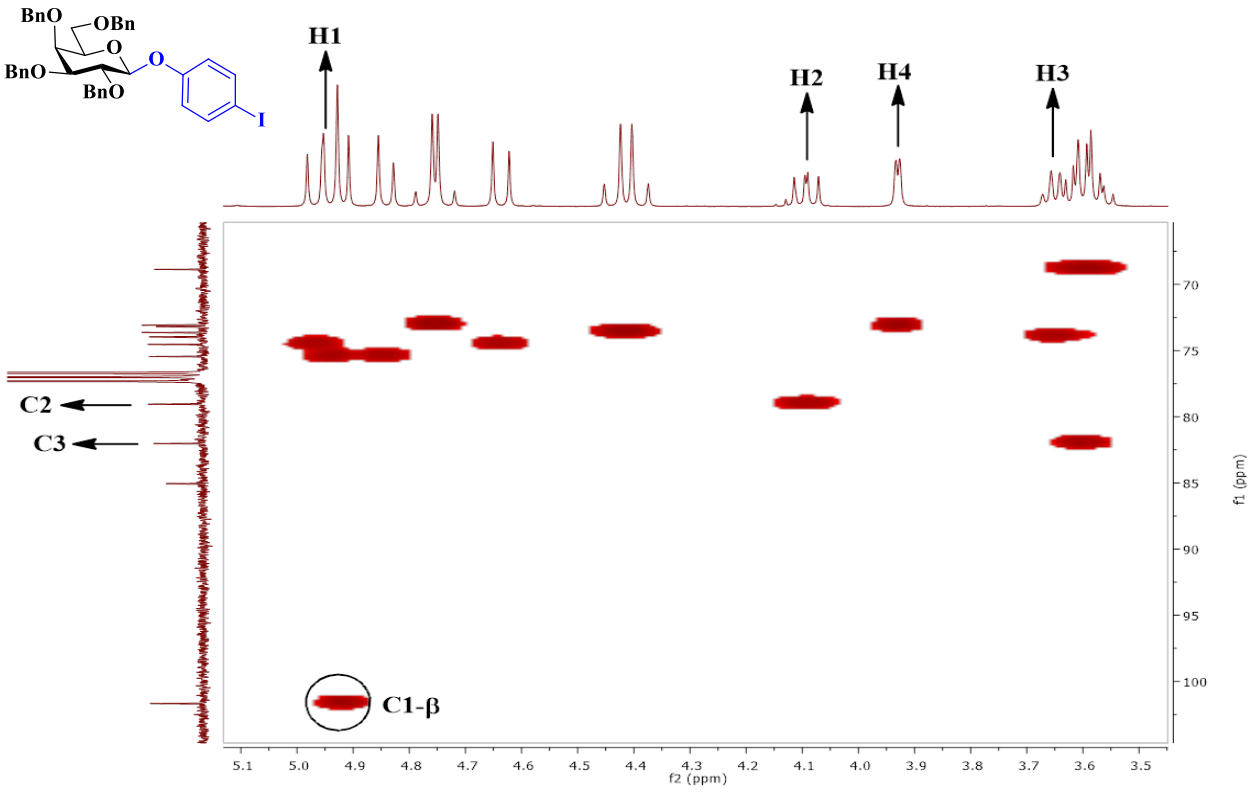
^{13}C {^{1}H} NMR spectrum of compound 7d (100 MHz, $CDCl_3$)



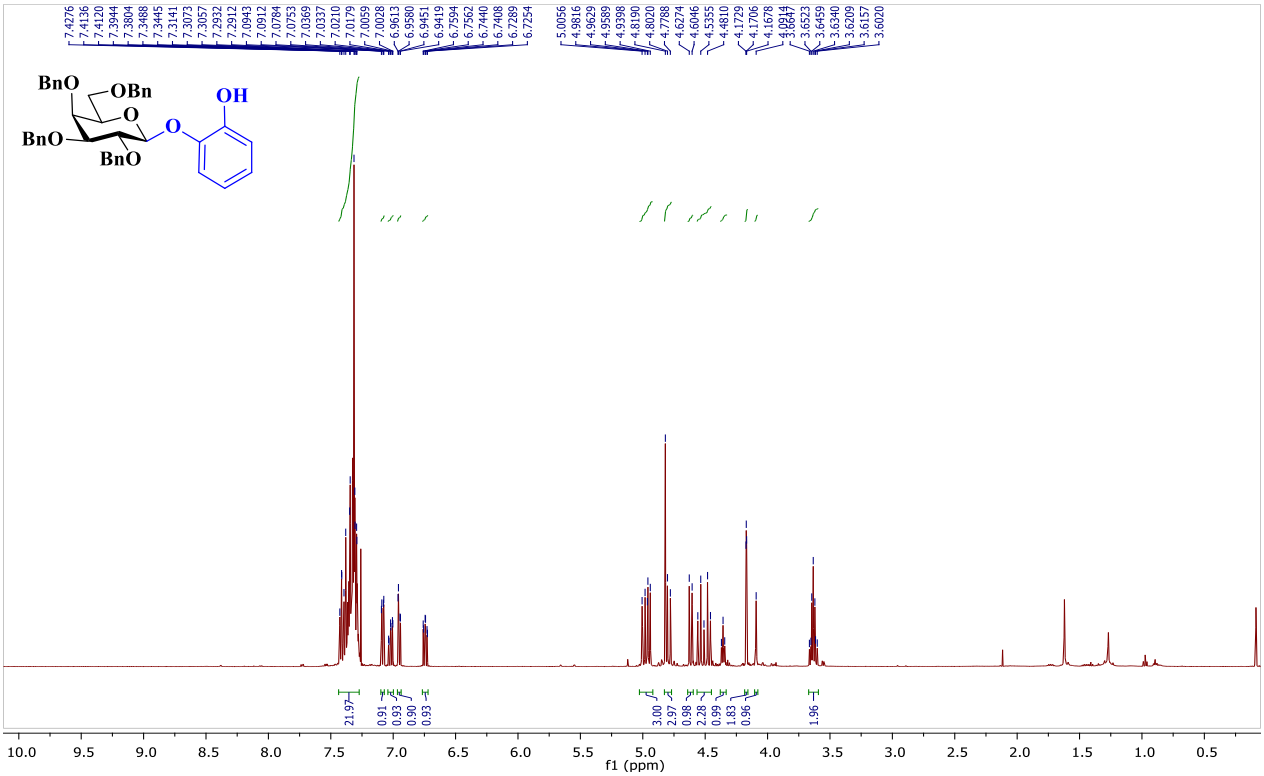
COSY spectrum of compound 7d



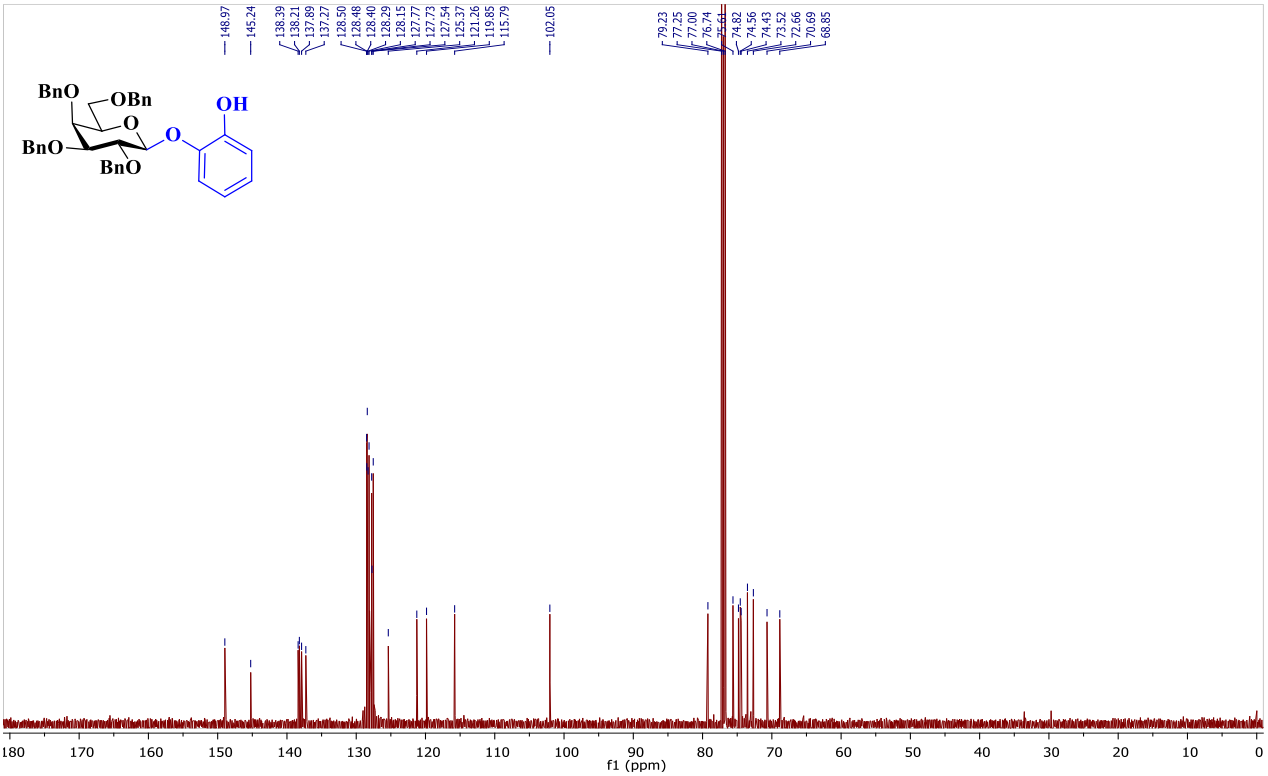
HSQC spectrum of compound 7d



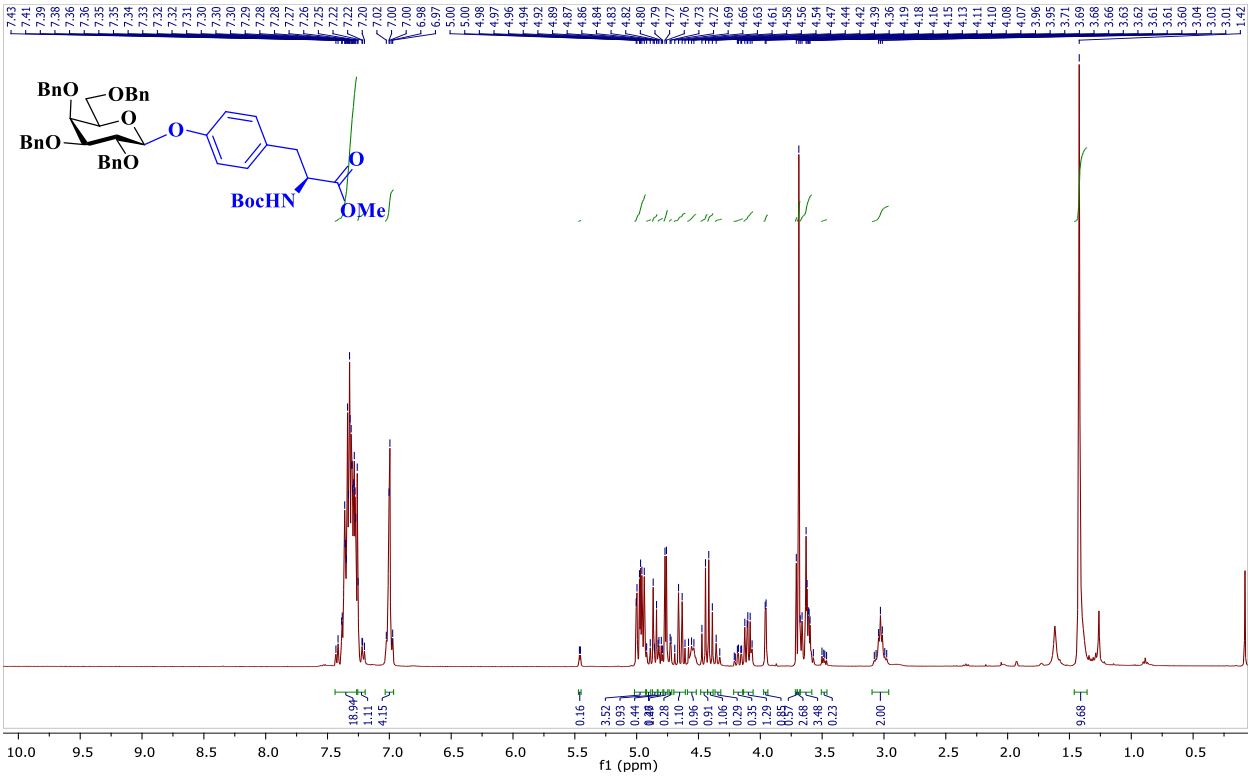
^{1}H NMR spectrum of compound 7e (400 MHz, $CDCl_3$)



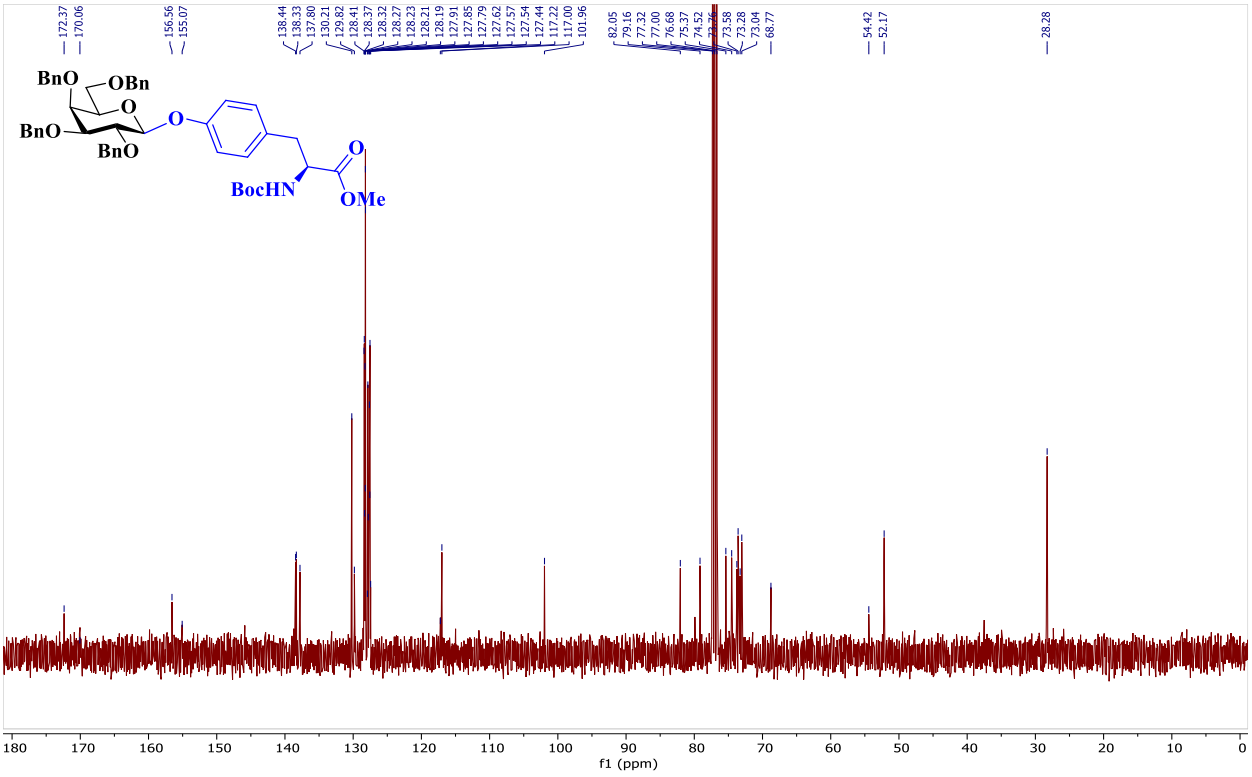
^{13}C {1H} NMR spectrum of compound 7e (100 MHz, $CDCl_3$)



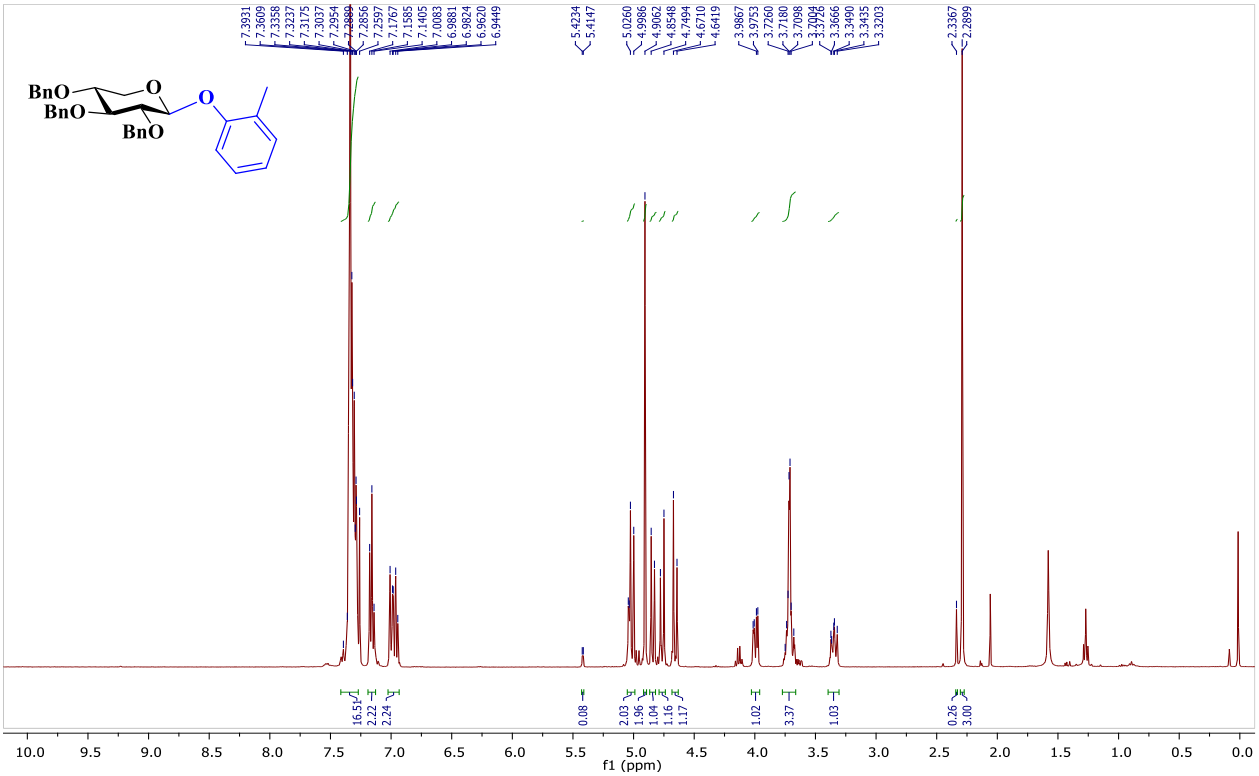
^{1}H NMR spectrum of compound 7f (400 MHz, $CDCl_3$)



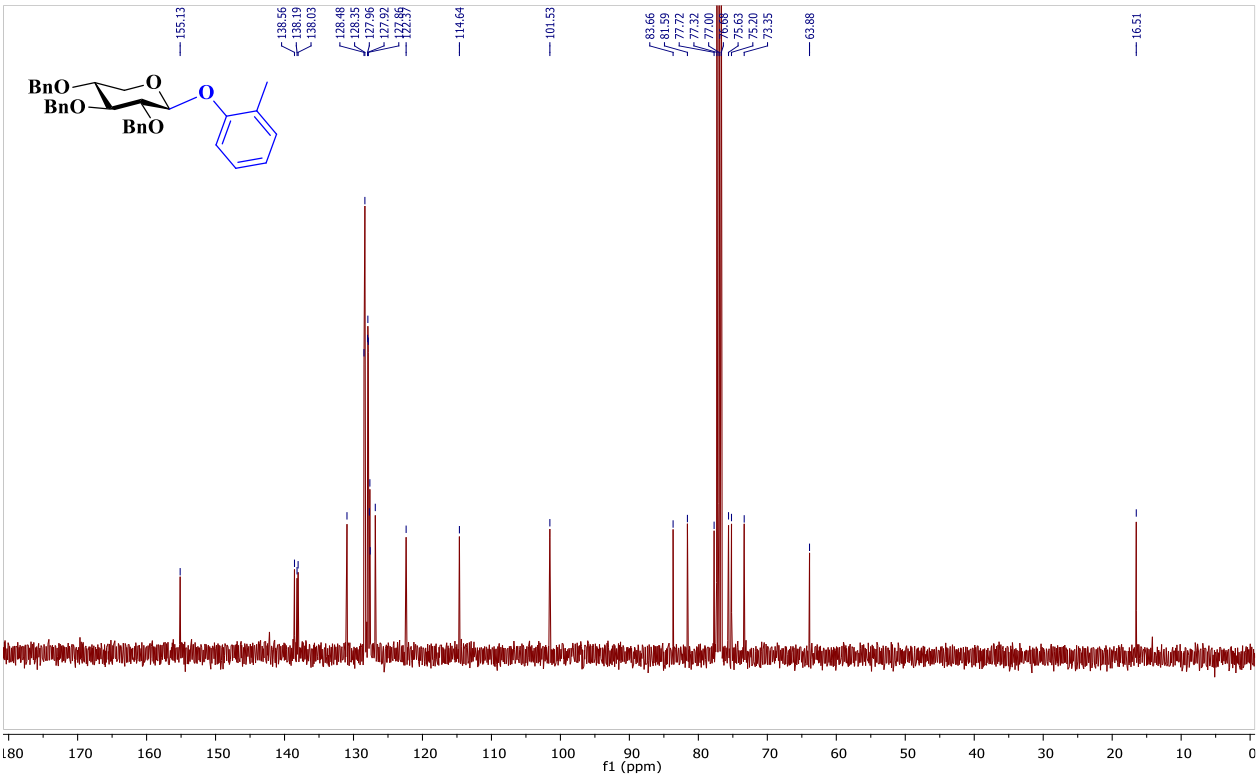
^{13}C {^{1}H}NMR spectrum of compound 7f (100 MHz, $CDCl_3$)



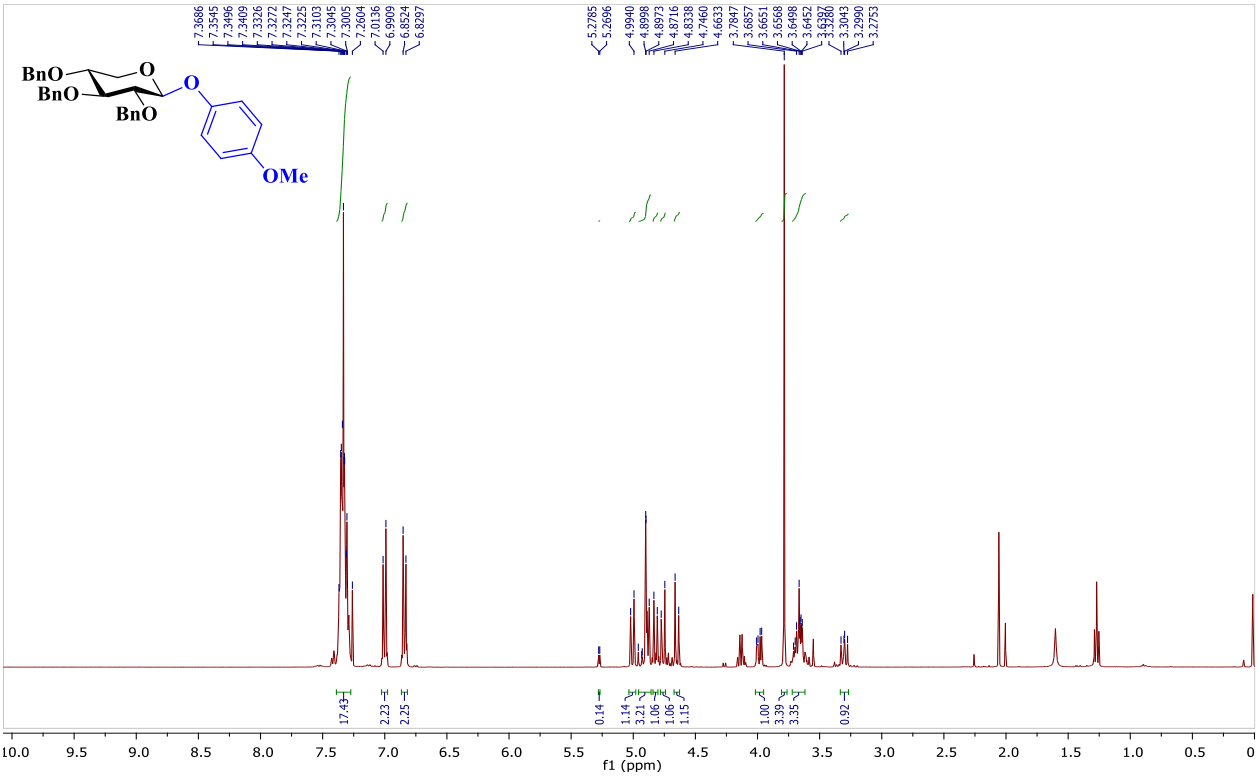
^{1}H NMR spectrum of compound 8a (400 MHz, $CDCl_3$)



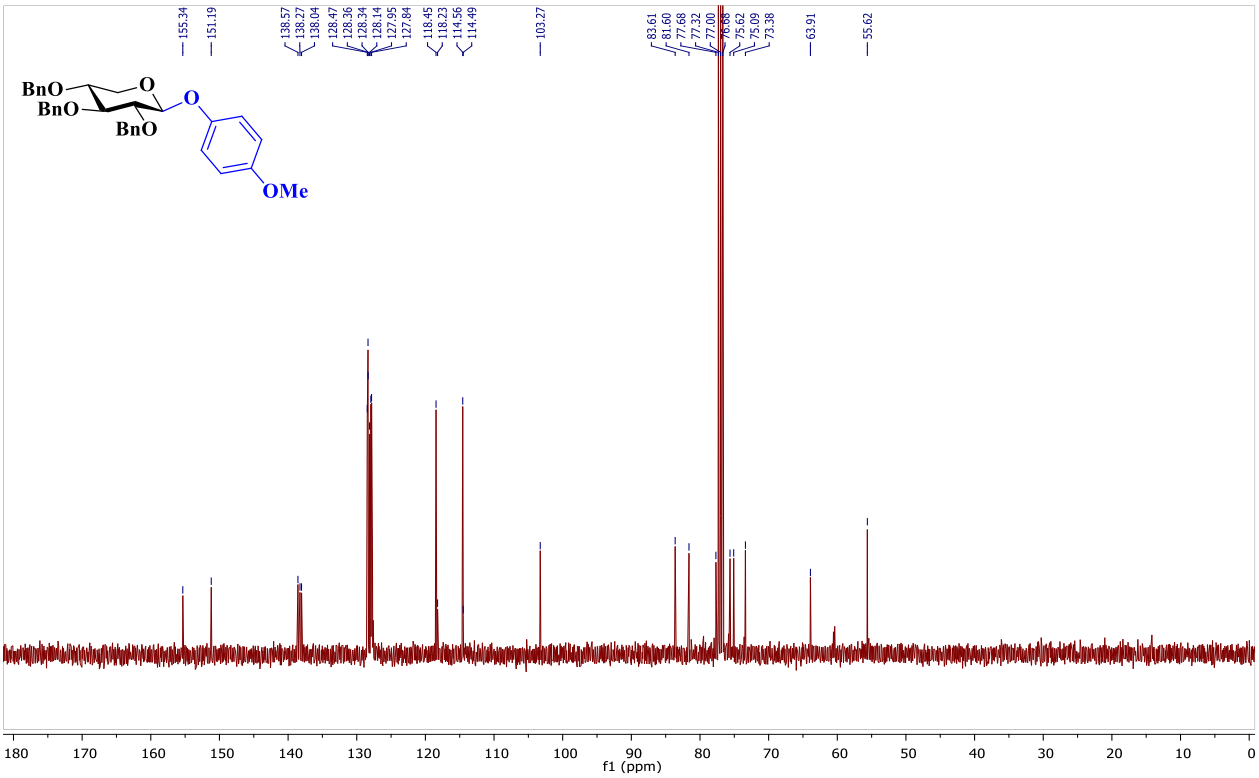
^{13}C {^{1}H} NMR spectrum of compound 8a (100 MHz, $CDCl_3$)



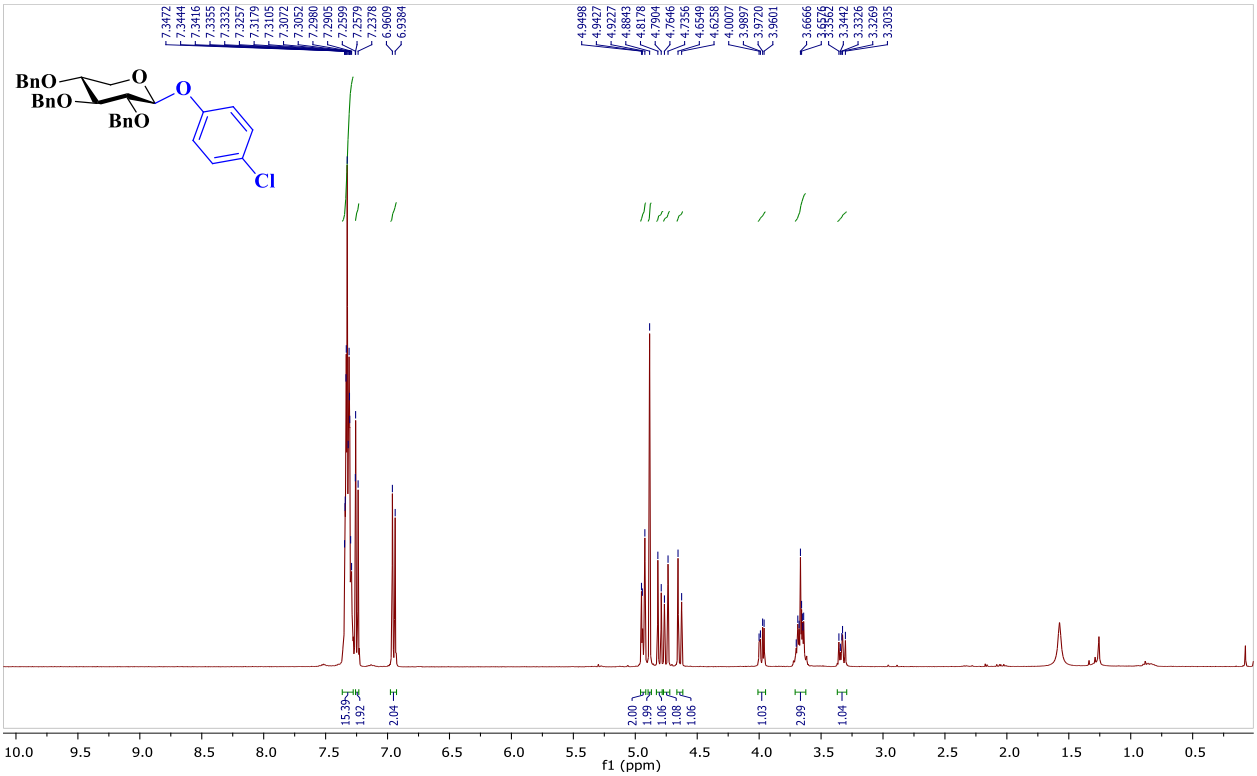
^{1}H NMR spectrum of compound 8b (400 MHz, $CDCl_3$)



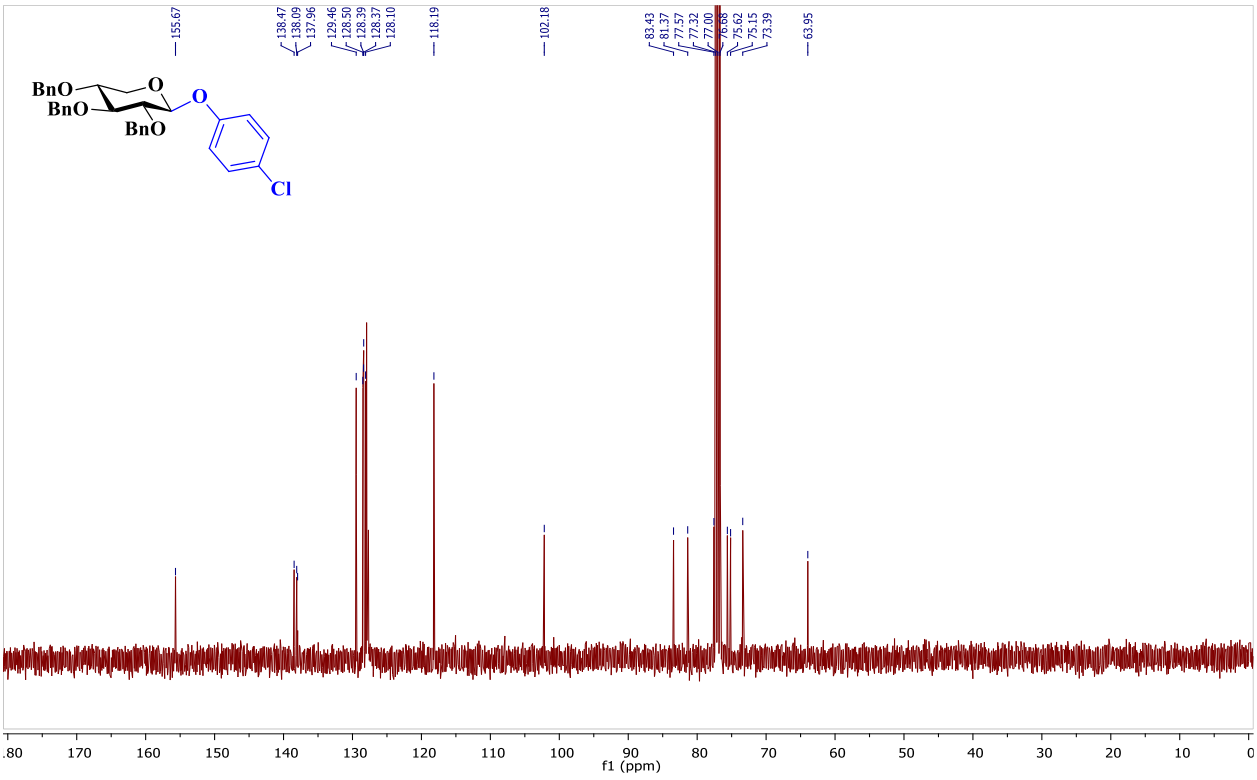
^{13}C {^{1}H} NMR spectrum of compound 8b (100 MHz, $CDCl_3$)



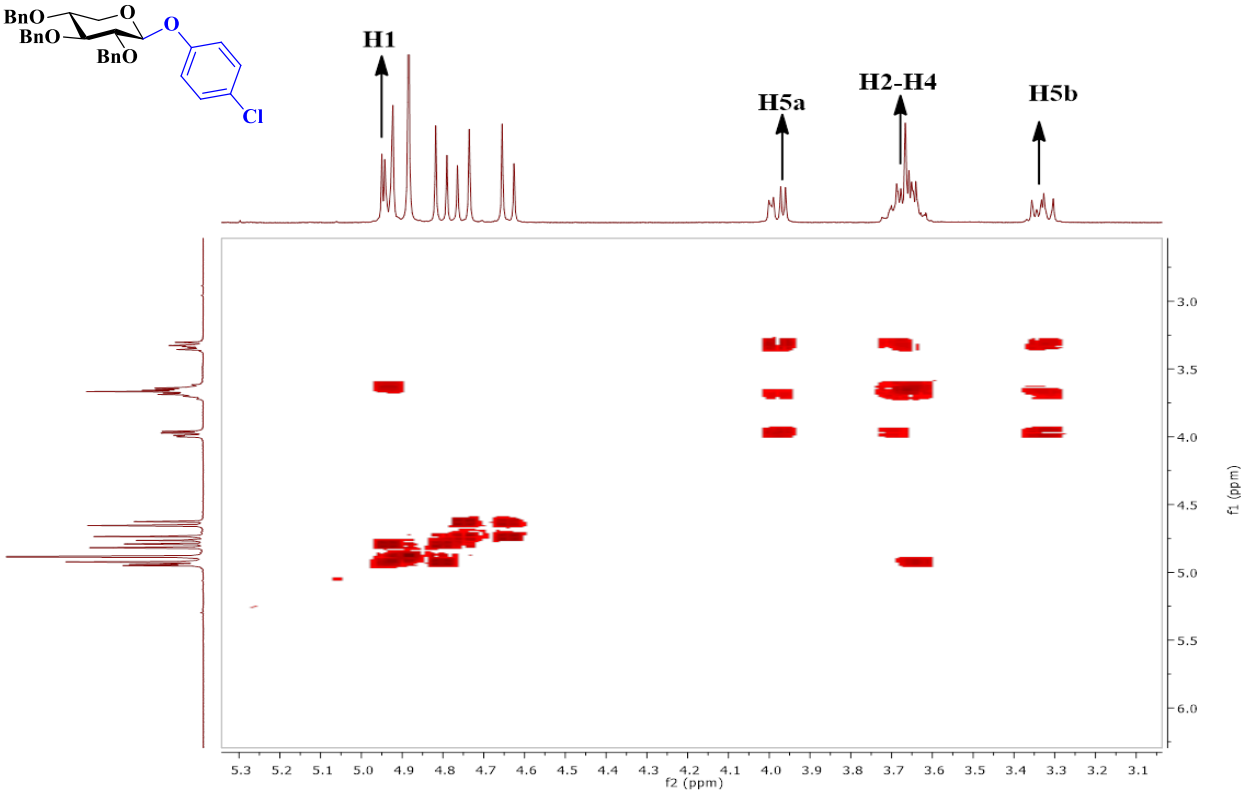
^{1}H NMR spectrum of compound 8c (400 MHz, $CDCl_3$)



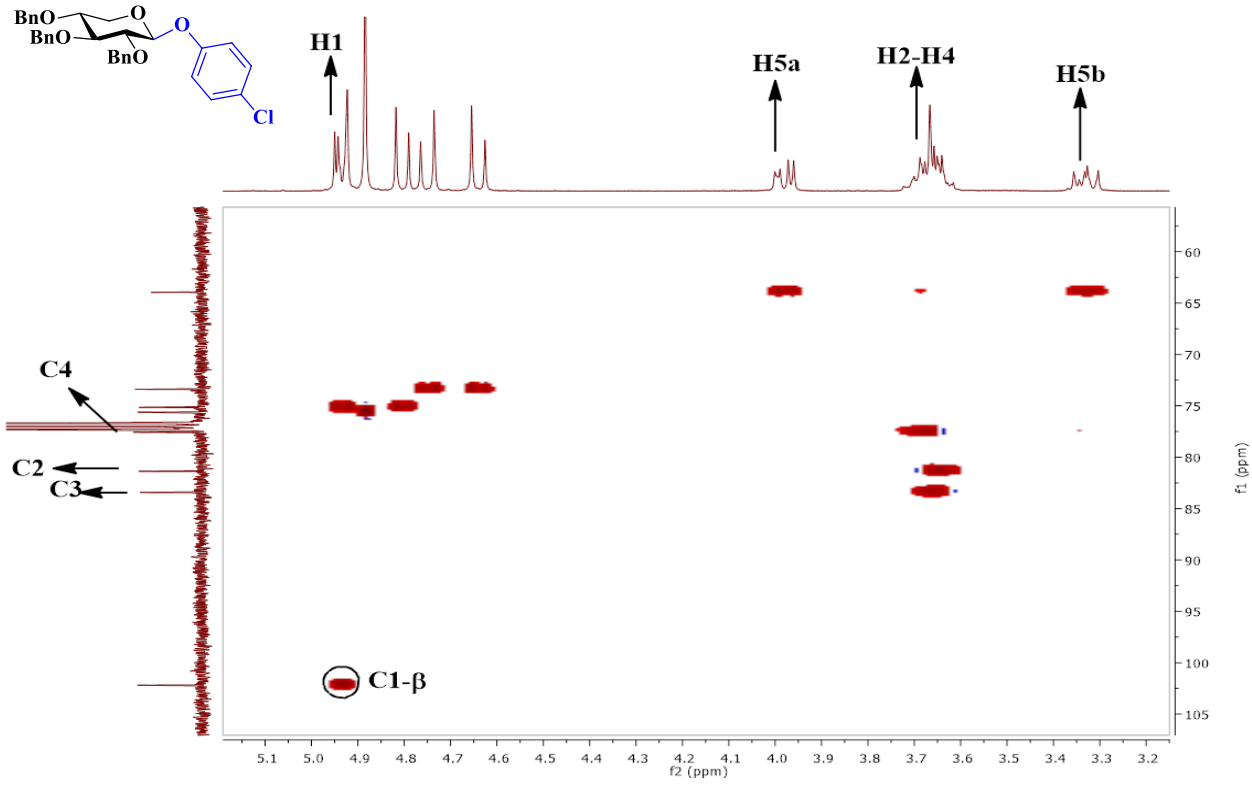
^{13}C {^{1}H} NMR spectrum of compound 8c (100 MHz, $CDCl_3$)



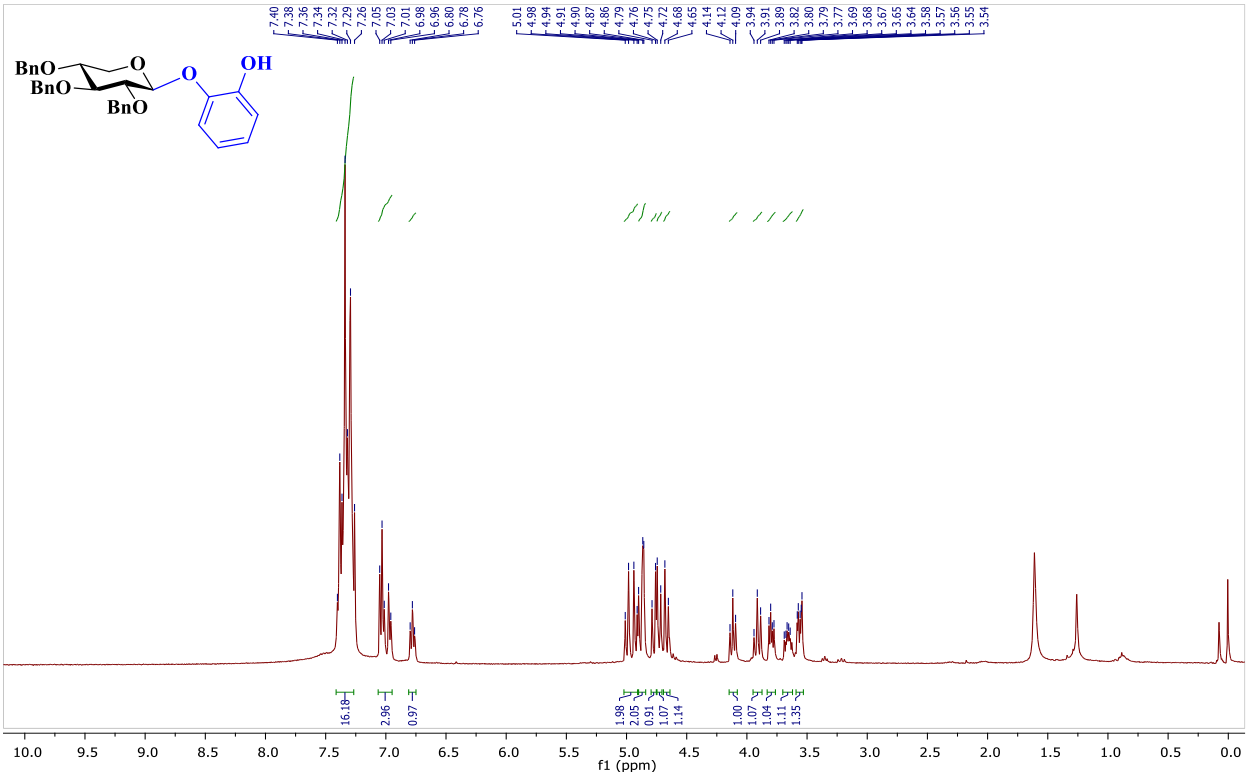
COSY spectrum of compound 8c



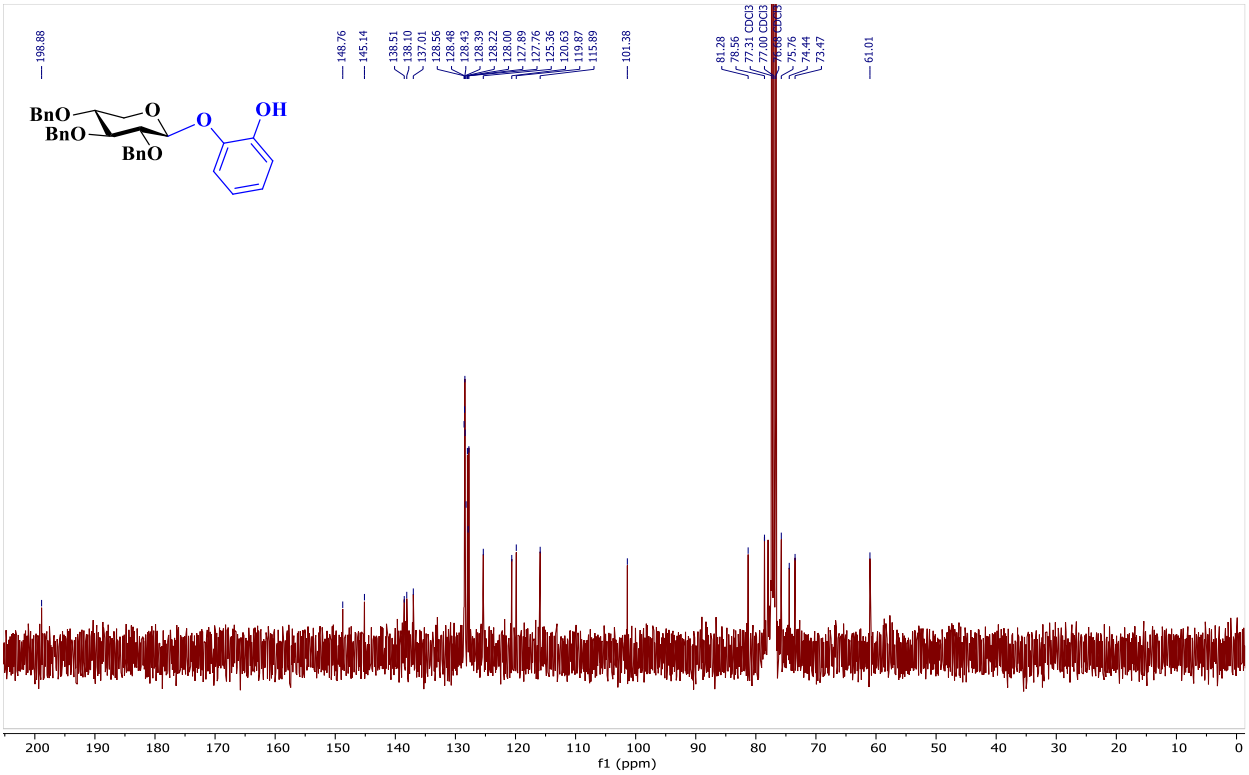
HSQC spectrum of compound 8c



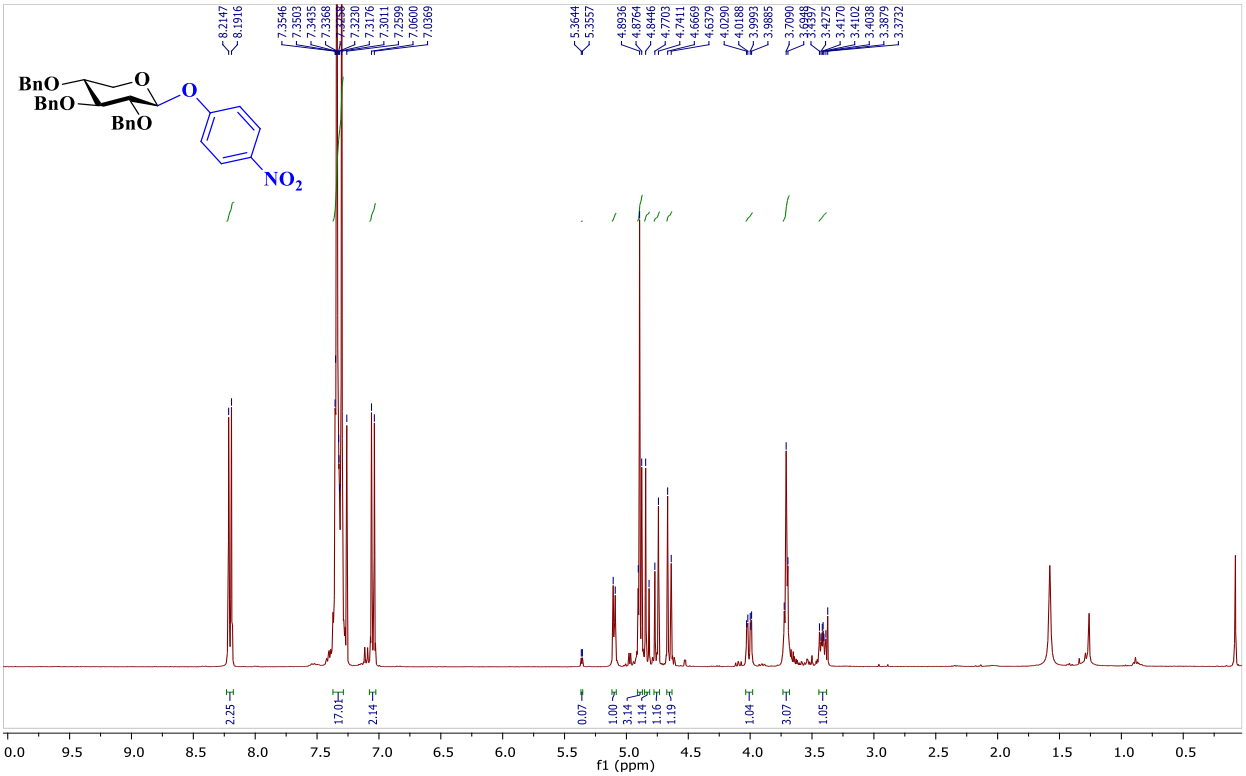
^{1}H NMR spectrum of compound 8d (400 MHz, $CDCl_3$)



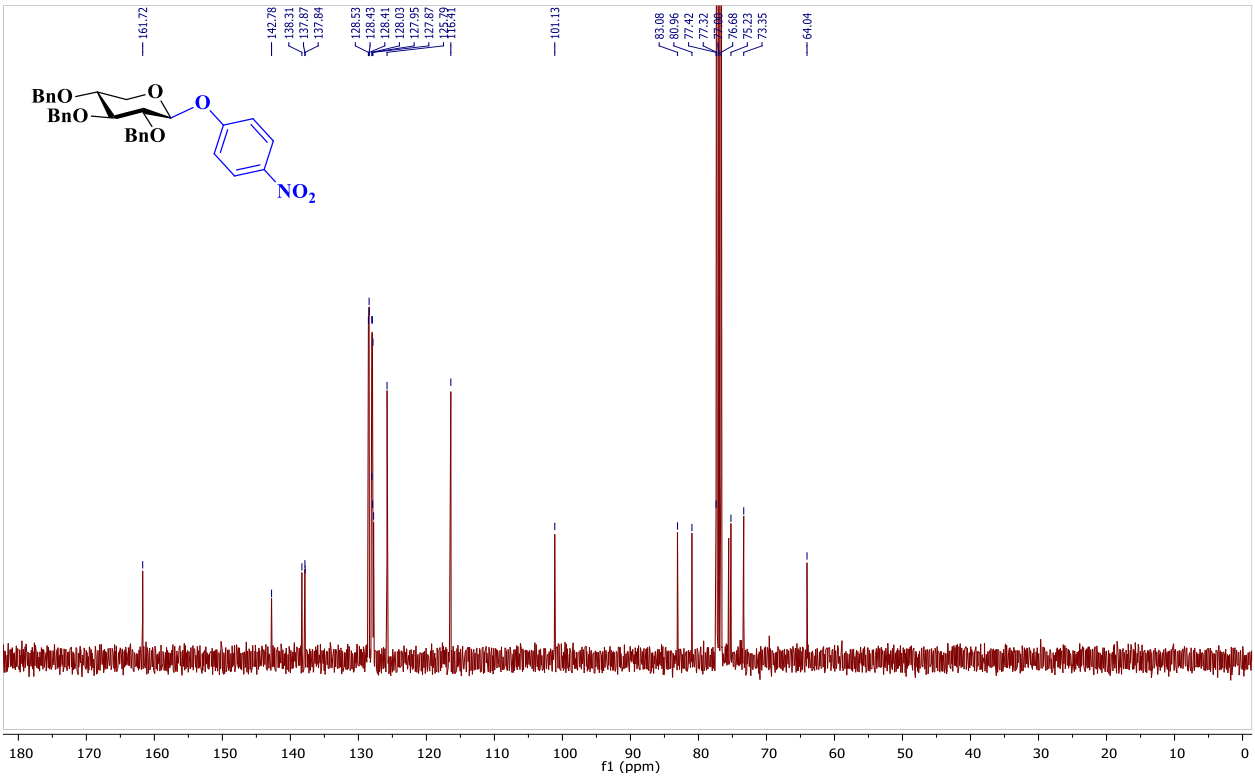
^{13}C {^{1}H} NMR spectrum of compound 8d (100 MHz, $CDCl_3$)



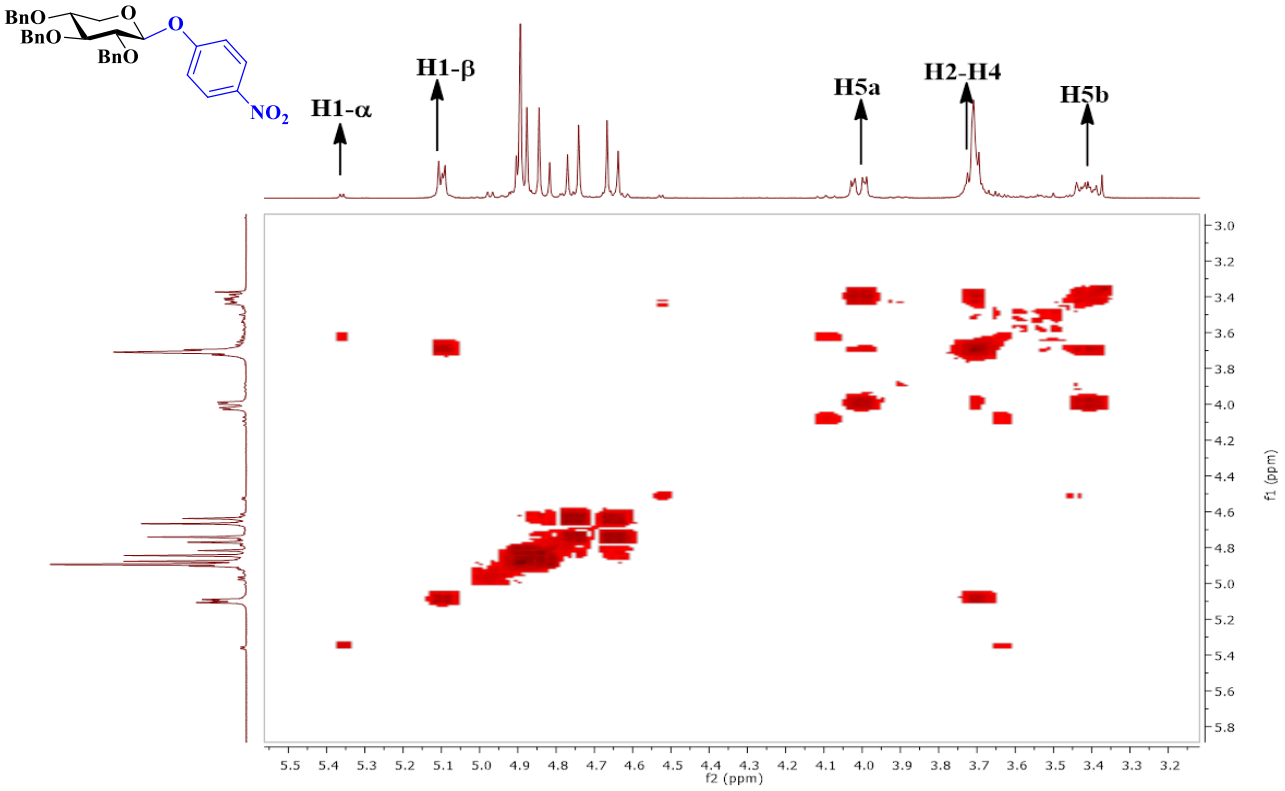
^{1}H NMR spectrum of compound 8e (400 MHz, $CDCl_3$)



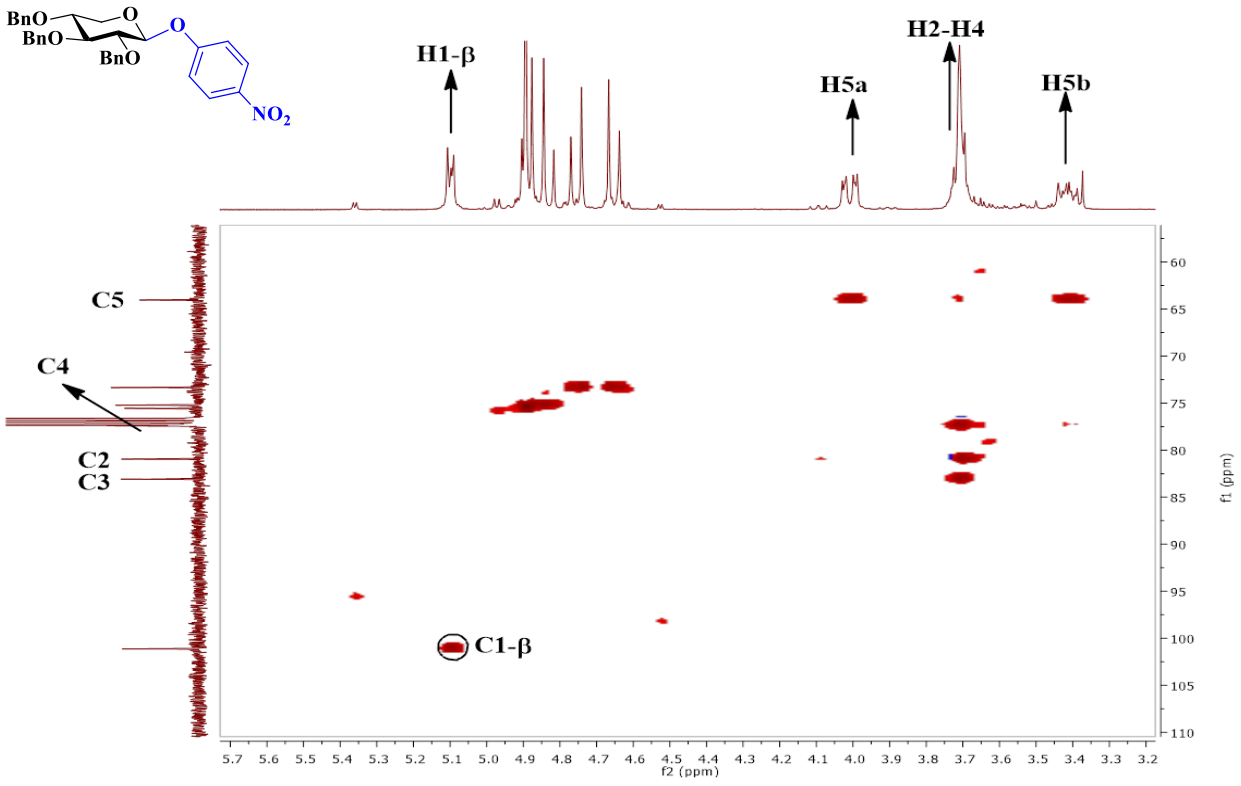
^{13}C {^{1}H}NMR spectrum of compound 8e (100 MHz, $CDCl_3$)



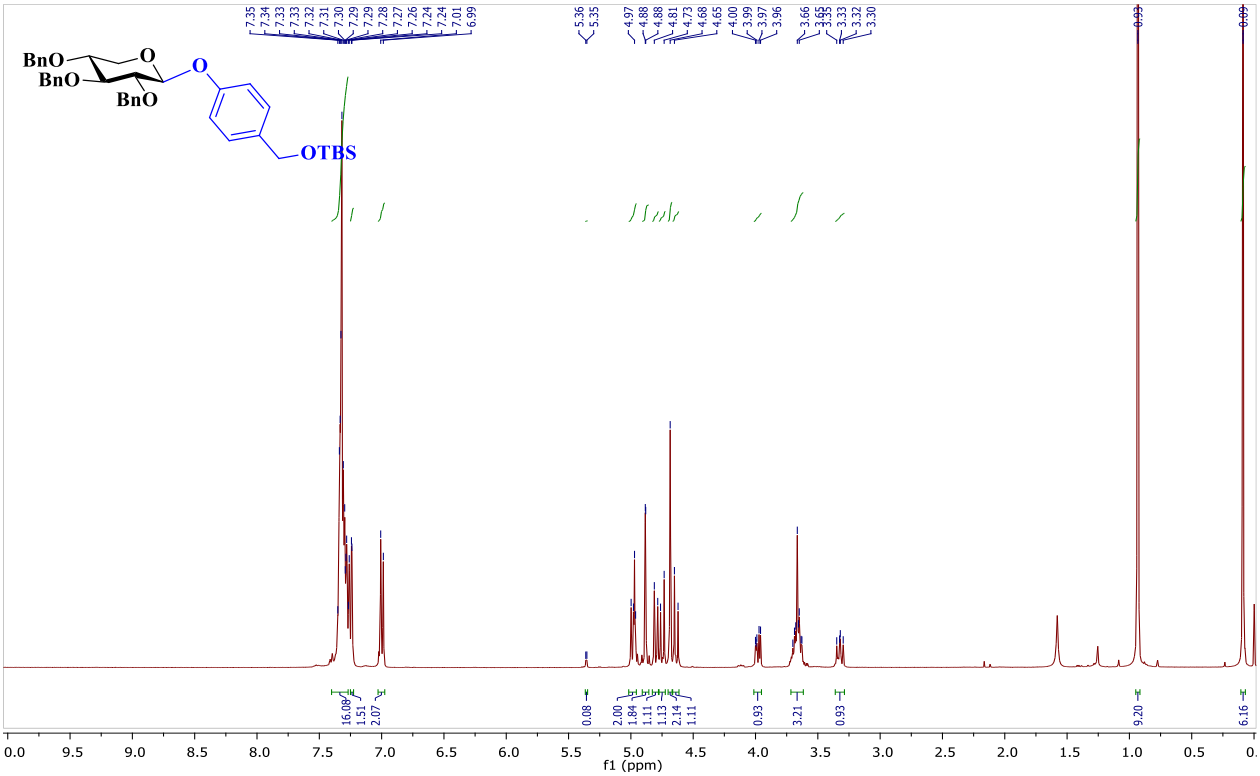
COSY spectrum of compound 8e



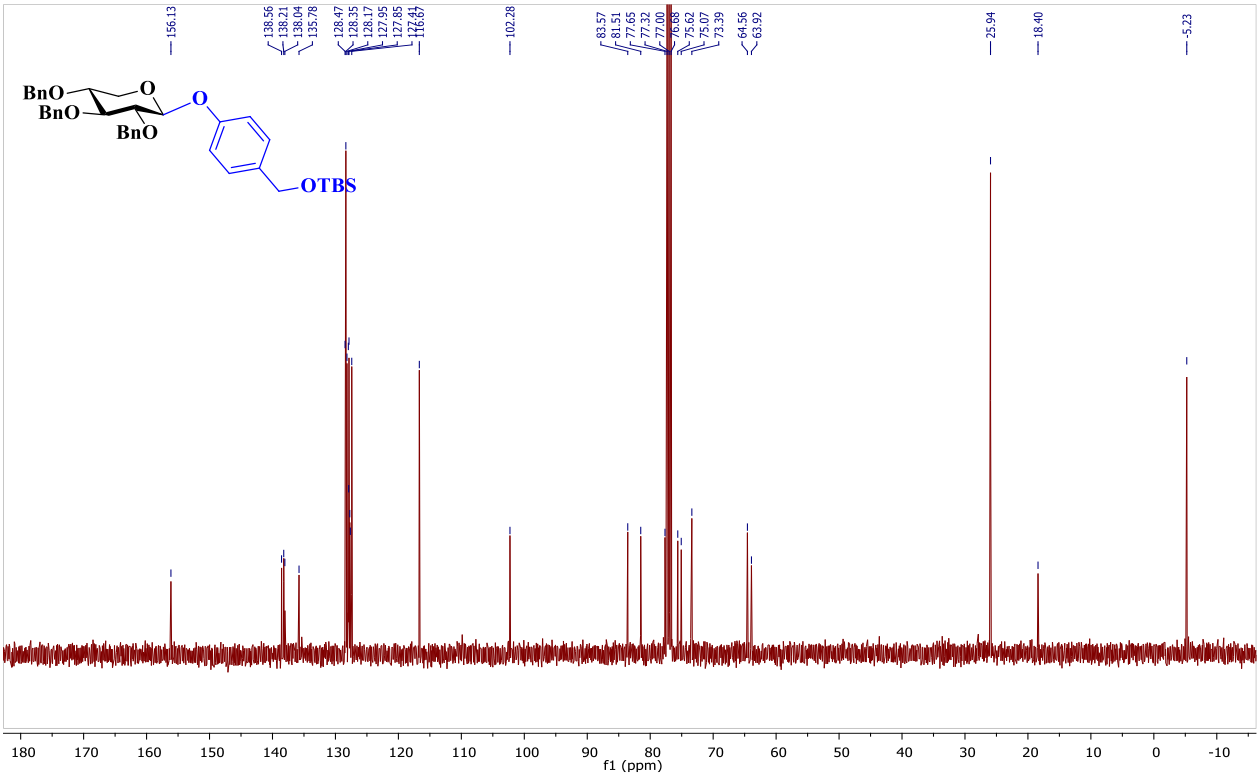
HSQC spectrum of compound 8e



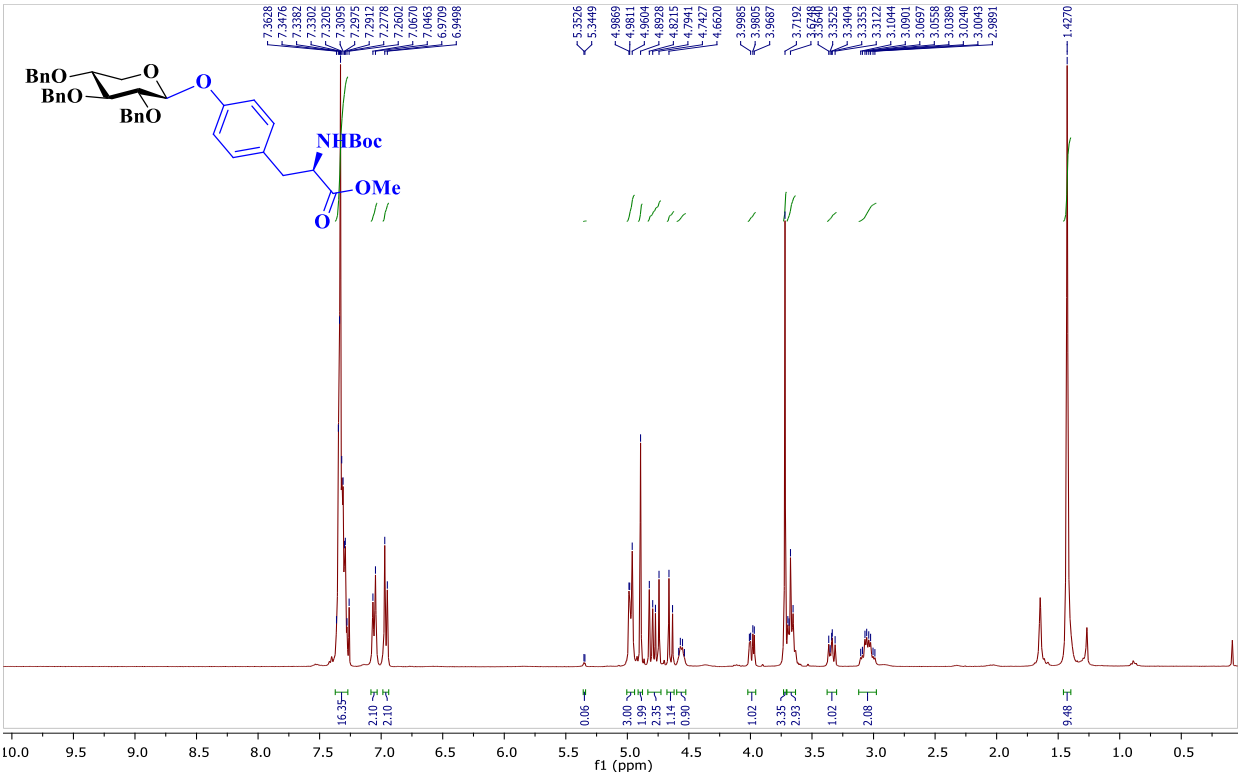
^{1}H NMR spectrum of compound 8f (400 MHz, $CDCl_3$)



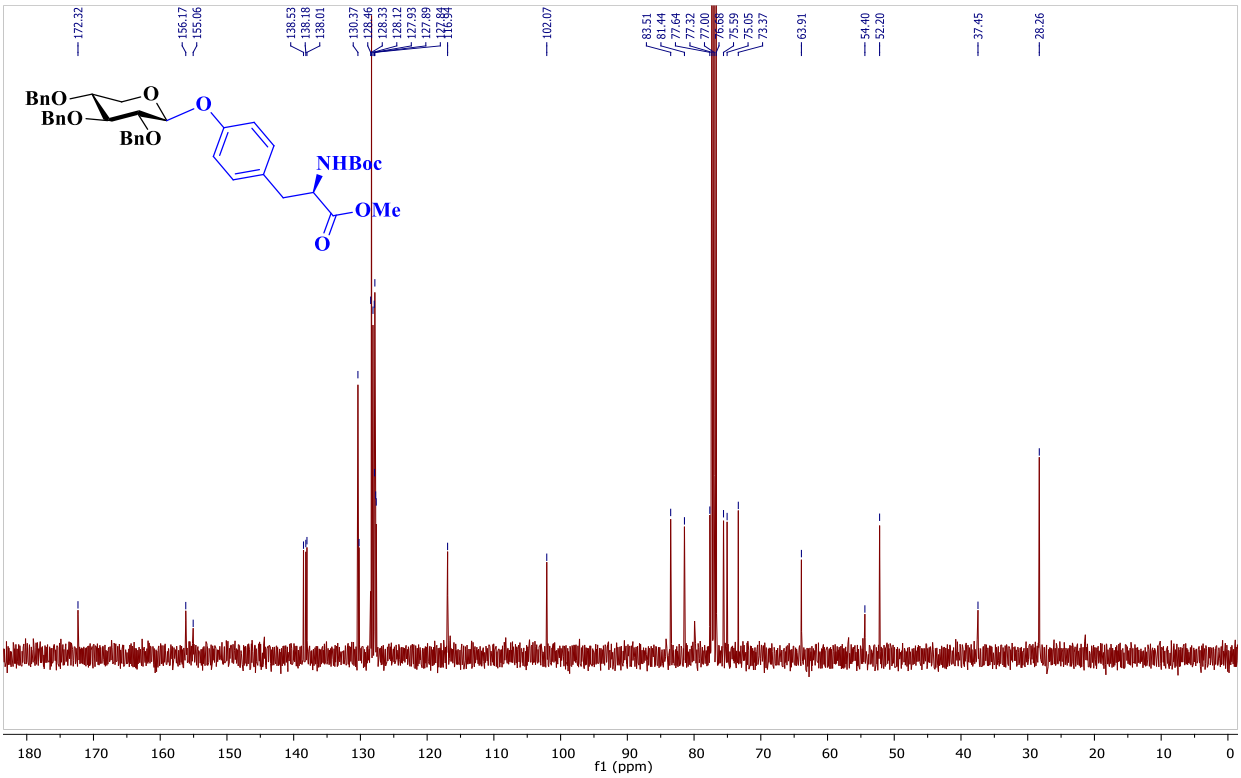
^{13}C {^{1}H} NMR spectrum of compound 8f (100 MHz, $CDCl_3$)



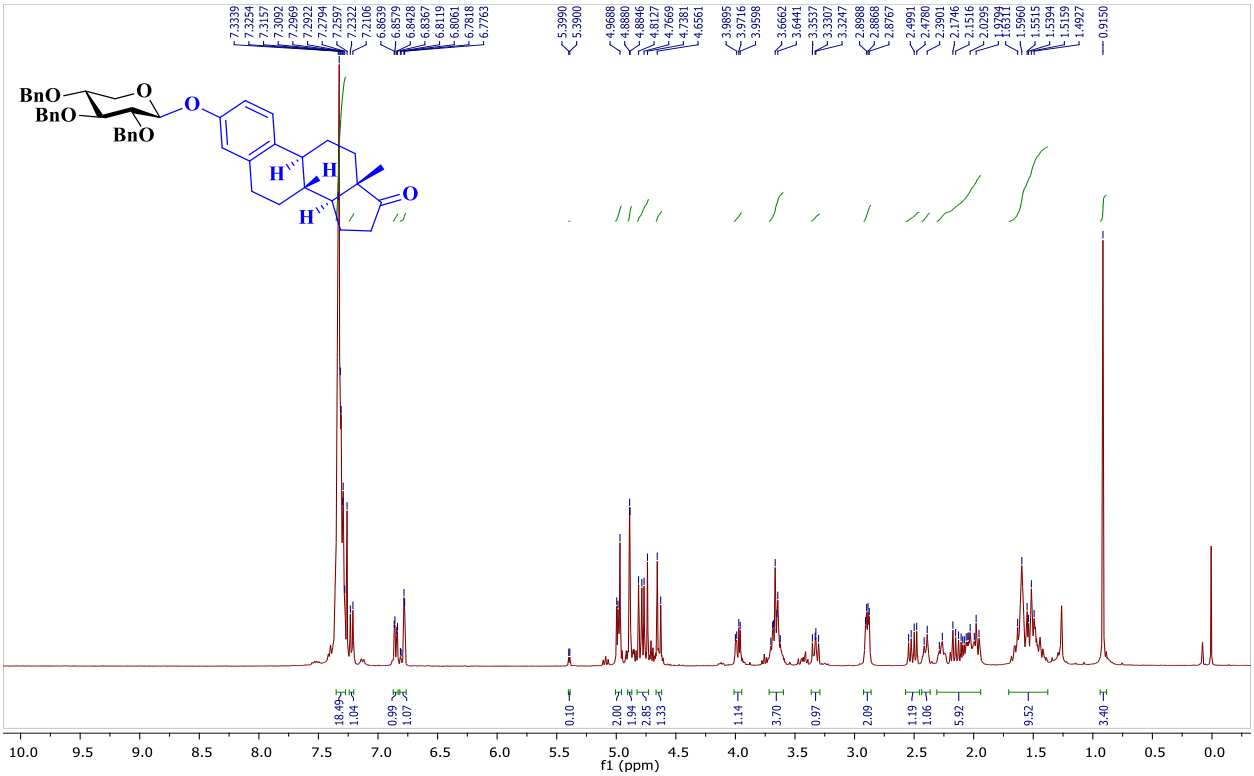
^{1}H NMR spectrum of compound 8g (400 MHz, $CDCl_3$)



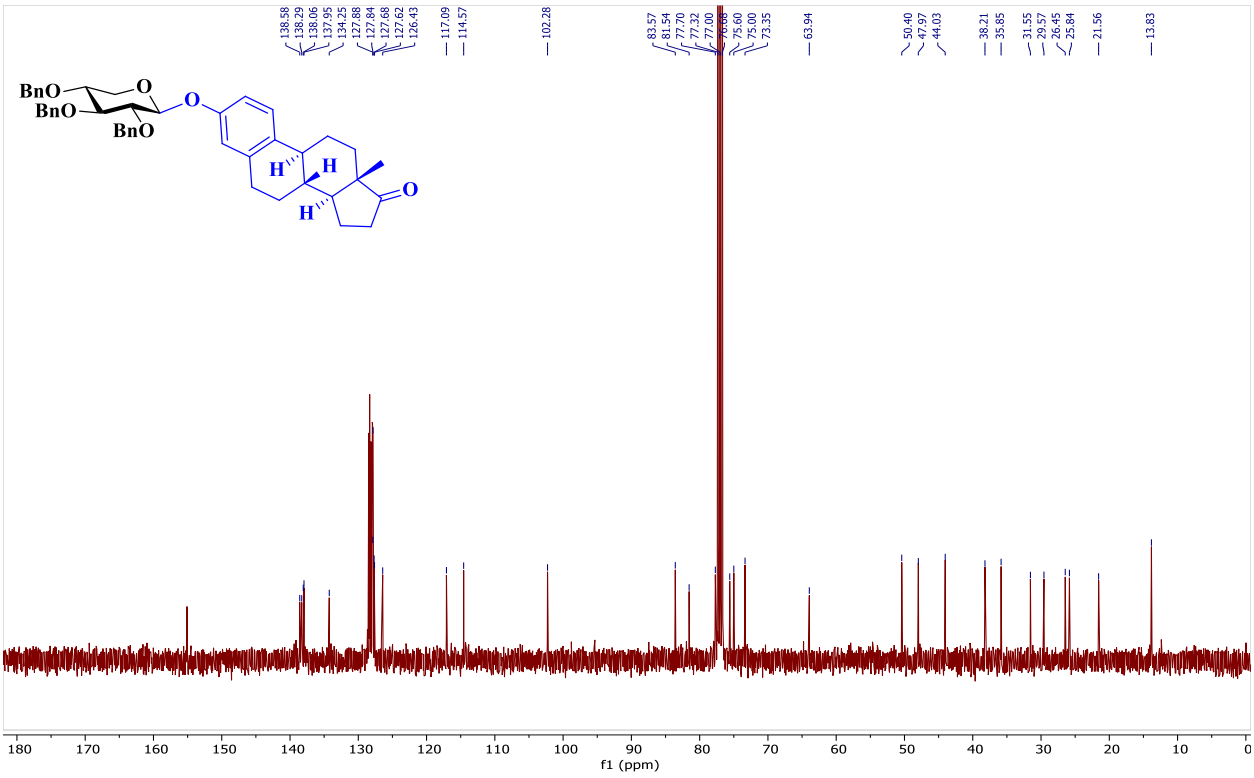
^{13}C {^{1}H} NMR spectrum of compound 8g (100 MHz, $CDCl_3$)



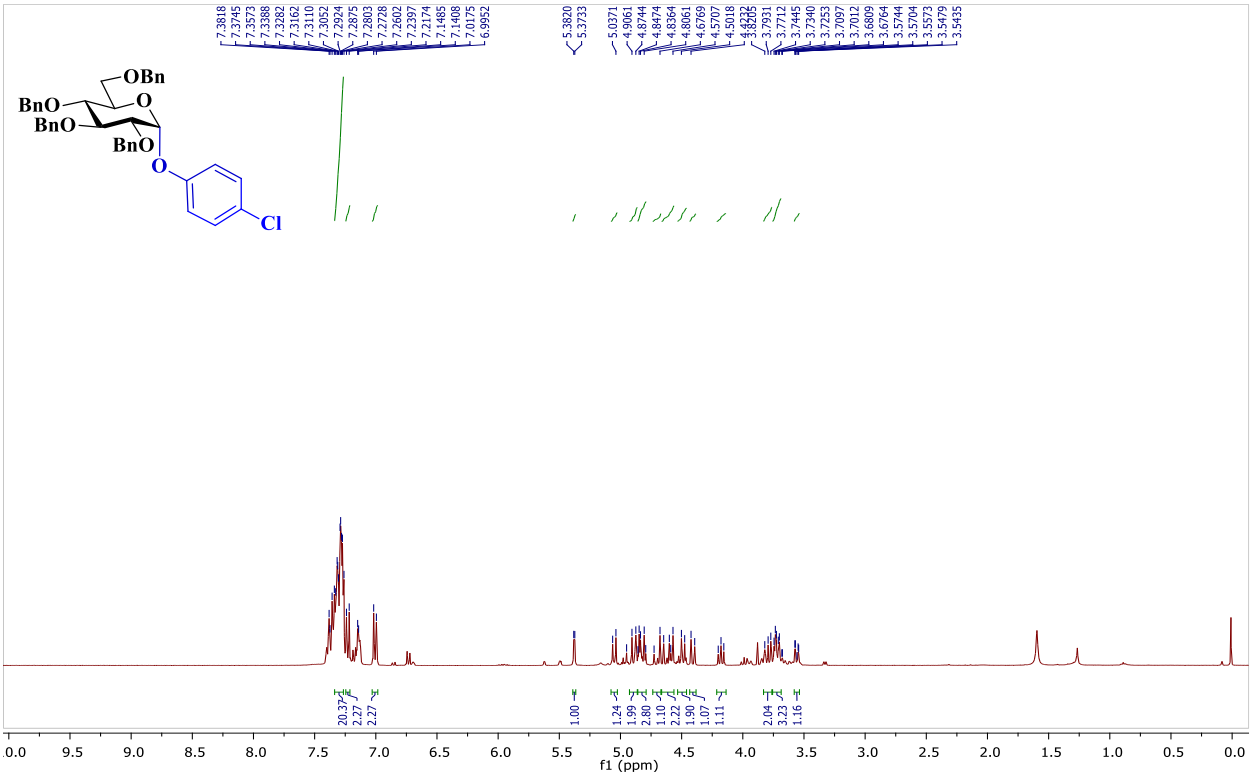
^{1}H NMR spectrum of compound 8h (400 MHz, $CDCl_3$)



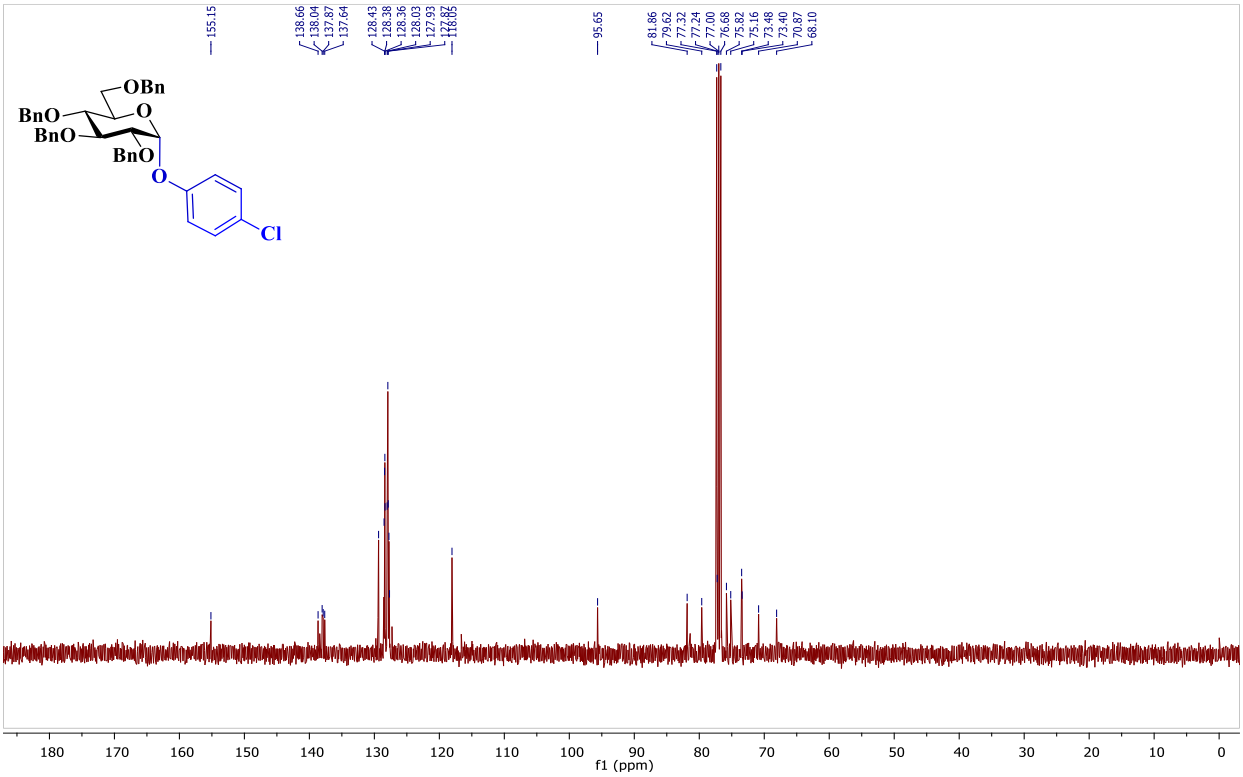
^{13}C {^{1}H} NMR spectrum of compound 8h (100 MHz, $CDCl_3$)



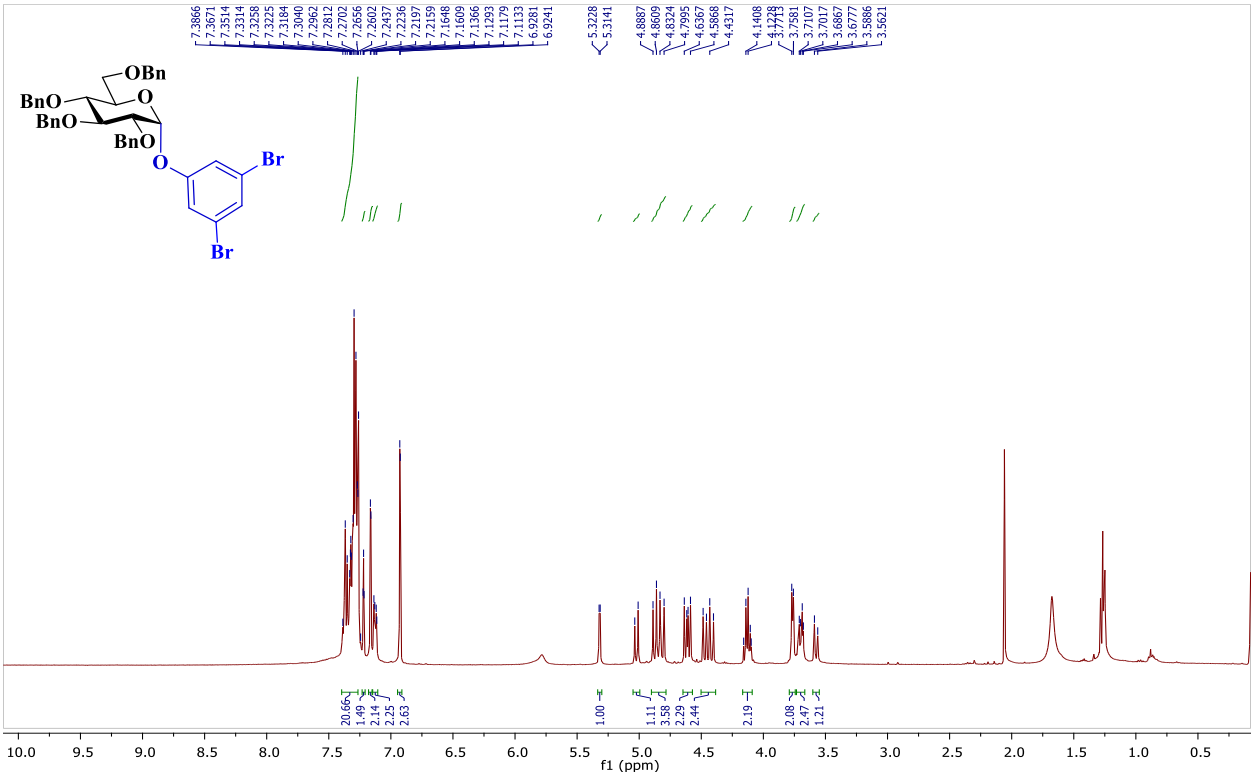
^{1}H NMR spectrum of compound 9a (400 MHz, $CDCl_3$)



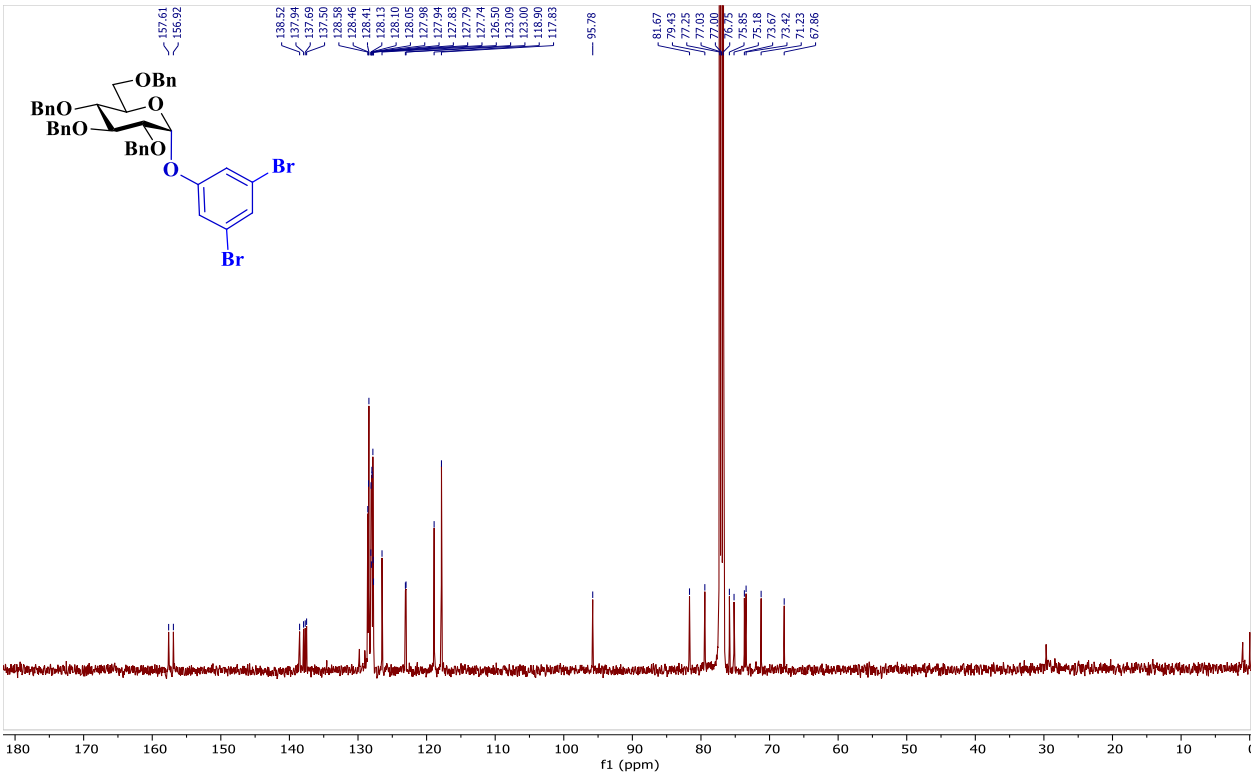
^{13}C {^{1}H} NMR spectrum of compound 9a (100 MHz, $CDCl_3$)



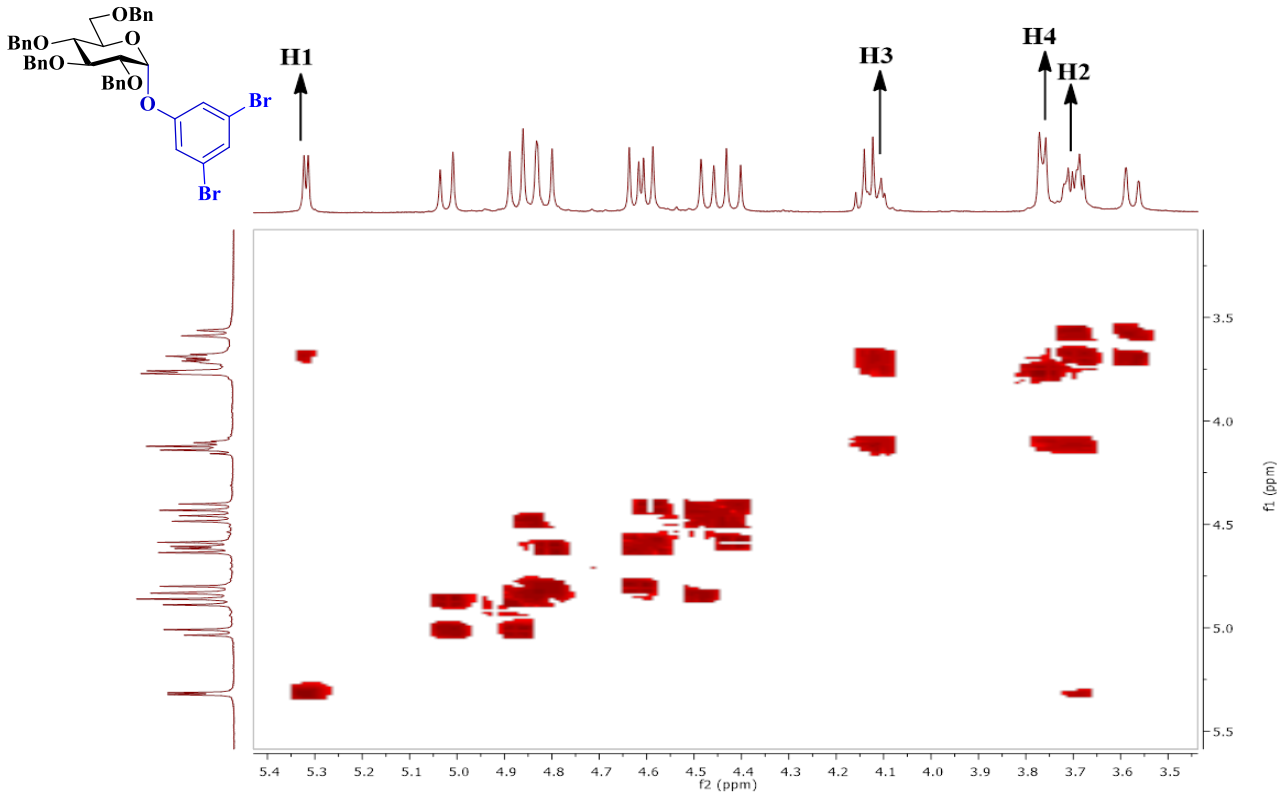
^{1}H NMR spectrum of compound 9b (400 MHz, $CDCl_3$)



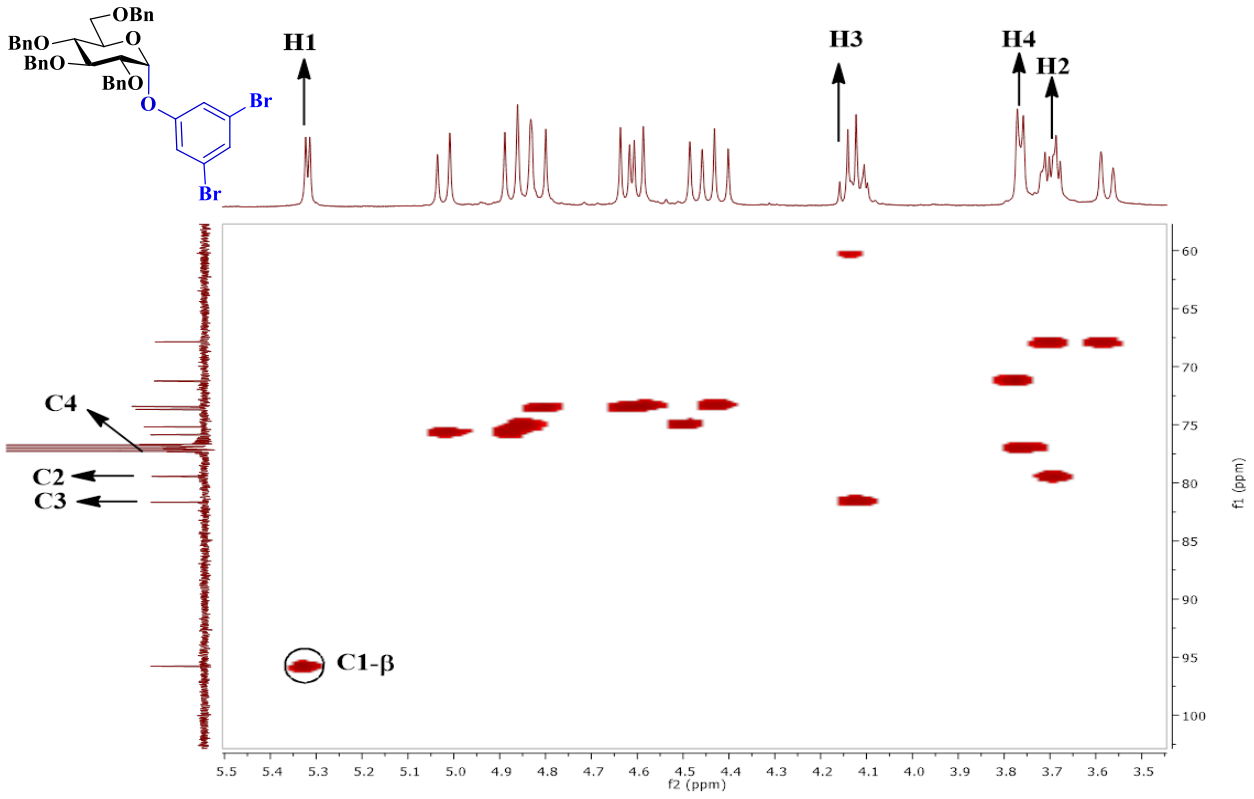
^{13}C {^{1}H} NMR spectrum of compound 9b (100 MHz, $CDCl_3$)



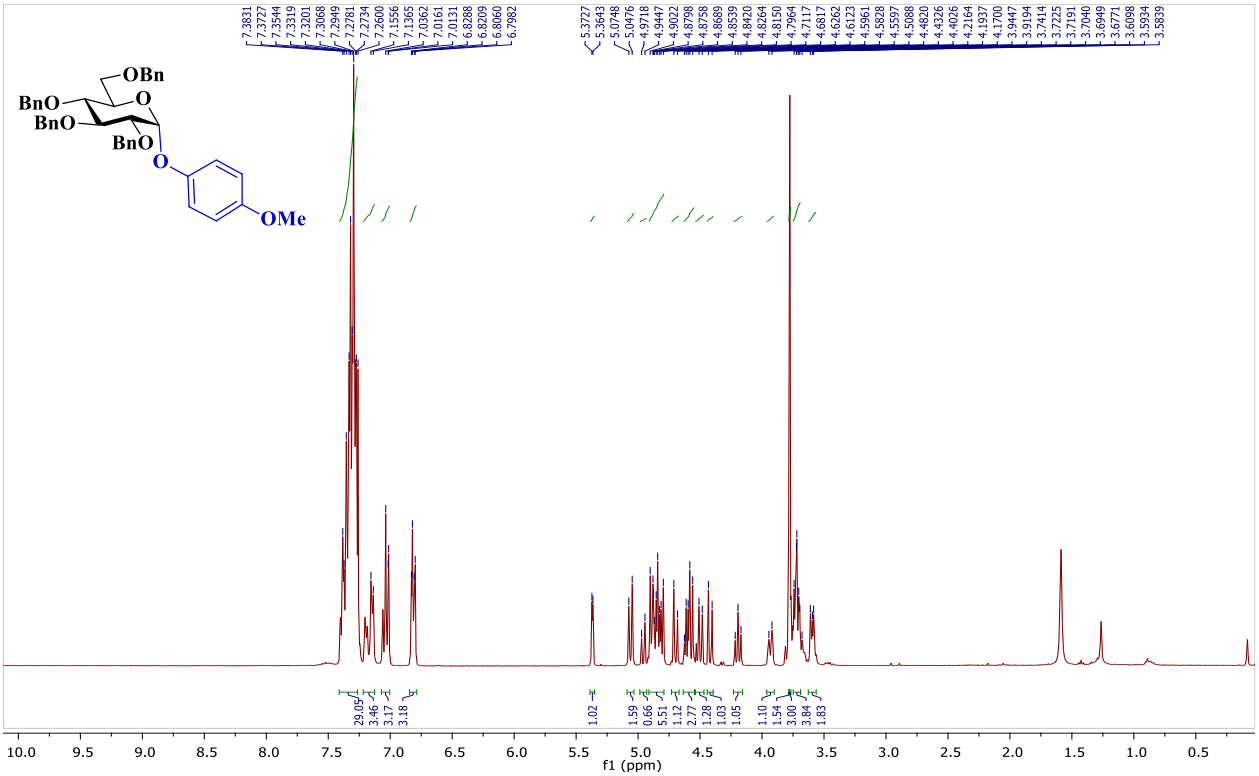
COSY spectrum of compound 9b



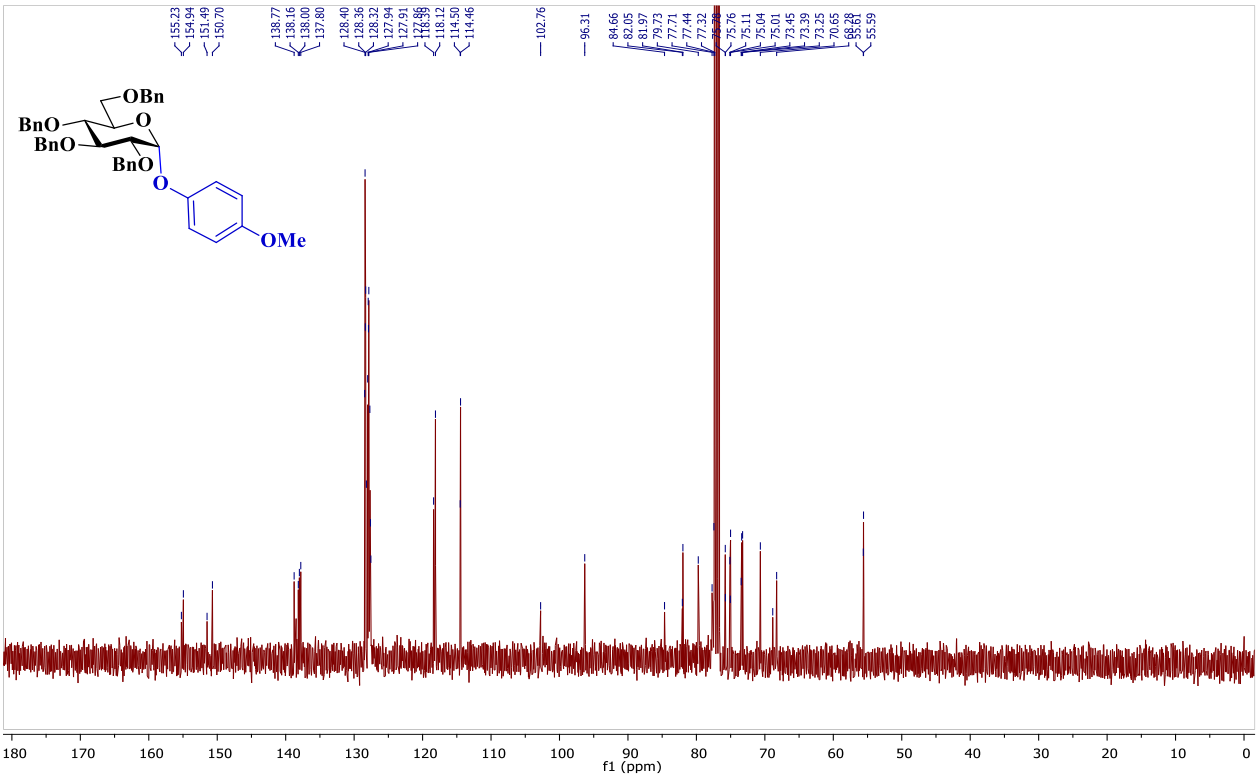
HSQC spectrum of compound 9b



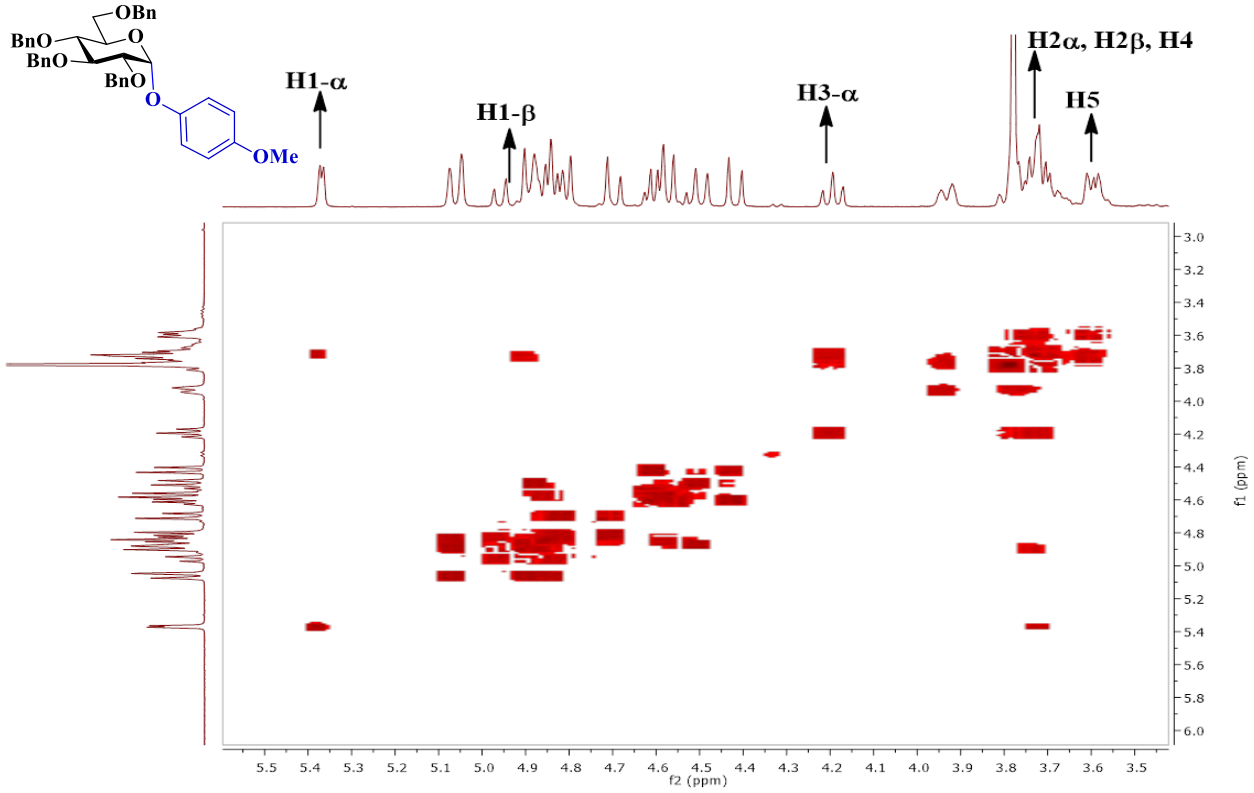
^{1}H NMR spectrum of compound 9c (400 MHz, $CDCl_3$)



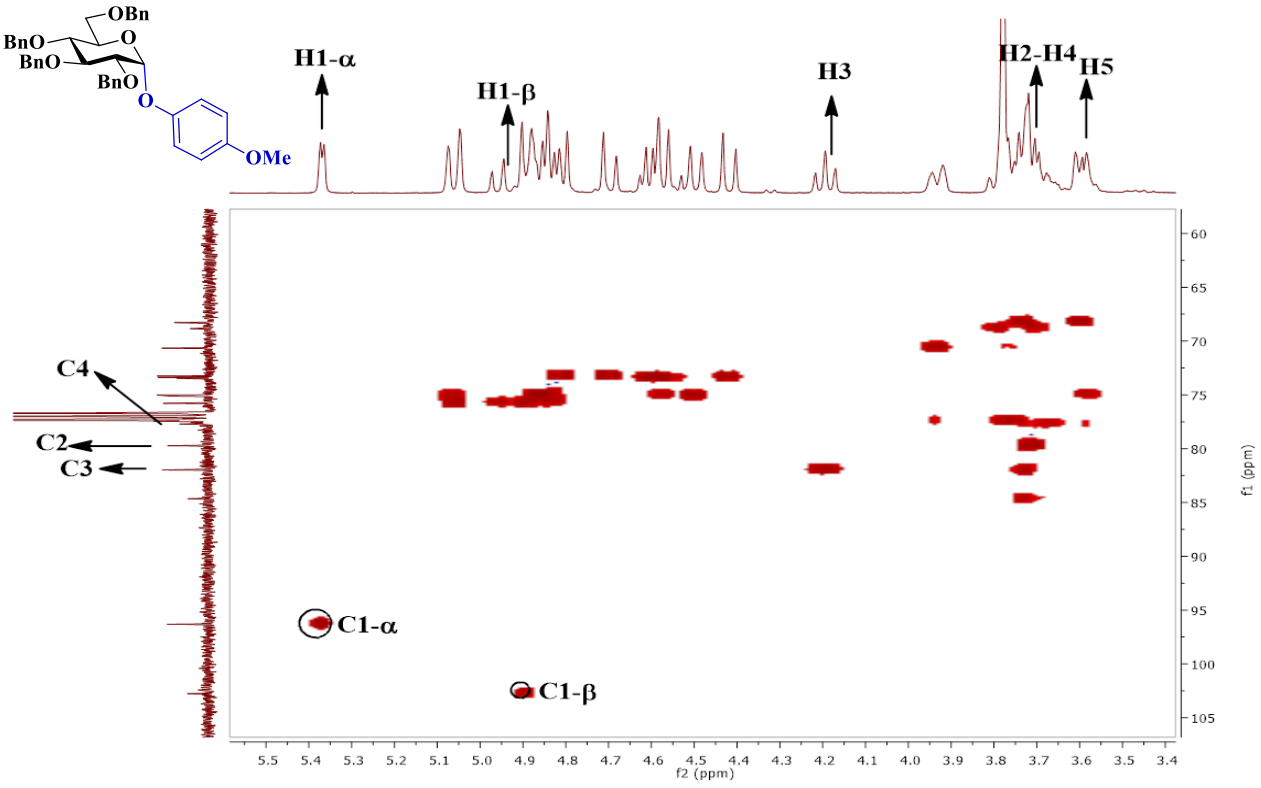
^{13}C {^{1}H} NMR spectrum of compound 9c (100 MHz, $CDCl_3$)



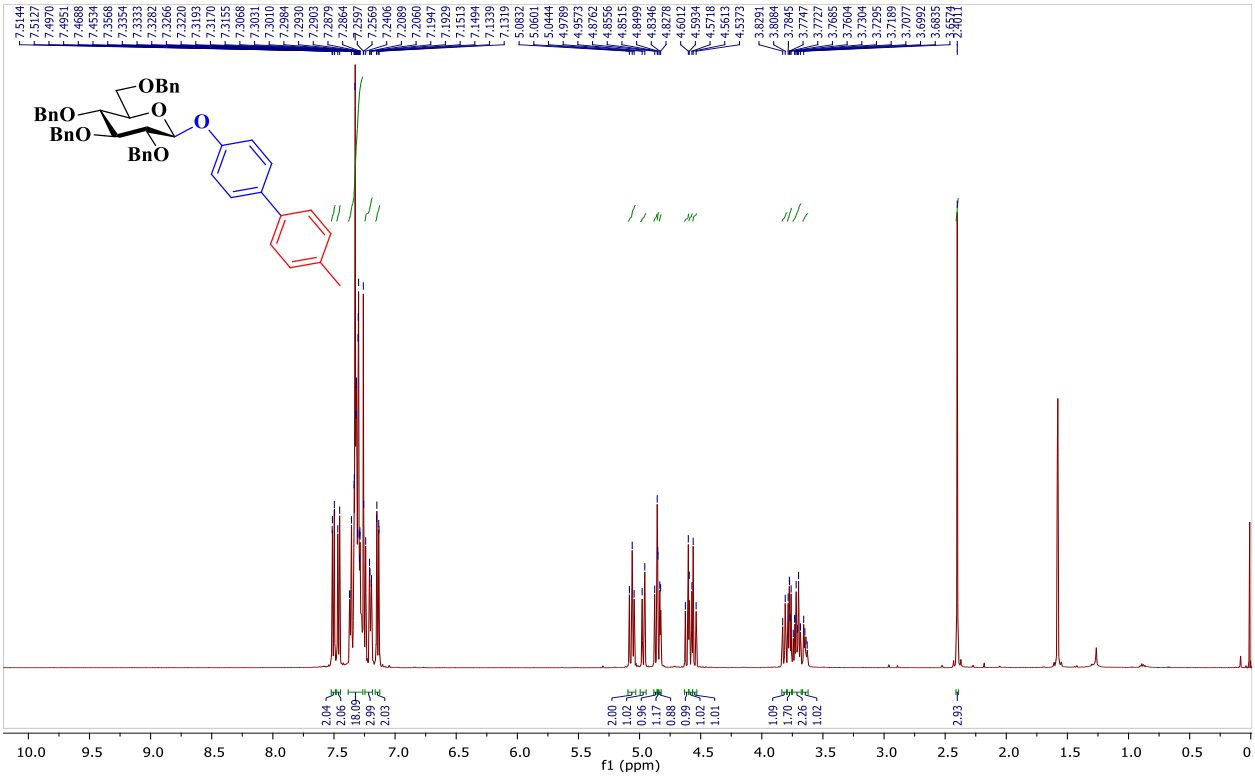
COSY spectrum of compound 9c



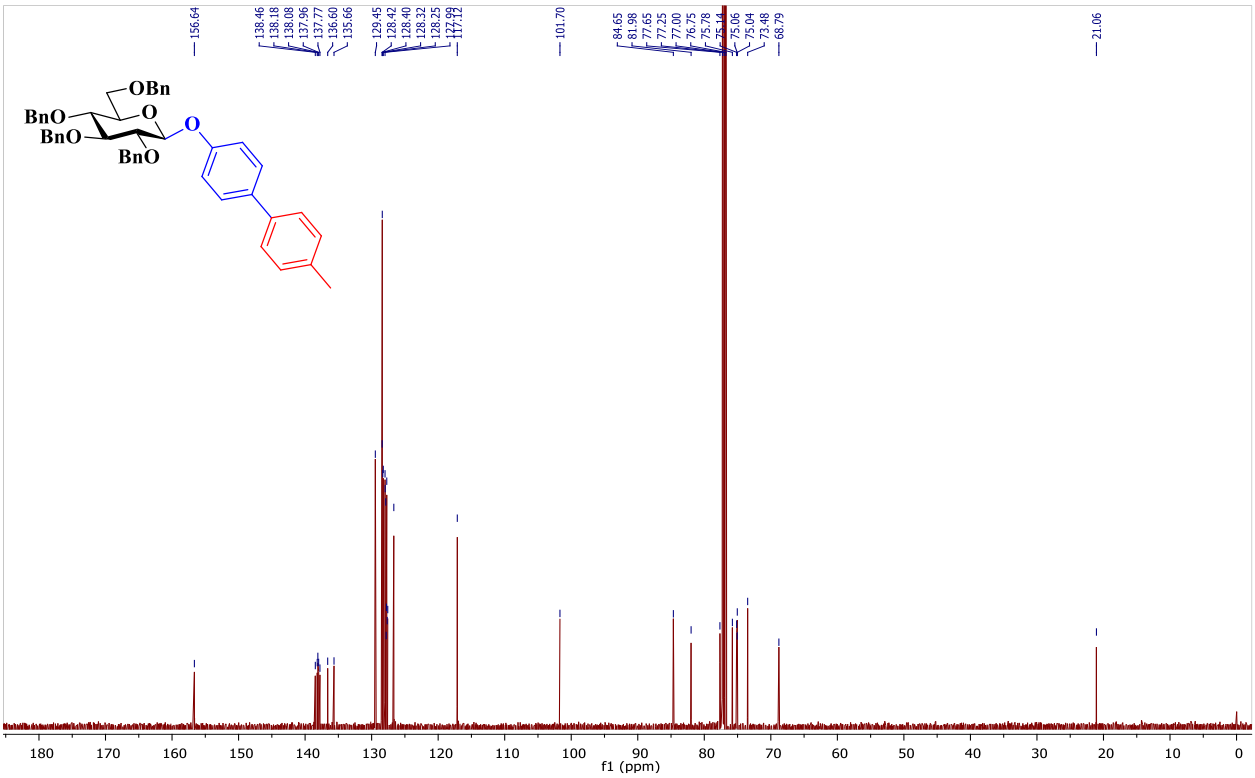
HSQC spectrum of compound 9c



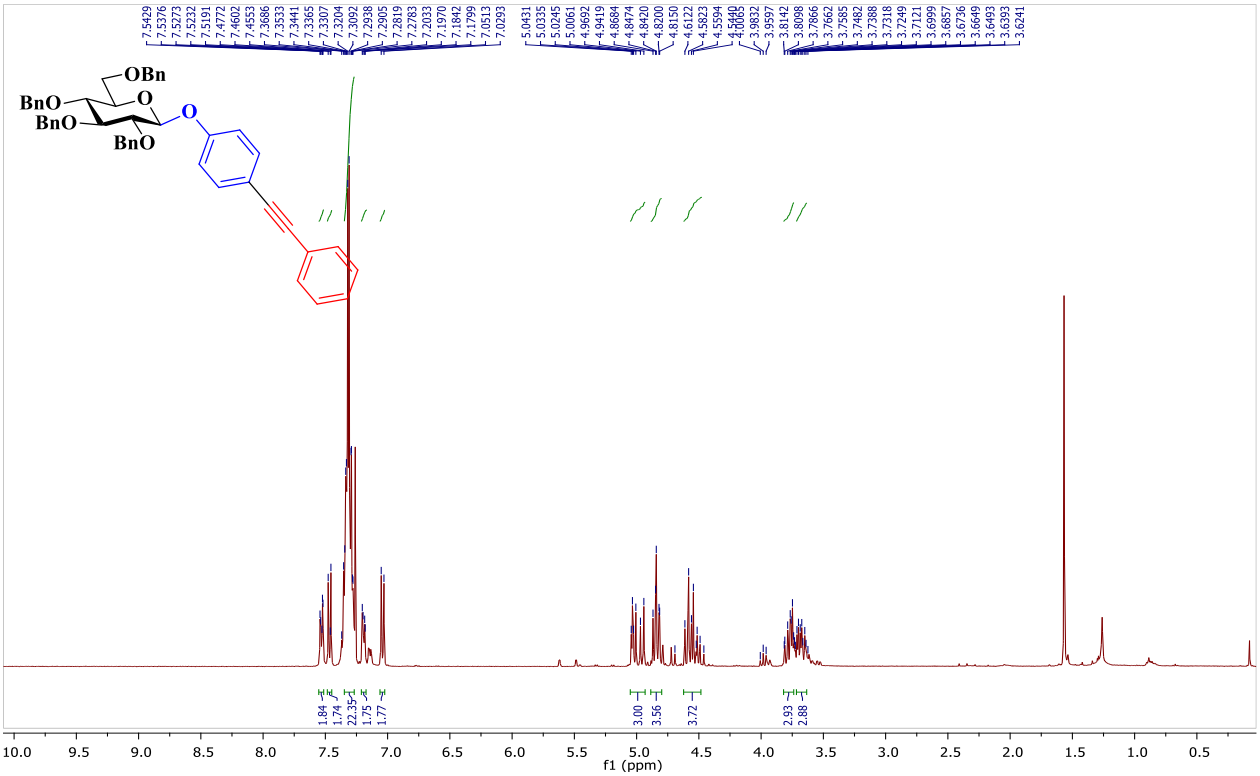
^{1}H NMR spectrum of compound 10a (500 MHz, $CDCl_3$)



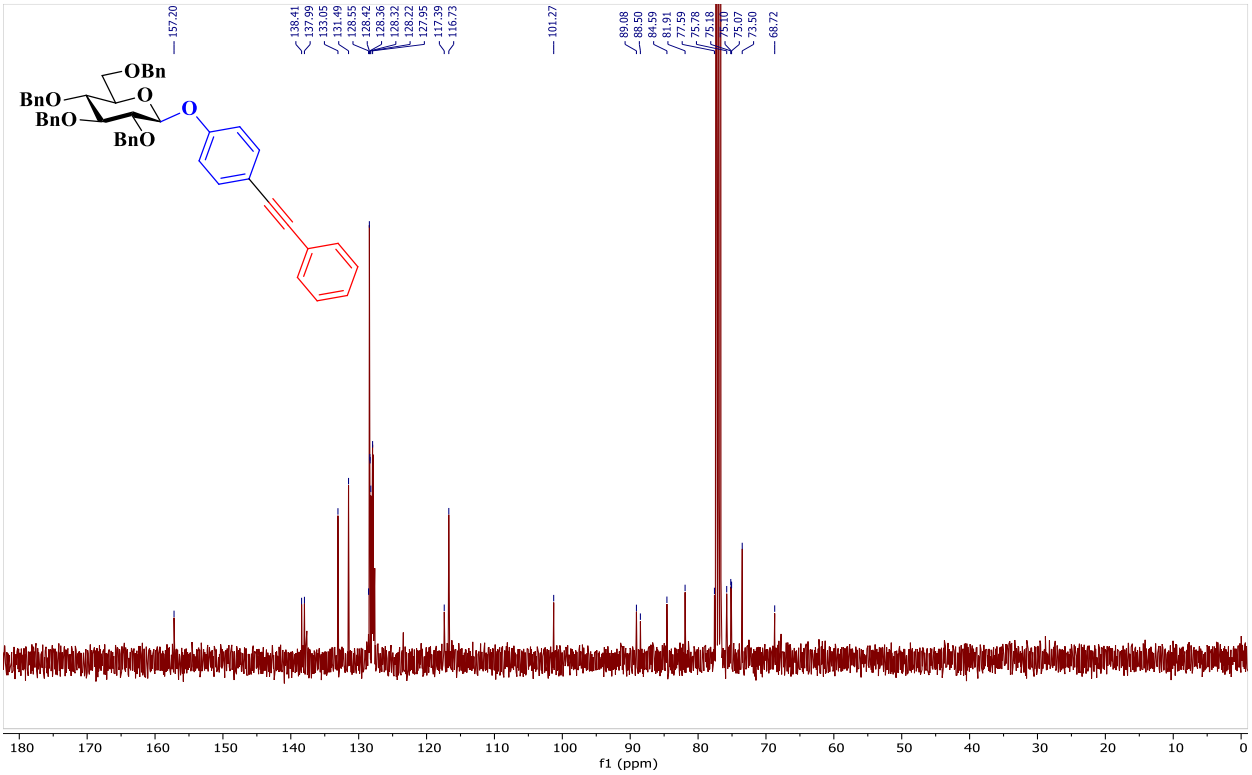
^{13}C {^{1}H} NMR spectrum of compound 10a (125 MHz, $CDCl_3$)



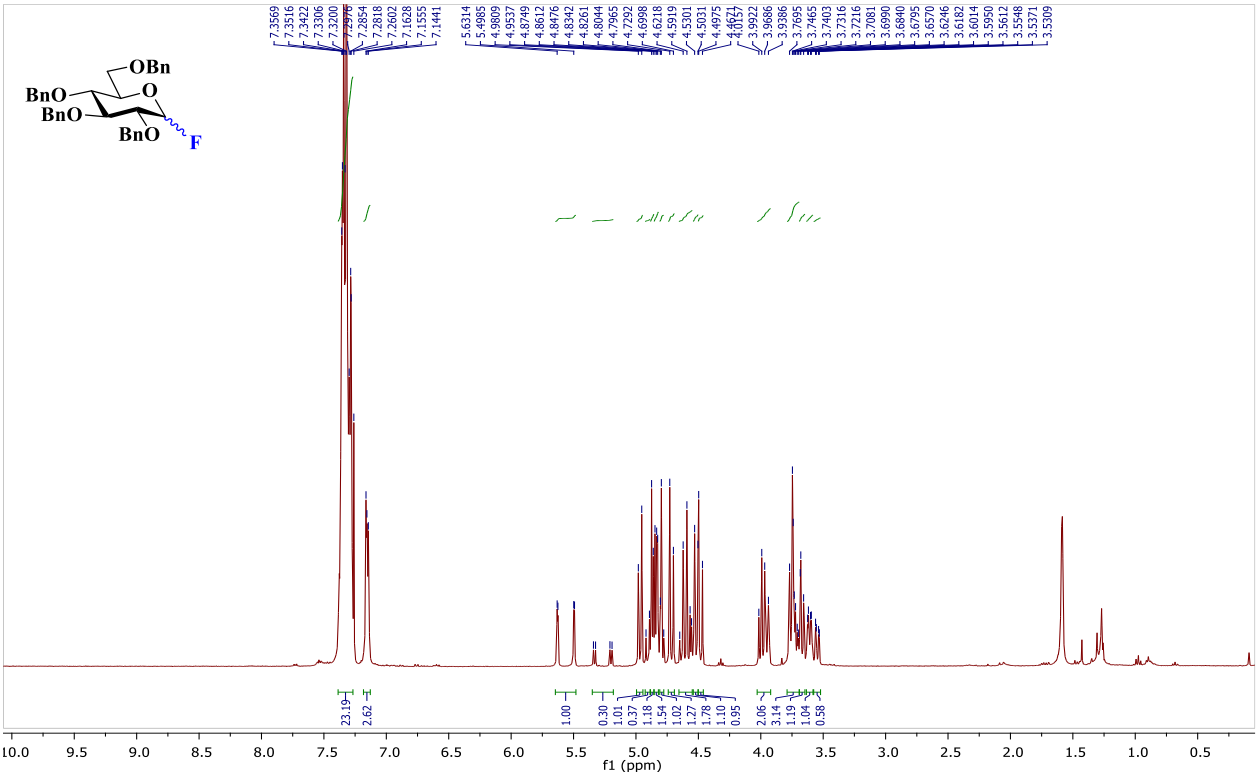
^{1}H NMR spectrum of compound 10b (400 MHz, $CDCl_3$)



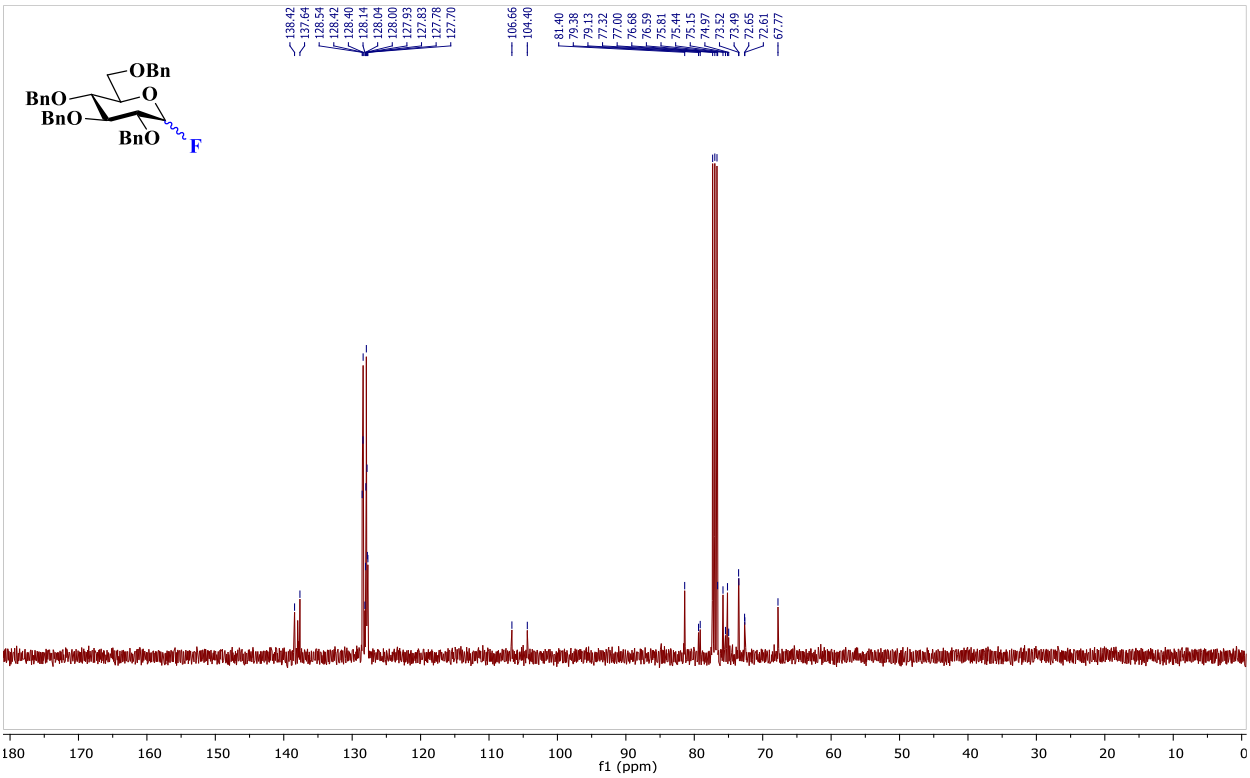
^{13}C {^{1}H} NMR spectrum of compound 10b (100 MHz, $CDCl_3$)



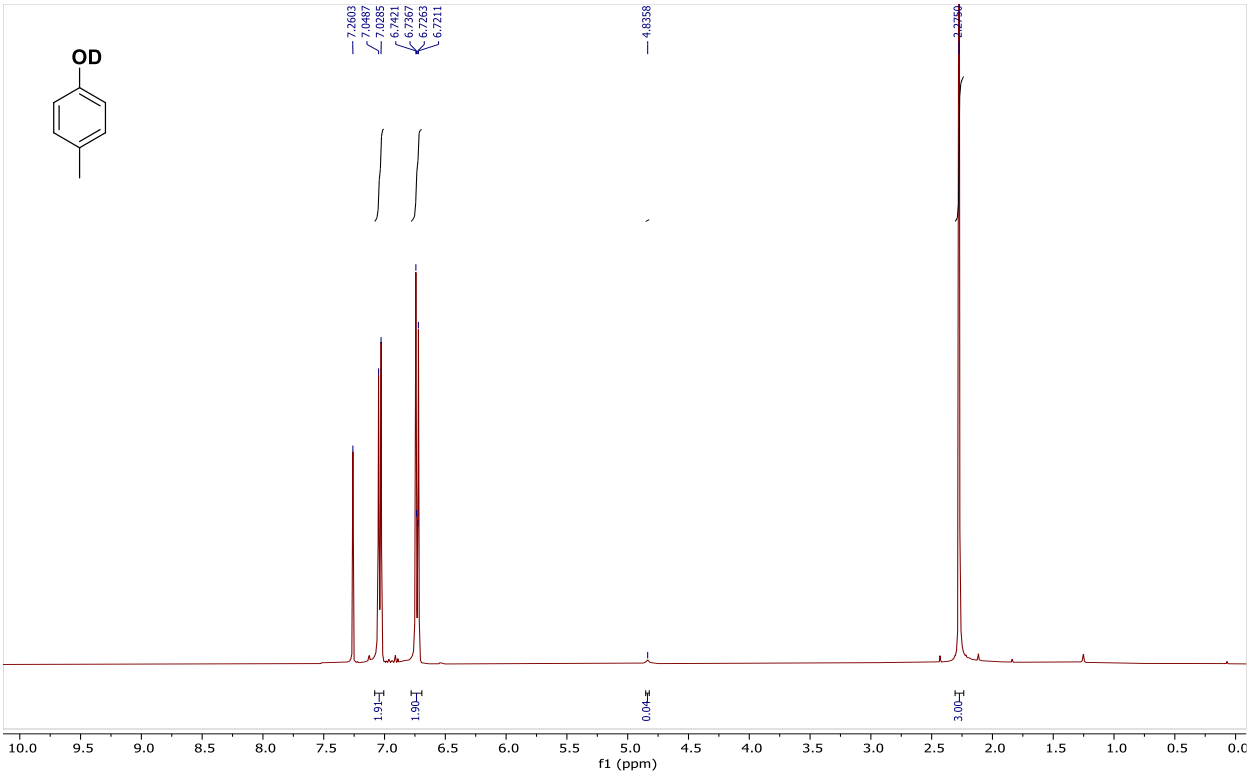
^{1}H NMR spectrum of compound 10c (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR spectrum of compound 10c (100 MHz, $CDCl_3$)



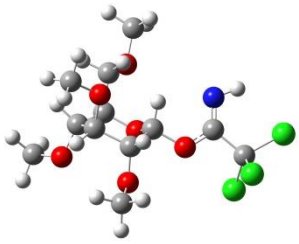
^{1}H NMR spectrum of compound 2-*d* (400 MHz, $CDCl_3$)



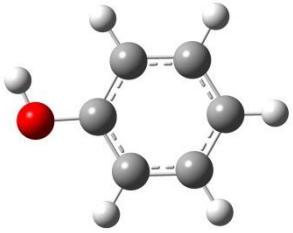
DFT Calculation Data

Density functional theory (DFT)[1] calculations were conducted using the Gaussian 16 program package[2]. For geometry optimization and harmonic frequency calculations, the popular hybrid functional B3LYP level of theory and the 6-31g(++)(d,p) Pople basis set is utilized. The bulk solvent effects were included by using the SMD model[3]. Geometry optimization and frequencies were calculated at 273.15 K and 1 atm pressure. All the structures were generated by Gaussview.

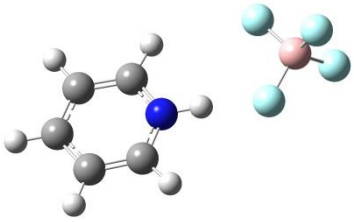
Overview of the calculated optimized structures:



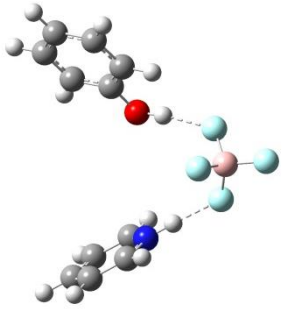
1b
E = -2355.969369 Hartree



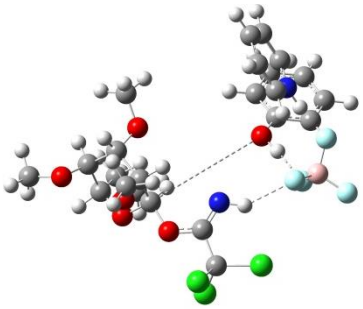
2a
E = -307.507615 Hartree



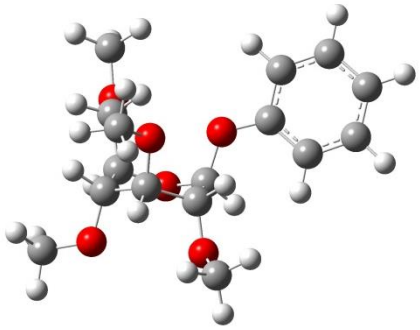
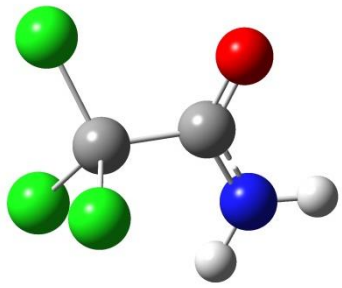
A
E = -673.434223 Hartree



A---2a (Int. I)
E = -980.947194 Hartree



(Int. II)
E = -3336.916300 Hartree

	
***O*-aryl Glycoside** **E = -1075.498780 Hartree**	**Trichloroacetamide** **E = -1588.001865 Hartree**

Reaction Coordinates:

1) Glycosyl donor (1b)

Number of imaginary frequencies = 0

Energy = -2355.969369 Hartree

Atom	Coordinates (Angstroms)		
	X	**Y**	**Z**
C	3.079621	-0.243104	0.397814
C	2.520574	-1.122624	-0.744802
C	1.011222	-1.435054	-0.599768
C	0.283750	-0.123934	-0.316476
C	0.762225	0.510079	0.846197
C	2.141308	0.929214	0.774960
C	2.336396	2.167745	-0.102051
O	-1.096034	-0.412607	-0.077613
C	-2.003651	0.537168	-0.357494
N	-1.732278	1.659318	-0.870599
O	3.334584	-1.095350	1.513133
C	4.348551	-0.618602	2.391853
O	2.674311	-0.451505	-1.998344
C	3.929041	-0.679062	-2.638134
O	1.678466	3.267234	0.513807
C	1.756559	4.453077	-0.265310

C	0.863915	-3.720547	0.055975
O	0.747828	-2.355004	0.442226
C	-3.404772	0.000559	0.043883
Cl	-4.689921	1.201387	-0.322973
Cl	-3.425969	-0.349162	1.809726
Cl	-3.750745	-1.511199	-0.879156
H	4.033514	0.179562	0.051667
H	3.079651	-2.065942	-0.751056
H	0.652465	-1.828252	-1.561546
H	0.357678	0.531359	-1.189168
H	2.368431	1.228396	1.801776
H	1.954746	2.016474	-1.120484
H	3.415719	2.374121	-0.181590
H	-2.556902	2.238299	-1.018010
H	4.472004	-1.376532	3.169514
H	5.303544	-0.486982	1.861631
H	4.074609	0.331571	2.870644
H	3.917187	-0.104725	-3.567645
H	4.773022	-0.340736	-2.022312
H	4.061720	-1.744333	-2.872677
H	1.230629	5.236672	0.286186
H	2.800923	4.763861	-0.421740
H	1.276340	4.320020	-1.246073
H	0.604357	-4.316405	0.934457
H	0.168050	-3.961314	-0.760735
H	1.884910	-3.979583	-0.255737

2) Phenol (2a)

Number of imaginary frequencies = 0

Energy = -307.507615 Hartree

Atom	**Coordinates (Angstroms)**		

	X	Y	Z
C	-0.269082	1.202037	-0.000000
C	1.129280	1.223747	-0.000000
C	1.860245	0.031365	-0.000000
C	1.177102	-1.190987	-0.000000
C	-0.218856	-1.227200	0.000000
C	-0.940019	-0.026903	0.000000
O	-2.308378	-0.114454	0.000000
H	-0.835700	2.130566	-0.000000
H	1.644921	2.180219	-0.000001
H	2.945930	0.053395	-0.000000
H	1.732419	-2.125016	0.000000
H	-0.756195	-2.170925	0.000000
H	-2.696376	0.775036	0.000003

3) Catalyst (A)

Number of imaginary frequencies = 0

Energy = -673.434223 Hartree

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-3.379163	-1.053092	0.012910
C	-2.014462	-1.291483	-0.011935
N	-1.158708	-0.250090	-0.027999
C	-1.562922	1.035680	-0.020421
C	-2.918336	1.323803	0.003748
C	-3.835222	0.268661	0.020503
H	-4.067445	-1.889975	0.025972
H	-1.572020	-2.279924	-0.019562
H	-0.145907	-0.450440	-0.048893

H	-0.782098	1.786178	-0.033645
H	-3.244053	2.357102	0.009511
H	-4.900507	0.475386	0.039529
B	2.583386	0.013472	0.006410
F	3.317592	-0.261514	1.169967
F	3.404683	-0.065071	-1.128088
F	1.531810	-0.962987	-0.117225
F	1.986658	1.287742	0.093368

4) Int. I

Number of imaginary frequencies = 0

Energy = -980.947194 Hartree

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
C	2.865462	-2.750923	-0.927735
C	2.559409	-1.412722	-1.116193
N	2.603976	-0.568300	-0.066624
C	2.934531	-0.959070	1.180272
C	3.249116	-2.287457	1.417725
C	3.213924	-3.192143	0.352405
H	2.829302	-3.430813	-1.770718
H	2.277950	-0.983298	-2.069720
H	2.368120	0.423851	-0.223254
H	2.932208	-0.190227	1.943362
H	3.513906	-2.602155	2.420168
H	3.455904	-4.236951	0.519026
B	0.872774	2.785749	0.006550
F	1.098637	4.163585	0.019341
F	-0.244468	2.488006	-0.822681
F	2.020359	2.123657	-0.539856
F	0.641610	2.297423	1.300872
C	-3.078107	0.439669	0.341637
C	-4.223071	-0.000441	1.012771
C	-4.735786	-1.282214	0.787645
C	-4.088858	-2.126153	-0.123460
C	-2.944538	-1.699606	-0.800580

C	-2.436765	-0.413434	-0.568179
O	-1.315908	-0.044277	-1.255865
H	-2.684545	1.436944	0.519508
H	-4.713749	0.667593	1.715650
H	-5.625692	-1.617950	1.311750
H	-4.476071	-3.124368	-0.310161
H	-2.439555	-2.348434	-1.510420
H	-1.039357	0.862308	-1.021571

5) Int. II

Number of imaginary frequencies = 0

Energy = -3336.9163 Hartree

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.839010	-2.817752	0.182028
C	2.946028	-2.188906	1.276517
C	2.897418	-0.641840	1.224948
C	2.647799	-0.210671	-0.222702
O	3.628189	-0.707849	-1.095469
C	3.664788	-2.144297	-1.200093
C	2.489104	-2.707642	-2.001816
O	2.763607	1.211440	-0.387538
C	1.670607	1.966930	-0.224881
N	0.565556	1.535911	0.214372
O	5.189538	-2.748667	0.637375
C	6.047374	-3.734561	0.072158
O	1.597217	-2.640579	1.130675
C	1.312740	-3.873924	1.787162
O	2.567784	-2.211469	-3.331299
C	1.481504	-2.645846	-4.139048
C	4.166825	0.120134	3.092599
O	4.100868	-0.051625	1.681312
C	2.011730	3.418030	-0.662633
Cl	0.599615	4.502856	-0.461981

Cl	2.502741	3.416813	-2.398177
Cl	3.371511	4.042225	0.347652
H	3.551659	-3.874845	0.086926
H	3.342676	-2.496186	2.251964
H	2.049310	-0.311518	1.839024
H	1.638307	-0.508478	-0.522939
H	4.568415	-2.330986	-1.786660
H	1.519374	-2.449669	-1.555270
H	2.568580	-3.806551	-2.003903
H	-0.171102	2.239945	0.254365
H	7.028239	-3.600337	0.535122
H	5.681955	-4.749562	0.288505
H	6.155834	-3.620535	-1.015126
H	0.258790	-4.093774	1.600002
H	1.921353	-4.700880	1.397387
H	1.478653	-3.789064	2.870268
H	1.627086	-2.215710	-5.133240
H	1.456538	-3.743153	-4.222743
H	0.518809	-2.299377	-3.735312
H	5.117134	0.617211	3.302795
H	3.342596	0.751810	3.454509
H	4.145296	-0.837878	3.630178
C	-2.694059	-0.655542	4.862933
C	-2.946019	0.285717	3.877649
N	-3.720304	-0.046582	2.825612
C	-4.272503	-1.266710	2.673199
C	-4.049323	-2.240839	3.633024
C	-3.252458	-1.931286	4.739281
H	-2.072300	-0.388850	5.709312
H	-2.555753	1.295726	3.889484
H	-3.899494	0.666554	2.102427

H	-4.873928	-1.417261	1.785281
H	-4.493255	-3.221706	3.511096
H	-3.067340	-2.681061	5.501735
B	-3.401380	2.670549	0.195065
F	-3.932068	3.944608	-0.012491
F	-3.129567	2.047918	-1.051704
F	-2.222492	2.734784	0.958445
F	-4.358052	1.866676	0.895450
C	-5.401590	-0.546322	-2.267481
C	-6.537277	-1.201216	-2.754041
C	-6.546668	-2.590119	-2.919653
C	-5.399644	-3.324206	-2.593253
C	-4.258596	-2.683430	-2.106146
C	-4.257732	-1.290354	-1.941846
O	-3.116967	-0.714892	-1.461959
H	-5.399358	0.533326	-2.144589
H	-7.417929	-0.616153	-3.005636
H	-7.431247	-3.092311	-3.299976
H	-5.390056	-4.403580	-2.720101
H	-3.364391	-3.246429	-1.854393
H	-3.216665	0.252197	-1.372642

6) *O*-aryl glycoside

Number of imaginary frequencies = 0

Energy = -1075.498780 Hartree

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.082043	-1.036162	-0.639949
C	4.461721	-1.241544	-0.504959
C	5.278954	-0.281415	0.093237
C	4.701721	0.906170	0.563124
C	3.332694	1.128328	0.431842

C	2.514523	0.159477	-0.174113
O	1.186483	0.485570	-0.253424
H	2.478352	-1.809331	-1.099967
H	4.890628	-2.170340	-0.871569
H	6.346336	-0.453124	0.195314
H	5.321181	1.665971	1.032079
H	2.877911	2.047532	0.788333
C	-2.447851	-0.113087	0.179351
C	-1.426848	-1.032220	0.879980
C	-0.266881	-1.480710	-0.035058
C	0.259575	-0.363584	-0.959013
O	-0.731660	0.440407	-1.517577
C	-1.777916	0.977493	-0.676882
C	-1.337208	2.197508	0.132193
O	-3.305932	-0.944677	-0.602644
C	-4.596260	-0.392804	-0.842791
O	-0.850548	-0.366256	2.005494
C	-1.601856	-0.496564	3.210331
O	-1.053512	3.261223	-0.771037
C	-0.586005	4.426093	-0.106504
C	-0.645254	-3.833688	-0.290681
O	-0.650930	-2.546169	-0.900330
H	-3.045998	0.380801	0.957626
H	-1.963537	-1.928167	1.215382
H	0.555157	-1.809006	0.614449
H	0.765594	-0.820061	-1.813303
H	-2.513457	1.333781	-1.404055
H	-0.462371	1.974893	0.751542
H	-2.166341	2.489700	0.797098
H	-5.159207	-1.142798	-1.404216
H	-5.119256	-0.181980	0.101930

H	-4.553077	0.529568	-1.437947
H	-1.053494	0.047929	3.983099
H	-2.608360	-0.065611	3.121654
H	-1.691008	-1.551237	3.506852
H	-0.400430	5.183278	-0.872921
H	-1.333307	4.811929	0.604138
H	0.349567	4.229915	0.438045
H	-0.882231	-4.552655	-1.078793
H	0.344031	-4.068870	0.127787
H	-1.398805	-3.922640	0.502937

7) Trichloroacetamide

Number of imaginary frequencies = 0

Energy = -1588.001865 Hartree

Atom	**Coordinates (Angstroms)**		
	X	**Y**	**Z**
O	1.566235	1.636424	-0.171372
C	1.302292	0.444927	-0.129187
N	2.202919	-0.549451	-0.124943
C	-0.203325	-0.015110	-0.008041
Cl	-1.290345	1.315912	-0.479427
Cl	-0.498090	-0.452287	1.722962
Cl	-0.546206	-1.451277	-1.049856
H	3.185676	-0.304238	-0.133872
H	1.959108	-1.529827	-0.089725

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