Supporting information

Glycosyl thiocarbamates as complementary building blocks for chemical glycosylation

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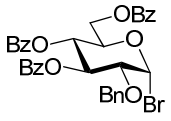
Content:

General remarks.

Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science). The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at < 40 ^{o}C. CH_2Cl_2 and $ClCH_2CH_2Cl$ were distilled from CaH_2 directly prior to application. Methanol was dried by refluxing with magnesium methoxide, distilled and stored under argon. Acetonitrile and pyridine were dried by refluxing with CaH_2 and then distilled and stored over molecular sieves (3 Å). Acetone was dried by refluxing with K_2CO_3 and then distilled and stored over molecular sieves (3 Å). KSCN was dried *in vacuo* at 150 ^{o}C for 24 h. Molecular sieves (3 Å or 4 Å), used for reactions, were crushed and activated *in vacuo* at 390 °C during 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. AgOTf was co-evaporated with toluene (3 x 10 mL) and dried *in vacuo* for 2-3 h directly prior to application. $Cu(OTf)_2$ was dried *in vacuo* for 1-2 h before using for glycosylation. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ at 300 MHz, ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75 MHz (Bruker Avance). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

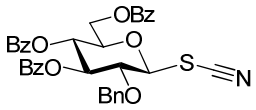
3,4,6-Tri-O-benzoyl-2-O-benzyl-α-D-glucopyranosyl bromide (12).



A solution of acetyl bromide (4 mL, 54.29 mmol) and methanol (2.1 mL, 54.29 mmol) in dichloromethane (25 mL) was added to a solution of 1,3,4,6-tetra-O-benzoyl-2-O-benzyl-D-

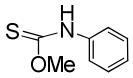
glucopyranose[1] (2.3 g, 3.393 mmol) in dichloromethane (15 mL) at 0 ^{o}C. The resulting reaction mixture was stirred for 2 h at 0 ^{o}C and then washed with water (1 x 15 mL), sat. aq. $NaHCO_3$ (15 mL), and water (3 x 15 mL). The organic layer was separated, dried with $MgSO_4$, concentrated in *vacuo* and dried to afford the title compound in 78% (1.7 g) yield, which was used directly in subsequent synthesis of **1a**. Spectral data of **12** was the same as reported previously.[2]

3,4,6-Tri-O-benzoyl-2-O-benzyl-β-D-glucopyranosyl thiocyanate (1a).



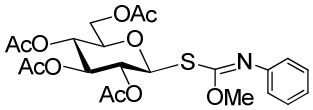
The title compound was obtained in accordance with the method reported previously.[3] 18-Crown-6 (85 mg, 0.3 mmol) and KSCN (312 mg, 3.0 mmol) were added to a stirred solution of bromide **12** (690 mg, 1.0 mmol) in dry acetone (2.6 mL) and the reaction mixture was stirred under argon for 2.5 h at rt. After that, the mixture was diluted with acetone (20 mL), the solid was filtered off, rinsed with acetone (3 x 5 mL) and the combined filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam in 65% (435 mg) yield. Analytical data for **1a**: R_f = 0.48 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{22}$ 21.1^{o} (c = 0.9, $CHCl_3$); ^{1}H n.m.r.: δ, 4.14 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 4.24 (m, 1H, $J_{5,6a}$ = 5.0, $J_{5,6b}$ = 2.9 Hz, H-5), 4.56 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.68 (dd, H-6b), 4.83 (dd, 2H, J^2 = 10.7 Hz, CH_2Ph), 4.94 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1), 5.70 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.93 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 7.27-8.12 (m, 25H, aromatic) ppm; ^{13}C n.m.r.: δ, 62.9, 68.9, 75.4, 75.9, 77.1, 79.1, 84.3, 108.5, 128.5 (x 3), 128.6 (x 2), 128.61 (x 2), 128.7 (x 6), 128.9, 129.6, 129.9 (x 2), 130.0 (x 4), 133.3, 133.6, 136.3, 165.3, 165.6, 166.2 ppm, HR-FAB MS$[M+Na]^+$ calcd for $C_{35}H_{29}NO_8SNa^+$ 646.1512, found 646.1501.

O-Methyl phenylcarbamothioate.



A solution of NaOMe in methanol (1M, 22.2 mL) was added to phenyl isothiocyanate (1.7 mL, 14.7 mmol) and the resulting mixture was stirred for 15 min at rt. After that, conc. HCl was added till the pH ~ 4-5. The resulting white precipitate was filtered off and the filtrate was concentrated *in vacuo*. The crude residue containing the title compound was used directly in subsequent reactions with glycosyl bromides. The analytical data of the title compound were the same as described previously.[4]

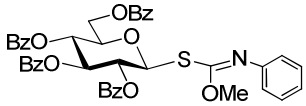
2,3,4,6-Tetra-O-acetyl-1-thio-β-D-glucopyranosyl O-methyl phenylcarbamothioate (13).



O-Methyl phenylcarbamothioate (HSNea, 61 mg, 0.364 mmol) and NaOH (9.7 mg, 0.243 mmol) were added to a stirring solution of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide[5] (100 mg, 0.243 mmol) in dry acetonitrile (1.2 mL) and the resulting reaction mixture was stirred for 1 h at rt. After that, the solid was filtered off and filtrate was washed with sat. aq. $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to afford the title compound as a white foam in 60% (73 mg) yield. Analytical data for **13**: R_f = 0.42 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{25}$ -1.9° (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 1.99, 2.01, 2.03, 2.09 (4s, 12H, 4 x $COCH_3$), 3.77 (m, 1H, $J_{5,6a}$ = 2.3 Hz, $J_{5,6b}$ = 4.7 Hz, H-5), 4.01 (s, 3H, OCH_3), 4.14 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.25 (dd, 1H, H-6b), 4.99 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 5.07 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.22 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 5.24 (dd, 1H,

$J_{1,2}$ = 10.4 Hz, H-1), 6.83-7.27 (m, 5H, aromatic) ppm; ^{13}C n.m.r.: δ, 20.7 (x 3), 20.9, 56.8, 62.2, 68.2, 69.9, 74.1, 76.3, 81.4, 121.5 (x 2), 124.4, 129.3 (x 2), 146.3, 154.5, 169.3, 169.5, 170.4, 170.8 ppm; HR-FAB MS[M+Na]$^+$ calcd for $C_{22}H_{27}NO_{10}SNa^+$ 520.1253, found 520.1263.

2,3,4,6-Tetra-O-benzoyl-1-thio-β-D-glucopyranosyl O-methyl phenylcarbamothioate (4c).

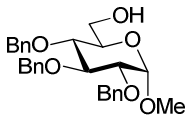


A solution of NaOMe in methanol (1M, ~0.1 mL) was added dropwise to a solution of thiocarbamate **12** (72 mg, 0.145 mmol) in methanol (1.0 mL) till pH ~ 9 and the resulting reaction mixture was kept for 1 h at rt. After that, Dowex (H^+) was added till pH ~ 7, the resin was filtered off and washed successively with methanol (5 x 5 mL). The combined filtrate was concentrated *in vacuo* and dried. The residue was dissolved in pyridine (1 mL) and benzoyl chloride (0.1 mL, 0.87 mmol) was added dropwise at 0 ^{o}C under argon. The external cooling was removed, the reaction mixture was allowed to warm to rt and stirred for 4 h total. After that, methanol (1 mL) was added, the volatiles were evaporated *in vacuo*, and the residue was co-evaporated with toluene (3 x 5 mL). The resulting residue was diluted with dichloromethane (100 mL) and washed with 1N aq. HCl (25 mL), water (25 mL), sat. aq. $NaHCO_3$ (25 mL), and water (3 x 25 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate - toluene gradient elution) to afford the title compound as a white foam in 83% (90 mg) yield. Analytical data for **4c**: R_f = 0.37 (ethyl acetate/toluene, 1.5/8.5, v/v); $[\alpha]_D^{21}$ 0.35^o (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 3.90 (s, 3H, OCH_3), 4.25 (m, 1H, $J_{5,6a}$ = 5.7 Hz, $J_{5,6b}$ = 2.9 Hz, H-5), 4.49 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.64 (dd, 1H, H-6b), 5.54 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 5.62 (d, 1H, $J_{1,2}$ = 10.2 Hz, H-1), 5.64 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.95 (dd, $J_{3,4}$ = 9.2 Hz, H-3), 6.72-8.06 (m, 25H, aromatic)

ppm; ^{13}C-n.m.r.: δ, 56.8, 63.4, 69.6, 70.6, 74.3, 77.4, 81.9, 121.5 (x 2), 124.2, 128.5 (x 2), 128.6 (x 6), 128.7 (x 2), 128.9 (x 2), 129.1, 129.2 (x 2), 129.8, 129.9 (x 3), 130.0 (x 3), 133.4, 133.5, 133.6, 133.7, 146.3, 154.5, 165.1, 165.4, 165.9, 166.3 ppm; HR-FAB MS[M+Na]$^+$ calcd for $C_{42}H_{35}NO_{10}SNa^+$ 768.1879, found 768.1896.

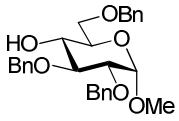
Characterization data for glycosyl acceptors 2, 5-7

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**).[6]



Analytical data for **2**: ^{1}H n.m.r.: δ, 3.33 (s, 3H, OCH_3), 3.45-3.52 (m, 2H, H-2, 4), 3.59-3.76 (m, 3H, H-5, 6a, 6b), 3.98 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.53 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.70 (dd, 2H, J^2 = 12.1 Hz, C*H*$_2$Ph), 4.73 (dd, 2H, J^2 = 11.0 Hz, C*H*$_2$Ph), 4.89 (dd, 2H, J^2 = 10.9 Hz, C*H*$_2$Ph), 7.21-7.34 (m, 15H, aromatic) ppm; ^{13}C n.m.r.: δ, 55.12, 61.76, 70.55, 73.33, 74.93, 77.24, 79.82, 81.83, 98.01, 127.42, 127.68, 127.74, 127.76 (x 3), 127.83 (x 2), 127.92 (x 2), 128.20 (x 2), 128.27 (x 4), 137.87, 138.48 ppm.

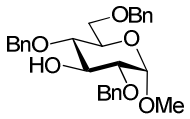
Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (5).[7]



Analytical data for **5**: ^{1}H n.m.r.: δ, 3.34 (s, 3H, OCH_3), 3.52 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 3.56-3.69 (m, 4H, H-4, 5, 6a, 6b), 3.74 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 4.52 (dd, 2H, J^2 = 12.2 Hz, CH_2Ph), 4.59 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.63 (dd, 2H, J^2 = 12.4 Hz, C*H*$_2$Ph), 4.84 (dd, 2H, J^2 = 11.4 Hz, C*H*$_2$Ph), 7.22-7.22 (m, 15H, aromatic) ppm; ^{13}C n.m.r.: δ, 55.36, 69.57, 70.02, 70.80,

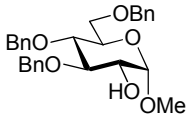
73.28, 73.69, 75.55, 79.71, 81.59, 98.32, 127.80 (x 3), 128.02, 128.14, 128.18 (x 2), 128.31 (x 2), 128.54 (x 2), 128.66 (x 2), 128.77 (x 2), 138.19, 138.24, 138.99 ppm.

Methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (6).[8]



Analytical data for **6**: R_f = 0.35 (ethyl acetate/toluene, 2/8, v/v); $[\alpha]_D^{27}$ +36° (c = 1, $CHCl_3$); ^{1}H n.m.r.: δ, 3.29 (s, 3H, OCH_3), 3.36 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 3.51 (dd, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.58-3.7 (m, 3H, H-5, 6a, 6b), 4.02 (dd, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 4.50 (dd, 2H, J^2 = 12.1 Hz, C*H*$_2$Ph), 4.61 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.62 (dd, 2H, J^2 = 11.1 Hz, C*H*$_2$Ph), 4.64 (dd, 2H, J^2 = 12.1 Hz, C*H*$_2$Ph), 7.15-7.33 (m, 15H, aromatic) ppm; ^{13}C n.m.r.: δ, 55.21, 68.51, 69.65, 73.11, 73.54, 73.63, 74.60, 77.29, 79.51, 97.60, 127.73, 127.76, 127.91 (x 2), 127.99 (x 2), 128.13, 128.17 (x 2), 128.42 (x 4), 128.61 (x 2), 137.94, 138.01, 138.45 ppm.

Methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7).[9]



Analytical data for **7**: ^{1}H n.m.r.: δ, 3.43 (s, 3H, OCH_3), 3.62-3.80 (m, 6H, H-2, 3, 4, 5, 6a, 6b), 4.58 (dd, 2H, J^2 = 12.1 Hz, C*H*$_2$Ph), 4.67 (dd, J^2 = 10.8 Hz, ½ C*H*$_2$Ph), 4.81 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 4.88 (m, 2H, J^2 = 11.2 Hz, C*H*$_2$Ph), 7.14-7.30 (m, 15H, aromatic) ppm. ^{13}C n.m.r.: δ, 55.32, 68.60, 70.54, 73.03, 73.64, 75.48, 77.60, 83.38, 99.53, 127.84, 127.97 (x 2), 128.03 (x 5), 128.51 (x 4), 128.57 (x 3), 138.05, 138.30, 138.79 ppm.

General procedures for glycosylation

In the presence of MeOTf (Method A). A mixture of a glycosyl donor (0.04 mmol), glycosyl acceptor (0.032 mmol), and freshly activated molecular sieves (3 Å, 90 mg) in 1,2-dichloroethane (0.5 mL) was stirred under argon at rt for 1.5 h. MeOTf (10 μL, 0.08 mmol) was added and the reaction mixture was stirred at rt for 22-48 h. After that, the solid was filtered off and the filtrate was washed successively with sat. aq. $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to afford the corresponding disaccharide.

In the presence of AgOTf (Method B): A mixture of glycosyl donor (0.04 mmol), glycosyl acceptor (0.032 mmol), and freshly activated molecular sieves (3 Å, 90 mg) in 1,2-dichloroethane (0.5 mL) was stirred under argon for 1.5 h. AgOTf (12.3 mg, 0.048 mmol) was added and the reaction mixture was stirred for 24 h. Upon completion, the solid was filtered off and the filtrate was washed with $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate-toluene gradient elution) to afford the corresponding oligosaccharide.

In the presence of $AgBF_4$ (Method C): A mixture of glycosyl donor (0.04 mmol), glycosyl acceptor (0.032 mmol), and freshly activated molecular sieves (3 Å, 90 mg) in 1,2-dichloroethane (0.5 mL) was stirred under argon for 1.5 h. $AgBF_4$ (9.3 mg, 0.048 mmol) was added and the reaction mixture was stirred for 5 min - 24 h. Upon completion, the solid was filtered off and the filtrate was washed with $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by

silica gel column chromatography (ethyl acetate-toluene gradient elution) to afford the corresponding oligosaccharide.

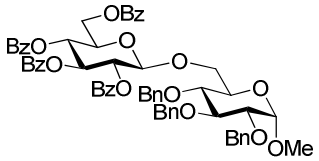
In the presence of $Cu(OTf)_2$ (Method D): A mixture of glycosyl donor (0.04 mmol), glycosyl acceptor (0.032 mmol), and freshly activated molecular sieves (4 Å, 90 mg) in 1,2-dichloroethane (0.5 mL) was stirred under argon for 1.5 h. $Cu(OTf)_2$ (17 mg, 0.048 mmol) was added and the reaction mixture was stirred for 10 min - 24 h. Upon completion, the solid was filtered off and the filtrate was washed with $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate-toluene gradient elution) to afford the corresponding disaccharide.

General Procedure for Competitive Glycosylations

A mixture of glycosyl donor **4b** (47 mg, 0.0645 mmol), glycosyl donor **4c** (48 mg, 0.0645 mmol), glycosyl acceptor **2** (20 mg, 0.043 mmol), and freshly activated molecular sieves (4 Å for $Cu(OTf)_2$ or 3 Å for MeOTf-promoted reactions, 140 mg) in 1,2-dichloroethane (1 mL) was stirred under argon at rt for 1h. $Cu(OTf)_2$ (28 mg, 0.0774 mmol) or MeOTf (16 μL, 0.129 mmol) was added and the resulting reaction mixture was stirred at rt. The reaction was monitored by TLC (ethyl acetate / toluene, 1/4, v/v); upon disappearance of the glycosyl acceptor **2** (1-1.5 h), the solid was filtered off, rinsed with CH_2Cl_2 (3 x 5 mL), and the combined filtrate was washed with sat. aq. $NaHCO_3$ (5 mL) and water (3 x 5 mL). The organic layer was separated, dried with $MgSO_4$, filtered and concentrated *in vacuo.* The residue was purified by column chromatography on silica gel (ethyl acetate – hexanes gradient elution) to afford disaccharide **8** in 88-97% yield and unreacted glycosyl donors.

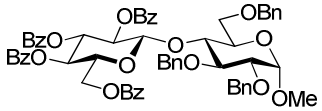
Characterization data for disaccharides 8-11

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (8).[10]



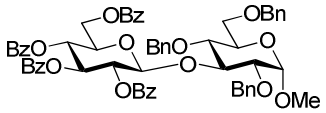
The title compound was synthesized by method D from glycosyl donor **4c** (30 mg, 0.04 mmol) and glycosyl acceptor **2** (15 mg, 0.032 mmol) in 90% (30 mg) yield. Analytical data for **8** was in agreement with that reported previously.[10]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (9).[10]



The title compound was synthesized by method D from glycosyl donor **4c** (30 mg, 0.04 mmol) and glycosyl acceptor **5** (15 mg, 0.032 mmol) in 78% (26 mg) yield. Analytical data for **9** was in agreement with that reported previously.[10]

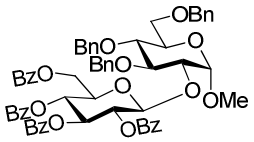
Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (10).



The title compound was synthesized by method D from glycosyl donor **4c** (30 mg, 0.04 mmol) and glycosyl acceptor **6** (15 mg, 0.032 mmol) in 74% (25 mg) yield. Analytical data for **10**: R_f =

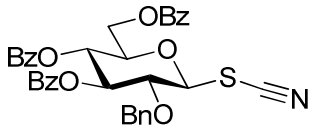
0.4 (ethyl acetate / toluene, 1/5, v/v), $[\alpha]_D^{27}$ -12.8^o (c = 1, $CHCl_3$), ^{1}H-n.m.r.: δ, 3.15 (s, 3H, OCH_3), 3.25 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.44-3.58 (m, 4H, H-4, 5, 6a, 6b), 4.03-4.07 (m, 1H, H-5'), 4.19 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.28 (dd, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 4.30 (dd, 2H, J^2 = 12.2 Hz, C*H*$_2$Ph), 4.30-4.50 (m, 2H, H-6a', 6b'), 4.70 (dd, 2H, J^2 = 10.8 Hz, C*H*$_2$Ph), 5.43 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 5.57 (dd, 1H, $J_{2',3'}$ = 9.7 Hz, H-2'), 5.63 (dd, 1H, $J_{4',5'}$ = 9.7 Hz, H-4'), 5.86 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 7.0-7.94 (m, 35H, aromatic) ppm; ^{13}C n.m.r.: δ, 55.19, 63,46, 68.59, 69.71, 70.05, 72.08, 72.68, 73.32, 73.66, 74.01, 75.07, 75.58, 79.51, 80.97, 97.84, 101.19, 127.62, 127.88, 128.07 (x 2), 128.14 (x 2), 128.25 (x 4), 128.29 (x 2), 128.38 (x 2), 128.46 (x 2), 128.54 (x 4), 128.64 (x 2), 128.67 (x 2), 128.99, 129.57, 129.79, 129.89 (x 2), 129.99 (x 4), 130.03 (x 2), 133.07, 133.39, 133.46, 133.54, 138.04, 138.11, 138.66, 165.34, 165.43, 166.02, 166.28 ppm; HR-FAB MS$[M+Na]^+$ calcd for $C_{62}H_{58}O_{15}Na^+$ 1065.3673, found 1065.3673.

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (11).[11]

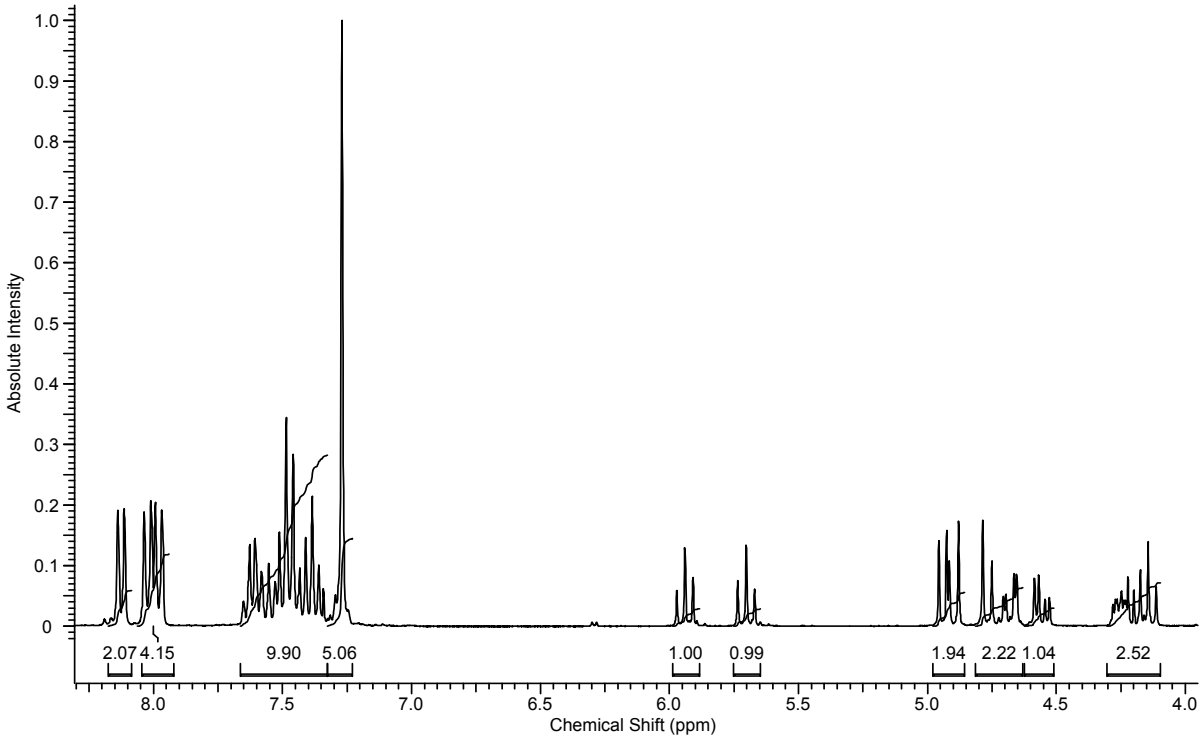


The title compound was synthesized by method D from glycosyl donor **4c** (30 mg, 0.04 mmol) and glycosyl acceptor **7** (15 mg, 0.032 mmol) in 75% (25 mg) yield. Analytical data for **11** was in agreement with that reported previously.[11]

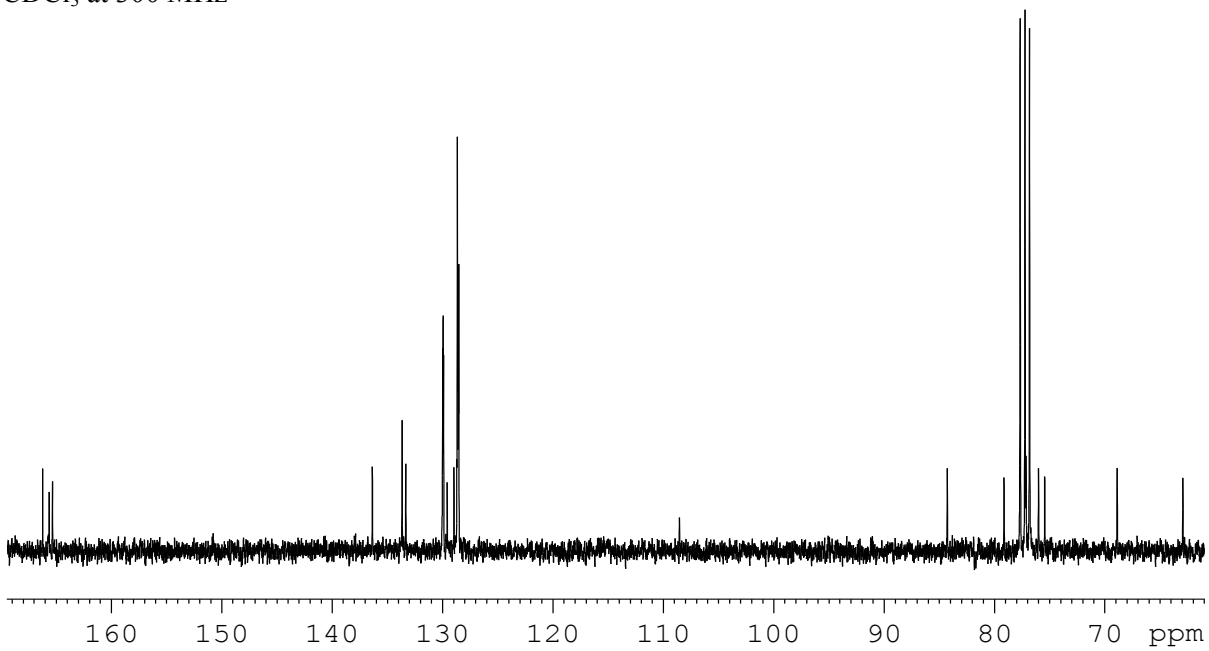
NMR spectra



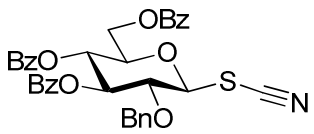
1a



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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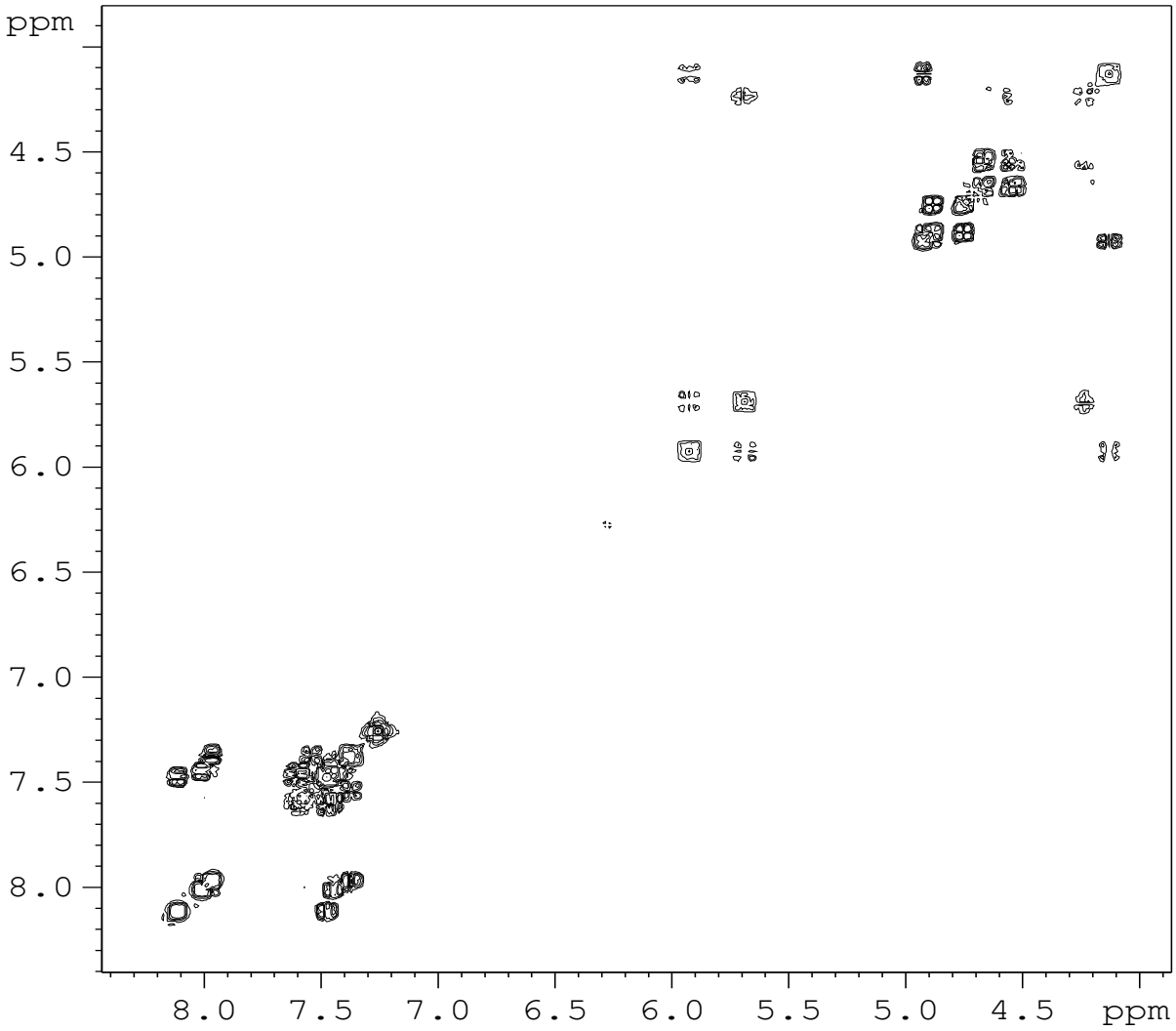

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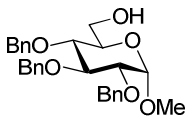

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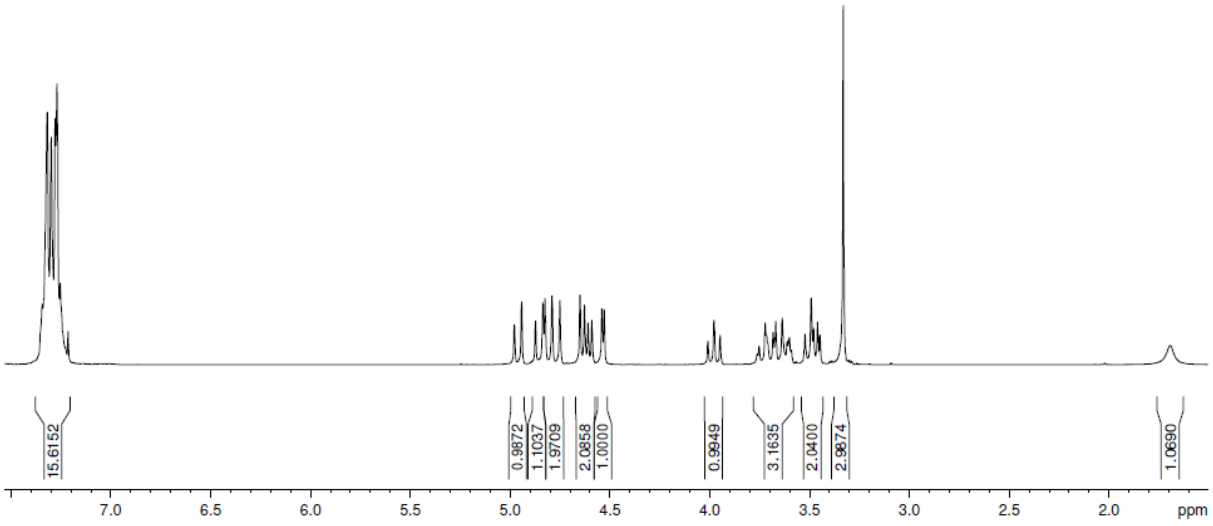
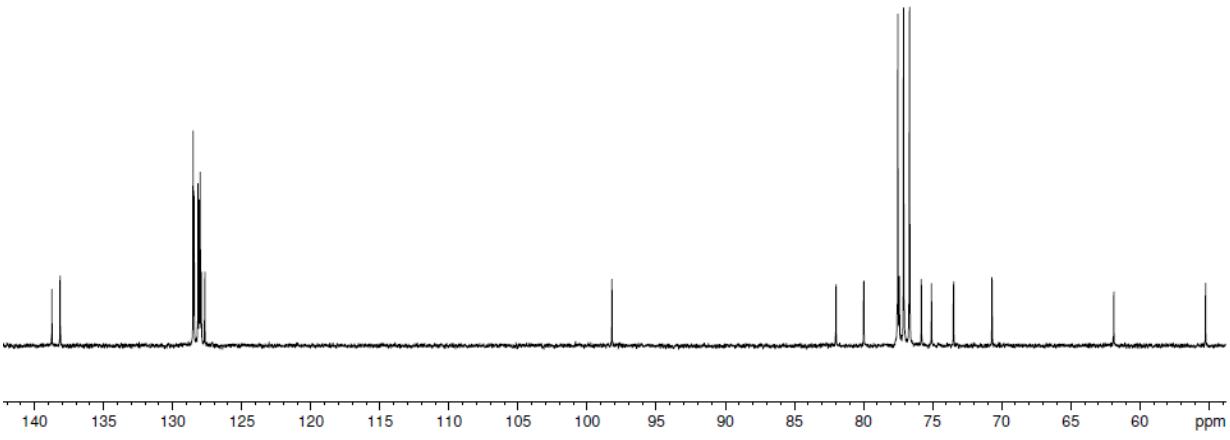
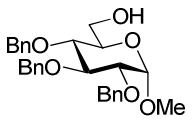


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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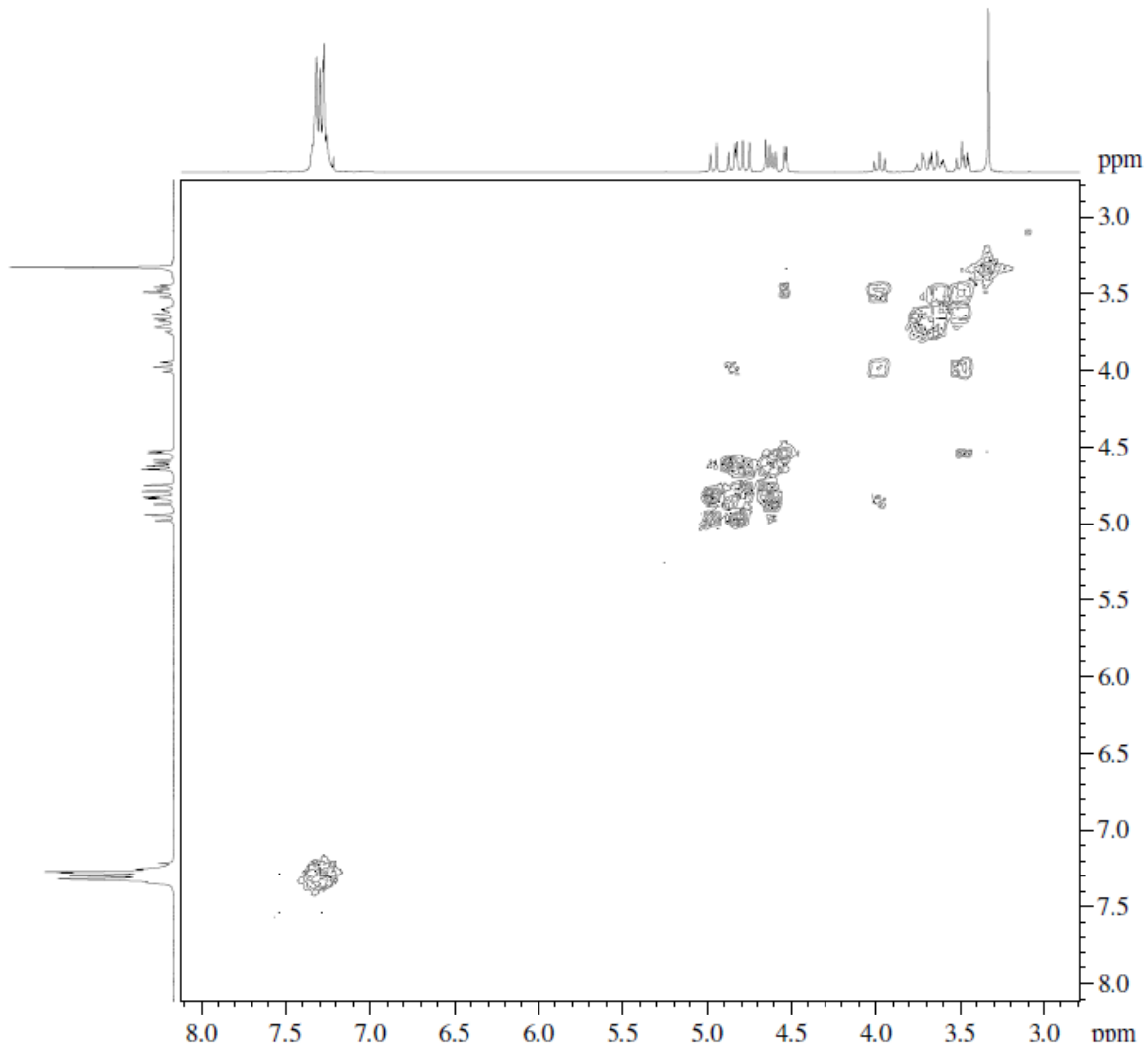
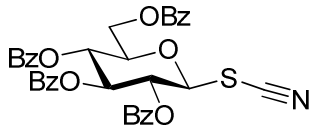
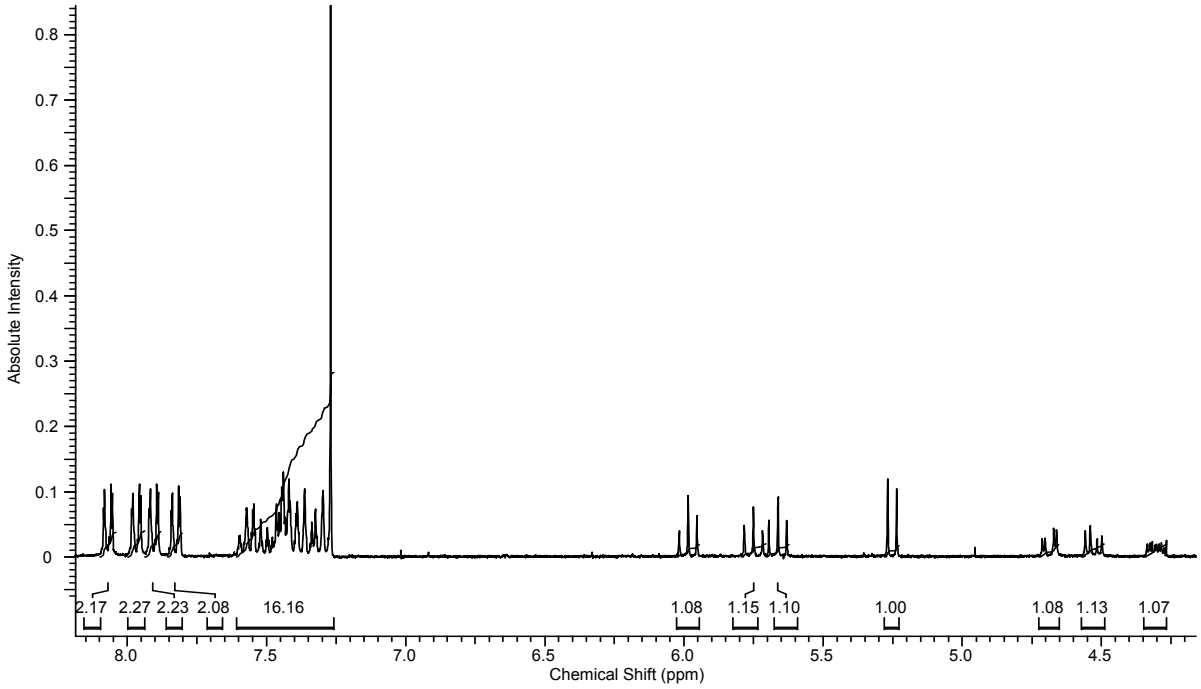


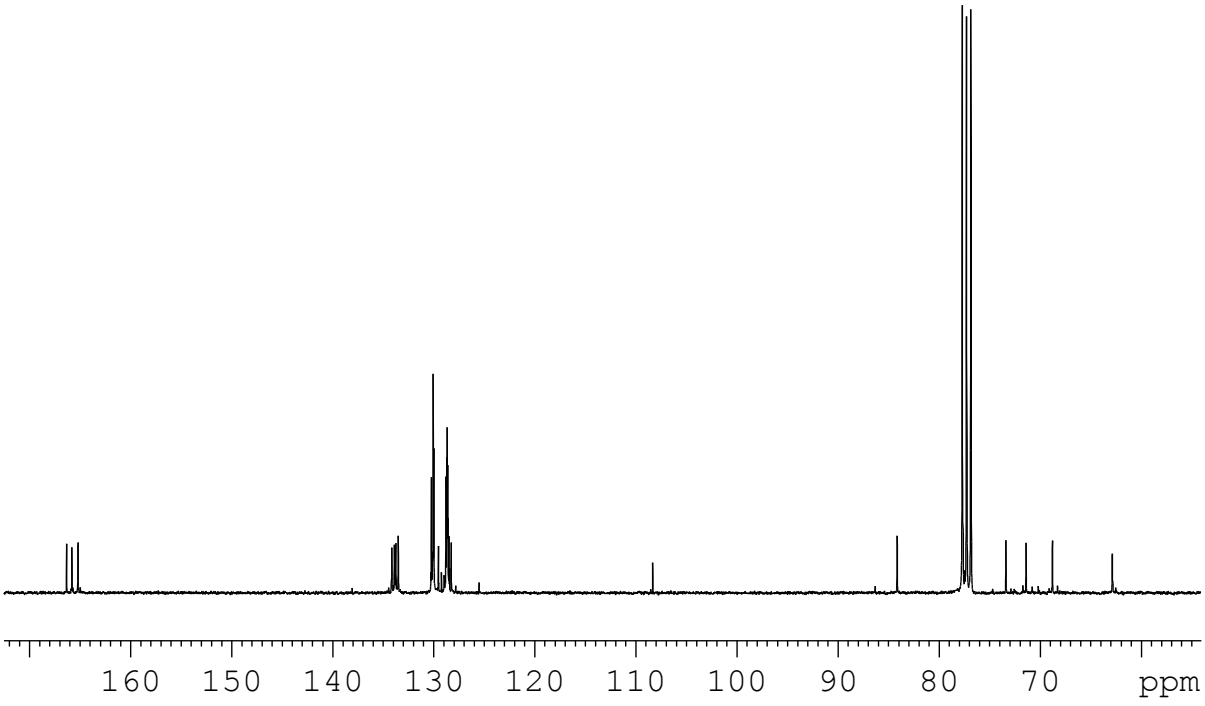
$CDCl_3$ at 300 MHz



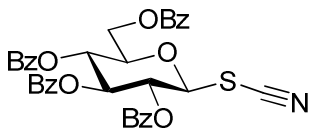
4a



CDCl3 at 300 MHz



CDCl3 at 300 MHz



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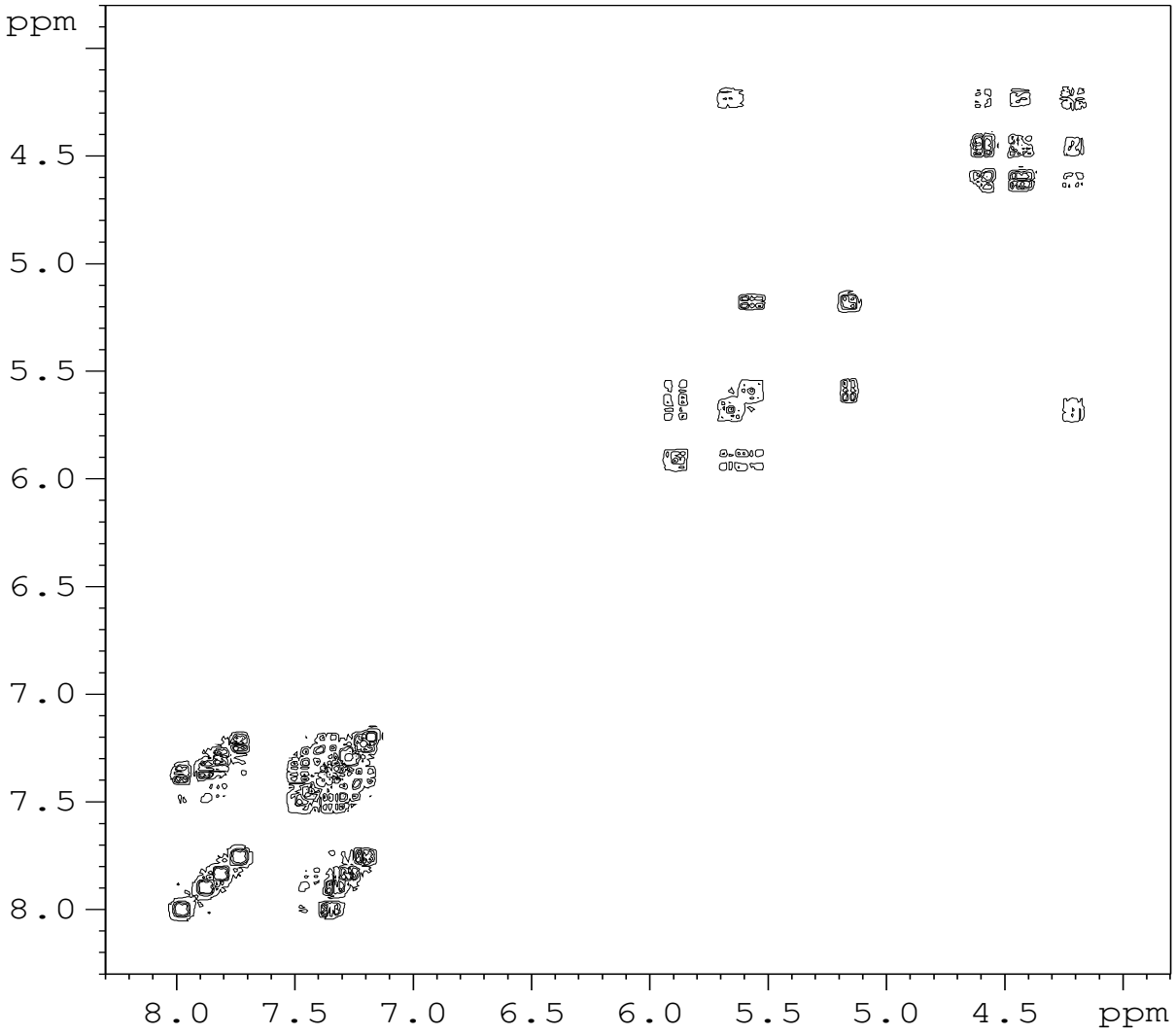
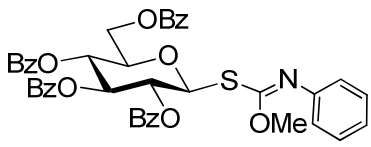


$CDCl_3$ at 300 MHz



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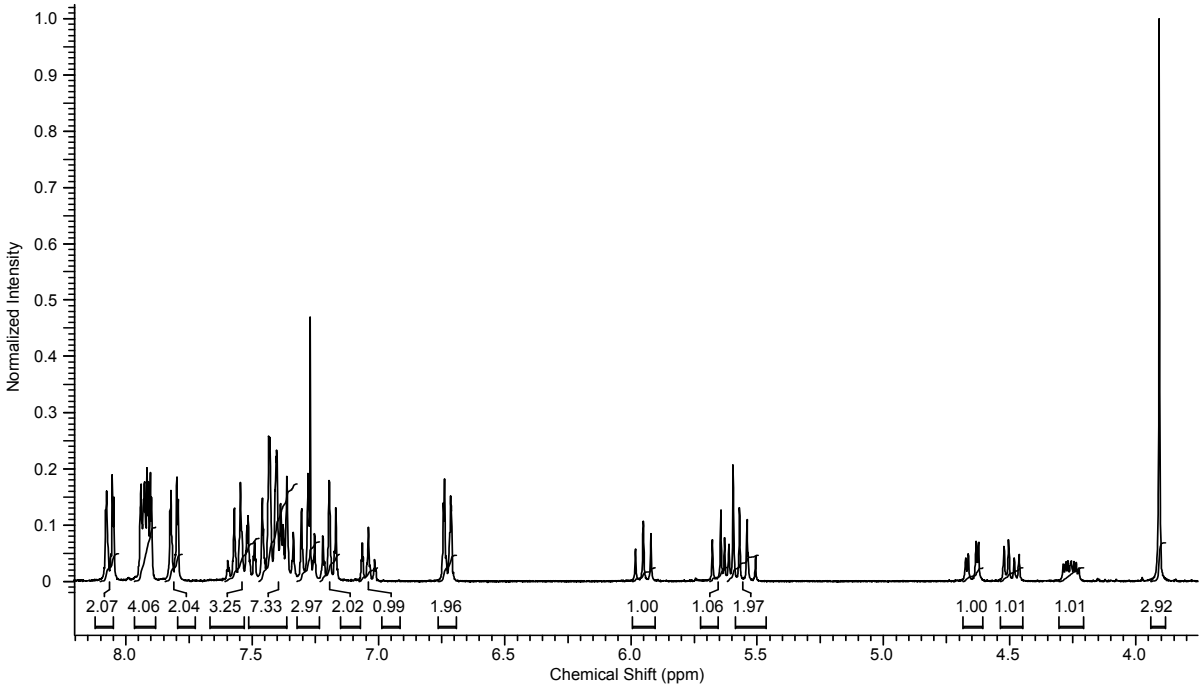
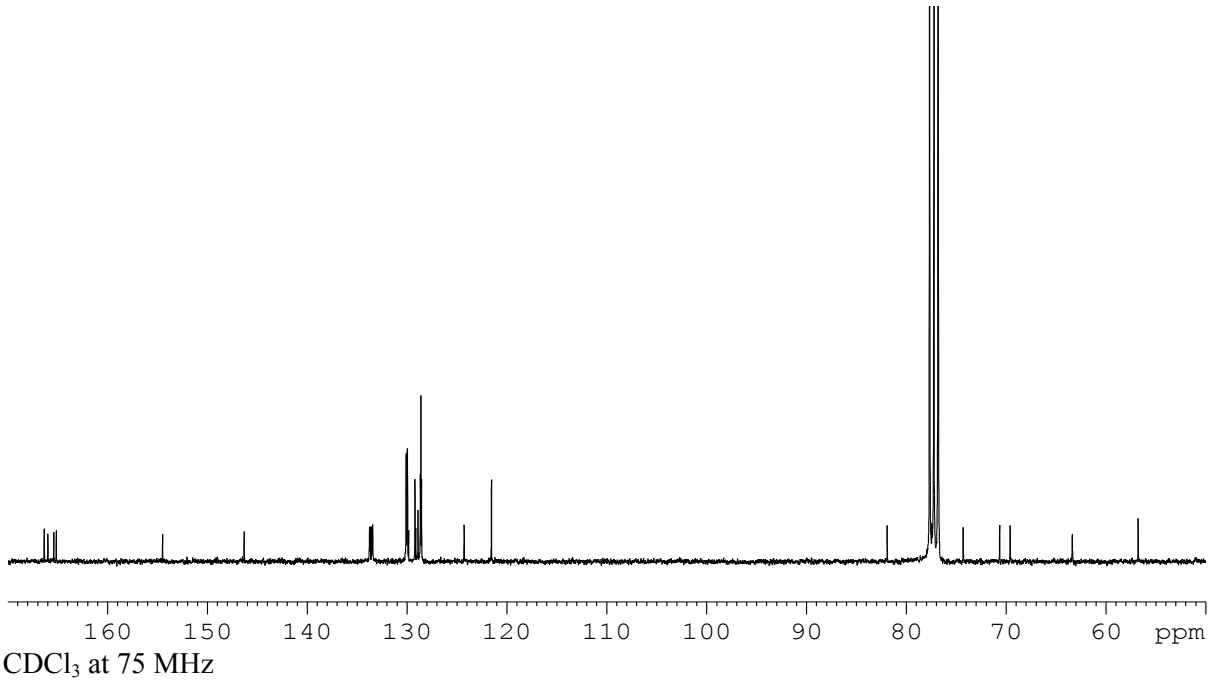
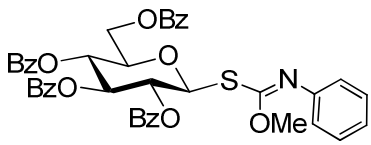


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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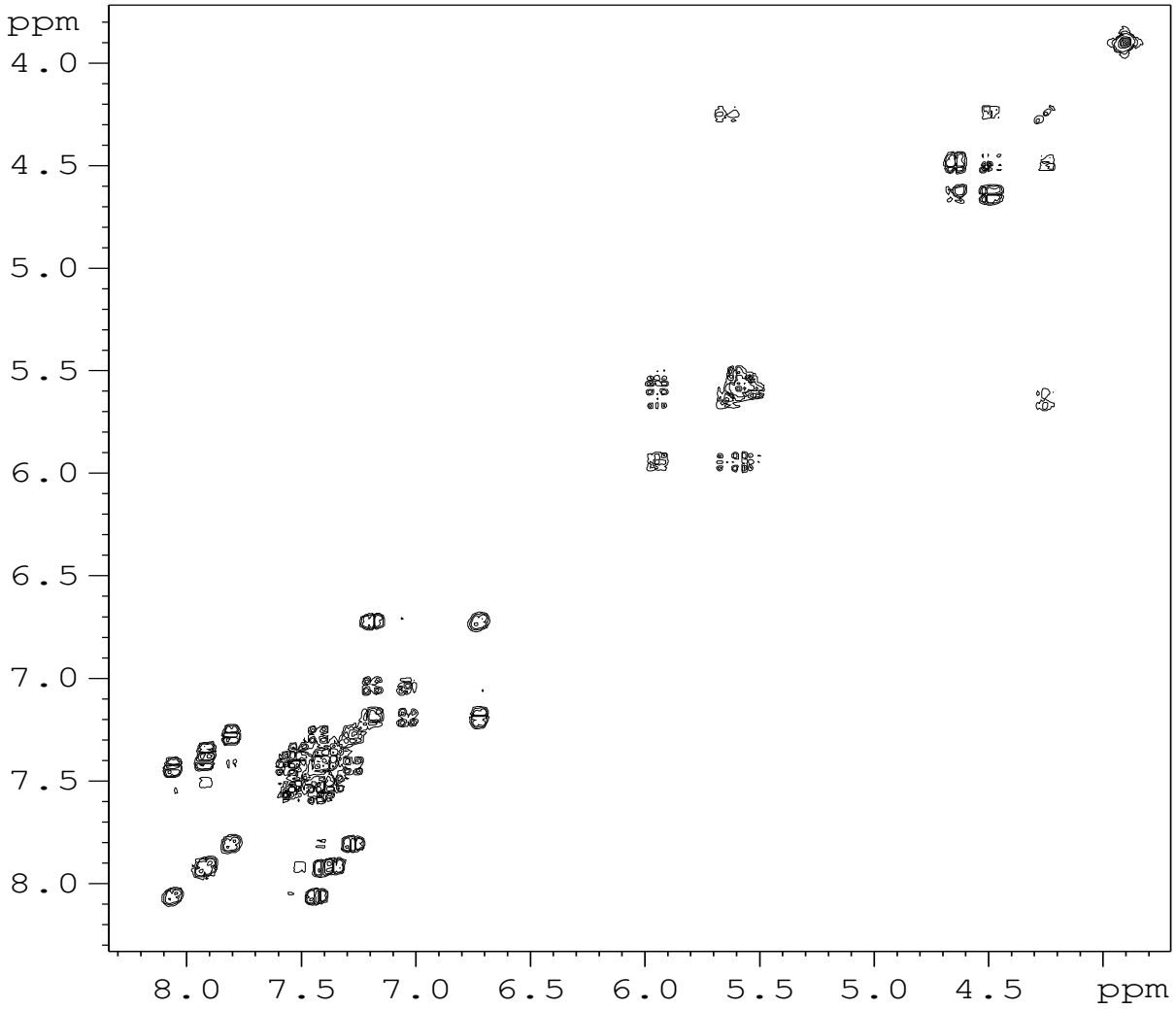

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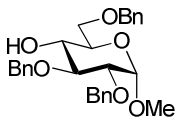

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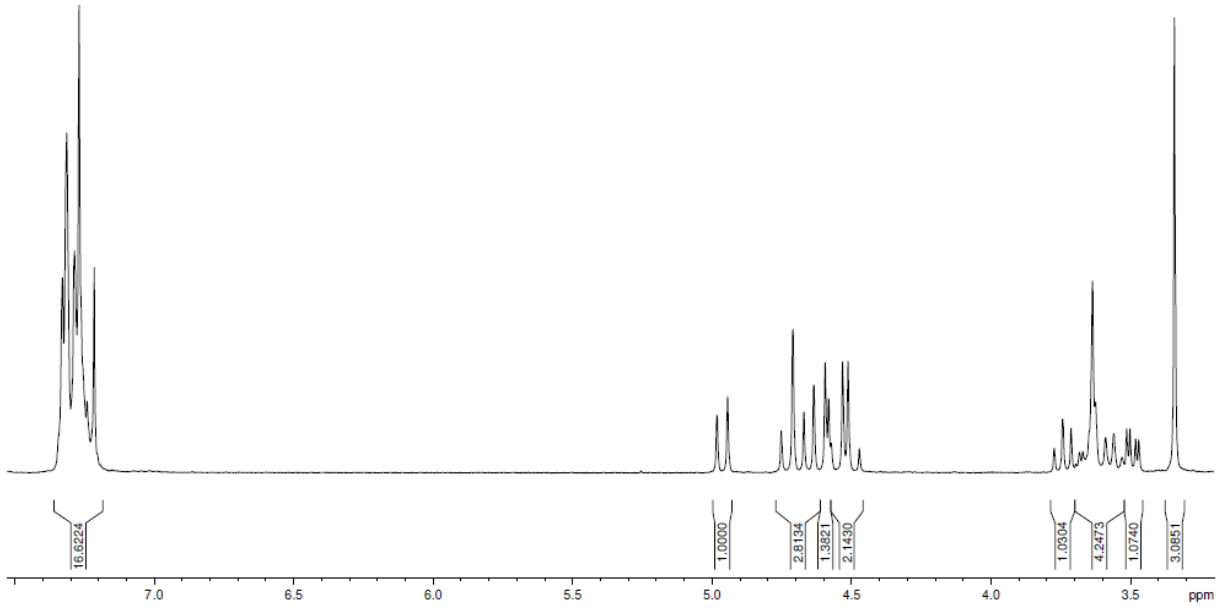

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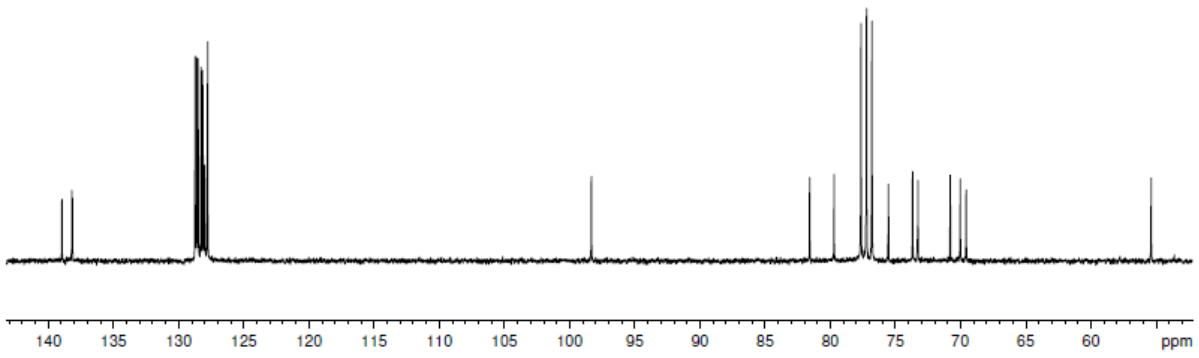

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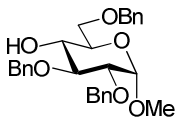

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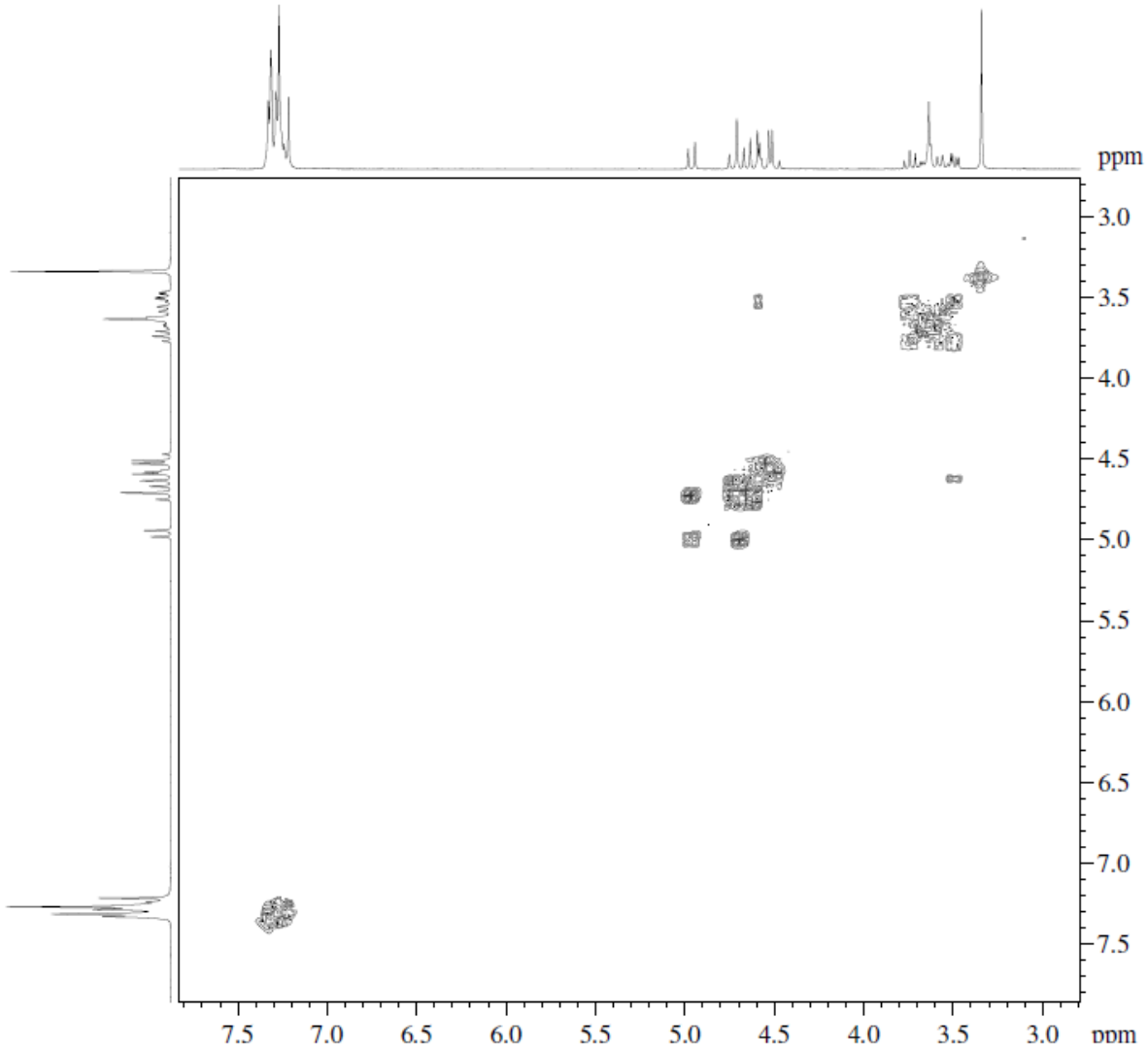

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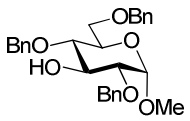

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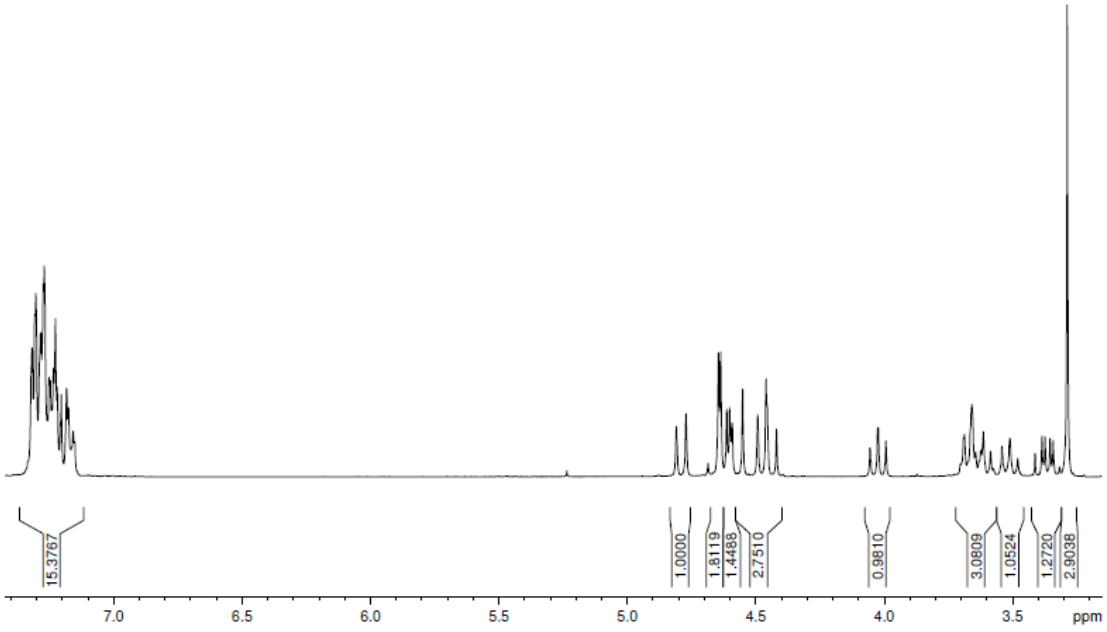

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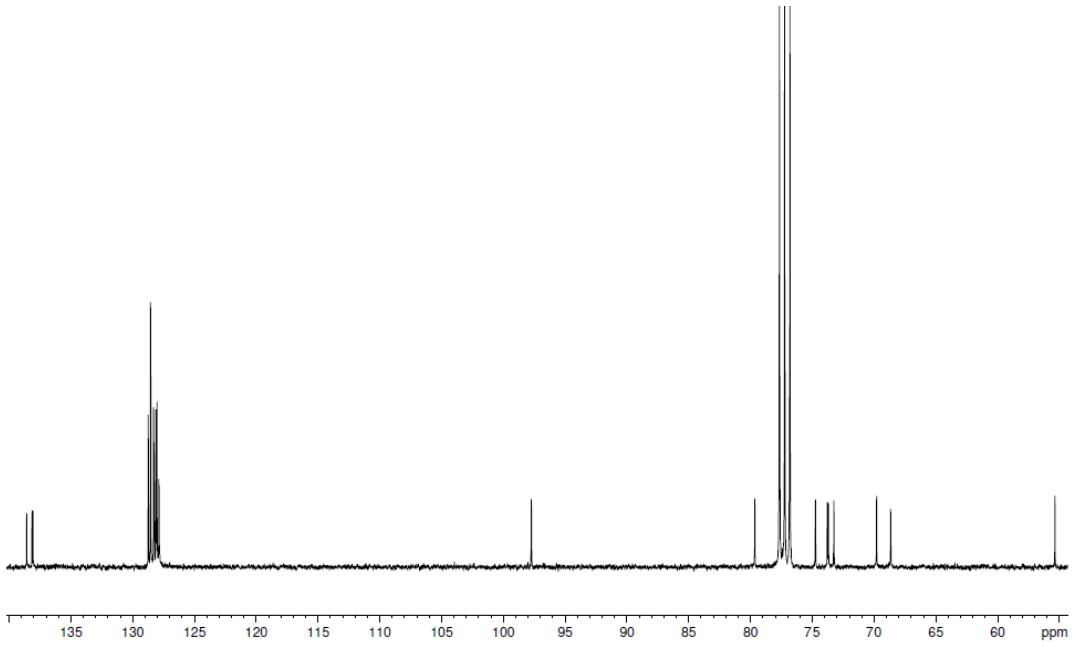

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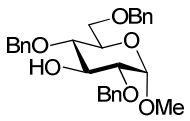

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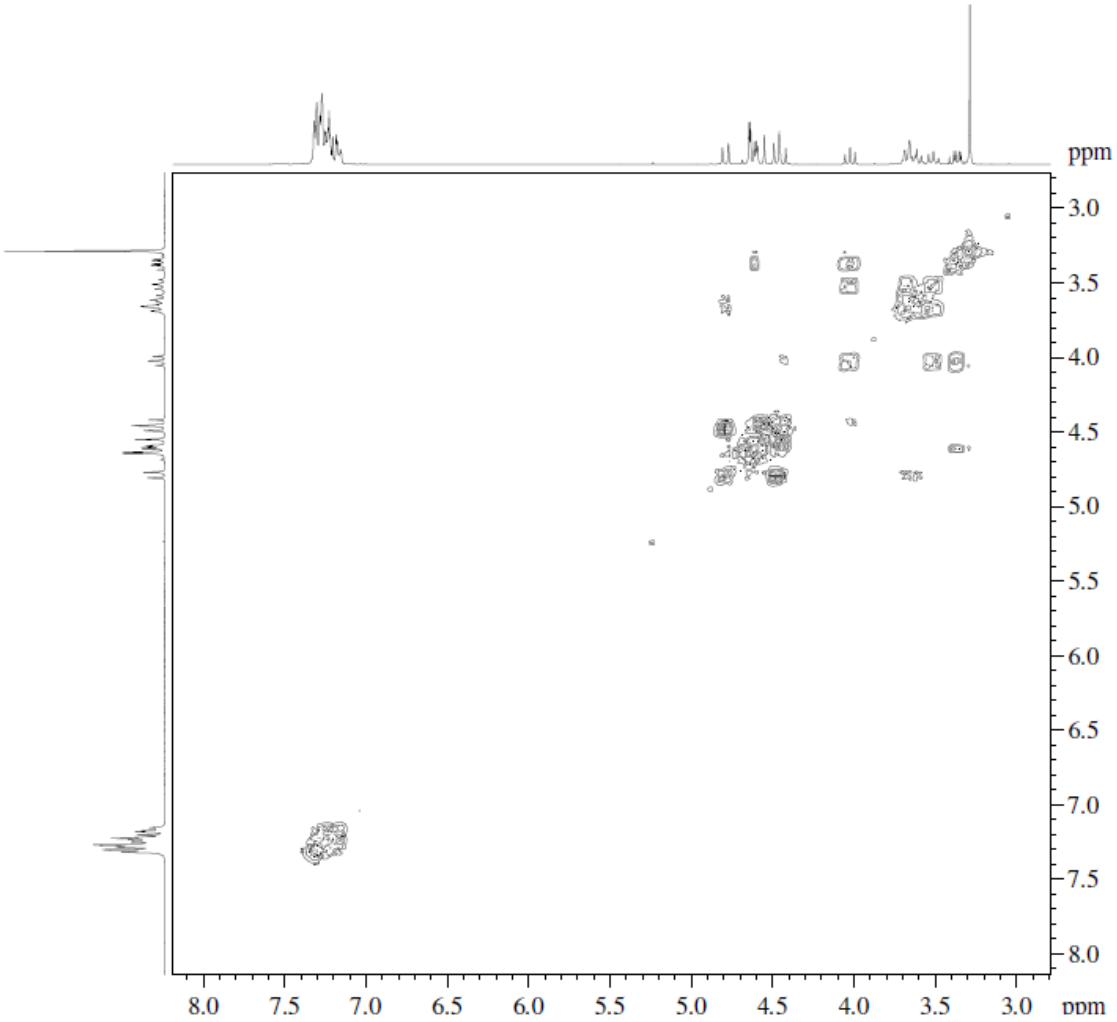
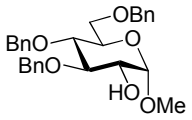


CDCl3 at 300 MHz



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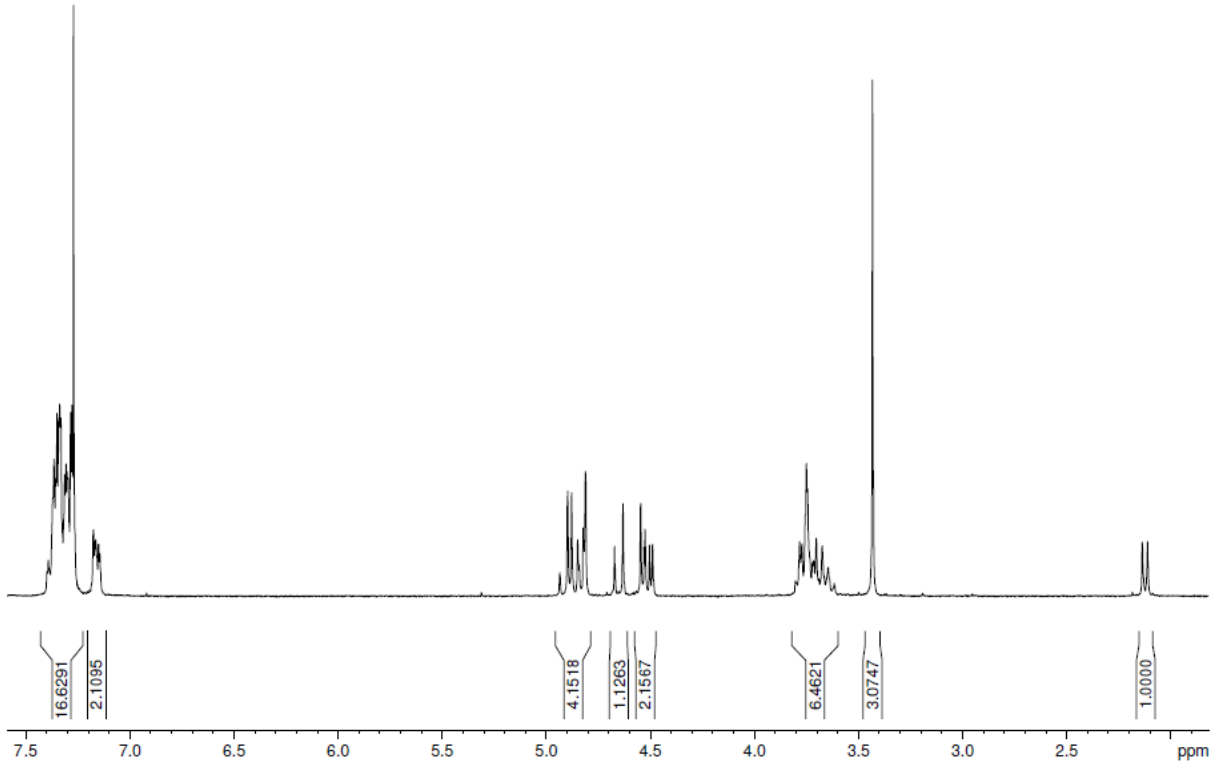
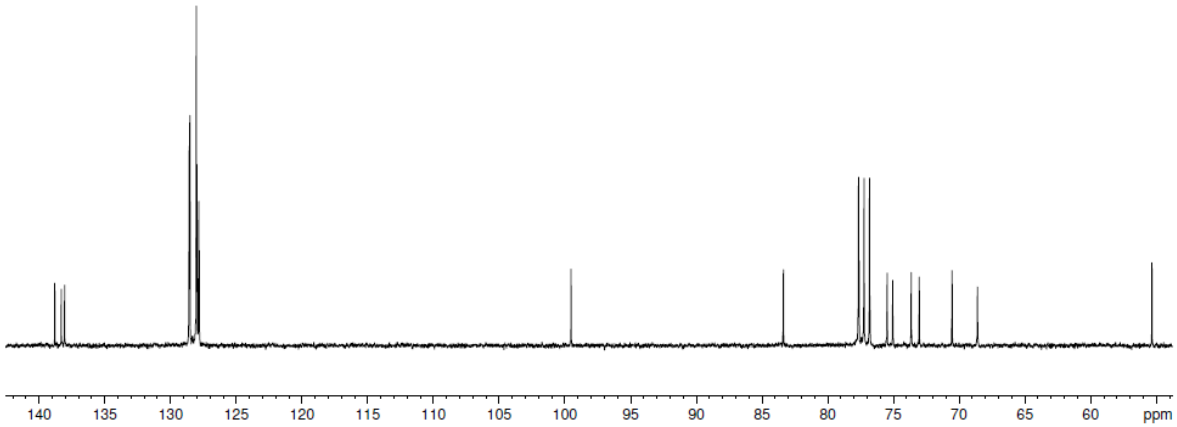
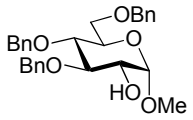


$CDCl_3$ at 300 MHz



CDCl3 at 75 MHz



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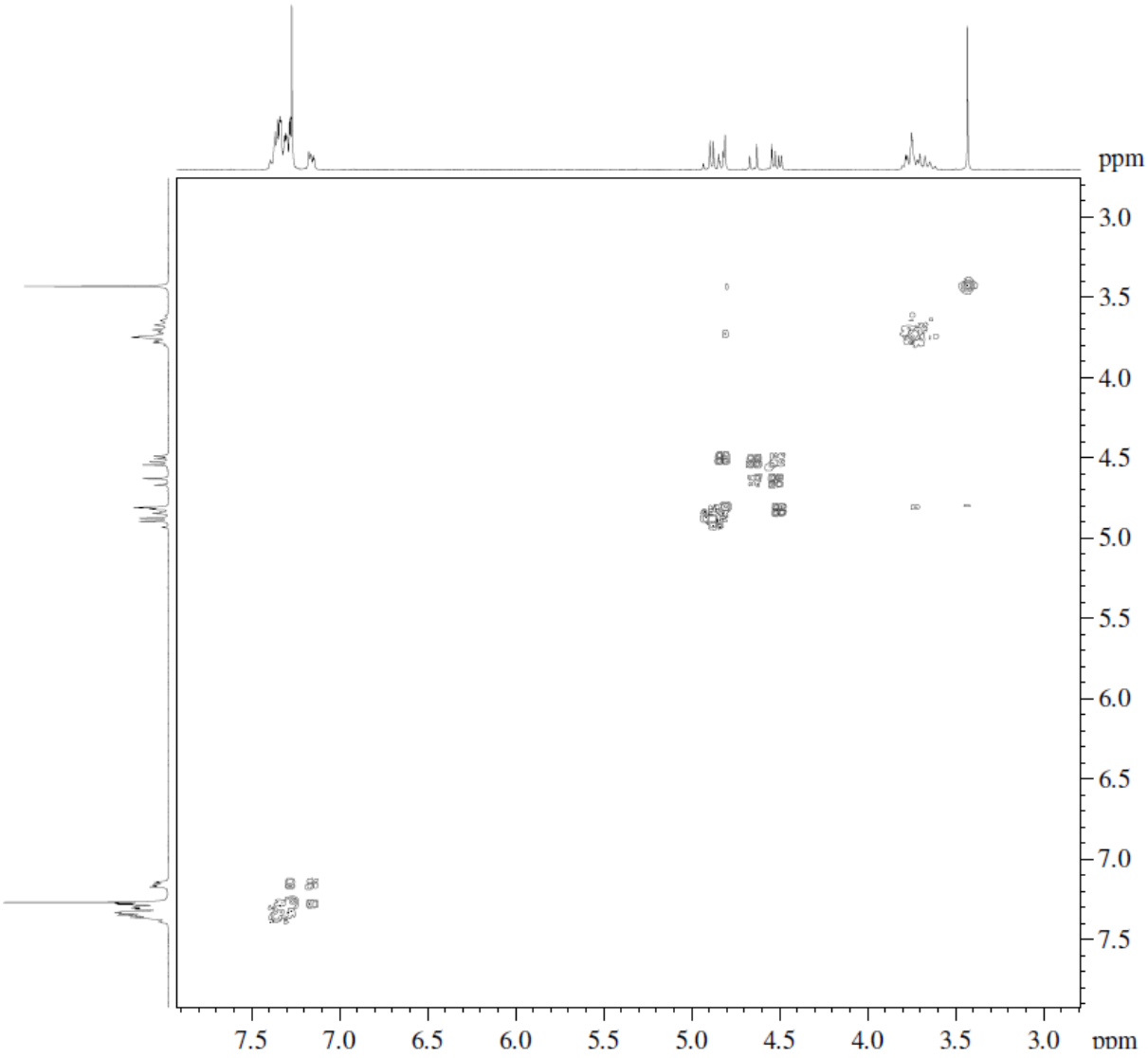
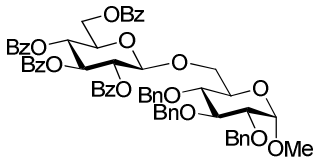


CDCl3 at 300 MHz



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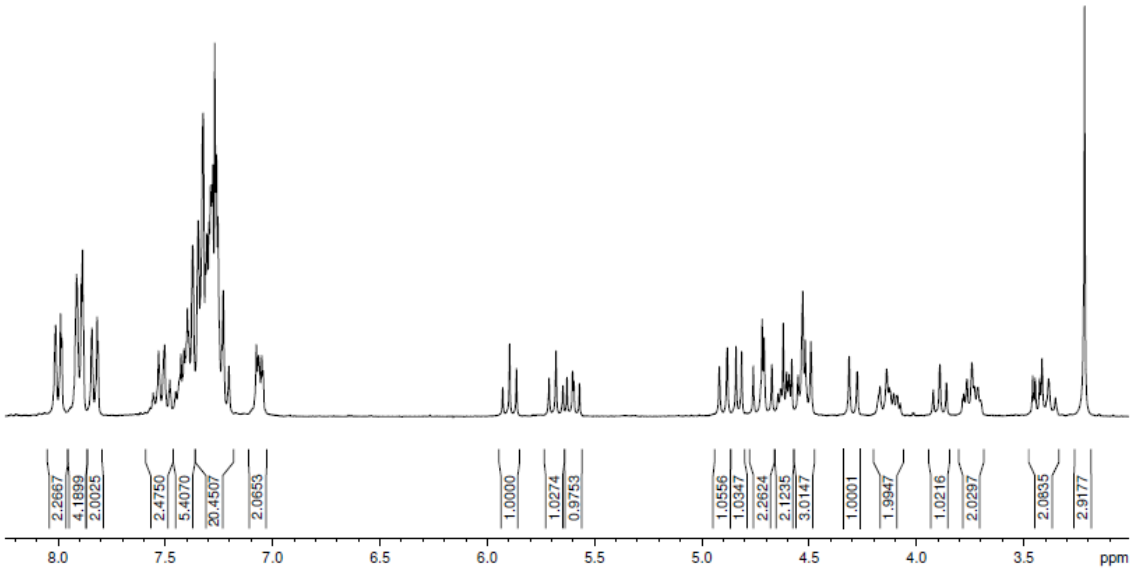
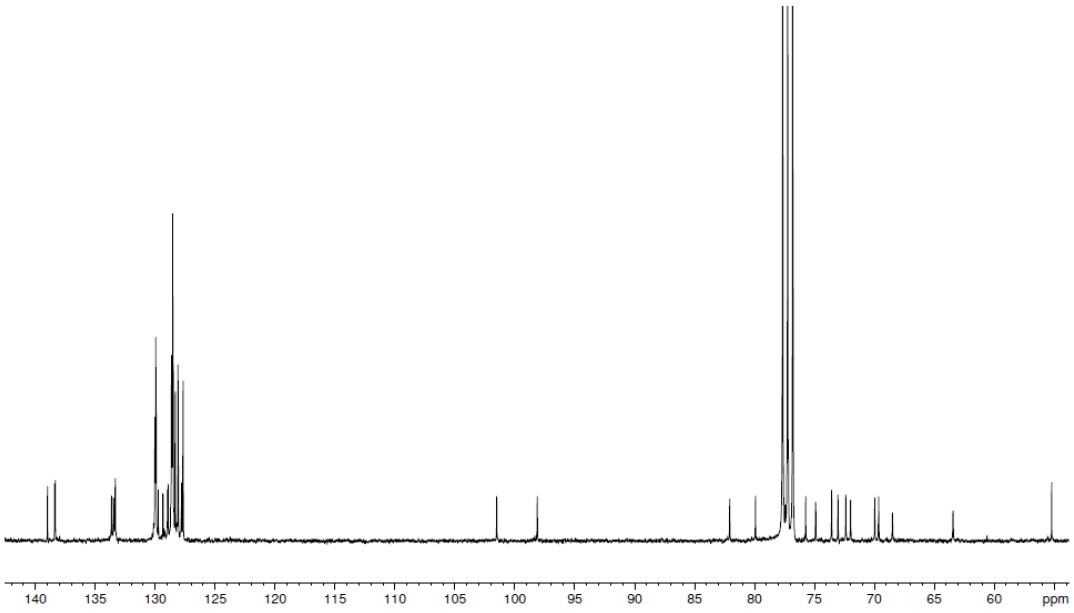


$CDCl_3$ at 300 MHz



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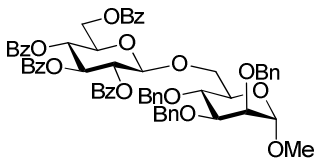

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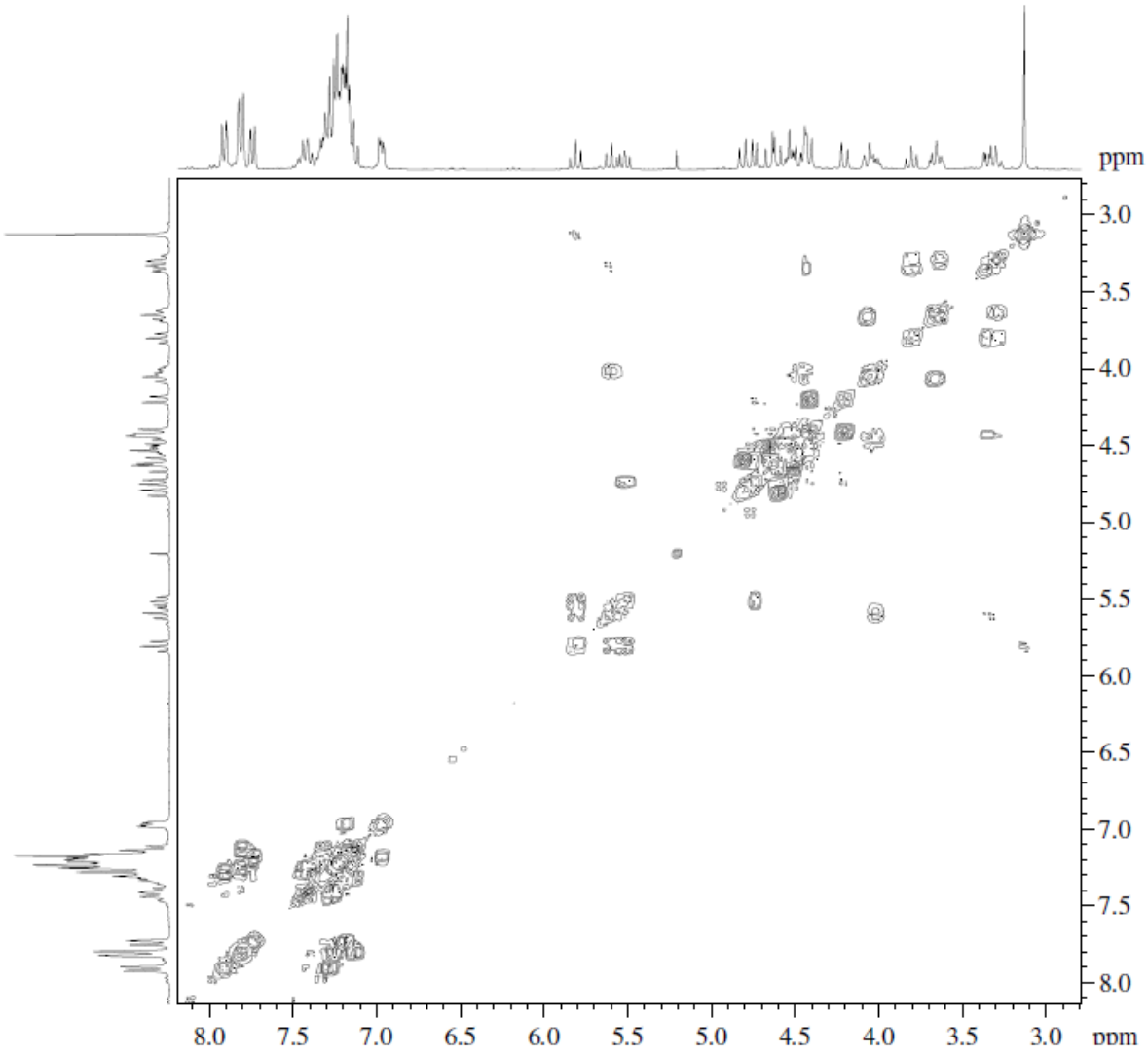

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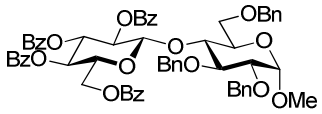

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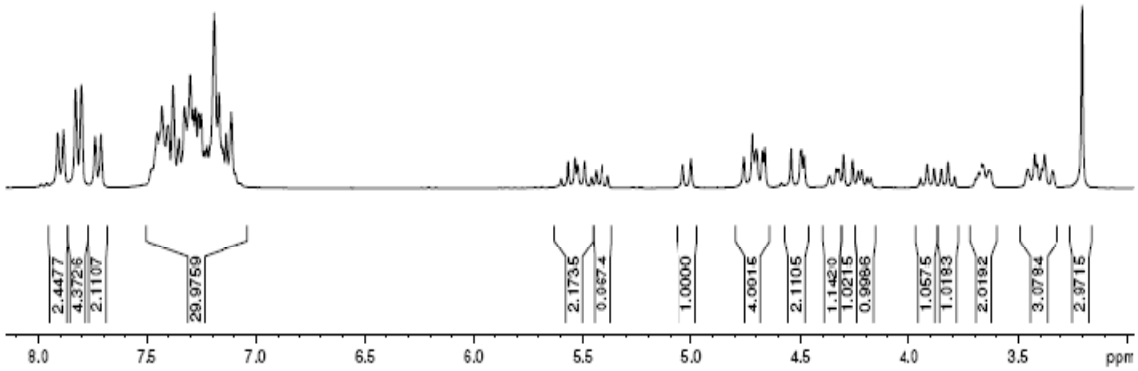
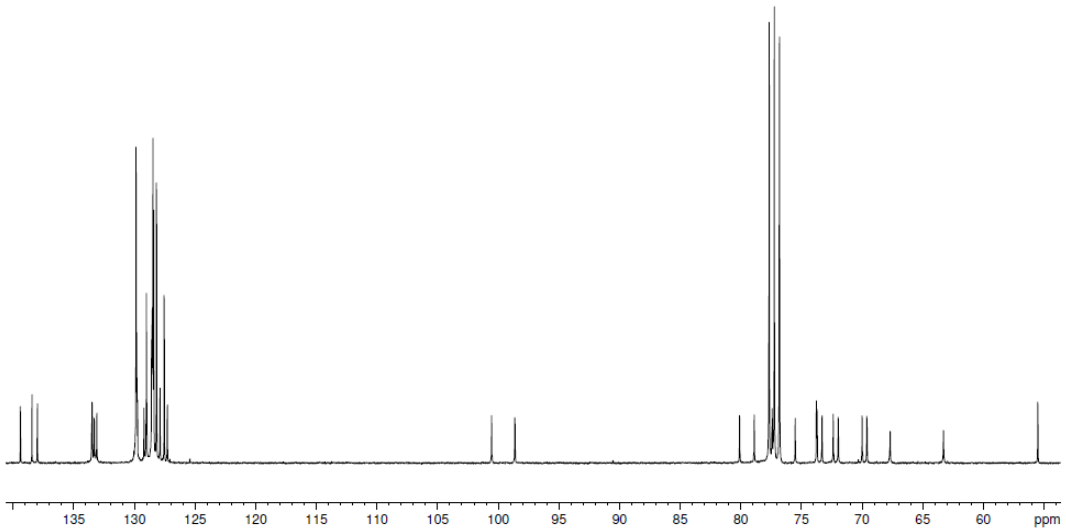
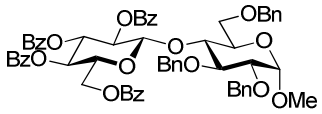


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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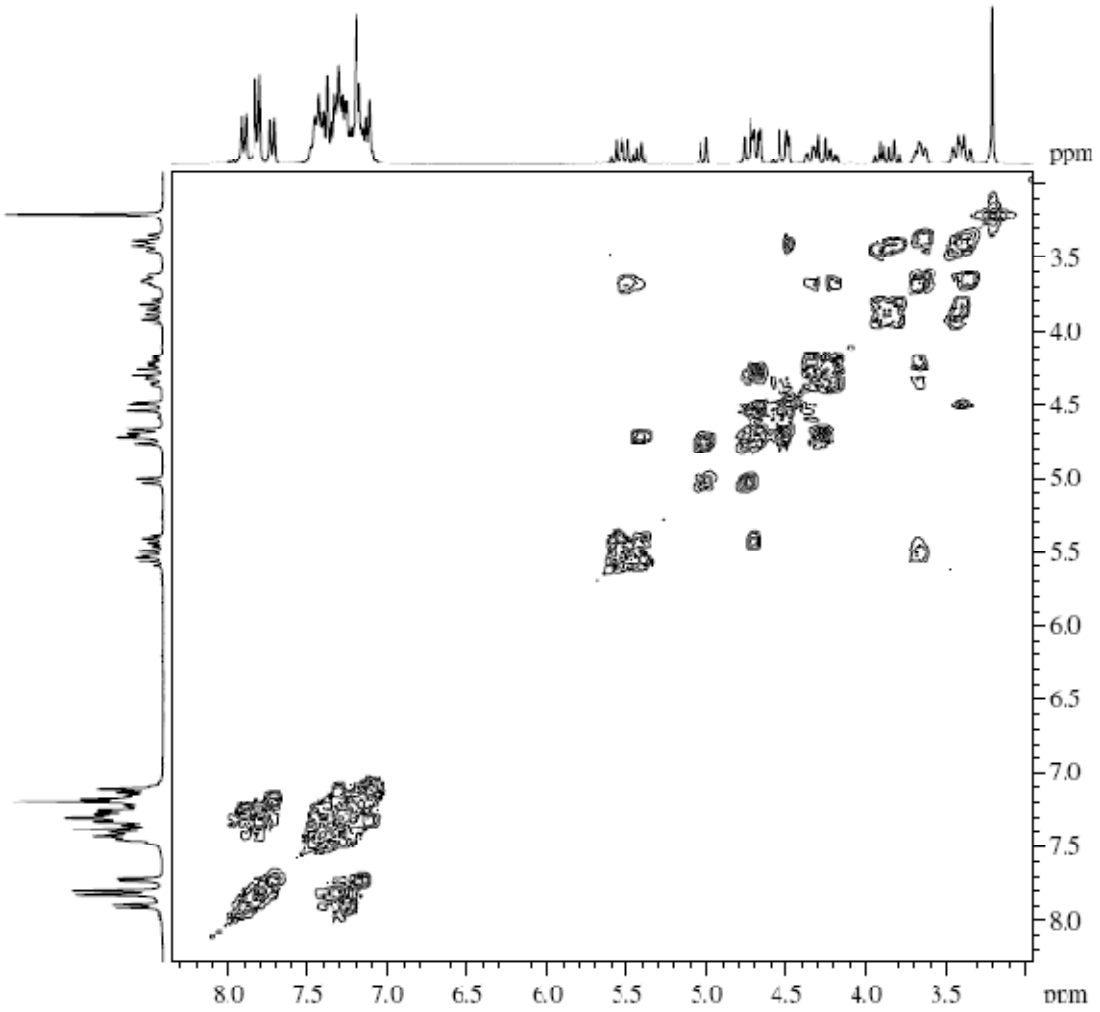

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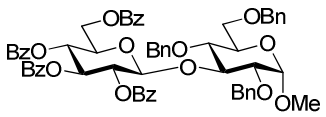

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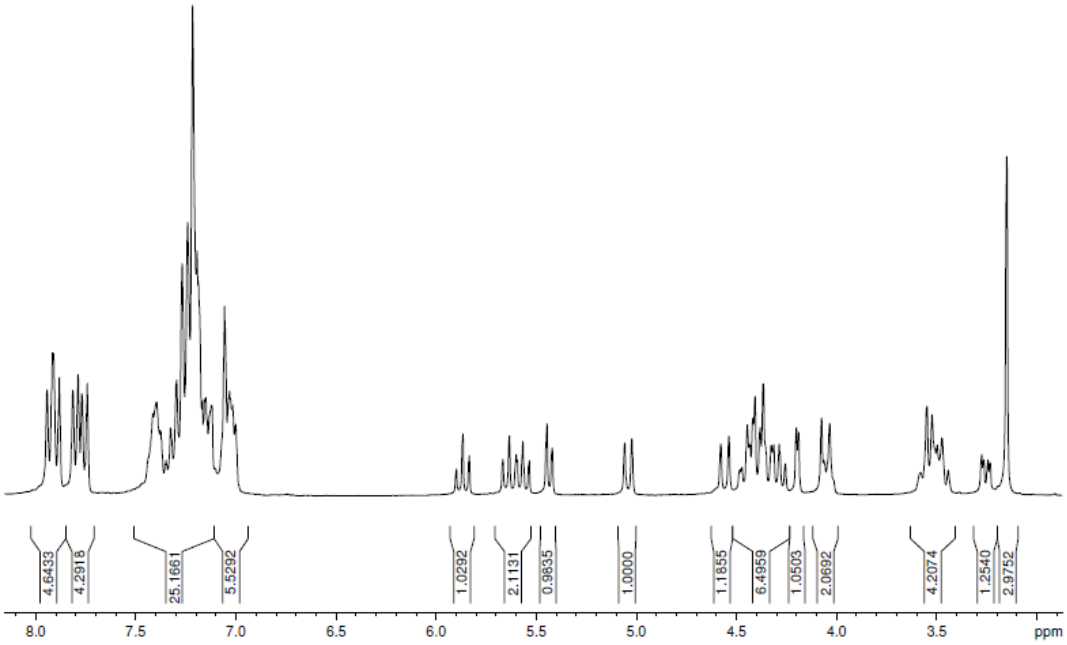
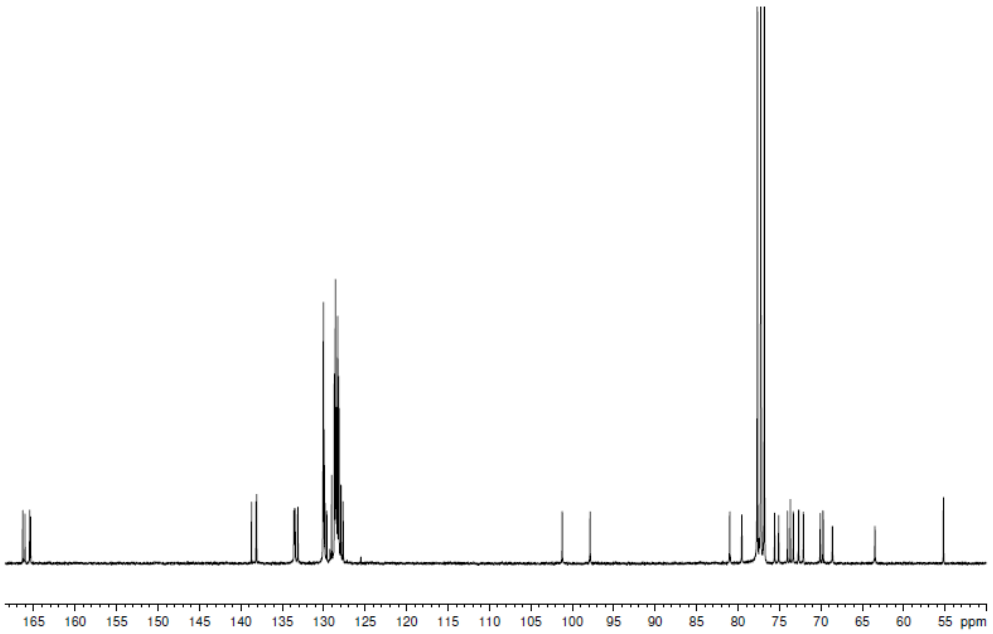
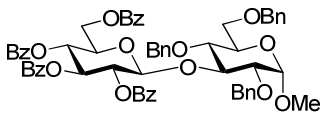


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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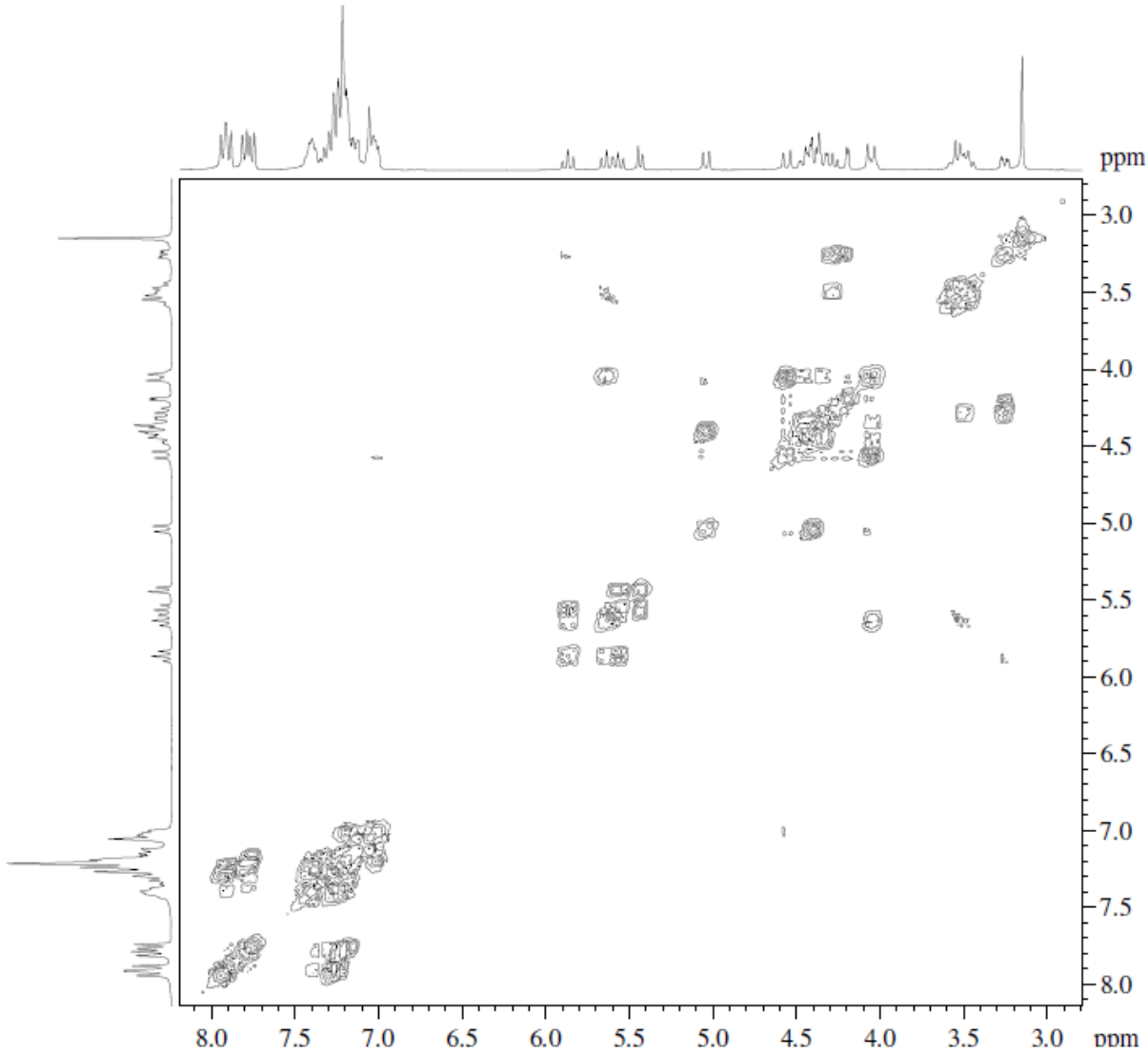
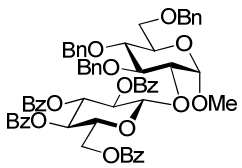
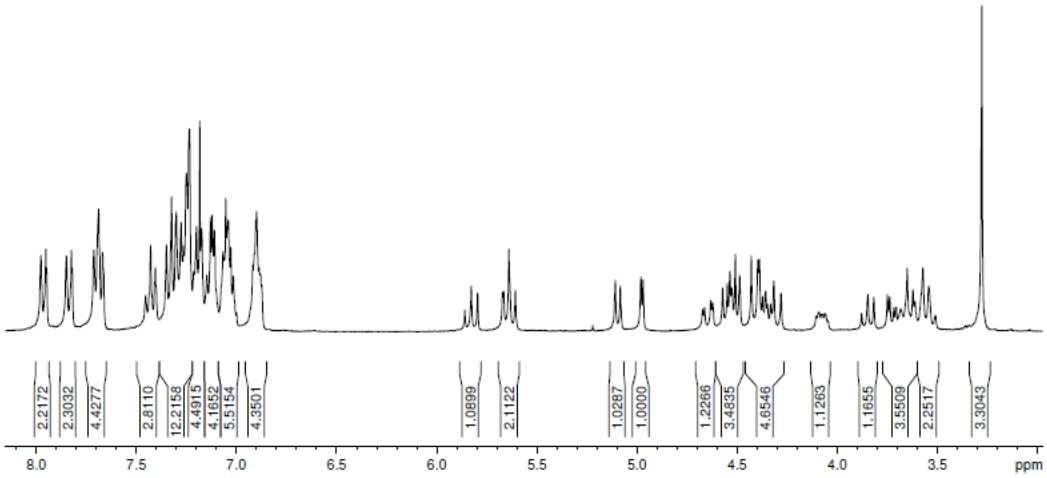


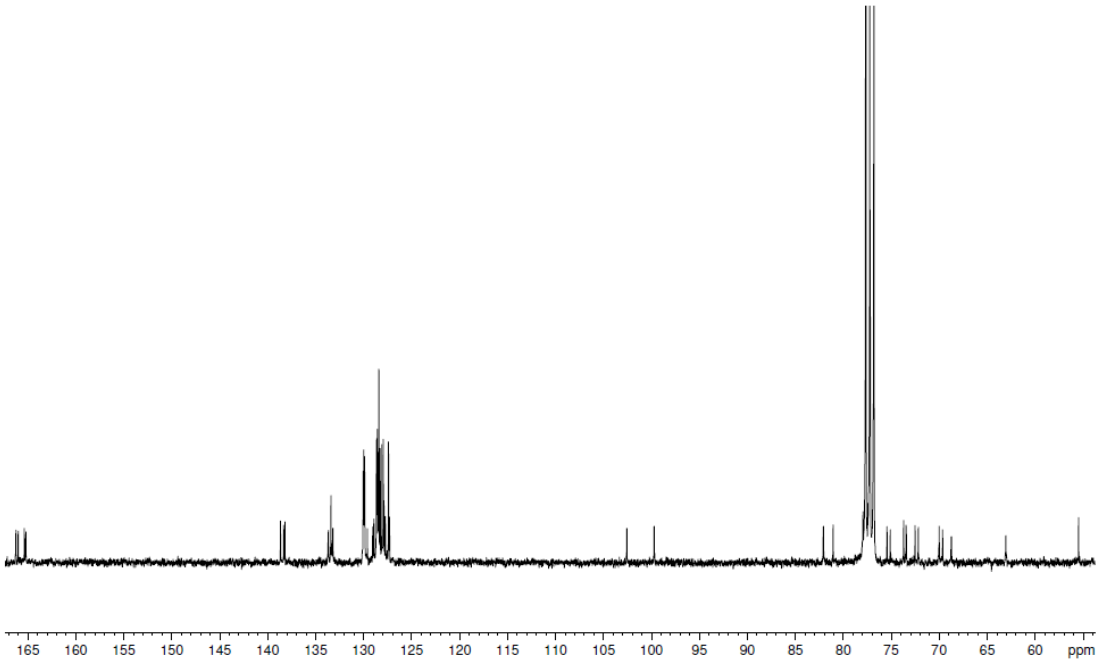
$CDCl_3$ at 300 MHz



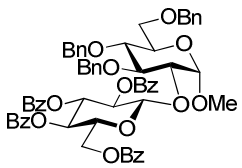
11



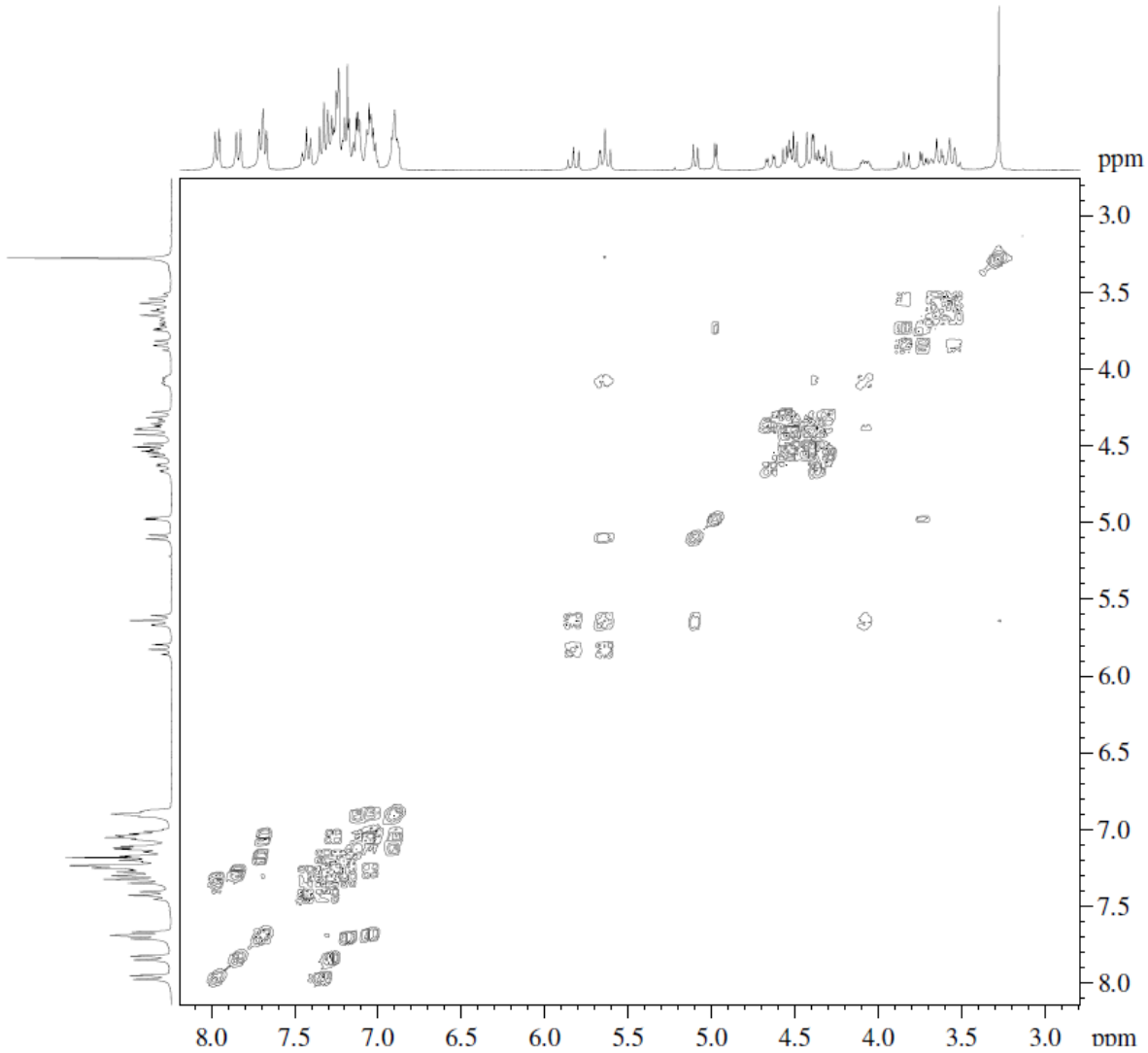
$CDCl_3$ at 300 MHz



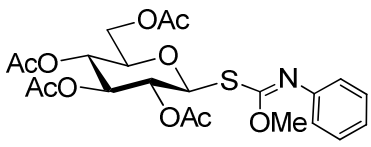
$CDCl_3$ at 75 MHz



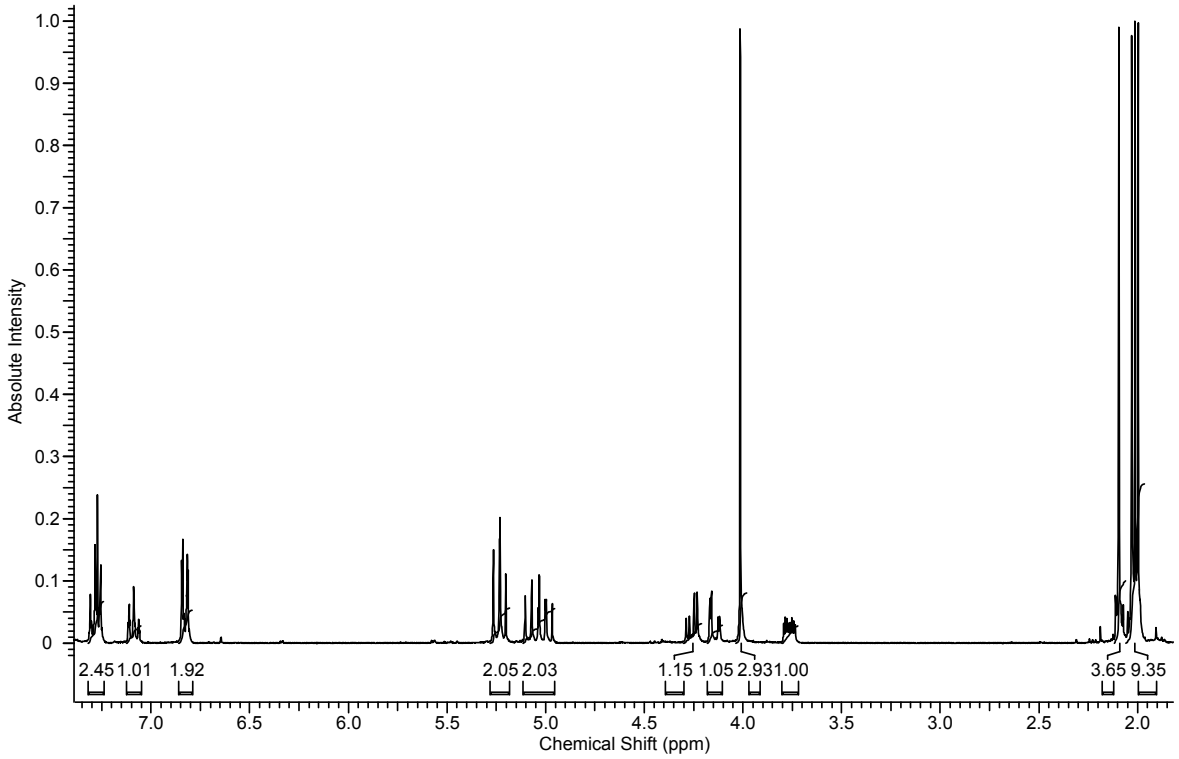
11



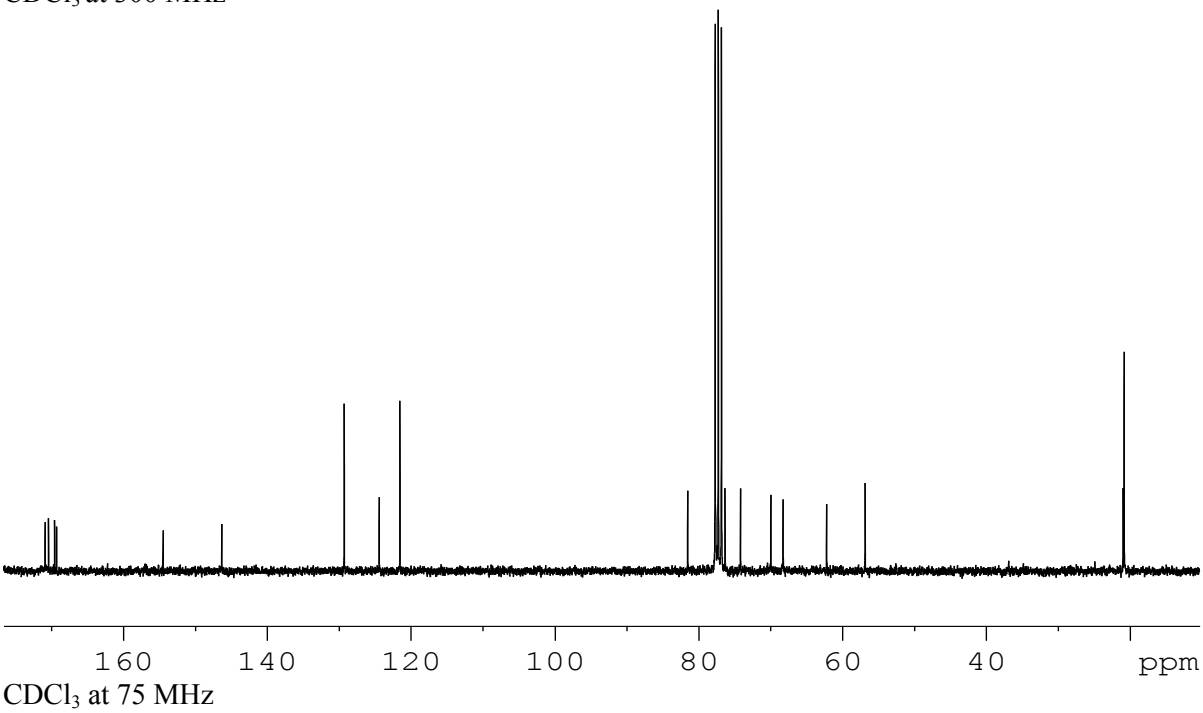
$CDCl_3$ at 300 MHz



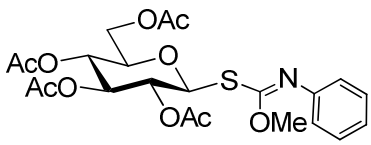
13



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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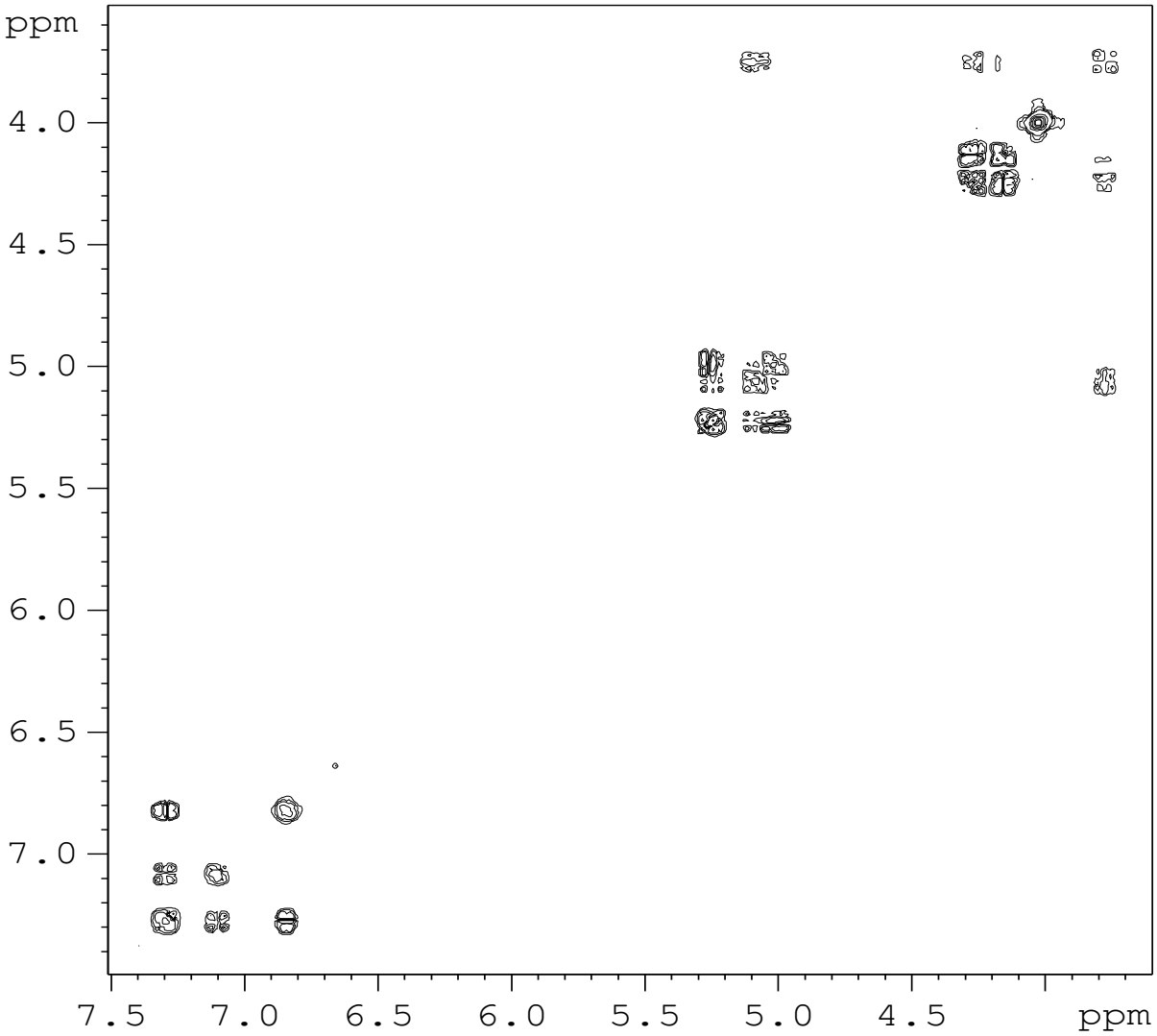

$CDCl_3$ at 300 MHz

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