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Supplementary Information

Iron(III) chloride-tandem catalysis for a one-pot regioselective protection of glucopyranosides

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General methods: Dichloromethane and acetonitrile were distilled from CaH_2. TLC (Silica Gel 60 F_{254}) was visualized under UV (254 nm) and by staining in a 5% ethanolic sulfuric acid solution. Silica gel SDS 60 ACC 35-70 mm was used for column chromatography. Melting points were measured on a Stuart SMP10 apparatus and are uncorrected. NMR spectra were recorded on Bruker DRX 300 or AV 360 or DPX 250 NMR spectrometers. Chemical shifts (in ppm) were determined relative to residual undeuterated solvent as an internal reference. Abbreviations of multiplicity were as follows: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad). Coupling constants in hertz (Hz) were measured from one-dimensional spectra. High-resolution mass spectra (positive mode ESI) were performed on a Bruker Daltonics micrOTOF-QII spectrometer. Optical rotations were measured on a Perkin Elmer 341 Polarimeter (*c* in g / 100 mL).

Procedure 1: persilylation of glucopyranoside derivatives: To a solution of the glucopyranoside derivative (10 mmol) in pyridine (10 mL) was added dropwise *via* syringe trimethylsilyl chloride (1.25 equiv per OH group). The solution was stirred overnight at room temperature and then diluted with AcOEt and H_2O. The organic layer was separated and washed twice with H_2O, dried over Na_2SO_4, filtred and concentrated *in vacuo*. The pyridine was then coevaporated twice with toluene to give the expected product.

Derivatives **1** and **2** were prepared in quantitative yields according to this procedure. The NMR data were in agreement with those previously reported in the literature: **1**[1,2], **2.**[2] Compound **9** was obtained in 92 % yield. Compound **13** was prepared starting from methyl α-D-maltoside[3] in 91% yield.

2,3,4,6,2',3',4',6'-Octa-*O*-trimethylsilyl-α,α-D-trehalose 9:

White solid; mp 80-82°C; $[\alpha]^{24}_D = +96$ ($c = 0.9$, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): 4.92 (d, $J_{1,2} = 3.2$ Hz, 1H, H-1), 3.89 (t, $J_{3,2} = J_{3,4} = 9.1$ Hz, 1H, H-3), 3.79 (m, 1H, H-5), 3.72-3.64 (m, 2H, H-6 & H-6'), 3.44 (t, $J_{4,3} = J_{4,5} = 9.1$ Hz, 1H, H-4), 3.39 (dd, $J_{2,1} = 3.1$ Hz, $J_{2,3} = 9.1$ Hz, 1H, H-2), 0.15 (bs, 18H, 2 $Si(CH_3)_3$), 0.13 (s, 9H, $Si(CH_3)_3$) 0.11 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): 94.4 (C-1), 73.6 (C-3), 73.2 (C-5), 72.9 (C-2), 71.8 (C-4), 62.2 (C-

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[3] S. Koto, M. Hirooka, T. Tashiro, M. Sakashita, M. Hatachi, T. Kono, M. Shimizu, N. Yoshida, S. Kurasawa, N. Sakuma, S. Sawazaki, A. Takeuchi, N. Shoya, E. Nakamura, *Carbohydr. Res.*, 2004, **339**, 2415.

6), 1.1 ($Si(CH_3)_3$), 1.0 ($Si(CH_3)_3$), 0.2 ($Si(CH_3)_3$), -0.3 ($Si(CH_3)_3$); ESI HRMS for $C_{36}H_{86}O_{11}Si_8$ $[M+Na]^+$: calcd 941.4222, found 941.4225.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-trimethysilyl-α-D-glucopyranosyl)-2,3,6-*O*-trimethysilyl-α-D-glucopyranoside 13:

Pale yellow oil; $[\alpha]^{16}_D$ = +78 (*c* = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): 5.24 (d, $J_{1',2'}$ = 3.5 Hz, 1H, H-1'), 4.66 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.02 (t, $J_{3,2} = J_{3,4}$ = 8.8 Hz, 1H, H-3), 3.99 (dd, $J_{6a,6b}$ = 11.3 Hz, $J_{6a,5}$ = 4.6 Hz, 1H, H-6a), 3.79 (dd, $J_{6b,6a}$ = 11.3 Hz, $J_{6b,5}$ = 1.9 Hz, 1H, H-6b), 3.76-3,69 (m, 4H, H-3', H-6a', H-6b' & H-4), 3.68-3.60 (m, 2H, H-5' & H-5), 3.55 (dd, $J_{2,3}$ = 8.8 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.53-3.48 (m, 1H, H-4'), 3.45 (dd, $J_{2',3'}$ = 8.5 Hz, $J_{2',1'}$ = 3.5 Hz, 1H, H-2'), 3.36 (s, 3H, OCH_3), 0.18 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$), 0.16 (2s, 18H, 2 $Si(CH_3)_3$), 0.15 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$), 0.13 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): 99.2 (C-1), 96.2 (C-1'), 75.3 (C-3'), 75,1 (C-3), 74.3 (C-4), 73.8 (C-2), 73.7 (C-2'), 73.0 (C-5'), 71.9 (C-4'), 70.6 (C-5), 62.5 (C-6), 62.0 (C-6'), 54.6 (OCH_3), 1.7 ($Si(CH_3)_3$), 1.2 ($Si(CH_3)_3$), 0.9 ($Si(CH_3)_3$), 0.8 ($Si(CH_3)_3$), 0.7 ($Si(CH_3)_3$), -0.1 ($Si(CH_3)_3$), -0.3 ($Si(CH_3)_3$); ESI HRMS for $C_{34}H_{80}O_{11}Si_7$ $[M+Na]^+$: calcd 883.3978, found 883.3953.

Procedure 2: preparation of 4,6-*O*-benzylidene-3-*O*-benzyl derivatives: To an ice-cold solution of the per-*O*-silylated glucopyranoside (0.207 mmol) and benzaldehyde (0.621 mmol; 3 equiv) in dichloromethane (360 μL) were added dropwise a solution of $FeCl_3·6H_2O$ in acetonitrile (90 μL of a 118 mM solution; 5 mol%) and triethylsilane (36 μL; 0.228 mmol; 1.1 equiv). The solution was stirred for 1.5 h at room temperature. For a large scale, a treatment of TBAF (1 M solution in THF) was required. The mixture was then diluted with ethyl acetate and neutralized with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography to give the expected product.

For the trehalose disaccharide, 6 equivalents of benzaldehyde and 2.2 equivalents of triethylsilane were required. The reaction was complete within 3 hours.

Derivatives **3**, **4** and **10** were prepared in 77, 71 and 61% yields respectively according to this procedure. The NMR data were in agreement with those previously reported in the literature: **3**[4], **4**[5], **10**[6].

Synthesis of compound 14: To a solution of the per-*O*-silylated maltoside **13** (86 mg; 0.100 mmol) and benzaldehyde (0.800 mmol; 8 equiv) in dichloromethane (200 μL) were added dropwise a solution of $FeCl_3{\cdot}6H_2O$ in acetonitrile (50 μL of a 300 mM solution; 15 mol%) and triethylsilane (64 μL; 0.400 mmol; 4 equiv). The solution was stirred overnight at room temperature. The mixture was then diluted with ethyl acetate and neutralized with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography to give the expected product (32 mg; 51%).

Methyl 4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-6-*O*-benzyl-α-D-glucopyranoside 14:

Colourless oil; $[\alpha]^{16}_D = +107$ ($c = 1$, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): 7.50-7.30 (m, 15H, Ar-H), 5.56 (s, 1H, CH-Ph), 5.18 (d, $J_{1',2'} = 3.6$ Hz, 1H, H-1'), 4.99 (d, $J = 11.7$ Hz, 1H, CH_2-Ph), 4.81 (d, $J_{1,2} = 4.0$ Hz, 1H, H-1), 4.75 (d, $J = 11.7$ Hz, 1H, CH_2-Ph), 4.61 (d, $J = 11.7$ Hz, 1H, CH_2-Ph), 4.57 (d, $J = 11.7$ Hz, 1H, CH_2-Ph), 4.11 (dd, $J_{6a',6b'} = 10.1$ Hz, $J_{6a',5'} = 4.6$ Hz, 1H, H-6a'), 3.93 (ddd, $J_{5',6b'} = 10.1$ Hz, $J_{5',4'} = 9.4$ Hz, $J_{5',6a'} = 4.6$ Hz, 1H, H-5'), 3.88 (2t, $J_{3,2} = J_{3,4} = J_{3',2'} = J_{3',4'} = 9.4$ Hz, 2H, H-3 & H-3'), 3.79-3.74 (m, 3H, H-5, H-6a & H-6b), 3.76 (dd, $J_{2',3'} = 9.4$ Hz, $J_{2',1'} = 3.6$ Hz, 1H, H-2'), 3.69 (t, $J_{6b',6a'} = J_{6b',5'} = 10.1$ Hz, 1H, H-6b'), 3.68-3.64 (m, 1H, H-4), 3.63 (t, $J_{4',3'} = J_{4',5'} = 9.4$ Hz, 1H, H-4'), 3.60 (dd, $J_{2,3} = 9.4$ Hz, $J_{2,1} = 4.0$ Hz, 1H, H-2), 3.45 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): 138.4, 138.0, 137.3, 129.0, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 127.7, 126.1 (C-Ar), 101.9 (C-1'), 101.3 (CH-Ph), 99.2 (C-1), 81.9 (C-4'), 81.4 (C-4), 78.4 (C-3 or C-3'), 74.8 (CH_2-Ph), 74.4 (C-3' or C-3), 73.7 (CH_2-Ph), 73.0 (C-2'), 71.8 (C-2), 69.6 (C-5), 68.8 (C-6'), 68.8 (C-6), 63.7 (C-5'), 55.4 (OCH_3); ESI HRMS for $C_{34}H_{40}O_{11}$ $[M+Na]^+$: calcd 647.2463, found 647.2447.

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[4] C. L. Battistelli, C. D. Castro, A. Iadonisi, R. Lanzetta, L. Mangoni, M. Parrilli, *J. Carbohydr. Chem.*, 1999, **18**, 69.

[5] E. Bousquet, M. Khitri, L. Lay, F. Nicotra, L. Panza, G. Russo, *Carbohydr. Res.*, 1998, **311**, 171.

[6] C. Vincent, M. Martín-Lomas, S. Penadés, *Carbohydr. Res.,* 1989, **194**, 308.

Acetylated 14[7] **(Methyl 4-*O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-2,3-di-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranoside):**

Colourless oil; ^{1}H NMR ($CDCl_3$, 360 MHz): 7.52-7.28 (m, 15H, Ar-H), 5.57 (s, 1H, CH-Ph), 5.56 (t, $J_{3,2} = J_{3,4}$ = 9.8 Hz, 1H, H-3), 5.38 (d, $J_{1',2'}$ = 4.0 Hz, 1H, H-1'), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.88 (d, J = 11.7 Hz, 1H, CH_2-Ph), 4.85 (dd, $J_{2',3'}$ = 9.5 Hz, $J_{2',1'}$ = 4.0 Hz, 1H, H-2'), 4.81 (dd, $J_{2,3}$ = 9.8 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 4.69 (d, J = 11.7 Hz, 1H, CH_2-Ph), 4.68 (d, J = 11.7 Hz, 1H, CH_2-Ph), 4.63 (d, J = 11.7 Hz, 1H, CH_2-Ph), 4.16 (t, $J_{4,3} = J_{4,5}$ = 9.8 Hz, 1H, H-4), 4.13 (dd, $J_{6a',6b'}$ = 10.1, Hz, $J_{6a',5'}$ = 4.8 Hz, 1H, H-6a'), 3.94 (t, $J_{3',2'} = J_{3',4'}$ = 9.5 Hz, 1H, H-3'), 3.93-3.87 (m, 2H, H-5 & H-6a or H-6b), 3.84 (ddd, $J_{5',6b'}$ = 10.1 Hz, $J_{5',4'}$ = 9.5 Hz, $J_{5',6a'}$ = 4.8 Hz 1H, H-5'), 3.75-3.68 (m, 1H, H-6b or H-6a), 3.68 (t, $J_{4',3'} = J_{4',5'}$ = 9.5 Hz, 1H, H-4'), 3.65 (t, $J_{6b',6a'} = J_{6b',5'}$ = 10.1 Hz, 1H, H-6b'), 3.41 (s, 3H, OCH_3), 2.08 (s, 3H, CH_3-CO), 2.05 (s, 3H, CH_3-CO), 2.02 (s, 3H, CH_3-CO); ^{13}C NMR ($CDCl_3$, 62.5 MHz): 170.8, 170.3, 170.0 (CH_3-CO), 138.5, 138.0, 137.3, 128.9, 128.3, 128.3, 128.2, 127.6, 127.5, 127.4, 126.0 (C-Ar), 101.2 (CH-Ph), 96.7 (C-1), 96.2 (C-1'), 81.9 (C-4'), 76.0 (C-3'), 74.9 (CH_2-Ph), 73.6 (CH_2-Ph), 72.9 (C-3), 72.4 (C-2'), 71.5 (C-2), 71.2 (C-4), 69.4 (C-5), 68.6 (C-6), 68.5 (C-6'), 63.5 (C-5'), 55.3 (OCH_3), 21.0 (CH_3-CO), 20.8 (CH_3-CO), 20.7 (CH_3-CO); ESI HRMS for $C_{40}H_{46}O_{14}$ $[M+Na]^+$: calcd 773.2780, found 773.2762.

Preparation of 4,6-*O*-benzylidene-3-*O*-benzyl-2-*O*-ester derivatives: Following the procedure 2, acylating reagent (1.035 mmol; 5 equiv) was added before the treatment (aqueous solution). The solution was then stirred overnight at the indicated temperature. The treatment was similar that for procedure 2. The crude product was purified by silica gel chromatography to give the orthogonally protected sacharide.

For the trehalose disaccharide, 10 equivalents of the acylating reagent and 5 mol% of $FeCl_3 \cdot 6H_2O$ were added.

Derivatives **5a**, **5c** and **6** were prepared in 64, 60 and 60% yields respectively according to this procedure. The NMR data were in agreement with those previously reported in the literature: **5a**[2,8], **5c**[2], **6**[5]. The compounds **5b** and **11** (NMR data partially reported[6]) were isolated in 58 and 41% yields respectively.

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[7] Compound **Y** was acylated quantitatively with an excess of acetic anhydride in pyridine.

[8] C.-C. Wang, J.-C. Lee, S.-Y. Luo, S. S. Kulkarni, Y.-W. Huang, C.-C. Lee, K.-L. Chang, S.-C. Hung, *Nature,* 2007, **446**, 896

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-palmitoyl-α-D-glucopyranoside 5b:
White solid; mp 58-60°C; $[\alpha]^{24}_{D}$ = +49 (*c* = 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 360MHz): 7.53-7.26 (m, 10H, Ar-H), 5.61 (s, 1H, CH-Ph), 4.96 (d, 1H, $J_{1,2}$ = 3.7 Hz H-1), 4.92 (dd, $J_{2,1}$ = 3.7 Hz, $J_{2,3}$ = 9.4 Hz, 1H, H-2), 4.90 (d, *J* = 11.8 Hz, 1H, CH_2-Ph), 4.73 (d, *J* = 11.8 Hz, 1H, CH_2-Ph), 4.33 (dd, $J_{6',5}$ = 4,5 Hz, $J_{6',6}$ = 10.0 Hz, 1H, H-6'), 4.06 (t, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.89 (ddd, $J_{5,4}$ = 9.4 Hz, $J_{5,6}$ = 10.0 Hz, $J_{5,6'}$ = 4,5 Hz, 1H, H-5), 3.80 (t, $J_{6,5}$ = $J_{6,6'}$ = 10.0 Hz, 1H, H-6), 3.74 (t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4), 3.41 (s, 3H, OCH_3), 2.35 (m, 2H, H-7), 1.64 (m, 2H, H-8), 1.28 (bs, 24H, H-9 to H-20), 0.91(bt, *J* = 6.8 Hz, 3H, H-21); ^{13}C NMR ($CDCl_3$, 90 MHz): 173.2 (CH_3-CO), 138.5, 137.4, 128.9, 128.2, 127.6, 127.5, 126.1 (Ar-C), 101.4 (CH-Ph), 97.9 (C-1), 82.1 (C-4), 76.2 (C-3), 74.8 (CH_2-Ph), 72.9 (C-2), 69.0 (C-6), 62.3 (C-5), 55.3 (OCH_3), 34.2 (C-7), 31.9, 29.7, 29.65, 29.60, 29.5, 29.3, 29.2, 29.1, 24.9, 22.7 (C-8 to C-20), 14.1 (C-21); ESI HRMS for $C_{37}H_{54}O_7$ $[M+Na]^+$: calcd 633.3767, found 633.3755.

2,2'-di-*O*-acetyl-3,3'-di-*O*-benzyl-4,6:4',6'-di-*O*-benzylidene-α,α-D-trehalose 11:
White solid; mp 190-192°C; $[\alpha]^{24}_{D}$ = +94 (*c* = 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 360MHz): 7.56-7.26 (m, 10H, Ar-H), 5.62 (s, 1H, CH-Ph), 5.31 (d, $J_{1,2}$ = 3.9 Hz, 1H, H-1), 4.97 (dd, $J_{2,1}$ = 3.9 Hz, $J_{2,3}$ = 9.4 Hz, 1H, H-2), 4.96 (d, *J* = 11.7 Hz, 1H, CH_2-Ph), 4.76 (d, *J* = 11.7 Hz, 1H, CH_2-Ph), 4.20 (dd, $J_{6',5}$ = 4,8 Hz, $J_{6',6}$ = 10.4 Hz, 1H, H-6'), 4.09 (t, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1H, H-3), 3.88 (ddd, $J_{5,4}$ = 9.4 Hz, $J_{5,6}$ = 10,4 Hz, $J_{5,6'}$ = 4,8 Hz, 1H, H-5), 3.79 (t, $J_{6,5}$ = $J_{6,6'}$ = 10.4 Hz, 1H, H-6), 3.78 (t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4), 2.16 (s, 3H, CH_3-CO); ^{13}C NMR ($CDCl_3$, 90 MHz): 170.0 (CH_3-CO), 138.4, 137.2, 129.0, 128.3, 128.2, 127.6, 127.5, 126.0 (Ar-C), 101.5 (CH-Ph), 93.4 (C-1), 81.8 (C-4), 76.2 (C-3), 74.9 (CH_2-Ph), 72.4 (C-2), 68.7 (C-6), 63.3 (C-5), 20.7 (CH_3-CO); ESI HRMS for $C_{44}H_{46}O_{13}$ $[M+Na]^+$: calcd 805.2831, found 805.2831.

Preparation of 3,6-*O*-dibenzyl derivatives: Following the procedure 1, a solution of $FeCl_3 \cdot 6H_2O$ in acetonitrile (90 μL of a 118 mM solution; 5 mol%) and triethylsilane (164 μL; 1.035 mmol; 5 equiv) were added before the treatment (TBAF or aqueous solution). The solution was then stirred overnight at room temperature. The treatment was similar that for procedure 2. The crude product was purified by silica gel chromatography to give the expected compound.

For the trehalose disaccharide, 10 equivalents of triethylsilane and 15 mol% of $FeCl_3 \cdot 6H_2O$ were added.

Derivative **7** was prepared in 55% yield according to this procedure. The NMR data were in agreement with those previously reported in the literature.[9,4] The compounds **8** and **12** were obtained in 54 and 28% yields respectively.

Phenyl 3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside 8:

White solid; $[\alpha]^{20}_D$ = -58 (c = 0.5, $CHCl_3$); mp 85-87°C; ^1H NMR ($CDCl_3$, 360 MHz): 7.60-7.53 (m, 2H, Ar-H), 7.44-7.24 (m, 13H, Ar-H), 4.98 (d, J = 11.5 Hz, 1H, CH_2-Ph), 4.84 (d, J = 11.5 Hz, 1H, CH_2-Ph), 4.63 (d, J = 11.9 Hz, 1H, CH_2-Ph), 4.59 (d, J = 11.9 Hz, 1H, CH_2-Ph), 4.55 (d, $J_{1,2}$ = 9.2 Hz, 1H, H-1), 3.84-3.75 (m, 2H, H-6 & H-6'), 3.64 (t, $J_{4,3} = J_{4,5}$ = 8.6 Hz, 1H, H-4), 3.55 (m, 1H, H-5), 3.50 (dd, $J_{2,1}$ = 9.2 Hz, $J_{2,3}$ = 8.6 Hz, 1H, H-2), 3.45 (t, $J_{3,4} = J_{3,2}$ = 8.6 Hz, 1H, H-3), 2.67 (bs, 1H, OH), 2.49 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$, 90 MHz): 138.5, 138.0 (Ar-Cq), 132.8, 131.8, 129.0, 128.6, 128.4, 128.1, 128.0, 127.9, 127.7, 127.6 (Ar-C), 88.4 (C-1), 85.2 (C-3), 78.5 (C-5), 74.9 (CH_2-Ph), 73.7 (CH_2-Ph), 72.3 (C-2), 71.2 (C-4), 70.3 (C-6); ESI HRMS for $C_{26}H_{28}O_5S$ $[M+Na]^+$: calcd 475.1555, found 475.1555.

3,6,3',6'-tetra-*O*-benzyl-α,α-D-trehalose 12:

Colourless oil; $[\alpha]^{27}_D$ = +81 (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 360MHz): 7.43-7.28 (m, 10H, Ar-H), 5.17 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 4.93 (d, J = 11.5 Hz, 1H, CH_2-Ph), 4.88 (d, J = 11.5 Hz, 1H, CH_2-Ph), 4.61 (d, J = 12.0 Hz, 1H, CH_2-Ph), 4.55 (d, J = 12.0 Hz, 1H, CH_2-Ph), 4.01 (m, 1H, H-5), 3.75-3.66 (m, 5H, H-2, H-3, H-4 & H-6), 2.69 (bs, 1H, OH), 2.23 (bs, 1H, OH); ^{13}C NMR ($CDCl_3$, 90 MHz): 138.6, 137.7, 128.6, 128.5, 128.0, 127.9, 127.8, 127.7 (Ar-C), 94.9 (C-1), 82.1 (C-3), 74.9 (CH_2-Ph), 73.7 (CH_2-Ph), 71.8, 71.6 (C-2 and C-4), 70.7 (C-5), 69.9 (C-6); ESI HRMS for $C_{40}H_{46}O_{11}$ $[M+Na]^+$: calcd 725.2932, found 725.2933.

Acetylated 12[10] (2,4,2',4'-tetra-*O*-acetyl-3,6,3',6'-tetra-*O*-benzyl-α,α-D-trehalose):

Colourless oil; ^1H NMR ($CDCl_3$, 250MHz): 7.40-7.26 (m, 10H, Ar-H), 5.27 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 5.14 (t, $J_{4,3} = J_{4,5}$ = 9.9 Hz, 1H, H-4), 5.01 (dd, $J_{2,1}$ = 3.6 Hz, $J_{2,3}$ = 9.9 Hz, 1H, H-2), 4.75 (d, J = 11.6 Hz, 1H, CH_2-Ph), 4.66 (d, J = 11.6 Hz, 1H, CH_2-Ph), 4.50 (d, H, J = 12.4 Hz, CH_2-Ph),), 4.45 (d, H, J = 12.4 Hz, CH_2-Ph), 4.04 (t, $J_{3,4} = J_{3,2}$ = 9.9 Hz, 1H, H-3), 4.02-3.93 (m, 1H, H-5), 3.56-3.43 (m, 2H, H-6a & H-6b), 1.99 (s, 3H, CH_3-CO), 1.93 (s, 3H, CH_3-CO); ^{13}C NMR ($CDCl_3$, 62.5 MHz): 169.7, 169.5 (CH_3-CO), 138.2, 137.6, 128.4, 128.3, 127.9,

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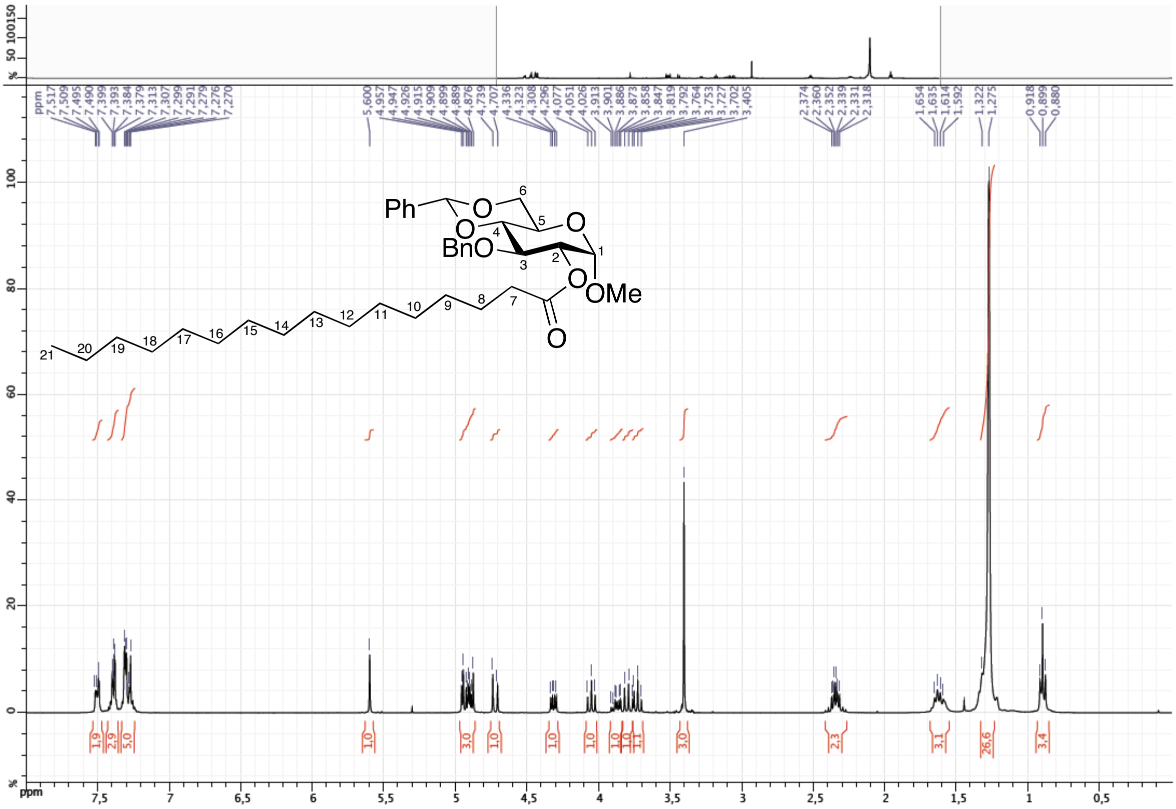
[9] T. Ogawa, Y. Takahashi, M. Matsui, *Carbohydr. Res.*, 1982, **102**, 207.

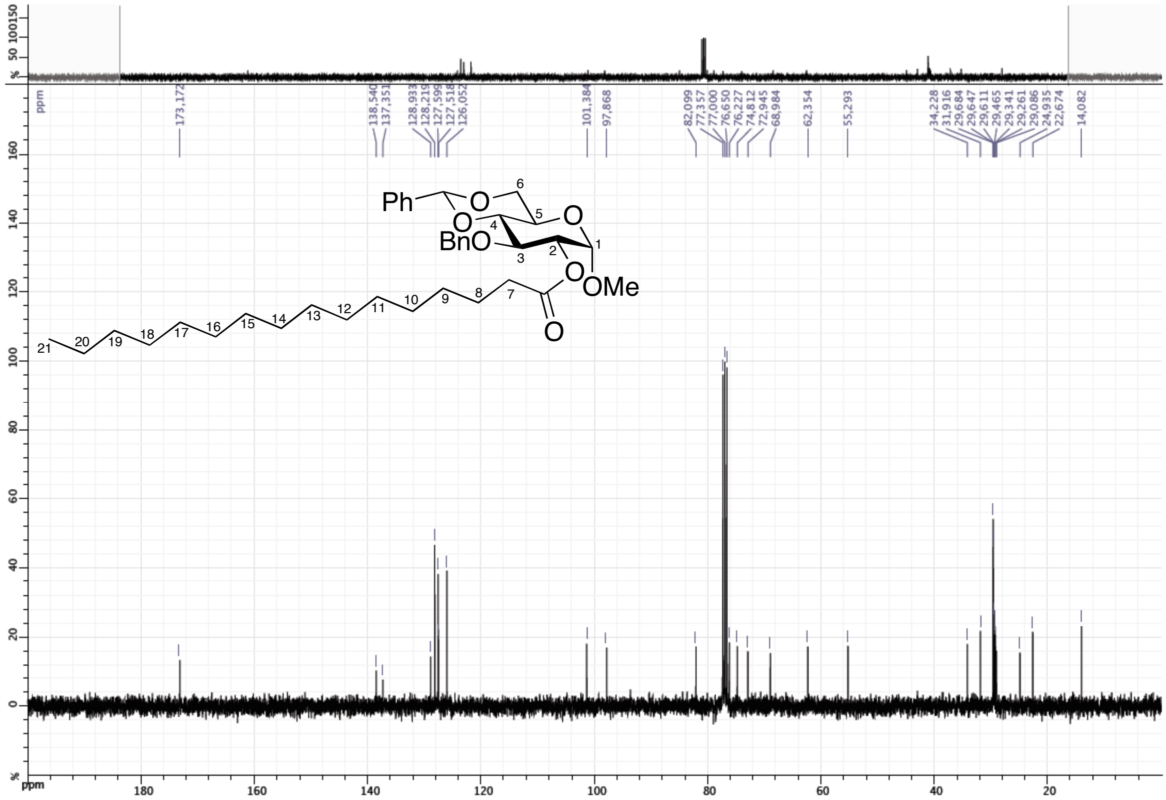
[10] Compound **12** was acylated quantitatively with an excess of acetic anhydride in pyridine

127.7, 127.5 (Ar-C), 93.0 (C-1), 76.9 (C-3), 74.2 (CH_2-Ph), 73.8 (CH_2-Ph), 72.0 (C-2), 70.9 (C-4), 69.9 (C-5), 69.4 (C-6), 20.9, 20.6 (CH_3-CO); ESI MS for $C_{48}H_{54}O_{15}$ $[M+Na]^+$: 893.45

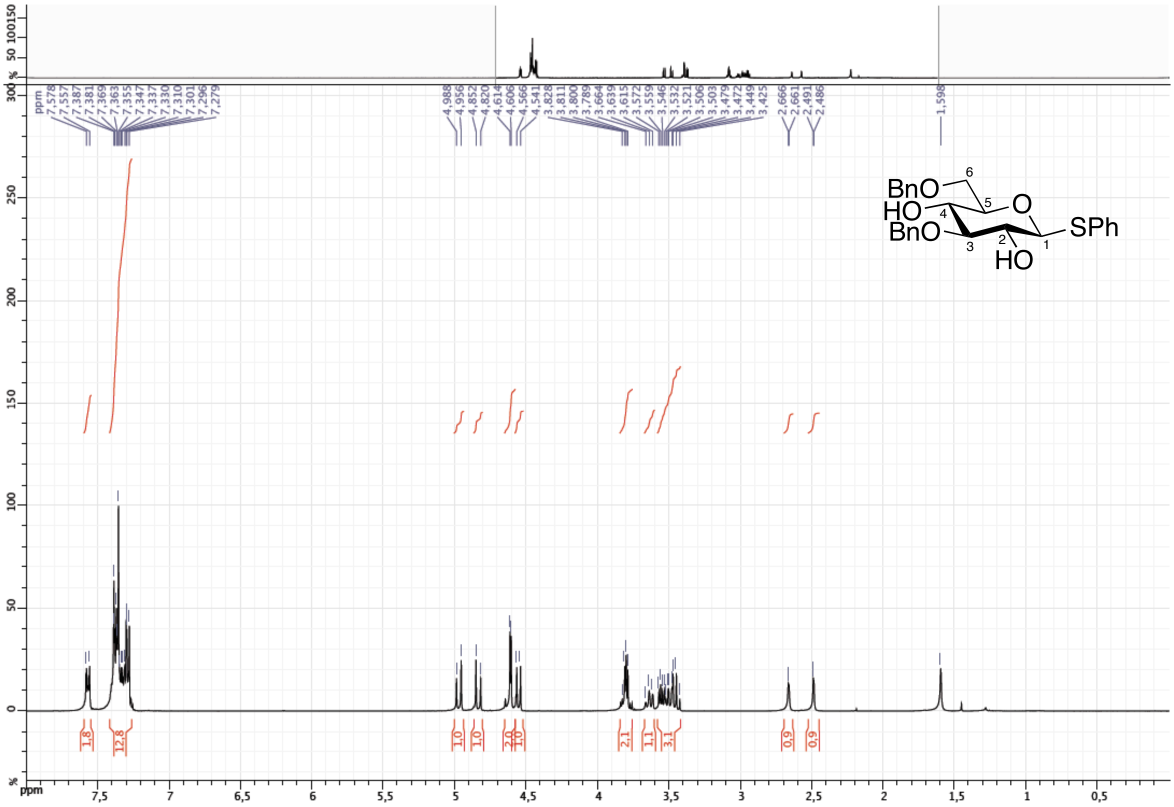
Copy of ^{1}H NMR spectrum of compound 5b (360 MHz, $CDCl_3$)



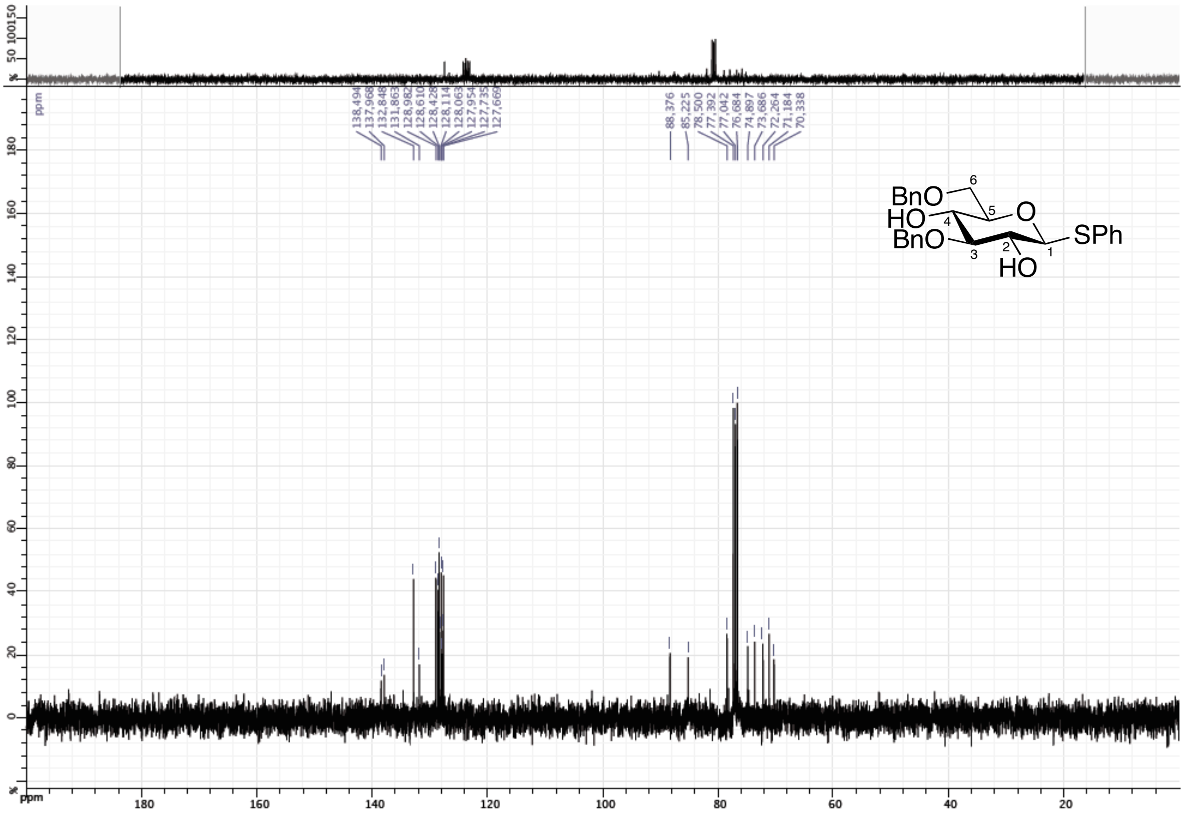
Copy of ^{13}C NMR spectrum of compound 5b (90 MHz, $CDCl_3$)



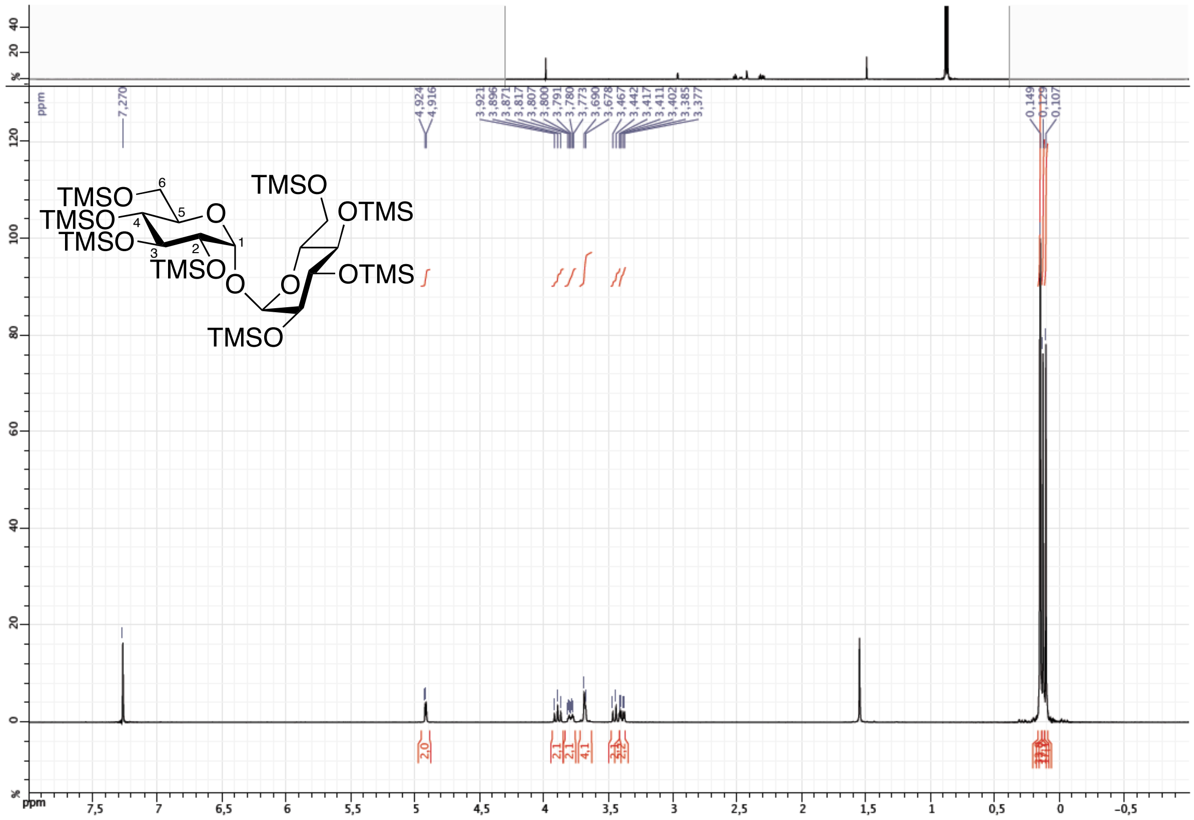
Copy of ^{1}H NMR spectrum of compound 8 (360 MHz, $CDCl_3$)



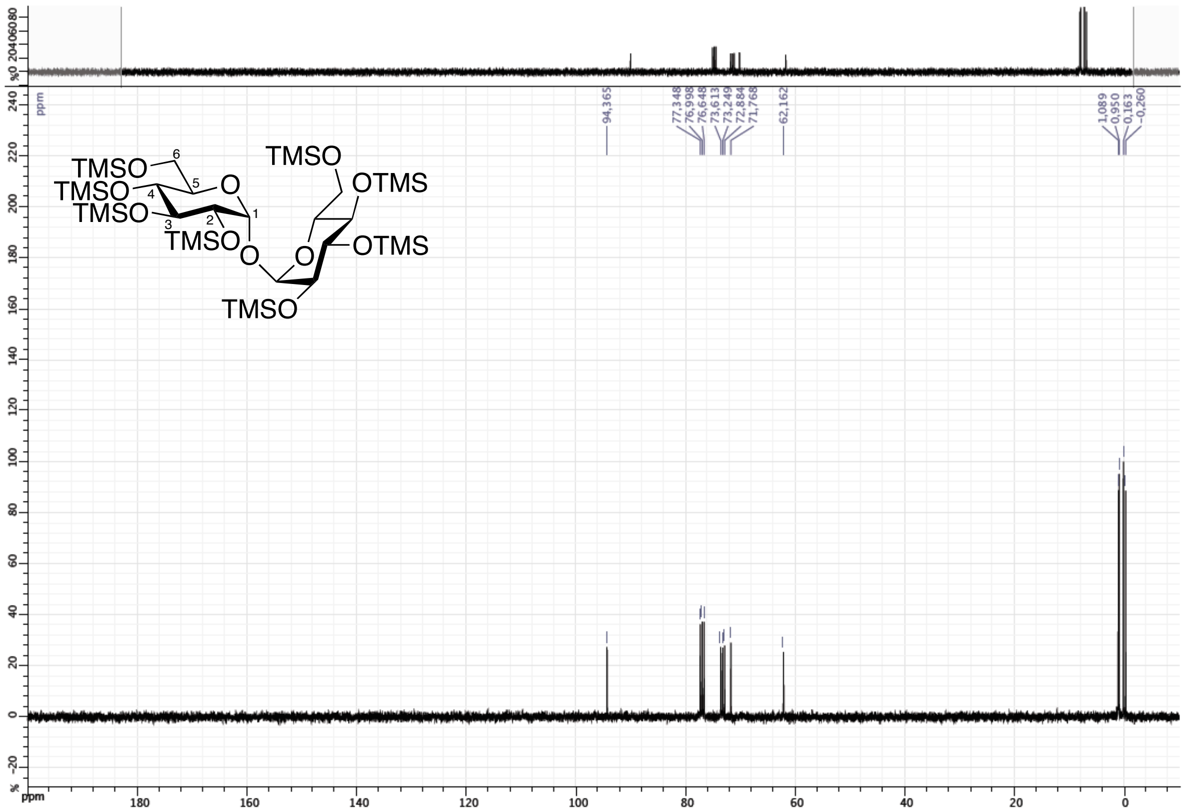
Copy of ^{13}C NMR spectrum of compound 8 (90 MHz, $CDCl_3$)



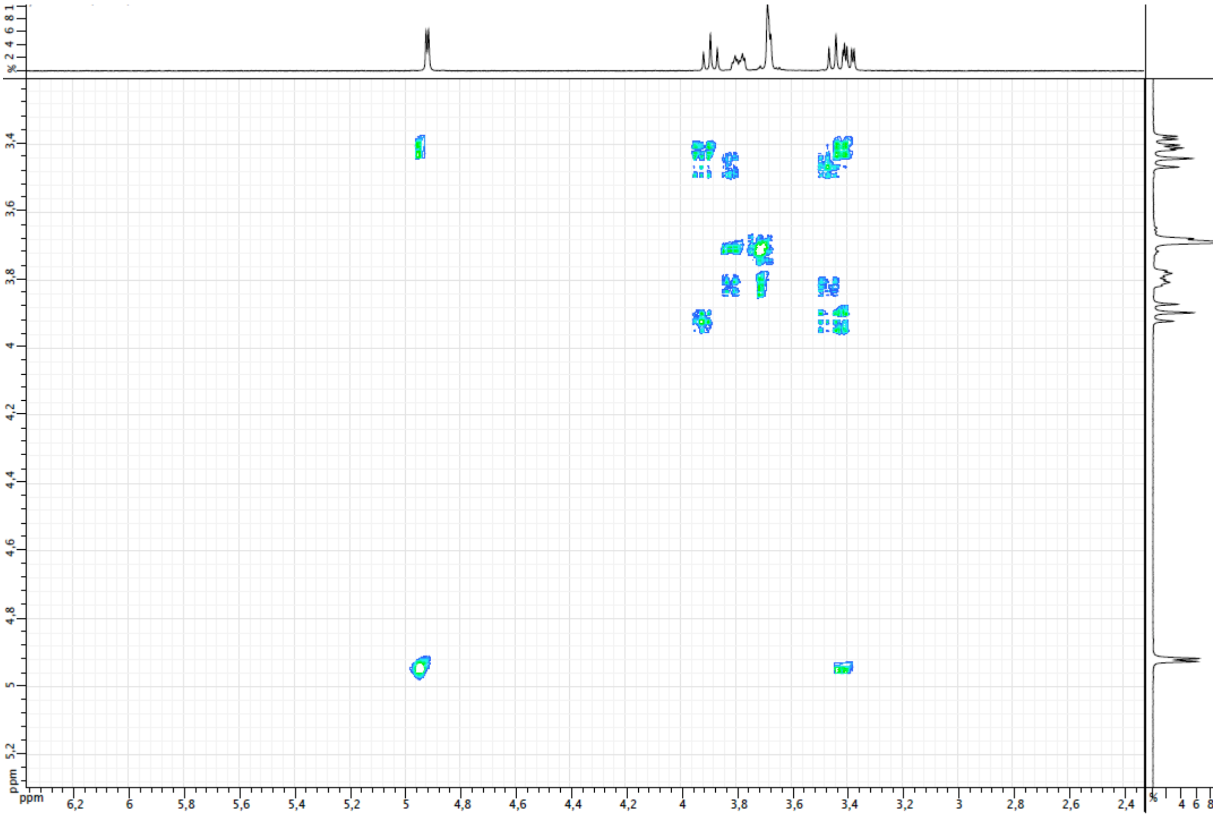
Copy of ^{1}H NMR spectrum of compound 9 (360 MHz, CDCl$_3$)



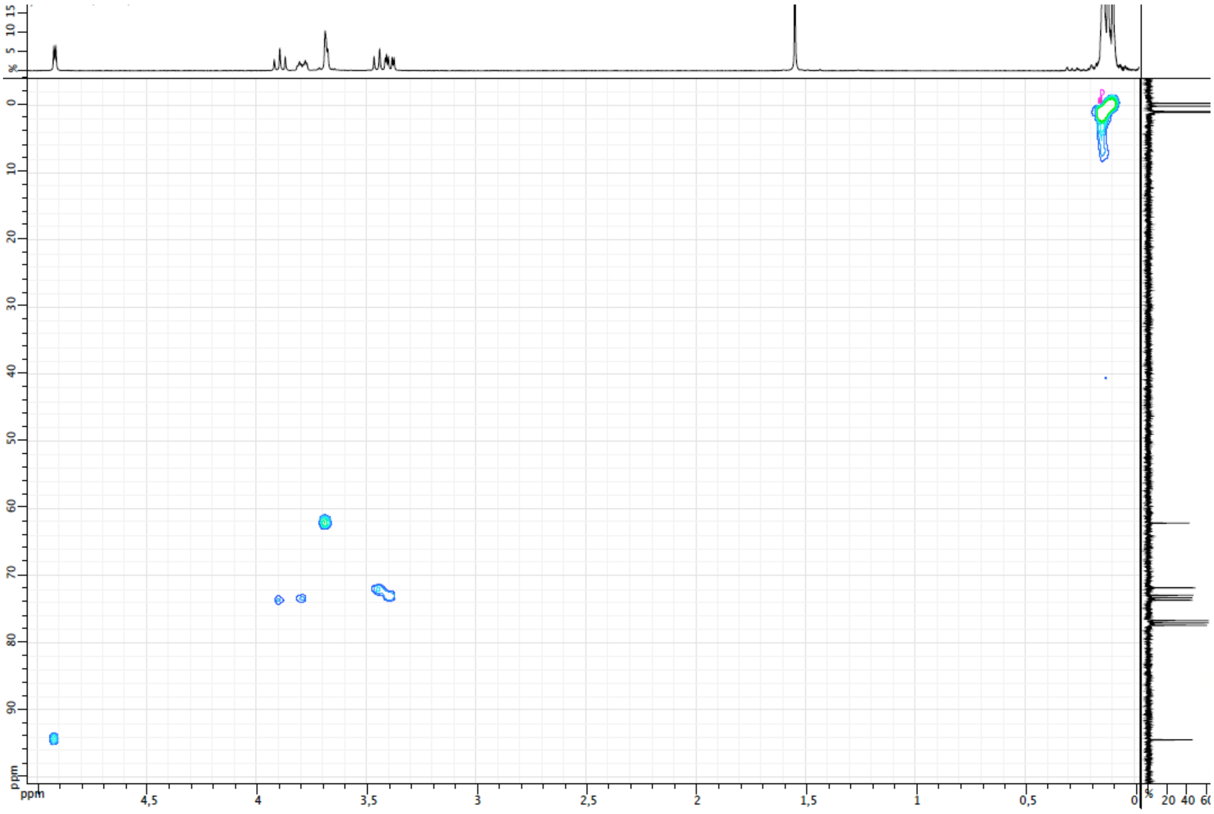
Copy of ^{13}C NMR spectrum of compound 9 (90 MHz, CDCl$_3$)



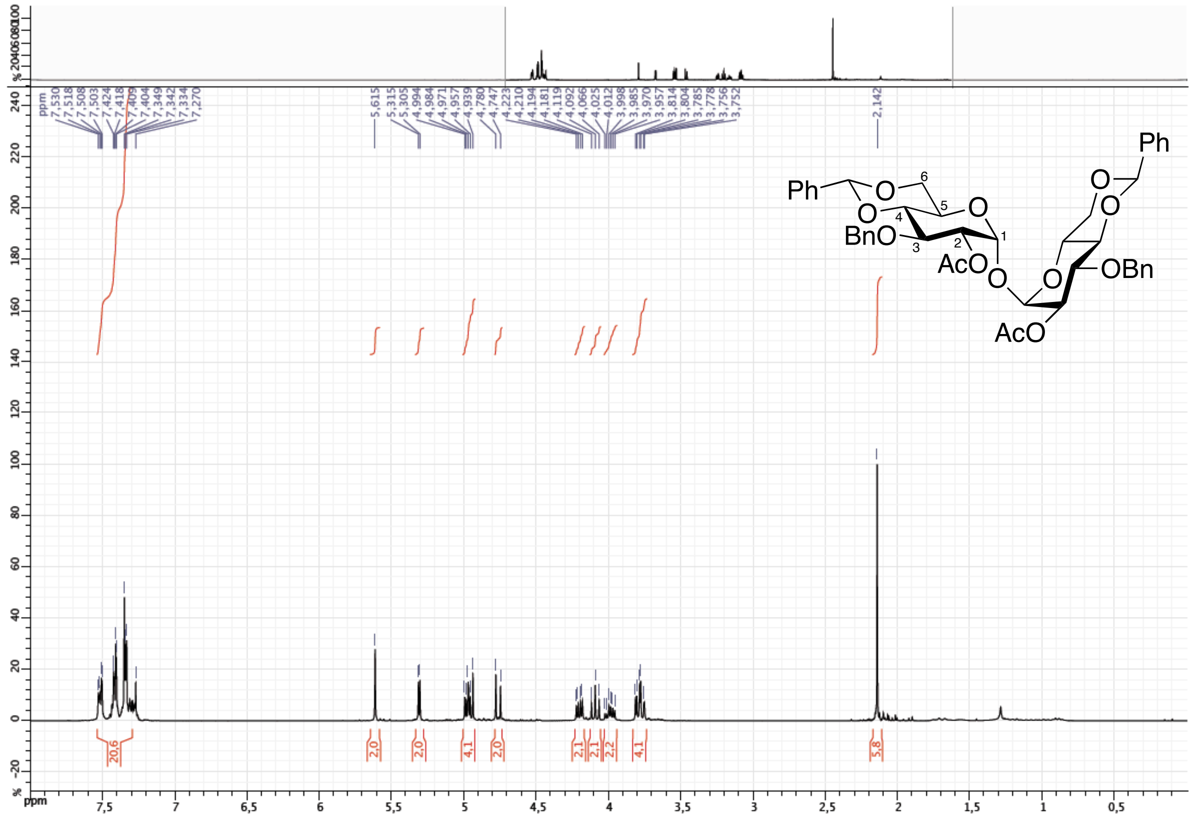
Copy of COSY spectrum of compound 9 (360 MHz, $CDCl_3$)



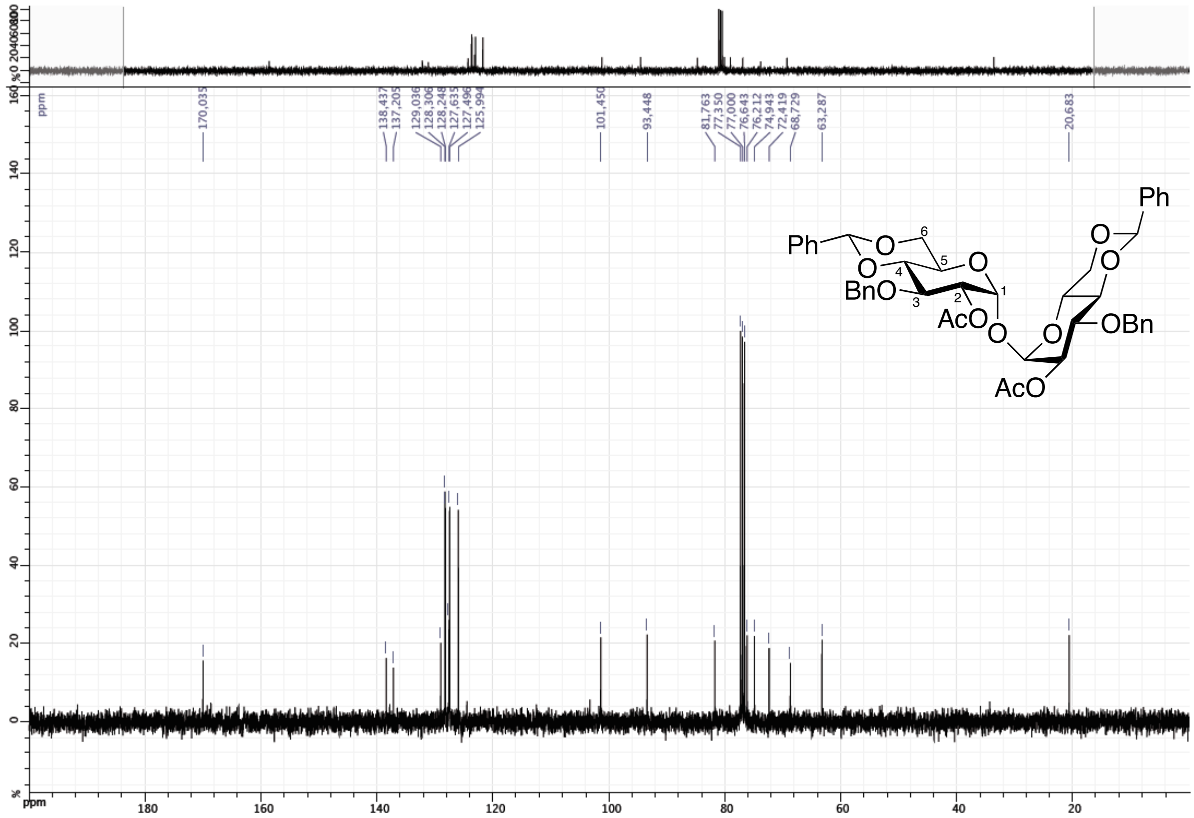
Copy of HSQC spectrum of compound 9 ($CDCl_3$)



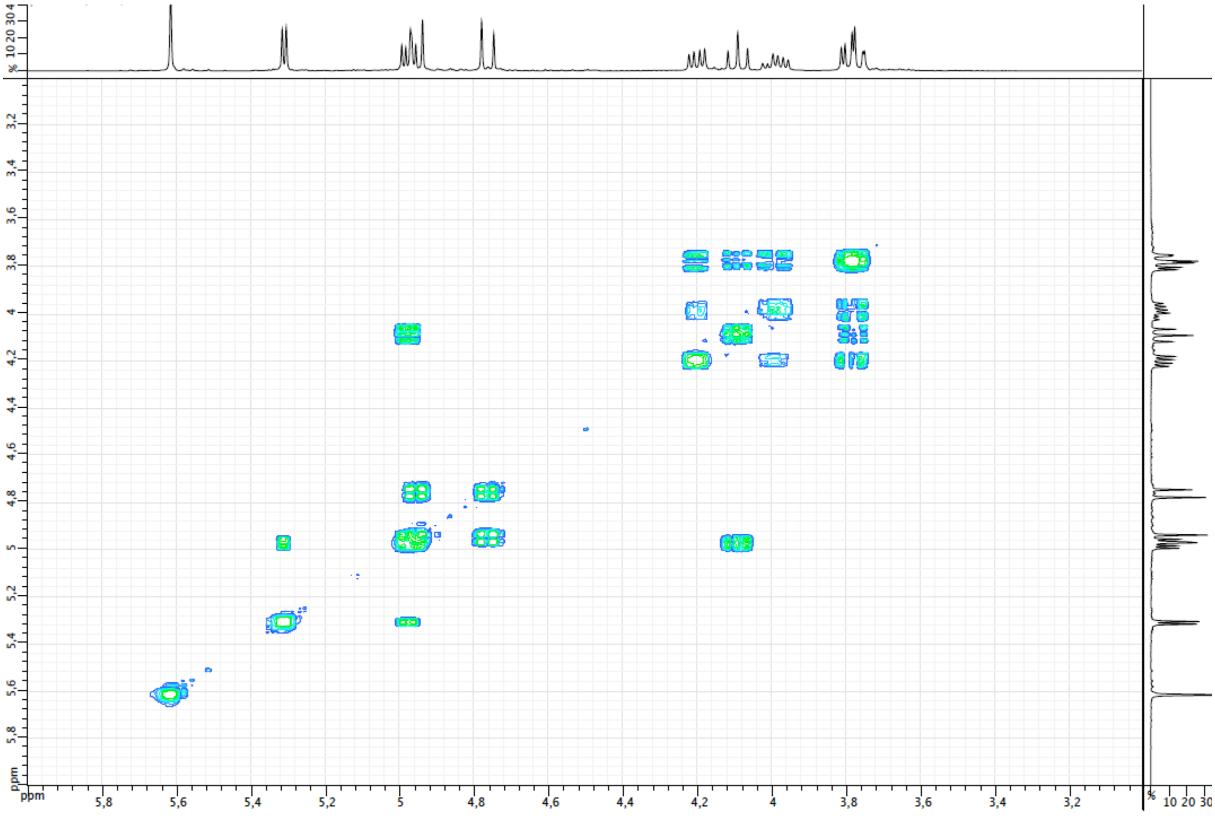
Copy of ^{1}H NMR spectrum of compound 11 (360 MHz, $CDCl_3$)



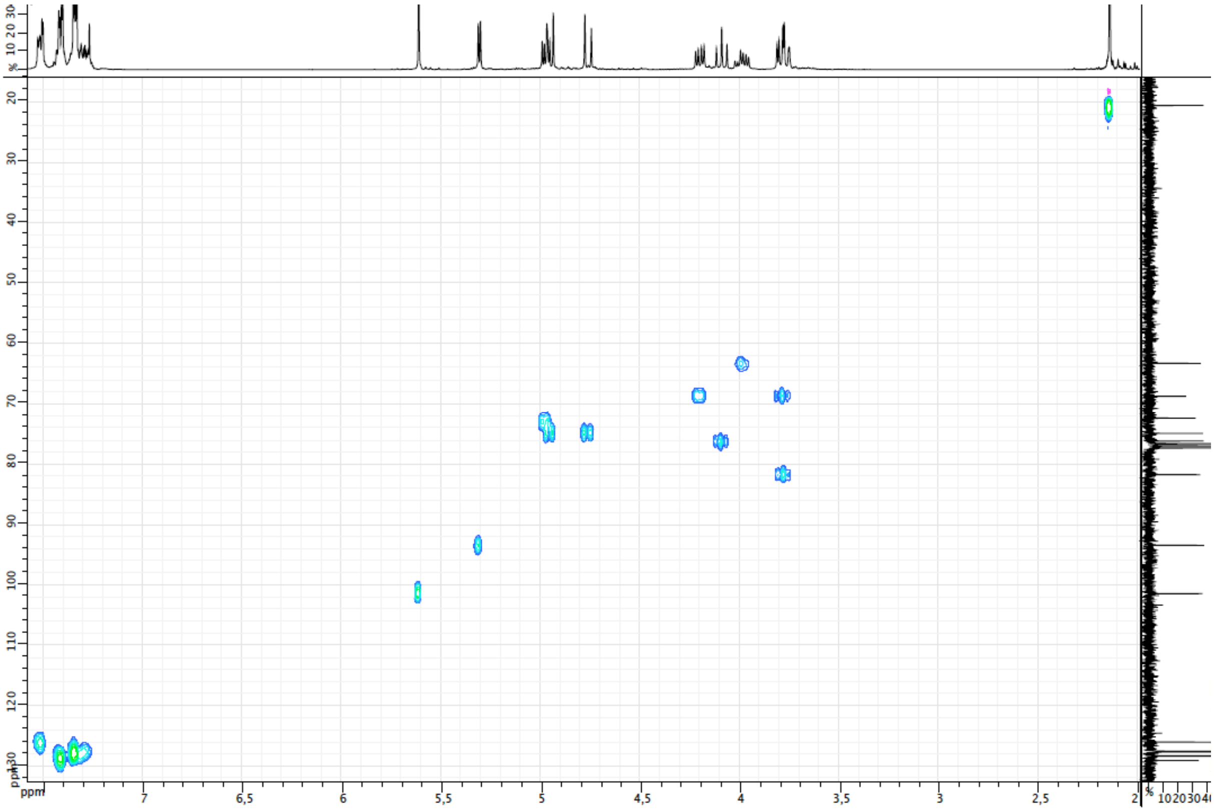
Copy of ^{13}C NMR spectrum of compound 11 (90 MHz, $CDCl_3$)



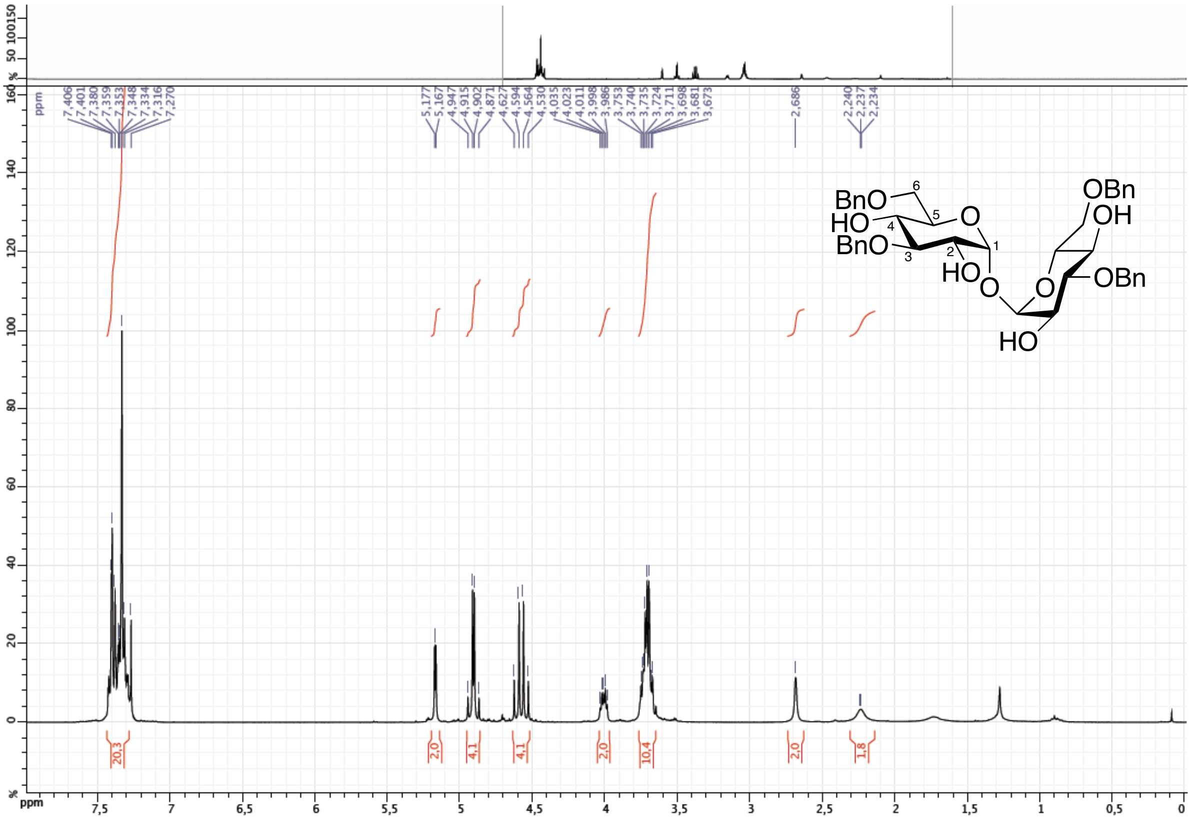
Copy of COSY spectrum of compound 11 (360 MHz, $CDCl_3$)



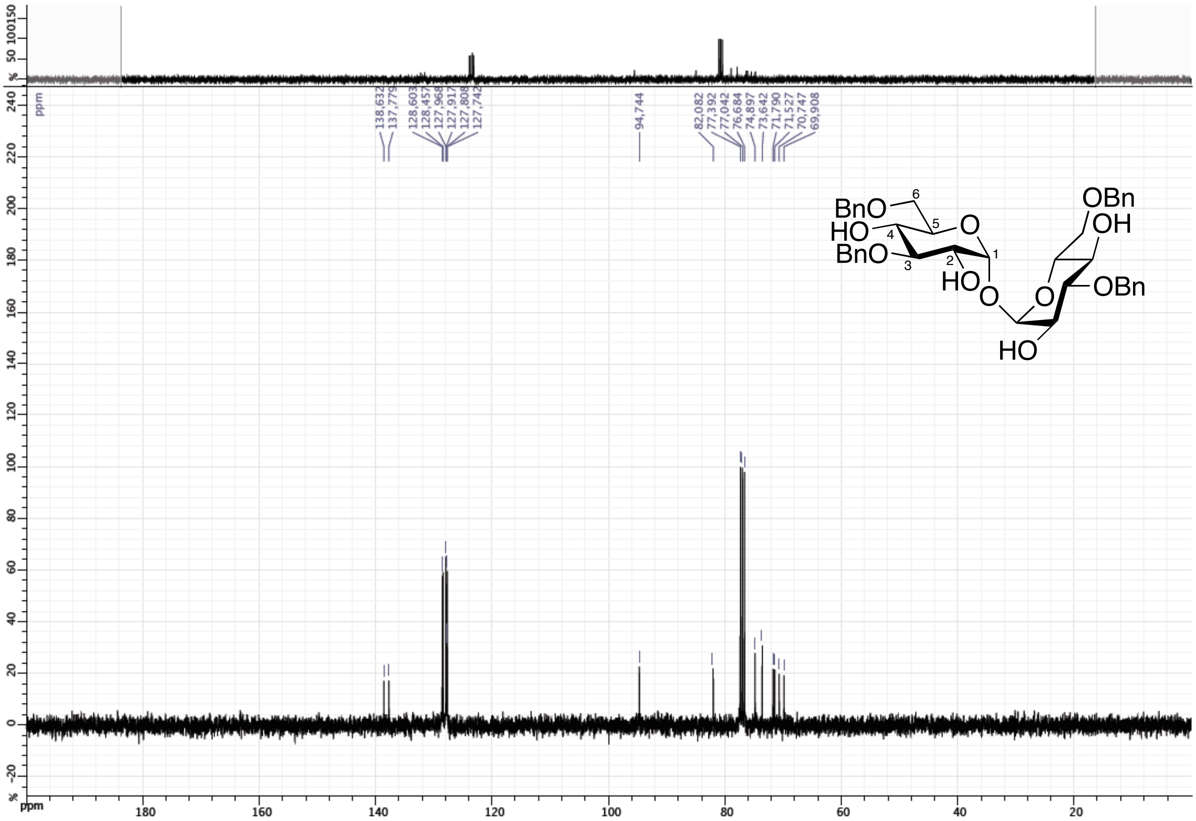
Copy of HSQC spectrum of compound 11 ($CDCl_3$)



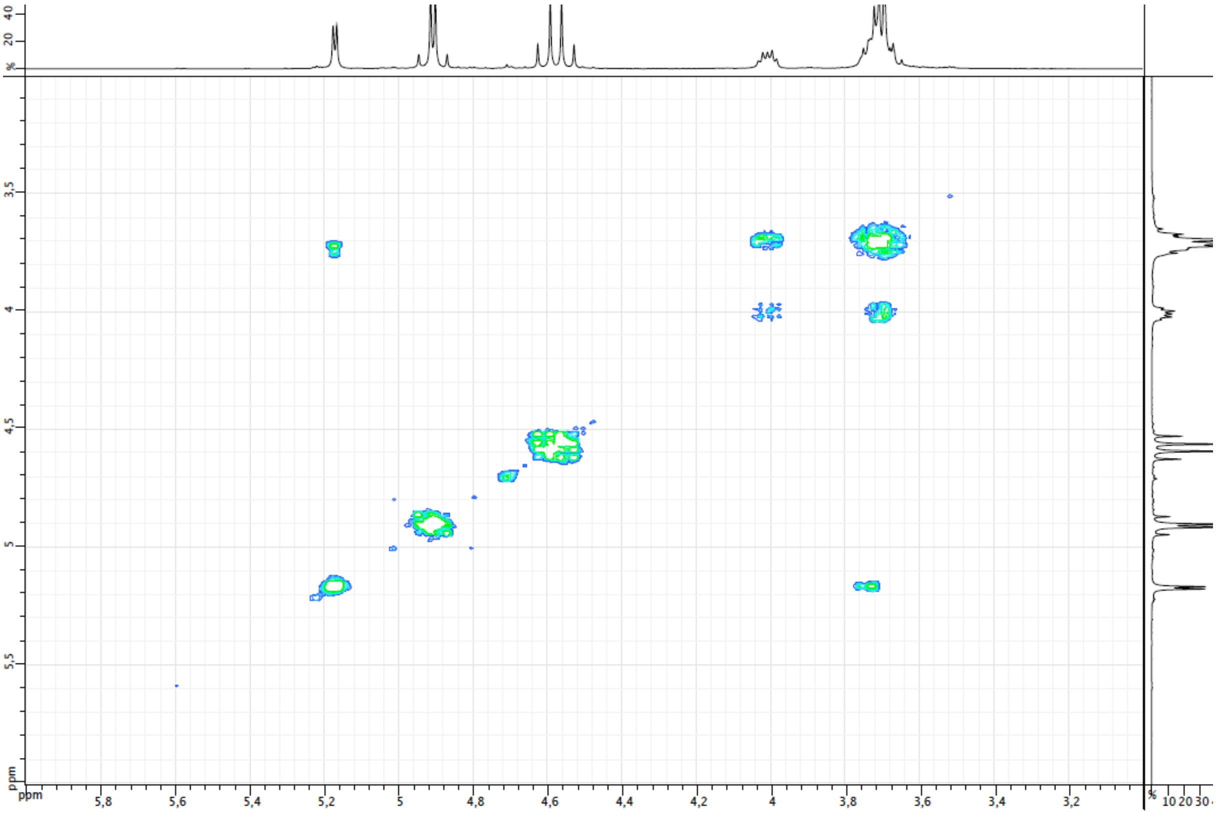
Copy of ^{1}H NMR spectrum of compound 12 (360 MHz, CDCl$_3$)



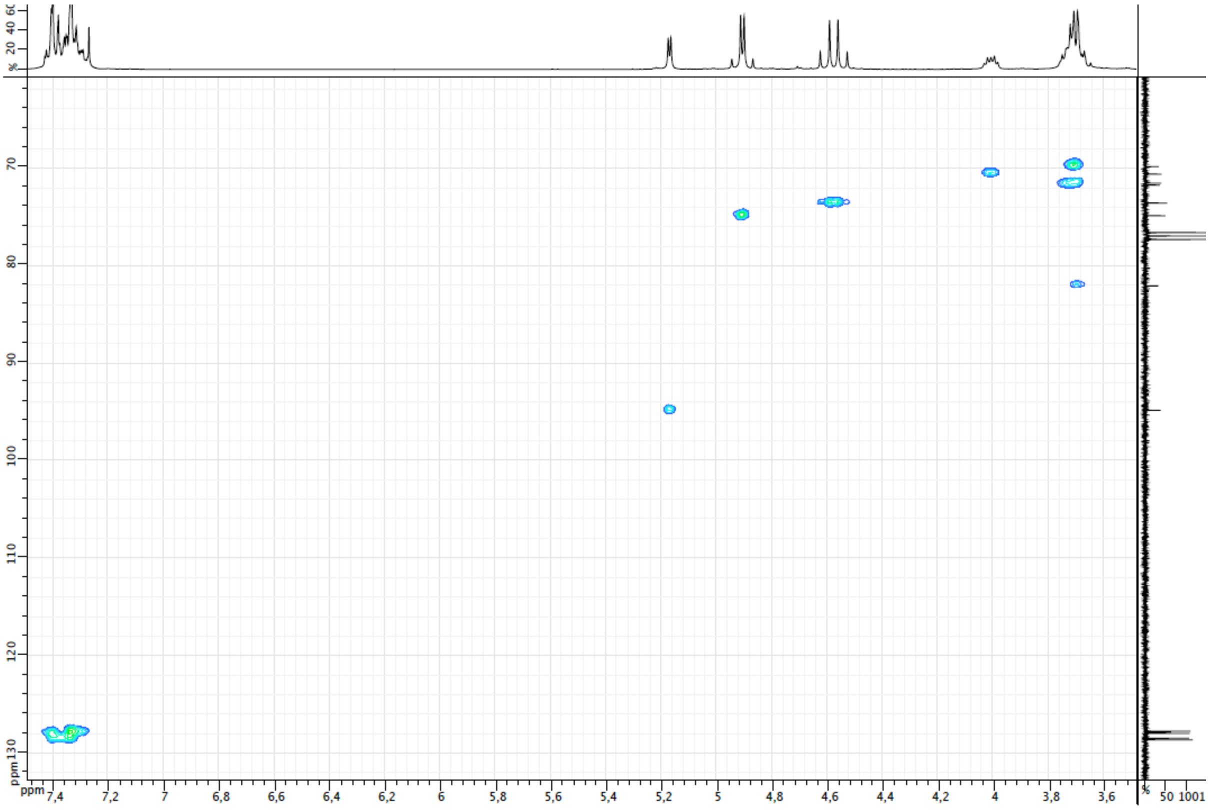
Copy of ^{13}C NMR spectrum of compound 12 (90 MHz, CDCl$_3$)



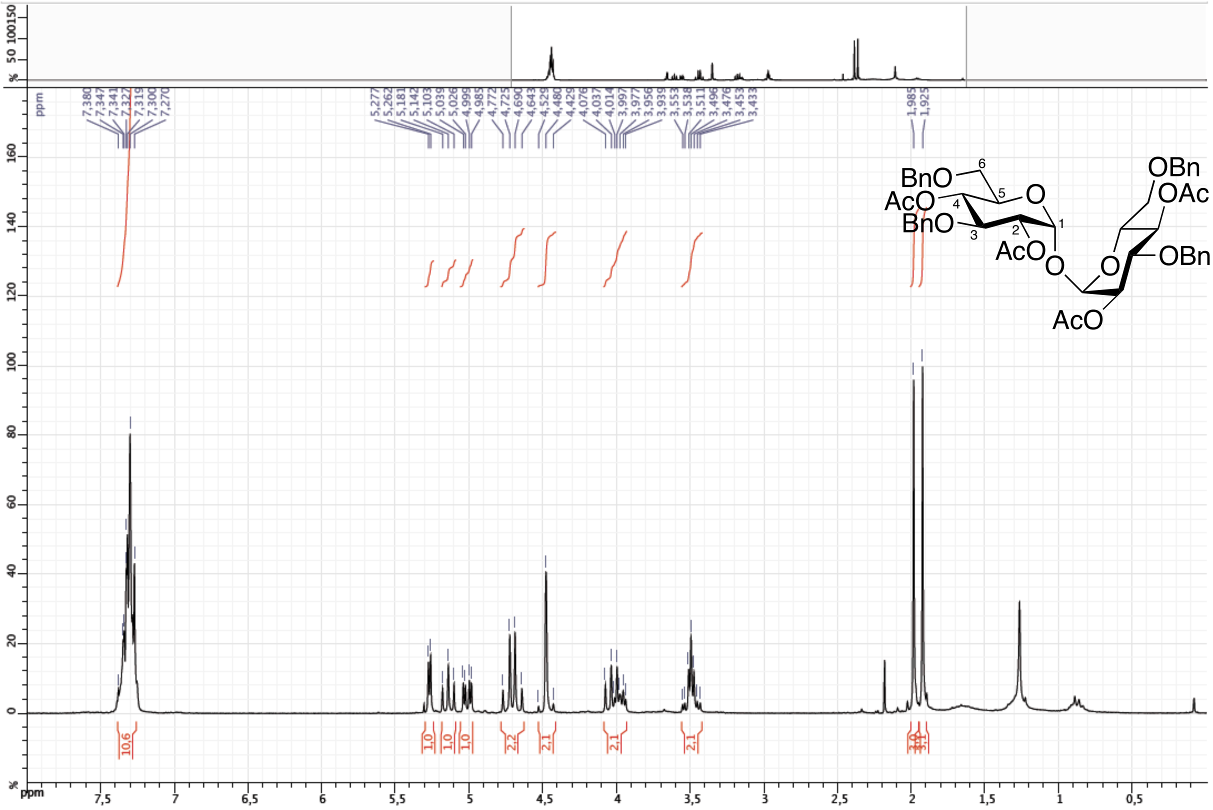
Copy of COSY spectrum of compound 12 (360 MHz, $CDCl_3$)



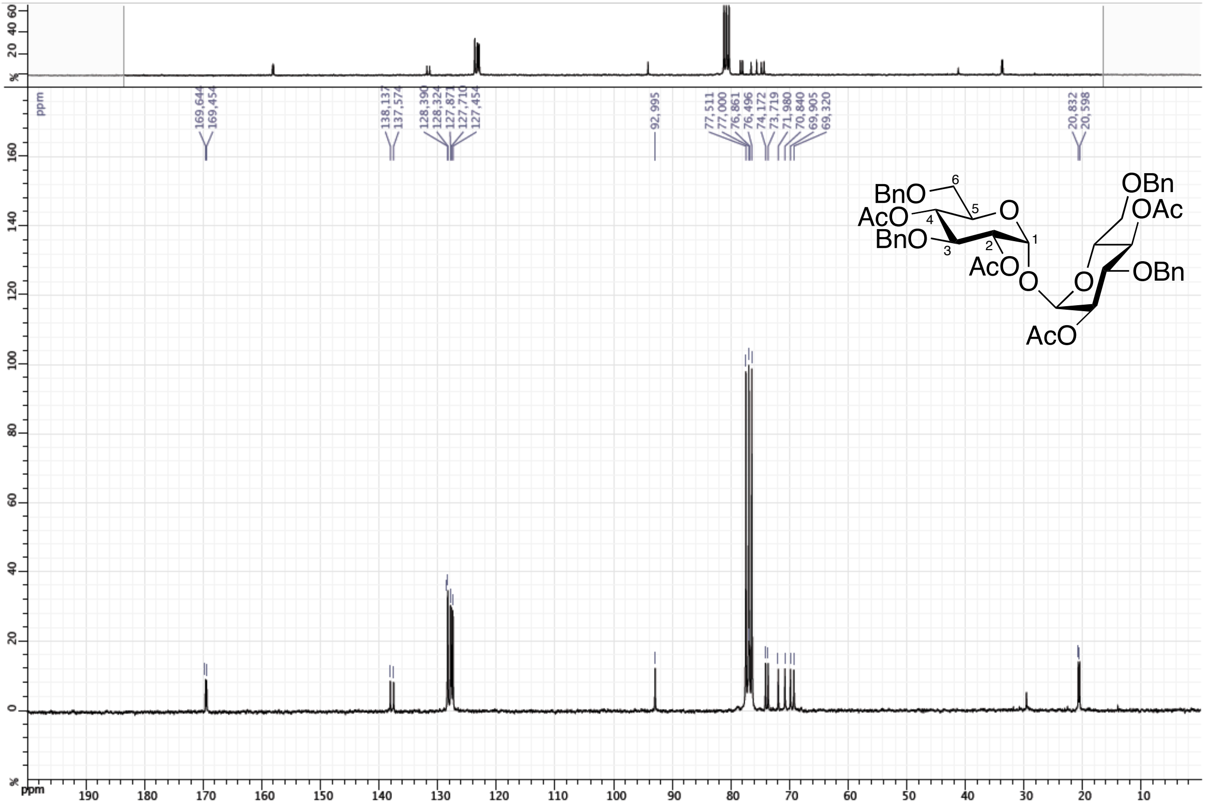
Copy of HSQC spectrum of compound 12 ($CDCl_3$)



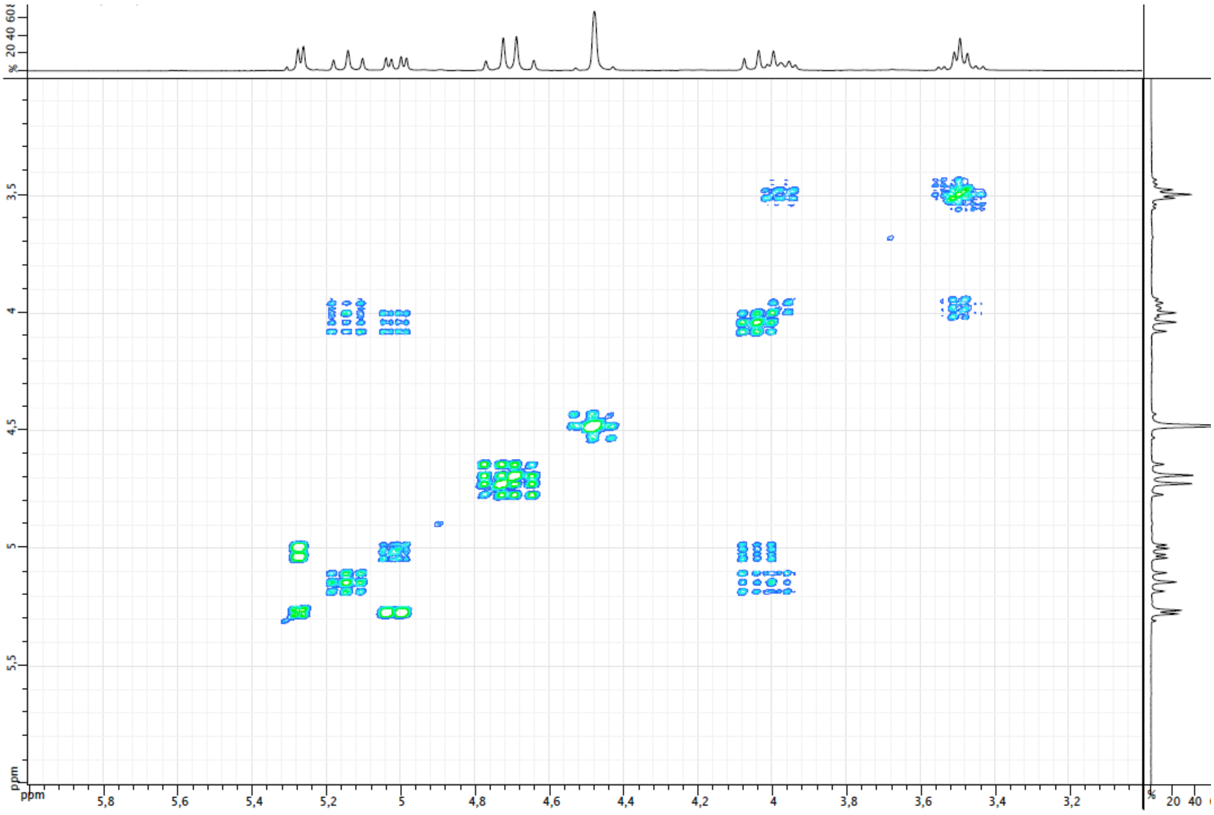
Copy of ^{1}H NMR spectrum of acetylated 12 (250 MHz, $CDCl_3$)



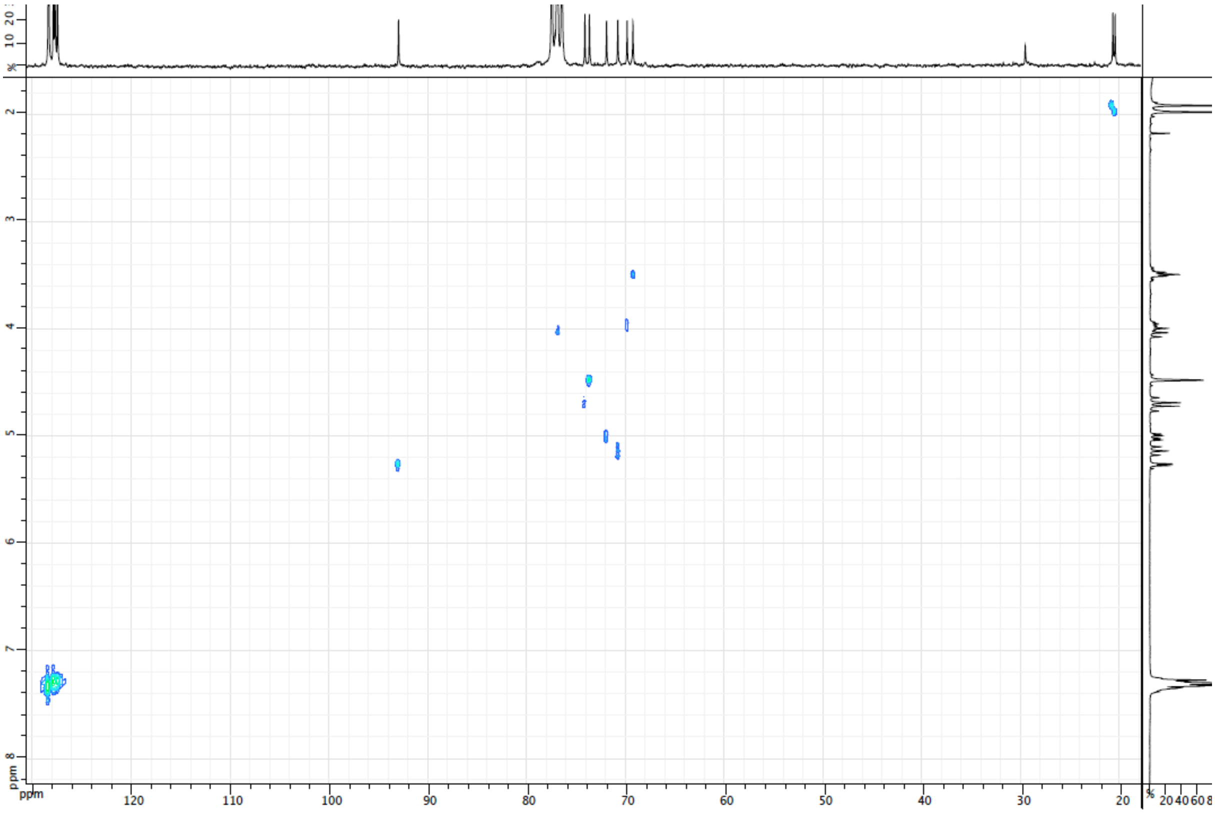
Copy of ^{13}C NMR spectrum of acetylated 12 (62.5 MHz, $CDCl_3$)



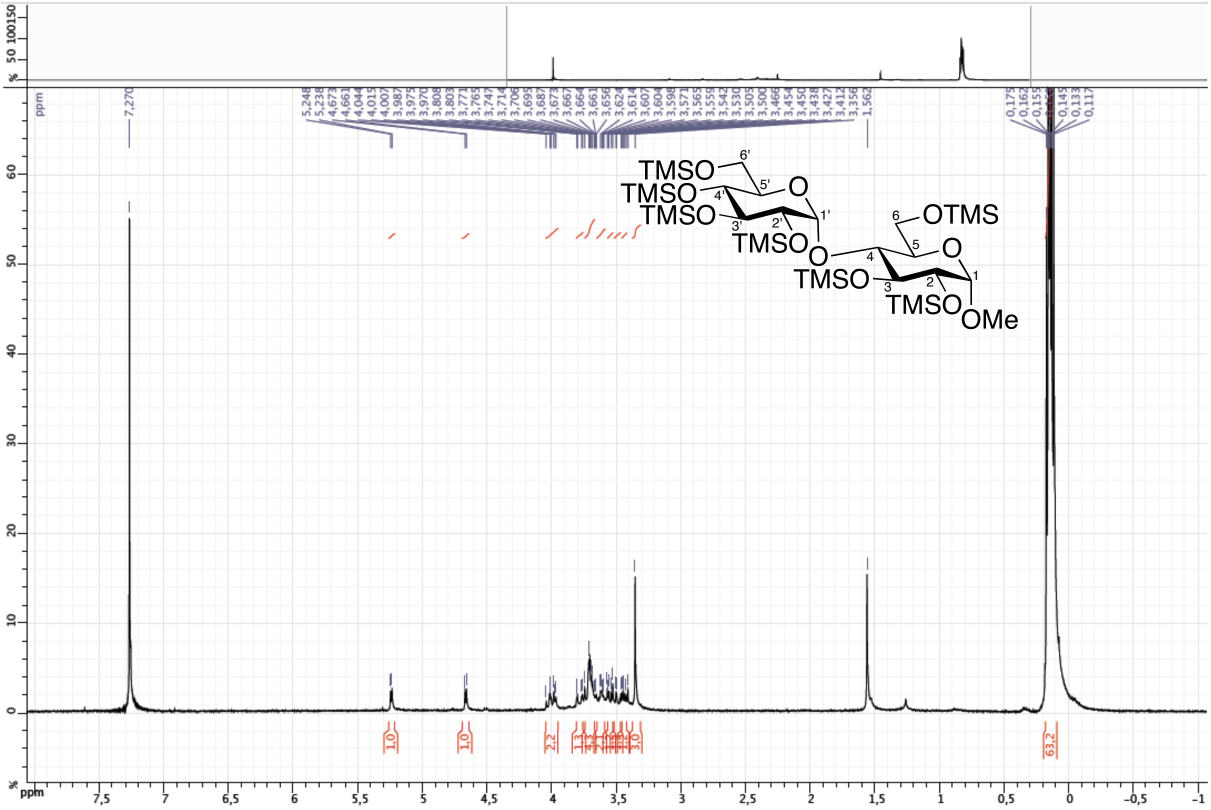
Copy of COSY spectrum of acetylated 12 (250 MHz, $CDCl_3$)



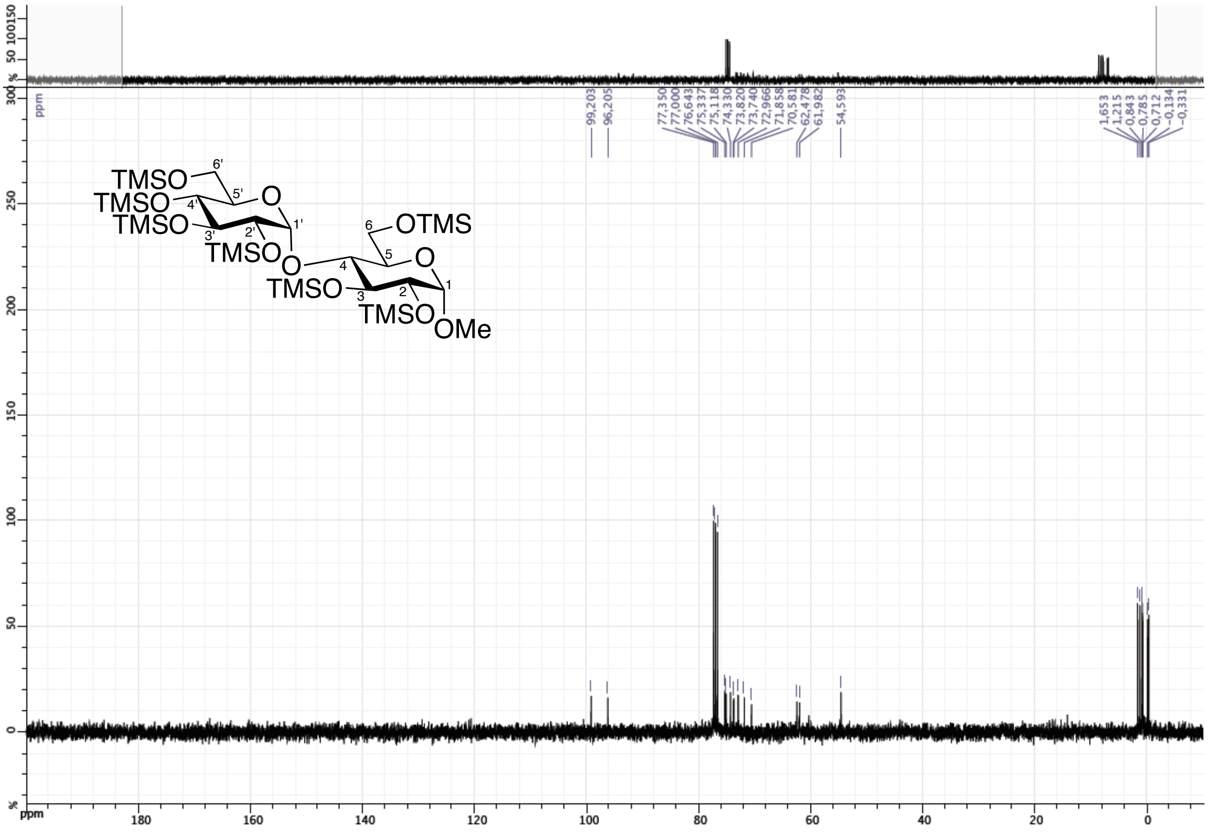
Copy of HSQC spectrum of acetylated 12 ($CDCl_3$)



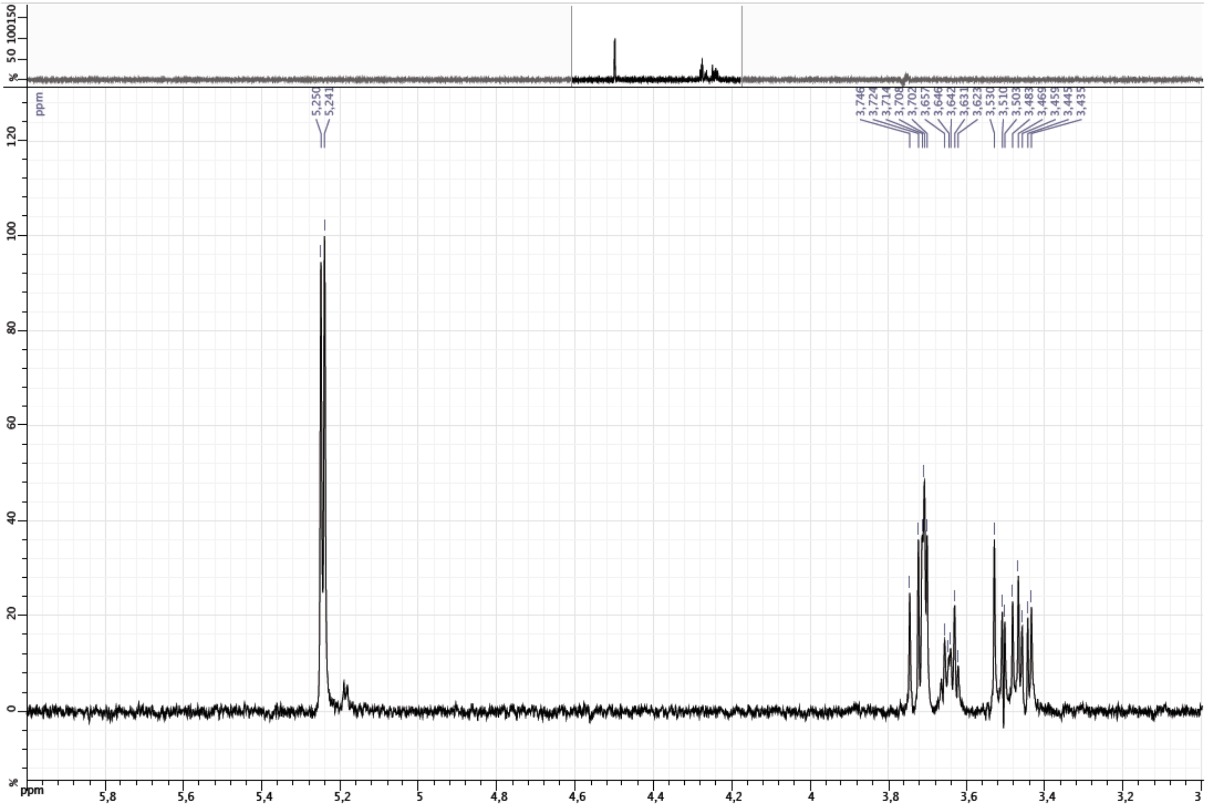
Copy of ^{1}H NMR spectrum of compound 13 (300 MHz, $CDCl_3$)



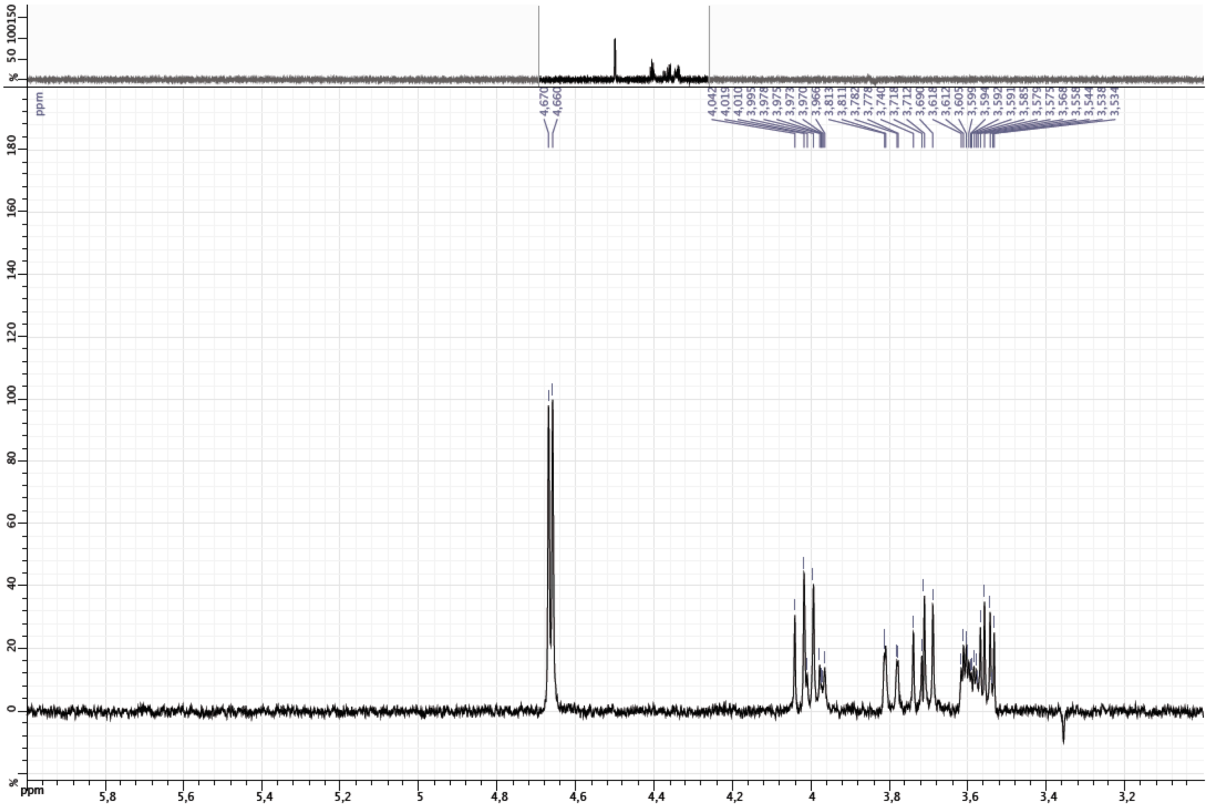
Copy of ^{13}C NMR spectrum of compound 13 (90 MHz, $CDCl_3$)



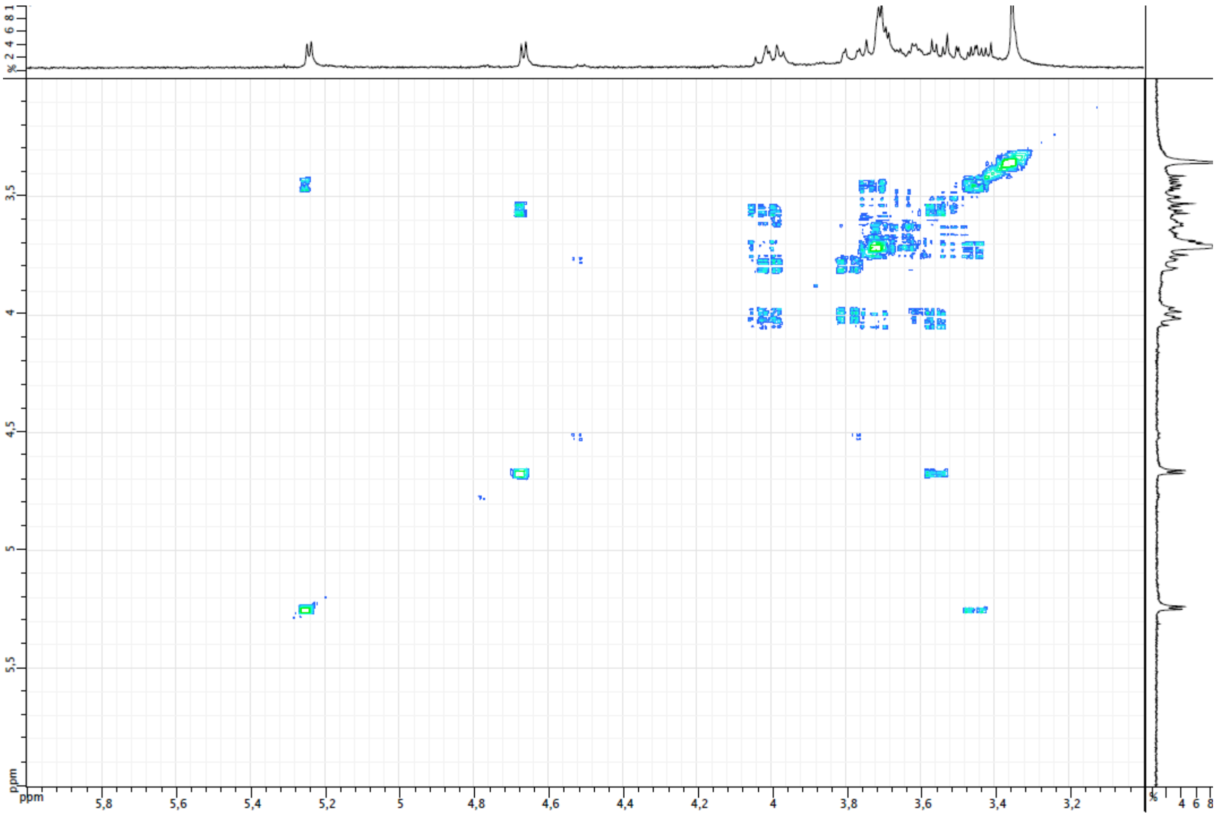
Copy of selective 1D TOCSY spectrum of compound 13 (360 MHz, O1: 1890 Hz, $CDCl_3$)



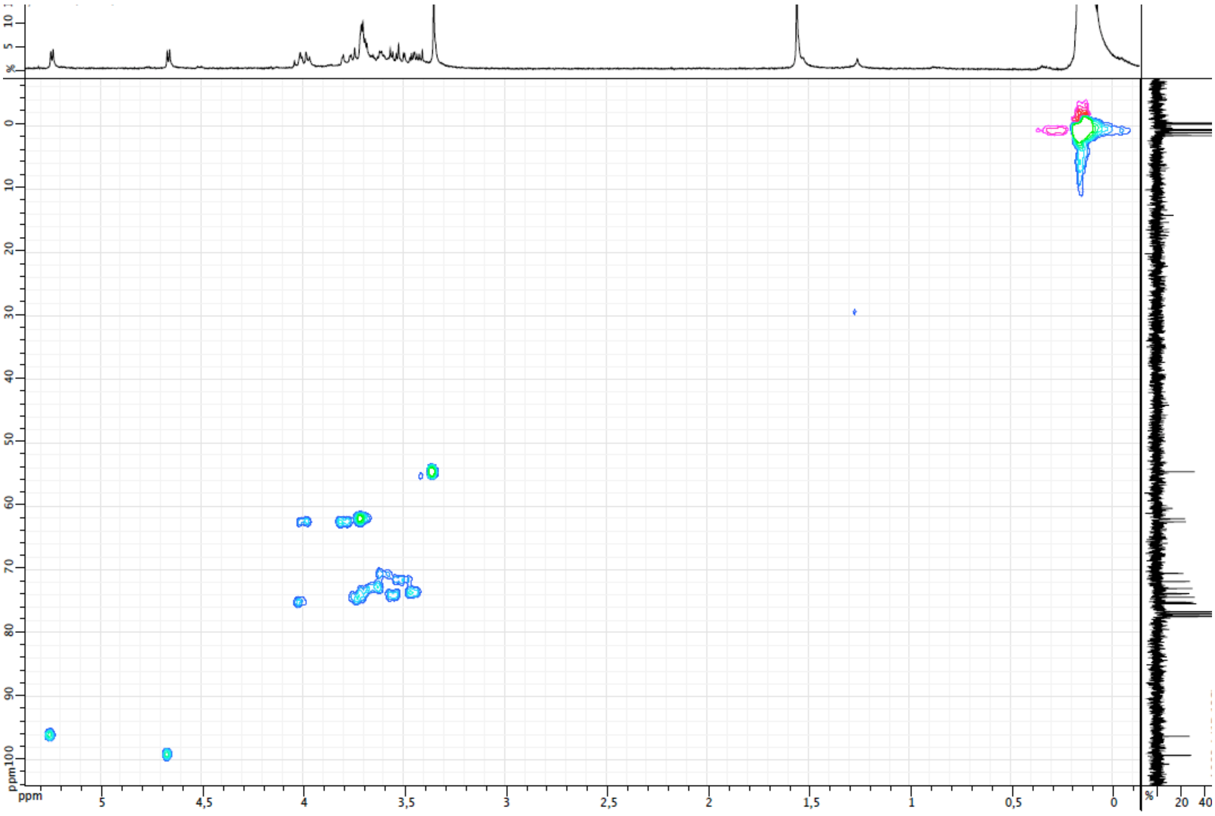
Copy of selective 1D TOCSY spectrum of compound 13 (360 MHz, O1: 1680 Hz, $CDCl_3$)



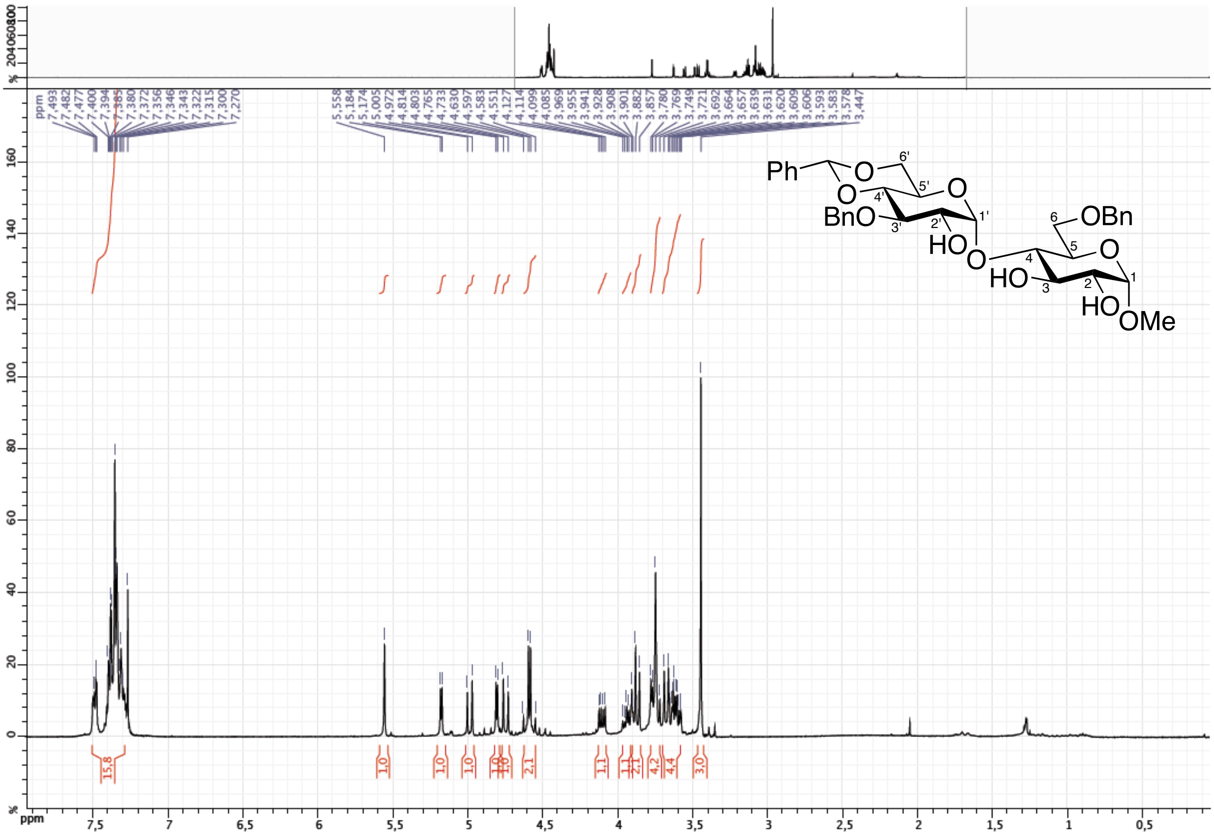
Copy of COSY spectrum of compound 13 (360 MHz, $CDCl_3$)



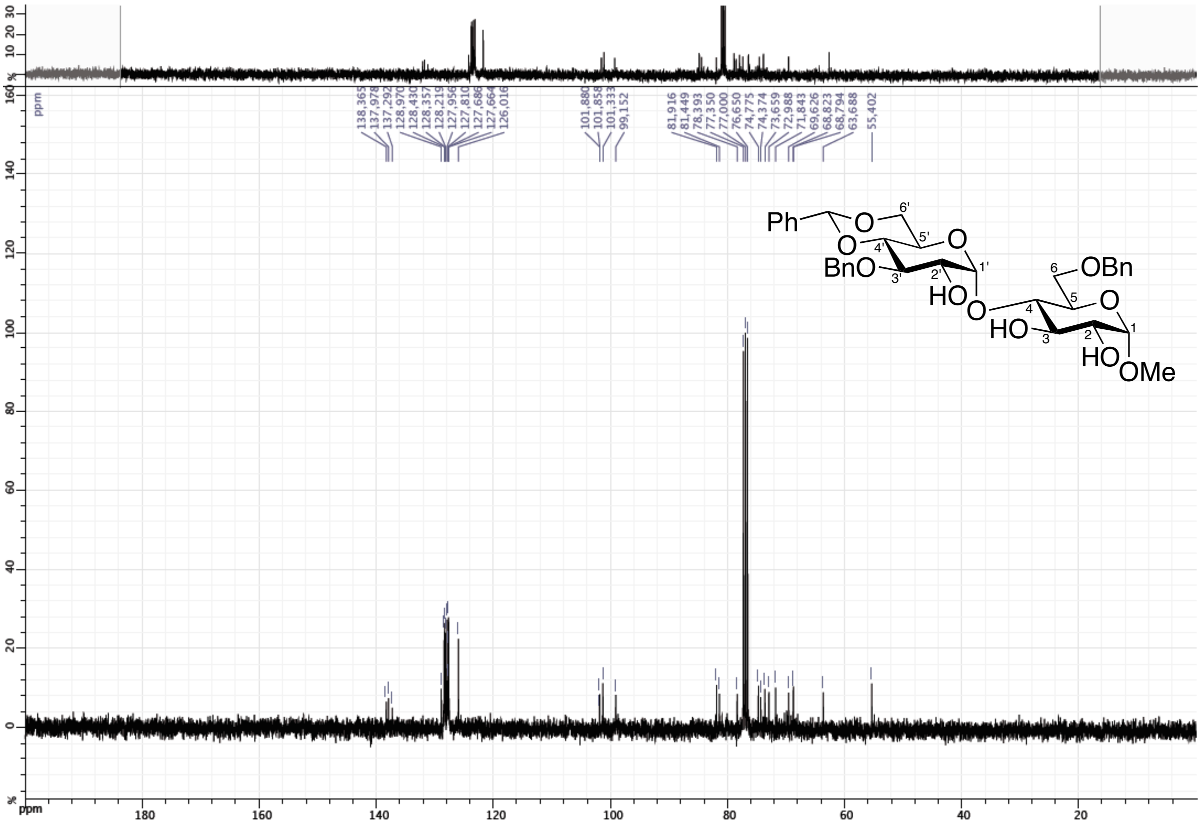
Copy of HSQC spectrum of compound 13 ($CDCl_3$)



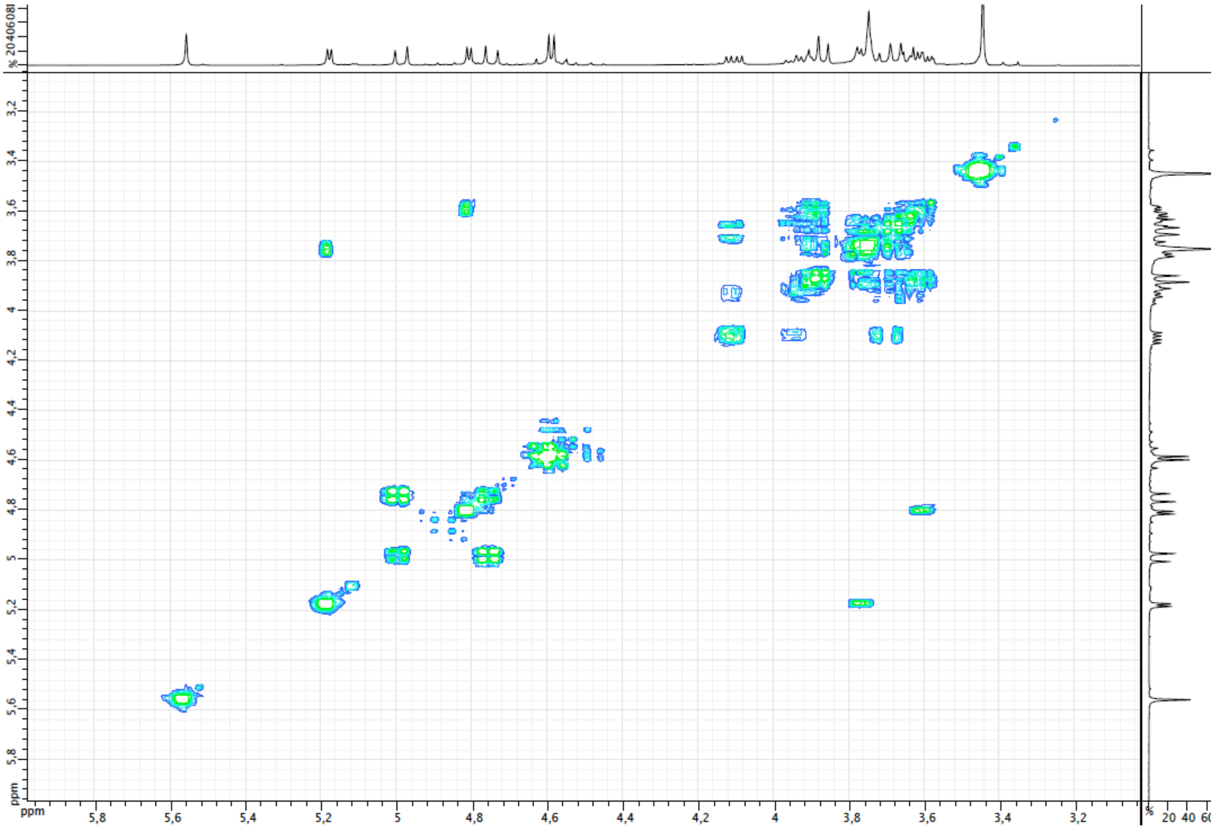
Copy of ^{1}H NMR spectrum of compound 14 (360 MHz, $CDCl_3$)



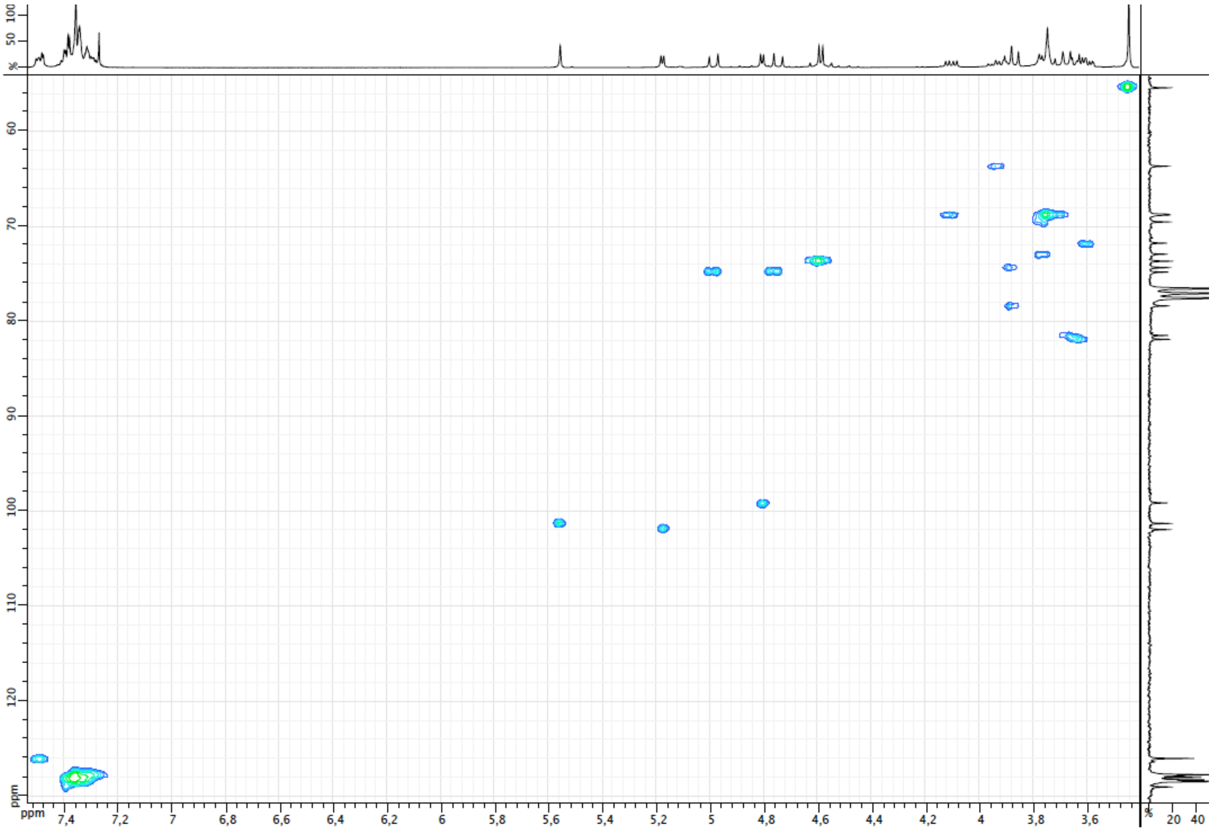
Copy of ^{13}C NMR spectrum of compound 14 (90 MHz, $CDCl_3$)



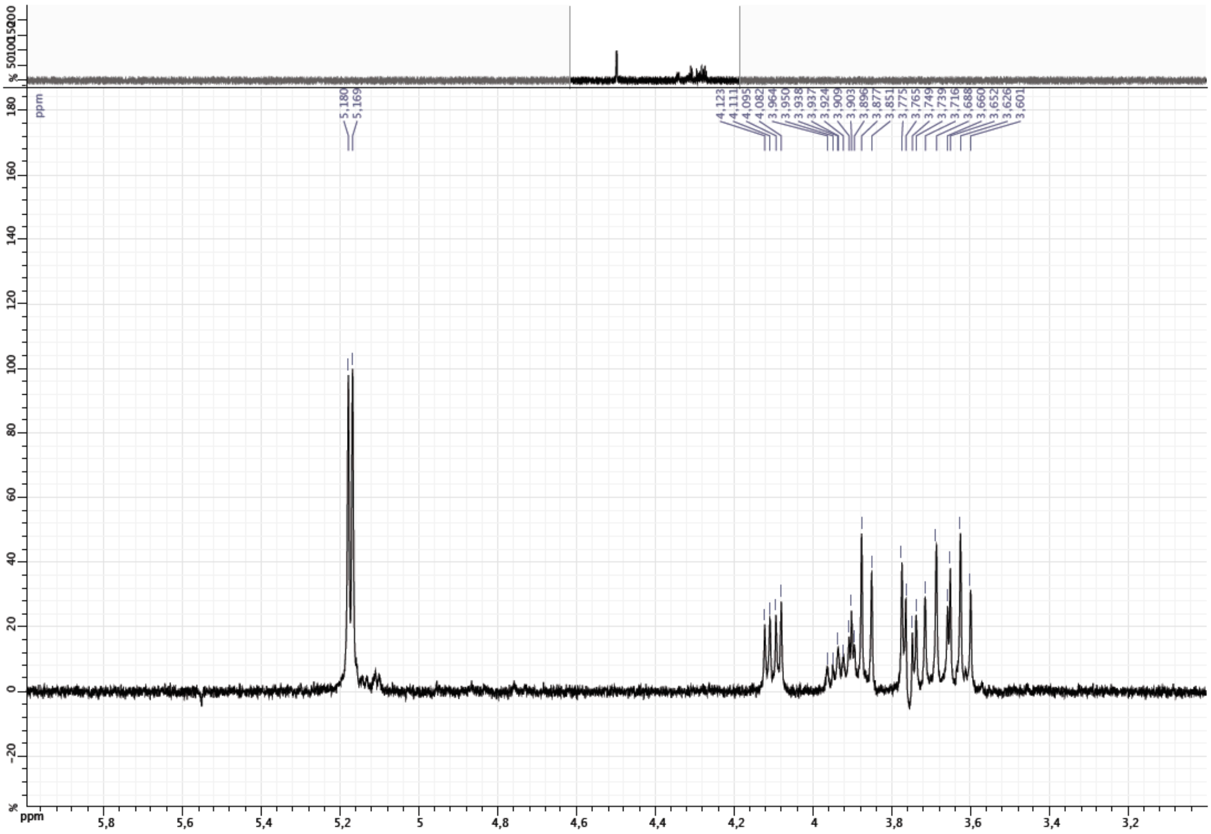
Copy of COSY spectrum of compound 14 (360 MHz, CDCl$_3$)



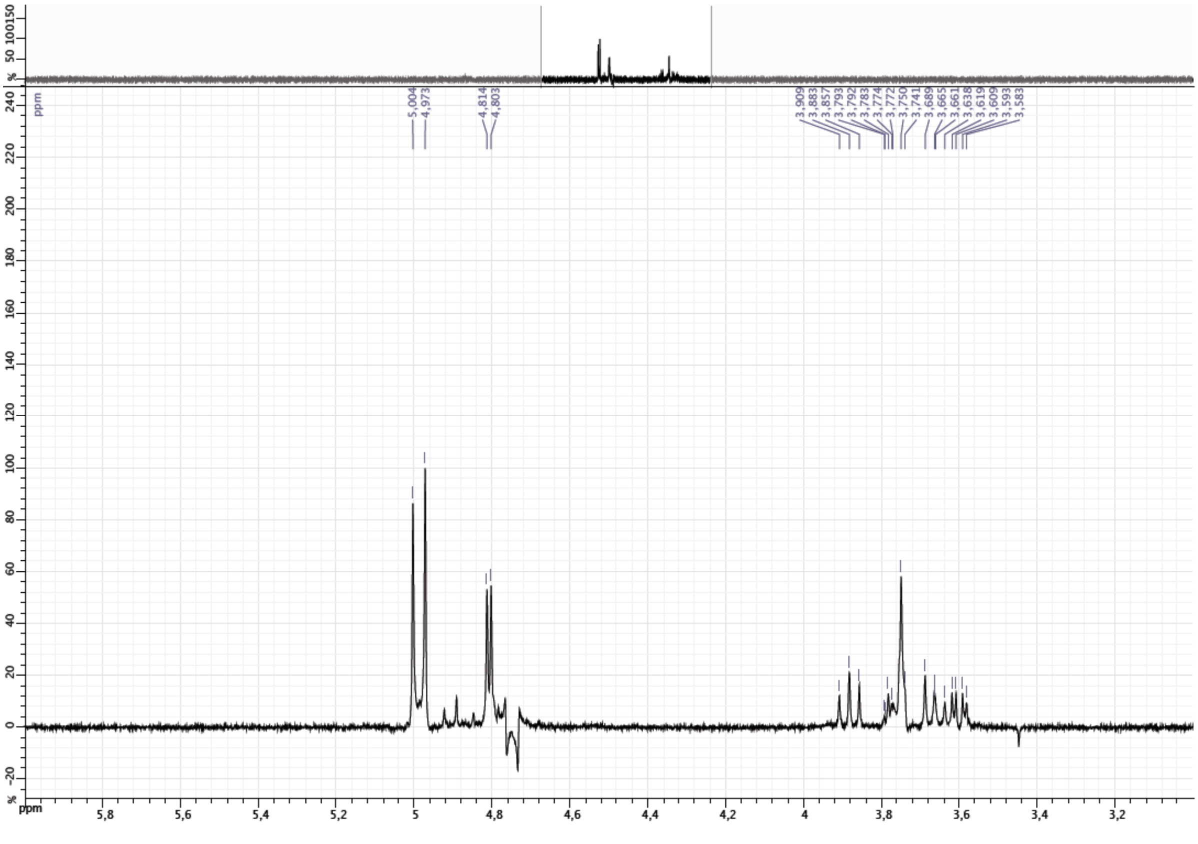
Copy of HSQC spectrum of compound 14 (CDCl$_3$)



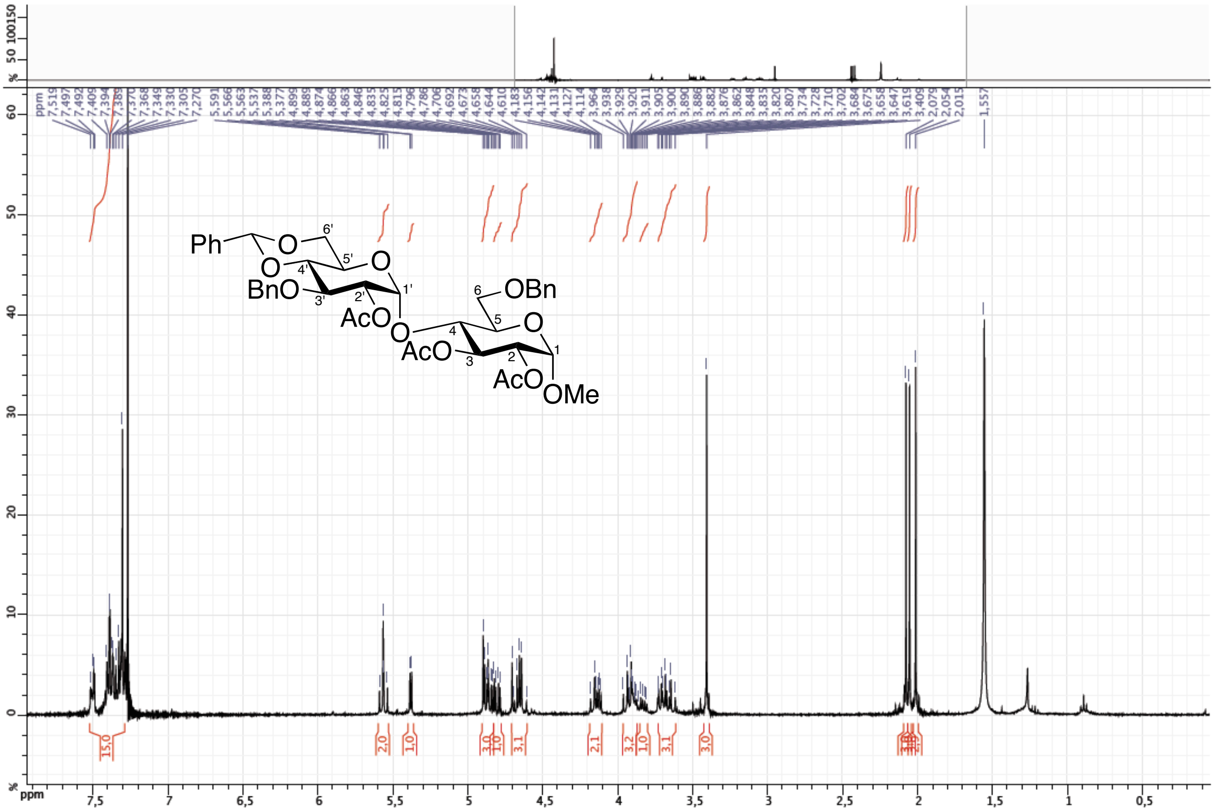
Copy of selective 1D TOCSY spectrum of compound 14 (360 MHz, O1: 1863 Hz, $CDCl_3$)



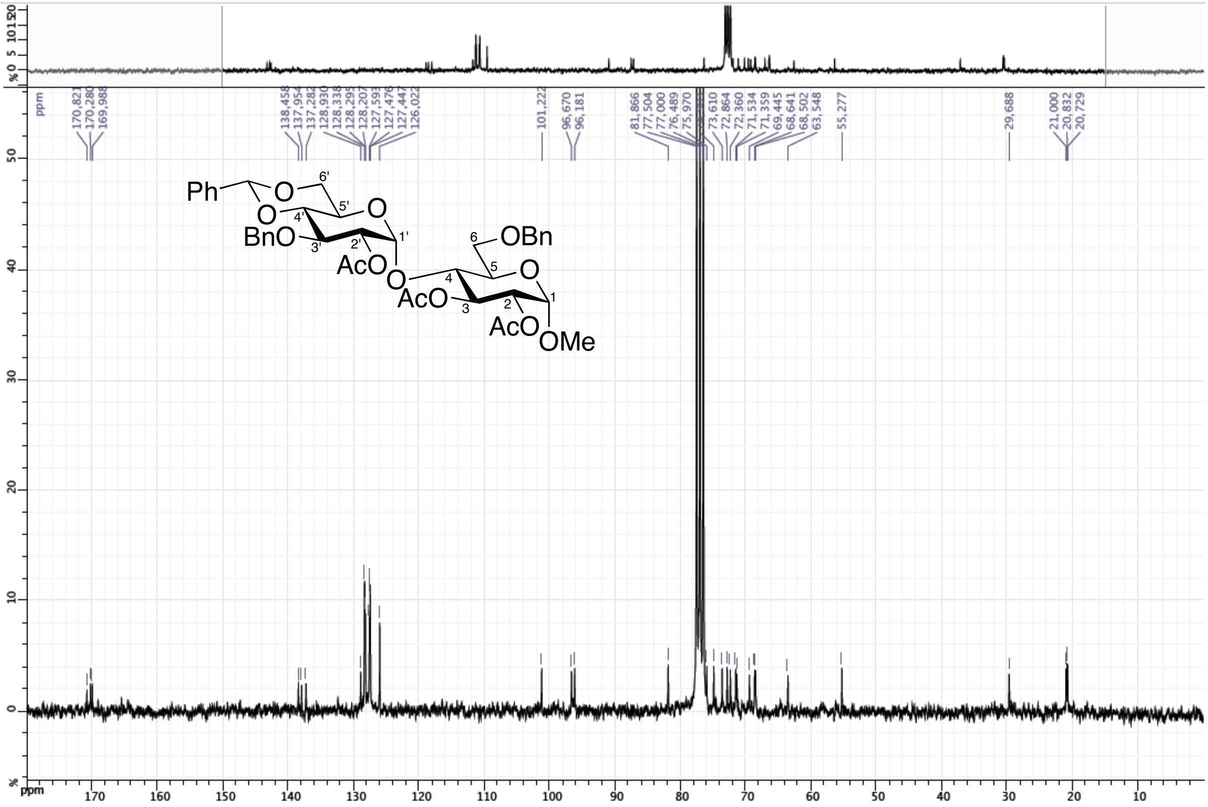
Copy of selective 1D TOCSY spectrum of compound 14 (360 MHz, O1: 1731 Hz, $CDCl_3$)



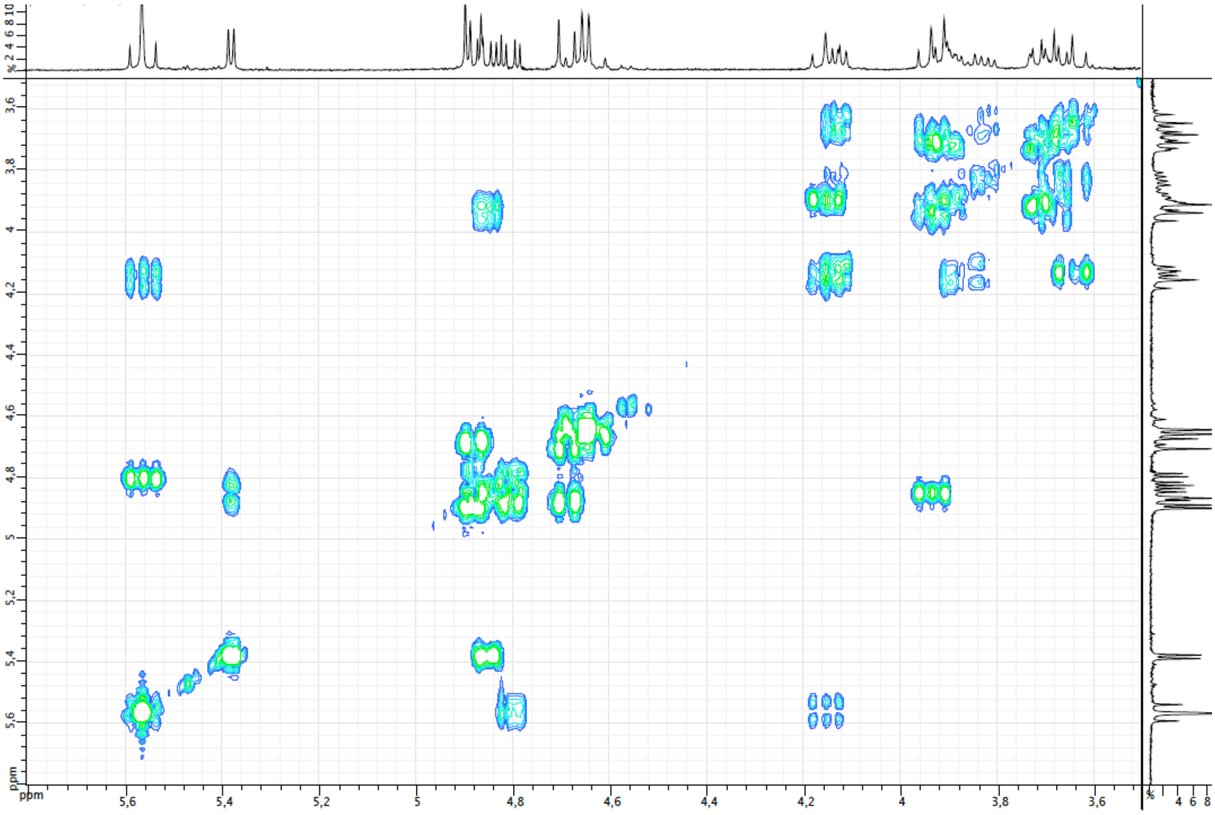
Copy of ^{1}H NMR spectrum of acetylated 14 (360 MHz, $CDCl_3$)



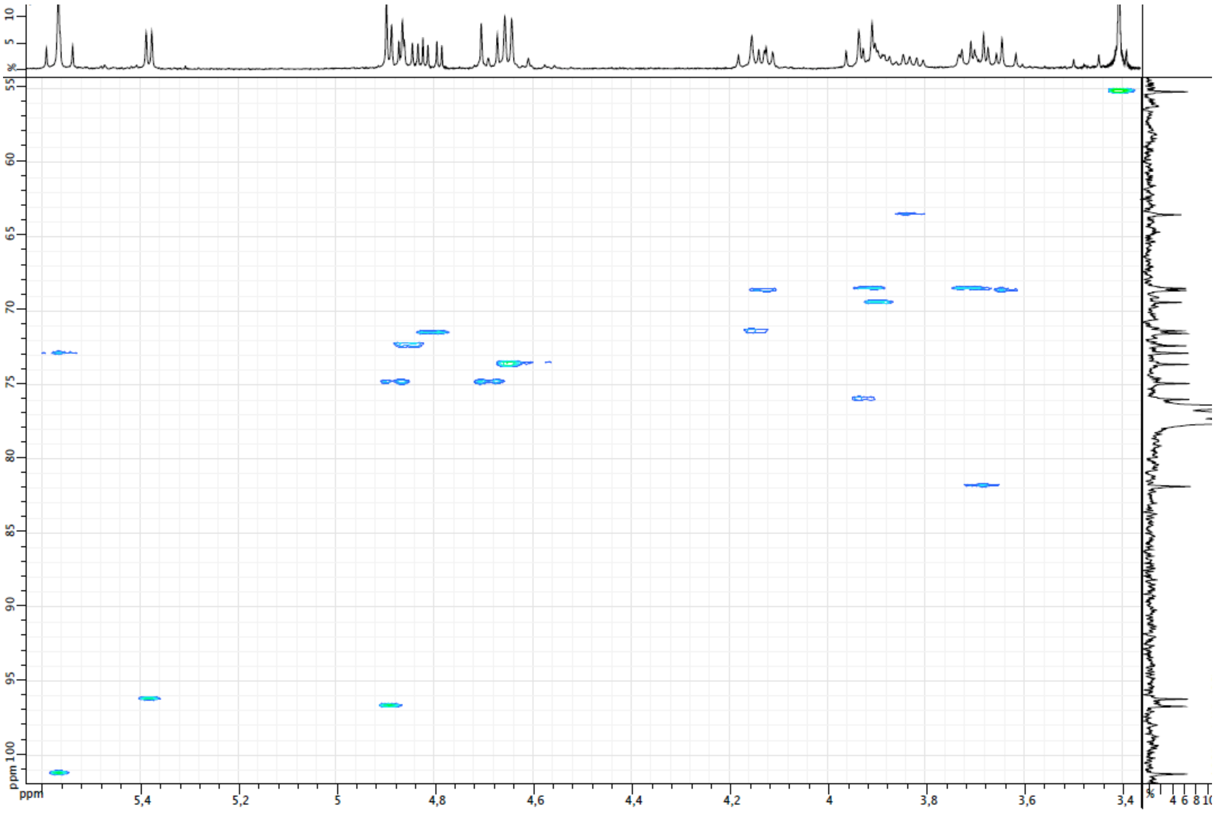
Copy of ^{13}C NMR spectrum of acetylated 14 (62.5 MHz, $CDCl_3$)



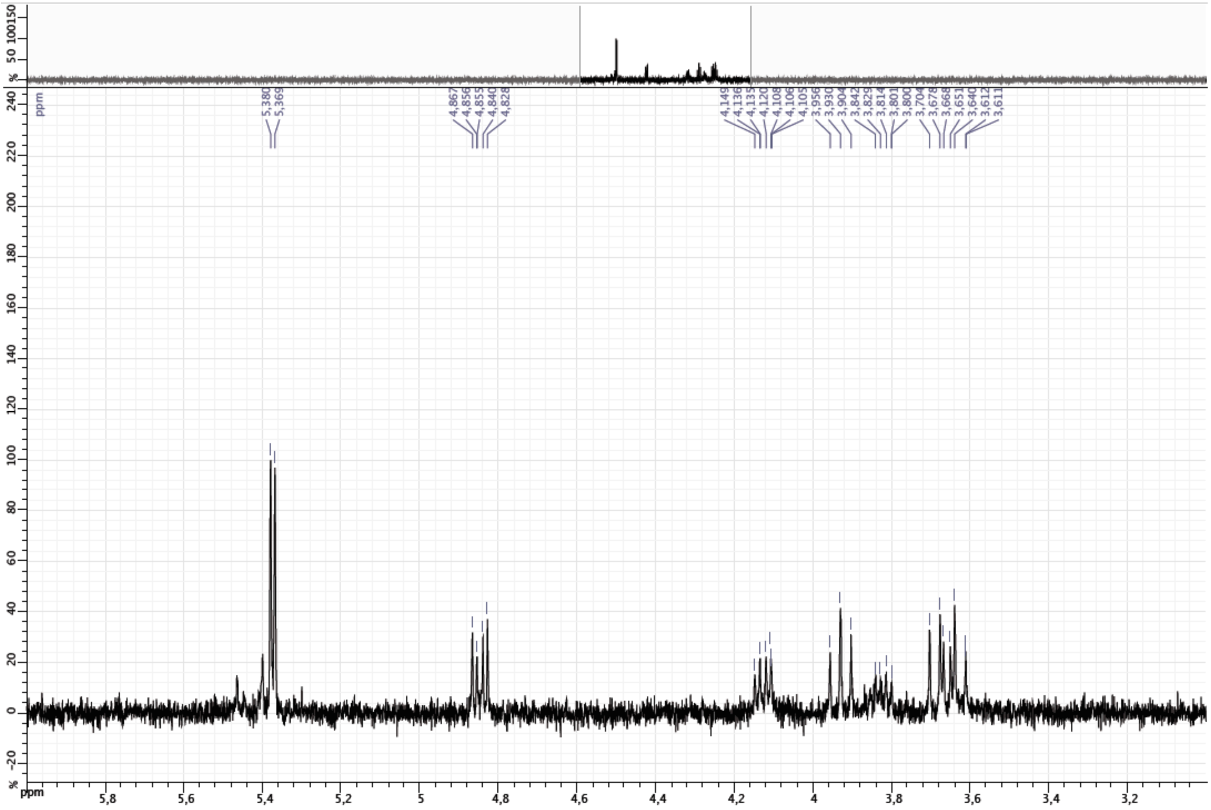
Copy of COSY spectrum of acetylated 14 (360 MHz, $CDCl_3$)



Copy of HSQC spectrum of acetylated 14 ($CDCl_3$)



Copy of selective 1D TOCSY spectrum of acetylated 14 (360 MHz, O1: 1938 Hz, CDCl$_3$)



Copy of selective 1D TOCSY spectrum of acetylated 14 (360 MHz, O1: 2003 Hz, CDCl$_3$)