Supporting information

for

2-Allylphenyl glycosides as complementary building blocks for oligosaccharide and glycoconjugate synthesis

Hemali D. Premathilake and Alexei V. Demchenko*

Address: Department of Chemistry and Biochemistry, University of Missouri – St. Louis, One University Boulevard, St. Louis, MO 63121, USA

Email: Alexei V. Demchenko - demchenkoa@umsl.edu

*Corresponding author

Experimental procedures, extended experimental data,
^{1}H and ^{13}C NMR spectra for all new compounds.

Content

Synthesis of glycosyl donors

2-Allylphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1a). 2-Allylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (see below for the synthesis, 1.00 g, 2.16 mmol) was dissolved in methanol (8 mL), and the pH was adjusted (pH 9) by careful addition of a 1 M solution of $NaOCH_3$ in MeOH (~0.1 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until neutral pH was reached. The resin was filtered off and rinsed with methanol (3 × 5 mL). The combined filtrate (~30 mL) was concentrated in vacuo and dried. The resultant solid was dissolved in DMF (14 mL) and benzyl bromide (1.41 mL, 11.82 mmol) was added. The resulting mixture was cooled to 0 °C and NaH (0.426 g, 17.74 mmol) was added portionwise. The reaction mixture was allowed to gradually warm to rt. After stirring for 1 h at rt, the reaction was quenched by stirring with ice water (50 mL). The organic phase was extracted with ethyl acetate/diethyl ether 1/1 (v/v, 3 × 40 mL) and the combined organic extract was washed with water (3 × 20 mL), the organic phase was separated, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford the title compound (1.3 g, 92%) as white crystals. Analytical data for **1a**: R_f 0.50 (ethyl acetate/hexanes 1:5, v/v); mp 94–97 °C (diethyl ether/hexanes); $[\alpha]_D^{23}$ +16.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 3.34–3.49 (m, 2H, PhC*H*$_2$CH=CH$_2$), 3.54–3.55 (m, 1H, H-5), 3.60–3.76 (m, 5H, H-2, H-3, H-4, H-6a, H-6b), 4.43–4.54 (m, 2H, C*H*$_2$Ph), 4.76–4.94 (m, 4H, 2×C*H*$_2$Ph), 4.94–5.00 (m, 4H, $J_{1,2}$ = 7.8 Hz, H-1, PhC*H*$_2$CH=C*H*$_2$, 1/2×C*H*$_2$Ph), 5.97–6.10 (m, 1H, PhCH$_2$*CH*=CH$_2$), 6.94–7.28 (m, 24H, aromatic) ppm; ^{13}C NMR: δ 34.3, 69.0, 73.7, 75.2, 75.3, 75.4, 76.0, 77.4, 78.0, 82.3, 85.1, 101.5, 115.6, 116.1, 122.8, 127.6, 127.7, 127.8, 127.9 (×4), 128.0 (×2),

128.1 (×2), 128.2 (×2), 128.5 (×2), 128.6 (×3), 128.7 (×2), 129.8, 130.1, 136.9, 138.2, 138.3, 138.4, 138.7, 155.1 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{43}H_{44}O_6Na^+$, 679.3036; found, 679.3058.

2-Allylphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (1b). 2-Allylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (see below for the synthesis, 5.40 g, 11.63 mmol) was dissolved in methanol (44 mL), and the pH was adjusted to pH 9 by careful addition of 1 M solution of $NaOCH_3$ in MeOH (~0.2 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until neutral pH. The resin was filtered off and washed with methanol (3 × 5 mL). The combined filtrate was concentrated in vacuo and dried. The residue was dissolved in dry pyridine (70 mL), the mixture was cooled to 0 °C and benzoyl chloride (7.2 mL, 62.5 mmol) was added dropwise. The reaction mixture was allowed to gradually warm to rt. After stirring for 1 h at rt, the reaction was quenched by the addition of methanol (5 mL). The resulting mixture was evaporated and coevaporated with toluene (3 × 10 mL) under reduced pressure. The residue was diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL) and water (3 × 10 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/hexane gradient elution) to afford the title compound (8.8 g, 90%) as white crystals. Analytical data for **1b**: R_f 0.58 (ethyl acetate/hexanes 4:10 v/v); mp 130–132 °C (diethyl ether/hexanes); $[\alpha]_D^{23}$ +26.7 (*c* 1, $CHCl_3$); ^{1}H NMR: δ 3.06 (d, 2H, *J* = 6.6 Hz, PhC*H*$_2$CH=CH$_2$), 4.18–4.26 (m, 1H, H-5), 4.39 (dd, 1H, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 6.8 Hz, H-6a), 4.54–4.69 (m, 3H, H-6b, PhCH$_2$CH=C*H*$_2$), 5.26 (d, 1H, $J_{1,2}$ = 6.0 Hz, H-1), 5.50–5.64 (m, 2H, H-4,

PhCH$_2$*CH*=CH$_2$), 5.77 (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 5.90 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 6.82–7.92 (m, 24H, aromatic) ppm; ^{13}C NMR: δ 34.0, 63.4, 69.9, 71.7, 72.8, 73.0, 99.9, 115.4, 115.7, 123.4, 128.5 (×2), 128.6 (×2), 128.7 (×3), 128.8 (×2), 128.9, 129.0, 129.3, 129.7, 129.8 (×3), 129.9 (×2), 130.0 (×2), 130.1 (×2), 130.2, 130.3, 133.4, 133.5, 133.8, 136.4, 154.8, 165.2, 165.5, 166.0, 166.2 ppm; HRMS–MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{43}H_{36}O_{10}Na$, 735.2205; found, 735.2194.

2-Allylphenyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (1c). A mixture of 3,4,6-tri-*O*-benzyl-1,2-*O*-methoxybenzylidene-α-D-glucopyranose [1] (0.360 g, 0.63 mmol), molecular sieves (4 Å, 400 mg) and 2-allylphenol (0.84 mL, 6.34 mmol) in dry dichloromethane (3.6 mL) was stirred under argon for 10 min at rt. TMSOTf (0.03 mL, 0.16 mmol) was added, and the resulting mixture was stirred at rt for 4 h. After that, the reaction mixture was filtered through celite, the filtrate was diluted with dichloromethane (30 mL) and then washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL), and water (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford the title compound (0.120 g, 28% yield) as a white solid. Analytical data for **1c**: R_f 0.59 (ethyl acetate/hexanes 3:10, v/v); $[\alpha]_D^{23}$ +26.4 (*c* 1, $CHCl_3$); ^{1}H NMR: δ 3.31 (d, 1H, *J* = 10.0 Hz, PhC*H*$_2$CH=CH$_2$), 3.85–4.06 (m, 5H, H-3, H-4, H-5, H-6a, H-6b), 4.71–5.01 (m, 8H, PhCH$_2$CH=C*H*$_2$, 3 × C*H*$_2$Ph), 5.21 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 5.76 (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 5.79–5.89 (m, 1H, PhCH$_2$*CH*=CH$_2$), 7.04–8.14 (m, 24H, aromatic) ppm; ^{13}C NMR: δ 33.98, 68.99, 73.6, 73.8, 75.3, 75.4, 75.7, 78.1, 82.9, 99.8, 115.2, 115.5, 122.9, 127.5, 127.8, 127.9, 128.0 (×2), 128.1, 128.2 (×4), 128.4 (×3), 128.5 (×2), 128.6 (×2), 128.7 (×2), 130.0 (×2), 130.1

(×2), 133.3, 136.7, 137.9, 138.0, 138.3, 155.2, 165.3 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{43}H_{42}O_2Na$ 693.2831, found 693.2834.

2-Allylphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (1d). 2-Allylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (see below for the synthesis, 2.00 g, 4.32 mmol) was dissolved in methanol (16 mL), and the pH was adjusted (pH 9) by careful addition of a 1 M solution of $NaOCH_3$ in MeOH (~0.1 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until neutral pH was reached. The resin was filtered off and washed with methanol (3 × 10 mL). The combined filtrate was concentrated in vacuo and dried. The resultant solid was dissolved in dry DMF (24 mL) and benzyl bromide (2.4 mL, 20.27 mmol). Then the reaction mixture was cooled down to 0 °C and NaH was added (0.73 g, 30.41 mmol) portionwise. The reaction mixture was allowed to warm up gradually. After stirring for 1 h at rt, the reaction was quenched by stirring with ice water (50 mL). The organic phase was extracted with ethyl acetate/diethyl ether 1:1 (v/v, 3 × 40 mL) and the combined organic extract was washed with water (3 × 20 mL). The organic phase was separated, dried with $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes gradient elution) to afford the title compound (2.6 g, 98%) as a white solid. Analytical data for **1d**: R_f 0.80 (ethyl acetate/hexanes 2:3, v/v); $[\alpha]_D^{24}$ −22.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 3.39–3.50 (m, 2H, PhC*H*$_2$CH=CH$_2$), 3.60–3.71 (m, 4H, H-3, H-4, H-6a, H-6b), 3.97 (m, 1H, H-5), 4.15 (dd, 1H, $J_{2,3}$ =8.3 Hz, H-2), 4.43 (dd, 2H, *J* = 11.6 Hz, C*H*$_2$Ph), 4.66 (d, 1H, ^2J = 8.4 Hz, 1/2 × C*H*$_2$Ph), 4.72–4.80 (s, 2H, C*H*$_2$Ph), 4.88–5.05 (m, 6H, $J_{1,2}$ = 7.8 Hz, H-1, PhCH$_2$CH=C*H*$_2$, 1.5×C*H*$_2$Ph), 5.96–6.01 (m, 1H, PhCH$_2$C*H*=CH$_2$), 6.96–7.34 (m, 24H, aromatic) ppm; ^{13}C NMR: δ 34.2, 69.1, 73.1, 73.2,

73.3, 73.8, 74.1, 74.5, 74.7, 75.7, 79.2, 82.7, 101.8, 115.1, 115.4, 116.0, 116.2, 127.7, 127.8, 127.9, 128.1, 128.2 (×2), 128.3, 128.4, 128.5 (×2), 128.6 (×3), 128.7 (×2), 129.7, 130.0, 136.9, 138.1, 138.5, 138.6, 138.7, 155.2 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{43}H_{44}O_6Na^+$ 679.3036, found 679.3019.

Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (24). Analytical data for the title compound was essentially the same as previously described [2].

Thiazolinyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (27). Analytical data for the title compound was essentially the same as previously described [3].

Tolyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (28). Analytical data for the title compound was essentially the same as previously described [4].

Phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (29). Analytical data for the title compound was essentially the same as previously described [5].

Synthesis of glycosyl acceptors

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (2). Analytical data for the title compound was essentially the same as previously described [1,6].

Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (3). Analytical data for the title compound was essentially the same as previously described [1,7].

Methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (4). Analytical data for the title compound was essentially the same as previously described [7,8].

Methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (5). Analytical data for the title compound was essentially the same as previously described [7,8].

Allylphenyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (13). To a stirred solution of 2-allylphenyl 2,3,4-tri-*O*-benzoyl-6-*O*-triphenylmethyl-β-D-glucopyranoside (see below for the synthesis, 1.1 g, 1.22 mmol) in CH_2Cl_2 (20 mL), water (0.2 mL) followed by trifluoroacetic acid (1.8 mL) were added until a persistent yellow color was obtained. The resultant mixture was stirred at rt for 45 min, diluted with CH_2Cl_2 (20 mL), and washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL), and water (3 × 10 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/hexanes gradient elution) to afford the title compound (0.7 g, 90%) as a white solid. Analytical data for **13**: R_f 0.56 (ethyl acetate/hexanes 2:5, v/v); $[\alpha]_D^{23}$ +15.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 3.13 (t, *J* =

6.2 Hz, 1H, OH), 3.35 (d, 2H, J = 6.5 Hz, PhCH_2CH=CH_2), 3.87–4.02 (m, 2H, H-6a, H-6b), 4.08–4.13 (m, 1H, H-5), 4.89 (m, 2H, PhCH_2CH=CH_2), 5.57 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 5.73 (dd, 1H, $J_{3,4}$= 9.7 Hz, H-4), 5.77–5.90 (m, 1H, PhCH_2CH=CH_2), 5.99 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 6.20 (dd, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 7.08–7.56 (m, 13H, aromatic), 7.95–8.09 (m, 6H, aromatic) ppm; ^{13}C NMR: δ 33.9, 61.6, 69.6, 71.7, 72.9, 75.1, 77.6, 99.6, 114.9, 115.7, 123.3, 127.6, 128.5 (×3), 128.7 (×3), 128.9 (×2), 129.3, 129.9 (×2), 129.9 (×2), 130.1 (×2), 130.4, 133.5 (x2), 133.9, 136.5, 154.7, 165.2, 165.9, 166.1 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{36}H_{32}O_9Na$ 631.1944, found 631.1937

Ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (15). Analytical data for the title compound was essentially the same as previously described [9].

Tolyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (17). Analytical data for the title compound was essentially the same as previously described [10].

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (19). Analytical data for the title compound was essentially the same as previously described [11].

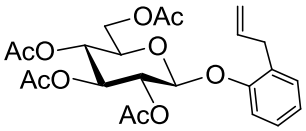
Phenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (21). Analytical data for the title compound was essentially the same as previously described [12].

2-Allylphenyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (25). A solution of 2-allylphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (see below for the synthesis, 0.42 g, 0.69 mmol) was dissolved in methanol (3.2 mL) and the pH was adjusted to pH 9 by

careful addition of a 1 M solution of $NaOCH_3$ in MeOH (~0.1 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until a neutral pH was reached. The resin was filtered off and washed with methanol (3 × 5 mL). The combined filtrate was concentrated in vacuo and dried. The residue was purified by column chromatography on silica gel (ethyl acetate/hexanes gradient elution) to afford the title compound (0.270 g, 69%) as a white solid. Analytical data for **25**: R_f 0.56 (ethyl acetate/hexanes 2:5, v/v); $[\alpha]_D^{23}$ −15.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 1.82 (s, 1H, OH), 3.35–3.44 (m, 2H, H-4, PhC*H*$_2$CH=CH$_2$), 3.55–3.75 (m, 4H, $J_{2,3}$ = 8.7 Hz, H-2, H-3, H-5, H-6a), 3.80 (dd, 1H, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6b}$ = 2.6 Hz, H-6b), 4.59 (d, ^2J = 10.9 Hz, 1H, 1/2 C*H*$_2$Ph), 4.74–4.98 (m, 7H, PhCH$_2$CH=C*H*$_2$, 2.5 × C*H*$_2$Ph), 5.04 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 5.83–5.96 (m, 1H, PhCH$_2$C*H*=CH$_2$), 6.91–7.24 (m, 19H, aromatic) ppm; ^{13}C NMR: δ 34.2, 62.2, 75.3, 75.5, 75.9, 82.3, 84.9, 101.1, 114.9, 116.2, 122.9, 127.7, 127.9 (×3), 128.0 (×2), 128.1 (×3), 128.3 (×3), 128.6 (×3), 128.7 (×3), 129.7, 130.4, 136.9, 138.0, 138.3, 138.6, 154.8 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{36}H_{38}O_6Na$ 589.2668, found 589.2676.

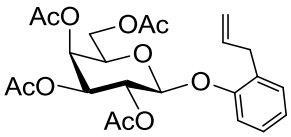
Synthesis of additional building blocks

2-Allylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (S1).



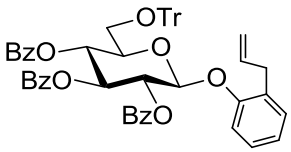
2-Allylphenol (1.37 mL, 10.25 mmol), $BF_3{\cdot}OEt_2$ (1.6 mL, 12.8 mmol), and triethylamine (0.36 mL, 2.56 mmol) were added to a stirred solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranoside (2.00 g, 5.13 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was kept for 16 h at rt, then it was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL), and water (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford the title compound (1.9 g, 90% yield) as white crystals. Analytical data for **S1**: R_f 0.50 (ethyl acetate/hexane 1:5, v/v); mp 145–148 °C (diethyl ether/hexanes); $[\alpha]_D^{23}$ −25.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 2.02 (s, 3H, OCH_3), 2.03 (s, 3H, OCH_3), 2.04 (s, 3H, OCH_3), 2.06 (s, 3H, OCH_3), 3.23–3.38 (m, 2H, PhC*H*$_2$CH=CH$_2$), 3.81–3.87 (m, 1H, H-5), 4.16 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.5 Hz, H-6b), 4.27 (dd, 1H, $J_{5,6a}$ = 5.5 Hz, H-6a), 4.95–5.05 (m, 3H, H-2, PhCH$_2$CH=C*H*$_2$), 5.12–5.19 (m, 1H; H-4), 5.24–5.35 (m, 2H, $J_{1,2}$ = 8.7 Hz, H-1, H-3), 5.83–5.96 (m, 1H, PhCH$_2$C*H*=CH$_2$), 6.97–7.18 (m, 4H, aromatic) ppm; ^{13}C NMR: δ 20.7, 20.8, 20.9, 21.0, 33.9, 62.1, 68.5, 71.2, 72.1, 72.9, 99.3, 115.4, 115.9, 123.5, 127.5, 130.0, 130.5, 136.6, 154.6, 169.3, 169.5, 170.4, 170.7 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{23}H_{28}O_{10}Na^+$, 487.1580; found, 487.1562.

2-Allylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (S2).



2-Allylphenol (1.37 mL, 10.25 mmol), $BF_3{\cdot}OEt_2$ (1.6 mL, 12.8 mmol), and triethylamine (0.36 mL, 2.56 mmol) were added to a stirred solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranoside (2.00 g, 5.13 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was kept for 16 h at rt, then it was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL), and water (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford the title compound (1.8 g, 89% yield) as white crystals. Analytical data for **S2**: R_f 0.51 (ethyl acetate/hexane 2:3, v/v); mp 98–101 (diethyl ether/hexanes); $[\alpha]_D^{24}$ −13.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ, 2.23–2.42 (m, 12H, 4 × OCH_3), 3.55–3.63 (m, 2H, PhCH_2CH=CH_2), 4.33 (m, 1H, H-5), 4.40 (dd, 1H, $J_{6a,6b}$ = 11.3 Hz, $J_{5,6a}$ = 6.1 Hz, H-6a), 4.48 (dd, 1H, $J_{5,6b}$ = 7.2 Hz, H-6b), 5.23 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.28 (t, 2H, PhCH_2CH=CH_2), 5.36 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 5.70 (dd, 1H, H-4), 5.78 (dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 6.12–6.24 (m, 1H, PhCH_2CH=CH_2), 7.10–7.29 (m, 4H; aromatic) ppm; ^{13}C NMR: δ 20.6, 20.7, 20.8, 20.9, 33.8, 61.5, 67.0, 68.6, 70.9, 71.0, 99.6, 115.1, 115.7, 123.3, 127.4, 129.8, 130.3, 136.6, 154.6, 169.3, 170.1, 170.3, 170.5 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{23}H_{28}O_{10}Na^+$, 487.1580; found, 487.1573.

2-Allylphenyl 2,3,4-tri-*O*-benzoyl-6-*O*-triphenylmethyl-β-D-glucopyranoside (S3).

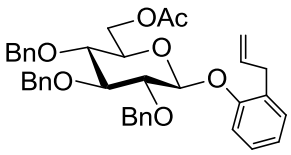


S3

Compound **S1** (1.00 g, 2.16 mmol) was dissolved in methanol (8 mL) and the pH was adjusted to pH 9 by careful addition of a 1 M solution of $NaOCH_3$ in MeOH (~0.1 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until neutral pH was reached. The resin was filtered off and rinsed with methanol (3 × 5 mL). The combined filtrate (~30 mL) was concentrated in vacuo and dried. The resultant solid was dissolved in pyridine (5.3 mL), and triphenylmethyl chloride (1.9 g, 6.76 mmol) was added and the resulting reaction mixture was stirred for 16 h. After that, the reaction mixture was cooled to 0 °C and benzoyl chloride (1.6 mL, 13.5 mmol) was added dropwise. The reaction mixture was allowed to gradually warm to rt and stirred for an additional 3 h at rt. The reaction was quenched by addition of methanol (10 mL), evaporated under reduced pressure and coevaporated with toluene (3 × 20 mL). The residue was diluted with CH_2Cl_2 (20 mL) and washed with water (10 mL), sat. aq. $NaHCO_3$ (10 mL) and water (3 × 10 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/hexanes gradient elution) to afford the title compound (1.5 g, 86%) as a white solid. Analytical data for **S3**: R_f 0.50 (ethyl acetate/hexanes 2:5, v/v); ^{1}H NMR: δ 3.33 (d, 2H, J = 6.5 Hz, PhCH_2CH=CH_2), 3.43 (dd, 1H, $J_{5,6a}$ = 2.2 Hz, $J_{6b,6a}$ = 10.7 Hz, H-6a), 3.52 (dd, 1H, $J_{5,6b}$ = 6.1Hz, H-6b), 4.03–4.09 (m, 1H, H-5), 4.80–4.92 (m, 2H, PhCH$_2$CH=CH_2), 5.40–5.43 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 5.65–5.72 (m, 1H, H-4), 5.76–5.89 (m, 1H, PhCH$_2$CH=CH$_2$), 5.93–6.01 (m, 2H, H-2, H-

3), 7.09–8.04 (m, 34H, aromatic) ppm; ^{13}C NMR: δ 34.1, 60.6, 62.6, 69.6, 71.9, 73.3, 74.5, 74.6, 87.2 (×2), 100.0, 115.6, 115.7, 115.9, 123.4 (×2), 127.2, 127.6 (×5), 127.9, 128.4, 128.5, 128.7 (×6), 129.0, 129.1, 129.2, 129.4, 129.9, 129.9, 130.0 (×2), 130.1, 130.2, 133.4, 133.4, 136.6, 143.7 (×5), 155.1, 165.1 (×2), 165.3 (×2), 166.0 (×2) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{55}H_{46}O_9Na$ 873.3072, found 873.3064.

2-Allylphenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (S4).



S4

To a stirred solution of a **1a** (0.1 g, 0.15 mmol) in Ac_2O/AcOH 2:1 (v/v, 0.9 mL) was added freshly prepared $ZnCl_2$ (166 mg, 1.22 mmol) solution in Ac_2O/AcOH 2:1 (v/v, 0.86 mL). The reaction mixture was stirred under argon for 4 h at rt. Upon completion, the reaction was quenched with H_2O, diluted with ethyl acetate (50 mL), and washed with water (20 mL), sat. aq. $NaHCO_3$ (20 mL) and water (3 × 20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to afford the title compound (98 mg, 99%) as a clear form. Analytical data for **S4**: R_f 0.51 (ethyl acetate/toluene 1:10, v/v); $[\alpha]_D^{23}$ −5.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 1.92 (s, 3H, OCH_3), 3.29–3.45 (m, 2H, PhCH_2CH=CH_2), 3.48–3.65 (m, 2H, H-4, H-5), 3.67–3.71 (m, 2H, H-2, H-3), 4.14 (dd, 1H, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6a}$ = 5.1 Hz, H-6a), 4.24 (dd, 1H, $J_{5,6b}$ = 1.7 Hz, H-6b), 4.51 (d, ^{2}J = 10.9 Hz, 1/2 CH_2Ph), 4.74–5.01 (m, 8H, H-1, PhCH_2CH=CH_2, 2.5 × CH_2Ph), 5.83–5.93 (m, 1H, PhCH_2CH=CH_2), 6.87–7.27 (m, 19H, aromatic) ppm; ^{13}C NMR: δ 20.9, 34.2, 63.3, 73.1, 75.2, 75.3, 75.9, 82.1, 85.0, 101.3, 115.5, 116.1,

123.0, 127.5, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4 (×3), 128.5, 128.6 (×3), 128.6, 128.7 (×3), 129.9, 130.2, 136.8, 137.7, 138.2, 138.4, 154.9, 170.8 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{38}H_{40}O_7Na$, 631.2674; found, 631.2665.

Data for di- and trisaccharides

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6a). Analytical data for the title compound was similar to that previously described [13].

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6b). Analytical data for the title compound was essentially the same as previously described [13].

Methyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6c). Analytical data for the title compound was essentially the same as previously described [14].

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (6d). Analytical data for the title compound was essentially the same as previously described [15].

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7a). Analytical data for the title compound was similar to that previously described [13].

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7d). Analytical data for the title compound was similar to that previously described [16].

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (8a). Analytical data for the title compound was similar to that previously described [17].

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (8d). Analytical data for the title compound was similar to that previously described [18].

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (9a). Analytical data for the title compound was similar to that previously described [19].

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (9b). Analytical data for the title compound was essentially the same as previously described [19].

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (9d). The title compound was obtained as a clear film from **1d** and **5** by Method C in 80% yield (α/β = 3.0/1). Selected analytical data for α-**9d**: ^{1}H NMR: δ 3.91 (dd, 1H, $J_{2,3}$ = 7.6 Hz, H-2), 4.02 (dd, 1H, $J_{2',3'}$ = 9.6 Hz, H'-2), 4.93 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.97 (d, 1H, $J_{1'2'}$ = 3.5 Hz, H'-1) ppm; ^{13}C NMR: δ 94.9 (C-1), 96.7 (C'-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{62}H_{66}O_{11}Na^+$, 1009.4503; found, 1009.4510.

2-[3-Iodo-2-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yl)propyl]oxyphenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (12). The title compound was isolated as a by-product from the synthesis of **6a** from **1a** and **2** by Method B in 15% yield. Selected analytical data for **12**: ^{1}H NMR: δ 3.74 (dd, 1H, $J_{2',3'}$ = 7.9 Hz, H'-2), 4.53 (d, $J_{1,2}$ = 4.1 Hz, H-1), 5.02 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H'-1) ppm; ^{13}C NMR: δ 10.6, 35.9, 55.3, 68.0, 68.8, 70.4, 73.5, 73.6, 73.7, 74.8, 75.2, 75.3, 75.4, 75.5, 75.8, 75.9, 77.4, 77.8, 77.9, 79.4, 79.9, 80.1, 82.2, 82.3, 82.4, 85.1, 85.2, 98.2, 101.8, 115.8, 122.8, 122.9, 127.1, 127.6, 127.7, 127.8, 127.9 (×2), 128.0 (×2), 128.1 (×2), 128.1 (×2), 128.2 (×2), 128.3, 128.4 (×2), 128.5 (×2), 128.6 (×4), 128.7 (×4), 128.9, 129.2, 132.2, 138.1, 138.2, 138.3, 138.4, 138.5, 138.6, 138.7, 138.8, 155.5 ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{71}H_{75}IO_{12}Na^+$, 1269.4201; found, 1269.4214.

2-Allylphenyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (14). The title compound was obtained as a clear film from **1a** and **13** by Method B in 78% yield (α/β = 1.0/1). Selected analytical data for α-**14**: ^{1}H NMR: δ 4.58 (d, 1H, $J_{1',2'}$ = 4.6 Hz, H'-1), 5.28 (d, $J_{1,2}$ = 7.8 Hz, H-1) ppm; ^{13}C NMR: δ 80.4 (C-1), 98.4 (C'-1) ppm; Selected analytical data for β-**14**: ^{1}H NMR: δ 4.42 (d, 1H, $J_{1',2'}$ = 11.0 Hz, H'-1) ppm; ^{13}C NMR: δ 82.2 (C-1), 100.1 (C'-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{70}H_{68}O_{14}Na^+$, 1155.4609; found, 1155.4623.

Ethyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (16). Analytical data for the title compound was essentially the same as previously described [2].

Tolyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (18). The title compound was obtained as a clear film from **6** and **15** by Method A in 75% yield (α/β = 2.4/1). Selected analytical data for α-**18**: ^{1}H NMR: δ 4.67 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H'-1), 4.85 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1) ppm; ^{13}C NMR: δ 86.1 (C-1), 97.6 (C'-1) ppm. Selected analytical data for β-**18**: ^{1}H NMR: δ 4.52 (d, 1H, $J_{1',2'}$ = 10.8 Hz, H'-1) ppm; ^{13}C NMR: δ 87.2 (C-1), 103.9 (C'-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{68}H_{64}O_{13}SNa^+$, 1143.3965; found, 1143.3970.

Phenyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (20). The title compound was obtained as a clear film from **1a** and **19** by Method B in 90% yield (α/β = 1.0/1). Selected analytical data for α-**20**: ^{1}H NMR: δ 3.95 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-3), 4.57 (d, 1H, $J_{1,2}$ = 9.3 Hz, H-1), 5.00 (d, 1H,

$J_{1',2'}$ = 3.5 Hz, H'-1) ppm; ^{13}C NMR: δ 89.2 (C-1), 96.6 (C'-1) ppm. Selected analytical data for β-**20**: ^{1}H NMR: δ 4.37 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H'-1); ^{13}C NMR: δ 95.2 (C-1), 103.4 (C'-1) ppm. HRMS–MS (*m*/*z*): [M + Na]$^{+}$ calcd for $C_{67}H_{68}O_{10}SNa^{+}$, 1087.4433; found, 1087.4406.

Phenyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (22). Analytical data for the title compound was essentially the same as previously described [19].

Phenyl 6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (23). The title compound was obtained as a clear film from donors **1c** and acceptor **21** by Method B in 75% yield. Selected analytical data for **23**: ^{1}H NMR: δ 3.65 (dd, 1H, $J_{6a,6b}$ = 9.3 Hz, H-6a), 3.81 (dd, 1H, $J_{5,6b}$ = 3.2 Hz, H-6b), 3.87–3.99 (m, 4H, H-5, H'-5, H'-6a, H'-6b), 4.08–4.14 (m, 2H, H'3, H'-4), 4.59 (d, 1H, ^{2}J = 12.2 Hz, 1/2 CH_2Ph), 4.70 (d, 1H, ^{2}J = 11.6 Hz, 1/2 CH_2Ph), 4.78–4.88 (m, 4H, 2 × CH_2Ph), 4.93 (d, 1H, $J_{1',2'}$ = 6.2 Hz, H'-1), 4.96 (d, 1H, $H_{1,2}$ = 5.2 Hz, H-1), 5.39–5.49 (m, 3H, H-2, H-4, H'-2), 5.88 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-3), 7.27–8.12 (m, 40H, aromatic) ppm; ^{13}C NMR: δ 68.8, 69.5, 70.5, 71.2, 73.7, 74.6, 74.9, 75.3, 77.6, 78.1, 78.5, 83.2, 101.3, 127.7, 127.9, 128.1 (×3), 128.3 (×3), 128.4 (×3), 128.5 (×3), 128.6 (×4), 128.9, 129.0, 129.1 (×3), 129.2 (×3), 129.3 (×2), 129.4 (×3), 129.5 (×2), 129.9 (×2), 130.0 (×3), 130.1 (×4), 130.2, 131.8, 133.2, 133.4, 133.5, 138.0, 138.1, 138.2, 165.2, 165.5, 165.6, 165.9 ppm; HRMS–MS (*m*/*z*): [M + Na]$^{+}$ calcd for $C_{67}H_{60}O_{14}SNa$, 1143.3604; found, 1143.3636

2-Allylphenyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (26). The title compound was obtained as a clear film from donors **24**, **27**–**29** and acceptor **25** by Method A in 82–90% yield. Selected analytical data for α-**26**: ^{1}H NMR: δ 4.37 (d, 1H, $J_{1',2'}$ = 2.7 Hz, H'-1) ppm; ^{13}C NMR: δ 97.6 (C-1), 100.6 (C'-1) ppm. Selected analytical data for β-**26**: ^{1}H NMR: δ 4.34 (d, 1H, $J_{1',2'}$ = 5.6 Hz, H'-1) ppm; ^{13}C NMR: δ 101.6 (C-1), 104.2 (C'-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{70}H_{72}O_{11}Na^+$, 1111.5057; found, 1111.4980.

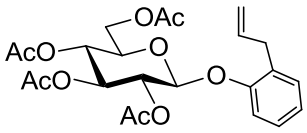
Methyl O-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (S5). The title compound was obtained from **2** and **26** by Method C in 80% yield and from **2** and **16** by Method C in 89% yield. Analytical data for the title compound was in accordance with that previously described [20].

Phenyl O-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (30). The title compound was obtained as a clear film from **26** and **21** by method B in 90% yield. Selected analytical data for α-**30**: ^{1}H NMR: δ 4.69 (d, 1H, $J_{1',2'}$ = 3.1 Hz, H'-1), 4.96 (d, 1H, $J_{1'',2''}$ = 2.3 Hz, H''-1) ppm; ^{13}C NMR: δ 97.4 (C-1), 97.5 (C'-1), 97.6 (C"-1) ppm. Selected analytical data for β-**31**: ^{1}H NMR: δ 5.27 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1) ppm; ^{13}C NMR: δ 99.7 (C-1), 99.8 (C'-1), 103.8 (C''-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{94}H_{90}O_{18}SNa^+$, 1561.5745; found, 1561.5731.

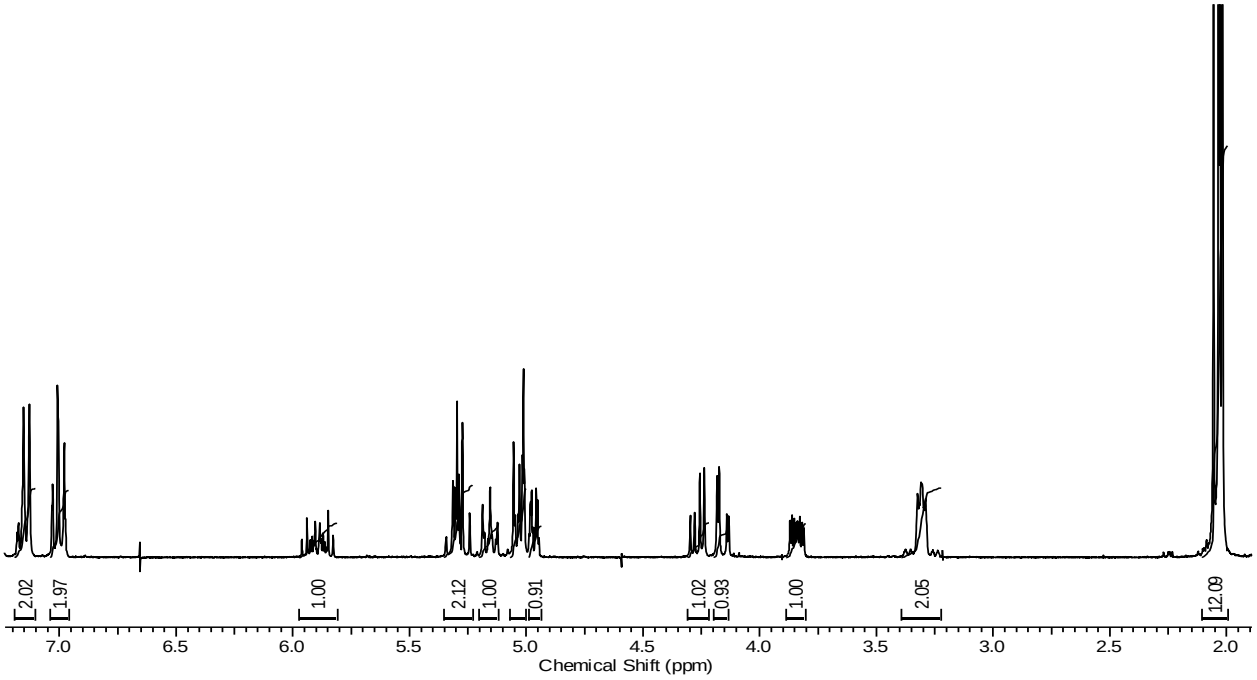
2-Allylphenyl O-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (31). The title compound was obtained as a colorless syrup from **16** and **25** by method A in 50% yield. Selected analytical data for β-**31**: ^{1}H NMR: δ 4.27 (d, 1H, $J_{1',2'}$ = 9.0 Hz, H'-1), 4.37 (d, 1H, $J_{1'',2''}$ = 7.1 Hz, H''-1), 5.25 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1) ppm; ^{13}C NMR: δ 98.2 (C-1), 102.0 (C'-1), 103.8 (C''-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{97}H_{100}O_{16}Na^+$, 1543.6909; found, 1543.6936.

2-Allylphenyl O-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (32). The title compound was obtained as a colorless syrup from **16** and **13** by method A in 80% yield. Selected analytical data for α-**32**: ^{1}H NMR: δ 4.67 (d, 1H, $J_{1',2'}$ = 3.2 Hz, H'-1), 4.90 (d, 1H, $J_{1'',2''}$ = 2.5 Hz, H''-1) ppm; ^{13}C NMR: δ 97.4 (C-1), 97.5 (C'-1), 97.6 (C"-1) ppm; Selected analytical data for β-**33**: ^{1}H NMR: δ 5.27 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1) ppm; ^{13}C NMR: δ 99.7 (C-1), 99.8 (C'-1), 103.8 (C''-1) ppm; HRMS–MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{97}H_{94}O_{19}Na^+$, 1585.7729; found, 1585.7762.

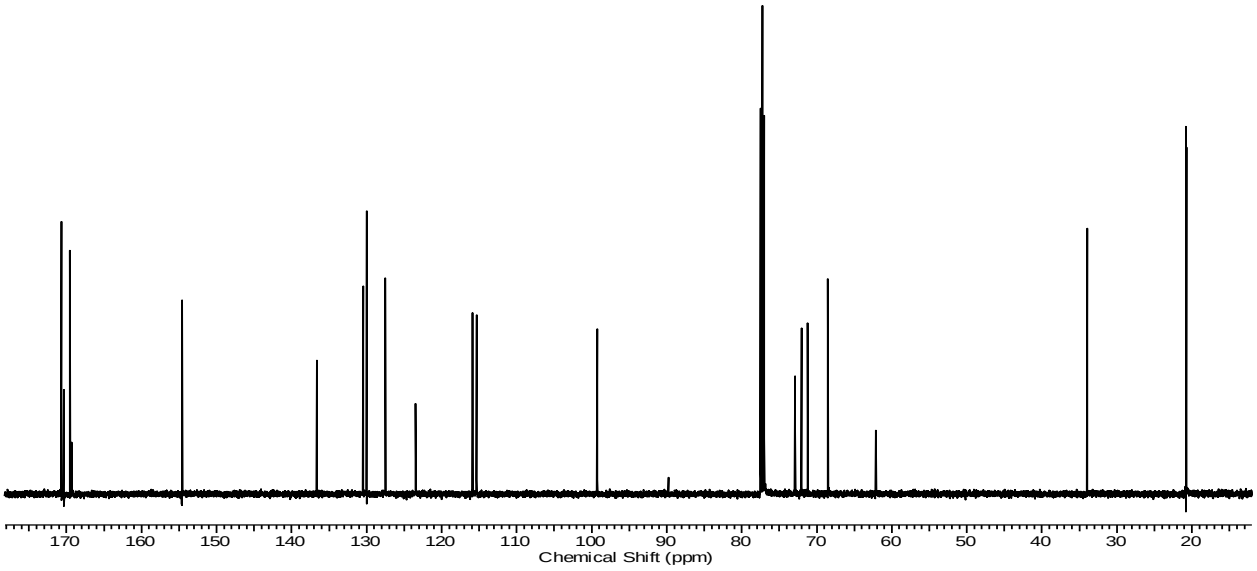
NMR spectra



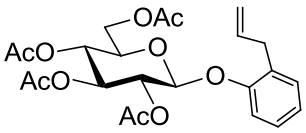
S1



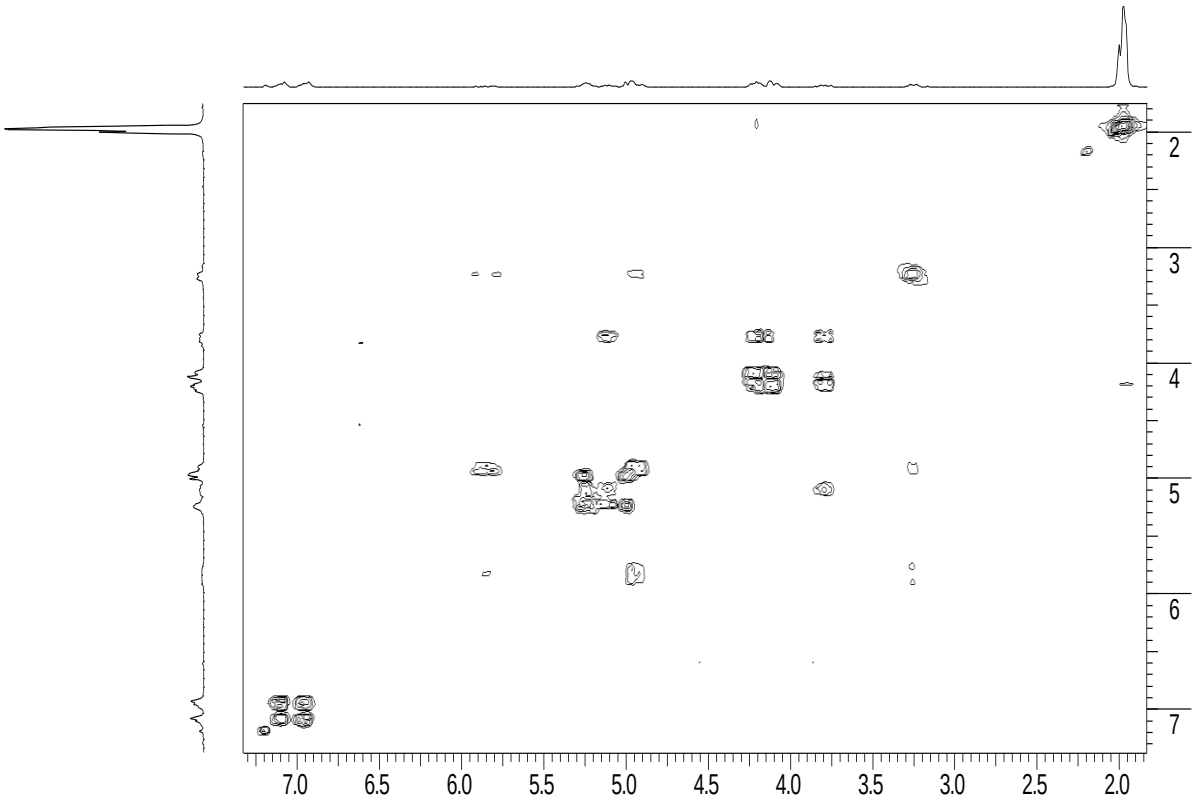
$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



S1



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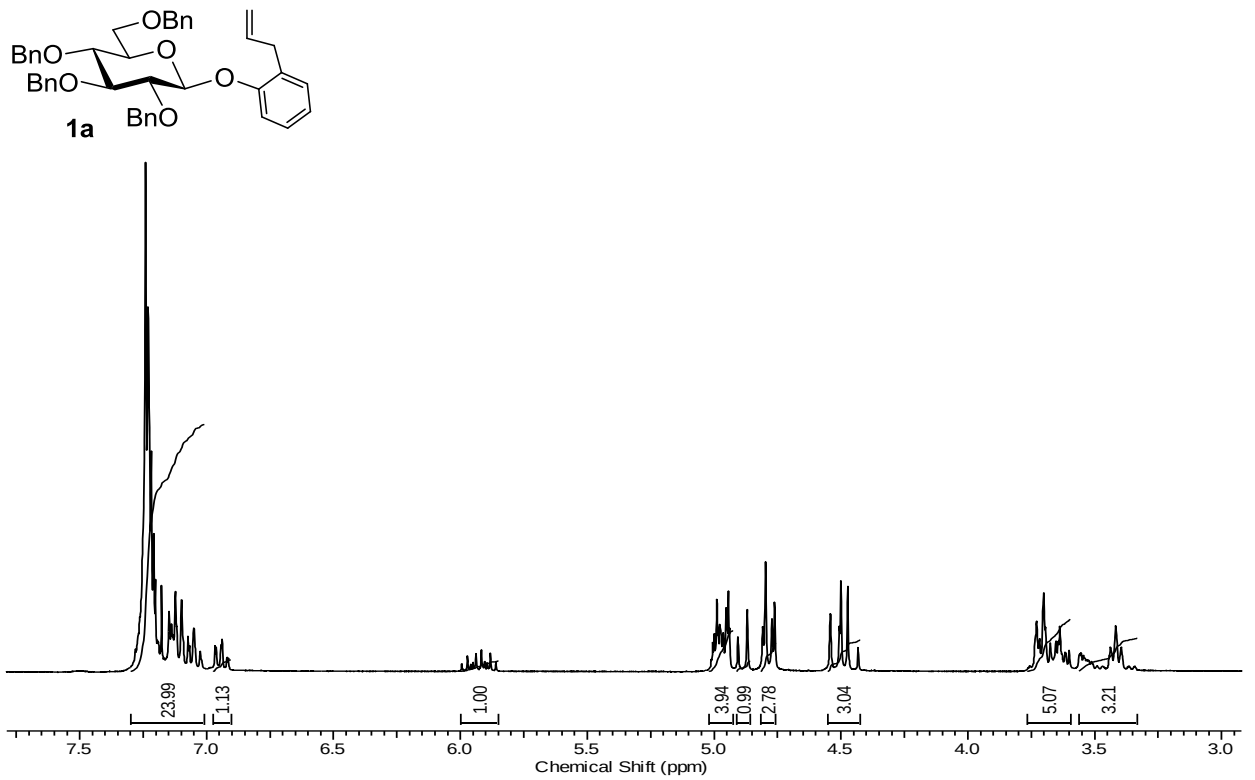

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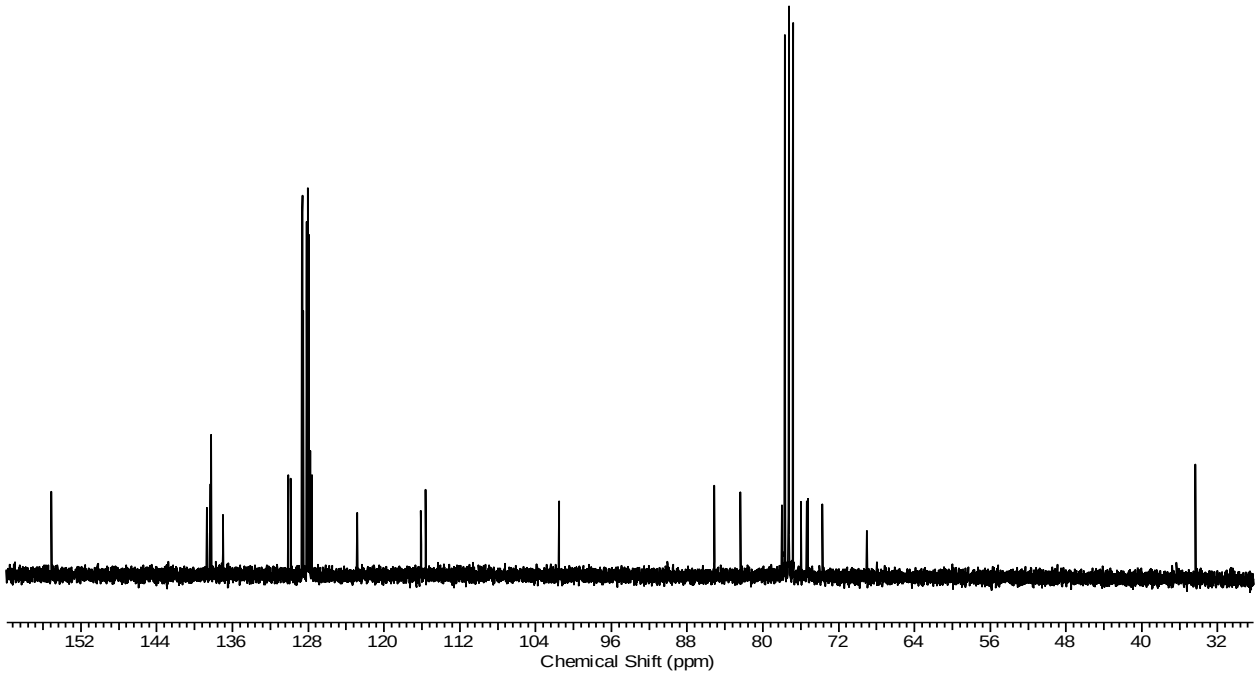
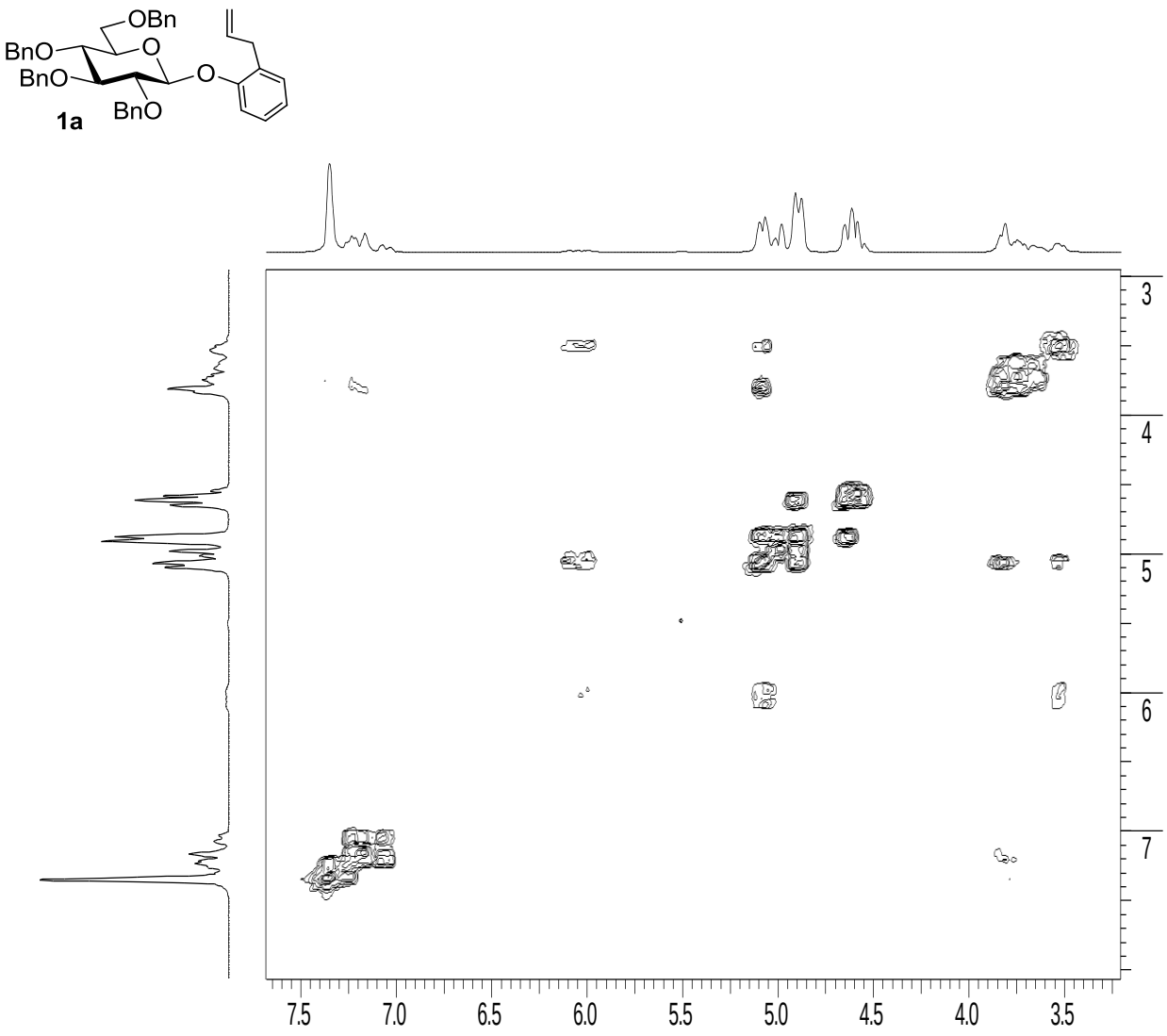


$CDCl_3$ at 75 MHz



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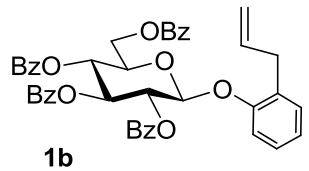
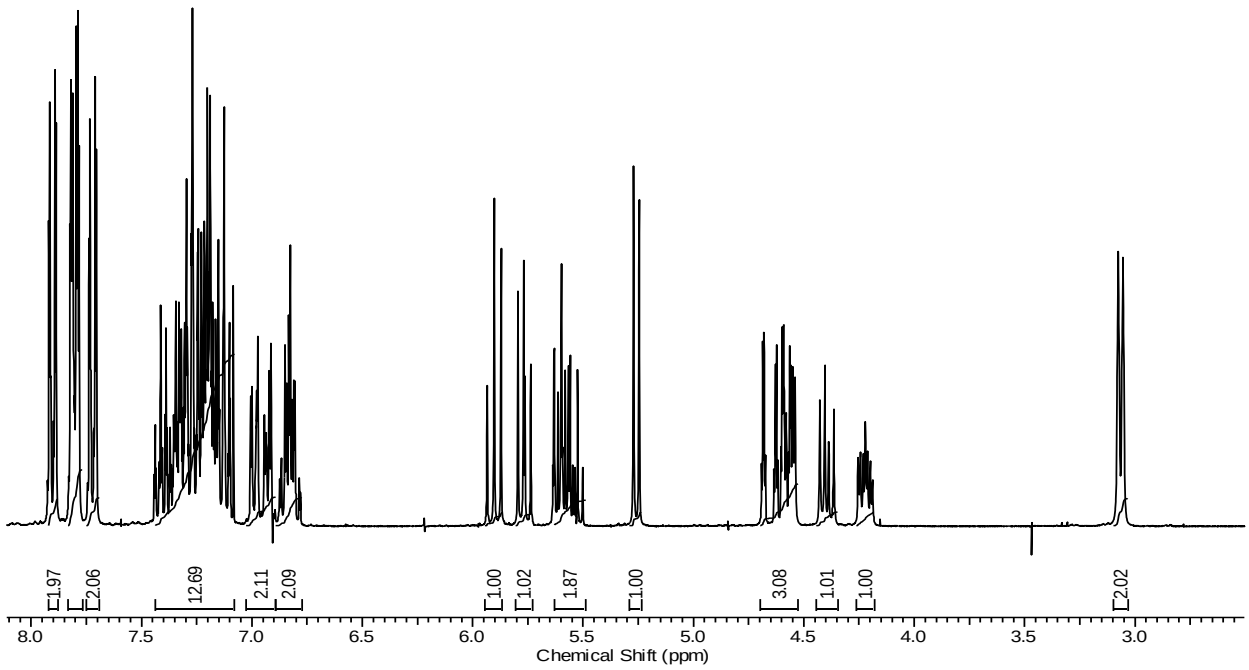
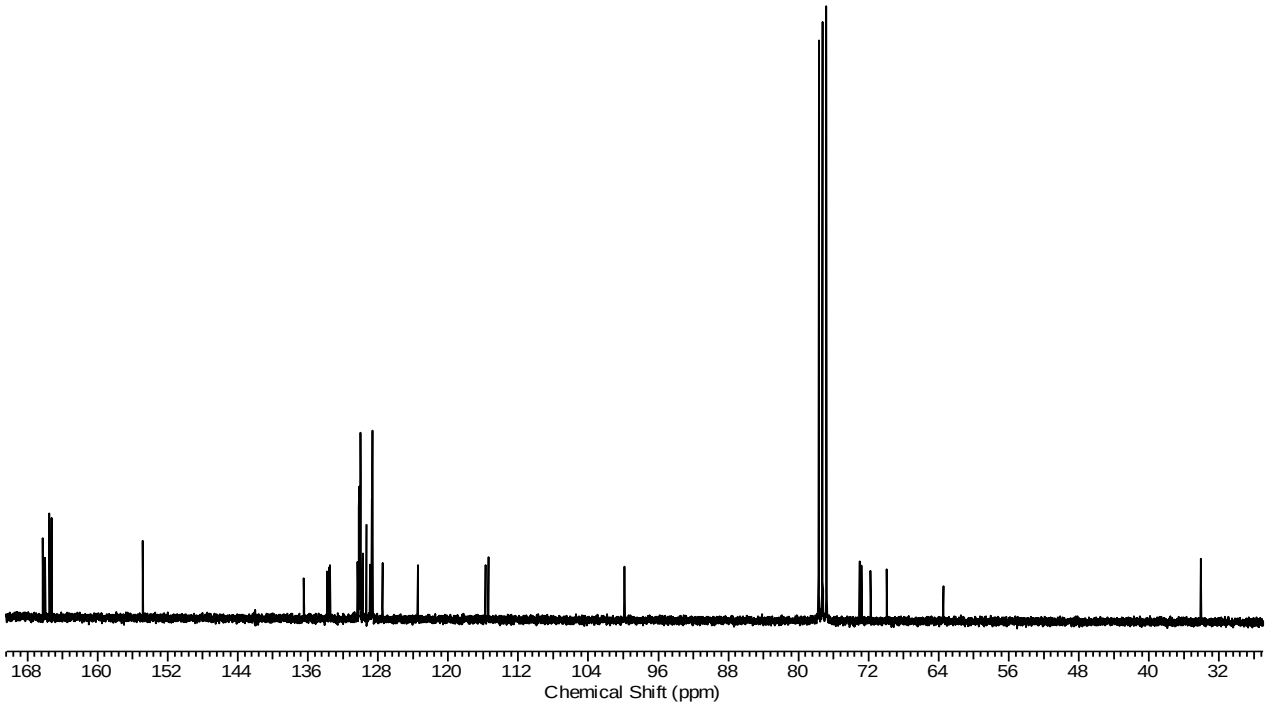


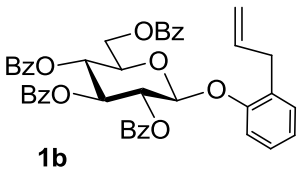
1b



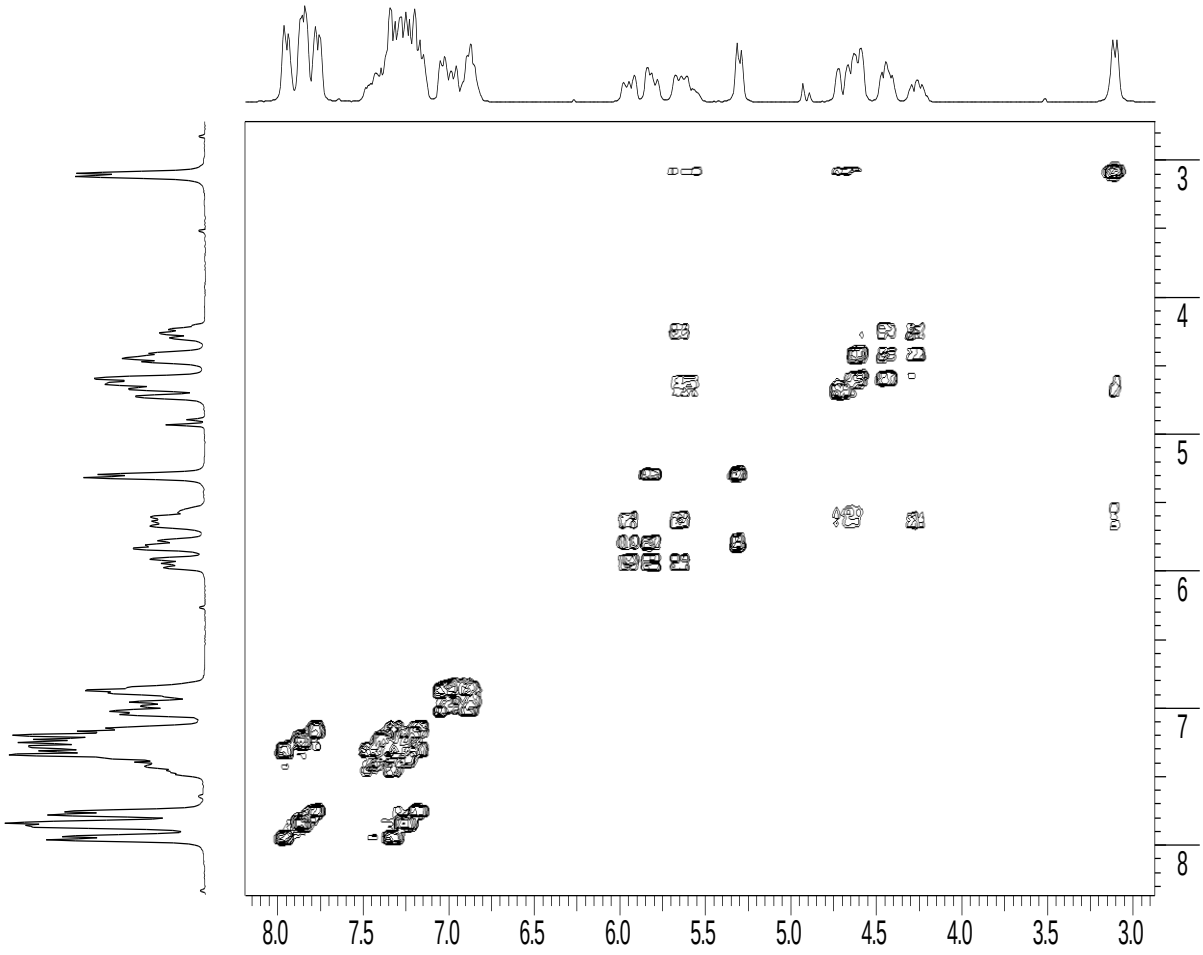
$CDCl_3$ at 300 MHz



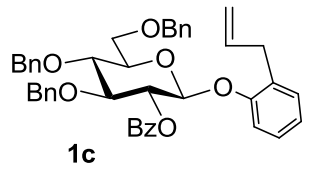
$CDCl_3$ at 75 MHz



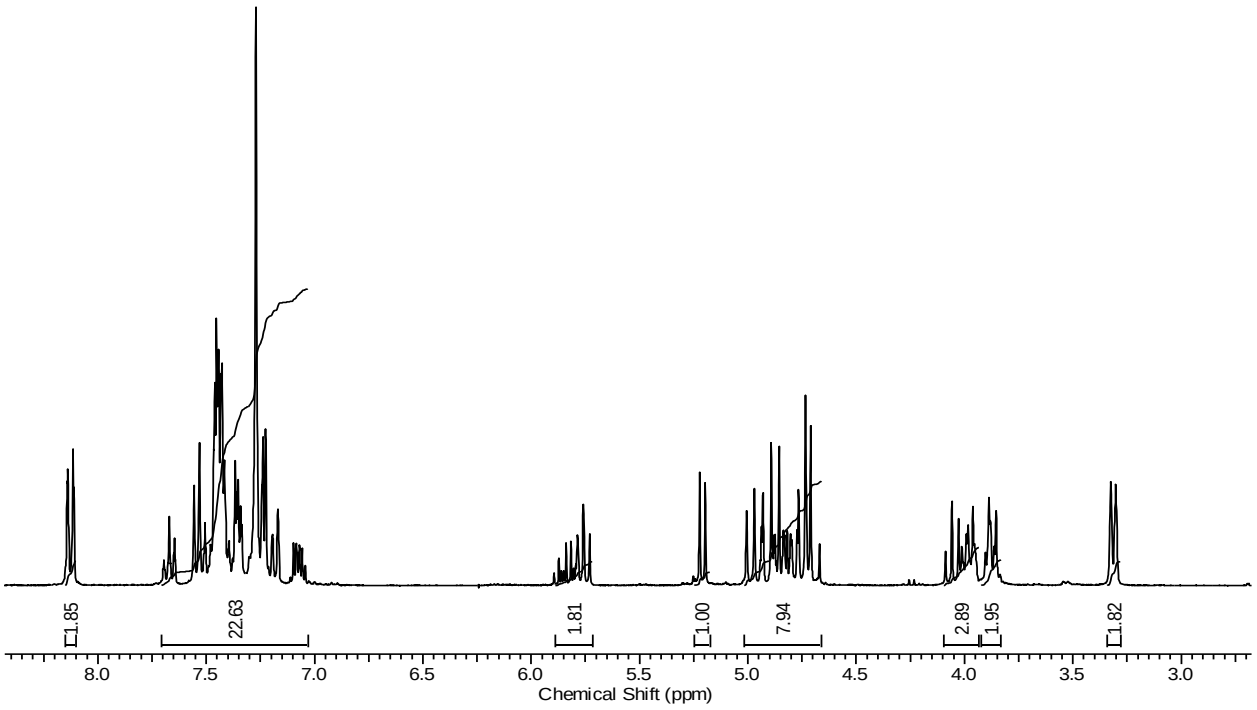
1b



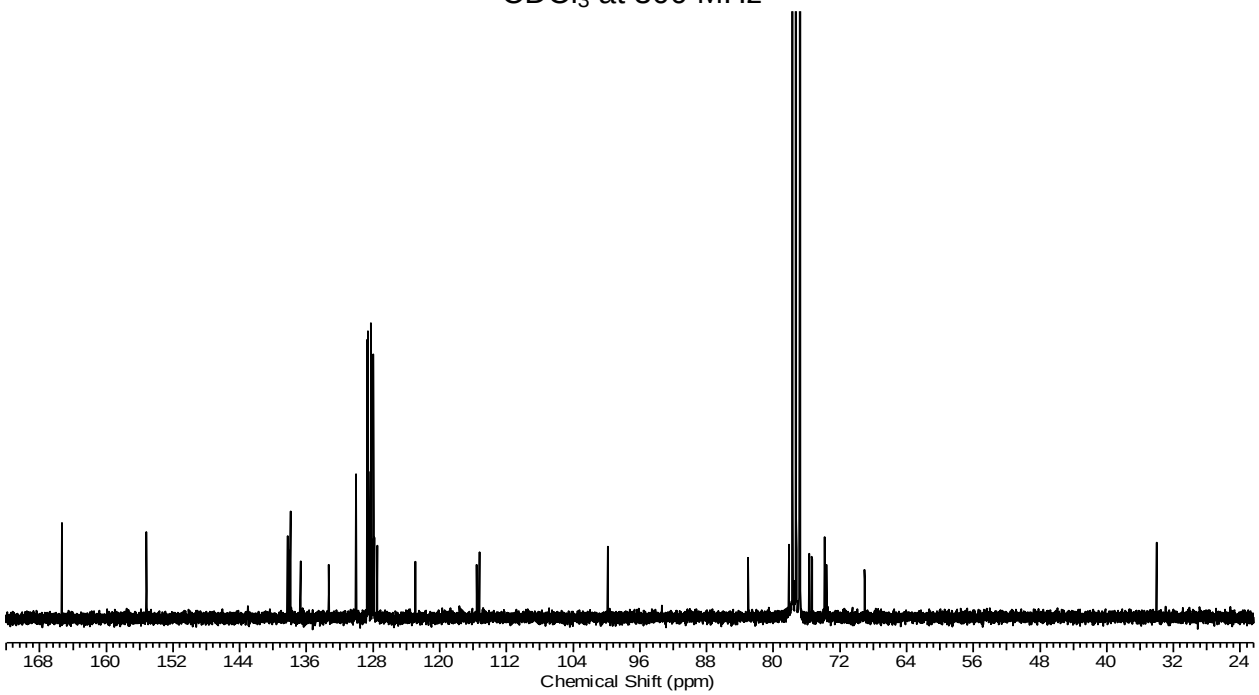
$CDCl_3$ at 300 MHz



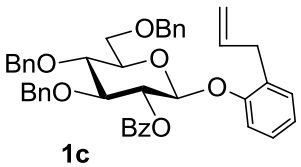
1c



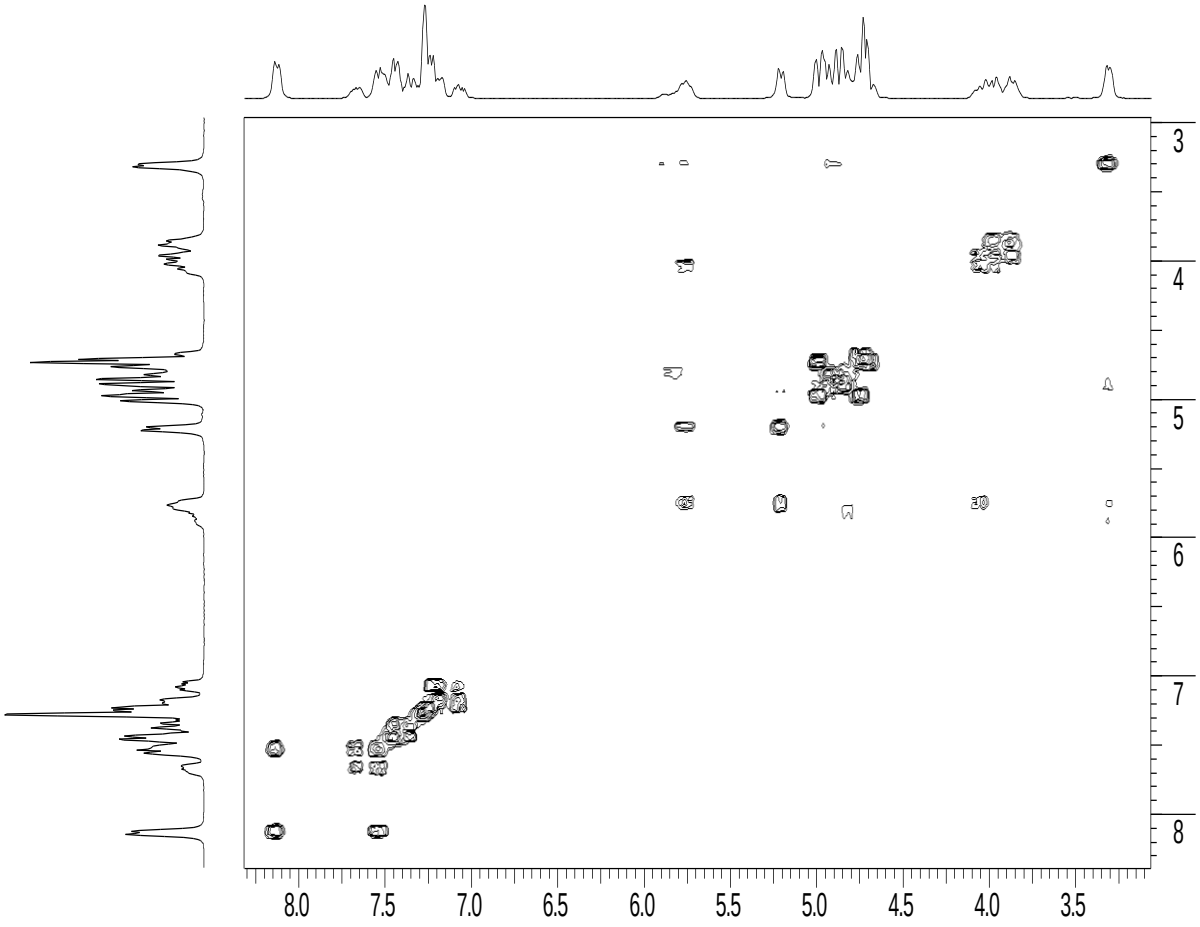
$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



1c



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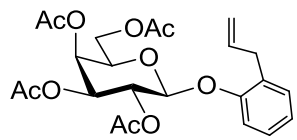
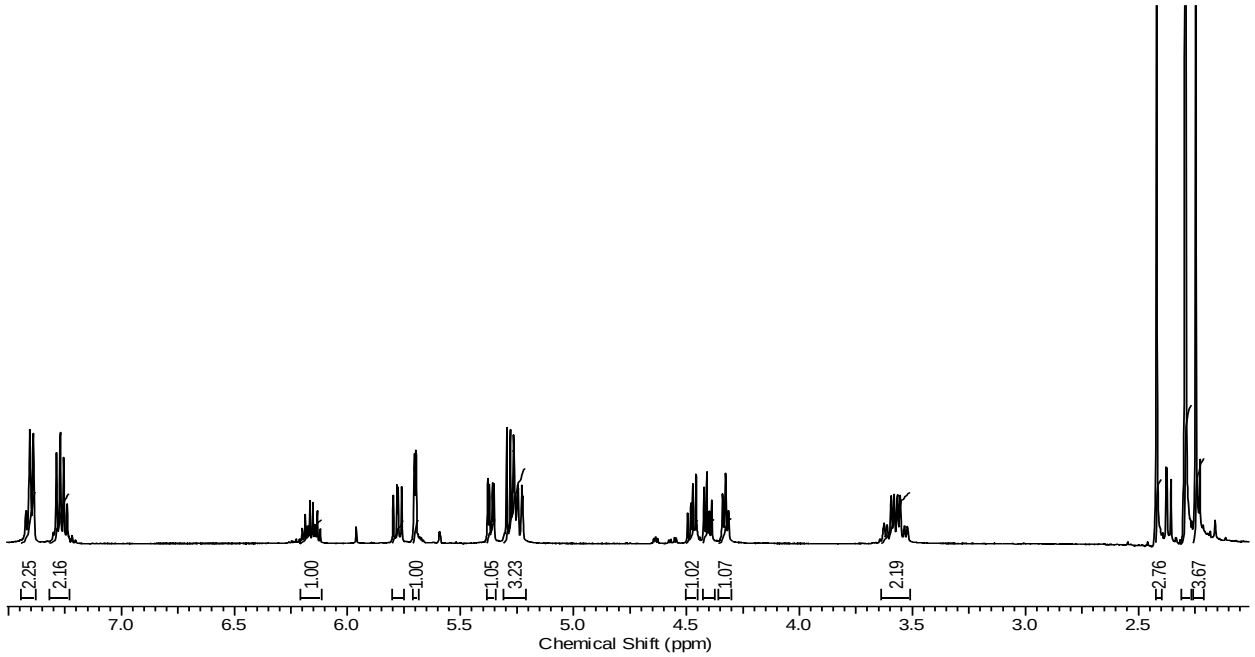
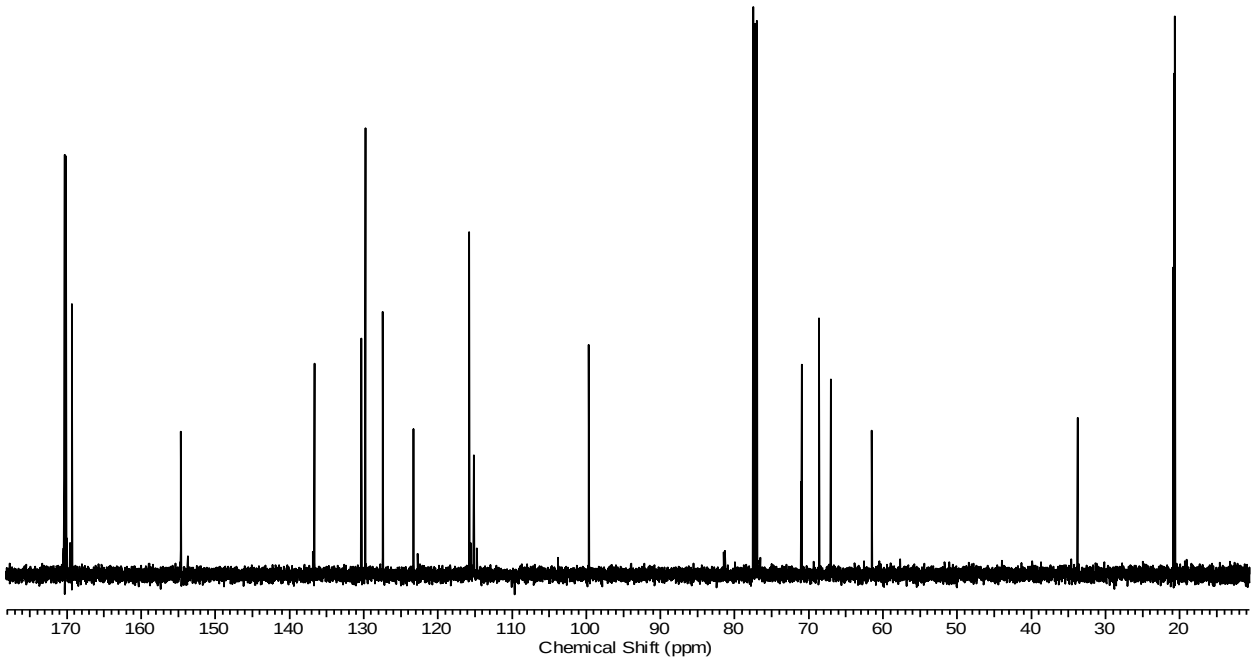


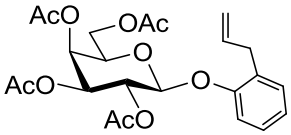
S2



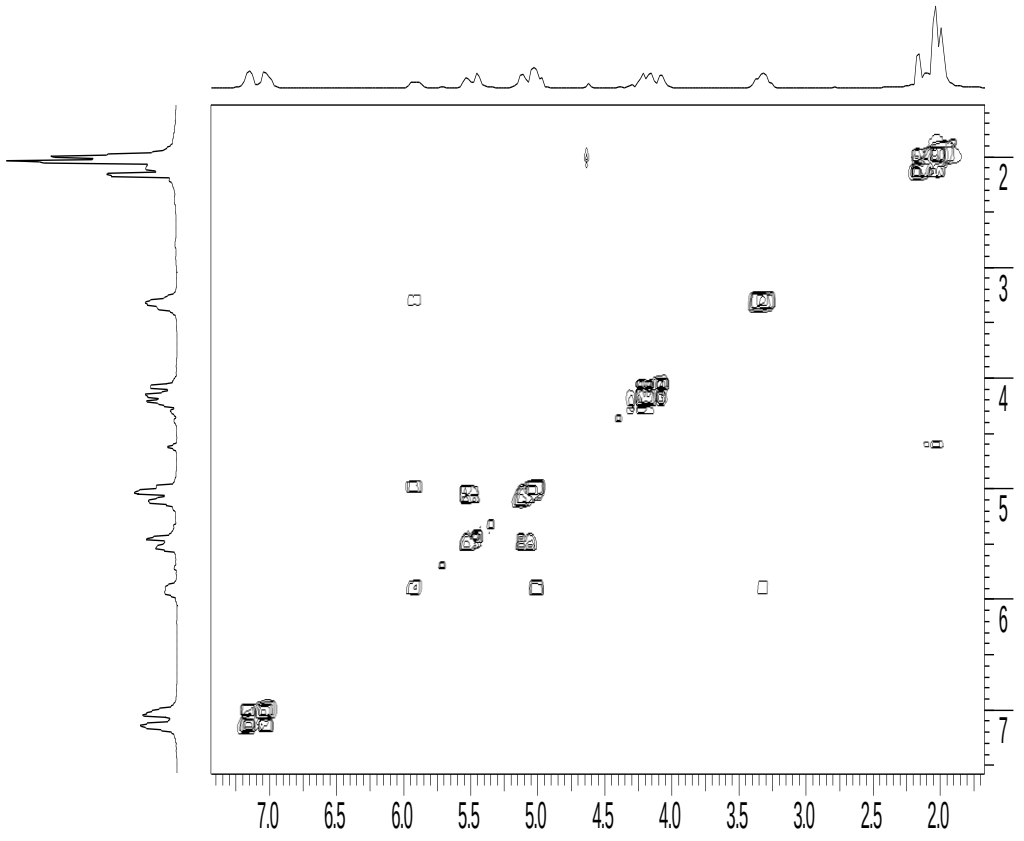
$CDCl_3$ at 300 MHz



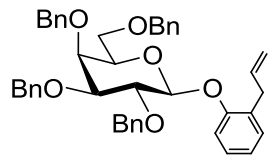
$CDCl_3$ at 75 MHz



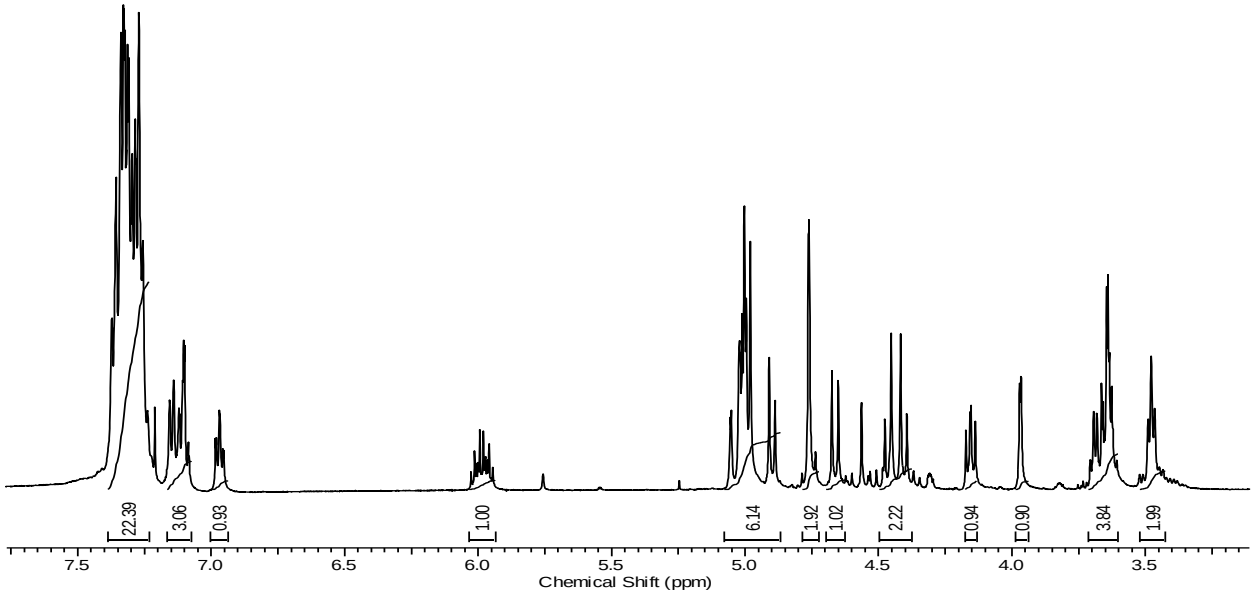
S2



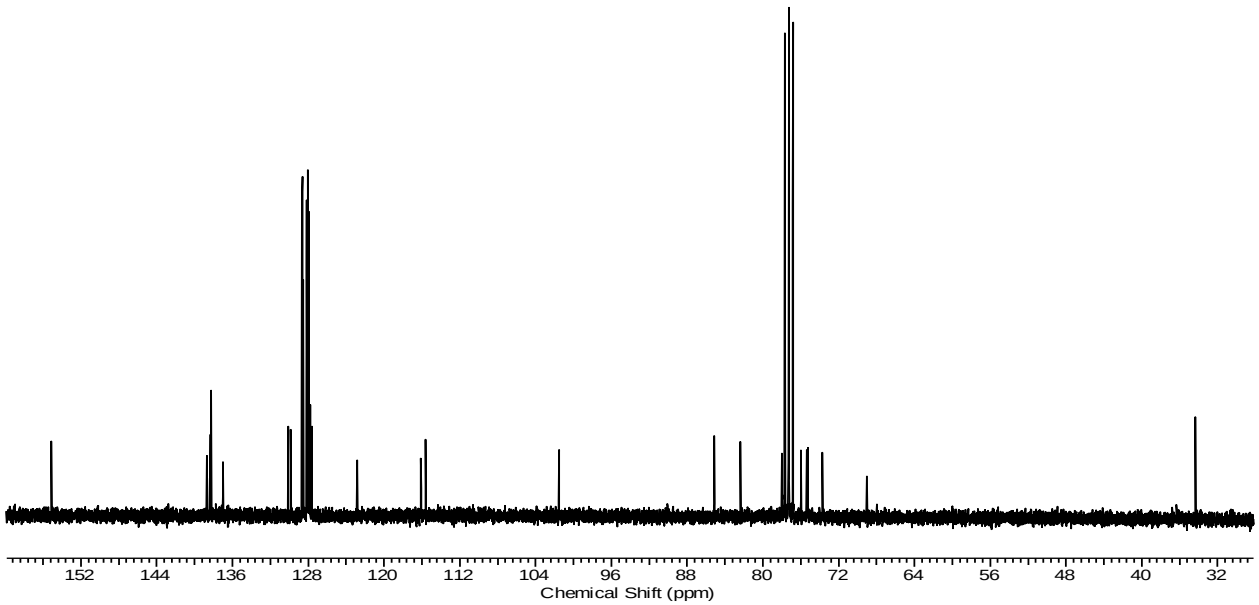
$CDCl_3$ at 300 MHz



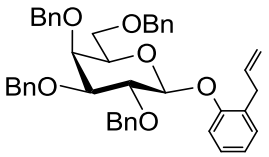
1d



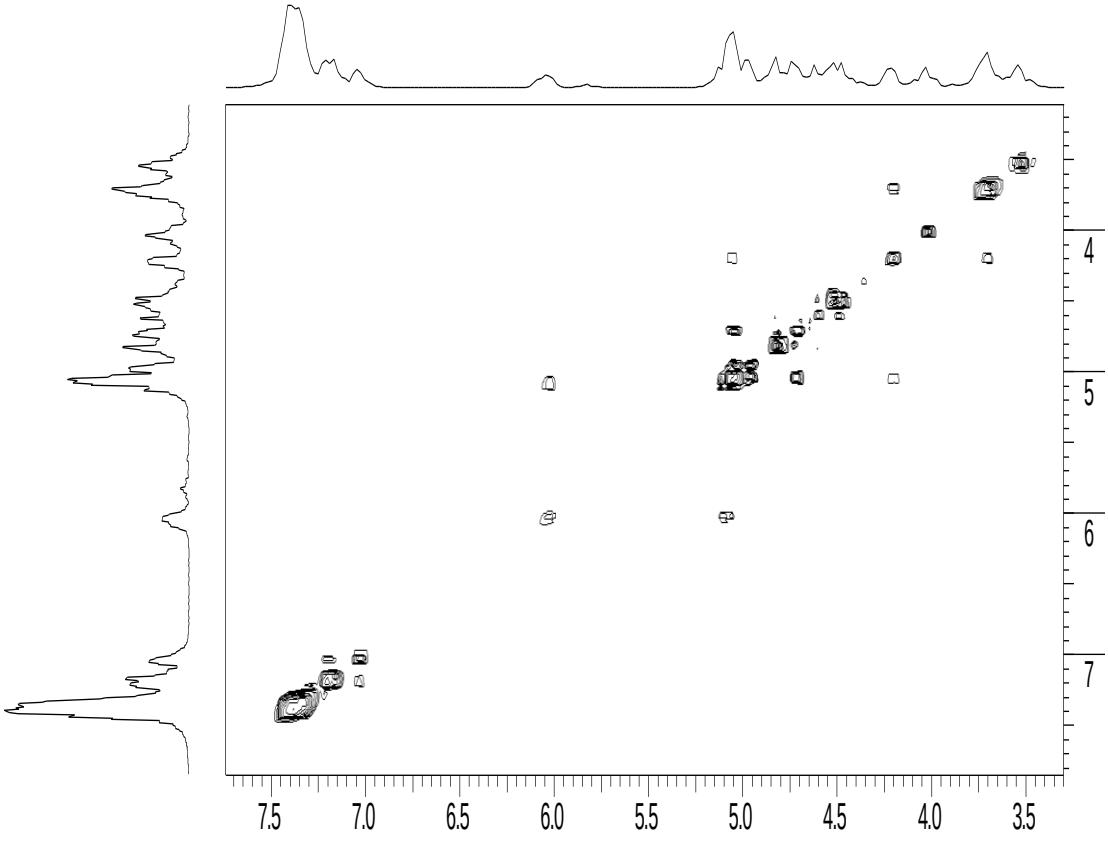
$CDCl_3$ at 300 MHz



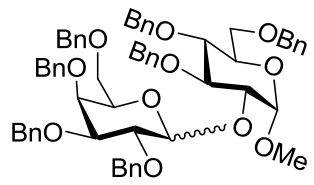
$CDCl_3$ at 75 MHz



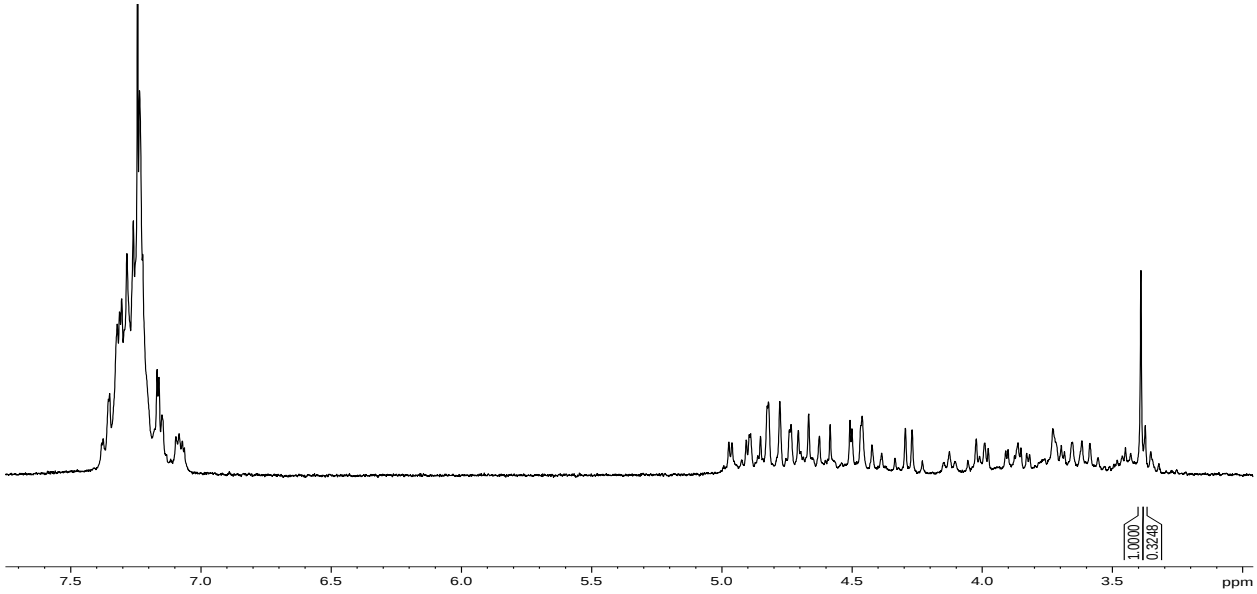
1d



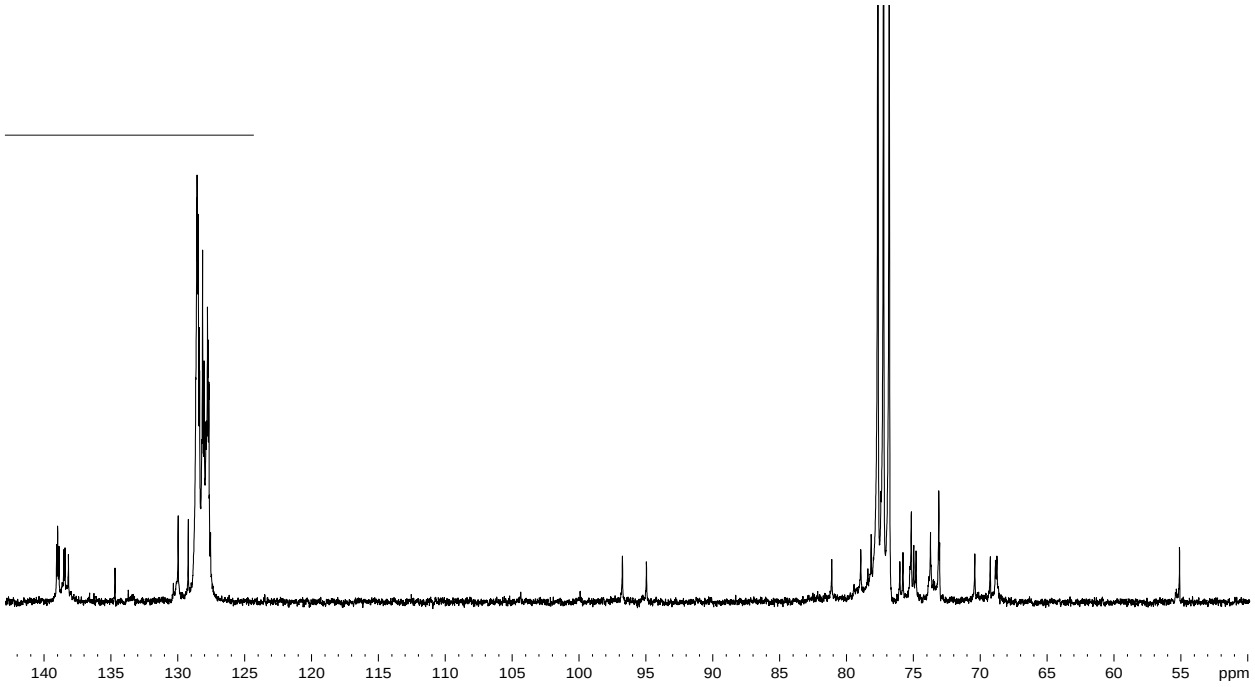
$CDCl_3$ at 300 MHz



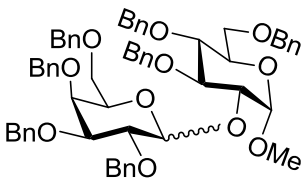
9d



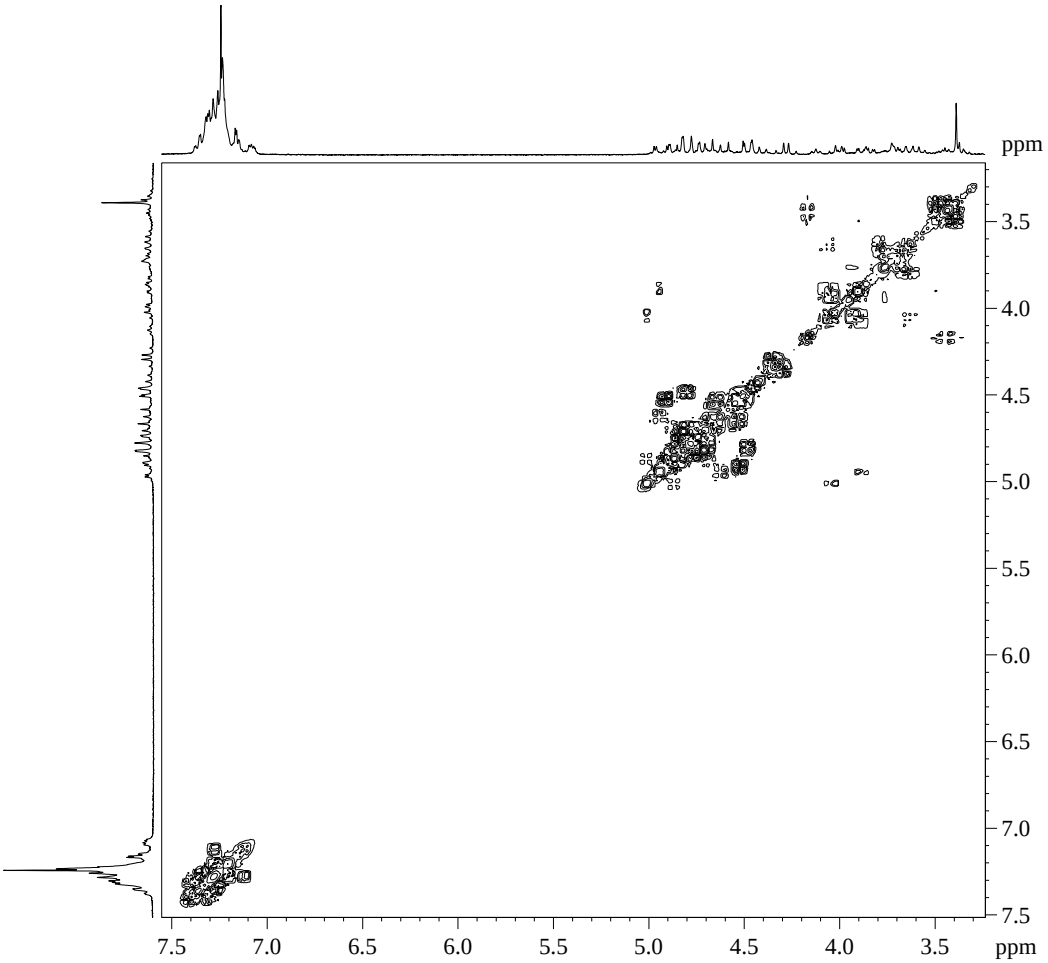
$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



9d



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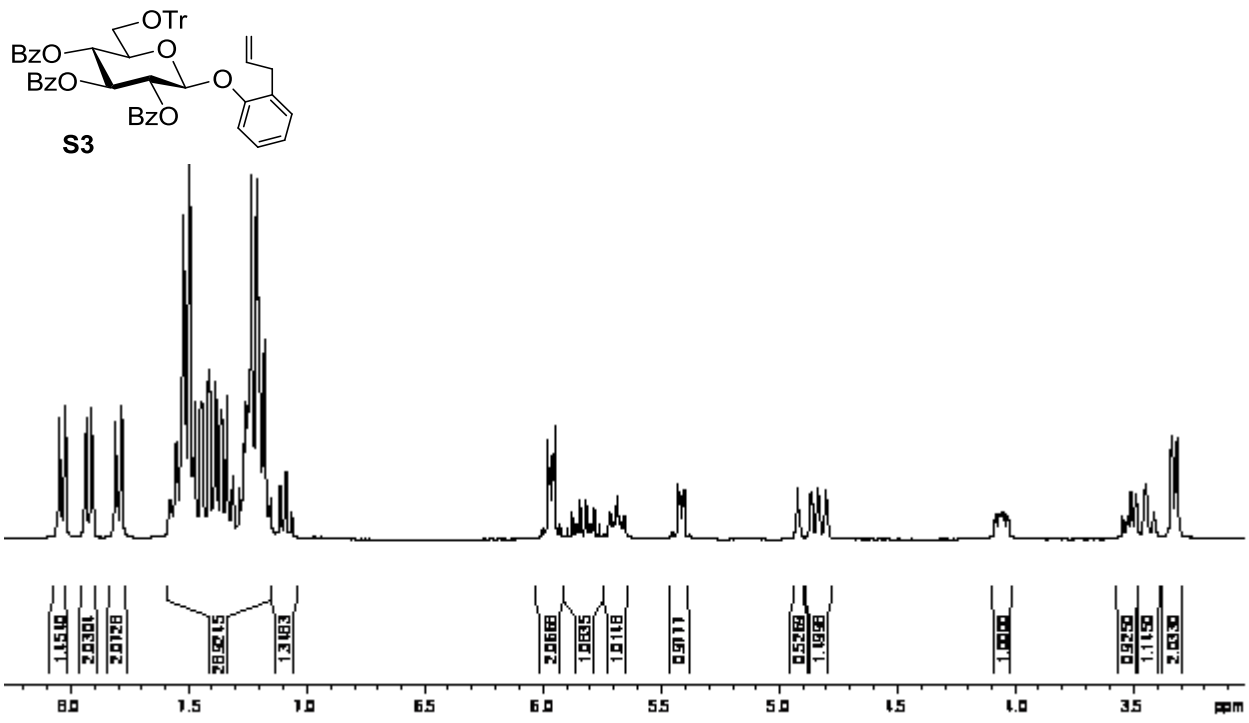
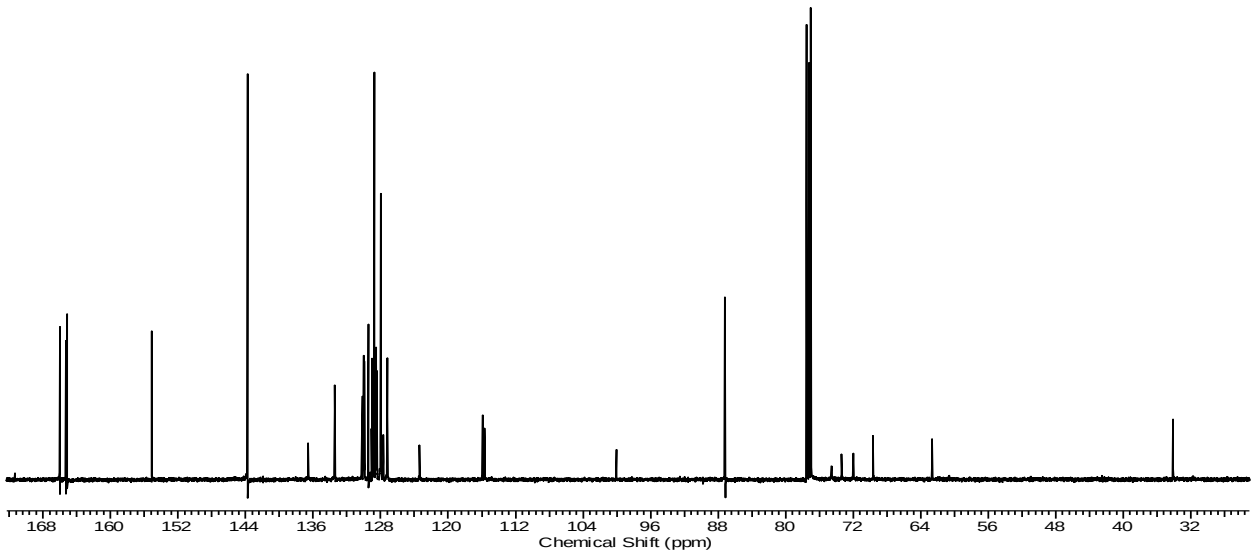
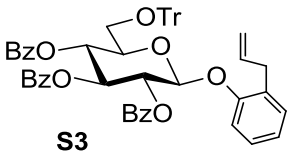


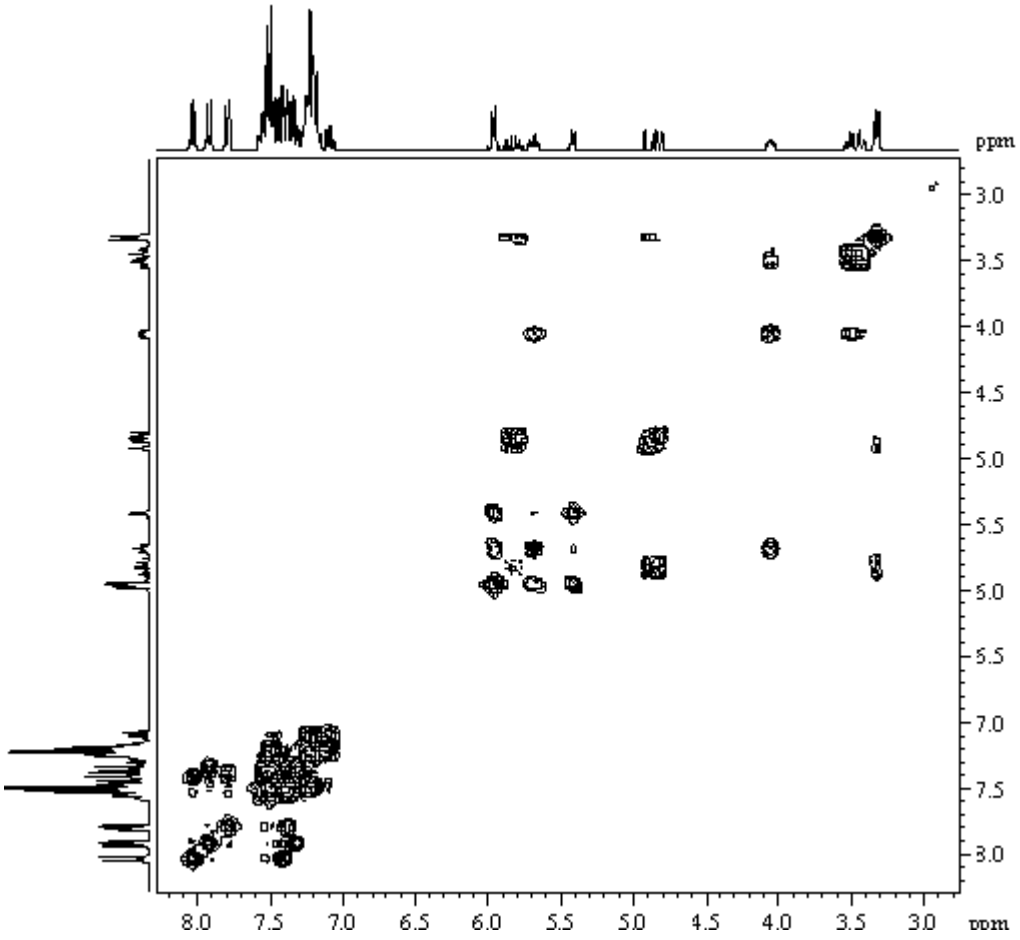
$CDCl_3$ at 300 MHz



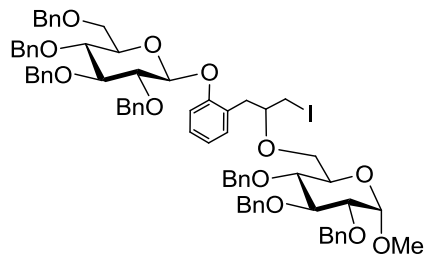
$CDCl_3$ at 75 MHz



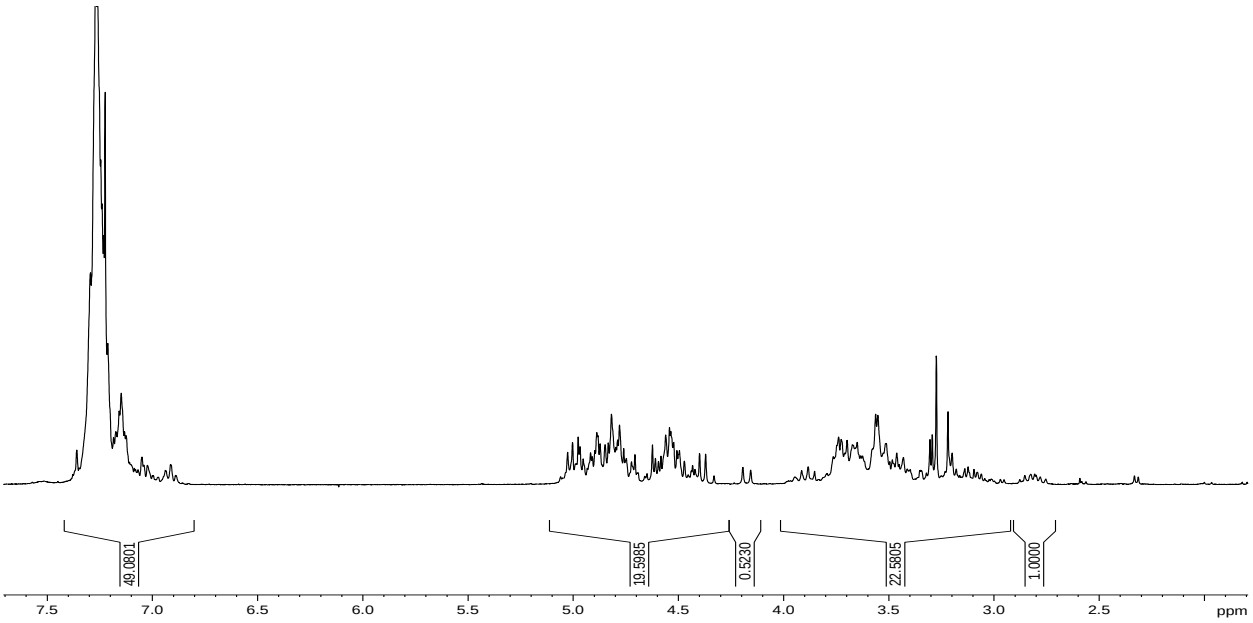
S3



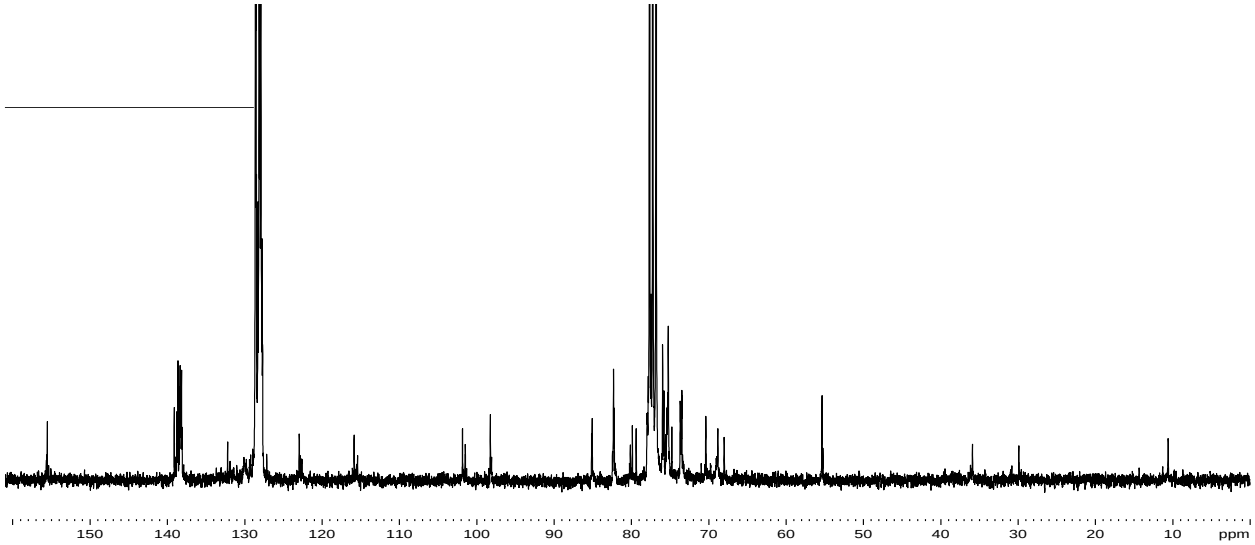
$CDCl_3$ at 300 MHz



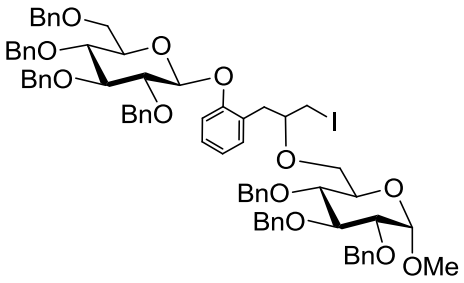
12



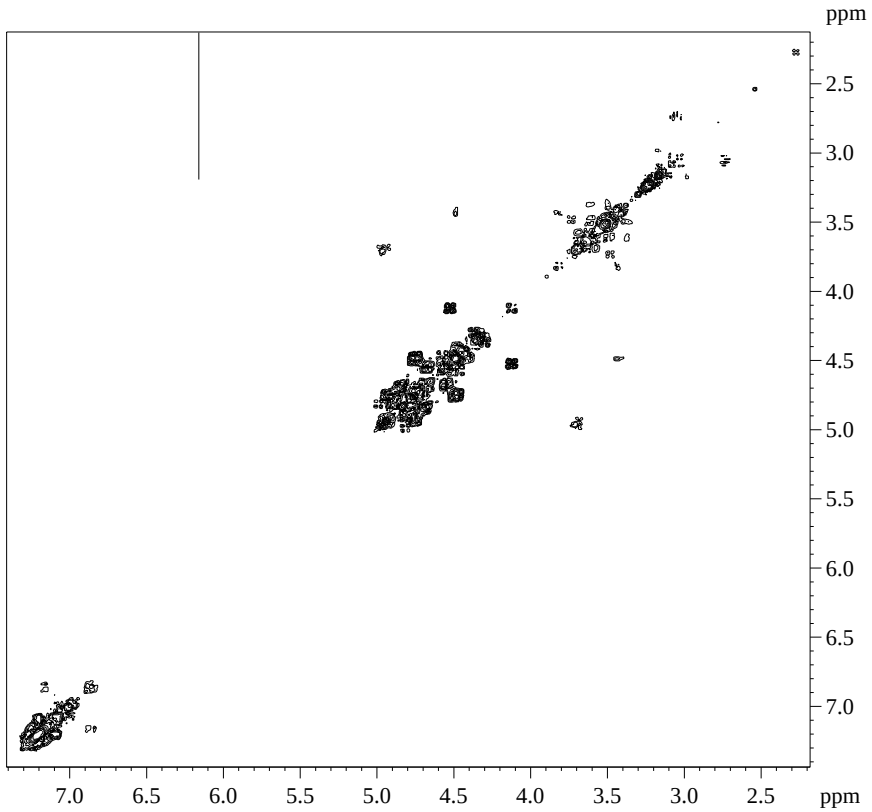
$CDCl_3$ at 300 MHz



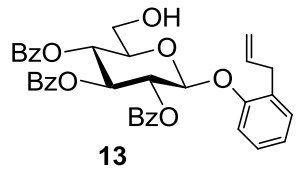
$CDCl_3$ at 75 MHz



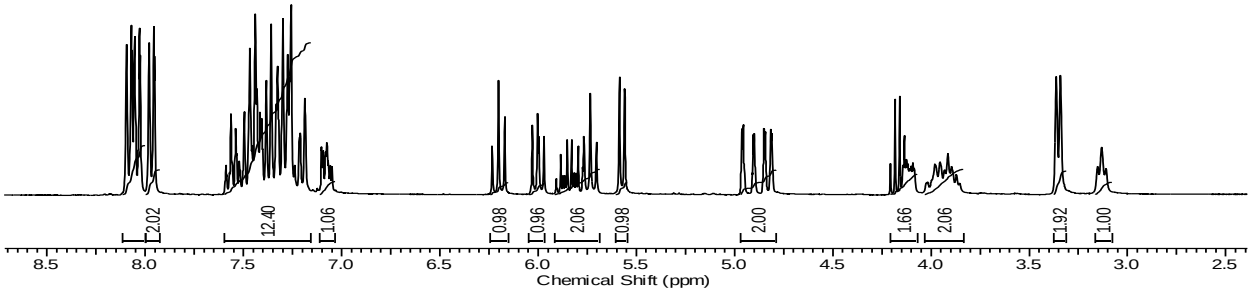
12



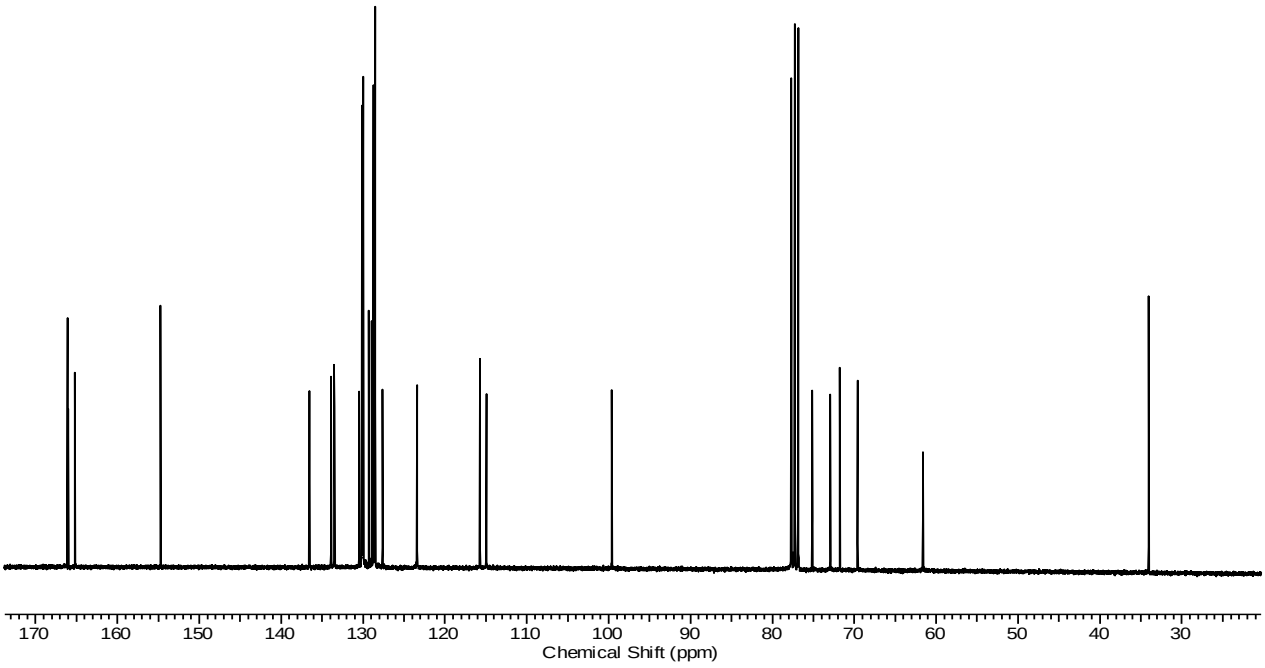
$CDCl_3$ at 300 MHz



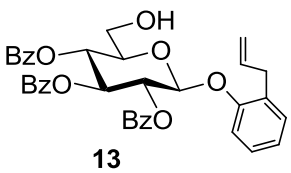
13



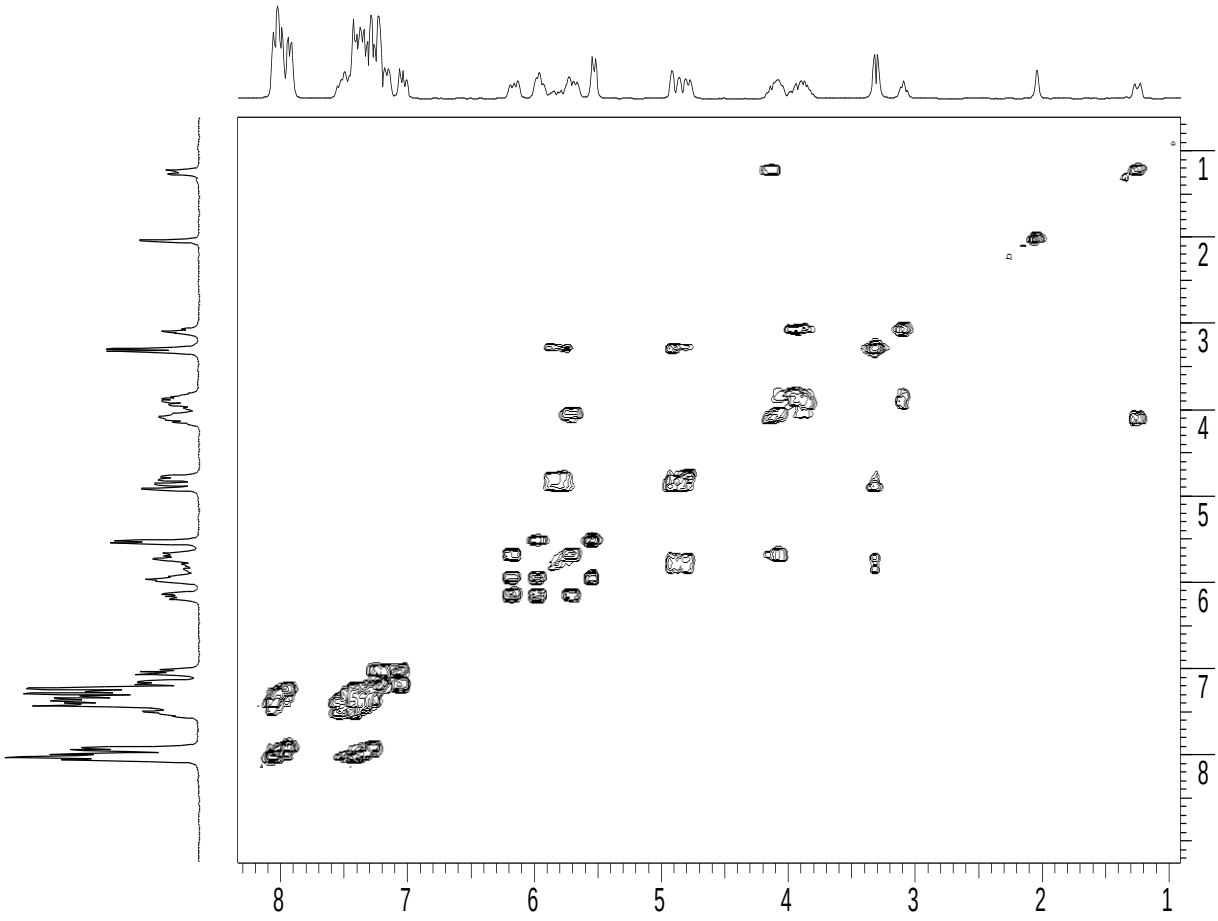
$CDCl_3$ at 300 MHz



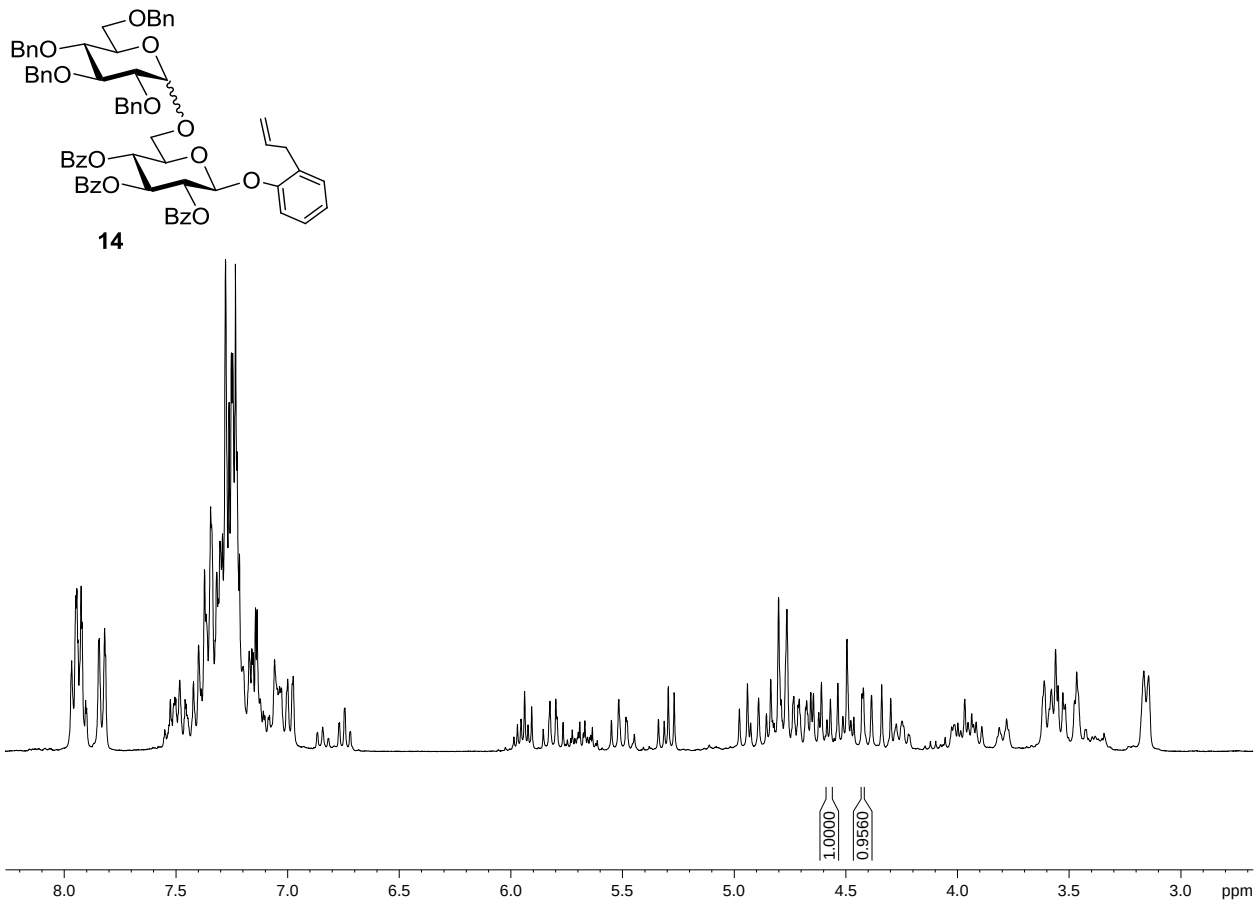
$CDCl_3$ at 75 MHz



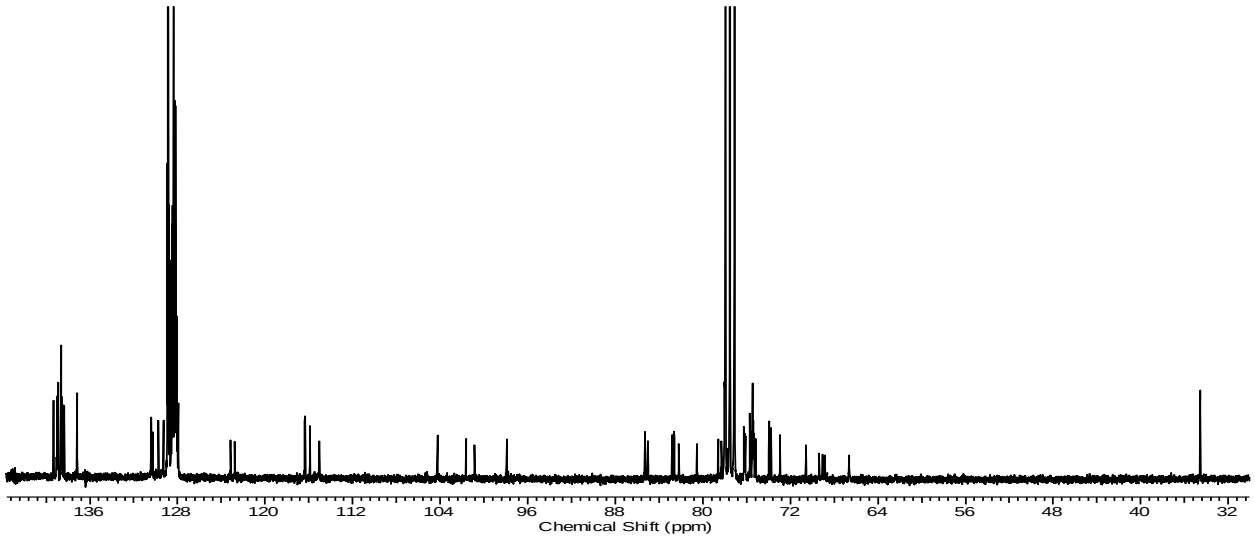
13



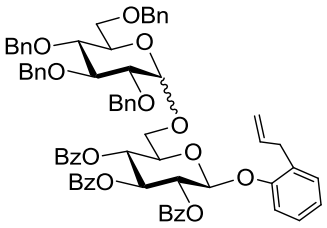
$CDCl_3$ at 300 MHz



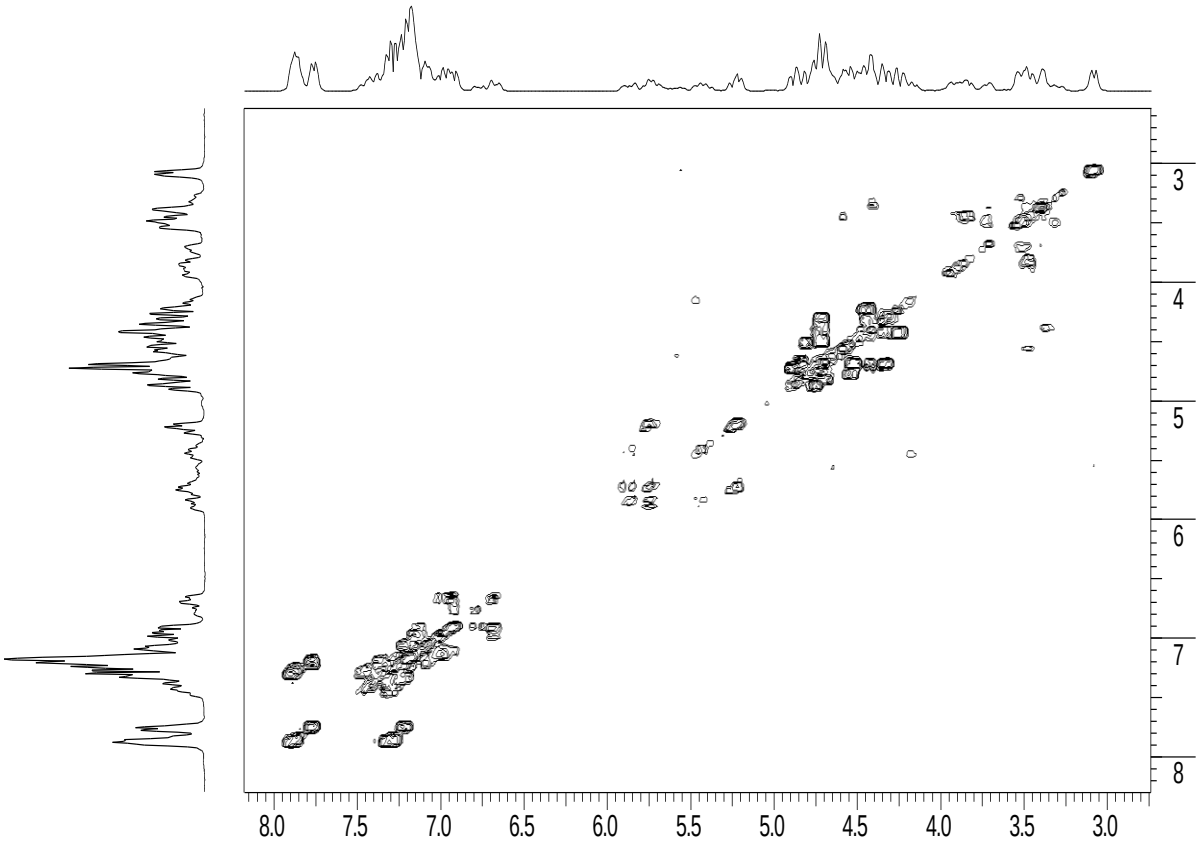
$CDCl_3$ at 300 MHz



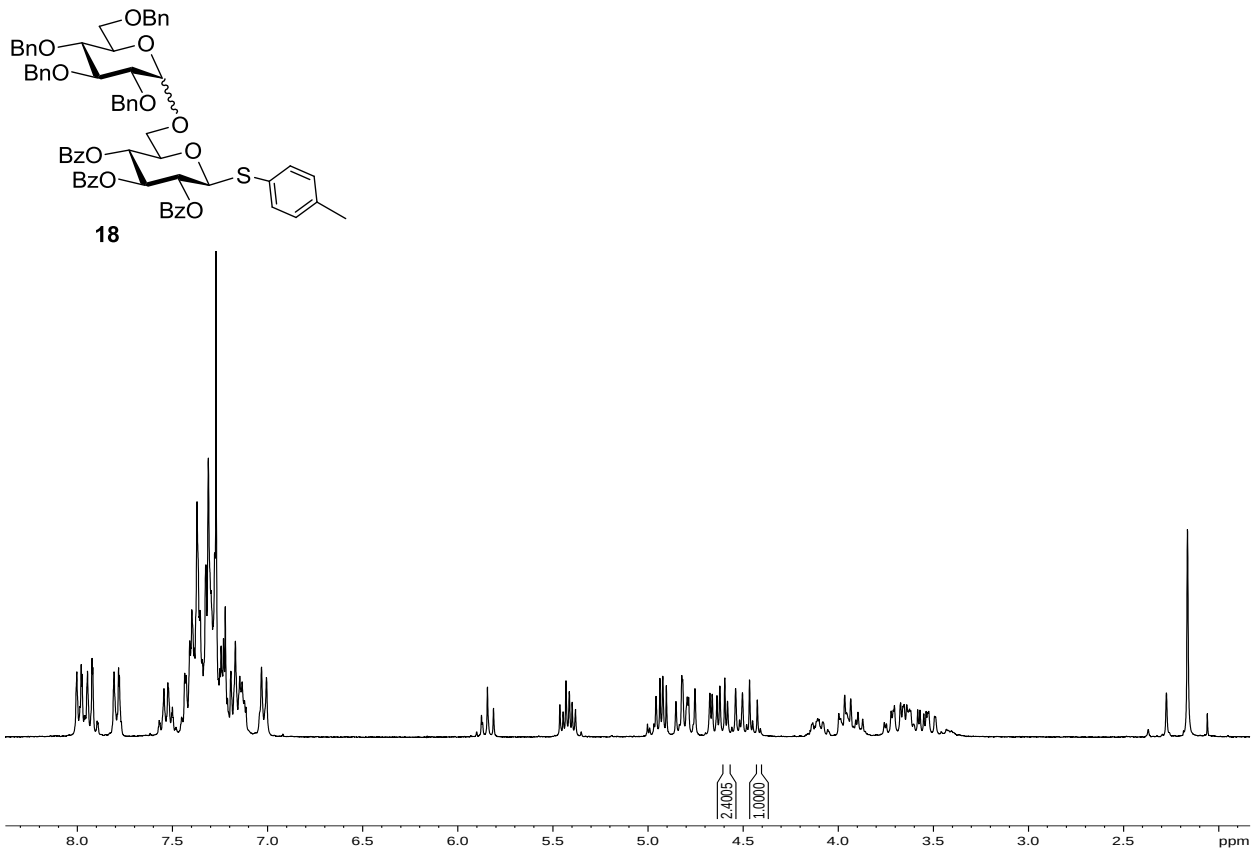
$CDCl_3$ at 75 MHz



14

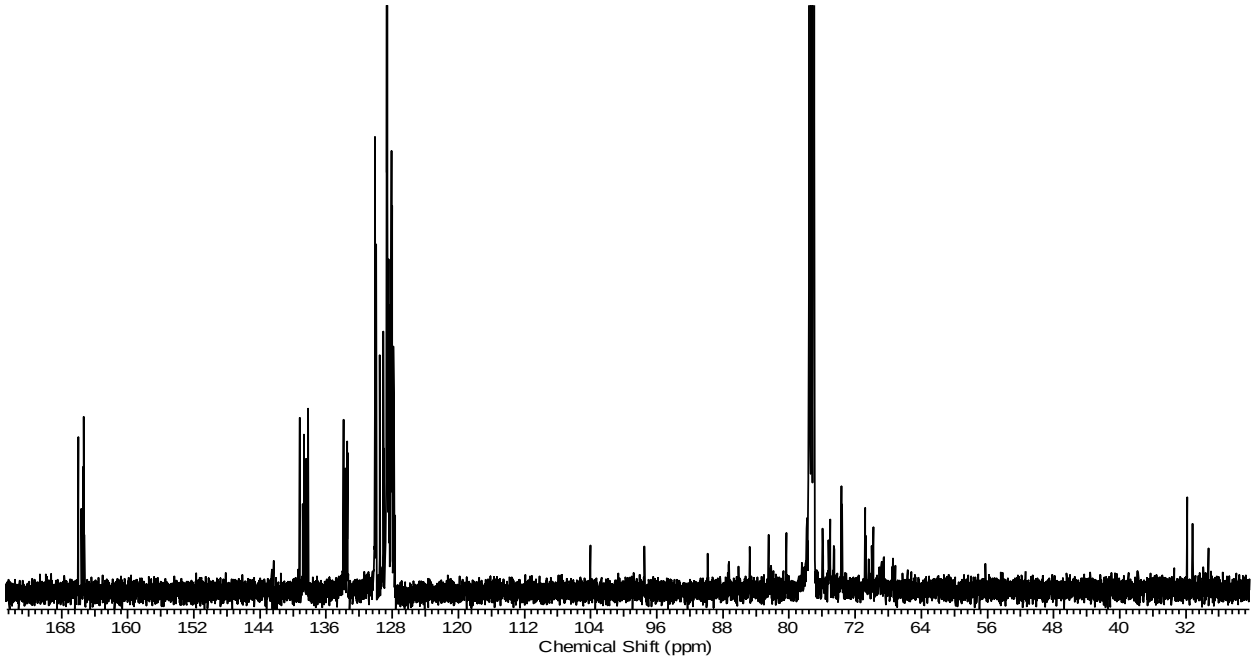


$CDCl_3$ at 300 MHz

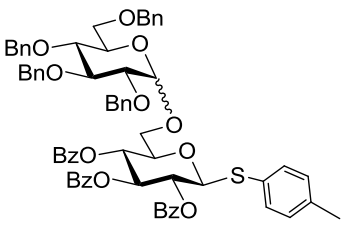


18

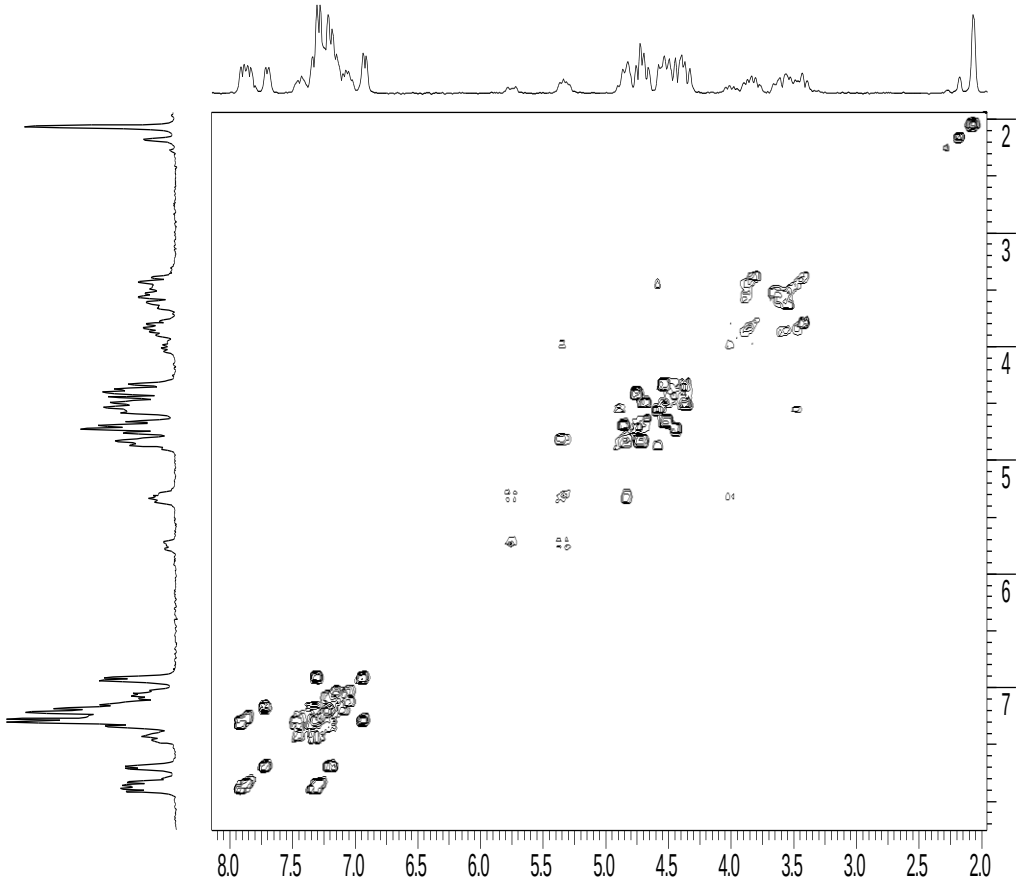
$CDCl_3$ at 300 MHz



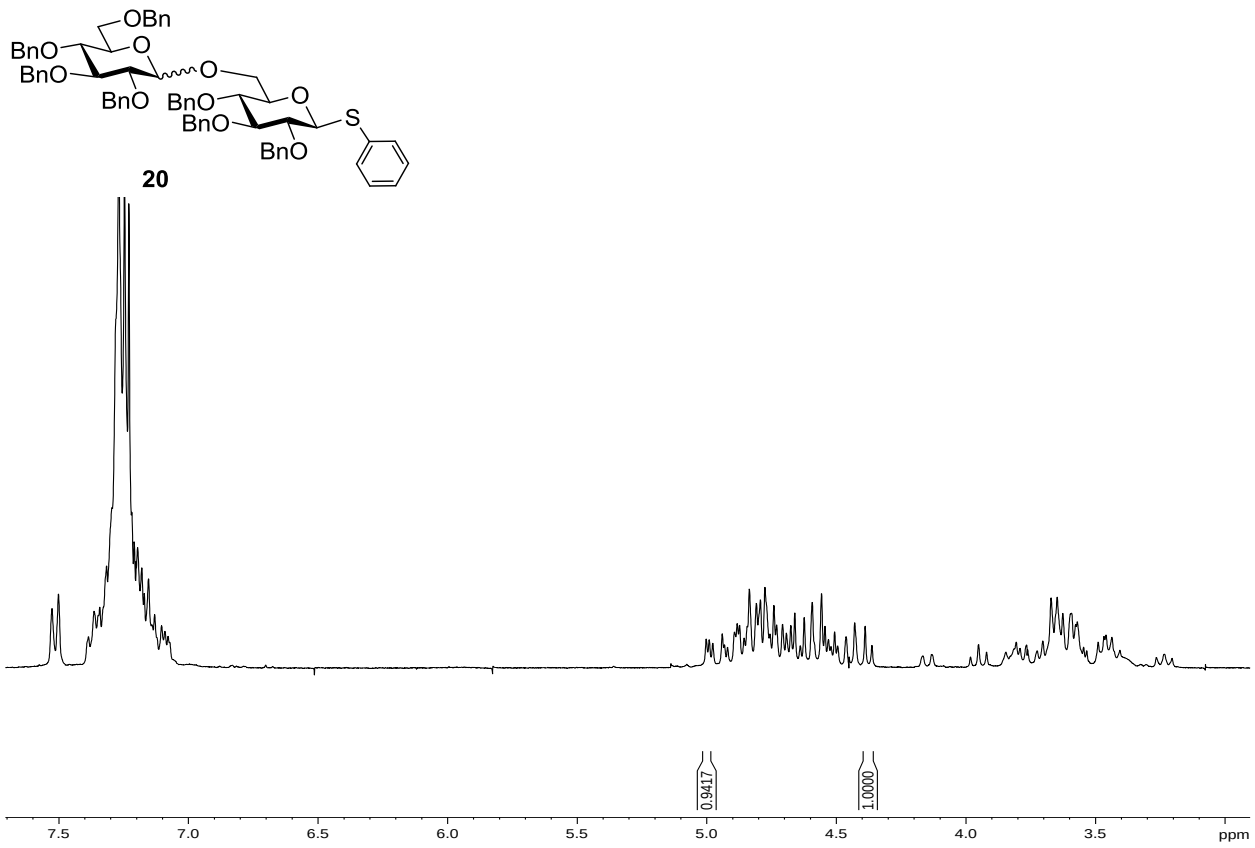
$CDCl_3$ at 75 MHz



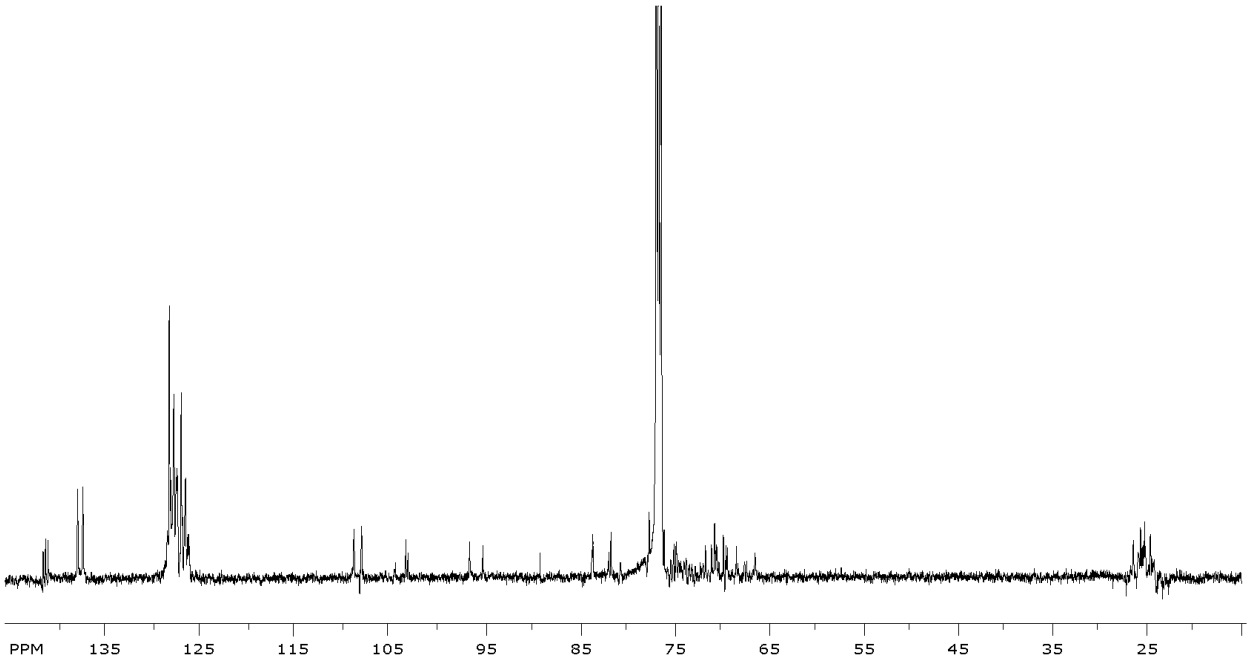
18



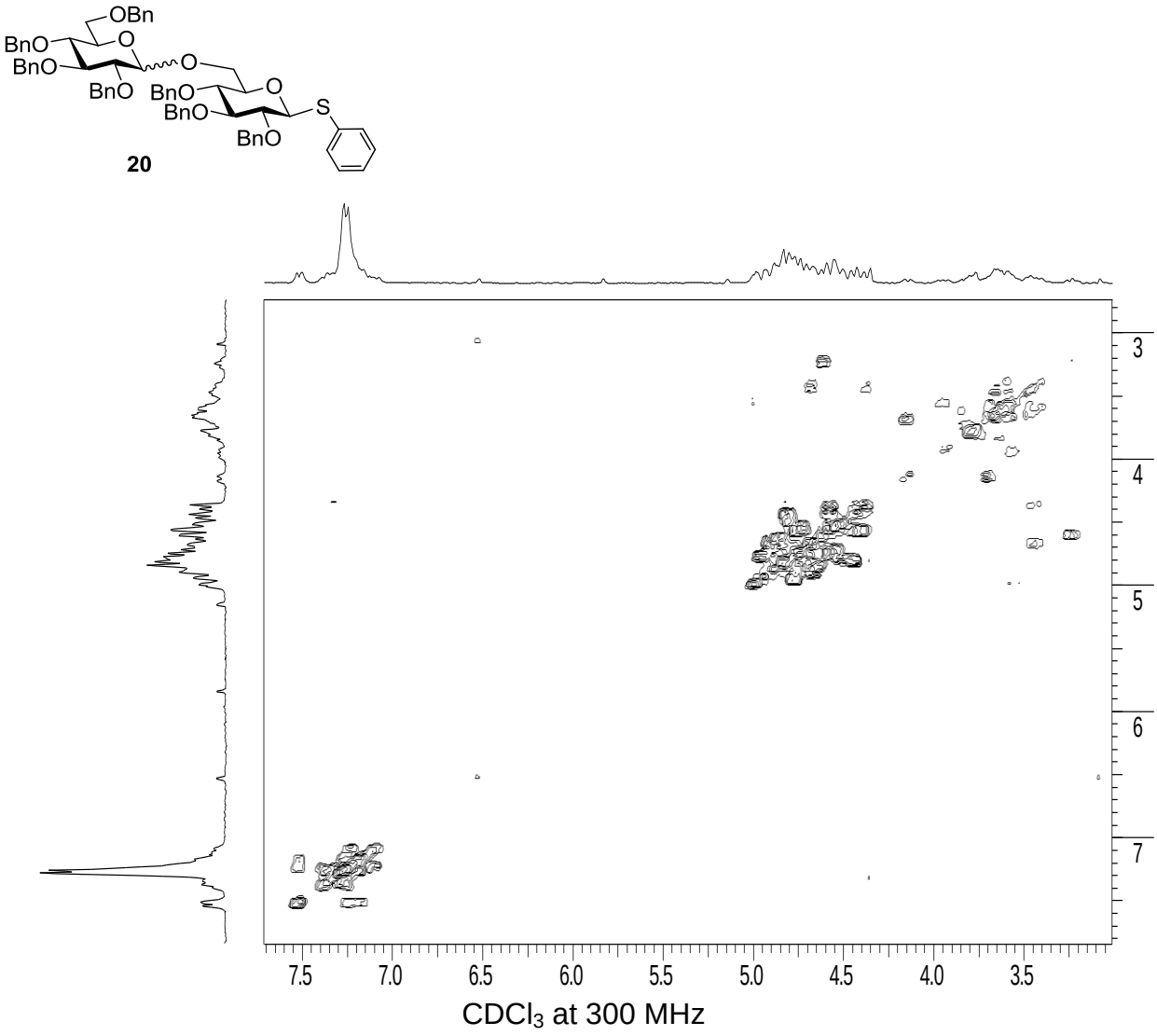
$CDCl_3$ at 300 MHz



$CDCl_3$ at 300 MHz

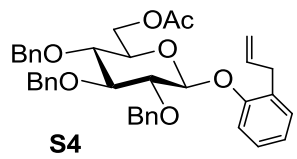


$CDCl_3$ at 125 MHz

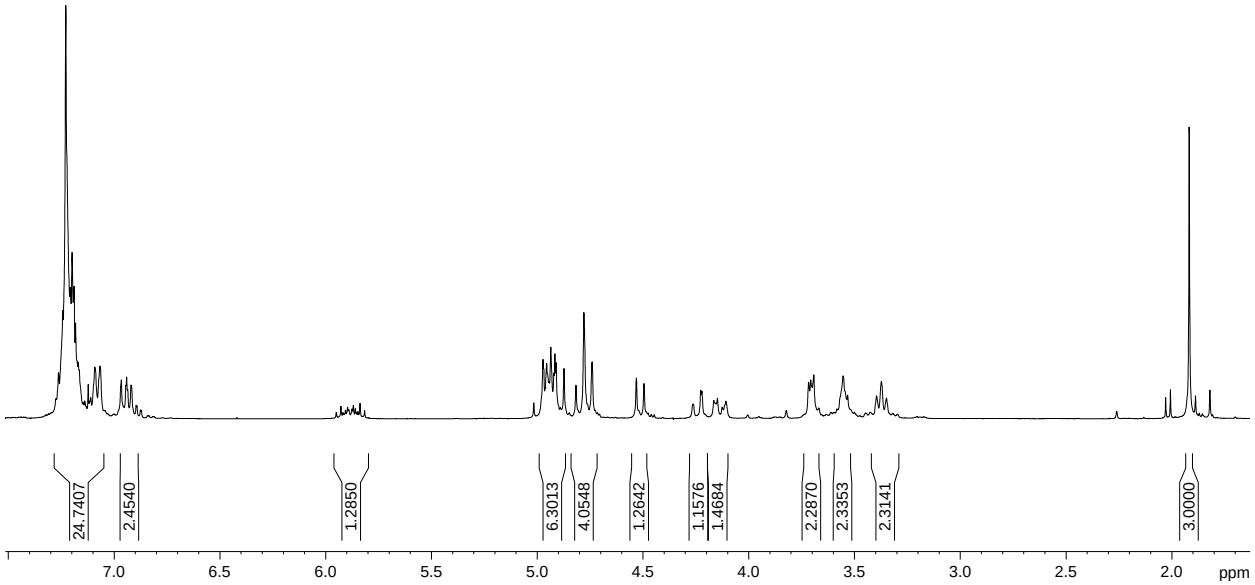


20

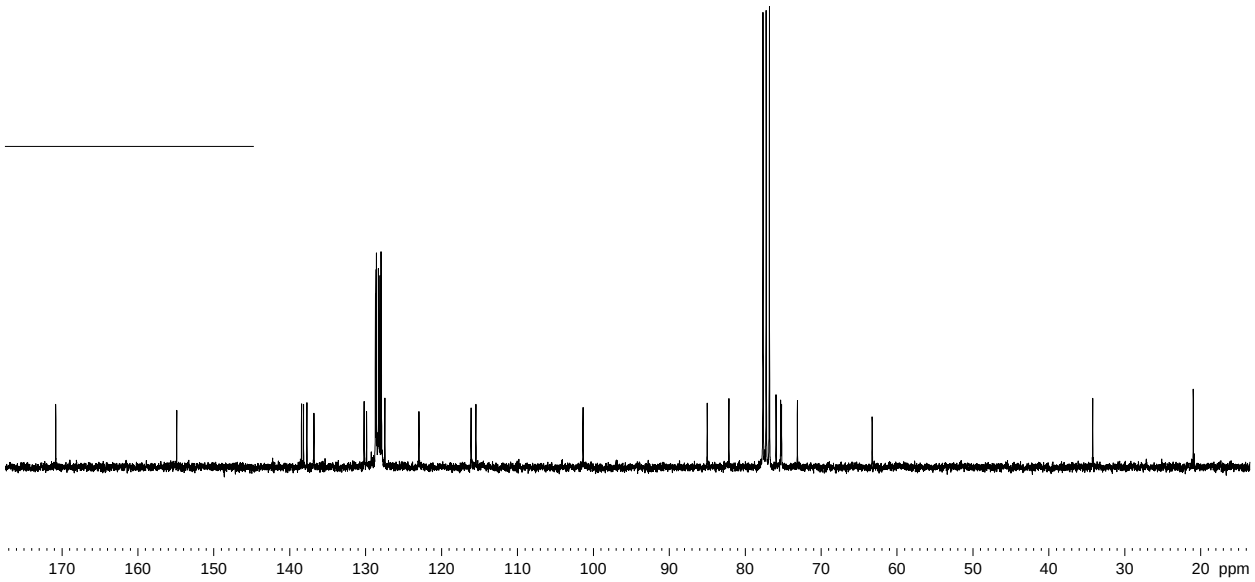
$CDCl_3$ at 300 MHz



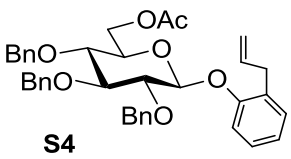
S4



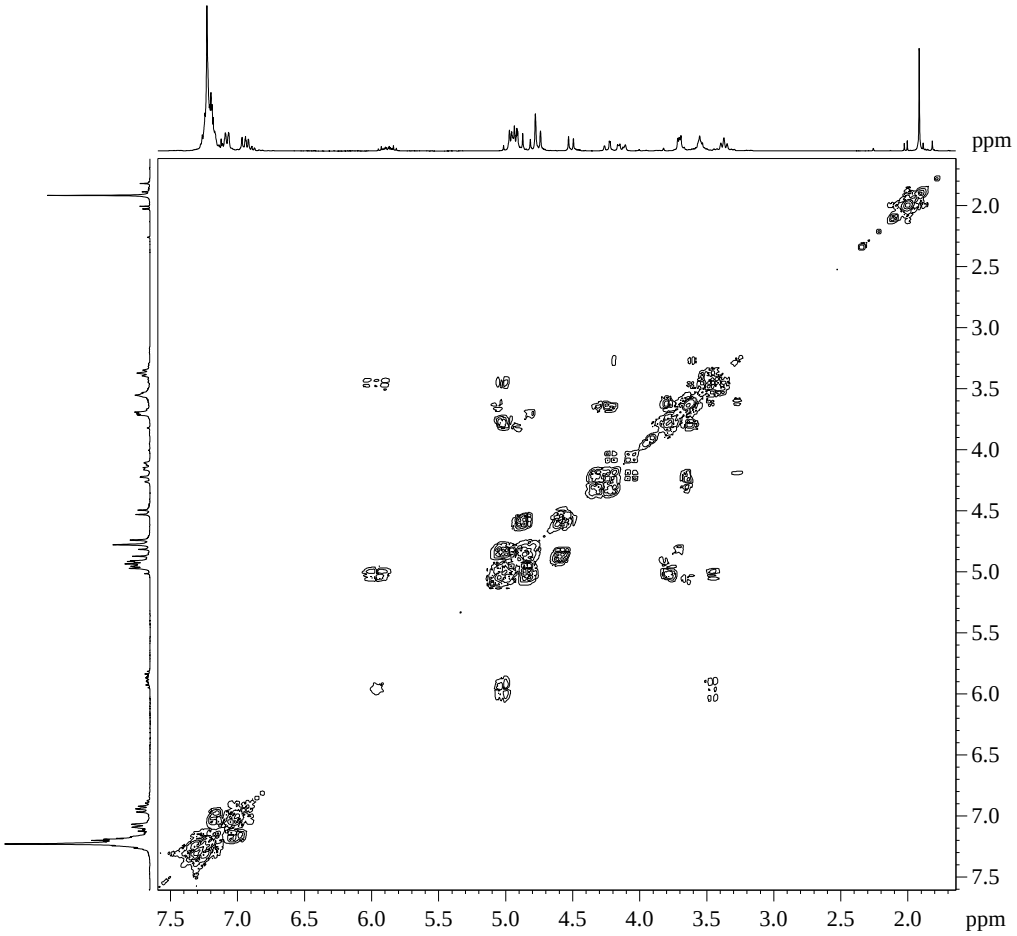
$CDCl_3$ at 300 MHz



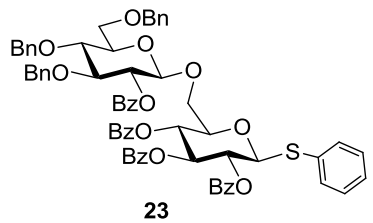
$CDCl_3$ at 75 MHz



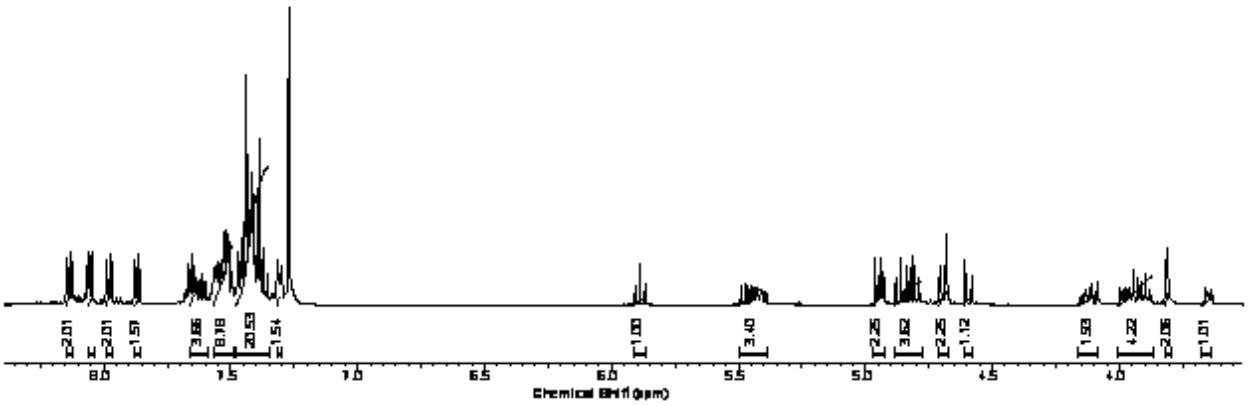
S4



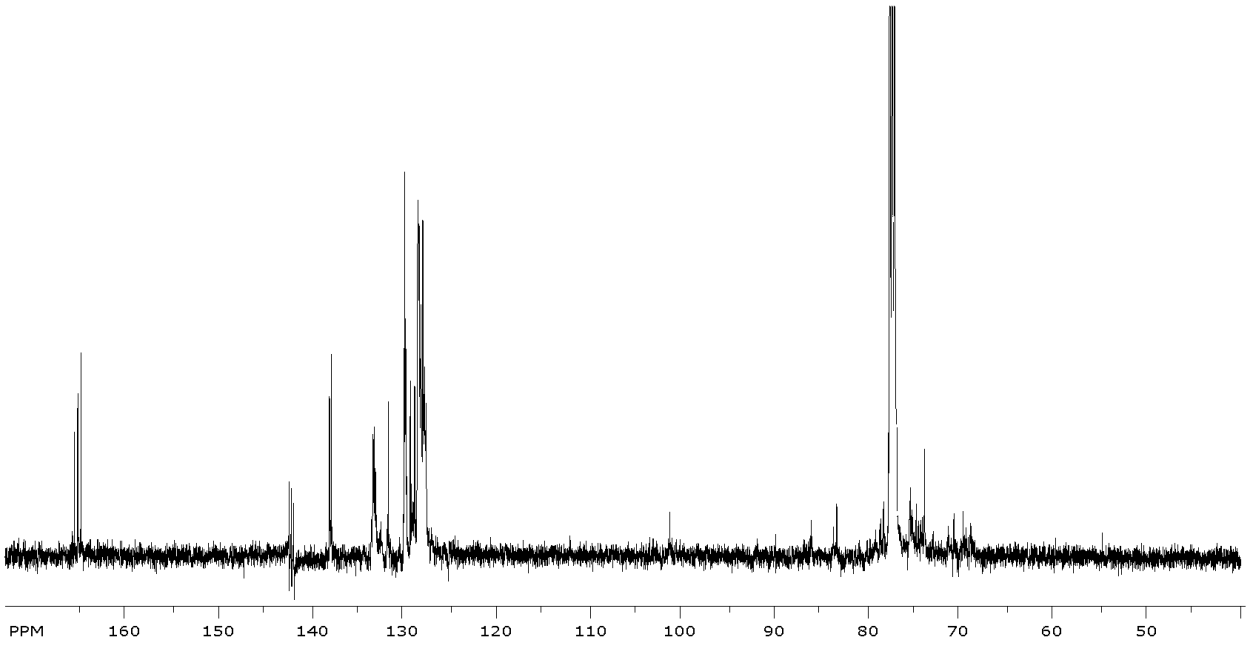
$CDCl_3$ at 300 MHz



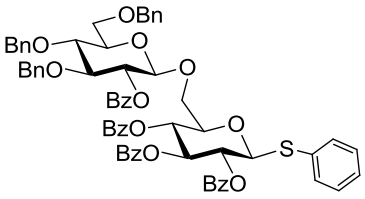
23



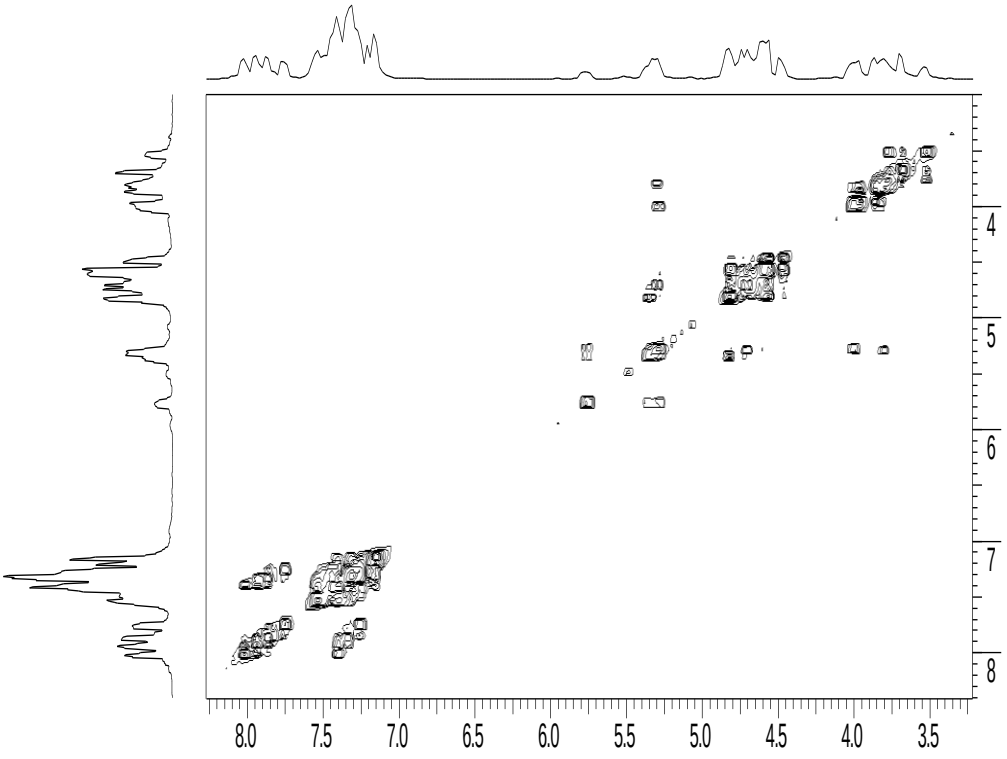
$CDCl_3$ at 300 MHz



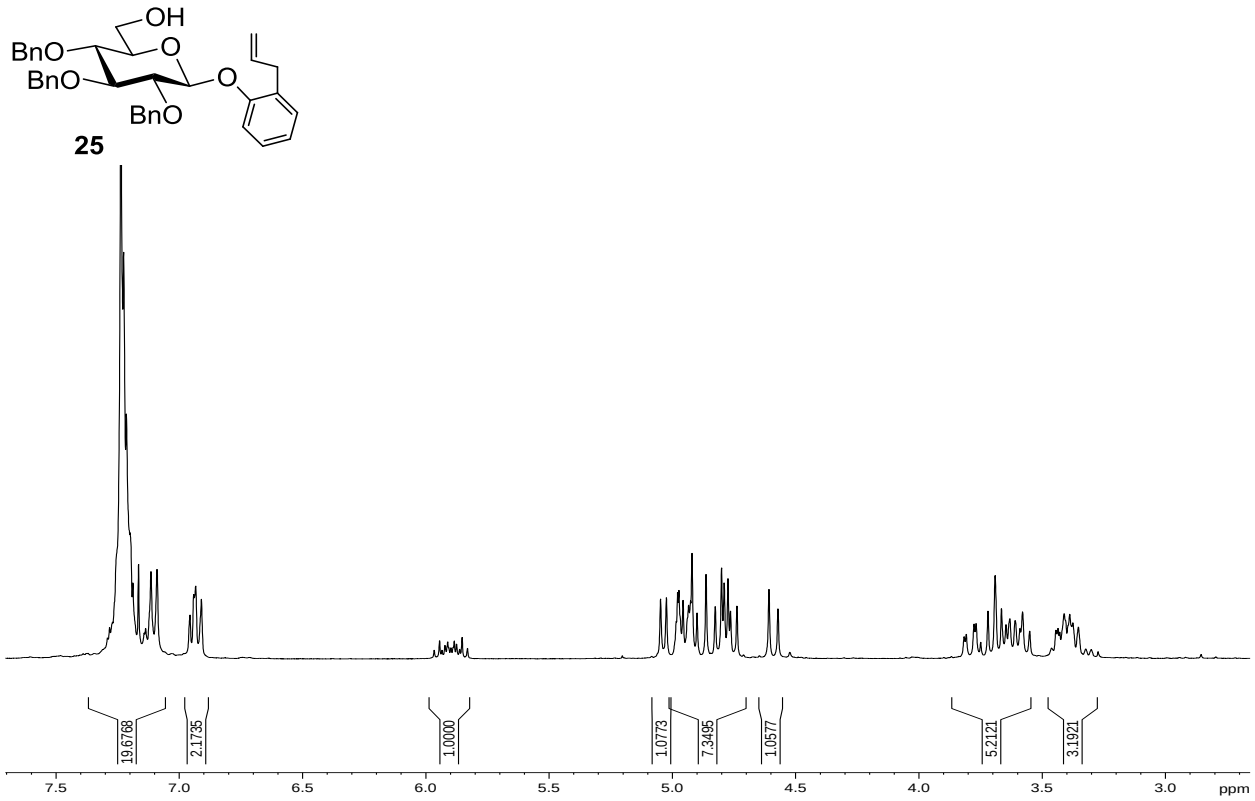
$CDCl_3$ at 125 MHz



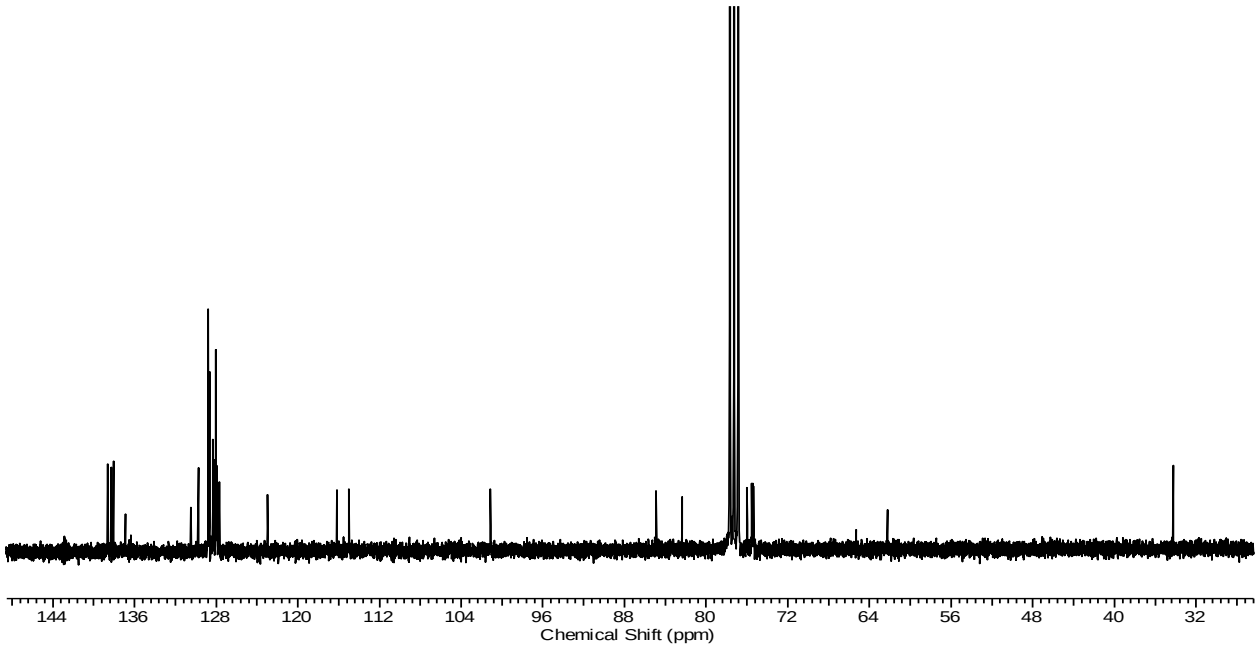
23



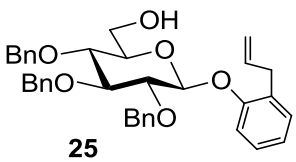
$CDCl_3$ at 300 MHz



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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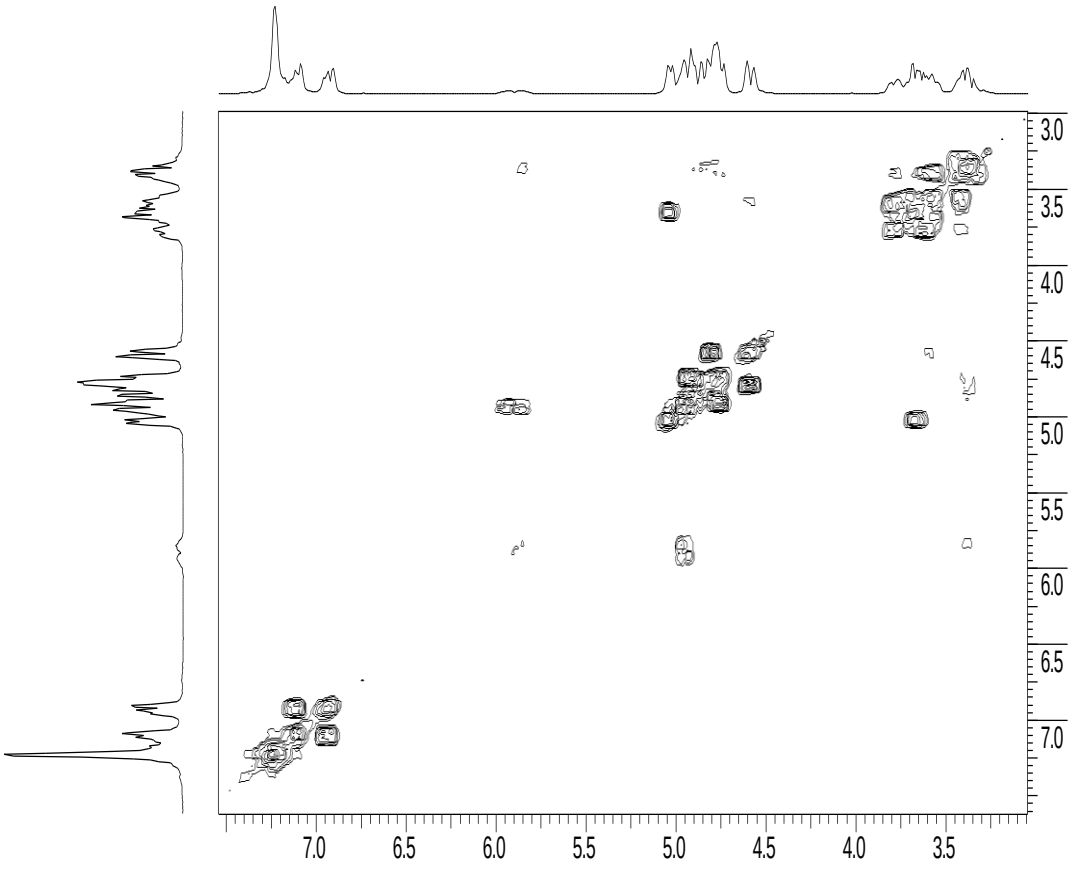
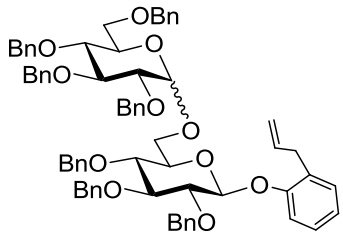


$CDCl_3$ at 300 MHz



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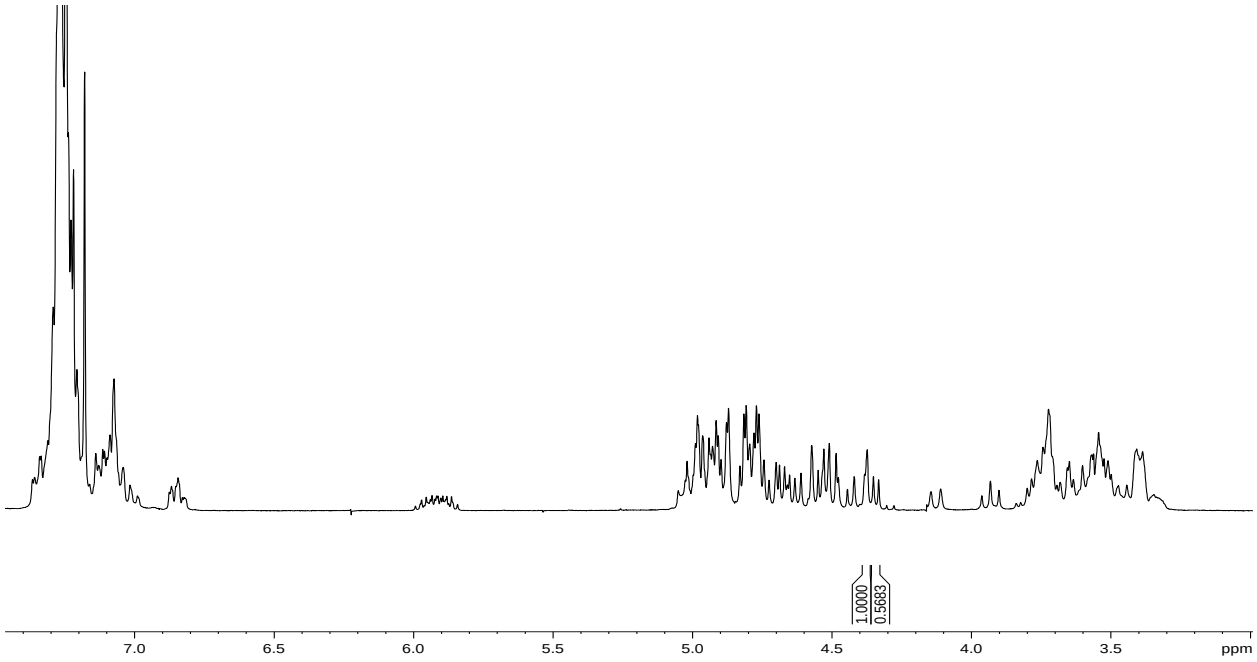
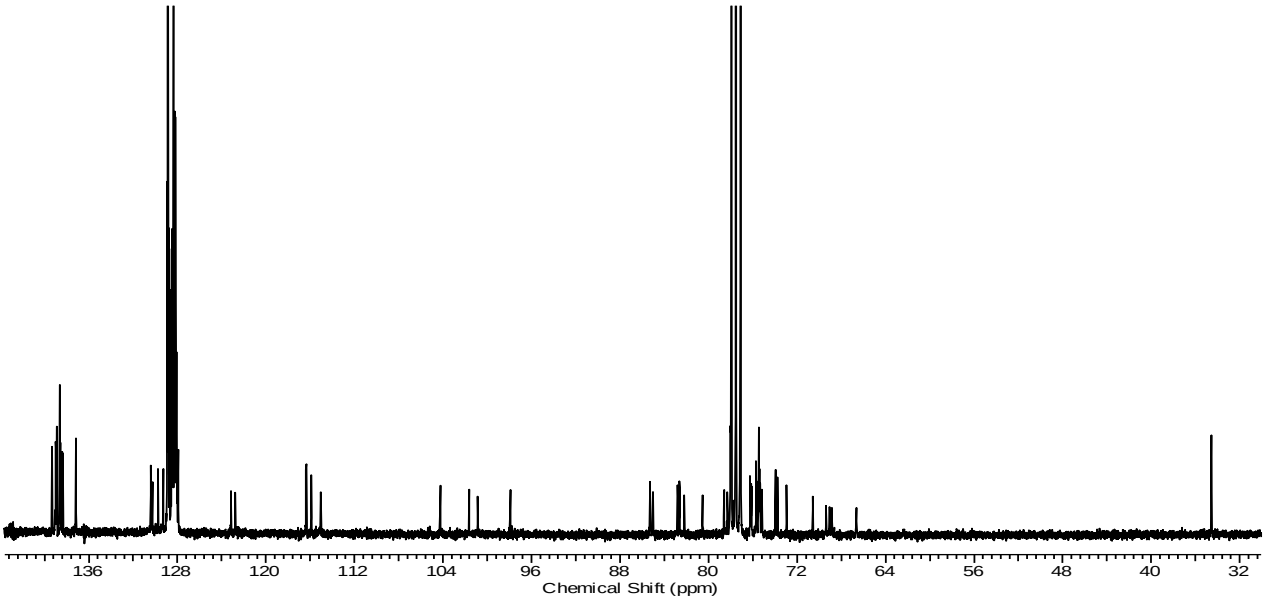
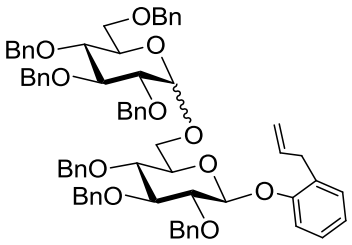


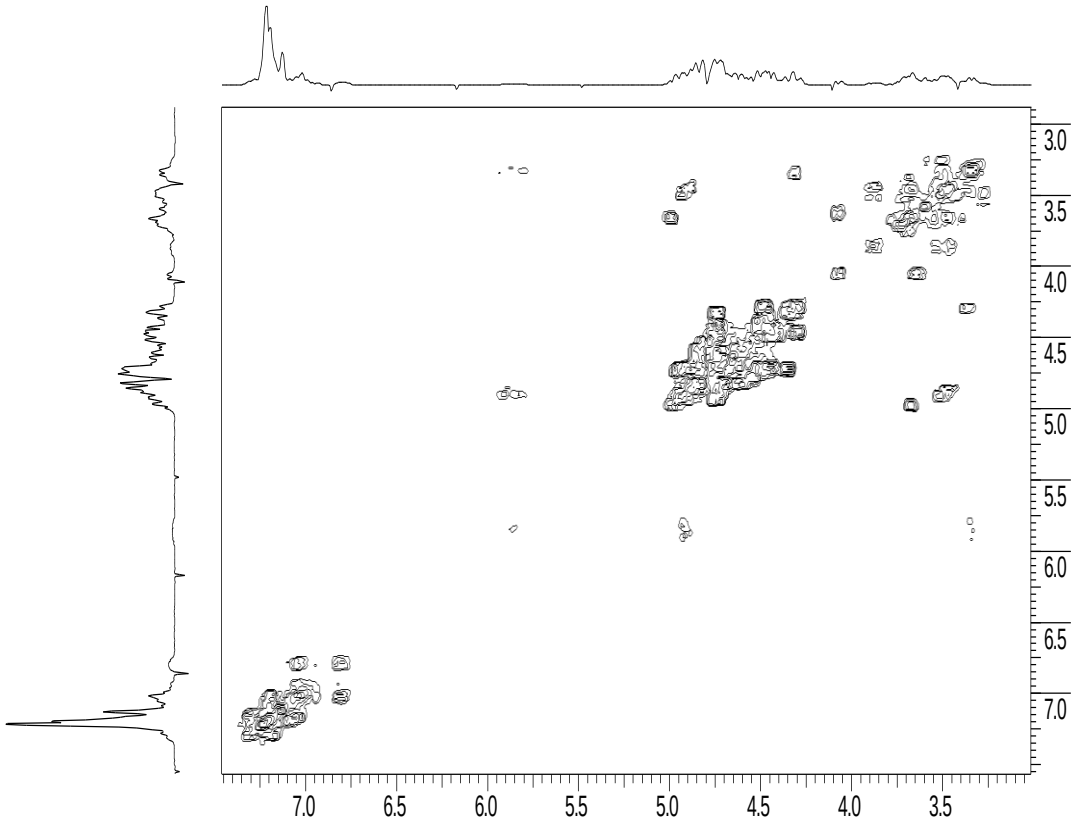
$CDCl_3$ at 300 MHz



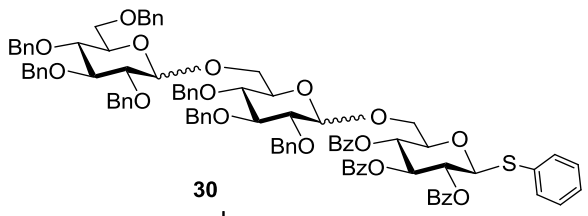
$CDCl_3$ at 75 MHz



26



$CDCl_3$ at 300 MHz



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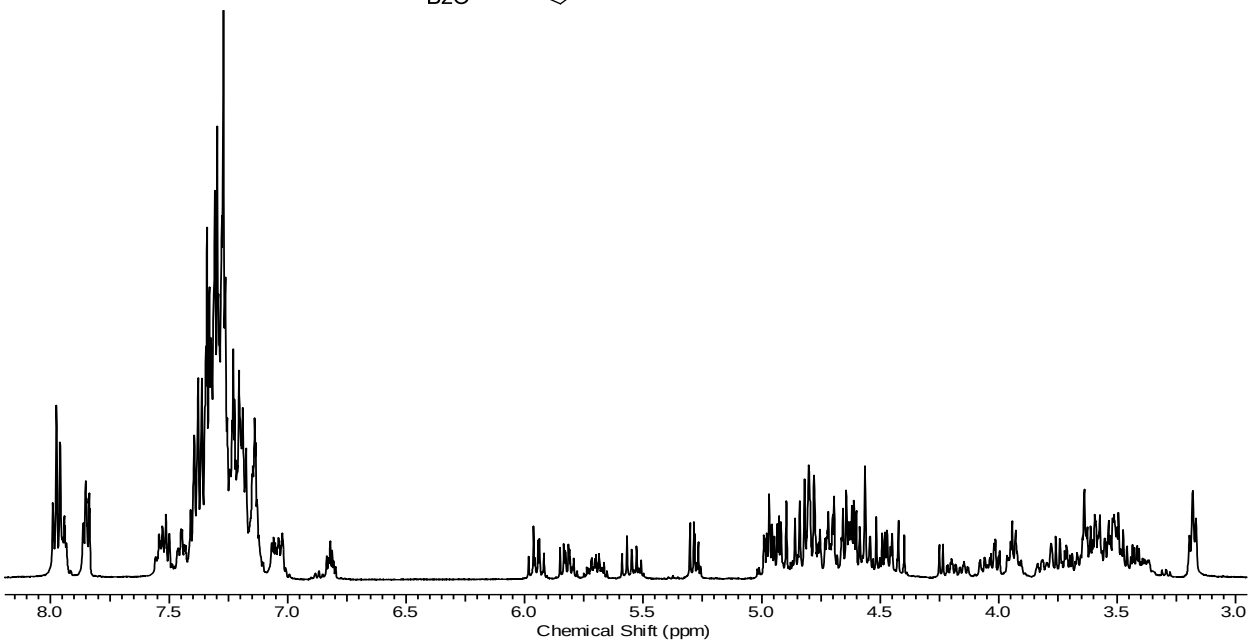
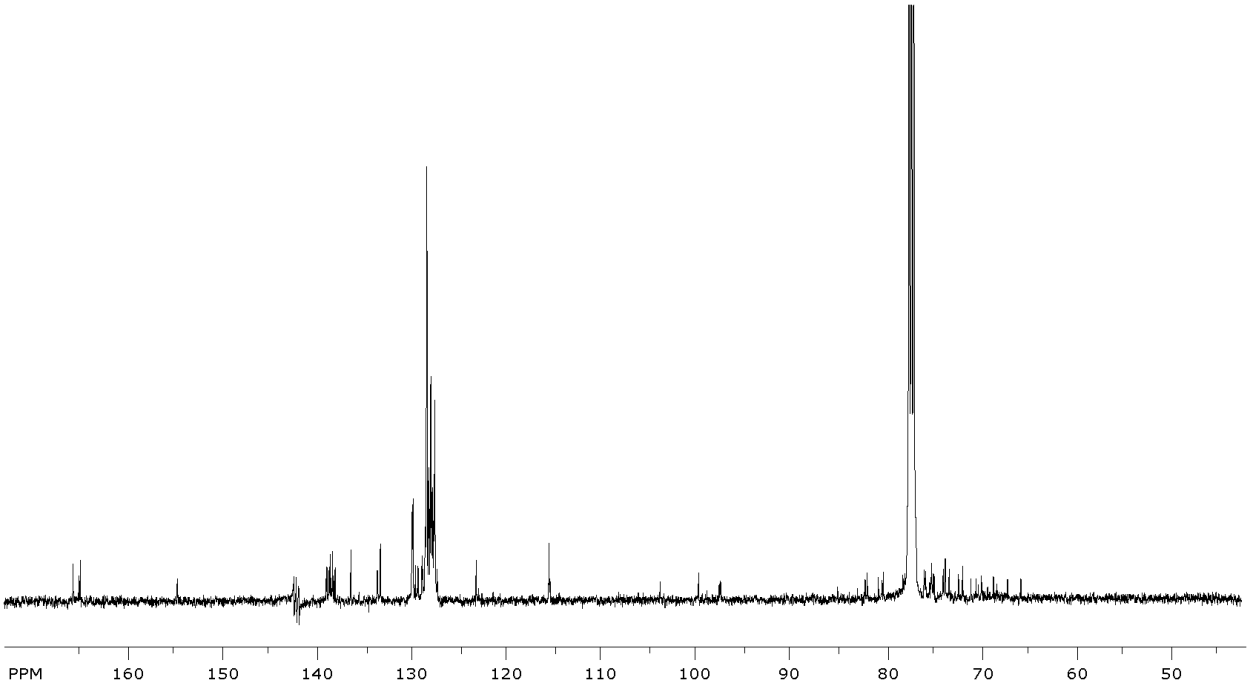
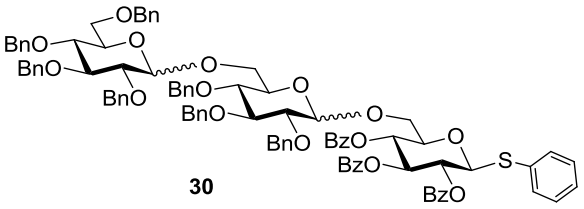


$CDCl_3$ at 300 MHz



$CDCl_3$ at 125 MHz



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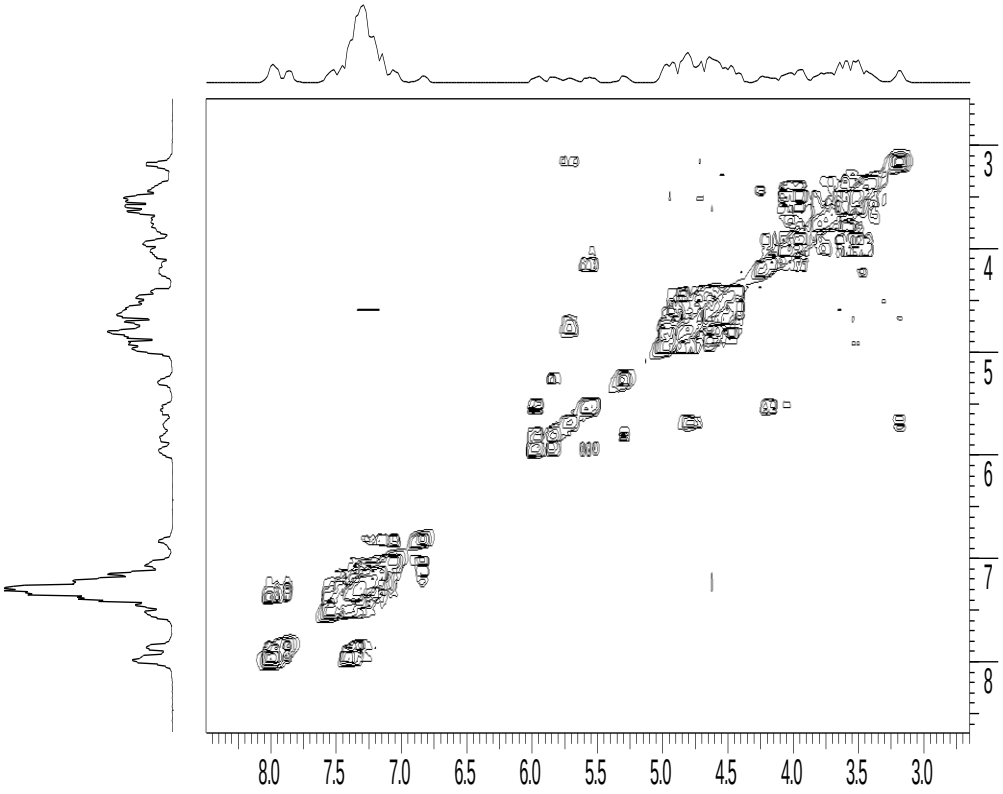
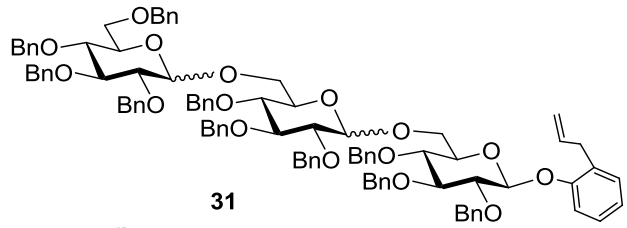


$CDCl_3$ at 300 MHz



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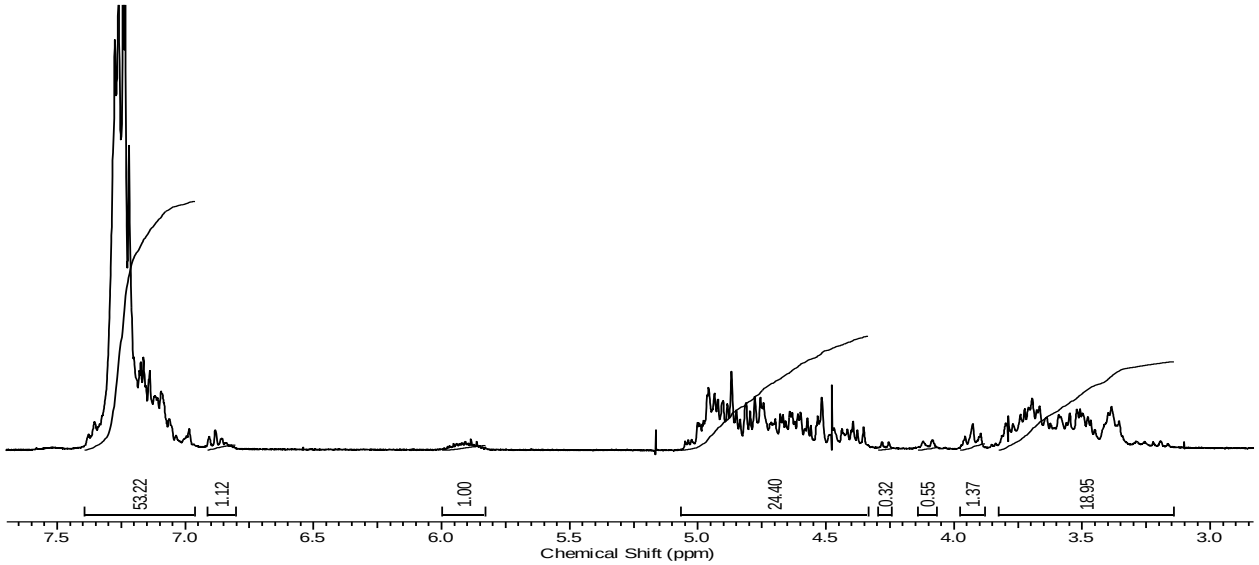
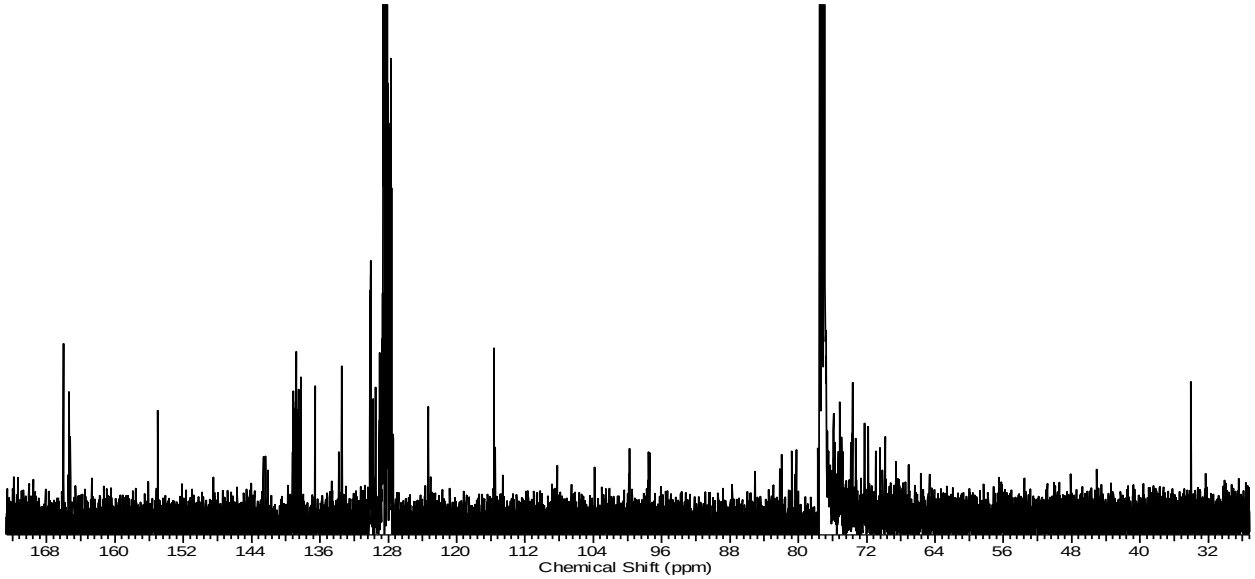
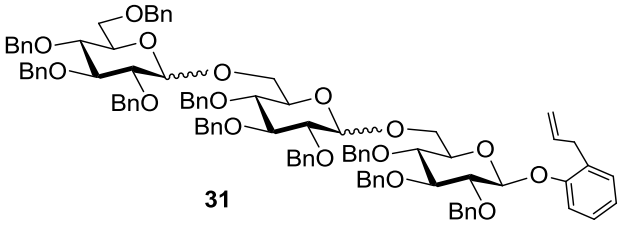


$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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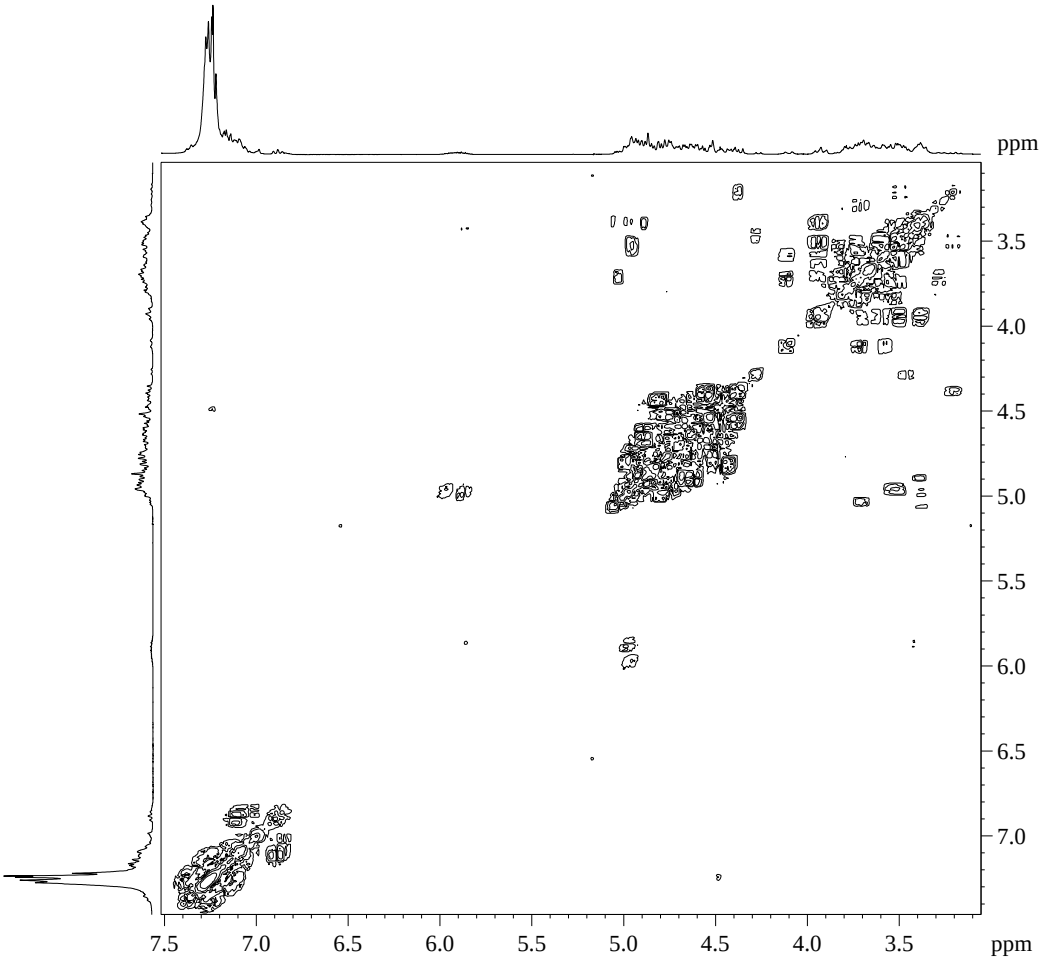
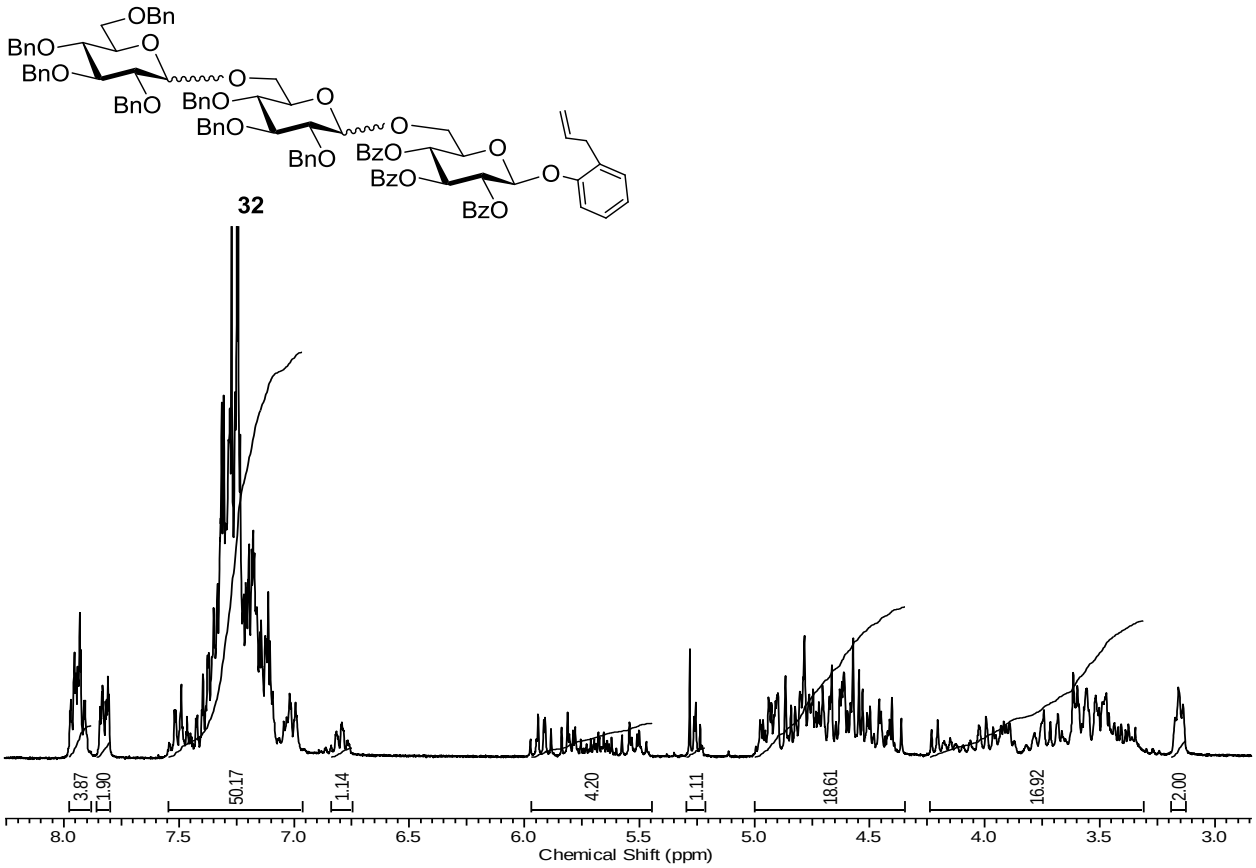
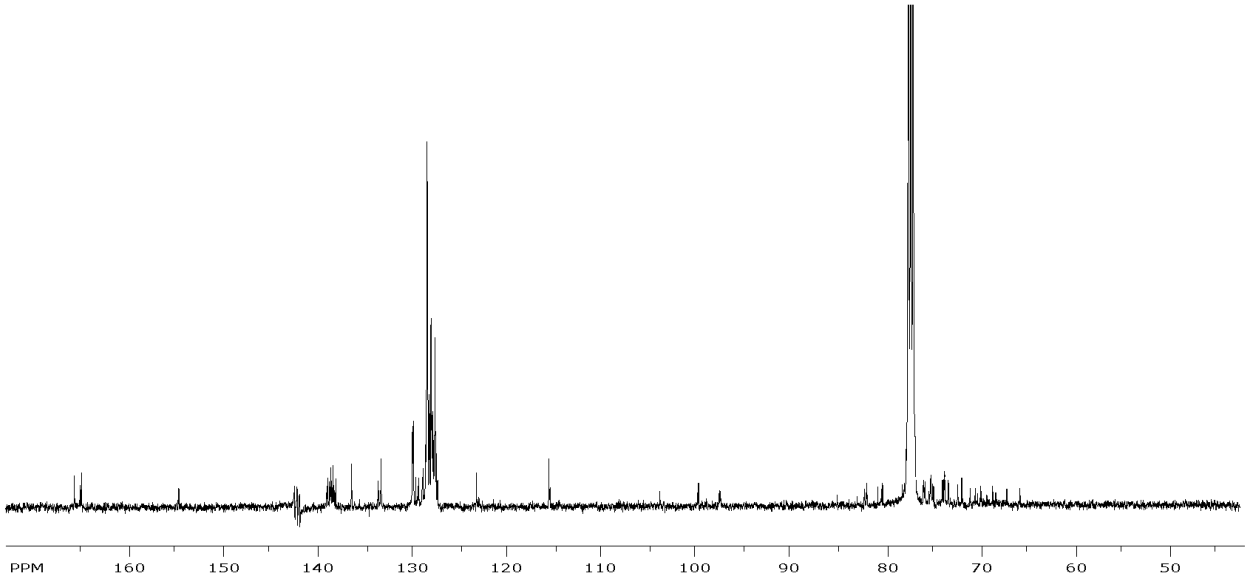


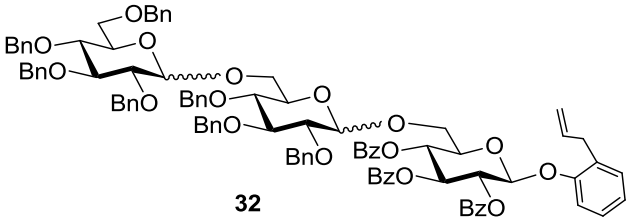
$CDCl_3$ at 300 MHz



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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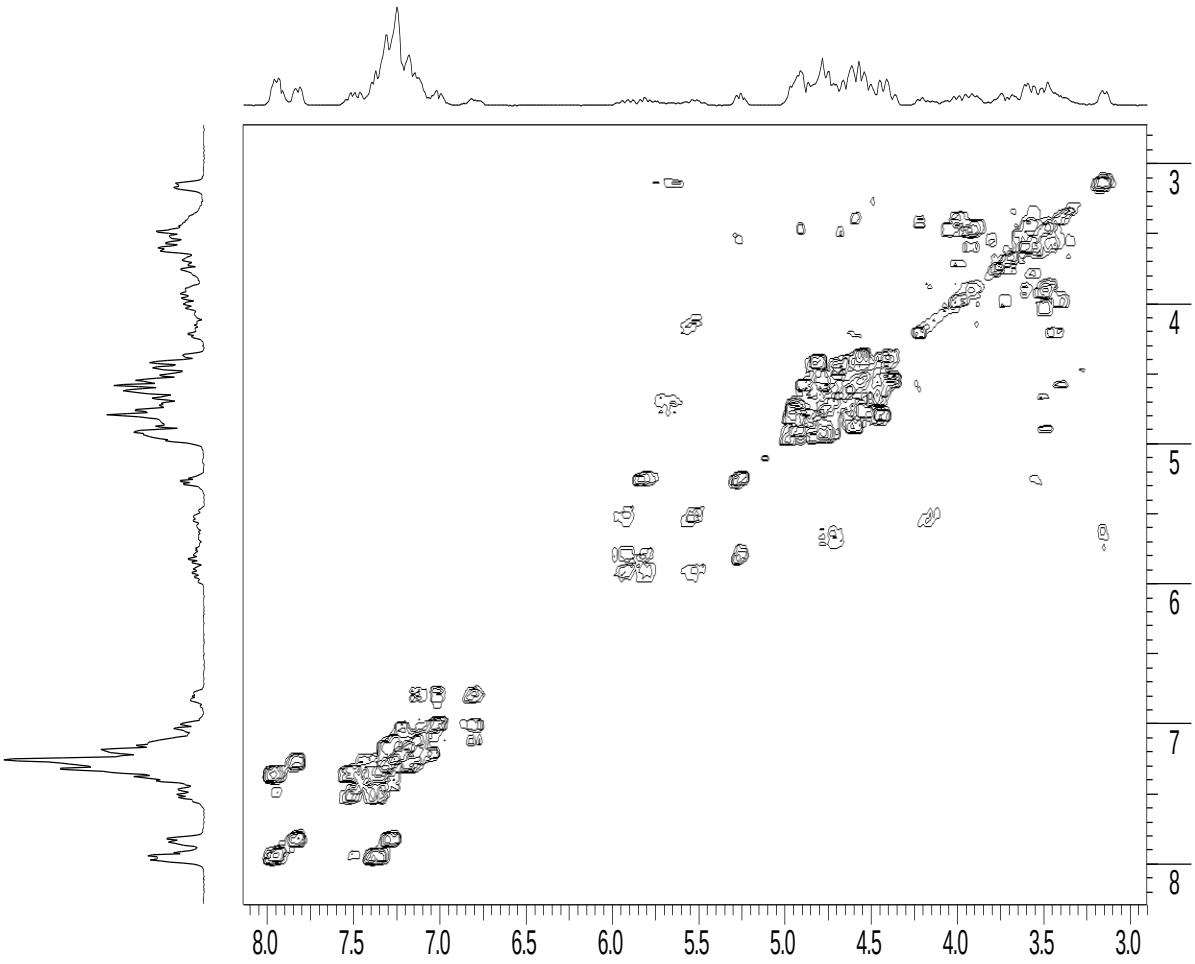

$CDCl_3$ at 300 MHz

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