Supporting Information

4-(Pyridin-2-yl)thiazole-2-yl thioglycosides as bidentate ligands for oligosaccharide synthesis via temporary deactivation

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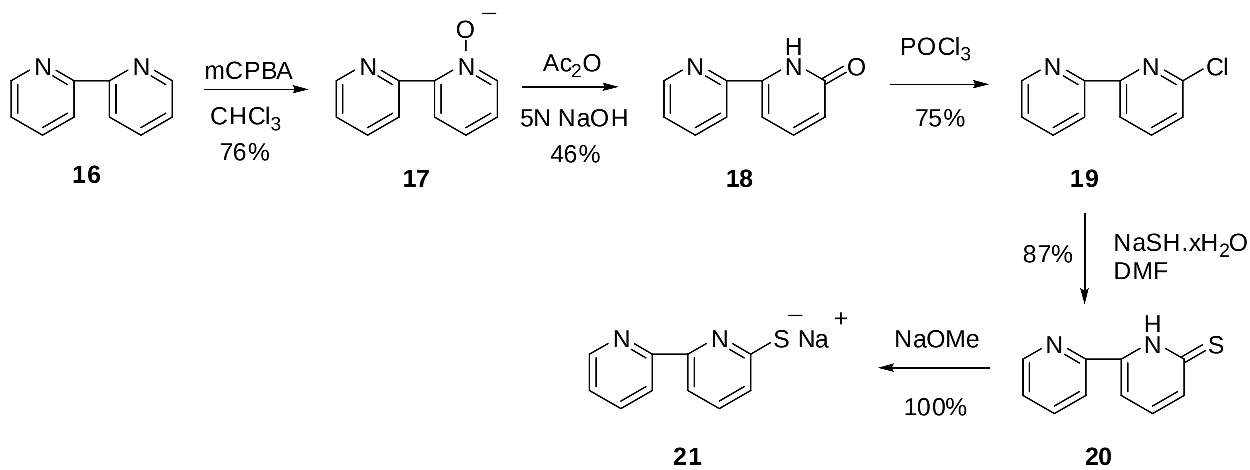
Contents:

General

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. DCM, DCE, and MeCN were distilled from CaH_2 directly prior to application. Methanol was dried by refluxing with magnesium methoxide, distilled and stored under argon. Pyridine was dried by refluxing with CaH_2 and then distilled and stored over molecular sieves (3Å). Molecular sieves (3Å or 4Å), 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 (Acros) was co-evaporated with toluene (3 x 10 mL) and dried *in vacuo* for 2-3 h directly prior to application. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-NMR spectra were recorded at 300MHz, ^{13}C-NMR spectra were recorded at 75MHz (Bruker Avance). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

Synthesis of bidentate aglycones

Synthesis of sodium 2,2'-bipyridine-6-thiolate (**21**).



2,2’-Bipyridine N-oxide (17) was obtained from 2,2’-bipyridine **16** as previously reported.[1]

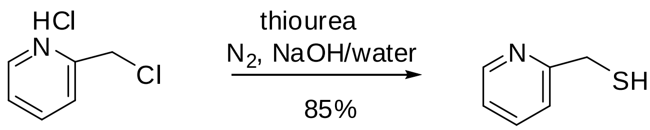
6-(Pyridin-2-yl)pyridine-2(1H)-one (18) was obtained from **17** as previously reported.[2]

6-Chloro-2,2’-bipyridine (19) was obtained from **18** as previously reported.[2]

6-(Pyridin-2-yl)pyridine-2(1H)-thione (20) was obtained from **19** as previously reported.[3] Analytical data for **20** was previously reported.[4]

Sodium 2,2'-bipyridine-6-thiolate (21). To a solution of **20** (3.43 mmol, 650 mg) in MeOH (30 mL) NaOMe solution (1N, 3.43 mmol Na in 20 mL methanol) was added. The reaction mixture was stirred under argon for 16 h at rt. Upon completion, methanol was evaporated and the residue was dried in *vacuo* to give the title compound as light brown solid (710 mg, 98% yield).

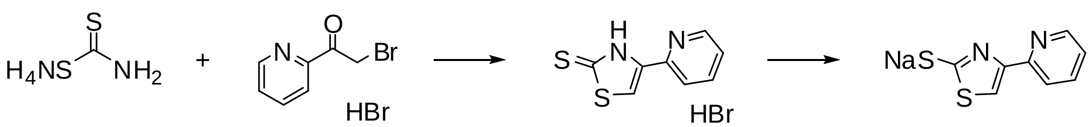
Synthesis of pyridin-2-ylmethanethiol (**23**).



22 **23**

The title compound was obtained from 2-(chloromethyl)pyridine hydrochloride hydrochloride (**22**) as previously reported.[5] Analytical data for **20** was previously reported.[6]

Synthesis of Sodium 4-(pyridin-2-yl)thiazole-2-thiolate (**2**).



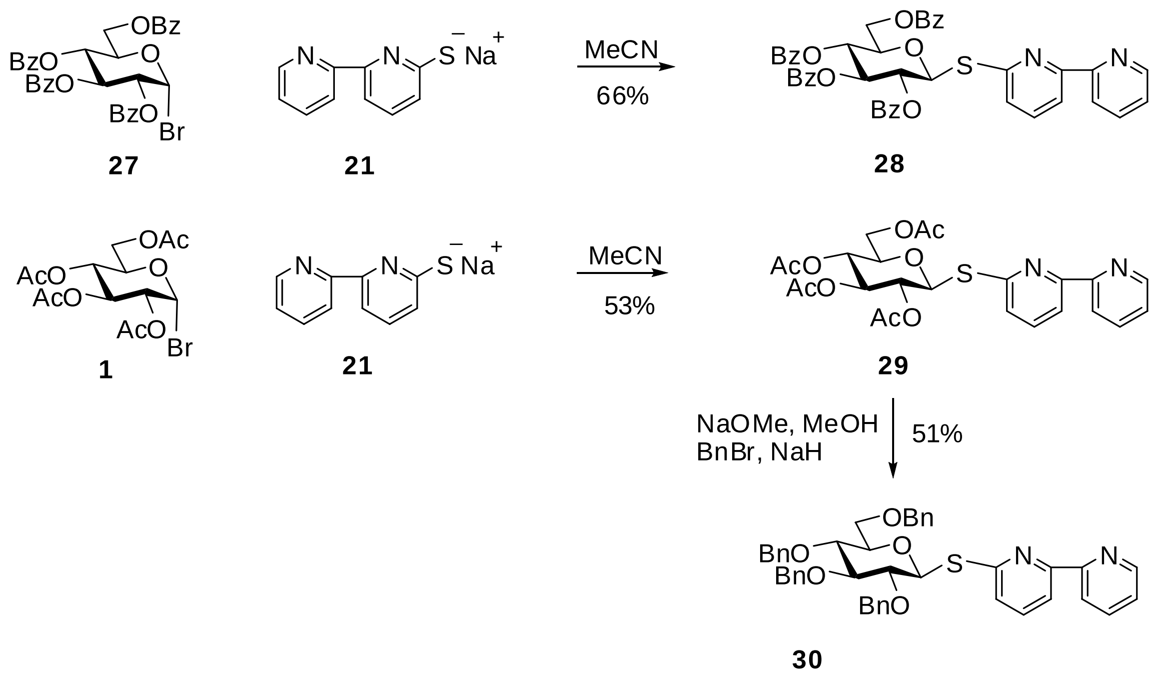
24 **25** **26** **2**

4-(pyridin-2-yl)thiazole-2(3H)-thione hydrobromide (26). To a solution of 2-(bromoacetyl)pyridine hydrobromide[7] (**25**, 22 mmol, 2.42 g) in ethanol (40 mL), ammonium dithiocarbamate[8] (**24**, 20 mmol, 5.6 g) was added portionwise. The reaction mixture was stirred for 6 h at rt. Upon completion, the bright yellow solid was filtered off, washed with isopropanol/diethyl ether (1/1, v/v, 50 mL) and dried in *vacuo*. The residue was crystallized from methanol to give the title compound as bright yellow crystals (2.53 g, 46% yield). Analytical data for **26**:[9] R_f = 0.62 (3/7 acetone/toluene); ^{1}H-n.m.r. : δ, 7.59 (s, 1H, C*H*S), 7.73 (m, 1H, H-5’), 8.05 (d, 1H, J= 8.1 Hz, H-3’), 8.29 (dt, 1H, J= 1.7 Hz, J= 8.1, H-4’), 8.73 (m, 1H, H-6’) ppm.; ^{13}C-n.m.r.: δ, 116.5, 121.7, 123.5, 138.7, 149.0, 151.6, 152.5, 180.5 ppm.

Sodium 4-(pyridin-2-yl)thiazole-2-thiolate (2). To a solution of **26** (7.3 mmol, 2 g) in methanol (60 mL) NaOMe solution, prepared from Na (334 mg, 14.6 mmol) and methanol (40 mL), was added. The reaction mixture was stirred under argon for 2 h at rt. Upon completion, methanol was evaporated off and the residue was dried in *vacuo* to give the title compound as light brown solid (1.56 g, 99% yield).

Synthesis of bidentate glycosyl donors

Synthesis of bipyridyl thioglycosides (**28-30**).

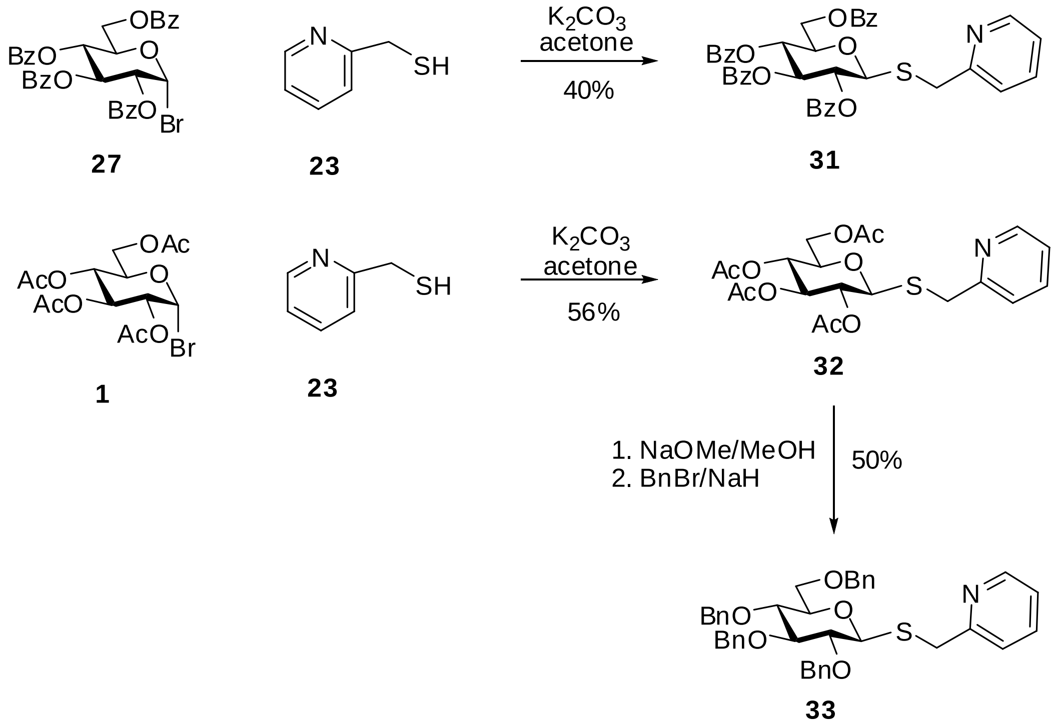


6-(Pyridin-2-yl)pyridin-2-yl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (28). To a solution of 2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl bromide[10] (**27**, 0.57 mmol, 374 mg) in MeCN (10 mL), **21** (0.85 mmol, 180 mg) was added. The reaction mixture was kept under argon for 17 h at rt, after that, it was diluted with CH_2Cl_2 (100 mL) and washed with water (20 mL), 1N aqueous NaOH (20 mL), and water (3 x 20 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white foam (157 mg, 36% yield). Analytical data for **28**: R_f = 0.50 (1/1 ethyl acetate/hexane), $[\alpha]_D^{22}$ = +107.0° (c = 1, $CHCl_3$); ^{1}H-n.m.r. : δ, 4.52 (m, 1H, H-5), 4.58 (dd, 1H, $J_{5,6b}$ = 6.7 Hz, $J_{6a,6b}$ = 12.0, H-6b), 4.71 (dd, 1H, $J_{5,6a}$ = 2.7 Hz, H-6a), 5.83 (dd, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 5.93 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 6.26 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 6.43 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 7.27-8.06 (m, 24H, aromatic), 8.27 (d, 1H, aromatic), 8.55 (1H, aromatic), 8.74 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 55.5, 69.6, 70.1, 70.8, 72.1, 73.0, 73.9, 79.6, 82.1, 97.9, 124.0, 125.0, 128.0, 128.0, 128.2, 128.3, 128.7, 137.9, 141.6, 148.1, 158.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{44}H_{34}N_2O_9SNa$ 789.1883, found 789.1886

6-(Pyridin-2-yl)pyridin-2-yl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (29). To a solution of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide[10] (**1**, 4.9 mmol, 2 g) in MeCN (40 mL), **21** (7.3 mmol, 1.55 g) was added. The reaction was kept under argon for 2 h at rt, after that, it was diluted with CH_2Cl_2 (200 mL) and washed with water (50 mL), 1N aqueous NaOH (50 mL), water (3x50 mL), the organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white foam (1.68 g, 66%). Analytical data for **29**: R_f = 0.40 (1/4 acetone/toluene), $[\alpha]_D^{21}$ = -34.9° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.81, 2.03, 2.03, 2.06 (s, 12H, $COCH_3$ x4), 3.97 (m, 1H, H-5), 4.14 (dd, 1H, $J_{5,6b}$= 2.3 Hz, H-6b), 4.19 (dd, 1H, $J_{5,6a}$= 6.7 Hz, $J_{6a,6b}$= 12.3 Hz, H-6a), 5.15 (dd, 1H, $J_{4,5}$= 9.9 Hz, H-4), 5.29 (dd, 1H, $J_{2,3}$= 9.4 Hz, H-2), 5.42 (dd, 1H, $J_{3,4}$= 9.3 Hz, H-3), 5.95 (d, 1H, $J_{1,2}$= 10.5 Hz, H-1), 7.19-8.68 (m, 7H, aromatic) ppm; ^{13}C-n.m.r.: δ, 20.6, 20.8, 62.4, 68.7, 69.4, 74.3, 76.4, 81.7, 118.2, 120.9, 123.2, 124.2, 137.1, 137.1, 137.7, 149.3, 149.5, 154.6, 155.6, 156.1, 169.6, 169.7, 170.4, 170.7 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{24}H_{26}N_2O_9SNa$ 541.1257, found 541.1256

6-(Pyridin-2-yl)pyridin-2-yl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (30). To a solution of compound **29** (0.75 mmol, 390 mg) in methanol (15 mL), 1N methanolic NaOMe soln. (0.2 mL) of was added (or until the pH = 8-9). The reaction mixture was kept under argon for 1 h at rt, after that, Dowex (H^+) was added until neutral pH. The resin was filtered off and washed successively with methanol (5 x 15 mL). The combined filtrate was concentrated *in vacuo* and dried to allow 6-(Pyridin-2-yl)pyridin-2-yl 1-thio-β-D-glucopyranoside as a white foam (260 mg, 98% yield). The crude mixture of the latter compound (0.74 mmol, 260 mg) was dissolved in DMF (10 mL) and BnBr (3.7 mmol, 0.44 mL) was added. The mixture was cooled to 0 ^oC and NaH (60% suspension in a mineral oil, 5.5 mmol, 222 mg) was added portionwise. The external cooling was then removed and the reaction mixture was stirred for additional 1 h at rt. Upon completion, the reaction mixture was poured in ice water (20 mL) and extracted with ethyl acetate/ether (1:1, v/v, 3x30 mL). The combined organic extract was dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white solid (267 mg, 51% yield). Analytical data for **30**: R_f= 0.40 (3/7 ethyl acetate/hexane), $[\alpha]_D^{22}$ = +0.72^o (c = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 3.75-3.83 (m, 5H, H-2,4,5,6a,6b), 3.92 (m, 1H, H-3), 4.47-4.66 (m, 3H, CH_2Ph), 4.83-5.03 (m, 5H, CH_2Ph), 5.76 (d, 1H, $J_{1,2}$= 10.1 Hz, H-1), 7.22-7.62 (m, 24H, aromatic), 8.23 (d, 1H, aromatic), 8.44 (1H, aromatic), 8.68 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 68.9, 73.4, 75.3, 75.6, 75.8, 78.0, 79.7, 80.6, 83.6, 87.0, 117.7, 121.2, 123.1, 123.9, 126.9, 127.6, 127.8, 127.8, 127.8, 127.9, 128.0, 128.2, 128.23, 128.3, 128.4, 128.5, 128.5, 130.2, 130.4, 136.9, 137.4, 137.9, 138.0, 138.1, 138.5, 149.1, 155.7, 156.0, 156.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{44}H_{42}N_2O_5$ SNa 733.2712**,** found 733.2710

Synthesis of picolyl thioglycosides (**31-33**).

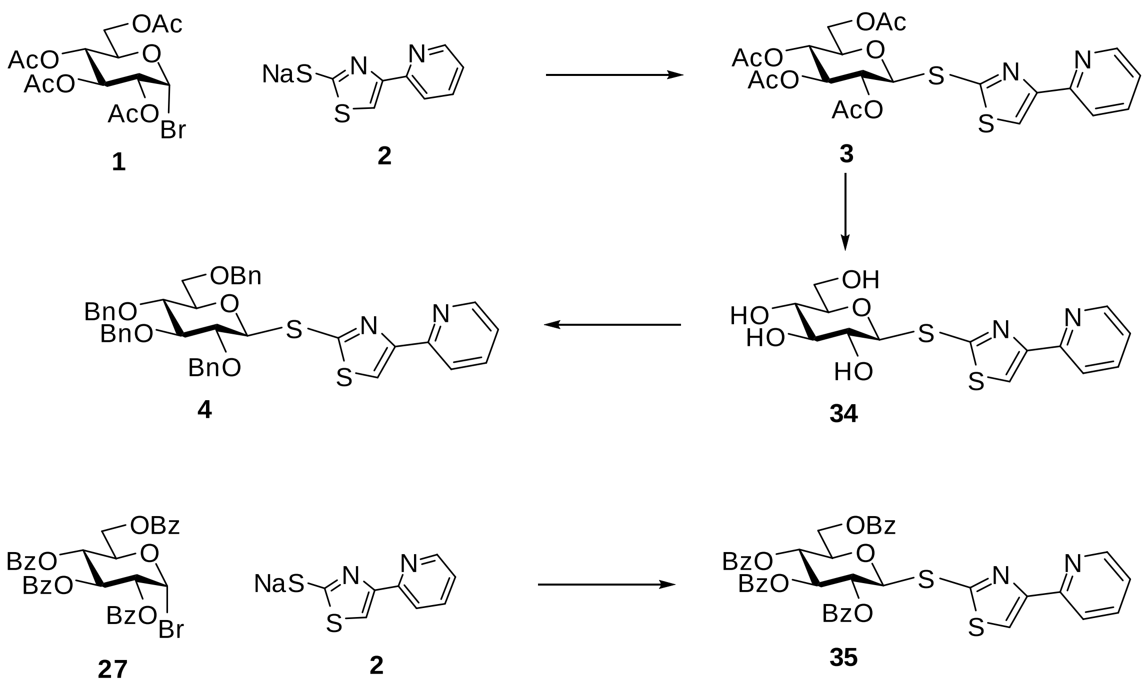


Picolyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (31). To a solution of **27** (1.51 mmol, 1 g) in acetone (10 mL), **23** (6.1 mmol, 0.76 g) and anhydrous potassium carbonate (6.1 mmol, 0.84 g) were added. The reaction mixture was kept under argon for 2 h at 70 ^{o}C, after that, it was diluted with toluene (150 mL) and washed with water (3 x 30 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white foam (40%). Analytical data for **31**: R_f = 0.40 (1/1 ethyl acetate/hexane); ^{1}H-n.m.r : δ, 3.96 (d, 1H, SCH_2), 4.10 (m, 1H, H-5), 4.17 (d, 1H, SCH_2), 4.44 (dd, 1H, $J_{5,6b}$= 5.0 Hz, H-6b), 4.53 (dd, 1H, $J_{5,6a}$= 3.2 Hz, $J_{6a,6b}$= 12.3 Hz, H-6a), 4.97 (d, 1H, $J_{1,2}$= 10.1 Hz, H-1), 5.59 (dd, 1H, $J_{2,3}$= 9.6 Hz, H-2), 5.67 (dd, 1H, $J_{4,5}$= 9.8 Hz, H-4), 5.88 (dd, 1H, $J_{3,4}$= 9.5 Hz, H-3), 7.13-8.05 (m, 23H, aromatic), 8.52 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 36.5, 63.5, 69.8, 70.9, 74.3, 76.4, 83.4, 122.3, 123.5, 128.5, 128.6, 128.6, 129.0, 129.3, 129.8, 129.9, 130.0, 130.0, 130.1, 133.4, 133.6, 136.9, 149.4, 158.2, 165.3, 166.0, 166.3 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{40}H_{34}NO_9SNa$ 704.1954, found 704.1940

Picolyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (32). To a solution of **1** (0.24 mmol, 100 mg) in acetone (2 mL), **23** (0.48 mmol, 61 mg) and anhydrous potassium carbonate (0.48 mmol, 67 mg) were added. The reaction was kept under argon for 24 h at rt, after that, it was diluted with toluene (40 mL) and washed with water (3 x 10 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white foam (35%). Analytical data for **32**: R_f = 0.20 (1/1 ethyl acetate/hexane); ^{1}H-n.m.r : δ, 1.98, 1.99, 2.01, 2.07 (s, 12H, $COCH_3$ x4), 3.66 (m, 1H, H-5), 3.92 (d, 1H, SCH_2), 4.03 (dd, 1H, $J_{5,6b}$= 2.3 Hz, H-6b), 4.05 (d, 1H, SCH_2), 4.18 (dd, 1H, $J_{5,6a}$= 4.8 Hz, $J_{6a,6b}$= 12.4 Hz, H-6a), 4.59 (d, 1H, $J_{1,2}$= 10.1 Hz, H-1), 5.01-5.12 (m, 2H, H-2,4), 5.18 (dd, 1H, $J_{3,4}$= 9.2 Hz, H-3), 7.16-8.53 (m, 4H, aromatic) ppm; ^{13}C-n.m.r.: δ, 20.7, 20.9, 36.2, 45.3, 62.2, 68.5, 70.1, 74.1, 75.9, 82.8, 122.5, 123.4, 123.9, 136.7, 136.9, 149.5, 150.0, 169.9, 170.4, 170.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{20}H_{25}NO_9SNa$ 478.1148, found 478.1150

Picolyl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (33). The title compound was obtained from **32** as a colorless syrup (150 mg, 37% yield) via deacetylation-benzylation sequence as described for the synthesis of **30**. Analytical data for **33**: R_f = 0.30 (1/9 acetone/toluene); ^{1}H-n.m.r : δ, 3.40-3.51 (m, 2H, H-2,4), 3.60-3.77 (m, 4H, H-3,5,6a,6b), 4.00 (d, 1H, SCH_2^a), 4.18 (d, 1H, SCH_2^b), 4.43 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.48-4.91 (m, 8H, CH_2Ph), 7.10-7.60 (m, 23H, aromatic) ppm; ^{13}C-n.m.r.: δ, 29.9, 36.5, 69.3, 73.7, 75.2, 75.6, 75.9, 77.4, 78.1, 79.2, 81.9, 84.0, 86.8, 122.1, 123.6, 127.8, 127.9, 128.0 (x7), 128.2 (x3), 128.5 (x3), 128.6 (x8), 128.7, 129.3 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{40}H_{41}NO_5SNa$ 670.2603, found 670.2610

Synthesis of pyridylthiazolyl thioglycosides (SPT, **3, 4, 34** and **35**).



4-(Pyridin-2-yl)thiazole-2-yl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (3). To a solution of **1** (0.49 mmol, 200 mg) in MeCN (3 mL), **2** (0.73 mmol, 158 mg) was added. The reaction mixture was kept under argon for 8 h at rt, after that, it was diluted with CH_2Cl_2 (50 mL) and washed with water (3 x 15 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane) to allow the title compound as a white foam (99%). Analytical data for **3**: R_f = 0.40 (1/4 acetone/toluene), $[\alpha]_D^{32}$ = -28.8° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.91, 1.93, 1.95, 1.99 (4s, 12H, 4 x $COCH_3$), 3.77-3.82 (m, 1H, H-5), 4.08 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, H-6b), 4.19 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, H-6a), 5.02-5.14 (m, 2H, H-2,4), 5.23 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 5.25 (dd, 1H, $J_{3,4}$= 9.1 Hz, H-3), 7.15-8.02 (m, 4H, aromatic), 8.50 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.5, 20.6, 20.6, 61.9, 68.1, 69.6, 73.7, 76.2, 84.6, 119.4, 121.2, 123.0, 137.0, 149.5, 151.8, 155.5, 159.0, 169.2, 169.3, 170.0, 170.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{22}H_{24}N_2O_9S_2Na$ 547.0821, found 547.0816

4-(Pyridin-2-yl)thiazole-2-yl 1-thio-β-D-glucopyranoside (34). To a solution of compound **3** (0.46 mmol, 243 mg) in methanol (5 mL), 1N methanolic NaOMe (0.2 mL) was added (or until pH = 8-9). The reaction was kept under argon for 30 min at rt, after that, Dowex (H^+) was added until neutral pH. The resin was filtered off and washed with methanol (5 x 15 mL). The combined filtrate was concentrated *in vacuo* and dried. The residue was purified by silica gel column chromatography (methanol/ DCM) to allow the title compound as a white foam (176 mg, 100% yield). Analytical data for **34**: R_f= 0.45 (methanol/dichloromethane, 1/4, v/v), $[\alpha]_D^{31}$ = -52.7° (c = 0.5, methanol); ^{1}H-n.m.r (300 MHz, CD_3OD): δ, ^{1}H-n.m.r.: δ, 3.37-3.47 (m, 4H, H-2,3,4,5), 3.73 (dd, 1H, $J_{5,6a}$= 4.8 Hz, $J_{6a,6b}$= 12.0 Hz, H-6a), 3.89 (dd, 1H, $J_{5,6b}$= 1.8 Hz, H-6b), 5.01 (d, 1H, $J_{1,2}$= 9.2 Hz, H-1), 7.37 (m, 1H, SCH=), 7.90 (m, 5H, aromatic), 8.56 (dd, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 61.6, 70.1, 72.9, 78.6, 81.6, 87.5, 88.0, 119.7, 121.7, 123.5, 138.2, 149.2, 154.0, 162.7; HR-FAB MS $[M+Na]^+$ calcd for $C_{14}H_{16}N_2O_5S_2$ 379.0398, found 379.0394

4-(Pyridin-2-yl)thiazole-2-yl 2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside (4). Compound **34** (0.5 mmol, 176 mg) was dissolved in DMF (3 mL) and BnBr (2.5 mmol, 0.3 mL) was added. The mixture was cooled down to 0 °C and NaH (60% suspension in mineral oil, 3.7

mmol, 148 mg) was added portionwise. The temperature was then allowed to gradually increase to rt and the reaction mixture was stirred for 20 h. Upon completion, the reaction mixture was poured in ice water (10 mL) and extracted with ethyl acetate/ether (1/1, v/v, 3 x 30 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white solid (232 mg, 65% yield). Analytical data for **4**: R_f = 0.63 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{32}$ = -11.6° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.63-3.70 (m, 2H, H-2,4), 3.71-3.77(m, 4H, H-3,5,6a,6b), 4.46-4.60 (m, 4H, CH_2Ph), 4.74-4.83 (m, 2H, CH_2Ph), 4.84 (d, 1H, $J_{1,2}$= 6.6 Hz, H-1), 4.88-5.00 (m, 2H, CH_2Ph), 7.14-8.04 (m, 24H, aromatic), 8.55 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 68.7, 73.5, 75.2, 75.6, 75.9, 77.6, 79.7, 80.6, 85.9, 86.6, 119.7, 121.4, 123.0, 127.7, 127.8 (x2), 127.8 (x3), 127.9, 128.0 (x2), 128.0, 128.4 (x2), 128.5 (x2), 128.5 (x6), 137.1, 137.8, 138.1, 138.2, 138.4, 149.4, 152.1, 155.4, 160.1 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{42}H_{40}N_2O_5S_2Na$ 739.2276, found 739.2268

4-(Pyridin-2-yl)thiazole-2-yl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (35). To a solution of bromide **27** (0.24 mmol, 160 mg) in MeCN (2 mL), 4-(pyridin-2'-yl) salt **2** (0.36 mmol, 79 mg) was added and the reaction mixture was kept under argon for 4 h at rt. After that, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with water (3 x 15 mL), the organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white solid (152 mg, 81% yield). Analytical data for **35**: R_f = 0.35 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{32}$ = 25.4° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 4.34-4.39 (m, 1H, H-5), 4.48-4.55 (dd, 1H, $J_{5,6b}$= 6.2 Hz, $J_{6a,6b}$= 12.2 Hz, H-6b), 4.64-4.69 (dd, 1H, $J_{5,6a}$= 2.7 Hz, H-6a), 5.70-5.76

(m, 3H, H-1,2,4), 6.06 (m, 1H, H-3), 7.16-8.06 (m, 24H, aromatic), 8.57 (d, 1H, H-1) ppm; ^{13}C-n.m.r.: δ, 60.5, 63.3, 69.5, 70.6, 74.0, 77.0, 85.1, 119.2, 121.4, 123.1, 128.4 (x2), 128.5 (x2), 128.5 (x2), 128.6 (x2), 128.7, 128.8, 129.6, 129.8 (x3), 129.9 (x2), 130.0 (x2), 130.1 (x2), 133.3, 133.5, 133.7, 133.7, 137.2, 149.5, 152.0, 155.5, 159.4, 165.3, 165.9, 166.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{42}H_{32}N_2O_9S_2Na$ 795.1447, found 594.1470

Glycosidation of bidentate glycosyl donors

General glycosylation procedures.

AgOTf-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor **36**[11] (0.026 mmol), and freshly activated molecular sieves (3Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. AgOTf (0.06 mmol) was added and the reaction mixture was stirred for 6-20 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3 x 10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

MeOTf-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (3Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. MeOTf (0.09 mmol) was added and the reaction mixture was stirred for 30 min-1h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

MeI-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (3Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. MeI (0.09 mmol) was added and the reaction mixture was stirred 24h at 55^{o}C. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

NIS/TfOH-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (4Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. NIS (0.06 mmol) and catalytic amount of TfOH (0.006 mmol) were added and the reaction mixture was stirred for 30 min-1h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with $Na_2S_2O_3$ (10 mL), and water (2x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

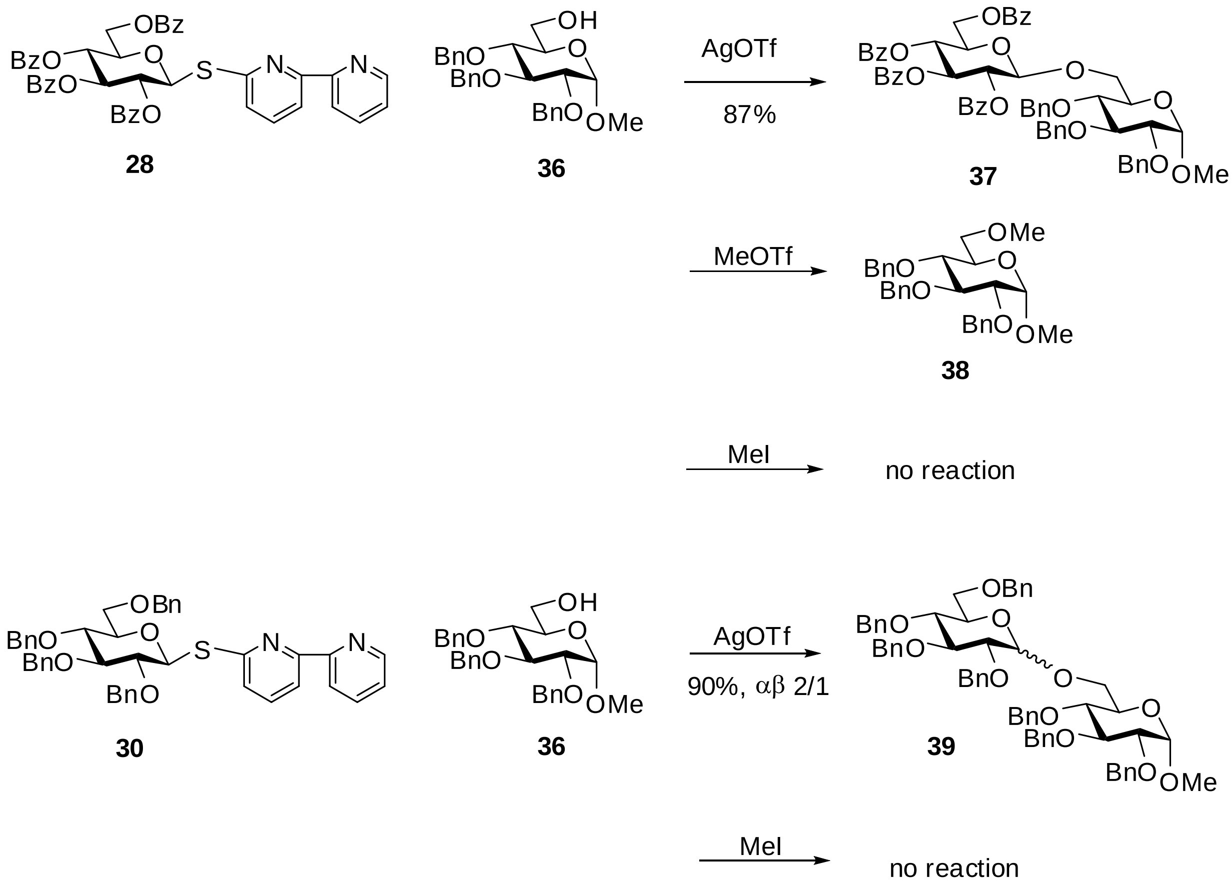
DMTST-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (4Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. DMTST (0.09 mmol) was added and the reaction mixture was stirred for 16h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

Br_2/AgOTf-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (4Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. Br_2 (0.06 mmol) and AgOTf (0.03 mmol) were added and the reaction mixture was stirred for 16 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

$Cu(OTf)_2$-promoted reaction. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (4Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. $Cu(OTf)_2$ (0.06 mmol) was added and the reaction mixture was stirred for 16h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic

phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

Glycosidation of bipyridyl glycosides

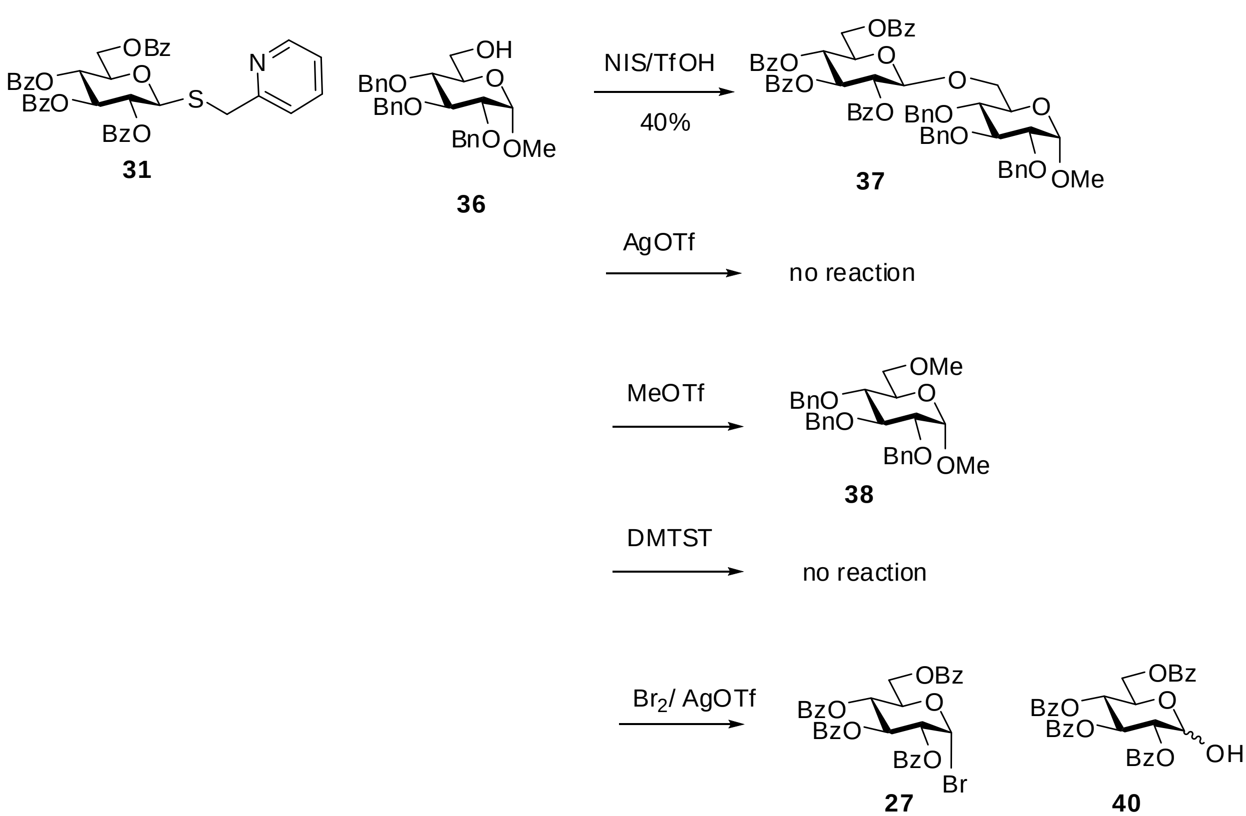


Methyl 6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**37**) was obtained as a white foam. Analytical data for **37** was reported previously.[12]

Methyl 2,3,4-tri-O-benzyl-6-O-methyl-α-D-glucopyranoside (38) The title compound was isolated as the major product from MeOTf-promoted glycosidation of **28** and **31** as a colorless syrup. Analytical data for **38** was reported previously.[13]

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (**39**) was obtained as a colorless syrup. Analytical data for **39** was reported previously.[14]

<u>Glycosidation of picolyl glycosides</u>



2,3,4,6-Tetra-O-benzoyl-D-glucopyranoside (40) was obtained as a by-product from Br_2/AgOTf-promoted glycosidation of **31** as colorless syrup.

Glycosidation of SPT glycosides

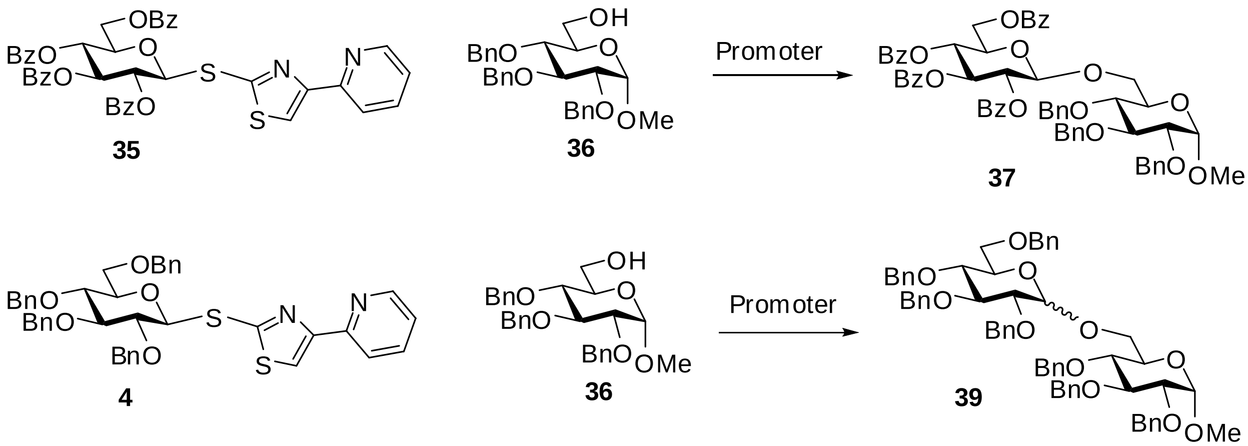
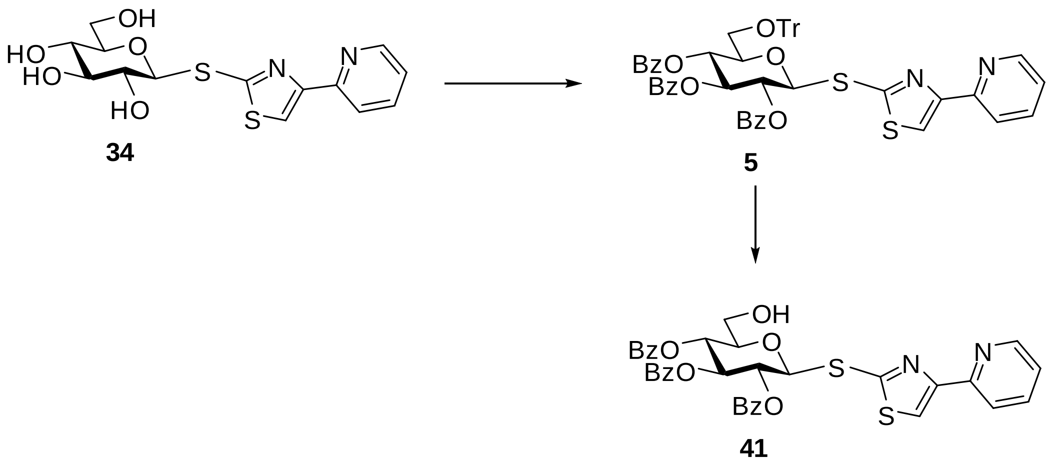


Table 1. Glycosidation of SPT donors **35** and **4**.

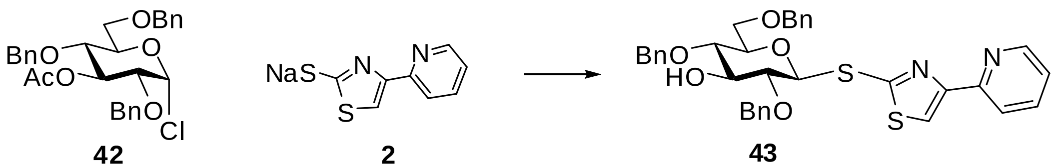
Entry	Donor	Promoter	Equiv.	Time	Product	Yield, %	α/β Ratio
1	**35**	AgOTf	2	17 h	**37**	82	β only
2	**35**	$Cu(OTf)_2$	3	3 days	**37**	79	β only
3	**35**	MeOTf	3	19 h	**37**	30	β only
4	**35**	NIS/TfOH	2/0.2	3 days	**37**	No rxn	–
5	**4**	AgOTf	2	15 h	**39**	84	2.0/1
6	**4**	$Cu(OTf)_2$	3	6 h	**39**	81	2.1/1
7	**4**	MeOTf	3	20 h	**39**	34	3.5/1
8	**4**	NIS/TfOH	2/0.2	16 h	**39**	41	1.5/1

Synthesis of bidentate glycosyl acceptors.

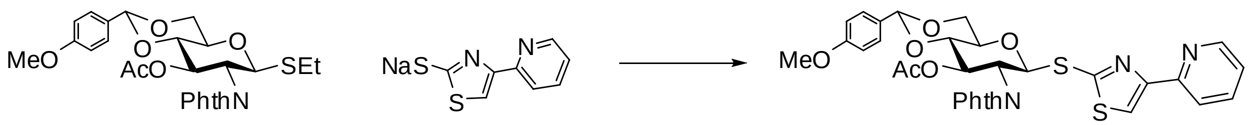


4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-6-triphenylmethyl-1-thio-β-D-glucopyranoside (5). Compound **34** (0.39 mmol, 140 mg) was dissolved in dry pyridine (3 mL) and triphenylmethyl chloride (0.78 mmol, 219 mg) was added. The reaction mixture was left for 16 h at rt, then cooled to 0 ^{o}C and benzoyl chloride (1.97 mmol, 0.23 mL) was added dropwise. The reaction mixture was stirred under argon for 5 h at rt, then it was quenched with methanol (5 mL). Volatile solvents were evaporated *in vacuo*, the residue was diluted with CH_2Cl_2 (50 mL) and the organic layer was washed with water (15 mL), saturated aq. $NaHCO_3$ (15 mL), water (15 mL), 1M HCl (15 mL), and water (3 x 15 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to give the title compound as a white foam (250 mg, 70% yield). Analytical data for **5**: R_f = 0.63 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{25}$ = 20.0^o (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.35 (dd, 1H, $J_{5,6a}$= 5.1 Hz, $J_{6a,6b}$= 10.8 Hz, H-6a), 3.43 (dd, 1H, $J_{5,6b}$= 2.3 Hz, H-6b), 4.05 (m, 1H, H-5), 5.58 (d, 1H, $J_{1,2}$= 10.0 Hz, H-1), 5.72 (dd, 1H, $J_{4,5}$= 9.8 Hz, H-4), 5.75 (dd, 1H, $J_{2,3}$= 9.9 Hz, H-2), 5.93 (dd, 1H, $J_{3,4}$= 9.5 Hz, H-3), 7.10-8.15 (m, 29H, aromatic, CH), 8.63 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 62.7, 69.3, 71.0, 74.5, 78.8, 85.5, 87.1, 121.7, 123.2, 127.1 (x2), 127.9 (x3), 128.4, 128.5, 128.6, 128.8 (x4), 129.0, 129.1, 129.2, 129.9, 130.0, 130.2, 133.4, 133.4, 133.7, 143.6, 164.9, 165.4, 166.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{54}H_{42}N_2O_8S_2Na$ 933.2280, found 933.2269.

4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-1-thio-β-D-glucopyranoside (41). Compound **5** (0.18 mmol, 162 mg) was dissolved in wet CH_2Cl_2 (5 mL) containing trifluoroacetic acid (0.1 mL). The reaction mixture was kept for 1 h at rt, then diluted with CH_2Cl_2 (50 ml.), transferred into a separatory funnel and washed with water (15 mL), saturated aq. $NaHCO_3$ (15 mL) and water (3 x 15 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the title compound as a white foam (81 mg, 68% yield). Analytical data for **41**: R_f= 0.38 (1/4 acetone/toluene), $[\alpha]_D^{31}$ = +58.4° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 2.95 (bs, 1H, OH), 3.70 (dd, 1H, $J_{5,6b}$= 5.0 Hz, $J_{6a,6b}$= 12.8 Hz, H-6b), 3.82 (dd, 1H, H-6a), 3.88-3.94 (m, 1H, H-5), 5.51 (dd, 1H, $J_{4,5}$= 9.7 Hz, H-4), 5.58 (dd, 1H, H-3), 5.60 (d, 1H, $J_{1,2}$= 3.3 Hz, H-1), 5.94-5.97 (m, 1H, H-2), 7.06-8.05 (m, 19H, aromatic), 8.52 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 21.6, 61.6, 69.3, 70.7, 74.0, 79.7, 85.3, 119.4, 121.5, 123.2, 125.5, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.2, 129.9, 130.1, 130.1, 133.5, 133.7, 133.9, 137.3, 149.6, 155.7, 159.7, 165.3, 165.9, 166.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{28}N_2O_8S_2Na$ 691.1185, found 691.1207.

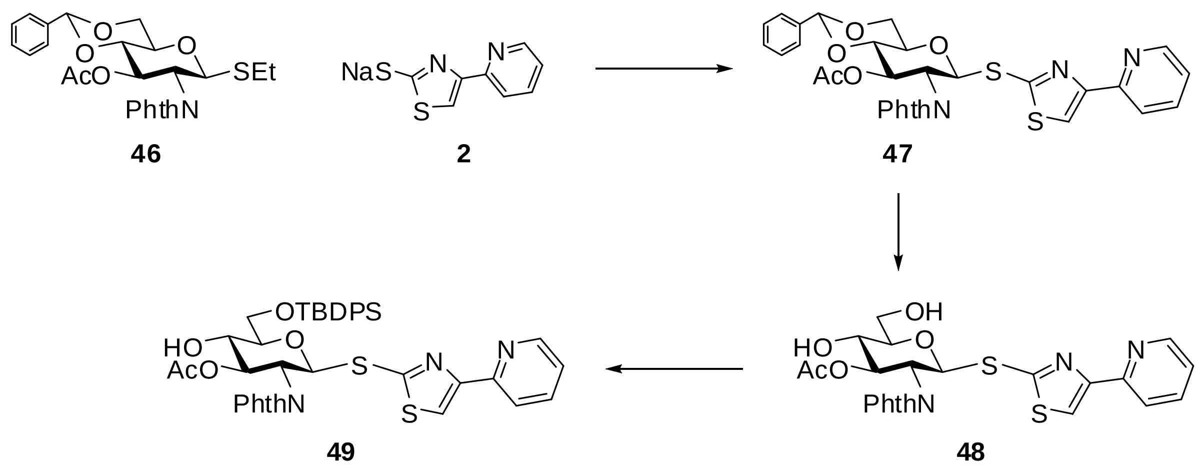


4-(Pyridin-2-yl)thiazole-2-yl 2,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside (43). Salt **2** (2.14 mmol, 463 mg) was added to a stirred solution of 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride[15] (**42**, 1.43 mmol, 730 mg) in dry acetonitrile (15 mL). The reaction mixture was stirred under argon for 2 h at rt, after that, it was diluted with toluene (100 mL) and washed with 1% aq. NaOH (20 mL) and water (3 x 20 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution). The intermediate was then dissolved in methanol (10 mL) containing 1M aq. $NaOCH_3$ (0.3 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 (5 x 15 mL). The combined filtrate was concentrated *in vacuo* and dried to afford the title compound as a white foam (630 mg, 70% yield). Analytical data for **43**: R_f= 0.48 (2/3 ethyl aceate/hexanes), $[\alpha]_D^{32}$ = -10.7° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 2.83 (bs, 1H, OH), 3.44 (dd, 1H, $J_{2,3}$= 8.8 Hz, H-2), 3.45-3.55 (m, 2H, H-4,6a), 3.67-3.77 (m, 3H, H-3,5-6b), 4.41-4.55 (m, 3H, CH_2Ph), 4.69 (dd, 2H, CH_2Ph), 4.88 (d, 1H, $J_{1,2}$= 9.8 Hz, H-1), 4.91 (d, 1H, CH_2Ph), 7.10-8.02 (m, 19H, aromatic), 8.50 (dd, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 68.8, 73.7, 74.9, 75.4, 77.3, 78.7, 79.6, 80.4, 85.7, 119.7, 121.5, 123.1, 127.8, 127.9 (x2), 128.1, 128.1 (x2), 128.3, 128.5 (x2), 128.5 (x2), 128.7 (x2), 128.8 (x2), 137.3, 138.0, 138.2, 138.3, 149.5, 152.2, 155.4, 160.3 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{35}H_{35}N_2O_5S_2$ 627.1987, found 627.1992.



44 **2** **45**

4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-2-deoxy-4,6-O-p-methoxybenzylidene-2-phthlimido-1-thio-β-D-glucopyranoside (45). The solution of ethyl 3-O-acetyl-2-deoxy-4,6-O-p-methoxybenzylidene-2-phthlimido-1-thio-β-D-glucopyranoside[16] (**44**, 3.78 mmol, 1.94 g), activated molecular sieves 3Å (1.9 g, 500 mg/mmol) in CH_2Cl_2 (57 mL, 15 mL/mmol) was stirred under argon for 1 h. Freshly prepared soln. Br_2/CH_2Cl_2 (1:165, v/v) was then added (36 mL, 9.4 mL/mmol) and the reaction mixture was kept for 5 min at rt. After that, CH_2Cl_2 was evaporated out from the reaction mixture at <30 ^oC. To the concentrated residue, dried acetonitrile (40 mL) was added, followed by the addition of salt (**2**, 11.3 mmol, 2.4 g). The reaction mixture was stirred under argon for 1 h at rt. Upon completion, the mixture was diluted with toluene (200 mL) and washed with 1% aq. NaOH (50 mL) and water (3x50 mL), the organic layer was separated and concentrated in *vacuo*. The residue was subjected to crystallization (CH_2Cl_2/hexane) to afford the title compound as white crystals (1.58 g, 65% yield). Analytical data for **45**: R_f = 0.48 (1/4 acetone/toluene), $[\alpha]_D^{27}$ = +105.1^o (c = 1, $CHCl_3$);m.p. 214 ^oC ; ^{1}H-n.m.r : δ, 1.94 (s, 3H, $COCH_3$), 3.74-3.86 (m, 5H, H-4,5,OCH_3), 4.32 (dd, 1H, $J_{5,6a}$= 5.0 Hz, $J_{6a,6b}$= 10.4 Hz, H-6a), 4.89 (dd, 1H, $J_{5,6b}$= 4.9 Hz, H-6b), 5.01 (dd, 1H, $J_{2,3}$= 5.6 Hz, H-2), 5.53 (s, 1H, CHPh), 6.36 (d, 1H, $J_{1,2}$= 5.6 Hz, H-1), 6.60 (dd, 1H, $J_{3,4}$= 9.4 Hz, H-3), 6.88-8.03 (m, 12H, aromatic), 8.55 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.0, 53.8, 55.4 (x2), 65.4, 66.5, 68.4, 81.1, 87.6, 101.7, 113.8 (x4), 119.2, 121.4, 123.1, 127.6 (x4), 129.5, 137.1, 149.5, 151.9, 155.7, 160.2, 168.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{32}H_{27}N_3O_8S_2Na$ 668.1137, found 668.1151.



4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside (47). The title compound was prepared from of ethyl 3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside[17] (**46**) white crystals (67% yield) as described for the synthesis of **45**. Analytical data for **47**: R_f= 0.33 (1/4 ethyl acetate/toluene); mp= 235°C; $[\alpha]_D^{32}$ = +107.6° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.95 (s, 3H, $COCH_3$), 3.79 (dd, 1H, $J_{4,5}$= 9.4 Hz, H-4), 3.85 (dd, 1H, $J_{6a,6b}$= 10.3 Hz, H-6b), 4.34 (dd, 1H, $J_{5,6a}$= 5.0 Hz, H-6a), 4.50 (m, 1H, H-5), 5.02 (dd, 1H, $J_{2,3}$= 5.6 Hz, H-2), 5.57 (s, 1H, CHPh), 6.37 (d, 1H, $J_{1,2}$= 5.6 Hz, H-1), 6.63 (dd, 1H, $J_{3,4}$= 9.3 Hz, H-3), 7.20 (dt, 1H, SCHC), 7.30-8.03 (m, 12H, aromatic), 8.55 (dd, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.9, 53.8, 65.3, 66.5, 68.5, 81.1, 87.5, 101.7, 119.3, 121.4, 123.1, 126.3, 128.4, 129.2, 136.9, 137.1, 149.4, 151.8, 155.6, 160.1, 168.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{31}H_{25}N_3O_7S_2Na$ 638.1032, found 638.1034.

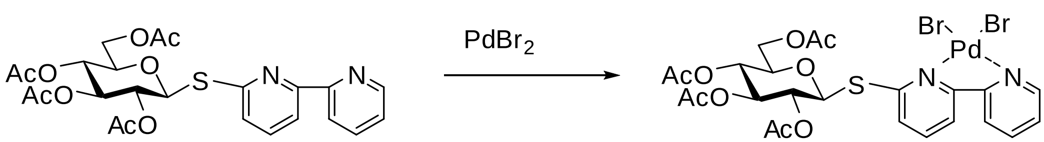
4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside (48). To a stirred solution of **47** (0.08 mmol, 50 mg) in wet CH_2Cl_2 (1 mL), 10% trifluoroacetic acid soln. in CH_2Cl_2 (1 mL) was added at 0 °C. The mixture was kept at 0 °C for 10 min, after that triethylamine (XX mL) was added. The resulting mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the title compound as a white solid (40 mg, 94% yield). Analytical data for **48**: R_f= 0.35 (1/1 acetone/toluene), $[\alpha]_D^{32}$ = 70.0° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 2.00 (s, 3H, $COCH_3$), 3.70 (bs, 1H, OH), 3.83 (dd, 1H, $J_{4,5}$= 8.9 Hz, H-4), 3.98 (d, 2H, $J_{5,6a}$= 3.6 Hz, H-6a,6b), 4.29 (m, 1H, H-5), 4.87 (dd, 1H, $J_{2,3}$= 5.2 Hz, H-2), 6.31 (d, 1H, $J_{1,2}$= 5.2 Hz, H-1), 6.37 (dd, 1H, $J_{3,4}$= 9.1 Hz, H-3), 7.18-7.27 (m, 3H, SCHC, aromatic), 7.71-8.01 (m, 5H, aromatic), 8.55 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 21.1, 21.6, 53.9, 62.0, 71.1, 71.6, 75.1, 77.4, 86.9, 119.5, 121.5, 123.2, 123.9, 125.5, 129.2, 134.7, 137.3, 149.5, 151.9, 155.7, 160.0, 172.5 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{24}H_{22}N_3O_7S_2$ 528.0899, found 528.0878.

4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-6-O-(*tert*-butyl)diphenylsilyl-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside (49). TBDPSCl (0.79 mmol, 0.2 mL) and imidazole (1.1 mmol, 75 mg) were added to a stirred solution of compound **48** (0.32 mmol, 166 mg) in DMF (1 mL). The reaction mixture was kept for 20 h at rt. Upon completion, the volatiles were evaporated, the crude residue was diluted in CH_2Cl_2 (50 mL), washed with water (15 mL), $NaHCO_3$ (15 mL), and water (3 x 15 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound as a white solid (240 mg, 99% yield). Analytical data for **49**: R_f = 0.55 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{25}$ = +81.2° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.06 (s, 9H, $3xCH_3$), 2.03 (s, 3H, $COCH_3$), 3.29 (d, 1H, OH), 3.94-4.00 (m, 2H, H-4,6b), 4.06-4.12 (m, 1H, H-6a), 4.20-4.28 (m, 1H, H-5), 4.88 (dd, 1H, $J_{2,3}$= 5.3 Hz, H-2), 6.30 (d, 1H, $J_{1,2}$= 5.2 Hz, H-1), 6.38 (dd, 1H, $J_{3,4}$= 9.2 Hz, H-3), 7.26-8.05 (m, 18H, aromatic), 8.57 (d, 1H, H-6’) ppm; ^{13}C-n.m.r.: δ, 19.4, 21.1, 26.9, 58.8, 63.0, 71.0, 75.1, 86.8, 119.2, 121.4, 123.0, 127.8, 127.9, 129.9, 133.2, 133.3, 135.7, 135.8, 137.2 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{40}H_{40}N_3O_7S_2Si$ 766.2077, found 766.2095.

Formation and stability of the bidentate complexes.

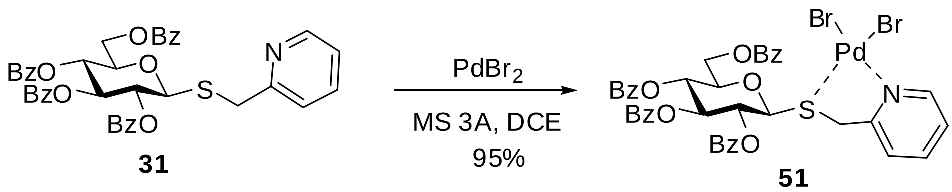
General procedure for the synthesis of the Palladium(II) complexes.

A solution of a glycoside (0.206 mmol), activated molecular sieves 3Å (1.65 g/mmol) in 1,2-dichloroethane was stirred under argon for 1 h at rt. $PdBr_2$ was then added (0.206-0.412 mmol) and the reaction mixture was stirred for 6-20 h at rt. After that, the solid was filtered-off, washed with CH_2Cl_2 and the combined filtrate was concentrated in vacuo to afford the Pd-complex. Typically, the complexes were used in glycosylations as is. If additional purification was desired, this could be achieved by column chromatography on silica gel or by crystallization.

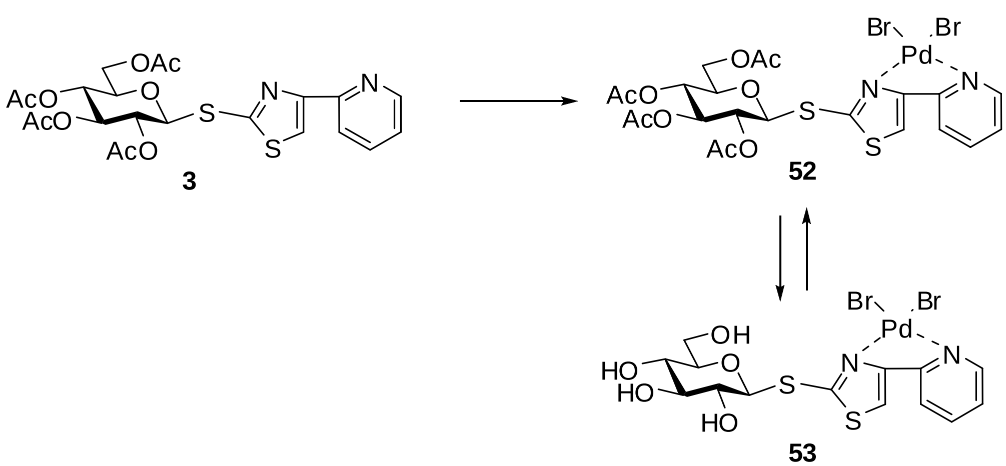


29 **50**

6-(Pyridin-2-yl)pyridin-2-yl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside /Palladium (II) complex (50) was obtained from complexation of **29** and $PdBr_2$ as dark yellow film in 80% yield. Analytical data for **50**: R_f = 0.6 (1/19 methanol/dichloromethane), ^{1}H-n.m.r : δ, 1.90, 2.03, 2.13, 2.23 (s, 12H, $COCH_3$ x4), 3.80 (m, 1H, H-5), 4.17 (dd, 1H, $J_{5,6b}$= 2.2 Hz, H-6b), 4.27 (dd, 1H, $J_{5,6a}$= 5.2 Hz, $J_{6a,6b}$= 12.4 Hz, H-6a), 4.56 (dd, 1H, $J_{2,3}$= 9.6 Hz, H-2), 4.74 (d, 1H, $J_{1,2}$= 10.1 Hz, H-1), 4.97 (dd, 1H, $J_{4,5}$= 9.8 Hz, H-4), 5.18 (dd, 1H, $J_{3,4}$= 9.4 Hz, H-3), 7.45-8.15 (m, 6H, aromatic), 9.39 (d, 1H, H-6’) ppm.



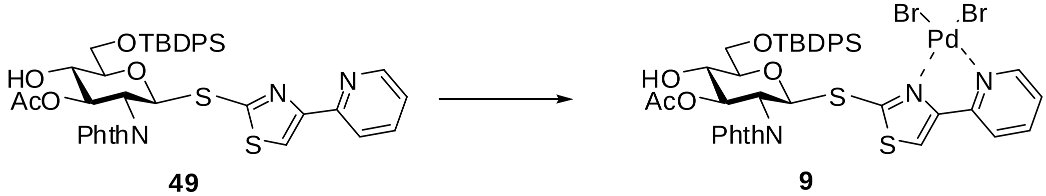
Picolyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside / Palladium (II) complex (51) was obtained from complexation of **31** and $PdBr_2$ as yellow foam in 95% yield. Analytical data for **51**: R_f = 0.40 (1/1 ethyl acetate/hexane); ^{1}H-n.m.r : δ, 4.13 (dd, 1H, $J_{5,6a}$= 6.2 Hz, $J_{6a,6b}$= 12.6 Hz, H-6a), 4.44-4.52 (m, 2H, H-5,6b), 4.57 (d, 1H, SCH_2), 4.85 (d, 1H, SCH_2), 5.63-5.73 (m, 3H, H-1,2,4), 6.06 (dd, 1H, $J_{3,4}$= 9.0 Hz, H-3), 7.11-8.10 (m, 23H, aromatic), 9.46 (d, 1H, H-6') ppm.



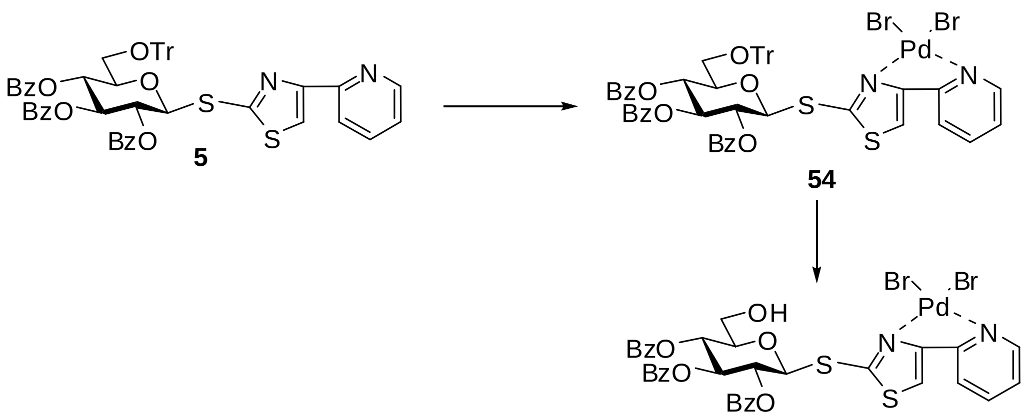
4-(Pyridin-2-yl)thiazole-2-yl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside / Palladium (II) complex (52) was obtained from complexation of **3** and $PdBr_2$ as yellow solid in 89% yield. Analytical data for **52**: R_f = 0.6 (1/19 methanol/dichloromethane); ^{1}H-n.m.r : δ, 1.91, 1.93, 1.95, 1.99 (4s, 12H, 4 x $COCH_3$), 3.77-3.82 (m, 1H, H-5), 4.08 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, H-6b), 4.19

(dd, 1H, $J_{5,6a}$ = 5.1 Hz, H-6a), 5.02-5.14 (m, 2H, H-2,4), 5.23 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 5.25 (dd, 1H, $J_{3,4}$= 9.1 Hz, H-3), 7.15-8.02 (m, 4H, aromatic), 8.50 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.5, 20.6, 20.6, 61.9, 68.1, 69.6, 73.7, 76.2, 84.6, 119.4, 121.2, 123.0, 137.0, 149.5, 151.8, 155.5, 159.0, 169.2, 169.3, 170.0, 170.4 ppm.

4-(Pyridin-2-yl)thiazole-2-yl 1-thio-β-D-glucopyranoside /Palladium (II) complex (53). To a solution of complex **53** (0.05 mmol, 40 mg) in methanol (3 mL), 1N methanolic NaOMe (50 μL) was added (or until pH = 8) at 0°C. The reaction was kept under argon for 4 h at 0 °C. Upon completion, the solvent was removed under reduced pressure and dried. The residue was purified by silica gel column chromatography (methanol/ DCM) to allow the title compound as a yellow solid (28 mg, 90% yield). Analytical data for **53**: R_f= 0.45 (methanol/dichloromethane, 1/4, v/v), ^{1}H-n.m.r (300 MHz, CD_3OD): δ, ^{1}H-n.m.r.: δ, 3.37-3.47 (m, 4H, H-2,3,4,5), 3.73 (dd, 1H, $J_{5,6a}$= 4.8 Hz, $J_{6a,6b}$= 12.0 Hz, H-6a), 3.89 (dd, 1H, $J_{5,6b}$= 1.8 Hz, H-6b), 5.01 (d, 1H, $J_{1,2}$= 9.2 Hz, H-1), 7.37 (m, 1H, SCH=), 7.90 (m, 5H, aromatic), 8.56 (dd, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 61.6, 70.1, 72.9, 78.6, 81.6, 87.5, 88.0, 119.7, 121.7, 123.5, 138.2, 149.2, 154.0, 162.7 ppm.



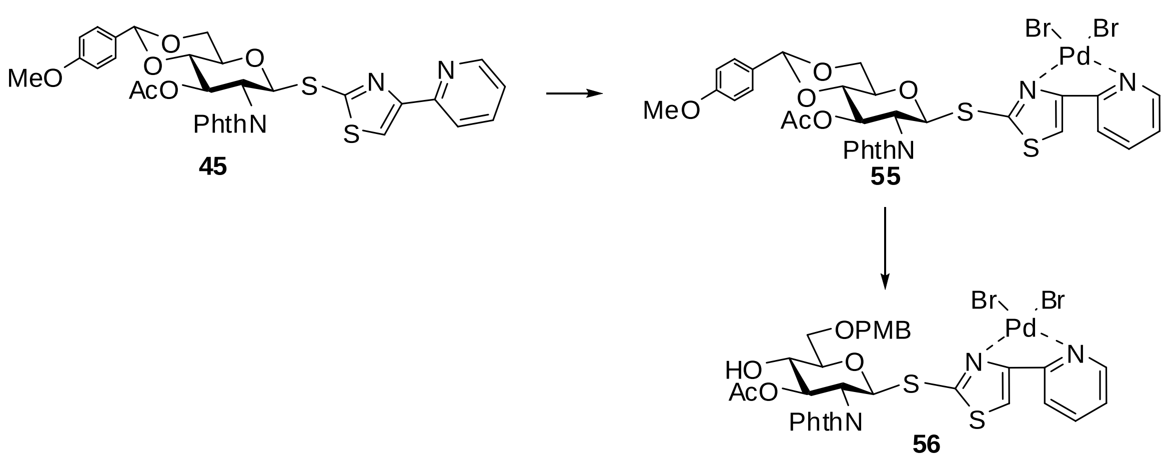
4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-6-O-*tert*-butyl diphenylsilyl-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (9). The title compound was obtained from **49** followed by chromatography on silica gel as yellow foam in 93% yield. Analytical data for **9**: R_f = 0.20 (1/4 acetone/toluene), $[\alpha]_D^{25}$ = +65.1° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.10 (s, 9H, $C(CH_3)_3$), 1.99 (s, 3H, $COCH_3$), 3.59 (d, 1H, OH), 3.92 (dd, 1H, $J_{4,5}$= 9.5 Hz, H-4), 4.13 (dd, 1H, $J_{5,6b}$= 1.6 Hz, H6b), 4.24 (dd, 1H, $J_{5,6a}$= 4.5 Hz, $J_{6a,6b}$= 11.6 Hz, H-6a), 4.40-4.47 (m, 1H, H-5), 4.88 (dd,1H, $J_{2,3}$= 5.6 Hz, H-2), 5.83 (d, 1H, $J_{1,2}$= 5.6 Hz, H-1), 6.48 (dd, 1H, $J_{3,4}$= 9.5 Hz, H-3), 7.01 (dt, 1H, SCH=), 7.39-7.85 (m, 17H, aromatic), 8.88 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 19.5, 21.2, 27.1, 29.8, 43.7, 53.3, 62.6, 70.4, 70.8, 75.1, 87.3, 122.6, 123.0, 123.9, 124.7, 127.9, 129.9, 129.9, 133.4, 135.8, 136.0, 139.8, 150.2, 151.1, 153.6, 171.4, 172.7 ppm.



4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-6-triphenylmethyl-1-thio-β-D-glucopyranoside /Palladium (II) complex (54). The title compound was obtained from **5** followed by chromatography on silica gel as yellow foam in 98% yield. Analytical data for **54**: R_f= 0.38 (1/9 methanol/dichloromethane); ^{1}H-n.m.r : δ, 3.46-3.52 (m, 2H, H-6a,6b), 4.14 (m, 1H, H-5), 5.29 (d, 1H, $J_{1,2}$= 9.8 Hz, H-1), 5.66 (dd, 1H, $J_{4,5}$= 9.7 Hz, H4), 5.73 (dd, 1H, $J_{2,3}$= 9.6 Hz, H-2), 5.93 (dd, 1H, $J_{3,4}$= 9.4 Hz, H-3), 6.97 (dt, 1H, SCH=), 7.10-8.00 (m, 33H, aromatic), 9.10 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 11.7, 14.3, 22.9, 29.3, 29.9, 61.3, 62.8, 69.1, 70.6, 73.9, 74.0, 79.1, 80.0, 82.3, 85.4, 87.7, 109.0, 125.2, 125.5, 127.5 (x3), 128.2 (x3), 128.5, 128.6 (x2), 128.8

(x3), 128.9 (x3), 129.3, 130.0 (x3), 130.2, 130.3, 133.7, 134.0, 140.3, 143.5, 147.1, 150.9, 151.0, 153.9, 165.1, 165.4, 165.9, 166.0, 174.5 ppm.

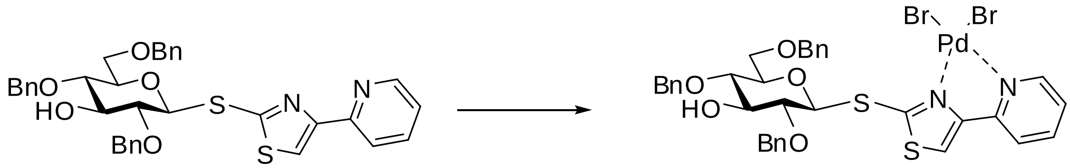
4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-1-thio-β-D-glucopyranoside/ Palladium (II) complex (6). The title compound was obtained from **54** in 94% yield as described for the synthesis of **41**. Analytical data for **6**: R_f= 0.48 (1/1 acetone/toluene); ^{1}H-n.m.r : δ, 3.51 (m ,1H, H-6b), 4.05 (m, 2H, H-6a, OH), 4.17 (m, 1H, H-5), 5.28 (d, 1H, $J_{1,2}$= 9.9 Hz, H-1), 5.80 (dd, 2H, $J_{4,5}$= 9.8 Hz, H-2,4), 6.10 (dd, 1H ,$J_{3,4}$= 9.4 Hz, H-3), 7.08 (m, 1H, SCH=), 7.26-8.18 (m, 18H, aromatic), 8.97 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 43.7, 61.3, 69.1, 70.6, 73.8, 77.4, 79.8, 85.3, 121.9, 123.2, 125.6, 128.5, 128.6 (x2), 128.7 (x2), 128.7 (x2), 128.8 (x3), 129.9, 130.1, 130.2, 133.5, 133.8, 134.1, 140.7, 150.2, 150.5, 153.3, 165.5, 165.9 (x2), 174.4 ppm.



4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-2-deoxy-4,6-O-*p*-methoxybenzylidene-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (55). The title compound was obtained from **45** followed by chromatography on silica gel as yellow foam in 61% yield. Analytical data for **55**: R_f = 0.58 (1/9 methanol/dichloromethane), $[\alpha]_D^{28}$ = 138.1° (c = 1,

$CHCl_3$); [1]H-n.m.r : δ, 1.92 (s, 3H, $COCH_3$), 3.77 (dd, 1H, $J_{4,5}$= 9.4 Hz, H-4), 3.79 (s, 3H, OCH_3), 3.85 (m, 1H, H-6a), 4.31-4.36 (m, 2H, H-5,6b), 4.98 (dd, 1H, $J_{2,3}$= 5.8 Hz, H-2), 5.50 (s, 1H, CHPh), 6.01 (d, 1H, $J_{1,2}$= 5.7 Hz, H-1), 6.52 (dd, 1H, $J_{3,4}$= 9.4 Hz, H-3), 6.85-8.28 (m, 12H, aromatic), 9.19 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.9, 53.0, 55.6, 65.5, 66.3, 68.2, 76.7, 80.7, 87.9, 101.6, 113.8 (x4), 122.7, 123.1, 124.3, 125.6, 127.6 (x4), 129.2, 129.3 (x2), 140.5, 150.9, 151.2, 154.6, 160.3, 169.0, 171.8 ppm.

4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-2-deoxy-6-O-*p*-methoxybenzyl-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (56). The solution of compound **55** (0.05 mmol, 50 mg), activated molecular sieves 3Å (3g/mmol) in DMF (1 mL) was stirred under argon for 1 h. Then $NaCNBH_3$ (0.54 mmol, 34.5 mg) was added and stirred for another 30 min. After that the reaction mixture was cooled down to 0^{o}C and added TFA (0.54 mmol, 41μL) dropwise. The reaction mixture was kept for 2 h at 0^{o}C. Upon completion, the reaction mixture was diluted in CH_2Cl_2 (50 mL), washed with water (15 mL), $NaHCO_3$ (15 mL), and water (3 x 15 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow compound **56** as yellow foam (31.5 mg, 69% yield). Analytical data for **56**: ^{1}H-n.m.r : δ, 1.98 (s, 3H, $COCH_3$), 3.80 (s, 3H, OCH_3), 3.92 (dd, 1H, $J_{4,5}$= 8.7 Hz, H-4), 4.00 (dd, 1H, $J_{5,6b}$= 1.6 Hz, H-6b), 4.13 (dd, 1H, $J_{5,6a}$= 3.8 Hz, $J_{6a,6b}$= 11.5 Hz, H-6a), 4.53-4.67 (m, 3H, H-5,CH_2PhOMe), 4.91 (dd, 1H, $J_{2,3}$= 5.6 Hz, H-2), 5.83 (d, 1H, $J_{1,2}$= 5.6 Hz, H-1), 6.44 (dd, 1H, $J_{3,4}$= 9.2 Hz, H-3), 6.87-8.09 (m, 12H, aromatic), 8.90 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.9, 53.0, 55.6, 55.8, 65.5, 66.3, 68.3, 77.4, 80.7, 101.7, 113.9 (x2), 114.5 (x2), 122.4, 122.5, 125.5, 127.7 (x2), 129.3, 130.2, 132.2 (x2), 140.3, 151.2, 154.8, 160.3, 164.8, 168.9, 172.0, 191.0 ppm.



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4-(Pyridin-2-yl)thiazole-2-yl 2,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside/ Palladium (II) complex (57). The title compound was obtained from **43** followed by chromatography on silica gel as yellow foam in 98% yield. Analytical data for **57**: R_f= 0.45 (1/4 acetone/toluene), $[\alpha]_D^{25}$ = 134.3° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 2.84 (bs, 1H, OH), 3.09 (m, 1H, H-5), 3.49-3.61 (m, 4H, H-2,4,6a,6b), 3.89 (dd, 1H, $J_{3,4}$= 8.5 Hz, H-3), 4.37-4.62 (m, 3H, CH_2Ph), 4.72 (d, 1H, $J_{1,2}$= 6.9 Hz, H-1), 4.75-4.99 (m, 3H, CH_2Ph), 7.00 (dd, 1H, SCH=), 7.18-8.06 (m, 18H, aromatic), 8.92 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 21.7, 29.9, 68.6, 73.6, 75.0, 76.5, 78.6, 78.6, 80.7, 85.1, 121.5, 123.3, 124,8, 125.5, 128.0, 128.1, 128.1, 128.3, 128.4, 128.6, 128.7, 128.8, 129.0, 129.2, 129.7, 137.3, 138.0, 138.3, 140.1, 150.3, 150.9, 153.0 ppm.

Glycosylation of bidentate glycosyl acceptors and decomplexation

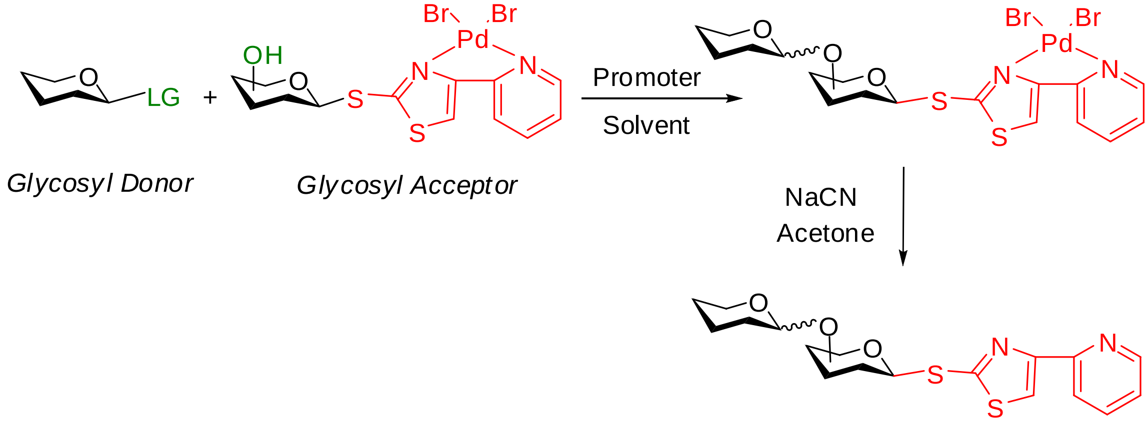
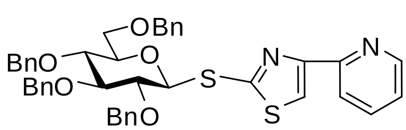


Table 2. Glycosylation of the temporary deactivated SPT acceptors.

Entry	donor	acceptor	promoter	time	product	yield, %	α/β ratio
1	**4**	**6**	AgOTf	1 h	**7**	90	1.5/1
2	**58**	**6**	AgOTf	10 min	**7**	85	1.1/1
3	**59**	**6**	AgOTf	2 h	**7**	89	1.2/1
4	**62**	**6**	TMSOTf	5 min	**7**	83	3.2/1
5	**64**	**6**	MeOTf	30 min	**7**	70	1.2/1
6	**4**	**57**	AgOTf	3 h	**67**	68	1.8/1
7	**58**	**57**	AgOTf	1 h	**67**	84	2.2/1
8	**59**	**57**	AgOTf	2 h	**67**	80	1.3/1
9	**62**	**57**	TMSOTf	5 min	**67**	71	2.5/1
10	**64**	**57**	MeOTf	1h	**67**	65	1.1/1
11	**35**	**6**	AgOTf	16 h	**66**	77	β only

12	**60**	**6**	AgOTf	20 min	**66**	81	β only
13	**61**	**6**	AgOTf	16 h	**66**	73	β only
14	**63**	**6**	TMSOTf	10 min	**66**	86	β only
15	**65**	**6**	MeOTf	30 min	**66**	70	β only
16	**35**	**57**	AgOTf	24 h	**68**	62	β only
17	**60**	**57**	AgOTf	1 h	**68**	79	β only
18	**61**	**57**	AgOTf	16 h	**68**	75	β only
19	**63**	**57**	TMSOTf	10 min	**68**	80	β only
20	**65**	**57**	MeOTf	4 h	**68**	60	β only

Glycosyl donors **4**, **35**, **58**,[18] **59**,[19] **60**,[18] **61**,[19] **62**,[20] **63**,[21] **64**,[22] **65**.[23]



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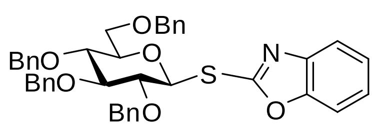

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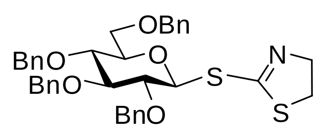

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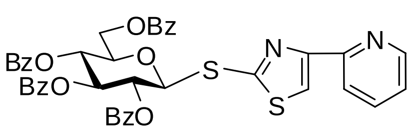

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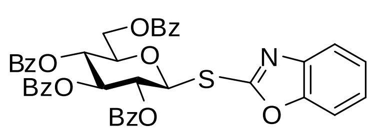

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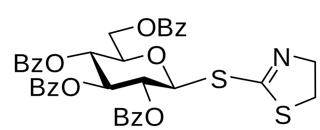

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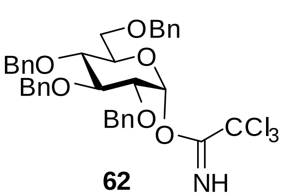

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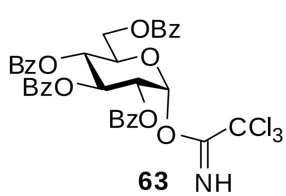

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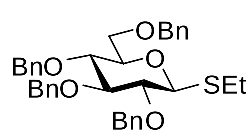

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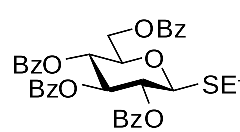

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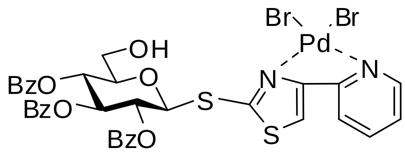
Glycosyl acceptors



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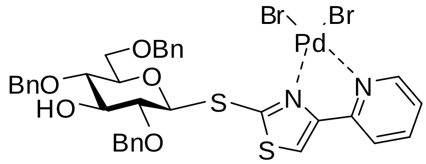

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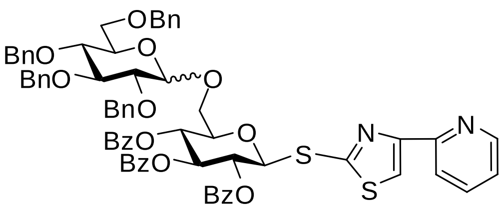
Disaccharides



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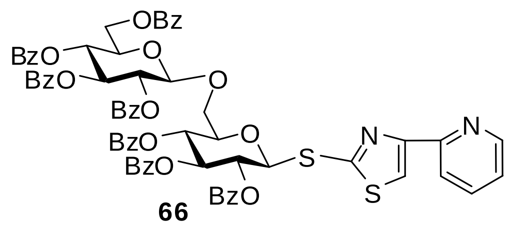

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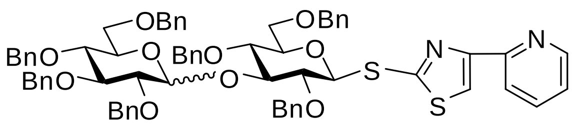

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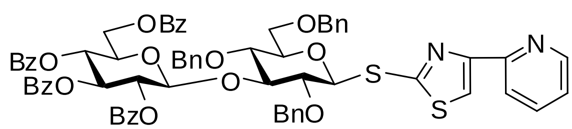

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General Glycosylation/Ligand Exchange Procedures.

AgOTf-promoted glycosylation procedure. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (3Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. AgOTf (0.06 mmol) was added and the reaction mixture was stirred for 6-20 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was then dissolved in acetone (1 mL) containing NaCN (0.1 mmol). The reaction mixture was stirred for 16 h at rt, the solid was filtered-off and washed with acetone (3 x 0.5 mL). The combined filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharides. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

MeOTf-promoted glycosylation procedure. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (3Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. MeOTf (0.09 mmol) was added and the reaction mixture was stirred for 30 min-1h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was then dissolved in acetone (1 mL) containing NaCN (0.1 mmol). The reaction mixture was stirred for 16 h at rt, the solid was filtered-off and washed with acetone (3 x 0.5 mL). The combined filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the corresponding disaccharides. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

TMSOTf-promoted glycosylation procedure. A mixture of the glycosyl donor (0.03 mmol), glycosyl acceptor (0.026 mmol), and freshly activated molecular sieves (4Å, 60 mg) in $(ClCH_2)_2$ (0.5 mL) was stirred under argon for 1.5 h. TMSOTf (0.06 mmol) was added and the reaction mixture was stirred for 1-3 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), saturated $NaHCO_3$ (10 mL) and water (3x10 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was then dissolved in acetone (1 mL) containing NaCN (0.1 mmol). The reaction mixture was stirred for 16 h at rt, the solid was filtered-off and washed with acetone (3 x 0.5 mL). The combined filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to allow the corresponding disaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

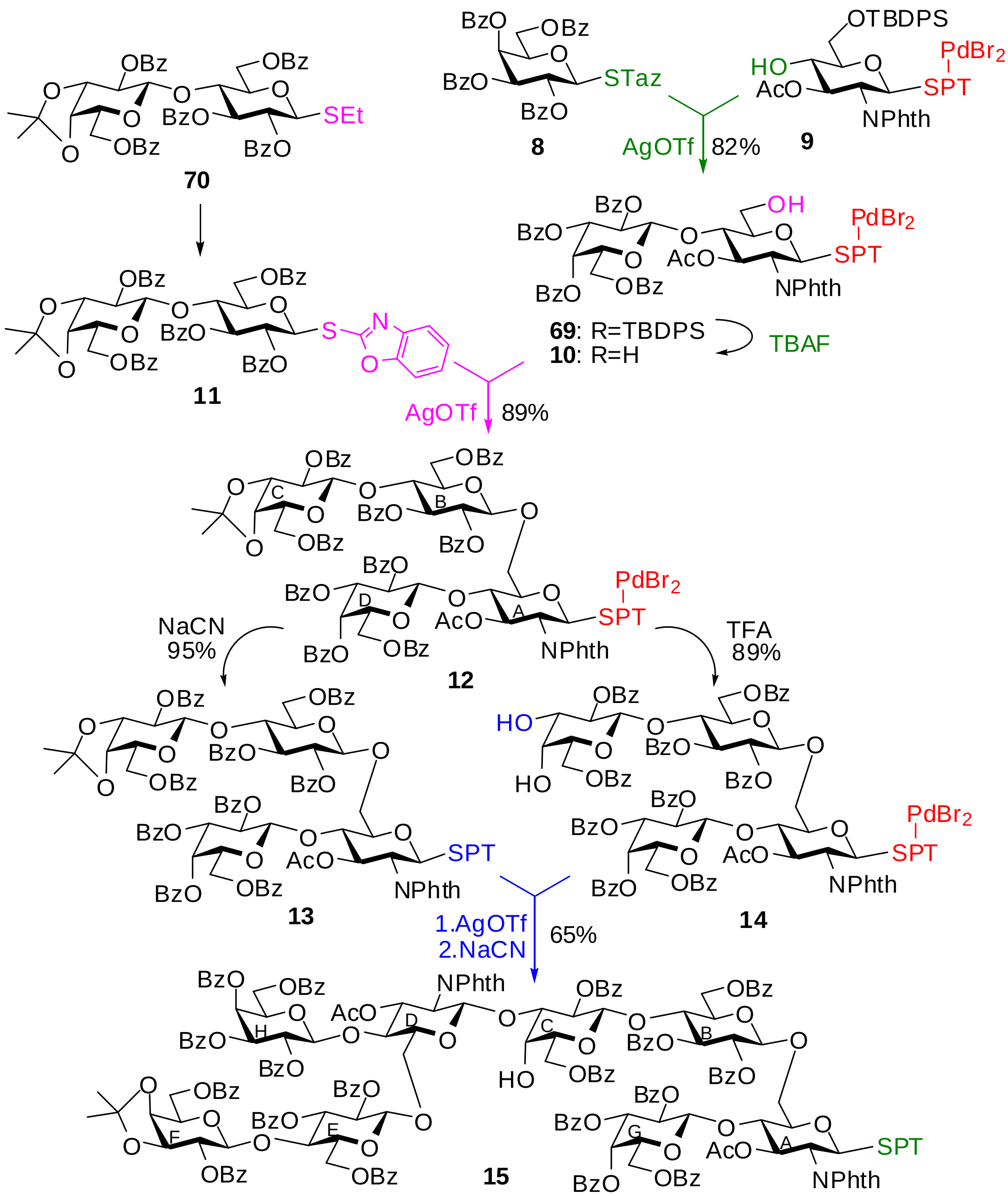
4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyl)-1-thio-D-glucopyranoside (7). Analytical data for α-**7**: R_f= 0.53 (2/3 ethyl acetate/hexanes); ^{1}H-n.m.r : δ, 3.39 (m, 1H, H-6b'), 3.50.3.70 (m, 3H, H-2',4',6a'), 3.78-3.90 (m, 2H, $J_{3',4'}$= 9.4 Hz, H-3',5'), 3.90-4.00 (m, 1H, H-6a), 4.18 (dd, 1H, $J_{6a,6b}$= 10.1 Hz, H-6b), 4.27-4.36 (m, 1H, H-5), 4.40-4.90 (m, 9H, H-1', CH_2Ph), 5.59 (d, 1H, $J_{1,2}$= 10.1 Hz, H-1), 5.67 (dd, 1H, $J_{4,5}$= 8.9 Hz, H-4), 5.81 (dd, 1H, H-3), 6.03 (dd, 1H, $J_{2,3}$= 9.4 Hz, H-2), 7.10-8.15 (m, 39H, aromatic), 8.60 (d, 1H, H-6') ppm; ^{13}C-n.m.r. (α/β–**7**) : δ, 14.3, 22.9, 29.6, 29.9, 32.1, 67.3, 68.5, 68.8, 69.1, 69.7, 69.9, 70.3, 70.7, 73.5, 73.6, 73.7, 74.3, 74.9, 75.0, 75.1, 75.7, 75.8, 77.4, 77.8, 78.0, 78.8, 80.1, 82.1, 82.3, 84.6, 84.9, 85.1, 97.6, 104.0, 119.0, 199.8, 121.5, 121.6, 123.0, 123.2, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 129.0, 129.0, 130.0, 130.1, 130.2, 133.5, 133.7, 133.7, 137.2, 137.3, 138.2, 138.3, 138.4, 138.5, 138.6, 138.7, 138.8, 139.2, 149.6, 152.2, 152.3, 155.4, 155.5, 159.5, 159.8, 165.3, 165.4, 165.6, 166.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{69}H_{62}N_2O_{13}S_2Na$ 1213.3591, found 1213.3630.

4-(Pyridin-2-yl)thiazole-2-yl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (66). Analytical data: R_f= 0.65 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{27}$ = +21.8° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.97 (dd, 1H, $J_{5',6a'}$= 6.9 Hz, $J_{6a',6b'}$= 11.6 Hz, H-6a'), 4.08-4.15 (m, 2H, H-5,6b'), 4.22 (m, 1H, H-5'), 4.40 (dd, 1H, $J_{5,6a}$= 4.7 Hz, $J_{6a,6b}$= 12.3 Hz, H-6a), 4.63 (dd, 1H, $J_{5,6b}$= 3.1 Hz, H-6b), 5.00 (d, 1H, $J_{1,2}$= 7.8 Hz, H-1), 5.37-5.52 (m, 3H, H-1',2,4'), 5.57 (dd, 1H, $J_{2',3'}$= 9.6 Hz, H-2'), 5.63 (dd, 1H, $J_{4,5}$= 9.7 Hz, H-4), 5.85 (dd, 1H, $J_{3,4}$= 9.6 Hz, H-3), 5.94 (dd, 1H, $J_{3',4'}$= 9.4 Hz, H-3'), 7.17-8.32 (m, 39H, aromatic), 8.67 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 62.9, 68.5, 69.6, 69.7, 70.7, 72.0, 72.5, 73.1, 74.1, 76.7, 78.7, 85.0, 101.4, 120.1, 120.5, 123.1, 128.5 (x4), 128.5 (x2), 128.6 (x2), 128.6 (x4), 128.7 (x2), 128.9, 128.9, 129.0, 129.0, 129.1, 129.4, 129.8, 129.9 (x2), 130.0 (x6), 130.0 (x4), 130.1 (x2), 133.3 (x2), 133.4, 133.4, 133.6, 133.6, 133.7, 137.1, 149.6, 152.2, 155.6, 159.2, 165.2, 165.3, 165.5, 165.8, 166.0, 166.3 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{68}H_{52}N_2O_{17}S_2Na$ 1269.2762, found 1269.2747.

4-(Pyridin-2-yl)thiazole-2-yl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-1-thio-D-glucopyranoside (67). Analytical data for α-**67**: R_f= 0.65 (2/3 ethyl acetate/hexanes); ^{1}H-n.m.r : δ, 3.44 (dd, 1H, $J_{5',6a'}$= 2.4 Hz, $J_{6a',6b'}$= 10.9 Hz, H-6b'), 3.49 (dd, 1H, $J_{5',6a'}$= 2.7 Hz, H-6a'), 3.68-3.73 (m, 2H, H-2',5'), 3.75-3.90 (m, 4H, H-2,5,6a,6b), 4.00 (dd, 1H, $J_{3',4'}$= 9.5 Hz, H-3'), 4.20 (m, 2H, H-3,4'), 4.30 (m, 1H, H-4), 4.38 (d, 1H, CH_2Ph), 4.52-5.10 (m, 13H, CH_2Ph), 5.06 (d, 1H, $J_{1,2}$= 9.6 Hz, H-1), 5.78 (d, 1H, $J_{1',2'}$= 3.6 Hz, H-1'), 7.17-8.23 (m, 39 H, aromatic), 8.73 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 68.2, 68.6, 70.3, 73.5, 73.7, 74.1, 75.0, 75.3, 75.6, 75.7, 77.4, 78.3, 78.7, 79.2, 79.5, 79.5, 79.6, 82.6, 86.8, 97.5, 120.2, 121.6, 123.1, 127.0, 127.6, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4, 128.5, 128.6, 128.6, 128.9, 129.2, 137.4, 138.0, 138.1, 138.2, 138.3, 138.5, 138.7, 138.9, 149.5, 152.2, 159.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{69}H_{68}N_2O_{10}S_2Na$ 1171.4213, found 1171.4243.

4-(Pyridin-2-yl)thiazole-2-yl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-benzoyl-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (68). Analytical data: R_f= 0.42 (1/4 ethyl acetate/toluene); ^{1}H-n.m.r : δ, 3.54 (m, 2H, H-2,5), 3.62-3.75 (m, 3H, H-4,6a,6b), 3.95 (m, 1H, H-5'), 4.21 (dd, 1H, $J_{3,4}$= 8.7 Hz, H-3), 4.40 (dd, 1H, $J_{5',6a'}$= 5.3 Hz, $J_{6a',6b'}$= 12.1 Hz, H-6a'), 4.45-4.60 (m, 5H, H-6b', CH_2Ph), 4.84 (d, 1H, CH_2Ph), 4.97 (d, 1H, $J_{1,2}$= 9.9 Hz, H-1), 5.11 (d, 1H, CH_2Ph), 5.46 (d, 1H, $J_{1',2'}$= 8.0 Hz, H-1'), 5.56-5.70 (m, 2H, $J_{2',3'}$= 9.9 Hz, $J_{4',5'}$= 9.7 Hz, H-2',4'), 5.86 (dd, 1H, $J_{3',4'}$= 9.7 Hz, H-3'), 7.19-8.05 (m, 39H, aromatic), 8.62 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 63.5, 68.9, 70.1, 72.3, 72.6, 73.1, 73.6, 75.1, 75.2, 75.4, 77.4, 79.6, 81.2, 83.0, 85.9, 100.7, 119.5, 121.5, 123.1, 127.8, 127.8, 128.0 (x2), 128.3 (x2), 128.4 (x3), 128.5 (x3), 128.5 (x4), 128.6 (x4), 128.7 (x2), 129.0 (x3), 129.3, 129.8, 129.9 (x3), 130.0 (x2), 130.0 (x2), 133.2, 133.5, 133.5, 133.6, 137.3, 137.6, 138.3, 138.5, 149.5, 152.2, 155.3, 160.3, 165.4, 165.4, 166.0, 166.2 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{69}H_{60}N_2O_{14}S_2Na$ 1227.3384, found 1227.3370.

Synthesis of octasaccharide SPn14



4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-6-O-(*tert*-butyl)diphenylsilyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (69). The title compound was obtained from **8** and **9**

as yellow foam in 79% yield by typical AgOTf-promoted glycosylation. Analytical data for **69**: R_f= 0.70 (1/9 methanol/dichloromethane), $[\alpha]_D^{28}$ = +156.1° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.08 (s, 9H, $C(CH_3)_3$), 1.97 (s, 3H, $COCH_3$), 3.72 (dd, 1H, $J_{6a',6b'}$= 11.6 Hz, H-6b'), 3.96 (dd, 1H, H-5'), 4.01 (dd, 1H, H-6a'), 4.23 (dd, 1H, $J_{5,6a}$= 7.1 Hz, $J_{5,6b}$= 6.2 Hz, H-5), 4.41-4.46 (m, 2H, H-4,6a), 4.58 (dd, 1H, $J_{6a,6b}$= 11.6 Hz, H-6b), 4.91 (dd, 1H, $J_{2,3}$= 5.8 Hz, H-2), 5.31 (d, 1H, $J_{1',2'}$= 8.1 Hz, H-1'), 5.52 (dd, 1H, $J_{3',4'}$=3.3 Hz, H-3'), 5.76 (d, 1H, $J_{1,2}$= 5.8 Hz, H-1), 5.85 (dd, 1H, $J_{2',3'}$= 8.0 Hz, H-2'), 5.96 (d, 1H, $J_{4',5'}$= 3.3 Hz, H-4'), 6.50 (dd, 1H, $J_{3,4}$= 9.2 Hz, H-3), 7.10-8.11 (m, 38H, aromatic), 9.08 (d, 1H, H-6') ppm;^{13}C-n.m.r.: δ, 19.6, 21.3, 27.2 (x3), 29.9, 53.4, 61.1, 62.2, 67.0, 68.2, 70.0, 71.7, 72.3, 73.5, 74.9, 76.7, 86.7, 100.3, 121.0, 122.3, 125.1, 125.5, 128.0 (x2), 128.1, 128.4 (x2), 128.5 (x2), 128.5 (x2), 128.6, 128.7, 128.8 (x2), 128.9, 128.9, 129.0, 129.0 (x2), 129.2, 129.7, 130.0, 130.0 (x2), 130.1 (x2), 130.2, 130.2, 130.3, 130.3, 130.7, 132.4, 133.3, 133.5, 133.5, 133.6, 133.7, 134.0, 135.7 (x2), 136.2, 136.4, 139.8, 151.0, 151.1, 154.1, 164.7, 165.6, 165.7, 166.2, 168.7, 173.5 ppm.

4-(Pyridin-2-yl)thiazole-2-yl 3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (10). To a solution of compound **69** (0.02 mmol, 30 mg) in THF (1 mL) was added 1M TBAF in THF (0.04 mmol, 40 μL) at 0°C. The reaction mixture was kept at 0°C for 10h. Upon completion, the reaction mixture was diluted in CH_2Cl_2 (50 mL), washed with water (15 mL), $NaHCO_3$ (15 mL), and water (3 x 15 mL). The organic phase was separated, dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (methanol/dichloromethane gradient elution) to allow compound **10** as yellow foam (21 mg, 82% yield). Analytical data for **10**: R_f= 0.43 (1/9 methanol/dichloromethane); ^{1}H-n.m.r : δ, 1.95 (s, 3H, $COCH_3$), 2.82 (bs, 1H, OH), 3.75 (dd, 1H, $J_{6a,6b}$= 11.9 Hz, H-6b), 3.81 (dd, 1H, H-6a), 4.04 (dd, 1H, H-5), 4.15 (dd, 1H, $J_{4,5}$= 9.8 Hz, H-4), 4.43-4.53 (m, 2H, H-6a',6b'), 4.58 (dd, 1H, $J_{5',6a'}$= 6.3 Hz, $J_{5',6b'}$= 5.9 Hz, H-5'), 4.85 (dd, 1H, $J_{2,3}$= 5.6 Hz, H-2), 5.20 (dd, 1H, $J_{2',3'}$= 3.5 Hz, H=2'), 5.70 (d, 1H, $J_{1,2}$= 5.6 Hz, H-1), 5.82 (m, 2H, $J_{1',2'}$= 4.7 Hz, H-1',3'), 6.02 (d, 1H, H-4'), 6.40 (dd, 1H, $J_{3,4}$= 9.2 Hz, H-3), 7.23-8.23 (m, 28H, aromatic), 9.14 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 21.4, 29.9, 53.1, 59.7, 61.7, 67.2, 68.2, 70.5, 71.2, 72.2, 73.8, 75.5, 76.7 (x2), 87.3, 100.7, 122.4, 122.8, 123.8, 125.4, 128.4, 128.5 (x2), 128.7, 128.8 (x5), 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 129.9 (x4), 130.0 (x6), 130.2, 133.5, 133.6, 133.8, 134.0, 151.2, 154.3, 164.9, 165.6, 165.8, 166.4, 168.0, 172.4 ppm.

2-Benzoxazolyl 2,3,6-tri-O-benzoyl-4-O-(2,6-di-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (11). The solution of ethyl 2,3,6-tri-O-benzoyl-4-O-(2,6-di-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside[24] (**70**, 3.56 mmol, 3.37 g), activated molecular sieves 3Å (1.1 g, 500mg/mmol) in CH_2Cl_2 (53 mL, 15 mL/mmol) was stirred under argon for 1 h. Freshly prepared soln. Br_2/CH_2Cl_2 (1:165) was then added (33 mL, 9.4 mL/mmol) and the reaction mixture was kept for 5 min at rt. After that, CH_2Cl_2 was evaporated out from the reaction mixture using cold water bath. The concentrated residue was diluted with dry acetone (20 mL) and potassium salt of 2-mercaptobenzoxazole (10.7 mmol, 2 g) was added. The reaction was stirred under argon for 2 h at rt. Upon completion, the mixture was diluted with toluene (300 mL) and washed with 1% aq. NaOH (60 mL) and water (3 x 60 mL), the organic layer was separated and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the title compound as a white foam (3.13 g, 85% yield). Analytical data for **11**: R_f = 0.48 (2/3 ethyl acetate/hexanes), $[\alpha]_D^{32}$ = -7.7° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.22 (s, 3H, CCH_3), 1.53 (s, 3H, CCH_3), 3.65 (dd, 1H, $J_{4,5}$= 8.5 Hz, H-4), 3.86 (dd, 1H, $J_{5,6a}$= 3.4 Hz, $J_{5,6b}$= 3.5 Hz, H-5), 4.06 (dd, 1H, $J_{3,4}$= 8.7 Hz, H-3), 4.11-4.18 (m, 2H, H-5', 6a), 4.23-4.31 (m, 2H, H-3', 6b), 4.36 (dd, 1H, H-6a'), 4.55 (d, 1H, $J_{1',2'}$= 8.2 Hz, H-1'), 4.67 (d, 1H, H-4'), 4.78 (dd, 1H, $J_{5',6b'}$= 2.2 Hz, $J_{6a',6b'}$= 12.3, H-6b'), 5.30 (dd, 1H, $J_{2',3'}$= 7.8 Hz, H-2'), 5.35 (dd, 1H, $J_{2,3}$= 9.2 Hz, H-2), 5.69 (d, 1H, $J_{1,2}$= 10.5 Hz, H-1), 7.00-7.94 (m, 29H, aromatic) ppm; ^{13}C-n.m.r.: δ, 21.9, 26.8, 28.1, 63.3, 64.1, 71.9, 72.7, 73.4, 73.9, 75.1, 76.9, 77.5, 82.6, 83.8, 102.0, 110.5, 111.7, 119.2, 124.7, 124.9, 125.8, 128.7 (x3), 128.9 (x3), 128.9 (x2), 129.0 (x2), 129.3, 129.5 (x3), 129.6, 129.7, 130.0 (x2), 130.0, 130.3 (x2), 130.4 (x2), 130.4 (x2), 133.3, 133.7, 133.8, 133.9, 138.3, 142.0, 152.3, 161.8, 165.7, 165.9, 166.0, 167.0 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{57}H_{49}NO_{16}SNa$ 1058.2670, found 1058.2697.

4-(Pyridin-2-yl)thiazole-2-yl O-(2,6-di-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (12). The title compound was prepared from **10** and **11** in the presence of AgOTf as yellow foam in 89% yield. Analytical data for **12**: R_f= 0.53 (1/4 acetone/toluene); ^{1}H-n.m.r : δ, 1.38 (s, 3H, CCH_3), 1.67 (s, 3H, CCH_3), 2.00 (s, 3H, $COCH_3$), 3.09 (dd, 1H, $J_{4B,5B}$= 6.9 Hz, H-4B), 3.19 (m, 1H, H-5B), 3.59 (dd, 1H, $J_{(6a)A,(6b)A}$= 9.4 Hz, H-(6a)A), 3.75 (m, 1H, H-(6b)A), 3.90 (dd, 1H, $J_{4A,5A}$= 9.4 Hz, H-4A), 3.95 (dd, 1H, $J_{(6a)B,(6b)B}$= 9.4 Hz, H-(6a)B), 4.06 (dd, 1H, $J_{3B,4B}$= 7.0 Hz, H-3B), 4.15 (m, 2H, H-(6a)D, (6b)D), 4.22 (m, 1H, H-5A), 4.28-4.31 (m, 2H, H-3C,5C), 4.35-4.40 (m, 2H, H-4C, (6b)B), 4.43 (d, 1H, $J_{1D,2D}$= 7.8 Hz, H-1D), 4.48 (dd, 1H, $J_{(6a)C,(6b)C}$= 7.8 Hz, H-(6b)C), 4.53 (dd, 1H, H-(6a)C), 4.62 (d, 1H,

$J_{1C,2C}$= 7.9 Hz, H-1C), 4.77 (dd, 1H, $J_{5D,(6a)D}$= 4.5 Hz, $J_{5D,(6b)D}$= 4.5 Hz, H-5D), 4.86 (dd, 1H, $J_{2A,3A}$= 6.0 Hz, H-2A), 5.16 (dd, 1H, $J_{3D,4D}$= 3.5 Hz, H-3D), 5.29 (dd, 2H, H-1B,2C), 5.38 (dd, 1H, $J_{2B,3B}$= 9.3 Hz, H-2B), 5.52 (d, 1H, $J_{4D,5D}$= 3.4 Hz, H-4D), 5.57 (dd, 1H, $J_{2D,3D}$= 7.8 Hz, H-2D), 5.75 (d, 1H, $J_{1A,2A}$= 6.0 Hz, H-1A), 6.34 (dd, 1H, $J_{3A,4A}$= 8.8 Hz, H-3A), 7.20-8.25 (m, 53H, aromatic), 9.27 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, δ, 20.9, 21.3, 21.7, 26.5, 27.8, 29.9, 53.6, 61.5, 62.6, 63.5, 67.2, 67.6, 68.3, 70.5, 70.7, 71.4, 71.8, 72.0, 72.3, 73.3, 73.5, 73.7, 76.2, 76.9, 77.7, 86.9, 101.0, 101.1, 101.5, 111.3, 119.3, 121.4, 123.0, 125.5, 128.4, 128.5, 128.7, 128.8, 128.9, 128.9, 128.9, 129.0, 129.1, 129.1, 129.2, 129.5, 129.5, 129.6, 129.7, 129.8, 129.9, 129.9, 130.0, 130.0, 130.3, 130.03, 133.4, 133.5, 133.7, 133.8, 133.8, 134.1, 137.0, 138.1, 149.5, 152.0, 155.4, 160.5, 164.9, 165.0, 165.1, 165.4, 165.5, 166.0, 166.5, 168.6, 170.1 ppm.

4-(Pyridin-2-yl)thiazole-2-yl O-(2,6-di-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside (13). The title compound was prepared from **12** via typical ligand exchange procedure with NaCN as white foam in 95% yield. Analytical data for **13**: R_f= 0.53 (1/4 acetone/toluene), $[\alpha]_D^{26}$ = 54.7° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.35 (s, 3H, CCH_3), 1.65 (s, 3H, CCH_3), 1.99 (s, 3H, $COCH_3$), 3.08 (m, 1H, H-4B), 3.13 (dd, 1H, H-5B), 3.66 (dd, 1H, $J_{5A,(6a)A}$= 2.9 Hz, $J_{(6a)A,(6b)A}$= 11.1 Hz, H-(6a)A), 3.80 (dd, 2H, H-3B, (6a)B), 3.89 (dd, 1H, $J_{4A,5A}$= 8.9 Hz, H-4A), 3.96 (m, 1H, H-5C), 4.02 (dd, 1H, $J_{(6a)B,(6b)B}$= 7.0 Hz, H-(6a)B), 4.17 (d, 1H, $J_{1D,2D}$= 7.7 Hz, H-1D), 4.22 (dd, 1H, $J_{5D,(6a)D}$= 2.1 Hz, $J_{(6a)D,(6b)D}$= 5.4 Hz, H-(6b)D), 4.25-4.47 (m, 7H, H-5A, (6b)B,3C,4C,(6a)C,(6b)C,(6a)D), 4.51 (d, 1H, $J_{1C,2C}$= 7.8 Hz, H-1C), 4.77 (dd, 1H, $J_{5D,(6a)D}$= 4.2 Hz, $J_{5D,(6b)D}$= 4.2 Hz, H-5D), 4.87 (dd, 1H, $J_{2A,3A}$= 5.7 Hz, H-2A), 5.24-5.36 (m, 4H, H-

1B,2B,2C,2D), 5.56 (d, 1H, $J_{4D,5D}$= 3.3 Hz, H-4D), 5.62 (d, 1H, $J_{3D,4D}$= 7.8 Hz, H-3D), 6.09 (d, 1H, $J_{1A,2A}$= 5.7 Hz, H-1A), 6.33 (dd, 1H, $J_{3A,4A}$= 8.7 Hz, H-3A), 7.18-8.25 (m, 53H, aromatic), 8.52 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 20.9, 21.3, 21.7, 26.5, 27.8, 29.9, 53.6, 61.5, 62.6, 63.5, 67.2, 67.6, 68.3, 70.5, 70.7, 71.4, 71.8, 72.0, 72.3, 73.3, 73.5, 73.7, 76.2, 76.9, 77.7, 86.9, 101.0, 101.1, 101.5, 111.3, 119.3, 121.4, 123.0, 125.5, 128.4, 128.5, 128.7, 128.8, 128.9, 128.9, 128.9, 129.0, 129.1, 129.1, 129.2, 129.5, 129.5, 129.6, 129.7, 129.8, 129.9, 129.9, 130.0, 130.0, 130.3, 130.03, 133.4, 133.5, 133.7, 133.8, 133.8, 134.1, 137.0, 138.1, 149.5, 152.0, 155.4, 160.5, 164.9, 165.0, 165.1, 165.4, 165.5, 166.0, 166.5, 168.6, 170.1 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{108}H_{91}N_3O_{31}S_2$ 1990.5156, found 1990.5164.

4-(Pyridin-2-yl)thiazole-2-yl O-(2,6-di-O-benzoyl-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside /Palladium (II) complex (14). Compound **12** (0.022 mmol, 50 mg) was dissolved in wet CH_2Cl_2 (2 mL) containing trifluoroacetic acid (0.05 mL). The reaction mixture was kept for 1 h at 0^{o}C, then diluted with CH_2Cl_2 (50 ml.), transferred into a separatory funnel and washed with water (15 mL), saturated aq. $NaHCO_3$ (15 mL) and water (3 x 15 mL). The organic phase was separated, dried, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the title compound as yellow foam (43 mg, 89% yield). Analytical data for **14**: R_f= 0.45 (1/9 methanol/dichloromethane); ^{1}H-n.m.r : δ, 2.04 (s, 3H, $COCH_3$), 3.18 (m, 1H, H-5B), 3.30 (m, 3H, H-4B, OHx2), 3.62 (dd, 1H, $J_{(6a)A,(6b)A}$= 9.4 Hz, H-(6a)A), 3.78 (dd, 1H, H-(6b)A), 3.80-3.92 (m, 3H, H-4A, 3C, 4C), 4.00-4.09 (m, 3H, H-3B, (6a)B, (6b)D), 4.18 (dd, 1H, H-5A), 4.23 (dd, 1H, H-(6b)B), 4.29 (dd, 1H, H-(6b)C), 4.39 (dd, 1H, H-5C), 4.48 (m, 2H, H-1D, (6a)D), 4.57 (dd, 1H, H-(6a)C), 4.68 (d, 1H, $J_{1C,2C}$= 7.9 Hz, H-1C), 4.75 (m, 1H, H-5D), 4.84 (dd, 1H, $J_{2A,3A}$= 5.9 Hz, H-2A), 5.21 (dd, 1H, $J_{3D,4D}$= 2.9 Hz, H-3D), 5.25-5.40 (m, 3H, H-1B,2B,2C), 5.55 (d, 1H, $J_{4D,5D}$= 2.9 Hz, H-4D), 5.58 (dd, 1H, $J_{2D,3D}$= 7.9 Hz, H-2D), 5.68 (d, 1H, $J_{1A,2A}$= 5.9 Hz, H-1A), 6.33 (dd, 1H, $J_{3A,4A}$= 9.1 Hz, H-3A), 7.20-8.20 (m, 53H, aromatic), 9.15 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 14.3, 21.0, 21.2, 22.9, 29.6, 29.9, 32.1, 53.1, 61.5, 62.7, 66.6, 67.6, 68.0, 68.7, 70.6, 70.7, 71.7, 72.1, 72.5, 72.7, 73.7, 74.1, 75.9, 76.7, 86.5, 100.6, 101.2, 101.4, 122.2, 125.4, 128.5, 128.9, 128.9, 128.9, 129.0, 129.3, 129.3, 129.4, 129.6, 129.6, 129.7, 129.9, 130.0, 130.2, 130.3, 133.5, 133.8, 133.9, 134.1, 134.3, 150.1, 151.1, 154.0, 164.8, 165.1, 165.5, 166.0, 166.7, 166.8, 168.7, 170.4, 173.0 ppm.

4-(Pyridin-2-yl)thiazole-2-yl O-(2,6-di-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-O-[3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-β-D-glucopyranosyl]-(1→3)-O-(2,6-di-O-benzoyl-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-3-O-acetyl-4-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-2-phthlimido-1-thio-β-D-glucopyranoside (15). The title compound was prepared from **13** and **14** using typical AgOTf-promoted glycosylation / ligand exchange with NaCN procedure as yellow foam in 65% yield. Analytical data for **15**: R_f= 0.28 (1/4 acetone/toluene), $[\alpha]_D^{27}$ = +54.8° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 1.57 (s, 3H, CCH_3), 1.84 (s, 3H, CCH_3), 2.36 (s, 6H, $COCH_3$), 3.21 (m, 2H, H-5B, OH), 3.30 (m, 1H, H-5E), 3.60-3.72 (m, 4H, H-4F,(6b)C,(6b)D,(6b)F), 3.74-3.97 (m, 7H, H-4A,5C,(6a)C,(6a)D,3F,(6a)F,(6a)G), 3.98-4.09 (m, 3H, H-(6a)A,4B,5G), 4.09-4.20 (m, 5H, $J_{1E,2E}$= 7.2 Hz, H-4C,5D,1E,4E,5F), 4.22-4.36 (m, 11H, $J_{1B,2B}$= 7.5 Hz, H-5A,(6b)A,1B,(6a)B,(6b)B,3C,4D,(6a)E,(6b)E,(6b)G,(6a)H), 4.40-

4.46 (m, 2H, H-2D,5H), 4.50 (d, 1H, $J_{1D,2D}$= 7.9 Hz, H-1D), 4.56 (d, 1H, $J_{1G,2G}$= 7.8 Hz, H-1G), 4.62 (d, 1H, $J_{1H,2H}$= 7.9 Hz, H-1H), 4.69 (d, 1H, $J_{1C,2C}$= 7.9 Hz, H-1C), 4.74 (dd, 1H, $J_{5H,(6b)H}$= 2.0 Hz, $J_{(6a)H,(6b)H}$= 12.2 Hz, H-(6b)H), 4.89 (dd, 1H, $J_{2A,3A}$= 5.7 Hz,H-2A), 5.19-5.26 (m, 2H, H-2C,3D), 5.31 (dd, 1H, $J_{3G,4G}$= 3.3 Hz, H-3G), 5.39 (dd, 1H, $J_{2E,3E}$= 7.2 Hz, H-2E), 5.44-5.51 (m, 3H, $J_{1F,2F}$=9.6 Hz, H-2B, 1F, 3H), 5.58-5.68 (m, 5H, H-3B,3E,2G,4G,2H), 5.81 (dd, 1H, $J_{2F,3F}$= 8.7 Hz, H-2F), 5.84 (d, 1H, $J_{4H,5H}$= 1.4 Hz, H-4H), 6.12 (d, 1H, $J_{1A,2A}$= 5.7 Hz, H-1A), 6.36 (dd, 1H, $J_{3A,4A}$= 8.7 Hz, H-3A), 7.15-8.20 (m, 102H, aromatic), 8.52 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 14.3, 14.4, 21.0, 21.3, 21.7, 22.9, 23.4, 26.4, 26.9, 27.7, 27.8, 29.6, 29.9, 30.4, 32.2, 53.7, 57.3, 61.2, 61.6, 62.4, 62.7, 63.1, 67.2, 67.6, 67.7, 68.3, 68.9, 70.4, 70.5, 70.7, 71.5, 71.6, 71.9, 72.0, 72.3, 72.4, 72.9, 73.4, 73.5, 73.5, 73.8, 73.8, 73.9, 75.4, 75.7, 77.7, 86.9, 92.8, 100.8, 101.1, 101.2, 101.5, 101.9, 111.1, 128.1, 128.4, 128.4, 128.5, 128.5, 128.7, 128.8, 128.8, 128.9, 128.9, 129.1, 129.1, 129.3, 129.3, 129.5, 129.5, 129.6, 129.6, 129.6, 129.7, 129.8, 129.9, 130.0, 130.1, 130.1, 130.3, 130.3, 130.4, 119.4, 121.4, 123.0, 123.7, 125.5, 126.2, 128.1, 128.4, 128.5, 128.5, 128.7, 128.8, 128.8, 128.9, 128.9, 128.9, 129.1, 129.3, 129.6, 129.6, 129.6, 129.7, 129.8, 129.9, 130.0, 130.3, 133.4, 133.4, 133.5, 133.6, 133.6, 133.7, 133.8, 134.0, 134.1, 134.3, 137.0, 138.1, 149.5, 152.1, 155.4, 160.5, 164.9, 165.1, 165.2, 165.2, 165.3, 165.5, 165.5, 165.6, 165.8, 165.9, 166.0, 166.1, 166.2, 166.3, 166.4, 168.1, 168.7, 170.1 ppm; HR-FAB MS $[M+H]^+$ calcd for $C_{205}H_{173}N_4O_{62}S_2$ 3745.9949, found 3745.9977.

X-ray structure determination of 6:

A crystal with approximate dimensions 0.49 x 0.06 x 0.03 mm^3 was mounted on a Mitgen cryoloop in a random orientation. Preliminary examination and data collection were performed using a Bruker Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. The data set consisted of a combination of ϖ and ϕ scans with scan width of 0.5° and counting time of 30 seconds/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2006) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of 9757 reflections from the complete data set. Collected data were corrected for systematic errors using SADABS based on the Laue symmetry using equivalent reflections.[25]

Crystal data and intensity data collection parameters are listed in Tables 1-6. Structure solution and refinement were carried out using the SHELXTL- PLUS software package.[26] The structure was solved by direct methods and refined successfully in the space group C_2. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms were treated using appropriate riding model (AFIX m3). One of the phenyl groups of the sugar moiety is disordered. The disorder was resolved with two rings of 50% occupancy atoms and was refined with restraints SIMU, ISOR and EADP (SHELXTL). A molecule of water and a molecule of acetone were located in the lattice. The final residual values and structure refinement parameters are listed below in Table1.

Complete listings of positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are listed as Tables 2-6 below. Table of calculated and observed structure factors are available in electronic format.

X-Ray data for complex 6.

Table 1. Crystal data and structure refinement for complex **6**.

Identification code	d14407/lt/Ning	
Empirical formula	$C_{38} H_{36} Br_2 N_2 O_{10} Pd S_2$	
Formula weight	1011.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 26.134(2) Å	α= 90°.
	b = 6.6651(5) Å	β= 118.580(4)°.
	c = 26.550(3) Å	γ = 90°.
Volume	4061.1(7) Å^3	

Z	4
Density (calculated)	1.654 Mg/m^3
Absorption coefficient	2.585 mm^{-1}
F(000)	2024
Crystal size	0.49 x 0.06 x 0.03 mm^3
Theta range for data collection	1.80 to 25.00°.
Index ranges	$-30 \le h \le 30$, $-7 \le k \le 7$, $-31 \le l \le 31$
Reflections collected	41064
Independent reflections	7012 [R(int) = 0.064]
Completeness to theta = 25.00°	99.6 %
Absorption correction	Numerical
Max. and min. transmission	0.9265 and 0.3640
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7012 / 145 / 481
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0851
R indices (all data)	R1 = 0.0717, wR2 = 0.0951
Absolute structure parameter	0.013(13)
Largest diff. peak and hole	0.897 and -0.624 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	-3298(1)	5775(1)	-118(1)	19(1)
Br(1)	-4144(1)	5729(2)	-1054(1)	32(1)
Br(2)	-3954(1)	5833(2)	276(1)	29(1)
S(1)	-1597(1)	5722(5)	1631(1)	29(1)
S(2)	-2802(1)	5744(5)	1524(1)	23(1)
O(1)	-1877(2)	5313(6)	2555(2)	32(1)
O(2)	-3073(2)	8783(6)	2204(2)	23(1)
O(3)	-3744(2)	6400(7)	2057(2)	54(2)
O(4)	-2469(2)	8902(9)	3425(2)	34(1)
O(5)	-2218(4)	12122(11)	3437(3)	84(3)
O(6)	-1279(2)	8067(7)	3926(2)	30(1)
O(7)	-1103(4)	5365(9)	4495(3)	96(3)
O(8)	-702(2)	4018(8)	3023(2)	45(1)
N(1)	-2722(2)	5757(14)	-439(2)	23(1)
N(2)	-2519(2)	5801(14)	654(2)	19(1)
C(1)	-2853(3)	5790(16)	-1003(2)	29(1)
C(2)	-2432(3)	5880(16)	-1165(3)	31(2)
C(3)	-1857(3)	5856(18)	-760(3)	39(2)

C(4)	-1709(2)	5803(18)	-180(2)	29(1)
C(5)	-2149(2)	5761(16)	-37(2)	23(1)
C(6)	-2042(2)	5733(17)	554(2)	22(1)
C(7)	-1522(2)	5752(17)	1034(2)	28(1)
C(8)	-2347(2)	5800(16)	1209(2)	22(1)
C(9)	-2303(3)	6765(10)	2218(3)	27(2)
C(10)	-2623(3)	7365(10)	2541(3)	21(2)
C(11)	-2186(3)	8374(10)	3092(3)	24(2)
C(12)	-1696(3)	6894(10)	3431(3)	27(2)
C(13)	-1413(3)	6197(10)	3085(3)	30(2)
C(14)	-3630(3)	8081(11)	1958(3)	31(2)
C(15)	-4054(4)	9523(12)	1558(4)	23(2)
C(16)	-3936(4)	11509(12)	1568(4)	32(3)
C(17)	-4357(4)	12761(14)	1165(4)	39(2)
C(18)	-4882(5)	12002(17)	745(4)	45(3)
C(19)	-4994(5)	10017(17)	748(5)	56(4)
C(20)	-4590(4)	8758(14)	1145(5)	50(3)
C(21)	-2446(3)	10820(30)	3569(3)	50(2)
C(22)	-2675(10)	11100(30)	3971(10)	93(5)
C(23)	-2585(11)	12950(30)	4242(12)	128(6)
C(24)	-2786(10)	13290(30)	4634(10)	180(8)
C(25)	-3077(9)	11770(30)	4755(7)	162(8)
C(26)	-3166(8)	9920(30)	4484(8)	187(8)

C(27)	-2965(8)	9590(30)	4091(8)	130(6)
C(22')	-2772(9)	11580(30)	3863(10)	93(5)
C(23')	-2656(10)	13390(30)	4159(12)	128(6)
C(24')	-3014(11)	14050(30)	4378(10)	180(8)
C(25')	-3490(10)	12890(30)	4302(8)	162(8)
C(26')	-3606(7)	11090(30)	4006(8)	187(8)
C(27')	-3247(8)	10430(30)	3786(7)	130(6)
C(28)	-1048(4)	7140(13)	4450(4)	48(2)
C(29)	-739(3)	8538(11)	4926(3)	36(2)
C(30)	-401(5)	7773(15)	5469(3)	81(4)
C(31)	-135(4)	8989(16)	5939(4)	74(3)
C(32)	-195(3)	10930(20)	5877(3)	57(3)
C(33)	-516(6)	11752(15)	5350(4)	114(5)
C(34)	-794(4)	10489(15)	4860(3)	57(3)
C(35)	-961(3)	4582(12)	3373(3)	46(2)
O(1S)	-330(3)	7425(10)	2652(3)	64(2)
C(1S)	62(7)	7660(20)	2554(5)	110(5)
C(2S)	382(8)	9490(30)	2537(9)	227(7)
C(3S)	221(2)	5819(13)	2356(2)	227(7)
O(2S)	-1264(2)	504(13)	2416(2)	69(2)

Table 3. Bond lengths [Å] and angles [°] for complex **6**.

Pd(1)-N(1)	2.055(4)	N(1)-C(5)	1.362(6)
Pd(1)-N(2)	2.087(4)	N(1)-C(1)	1.367(6)
Pd(1)-Br(2)	2.3969(7)	N(2)-C(8)	1.318(6)
Pd(1)-Br(1)	2.4110(7)	N(2)-C(6)	1.394(6)
S(1)-C(7)	1.687(6)	C(1)-C(2)	1.360(8)
S(1)-C(8)	1.731(5)	C(1)-H(1A)	0.9500
S(2)-C(8)	1.751(6)	C(2)-C(3)	1.367(8)
S(2)-C(9)	1.806(7)	C(2)-H(2A)	0.9500
O(1)-C(9)	1.422(7)	C(3)-C(4)	1.397(8)
O(1)-C(13)	1.470(7)	C(3)-H(3A)	0.9500
O(2)-C(14)	1.362(8)	C(4)-C(5)	1.372(7)
O(2)-C(10)	1.440(7)	C(4)-H(4A)	0.9500
O(3)-C(14)	1.220(8)	C(5)-C(6)	1.455(7)
O(4)-C(21)	1.326(16)	C(6)-C(7)	1.349(7)
O(4)-C(11)	1.442(8)	C(7)-H(7)	0.9500
O(5)-C(21)	1.196(14)	C(9)-C(10)	1.512(9)
O(6)-C(28)	1.371(10)	C(9)-H(9A)	1.0000
O(6)-C(12)	1.468(7)	C(10)-C(11)	1.516(9)
O(7)-C(28)	1.204(11)	C(10)-H(10A)	1.0000
O(8)-C(35)	1.437(9)	C(11)-C(12)	1.524(9)
O(8)-H(8A)	0.8400	C(11)-H(11A)	1.0000

C(12)-C(13)	1.502(9)	C(24)-H(24A)	0.9500
C(12)-H(12A)	1.0000	C(25)-C(26)	1.3900
C(13)-C(35)	1.508(9)	C(25)-H(25A)	0.9500
C(13)-H(13A)	1.0000	C(26)-C(27)	1.3900
C(14)-C(15)	1.467(11)	C(26)-H(26A)	0.9500
C(15)-C(16)	1.356(10)	C(27)-H(27A)	0.9500
C(15)-C(20)	1.398(13)	C(22')-C(23')	1.3900
C(16)-C(17)	1.388(12)	C(22')-C(27')	1.3900
C(16)-H(16A)	0.9500	C(23')-C(24')	1.3900
C(17)-C(18)	1.385(14)	C(23')-H(23B)	0.9500
C(17)-H(17A)	0.9500	C(24')-C(25')	1.3900
C(18)-C(19)	1.355(13)	C(24')-H(24B)	0.9500
C(18)-H(18A)	0.9500	C(25')-C(26')	1.3900
C(19)-C(20)	1.366(14)	C(25')-H(25B)	0.9500
C(19)-H(19A)	0.9500	C(26')-C(27')	1.3900
C(20)-H(20A)	0.9500	C(26')-H(26B)	0.9500
C(21)-C(22)	1.464(15)	C(27')-H(27B)	0.9500
C(21)-C(22')	1.494(15)	C(28)-C(29)	1.462(11)
C(22)-C(23)	1.3900	C(29)-C(34)	1.310(13)
C(22)-C(27)	1.3900	C(29)-C(30)	1.379(11)
C(23)-C(24)	1.3900	C(30)-C(31)	1.367(12)
C(23)-H(23A)	0.9500	C(30)-H(30A)	0.9500
C(24)-C(25)	1.3900	C(31)-C(32)	1.303(16)

C(31)-H(31A)	0.9500	N(2)-Pd(1)-Br(1)	174.70(12)
C(32)-C(33)	1.356(12)	Br(2)-Pd(1)-Br(1)	87.47(2)
C(32)-H(32A)	0.9500	C(7)-S(1)-C(8)	89.8(3)
C(33)-C(34)	1.423(12)	C(8)-S(2)-C(9)	98.9(3)
C(33)-H(33A)	0.9500	C(9)-O(1)-C(13)	111.6(5)
C(34)-H(34A)	0.9500	C(14)-O(2)-C(10)	116.1(5)
C(35)-H(35A)	0.9900	C(21)-O(4)-C(11)	116.4(6)
C(35)-H(35B)	0.9900	C(28)-O(6)-C(12)	116.6(6)
O(1S)-C(1S)	1.181(15)	C(35)-O(8)-H(8A)	109.5
C(1S)-C(3S)	1.472(16)	C(5)-N(1)-C(1)	117.6(4)
C(1S)-C(2S)	1.49(2)	C(5)-N(1)-Pd(1)	115.1(3)
C(2S)-H(2SA)	0.9800	C(1)-N(1)-Pd(1)	127.3(4)
C(2S)-H(2SB)	0.9800	C(8)-N(2)-C(6)	110.8(4)
C(2S)-H(2SC)	0.9800	C(8)-N(2)-Pd(1)	138.5(3)
C(3S)-H(3SA)	0.9800	C(6)-N(2)-Pd(1)	110.7(3)
C(3S)-H(3SB)	0.9800	C(2)-C(1)-N(1)	122.1(5)
C(3S)-H(3SC)	0.9800	C(2)-C(1)-H(1A)	119.0
O(2S)-H(1S)	0.9028	N(1)-C(1)-H(1A)	119.0
O(2S)-H(1S')	0.8499	C(1)-C(2)-C(3)	120.1(6)
N(1)-Pd(1)-N(2)	81.00(17)	C(1)-C(2)-H(2A)	119.9
N(1)-Pd(1)-Br(2)	178.69(17)	C(3)-C(2)-H(2A)	119.9
N(2)-Pd(1)-Br(2)	97.83(11)	C(2)-C(3)-C(4)	119.2(5)
N(1)-Pd(1)-Br(1)	93.70(12)	C(2)-C(3)-H(3A)	120.4

C(4)-C(3)-H(3A)	120.4	O(2)-C(10)-C(11)	108.8(5)
C(5)-C(4)-C(3)	118.6(5)	C(9)-C(10)-C(11)	107.5(5)
C(5)-C(4)-H(4A)	120.7	O(2)-C(10)-H(10A)	110.4
C(3)-C(4)-H(4A)	120.7	C(9)-C(10)-H(10A)	110.4
N(1)-C(5)-C(4)	122.4(5)	C(11)-C(10)-H(10A)	110.4
N(1)-C(5)-C(6)	114.6(4)	O(4)-C(11)-C(10)	109.3(5)
C(4)-C(5)-C(6)	123.0(5)	O(4)-C(11)-C(12)	109.3(5)
C(7)-C(6)-N(2)	114.1(5)	C(10)-C(11)-C(12)	108.3(5)
C(7)-C(6)-C(5)	127.2(5)	O(4)-C(11)-H(11A)	110.0
N(2)-C(6)-C(5)	118.6(4)	C(10)-C(11)-H(11A)	110.0
C(6)-C(7)-S(1)	111.7(4)	C(12)-C(11)-H(11A)	110.0
C(6)-C(7)-H(7)	124.2	O(6)-C(12)-C(13)	110.0(5)
S(1)-C(7)-H(7)	124.2	O(6)-C(12)-C(11)	103.8(5)
N(2)-C(8)-S(1)	113.5(4)	C(13)-C(12)-C(11)	111.1(5)
N(2)-C(8)-S(2)	125.9(4)	O(6)-C(12)-H(12A)	110.6
S(1)-C(8)-S(2)	120.5(3)	C(13)-C(12)-H(12A)	110.6
O(1)-C(9)-C(10)	107.6(5)	C(11)-C(12)-H(12A)	110.6
O(1)-C(9)-S(2)	110.6(4)	O(1)-C(13)-C(12)	106.8(5)
C(10)-C(9)-S(2)	110.7(5)	O(1)-C(13)-C(35)	106.7(5)
O(1)-C(9)-H(9A)	109.3	C(12)-C(13)-C(35)	113.9(6)
C(10)-C(9)-H(9A)	109.3	O(1)-C(13)-H(13A)	109.8
S(2)-C(9)-H(9A)	109.3	C(12)-C(13)-H(13A)	109.8
O(2)-C(10)-C(9)	109.2(5)	C(35)-C(13)-H(13A)	109.8

O(3)-C(14)-O(2)	121.8(6)	O(4)-C(21)-C(22)	110.8(14)
O(3)-C(14)-C(15)	125.4(7)	O(5)-C(21)-C(22')	113.1(15)
O(2)-C(14)-C(15)	112.7(6)	O(4)-C(21)-C(22')	121.3(14)
C(16)-C(15)-C(20)	120.3(10)	C(22)-C(21)-C(22')	16.4(14)
C(16)-C(15)-C(14)	122.6(9)	C(23)-C(22)-C(27)	120.0
C(20)-C(15)-C(14)	117.0(8)	C(23)-C(22)-C(21)	117.8(16)
C(15)-C(16)-C(17)	118.9(11)	C(27)-C(22)-C(21)	122.1(16)
C(15)-C(16)-H(16A)	120.6	C(22)-C(23)-C(24)	120.0
C(17)-C(16)-H(16A)	120.6	C(22)-C(23)-H(23A)	120.0
C(18)-C(17)-C(16)	121.1(10)	C(24)-C(23)-H(23A)	120.0
C(18)-C(17)-H(17A)	119.5	C(25)-C(24)-C(23)	120.0
C(16)-C(17)-H(17A)	119.5	C(25)-C(24)-H(24A)	120.0
C(19)-C(18)-C(17)	119.0(12)	C(23)-C(24)-H(24A)	120.0
C(19)-C(18)-H(18A)	120.5	C(24)-C(25)-C(26)	120.0
C(17)-C(18)-H(18A)	120.5	C(24)-C(25)-H(25A)	120.0
C(18)-C(19)-C(20)	121.0(13)	C(26)-C(25)-H(25A)	120.0
C(18)-C(19)-H(19A)	119.5	C(25)-C(26)-C(27)	120.0
C(20)-C(19)-H(19A)	119.5	C(25)-C(26)-H(26A)	120.0
C(19)-C(20)-C(15)	119.7(10)	C(27)-C(26)-H(26A)	120.0
C(19)-C(20)-H(20A)	120.2	C(26)-C(27)-C(22)	120.0
C(15)-C(20)-H(20A)	120.2	C(26)-C(27)-H(27A)	120.0
O(5)-C(21)-O(4)	125.2(7)	C(22)-C(27)-H(27A)	120.0
O(5)-C(21)-C(22)	123.6(16)	C(23')-C(22')-C(27')	120.0

C(23')-C(22')-C(21)	124.5(16)	C(31)-C(30)-C(29)	121.8(9)
C(27')-C(22')-C(21)	115.3(16)	C(31)-C(30)-H(30A)	119.1
C(22')-C(23')-C(24')	120.0	C(29)-C(30)-H(30A)	119.1
C(22')-C(23')-H(23B)	120.0	C(32)-C(31)-C(30)	119.7(8)
C(24')-C(23')-H(23B)	120.0	C(32)-C(31)-H(31A)	120.2
C(25')-C(24')-C(23')	120.0	C(30)-C(31)-H(31A)	120.2
C(25')-C(24')-H(24B)	120.0	C(31)-C(32)-C(33)	120.6(10)
C(23')-C(24')-H(24B)	120.0	C(31)-C(32)-H(32A)	119.7
C(24')-C(25')-C(26')	120.0	C(33)-C(32)-H(32A)	119.7
C(24')-C(25')-H(25B)	120.0	C(32)-C(33)-C(34)	119.8(11)
C(26')-C(25')-H(25B)	120.0	C(32)-C(33)-H(33A)	120.1
C(25')-C(26')-C(27')	120.0	C(34)-C(33)-H(33A)	120.1
C(25')-C(26')-H(26B)	120.0	C(29)-C(34)-C(33)	119.3(8)
C(27')-C(26')-H(26B)	120.0	C(29)-C(34)-H(34A)	120.3
C(26')-C(27')-C(22')	120.0	C(33)-C(34)-H(34A)	120.3
C(26')-C(27')-H(27B)	120.0	O(8)-C(35)-C(13)	110.9(6)
C(22')-C(27')-H(27B)	120.0	O(8)-C(35)-H(35A)	109.5
O(7)-C(28)-O(6)	121.8(9)	C(13)-C(35)-H(35A)	109.5
O(7)-C(28)-C(29)	125.7(9)	O(8)-C(35)-H(35B)	109.5
O(6)-C(28)-C(29)	112.5(7)	C(13)-C(35)-H(35B)	109.5
C(34)-C(29)-C(30)	118.8(7)	H(35A)-C(35)-H(35B)	108.1
C(34)-C(29)-C(28)	122.5(7)	O(1S)-C(1S)-C(3S)	113.0(13)
C(30)-C(29)-C(28)	118.7(8)	O(1S)-C(1S)-C(2S)	132.3(16)

C(3S)-C(1S)-C(2S)	114.4(14)	C(1S)-C(3S)-H(3SA)	109.5
C(1S)-C(2S)-H(2SA)	109.5	C(1S)-C(3S)-H(3SB)	109.5
C(1S)-C(2S)-H(2SB)	109.5	H(3SA)-C(3S)-H(3SB)	109.5
H(2SA)-C(2S)-H(2SB)	109.5	C(1S)-C(3S)-H(3SC)	109.5
C(1S)-C(2S)-H(2SC)	109.5	H(3SA)-C(3S)-H(3SC)	109.5
H(2SA)-C(2S)-H(2SC)	109.5	H(3SB)-C(3S)-H(3SC)	109.5
H(2SB)-C(2S)-H(2SC)	109.5	H(1S)-O(2S)-H(1S')	101.2

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for complex **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	18(1)	14(1)	20(1)	-2(1)	5(1)	-1(1)
Br(1)	27(1)	38(1)	23(1)	0(1)	5(1)	-2(1)
Br(2)	19(1)	36(1)	24(1)	-3(1)	5(1)	-1(1)
S(1)	18(1)	24(1)	31(1)	-1(2)	1(1)	2(2)
S(2)	20(1)	21(1)	20(1)	3(1)	2(1)	-3(2)
O(1)	35(3)	24(4)	23(2)	0(2)	2(2)	10(2)
O(2)	19(3)	22(2)	25(3)	3(2)	8(2)	-3(2)
O(3)	29(3)	32(4)	84(4)	20(3)	13(3)	-8(2)
O(4)	26(3)	54(4)	21(3)	6(3)	10(2)	-4(3)
O(5)	171(9)	34(4)	93(6)	-13(4)	100(7)	2(5)
O(6)	24(3)	33(3)	18(3)	3(2)	-2(2)	7(2)
O(7)	165(7)	32(5)	24(3)	11(3)	-10(4)	16(4)
O(8)	34(3)	44(3)	35(3)	-11(2)	-2(3)	14(2)
N(1)	32(3)	13(2)	26(3)	0(5)	17(2)	3(5)
N(2)	21(2)	8(2)	24(3)	-5(5)	8(2)	-4(5)
C(1)	41(4)	11(3)	35(3)	-1(6)	19(3)	2(6)
C(2)	51(4)	11(3)	43(4)	8(5)	33(4)	4(6)
C(3)	48(4)	20(3)	68(5)	-5(7)	44(4)	-1(7)

C(4)	25(3)	18(3)	44(4)	0(6)	16(3)	1(6)
C(5)	25(3)	6(2)	39(3)	-2(6)	16(3)	3(6)
C(6)	16(3)	12(2)	34(3)	1(6)	10(3)	8(5)
C(7)	17(3)	16(3)	45(4)	-6(6)	10(3)	-3(6)
C(8)	17(3)	11(2)	24(3)	-6(5)	-1(2)	-2(6)
C(9)	27(4)	21(3)	18(4)	1(3)	-1(4)	5(3)
C(10)	12(4)	26(3)	24(4)	8(3)	7(3)	1(3)
C(11)	25(4)	25(4)	20(4)	0(3)	8(3)	-2(3)
C(12)	21(4)	34(4)	14(4)	-4(3)	-2(3)	-3(3)
C(13)	29(4)	27(6)	18(3)	0(3)	-2(3)	11(3)
C(14)	18(4)	34(4)	35(4)	-2(3)	9(4)	0(3)
C(15)	10(4)	29(5)	21(5)	0(4)	0(4)	0(4)
C(16)	21(5)	38(5)	33(5)	8(3)	9(4)	4(3)
C(17)	45(7)	42(5)	34(5)	4(4)	23(5)	8(5)
C(18)	40(7)	61(8)	31(6)	15(5)	15(6)	26(6)
C(19)	18(5)	56(7)	68(8)	-11(5)	0(5)	14(4)
C(20)	30(6)	32(5)	73(7)	-6(5)	12(5)	-9(4)
C(21)	52(5)	71(6)	35(4)	1(9)	27(4)	17(9)
C(22)	160(11)	76(14)	114(10)	51(9)	123(10)	62(9)
C(23)	261(15)	78(12)	133(12)	41(9)	165(12)	92(11)
C(24)	312(19)	147(17)	185(16)	69(13)	204(14)	135(15)
C(25)	241(17)	184(18)	181(15)	107(12)	198(14)	107(14)
C(26)	222(16)	256(19)	181(16)	109(14)	175(13)	146(15)

C(27)	150(13)	176(15)	143(13)	111(10)	135(11)	148(11)
C(22')	160(11)	76(14)	114(10)	51(9)	123(10)	62(9)
C(23')	261(15)	78(12)	133(12)	41(9)	165(12)	92(11)
C(24')	312(19)	147(17)	185(16)	69(13)	204(14)	135(15)
C(25')	241(17)	184(18)	181(15)	107(12)	198(14)	107(14)
C(26')	222(16)	256(19)	181(16)	109(14)	175(13)	146(15)
C(27')	150(13)	176(15)	143(13)	111(10)	135(11)	148(11)
C(28)	47(6)	38(5)	36(5)	5(4)	0(4)	11(4)
C(29)	30(4)	44(5)	19(4)	-6(3)	1(4)	-1(4)
C(30)	107(9)	49(6)	26(5)	-7(4)	-17(5)	12(6)
C(31)	80(8)	71(7)	25(5)	11(5)	-11(5)	8(6)
C(32)	55(5)	74(7)	20(4)	-3(7)	-1(4)	-38(8)
C(33)	177(13)	51(6)	41(7)	-1(5)	-7(8)	-44(7)
C(34)	79(6)	33(6)	25(4)	1(4)	-2(4)	-14(5)
C(35)	37(5)	47(5)	28(5)	-2(4)	-4(4)	18(4)
O(1S)	44(4)	81(5)	69(5)	-17(4)	29(4)	-17(3)
C(1S)	142(14)	138(13)	49(7)	-11(7)	45(9)	-22(11)
C(2S)	220(14)	228(16)	319(18)	70(15)	198(15)	-56(14)
C(3S)	220(14)	228(16)	319(18)	70(15)	198(15)	-56(14)
O(2S)	62(3)	64(5)	56(3)	-14(4)	8(3)	-20(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for complex **6**.

	x	y	z	U(eq)
H(8A)	-862	2970	2840	68
H(1A)	-3250	5750	-1290	35
H(2A)	-2538	5960	-1560	37
H(3A)	-1562	5874	-872	46
H(4A)	-1312	5796	109	35
H(7)	-1157	5779	1036	33
H(9A)	-2104	7969	2166	32
H(10A)	-2794	6157	2628	26
H(11A)	-2026	9605	3003	29
H(12A)	-1844	5725	3560	33
H(13A)	-1236	7365	2989	36
H(16A)	-3572	12034	1847	38
H(17A)	-4284	14161	1177	46
H(18A)	-5160	12860	460	54
H(19A)	-5358	9494	469	67
H(20A)	-4673	7368	1141	60
H(23A)	-2387	13990	4159	154

H(24A)	-2725	14551	4820	216
H(25A)	-3214	11998	5023	194
H(26A)	-3364	8885	4566	224
H(27A)	-3026	8324	3906	156
H(23B)	-2331	14180	4211	154
H(24B)	-2935	15281	4580	216
H(25B)	-3735	13341	4452	194
H(26B)	-3931	10299	3953	224
H(27B)	-3327	9197	3584	156
H(30A)	-351	6361	5518	97
H(31A)	93	8424	6309	88
H(32A)	-11	11774	6204	69
H(33A)	-555	13168	5308	137
H(34A)	-1017	11053	4489	68
H(35A)	-655	5077	3748	55
H(35B)	-1145	3393	3443	55
H(2SA)	261	10640	2685	341
H(2SB)	294	9758	2141	341
H(2SC)	802	9276	2775	341
H(3SA)	1	4683	2389	341
H(3SB)	640	5568	2593	341
H(3SC)	129	5979	1954	341
H(1S)	-908	772	2456	103

H(1S')	-1344	-599	2234	103

Table 6. Torsion angles [°] for complex **6**.

N(2)-Pd(1)-N(1)-C(5)	0.3(7)
Br(2)-Pd(1)-N(1)-C(5)	27(11)
Br(1)-Pd(1)-N(1)-C(5)	-179.5(7)
N(2)-Pd(1)-N(1)-C(1)	-178.0(10)
Br(2)-Pd(1)-N(1)-C(1)	-152(10)
Br(1)-Pd(1)-N(1)-C(1)	2.2(9)
N(1)-Pd(1)-N(2)-C(8)	-179.0(12)
Br(2)-Pd(1)-N(2)-C(8)	1.6(12)
Br(1)-Pd(1)-N(2)-C(8)	-177(2)
N(1)-Pd(1)-N(2)-C(6)	-1.7(7)
Br(2)-Pd(1)-N(2)-C(6)	178.8(7)
Br(1)-Pd(1)-N(2)-C(6)	1(3)
C(5)-N(1)-C(1)-C(2)	-1.8(16)
Pd(1)-N(1)-C(1)-C(2)	176.5(8)
N(1)-C(1)-C(2)-C(3)	2.7(16)
C(1)-C(2)-C(3)-C(4)	-2.0(17)
C(2)-C(3)-C(4)-C(5)	0.5(19)
C(1)-N(1)-C(5)-C(4)	0.2(17)
Pd(1)-N(1)-C(5)-C(4)	-178.3(9)
C(1)-N(1)-C(5)-C(6)	179.7(9)
Pd(1)-N(1)-C(5)-C(6)	1.3(12)

C(3)-C(4)-C(5)-N(1)	0.4(18)
C(3)-C(4)-C(5)-C(6)	-179.1(10)
C(8)-N(2)-C(6)-C(7)	-2.1(13)
Pd(1)-N(2)-C(6)-C(7)	179.8(8)
C(8)-N(2)-C(6)-C(5)	-178.9(10)
Pd(1)-N(2)-C(6)-C(5)	3.0(12)
N(1)-C(5)-C(6)-C(7)	-179.2(10)
C(4)-C(5)-C(6)-C(7)	0(2)
N(1)-C(5)-C(6)-N(2)	-2.9(15)
C(4)-C(5)-C(6)-N(2)	176.6(10)
N(2)-C(6)-C(7)-S(1)	3.2(13)
C(5)-C(6)-C(7)-S(1)	179.7(9)
C(8)-S(1)-C(7)-C(6)	-2.6(9)
C(6)-N(2)-C(8)-S(1)	0.1(12)
Pd(1)-N(2)-C(8)-S(1)	177.4(7)
C(6)-N(2)-C(8)-S(2)	-176.5(8)
Pd(1)-N(2)-C(8)-S(2)	0.7(18)
C(7)-S(1)-C(8)-N(2)	1.4(10)
C(7)-S(1)-C(8)-S(2)	178.2(7)
C(9)-S(2)-C(8)-N(2)	-158.2(10)
C(9)-S(2)-C(8)-S(1)	25.4(7)
C(13)-O(1)-C(9)-C(10)	-67.8(7)
C(13)-O(1)-C(9)-S(2)	171.2(4)

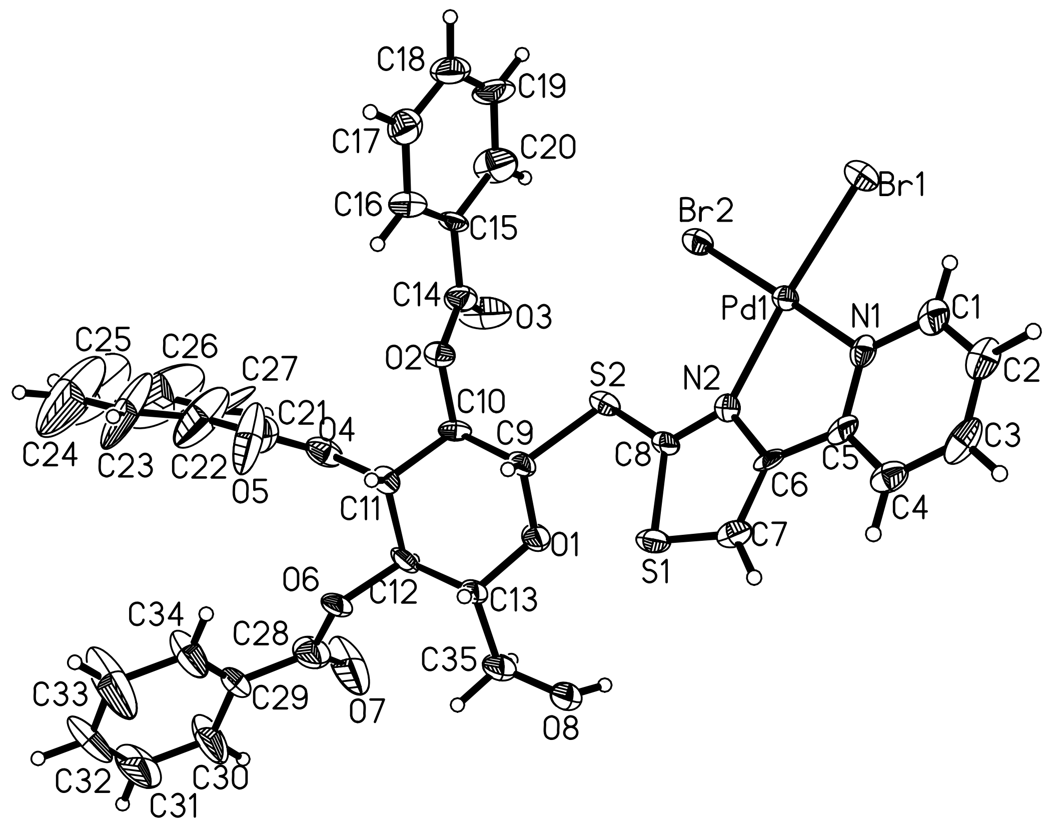
C(8)-S(2)-C(9)-O(1)	-74.6(6)
C(8)-S(2)-C(9)-C(10)	166.3(5)
C(14)-O(2)-C(10)-C(9)	106.9(6)
C(14)-O(2)-C(10)-C(11)	-136.0(6)
O(1)-C(9)-C(10)-O(2)	-178.0(5)
S(2)-C(9)-C(10)-O(2)	-57.0(6)
O(1)-C(9)-C(10)-C(11)	64.1(6)
S(2)-C(9)-C(10)-C(11)	-175.0(4)
C(21)-O(4)-C(11)-C(10)	-123.6(6)
C(21)-O(4)-C(11)-C(12)	118.0(6)
O(2)-C(10)-C(11)-O(4)	64.0(6)
C(9)-C(10)-C(11)-O(4)	-177.8(5)
O(2)-C(10)-C(11)-C(12)	-177.0(5)
C(9)-C(10)-C(11)-C(12)	-58.9(7)
C(28)-O(6)-C(12)-C(13)	-105.3(7)
C(28)-O(6)-C(12)-C(11)	135.8(6)
O(4)-C(11)-C(12)-O(6)	-65.6(6)
C(10)-C(11)-C(12)-O(6)	175.5(5)
O(4)-C(11)-C(12)-C(13)	176.3(5)
C(10)-C(11)-C(12)-C(13)	57.3(7)
C(9)-O(1)-C(13)-C(12)	63.4(7)
C(9)-O(1)-C(13)-C(35)	-174.4(6)
O(6)-C(12)-C(13)-O(1)	-171.5(5)

C(11)-C(12)-C(13)-O(1)	-57.1(7)
O(6)-C(12)-C(13)-C(35)	71.1(7)
C(11)-C(12)-C(13)-C(35)	-174.6(6)
C(10)-O(2)-C(14)-O(3)	6.0(9)
C(10)-O(2)-C(14)-C(15)	-171.9(6)
O(3)-C(14)-C(15)-C(16)	162.8(10)
O(2)-C(14)-C(15)-C(16)	-19.5(13)
O(3)-C(14)-C(15)-C(20)	-18.9(13)
O(2)-C(14)-C(15)-C(20)	158.8(8)
C(20)-C(15)-C(16)-C(17)	0.2(17)
C(14)-C(15)-C(16)-C(17)	178.4(7)
C(15)-C(16)-C(17)-C(18)	-2.1(16)
C(16)-C(17)-C(18)-C(19)	3.0(17)
C(17)-C(18)-C(19)-C(20)	-2(2)
C(18)-C(19)-C(20)-C(15)	0.3(19)
C(16)-C(15)-C(20)-C(19)	0.7(17)
C(14)-C(15)-C(20)-C(19)	-177.6(9)
C(11)-O(4)-C(21)-O(5)	1.1(11)
C(11)-O(4)-C(21)-C(22)	-172.0(11)
C(11)-O(4)-C(21)-C(22')	173.9(11)
O(5)-C(21)-C(22)-C(23)	-4.6(17)
O(4)-C(21)-C(22)-C(23)	168.7(8)
C(22')-C(21)-C(22)-C(23)	-59(6)

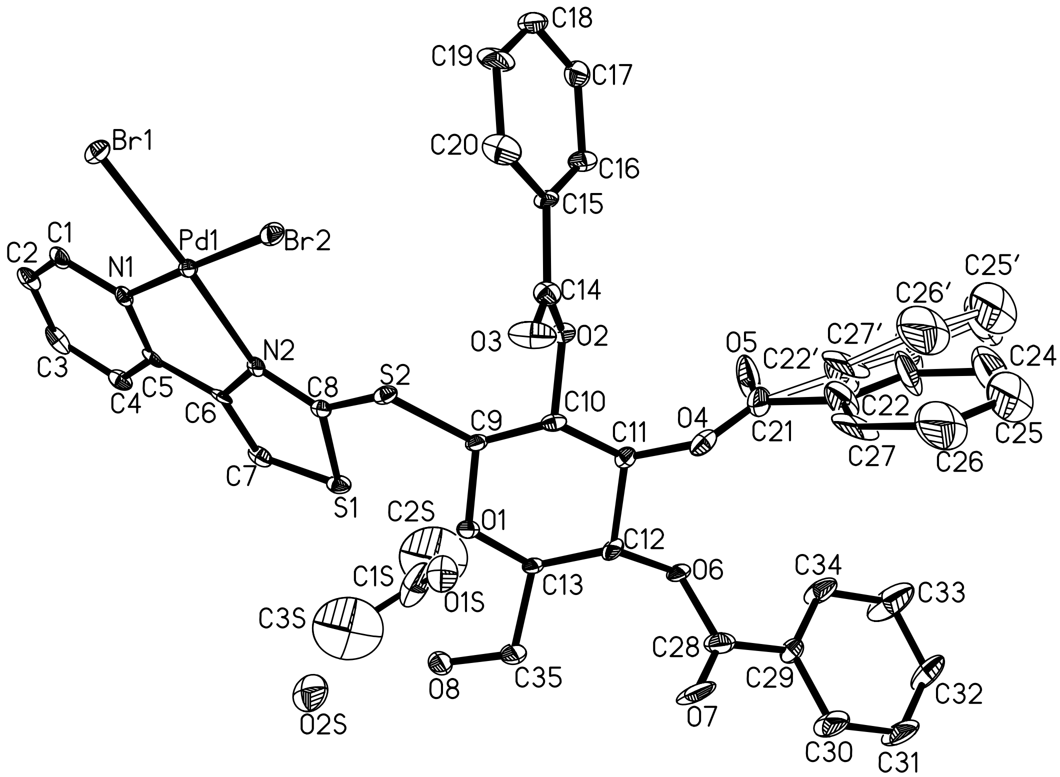
O(5)-C(21)-C(22)-C(27)	176.5(11)
O(4)-C(21)-C(22)-C(27)	-10.2(18)
C(22')-C(21)-C(22)-C(27)	122(7)
C(27)-C(22)-C(23)-C(24)	0.0
C(21)-C(22)-C(23)-C(24)	-179.0(18)
C(22)-C(23)-C(24)-C(25)	0.0
C(23)-C(24)-C(25)-C(26)	0.0
C(24)-C(25)-C(26)-C(27)	0.0
C(25)-C(26)-C(27)-C(22)	0.0
C(23)-C(22)-C(27)-C(26)	0.0
C(21)-C(22)-C(27)-C(26)	178.9(19)
O(5)-C(21)-C(22')-C(23')	-24.3(14)
O(4)-C(21)-C(22')-C(23')	162.2(8)
C(22)-C(21)-C(22')-C(23')	108(7)
O(5)-C(21)-C(22')-C(27')	150.8(11)
O(4)-C(21)-C(22')-C(27')	-22.7(17)
C(22)-C(21)-C(22')-C(27')	-77(6)
C(27')-C(22')-C(23')-C(24')	0.0
C(21)-C(22')-C(23')-C(24')	174.8(17)
C(22')-C(23')-C(24')-C(25')	0.0
C(23')-C(24')-C(25')-C(26')	0.0
C(24')-C(25')-C(26')-C(27')	0.0
C(25')-C(26')-C(27')-C(22')	0.0

C(23')-C(22')-C(27')-C(26')	0.0
C(21)-C(22')-C(27')-C(26')	-175.3(15)
C(12)-O(6)-C(28)-O(7)	12.2(14)
C(12)-O(6)-C(28)-C(29)	-167.8(6)
O(7)-C(28)-C(29)-C(34)	-165.7(11)
O(6)-C(28)-C(29)-C(34)	14.3(12)
O(7)-C(28)-C(29)-C(30)	11.1(16)
O(6)-C(28)-C(29)-C(30)	-168.9(8)
C(34)-C(29)-C(30)-C(31)	1.7(16)
C(28)-C(29)-C(30)-C(31)	-175.2(10)
C(29)-C(30)-C(31)-C(32)	-0.7(18)
C(30)-C(31)-C(32)-C(33)	-0.3(18)
C(31)-C(32)-C(33)-C(34)	0.5(19)
C(30)-C(29)-C(34)-C(33)	-1.5(15)
C(28)-C(29)-C(34)-C(33)	175.2(10)
C(32)-C(33)-C(34)-C(29)	0.5(18)
O(1)-C(13)-C(35)-O(8)	63.6(8)
C(12)-C(13)-C(35)-O(8)	-178.8(6)

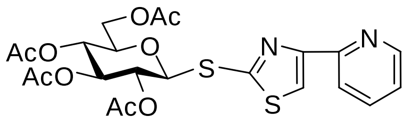
Projection view of the molecule with 50% thermal ellipsoids- disorder and solvents not shown:



Projection view of the molecule with 50% thermal ellipsoids:



Copies of NMR spectra



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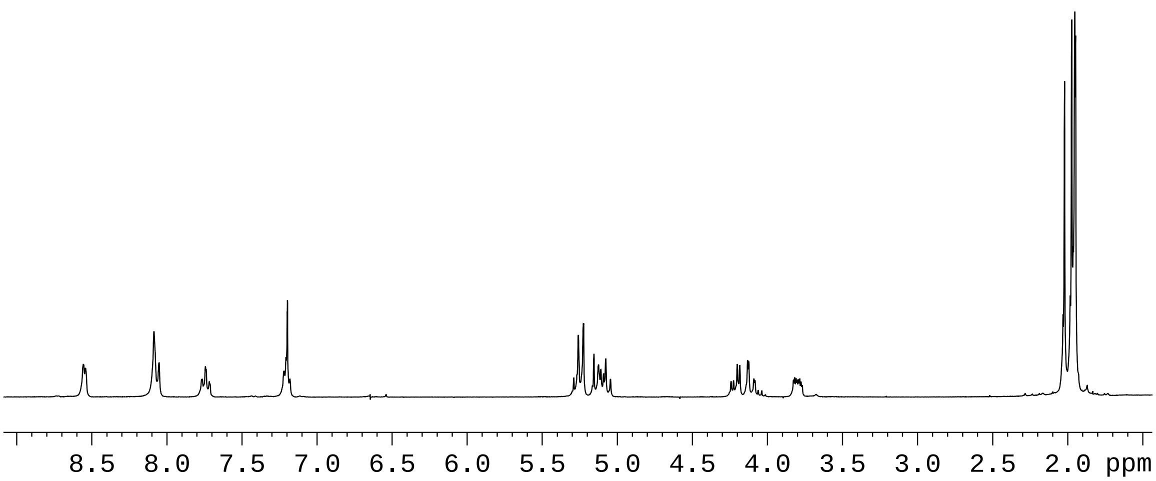

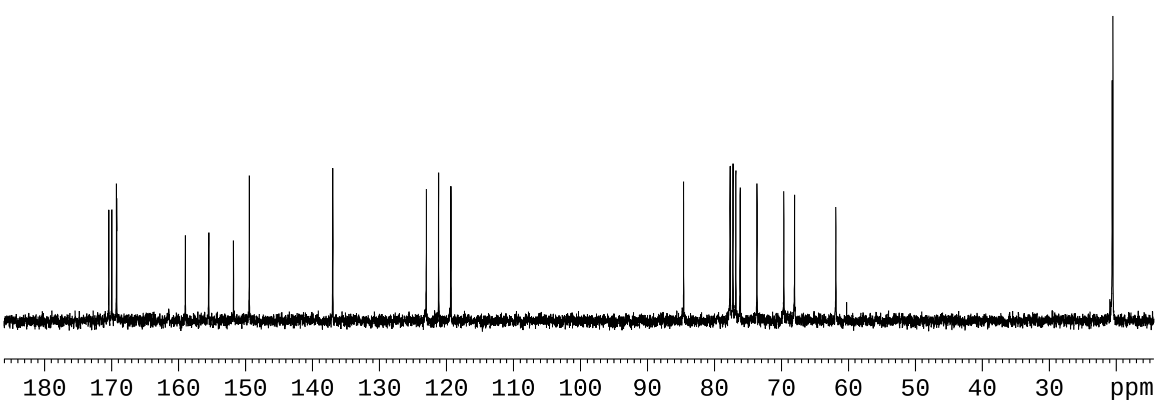

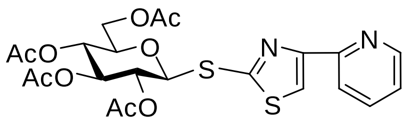

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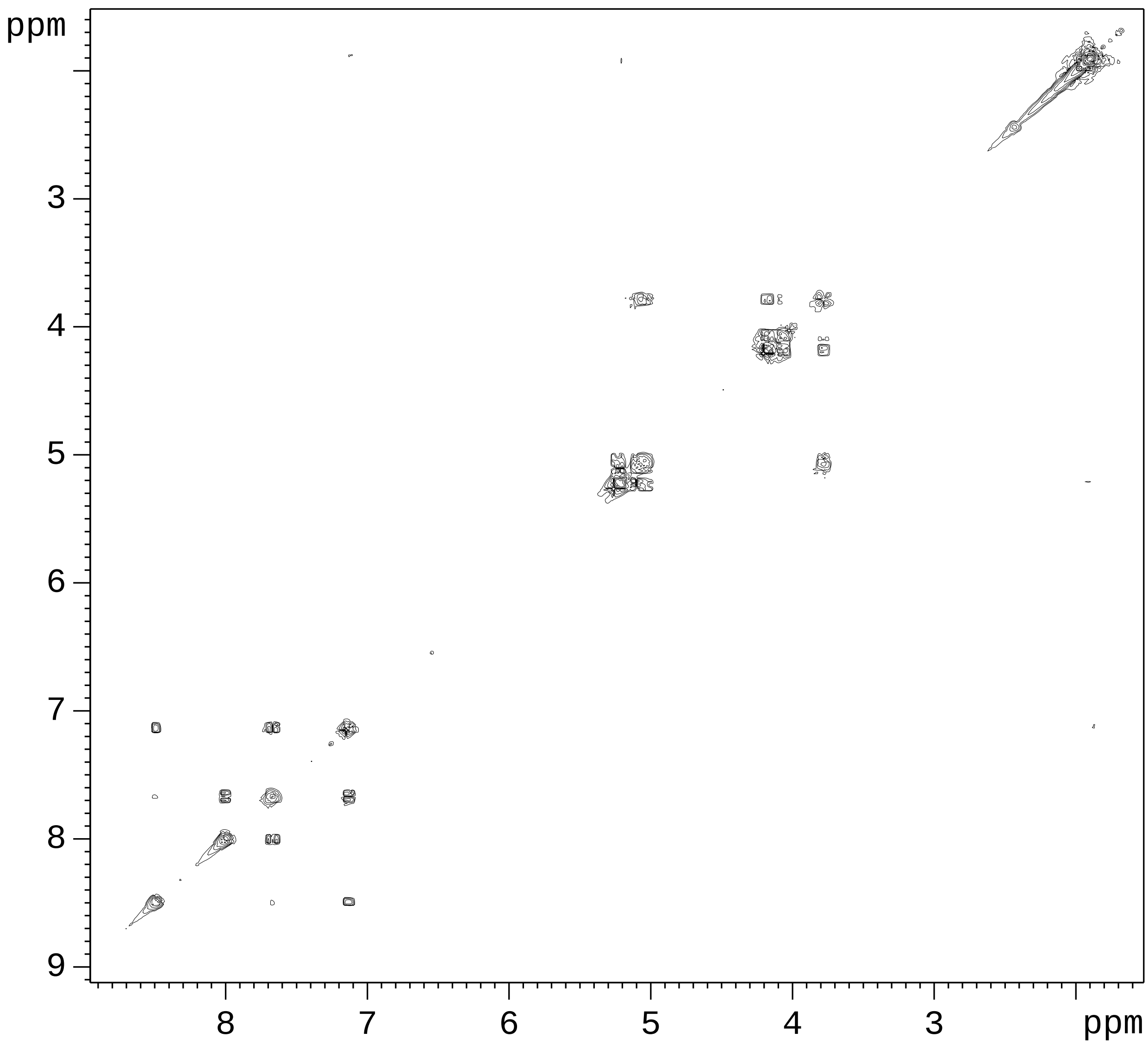

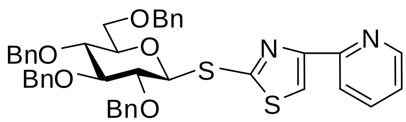

OBn
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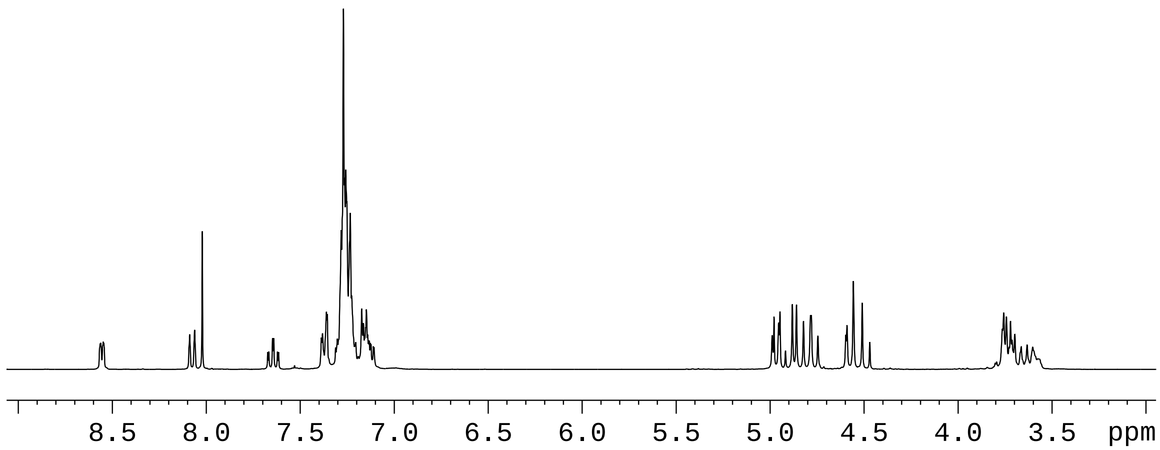
BnO
BnO
O
S
N
S
N

4



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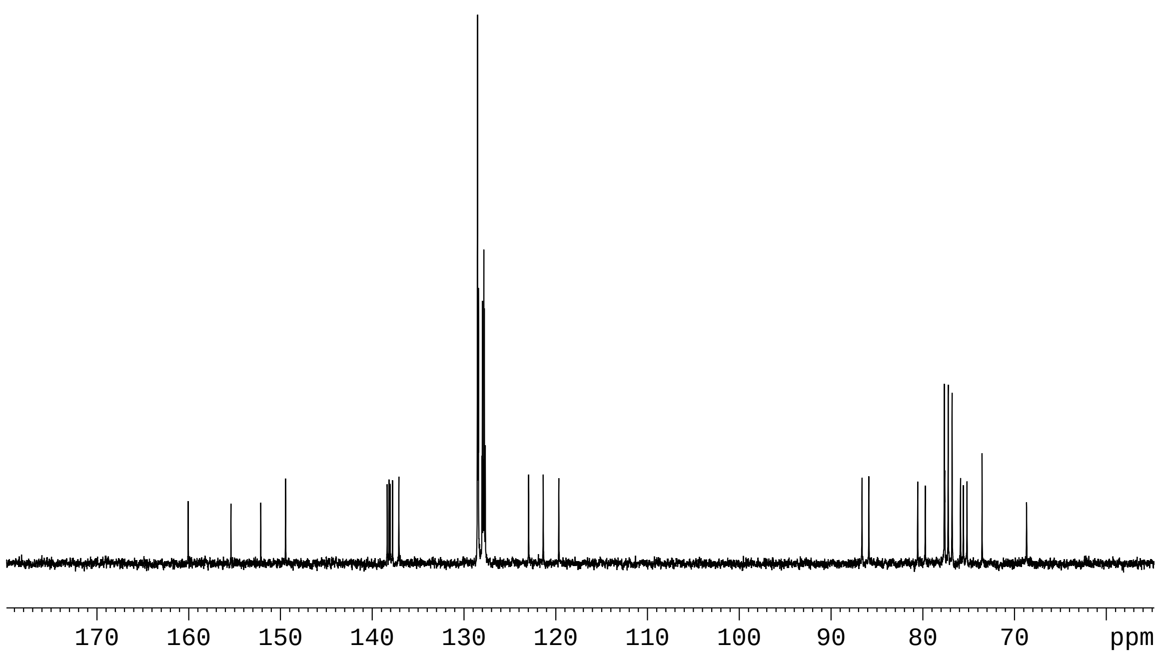

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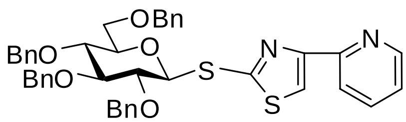
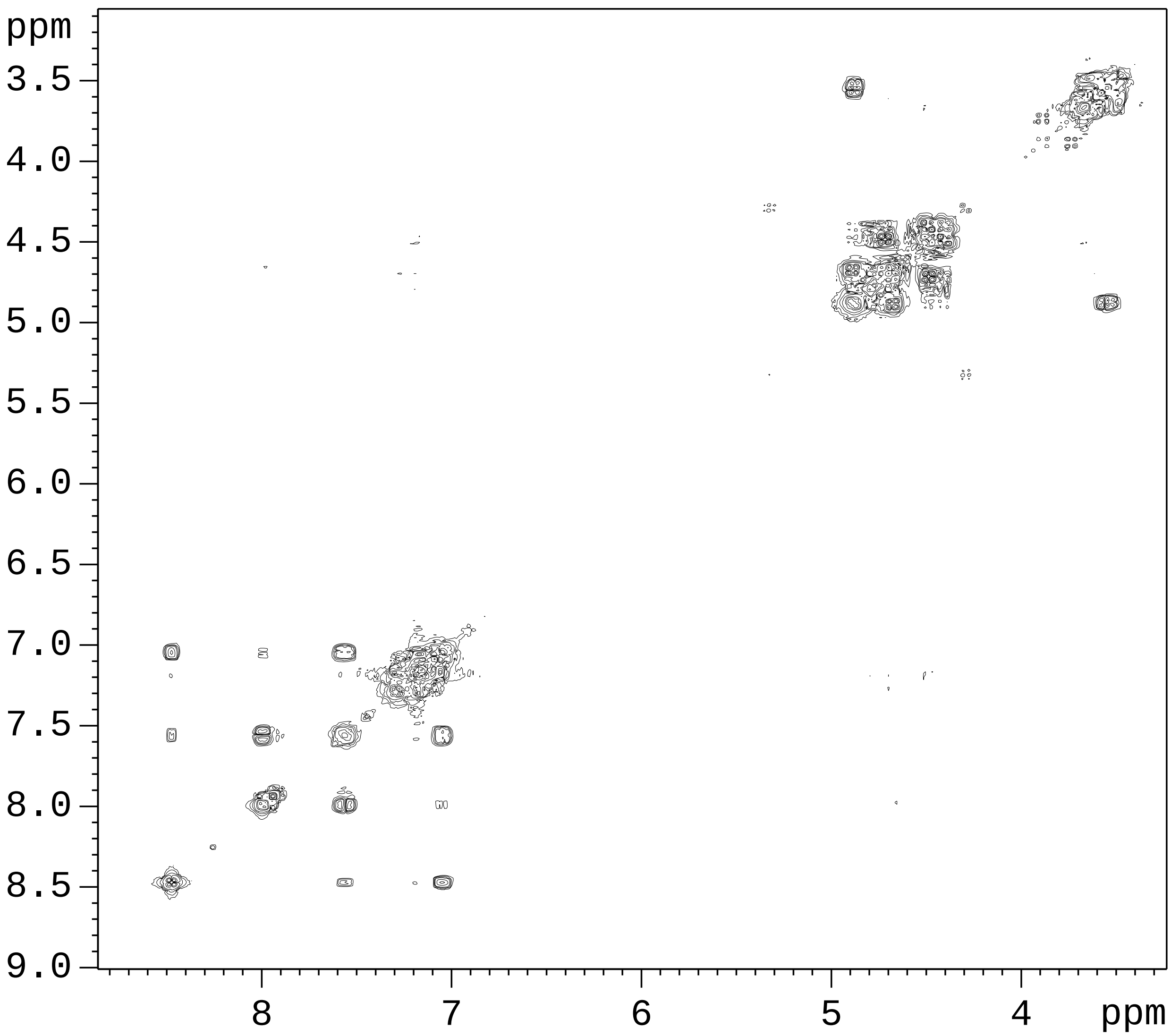

OBn
BnO
BnO
BnO
O
S
N
S
N

4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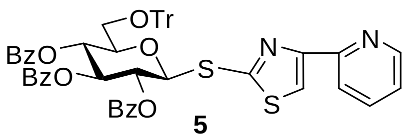
6.5
7.0
7.5
8.0
8.5
9.0
8
7
6
5
4
ppm



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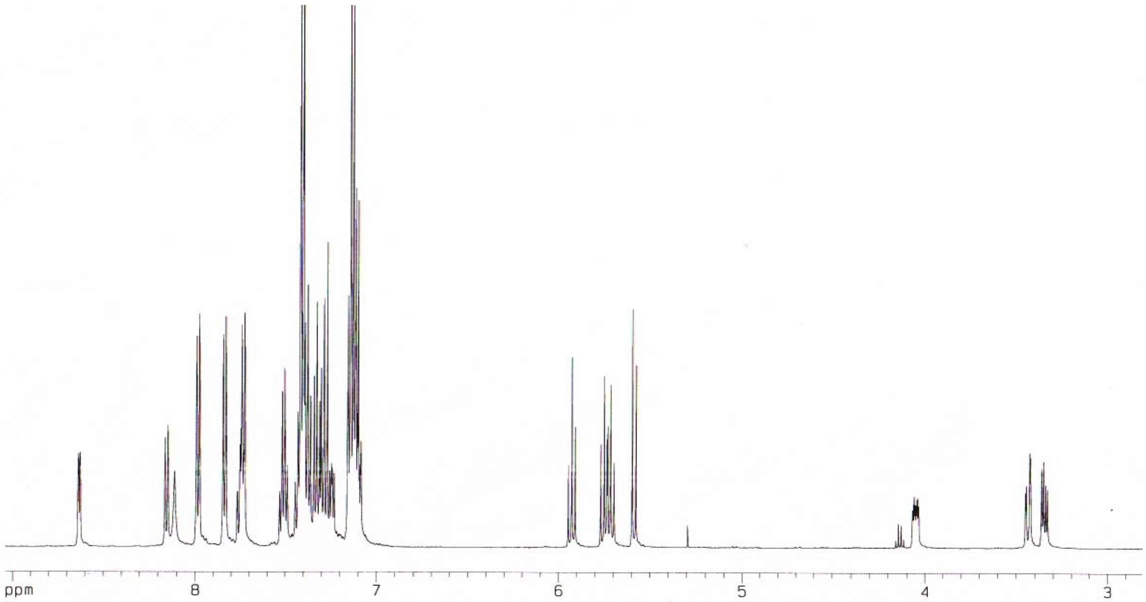

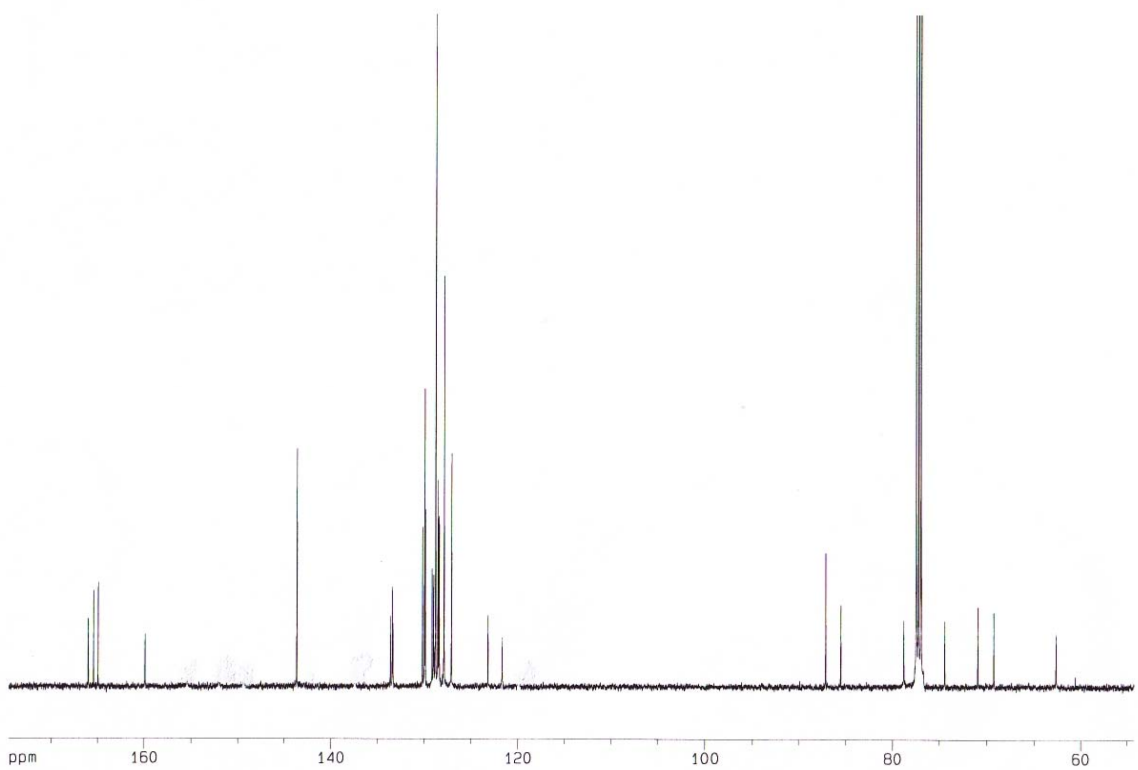

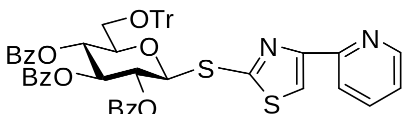
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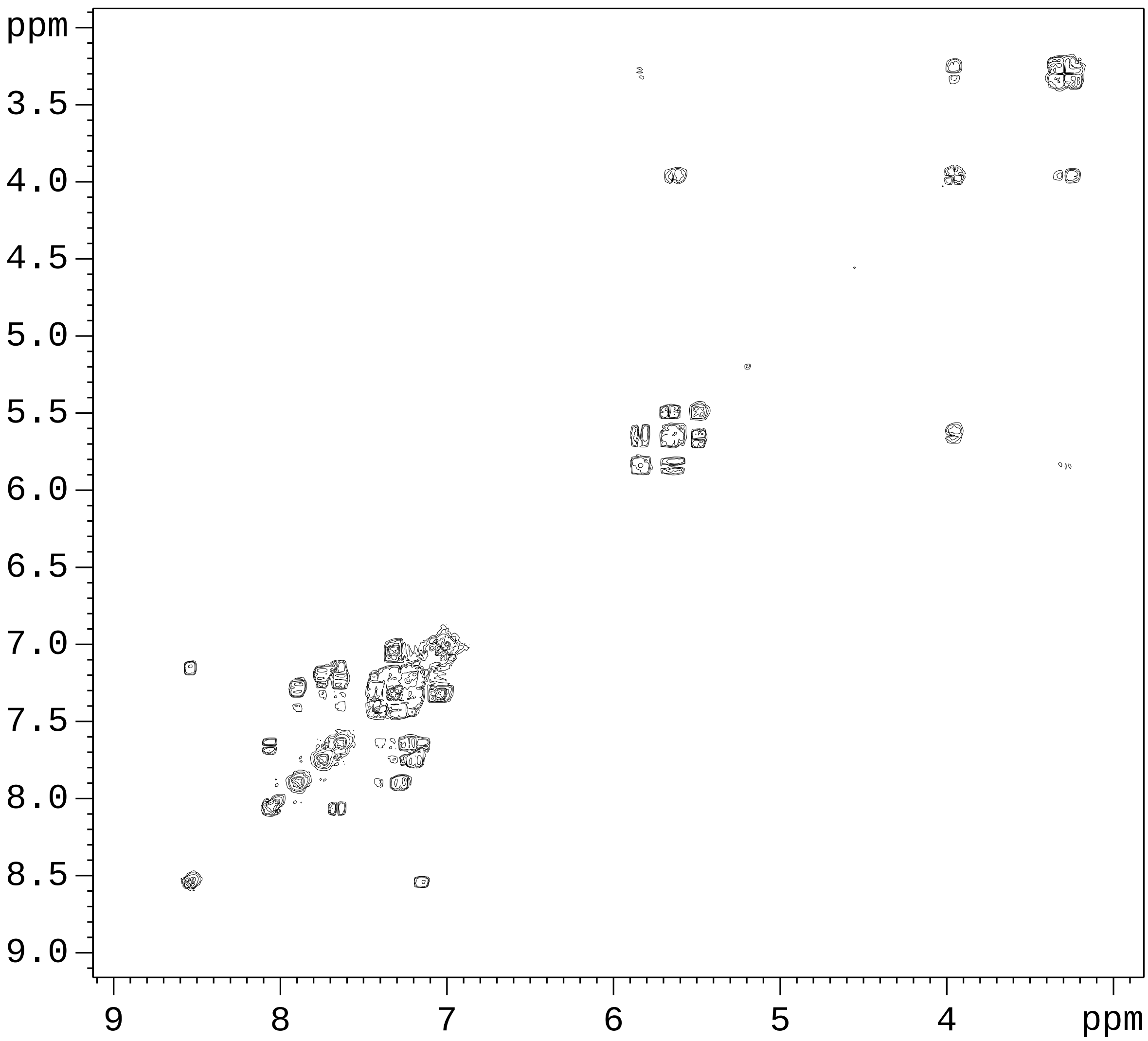
BzO
BzO
BzO
O
S
N
S
N

5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7.0
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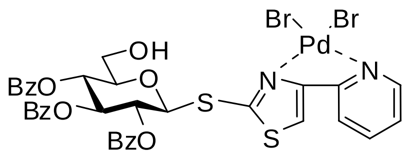
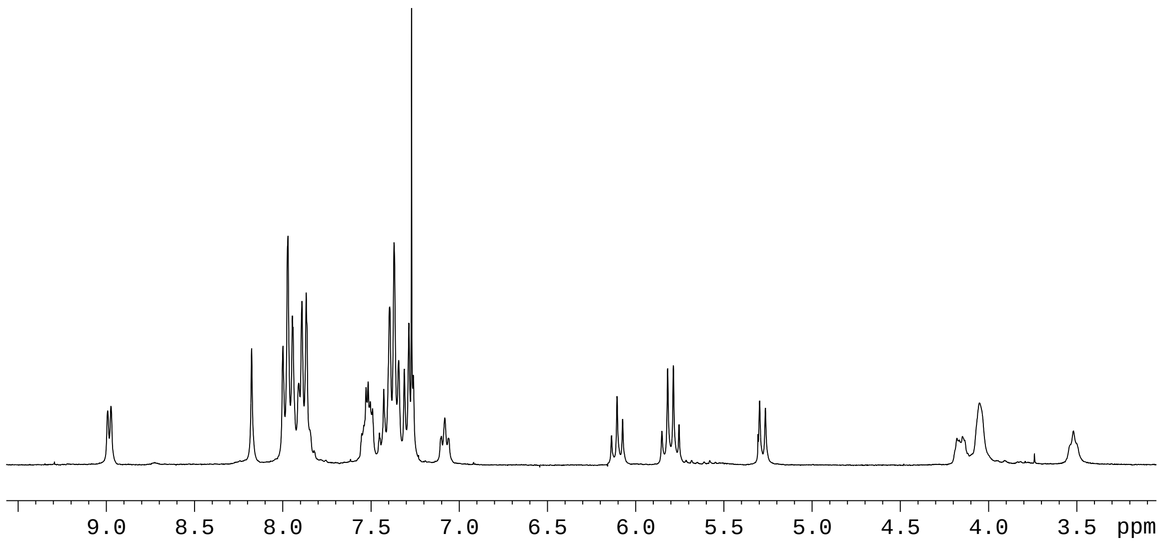
8.0
8.5
9.0
9
8
7
6
5
4
ppm


Br
Br
Pd
N
N
OH
O
BzO
BzO
BzO
S
S

6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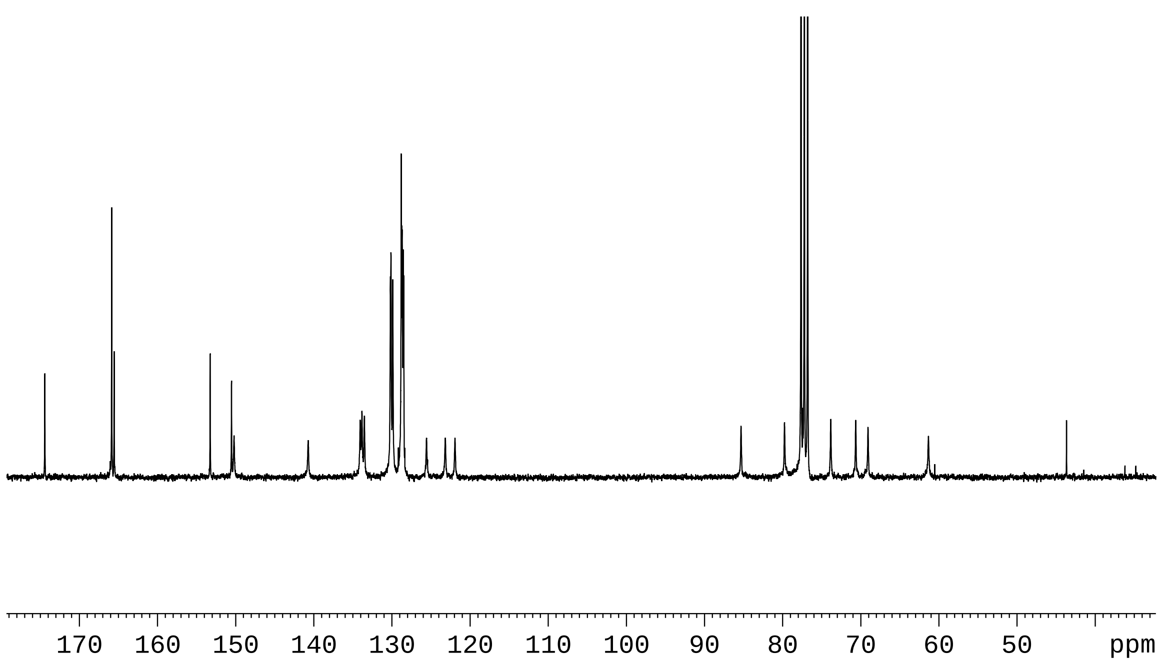
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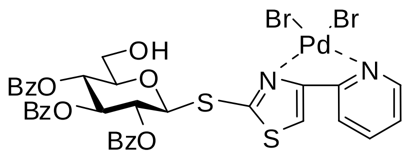
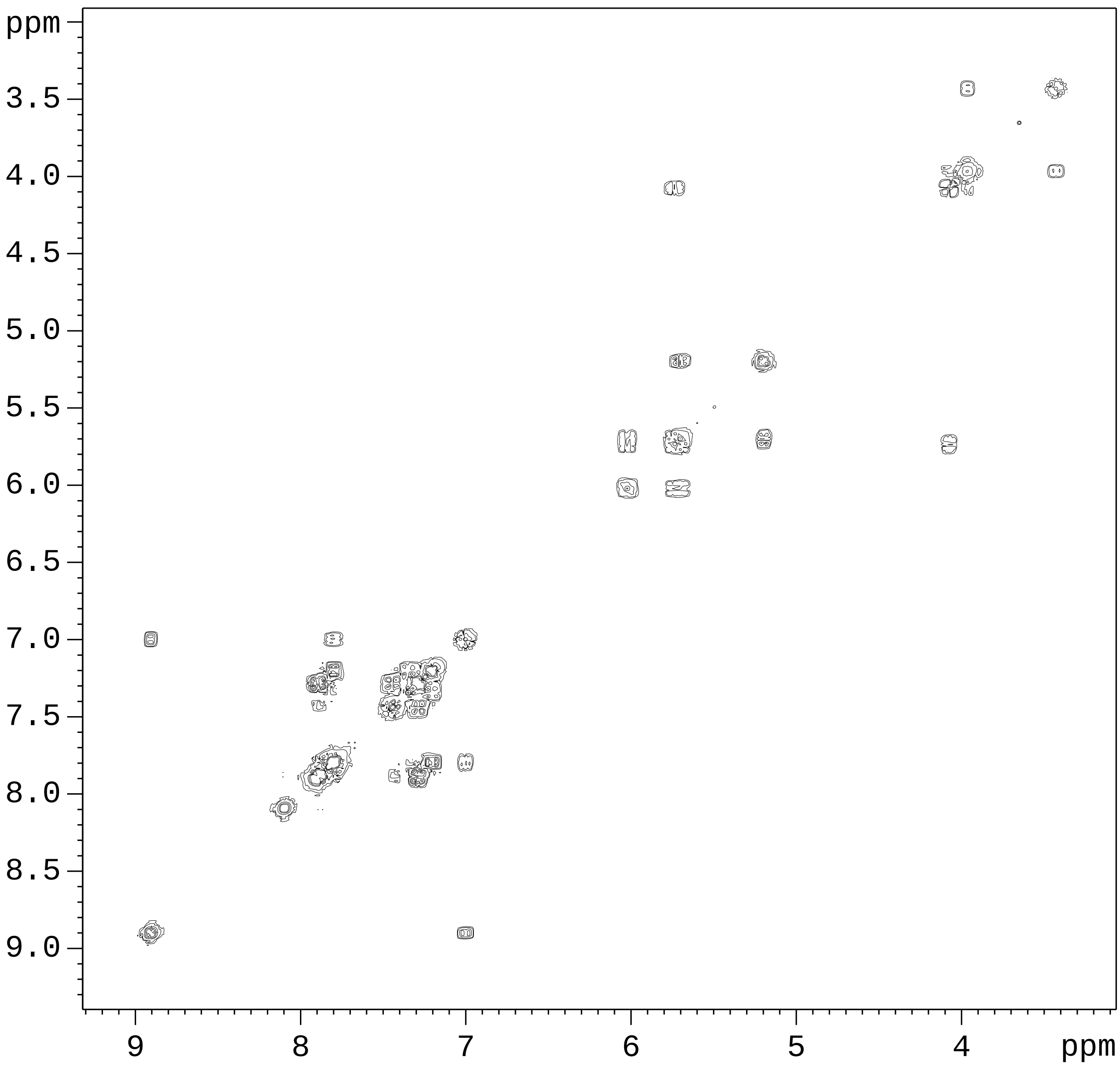

Br
Br
Pd
N
N
OH
O
BzO
BzO
BzO
S
S

6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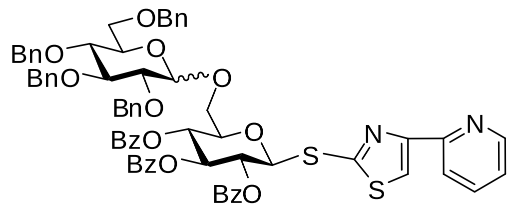
7.0
7.5
8.0
8.5
9.0
9
8
7
6
5
4
ppm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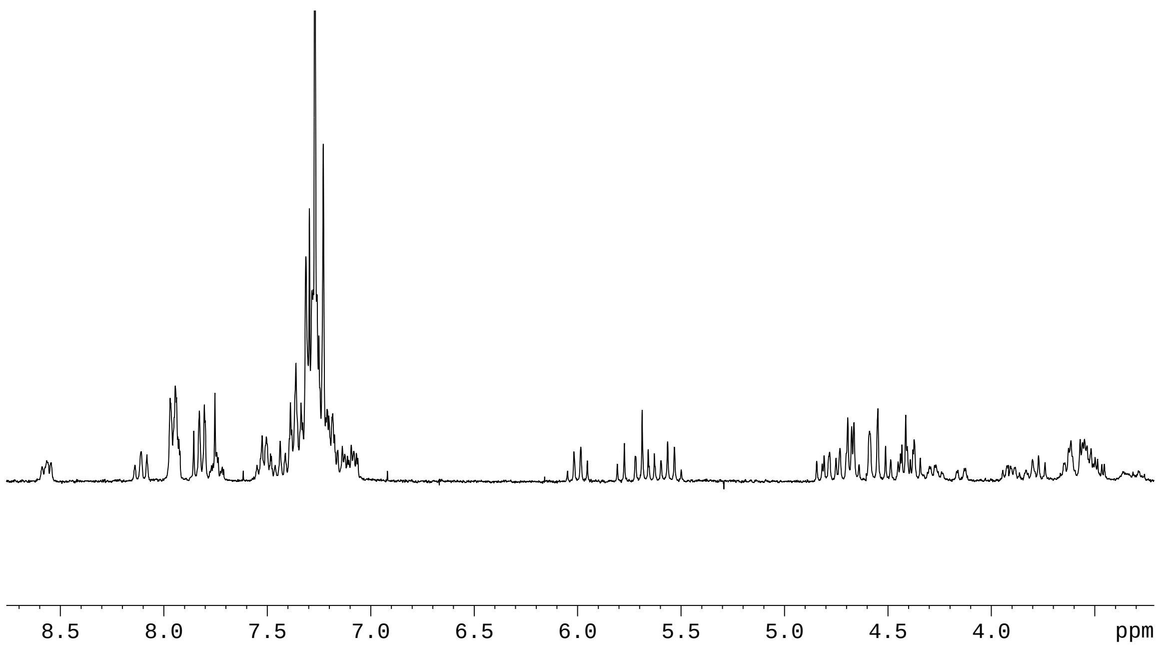
BnO
BnO
O
O
BnO
BzO
BzO
O
S
N
N
S
BzO

7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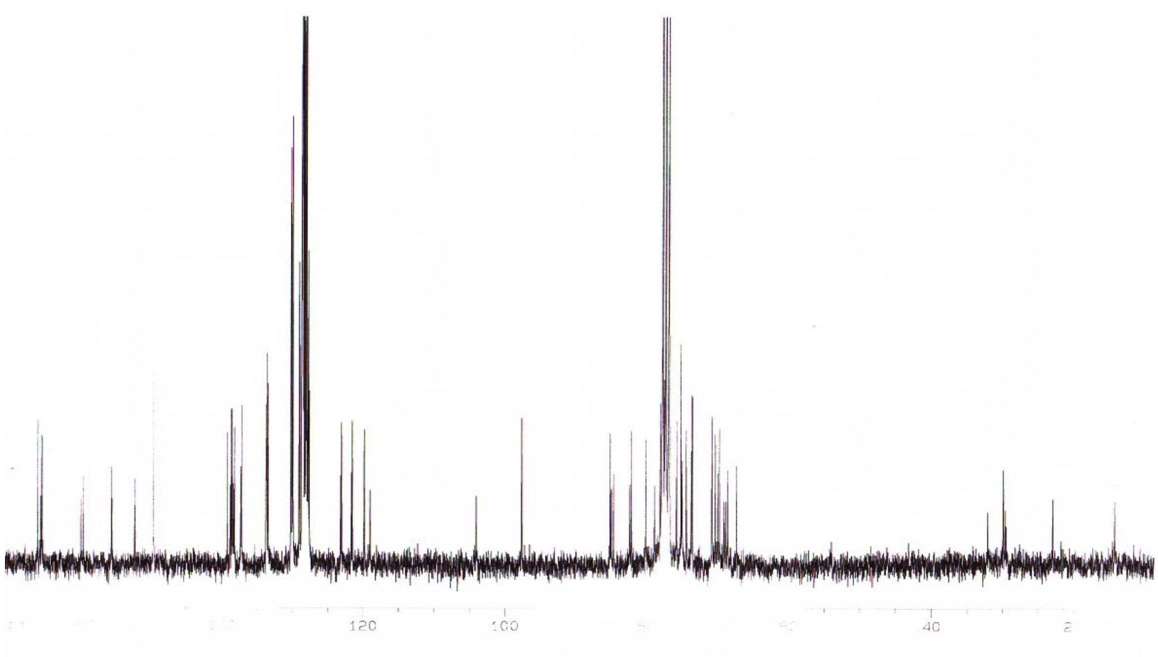
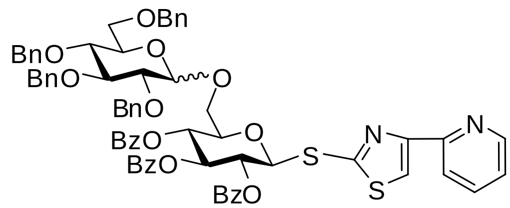
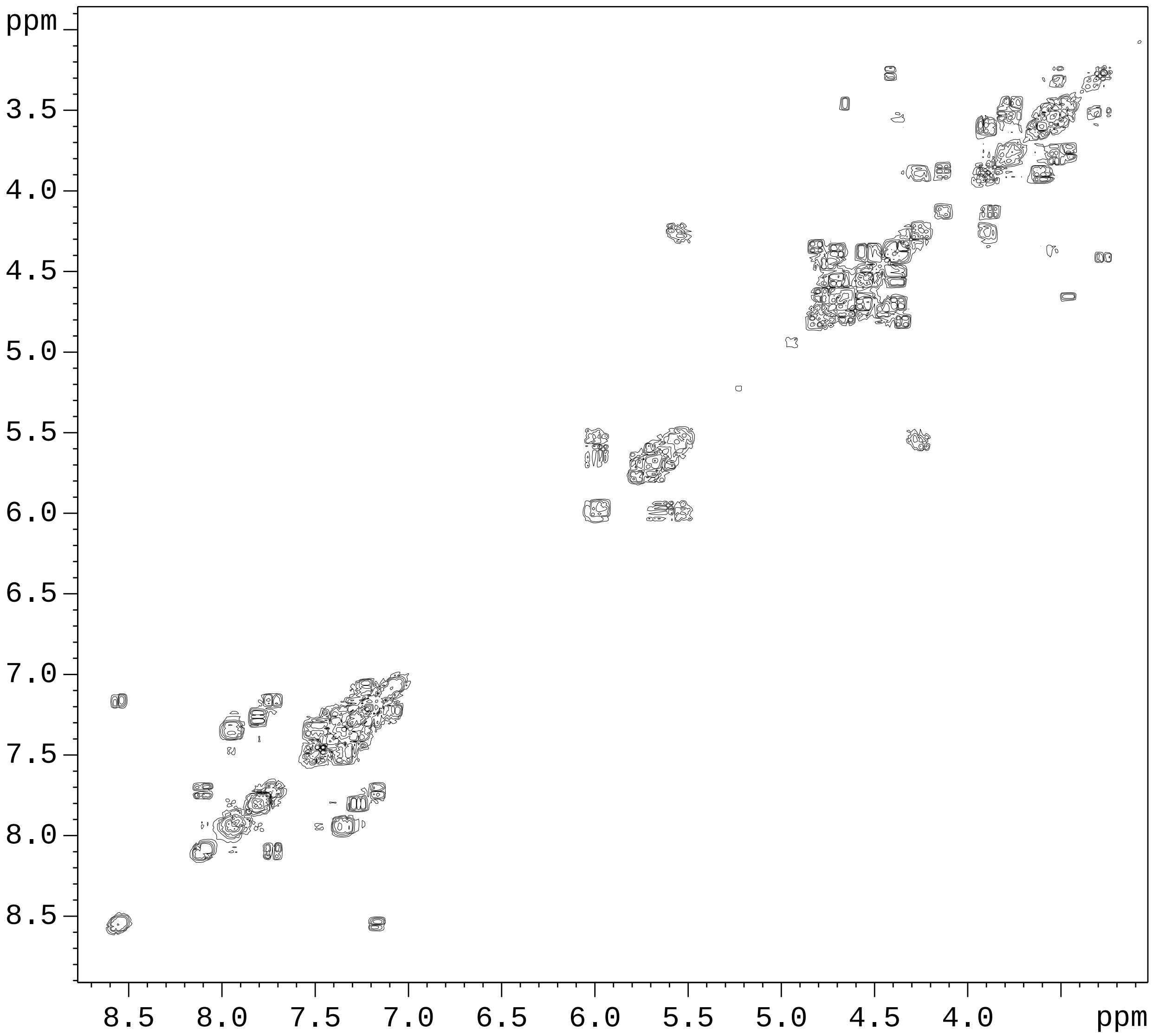
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


120
100
40


OBn
BnO
BnO
BnO
O
O
BzO
BzO
BzO
O
S
N
S
N

7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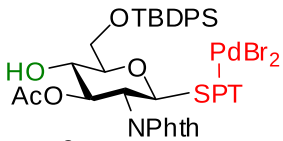
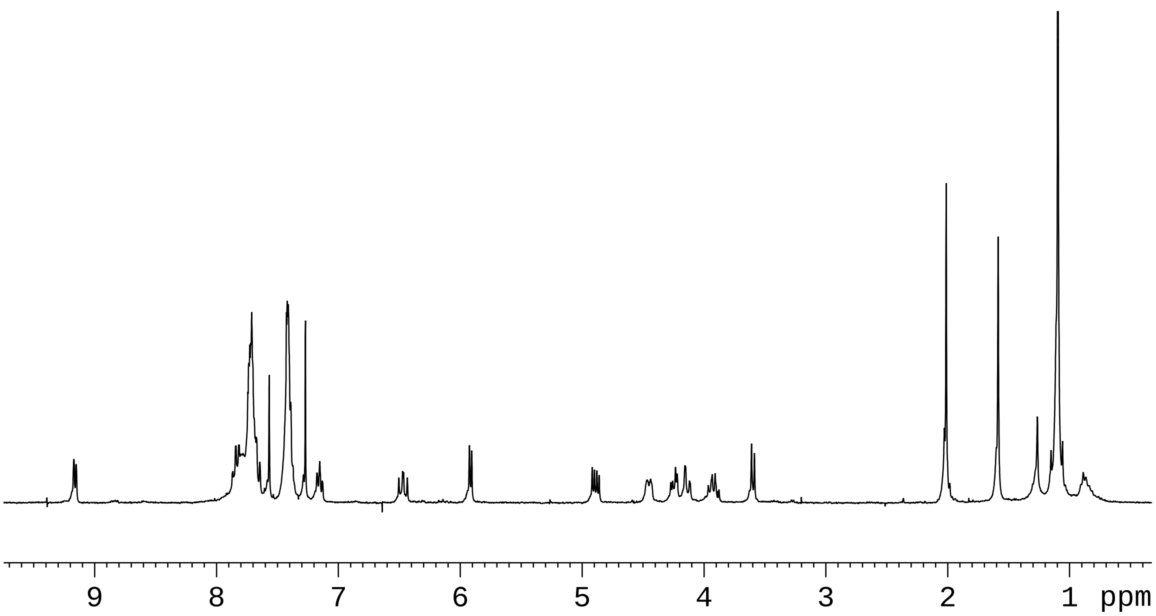
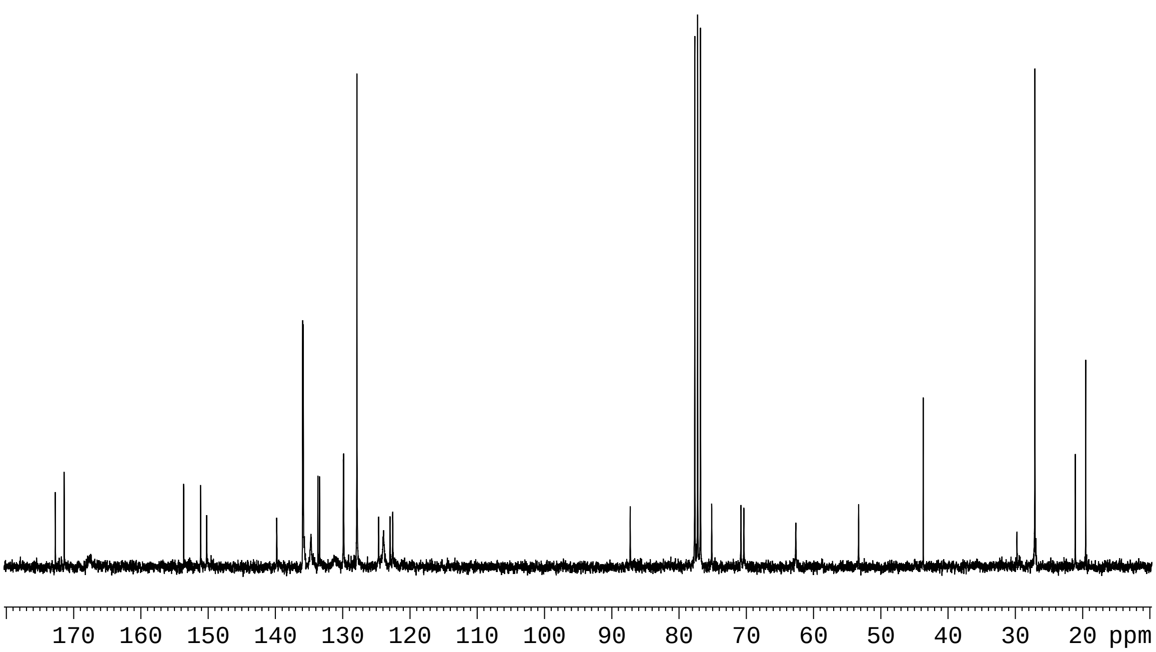
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


OTBDPS
PdBr2
HO
O
AcO
SPT
NPhth

9


9
8
7
6
5
4
3
2
1 ppm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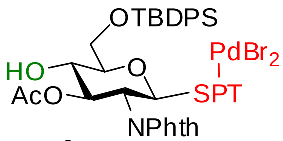
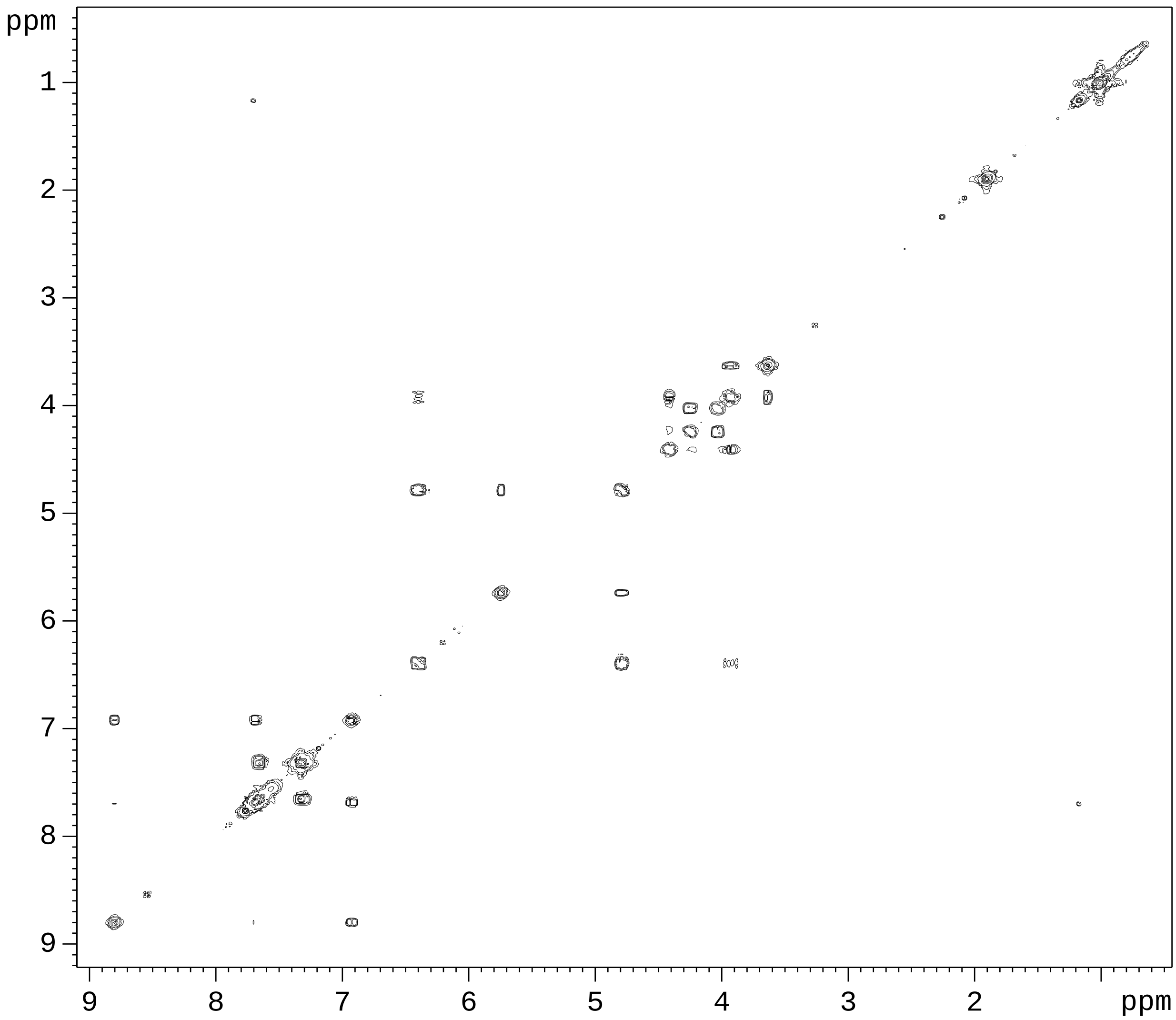
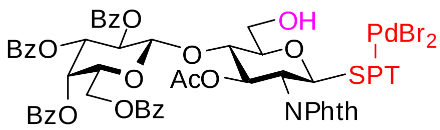
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20 ppm



9

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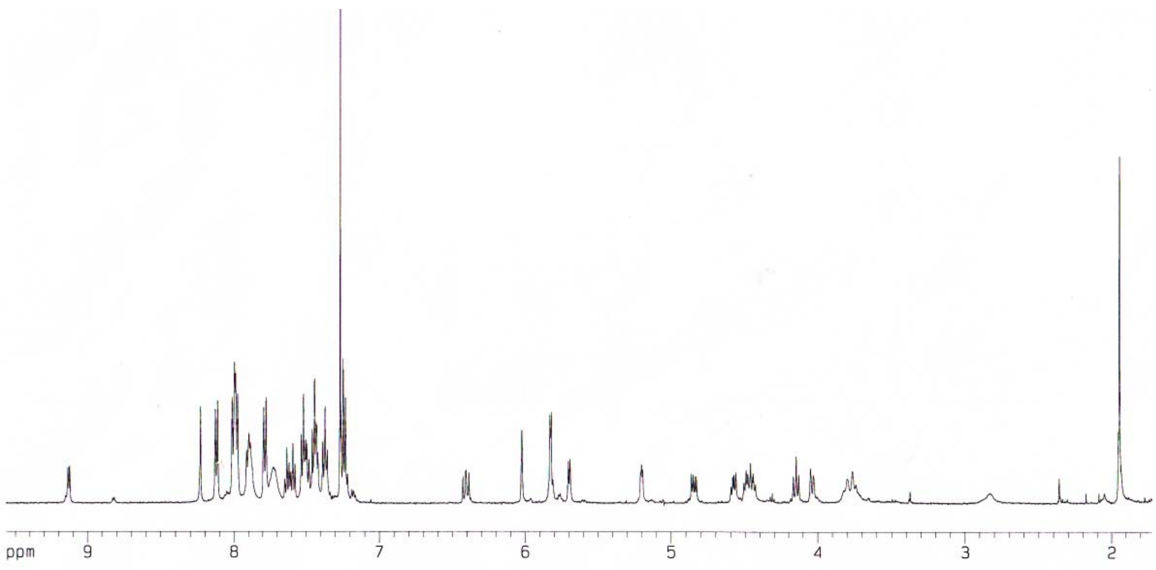
O
AcO
OH
O
PdBr2
SPT
NPhth
BzO
OBz

10


ppm
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3
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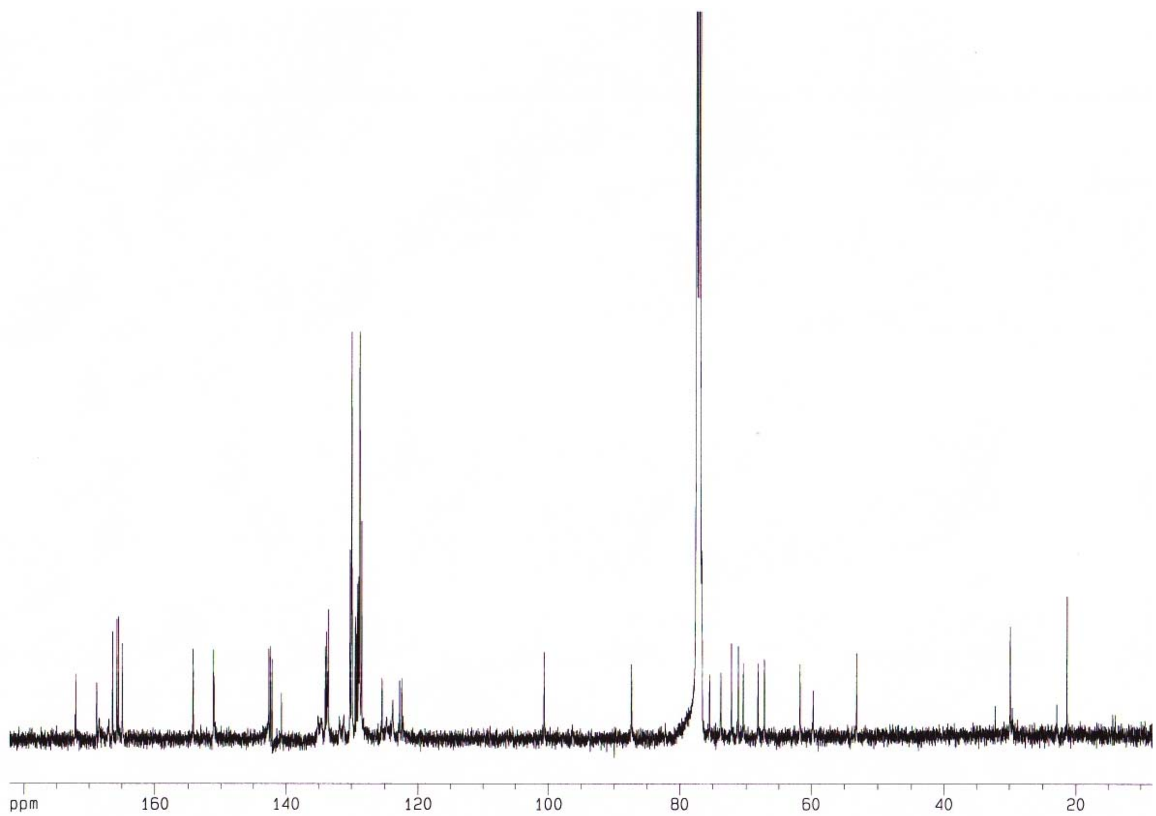
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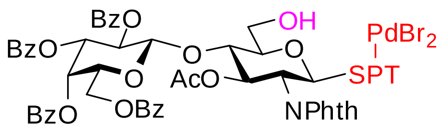
20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BzO
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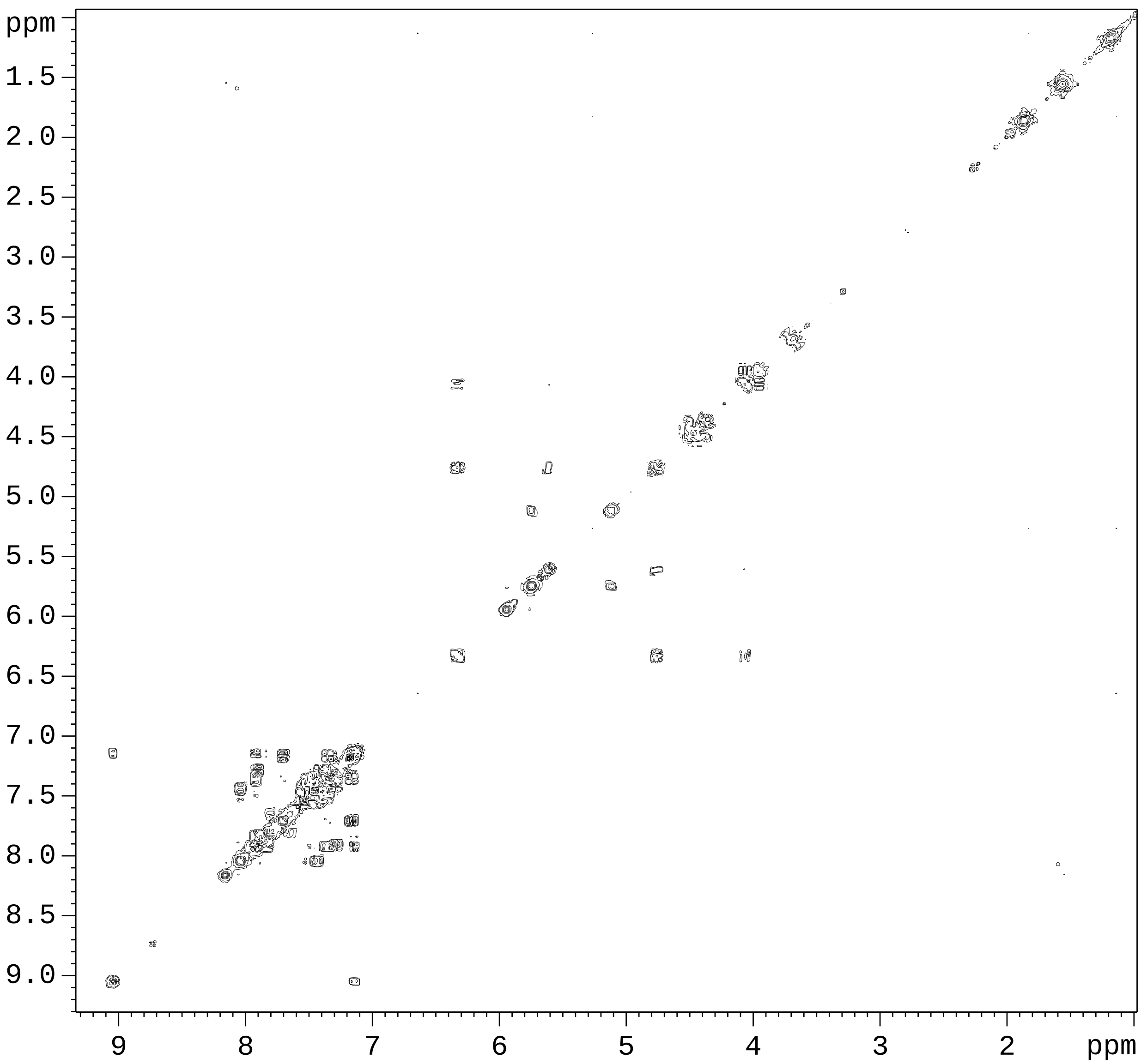
BzO
OBz
O
AcO
OH
O
PdBr2
SPT
NPhth

10


ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
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7.5
8.0
8.5
9.0
9
8
7
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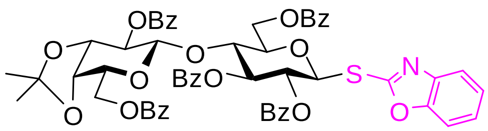
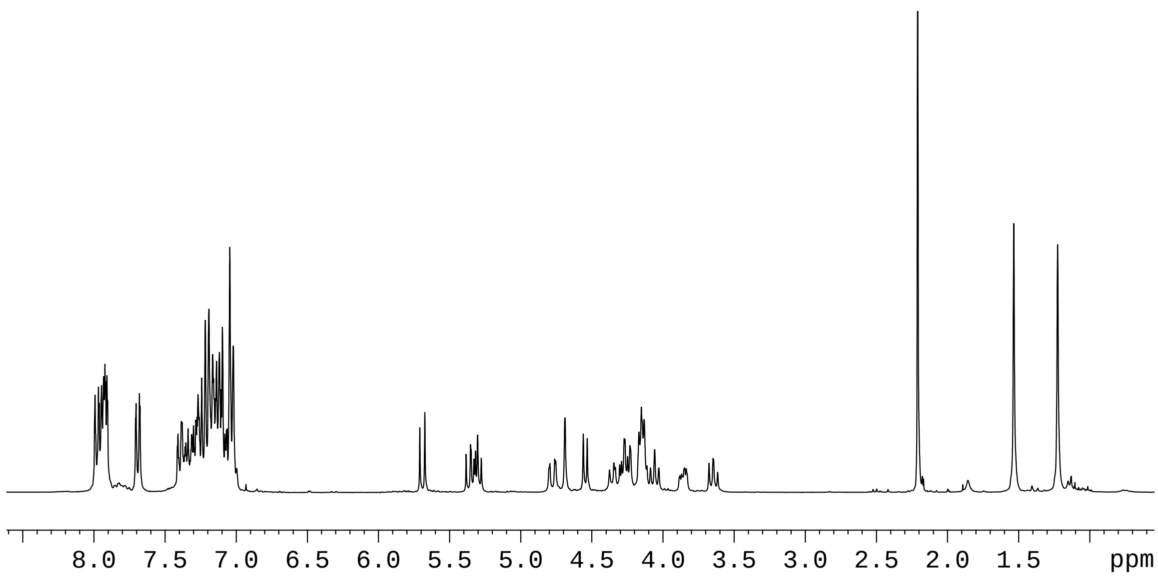
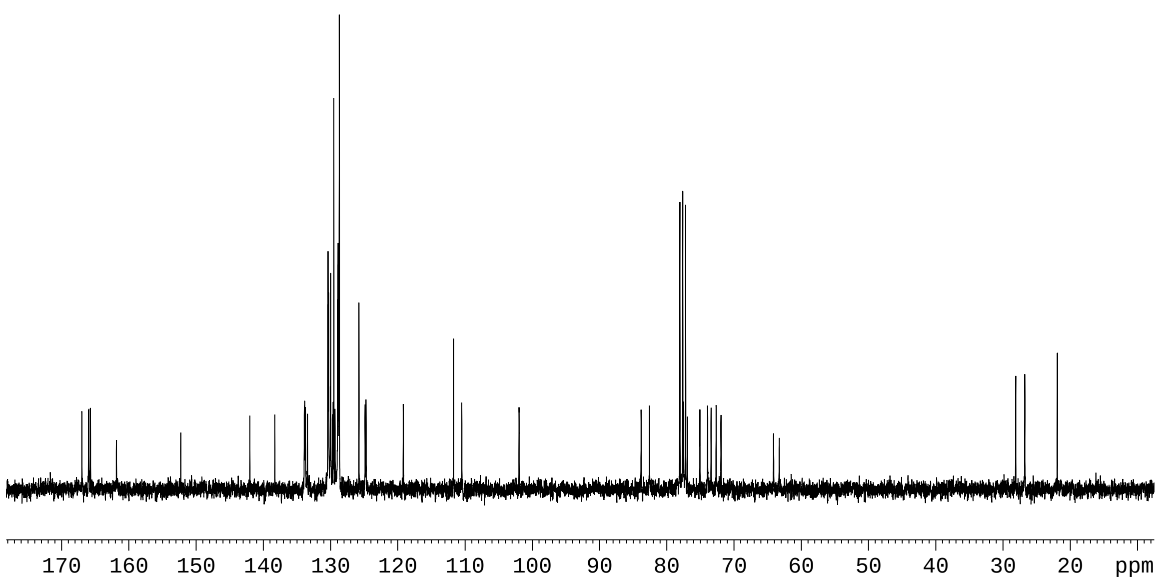
5
4
3
2
ppm


OBz
OBz
O
O
O
O
BzO
O
OBz
BzO
S
N
O

11


8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm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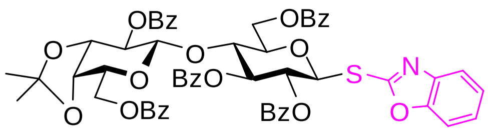

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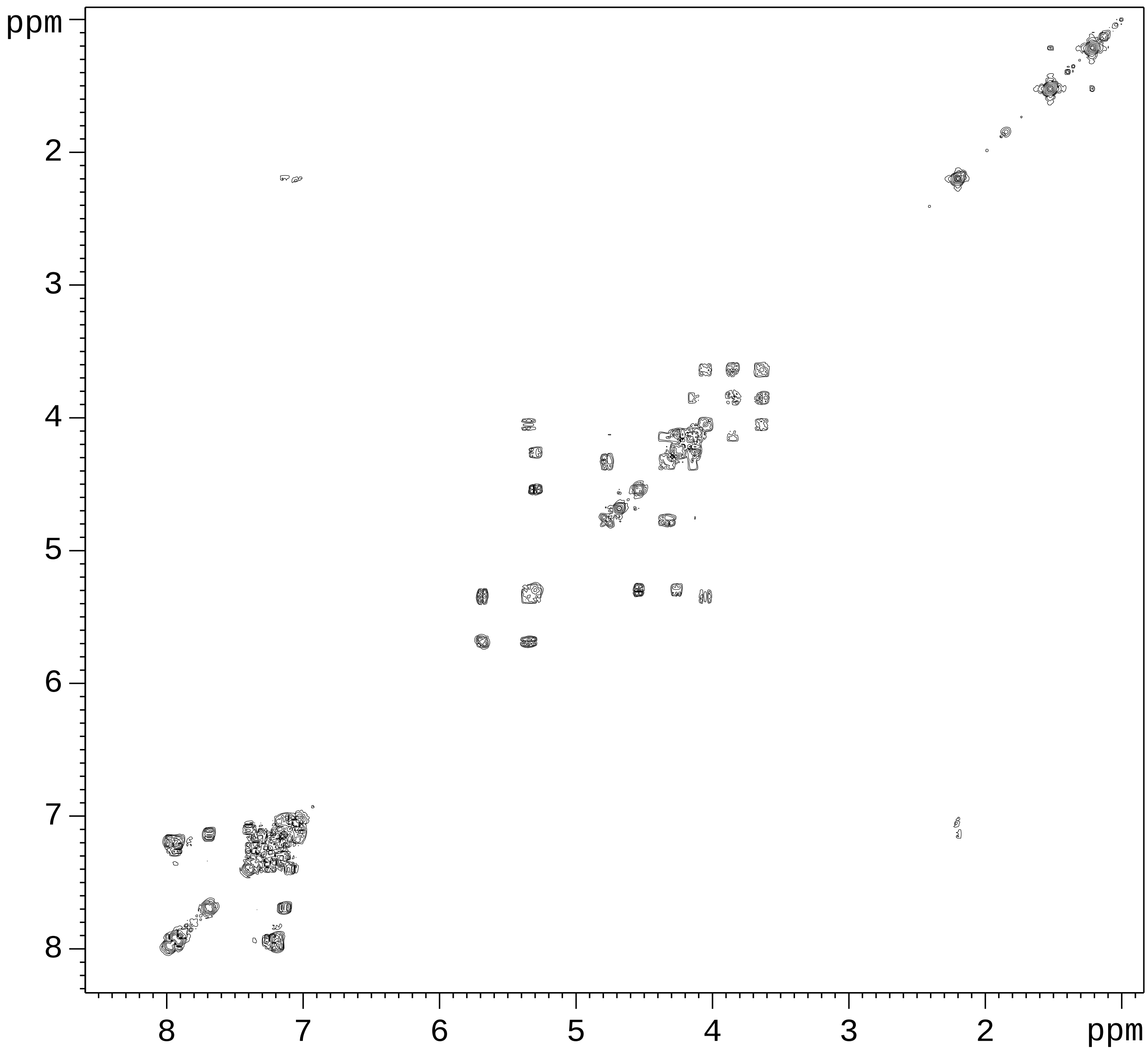
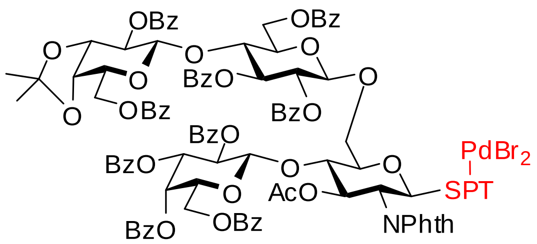
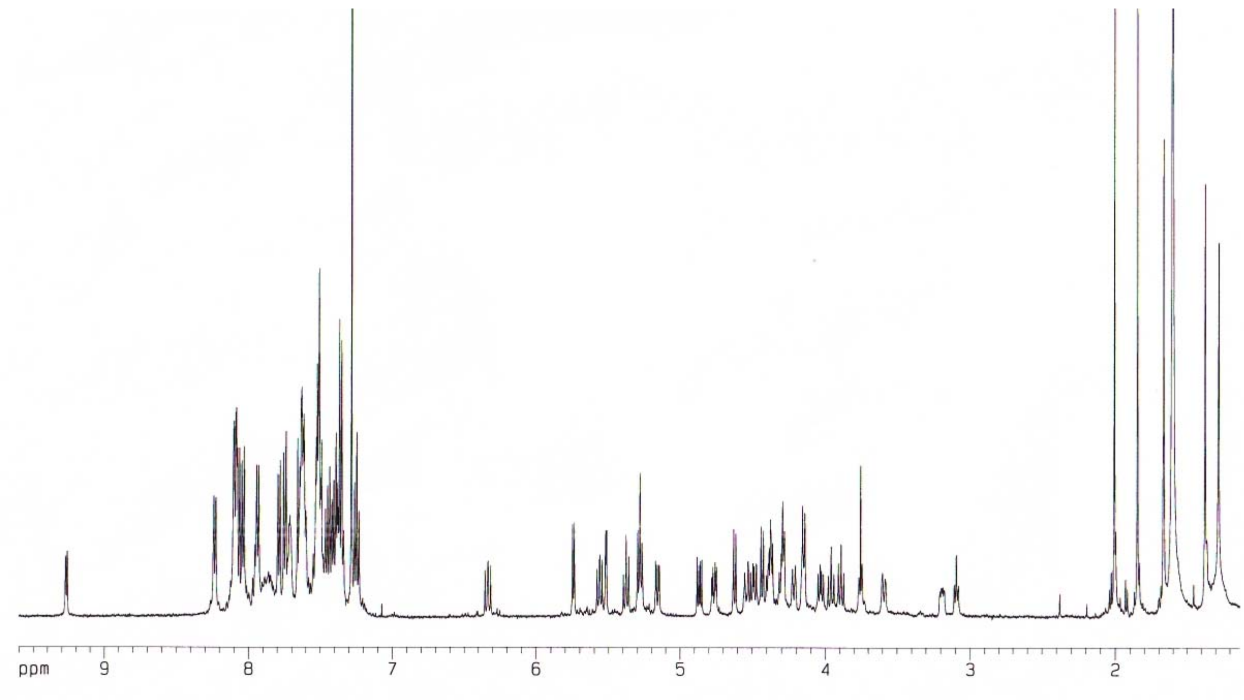



OBz
OBz
BzO
BzO
OBz
BzO
BzO
BzO
AcO
BzO
OBz
PdBr2
SPT
NPhth

12


ppm
9
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5
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3
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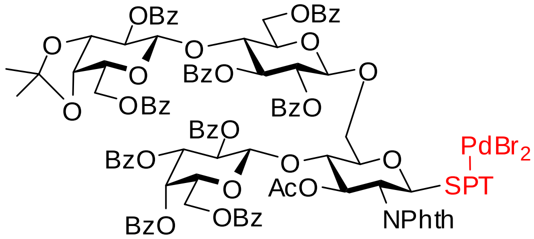
OBz
OBz
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O
BzO
O
O
BzO
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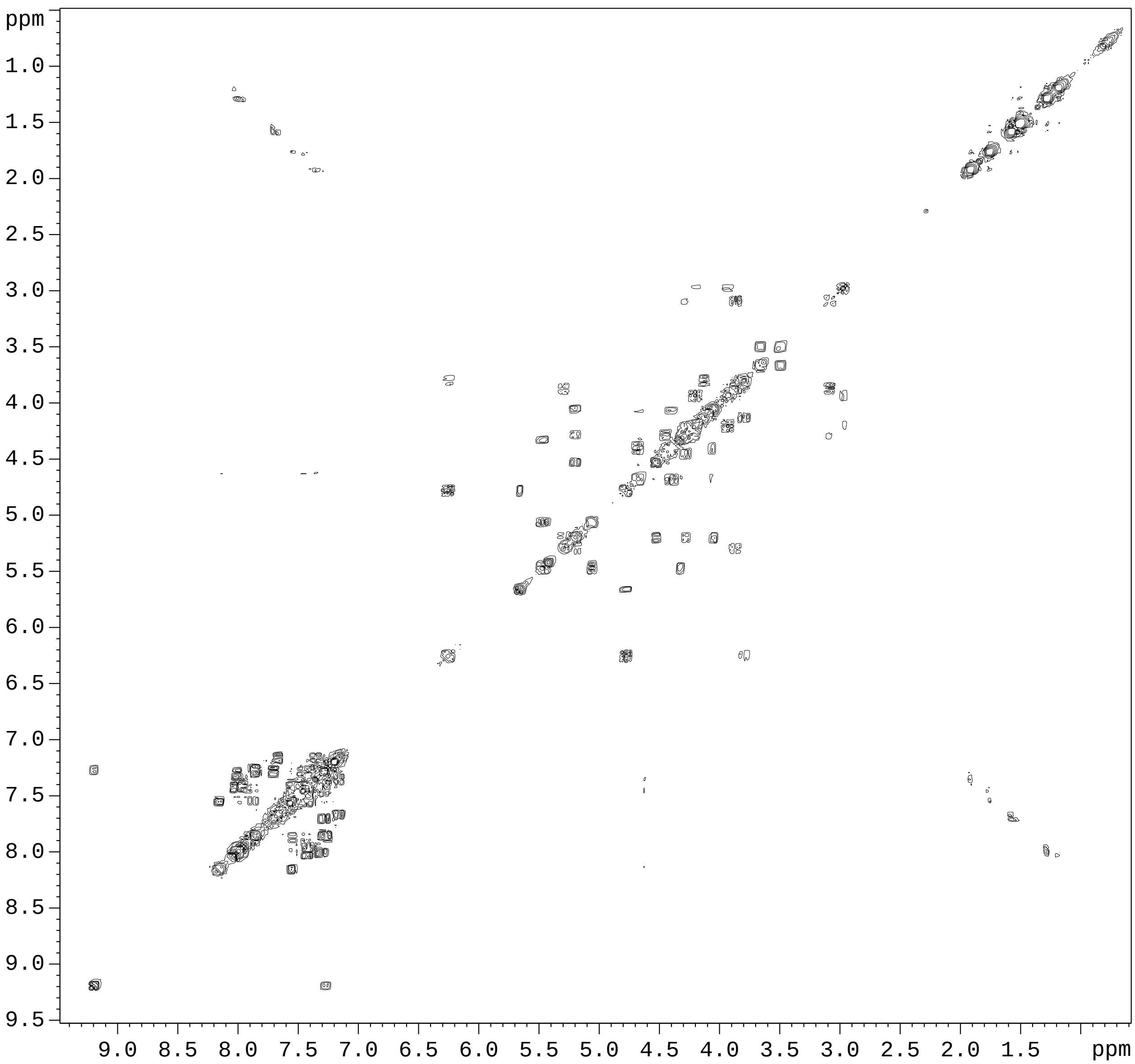
OBz
BzO
BzO
O
O
AcO
PdBr$_2$
SPT
O
BzO
OBz
NPhth

12


ppm
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4.5
5.0
5.5
6.0
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7.5
8.0
8.5
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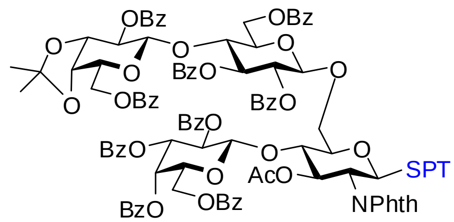
ppm


OBz
OBz
O
BzO
O
O
O
OBz
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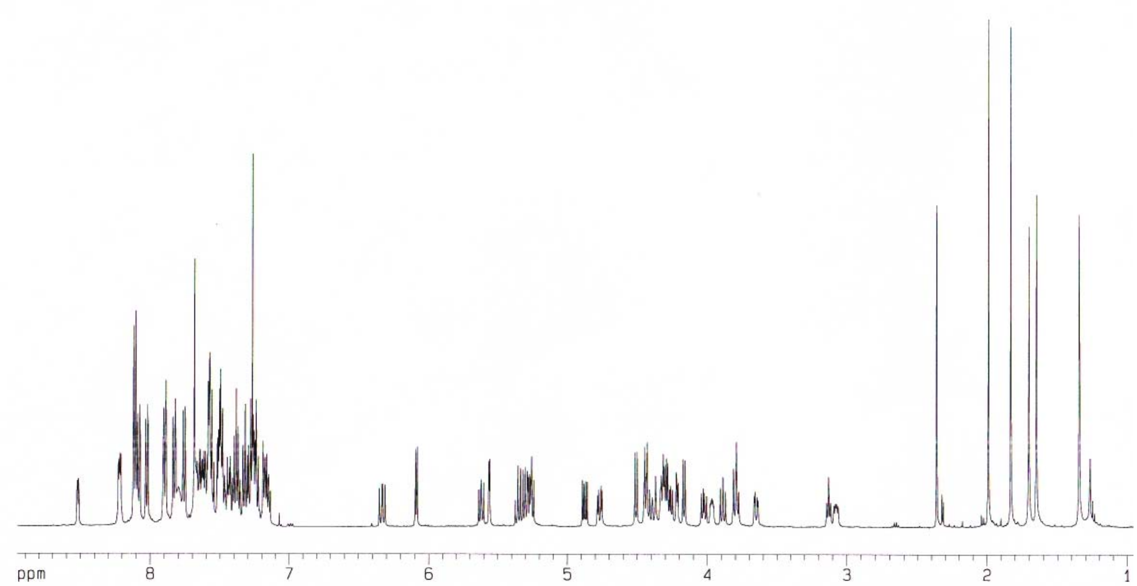
O
BzO
BzO
O
BzO
O
AcO
O
SPT
BzO
OBz
NPhth

13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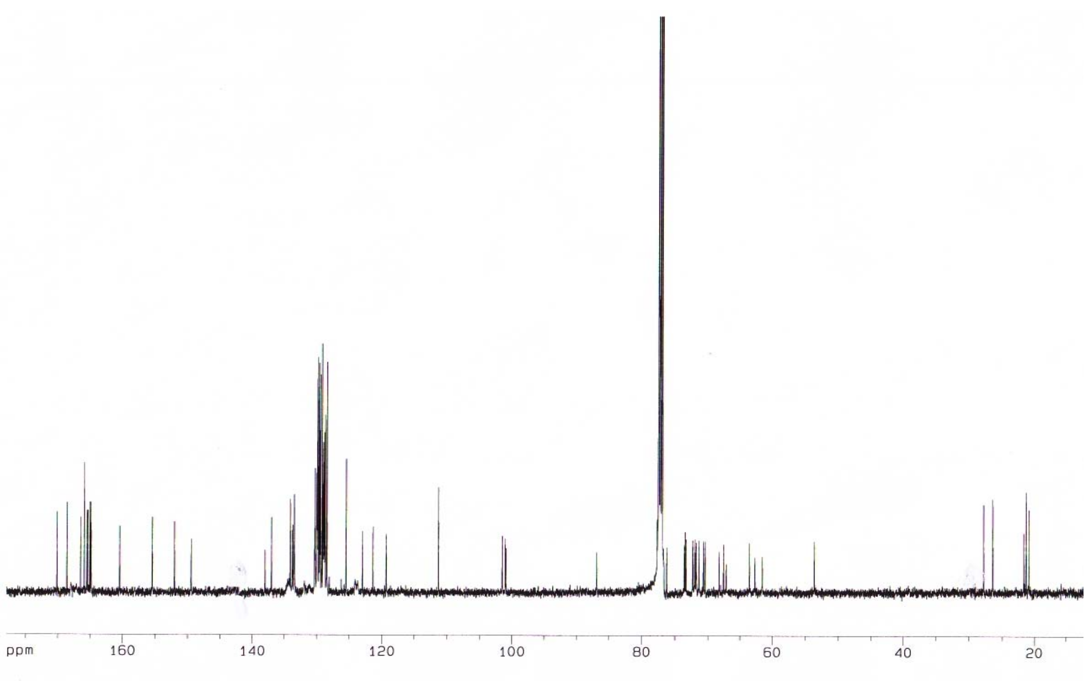
4
3
2
1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80
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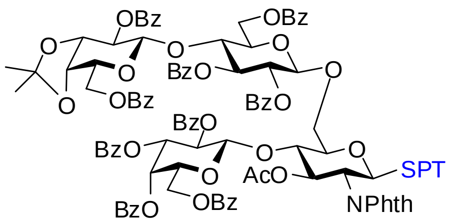
OBz
OBz
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O
BzO
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BzO
OBz
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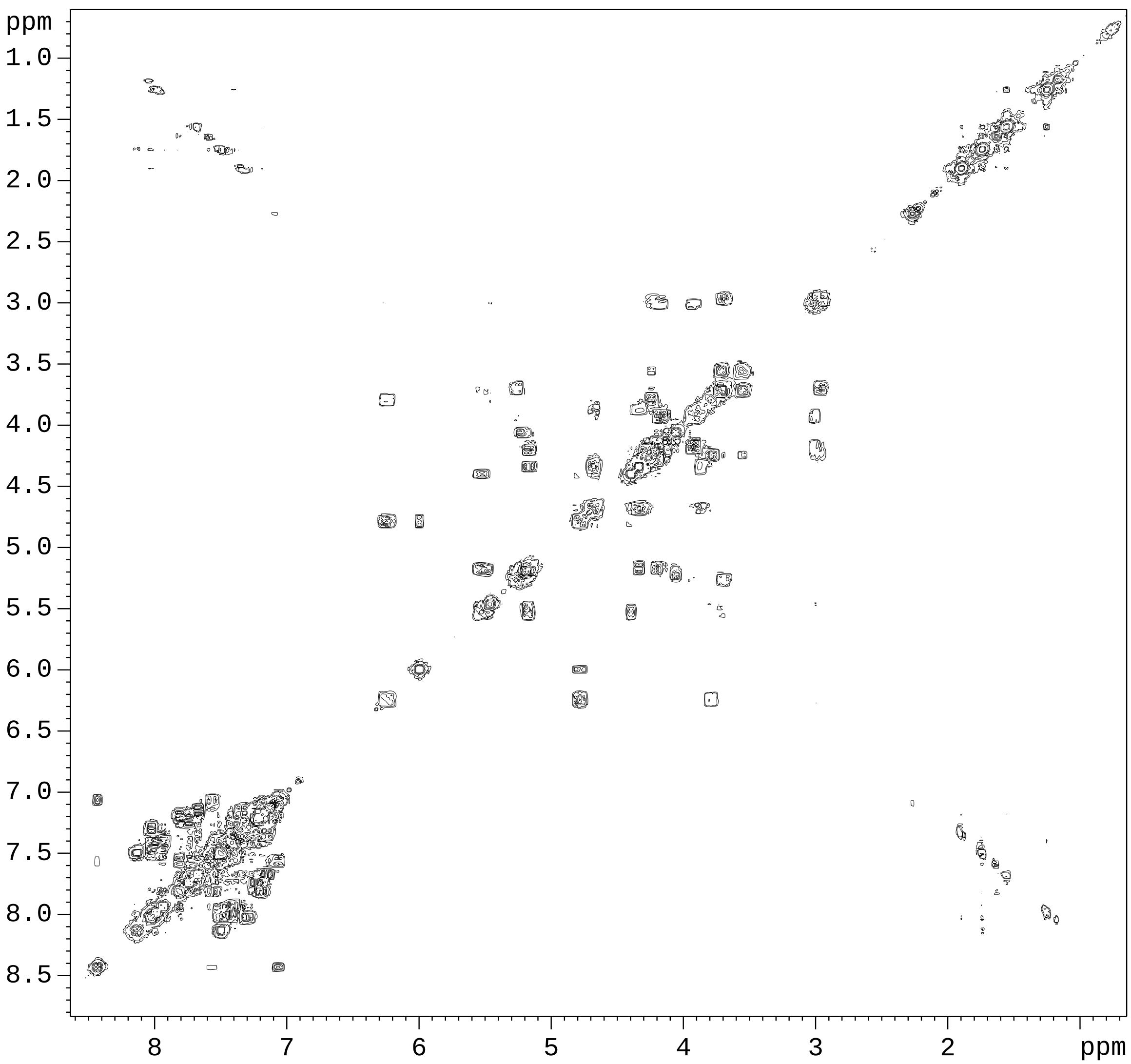
BzO
BzO
O
O
AcO
O
SPT
BzO
OBz
NPhth

13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2.5
3.0
3.5
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4.5
5.0
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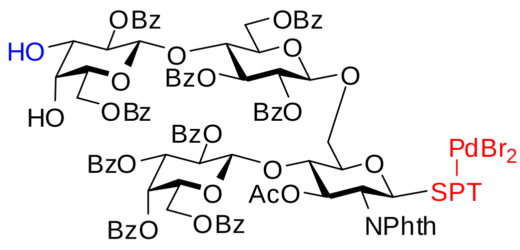
7.0
7.5
8.0
8.5
8
7
6
5
4
3
2
ppm


HO
OBz
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OBz
O
BzO
BzO
O
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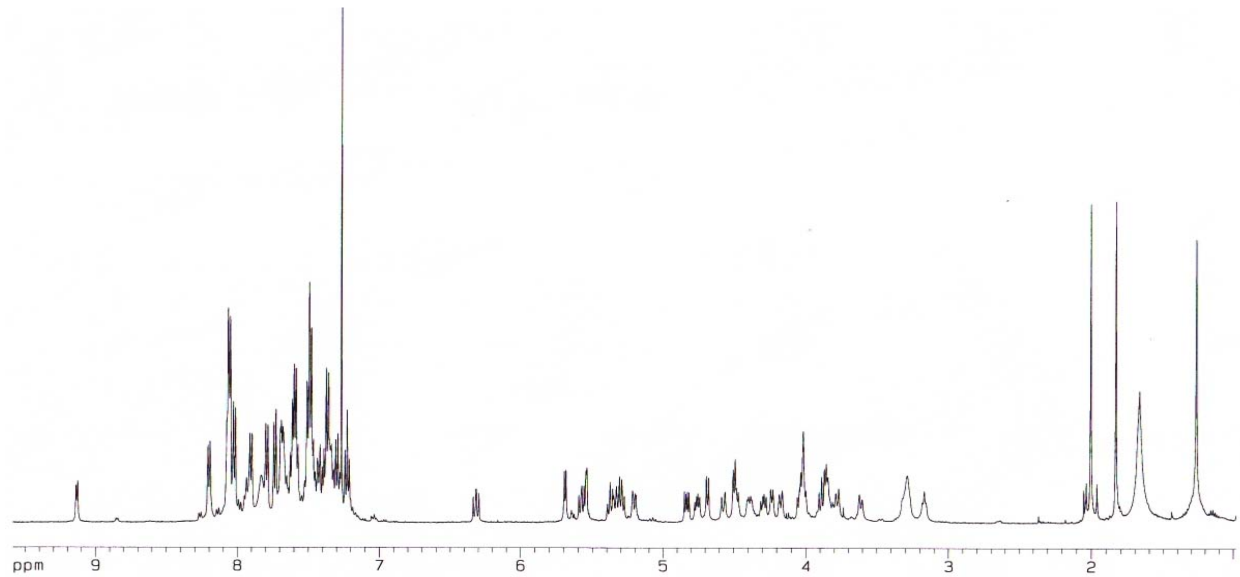
OBz
BzO
BzO
O
O
PdBr2
SPT
AcO
BzO
OBz
NPhth

14


ppm
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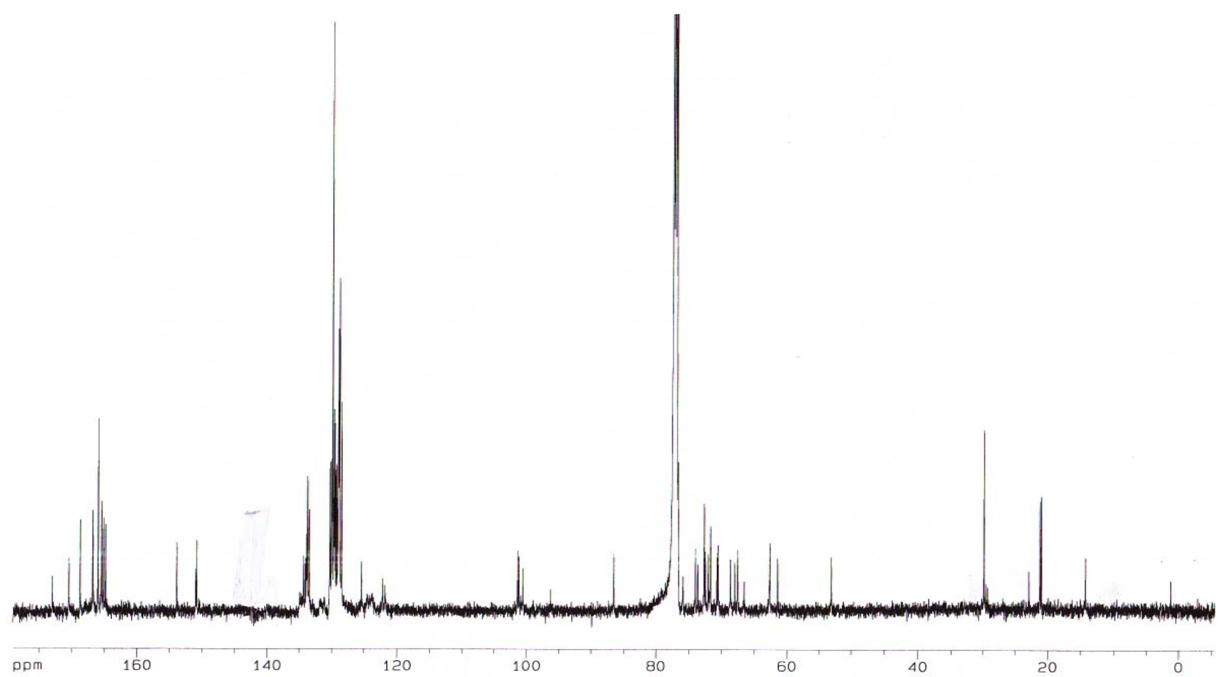
5
4
3
2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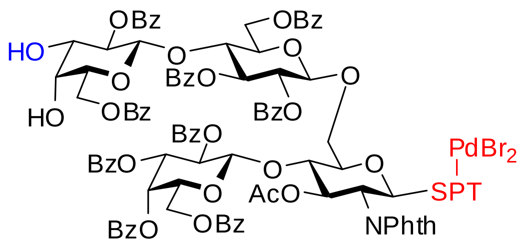

HO
OBz
O
OBz
O
BzO
O
BzO
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HO
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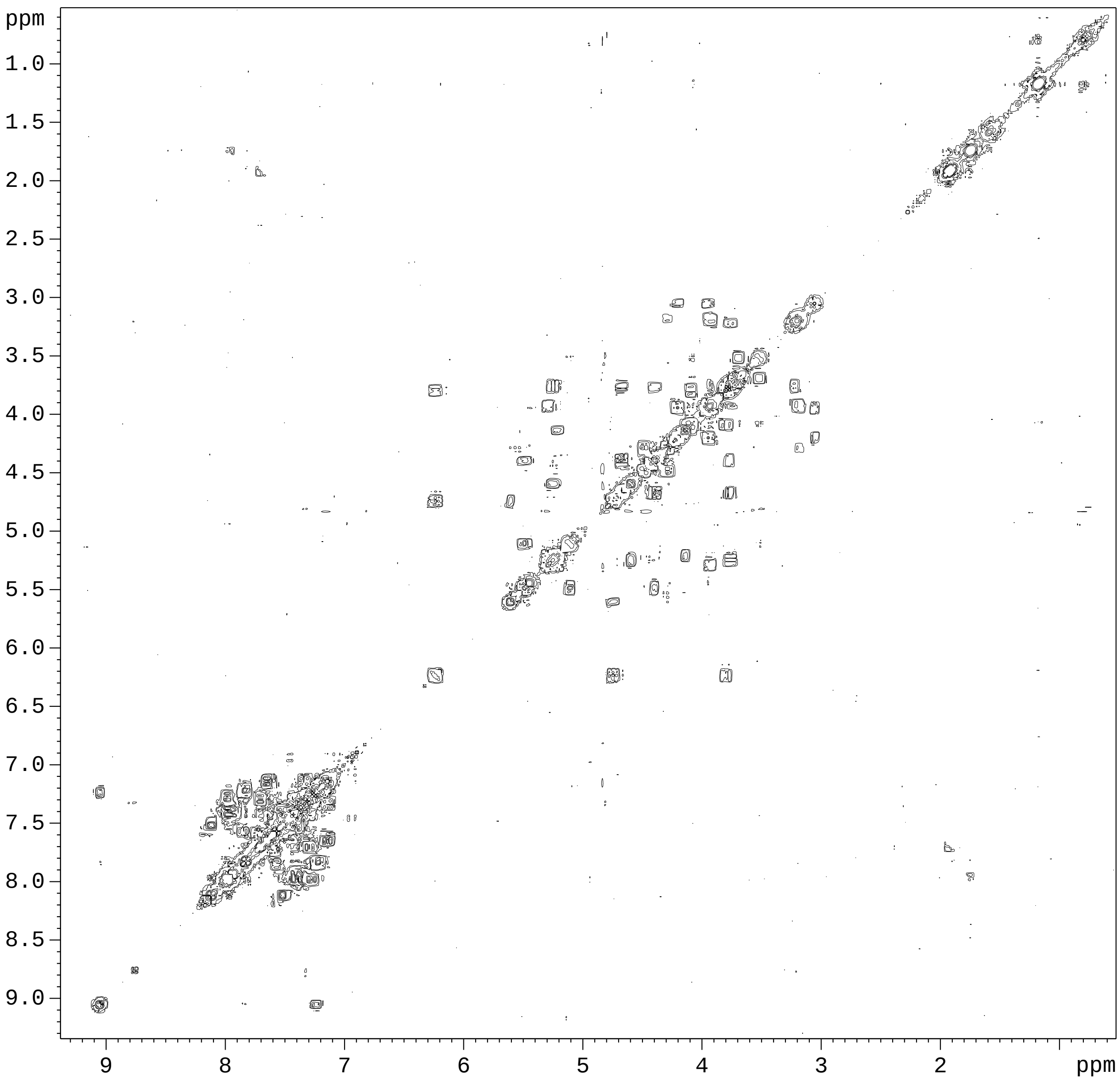
BzO
PdBr2
BzO
O
O
SPT
O
AcO
BzO
OBz
NPhth

14



ppm
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3.5
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4.5
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8.5
9.0
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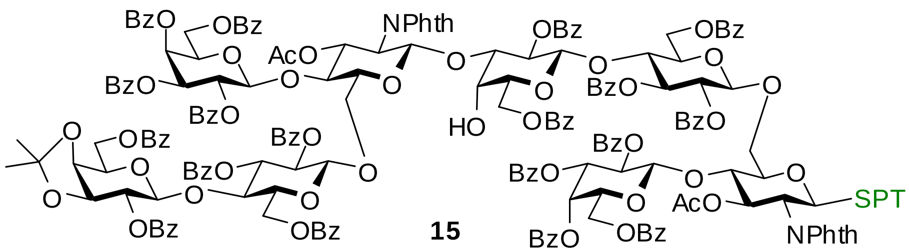
4
3
2
ppm


BzO
OBz
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AcO
NPhth
OBz
OBz
BzO
O
O
BzO
BzO
O
HO
OBz
BzO
O
OBz
BzO
BzO
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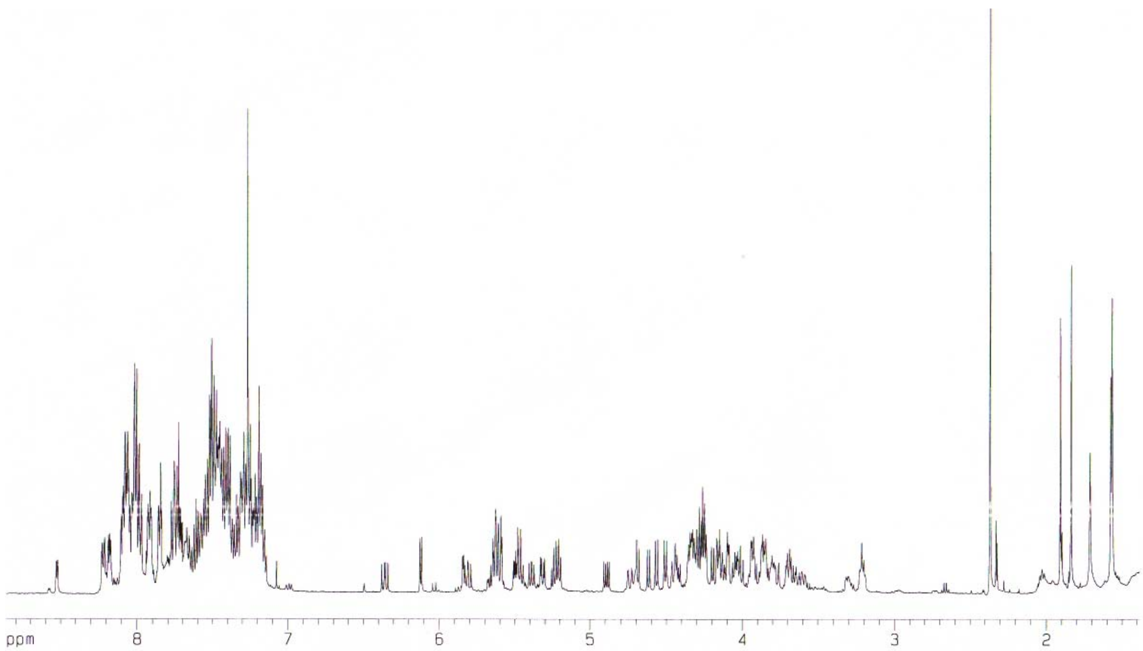
BzO
O
OBz
BzO
AcO
SPT
OBz
OBz
BzO
OBz
NPhth
15


ppm
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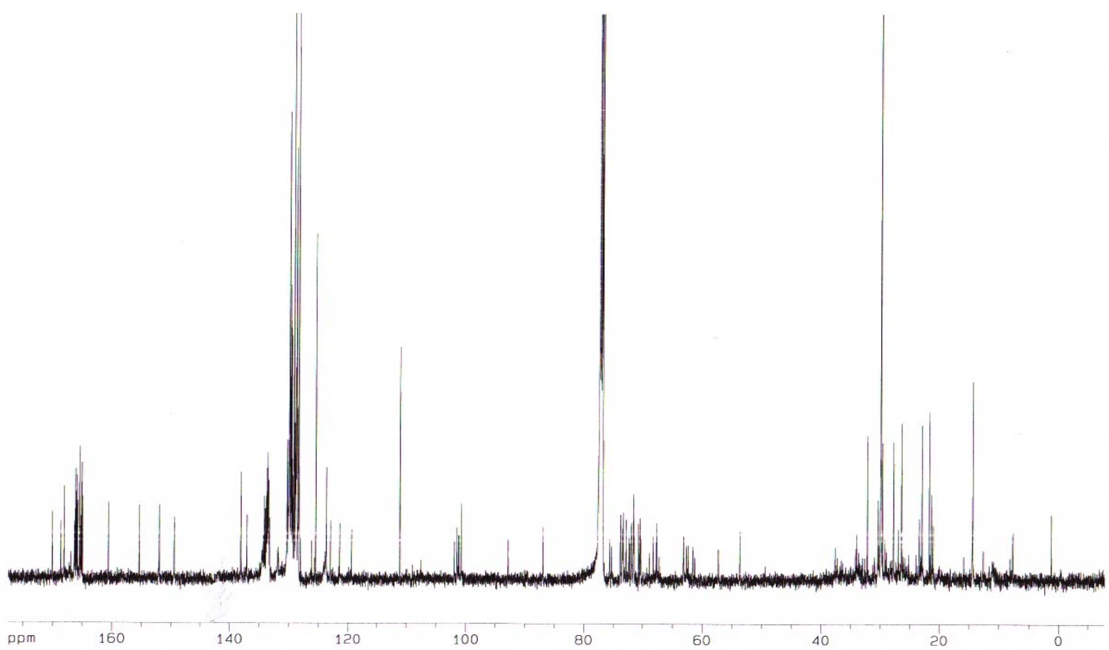
5
4
3
2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20
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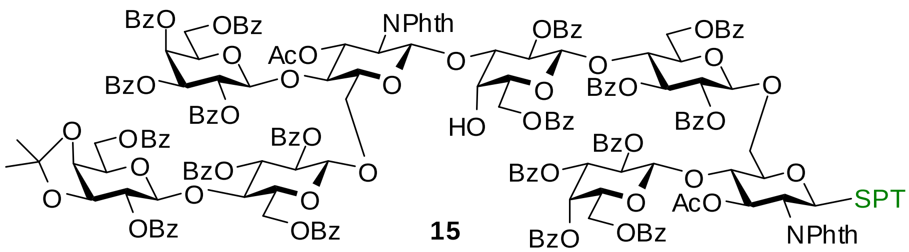

BzO
OBz
O
AcO
NPhth
O
O
OBz
O
OBz
O
O
BzO
O
BzO
O
HO
OBz
BzO
O
OBz
BzO
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BzO
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O
BzO
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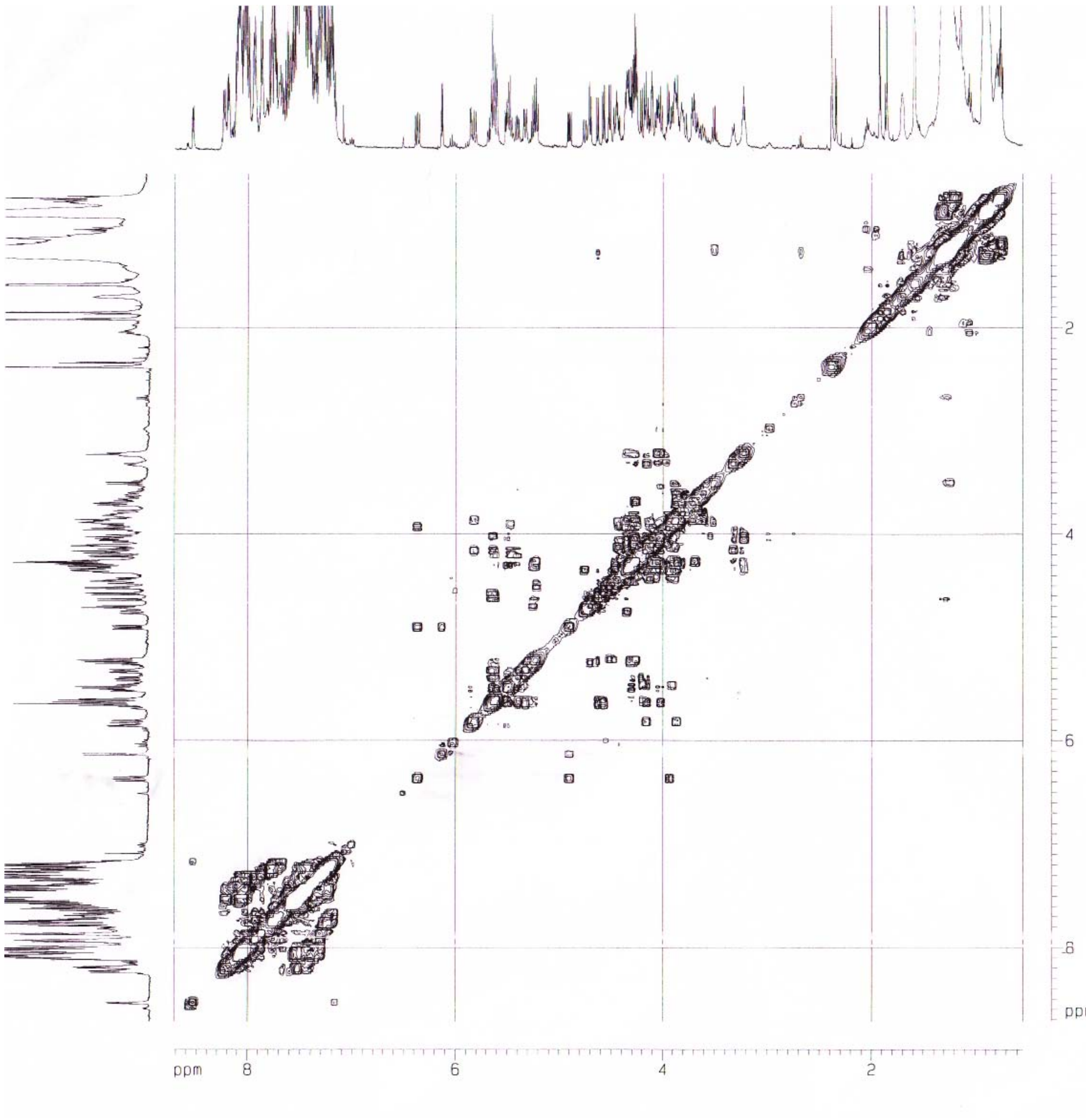
O
AcO
O
SPT
OBz
OBz
BzO
OBz
NPhth

15



ppm
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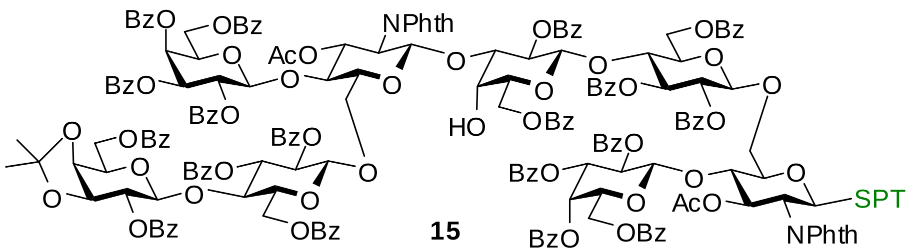
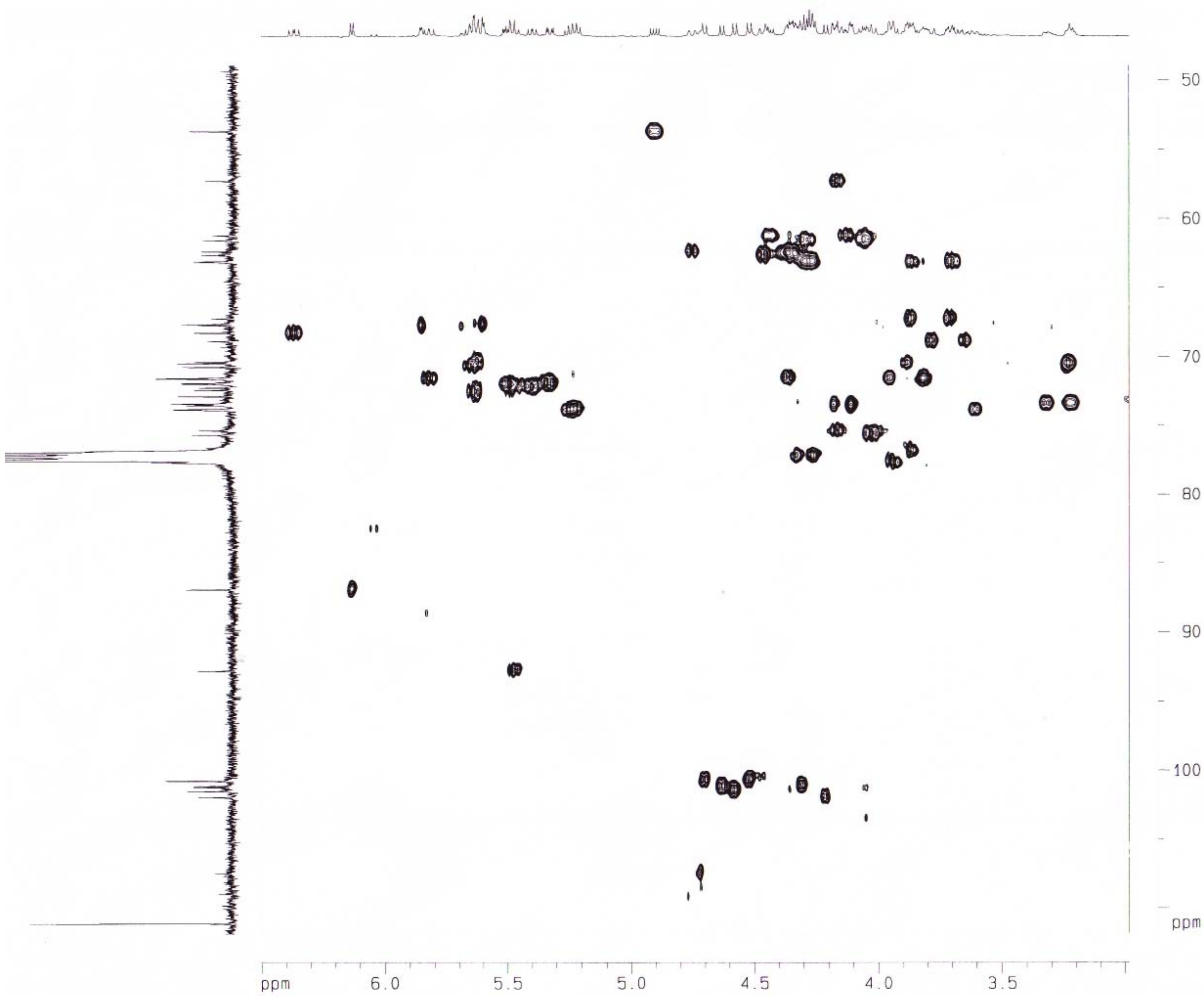
4
2
2
4
6
8
ppm


15
SPT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5.0
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3.5
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90
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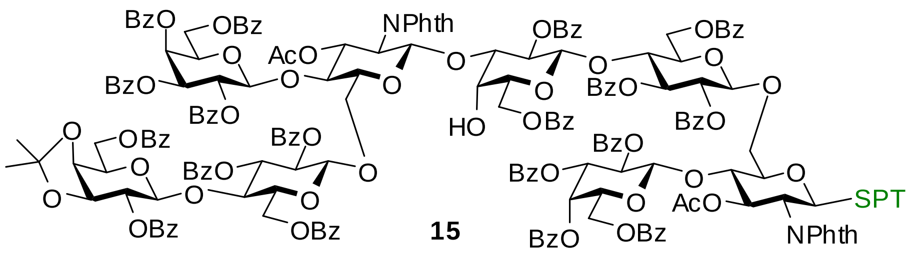
BzO
OBz
NPhth
OBz
OBz
AcO
O
O
O
BzO
O
O
BzO
O
O
HO
BzO
OBz
BzO
OBz
BzO
OBz
BzO
O
O
SPT
BzO
O
O
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O
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AcO
O
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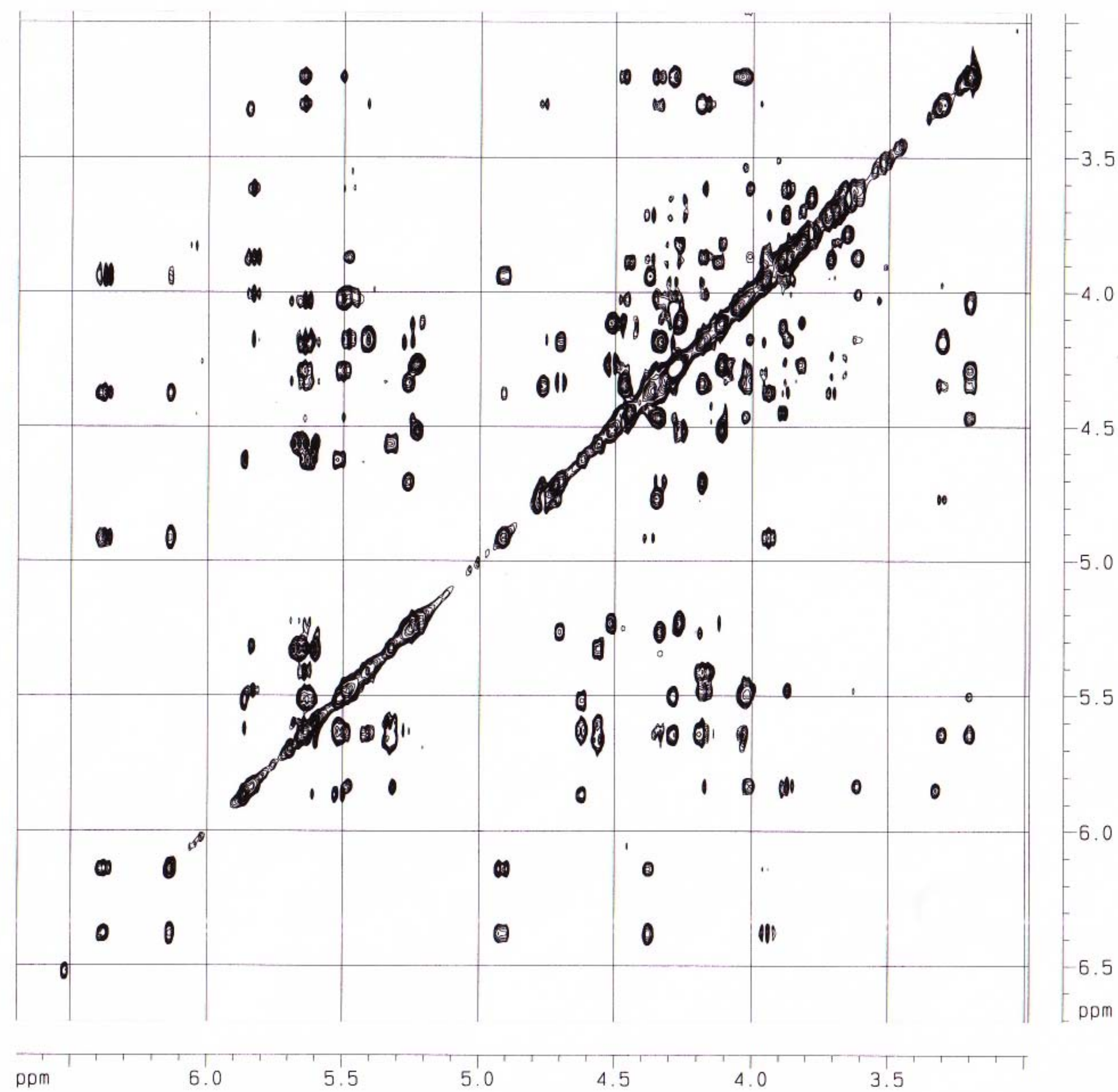
BzO
OBz
NPhth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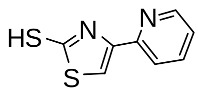
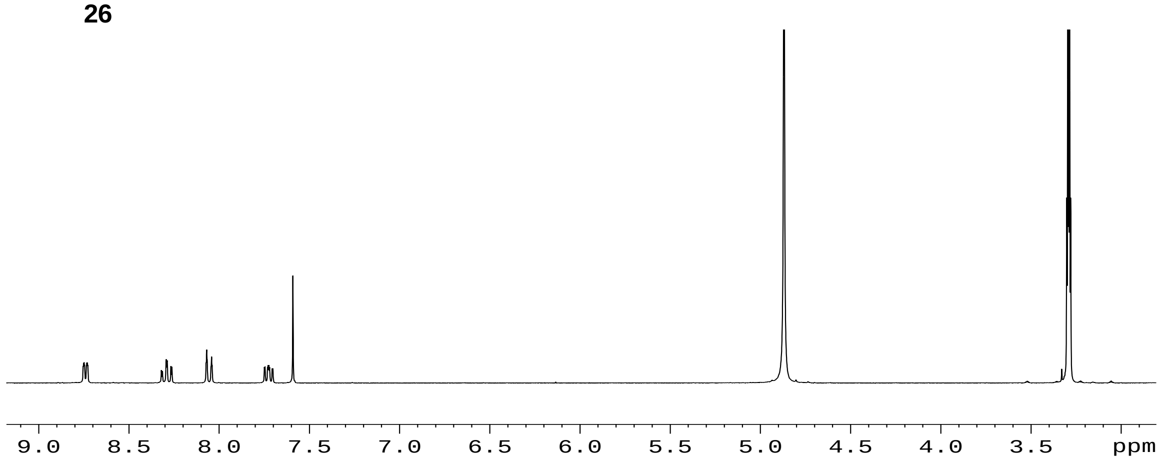
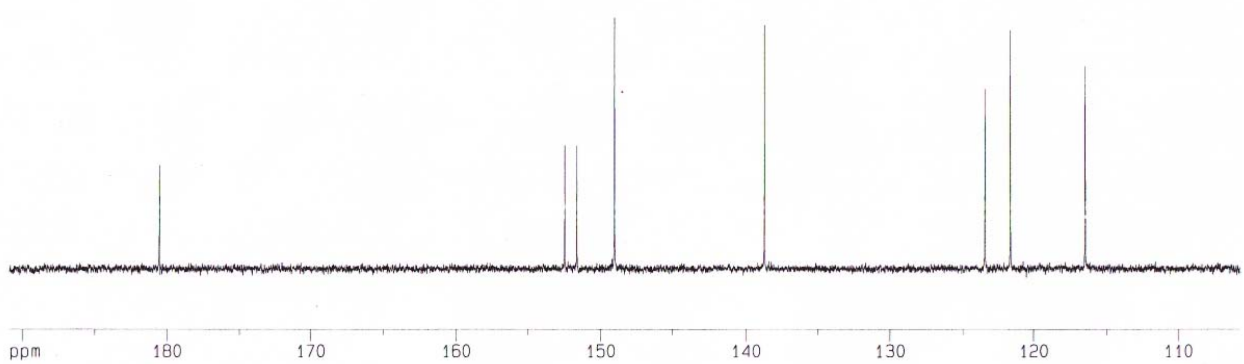
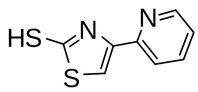
4.0
4.5
5.0
5.5
6.0
6.5
ppm
ppm
6.0
5.5
5.0
4.5
4.0
3.5



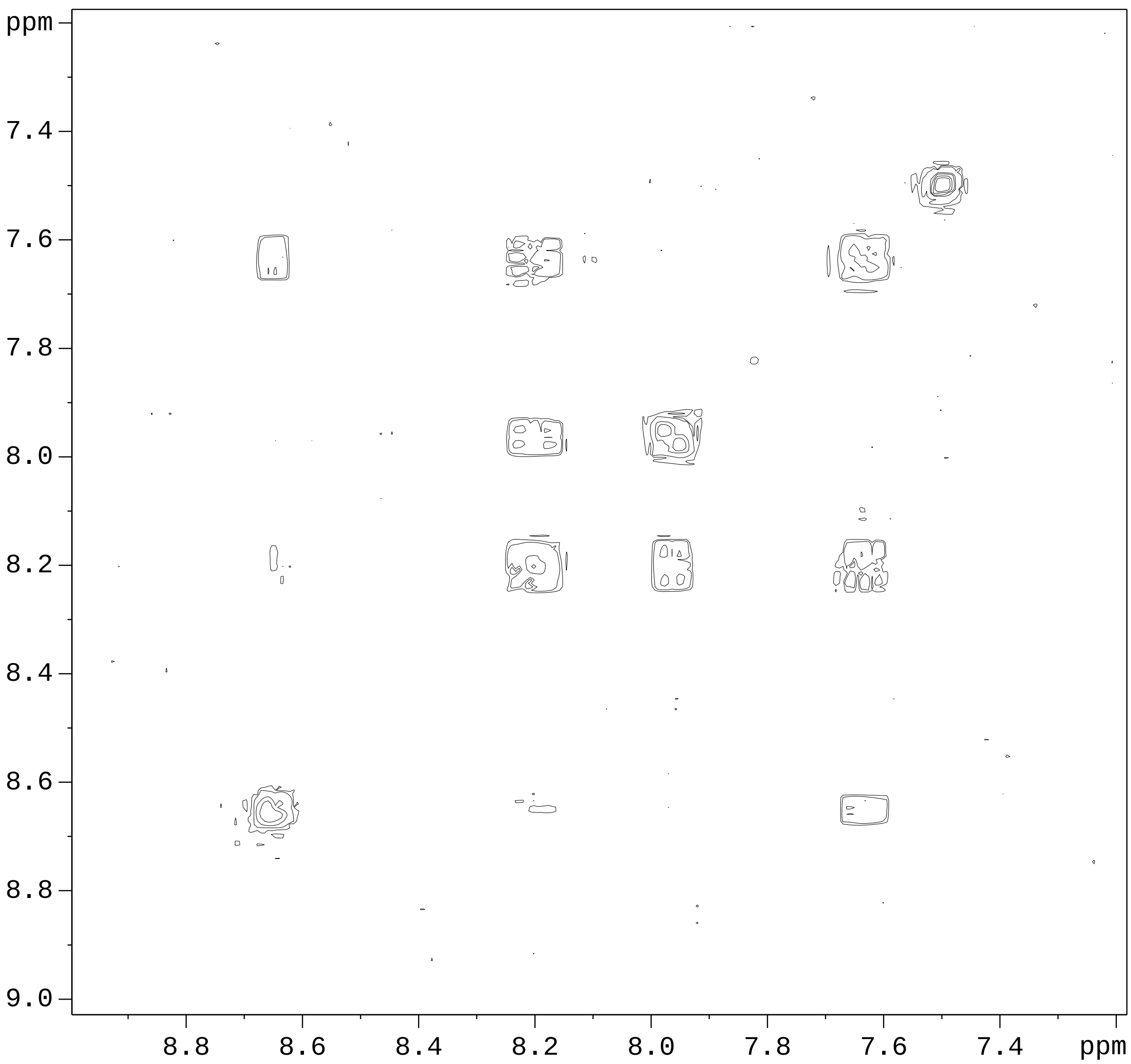
26

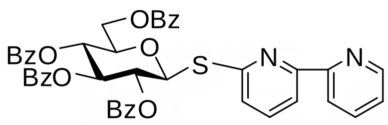

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm


ppm 180 170 160 150 140 130 120 110

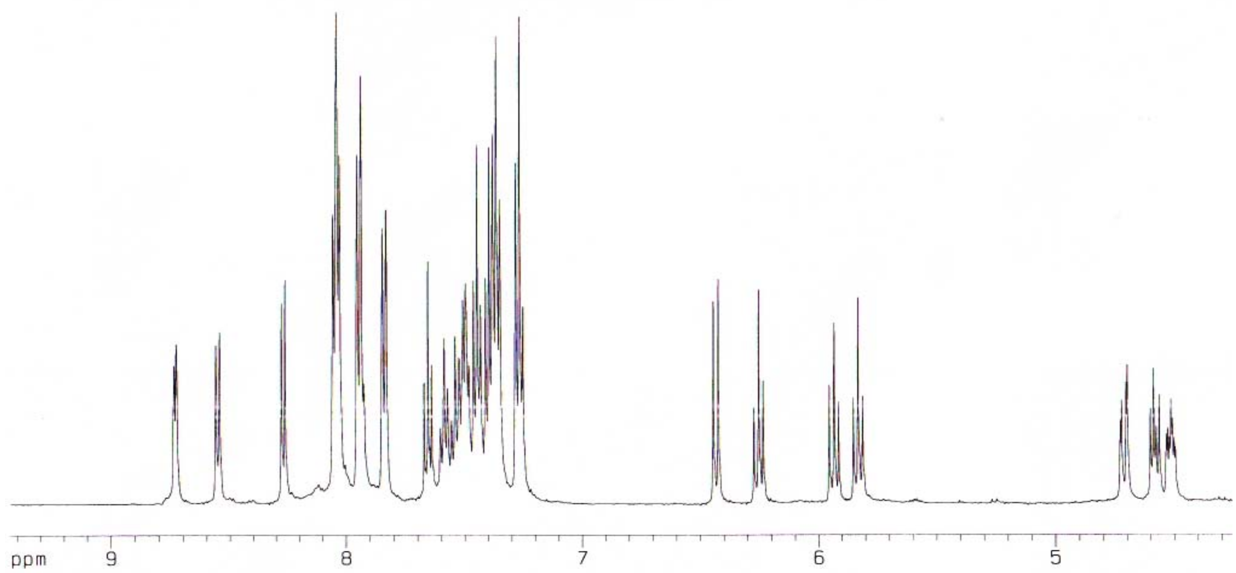


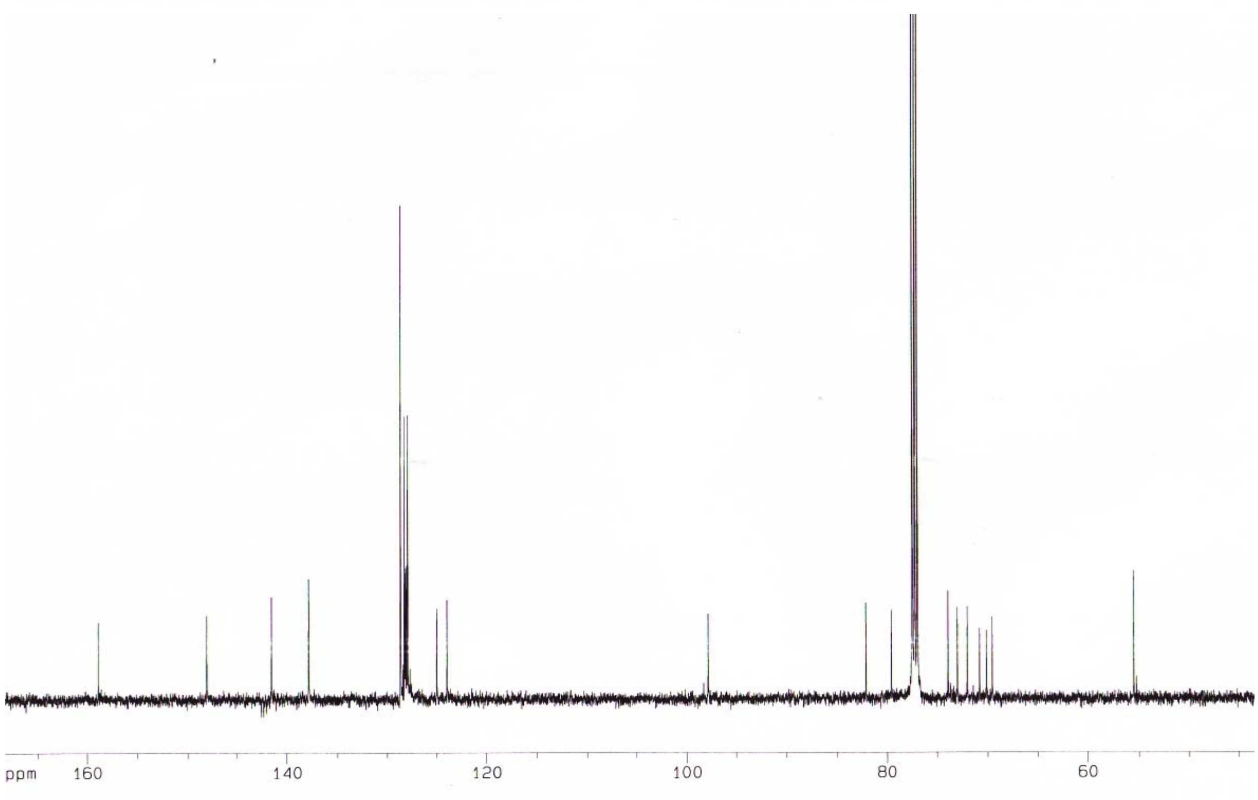
26

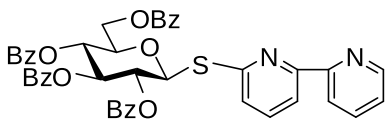




28







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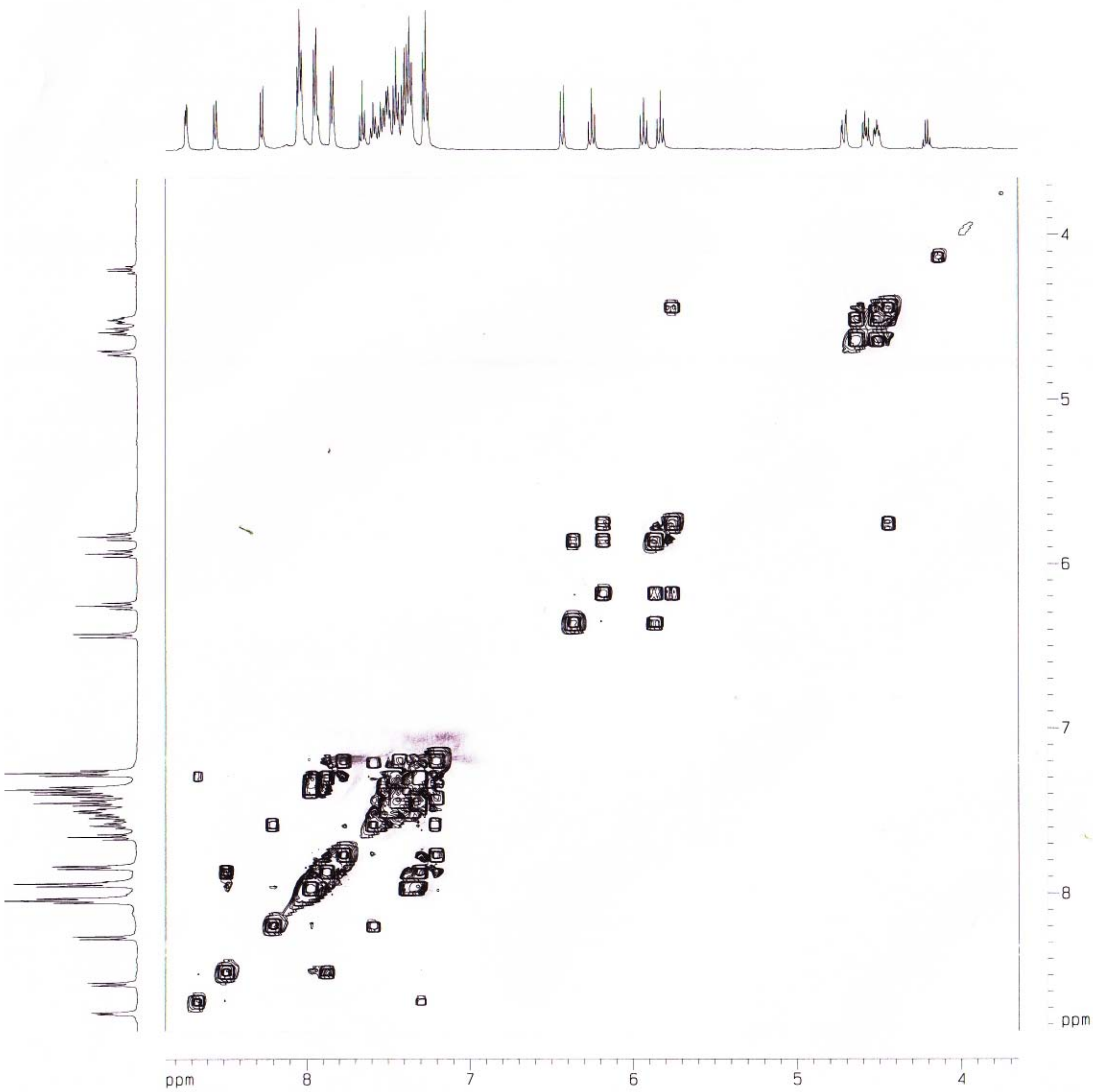
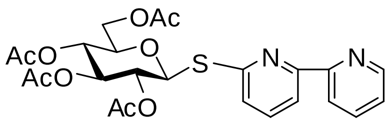
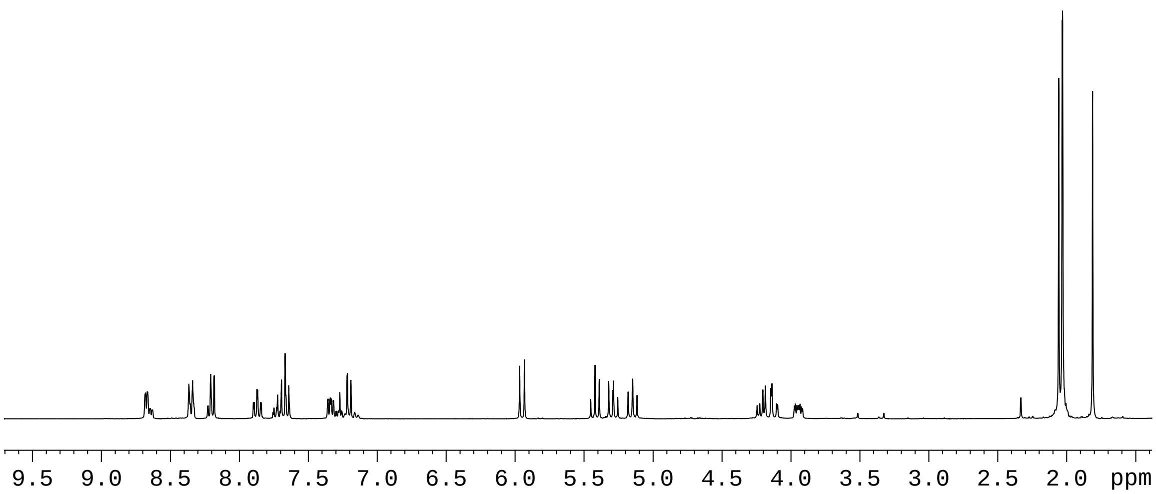
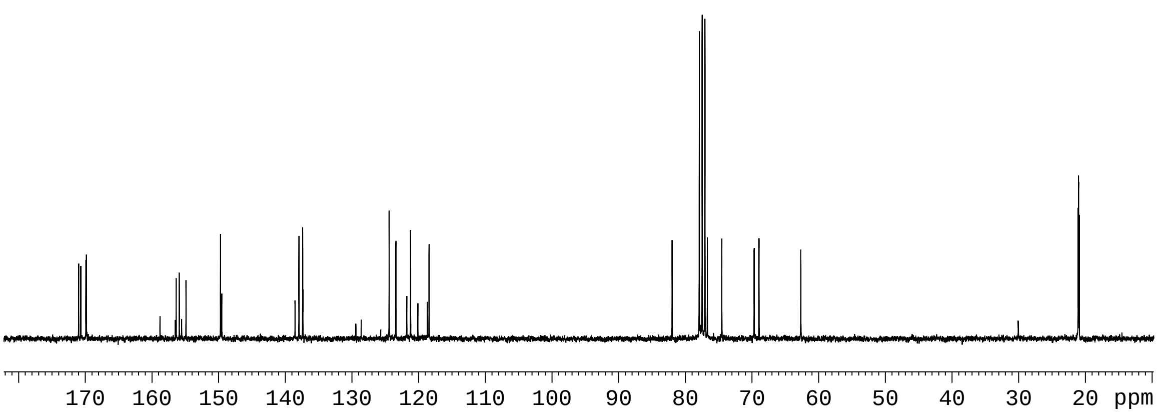



OAc
AcO
AcO
O
S
N
N
AcO

29


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm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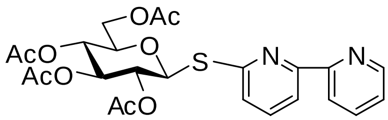

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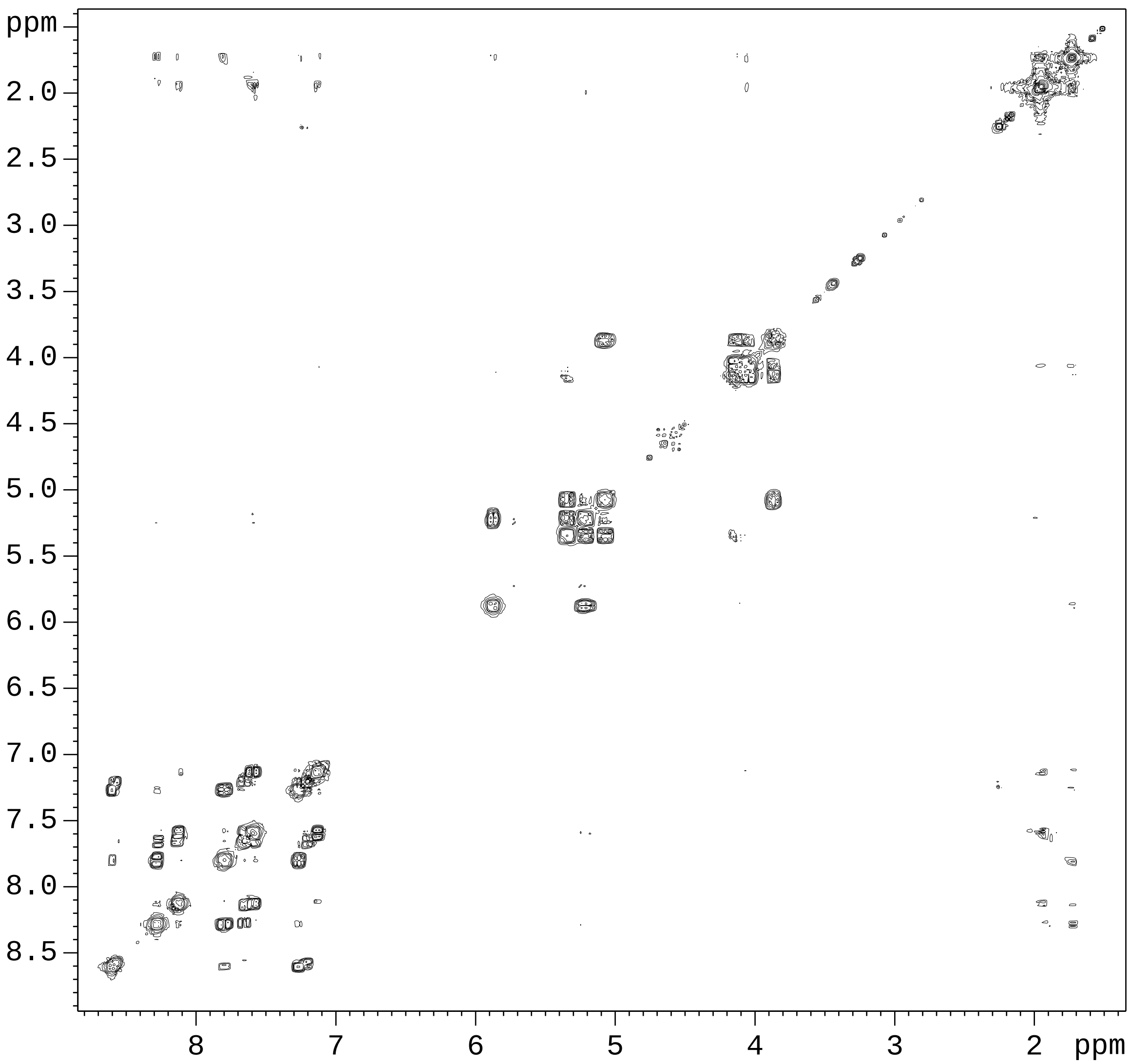
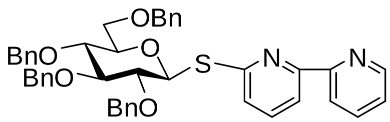
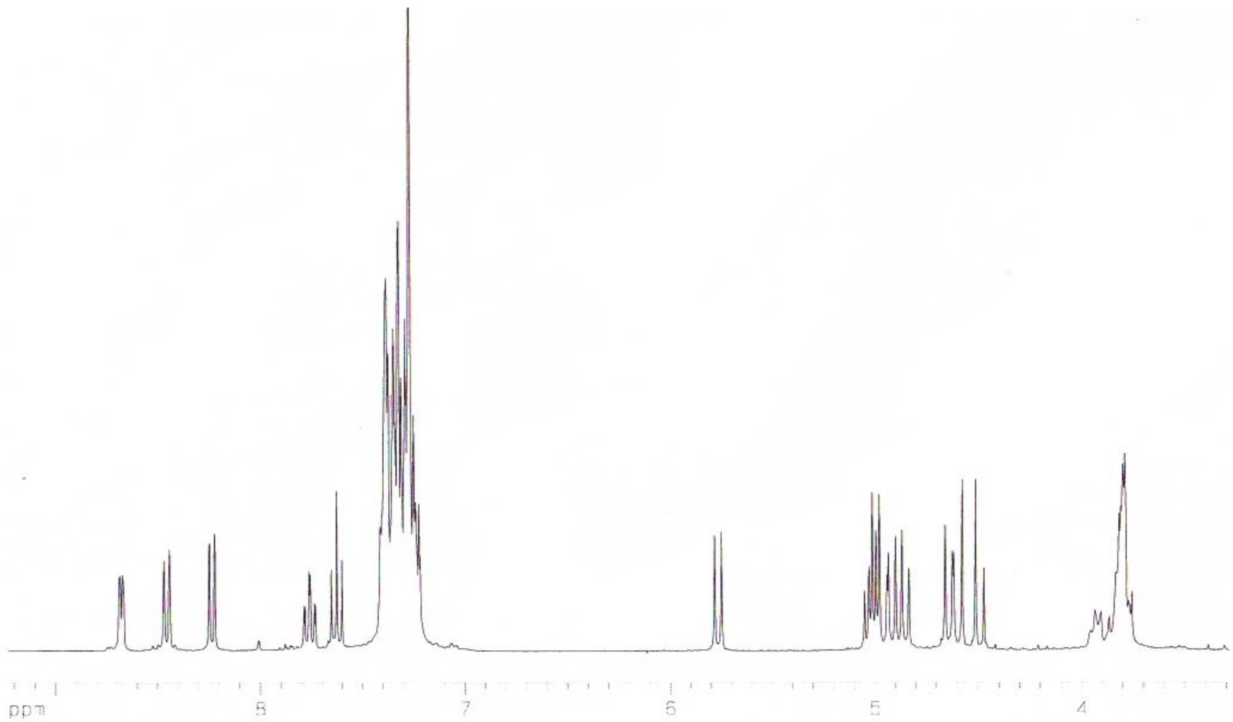


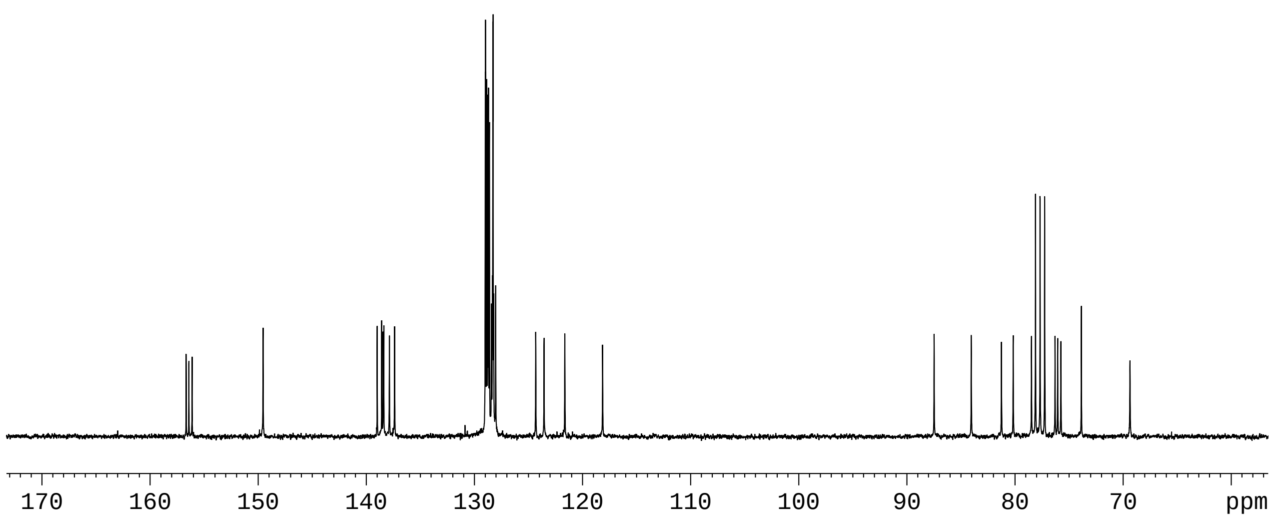


OBn
BnO
BnO
O
S
N
N
BnO

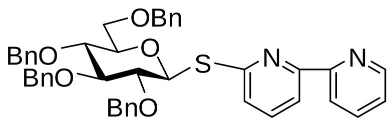
30



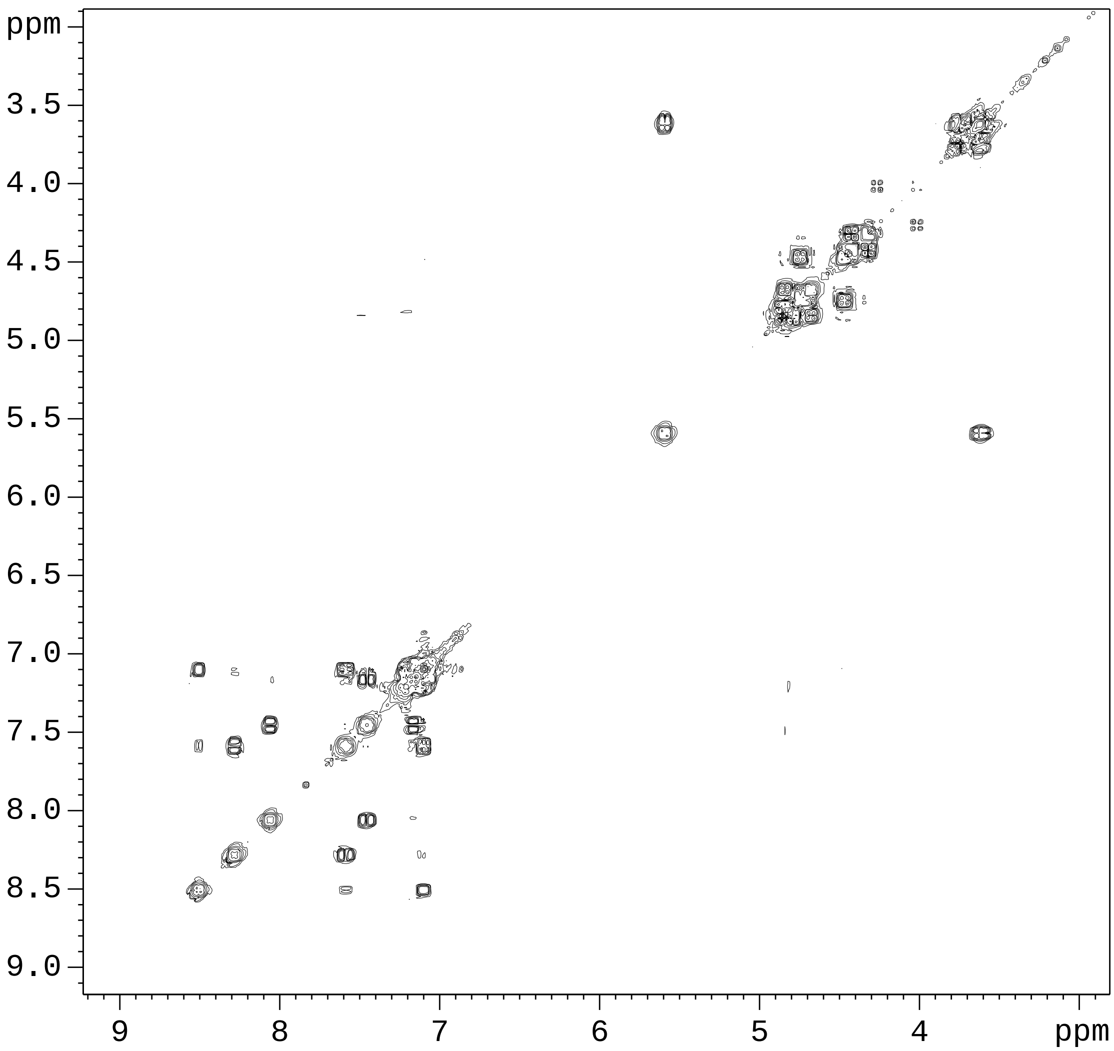
ppm
8
7
6
5
4



170 160 150 140 130 120 110 100 90 80 70 ppm


OBn
BnO
BnO
O
S
N
N
BnO

30


ppm
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8.0
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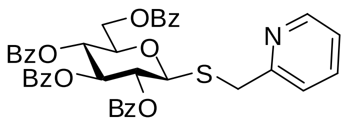
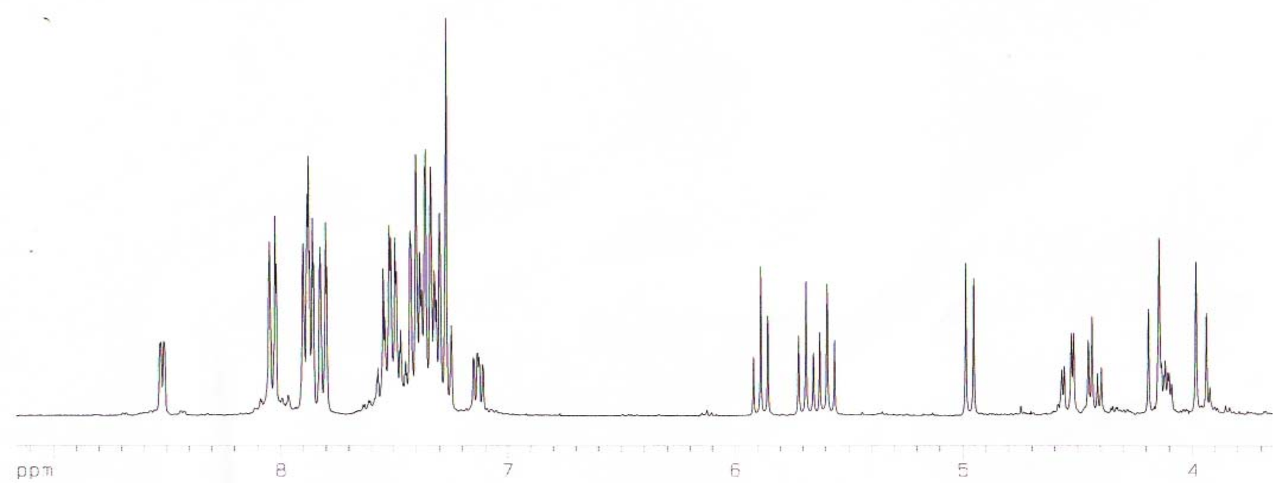
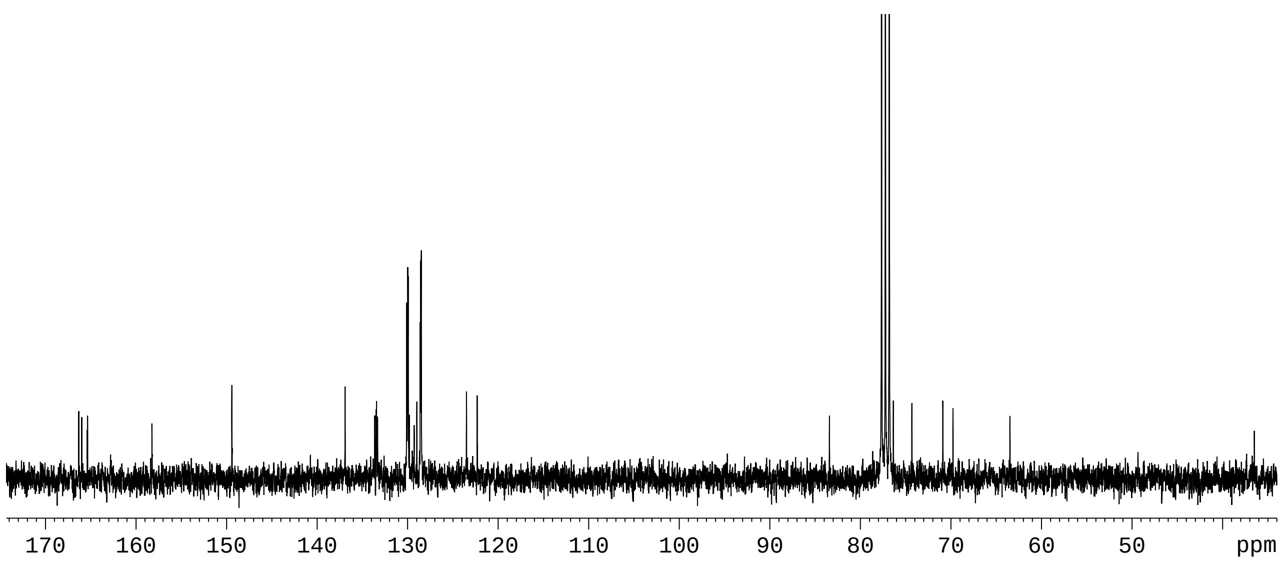
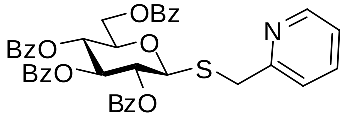
6
5
4
ppm


OBz
BzO
BzO
O
S
N
BzO

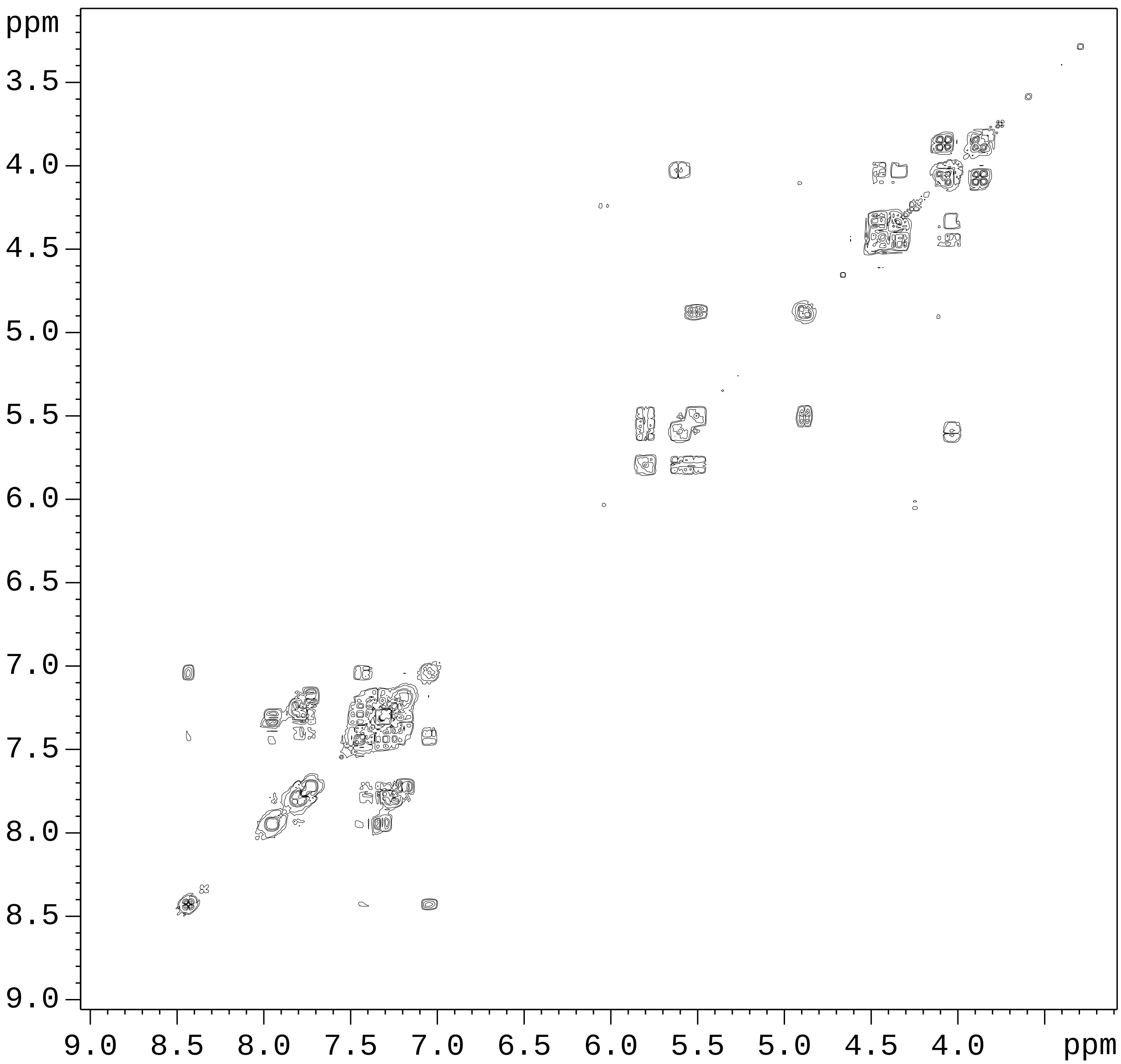
31

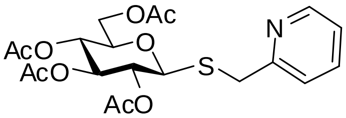

ppm
8
7
6
5
4


170
160
150
140
130
120
110
100
90
80
70
60
50
ppm

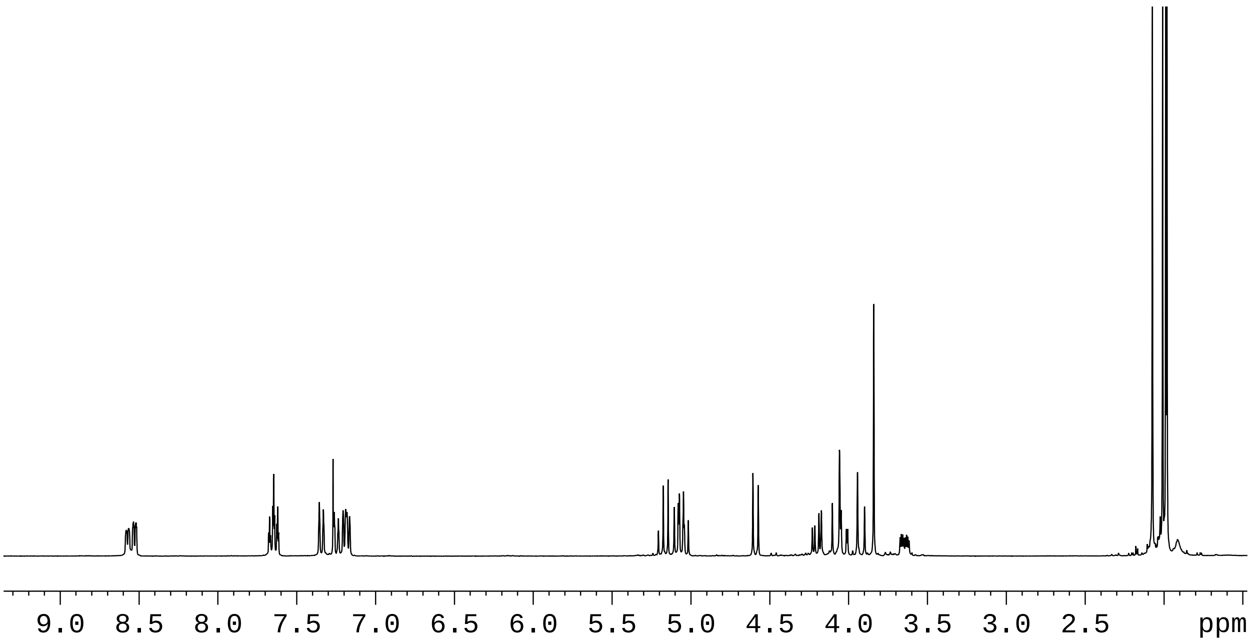

OBz
BzO
BzO
O
S
N
BzO

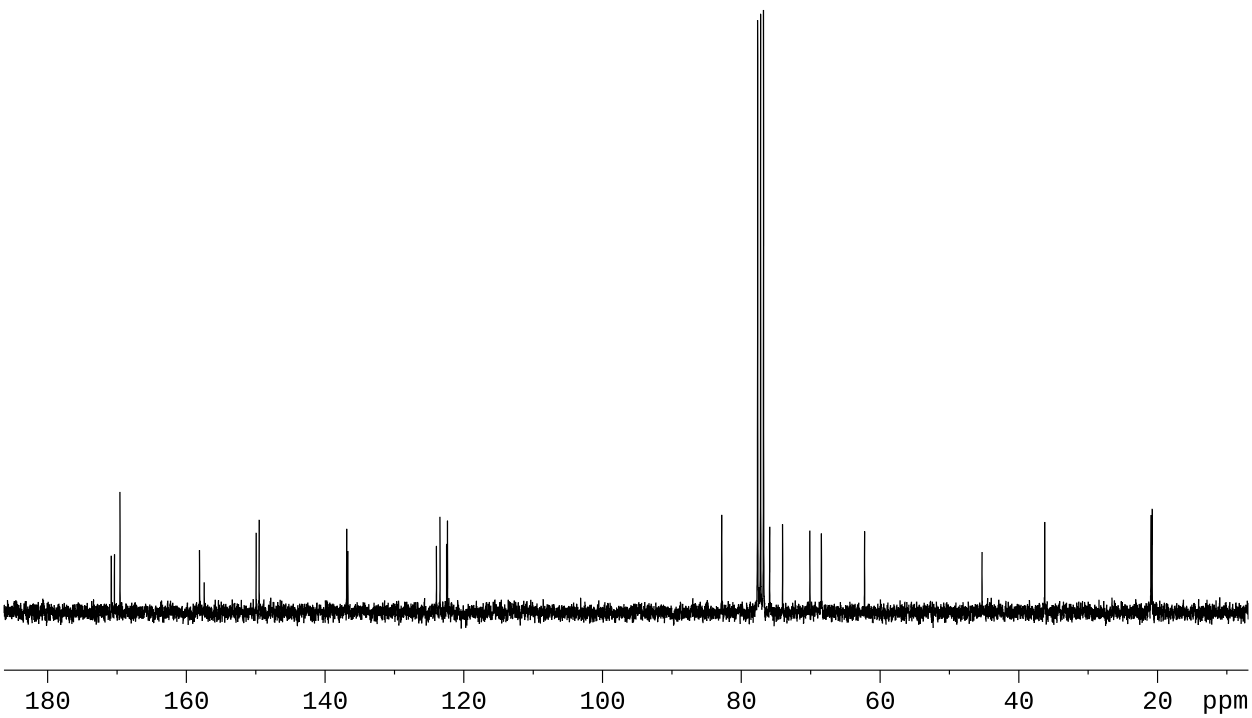
31

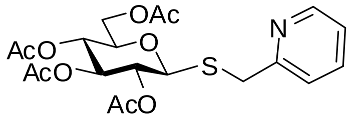

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


OAc
AcO
AcO
O
N
S
AcO

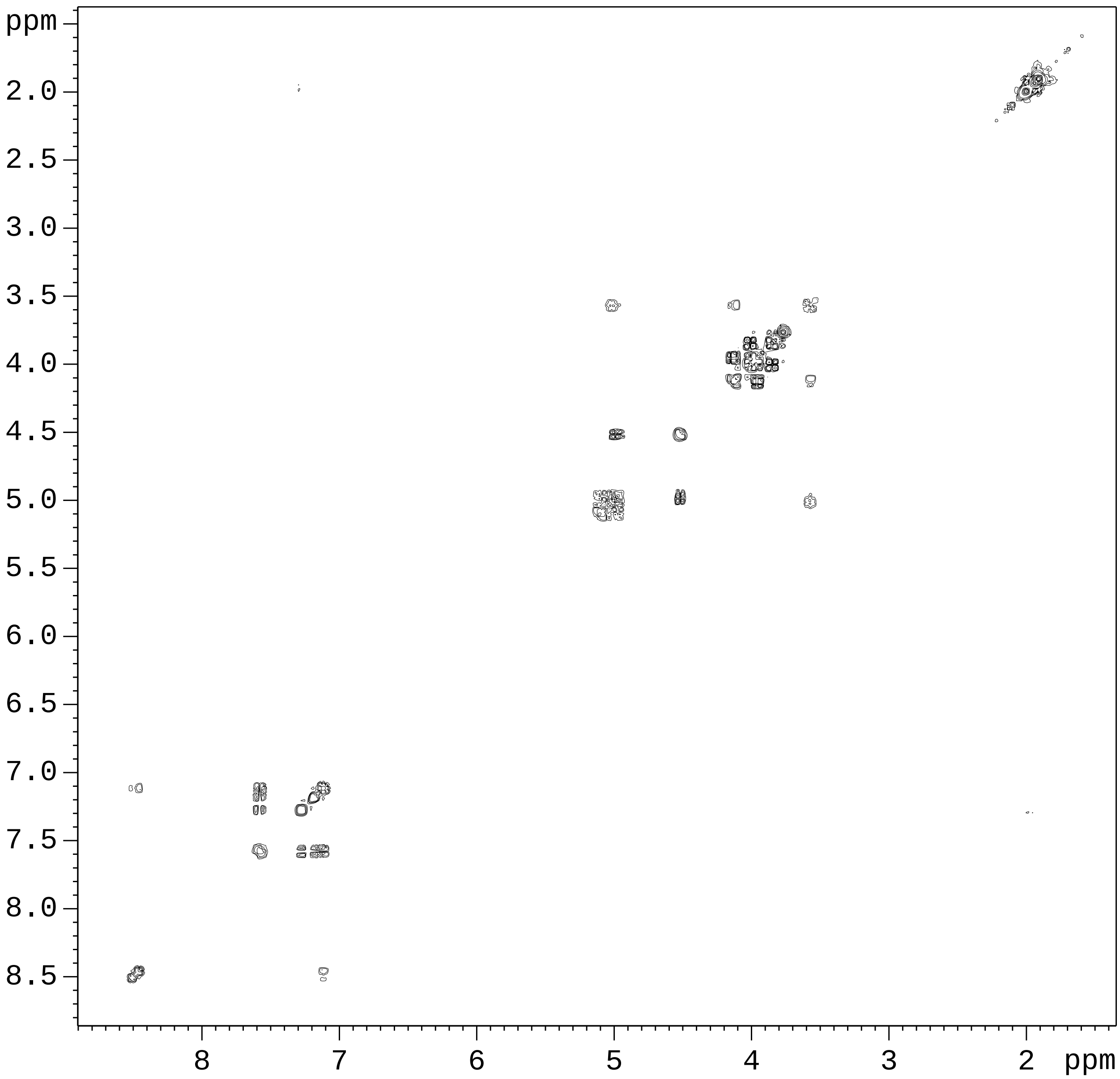
32

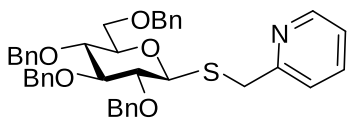

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm


180 160 140 120 100 80 60 40 20 ppm

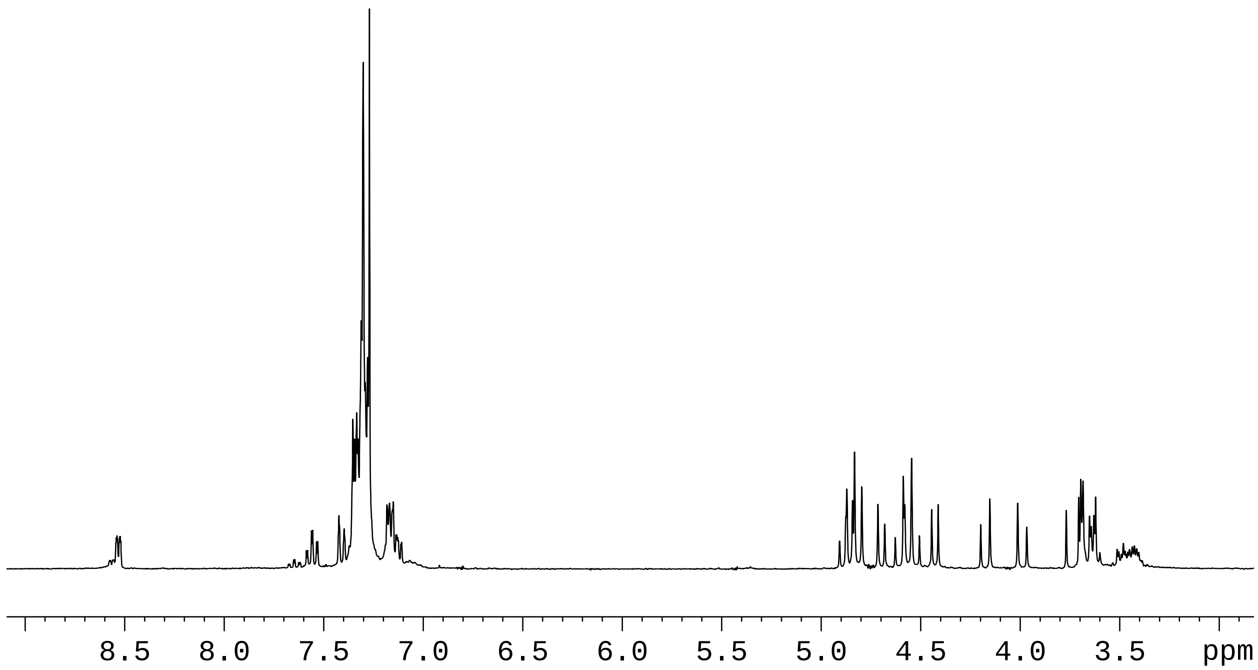

OAc
AcO
AcO
AcO
O
S
N

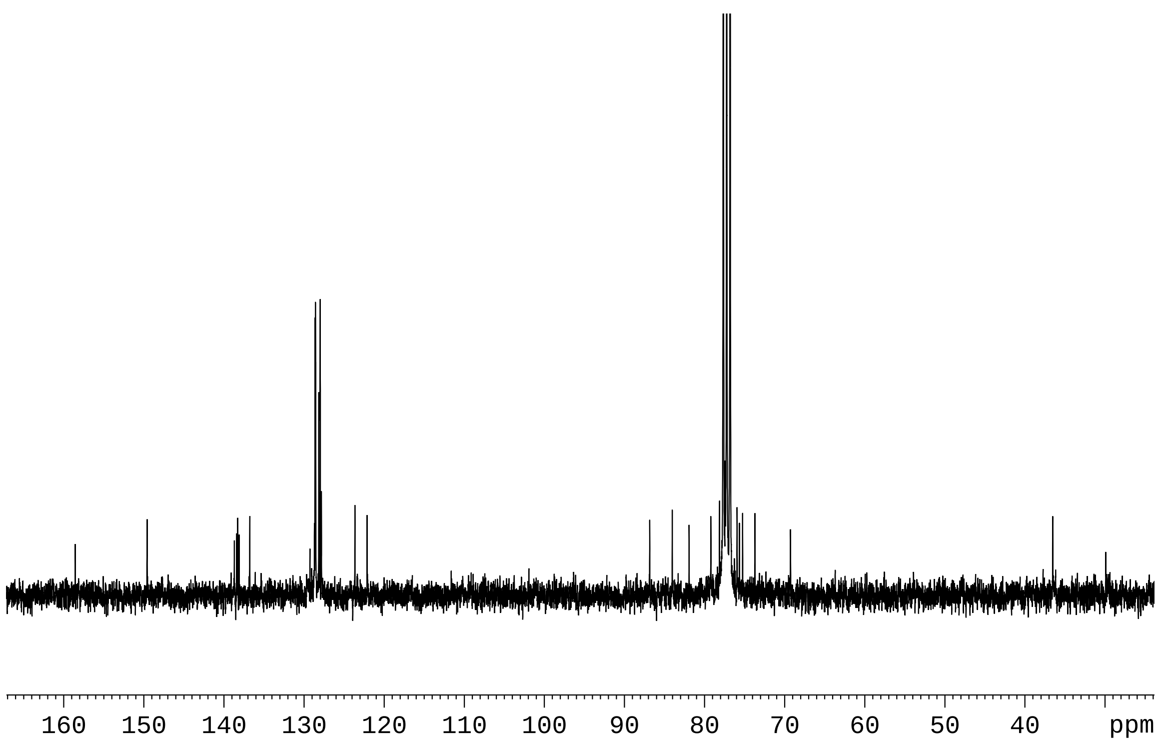
32

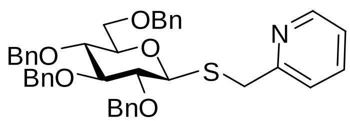

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8
7
6
5
4
3
2
ppm


OBn
O
BnO
BnO
BnO
S
N

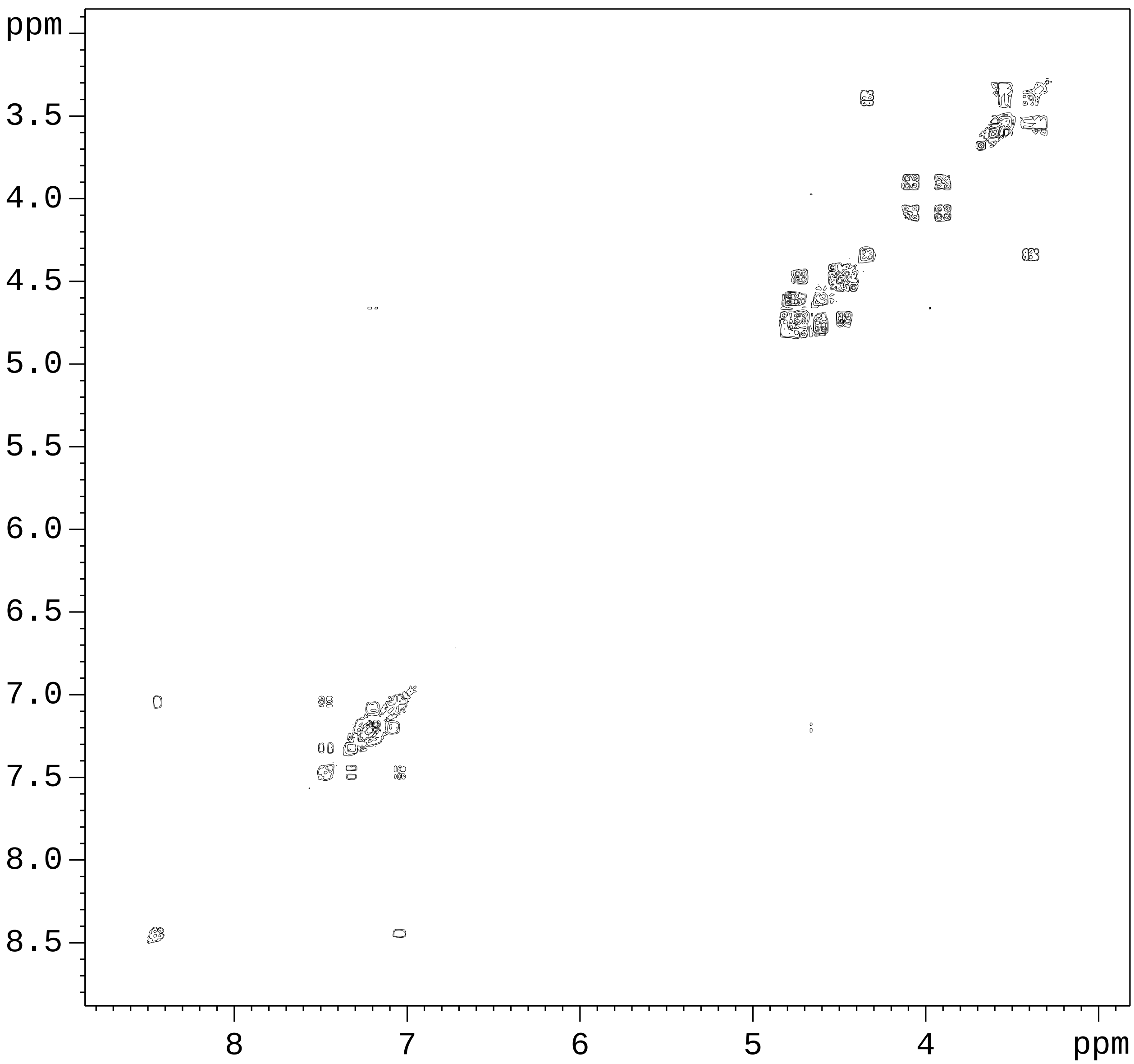
33

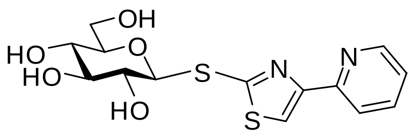

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

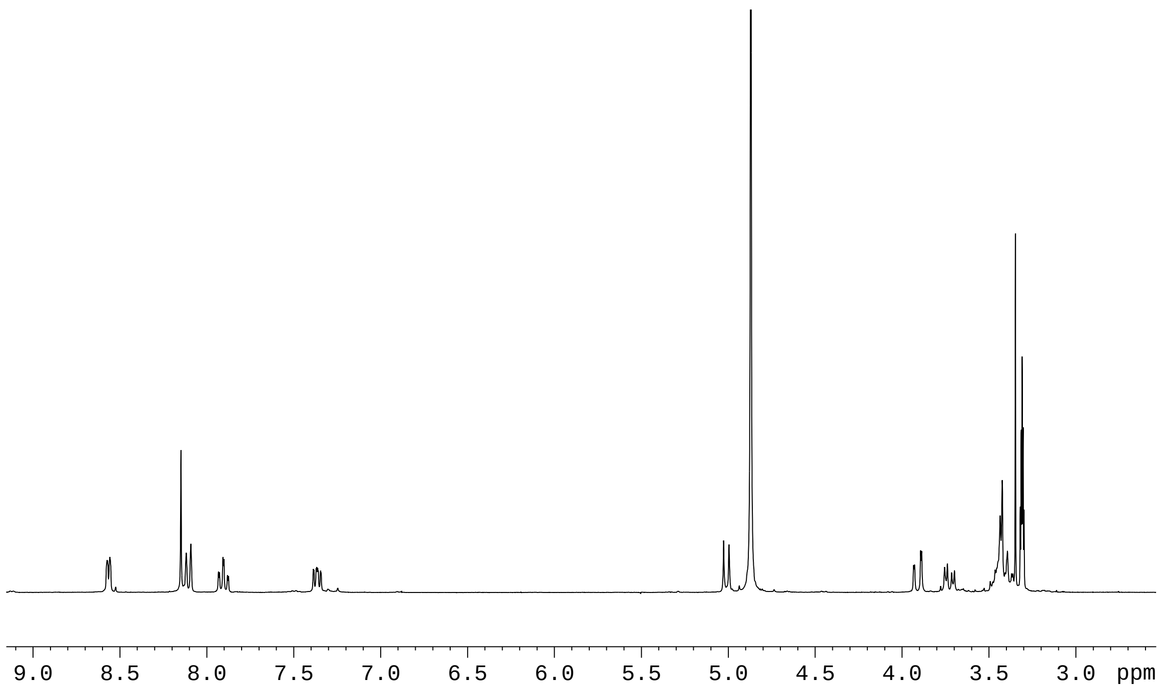


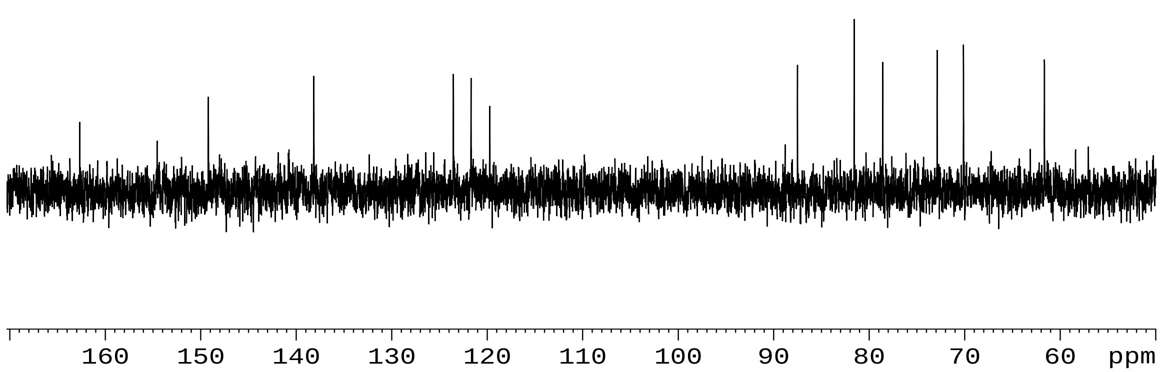
33

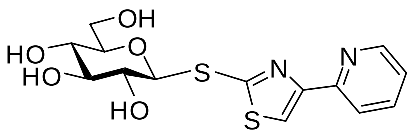



OH
HO
O
HO
S
N
N
HO
S

34

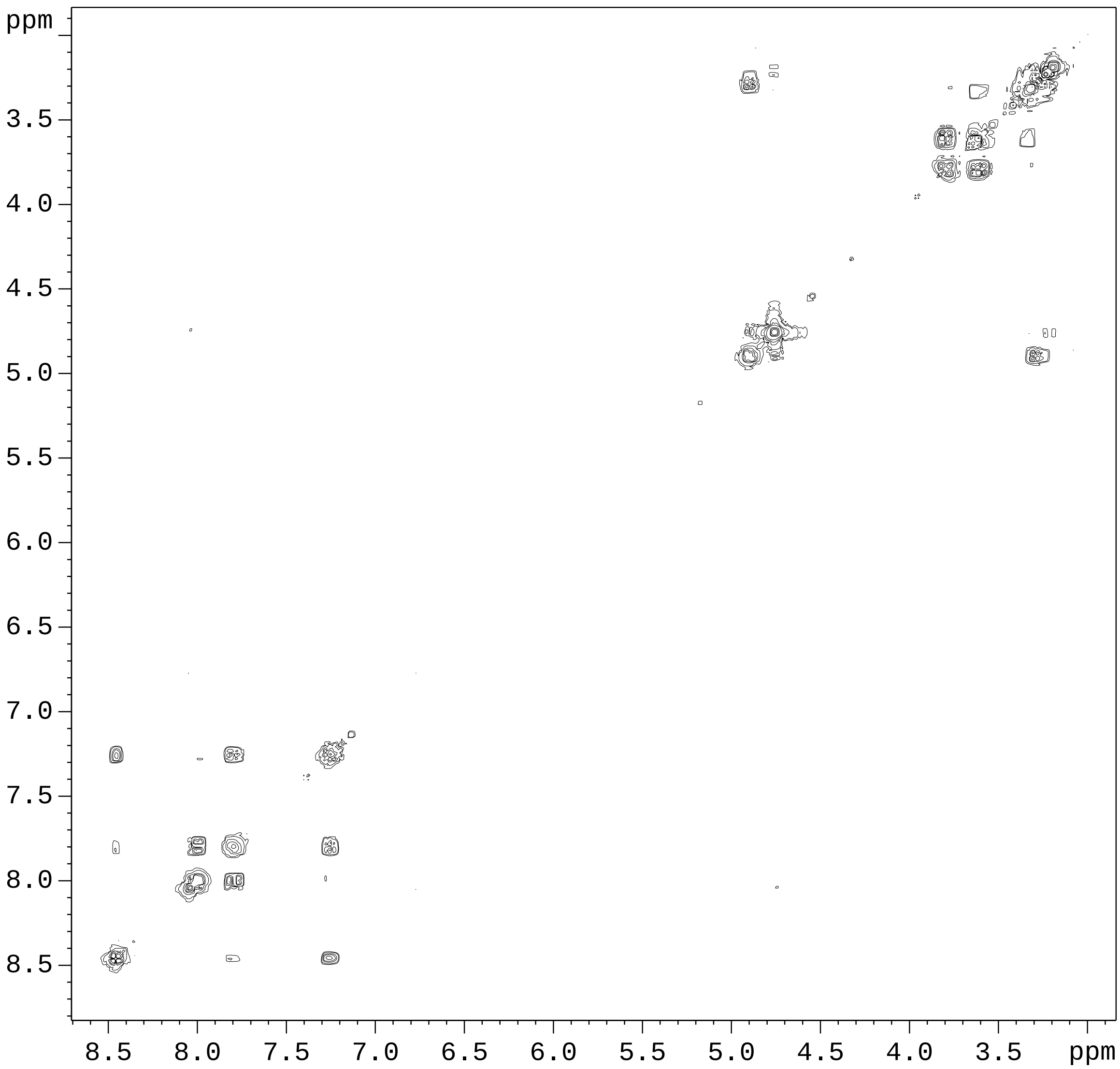

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


160
150
140
130
120
110
100
90
80
70
60
ppm



OH
HO
O
HO
S
N
N
HO
S

34



ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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7.5
7.0
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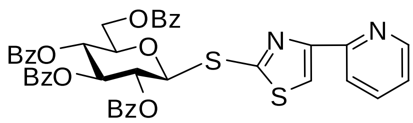
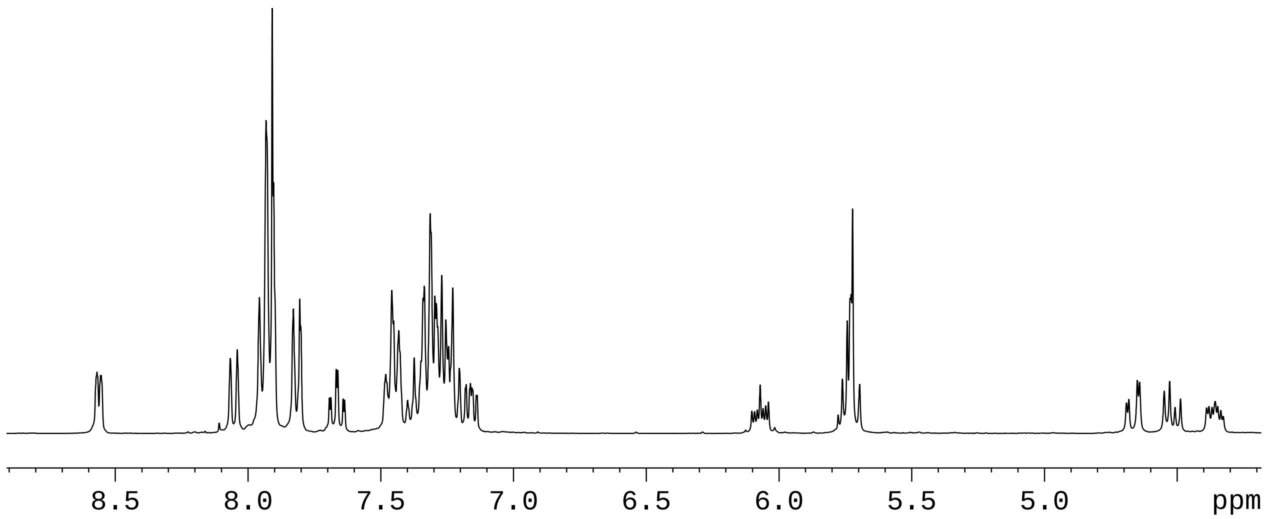
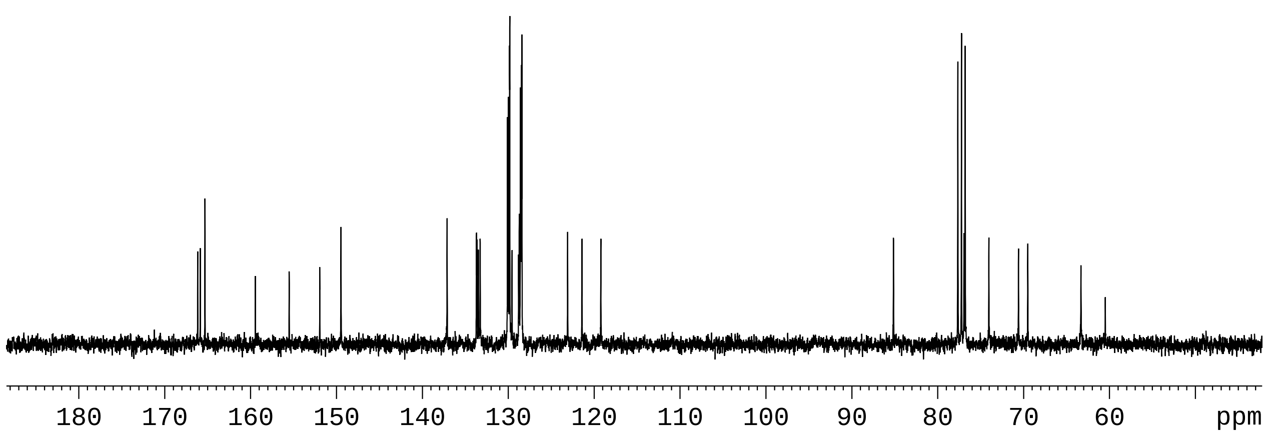
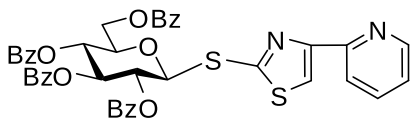
5.0
4.5
4.0
3.5
ppm


OBz
BzO
BzO
BzO
O
S
N
S
N

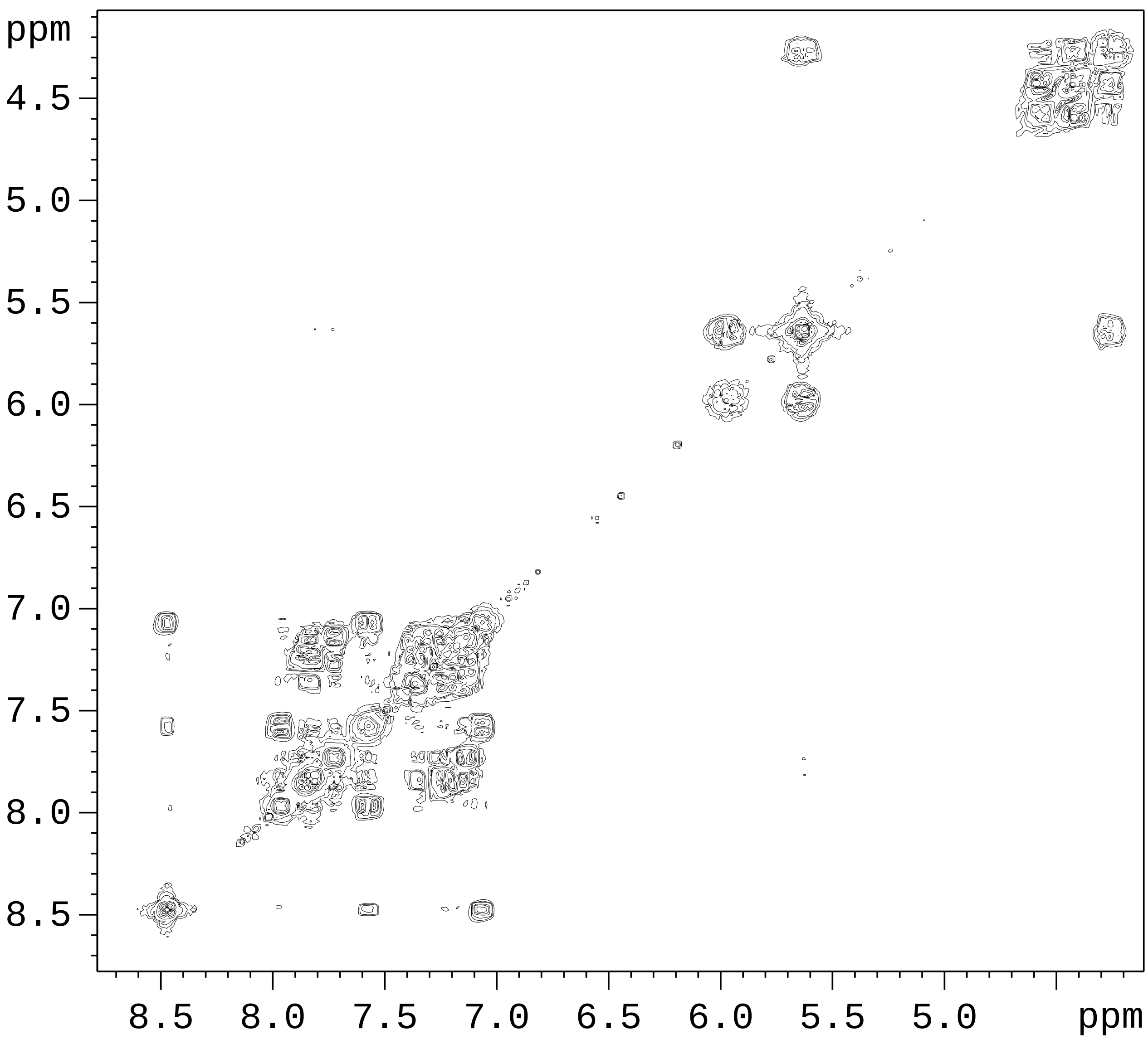
35

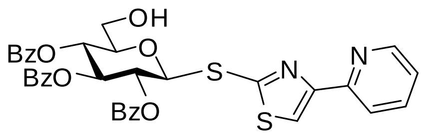

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


180
170
160
150
140
130
120
110
100
90
80
70
60
ppm

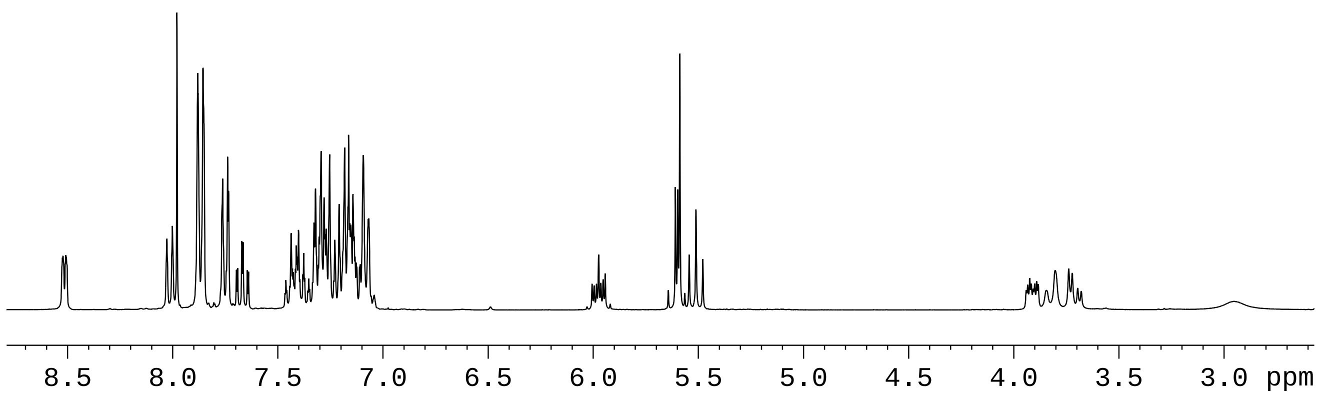

OBz
BzO
BzO
BzO
O
S
N
S
N

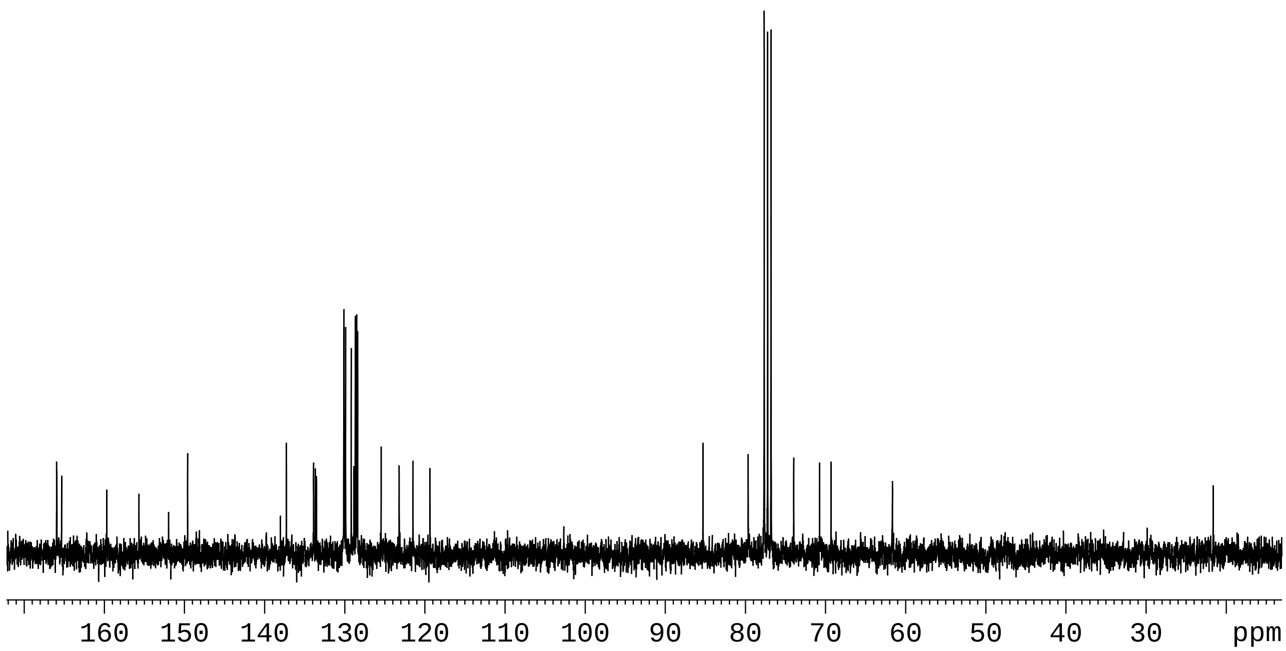
35

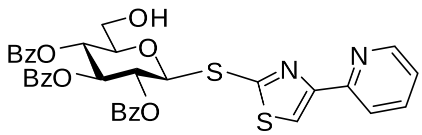

ppm
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


OH
BzO
O
BzO
S
N
N
BzO
S

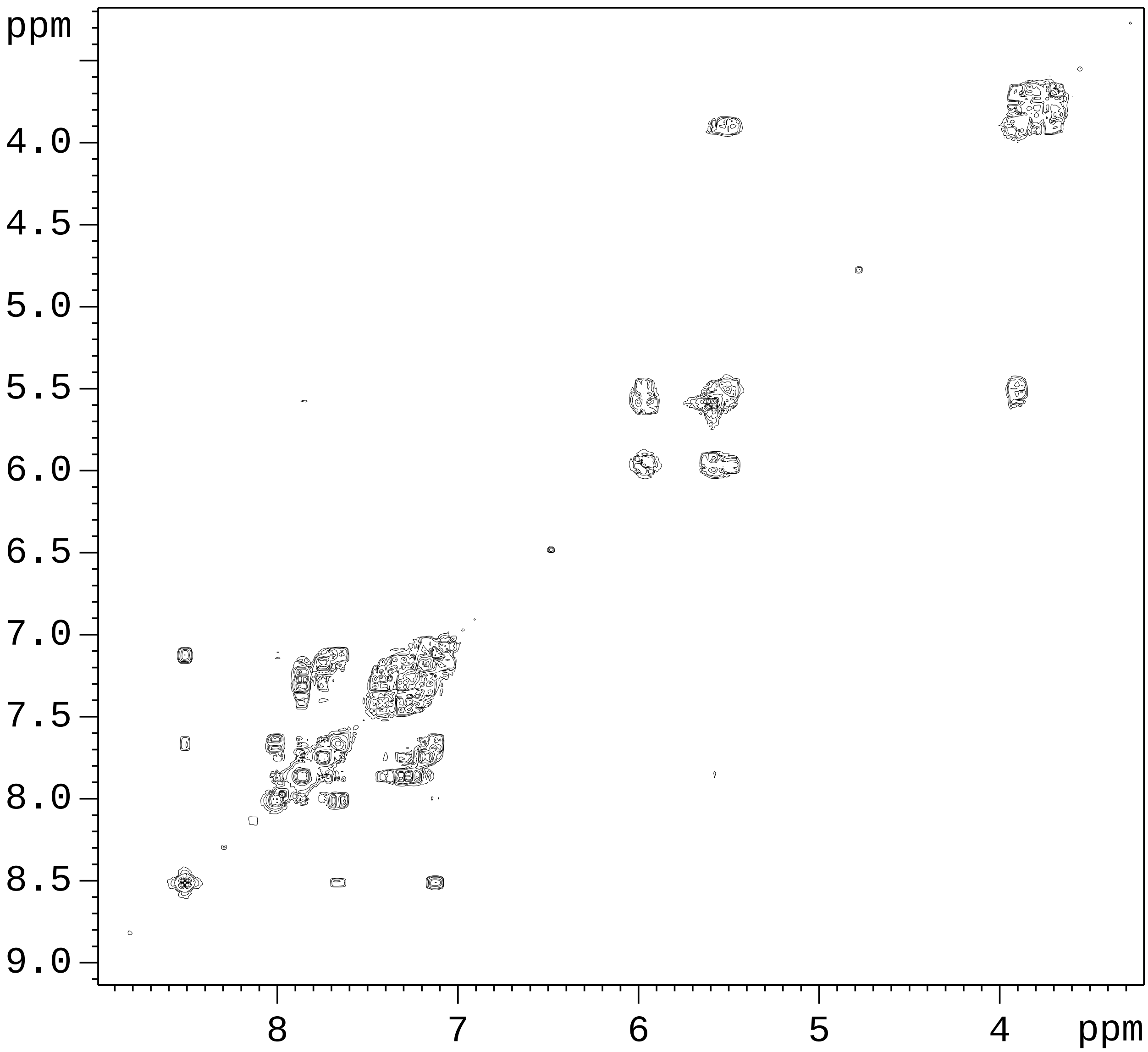
41

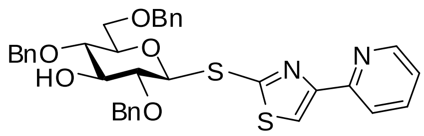

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm


160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

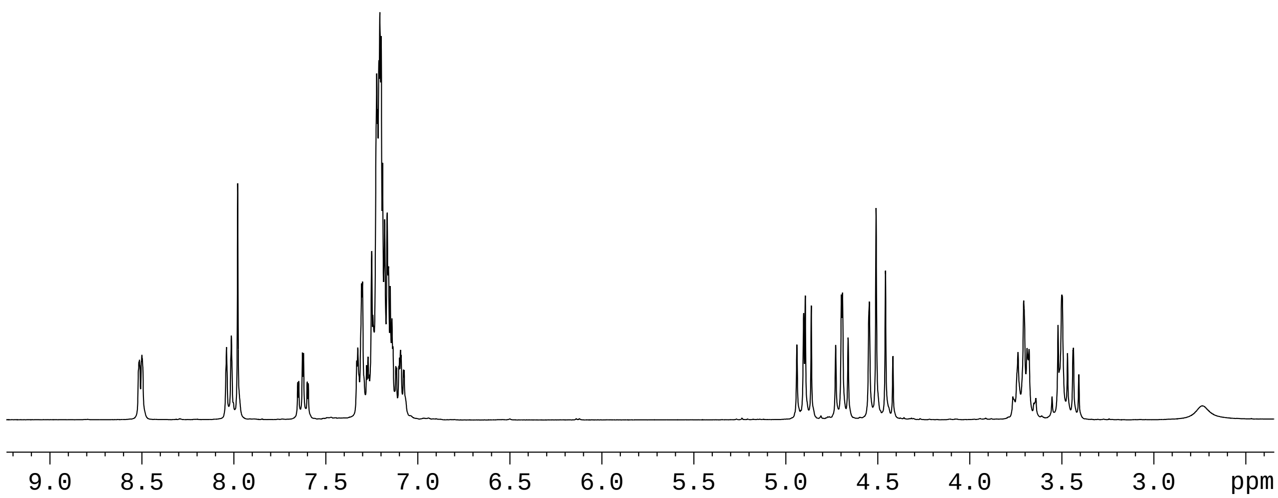


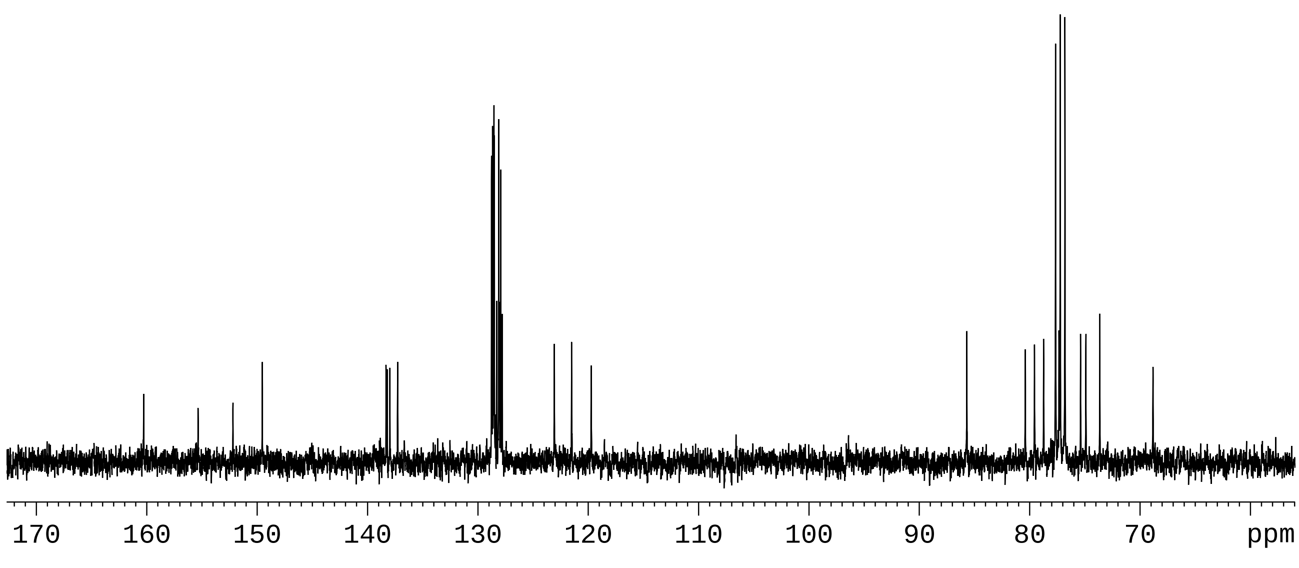
41

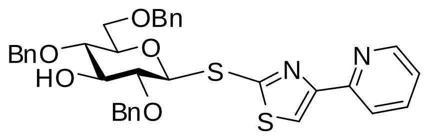



OBn
BnO
O
HO
S
N
N
BnO
S

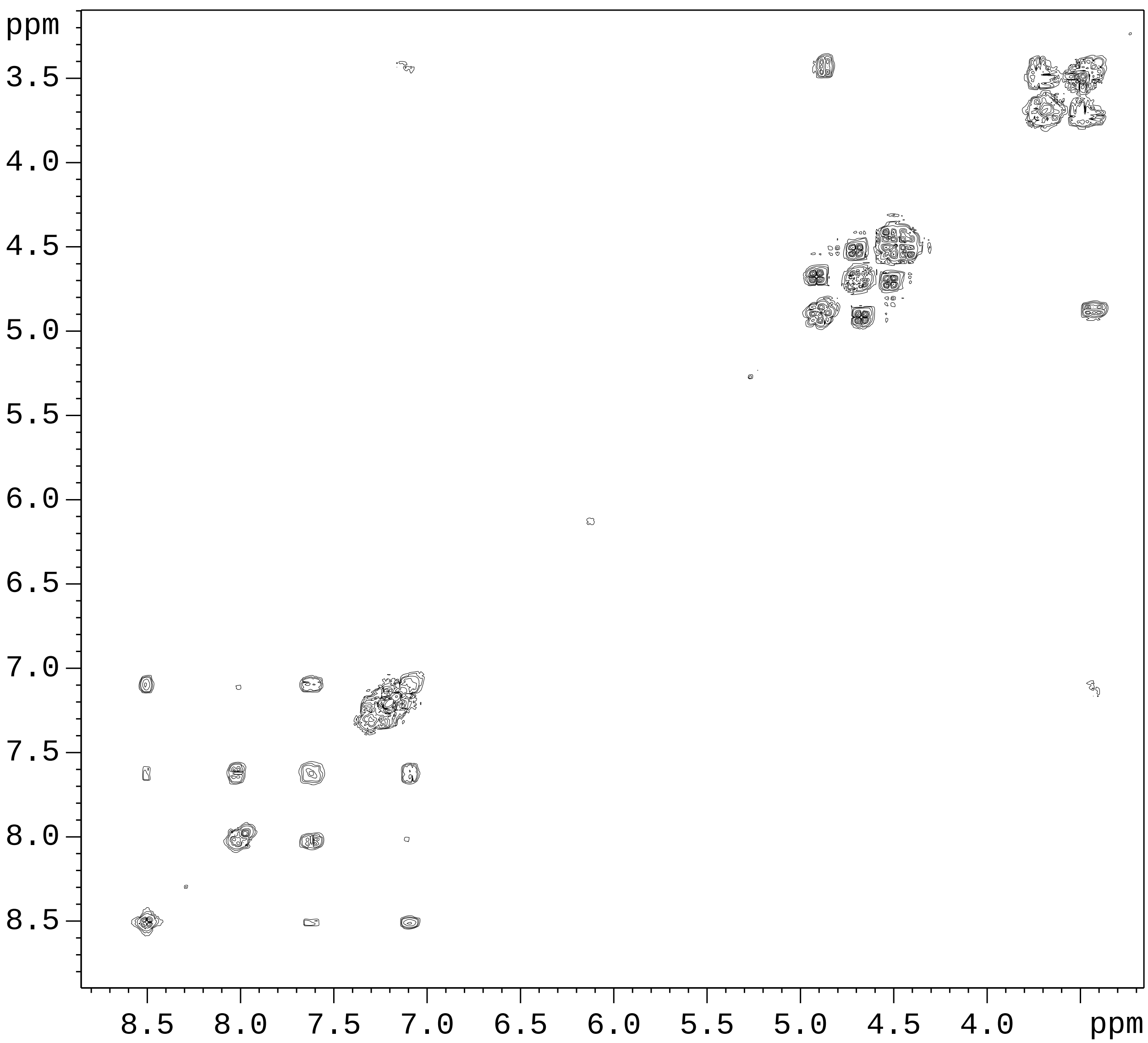
43

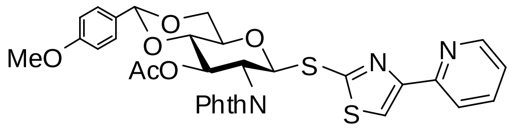

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm


170 160 150 140 130 120 110 100 90 80 70 ppm

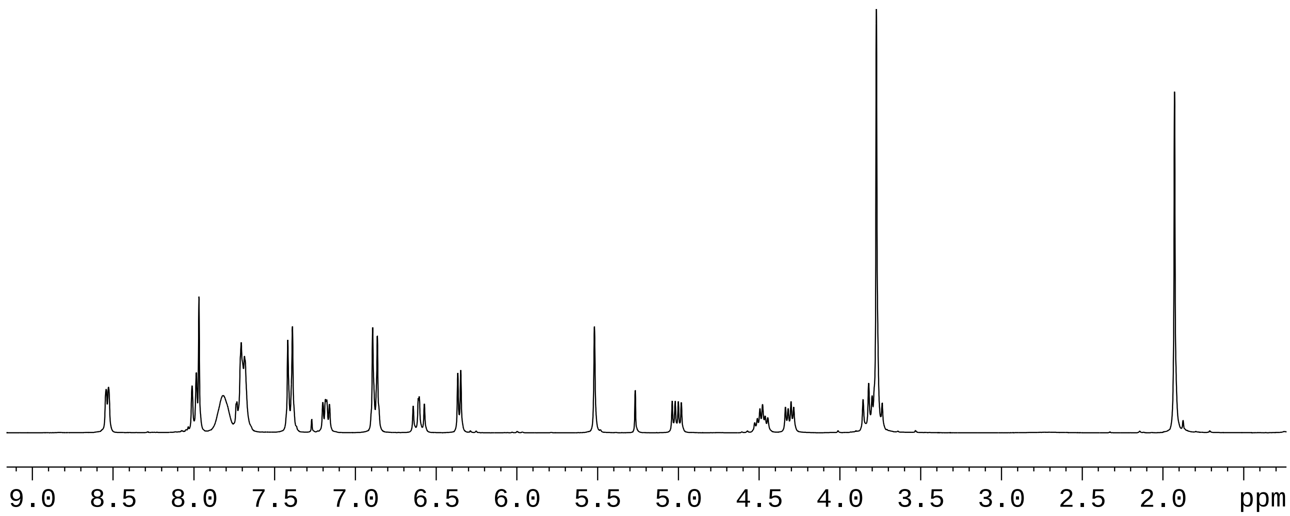

OBn
BnO
O
HO
S
N
N
BnO
S

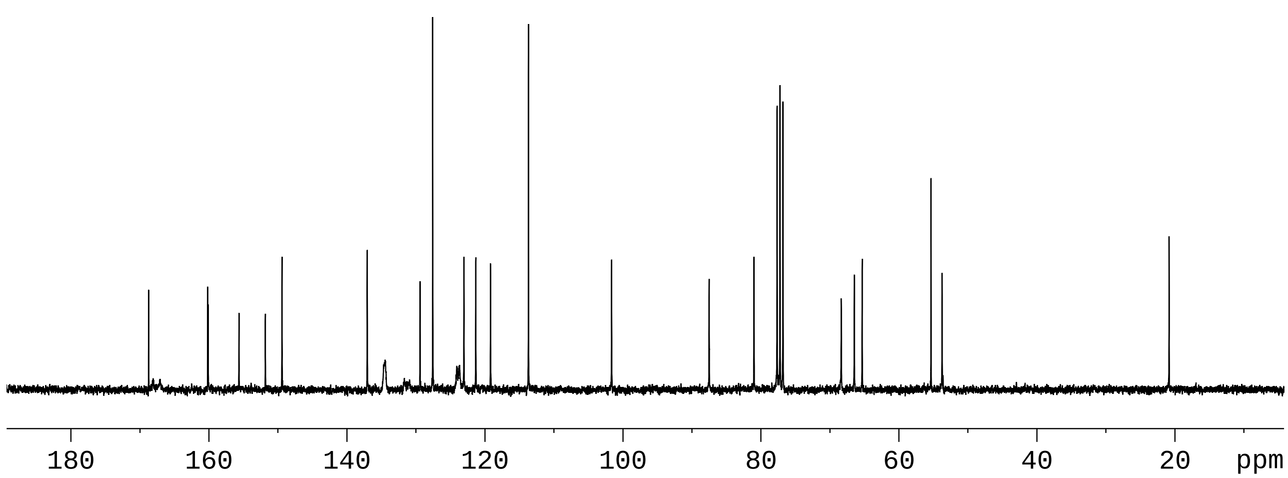
43

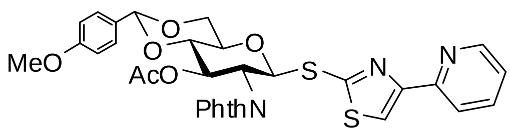

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


MeO
O
O
O
AcO
S
N
N
S
PhthN

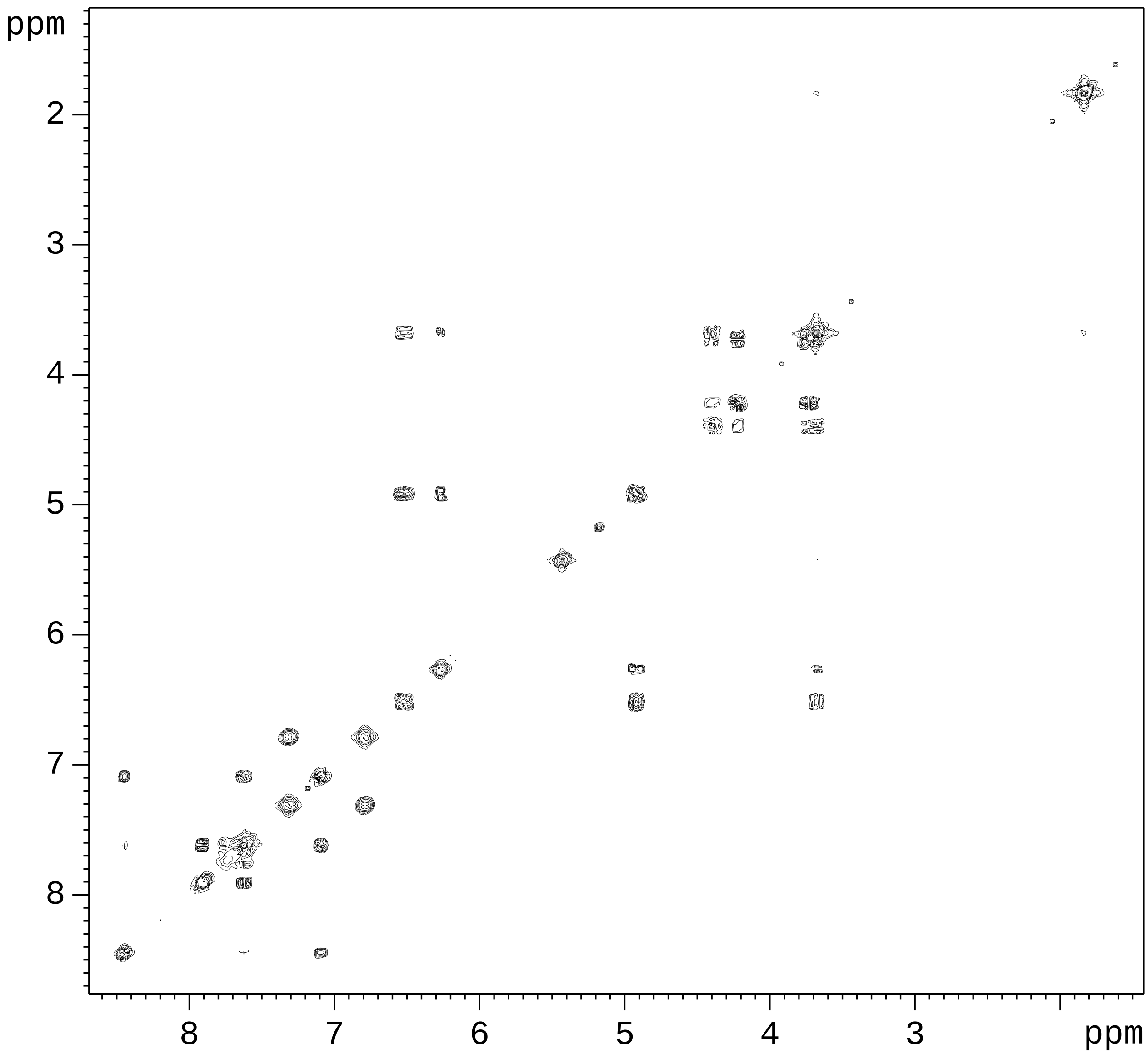
45

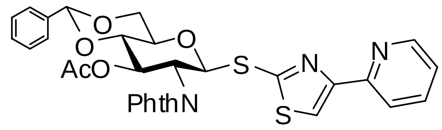

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


180
160
140
120
100
80
60
40
20
ppm

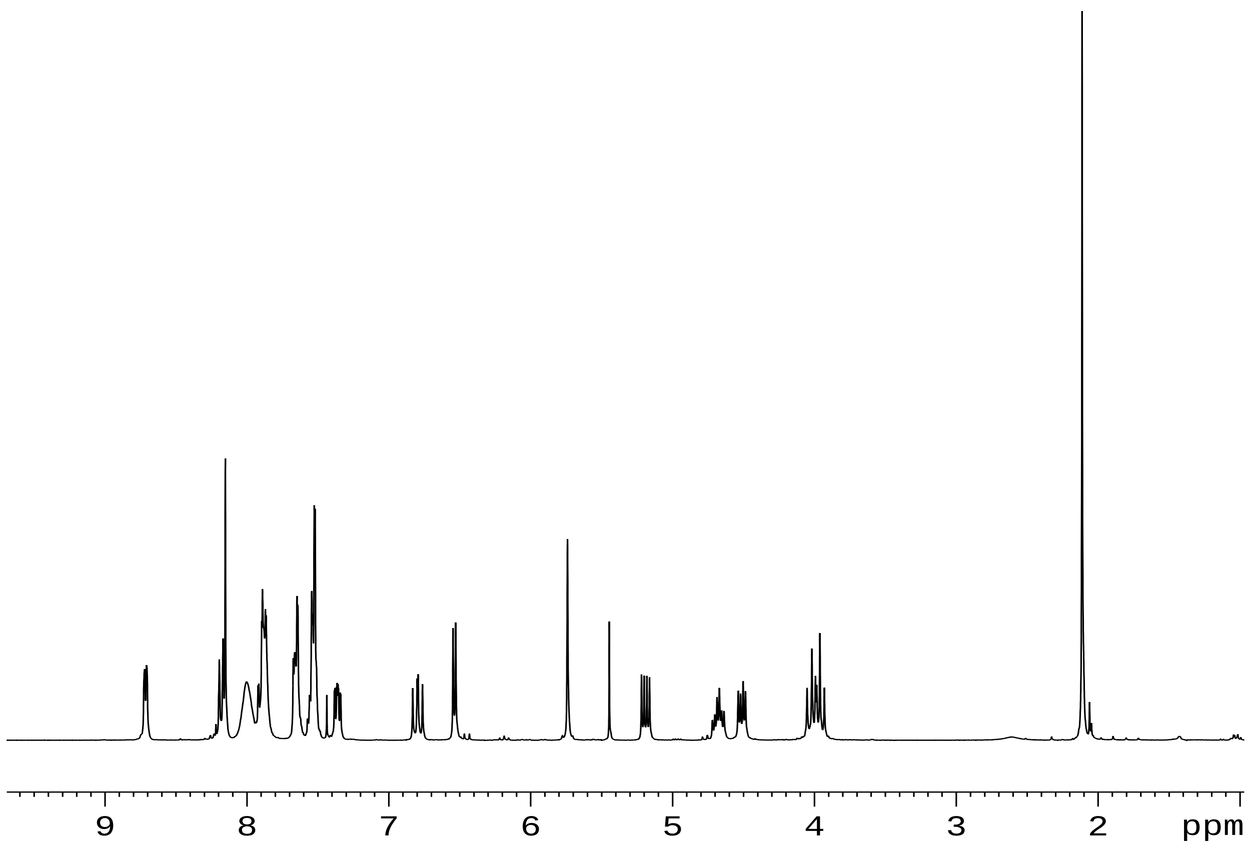


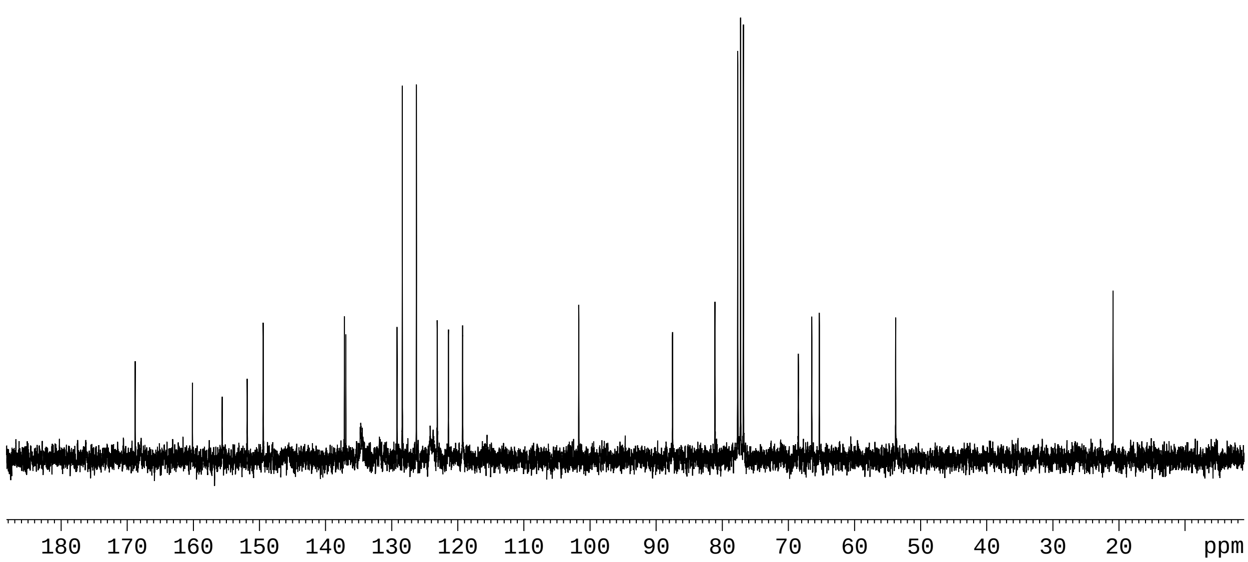
45

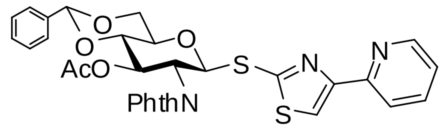



O
O
AcO
PhthN
S
N
S
N

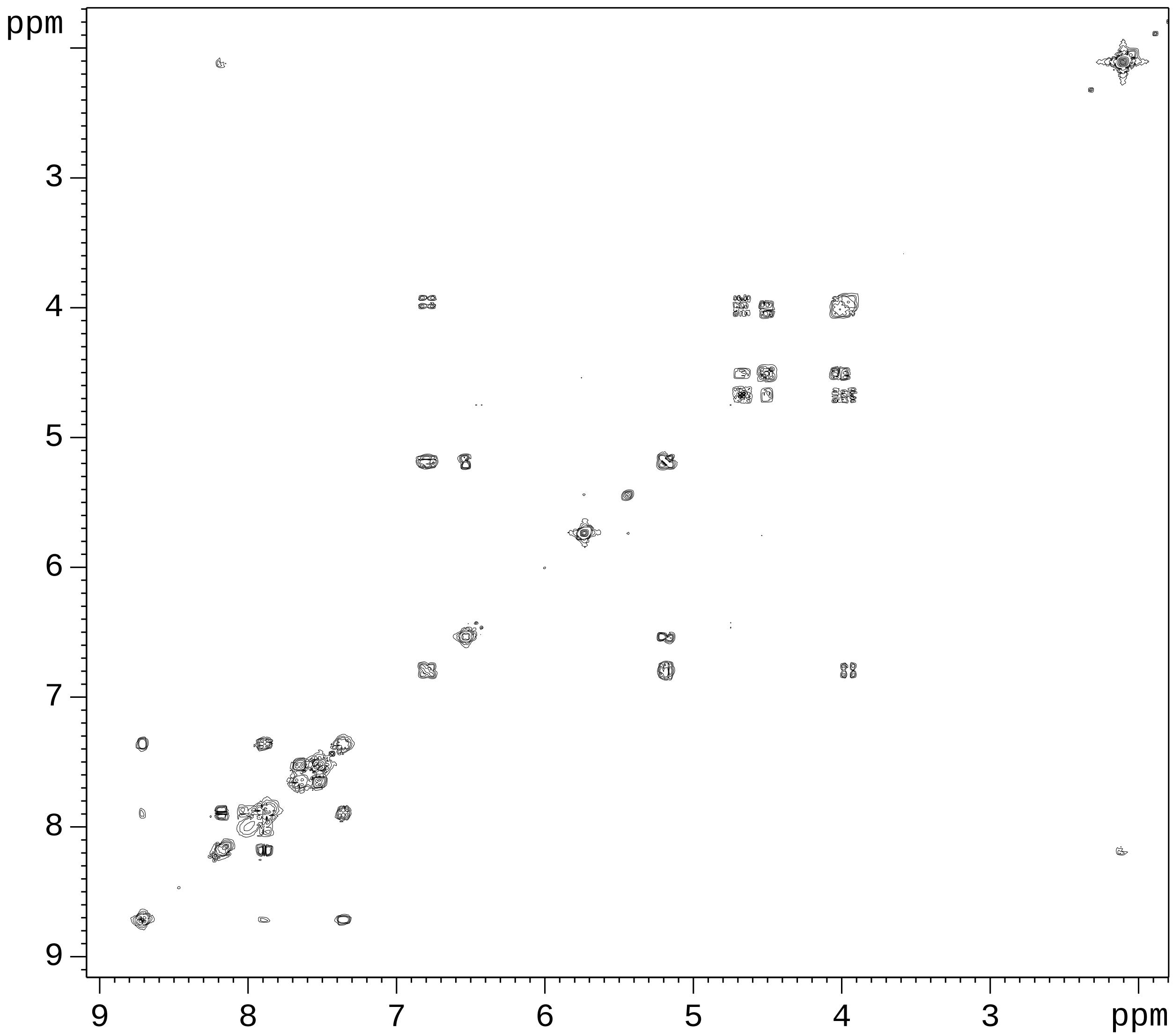
47

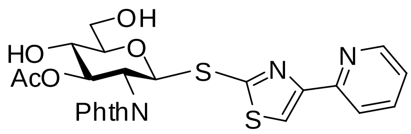

9
8
7
6
5
4
3
2
ppm


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

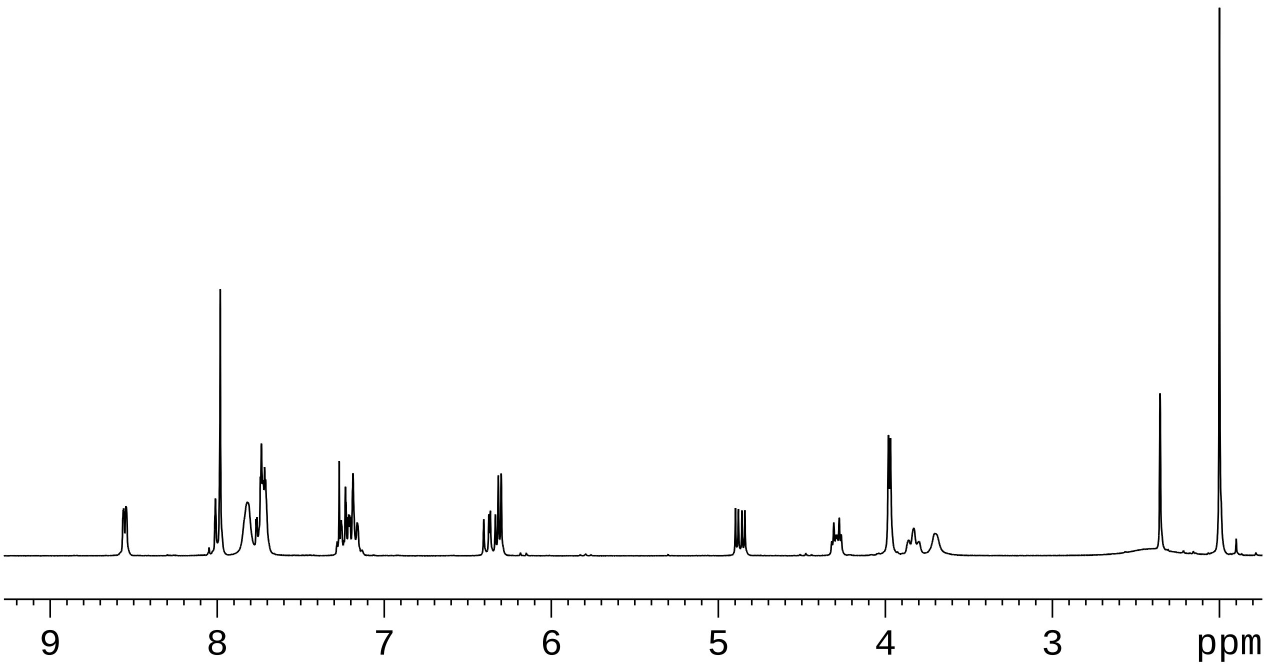


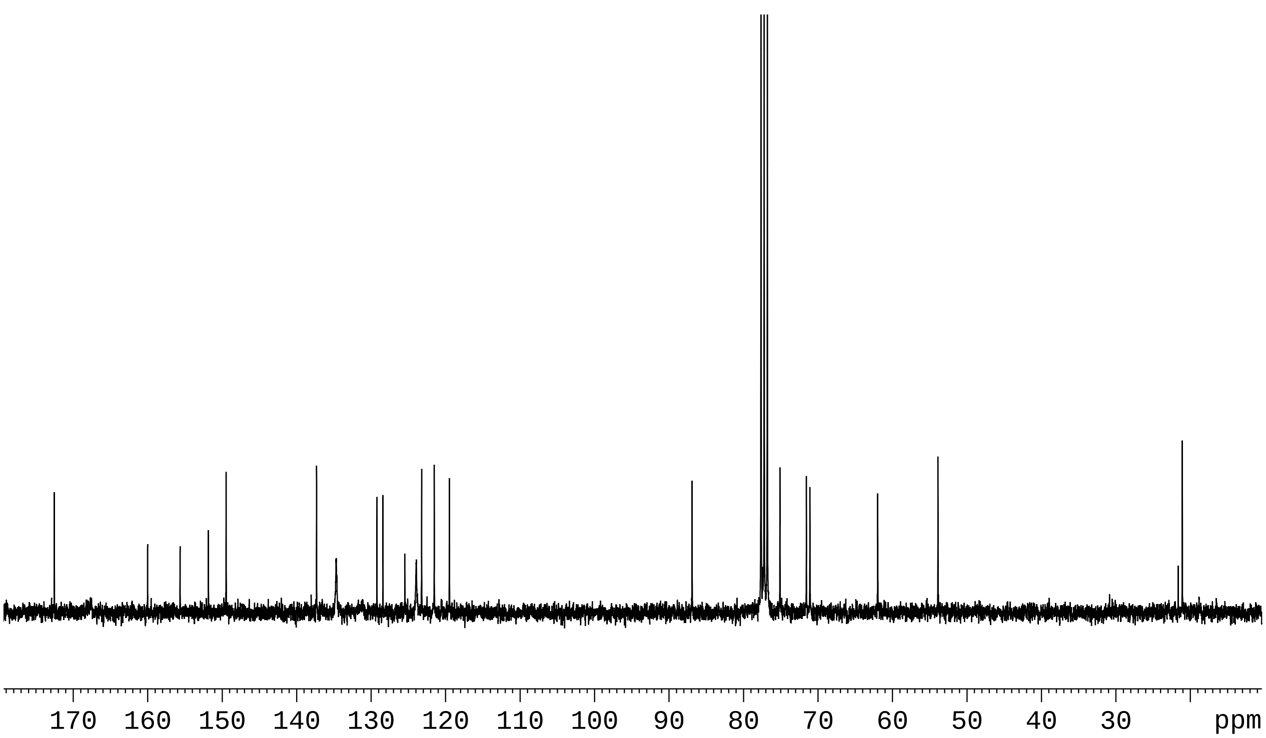
47

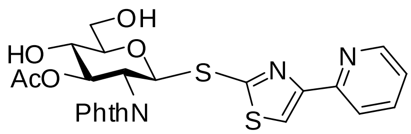



OH
HO
O
AcO
S
N
N
PhthN
S

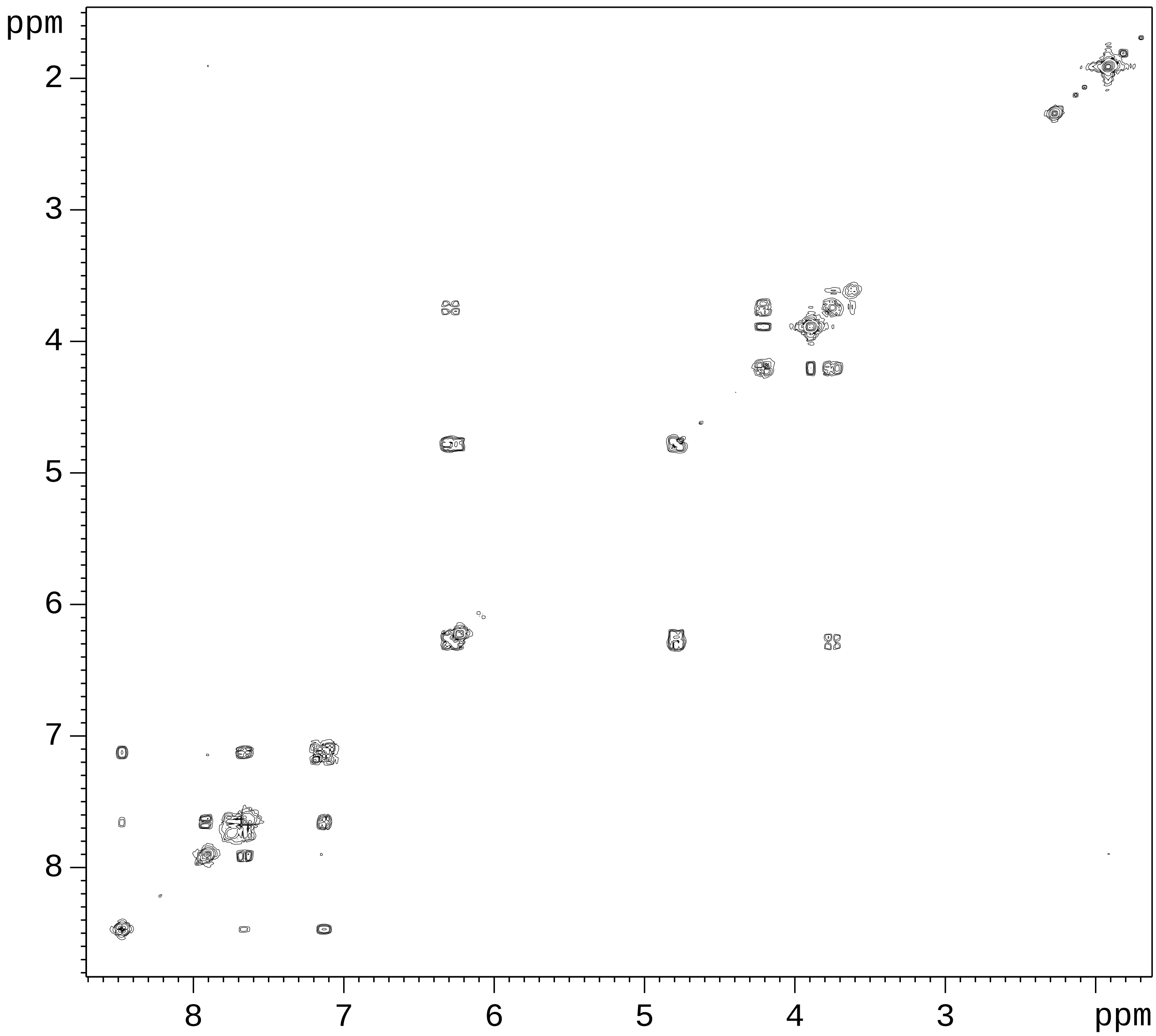
48

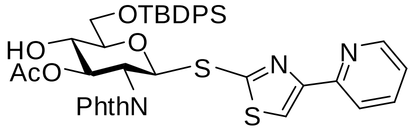

9
8
7
6
5
4
3
ppm


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

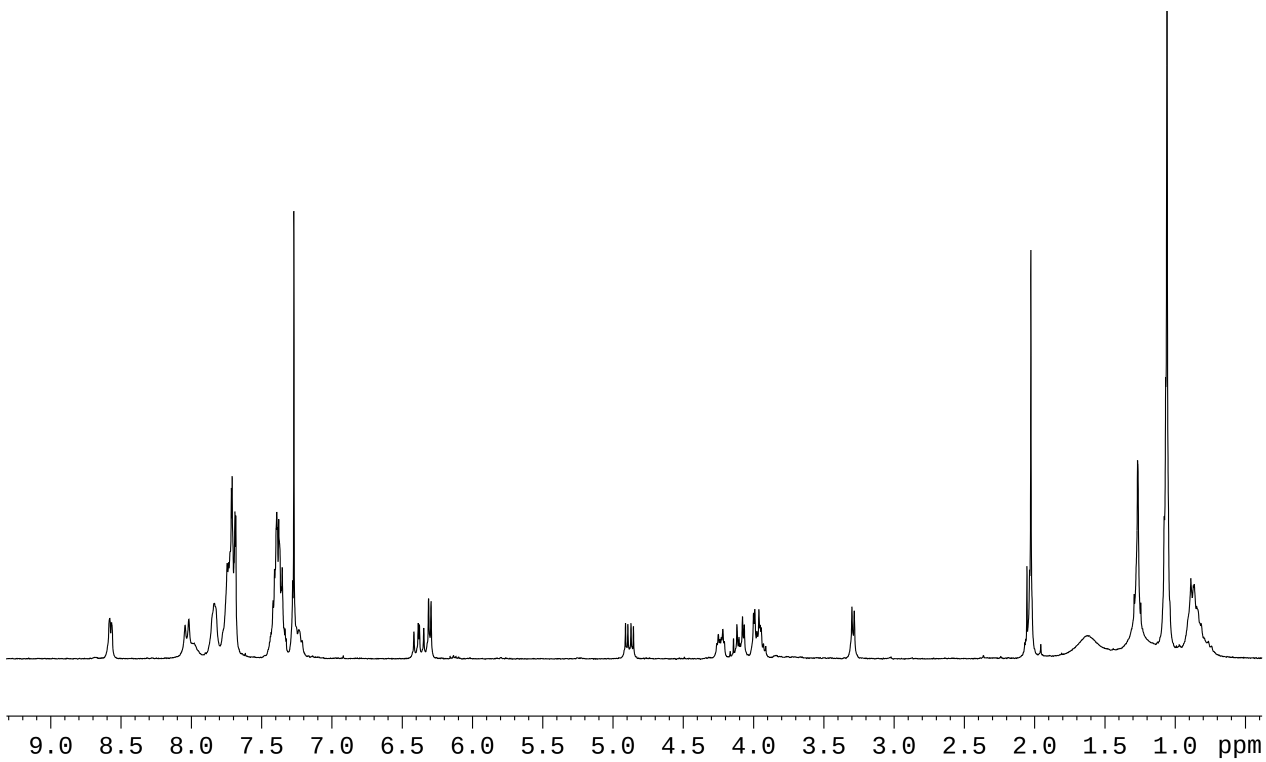


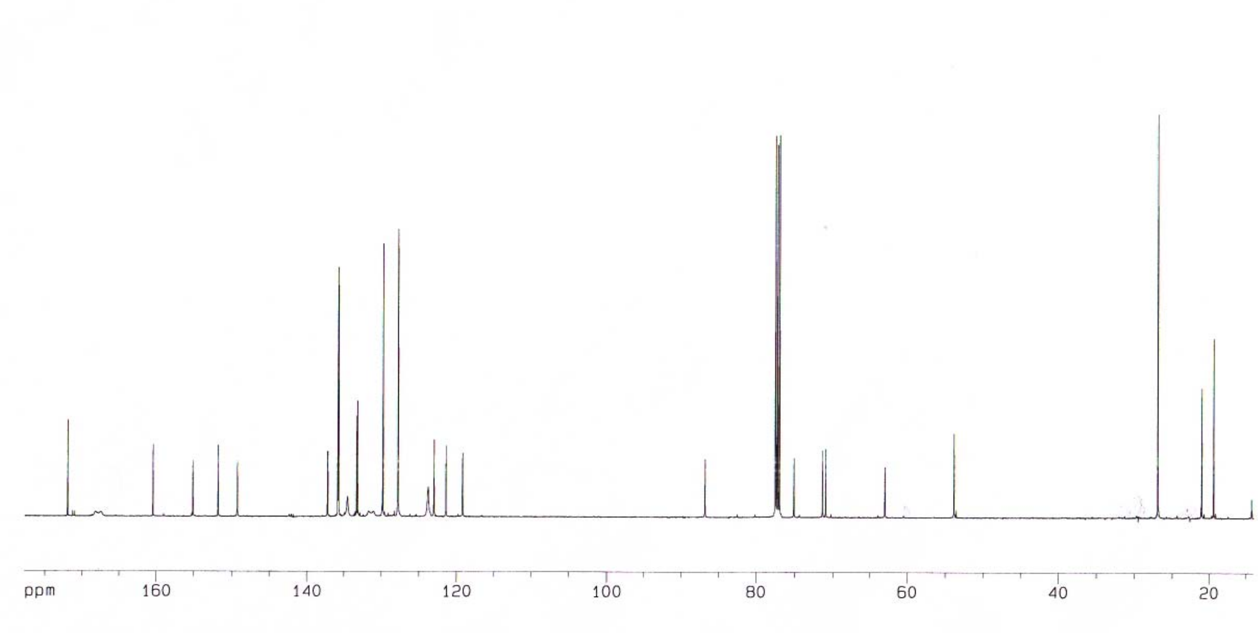
48

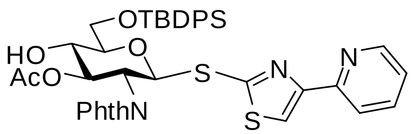



OTBDPS
HO
O
AcO
S
N
N
PhthN
S

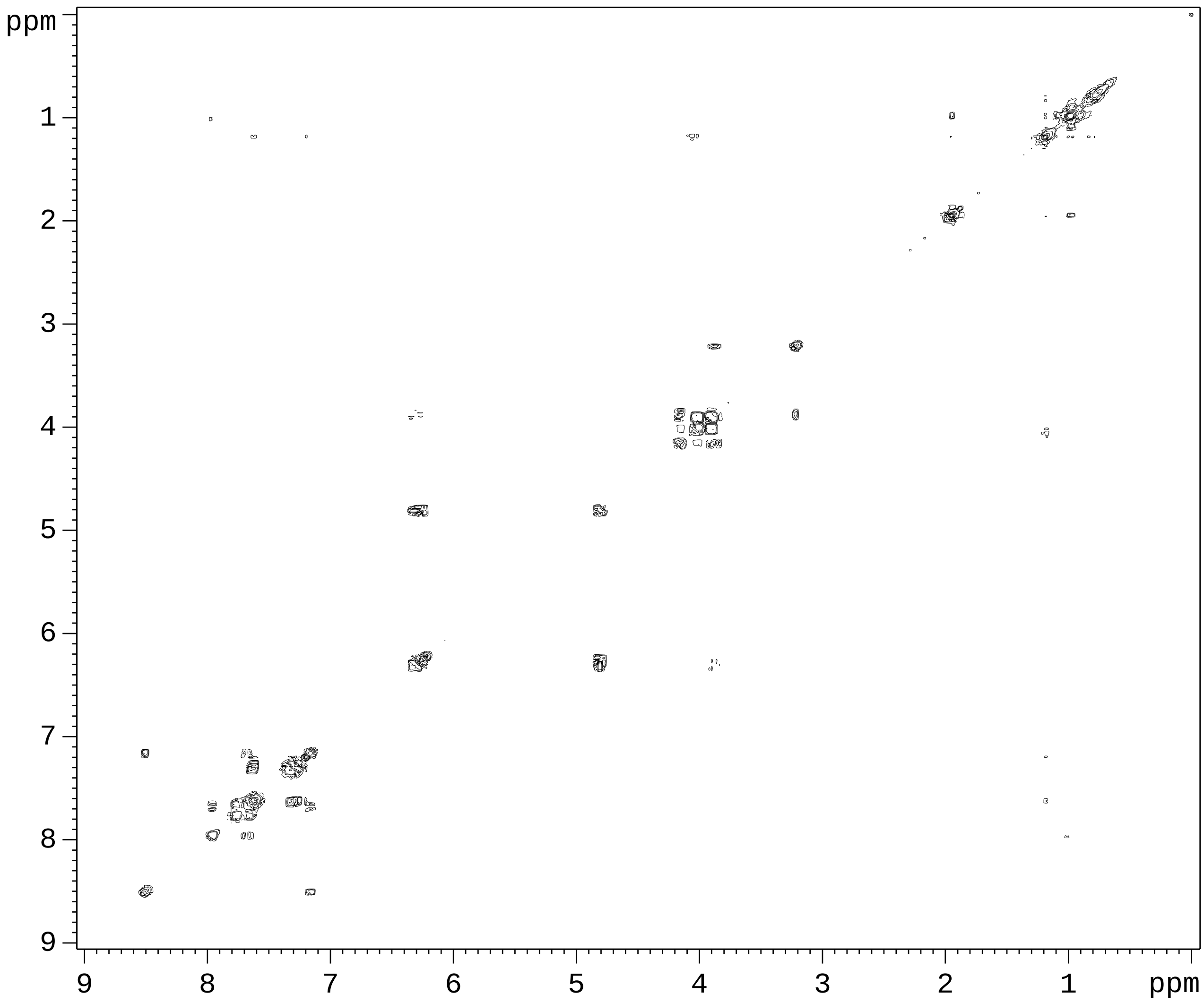
49

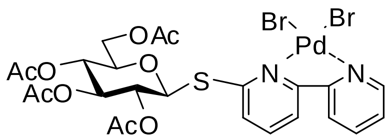

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


ppm 160 140 120 100 80 60 40 20

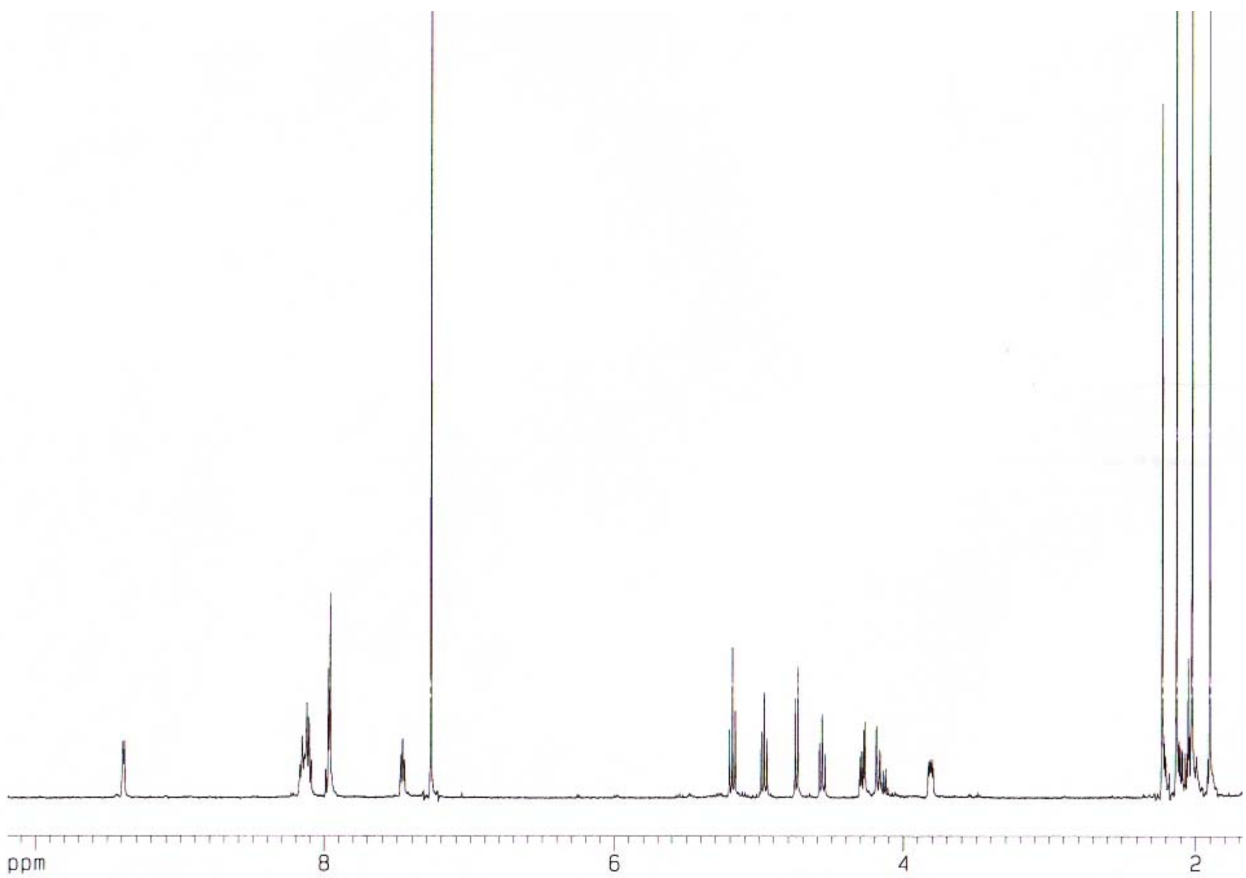


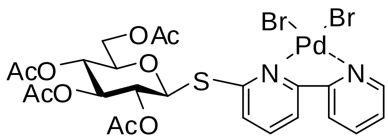
49



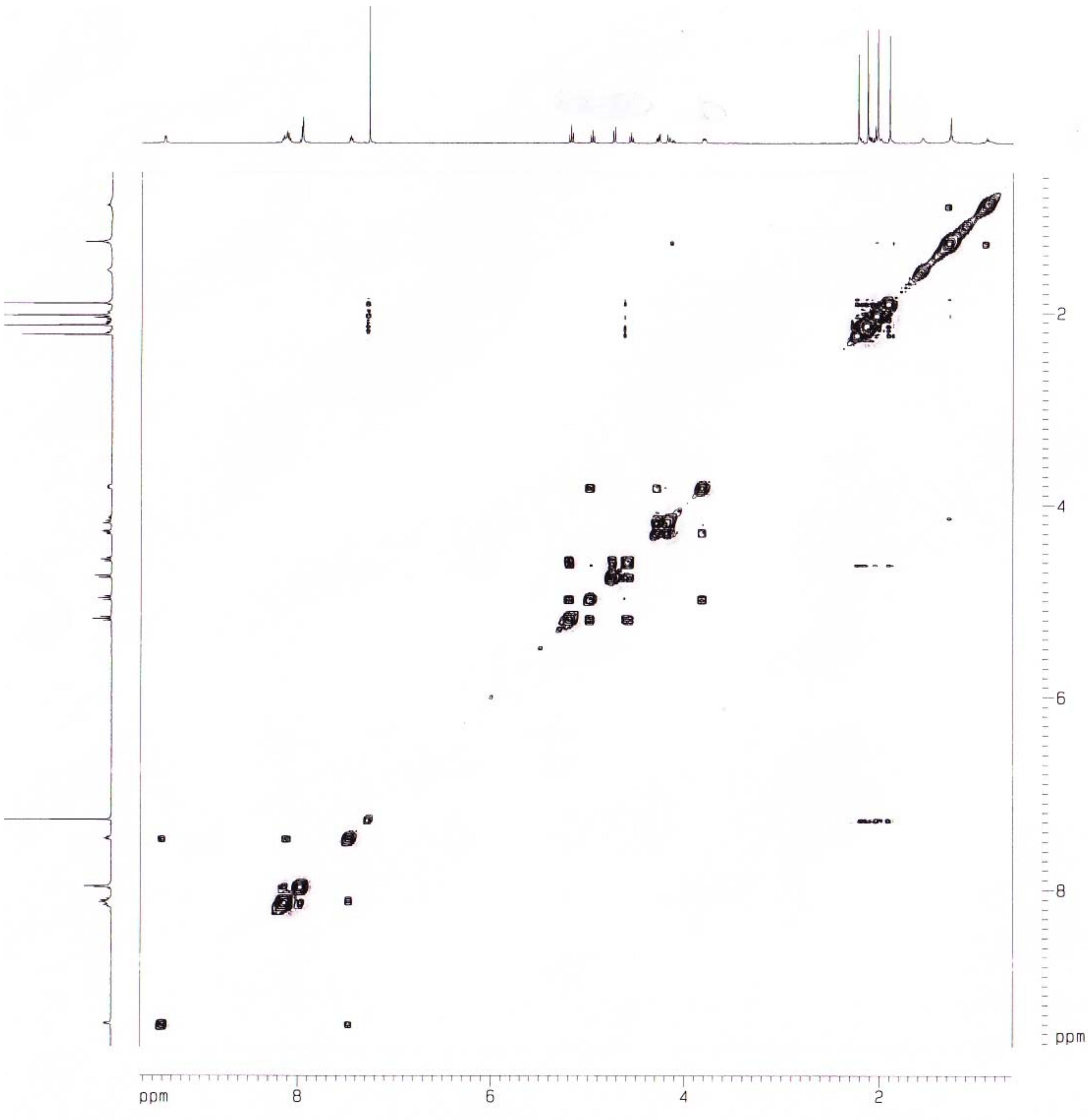


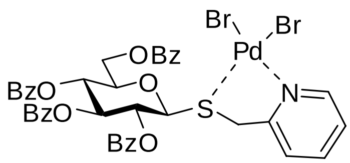
50





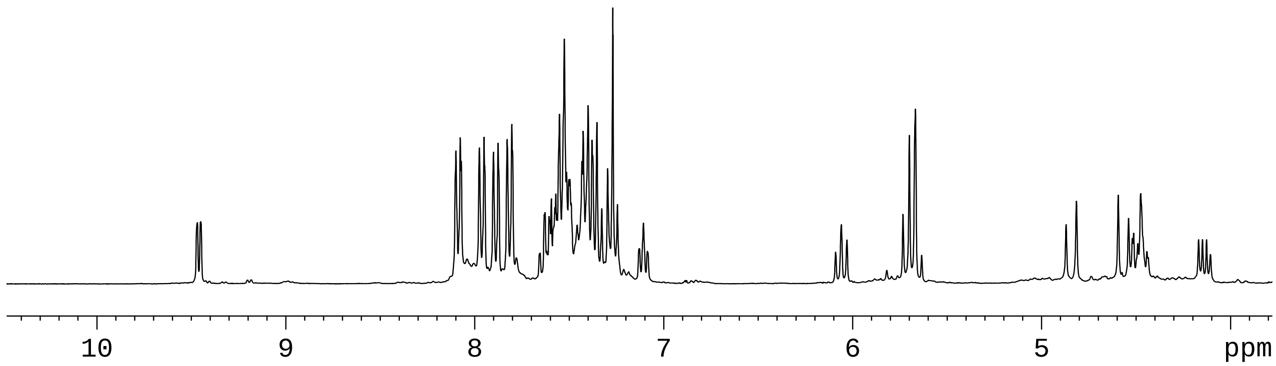
50



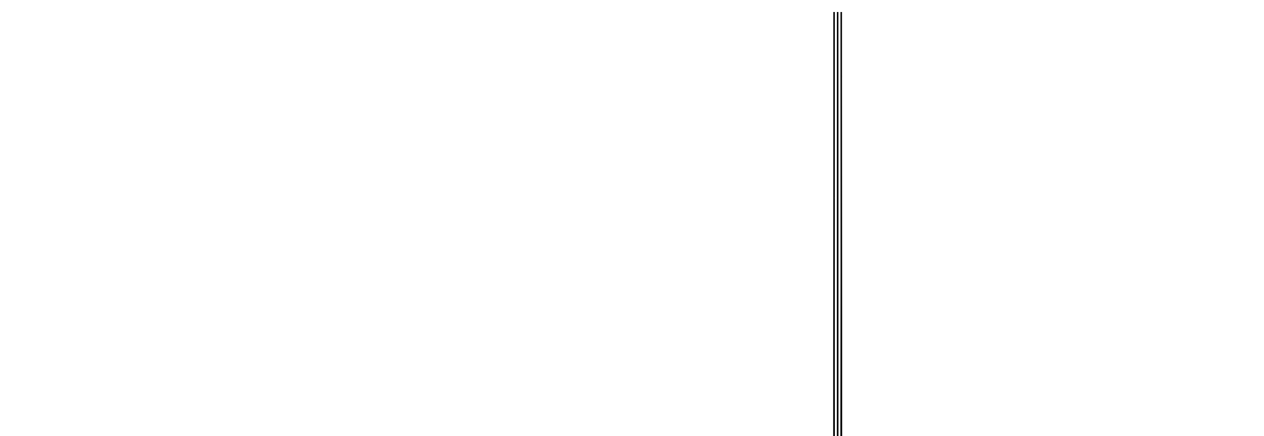


Br
Br
Pd
OBz
BzO
BzO
BzO
O
S
N

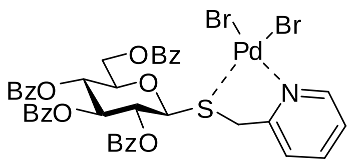
51



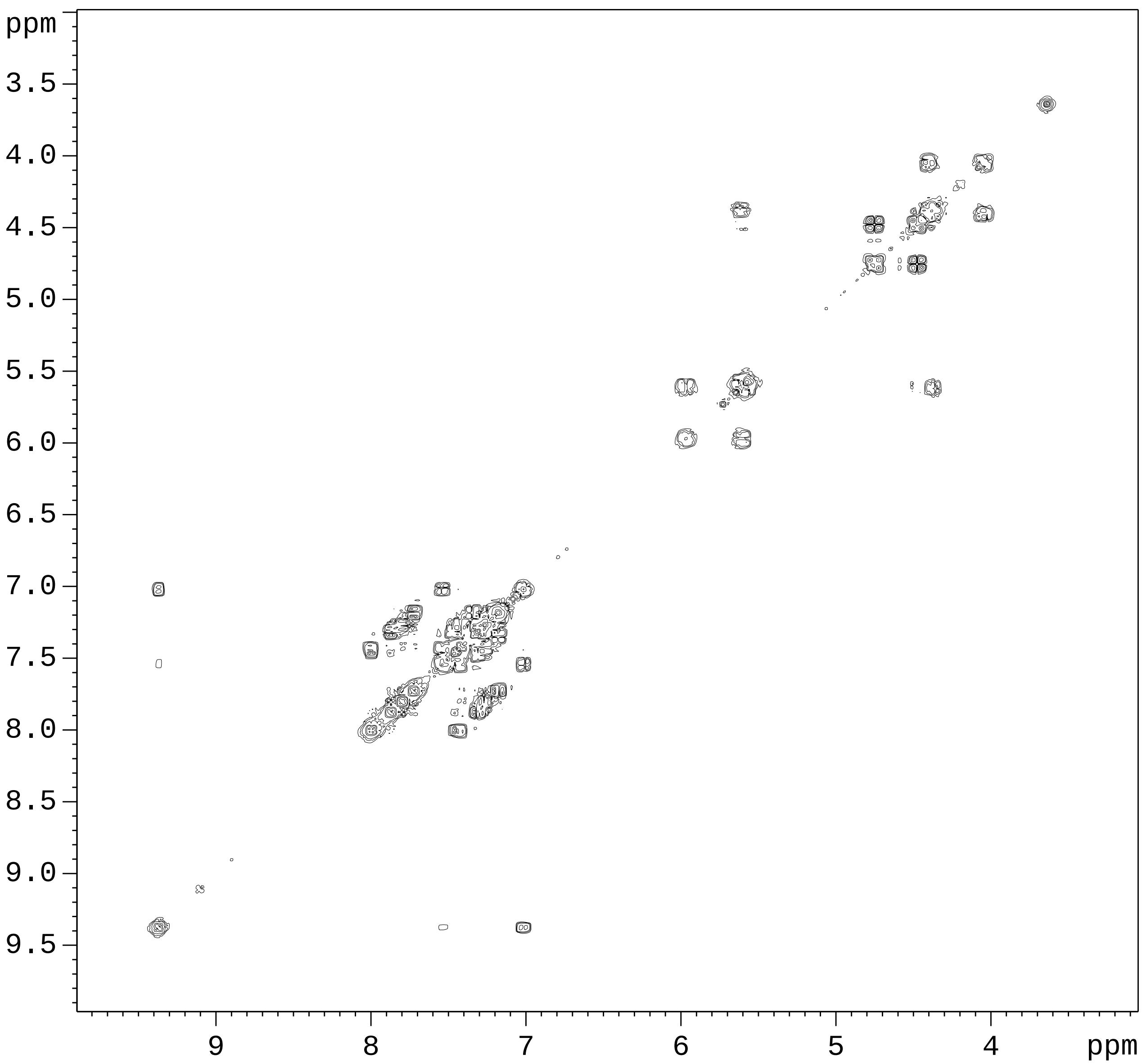
10
9
8
7
6
5
ppm



170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm


Br
Br
Pd
OBz
BzO
O
N
BzO
S
BzO

51


ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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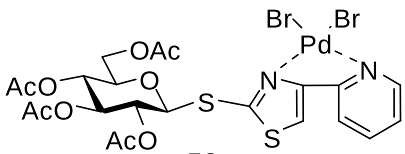
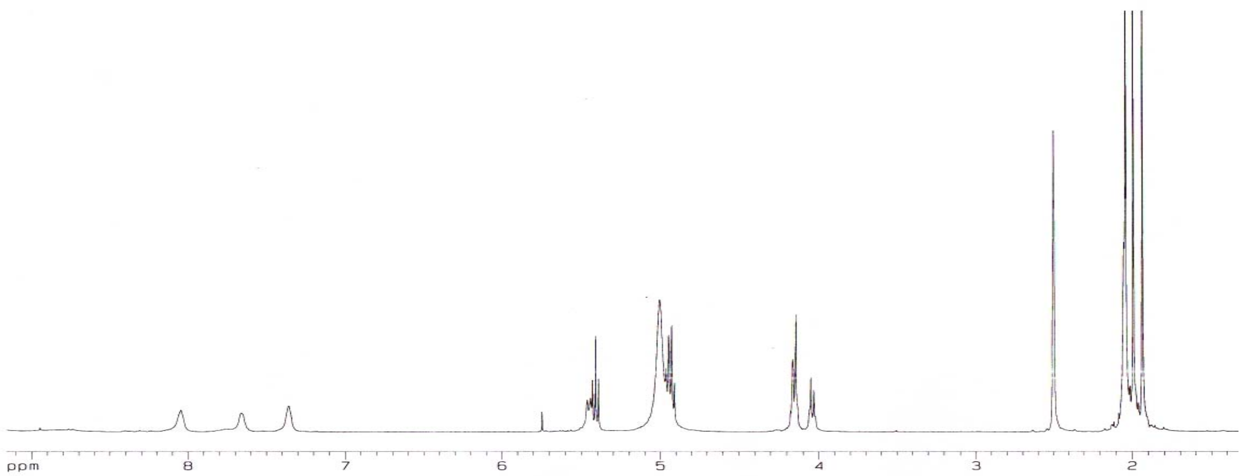
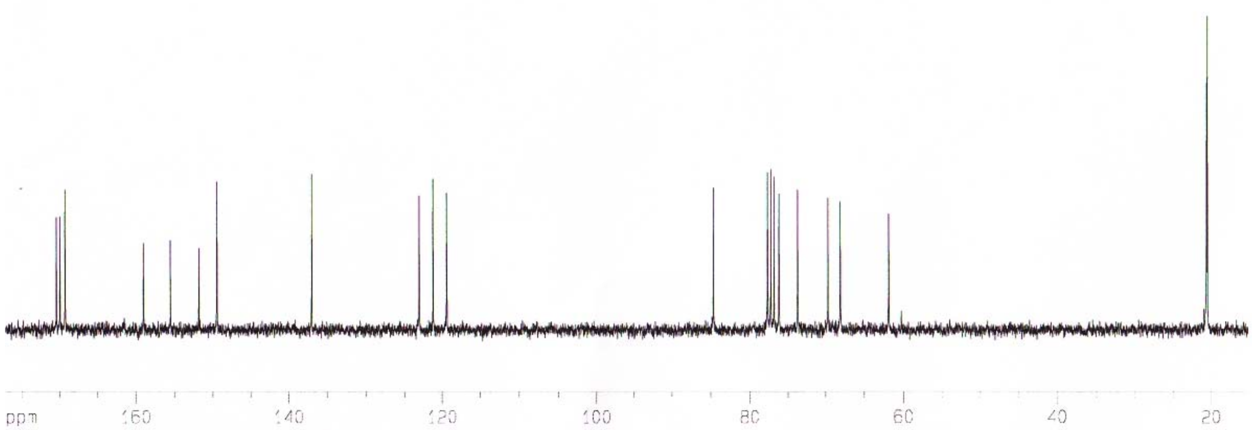
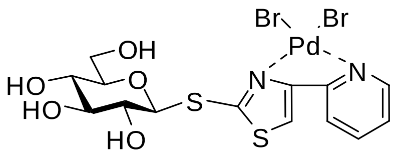
7
6
5
4
ppm


Br
Br
Pd
OAc
N
N
AcO
O
AcO
S
AcO
S

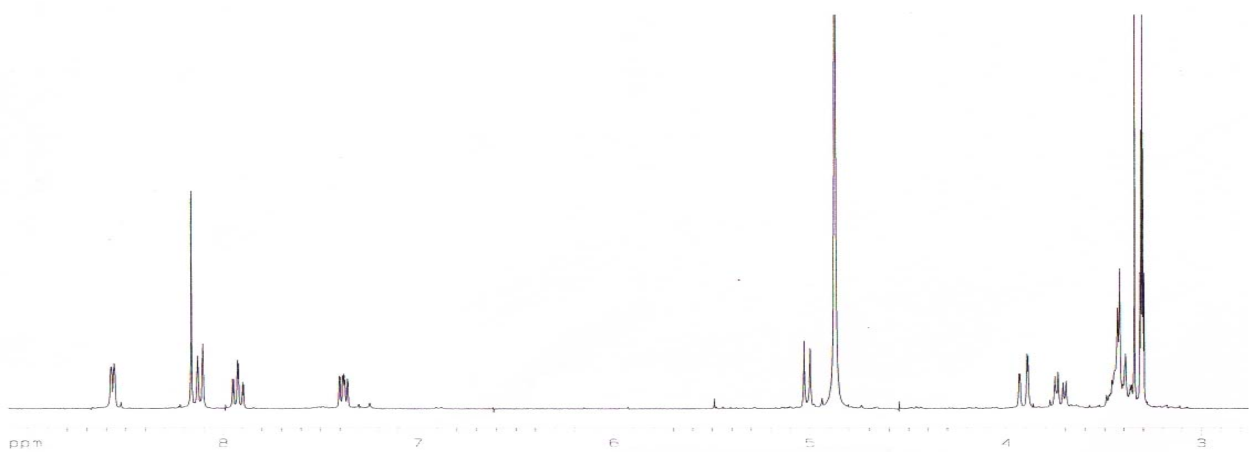
52

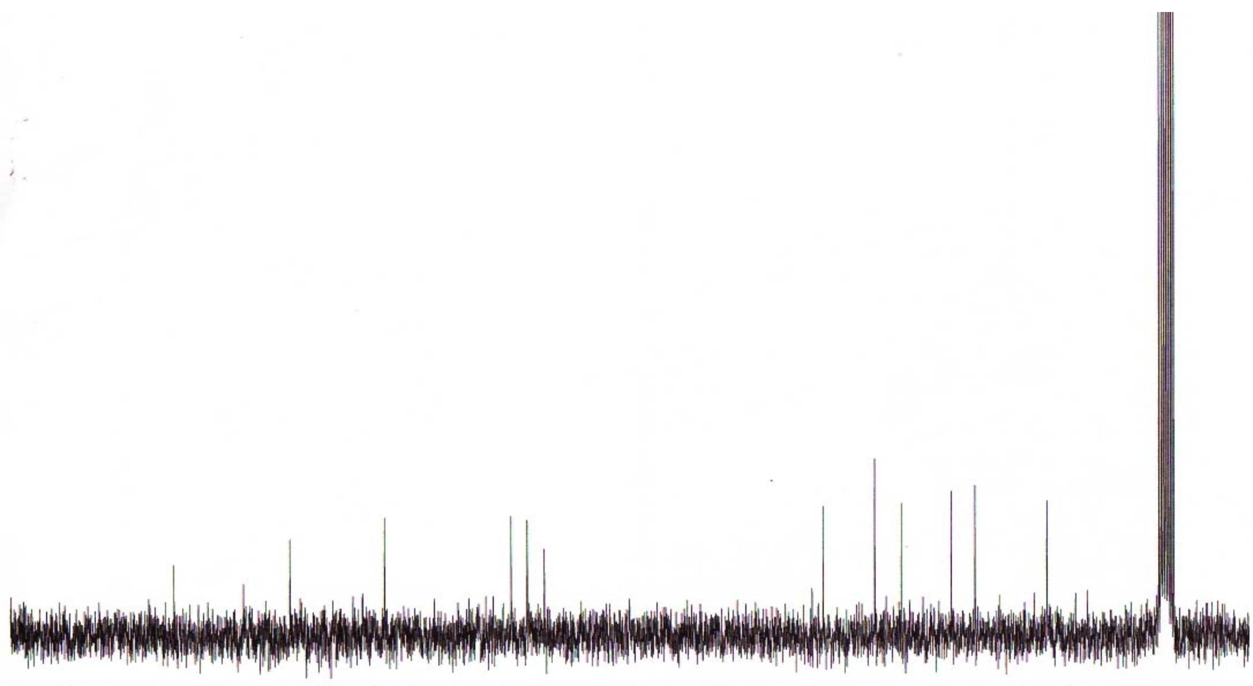

ppm
8
7
6
5
4
3
2

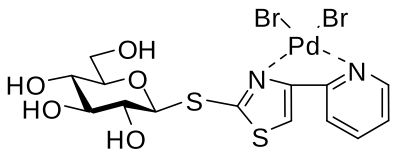

ppm
160
140
120
100
80
60
40
20



53

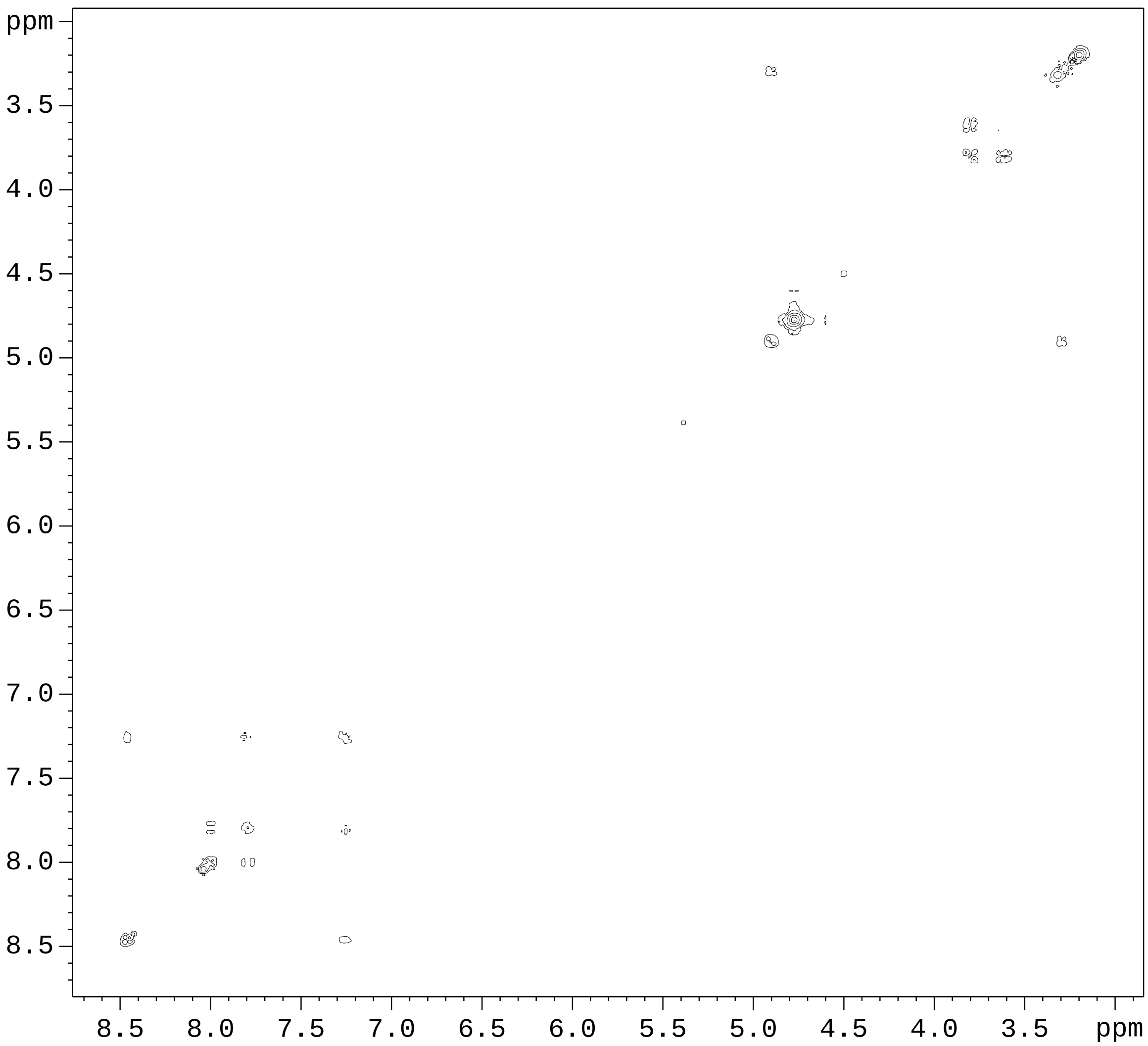




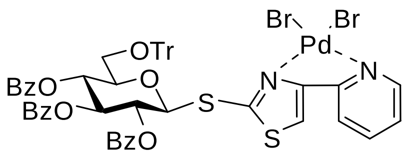


Br
Br
Pd
N
N
OH
O
HO
HO
HO
S
S

53

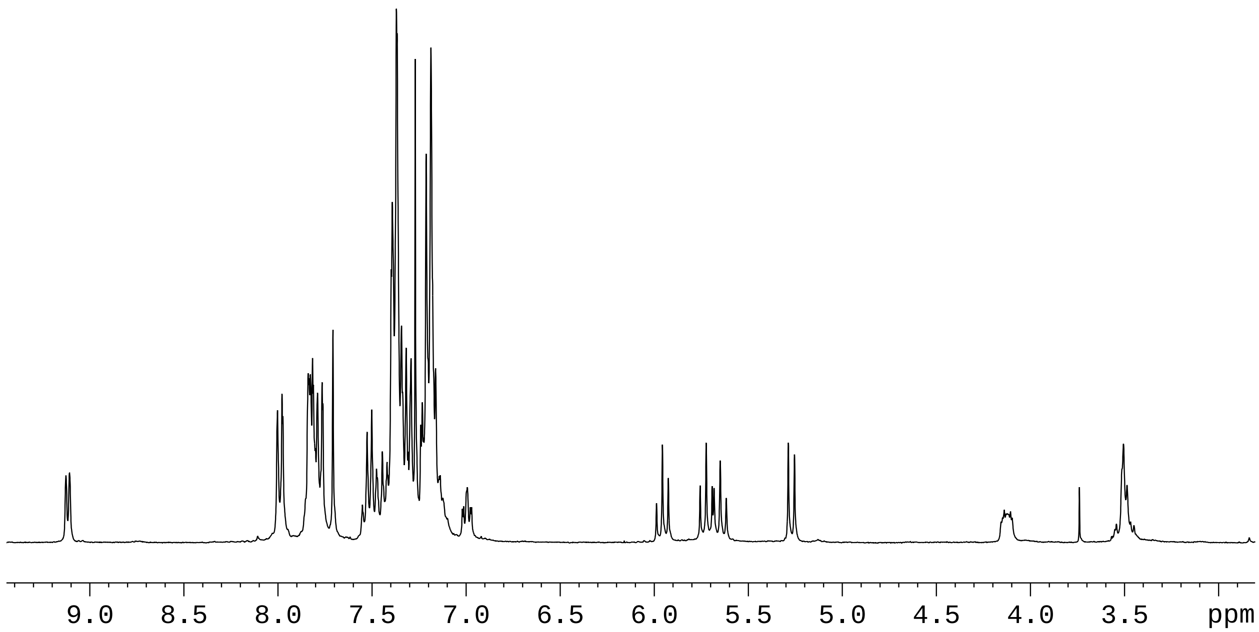


ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

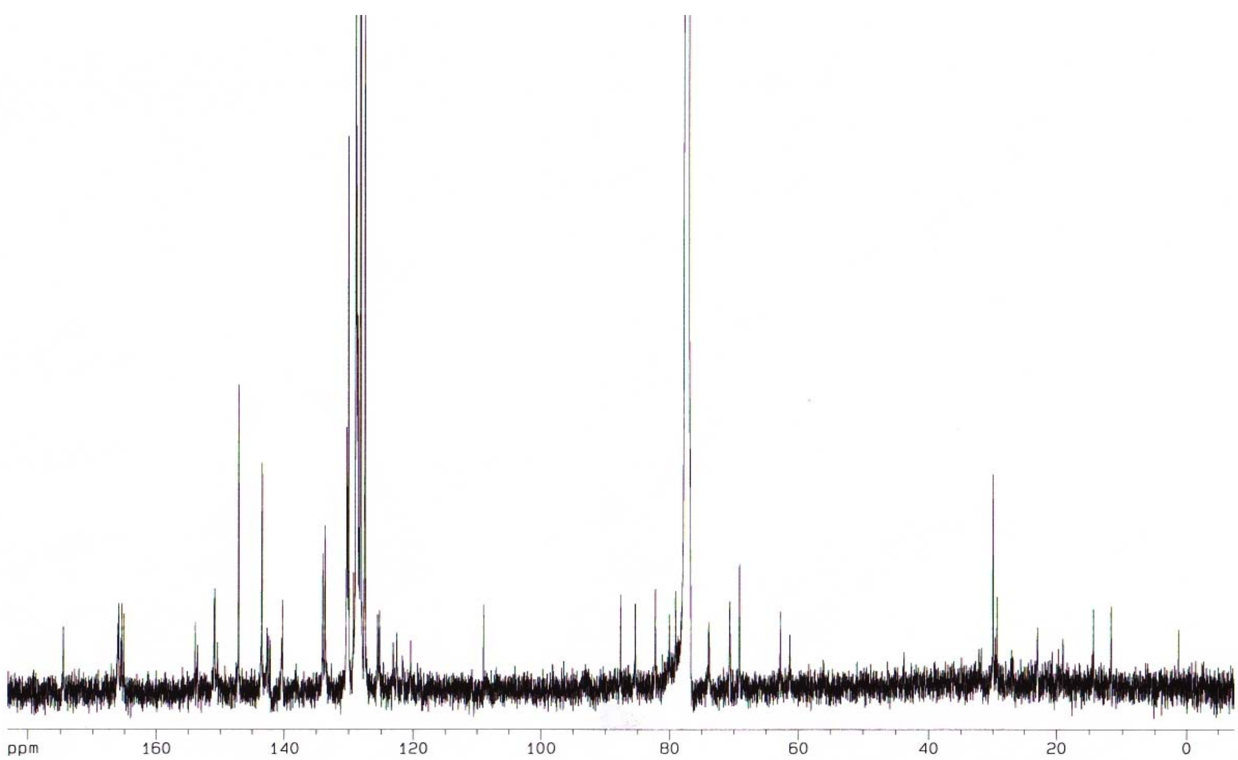


Br
Br
Pd
N
N
OTr
O
BzO
BzO
BzO
S
S

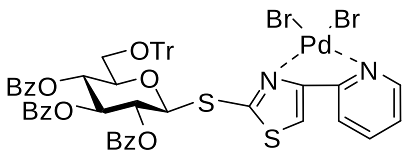
54



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm

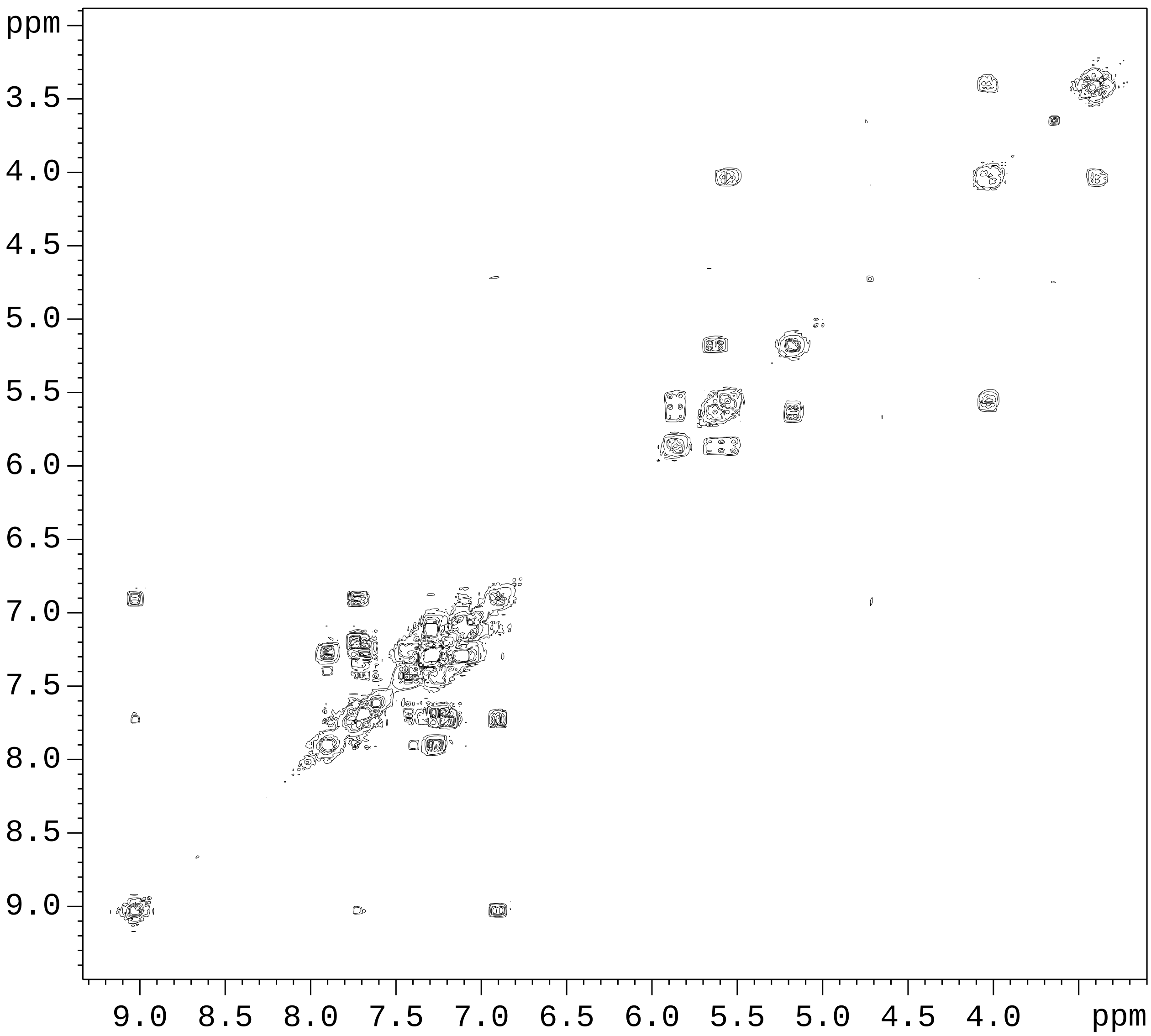


ppm 160 140 120 100 80 60 40 20 0

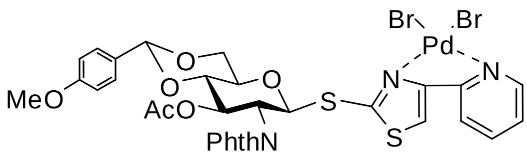


Br
Br
Pd
N
N
OTr
O
BzO
BzO
BzO
S
S

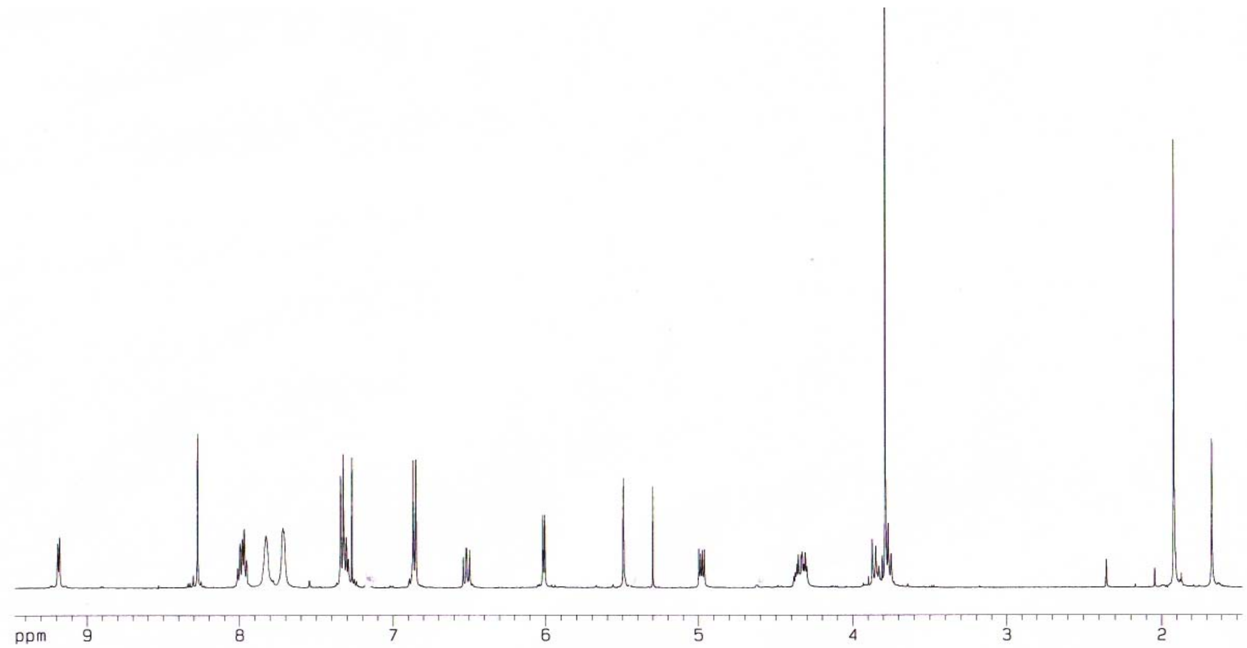
54

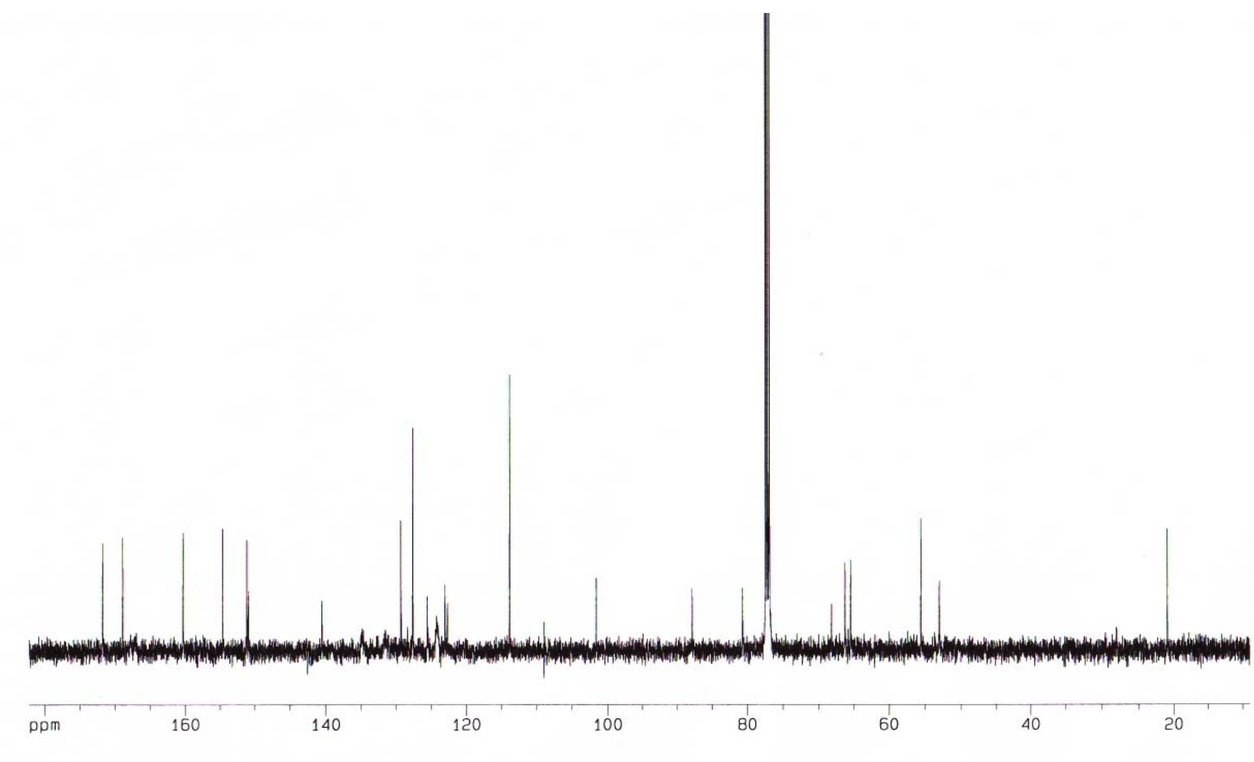


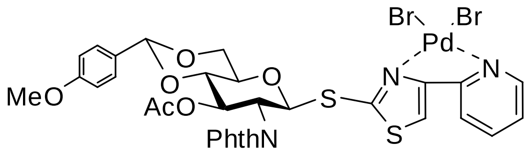
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


Br
Br
Pd
N
N
MeO
O
O
O
AcO
S
S
PhthN

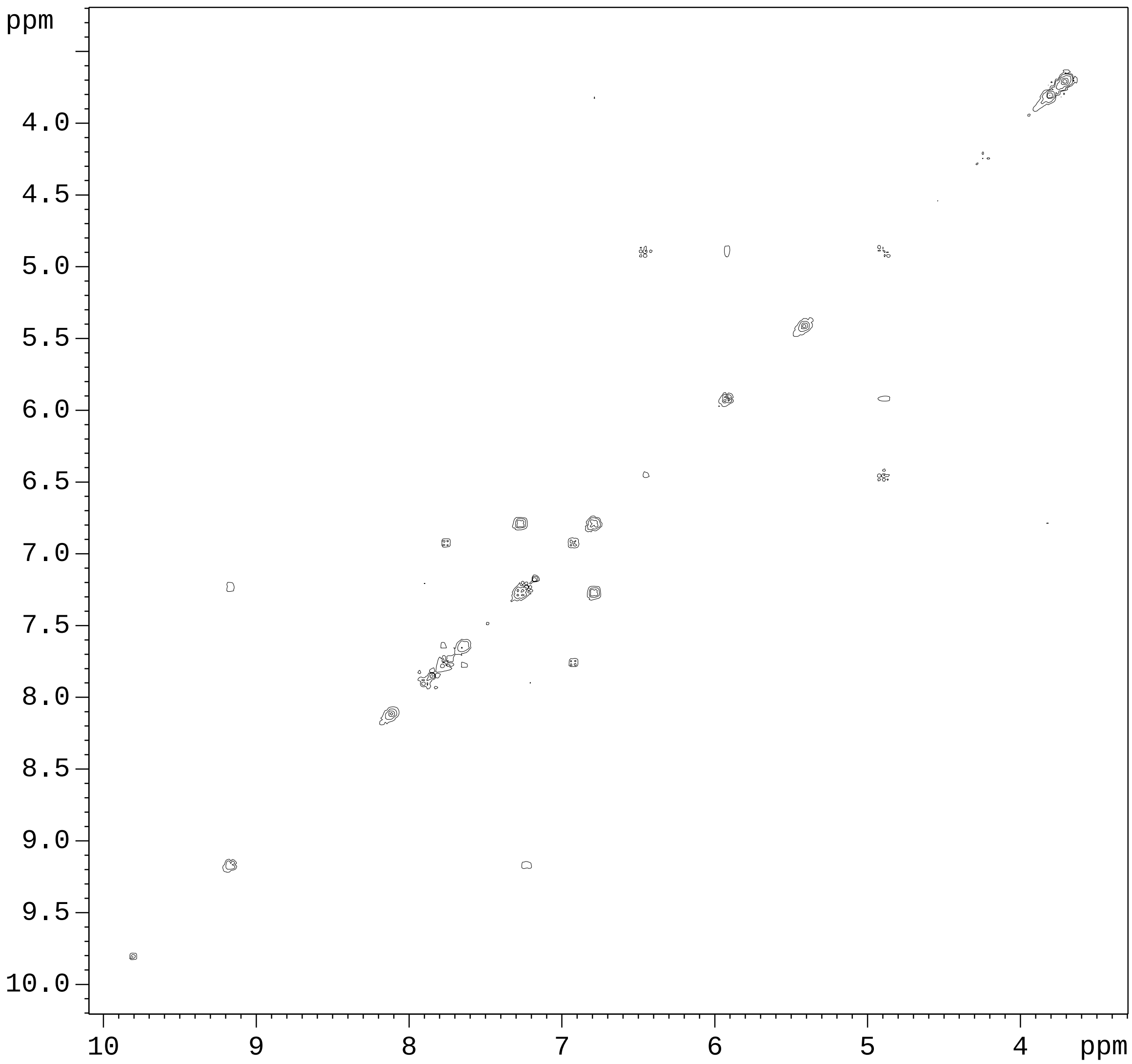
55

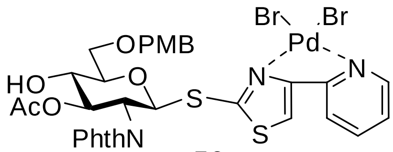

ppm 9 8 7 6 5 4 3 2


ppm 160 140 120 100 80 60 40 20

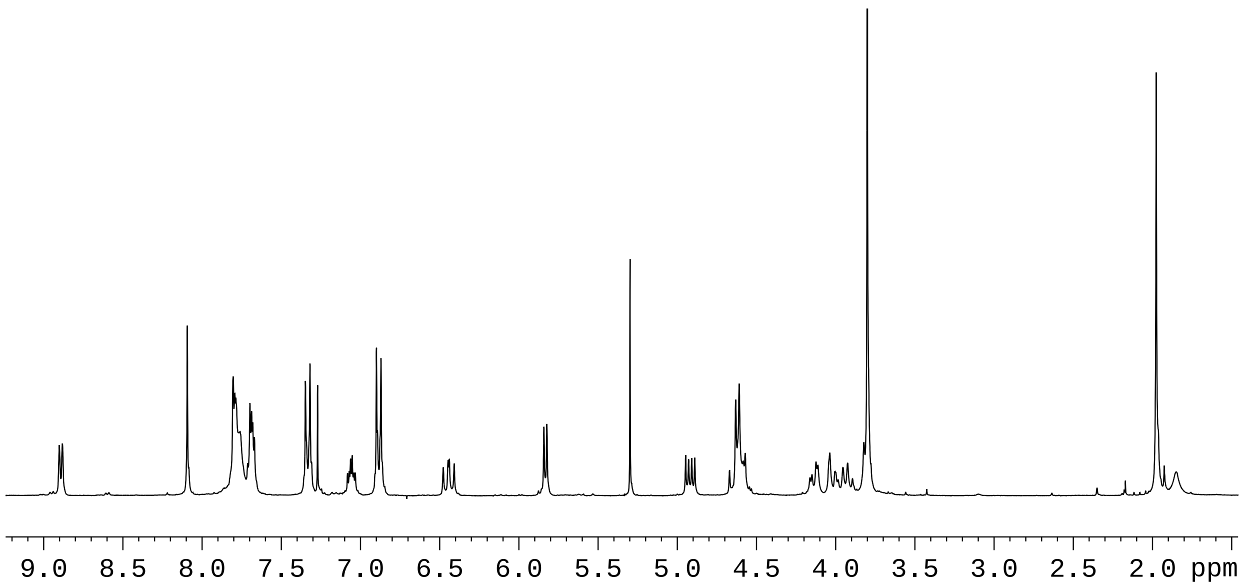

Br
Br
Pd
N
N
S
S
O
O
O
MeO
AcO
PhthN

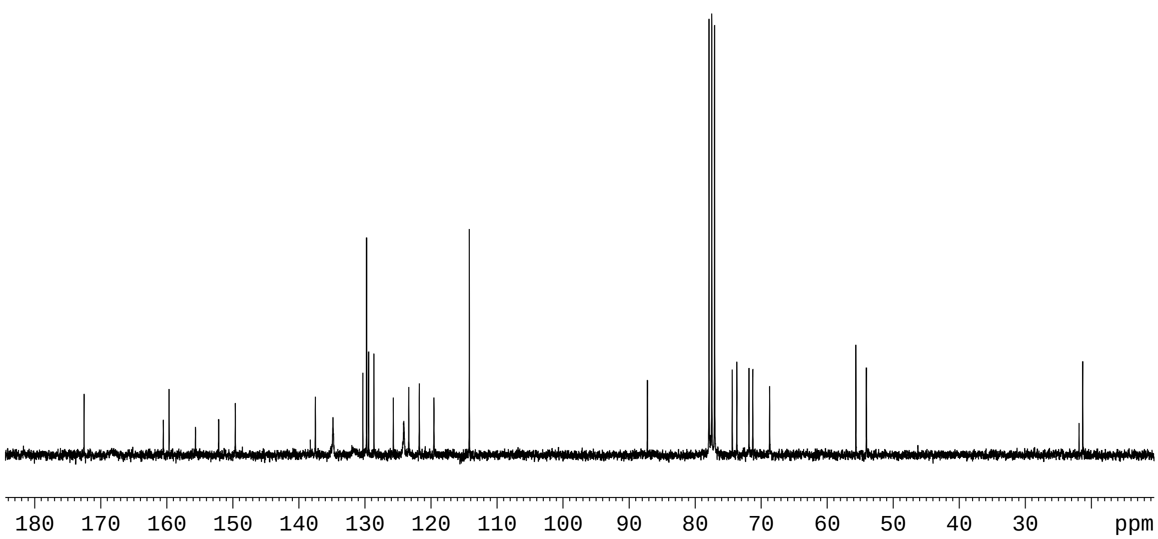
55

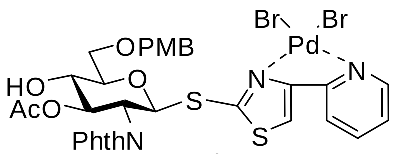

ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10
9
8
7
6
5
4
ppm


Br
Br
Pd
N
N
OPMB
O
HO
AcO
S
S
PhthN

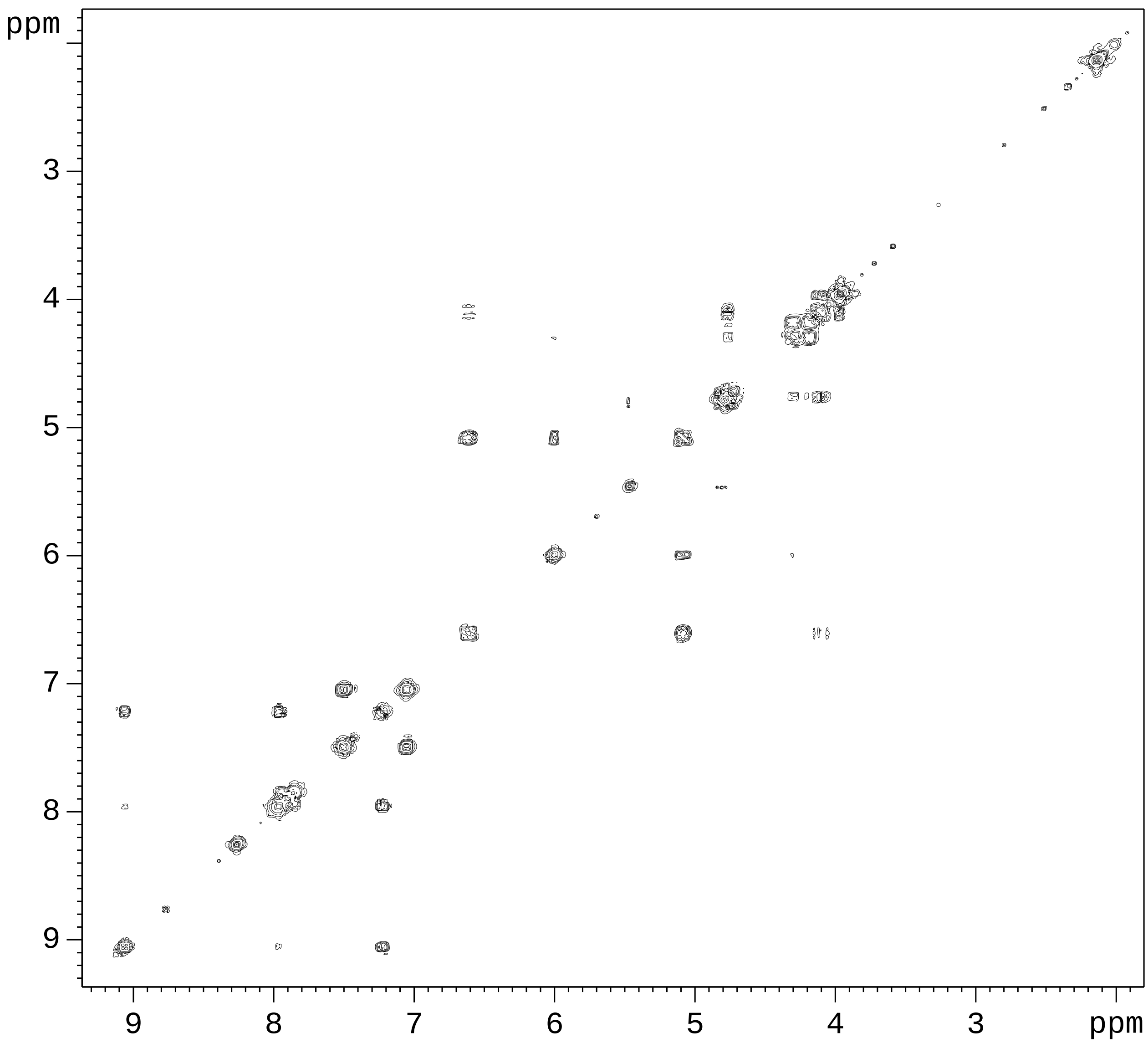
56

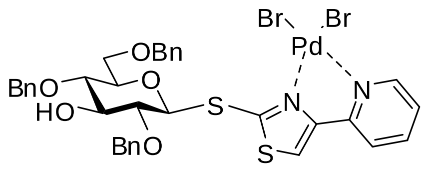

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

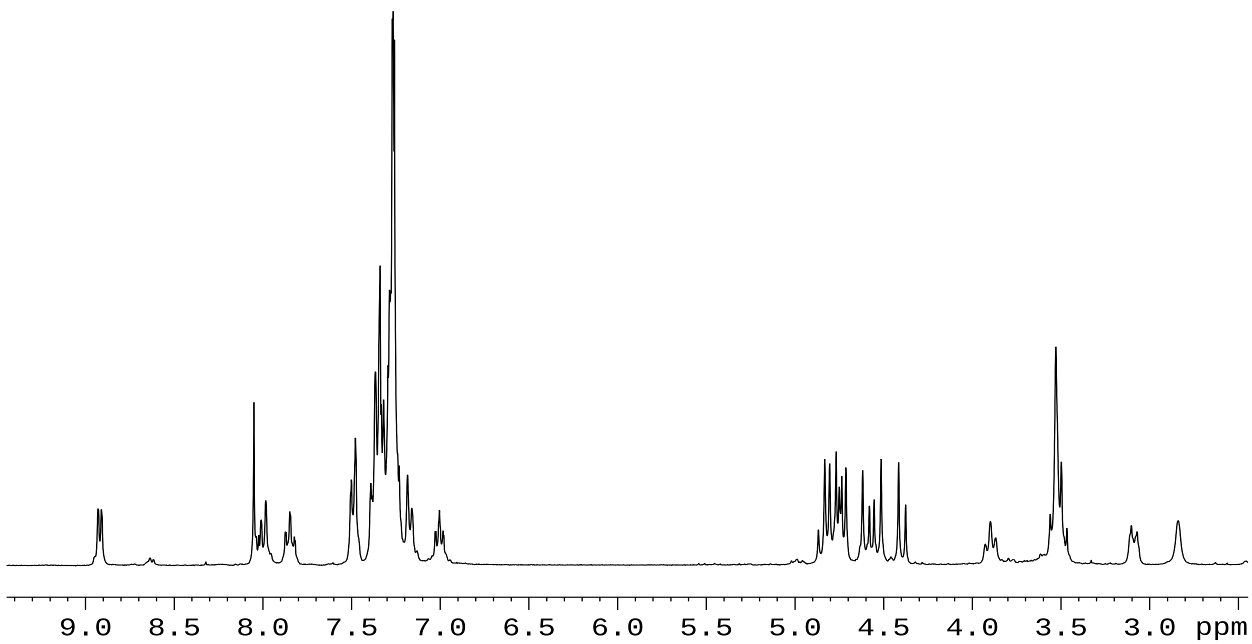


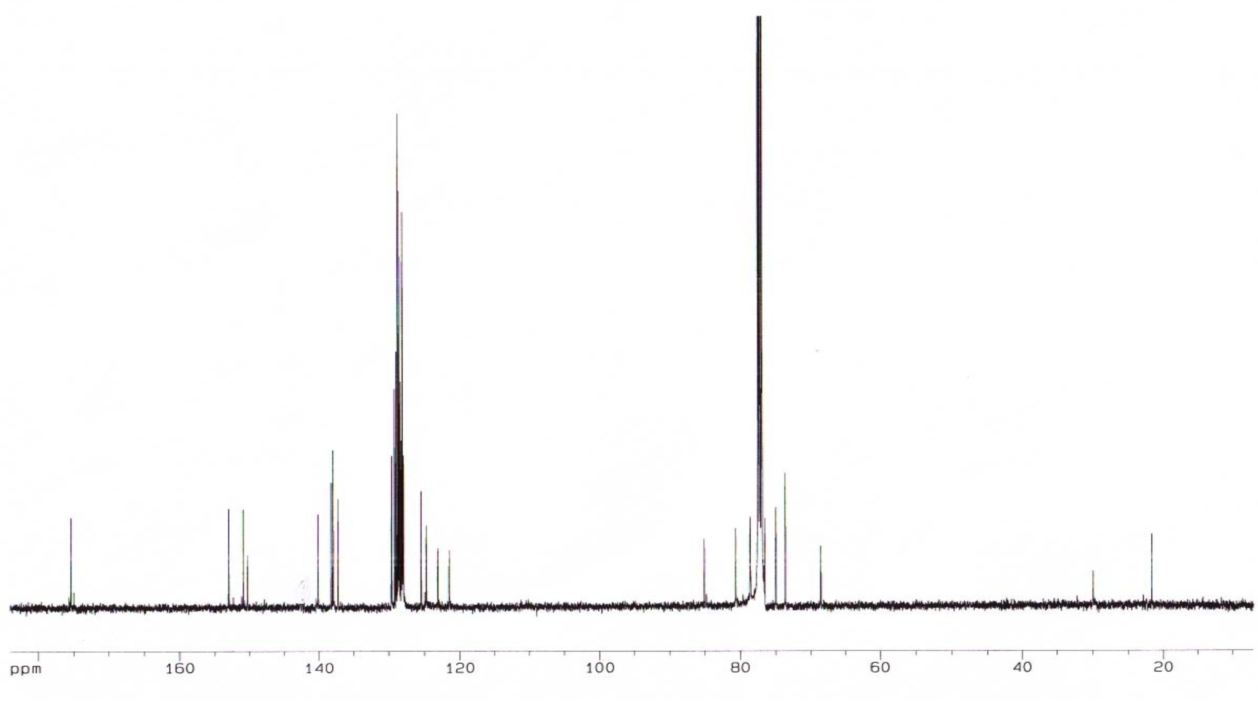
56

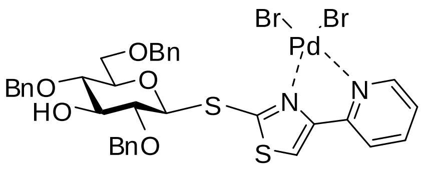



Br
Br
Pd
OBn
O
BnO
HO
S
N
N
BnO
S

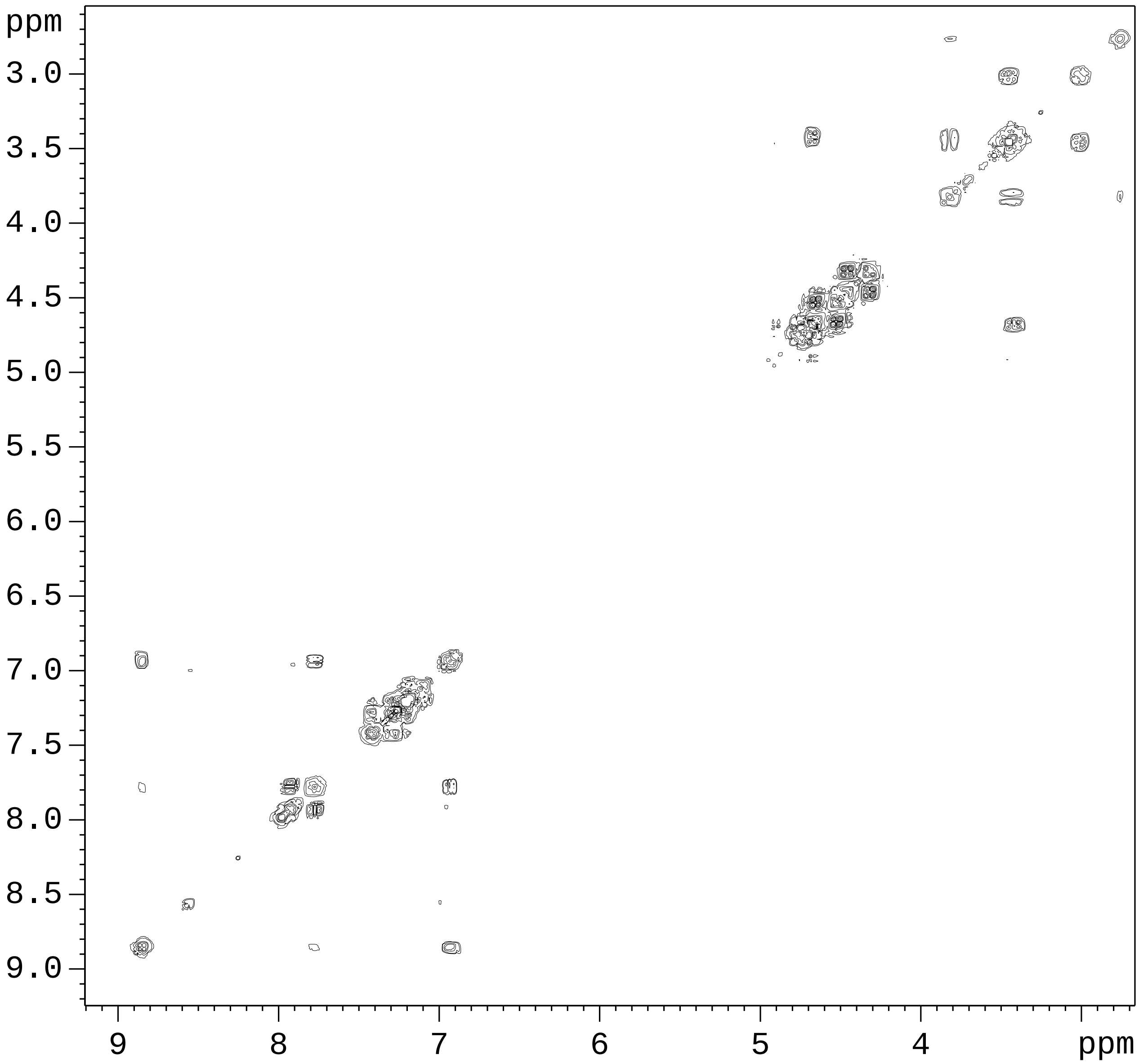
57

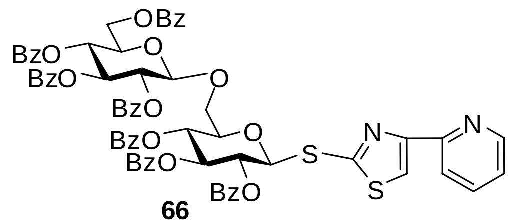

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm


ppm 160 140 120 100 80 60 40 20

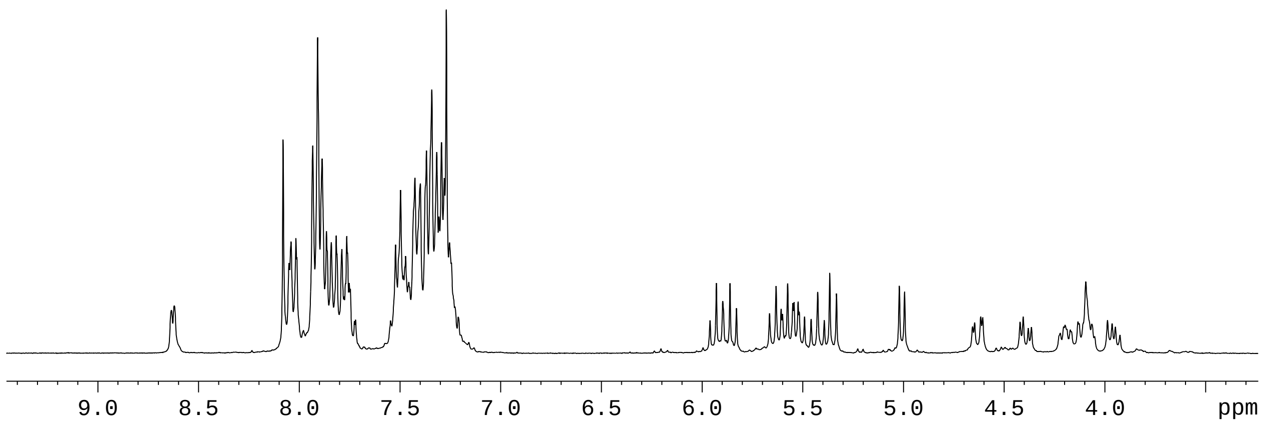

Br
Br
Pd
OBn
BnO
O
HO
S
N
N
BnO
S

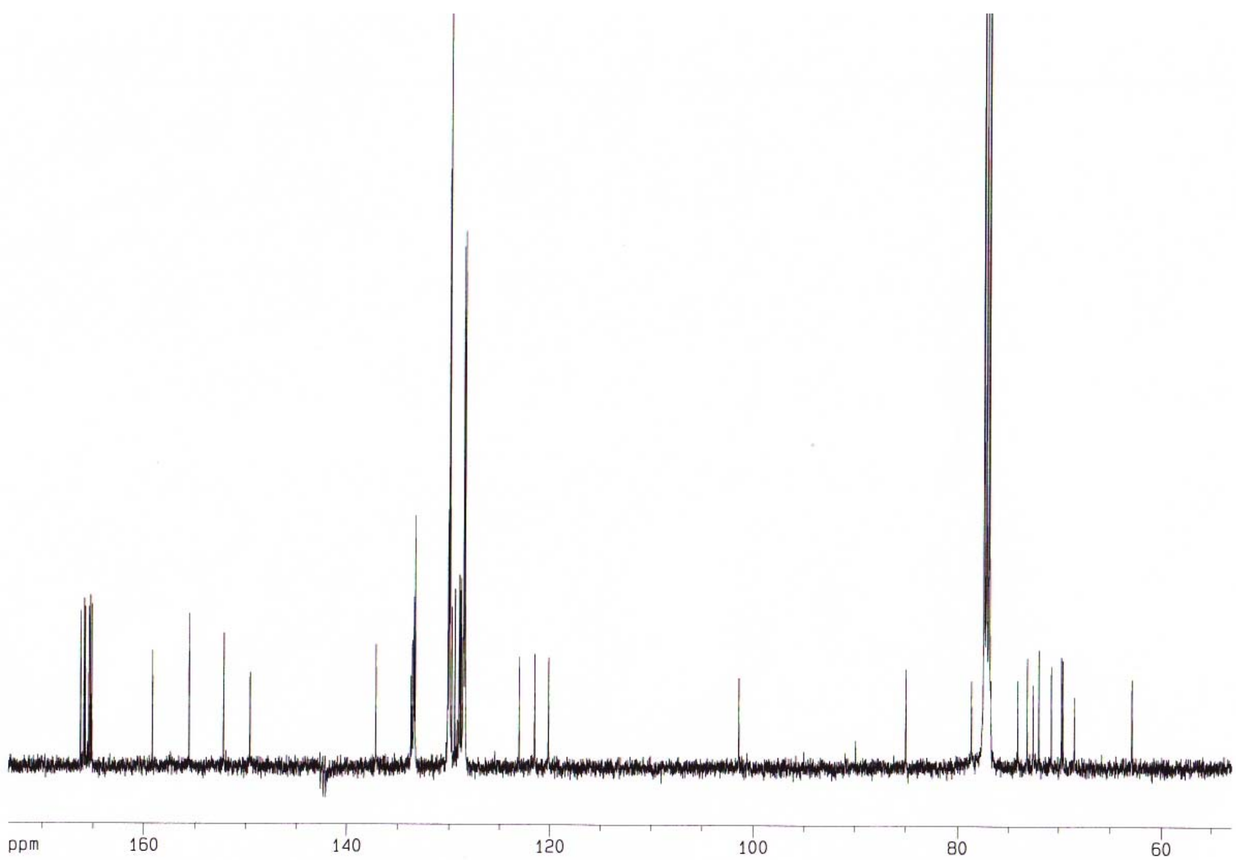
57

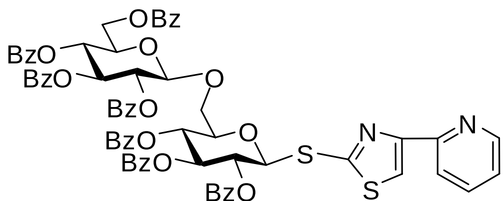

ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9
8
7
6
5
4
ppm


OBz
BzO
BzO
O
O
BzO
BzO
BzO
O
S
N
S
N
BzO

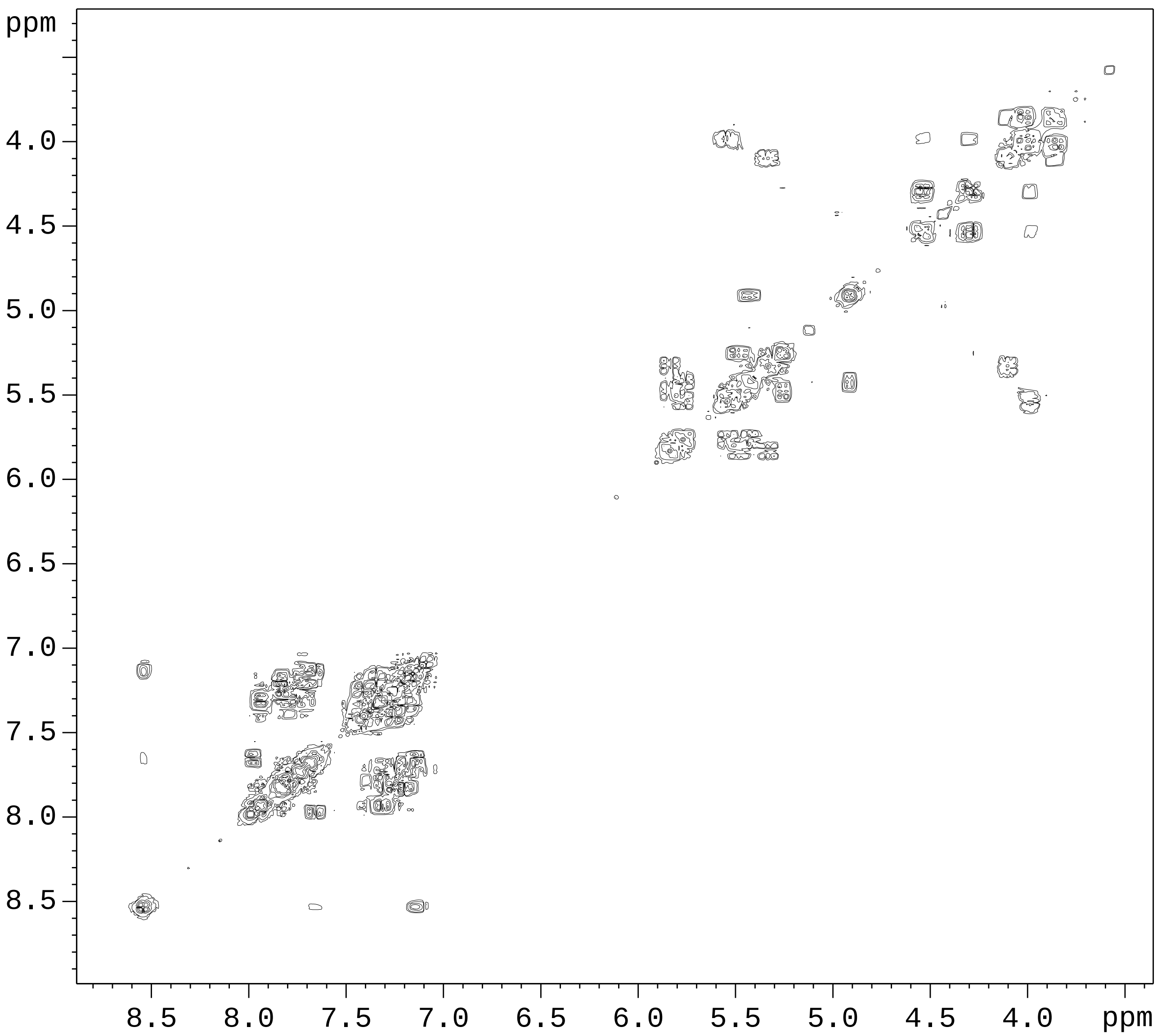
66

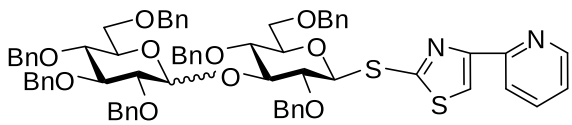

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


ppm
160
140
120
100
80
60


OBz
BzO
BzO
BzO
O
O
BzO
BzO
O
BzO
S
N
S
N

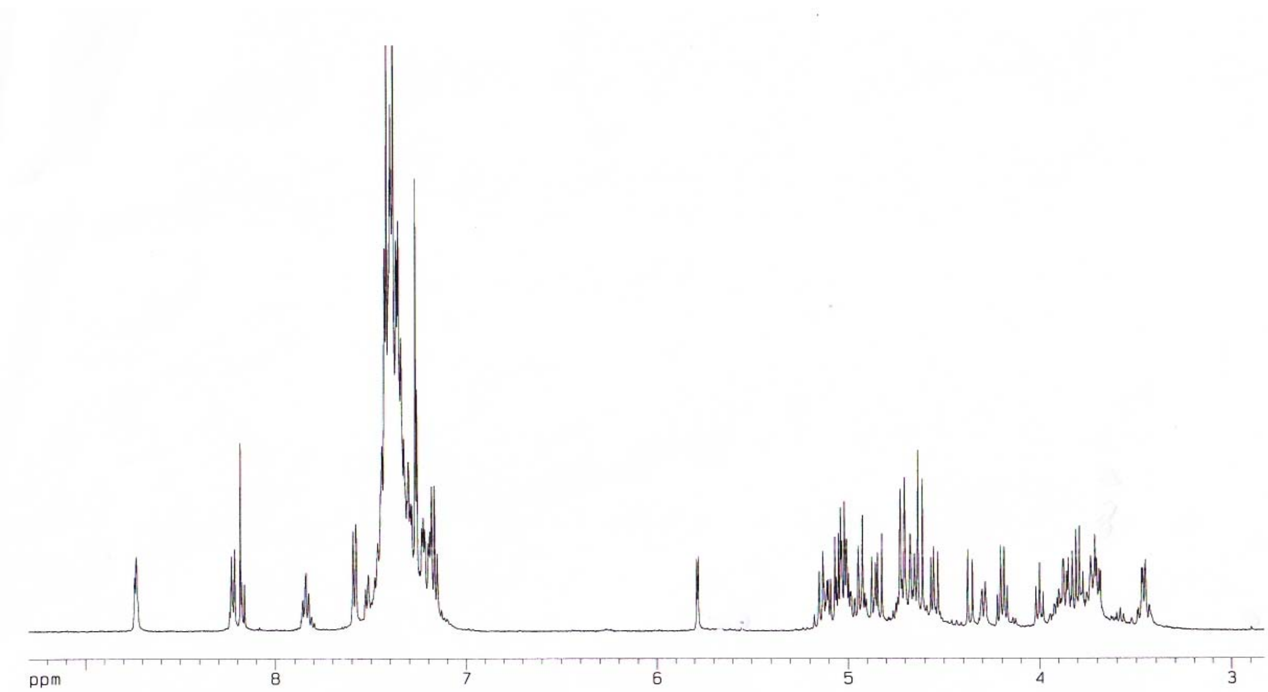
66


ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

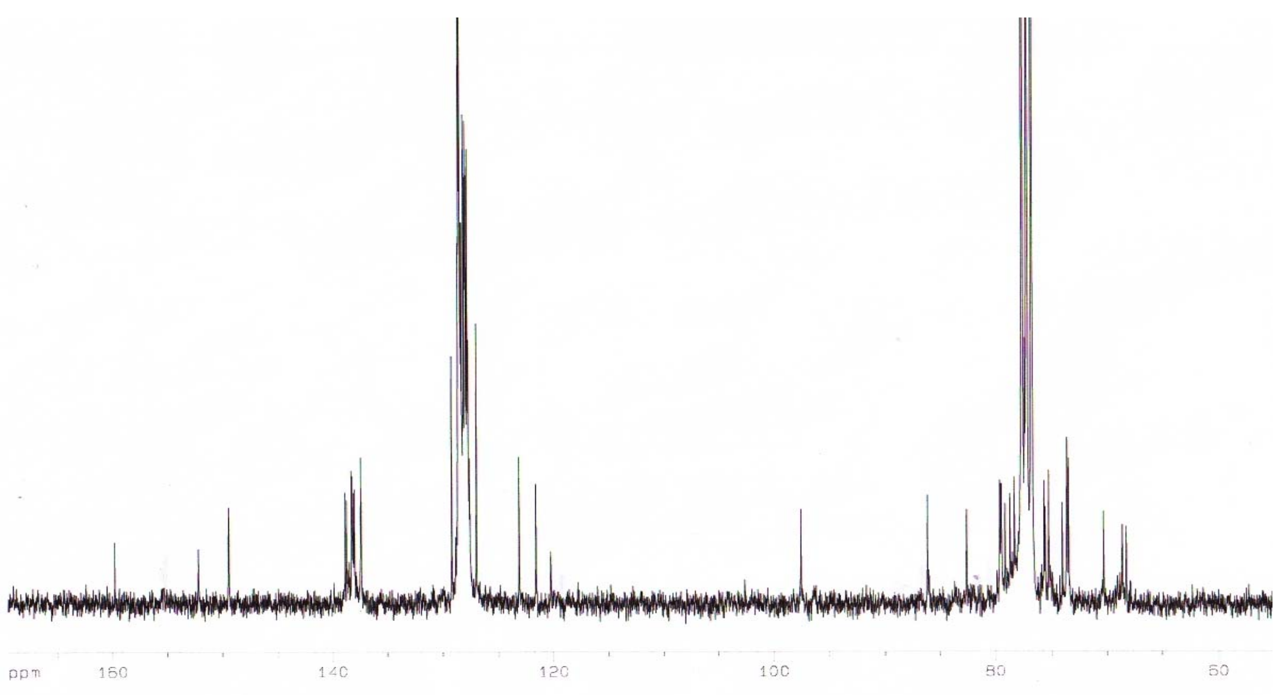


OBn
OBn
BnO
BnO
BnO
BnO
O
O
O
S
N
S
N
BnO
BnO

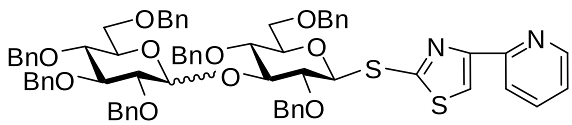
67



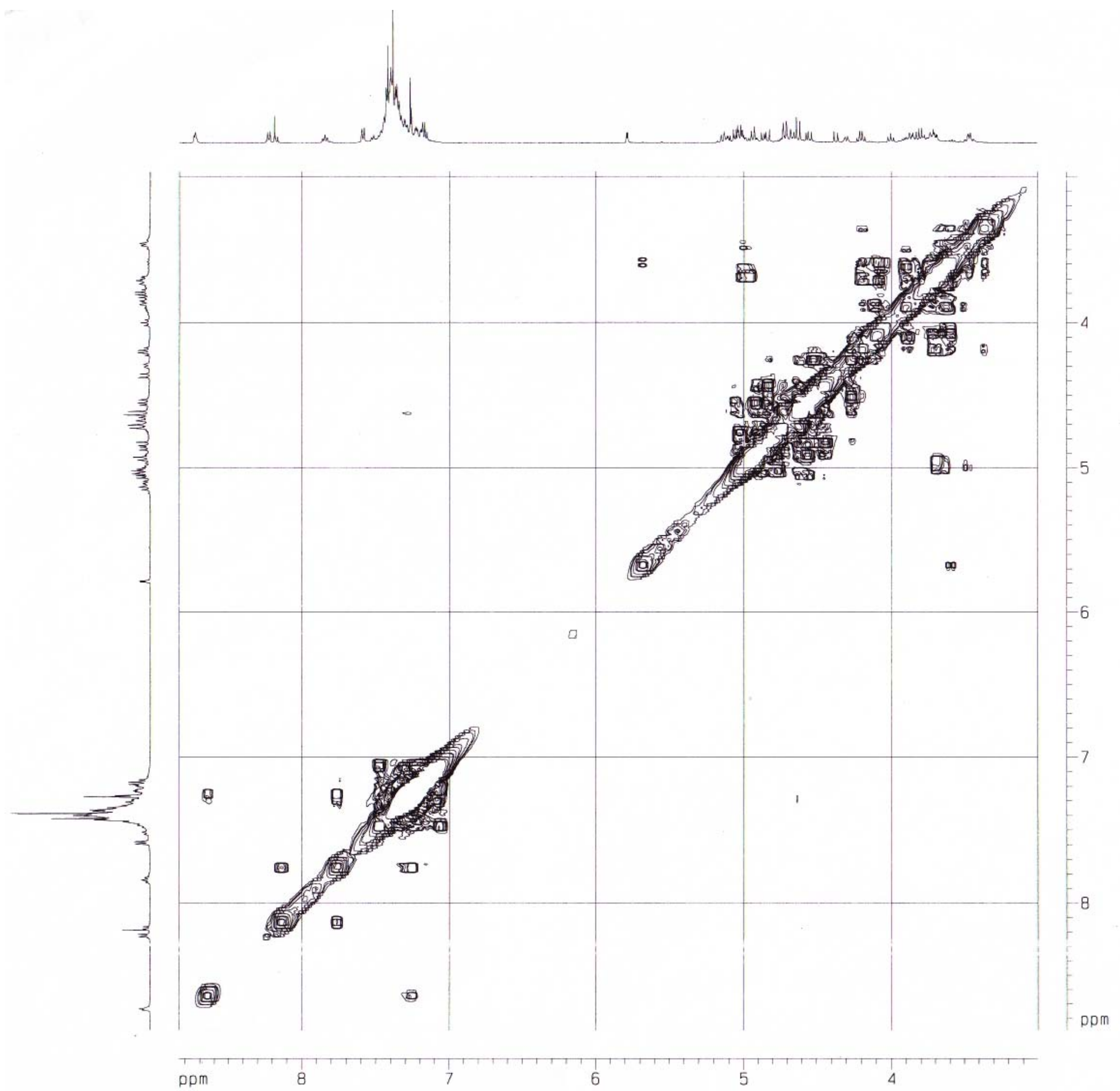
ppm
8
7
6
5
4
3

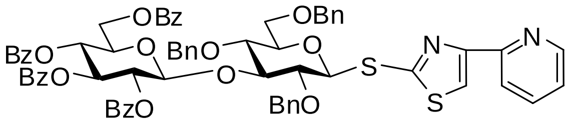


ppm
160
140
120
100
80
60

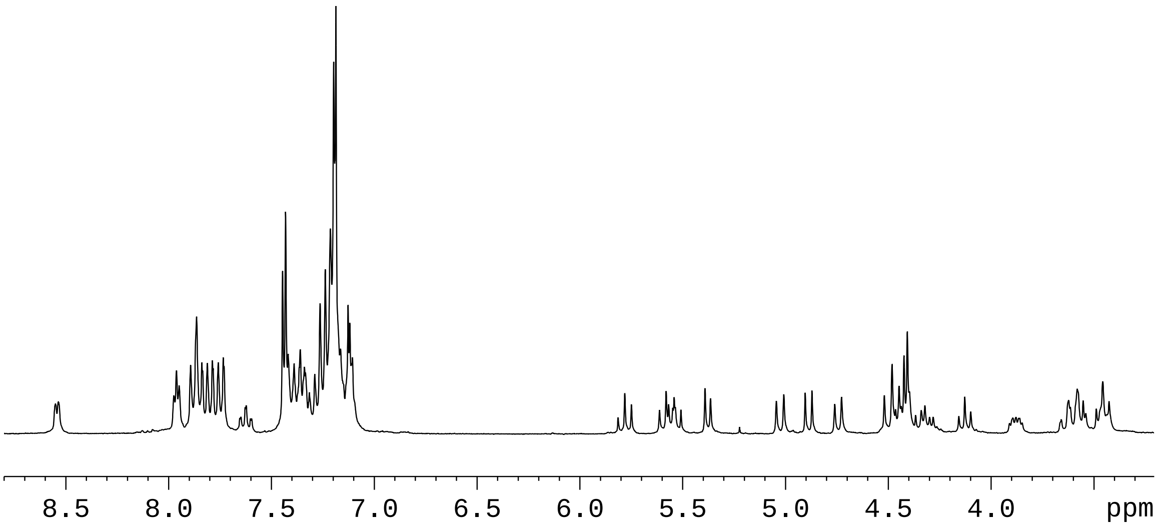


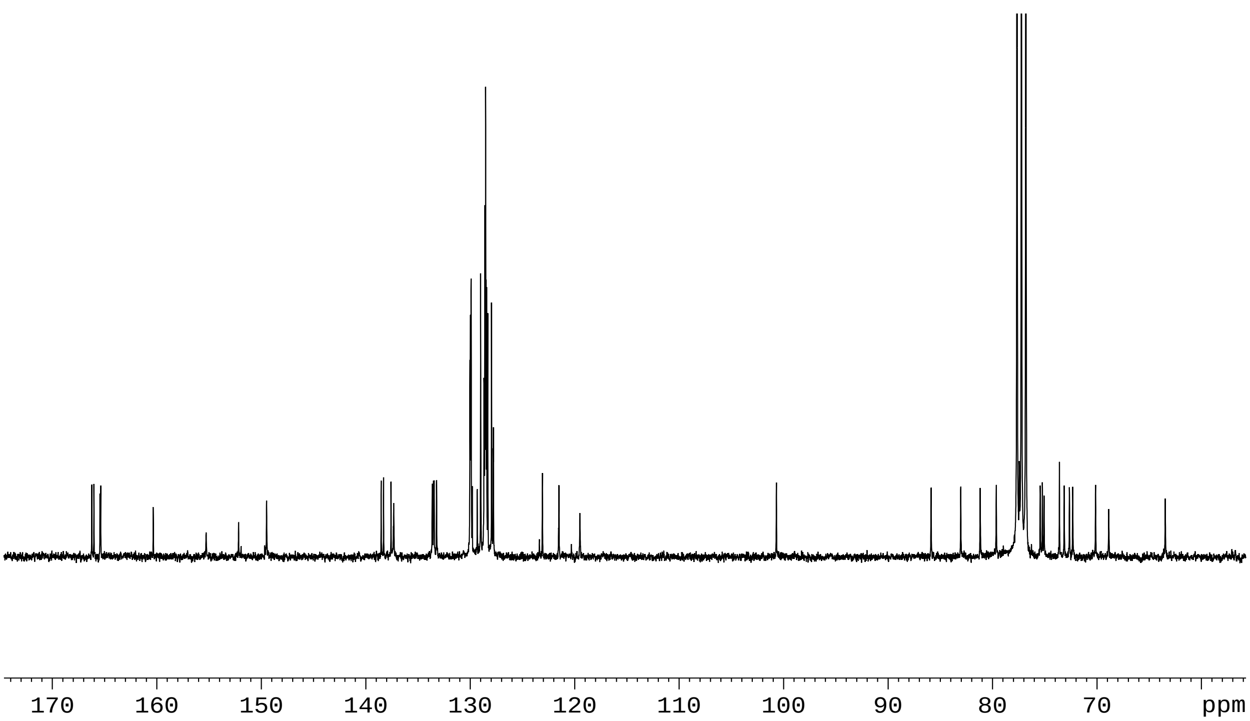
67

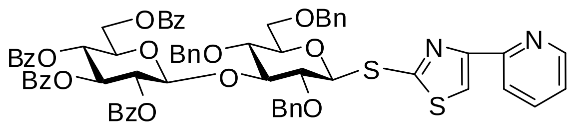



OBz
BzO
O
BzO
BzO
BnO
O
OBn
O
BnO
S
N
S
N

68

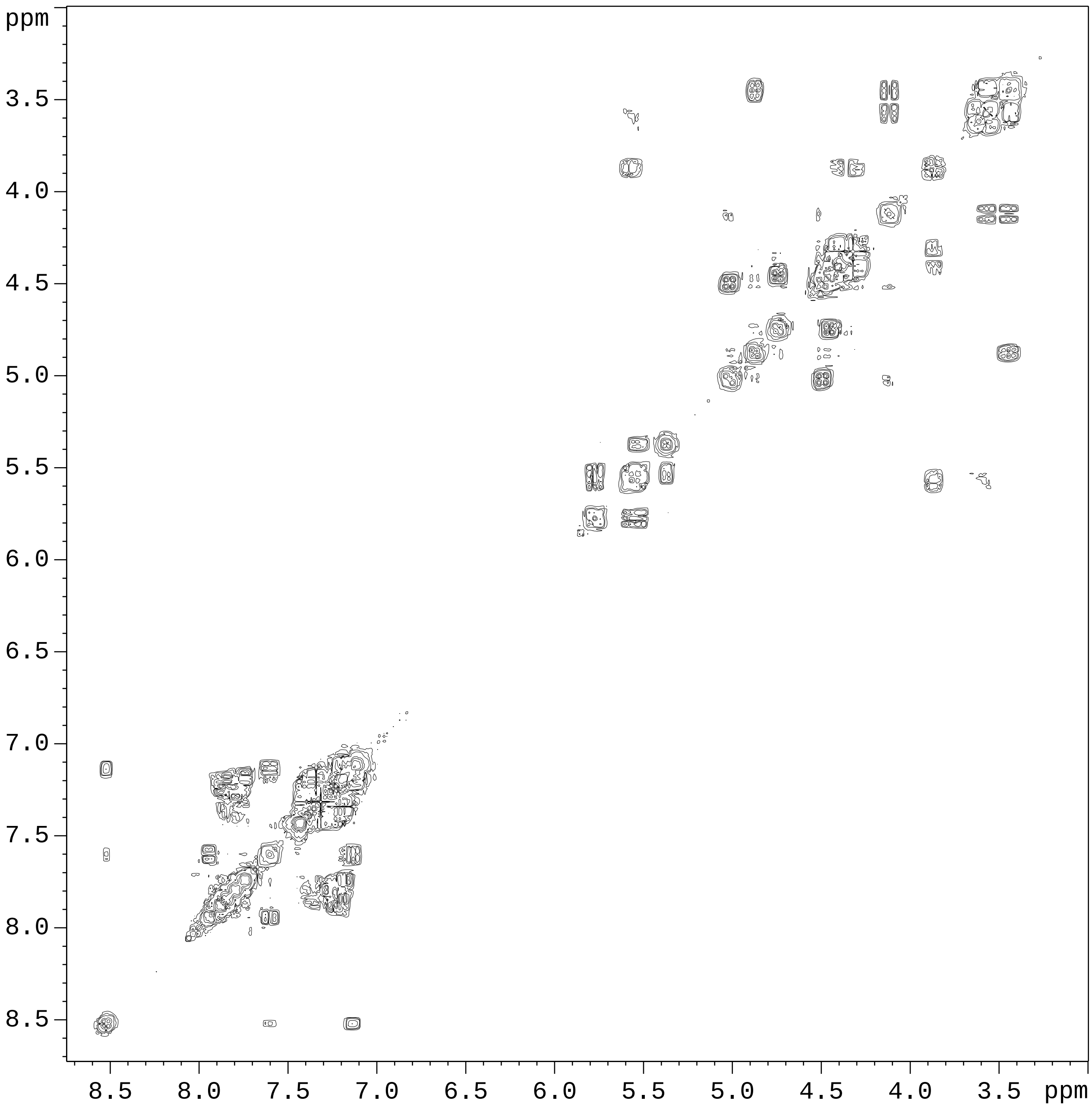

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


170
160
150
140
130
120
110
100
90
80
70
ppm

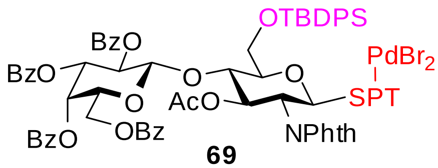


OBz
BzO
BzO
BzO
O
BnO
O
OBn
O
BnO
S
N
S
N

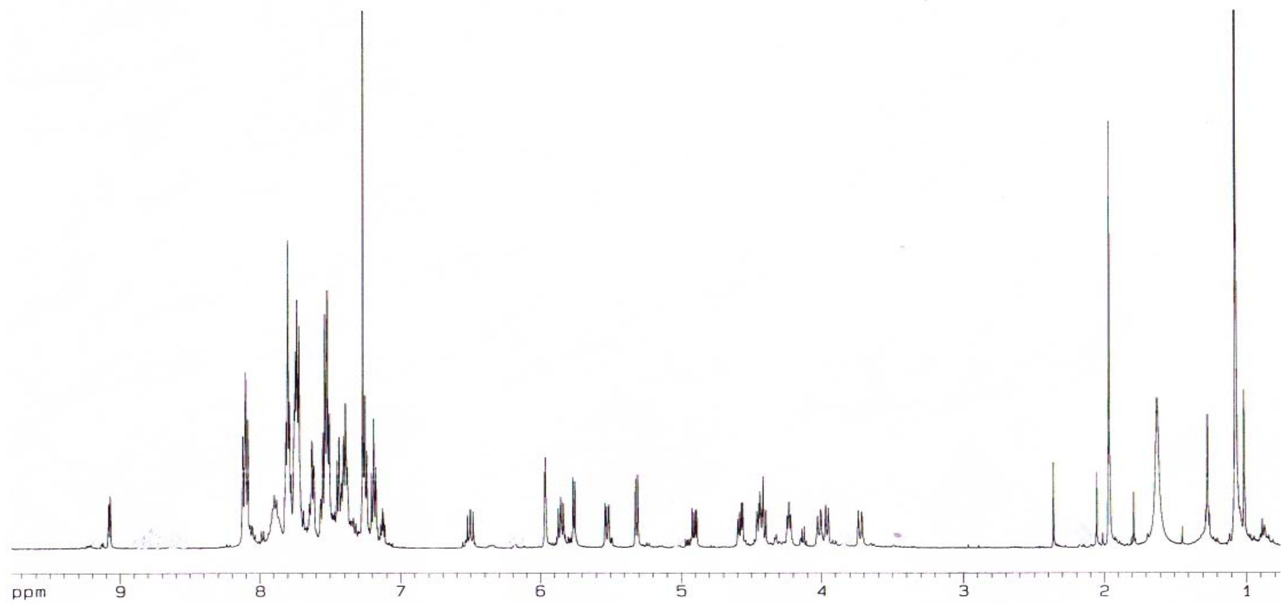
68

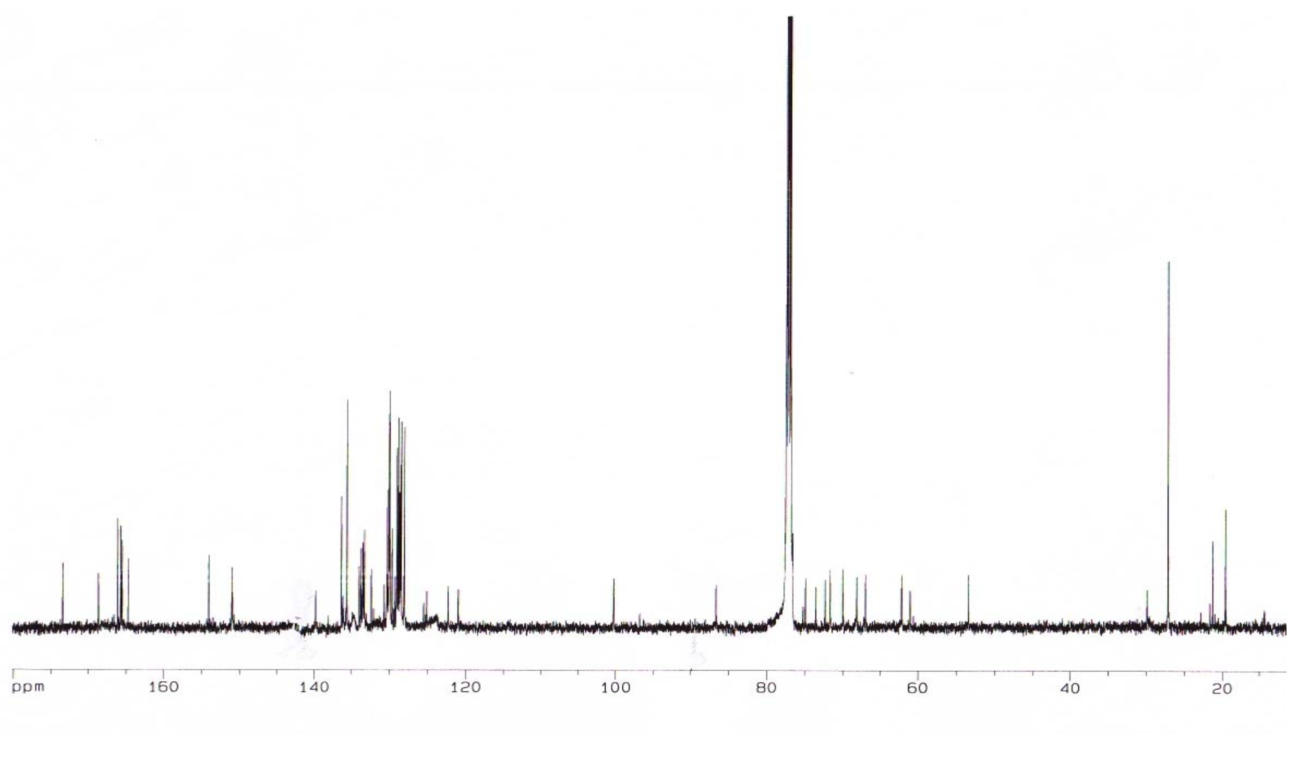


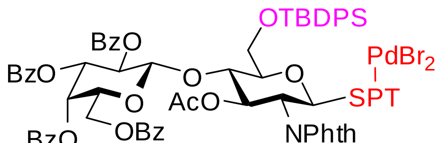
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm


OTBDPS
PdBr2
BzO
BzO
O
SPT
O
AcO
O
BzO
OBz
NPhth

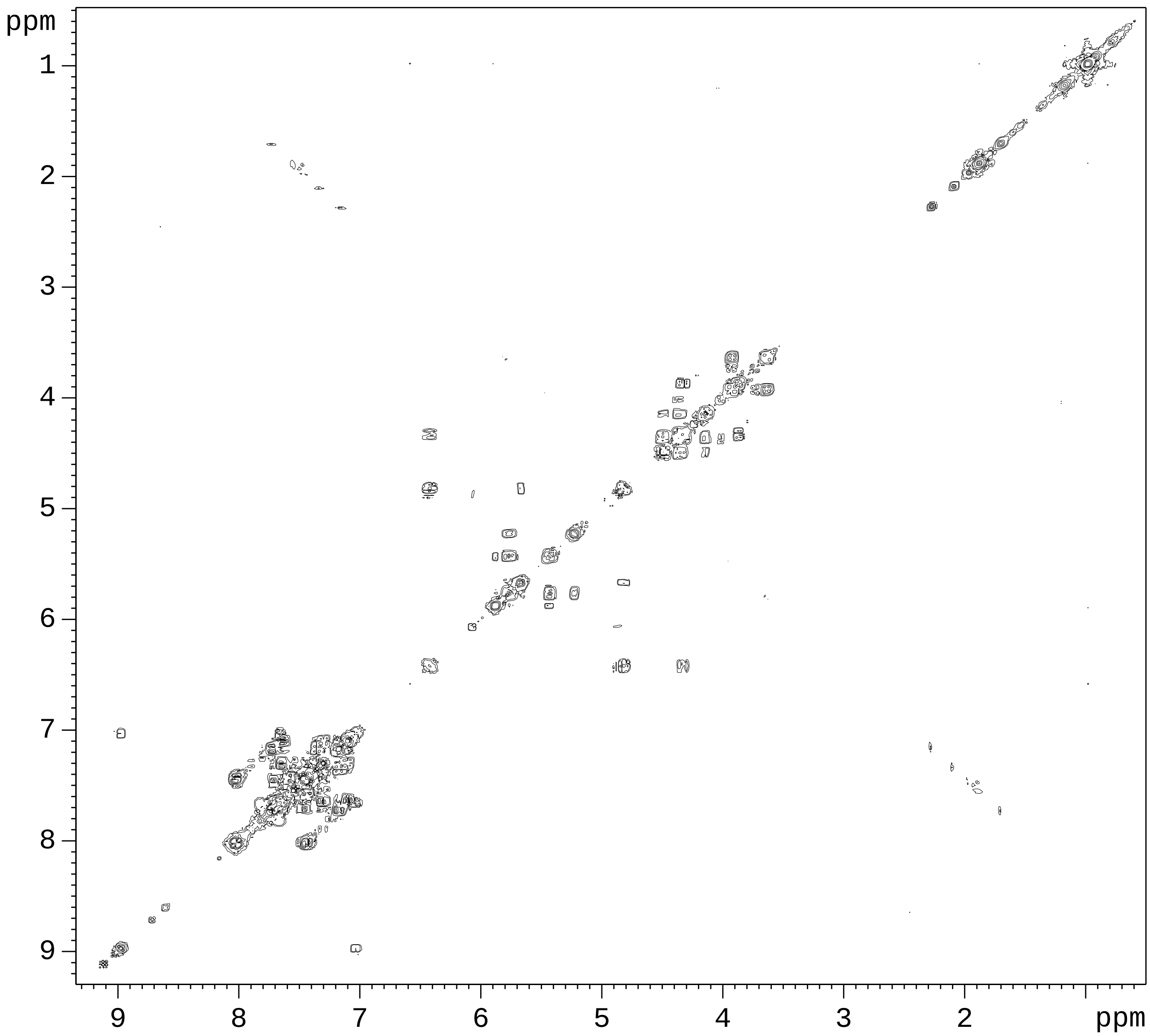
69


ppm
9
8
7
6
5
4
3
2
1


ppm
160
140
120
100
80
60
40
20


OTBDPS
PdBr2
BzO
BzO
O
O
AcO
SPT
BzO
OBz
NPhth

69


ppm
1
2
3
4
5
6
7
8
9
9
8
7
6
5
4
3
2
ppm

References

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