Supporting information

Coordination chemistry approach to the long-standing challenge of stereocontrolled chemical glycosylation

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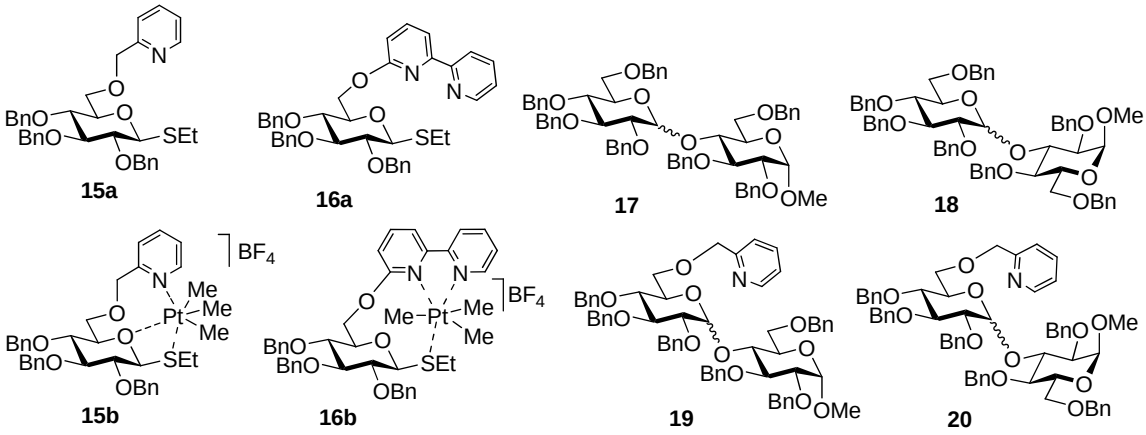
Table 1S. Extended experimental data



Entry SI	Entry article	Donor	Acceptor	Promoter	Product	Time	Yield, %	α/β
1	1.1	**1a**	**3**	MeOTf	**4**	10 min	92	1/1
2	1.3	**2a**	**3**	$Cu(OTf)_2$	**4**	1 h	95	1.5/1
3		**2a**	**11**	$Cu(OTf)_2$	**17**	5 h	90	2.4/1
4		**2a**	**12**	$Cu(OTf)_2$	**18**	6 h	87	2.1/1
5	2.1	**5a**	**3**	AgOTf	**7**	22 h	66	1.1/1
6		**5a**	**11**	AgOTf	**19**	4 days	42	2.8/1
7		**5a**	**12**	AgOTf	**20**	4 days	58	2.2/1
8	2.2	**6a**	**3**	$Cu(OTf)_2$	**7**	16 h	83	2/1
9		**6a**	**11**	$Cu(OTf)_2$	**19**	2 days	75	2.4/1
10		**6a**	**12**	$Cu(OTf)_2$	**20**	2 days	72	1.8/1
11	3.1	**8a**	**3**	AgOTf	**10**	14 h	82	1.5/1
12		**8a**	**11**	AgOTf	**13**	2 days	55	2.7/1
13		**8a**	**12**	AgOTf	**14**	2 days	66	2.1/1
14	3.2	**9a**	**3**	$Cu(OTf)_2$	**10**	2 days	73	1.7/1
15	4.1	**9a**	**11**	$Cu(OTf)_2$	**13**	5 days	53	2.2/1
16	4.2	**9a**	**12**	$Cu(OTf)_2$	**14**	5 days	61	2/1
17		**15a**	**3**	NIS/TfOH	**7**	1 h	70	1.2/1

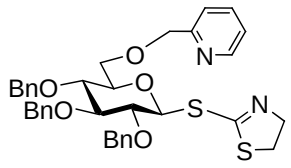
Entry SI	Entry article	Donor	Acceptor	Promoter	Product	Time	Yield, %	α/β
18		**16a**	**3**	NIS/TfOH	**10**	3 h	72	1.8/1
19		**16a**	**3**	DMTST	**10**	4 h	76	1/1
20	1.2	**1b**	**3**	MeOTf	NR	48 h	-	-
21		**1c**	**3**	MeOTf	NR	48 h	-	-
22		**1d**	**3**	MeOTf	NR	48 h	-	-
23	1.4	**2b**	**3**	$Cu(OTf)_2$	**4**	20 h	62	2.4/1
24	1.5	**2c**	**3**	$Cu(OTf)_2$	**4**	15 h	88	2.5/1
25	1.6	**2d**	**3**	$Cu(OTf)_2$	**4**	16 h	79	2.3/1
26	2.3	**5b**	**3**	AgOTf	**7**	20 h	58	2.1/1
27		**5b**	**11**	AgOTf	**19**	2 days	42	2.5/1
28		**5b**	**12**	AgOTf	**20**	2 days	48	3/1
29	2.4	**6b**	**3**	$Cu(OTf)_2$	**7**	62	24 h	5.2/1
30		**6b**	**11**	$Cu(OTf)_2$	**19**	51	3 days	4.2/1
31		**6b**	**12**	$Cu(OTf)_2$	**20**	56	3 days	5.8/1
32	3.3	**8b**	**3**	AgOTf	**10**	16 h	67	2.2/1
33		**8b**	**11**	AgOTf	**13**	4 days	47	4.5/1
34		**8b**	**12**	AgOTf	**14**	4 days	50	3/1
35	3.4	**9b**	**3**	$Cu(OTf)_2$	**10**	24 h	65	9.4/1
36	4.3	**9b**	**11**	$Cu(OTf)_2$	**13**	3 days	50	7.2/1
37	4.4	**9b**	**12**	$Cu(OTf)_2$	**14**	3 days	48	6/1
38		**15b**	**3**	NIS/TfOH	NR	48 h	-	-
39		**15b**	**3**	MeOTf	NR	48 h	-	-
40		**16b**	**3**	NIS/TfOH	NR	48 h	-	-
41		**16b**	**3**	DMTST	NR	48 h	-	-
42		**16b**	**3**	MeOTf	NR	48 h	-	-

NR – no reaction

General

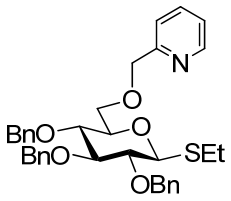
Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol or potassium permanganate solution. Solvents were removed under reduced pressure at <40 ^{o}C. DCM and 1,2-DCE 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). Acetone was dried under argon over P_2O_5, distilled and stored under argon. Hexanes were dried over $CaCl_2$, distilled and stored over molecular sieves (3Å). Reagent grade solvents such as N,N-dimethylformamide was purchased from Acros. Molecular sieves (3Å), 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. Optical rotations were measured at 'Jasco P-1020' polarimeter. ^{1}H-NMR spectra were recorded at 300, 400 MHz and 500 MHz, ^{13}C-NMR spectra were recorded at 75, 125 and 201 MHz (Bruker Avance 300 and 800, VXR 400 and Varian Unity 500). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer. ESI mass spectra were obtained on a Finnigan LCQ spectrometer (Thermo Electron Corp.) and Bruker Apex III Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, Billerica, USA).

Preparation of glycosyl donors.



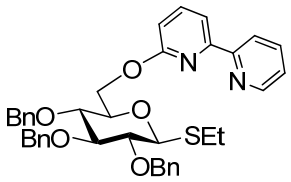
6a

2-Thiazolinyl 2,3,4-tri-O-benzyl-6-O-picolyl-1-thio-β-D-glucopyranoside (6a). To a solution of 2-bromomethylpyridine hydrobromide (495 mg, 1.96 mmol) in DMF (3 mL) NaH (60% dispersion in mineral oil, 84 mg, 2.1 mmol) was added portionwise at 0 ^{o}C and reaction mixture was stirred for 30 min. After that, a solution of 2-thiazolinyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside[1] (360 mg, 0.65 mmol) in DMF (2 mL) was added dropwise, followed by the addition of NaH (52 mg, 1.3 mmol). 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 and extracted 3 times with ethyl acetate/ether (1/1, v/v). The combined organic layer was dried with anhydrous $MgSO_4$, concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound **6a** as a colorless syrup (228 mg, 55% yield). Analytical data for **6a**: R_f = 0.25 (ethyl acetate/hexanes, 3/2, v/v); ^{1}H-n.m.r : δ, 3.30 (t, 2H, CH_2S), 3.57 (m, 2H, H-2,4), 3.70-3.73 (m, 2H, H-3,5), 3.79-3.82 (m, 2H, H-6a,6b), 4.02-4.23 (m, 2H, CH_2N), 4.57-4.87 (m, 8H, CH_2Ph), 7.10-7.60 (m, 18H, aromatic), 8.47 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 35.1, 64.4, 69.4, 74.2, 75.1, 75.7, 75.9, 76.8, 77.2, 79.3, 81.0, 84.7, 86.7, 121.5, 122.4, 127.8, 127.9, 127.9, 128.0, 128.0 (x 2), 128.4 (x 2), 128.5 (x 2), 128.6 (x 2), 136.7, 137.7, 138.1, 138.4, 149.0, 158.6, 163.7 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{36}H_{38}N_2O_5S_2Na$ 665.2120, found 665.2131



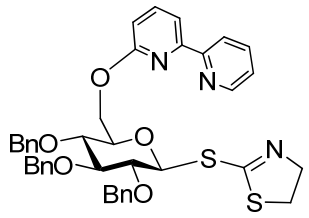
15a

Ethyl 2,3,4-tri-O-benzyl-6-O-picolyl-1-thio-β-D-glucopyranoside (15a). To a solution of 2-bromomethylpyridine hydrobromide (154 mg, 0.61 mmol) in DMF (1 mL) NaH (60% dispersion in mineral oil, 26 mg, 0.65 mmol) was added portionwise at 0 ^{o}C and reaction mixture was stirred for 30 min. After that a solution of ethyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside[2] (100 mg, 0.20 mmol) in DMF (1 mL) was added dropwise, followed by the addition of NaH (16.2 mg, 0.4 mmol). The temperature was then allowed to gradually increase to rt and the reaction mixture was stirred for 3 h. Upon completion, the reaction mixture was poured in ice water and extracted 3 times with ethyl acetate/ether (1/1, v/v). The combined organic layer was dried with anhydrous $MgSO_4$, concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound **15a** as a white foam (102 mg, 86% yield). Analytical data for **15a**: R_f = 0.50 (ethyl acetate/hexanes, 1/1, v/v); ^{1}H-n.m.r : δ, 1.32 (t, 3H, $SCH_2\mathit{CH_3}$), 2.77 (m, 2H, $S\mathit{CH_2}CH_3$), 3.56 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.70-3.80 (m, 3H, H-3,4,5), 4.55 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.60-4.98 (m, 6H, CH_2Ph), 6.80 (d, 1H, aromatic), 7.20-7.40 (m, 16H, aromatic), 7.71 (t, 2H, aromatic), 8.02 (d, 1H, aromatic), 8.31 (d, 1H, aromatic), 8.65 (d, 1H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.2, 25.2, 64.6, 75.3, 75.6, 75.8, 77.8, 78.2, 82.0, 85.3, 86.8, 111.6, 114.0, 121.1, 121.1, 127.9, 128.0 (x 2), 128.1, 128.2 (x 2), 128.3, 128.4 (x 2), 128.4 (x 2), 128.5 (x 2), 128.5 (x 2), 136.8, 138.0, 138.1, 138.6, 139.6, 149.1, 153.8, 156.0, 162.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{39}NO_5SNa$ 608.2447, found 608.2445.



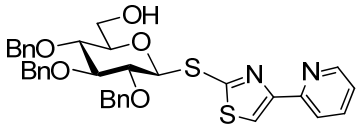
16a

Ethyl 2,3,4-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside (16a). Ethyl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside[2] (2.32 g, 4.7 mmol) was dissolved in DMF (15 mL). After that, 6-chloro-2,2'-bipyridine[3] (9.4 mmol, 1.8 g) was added. The reaction mixture was cooled down to 0 ^{o}C and NaH (60% suspension in mineral oil, 0.75 g, 18.8 mmol) was added portionwise. The temperature was then allowed to gradually increase to rt and the reaction mixture was stirred for 16 h. Upon completion, the reaction mixture was poured in ice water and extracted 3 times with ethyl acetate/ether (1/1, v/v). The combined organic layer was dried with anhydrous $MgSO_4$, concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the title compound **16a** as a colorless syrup (2.59 g, 85% yield). Analytical data for **16a**: R_f = 0.65 (ethyl acetate/hexanes, 1/1, v/v); ^{1}H-n.m.r : δ, 1.32 (t, 3H, $SCH_2\mathit{CH_3}$), 2.77 (m, 2H, $S\mathit{CH_2}CH_3$), 3.56 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.70-3.80 (m, 3H, H-3,4,5), 4.55 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.60-4.98 (m, 6H, CH_2Ph), 6.80 (d, 1H, aromatic), 7.20-7.40 (m, 16H, aromatic), 7.71 (t, 2H, aromatic), 8.02 (d, 1H, aromatic), 8.31 (d, 1H, aromatic), 8.65 (d, 1H, aromatic) ppm; ^{13}C-n.m.r.: δ, 15.2, 25.2, 64.6, 75.3, 75.6, 75.8, 77.8, 78.2, 82.0, 85.3, 86.8, 111.6, 114.0, 121.1, 121.1, 127.9, 128.0 (x 2), 128.1, 128.2 (x 2), 128.3, 128.4 (x 2), 128.4 (x 2), 128.5 (x 2), 128.5 (x 2), 136.8, 138.0, 138.1, 138.6, 139.6, 149.1, 153.8, 156.0, 162.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{39}NO_5SNa$ 608.2447, found 608.2445.



9a

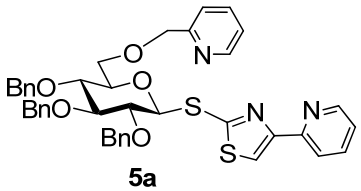
2-Thiazolinyl 2,3,4,-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside (9a). The solution of ethyl 2,3,4,-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside (**16a**, 700 mg, 1.09 mmol), activated molecular sieves (3Å, 600 mg) in CH_2Cl_2 (16 mL) was stirred under argon for 1 h. Freshly prepared Br_2/CH_2Cl_2 (1/165, v/v) was then added (10.2 mL) and the reaction mixture was kept for 5 min at rt. After that, CH_2Cl_2 was evaporated out under reduced pressure at rt and dried in *vacuo*. The residue was redissolved in dry acetonitrile (20 mL), 2-mercaptothiazoline sodium salt[1] (462 mg, 3.27 mmol) was added and the resulting mixture was stirred under argon for 1 h at rt. The reaction mixture was then diluted with toluene (200 mL) and washed with 1% aq. NaOH (50 mL) and water (3 x 50 mL). The organic layer was separated, dried, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to allow the title compound **9a** as a colorless syrup (372 mg, 48% yield). Analytical data for **9a**: R_f = 0.50 (ethyl acetate/toluene, 3/7, v/v); ^{1}H-n.m.r : δ, 3.28 (t, 2H, CH_2S), 3.31 (dd, 1H, $J_{3,4}$ = 7.8 Hz, H-3), 3.65-3.71 (m, 2H, H-2, 4), 3.86 (m, 3H, H-5, 6a, 6b), 4.16 (m, 2H, CH_2N), 4.57-4.94 (m, 6H, CH_2Ph), 5.35 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 6.80 (d, 1H, aromatic), 7.12-7.33 (m, 16H, aromatic), 7.64 (t, 2H, aromatic), 8.02 (h, 1H, aromatic), 8.65 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 33.6, 35.0, 64.1, 64.4, 75.2, 75.6, 75.8, 78.0, 80.9, 84.8, 86.7, 111.6, 114.0, 121.1, 123.6, 127.6, 127.8 (x 3), 128.0, 128.1 (x 2), 128.3 (x 2), 128.4 (x 2), 128.4 (x 2), 128.5 (x 2), 136.8, 137.6, 137.8, 138.3, 139.5, 149.1, 153.3, 155.9, 162.7, 163.7 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{40}H_{39}N_3O_5S_2Na$ 728.2229, found 728.2223.



21

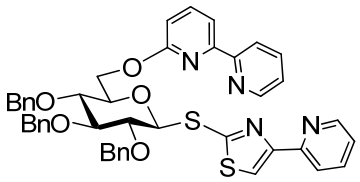
4-(Pyridin-2-yl)thiazol-2-yl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (21). 4-(Pyridin-2-yl)thiazol-2-yl 1-thio-β-D-glucopyranoside[4] (1.17 g, 3.4 mmol) was dissolved in dry pyridine (10 mL) and triphenylmethyl chloride (1.43 g, 5.1 mmol) was added. The reaction mixture was left for 16 h at rt. After that, solvent was removed under reduced pressure and dried in *vacuo*. The residue was then dissolved in DMF (15 mL) and benzyl bromide (0.83 mL, 7.0 mmol) was added. The mixture was cooled down to 0 ^{o}C and 60% NaH (0.42 g, 10.5 mmol) was added portionwise. The temperature was allowed to gradually increase to rt and the reaction mixture was stirred for 4 h. Upon completion, the reaction mixture was poured in ice-water and extracted with ethyl acetate/ether (1/1, v/v, 3 x 35 mL). The combined organic layer was dried with anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude residue was dissolved in wet CH_2Cl_2 (30 mL) containing trifluoroacetic acid (3 mL) and the reaction mixture was kept for 1 h at rt. After that, the mixture was diluted with CH_2Cl_2 (200 mL), transferred into a separatory funnel and washed with water (50 mL), saturated aq. $NaHCO_3$ (50 mL) and water (3 x 50 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 **21** as a white amorphous solid (850 mg, 40% yield over 3 steps). Analytical data for **21**: R_f= 0.48 (acetone/toluene, 3/7, v/v), $[\alpha]_D^{20}$ = -19.7^{o} (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.46-3.65 (m, 3H, H-2, 3, 5), 3.65-3.80 (m, 2H, H-4, 6b), 3.87 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 4.60-4.95 (m, 6H, CH_2Ph), 5.04 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 7.02-7.36 (m, 16H, aromatic), 7.70 (m, 1H, aromatic), 8.06 (m, 2H, aromatic), 8.57 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: δ, 29.9, 62.1, 75.4, 75.8, 76., 80.1, 80.7, 86.1, 86.6, 119.7, 121.5, 123.2, 128.0 (x 2), 128.1 (x 2), 128.2 (x 2), 128.5 (x 2), 128.5 (x 2), 128.7, 128.7 (x 2), 128.7 (x 2), 137.3, 137.8,

138.0, 138.4, 149.7, 152.2, 155.8, 159.9 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{35}H_{34}N_2O_5S_2Na$ 649.1827, found 649.1827.



5a

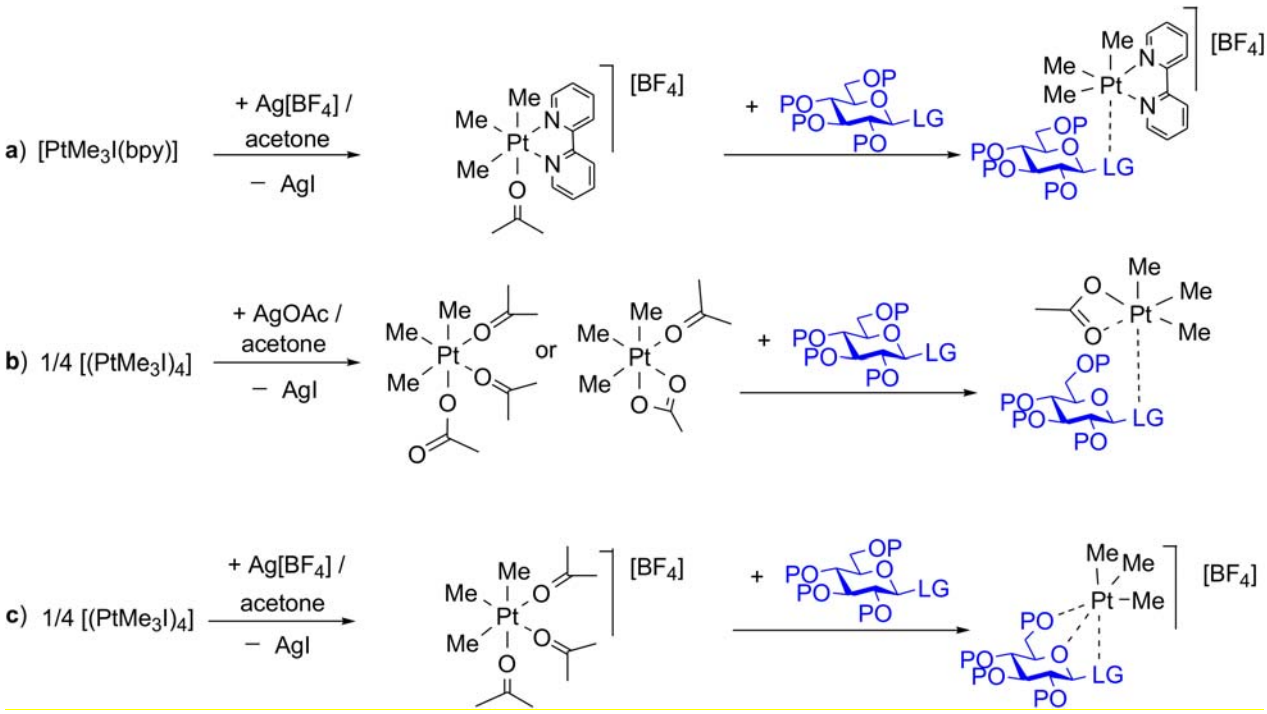
4-(Pyridin-2-yl)thiazol-2-yl 2,3,4-tri-O-benzyl-6-O-picolyl-1-thio-β-D-glucopyranoside (5a). NaH (60% dispersion in mineral oil, 174 mg, 4.4 mmol) was added portionwise to a solution of 2-bromomethylpyridine hydrobromide (1.03 g, 4.1 mmol) in DMF (5 mL) and the reaction mixture was stirred at 0 ^oC for 30 min. After that, a solution of 4-(pyridin-2-yl)thiazol-2-yl 2,3,4-tri-O-benzyl-1-thio-β-D-glucopyranoside (**21**) (850 mg, 1.36 mmol) in DMF (5 mL) was added dropwise, followed by the addition of NaH (109 mg, 2.7 mmol). The temperature was then allowed to gradually increase to rt and the reaction mixture was stirred for 1 h. The resulting mixture was poured in ice-water and extracted with ethyl acetate/ether (1/1, v/v, 3 x 20 mL). The combined organic layer was dried with anhydrous $MgSO_4$, concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (acetone/toluene gradient elution) to allow the title compound **5a** as a pale yellow syrup (760 mg, 78% yield). Analytical data for **5a**: R_f = 0.55 (1/1 acetone/toluene), $[\alpha]_D^{20}$ = -12.9^o (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.71 (m, 2H, H-2, 4), 3.83 (m, 2H, H-3, 5), 3.91 (m, 2H, H-6a, 6b), 4.69-5.06 (m, 7H, CH_2Ph), 5.06-5.10 (m, 2H, H-1, CH_2Ph), 7.10-7.68 (m, 2H, aromatic), 8.11-8.17 (m, 2H, aromatic), 8.54 (d, 1H, H-6'), 8.62 (d, 1H, H-6') ppm; ^{13}C-n.m.r.: 69.8, 74.7, 75.6, 76.0, 78.0, 79.9, 81.0, 86.3, 87.0, 120.0, 121.7, 121.8, 122.7, 123.4, 128.3 (x 3), 128.4 (x 3), 128.4, 128.7 (x 2), 128.8, 128.9 (x 4), 137.0, 137.4, 138.2, 138.4, 138.7, 149.4, 149.9, 152.5, 155.9, 158.8, 160.4 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{41}H_{39}N_3O_5S_2Na$ 740.2229, found 740.2227.



8a

4-(Pyridin-2-yl)thiazol-2-yl 2,3,4-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside (8a). The solution of ethyl 2,3,4-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside (**16a**, 600 mg, 0.93 mmol), activated molecular sieves (3Å, 460 mg) in CH_2Cl_2 (14 mL) was stirred under argon for 1 h. Freshly prepared Br_2/CH_2Cl_2 (1/165, v/v) was then added (8.7 mL) and the reaction mixture was kept for 5 min at rt. After that, CH_2Cl_2 was evaporated out under reduced pressure at rt and dried in *vacuo*. The residue was dissolved in dry acetonitrile (10 mL) and 4-(pyridin-2'-yl)thiazole-2(3H)-thione sodium salt[4] (600 mg, 2.78 mmol) was added and the reaction mixture was stirred under argon for 2 h at rt. The resulting mixture was diluted with toluene (200 mL) and washed with 1% aq. NaOH (50 mL) and water (3 x 50 mL), the organic layer was separated, dried, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/toluene gradient elution) to allow the title compound **8a** as a colorless syrup (330 mg, 46% yield). Analytical data for **8a**: R_f = 0.40 (3/7 ethyl acetate/toluene), $[\alpha]_D^{20}$ = 32.5° (c = 1, $CHCl_3$); ^{1}H-n.m.r : δ, 3.64 (m, 2H, H-2, 4), 3.77-3.85 (m, 4H, H-3, 5, 6a, 6b), 4.55-4.98 (m, 6H, CH_2Ph), 5.01 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 6.70 (d, 1H, aromatic), 7.12-7.34 (m, 20H, aromatic), 7.63 (m, 2H, aromatic), 7.98-8.06 (m, 2H, aromatic), 8.54-8.58 (dd, 2H, aromatic) ppm; ^{13}C-n.m.r.: 62.2. 73.5, 73.7, 74.0, 75.9, 76.4, 78.7, 84.0, 84.8, 109.7, 112.2, 117.6, 118.2, 119.3, 119.5 (x 2), 121.1, 121.3, 121.7, 126.0 (x 2), 126.0, 126.2, 126.2, 126.3 (x 2), 126.4, 126.4, 126.5, 126.5 (x 2), 126.6 (x 2), 126.6 (x 2), 126.7 (x 2), 127.2, 134.9, 135.2, 135.2, 135.8, 135.9, 136.4, 137.7, 147.2, 147.6, 147.7, 150.3, 151.5, 153.5, 154.0, 158.2, 160.8 ppm; HR-FAB MS $[M+Na]^+$ calcd for $C_{45}H_{40}N_4O_5S_2Na$ 803.2338, found 803.2330.

General procedures for the preparation of Pt(IV) complexes



PtMe$_3$-carbohydrate complexes:

A mixture of [PtMe$_3$I(bpy)][5] (50 mg, 0.096mmol) and Ag[BF$_4$] (18.6 mg, 0.096 mmol) (**a**), [(PtMe$_3$I)$_4$][6] (50 mg, 0.034mmol) and AgOAc (23 mg, 0.136 mmol) (**b**) and [(PtMe$_3$I)$_4$] (30 mg, 0.02mmol) and Ag[BF$_4$] (16 mg, 0.083 mmol) (**c**), respectively, was dried under *vacuo* for 2 h. Dry acetone (6 mL) was added to the mixture in a very secured anaerobic condition. The reaction mixture was stirred at rt under atmosphere of argon for 2-20 h upon completion, AgI precipitate was removed from the reaction mixture by filtration, the filtrate was then added to another Schlenk flask containing a glycosyl donor (0.136 mmol). The reaction mixture was kept at rt under argon for 2-20 h to completion. After that, solvent was removed under reduced pressure, DCM (1 mL) and hexanes (3 mL) were added to the crude mixture to obtain the corresponding Pt(IV) complex as a syrup or precipitate. The residue will be used as is for glycosylation without column purification.

[$PtMe_3$(ch)][BF_4] 1b (ch = Ethyl-2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside)

Yield: 53 mg (70%). ^{1}H-n.m.r.: 1.18 (s+d, br, 9H, $^2J_{Pt,H}$ = 75.9 Hz, $PtMe_3$), 1.34 (t, br, 3H, SCH_2CH_3), 2.93 (m, br, 1H, SCH_2CH_3), 3.07 (m, br, 1H, SCH_2CH_3), 3.62 (m, br, 4H, H-2, 4, 6a, 6b), 3.73 (m, br, 2H, H-3, 5), 4.87-4.44 (m, br, 9H, H-1, $CH_2C_6H_5$), 7.36-7.12 (m, 20 H, $CH_2C_6H_5$, aromatic). ^{13}C-n.m.r.: –11.3 (s+d, br, $PtMe_3$), 14.3 (SCH_2CH_3), 25.5 (SCH_2CH_3), 67.6 (C-6), 73.4 ($CH_2C_6H_5$), 75.0 ($CH_2C_6H_5$), 75.3 ($CH_2C_6H_5$), 75.6 ($CH_2C_6H_5$), 77.3 (C-5), 79.2 (br, C-2), 80.0 (br, C-4), 83.2 (br, C-1), 85.1 (C-3), 127.6-138.0 ($CH_2C_6H_5$, aromatic). ESI-MS: ([$PtMe_3$(ch)]$^+$) *m*/*z* (obsd./calc. %) 823 (51/69), 824 (100/100), 825 (86/93), 826 (30/36), 827 (19/26).

[$PtMe_3$(bpy)(ch)][BF_4] 2c (ch = 2-Thiazolinyl-2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside)

Yield: 72 mg (72%). ^{1}H-n.m.r.: 0.45 (s+d, 3H, $^2J_{Pt,H}$ = 72.2 Hz, ch_{trans}-PtMe), 1.21 (s+d, 3H, $^2J_{Pt,H}$ = 67.2 Hz, N_{trans}-PtMe), 1.23 (s+d, 3H, $^2J_{Pt,H}$ = 68.1 Hz, N_{trans}-PtMe), 3.00 (m, 2H, SCH_2), 3.44 (m, 3H, H-2, 4, NCH_2), 3.66 (m, 4H, H-3, 5, 6a, 6b), 3.86 (m, 1H, NCH_2), 4.41-4.86 (m, 9H, H-1, $CH_2C_6H_5$), 7.11-7.38 (m, 20H, $CH_2C_6H_5$, aromatic), 7.56 (m, 1H, H-5′$_{bpy}$), 7.66 (m, 1H, H-5$_{bpy}$), 8.10 (m, 1H, H-4′$_{bpy}$), 8.15 (m, 1H, H-4$_{bpy}$), 8.57 (d, 2H, H-3$_{bpy}$, 3′$_{bpy}$), 8.81 (d, 1H, H-6′$_{bpy}$), 8.87 (d, 1H, H-6$_{bpy}$). ^{13}C-n.m.r.: –5.7 (s+d, $^1J_{Pt,C}$ = 657.1 Hz, ch_{trans}-PtMe), –4.0 (s+d, $^1J_{Pt,C}$ = 623.4 Hz, N_{trans}-PtMe), –3.7 (s+d, $^1J_{Pt,C}$ = 609.7 Hz, N_{trans}-PtMe), 32.1 (SCH_2), 64.4 (NCH_2), 68.3 (C-6), 73.3 (2 × $CH_2C_6H_5$), 75.0 ($CH_2C_6H_5$), 75.7 ($CH_2C_6H_5$), 77.3 (C-5), 79.3 (C-4), 79.7 (C-2), 85.6 (C-1), 86.4 (C-3), 125.2 (C-3$_{bpy}$, 3′$_{bpy}$), 127.6-128.7 (C-5$_{bpy}$, 5′$_{bpy}$, $CH_2C_6H_5$, aromatic), 137.2-138.7 ($CH_2C_6H_5$, aromatic), 141.0 (C-4$_{bpy}$, 4′$_{bpy}$), 147.1 (C-6$_{bpy}$, C-6′$_{bpy}$). ESI-MS: ([$PtMe_3$(bpy)(ch)]$^+$) *m*/*z* (obsd./calc. %) 1036 (55/61), 1037 (96/99), 1038 (100/100), 1039 (43/49), 1040 (25/33), 1041 (13/14).

[$PtMe_3$(OAc)(ch)] 2d (ch = 2-Thiazolinyl-2,3,4,6-tetra-O-benzyl-1-thio-β-D-glucopyranoside) Yield: 102 mg (80%). ^{1}H-n.m.r.: 1.17 (s+d, br, 9H, $^2J_{Pt,H}$ = 74.4 Hz, $PtMe_3$), 1.91 (s, 3H, $CH_3C(O)O$), 3.25 (m, 2H, SCH_2), 3.59 (m, 2H, H-2, 4), 3.75 (m, 4H, H-3, 5, 6a, 6b), 4.20 (m, br, 1H, NCH_2), 4.46 (m, br, 1H, NCH_2), 4.55-4.96 (m, 9H, H-1, $CH_2C_6H_5$), 7.17-7.38 (m, 20H, $CH_2C_6H_5$, aromatic). ^{13}C-n.m.r.: –11.3 (s+d, br, $^1J_{Pt,C}$ = 740.4 Hz, $PtMe_3$), 25.4 ($CH_3C(O)O$), 32.4 (SCH_2), 63.6 (NCH_2), 68.5 (C-6), 73.4 ($CH_2C_6H_5$), 75.1 ($CH_2C_6H_5$), 75.8 (2 × $CH_2C_6H_5$), 77.4 (C-5), 79.4 (C-4), 80.6 (C-2), 85.9 (C-1), 86.6 (C-3), 127.6-128.4 ($CH_2C_6H_5$, aromatic), 137.2-138.1 ($CH_2C_6H_5$, aromatic). ESI-MS: $[PtMe_3(ch)]^+$ *m*/*z* (obsd./calc.%) 880 (63/68), 881 (100/100), 882 (90/97), 883 (38/42), 884 (28/30), 885 (9/11).

[$PtMe_3$(ch)][BF_4] 9b (ch = 2-Thiazolinyl-2,3,4,-tri-O-benzyl-6-O-(2,2'-bipyridin-6-yl)-1-thio-β-D-glucopyranoside)

^{1}H-n.m.r.: δ 0.81 (s+d, 3H, $^2J_{Pt,H}$ = 73.0 Hz, PtMe), 1.31 (s+d, 3H, $^2J_{Pt,H}$ = 71.4 Hz, PtMe), 1.75 (s+d, 3H, $^2J_{Pt,H}$ = 70.5 Hz, PtMe), 2.99 (m, br, 1H, SCH_2), 3.27 (m, 1H, SCH_2), 3.40 (dd, 1H, H-2), 3.70 (dd, 1H, H-4), 3.93 (m, 2H, H-3, 5), 4.36 (m, 2H, NCH_2), 4.51-4.98 (m, 8H, $CH_2C_6H_5$, H6a, 6b), 5.21 (d, 1H, H-1, $^3J_{H,H}$ = 9.96 Hz), 7.02-7.43 (m, 15H, $CH_2C_6H_5$, aromatic), 7.48 (d, 1H, H-5_{bpy}), 7.73 (d, 1H, H-3_{bpy}), 7.97 (t, 1H, H-$5'_{bpy}$), 8.11 (t, 1H, H-4_{bpy}), 8.36 (m, 2H, H-$4'_{bpy}$, $3'_{bpy}$), 9.16 (d, 1H, H-$6'_{bpy}$). ^{13}C-n.m.r.: –8.1 (PtMe, $^1J_{Pt,C}$ = 688.2 Hz), –4.9 (PtMe, $^1J_{Pt,C}$ = 639.9 Hz), 0.2 (PtMe, $^1J_{Pt,C}$ = 726.4 Hz), 33.9 (SCH_2), 65.1 (NCH_2), 65.7 (C-6), 75.5 ($CH_2C_6H_5$), 75.7 ($CH_2C_6H_5$), 75.8 ($CH_2C_6H_5$), 78.3 (C-4), 79.0 (C-5), 83.9 (C-2), 86.6 (C-3), 89.3 (C-1), 111.5 (C-5_{bpy}), 118.5 (C-3_{bpy}), 125.9 (C-$3'_{bpy}$), 129.2-128.1 (C-$5'_{bpy}$, $CH_2C_6H_5$, aromatic), 138.8 ($CH_2C_6H_5$, aromatic), 139.1 ($CH_2C_6H_5$, aromatic), 139.2 ($CH_2C_6H_5$, aromatic), 141.5 (C-$4'_{bpy}$), 144.3 (C-4_{bpy}), 147.5 (C-$6'_{bpy}$). ESI-MS: $[PtMe_3(ch)]^+$ *m*/*z* (obsd./calc.%) 944 (66/66), 945 (99/100), 946 (100/98), 947 (47/45), 948 (30/31).

General procedures for glycosylation

AgOTf-promoted glycosylation procedure. A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. AgOTf (0.22 mmol) was added and the reaction mixture was stirred until the starting materials disappear on TLC. 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 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 (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. MeOTf (0.33 mmol) was added and the reaction mixture was stirred until the starting materials disappear on TLC. 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 were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

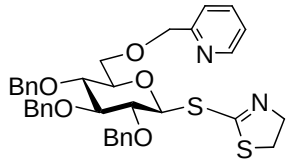
$Cu(OTf)_2$-promoted glycosylation procedure. A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. $Cu(OTf)_2$ (0.33 mmol) was added and the reaction mixture was stirred until the starting materials disappear on TLC. 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 were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

NIS/TfOH-promoted glycosylation procedure. A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. NIS (0.22 mmol) and a catalytic amount of TfOH (0.02 mmol) were added and the reaction mixture was stirred until the starting materials disappear on TLC. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with water (10 mL), $Na_2S_2O_3$ (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 were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

DMTST-promoted glycosylation procedure. A mixture of the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (4Å, 200 mg) in $(ClCH_2)_2$ (2 mL) was stirred under argon for 1.5 h. DMTST (0.33 mmol) was added and the

reaction mixture was stirred until the starting materials disappear on TLC. 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 were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

Spectra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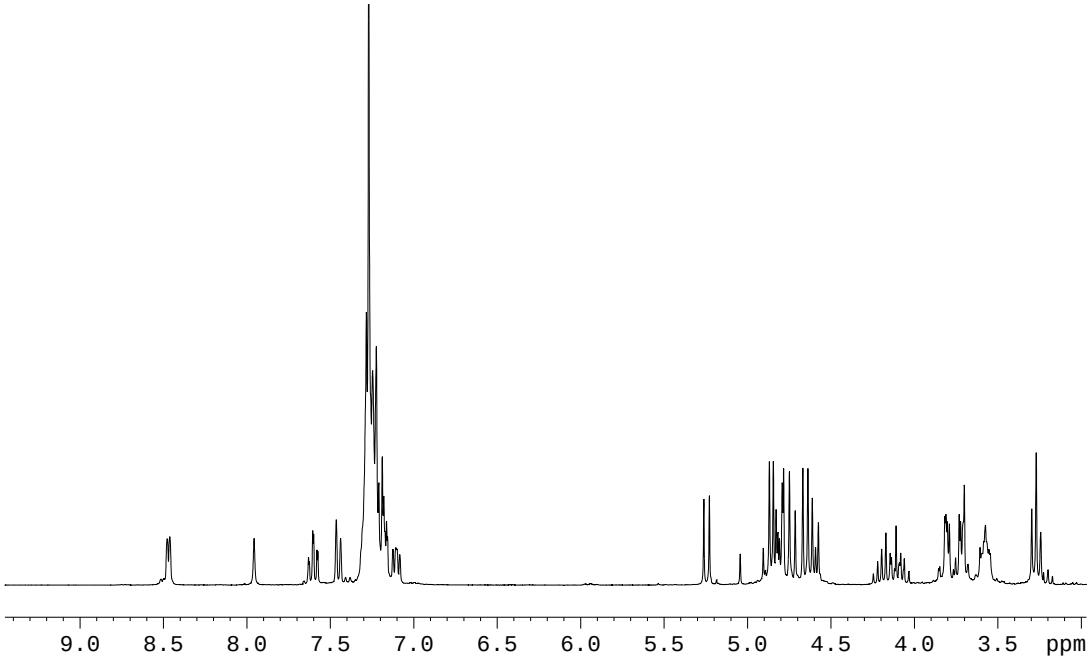
O
BnO
S
N
BnO
S

6a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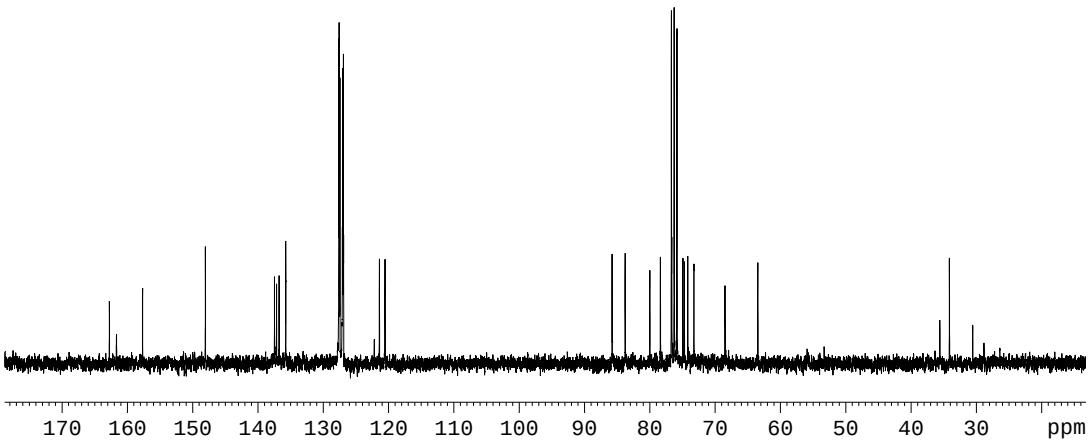
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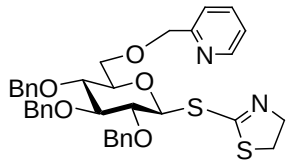
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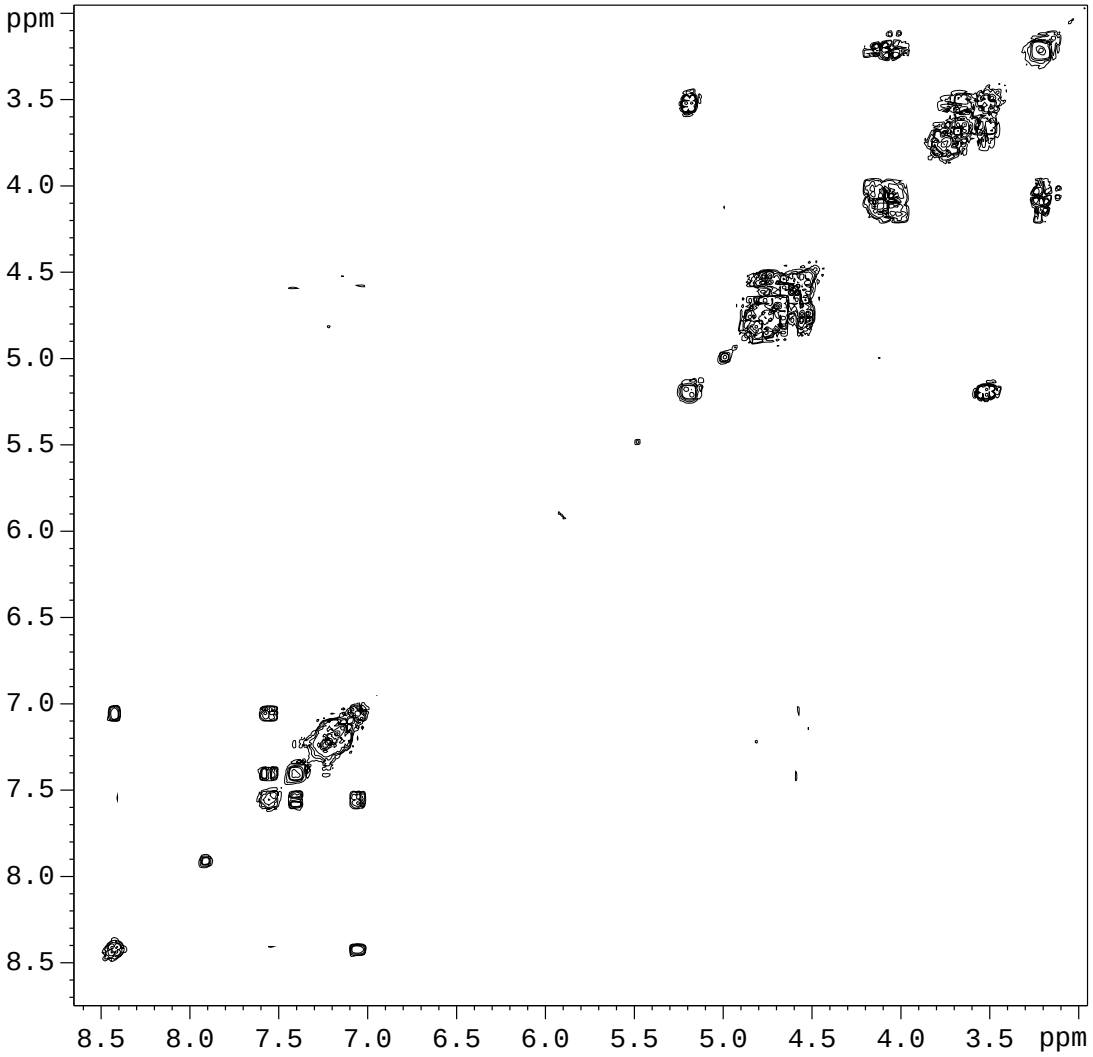
S

6a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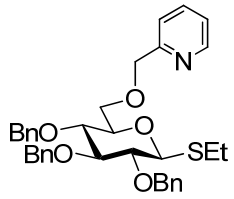

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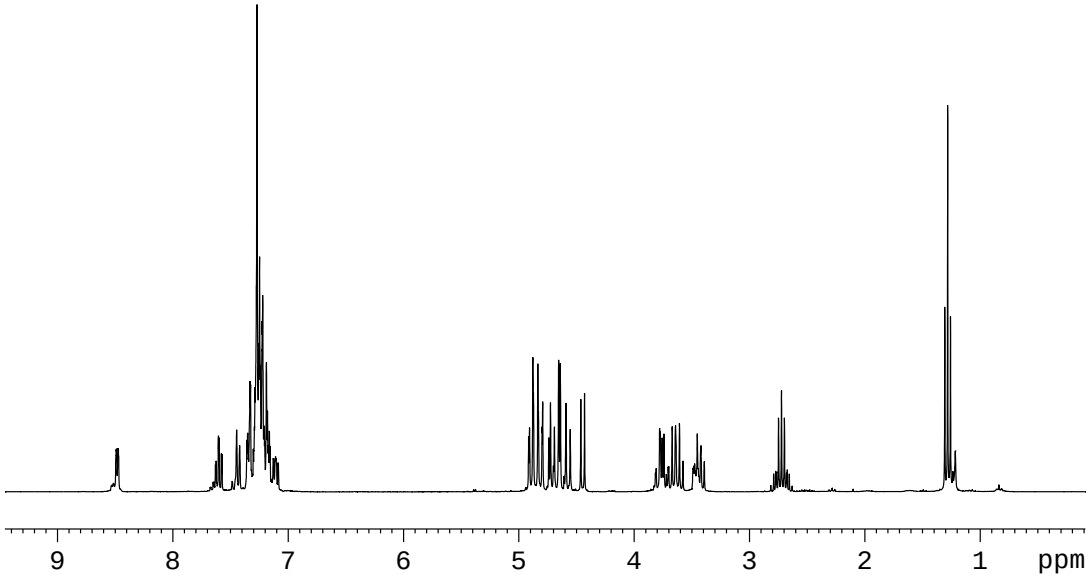

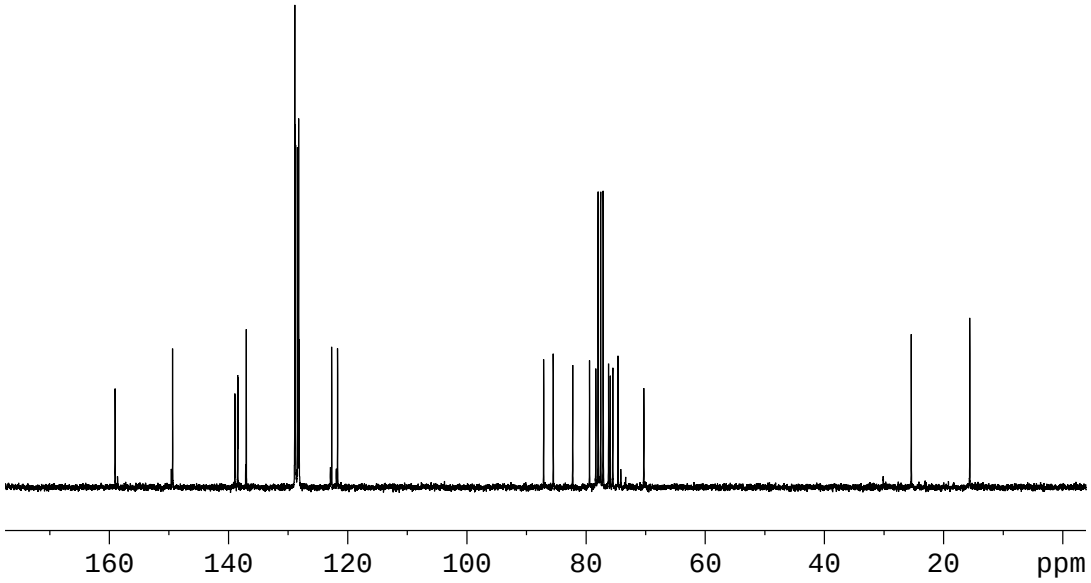

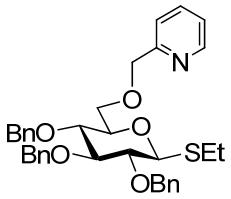

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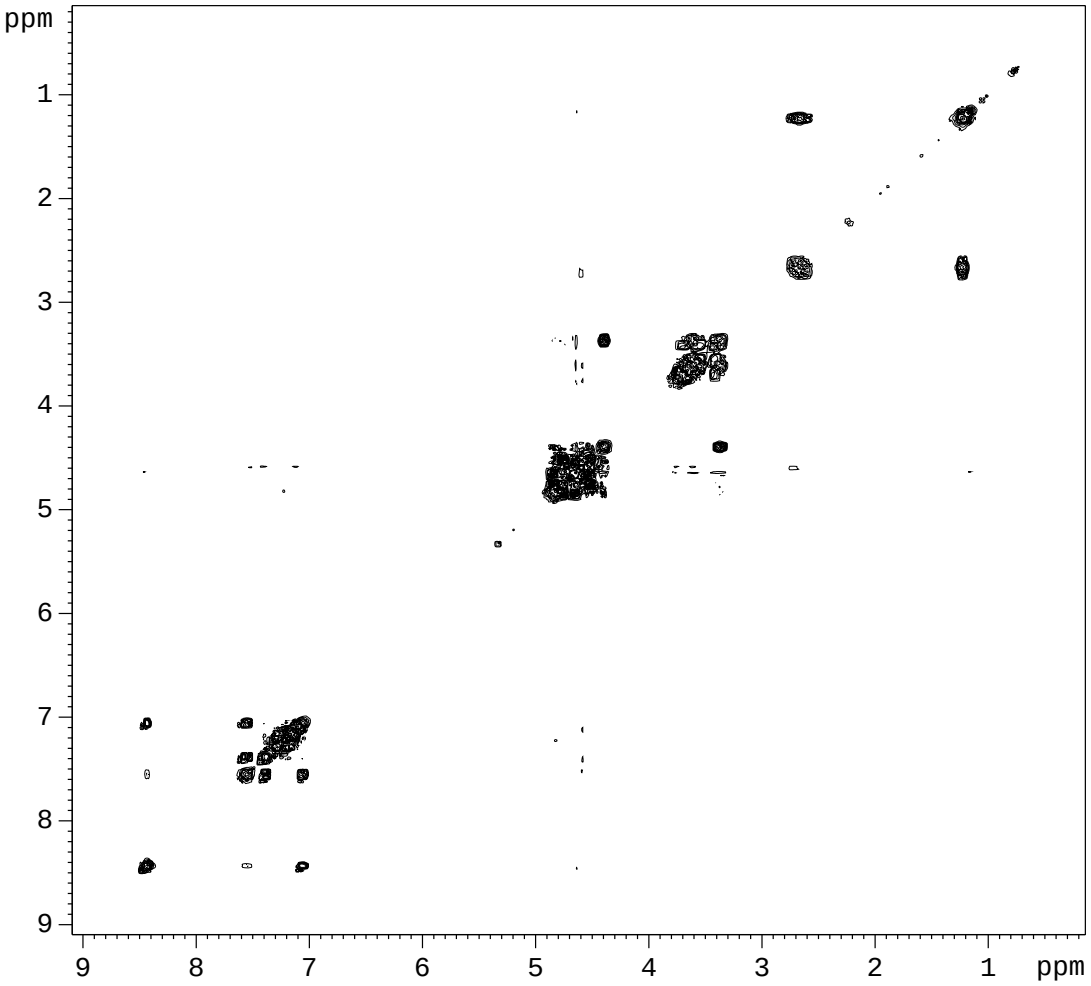

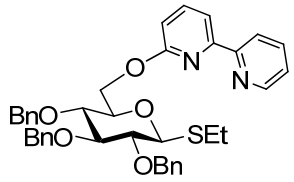
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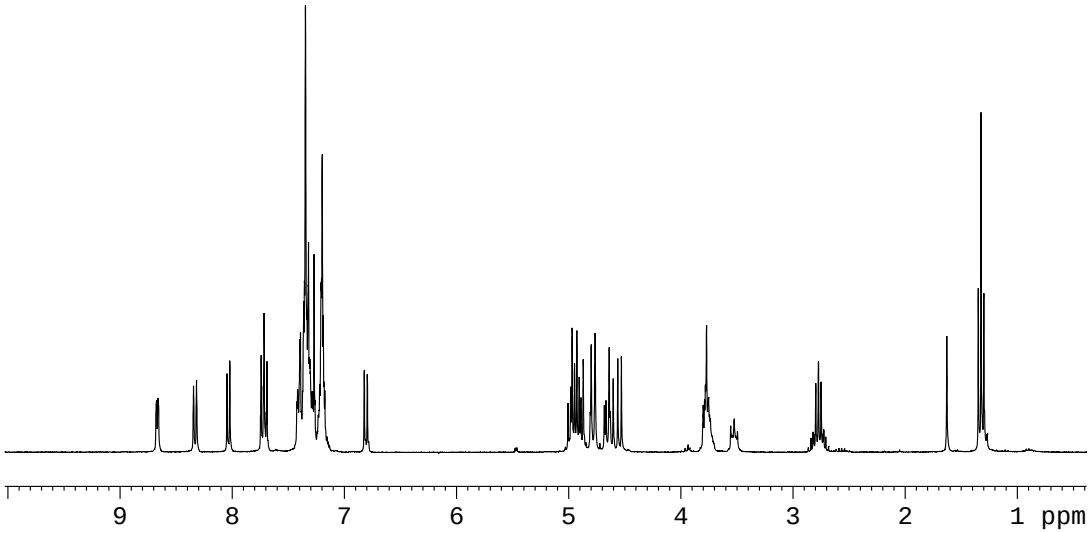
16a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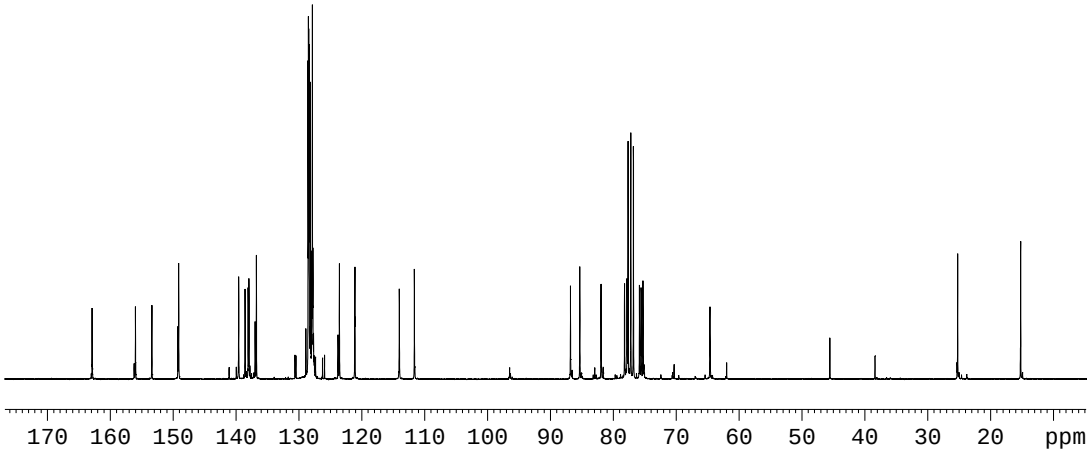
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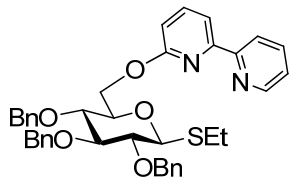

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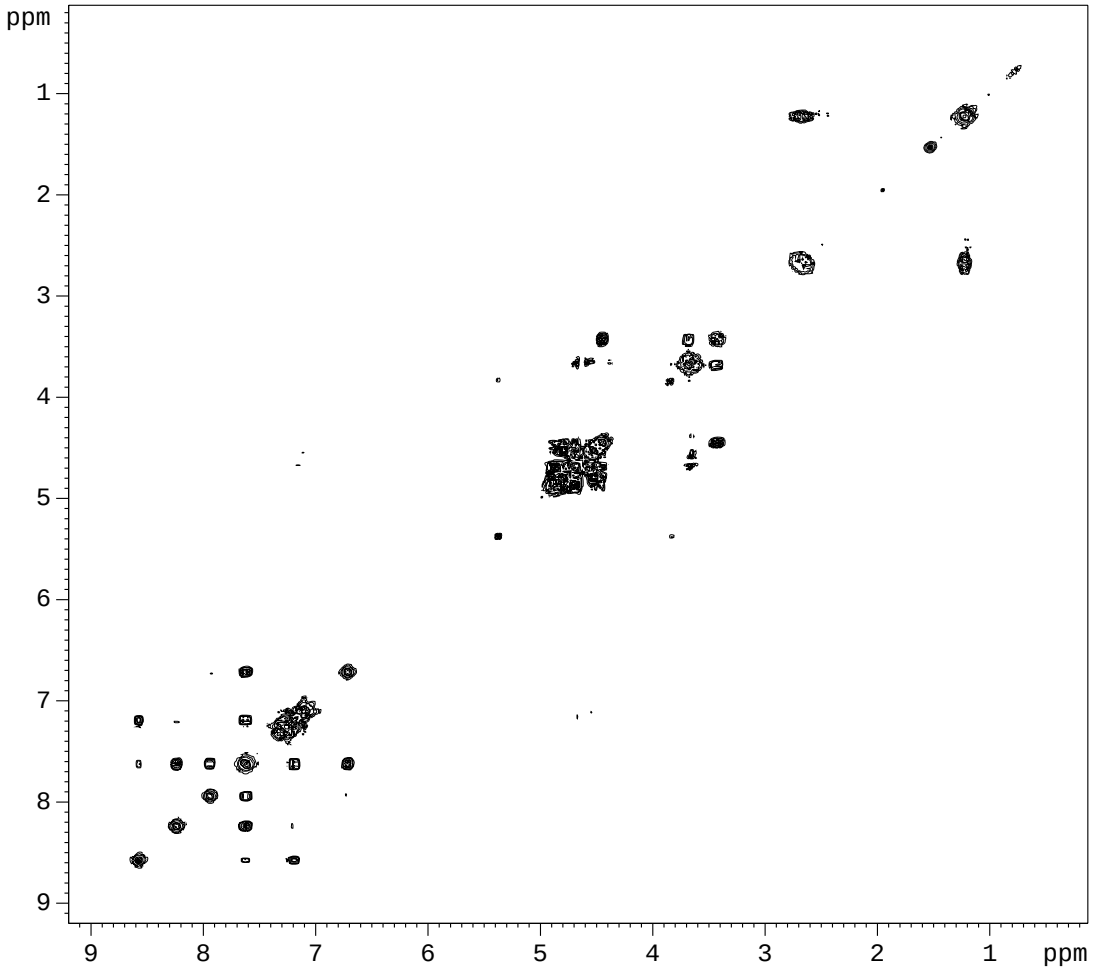

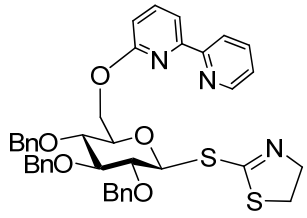
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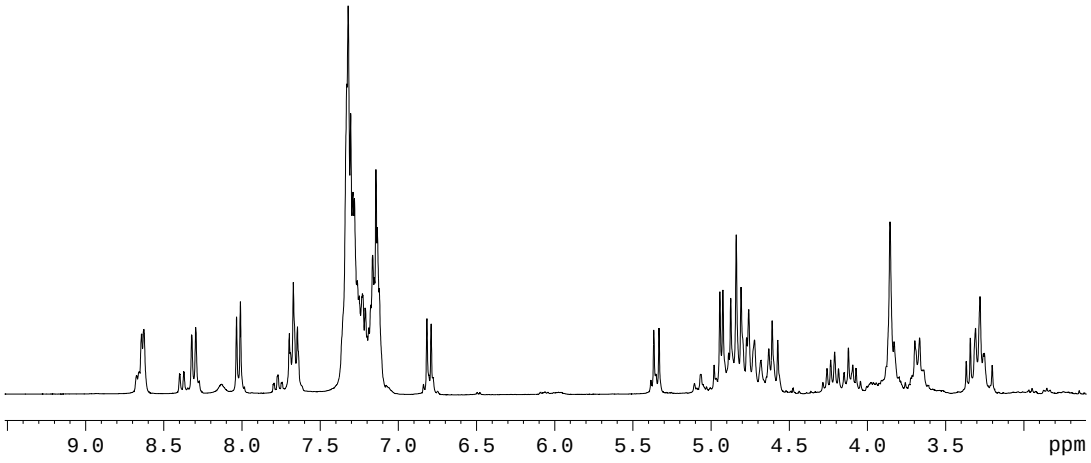
S
N
S

9a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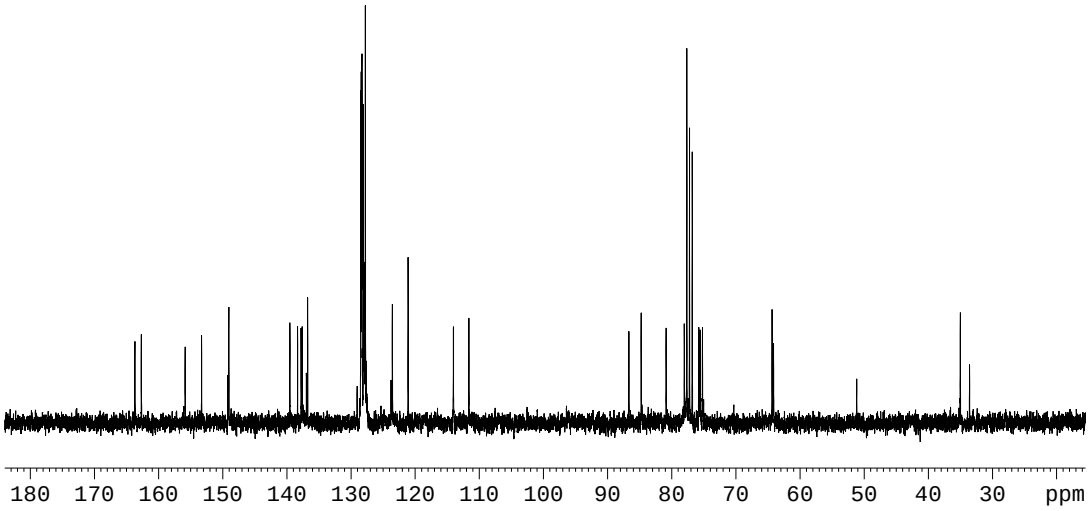
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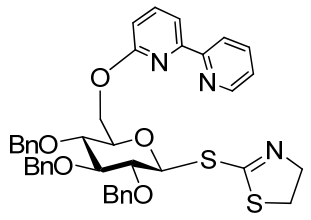
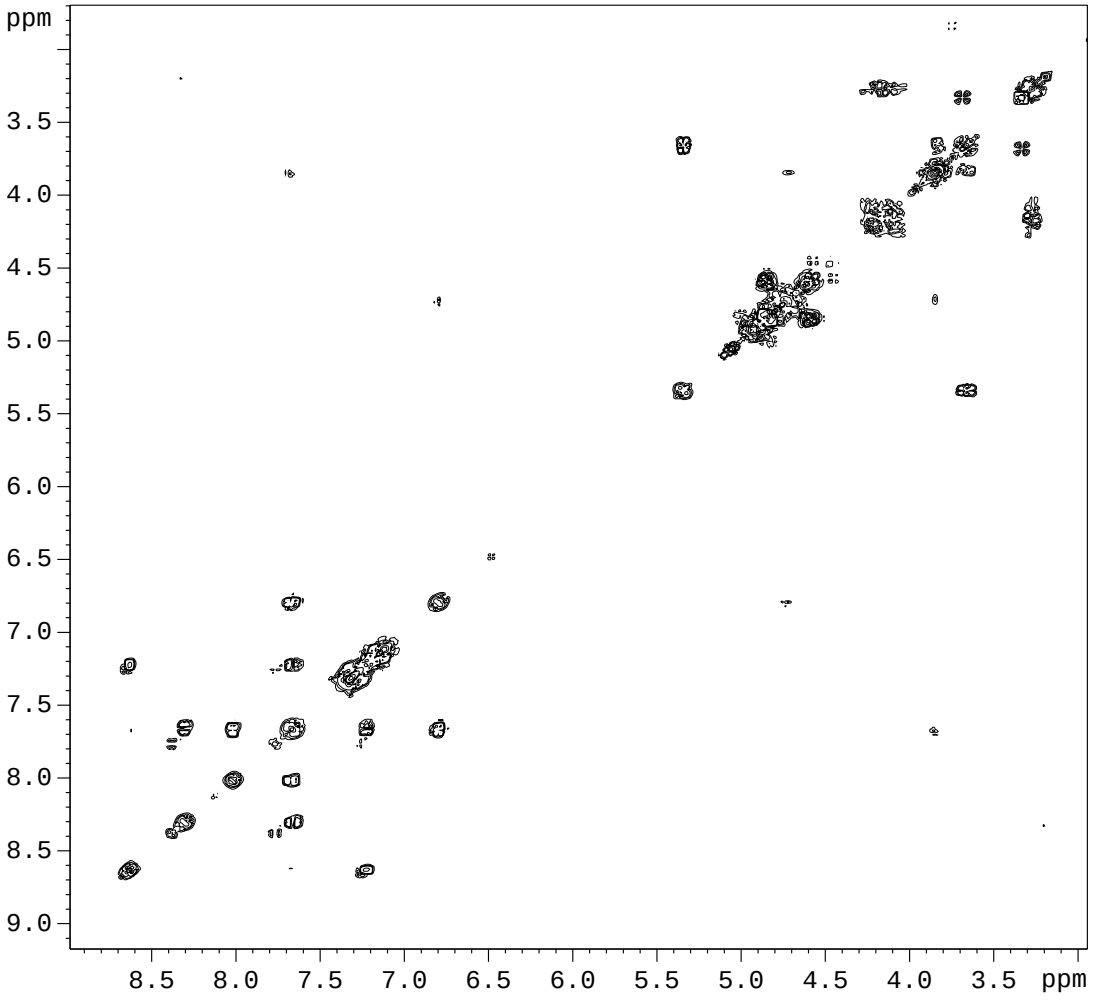
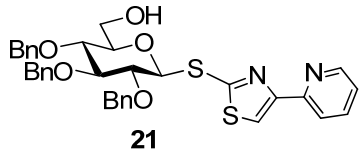
30
ppm

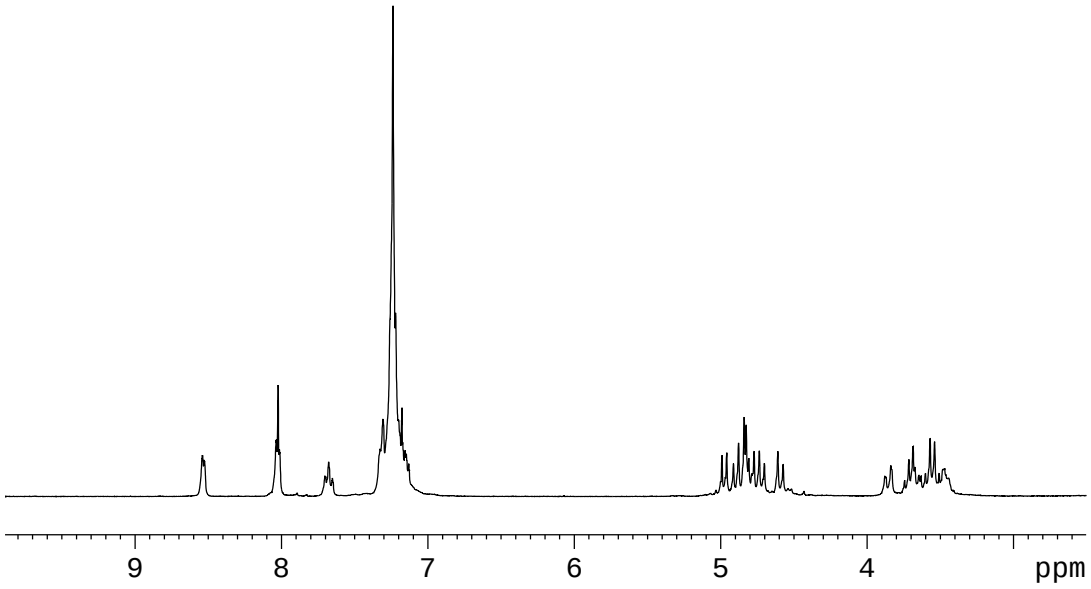

N
N
O
BnO
BnO
BnO
O
S
N
S

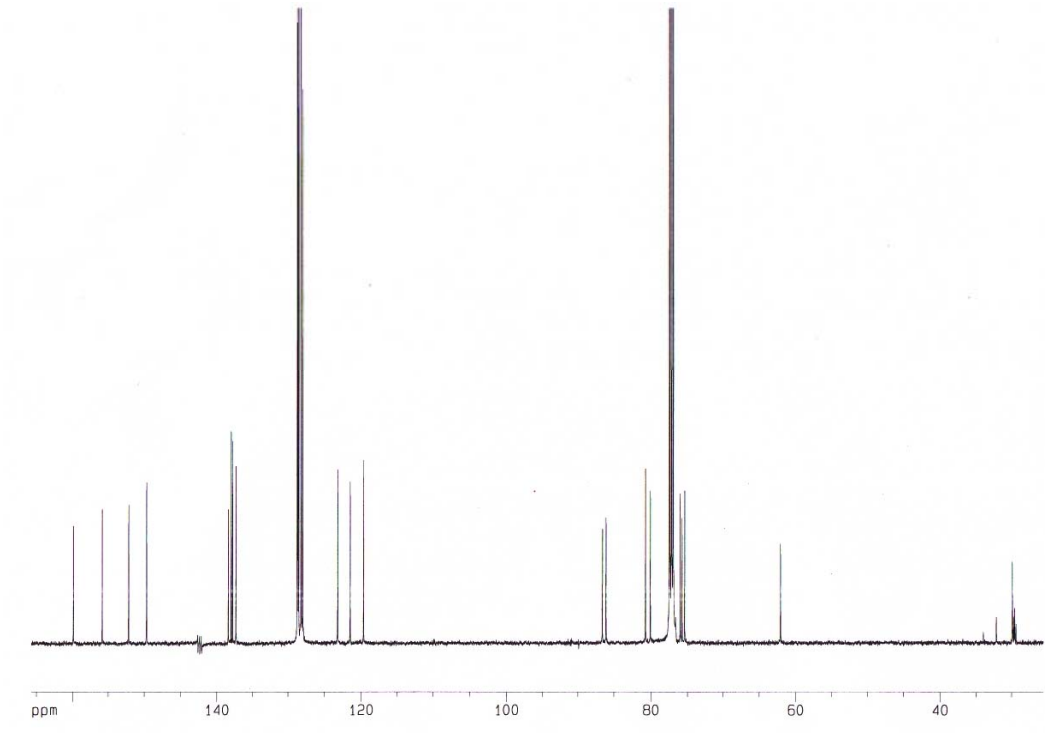
9a

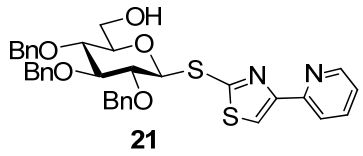

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm



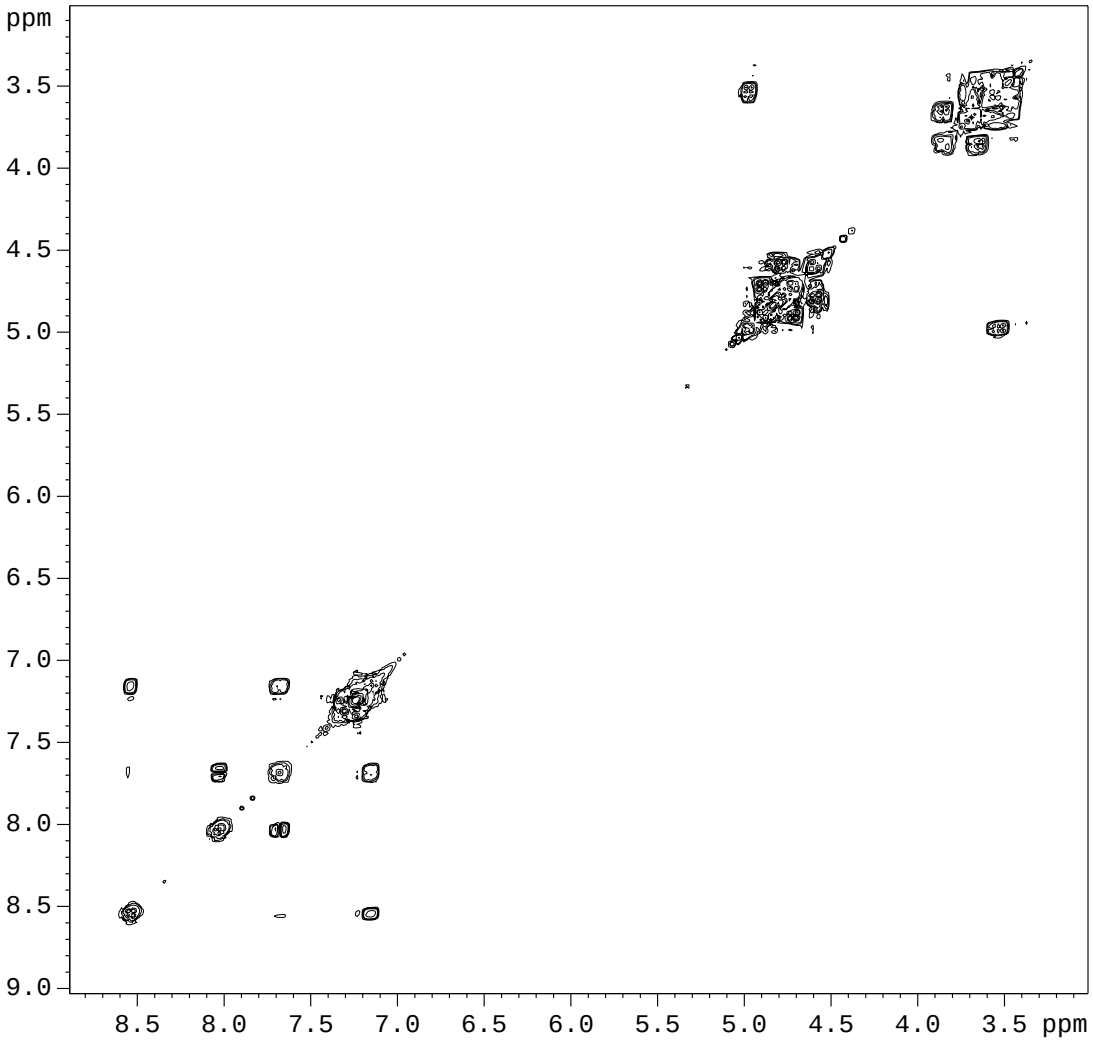
21

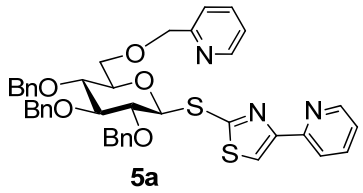




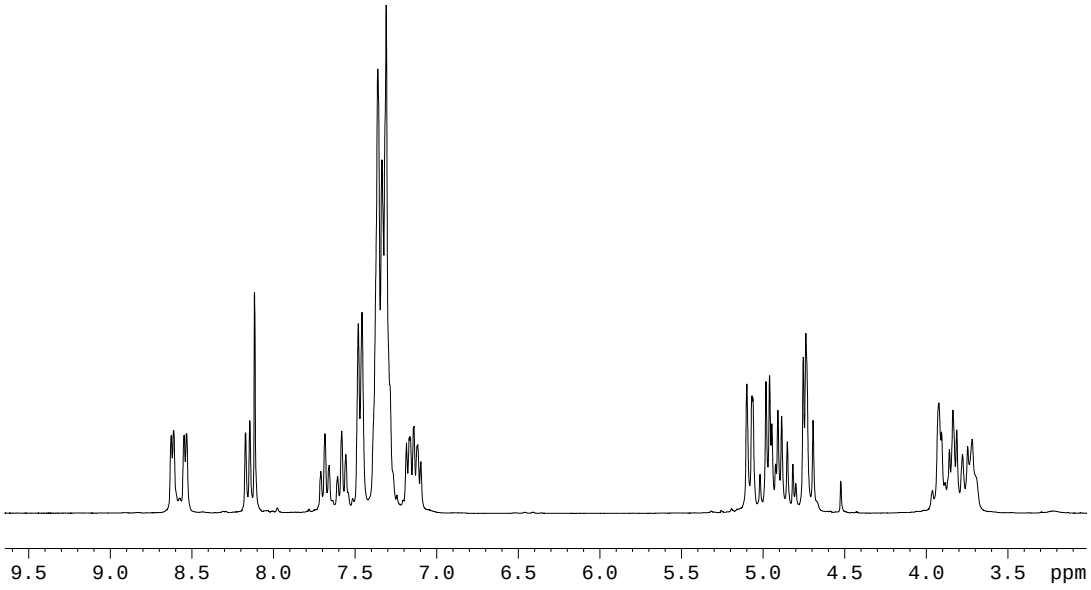

OH
O
BnO
BnO
BnO
S
N
N
S

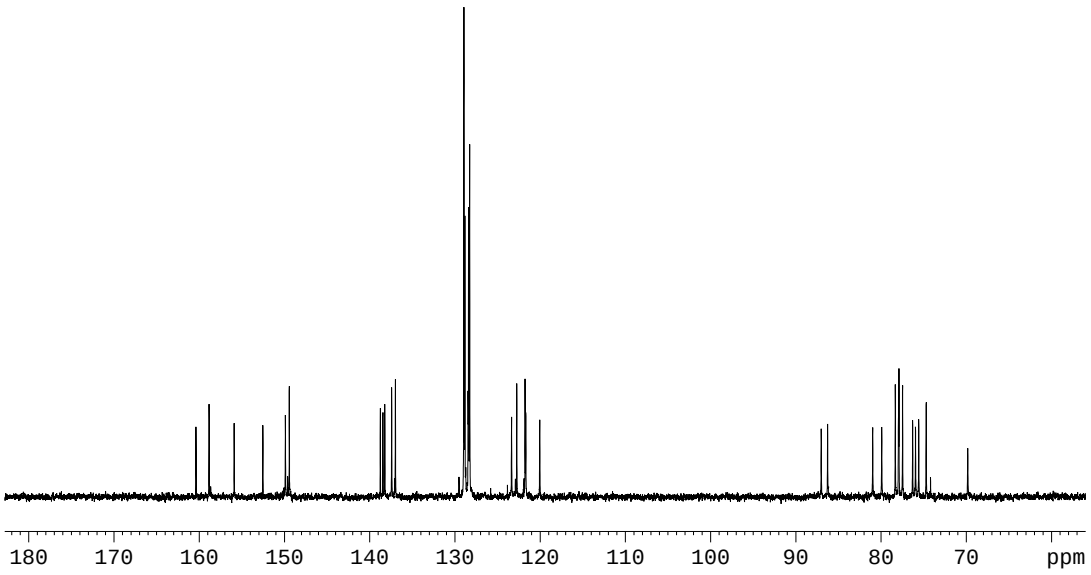
21

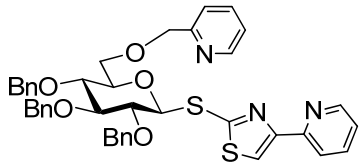

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm


O
N
BnO
O
BnO
S
N
N
BnO
S

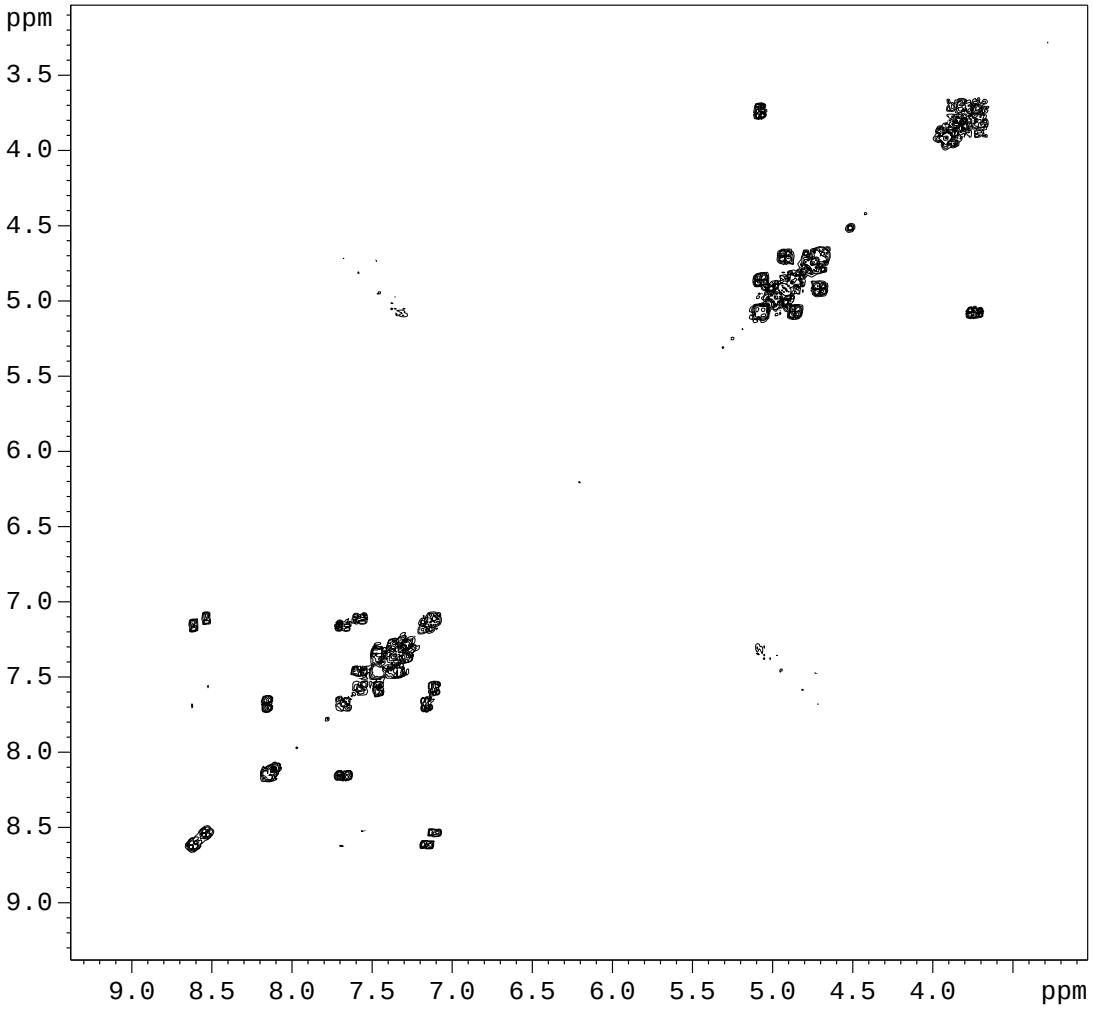
5a

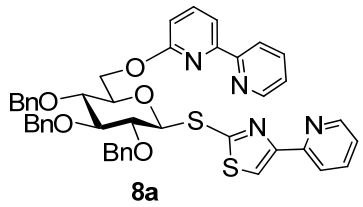

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm


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

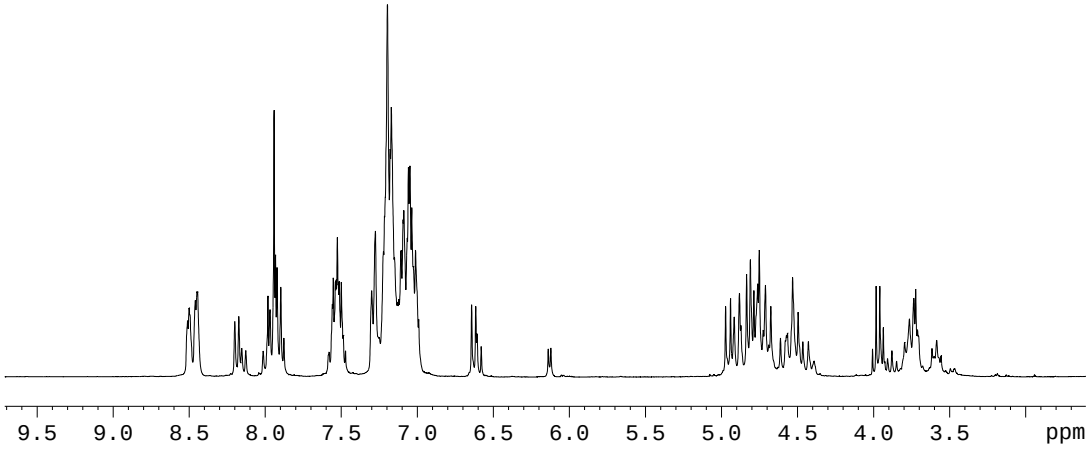

O
N
BnO
O
BnO
S
N
N
BnO
S

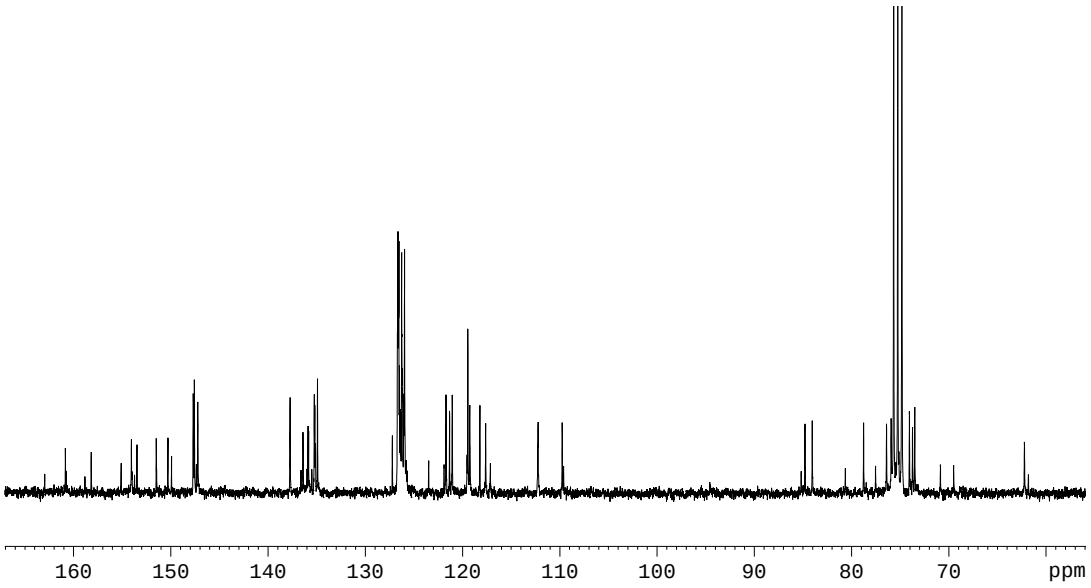
5a

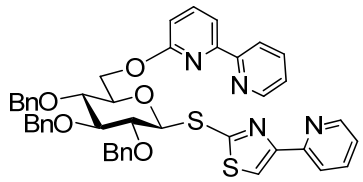

ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 ppm


O
N
N
BnO
O
BnO
S
N
N
BnO
S

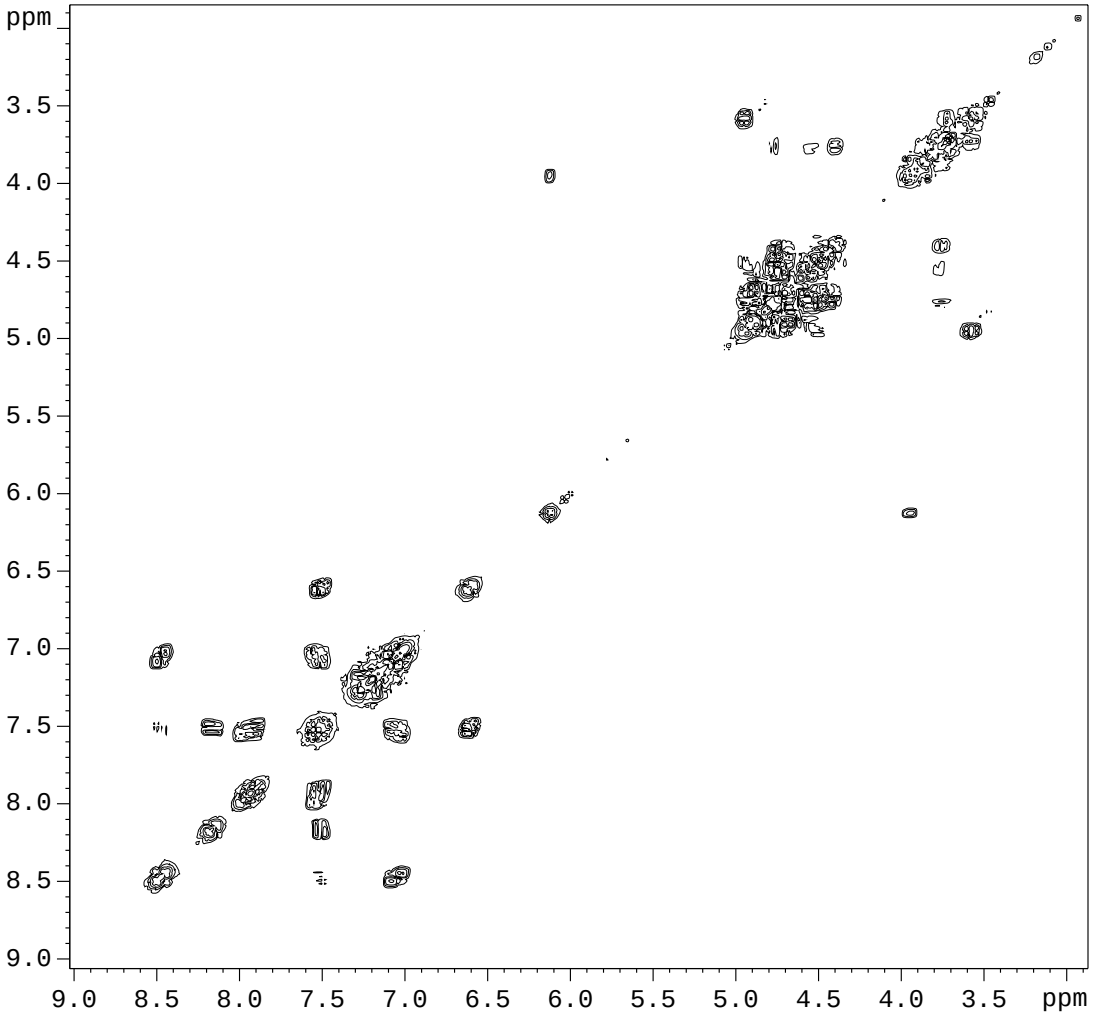
8a


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
ppm


160
150
140
130
120
110
100
90
80
70
ppm


O
N
N
O
BnO
BnO
S
N
N
BnO
S

8a


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 3.5 ppm

References

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