Supporting information

Unexpected orthogonality of S-benzoxazolyl and S-thiazolinyl derivatives: application to expeditious oligosaccharide assembly

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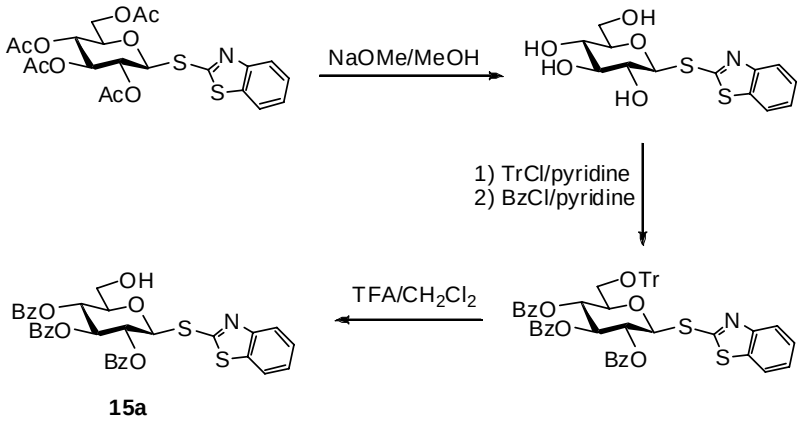
Content

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. Solvents were removed under reduced pressure at <40 ^{o}C. CH_2Cl_2, $ClCH_2CH_2Cl$, 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 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 300 or 500 MHz, ^{13}C-NMR spectra were recorded at 75 or 125 MHz. HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.

Benzothiazol-2-yl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (15a).



15a

Benzothiazol-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[1] (550 mg, 1.1 mmol) was dissolved in methanol (5 mL) and the pH 8-9 was adjusted by careful addition of 1M solution of $NaOCH_3$ in MeOH (~0.1 mL). The reaction mixture was kept for 1 h at rt, then Dowex (H^+) was added until neutral pH. The resin was filtered off and washed with methanol (3 x 5 mL). The combined filtrate was concentrated *in vacuo* and dried. The residue was dissolved in dry pyridine (5.0 mL) and triphenylmethyl chloride (439 mg, 1.57 mmol) was added. The reaction mixture was left stirring for 16 h at rt. After that, the reaction mixture was cooled to 0 °C and benzoyl chloride (0.49 mL, 4.21 mmol) was added dropwise. The reaction mixture was allowed to gradually warm up. Upon stirring for 3 h at rt, the reaction was quenched with methanol (5 mL), co-evaporated with toluene (3 x 10 mL), then diluted with dichloromethane (20 mL) and washed with 1N HCl (10 mL), water (10 mL), sat. $NaHCO_3$ (10 mL), and water (3 x 10 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate-toluene gradient elution). After that, the product was dissolved in dichloromethane (10 mL) containing one drop of water and trifluoroacetic acid (0.2 mL) was added dropwise. Upon completion, the reaction was then diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ (10 mL) and water (3 x

15 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate-toluene gradient elution) to obtain **15a** as yellow amorphous solid in 64% yield. R_f = 0.35 (ethyl acetate/toluene, 1.5/8.5, v/v); $[\alpha]_D^{23}$ = 0.48 (c = 1.0, $CHCl_3$); ^{1}H n.m.r.: δ, 2.75 (broad s, 1H, OH), 3.86 (m, 2H, H-6a, 6b), 4.06 (m, 1H, H-5), 5.62 (dd, 1H, $J_{4,5}$ = 4.7 Hz, H-4), 5.74 (dd, 1H, $J_{2,3}$ = 4.5 Hz, H-2), 5.97 (d, 1H, $J_{1.2}$ = 10.2 Hz, H-1), 6.11 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 7.2- 8.10 (m, 19H, aromatic) ppm; ^{13}C-n.m.r.: δ, 60.6, 61,7, 69.4, 70.8, 74.0, 79.7, 84.4, 121.3, 122.5, 125.2, 126.6, 128.6 (×4), 128.7, 128.7 (×2), 128.8, 128.9, 129.9 (×2), 130.1 (×3), 133.6, 133.7, 134.0, 135.8, 152.9, 162.4, 165.4, 165.9, 166.1 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{34}H_{27}NO_8S_2Na$ 664.1076, found 664.1085.

General glycosylation procedures

Method A. A typical 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 h. MeOTf (0.33 mmol) was added and the reaction mixture was stirred for 20 min – 2 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.

Method B. A typical MeI - 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 h, then MeI (1.0-1.5 mmol) was added. The reaction mixture was stirred for 60 h at rt. Upon completion, the reaction mixture was diluted with CH_2Cl_2, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL), the organic phase was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the corresponding di- or oligosaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

Method C – A typical BnBr- 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 h, then BnBr (0.33-0.99 mmol) was added. The reaction mixture was stirred for 24-36 h at 55 °C. Upon completion, the reaction mixture was diluted with CH_2Cl_2, the solid was filtered-off and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL), the organic phase was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to allow the corresponding di- or oligosaccharide. Anomeric ratios (if applicable) were determined by comparison of the integral intensities of relevant signals in ^{1}H-n.m.r. spectra.

Method D – A typical Bi(OTf)$_3$- promoted glycosylation procedure: A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $(ClCH_2)_2$ (2mL) was stirred under argon for 1 h. The reaction mixture was cooled down at 0°C and then $Bi(OTf)_3$ (0.22 mmol) was added into the solution. After that the reaction mixture was stirred for 1-2 h at rt. Upon completion, the reaction mixture was diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3 × 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford a di- or oligosaccharide derivative.

Method E – A typical AgOTf- promoted glycosylation procedure: A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $(ClCH_2)_2$ (2mL) was stirred under argon for 1 h. Freshly conditioned AgOTf (0.22 mmol) was added and the reaction mixture was stirred for 1–2 h at rt and then diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3 × 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford an oligosaccharide derivative.

Method F – A typical $AgBF_4$- promoted glycosylation procedure: A mixture the glycosyl donor (0.11 mmol), glycosyl acceptor (0.10 mmol), and freshly activated molecular sieves (3 Å, 200 mg) in $(ClCH_2)_2$ (2mL) was stirred under argon for 1 h. $AgBF_4$ (0.22 mmol) was added and the reaction mixture was stirred for 2 h at rt and then diluted with CH_2Cl_2, the solid was filtered-off, and the residue was washed with CH_2Cl_2. The combined filtrate (30 mL) was washed with 20% aq. $NaHCO_3$ (15 mL) and water (3 × 10 mL), and the organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane gradient elution) to afford an oligosaccharide derivative.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (**5**). The title compound was obtained as a colorless syrup by a range of methods in 87-90% yield (see *Table 1* of the manuscript). Analytical data for **8** was in good agreement with those reported previously.[2]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-D-glucopyranosyl)-α-D-glucopyranoside (**9**). The title compound was obtained as a white foam by a variety of methods shown in *Table 1* in the manuscript in 79-97% yield. Analytical data for **9** was in good agreement with those reported previously.[3]

Benzothiazol-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 (16a). The title compound was obtained by *Method C* from **6** and **15a** in 70% yield as a white foam. Analytical data for **16a**: R_f = 0.6 (ethyl acetate/toluene, 1/4, v/v); $[\alpha]_D^{24}$ +49.9 (*c* = 1, $CHCl_3$); ^{1}H-n.m.r; δ, 3.58 (m, 2H, H-6a,6b), 4.12 (m, 2H, H-5,5'), 4.36 (dd, 1H, $J_{5',6b'}$ = 7.4 Hz, H-6b'), 4.48 (dd, 1H, $J_{5',6a'}$ = 2.8 Hz, $J_{6a',6b'}$ = 12.1 Hz, H-6a'), 4.60 (m, 1H, H-4), 5.44 (d, 1H, $J_{4',5'}$ = 8.7 Hz, H-4'), 5.72 (m, 2H, H-3,3'), 5.85 (d, 1H, $J_{1,2}$ = 10.1 Hz, H-1), 5.93 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, H-2'), 5.95 (dd, 1H, $J_{2,3}$ = 5.0 Hz, H-2), 7.1-8.10 (m, 39H, aromatic); 13C-n.m.r.: δ, 63.1, 64.2, 67.7, 68.6, 69.3, 69.3, 70.8, 72.1, 74.3, 77.4, 84.6, 98.0, 121.2 (×2), 122. 5, 125.1, 125.5, 126.5, 126.7 (×2), 128.4 (×2), 128.4 (×2), 128.5 (×3), 128.6 (×2), 128.6 (×3), 128.7 (×2), 128.7 (×2), 128.9, 128.9, 129.0, 129.2 (×2), 129.4, 129.9 (×2), 129.9 (×5), 130.1 (×2), 130.1 (×3), 130.3 (×2), 133.1, 133.7 (×2), 133.7, 134.5, 135.9, 152. 9, 162.5, 164.5, 165.3 (×2), 165.9, 166.2 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{68}H_{53}NO_{17}S_2Na$ 1242.2653, found 1242.2683.

Benzoxazol-2-yl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (16b). The title compound was obtained from 2-thiazolinyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**1**)[4] and benzoxazolyl 2,3,4-tetra-*O*-benzyl-1-thio-

β-D-glucopyranoside (**15b**)[5] by *Method B* in 82% yield and *Method C* in 85% yield, as colorless syrup. Analytical data for **16b**: R_f = 0.52 (ethyl acetate/hexane, 3/7, v/v); ^{1}H-n.m.r; δ, 3.28 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 3.82 (dd, $J_{3',4'}$ = 9.2 Hz, H-3'), 3.42-3.82 (m, 10H, H-3, 4, 5, 6a, 6b, 2', 4', 5', 6a', 6b'), 4.43-4.95 (m, 14H, C*H*$_2$Ph), 4.98 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.09 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1'), 5.38 (d, 1H, $J_{1,2}$ = 10.1 Hz, H-1), 7.10-7.65 (m, 39H, aromatic); ^{13}C NMR: δ, 65.5, 68.7, 70.4, 72.3, 73.5, 75.0, 75.3, 75.7, 75.8, 77.4, 79.8, 80.3, 80.8, 81.8, 85.0, 86.7, 97.3, 119.2, 124.4, 124.6, 127.6 (×2), 127.6 (×2), 127.7 (×2), 127.8 (×2), 127.8 (×3), 128.0 (×3), 128.0 (×3), 128.1 (×3), 128.3 (×3), 128.5 (×3), 128.5 (×3), 128.6 (×3), 128.6 (×3), 128.7 (×2), 137.7, 138.2, 138.4, 138.5, 138.7, 138.7, 138.8, 139.0, 142.0, 152.0, 161.7 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{68}H_{67}NO_{11}SNa$ 1128.4333, found 1128.4368.

Benzoxazol-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 (16c). The title compound was obtained by *Method C* from 2-thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**6**)[4] and benzoxazolyl 2,3,4-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**15c**)[6] in 76% yield as colorless syrup. Analytical data for **16c**: R_f = 0.45 (ethyl acetate/hexane, 7/3, v/v); $[\alpha]_D^{24}$= 48.5 (*c* = 1, $CHCl_3$]; ^{1}H-n.m.r; δ, 3.53 (dd, 1H, $J_{5,6b}$ = 8.3 Hz, H-6b), 3.86 (dd, 1H, $J_{6a,6b}$ = 4.8 Hz, H-6a), 4.12 (m, 1H, H-5'), 4.15 (m, 1H, H-5), 4.34 (dd, 1H, $J_{5,6b'}$ = 7.9 Hz, H-6b), 4.47 (dd, 1H, $J_{6a',6b'}$ = 2.6 Hz), 4.74 (m, 1H, H-2), 5.43 (d, 1H, $J_{4',5'}$ = 8.4 Hz, H-4'), 5.68 (dd, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 5.72 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.90-5.99 (m, 3H, H-1, 1', 2'), 7.09-8.10 (m, 39H, aromatic); ^{13}C NMR: δ, 63.3, 64.4, 67.8, 68.8, 79.4, 71.0, 72.3, 74.5, 77.6, 84.3, 110.5, 119.2, 121.4, 124.9, 124.9, 126.9 (×2), 128.7 (×5), 128.8 (×5), 128.9 (×2), 129.0, 129.1, 129.2, 129.5, 129.5, 130.5 (×3), 130.1 (×5), 130.3 (×5), 130.5 (×2), 133.3, 133.7, 133.8 (×3), 133.9, 134.7, 141.9, 152.2, 164.7, 165.5, 165.5,

165.6, 166.1, 166.4 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{68}H_{53}NO_{18}SNa$ 1226.2281, found 1226.2283.

2-Thiazolinyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (16d). The title compound was obtained by *Method D* from benzoxazolyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**7**)[1] and 2-thiazolinyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**15d**)[4] in 69% yield as a white foam. Analytical data for **16d** was in a good agreement with those reported previously.[7]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-b-D-glucopyranosyl]-β-D-glucopyranoside (17a). The title compound was obtained as a colorless syrup by *Method E* from methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**4**)[8] and **16c** in 72% yield and *Method F* from **4** and **16a** in 75% yield and from **4** and **16d** in 81% yield. Analytical data for **17a** was in a good agreement with those reported previously.[9]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-D-glucopyranosyl]-α-D-glucopyranoside (17b). The title compound was obtained by *Method E* from **4** and **16b** in 92% yield as a white amorphous solid. Analytical data for α/β–**17b**; R_f = 0.48 (ethyl acetate/hexane, 3:7, v/v); ^{13}C-n.m.r.: δ, 55.4, 70.7, 70.8, 72.4, 72.5., 72,6, 73.5, 73.6, 73.6, 75.1, 75,1, 75.2, 75.6, 75.7, 75.7, 75.7, 75.8, 75.9, 77.4, 78.0, 80.0, 80.3, 80.3, 80.4, 80.5, 81.9, 82.1, 82.3, 82.4, 84.9, 97.3, 97.4, 97.5, 98.1, 98.2, 98.2, 103.7, 127.7, 127.7, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.3, 128.5, 128.5, 128.6, 128.6,

138.2, 138.3, 138.4, 138.5, 138.6, 138.6, 138.7, 138.8, 138.9, 139.0, HR FAB MS $[M+Na]^+$ calcd for $C_{89}H_{94}O_{16}Na$ 1441.6440, found 1441.6437.

2-Thiazolinyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-1-thio-β–D-glucopyranoside (17c). The title compound was obtained by *Method D* from **16c** and **15d** in 62 % yield as white foam. Analytical data for **17c**: R_f = 0.46 (ethyl acetate/toluene, 1/4, v/v); $[\alpha]_D^{21}$= 5.84 (*c* = 1, $CHCl_3$); ^{1}H-n.m.r; δ, 3.29-3.39 (m, 2H, CH_2S), 3.59 (m, 1H, H-6a'), 3.85 (m, 2H, H-5',6b"), 4.00 (m, 1H, 6a"), 4.13-4.29 (m, 2H, CH_2N), 4.44 (m, 2H, H-5, 6a'), 4.66 (m, 1H, H-6b), 4.67 (d, 1H, $J_{1",2"}$ = 7.8 Hz, H-1"), 5.04 (dd, 1H, $J_{4",5"}$ = 9.5 Hz, H-4"), 5.11 (dd, 1H, $J_{2",3"}$ = 7.8 Hz, H-2"), 5.21 (d, 1H, $J_{1',2'}$ = 7.9, H-1'), 5.27 (dd, 1H, $J_{2',3'}$ = 4.0 Hz, H-2'), 5.59-5.62 (m, 2H, H-3", 4'), 5.65 (dd, 1H, $J_{4,5}$ = 8.3 Hz, H-4), 5.77 (dd, 1H, $J_{2,3}$ = 7.1 Hz, H-2), 5.78 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 5.91 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 6.15 (dd, 1H, $J_{3',4'}$ = 9.7 Hz, H-3'), 7.15-8.10 (m, 50H, aromatic); ^{13}C-n.m.r.: δ, 58.8, 63.5, 64.4, 68.2, 68.4, 69.8, 69.9, 70.6, 70.8, 72.0, 72.3, 72.5, 72.9, 73.0, 74.2, 74.3, 83.5, 100.2, 101.5, 125.5 (×2), 127.2, 127.9, 128.4 (×2), 128.4 (×2), 128.5 (×2), 128.5 (×2), 128.5 (×3), 128.6 (×2), 128.6 (×4), 128.8 (×2), 128.8, 128.9 (×2), 129.0, 129.1, 129.1 (×3), 129.2 129.3, 129.4 (×2), 129.5, 129.8, 129.9 (×2), 130.0 (×3), 130.0 (×5), 130.1(×3), 130.1 (×2), 130.2 (×2), 130.3(×2), 130.3 (×2), 133.3, 133.3, 133.4 (×2), 133.5 (×2), 133.6, 133.6, 165.2, 165.3, 165.4, 165.6 (×2), 166.0, 166.0, 166.4 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{91}H_{75}NO_{25}S_2Na$ 1668.3967, found 1668.4023.

Benzoxazol-2-yl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-1-thio-β–D-glucopyranoside (17d). The title

compound was obtained by *Method B* from **16d**[7] and **15c** in 67% yield as a colorless syrup. Analytical data for **17d**: R_f = 0.48 (ethyl acetate/toluene, 1.5/8.5, v/v); $[\alpha]_D^{28}$= 47.4 (*c* = 1, $CHCl_3$); ^{1}H-n.m.r.: δ, 3.43-3.45 (m, 2H, H-6a, 6b), 3.66 (dd, 1H, $J_{5',6a'}$ = 5.5 Hz, $J_{6a',6b'}$ = 11.5 Hz, H-6a'), 3.84 (m, 1H, H-5'), 4.06-4.16 (m, 3H, H-5, 5'', 6b'), 4.30 (dd, 1H, $J_{5'',6a''}$ = 5.1 Hz, $J_{6a'',6b''}$ = 12.1 Hz, H-6a''), 4.54-4.58 (m, 2H, H-4, 6b''), 4.95 (d, 1H, $J_{1',2'}$ = 11.0 Hz, H-1'), 5.22 (dd, 1H, H-4'), 5.50-5.55 (m, 2H, H-2', 3'), 5.60-5.69 (m, 2H, H-3'', 4''), 5.71 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 5.77 (d, 1H, $J_{1'',2''}$ = 5.3 Hz, H-1''), 5.86 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 5.95 (d, 1H, $J_{2'',3''}$ = 9.5 Hz), 5.96 (d, 1H, $J_{1,2}$ = 10.3 Hz, H-1), 7.15-8.10 (m, 54H, aromatic); ^{13}C-n.m.r.: δ, 60.6, 63.0, 63.3, 68.1, 68.6, 69.3, 69.5, 69.98, 70.8, 71.7, 72.4, 72.4, 73.2, 74.3, 76.7, 77.6, 77.7, 84.1, 97.8, 102.0, 110.3, 119.1, 121.1, 124.6, 124.8, 126.6, 128.2 (×2), 128.4 (×2), 128.4 (×2), 128.5 (×4), 128.6 (×4), 128.8, 128.9, 129.0, 129.1, 129.1, 129.2, 129.4 (×3), 129.7, 129.8 (×2), 129.9 (×4), 130.0 (×4), 130.0 (×4), 130.0 (×4), 130.10 (×2), 130.3, 133.1, 133.2, 133.3 (×2), 133.4, 133.5, 133.6 (×2), 133.6, 134.4, 141.7, 152.0, 161.4, 164.5, 165.1, 165.2, 165.2, 165.4, 165.9, 166.0, 166.3 ppm; HR FAB MS $[M+Na]^+$ calcd for $C_{95}H_{75}NO_{26}SNa$ 1700.4196, found 1700.4182.

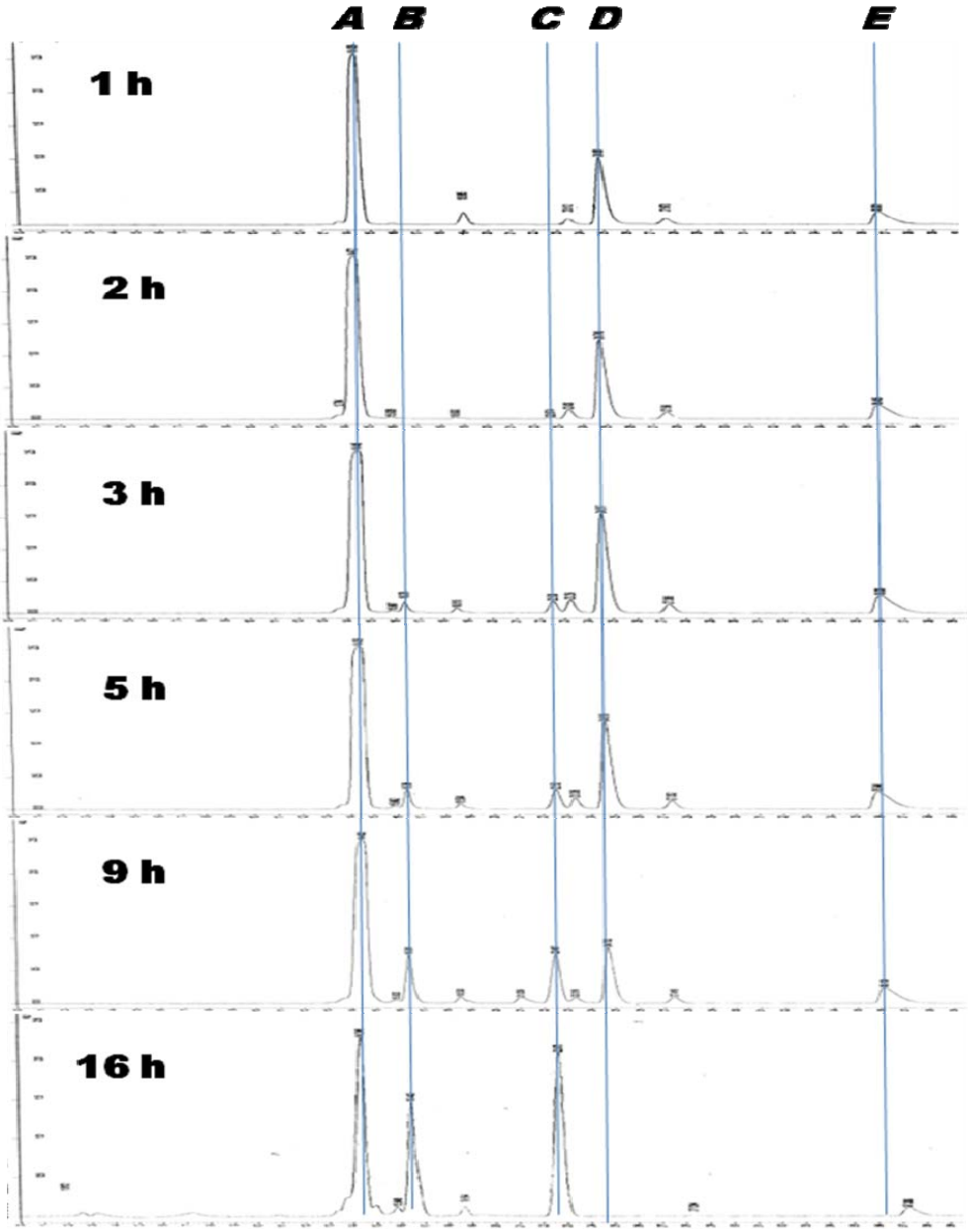
Aglycone isolation

3-Benzyl-thiazolidine-2-thione (13). The title compound was isolated by column chromatography from the reaction mixture resulted from glycosylation between **1** and **7**. Analytical data for **13** was reported previously.[10] The structure of **13** was confirmed by UV spectrometry with absorption maximum at 277 nm. X-ray structure determination data for **13** is presented below on page S28.

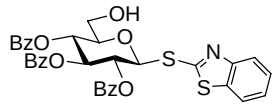
2-(Benzylthio)-benzoxazole (14). The title compound was isolated by column chromatography from the reaction mixture resulted from glycosylation between **3** and **7**. Analytical data for **14** was reported previously.[11] The structure of **14** was confirmed by UV spectrometry with two absorption maxima at 280 and 290 nm.[12] X-ray structure determination data for **14** is presented below on page S35.

HPLC Monitoring

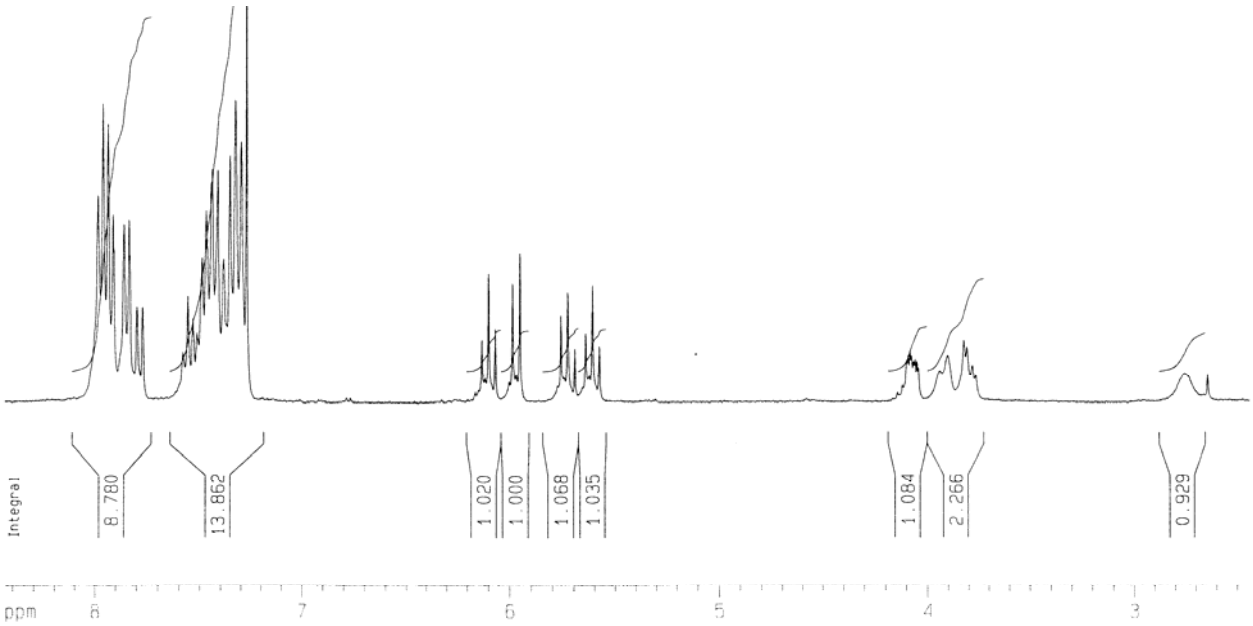
The analyses were carried out on a Supelcosil LC-SI Semi Prep (250mm×10mm i.d., 5μm) (Supelco, Bellefonte, PA, USA) The mobile phase was ethyl acetate/hexane (30/70, v/v), under isocratic conditions. The sample analysis (injection volume 20 μL) was performed for 60 min at rt with the flow rate 1.0 mL/min and UV detection at 254 nm.



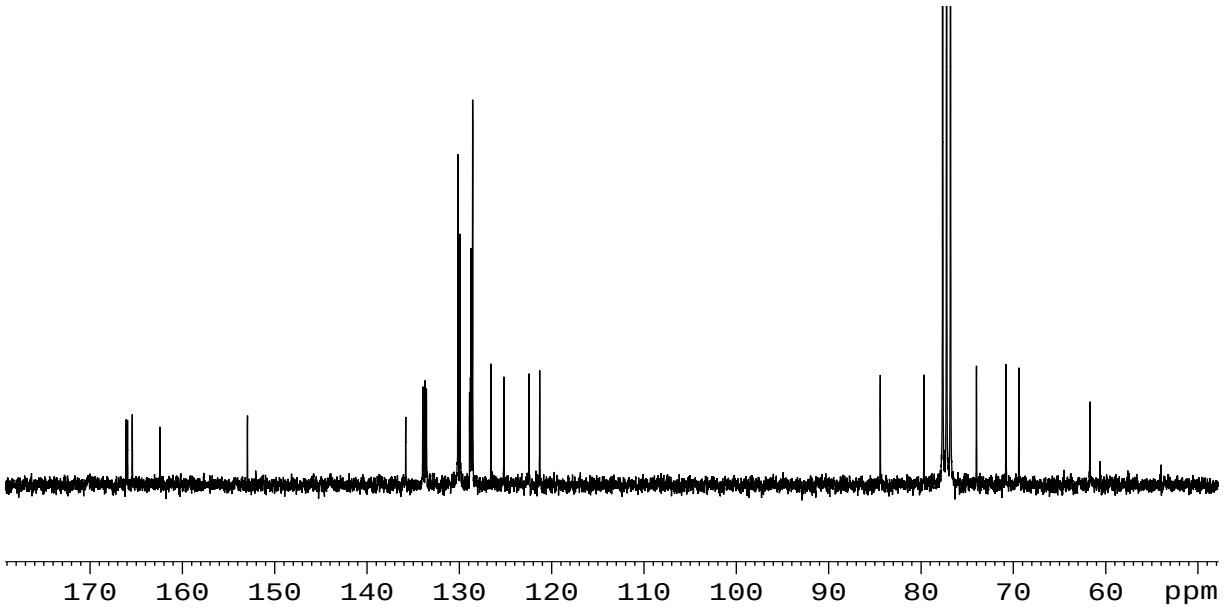
NMR Spectra



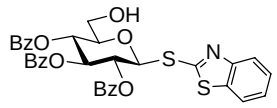
15a



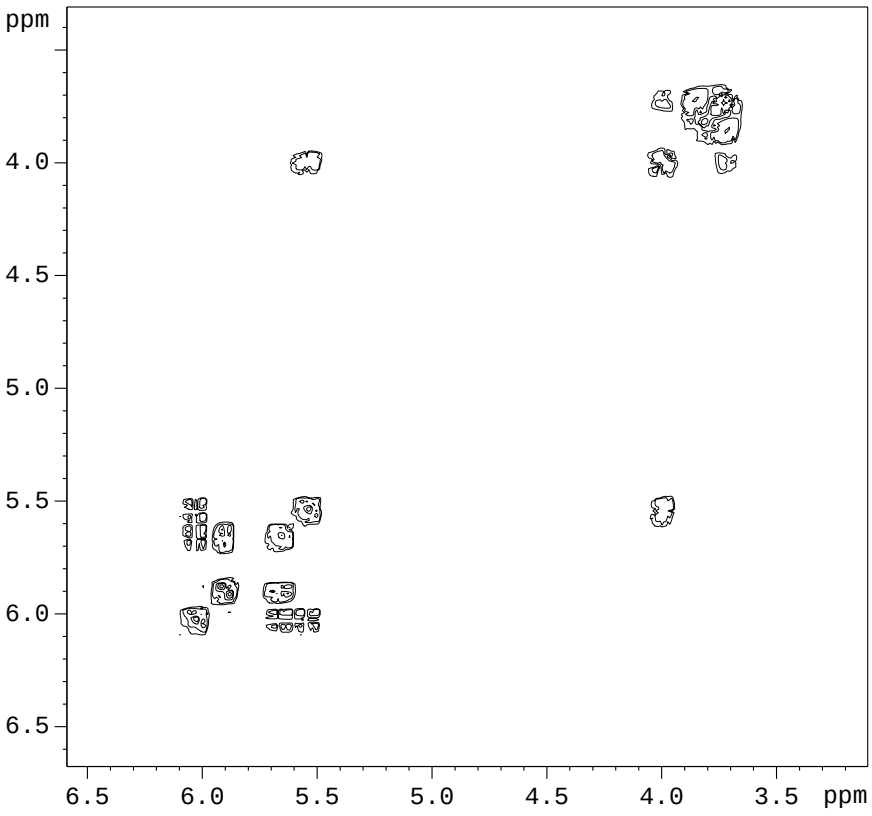
$CDCl_3$ at 300 MHz



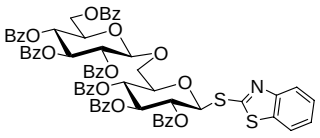
$CDCl_3$ at 75 MHz



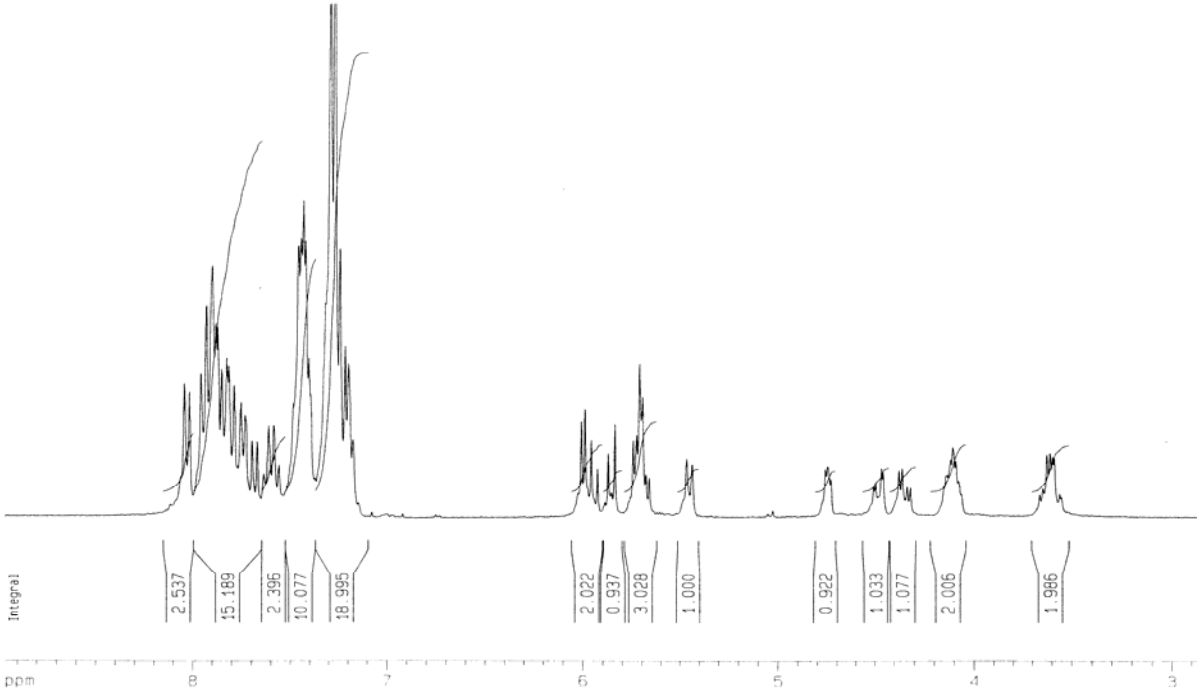
15a



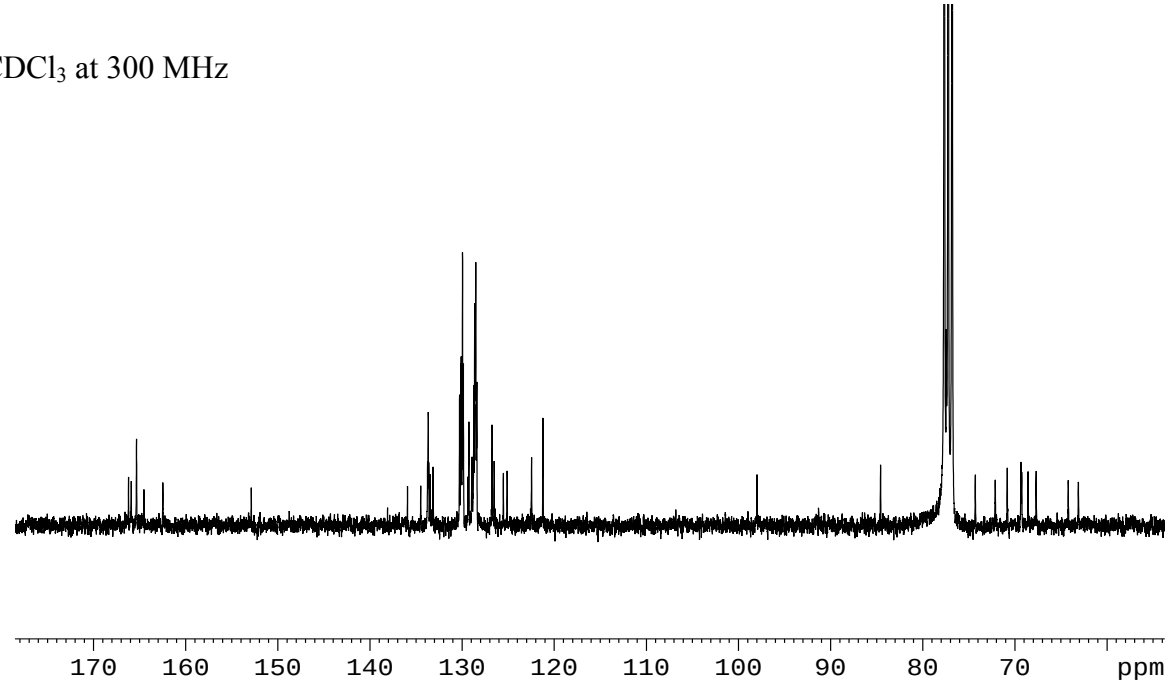
$CDCl_3$ at 300 MHz



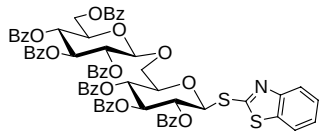
16a



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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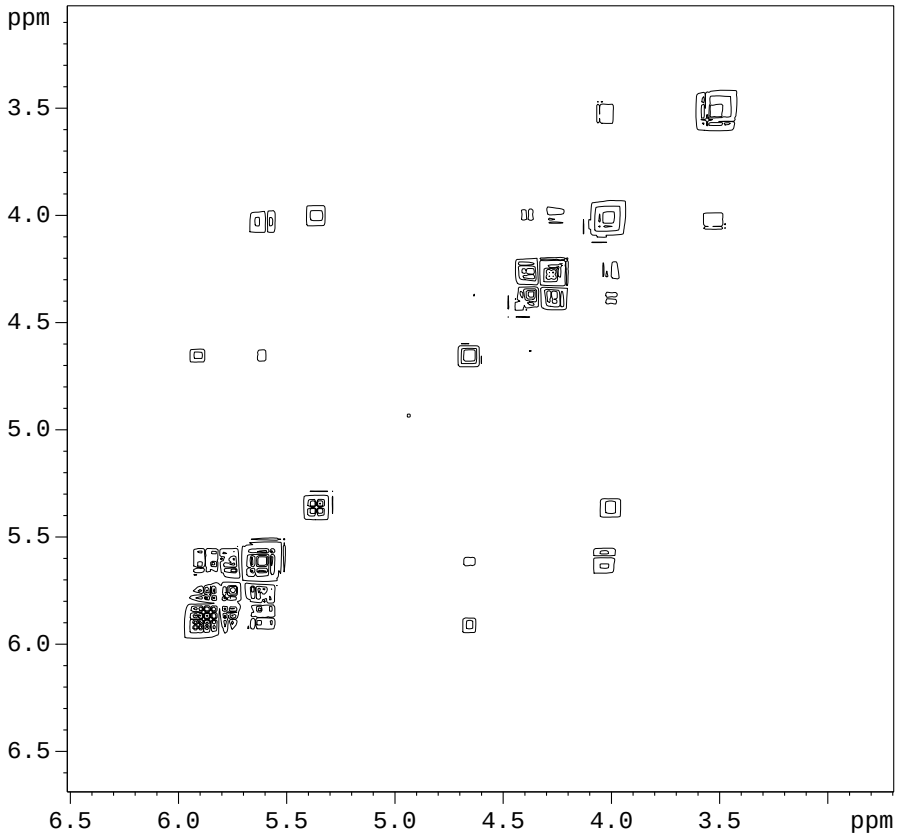
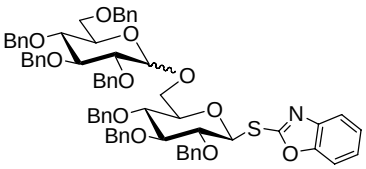
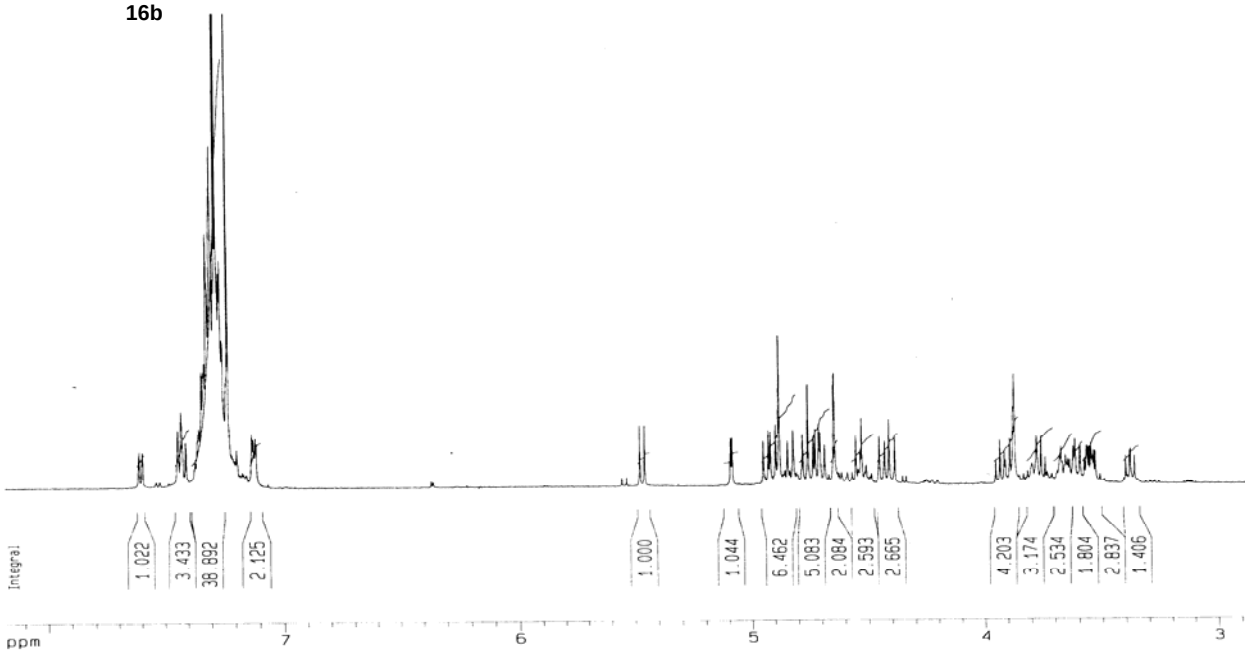


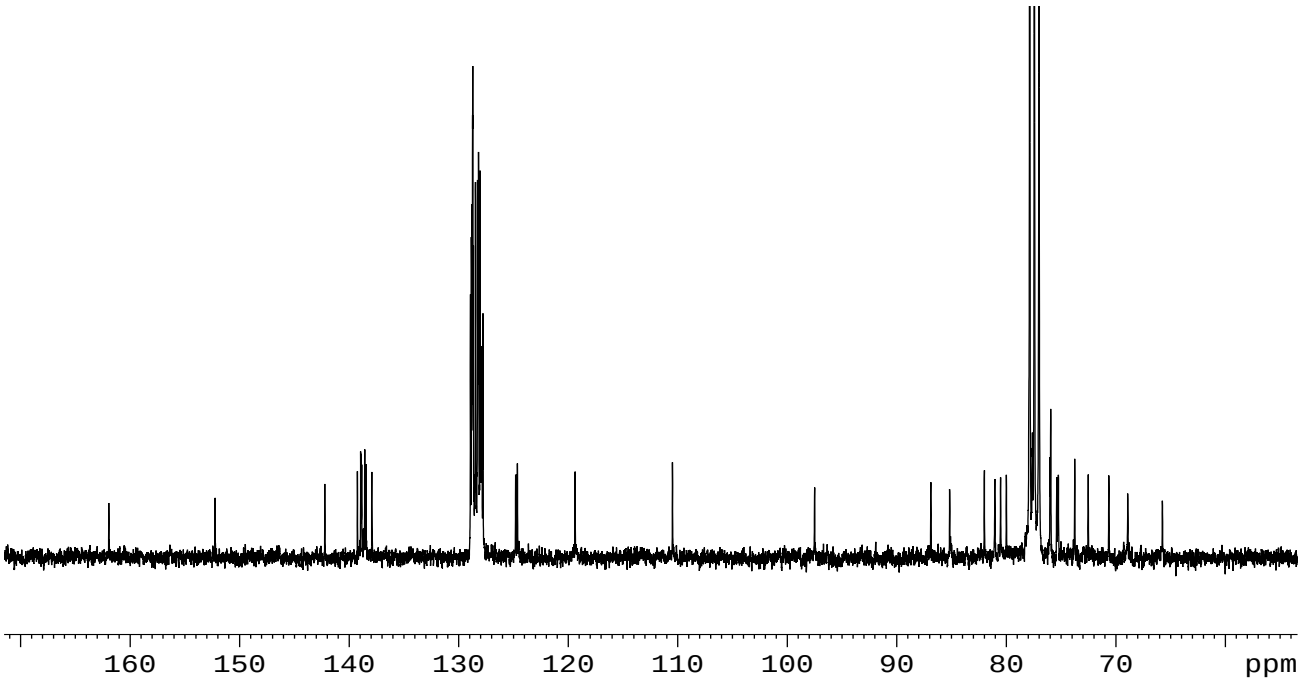
$CDCl_3$ at 300 MHz



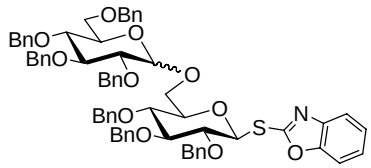
16b



$CDCl_3$ at 500 MHz



$CDCl_3$ at 75 MHz



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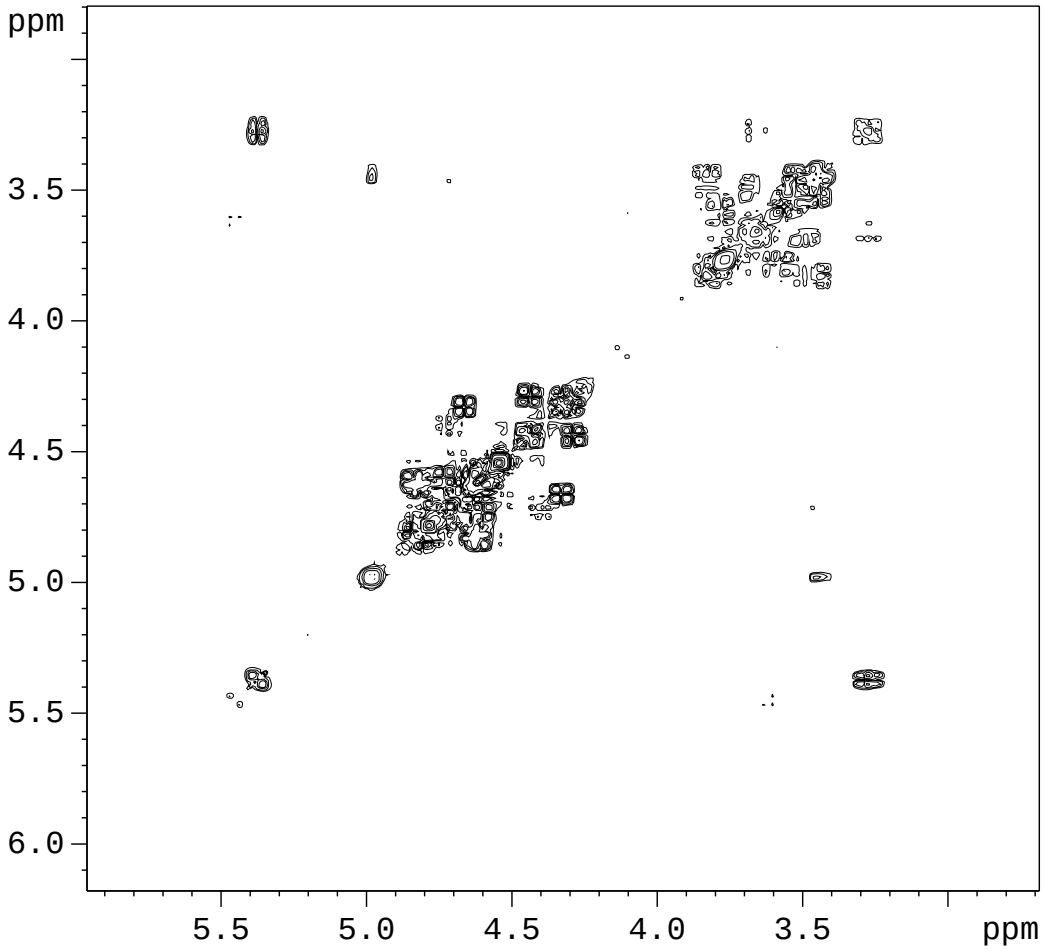
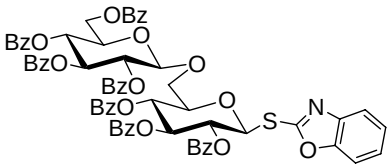
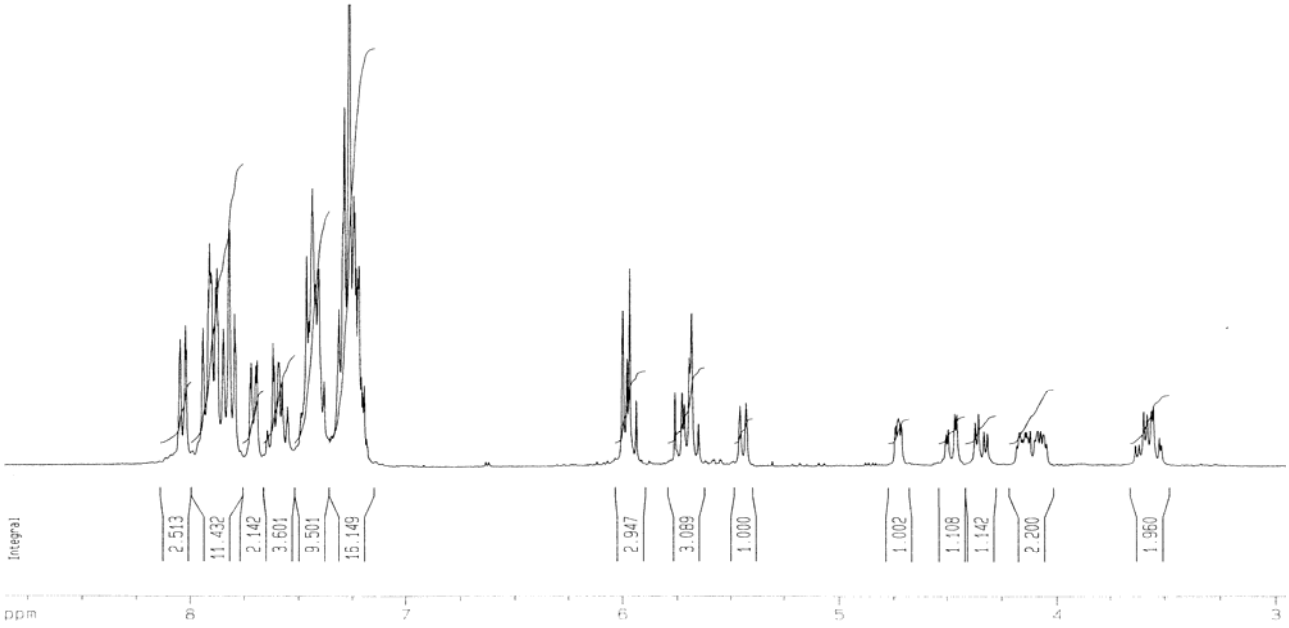


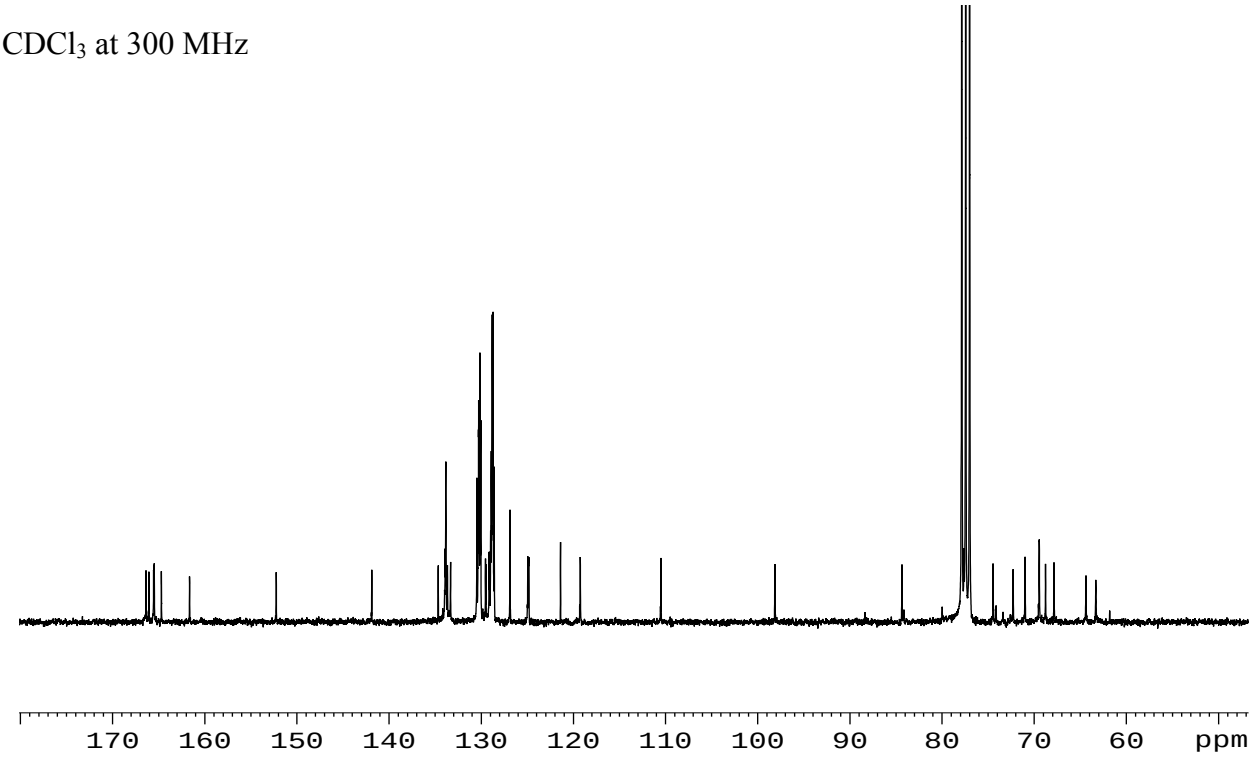
$CDCl_3$ at 300 MHz



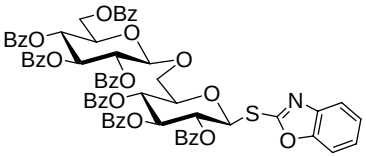
16c



$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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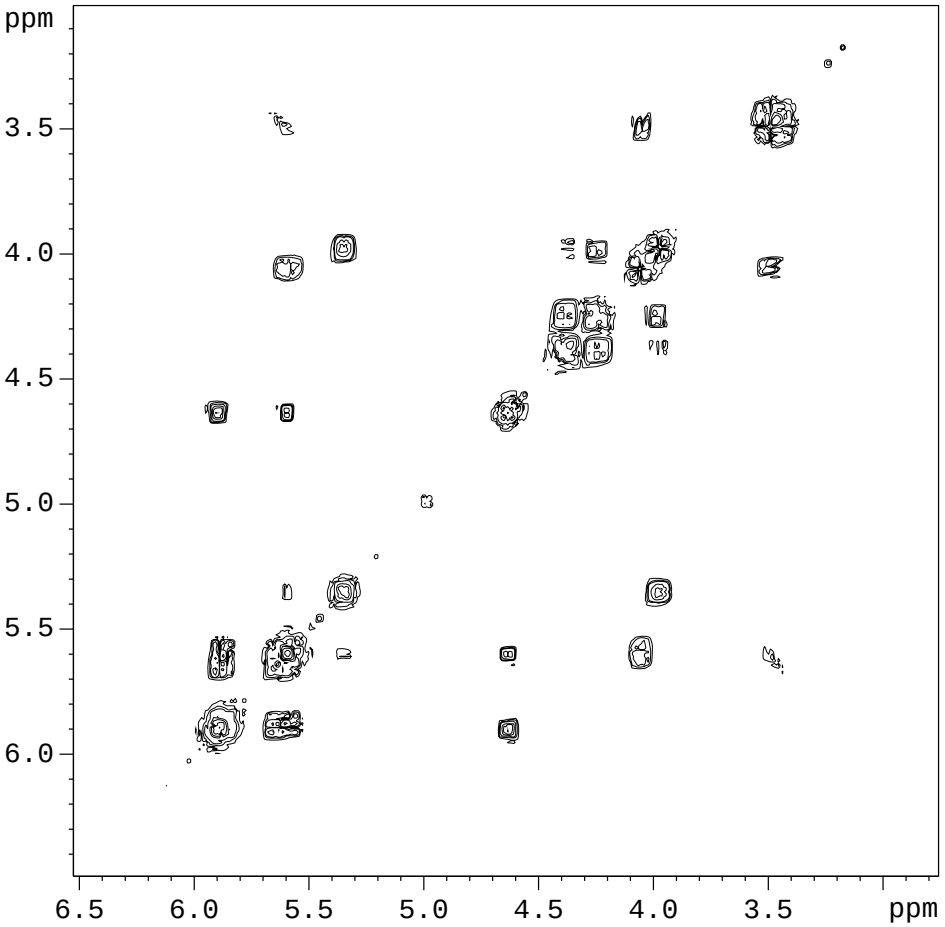
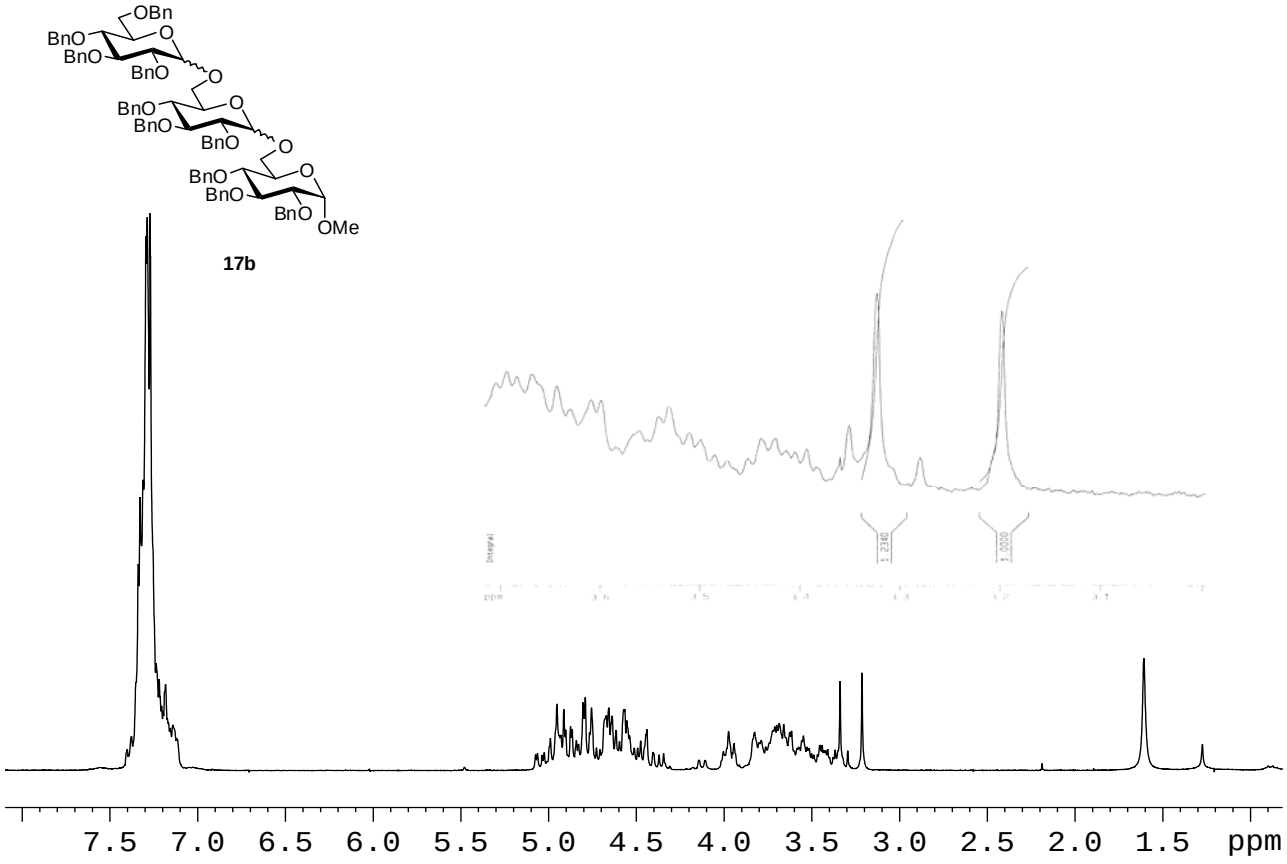
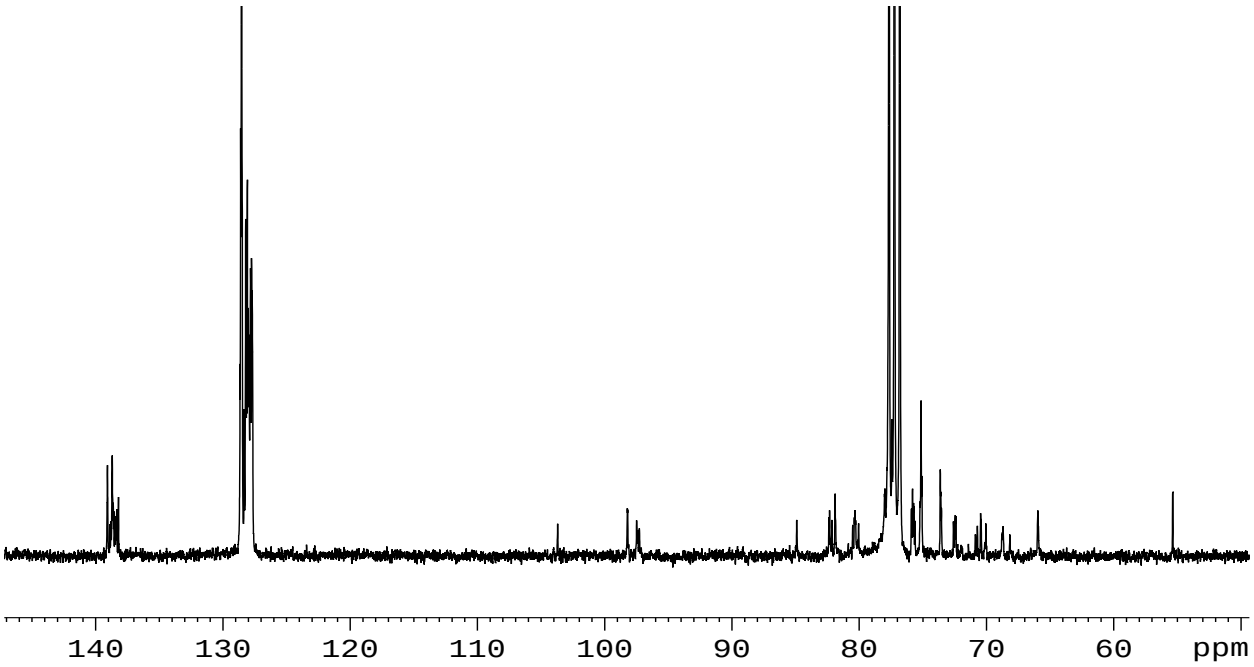


$CDCl_3$ at 300 MHz

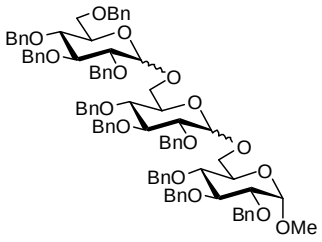


17b

$CDCl_3$ at 300 MHz



$CDCl_3$ at 75 MHz



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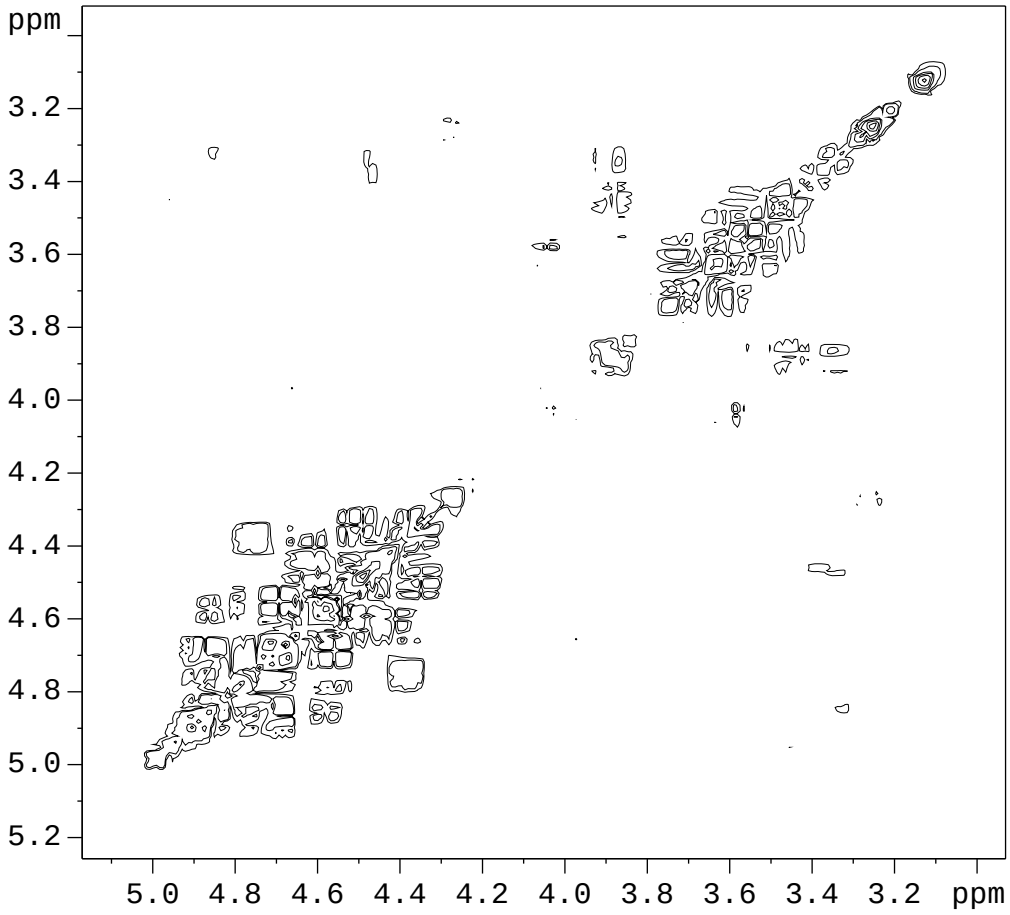
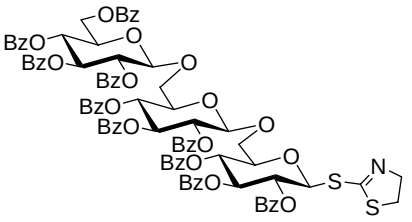


$CDCl_3$ at 300 MHz



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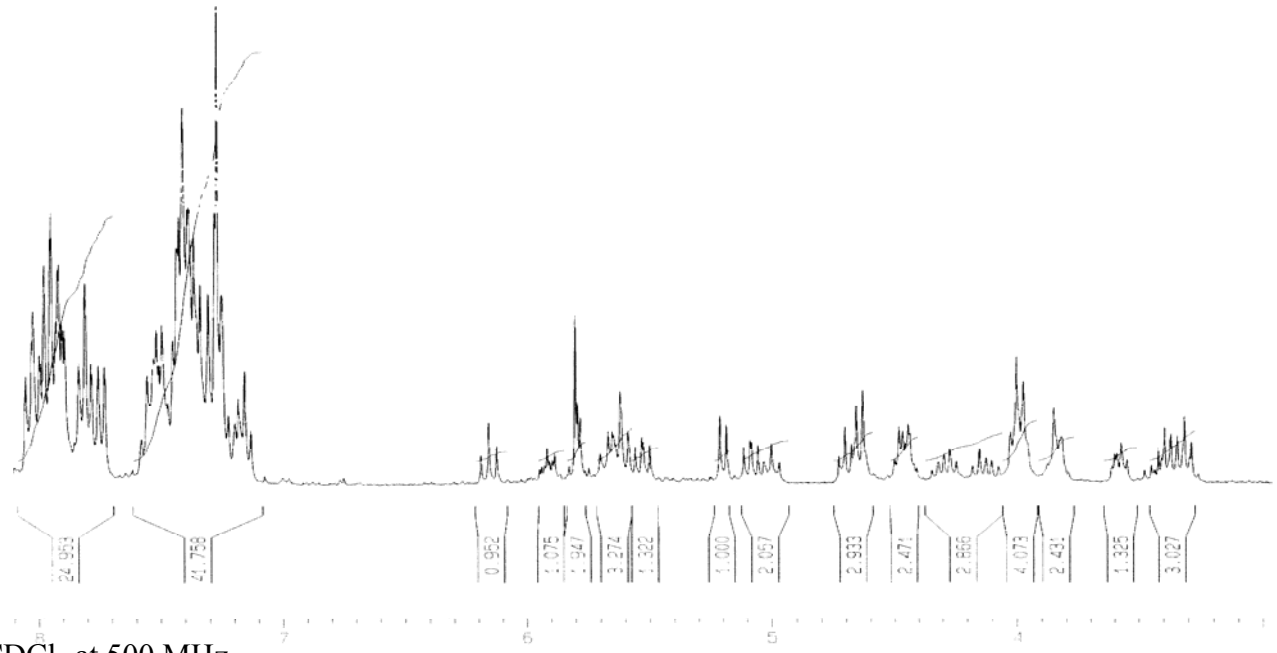
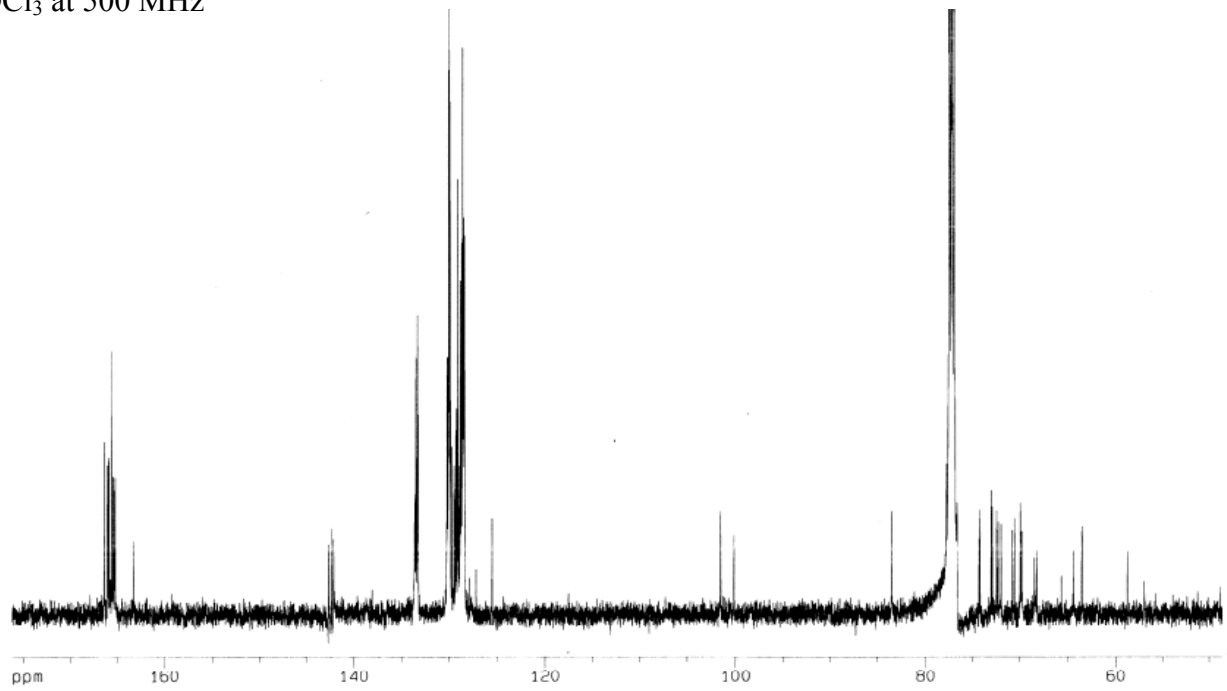
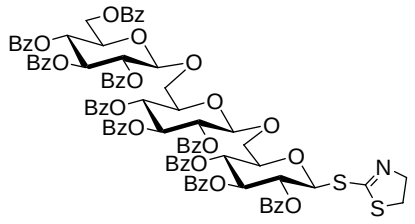


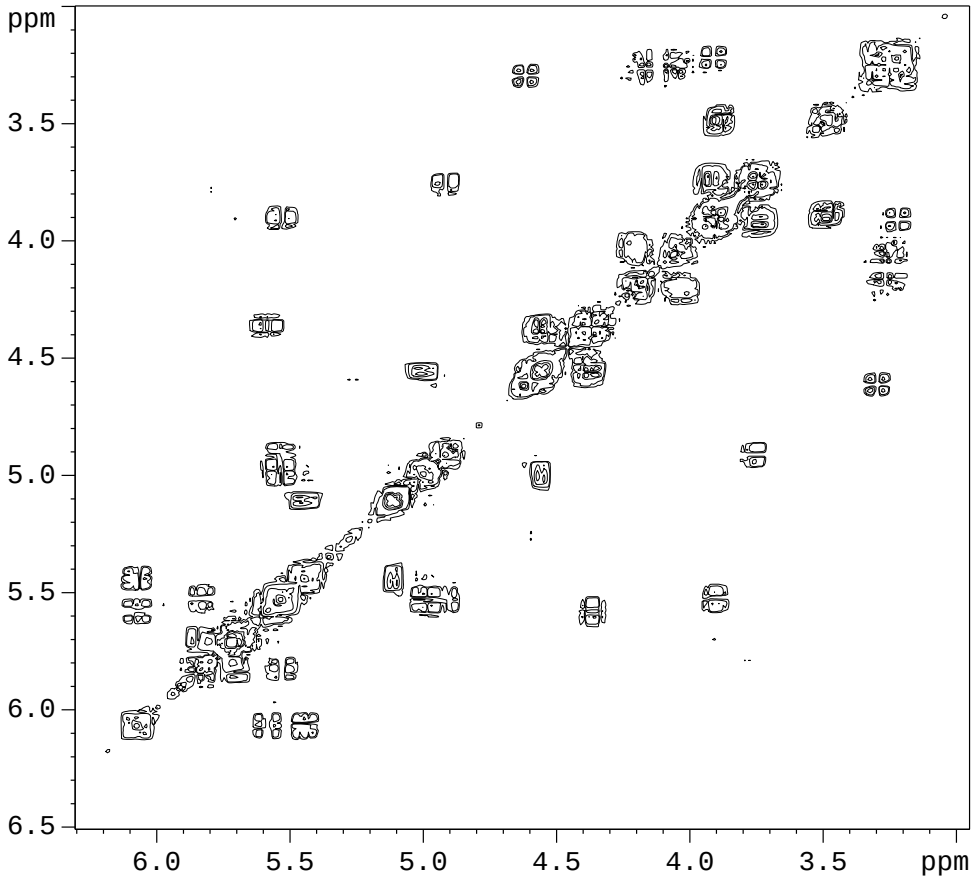
$CDCl_3$ at 500 MHz



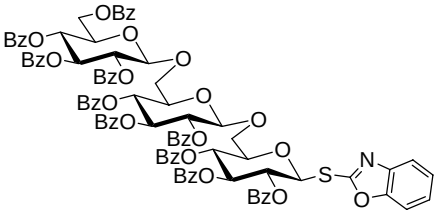
$CDCl_3$ at 125 MHz



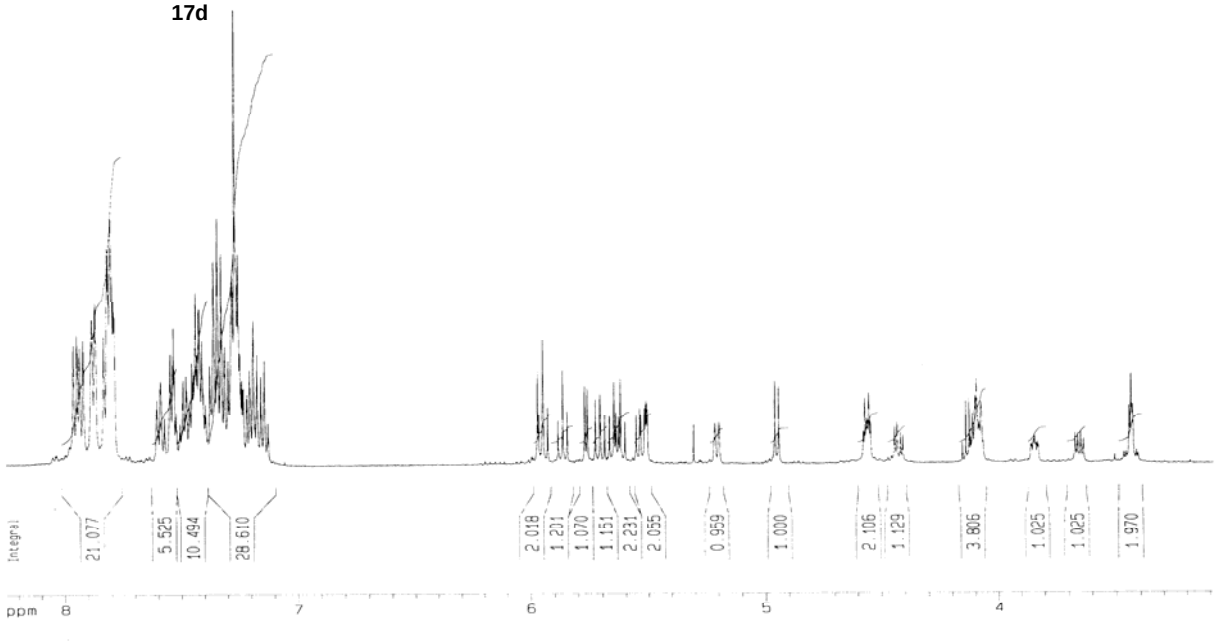
17c



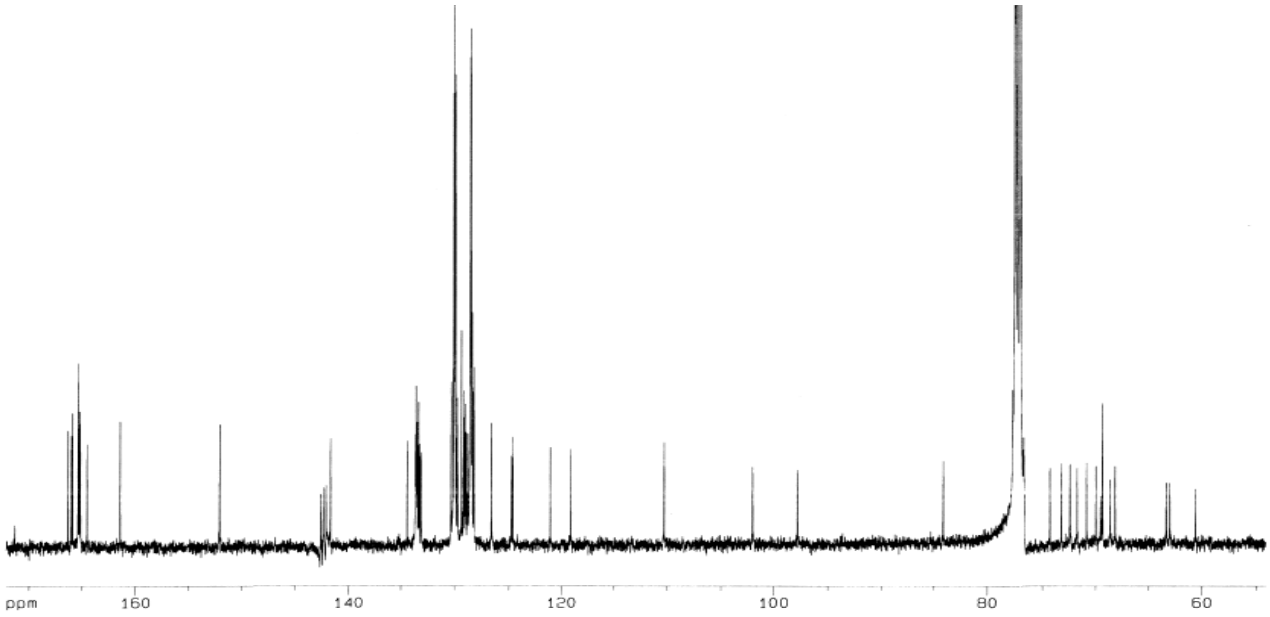
$CDCl_3$ at 300 MHz



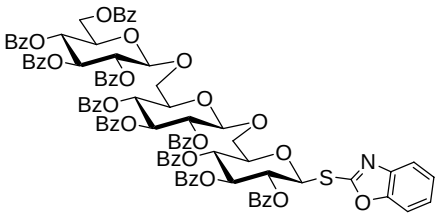
17d



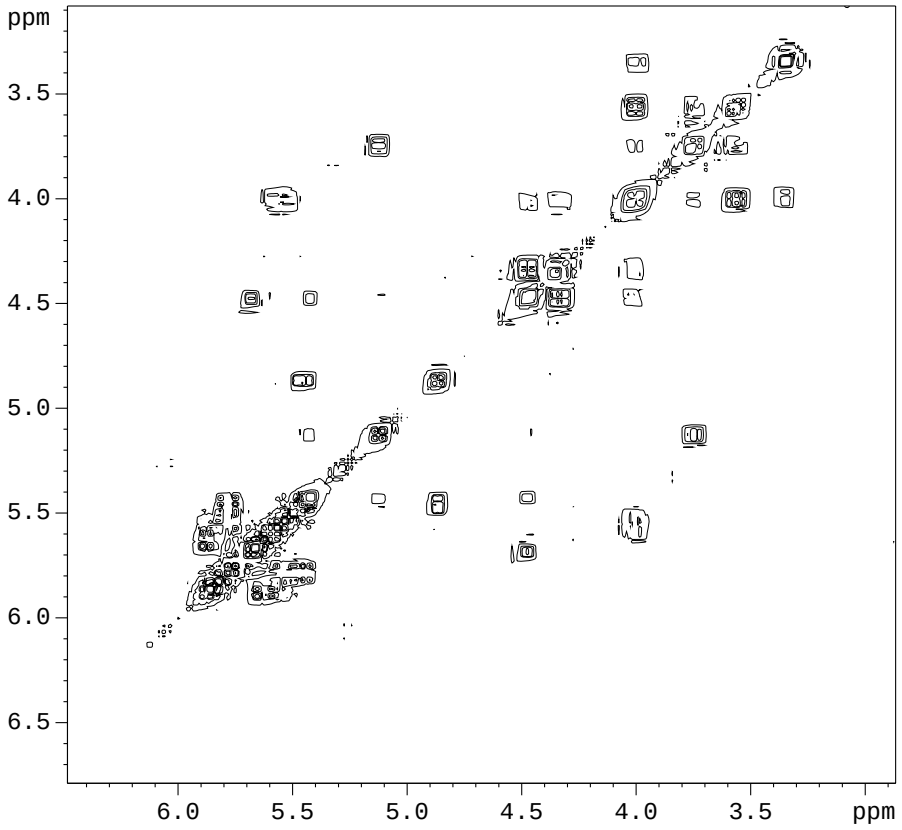
$CDCl_3$ at 500 MHz



$CDCl_3$ at 125 MHz



17d



$CDCl_3$ at 300 MHz

X-Ray data for compound 13

Table 1. Crystal data and structure refinement for **13** (avd8608).

Empirical formula	$C_{10}\ H_{11}\ N\ S_2$	
Formula weight	209.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.0126(10) Å	α= 90°.
	b = 9.7287(11) Å	β= 91.240(5)°.
	c = 12.6512(12) Å	γ = 90°.
Volume	985.96(19) $Å^3$	
Z	4	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.489 mm^{-1}	
F(000)	440	
Crystal size	0.35 x 0.23 x 0.09 mm^3	
Theta range for data collection	3.22 to 27.46°.	
Index ranges	-10≤h≤10, -12≤k≤12, -16≤l≤16	
Reflections collected	21284	
Independent reflections	2259 [R(int) = 0.0296]	
Completeness to theta = 27.46°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9573 and 0.8486	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2259 / 0 / 118	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0781	
R indices (all data)	R1 = 0.0327, wR2 = 0.0799	
Largest diff. peak and hole	0.410 and -0.371 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **13**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6921(1)	4298(1)	2967(1)	17(1)
S(2)	7693(1)	1304(1)	2797(1)	20(1)
N(1)	8031(2)	3218(1)	1279(1)	13(1)
C(1)	7609(2)	2871(1)	2260(1)	13(1)
C(2)	7217(3)	5458(2)	1877(2)	38(1)
C(3)	7820(3)	4658(2)	973(1)	29(1)
C(4)	8654(2)	2239(2)	513(1)	15(1)
C(5)	10537(2)	2230(1)	430(1)	13(1)
C(6)	11592(2)	2852(2)	1177(1)	16(1)
C(7)	13320(2)	2780(2)	1076(1)	20(1)
C(8)	14000(2)	2079(2)	235(1)	21(1)
C(9)	12951(2)	1457(2)	-521(1)	19(1)
C(10)	11232(2)	1540(2)	-423(1)	16(1)

Table 3. Bond lengths [Å] and angles [°] for **13**.

S(1)-C(1)	1.7480(15)	C(3)-C(2)-H(2A)	110.0
S(1)-C(2)	1.8023(18)	S(1)-C(2)-H(2A)	110.0
S(2)-C(1)	1.6691(14)	C(3)-C(2)-H(2B)	110.0
N(1)-C(1)	1.3369(18)	S(1)-C(2)-H(2B)	110.0
N(1)-C(4)	1.4552(18)	H(2A)-C(2)-H(2B)	108.4
N(1)-C(3)	1.4618(19)	N(1)-C(3)-C(2)	109.84(13)
C(2)-C(3)	1.473(2)	N(1)-C(3)-H(3A)	109.7
C(2)-H(2A)	0.9900	C(2)-C(3)-H(3A)	109.7
C(2)-H(2B)	0.9900	N(1)-C(3)-H(3B)	109.7
C(3)-H(3A)	0.9900	C(2)-C(3)-H(3B)	109.7
C(3)-H(3B)	0.9900	H(3A)-C(3)-H(3B)	108.2
C(4)-C(5)	1.515(2)	N(1)-C(4)-C(5)	113.96(12)
C(4)-H(4A)	0.9900	N(1)-C(4)-H(4A)	108.8
C(4)-H(4B)	0.9900	C(5)-C(4)-H(4A)	108.8
C(5)-C(6)	1.393(2)	N(1)-C(4)-H(4B)	108.8
C(5)-C(10)	1.396(2)	C(5)-C(4)-H(4B)	108.8
C(6)-C(7)	1.395(2)	H(4A)-C(4)-H(4B)	107.7
C(6)-H(6)	0.9500	C(6)-C(5)-C(10)	119.10(13)
C(7)-C(8)	1.386(2)	C(6)-C(5)-C(4)	122.79(13)
C(7)-H(7)	0.9500	C(10)-C(5)-C(4)	118.10(13)
C(8)-C(9)	1.397(2)	C(5)-C(6)-C(7)	120.35(14)
C(8)-H(8)	0.9500	C(5)-C(6)-H(6)	119.8
C(9)-C(10)	1.388(2)	C(7)-C(6)-H(6)	119.8
C(9)-H(9)	0.9500	C(8)-C(7)-C(6)	120.15(14)
C(10)-H(10)	0.9500	C(8)-C(7)-H(7)	119.9
C(1)-S(1)-C(2)	93.29(7)	C(6)-C(7)-H(7)	119.9
C(1)-N(1)-C(4)	123.38(12)	C(7)-C(8)-C(9)	119.87(14)
C(1)-N(1)-C(3)	117.24(12)	C(7)-C(8)-H(8)	120.1
C(4)-N(1)-C(3)	119.37(12)	C(9)-C(8)-H(8)	120.1
N(1)-C(1)-S(2)	126.85(11)	C(10)-C(9)-C(8)	119.83(14)
N(1)-C(1)-S(1)	111.30(10)	C(10)-C(9)-H(9)	120.1
S(2)-C(1)-S(1)	121.85(8)	C(8)-C(9)-H(9)	120.1
C(3)-C(2)-S(1)	108.28(12)	C(9)-C(10)-C(5)	120.70(14)
		C(9)-C(10)-H(10)	119.7
		C(5)-C(10)-H(10)	119.7

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **13**. 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}
S(1)	22(1)	16(1)	13(1)	-1(1)	2(1)	3(1)
S(2)	33(1)	13(1)	15(1)	3(1)	-1(1)	0(1)
N(1)	14(1)	13(1)	13(1)	0(1)	1(1)	0(1)
C(1)	13(1)	14(1)	13(1)	-1(1)	-1(1)	-1(1)
C(2)	71(2)	15(1)	29(1)	6(1)	24(1)	8(1)
C(3)	53(1)	16(1)	18(1)	5(1)	8(1)	8(1)
C(4)	14(1)	17(1)	13(1)	-4(1)	1(1)	-1(1)
C(5)	13(1)	12(1)	14(1)	3(1)	2(1)	0(1)
C(6)	18(1)	15(1)	15(1)	-1(1)	0(1)	-1(1)
C(7)	17(1)	19(1)	23(1)	1(1)	-4(1)	-4(1)
C(8)	13(1)	21(1)	28(1)	3(1)	2(1)	-1(1)
C(9)	19(1)	17(1)	21(1)	0(1)	5(1)	1(1)
C(10)	17(1)	15(1)	14(1)	-1(1)	1(1)	-2(1)

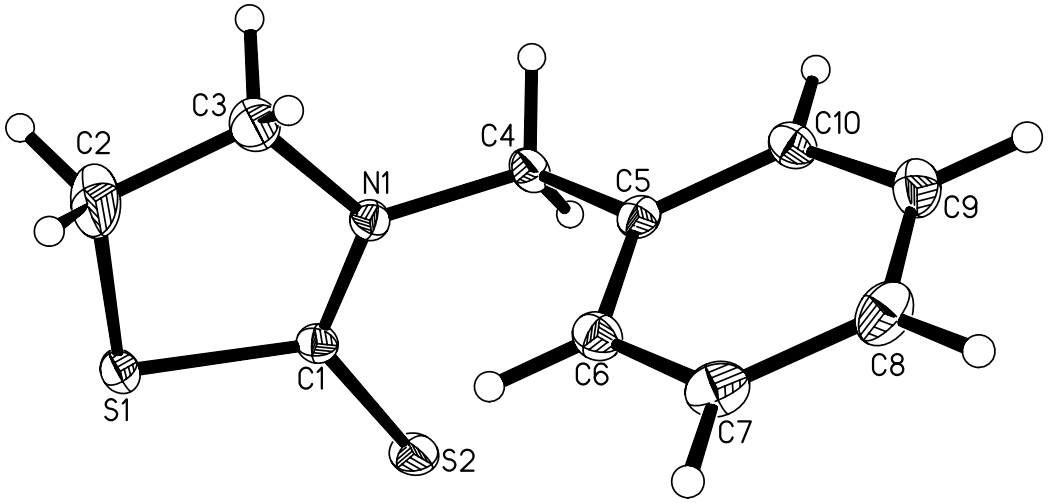
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **13**.

	x	y	z	U(eq)
H(2A)	6149	5916	1684	46
H(2B)	8042	6175	2077	46
H(3A)	7008	4726	375	35
H(3B)	8899	5036	741	35
H(4A)	8156	2456	-191	17
H(4B)	8277	1306	710	17
H(6)	11132	3328	1758	19
H(7)	14033	3213	1586	23
H(8)	15177	2021	171	25
H(9)	13412	979	-1100	23
H(10)	10521	1124	-941	19

Table 6. Torsion angles [°] for **13**.

C(4)-N(1)-C(1)-S(2)	-0.3(2)
C(3)-N(1)-C(1)-S(2)	178.70(13)
C(4)-N(1)-C(1)-S(1)	179.77(10)
C(3)-N(1)-C(1)-S(1)	-1.25(17)
C(2)-S(1)-C(1)-N(1)	-0.10(13)
C(2)-S(1)-C(1)-S(2)	179.95(12)
C(1)-S(1)-C(2)-C(3)	1.33(17)
C(1)-N(1)-C(3)-C(2)	2.3(2)
C(4)-N(1)-C(3)-C(2)	-178.71(16)
S(1)-C(2)-C(3)-N(1)	-2.1(2)
C(1)-N(1)-C(4)-C(5)	-98.38(16)
C(3)-N(1)-C(4)-C(5)	82.66(17)
N(1)-C(4)-C(5)-C(6)	14.16(19)
N(1)-C(4)-C(5)-C(10)	-167.21(12)
C(10)-C(5)-C(6)-C(7)	-0.3(2)
C(4)-C(5)-C(6)-C(7)	178.28(13)
C(5)-C(6)-C(7)-C(8)	-0.5(2)
C(6)-C(7)-C(8)-C(9)	0.8(2)
C(7)-C(8)-C(9)-C(10)	-0.2(2)
C(8)-C(9)-C(10)-C(5)	-0.6(2)
C(6)-C(5)-C(10)-C(9)	0.9(2)
C(4)-C(5)-C(10)-C(9)	-177.82(13)

Projection view of the molecule **13** with 50% thermal ellipsoids:



X-Ray data for compound 14

Table 1. Crystal data and structure refinement for **14** (avd13307).

Empirical formula	$C_{14}H_{11}NOS$	
Formula weight	241.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 4.6217(3) Å	α= 90°.
	b = 11.4672(6) Å	β= 90°.
	c = 21.6268(12) Å	γ = 90°.
Volume	1146.18(11) $Å^3$	
Z	4	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	0.262 mm^{-1}	
F(000)	504	
Crystal size	0.41 x 0.34 x 0.16 mm^3	
Theta range for data collection	3.34 to 31.04°.	
Index ranges	$-6\le h\le 6$, $-16\le k\le 16$, $-30\le l\le 31$	
Reflections collected	18698	
Independent reflections	3662 [R(int) = 0.042]	
Completeness to theta = 31.04°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9592 and 0.9000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3662 / 0 / 198	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0745	
R indices (all data)	R1 = 0.0366, wR2 = 0.0766	
Absolute structure parameter	0.04(6)	
Largest diff. peak and hole	0.309 and -0.220 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4076(1)	3358(1)	2032(1)	18(1)
O(1)	7728(2)	5095(1)	2070(1)	18(1)
N(1)	6962(3)	4452(1)	1093(1)	16(1)
C(1)	9382(3)	5771(1)	1680(1)	17(1)
C(2)	11238(3)	6670(1)	1830(1)	23(1)
C(3)	12659(3)	7185(1)	1337(1)	26(1)
C(4)	12204(3)	6821(1)	729(1)	25(1)
C(5)	10304(3)	5919(1)	588(1)	22(1)
C(6)	8919(3)	5389(1)	1081(1)	16(1)
C(7)	6385(3)	4340(1)	1674(1)	16(1)
C(8)	3117(3)	2457(1)	1368(1)	19(1)
C(9)	5398(3)	1592(1)	1188(1)	15(1)
C(10)	6703(3)	1645(1)	608(1)	16(1)
C(11)	8737(3)	814(1)	433(1)	19(1)
C(12)	9474(3)	-73(1)	839(1)	19(1)
C(13)	8203(3)	-128(1)	1418(1)	19(1)
C(14)	6159(3)	693(1)	1590(1)	18(1)

Table 3. Bond lengths [Å] and angles [°] for **14**.

		O(1)-C(1)-C(2)	128.41(12)
S(1)-C(7)	1.7336(13)	O(1)-C(1)-C(6)	108.04(11)
S(1)-C(8)	1.8227(14)	C(2)-C(1)-C(6)	123.54(13)
O(1)-C(7)	1.3671(15)	C(1)-C(2)-C(3)	115.60(13)
O(1)-C(1)	1.3771(16)	C(1)-C(2)-H(2)	123.0(11)
N(1)-C(7)	1.2917(17)	C(3)-C(2)-H(2)	121.4(11)
N(1)-C(6)	1.4049(17)	C(2)-C(3)-C(4)	121.80(14)
C(1)-C(2)	1.3792(19)	C(2)-C(3)-H(3)	119.7(11)
C(1)-C(6)	1.3854(17)	C(4)-C(3)-H(3)	118.4(11)
C(2)-C(3)	1.385(2)	C(5)-C(4)-C(3)	121.67(14)
C(2)-H(2)	0.927(17)	C(5)-C(4)-H(4)	118.2(11)
C(3)-C(4)	1.394(2)	C(3)-C(4)-H(4)	120.1(11)
C(3)-H(3)	0.916(19)	C(6)-C(5)-C(4)	116.69(13)
C(4)-C(5)	1.390(2)	C(6)-C(5)-H(5)	123.1(9)
C(4)-H(4)	0.945(18)	C(4)-C(5)-H(5)	120.2(9)
C(5)-C(6)	1.3848(19)	C(5)-C(6)-C(1)	120.68(13)
C(5)-H(5)	0.970(16)	C(5)-C(6)-N(1)	130.42(12)
C(8)-C(9)	1.4989(18)	C(1)-C(6)-N(1)	108.90(11)
C(8)-H(8A)	0.979(18)	N(1)-C(7)-O(1)	116.97(11)
C(8)-H(8B)	1.015(18)	N(1)-C(7)-S(1)	128.69(10)
C(9)-C(14)	1.3931(17)	O(1)-C(7)-S(1)	114.34(9)
C(9)-C(10)	1.3931(17)	C(9)-C(8)-S(1)	114.10(9)
C(10)-C(11)	1.3910(19)	C(9)-C(8)-H(8A)	111.3(10)
C(10)-H(10)	0.942(15)	S(1)-C(8)-H(8A)	101.1(10)
C(11)-C(12)	1.3855(18)	C(9)-C(8)-H(8B)	114.4(10)
C(11)-H(11)	0.980(16)	S(1)-C(8)-H(8B)	107.3(10)
C(12)-C(13)	1.386(2)	H(8A)-C(8)-H(8B)	107.6(15)
C(12)-H(12)	0.951(18)	C(14)-C(9)-C(10)	119.03(12)
C(13)-C(14)	1.3848(19)	C(14)-C(9)-C(8)	120.35(12)
C(13)-H(13)	0.980(19)	C(10)-C(9)-C(8)	120.58(11)
C(14)-H(14)	0.974(18)	C(11)-C(10)-C(9)	120.48(12)
		C(11)-C(10)-H(10)	119.2(10)
C(7)-S(1)-C(8)	99.63(6)	C(9)-C(10)-H(10)	120.3(10)
C(7)-O(1)-C(1)	102.98(10)	C(12)-C(11)-C(10)	119.81(13)
C(7)-N(1)-C(6)	103.11(10)	C(12)-C(11)-H(11)	119.3(9)

C(10)-C(11)-H(11)	120.9(9)	C(12)-C(13)-H(13)	119.6(12)
C(11)-C(12)-C(13)	120.11(13)	C(13)-C(14)-C(9)	120.50(12)
C(11)-C(12)-H(12)	118.5(10)	C(13)-C(14)-H(14)	120.0(10)
C(13)-C(12)-H(12)	121.4(10)	C(9)-C(14)-H(14)	119.4(10)
C(14)-C(13)-C(12)	120.08(12)		
C(14)-C(13)-H(13)	120.1(12)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **14**. 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}
S(1)	19(1)	17(1)	19(1)	0(1)	4(1)	1(1)
O(1)	19(1)	18(1)	17(1)	-3(1)	-2(1)	2(1)
N(1)	16(1)	14(1)	17(1)	-1(1)	-1(1)	1(1)
C(1)	15(1)	15(1)	21(1)	0(1)	-2(1)	3(1)
C(2)	22(1)	18(1)	30(1)	-4(1)	-8(1)	2(1)
C(3)	19(1)	17(1)	43(1)	3(1)	-4(1)	0(1)
C(4)	20(1)	20(1)	36(1)	9(1)	6(1)	3(1)
C(5)	23(1)	19(1)	23(1)	2(1)	3(1)	4(1)
C(6)	16(1)	13(1)	20(1)	0(1)	-1(1)	4(1)
C(7)	14(1)	14(1)	20(1)	-1(1)	-1(1)	4(1)
C(8)	13(1)	19(1)	23(1)	-2(1)	-1(1)	1(1)
C(9)	12(1)	15(1)	18(1)	-1(1)	-2(1)	-3(1)
C(10)	18(1)	14(1)	16(1)	1(1)	-2(1)	-2(1)
C(11)	21(1)	17(1)	17(1)	-2(1)	2(1)	-2(1)
C(12)	21(1)	15(1)	21(1)	-2(1)	1(1)	1(1)
C(13)	21(1)	16(1)	21(1)	4(1)	-1(1)	-1(1)
C(14)	18(1)	18(1)	18(1)	2(1)	2(1)	-3(1)

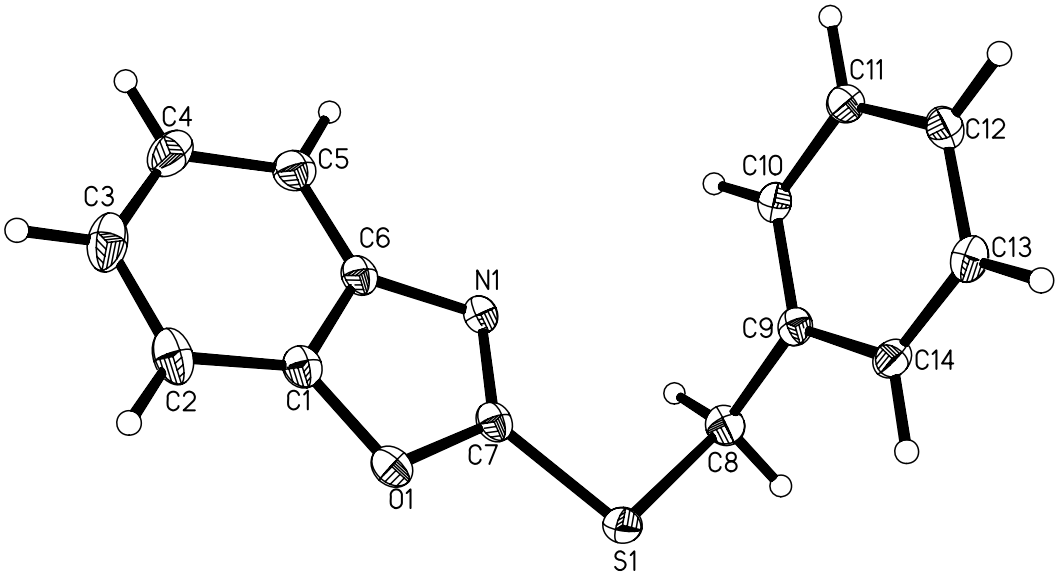
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **14**.

	x	y	z	U(eq)
H(2)	11550(40)	6917(14)	2233(8)	25(5)
H(3)	13840(40)	7814(16)	1404(8)	31(5)
H(4)	13220(40)	7181(16)	401(8)	31(5)
H(5)	10020(40)	5681(13)	162(7)	17(4)
H(8A)	1380(40)	2066(14)	1521(8)	24(4)
H(8B)	2500(40)	3003(16)	1023(8)	31(5)
H(10)	6250(40)	2256(14)	334(7)	16(4)
H(11)	9670(40)	851(12)	27(7)	14(4)
H(12)	10840(40)	-640(14)	708(8)	26(4)
H(13)	8880(50)	-709(16)	1717(9)	36(5)
H(14)	5320(40)	670(14)	2003(8)	27(4)

Table 6. Torsion angles [°] for **14**.

C(7)-O(1)-C(1)-C(2)	-178.84(13)
C(7)-O(1)-C(1)-C(6)	0.35(13)
O(1)-C(1)-C(2)-C(3)	179.04(13)
C(6)-C(1)-C(2)-C(3)	0.0(2)
C(1)-C(2)-C(3)-C(4)	0.7(2)
C(2)-C(3)-C(4)-C(5)	-0.1(2)
C(3)-C(4)-C(5)-C(6)	-1.0(2)
C(4)-C(5)-C(6)-C(1)	1.60(19)
C(4)-C(5)-C(6)-N(1)	-178.31(13)
O(1)-C(1)-C(6)-C(5)	179.63(12)
C(2)-C(1)-C(6)-C(5)	-1.1(2)
O(1)-C(1)-C(6)-N(1)	-0.44(14)
C(2)-C(1)-C(6)-N(1)	178.79(12)
C(7)-N(1)-C(6)-C(5)	-179.74(14)
C(7)-N(1)-C(6)-C(1)	0.34(14)
C(6)-N(1)-C(7)-O(1)	-0.12(15)
C(6)-N(1)-C(7)-S(1)	179.25(10)
C(1)-O(1)-C(7)-N(1)	-0.15(14)
C(1)-O(1)-C(7)-S(1)	-179.61(8)
C(8)-S(1)-C(7)-N(1)	6.44(14)
C(8)-S(1)-C(7)-O(1)	-174.18(9)
C(7)-S(1)-C(8)-C(9)	78.05(10)
S(1)-C(8)-C(9)-C(14)	64.43(14)
S(1)-C(8)-C(9)-C(10)	-118.16(12)
C(14)-C(9)-C(10)-C(11)	-0.03(18)
C(8)-C(9)-C(10)-C(11)	-177.47(12)
C(9)-C(10)-C(11)-C(12)	-0.06(19)
C(10)-C(11)-C(12)-C(13)	-0.4(2)
C(11)-C(12)-C(13)-C(14)	1.0(2)
C(12)-C(13)-C(14)-C(9)	-1.1(2)
C(10)-C(9)-C(14)-C(13)	0.59(19)
C(8)-C(9)-C(14)-C(13)	178.05(12)

Projection view of the molecule **14** with 50% thermal ellipsoids:



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