Electronic Supporting Information (ESI)

Synthesis of Galactomannans Fragments to help NMR Assignment of Polysaccharides extracted from Lichens

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General experimental Details. All reagents were purchased from commercial sources and were used without further purification unless noted. **4**, **7**, **11a**, **14**, **21** were synthesized according to literature procedures.[1] Unless otherwise stated, all reactions were monitored by TLC on Silica Gel 60 F_{254}. TLC spots were detected under 254 nm UV-light or by staining with cerium ammonium molybdate solution. For reactions that proceeded by heating, a metallic heating mantle was used. Column chromatography was performed on Silica Gel (50 µm). High Resolution Masses were recorded in positive mode using direct Electrospray ionization on a Waters Q-Tof 2 spectrometer.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.13 MHz for ^{1}H, equipped with a BBFO probe with a Z-gradient coil and a GREAT 1/10 gradient unit or on a Bruker Avance III operating at 500.13 MHz for ^{1}H equipped with a 5 mm TCI cryo-probe. All experiments were carried out at 25 °C and references for chemical shifts are external. Coupling constants *J* were calculated in Hertz (Hz). Proton and carbon NMR peaks were unambiguously assigned by COSY (double quantum filtered with gradient pulse for selection), HSQC (gradient echo-anti echo selection and shape pulse), HMBC (echo-anti echo gradient selection, magnitude mode) correlation experiments as well as TOCSY. Mutiplicity are annotated as s (singlet), d (doublet), t (triplet), m (multiplet) or o (overlapping signals). For linear oligosaccharides, the letters a, b, c were attributed starting from the reducing glycosyl residue. For branched oligosaccharides, the letter a was for the reducing entity, b for the glycosyl residue linked to *O*-4 of the reducing Man*p* unit, and c for the residue linked to *O*-6 of the same entity.

The zg30 Bruker pulse program was used for 1D ^{1}H NMR, with a TD of 64k, a relaxation delay d1 = 2s and 32 scans or more. The spectrum width was set to 18 ppm. 2D COSY experiments were acquired using the cosygpdqf pulse program. Matrices consisting of 256-512 (t1)×2048 (t2) complex data points were recorded. AQ time of 0.25 s to 0.5 s was used. Processing was performed with a QSINE function in both dimensions (SSB=0). 2D TOCSY experiments were acquired using the dipsi2sisp pulse program with a mixing time of 150 ms in major cases. Matrices consisting of 256-400 (t1)×4k-8k (t2) complex data points were recorded; 8 to 16 scans are carried out per t1 increment with 1.5 s recovery delay (d1) and AQ time of 0.3 s to 0.7 s. Processing was performed with a QSINE function in both dimensions (SSB=2). ^{13}C NMR spectra were recorded at 100.61 MHz or at 125.13 MHz on cryo-probe. Several sequences as jmod, dept135 or zgpg30 were used with n*1024 scans depending on the concentration of the sample. TD was set to 64k and a relaxation delay of 2 s for a spectral width of 220 ppm was used.

2D HSQC (^{1}H-^{13}C) experiments were acquired using the hsqcetgpsisp2.2 pulse program for high sensitivity with an AQ=0.25 s to 0.5 s, d1=1.5 s, ns=2 to 24 depending on the concentration. Generally, 256 experiences were acquired (t1). Fourier transform was performed in both dimensions with a SINE function (SSB=3). 2D HMBC (^{1}H-^{13}C) experiments were performed with either the hmbcplrndqf or the impact-hmbc pulse program. D1 was set to 0.3 s to 1.5 s, delay d6 for the evolution of long-range coupling was set to 65 ms, NS was depending on the concentration and the number of series was set at 256 to 512(t1). All the data were processed with a SINE function in both dimensions (SSB=3). To identify the ^{1}H frequency of the mixture of anomers, the 1D-Tocsy experiment (selcssfdizs.2) from the Bruker library was used with 150 ms for mixing time and 16 for TD0 when the highest selectivity was required.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α,β-D-mannopyranose (5a). This synthesis was performed according to general procedure A1 starting from thioglycoside **4a** (720 mg, 0.62 mmol), *N*-iodosaccharin (574 mg, 1.86 mmol), in a 9:1:5 DCM/H_2O/CH_3CN mixture (15 mL), at RT for 2.5 h. Flash-chromatography eluting with Cyclohexane/AcOEt (gradient from 9:1 to 1:1) afforded **5a** (524 mg, 79%) as a white solid. TLC: (cyclohexane/AcOEt, 65:35): R_f=0.3.
5aα: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11-7.87 (13H, m, Ph), 7.82 (2H, dd, *J* 8.4, 1.2, Ph), 7.63-7.20 (20H, m, Ph), 6.02 (1H, dd, $J_{3a,4a}$ 10.1, $J_{3a,2a}$ 3.2, H-3a), 6.00-5.94 (1H, m, H-5b), 5.74 (1H, dd, $J_{2a,3a}$ 3.2, $J_{2a,1a}$

[1] B. Favreau, O. Yeni, S. Ollivier, J. Boustie, F. Le Dévéhat, J.-P. Guégan, M. Fanuel, H. Rogniaux, R. Brédy, I. Compagnon, D. Ropartz, L. Legentil and V. Ferrières, *J. Org. Chem.*, 2021, **86**, 6390-6405.

1.3, H-2a), 5.73 (1H, t, $J_{4a,3a}$= $J_{4a,5a}$ 10.1, H-4a), 5.66 (1H, dd, $J_{3b,4b}$ 5.9, $J_{3b,2b}$ 1.5, H-3b), 5.62 (1H, s, H-1b), 5.49 (1H, d, $J_{2b,3b}$ 1.5, H-2b), 5.42 (1H, s, H-1a), 4.80-4.67 (4H, m, H-5a, H-4b, H-6b), 4.01 (1H, dd, $J_{6a,6'a}$ 12.6 $J_{6a,5a}$ 7.9, H-6a), 3.93 (1H, dd, $J_{6'a,6a}$ 12.6 $J_{6'a,5a}$ 2.2, H-6'a). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.32, 166.29, 166.01, 165.89, 165.79, 165.65, 165.52 (CO), 133.79, 133.63, 133.60, 133.48, 133.26, 133.23, 130.14, 130.06, 130.01, 129.97, 129.90, 129.85, 129.69, 129.47, 129.45, 129.31, 129.09, 128.97, 128.79, 128.72, 128.67, 128.61, 128.56, 128.52, 128.49, 128.39 (Ph), 107.35 (C-1b), 92.54 (C-1a), 83.41 (C-2b), 80.63 (C-4b), 77.48 (C-3b), 71.56 (C-5a), 71.13 (C-2a), 70.51 (C-5b), 69.83 (C-3a), 68.19 (C-6a), 67.86 (C-4a), 63.59 (C-6b).
5aβ: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.53 (1H, s, H-1b), 5.17 (1H, s, H-1a). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 107.35 (C-1b), 92.54 (C-1a).
HRMS (ESI): calcd for $C_{67}H_{54}O_{17}SNa$ $[M+Na]^+$ 1185.2979, found 1185.2975.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (6a). To a solution of **5a** (542 mg, 0.51 mmol) in anhydrous DCM (10 mL) was added at -15 °C trichloroacetonitrile (255 µL, 2.55 mmol) followed by DBU (22 µL, 0.15 mmol). The mixture was stirred at -15 °C for 2h. Then, solvent was evaporated under vacuo and the resulting residue was purified by column chromatography (cyclohexane/AcOEt, 9:1 to 7:3) to give the desired compound **6a** (526 mg, 85%) as an oil. TLC: (cyclohexane/AcOEt, 7:3): R_f=0.45. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.80 (1H, s, NH), 8.07 (2H, dd, *J* 8.4, 1.2, Ph), 8.02 (2H, dd, *J* 8.4, 1.2, Ph), 7.97-7.90 (9H, m, Ph), 7.81 (2H, dd, *J* 8.5, 1.0, Ph), 7.56-7.40 (10H, m, Ph), 7.37-7.23 (10H, m, Ph), 6.55 (1H, d, $J_{1a,2a}$ 1.9, H-1a), 6.08 (1H, t, $J_{4a,3a}$= $J_{4a,5a}$ 10.0, H-4a), 5.97 (1H, dd, $J_{3a,4a}$ 10.0, $J_{3a,2a}$ 3.3, H-3a), 6.01-5.96 (1H, m, H-5b), 5.91 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.9, H-2a), 5.61 (1H, dd, $J_{3b,4b}$ 5.2, $J_{3b,2b}$ 1.4, H-3b), 5.57 (1H, d, $J_{2b,3b}$ 1.4, H-2b), 5.48 (1H, s, H-1b), 4.72 (1H, dd, $J_{6b,6'b}$ 12.0 $J_{6b,5b}$ 4.3, H-6b), 4.69 (1H, dd, $J_{6'b,6b}$ 12.0 $J_{6'b,5b}$ 5.0, H-6'b), 4.64 (1H, dd, $J_{4b,3b}$ 5.2, $J_{4b,5b}$ 3.8, H-4b), 4.52 (1H, ddd, $J_{5a,4a}$ 10.0, $J_{5a,6'a}$ 5.2, $J_{5a,6a}$ 2.4, H-5a), 4.04 (1H, dd, $J_{6a,6'a}$ 12.0 $J_{6a,5a}$ 2.4, H-6a), 3.89 (1H, dd, $J_{6'a,6a}$ 12.0 $J_{6'a,5a}$ 5.2, H-6'a). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.22, 165.82, 165.69, 165.62, 165.59, 165.38, 165.24 (CO), 159.91 (CN), 133.89, 133.67, 133.45, 133.32, 133.17, 130.07, 130.01, 129.89, 129.86, 129.69, 129.59, 129.20, 129.09, 128.99, 128.94, 128.91, 128.80, 128.62, 128.54, 128.48, 128.47, 128.42 (Ph), 106.51 (C-1b), 94.68 (C-1a), 90.79 (CCl_3), 81.88 (C-2b, C-4b), 77.64 (C-3b), 73.30 (C-5a), 70.45 (C-5b), 69.81 (C-3a), 68.93 (C-2a), 66.65 (C-4a), 66.08 (C-6a), 63.72 (C-6b). HRMS (ESI): calcd for $C_{63}H_{50}Cl_3NO_{18}Na$ $[M+Na]^+$ 1236.1991, found 1236.1994.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-1-thio-α-D-mannopyranoside (8a). Applying procedure C with **6a** (473 mg, 0.39 mmol), **7** (115 mg, 0.32 mmol), activated 4Å molecular sieves (100 mg), TMSOTf (0.02 M in CH_2Cl_2, 1.6 mL, 0.032 mmol) in anhydrous CH_2Cl_2 (10 mL), at -15 °C for 1 h, and purifying by flash chromatography (cyclohexane/AcOEt, gradient from 9:1 to 7:3) afforded **8a** (377 mg, 88%) as a white product. TLC: (cyclohexane/AcOEt, 65:35): R_f=0.39. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.06 (2H, dd, *J* 8.4, 1.2, Ph), 8.00 (2H, dd, *J* 8.4, 1.2, Ph), 7.98-7.89 (9H, m, Ph), 7.81 (2H, dd, *J* 8.5, 1.3, Ph), 7.60-7.41 (13H, m, Ph), 7.41-7.25 (12H, m, Ph), 6.04 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 9.8, H-4b), 5.94 (1H, td, $J_{5c,6'c}$ 7.0, $J_{5c,4c}$ = $J_{5c,6c}$ 4.5, H-5c), 5.82 (1H, dd, $J_{3b,4b}$ 9.8, $J_{3b,2b}$ 3.0, H-3b), 5.83 (1H, s, H-1a), 5.78 (1H, dd, $J_{2b,3b}$ 3.0, $J_{2b,1b}$ 2.2, H-2b), 5.74 (1H, d, $J_{1b,2b}$ 2.2, H-1b), 5.63 (1H, d, $J_{3c,4c}$ 5.0, H-3c), 5.60 (1H, s, H-2c), 5.46 (1H, s, H-1c), 4.70 (1H, dd, $J_{6c,6'c}$ 12.0 $J_{6c,5c}$ 4.5, H-6c), 4.68-4.63 (1H, m, H-4c), 4.65 (1H, dd, $J_{6'c,6c}$ 12.0, $J_{6'c,5c}$ 7.0, H-6'c), 4.54-4.49 (1H, m, H-5a), 4.49 (1H, t, $J_{3a,4a}$ = $J_{3a,2a}$ 6.7, H-3a), 4.44-4.36 (3H, m, H-2a, H-6a), 4.30 (1H, ddd, $J_{5b,4b}$ 9.8, $J_{5b,6'b}$ 4.9, $J_{5b,6b}$ 2.7, H-5b), 4.10-4.04 (1H, m, H-4a), 4.06 (1H, dd, $J_{6b,6'b}$ 11.3, $J_{6b,5b}$ 2.7, H-6b), 3.82 (1H, dd, $J_{6'b,6b}$ 11.3, $J_{6'b,5b}$ 4.9, H-6'b), 1.91 (3H, $COCH_3$), 1.47 (3H, s, CCH_3), 1.30 (3H, s, CCH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 170.74, 166.28, 166.00, 165.96, 165.77, 165.74, 165.66, 165.60 (CO), 133.89, 133.77, 133.73, 133.66, 133.61, 133.59, 133.44, 133.24, 132.80, 132.60, 130.22, 130.18, 130.14, 130.13, 130.10, 129.95, 129.92, 129.63, 129.61, 129.54, 129.50, 129.50, 129.46, 128.96, 128.81, 128.80, 128.78, 128.74, 128.70, 128.34 (Ph), 110.52 ($C(CH_3)_2$), 106.86 (C-1c), 96.85 (C-1b), 84.40 (C-1a), 82.24, 82.17 (C-4c, C-2c), 78.28 (C-3a), 77.86 (C-3c), 76.74 (C-2a), 74.26 (C-4a), 71.18 (C-5b), 70.72 (C-5c), 70.62 (C-2b), 70.50 (C-3b), 67.95 (C-5a), 67.24 (C-4b),

66.54 (C-6b), 63.92, 63.76 (C-6a, C-6c), 28.08, 26.45 ($C(CH_3)_2$), 20.93 ($COCH_3$). HRMS (ESI): calcd for $C_{78}H_{70}O_{23}SNa$ $[M+Na]^+$ 1429.3926, found 1429.3927.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-acetyl-1-thio-α-D-mannopyranoside (9a). To a solution of **8a** (123 mg, 0.087 mmol) in DCM (5 ml) was added at RT trifluoroacetic acid (56 µL, 0.61 mmol) and DTT (13 mg, 0.087 mmol). After 3h stirring, the reaction was quenched with triethylamine and solvent was evaporated *in vacuo*. The resulting residue was purified by column chromatography (cyclohexane/AcOEt, 9:1 to 3:2) to give the desired compound **9a** (48 mg, 41%) as an oil. TLC: (cyclohexane/AcOEt, 3:2): R_f=0.28. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.05 (4H, td, *J* 7.9, 1.3, Ph), 8.00 (2H, dd, *J* 9.1, 1.4, Ph), 7.97 (2H, dd, *J* 8.4, 1.3, Ph), 7.92 (2H, dd, *J* 8.2, 1.3, Ph), 7.89 (2H, dd, *J* 8.1, 1.3, Ph), 7.82 (2H, dd, *J* 8.4, 1.4, Ph), 7.60-7.43 (11H, m, Ph), 7.40-7.26 (15H, m, Ph), 5.98 (1H, ddd, $J_{5c,6'c}$ 6.8, $J_{5c,4c}$ 4.5, $J_{5c,6c}$ 3.3, H-5c), 5.87 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 9.9, H-4b), 5.84 (1H, dd, $J_{3b,4b}$ 9.9, $J_{3b,2b}$ 2.9, H-3b), 5.79 (1H, dd, $J_{2b,3b}$ 2.9, $J_{2b,1b}$ 1.9, H-2b), 5.76 (1H, d, $J_{1b,2b}$ 1.9, H-1b), 5.61-5.59 (2H, m, H-2c, H-3c), 5.53 (1H, d, $J_{1a,2a}$ 1.3, H-1a), 5.50 (1H, s, H-1c), 4.74-4.65 (3H, m, H-4c, H-6c), 4.58-4.42 (4H, m, H-5a, H-6a, H-5b), 4.22-4.18 (3H, m, H-2a, H-3a, H-4a), 4.04 (1H, dd, $J_{6b,6'b}$ 11.8, $J_{6b,5b}$ 2.3, H-6b), 3.92 (1H, dd, $J_{6'b,6b}$ 11.8, $J_{6'b,5b}$ 7.1, H-6'b), 3.40 (1H, d, *J* 7.9, OH), 3.08 (1H, d, *J* 5.2, OH), 1.92 (3H, $COCH_3$). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 170.86, 166.41, 166.39, 166.13, 166.06, 165.88, 165.80 (CO), 133.95, 133.91, 133.84, 133.80, 133.69, 133.65, 133.47, 132.46, 132.42, 130.51, 130.27, 130.22, 130.18, 130.16, 130.15, 130.05, 129.97, 129.94, 129.81, 129.65, 129.55, 129.48, 129.47, 129.44, 129.27, 129.00, 128.94, 128.85, 128.77, 128.75, 128.72, 128.68, 128.58, 128.10 (Ph), 107.25 (C-1c), 98.00 (C-1b), 88.14 (C-1a), 82.58 (C-2c), 81.78 (C-4c), 77.99 (C-3c), 74.93 (C-4a), 73.24, 72.41 (C-2a, C-3a), 71.59 (C-5b), 70.97 (C-2b), 70.62, 70.55 (C-3b, C-5c), 69.77 (C-5a), 67.46 (C-4b), 67.20 (C-6b), 64.06, 63.93 (C-6a, C-6c), 20.93 ($COCH_3$). HRMS (ESI): calcd for $C_{75}H_{66}O_{23}SNa$ $[M+Na]^+$ 1389.3613, found 1389.3609.

Phenyl β-D-galactofuranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-1-thio-α-D-mannopyranoside (10a). This synthesis was performed according to general procedure B starting from **9a** (132 mg, 0.096 mmol), MeONa (0.054 M in MeOH, 357 µL, 0.019 mmol), in MeOH (5 mL) to give **10a** (56 mg, 97%) as a white solid. TLC: (AcOEt/AcOH/H_2O, 7:2:2): R_f=0.25. ^{1}H NMR (D_2O, 400 MHz): δ 7.63-7.55 (2H, m, Ph), 7.47-7.38 (3H, m, Ph), 5.52 (1H, d, $J_{1a,2a}$ 1.9, H-1a), 5.21 (1H, d, $J_{1b,2b}$ 1.9, H-1b), 5.05 (1H, d, $J_{1c,2c}$ 1.9, H-1c), 4.23 (1H, td, $J_{5a,4a}$ 9.5, $J_{5a,6a}$ 3.9, H-5a), 4.19 (1H, dd, $J_{2a,3a}$ 3.4, $J_{2a,1a}$ 1.9, H-2a), 4.13 (1H, dd, $J_{2c,3c}$ 3.7, $J_{2c,1c}$ 1.9, H-2c), 4.09 (1H, dd, $J_{2b,3b}$ 3.3, $J_{2b,1b}$ 1.9, H-2b), 4.09-4.04 (2H, m, H-3c, H-6b), 4.02-3.98 (2H, m, H-3a, H-4c), 3.87 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.5, H-4a), 3.86-3.81 (5H, m, H-6a, H-3b, H-5b, H-5c), 3.73 (1H, dd, $J_{6c,6'c}$ 11.8, $J_{6c,5c}$ 4.5, H-6c), 3.75-3.67 (2H, m, H-4b, H-6'b), 3.66 (1H, dd, $J_{6'c,6c}$ 11.8, $J_{6'c,5c}$ 7.5, H-6'c). ^{13}C NMR (D_2O, 100 MHz): δ 132.58, 132.25, 129.40, 128.34 (Ph), 107.70 (C-1c), 101.76 (C-1b), 87.85 (C-1a), 82.74 (C-4c), 81.01 (C-2c), 76.78 (C-3c), 75.24 (C-4a), 72.59 (C-5b), 72.24 (C-5a), 71.70 (C-2a), 71.31 (C-3a), 70.79 (C-5c), 70.24 (C-2b), 70.17 (C-3b), 66.77 (C-6b), 66.56 (C-4b), 62.72 (C-6c), 60.88 (C-6a). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1674.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranose (5b). This synthesis was performed according to general procedure A1 starting from thioglycoside **4b** (1.05 g, 1.14 mmol), *N*-iodosaccharin (1.45 g, 3.99 mmol), in a 5:1:5 DCM/H_2O/CH_3CN mixture (11 mL), at RT for 2.5 h. Flash-chromatography eluting with Cyclohexane/AcOEt (gradient from 9:1 to 1:1) afforded **5b** (675 mg, 72%) as an orange solid. TLC: (cyclohexane/AcOEt, 1:1): R_f=0.16. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (2H, dd, *J* 7.6, 1.2, Ph), 7.95 (2H, dd, *J* 8.3, 1.1, Ph), 7.80 (2H, dd, *J* 8.5, 1.1, Ph), 7.61 (1H, tt, *J* 7.3, 2.0, Ph) 7.56-7.50 (3H, m, Ph), 7.45-7.36 (3H, m, Ph), 7.28-7.22 (2H, m, Ph), 5.94 (1H, dd, $J_{3a,4a}$ 10.1, $J_{3a,2a}$ 3.4, H-3a), 5.76 (1H, t, $J_{4a,3a}$ = $J_{4a,5a}$ 10.1, H-4a), 5.71 (1H, dd, $J_{2a,3a}$ 3.4, $J_{2a,1a}$ 1.8, H-2a), 5.47 (1H, d, $J_{1a,2a}$ 1.8, H-1a), 5.36 (1H, dd, $J_{4b,3b}$ 3.3, $J_{4b,5b}$ 1.2, H-4b), 5.24 (1H, dd, $J_{2b,3b}$ 10.5, $J_{2b,1b}$ 7.9, H-2b), 5.02 (1H, dd, $J_{3b,2b}$ 10.5, $J_{3b,4b}$ 3.3, H-3b), 4.58-4.52 (1H, m, H-5a), 4.52 (1H, d, $J_{1b,2b}$ 7.9, H-1b), 4.15-4.05 (3H, m, H-6a, H-6b), 3.86 (1H, td, $J_{5b,6b}$ 6.6, $J_{5b,4b}$ 1.2, H-5b), 3.77 (1H, dd, $J_{6'a,6a}$ 10.9, $J_{6'a,5a}$ 6.9, H-6'a), 2.11 (6H, s, $COCH_3$), 1.99 (6H,s, $COCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.55,

170.37, 170.30, 170.27, 165.75, 165.67, 165.55 (CO), 133.66, 133.65, 133.27, 130.17, 129.91, 129.83, 129.46, 129.27, 129.09, 128.78, 128.65, 128.41 (Ph), 101.87 (C-1b), 92.51 (C-1a), 71.01, 70.92, 70.87 (C-2a, C-3b, C-5b), 69.92, 69.87 (C-3a, C-5a), 69.20 (C-6a), 69.04 (C-2b), 67.33 (C-4a), 67.14 (C-4b), 61.43 (C-6b), 21.04, 20.79, 20.76 ($CO\mathit{C}H_3$). HRMS (ESI): calcd for $C_{47}H_{46}O_{17}SNa$ $[M+Na]^+$ 937.2353, found 937.2353.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (6b). To a solution of **5b** (320 mg, 0.39 mmol) in anhydrous DCM (5 mL) was added at 0 °C trichloroacetonitrile (117 µL, 1.17 mmol) followed by DBU (12 µL, 0.08 mmol). The mixture was allowed to warm-up to RT and reaction was followed by TLC (cyclohexane/AcOEt, 7:3). After 2h, no starting material remained. So, solvent was evaporated under *vacuo* and the resulting residue was purified by column chromatography (cyclohexane/AcOEt, 9:1 to 7:3) to give the desired compound **6b** (231 mg, 61%) as an oil. TLC: (cyclohexane/AcOEt, 6:4): R_f=0.38. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.93 (1H, s, NH), 8.14 (2H, dt, *J* 7.0, 1.2, Ph), 7.97 (2H, dt, *J* 8.3, 1.2, Ph), 7.79 (2H, dt, *J* 8.3, 1.3, Ph), 7.67 (1H, tt, *J* 8.3, 1.3, Ph), 7.61-7.52 (3H, m, Ph), 7.49-7.38 (3H, m, Ph), 7.32-7.26 (2H, m, Ph), 6.54 (1H, d, $J_{1a,2a}$ 1.9, H-1a), 5.98 (1H, t, $J_{4a,3a}$ = $J_{4a,5a}$ 10.1, H-4a), 5.90 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.9, H-2a), 5.86 (1H, dd, $J_{3a,4a}$ 10.1, $J_{3a,2a}$ 3.3, H-3a), 5.35 (1H, dd, $J_{4b,3b}$ 3.6, $J_{4b,5b}$ 1.3, H-4b), (1H, dd, $J_{2b,3b}$ 10.5, $J_{2b,1b}$ 8.0, H-2b), 5.23 (1H, dd, $J_{3b,2b}$ 10.5, $J_{3b,4b}$ 3.6, H-3b), 4.51 (1H, d, $J_{1b,2b}$ 8.0, H-1b), 4.48 (1H, ddd, $J_{5a,4a}$ 10.1, $J_{5a,6'a}$ 4.2, $J_{5a,6a}$ 2.1, H-5a), 4.16 (1H, dd, $J_{6a,6'a}$ 11.1, $J_{6a,5a}$ 2.1, H-6a), 4.11-4.05 (2H, m, H-6b), 3.88 (1H, td, $J_{5b,6b}$ 6.7, $J_{5b,4b}$ 1.3, H-5b), 3.73 (1H, dd, $J_{6'a,6a}$ 11.1, $J_{6'a,5a}$ 4.2, H-6'a), 2.13 (3H, s, $COCH_3$), 2.10 (3H, s, $COCH_3$), 1.98 (3H, s, $COCH_3$), 1.97 (3H, s, $COCH_3$). ^{13}C NMR (CD_2Cl_2, 100 MHz): 170.59, 170.57, 170.40, 169.97, 165.69, 165.35 (CO), 160.19 (CN), 134.06, 133.91, 133.69, 130.51, 130.08, 129.93, 129.45, 129.42, 129.38, 129.16, 128.88, 128.74 (Ph), 101.50 (C-1b), 95.12 (C-1a), 90.96 (CCl_3), 72.71 (C-5a), 71.34, 71.22 (C-3b, C-5b), 70.64 (C-3a), 69.09 (C-2a), 68.76 (C-2b), 67.49 (C-4b), 67.38 (C-6a), 66.11 (C-4a), 61.74 (C-6b), 21.00, 20.83, 20.80 ($CO\mathit{C}H_3$). HRMS (ESI): calcd for $C_{41}H_{42}O_{18}Na$ $[M+Na]^+$ 845.2269, found 845.2273.

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-1-thio-α-D-mannopyranoside (8b). Applying procedure C with **6b** (255 mg, 0.21 mmol), **7** (75 mg, 0.21 mmol), activated 4A molecular sieves (100 mg), TMSOTf (0.02 M in CH_2Cl_2, 1 mL, 0.02 mmol) in anhydrous CH_2Cl_2 (10 mL), at -15 °C for 3 h, and purifying by flash chromatography (cyclohexane/AcOEt, gradient from 9:1 to 1:1) afforded **8b** (166 mg, 67%) as a white solid. TLC: (cyclohexane/AcOEt, 3:2): R_f=0.31. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.14 (2H, dt, *J* 7.2, 1.5, Ph), 7.96 (2H, dt, *J* 8.6, 1.5, Ph), 7.79 (2H, dt, *J* 8.4, 1.5, Ph), 7.65 (1H, tt, *J* 7.2, 1.4, Ph), 7.61-7.52 (5H, m, Ph), 7.48-7.32 (6H, m, Ph), 7.31-7.25 (2H, m, Ph), 5.92 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 9.8, H-4b), 5.82 (1H, s, H-1a), 5.76 (1H, dd, $J_{2b,3b}$ 3.2, $J_{2b,1b}$ 1.8, H-2b), 5.72 (1H, dd, $J_{3b,4b}$ 9.8, $J_{3b,2b}$ 3.2, H-3b), 5.64 (1H, d, $J_{1b,2b}$ 1.8, H-1b), 5.34 (1H, dd, $J_{4c,3c}$ 3.5, $J_{4c,5c}$ 1.2, H-4c), 5.60 (1H, dd, $J_{2c,3c}$ 10.2, $J_{2c,1c}$ 8.0, H-2c), 4.98 (1H, dd, $J_{3c,2c}$ 10.2, $J_{3c,4c}$ 3.5, H-3c), 4.48 (1H, d, $J_{1c,2c}$ 8.0, H-1c), 4.48-4.43 (2H, m, H-3a, H-5a), 4.41 (1H, dd, $J_{2a,3a}$ 5.5, $J_{2a,1a}$ 1.0, H-2a), 4.36 (1H, dd, $J_{6a,6'a}$ 12.0, $J_{6a,5a}$ 4.9, H-6a), 4.32 (1H, dd, $J_{6'a,6a}$ 12.0, $J_{6'a,5a}$ 3.0, H-6'a), 4.19 (1H, ddd, $J_{5b,4b}$ 9.8, $J_{5b,6'b}$ 3.8, $J_{5b,6b}$ 1.9, H-5b), 4.11 (1H, dd, $J_{6b,6'b}$ 11.0, $J_{6b,5b}$ 1.9, H-6b), 4.10-4.05 (2H, m, H-6c), 3.99 (1H, dd, $J_{4a,3a}$ 10.3, $J_{4a,5a}$ 7.0, H-4a), 3.87 (1H, td, $J_{5c,6c}$ 6.4, $J_{5c,4c}$ 1.2, H-5c), 3.69 (1H, dd, $J_{6'b,6b}$ 11.0, $J_{6'b,5b}$ 3.8, H-6'b), 2.16 (3H, $COCH_3$), 2.09 (3H, $COCH_3$), 2.01 (3H, $COCH_3$), 1.97 (6H, $COCH_3$), 1.57 (3H, s, CCH_3), 1.37 (3H, s, CCH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 170.89, 170.60, 170.58, 170.39, 170.10, 165.84, 165.76, 165.28 (CO), 133.84, 133.77, 133.57, 133.21, 132.66, 130.47, 130.06, 129.92, 129.73, 129.64, 129.52, 129.11, 128.87, 128.69, 128.32 (Ph), 110.61 ($\mathit{C}(CH_3)_2$), 101.48 (C-1c), 97.18 (C-1b), 84.42 (C-1a), 78.19 (C-3a), 76.69 (C-2a), 74.49 (C-4a), 71.42 (C-3c), 71.20 (C-5c), 70.90 (C-3b), 70.74 (C-5b), 70.61 (C-2b), 68.77 (C-2c), 67.88 (C-5a), 67.52 (C-4c), 67.31 (C-6b), 66.45 (C-4b), 63.49 (C-6a), 61.75 (C-6c), 28.13, 26.45 ($C(\mathit{C}H_3)_2$), 21.03, 20.98, 20.81 ($COCH_3$). HRMS (ESI): calcd for $C_{58}H_{62}O_{23}SNa$ $[M+Na]^+$ 1181.3300, found 1181.3298.

Phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-acetyl-1-thio-α-D-mannopyranoside (9b). To a solution of **8b** (145 mg, 0.125 mmol) in CH_2Cl_2 (5 ml) was added at RT trifluoroacetic acid (50 µL, 0.625 mmol). The reaction mixture was stirred for 18h. Then the reaction was quenched with triethylamine and solvent was evaporated *in vacuo*. The resulting residue was purified by column chromatography (cyclohexane/AcOEt, 9:1 to 3:2) to give the desired compound **9b** (92 mg, 66%) as an oil. TLC: (cyclohexane/AcOEt, 1:1): R_f=0.24. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.11 (2H, dd, *J* 8.4, 1.5, Ph), 7.97 (2H, dd, *J* 8.6, 1.4, Ph), 7.80 (2H, dd, *J* 8.3, 1.3, Ph), 7.64 (1H, tt, *J* 7.6, 1.1, Ph), 7.58-7.52 (5H, m, Ph), 7.49-7.25 (8H, m, Ph), 5.87-5.46 (3H, m, H-2b, H-3b, H-4b), 5.71 (1H, d, $J_{1b,2b}$ 1.7, H-1b), 5.59 (1H, d, $J_{1a,2a}$ 1.5, H-1a), 5.35 (1H, dd, $J_{4c,3c}$ 3.6, $J_{4c,5c}$ 1.2, H-4c), 5.23 (1H, dd, $J_{2c,3c}$ 10.4, $J_{2c,1c}$ 7.9, H-2c), 5.01 (1H, dd, $J_{3c,2c}$ 10.4, $J_{3c,4c}$ 3.6, H-3c), 4.52 (1H, ddd, $J_{5a,4a}$ 9.9, $J_{5a,6'a}$ 5.2, $J_{5a,6a}$ 3.0, H-5a), 4.49 (1H, d, $J_{1c,2c}$ 7.9, H-1c), 4.45 (1H, dd, $J_{6a,6'a}$ 11.8, $J_{6a,5a}$ 5.2, H-6a), 4.41 (1H, dd, $J_{6'a,6a}$ 11.8, $J_{6'a,5a}$ 3.0, H-6'a), 4.33 (1H, ddd, $J_{5b,4b}$ 9.9, $J_{5b,6'b}$ 6.2, $J_{5b,6b}$ 1.8, H-5b), 4.21-4.11 (3H, m, H-2a, H-3a, H-6b), 4.11-4.01 (3H, m, H-4a, H-6c), 3.88 (1H, dd, $J_{5c,6c}$ 6.2, $J_{5c,4c}$ 1.2, H-5c), 3.69 (1H, dd, $J_{6'b,6b}$ 10.1, $J_{6'b,5b}$ 6.2, H-6'b), 3.28 (1H, d, $J_{OH,2a}$ 10.1, OH-2), 3.18 (1H, d, $J_{OH,3a}$ 10.1, OH-3), 2.15 (3H, $COCH_3$), 2.10 (3H, $COCH_3$), 2.07 (3H, $COCH_3$), 1.97 (3H, $COCH_3$), 1.90 (3H, $COCH_3$). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 171.06, 170.58, 170.39, 165.99, 165.87, 165.65 (CO), 133.94, 133.89, 133.81, 133.65, 132.38, 130.35, 130.10, 129.95, 129.71, 129.57, 129.50, 129.49, 129.08, 128.89, 128.72, 128.15 (Ph), 101.56 (C-1c), 98.04 (C-1b), 88.15 (C-1a), 74.43 (C-4a), 73.17 (C-2a), 72.56 (C-3a), 71.19, 71.15 (C-3c, C-5c), 70.88, 70.70 (C-2b, C-3b, C-5b), 69.81 (C-5a), 69.28 (C-2c), 68.45 (C-6b), 67.41 (C-4c), 66.91 (C-4b), 63.61 (C-6a), 61.70 (C-6c), 21.10, 20.79, 20.71 ($COCH_3$). HRMS (ESI): calcd for $C_{55}H_{58}O_{23}SNa$ $[M+Na]^+$ 1141.2987, found 1141.2990.

Phenyl β-D-galactopyranosyl-(1→6)-α-D-mannopyranosyl-(1→4)-1-thio-α-D-mannopyranoside (10b). This synthesis was performed according to general procedure B starting from **9b** (140 mg, 0.125 mmol), MeONa (0.054 M in MeOH, 230 µL, 0.012 mmol), in MeOH (5 mL) to give **10b** (65 mg, 87%) as a white solid. TLC: (AcOEt/AcOH/H_2O, 6:2:2): R_f=0.12. ^{1}H NMR (D_2O, 400 MHz): δ 7.61-7.56 (2H, m, Ph), 7.46-7.38 (3H, m, Ph), 5.52 (1H, d, $J_{1a,2a}$ 1.9, H-1a), 5.23 (1H, d, $J_{1b,2b}$ 2.0, H-1b), 4.44 (1H, d, $J_{1c,2c}$ 7.7, H-1c), 4.25-4.19 (2H, m, H-5a, H-6b), 4.18 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.9, H-2a), 4.09 (1H, dd, $J_{2b,3b}$ 3.1, $J_{2b,1b}$ 2.0, H-2b), 4.00 (1H, dd, $J_{3a,4a}$ 9.2, $J_{3a,2a}$ 3.3, H-3a), 3.92 (1H, d, $J_{4c,3c}$ 3.5, H-4c), 3.91-3.76 (9H, m, H-4a, H-6a, H-3b, H-4b, H-5b, H-6'b, H-6c), 3.70 (1H, dd, $J_{5c,6'c}$ 7.8, $J_{5c,6c}$ 4.2, H-5c), 3.66 (1H, dd, $J_{3c,2c}$ 9.8, $J_{3c,4c}$ 3.5, H-3c), 3.57 (1H, dd, $J_{2c,3c}$ 9.8, $J_{2c,1c}$ 7.7, H-2c). ^{13}C NMR (D_2O, 100 MHz): δ 132.55, 132.30, 129.42, 128.34 (Ph), 103.37 (C-1c), 101.74 (C-1b), 87.87 (C-1a), 75.15 (C-4a), 75.06 (C-5c), 72.67 (C-5b), 72.59 (C-3c), 72.18 (C-5a), 71.75 (C-2a), 71.39 (C-3a), 70.81 (C-2c), 70.24, 70.20 (C-2b, C-3b), 68.65 (C-6b, C-4c), 66.34 (C-4b), 61.02, 60.89 (C-6a, C-6c). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1680.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α,β-D-mannopyranose (12a). This synthesis was performed according to general procedure A2 starting from thioglycoside **11a** (500 mg, 0.54 mmol), *N*-bromosuccinimide (286 mg, 1.07 mmol), in a 9:1 acetone/H_2O mixture (10 mL), at RT for 3 h. Flash-chromatography eluting with CH_2Cl_2/AcOEt (gradient from 8:2 to 7:3) afforded **12a** (336 mg, 75%, ratio α/β : 4:1) as a white solid.

12aα: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (2H, dd, *J* 8.4, 1.3, Ph), 8.06 (2H, dd, *J* 8.5, 1.3, Ph), 7.97 (2H, dd, *J* 8.3, 1.5, Ph), 7.85 (2H, dd, *J* 8.5, 1.3, Ph), 7.59 (1H, tt, *J* 7.3, 1.2, Ph), 7.56-7.48 (3H, m, Ph), 7.47-7.42 (2H, m, Ph), 7.39-7.32 (4H, m, Ph), 7.28-7.23 (2H, m, Ph), 6.17 (1H, td, $J_{5b,6'b}$ 8.0, $J_{5b,4b}$ = $J_{5b,6b}$ 3.3, H-5b), 5.61 (1H, dd, $J_{3b,4b}$ 5.3, $J_{3b,2b}$ 1.1, H-3b), 5.46 (1H, d, $J_{1a,OH}$ 3.8, H-1a), 5.40 (1H, s, H-1b), 5.37 (1H, d, $J_{2b,3b}$ 1.1, H-2b), 4.84 (1H, dd, $J_{4b,3b}$ 5.3, $J_{4b,5b}$ 3.3, H-4b), 4.79 (1H, dd, $J_{6b,6'b}$ 12.1, $J_{6b,5b}$ 3.3, H-6b), 4.74 (1H, dd, $J_{6'b,6b}$ 12.1, $J_{6'b,5b}$ 8.0, H-6'b), 4.59 (1H, dd, $J_{6a,6'a}$ 12.1, $J_{6a,5a}$ 2.2, H-6a), 4.33-4.26 (2H, m, H-3a, H-6'a), 4.18 (1H, d, $J_{2a,3a}$ 5.6, H-2a), 4.10 (1H, ddd, $J_{5a,4a}$ 10.1, $J_{5a,6'a}$ 4.3, $J_{5a,6a}$ 2.2, H-5a), 3.87 (1H, dd, $J_{4a,5a}$ 10.1, $J_{4a,3a}$ 7.1, H-4a), 2.76 (1H, d, $J_{OH,1a}$ 3.8, OH), 2.07 (3H, s, $COCH_3$), 1.65 (3H, s, $C(CH_3)_2$), 1.36 (3H, s, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.83, 166.42, 165.96, 165.89, 165.77 (CO), 133.70, 133.55, 133.38, 133.22, 130.18, 130.08, 129.99, 129.89, 128.65, 128.59, 128.56, 128.51

(Ph), 109.94 (*C*$(CH_3)_2$), 105.58 (C-1b), 92.41 (C-1a), 82.30 (C-2b), 81.59 (C-4b), 77.42 (C-3b), 77.10 (C-3a), 75.96 (C-2a), 74.29 (C-4a), 70.32 (C-5b), 67.34 (C-5a), 64.84 (C-6b), 62.70 (C-6a), 27.99, 26.46 (*C*$(CH_3)_2$), 21.12 (CO*C*H_3).

12aβ: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.08 (2H, m, Ph), 8.05-8.02 (2H, m, Ph), 7.99-7.96 (2H, m, Ph), 7.88-7.85 (2H, m, Ph), 7.59 (1H, tt, *J* 7.3, 1.2, Ph), 7.56-7.48 (3H, m, Ph), 7.47-7.42 (2H, m, Ph), 7.39-7.32 (4H, m, Ph), 7.28-7.23 (2H, m, Ph), 6.13 (1H, td, $J_{5b,6'b}$ 7.7, $J_{5b,4b}$=$J_{5b,4b}$ 3.5, H-5b), 5.61 (1H, dd, $J_{3b,4b}$ 5.3, $J_{3b,2b}$ 1.1, H-3b), 5.39 (1H, s, H-1b), 5.38 (1H, d, $J_{2b,3b}$ 1.2, H-2b), 5.04 (1H, dd, $J_{1a,OH}$ 11.1, $J_{1a,2a}$ 2.3, H-1a), 4.82-4.70 (3H, m, H-4b, H-6b), 4.43 (1H, dd, $J_{6a,6'a}$ 11.8, $J_{6a,5a}$ 3.5, H-6a), 4.36 (1H, t, $J_{3a,4a}$ = $J_{3a,2a}$ 6.3, H-3a), 4.33-4.26 (1H, m, H-6'a), 4.23 (1H, dd, $J_{2a,3a}$ 6.3, $J_{2a,1a}$ 2.3, H-2a), 3.96 (1H, dd, $J_{4a,5a}$ 7.6, $J_{4a,3a}$ 6.3, H-4a), 3.77 (1H, ddd, $J_{5a,4a}$ 7.6, $J_{5a,6'a}$ 5.4, $J_{5a,6a}$ 3.5, H-5a), 3.63 (1H, d, $J_{OH,1a}$ 11.1, OH), 2.07 (3H, s, COCH_3), 1.65 (3H, s, C$(CH_3)_2$), 1.36 (3H, s, C$(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.83, 166.42, 165.96, 165.89, 165.77 (CO), 133.70, 133.55, 133.38, 133.22, 130.18, 130.08, 129.99, 129.89, 128.65, 128.59, 128.56, 128.51 (Ph), 109.94 (*C*$(CH_3)_2$), 105.58 (C-1b), 92.41 (C-1a), 82.30 (C-2b), 81.59 (C-4b), 78.01 (C-3a), 77.42 (C-3b), 74.57 (C-2a), 73.36 (C-5a), 73.27 (C-4a), 70.32 (C-5b), 64.84 (C-6b), 62.70 (C-6a), 27.99, 26.46 (*C*$(CH_3)_2$), 21.12 (CO*C*H_3).
HRMS (ESI): calcd for $C_{45}H_{44}O_{16}Na$ $[M+Na]^+$ 863.2527, found 863.2524.

2,3,5,6-Tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α-D-mannopyranosyl trichloroacetimidate (13a). Donor **13a** was obtained according to general procedure D starting from **12a** (968 mg, 1.15 mmol), Cs_2CO_3 (112 mg, 0.346 mmol), trichloroacetonitrile (578 µL, 5.77 mmol) in CH_2Cl_2 (25 mL) for 24 h at RT. After work-up, a flash-chromatography eluting with cyclohexane/AcOEt (gradient from 7:3 to 6:4) afforded the desired product (980 mg, 86%) as a white solid. δ ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73 (1H, s, NH), 8.11 (2H, dd, *J* 8.6, 1.3, Ph), 8.06 (2H, d, *J* 8.4, 1.1, Ph), 7.98 (2H, d, *J* 8.4, 1.3, Ph), 7.85 (2H, d, *J* 8.6, 1.3, Ph), 7.62-7.41 (4H, m, Ph), 7.48-7.41 (2H, m, Ph), 7.40-7.31 (4H, m, Ph), 7.30-7.23 (2H, m, Ph), 6.53 (1H, s, H-1a), 6.17 (1H, td, $J_{5b,6'b}$ 7.9, $J_{5b,6b}$ = $J_{5b,4b}$ 3.5, H-5b), 5.64 (1H, d, $J_{3b,4b}$ 5.4, H-3b), 5.40 (1H, s, H-1b), 5.37 (1H, d, $J_{2b,3b}$ 1.0, H-2b), 4.84 (1H, dd, $J_{4b,3b}$ 5.4, $J_{4b,5b}$ 3.4, H-4b), 4.80 (1H, dd, $J_{6b,6'b}$ 12.2, $J_{6b,5b}$ 3.5, H-6b), 4.74 (1H, dd, $J_{6'b,6b}$ 12.2, $J_{6'b,5b}$ 7.9, H-6'b), 4.56 (1H, dd, $J_{6a,6'a}$ 12.3, $J_{6a,5a}$ 2.0, H-6a), 4.41-4.30 (3H, m, H-2a, H-3a, H-6'a), 4.06 (1H, ddd, $J_{5a,4a}$ 10.5, $J_{5a,6'a}$ 4.5, $J_{5a,6a}$ 2.0, H-5a), 3.94 (1H, dd, $J_{4a,5a}$ 10.5, $J_{4a,3a}$ 7.0, H-4a), 2.03 (s, 3H, COCH_3), 1.67 (s, 3H, C$(CH_3)_2$), 1.39 (s, 3H, C$(CH_3)_2$), ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 170.69, 166.48, 166.16, 166.11, 166.01 (CO), 160.42 (CN), 133.98, 133.87, 133.72, 133.50, 130.25, 130.21, 130.15, 130.09, 129.98, 129.57, 129.28, 128.93, 128.89, 128.88, 128.81 (Ph), 110.63 (*C*$(CH_3)_2$), 106.01 (C-1b), 95.37 (C-1a), 91.33 (CCl_3), 82.62 (C-2b), 81.95 (C-4b), 77.72 (C-3b), 77.59 (C-3a), 75.11 (C-2a), 74.17 (C-4a), 70.63 (C-5b), 70.16 (C-5a), 64.88 (C-6b), 62.43 (C-6a), 28.00, 26.47 (C(*C*$H_3)_2$), 20.99 (CO*C*H_3).
HRMS (ESI): calcd for $C_{47}H_{44}Cl_3NO_{16}Na$ $[M+Na]^+$ 1006.1623, found 1006.1626.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (15a). Applying procedure C with **13a** (55 mg, 0.06 mmol), **14** (28 mg, 0.05 mmol), activated 4A molecular sieves (100 mg), TMSOTf (0.02 M in CH_2Cl_2, 0.250 mL, 0.005 mmol) in anhydrous CH_2Cl_2 (5 mL), at 0 °C for 3 h, and purifying by flash chromatography (cyclohexane/AcOEt, gradient from 9:1 to 8:2) afforded 22 (59 mg, 88%) as a white product. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.03 (6H, m, Ph), 8.00-7.94 (4H, m, Ph), 7.82 (4H, t, *J* 8.8, Ph), 7.64-7.56 (4H, m, Ph), 7.56-7.41 (9H, m, Ph), 7.41-7.30 (8H, m, Ph), 7.29-7.21 (5H, m, Ph), 6.16 (1H, td, $J_{5c,6'c}$ 8.1, $J_{5c,4c}$ = $J_{5c,6c}$ 3.00, H-5c), 5.94 (1H, dd, $J_{2a,3a}$ 2.5, $J_{2a,1a}$ 2.0, H-2a), 5.86-5.80 (2H, m, H-3a, H-4a), 5.80 (1H, d, $J_{1a,2a}$ 2.0, H-1a), 5.57 (1H, d, $J_{3c,4c}$ 5.3, H-3c), 5.34-5.32 (2H, m, H-1c, H-2c), 4.97 (1H, tt, $J_{5a,4a}$ = $J_{5a,6'a}$ 7.8, $J_{5a,6a}$ 1.8, H-5a), 4.81-4.77 (3H, m, H-1b, H-4c, H-6c), 4.71 (1H, dd, $J_{6'c,6c}$ 12.2, $J_{6'c,5c}$ 8.1, H-6'c), 4.46 (1H, dd, $J_{6b,6'b}$ 12.0, $J_{6b,5b}$ 2.5, H-6b), 4.22 (1H, dd, $J_{6'b,6b}$ 12.0, $J_{6'b,5b}$ 5.1, H-6'b), 4.15 (1H, dd, $J_{6a,6'a}$ 12.3, $J_{6a,5a}$ 1.8, H-6a), 4.10 (1H, dd, $J_{3b,4b}$ 6.3, $J_{3b,2b}$ 5.6, H-3b), 4.04 (1H, dd, $J_{2b,3b}$ 5.6, $J_{2b,1b}$ 1.8, H-2b), 3.97-3.91 (2H, m, H-6'a, H-4b), 3.47 (1H, ddd, $J_{5b,4b}$ 9.8, $J_{5b,6'b}$ 5.1, $J_{5b,6b}$ 2.5, H-5b), 1.94 (s, 3H, COCH_3), 1.64 (s, 3H, C$(CH_3)_2$), 1.37 (s, 3H, C$(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.61, 166.31, 165.88, 165.82, 165.77, 165.76, 165.63, 165.48 (CO), 133.73, 133.68, 133.50, 133.39, 133.35, 133.19, 132.85, 132.47, 130.10, 130.01, 129.92, 129.90, 129.83,

129.68, 129.66, 129.29, 129.26, 129.13, 128.98, 128.83, 128.79, 128.73, 128.62, 128.59, 128.53, 128.49, 128.46, 128.44, 128.10 (Ph), 111.09 ($C(CH_3)_2$), 105.57 (C-1c), 99.22 (C-1b), 85.42 (C-1a), 82.26 (C-2c), 81.61 (C-4c), 78.85 (C-3b), 77.38 (C-3c), 74.69 (C-4b), 74.22 (C-2b), 72.31 (C-5b), 72.13 (C-5a), 71.97 (C-2a), 70.46 (C-3a), 70.26 (C-5c), 68.37 (C-6a), 67.31 (C-4a), 64.68 (C-6c), 63.03 (C-6b), 27.84 ($C(CH_3)_2$), 26.52 ($C(CH_3)_2$), 20.87 ($COCH_3$). HRMS (ESI): calcd for $C_{78}H_{70}O_{23}SNa$ $[M+Na]^+$ 1429.3926, found 1429.3920.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzoyl-1-thio-α-D-mannopyranoside (16a). A solution of **15a** (50 mg, 0.04 mmol) in acetic acid/H_2O 70:30 mixture (9 mL) was stirred at 80 °C for 15 h. Then toluene was added to the solution and co-evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/AcOEt gradient from 8:2 up to 7:3) to give **16a** (27 mg, 56%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12-8.06 (4H, m, Ph), 8.03-7.97 (6H, m, Ph), 7.88-7.81 (4H, m, Ph), 7.64-7.58 (3H, m, Ph), 7.58-7.46 (7H, m, Ph), 7.46-7.26 (16H, m, Ph), 6.03 (1H, ddd, $J_{5c,6'c}$ 6.4, $J_{5c,6c}$ 4.6, $J_{5c,4c}$ 3.8, H-5c), 5.94 (1H, dd, $J_{2a,3a}$ 3.0, $J_{2a,1a}$ 1.7, H-2a), 5.91 (1H, t, $J_{4a,3a}$ = $J_{4a,5a}$ 9.6, H-4a), 5.86 (1H, dd, $J_{3a,4a}$ 9.6, $J_{3a,2a}$ 3.0, H-3a), 5.76 (1H, d, $J_{1a,2a}$ 1.7, H-1a), 5.64 (1H, dd, $J_{3c,4c}$ 5.3, $J_{3c,2c}$ 1.7, H-3c), 5.37 (1H, d, $J_{2c,3c}$ 1.7, H-2c), 5.34 (1H, s, H-1c), 4.95 (1H, dd, $J_{4c,3c}$ 5.3, $J_{4c,5c}$ 3.8, H-4c), 4.97 (1H, ddd, $J_{5a,4a}$ 9.6, $J_{5a,6'a}$ 6.8, $J_{5a,6a}$ 2.0, H-5a), 4.79 (1H, dd, $J_{6c,6'c}$ 12.0, $J_{6c,5c}$ 4.6, H-6c), 4.75 (1H, dd, $J_{6'c,6c}$ 12.0, $J_{6'c,5c}$ 6.4, H-6'c), 4.50 (1H, d, $J_{1b,2b}$ 0.9, H-1b), 4.40 (1H, dd, $J_{6b,6'b}$ 12.0, $J_{6b,5b}$ 2.3, H-6b), 4.31 (1H, dd, $J_{6'b,6b}$ 12.0, $J_{6'b,5b}$ 4.9, H-6'b), 4.15 (1H, dd, $J_{6a,6'a}$ 11.5, $J_{6a,5a}$ 2.0, H-6a), 4.01 (1H, t, $J_{2b,3b}$ = $J_{2b,OH}$ 3.0, H-2b), 3.89 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 9.0, H-4b), 3.83 (1H, dd, $J_{6'a,6a}$ 11.5, $J_{6'a,5a}$ 6.8, H-6'a), 3.59 (1H, ddd, $J_{3b,4b}$ 9.0, $J_{3b,OH}$ 6.7, $J_{3b,2b}$ 3.0, H-3b), 3.50-3.45 (1H, m, H-5b), 3.47 (1H, d, $J_{OH,3b}$ 6.7, OH-3b), 2.36 (1H, d, $J_{OH,2b}$ 3.0, OH-2b),1.89 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.70, 166.33, 165.94, 165.83, 165.76, 165.52, 165.46 (CO), 133.86, 133.81, 133.73, 133.63, 133.48, 133.45, 133.29, 132.70, 132.62, 132.49, 130.14, 130.06, 130.01, 129.99, 129.93, 129.87, 129.67, 129.53, 129.40, 129.37, 129.34, 129.00, 128.81, 128.71, 128.61, 128.58, 128.52, 128.49 (Ph), 107.04 (C-1c), 100.73 (C-1b), 85.70 (C-1a), 82.51 (C-2c), 81.77 (C-4c), 77.63 (C-3c), 76.32 (C-4b), 72.78 (C-5b), 72.57 (C-3b), 71.89 (C-2a), 71.21 (C-5a), 70.53 (C-2b), 70.39 (C-3a, C-5c), 68.69 (C-6a), 67.36 (C-4a), 63.51 (C-6c), 62.88 (C-6b), 20.88 ($COCH_3$). HRMS (ESI): calcd for $C_{75}H_{66}O_{23}SNa$ $[M+Na]^+$ 1389.3613, found 1389.3610.

Phenyl β-D-galactofuranosyl-(1→4)-α-D-mannopyranosyl-(1→6)-1-thio-α-D-mannopyranoside (17a). This synthesis was performed according to general procedure B starting from **16a** (100 mg, 0.07 mmol), MeONa (0.54 M in MeOH, 3 µL, 0.014 mmol), in MeOH (5 mL). After stirring for 18 h, purification gave **17a** (42 mg, 97%) as a white solid. ^{1}H NMR (D_2O, 500 MHz): δ 7.63-7.58 (2H, m, Ph), 7.47-7.40 (3H, m, Ph), 5.57 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 5.06 (1H, d, $J_{1c,2c}$ 1.7, H-1c), 4.56 (1H, s, H-1b), 4.33 (1H, ddd, $J_{5a,4a}$ 10.1, $J_{5a,6'a}$ 6.2, $J_{5a,6a}$ 1.8, H-5a), 4.24 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.6, H-2a), 4.14-4.08 (4H, m, H-6a, H-2c, H-3c, H-4c), 3.93-3.85 (3H, m, H-3a, H-6'a, H-6b), 3.85-3.80 (m, 1H, H-5c), 3.82 (1H, d, $J_{2b,3b}$ 3.3, H-2b), 3.78-3.63 (5H, m, H-4a, H-4b, H-6'b, H-6c), 3.58 (1H, dd, $J_{3b,4b}$ 9.5, $J_{3b,2b}$ 3.3, H-3b), 3.37 (1H, ddd, $J_{5b,4b}$ 9.8, $J_{5a,6'a}$ 5.5, $J_{5a,6a}$ 2.1, H-5b). ^{13}C NMR (D_2O, 126 MHz): δ 132.41, 132.12, 129.49, 128.40 (Ph), 107.89 (C-1c), 100.04 (C-1b), 87.74 (C-1a), 82.58 (C-2c), 80.93 (C-4c), 75.90 (C-3c), 75.14, 74.97 (C-4b, C-5b), 73.00 (C-5a), 71.44 (C-3b), 71.20 (C-2a), 70.96 (C-3a), 70.47 (C-5c), 70.17 (C-2b), 67.84 (C-6a), 66.96 (C-4a), 62.66 (C-6c), 60.38 (C-6b). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1669.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-1-thio-α-D-mannopyranoside (11b). Applying procedure C with 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl trichloroacetimidate (1.38 g, 1.86 mmol), **7** (550 mg, 1.55 mmol), activated 4A molecular sieves (300 mg), TMSOTf (28 µL, 0.155 mmol) in anhydrous CH_2Cl_2 (80 mL), at 0 °C for 3 h, and purifying by flash chromatography (cyclohexane/AcOEt, gradient from 9:1 to 4:1) afforded **11b** (1.3 g, 91%) as a white product. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (2H, dd, *J* 8.6, 1.4, Ph), 8.05 (2H, dd, *J* 8.5, 1.5, Ph), 7.94 (2H, dd, *J* 8.7, 1.3, Ph), 7.76 (2H, dd, *J* 8.4, 1.5, Ph), 7.63 (1H, tt, *J* 7.4, 1.3, Ph), 7.56 (1H, tt, *J* 7.6, 1.1, Ph), 7.52-7.47 (3H, m, Ph), 7.46-7.40 (5H, m, Ph), 7.39-7.34 (2H, m, Ph), 7.26-7.22

(5H, m, Ph), 5.99 (1H, dd, $J_{4b,3b}$ 3.5, $J_{4b,5b}$ 1.2, H-4b), 5.78 (1H, dd, $J_{2b,3b}$ 10.3, $J_{2b,1b}$ 8.1, H-2b), 5.71 (1H, s, H-1a), 5.66 (1H, dd, $J_{3b,2b}$ 10.3, $J_{3b,4b}$ 3.5, H-3b), 5.09 (1H, d, $J_{1b,2b}$ 8.1, H-1b), 4.68 (1H, dd, $J_{6b,6'b}$ 11.1, $J_{6b,5b}$ 7.0, H-6b), 4.56 (1H, dd, $J_{3a,4a}$ 6.9, $J_{3a,2a}$ 5.7, H-3a), 4.48 (1H, dd, $J_{6'b,6b}$ 11.1, $J_{6'b,5b}$ 6.2, H-6'b), 4.38-4.34 (1H, m, H-5b), 4.32 (1H, ddd, $J_{5a,4a}$ 10.0, $J_{5a,6'a}$ 5.3, $J_{5a,6a}$ 2.3, H-5a), 4.20-4.15 (2H, m, H-2a, H6a), 3.95 (1H, dd, $J_{6'a,6a}$ 12.0, $J_{6'a,5a}$ 5.3, H-6'a), 3.82 (1H, dd, $J_{4a,5a}$ 10.0, $J_{4a,3a}$ 6.9, H-4a), 1.56 (s, 3H, $COCH_3$), 1.53 (s, 3H, $C(CH_3)_2$), 1.15 (s, 3H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.15, 166.01, 165.65, 165.54, 165.12 (CO), 133.63, 133.33, 133.31, 133.29, 132.87, 131.70, 130.08, 129.78, 129.76, 129.75, 129.62, 129.04, 128.95, 128.68, 128.63, 128.47, 128.46, 128.28, 127.68 (Ph), 109.56 ($C(CH_3)_2$), 101.15 (C-1b), 83.90 (C-1a), 78.44 (C-4a), 76.60 (C-3a), 75.95 (C-2a), 71.70 (C-5b), 71.59 (C-3b), 69.99 (C-2b), 68.25 (C-4b), 67.21 (C-5a), 62.51 (C-6a), 62.06 (C-6b), 28.18, 26.12 ($C(CH_3)_2$, 20.19 ($COCH_3$). HRMS (ESI): calcd for $C_{51}H_{48}O_{15}SNa$ $[M+Na]^+$ 955.2612, found 955.2621.

2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α,β-D-mannopyranose (12b). This synthesis was performed according to general procedure A2 starting from thioglycoside **11b** (1.5 g, 1.61 mmol), *N*-bromosuccinimide (1.14 g, 6.43 mmol), in a 9:1 acetone/H_2O mixture (20 mL), at RT for 6 h. Flash-chromatography eluting with cyclohexane/AcOEt (gradient from 8:2 to 7:3) afforded **12b** (940 mg, 70%, ratio α/β : 4:1) as a white solid.

12bα: ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (2H, dd, *J* 8.3, 1.7, Ph), 8.04 (2H, dd, *J* 8.4, 1.7, Ph), 7.95 (2H, dd, *J* 8.3, 1.5, Ph), 7.79-7.74 (2H, m, Ph), 7.65-7.59 (1H, m, Ph), 7.58-7.46 (4H, m, Ph), 7.45-7.34 (5H, m, Ph), 7.26-7.20 (2H, m, Ph), 5.99 (1H, dd, $J_{4b,3b}$ 3.6, $J_{4b,5b}$ 1.0, H-4b), 5.77 (1H, dd, $J_{2b,3b}$ 10.4, $J_{2b,1b}$ 8.0, H-2b), 5.67 (1H, dd, $J_{3b,2b}$ 10.4, $J_{3b,4b}$ 3.6, H-3b), 5.33 (1H, d, $J_{1a,OH}$ 4.1, H-1a), 5.08 (1H, d, $J_{1b,2b}$ 8.0, H-1b), 4.65 (1H, dd, $J_{6b,6'b}$ 11.3, $J_{6b,5b}$ 7.0, H-6b), 4.57 (1H, dd, $J_{3a,4a}$ 6.9, $J_{3a,2a}$ 5.8, H-3a), 4.47 (1H, dd, $J_{6'b,6b}$ 11.3, $J_{6'b,5b}$ 6.1, H-6'b), 4.39- 4.34 (2H, m, H-5b, H-6a), 4.06 (1H, d, $J_{2a,3a}$ 5.8, H-2a), 4.05-4.00 (1H, m, H-5a), 3.95 (1H, dd, $J_{6'a,6a}$ 11.8, $J_{6'a,5a}$ 4.6, H-6'a), 3.79 (1H, dd, $J_{4a,5a}$ 9.7, $J_{4a,3a}$ 6.9, H-4a), 3.08 (1H, d, $J_{OH,1a}$ 4.1, OH), 1.63 (s, 3H, $COCH_3$), 1.52 (s, 3H, $C(CH_3)_2$), 1.16 (s, 3H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.65, 166.19, 165.79, 165.69, 165.31 (CO), 133.76, 133.50, 133.47, 133.45, 133.40, 130.20, 129.90, 129.88, 129.87, 129.70, 129.23, 129.08, 128.81, 128.75, 128.62, 128.60, 128.56, 128.42 (Ph), 109.48 ($C(CH_3)_2$), 101.31 (C-1b), 92.22 (C-1a), 77.90 (C-4a), 76.58 (C-3a), 75.66 (C-2a), 71.82 (C-5b), 71.69 (C-3b), 70.16 (C-2b), 68.40 (C-4b), 66.38 (C-5a), 62.60 (C-6a), 62.27 (C-6b), 28.21, 26.09 ($C(CH_3)_2$), 20.40 ($COCH_3$).

12bβ: ^1H NMR ($CDCl_3$, 400 MHz): δ 8.12-8.07 (2H, m, Ph), 8.04-8.00 (2H, m, Ph), 7.97-7.93 (2H, m, Ph), 7.79-7.74 (2H, m, Ph), 7.65-7.59 (1H, m, Ph), 7.58-7.46 (4H, m, Ph), 7.45-7.34 (5H, m, Ph), 7.26-7.20 (2H, m, Ph), 5.99 (1H, dd, $J_{4b,3b}$ 3.6, $J_{4b,5b}$ 1.0, H-4b), 5.74 (1H, dd, $J_{2b,1b}$ 7.9, $J_{2b,3b}$ 7.0, H-2b), 5.64 (1H, dd, $J_{3b,2b}$ 7.0, $J_{3b,4b}$ 3.6, H-3b), 4.98 (1H, d, $J_{1b,2b}$ 7.9, H-1b), 4.80 (1H, dd, $J_{1a,OH}$ 10.9, $J_{1a,2a}$ 2.1, H-1a), 4.69-4.62 (2H, m, H-3a, H-6b), 4.47-4.41 (1H, m, H-6'b), 4.39-4.34 (1H, m, H-5b), 4.20 (1H, dd, $J_{2a,3a}$ 6.8, $J_{2a,1a}$ 2.1, H-2a), 4.23-4.19 (1H, m, H-6a), 4.05-4.00 (1H, m, H-6'a), 3.79 (1H, dd, $J_{4a,5a}$ 9.7, $J_{4a,3a}$ 6.9, H-4a), 3.77-3.72 (1H, m, H-5a), 3.64 (1H, d, $J_{OH,1a}$ 10.9, OH), 1.80 (s, 3H, $COCH_3$), 1.50 (s, 3H, $C(CH_3)_2$), 1.25 (s, 3H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.65, 166.19, 165.79, 165.69, 165.31 (CO), 133.76, 133.50, 133.47, 133.45, 133.40, 130.20, 129.90, 129.88, 129.87, 129.70, 129.23, 129.08, 128.81, 128.75, 128.62, 128.60, 128.56, 128.42 (Ph), 110.73 ($C(CH_3)_2$), 101.31 (C-1b), 91.94 (C-1a), 77.90 (C-4a), 76.58 (C-3a), 73.96 (C-2a), 73.92 (C-5a), 71.87 (C-5b), 71.56 (C-3b), 69.89 (C-2b), 68.27 (C-4b), 63.95 (C-6a), 62.20 (C-6b), 27.14, 25.76 ($C(CH_3)_2$), 20.62 ($COCH_3$).
HRMS (ESI): calcd for $C_{45}H_{44}O_{16}Na$ $[M+Na]^+$ 863.2527, found 863.2524.

2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α-D-mannopyranosyl trichloroacetimidate (13b). Donor **13b** was obtained according to general procedure D starting from **12b** (890 mg, 1.05 mmol), Cs_2CO_3 (345 mg, 1.05 mmol), trichloroacetonitrile (317 µL, 3.17 mmol) in CH_2Cl_2 (20 mL) for 24 h at RT. After work-up, a flash-chromatography eluting with cyclohexane/AcOEt (gradient from 7:3 to 6:4) afforded the desired product (773 mg, 74%) as an oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.69 (1H, s, NH), 8.10 (2H, dd, *J* 8.3, 1.4, Ph), 8.04 (2H, dd, *J* 8.3, 1.5, Ph), 7.94 (2H, dd, *J* 8.3, 1.2, Ph), 7.76 (2H, dd, *J* 8.5, 1.3, Ph), 7.62 (1H, tt, *J* 7.5, 1.2, Ph), 7.54 (1H, tt, *J* 7.3, 1.3, Ph), 7.53-7.46 (3H, m, Ph), 7.45-7.34 (5H, m, Ph), 7.25-7.19 (2H, m, Ph), 6.43 (1H, s, H-1a),

6.00 (1H, dd, $J_{4b,3b}$ 3.4, $J_{4b,5b}$ 1.2, H-4b), 5.78 (1H, dd, $J_{2b,3b}$ 10.3, $J_{2b,1b}$ 8.1, H-2b), 5.68 (1H, dd, $J_{3b,2b}$ 10.3, $J_{3b,4b}$ 3.4, H-3b), 5.10 (1H, d, $J_{1b,2b}$ 8.1, H-1b), 4.69 (1H, dd, $J_{6b,6'b}$ 11.3, $J_{6b,5b}$ 6.5, H-6b), 4.64 (1H, dd, $J_{3a,4a}$ 7.0, $J_{3a,2a}$ 6.1, H-3a), 4.47 (1H, dd, $J_{6'b,6b}$ 11.3, $J_{6'b,5b}$ 6.5, H-6'b), 4.38 (1H, td, $J_{5b,6b}$ 6.5, $J_{5b,4b}$ 1.2, H-5b), 4.34 (1H, dd, $J_{6a,6'a}$ 11.9, $J_{6a,5a}$ 2.3, H-6a), 4.16 (1H, d, $J_{2a,3a}$ 6.1, H-2a), 4.00 (1H, ddd, $J_{5a,4a}$ 10.2, $J_{5a,6'a}$ 4.7, $J_{5a,6a}$ 2.3, H-5a), 3.93 (1H, dd, $J_{6'a,6a}$ 11.9, $J_{6'a,5a}$ 4.7, H-6'a), 3.85 (1H, dd, $J_{4a,5a}$ 10.2, $J_{4a,3a}$ 7.0, H-4a), 1.58 (s, 3H, $COCH_3$), 1.56 (s, 3H, $C(CH_3)_2$), 1.18 (s, 3H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.25, 166.11, 165.77, 165.66, 165.27 (CO), 160.22 (CN), 133.78, 133.52, 133.47, 133.41, 130.19, 129.89, 129.86, 129.73, 129.12, 129.06, 128.77, 128.75, 128.64, 128.54, 128.42 (Ph), 109.98 ($C(CH_3)_2$), 101.51 (C-1b), 95.19 (C-1a), 90.97 (CCl_3), 77.72 (C-4a), 76.96 (C-3a), 74.43 (C-2a), 71.87 (C-5b), 71.65 (C-3b), 70.09 (C-2b), 68.71 (C-5a), 68.37 (C-4b), 62.09, 62.05 (C-6a, C-6b), 28.24, 26.13 ($C(CH_3)_2$), 20.26 ($COCH_3$). HRMS (ESI): calcd for $C_{47}H_{44}Cl_3NO_{16}Na$ $[M+Na]^+$ 1006.1623, found 1006.16222.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-isopropylidene-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (15b). Applying procedure C with **13b** (730 mg, 0.74 mmol), **14** (392 mg, 0.67 mmol), activated 4A molecular sieves (100 mg), TMSOTf (0.2 M in CH_2Cl_2, 1.0 mL, 0.20 mmol) in anhydrous CH_2Cl_2 (10 mL), at 0 °C for 3 h, and purifying by flash chromatography (cyclohexane/AcOEt, gradient from 9:1 to 8:2) afforded **15b** (834 mg, 80%) as a white product. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (2H, dd, *J* 8.4, 1.5, Ph), 8.07 (2H, dd, *J* 8.8, 1.3, Ph), 8.05 (2H, dd, *J* 8.4, 1.7, Ph), 7.93 (2H, dd, *J* 8.4, 1.4, Ph), 7.90 (2H, dd, *J* 8.4, 1.4, Ph), 7.82 (2H, dd, *J* 8.3, 1.4, Ph), 7.74 (2H, dd, *J* 8.3, 1.4, Ph), 7.64-7.27 (26H, m, Ph), 5.94 (1H, dd, $J_{4c,3c}$ 3.6, $J_{4c,5c}$ 1.2, H-4c), 5.92 (1H, dd, $J_{2a,3a}$ 3.2, $J_{2a,1a}$ 1.6, H-2a), 5.82 (1H, t, $J_{4a,3a} = J_{4a,5a}$ 9.9, H-4a), 5.78 (1H, dd, $J_{3a,4a}$ 9.9, $J_{3a,2a}$ 3.2, H-3a), 5.70 (1H, dd, $J_{2c,3c}$ 10.4, $J_{2c,1c}$ 8.0, H-2c), 5.63 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 5.43 (1H, dd, $J_{3c,2c}$ 10.4, $J_{3c,4c}$ 3.6, H-3c), 4.89 (1H, d, $J_{1c,2c}$ 8.0, H-1c), 4.90-4.84 (1H, m, H-5a), 4.73 (1H, d, $J_{1b,2b}$ 2.3, H-1b), 4.70 (1H, dd, $J_{6c,6'c}$ 11.1, $J_{6c,5c}$ 6.2, H-6c), 4.49 (1H, t, $J_{3b,4b} = J_{3b,2b}$ 6.4, H-3b), 4.37 (1H, dd, $J_{6'c,6c}$ 11.1, $J_{6'c,5c}$ 7.2, H-6'c), 4.26-4.22 (1H, m, H-5c), 4.23 (1H, dd, $J_{6b,6'b}$ 11.8, $J_{6b,5b}$ 2.7, H-6b), 4.04 (1H, dd, $J_{2b,3b}$ 6.4, $J_{2b,1b}$ 2.3, H-2b), 4.02 (1H, dd, $J_{6a,6'a}$ 11.8, $J_{6a,5a}$ 1.9, H-6a), 3.99 (1H, dd, $J_{4b,5b}$ 9.4, $J_{4b,3b}$ 6.4, H-4b), 3.83 (1H, dd, $J_{6'b,6b}$ 11.8, $J_{6'b,5b}$ 5.3, H-6'b), 3.81 (1H, dd, $J_{6'a,6a}$ 11.8, $J_{6'a,5a}$ 7.0, H-6'a), 3.53 (1H, ddd, $J_{5b,4b}$ 9.4, $J_{5b,6'b}$ 5.3, $J_{5b,6b}$ 2.7, H-5b), 1.63 (s, 3H, $COCH_3$), 1.61 (s, 3H, $C(CH_3)_2$), 1.30 (s, 3H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.30, 166.18, 165.70, 165.63, 165.60, 165.55, 165.52, 165.16 (CO), 133.74, 133.68, 133.56, 133.50, 133.41, 133.03, 132.12, 130.16, 129.92, 129.85, 129.58, 129.43, 129.38, 129.13, 129.01, 129.00, 128.94, 128.90, 128.83, 128.74, 128.66, 128.64, 128.62, 128.58, 128.47, 128.41, 128.01 (Ph), 110.87 ($C(CH_3)_2$), 101.36 (C-1c), 98.43 (C-1b), 85.48 (C-1a), 78.05, 77.97 (C-3b, C-4b), 73.69 (C-2b), 72.08 (C-2a), 71.86 , 71.56 (C-5a, C-5b), 71.56, 71.52 (C-3c, C-5c), 70.63 (C-3a), 69.90 (C-2c), 68.12 (C-4c), 67.61(C-6a), 67.24 (C-4a), 63.39 (C-6b), 61.92 (C-6c), 27.55, 26.00 ($C(CH_3)_2$), 20.42 ($COCH_3$). HRMS (ESI): calcd for $C_{78}H_{70}O_{23}SNa$ $[M+Na]^+$ 1429.3926, found 1429.3924.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (16b). A solution of **15b** (830 mg, 0.59 mmol) in acetic acid/H_2O 70:30 mixture (15 mL) was stirred at 80 °C for 15 h. Then toluene was added to the solution and co-evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/AcOEt gradient from 7:3 up to 1:1) to give **16b** (650 mg, 81%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12-8.04 (6H, m, Ph), 7.95 (2H, dd, *J* 8.5, 1.5, Ph), 7.92 (2H, dd, *J* 8.6, 1.3, Ph), 7.82 (2H, dd, *J* 8.5, 1.3, Ph), 7.75 (2H, dd, *J* 8.5, 1.3, Ph), 7.68-7.20 (26H, m, Ph), 5.99 (1H, dd, $J_{4c,3c}$ 3.5, $J_{4c,5c}$ 1.1, H-4c), 5.92 (1H, dd, $J_{2a,3a}$ 2.8, $J_{2a,1a}$ 1.6, H-2a), 5.87-5.80 (3H, m, H-3a, H4a, H-2c), 5.71 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 5.59 (1H, dd, $J_{3c,2c}$ 10.6, $J_{3c,4c}$ 3.5, H-3c), 4.91-4.85 (1H, m, H-5a), 4.88 (1H, d, $J_{1c,2c}$ 8.1, H-1c), 4.60-4.57 (2H, m, H-6c), 4.46-4.42 (2H, m, H-1b, H-5c), 4.23 (1H, d, $J_{OH,3b}$ 1.8, OH-3b), 4.10-4.05 (3H, m, H-6a, H-6b), 4.01 (1H, dd, $J_{2b,3b}$ 3.3, $J_{2b,OH}$ 1.6, H-2b), 3.82 (1H, t, $J_{4b,5b} = J_{4b,3b}$ 9.2, H-4b), 3.77 (1H, dd, $J_{6'a,6a}$ 11.6, $J_{6'a,5a}$ 7.1, H-6'a), 6.68 (1H, ddd, $J_{3b,4b}$ 9.2, $J_{3b,2b}$ 3.3, $J_{3b,OH}$ 1.8, H-3b), 3.37 (1H, ddd, $J_{5b,4b}$ 9.2, $J_{5b,6'b}$ 5.2, $J_{5b,6b}$ 2.0, H-5b), 4.23 (1H, d, $J_{OH,2b}$ 1.6, OH-2b), 1.74 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.27, 166.16, 165.87, 165.56, 165.53,

165.51, 165.45, 165.23 (CO), 133.93, 133.79, 133.75, 133.63, 133.56, 133.43, 132.88, 132.59, 130.16, 130.09, 130.03, 129.96, 129.92, 129.90, 129.86, 129.35, 129.26, 129.01, 128.89, 128.85, 128.82, 128.77, 128.69, 128.66, 128.62, 128.58, 128.48 (Ph), 102.17 (C-1c), 100.66 (C-1b), 85.72 (C-1a), 79.51 (C-4b), 72.35 (C-5c), 72.21, 72.12 (C-3b, C-5b), 71.88 (C-2a), 71.55 (C-3c), 71.37 (C-5a), 70.40 (C-3a), 69.98 (C-2b), 69.59 (C-2c), 68.72 (C-6a), 68.05 (C-4c), 67.35 (C-4a), 62.50, 62.33 (C-6b, C-6c), 20.63 ($COCH_3$). HRMS (ESI): calcd for $C_{75}H_{66}O_{23}SNa$ $[M+Na]^+$ 1389.3613, found 1389.3612.

Phenyl β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl-(1→6)-1-thio-α-D-mannopyranoside (17b). This synthesis was performed according to general procedure B starting from **16b** (40 mg, 0.03 mmol), MeONa (0.05 M in MeOH, 200 µL, 0.01 mmol), in MeOH (5 mL). After stirring for 18 h, purification gave **17b** (12 mg, 63%) as a white solid. ^{1}H NMR (D_2O, 400 MHz): δ 7.62-7.55 (2H, m, Ph), 7.50-7.37 (3H, m, Ph), 5.56 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 4.84 (1H, d, $J_{1b,2b}$ 1.9, H-1b), 4.42 (1H, d, $J_{1c,2c}$ 7.7, H-1c), 4.35 (1H, ddd, $J_{5a,4a}$ 10.2, $J_{5a,6'a}$ 6.9, $J_{5a,6a}$ 2.0, H-5a), 4.24 (1H, dd, $J_{2a,3a}$ 3.4, $J_{2a,1a}$ 1.6, H-2a), 3.97-3.85 (5H, m, H-3a, H-6a, H-2b, H-4c, H-6c), 3.85-3.67 (9H, m, H-4a, H-6'a, H-3b, H-4b, H-5b, H-6b, H-5c, H-6'c), 3.67 (1H, dd, $J_{3c,2c}$ 10.0, $J_{3c,4c}$ 3.4, H-3c), 3.57 (1H, dd, $J_{2c,3c}$ 10.0, $J_{2c,1c}$ 7.7, H-2c). ^{13}C NMR (D_2O, 100 MHz): δ 132.32, 132.11, 129.46, 128.35 (Ph), 102.99 (C-1c), 99.06 (C-1b), 87.59 (C-1a), 76.42 (C-5c), 75.33 (C-4b), 72.52 (C-3c), 71.53 (C-5a), 71.21 (C-2a, C-5b), 71.13 (C-3a), 70.95 (C-2c), 69.40 (C-2b), 69.21 (C-3b), 68.58 (C-4c), 67.25 (C-4a), 65.93 (C-6a), 61.13 (C-6b), 60.25 (C-6c). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1680.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-1-thio-α-D-mannopyranoside (18a). A solution of **11a** (350 mg, 0.38 mmol) in acetic acid/H_2O 70:30 mixture (10 mL) was stirred at 80 °C for 15 h. Then toluene was added to the solution and co-evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/AcOEt gradient from 9:3 up to 3:2) to give **18a** (260 mg, 78%) as a white solid. Spectral data are in accordance with the literature.[1]

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-1-thio-α-D-thiomannopyranoside (19a). To a solution of **18a** (180 mg, 0.20 mmol) in anhydrous pyridine (4 mL) was added benzoyl chloride (60 µL, 0.50 mmol). The mixture was stirred at RT and the reaction was monitored by TLC (cyclohexane/AcOEt 7:3). After 18 h, no starting material remained. Water was therefore added and the mixture was diluted with CH_2Cl_2. The resulting organic layer was washed with aqueous 10% HCl then with an aqueous saturated $NaHCO_3$ solution, and water. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/AcOEt 9:1) to give **19a** (168 mg, 76%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (2H, dd, *J* 8.4, 1.3, Ph), 8.01 (2H, dd, *J* 8.4, 1.3, Ph), 7.92-7.87 (4H, m, Ph), 7.86 (2H, dd, *J* 8.4, 1.3, Ph), 7.81 (2H, dd, *J* 8.7, 1.1, Ph), 7.63-7.58 (2H, m, Ph), 7.55 (2H, dd, *J* 8.3, 1.3, Ph), 7.51- 7.43 (8H, m), 7.38- 7.29 (6H, m, Ph), 7.26-7.18 (5H, m, Ph), 5.83 (1H, dd, $J_{3a,4a}$ 9.6, $J_{3a,2a}$ 3.3, H-3a), 5.82 (1H, s, H-1a), 5.69-5.64 (3H, m, H-2a, H-3b, H-5b), 5.44 (1H, s, H-1b), 5.39 (1H, d, $J_{2b,3b}$ 1.3, H-2b), 4.71 (1H, ddd, $J_{5a,4a}$ 9.6, $J_{5a,6'a}$ 4.3, $J_{5a,6a}$ 2.2, H-5a), 4.63 (1H, dd, $J_{6a,6'a}$ 12.0, $J_{6a,5a}$ 2.2, H-6a), 4.59 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.6, H-4a), 4.55 (1H, dd, $J_{6'a,6a}$ 12.0, $J_{6'a,5a}$ 4.3, H-6'a), 4.50 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 4.4, H-4b), 4.37 (1H, dd, $J_{6b,6'b}$ 12.0, $J_{6b,5b}$ 7.8, H-6b), 4.28 (1H, dd, $J_{6'b,6b}$ 12.0, $J_{6'b,5b}$ 3.3, H-6'b), 2.08 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.55, 166.04, 165.84, 165.71, 165.59, 165.41, 165.30 (CO), 133.76, 133.73, 133.60, 133.53, 133.27, 133.17, 133.03, 132.33, 130.15, 130.00, 129.98, 129.84, 129.76, 129.69, 129.56, 129.52, 129.37, 128.92, 128.74, 128.64, 128.56, 128.48, 128.44, 128.23 (Ph), 107.42 (C-1b), 85.99 (C-1a), 82.69 (C-2b), 82.28 (C-4b), 77.20 (C-3b), 72.99 (C-4a), 72.33 (C-2a), 70.92 (C-3a), 70.86 (C-5b), 70.24 (C-5a), 63.37, 62.77 (C6b, C6a), 20.97 ($COCH_3$). HRMS (ESI): calcd for $C_{62}H_{52}O_{17}SNa$ $[M+Na]^+$ 1123.2823, found 1123.2825.

Phenyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-di-*O*-benzoyl-1-thio-α-D-thiomannopyranoside (20a). To a solution of **19a** (165 mg, 0.15 mmol) in anhydrous MeOH (5 mL)

and anhydrous CH_2Cl_2 (2 mL) was added acetyl chloride (21 µL, 0.30 mmol). After stirring at RT for 16 h, aqueous saturated $NaHCO_3$ was added and the resulting mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give **20a** (130 mg, 82%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (2H, dd, *J* 8.5, 1.3, Ph), 8.02 (2H, dd, *J* 8.5, 1.3, Ph), 7.93- 7.88 (4H, m, Ph), 7.86 (2H, dd, *J* 8.5, 1.3, Ph), 7.81 (2H, dd, *J* 8.4, 1.3, Ph), 7.64-7.58 (2H, m, Ph), 7.56-7.53 (2H, m, Ph), 7.52-7.44 (7H, m, Ph), 7.37-7.30 (6H, m, Ph), 7.25-7.19 (6H, m, Ph), 5.87 (1H, dd, $J_{3a,4a}$ 9.6, $J_{3a,2a}$ 3.5, H-3a), 5.83 (1H, dd, $J_{2a,3a}$ 3.5, $J_{2a,1a}$ 1.6, H-2a), 5.71 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 5.68-5.64 (2H, m, H-3b, H-5b), 5.57 (1H, s, H-1b), 5.38 (1H, d, $J_{2b,3b}$ 1.2, H-2b), 4.76 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.6, H-4a), 4.51 (1H, td, $J_{5a,4a}$ 9.6, $J_{5a,6a}$ 2.4, H-5a), 4.44 (1H, dd, $J_{4b,3b}$ 4.6, $J_{4b,5b}$ 4.0, H-4b), 4.38 (1H, dd, $J_{6b,6'b}$ 12.1, $J_{6b,5b}$ 7.8, H-6b), 4.28 (1H, dd, $J_{6'b,6b}$ 12.1, $J_{6'b,5b}$ 3.3, H-6'b), 4.20 (1H, ddd, $J_{6a,6'a}$ 12.0, $J_{6a,OH}$ 8.8, $J_{6a,5a}$ 2.4, H-6a), 3.98 (1H, ddd, $J_{6'a,6a}$ 12.0, $J_{6'a,OH}$ 4.0, $J_{6'a,5a}$ 2.4, H-6'a), 2.16 (1H, dd, $J_{OH,6a}$ 8.8, $J_{OH,6'a}$ 4.0, OH-6a). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.18, 166.00, 165.73, 165.62, 165.36 (CO), 133.74, 133.63, 133.54, 133.25, 133.15, 133.12, 132.36, 130.17, 130.03, 130.01, 129.99, 129.94, 129.82, 129.69, 129.56, 129.48, 129.42, 129.39, 128.97, 128.84, 128.67, 128.64, 128.53, 128.45, 128.20 (Ph), 107.26 (C-1b), 86.32 (C-1a), 82.80 (C-2b), 82.25 (C-4b), 77.24 (C-3b), 73.34 (C-4a), 72.71 (C-2a), 71.80 (C-3a), 70.83 (C-5b), 70.28 (C-5a), 63.46 (C-6b), 61.17 (C-6a). HRMS (ESI): calcd for $C_{60}H_{50}O_{16}SNa$ $[M+Na]^+$ 1081.2717, found 1081.2715.

Phenyl [2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)]-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3-di-*O*-benzoyl-1-thio-α-D-mannopyranoside (22a). This glycosylation was performed according to general procedure C starting from acceptor **20a** (100 mg, 0.10 mmol), donor **21** (85 mg, 0.11 mmol), activated 4Å molecular sieves (100 mg), TMSOTf (0.02 M in CH_2Cl_2, 0.5 mL, 0.001 mmol), in anhydrous CH_2Cl_2, and stirring at 0 °C for 2 h. At the end of the C procedure, the residue was purified by column chromatography on silica gel (cyclohexane/AcOEt gradient from 9:1 up to 8:2) to give **22a** (116 mg, 75%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.07 (4H, m, Ph), 8.04 (2H, dd, *J* 8.4, 1.3, Ph), 7.96 (2H, dd, *J* 8.4, 1.3, Ph), 7.94-7.88 (6H, m, Ph), 7.82 (2H, dd, *J* 8.4, 1.3, Ph), 7.79 (2H, dd, *J* 8.4, 1.2, Ph), 7.70 (2H, dd, *J* 8.4, 1.3, Ph), 7.59-7.52 (5H, m, Ph), 7.50-7.30 (19H, m, Ph), 7.30-7.17 (11H, m, Ph), 6.12 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 10.0, H-4b), 5.94 (1H, dd, $J_{3b,4b}$ 10.0, $J_{3b,2b}$ 3.2, H-3b), 5.90 (1H, dd, $J_{2a,3a}$ 3.5, $J_{2a,1a}$ 1.6, H-2a), 5.87 (1H, dd, $J_{3a,4a}$ 9.8, $J_{3a,2a}$ 3.5, H-3a), 5.88 (1H, dd, $J_{2b,3b}$ 3.2, $J_{2b,1b}$ 1.6, H-2b), 5.75 (1H, ad, $J_{3c,4c}$ 4.8, H-3c), 5.73 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 5.70 (1H, td, $J_{5c,6c}$ 7.6, $J_{5c,4c}$ = $J_{5c,6'c}$ 3.7, H-5c), 5.65 (1H, s, H-1c), 5.50 (1H, d, $J_{2c,3c}$ 1.1, H-2c), 5.36 (1H, d, $J_{1b,2b}$ 1.6, H-1b), 4.76 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.8, H-4a), 4.71 (1H, ddd, $J_{5a,4a}$ 9.8, $J_{5a,6a}$ 3.9, $J_{5a,6'a}$ 1.5, H-5a), 4.61 (1H, dd, $J_{6b,6'b}$ 11.7, $J_{6b,5b}$ 2.0, H-6b), 4.58 (1H, dd, $J_{4c,3c}$ 4.8, $J_{4c,5c}$ 3.7, H-4c), 4.44 (1H, dd, $J_{6a,6'a}$ 12.2, $J_{6a,5a}$ 3.9, H-6a), 4.44 (1H, dd, $J_{6c,6'c}$ 12.2, $J_{6c,5c}$ 7.6, H-6c), 4.39 (1H, ddd, $J_{5b,4b}$ 10.0, $J_{5b,6'b}$ 3.5, $J_{5b,6b}$ 2.0, H-5b), 4.37 (1H, dd, $J_{6'c,6c}$ 12.2, $J_{6'c,5c}$ 3.7, H-6'c), 4.37 (1H, dd, $J_{6'b,6b}$ 11.7, $J_{6'b,5b}$ 3.5, H-6'b), 4.17 (1H, dd, $J_{6'a,6a}$ 12.2, $J_{6'a,5a}$ 1.5, H-6'a). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.26, 166.18, 165.99, 165.79, 165.69, 165.64,165.61, 165.42, 165.24, 165.01 (CO), 133.77, 133.47, 133.41, 133.31, 133.22, 133.15, 133.10, 133.07, 132.37, 130.16, 130.06, 129.96, 129.92, 129.88, 129.85, 129.58, 129.57, 129.46, 129.43, 129.33, 129.13, 128.84, 128.66, 128.61, 128.58, 128.54, 128.44, 128.40, 128.31, 128.20 (Ph), 107.55 (C-1c), 98.55 (C-1b), 86.40 (C-1a), 82.76 (C-2c), 82.32 (C-4c), 77.20 (C-3c), 72.68, 72.61 (C-4a, C-5a), 72.39 (C-2a), 71.26 (C-2b), 70.39, 70.34, 70.27 (C-3a, C-3b, C-5c), 69.23 (C-5b), 66.73 (C-4b), 66.09 (C-6a), 63.43 (C-6c), 62.66 (C-6b). HRMS (ESI): calcd for $C_{94}H_{76}O_{25}SNa$ $[M+Na]^+$ 1659.4294, found 1659.4300.

Phenyl [β-D-galactofuranosyl-(1→4)]-α-D-mannopyranosyl-(1→6)-1-thio-α-D-mannopyranoside (23a). Deacylation was performed according to general procedure B starting from **22a** (100 mg, 0.06 mmol), MeONa (0.54 M in MeOH, 20 µL, 0.01 mmol), in anhydrous MeOH (4 mL). The mixture was stirred for 18 h at RT. At the end of the B procedure, **23a** was isolated (25 mg, 71%) as a white solid. ^{1}H NMR (D_2O, 500 MHz): δ 7.61-7.52 (2H, m, Ph), 7.47-7.38 (3H, m, Ph), 5.55 (1H, s, H-1a), 5.10 (1H, d, $J_{1c,2c}$ 2.3, H-1c), 4.83 (1H, s, H-1b), 4.41 (1H, ddd, $J_{5a,4a}$ 9.8, $J_{5a,6'a}$ 6.2, $J_{5a,6a}$ 2.3, H-5a), 4.27 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.3, H-2a), 4.14-4.09 (3H, m, H-2c, H-3c, H-4c), 4.00 (1H, dd, $J_{3a,4a}$ 9.3, $J_{3a,2a}$ 3.3, H-3a), 3.93 (1H, dd, $J_{6a,6'a}$ 11.6, $J_{6a,5a}$ 6.2, H-6a), 3.88-3.82 (4H, m, H-4a, H-2b, H-6b, H-5c), 3.77-3.61 (6H, m,

H-6'a, H-3b, H-4b, H-6'b, H-6c), 3.58 (1H, ddd, $J_{5b,4b}$ 9.6, $J_{5b,6'b}$ 6.1, $J_{5b,6b}$ 2.3, H-5b). ^{13}C NMR (D_2O, 126 MHz): δ 132.31, 132.09, 129.44, 128.33 (Ph), 107.75 (C-1c), 99.82 (C-1b), 87.46 (C-1a), 82.63 (C-2c), 81.08 (C-4c), 75.99 (C-3c), 75.72 (C-4a), 72.77 (C-5b), 71.04 (C-2a), 70.48 (C-3b, C-5a), 70.42 (C-5c), 69.85 (C-2b), 69.56 (C-3a), 66.60 (C-4b), 65.81 (C-6a), 62.74 (C-6c), 60.81 (C-6b). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1672.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-1-thio-α-D-mannopyranoside (18b). A solution of **11b** (500 mg, 0.53 mmol) in acetic acid/H_2O 70:30 mixture (10 mL) was stirred at 80 °C for 15 h. Then toluene was added to the solution and co-evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/AcOEt gradient from 9:3 up to 3:2) to give **18b** (250 mg, 54%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.07 (4H, m, Ph), 7.95 (2H, dd, *J* 8.5, 1.3, Ph), 7.77 (2H, dd, *J* 8.5, 1.3, Ph), 7.65 (1H, tt, *J* 7.4, 1.3, Ph), 7.58 (1H, tt, *J* 7.2, 1.3, Ph), 7.54-7.50 (3H, m, Ph), 7.47-7.36 (7H, m, Ph), 7.27-7.21 (5H, m, Ph), 6.00 (1H, dd, $J_{4b,3b}$ 3.5, $J_{4b,5b}$ 1.1, H-4b), 5.90 (1H, dd, $J_{2b,3b}$ 10.4, $J_{2b,1b}$ 8.0, H-2b), 5.60 (1H, dd, $J_{3b,2b}$ 10.4, $J_{3b,4b}$ 3.5, H-3b), 5.52 (1H, d, $J_{1a,2a}$ 1.3, H-1a), 4.87 (1H, d, $J_{1b,2b}$ 8.0, H-1b), 4.63 (1H, dd, $J_{6b,6'b}$ 11.7, $J_{6b,5b}$ 4.7, H-6b), 4.57 (1H, dd, $J_{6'b,6b}$ 11.7, $J_{6'b,5b}$ 8.0, H-6'b), 4.49 (1H, s, OH-3), 4.48 (1H, ddd, $J_{5b,6'b}$ 8.0, $J_{5b,6b}$ 4.7, $J_{5b,4b}$ 1.1, H-5b), 4.31 (1H, ddd, $J_{5a,4a}$ 9.9, $J_{5a,6a}$ 4.9, $J_{5a,6'a}$ 2.2, H-5a), 4.22 (1H, td, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ = $J_{2a,OH}$ 1.3, H-2a), 4.09 (1H, dd, $J_{6a,6'a}$ 12.0, $J_{6a,5a}$ 4.9, H-6a), 4.05 (1H, dd, $J_{6'a,6a}$ 12.0, $J_{6'a,5a}$ 2.2, H-6'a), 3.99 (1H, dd, $J_{3a,4a}$ 8.9, $J_{3a,2a}$ 3.3, H-3a), 3.82 (1H, dd, $J_{4a,5a}$ 9.9, $J_{4a,3a}$ 8.9, H-4a), 2.58 (1H, d, $J_{OH,2a}$ 1.3, OH-2), 1.88 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.31, 166.16, 165.61, 165.59, 165.20 (CO), 134.02, 133.77, 133.61, 131.67, 130.20, 130.02, 129.99, 129.93, 129.25, 129.14, 128.91, 128.81, 128.72, 128.65, 128.60, 128.57, 128.51, 127.69 (Ph), 102.27 (C-1b), 86.80 (C-1a), 80.31 (C-4a), 72.55 (C-5a), 71.67 (C-4b), 71.58 (C-3b), 70.17 (C-5b), 69.48 (C-2b), 68.94 (C-3a), 68.09 (C-2a), 62.62, 62.57 (C-6a, C-6b), 20.81 ($COCH_3$). HRMS (ESI): calcd for $C_{48}H_{44}O_{15}SNa$ $[M+Na]^+$ 915.2299, found 915.2305.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-1-thio-α-D-thiomannopyranoside (19b). To a solution of **18b** (250 mg, 0.28 mmol) in mixture anhydrous pyridine / DCM (5/5 mL) was added benzoyl chloride (80 µL, 0.69 mmol). The mixture was stirred at RT and the reaction was monitored by TLC (cyclohexane/AcOEt 3:2). After 18 h, no starting material remained. Water was therefore added and the mixture was diluted with CH_2Cl_2. The resulting organic layer was washed with aqueous 10% HCl then with an aqueous saturated $NaHCO_3$ solution, and water. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/AcOEt 9:1) to give **19a** (258 mg, 84%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (2H, dd, *J* 8.5, 1.4, Ph), 8.01 (2H, dd, *J* 8.5, 1.4, Ph), 7.97 (2H, dd, *J* 8.5, 1.3, Ph), 7.94 (2H, dd, *J* 8.4, 1.3, Ph), 7.87 (2H, dd, *J* 8.5, 1.3, Ph), 7.73 (2H, dd, *J* 8.4, 1.4, Ph), 7.60 (2H, tt, *J* 7.4, 1.3, Ph), 7.55-7.36 (12H, m, Ph), 7.32 (2H, dd, *J* 8.2, 7.4, Ph), 7.30-7.24 (5 H, m, Ph), 7.22 (2H, dd, *J* 8.3, 7.4, Ph), 5.87 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.8, H-2a), 5.84-5.80 (2H, m, H-3a, H-4b), 5.75 (1H, dd, $J_{2b,3b}$ 10.4, $J_{2b,1b}$ 7.9, H-2b), 5.60 (1H, d, $J_{1a,2a}$ 1.8, H-1a), 5.51 (1H, dd, $J_{3b,2b}$ 10.4, $J_{3b,4b}$ 3.3, H-3b), 4.96 (1H, d, $J_{1b,2b}$ 7.9, H-1b), 4.56 (1H, ddd, $J_{5a,4a}$ 9.6, $J_{5a,6'a}$ 4.5, $J_{5a,6a}$ 2.1, H-5a), 4.42 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.6, H-4a), 4.37 (1H, dd, $J_{6a,6'a}$ 12.0, $J_{6a,5a}$ 2.1, H-6a), 4.29 (1H, dd, $J_{6'a,6a}$ 12.0, $J_{6'a,5a}$ 4.5, H-6'a), 4.09 (1H, dd, $J_{6b,6'b}$ 10.9, $J_{6b,5b}$ 5.2, H-6b), 3.94 (1H, dd, $J_{5b,6'b}$ 8.6, $J_{5b,6b}$ 5.2, H-5b), 3.81 (1H, dd, $J_{6'b,6b}$ 10.9, $J_{6'b,5b}$ 8.6, H-6'b), 1.89 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 170.34, 165.69, 165.46, 165.32, 165.05, 165.03 (CO), 133.75, 133.69, 133.58, 133.55, 133.45, 133.36, 133.08, 132.26, 130.12, 130.01, 129.93, 129.91, 129.80, 129.61, 129.58, 129.33, 129.30, 129.03, 129.00, 128.75, 128.66, 128.64, 128.55, 128.42, 128.17 (Ph), 101.65 (C-1b), 86.01 (C-1a), 74.67 (C-4a), 72.18 (C-5a), 71.83 (C-4b), 71.25 (C-3b), 70.60 (C-5b), 70.38, 70.22 (C-3a, C-2b), 67.49 (C-2a), 62.46 (C-6b), 60.83 (C-6a), 20.68 ($COCH_3$). HRMS (ESI): calcd for $C_{62}H_{52}O_{17}SNa$ $[M+Na]^+$ 1123.2823, found 1123.2824.

Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-1-thio-α-D-thiomannopyranoside (20b). To a solution of **20b** (250 mg, 0.22 mmol) in anhydrous MeOH (5 mL)

and anhydrous CH_2Cl_2 (2 mL) was added acetyl chloride (32 µL, 0.45 mmol). After stirring at RT for 16 h, aqueous saturated $NaHCO_3$ was added and the resulting mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/AcOEt 4:1) to give **20b** (190 mg, 80%) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08-7.98 (6H, m, Ph), 7.94-7.86 (4H, m, Ph), 7.74 (2H, dd, *J* 8.4, 1.3, Ph), 7.66-7.57 (2H, m, Ph), 7.56-7.35 (13H, m, Ph), 7.33-7.19 (8H, m, Ph), 5.87 (1H, dd, $J_{2a,3a}$ 3.4, $J_{2a,1a}$ 1.9, H-2a), 5.85 (1H, d, $J_{4b,3b}$ 3.3, H-4b), 5.79 (1H, dd, $J_{3a,4a}$ 9.8, $J_{3a,2a}$ 3.4, H-3a), 5.75 (1H, dd, $J_{2b,3b}$ 10.5, $J_{2b,1b}$ 7.9, H-2b), 5.63 (1H, d, $J_{1a,2a}$ 1.9, H-1a), 5.54 (1H, dd, $J_{3b,2b}$ 10.5, $J_{3b,4b}$ 3.3, H-3b), 5.10 (1H, d, $J_{1b,2b}$ 7.9, H-1b), 4.66 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.8, H-4a), 4.27 (1H, ddd, $J_{5a,4a}$ 9.8, $J_{5a,6a}$ 2.4, $J_{5a,6'a}$ 2.0, H-5a), 4.16-4.09 (2H, m, H-5b, H-6b), 3.90-3.82 (2H, m, H-6a, H-6'b), 3.7 (1H, ddd, $J_{6'a,6a}$ 12.4, $J_{6'a,OH}$ 3.7, $J_{6'a,5a}$ 2.0, H-6'a), 1.77 (1H, dd, $J_{OH,6a}$ 9.6, $J_{OH,6'a}$ 3.7, OH-6). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 165.8, 165.7, 165.3, 165.0 (CO), 133.7, 133.7, 133.6, 133.5, 133.4, 133.1, 132.3, 130.1, 130.0, 129.9, 129.8, 129.6, 129.3, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2 (Ph), 101.5 (C-1b), 86.2 (C-1a), 73.1 (C-4a), 72.8 (C-5a), 72.6 (C-4b) 71.9 (C-3b), 71.1 (C-5b), 70.2 (C-3a, C-2b), 67.6 (C-2a), 61.0 (C-6b), 60.7 (C-6a). HRMS (ESI): calcd for $C_{60}H_{50}O_{16}SNa$ $[M+Na]^+$ 1081.2717, found 1081.2715.

Phenyl [2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)]-2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3-di-*O*-benzoyl-1-thio-α-D-mannopyranoside (22b). This glycosylation was performed according to general procedure C starting from acceptor **20b** (120 mg, 0.11 mmol), donor **21** (100 mg, 0.13 mmol), activated 4Å molecular sieves (100 mg), TMSOTf (0.02 M in CH_2Cl_2, 0.6 mL, 0.01 mmol), in anhydrous CH_2Cl_2, and stirring at 0 °C for 2 h. At the end of the C procedure, the residue was purified by column chromatography on silica gel (cyclohexane/AcOEt gradient from 4:1 up to 7:3) to give **22b** (167 mg, 92%) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13-7.99 (10H, m, Ph), 7.96 (2H, dd, *J* 8.3, 1.4, Ph), 7.89 (2H, dd, *J* 8.3, 1.4, Ph), 7.81 (2H, dd, *J* 8.4, 1.1, Ph), 7.78 (2H, dd, *J* 8.3, 1.4, Ph), 7.72 (2H, dd, *J* 8.4, 1.4, Ph), 7.61-7.55 (3H, m, Ph), 7.52-7.47 (3H, m, Ph), 7.45-7.26 (22H, m, Ph), 7.24-7.12 (7H, m, Ph), 6.20 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 10.2, H-4b), 6.00 (1H, dd, $J_{3b,4b}$ 10.2, $J_{3b,2b}$ 3.3, H-3b), 5.94 (1H, dd, $J_{4c,3c}$ 3.3, $J_{4c,5c}$ 1.2, H-4c), 5.92 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.7, H-2a), 5.84 (1H, dd, $J_{3a,4a}$ 9.8, $J_{3a,2a}$ 3.3, H-3a), 5.81 (1H, dd, $J_{3c,2c}$ 10.4, $J_{3c,4c}$ 3.3, H-3c), 5.76 (1H, dd, $J_{2b,3b}$ 3.3, $J_{2a,1a}$ 2.0, H-2b), 5.75 (1H, dd, $J_{2c,3c}$ 10.4, $J_{2c,1c}$ 7.7, H-2c), 5.70 (1H, d, $J_{1a,2a}$ 1.7, H-1a), 5.35 (1H, d, $J_{1c,2c}$ 7.7, H-1c), 5.16 (1H, d, $J_{1b,2b}$ 2.0, H-1b), 4.72 (1H, dd, $J_{6b,6'b}$ 12.2, $J_{6b,5b}$ 3.3, H-6b), 4.71 (1H, t, $J_{4a,5a}$ = $J_{4a,3a}$ 9.9, H-4a), 4.55 (1H, ddd, $J_{5a,4a}$ 9.8, $J_{5a,6a}$ 4.1, $J_{5a,6'a}$ 1.3, H-5a), 4.50 (1H, dd, $J_{6'b,6b}$ 12.2, $J_{6'b,5b}$ 3.3, H-6'b), 4.44 (1H, ddd, $J_{5c,6'c}$ 8.8, $J_{5c,6c}$ 5.2, $J_{5c,4c}$ 1.2, H-5c), 4.39 (1H, td, $J_{5b,4b}$ 10.2, $J_{5b,6b}$ 3.3, H-5b), 4.25 (1H, dd, $J_{6c,6'c}$ 10.8, $J_{6c,5c}$ 5.2, H-6c), 4.09 (1H, dd, $J_{6a,6'a}$ 12.4, $J_{6a,5a}$ 4.1, H-6a), 3.93 (1H, dd, $J_{6'c,6c}$ 10.8, $J_{6'c,5c}$ 8.8, H-6'c), 3.85 (1H, dd, $J_{6'a,6a}$ 12.4, $J_{6'a,5a}$ 1.3, H-6'a). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 166.28, 165.84, 165.77, 165.69, 165.63, 165.59, 165.35, 165.07, 164.93 (CO), 133.68, 133.56, 133.52, 133.47, 133.44, 133.36, 133.32, 133.25, 133.05, 131.99, 130.08, 129.95, 129.93, 129.90, 129.87, 129.83, 129.76, 129.73, 129.53, 129.49, 129.39, 129.28, 129.11, 129.07, 128.89, 128.80, 128.73, 128.67, 128.65, 128.55, 128.40, 128.04 (Ph), 101.64 (C-1c), 98.42 (C-1b), 86.37 (C-1a), 74.13 (C-4a), 72.67 (C-2a), 72.42 (C-5a), 71.89 (C-3c), 71.38 (C-5c), 70.92 (C-2b), 70.31 (C-3a, C-3b, C-2c), 69.56 (C-5b), 67.87 (C-4c), 66.69 (C-4b), 65.98 (C-6a), 62.58 (C-6b), 61.03 (C-6c). HRMS (ESI): calcd for $C_{94}H_{76}O_{25}SNa$ $[M+Na]^+$ 1659.4294, found 1659.4299.

Phenyl [β-D-galactopyranosyl-(1→4)]-α-D-mannopyranosyl-(1→6)-1-thio-α-D-mannopyranoside (23b). Deacylation was performed according to general procedure B starting from **22b** (140 mg, 0.086 mmol), MeONa (0.54 M in MeOH, 50 µL, 0.02 mmol), in anhydrous MeOH (5 mL). The mixture was stirred for 18 h at RT. At the end of the B procedure, **23b** was isolated (38 mg, 75%) as a white solid. ^{1}H NMR (D_2O, 500 MHz): δ 7.62-7.57 (2H, m, Ph), 7.48-7.39 (3H, m, Ph), 5.57 (1H, d, $J_{1a,2a}$ 1.6, H-1a), 4.85 (1H, d, $J_{1b,2b}$ 1.8, H-1b), 4.48-4.44 (1H, m, H-5a), 4.45 (1H, d, $J_{1c,2c}$ 7.8, H-1c), 4.31 (1H, dd, $J_{2a,3a}$ 3.3, $J_{2a,1a}$ 1.6, H-2a), 4.02 (1H, dd, $J_{3a,4a}$ 9.4, $J_{3a,2a}$ 3.3, H-3a), 3.95 (1H, dd, $J_{6a,6'a}$ 11.8, $J_{6a,5a}$ 6.5, H-6a), 3.94-3.93 (1H, m, H-4c), 3.91 (1H, t, $J_{4a,3a}$ = $J_{4a,5a}$ 9.4, H-4a), 3.89 (1H, dd, $J_{6'a,6a}$ 11.8, $J_{6'a,5a}$ 2.2, H-6'a), 3.87 (1H, dd, $J_{6b,6'b}$ 12.0, $J_{6b,5b}$ 1.8, H-6b), 3.83 (1H, dd, $J_{2b,3b}$ 3.2, $J_{2b,1b}$ 1.8, H-2b), 3.81 (1H, dd, $J_{6c,6'c}$

9.8, $J_{6c,5c}$ 2.0, H-6c), 3.77 (1H, dd, $J_{6'c,6c}$ 9.8, $J_{6'c,5c}$ 3.7, H-6'c), 3.76-3.72 (1H, m, H-5c), 3.74 (1H, dd, $J_{6'b,6b}$ 12.0, $J_{6'b,5b}$ 5.7, H-6'b), 3.70-3.68 (2H, m, H-3b, H-3c), 3.64 (1H, t, $J_{4b,3b}$ = $J_{4b,5b}$ 9.9, H-4b), 3.64-3.61 (1H, m, H-5b), 3.58 (1H, dd, $J_{2c,3c}$ 10.0, $J_{2c,1c}$ 7.8, H-2c). ^{13}C NMR (D_2O, 126 MHz): δ 132.28, 132.07, 129.43, 128.33 (Ph), 103.06 (C-1c), 99.63 (C-1b), 87.34 (C-1a), 76.97 (C-4a), 75.48 (C-5c), 72.78 (C-5b), 72.49 (C-3c), 70.89 (C-2c), 70.68 (C-2a), 70.49 (C-3b), 70.36 (C-5a), 69.84 (C-2b), 69.76 (C-3a), 68.59 (C-4c), 66.62 (C-4b), 65.59 (C-6a), 61.11 (C-6c), 60.92 (C-6b). HRMS (ESI): calcd for $C_{24}H_{36}O_{15}SNa$ $[M+Na]^+$ 619.1673, found 619.1670.

^{1}H and ^{13}C chemical shifts tables of trisaccharide 1-3

For linear oligosaccharides, the letters a, b, c were attributed starting from the reducing glycosyl residue. For branched oligosaccharides, the letter a was for the reducing entity, b for the glycosyl residue linked to *O*-4 of the reducing Man*p* unit, and c for the residue linked to *O*-6 of the same entity.

Table S1a: ^{1}H and ^{13}C NMR chemical shifts tables of Gal*f*-(1,6)-Man*p*-(1,4)-Man*p* (**1a**) in D_2O

^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
1aα	**Man a**	5,17	3,90*	3,97	3,79*	3,81-3,89	3,89*;3,79
	Man b	5,2	4,07*	3,81*	3,70	3,82*	4,05*; 3,69*
	Gal c	5,05	4,14	4,07	4,00	3,85*	3,65 ; 3,76
1aβ	**Man a**	4,85	3,90*	3,71*	3,63-3,76	3,53-3,44	3,78-3,86 3,75-3,61
	Man b	5,25	4,07*	3,81*	3,70	3,92-3,76	4,09-4,03 3,76-3,63
	Gal c	5,05	4,14	4,07	4,00	3,92-3,76	3,65 ; 3,76

* ^{1}H chemical shift was determined according to HSQC correlation spot.

^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
1aα	**Man a**	93,83	71,17	70,60	75,1	71,03 ; 70,87	61,19
	Man b	101,74	70,27		66,62	72,56	66,8
	Gal c	107,75	81,05	76,85	82,83	71,03 ; 70,87	62,76
1aβ	**Man a**	93,61	71,17	73,48	74,77 ; 74,69		60,93
	Man b	101,74	70,27		66,62	72,56	66,8
	Gal c	107,75	81,05	76,85	82,83	70,87	62,76

Table S1b: ^{1}H and ^{13}C NMR chemical shifts tables of Gal*p*-(1,6)-Man*p*-(1,4)-Man*p* (**1b**) in D_2O

^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
1bα	**Man a**	5,17	3,89*	3,97	3,80*	3,89*	3,94-3,85 3,84-3,69
	Man b	5,22	4,07	3,82*	3,78*	3,86*	4,22 ; 3,87*
	Gal c	4,45	3,57	3,67	3,93*	3,71*	3,84-3,69
1bβ	**Man a**	4,89	3,89*	3,97	3,81*	3,47	3,94-3,85 3,84-3,69
	Man b	5,22	4,06	3,82*	3,78*	3,86*	4,22 ; 3,87*
	Gal c	4,45	3,57	3,67	3,93*	3,71*	3,84-3,69

* ^{1}H chemical shift was determined according to HSQC correlation spot.

^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
1bα	**Man a**	93,78	71,13	70,61	74,94	70,90	61,16 ; 61,01
	Man b	101,71	70,21		66,33	72,62 ; 72,59	68,66
	Gal c	103,36	70,81	72,62 ; 72,59	68,66	75,14	61,16 ; 61,01
1bβ	**Man a**	93,57	71,70	70,61	71,48	74,58	61,16 ; 61,01
	Man b	101,65	70,21		66,33	72,62 ; 72,59	68,66
	Gal c	103,33	70,81	72,62 ; 72,59	68,66	75,14	61,16 ; 61,01

Table S2a: ^{1}H and ^{13}C NMR chemical shifts tables of Gal*f*-(1,6)-Man*p*-(1,4)-Man*p* (**2a**) in D_2O

^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
2aα	**Man a**	5,17	3,94*	3,83*	3,71*	3,95*	4,17 ; 3,85*
	Man b	4,72	4,10	3,76*	3,74*	3,52-3,46	3,94* ; 3,79*
	Gal c	5,08	4,10	4,10	4,10	3,89-3,77	3,77-3,59
2aβ	**Man a**	4,91	3,94*	3,83*	3,62*	3,85*	4,20 ; 3,83*
	Man b	4,73	4,10	3,76*	3,74*	3,56-3,50	3,94* ; 3,74*
	Gal c	5,08	4,10	4,10	4,10	3,84*	3,77-3,59

* ^{1}H chemical shift was determined according to HSQC correlation spot.

^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
2aα	**Man a**	94,09	70,58	70,48	66,67	71,24	68,6
	Man b	100,44	70,23	71,44	75,14	75,04	60,43
	Gal c	107,91	82,62	75,91	80,91	70,12	62,67
2aβ	**Man a**	93,72	70,58	70,48	66,43	71,16	68,56
	Man b	100,47	70,23	71,44	72,94	74,9	61,04
	Gal c	107,91	82,62	75,91	80,91	70,12	62,67

Table S2b: ^{1}H and ^{13}C NMR chemical shifts tables of Gal*p*-(1,6)-Man*p*-(1,4)-Man*p* (**2b**) in D_2O

^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
2bα	**Man a**	5,17	3,93*	3,83*	3,74*	3,93*	3,98* ; 3,74*
	Man b	4,91	4,06	3,97*	3,88*	3,83*	3,84-3,72
	Gal c	4,45	3,55	3,68	3,93*	3,75*	3,96* ; 3,85*
2bβ	**Man a**	4,90	3,93*	3,94*	3,65*	3,52*	3,93* ; 3,79*
	Man b	4,92	4,06	3,97*	3,83*	3,88*	3,84-3,72
	Gal c	4,45	3,55	3,68	3,93*	3,75*	3,96* ; 3,85*

* ^{1}H chemical shift was determined according to HSQC correlation spot.

^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
2bα	**Man a**	94,17	70,58	70,41	66,66	70,63	65,91
	Man b	99,33	69,41	69,32	76,4	71,28	61,1
	Gal c	103,02	70,95	72,50	68,59	75,37	60,23
2bβ	**Man a**	83,81	73,14	71,14	66,45	74,25	65,99
	Man b	99,39	69,38	69,3	76,40	71,28	61,1
	Gal c	103,02	70,95	72,5	68,59	75,37	60,23

Table S3a: ^{1}H and ^{13}C NMR chemical shifts tables of Man*p*-(1,6)-[Gal*f*-(1,4)-]Man*p* (**3a**) in D_2O

^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
3aα	**Man a**	5,17	3,98*	3,96*	3,87*	4,04*	4,01* ; 3,75*
	Man b	4,93	4,03*	3,86*	3,68*	3,68*	3,90* ; 3,78*
	Gal c	5,11	4,11	4,10	4,11	3,83*	3,71-3,63
3aβ	**Man a**	4,90	3,98*	3,96*	3,78*	3,61*	3,96* ; 3,81*
	Man b	4,94	4,03*	3,86*	3,768*	3,68*	3,90* ; 3,78*
	Gal c	5,11	4,11	4,10	4,11	3,83*	3,71-3,63

* ^{1}H chemical shift was determined according to HSQC correlation spot.

^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
3aα	**Man a**	93,88	70,50 ; 70,49	68,76	75,25	69,86	66,15
	Man b	100,34	69,65	70,44	66,62	72,92	60,84
	Gal c	107,77	82,66	76,06	81,04	70,50 ; 70,49	62,68
3aβ	**Man a**	93,77	70,50 ; 70,49	68,76	74,95	73,38	66,06
	Man b	100,3	69,65	70,44	66,62	72,92	60,87
	Gal c	107,73	82,75	76,06	81,00	70,50 ; 70,49	62,68

Table S3b: ^{1}H and ^{13}C NMR chemical shifts tables of Man*p*-(1,6)-[Gal*p*-(1,4)-]Man*p* (**3b**) in D_2O

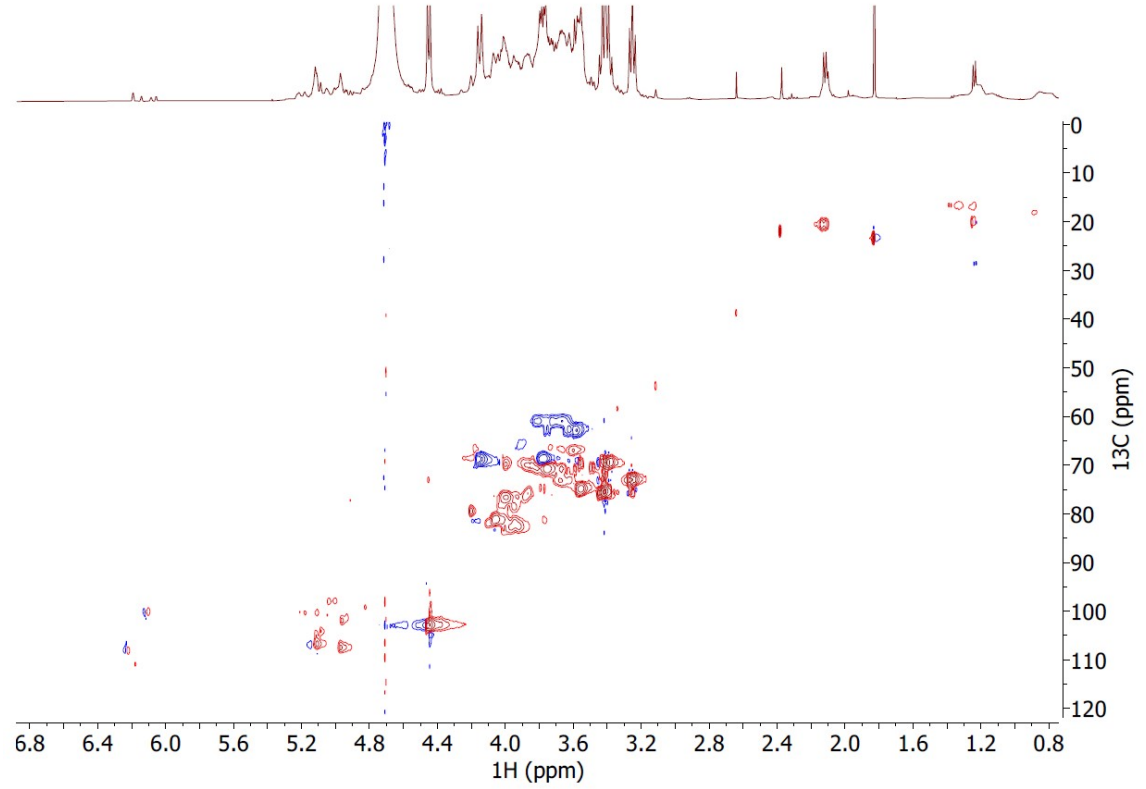
^{1}H NMR		H-1	H-2	H-3	H-4	H-5	H-6
3bα	**Man a**	5,17	4,00*	3,86*	3,93*	4,07*	4,04* ; 3,84*
	Man b	4,93	4,02*	3,84*	3,67*	3,72*	3,90* ; 3,77*
	Gal c	4,44	3,55*	3,67*	3,92*	3,74*	3,87-3,70
3bβ	**Man a**	4,91	4,00*	3,86*	3,83*	3,55*	4,00* ; 3,89*
	Man b	4,94	4,02*	3,84*	3,67*	3,72*	3,90* ; 3,77*
	Gal c	4,44	3,55*	3,67*	3,92*	3,74*	3,87-3,70

* ^{1}H chemical shift was determined according to HSQC correlation spot.

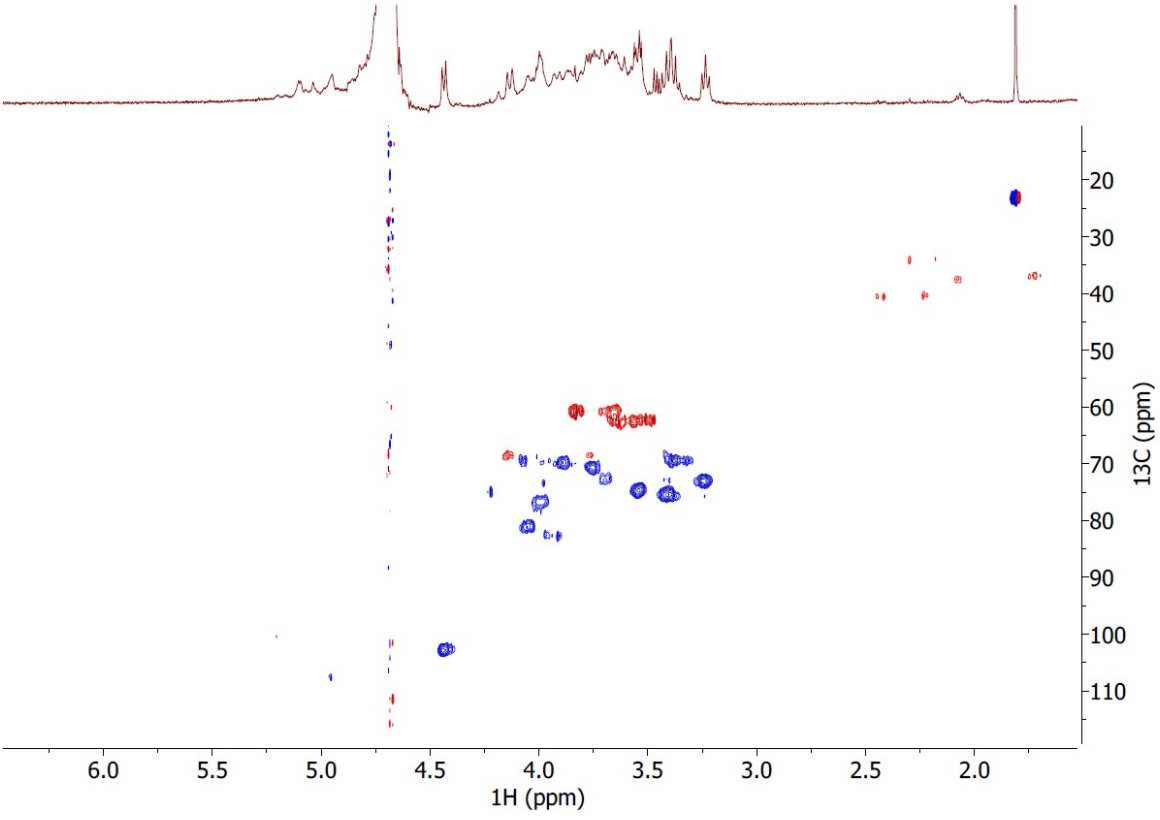
^{13}C NMR		C-1	C-2	C-3	C-4	C-5	C-6
3bα	**Man a**	93,8	69,84	68,92	76,32	69,62	65,99
	Man b	100,22	70,03	70,52	66,61	72,89	60,95
	Gal c	102,99	70,89	72,45	68,61	75,49	61,13
3bβ	**Man a**	93,67	69,81	68,92	75,92	73,45	65,91
	Man b	100,17	70,03	70,5	66,65	72,84	60,95
	Gal c	102,99	70,9	72,45	68,61	75,49	61,13

2D HSQC maps of lichen extracts

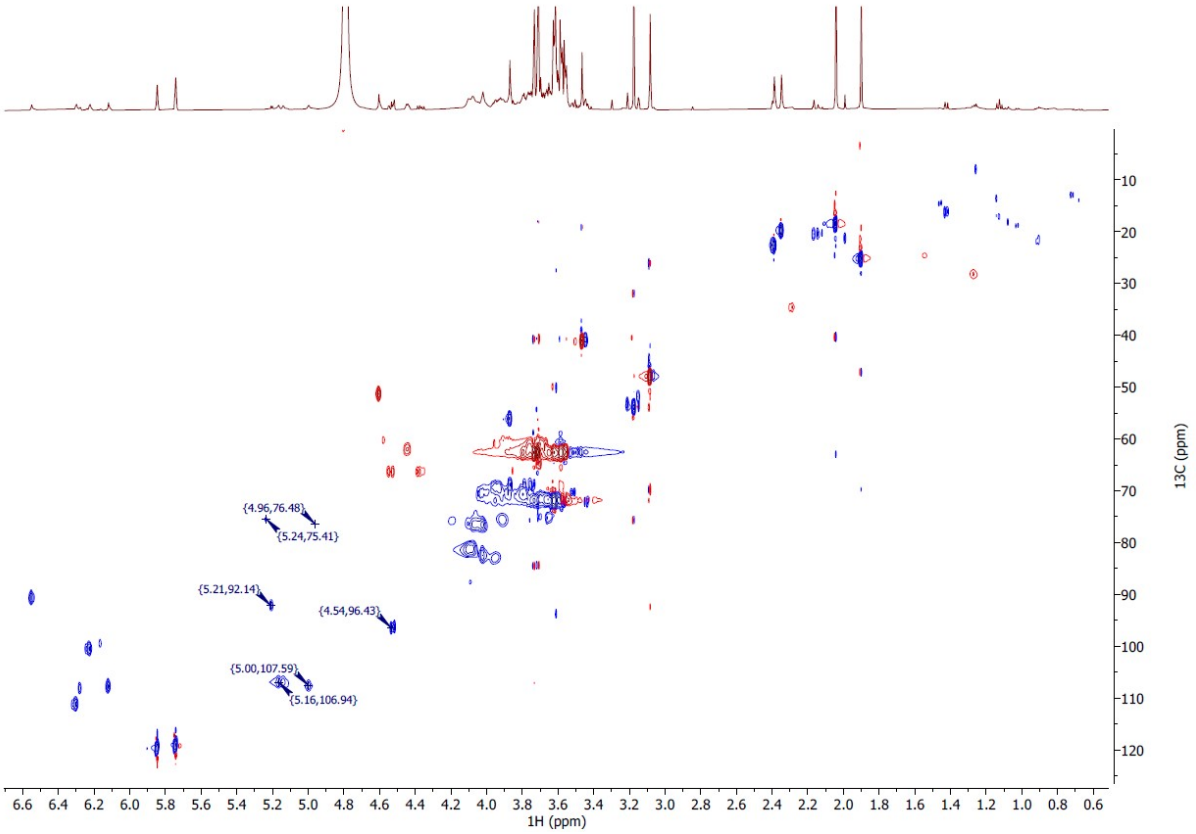
HSQC map of the fraction A2 of *Lasalia pustulata*



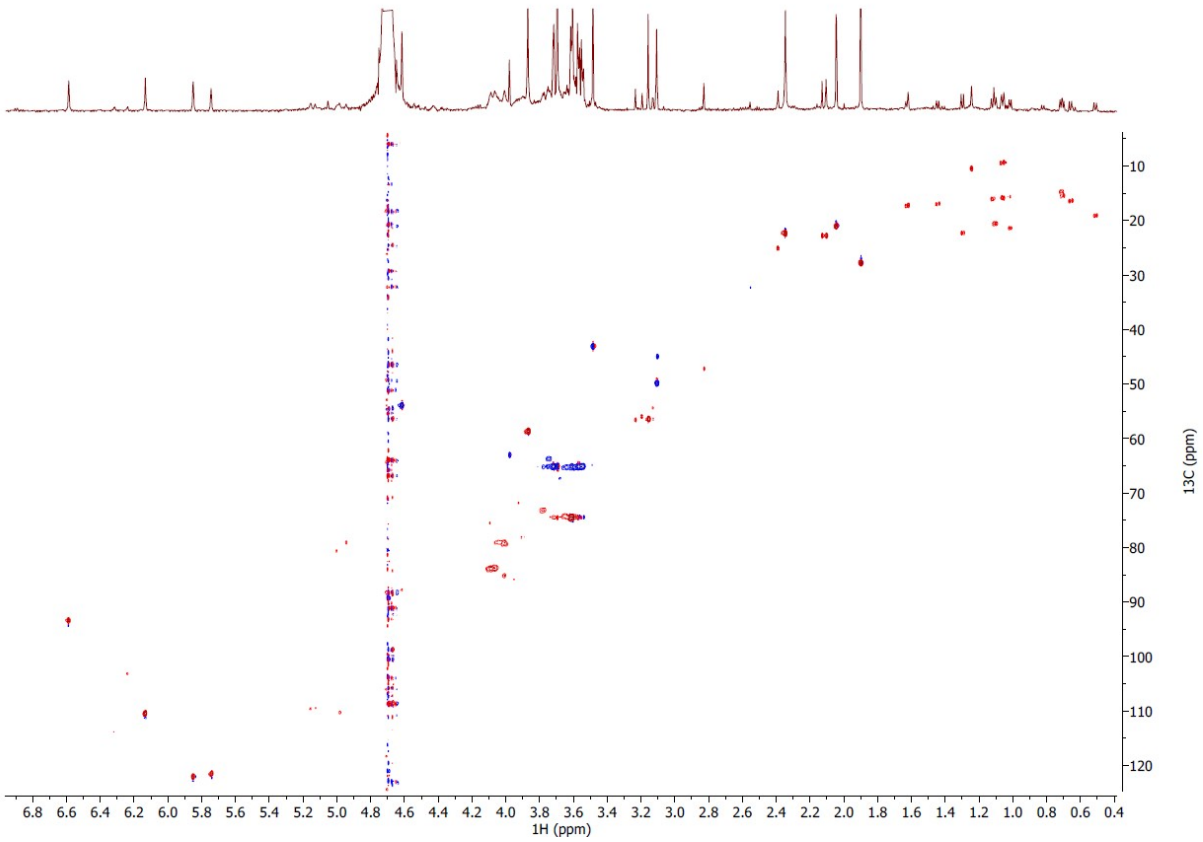
HSQC map of the fraction F1S of *Lasalia pustulata*



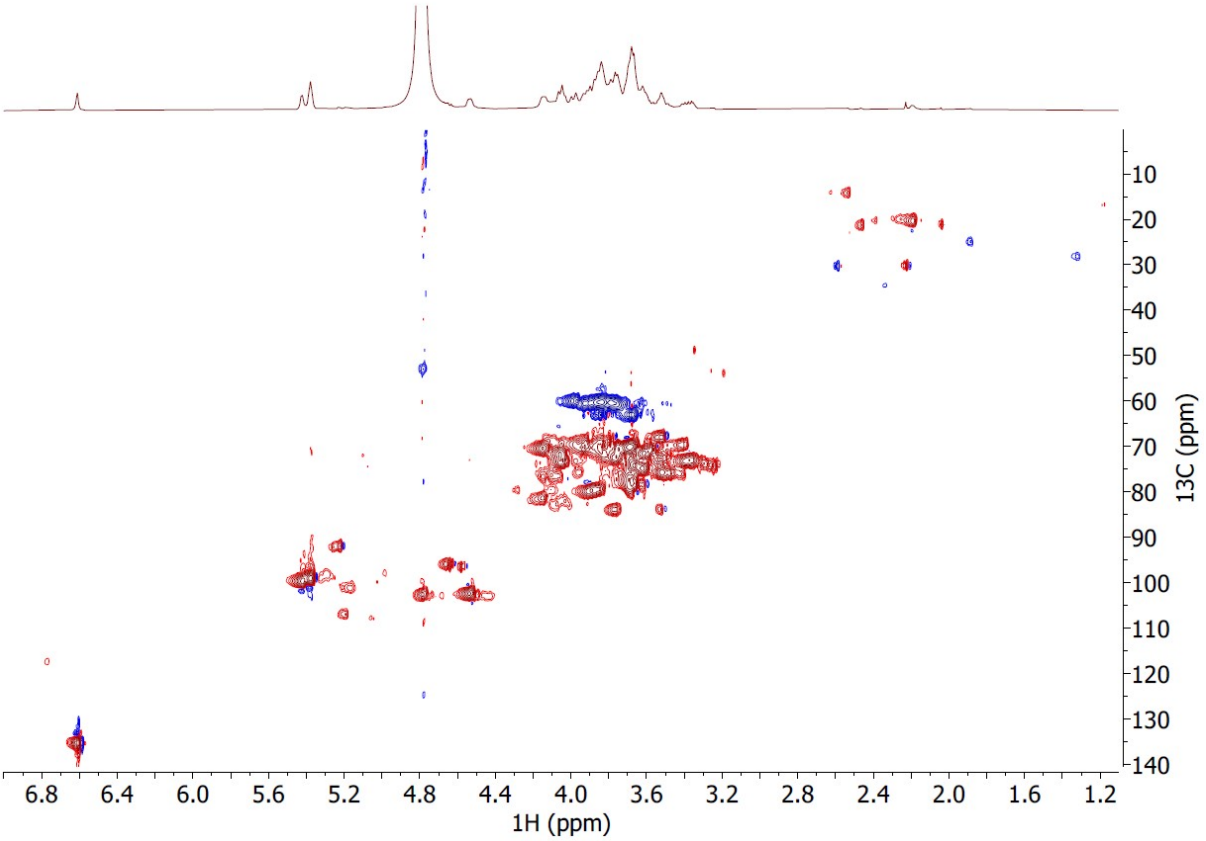
HSQC map of the fraction A2 of *Roccella fuciformis*



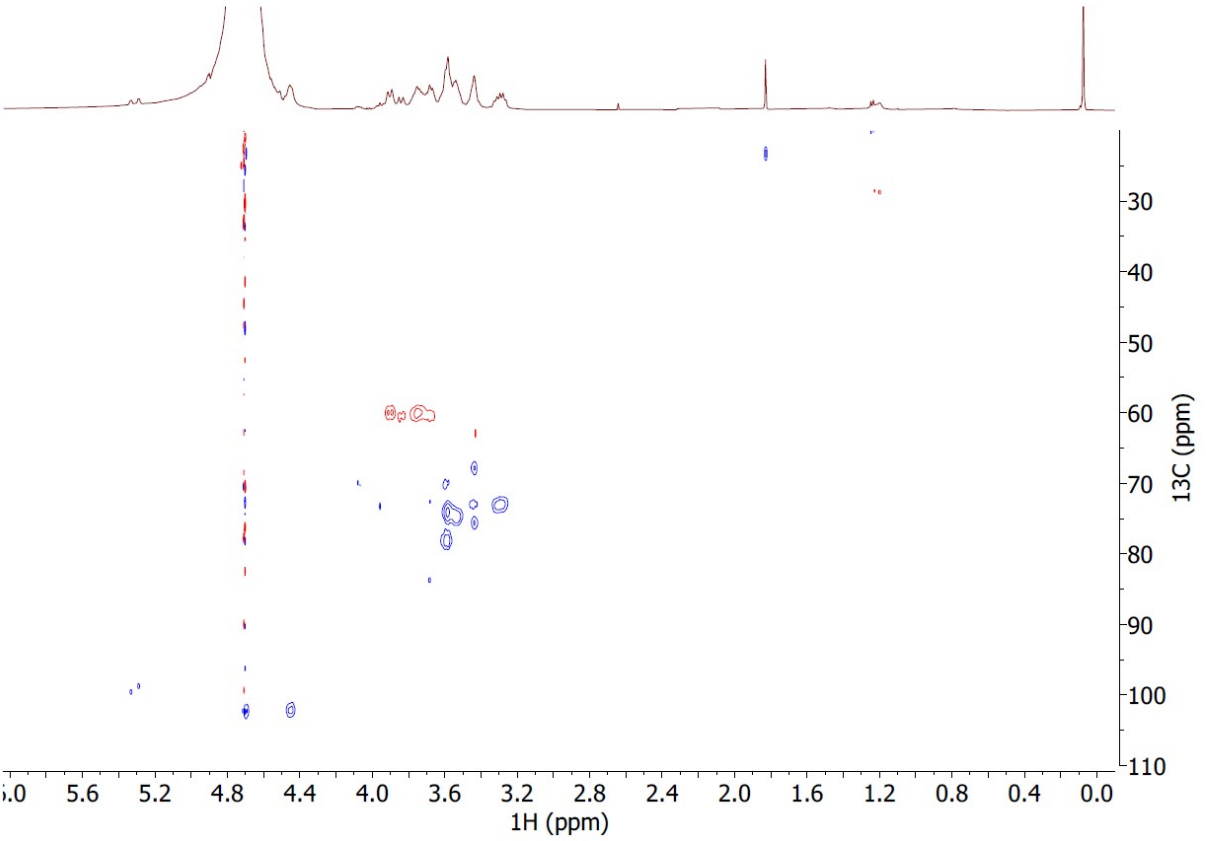
HSQC map of the fraction F1S of *Roccella fuciformis*



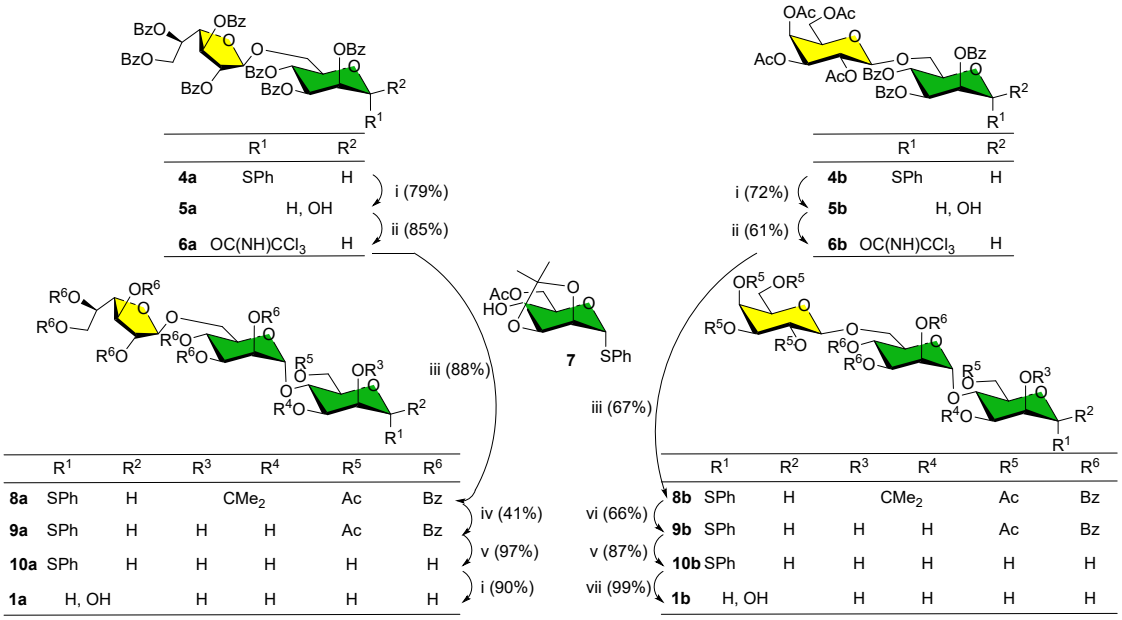
HSQC map of the fraction A2 of *Cetraria islandica*



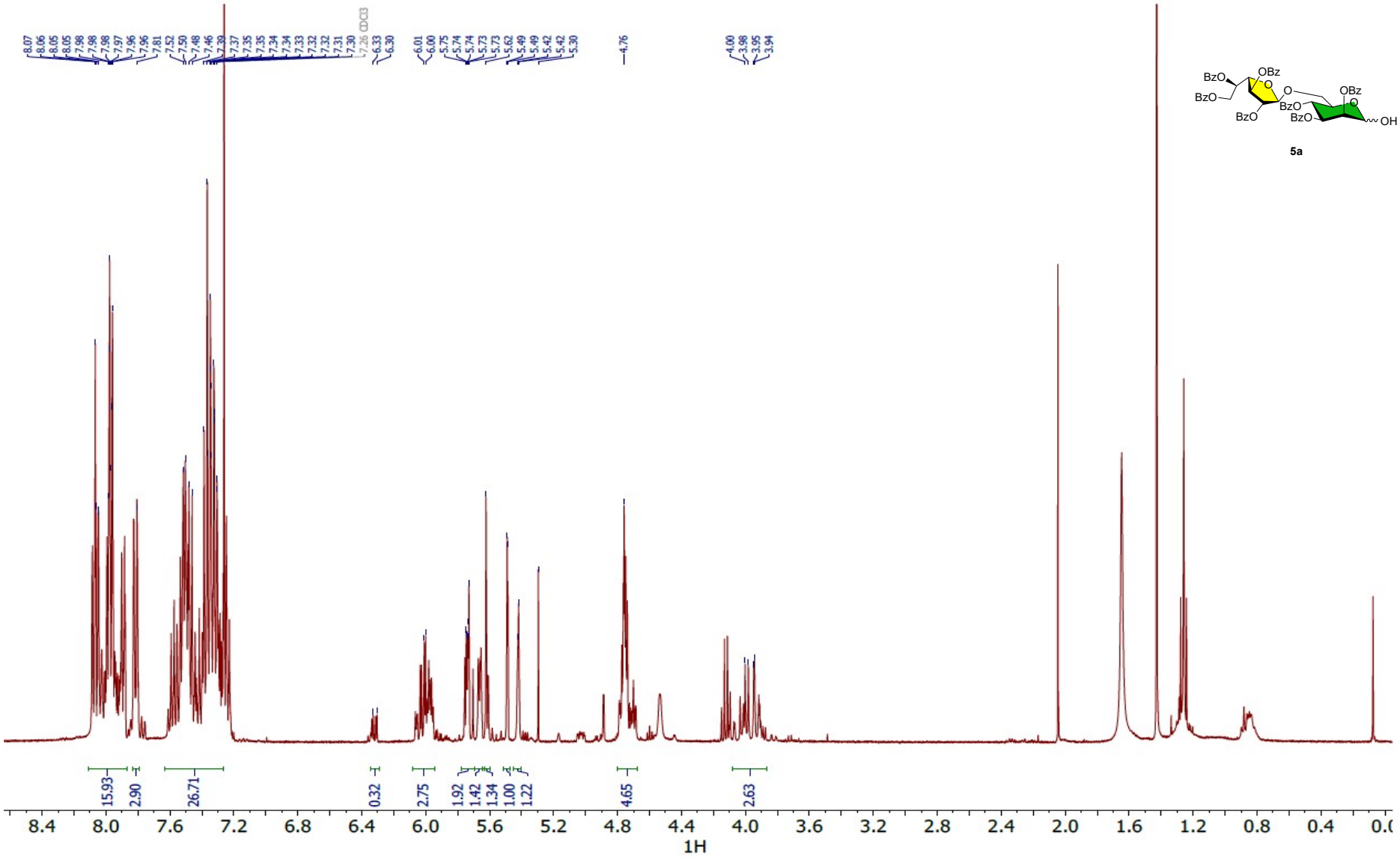
HSQC map of the fraction F1S of *Cetraria islandica*



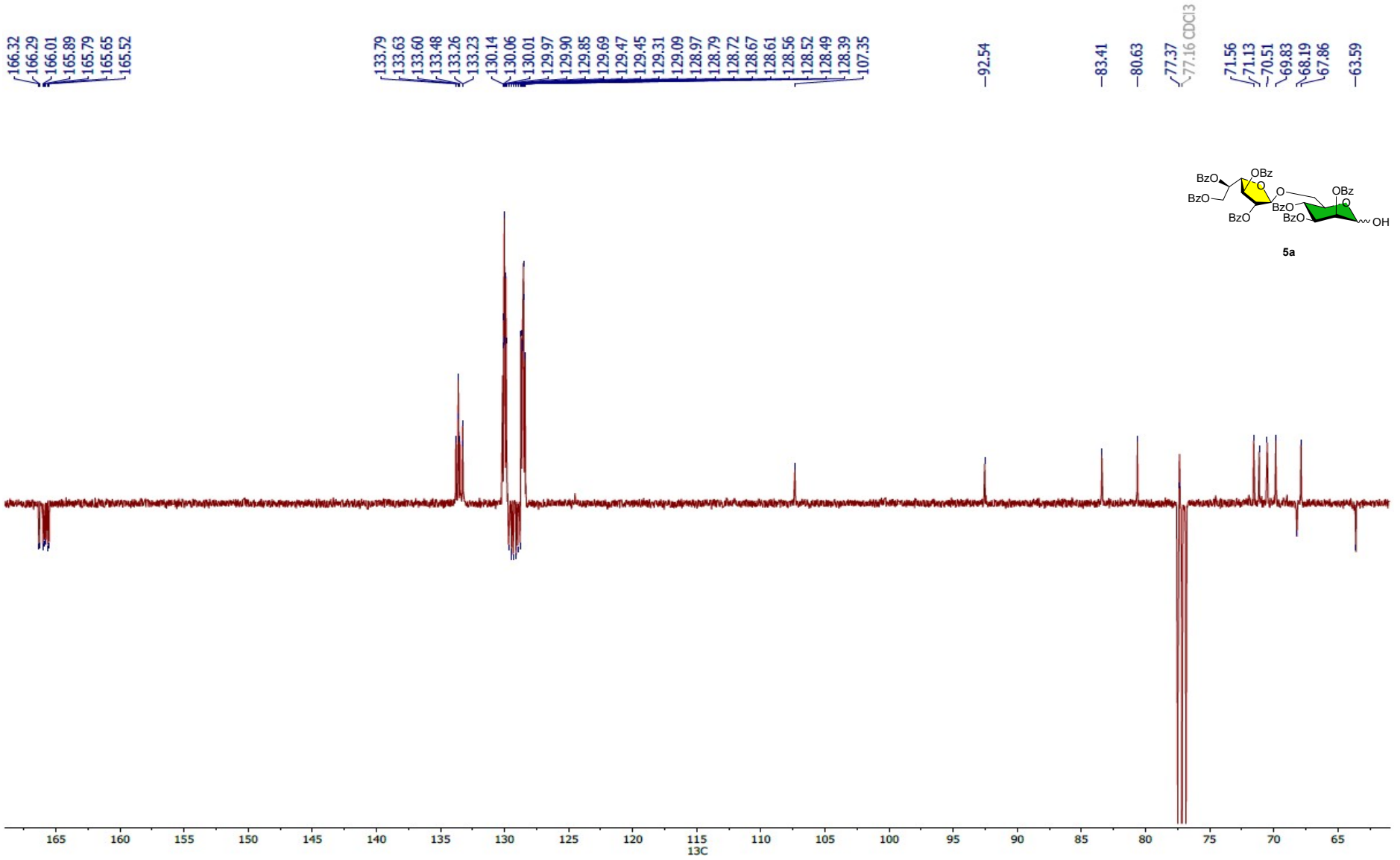
^{1}H and ^{13}C NMR Spectrum of trisaccharides 1 based on Man*p*-(1,4)-Man*p* skeleton



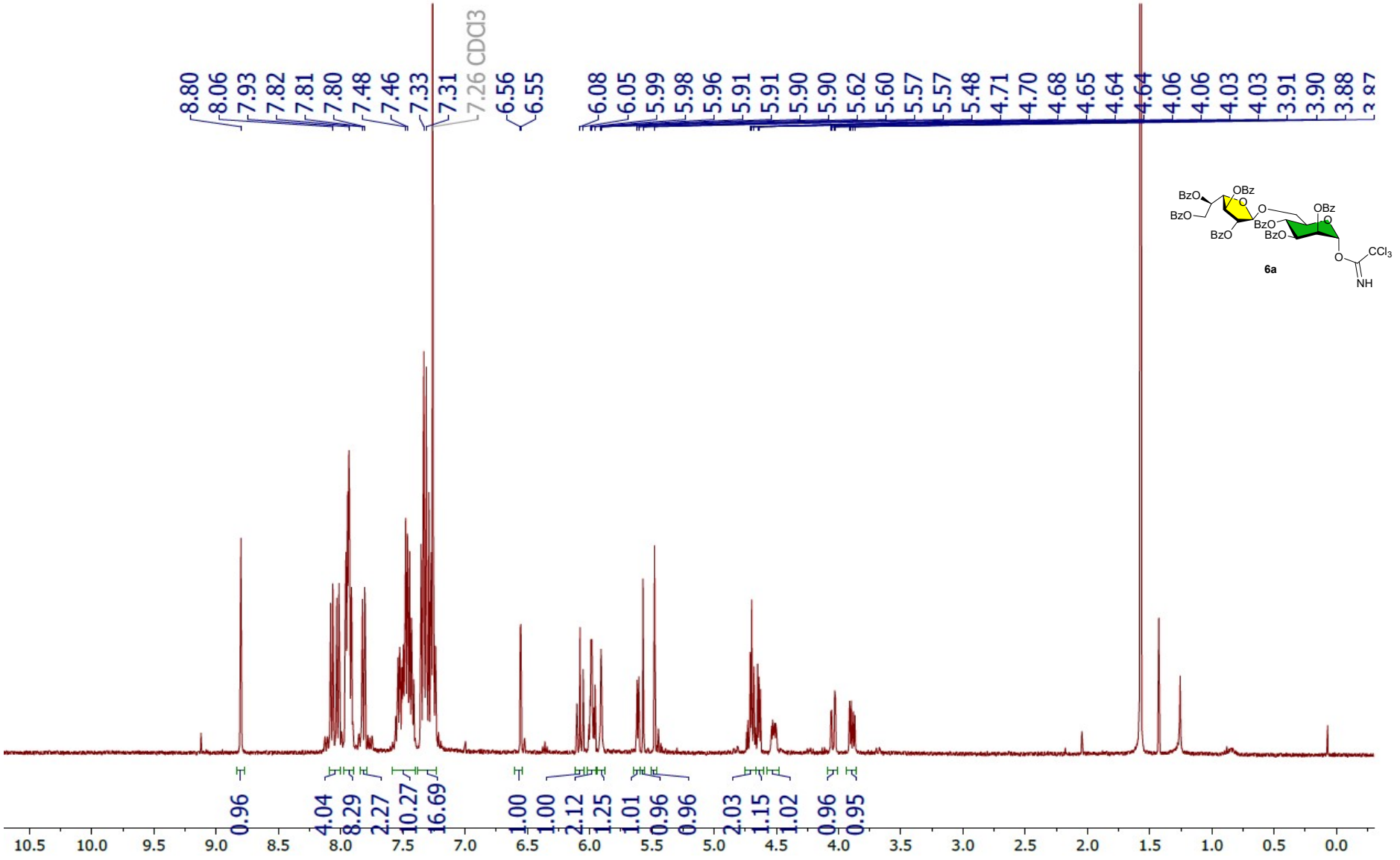
Reagents and conditions: (i) *N*-Iodosaccharin, $H_2O/CH_3CN/CH_2Cl_2$; (ii) Cl_3CCN, DBU, CH_2Cl_2; (iii) **5**, TMSOTf, CH_2Cl_2; (iv) TFA, DTT, CH_2Cl_2; (v) NaOMe, MeOH; (vi) TFA, CH_2Cl_2; (vii) *N*-bromosuccinimide, Acetone/H_2O



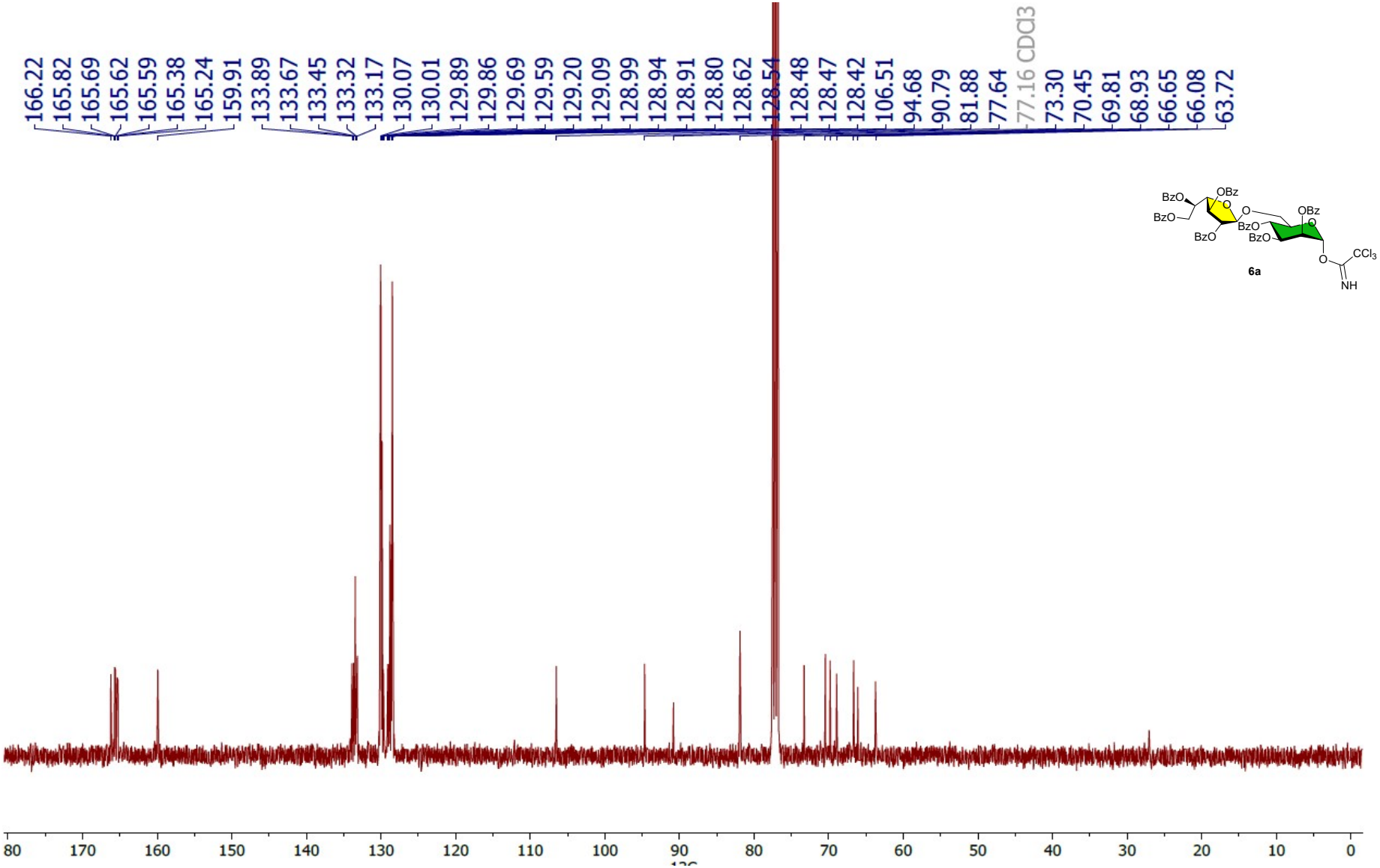
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **5a**



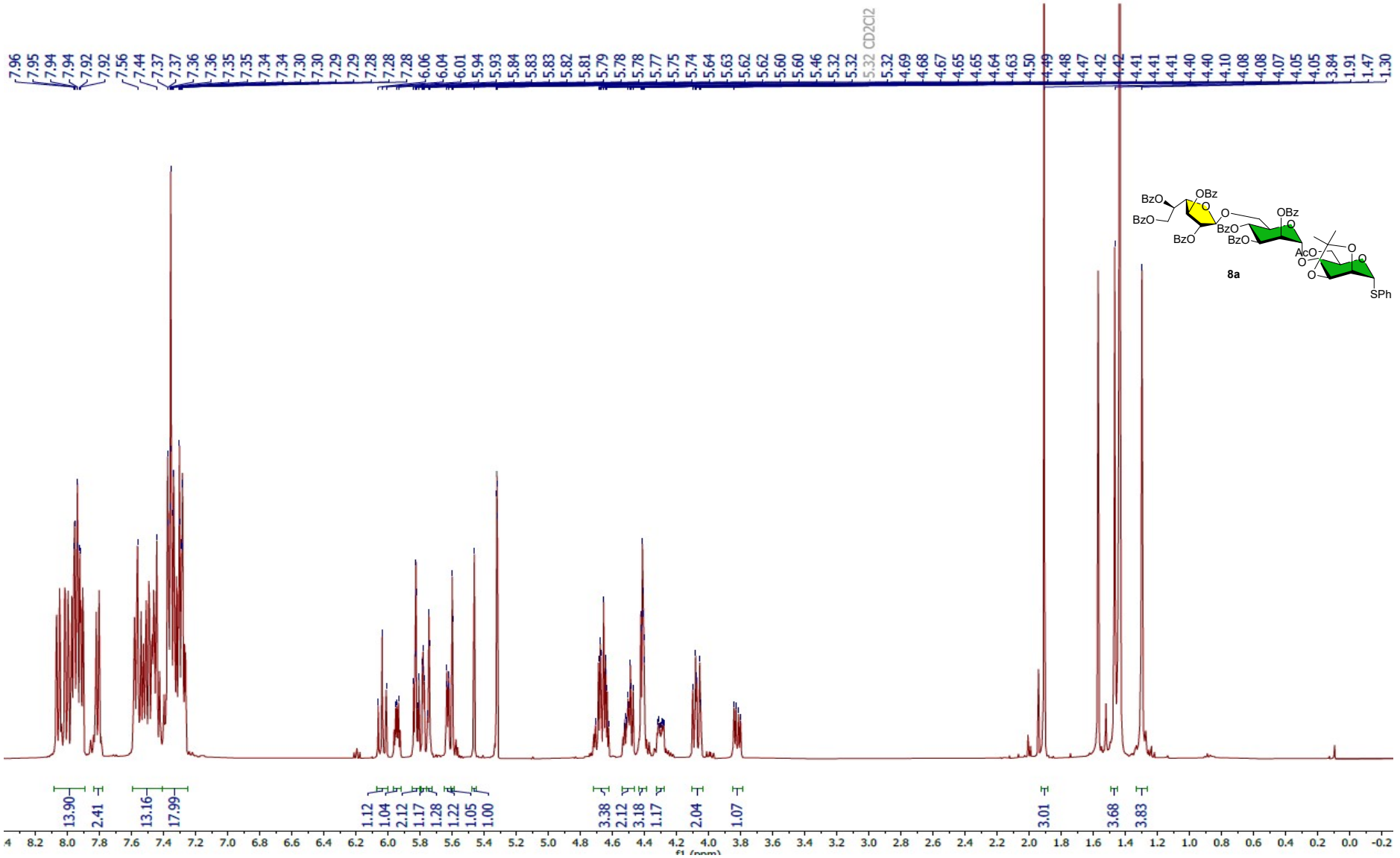
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **5a**



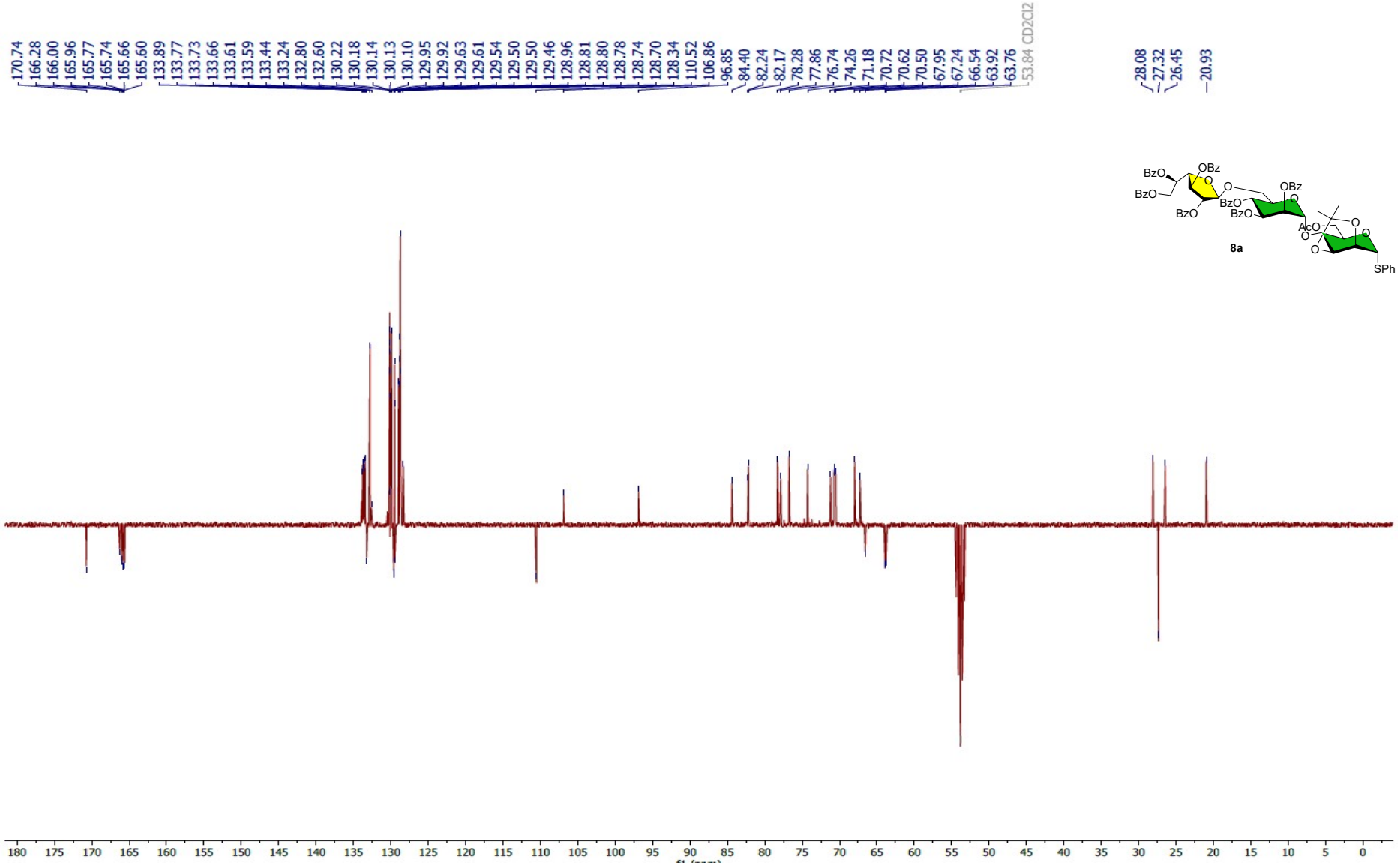
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **6a**


166.22
165.82
165.69
165.62
165.59
165.38
165.24
159.91
133.89
133.67
133.45
133.32
133.17
130.07
130.01
129.89
129.86
129.69
129.59
129.20
129.09
128.99
128.94
128.91
128.80
128.62
128.54
128.48
128.47
128.42
106.51
94.68
90.79
81.88
77.64
77.16 CDCl3
73.30
70.45
69.81
68.93
66.65
66.08
63.72
BzO
OBz
O
BzO
BzO
BzO
OBz
O
BzO
O
CCl3
NH
6a
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

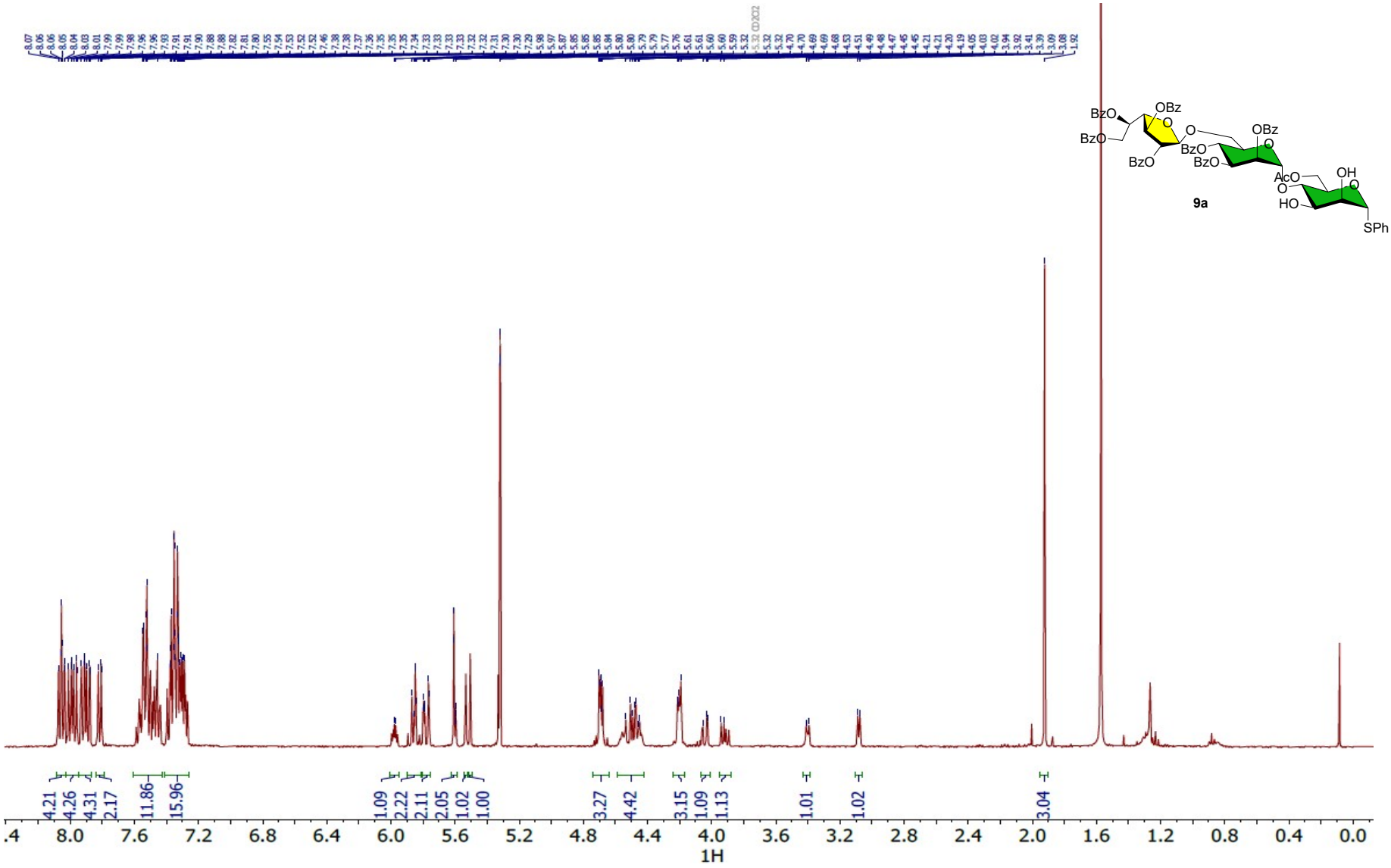
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **6a**



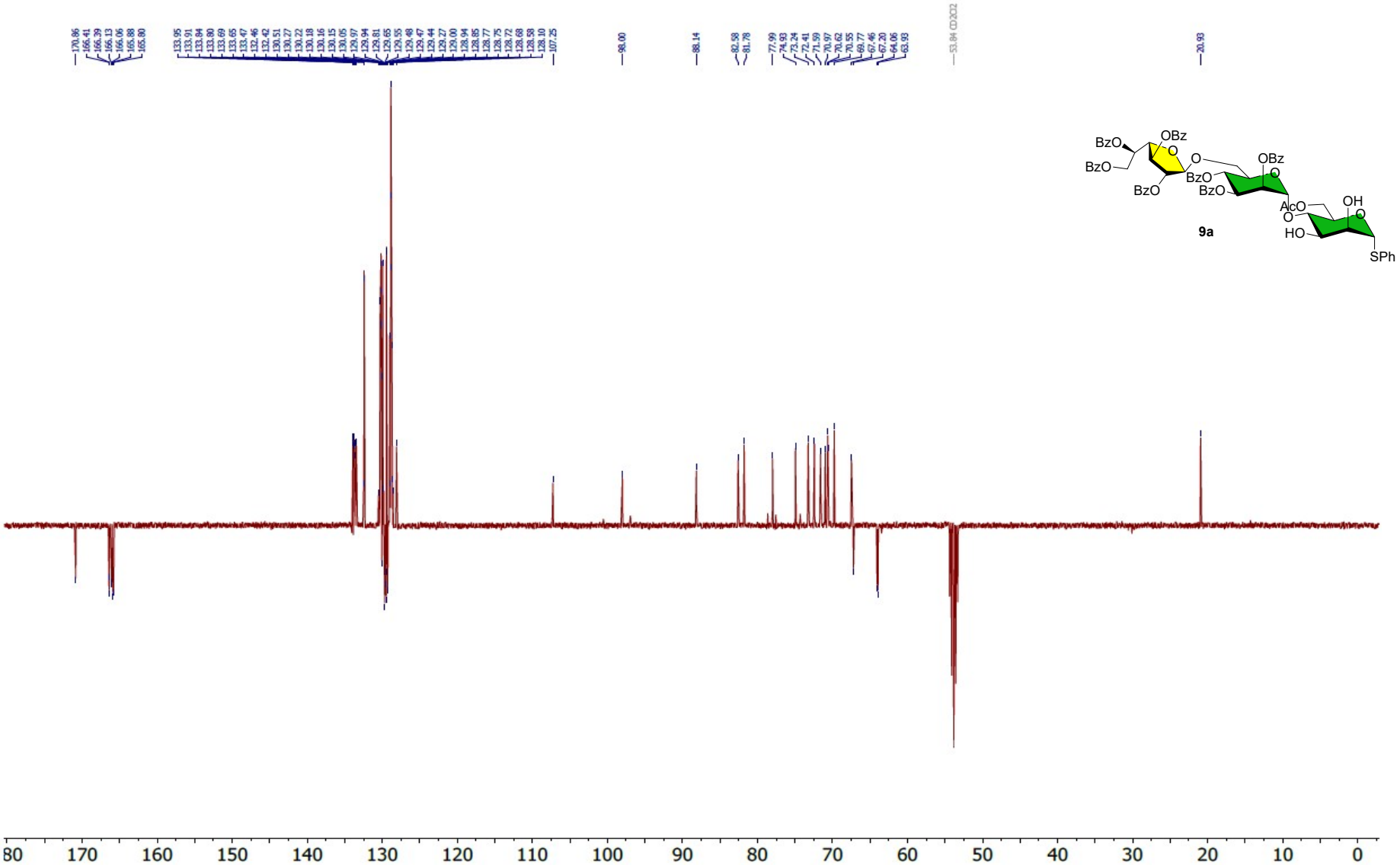
^{1}H NMR (CD_2Cl_2, 400 MHz) of compound **8a**



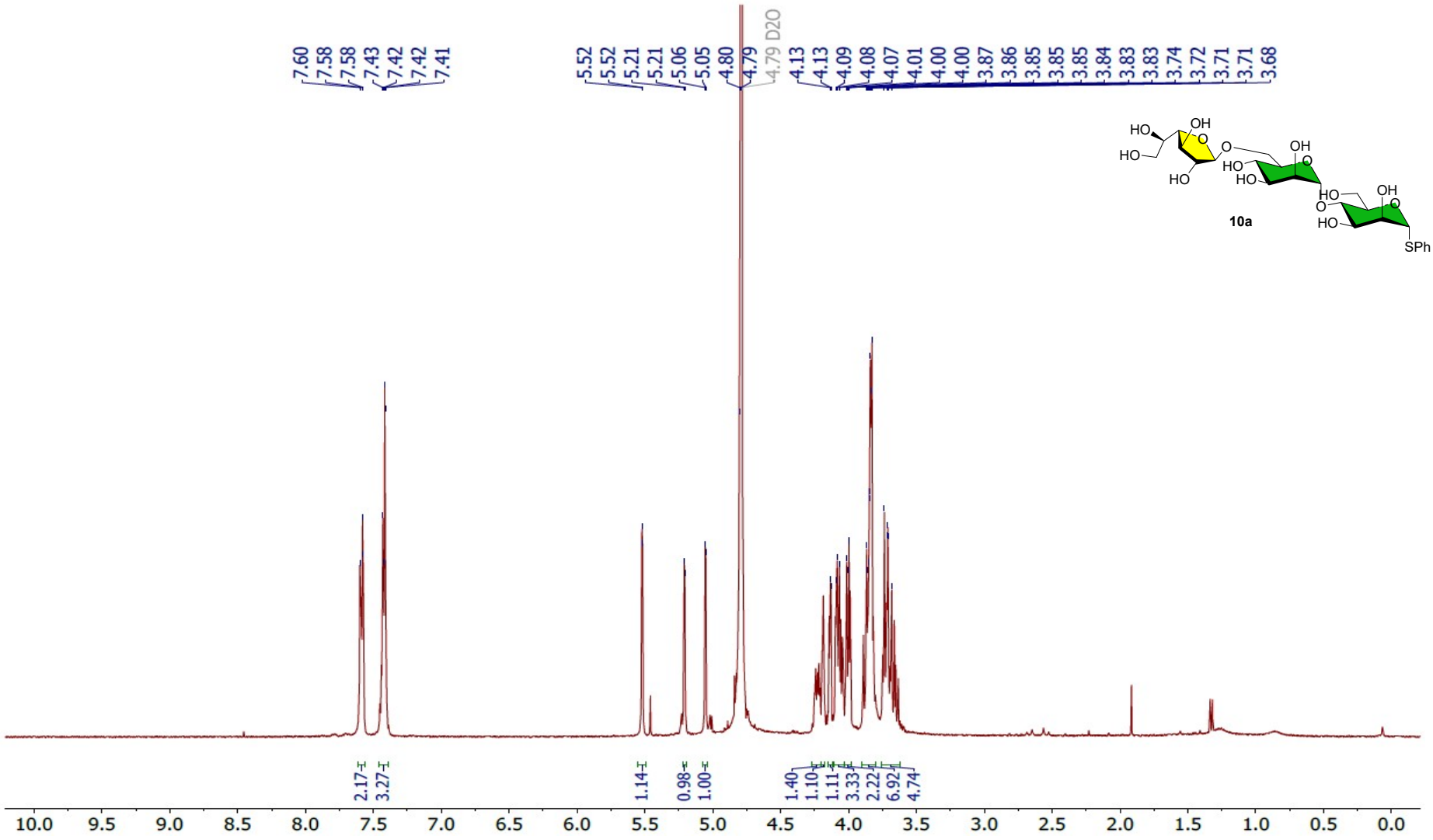
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **8a**



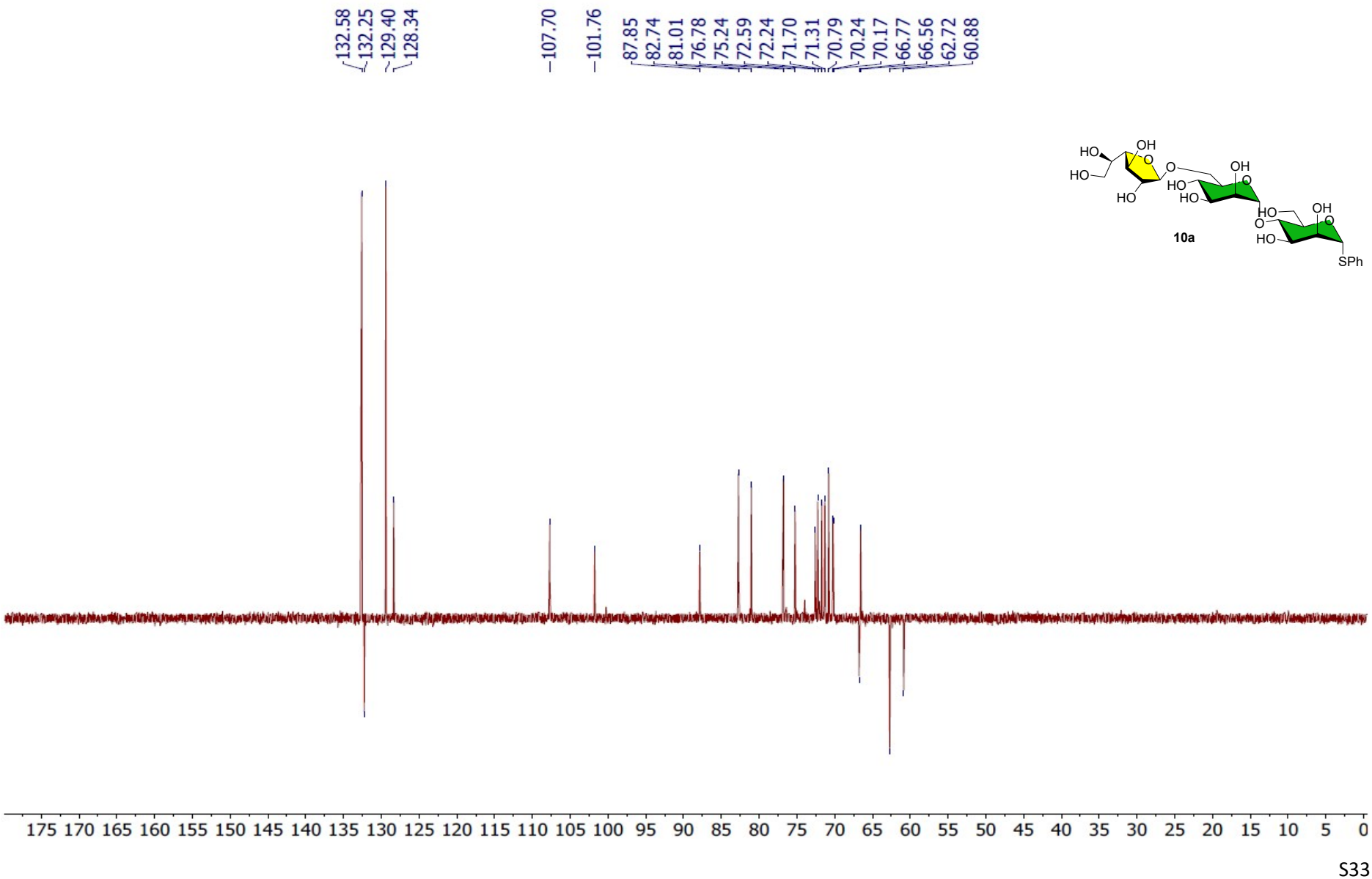
^{1}H NMR (CD_2Cl_2, 400 MHz) of compound **9a**



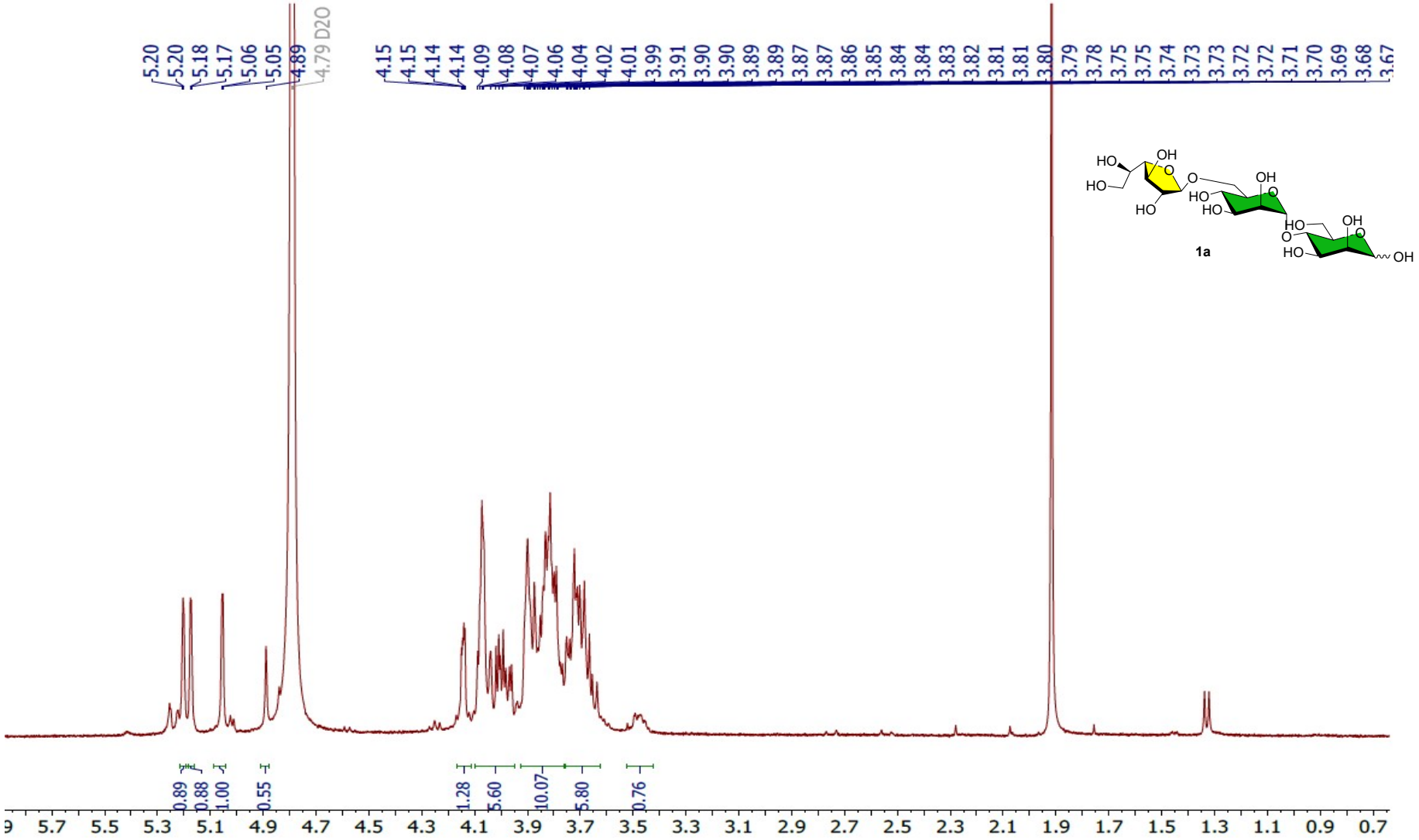
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **9a**



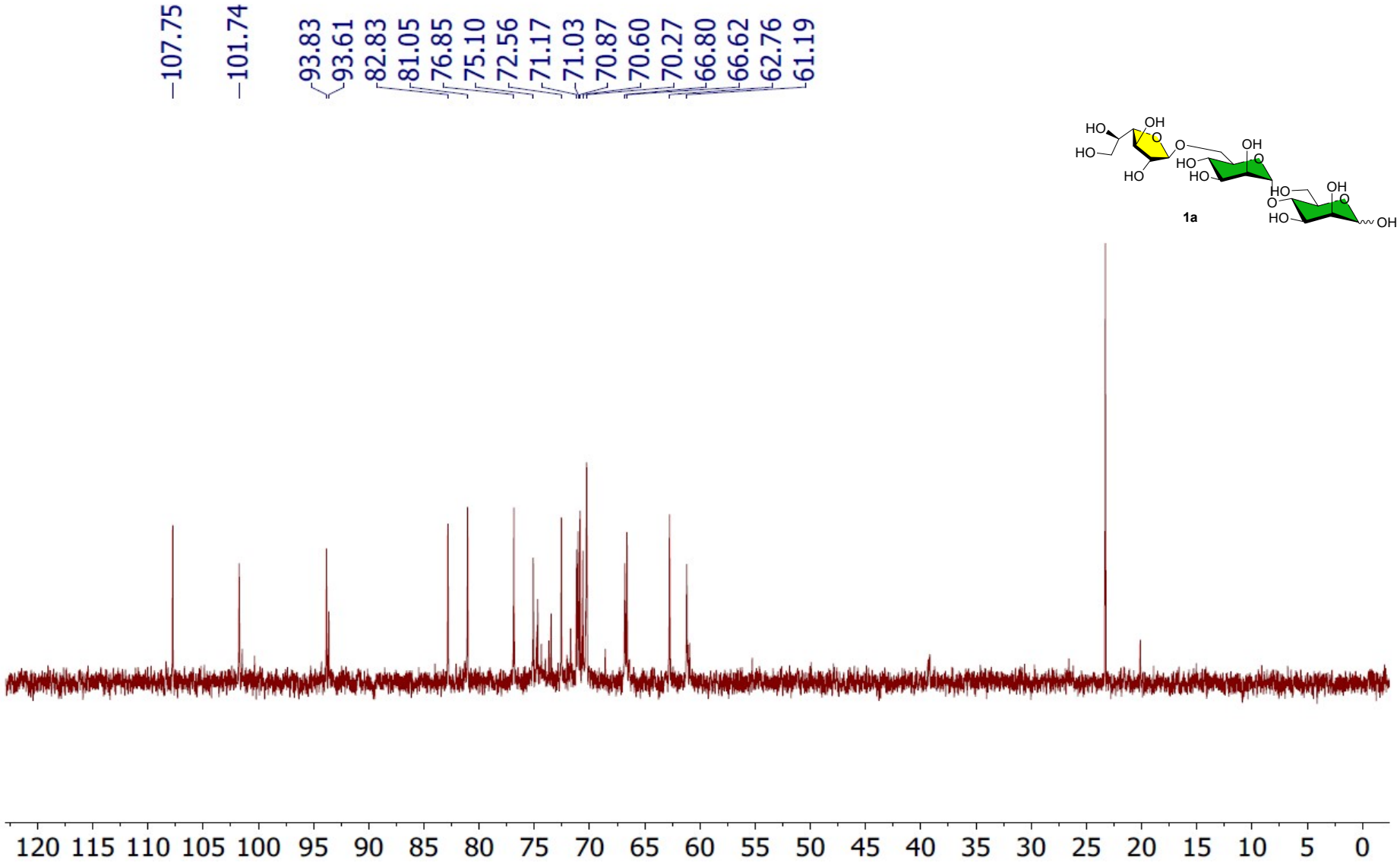
^{1}H NMR (D_2O, 400 MHz) of compound **10a**



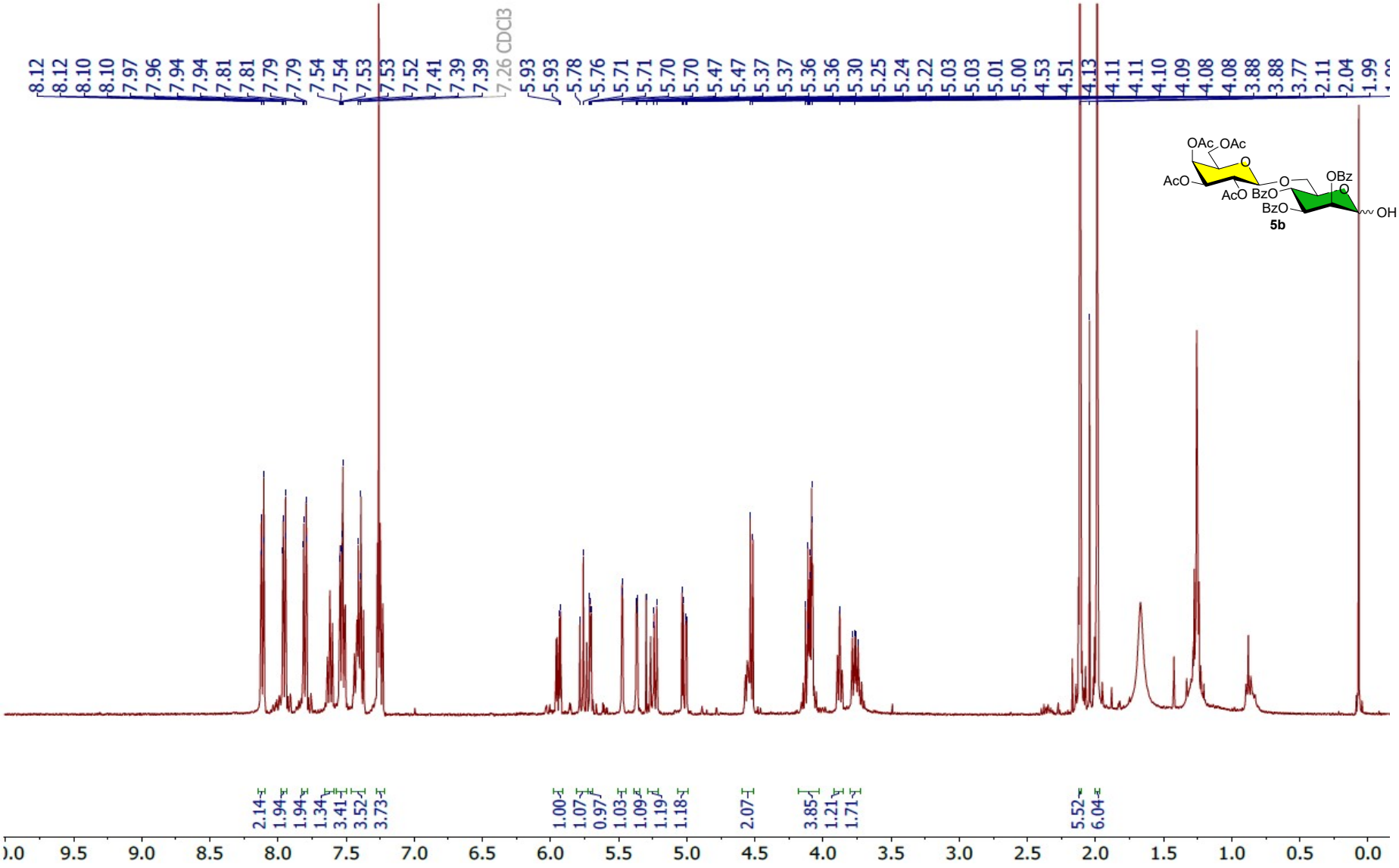
^{13}C NMR (D_2O, 100 MHz) of compound **10a**



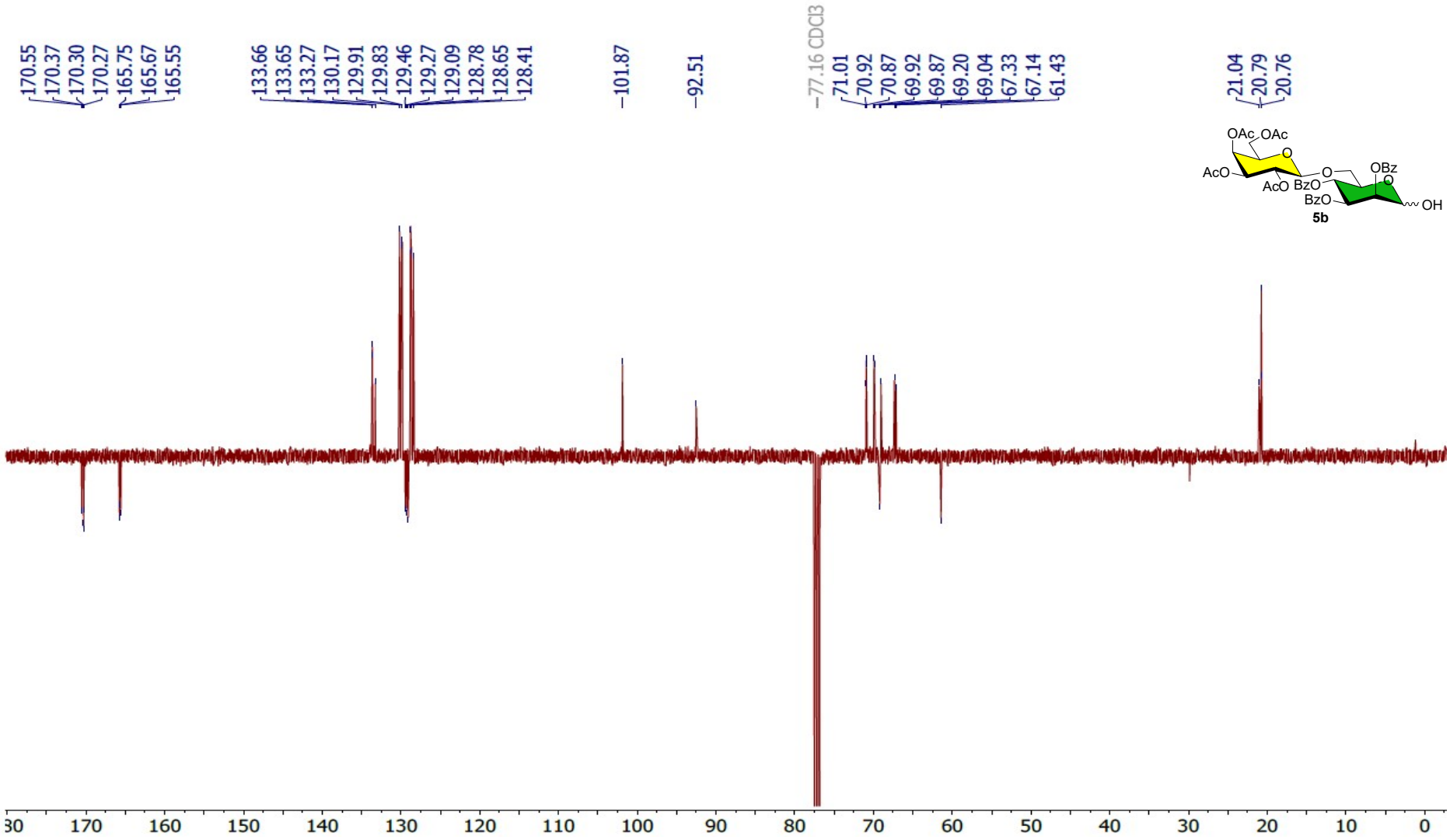
^{1}H NMR (D_2O, 400 MHz) of compound **1a**



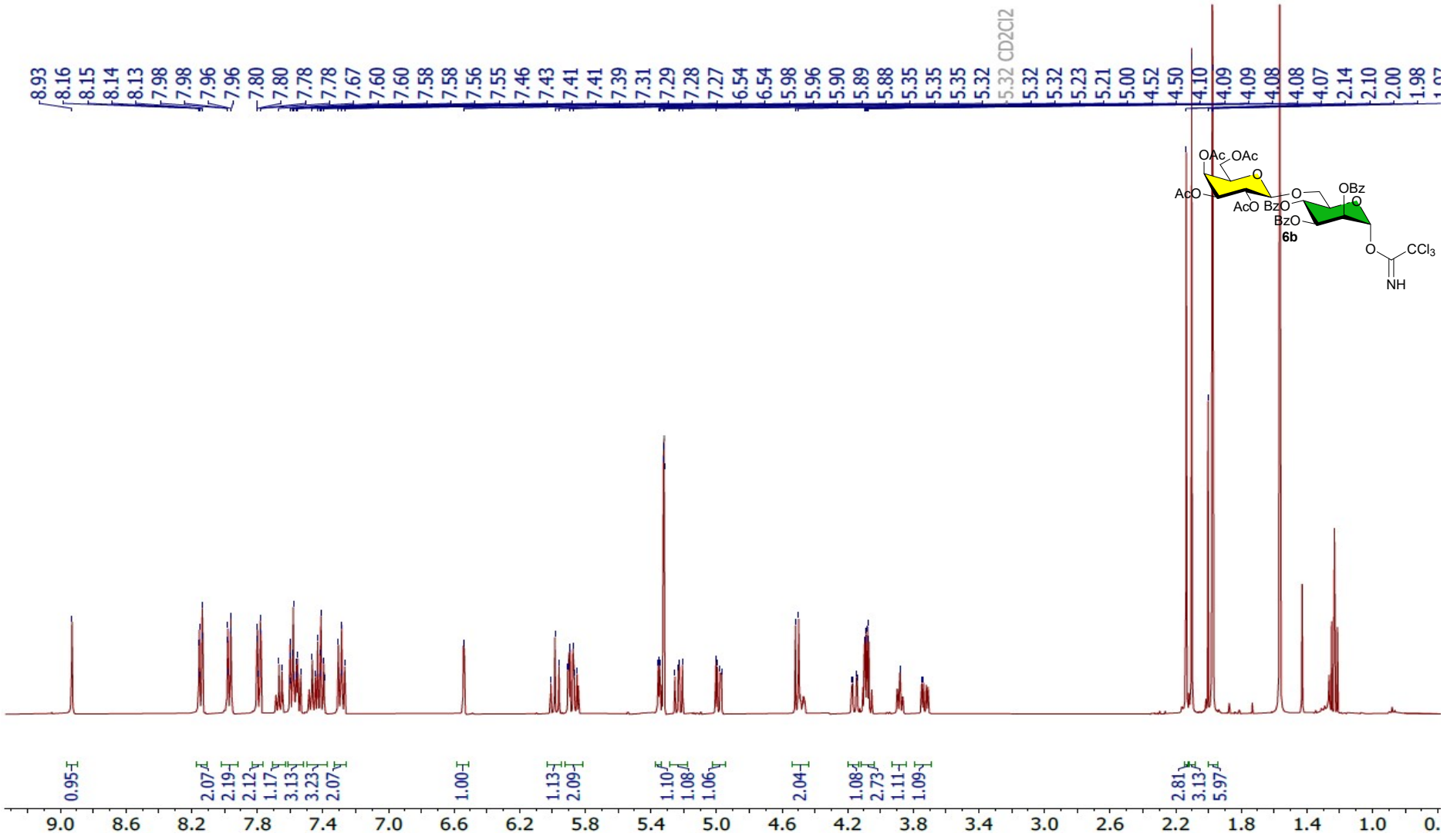
^{13}C NMR (D_2O, 100 MHz) of compound **1a**



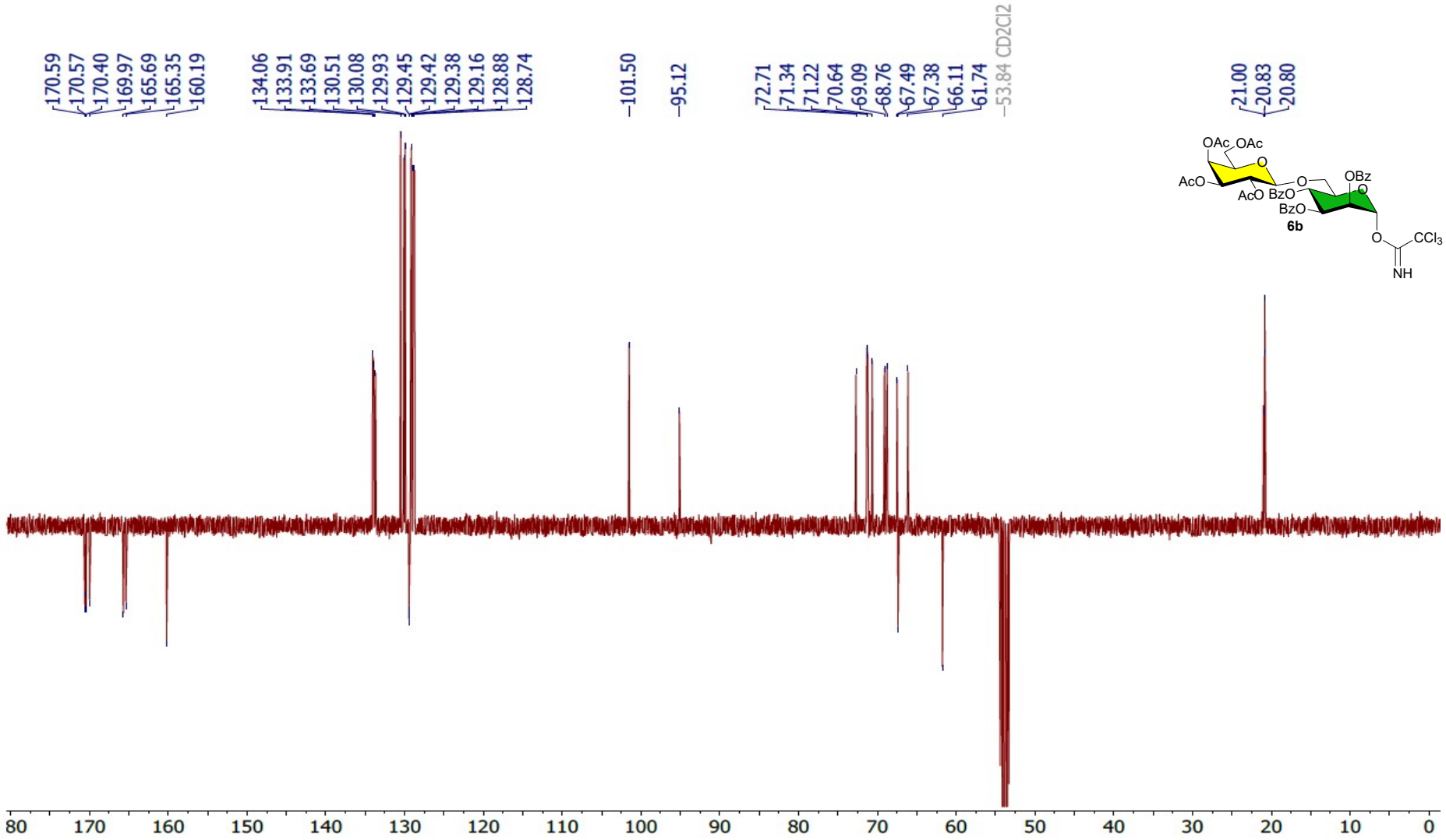
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **5b**



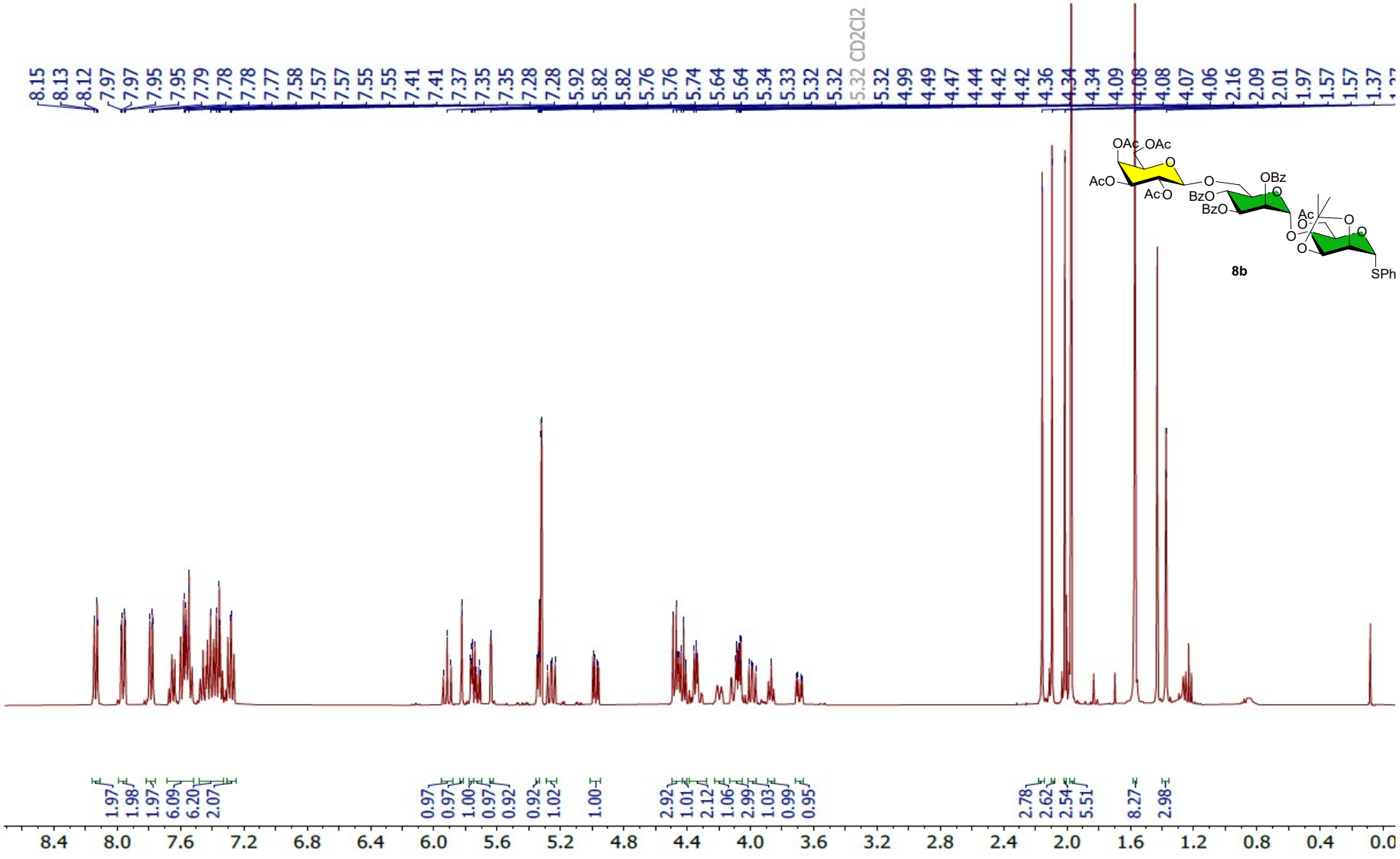
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **5b**



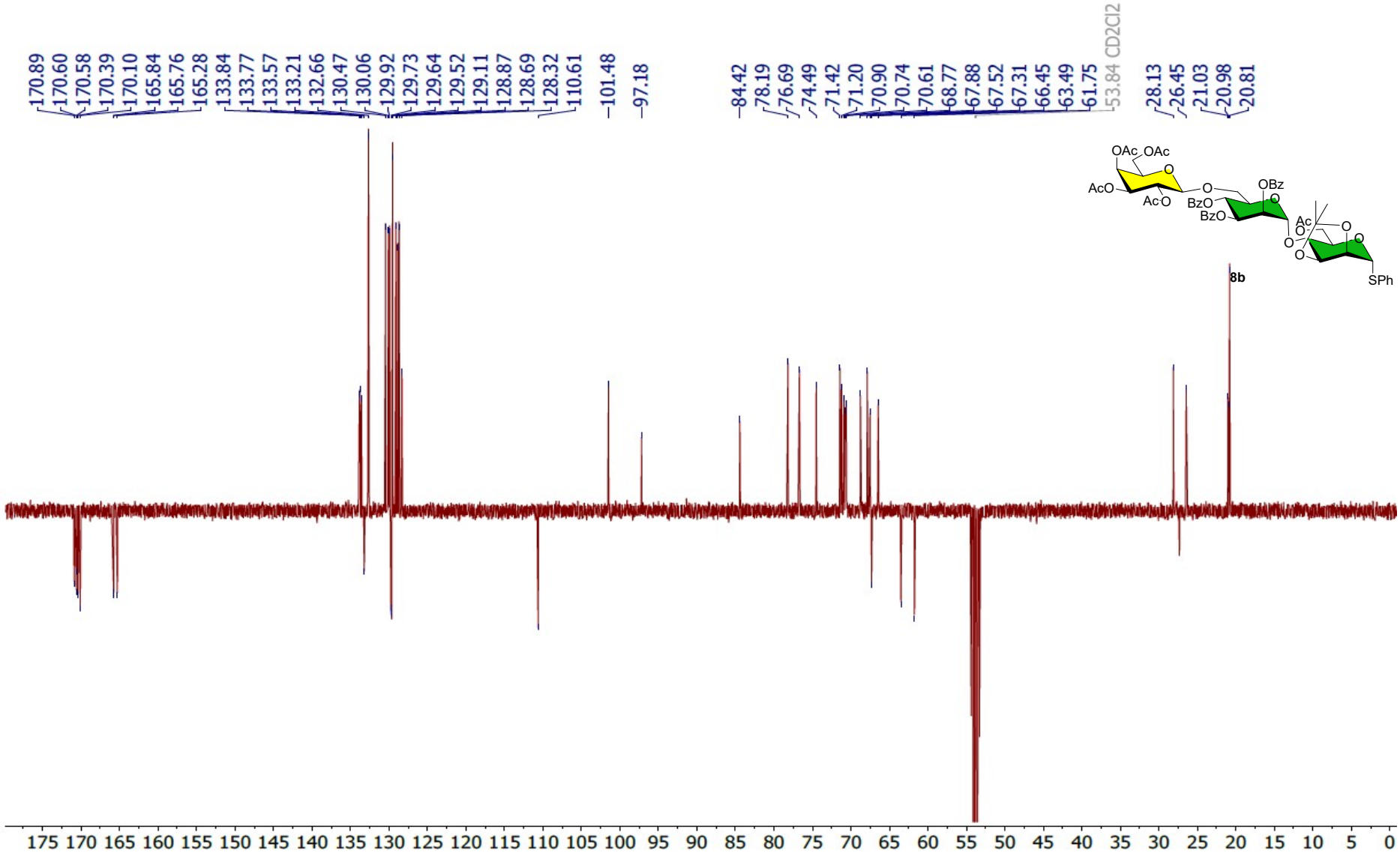
^{1}H NMR (CD_2Cl_2, 400 MHz) of compound **6b**



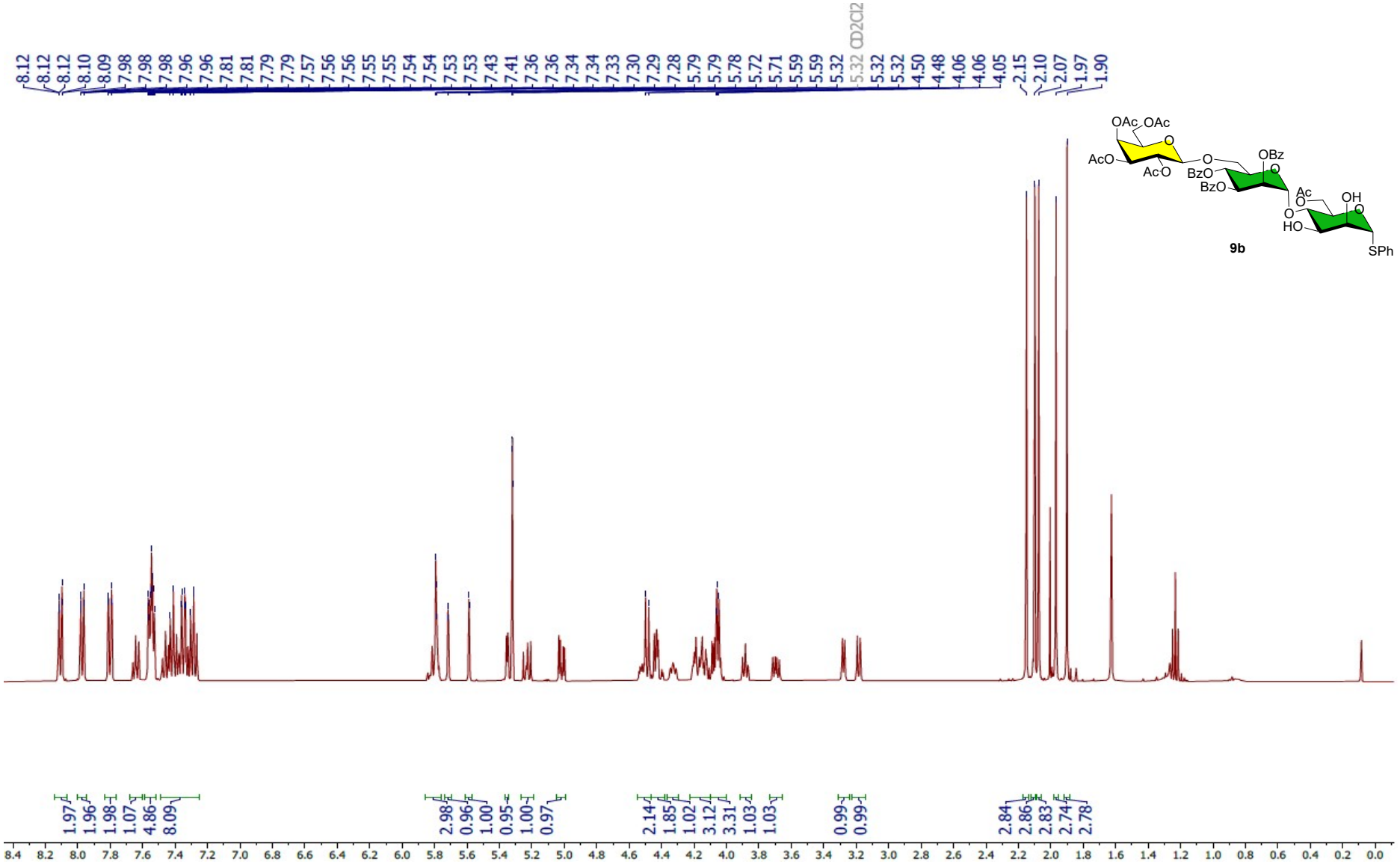
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **6b**



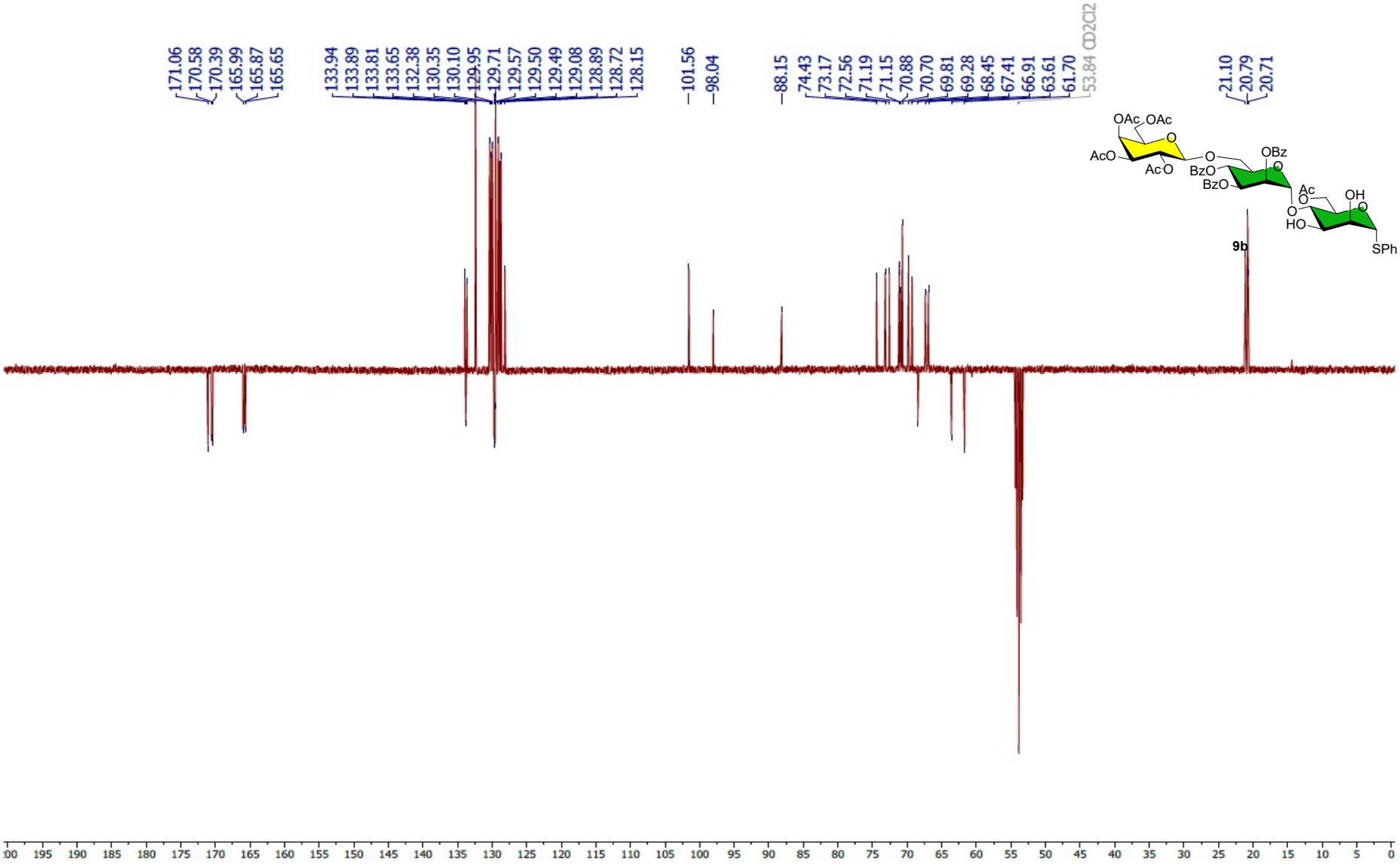
^{1}H NMR (CD_2Cl_2, 400 MHz) of compound **8b**



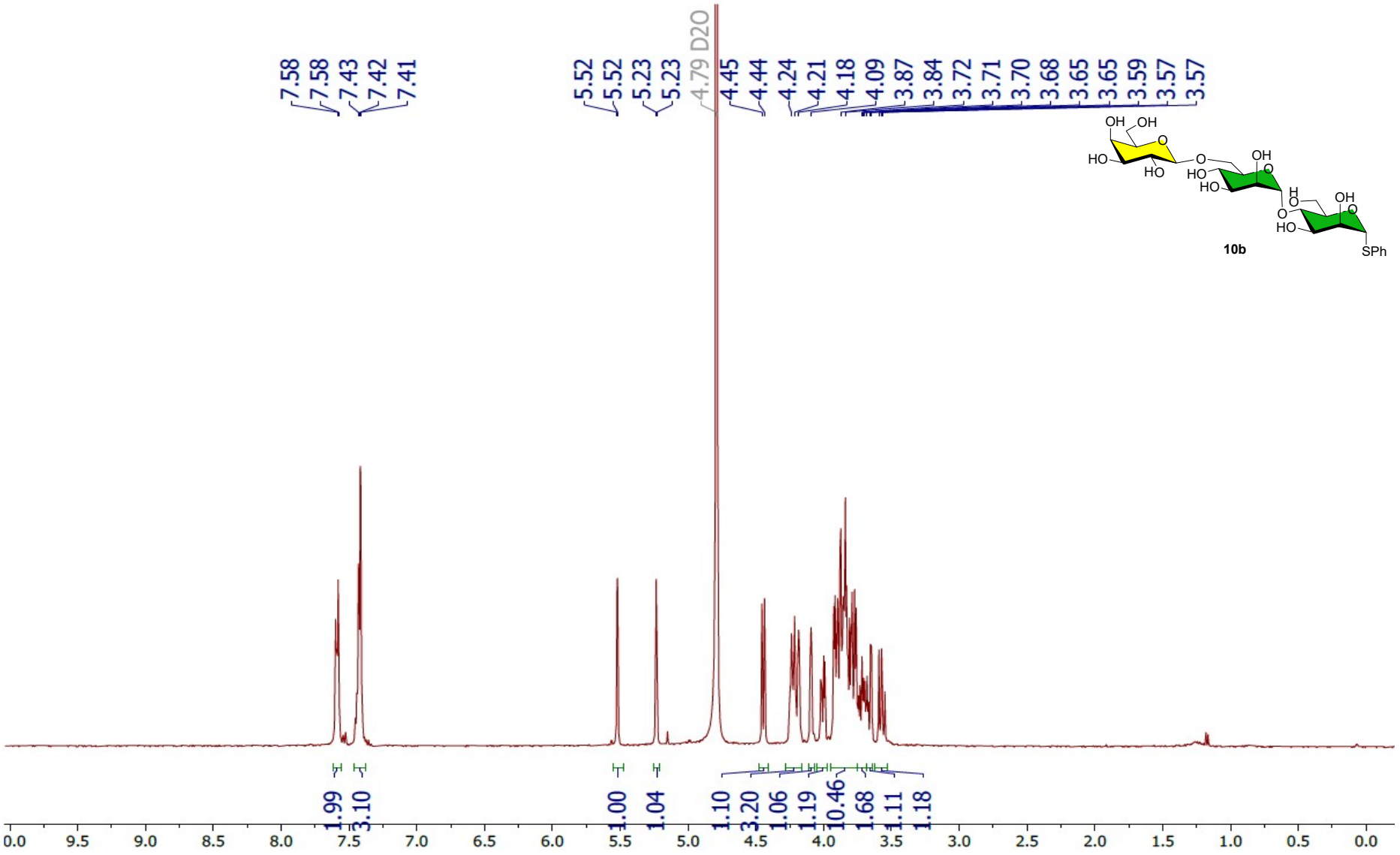
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **8b**



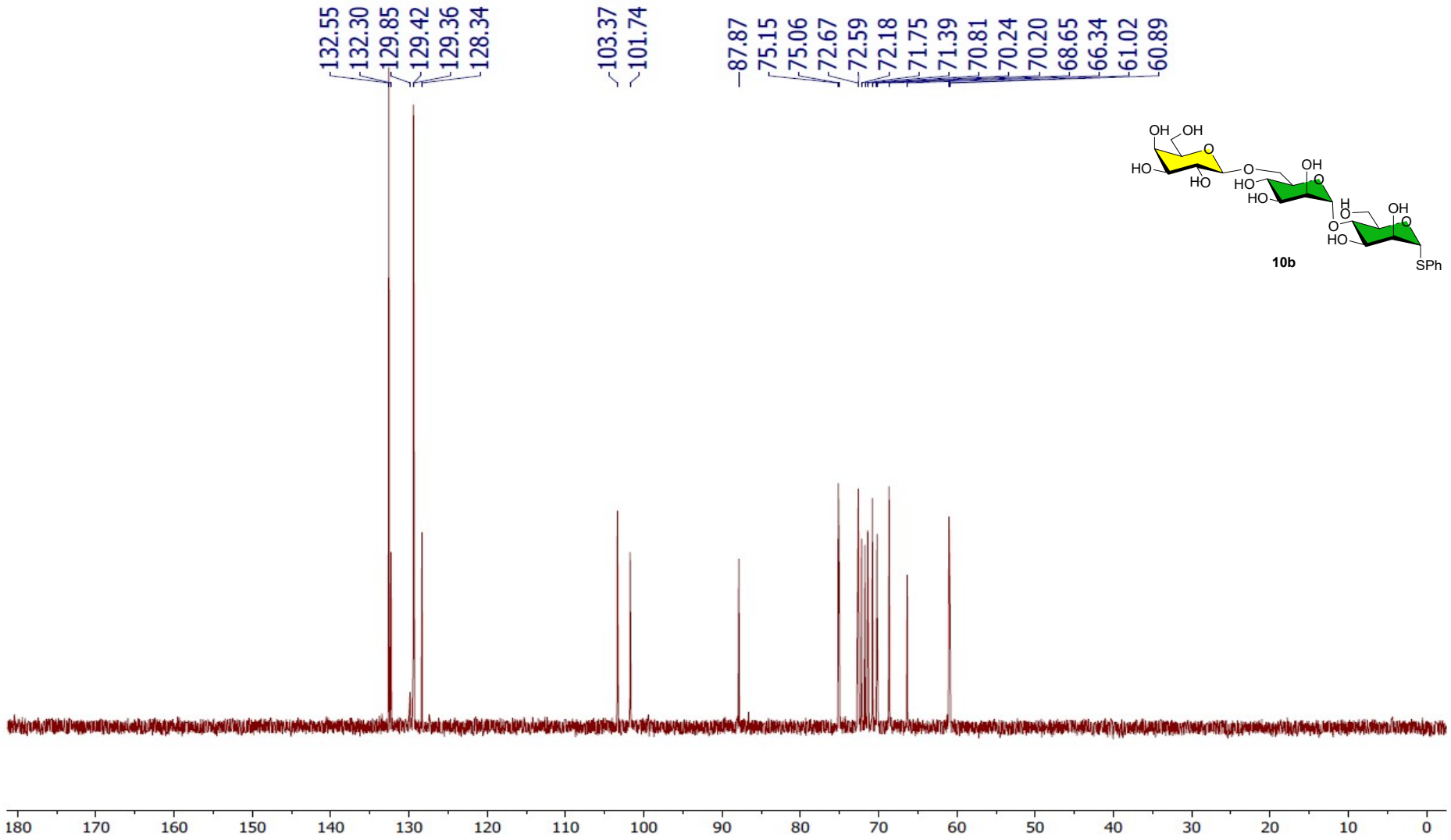
^{1}H NMR (CD_2Cl_2, 400 MHz) of compound **9b**



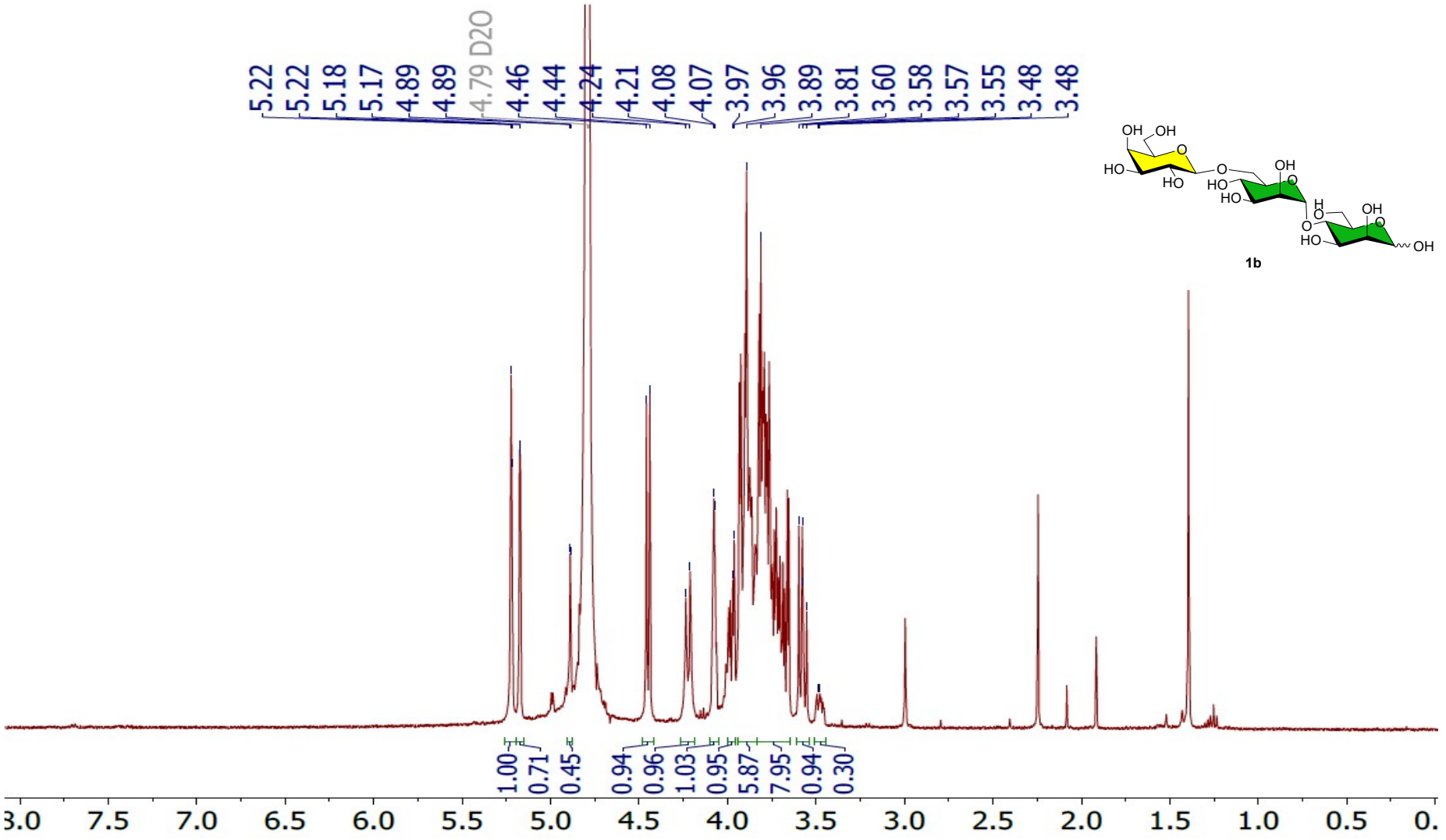
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **9b**



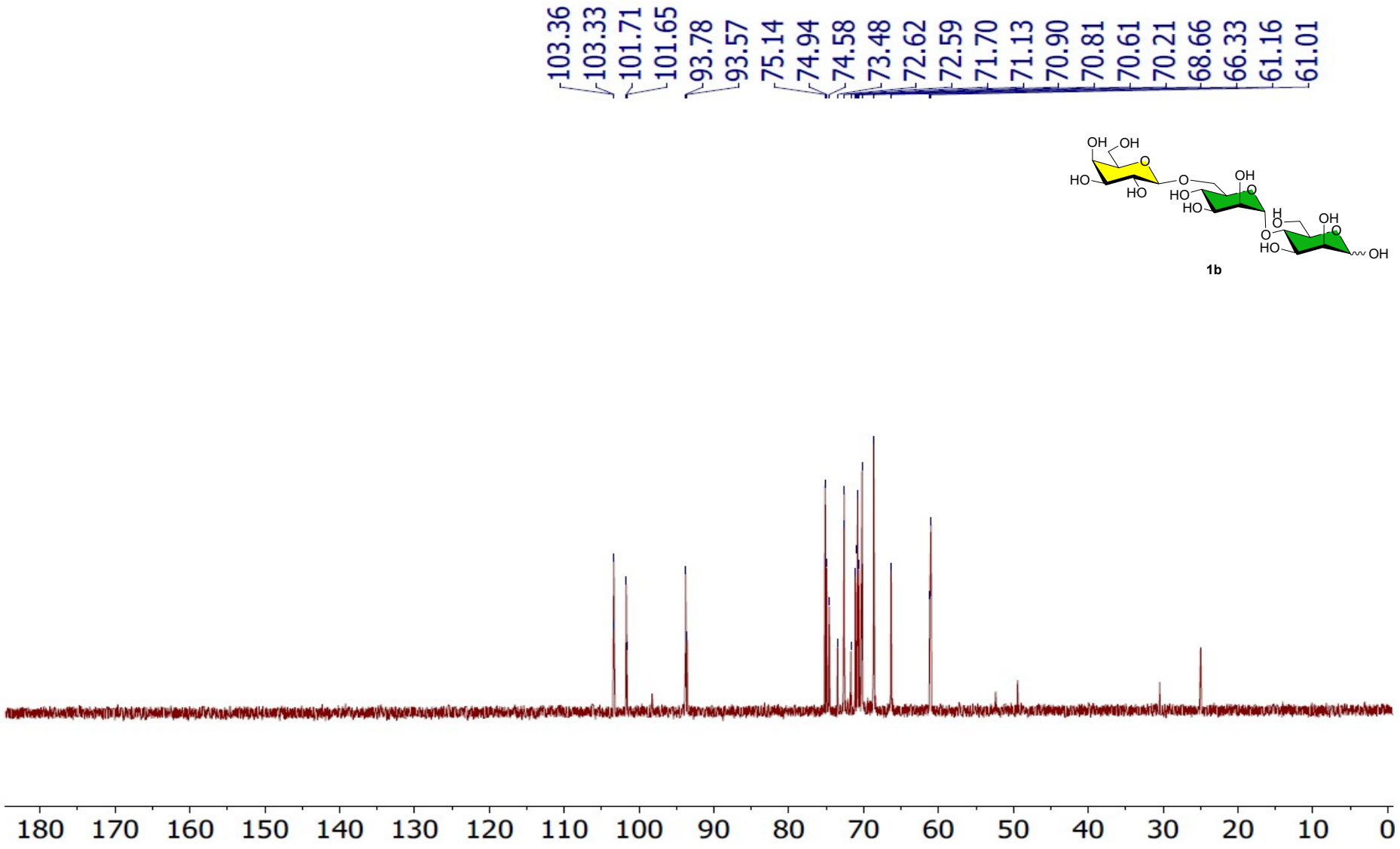
^{1}H NMR (D_2O, 400 MHz) of compound **10b**



^{13}C NMR (D_2O, 100 MHz) of compound **10b**

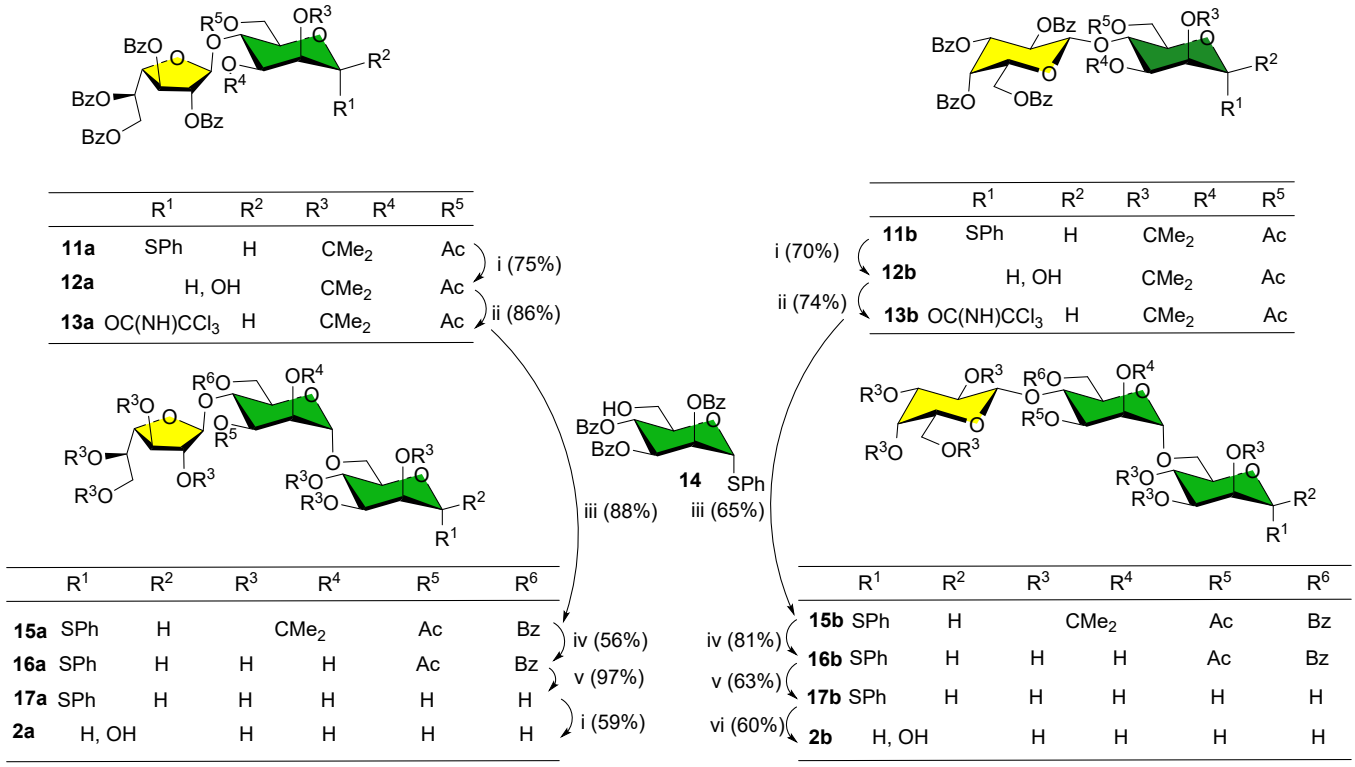


^{1}H NMR (D_2O, 400 MHz) of compound **1b**



^{13}C NMR (D_2O, 100 MHz) of compound **1b**

^{1}H and ^{13}C NMR Spectrum of trisaccharides 2 based on Man*p*-(1,6)-Man*p* skeleton



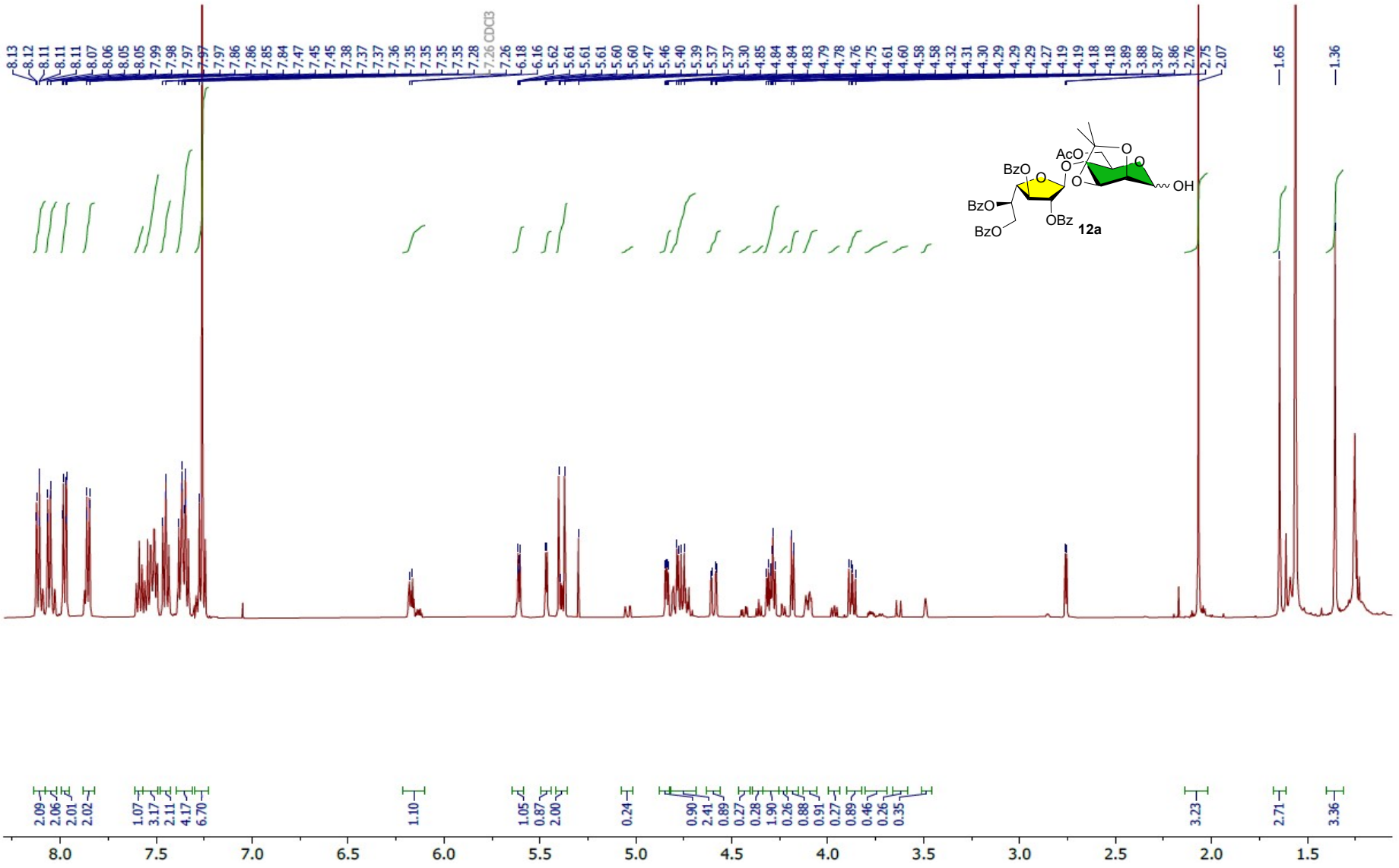
	R^1	R^2	R^3	R^4	R^5
11a	SPh	H	CMe_2		Ac
12a	H, OH		CMe_2		Ac
13a	$OC(NH)CCl_3$	H	CMe_2		Ac

	R^1	R^2	R^3	R^4	R^5
11b	SPh	H	CMe_2		Ac
12b	H, OH		CMe_2		Ac
13b	$OC(NH)CCl_3$	H	CMe_2		Ac

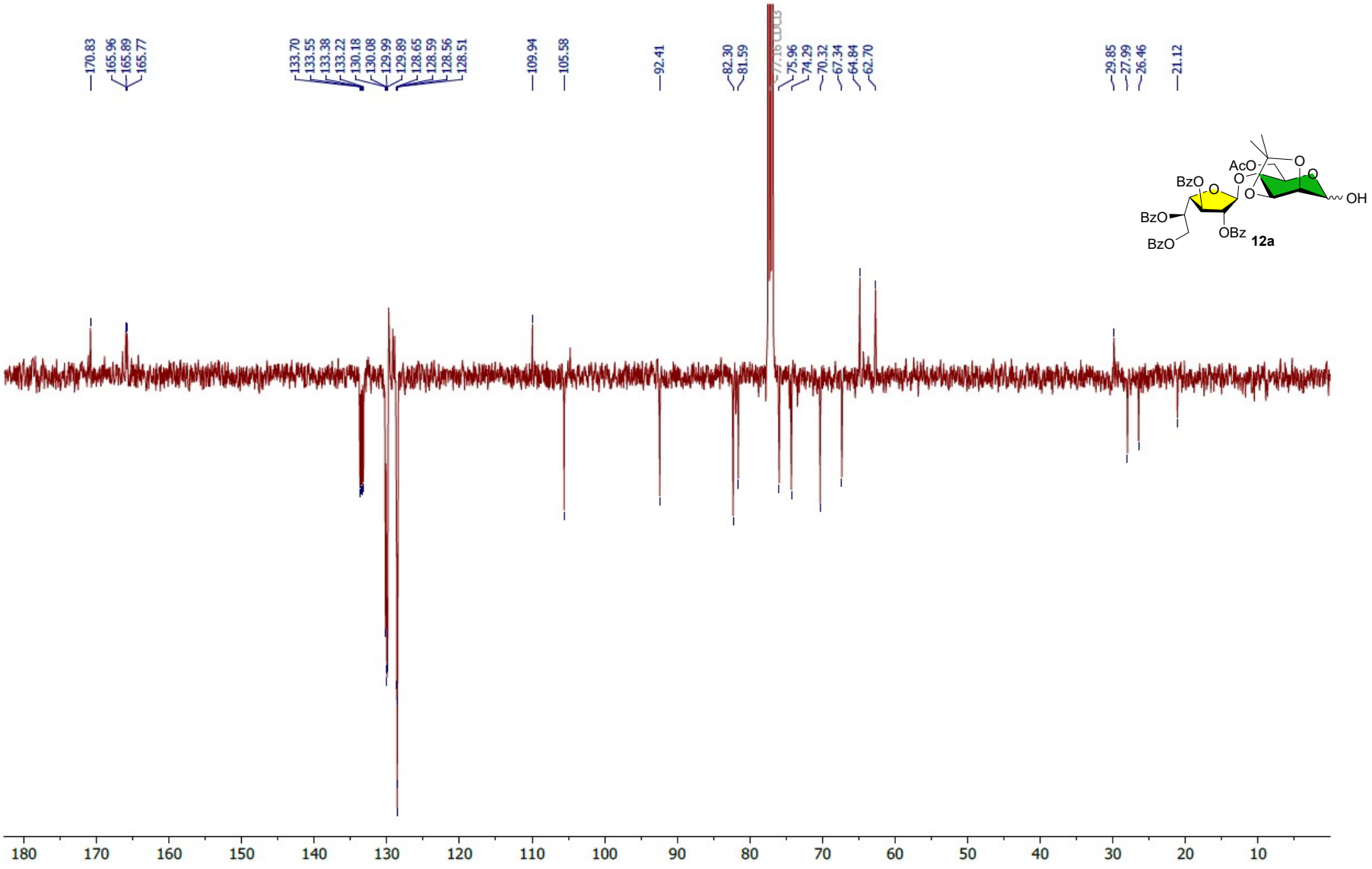
	R^1	R^2	R^3	R^4	R^5	R^6
15a	SPh	H	CMe_2		Ac	Bz
16a	SPh	H	H	H	Ac	Bz
17a	SPh	H	H	H	H	H
2a	H, OH		H	H	H	H

	R^1	R^2	R^3	R^4	R^5	R^6
15b	SPh	H	CMe_2		Ac	Bz
16b	SPh	H	H	H	Ac	Bz
17b	SPh	H	H	H	H	H
2b	H, OH		H	H	H	H

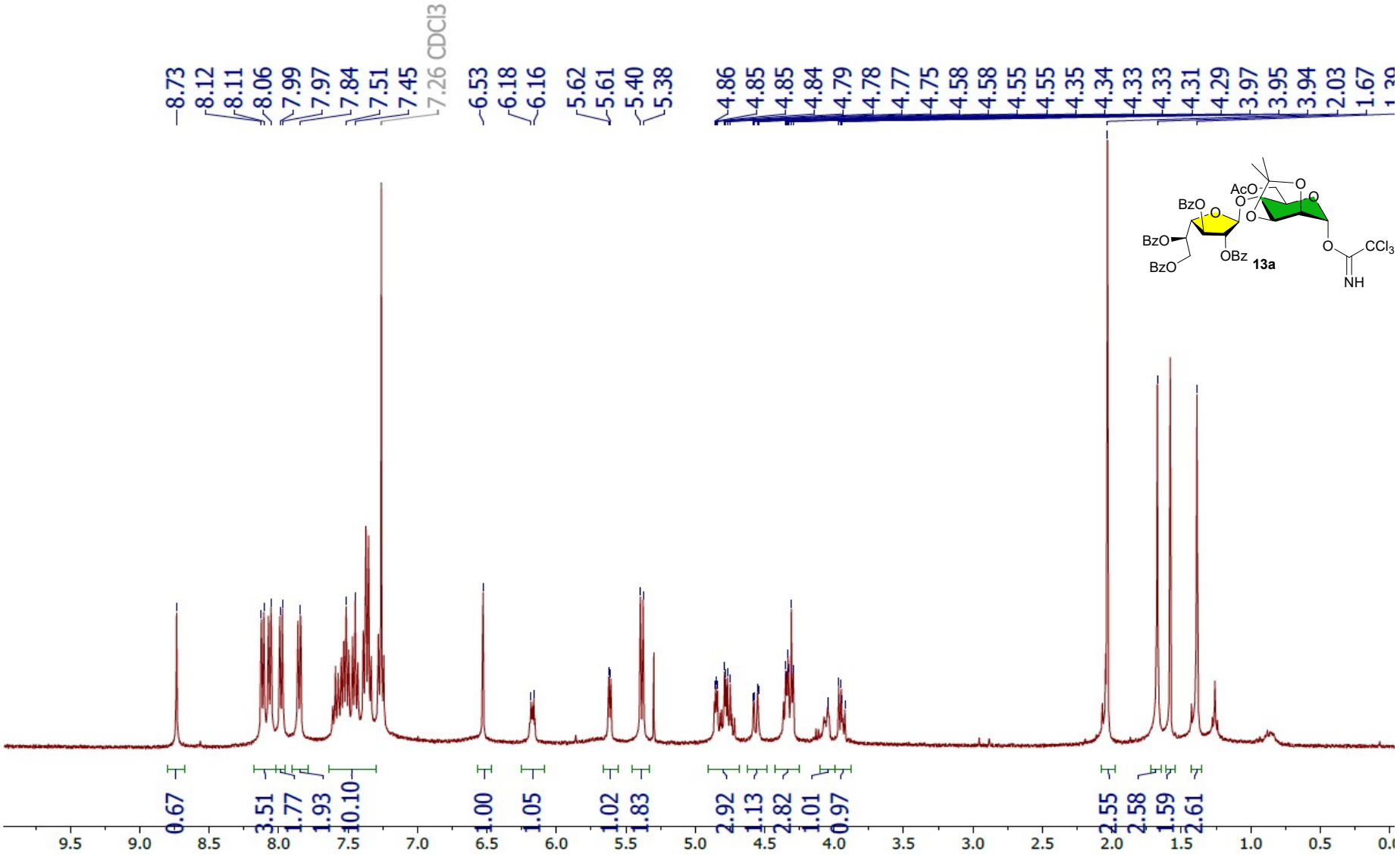
Reagents and conditions: (i) NBS, H_2O/Me_2CO; (ii) Cl_3CCN, $CsCO_3$, CH_2Cl_2; (iii) **14**, TMSOTf, CH_2Cl_2; (iv) AcOH, H_2O; (v) NaOMe, MeOH; (vi) NIS, CH_3CN/H_2O.



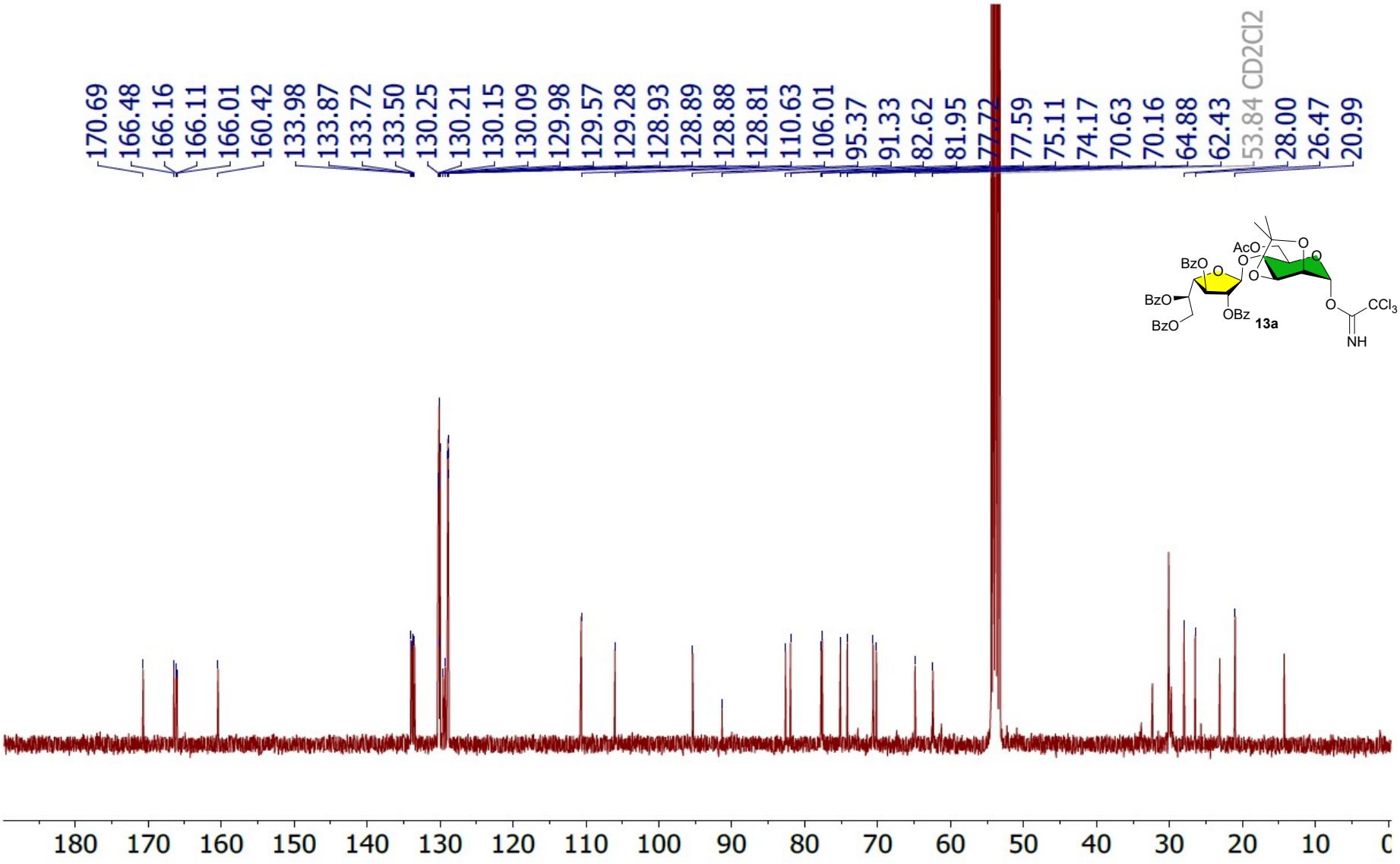
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **12a**



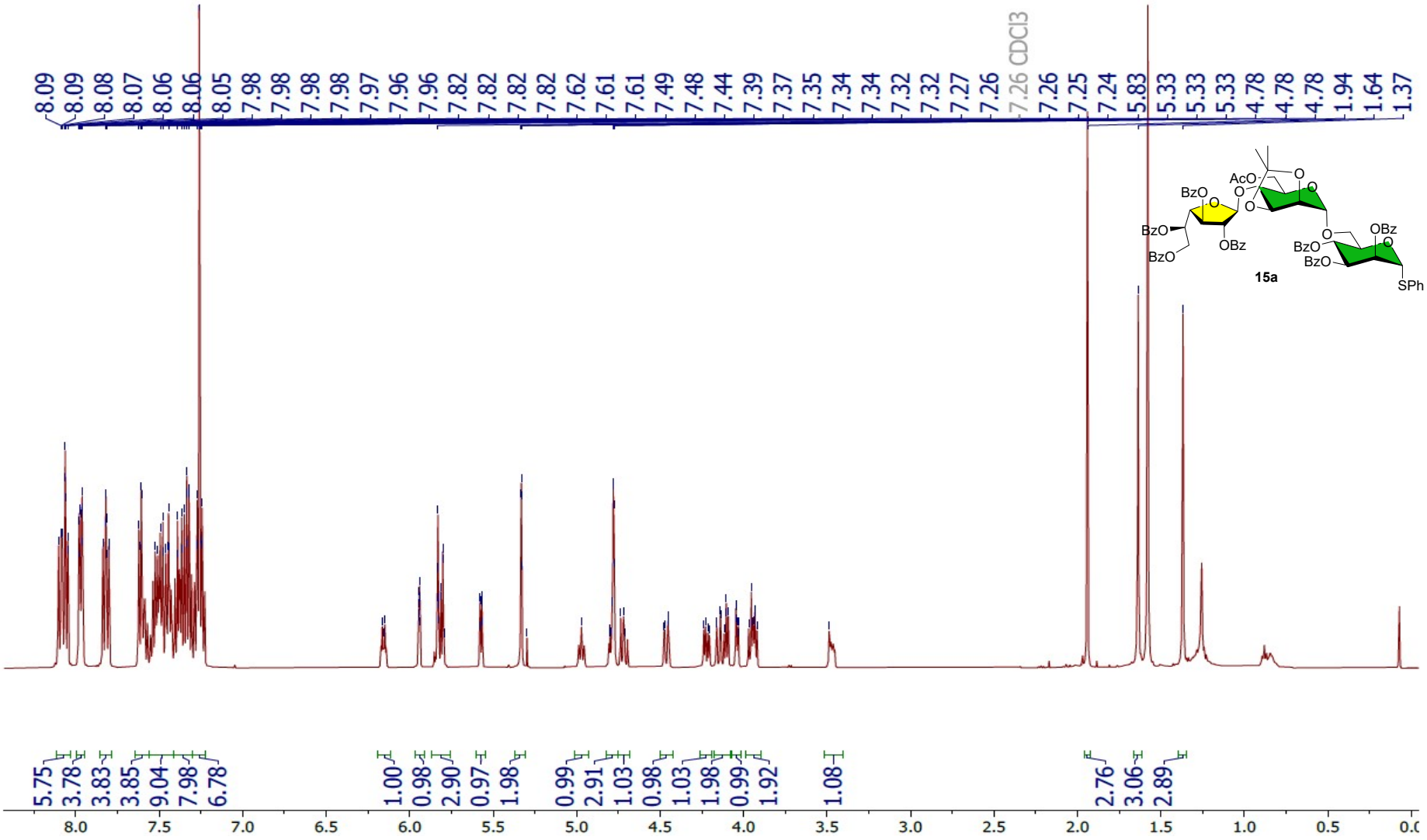
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **12a**



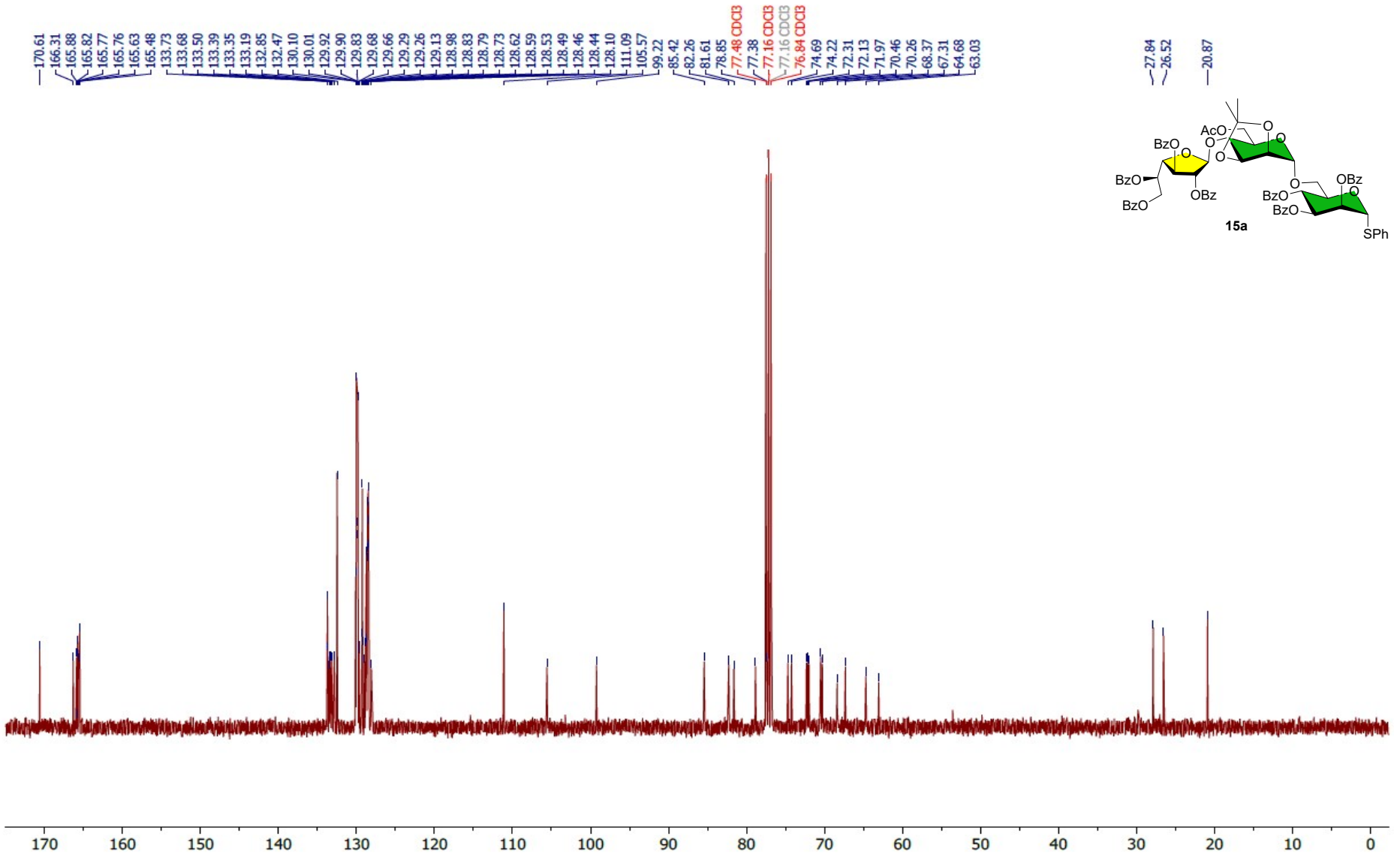
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **13a**



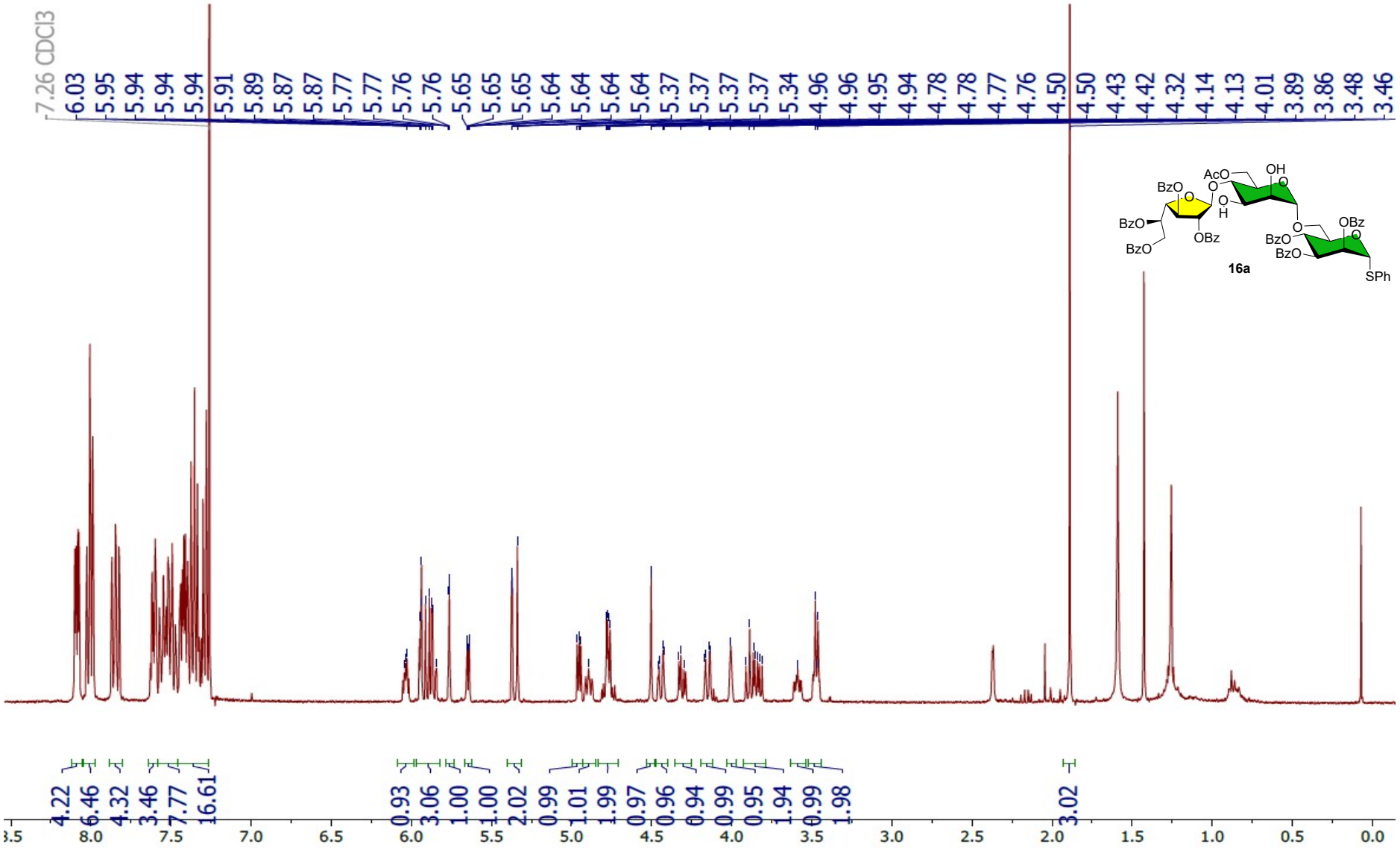
^{13}C NMR (CD_2Cl_2, 100 MHz) of compound **13a**



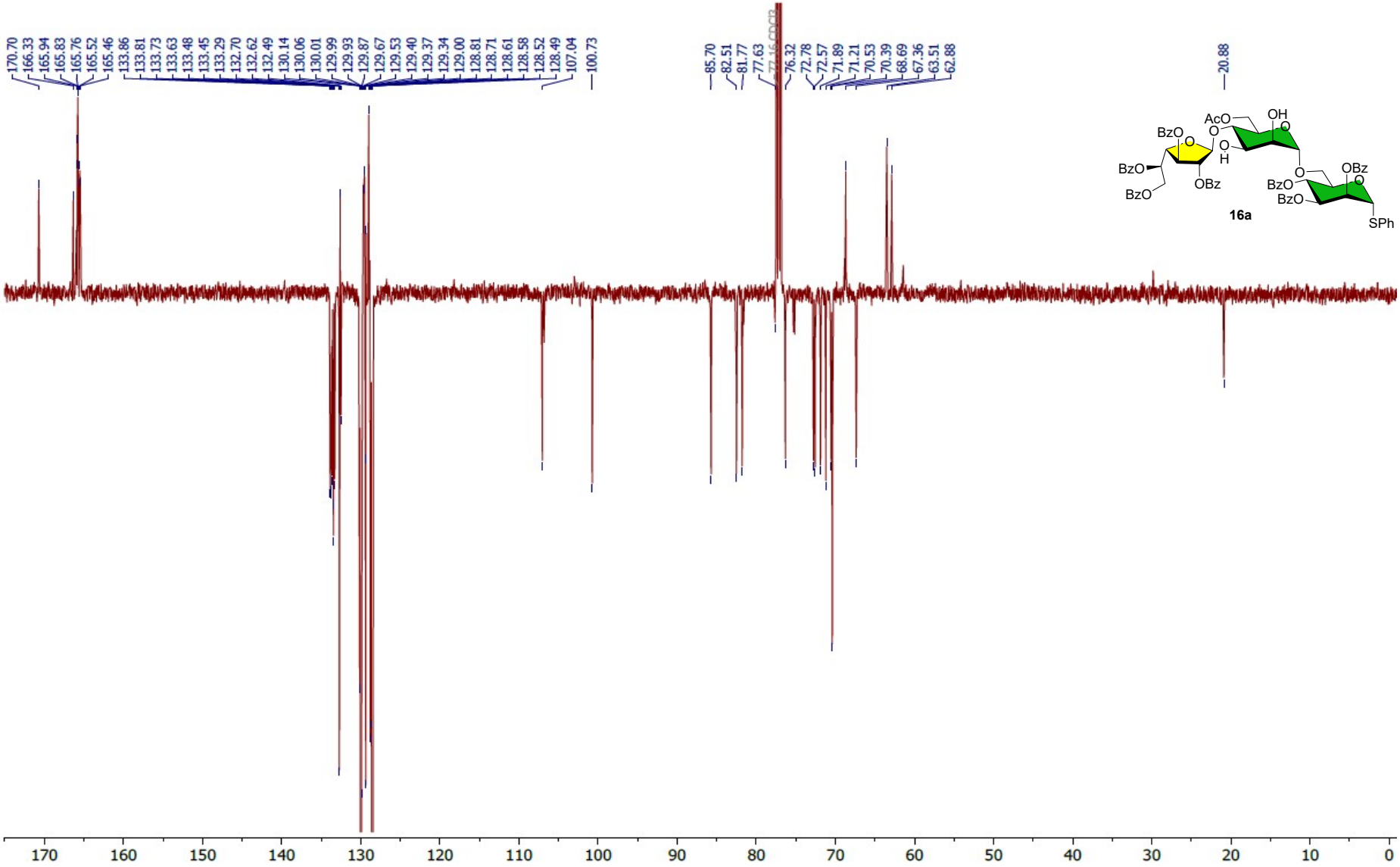
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **15a**



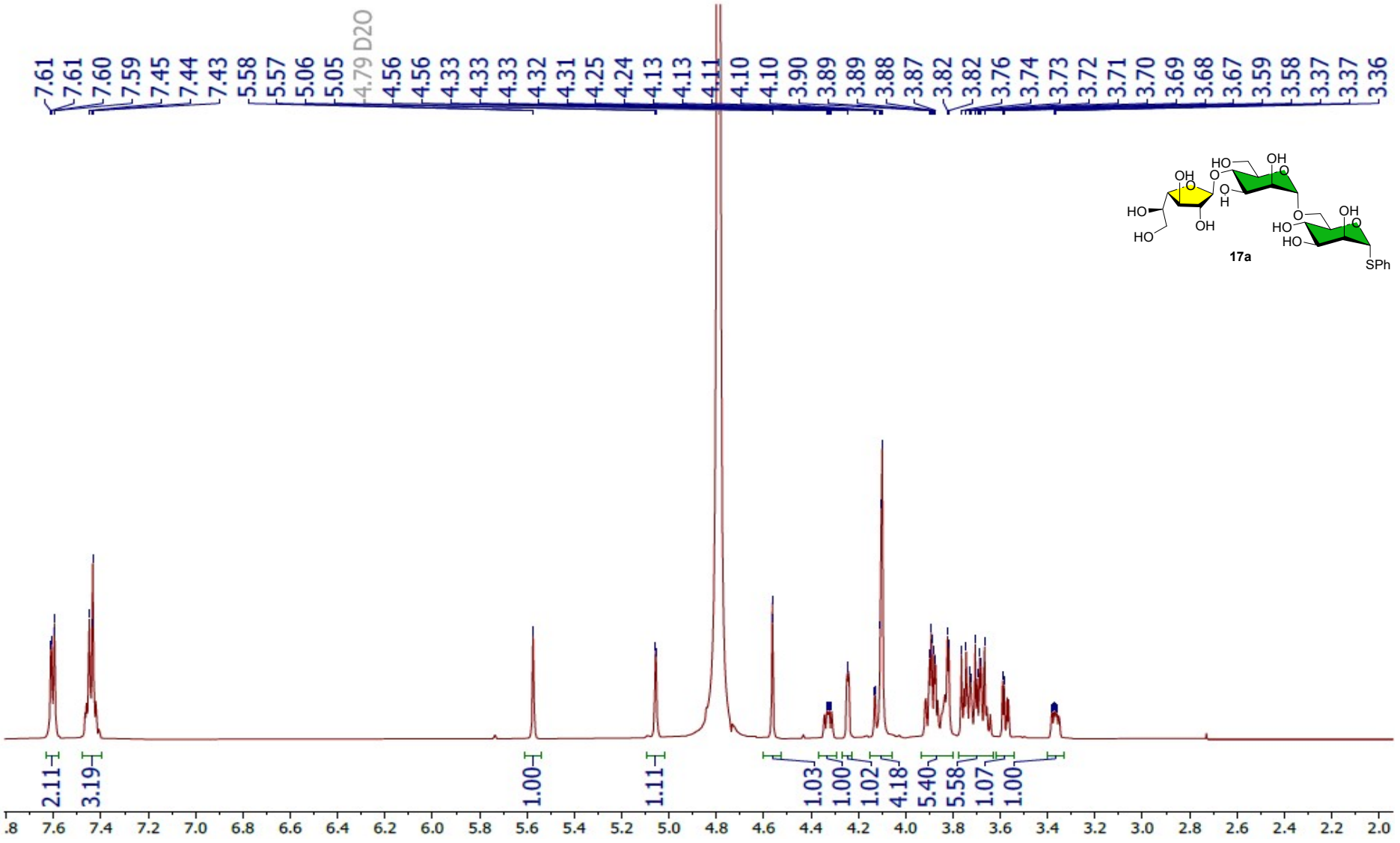
^{13}C NMR ($CDCl_3$, 126 MHz) of compound **15a**



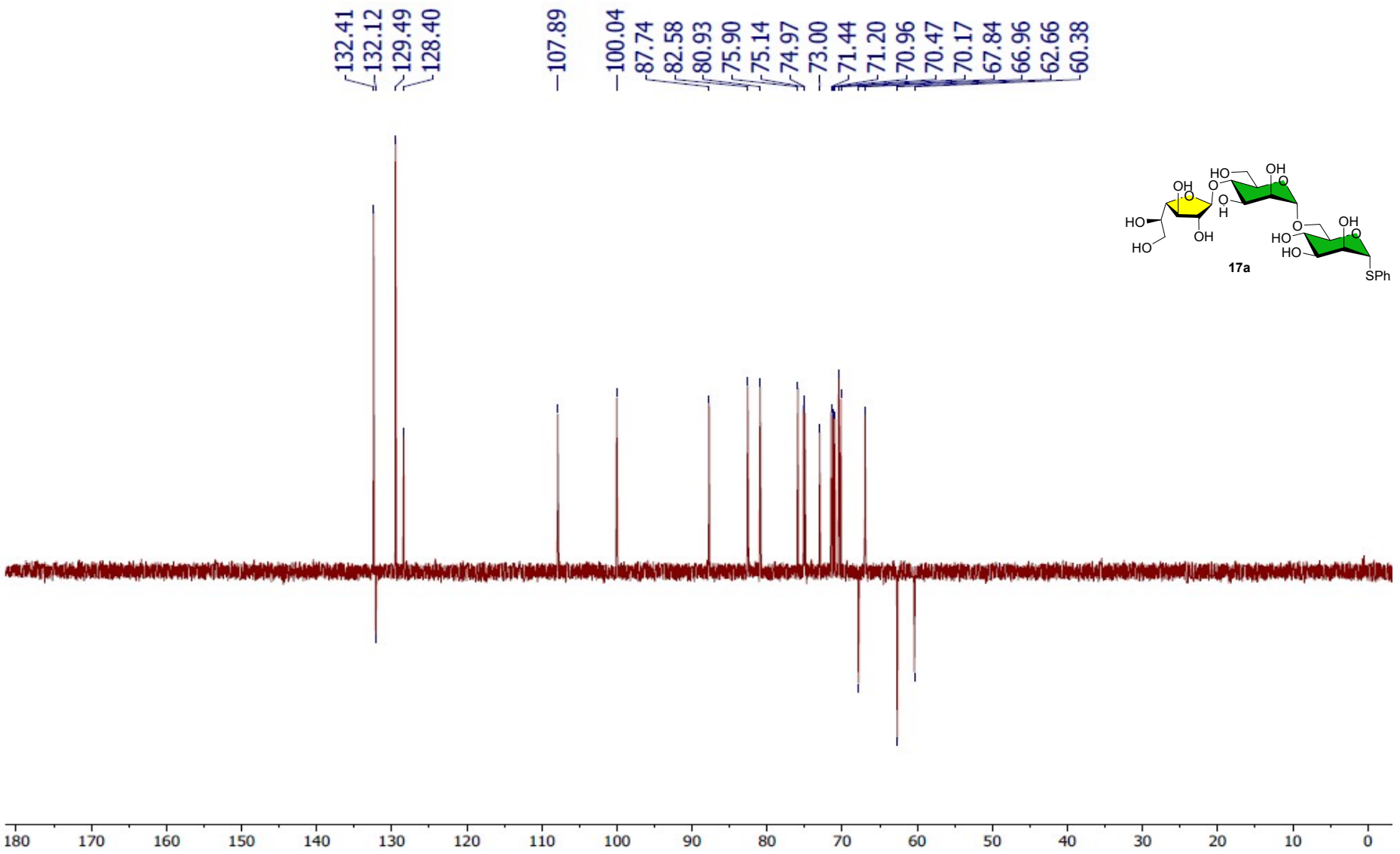
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **16a**



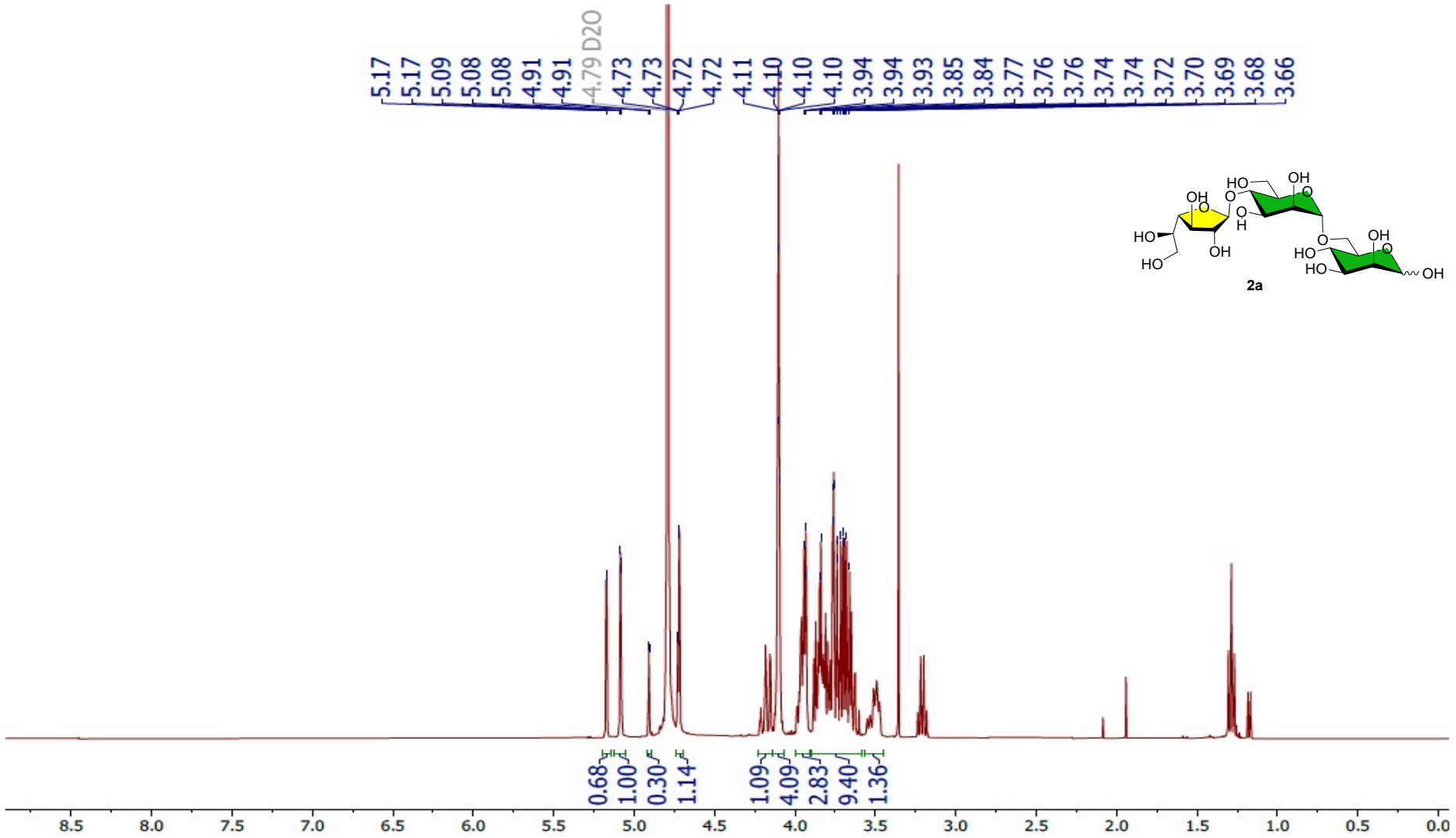
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **16a**



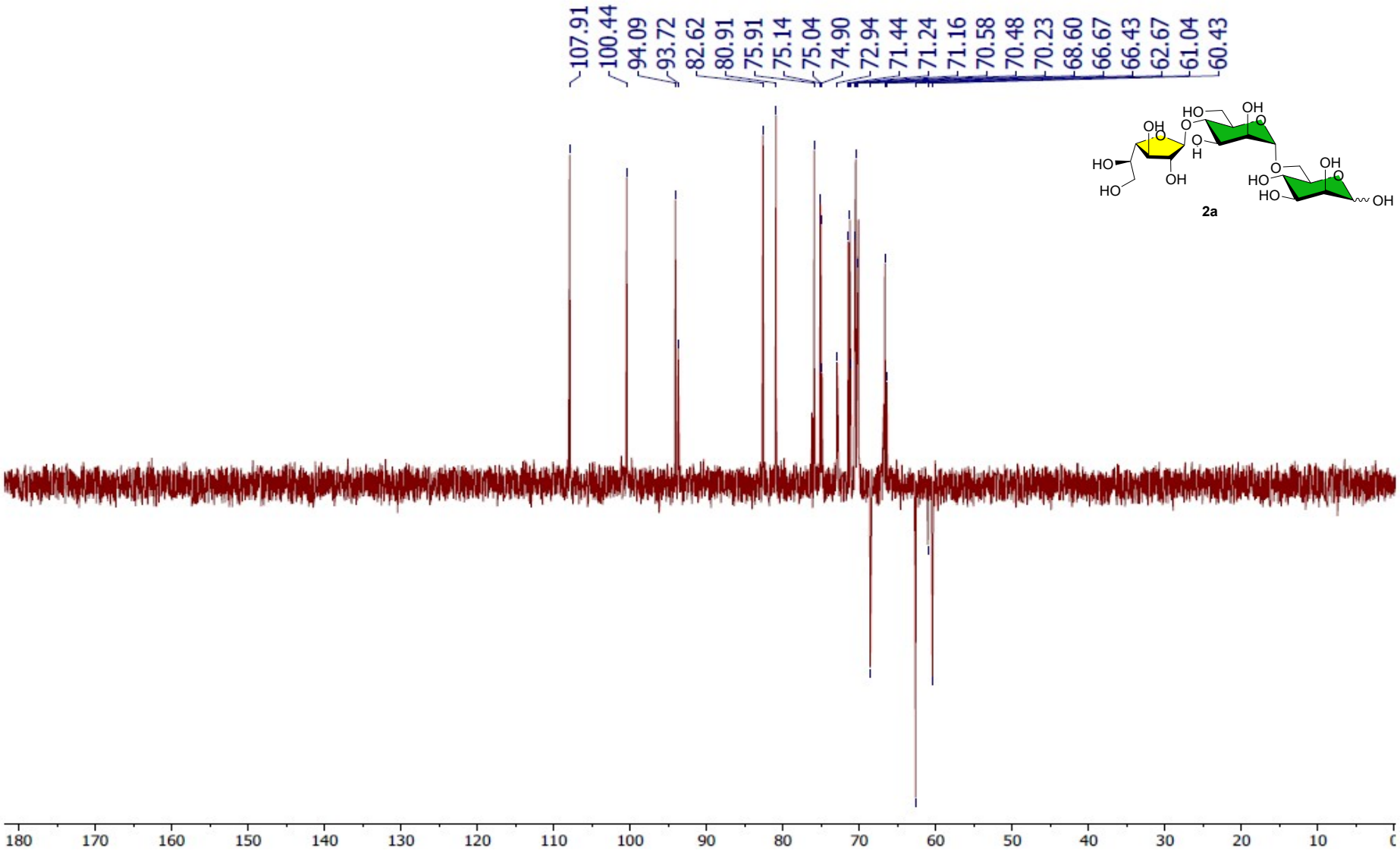
^{1}H NMR (D_2O, 500 MHz) of compound **17a**



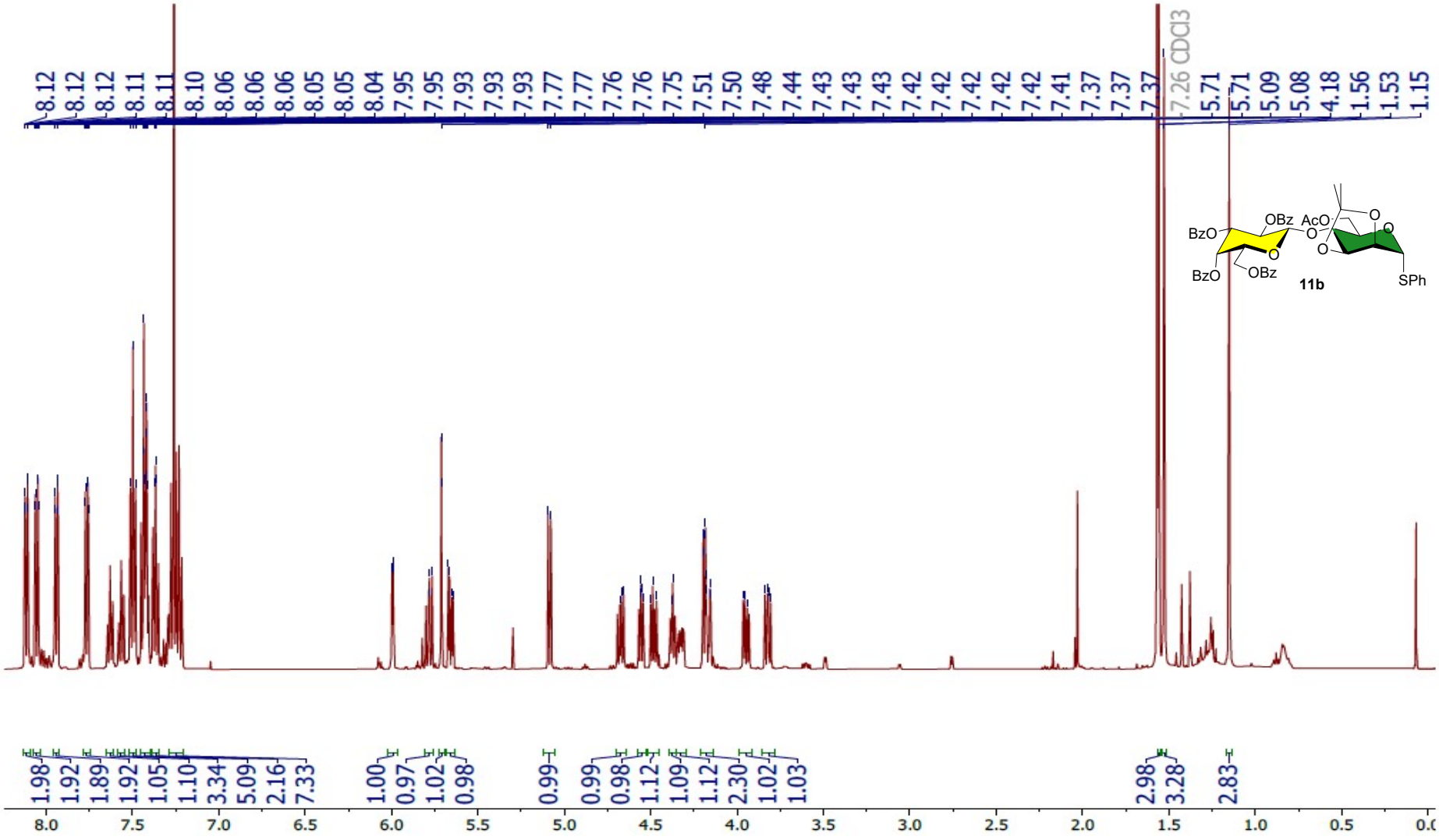
^{13}C NMR (D_2O, 126 MHz) of compound **17a**



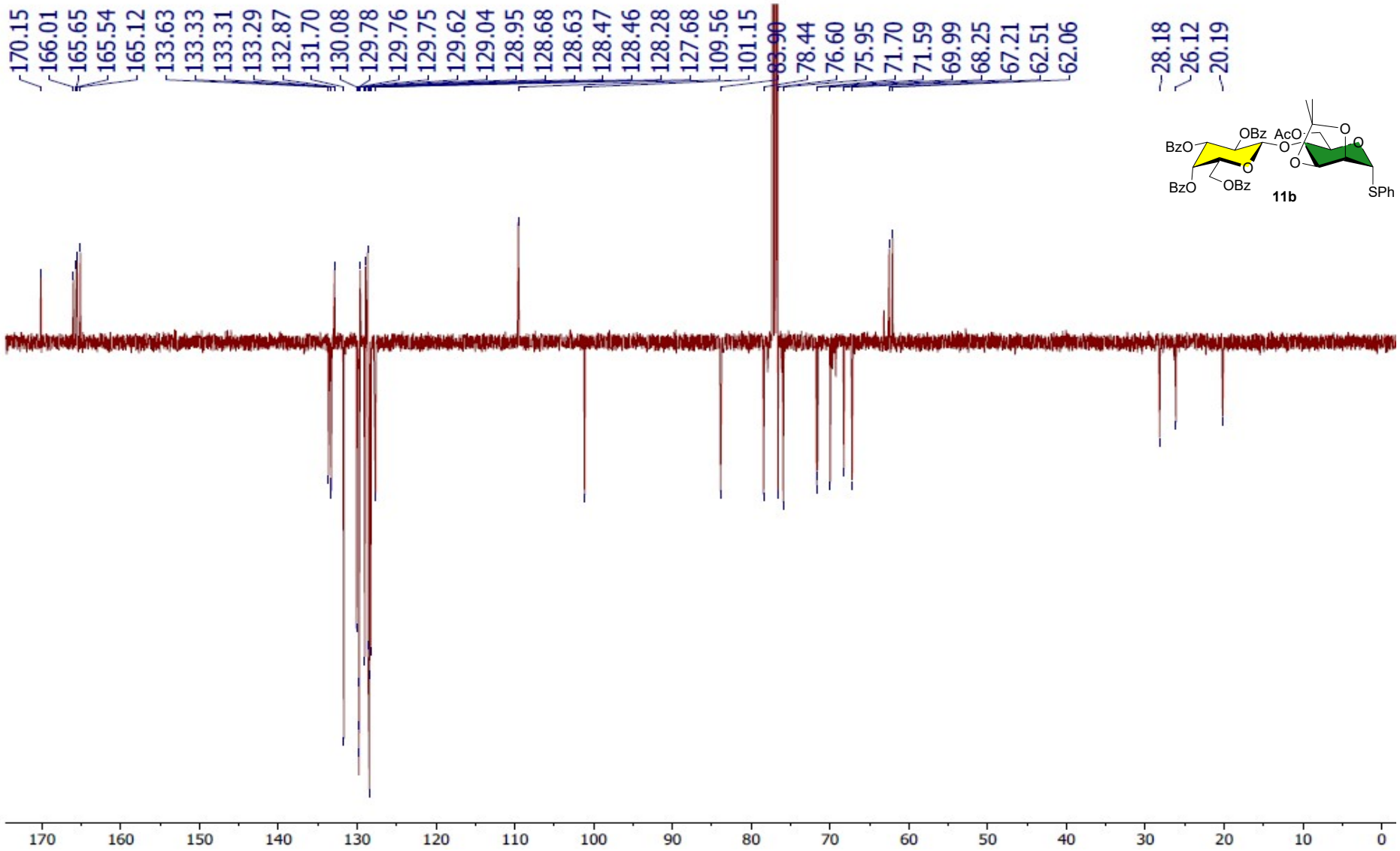
^{1}H NMR (D_2O, 500 MHz) of compound **2a**



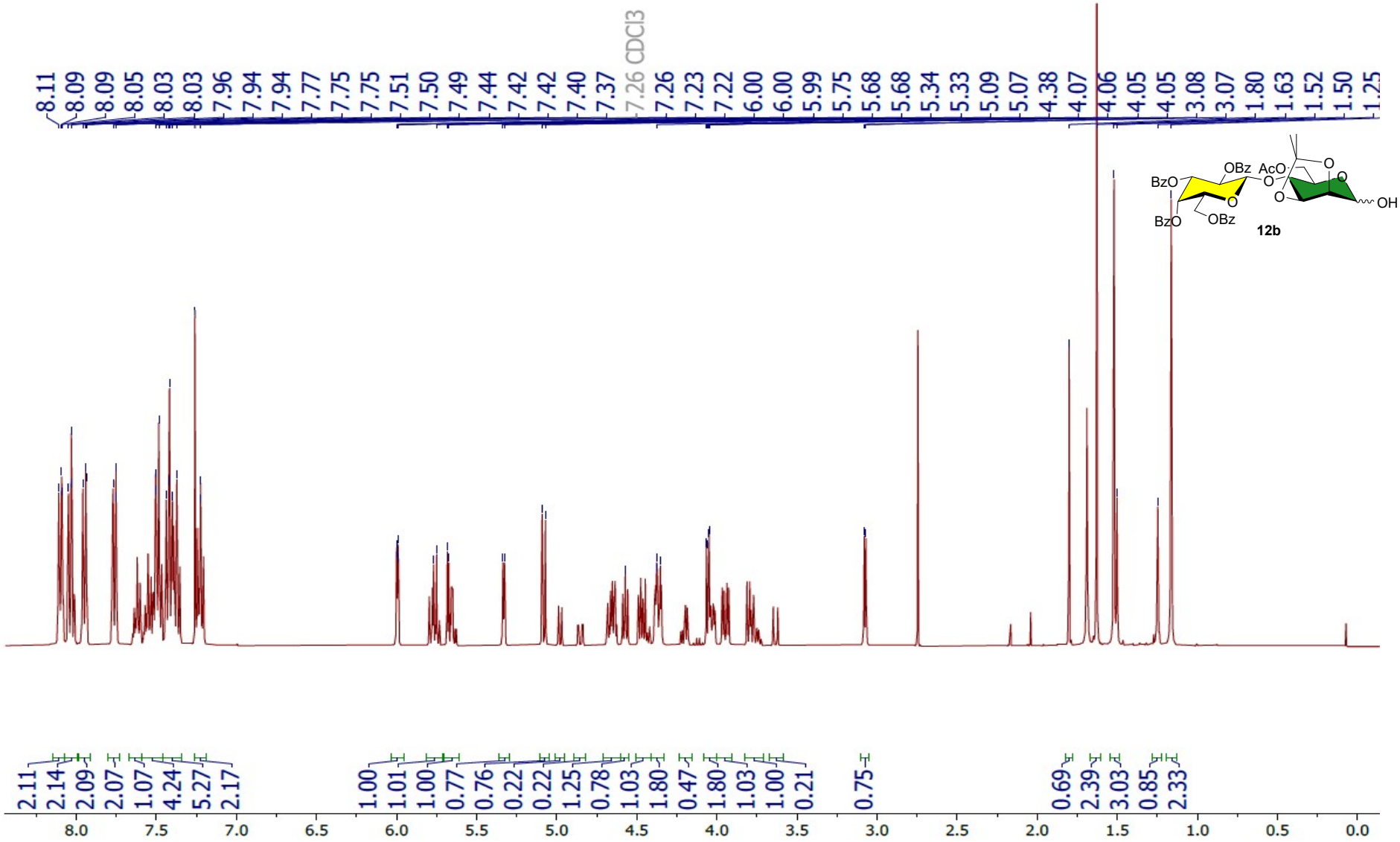
^{13}C NMR (D_2O, 126 MHz) of compound **2a**



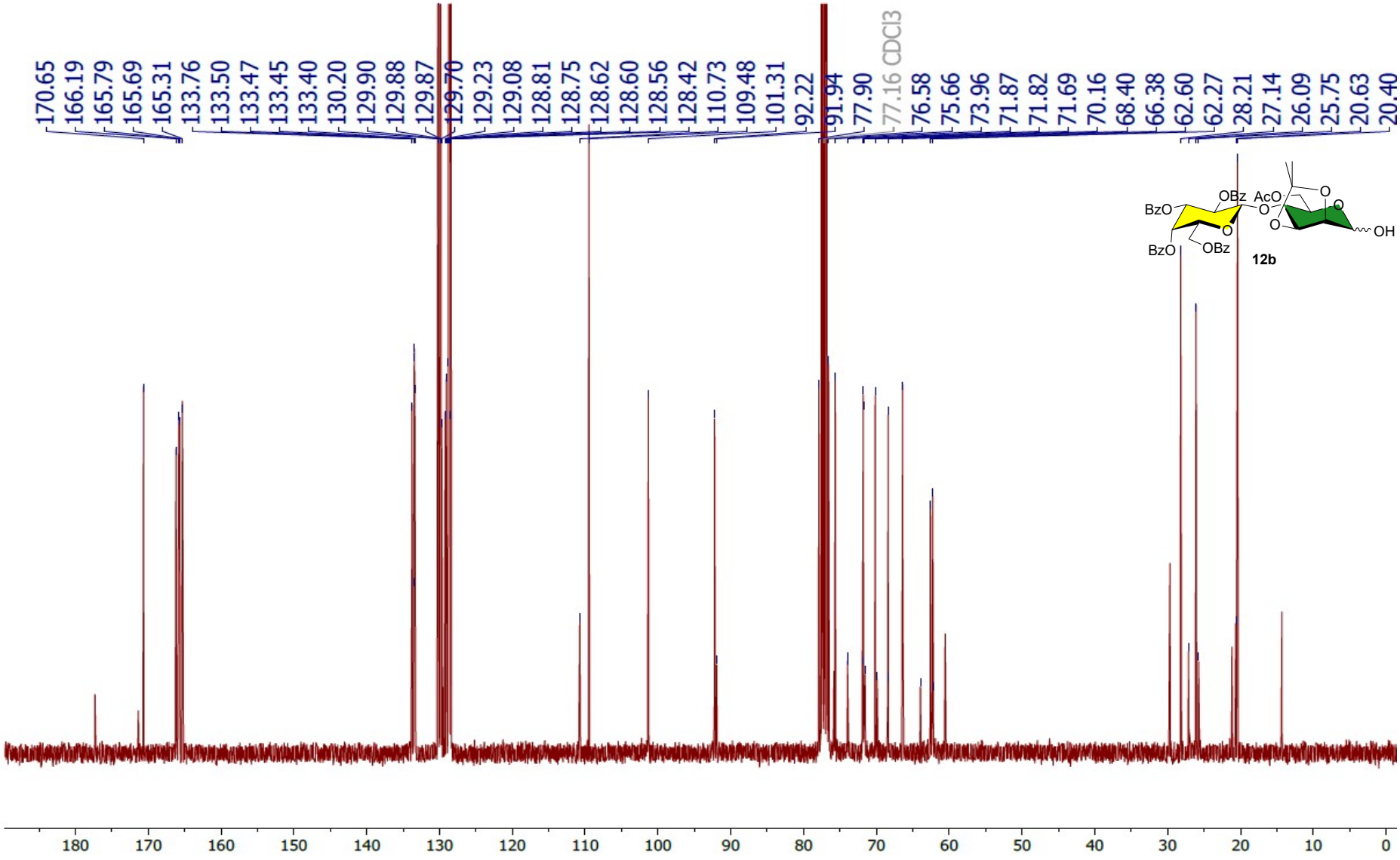
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **11b**



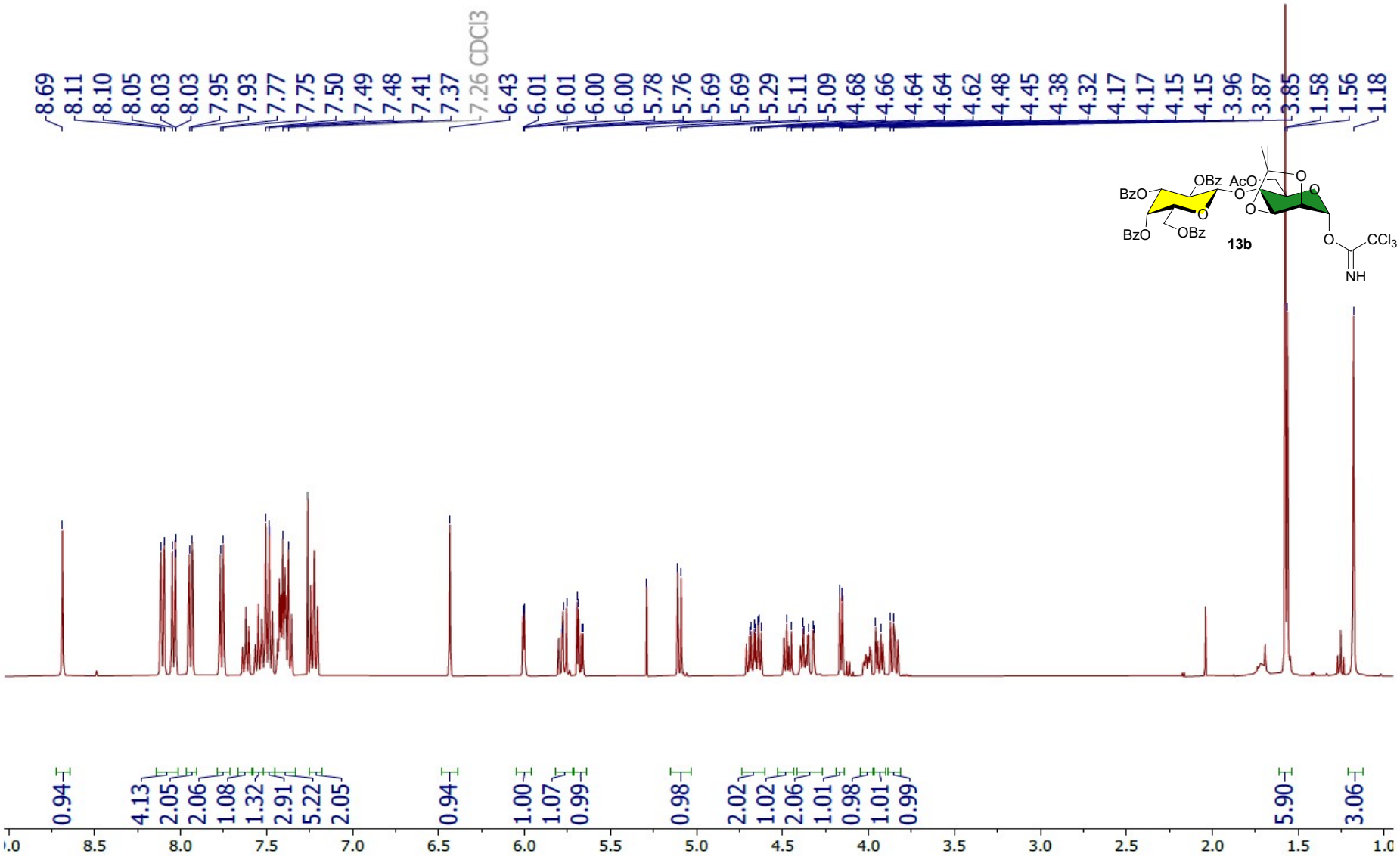
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **11b**



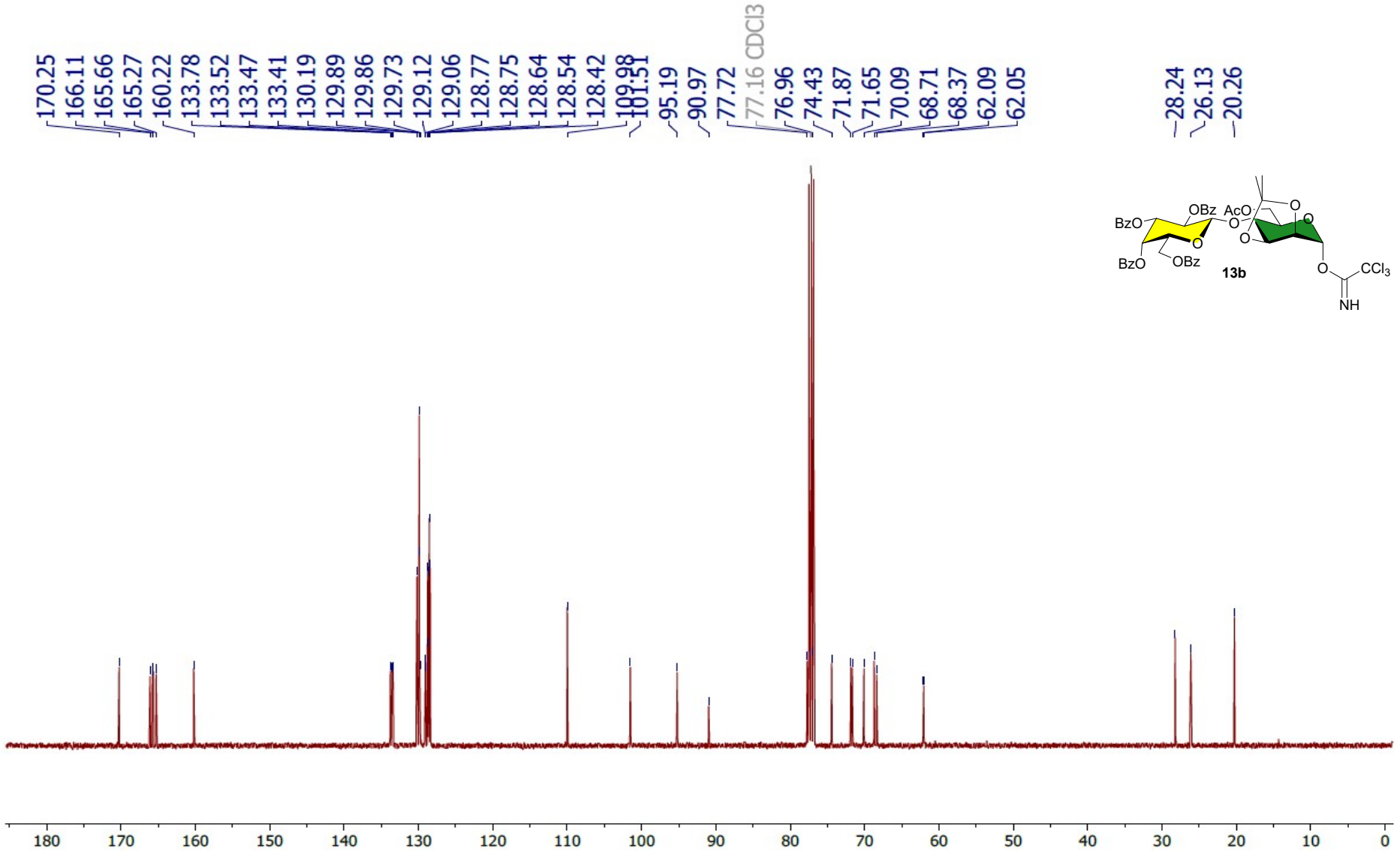
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **12b**



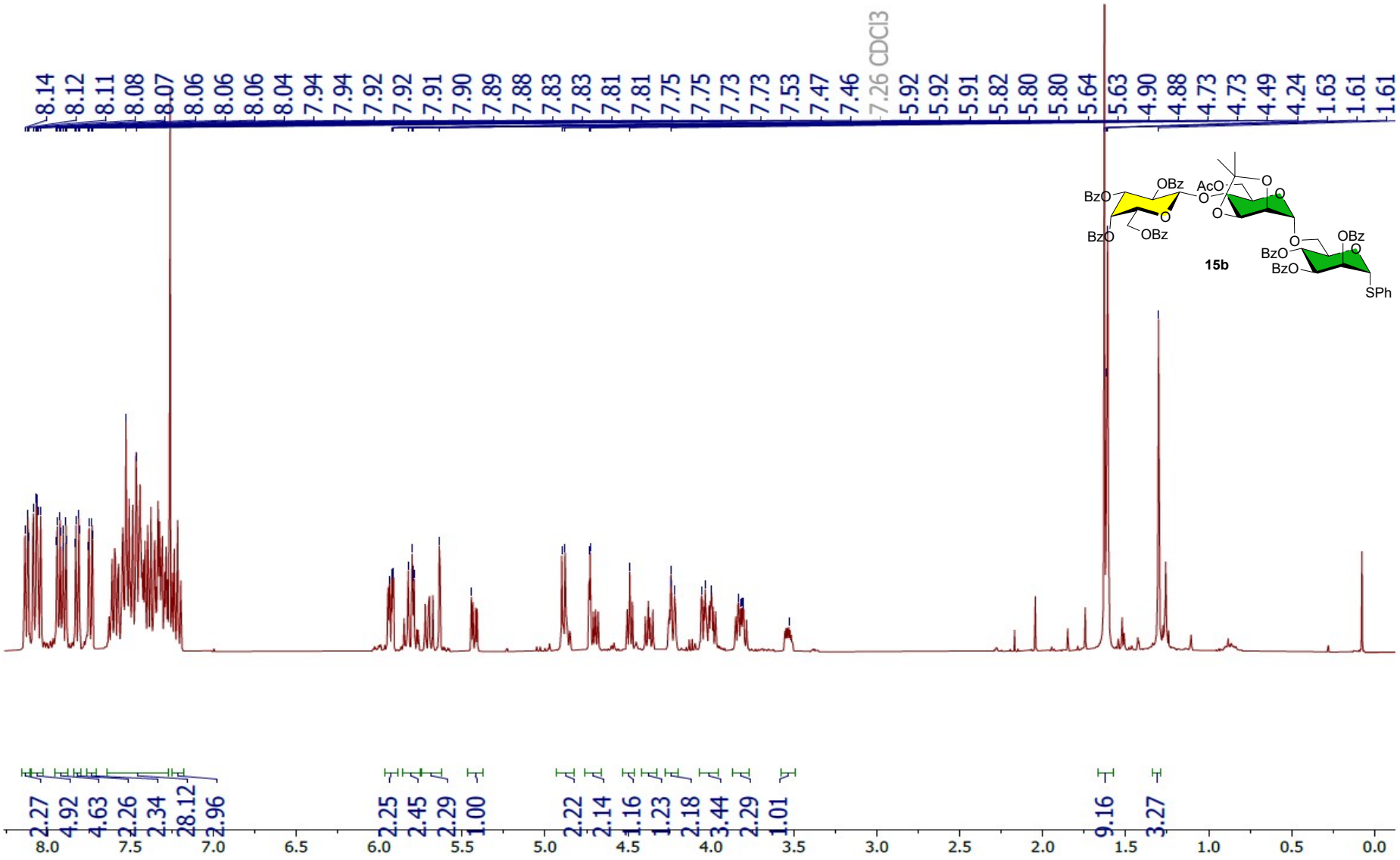
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **12b**



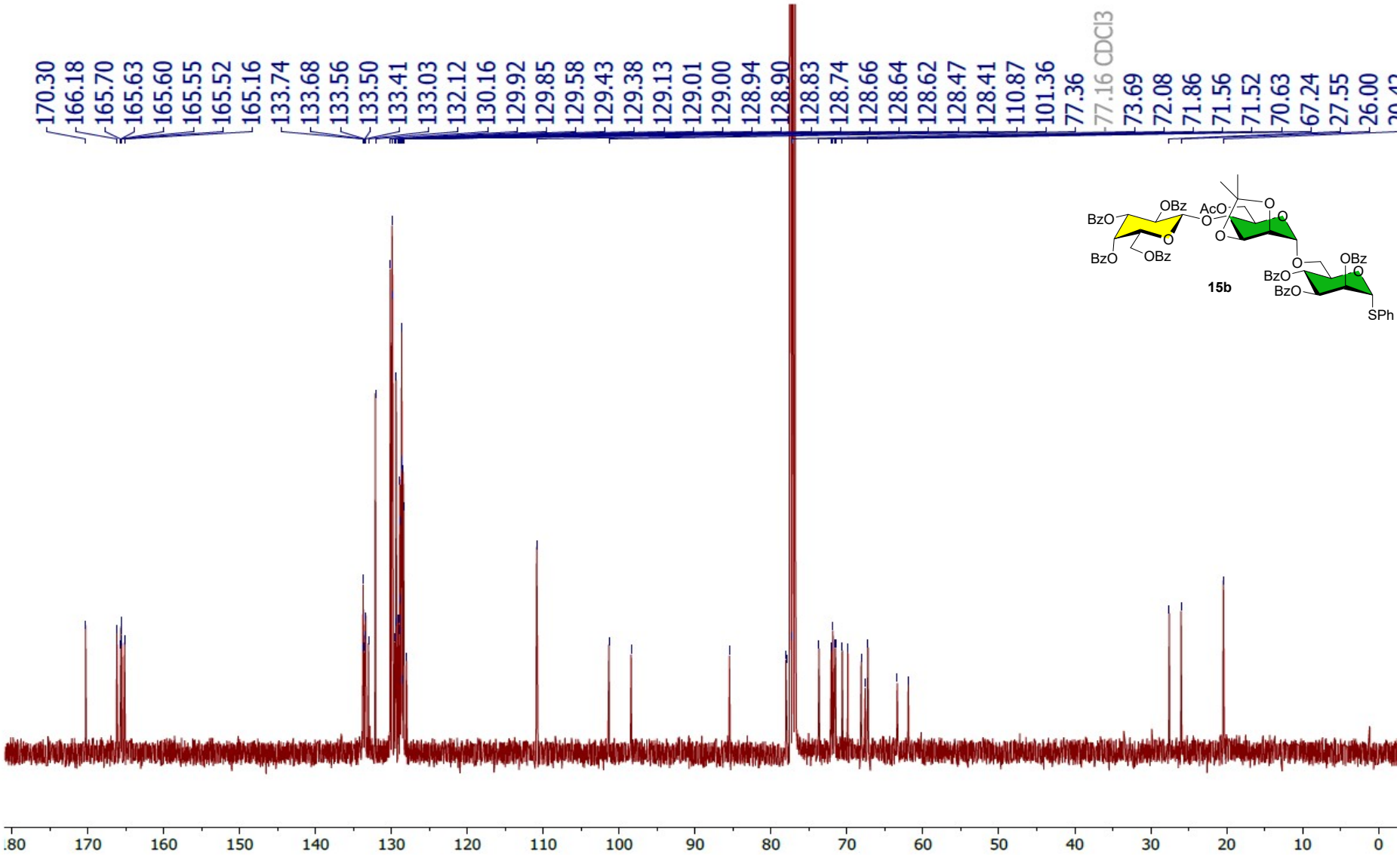
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **13b**



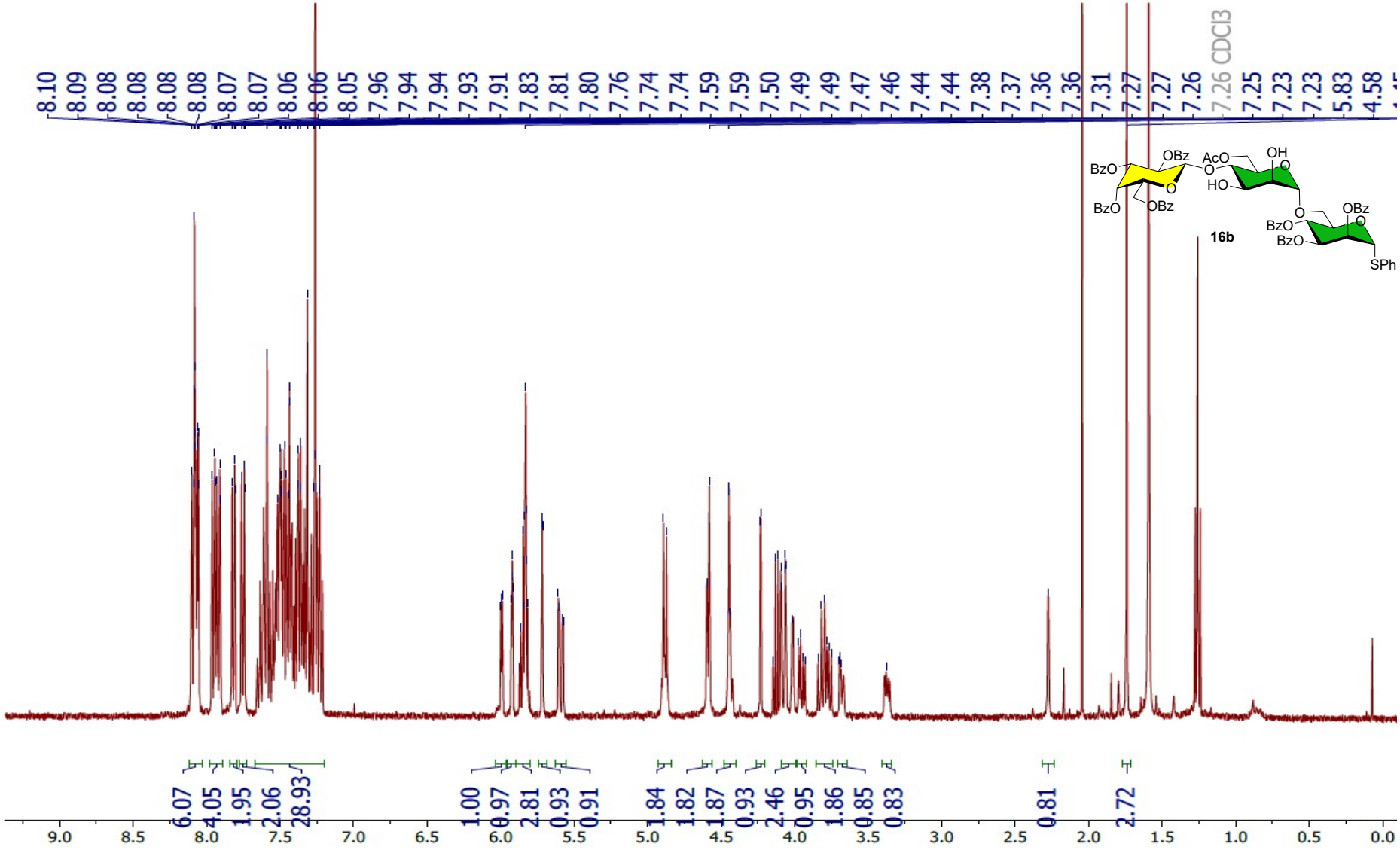
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **13b**



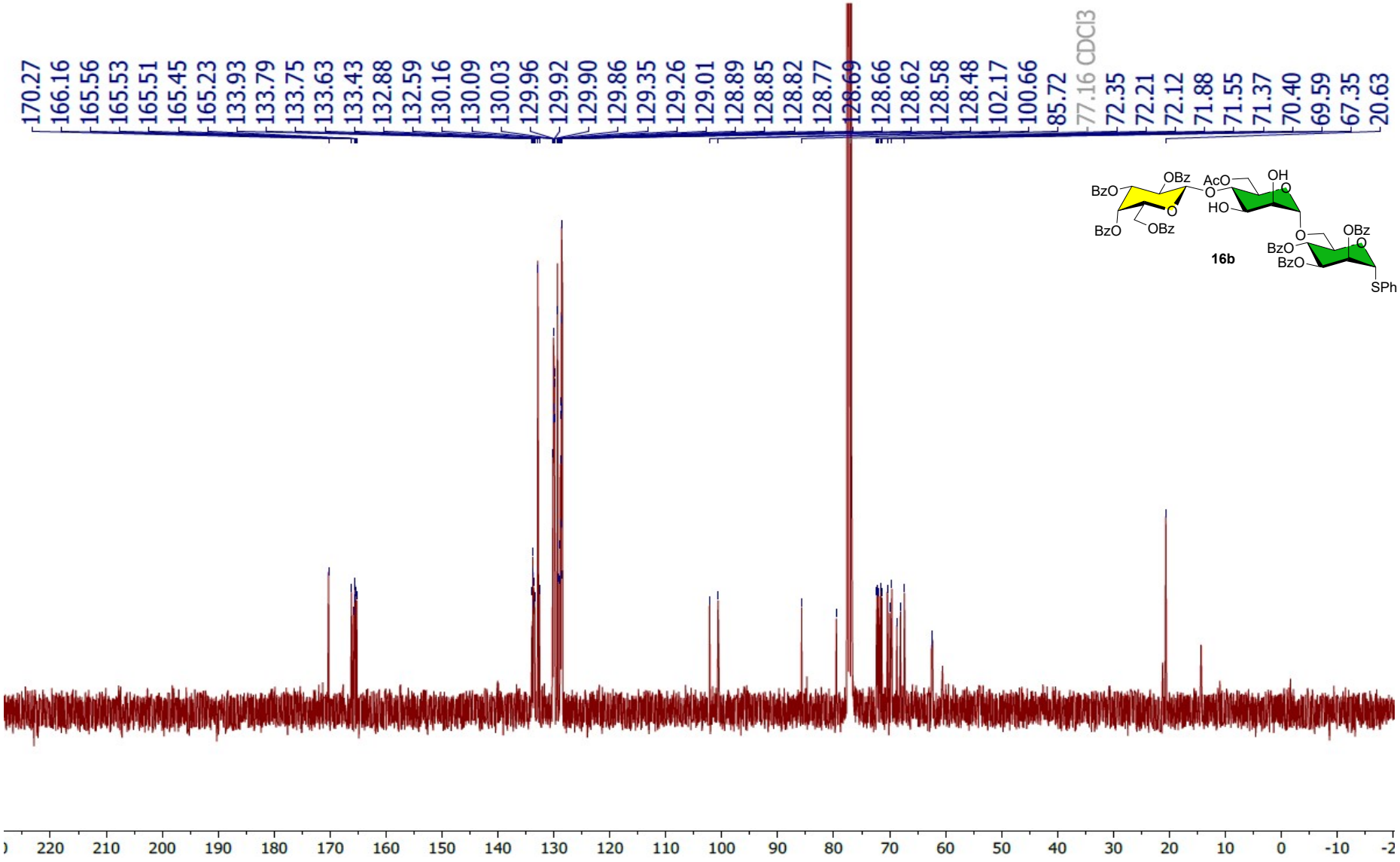
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **15b**



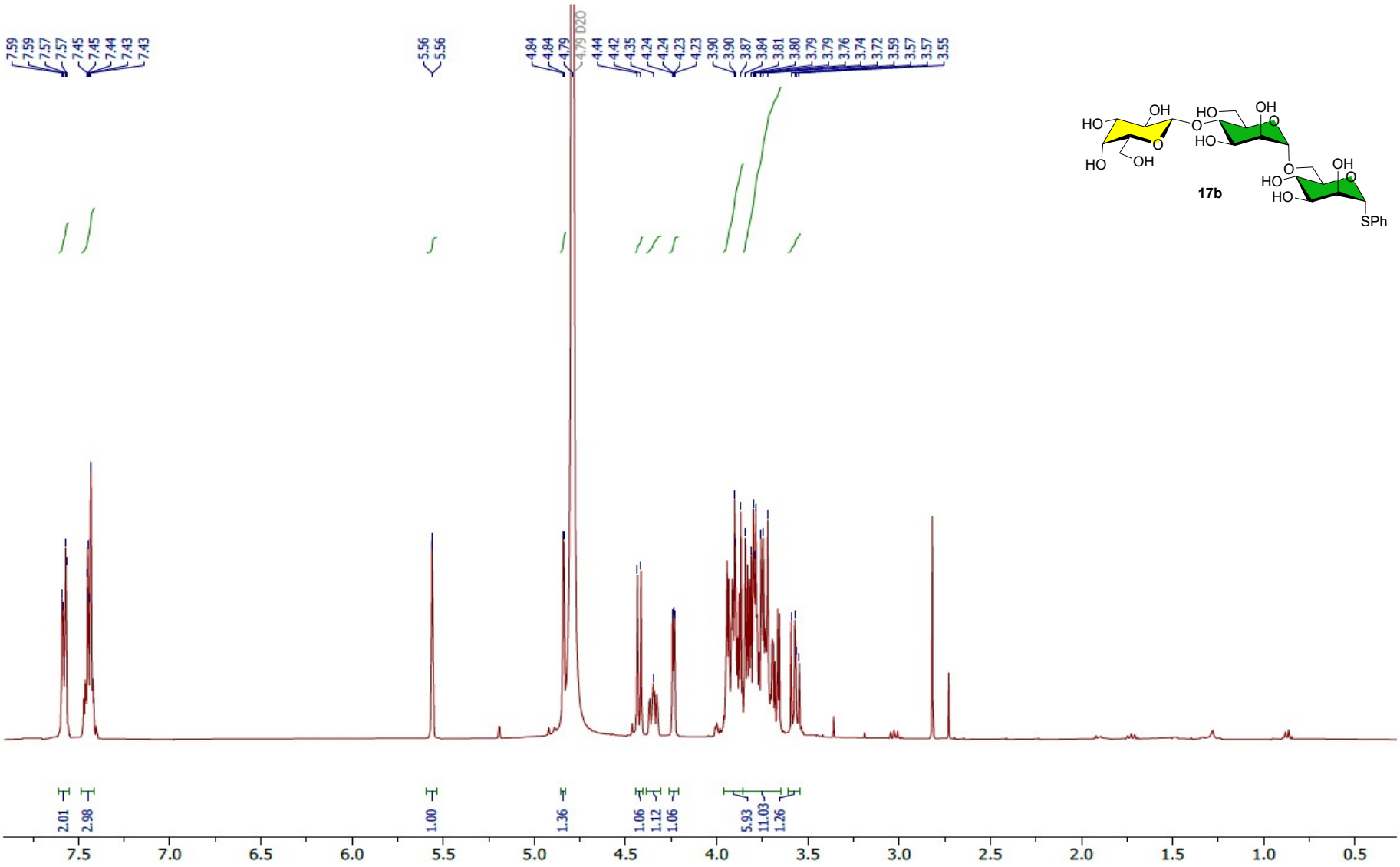
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **15b**



^{1}H NMR ($CDCl_3$, 400 MHz) of compound **16b**

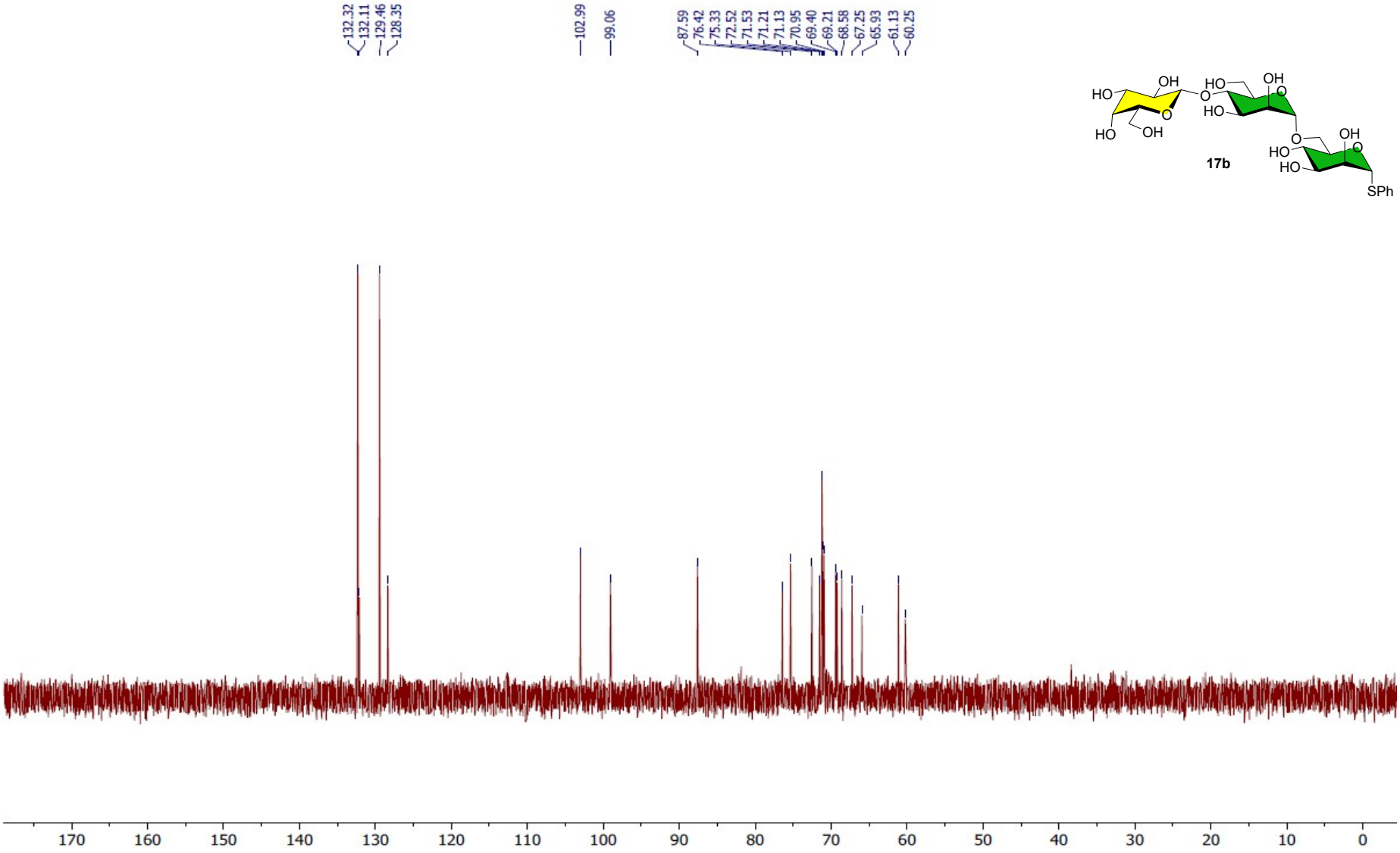


^{13}C NMR ($CDCl_3$, 100 MHz) of compound **16b**

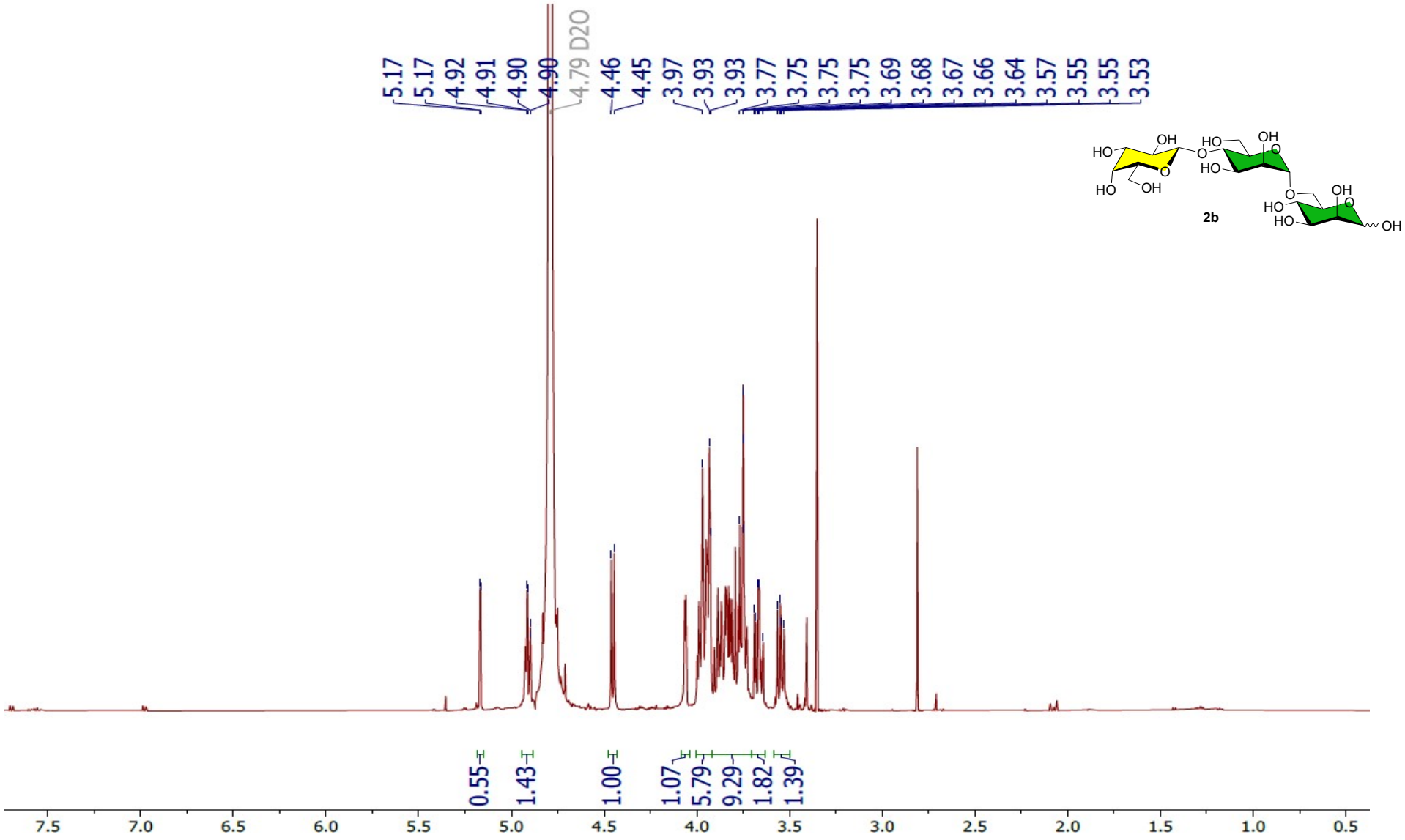


17b

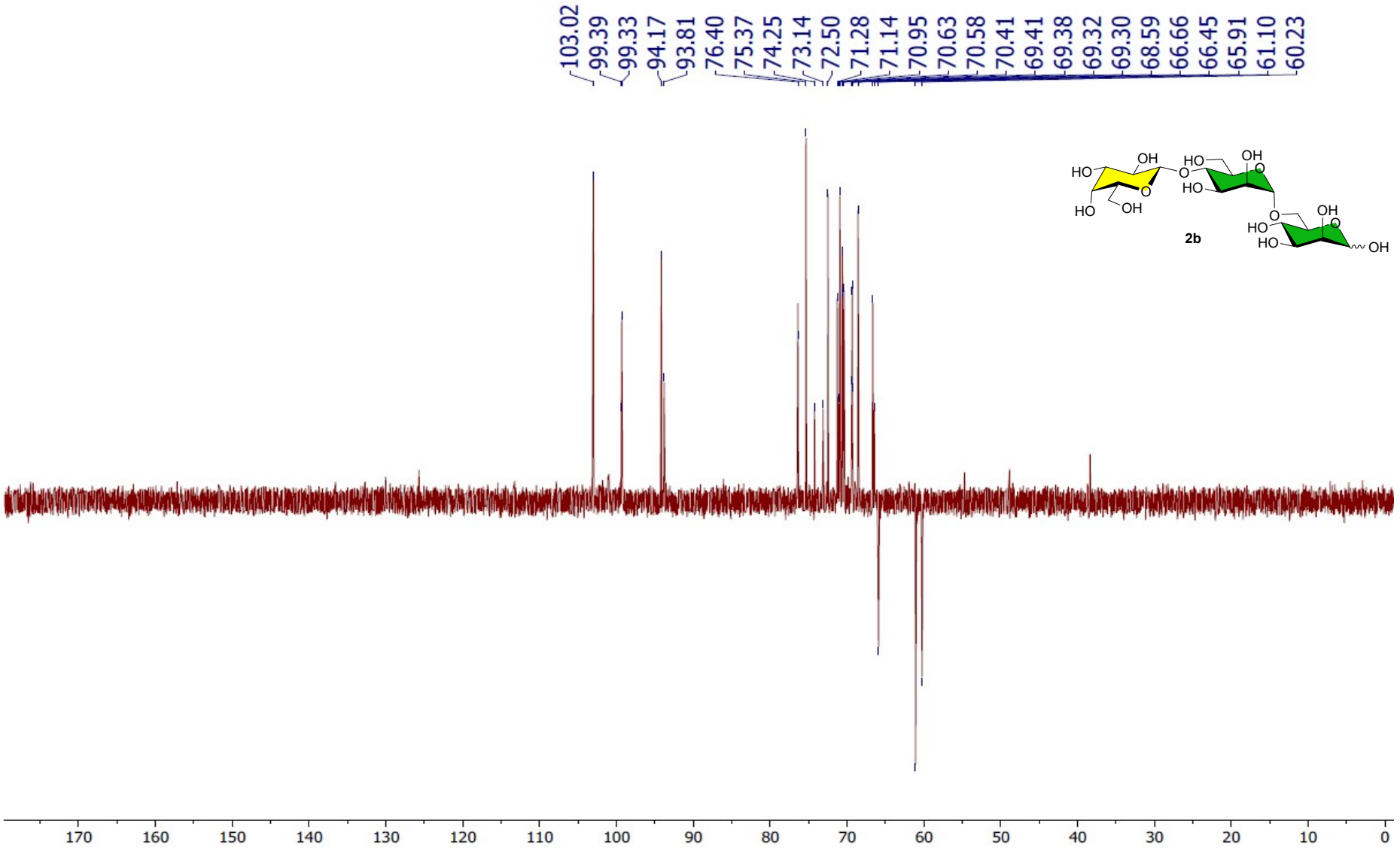
^{1}H NMR (D_2O, 400 MHz) of compound **17b**



^{13}C NMR (D_2O, 100 MHz) of compound **17b**

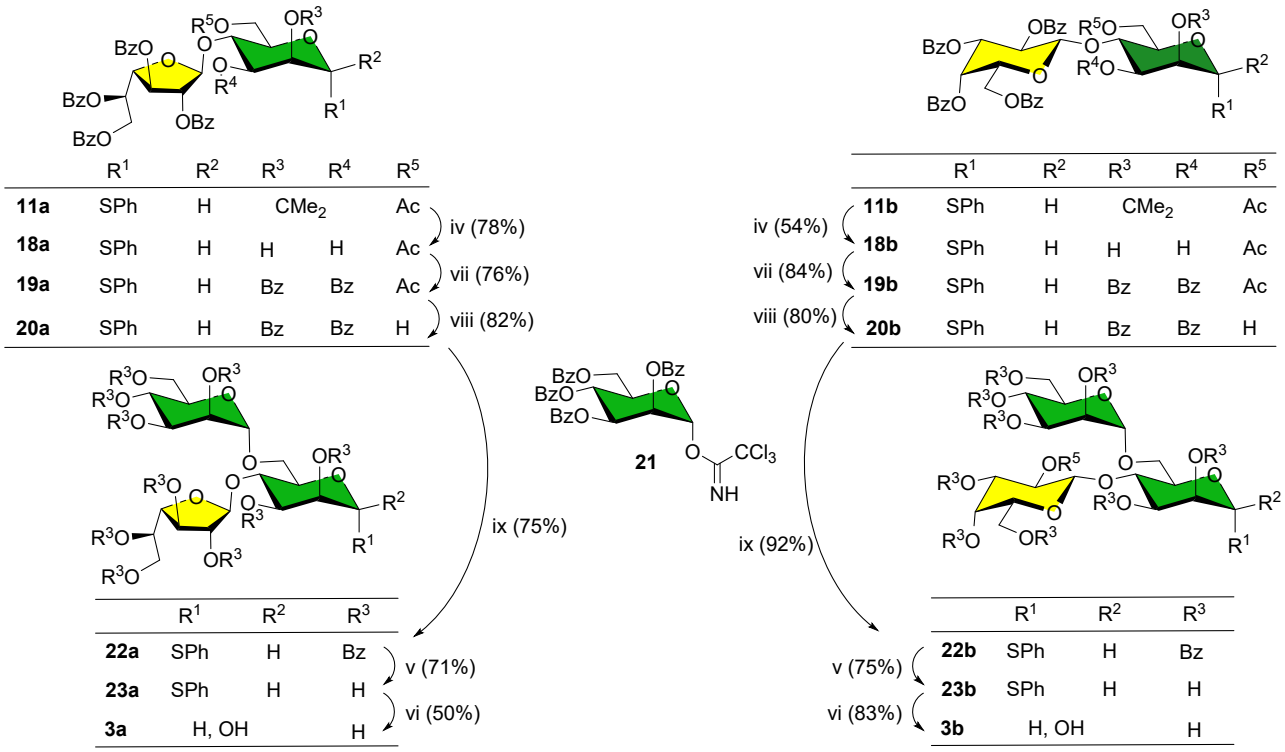


^{1}H NMR (D_2O, 500 MHz) of compound **2b**

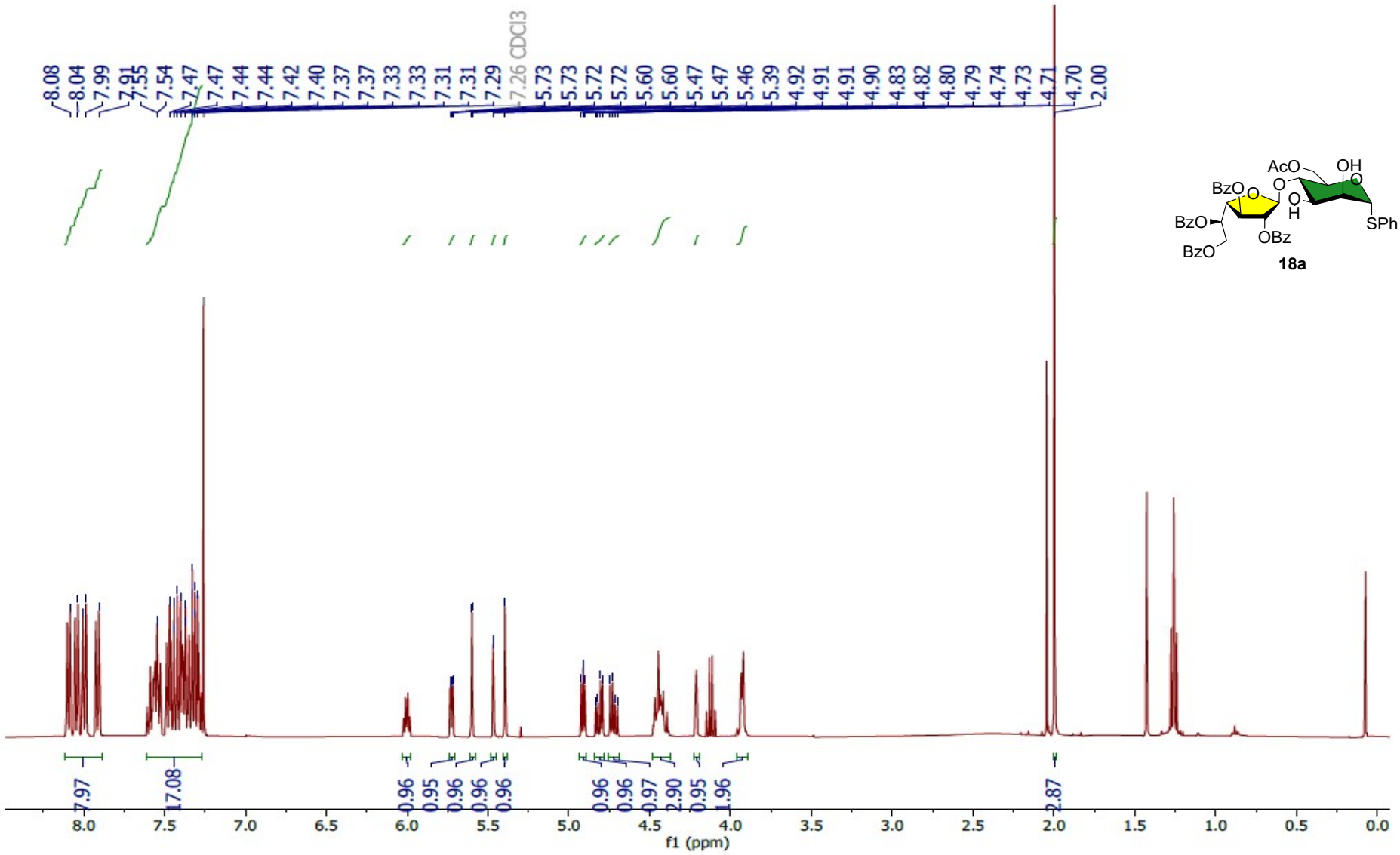


^{13}C NMR (D_2O, 125 MHz) of compound **2b**

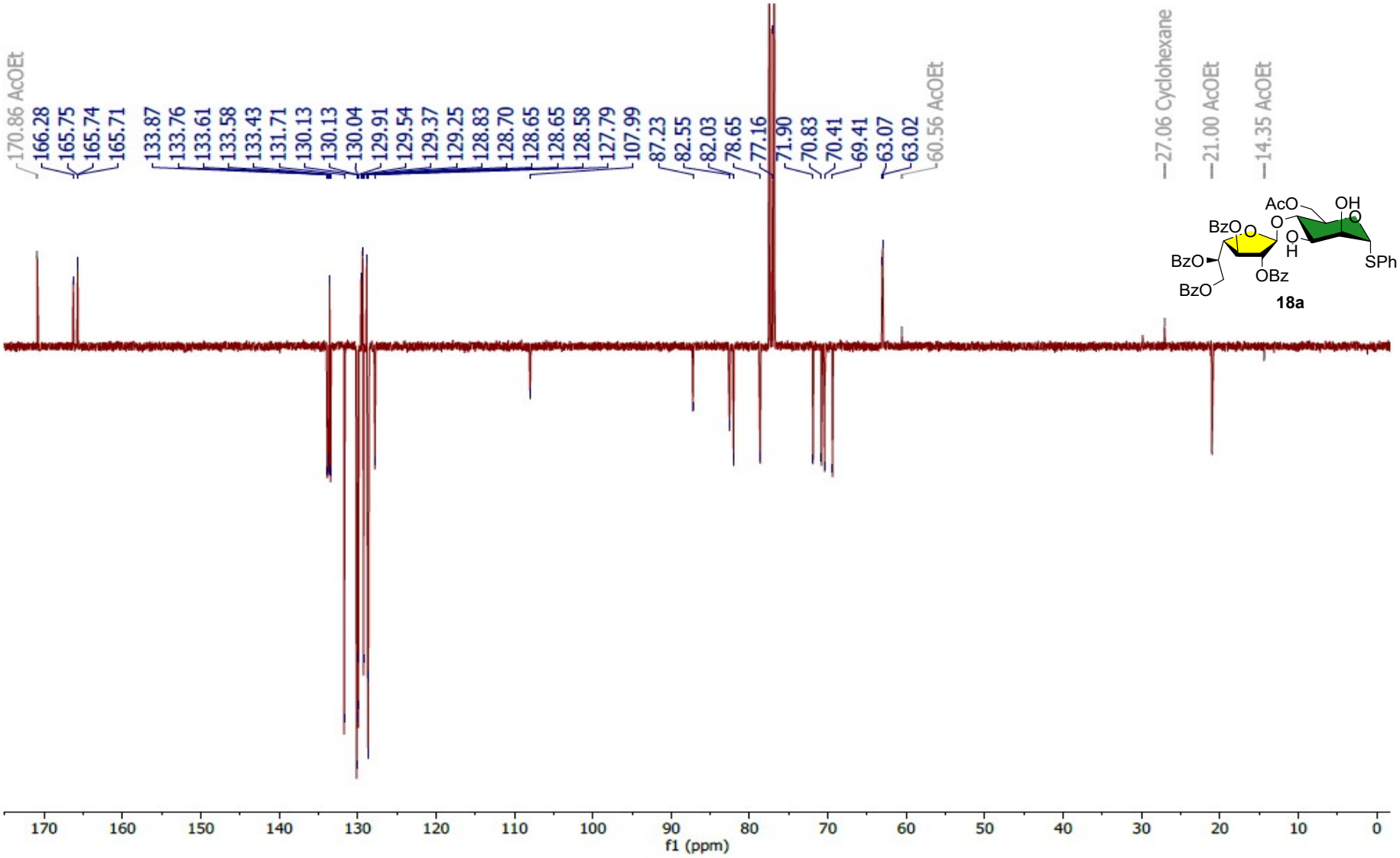
^{1}H and ^{13}C NMR Spectrum of trisaccharides 3 based on Man*p*-(1,6)-Man*p* skeleton



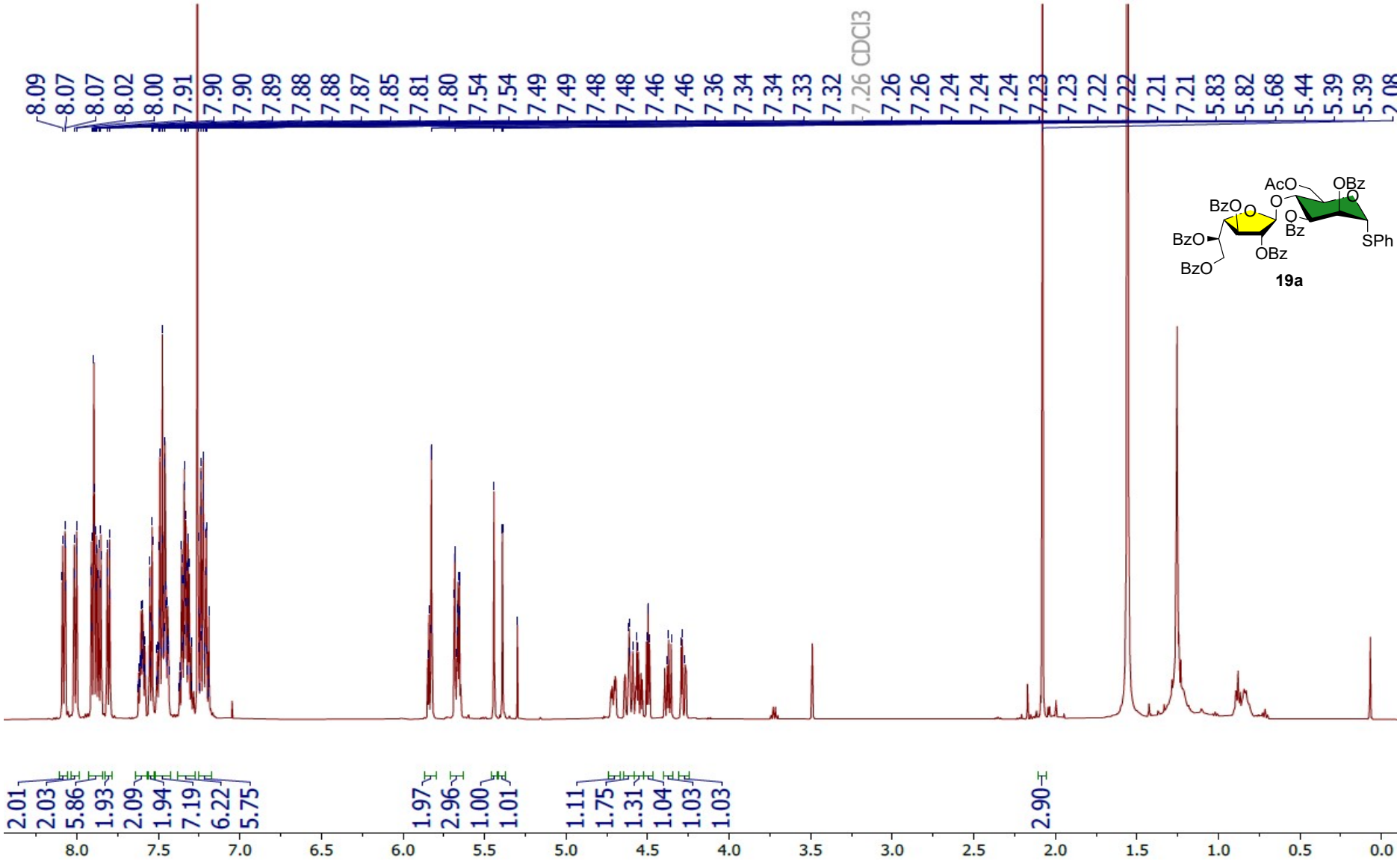
Reagents and conditions: (iv) AcOH, H_2O; (v) NaOMe, MeOH; (vi) NIS, CH_3CN/H_2O; (vii) BzCl, Pyr; (viii) AcCl, MeOH; (ix) **21**, TMSOTf, CH_2Cl_2.



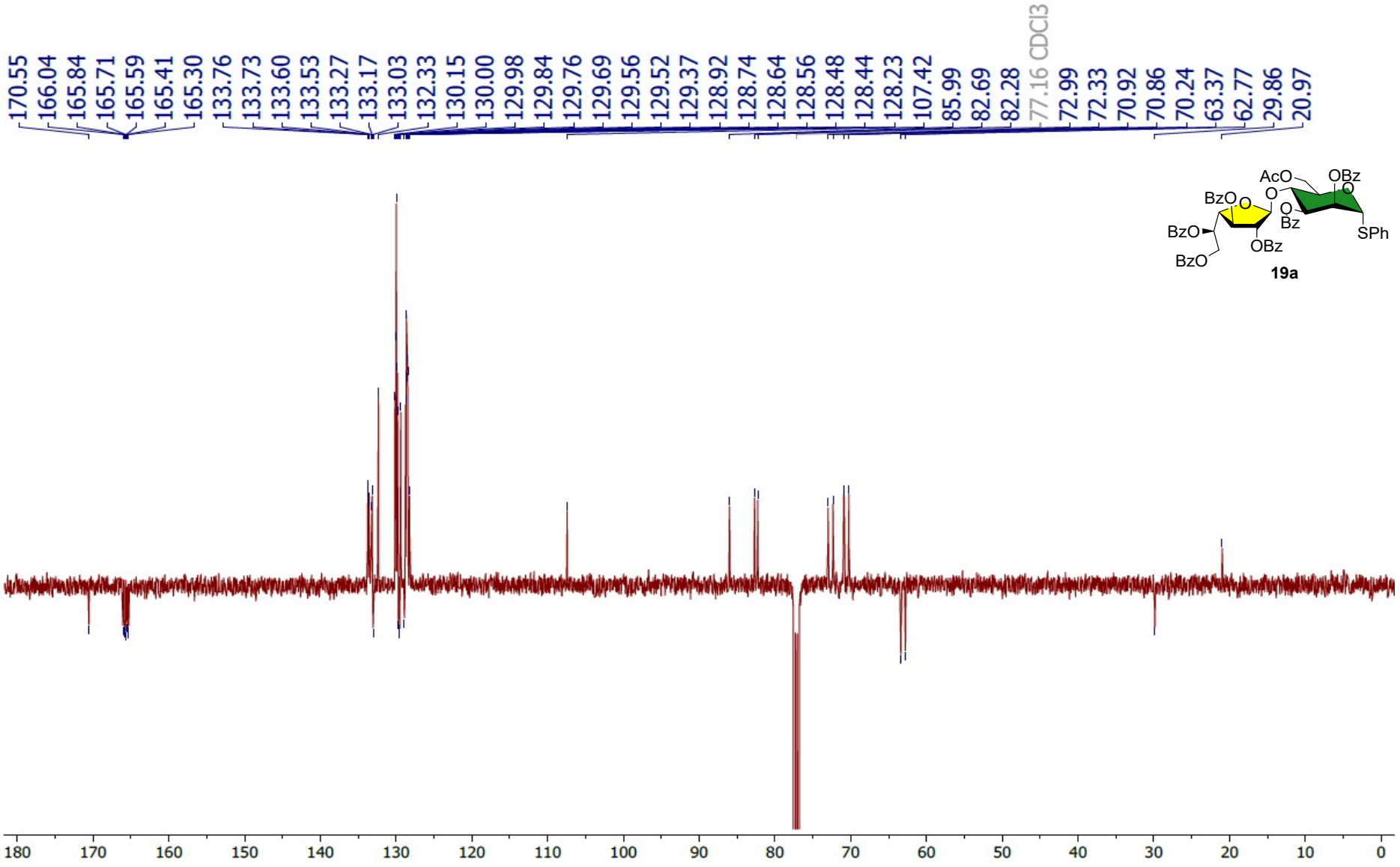
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **18a**



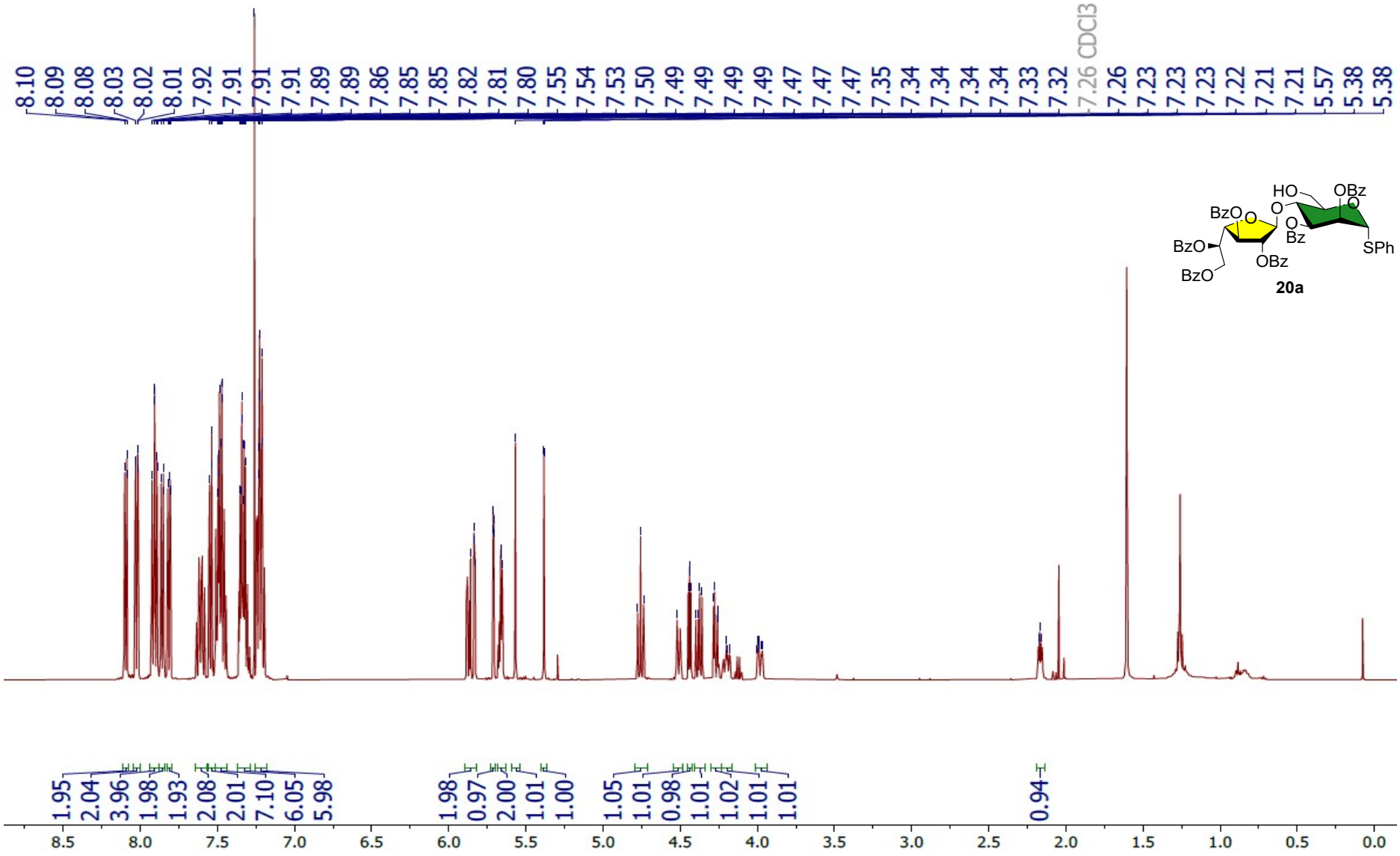
^{13}C NMR ($CDCl_3$, 100 MHz) of compound **18a**



^{1}H NMR ($CDCl_3$, 500 MHz) of compound **19a**



^{13}C NMR ($CDCl_3$, 125 MHz) of compound **19a**



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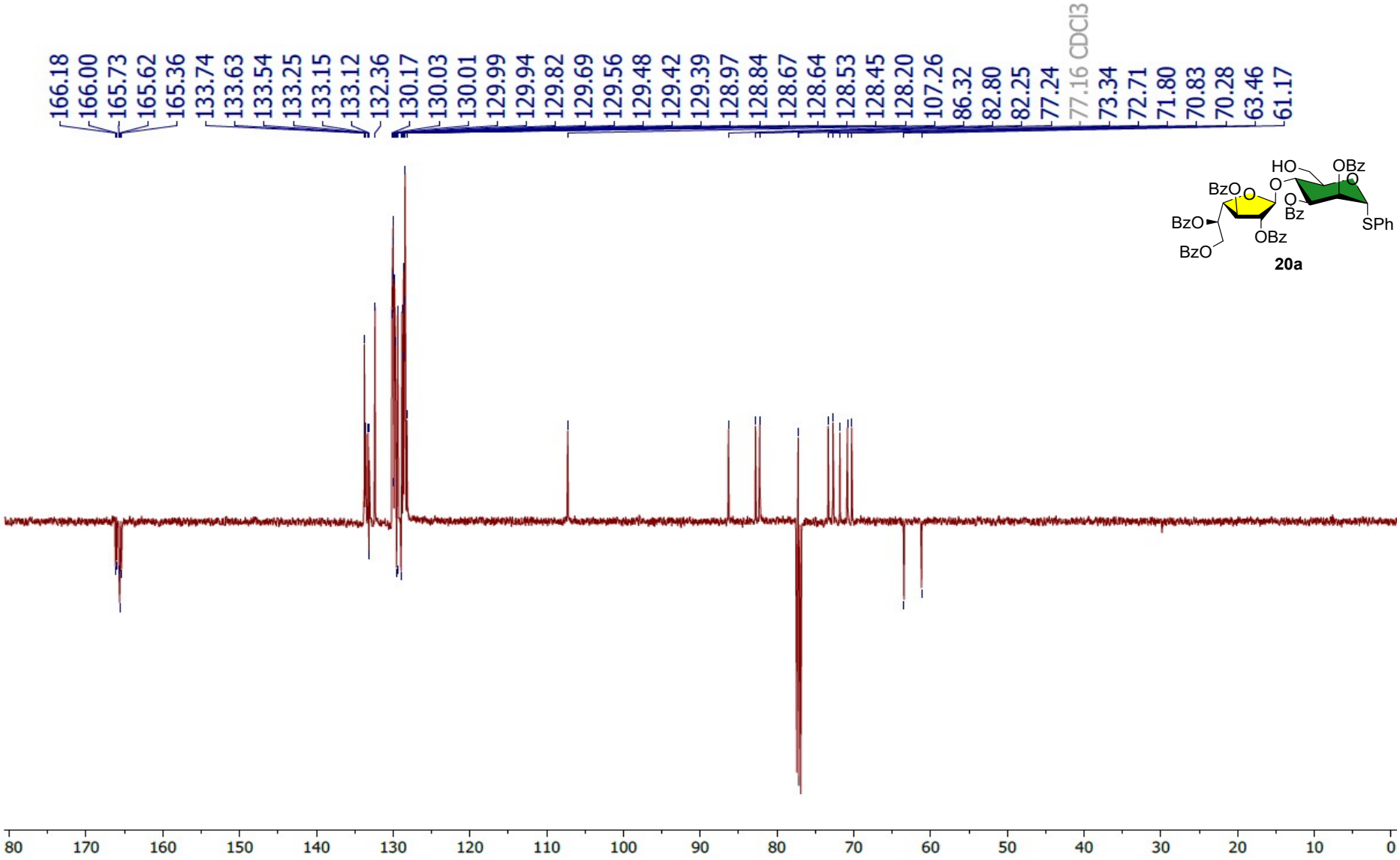
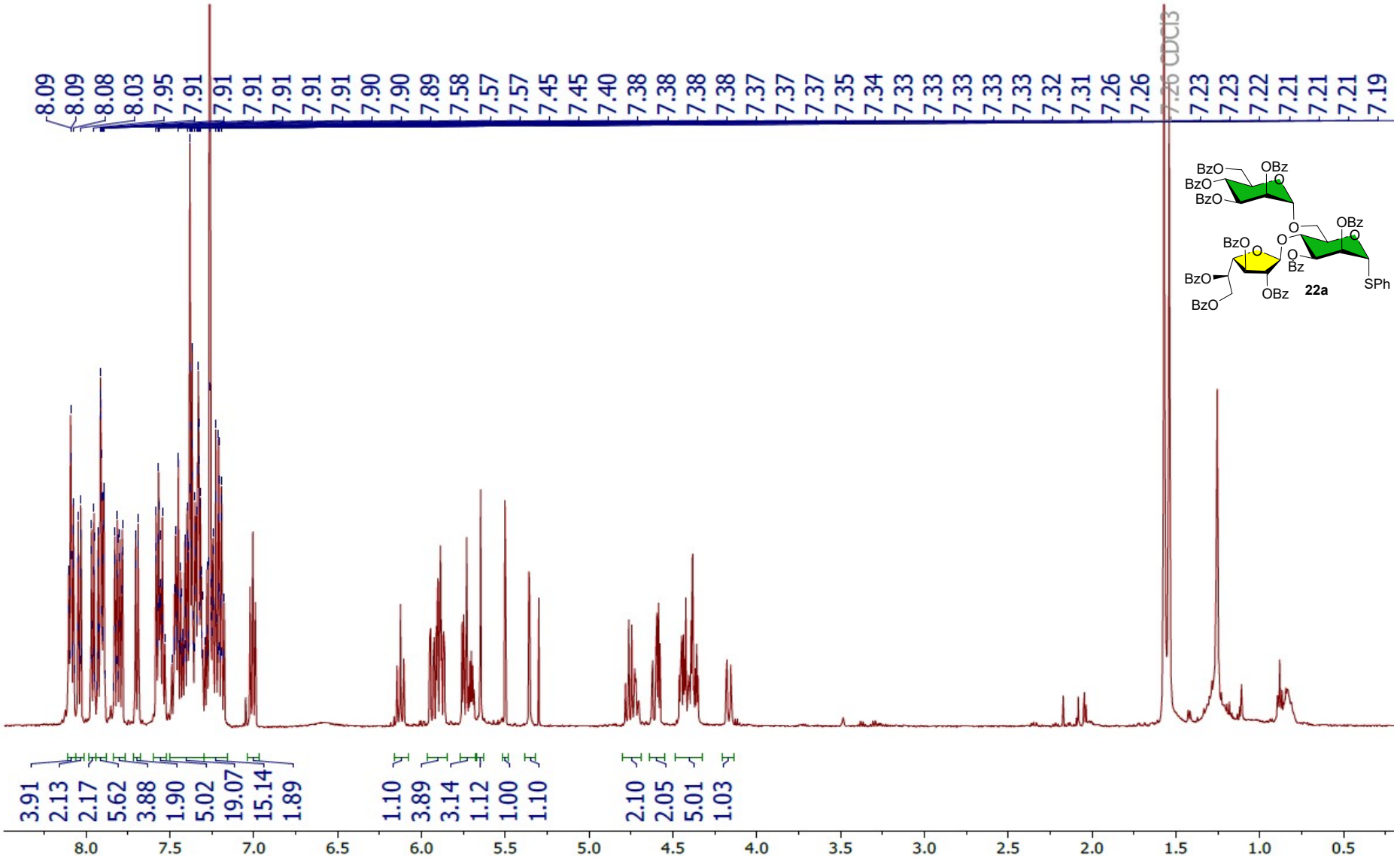
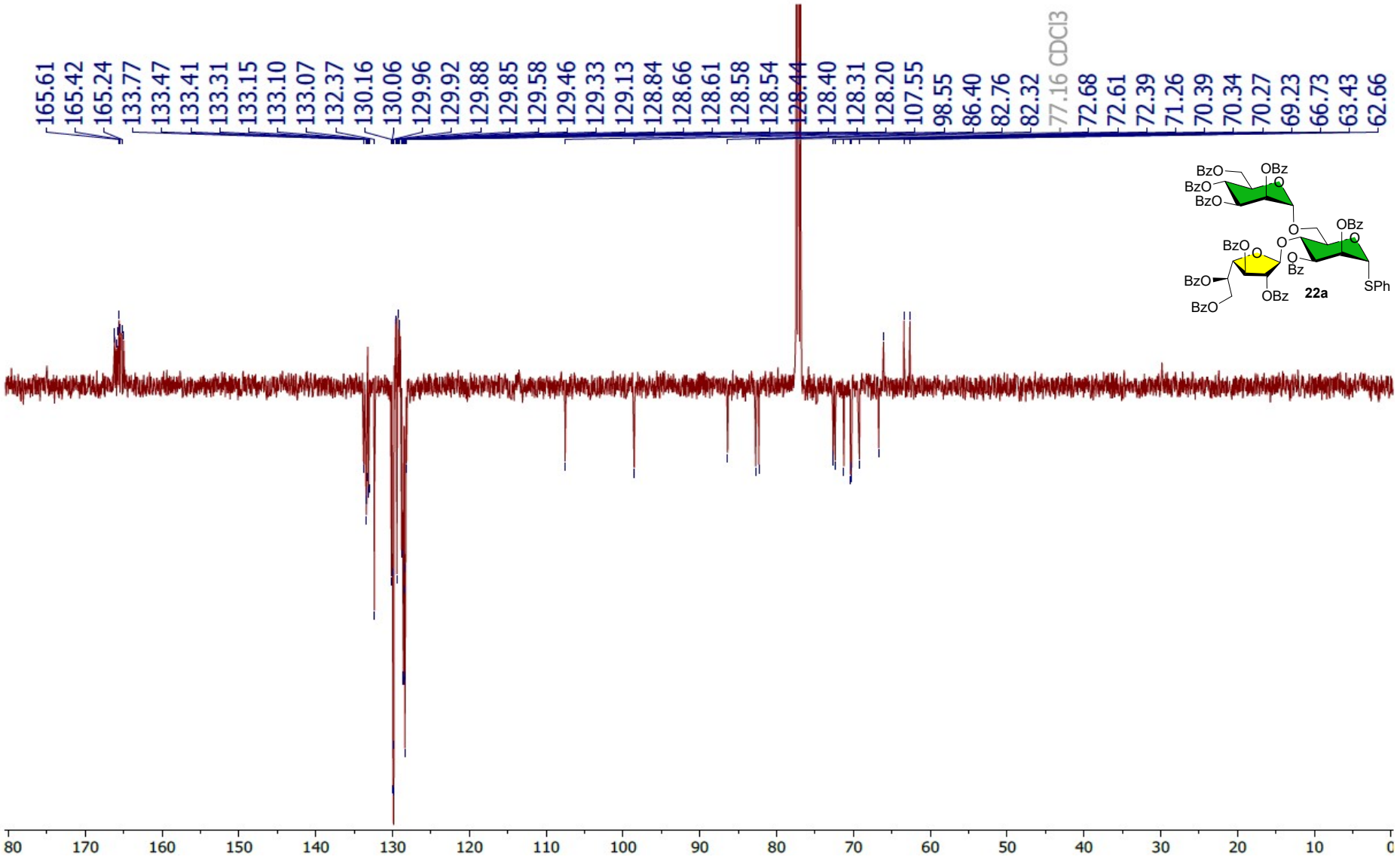


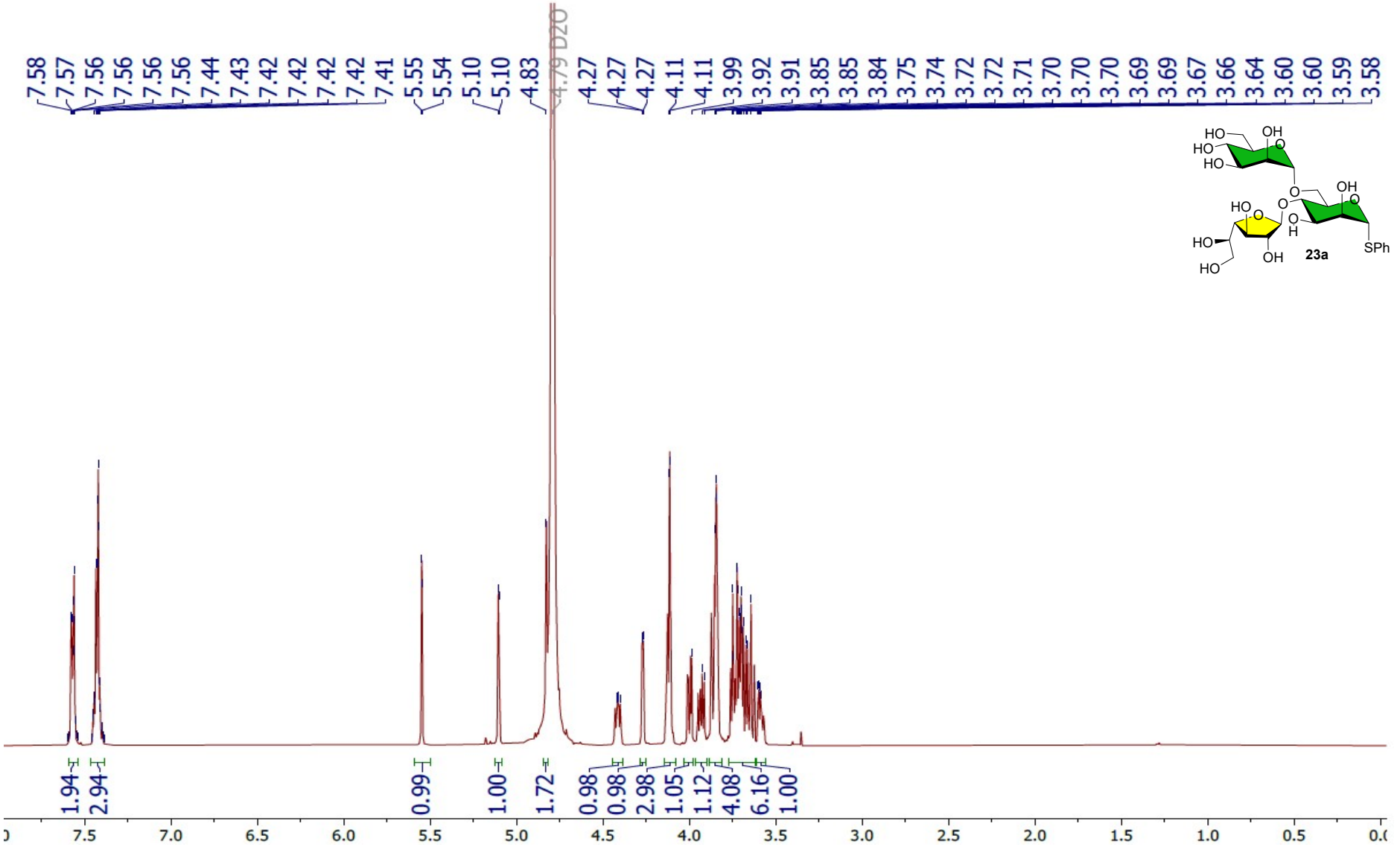
^{13}C NMR ($CDCl_3$, 125 MHz) of compound **20a**



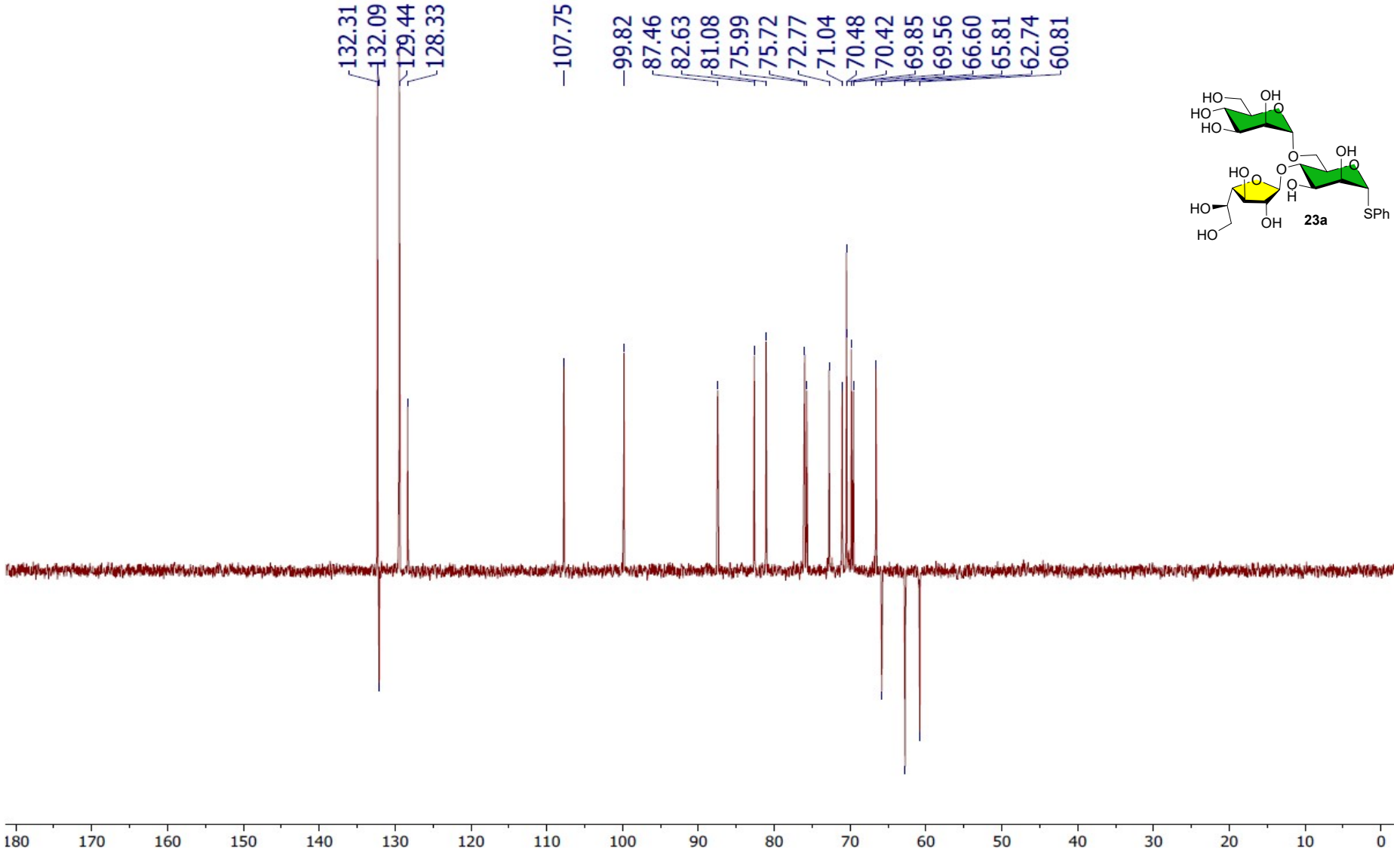
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **22a**



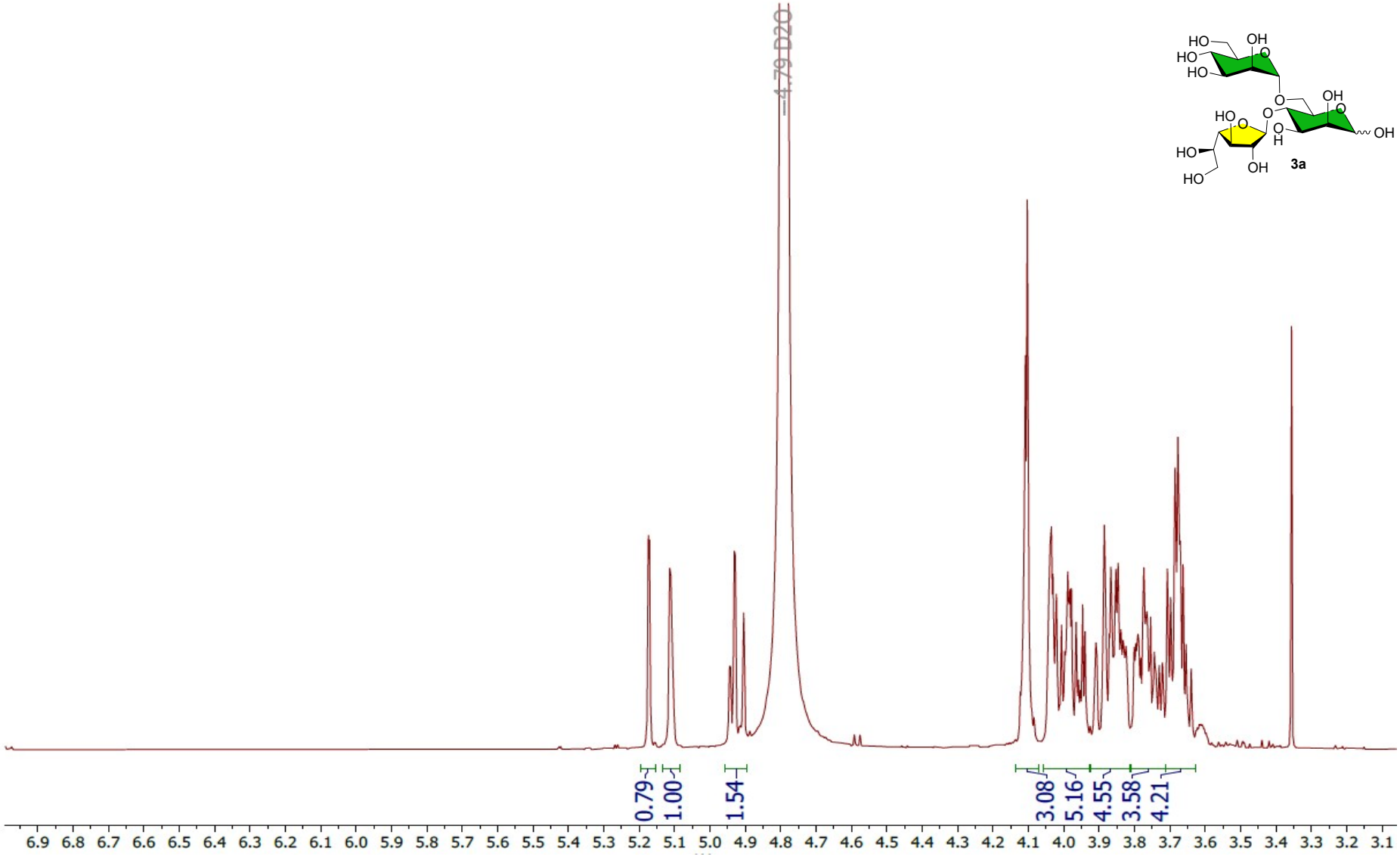
^{13}C NMR ($CDCl_3$, 125 MHz) of compound **22a**



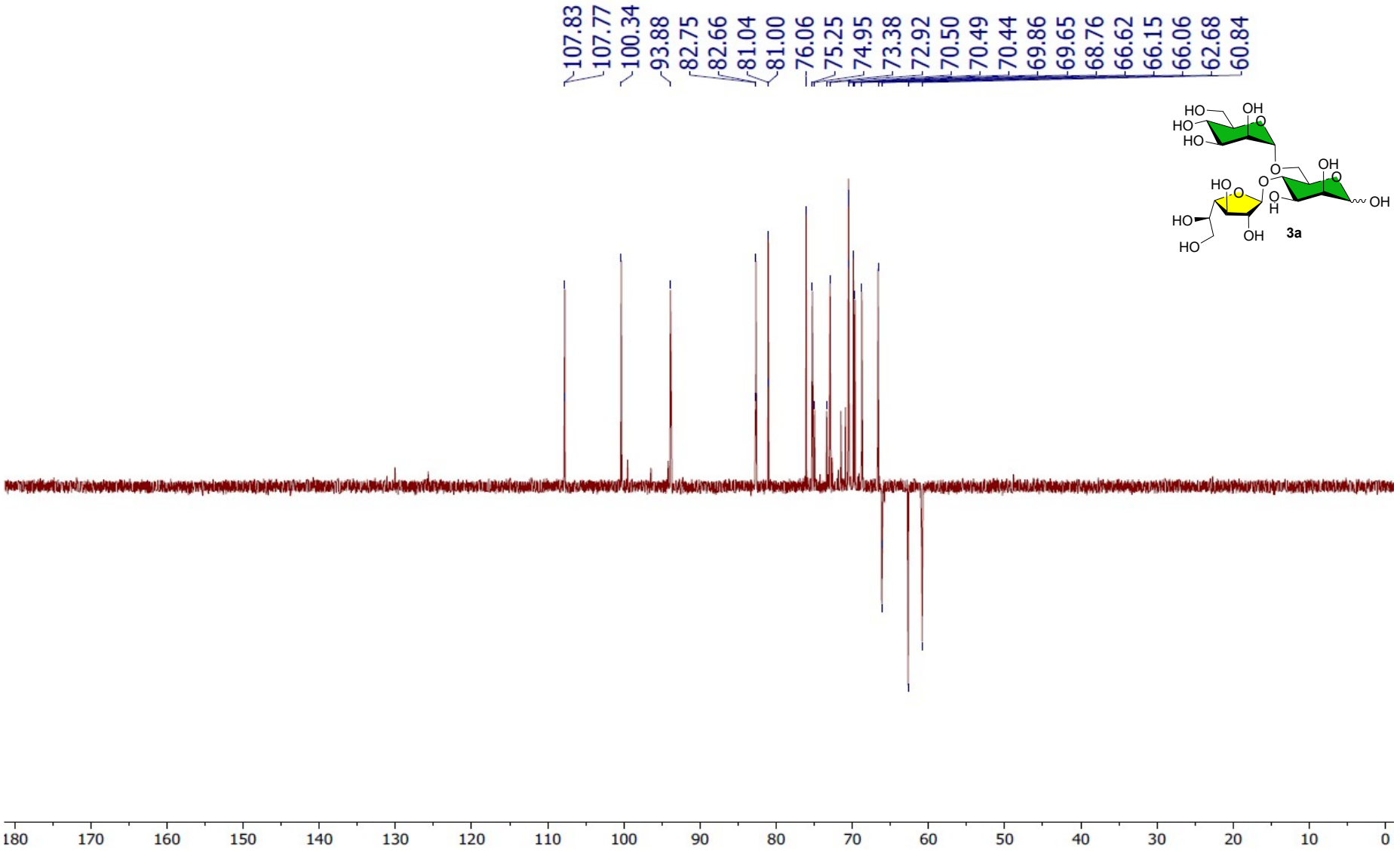
^{1}H NMR (D_2O, 500 MHz) of compound **23a**



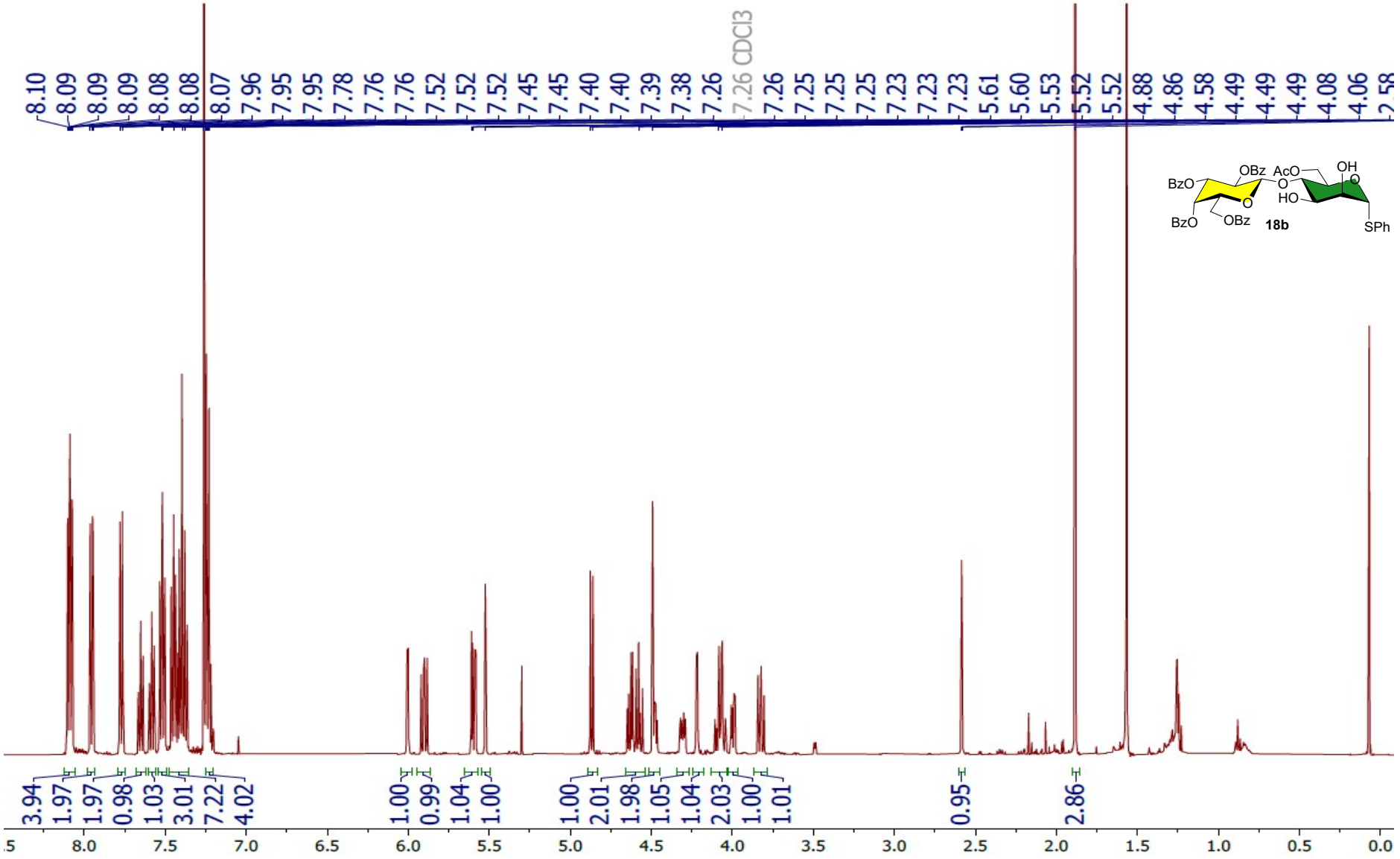
^{13}C NMR (D_2O, 125 MHz) of compound **23a**



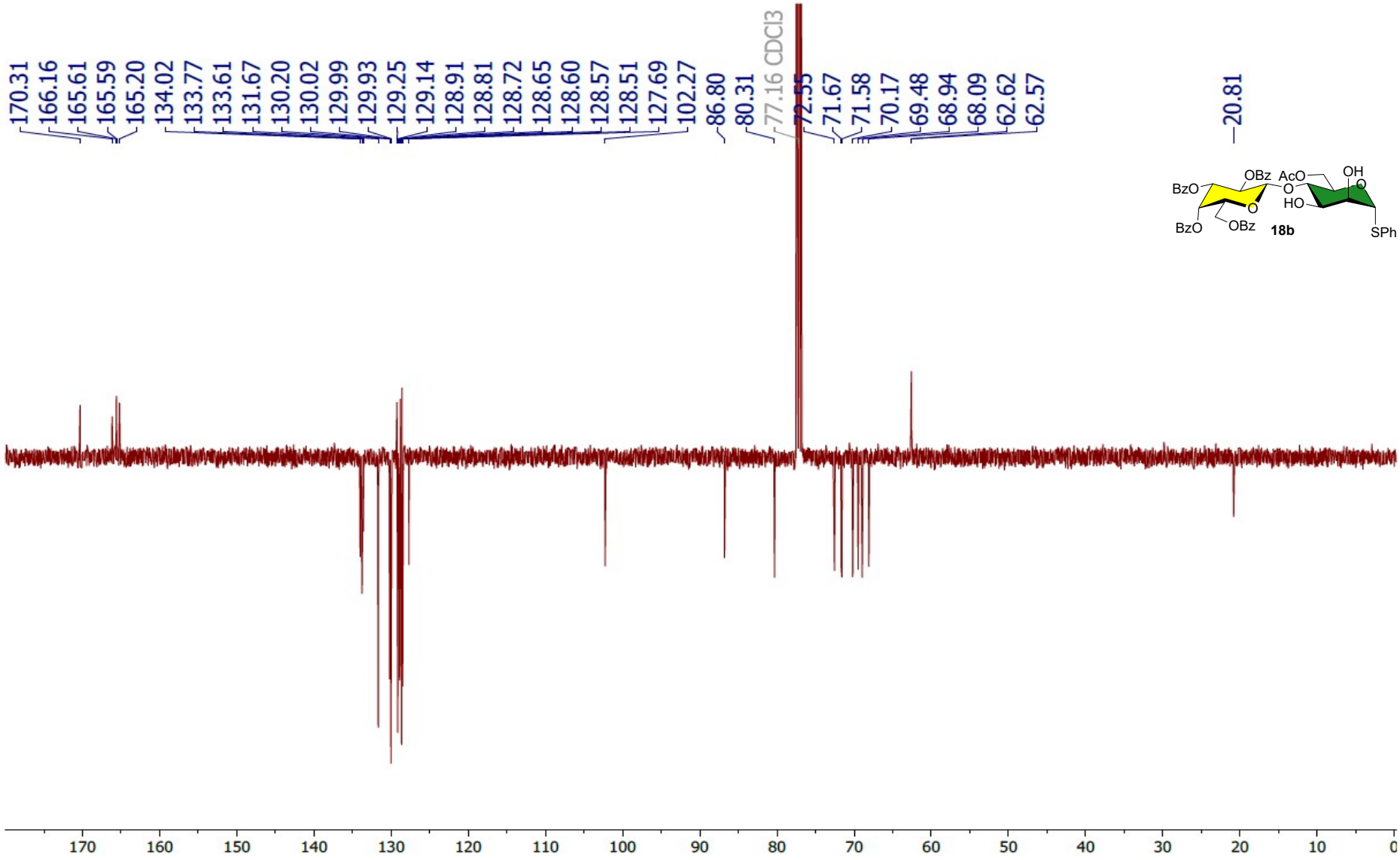
^{1}H NMR (D_2O, 500 MHz) of compound **3a**



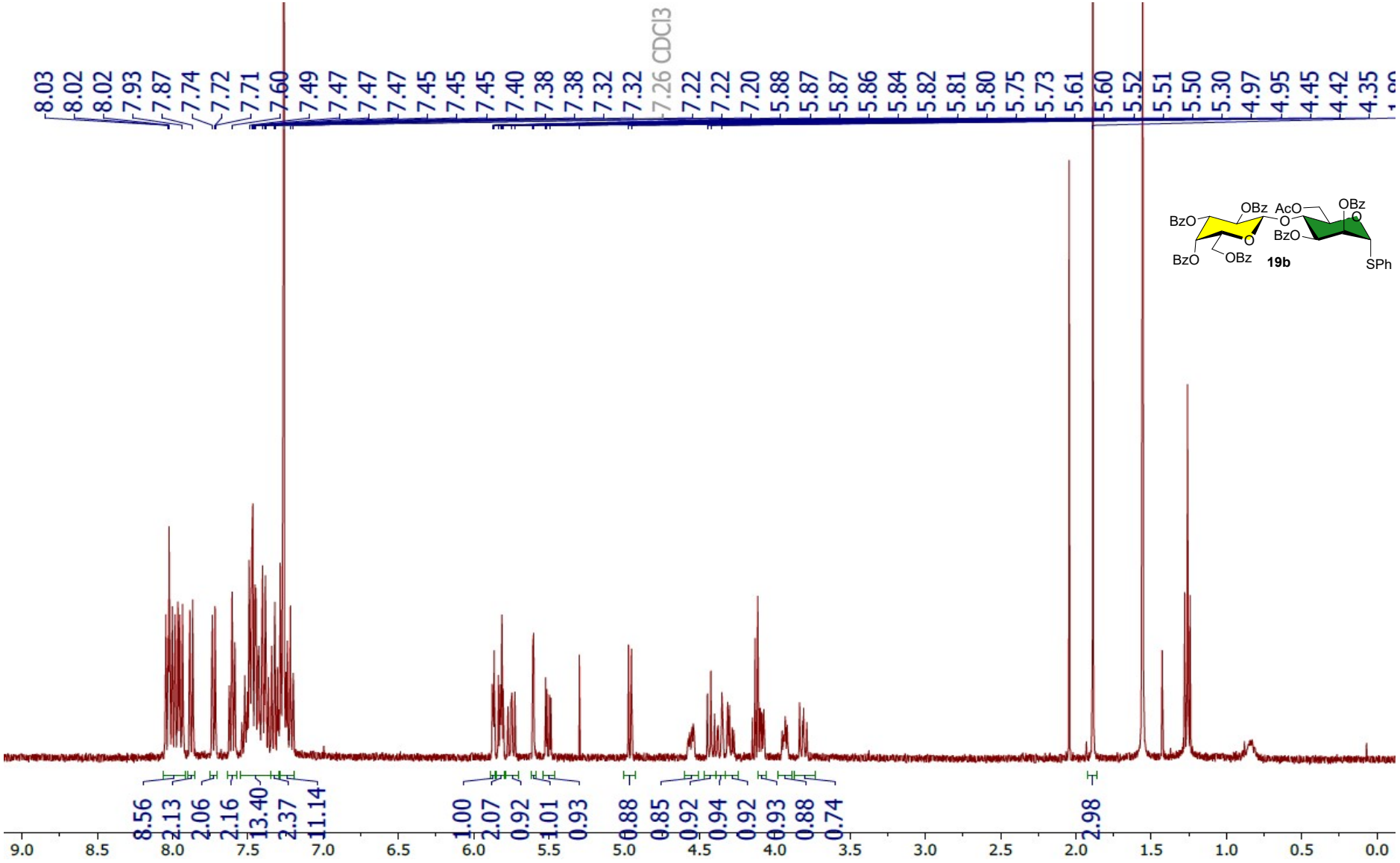
^{13}C NMR (D_2O, 125 MHz) of compound **3a**



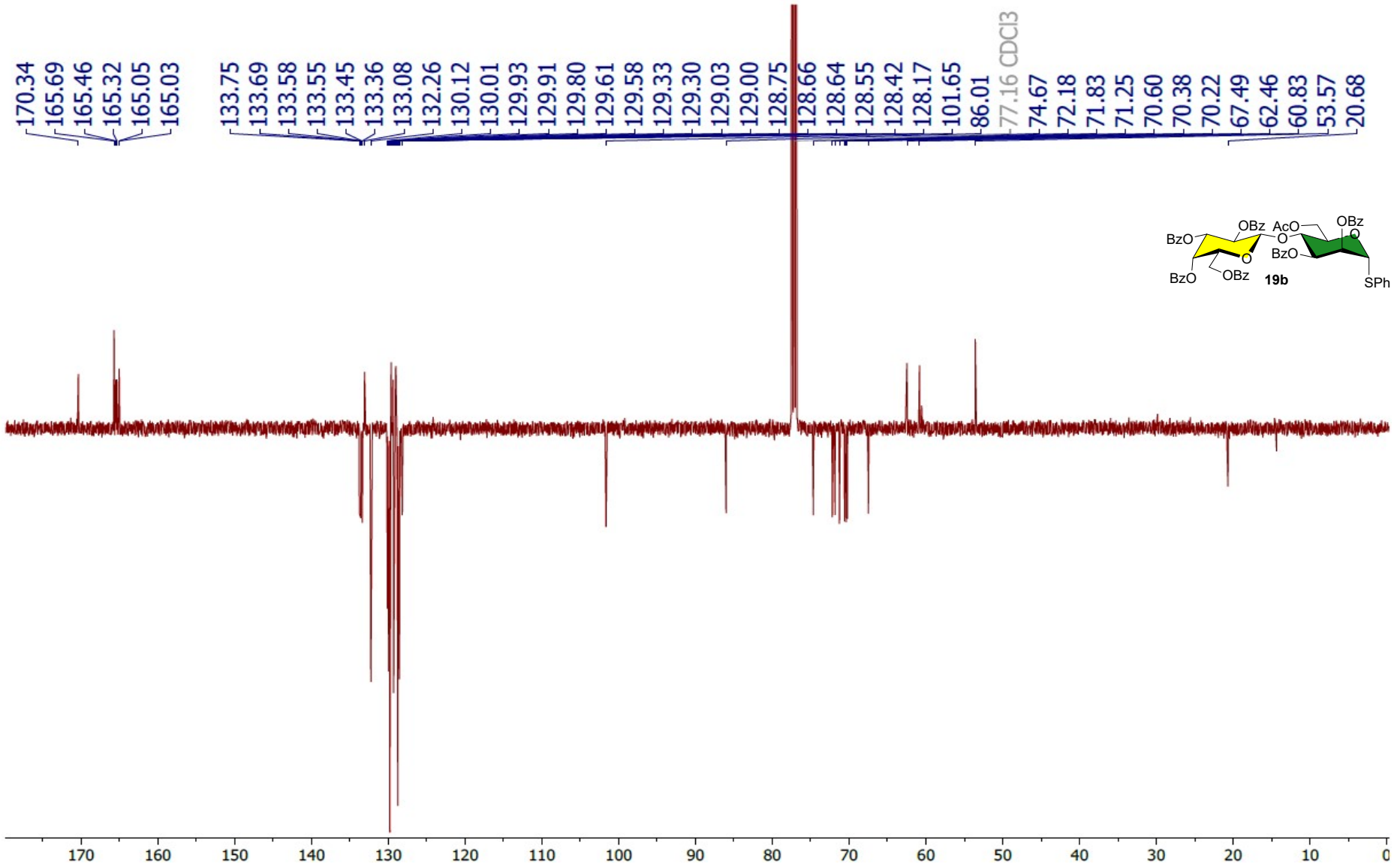
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **18b**



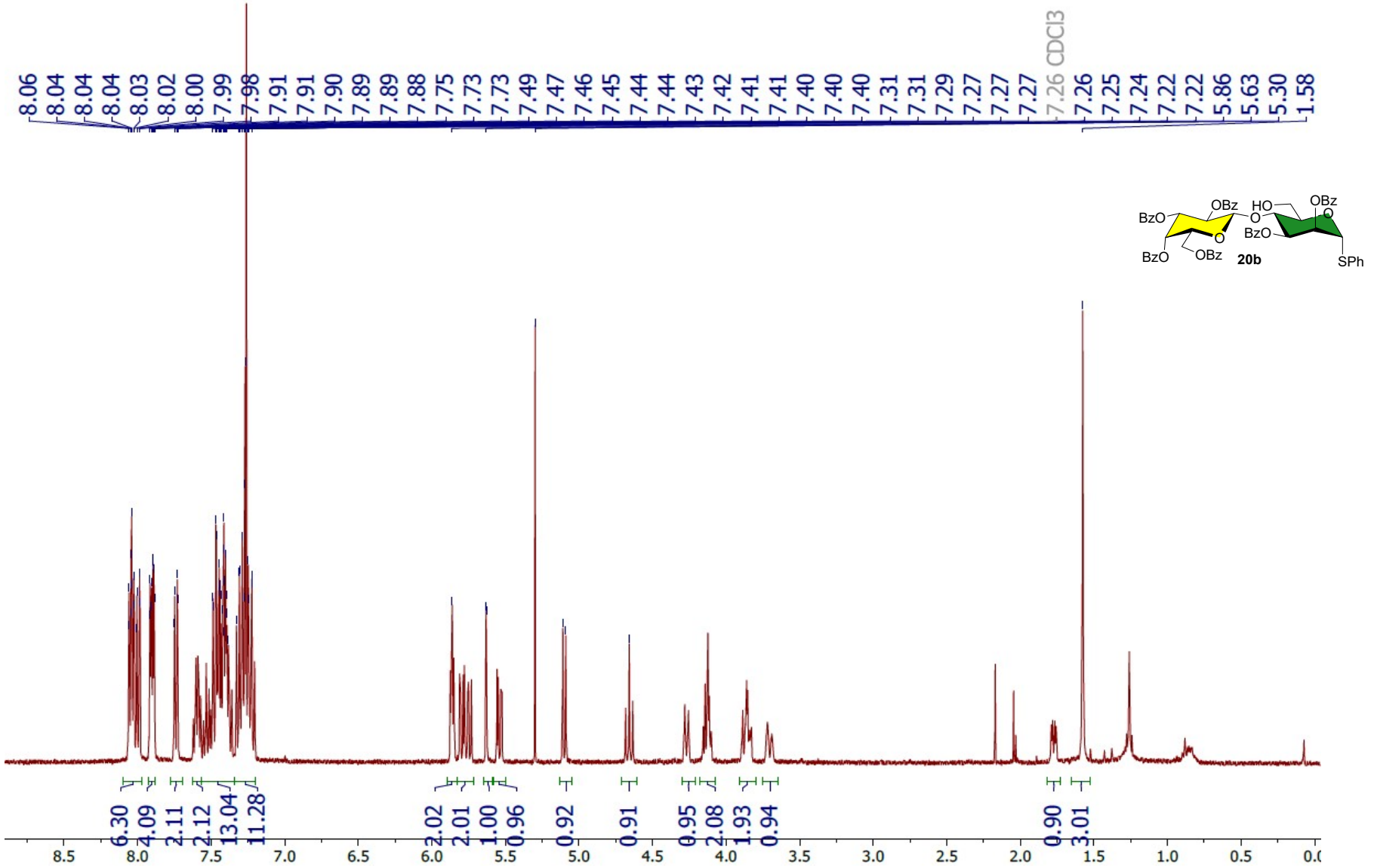
^{13}C NMR ($CDCl_3$, 125 MHz) of compound **18b**



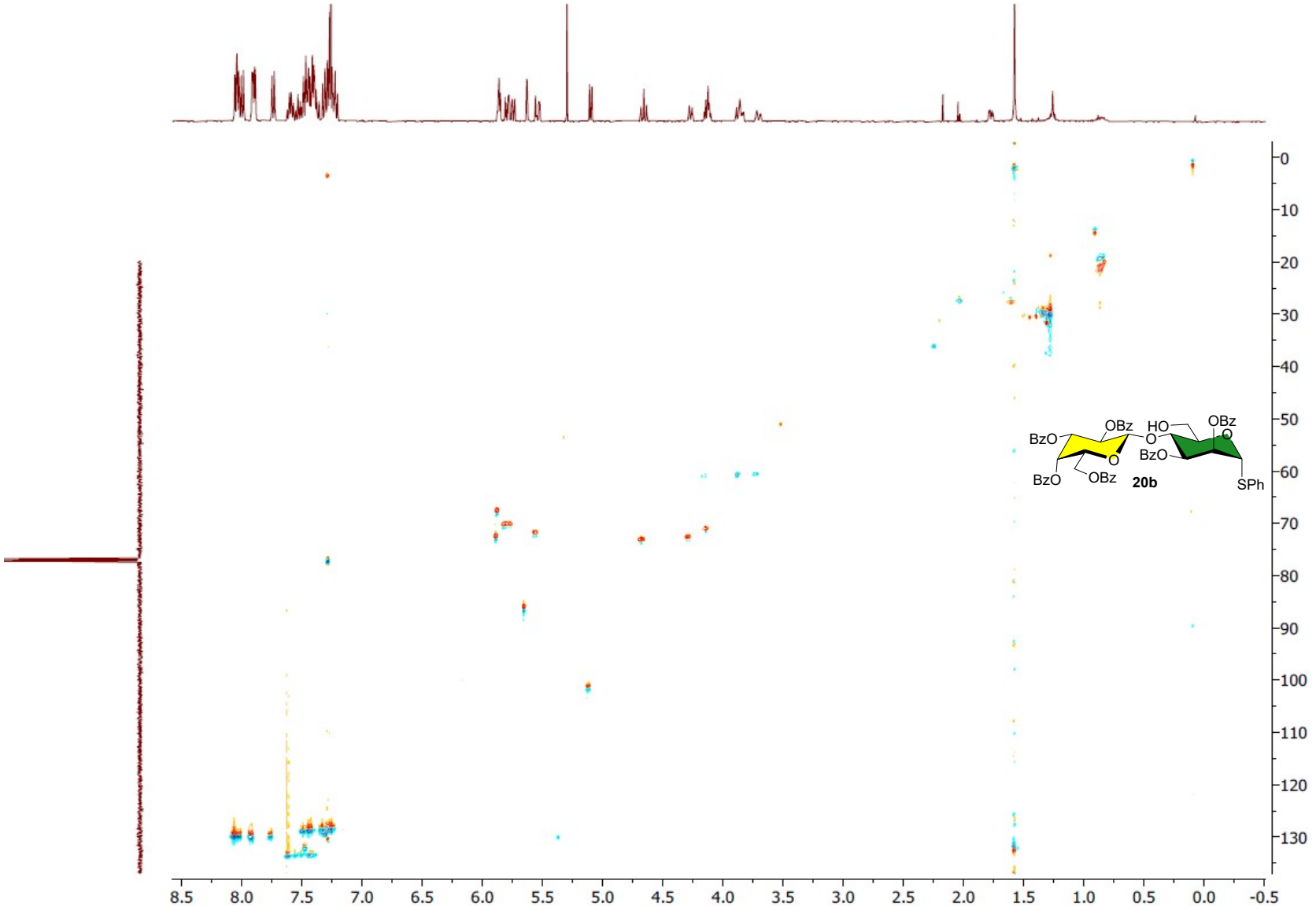
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **19b**



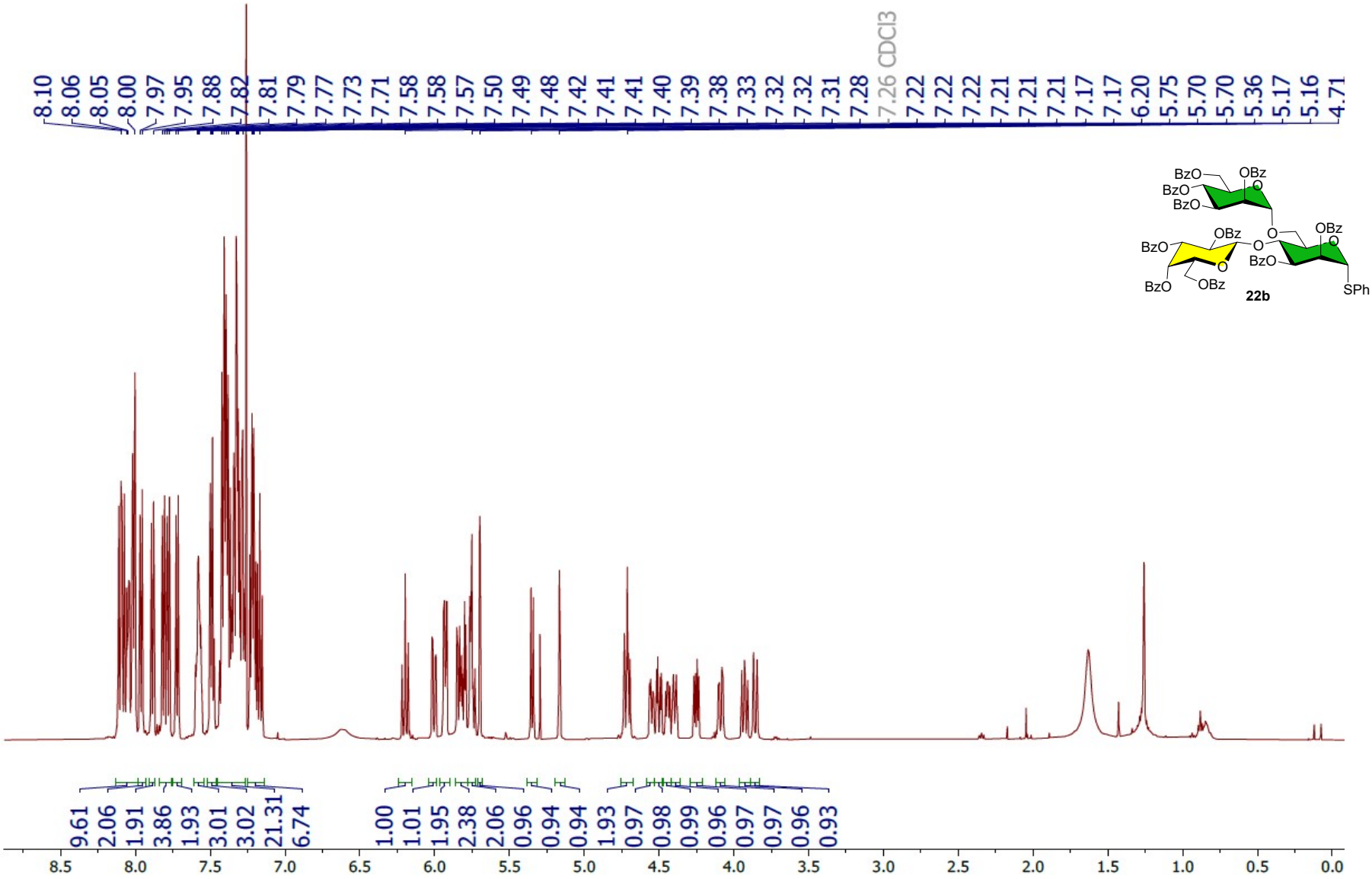
^{13}C NMR ($CDCl_3$, 125 MHz) of compound **19b**



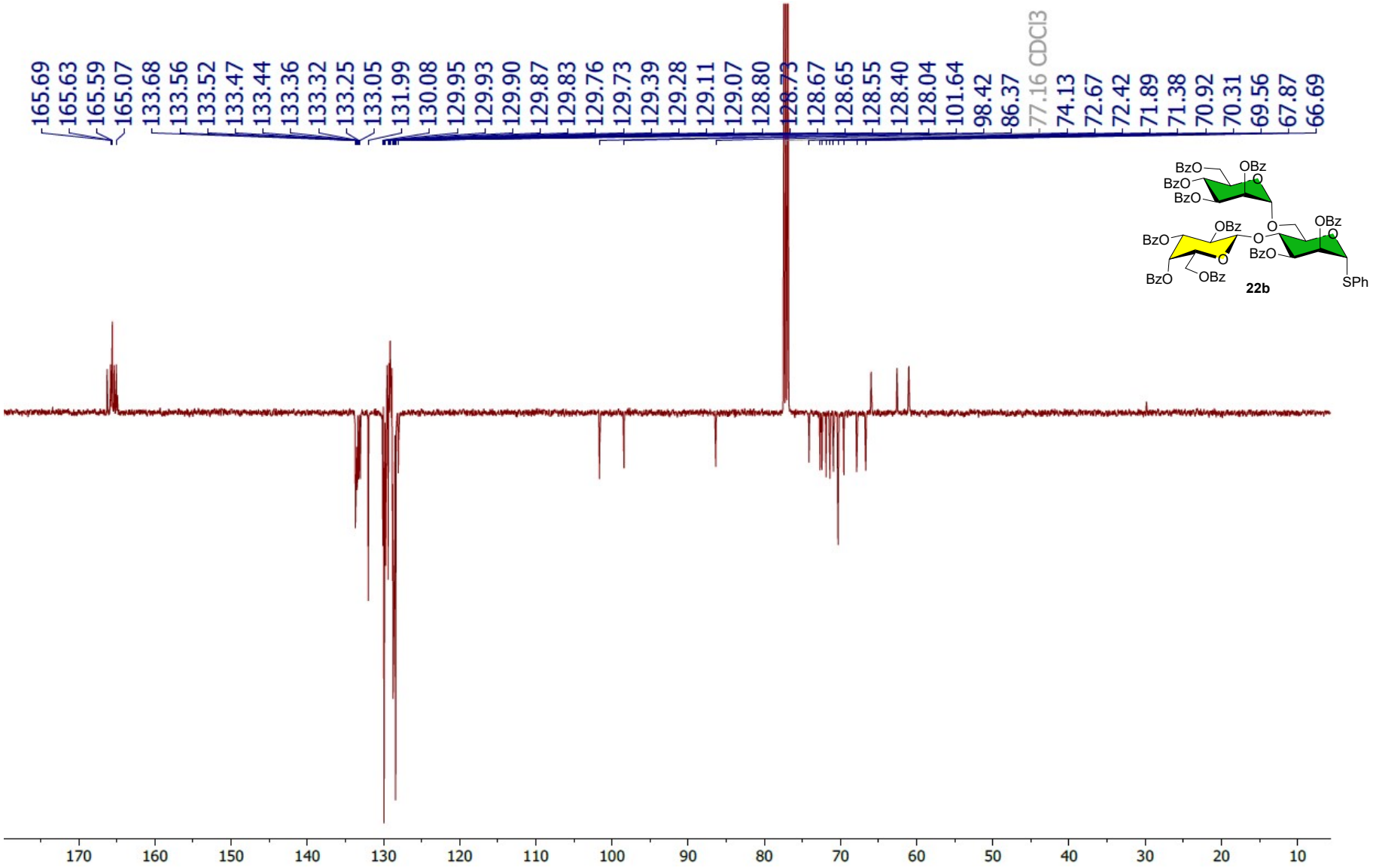
^{1}H NMR ($CDCl_3$, 400 MHz) of compound **20b**



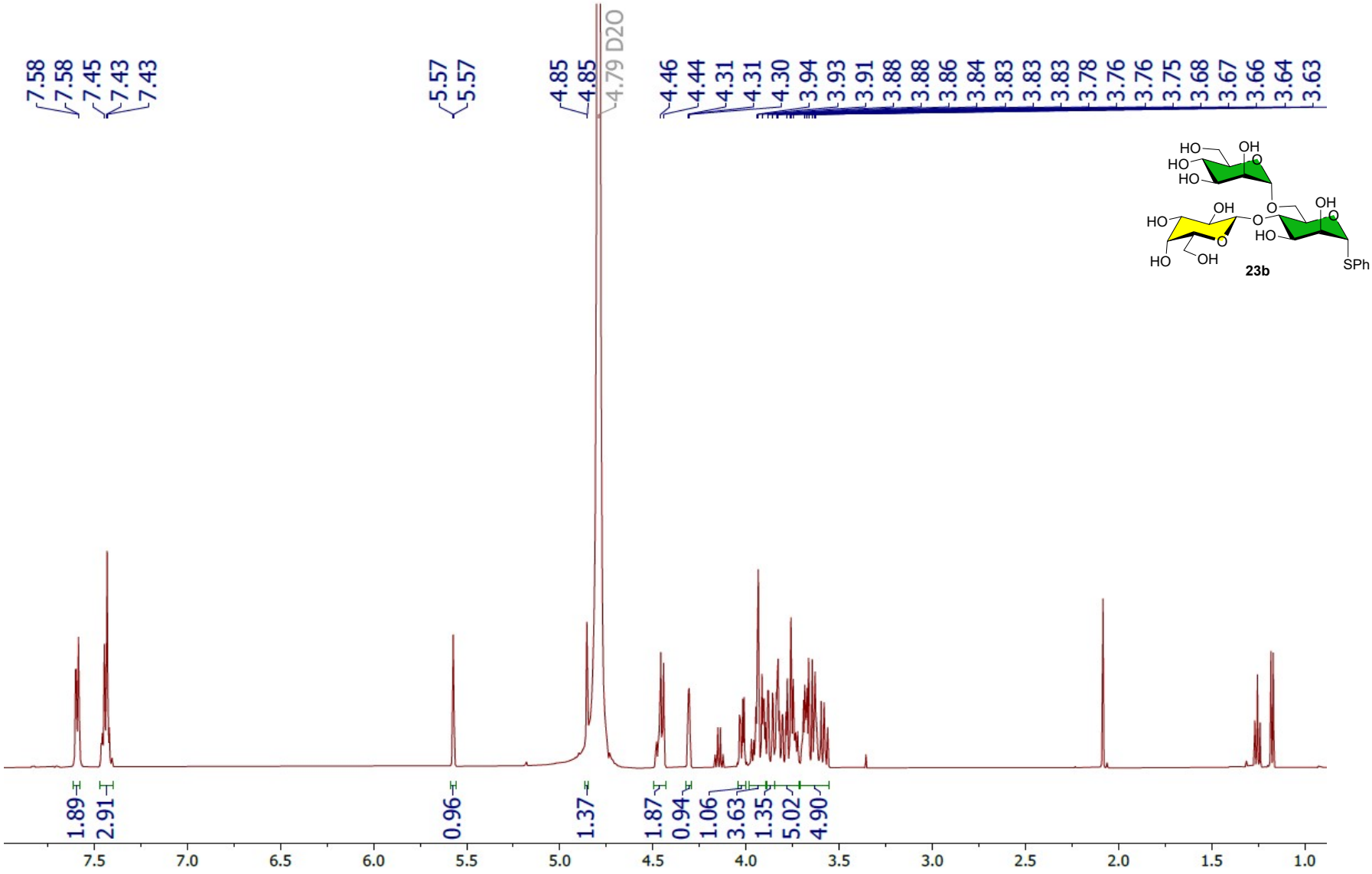
^{1}H-^{13}C HSQC ($CDCl_3$, 400 MHz) of compound **20b**



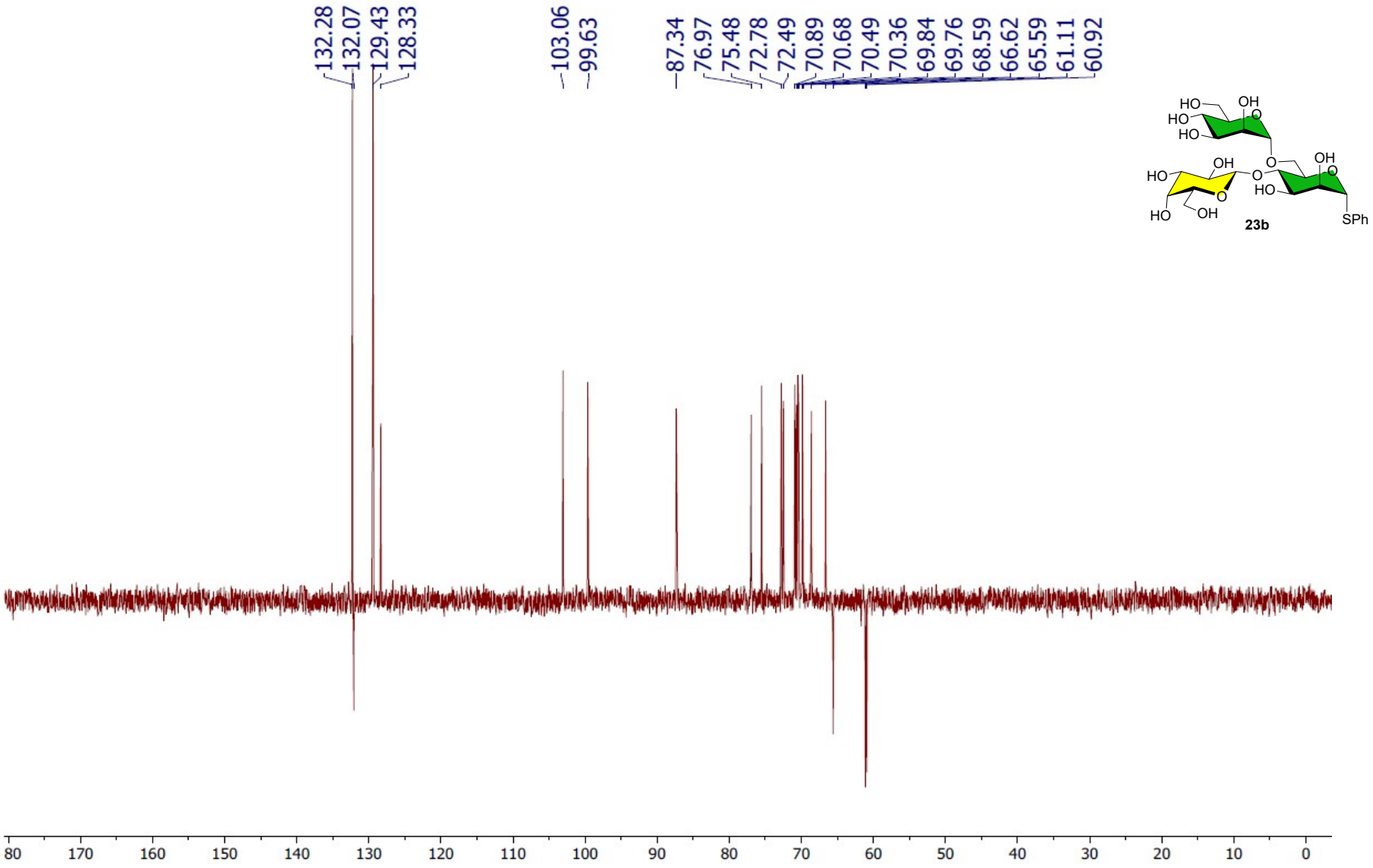
^{1}H NMR ($CDCl_3$, 500 MHz) of compound **22b**



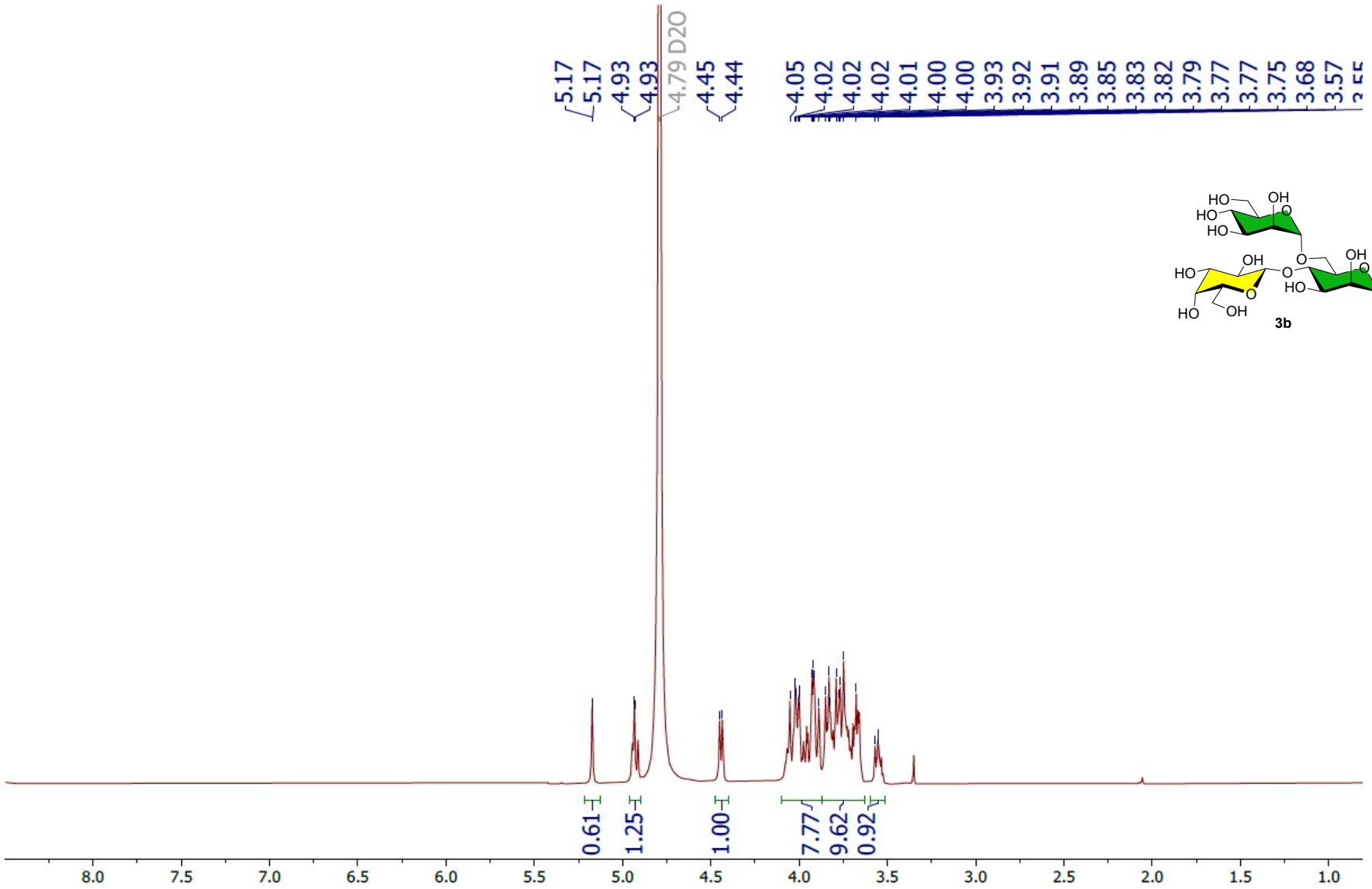
^{13}C NMR ($CDCl_3$, 125 MHz) of compound **22b**



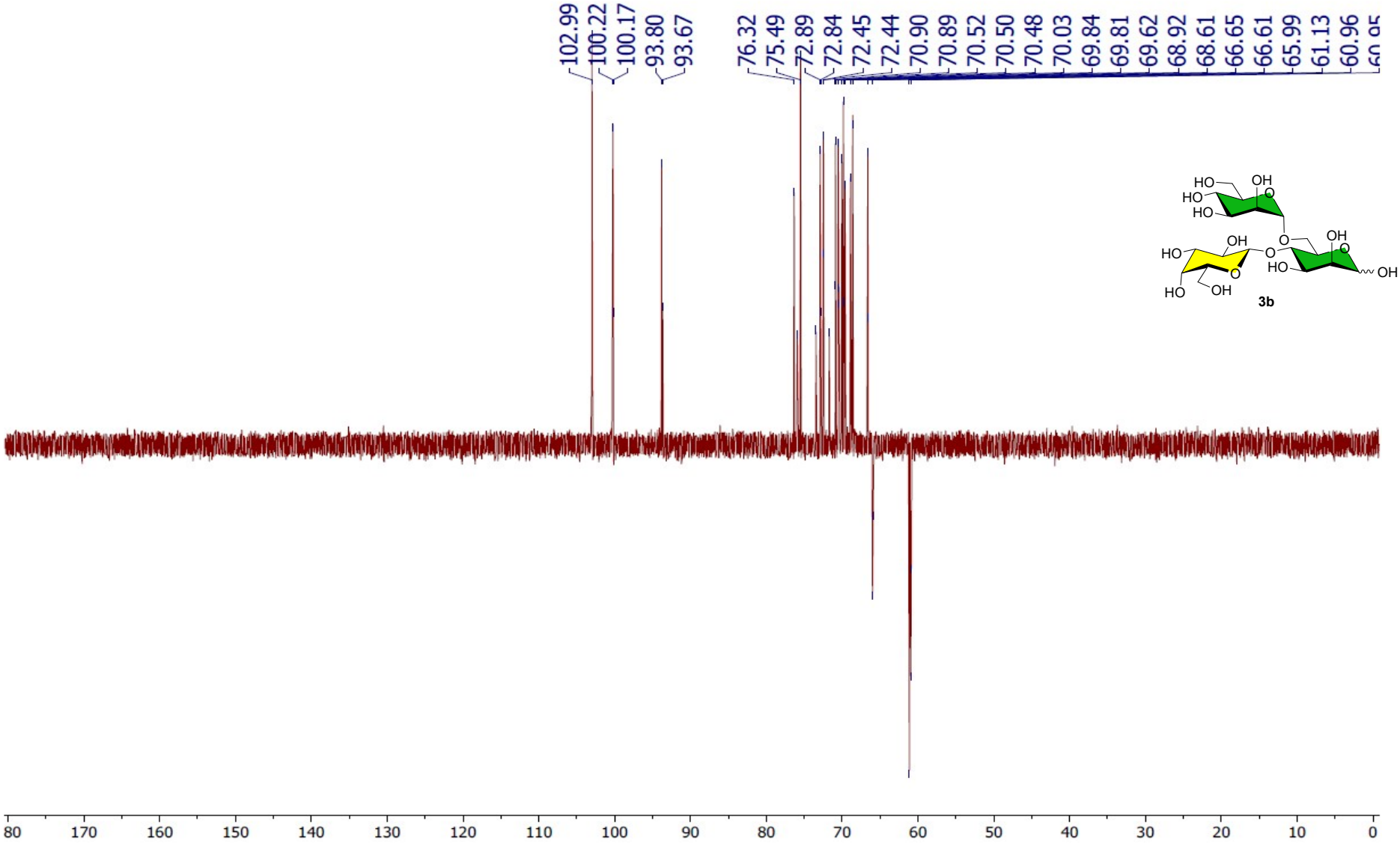
^{1}H NMR (D_2O, 500 MHz) of compound **23b**



^{13}C NMR (D_2O, 125 MHz) of compound **23b**



^{1}H NMR (D_2O, 500 MHz) of compound **3b**



^{13}C NMR (D_2O, 125 MHz) of compound **3b**