SUPPORTING INFORMATION

RAPID ACCESS TO 1,6-ANHYDRO-β-L-HEXOPYRANOSE DERIVATIVES VIA DOMINO REACTION: SYNTHESIS OF L-ALLOSE AND L-GLUCOSE

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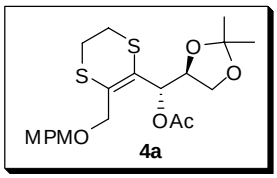
CONTENTS

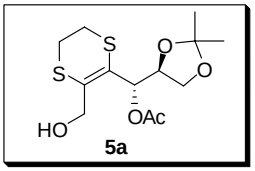
All moisture-sensitive reactions were performed under nitrogen atmosphere using oven-dried glassware. Solvents were dried over standard drying agents and freshly distilled prior to use. Reactions were monitored by TLC (precoated silica gel plate F_{254}, Merck). Column chromatography: Merck Kieselgel 60 (70-230 mesh); flash chromatography: Merck Kieselgel 60 (230-400 mesh). Melting points are uncorrected and were determined with a capillary apparatus. Optical rotations were measured at 25 ± 2 °C in the stated solvent. ^{1}H and ^{13}C NMR spectra were recorded on NMR spectrometers operating at 200, 300, 400 or 500 MHz and 50, 75, 100 or 125 MHz, respectively. Combustion analyses were performed using CHNS analyzer.



4a

Compound 4a. The *anti*-diastereomer afforded by reaction of **1** with **2** (according to ref. 9) was acetylated by treatment with Ac_2O in pyridine overnight at room temperature. Then solvent removal under reduced pressure and chromatography of the crude residue on silica gel (hexane/EtOAc = 7:3) gave the pure **4a** (98% yield): oily, $[\alpha]^{25}_{D}$ +27.0 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, C_6D_6): δ 1.27 (s, 3H), 1.35 (s, 3H), 1.71 (s, 3H), 2.42-2.49 (m, 3H), 2.55-2.61 (m, 1H), 3.27 (s, 3H), 3.99 (dd, *J* = 6.5 Hz, *J* = 8.5 Hz, 1H), 4.08 (dd, *J* = 6.5 Hz, *J* = 8.5 Hz, 1H), 4.29 (d, *J* = 12.2 Hz, 1H), 4.48 (s, 3H), 4.63 (d, *J* = 12.2 Hz, 1H), 6.26 (d, *J* = 5.9 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6): δ 20.3, 25.6, 26.5, 26.9, 29.5, 54.7, 66.6, 70.9, 72.1, 73.2, 76.7, 109.4, 114.0, 125.1, 129.2, 129.9, 130.8, 159.8, 169.0. Anal. calcd for $C_{21}H_{28}O_6S_2$: C 57.25, H 6.41, S 14.56. Found: C 57.08, H 6.44, S 14.63.

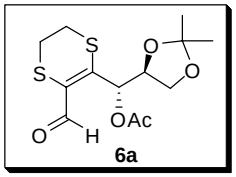
Compound 4b. Synthetic procedure and characterization data have been previously described according to ref. 9.



5a

Compound 5a. To a stirred 9:1 CH_2Cl_2/H_2O emulsion (100 mL) containing the MPM ether **4a** (1.08 g, 2.46 mmol), DDQ (0.84 g, 3.68 mmol) was added in one portion at room temperature. After 3h, H_2O was added and the resulting mixture was extracted with CH_2Cl_2; the organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure. Chromatography of the crude residue over silica gel (hexane/acetone = 9:1) gave the pure **5a** (0.57 g; 72% yield): oily, $[\alpha]^{25}_D$ +31.0 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 3H), 1.42 (s, 3H), 2.05 (s, 3H), 3.02-3.08 (m, 2H), 3.16-3.22 (m, 2H), 3.76 (dd, *J* = 6.3 Hz, *J* = 8.7 Hz, 1H), 4.10 (dd, *J* = 6.3 Hz, *J* = 8.7 Hz, 1H), 4.10 (bd, *J* = 13.0 Hz, 1H), 4.26 (bd, *J* = 13.0 Hz, 1H), 4.38-4.43 (m, 1H), 5.60 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.1, 26.2, 27.0, 29.7, 29.9, 63.3, 67.3, 73.8, 74.2, 108.7, 124.5, 128.5, 170.1. Anal. calcd for $C_{13}H_{20}O_5S_2$: C, 48.73; H, 6.29, S 20.01. Found: C, 48.60; H 6.32, S 20.08.

Compound 5b. Synthetic procedure and characterization data have been previously described according to ref. 9.

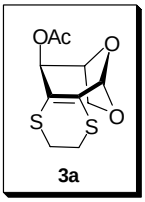


6a

Compound 6a. A solution of alcohol **5a** (0.56 g, 1.8 mmol) in pyridine (4 mL) was added in one portion to a stirred suspension of PCC (0.54 g, 2.50 mmol) and Celite (0.54 g) in Py (14 mL) at room temperature. The resulting mixture was stirred for 8 h and then diluted with 20 mL of anhydrous Et_2O, kept in an ultrasound bath for 30 min and filtered on a Celite pad. After solvent removal under reduced pressure, chromatography of the crude residue over silica gel (hexane/acetone = 9:1) gave the pure **6a** (0.54 g, 97% yield): oily, $[\alpha]^{25}_D$ +68.2 (*c* 0.8, $CHCl_3$). ^{1}H

NMR (200 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.39 (s, 3H), 2.11 (s, 3H), 3.05-3.18 (m, 2H), 3.20-3.26 (m, 2H), 3.91 (dd, *J* = 5.4 Hz, *J* = 9.3 Hz, 1H), 4.14 (dd, *J* = 6.4 Hz, *J* = 8.8 Hz, 1H), 4.31-4.43 (m, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 10.0 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.6, 25.0, 25.9, 26.4, 29.1, 66.8, 72.5, 75.7, 110.6, 130.6, 147.2, 169.2, 182.9. Anal. calcd for $C_{13}H_{18}O_5S_2$: C 49.04, H 5.70, S 20.14. Found: C 49.19, H 5.67, S 20.20.

Compound 6b. Synthetic procedure and characterization data have been previously described according to ref. 9.

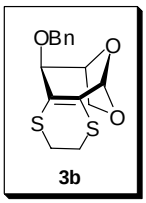


3a

Compound 3a. *Method A*: amberlyst 15 (4.8 g, previously washed with anhydrous MeOH) was added in one portion to a stirred solution of aldehyde **6a** (0.48 g, 1.51 mmol) in methanol (40 mL) at 0 °C. After 10 min, the suspension was warmed to room temperature and stirred for 1h. Then the solid was filtered off and washed with AcOEt; the organic phase, diluted with AcOEt, was washed with brine until neutrality, dried (Na_2SO_4) and concentrated under reduced pressure. The crude residue was dissolved in $CHCl_3$ (80 mL) and amberlyst 15 (4.8 g, previously washed with anhydrous $CHCl_3$) was added in one portion at 0 °C. After 10 min, the suspension was warmed to room temperature and further stirred for 1h. Then the solid was filtered off, washed with $CHCl_3$ and the resulting solution washed with saturated $NaHCO_3$ solution and brine. The organic layers were dried (Na_2SO_4) and the solvent evaporated under reduced pressure. Chromatography of the crude residue over silica gel (hexane/acetone = 90:1) gave the pure **3a** (0.31 g, 80% o.y.).

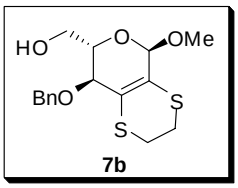
Method B: to a stirred 18:1 CH_2Cl_2/H_2O emulsion (7 mL) containing the ether **4a** (0.44 g, 1.0 mmol), DDQ (0.45 g, 2.00 mmol) was added in one portion at room temperature; then the reaction was warmed until reflux and stirred for 48 h. Hence, H_2O was added and the mixture was extracted

with CH_2Cl_2; the organic layer was dried (Na_2SO_4) and the solvent evaporated. Chromatography of the crude residue (hexane/acetone = 9:1) gave the pure **3a** (0.23 g, 89% yield): oily, $[\alpha]^{25}_D$ -32.0 (*c* 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 3.19-3.27 (m, 4H), 3.68 (dd, *J* = 1.9 Hz, *J* = 8.1 Hz, 1H), 3.98 (dd, *J* = 6.6 Hz, *J* = 8.0 Hz, 1H), 4.70-4.72 (m, 1H), 4.85 (d, *J* = 1.3 Hz, 1H), 5.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.5, 27.9, 29.7, 63.8, 70.5, 75.2, 98.9, 128.8, 130.9, 172.6. Anal. calcd for $C_{10}H_{12}O_4S_2$: C 46.14, H 4.65, S 24.63. Found: C 46.00, H 4.63, S 24.55.



3b

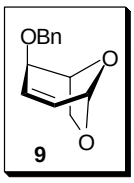
Compound 3b. Following both methods reported with regards to the synthesis of compound **3a**, the pure **3b** was afforded by double cyclization from aldehyde **6b** (94% o.y.) or by domino reaction starting from MPM ether **4b** (92% yield): white solid, mp 132.3-134.4 °C (from MeOH); $[\alpha]^{25}_D$ +12.5 (*c* 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.16-3.29 (m, 4H), 3.56 (dd, *J* = 2.0 Hz, *J* = 7.7 Hz, 1H), 3.58 (d, *J* = 1.0 Hz, 1H), 3.98 (dd, *J* = 6.8 Hz, *J* = 7.7 Hz, 1H), 4.72 (s, 2H), 4.80-4.82 (m, 1H), 5.24 (s, 1H), 7.29-7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 27.7, 64.0, 70.2, 76.6, 77.0, 98.8, 118.9, 126.8, 127.7, 128.0, 128.3, 137.9. Anal. calcd for $C_{15}H_{16}O_3S_2$: C 58.41, H 5.23, S 20.79. Found: C 58.59, H 5.25, S 20.71.



7b

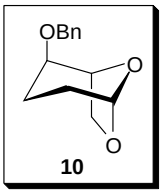
Compound 7b. Amberlyst 15 (3.5 g, previously washed with anhydrous MeOH) was added in one portion to a stirred solution of **3b** (0.35 g, 1.14 mmol) in methanol (30 mL) at 0 °C. After 10 min, the suspension was warmed to room temperature and stirred for 1h. Then the solid was filtered off and washed with AcOEt; the organic phase, diluted with AcOEt, was washed with brine until

neutrality, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography over silica gel (CH_2Cl_2) gave the pure **7b** (0.33 g, 85% yield): white solid, mp 78.9-80.2 °C (from MeOH); $[\alpha]^{25}_D$ +55.2 (*c* 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, C_6D_6): δ 2.30-2.43 (m, 3H), 2.55-2.62 (m, 1H), 3.12 (s, 3H), 3.54-3.63 (m, 1H), 4.12-4.16 (m, 1H), 4.28 (d, *J* = 11.2 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* =11.2 Hz, 1H), 4.74 (s, 1H), 7.03-7.18 (m, 3H), 7.38 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6): δ 26.4, 27.6, 55.1, 61.8, 70.7, 72.8, 74.2, 98.4, 122.3, 125.6, 127.6, 127.8, 128.2, 128.4, 138.3. Anal. calcd for $C_{16}H_{20}O_4S_2$: C 56.44, H 5.92, S 18.84. Found: C 56.25, H 5.94, S 18.91.

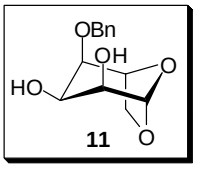


9

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-β-L-*erytro*-hex-2-enopyranose (9). A solution of **3b** (0.30 g, 0.97 mmol) in acetone (12 mL) was added in one portion to a stirred suspension of Raney-Ni (W2) (3.0 g, washed with acetone) in the same solvent (10 mL) at 0 °C and under nitrogen atmosphere. The suspension was warmed to room temperature and further stirred for 2h, then the solid was filtered off and washed with acetone. The filtrate was evaporated under reduced pressure to afford a crude residue which chromatography over silica gel (CH_2Cl_2) gave the pure **9** (0.16 g, 75% yield): oily; $[\alpha]^{25}_D$ -154.0 (*c* 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.40 (dd, *J* =1.9 Hz, *J* =7.5 Hz, 1H), 3.53 (d, *J* =4.4 Hz, 1H), 3.92 (appt, *J* = 6.6 Hz, *J* = 7.3 Hz, 1H), 4.68 (d, *J* =12.2 Hz, 1H), 4.70 (d, *J* =12.2 Hz, 1H), 4.78-4.82 (m, 1H), 5.57 (d, *J* = 3.1 Hz, 1H), 5.85 (ddd, *J* =1.8 Hz, *J* = 3.6 Hz, *J* =9.6 Hz, 1H), 6.14 (dd, *J* =3.1 Hz, *J* = 9.6 Hz, 1H), 7.25-7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.0, 70.6, 73.0, 74.0, 95.4, 124.0, 126.8, 127.7, 128.4, 131.3, 138.1. Anal. calcd for $C_{13}H_{14}O_3$: C 71.54, H 6.47. Found: C 71.78, H 6.44.



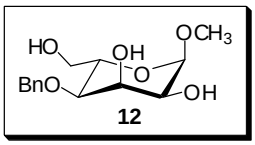
1,6-anhydro-4-*O*-benzyl-2,3-dideoxy-β-L-*erytro*-pyranose (10). Under similar conditions reported above, treatment of **3b** (0.30 g, 1.37 mmol) in acetone with an excess of Raney-Ni (W2) (6.0 g, wet) afforded, after common work-up and purification procedures, the pure **10** (0.25 g, 82% yield): oily, $[\alpha]^{25}_{D}$ -63.0 (*c* 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.80 (bdd, *J* = 5.8 Hz, *J* = 14.2 Hz, 1H), 1.83-1.92 (m, 2H), 1.97 (ddd, *J* = 6.3 Hz, *J* = 13.2 Hz, *J* = 19.0 Hz, 1H), 3.38 (s, 1H), 3.74-3.81 (m, 2H), 4.56-4.60 (m, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 5.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0, 29.3, 66.1, 70.1, 72.9, 74.9, 101.7, 127.6, 127.8, 128.3, 138.2. Anal. calcd for $C_{13}H_{16}O_3$: C 70.89, H 7.32. Found: C 70.94, H 7.33.



1,6-Anhydro-4-*O*-benzyl-β-L-*allo*pyranose (11). To a solution of **9** (0.15 g, 0.69 mmol) in pyridine (5.0 mL), cooled at 0 °C, OsO_4 (0.17 g, 0.69 mmol) was added and the resulting mixture was stirred overnight at room temperature; then the reaction was quenched with a saturated Na_2SO_3 solution and evaporated under reduced pressure. Chromatography of the crude residue over silica gel (CH_2Cl_2/MeOH = 95/5) afforded the pure **11** (0.16 g, 91% yield) as single diastereomer: white crystals, mp 109.0-110.3 °C (from hexane/acetone); $[\alpha]^{25}_{D}$ +71.1 (*c* 0.8, $CHCl_3$), [lit. data for ***ent*-11**: mp 113 °C, $[\alpha]^{25}_{D}$ -79.0 and mp 109-111 °C, $[\alpha]^{25}_{D}$ -76.0)][†]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (bs, 1H), 2.82 (bs, 1H), 3.60 (bt, *J* = 1.8 Hz, 1H), 3.70 (dd, *J* = 5.4 Hz, *J* = 7.4 Hz, 1H), 3.87 (dd, *J* = 1.8 Hz, *J* = 5.6 Hz, 1H), 4.02-4.08 (m, 1H), 4.12 (d, *J* = 7.4 Hz, 1H), 4.57 (bd, *J* = 5.4 Hz,

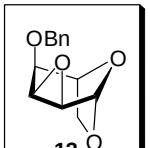
[†] Černý M., Kalvoda, L., Pacák J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 1143-1156 and Cruzado, M.C.; Martin-Lomas, M. *Carbohydr. Res.* **1988**, *175*, 193-199.

1H), 4.62 (d, *J* = 12.4 Hz, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 5.40 (s, 1H), 7.28-7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.8, 66.6, 68.8, 71.5, 74.0, 78.2, 101.4, 127.7, 127.9, 128.5, 137.4. Anal. calcd for $C_{13}H_{16}O_5$: C 61.90, H 6.39. Found: C 61.71, H 6.41.



12

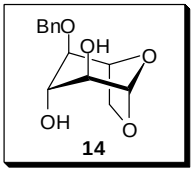
Methyl 4-*O*-benzyl-α-L-*allo*pyranoside (**12**). To a solution of **11** (0.15 g, 0.60 mmol) in MeOH (8 mL) a catalytic amount of trimethylsilyl trifluoromethansulfonate (TfOTMS, 0.06 mmol) was added and the resulting reaction mixture was stirred at 50 °C for 48 h. Then the reaction was quenched with solid $NaHCO_3$ and the solvent evaporated under reduced pressure. Chromatography of the crude residue over silica gel (CH_2Cl_2/MeOH = 9/1) gave the pure **12** (0.16 g, 92% yield) as single anomer: amorphus, $[\alpha]^{25}_D$ -70.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD): δ 3.36 (s, 3H), 3.47-3.54 (m, 1H), 3.58 (t, *J* = 9.7 Hz, 1H), 3.62 (dd, *J* = 5.4 Hz, *J* = 12.2 Hz, 1H), 3.68-3.74 (m, 2H), 3.77 (dd, *J* = 3.4 Hz, *J* = 9.2 Hz, 1H), 4.55 (d, *J* = 10.7 Hz, 1H), 4.58 (s, 1H), 4.84 (d, *J* = 10.7 Hz, 1H), 7.19 (t, *J* = 6.8 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 62.7, 72.6, 73.0, 73.5, 75.9, 76.8, 102.7, 128.6, 129.1, 129.3, 140.1. Anal. calcd for $C_{14}H_{20}O_6$: C 59.14, H 7.09. Found: C 59.00, H 7.06.



13

1,6:2,3-Dianhydro-4-*O*-benzyl-β-L-*allo*pyranose (13). Na_2EDTA (4.0 x 10^{-4} M, 3.45 mL) and CF_3COCH_3 (0.61 mL) were added to a solution of **9** (0.15 g, 0.69 mmol) in CH_3CN (6.9 mL) at 0 °C. After a few minutes a mixture of $NaHCO_3$ (0.43 g) and Oxone® (1.72 g) was added over 1 h and the whole resulting mixture was stirred for 30 min at the same temperature. Then the reaction was diluted with H_2O and extracted with CH_2Cl_2. The extracts were washed with brine, dried (Na_2SO_4),

and evaporated under reduced pressure. Chromatography of the crude residue over silica gel (hexane/acetone = 8:2) afforded the pure **13** (0.15 g, 92% yield) as single diastereoisomer: white solid, mp 74.2-76.0 °C (from MeOH); $[\alpha]^{25}_{D}$ -117.3 (c 1.8, $CHCl_3$), [lit. data for ***ent*-13**: mp 74.0-76.0 °C, $[\alpha]^{25}_{D}$ +127.0 and mp 75.0-79.0 °C, $[\alpha]^{25}_{D}$ +119.0][‡]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.09 (dd, *J* = 0.9 Hz, *J* = 4.4 Hz, 1H), 3.29-3.34 (m, 1H), 3.45 (d, *J* = 4.4 Hz, 1H), 3.62 (dd, *J* = 1.9 Hz, *J* = 7.8 Hz, 1H), 3.88 (appt, *J* = 7.1 Hz, *J* = 7.8 Hz, 1H), 4.51 (dt, *J* = 1.9 Hz, *J* = 7.1 Hz, 1H), 4.74 (d, *J* = 12.4 Hz, 1H), 4.87 (d, *J* =12.4 Hz, 1H), 5.65 (d, *J* = 0.9 Hz, 1H), 7.28-7.47 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 47.5, 47.8, 65.4, 70.7, 72.3, 75.4, 97.1, 127.8, 127.9, 128.4, 137.6. Anal. calcd for $C_{13}H_{14}O_4$: C 66.66, H 6.02. Found C 66.87, H 6.04.

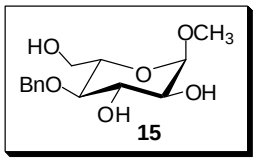


14

1,6-Anhydro-4-*O*-benzyl-β-L-*gluco*pyranose (14). The epoxide **13** (0.14 g, 0.60 mmol) was refluxed for 48 h in a 1M aqueous solution of KOH (8 ml). Then 1N HCl was carefully added at 0 °C until neutrality. The white solid was filtered off and washed with AcOEt, the solvent removed under reduced pressure to afford crude **14**, which was directly used in the next reaction. A sample of crude **14** was purified by SiO_2 chromatography (CH_2Cl_2/MeOH = 95/5) and characterized. White crystals, m.p. 51-53, $[\alpha]^{25}_{D}$ +40.2 (c 1.5, EtOH), [lit. data for ***ent*-14**: mp 53.0.-54.0 °C, $[\alpha]^{25}_{D}$ -43.0 and mp 50.0.-52.0 °C, $[\alpha]^{25}_{D}$ -41.0][§]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.52 (bs, 1H), 2.75 (bs, 1H), 3.45 (s, 1H), 3.55 (bs, 1H), 3.78 (dd, *J* = 5.4 Hz, *J* = 7.8 Hz, 1H), 3.94 (bs, 1H), 4.15 (d, *J* = 7.8 Hz, 1H), 4.63 (bd, *J* = 7.3 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.70 (d, *J* = 11.7 Hz, 1H), 5.52 (s, 1H), 7.30-7.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.3, 69.8, 70.4, 71.3, 74.3, 76.6, 102.0, 127.6, 127.8, 128.4, 137.0. Anal. calcd for $C_{13}H_{16}O_5$: C 61.90, H 6.39. Found: C 62.12, H 6.52.

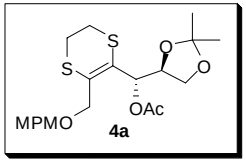
(‡) (a) Černý, M.; Trnka, T.; Beran, P.; Pacák, J. *Collect. Czech. Chem. Commun.* **1969**, *34*, 3377-3382. (b) Grindley, T. B.; Reimer, G. J.; Kralovek, J. *Can. J. Chem.* **1987**, *65*, 1065-1071.

§ (a) Seib, P. A. *Carbohydr. Res.* **1968**, *8*, 101-109. (b) Cruzado, M.C.; Martin-Lomas, M. *Carbohydr. Res.* **1988**, *175*, 193-199..



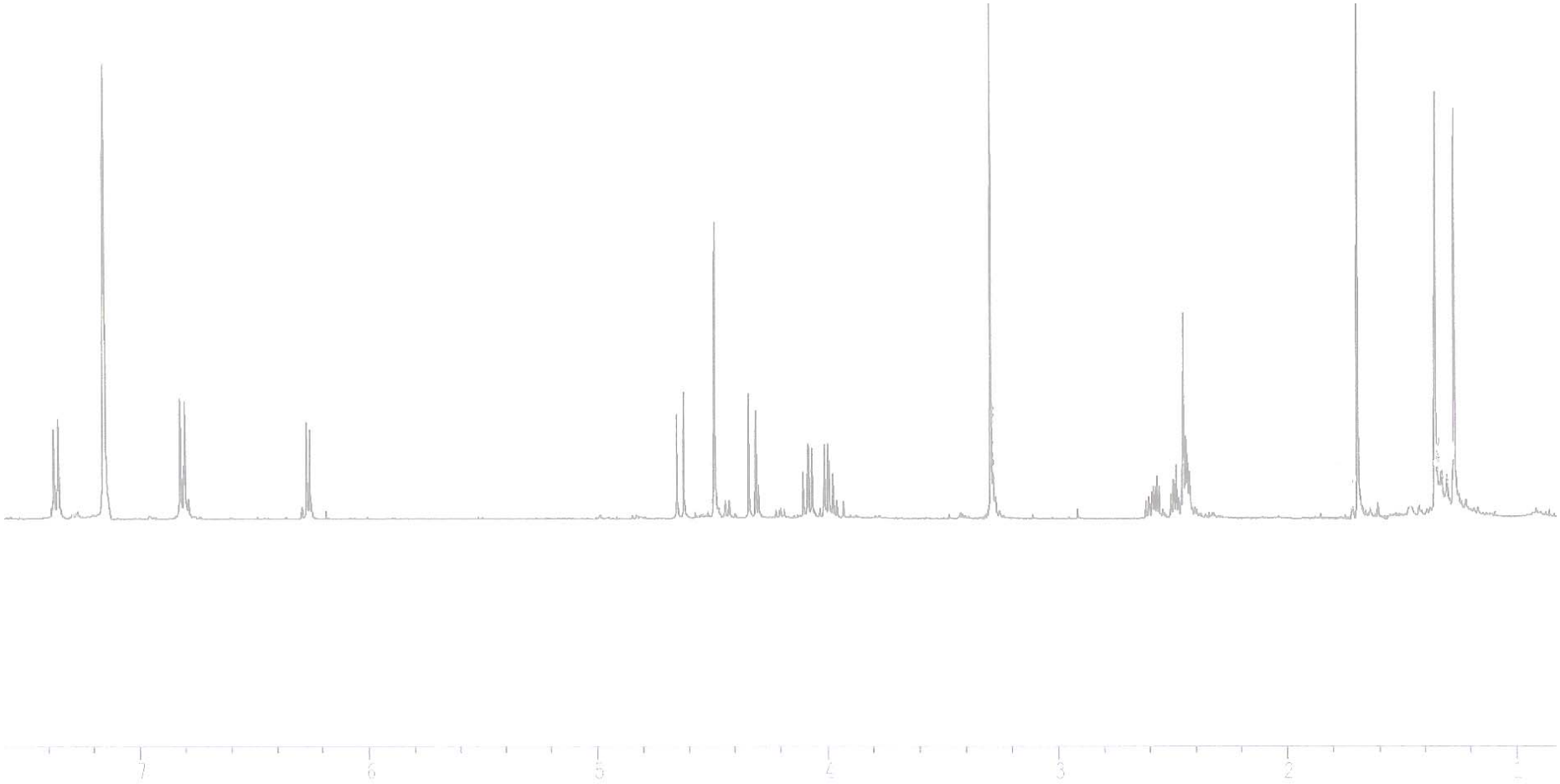
Methyl 4-*O*-benzyl-α-L-*gluco*pyranoside (**15**). The crude **14**, coevaporated three times with toluene, was dissolved in MeOH (10 mL) and a catalytic amount of TfOTMS (10.9 μL, 0.06 mmol) was added. The resulting reaction mixture was stirred at 50 °C for 48 h; then the reaction was quenched with solid $NaHCO_3$ and the solvent evaporated under reduced pressure. Chromatography of the crude residue over silica gel (CH_2Cl_2/MeOH = 9/1) gave the pure **15** (0.16 g, 93% from **13** yield): white crystals, mp 125-127 °C, $[\alpha]^{25}_D$ -144.2 (c 1.2, MeOH), [lit. data for ***ent*-15**: mp 126.0-127.0 °C, $[\alpha]^{25}_D$ +154.0][**]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.41 (s, 3H), 3.46 (t, *J* = 9.5 Hz, 1H), 3.51 (dd, *J* = 3.1 Hz, *J* = 9.5 Hz, 1H), 3.65 (dt, *J* = 3.2 Hz, *J* = 9.5 Hz, 1H), 3.67-3.73 (m, 1H), 3.76 (dd, *J* = 3.2 Hz, *J* = 11.7 Hz, 1H), 3.84 (dd, *J* = 3.2 Hz, *J* = 11.7 Hz, 1H), 3.86 (t, *J* = 9.5 Hz, 1H), 4.73 (d, *J* = 11.2 Hz, 1H), 4.77 (d, *J* = 3.1 Hz, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 7.25-7.38 (m, 5H). ^{13}C NMR (100 MHz, CD_3OD): δ 54.0, 60.8, 61.3, 72.3, 74.0, 74.3, 78.0, 99.7, 127.1, 127.5, 127.7, 138.5. Anal. calcd for $C_{14}H_{20}O_6$: C 59.14, H 7.09. Found: C 58.95, H 7.06.

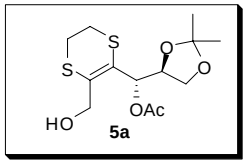
(**) Satomura, S.; Iwata, T.; Sakata, Y.; Omichi, K.; Ikenaka, T. *Carbohydr. Res.* **1988**, *176*, 107-116.



4a

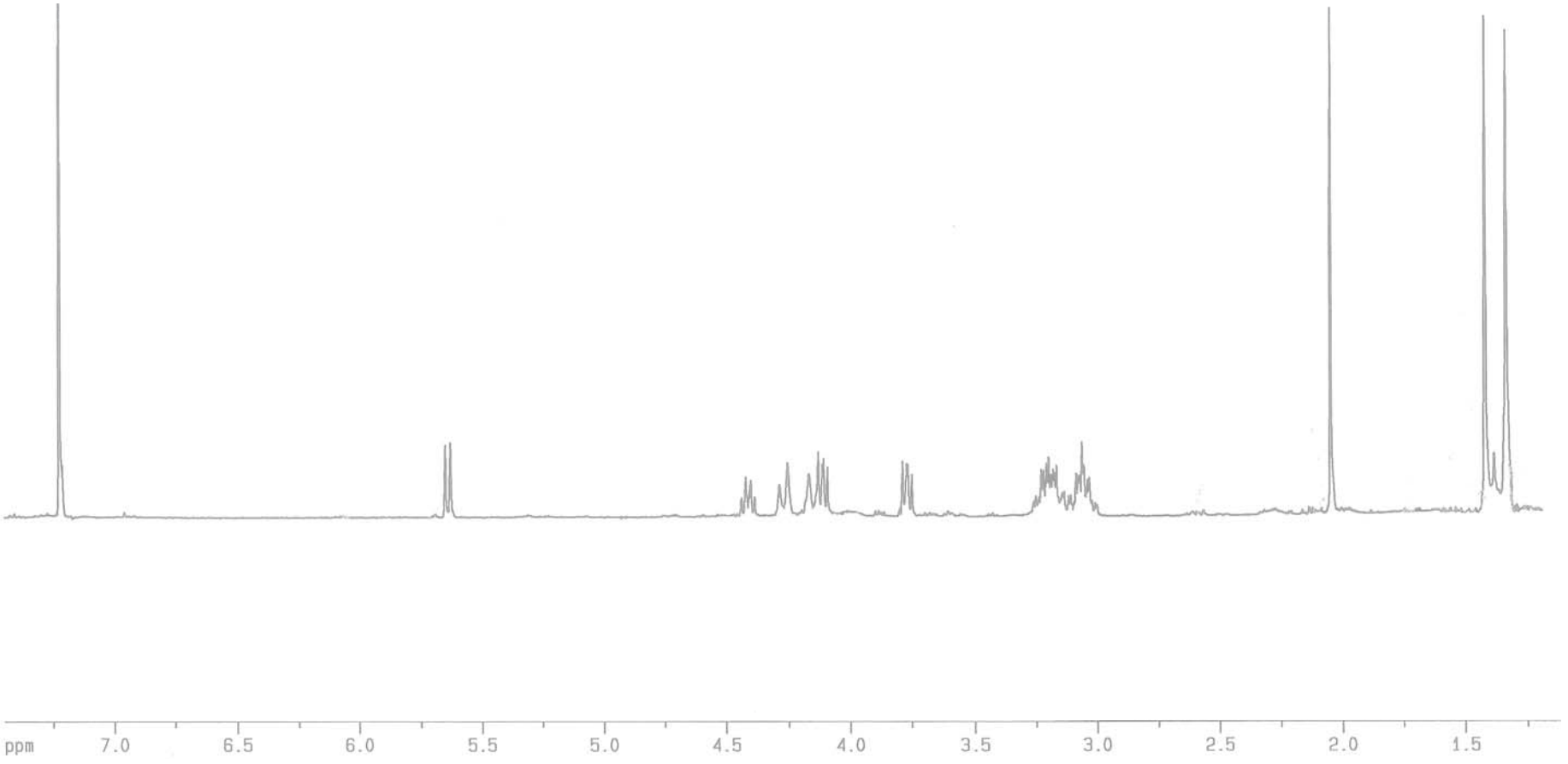
400 MHz, C_6D_6

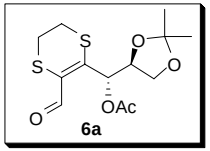




5a

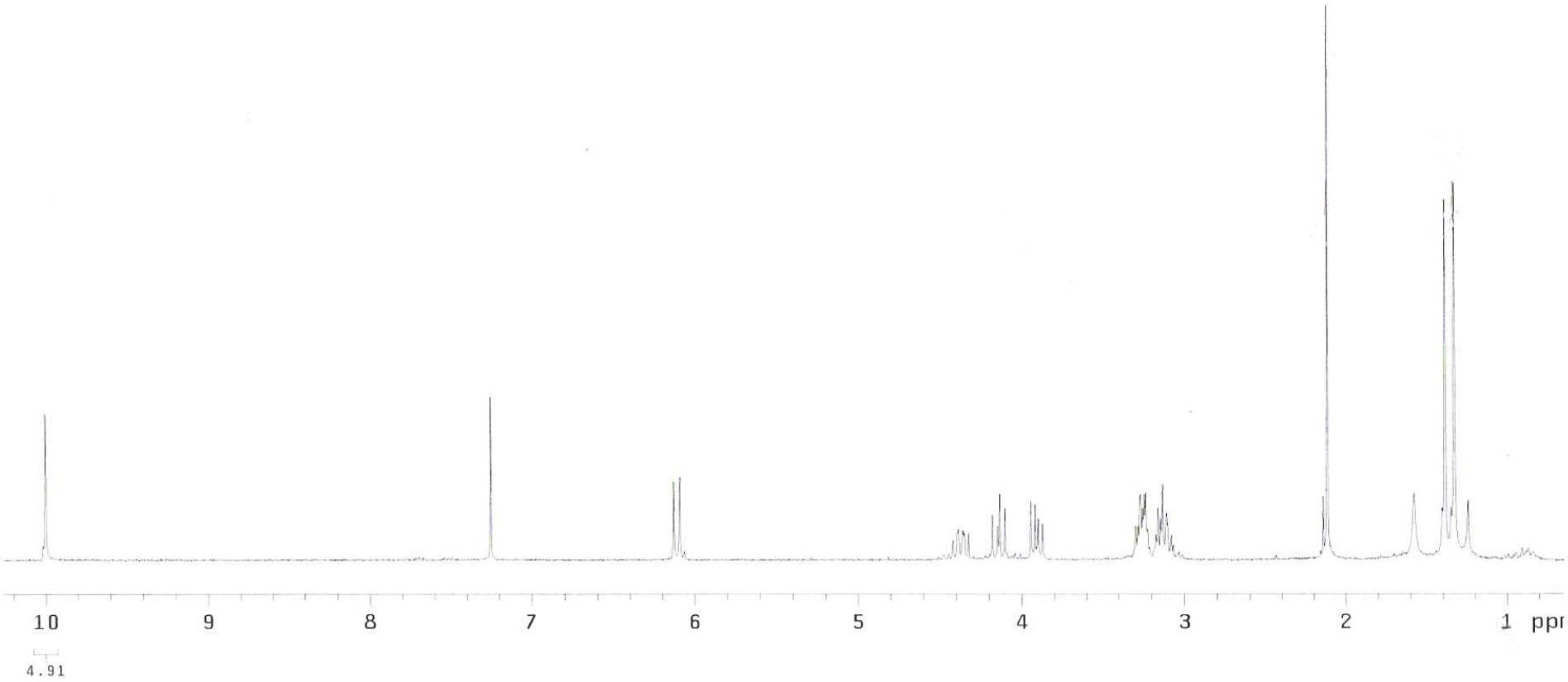
400 MHz, $CDCl_3$

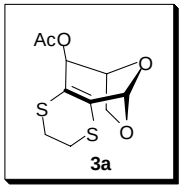




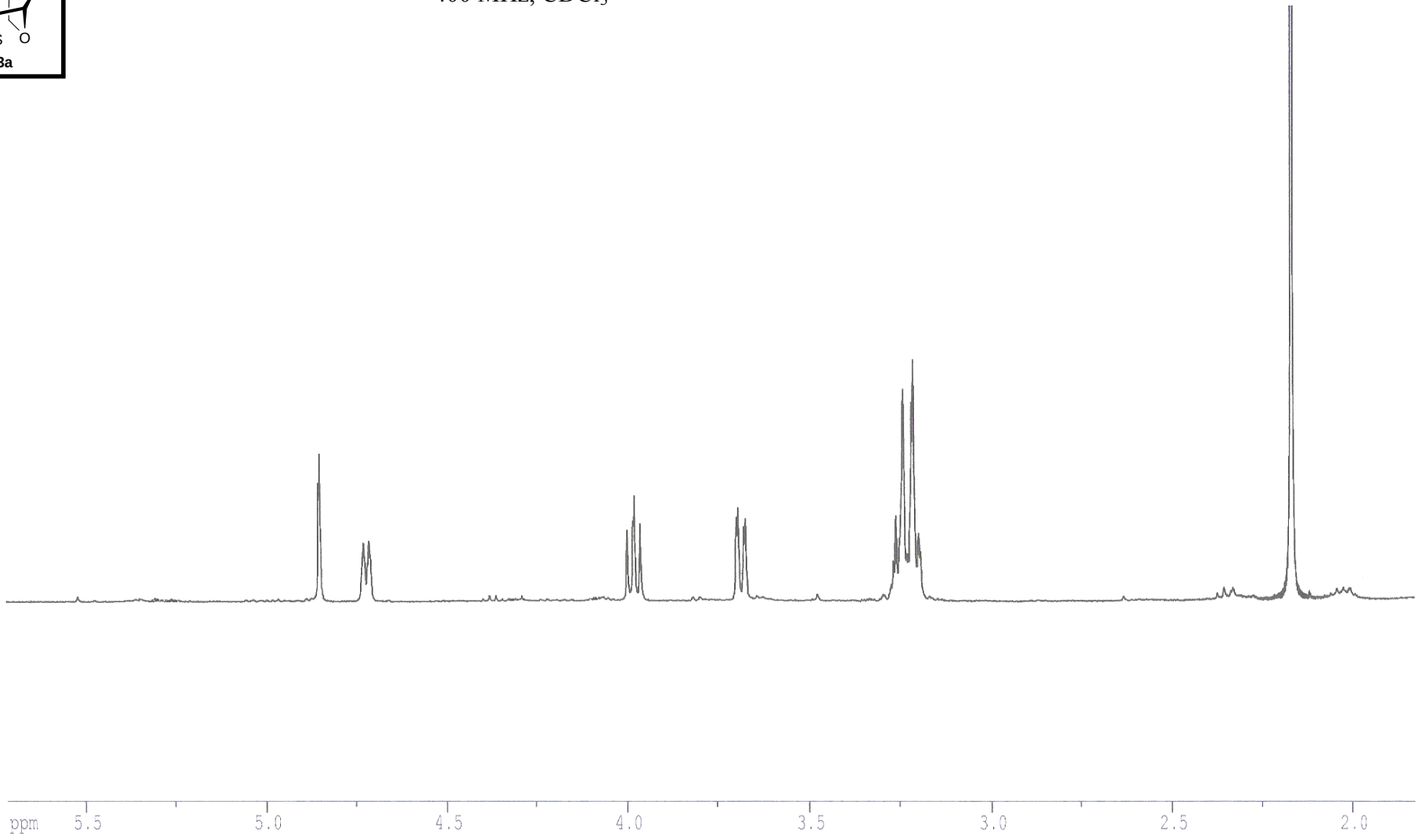
6a

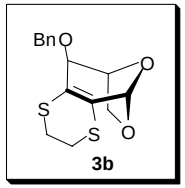
200 MHz, $CDCl_3$





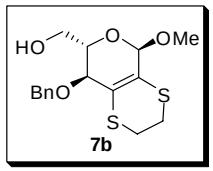
400 MHz, $CDCl_3$



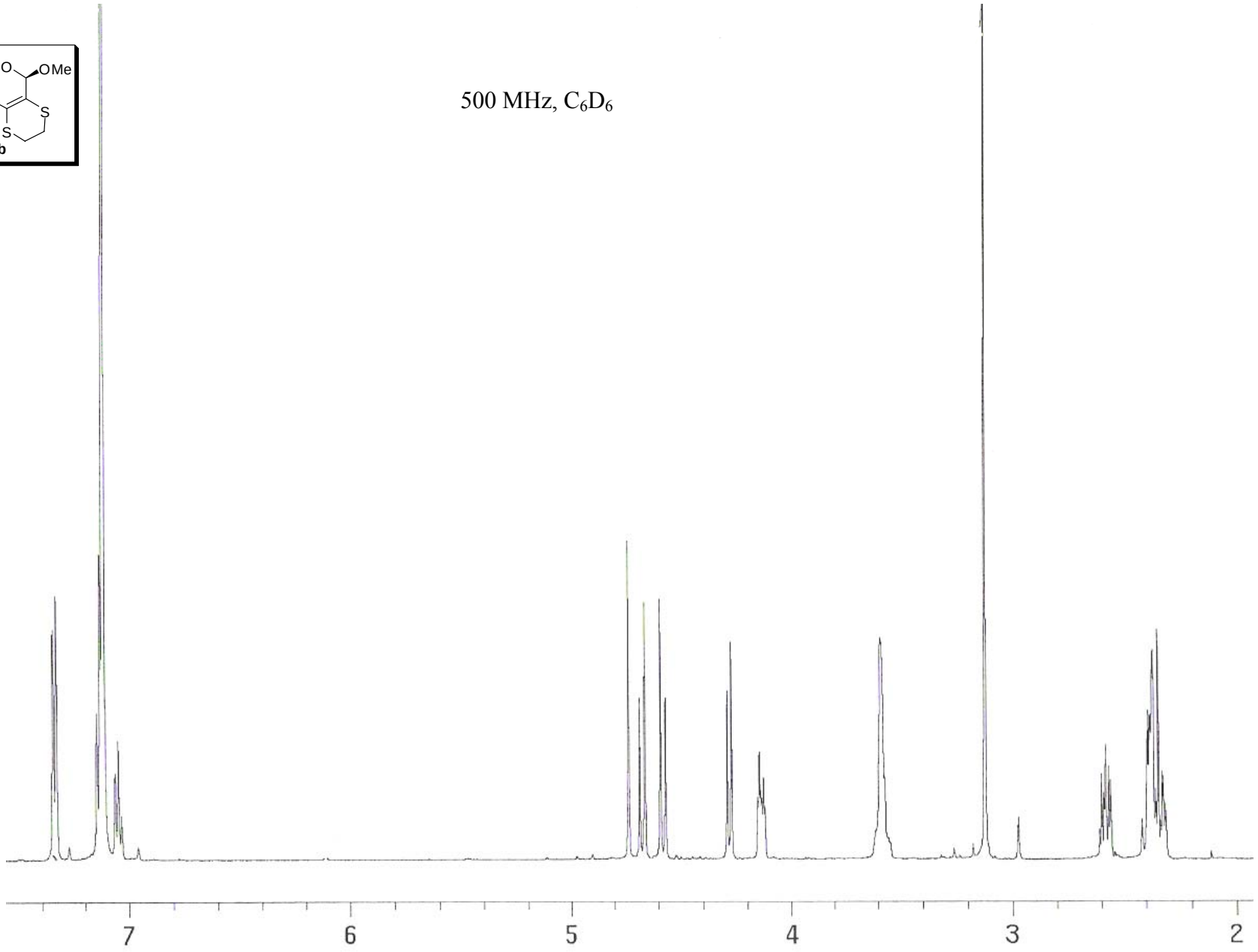


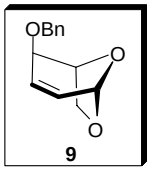
3b

400 MHz, $CDCl_3$

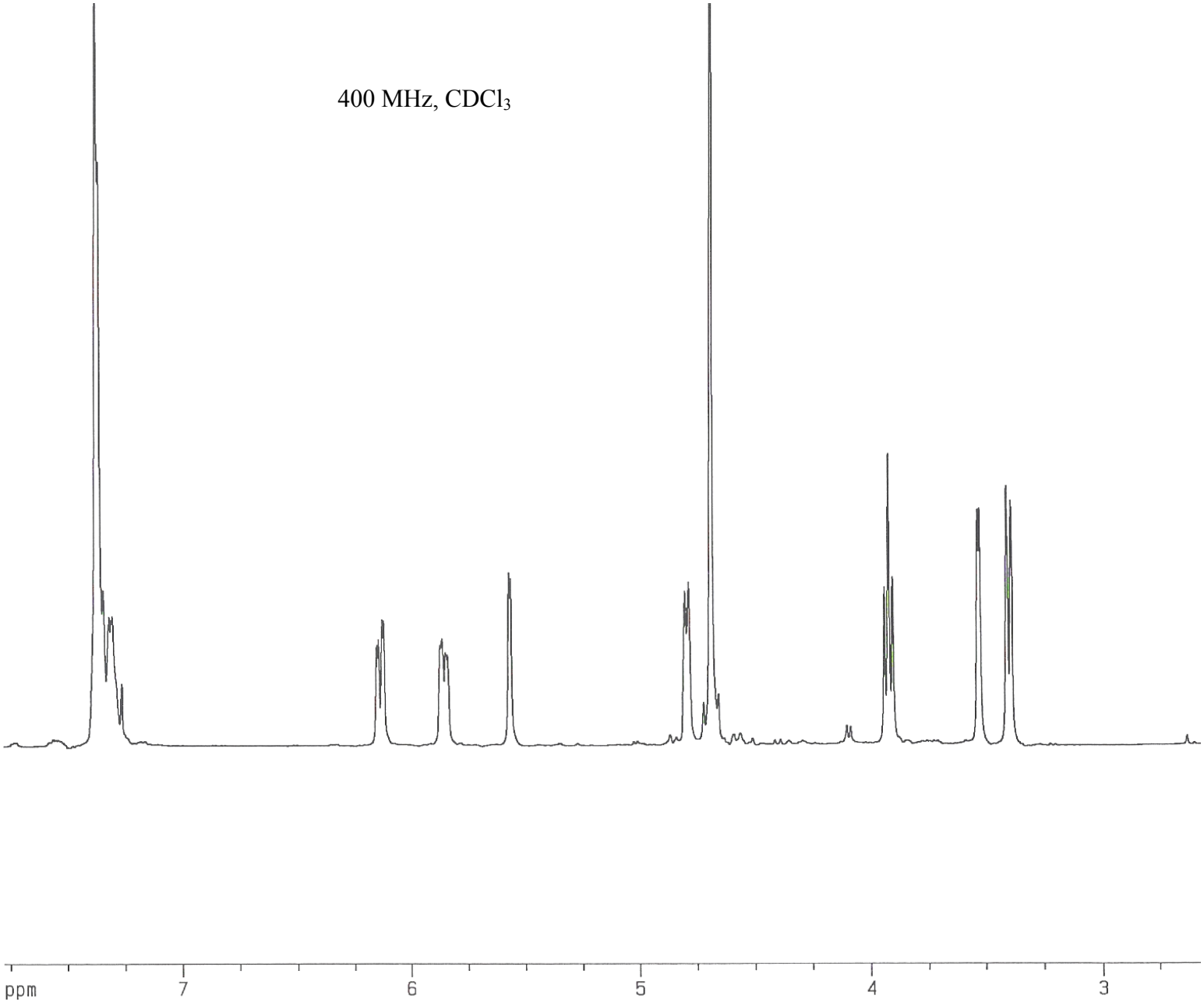


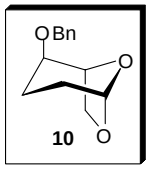
500 MHz, C_6D_6



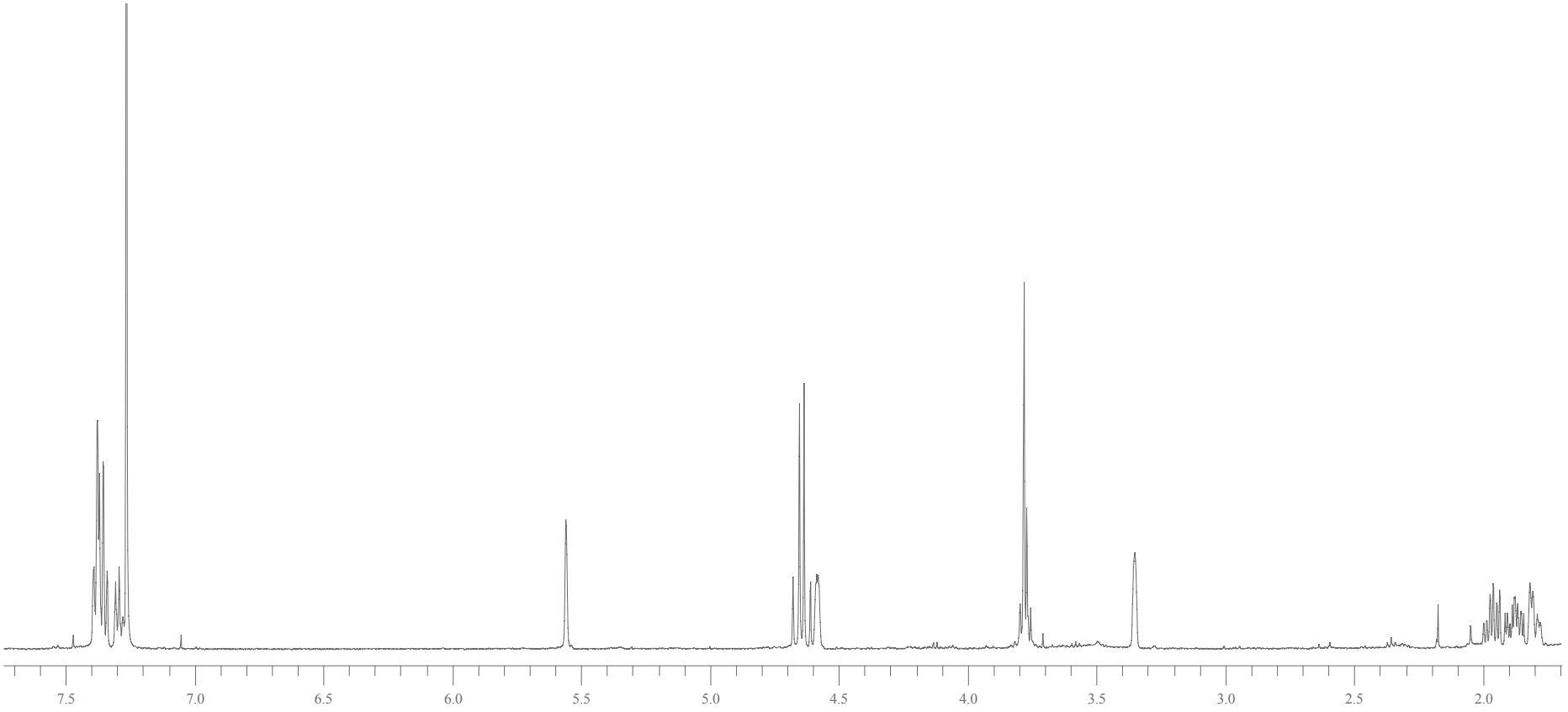


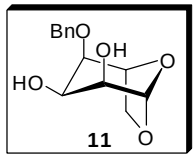
400 MHz, $CDCl_3$



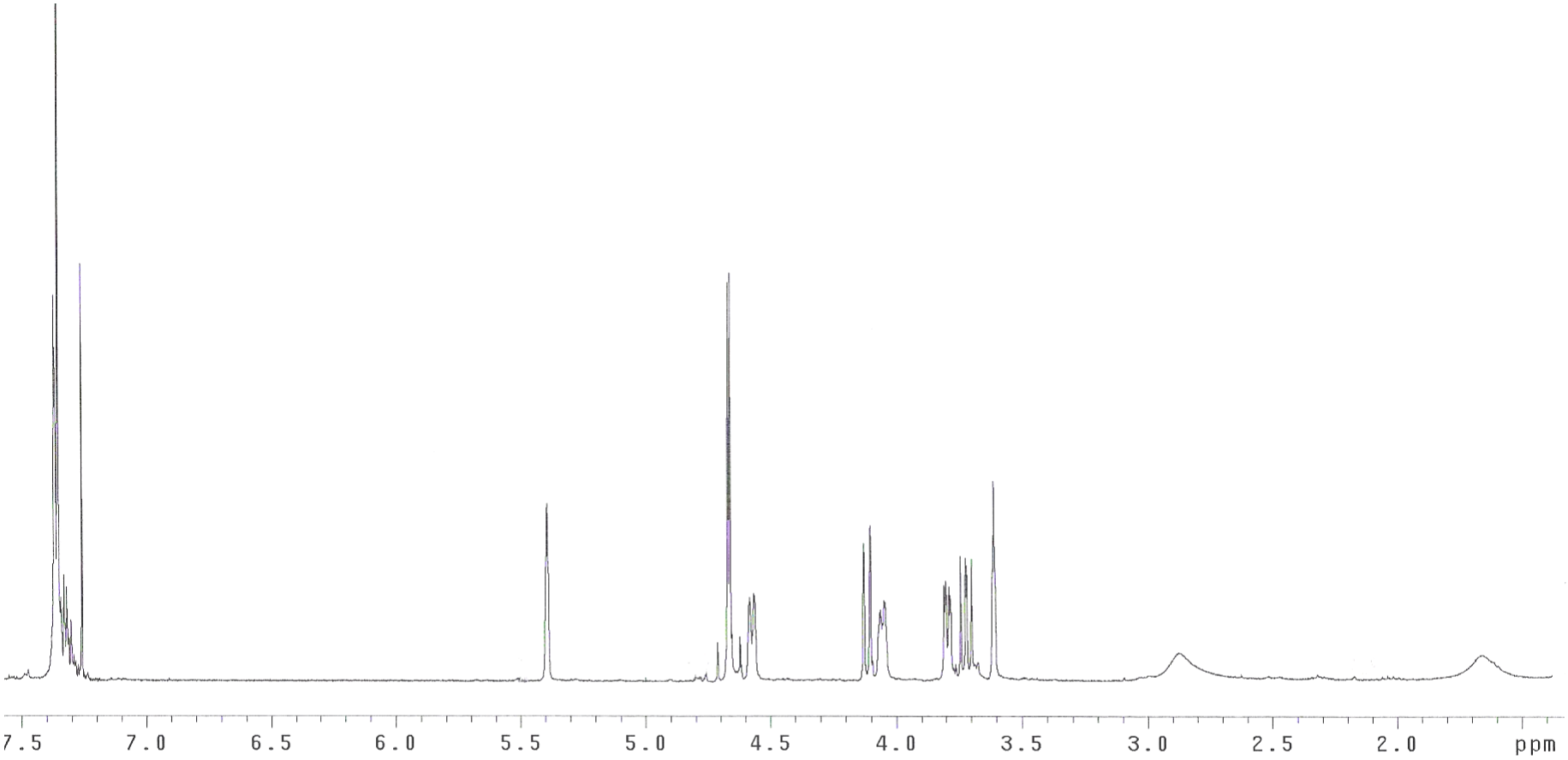


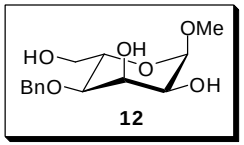
500 MHz, $CDCl_3$





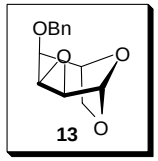
300 MHz, $CDCl_3$





12

400 MHz, CD_3OD



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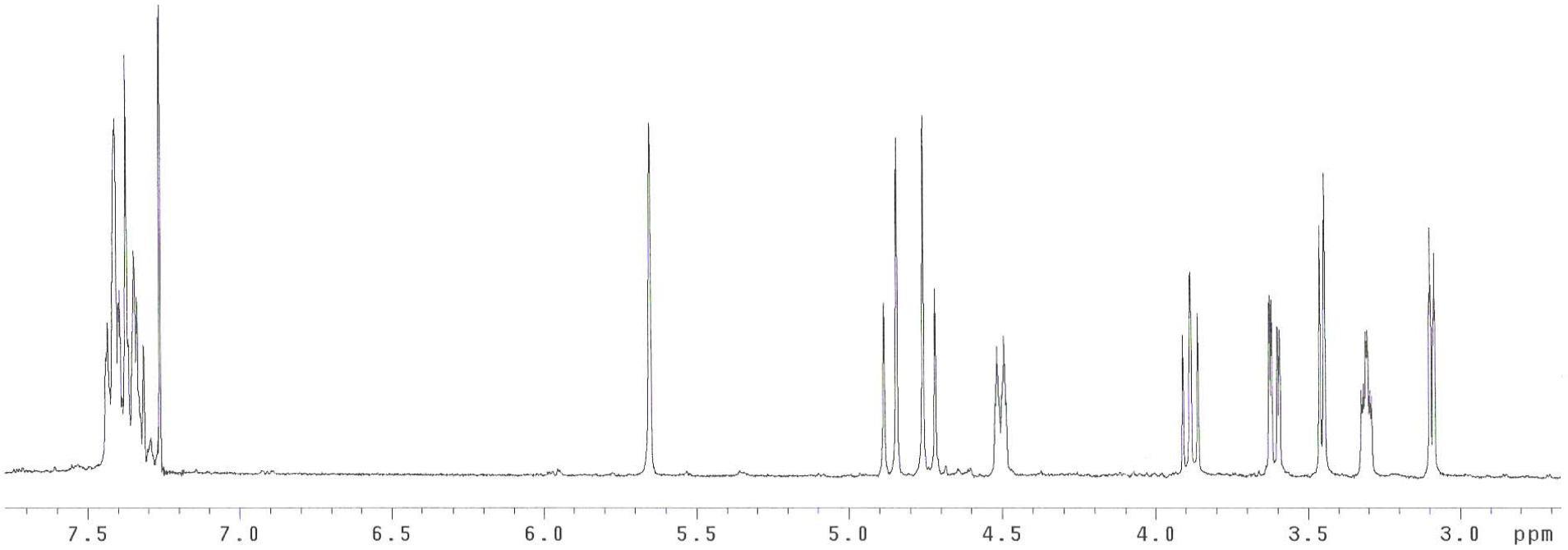
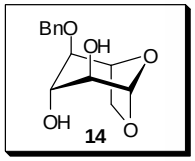
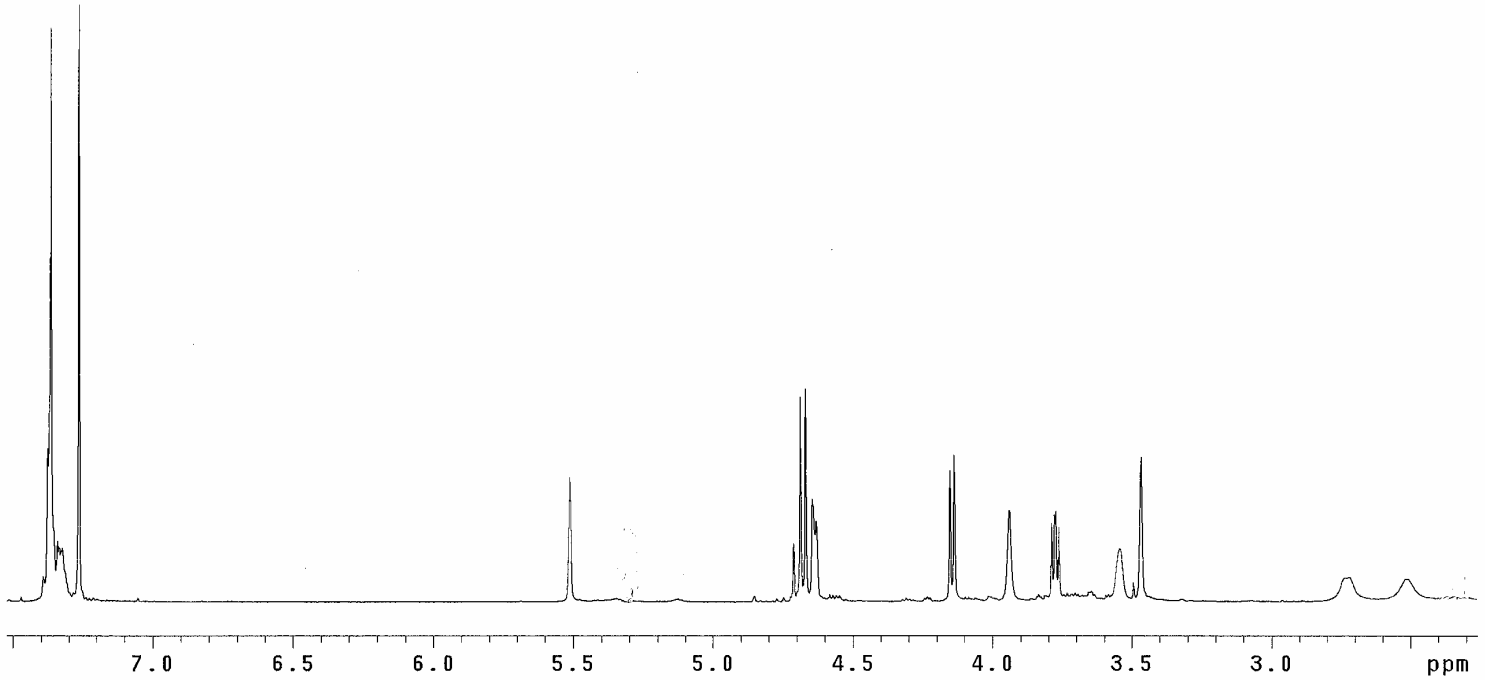
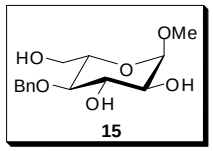


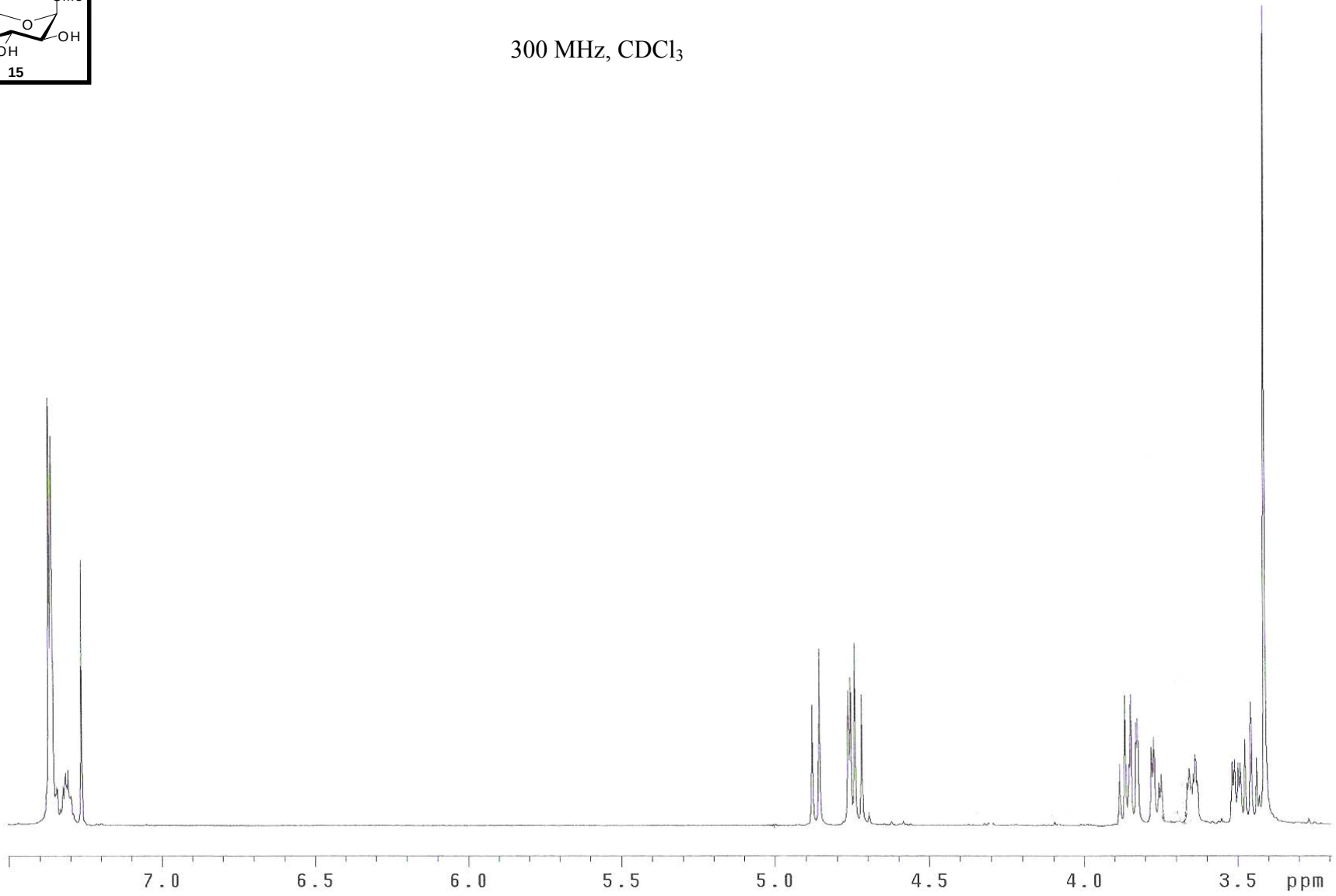


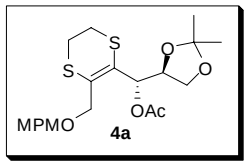
500 MHz, $CDCl_3$





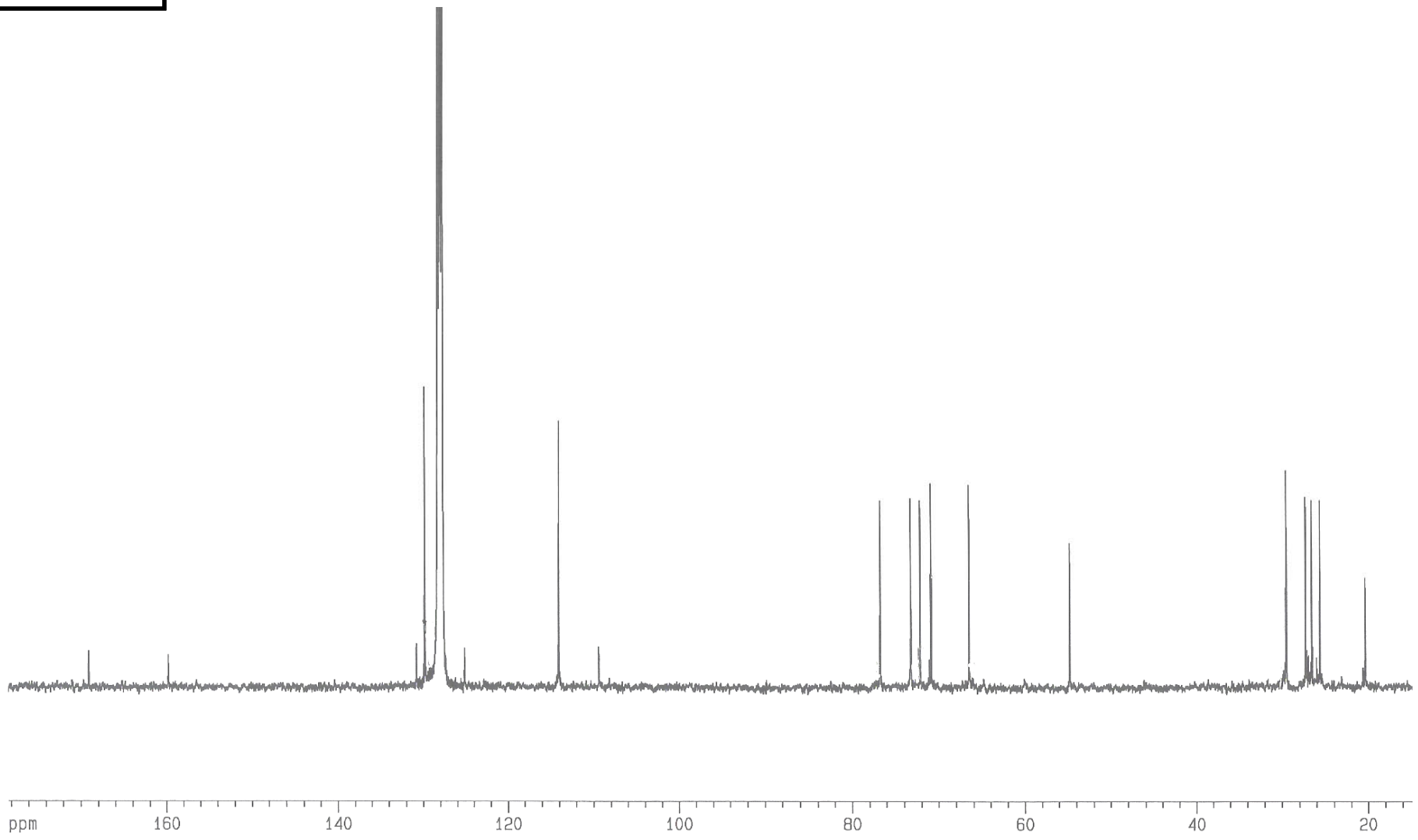
300 MHz, $CDCl_3$

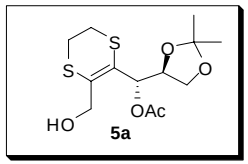




4a

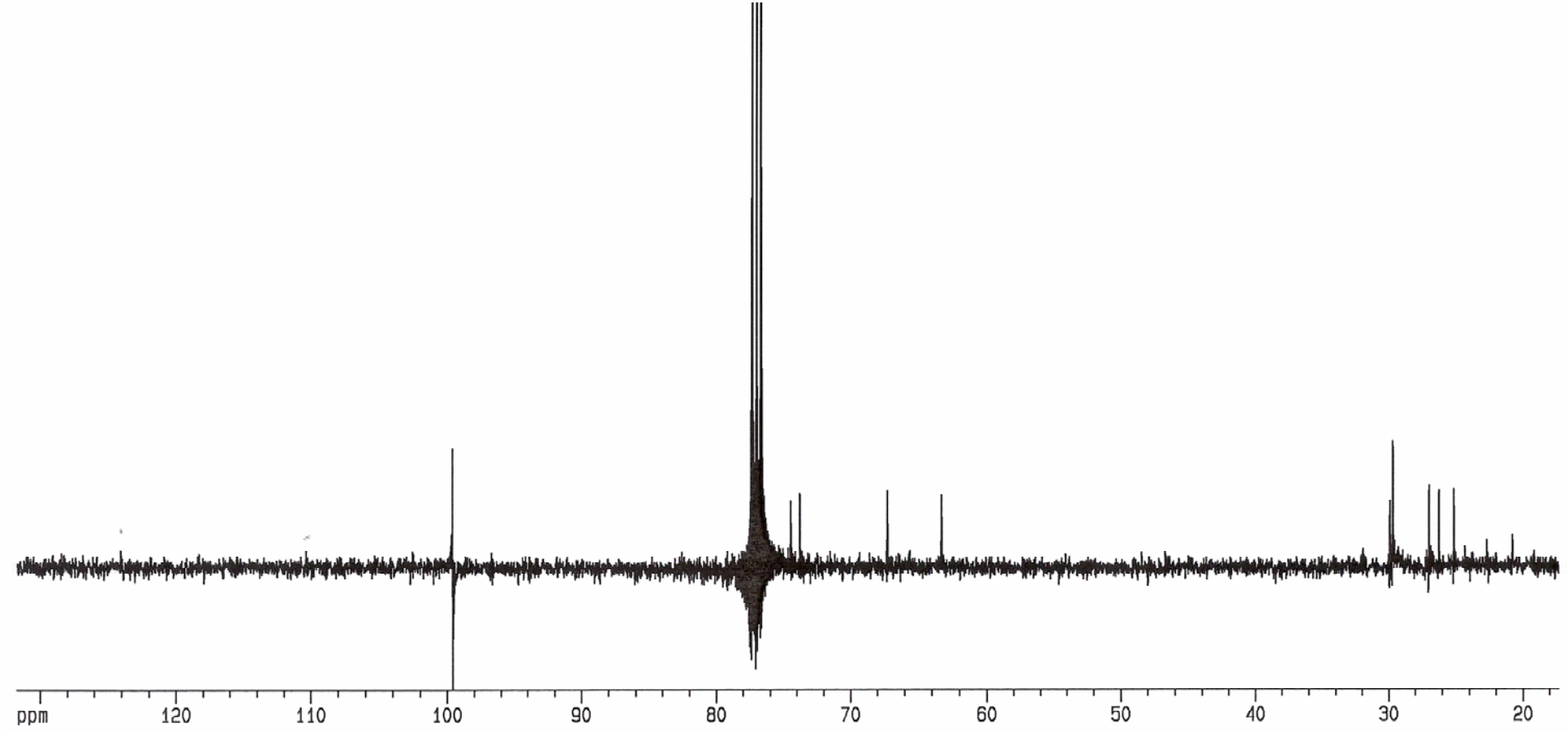
100 MHz, C_6D_6

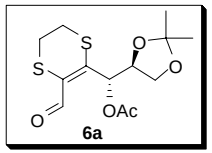




5a

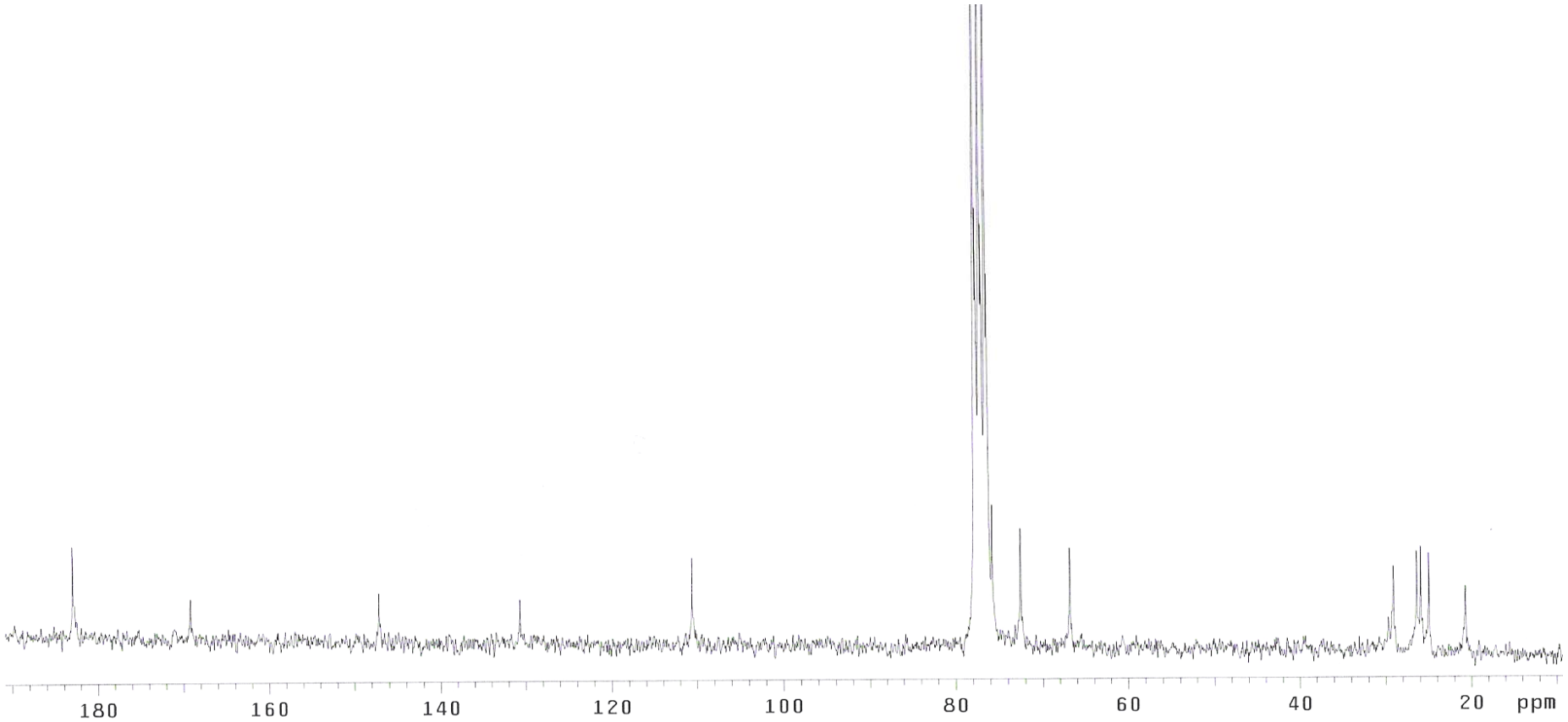
100 MHz, $CDCl_3$

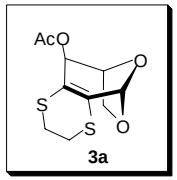




6a

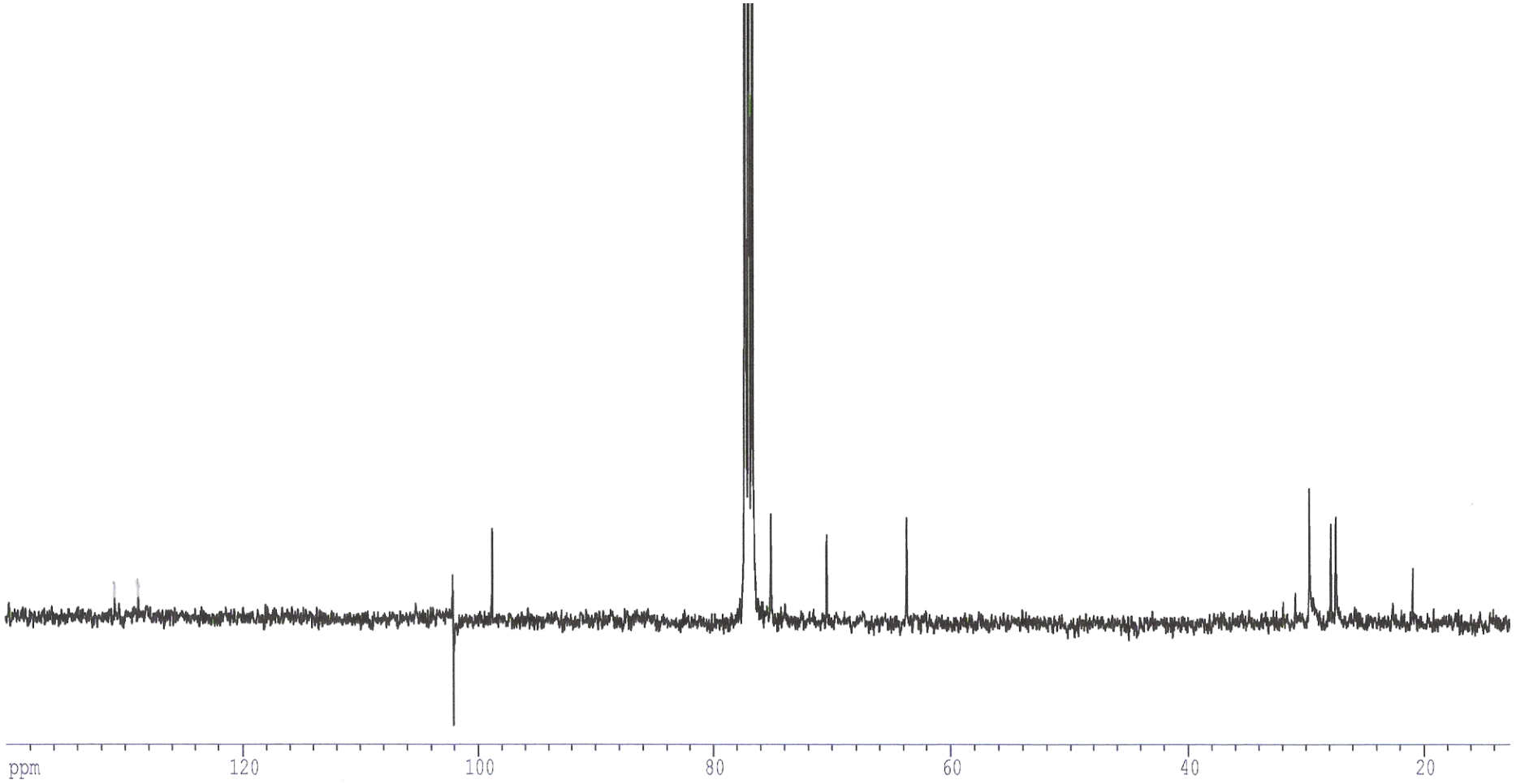
50 MHz, $CDCl_3$

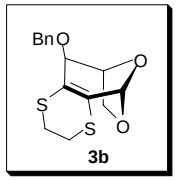




3a

100 MHz, $CDCl_3$





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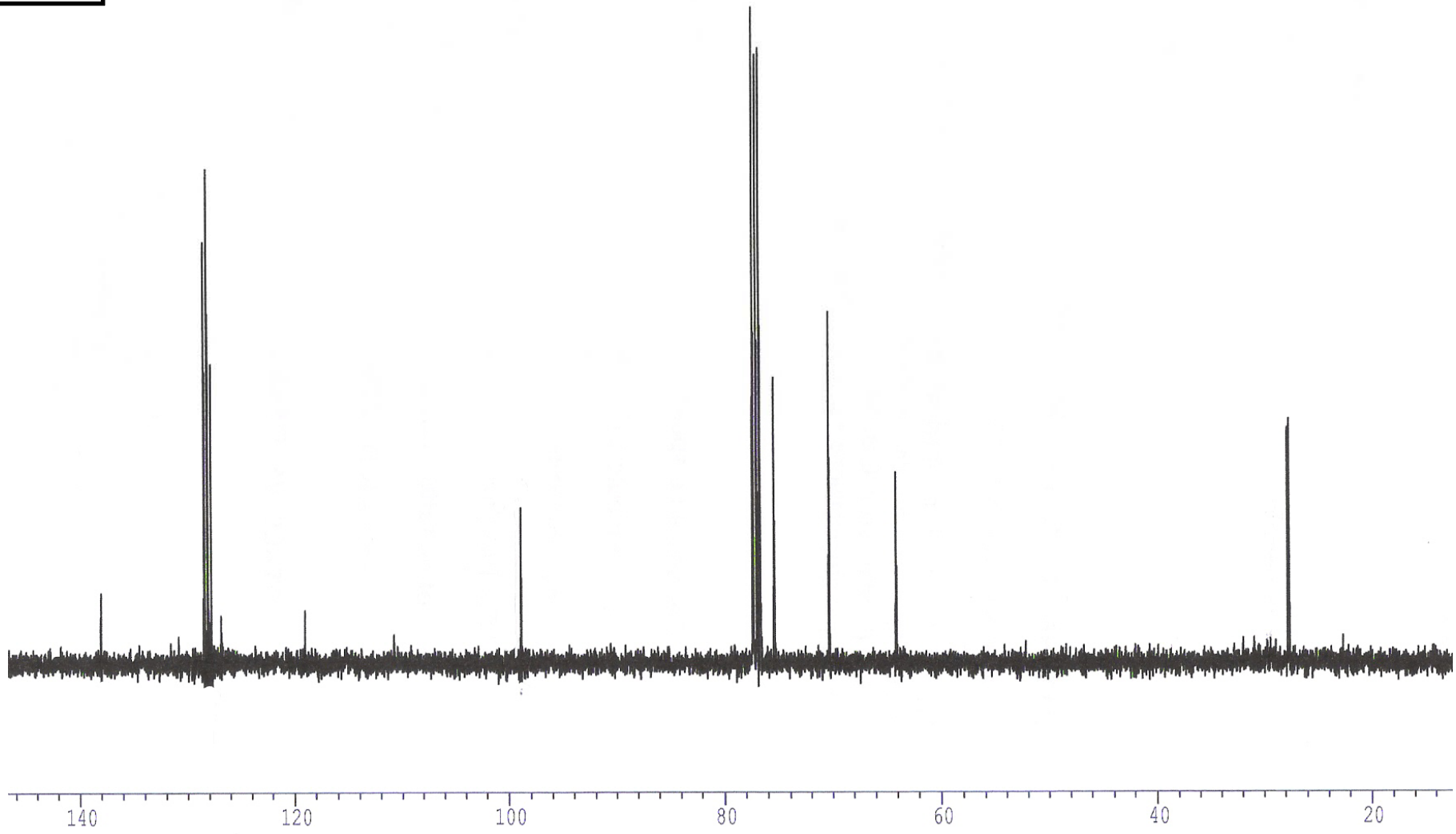
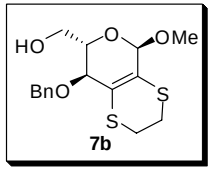
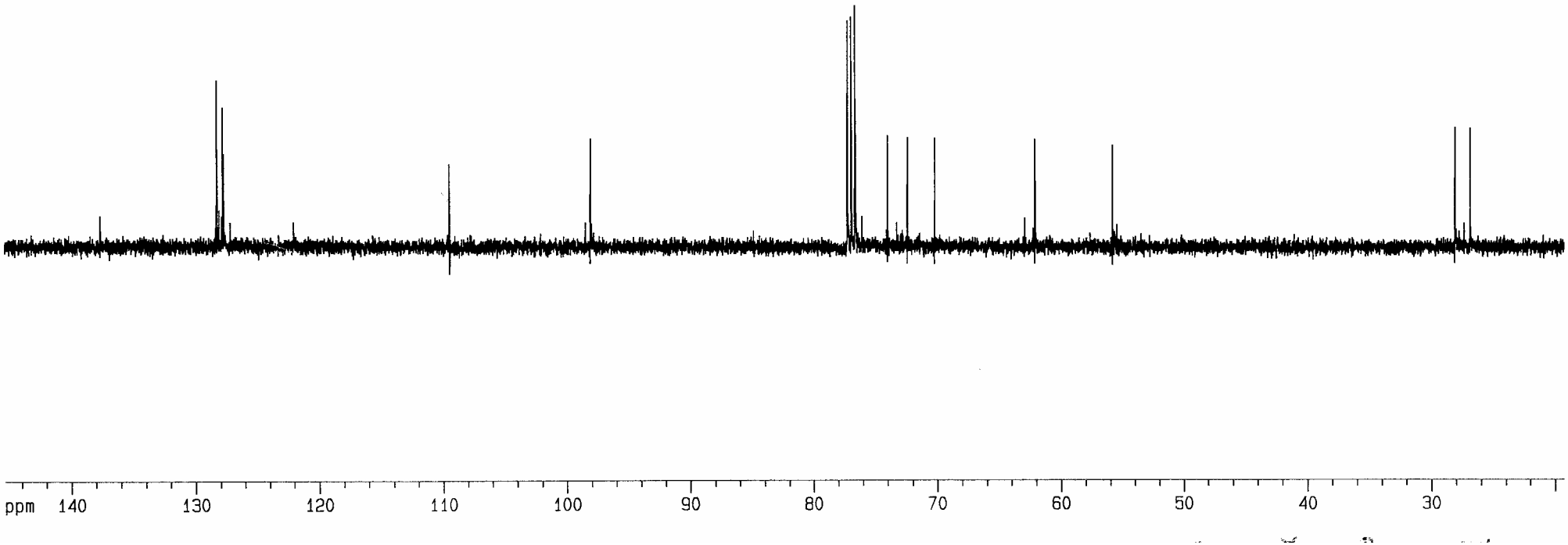
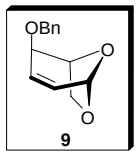


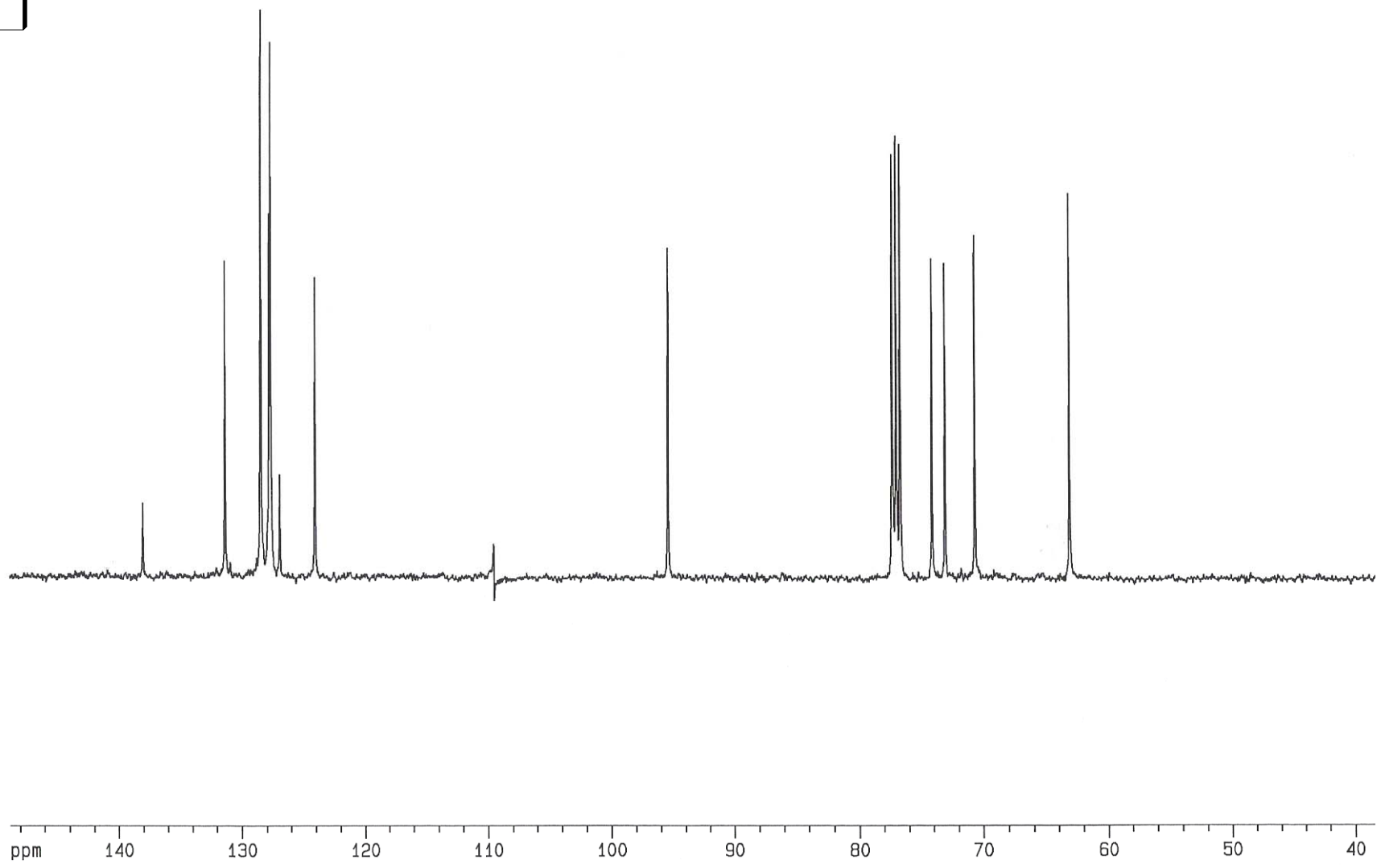


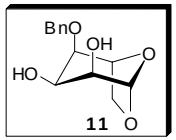
100 MHz, C_6D_6



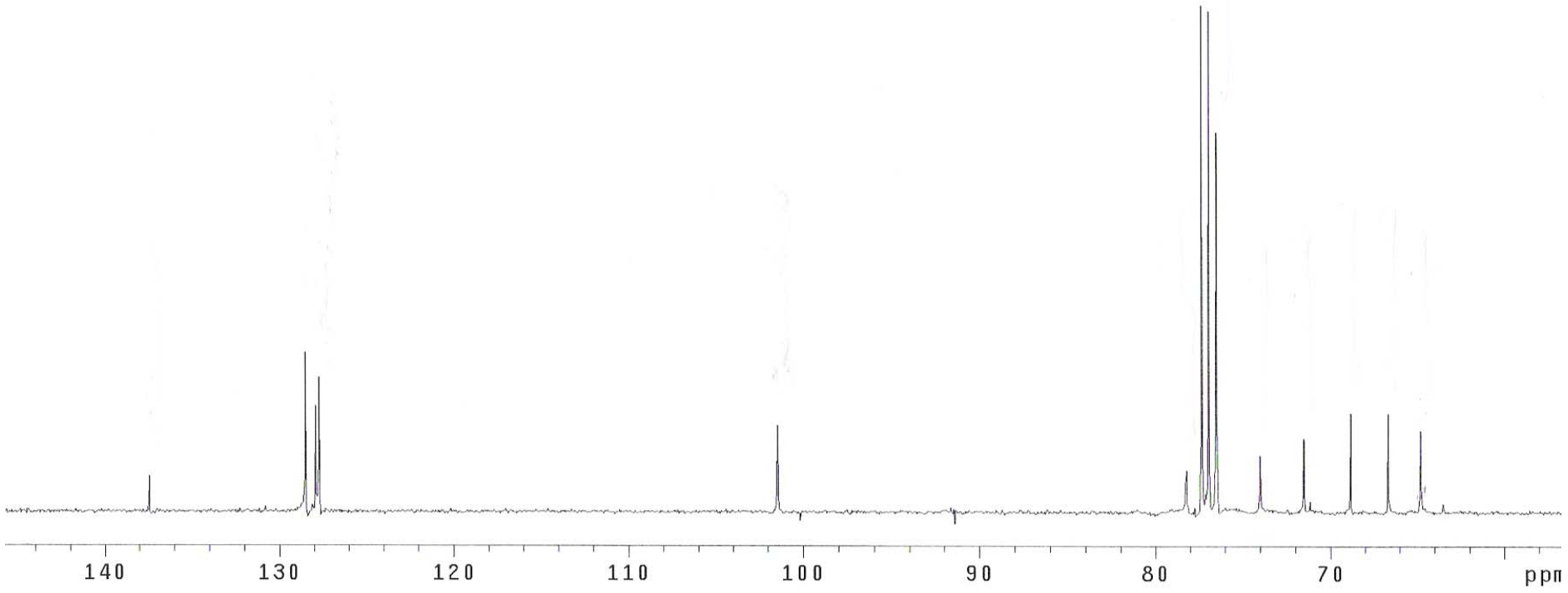


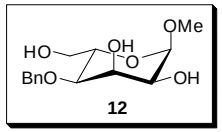
100 MHz, $CDCl_3$



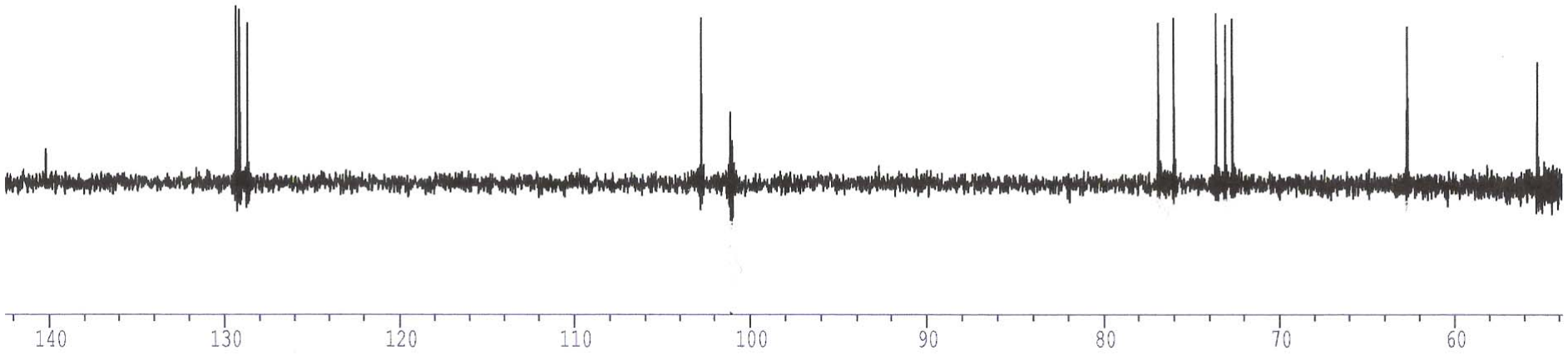


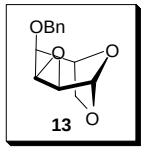
75 MHz, $CDCl_3$



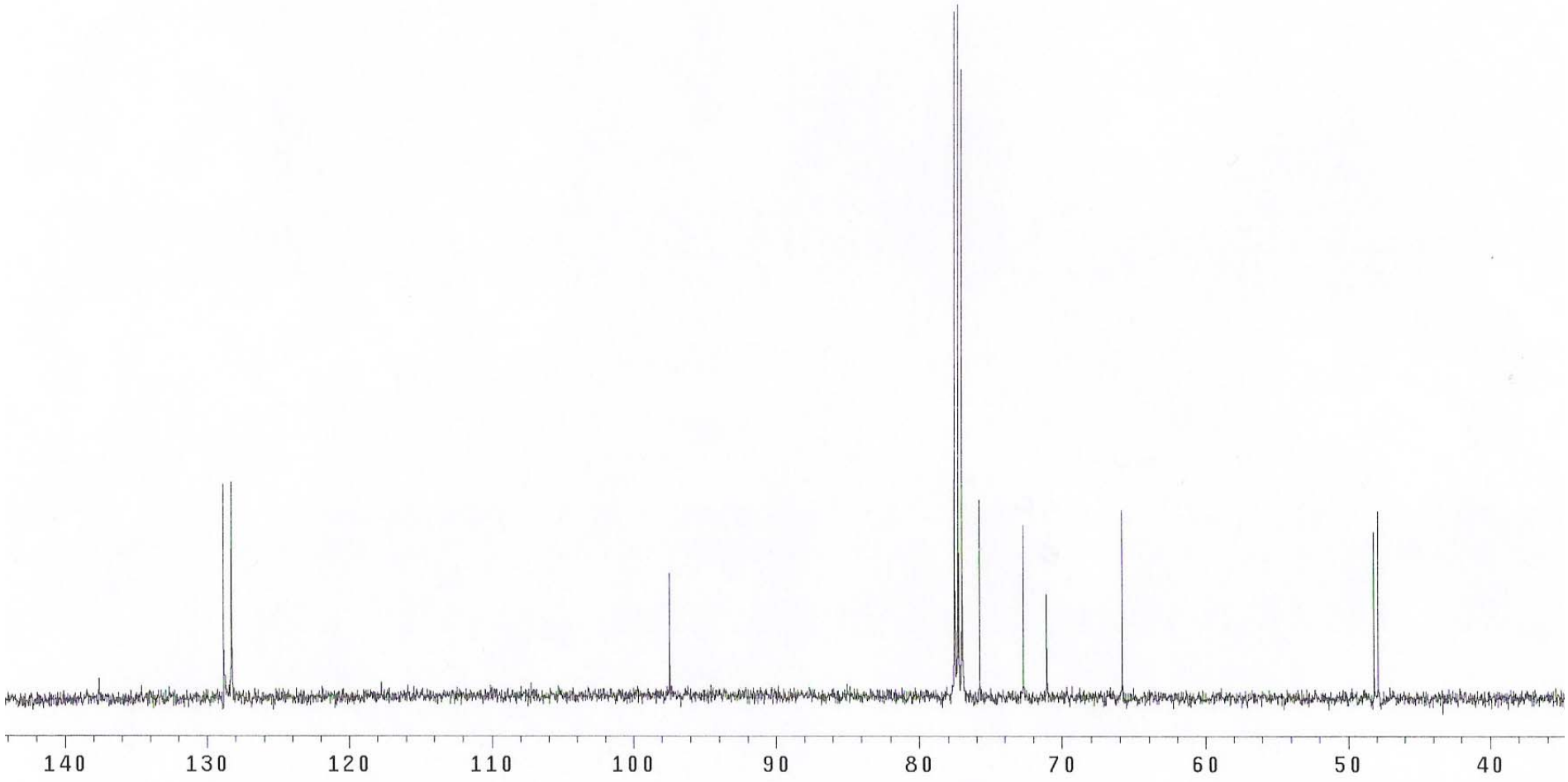


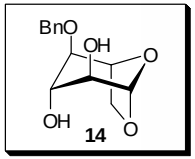
100 MHz, CD_3OD



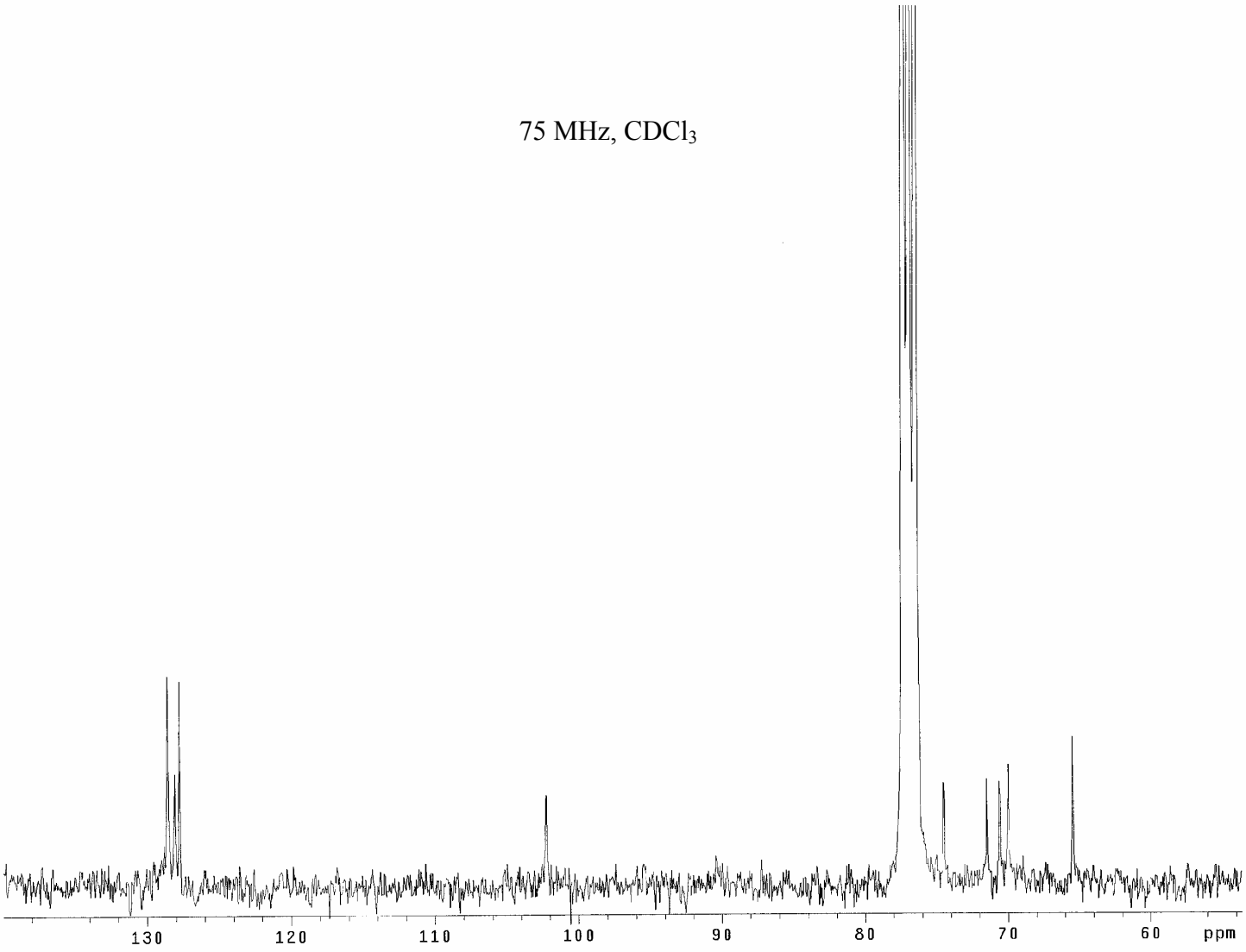


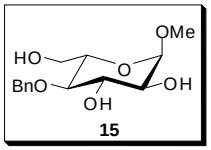
125 MHz, $CDCl_3$





75 MHz, $CDCl_3$





100 MHz, CD_3OD