Supporting Information for:

Monolithiocavitands: Versatile Intermediates For New Cavitand-Based Hosts

Jacob L. Irwin and Michael S. Sherburn*

School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

Contents (41 pages):

General Experimental Details

^{1}H NMR spectra were recorded on a Bruker AC 200B spectrometer (200.13 MHz) or a Bruker AM 400 (400.21 MHz) spectrometer in $CDCl_3$ or benzene-d_6. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane or residual protiosolvent as internal reference and are reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* in Hz) and integration (number of protons). ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker AM 400 (100.64 MHz) spectrometer in $CDCl_3$ or benzene-d_6 at ambient temperature with complete proton decoupling. Data is expressed in parts per million (ppm) shift relative to $CDCl_3$ (77.0 ppm) or C_6D_6 (128 ppm) and are reported as position (δ). Melting points were recorded on a Reichert heating stage with microscope and are uncorrected. Elemental analyses were obtained at the Campbell Microanalytical Laboratory at the Department of Chemistry, University of Otago, New Zealand. All compounds were dried before analysis at *ca*. 50 ºC and 0.1 mmHg for 36-45 h. Mass spectra were recorded on a VG ZAB-2SEQ instrument using a cesium ion gun at ca. 25 kV to produce a beam of fast Cs^+ ions. Compounds were prepared for infrared spectroscopic analysis as mixtures in KBr and the spectra collected by measurement of reflectance. High performance liquid chromatography (HPLC) was carried out using a Waters Associates system consisting of a Model M-6000A pump, a millipore model U6K injector and a model 440 UV detector at 254 nm. A Whatman Partisil 10 M9 semipreparative column of outer diameter 12.80 mm, inner diameter 9.40 mm, length 500.0 mm and particle size 10.0 μm was employed. $B(OMe)_3$ was dried by distillation from sodium metal. Solvents and reagents were purified according to the procedures outlined by Perrin and Armarego. [Purification of Laboratory Chemicals; D.D. Perrin, W.L.F. Armarego; 3rd Ed., Pergamon Press, 1988].

Experimental Procedures and Product Characterization Data

Standard procedure for generation of THF solutions of tribromo-monolithio bowl 6. A two-necked round-bottomed flask, equipped with a stir bar, a gas inlet to Ar/vacuum double manifold and a ground-glass stopper, was flame dried under reduced pressure. After cooling o ambient temperature, the flask was charged with the bromocavitand precursor and dry, freshly distilled THF (10 mL/mmol of cavitand). The solvent was removed by evaporation under vacuum and the residue was heated to 80 ºC at 0.1 mmHg for 1 h. The vacuum was replaced with Ar and the dissolution-evaporation procedure was repeated two more times. To a solution of the dried bromocavitand in THF (50 mL/mmol of cavitand) at -78 ºC (bath temperature) was rapidly added *n*-butyllithium (1.1 equiv, freshly titrated; at ca. 1.5 M in hexanes). After 20 minutes, the electrophile was introduced at -78 ºC. Reaction times and workup procedures vary. See below for details.

Preparation of Tribromo-monosubstituted bowls 7-16 (Table 1)

Tribromomonol bowl 7. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added trimethyl borate (24.7 μL, 0.220 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was cooled to -78 °C, quenched with a 1:1 mixture of 30% aqueous H_2O_2 and 3.0 M aqueous NaOH (1 mL) then stirred at 25 ºC for 18 h. After the cautious addition of 10% aqueous sodium metabisulfite solution (10%, 20 mL), the products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (279 mg). Column chromatography (13 g SiO_2, 6:1 hexane/ethyl acetate) gave *monol derivative* **7** as a white solid (191 mg, 68%): R_f = 0.21 (9:1 hexane/ethyl acetate); mp 105-106 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 3H), 6.60 (s, 1H), 5.95 (d, *J* = 7.6 Hz, 2H), 5.93 (d, *J* = 7.6 Hz, 2H), 5.63 (s, 3H), 4.85 (t, *J* = 8.0 Hz, 2H), 4.78 (t, *J* = 8.0 Hz, 2H), 4.41 (d, *J* = 7.2 Hz, 2H), 4.38 (d, *J* = 7.2 Hz, 2H), 2.21-2.17 (br

m, 8H), 1.41-1.24 (br m, 72H), 0.87 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 152.0, 151.8, 142.0, 141.3, 139.6, 139.2, 139.1, 138.2, 119.2, 119.1, 113.4, 114.2, 109.5, 99.1, 98.4, 37.6, 37.2, 31.9, 29.8, 29.7, 29.7, 29.4, 27.8, 27.7, 22.8, 22.7, 14.1; IR (KBr) 3498, 3371, 2922, 2852, 1585, 1467, 971 cm^{-1}; FAB-MS *m/z* 1404.8 (M^+, 100); Anal. Calcd for $C_{76}H_{109}Br_3O_9$: C, 64.90; H, 7.81; Found: C, 65.12; H, 7.95.

Tribromo-monoiodo bowl 8. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added iodine (101 mg, 0.400 mmol) dissolved in THF (1 mL). After warming to 25 ºC over the course of 1 h the yellow reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with 10 % aqueous sodium thiosulfate solution (2 × 40 mL), saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (238 mg). Column chromatography (13 g SiO_2, 3:1 hexane/CH_2Cl_2) gave *monoiodide derivative* **8** as a white solid (216 mg, 71%): R_f = 0.67 (1:1 hexane/CH_2Cl_2); mp 95-96 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 7.03 (s, 3H), 5.95 (d, J = 7.4 Hz, 2H), 5.94 (d, J = 7.4 Hz, 2H), 4.85 (t, J = 8.0 Hz, 2H), 4.39 (d, J = 7.4 Hz, 2H), 4.34 (d, J = 7.4 Hz, 2H), 2.23-2.17 (br m, 8H), 1.41-1.24 (br m, 72H), 0.88 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.4, 139.2, 138.6, 120.7, 119.0, 113.5, 98.5, 98.4, 93.1, 37.7, 37.6, 31.9, 30.0, 29.9, 29.7, 29.4, 27.7, 22.7, 14.1; IR (KBr) 2923, 2850, 1469, 1299, 1091, 967 cm^{-1}; FAB-MS *m/z* 1516.3 (M^+, 100); Anal. Calcd for $C_{76}H_{108}Br_3IO_8$: C, 60.20; H, 7.18; Found: C, 60.50; H, 7.19.

Tribromo-mono(trimethylsilyl) bowl 9. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added trimethylsilyl chloride (31 μL, 0.400 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (276 mg). Column chromatography (13 g SiO_2, 9:1→7:3

hexane/CH_2Cl_2) gave *monoTMS derivative* **9** as a white solid (66 mg, 22%): R_f = 0.50 (9:1 hexane/CH_2Cl_2); mp 45-47 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 7.08 (s, 1H), 7.05 (s, 2H), 5.95 (d, *J* = 7.4 Hz, 2H), 5.83 (d, *J* = 7.4 Hz, 2H), 4.85 (t, *J* = 8.0 Hz, 2H), 4.76 (t, *J* = 8.0 Hz, 2H), 4.37 (d, *J* = 7.4 Hz, 2H), 4.37 (d, *J* = 7.4 Hz, 2H), 2.23-2.10 (br m, 8H), 1.41-1.22 (br m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.4, 152.0, 151.9, 139.5, 139.3, 138.9, 137.6, 126.0, 123.0, 119.2, 118.9, 113.2, 113.1, 99.3, 98.6, 37.7, 37.3, 31.9, 30.4, 29.9, 29.8, 29.7, 29.4, 27.8, 27.7, 22.7, 14.1, 1.7; IR (KBr) 2920, 2851, 1568, 1467, 1409, 1302, 965, 838 cm^{-1}; FAB-MS *m/z* 1464.6 (M^+, 100); Anal. Calcd for $C_{79}H_{117}Br_3O_8Si$: C, 64.88; H, 8.06; Found: C, 64.83; H, 8.57.

Tribromo-mono(methylthiyl) bowl 10. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added methyl disulfide (20 μL, 0.220 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (283 mg). Column chromatography (14 g SiO_2, 9:1→7:3 hexane/CH_2Cl_2) gave *monomethylsulfide derivative* **10** as a white solid (231 mg, 80%): R_f = 0.20 (9:1 hexane/CH_2Cl_2); mp 100-101 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 4H), 5.95 (d, *J* = 7.4 Hz, 2H), 5.94 (d, *J* = 7.4 Hz, 2H), 4.84 (t, *J* = 7.9 Hz, 2H), 4.83 (t, *J* = 7.9 Hz, 2H), 4.38 (d, *J* = 7.4 Hz, 4H), 4.35 (d, *J* = 7.4 Hz, 4H), 2.35 (s, 3H), 2.21-2.17 (br m, 8H), 1.41-1.24 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 152.2, 152.0, 151.9, 139.3, 139.2, 138.5, 124.5, 119.9, 119.0, 113.5, 113.4, 98.8, 98.4, 37.6, 37.5, 31.9, 30.0, 29.9, 29.7, 29.4, 27.8, 27.7, 22.7, 17.7, 14.1; IR (KBr) 2924, 2852, 1467, 1416, 1299, 961 cm^{-1}; FAB-MS *m/z* 1435.8 (M^+, 100); Anal. Calcd for $C_{77}H_{111}Br_3O_8S$: C, 64.38; H, 7.79; Found: C, 64.40; H, 7.86.

Tribromo-monothiol bowl 11. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added sulfur flowers (7.7 mg, 0.240 mmol). After warming to 25 ºC over the course of 1 h the reaction

mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with 10 % aqueous hydrochloric acid (1 × 30 mL), saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (298 mg). Column chromatography (14 g SiO_2, 7:3→2:1 hexane/CH_2Cl_2) gave *monothiol derivative* **11** as a white solid (106 mg, 37%): R_f = 0.48 (7:3 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (s, 4H), 5.90 (d, *J* = 7.4 Hz, 2H), 5.73 (d, *J* = 7.4 Hz, 2H), 5.15 (t, *J* = 8.1 Hz, 2H), 5.10 (t, *J* = 8.1 Hz, 2H), 4.42 (d, *J* = 7.4 Hz, 2H), 4.32 (d, *J* = 7.4 Hz, 2H), 3.70 (s, 1H), 2.25-2.22 (br m, 8H), 1.32-1.28 (br m, 72H), 0.92 (t, *J* = 2.1 Hz, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.9, 152.8, 152.7, 152.6, 150.8, 140.0, 139.9, 139.8, 139.7, 138.7, 123.6, 119.6, 119.3, 116.2, 114.5, 114.3, 98.8, 98.6, 38.2, 38.0, 32.4, 30.4, 30.1, 29.8, 28.1, 23.1, 14.3; IR (KBr) 2923, 2845, 2361, 1654, 1455, 959 cm^{-1}.

Tribromo-monomethyl bowl 12. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added methyl iodide (25 μL, 0.400 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (280 mg). Column chromatography (14 g SiO_2, 2:1→1:1 hexane/CH_2Cl_2) gave *monomethyl derivative* **12** as a white solid (152 mg, 54%): R_f = 0.27 (2:1 hexane/CH_2Cl_2); mp 72-73 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 3H), 6.92 (s, 1H), 5.95 (d, *J* = 7.4 Hz, 2H), 5.91 (d, *J* = 7.4 Hz, 2H), 4.85 (t, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 8.0 Hz, 2H), 4.35 (dd, *J* = 7.4 Hz, 4H), 2.21-2.17 (br m, 8H), 1.99 (s, 3H), 1.41-1.24 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 152.2, 151.9, 151.7, 139.8, 139.3, 138.9, 137.6, 124.5, 119.2, 119.1, 117.2, 113.3, 113.1, 98.5, 98.4, 37.6, 37.3, 31.9, 30.0, 29.8, 29.7, 29.7, 29.4, 27.8, 27.7, 22.7, 14.1, 10.3; IR (KBr) 2924, 2852, 1468, 1301, 1092, 971 cm^{-1}; FAB-MS *m/z* 1404.6 (M^+, 100); Anal. Calcd for $C_{77}H_{111}Br_3O_8$: C, 65.85; H, 7.97; Found: C, 65.84; H, 8.05.

Tribromo-monocarboxaldehyde bowl 13. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added dimethylformamide (30.8 μL, 0.400 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with 10 % aqueous hydrochloric acid (1 × 40 mL), saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (275 mg). Column chromatography (13 g SiO_2, 3:1 → 1:2 hexane/CH_2Cl_2) gave *monoaldehyde derivative* **13** as a low melting point white solid (160 mg, 57%): R_f = 0.56 (3:7 hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6) δ 10.11 (s, 1H), 7.58 (s, 1H), 7.34 (s, 3H), 5.87 (d, *J* = 7.4 Hz, 2H), 5.77 (d, *J* = 7.4 Hz, 2H), 5.15 (t, *J* = 8.1 Hz, 2H), 5.13 (t, *J* = 8.1 Hz, 2H), 4.40 (d, *J* = 7.6 Hz, 2H), 4.37 (d, *J* = 7.6 Hz, 2H), 2.24-2.22 (br m, 8H), 1.32 (br s, 72H), 0.92 (t, *J* = 2.1 Hz, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 189.4, 155.3, 152.9, 152.8, 139.9, 139.8, 139.7, 139.6, 128.5, 125.3, 125.0, 119.3, 119.2, 114.6, 114.5, 99.6, 99.3, 38.2, 37.3, 32.4, 30.4, 30.1, 29.8, 28.2, 28.1, 23.1, 14.3; IR (KBr) 2923, 2852, 1697, 1467, 969 cm^{-1}.

Tribromo-monocarboxymethyl bowl 14. To the monolithiocavitand solution generated from tetrabromide **1**[8] (294 mg, 0.200 mmol) in THF (10 mL) at -78 °C was added methyl chloroformate (31 μL, 0.400 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (287 mg). Column chromatography (14 g SiO_2, 2:1 → 1:2 hexane/CH_2Cl_2) gave *monoester derivative* **14** as a white solid (207 mg, 72%): R_f = 0.71 (3:7 hexane/CH_2Cl_2); mp 44-46 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.02 (s, 3H), 5.93 (d, *J* = 7.4 Hz, 2H), 5.79 (d, *J* = 7.4 Hz, 2H), 4.85 (t, *J* = 8.0 Hz, 2H), 4.80 (t, *J* = 8.0 Hz, 2H), 4.48 (d, *J* = 7.4 Hz, 2H), 4.36 (d, *J* = 7.4 Hz, 2H), 3.87 (s, 3H), 2.21-2.17 (br m, 8H), 1.41-1.24 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5,

152.2, 152.0, 150.7, 139.2, 139.0, 138.8, 138.5, 123.9, 121.7, 118.9, 118.7, 113.7, 113.6, 98.9, 98.3, 52.9, 37.6, 36.8, 31.9, 29.9, 29.7, 29.3, 27.7, 22.6, 14.0; IR (KBr) 2925, 2852, 1746, 1470, 1470, 963 cm^{-1}; FAB-MS *m/z* 1448.6 (M+, 100); Anal. Calcd for $C_{78}H_{111}Br_3O_{10}$: C, 64.68; H, 7.72; Found: C, 64.83; H, 7.84.

Tribromo-monoacyl bowl 15. To the monolithiocavitand solution generated from tetrabromide **1**[8] (1.47 g, 1.00 mmol) in THF (50 mL) at -78 °C was added methyl acetate (159 μL, 2.00 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was quenched with sat. NH_4Cl (50 mL). The products were extracted into ethyl acetate (3 × 50 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 50 mL), saturated brine (1 × 50 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (1.43 g). Column chromatography (80 g SiO_2, 7:3 → 1:1 → 3:7 hexane/CH_2Cl_2) gave *monomethylketone derivative* **15** (422 mg, 29%) and tribromo-monoprotio bowl **2** (451 mg, 32%) as white solids. Characterization data for **15**: R_f = 0.38 (9:1 hexane/CH_2Cl_2); mp 59-60 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.01 (s, 3H), 5.94 (d, *J* = 7.4 Hz, 2H), 5.75 (d, *J* = 7.4 Hz, 2H), 4.85 (t, *J* = 8.0 Hz, 2H), 4.78 (t, *J* = 8.0 Hz, 2H), 4.50 (d, *J* = 7.4 Hz, 4H), 4.27 (d, *J* = 7.4 Hz, 4H), 2.49 (s, 3H), 2.21-2.17 (br m, 8H), 1.41-1.24 (br m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 152.2, 152.1, 149.9, 139.2, 139.0, 138.8, 138.7, 131.6, 121.1, 118.9, 118.6, 113.8, 113.7, 99.2, 98.4, 32.2, 31.9, 29.9, 29.7, 29.4, 27.8, 27.1, 22.7, 14.1; IR (KBr) 2924, 2852, 1710, 1580, 1460, 1092, 961 cm^{-1}; FAB-MS *m/z* 1431.3 (M^+, 100); Anal. Calcd for $C_{78}H_{111}Br_3O_9$: C, 65.40; H, 7.81; Found: C, 65.57; H, 7.85.

Tribromo-monophenacyl bowl 16. To the monolithiocavitand solution generated from tetrabromide **1**[8] (1.47 g, 1.00 mmol) in THF (50 mL) at -78 °C was added methyl benzoate (137 μL, 1.10 mmol). After warming to 25 ºC over the course of 3 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 50 mL), the combined organic phases were washed with saturated brine (1 × 50 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (1.53 g). Column chromatography (90 g SiO_2, 7:3 → 1:1 → 3:7 hexane/CH_2Cl_2) gave

monophenylketone derivative **14** as a white solid (627 mg, 42%): R_f = 0.47 (4:6 hexane/CH_2Cl_2); mp 53-54 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.61 (td, *J* = 6.3, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.22 (s, 1H), 7.04 (s, 3H), 5.94 (d, *J* = 7.3 Hz, 2H), 5.61 d (7.4, 2H), 4.86 (t, *J* = 8.1 Hz, 2H), 4.80 (t, *J* = 8.1 Hz, 2H), 4.55 (d, *J* = 7.4 Hz, 4H), 4.30 (d, *J* = 7.4 Hz, 4H), 2.35-2.20 (br m, 8H), 1.42-1.24 (br m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 152.3, 152.2, 152.1, 150.8, 139.1, 139.0, 138.9, 138.6, 136.2, 134.3, 129.7, 129.4, 128.7, 121.5, 118.9, 118.6, 113.9, 113.8, 99.1, 98.4, 37.6, 36.9, 31.9, 30.0, 29.7, 29.4, 27.8, 27.7, 22.7, 14.1; IR (KBr) 3002, 2921, 2853, 1674, 1581, 1467, 1092, 963 cm^{-1}; FAB-MS *m/z* 1494.2 (M^+, 100); Anal. Calcd for $C_{83}H_{113}Br_3O_9$: C, 66.70; H, 7.62; Found: C, 66.78; H, 7.73.

Preparation of carbon-linked *bis*-bowl 18 (Scheme 1)

***Bis*-bowl 18**. To the monolithiocavitand solution generated from tetrabromide **1**[8] (1.47 g, 1.00 mmol) in THF (50 mL) at -78 °C was added dimethyl benzene-1,4-dicarboxylate **17** (93.2 mg, 0.480 mmol). After warming to 25 ºC over the course of 2 h the reaction mixture was quenched with water (30 mL). The products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (1.48 g). Radial chromatography (4 mm rotor, 1:9 hexane/CH_2Cl_2) gave a chromatographically homogeneous mixture of the desired product and the monobowl-monoester (682 mg). The mixture (682 mg) was dissolved in THF (15 mL) - H_2O (4 mL) and lithium hydroxide (50 mg) was added. The solution was stirred at 25 ºC for 3 h before being partitioned between ethyl acetate (100 mL) and water (50 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid. Column chromatography (10 g SiO_2, diethyl ether) gave *bis-bowl* **18** as a white powder (407 mg, 28%): R_f = 0.31 (4:6 hexane/CH_2Cl_2); mp 94-95 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 4H), 7.23 (s, 2H), 7.04 (s, 6H), 5.94 (d, *J* = 7.3 Hz, 4H), 5.60 (d, *J* = 7.3 Hz, 4H), 4.86 (t, *J* = 8.0 Hz, 4H), 4.78 (t, *J* = 8.0 Hz, 4H), 4.54 (d, *J* = 7.3 Hz, 4H), 4.29 (d, *J* = 7.3 Hz, 4H), 2.34-2.15 (br m, 16H), 1.42-1.24 (br m, 144H), 0.88 (t, *J* = 6.8 Hz, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7,

152.3, 152.1, 152.0, 150.8, 139.8, 139.2, 139.1, 139.0, 138.3, 129.9, 128.8, 121.9, 118.9, 118.6, 113.8, 113.7, 37.6, 36.9, 31.9, 29.9, 29.8, 29.7, 29.3, 27.8, 27.7, 22.6, 14.1; IR (KBr) 2924, 2852, 1675, 1584, 1467, 1301, 963 cm^{-1}; Anal. Calcd for $C_{160}H_{220}Br_6O_{18}$: C, 66.02; H, 7.62; Found: C, 66.31; H, 7.73.

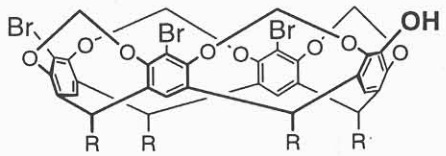
Preparation of "triple functionality" bowls 19-22 (Schemes 2 and 3)

***A,B*-Dibromo-*C*-hydroxy-*D*-protio bowl (±)-19** and ***A,C*-dibromo-*B*-hydroxy-*D*-protio bowl 20**. To the solution of monolithiocavitands generated from tribromide **2a**[8] (1.39 g, 1.00 mmol) in THF (50 mL) at -78 °C was added trimethyl borate (168 μL, 1.50 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was cooled to -78 °C, quenched with a 1:1 mixture of 30% aqueous H_2O_2 and 3.0 M aqueous NaOH (5 mL) then stirred at 25 ºC for 18 h. After the cautious addition of 10% aqueous sodium metabisulfite solution (10%, 20 mL), the products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 80 mL), saturated brine (1 × 80 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (1.37 g). Column chromatography (200 g SiO_2, 4:1 hexane/ethyl acetate) gave a mixture of the two regioisomeric *dibromo-monohydroxy-monoprotio derivatives* **19** and **20** as a white solid (1.11 g). These were separated by normal phase HPLC (86.6:12.4:1 hexane/ethyl acetate/acetic acid). Both the slower eluting, major, chiral isomer **19** (545 mg, 41%) and the faster eluting, minor, achiral isomer **20** (465 mg, 35%) were obtained as a white powders. Characterization data for **20**: R_f = 0.52 (7:3 hexane/ethyl acetate); mp 141-142 °C ($CHCl_3$/EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.07 (s, 2H), 6.64 (s, 1H), 6.54 (s, 1H), 5.96 (d, *J* = 7.1 Hz, 2H), 5.86 (d, *J* = 7.2 Hz, 2H), 5.25 (br s, 1H), 4.80 (t, *J* = 7.9 Hz, 2H), 4.78 (t, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 7.2 Hz, 4H), 2.21-2.18 (br m, 8H), 1.42-1.27 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.1, 152.0, 142.1, 141.3, 139.5, 139.4, 138.4, 138.3, 121.0, 119.2, 116.9, 113.1, 109.8, 99.2, 99.0, 37.3, 37.2, 32.0, 30.0, 29.8, 29.7, 29.5, 27.9, 22.8, 14.1; IR (KBr) 3454, 2927, 2852, 1587, 1465, 1296, 1091, 979 cm^{-1}; Anal. Calcd for $C_{76}H_{110}Br_2O_9$: C, 68.76; H, 8.35; Found: C, 68.67; H, 8.65. Characterization data for **(±)-19**: R_f = 0.46 (7:3 hexane:ethyl acetate); mp 82-83 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09

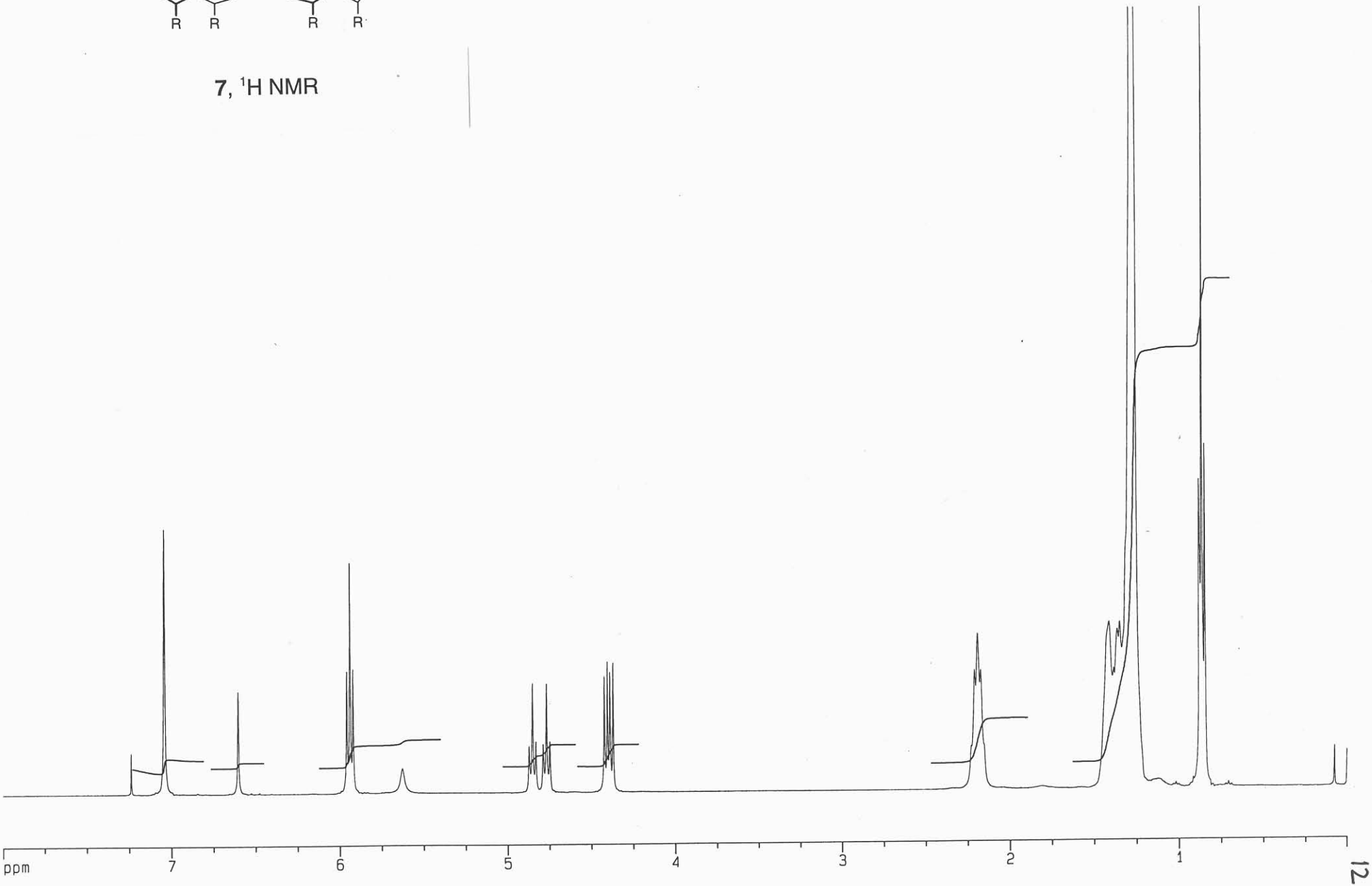
(s, 1H), 7.07 (s, 2H), 6.63 (s, 1H), 6.54 (s, 1H), 5.96 (d, *J* = 7.1 Hz, 1H), 5.95 (d, *J* = 7.0 Hz, 1H), 5.86 (d, *J* = 7.2 Hz, 1H), 5.85 (d, *J* = 6.9 Hz, 1H), 5.10 (br s, 1H), 4.87 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 7.8 Hz, 1H), 4.78 (t, *J* = 7.9 Hz, 1H), 4.72 (t, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 7.0 Hz, 1H), 4.42 (d, *J* = 7.2 Hz, 2H), 4.38 (d, *J* = 7.4 Hz, 1H), 2.23-2.17 (br m, 8H), 1.42-1.27 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 154.7, 152.2, 152.1, 151.9, 142.2, 141.8, 141.1, 139.7, 139.6, 139.2, 139.1, 138.6, 138.5, 138.1, 138.0, 120.9, 119.3, 119.0, 116.6, 113.3, 113.0, 109.5, 99.6, 99.1, 99.0, 98.5, 37.7, 37.2, 37.0, 36.5, 31.9, 29.9, 29.8, 29.7, 29.4, 27.8, 27.7, 27.6, 22.7, 14.1; IR (KBr) 3390, 2927, 2850, 1587, 1460, 1291, 1090, 967 cm^{-1}; Anal. Calcd for $C_{76}H_{110}Br_2O_9$: C, 68.76; H, 8.35; Found: C, 68.50; H, 8.29.

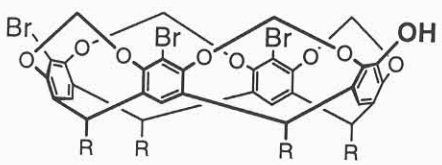
***A*-Bromo-*C*-hydroxy-*B,D*-diprotio bowl 21**. To the monolithiocavitand solution generated from A,C-dibromide **3a**[8] (262 mg, 0.200 mmol) in THF (50 mL) at -78 °C was added trimethyl borate (34 μL, 0.300 mmol). After warming to 25 ºC over the course of 1 h the reaction mixture was cooled to -78 °C, quenched with a 1:1 mixture of 30% aqueous H_2O_2 and 3.0 M aqueous NaOH (1 mL) then stirred at 25 ºC for 18 h. After the cautious addition of 10% aqueous sodium metabisulfite solution (10%, 20 mL), the products were extracted into ethyl acetate (3 × 40 mL), the combined organic phases were washed with saturated aqueous sodium hydrogen carbonate solution (1 × 40 mL), saturated brine (1 × 40 mL), dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a white solid (277 mg). Column chromatography (13 g SiO_2, 9:1→8:2→1:1 hexane/ ethyl acetate) gave *achiral monobromo-monohydroxy-diprotio bowl* **21** as a white solid (107 mg, 44%): R_f = 0.34 (7:3 hexane/ethyl acetate); mp 111-112 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.08 (s, 1H), 6.64 (s, 1H), 6.51 (s, 2H), 5.86 (d, *J* = 7.2 Hz, 4H), 5.38 (br s, 1H), 4.80 (t, *J* = 8.0 Hz, 2H), 4.72 (t, *J* = 8.0 Hz, 2H), 4.46 (d, *J* = 7.0 Hz, 2H), 4.41 (d, *J* = 7.2 Hz, 2H), 2.27-2.20 (br m, 8H), 1.42-1.22 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 154.7, 152.0, 142.0, 140.9, 139.4, 138.7, 138.3, 138.2, 121.1, 119.0, 116.5, 113.1, 109.5, 99.6, 99.0, 37.0, 36.5, 31.9, 29.9, 29.8, 29.7, 29.4, 27.9, 27.8, 22.7, 14.1**;** IR (KBr) 3433, 2923, 2852, 1572, 1490, 1295, 975 cm^{-1}; FAB-MS *m/z* 1247.7 (M^+, 100); Anal. Calcd for $C_{76}H_{111}BrO_9$: C, 73.11; H, 8.96; Found: C, 74.86; H, 9.23

***A*-Bromo-*B*-hydroxy-*C,D*-diprotio bowl (±)-22**. From the monolithiocavitand solution generated from A,B-dibromide **4a**[8] (262 mg, 0.200 mmol) in THF (50 mL), a procedure identical to that described for the conversion of **3a** → **21** gave *chiral monobromo-monohydroxy-diprotio bowl* **(±)-22** as a white solid (82.7 mg, 33%): R_f = 0.41 (7:3 hexane/ethyl acetate); mp 148-149 °C ($CHCl_3$/^{i}PrOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 2H), 7.07 (s, 1H), 6.64 (s, 1H), 6.51 (s, 2H), 5.95 (d, *J* = 7.1 Hz, 1H), 5.86 (d, *J* = 7.2 Hz, 1H), 5.85 (d, *J* = 7.0 Hz, 1H), 5.75 (d, *J* = 7.2 Hz, 1H), 5.45 (br s, 1H), 4.79 (t, *J* = 7.9 Hz, 1H), 4.75 (t, *J* = 8.5 Hz, 1H), 4.71 (t, *J* = 7.9 Hz, 2H), 4.45 (d, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 7.2 Hz, 1H), 4.40 (d, *J* = 7.4 Hz, 2H), 2.24-2.17 (br m, 8H), 1.42-1.27 (br m, 72H), 0.87 (t, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 154.9, 154.8, 154.8, 152.0, 151.9, 142.1, 141.8, 139.6, 139.5, 138.7, 134.6, 138.4, 138.3, 138.1, 138.0, 120.8, 120.7, 119.3, 116.6, 116.4, 112.8, 109.6, 99.6, 99.5, 99.2, 99.0, 37.2, 37.0, 36.5, 36.3, 31.9, 29.9, 29.8, 29.7, 29.4, 27.9, 27.8, 22.7, 14.1; IR (KBr) 3381, 2923, 2859, 1576, 1490, 1296, 981 cm^{-1}; FAB-MS *m/z* 1247.7 (M^+, 100); Anal. Calcd for $C_{76}H_{111}BrO_9$: C, 73.11; H, 8.96; Found: C, 73.16; H, 9.02. No separation in HPLC traces was observed for the enantiomers of **(±)-22** in a variety of solvents using the following chiral columns: Macher-Nugel Nucleosil Chiral-2; Rexchrom Pirkle Type 1-A; Jones Apex Chiralpack; Merck Hibar Chiraspher.

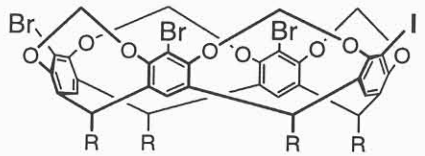


7, ^{1}H NMR

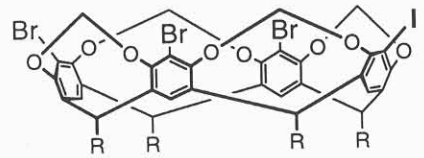




7, ^{13}C NMR



8, ^{1}H NMR



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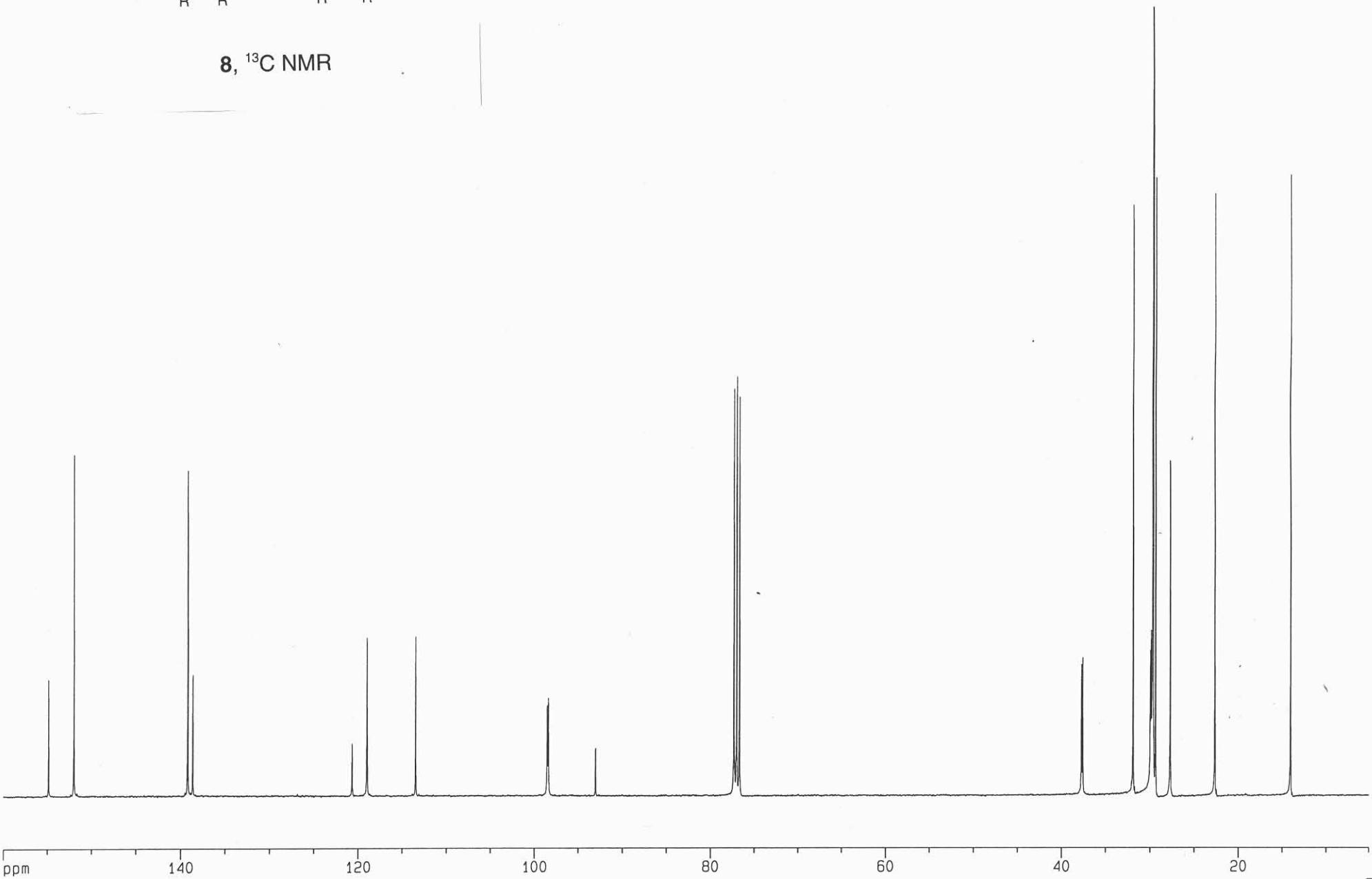
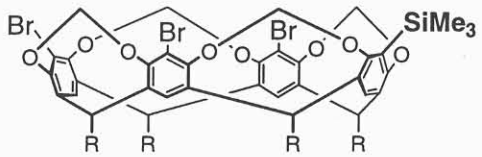
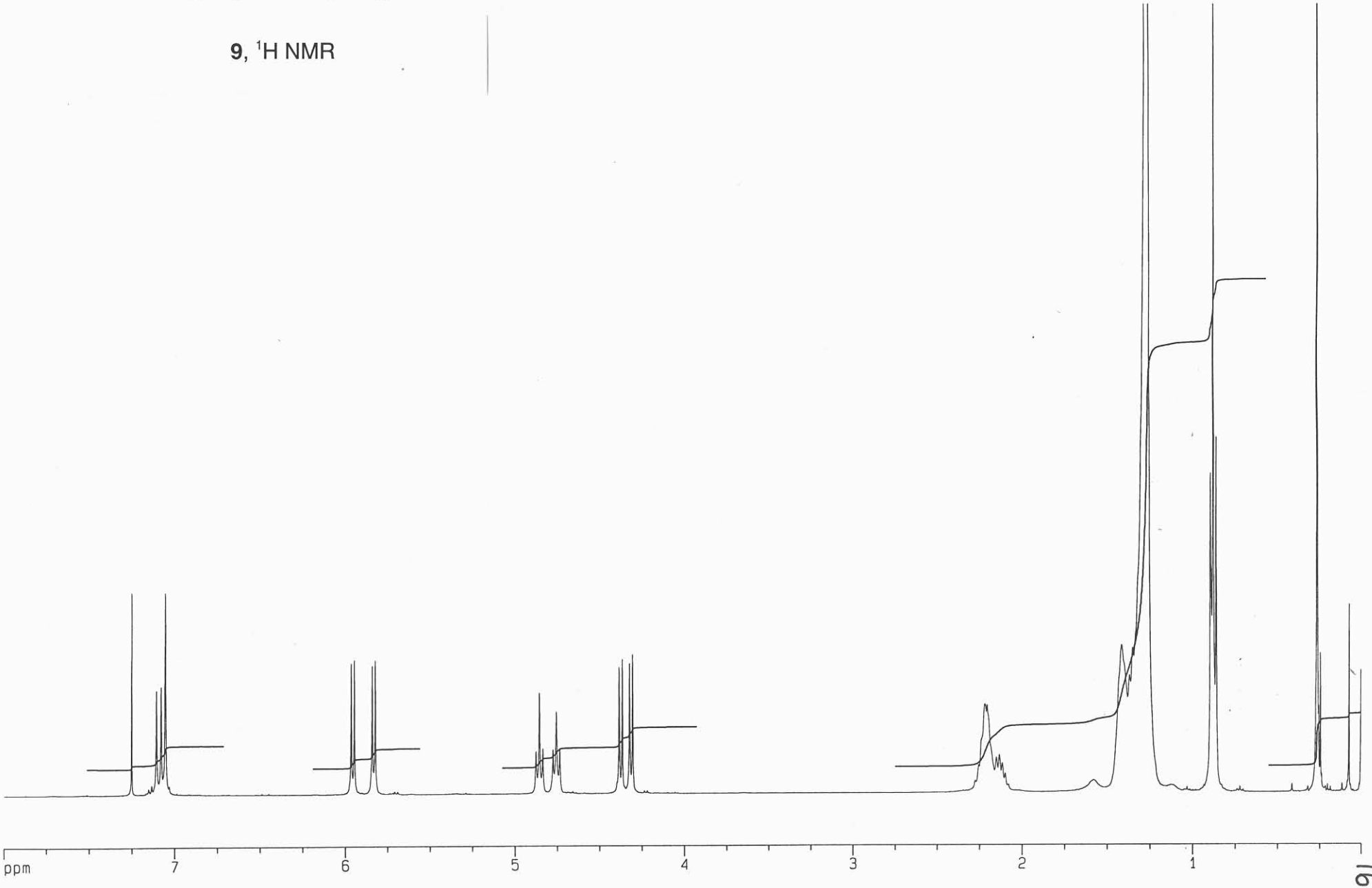
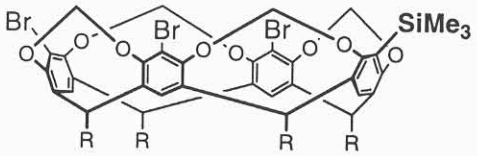




9, ^{1}H NMR





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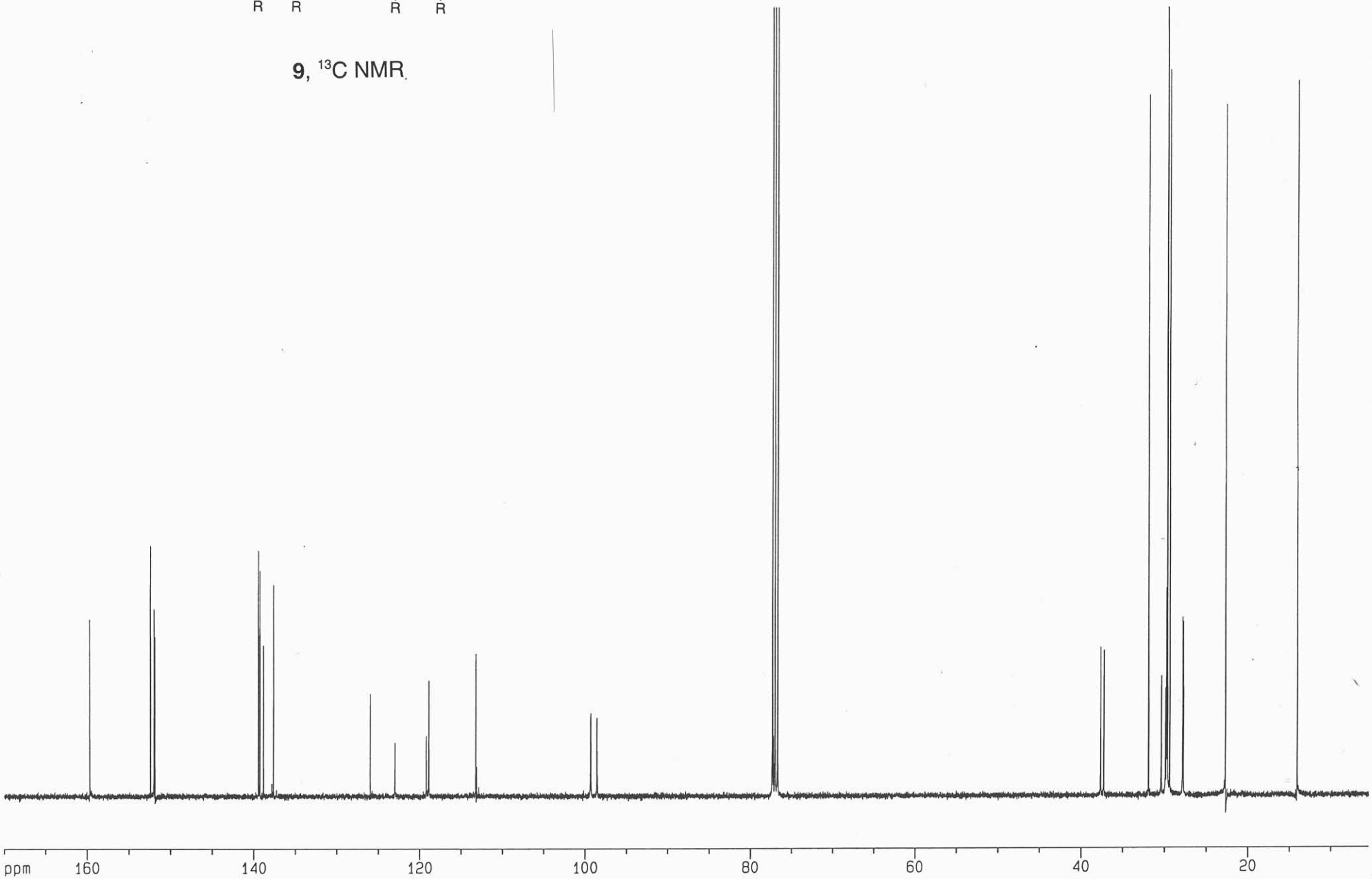
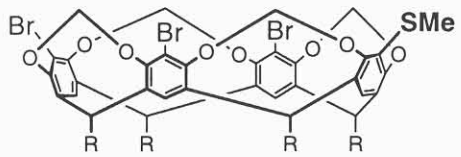
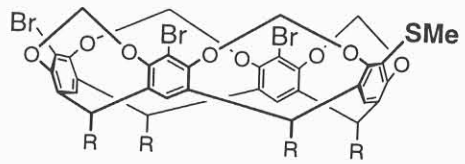




10, ^{1}H NMR



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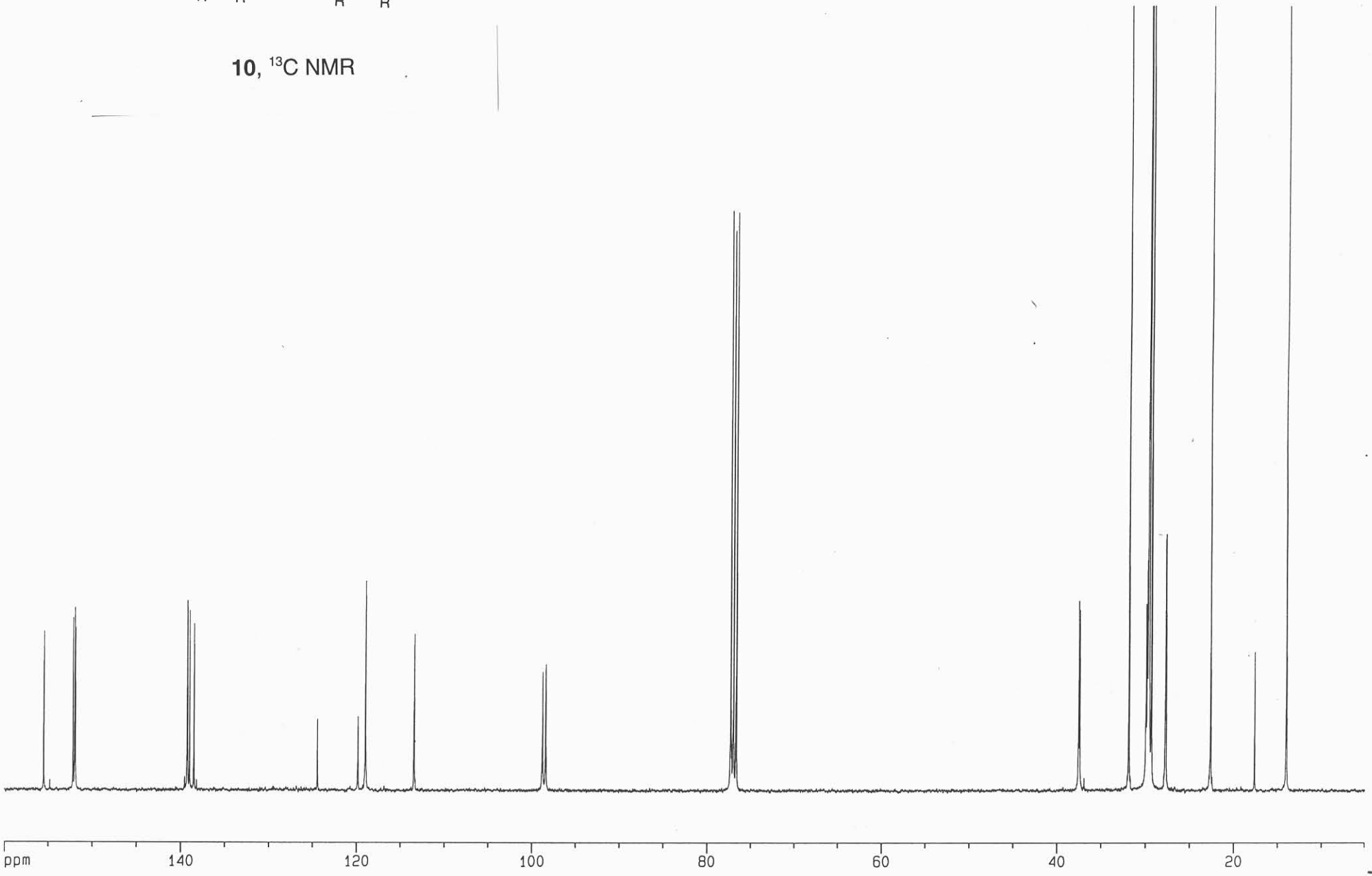
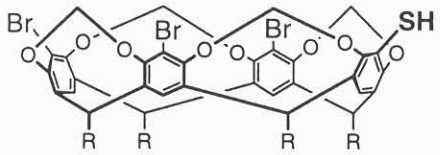
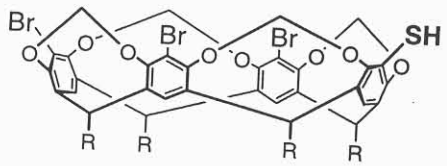




11, ^{1}H NMR



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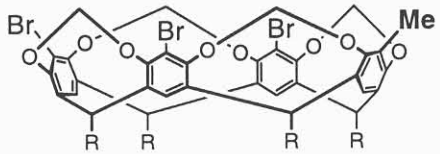
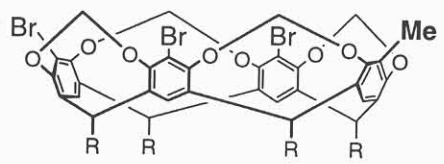


12, ^{1}H NMR



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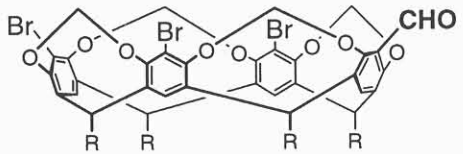

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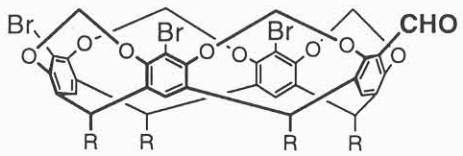

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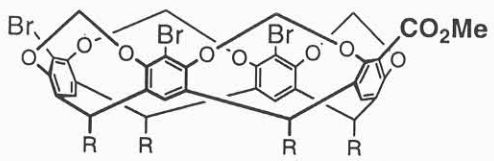
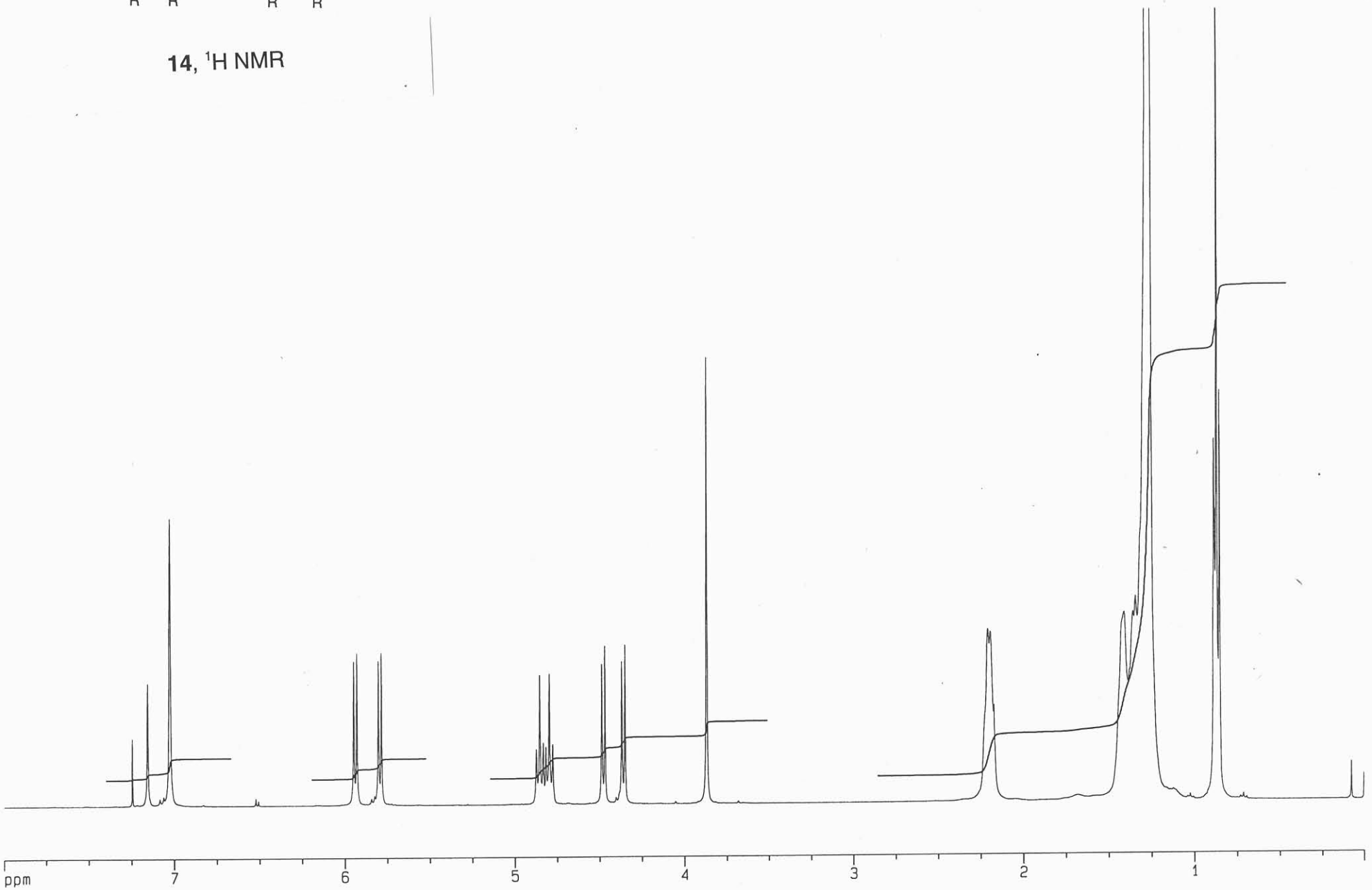
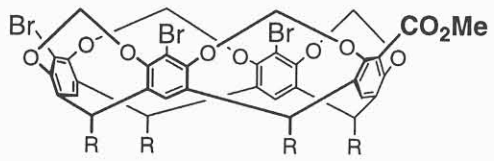


14, ^{1}H NMR





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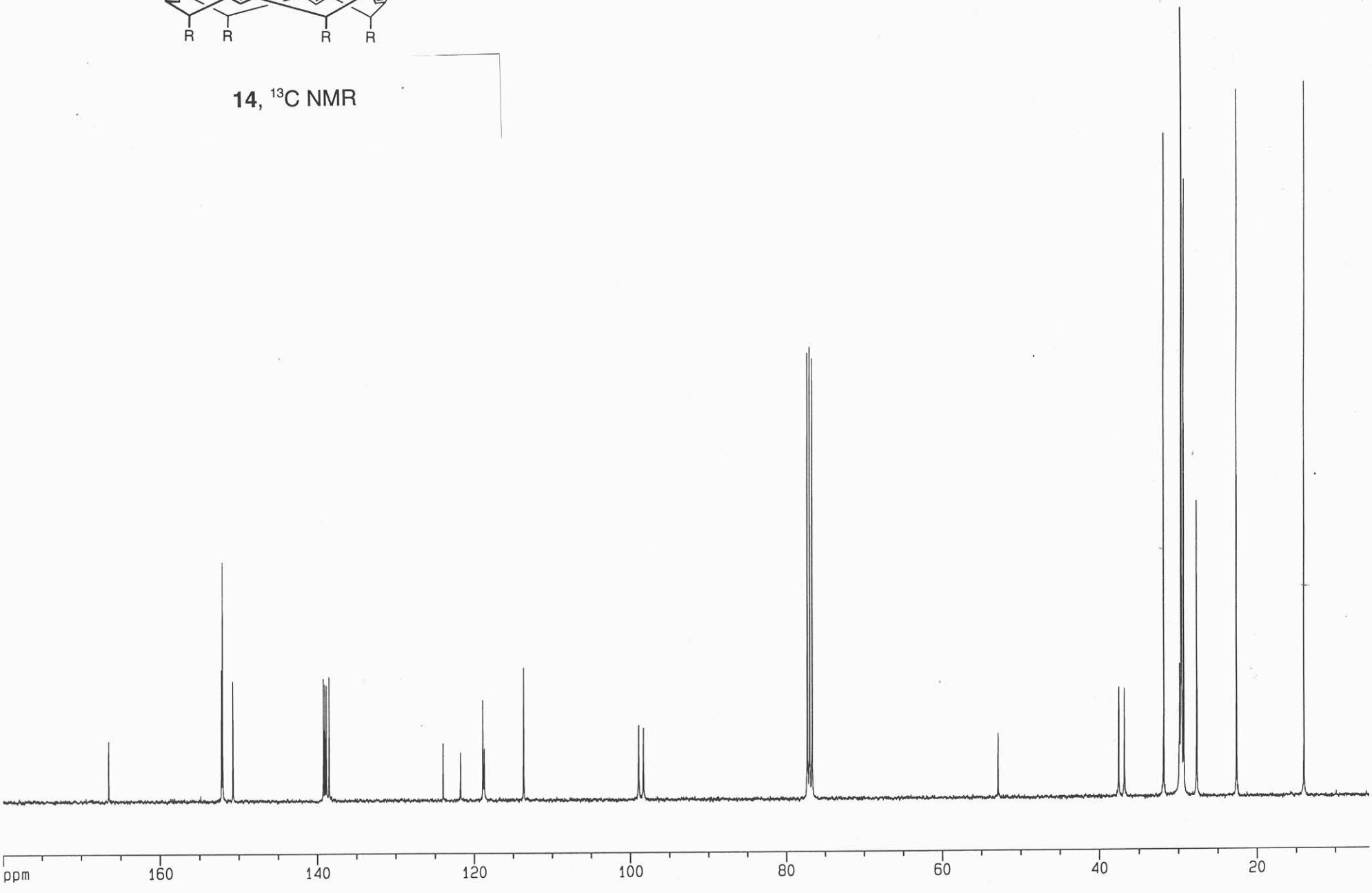
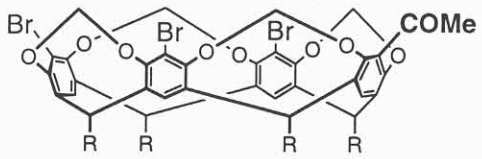
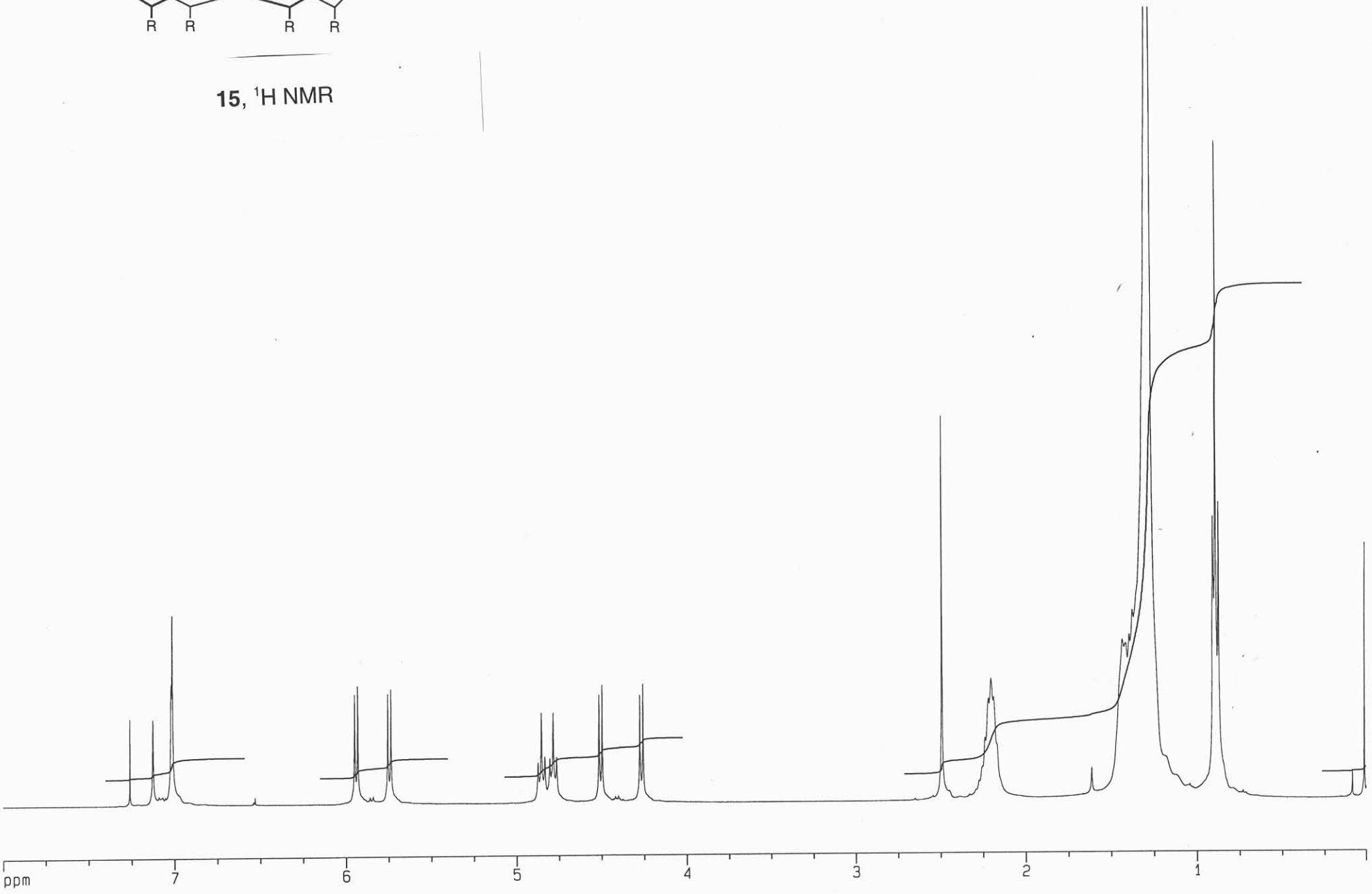
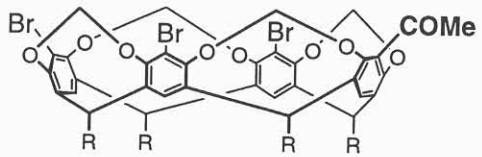




15, ^{1}H NMR





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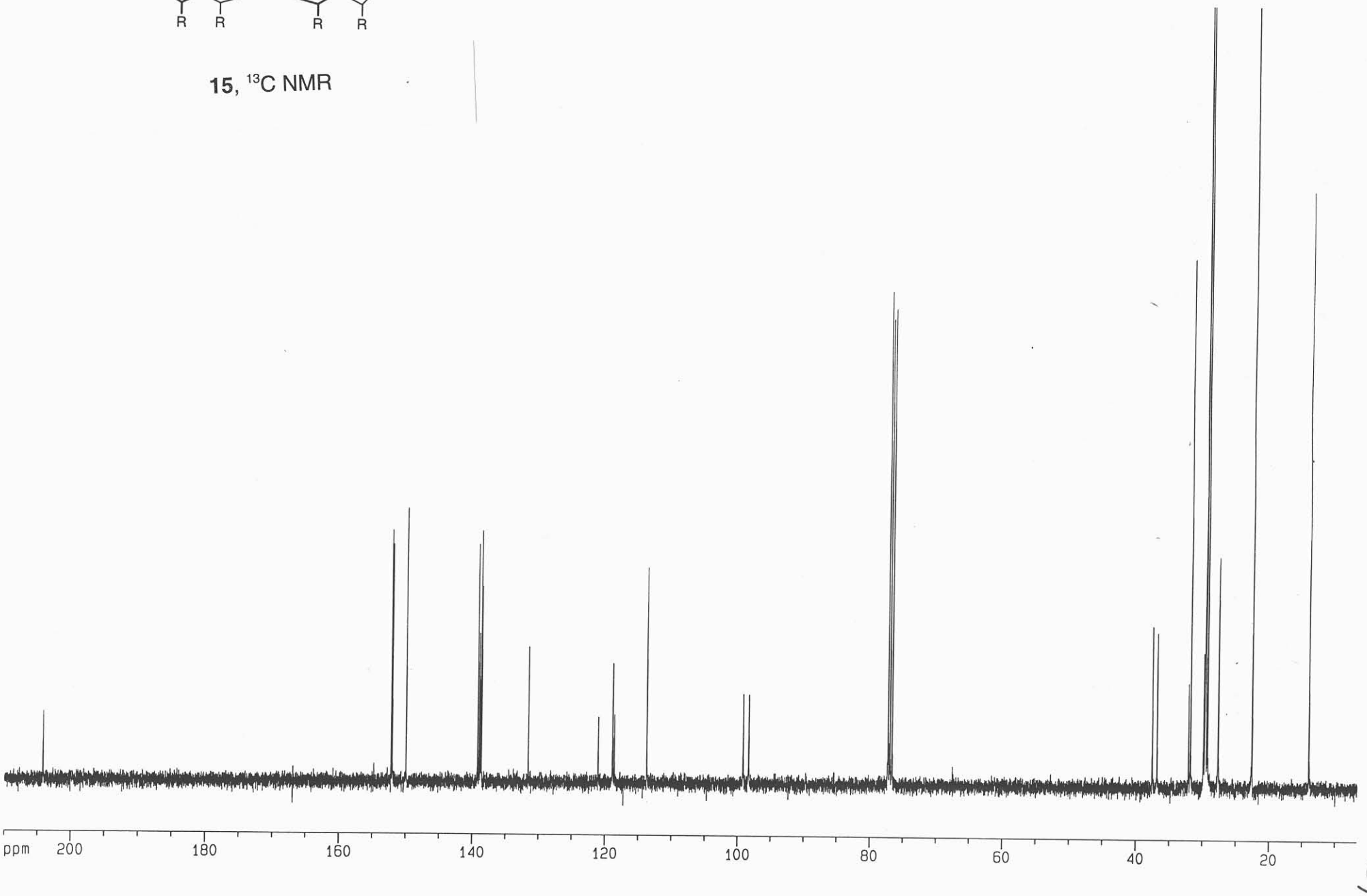
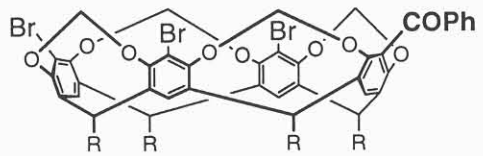
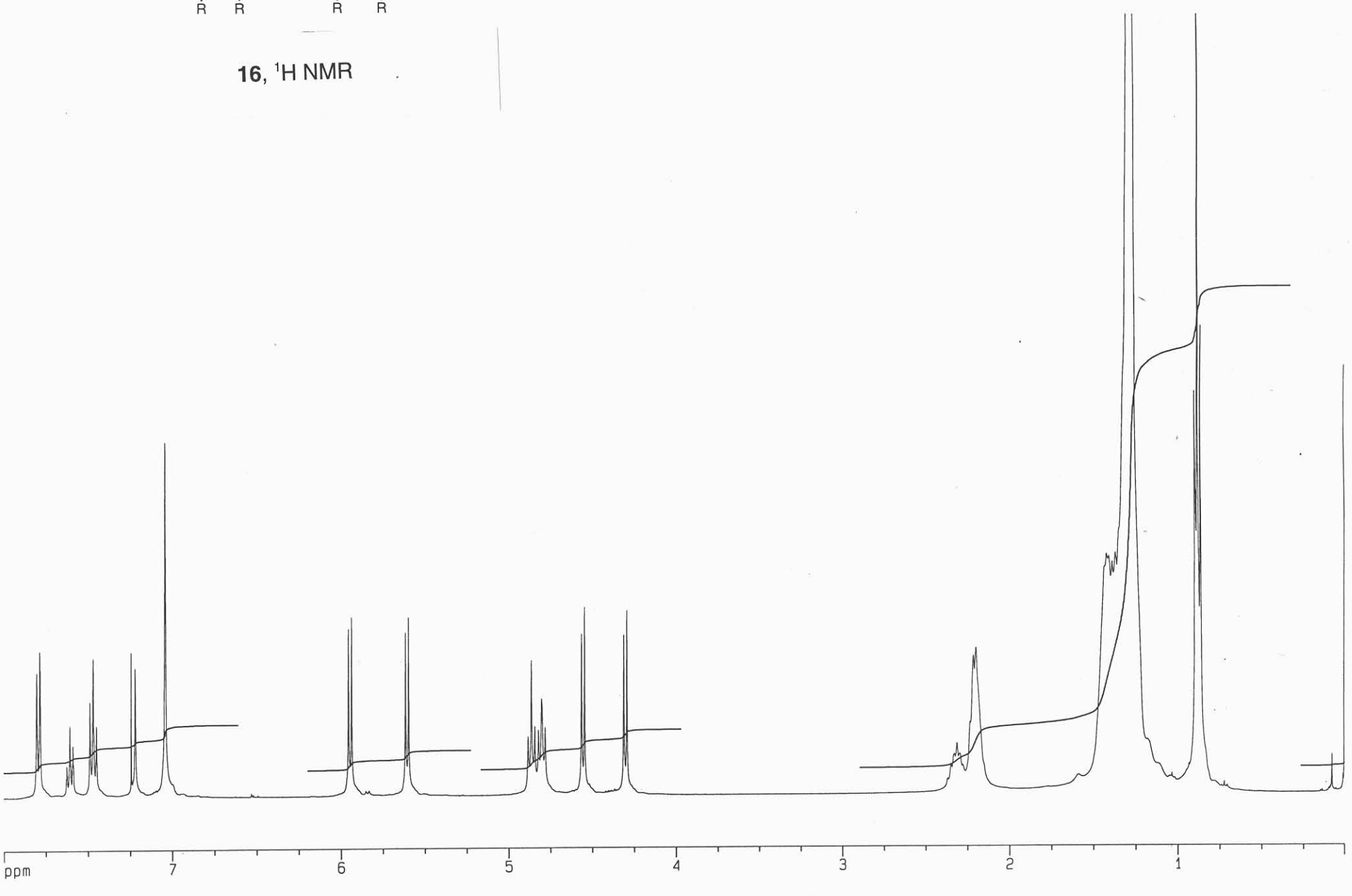
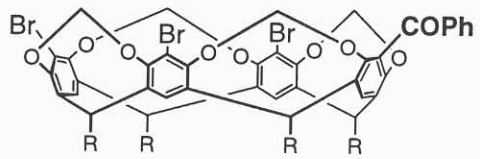


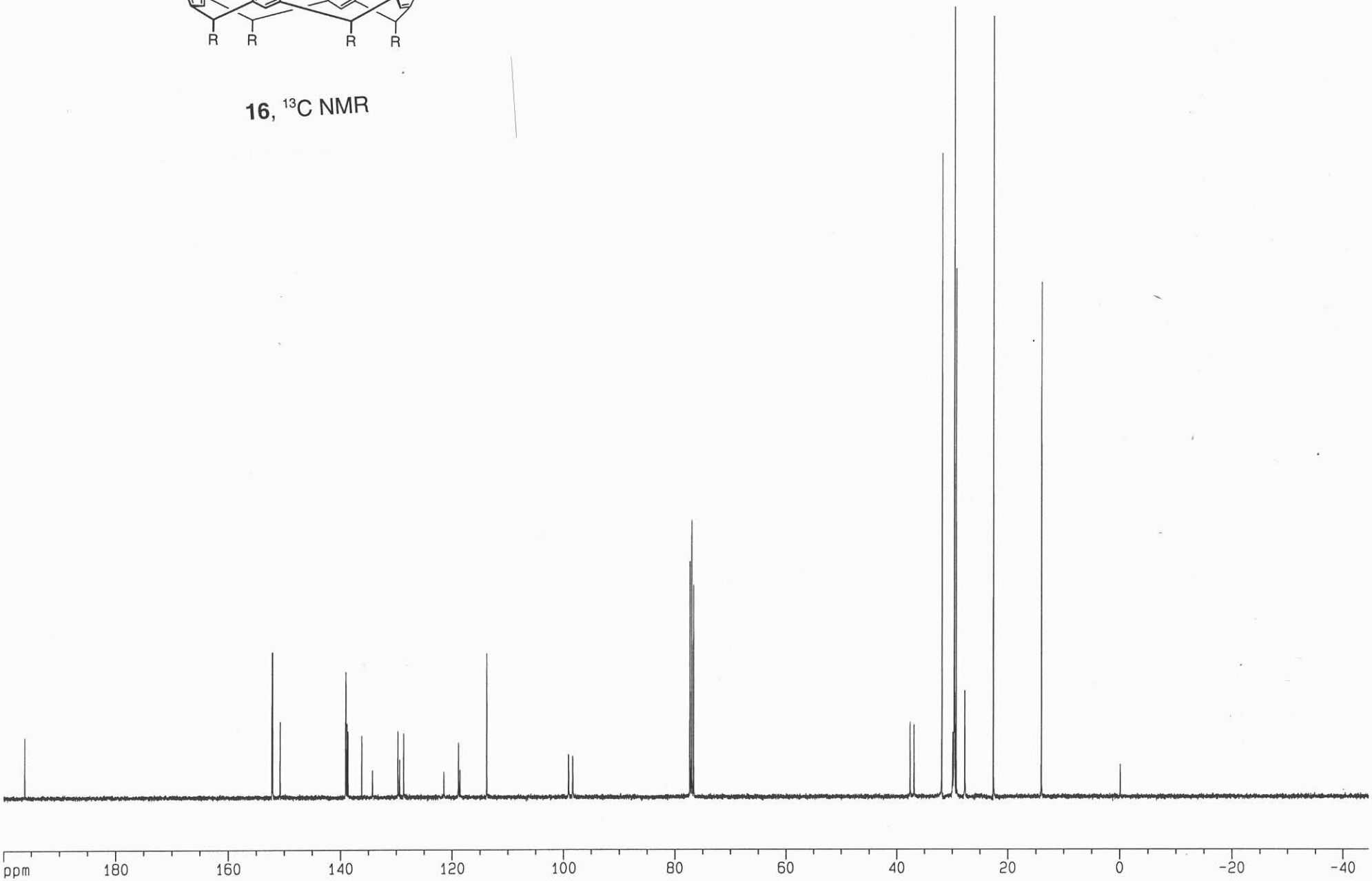


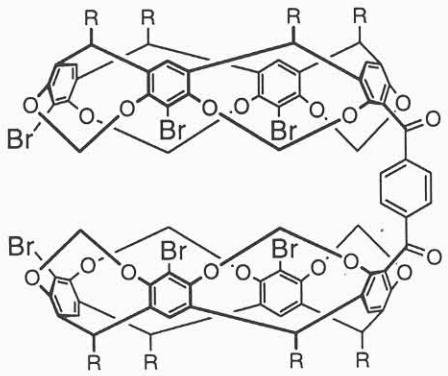
16, ^{1}H NMR



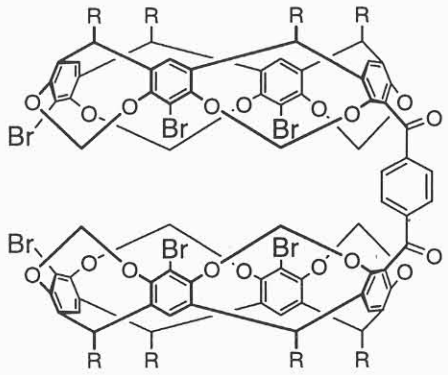


16, ^{13}C NMR

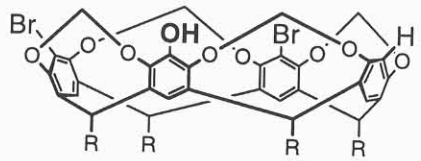




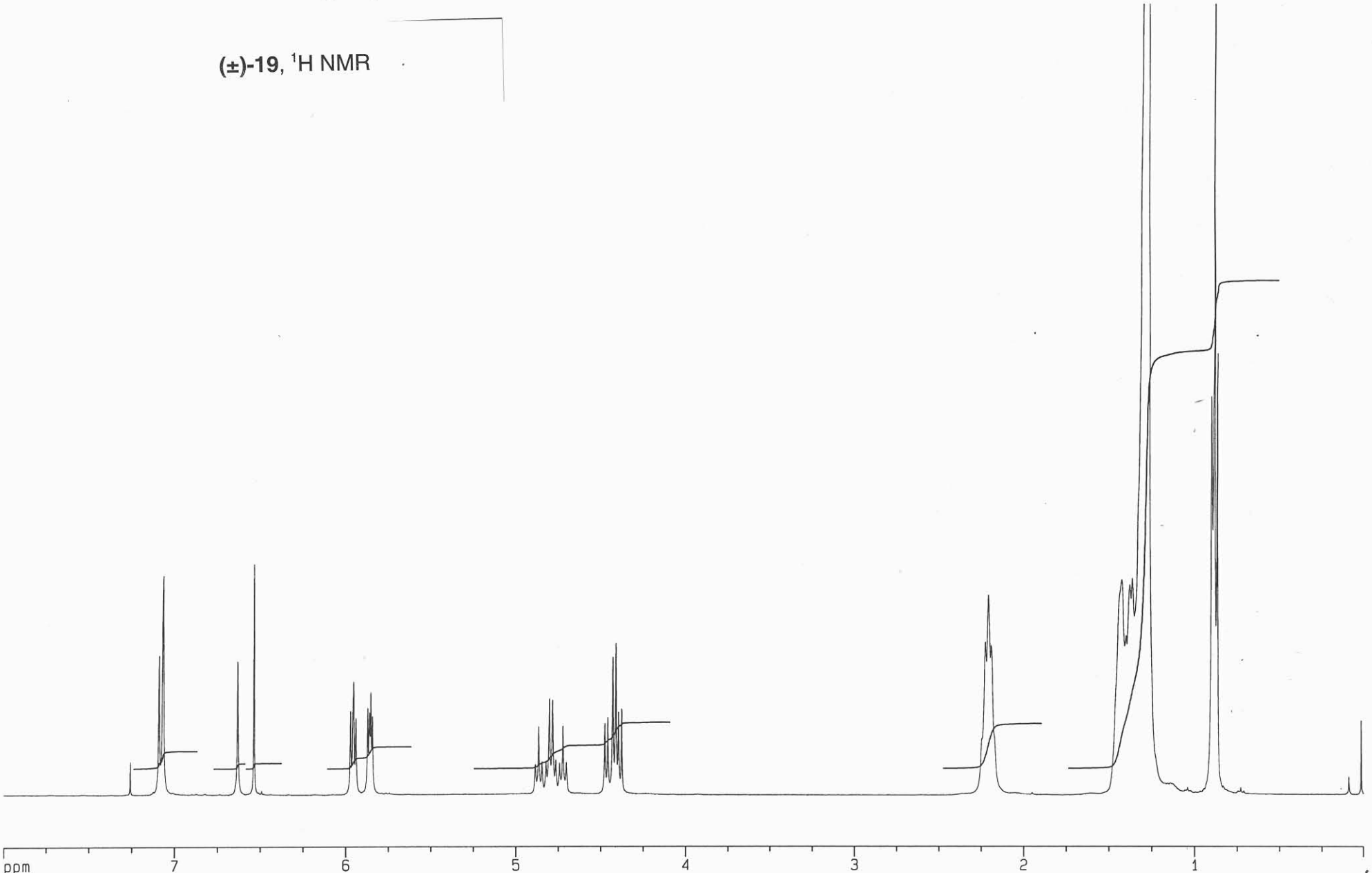
18, ^{1}H NMR

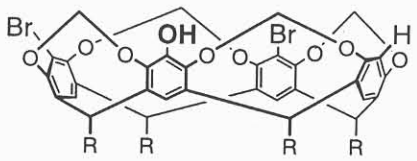


18, ^{13}C NMR

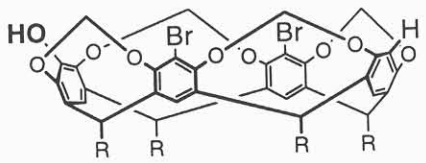


(±)-19, ^{1}H NMR

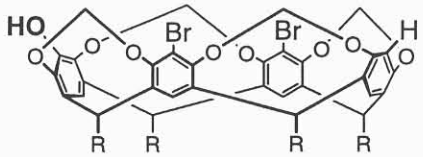




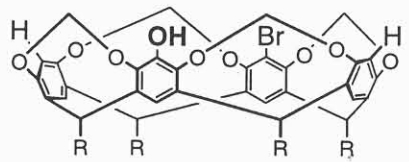
(±)-19, ^{13}C NMR



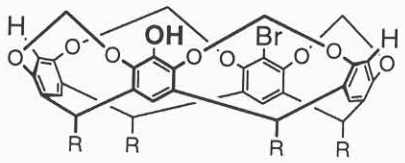
20, ^{1}H NMR



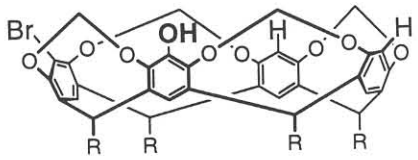
20, ^{13}C NMR



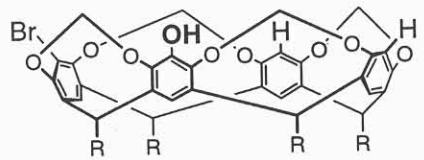
21, ^{1}H NMR



21, ^{13}C NMR



(±)-22, ^{1}H NMR



(±)-22, ^{13}C NMR