

# Supplementary Material

## Experimental Section

### General

The starting materials were purchased from Aldrich Chemical Company. Dimethylacetamide (DMA) was dried by stirring over BaO for 24 hours followed by distillation under reduced pressure. It was stored over molecular sieves (3A) and degassed prior to use. Other reagents were used as received. All reactions were run under a nitrogen atmosphere.

Flash chromatography (Silica gel 60 Å, 200–400 mesh; Natland International) was used for product purification. Unless otherwise noted, NMR spectra were recorded in CDCl<sub>3</sub>. MS analysis was performed with either MALDI or electron spray techniques. Elemental analysis was performed by Atlantic Microlab Inc. Melting points are uncorrected.

### Synthesis of *tris*-bridged DCC 5a

To an oven dried flask containing 15 mL of DMA was added 250 mg (0.276 mmol) of phenethyl octol **1**. To this solution was added 3 equiv (0.83 mmol, 338 mg) of 3,5 dibromobenzal bromide<sup>16</sup> and 6.6 equiv (1.82 mmol, 270 µL) of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU). The reaction mixture was warmed to 35 °C and stirred for 48 h. After this time the solvent was removed under reduced pressure, the crude product dissolved in a minimum of 3:7 acetone–CHCl<sub>3</sub>, and the resulting solution run through a silica plug. The solvent from the resulting solution was removed under reduced pressure. The crude product was then dissolved in 100% CHCl<sub>3</sub> and wet loaded onto a 100% hexane silica column. Chromatography with a (step-wise) graduated mobile phase (100% hexane to 50% hexane/CHCl<sub>3</sub> to 100% CHCl<sub>3</sub>) afforded the pure product as a brownish-yellow solid in 34%

yield: mp 195 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone) δ 2.71 (m, 16H), 4.57 (t, 1H, *J* = 6.8 Hz), 4.96 (t, 3H, *J* = 7.0 Hz), 5.48 (s, 1H), 5.59 (s, 2H), 6.67 (s, 2H), 7.07 (s, 2H), 7.23 (m, 20 H), 7.77 (s, 2H), 7.79 (t, 1H, *J* = 2.0 Hz), 7.82 (t, 2H, *J* = 2.0 Hz), 7.88 (s, 2H), 7.89 (m, 2H), 7.91 (m, 4H), 9.24 (s, 2H); MALDI MS *m/z* (M + Ag<sup>+</sup>)<sup>+</sup> 1748.95; Anal. Calcd. for C<sub>81</sub>H<sub>62</sub>O<sub>8</sub>Br<sub>6</sub>: C, 59.22; H, 3.80. Found: C, 58.93; H, 3.86.

### Synthesis of A/C *bis*-bridged DCC 4a

The synthetic procedure was identical to those used in the formation of DCC **5a**. Chromatography with a (step-wise) graduated mobile phase (100% hexane to 50% hexane/CHCl<sub>3</sub> to 100% CHCl<sub>3</sub> to 1% acetone/CHCl<sub>3</sub>) afforded the product as a brownish yellow solid in 3% yield: mp > 200 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone) δ 2.68 (m, 16H), 4.52 (t, 2H, *J* = 7.2 Hz), 4.84 (m, 2H), 5.62 (s, 2H), 6.57 (s, 4H), 7.16 (m, 20 H), 7.81 (s, 4H), 7.84 (t, 2H, *J* = 1.8 Hz), 7.92 (m, 4H), 8.97 (s, 4H); MALDI MS *m/z* (M + Ag<sup>+</sup>)<sup>+</sup> 1505.09; Anal. Calcd. for C<sub>74</sub>H<sub>60</sub>O<sub>8</sub>Br<sub>4</sub> + 2 H<sub>2</sub>O: C, 62.06; H, 4.50. Found: C, 61.93; H, 4.49.

### Synthesis of A/B *bis*-bridged DCC 3a

To an oven dried flask containing 15 mL of DMA was added 250 mg (0.276 mmol) of phenethyl octol **1**. To this solution was added 2 equiv (0.55 mmol, 225 mg) of 3,5-dibromobenzal bromide{1391} and 4.4 equiv (1.22 mmol, 182 μL) of DBU. The resulting mixture was stirred at rt for 48 h. The solvent was removed under reduced pressure and the crude product was dissolved in the minimum of 3:7 acetone–CHCl<sub>3</sub> and the resulting solution run through a silica plug. The solvent from the resulting solution was removed under reduced pressure. The crude product was then dissolved in 100% CHCl<sub>3</sub> and wet loaded onto a 100% hexane silica column. Chromatography with a (step-wise) graduated mobile phase (100% hexane to 50% hexane/CHCl<sub>3</sub> to 100% CHCl<sub>3</sub> to 1% acetone/CHCl<sub>3</sub> to 10% acetone/CHCl<sub>3</sub>) afforded the product as a brownish yellow solid in 13% yield: mp 195 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone) δ 2.64 (m, 16H), 4.47 (t, 2H, *J* = 7.0 Hz), 4.92 (m, 2H), 5.56 (s, 2H), 6.49

(s, 2H), 6.54 (s, 1H), 7.05 (s, 1H), 7.21 (m, 20H), 7.59 (s, 1H), 7.79 (s, 2H), 7.82 (t, 2H,  $J = 1.8$  Hz), 7.86 (s, 1H), 7.91 (m, 4H), 8.58 (s, 2H), 9.06 (s, 2H); MALDI MS  $m/z$  ( $M + Ag^+$ )<sup>+</sup> 1505.12; Anal. Calcd. for  $C_{74}H_{60}O_8Br_4 + 2 H_2O$ : C, 62.06; H, 4.50. Found: C, 61.76; H, 4.32.

### Synthesis of *mono*-bridged DCC 2a

The synthetic procedure was identical to those used in the formation of DCC 3a. Chromatography with a (step-wise) graduated mobile phase (100% hexane to 50% hexane/ $CHCl_3$  to 100%  $CHCl_3$  to 1% acetone/ $CHCl_3$  to 10% acetone/ $CHCl_3$  to 30% acetone/ $CHCl_3$ ) afforded the product as a brownish yellow solid in 13% yield: mp 182 °C;  $^1H$  NMR (400 MHz,  $d_6$ -Acetone)  $\delta$  2.62 (m, 16H), 4.43 (m, 3H), 4.83 (m, 1H), 5.57 (s, 1H), 6.39 (s, 2H), 6.46 (s, 2H), 7.19 (m, 20H), 7.71 (s, 2H), 7.84 (m, 3H), 7.90 (m, 2H), 8.68 (s, 2H), 8.77 (s, 2H), 8.85 (s, 2H); MALDI MS  $m/z$  ( $M + Ag^+$ )<sup>+</sup> 1258.9; Anal. Calcd. for  $C_{67}H_{58}O_8Br_2 + 3 H_2O$ : C, 66.90; H, 5.36. Found: C, 67.24; H, 5.06.

### Synthesis of *tris*-bridged DCC 5b

To an oven dried flask containing 15 mL of DMA, was added 250 mg (0.276 mmol) of phenethyl octol 1. To this solution was added 3.0 equiv (0.83 mmol, 273 mg) of 4-bromobenzal bromide<sup>16</sup> and 6.0 equiv (1.66 mmol, 248  $\mu$ L) of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU). The reaction mixture was warmed to 47 °C and stirred for 24 h. After this time the solvent was removed under reduced pressure, the crude product dissolved in a minimum of  $CHCl_3$ , and the resulting solution run through a silica plug. The solvent from the resulting solution was removed under reduced pressure. The crude product was then dissolved in 40%  $CHCl_3$  in hexane and wet loaded onto a silica column. Chromatography with a (step-wise) graduated mobile phase (40% chloroform in hexane to 100% chloroform) afforded the pure product as a buff solid in 35% yield: mp 215-217 °C;  $^1H$  NMR (400 MHz)  $\delta$  2.67 (m, 16H), 4.43 (t, 1H,  $J = 7.8$  Hz), 4.99 (m, 3H), 5.38 (s, 1H), 5.46 (s, 2H), 6.53 (s, 2H), 6.67 (s, 2H), 6.93 (s, 2H), 7.19 (m, 22 H), 7.33 (s, 2H), 7.60 (m, 12H); MALDI MS  $m/z$  ( $M + Ag^+$ )<sup>+</sup> 1513.07; Anal. Calcd. for  $C_{81}H_{65}O_8Br_3$ : C, 69.19; H, 4.66. Found: C, 68.91; H, 4.63.

## Synthesis of 2-Bromo-6-(dibromomethyl) pyridine (**7**)

In a round bottomed flask containing 9 mL of dry dichloromethane was added 1.56 mL (7.80 mmol) of  $\text{P(OPh)}_3$ . The temperature of this solution was reduced to 0 °C before 6 mL of a freshly made 1.35 M  $\text{Br}_2$  solution in dichloromethane (7.80 mmol) was added. The temperature of the  $\text{P(PhO)}_3\text{Br}_2$  solution was then reduced to -10 °C and a solution of 2-bromo-6-pyridinecarboxaldehyde{1467} (500 mg, 2.68 mmol in 5 mL) was added drop-wise. After 30 minutes 6 g of silica was added and the solvent of the reaction removed under reduced pressure. Dry loading (*Caution irritant*), column chromatography with 5% ethyl acetate in hexane and removal of the solvent under reduce pressure gave the desired tribromide in 50% yield as a colorless solid: mp 133–134 °C;  $^1\text{H}$  NMR (400MHz)  $\delta$  6.59 (s, 1H), 7.46 (d, 1H,  $J = 7.8$  Hz), 7.67 (t, 1H,  $J = 7.8$  Hz), 7.83 (d, 1H,  $J = 7.8$  Hz); ES MS  $m/z$  ( $\text{M} + \text{H}^+$ ) $^+$  329.7; Anal. Calcd. for  $\text{C}_6\text{H}_4\text{Br}_3\text{N}$ : C, 21.85; H, 1.22. Found: C, 22.08; H, 1.16.

## Synthesis of DCCs **9** and **10**.

To an oven dried flask containing 2 mL of DMA, was added 100 mg ( $7.12 \times 10^{-5}$  mol) of *tris*-bridged DCC **5b**. To this solution was added 2.0 equiv ( $1.42 \times 10^{-4}$  mol, 47 mg) of 2-Bromo-6-(dibromomethyl) pyridine **7** and 2.0 equiv ( $1.42 \times 10^{-4}$  mol, 21.2  $\mu\text{L}$ ) of DBU. The reaction mixture was warmed to 60 °C and stirred for 36 h. After this time the solvent was removed under reduced pressure. The crude product was then dissolved in 40%  $\text{CHCl}_3$  in hexane and wet loaded onto a silica column. Column chromatography (mobile phase 40% chloroform in hexane) afforded first the desired  $\text{C}_{\text{v4}}$  DCC **9**, followed by the  $\text{C}_s$  symmetry miss-bridged DCC **10**, as colorless solids in 54 and 16% yield respectively.

**DCC 9**: mp >250 °C;  $^1\text{H}$  NMR (400 MHz)  $\delta$  2.70 (m, 16H), 4.99 (t, 1H,  $J = 8.0$  Hz), 5.05 (t, 3H,  $J = 8.0$  Hz), 5.32 (s, 1H), 5.45 (s, 2H), 5.49 (s, 1H), 6.71 (s, 4H), 7.23 (m, 20H), 7.30 (s, 4H), 7.57 (m, 13H), 7.65 (t, 1H,  $J = 7.8$  Hz), 7.78 (d, 1H,  $J = 7.8$  Hz); MALDI MS  $m/z$  ( $\text{M} + \text{Ag}^+$ ) $^+$  1682.28; Anal. Calcd. for  $\text{C}_{87}\text{H}_{67}\text{Br}_4\text{NO}_8$ : C, 66.38; H, 4.29. Found: C, 66.24; H, 4.27.

**DCC 10:** mp >250 °C; <sup>1</sup>H NMR (500 MHz) δ 2.70 (m, 16H), 4.94 (m, 3H), 5.06 (t, 1H, *J* = 7.5 Hz), 5.09 (s, 2H), 5.38 (s, 1H), 5.81 (s, 2H), 6.63 (s, 1H), 6.69 (s, 2H), 6.81 (d, 1H, *J* = 8.0 Hz), 7.29 (m, 30H), 7.51 (d, 4H, *J* = 8.5 Hz), 7.62 (m, 4H); MALDI MS *m/z* (*M* + Ag<sup>+</sup>)<sup>+</sup> 1681.94; Anal. Calcd. for C<sub>87</sub>H<sub>67</sub>Br<sub>4</sub>NO<sub>8</sub>: C, 66.38; H, 4.29. Found: C, 66.17; H, 4.32.

### Synthesis of 2-Bromo-5-(dibromomethyl) pyridine (8)

To a round bottomed flask containing 50 mL of benzene was added 1.60 g (9.30 mmol) of 2-bromo-5-methylpyridine, 2.2 equiv of NBS (20.5 mmol, 3.64 g) and 0.2 equiv of benzoyl peroxide (0.186 mmol, 450 mg). The reaction mixture was heated to 60 °C for 24 h. After this time the solvent was removed under reduced pressure, the crude product taken up in a minimum amount of 1:1 chloroform hexane, and run through a short plug of silica. The solvent of the resulting solution was removed under reduced pressure. Column chromatography (gravity column with mobile phase 2:1 hexane chloroform) separated the desired dibromomethyl pyridine (from the bromomethyl and tribromomethyl side products) as a colorless solid in 41% yield: mp 88-90 °C; <sup>1</sup>H NMR (400 MHz) δ 6.61 (s, 1H), 7.56 (d, 1H, *J* = 8.7 Hz), 7.88 (dd, 1H, *J* = 8.1 and 2.9 Hz), 8.47 (d, 1H, *J* = 2.7 Hz); ES MS *m/z* (*M* + H<sup>+</sup>)<sup>+</sup> 329.7; Anal. Calcd. for C<sub>6</sub>H<sub>4</sub>Br<sub>3</sub>N: C, 21.85; H, 1.22. Found: C, 22.10; H, 1.19.

### Synthesis of DCC 11

Following the procedure for the formation of DCC **9** (see above) column chromatography (mobile phase 30% chloroform in hexane) afforded DCC **11** as a colorless solid in 64% yield: mp >250 °C; <sup>1</sup>H NMR (400 MHz) δ 2.70 (m, 16H) 5.00 (t, 1H, *J* = 7.6 Hz), 5.05 (t, 3H, *J* = 8.0 Hz), 5.41 (s, 1H), 5.43 (s, 2H), 5.50 (s, 1H), 6.68 (s, 4H), 7.25 (m, 24H), 7.59 (m, 13H), 7.89 (dd, 1H, *J* = 7.8 and 2.7 Hz), 8.65 (d, 1H, *J* = 2.7 Hz); MALDI MS *m/z* (*M* + Ag<sup>+</sup>)<sup>+</sup> 1681.68; Anal. Calcd. for C<sub>87</sub>H<sub>67</sub>Br<sub>4</sub>NO<sub>8</sub>: C, 66.38; H, 4.29. Found: C, 65.99; H, 4.25.

### Synthesis of DCC **6b** from *tris*-bridged DCC **5b**

Following the procedure for the formation of DCC **9** (see above) column chromatography (mobile phase 30% chloroform in hexane) afforded known DCC **6b**{1391} in an 84% yield.

### Synthesis of A/C *bis*-bridged DCC **4b**

To an oven dried flask containing 15 mL of DMA was added 250 mg (0.276 mmol) of phenethyl octol **1**. To this solution was added 2 equiv (0.553 mmol, 181.8 mg) of *p*-bromo benzal bromide and 4.4 equiv (1.22 mmol, 182  $\mu$ L) of DBU. The reaction was stirred at 25 °C for 48 h. After this time the solvent was removed under reduced pressure, the crude product was dissolved in a minimum of 3:7 acetone  $\text{CHCl}_3$ , and the resulting solution run through a silica plug. The solvent from the resulting solution was then removed under reduced pressure. The crude product was then dissolved in 100%  $\text{CHCl}_3$  and wet loaded onto a 100% hexane silica column. Chromatography with a graduated mobile phase (100% hexane to 50% hexane/ $\text{CHCl}_3$  to 100%  $\text{CHCl}_3$  to 1% acetone/99%) afforded a light brown/orange solid in 2% yield: mp 180 °C;  $^1\text{H}$  NMR (400 MHz,  $d_6$ -Acetone)  $\delta$  2.67 (m, 16H), 4.52 (t, 2H,  $J$  = 7.0 Hz), 4.87 (t, 2H,  $J$  = 3.6 Hz), 5.57 (s, 2H), 6.55 (s, 4H), 7.21 (m, 20H), 7.67 (d, 4 H,  $J$  = 8.6 Hz), 7.72 (d, 4 H,  $J$  = 8.6 Hz), 7.81 (s, 4H); 8.94 (s, 4H); MALDI MS  $m/z$  ( $\text{M} + \text{Ag}^+$ )<sup>+</sup> 1347.47; Anal. Calcd. for  $\text{C}_{74}\text{H}_{62}\text{O}_8\text{Br}_2 + 2 \text{H}_2\text{O}$ : C, 69.70; H, 5.22. Found: C, 69.53; H, 5.18.

### Synthesis of A/B *bis*-bridged DCC **3b**

The synthetic procedure was identical to those used in the formation of DCC **4b**. Chromatography with a graduated mobile phase (100% hexane to 50% hexane/ $\text{CHCl}_3$  to 100%  $\text{CHCl}_3$  to 1% acetone/99%  $\text{CHCl}_3$  to 10% acetone/90%  $\text{CHCl}_3$ ) afforded a light brown/orange solid in 14% yield: mp > 200 °C;  $^1\text{H}$  NMR (400 MHz,  $d_6$ -Acetone)  $\delta$  2.61 (m, 16H), 4.46 (t, 2H,  $J$  = 7.2 Hz), 4.94 (t, 2H,  $J$  = 5.4 Hz), 5.50 (s, 2H), 6.45 (s, 2H), 6.54 (s, 1H), 6.87 (s, 1H), 7.22 (m, 20H), 7.60 (s, 1H), 7.65 (d, 4 H,  $J$  = 8.2 Hz), 7.70 (d, 4 H,  $J$  = 8.2 Hz), 7.79 (s, 2H), 7.86 (s, 1H), 8.56 (s, 2H),

9.08 (s, 2H); MALDI MS  $m/z$  ( $M + Ag^+$ )<sup>+</sup> 1347.30; Anal. Calcd. for  $C_{74}H_{62}O_8Br_2 + H_2O$ : C, 70.70; H, 5.13. Found: C, 71.01; H, 5.28

### Synthesis of *mono*-bridged DCC **2b**

The synthetic procedure was identical to those used in the formation of DCC **4b**. Chromatography with a graduated mobile phase (100% hexane to 50% hexane/ $CHCl_3$  to 100%  $CHCl_3$  to 1% acetone/99%  $CHCl_3$  to 10% acetone/90%  $CHCl_3$  to 30% acetone/70%  $CHCl_3$ ) afforded a light brown/orange solid in 11% yield: mp 190 °C;  $^1H$  NMR (400 MHz,  $d_6$ -Acetone)  $\delta$  2.65 (m, 16H), 4.42 (m, 3H), 4.86 (t, 1H,  $J = 3.4$  Hz), 5.53 (s, 1H), 6.39 (s, 2H), 6.45 (s, 2H), 7.20 (m, 20H), 7.70 (m, 4H), 7.83 (s, 4H), 8.62 (s, 2H), 8.75 (s, 2H), 8.85 (s, 2H); MALDI MS  $m/z$  ( $M + Ag^+$ )<sup>+</sup> 1179.24; Anal. Calcd. for  $C_{67}H_{59}O_8Br + 2.5 H_2O$ : C, 72.0; H, 5.77. Found: C, 72.14; H, 5.64.

### Synthesis of DCC **6b** from tetrol **3b**

To an oven dried flask containing 10 mL of DMA was added 50 mg ( $4.04 \times 10^{-5}$  mol) of **3b**. To this solution was added 4.0 equiv (0.161 mmol, 106 mg) of 4-bromobenzal bromide and 4.4 equiv (0.177 mmol, 26.5  $\mu$ L) of DBU. The reaction was stirred for 30 h at 60 °C. After this period the solvent was removed under reduced pressure, the crude product dissolved in a minimum of 3:7 acetone- $CHCl_3$ , and the solution run through a silica plug. The solvent of the resulting solution was then removed under reduced pressure. The product was then dissolved in 100%  $CHCl_3$  and wet loaded onto a 100% hexane silica column. Chromatography with a graduated mobile phase (100% hexane to 50% hexane/ $CHCl_3$ ) afforded the known DCC **6b** in 61% yield.

### Synthesis of DCC **6b** from tetrol **4b**

The synthetic procedure was identical to those used in the conversion of tetrol **3b** to DCC **6b**. Chromatography afforded the known DCC{1391} as colorless solid in 62% yield.

### Synthesis of DCC **12** from tetrol **3b**

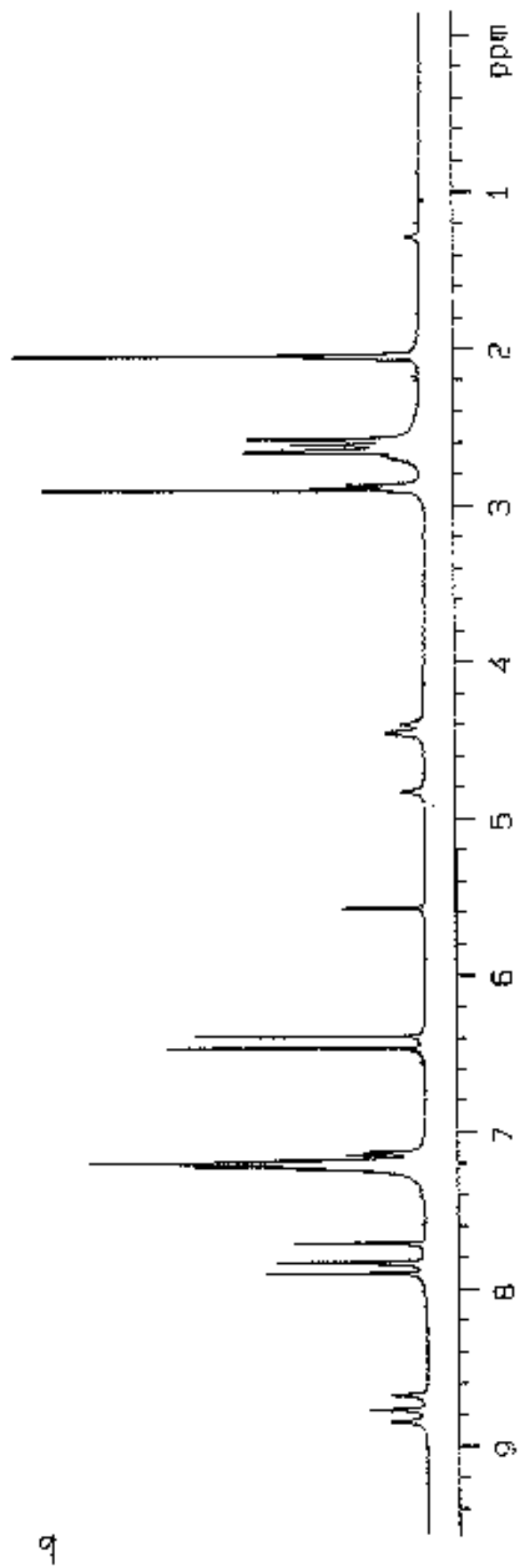
The synthetic procedure was identical to those used in the conversion of tetrol **3b** to DCC **6b**. The crude product was then dissolved in 100% CHCl<sub>3</sub> and wet loaded onto a 100% hexane silica column. Chromatography with a graduated mobile phase (100% hexane to 50% hexane/CHCl<sub>3</sub>) afforded DCC **12** as a colorless solid in 65% yield: mp > 200 °C; <sup>1</sup>H NMR (400 MHz) δ 2.69 (m, 16H), 5.04 (t, 4H, *J* = 7.8 Hz), 5.46 (s, 4H), 6.71 (m, 4H), 7.26 (m, 24H), 7.30 (s, 4H), 7.35 (m, 2H), 7.59 (m, 8H), 7.87 (s, 2H); MALDI MS *m/z* (M + Ag<sup>+</sup>)<sup>+</sup> 1680.33; Anal. Calcd. for C<sub>88</sub>H<sub>68</sub>O<sub>8</sub>Br<sub>4</sub>: C, 67.19; H, 4.36. Found: C, 67.02; H, 4.34.

### Synthesis of DCC **13** from tetrol **4b**

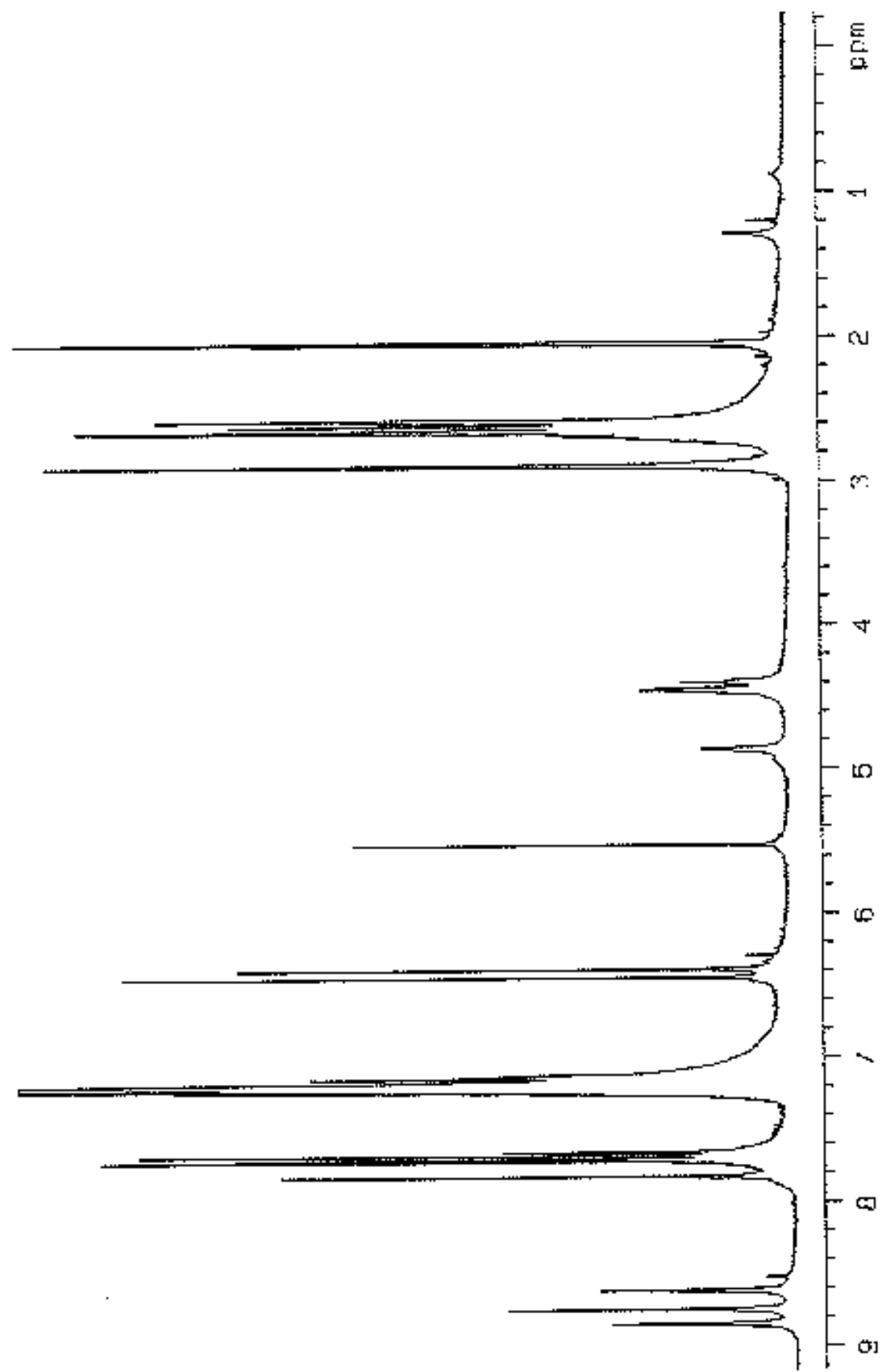
The synthetic procedure was identical to those used in the conversion of tetrol **3b** to DCC **6b**. The crude product was then dissolved in 100% CHCl<sub>3</sub> and wet loaded onto a 100% hexane silica column. Chromatography with a graduate mobile phase (100% hexane to 50% hexane/CHCl<sub>3</sub>) afforded DCC **13** as a colorless solid in 59% yield: mp >200 °C; <sup>1</sup>H NMR (400 MHz) δ 2.67 (m, 16H), 5.04 (t, 4H, *J* = 7.6 Hz), 5.45 (s, 4H), 6.70 (m, 4H), 7.26 (m, 24H), 7.29 (s, 4H), 7.34 (m, 2H), 7.59 (m, 8H), 7.86 (m, 2H, *J* = 1.8 Hz); MALDI MS *m/z* (M + Ag<sup>+</sup>)<sup>+</sup> 1680.83; Anal. Calcd. for C<sub>88</sub>H<sub>68</sub>O<sub>8</sub>Br<sub>4</sub> + H<sub>2</sub>O: C, 66.43; H, 4.43. Found: C, 66.56; H, 4.30.



2a

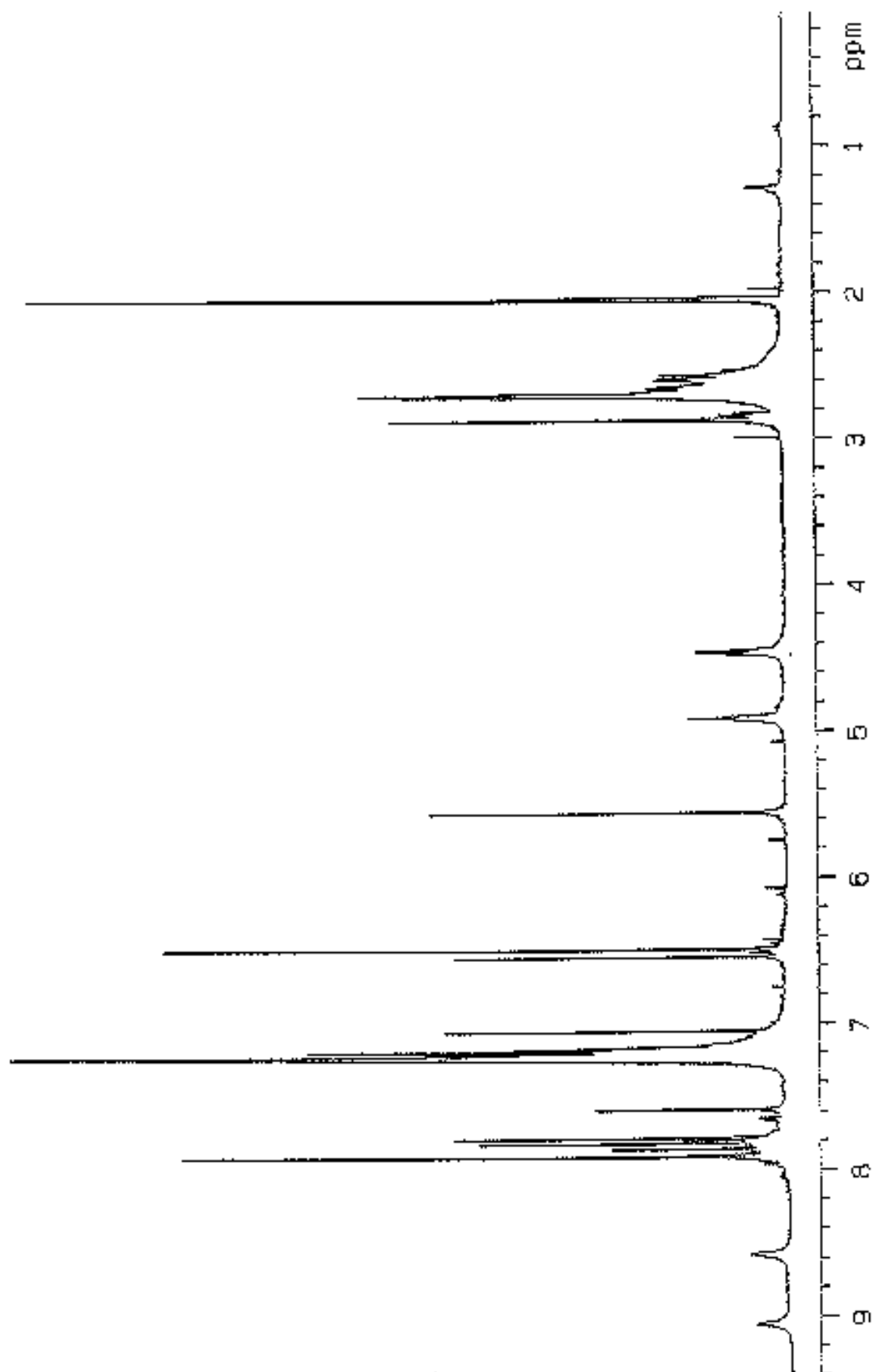


2b



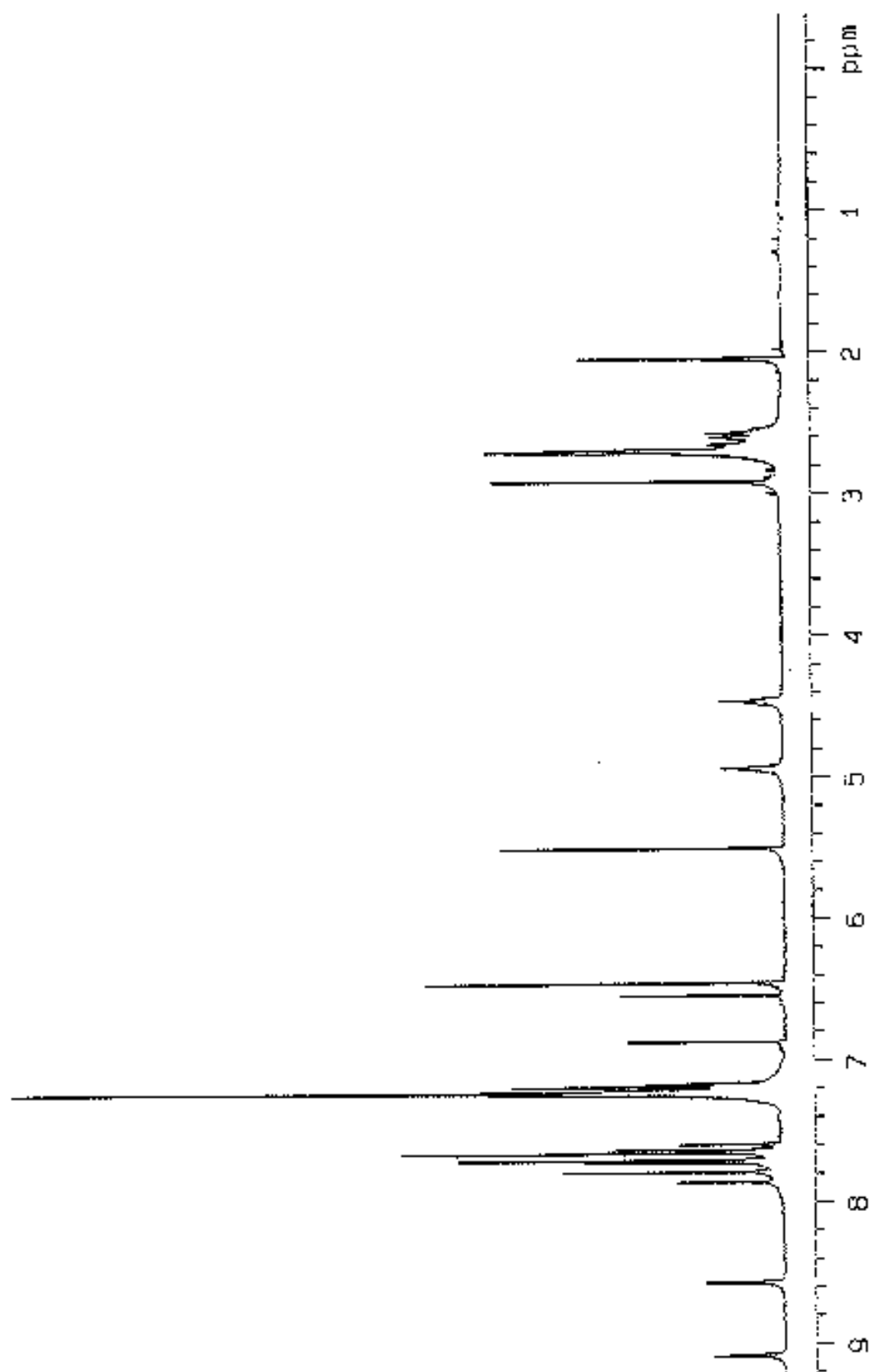
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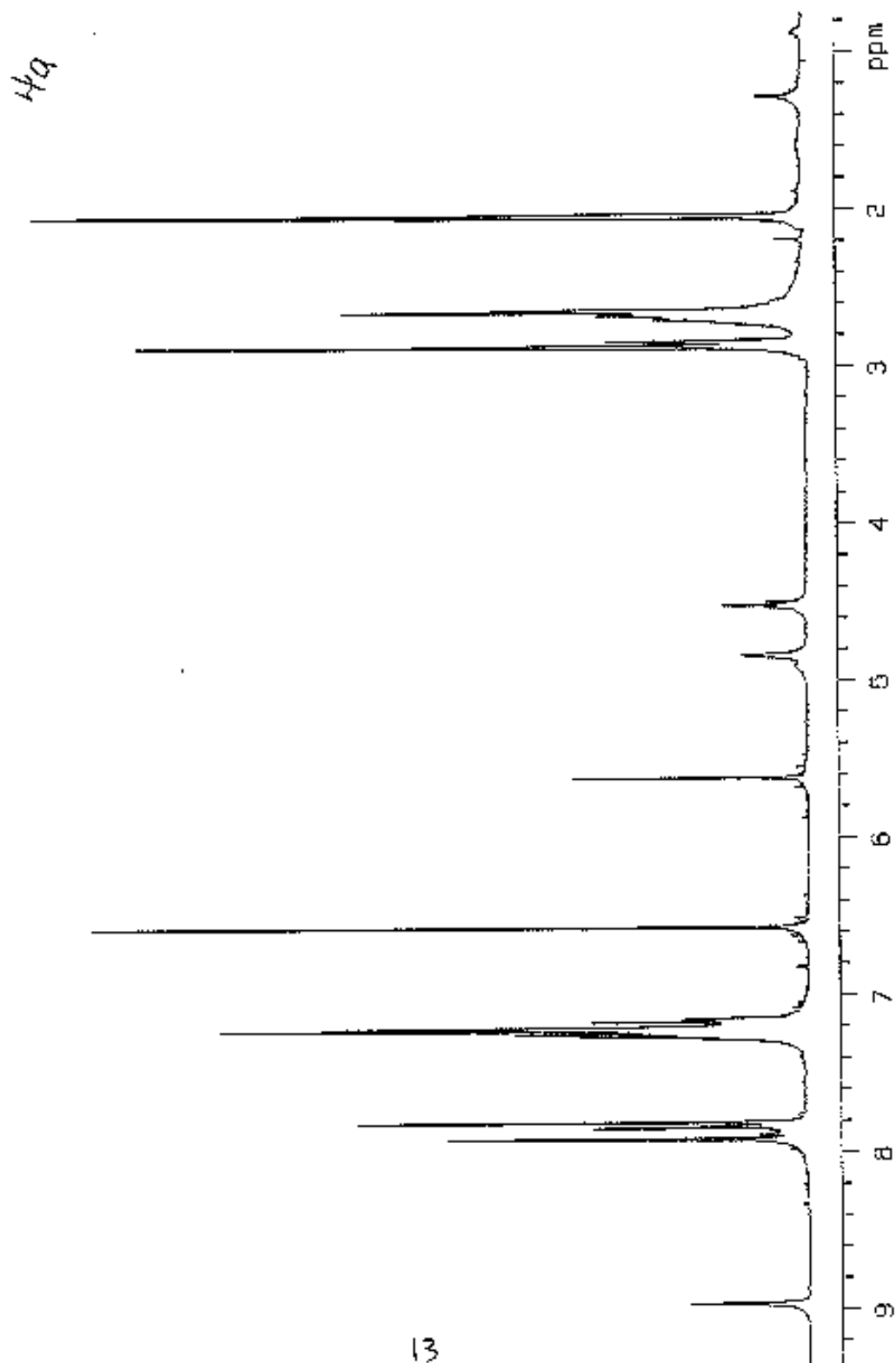
3a

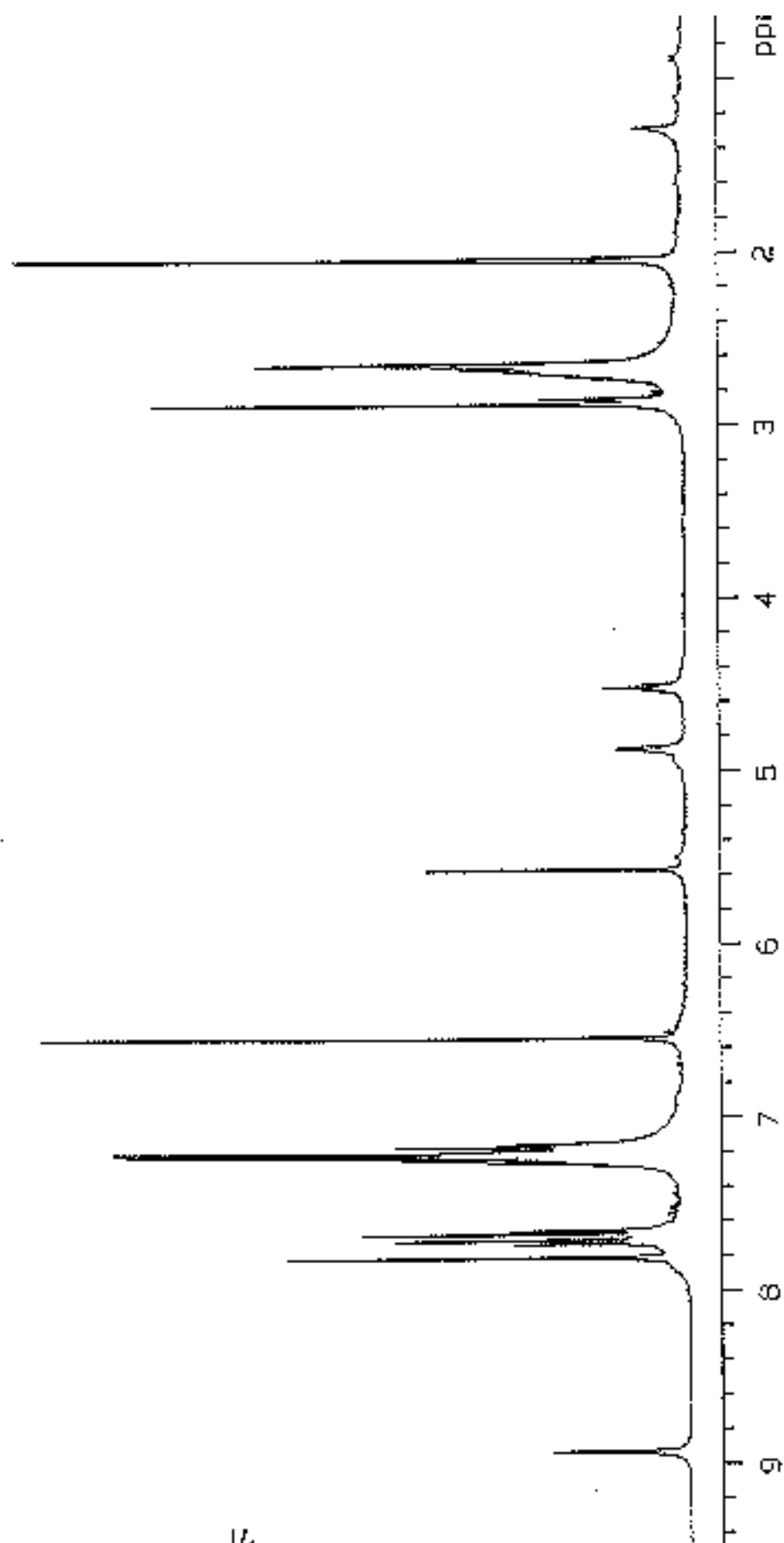


11

9b

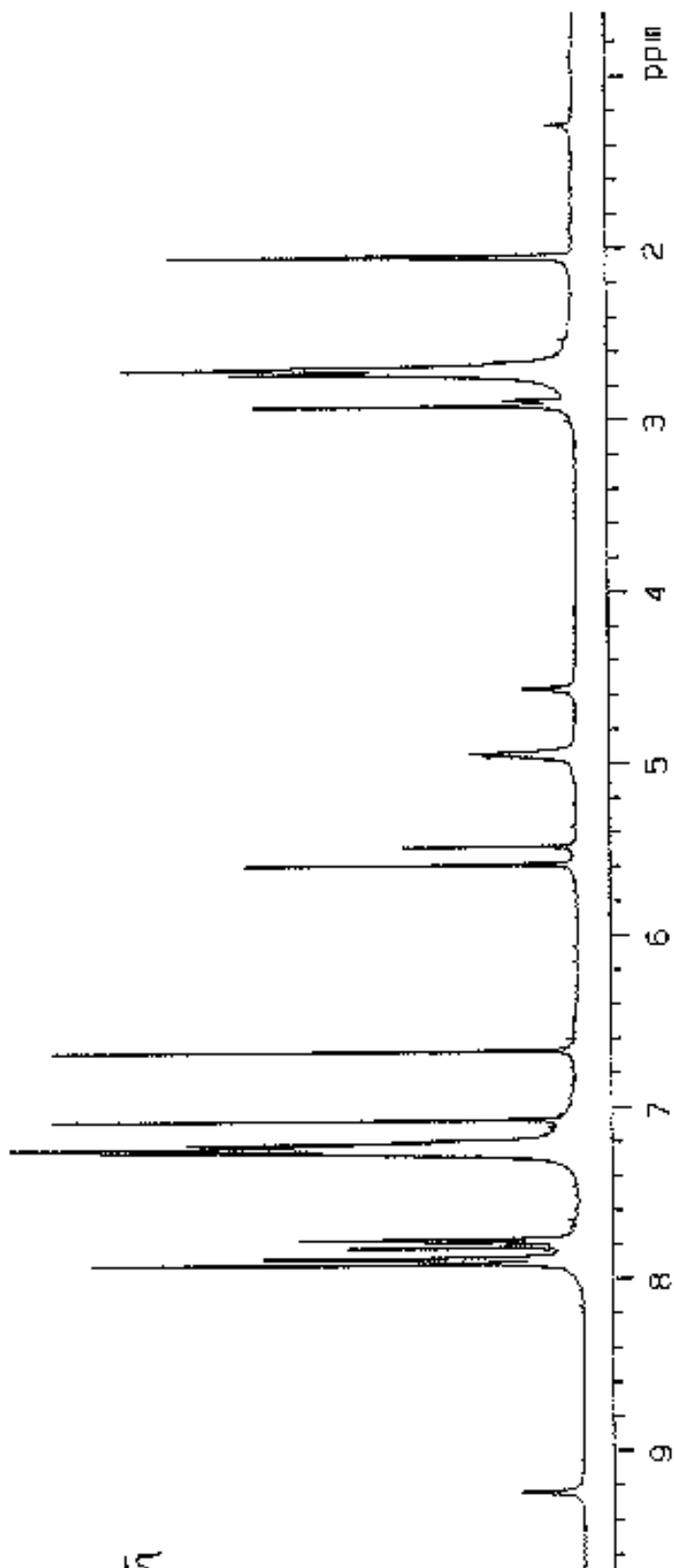




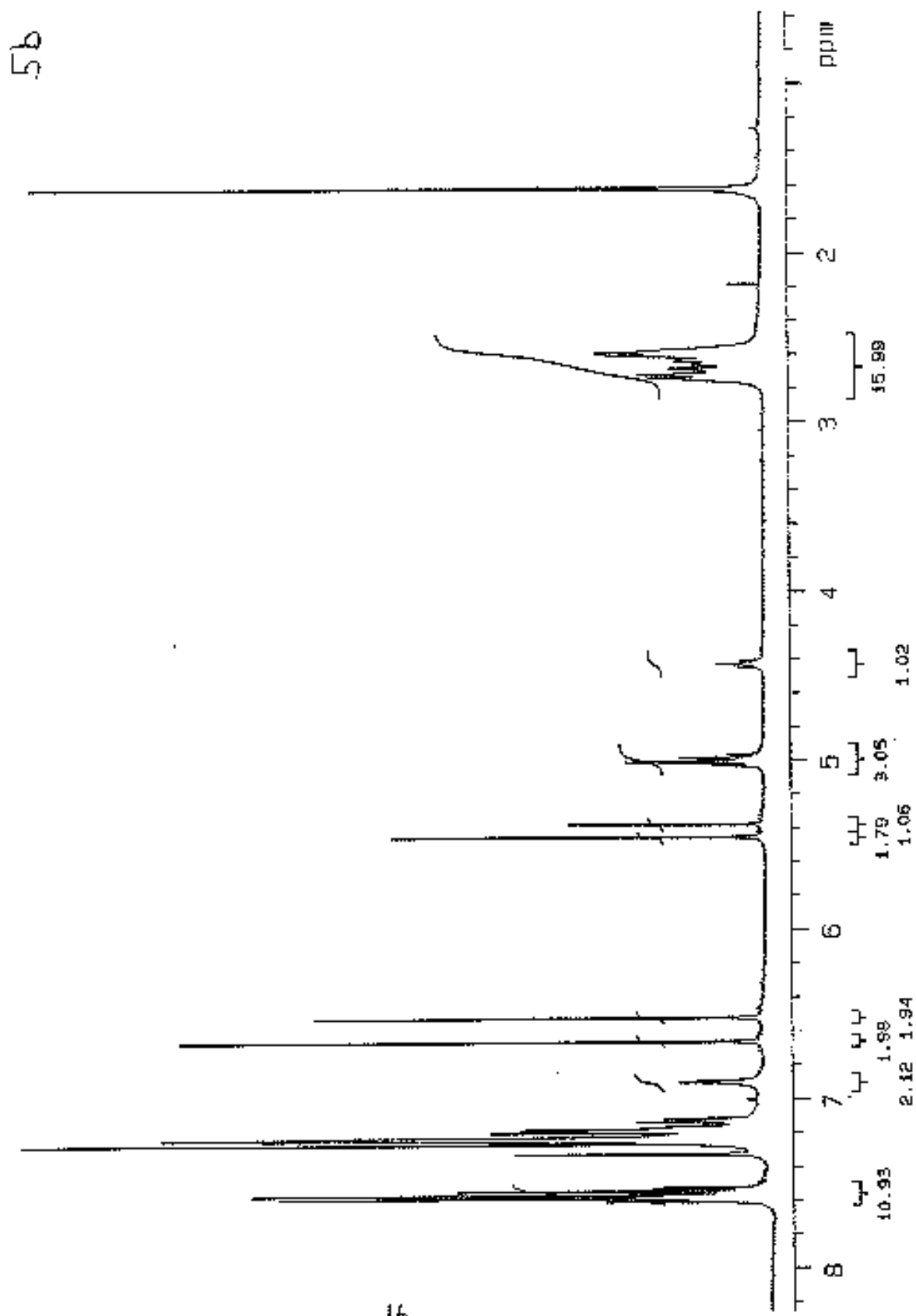


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5a



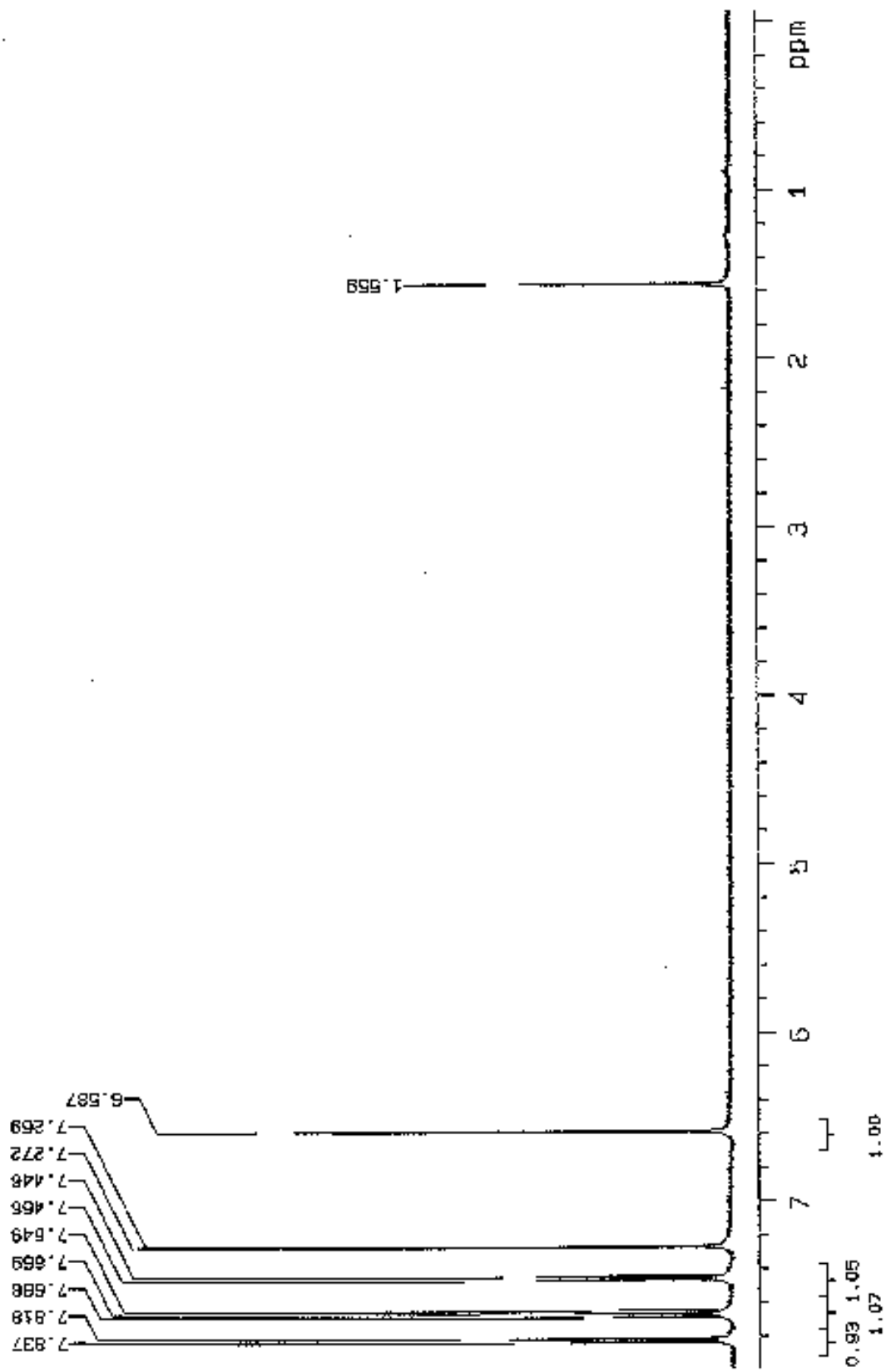
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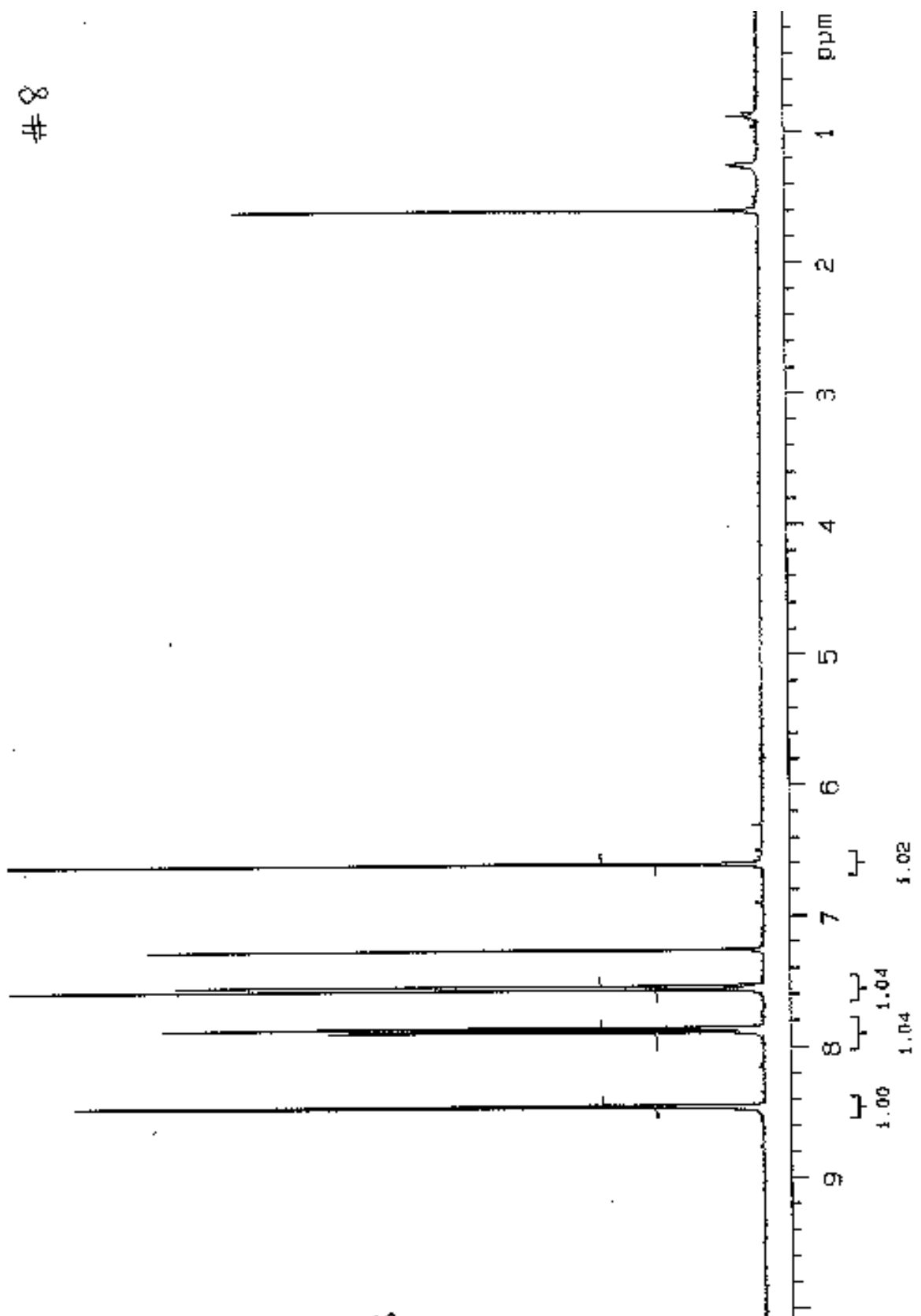


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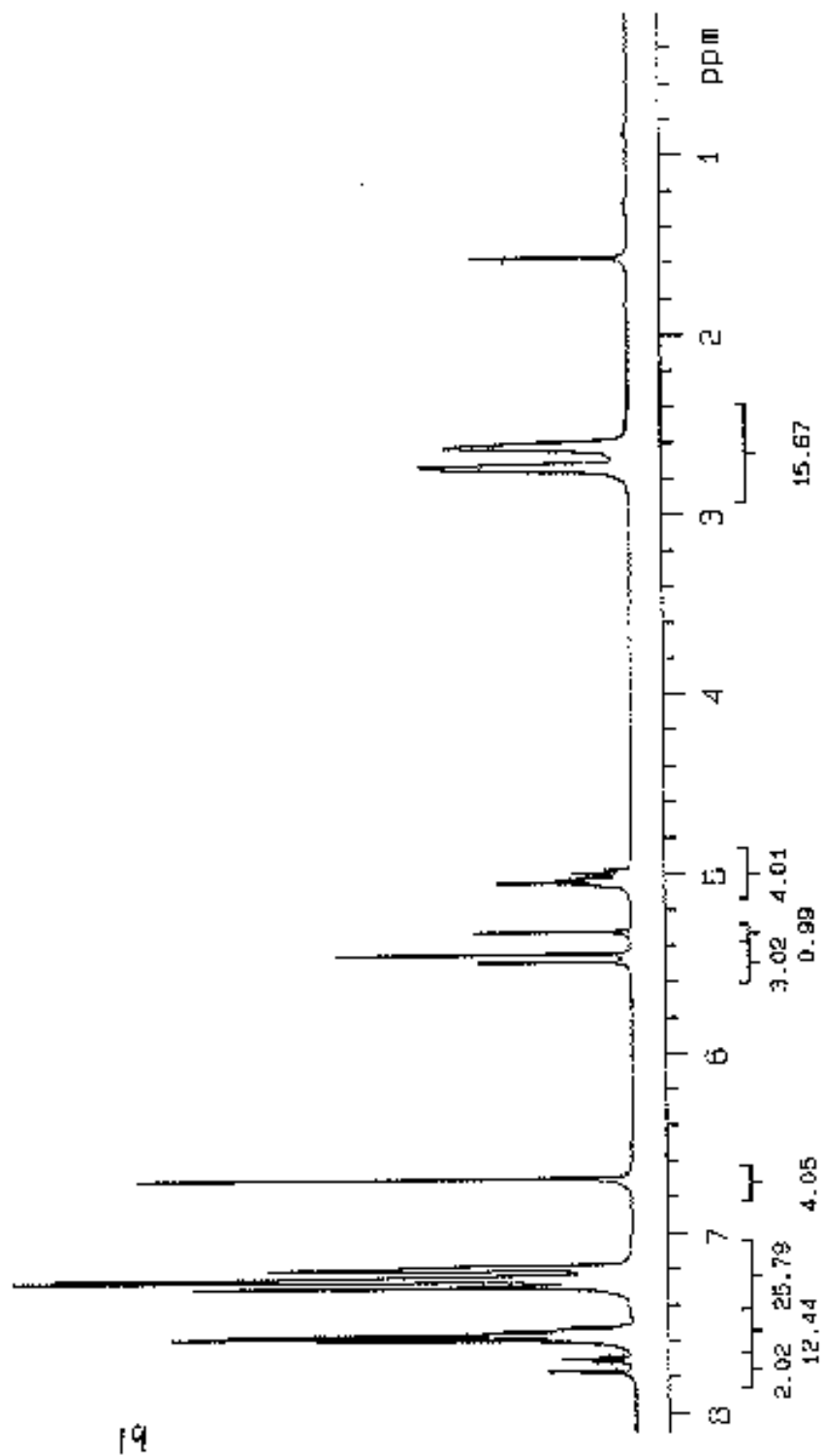
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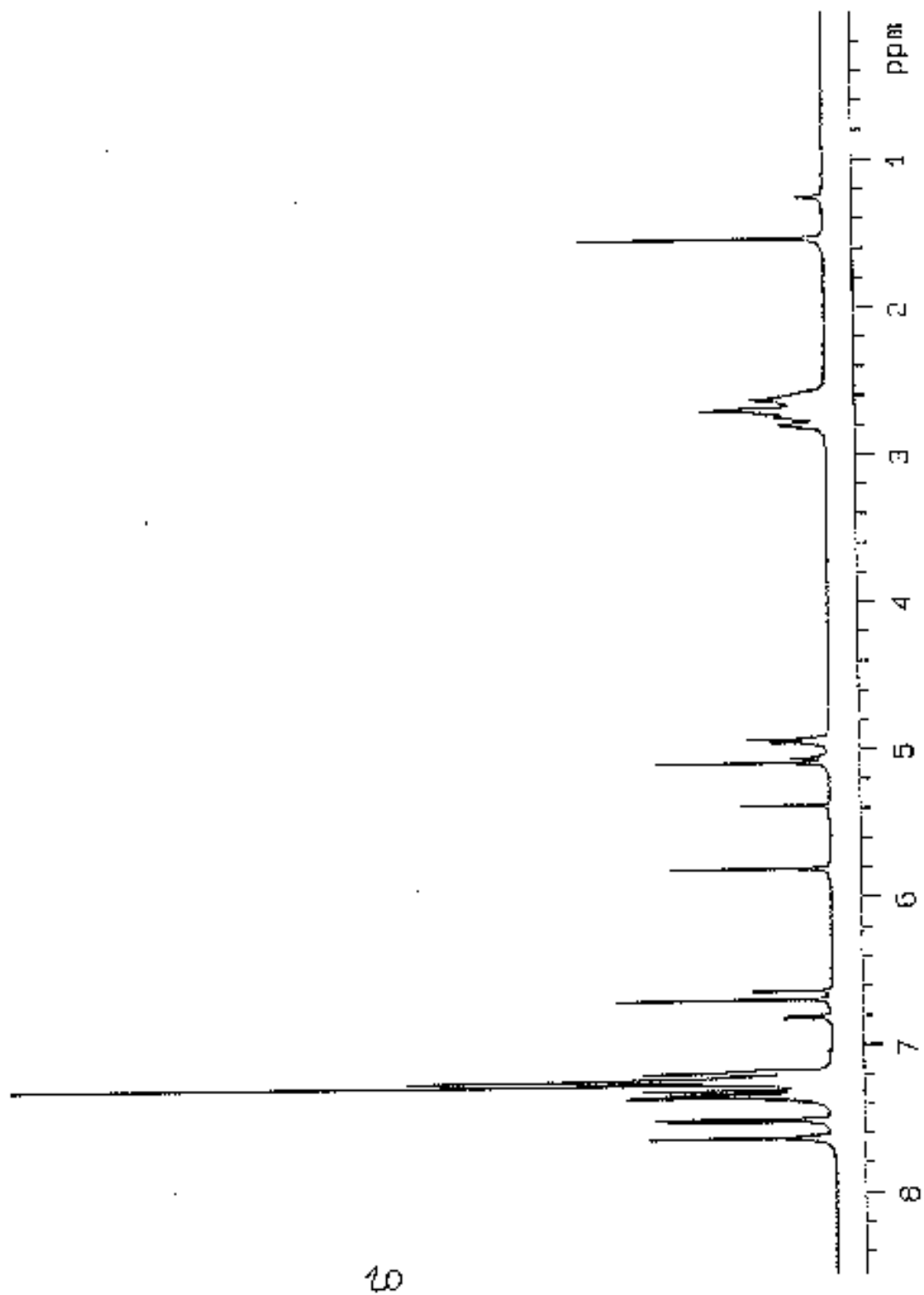


18

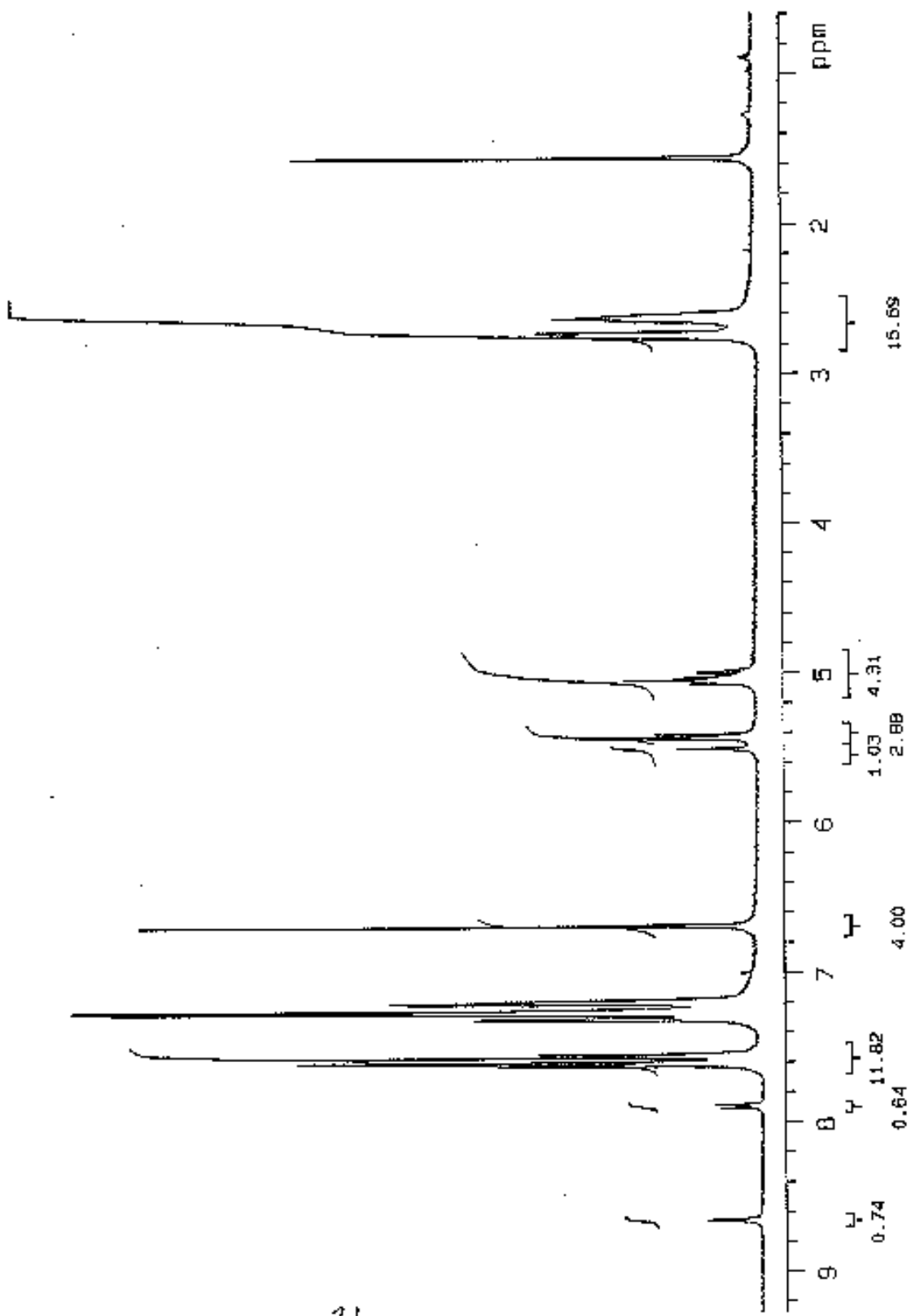
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#10

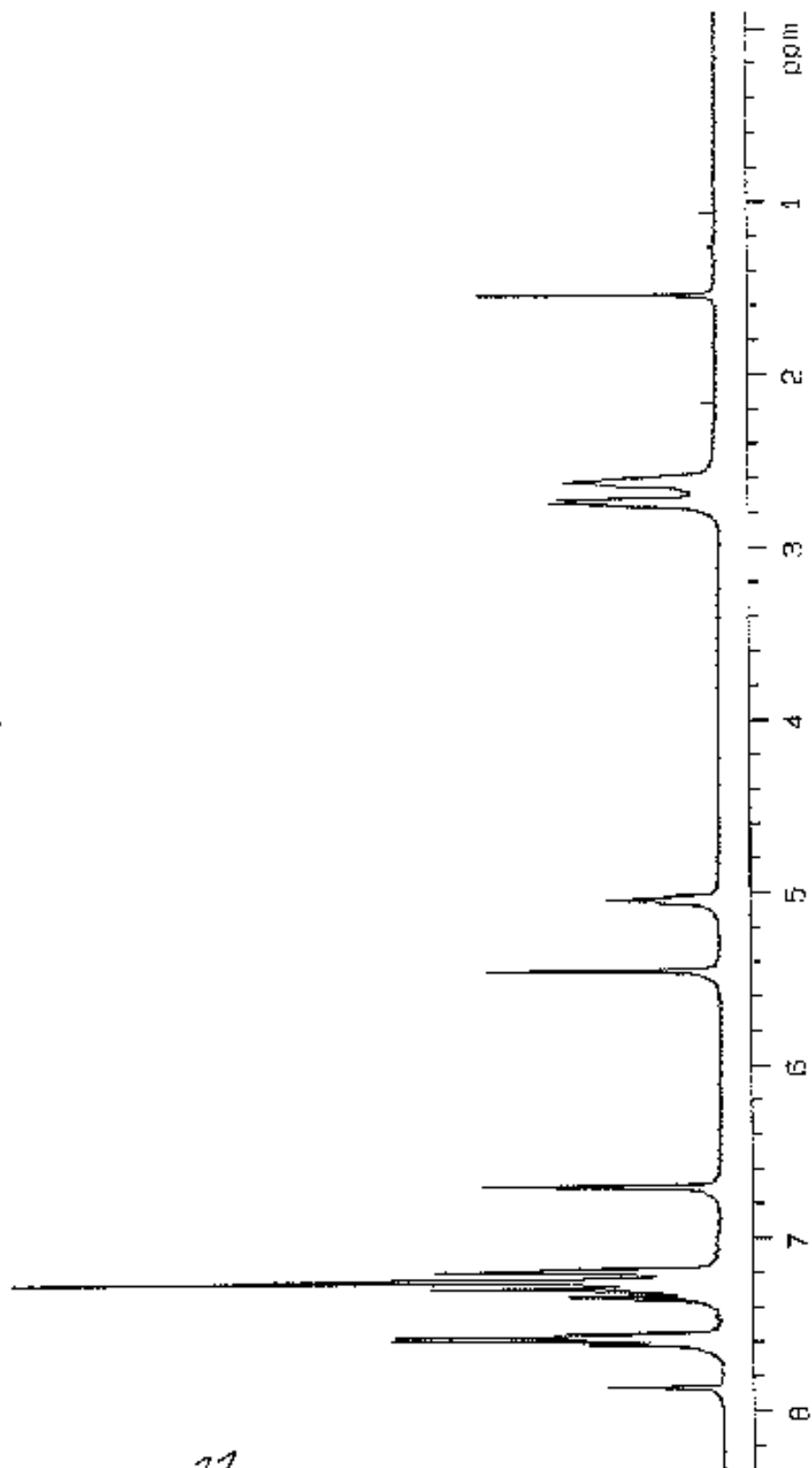


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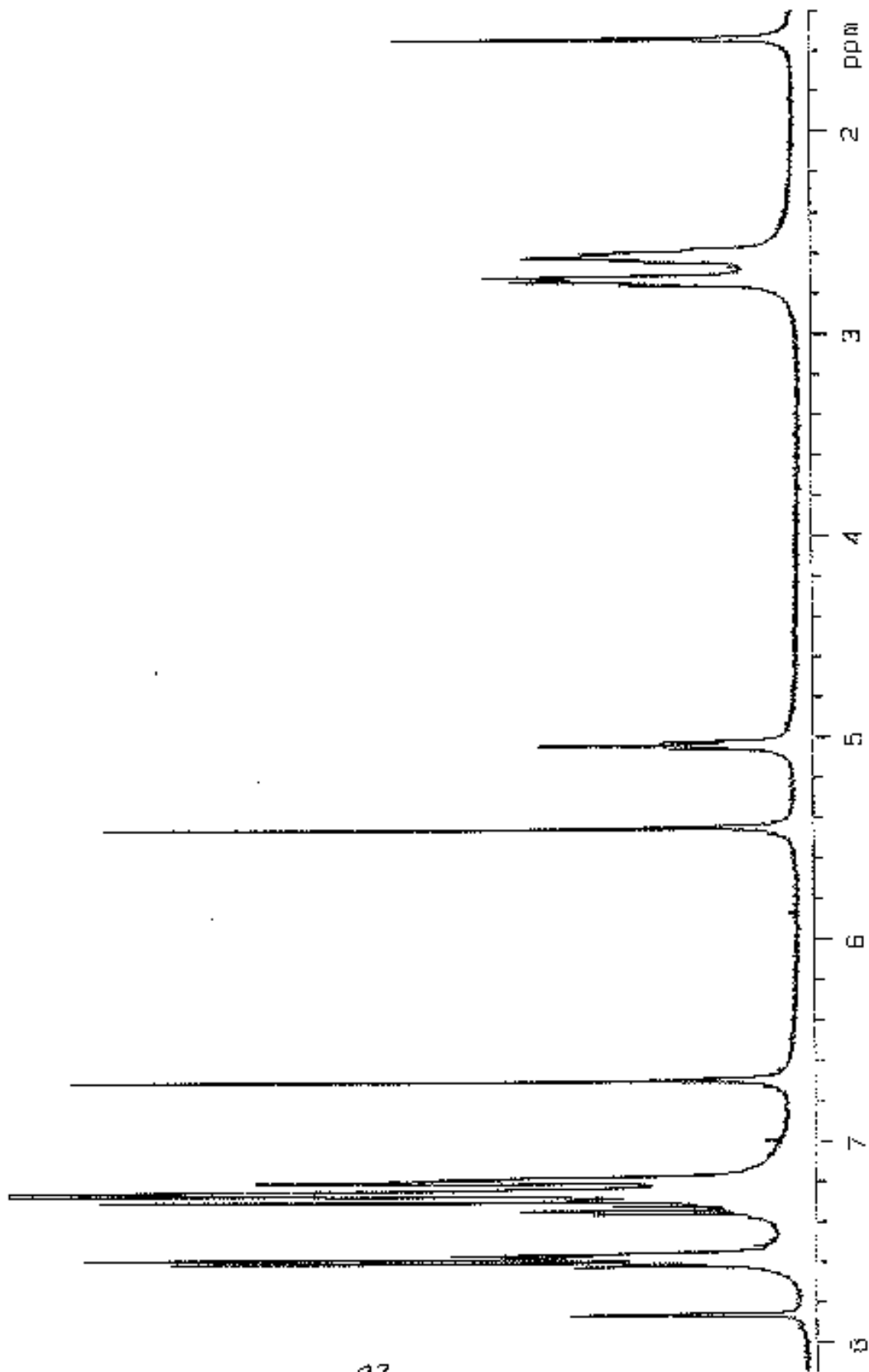


21

#12



#13



23