Chemical Communications

Two Guest Complexation Modes in a Cyclotriveratrylene-Based Molecular Container

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SUPPORTING INFORMATION

	Page
Experimental procedures and characterization data for all new compounds	S2–S4
^{1}H and ^{13}C NMR spectra of **2**	S5–S6
^{1}H and ^{13}C NMR spectra of **3**	S7–S8
^{1}H and ^{13}C NMR spectra of **4**	S9–S10
^{1}H and ^{13}C NMR spectra of **1**	S11–S12
Variable-temperature ^{1}H NMR spectra [400 MHz, $CDCl_3/CD_3CN$ (1:1)] of an equimolar mixture (5 mM) of **1** and BPBD·$2PF_6$	S13
^{1}H NMR spectra [400 MHz, $CDCl_3/CD_3CN$ (1:1)] of dilution an equimolar mixture of **1** and DMDAP·$2PF_6$	S14
Partial ^{1}H NMR spectra [400 MHz, $CDCl_3/CD_3CN$ (1:1), 298 K] of the mixtures of molecular container **1** and BPBD•$2PF_6$	S15

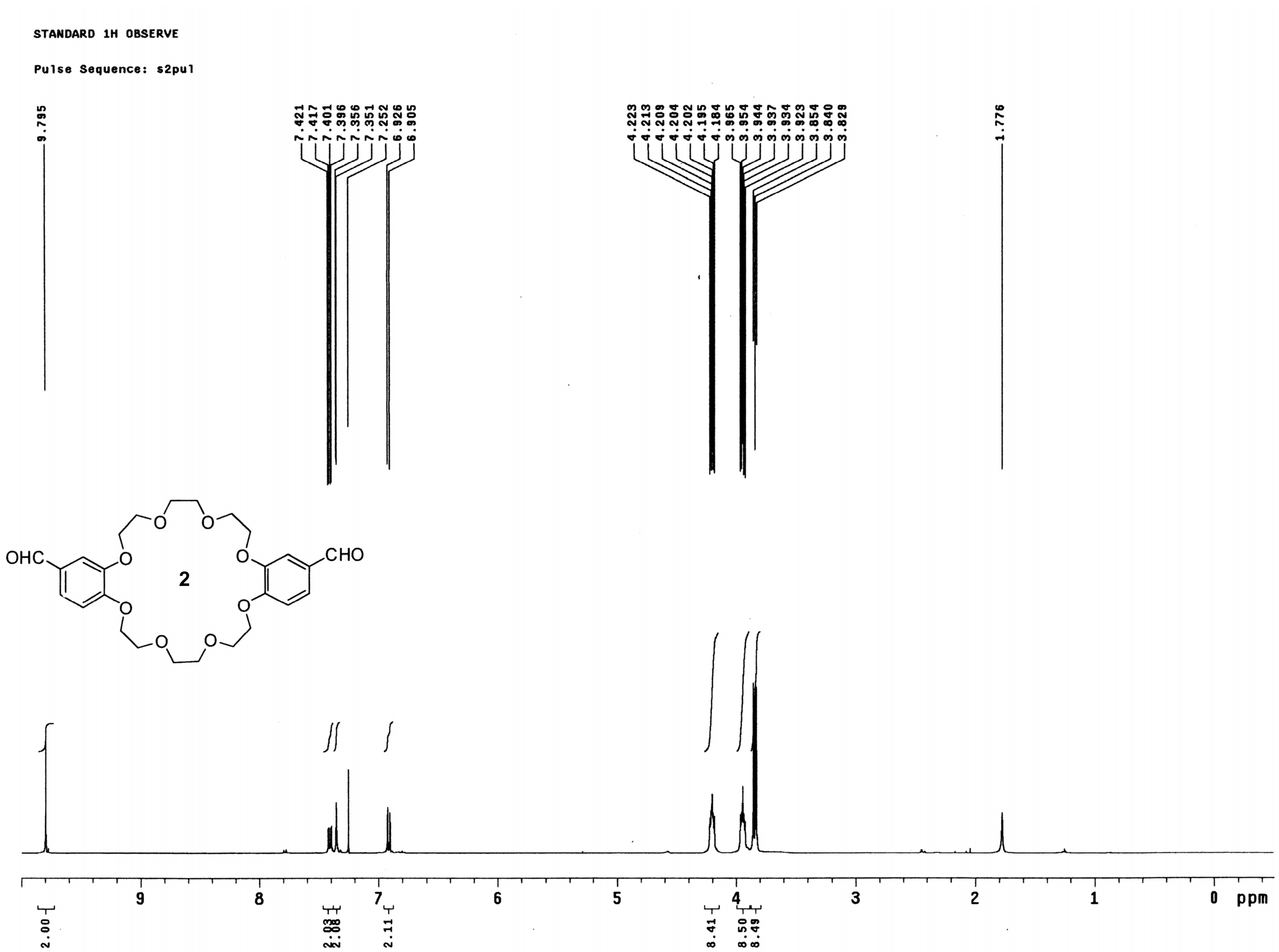
General Methods: All glassware, stirrer bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_2Cl_2 and MeCN were obtained by distillation from CaH_2 under N_2. Reactions were conducted under N_2 or Ar atmospheres. Thin layer chromatography (TLC) was performed on Merck 0.25-mm silica gel (Merck Art. 5715). Column chromatography was performed over Kieselgel 60 (Merck, 70–230 mesh). Melting points are uncorrected. In NMR spectra, the deuterated solvent was used as the lock, while either the solvent's residual protons or TMS was employed as the internal standard. Chemical shifts are reported in parts per million (ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad).

Crown Ether 2: A DMF solution (85 mL) of 3,4-dihydroxybenzaldehyde (5.5 g, 39.8 mmol), K_2CO_3 (5.5 g, 39.8 mmol) and triethylene glycol bistosylate (9.1 g, 19.9 mmol) was stirred at 60 °C for 5 h. After the organic solvent was removed under reduced pressure, the residue was partitioned between H_2O (250 mL) and CH_2Cl_2 (250 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to afford the crude diol (8.33 g), which was then dissolved with triethyleneglycol bistosylate (9.1 g, 19.9 mmol) in DMF (250 mL). This solution was slowly added to a mixture of K_2CO_3 (23.6 g, 170 mmol) and tetra-*n*-butylammonium iodide (496 mg, 1.07 mmol) in DMF (1200 mL) and then the combined mixture was stirred at 60 °C for 4 days. After removing the organic solvent under reduced pressure, the residue was partitioned between H_2O (250 mL) and CH_2Cl_2 (250 mL). The organic layer was separated, dried ($MgSO_4$), concentrated, and washed with MeOH (20 mL) to afford the dialdehyde **2** as a white solid (1.65 g, 17%). M.p.: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.83–3.85 (m, 8H), 3.92–3.96 (m, 8H), 4.18–4.22 (m, 8H), 6.91 (d, J = 8.4 Hz, 2H), 7.35 (s, 2H), 7.41 (d, J = 8.4 Hz, 2H), 9.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 69.3, 69.4, 69.5, 69.7, 71.4, 71.6, 110.7, 111.6, 126.7, 123.0, 148.9, 154.0, 190.6; HR-MS(ESI): *m/z* calcd for $[M + H]^+$ $C_{26}H_{33}O_{10}$ 505.2074, found 505.2074.

Crown Ether 3: Sodium borohydride (476 mg, 12.5 mmol) was added to a solution of the macrocycle **2** (6.35 g, 12.6 mmol) in MeOH and CH_2Cl_2 (9:1, 100 mL) and the mixture was stirred at room temperature for 3 h. After removing the organic solvent under reduced pressure, the residue was partitioned between H_2O (250 mL) and CH_2Cl_2 (250 mL). The organic layer was dried ($MgSO_4$) and concentrated to afford the diol (4.4 g, 8.7 mmol), which was then mixed with sodium acetate (357 mg, 4.35 mmol) and 4Å molecular sieves (4.0 g) in CH_2Cl_2 (80 mL). A solution of pyridinium chlorochromate (1.41 g, 6.53 mmol) in CH_2Cl_2 (95 mL) was added over 30 min and then the mixture was stirred at room temperature for 1.5 h before being filtrated through Celite. The filtrate was washed with H_2O (2 × 20 mL) and then the separated organic phase was dried ($MgSO_4$), concentrated, and purified (SiO_2, EtOAc) to afford the alcohol **3** as a white solid (2.0 g, 31%). M.p. 103–104 °C; ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.80–3.84 (m, 8H), 3.87–3.94 (m, 8H), 4.10–4.14 (m, 4H), 4.16–4.20 (m, 4H), 4.55 (s, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 6.90 (d, *J* = 8 Hz, 1H), 7.32 (s, 1H), 7.37 (d, *J* = 8 Hz, 1H), 9.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 64.8, 68.9, 68.9, 69.0, 69.1, 69.1, 69.3, 69.5, 70.9, 71.0, 71.2 (two signals are missing, possibly because of signal overlap), 110.5, 111.4, 112.3, 113.2, 119.4, 126.4, 129.6, 133.7, 147.7, 148.3, 148.5, 153.7, 190.34; HR-MS(ESI): *m/z* calcd for $[M + H]^+$ $C_{26}H_{35}O_{10}^+$ 507.2230, found 507.2231.

Molecular Container 4: Scandium triflate (87 mg, 0.2 mmol) was added to a CH_3CN (40 mL) solution of the macrocycle **3** (2.0 g, 4.1 mmol) and then the mixture was heated at 60 °C for 12 h. After removing the organic solvent under reduced pressure, the residue was partitioned between H_2O (50 mL) and CH_2Cl_2 (100 mL). The separated organic layers was dried ($MgSO_4$), concentrated, and chromatographied (SiO_2; $MeOH/CH_2Cl_2$, 3:97) to afford the trialdehyde **4** as a pale-yellow oil (725 mg, 38%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.43 (d, *J* = 13.2 Hz, 3H), 3.70–3.74 (m, 24H), 3.80–3.88 (m, 24H), 4.02–4.06 (m, 12H), 4.07–4.10 (m, 12H), 4.64 (d, *J* = 13.2 Hz, 3H), 6.76 (s, 6H), 6.88 (d, *J* = 8 Hz, 3H), 7.32 (s, 3H), 7.35 (d, *J* = 8 Hz, 3H), 9.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 36.7, 69.3, 69.4, 69.4, 69.6, 69.7, 69.9, 71.1, 71.3, 71.4 (three aliphatic signals are missing, possibly because of signal overlap), 110.6, 111.5, 115.9, 126.5, 129.7, 132.1, 147.0, 148.5, 153.6 (three aromatic signals are missing, possibly because of signal overlap), 190.0; HR-MS(ESI): *m/z* calcd for $[M + H]^+$ $C_{78}H_{97}O_{27}^+$ 1465.6217, found 1465.6218.

Molecular Container 1: $NaBH_4$ (95 mg, 2.5 mmol) was added to a solution of the molecular container **4** (1.22 g, 0.84 mmol) in MeOH and CH_2Cl_2 (9:1, 15 mL) and then the mixture was stirred at room temperature for 2 h. After removing the organic solvent under reduced pressure, the residue was partitioned between H_2O (150 mL) and CH_2Cl_2 (150 mL). The separated organic layers were dried ($MgSO_4$) and concentrated to afford the crude triol (1.02 g), which was then mixed with $Sc(OTf)_3$ (34 mg, 0.07 mmol) in CH_3CN (220 mL) and heated at 60 °C for 12 h. The organic solvent was removed under reduced pressure and the residue partitioned between H_2O (200 mL) and CH_2Cl_2 (300 mL); the separated organic layers was dried ($MgSO_4$), concentrated, and purified (SiO_2, $MeOH/CH_2Cl_2$, 5:95) to afford the molecular container **1** as a white solid (128 mg, 11%). M.p. >150 °C (decomposed); ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 3.45 (d, *J* = 14 Hz, 6H), 3.58–3.64 (m, 12H), 3.64–3.80 (m, 12H), 3.80–3.90 (m, 24H), 3.91–4.08 (m, 24H), 4.65 (d, J = 14 Hz, 6H), 6.77 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 36.6, 69.7, 69.9, 71.3, 115.8, 132.0, 147.1; HR-MS(ESI): *m/z* calcd for $[M + H]^+$ $C_{78}H_{97}O_{24}$ 1417.6370, found 1417.6301.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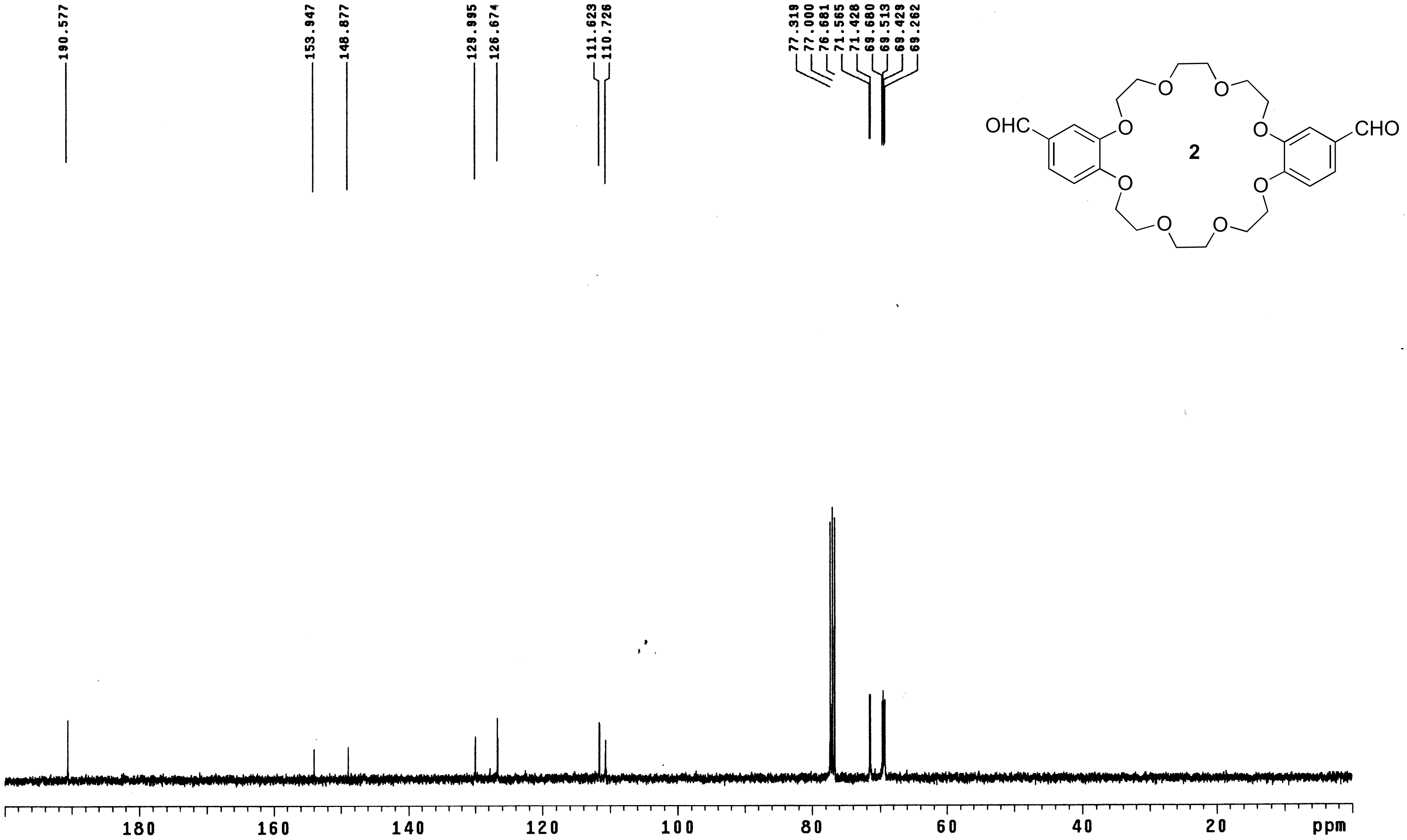

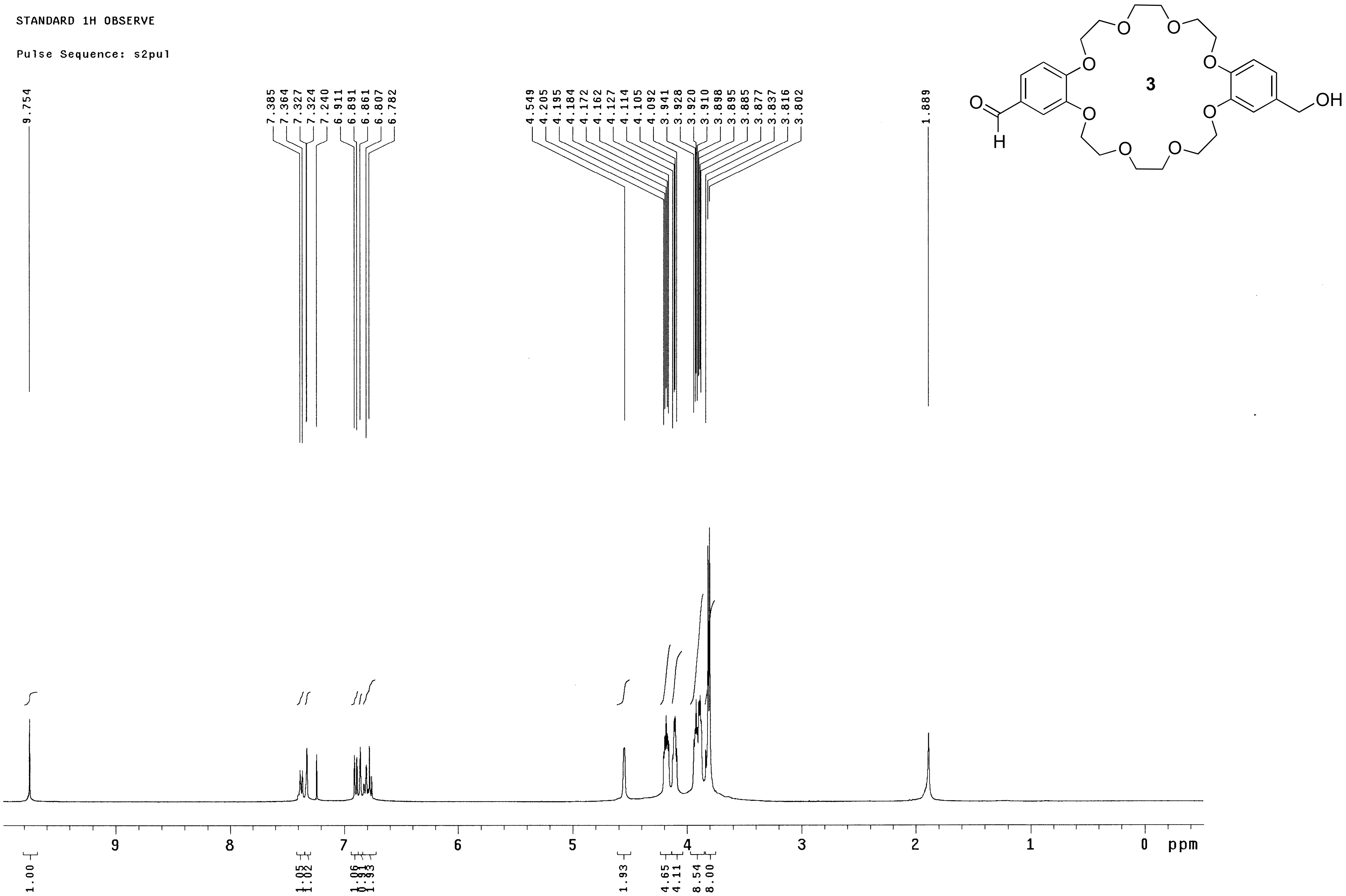
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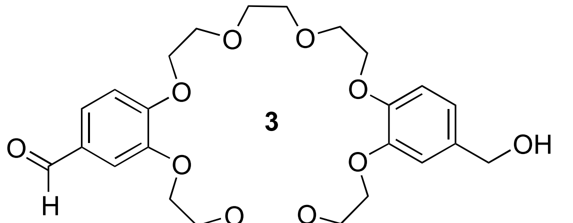

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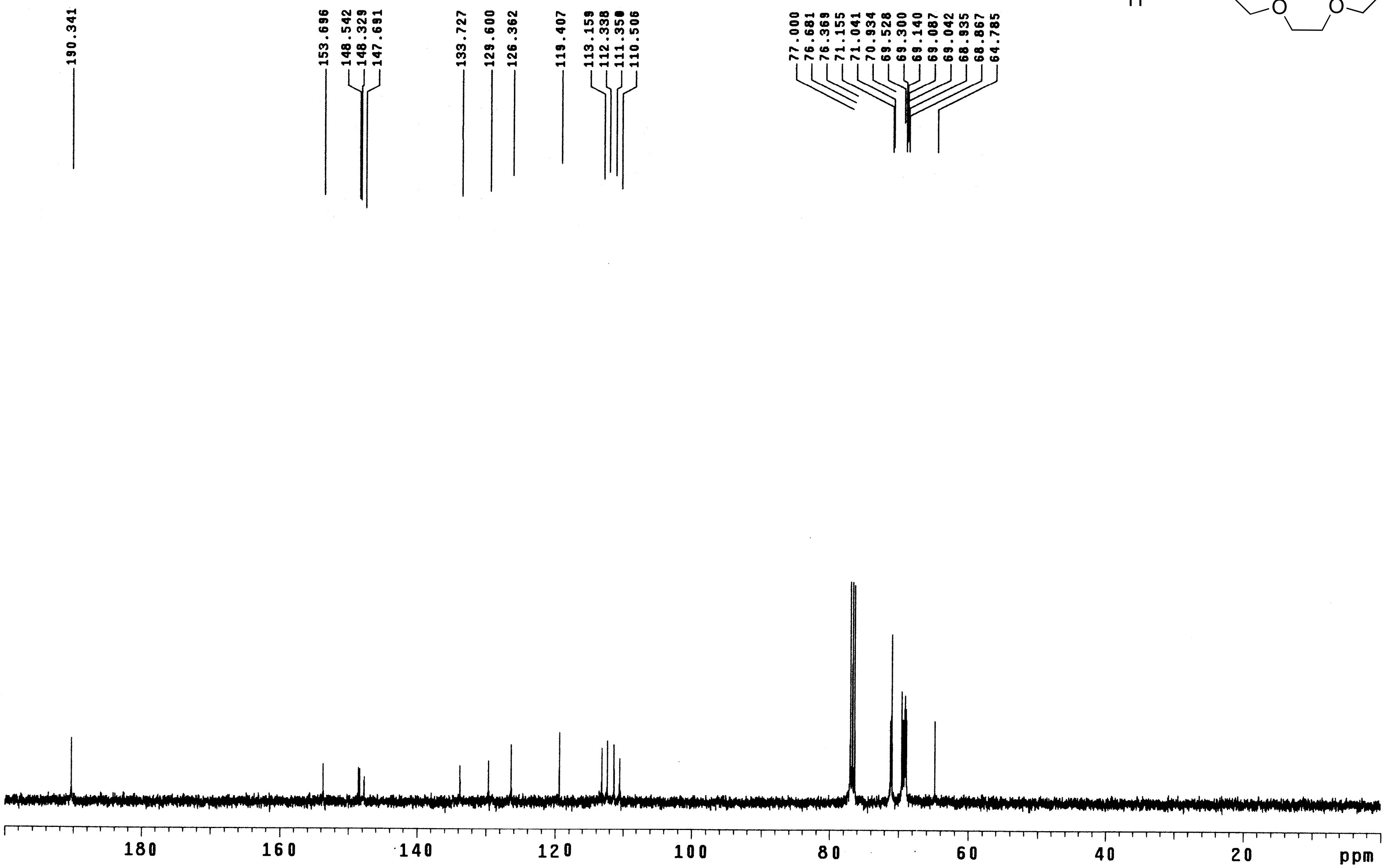

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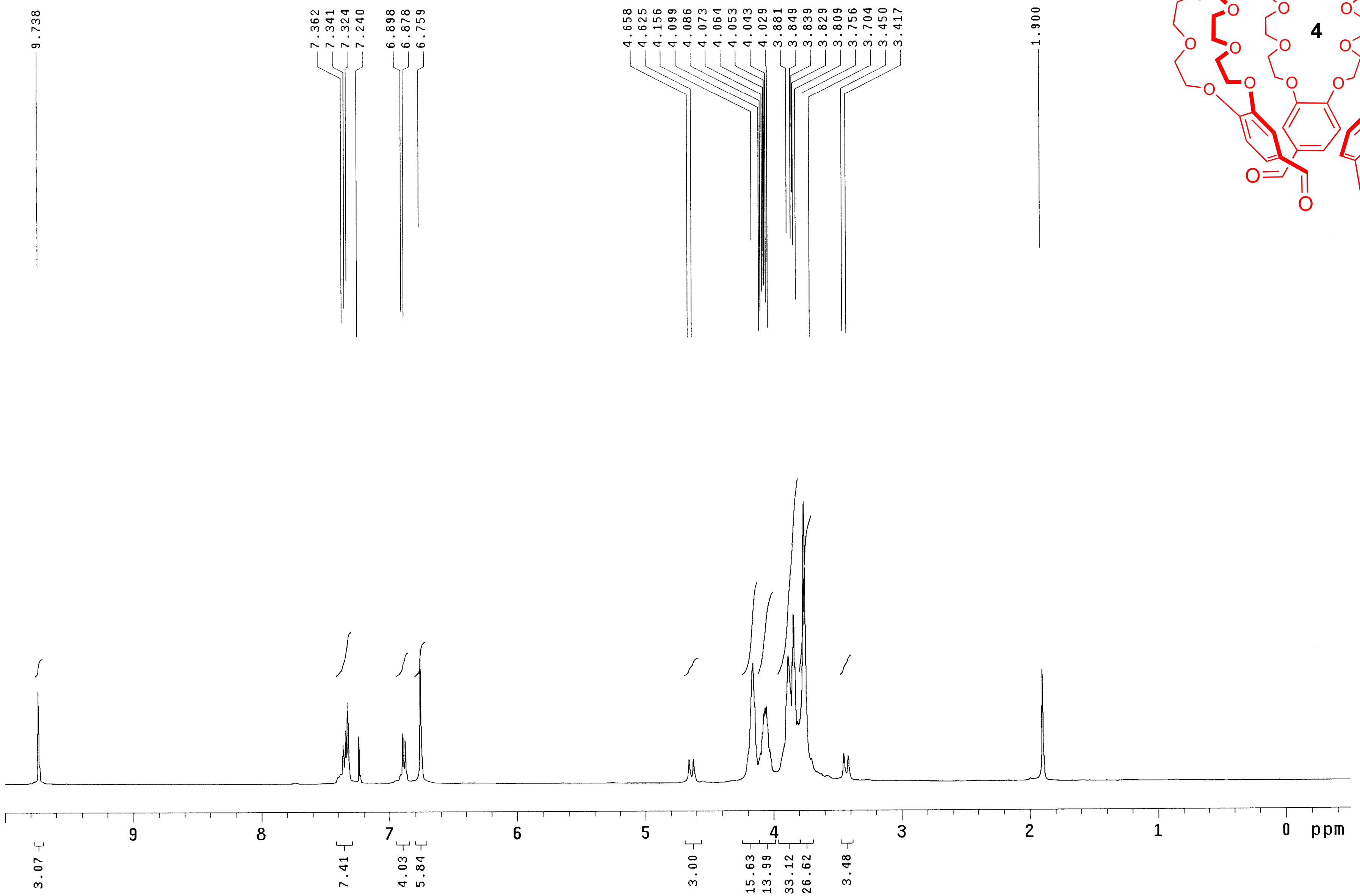

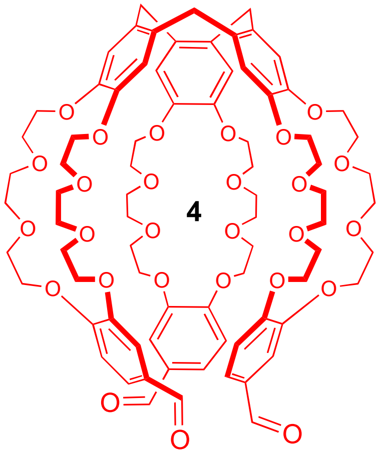

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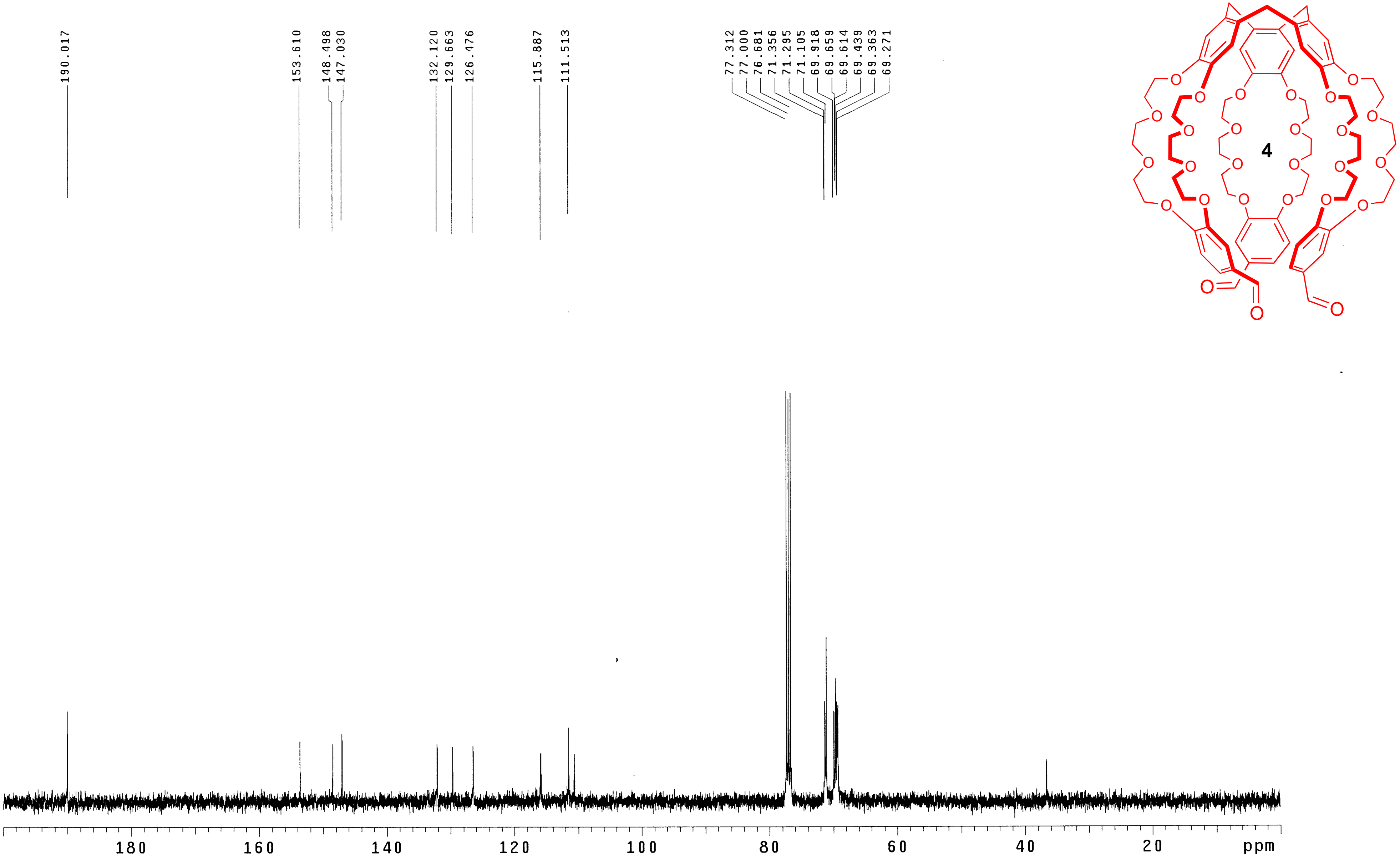

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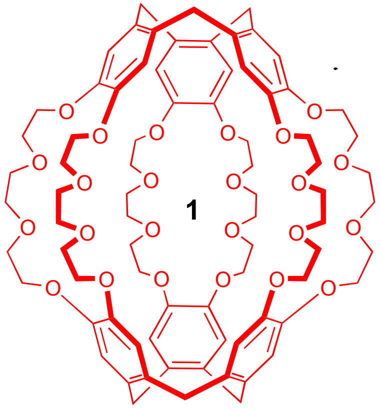

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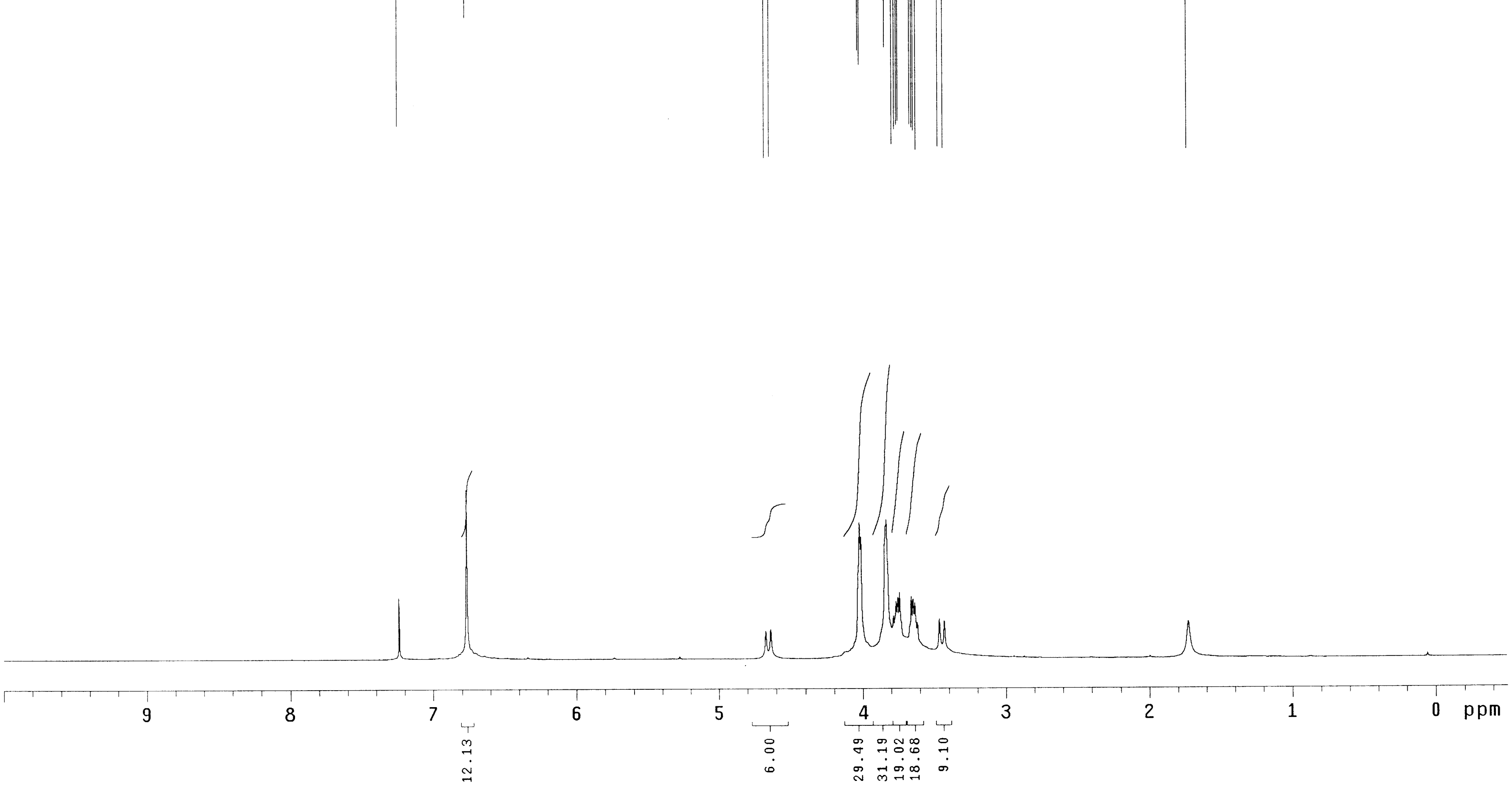

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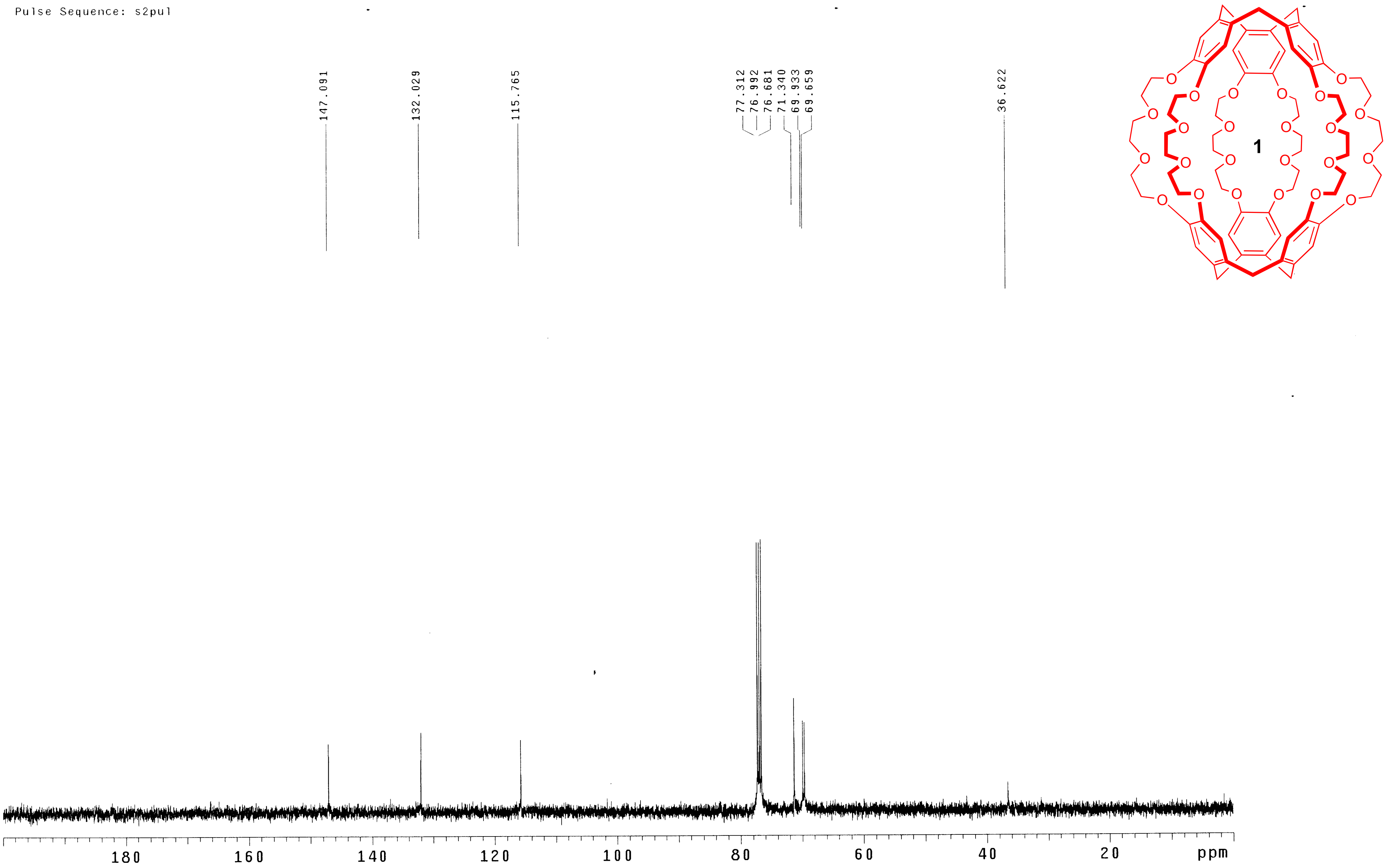
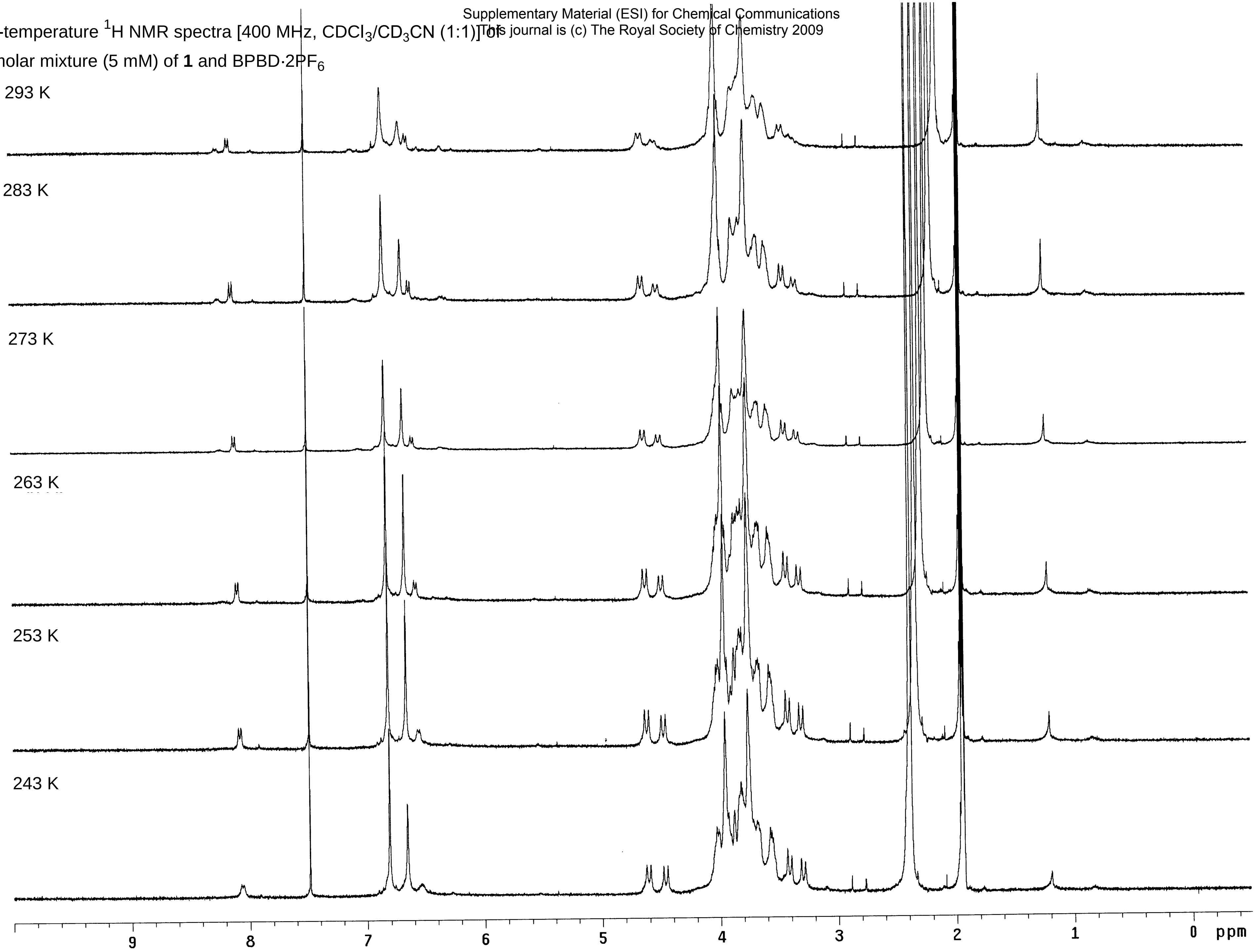
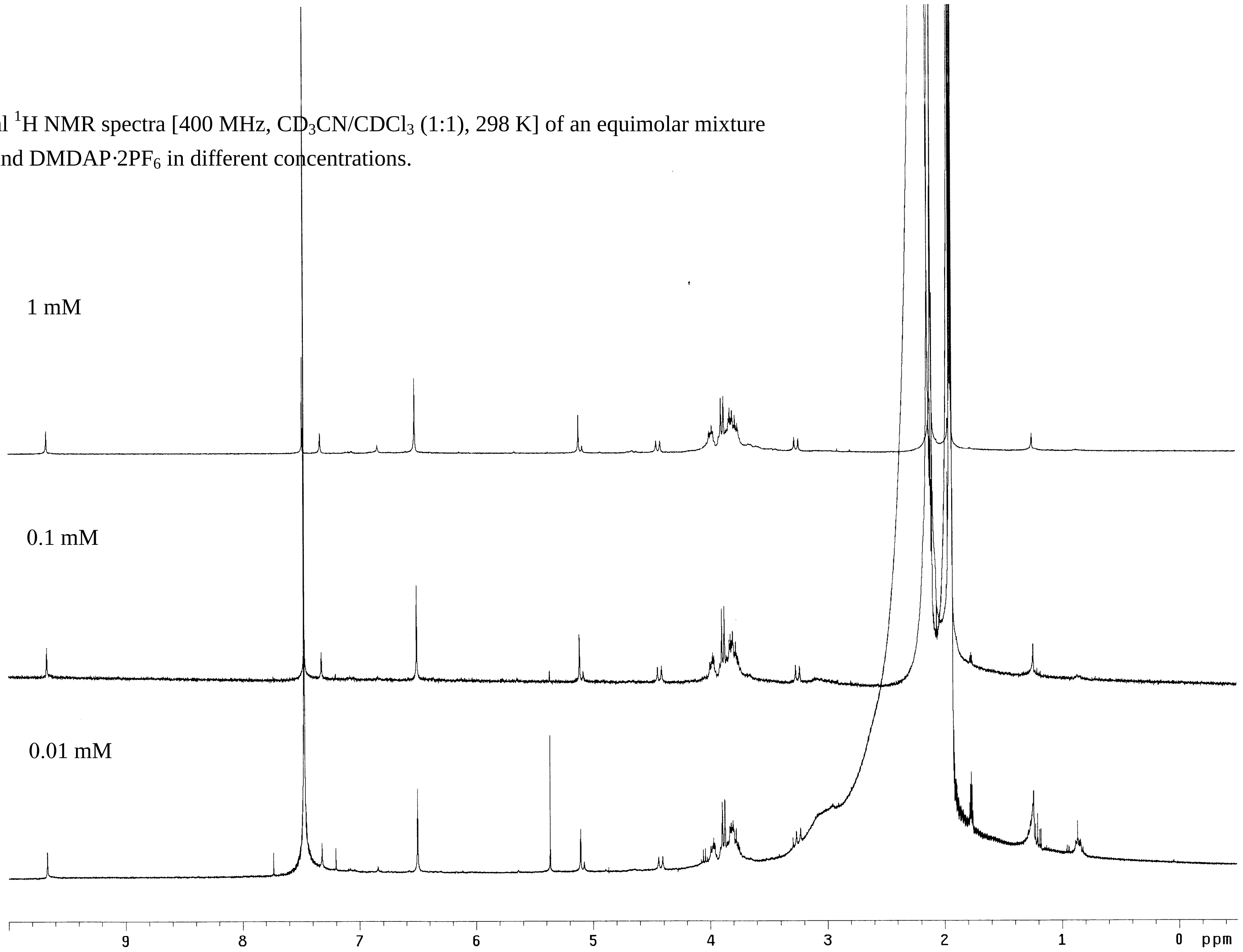
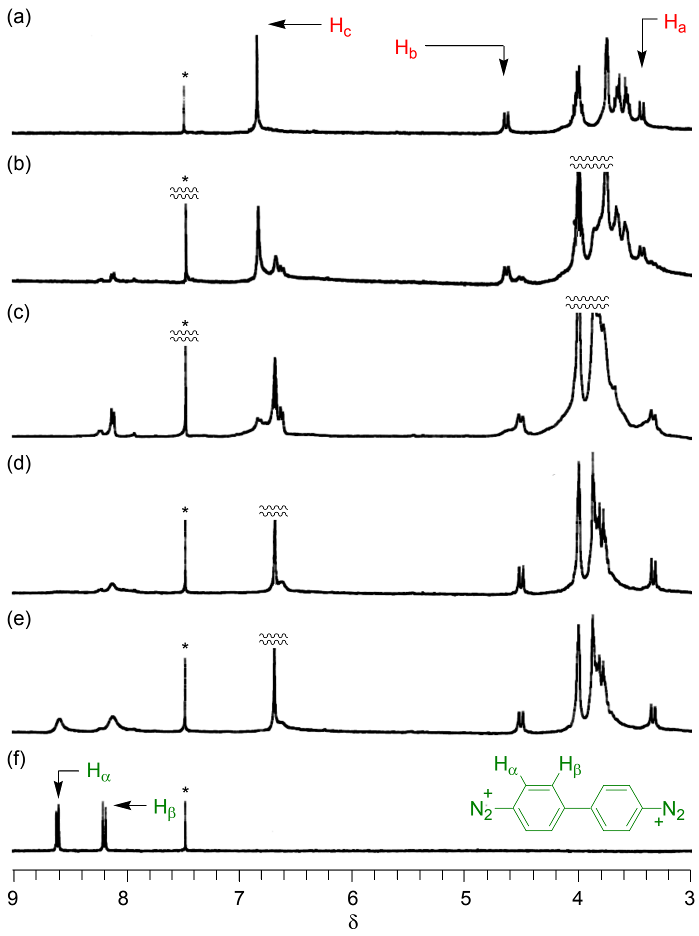


Variable-temperature ^{1}H NMR spectra [400 MHz, $CDCl_3/CD_3CN$ (1:1)] of an equimolar mixture (5 mM) of **1** and BPBD·2PF_6



Partial ^{1}H NMR spectra [400 MHz, $CD_3CN/CDCl_3$ (1:1), 298 K] of an equimolar mixture of **1** and DMDAP·$2PF_6$ in different concentrations.





Partial ^{1}H NMR spectra [400 MHz, $CDCl_3/CD_3CN$ (1:1), 298 K] of (a) the molecular container **1**, (b–e) mixtures of **1** and BPBD•2PF$_6$ [(b) 10:3 (2 mM:0.6 mM); (c) 10:8 (2 mM:1.6 mM); (d) 1:1 (2 mM:2 mM); (e) 1:2 (2 mM:4 mM)], and (f) BPBD•2PF$_6$.