Conformational polymorphism and amphiphilic properties of resorcinarene octapodands

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Contents:

Synthetic procedures

Octapodand 1:

Tetramethyl resorcinarene (0.27 g, 0.50 mmol), dibenzo-18-crown-6 (0.17 g, 0.49 mmol) and Cs_2CO_3 (3.25 g, 10.0 mmol) were suspended in dry acetonitrile (25 ml) under nitrogen atmosphere and refluxed for 30 minutes followed by the addition of *o*-nitro-*N*-(2-toluenesulfonyloxyethyl)aniline[1] (1.37 g, 4.07 mmol) in acetonitrile (15 ml). The resulting yellow suspension was refluxed for 40 hours and filtrated with suction. The precipitate was extracted with dichloromethane and the resulting dichloromethane solution was washed with water, dried over $MgSO_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO_2; $CHCl_3$:MeOH 9:1 + 0.25 % triethylamine) and recrystallized from hot acetone to provide dark orange crystals (0.29 g, 31 %), or dissolved in acetone and precipitated from water (yield 44 %). mp 228–229 °C (crystalline) and 98–100 °C (amorphous); (Found C, 61.9; H, 5.0; N, 12.1. $C_{96}H_{96}N_{16}O_{24}$ requires C, 62.1; H, 5.2; N, 12.1%); δ_H (500 MHz, [D$_6$]DMSO, 120 °C) 1.33 (d, ^3J (H,H) = 7.1, 12H; CH_3), 3.39–3.48 (br, 8H; OCH$_2$CH_2N), 3.48–3.57 (br, 8H; OCH$_2$CH_2N), 3.85–3.95 (br, 8H; OCH_2CH$_2$N), 4.07–4.16 (br, 8H; OCH_2CH$_2$N), 4.63 (q, ^3J (H,H) = 7.1, 4H; ArC*H*), 6.50 (s, 4H; Ar*H*), 6.61 (br s, 4H; Ar*H*), 6.65 (m, 8H; Ar*H*), 6.95 (d, ^3J (H,H) = 8.7, 8H; Ar*H*), 7.44 (m, 8H; Ar*H*), 7.92 (br s, 8H; N*H*), 7.99 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*); δ_C(126 MHz, [D$_6$]DMSO, 120 °C) 19.3 (CH_3), 29.6 (Ar*C*H), 41.8 (OCH$_2$*C*H$_2$N), 67.0 (O*C*H$_2$CH$_2$N), 99.8 (*Ar*H), 113.6 (*Ar*H), 114.8 (*Ar*H), 124.4 (*Ar*CH), 125.4 (*Ar*H), 127.6 (*Ar*H), 131.5 (*Ar*NH), 135.4 (*Ar*H), 144.3 (*Ar*NO$_2$), 153.8 (*Ar*OCH$_2$); *m/z* (ESI-TOF) 1896 (M + K$^+$, 18%), 1880 (M + Na$^+$, 100), 1858 (M + H$^+$, 15).

Octapodand 2:

Tetraethyl resorcinarene (0.30 g, 0.50 mmol), dibenzo-18-crown-6 (0.19 g, 0.53 mmol) and K_2CO_3 (1.39 g, 10.0 mmol) were suspended in dry acetonitrile (25 ml) under nitrogen atmosphere and refluxed for 30 minutes followed by the addition of *o*-nitro-*N*-(2-toluenesulfonyloxyethyl)aniline (1.37 g, 4.08 mmol) in acetonitrile (10 ml). The resulting yellow suspension was refluxed for 22 hours and filtrated with suction. The precipitate was extracted with dichloromethane and the resulting dichloromethane solution was washed with water, dried over $MgSO_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO_2; $CHCl_3$:MeOH 9:1 + 0.25 % triethylamine) and recrystallized from hot acetone to provide orange crystalline product (0.22g, 23 %), or dissolved in acetone and precipitated from water (yield 54 %). mp 195–196 °C (crystalline) and 192–193 °C (amorphous); (Found C, 62.5; H, 5.4; N, 11.4. $C_{100}H_{104}N_{16}O_{24}\cdot 0.5(CH_3)_2CO$ requires C, 62.7; H, 5.55; N, 11.5%); δ_H(500 MHz, [D6]DMSO, 30 °C) 0.71 (t, ^3J (H,H) = 7.2, 12H; CH_3), 1.77 (m, 8H; CH_2), 3.40–3.48 (m, 8H; OCH_2CH_2N), 3.50–3.59 (m, 8H; OCH_2CH_2N), 3.87–3.97 (m, 8H; OCH_2CH_2N), 4.04–4.13 (m, 8H; OCH_2CH_2N), 4.53 (t, ^3J (H,H) = 7.7, 4H; ArC*H*), 6.47 (s, 4H; Ar*H*), 6.63 (m, 8H; Ar*H*), 6.81 (br s, 4H; Ar*H*), 6.93 (d, ^3J (H,H) = 8.6, 8H; Ar*H*), 7.44 (m, 8H; Ar*H*), 7.97 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.16 (t, ^3J (H,H) = 5.4, 8H, N*H*); δ_C(126 MHz, [D_6]DMSO, 30 °C) 12.2 (CH_3), 28.0 (CH_2), 35.6 (Ar*C*H), 41.9 (OCH_2CH_2N), 66.6 (OCH_2CH_2N), 98.4 (*Ar*H), 114.2 (*Ar*H), 115.3 (*Ar*H), 125.5 (*Ar*H), 125.7 (*Ar*CH), 126.1 (*Ar*H), 131.1 (*Ar*NH), 136.4 (*Ar*H), 144.8 (*Ar*NO_2), 154.3 (*Ar*OCH_2);); *m/z (*ESI-TOF) 1953 (M + K^+, 9%), 1936 (M + Na^+, 100), 1914 (M + H^+, 14).

Octapodand 3:

Tetrapentyl resorcinarene (0.20 g, 0.26 mmol) and K_2CO_3 (0.58 g, 4.20 mmol) were suspended in dry acetonitrile (20 ml) under nitrogen atmosphere and refluxed for 15 minutes followed by the addition of *o*-nitro-*N*-(2-methanesulfonyloxyethyl)aniline (0.59 g, 2.30 mmol) in acetonitrile (15 ml). The resulting yellow suspension was refluxed for 21 hours, filtrated with suction and evaporated under reduced pressure. The residue was suspended in water and extracted with dichloromethane; organic layer was dried over $MgSO_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO_2; $CHCl_3$:MeOH 9:1), dissolved in acetone and precipitated from water with an addition of NaCl. The resulting bright yellow powder (0.22 g, 40 %) was filtrated with suction and dried under vacuum. mp 88–91 °C; (Found C, 64.3; H, 6.0; N, 10.5. $C_{112}H_{128}N_{16}O_{24}$ requires C, 64.6; H, 6.2; N, 10.8%); δ_H(500 MHz, [D_6]DMSO, 30 °C) 0.67 (t, ^3J (H,H) = 6.9, 12H; CH_3), 1.08 (br s, 24H; CH_2), 1.69 (br s, 8H; $ArCHCH_2$), 3.35–3.60 (br, 16H; OCH_2CH_2N), 3.83–3.95 (br, 8H; OCH_2CH_2N), 4.04–4.21 (br, 8H; OCH_2CH_2N), 4.57 (t, ^3J (H,H) = 7.4, 4H; ArC*H*), 6.48 (br s, 4H; Ar*H*), 6.65 (m, 8H; Ar*H*), 6.93 (d, ^3J (H,H) = 8.6, 8H; Ar*H*), 7.45 (m, 8H; Ar*H*), 8.00 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.15 (br s, 4H; N*H*), 4 Ar*H*'s not visible; δ_H(500 MHz, [D_6]acetone, 30 °C) 0.77 (t, ^3J (H,H) = 7.1, 12H; CH_3), 1.14–1.38 (m, 24H; CH_2), 1.86 (m, 8H; $ArCHCH_2$), 3.42–3.66 (br, 16H; OCH_2CH_2N), 3.91–4.11 (br, 8H; OCH_2CH_2N), 4.13–4.28 (br, 8H; OCH_2CH_2N), 4.71 (t, ^3J (H,H) = 7.4, 4H; ArC*H*), 6.60 (br s, 4H; Ar*H*), 6.65 (m, 8H; Ar*H*), 6.96 (m, 8H; Ar*H*), 7.46 (m, 8H; Ar*H*), 8.05 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.20 (br s, 8H; N*H*), 4 Ar*H*'s not visible; δ_C (126 MHz, [D_6]DMSO, 30 °C) 13.7 (CH_3), 22.0 (CH_2), 27.1 (CH_2), 31.4 (CH_2), 34.2 ($ArCHCH_2$), 34.7 (Ar*C*H), 42.2 (OCH_2CH_2N), 66.5 (OCH_2CH_2N), 98.6 (*Ar*H), 114.1 (*Ar*H), 115.4 (*Ar*H), 125.6 (*Ar*CH), 126.1 (*Ar*H), 131.1 (*Ar*NH), 136.4 (*Ar*H), 144.9 (*Ar*NO_2), 154.3 (*Ar*OCH_2), one resorcinarene core *Ar*H not visible; δ_C(126 MHz, [D_6]acetone, 30 °C) 14.4 (CH_3), 23.5 (CH_2), 28.7 (CH_2), 33.0 (CH_2), 35.8 ($ArCHCH_2$), 36.3 (Ar*C*H), 43.5 (OCH_2CH_2N), 68.1 (OCH_2CH_2N), 115.1 (*Ar*H), 116.3 (*Ar*H), 127.2 (*Ar*CH), 127.3 (*Ar*H), 132.9 (*Ar*NH), 137.2 (*Ar*H), 146.2 (*Ar*NO_2), 155.9 (*Ar*OCH_2), resorcinarene core *Ar*H's not visible; *m/z (*ESI-TOF) 2121 (M + K^+, 31%), 2105 (M + Na^+, 100).

Octapodand 4:

Tetranonyl resorcinarene (0.70 g, 0.71 mmol), dibenzo-18-crown-6 (0.41 g, 1.14 mmol) and Cs_2CO_3 (3.70 g, 11.3 mmol) were suspended in dry acetonitrile (35 ml) under nitrogen atmosphere and refluxed for 15 minutes followed by the addition of *o*-nitro-*N*-(2-toluenesulfonyloxyethyl)aniline (1.90 g, 5.64 mmol) in acetonitrile (15 ml). The resulting yellow suspension was refluxed for 44 hours, filtrated with suction and evaporated under reduced pressure. The residue was suspended in water and extracted with dichloromethane; organic layer was dried over $MgSO_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO_2; $CHCl_3$:MeOH 9:1), dissolved in acetone and precipitated from water with an addition of NaCl. The resulting bright yellow powder (1.0 g, 62 %) was filtrated with suction and dried under vacuum. mp 69–70 °C; (Found C, 66.8; H, 6.9; N, 9.3. $C_{128}H_{160}N_{16}O_{24}$ requires C, 66.65; H, 7.0, N, 9.7%); δ_H(500 MHz, [D_6]DMSO, 30 °C) 0.78 (t, ^3J (H,H) = 7.2, 12H; CH_3), 0.99–1.21 (m, 56H; CH_2), 1.67 (m, 8H; $ArCHCH_2$), 3.37–3.58 (br, 16H; OCH_2CH_2N), 3.85–3.96 (br, 8H; OCH_2CH_2N), 4.05–4.23 (br, 8H; OCH_2CH_2N), 4.57 (t, ^3J (H,H) = 7.4, 4H; ArC*H*), 6.48 (s, 4H; Ar*H*), 6.64 (m, 8H; Ar*H*), 6.94 (d, ^3J (H,H) = 8.3, 8H; Ar*H*), 7.45 (m, 8H; Ar*H*), 7.99 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.16 (br s, 8H; N*H*), resorcinarene core Ar*H* overlapps with Ar*H* at 6.64 ppm; δ_H (500 MHz, [D$_6$]acetone, 30 °C) 0.85 (t, ^3J (H,H) = 7.0, 12H; C*H*$_3$), 1.12–1.33 (m, 56H; C*H*$_2$), 1.87 (m, 8H; ArCHC*H*$_2$), 3.45–3.68 (br, 16H; OCH$_2$C*H*$_2$N), 3.92–4.10 (br, 8H; OC*H*$_2$CH$_2$N), 4.15–4.27 (br, 8H; OC*H*$_2$CH$_2$N), 4.72 (t, ^3J (H,H) = 7.4, 4H; ArC*H*), 6.61 (br s, 4H; Ar*H*), 6.66 (m, 8H; Ar*H*), 6.83 (br, 4H; Ar*H*) 6.96 (d, ^3J (H,H) = 9.1, 8H; Ar*H*), 7.47 (m, 8H; Ar*H*), 8.05 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.20 (br s, 8H; N*H*); δ_C(126 MHz, [D$_6$]DMSO, 30 °C) 13.8 (*C*H$_3$), 21.9 (*C*H$_2$), 27.3 (*C*H$_2$), 28.6 (*C*H$_2$), 28.9 (*C*H$_2$), 29.0 (*C*H$_2$), 29.2 (*C*H$_2$), 31.2 (*C*H$_2$), 34.1 (ArCH*C*H$_2$), 34.9 (Ar*C*H), 41.9 (OCH$_2$*C*H$_2$N), 66.5 (O*C*H$_2$CH$_2$N), 114.1 (*Ar*H), 115.4 (*Ar*H), 125.6 (*Ar*CH), 126.1 (*Ar*H), 131.1 (*Ar*NH), 136.4 (*Ar*H), 144.9 (*Ar*NO$_2$), 154.3 (*Ar*OCH$_2$), resorcinarene core *Ar*H's not visible; δ_C(126 MHz, [D$_6$]acetone, 30 °C) 14.4 (*C*H$_3$), 23.4 (*C*H$_2$), 29.0 (*C*H$_2$), 30.4 (*C*H$_2$), 30.5 (*C*H$_2$) 30.7 (*C*H$_2$), 30.8 (*C*H$_2$), 32.7 (*C*H$_2$), 35.8 (ArCH*C*H$_2$), 36.3 (Ar*C*H), 43.5 (OCH$_2$*C*H$_2$N), 68.1 (O*C*H$_2$CH$_2$N), 115.1 (*Ar*H), 116.3 (*Ar*H), 127.2 (*Ar*CH), 127.3 (*Ar*H), 132.9 (*Ar*NH), 137.2 (*Ar*H), 146.2 (*Ar*NO$_2$), 156.0 (*Ar*OCH$_2$); resorcinarene core *Ar*H's not visible; *m/z (*ESI-TOF) 2345 (M + K$^+$, 32%), 2329 (M + Na$^+$, 100).

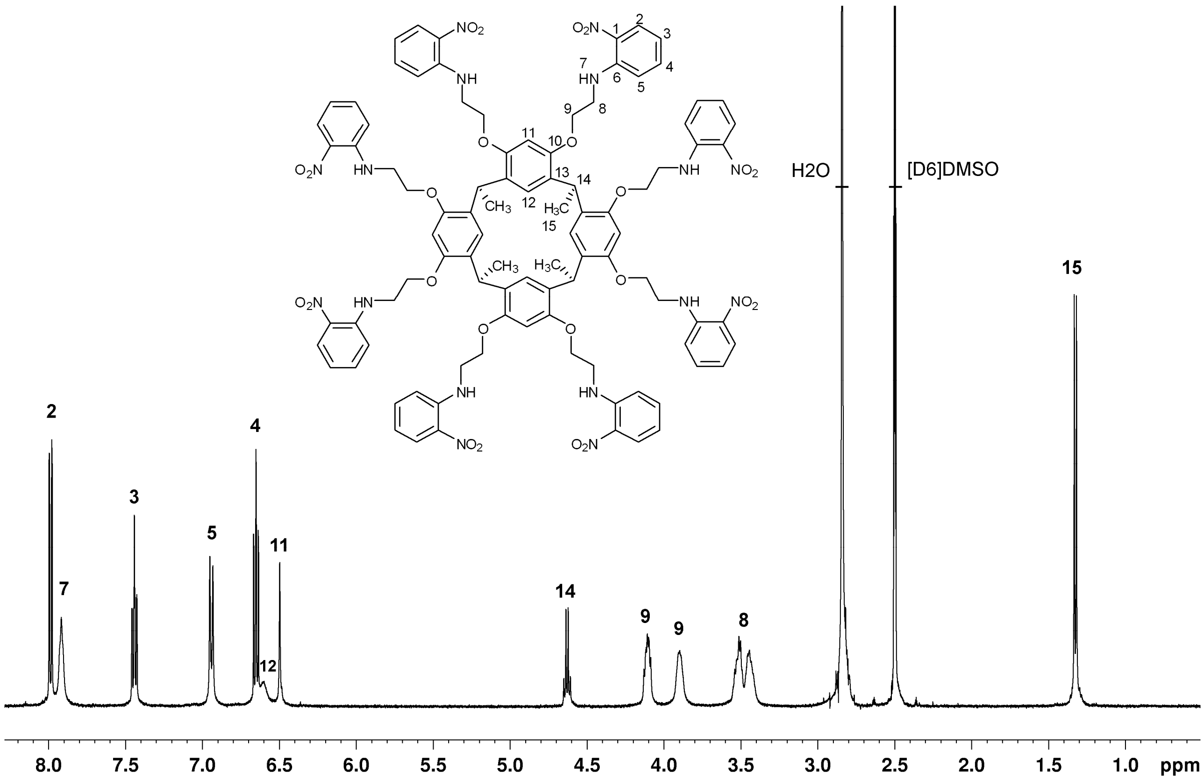
Octapodand 5 procedure A:

Tetra-1-decenyl resorcinarene[2] (0.47 g, 0.45 mmol), dibenzo-18-crown-6 (0.26 g, 0.73 mmol) and Cs$_2$CO$_3$ (2.38 g, 7.29 mmol) were suspended in dry acetonitrile (30 ml) under nitrogen atmosphere and refluxed for 15 minutes followed by the addition of *o*-nitro-*N*-(2-toluenesulfonyloxyethyl)aniline (1.28 g, 3.81 mmol) in acetonitrile (20 ml). The resulting yellow suspension was refluxed for 24 hours, filtrated with suction and evaporated under reduced pressure. The residue was suspended in water and extracted with dichloromethane; organic layer was dried over MgSO$_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO$_2$; CHCl$_3$:MeOH), dissolved in acetone and precipitated from water with an addition of NaCl. The product was filtrated with suction and dried under vacuum at 60 °C to provide glassy orange solid (0.57 g, 53 %). mp 56–58 °C; (Found C, 67.4; H, 6.9; N, 9.5. $C_{132}H_{160}N_{16}O_{24}$ requires C, 67.3; H, 6.85; N, 9.5%); δ_H(500 MHz, [D$_6$]DMSO, 30 °C) 0.93–1.16 (m, 40H; C*H*$_2$), 1.21 (m, 8H; C*H*$_2$), 1.67 (m, 8H; ArCHC*H*$_2$), 1.90 (m, 8H; C*H*$_2$CH=CH$_2$), 3.42 (br, 8H; OCH$_2$C*H*$_2$N), 3.52 (br, 8H; OCH$_2$C*H*$_2$N), 3.90 (br, 8H; OC*H*$_2$CH$_2$N) 4.11 (br, 8H; OC*H*$_2$CH$_2$N), 4.57 (t, ^3J (H,H) = 7.3, 4H; ArC*H*), 4.85–4.93 (m, 8H; CH=C*H*$_2$), 5.71 (m, 4H; C*H*=CH$_2$), 6.48 (br s, 4H; Ar*H*), 6.64 (m, 8H; Ar*H*), 6.93 (d, ^3J (H,H) = 8.5, 8H; Ar*H*), 7.45 (m, 8H, Ar*H*), 7.99 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.16 (br, 8H, N*H*), resorcinarene core Ar*H* overlaps with Ar*H* at 6.64 ppm; δ_H(500 MHz, [D$_6$]acetone, 30 °C) 1.14–1.35 (m, 48H; C*H*$_2$), 1.87 (m, 8H; ArCHC*H*$_2$), 1.99 (m, 8H; C*H*$_2$CH=CH$_2$), 3.46–3.64 (br, 16H; OCH$_2$C*H*$_2$N), 4.02 (br, 8H; OC*H*$_2$CH$_2$N), 4.21 (br, 8H; OC*H*$_2$CH$_2$N), 4.72 (t, ^3J (H,H) = 7.5, 4H; ArC*H*), 4.86–4.98 (m, 8H; CH=C*H*$_2$), 5.75 (m, 4H; C*H*=CH$_2$), 6.61 (br s, 4H; Ar*H*), 6.66 (m, 8H; Ar*H*), 6.83 (br, 4H; Ar*H*), 6.96 (d, ^3J (H,H) = 8.6, 8H; Ar*H*), 7.46 (m, 8H; Ar*H*), 8.05 (dd, ^3J (H,H) = 8.6, ^4J (H,H) = 1.6, 8H; Ar*H*), 8.21 ppm (br s, 8H; N*H*); δ_C(126 MHz, [D$_6$]DMSO, 30 °C) 27.4 (*C*H$_2$), 28.2 (*C*H$_2$), 28.4 (*C*H$_2$), 28.8 (*C*H$_2$), 29.0 (*C*H$_2$), 29.2 (*C*H$_2$), 33.1 (*C*H$_2$CH=CH$_2$), 34.2 (ArCH*C*H$_2$), 34.8 (Ar*C*H), 42.0 (OCH$_2$*C*H$_2$N), 66.6 (O*C*H$_2$CH$_2$N), 114.1 (CH=*C*H$_2$), 114.3 (*Ar*H), 115.4 (*Ar*H), 125.6 (*Ar*CH), 126.1 (*Ar*H), 131.1 (*Ar*N), 136.4 (*Ar*H), 138.6 (*C*H=CH$_2$), 144.9 (*Ar*N), 154.3 (*Ar*OCH$_2$), resorcinarene core *Ar*H's not visible; δ_C(126 MHz, [D$_6$]acetone, 30 °C) 29.0 (*C*H$_2$), 29.8 (*C*H$_2$), 30.1 (*C*H$_2$), 30.4 (*C*H$_2$), 30.6 (*C*H$_2$), 30.8 (*C*H$_2$), 34.5 (*C*H$_2$CH=CH$_2$), 35.8 (ArCH*C*H$_2$), 36.3 (Ar*C*H), 43.5 (OCH$_2$*C*H$_2$N), 68.1 (O*C*H$_2$CH$_2$N), 114.6 (CH=*C*H$_2$), 115.1 (*Ar*H), 116.3 (*Ar*H), 127.2 (*Ar*CH), 127.3 (*Ar*H), 132.9 (*Ar*NH), 137.2 (*Ar*H), 139.9 (*C*H=CH$_2$), 146.2 (*Ar*NO$_2$), 156.0 (*Ar*OCH$_2$), resorcinarene core *Ar*H's not visible; *m/z (*ESI-TOF) 2394 (M + K$^+$, 38%), 2378 (M + Na$^+$, 100).

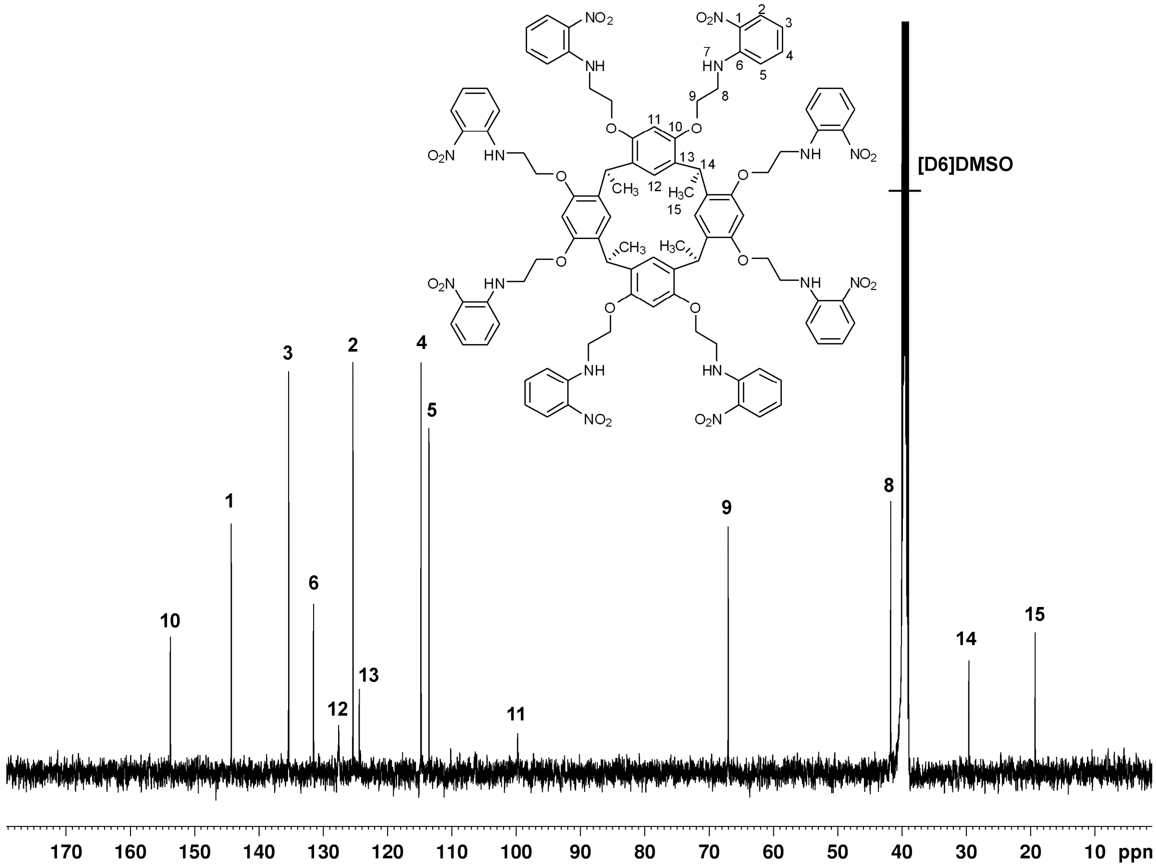
Octapodand 5 procedure B:

Tetra-1-decenyl resorcinarene (0.20 g, 0.19 mmol) and K$_2$CO$_3$ (0.43 g, 3.10 mmol) were suspended in dry acetonitrile (30 ml) under nitrogen atmosphere and refluxed for 15 minutes followed by the addition of *o*-nitro-*N*-(2-methanesulfonyloxyethyl)aniline (0.43 g, 1.70 mmol) in acetonitrile (10ml). The resulting yellow suspension was refluxed for 46 hours, filtrated with suction and evaporated under reduced pressure. The residue was suspended in water and extracted with dichloromethane; organic layer was dried over MgSO$_4$ and evaporated to dryness. The product was purified with flash chromatography (SiO$_2$; CHCl$_3$:MeOH), dissolved in acetone and precipitated from water with an addition of NaCl. The resulting bright yellow powder (0.30 g, 65 %) was filtrated with suction and dried under vacuum, mp 75–77 °C.

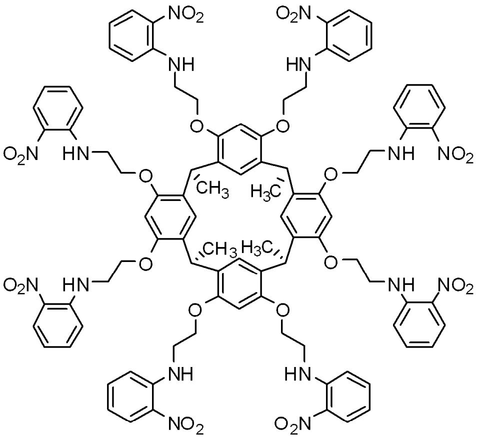
1H NMR spectrum of **1** in [D6]DMSO at 120 C

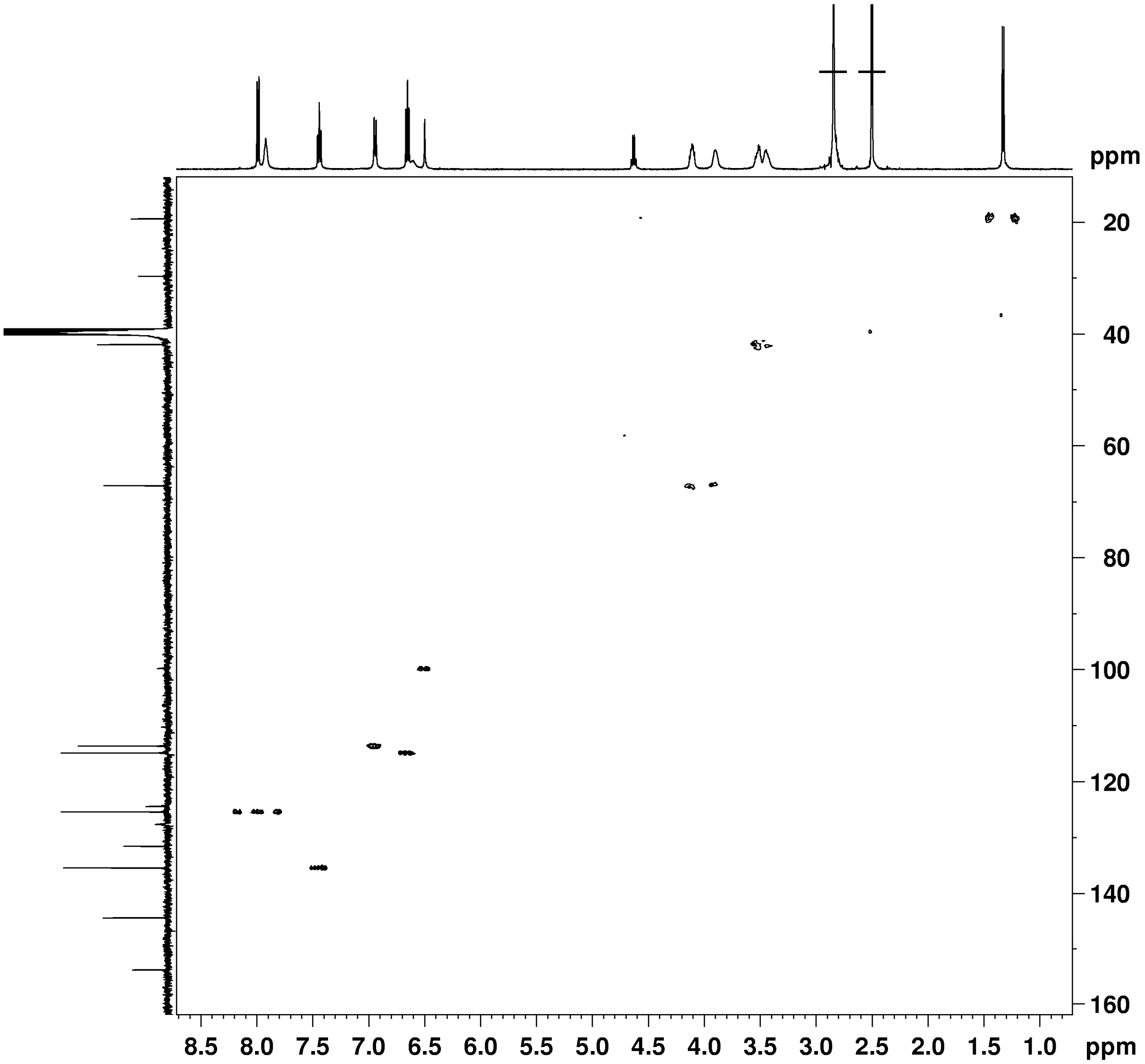


13C NMR spectrum of 1 in [D6]DMSO at 120 C

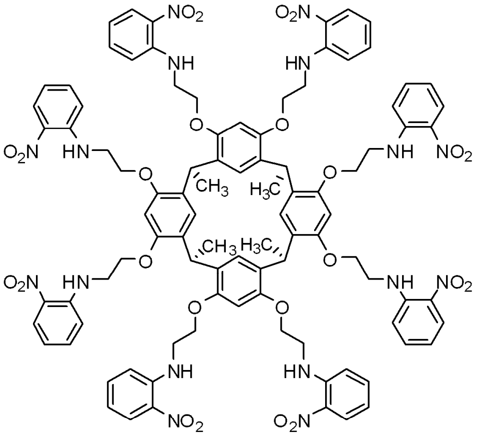


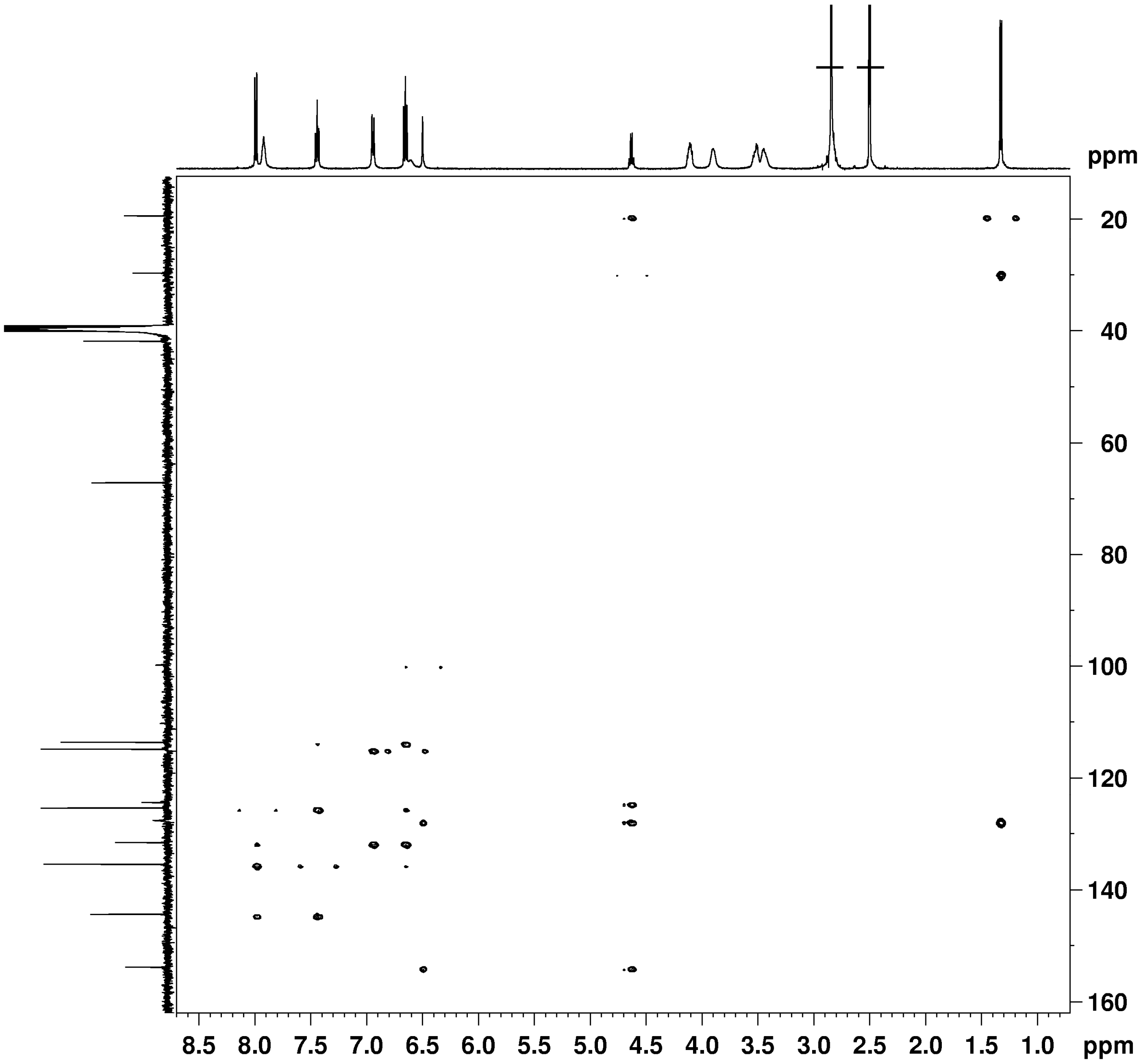
1H, 13C HMQC spectrum of 1 in [D6]DMSO at 120 C



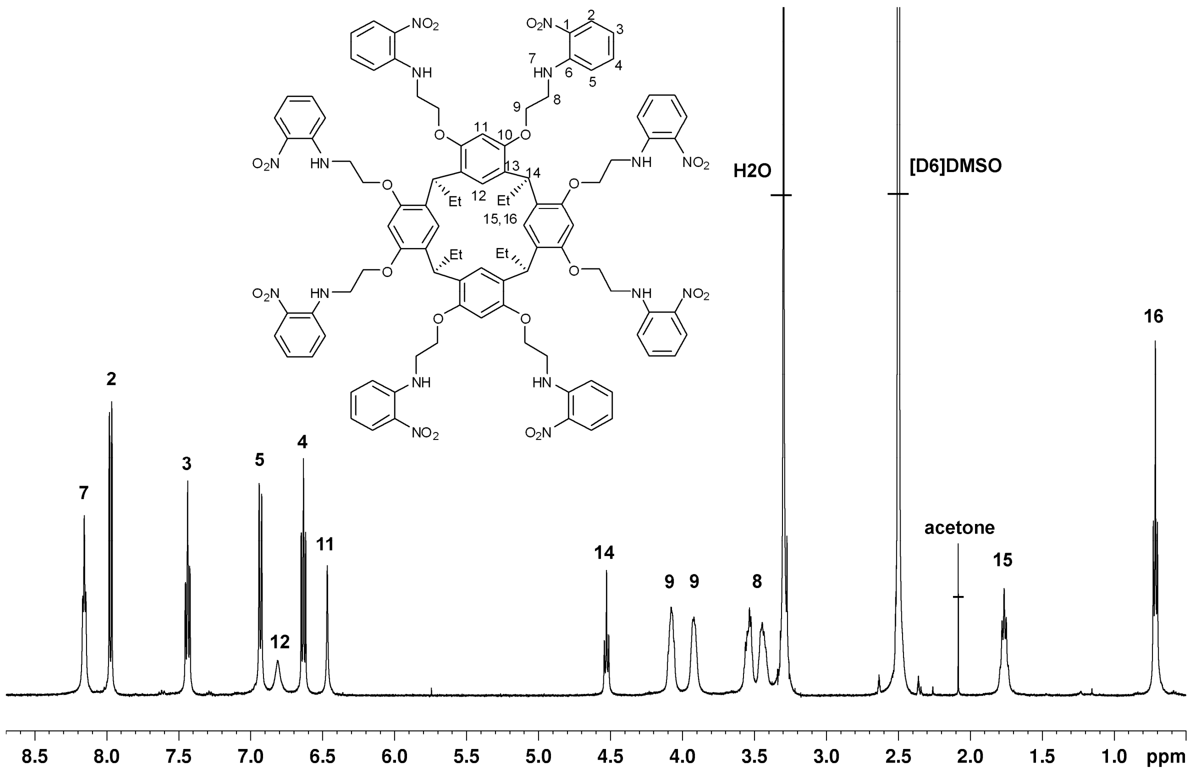


1H, 13C HMBC spectrum of 1 in [D6]DMSO at 120 C

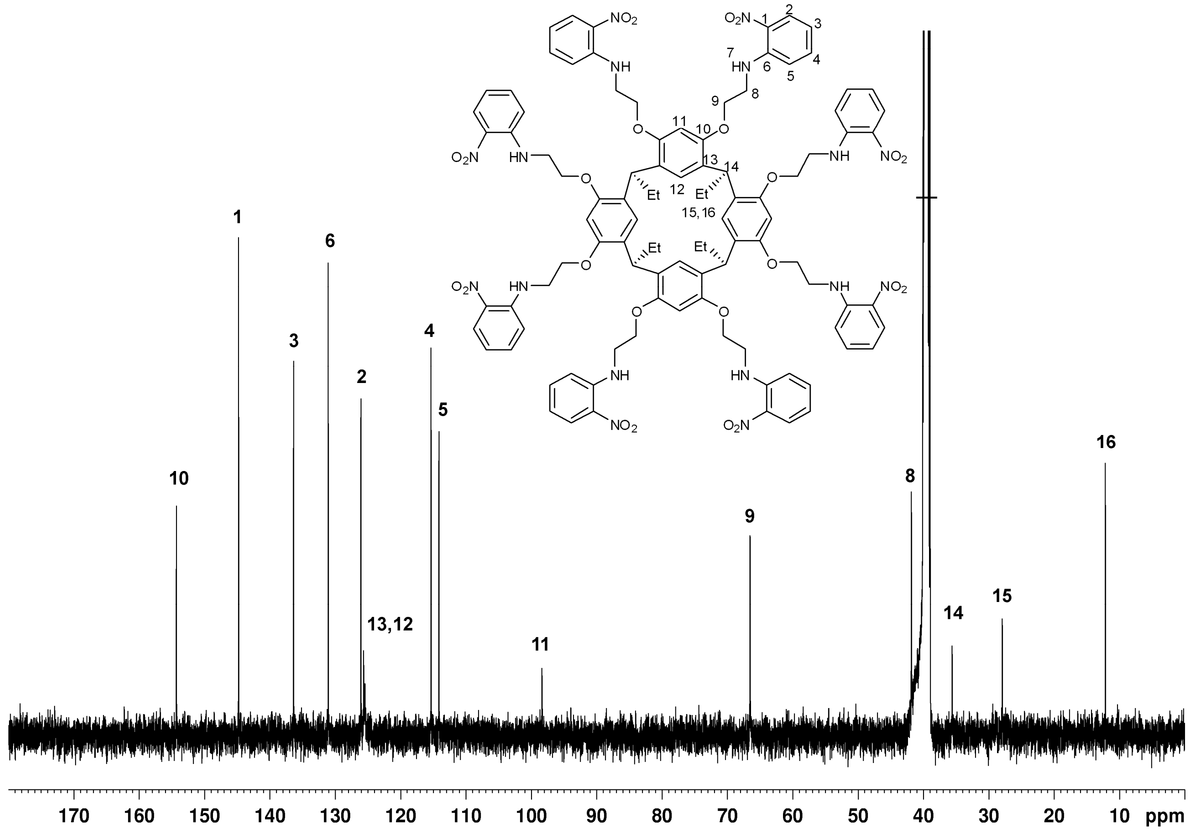




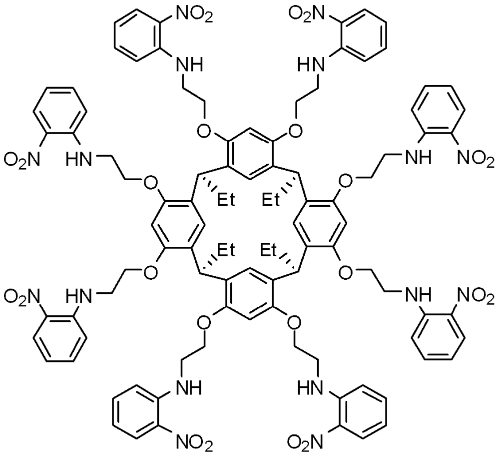
1H NMR spectrum of 2 in [D6]DMSO at 30 C

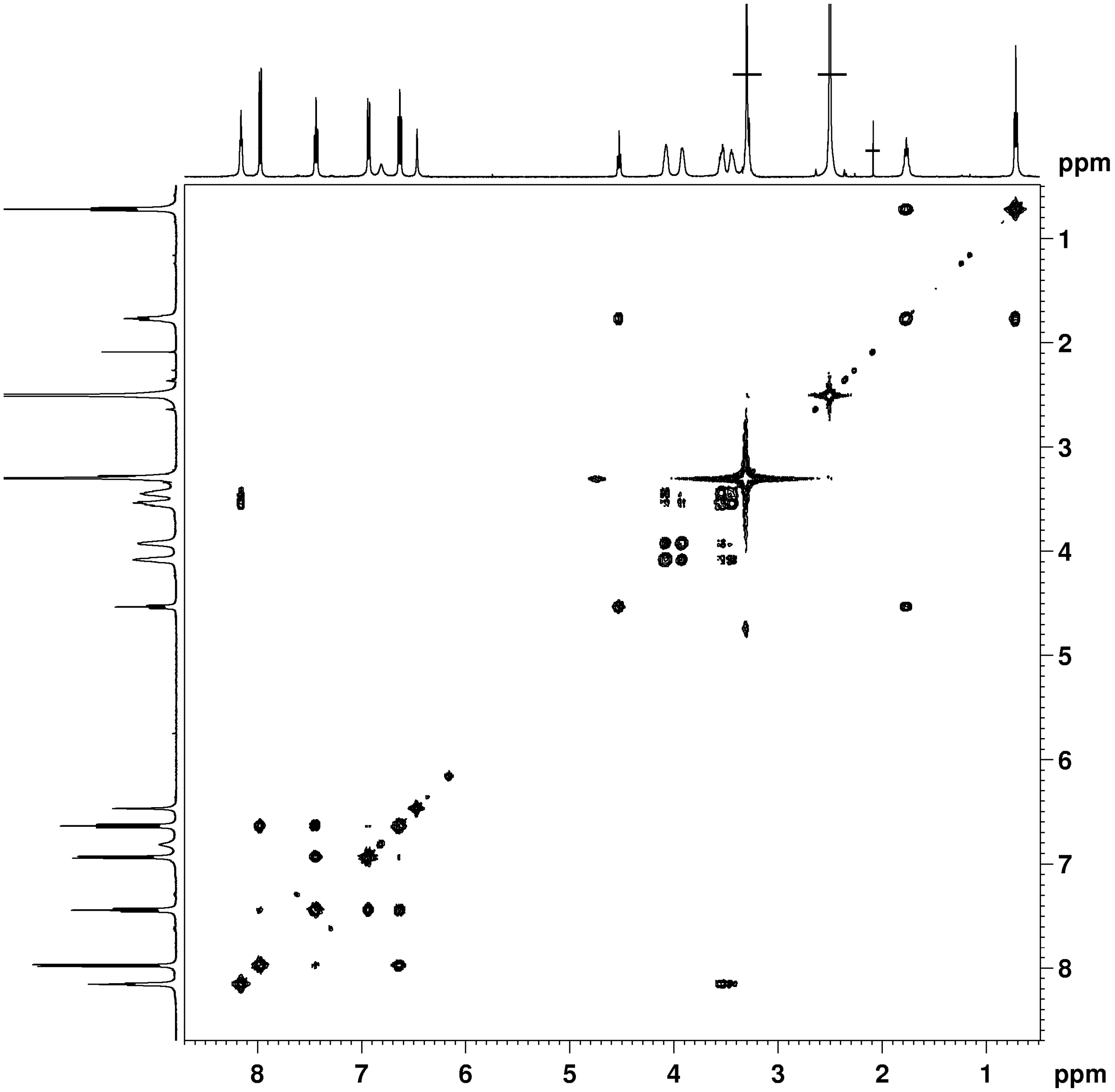


13C NMR spectrum of 2 in [D6]DMSO at 30 C

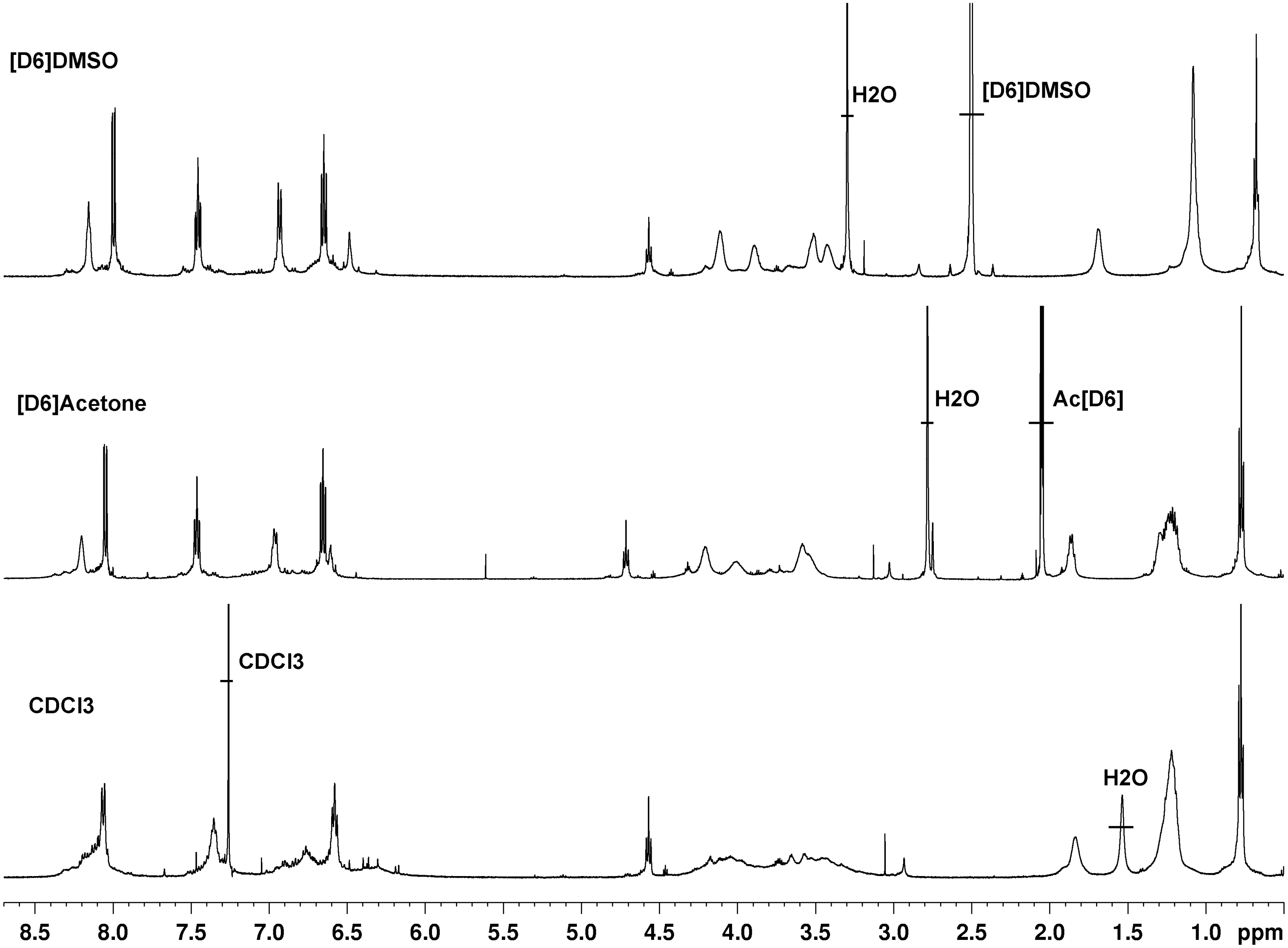


1H, 1H COSY spectrum of 2 in [D6]DMSO at 30 C

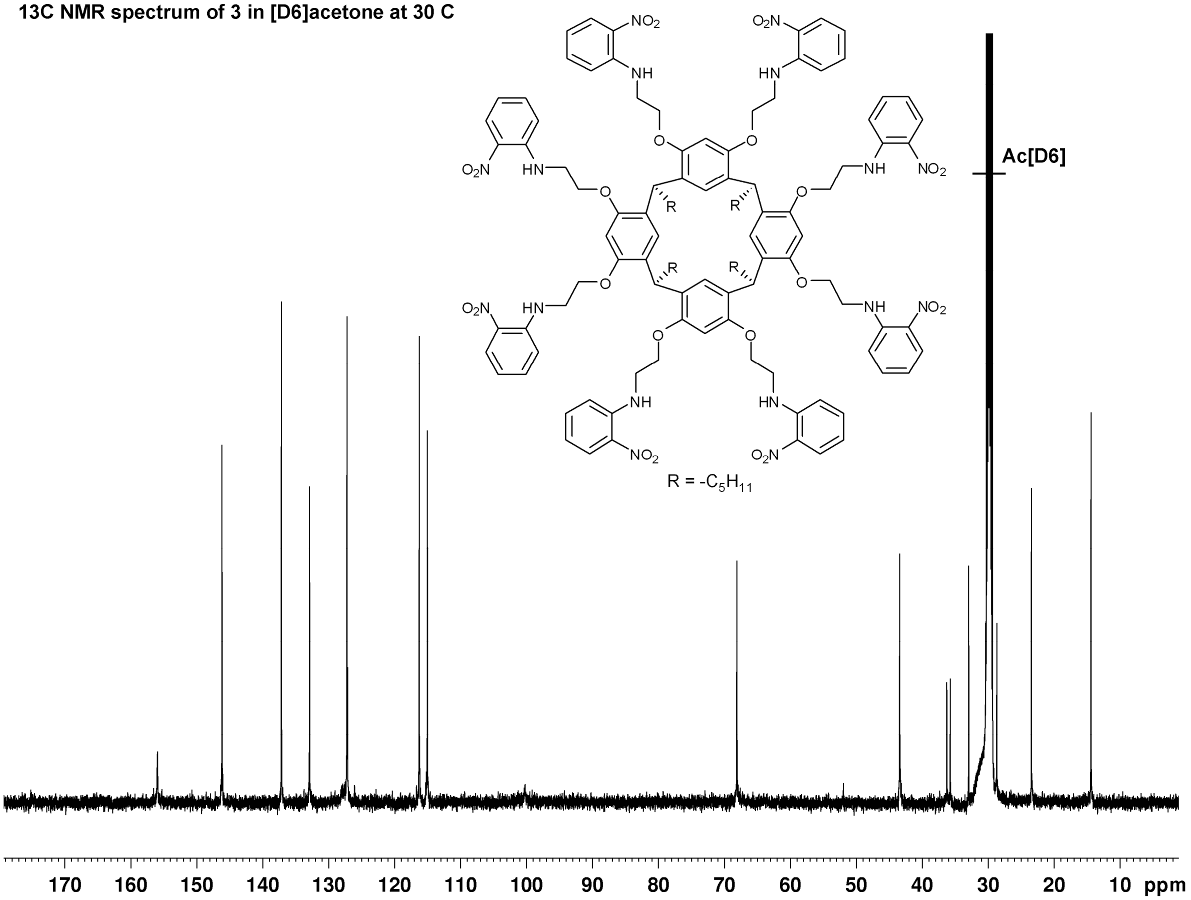




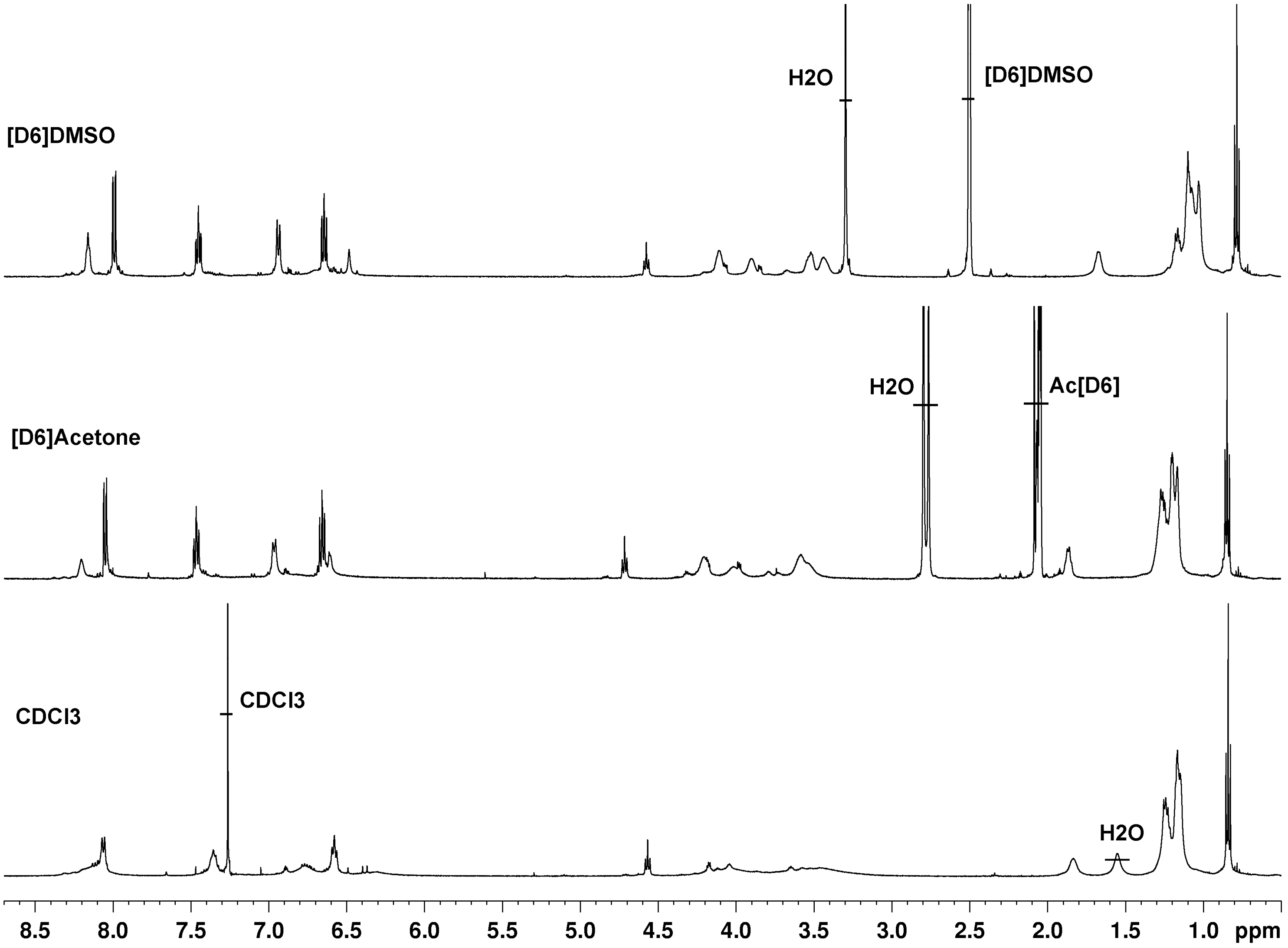
1H NMR spectra of 3 at 30 C



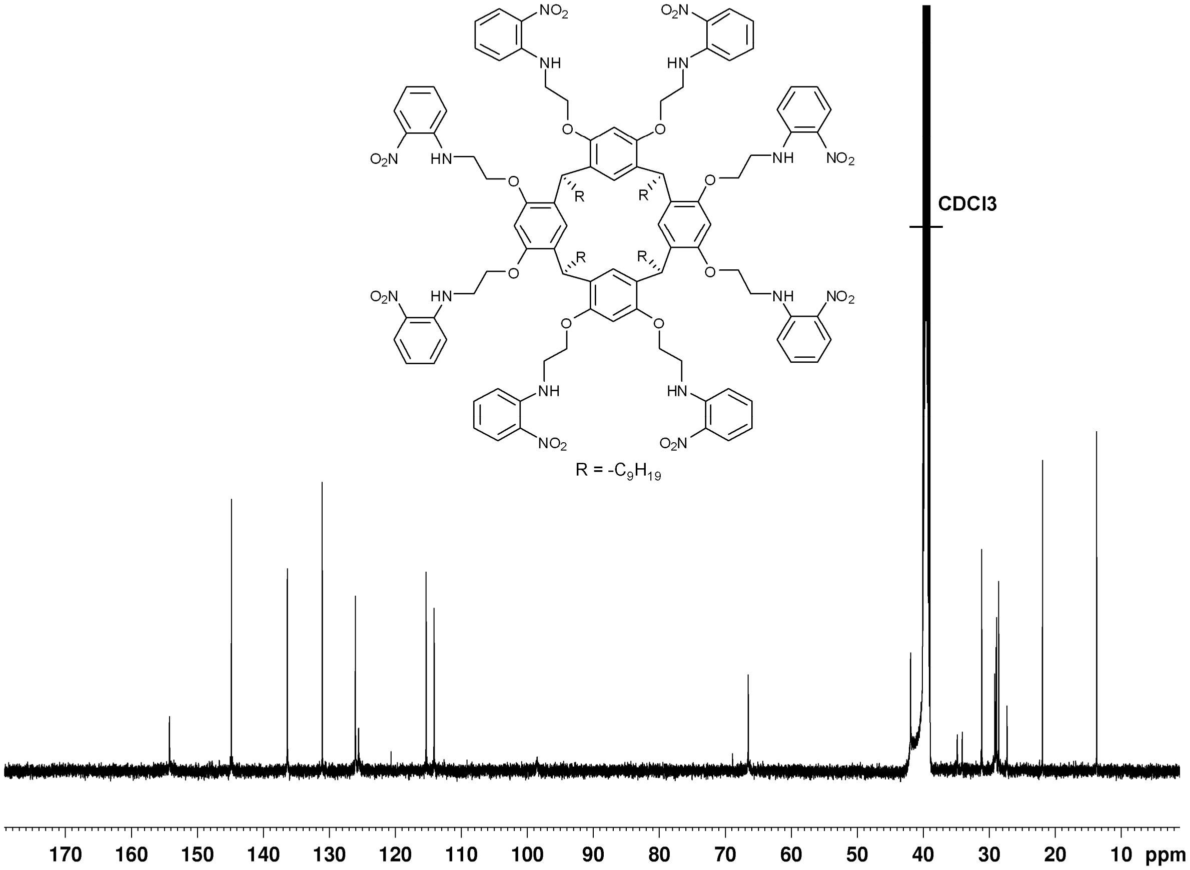
13C NMR spectrum of 3 in [D6]acetone at 30 C



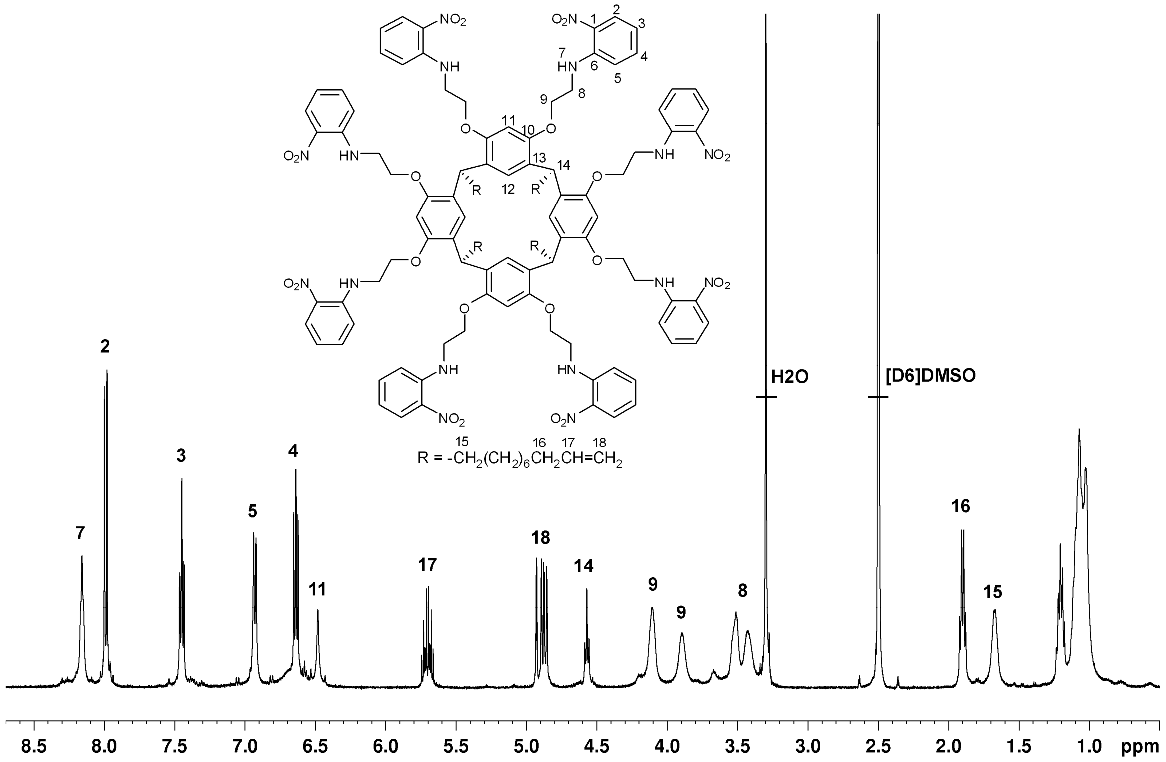
1H NMR spectra of 4 at 30 C



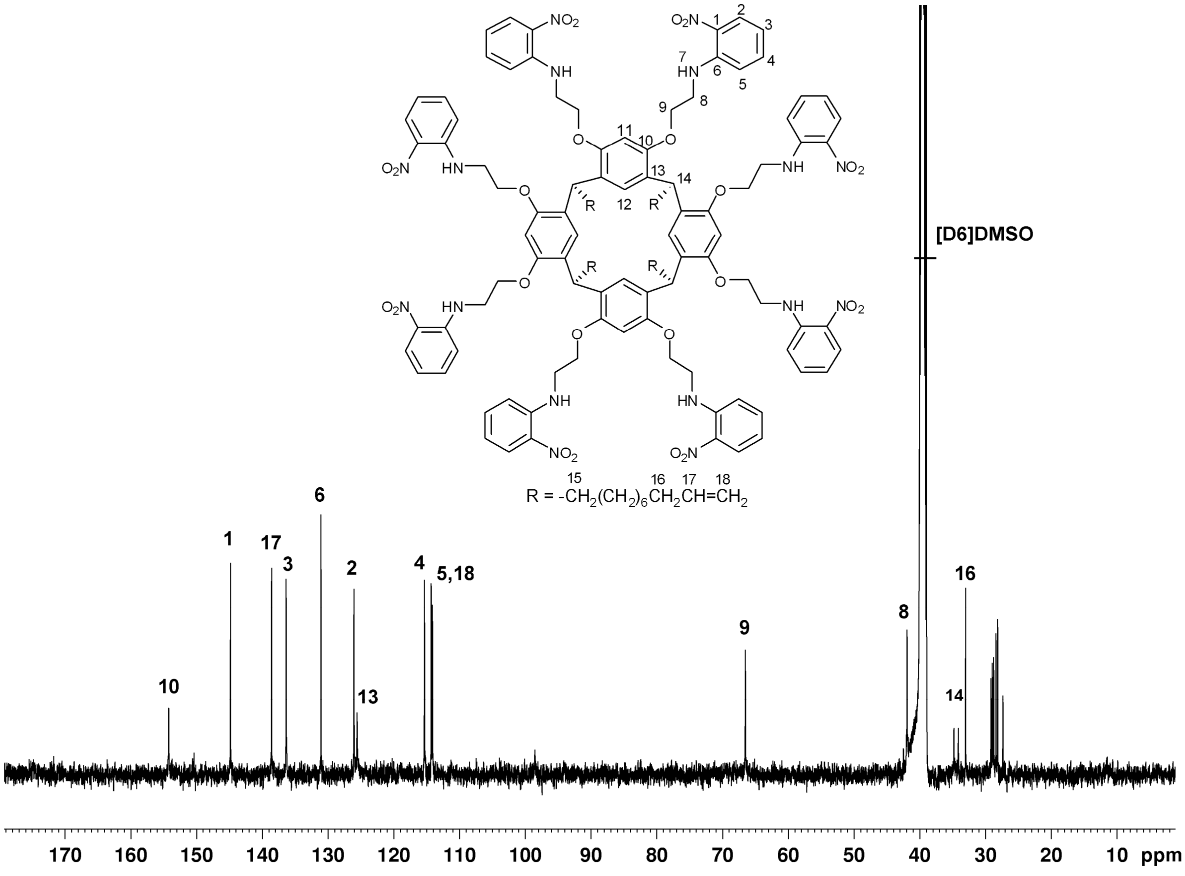
13C NMR spectrum of 4 in [D6]DMSO at 30 C



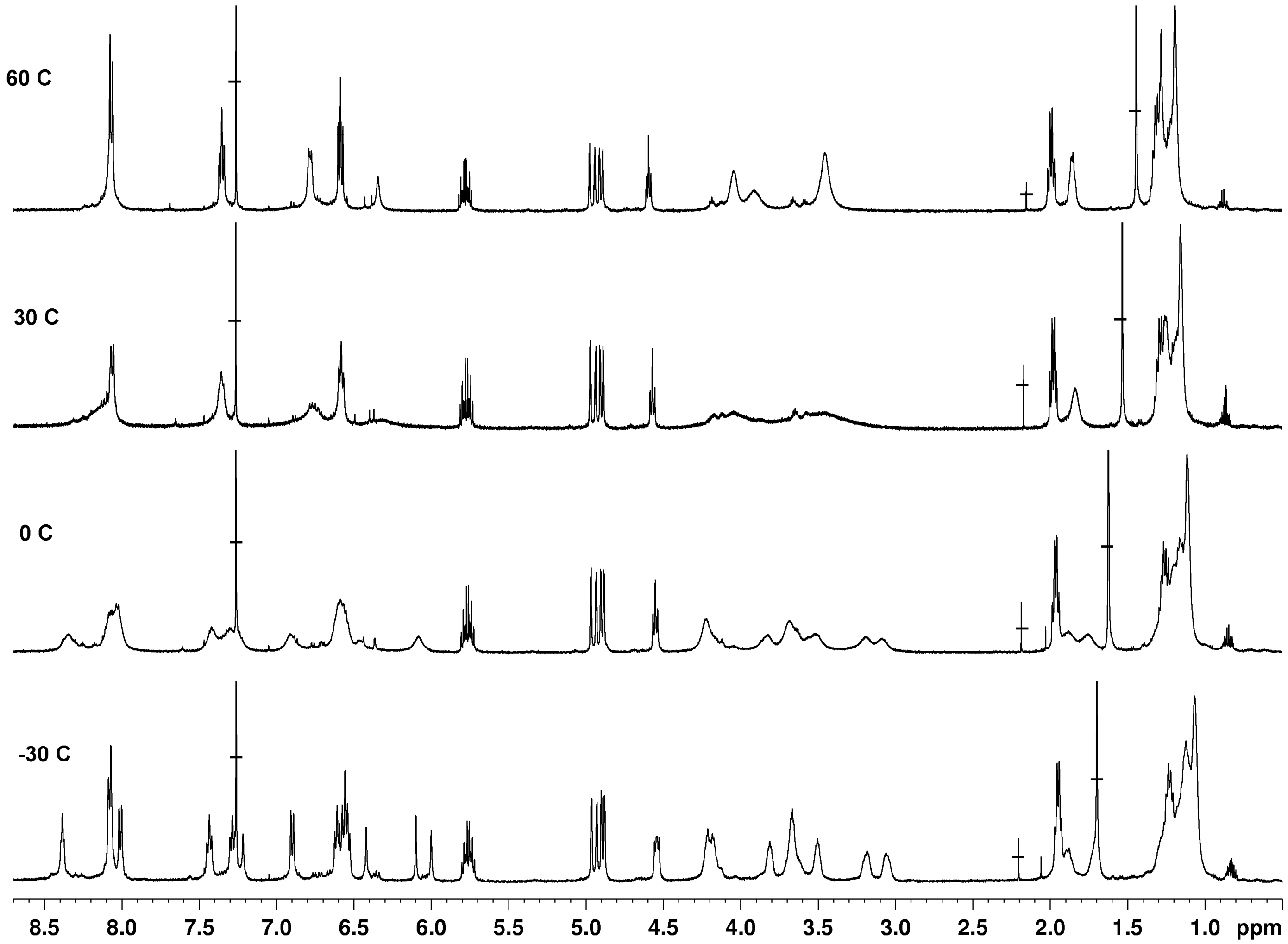
1H NMR spectra of 5 in [D6]DMSO at 30 C



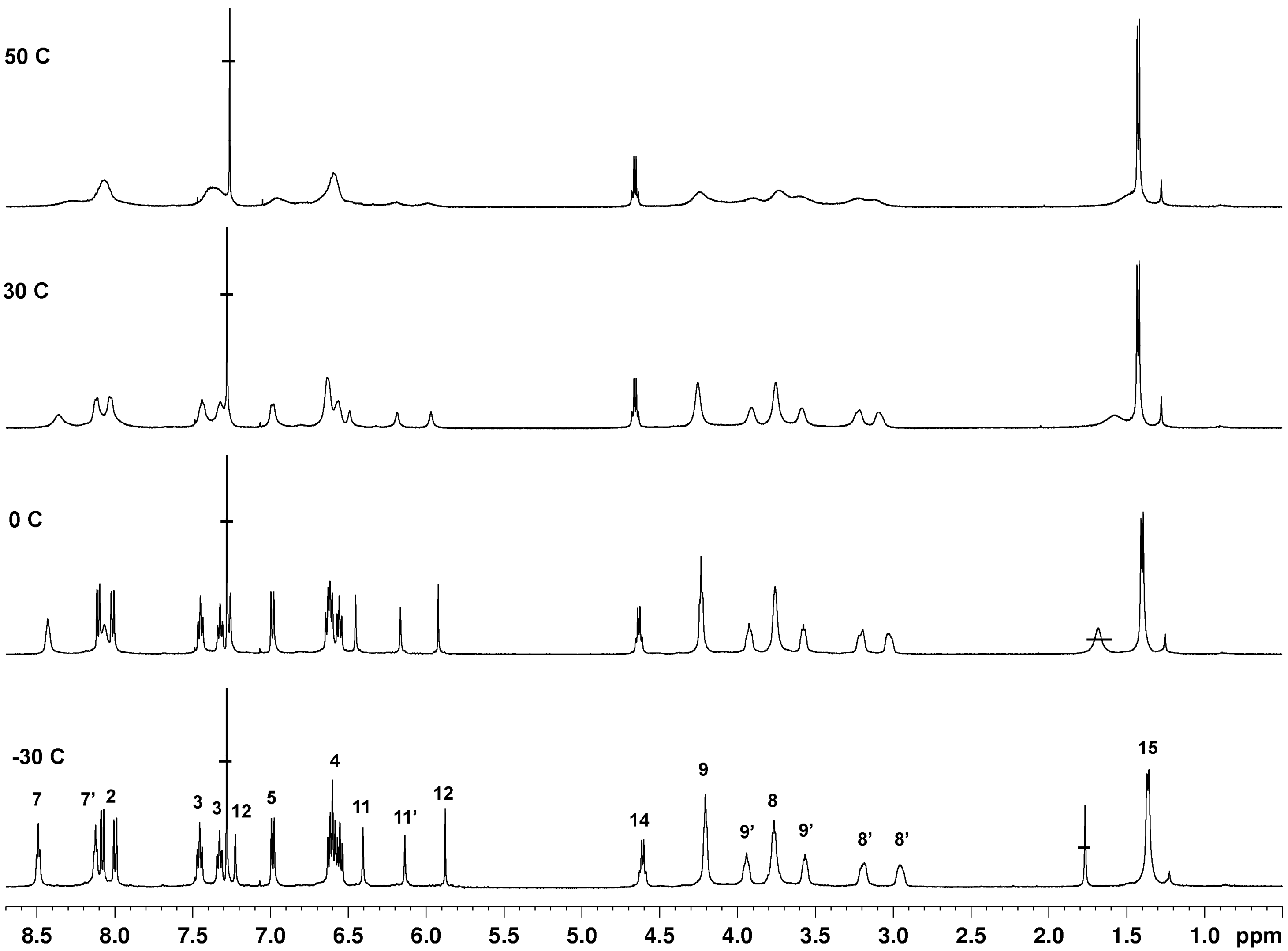
13C NMR spectrum of 5 in [D6]DMSO at 30 C



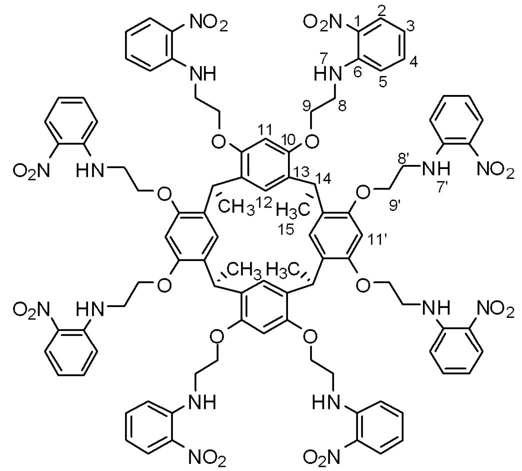
1H NMR spectra of 5 in CDCl3

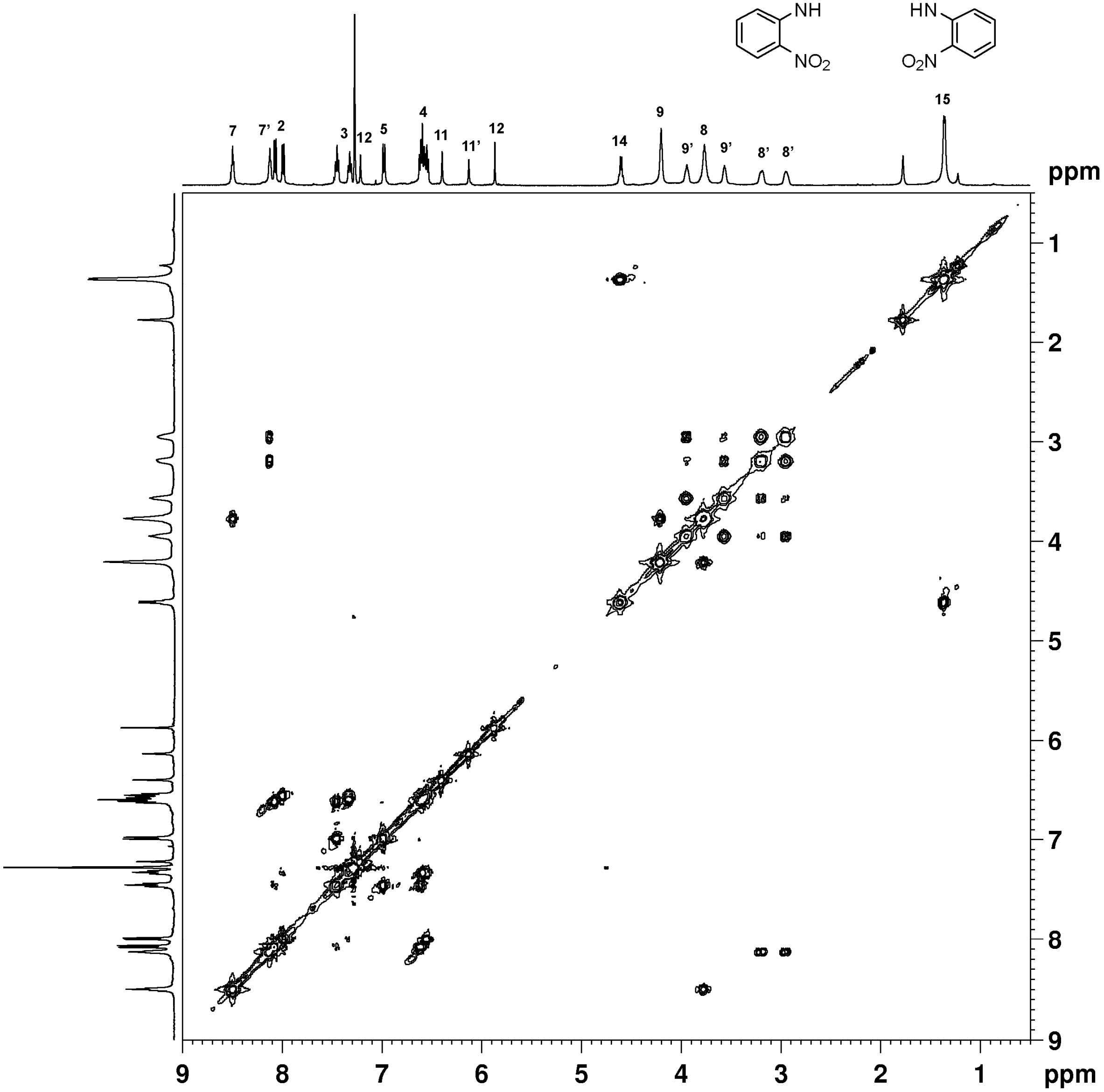


1H NMR spectra of 1 in CDCl3



1H, 1H COSY spectrum of 1 in CDCl3 at -30 C





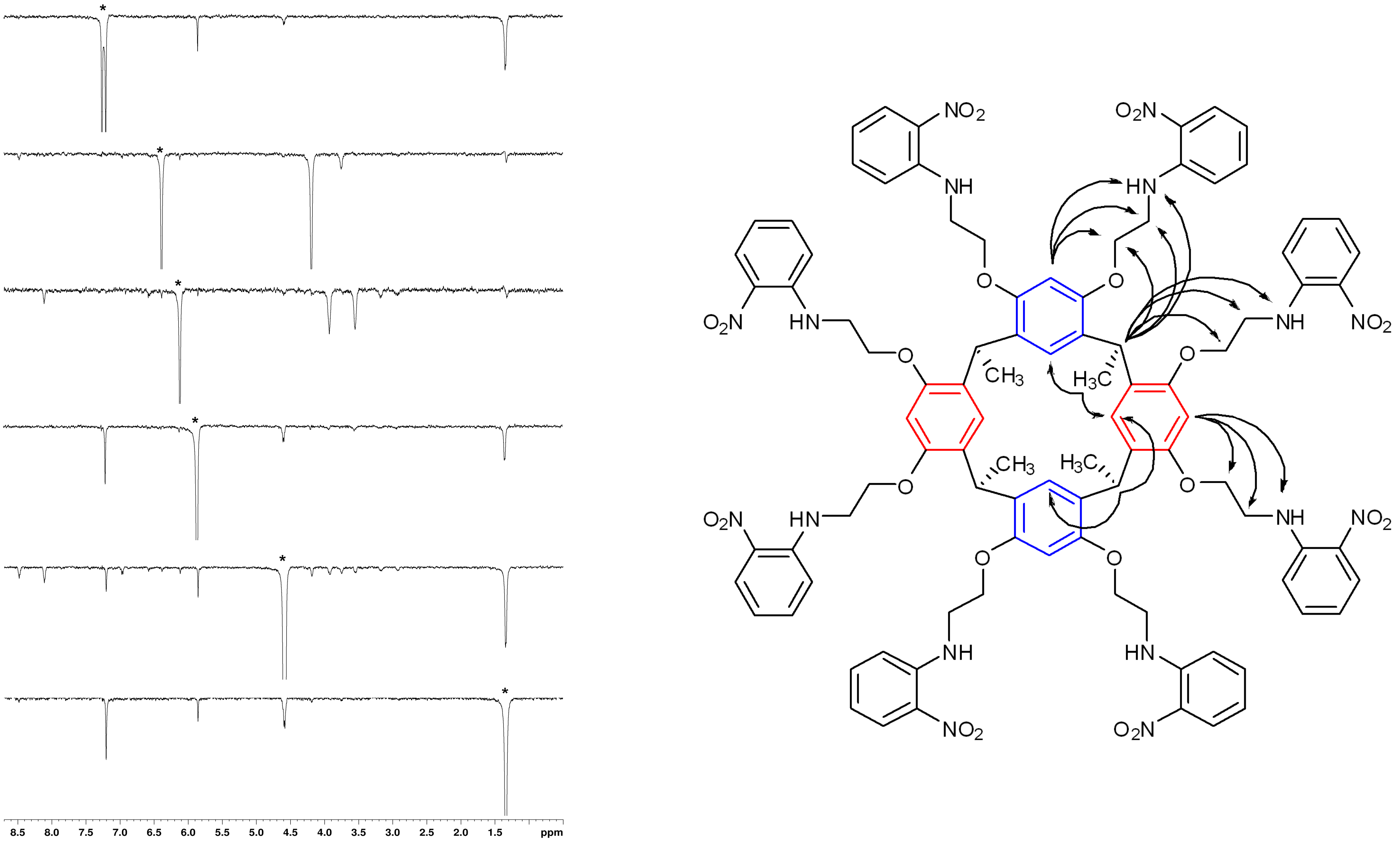
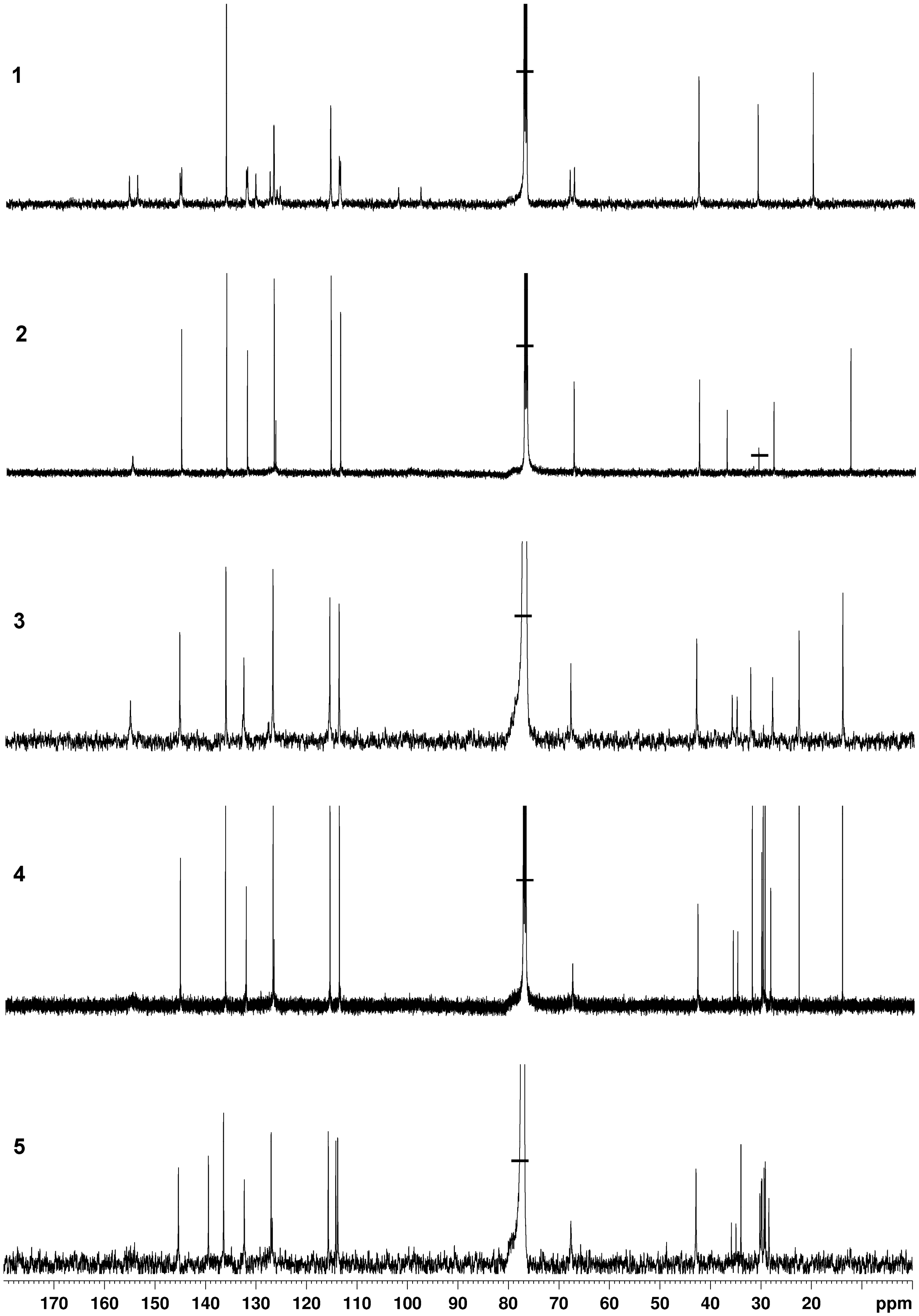
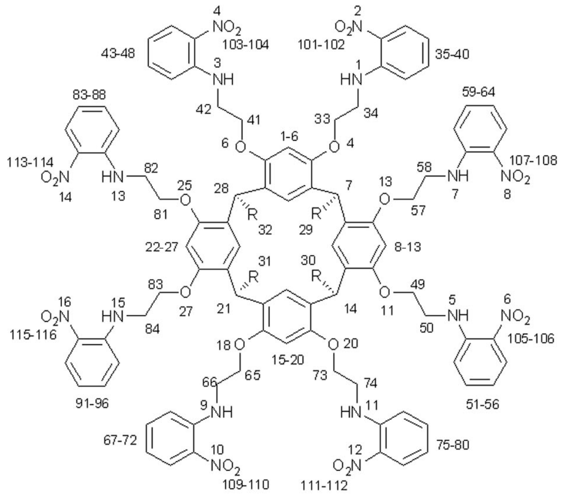


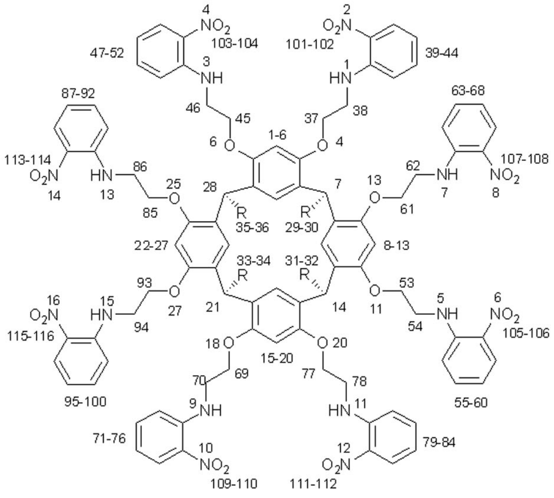
Figure 1. 1D NOE spectra of **1** in $CDCl_3$ at -30 ºC; 55 ms, 61.9 dB irradiation at a resonance frequency marked with an asterisk. Negative NOE from each resonance is indicated in a scheme, blue and red phenyl rings are magnetically non-equivalent.

13C NMR spectra of 1-5 in CDCl3 at 30 C

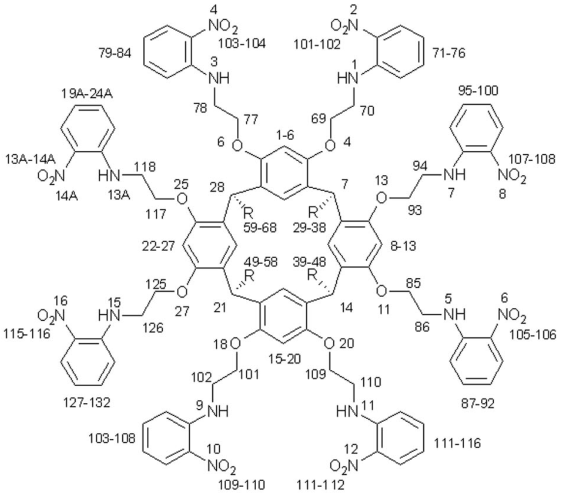




1: R = -CH_3



2: R = -CH_2CH_3



5: R = -$(CH_2)_8CH=CH_2$

Figure 2. Full crystallographic numbering of **1**, **2** and **5**.

Details of X-ray structure analysis

Structure 1A: Amine hydrogens H1N, H3N, H5N, H7N, H9N, H13N and H15N were located from the difference Fourier map. DFIX was used for amine hydrogen H15N.

Structure 1B: Disordered nitroaniline rings over two positions: (N7, C59–C64, N8, O57, O58) with site occupancy of A:B = 0.5:0.5, (N13, C83–C88, N14, O53, O54) with site occupancy of A:B = 0.7:0.3, (C89–C90) with site occupancy of A:B = 0.5:0.5 and (N15, C91–C96, N14, O55, O56) with site occupancy of A:B = 0.6:0.4, which cause five checkCIF A-level alerts. Amine hydrogens H1N, H3N, H5N, H9N and H11N were located from the difference Fourier map. Restrains EXYZ, EADP and SADI were used for the disordered part; disordered benzene rings were constrained using AFIX. DFIX was used for amine hydrogens H1N, H3N, H5N, H9N and H11N.

Structure 2A: Disordered C34 over two positions with site occupancy of A:B = 0.7:0.3. Amine hydrogens H1N, H7N, H9N and H11N were located from the difference Fourier map. Restrain SADI was used for amine hydrogens H1N, H7N, H9N and H11N. Benzene ring C87–C92 was constrained using AFIX. Residual electron density is located around side arm O27 with Q1 next to O116 but reasonable disorder model could not be constructed. Large atomic displacement parameters of the nitroaniline side arms cause a checkCIF A-level alert.

Structure 2B: Disordered nitroaniline ring (N7, C63–C68, N8, O50, O51) with site occupancy A:B = 0.6:0.4, which causes a checkCIF A-level alert. Amine hydrogens H3N, H5N, H11N, H13N and H15N were located from the difference Fourier map. Restrain SADI was used for amine hydrogens H3N, H5N, H11N, H13N and H15N. Restrain SADI was used for the disordered part of the molecule; disordered benzene ring was constrained using AFIX.

Structure 2C: Amine hydrogens H1N, H3N, H5N, H7N, H9N, H11N, H13N and H15N were located from the difference Fourier map. SQUEEZE[3] was applied to remove residual electron density caused by badly disordered nitromethane molecule.

Structure 2D: Amine hydrogens H1N, H3N, H5N, H7N, H9N, H13N, H11N and H15N were located from the difference Fourier map. SQUEEZE was applied to remove residual electron density caused by diffuse water molecules. Restrain SADI was used for all amine hydrogens. Disordered acetonitrile over two positions with site occupancy of 0.8:0.2. Constrain EXYZ, EADP and DFIX were used for the disordered part. Residual electron density around the disordered acetonitrile molecule.

Structure 5A: Data completeness was 70 % due to poorly diffracting crystal. Disordered C33–C34 over two positions with site occupancy of A:B = 0.5:0.5, disordered nitroaniline ring (N13, C19-C24, N14, O13, O14) with site occupancy of A:B = 0.5:0.5. Restrains SAME and SADI were used for the disordered part. DFIX was used for C32–C38, C45–C48, C55–C58, C65–C68. Low quality of the crystal and disorder cause several checkCIF A-level alerts.

Table 1. Orientation of sidearm nitrogroups. ‘Out’ refers to the direction outwards the resorcinarene cavity and ‘in’ towards the cavity.

Structure	O4	O6	O11	O13	O18	O20	O25	O27
1A	out	out	horizontal	horizontal	out	vertical	down	down
1B	vertical	vertical	down	vertical[a]	vertical	vertical	vertical[a]	vertical[a]
2A	in	vertical	down	up	vertical	out	up	up
2B	vertical	vertical	down	vertical[a]	vertical	vertical	up	up
2C	vertical	vertical	down	down	vertical	vertical	up	up
2D	vertical	vertical	down	down	vertical	vertical	up	up
5A	in	in	up	up	out	out	up[a]	up

[a] disordered benzene ring

Table 2. List of intermolecular hydrogen bonds with bond lengths (D-A) in ångströms.

Structure	D-A / Å	D-A / Å	D-A / Å
1B	N5-O105 / 3.024(5)		
2A	N3-O103 / 3.421(6)	N5-O200 / 3.127(7)	N15-O109 / 3.125(7)
2B	N5-O105 / 3.074(8)	N15-O200 / 3.091(8)	
2C	N5-O105 / 3.038(5)		
2D	N5-O105 / 3.031(4)	N15-O50A / 3.107(5)	

Table 3. π-π interactions between aromatic rings.

Structure	**intermolecular face-to-face**	**intermolecular edge-to-face**	**intramolecular face-to-face**
1A	C75-C80⋯C1-C6	C51-C56⋯C22-C27	
	C59-C64⋯C67-C72		
	C35-C40⋯C43-C48		
1B	C35-C40⋯C35-C40	C75-C80⋯C67-C72	C43-C48⋯C67-C72
	C59-C64⋯C83-C88⋯C51-C56⋯C91-C96		
2A	C39-C44⋯C79-C84		C47-C52⋯C71-C76
	C63-C68⋯C87-C92⋯C55-C60⋯C95-C100		
2B	C39-C44⋯C39-C44	C71-C76⋯C39-C44	
	C47-C52⋯C79-C84	C79-C84⋯C71-C76	
	C63-C68⋯C87-C92⋯C55-C60⋯C95-C100		
2C	C39-C44⋯C39-C44	C71-C76⋯C39-C44	
	C47-C52⋯C79-C84	C79-C84⋯C71-C76	
	C55-C60⋯C95-C100⋯C63-C68⋯C87-C92		
2D	C39-C44⋯C39-C44	C71-C76⋯C39-C44	
	C47-C52⋯C79-C84	C79-C84⋯C71-C76	
	C63-C68⋯C87-C92⋯C55-C60⋯C95-C100		
5A	C71-C76⋯C103-C108		
	C79-C84⋯C111-C116		

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