

## Supporting Information

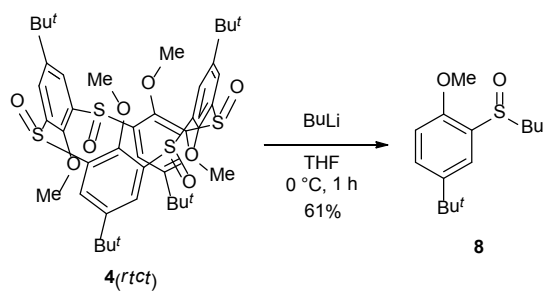
# Regioselective synthesis of 1,2- and 1,3-diaminothiocalix[4]arenes via nucleophilic aromatic substitution and their X-ray structures

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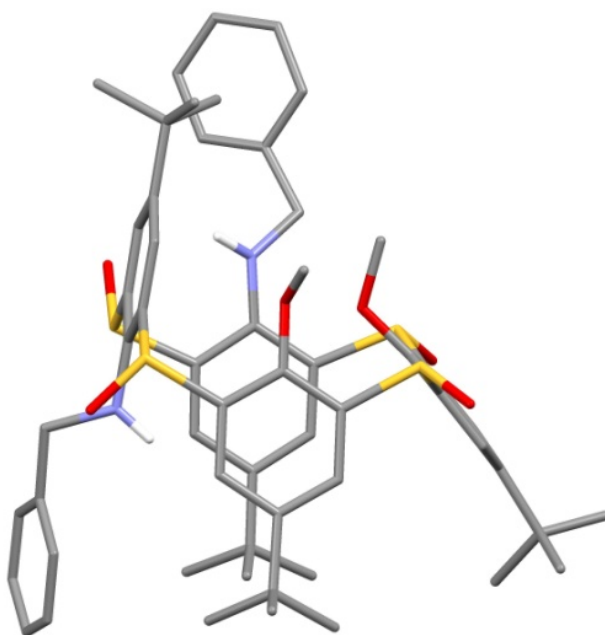
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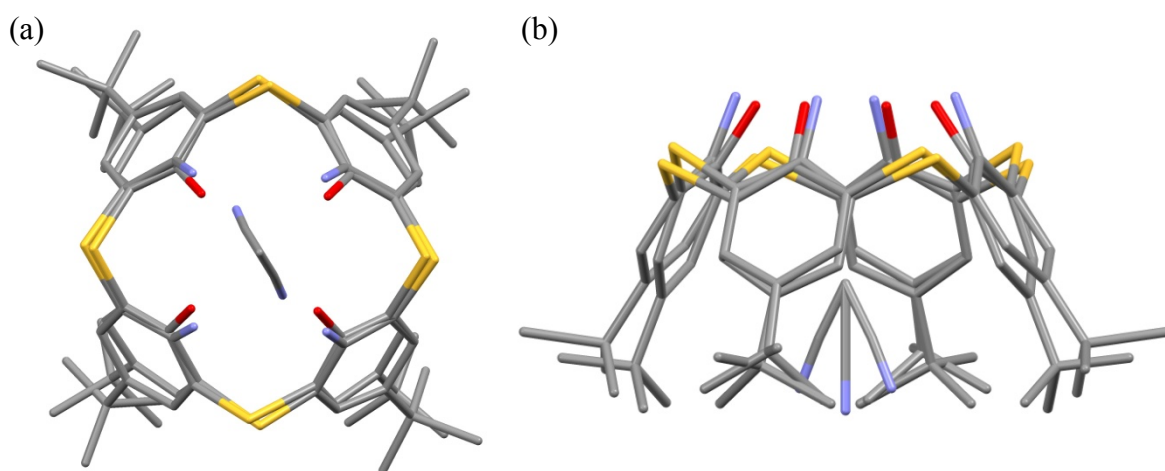
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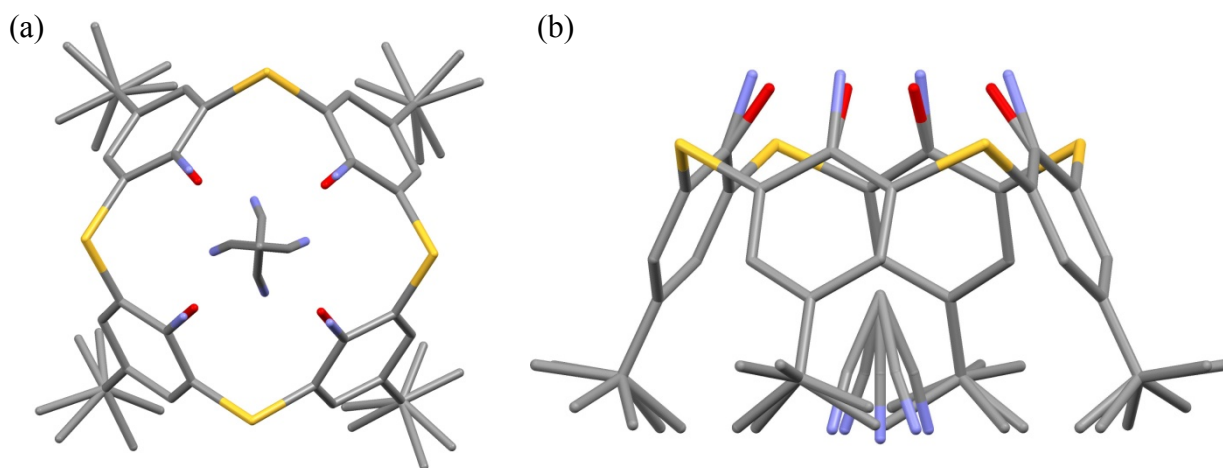
**Scheme S1.** Reaction of compound **4**(*rtct*) with butyllithium.



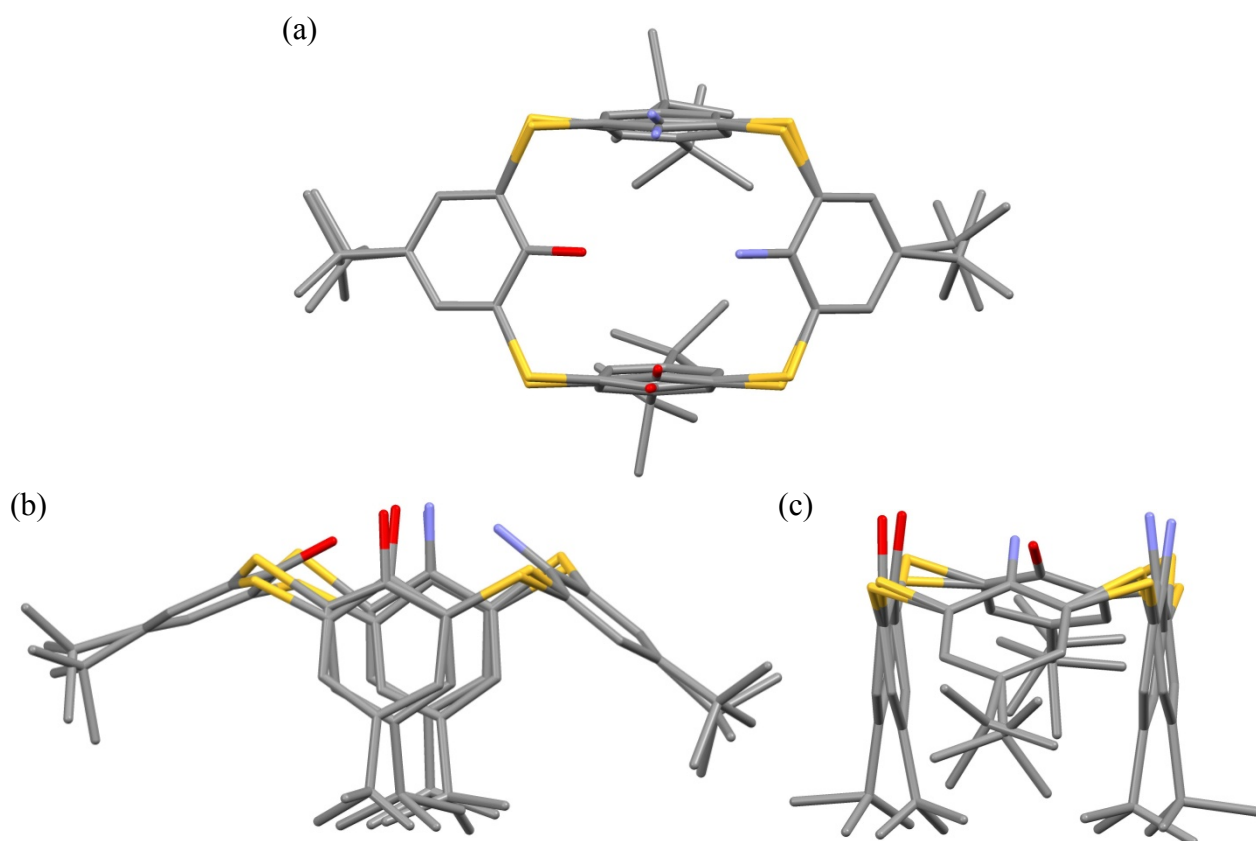
**Fig. S1.** X-ray structure of di(benzylamine) **7c**. Hydrogen atoms except for NH and solvent molecules are omitted for clarity.



**Fig. S2.** X-ray structure of **5b**·CH<sub>3</sub>CN: (a) Top view and (b) side view of disordered structure. Protons of the NH<sub>2</sub> and OH groups were not found. Hydrogen atoms are omitted for clarity.



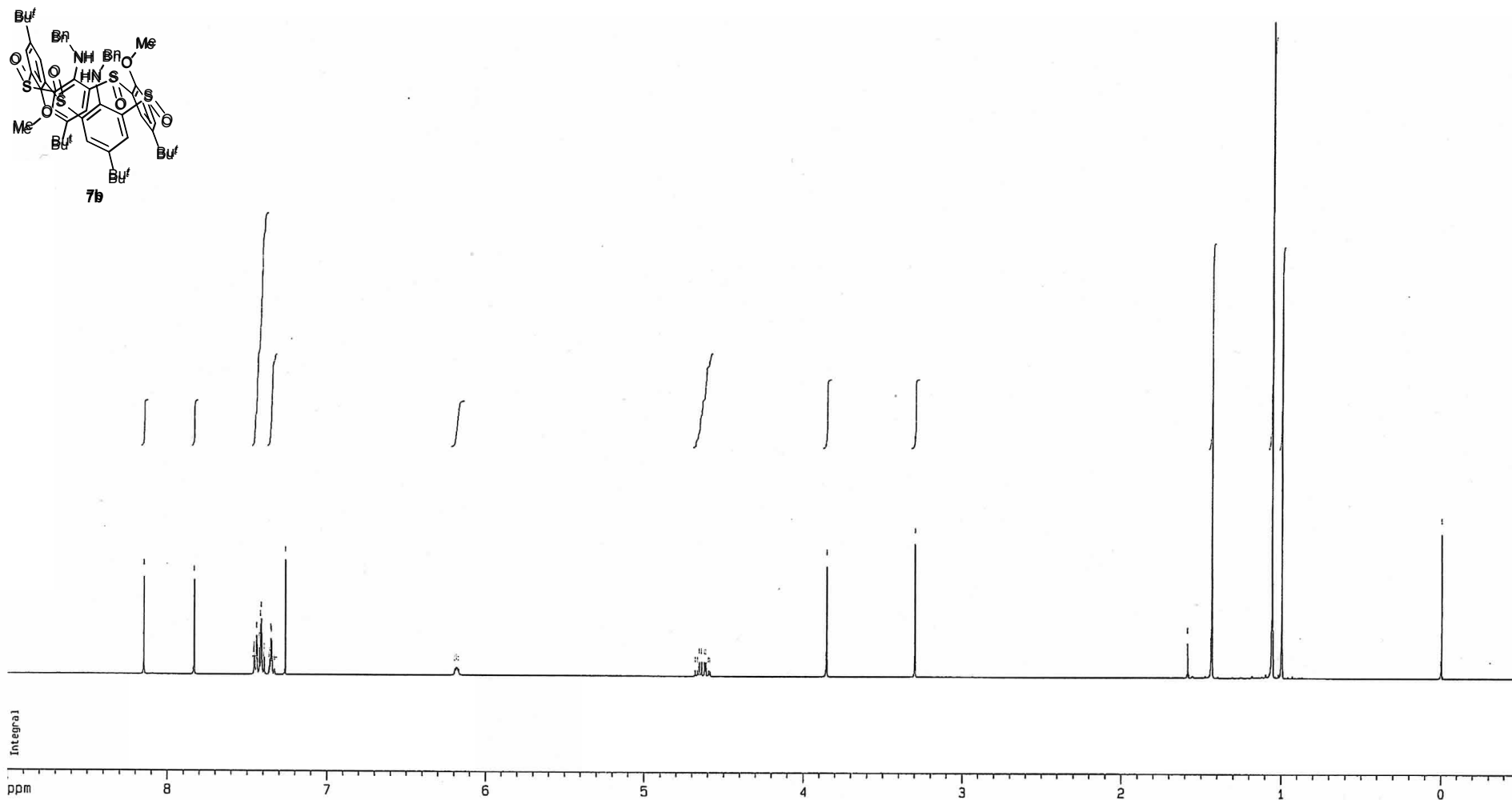
**Fig. S3.** X-ray structure of **5c**·CH<sub>3</sub>CN: (a) Top view and (b) side view of disordered structure. Protons of the NH<sub>2</sub> and OH groups were not found. Hydrogen atoms are omitted for clarity.



**Fig. S4.** X-ray structure of **5c**·CH<sub>3</sub>CN: (a) Top view and (b, c) side views of disordered structure. Protons of the NH<sub>2</sub> and OH groups were not found. Hydrogen atoms are omitted for clarity.

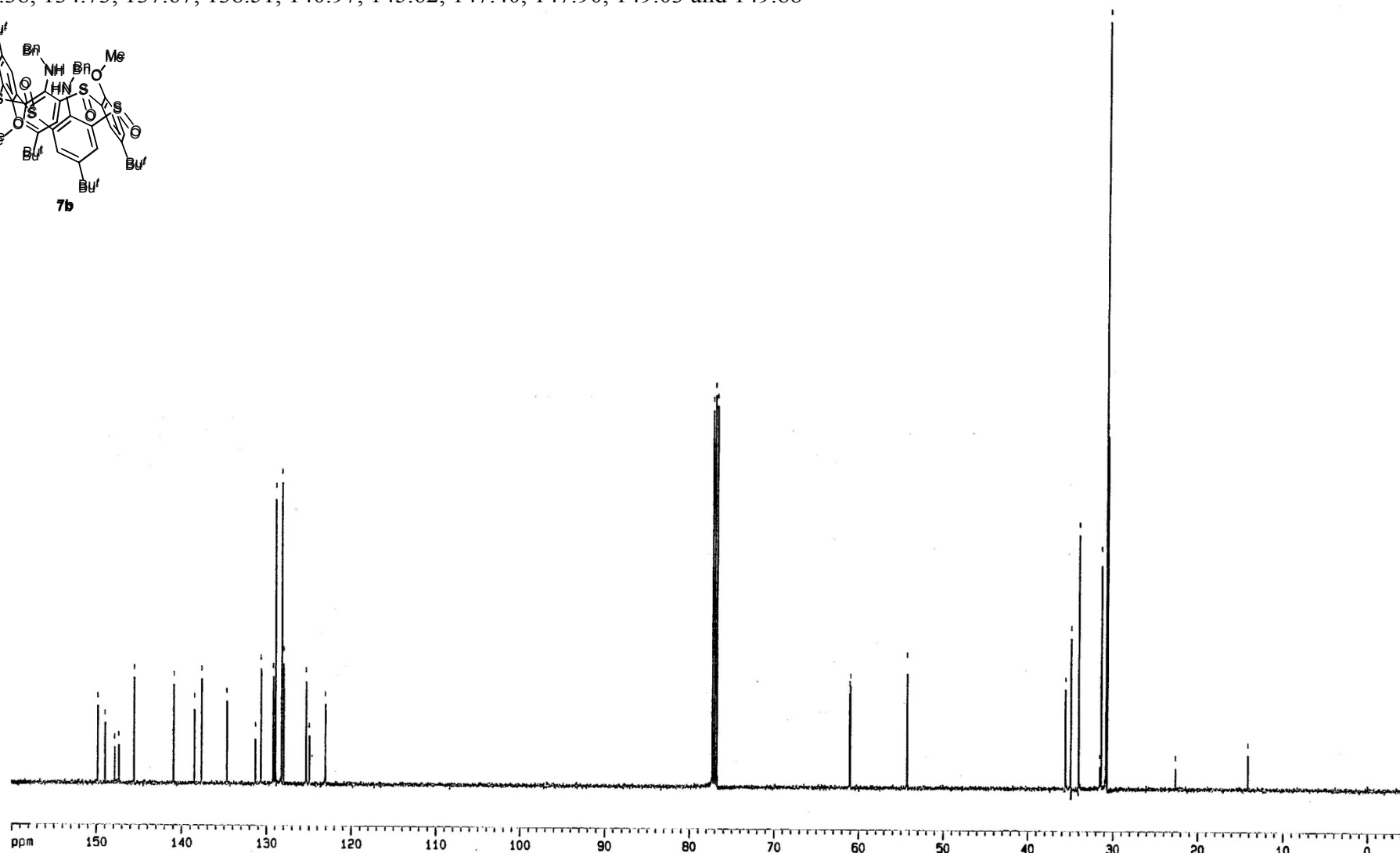
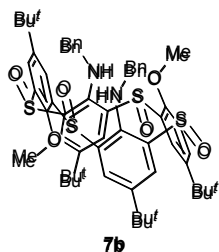
**25,27-Di(benzylamino)-26,28-dimethoxy-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (7b)**

$\delta_{\text{H}}$  (400 MHz) 1.00 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.06 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 1.44 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 3.30 (3 H, s, OCH<sub>3</sub>), 3.85 (3 H, s, OCH<sub>3</sub>), 4.60 (2 H, dd, *J* 12.7 and 5.66, NHCH<sub>2</sub> × 2), 4.66 (2 H, dd, *J* 12.7 and 5.66, NHCH<sub>2</sub> × 2), 6.17 (2 H, t, *J* 5.66, NHCH<sub>2</sub> × 2), 7.33–7.45 (14 H, m, ArH), 7.83 (2 H, s, ArH) and 8.15 (2 H, s, ArH)



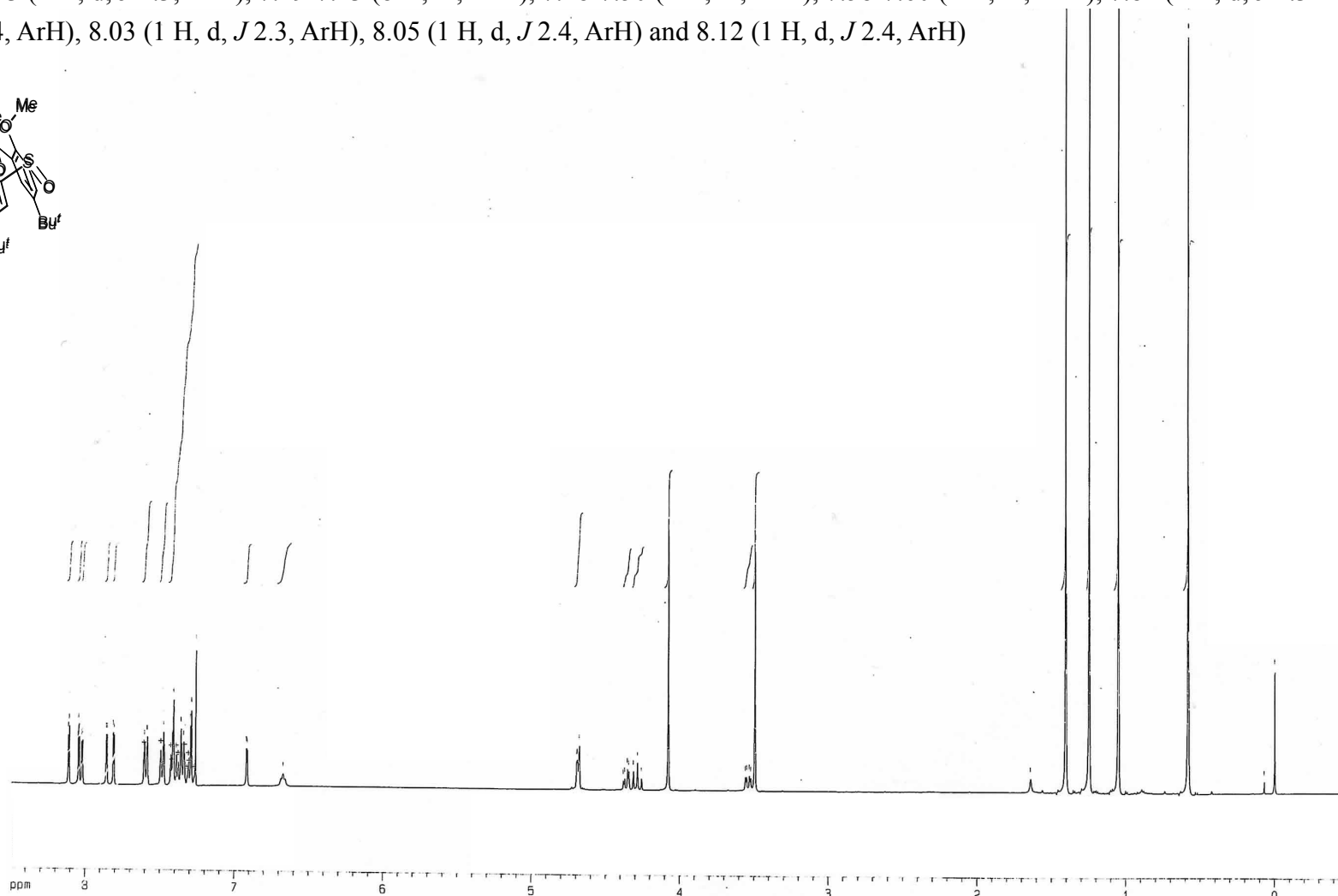
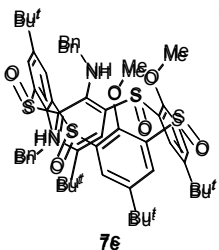
**25,27-Di(benzylamino)-26,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (7b)**

$\delta_C$  (100 MHz) 30.72, 30.84, 31.42, 34.06, 34.97, 35.62, 54.34, 61.03, 61.12, 123.12, 125.00, 125.37, 128.03, 128.27, 128.99, 129.25, 130.70, 131.38, 134.73, 137.67, 138.51, 140.97, 145.62, 147.40, 147.90, 149.03 and 149.88



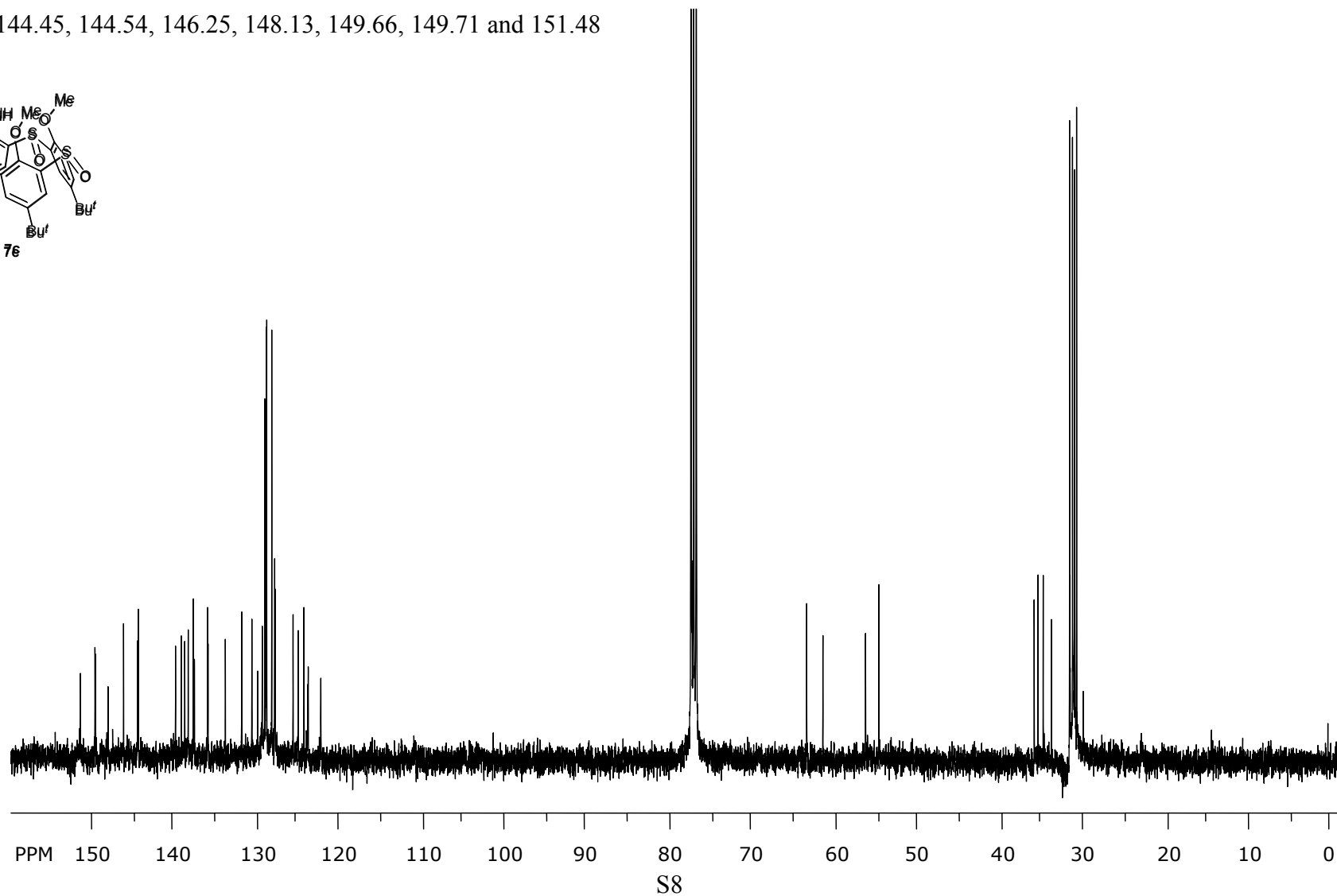
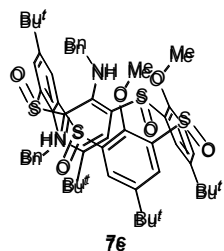
**25,26-Di(benzylamino)-27,28-dimethoxy-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (7c)**

$\delta_{\text{H}}$  (400 MHz) 0.59 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.05 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.25 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.41 [9 H, s, C(CH<sub>3</sub>)<sub>3</sub>], 3.49 (3 H, s, OCH<sub>3</sub>), 3.54-3.57 (1 H, m, ArNHCH<sub>2</sub>), 4.08 (3 H, s, OCH<sub>3</sub>), 4.29 (1 H, t, *J* 10.1 Hz, NHCH<sub>2</sub>), 4.34-4.40 (1 H, m, NHCH<sub>2</sub>), 4.68-4.70 (2 H, m, NHCH<sub>2</sub>), 6.65 (1 H, br, NHCH<sub>2</sub>), 6.93 (1 H, d, *J* 2.3, ArH), 7.29-7.43 (8 H, m, ArH), 7.48-7.50 (2 H, m, ArH), 7.58-7.60 (2 H, m, ArH), 7.81 (1 H, d, *J* 2.3 Hz, ArH), 7.86 (1 H, d, *J* 2.4, ArH), 8.03 (1 H, d, *J* 2.3, ArH), 8.05 (1 H, d, *J* 2.4, ArH) and 8.12 (1 H, d, *J* 2.4, ArH)



**25,26-Di(benzylamino)-27,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (7c)**

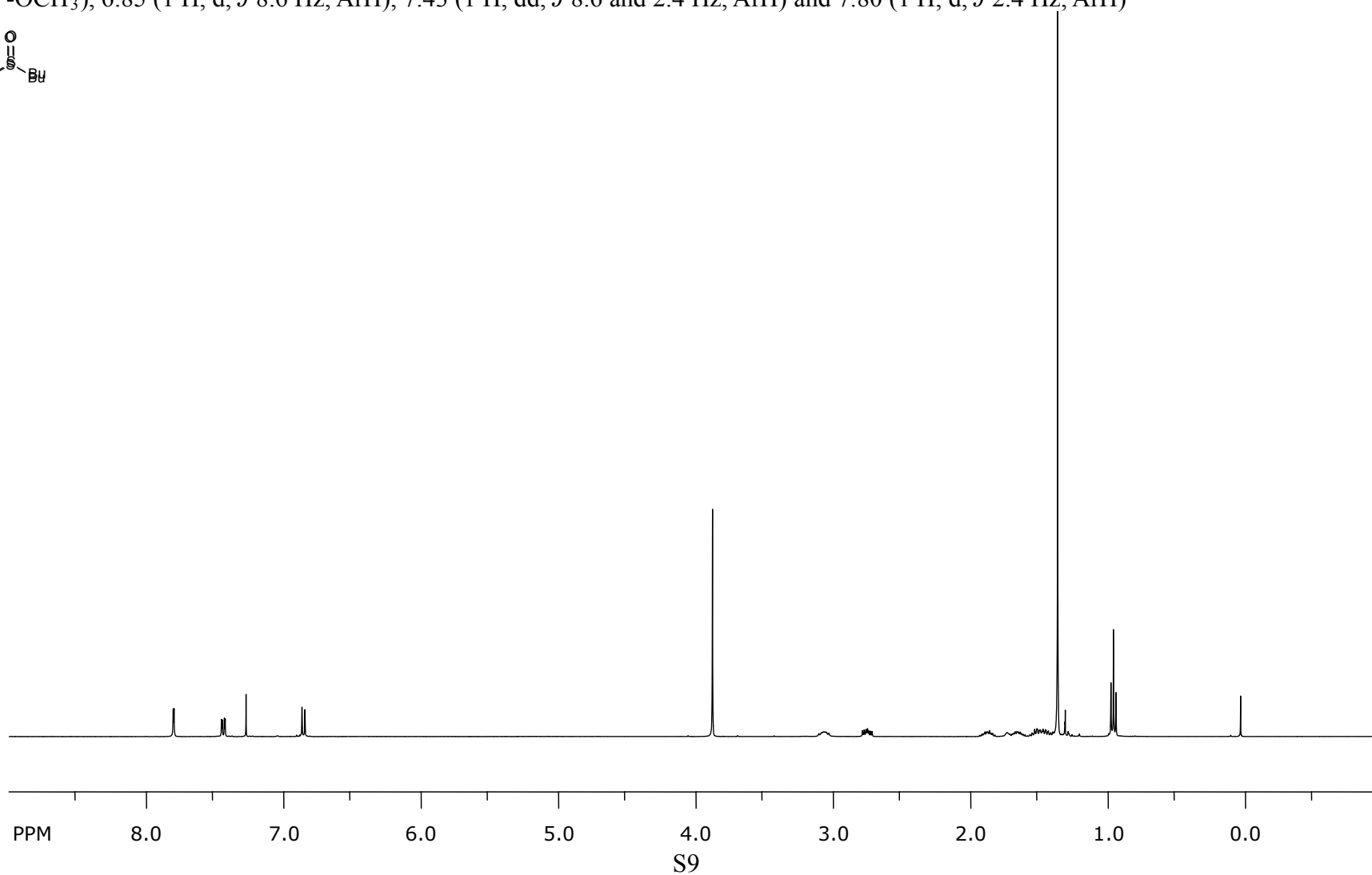
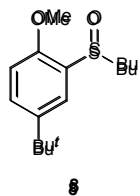
$\delta_C$  (100 MHz) 30.51, 30.75, 31.01, 31.37, 33.56, 34.57, 35.19, 35.66, 54.54, 56.15, 61.32, 63.29, 122.30, 123.83, 123.91, 124.34, 125.04, 125.67, 127.84, 127.91, 128.26, 128.87, 128.94, 129.11, 129.41, 130.00, 130.67, 131.90, 133.89, 136.01, 136.05, 137.65, 137.78, 138.41, 138.83, 139.25, 139.94, 144.45, 144.54, 146.25, 148.13, 149.66, 149.71 and 151.48





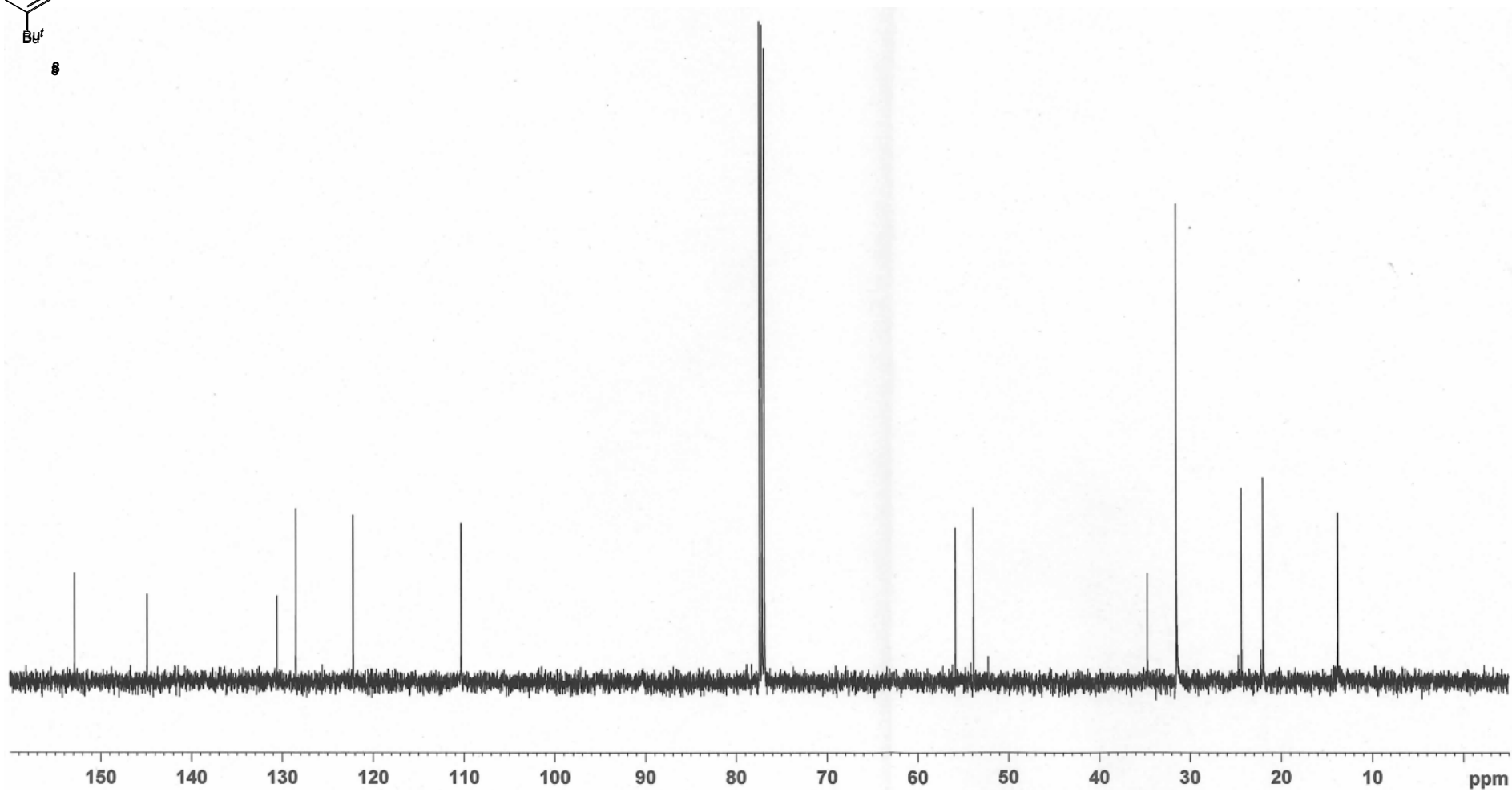
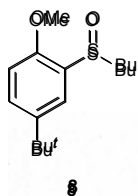
**4-tert-Butyl-2-(butylsulfinyl)-1-methoxybenzene (8)**

$\delta_{\text{H}}$  (400 MHz) 0.93 (3 H, t,  $J$  7.3 Hz,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.34 [9 H, s,  $\text{C}(\text{CH}_3)_3$ ], 1.39-1.52 (2 H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.58-1.67 (1 H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.80-1.91 (1 H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.69-2.76 (1 H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.01-3.08 (1 H, m,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.86 (3 H, s,  $-\text{OCH}_3$ ), 6.85 (1 H, d,  $J$  8.6 Hz, ArH), 7.43 (1 H, dd,  $J$  8.6 and 2.4 Hz, ArH) and 7.80 (1 H, d,  $J$  2.4 Hz, ArH)



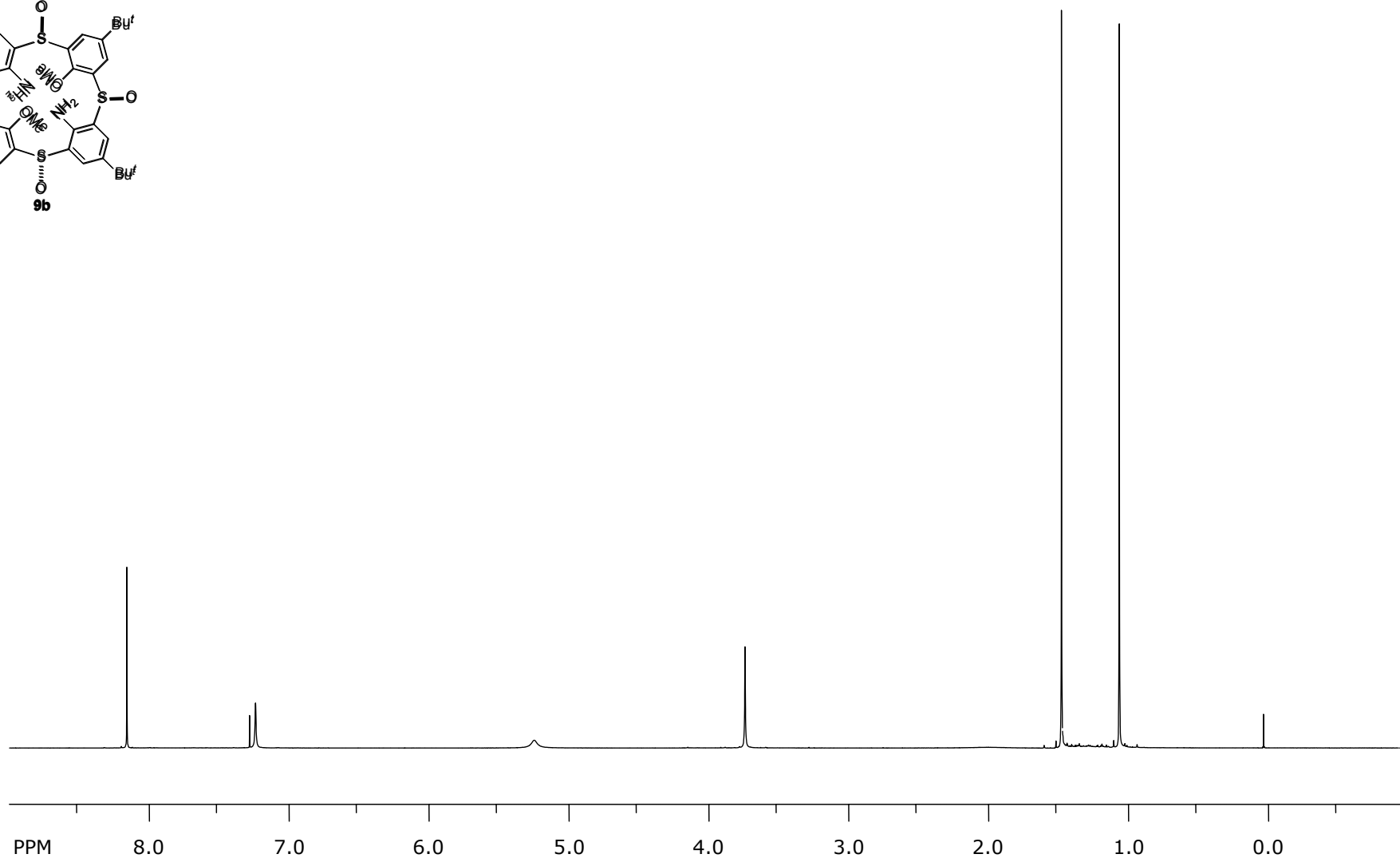
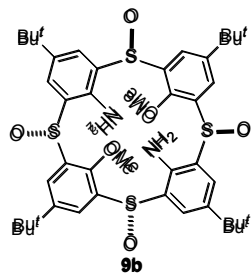
**4-*tert*-Butyl-2-(butylsulfinyl)-1-methoxybenzene (8)**

$\delta_C$  (125 MHz) 13.77, 21.98, 24.39, 31.52, 34.74, 53.84, 55.83, 110.30, 122.19, 128.51, 130.59, 144.87 and 152.84



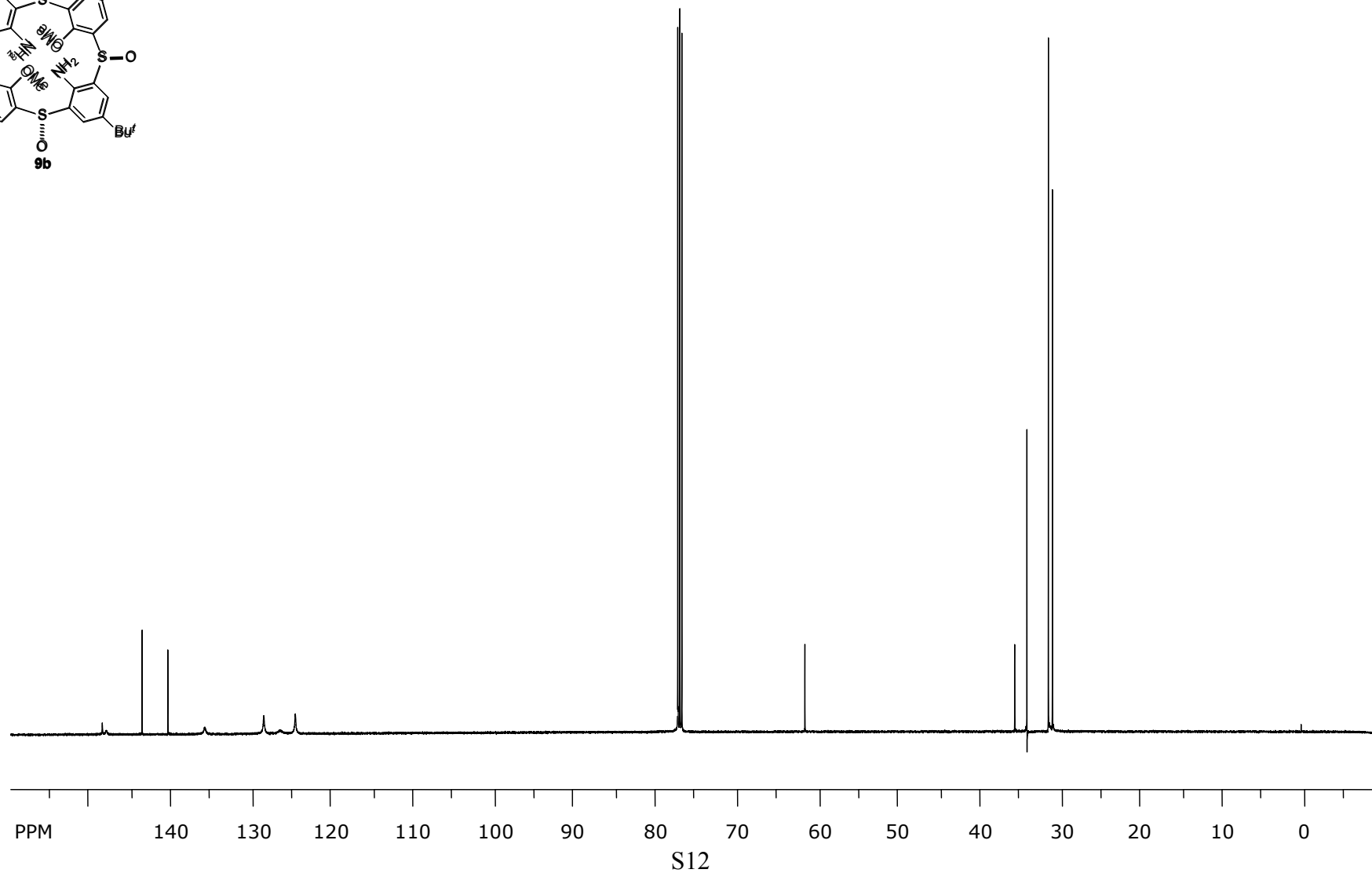
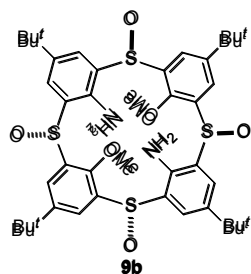
**25,27-Diamino-26,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (9b)**

$\delta_{\text{H}}$  (500 MHz) 1.03 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 1.45 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 3.72 (6 H, s, OCH<sub>3</sub> × 2), 5.23 (4 H, s, NH<sub>2</sub> × 2), 7.24 (4 H, s, ArH × 2) and 8.16 (4 H, s, ArH × 2)



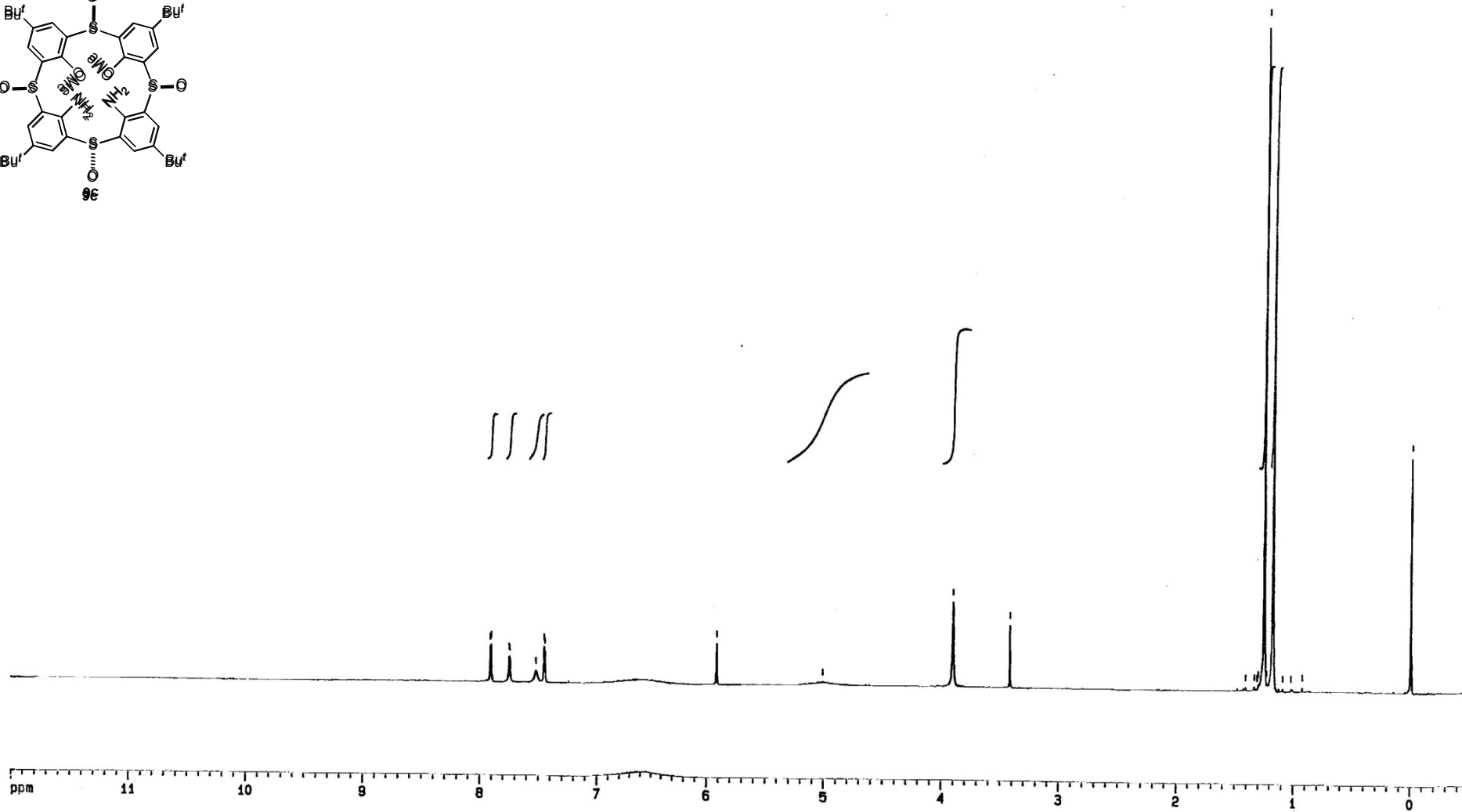
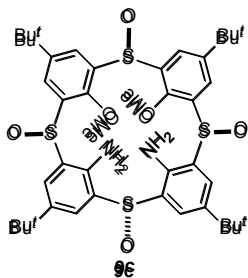
**25,27-Diamino-26,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (9b)**

$\delta_C$  (125 MHz) 30.84, 31.34, 33.99, 35.51, 61.53, 124.72, 126.66, 128.62, 135.93, 140.52, 143.71, 148.17 and 148.65



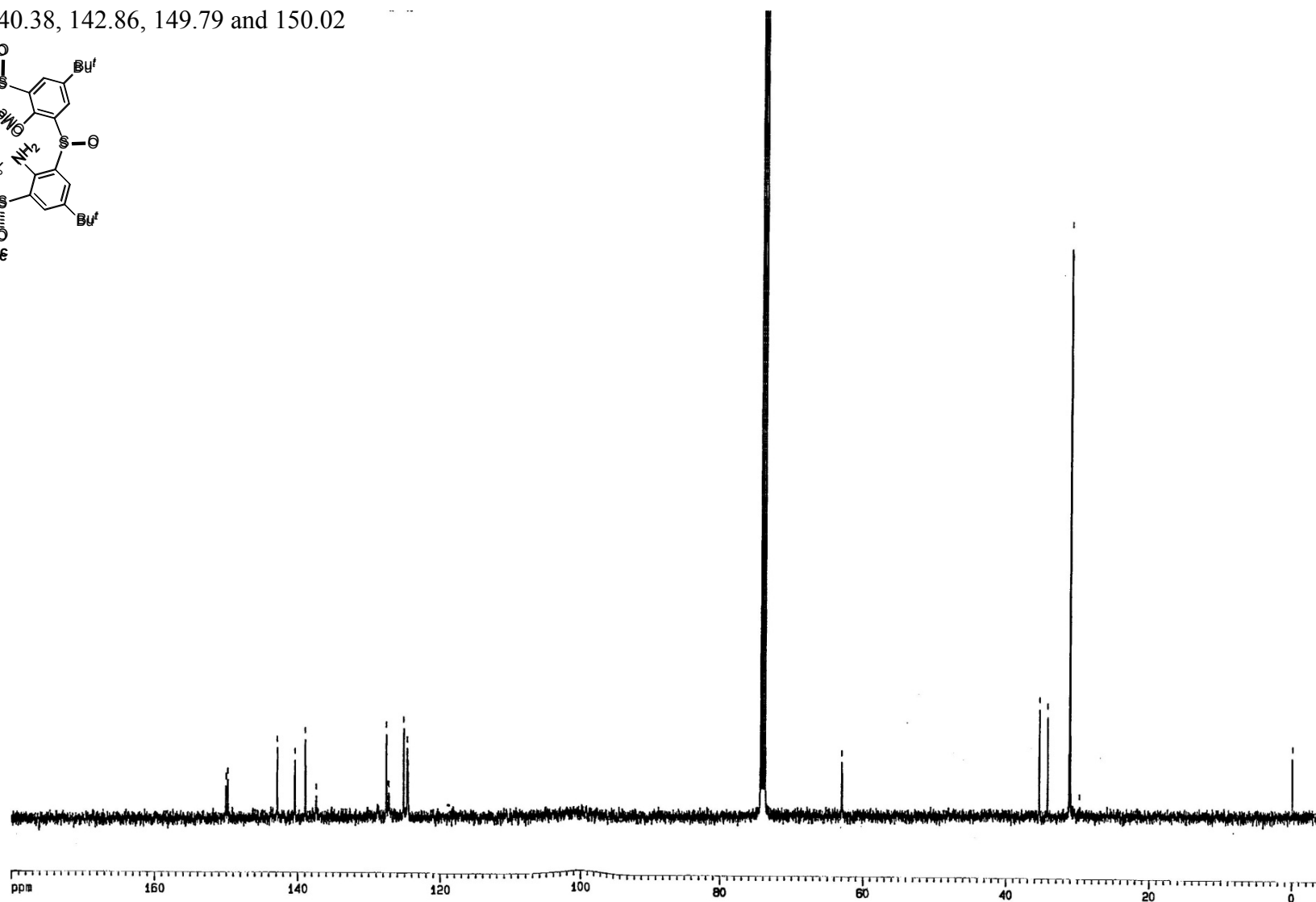
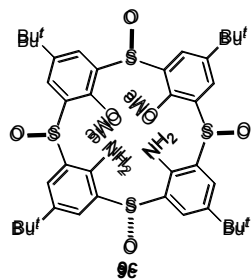
**25,26-Diamino-27,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (9c)**

$\delta_{\text{H}}$  (400 MHz, [ $^2\text{H}_2$ ]-1,1,2,2-tetrachloroethane, 383 K): 1.18 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 1.25 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 3.90 (6 H, s,  $\text{OCH}_3 \times 2$ ), 5.01 (4 H, s,  $\text{NH}_2 \times 2$ ), 7.45 (2 H, d,  $J$  2.2 Hz, ArH), 7.52 (2 H, br s, ArH), 7.75 (2 H, d,  $J$  2.2 Hz, ArH) and 7.91 (2 H, d,  $J$  2.2 Hz, ArH)



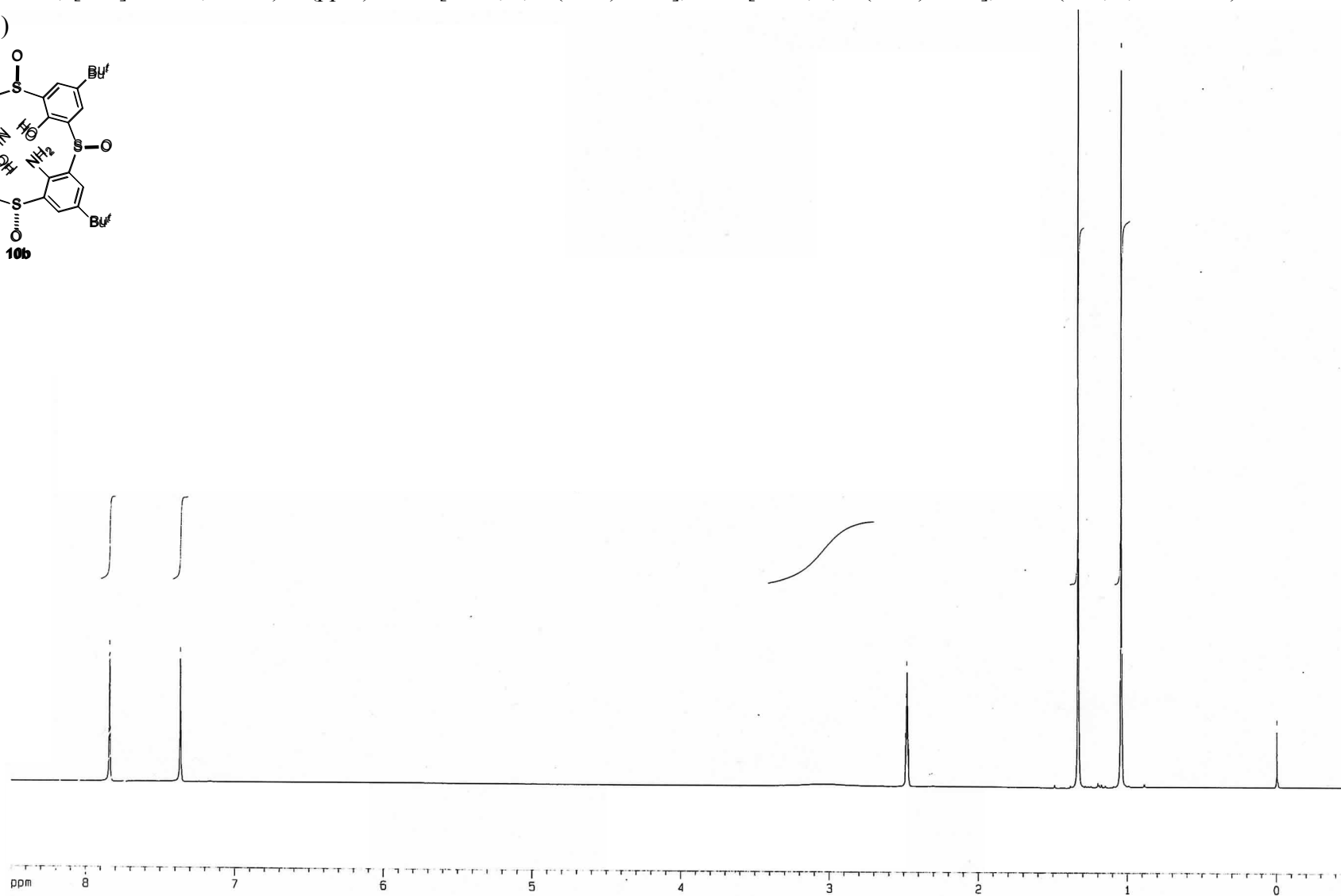
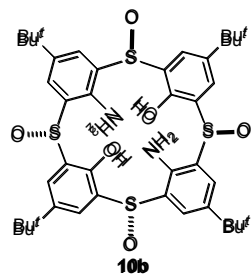
**25,26-Diamino-27,28-dimethoxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (9c)**

$\delta_C$  (100 MHz,  $[\text{D}_2]$ -1,1,2,2-tetrachloroethane, 383 K): 31.13, 31.18, 34.23, 35.39, 62.99, 124.53, 124.65, 125.15, 127.24, 127.58, 128.80, 137.41, 138.92, 140.38, 142.86, 149.79 and 150.02



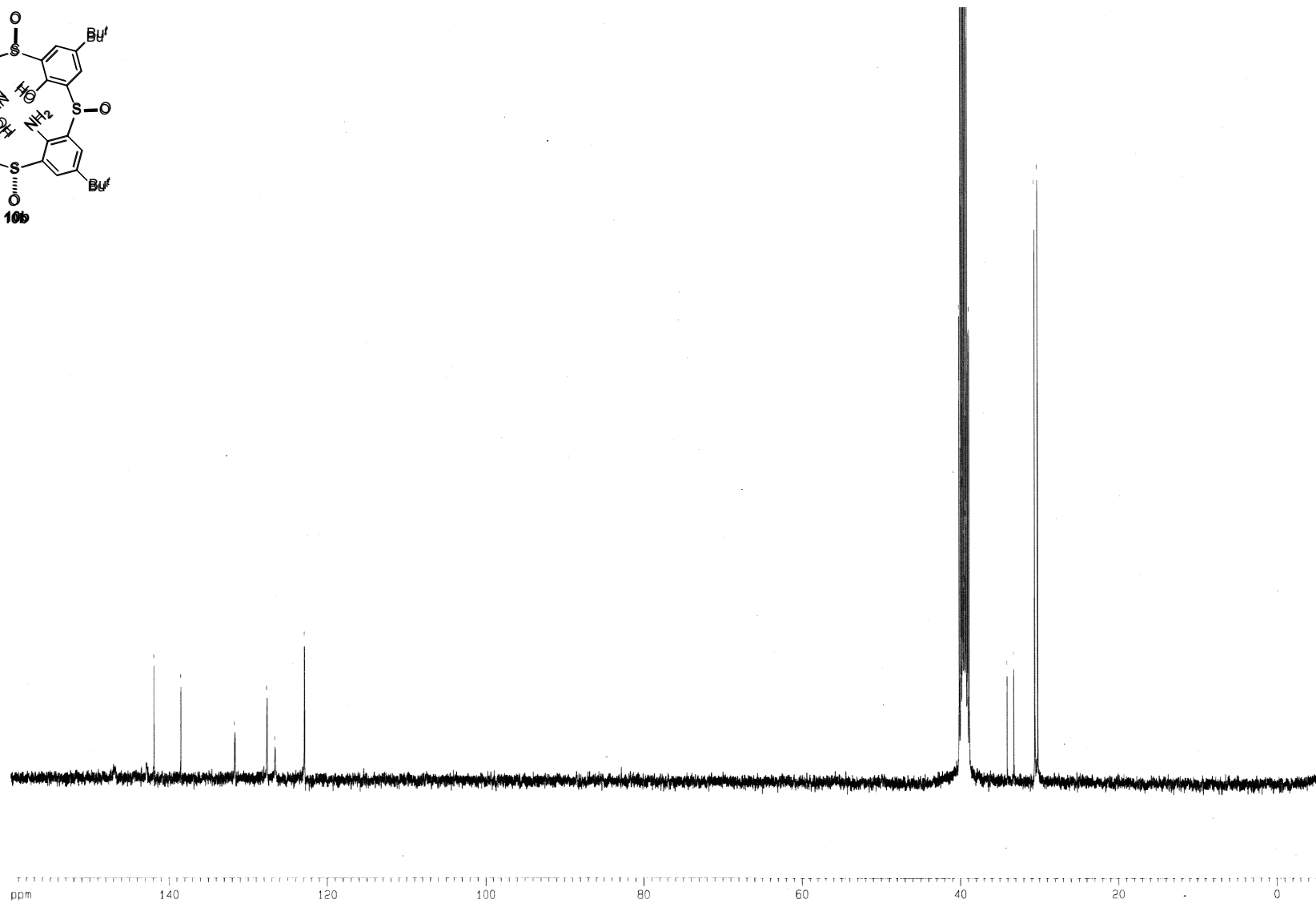
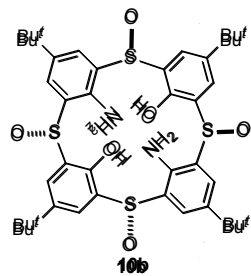
**25,27-Diamino-26,28-dihydroxy-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (10b)**

$\delta_{\text{H}}$  (400 MHz,  $[\text{}^2\text{H}_6]\text{DMSO}$ , 353K)  $\delta$  (ppm): 1.05 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 1.34 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 7.37 (4 H, s, ArH  $\times 2$ ) and 7.84 (4 H, s, ArH  $\times 2$ )



**25,27-Diamino-26,28-dihydroxy-tetra-*p-tert*-butylsulfinylcalix[4]arene (10b)**

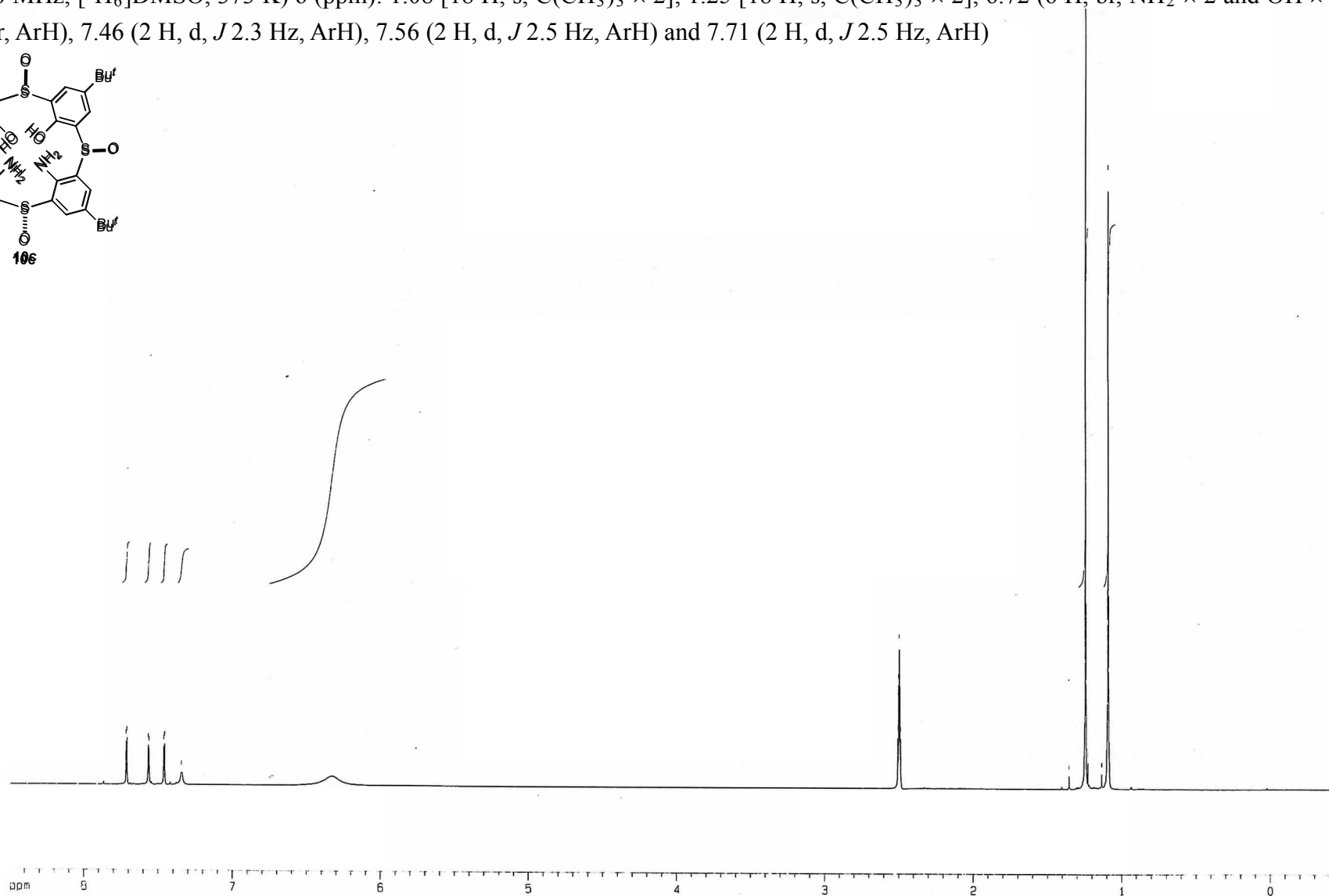
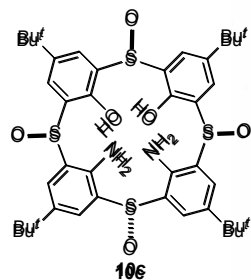
$\delta_C$  (100 MHz,  $[\text{D}_6]\text{DMSO}$ , 353K)  $\delta$  (ppm): 30.24, 30.62, 33.27, 34.13, 122.93, 126.64, 127.66, 131.73, 138.55, 141.93, 142.90, 142.90 and 147.05





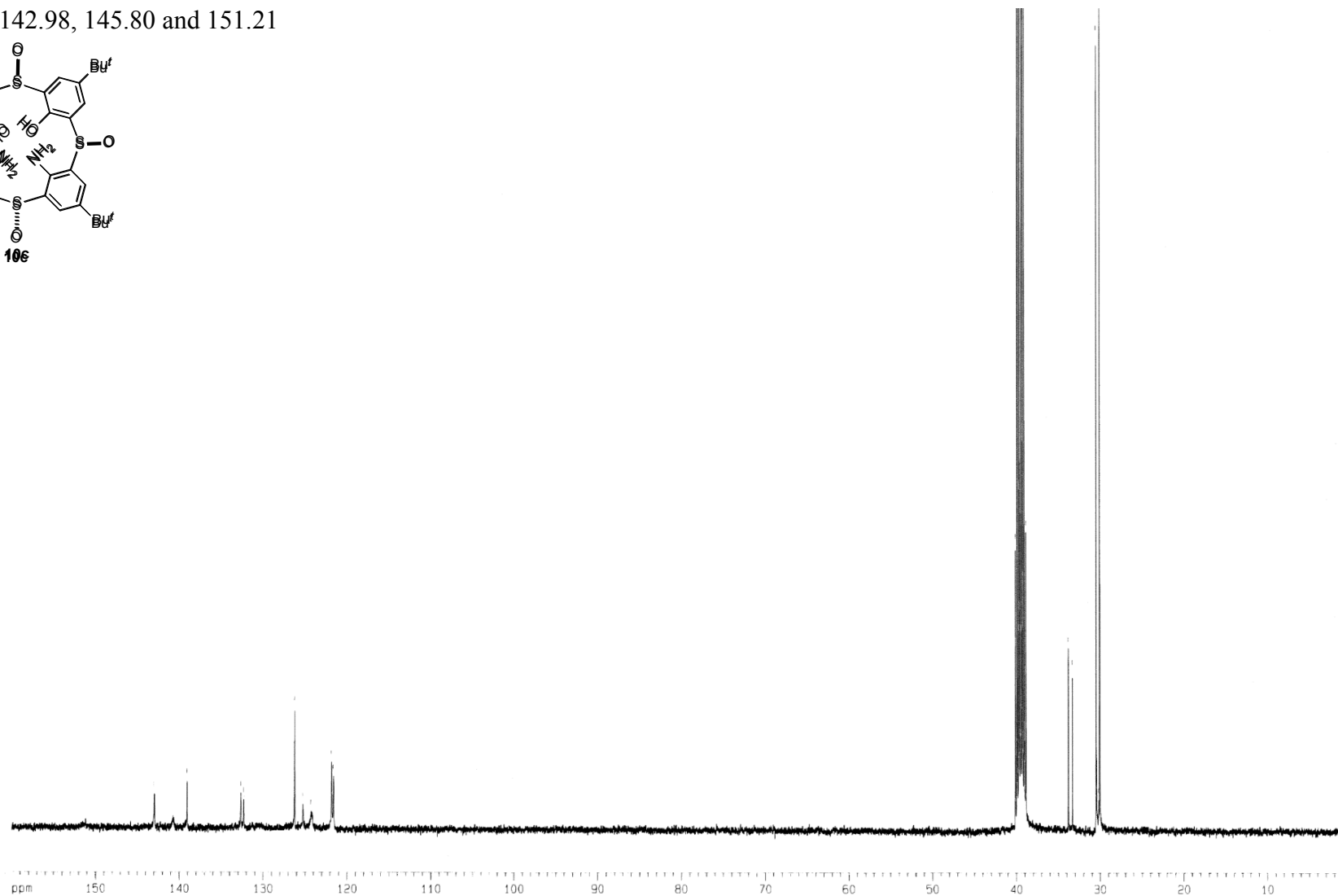
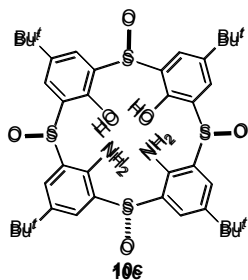
**25,26-Diamino-27,28-dihydroxy-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (10c)**

$\delta_{\text{H}}$  (400 MHz, [ $^2\text{H}_6$ ]DMSO, 373 K)  $\delta$  (ppm): 1.08 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 1.25 [18 H, s,  $\text{C}(\text{CH}_3)_3 \times 2$ ], 6.72 (6 H, br,  $\text{NH}_2 \times 2$  and  $\text{OH} \times 2$ ), 7.34 (2 H, br, ArH), 7.46 (2 H, d,  $J$  2.3 Hz, ArH), 7.56 (2 H, d,  $J$  2.5 Hz, ArH) and 7.71 (2 H, d,  $J$  2.5 Hz, ArH)



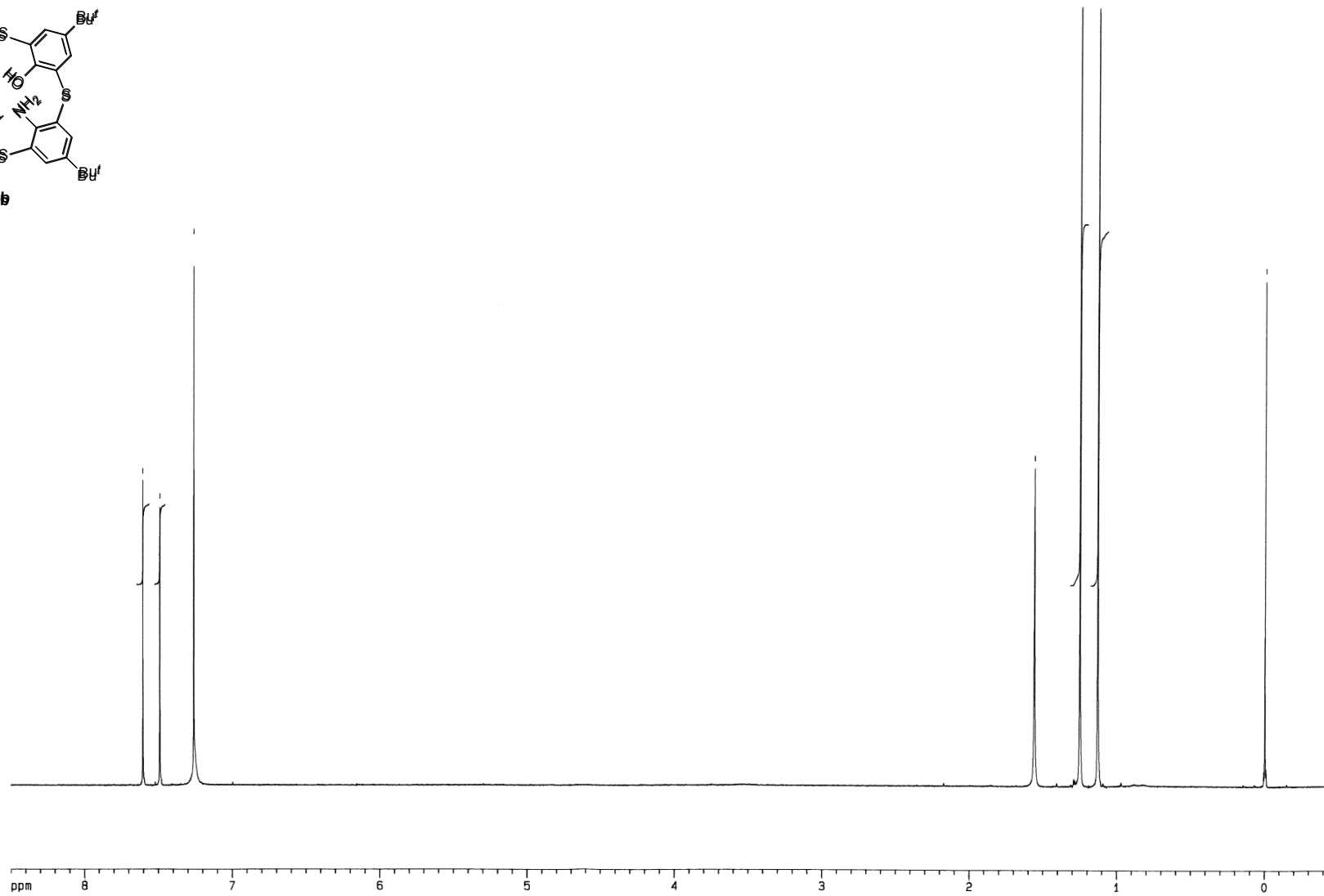
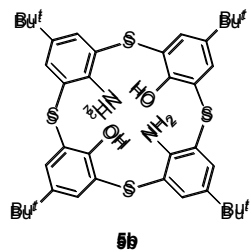
**25,26-Diamino-27,28-dihydroxy-tetra-*p*-*tert*-butylsulfinylcalix[4]arene (10c)**

$\delta_c$  (100 MHz, [ $^2\text{H}_6$ ]DMSO, 373 K)  $\delta$  (ppm): 30.11, 30.53, 33.34, 33.83, 121.64, 121.86, 124.29, 125.26, 126.27, 132.34, 132.70, 139.08, 140.77, 142.77, 142.98, 145.80 and 151.21



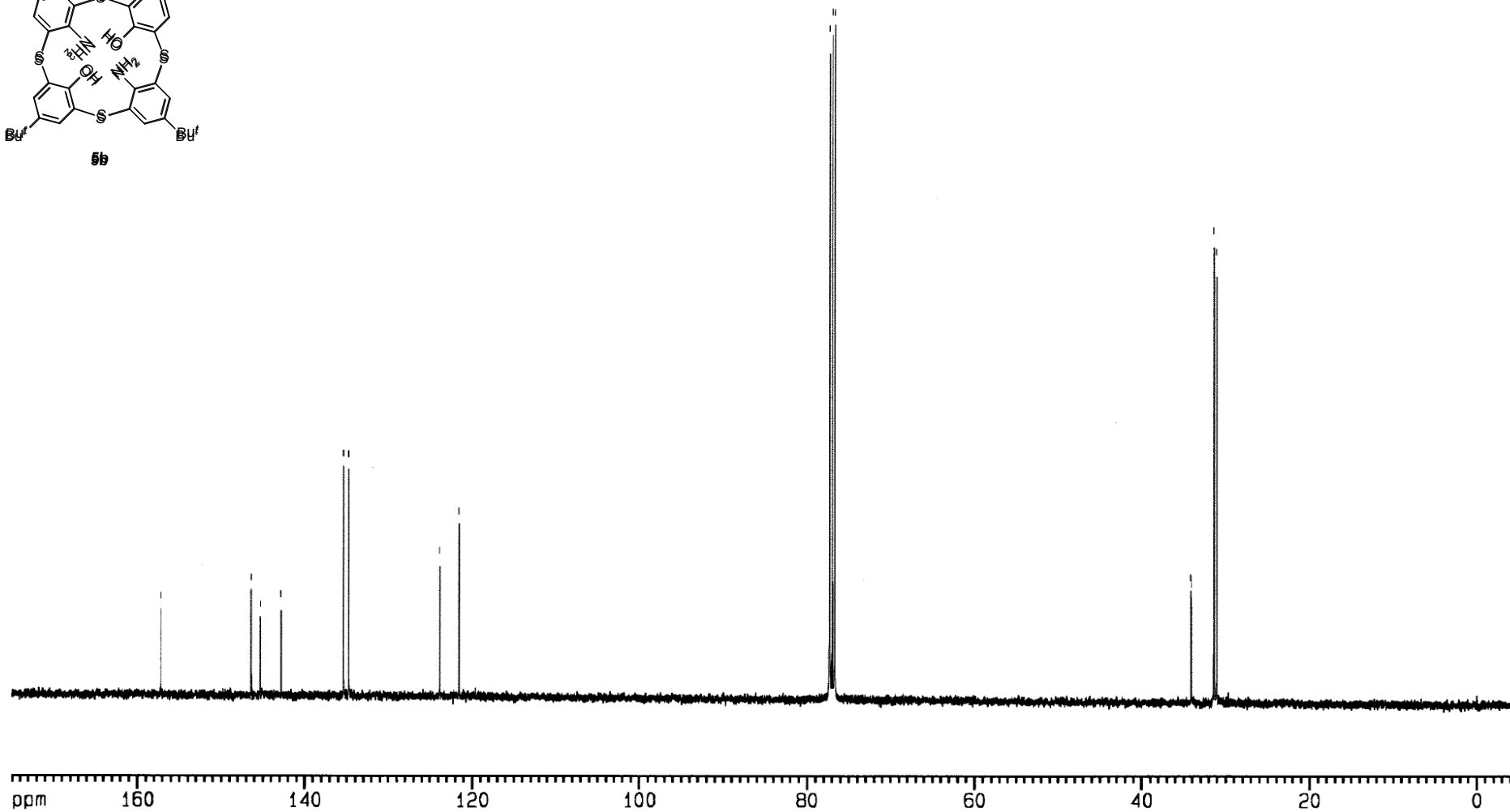
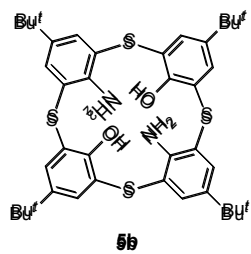
**25,27-Diamino-26,28-dihydroxy-tetra-*p*-*tert*-butylthiacalix[4]arene (5b)**

$\delta_{\text{H}}$  (400 MHz) 1.13 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 1.25 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 7.49 (4 H, s, ArH × 2) and 7.61 (4 H, s, ArH × 2)



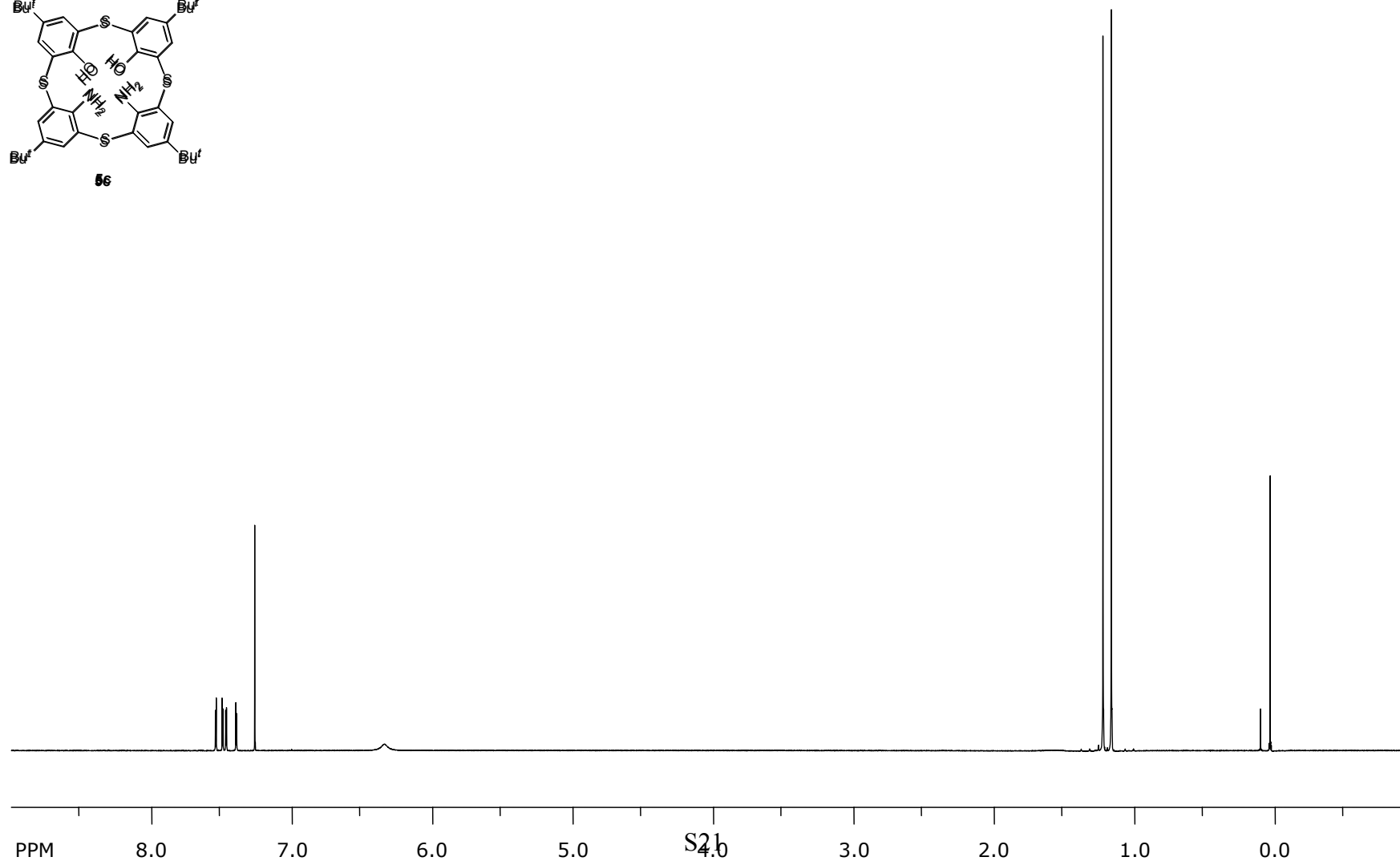
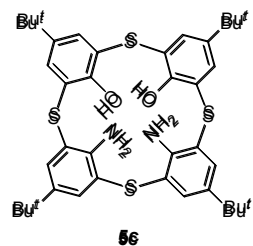
**25,27-Diamino-26,28-dihydroxy-tetra-*p*-*tert*-butylthiacalix[4]arene (5b)**

$\delta_C$  (100 MHz) 31.05, 31.39, 34.04, 34.14, 121.60, 123.89, 134.79, 135.41, 142.85, 145.31, 146.42 and 157.21



**25,26-Diamino-27,28-dihydroxy-tetra-*p*-*tert*-butylthiacalix[4]arene (5c)**

$\delta_{\text{H}}$  (400 MHz) 1.14 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 1.20 [18 H, s, C(CH<sub>3</sub>)<sub>3</sub> × 2], 6.32 (6 H, br, NH<sub>2</sub> × 2 and OH × 2), 7.39 (2 H, d, *J* 2.3 Hz, ArH), 7.47 (2 H, d, *J* 2.3 Hz, ArH), 7.49 (2 H, d, *J* 2.5 Hz, ArH), and 7.54 (2 H, d, *J* 2.5 Hz, ArH)



**25,26-Diamino-27,28-dihydroxy-tetra-*p*-*tert*-butylthiacalix[4]arene (5c)**

$\delta_C$  (100 MHz) 31.16, 31.24, 33.95, 34.09, 119.75, 120.12, 120.61, 120.99, 134.15, 134.23, 134.42, 134.77, 142.58, 143.69, 146.70 and 155.38

