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# Novel first-generation dendrimers on calix[4]resorcinol core equipped with multiple triazole units

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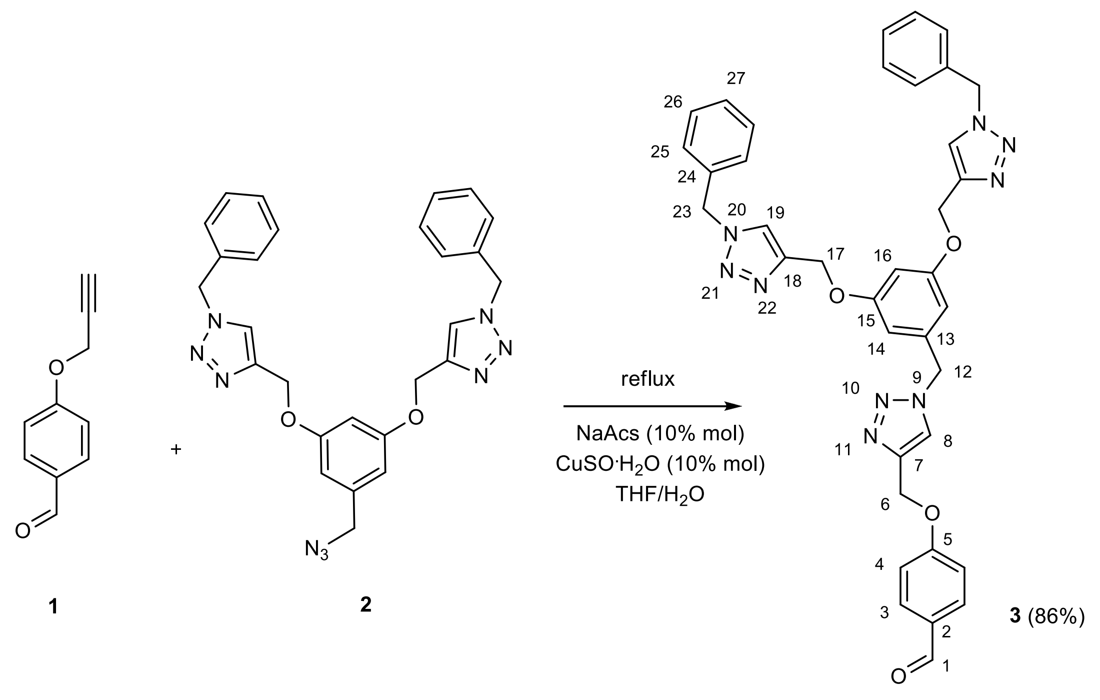
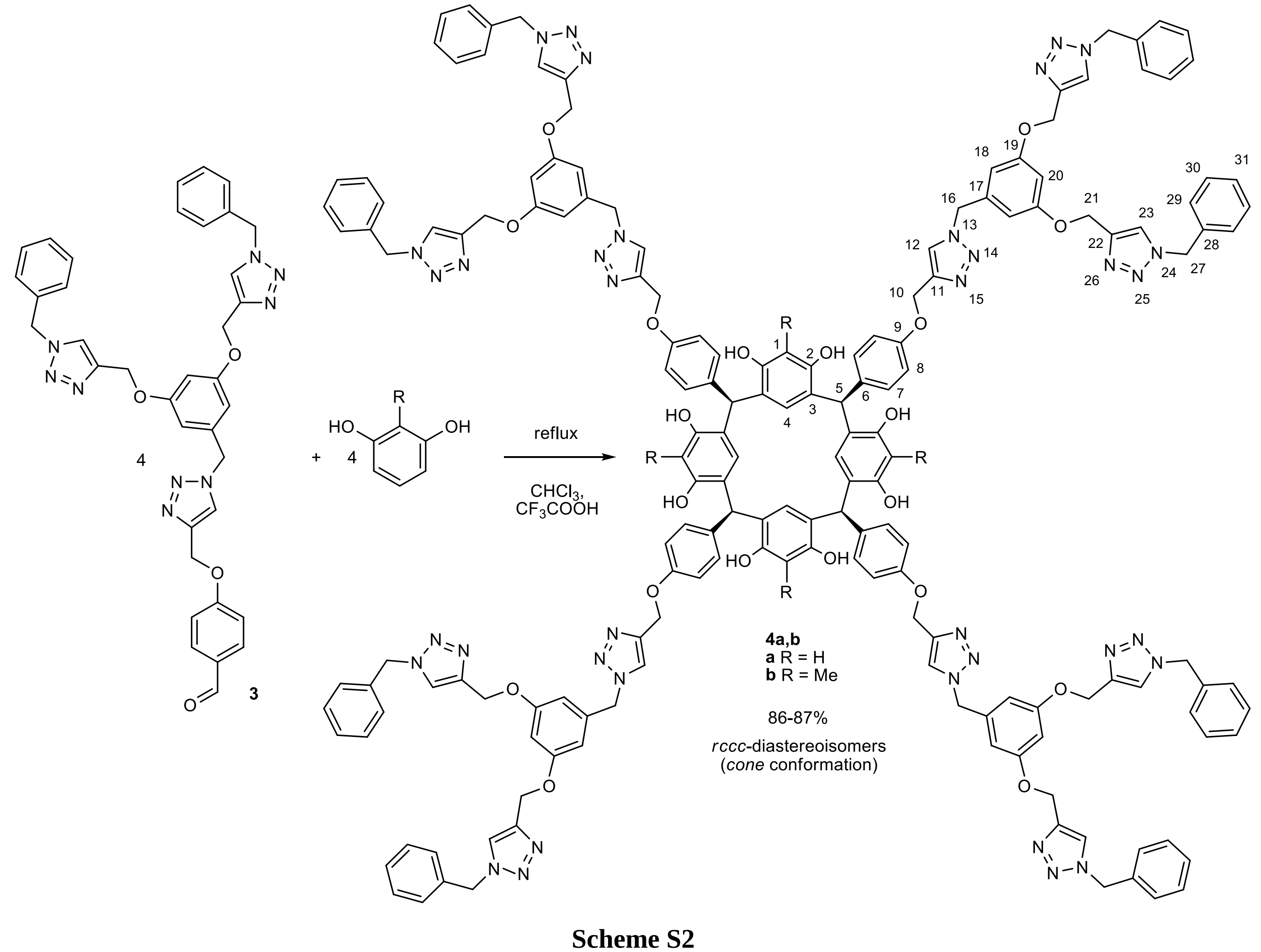
## General

NMR experiments were performed on a Bruker AVANCE **III**-500 spectrometer at 303 K equipped with 5 mm broadband probehead working at 500.1 MHz in $^1$H, 125.8 MHz in $^{13}$C and 50.7 MHz in $^{15}$N NMR experiments. Chemical shifts were reported relative to residual signal of deuterated solvents. IR spectra of solid compounds have been registered using Bruker Vector-27 FTIR spectrometer in the 400–4000 cm$^{-1}$ range (optical resolution 4 cm$^{-1}$). The samples were prepared as KBr pellets. The MALDI mass spectra were recorded on an Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) operated in the linear mode with the registration of positively charged ions or negatively charged ions. A Nd:YAG laser ($\lambda$ = 355 nm, repetition rate 100 Hz) was used. The mass spectra were obtained with an accelerating voltage of 25 kV and an ion extraction delay time of 30 ns. The resulting mass spectra were formed due to multiple laser irradiation of the crystal (50 shots). The metal target MTP AnchorChipTM was used. Portions (0.5 μl) of a 1% matrix solution in acetonitrile and of a 0.1% sample solution in methanol were consecutively applied onto the target and evaporated. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix. The polyethylene glycol was used to calibrate the mass scale of the device. The data were obtained using the FlexControl program (Bruker Daltonik GmbH, Germany) and processed using the FlexAnalysis 3.0 program (Bruker Daltonik GmbH, Germany). The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The elemental analysis was carried out on a CHNS analyzer EuroEA3028-HT-OM (Eurovector SpA, Italy). The samples were weighed on Sartorius CP2P (Germany) microbalances in tin capsules. Callidus 4.1 software was used to perform quantitative measurements and evaluate the data received.



**Scheme S1**



**Scheme S2**

*Experimental procedure for preparation and spectroscopic data of 4-{3,5-bis[(1-benzyl-1H-1,2,3-triazol-4-yl)methoxy]benzyloxy}benzaldehyde* (**3,** Scheme S1).

To a suspension of 4propargyloxybenzaldehyde (0.28 g, 1.73 mmol), sodium ascorbate (0.04 g, 0.21 mmol) and $CuSO_4{\cdot}5H_2O$ (0.05 g, 0.21 mmol) in a mixture of THF/$H_2O$ (25+15 ml), 4,4'-[(5-azidomethyl-1,3-phenylene)bis(oxymethylene)]bis(1-benzyl-1*H*-1,2,3-triazole) (1.46 g, 2.10 mmol) was added. The mixture was stirred at reflux for 24 h. The complete conversion of 4-propargyloxybenzaldehyde was monitored by TLC. Then the reaction mixture was diluted with $H_2O$ (20 mL) and extracted with chloroform (3 x 15 mL). The combined organic layers were evaporated, and the crude product was purified by column chromatography using dichloromethane/methanol (10:0.5) as the eluent. Pure compound **3** was obtained as white solid (0.98 g, 86 % yield, $R_f$ = 0.49), m. p. 61–62 °C. $^1$H NMR (600.1 MHz, DMSO-$d_6$): δ 5.09 (s, 2H, H17), 5.27 (s, 2H, H6), 5.52 (s, 2H, H12), 5.60 (s, 2H, H23), 6.57 (d, $^4J_{HH}$ 2.2 Hz, 2H, H14), 6.71 (t, $^4J_{HH}$ 2.2 Hz, 1H, H16), 7.22 (d, $^3J_{HH}$ 8.7 Hz, 2H, H4), 7.31-7.37 (m, 10H, H25-H27), 7.86 (d, $^3J_{HH}$ 8.7 Hz, 2H, H3), 8.25 (s, 1H, H19), 8.31 (s, 1H, H8), 9.86 (s, 1H, H1) ppm. $^{13}$C (150.9 MHz, DMSO-$d_6$): δ 52.7 (C12), 52.8 (C23), 61.2 (C17), 61.4 (C6), 100.9 (C16), 107.2 (C14), 115.2 (C4), 124.7 (C19), 124.9 (C8), 127.9 (C25), 128.1 (C27), 128.7 (C26), 129.8 (C2), 135.9 (C24), 131.7 (C3), 138.0 (C13), 142.3 (C7), 142.6 (C18), 159.3 (C15), 162.9 (C5), 191.2 (C1) ppm. $^{15}$NMR (61 MHz, DMSO-$d_6$): δ 249.3 (N9), 251.5 (N20), 353.7 (N11), 353.9 (N22), 363.2 (N21), 364.1 (N10) ppm. IR $\nu_{max}$ (KBr): 1688 cm$^{-1}$ (C=O) cm$^{-1}$. Anal. Calcd. for $C_{37}H_{33}N_9O_3$ (%): C, 68.19; H, 5.10; N, 19.34. Found: C, 67.97; H, 5.12; N, 19.49. MALDI-MS: *m/z* = 690.3 [M+K]$^+$ (calcd. M = 651.7).

*Experimental procedure for preparation and spectroscopic data of compound* **4a** (Scheme S2).

A mixture of resorcinol (0.03 g, 0.31 mmol) and dendron **3** (0.2 g, 0.31 mmol) in $CHCl_3$ (20 mL) and trifluoroacetic acid (2 mL) was stirred at reflux for 24 h under an inert atmosphere. Then solvent was evaporated to dryness, and the residue was triturated in diethyl ether. After drying in *vacuo* (40 ºC, 0.06 Torr), pure **4a** as *rccc*-diastereoisomer was obtained (0.20 g, 87%) as a beige powder. Mp > 80 ºC (dec). $^1$H NMR (600.1 MHz, DMSO-*d*$_6$): δ 5.03 (s, 8H, H10), 5.04 (s, 8H, H21), 5.38 (s, 8H, H16), 5.55 (s, 8H, H27), 5.60 (s, 4H, H5), 6.13 (s, 4H, H1), 6.25 (brs, 4H, H4), 6.54 (d, $^4J_{HH}$ 2.2 Hz, 8H, H18), 6.64 (m, 8H, H7), 6.65 (m, 8H, H8), 6.66 (m, 4H, H20), 7.26 (m, 8H, H31), 7.27 (m, 16H, H30), 7.30 (s, 16H, H29), 8.14 (s, 4H, H12), 8.19 (s, 4H, H23), 8.49 (br.m, 8H, OH) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): δ 40.6 (C5), 52.7 (C16), 52.8 (C27), 61.0 (C10), 61.1 (C21), 100.9 (C20), 102.2 (C1), 107.2 (C18), 113.4 (C8), 120.6 (C6), 124.3 (C12), 124.6 (C23), 127.9 (C30), 128.1 (C31), 128.7 (C29), 129.3 (C4), 129.4 (C7), 135.8 (C28), 137.9 (C17), 138.2 (C3), 142.7 (C22), 143.4 (C11), 152.4 (C2), 155.4 (C9), 159.3 (C19) ppm. $^{15}$NMR (61 MHz, DMSO-$d_6$): δ 251.3 (N13), 251.4 (N24), 354.1 (N15), 354.2 (N26), 363.7 (N14), 363.9 (N25). IR $\nu_{max}$ (KBr): 3100–3600 (OH) cm$^{-1}$. Anal. Calcd for $C_{172}H_{148}N_{36}O_{20}$ (%): C, 67.97; H, 4.91; N, 16.59. Found: 67.73; H, 4.87; N, 16.78. MALDI-MS: *m/z* = 3040.6 [M+H]$^+$ (calcd M = 3039.2).

*Experimental procedure for preparation and spectroscopic data of compound* **4b** (Scheme S2).

Compound **4b** as *rccc*-diastereoisomer was obtained as a beige powder in a yield of 0.37 g (88%) similarly to the synthesis of compound **4a** by the reaction of 2-methylresorcinol (0.067 g, 0.54 mmol) and aldehyde **3** (0.35 g, 0.54 mmol). Mp > 115 ºC (dec). $^1$H NMR (600.1 MHz, DMSO-*d*$_6$): δ 1.91 (s, 12H, $CH_3$), 5.05 (s, 8H, H21), 5.08 (s, 8H, H10), 5.38 (s, 8H, H16), 5.55 (s, 8H, H27), 5.58 (s, 4H, H5), 6.04 (s, 4H, H4), 6.57 (m, 8H, H18), 6.54 (m, 8H, H7), 6.67 (m, 8H, H8), 6.68 (m, 4H, H20), 7.28 (m, 8H, H30), 7.30 (m, 16H, H31), 7.32 (s, 16H, H29), 8.14 (s, 4H, H12), 8.19 (s, 4H, H23) ppm. $^{13}$C NMR (150.9 MHz, DMSO-*d*$_6$): δ 9.9 ($\underline{C}H_3$), 41.9 (C5), 52.6 (C16), 52.8 (C27), 61.0 (C10), 61.1 (C21), 100.9 (C20), 107.2 (C18), 111.2 (C1), 113.5 (C8), 122.4 (C3), 124.3 (C12), 124.6 (C23), 127.9 (C30), 128.1 (C31), 128.7 (C29), 129.6 (C7), 135.8 (C28), 135.9 (C6), 137.9 (C17), 142.7 (C22), 143.3 (C11), 150.4 (C2), 155.6 (C9), 159.3 (C19) ppm. IR $\nu_{max}$ (KBr): 3100–3600 (OH) cm$^{-1}$. Anal. Calcd for $C_{176}H_{156}N_{36}O_{20}$ (%): C, 68.29; H, 5.08; N, 16.29. Found: 68.35; H, 5.01; N, 16.31. MALDI-MS: *m/z* = 3118.4 [M+Na]$^+$, 3134.1 [M+Na]$^+$ (calcd M = 3095.4).

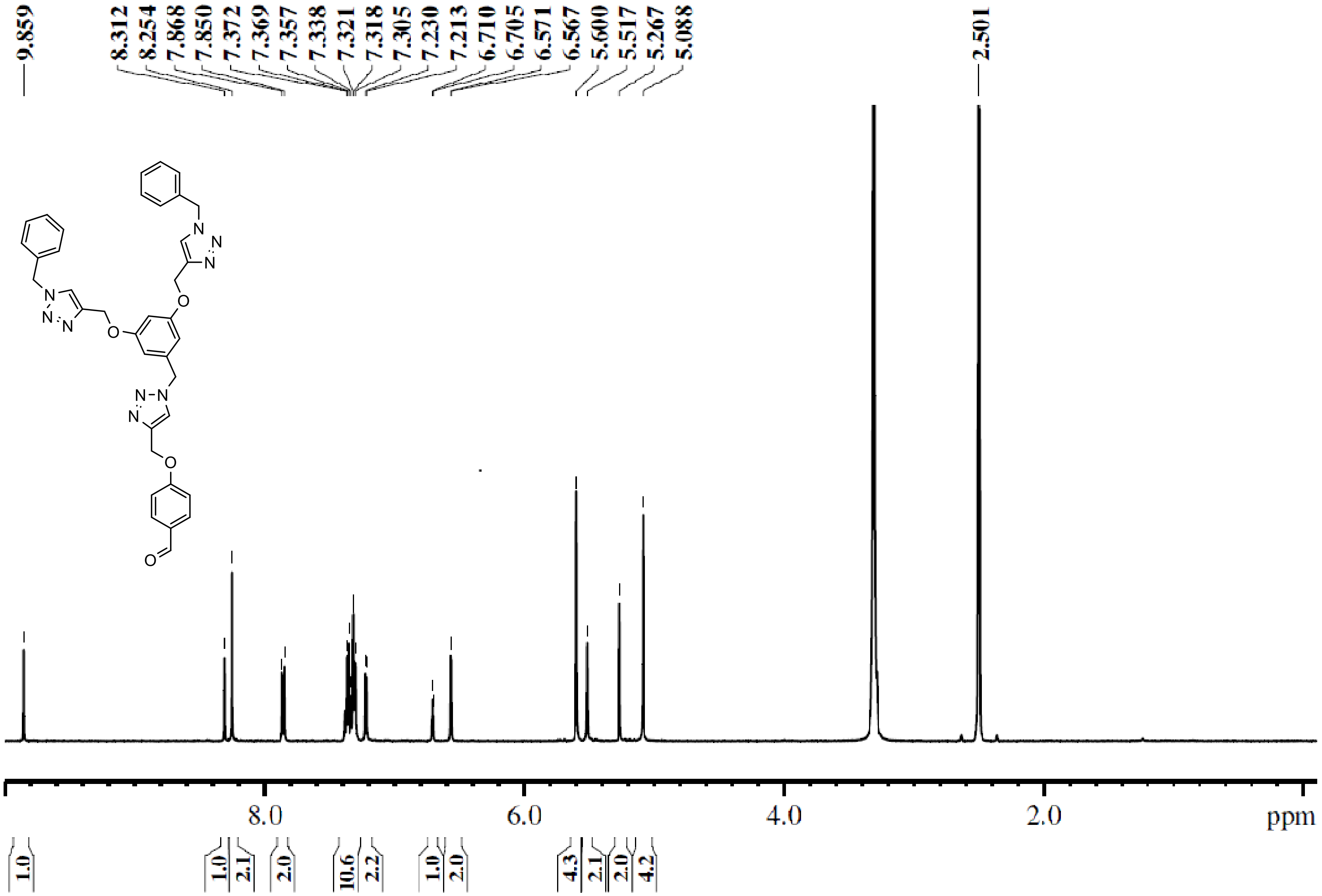


**Figure S1.** $^1$H NMR spectrum of 4-{3,5-bis[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]benzyloxy}benzaldehyde (**3**) in DMSO-$d_6$ (T=303 K).

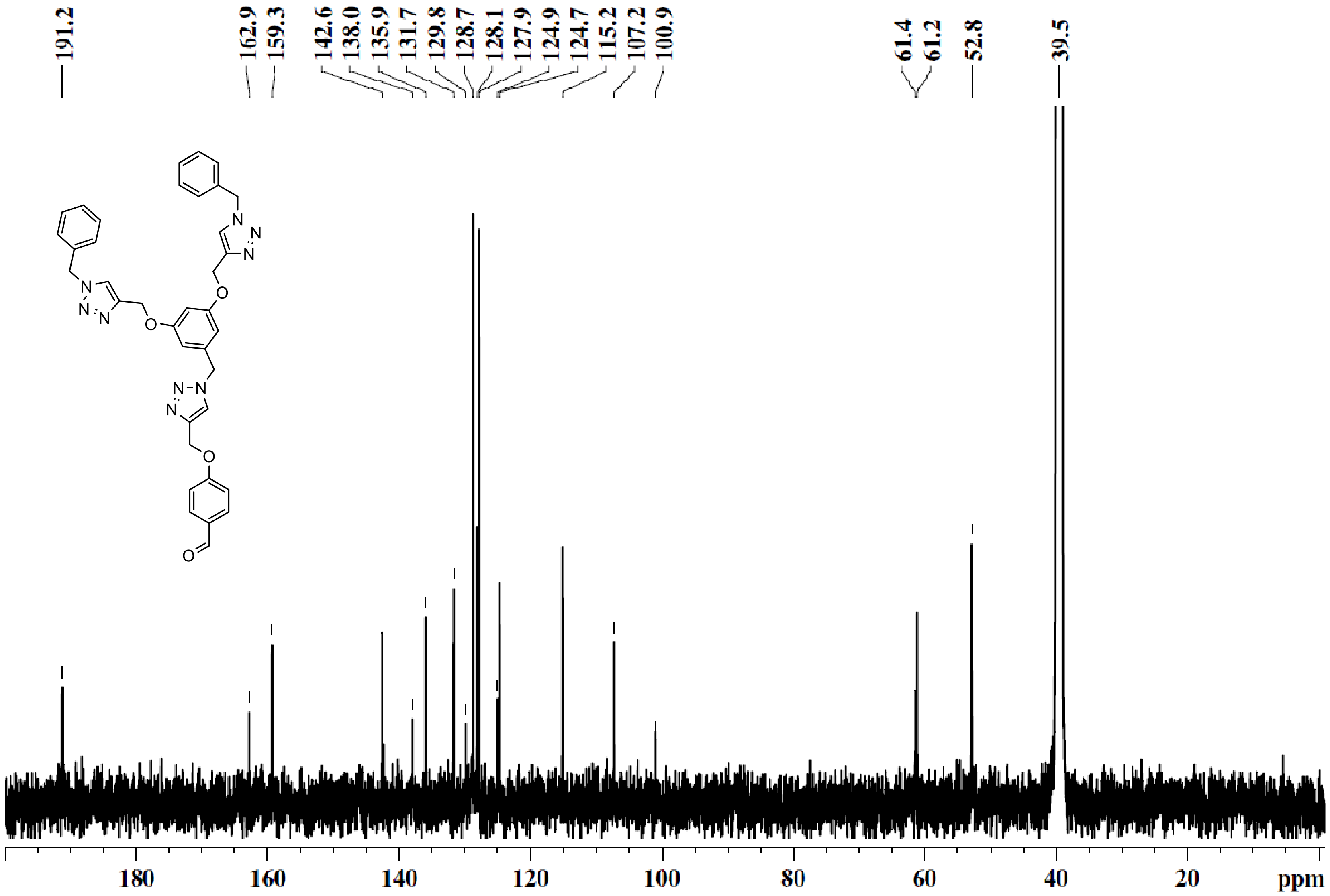


**Figure S2.** $^{13}$C NMR spectrum of spectrum of 4-{3,5-bis[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]benzyloxy}benzaldehyde (**3**) in DMSO-$d_6$ (T=303 K).

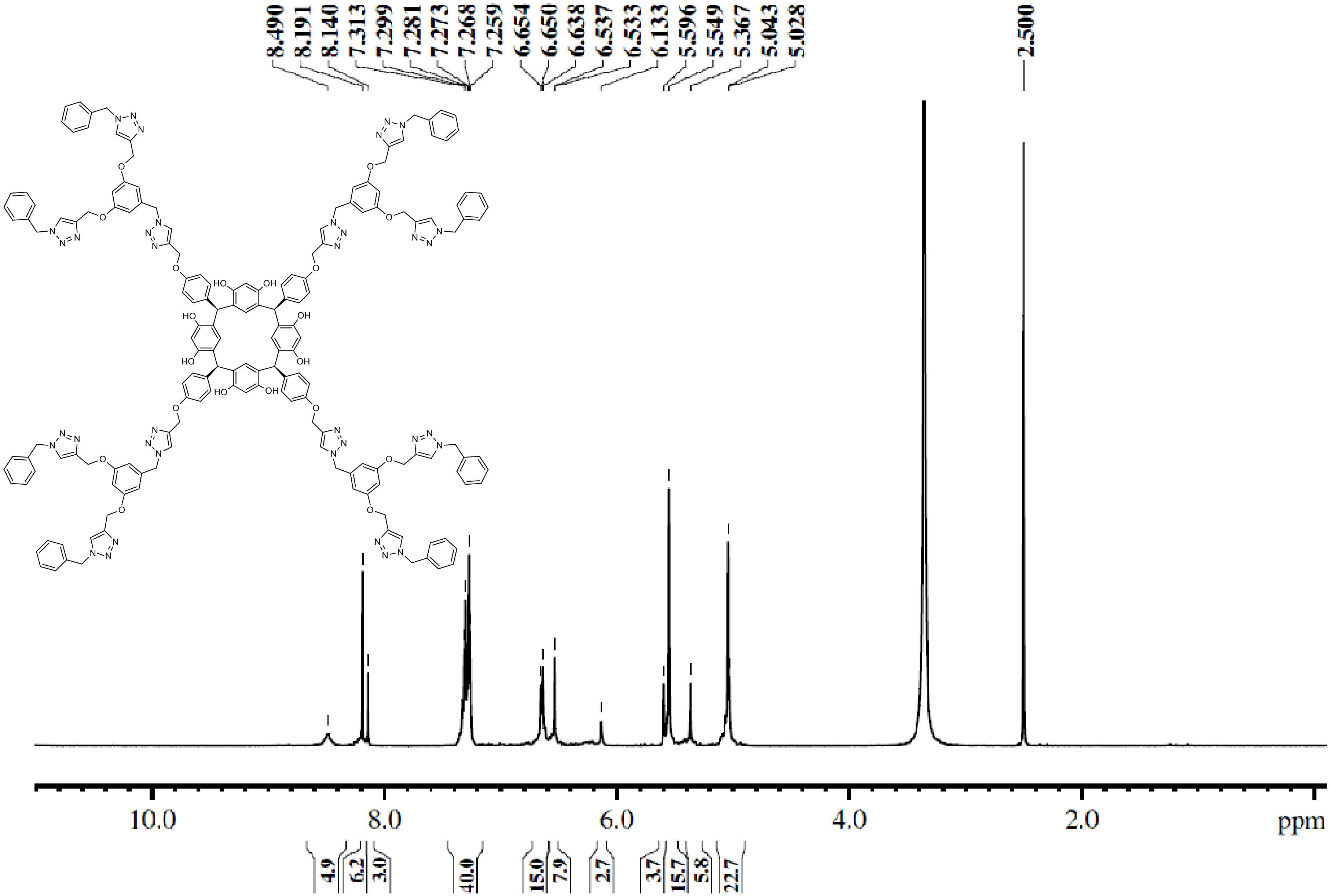


**Figure S3.** $^1$H NMR spectrum of calix[4]resorcinol **4a** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

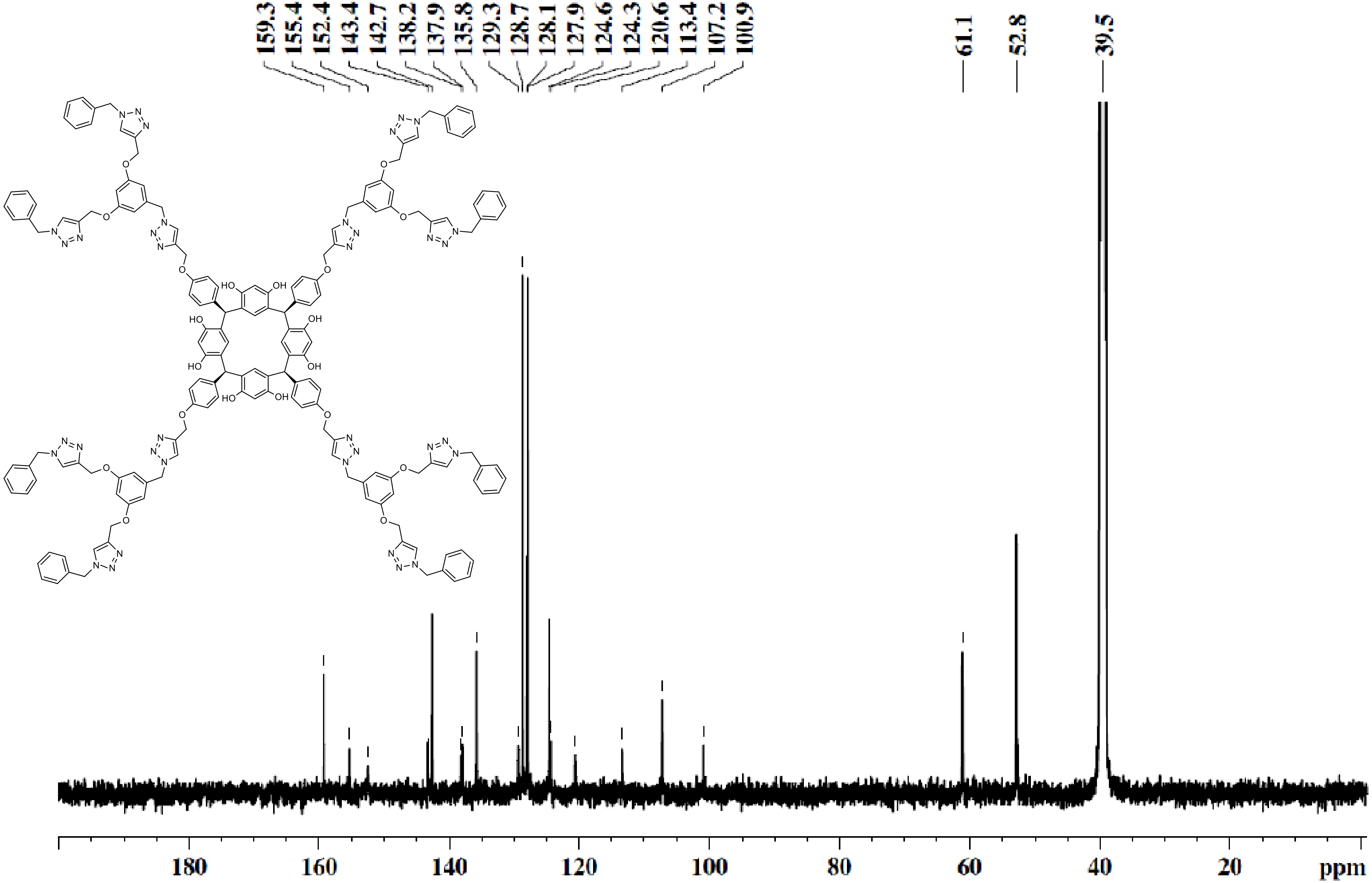


**Figure S4.** $^{13}$C NMR spectrum of calix[4]resorcinol **4a** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

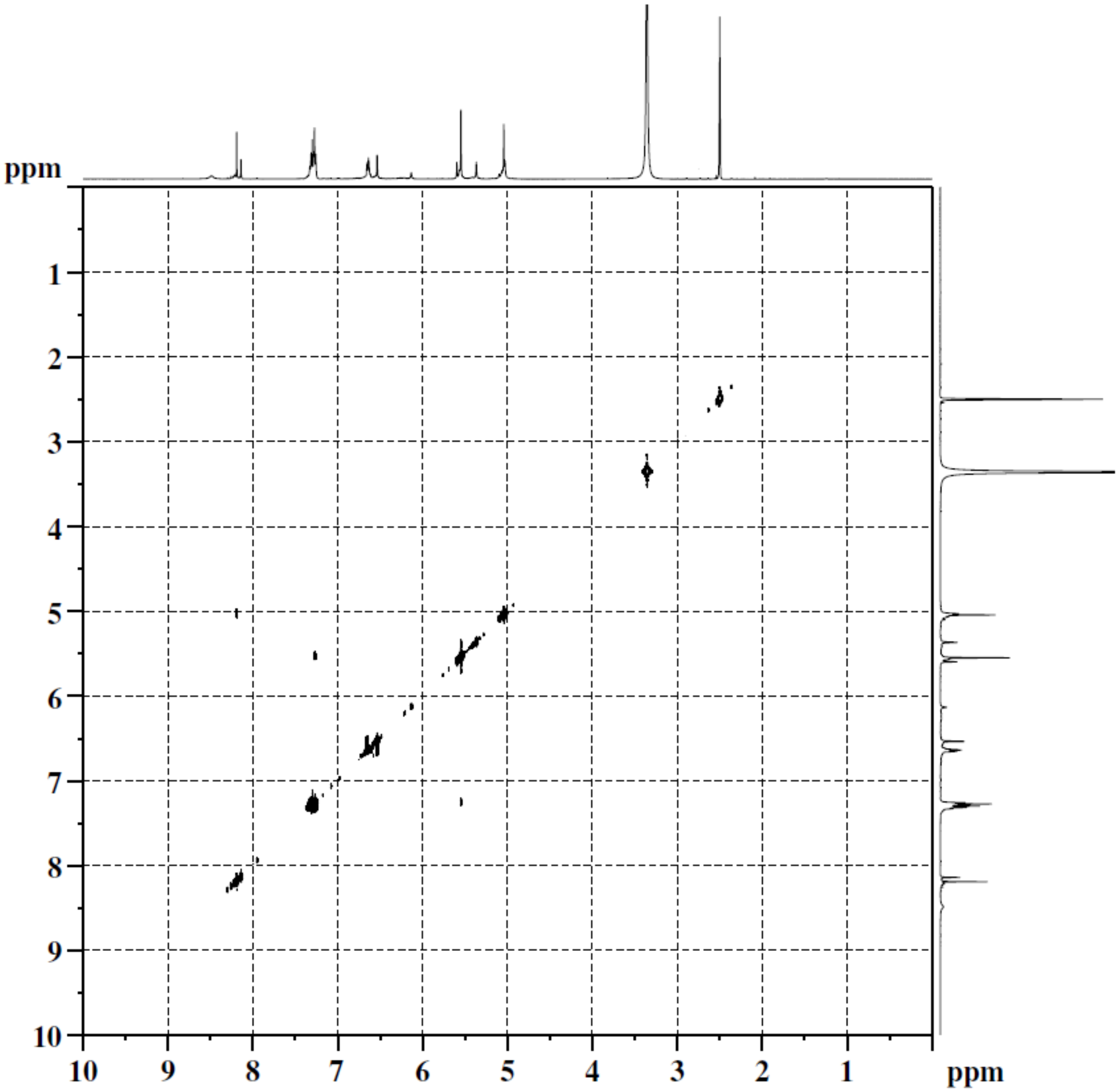


**Figure S5** COSY NMR spectrum of calix[4]resorcinol **4a** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

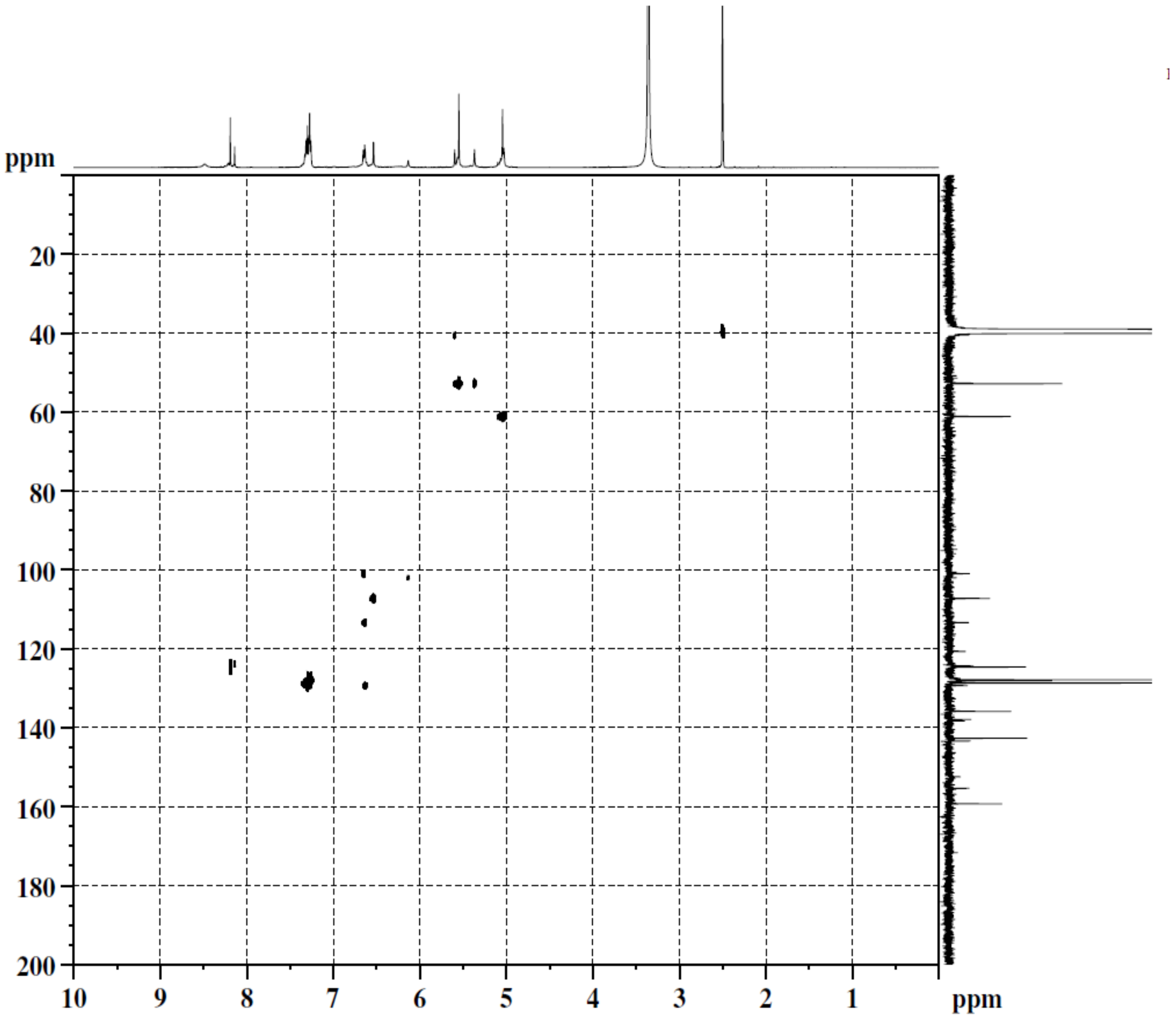


**Figure S6** HSQC ($^{13}$C) NMR spectrum of calix[4]resorcinol **4a** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

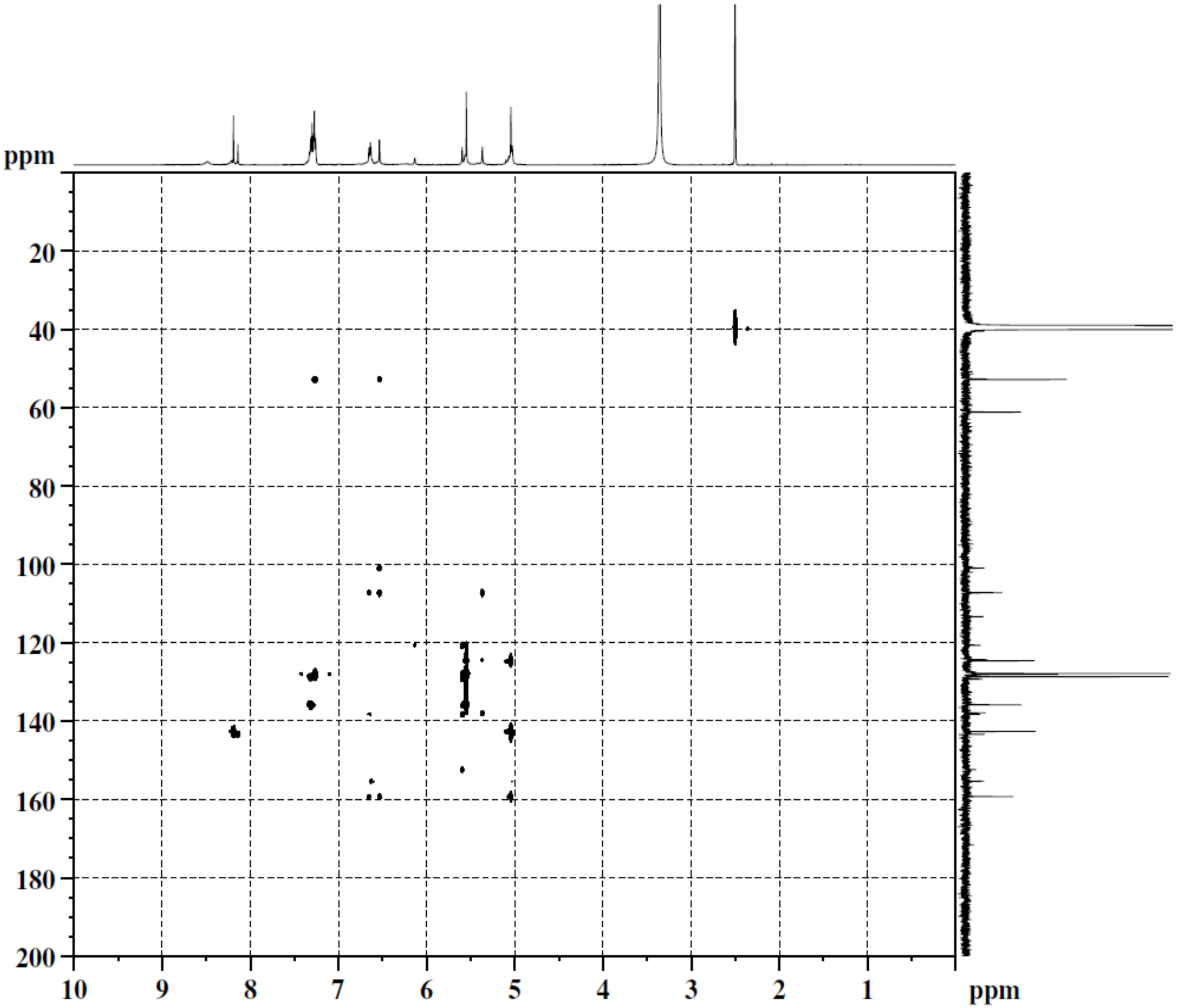


**Figure S7** HMBC ($^{13}$C) NMR spectrum of calix[4]resorcinol **4a** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

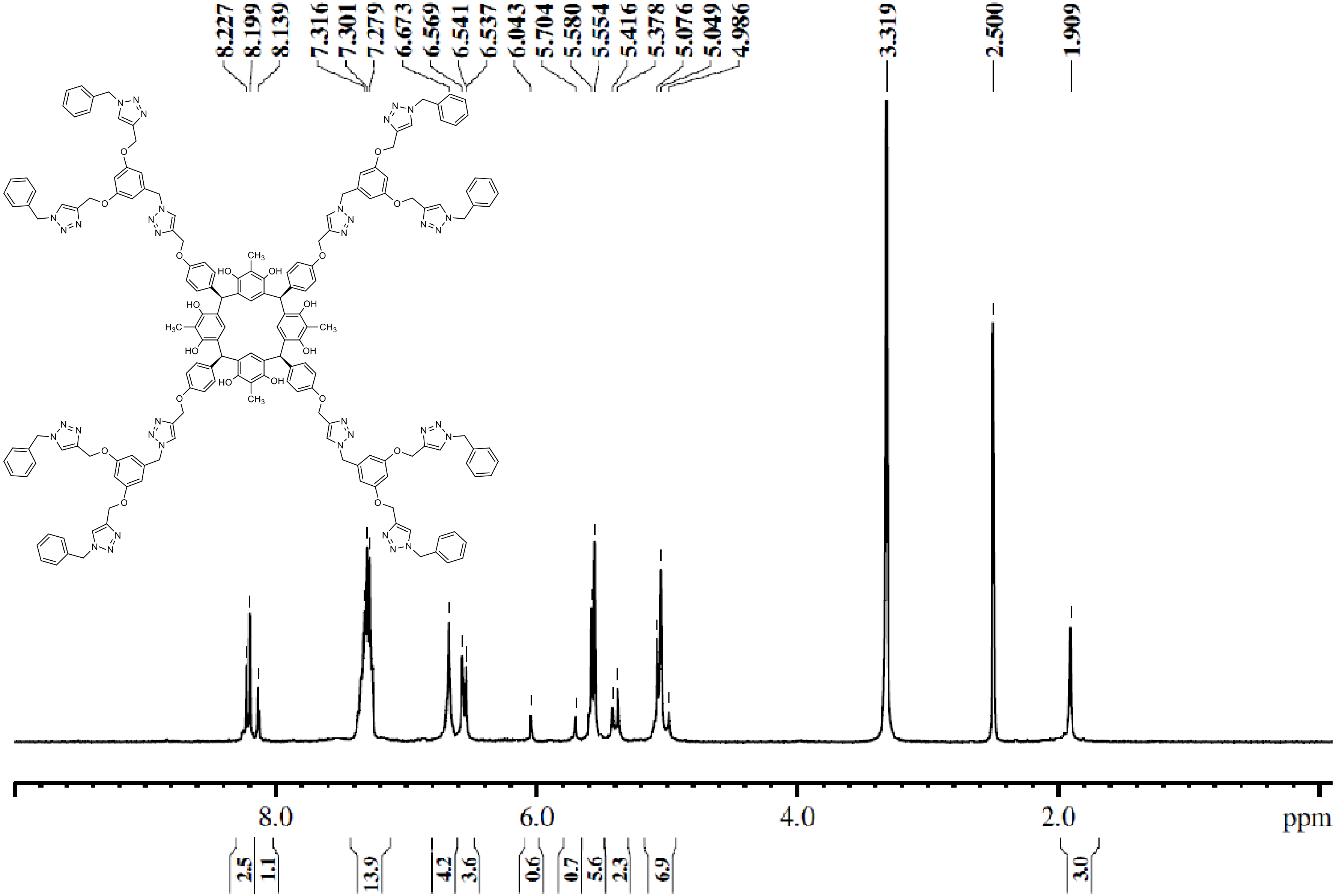


**Figure S8.** $^1$H NMR spectrum of calix[4]resorcinol **4b** (*rccc*-diastereoisomer) in DMSO-*d*$_6$ (T=303 K).

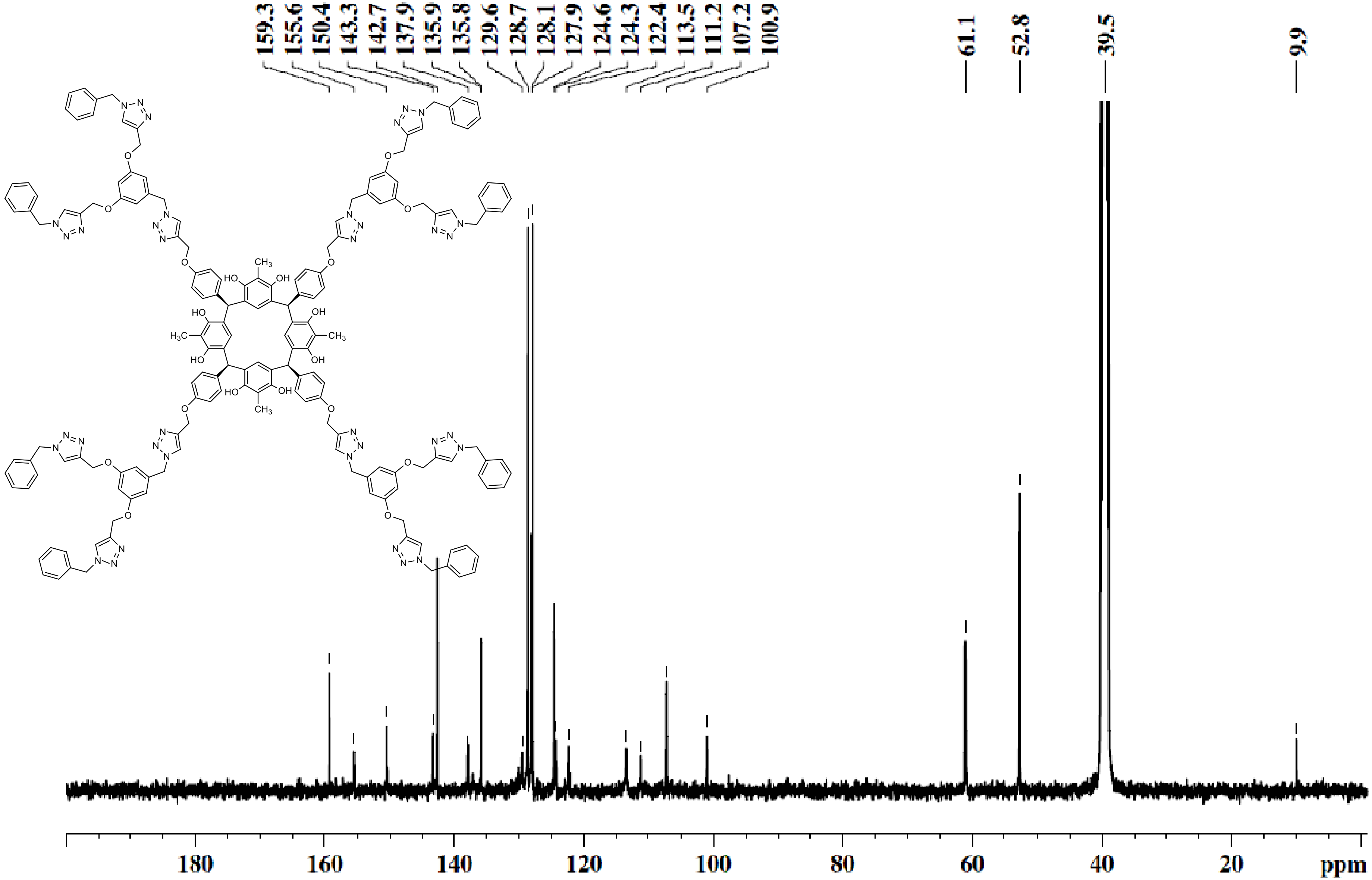


**Figure S9.** $^{13}$C NMR spectrum of calix[4]resorcinol **4b** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

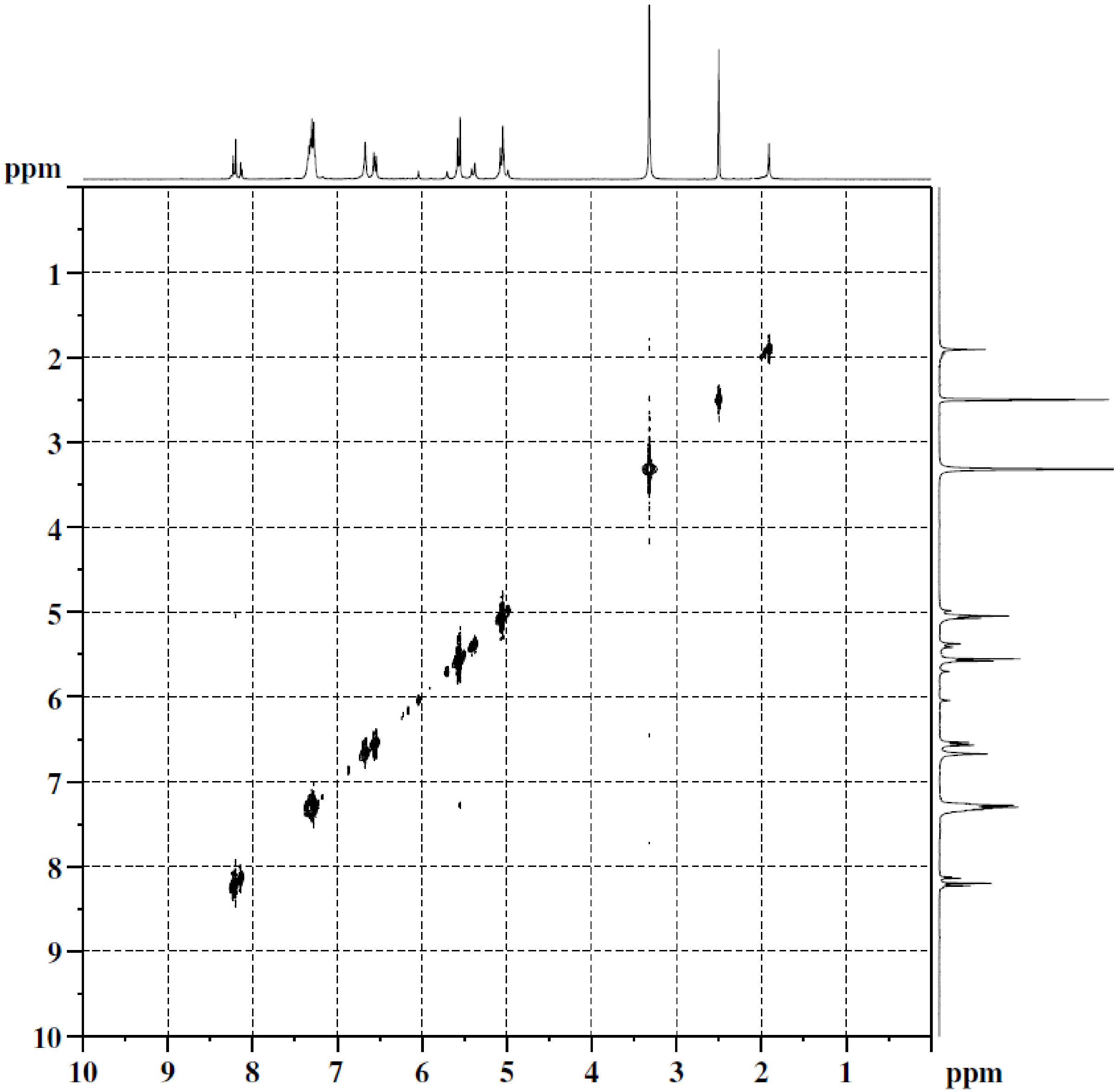


**Figure S10** COSY NMR spectrum of calix[4]resorcinol **4b** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

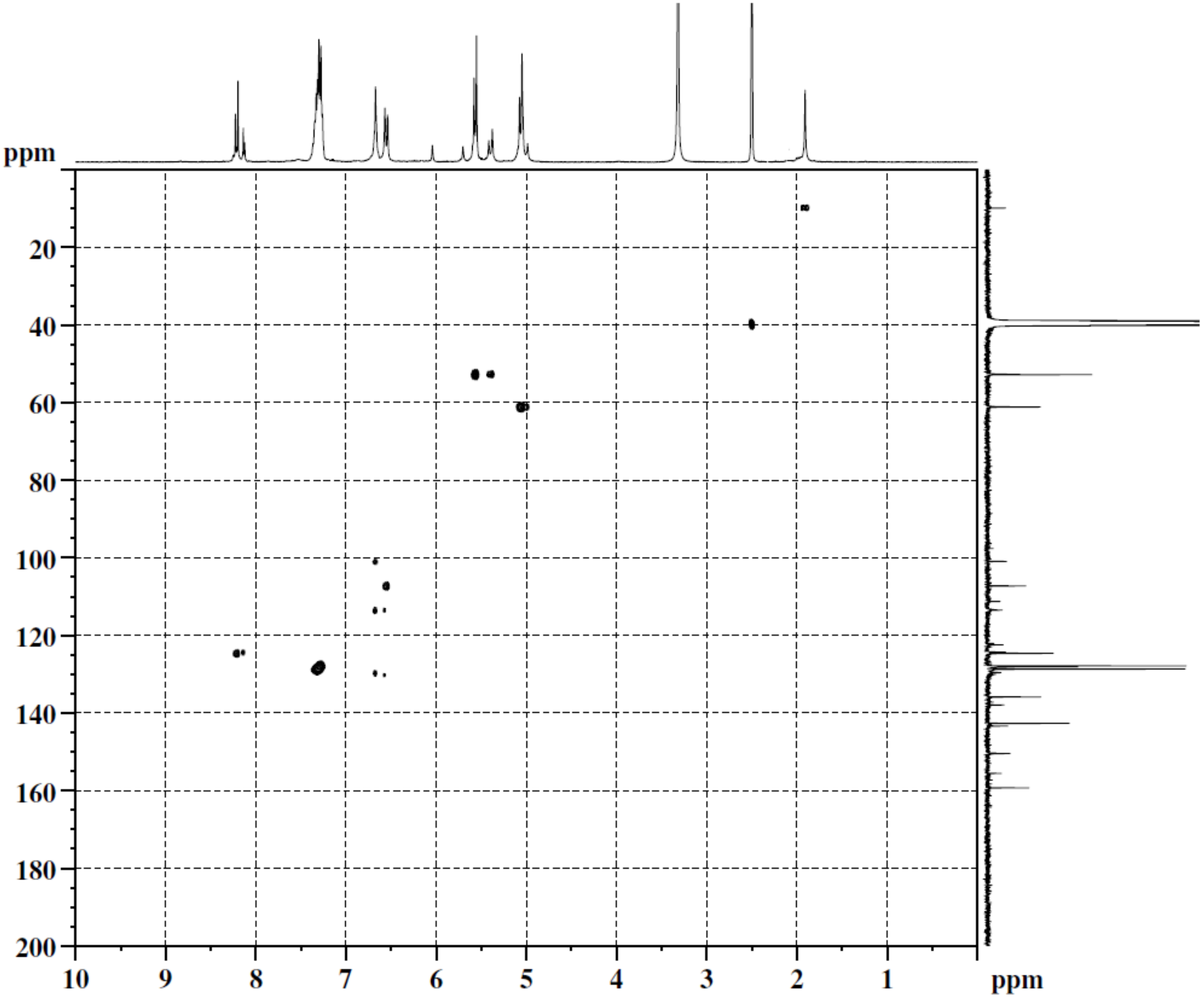


**Figure S11** HSQC ($^{13}$C) NMR spectrum of calix[4]resorcinol **4b** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).

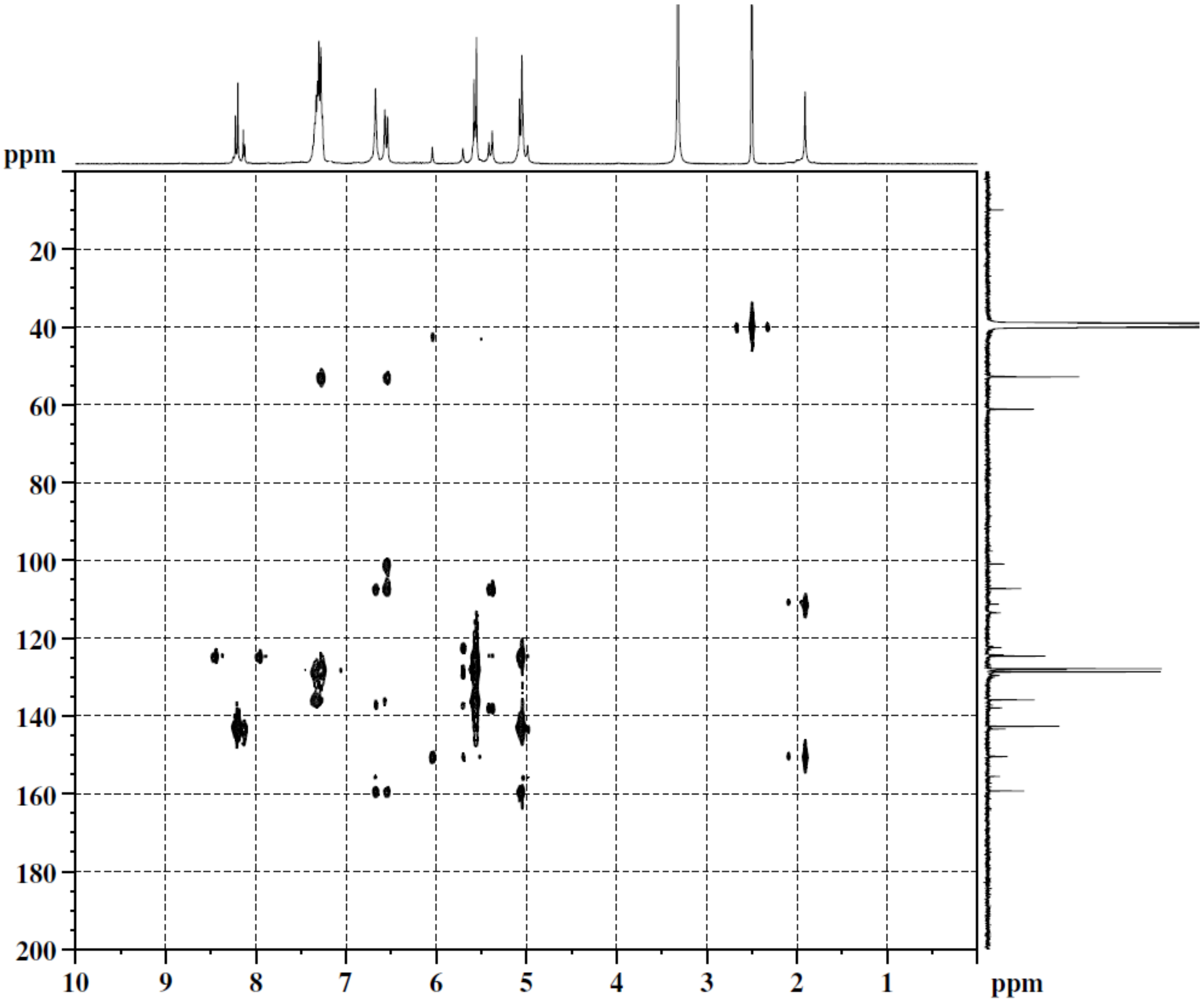


**Figure S12** HMBC ($^{13}$C) NMR spectrum of calix[4]resorcinol **4b** (*rccc*-diastereoisomer) in DMSO-$d_6$ (T=303 K).