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Synthesis and structural features of new calix[4]resorcinols with anthracene- and pyrene-ended isoxazole-containing fragments

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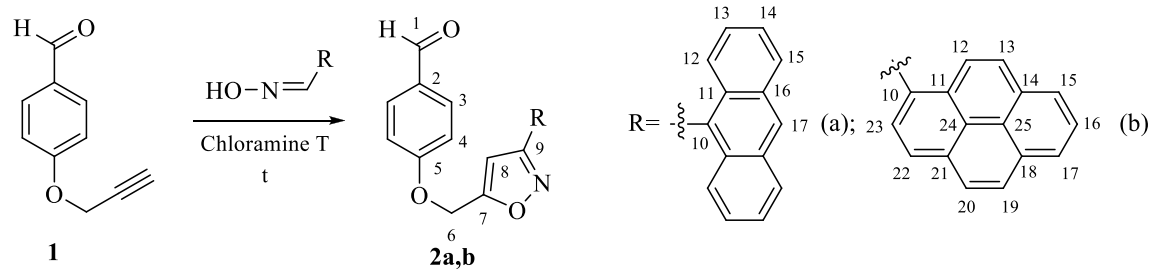
General

NMR experiments were performed on a Bruker AVANCE-600 spectrometer at 303K equipped with 5 mm broadband probehead working at 500 MHz in ^{1}H and 125 MHz in ^{13}C NMR experiments. Chemical shifts were reported relative to residual signal of deuterated solvents. IR spectra of obtained 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 ESI MS measurements were performed using an AmazonX ion trap mass spectrometer (Bruker Daltonic GmbH, Germany) in positive (and/or negative) mode in the mass range of 70–3000. The capillary voltage was −3500 V, nitrogen drying gas – 10 $L \cdot min^{-1}$, desolvation temperature – 250 °C. An methanol/water solution (70:30) was used as a mobile phase at a flow rate of 0.2 mL/min by binary pump (Agilent 1260 chromatograph, USA). The sample was dissolved in methanol to a concentration of 10-6 $g \cdot L^{-1}$. The instrument was calibrated with a tuning mixture (Agilent G2431A, USA). For instrument control and data acquiring the TrapControl 7.0 software (Bruker Daltonik GmbH, Germany) was used. Data processing was performed by DataAnalysis 4.0 SP4 software (Bruker Daltonik GmbH, Germany). 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 (λ = 355 nm, repetition rate 100 Hz) was used. The mass spectrum was obtained with an accelerating voltage of 25 kV and an ion extraction delay time of 30 ns. The resulting mass spectrum was 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 was 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 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.



1 **2a,b** **86-97%**

Scheme S1

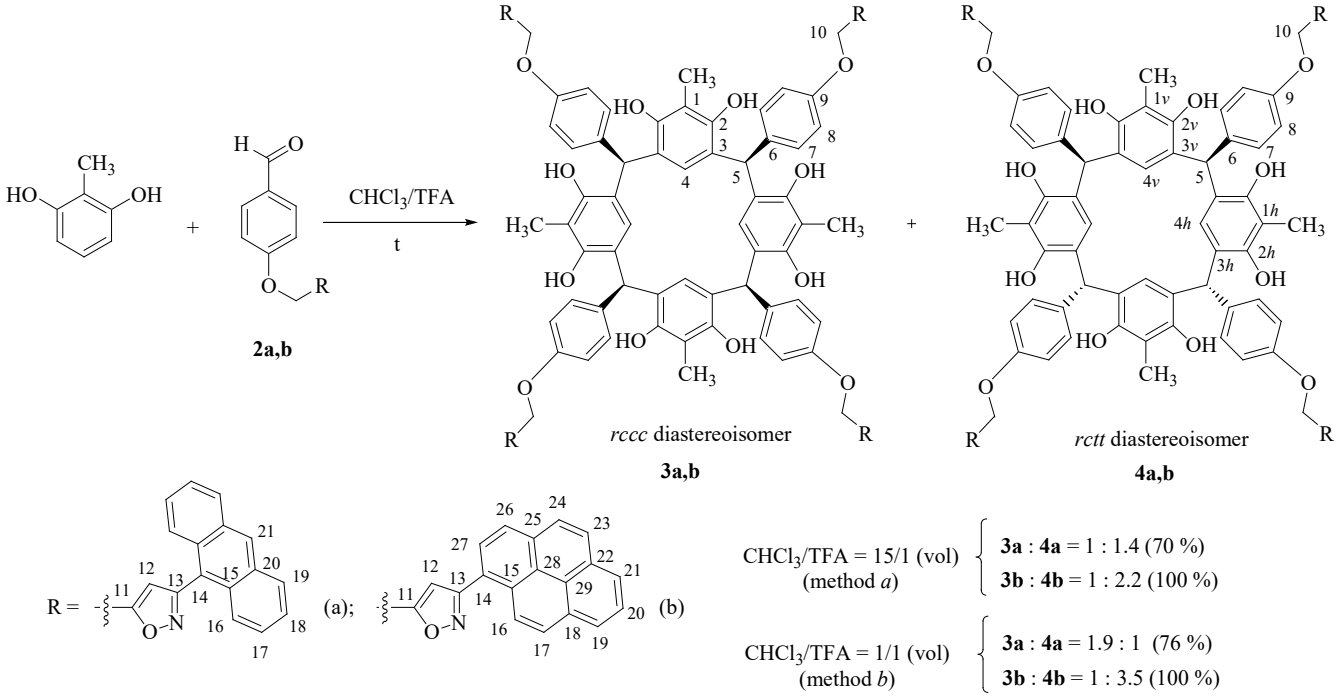
Experimental procedure for preparation and spectroscopic data of 4-{[3-(anthracen-9-yl)isoxazol-5-yl]methoxy}benzaldehyde (**2a**)

To the suspension of 4-(2-propyn-1-yloxy)benzaldehyde (**1**) (0.50 g, 3.13 mmol) in EtOH (70 mL) was added anthracene-9-carbaldehyde oxime[S1] (0.35 g, 1.58 mmol) and chloramine-T (0.36 g, 1.59 mmol). The reaction mixture was heated at reflux in argon atmosphere for 2.5 h. Then a second portion of oxime (1.58 mmol) and chloramine-T (1.59 mmol) was added. Refluxing was continued for another 2.5 h prior to the third addition of oxime and chloramine-T in the same quantities. After 2.5 h refluxing the water (200 mL) was added to the reaction mixture. The mixture was extracted with chloroform (20 mL×3), organic layers were combined and dried over anhydrous $MgSO_4$. Then solvent was evaporated and crude product was purified by column chromatography using the mixture dichloromethane/methanol (10:1) as eluent. The pure compound **2a** was obtained as light yellow solid (1.15 g, 97 % yield, R_f = 0.19), m. p. 127–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.64 (s, 2H, H6), 7.06 (s, 1H, H8), 7.37 (d, $^3J_{HH}$ 8.8 Hz, 2H, H4), 7.55 (t, $^3J_{HH}$ 8.8 Hz, 2H, H13), 7.59 (t, $^3J_{HH}$ 8.8 Hz, 2H, H14), 7.70 (dd, $^3J_{HH}$ 8.7 Hz, $^4J_{HH}$ 1.1 Hz, 2H, H12), 7.95 (t, $^3J_{HH}$ 8.8 Hz, 2H, H3), 8.20 (d, $^3J_{HH}$ 8.8 Hz, 2H, H15), 8.83 (s, 1H, H17), 9.93 (s, 1H, H1) ppm. ^{13}C (125 MHz, $CDCl_3$): δ 60.9 (s, C6), 107.9 (s, C8), 115.5 (s, C4), 122.4 (s, C10), 124.9 (s, C12), 125.7 (s, C14), 127.1 (s, C13), 128.7 (s, C15), 129.1 (s, C17), 129.9 (s, C11), 130.5 (s, C2), 130.7 (s, C16), 131.9 (s, C3), 160.4 (s, C9), 162.4 (s, C5), 167.9 (s, C7), 191.5 (s, C1) ppm. IR ν_{max} (KBr): 1602 (C=N), 1696 (C=O) cm^{-1}. Anal. Calcd. for $C_{25}H_{17}NO_3$ (%): C, 79.14; H, 4.52; N, 3.69. Found: C, 79.13; H, 4.56; N, 3.79. ESI-MS: *m/z* = 380 $[M+H]^+$, 402 $[M+Na]^+$ (calcd. M = 379).

Experimental procedure for preparation and spectroscopic data of 4-{[3-(pyren-1-yl)isoxazol-5-yl]methoxy}benzaldehyde (**2b**)

Aldehyde **2b** was obtained as a light yellow powder with an yield of 0.96 g (86%) according to a method analogous to that used to prepare **2a** by treatment of **1** (0.44 g, 2.75 mmol) with 1-pyrene carboxaldehyde oxime[S2] (0.33 g, 1.35 mmol) and chloramine-T (0.31 g, 1.36 mmol) three times. The crude product was purified by column chromatography using dichloromethane as eluent (R_f = 0.14). Mp 171–172 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.61 (s, 2H, H6), 7.34 (s, 1H, H8), 7.36 (d, $^3J_{HH}$ 8.8 Hz, 2H, H4), 7.94 (d, $^3J_{HH}$ 8.9 Hz, 2H, H3), 8.14 (t, $^3J_{HH}$ 7.6 Hz, 1H, H16), 8.26 (d, $^3J_{HH}$ 9.0 Hz, 1H, H20), 8.30 (d, $^3J_{HH}$ 9.0 Hz, 1H, H19), 8.32 (d, $^3J_{HH}$ 9.3 Hz, 1H, H13), 8.33 (d, $^3J_{HH}$ 8.1 Hz, 1H, H23), 8.37 (d, $^3J_{HH}$ 7.6 Hz, 1H, H15), 8.39 (d, $^3J_{HH}$ 7.6 Hz, 1H, H17), 8.42

(d, $^3J_{HH}$ 8.1 Hz, 1H, H22), 8.71 (d, $^3J_{HH}$ 9.3 Hz, 1H, H12), 9.92 (s, 1H, H1) ppm. ^{13}C (125 MHz, $CDCl_3$): δ 60.7 (s, C6), 106.2 (s, C8), 115.3 (s, C4), 122.7 (s, C24), 123.6 (s, C25), 124.1 (s, C11), 124. (s, C12), 125.0 (s, C22), 125.7 (s, C15), 126.1 (s, C17), 126.7 (s, C16), 127.2 (s, C20), 127.6 (s, C23), 128.2 (s, C21), 128.6 (s, C19), 128.9 (s, C13), 130.1 (s, C14), 130.4 (s, C2), 130.8 (s, C18), 131.8 (s, C3), 131.9 (s, C10), 162.4 (s, C5), 162.6 (s, C9), 167.4 (s, C7), 191.4 (s, C1) ppm. IR ν_{max} (KBr): 1600 (C=N), 1698 cm^{-1} (C=O) cm^{-1}. Anal. Calcd. for $C_{27}H_{17}NO_3$ (%): C, 80.38; H, 4.25; N, 3.47. Found: C, 80.31; H, 4.28; N, 3.49. ESI-MS: *m/z* = 380 $[M+H]^+$, 402 $[M+Na]^+$ (calcd. M = 379).



Scheme S2

Experimental procedure for preparation and spectroscopic data of anthracene-ended isoxazole-containing calix[4]resorcinols rccc **3a** *and rctt* **4a** *diastereoisomers*

<u>*Method a*</u>: A mixture of 2-methylresorcinol (0.1 g, 0.81 mmol) and aldehyde **2a** (0.3 g, 0.81 mmol) in $CHCl_3$ (15 mL) and TFA (1 mL) was stirred under reflux for 32 h under an argon atmosphere. The precipitate formed was filtered, washed sequentially with $CHCl_3$ and Et_2O. The washing procedure was repeated until only a colorless filtrate was observed. After drying *in vacuo* (40 ºC, 0.06 Torr) pure **4a** as its *rctt* isomer in *chair* conformation was obtained (0.09 g, 24%) as a white powder. Filtrate was evaporated and the crude product was subjected to flash chromatography with CH_2Cl_2–MeOH (10:0.5) affording additional amount 0.06 g (16%) of pure *rctt* diastereoisomer **4a** (R_f=0.53) and pure *rccc* diastereoisomer **3a** in the *cone* conformation as a beige powder (0.11 g , 30%, R_f=0.27). The *rccc*/*rctt* distereoisomers ratio was 1:1.4, total yield 70%.

<u>*Method b*</u>: Calix[4]resorcinols **3a** (*rccc*) and **4a** (*rctt*) in a 1.9:1 ratio were obtained upon condensation of 2-methylresorcinol (0.1 g, 0.81 mmol) with aldehyde **2a** (0.3 g, 0.81 mmol) in $CHCl_3$ (15 mL) and TFA (15 mL). Reaction mixture was stirred under reflux for 32 h under an argon atmosphere. *Rctt* isomer **4a** (yield 0.10

g, 26%) and *rccc* isomer **3a** (yield 0.19 g, 50%) were isolated as described above with overall yield 0.29 g (76 %).

***Calix[4]resorcinol rccc diastereoisomer* 3a**: m.p. > 175 ºC (dec). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.96 (s, 12H, CH_3), 5.42 (s, 8H, H10), 5.78 (s, 4H, H5), 6.11 (s, 4H, H4), 6.79 (d, $^3J_{HH}$ 8.6 Hz, 8H, H7), 6.82 (d, $^3J_{HH}$ 8.6 Hz, 8H, H8), 6.88 (s, 4H, H12), 7.19 (t, $^3J_{HH}$ 7.7 Hz, 8H, H18), 7.39 (t, $^3J_{HH}$ 7.7 Hz, 8H, H17), 7.59 (d, $^3J_{HH}$ 8.6 Hz, 8H, H19), 8.06 (d, $^3J_{HH}$ 8.6 Hz, 8H, H16), 8.70 (s, 4H, H21) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 10.0 (s, $\underline{C}H_3$), 42.1 (s, C5), 60.7 (s, C10), 107.2 (s, C12), 111.3 (s, C1), 113.7 (s, C8), 122.4 (s, C3), 122.4 (s, C14), 124.8 (s, C16), 125.4 (s, C18), 126.6 (s, C17), 127.4 (s, C4), 128.4 (s, C19), 128.8 (s, C21), 129.7 (s, C7), 129.8 (s, C15), 130.5 (s, C20), 138.1 (s, C6), 150.6 (s, C2), 155.2 (s, C9), 160.2 (s, C13), 168.8 (s, C11) ppm. IR ν_{max} (KBr): 1605 (C=N), 3100–3650 (OH) cm^{-1}. Anal. Calcd. for $C_{128}H_{92}N_4O_{16}$ (%): C, 79.16; H, 4.77; N, 2.88. Found: C, 79.12; H, 4.75; N, 2.98. MALDI-MS, *m/z*: 1943 $[M+H]^+$, 1965 $[M+Na]^+$ (calcd. M = 1942). †

***Calix[4]resorcinol rctt diastereoisomer* 4a**: m.p. > 160 ºC (dec). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.95 (s, 12H, CH_3^h), 2.14 (s, 12H, CH_3^v), 5.42 (s, 8H, H10), 5.49 (s, 2H, H4^v), 5.65 (s, 4H, H5), 6.23 (s, 2H, H4^h), 6.67 (d, $^3J_{HH}$ 8.7 Hz, 8H, H8), 6.73 (d, $^3J_{HH}$ 8.7 Hz, 8H, H7), 6.93 (s, 4H, H12), 7.24 (s, 2H, OH^v), 7.34 (t, $^3J_{HH}$ 8.8 Hz, 8H, H17), 7.48 (t, $^3J_{HH}$ 8.8 Hz, 8H, H18), 7.60 (s, 2H, OH^h), 7.65 (d, $^3J_{HH}$ 8.8 Hz, H16), 8.14 (d, $^3J_{HH}$ 8.8 Hz, H19), 8.76 (s, H21) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 9.6 (s, $\underline{C}H_3^v$), 9.9 (s, $\underline{C}H_3^h$), 42.8 (s, C5), 60.9 (s, C10), 107.2 (s, C12), 110.6 (s, C1^v), 111.0 (s, C1^h), 113.7 (s, C8), 122.2 (s, C3^v), 122.5 (s, C14), 122.8 (s, C3^h), 124.9 (s, C16), 125.5 (s, C18), 125.6 (s, C4^h), 126.7 (s, C17), 128.1 (s, C4^v), 128.5 (s, C19), 128.8 (s, C21), 129.8 (s, C20), 130.2 (s, C7), 130.6 (s, C15), 136.7 (s, C6), 150.4 (s, C2^v), 150.6 (s, C2^h), 155.2 (s, C9), 160.2 (s, C13), 168.9 (s, C11) ppm. IR ν_{max} (KBr): 1606 (C=N), 3100–3650 (OH) cm^{-1}. Anal. Calcd. for $C_{128}H_{92}N_4O_{16}$ (%): C, 79.16; H, 4.77; N, 2.88. Found: C, 79.12; H, 4.71; N, 2.91. MALDI-MS, *m/z*: 1943 $[M+H]^+$, 1965 $[M+Na]^+$ (calcd. M = 1942).

Experimental procedure for preparation and spectroscopic data of pyrene-ended isoxazole-containing calix[4]resorcinols rccc **3b** *and rctt* **4b** *diastereoisomers*

<u>*Method a*</u>: Calix[4]resorcinol *rccc* **3b** and *rctt* **4b** diastereoisomers in a 1 : 2.2 ratio with total yield of 0.41 g (100%) were obtained by treatment of 2-methylresorcinol (0.1 g, 0.81 mmol) with aldehyde **2b** (0.32 g, 0.81 mmol) in $CHCl_3$ (15 mL) and TFA (1 mL) at reflux for 5.5 h under an argon atmosphere. The precipitate formed was filtered, washed sequentially with $CHCl_3$ and Et_2O. After drying in *vacuo* (40 ºC, 0.06 Torr) pure **4b** as its *rctt* diastereoisomer in *chair* conformation was obtained (0.28 g, 68%) as a white powder. The filtrate was evaporated and the residue was recrystallized from diethyl ether into hexane to afford after drying in *vacuo* the pure *rccc* diastereoisomer **3b** (0.13 g, 32%) as a beige powder.

† In the NMR spectra of *rccc* diastereoisomer calix[4]resorcinols **3a,b** the one signal corresponds to each group of atoms, which indicates the existence of a highly symmetric *cone* conformation in solutions of these compounds. In the NMR spectra of *rctt* diastereoisomer calix[4]resorcinols **4a,b** in *chair* conformation the doubling of the signals of protons or carbon atoms of resorcinol residues is observed, i.e. opposite resorcinol aromatic rings are arranged vertically (*v*) or horizontally (*h*) with respect to the macrocycle cavity, as it was established in our earlier studies.[S3-S4]

Method b: Calix[4]resorcinols *rccc* **3b** and *rctt* **4b** in a 1:3.5 ratio were obtained upon condensation of 2-methylresorcinol (0.1 g, 0.81 mmol) with aldehyde **2b** (0.32 g, 0.81 mmol) in $CHCl_3$ (15 mL) and TFA (15 mL). Reaction mixture was stirred under reflux for 5.5 h under an argon atmosphere. *Rccc* isomer **3b** (yield 0.09 g, 22%) and *rctt* isomer **4b** (yield 0.32 g, 78%) were isolated as described above with overall yield 0.41 g (100 %).

***Calix[4]resorcinol rccc diastereoisomer* 3b**: m.p. > 180 ºC (dec). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.96 (s, 12H, CH_3), 5.43 (s, 8H, H10), 5.83 (s, 4H, H5), 6.14 (s, 4H, H4), 6.83 (d, $^3J_{HH}$ 7.9 Hz, 8H, H7), 6.92 (d, $^3J_{HH}$ 7.9 Hz, 8H, H8), 7.14 (s, 4H, H12), 7.46 (br.s, 8H, OH), 7.78 (d, $^3J_{HH}$ 9.0 Hz, 4H, H26), 7.83 (d, $^3J_{HH}$ 9.3 Hz, 4H, H21), 7.90 (m, 8H, H17, H19), 7.93 (m, 8H, H23), 7.98 (d, $^3J_{HH}$ 8.5 Hz, 4H, H27), 8.02 (d, $^3J_{HH}$ 8.2 Hz, 4H, H24), 8.17 (m, 4H, H20), 8.44 (d, $^3J_{HH}$ 9.1 Hz, 4H, H16). ^{13}C NMR (125 MHz, DMSO-d_6): δ 10.0 (s, $\underline{C}H_3$), 42.1 (s, C5), 60.6 (s, C10), 105.4 (s, C12), 111.4 (s, C1), 113.7 (s, C8), 122.4 (s, C28), 122.5 (s, C3), 123.2 (s, C29), 123.7 (s, C15), 124.1 (s, C26), 124.5 (s, C19), 125.2 (s, C16), 125.7 (s, C20), 126.2 (s, C24), 126.7 (s, C21), 127.0 (s, C4), 127.8 (s, C23), 128.1 (s, C27), 128.2 (s, C25, C17), 129.7 (s, C14), 129.9 (s, C7), 130.4 (s, C18), 131.4 (s, C22), 138.2 (s, C6), 150.6 (s, C2), 155.4 (s, C9), 162.4 (s, C13), 168.1 (s, C11) ppm. IR ν_{max} (KBr): 1605 (C=N), 3100–3650 (OH) cm^{-1}. Anal. Calcd. for $C_{136}H_{92}N_4O_{16}$ (%): C, 80.14; H, 4.55; N, 2.75. Found: C, 80.11; H, 4.53; N, 2.78. MALDI-MS, *m/z*: 2039 $[M+H]^+$ (calcd. M = 2038).

***Calix[4]resorcinol rctt diastereoisomer* 4b**: m.p. > 195 ºC (dec). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.95 (s, 12H, CH_3^h), 2.18 (s, 12H, CH_3^v), 5.34 (s, 8H, H10), 5.54 (s, 2H, H4^v), 5.67 (s, 4H, H5), 6.25 (s, 2H, H4^h), 6.71 (d, $^3J_{HH}$ 8.6 Hz, 8H, H7), 6.78 (d, $^3J_{HH}$ 8.7 Hz, 8H, H8), 7.14 (s, 4H, H12), 7.30 (s, 2H, OH^v), 7.61 (s, 2H, OH^h), 7.88 (d, $^3J_{HH}$ 9.5 Hz, 4H, H17), 7.92 (d, $^3J_{HH}$ 9.0 Hz, 4H, H24), 7.98 (d, $^3J_{HH}$ 7.6 Hz, 4H, H20), 8.00 (d, $^3J_{HH}$ 8.1 Hz, 4H, H26), 8.04 (d, $^3J_{HH}$ 7.5 Hz, 4H, H21), 8.06 (d, $^3J_{HH}$ 8.1 Hz, 4H, H27), 8.07 (d, $^3J_{HH}$ 9.0 Hz, 4H, H23), 8.22 (d, $^3J_{HH}$ 7.6 Hz, 4H, H19), 8.50 (d, $^3J_{HH}$ 9.5 Hz, 4H, H16) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 9.9 (s, $\underline{C}H_3^v$), 10.0 (s, $\underline{C}H_3^h$), 43.2 (s, C5), 60.9 (s, C10), 105.2 (s, C12), 110.7 (s, C1^v), 111.0 (s, C1^h), 113.7 (s, C8), 122.2 (s, C3^v), 122.5 (s, C3^h), 123.0 (s, C28), 123.3 (s, C15), 123.8 (s, C29), 124.2 (s, C16), 124.6 (s, C26), 125.3 (s, C21), 125.7 (s, C4^h), 125.8 (s, C19), 126.3 (s, C20), 126.8 (s, C24), 127.2 (s, C27), 127.9 (s, C23), 128.1 (s, C4^v), 128.2 (s, C25), 128.3 (s, C17), 129.8 (s, C18), 130.3 (s, C14), 130.3 (s, C7), 130.5 (s, C22), 136.8 (s, C6), 150.4 (s, C2^v), 150.7 (s, C2^h), 155.4 (s, C9), 162.5 (s, C13), 168.2 (s, C11) ppm. IR ν_{max} (KBr): 1605 (C=N), 3100–3650 (OH) cm^{-1}. Anal. Calcd. for $C_{136}H_{92}N_4O_{16}$ (%): C, 80.14; H, 4.55; N, 2.75. Found: C, 79.99; H, 4.51; N, 2.71. MALDI-MS, *m/z*: 2039 $[M+H]^+$, 2061 $[M+Na]^+$ (calcd. M = 2038).

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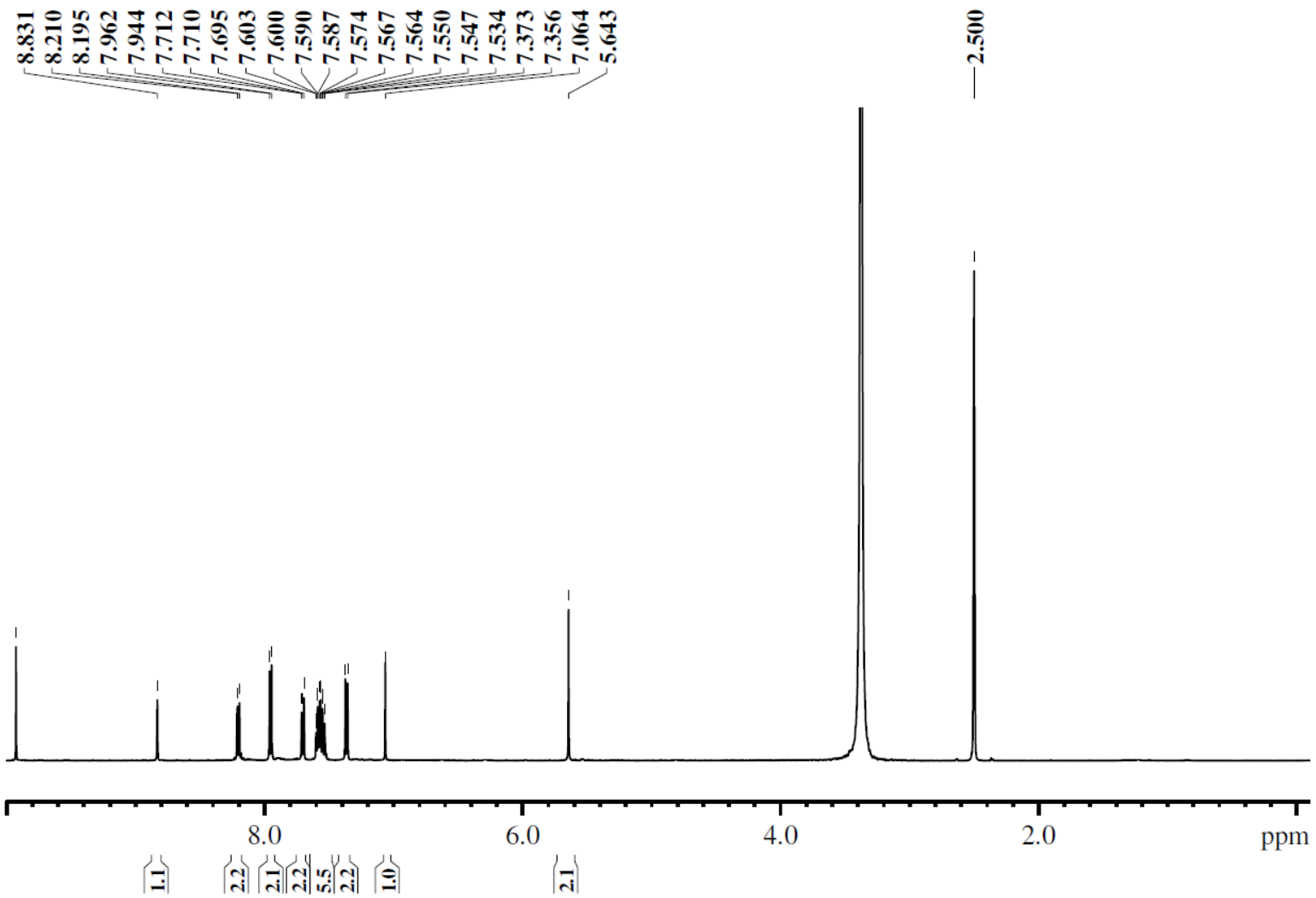

Figure S1. ^{1}H NMR spectrum of 4-((3-(anthracen-9-yl)isoxazol-5-yl)methoxy)benzaldehyde (**2a**) in $CDCl_3$ (T=303 K)

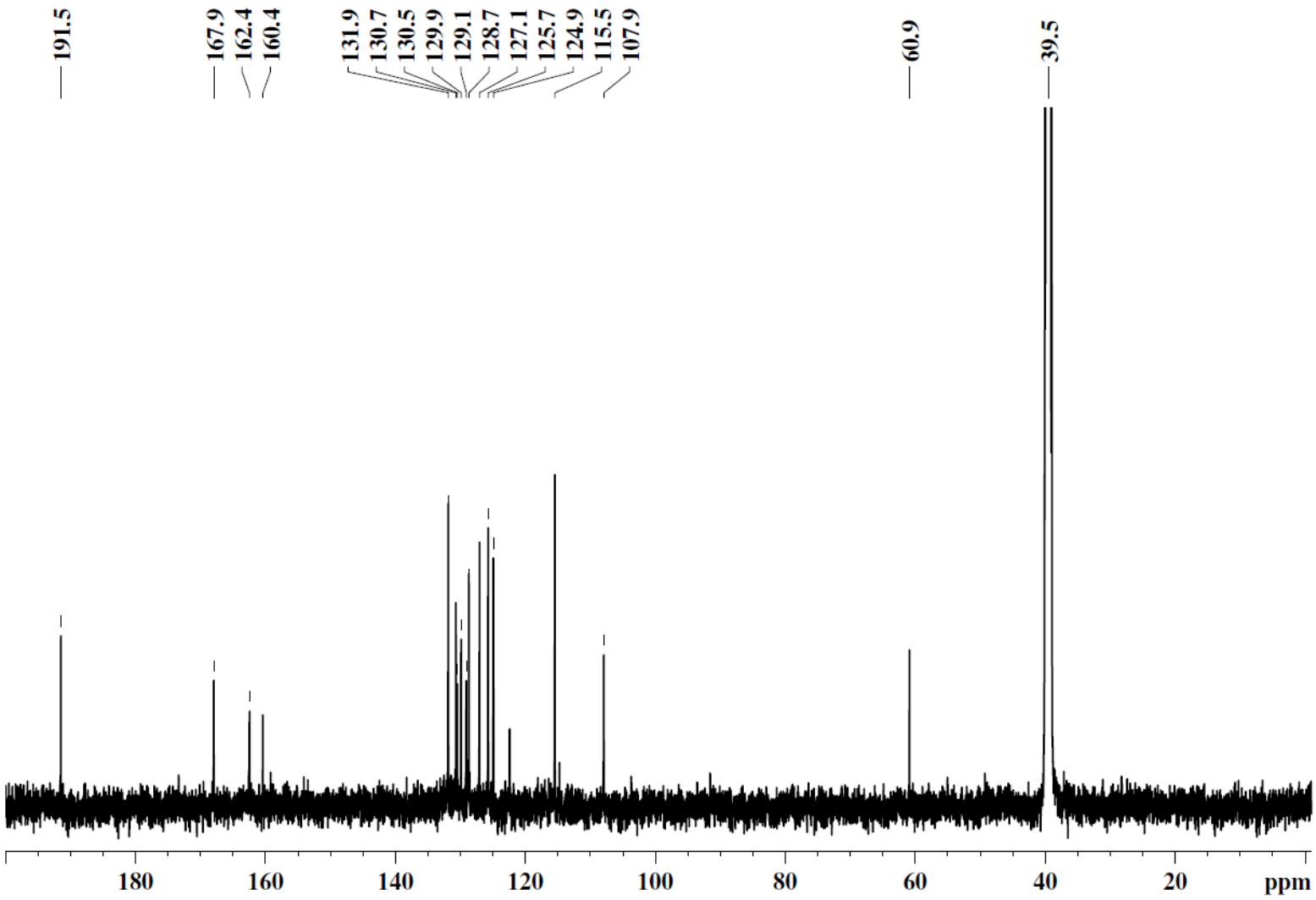

Figure S2. ^{13}C NMR spectrum of 4-((3-(anthracen-9-yl)isoxazol-5-yl)methoxy)benzaldehyde (**2a**) in $CDCl_3$ (T=303 K)

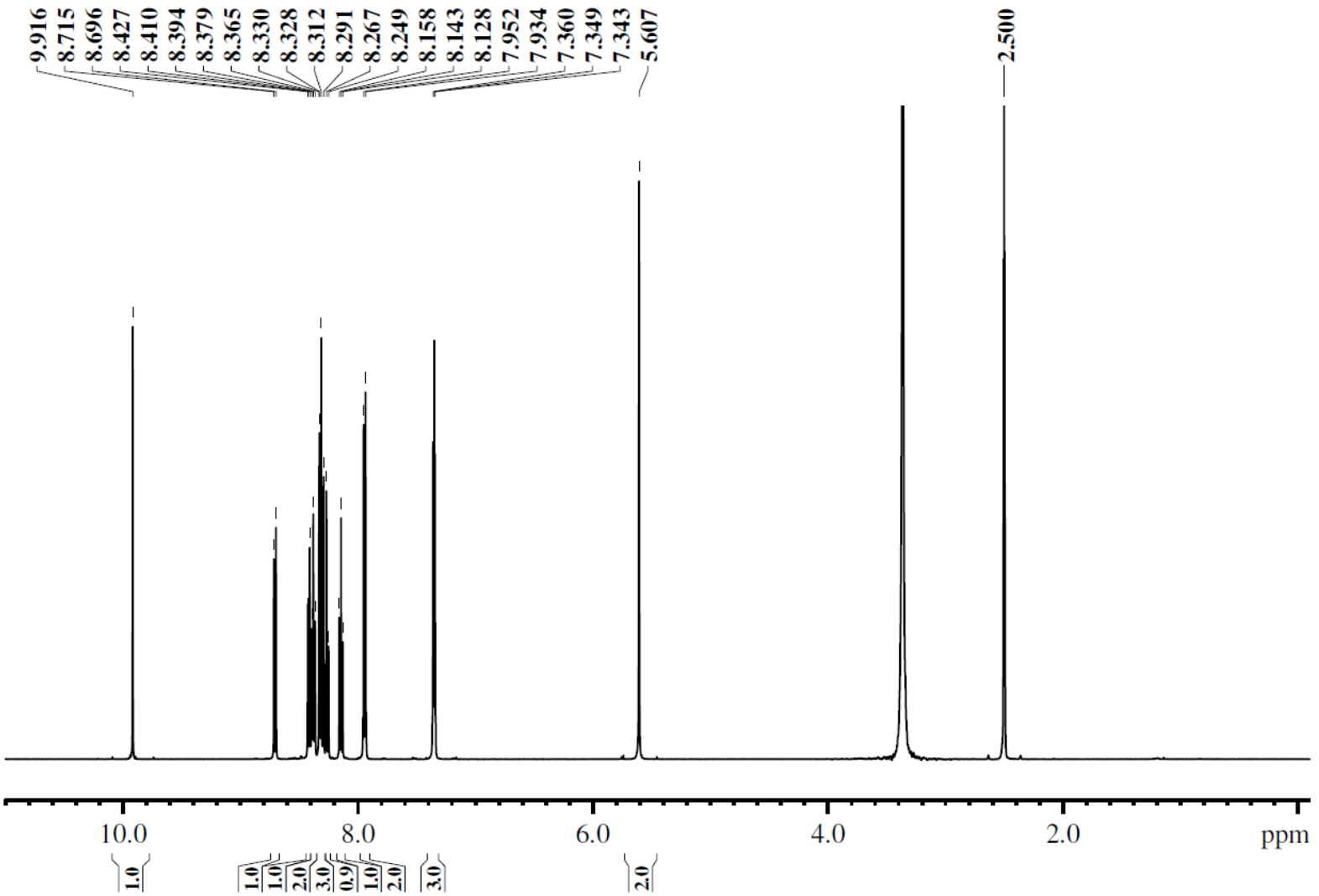

Figure S3. ^{1}H NMR spectrum of 4-((3-(pyren-1-yl)isoxazol-5-yl)methoxy)benzaldehyde (**2b**) in $CDCl_3$ (T=303 K)

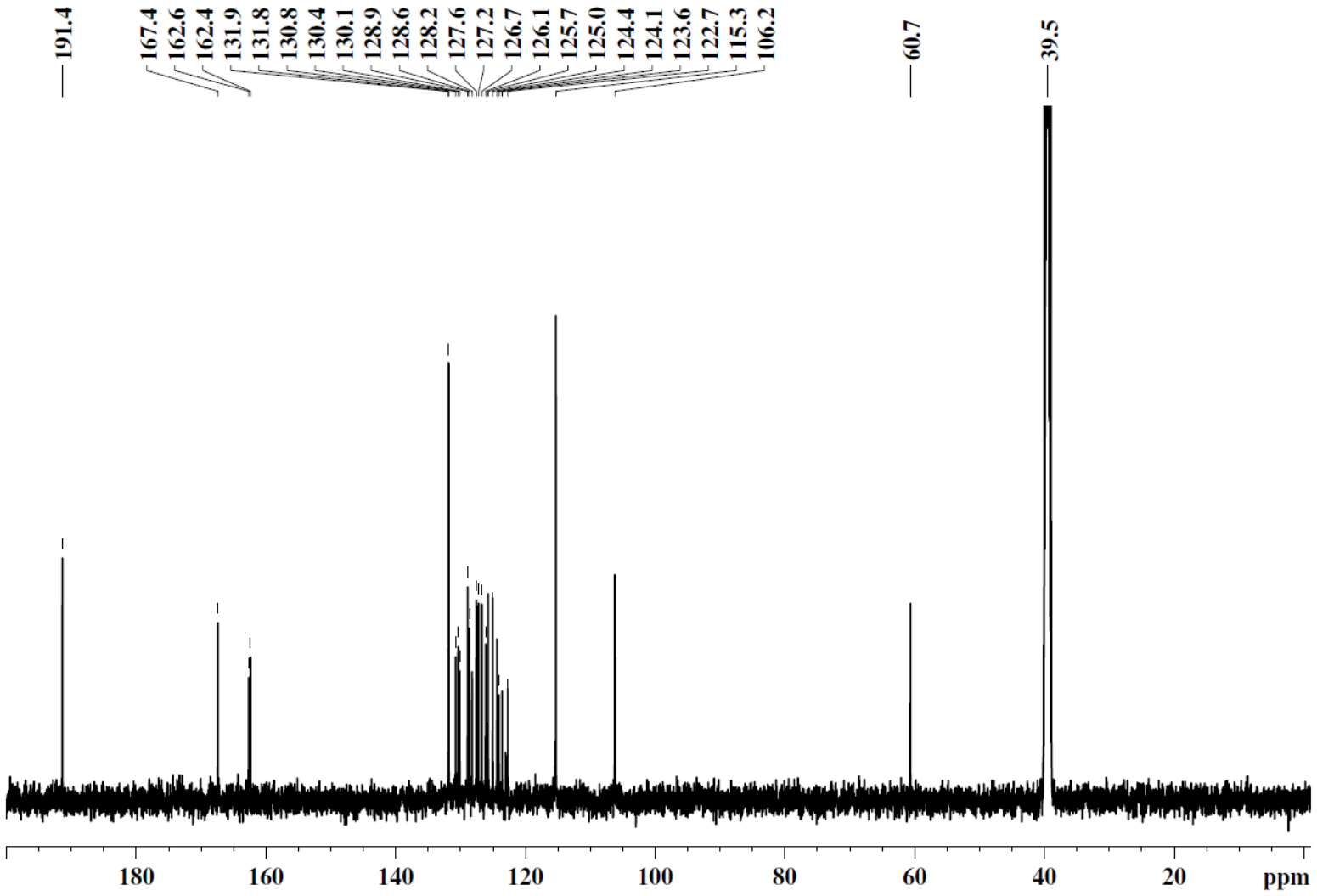

Figure S4. ^{13}C NMR spectrum of 4-((3-(pyren-1-yl)isoxazol-5-yl)methoxy)benzaldehyde (**2b**) in $CDCl_3$ (T=303 K)

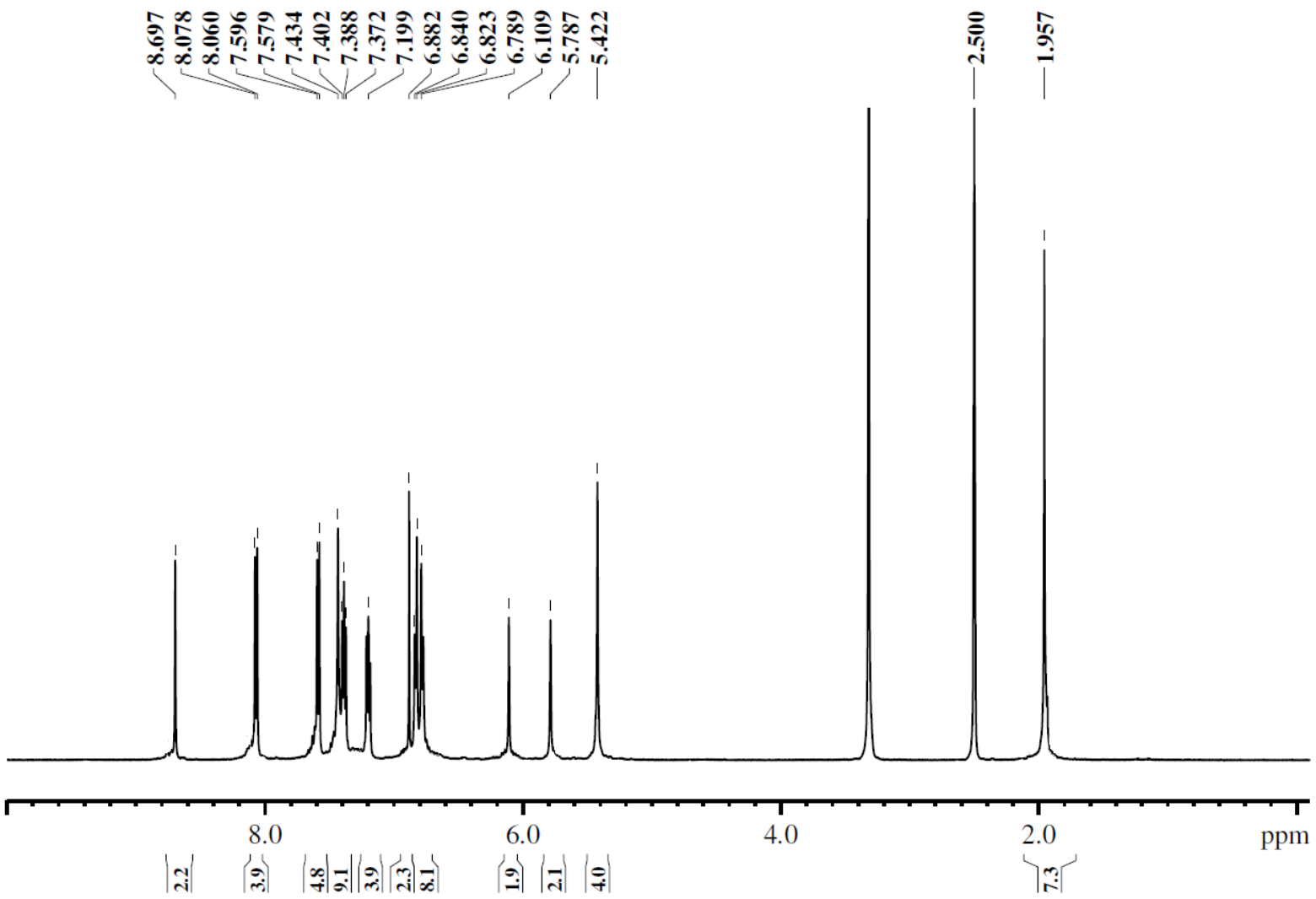

Figure S5. ^{1}H NMR spectrum of calix[4]resorcinol **3a** (*rccc* diastereoisomer in *cone* conformation) in DMSO-d_6 (T=303 K)

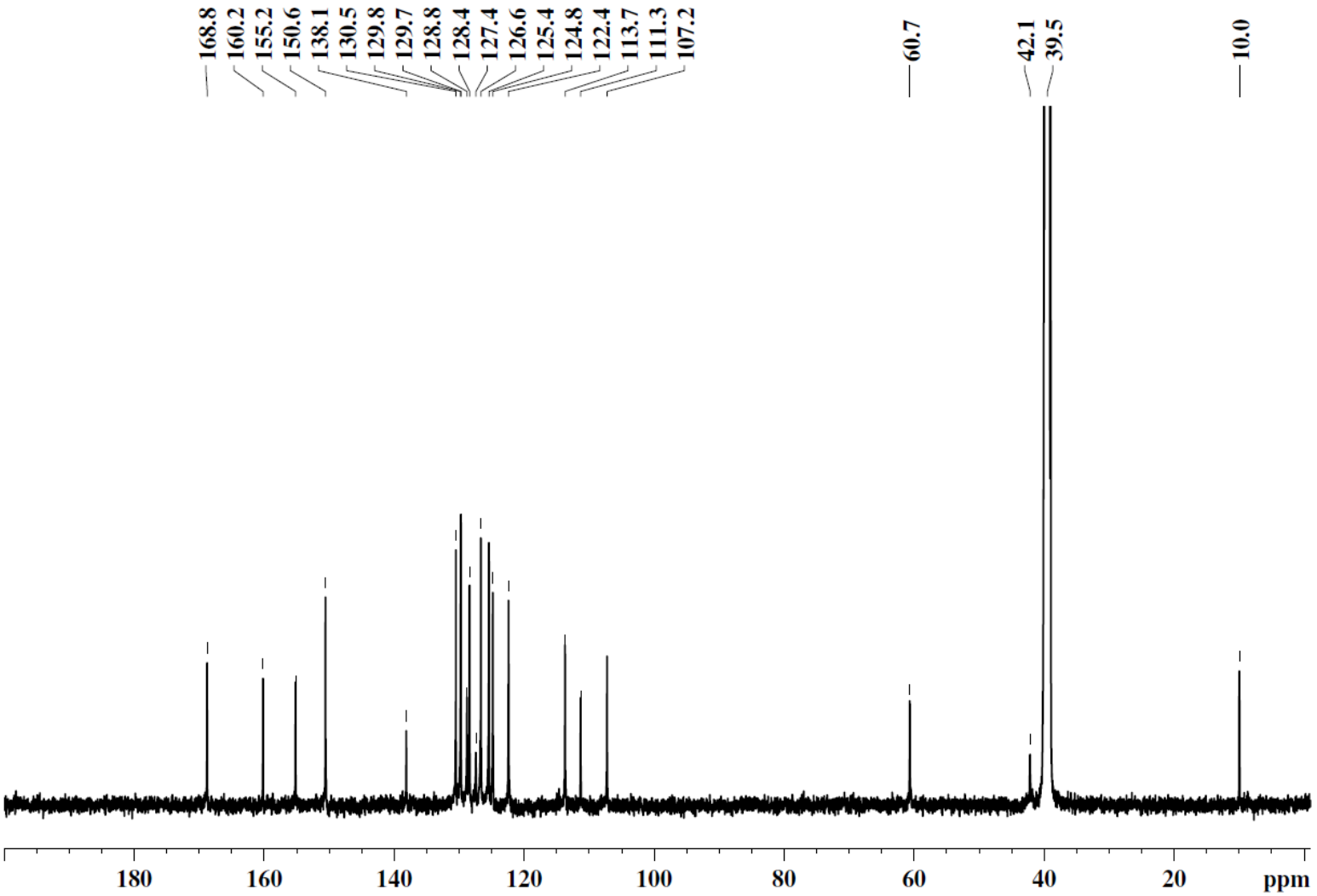

Figure S6. ^{13}C NMR spectrum of calix[4]resorcinol **3a** (*rccc* diastereoisomer in *cone* conformation) in DMSO-d_6 (T=303 K)

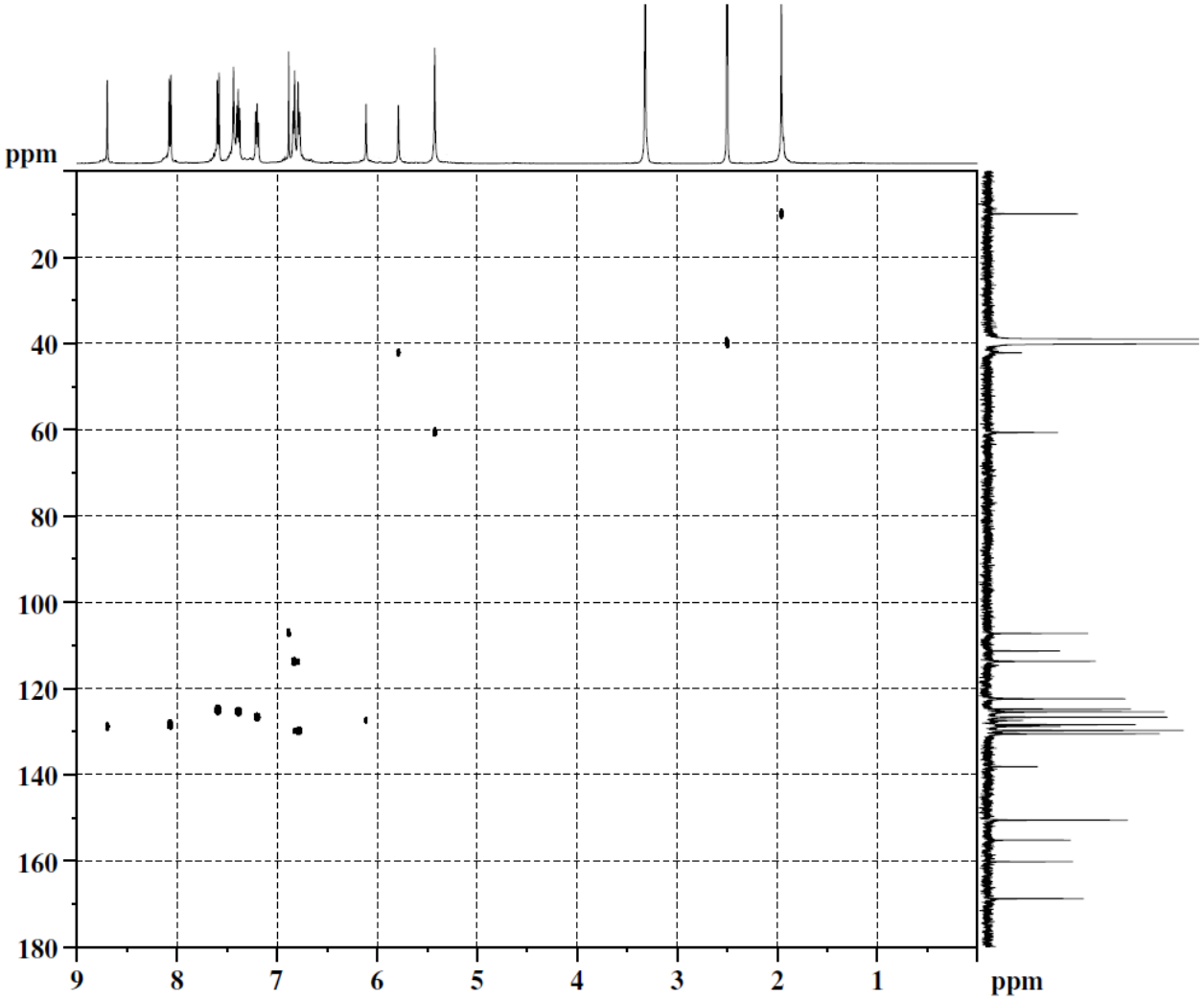

Figure S7. HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **3a** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

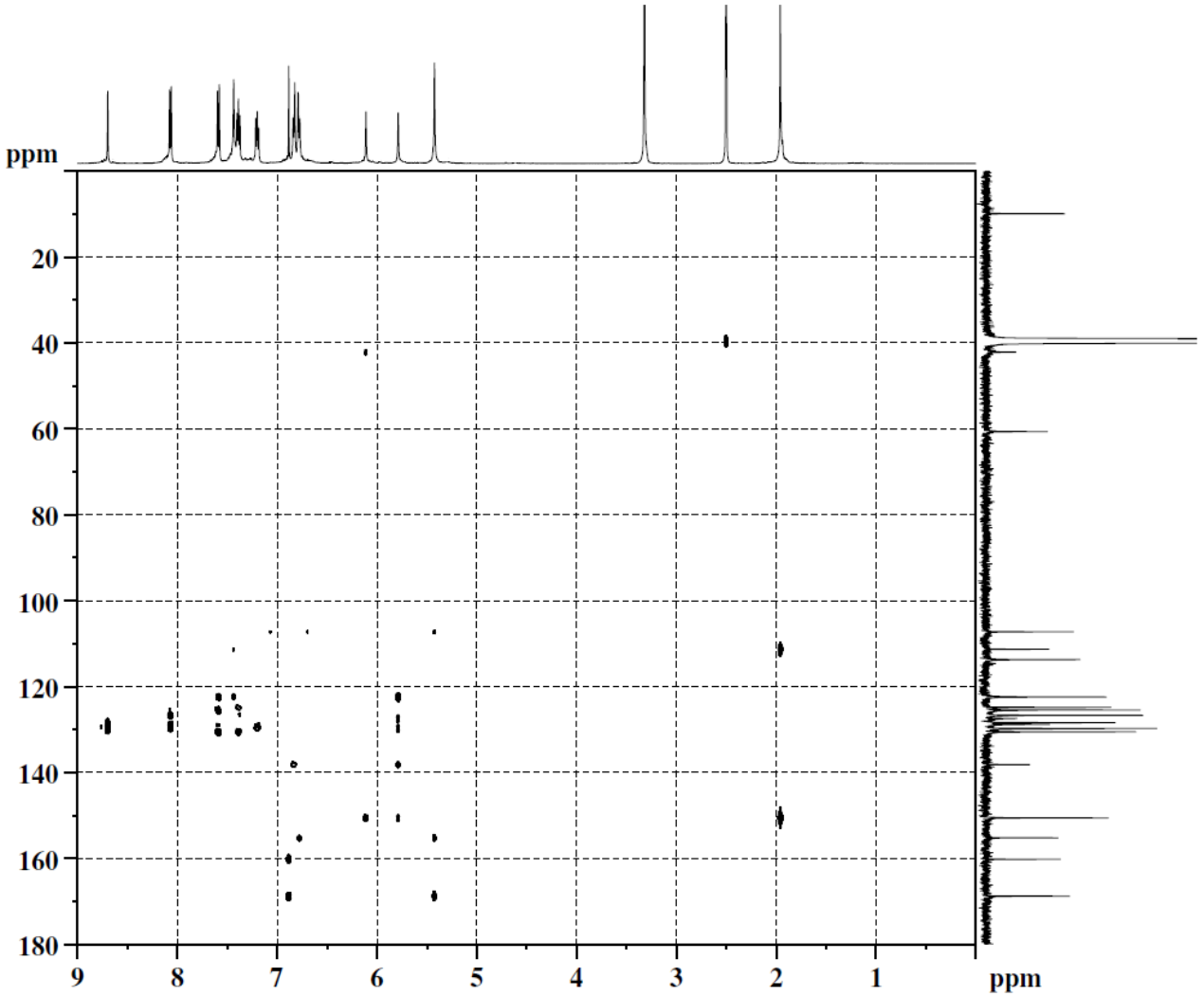

Figure S8. HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **3a** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

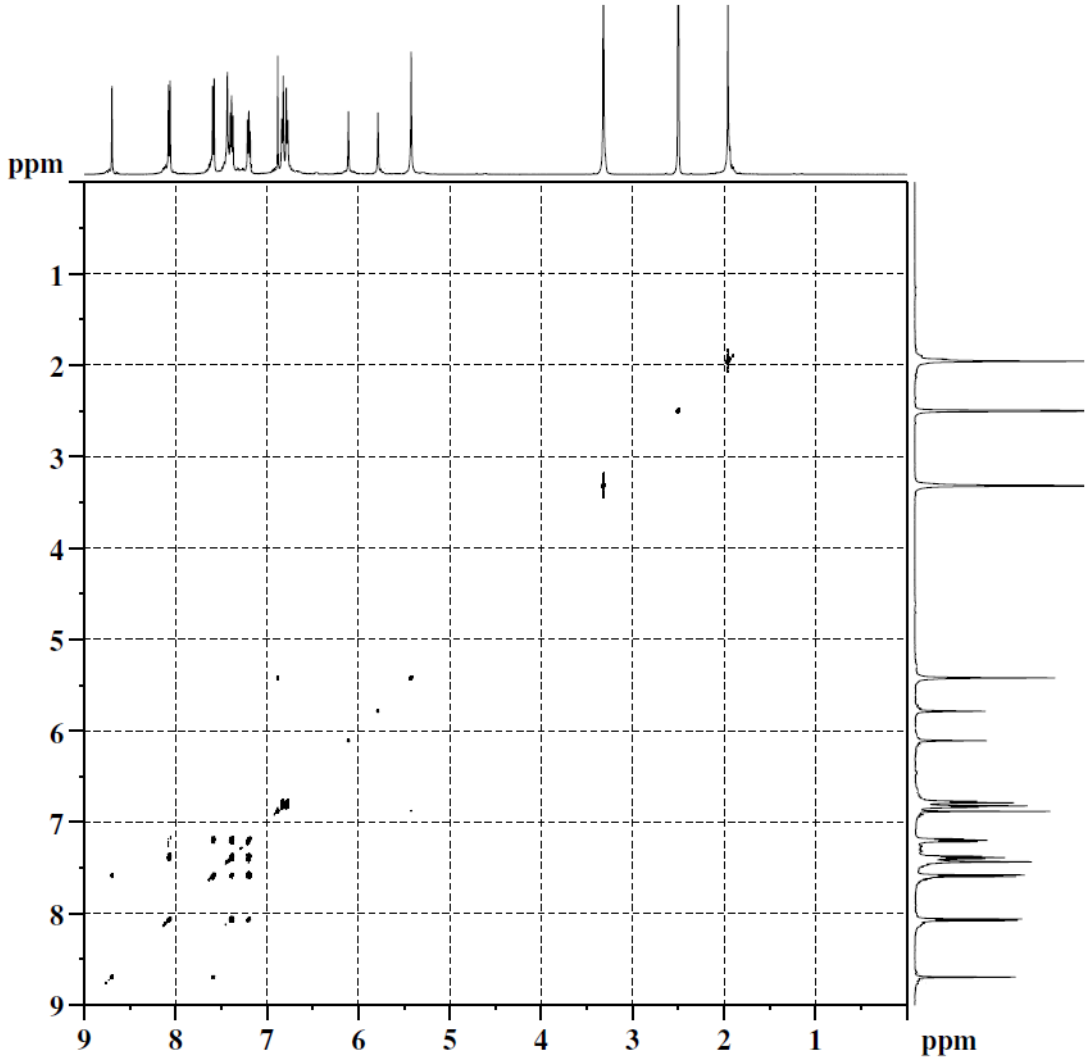

Figure S9. COSY NMR spectrum of calix[4]resorcinol **3a** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

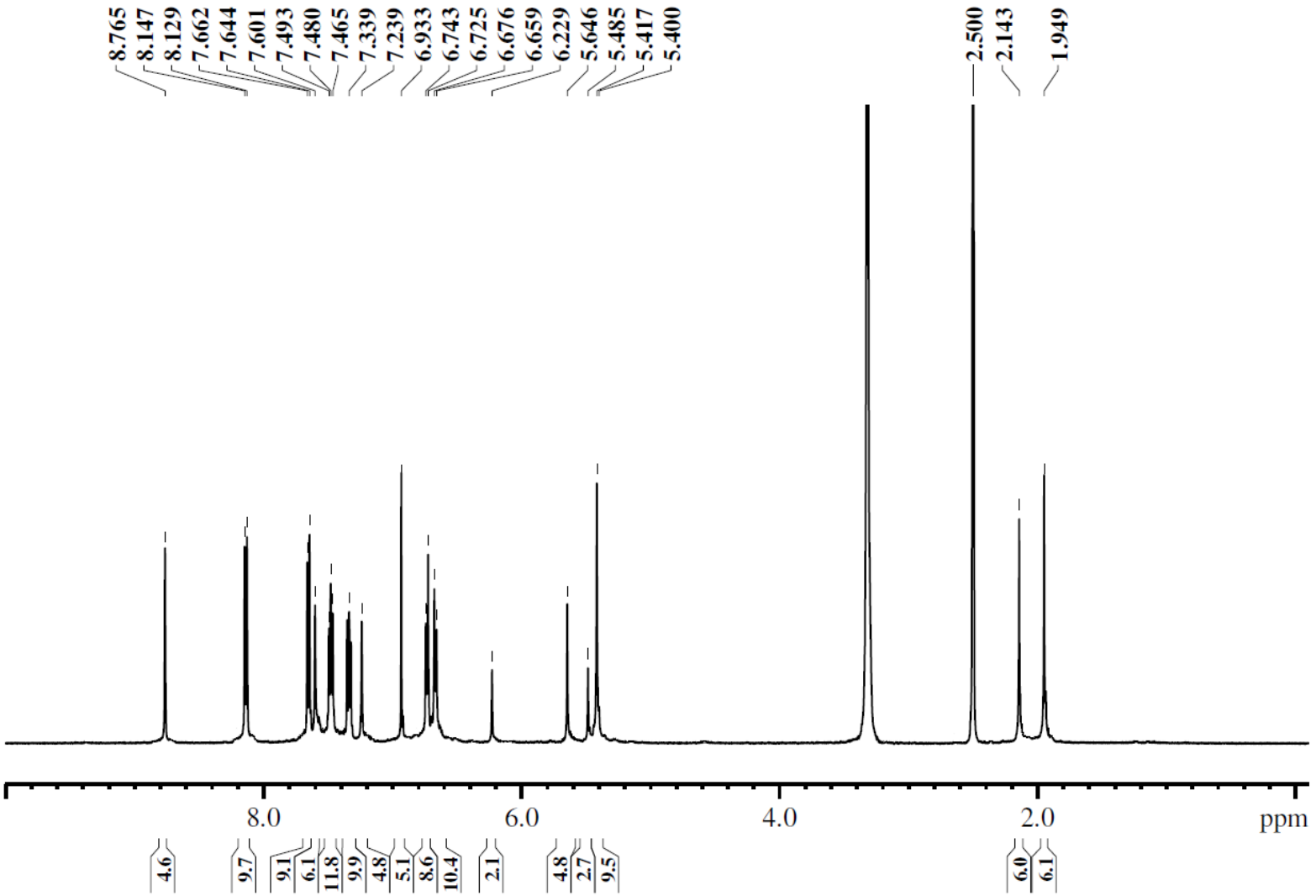

Figure S10. ^{1}H NMR spectrum of calix[4]resorcinol **4a** (*rctt* diastereoisomer in *chair* conformation) in DMSO-d_6 (T=303 K)

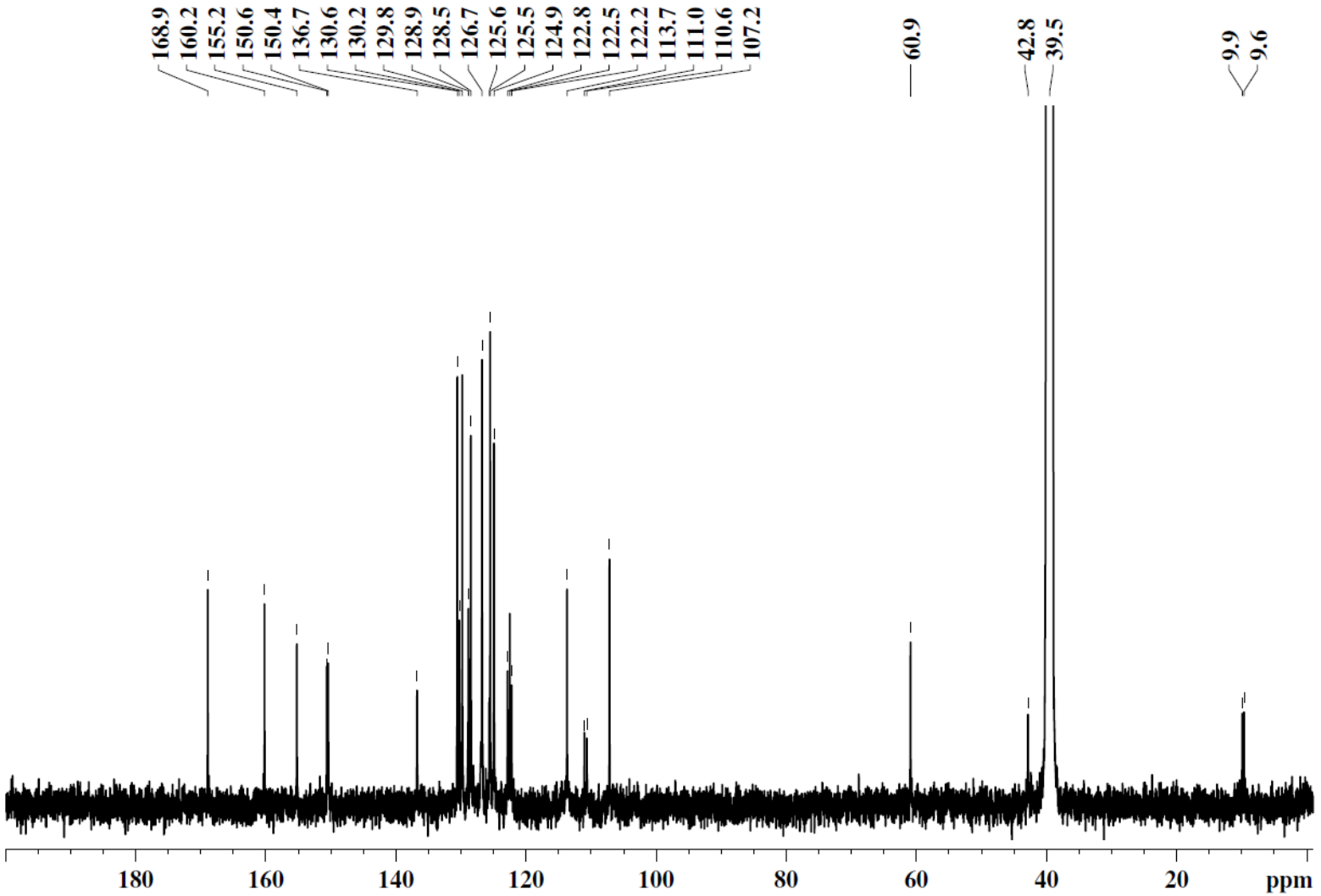

Figure S11. ^{13}C NMR spectrum of calix[4]resorcinol **4a** (*rctt* diastereoisomer in *chair* conformation) in DMSO-d_6 (T=303 K)

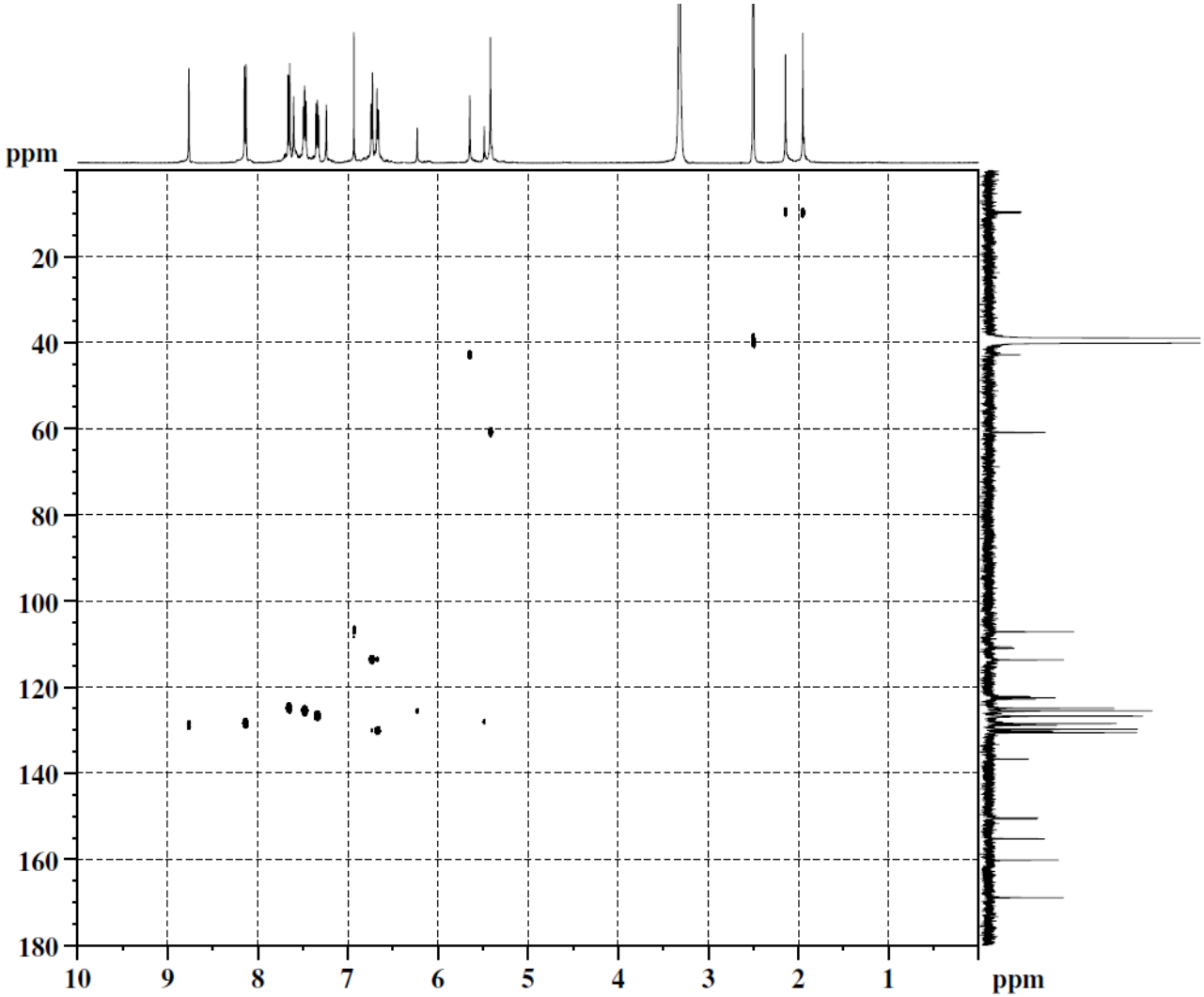

Figure S12. HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **4a** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)

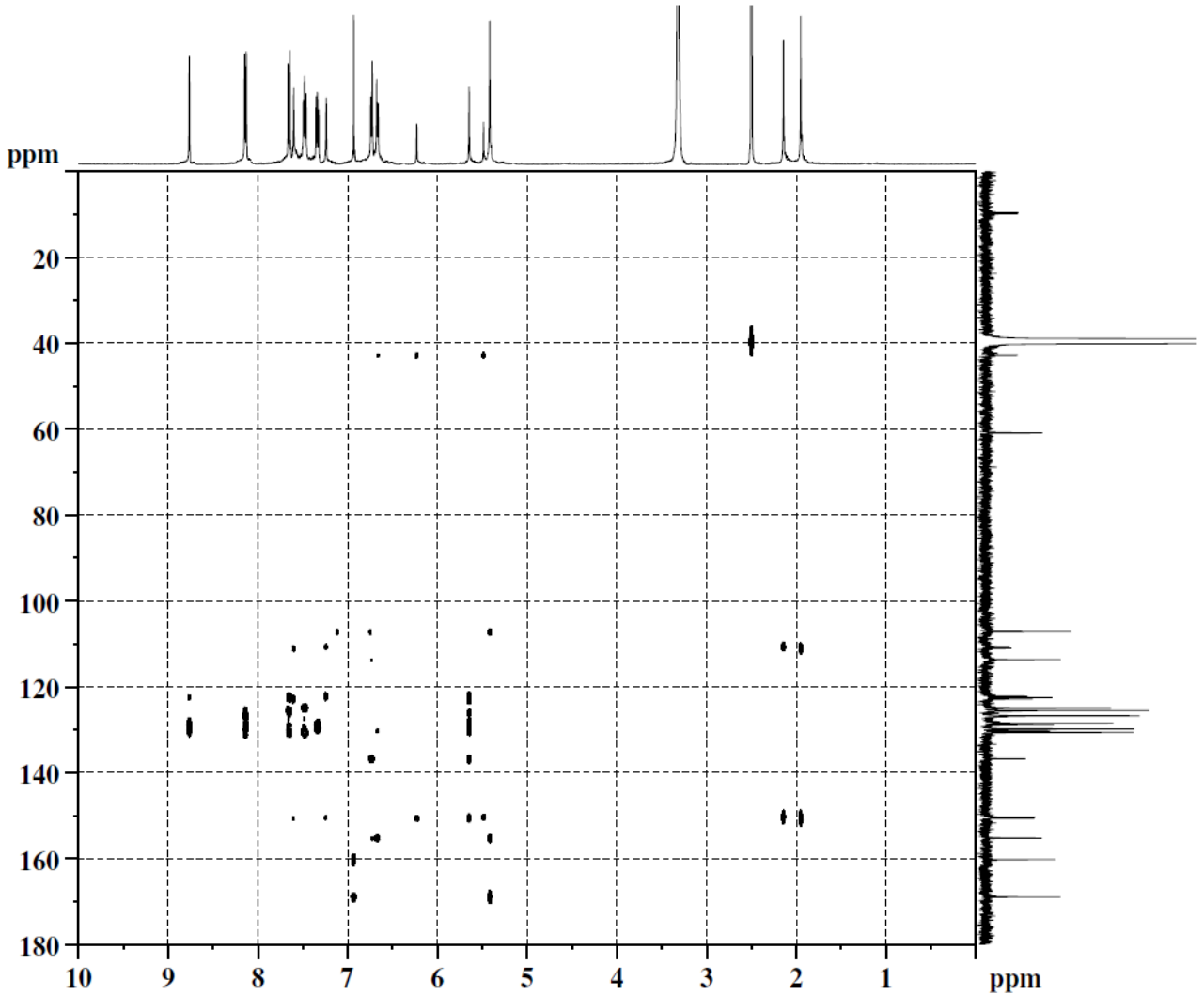

Figure S13. HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **4a** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)

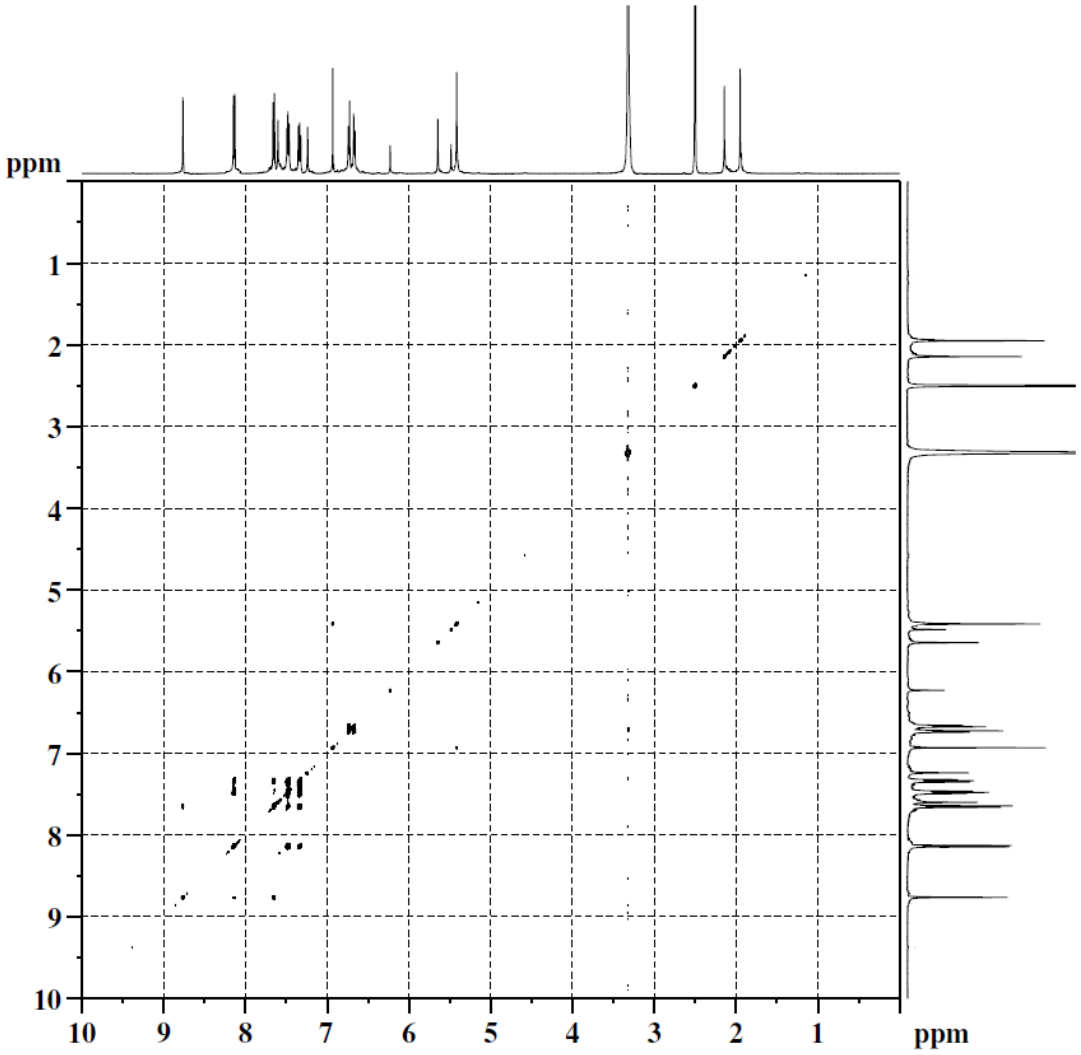

Figure S14. COSY NMR spectrum of calix[4]resorcinol **4a** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)

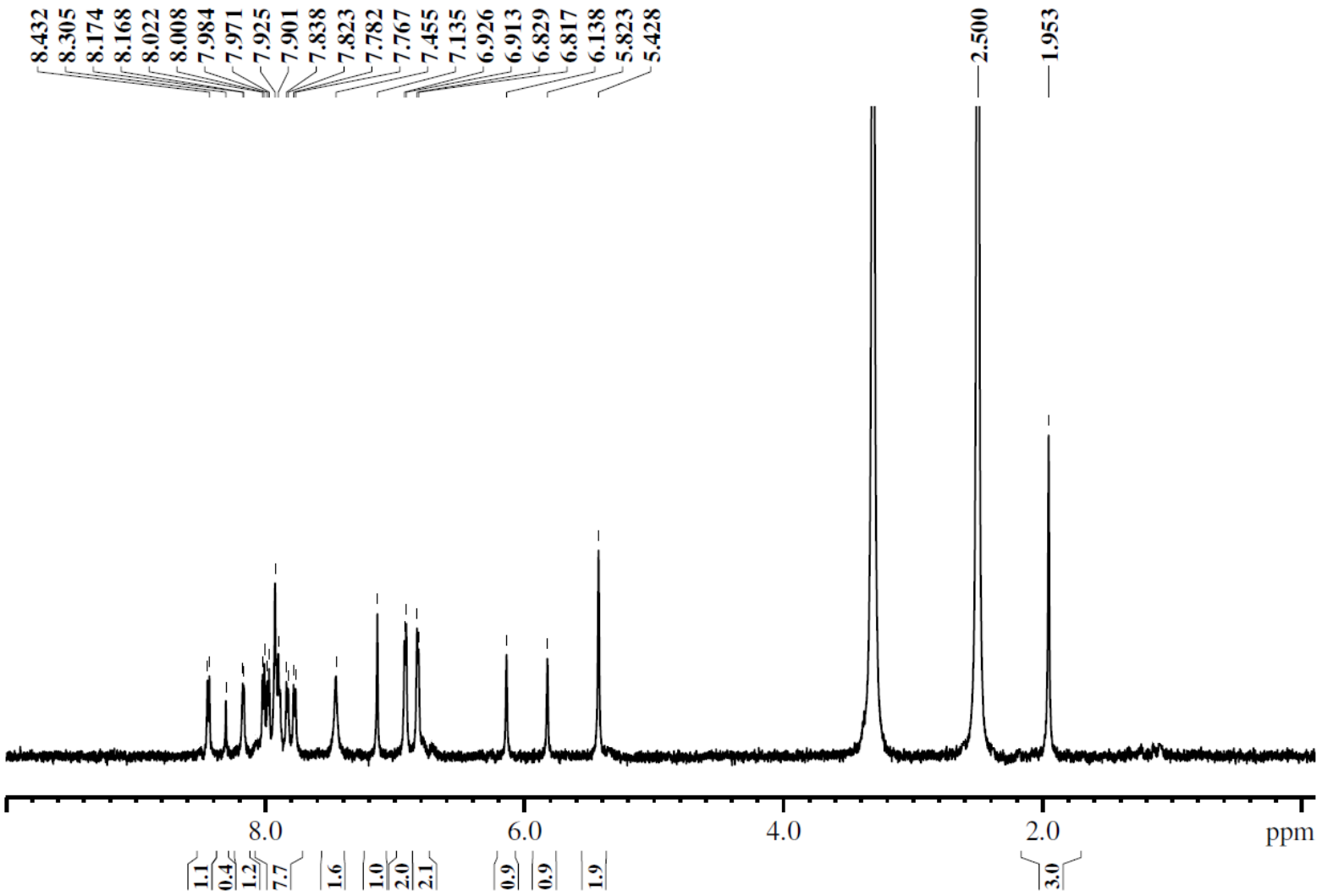

Figure S15. ^{1}H NMR spectrum of calix[4]resorcinol **3b** (*rccc* diastereoisomer) in DMSO-d_6 (T=303 K)

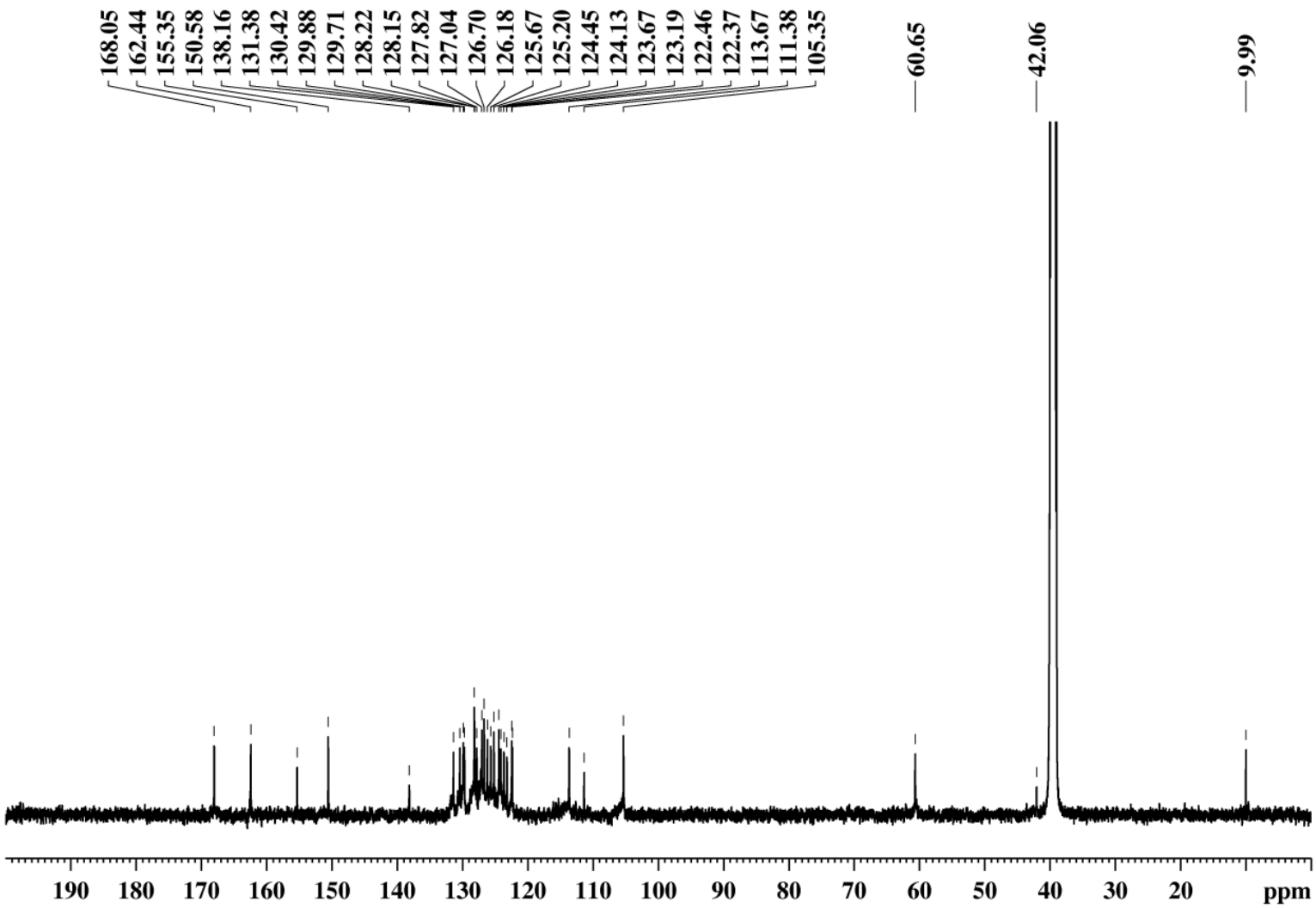

Figure S16. ^{13}C NMR spectrum of calix[4]resorcinol **3b** (*rccc* diastereoisomer) in DMSO-d_6 (T=303 K)

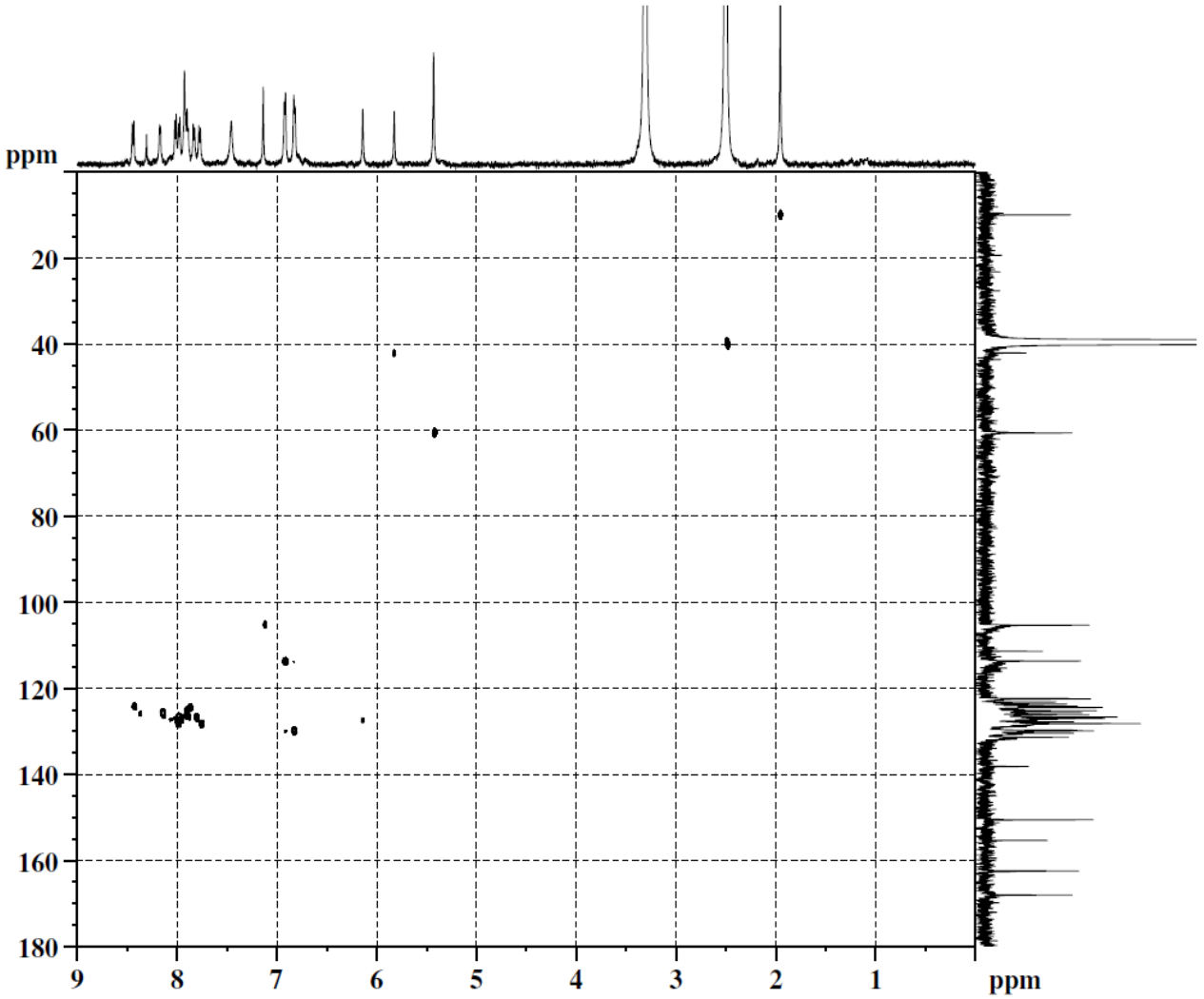

Figure S17. HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **3b** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

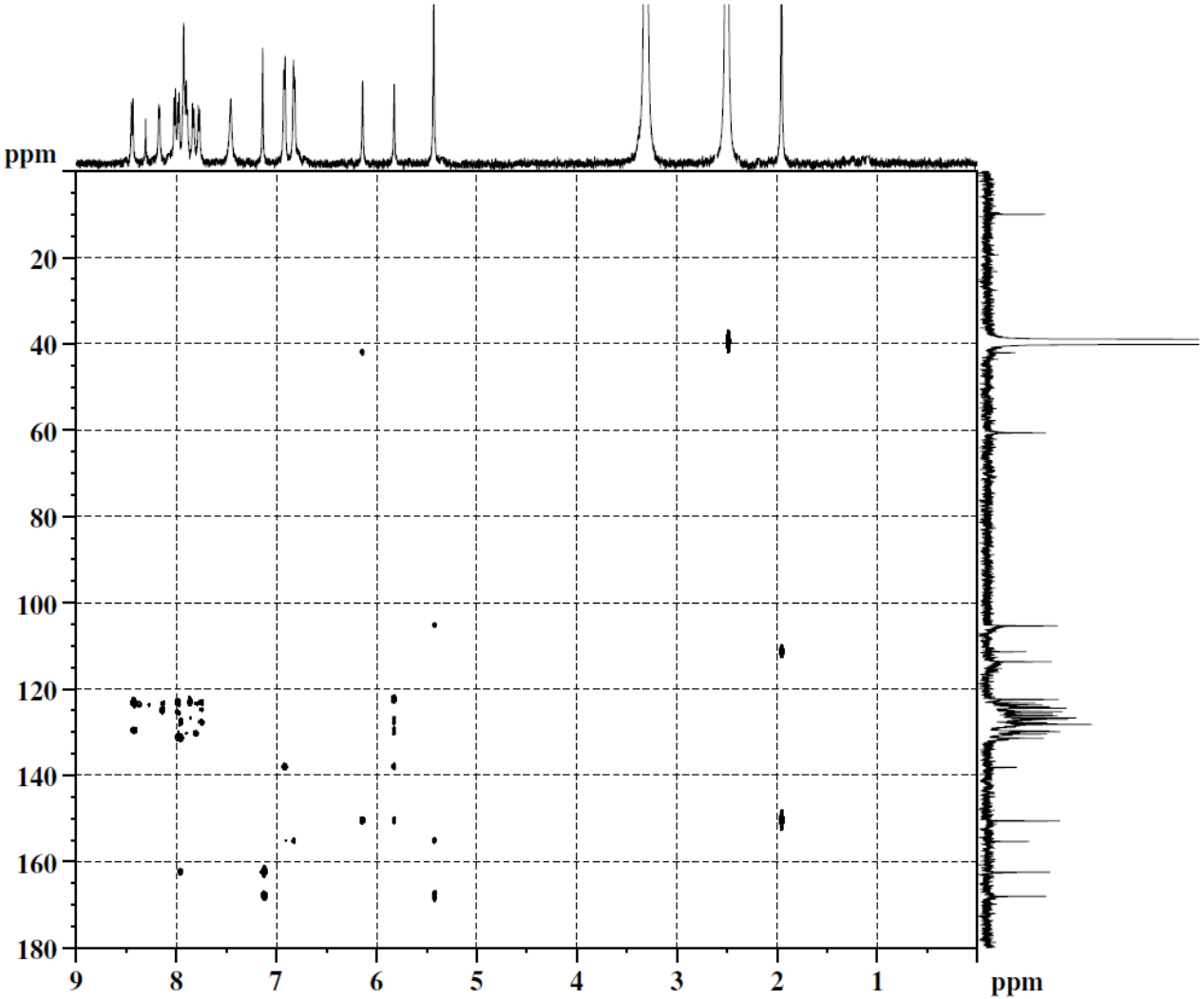

Figure S18. HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **3b** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

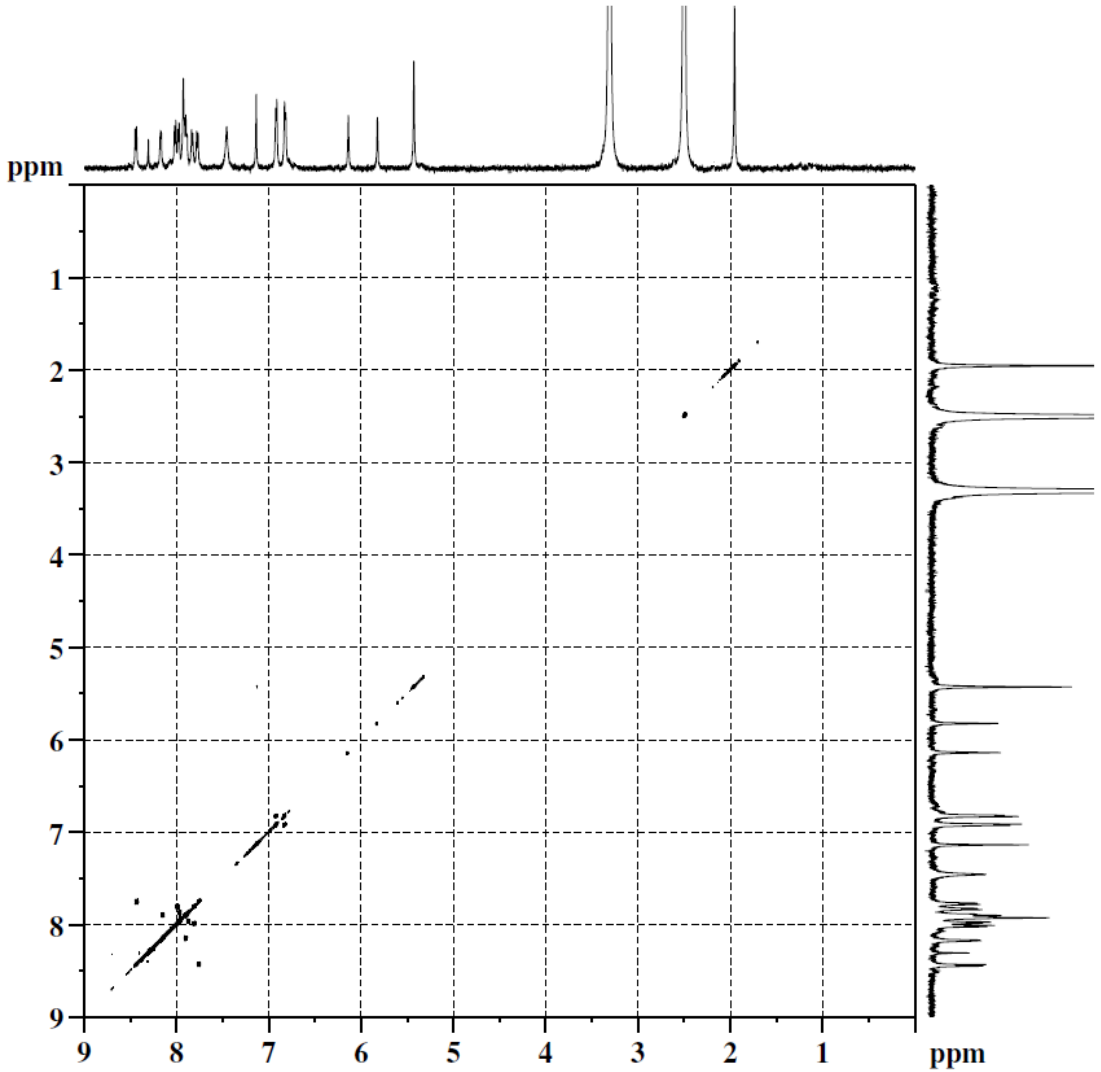

Figure S19. COSY NMR spectrum of calix[4]resorcinol **3b** (*rccc* isomer in *cone* conformation) in DMSO-d_6 (T=303 K)

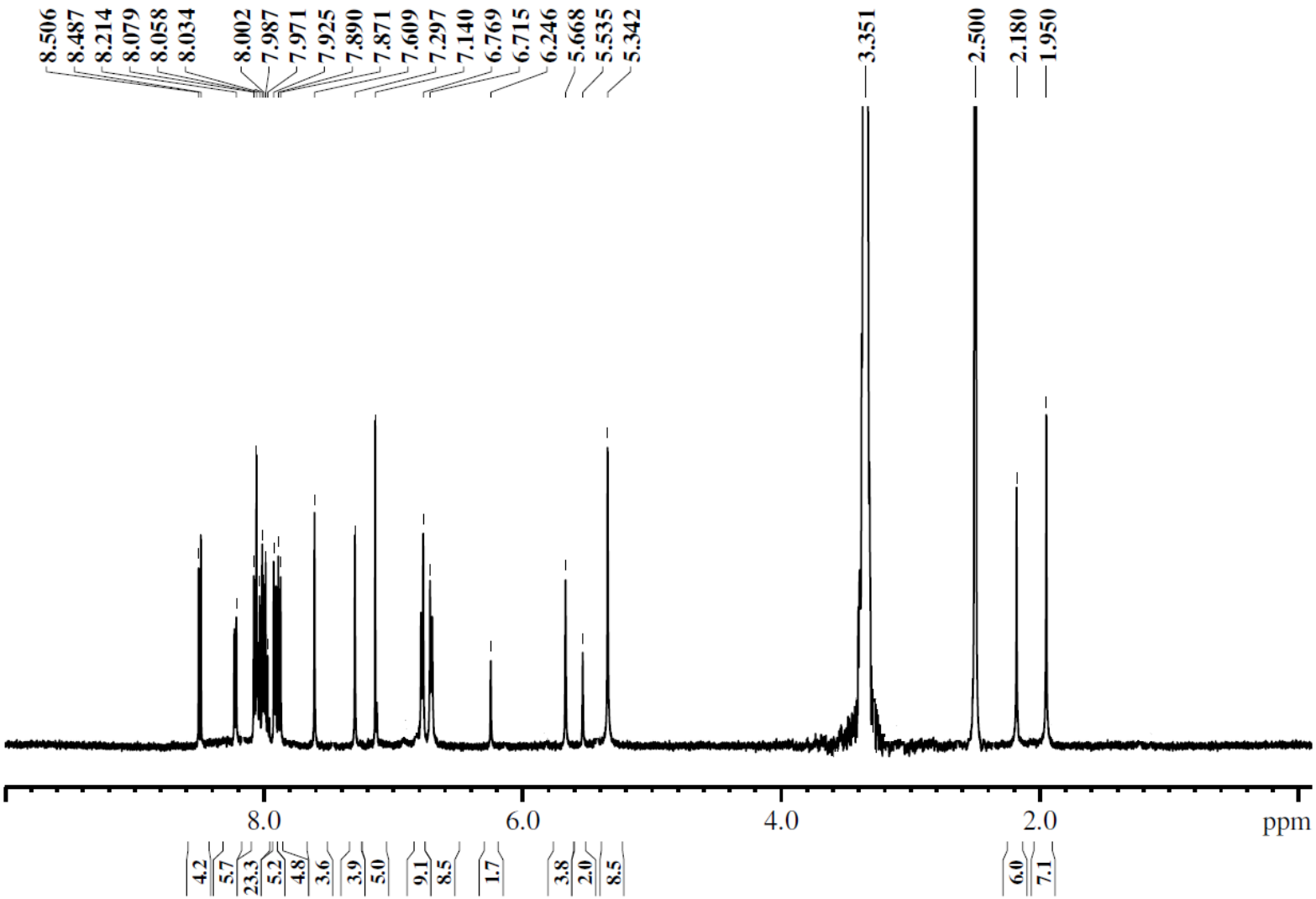

Figure S20. ^{1}H NMR spectrum of calix[4]resorcinol **4b** (*rctt* diastereoisomer in *chair* conformation) in DMSO-d_6 (T=303 K)

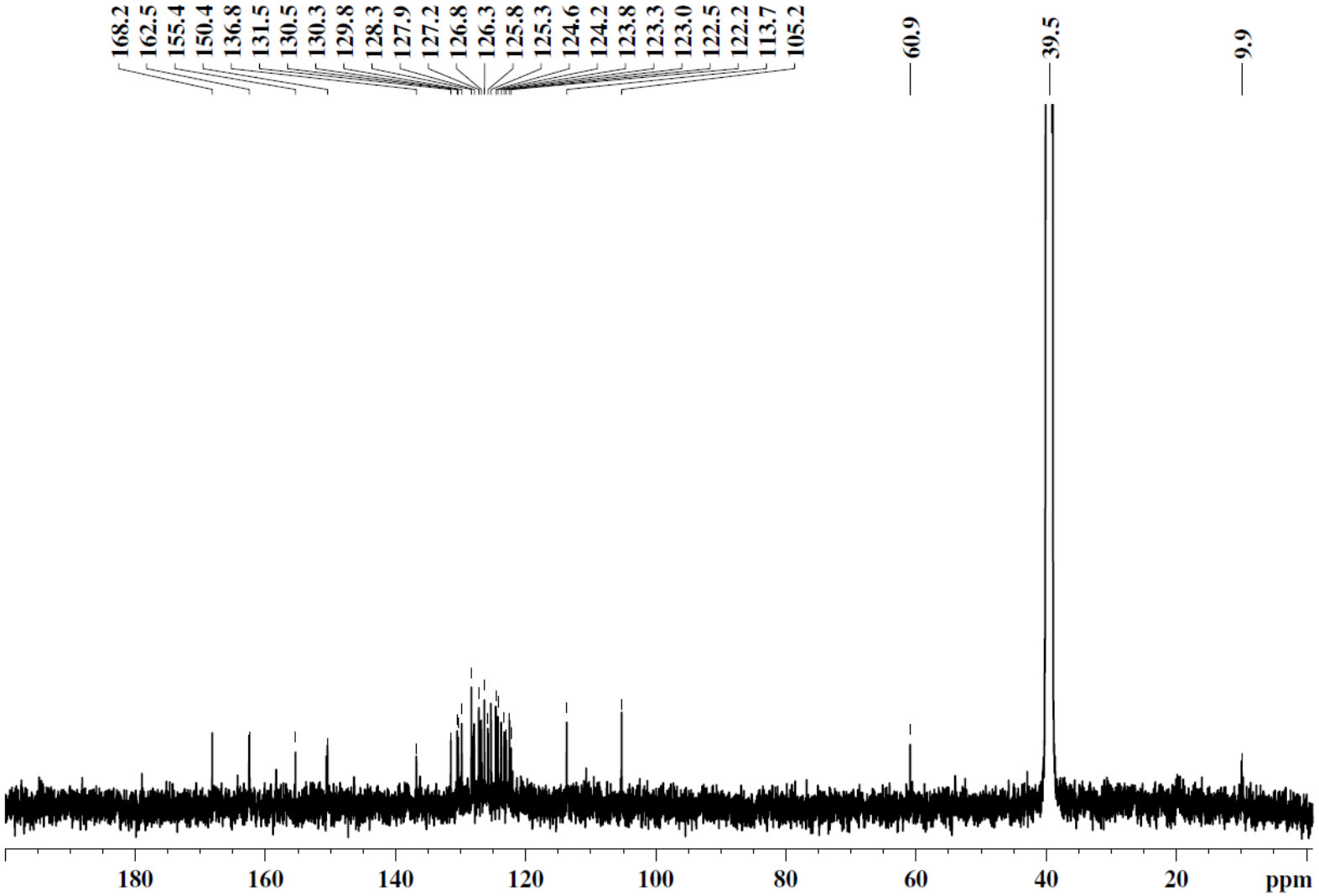

Figure S21. ^{13}C NMR spectrum of calix[4]resorcinol **4b** (*rctt* diastereoisomer in *chair* conformation) in DMSO-d_6 (T=303 K)

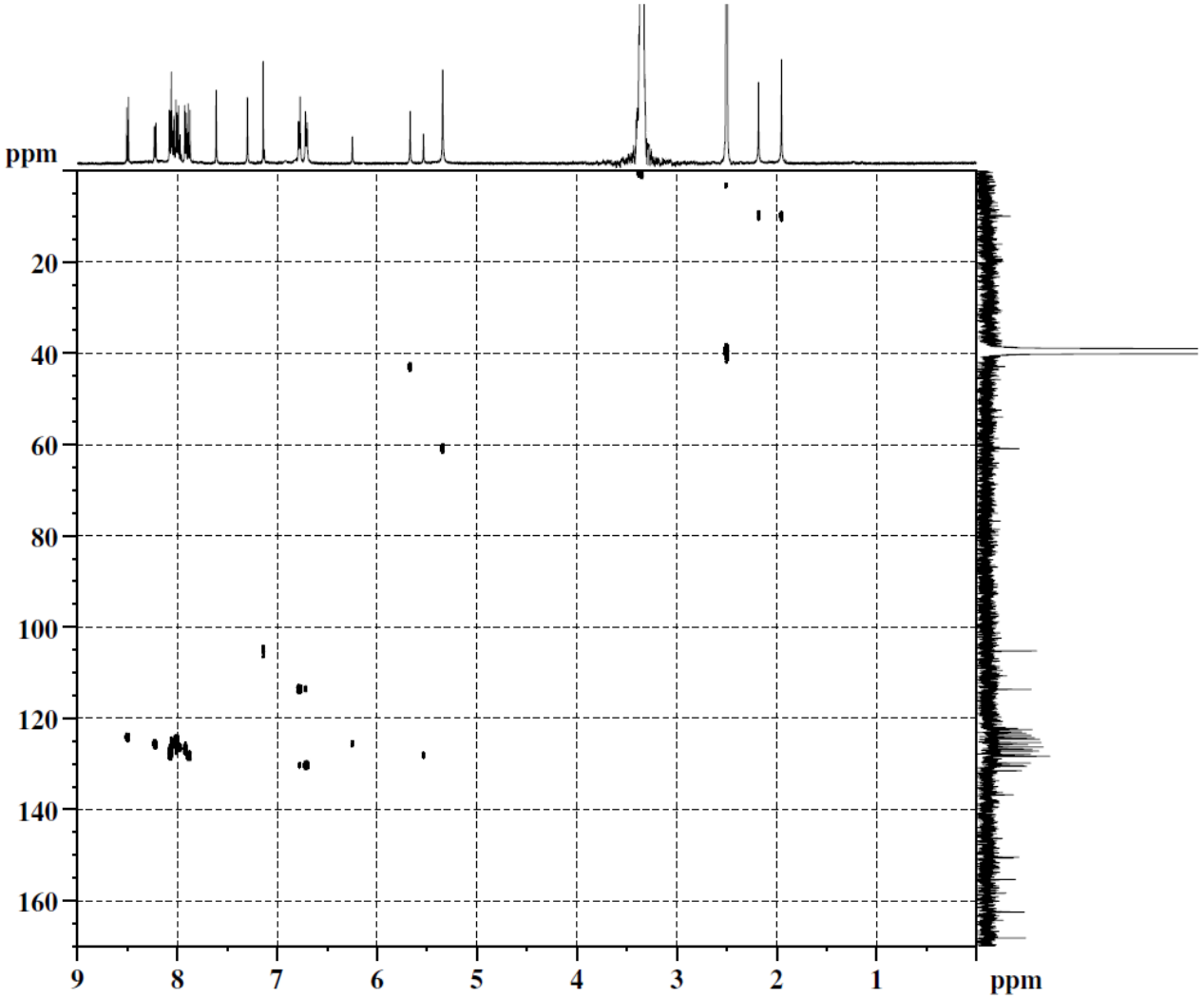

Figure S22. HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **4b** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)

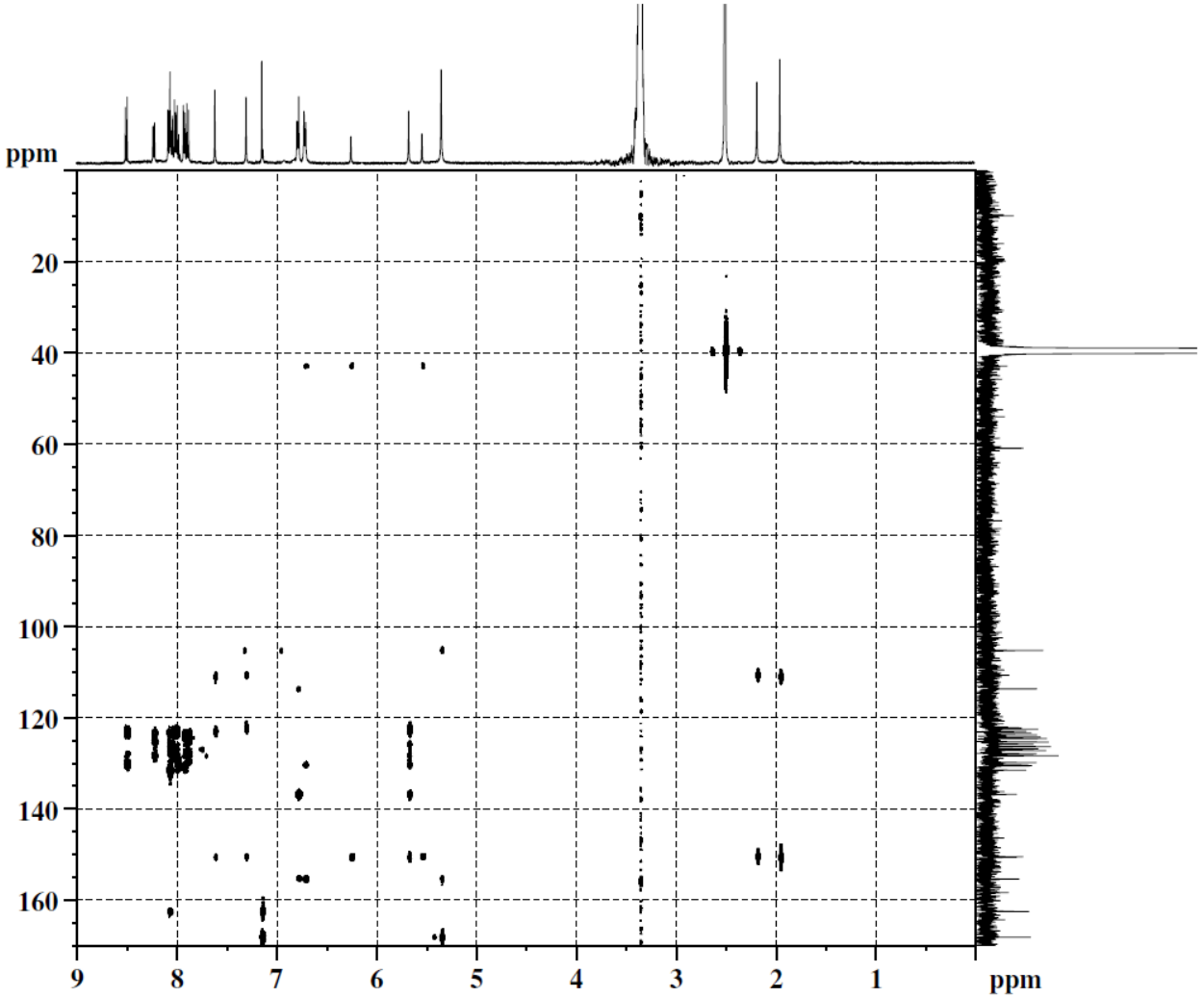

Figure S23. HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **4b** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)

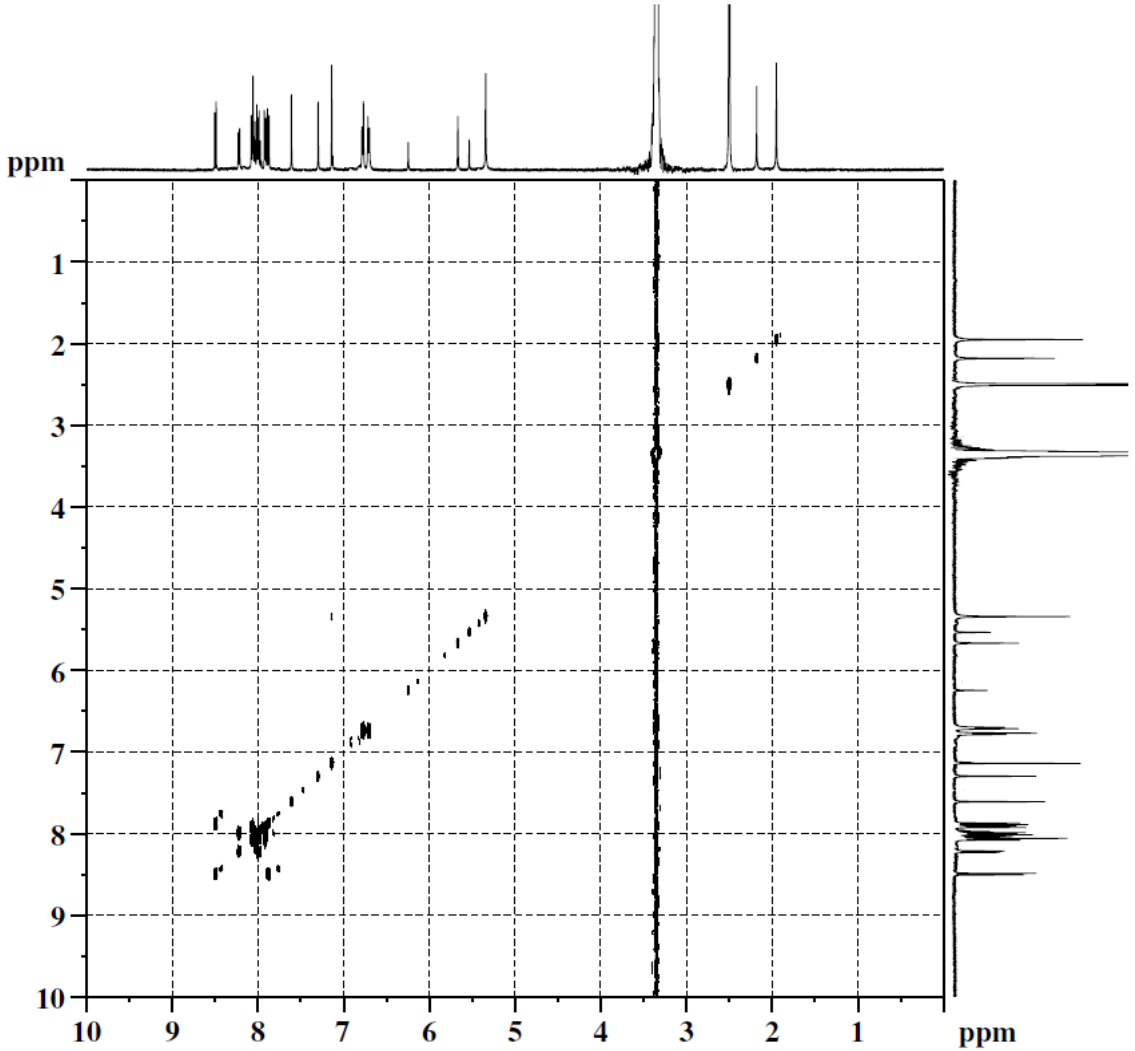

Figure S24. COSY NMR spectrum of calix[4]resorcinol **4b** (*rctt* isomer in *chair* conformation) in DMSO-d_6 (T=303 K)