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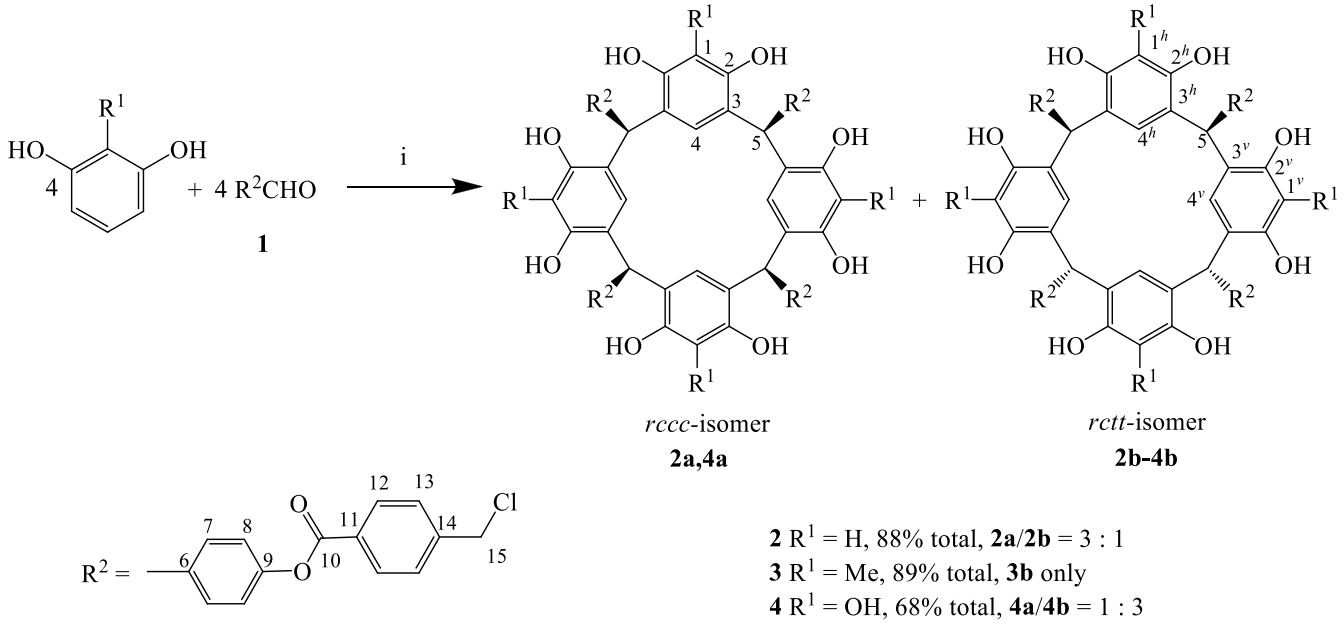
Synthesis and structure of new chlorine containing calix[4]resorcinols

Irina R. Knyazeva, Victor V. Syakaev, Olga A. Lodochnikova and Alexander R. Burilov

General

NMR experiments were carried out at 303 K using a Bruker AVANCE-600 spectrometer equipped with 5 mm broadband probe-head working at 600.1 MHz for ^{1}H and 150.9 MHz for ^{13}C experiments. Chemical shifts were expressed in ppm relative to the residual signals of deuterated solvents. IR spectra of solid compounds were registered using a Bruker Vector-27 FTIR spectrometer in 400–4000 cm^{-1} range at optical resolution 4 cm^{-1}, the samples were prepared as KBr pellets. MALDI mass spectra were recorded using an Ultraflex III TOF/TOF mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) operated in the linear mode with registration of positively charged ions or negatively charged ions. A Nd:YAG laser with λ = 355 nm and repetition frequency 100 Hz was used for the sample irradiation. The mass spectra were obtained with an accelerating voltage of 25 kV and an ion extraction delay time of 30 ns and were produced by the multiple laser irradiation of the crystal (50 shots). Portions (0.5 μl) of an 1% 2,5-dihydroxybenzoic acid matrix solution in acetonitrile and a 0.1% sample solution in methanol were consecutively applied onto a metal target MTP AnchorChip and evaporated. Polyethylene glycol was used to calibrate the mass scale, data were obtained using a FlexControl program (Bruker Daltonik GmbH, Germany) and processed by a FlexAnalysis 3.0 program (Bruker Daltonik GmbH, Germany). Elemental analysis was carried out using an EuroEA3028-HT-OM CHNS analyzer (Eurovector SpA, Italy). The samples were weighed in tin capsules on a Sartorius CP2P microbalance (Germany). Callidus 4.1 software was used to perform quantitative measurements and to evaluate the data received.



Scheme S1 *Reagents and conditions*: i, CF_3COOH, $CHCl_3$, 60–65 ºC, 24 h.

Experimental procedure for preparation and spectroscopic data of 4'-formylphenyl 4-(chloromethyl)benzoate **1**. To the suspension of 4-hydroxybenzaldehyde (0.98 g, 8.03 mmol) in CH_2Cl_2 (15 ml), a solution of 4-(chloromethyl)benzoyl chloride (1.88 g, 9.64 mmol) in CH_2Cl_2 (10 ml) was added dropwise, then triethylamine (0.97 g, 9.64 mmol) was added at room temperature, and the reaction mixture was stirred under reflux in an argon atmosphere for 6 h. Then the reaction mixture was diluted with H_2O (40 ml) and extracted with CH_2Cl_2 (3 x 15 ml). The combined organic extracts were evaporated, and the crude product was purified by column chromatography with CH_2Cl_2 as eluent. The pure compound **1** was obtained as white solid (2.0 g, 89 %), R_f = 0.38, mp 96–97 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$) δ: 4.67 (s, 2H, CH_2), 7.43 (d, $^3J_{HH}$ 8.6 Hz, 2H, CH^{Ar}), 7.57 (d, $^3J_{HH}$ 8.4 Hz, 2H, CH^{Ar}), 7.99 (d, $^3J_{HH}$ 8.6 Hz, 2H, CH^{Ar}), 8.21 (d, $^3J_{HH}$ 8.4 Hz, 2H, CH^{Ar}), 10.04 (s, 1H, CHO). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 45.4 (CH_2), 122.7 (CH^{Ar}), 129.0 (CH^{Ar}), 129.1 (C^{Ar}), 130.9 (CH^{Ar}), 131.5 (CH^{Ar}), 134.4 (C^{Ar}), 143.7 (C^{Ar}), 155.8 (C^{Ar}), 164.2 (O–C=O), 191.1 (CHO). IR (KBr, ν/cm^{-1}): 1692 (H–C=O), 1728 (O–C=O). Found (%): C, 65.63; H, 4.01; Cl, 12.89. Calc. for $C_{15}H_{11}ClO_3$ (%): C, 65.58; H, 4.04; Cl, 12.91.

Experimental procedure for preparation and spectroscopic data of compounds **2a** *and* **2b**. A mixture of resorcinol (0.08 g, 0.73 mmol) and aldehyde **1** (0.20 g, 0.73 mmol) in $CHCl_3$ (10 ml) and TFA (1 ml) was stirred with heating at 60–65 ºC for 24 h in an argon atmosphere. The precipitate formed was filtered off, washed sequentially with $CHCl_3$ and Et_2O, the washing procedure was repeated until a colorless filtrate was observed. After drying *in vacuo* at 40 ºC and 0.06 Torr, the crude product (mixture of compounds **2a** and **2b** in a 3 : 1 ratio by ^{1}H NMR spectroscopy, in total yield 0.24 g, 88%) was subjected to flash chromatography with CH2Cl2–MeOH (100 : 1) affording pure *rccc*-diastereomer **2a** and *rctt*-diastereomer **2b**.

Rctt-*isomer* **2b** *in* chair *conformation*: slightly brown powder, yield 0.15 g (56 %), R_f = 0.53, mp > 150 °C (dec.). ^{1}H NMR (600.1 MHz, DMSO-d_6) δ: 4.78 (s, 8H, H-15), 5.61 (s, 4H, H-5), 5.63 (s, 2H, H-4^{horizontal}), 6.22 (s, 2H, H-1^{vertical}), 6.36 (s, 2H, H-4^{vertical}), 6.36 (s, 2H, H-1^{horizontal}), 6.71 (d, $^3J_{HH}$ 8.6 Hz, 8H, H-7), 6.87 (d, $^3J_{HH}$ 8.6 Hz, 8H, H-8), 7.35 (d, $^3J_{HH}$ 8.3 Hz, 8H, H-13), 7.88 (d, $^3J_{HH}$ 8.3 Hz, 8H, H-12). ^{13}C NMR (150.9 MHz, DMSO-d_6) δ: 41.5 (C-5), 45.1 (C-15), 101.3 (C-1^{horizontal}), 101.7 (C-1^{vertical}), 120.1 (C-3^{vertical}), 120.5 (C-8), 120.8 (C-3^{horizontal}), 128.7 (C-11), 128.8 (C-13), 129.3 (C-4^{vertical}), 129.6 (C-7), 129.7 (C-12), 131.8 (C-4^{horizontal}), 141.9 (C-6), 142.9 (C-14), 147.7 (C-9), 150.8 (C-2^{vertical}), 163.8 (C-10). IR (KBr, ν/cm^{-1}): 1736 (C=O), 3100–3650 (OH). Found (%): C, 68.88; H, 4.28; N, 9.57. Calc. for $C_{84}H_{60}Cl_4O_{16}$ (%): C, 68.76; H, 4.12; Cl, 9.67. MALDI-MS, *m/z*: 1467 $[M+H]^+$, 1489 $[M+Na]^+$, calc. *M* = 1466.

Rccc-*isomer* **2a** *in* cone *conformation*: white powder, yield 0.05 g (19 %), R_f = 0.10, mp > 160 °C (dec.). ^{1}H NMR (600.1 MHz, DMSO-d_6) δ: 4.77 (s, 8H, H-15), 5.72 (s, 4H, H-5), 6.22 (s, 4H, H-1), 6.56 (br.s, 4H, H-4), 6.78 (d, $^3J_{HH}$ 8.6 Hz, 8H, H-7), 6.95 (d, $^3J_{HH}$ 8.6 Hz, 8H, H-8), 7.33 (d, $^3J_{HH}$ 8.3 Hz, 8H, H-13), 7.87 (d, $^3J_{HH}$ 8.3 Hz, 8H, H-12), 8.67 (s, 8H, OH). ^{13}C NMR (150.9 MHz, DMSO-d_6) δ: 40.8 (C-5), 45.0 (C-15), 102.2 (C-1), 120.0 (C-3), 120.3 (C-8), 128.7 (C-11), 128.8 (C-13), 129.1 (C-7), 129.7 (C-12), 143.6 (C-6), 142.9 (C-14), 147.7 (C-9), 152.6 (C-2), 163.9 (C-10). IR (KBr, ν/cm^{-1}): 1735 (C=O), 3100–3650 (OH). Found (%): C, 68.82; H, 4.16; N, 9.72. Calc. for $C_{84}H_{60}Cl_4O_{16}$ (%): C, 68.76; H, 4.12; Cl, 9.67. MALDI-MS, *m/z*: 1467 $[M+H]^+$, 1489 $[M+Na]^+$, calc. *M* = 1466.

Experimental procedure for preparation and spectroscopic data of compound **3b**. Only *rctt*-isomer **3b** in *chair* conformation was obtained as a white powder in a yield of 0.24 g (89%) under the same conditions as compounds **2a** and **2b** by reaction of 2-methylresorcinol (0.10 g, 0.81 mmol) and aldehyde **1** (0.22 g, 0.81 mmol), mp > 240 ºC (dec). ^{1}H NMR (600.1 MHz, DMSO-d_6) δ: 1.97 (s, 6H, Me^{vertical}), 2.09 (s, 6H, Me^{horizontal}), 4.76 (s, 8H, H-15), 5.47 (s, 2H, H-4^{vertical}), 5.72 (s, 4H, H-5), 6.22 (s, 2H, H-4^{horizontal}), 6.75 (d, $^{3}J_{HH}$ 8.5 Hz, 8H, H-7), 6.88 (d, $^{3}J_{HH}$ 8.5 Hz, 8H, H-8), 7.33 (d, $^{3}J_{HH}$ 8.4 Hz, 8H, H-13), 7.88 (d, $^{3}J_{HH}$ 8.4 Hz, 8H, H-12). ^{13}C NMR (150.9 MHz, DMSO-d_6) δ: 9.8 (Me^{horizontal}), 10.1 (Me^{vertical}), 43.3 (C-15), 45.3 (C-5), 111.0 (C-1^{vertical}), 111.3 (C-1^{horizontal}), 120.5 (C-8), 122.1 (C-3^{horizontal}), 123.0 (C-3^{vertical}), 125.8 (C-4^{vertical}), 126.3 (C-13), 128.2 (C-4^{horizontal}), 129.5 (C-12), 130.1 (C-7), 141.2 (C-6), 143.2 (C-14), 148.2 (C-11), 148.6 (C-9), 150.7 (C-2^{vertical}), 150.8 (C-2^{horizontal}), 164.5 (C-10). IR (KBr, ν/cm^{-1}): 1738 (C=O), 3100–3650 (OH). Found (%): C, 69.08; H, 4.59; Cl, 9.44. Calc. for $C_{88}H_{68}Cl_4O_{16}$ (%): C, 69.39; H, 4.50; Cl, 9.31. MALDI-MS, *m/z*: 1523 $[M]^+$, 1524 $[M+H]^+$, 1546 $[M+Na]^+$, calc. *M* = 1523.

Experimental procedure for preparation and spectroscopic data of compounds **4a** and **4b**. The mixture of **4a** and **4b** in an 1 : 3 ratio by ^{1}H NMR spectroscopy with total yield 0.19 g (68%) was obtained under the same conditions as compounds **2a** and **2b** by reaction of pyrogallol (0.1 g, 0.73 mmol) and aldehyde **1** (0.20 g, 0.73 mmol). Sequential recrystallization from acetone and ethanol gave pure *rctt*-isomer 4b in *chair* conformation as a light-pink powder (0.12 g, 43%), mp > 210 °C (dec.). ^{1}H NMR (600.1 MHz, DMSO-d_6) δ: 4.77 (s, 8H, H-15), 5.28 (s, 2H, H-4^{horizontal}), 5.75 (s, 4H, H-5), 6.03 (s, 2H, H-4^{vertical}), 6.71 (d, $^{3}J_{HH}$ 8.6 Hz, 8H, H-7), 6.87 (d, $^{3}J_{HH}$ 8.6 Hz, 8H, H-8), 7.34 (d, $^{3}J_{HH}$ 8.3 Hz, 8H, H-13), 7.78 (s, 4H, OH^{horizontal}), 7.87 (d, $^{3}J_{HH}$ 8.3 Hz, 8H, H-12), 7.93 (s, 4H, OH^{vertical}). ^{13}C NMR (150.9 MHz, DMSO-d_6) δ: 42.5 (C-5), 45.1 (C-15), 119.6 (C-4^{vertical}), 119.9 (C-8), 121.5 (C-3^{horizontal}), 122.7 (C-4^{horizontal}), 128.7 (C-11), 128.8 (C-13), 129.6 (C-12), 129.6 (C-7), 131.6 (C-1^{horizontal}), 131.9 (C-1^{vertical}), 141.3 (C-3^{vertical}), 141.8 (C-6), 142.2 (C-2^{vertical}), 142.3 (C-2^{horizontal}), 142.9 (C-14), 147.7 (C-9), 163.8 (C-10). IR (KBr, ν/cm^{-1}): 1736 (C=O), 3100–3650 (OH). Found (%): C, 65.86; H, 4.03; Cl, 9.21. Calc. for $C_{84}H_{60}Cl_4O_{20}$ (%): C, 65.89; H, 3.95; Cl, 9.26. MALDI-MS, *m/z*: 1532 $[M+H]^+$, 1554 $[M+Na]^+$, calc. *M* = 1531).

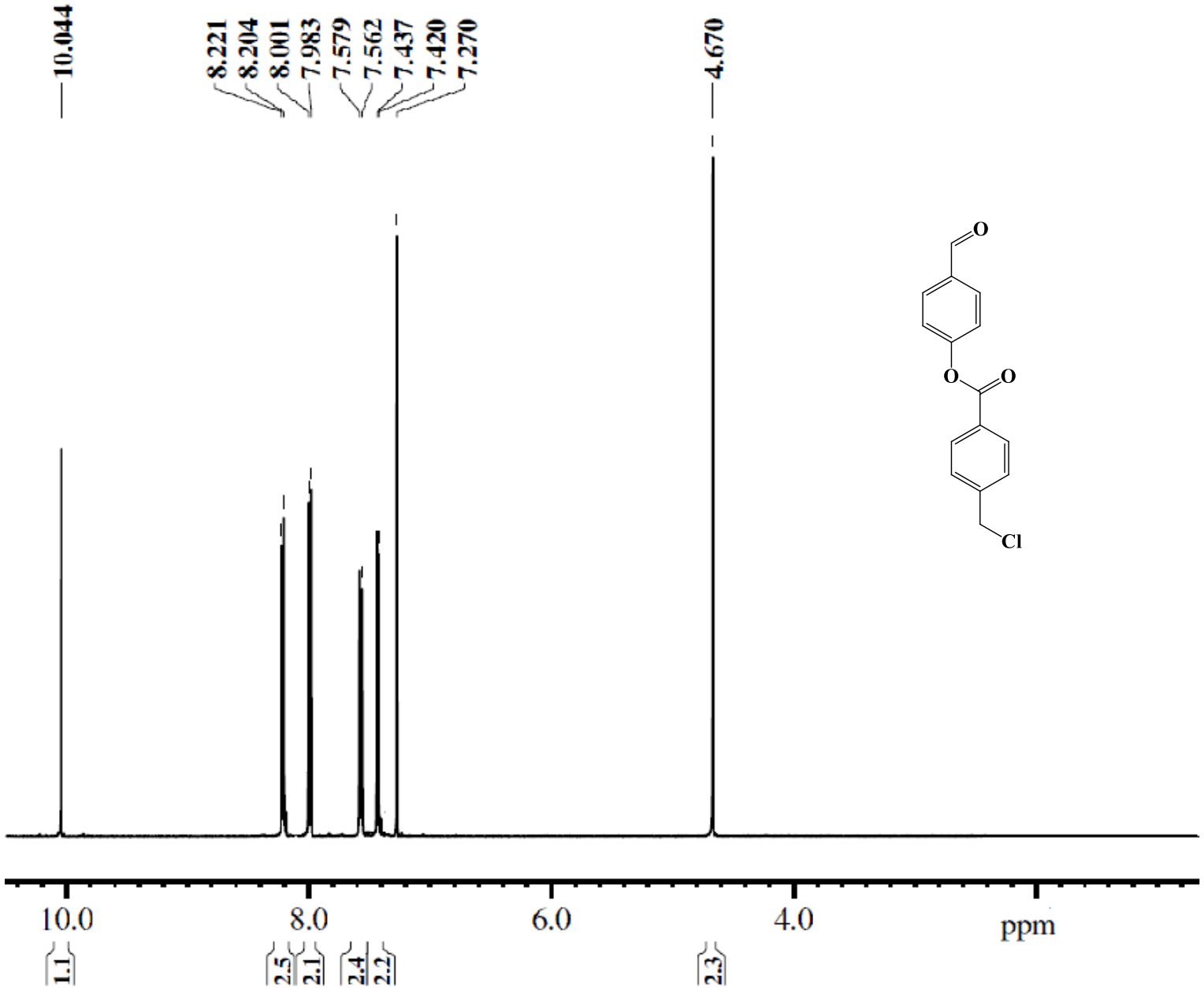


Figure S1 ^{1}H NMR spectrum of 4'-formylphenyl 4-(chloromethyl)benzoate **1** in $CDCl_3$ at 303 K.

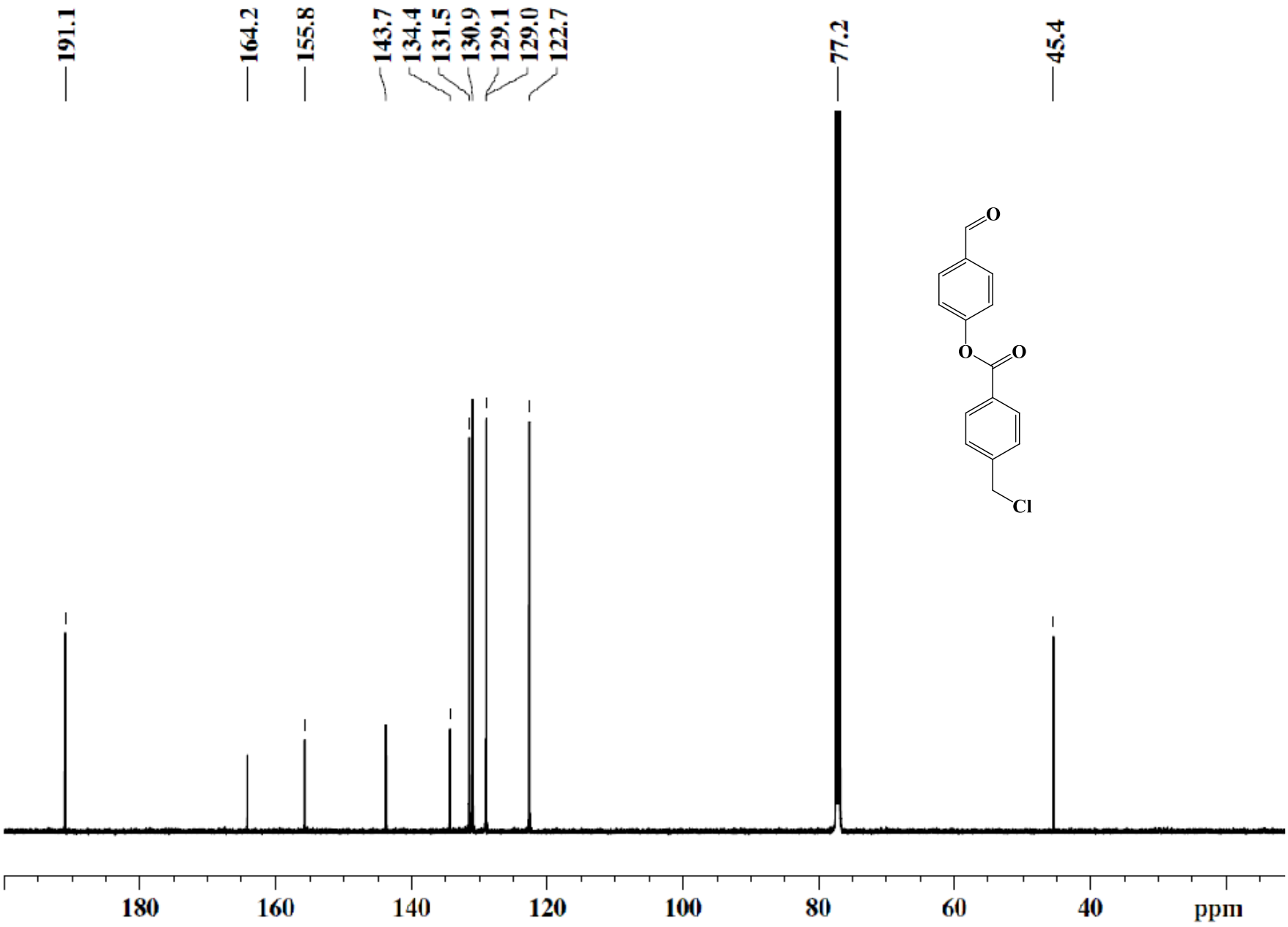


Figure S2 ^{13}C NMR spectrum of 4'-formylphenyl 4-(chloromethyl)benzoate **1** in $CDCl_3$ at 303 K.

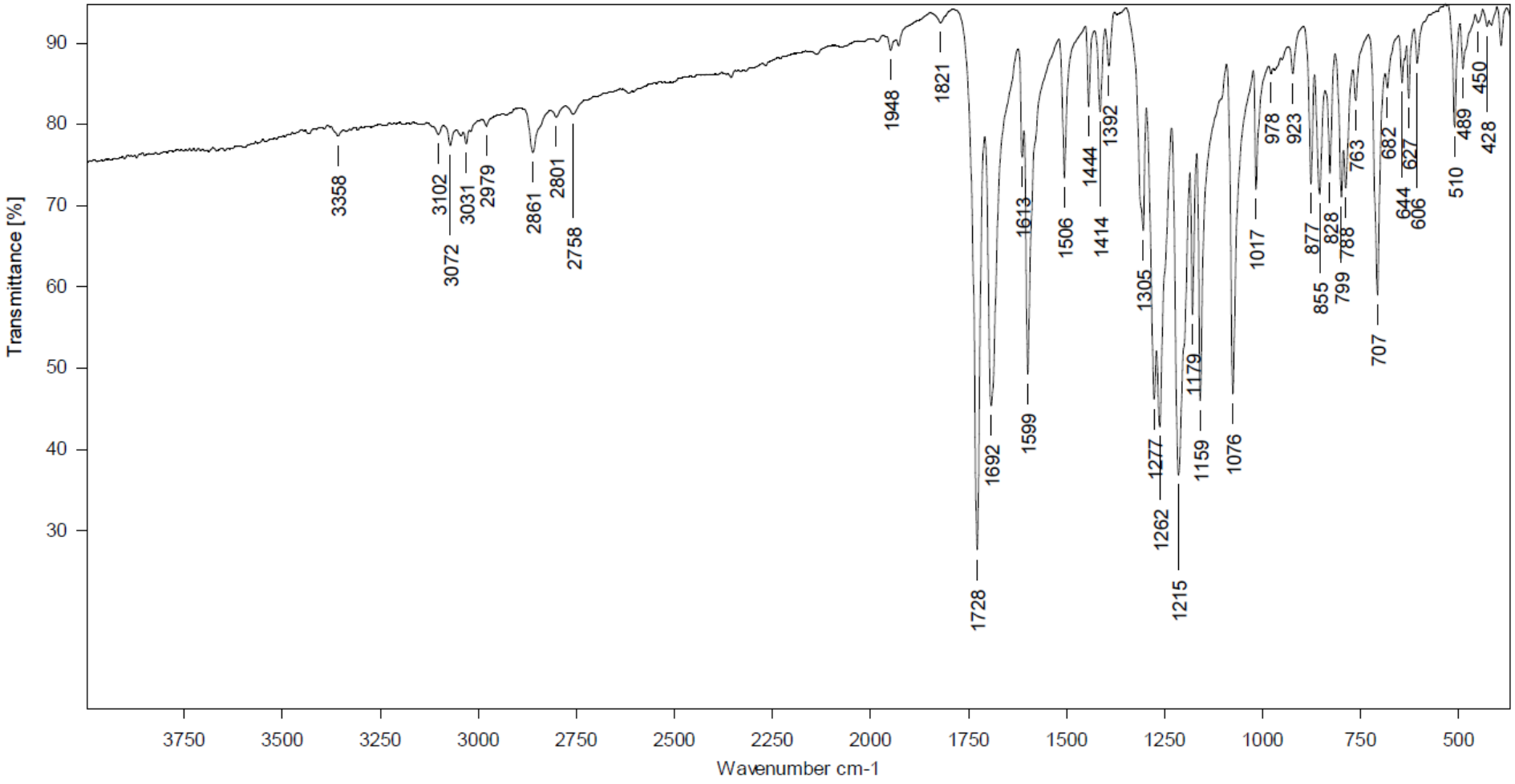


Figure S3 IR spectrum of 4'-formylphenyl 4-(chloromethyl)benzoate **1**.

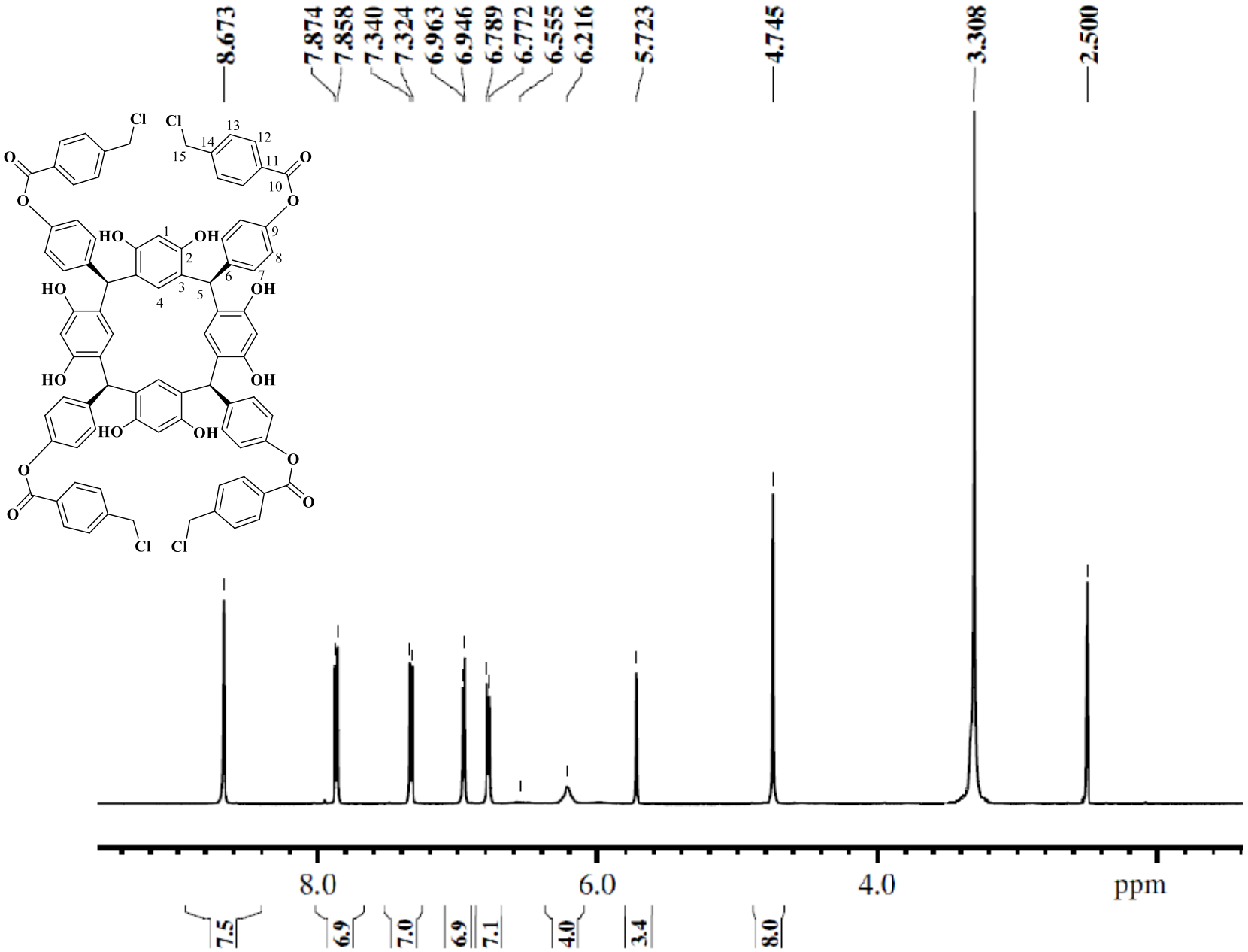


Figure S4 ^{1}H NMR spectrum of calix[4]resorcinol **2a** (*rccc*-isomer in *cone* conformation) in DMSO-d_6 at 303 K.

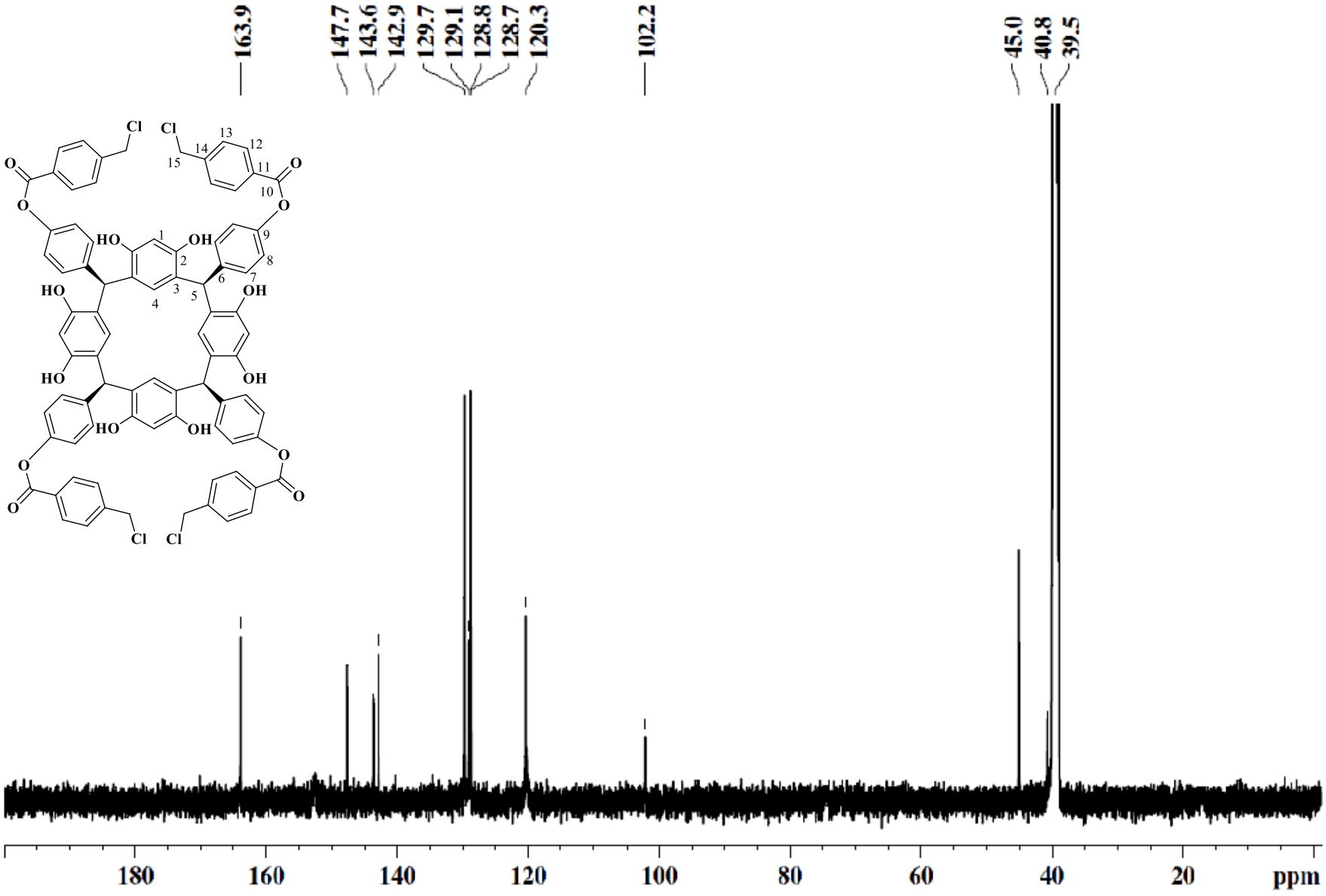


Figure S5 ^{13}C NMR spectrum of calix[4]resorcinol **2a** (*rccc*-isomer in *cone* conformation) in DMSO-d_6 at 303 K.

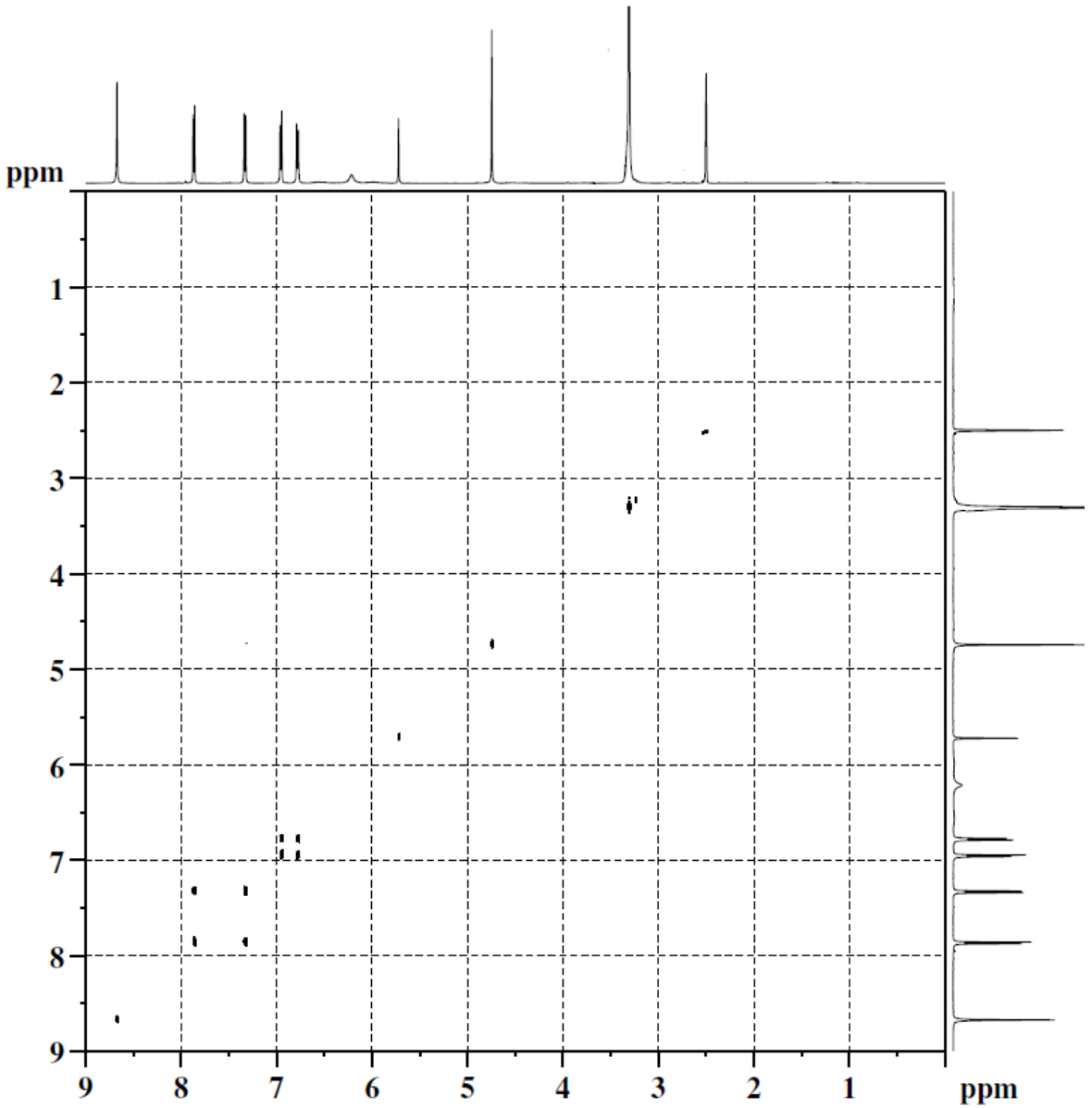


Figure S6 COSY NMR spectrum of calix[4]resorcinol **2a** (*rccc*-isomer in *cone* conformation) in DMSO-d_6 at 303 K.

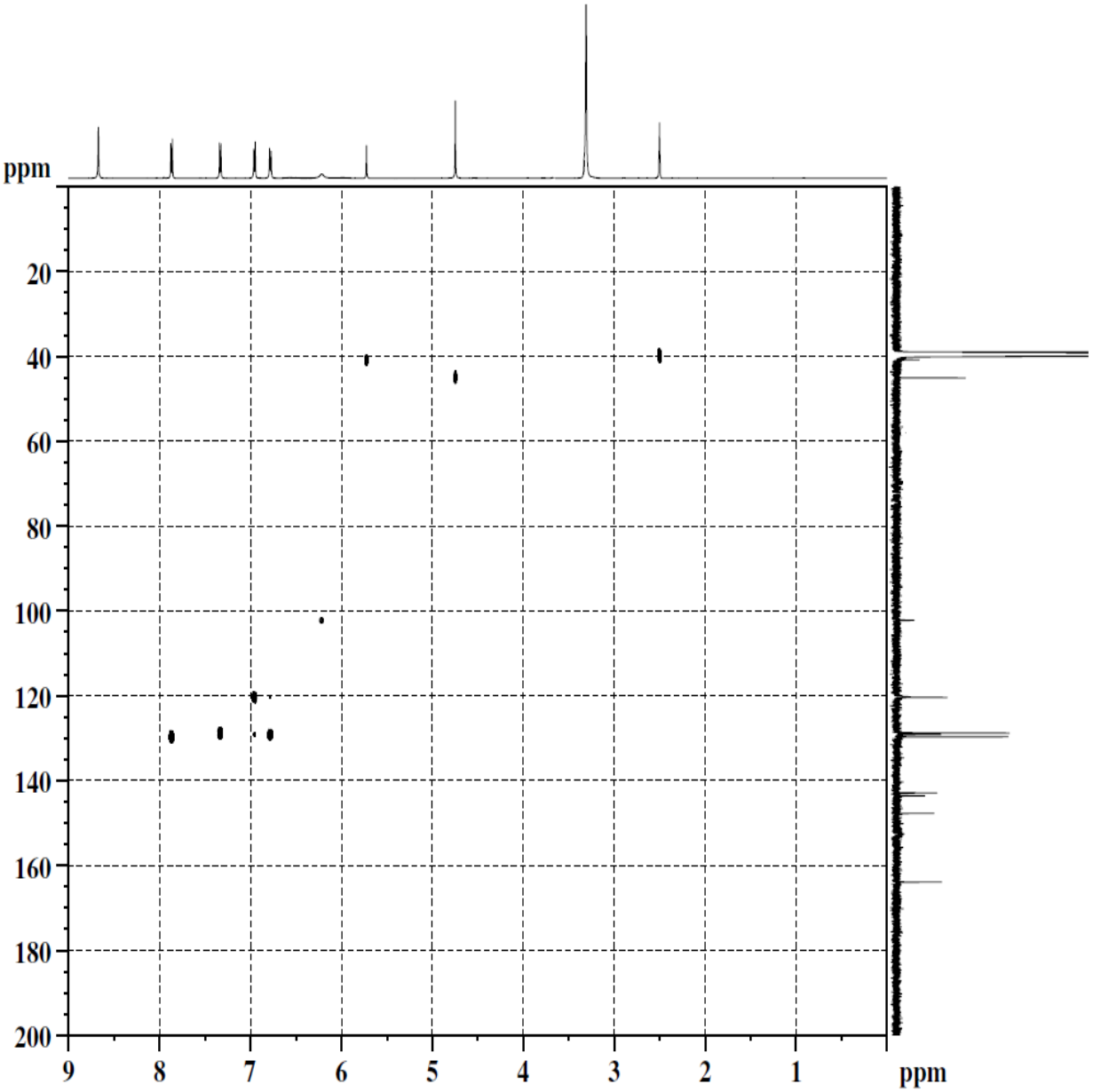


Figure S7 HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **2a** (*rccc*-isomer in *cone* conformation) in DMSO-d_6 at 303 K.

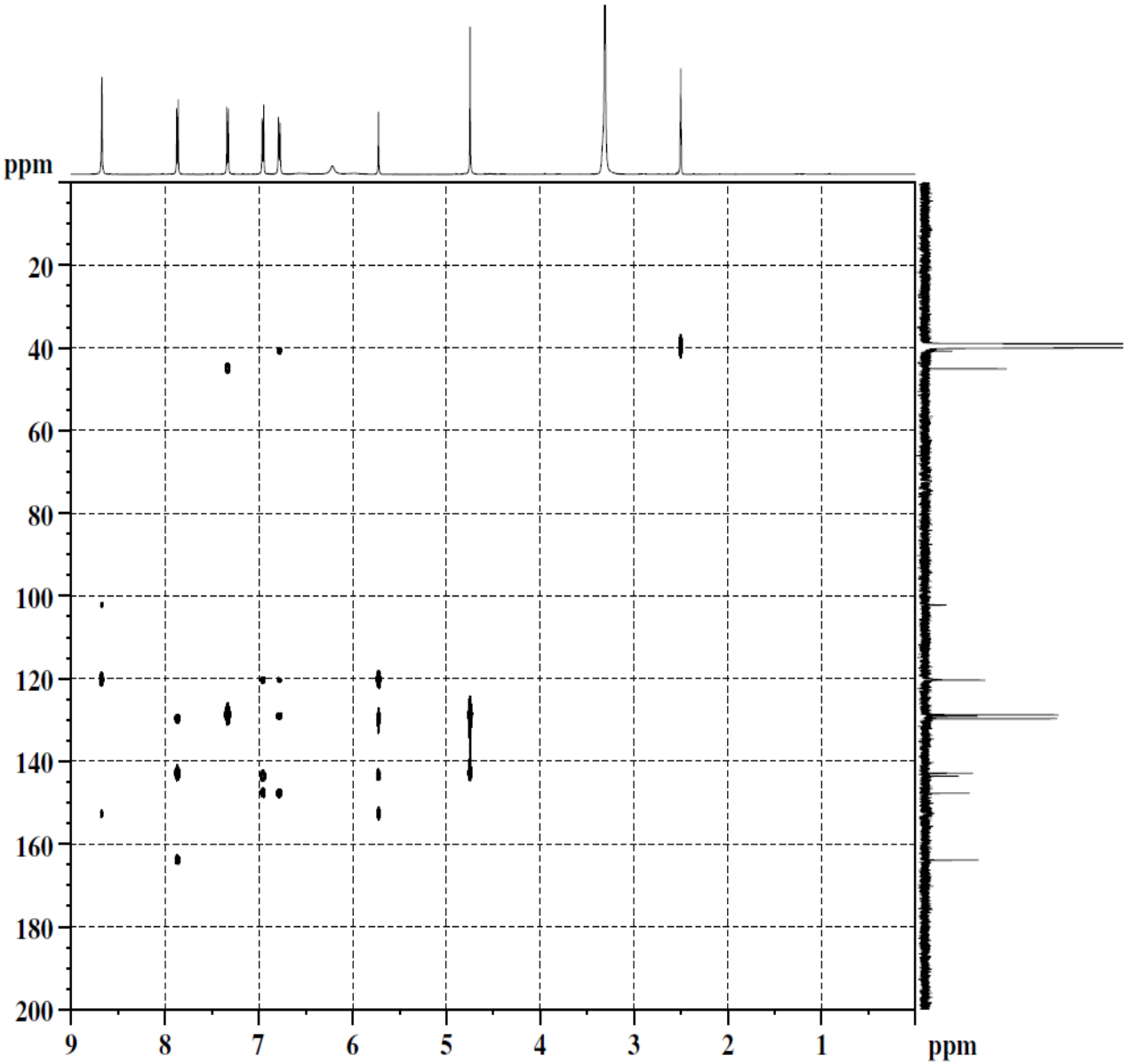


Figure S8 HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **2a** (*rccc*-isomer in *cone* conformation) in DMSO-d_6 at 303 K.

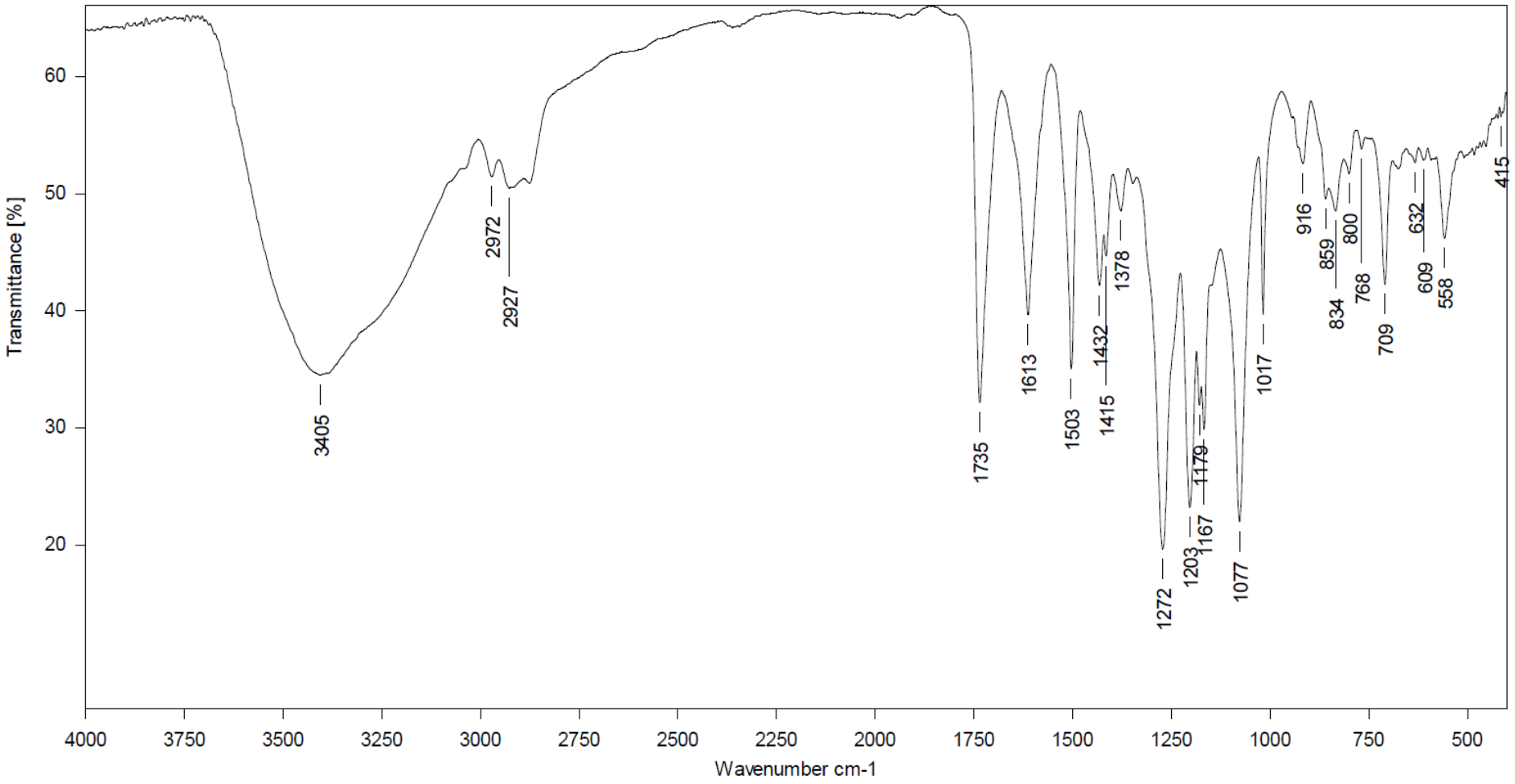


Figure S9 IR spectrum of calix[4]resorcinol **2a**.

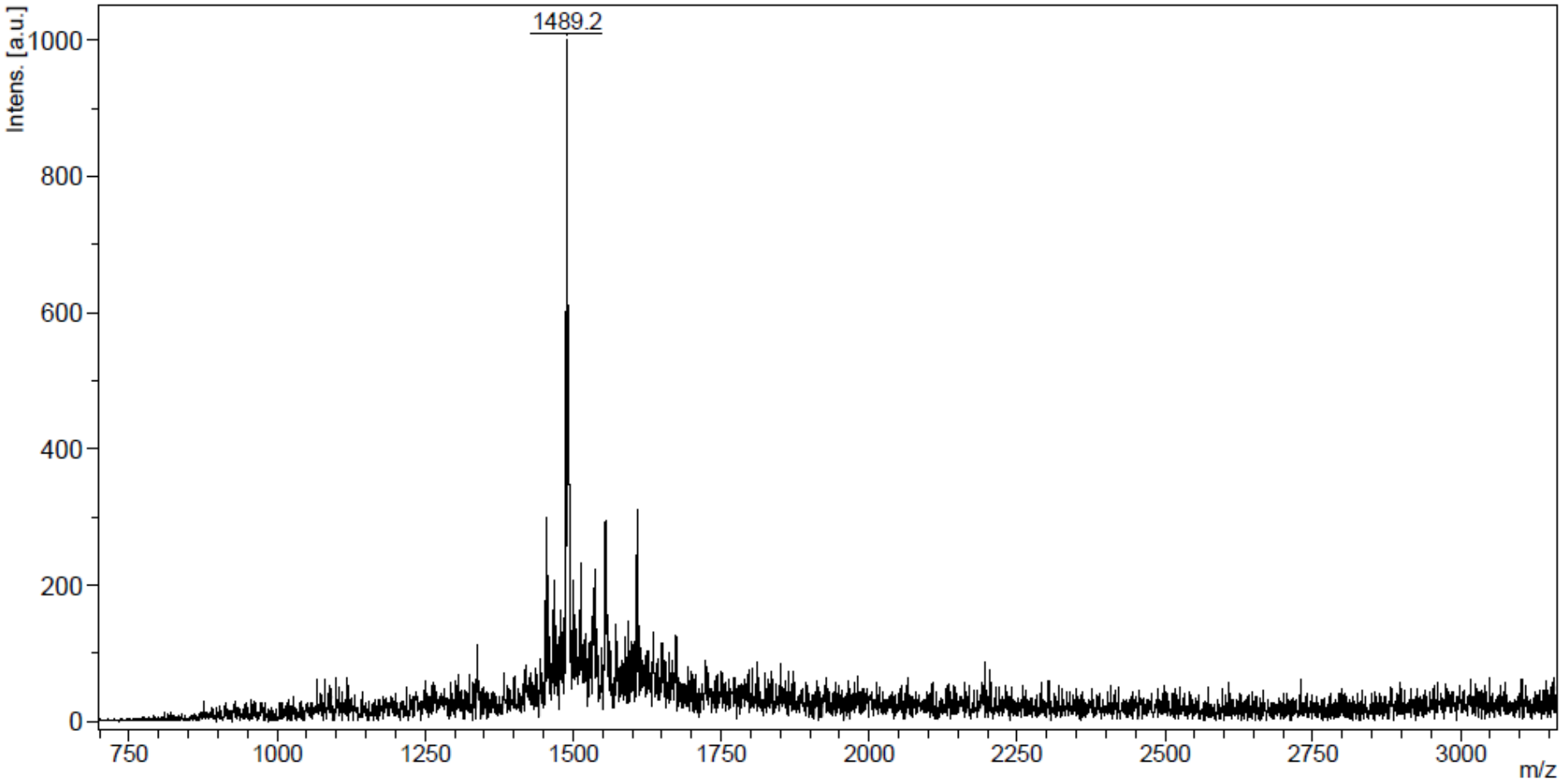


Figure S10 MALDI-MS spectrum of calix[4]resorcinol **2a**.

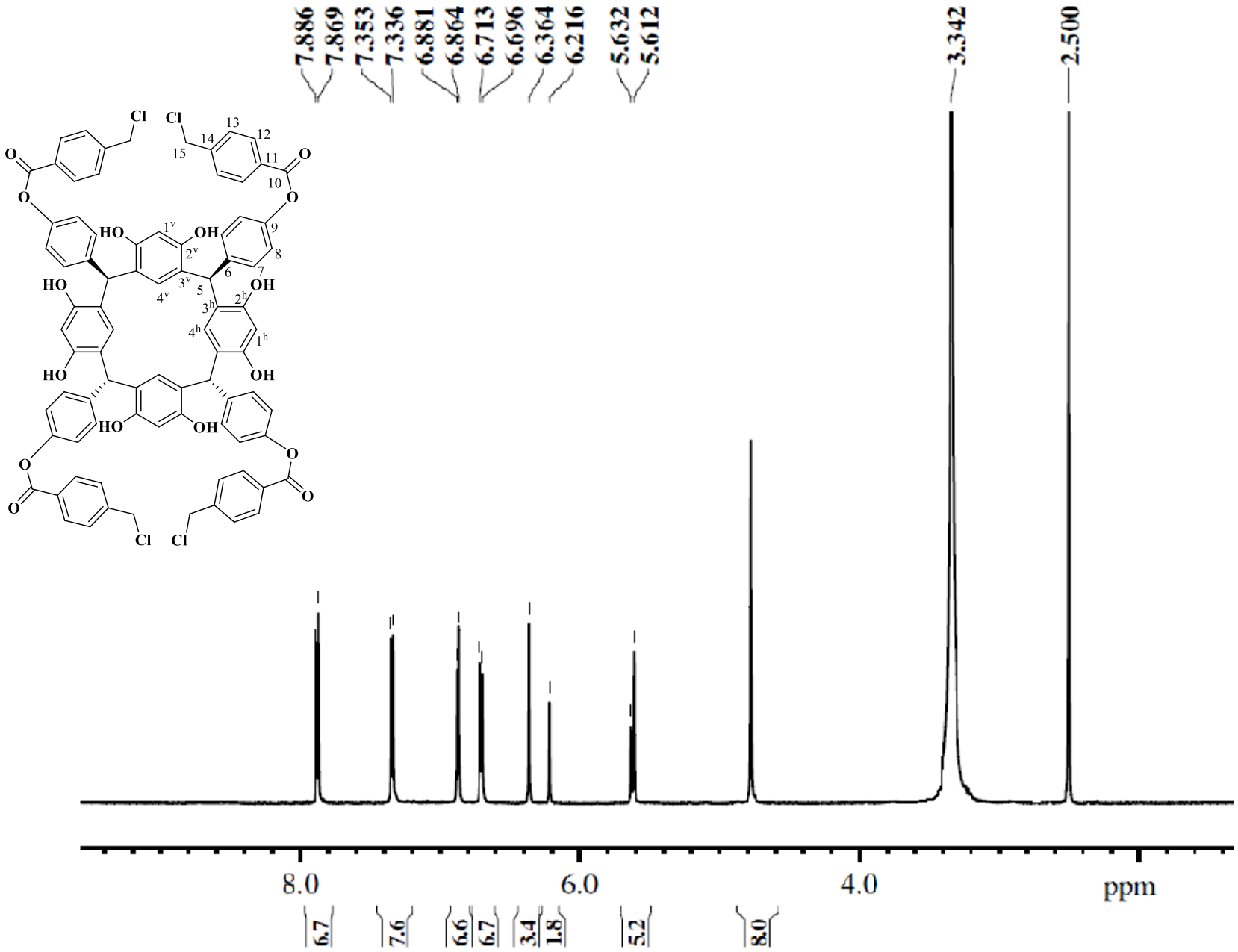


Figure S11 ^{1}H NMR spectrum of calix[4]resorcinol **2b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

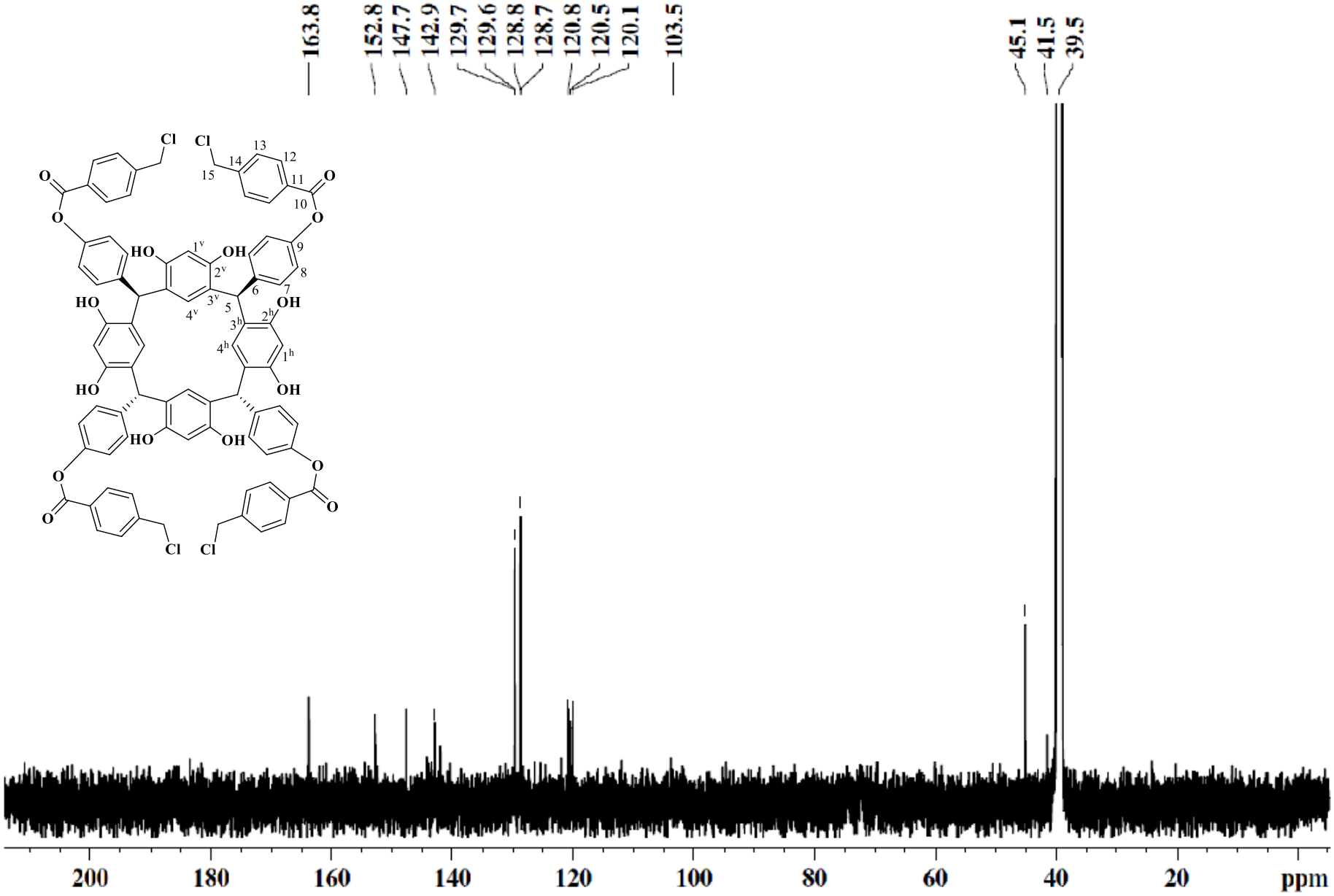


Figure S12 ^{13}C NMR spectrum of calix[4]resorcinol **2b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

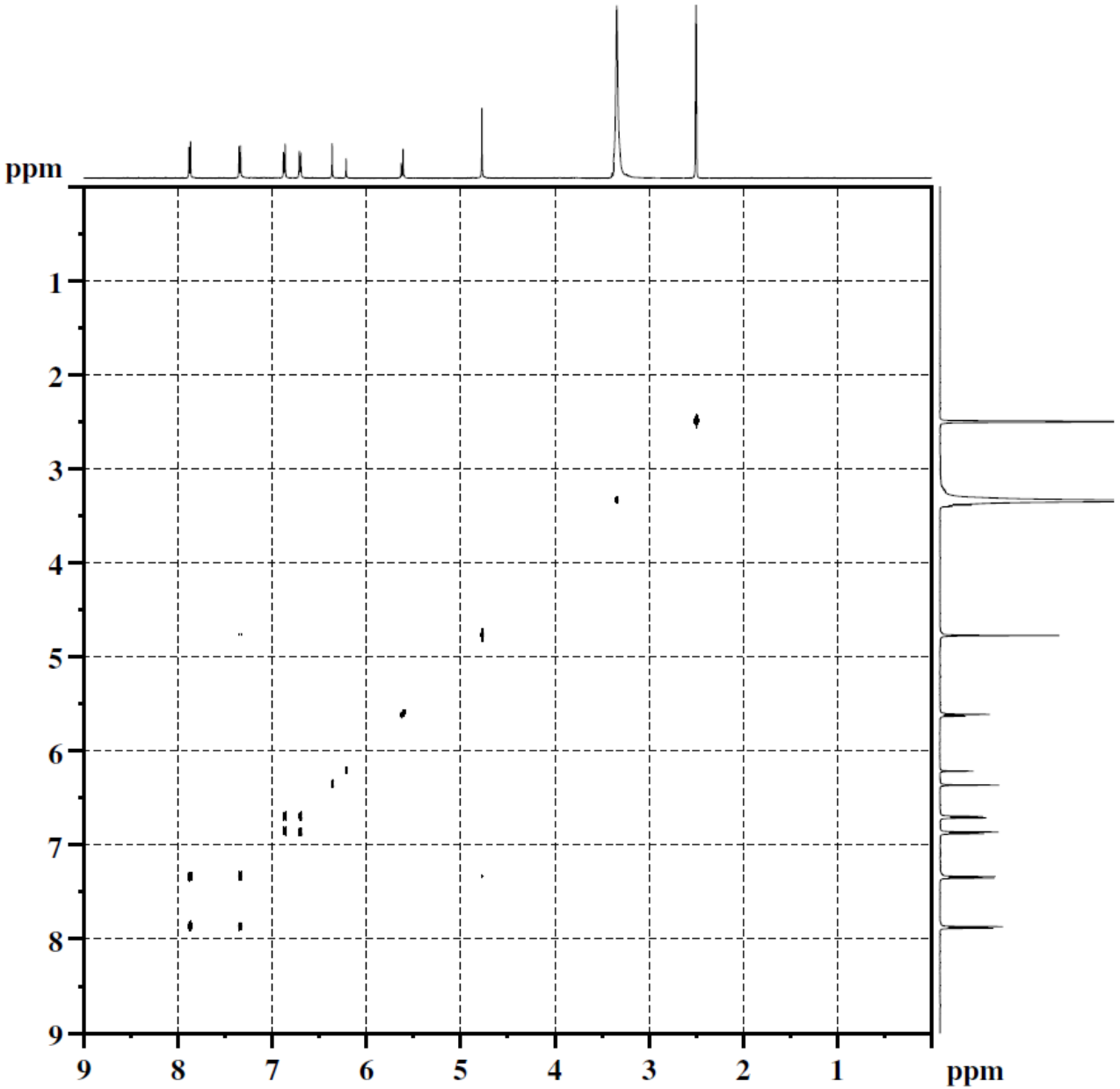


Figure S13 COSY NMR spectrum of calix[4]resorcinol **2b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

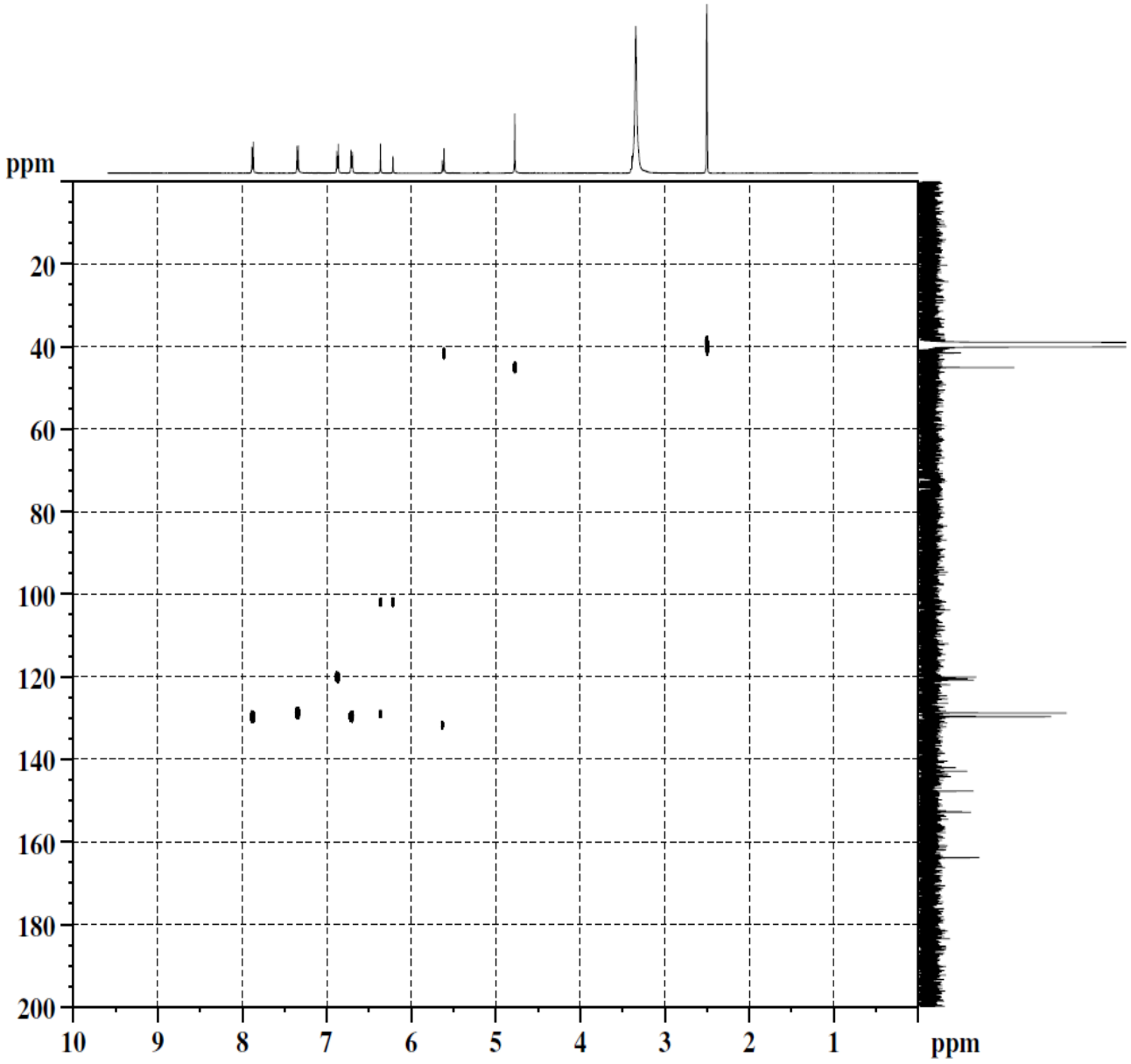


Figure S14 HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **2b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

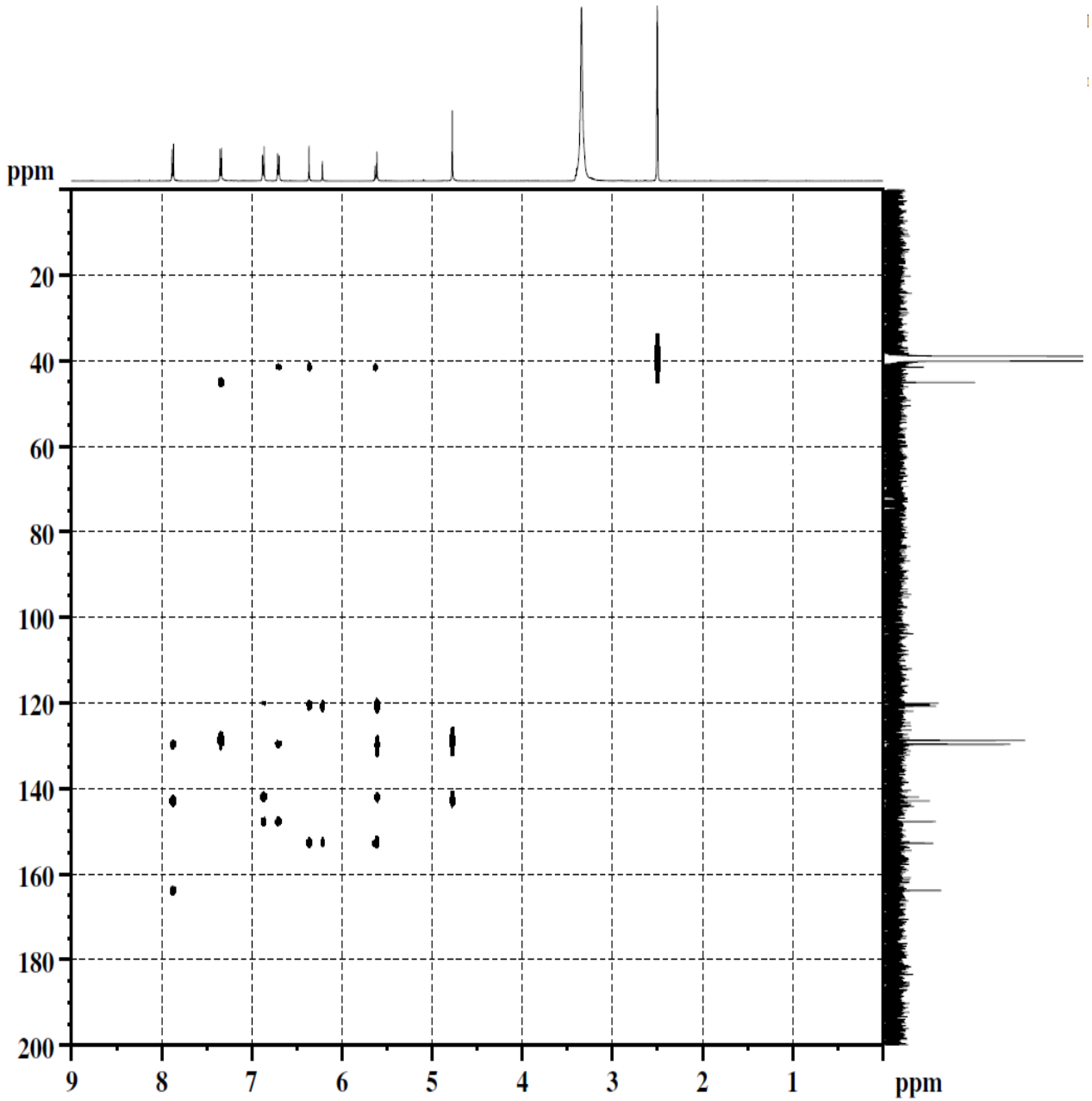


Figure S15 HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **2b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

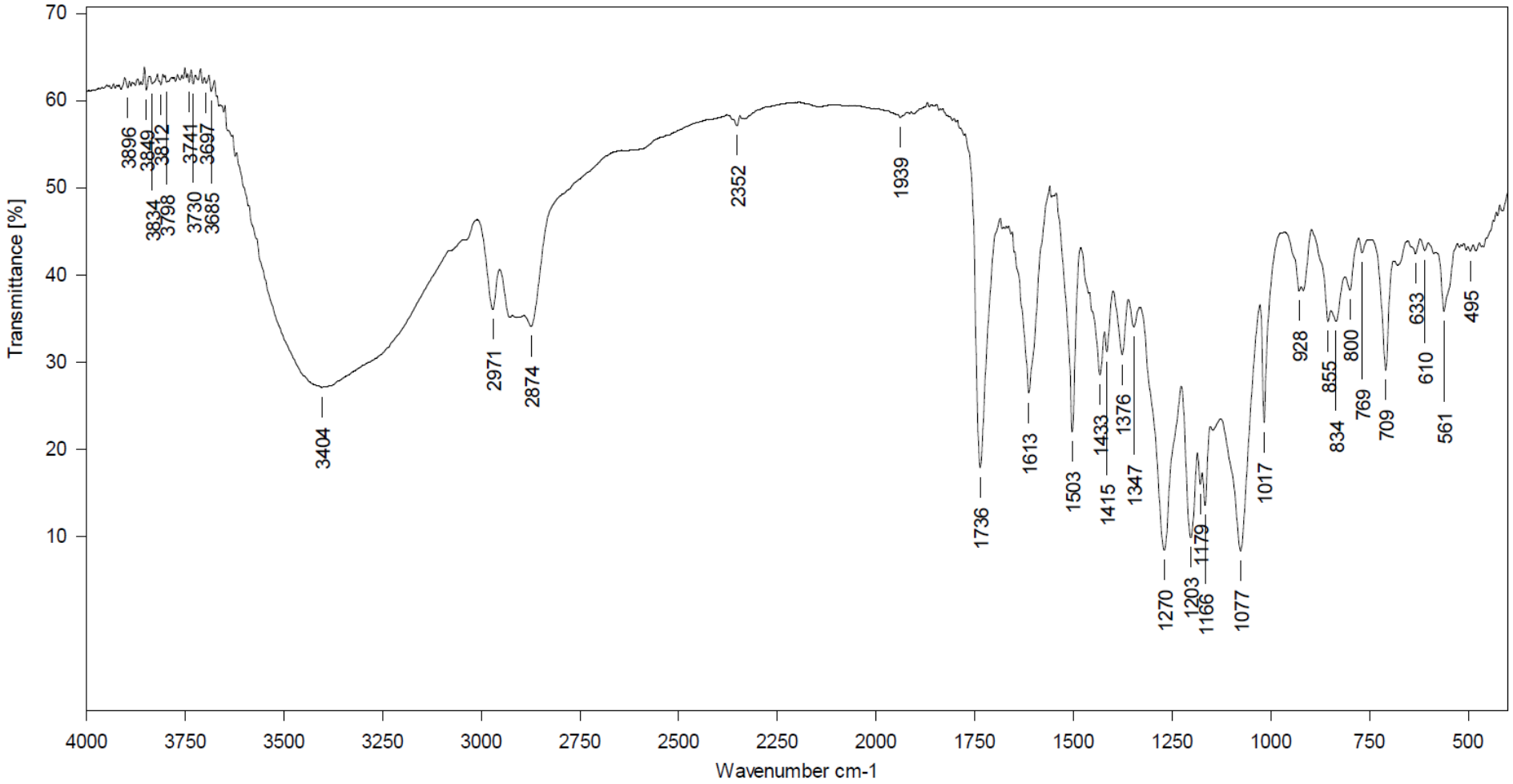


Figure S16 IR spectrum of calix[4]resorcinol **2b**.

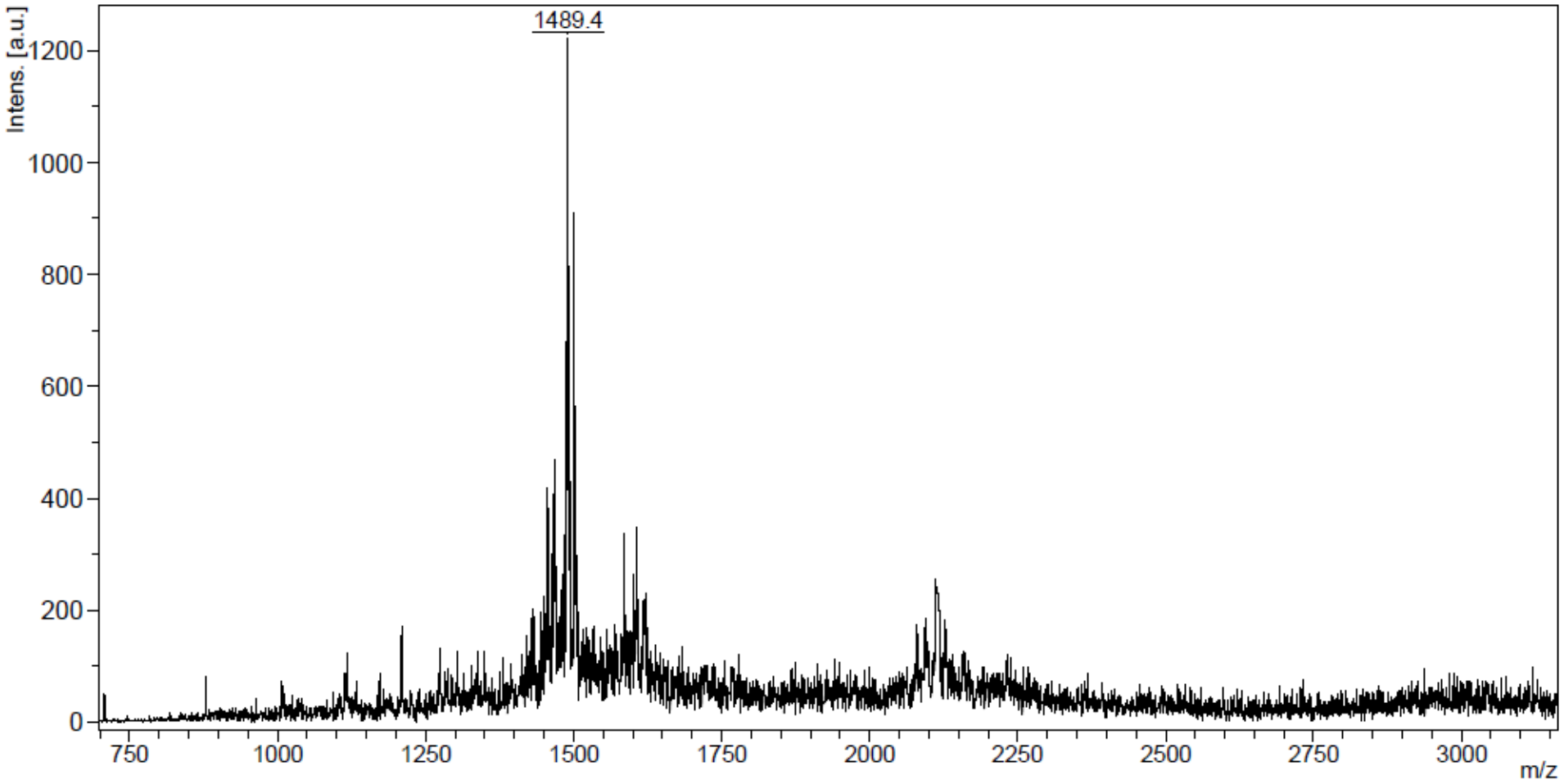


Figure S17 MALDI-MS spectrum of calix[4]resorcinol **2b**.

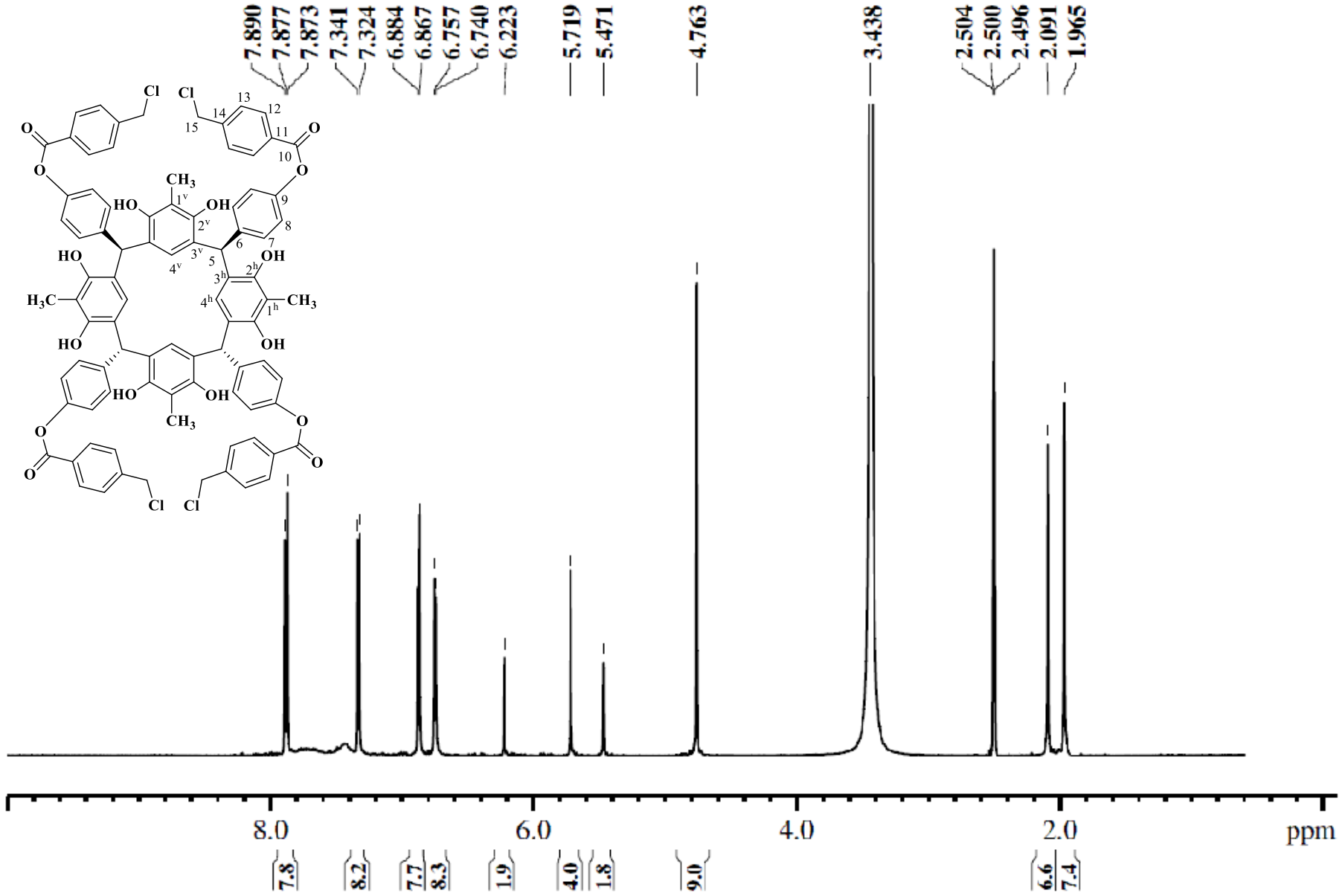


Figure S18 ^{1}H NMR spectrum of calix[4]resorcinol **3b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

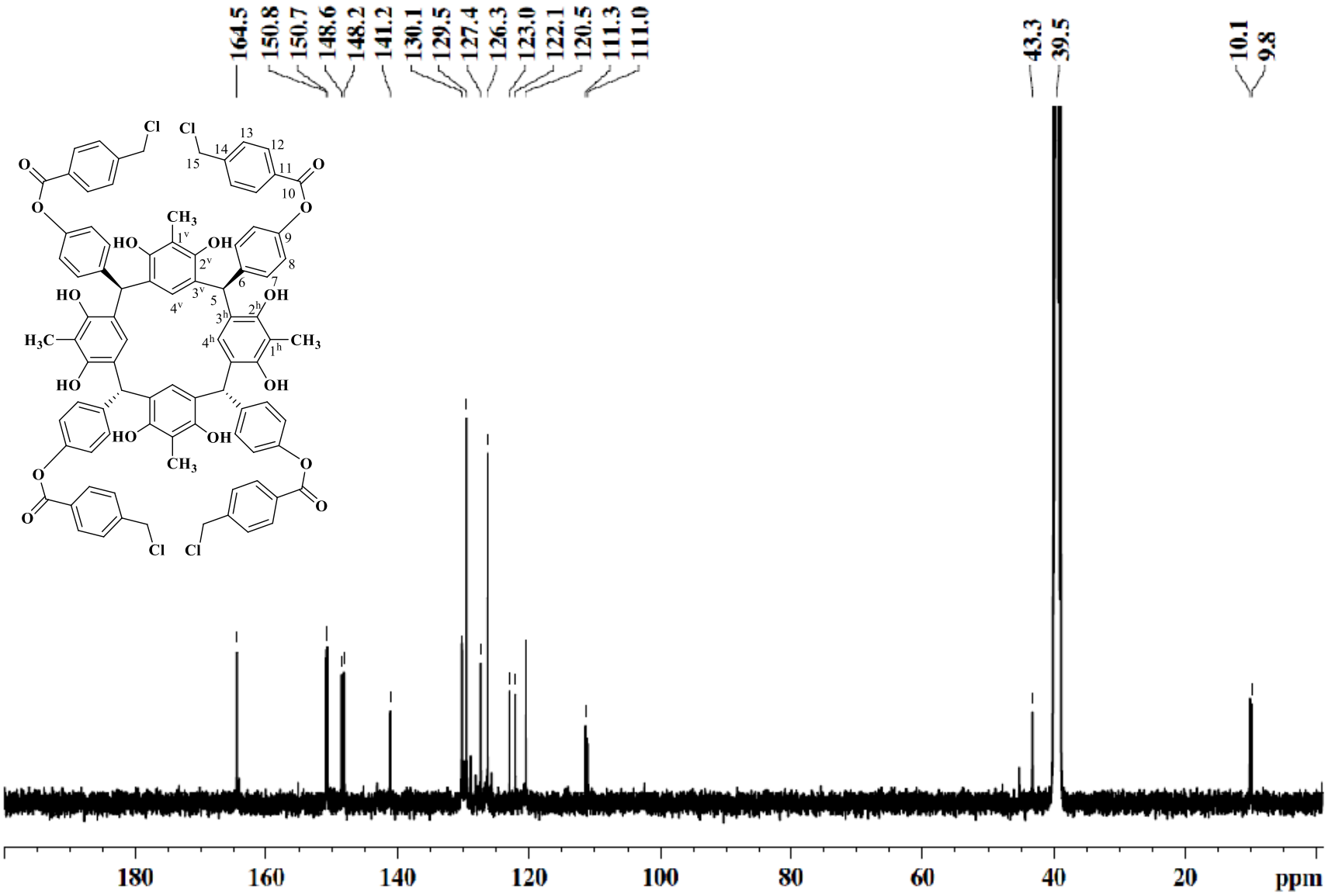


Figure S19 ^{13}C NMR spectrum of calix[4]resorcinol **3b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

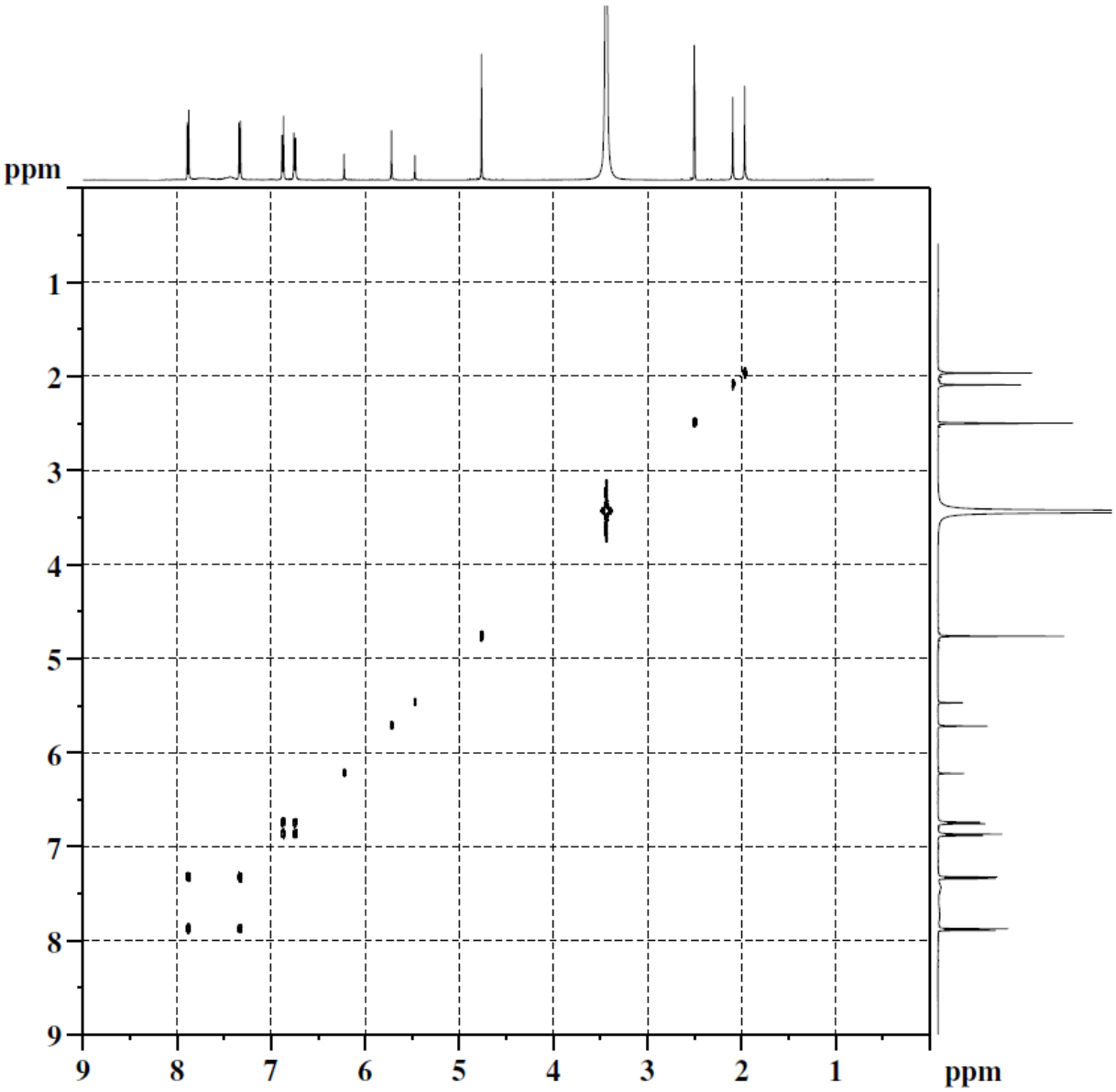


Figure S20 COSY NMR spectrum of calix[4]resorcinol **3b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

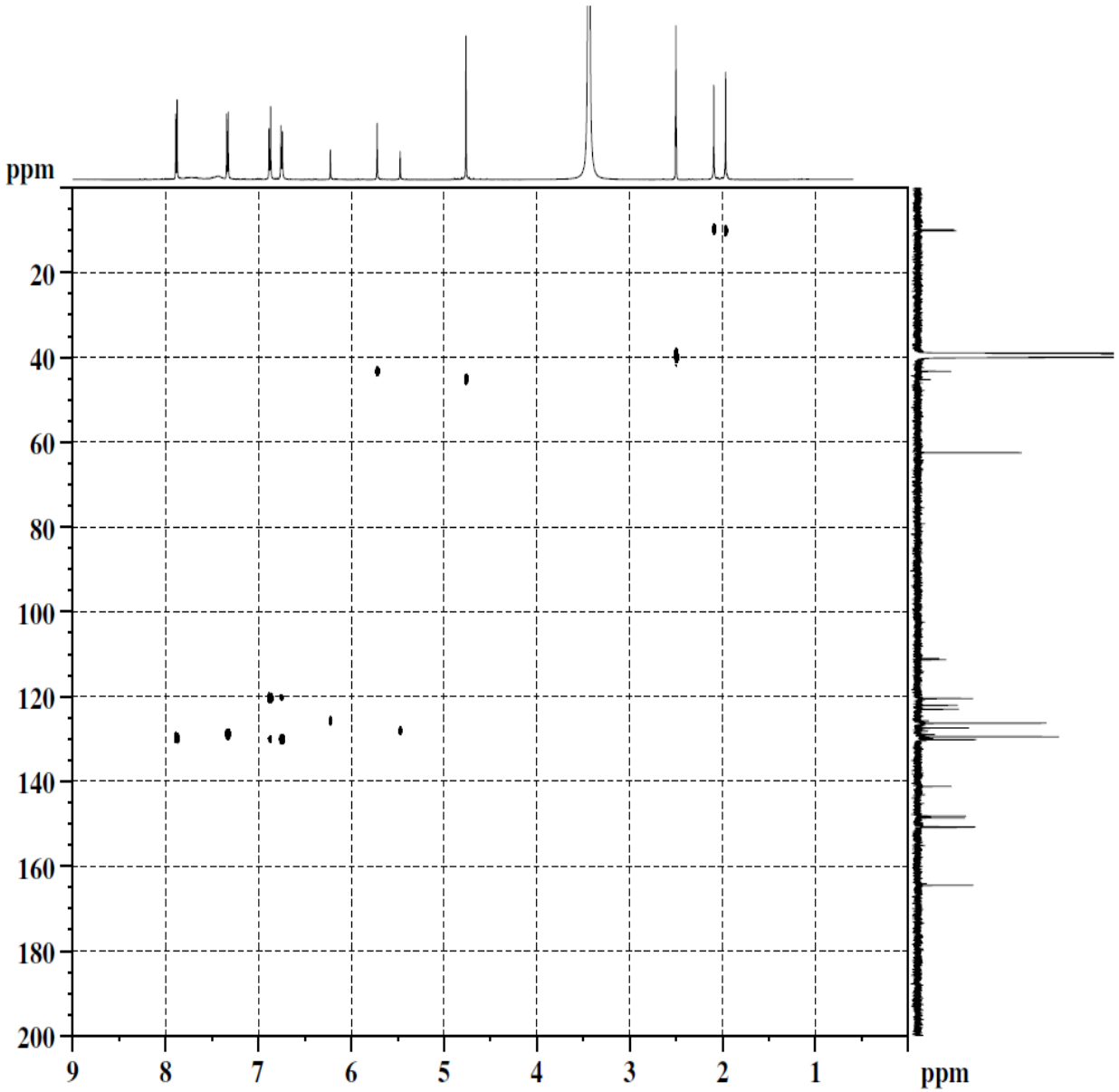


Figure S21 HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **3b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

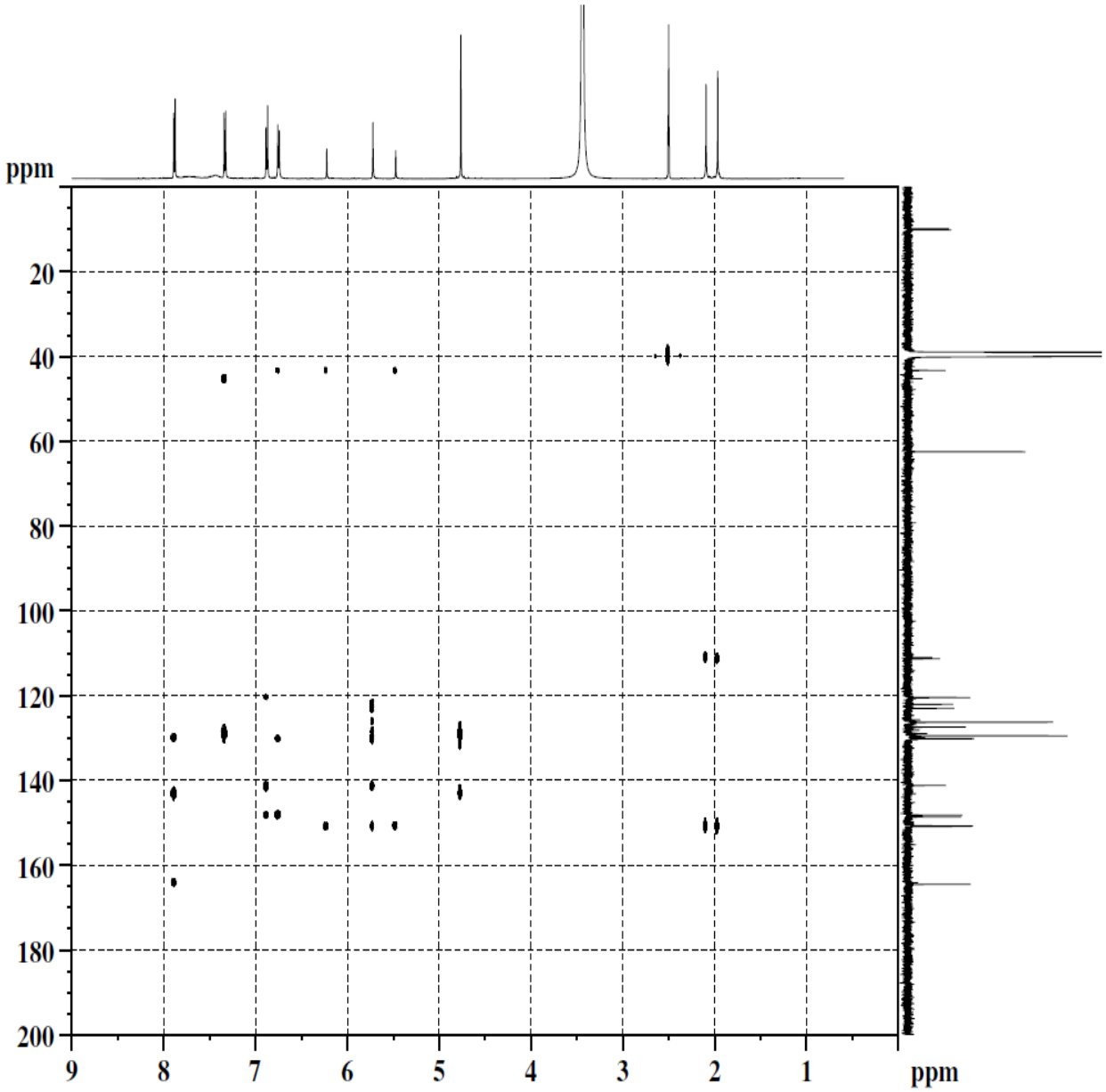


Figure S22 HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **3b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

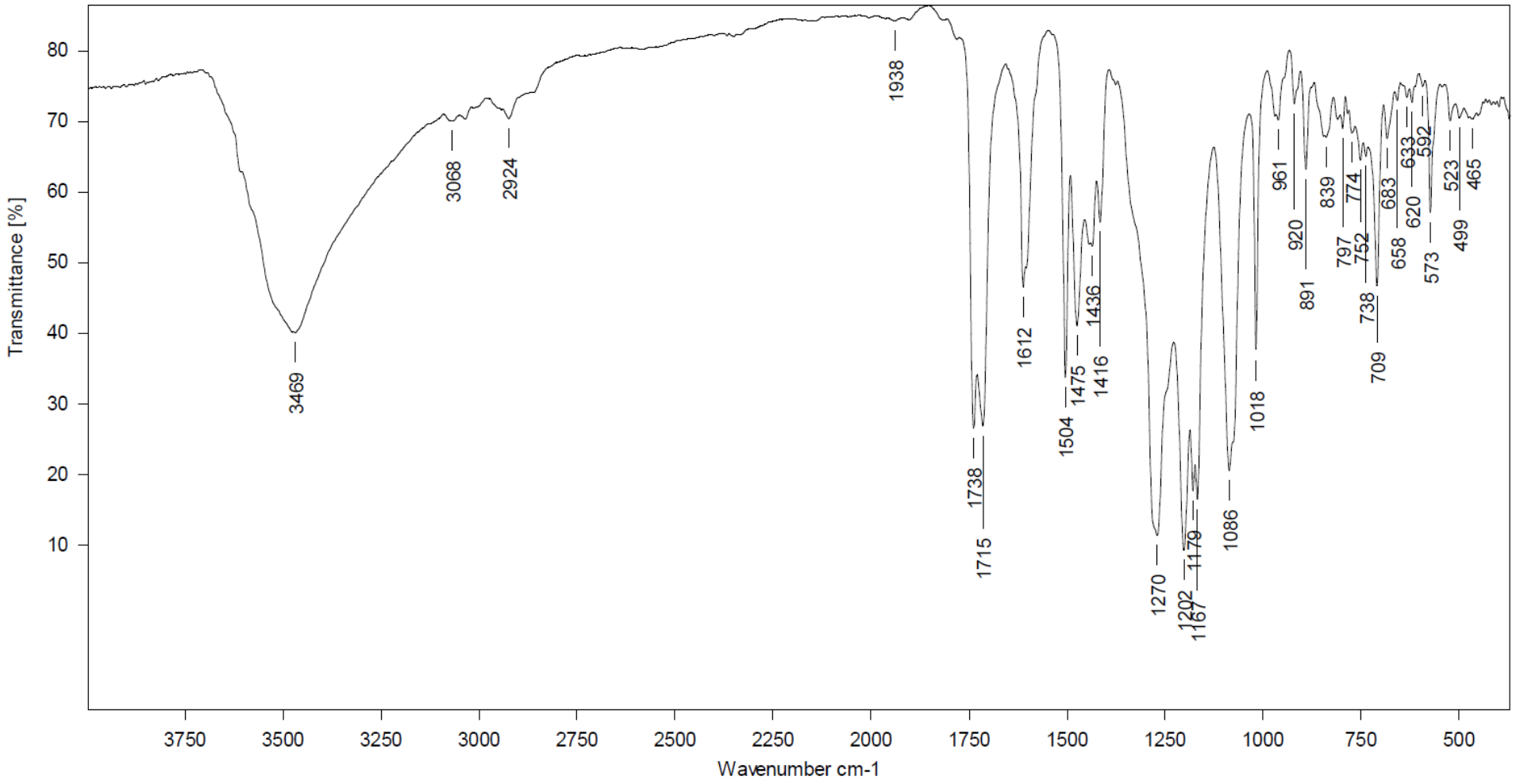


Figure S23 IR spectrum of calix[4]resorcinol **3b**.

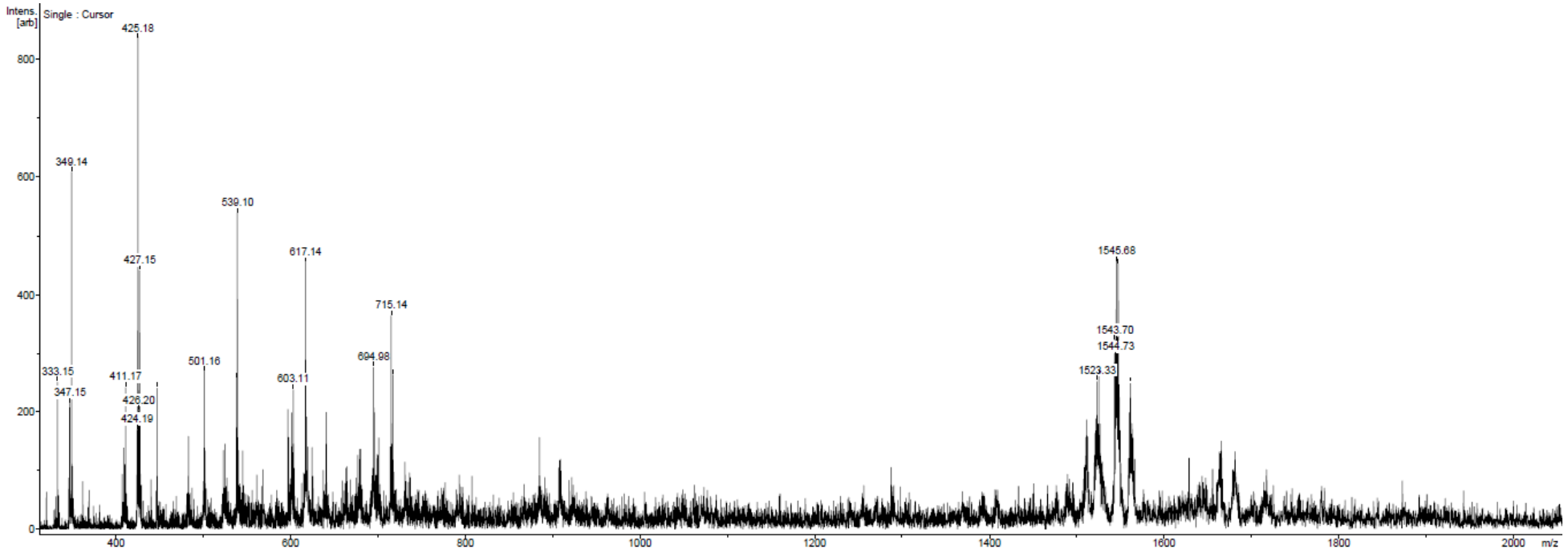


Figure S24 MALDI-MS spectrum of calix[4]resorcinol **3b**.

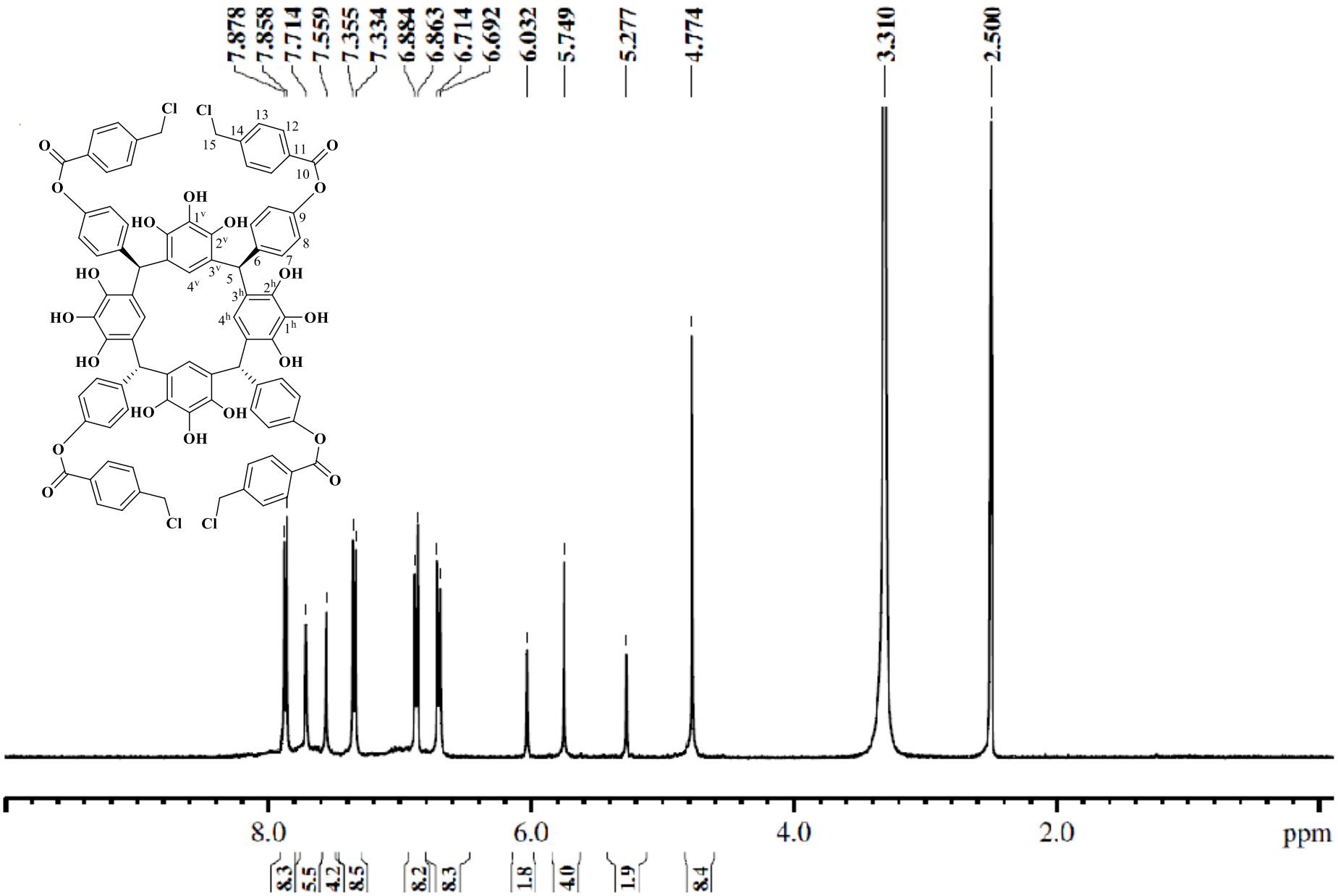


Figure S25 ^{1}H NMR spectrum of calix[4]resorcinol **4b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

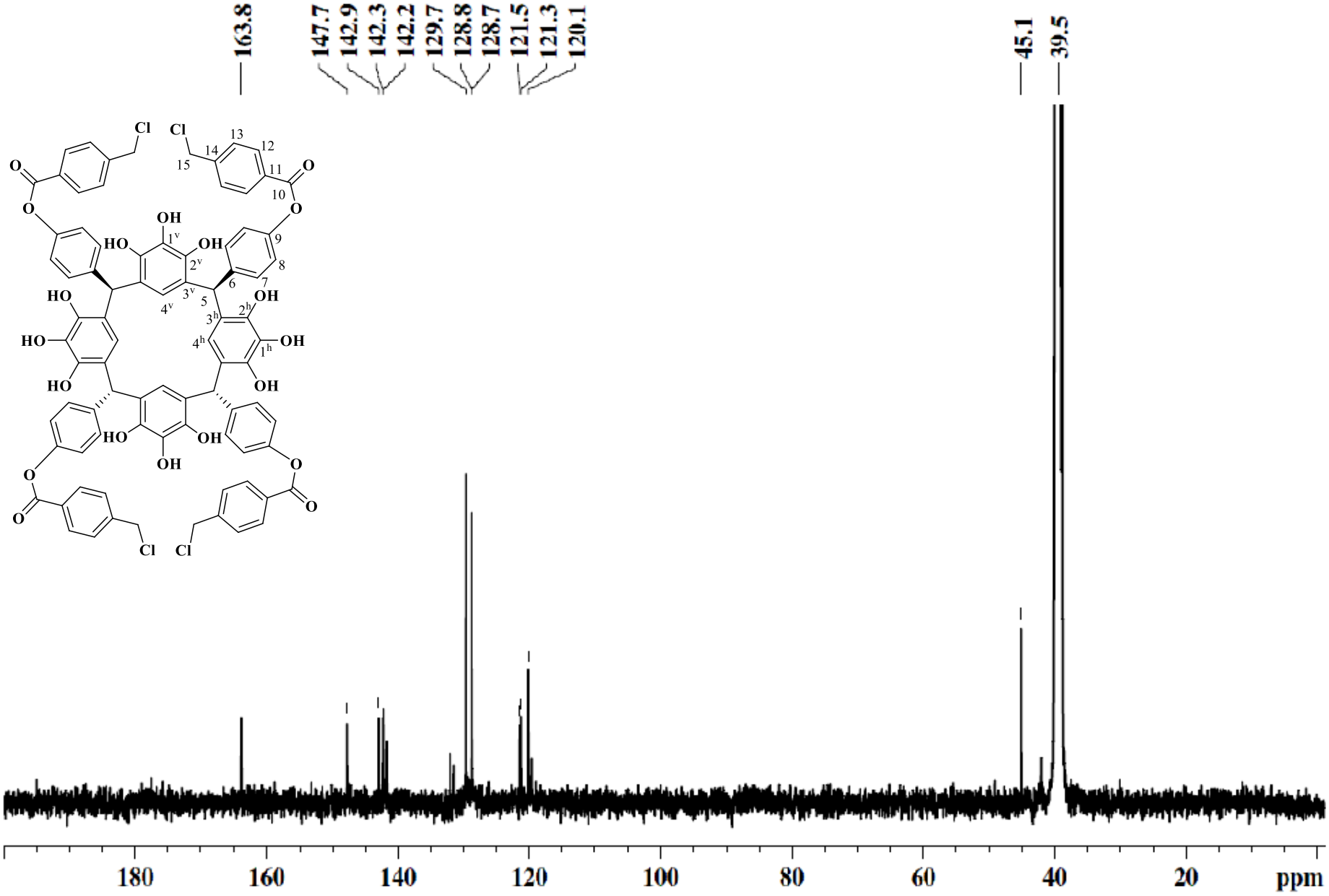


Figure S26 ^{13}C NMR spectrum of calix[4]resorcinol **4b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

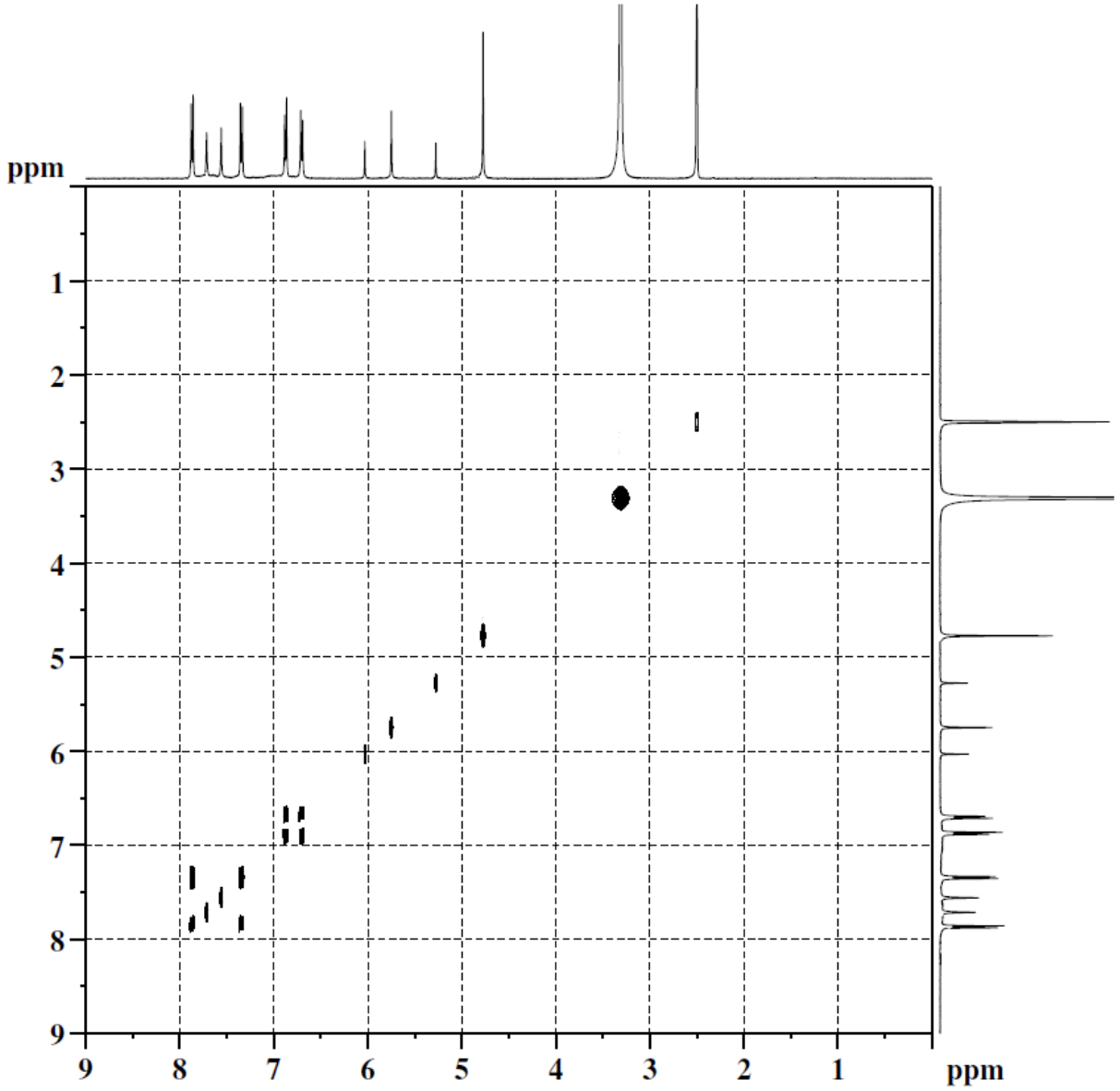


Figure S27 COSY NMR spectrum of calix[4]resorcinol **4b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

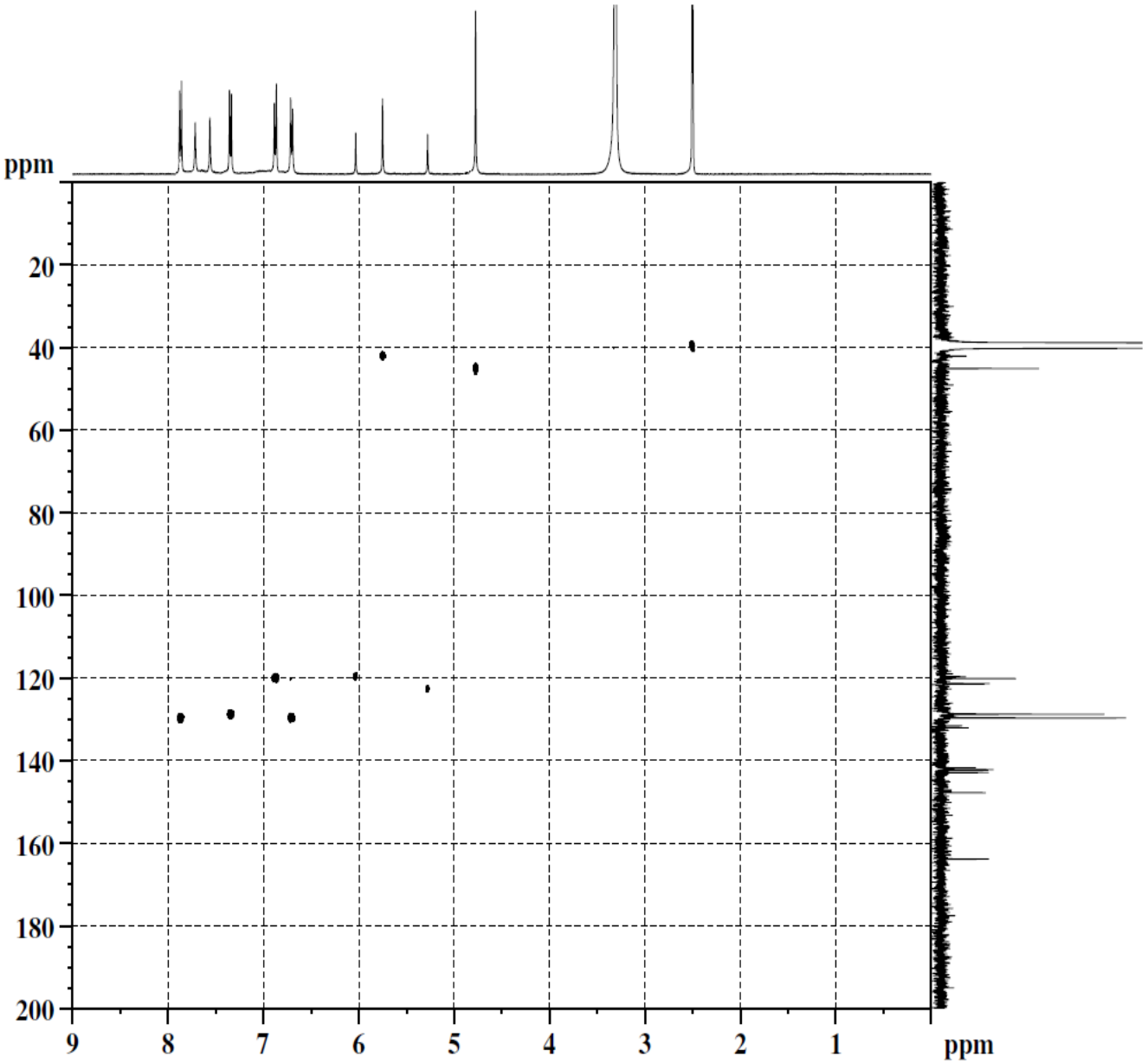


Figure S28 HSQC (^{13}C) NMR spectrum of calix[4]resorcinol **4b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

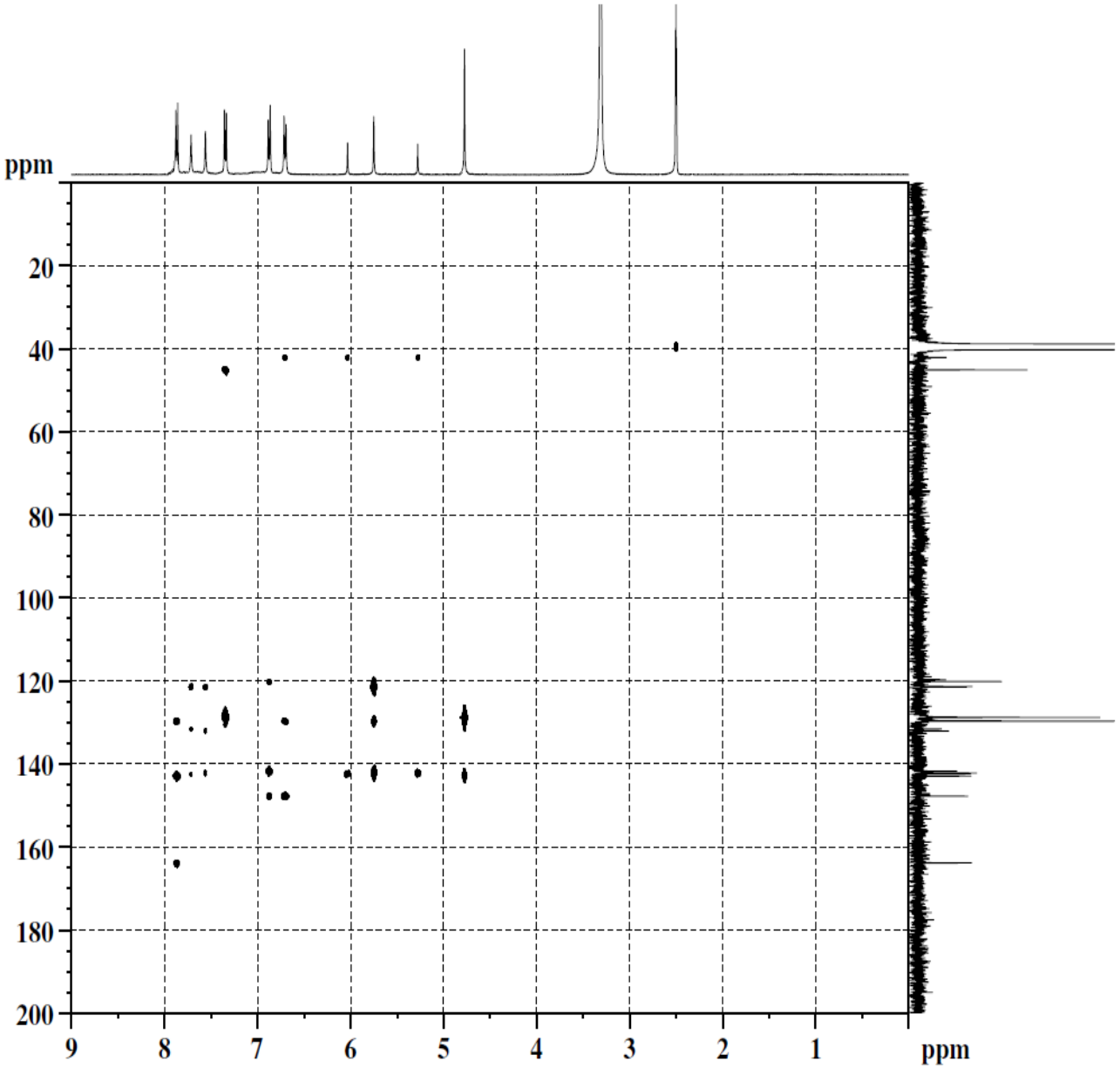


Figure S29 HMBC (^{13}C) NMR spectrum of calix[4]resorcinol **4b** (*rctt*-isomer in *chair* conformation) in DMSO-d_6 at 303 K.

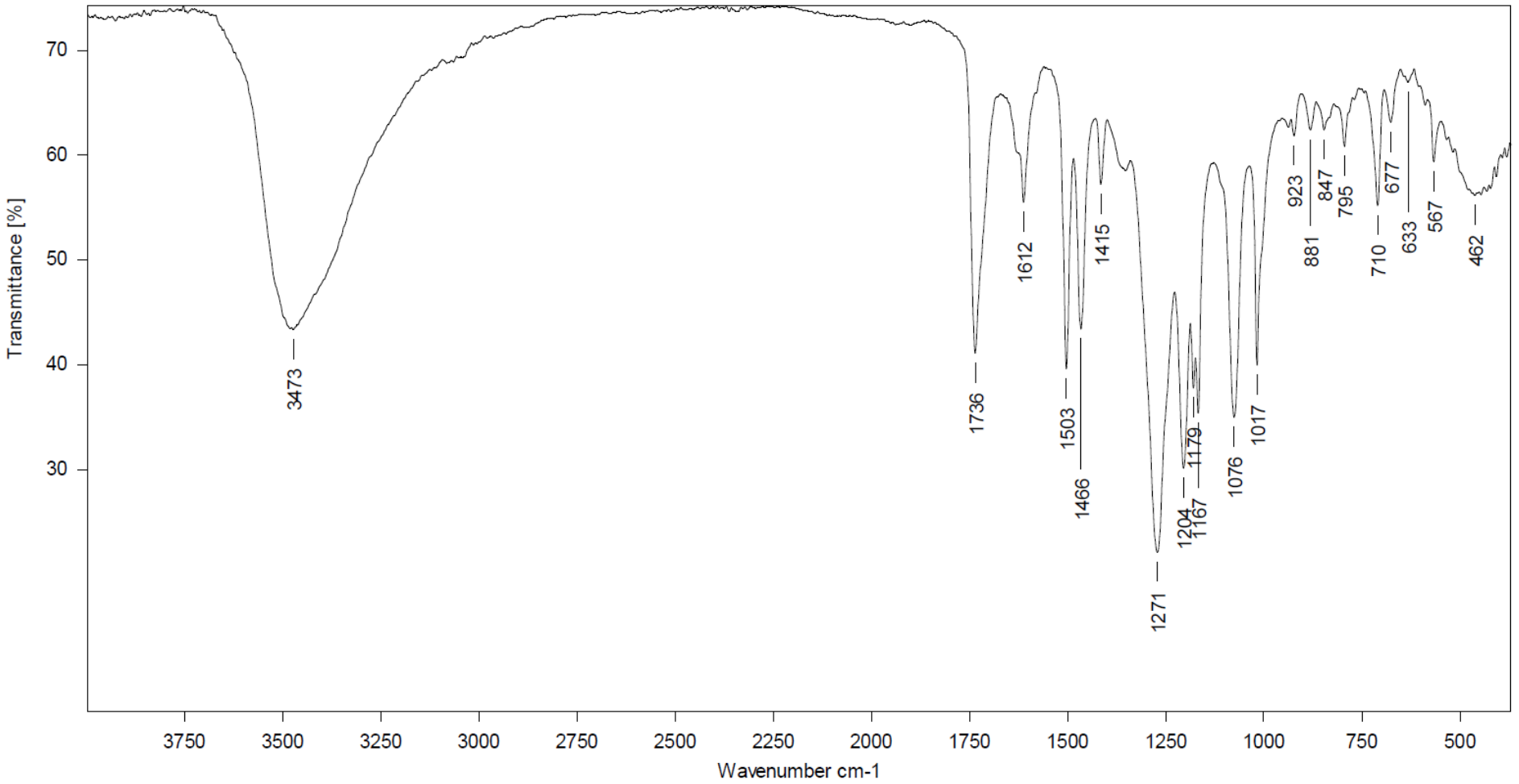


Figure S30 IR spectrum of calix[4]resorcinol **4b**.

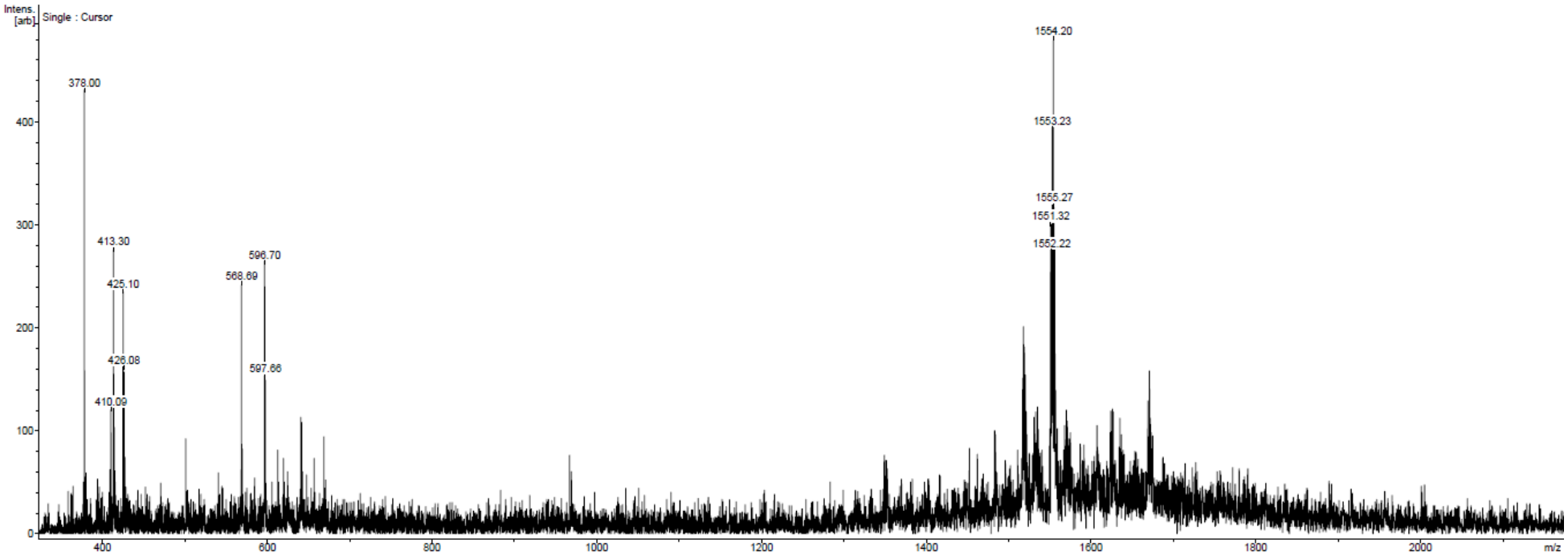


Figure S31 MALDI-MS spectrum of calix[4]resorcinol **4b**.