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Photophysical properties of new anthracene-ended calix[4]resorcinols

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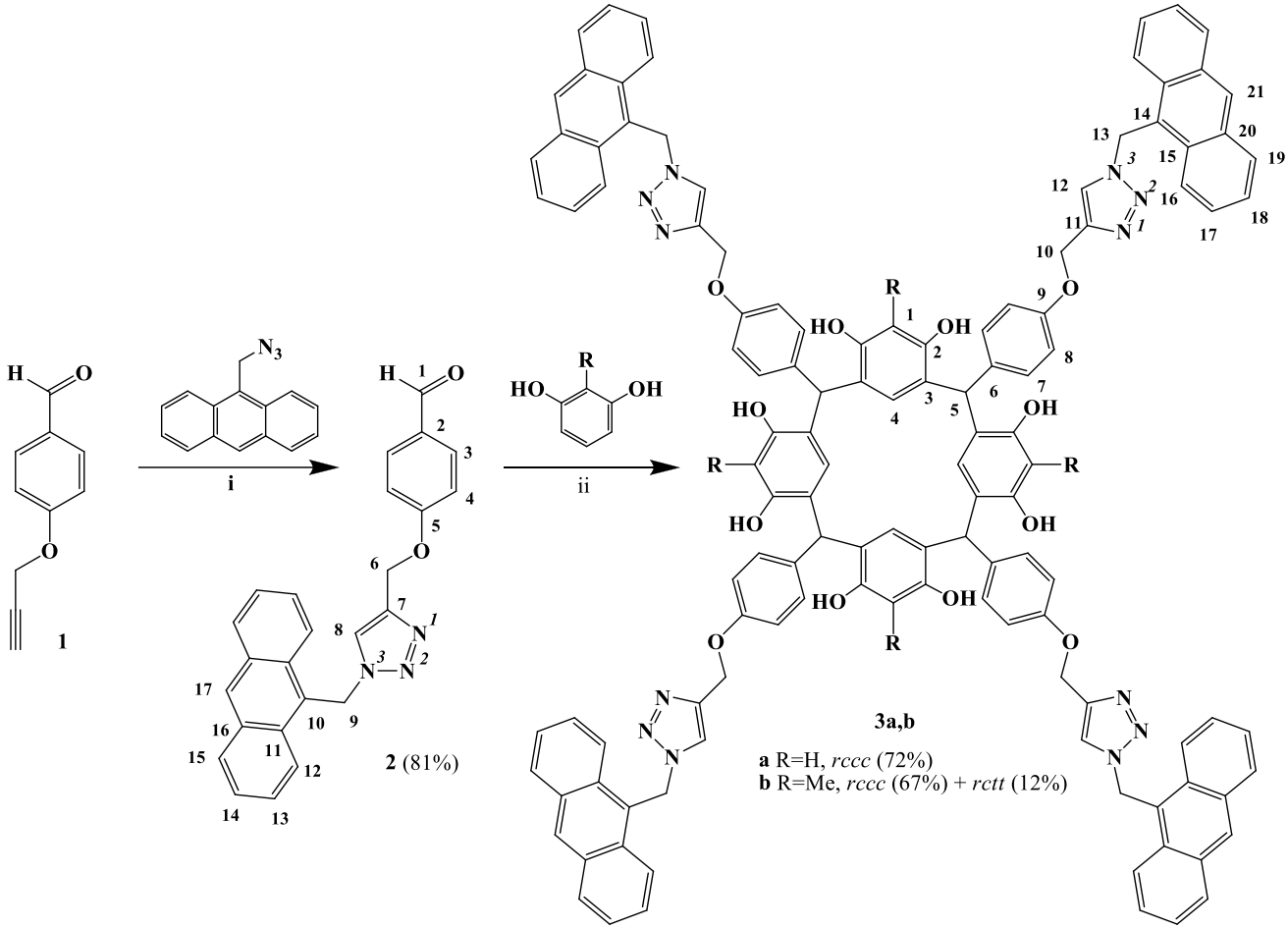
General

NMR experiments were performed on a Bruker AVANCE-600 spectrometer at 303K equipped with 5 mm broadband probehead working at 600.1 MHz in ^{1}H and 150.9 MHz in ^{13}C 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 (λ = 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. 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 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. Electronic absorption (UV-Vis) and steady state fluorescence spectra were recorded at room temperature on a Perkin-Elmer Lambda 35 spectrometer and a Cary Eclipse Fluorescence Spectrophotometer (Varian), respectively, using 10 mm quartz cells. Absorption spectra were registered with a scan speed of 480 nm min^{-1}, using a spectral width of 1 nm. All samples were prepared as solutions in THF with the concentrations ~10^{-5} mol dm^{-3}. The absorbance at

excitation wavelength was less than 0.1 to avoid the "inner filter effect". Fluorescence quantum yields for anthracene bands, excited at 366 nm, were measured using ethanol solution of anthracene as the standard (λ_{exc} = 366 nm, φ = 0.27 [S1,S2]), for bands near 550 nm ethanol solution of fluorescein as the standard (λ_{exc} = 488 nm, φ = 0.92 [S3]) has been used. Appropriate corrections were made for the optical density of the solutions and the refractive index of the medium [S4].



Scheme S1 *Reagents and conditions:* i, $CuSO_4 \cdot 5H_2O$, Na-ascorbate, THF, H_2O, 60-65 °C, 24 h; ii, CF_3CO_2H, $CHCl_3$.

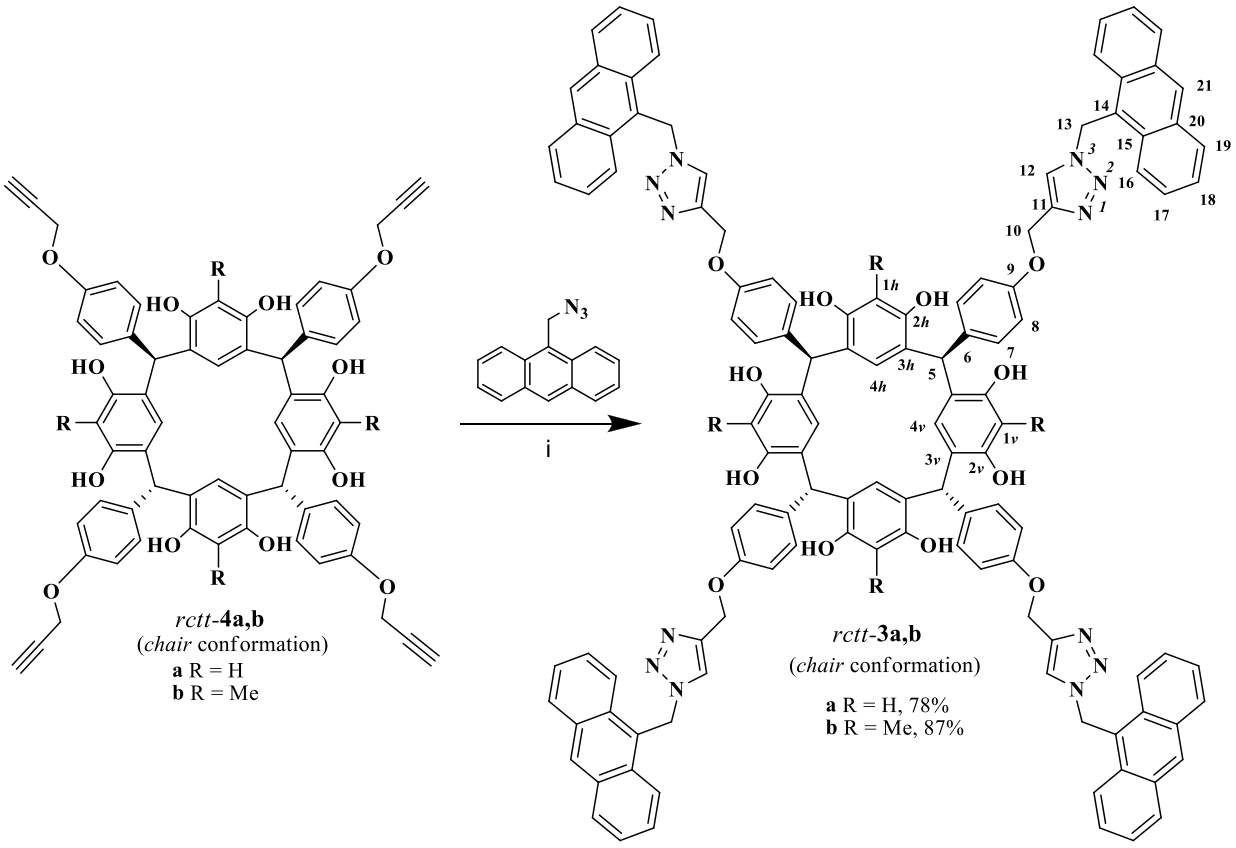
4-{[1-(Anthracen-9-ylmethyl)-1*H*-1,2,3-triazol-4-yl]methoxy}benzaldehyde 2. To a suspension of 4-propargyloxybenzaldehyde **1** (0.50 g, 3.13 mmol), sodium ascorbate (0.12 g, 0.63 mmol) and $CuSO_4 \cdot 5H_2O$ (0.16 g, 0.63 mmol) in the mixture of THF/H_2O (70:30 ml) the 9-(azidomethyl)anthracene (1.46 g, 6.25 mmol) was added. The reaction mixture was stirred at reflux for 24 h under an inert atmosphere (TLC control for conversion of **1**). The yellow precipitate was filtered, washed sequentially with water and diethyl ether. The crude product was purified by column chromatography using the mixture dichloromethane/methanol (10:1) as eluent. Pure compound **2** was obtained as yellow solid (1.0 g, 81 % yield, R_f = 0.7), m. p. 168–169 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$): δ 5.11 (s, 2H, H6), 6.57 (s, 2H, H9), 6.98 (d, $^3J_{HH}$ 8.8 Hz, 2H, H4), 7.23 (s, 1H, H8), 7.56 (t, $^3J_{HH}$ 8.8 Hz, 2H, H14), 7.62 (t, $^3J_{HH}$ 8.8 Hz, 2H, H13), 7.76 (d, $^3J_{HH}$ 8.8 Hz, 2H, H3), 8.10 (d, $^3J_{HH}$ 8.8 Hz, 2H, H15), 8.30 (d, $^3J_{HH}$ 8.8 Hz, 2H,

H12), 8.61 (s, 1H, H17), 9.85 (s, 1H, H1) ppm. ^{13}C (150.9 MHz, $CDCl_3$): δ 46.8 (s, C9), 62.2 (s, C6), 115.3 (s, C4), 122.8 (s, C8), 123.0 (s, C12), 123.6 (s, C16), 125.7 (s, C14), 128.0 (s, C13), 129,8 (s, C15), 130.3 (s, C17), 130.5 (s, C2), 131.0 (s, C11), 131.7 (s, C10), 132.1 (s, C3), 143.3 (s, C7), 163.2 (s, C5), 190.9 (s, C1) ppm. ^{15}N MR (61 MHz, DMSO-d_6): δ 250.5 (N3), 347.3 (N1), 362.9 (N2) ppm. IR ν_{max} (KBr): 1693 cm^{-1} (C=O) cm^{-1}. Anal. Calcd. for $C_{25}H_{19}N_3O_2$ (%): C, 76.32; H, 4.87; N, 10.68. Found: C, 75.93; H, 4.98; N, 10.89. MALDI-MS: *m/z* = 394 $[M+H]^+$, 416 $[M+Na]^+$ (calcd. M = 393).

2,8,14,20-Tetrakis(4-{[1-(anthracen-9-ylmethyl)-1*H*-1,2,3-triazol-4-yl]methoxy}phenyl)-4,6,10,12,16,18,22,24-octahydroxycalix[4]arene *rccc*-**3a** *(method A):* A mixture of resorcinol (0.10 g, 0.89 mmol) and aldehyde **2** (0.35 g, 0.89 mmol) in $CHCl_3$ (30 mL) and trifluoroacetic acid (2 mL) was stirred at 45–50 ºC for 24 h under an inert 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. Sequential recrystallization from acetone and drying in vacuo (40 ºC, 0.06 Torr) gave the calix[4]resorcinol **3a** as its *rccc*-isomer in *cone* conformation was obtained (0.31 g, 72%) as a beige powder, mp>140 ºC (dec). ^{1}H NMR (600.1 MHz, DMSO-d_6): δ 4.82 (s, 8H, H10), 5.56 (s, 4H, H5), 6.11 (s, 4H, H1), 6.21 (s, 4H, H4), 6.43 (s, 8H, H13), 6.54 (m, 8H, H7), 6.55 (m, 8H, H8), 7.40 (m, 8H, H18), 7.47 (m, 8H, H17), 7.95 (s, 4H, H12), 8.03 (m, 8H, H19), 8.50 (m, 8H, H16), 8.55 (s, 4H, H21) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 40.5 (s, C5), 45.3 (s, C13), 60.8 (s, C10), 102.1 (s, C1), 113.3 (s, C8), 120.6 (s, C20), 123.8 (s, C12), 123.9 (s, C16), 125.2 (s, C18), 125.5 (s, C6), 127.0 (s, C17), 128.9 (s, C19), 129.1 (s, C4), 129.2 (s, C7), 129.3 (s, C21), 130.2 (s, C15), 130.9 (s, C14), 138.0 (s, C3), 143.0 (s, C11), 152.4 (s, C2), 155.1 (s, C9) ppm. IR ν_{max} (KBr): 3100–3600 (OH) cm^{-1}. Anal. Calcd for $C_{124}H_{92}N_{12}O_{12}$ (%): C, 76.69; H, 4.77; N, 8.65. Found: 76.72; H, 4.83; N, 8.81. MALDI-MS: *m/z* = 1943.0 $[M+H]^+$, 1965.0 $[M+Na]^+$ (calcd M = 1942.0).

2,8,14,20-Tetrakis(4-{[1-(anthracen-9-ylmethyl)-1*H*-1,2,3-triazol-4-yl]methoxy}phenyl)-4,6,10,12,16,18,22,24-octahydroxy-5,11,17,23-tetramethylcalix[4]arenes *rccc*-**3b** and *rctt*-**3b** *(method A):* The mixture of **4a,b** with overall yield 0.26 g (79%) was obtained according to analogous to that used to prepare **3a** by treatment of 2-methylresorcinol (0.08 g, 0.66 mmol) with aldehyde **2** (0.26 g, 0.66 mmol). Sequential recrystallization from acetone and ethanol gave pure *rctt*- and *rccc*-isomers. ***rccc*-Isomer 3b in *cone* conformation**: beige powder , yield 0.22 g (67%), mp>175ºC (dec). ^{1}H NMR (600.1 MHz, DMSO-d_6): δ 1.87 (s, 6H, CH_3), 4.82 (s, 8H, H10), 5.66 (s, 4H, H5), 5.98 (s, 4H, H4), 6.44 (s, 8H, H13), 6.46 (d, $^3J_{HH}$ 8.9 Гц, 8H, H8), 6.57 (d, $^3J_{HH}$ 8.9 Гц, 8H, H7), 7.32 (s, 8H, OH), 7.41 (t, $^3J_{HH}$ 8.8 Гц, 8H, H18), 7.45 (t, $^3J_{HH}$ 8.8 Гц, 8H, H17), 7.94 (s, 4H, H12), 7.98 (d, $^3J_{HH}$ 8.8 Гц, 8H, H19), 8.46 (d, $^3J_{HH}$ 8.8 Гц, 8H, H16), 8.55 (s, 4H, H21) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 9.9 (s, $\underline{C}H_3$), 42.2 (s, C5), 45.3 (s, C13), 61.1 (s, C10), 111.2 (s, C1), 113.5 (s, C8), 122.4 (s, C12), 122.5 (s, C3), 123.8 (s, C16), 125.2 (s, C18), 125.5 (s, C17), 126.9 (s, C4), 128.9 (s, C19), 129.0 (s, C21), 129.5 (s, C14), 130.1 (s, C15), 130.2 (s, C7), 130.9 (s, C20), 136.3 (s, C6), 143.0 (s, C11), 150.4 (s, C2), 155. (s, C9) ppm. IR ν_{max}

(KBr): 3100–3600 (OH) cm^{-1}. Anal. Calcd for $C_{128}H_{100}N_{12}O_{12}$ (%): C, 76.94; H, 5.04; N, 8.41. Found: 76.90; H, 5.11; N, 8.36. MALDI-MS: *m/z* = 1999.0 $[M+H]^+$, 2021.0 $[M+Na]^+$ (calcd M = 1998.0). ***rctt*-Isomer 3b in *chair* conformation**: light yellow powder, yield 0.04 g (12%), mp > 200 ºC (dec.). ^{1}H NMR (600.1 MHz, DMSO-d_6): δ 1.89 (s, 6H, CH_3^v), 2.04 (s, 6H, CH_3^h), 4.75 (s, 8H, H10), 5.41 (s, 2H, $H4^h$), 5.51 (s, 4H, H5), 6.09 (s, 2H, $H4^v$), 6.44 (d, $^3J_{HH}$ 8.9 Гц, 8H, H8), 6.48 (d, $^3J_{HH}$ 8.9 Гц, 8H, H7), 6.50 (s, 8H, H13), 7.12 (s, 4H, OH^h), 7.49 (t, $^3J_{HH}$ 8.8 Гц, 8H, H18), 7.50 (s, 4H, OH^v), 7.52 (t, $^3J_{HH}$ 8.8 Гц, 8H, H17), 7.92 (s, 4H, H12), 8.03 (d, $^3J_{HH}$ 8.8 Гц, 8H, H19), 8.51 (d, $^3J_{HH}$ 8.8 Гц, 8H, H16), 8.60 (s, 4H, H21) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 9.9 (s, $\underline{C}H_3^h$), 10.2 (s, $\underline{C}H_3^v$), 43.2 (s, C5), 45.9 (s, C13), 61.4 (s, C10), 111.0 (s, $C1^h$), 111.4 (s, $C1^v$), 113.6 (s, C8), 122.6 (s, $C3^h$), 123.1 (s, $C4^h$), 123.3 (s, $C3^v$), 123.6 (s, C12), 124.3 (s, C16), 125.7 (s, C18), 125.8 (s, $C4^v$), 126.0 (s, C20), 127.3 (s, C17), 129.4 (s, C19), 129.5 (s, C21), 130.3 (s, C7), 130.6 (s, C15), 131.5 (s, C14), 136.3 (s, C6), 143.5 (s, C11), 150.6 (s, $C2^h$), 151.0 (s, $C2^v$), 156.0 (s, C9) ppm. IR ν_{max} (KBr): 3100–3600 (OH) cm^{-1}. Anal. Calcd for $C_{128}H_{100}N_{12}O_{12}$ (%): C, 76.94; H, 5.04; N, 8.41. Found: 76.85; H, 4.96; N, 8.46. MALDI-MS: m/z = 1999 $[M+H]^+$, 2021 $[M+Na]^+$ (calcd. M = 1998).



Scheme S2 *Reagents and conditions:* i, $CuSO_4 \cdot 5H_2O$, Na-ascorbate, THF, H_2O, rt, 60–65 ºC, 18 h.

Calixarene *rctt*-**3a** *(method B):* To a suspension of calix[4]resorcinol **4a** (0.15 g, 0.15 mmol), sodium ascorbate (0.02 g, 0.12 mmol) and $CuSO_4 \cdot 5H_2O$ (0.03 g, 0.12 mmol) in THF (45 mL) and H_2O (10 mL), 9-(azidomethyl)anthracene (0.16 g, 1.2 mmol) was added. The mixture was stirred at 60–65 ºC for 18 h under an inert atmosphere. The precipitate was filtered, washed sequentially with H_2O and Et_2O. After

drying in vacuo (40 ºC, 0.06 Torr) pure *rctt*-**3a** in the *chair* conformation was obtained (0.23 g, 79%) as beige powder. Mp > 210 ºC (dec.). ^{1}H NMR (600.1 MHz, DMSO-d_6): δ 4.73 (s, 8H, H10), 5.44 (s, 4H, H5), 5.60 (s, 2H, H4^{v}), 6.11 (s, 2H, H1^{v}), 6.25 (s, 2H, H4^{h}), 6.26 (s, 2H, H1^{h}), 6.41 (d, $^{3}J_{HH}$ 8.8 Гц, 8H, H7), 6.44 (d, $^{3}J_{HH}$ 8.8 Гц, 8H, H8), 6.46 (s, 8H, H13), 7.45 (t, $^{3}J_{HH}$ 8.2 Гц, 8H, H18), 7.51 (t, $^{3}J_{HH}$ 8.2 Гц, 8H, H17), 7.69 (s, 4H, H12), 7.86 (s, 4H, H12), 8.02 (d, $^{3}J_{HH}$ 8.2 Гц, 8H, H19), 8.46 (d, $^{3}J_{HH}$ 8.2 Гц, 8H, H16), 8.31 (s, 8H, OH), 8.58 (s, 4H, H21) ppm. ^{13}C NMR (150.9 MHz, DMSO-d_6): δ 41.2 (s, C5), 45.4 (s, C13), 61.0 (s, C10), 101.8 (s, C1), 113.3 (s, C8), 120.9 (s, C3^{h}), 121.3 (s, C3^{v}), 123.6 (s, C12), 123.7 (s, C16), 125.2 (s, C18), 125.4 (s, C14), 127.0 (s, C17), 129.0 (s, C19), 129.1 (s, C21), 129.2 (s, C4^{v}), 129.6 (s, C7), 130.2 (s, C15), 130.9 (s, C20), 131.7 (s, C4^{h}), 136.7 (s, C6), 143.1 (s, C11), 152.4 (s, C2^{v}), 152.5 (s, C2^{h}), 155.2 (s, C9) ppm. ^{15}NMR (61 MHz, DMSO-d_6): δ 250.0 (N3), 350.1 (N1), 362.1 (N2) ppm. IR ν_{max} (KBr): 3100–3600 (OH) cm^{-1}. Anal. Calcd for $C_{124}H_{92}N_{12}O_{12}$ (%): C, 76.69; H, 4.77; N, 8.65. Found: 76.70; H, 4.84; N, 8.76. MALDI-MS: *m/z* = 1943 $[M+H]^+$, 1965 $[M+Na]^+$ (calcd M = 1942).

Calixarene *rctt*-**3b** *(method B)*: Compound *rctt*-**3b** in *chair* conformation was obtained as a light yellow powder with an yield of 0.35 g (95%) according to a method analogous to that used to prepare *rctt*-**3a** by treatment of tetraalkyne **4b** (0.20 g, 0.19 mmol) with sodium ascorbate (0.03 g, 0.15 mmol), $CuSO_4 \cdot 5H_2O$ (0.4 g, 0.15 mmol) and 9-(azidomethyl)anthracene (0.35 g, 1.5 mmol). Mp > 200 ºC (dec.). NMR (^{1}H, ^{13}C) data of compound *rctt*-**3b** synthesized by methods *A* and *B* are identical. IR ν_{max} (KBr): 3100–3600 (OH) cm^{-1}. Anal. Calcd for $C_{128}H_{100}N_{12}O_{12}$ (%): C, 76.94; H, 5.04; N, 8.41. Found: 76.85; H, 4.96; N, 8.46. MALDI-MS: m/z = 1999 $[M+H]^+$, 2021 $[M+Na]^+$ (calcd. M = 1998).

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S3. D. Magde, R. Wong, P.G. Seybold, *Photochem. Photobiol*., 2002, **75**, 327.
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Table S1 The integral quantum yield of emission φ for compounds **2**–**4**.

compound	λ_{exc}/nm	Standard/solvent	Φ_f	λ_{exc}/nm	Standard/solvent	Φ_f
2	366	anthracene/ethanol	0.22			–
3a	366	anthracene/ethanol	0.02	488	fluorescein/ethanol	<0.01
3b	366	anthracene/ethanol	0.02			–
4a	366	anthracene/ethanol	0.04	488	fluorescein/ethanol	<0.01
4b	366	anthracene/ethanol	0.01			–

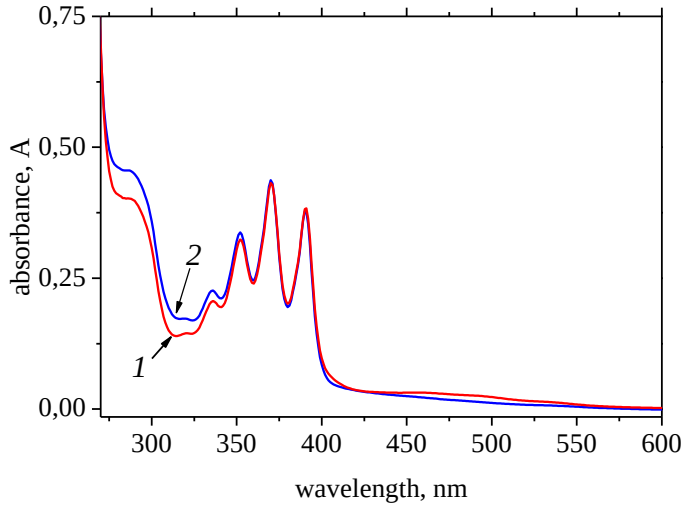

Figure S1 Absorption spectra of calix[4]resorcinols *rccc*-**3a** (*1*) and *rctt*-**3a** (*2*) in DMSO, c=10^{-5} mol/l.

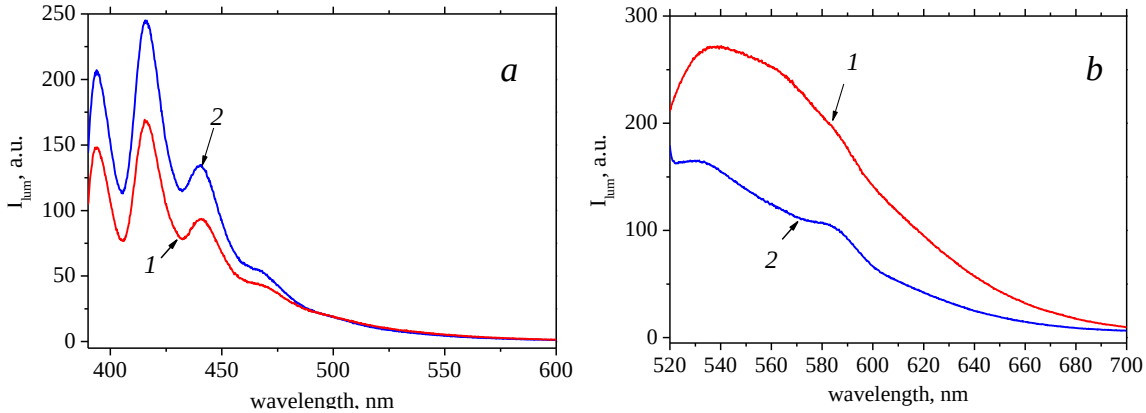

Figure S2 Emission spectra of *rccc*-**3a** (*1*) and *rctt*-**3a** (*2*) in THF solution (*C*=10^{-4} mol·l), excitation wavelengths: 380 nm (*a*) and 500 nm (*b*).

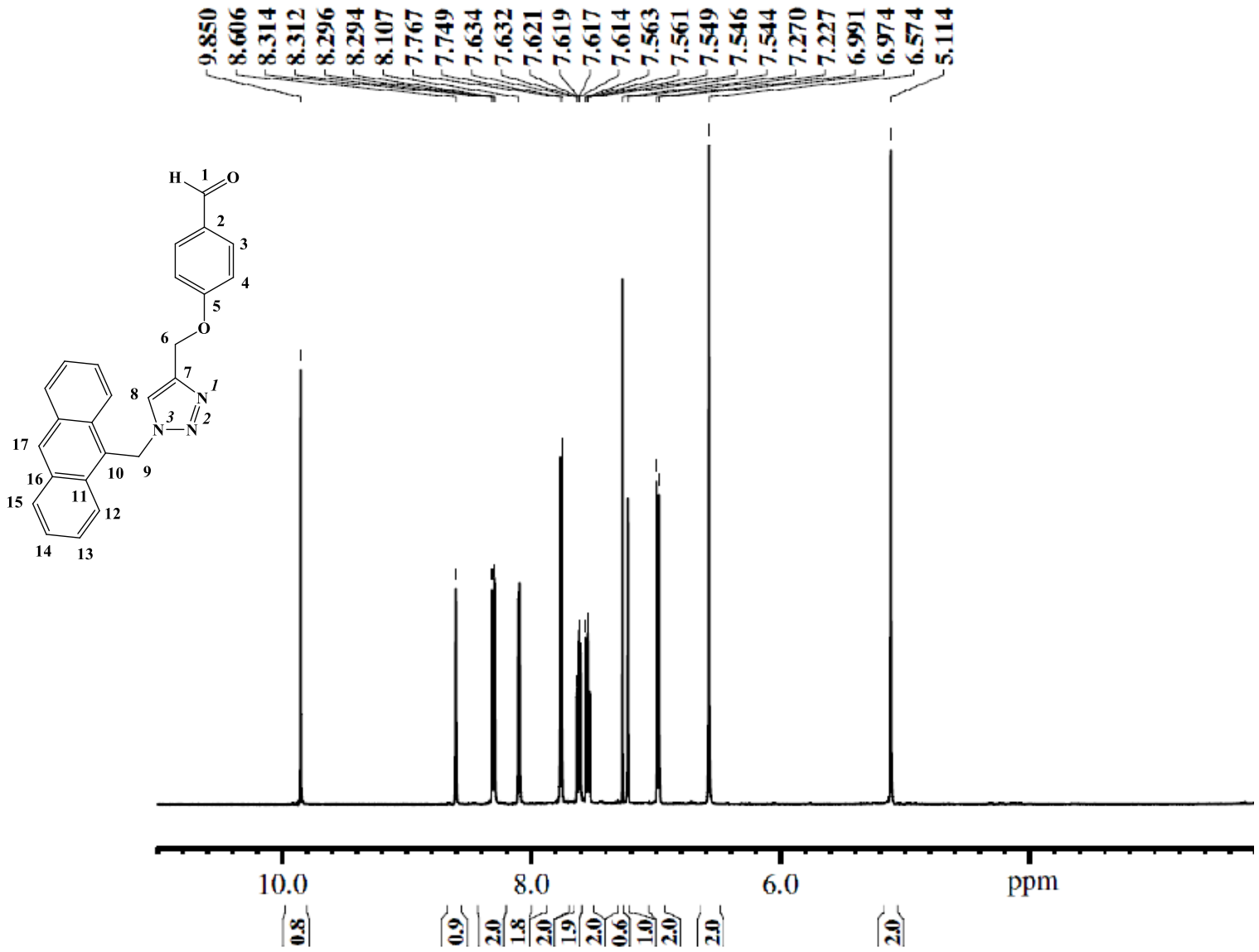

Figure S3 ^{1}H NMR spectrum of 4-((1-(anthracen-9-ylmethyl)-1H-[1,2,3]triazol-4-yl)methoxy)benzaldehyde (**2**) in $CDCl_3$ (T=303 K).

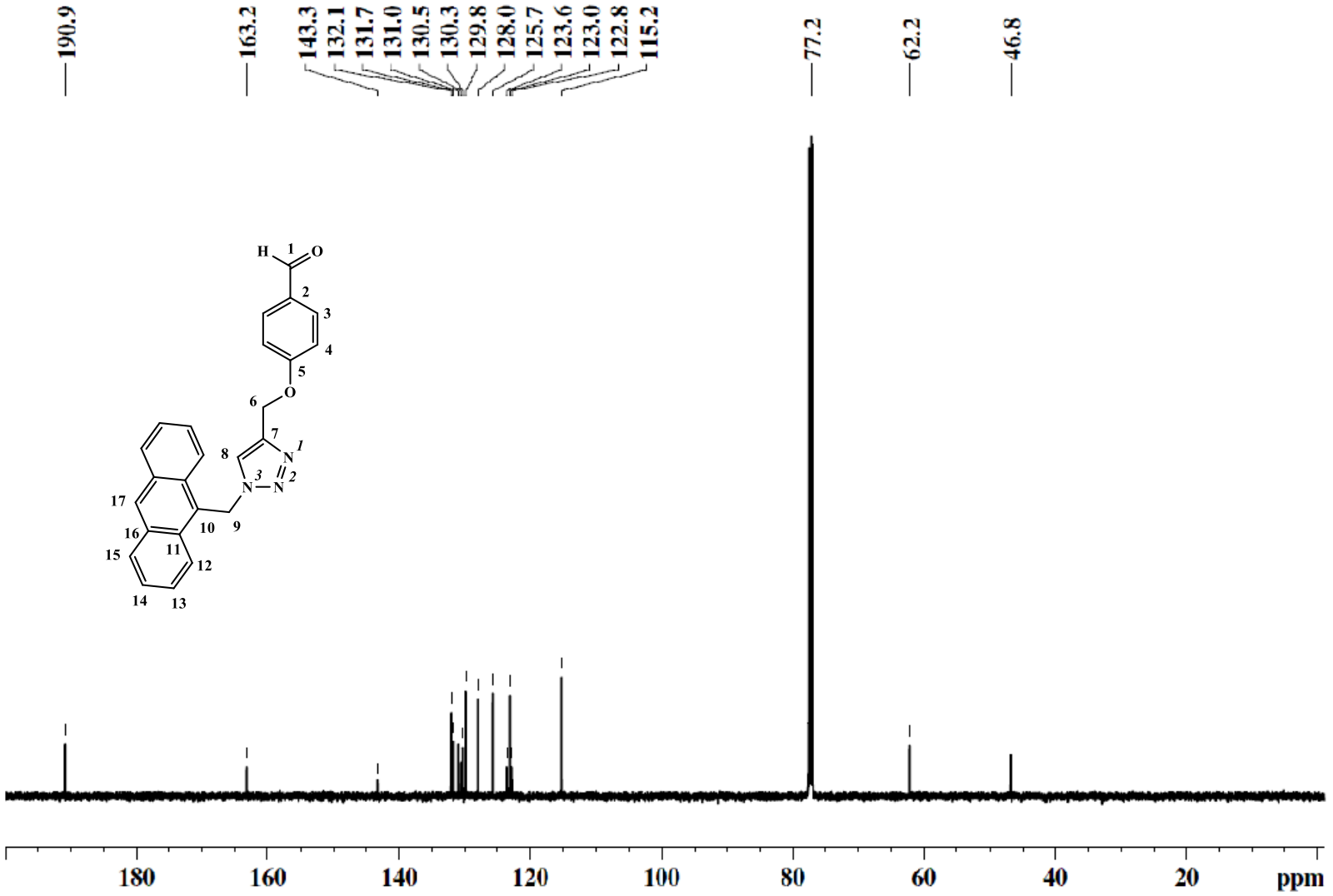

Figure S4 ^{13}C NMR spectrum of 4-((1-(anthracen-9-ylmethyl)-1H-[1,2,3]triazol-4-yl)methoxy)benzaldehyde (**2**) in $CDCl_3$ (T=303 K).

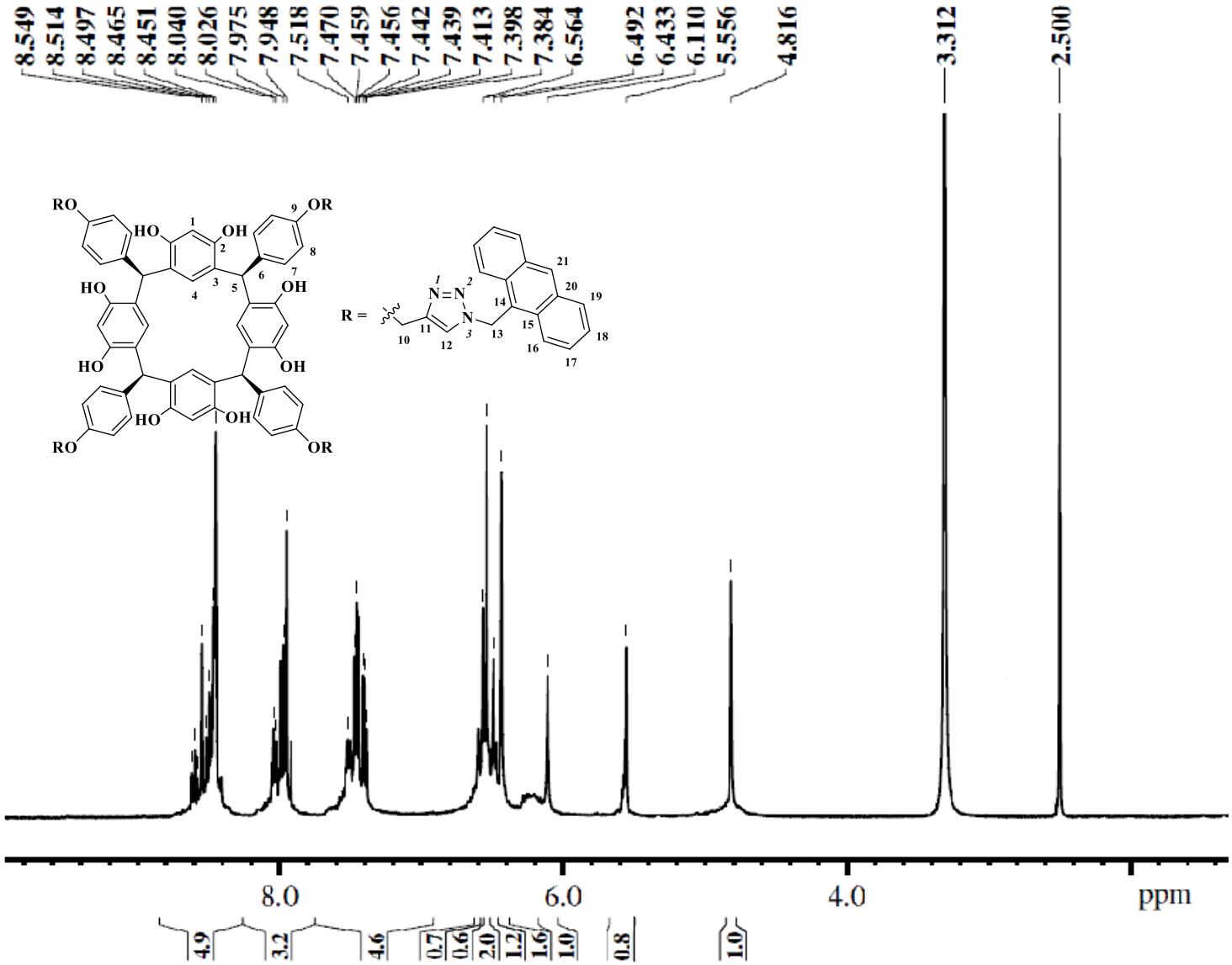

Figure S5 ^{1}H NMR spectrum of calix[4]resorcinol *rccc*-**3a** (*cone* conformation) in DMSO-d_6 (T=303 K).

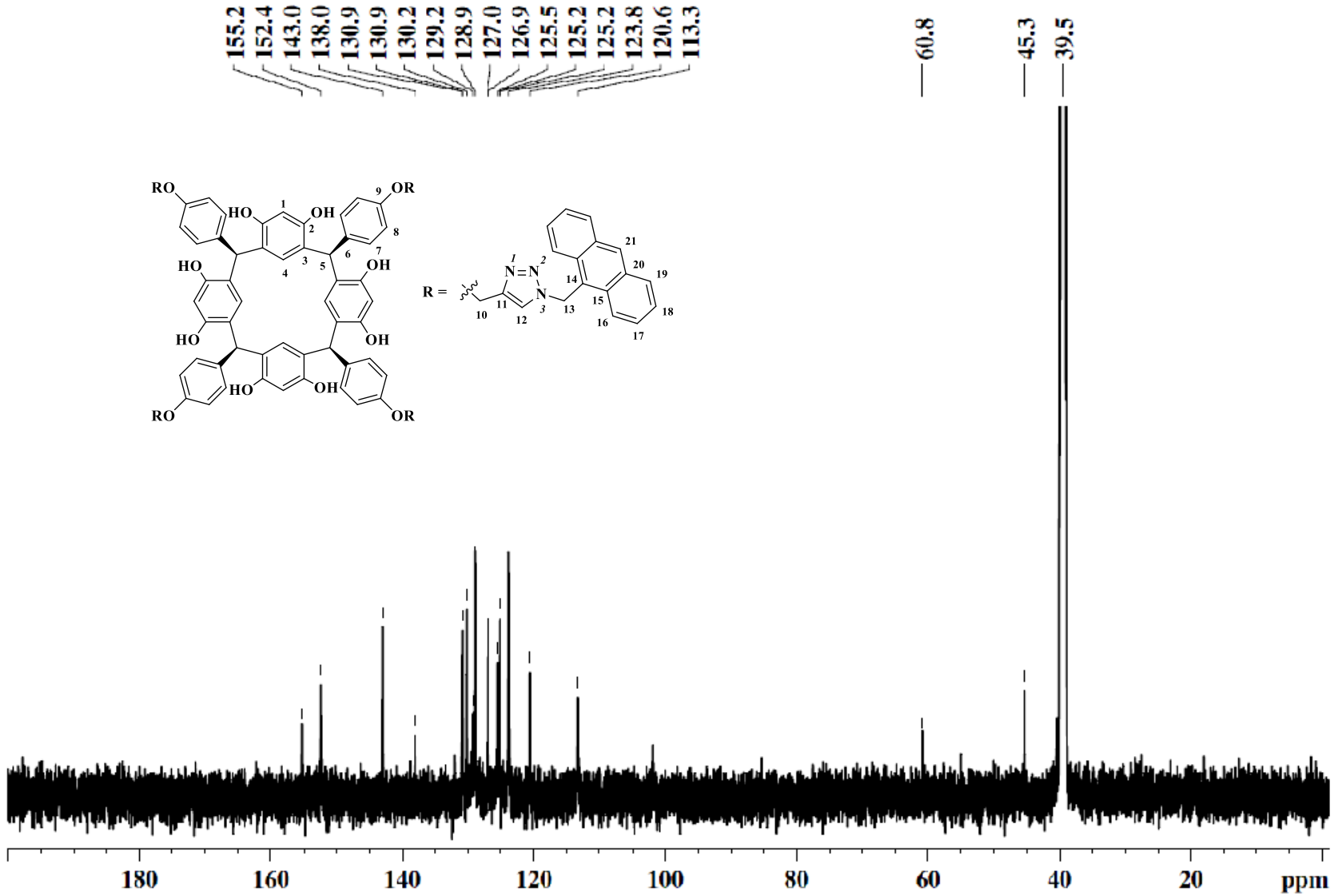

Figure S6 ^{13}C NMR spectrum of calix[4]resorcinol *rccc*-**3a** (*cone* conformation) in DMSO-d_6 (T=303 K).

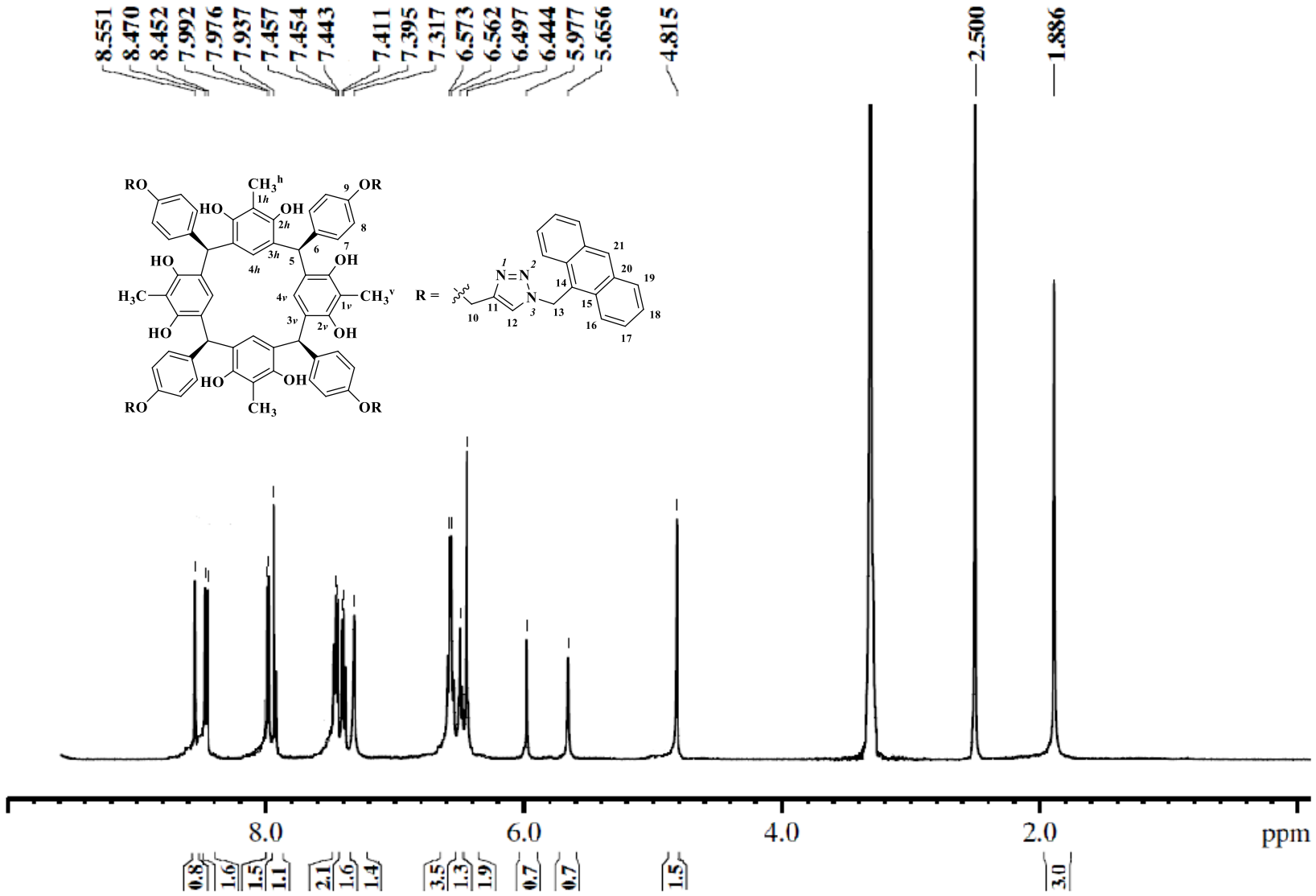

Figure S7 ^{1}H NMR spectrum of calix[4]resorcinol *rccc*-**3b** (*cone* conformation) in DMSO-d_6 (T=303 K).

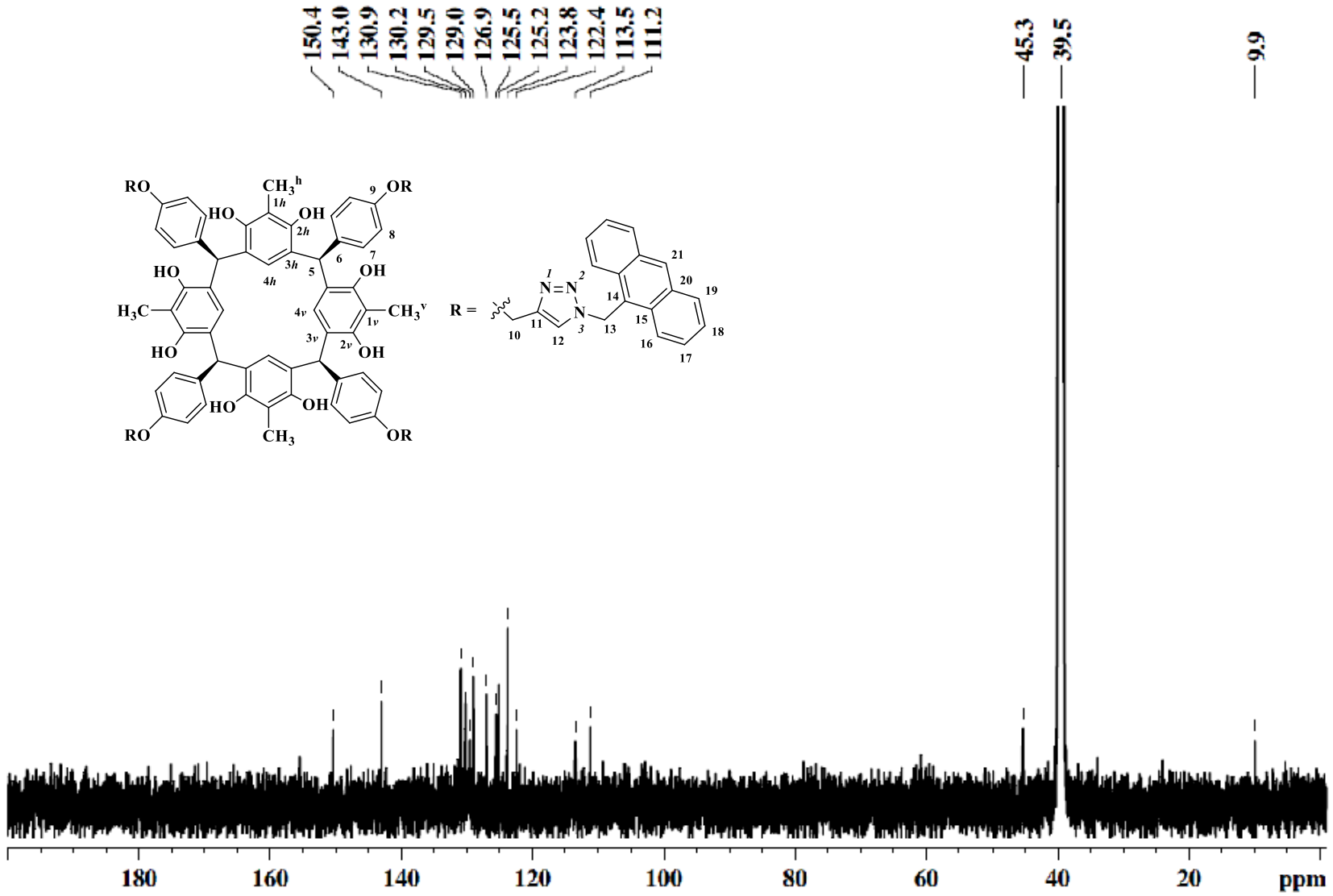

Figure S8 ^{13}C NMR spectrum of calix[4]resorcinol *rccc*-**3b** (*cone* conformation) in DMSO-d_6 (T=303 K).

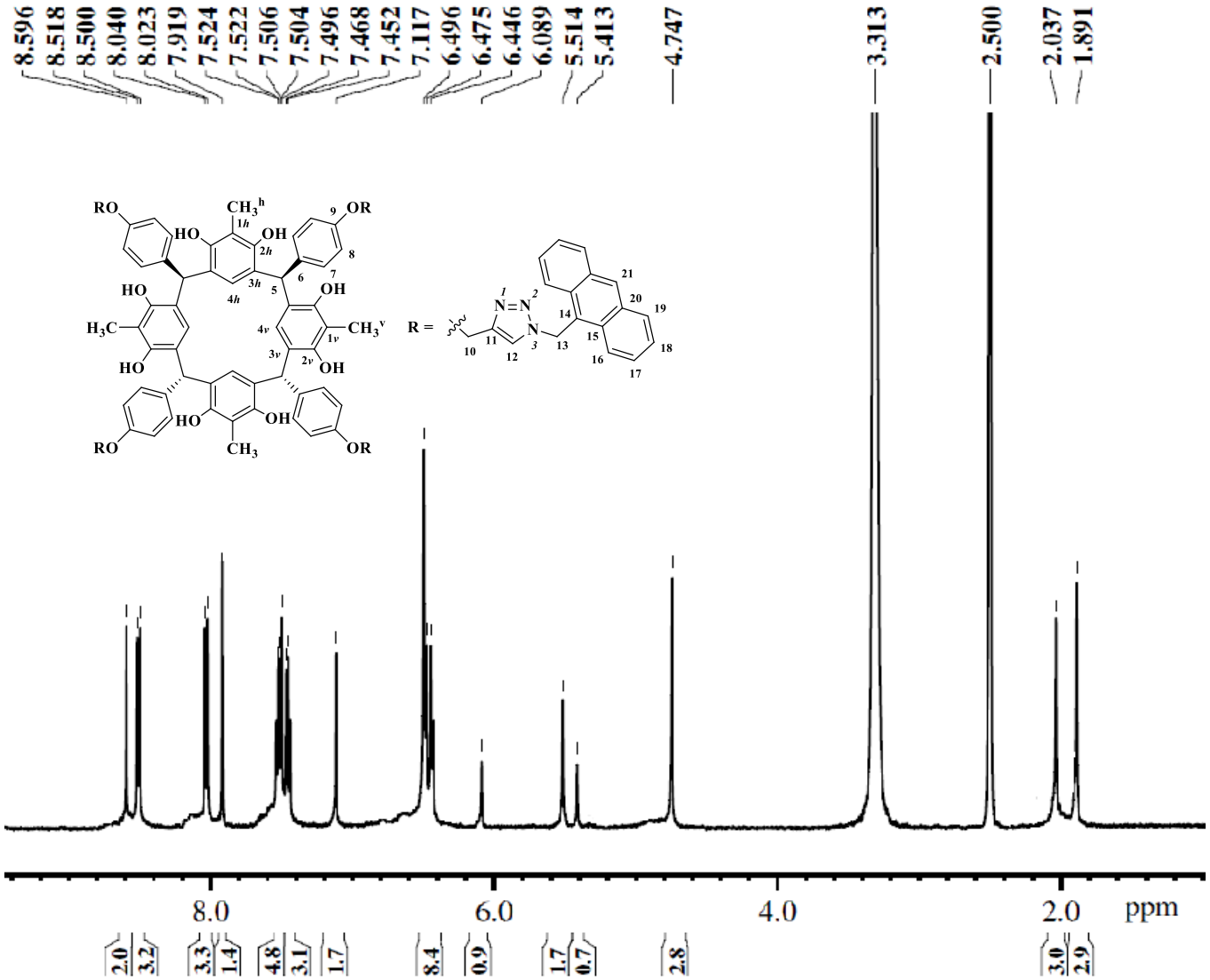

Figure S9 ^{1}H NMR spectrum of calix[4]resorcinol *rctt*-3**b** (*chair* conformation) in DMSO-d_6 (T=303 K).

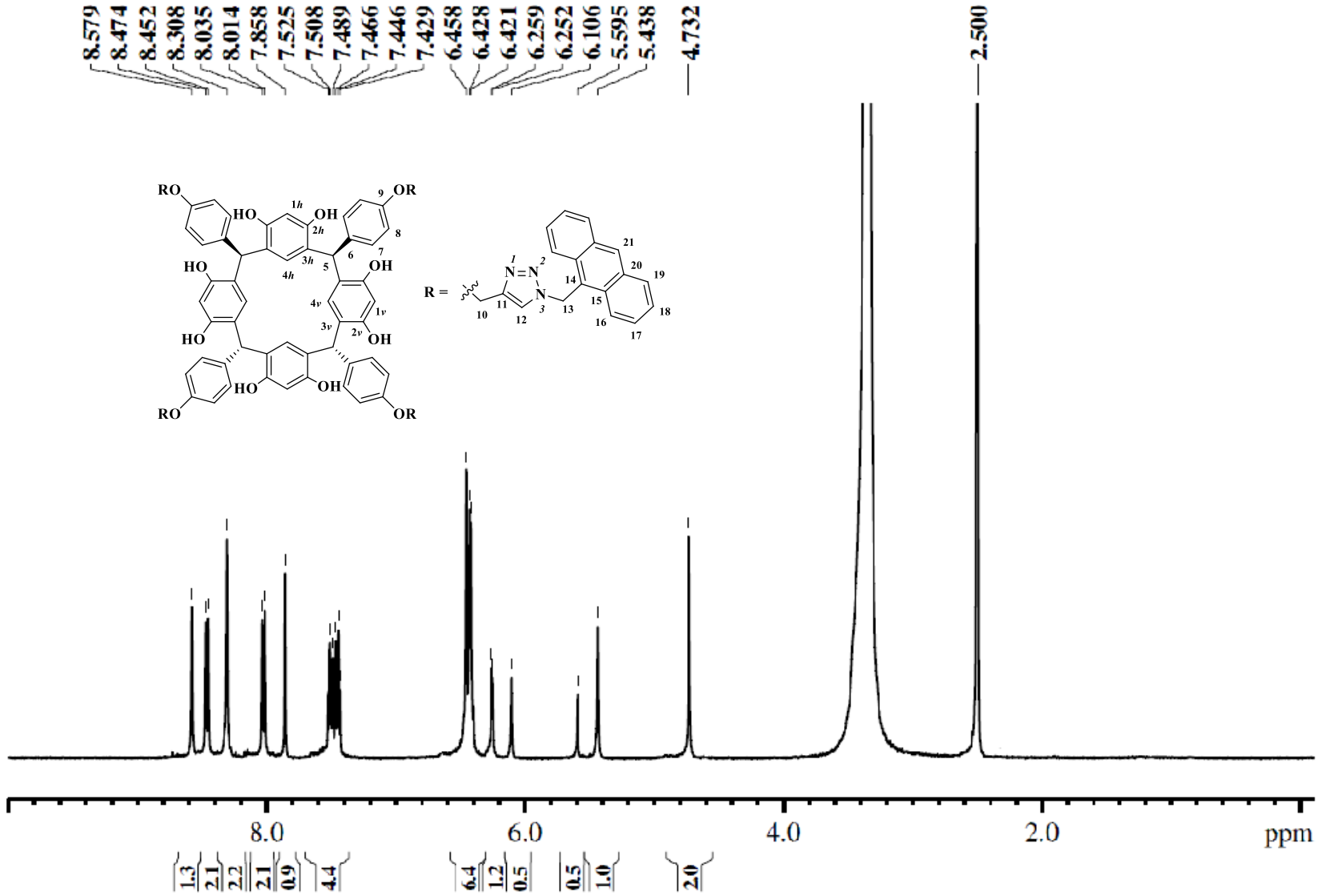

Figure S10 ^{1}H NMR spectrum of calix[4]resorcinol *rctt*-**3a** (*chair* conformation) in DMSO-d_6 (T=303 K).

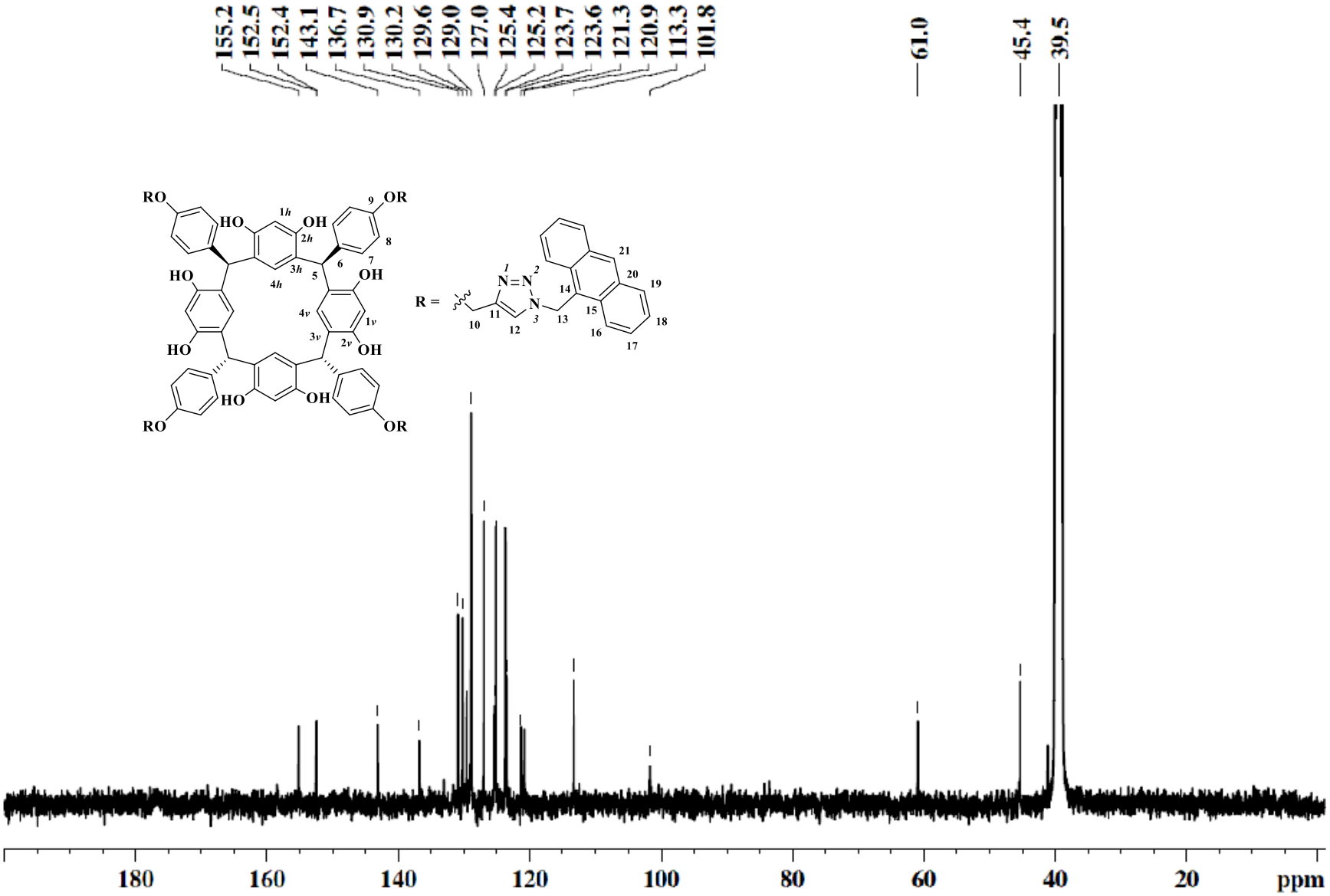

Figure S11 ^{13}C NMR spectrum of calix[4]resorcinol *rctt*-**3a** (*chair* conformation) in DMSO-d_6 (T=303 K).