Supplementary Information

Stereospecific synthesis of resorsin[4]arenes and pyrogallol [4]arene macrocycles in dynamic thin films

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1. General Experimental

All commercially obtained chemicals were used without any further purification unless otherwise stated. Resorcinol and pyrogallol were obtained from Sigma-Aldrich and Fluka, respectively. Acetaldehyde, butyryldehyde, heptaldehyde, benzaldehyde and vanillin were purchased from Sigma, Fluka, Fluka, Univar and Unilab respectively. Thin layer chromatography (TLC) was conducted with Silica gel 60 F_{254}. Visualization of products was effected by ultraviolet light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on Varian NMR spectrometer at 400 MHz and 100 MHz, respectively. Mass spectra were recorded with a Waters LCT Premier XE spectrometer, run in W-mode, using the ESI method, with MeCN:H_2O (9:1) as a matrix.

2. Synthesis

2.1 General route for the synthesis of calix[4]arens (4a-i) using VFD

To a solution of resorcinol (2.5 mmol) or pyrogallol (2.5 mmol) in ethanol (2.5 ml), the respective aldehyde (2.5 mmol) was added. Hydrochloric acid (0.125 mL, 10 M) was then added and the solution was stirred at ambient temperature for 5 mins and was passed through the VFD. The temperature, rotational speed, angle of inclination and flow rate of the VFD were fixed at respectively 80^0C, 7,000 rpm, 45° inclination angle and 1 mL/min. Only one feed jet was used for passing the solution into the glass tube. After one pass, water (50 mL) was added and the precipitate was collected by vacuum filtration. The product was further purified by recrystallisation from ethanol to give the calixarenes **4a-i** as light brown solids.

2.2 Synthesis of predominant C_{4v} isomer of 4h from the mixture of C_{4v} and C_{2h} isomers of 4h:

To a solution of the mixture of C_{4v} and C_{2h} isomers of **4h** (1 mmol) in ethanol (1 mL), hydrochloric acid (0.1 mL, 10 M) was added (for acetic acid 0.1 mL, 17 M and 4-toluenesulfonic acid 1 mmol). It was rotated under confined mode of the VFD at 7000 rpm, 60°C and 45° inclination angle for one hour. Completion of the reaction was confirmed by ^{1}H NMR (400 MHz) spectroscopy. The precipitate was collected by vacuum filtration and the product was further purified by recrystallisation from ethanol and obtained as a light brown solid, with mass return being obtained.

3. Characterization of calix[4]arenes (4a-i)

4a: 32%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[1]

4b: 43%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[2]

4c: 40%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[3]

4d: 42%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[4]

4e: 42%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[5]

4f: 75%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[6]

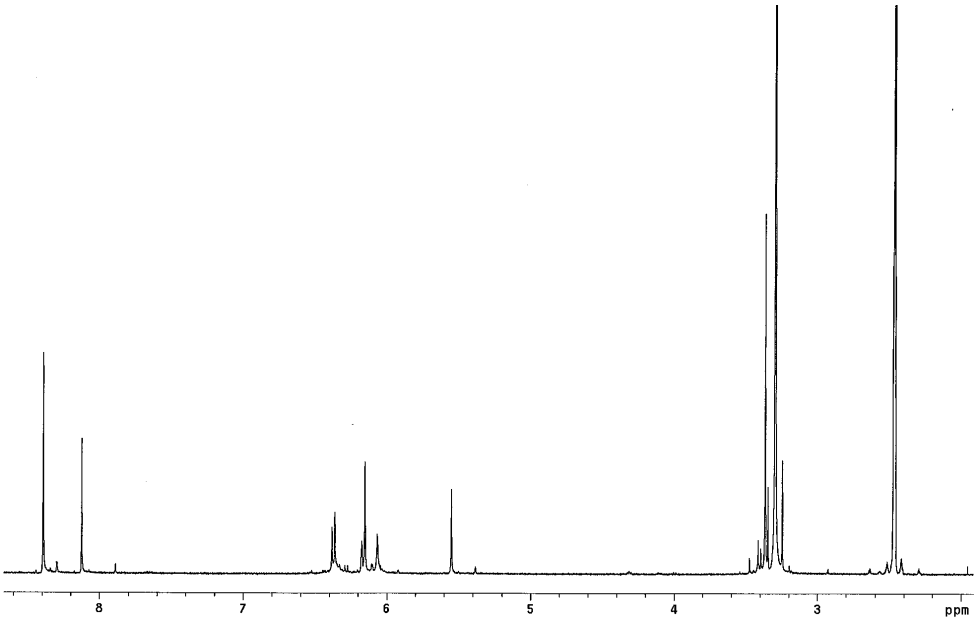
4g: 56%. ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[2]

4h (***C*** $_{2h}$): ^{13}C and ^{1}H NMR spectra of this compound were similar to that found in the literature.[7]

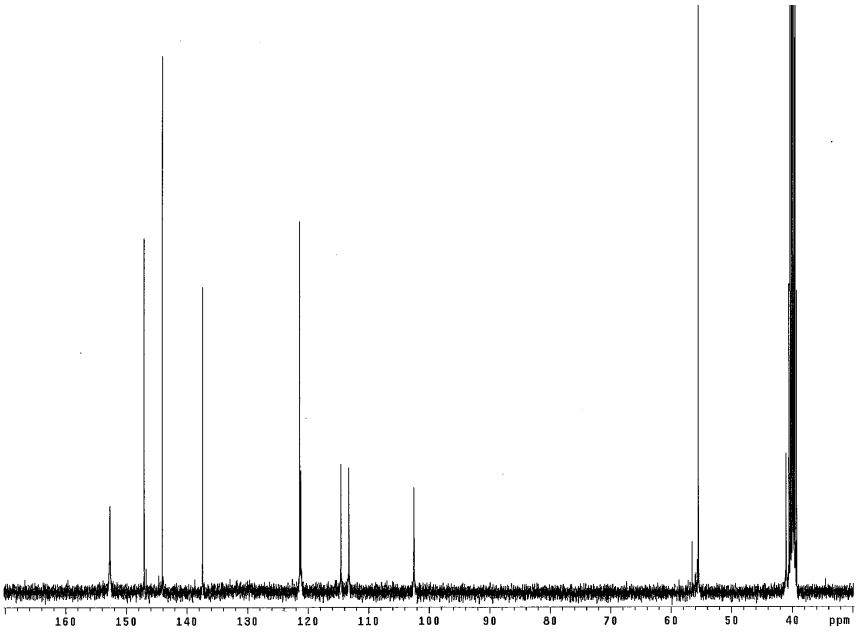
4h (***C*** $_{4v}$): 92%. δ_H (400 MHz, d_6-DMSO) 3.4 (s, 12H, $-OCH_3$), 5.59 (s, 4H, bridging –CH), 6.1-6.4 (m, 20H, ArH), 8.15 (s, 4H, -OH of pendant arms), 8.42 (s, 8H, -OH of the core). δ_C (100.5 MHz, d_6-DMSO) 152.8, 147.0, 144.0, 137.4, 121.4, 121.2, 114.6, 113.2, 102.5, 54.5. HR-MS *m*/*z* 977.3056 $(M+H)^+$ requires 977.3021.

4i (***C*** $_{2v}$): 84%. δ_H (400 MHz, d_6-DMSO) 3.42 (s, 12H, $-OCH_3$), 5.54 (s, 4H, bridging –CH), 5.57 (s, 2H, pyrogallol-H), 6.04 (s, 2H, pyrogallol-H), 6.07 (d, J=1.77 Hz, 2H, ArH), 6.09 (d, J=1.77 Hz, 2H, ArH), 6.15 (d, J=1.74 Hz, 4H, ArH), 6.29 (s, 2H, ArH), 6.32 (s, 2H, ArH), 7.25 (s, 4H, -OH of the pendant arms), 7.48 (s, 4H, -OH of the core), 7.66 (s, 2H, -OH of the core), 7.73 (s, 2H, -OH of the core), 7.95 (s, 4H, -OH of the core). δ_C (100.5 MHz, d_6-DMSO) 146.7, 143.9, 142.1, 141.6, 135.1, 132.3, 131.9, 123.0, 122.2, 121.9, 121.5, 119.3, 114.4, 113.6, 55.6. HR-MS *m*/*z* 1041.2844 $(M+H)^+$ requires 1041.2817.

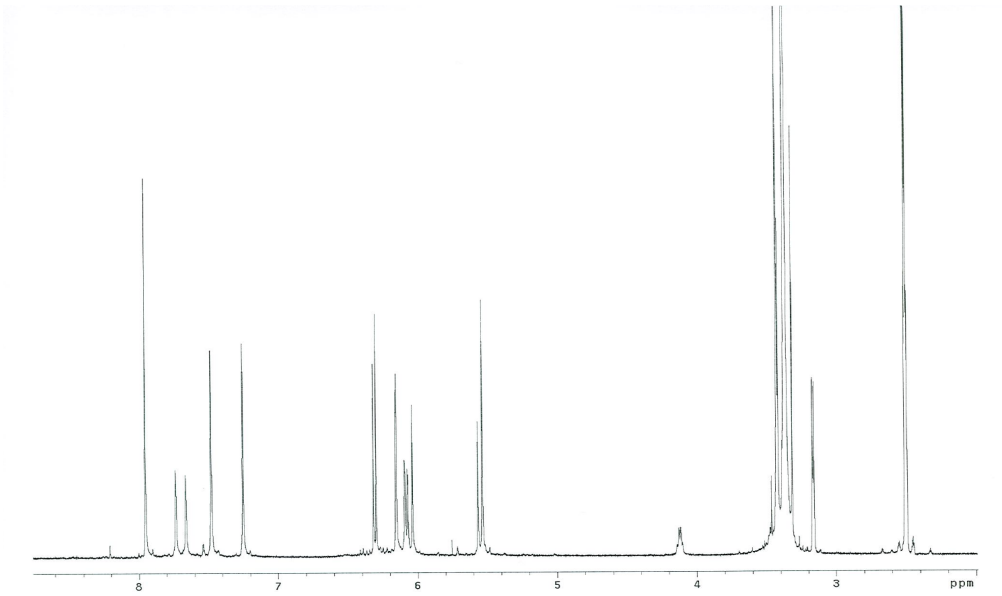
^{1}H NMR spectrum of **4h** ($\mathbf{C_{4v}}$)



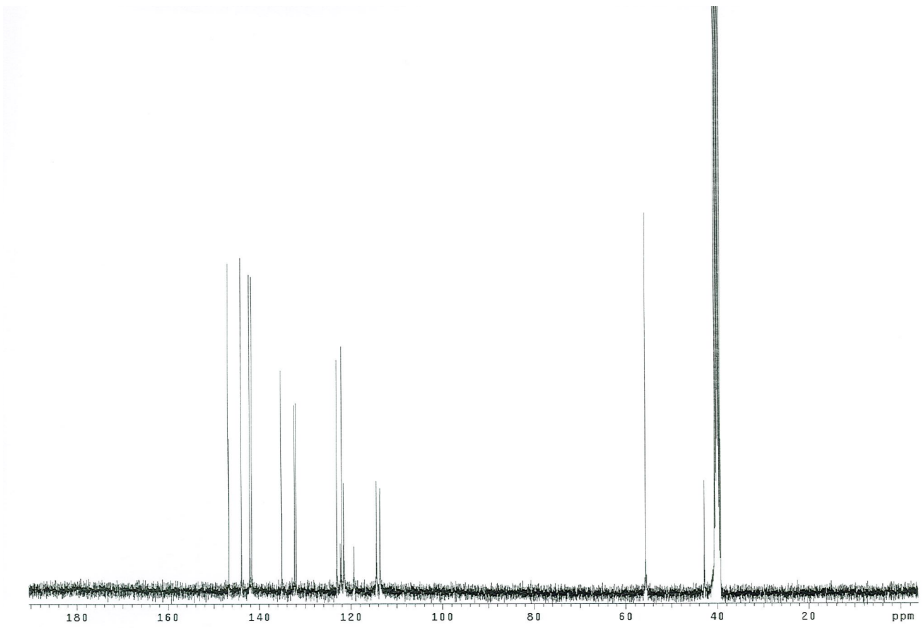
^{13}C NMR spectrum of **4h** ($\mathbf{C_{4v}}$)



^{1}H NMR spectrum of **4i** ($\mathbf{C_{2v}}$)



^{13}C NMR spectrum of **4i** ($\boldsymbol{C_{2v}}$)



4. References

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