

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Inherently chiral heterocyclic resorcinarenes using Diels-Alder reaction

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## 1. Experimental part

All NMR spectra were measured at 400 MHz, with a Bruker DRX 400 spectrometer. Mass spectra were recorded with SYNAPT (Waters) mass spectrometer with the electrospray (ESI) technique using HPLC/MS grade solvents. X-ray diffraction experiments for **4** were performed on a Super NOVA diffractometer. The crystal structures were solved with SHELXS and refined with SHELXL. The chromatographic separation of the benzopyrane derivative of resorcinarene **4** into enantiomers made using Thermo Fischer Scientific UltiMate 3000 chromatograph with the Nucleocel delta S column from Macherey&Nagel. Optical rotation spectra (ECD) of the obtained fractions were measured using a polarimeter Jasco P-2000. Melting points were recorded with a Boëtius melting point instrument and are uncorrected. Reactions were monitored by thin layer chromatography (TLC) on plastic sheets coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualized by UV radiation at a wavelength of 254 nm. Reagents and solvents were obtained from Sigma-Aldrich, Fluka and Merck and were used without purification.

**General procedure for synthesis of rac-4:**  $\alpha$ -Methylstyrene (5 ml) was added to the *N,N*-dimethylamino derivative of resorcinarene (**1a**, 0.2 g, 0.212 mmol) and the mixture was placed into an oil bath at a temperature of 140°C. The heating was continued for 7 hours, followed by cooling, and adding methanol (10 ml). The resulting mixture was placed in a refrigerator at about 6°C for 24 h. Then the obtained precipitate was filtered off and washed with methanol, dried and separated chromatographically using *n*-hexane:ethyl acetate as eluent. Crystallization from ethyl acetate yielded fine crystals of the resorcinarene derivative **4**.

Rac-**4**: White solid. mp >300 °C (EtOAc): <sup>1</sup>H NMR (CDCl<sub>3</sub>/400 MHz):  $\delta_{\text{H}}$  1.02 (24H, d, J = 6.7 Hz, CH<sub>3</sub>), 1.48–1.52 (4H, m, CH), 1.65 (s, 12H, CH<sub>3</sub>), 1.67–1.68 (4H, m, CH<sub>2</sub>), 1.98–2.08 (16H, m, CH<sub>2</sub>), 2.14–2.18 (4H, m, CH<sub>2</sub>), 2.53–2.61 (4H, m, CH<sub>2</sub>), 4.46 (4H, t, J=7.6 Hz, CH), 6.67 (4H, s, ArH), 6.67–6.81 (20H, m, ArH), 7.10 (4H, s, OH): <sup>13</sup>C NMR (CDCl<sub>3</sub>/100 MHz):  $\delta_{\text{C}}$  17.7, 22.9, 23.3, 25.9, 27.8, 31.4, 44.0, 79.5, 109.6, 121.7, 123.4, 123.5, 126.6, 127.8, 144.3, 148.4, 149.6.; ESI-MS calcd for C<sub>84</sub>H<sub>96</sub>O<sub>8</sub>: m/z 1233.7183; found: 1233.7161 [M+H]<sup>+</sup>.

## 2. Analytical data (NMR and MS spectra) of 4.

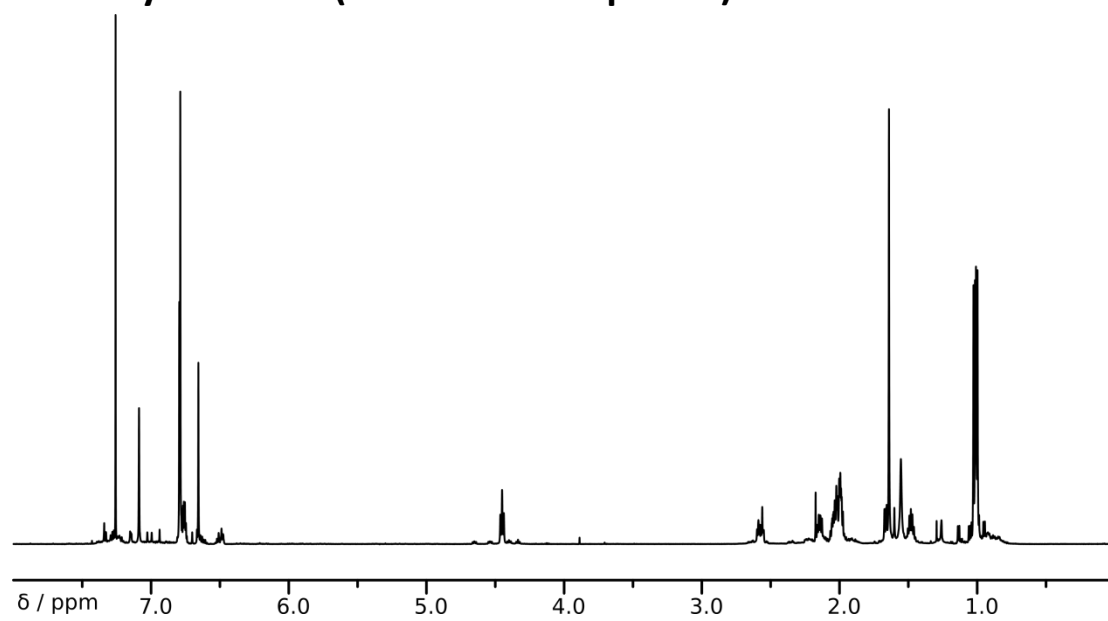


Figure S1.  $^1\text{H}$  NMR spectrum of 4 ( $\text{CDCl}_3$ , 600 MHz).

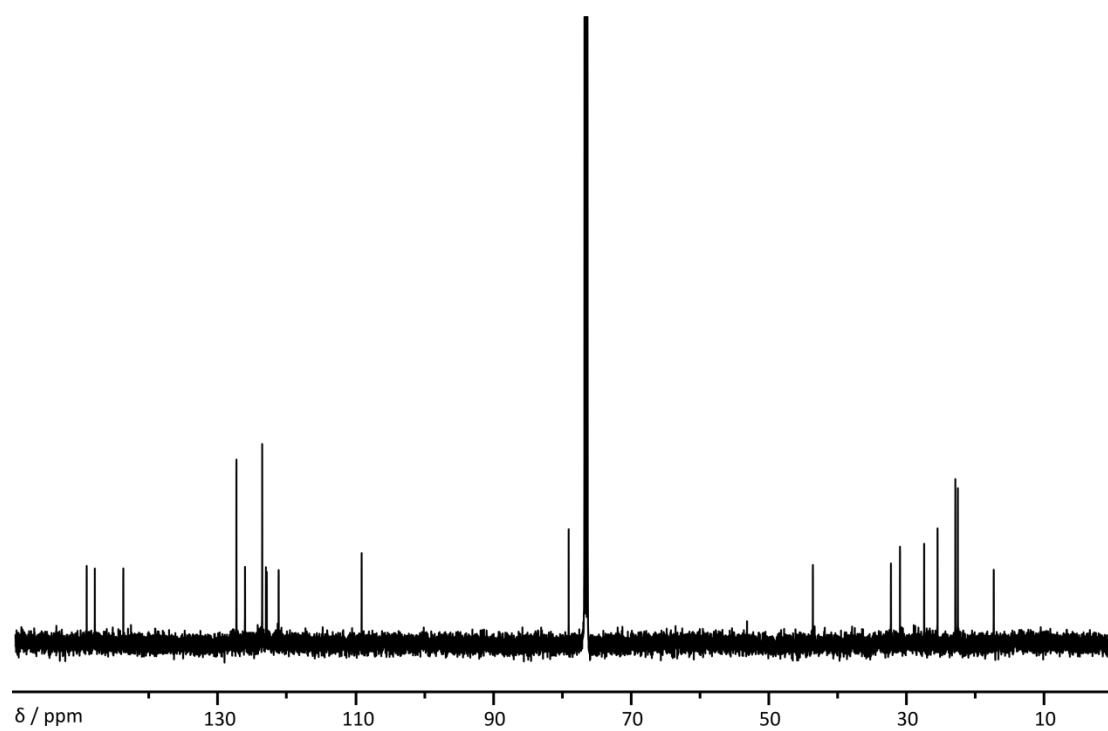
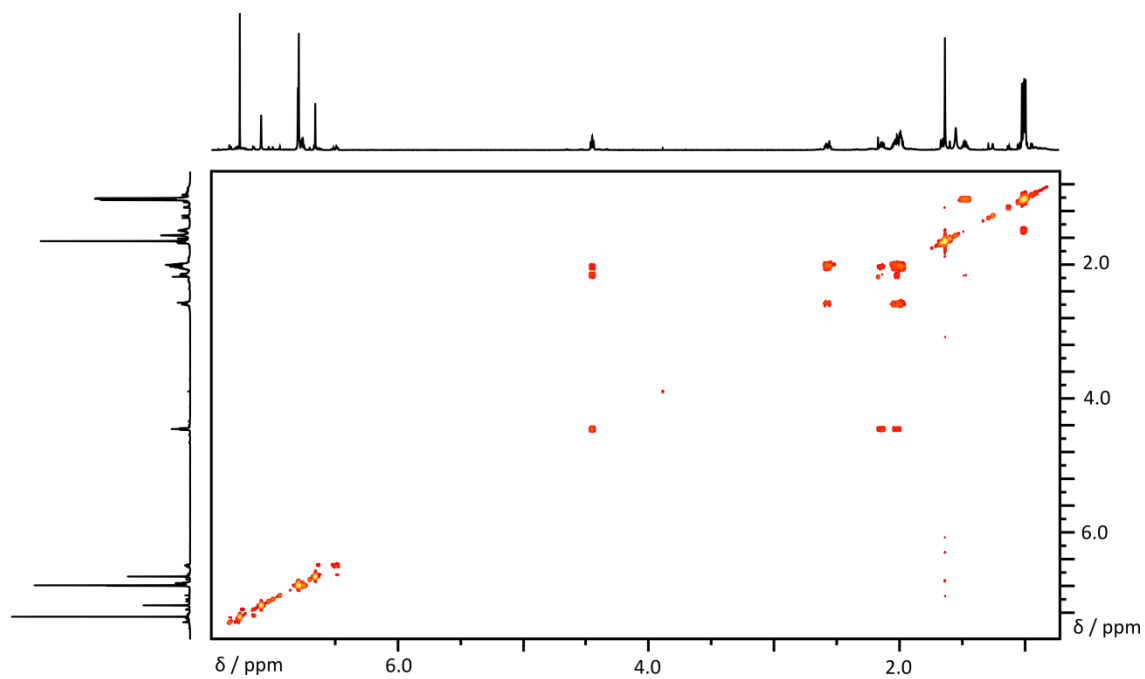
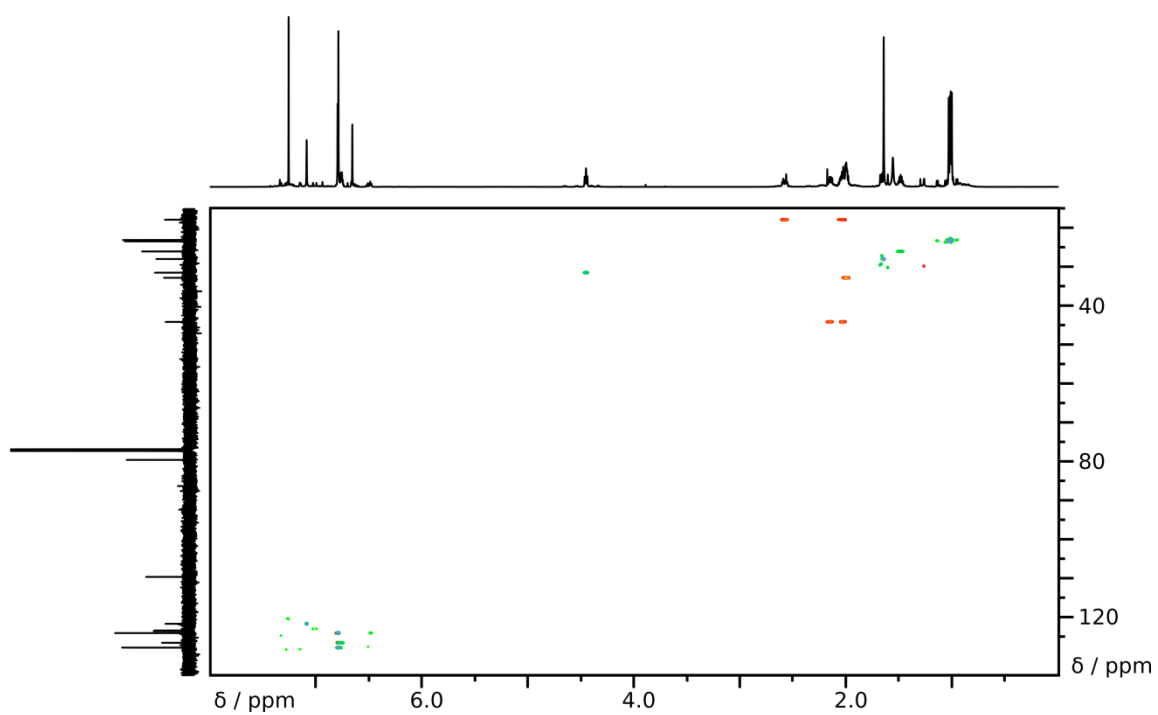


Figure 2.  $^{13}\text{C}$  NMR spectrum of 4 ( $\text{CDCl}_3$ , 150 MHz).



**Figure S3.** COSY spectrum of **4** ( $\text{CDCl}_3$ , 600 MHz).



**Figure S4.**  $^1\text{H} - ^{13}\text{C}$  HSQC spectrum of **4** ( $\text{CDCl}_3$ , 600 MHz).

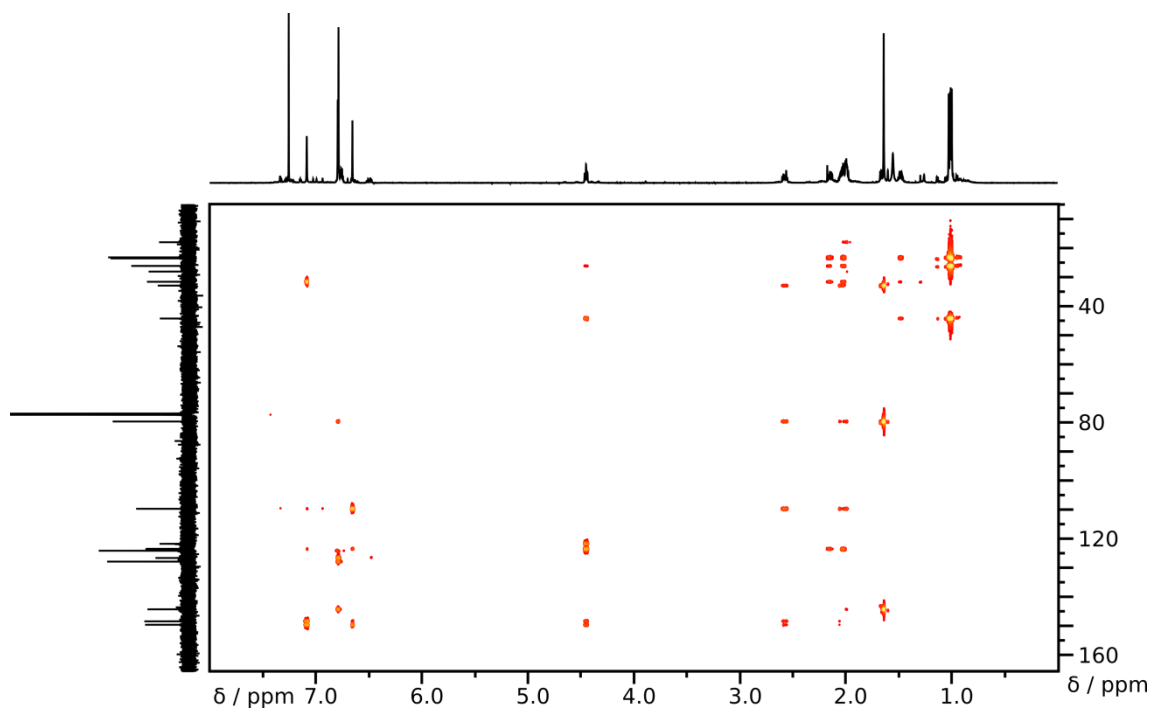


Figure S5.  $^1\text{H} - ^{13}\text{C}$  HMBC spectrum of **4** ( $\text{CDCl}_3$ , 600 MHz).

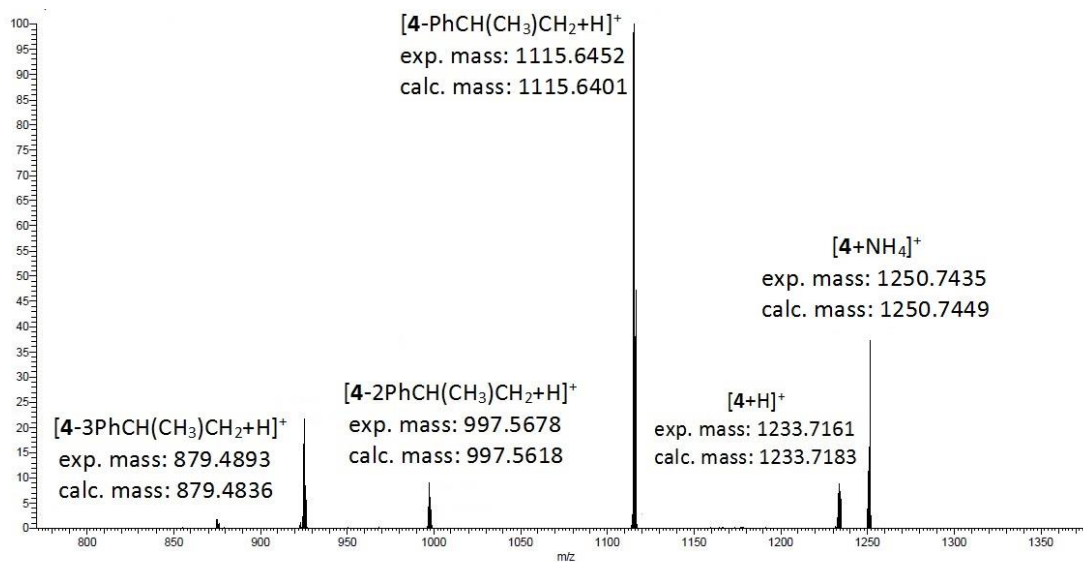
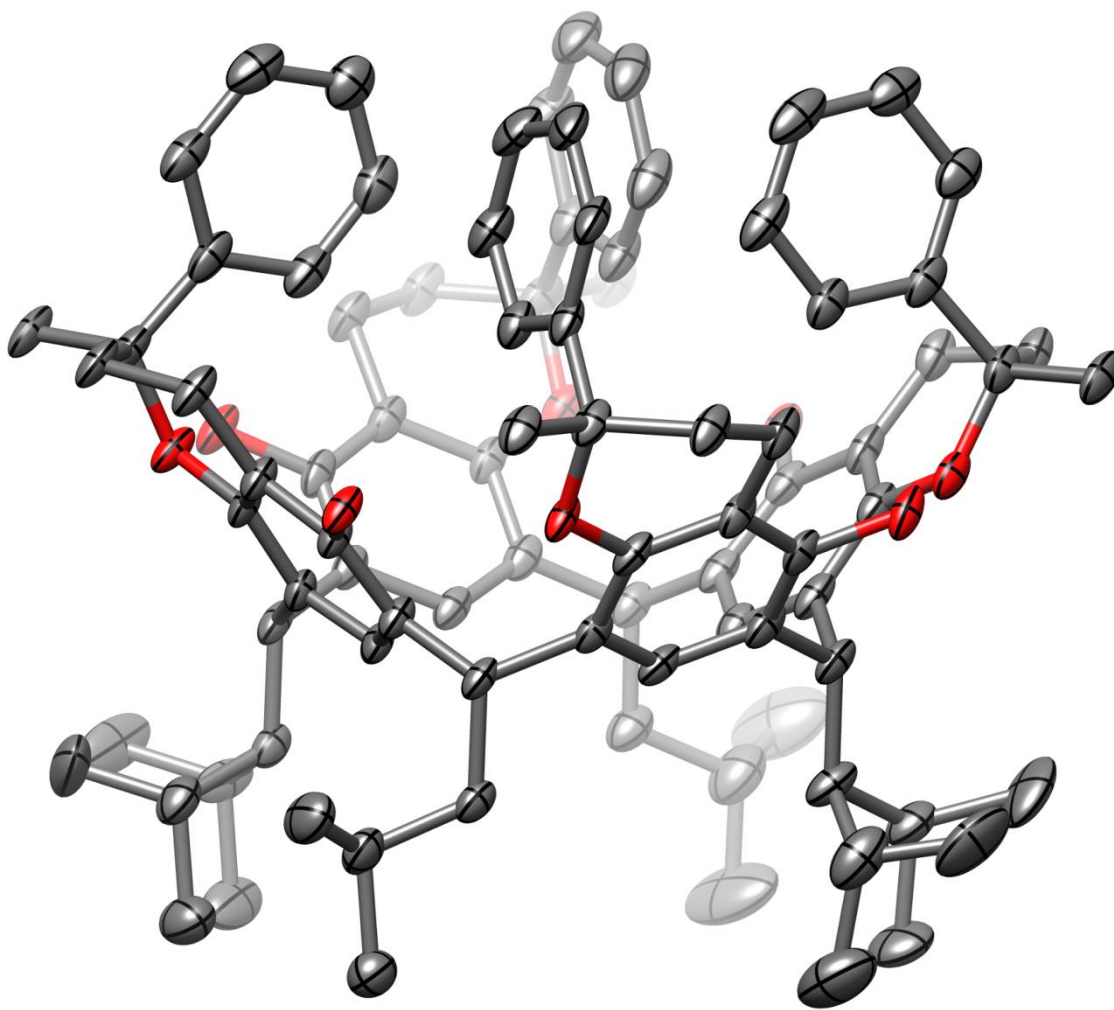


Figure S6. ESI-MS/MS spectrum of **4**. High resolution  $m/z$  values are given for each peak.

### 3. Crystallographic data for 4.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC 1405479 (**4**). Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:  $\dagger$ 44 1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk/conts/retrieving/.html](http://www.ccdc.cam.ac.uk/conts/retrieving/.html)).

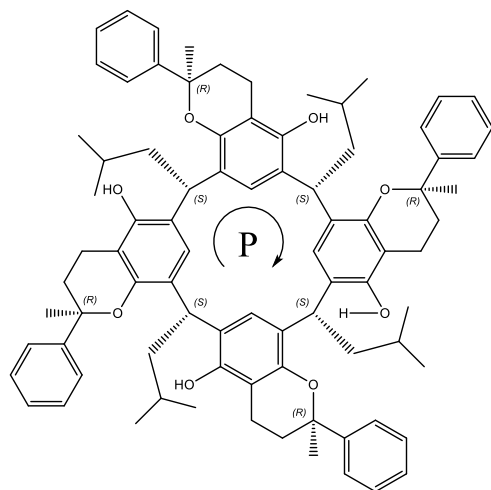


**Figure S7.** ORTEP representation of the crystal structure of **4**. Thermal ellipsoids depicted at 50% probability.

**Table S1.** Details of the X-ray measurement and structure refinement for **4**.

<b>Crystal data for 4</b>	
Molecular formula	C <sub>84</sub> H <sub>96</sub> O <sub>8</sub>
Formula weight	1233.60
Temperature (K)	100
X-ray source	sealed X-ray tube (Agilent SuperNova)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions a/b/c (Å) α/β/γ (°)	16.2545(7) 16.3681(9) 19.4099(7) 101.233(4) 109.150(4) 90.535(4)
Unit cell volume (Å <sup>3</sup> )	4769.9(4)
Z	2
Calculated density (g/cm <sup>3</sup> )	0.859
Linear absorption coefficient (mm <sup>-1</sup> )	0.054
F(000)	1328
θ range for data collection (°)	25.000 – 1.429
Resolution, d <sub>min</sub> (Å)	0.82
Index ranges	-13 < h < 19 -19 < k < 19 -23 < l < 22
Reflections collected	36541
Independent reflections	16771 (R <sub>int</sub> = 0.0606)
Completeness to θ <sub>max</sub>	0.998
<b>Refinement statistics</b>	
Final R index [I>2σ(I)]	0.0996
R index [all data]	0.1204
Goodness-of-fit	1.217
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.916 / -0.458

## 4. Calculation of the heat of formation of diastereoisomers of 4.



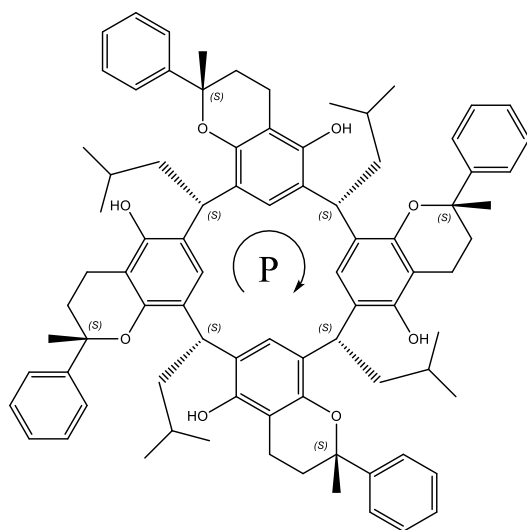
*(P,R,S)*-diastereoisomer

Empirical Formula: C<sub>84</sub> H<sub>96</sub> O<sub>8</sub> = 188 atoms

PM7 CHARGE= 0 GRAPHF +  
AUX BONDS DENSITY PI ENPART +  
MMOK  
Alfa-metylostyren-poprawiony

GEOMETRY OPTIMISED USING EIGENVECTOR FOLLOWING (EF).  
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION = -378.79803 KCAL/MOL = -1584.89094 KJ/MOL  
TOTAL ENERGY = -13979.00971 EV  
ELECTRONIC ENERGY = -287633.70787 EV  
CORE-CORE REPULSION = 273654.69816 EV  
GRADIENT NORM = 0.95291  
DIPOLE = 3.80871 DEBYE POINT GROUP: C1  
NO. OF FILLED LEVELS = 240  
IONIZATION POTENTIAL = 8.259589 EV  
HOMO LUMO ENERGIES (EV) = -8.260 0.294  
MOLECULAR WEIGHT = 1233.678  
COSMO AREA = 844.40 SQUARE ANGSTROMS  
COSMO VOLUME = 1540.30 CUBIC ANGSTROMS



*(P,S,S)*-diastereoisomer

Empirical Formula: C<sub>84</sub> H<sub>96</sub> O<sub>8</sub> = 188 atoms

PM7 CHARGE= 0 GRAPHF +  
AUX BONDS DENSITY PI ENPART +  
MMOK  
Alfa-metylostyren-poprawiony S

GEOMETRY OPTIMISED USING EIGENVECTOR FOLLOWING (EF).  
SCF FIELD WAS ACHIEVED

HEAT OF FORMATION = -356.30058 KCAL/MOL = -1490.76165 KJ/MOL  
TOTAL ENERGY = -13979.07792 EV  
ELECTRONIC ENERGY = -267561.40682 EV  
CORE-CORE REPULSION = 253582.32890 EV  
GRADIENT NORM = 0.97540  
DIPOLE = 3.69901 DEBYE POINT GROUP: C1  
NO. OF FILLED LEVELS = 240  
IONIZATION POTENTIAL = 8.152676 EV  
HOMO LUMO ENERGIES (EV) = -8.153 0.154  
MOLECULAR WEIGHT = 1233.678  
COSMO AREA = 1022.84 SQUARE ANGSTROMS  
COSMO VOLUME = 1563.71 CUBIC ANGSTROMS

**Figure S8.** Semiempirical calculation of the heat of formation ( $\Delta H$ ) of *(P,R,S)* and *(P,S,S)* diastereoisomers of **4** with the use of the program MOPAC2012 – PM7 method.