

## Supporting Information

for

# ***N,N'*-(Hexane-1,6-diyl)bis(4-methyl-*N*-(oxiran-2-ylmethyl)benzenesulfonamide): Synthesis via cyclodextrin mediated *N*-alkylation in aqueous solution and further Prilezhaev epoxidation**

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## **Additional spectra and experimental data**

### **Content:**

- Synthesis and spectral data of **3**
- Spectral data of **5**, synthesized CD mediated in aqueous solution
- Synthesis and spectral data of **8**
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### Synthesis of **3**

62.9 mmol of *p*-toluenesulfonyl chloride (**1**) were dispersed in 17 mL of diethyl ether and cooled with an ice bath. A solution of 63.8 mmol of sodium hydroxide and 31.4 mmol of hexamethylenediamine (**2**) in 15 mL of double distilled water was added dropwise. Afterwards, the suspension was stirred thoroughly for 24 h at room temperature. The product was filtered off and recrystallized in 355 mL methanol. After drying in vacuo, 22.4 mmol (71% yield) of colorless crystals of **3** were obtained.

$^1\text{H}$  NMR (600 MHz, DMSO- $d_6$ ,  $\delta$  [ppm]): 8.17 (m, 4H, Ar-H), 7.84 (m, 4H, Ar-H), 6.76 (t, 2H, N-H), 3.29 (m, 4H, N-CH<sub>2</sub>), 2.86 (s, 6H, Ar-CH<sub>3</sub>), 1.86 (m, 4H, CH<sub>2</sub>), 1.67 (m, 4H, CH<sub>2</sub>);  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ ,  $\delta$  [ppm]): 153.3 (2C, Ar-CH<sub>3</sub>), 148.9 (2C, RO<sub>2</sub>S-(C)-Ar), 140.0 (4C, CH, Ar), 137.4 (4C, CH, Ar), 53.4 (2C, N-CH<sub>2</sub>), 36.4 (4C, CH<sub>2</sub>), 31.0 (2C, Ar-CH<sub>3</sub>); IR (diamond):  $\nu$  (cm<sup>-1</sup>) = 3267 (br, -NH-), 2943, 2883, 2859 (m, -CH<sub>2</sub>-, Ar-CH<sub>3</sub>), 1597 (m, C-C, Ar), 1417 (m, R<sub>2</sub>-N-CH<sub>2</sub>-), 1312, 1148 (v, R-SO<sub>2</sub>-NH-), 1093 (m, Ar-S-), 938 (m, R-SO<sub>2</sub>-NH-), 813 (s, Ar-H (neighbouring)); MS-ESI,  $m/z$ : 425.4 [M + H]<sup>+</sup>; mp: 153 °C.

### Spectral data for the CD mediated synthesis of **5** in aqueous solution

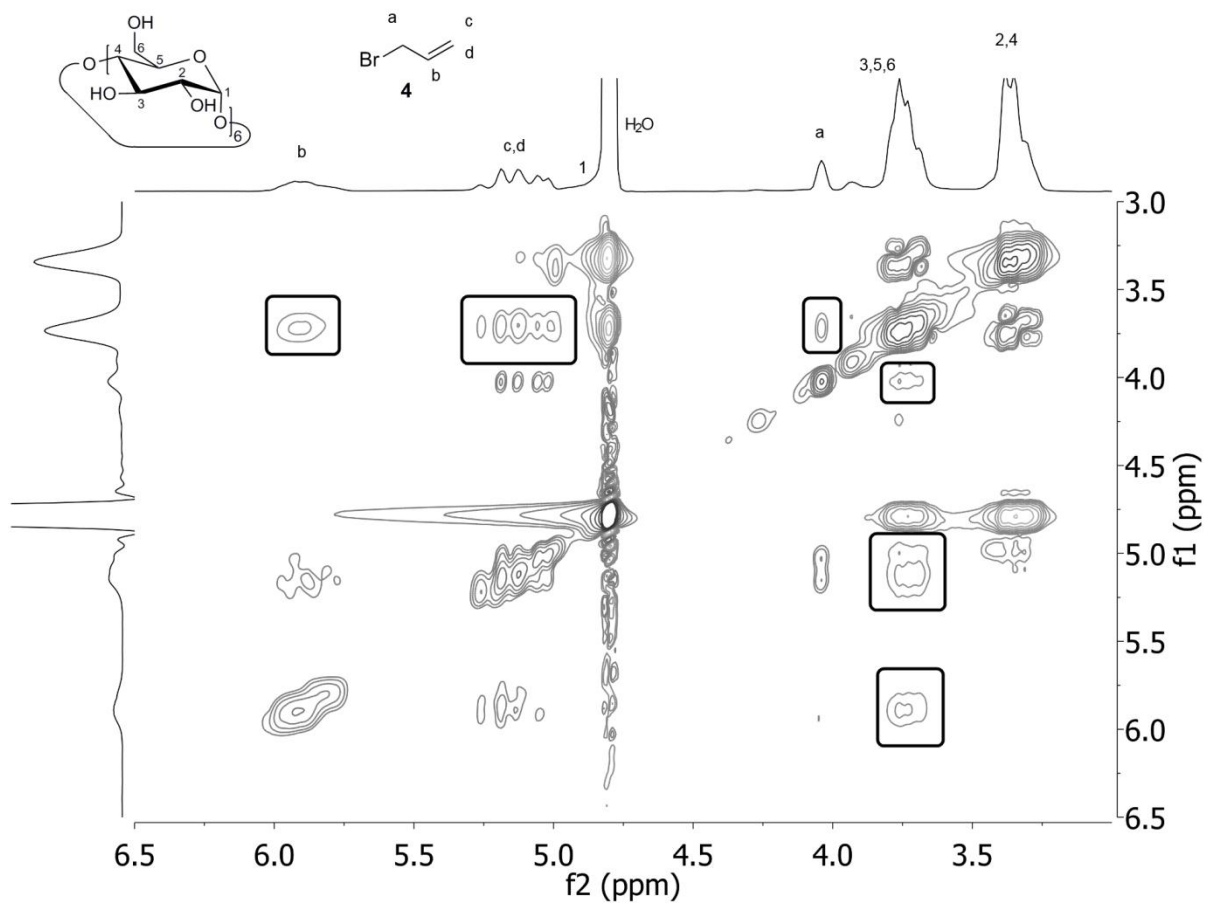
$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ,  $\delta$  [ppm]): 7.68 (d, 4H,  $J$  = 8.3 Hz, Ar-H), 7.41 (d, 4H,  $J$  = 7.9 Hz, Ar-H), 5.60 (ddt, 2H,  $J$  = 6.3, 10.1, 17.1 Hz, H<sub>2</sub>C=CH-CH<sub>2</sub>-), 5.21 (dd, 2H,  $J$  = 17.2, 1.7 Hz, CH<sub>2</sub>, *trans*), 5.11 (dd, 2H,  $J$  = 10.1, 1.6 Hz, CH<sub>2</sub>, *cis*), 3.73 (d, 4H,  $J$  = 6.3 Hz, Allyl-CH<sub>2</sub>-), 2.99 (t, 4H,  $J$  = 7.4 Hz, N-CH<sub>2</sub>-), 2.39 (s, 6H, Ar-CH<sub>3</sub>), 1.38 (m, 4H, -CH<sub>2</sub>-), 1.14 (m, 4H, -CH<sub>2</sub>-);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ,  $\delta$  [ppm]): 143.0 (2C, Ar(C)-CH<sub>3</sub>), 136.6 (2C, RO<sub>2</sub>S-(C)Ar), 133.5 (2C, R-CH=CH<sub>2</sub>), 129.8 (4C, Ar(C)),

126.9 (4C, Ar(C)), 118.5 (2C, RHC=CH<sub>2</sub>), 50.1 (2C, N-CH<sub>2</sub>-CHR), 47.1 (2C, N-CH<sub>2</sub>-CH<sub>2</sub>R), 27.5 (2C, -CH<sub>2</sub>-), 25.5 (2C, -CH<sub>2</sub>-), 20.9 (2C, -CH<sub>3</sub>); IR (diamond):  $\nu$  (cm<sup>-1</sup>) = 2951, 2918, 2855 (m, -CH<sub>2</sub>-, Ar-CH<sub>3</sub>), 1652 (w, C=C), 1597 (m, Ar), 1336, 1155 (v, R-SO<sub>2</sub>-NR<sub>2</sub>), 1089 (m, Ar-S-), 964 (v, -CH<sub>2</sub>-), 933 (m, R-SO<sub>2</sub>-NR<sub>2</sub>), 815 (s, Ar-H (neighbouring)); MS-ESI,  $m/z$ : 505.4 [M+H]<sup>+</sup>, 527 [M+Na]<sup>+</sup>; mp: 70 °C.

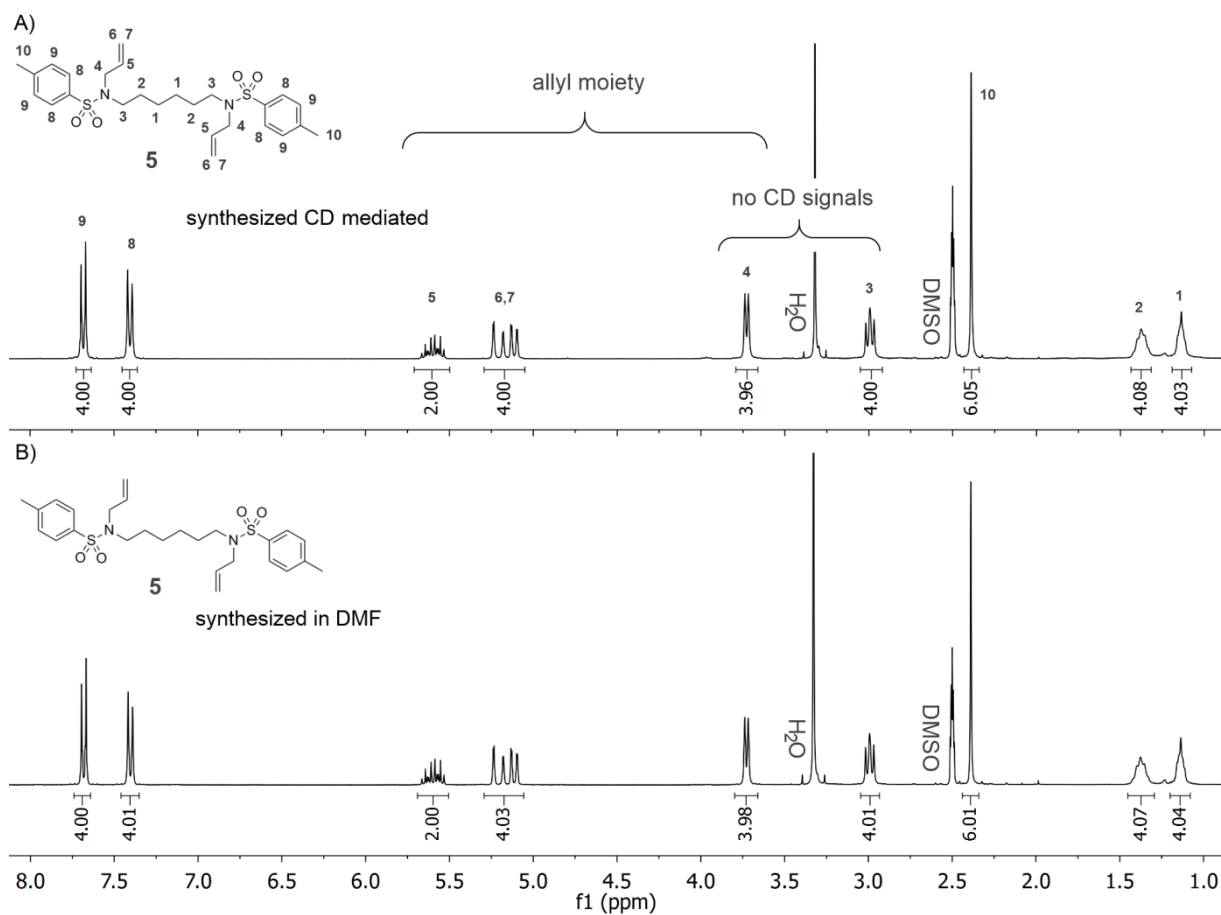
### Synthesis of 8 [1]

A mixture of L-(+)-lysine monohydrochloride (**7**, 20 g, 109.5 mmol), sodium hydroxide (4.38 g, 109.5 mmol), aluminium oxide (60 g, 589 mmol) and 300 mL *n*-butanol were heated to reflux for 48 h in a reaction vessel equipped with a water trap. Subsequently, the mixture was filtrated and the obtained pale yellow solution was concentrated under reduced pressure. After precipitation in diethyl ether, filtration, and drying in vacuo 8.1 g (63.2 mmol = 57.7%) of colorless / pale yellow crystals were received.

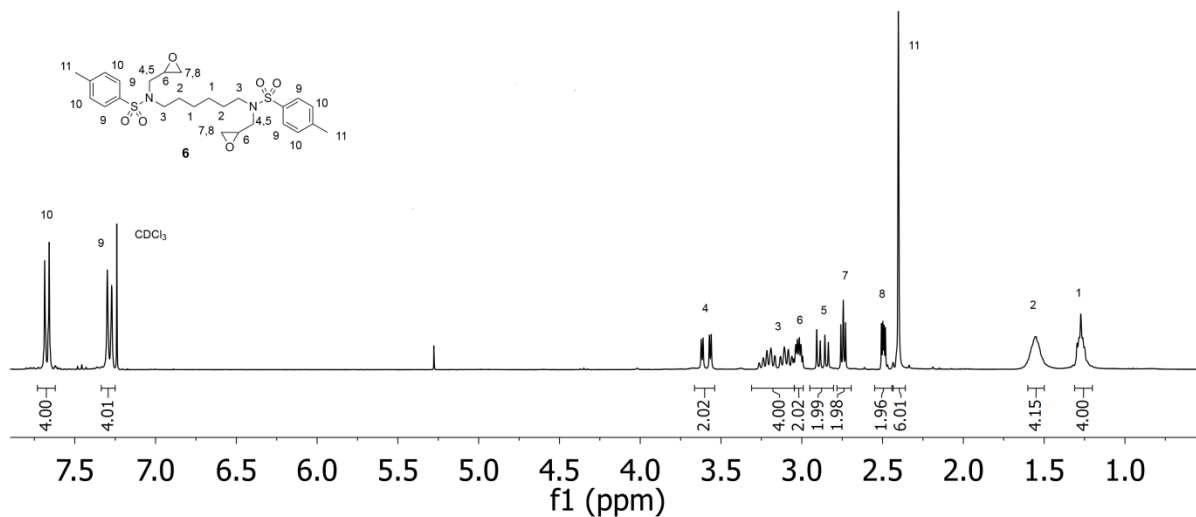
<sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O,  $\delta$  [ppm]): 3.73 (dd,  $J$  = 11.0, 1.9 Hz, 1H, CH), 3.26 (m, 2H, RHN-CH<sub>2</sub>-R), 2.02 – 1.30 (m, 6H, (CH<sub>2</sub>)<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O,  $\delta$  [ppm]): 181.3 (1C, C(O)), 52.7 (1C, CH), 41.3 (1C, RHN-CH<sub>2</sub>-R), 32.4 (1C, RHC-CH<sub>2</sub>-R), 27.7 (1C, CH<sub>2</sub>), 27.6 (1C, CH<sub>2</sub>); IR (diamond):  $\nu$  (cm<sup>-1</sup>) = 3355, 3283 (br, NH), 2930, 2909, 2849 (m, CH, CH<sub>2</sub>), 1648 (s, amide); MS-ESI,  $m/z$ : 129.1 [M+H]<sup>+</sup>; mp: 65–69 °C;



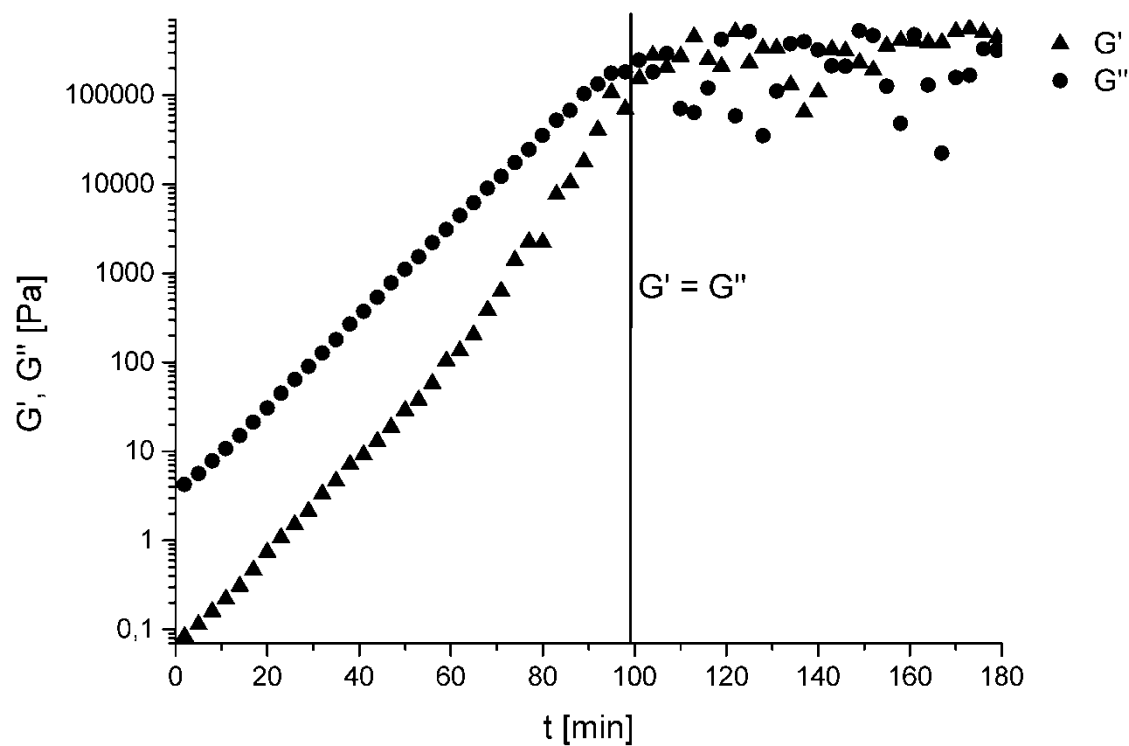
**Figure S1:** 2D NMR ROESY of the complex of **4** with  $\alpha$ -CD in  $\text{D}_2\text{O}$ .



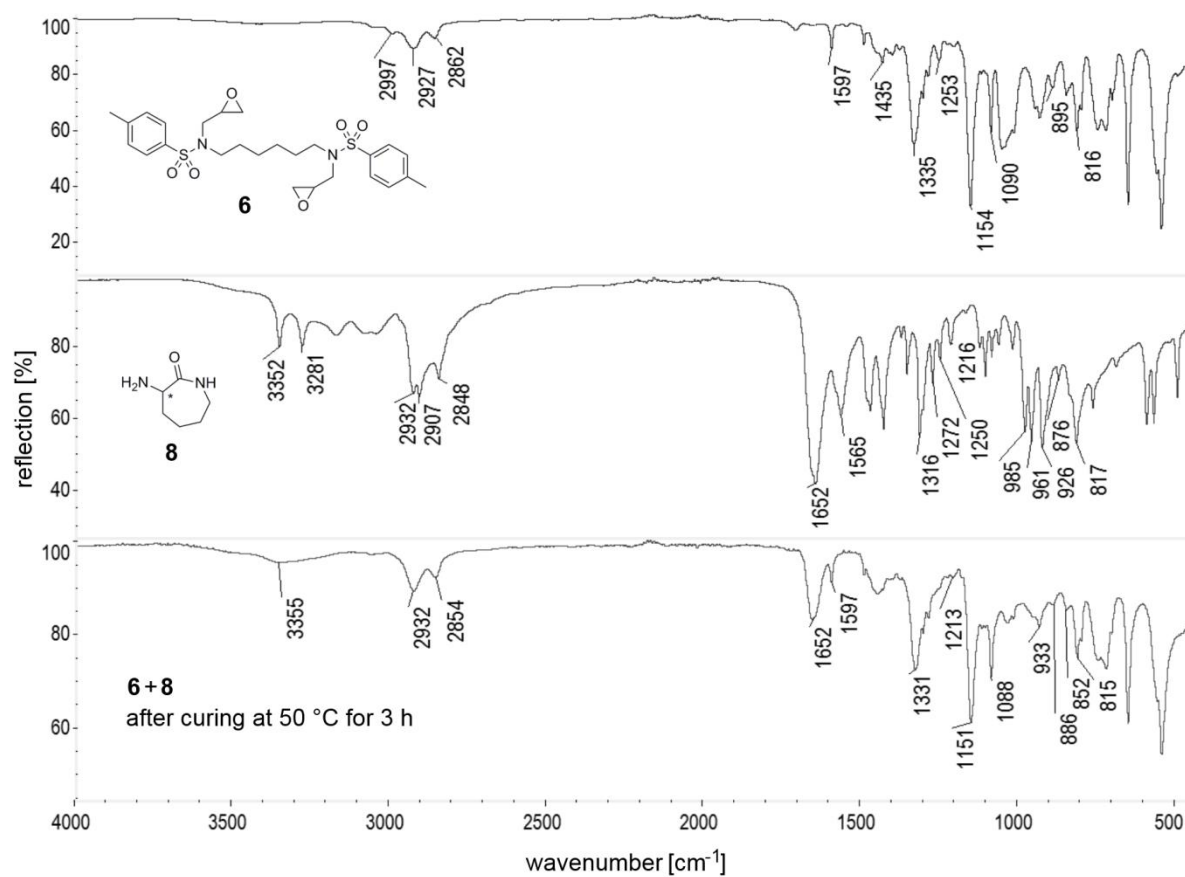
**Figure S2:**  $^1\text{H}$  NMR spectra ( $\text{DMSO}-d_6$ ) of the dialkylated sulfonamide **5**, synthesized CD mediated in aqueous solution (A) and in organic solution (*N,N*-dimethylformamide = DMF) (B).



**Figure S3:**  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$ .



**Figure S4:** Oscillatory rheological measurement of BADGE with **8** at  $50\text{ }^\circ\text{C}$ .



**Figure S5:** IR spectra of **6**, of **8**, and of a mixture of **6** and **8** after curing at 50 °C for 3 h.

## Reference

1. Frost, J. W.; Board of trustees of Michigan State University. Synthesis of Caprolactam from Lysine. WO Patent 123669A1, December 29, 2005.