



## Supporting Information

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## **Polysulfone: Catalysts for Alkene Isomerization**

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### **Materials and methods**

#### **General**

Reagents were purchased from Fluka and used without further purification unless stated otherwise.  $\text{CD}_2\text{Cl}_2$  was dried over  $\text{CaH}_2$  and freshly distilled under  $\text{N}_2$  prior to use.

Sulfur dioxide was dried by passing through a column filled with  $\text{P}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$  for drying (Fluka 06400),  $\text{Al}_2\text{O}_3$  basic activated Type 5016A Brockman I (Aldrich 19,944-3).

Instruments utilized for kinetics, analysis and characterization of compounds:  $^1\text{H}$ -NMR,  $^2\text{H}$ -NMR,  $^2\text{H}\{^1\text{H}\}$ -NMR,  $^{13}\text{C}$ -NMR: Bruker DPX-400 FT. IR spectra: Perkin-Elmer Paragon 1000 FT-IR spectrometer; mass spectra:

Nermag R 10-10C mass spectrometer in chemical ionization (CI) mode; microanalysis: Ilse Beetz Laboratory, Kronach (Germany).

### Kinetics of Isomerization of Methylidenecyclopentane (**1**) with Various Amounts of SO<sub>2</sub>

In a NMR tube was added a solution of methylidenecyclopentane (**1**) (0.23324 mol/kg) and toluene (0.02356 mol/kg) in anh. CD<sub>2</sub>Cl<sub>2</sub>, (**1**/SO<sub>2</sub>=1/1.1) = 0.35310 g; m(**1**/SO<sub>2</sub>)=1/5)= 0.35220 g; m(**1**/SO<sub>2</sub>) = 1/24.7)= 0.35100 g). Solution was degassed on the vac. line by freeze/thaw cycles 3 times. Different amounts of SO<sub>2</sub> were measured, degassed and transferred on the vacuum line to the CD<sub>2</sub>Cl<sub>2</sub> solution frozen at -196 °C. NMR tube was sealed *in vacuo* and reactions were followed at 0 °C by <sup>1</sup>H-NMR.

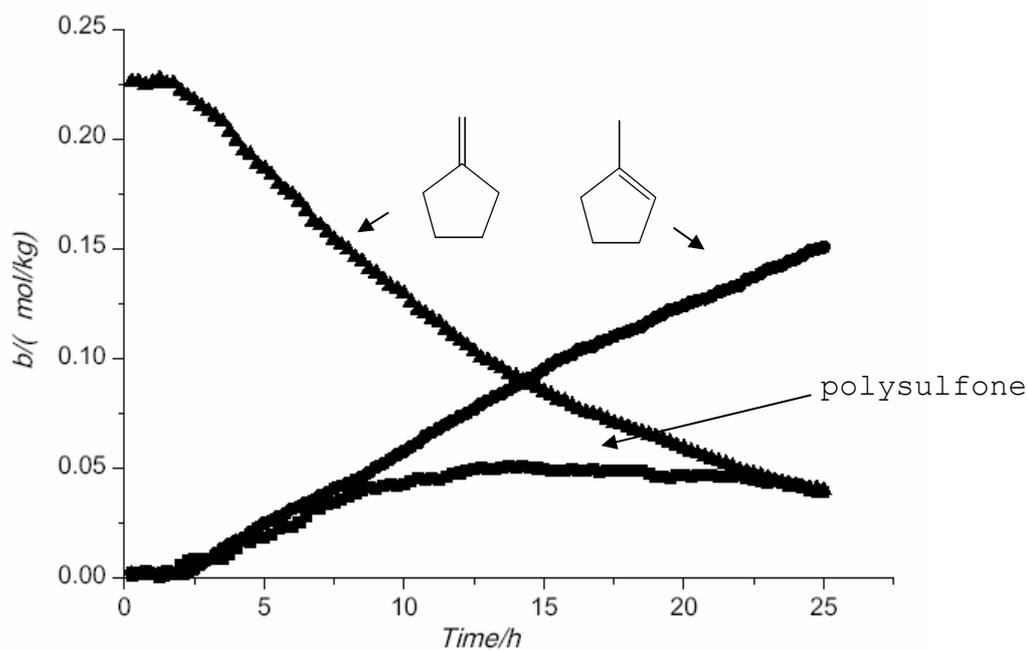


Figure SM1. Kinetics of the SO<sub>2</sub>-promoted isomerization **1**→**4**, in CD<sub>2</sub>Cl<sub>2</sub>, 0°C, 1.1 equivalent of SO<sub>2</sub>

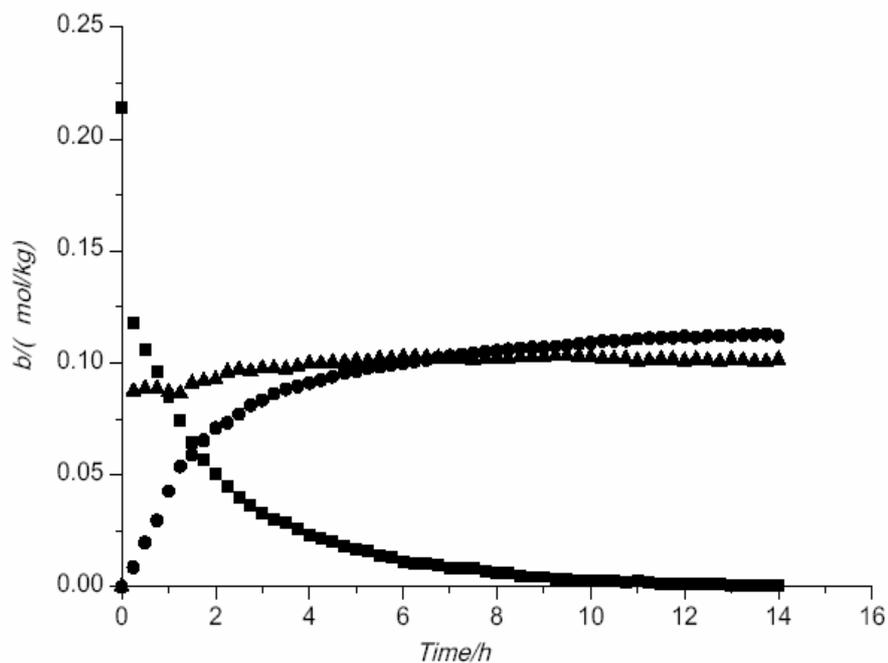


Figure SM2. Kinetic of the  $\text{SO}_2$ -promoted isomerization **1**→**4** in  $\text{CD}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 6 equivalents of  $\text{SO}_2$ . (integrals: ■ methylidenecyclopentane (**1**), ● 1-methylcyclopentene (**4**), ▲ poly(methylidenecyclopentane-sulfone) (**PS**)).

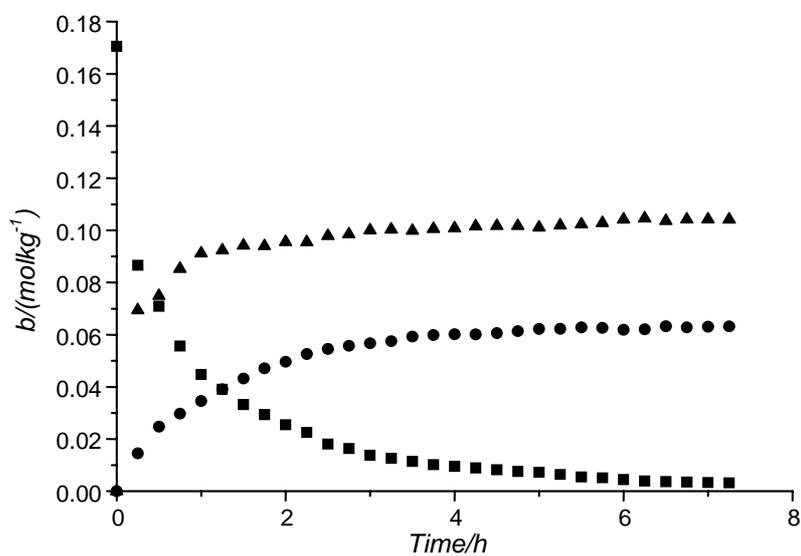


Figure SM3. Kinetic of the  $\text{SO}_2$ -promoted isomerization **1**→**4** in  $\text{CD}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 24.7 equivalents of  $\text{SO}_2$ . (integrals: ■ methylidenecyclopentane (**1**), ● 1-methylcyclopentene (**4**), ▲ poly(methylidenecyclopentane-sulfone) (**PS**)).

**Example of the Inhibition of 1→4 isomerization catalyzed by SO<sub>2</sub>  
(Bu<sub>3</sub>SnH)**

In a NMR tube was added a solution of methylenecyclopentane (**1**) (0.22958 mol/kg), toluene (0.02302 mol/kg) and Bu<sub>3</sub>SnH (3.43 mg, 0.011785 mmol) in anh. CD<sub>2</sub>Cl<sub>2</sub>, (m(solution)=0,50050 g). Solution was degassed on the vac. line by freeze/thaw cycles 3 times. SO<sub>2</sub> (high excess) was degassed and transferred on the vacuum line to the CD<sub>2</sub>Cl<sub>2</sub> solution frozen at -196 °C. NMR tube was sealed *in vacuo* and reaction was followed at 0 °C by <sup>1</sup>H-NMR. Reaction was still inhibited after 24 hours.

Same experiments were carried out with CH<sub>2</sub>I<sub>2</sub> and TEMPO that also completely inhibited the isomerization.

**Poly(methylenecyclopentane-sulfone) (PS)**

Methylenecyclopentane (**1**) was purified by distillation. SO<sub>2</sub> (1.6 ml, 0.0358 mol) was transferred to frozen methylenecyclopentane (**1**) (1.0012 g, 0.0122 mol) on the vacuum line. Mixture was allowed to warm to -20 °C. After 2 hours, at this temperature, the excess of SO<sub>2</sub>, non-reacted methylenecyclopentene (**1**) and 1-methylcyclopentene (**4**) were evaporated under reduced pressure (0.001 Torr). Poly(methylenecyclopentane-sulfone) (**PS**) (1.332 g, 75 %) was powdered and neutralized with 5 % aqueous solution of NaOH till pH=7

and washed 3 times by turns with water and  $\text{CH}_2\text{Cl}_2$ . Neutralized polymer was dried on the vacuum line overnight.

$^{13}\text{C}$ -NMR (solid): 107.5, 74.1, 52.4, 33.8, 28.05. IR (KBr): 2960, 2879, 1635, 1445, 1389, 1306, 1125. Anal. Calc. for monomer unit  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$  (146.20): C 49.29 %, H 6.89 %, O 21.89 %, S 21.93 %; found: C 48.15 %, H 6.72 %, O 20.21 %, S 20.61 %

#### **Titration of Sulfinic Acid Ends in Poly-(Methylidenecyclopentane-Sulfone) (PS)**

Powdered poly(methylidenecyclopentane-sulfone) (**PS**) (1.0373 g) was added to water (51.4139 g) and mixture stirred for 1 hour at room temperature. Titration was followed by automatic dosimat "METRUM 725". pH-meter was calibrated with two standard buffers pH 4.0 and pH 7.0. NaOH ( $0.01 \text{ mol/dm}^3$ , equivalent point 0.0904 mL, Fluka 72083) was used as a titrant reagent.

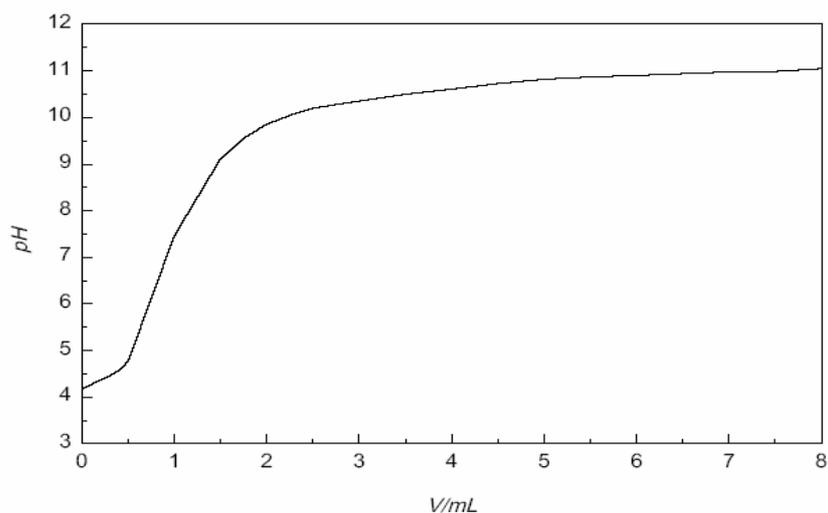


Figure SM4. Titration of poly(methylidenecyclopentane-sulfone) (**PS**) by NaOH ( $0.01 \text{ mol/dm}^3$ , equivalent point 0.0904 mL);

**Electron Spin Resonance of Copolymerization of Methylidenecyclopentane (1) and SO<sub>2</sub>**

In a ESR tube was added methylidenecyclopentane (1) (0.3142 g, 3.825 mmol) and dry SO<sub>2</sub> (0.2 ml, 44.76 mmol). ESR tube was sealed *in vacuo* and kept in liq. N<sub>2</sub>. The tube was placed in ESR probe and spectrum was recorded immediately after the tube was heated to room temperature.

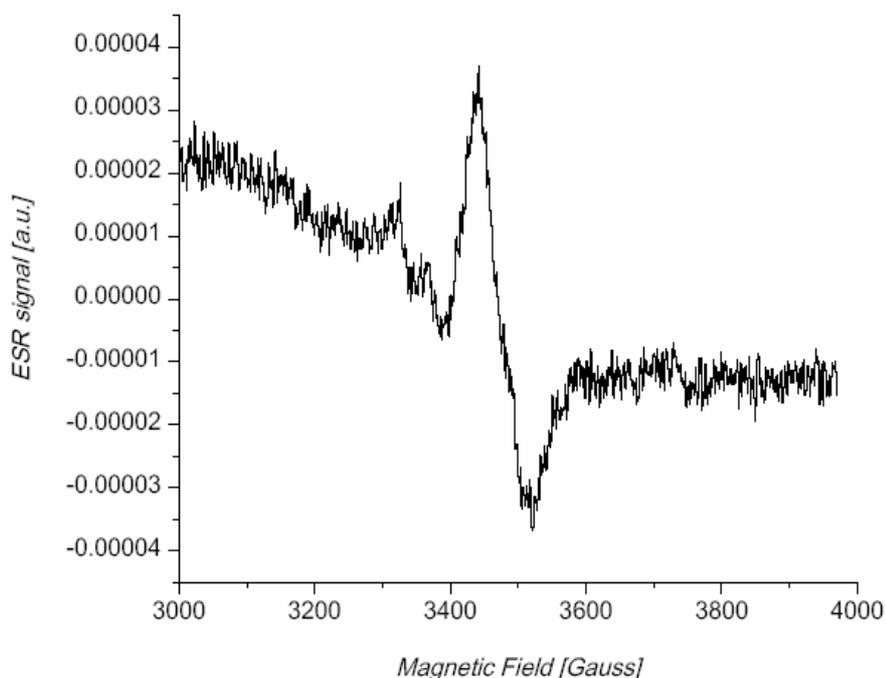


Figure SM5. ESR spectrum of polymerization of methylidenecyclopentane (1) and SO<sub>2</sub> at room temperature.

In a ESR tube was added methylidenecyclopentane (1) (0.3021 g, 3.6779 mmol) and dry SO<sub>2</sub> (0.2 ml, 44.76 mmol). ESR tube was sealed *in vacuo* and kept in liq. N<sub>2</sub>. The tube was placed in ESR probe. After

heating to  $-40\text{ }^{\circ}\text{C}$  the tube was immediately frozen by helium to 4 K and spectrum was recorded.

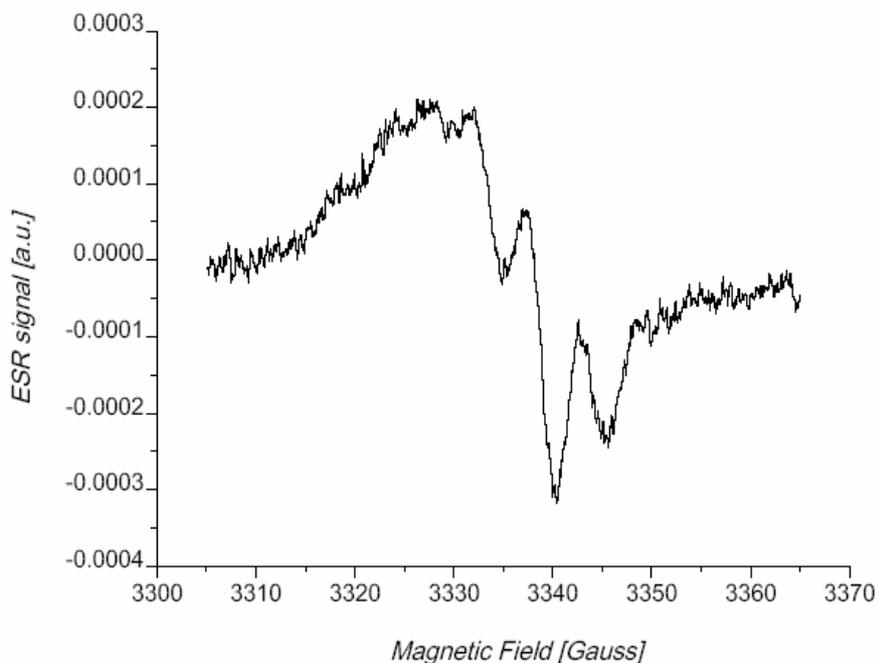


Figure SM6. ESR spectrum of polymerization of methylenecyclopentane (**1**) and  $\text{SO}_2$  at 4 K.

**Example of the Inhibition of 1→4 Isomerization Catalyzed by Polysulfone (PS) ( $\text{Bu}_3\text{SnH}$ )**

In a NMR tube was added a solution of methylenecyclopentane (**1**) (0.23056 mol/kg), toluene (0.02434 mol/kg) and  $\text{Bu}_3\text{SnH}$  (2.69 mg, 0.009242 mmol) in anh.  $\text{CD}_2\text{Cl}_2$ , ( $m(\text{solution})=0.40320\text{ g}$ ). The solution was degassed on the vac. line by freeze/thaw cycles 3 times and transferred to another NMR tube with poly(methylenecyclopentane-sulfone) (**PS**) (8 mg). The NMR tube was sealed *in vacuo* and reaction

was followed at 0 °C by  $^1\text{H-NMR}$ . The reaction was still inhibited after one day at 0 °C.

A same experiment was carried out with TEMPO (5 % mol) which also completely inhibits the reaction.

#### **Isomerization Reaction 1→4 Catalyzed by $(\text{PhSO}_2)_2$**

In a pyrex tube was added a solution of methylenecyclopentane (**1**) (100 mg, 1.2174 mmol), and toluene (11.51 mg, 0.1249 mmol) in anh.  $\text{CDCl}_3$  (2.4378 g) and diphenyldisulfone (16.9 mg, 0.0599 mmol, 4.9 % mol). Solution was irradiated (high pressure, Hg lamp-pyrex flask) and stirred for 6 h. Reaction conversion was 75 % by  $^1\text{H-NMR}$  of the crude reaction mixture. A back precipitate was formed.

$^1\text{H-NMR}$ : 0.8-2.9 (broad), 4.0 (broad), 7.3-7.9. Elemental analysis: 65,76 % C 6,61% H.

A experiment was also carried out by heating of same reaction mixture to 120 °C under pressure. Reaction conversion was 71 % by  $^1\text{H-NMR}$  of the crude reaction mixture.

#### **Methylened- $_2$ -cyclopentane-2,2,5,5- $_4$ (**6**)<sup>[1]</sup>**

In flame dry round bottom flask, to NaH (2.439 g, 0.056 mol, 55 %) and of methyl- $_3$ -triphenylphosphonium bromide (20.0 g, 0.056 mol) was added approximately 80 ml of  $\text{DMSO-}d_6$  under Ar atmosphere. After addition of the solvent, the temperature was raised over the period of 1 hour, to 60-70°C and maintained at this temperature for 3 hours.

The formation of intermediate methylened<sub>2</sub>-triphenylphosphorane was evidenced by the appearance of a yellow color shortly after the stirring had begun. The mixture was then cooled to 30 °C and cyclopentanone-2,2,5,5-d<sub>4</sub> (**8**) (4.81 g, 0.0546 mol, 99.2 % deuterium) was added dropwise. The mixture was heated to 80-95 °C over a period of 1 hour and maintained at this temperature overnight. The product was isolated from liquid nitrogen cooled trap and purified using preparative gas chromatography (column: C-20m 2%/Chromosorb G-AW 6080 mesh). This procedure yielded with 69 % of methylened<sub>2</sub>-cyclopentane-2,2,5,5-d<sub>4</sub> (**6**) (3.33 g, 0.0378 mol, methylened group 99.1 % deuterium; position 2 98.4 % deuterium).

<sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 0 °C): 1.62 (s, 4H, H-C(3), H-C(4)).

<sup>2</sup>H-NMR (61,44 MHz, CDCl<sub>3</sub>, 0 °C): 4.92 (2D, D-CC(1)), 2.28 (4D, D-

C(2), D-C(5)). <sup>13</sup>C-NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 153.07 (s, C(1)), 103.75

(quintet, J<sub>CD</sub>= 20.26, (CD<sub>2</sub>)), 32.22 (quintet, J<sub>CD</sub>=20.26, C(2), C(5)),

26.42 (t, J<sub>CD</sub>= 129.63, C(3), C(4)). IR (film): 2954, 2878, 2262, 2139,

2065, 1521, 1372.

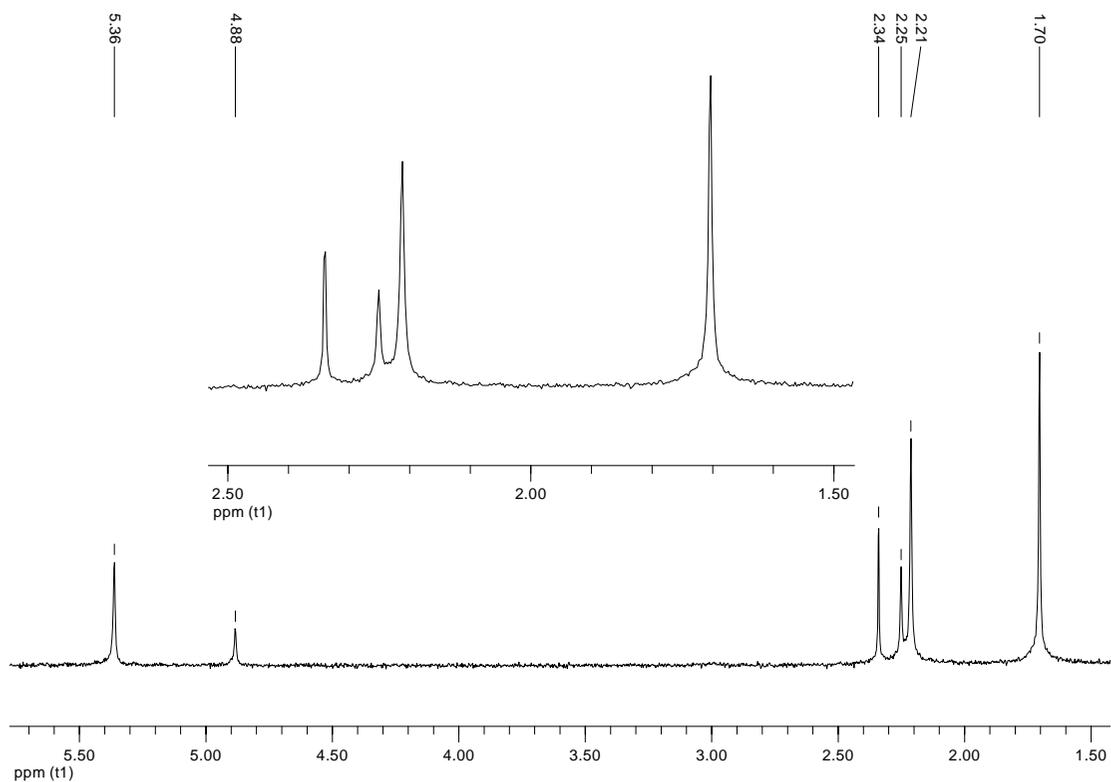
#### **Isomerization of 9→10 Catalyzed by (PhSO<sub>2</sub>)<sub>2</sub>**

In a cylinder was added a solution of methylened<sub>2</sub>-cyclopentane-2,2,5,5-d<sub>4</sub> (**6**) (0.47852 mol/kg), toluene (0.03893 mol/kg) and toluene-d<sub>8</sub> (0.18364 mol/kg) in anh. CDCl<sub>3</sub> (m(solution)=0,41432 g). Solution was degassed on the vac. line by freeze/thaw cycles 3 times and transferred under vacuum to a NMR tube which contained (PhSO<sub>2</sub>)<sub>2</sub>

**SM10**

(2.80 mg, 0.00991 mmol, 5 % mol). The NMR tube was sealed under vacuum and irradiated (high pressure Hg lamp) with light over 2 h at room temperature. The formation of 1-trideuteromethylcyclopentane was monitored by  $^2\text{H}\{^1\text{H}\}$ -NMR.

Figure SM7.  $^2\text{H}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture (isomerisation **6**→1-trideuteromethylcyclopentane-2,5,5- $\text{d}_6$ ) catalyzed by diphenyl-disulfone at room temperature.  $^2\text{H}\{^1\text{H}\}$ -NMR (61.44 MHz,  $\text{CDCl}_3$ , 25 °C): 1-trideuteromethylcyclopentane-2,5,5- $\text{d}_6$ : 1.71 (3D,  $\text{CD}_3$ ), 2.22 (2D, D-C(3)), 5.37 (1D, D-C(2)), methylened- $\text{d}_2$ -cyclopentane-2,2,5,5- $\text{d}_4$ : 2.35 (4D, -D-C(2), D-C(5)), 4.89 (2D,  $\text{CD}_2$ ); toluene- $\text{d}_8$ : 2.35 (3D,  $\text{CD}_3$ ).



### Cross Isomerization Catalyzed by Polysulfone (PS)

In a cylinder was added a solution of methylenedicyclopentane-2,2,5,5-d<sub>4</sub> (**6**) (0.18846 mol/kg), methylenedicyclopentane (**1**) (0.19997 mol/kg), toluene (0.03893 mol/kg) and toluene-d<sub>8</sub> (0.18364 mol/kg) in anh. CDCl<sub>3</sub> which was neutralized and dried (m(solution)=0,41432 g). Solution was degassed on the vac. line by freeze/thaw cycles 3 times. Poly(methylenedicyclopentane-sulfone) (**PS**) (3.04 mg), was degassed and frozen at -196 °C. Solution of olefins in CD<sub>2</sub>Cl<sub>2</sub> was transferred on the vacuum line to the NMR tube which was sealed *in vacuo*. Reaction was followed by <sup>1</sup>H-NMR and <sup>2</sup>H{<sup>1</sup>H}-NMR at 0 °C.

Figure SM8.  $^2\text{H}\{^1\text{H}\}$ -NMR spectrum of the reaction mixture in cross isomerization experiment.  $^2\text{H}\{^1\text{H}\}$ -NMR (61,44 MHz,  $\text{CDCl}_3$ , 0 °C): 1-trideuteromethylcyclopentane-2,5,5- $\text{d}_6$ : 1.72 (3D,  $\text{CD}_3$ ), 2.22 (2D, D-C(3)), 5.38 (1D, D-C(2)); 1-dideuteromethylcyclopentane-2,5,5- $\text{d}_5$ : 1.74 (2D,  $\text{CD}_2$ ), 2.22 (2D, D-C(3)), 5.38 (1D, D-C(2)); 1-monodeuteromethylcyclopentane- $\text{d}_1$ : 1.76 (1D, CD); methylened- $\text{d}_2$ -cyclopentane-2,2,5,5- $\text{d}_4$ : 2.35 (4D, D-C(2), D-C(5)), 4.90 (2D,  $\text{CD}_2$ ); toluene- $\text{d}_8$ : 2.36 (3D,  $\text{CD}_3$ ).

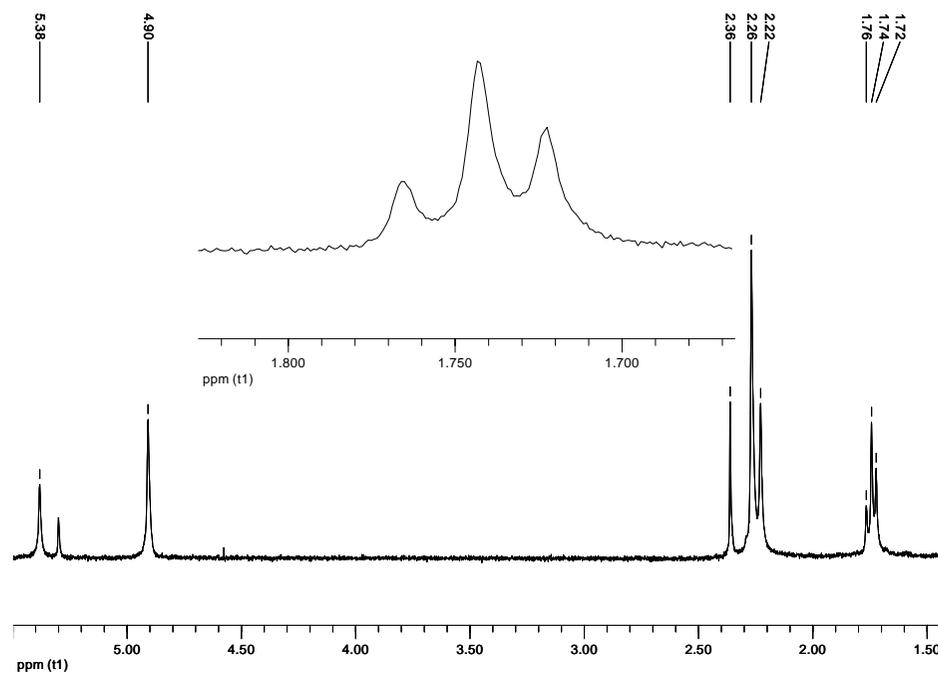
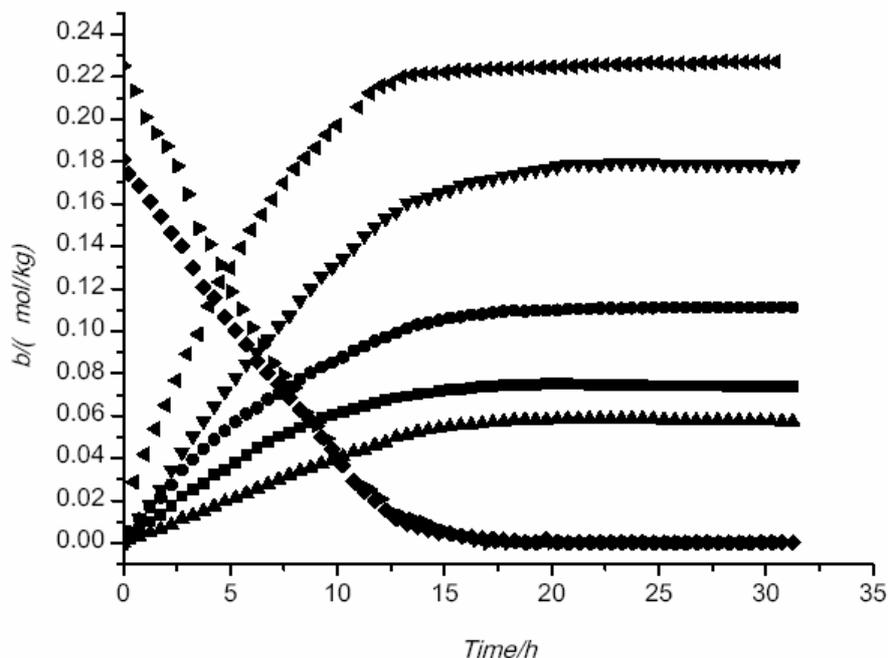


Figure SM9. Kinetic of the cross isomerization: Integrals of peaks:

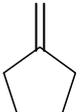
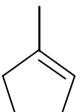
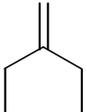
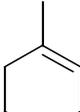
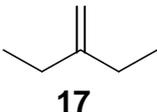
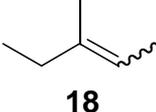
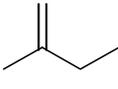
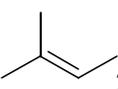
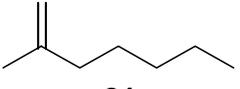
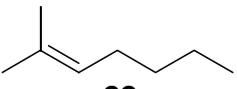
$^2\text{H}\{^1\text{H}\}$ -NMR:  $\blacksquare$   $\text{CDH}_2$ ,  $\bullet$   $\text{CD}_2\text{H}$ ,  $\blacktriangle$   $\text{CD}_3$ ,  $\blacktriangledown$   $\text{CD}$  (olefinic),  $\blacklozenge$   $\text{CD}_2$  (olefinic),  $^1\text{H}$ -NMR:  $\blacktriangleleft$   $\text{CH}$  (olefinic),  $\blacktriangleright$   $\text{CH}_2$  (olefinic)



### Isomerization of Olefins Catalyzed by Polysulfone (PS)

In a measuring cylinder was added a solution of olefin (0.092 mmol) and toluene (0.0092 mmol) in anh.  $\text{CD}_2\text{Cl}_2$  (0,4 g). Solution was degassed on the vac. line by freeze/thaw cycles 3 times. Solution was degassed on the vac. line by freeze/thaw cycles 3 times and transfer to another NMR tube with poly(methylidenecyclopentane-sulfone) (**PS**) (5 % mass). The isomerized products showed spectral data identical to those reported for these compounds. Conversion rates were determined by  $^1\text{H}$  NMR signal integration with toluene as standard reference (SM Table 2).

Table SM1. Conversion rates for isomerized products.

		Conversions
	$\longrightarrow$	
<b>13</b>		<b>14</b>
		<b>13/14=1:99</b>
	$\longrightarrow$	
<b>15</b>		<b>16</b>
		<b>15/16=6:94</b>
	$\longrightarrow$	
<b>17</b>		<b>18</b>
		<b>17/18=3:97</b>
	$\longrightarrow$	
<b>19</b>		<b>20</b>
		<b>19/20=1:99</b>
	$\longrightarrow$	
<b>21</b>		<b>22</b>
		<b>21/22=15:85</b>

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1. T. B. Malloy, Jr., F. Fisher, J. Laane, R. M. Hedges, *J. Mol. Spectrosc.* **1971**, *40*, 239-6; b) T. B. Malloy, Jr., R. M. Hedges, F. Fisher, *J. Org. Chem.* **1970**, *35*, 4256-7; c) R. L. Lipnick, *J. Mol. Struct.* **1974**, *21*, 411-21; d) L. E. Bauman, J. Laane, *J. Phys. Chem.* **1988**, *92*, 1040-51; e) P. D. Ellis, G. E. Maciel, *J. Am. Chem. Soc.* **1970**, *92*, 5829-33.