

## **Supporting Information**

for

Selective ring-opening metathesis polymerization (ROMP) of cyclobutenes. Unsymmetrical ladderphane containing polycyclobutene and polynorbornene strands

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<sup>1</sup>H and <sup>13</sup>C NMR spectra of both monomers and polymers, as well as GPC and kinetic investigation results

**Figure S1**: (a) Monomer conversion vs. time for **4** (solid square) and **5** (open circle) (0 °C, DCM- $d_2$ ); (b) First-order decay of **4** (solid square) and **5** (open circle) (0 °C, DCM- $d_2$ ).

**Figure S2:** (a) Monomer conversion vs. time for **4** (solid square) and **5** (open circle) (0 °C, THF- $d_8$ ); Right: Second-order decay of **4** (solid square) (0 °C, THF- $d_8$ ).

**Figure S3:** (a) <sup>1</sup>H (400 MHz) and (b) <sup>13</sup>C (100 MHz) NMR spectra of **9**..

**Figure S4:** (a) <sup>1</sup>H (400 MHz) and (b) <sup>13</sup>C (100 MHz) NMR spectra of **14**.

**Figure S5:** (a)  ${}^{1}$ H (400 MHz) and (b)  ${}^{13}$ C (100 MHz) NMR spectra of **8**.

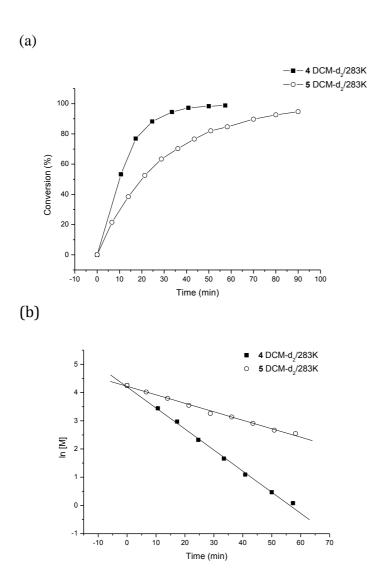
**Figure S6:** (a)  ${}^{1}$ H (400 MHz) and (b)  ${}^{13}$ C (100 MHz) NMR spectra of **7**.

Figure S7: <sup>1</sup>H (400 MHz) and (b) <sup>13</sup>C (100 MHz) spectra of 19.

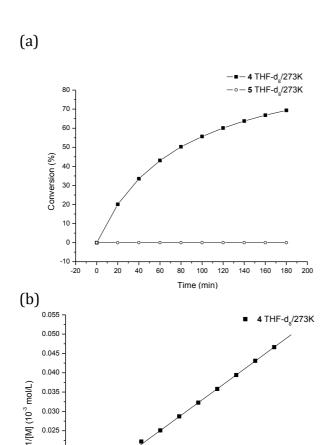
**Figure S8:** Kinetics of the **6**-catalyzed reaction of **4** in CD<sub>2</sub>Cl<sub>2</sub> at 10 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every ten minutes.

**Figure S9:** Kinetics of the **6**-catalyzed reaction of **5** in CD<sub>2</sub>Cl<sub>2</sub> at 10 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every ten minutes.

**Figure S10:** Kinetics of the **6**-catalyzed reaction of **4** in THF at 0 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every twenty minutes.



**Figure S1:** (a) Monomer conversion vs time for **4** (solid square) and **5** (open circle) (0  $^{\circ}$ C, DCM- $d_2$ ); (b) First-order decay of **4** (solid square) and **5** (open circle) (0  $^{\circ}$ C, DCM- $d_2$ ).



0.025 0.020 0.015 0.010

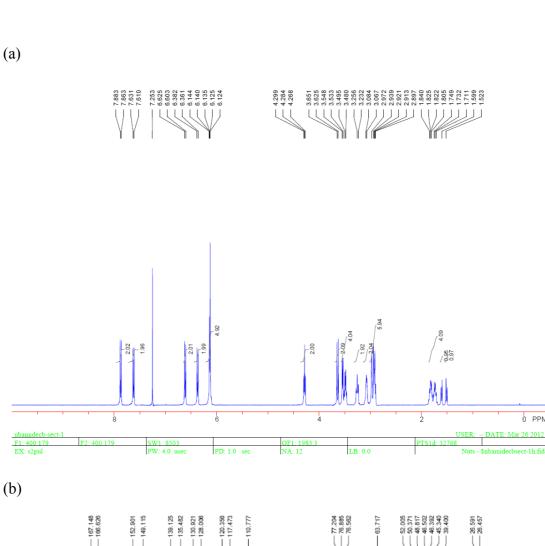
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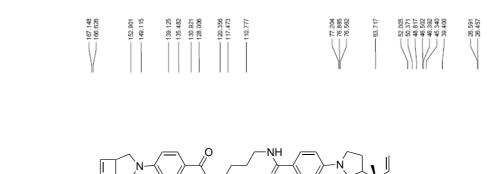
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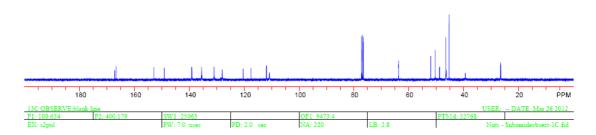
**Figure S2:** (a) Monomer conversion vs time for **4** (solid square) and **5** (open circle)  $(0 \, {}^{\circ}\text{C}, \text{THF-}d_8)$ ; (b) Second-order decay of **4** (solid square)  $(0 \, {}^{\circ}\text{C}, \text{THF-}d_8)$ .

80 100 120 140 160 180 200 220

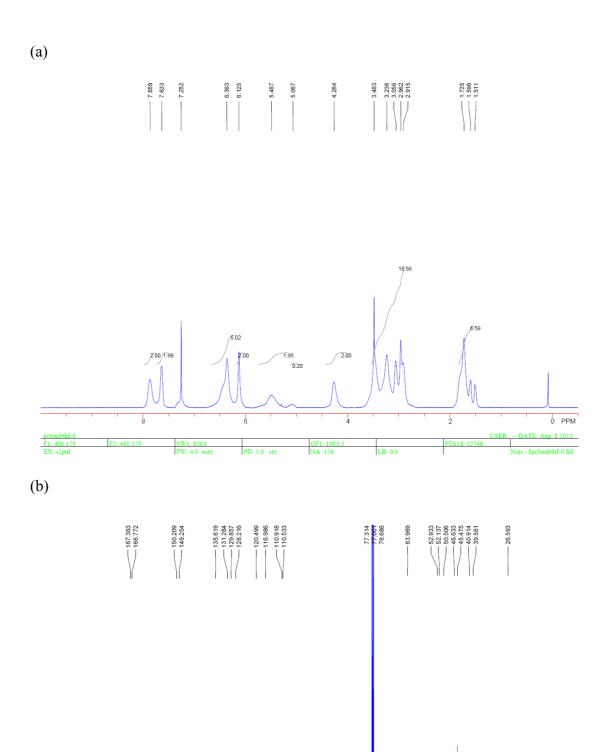
Time (min)







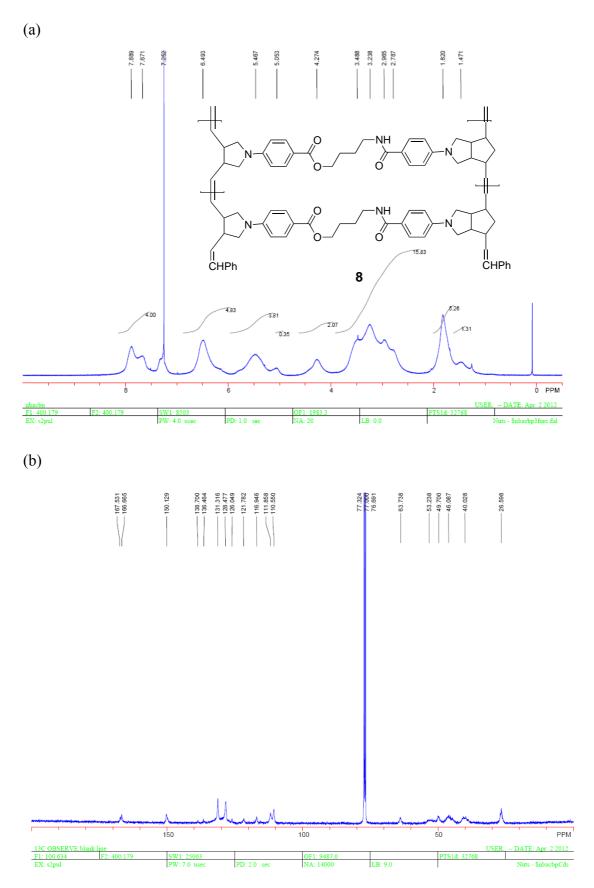
**Figure S3:** (a)  $^{1}$ H (400 MHz) and (b)  $^{13}$ C NMR (100 MHz) spectra of **9**.



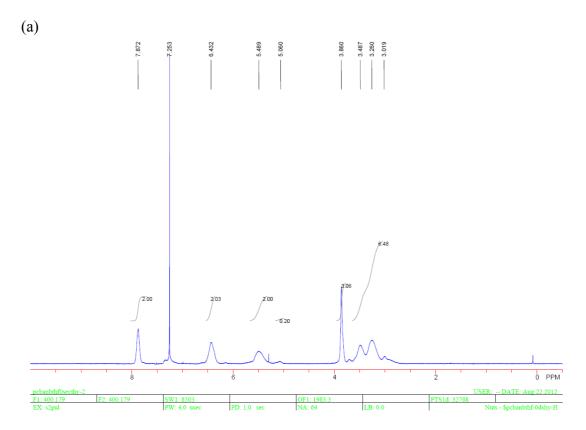
**Figure S4:** (a)  ${}^{1}$ H (400 MHz) and (b)  ${}^{13}$ C (100 MHz) NMR spectra of **14**.

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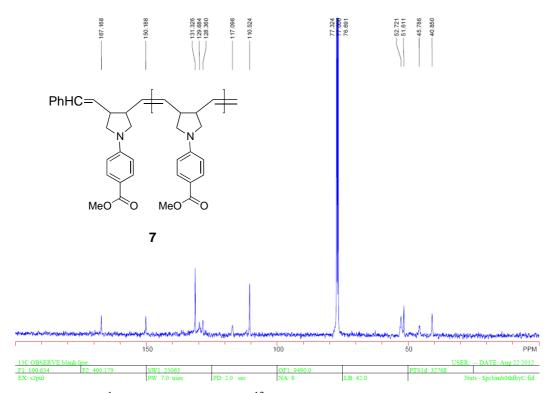
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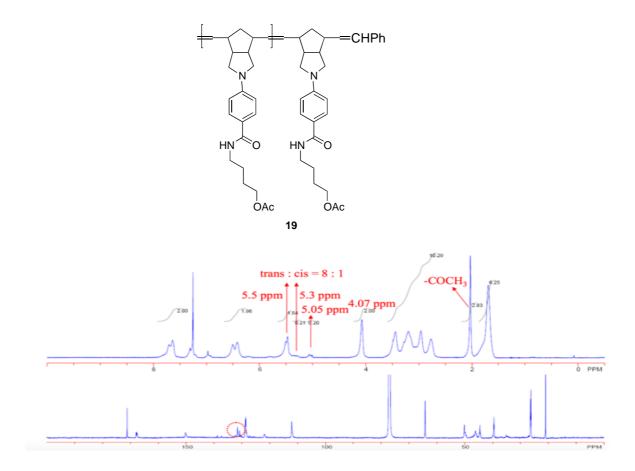
**Figure S5:** (a)  $^{1}$ H (400 MHz) and (b)  $^{13}$ C (100 MHz) NMR spectra of **8**.



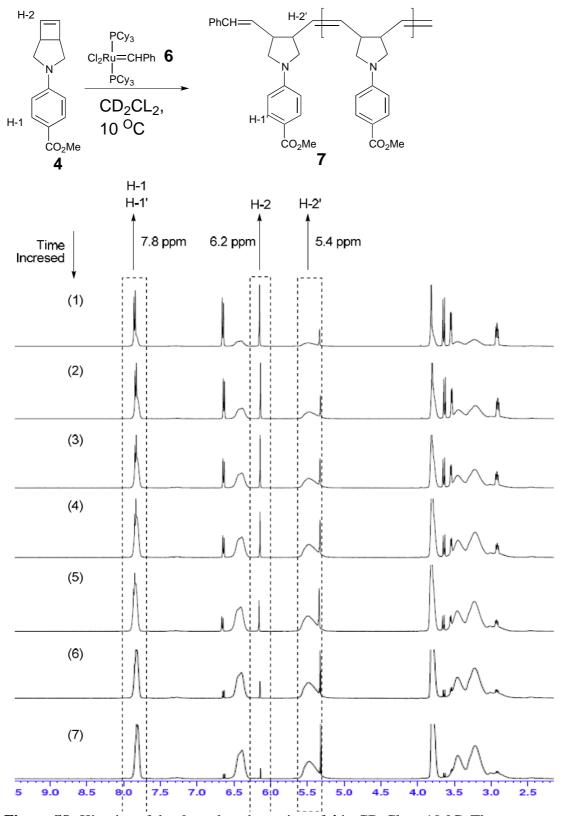




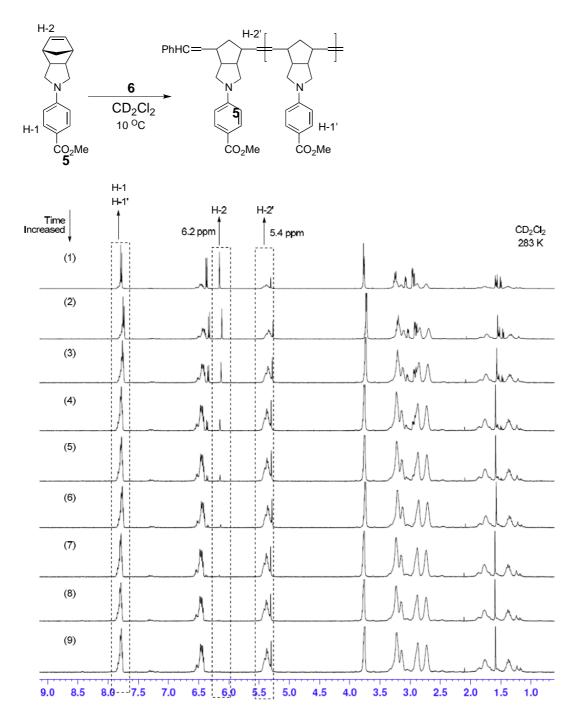
**Figure S6:** (a)  $^{1}$ H (400 MHz) and (b)  $^{13}$ C (100 MHz) NMR spectra of **7**.



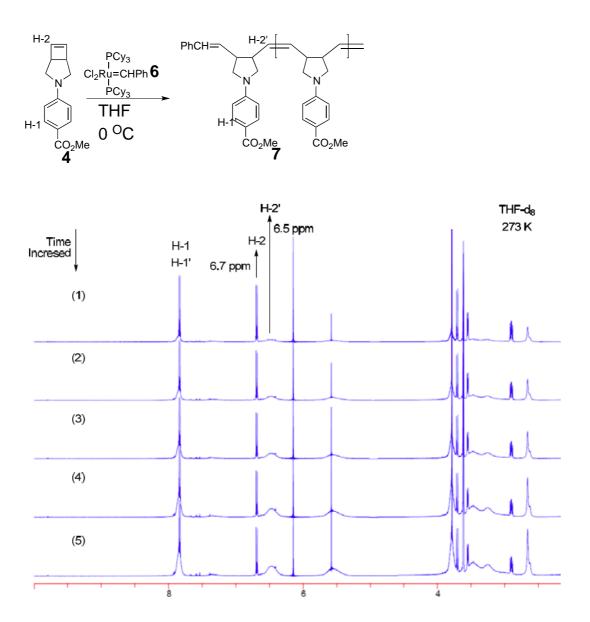
**Figure S7:** (a)  ${}^{1}$ H (400 MHz) and (b)  ${}^{13}$ C (100 MHz) NMR spectra of **19**.



**Figure S8:** Kinetics of the **6**-catalyzed reaction of **4** in CD<sub>2</sub>Cl<sub>2</sub> at 10 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every ten minutes.



**Figure S9:** Kinetics of the **6**-catalyzed reaction of **5** in CD<sub>2</sub>Cl<sub>2</sub> at 10 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every ten minutes.



**Figure S10**: Kinetics of the **6**-catalyzed reaction of **4** in THF at 0 °C The reaction was monitored by the decrease of the peak intensity for H-2 using the peaks for H-1 and H-1' as the internal reference. The spectra were recorded every twenty minutes.