## **Electronic Supplementary Information**

## Ethyleneglycol Tungsten Complexes of calix[6 and 8] arenes: Synthesis, Characterization and ROP of $\epsilon$ -caprolactone

Yuanzhuo Li,<sup>a</sup> Ke-Qing Zhao,<sup>a</sup> Chun Feng, <sup>a</sup> Mark R.J. Elsegood,<sup>b</sup> Timothy J. Prior,<sup>c</sup> Xinsen Sun,<sup>c</sup> and Carl Redshaw<sup>a,c\*</sup>

Figure S1. Crystals of sample 3



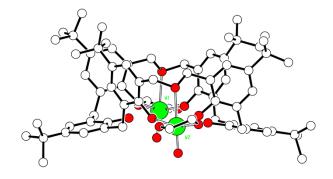


Figure S2. Side view of 5

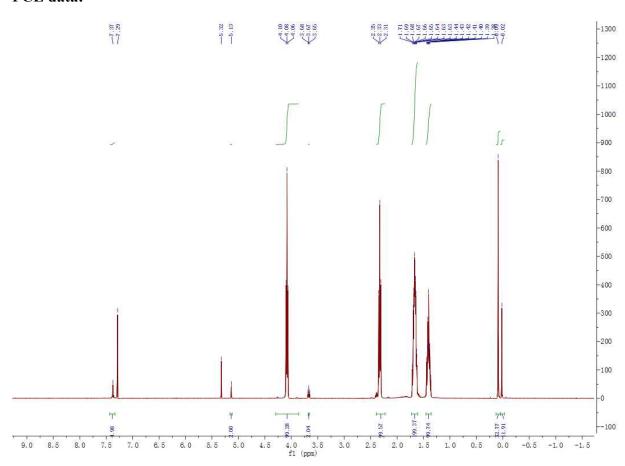
<sup>&</sup>lt;sup>a</sup> College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610066, China.

<sup>&</sup>lt;sup>b</sup> Chemistry Department, Loughborough University, Leicestershire, LE11 3TU, UK

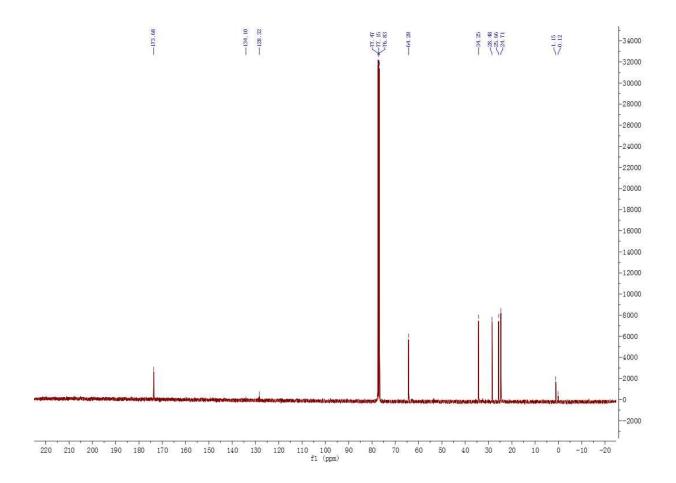
<sup>&</sup>lt;sup>c</sup> Department of Chemistry, University of Hull, Hull, HU6 7RX, UK



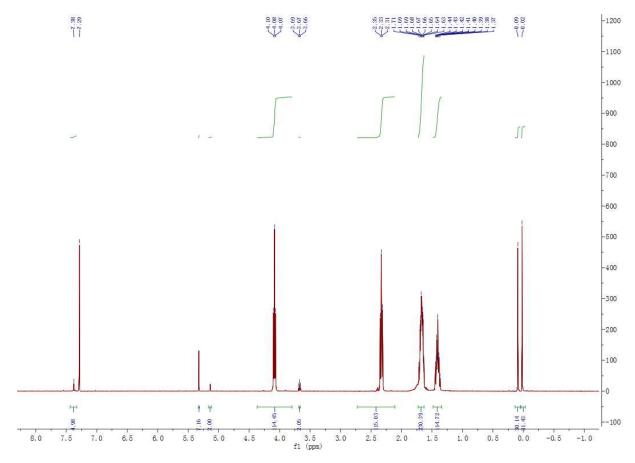
## PCL data:



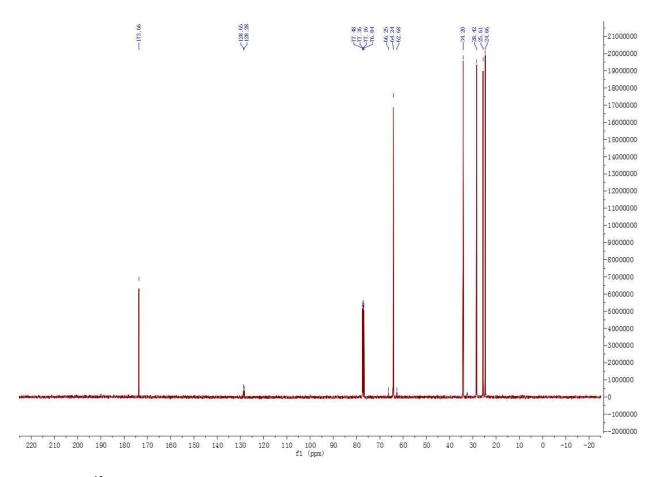
**Figure S3**. <sup>1</sup>H NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre- catalyst **1** with BnOH.



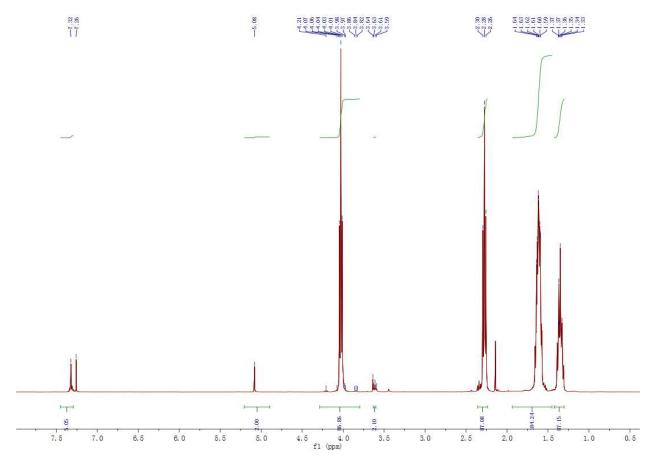
**Figure S4**. <sup>13</sup>C NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre- catalyst **1** with BnOH.



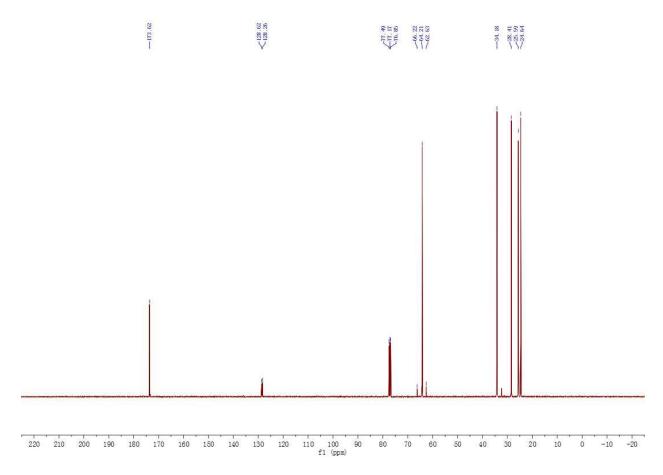
**Figure S5**. <sup>1</sup>H NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **2** with BnOH.



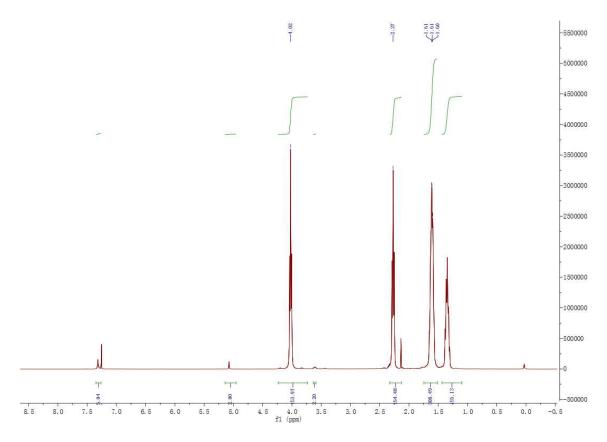
**Figure S6**. <sup>13</sup>C NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **2** with BnOH.



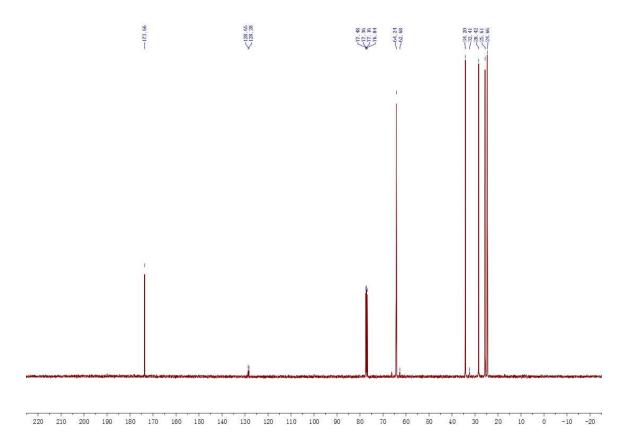
**Figure S7**. <sup>1</sup>H NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **5** with BnOH.



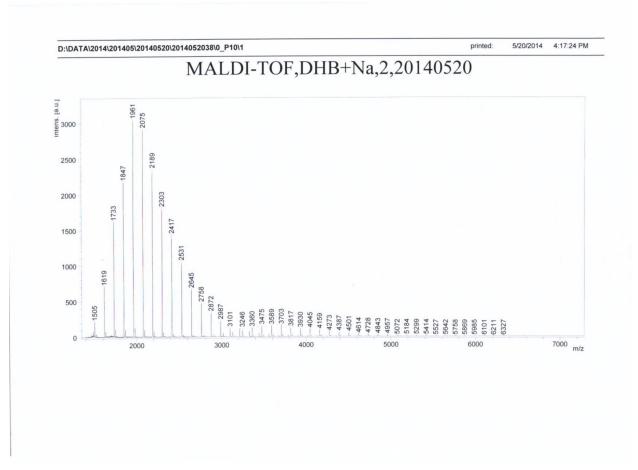
**Figure S8**. <sup>13</sup>C NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **5** with BnOH.



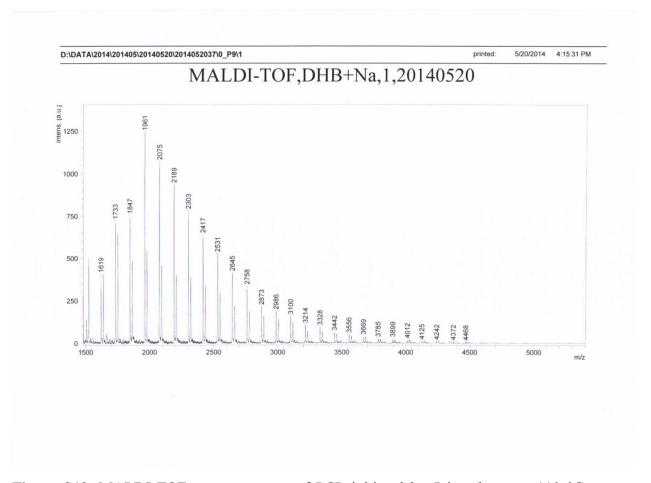
**Figure S9**. <sup>1</sup>H NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **6** with BnOH.



**Figure S10**. <sup>13</sup>C NMR spectrum of PCL in CDCl<sub>3</sub> catalyzed by tungsten pre-catalyst **6** with BnOH.

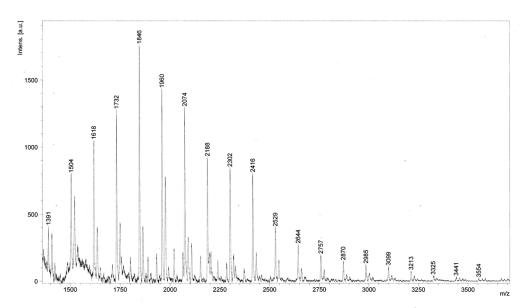


**Figure S11.** MALDI-TOF mass spectrum of PCL initiated by **2** in toluene at 110 °C, [CL]/[2]/[BnOH] = 400:1:1 (Table 2, entry 3). 114.14\*n + 108 + 1 + 22 for BnO-(CL)n-H+Na



**Figure S12.** MALDI-TOF mass spectrum of PCL initiated by **5** in toluene at 110 °C, [CL]/[5]/[BnOH] = 400:1:1 (Table 2, entry 5). 114.14\*n + 108 + 1 + 22 for BnO-(CL)n-H+Na

## MALDI-TOF,CCA,w4,20140617



**Figure S13.** MALDI-TOF mass spectrum of PCL initiated by **6** in toluene at 110 °C, [CL]/[**6**]/[BnOH] =400:1:1 (Table 2, entry 6). 114.14\*n + 108 + 1 + 22 for BnO-(CL)n-H+Na