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**Ether-substituted group 4 metallocene complexes: cytostatic effects and applications in ethylene polymerization §**

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**Supplementary Material**

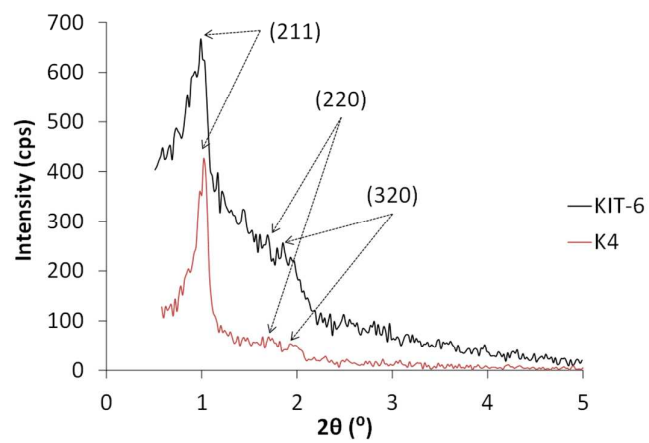
**Table S1. Crystallographic data of 8 and 4a.**

| Compound                                            | 8                                                                 | 4a                                                  |
|-----------------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------|
| Empirical formula                                   | C <sub>22</sub> H <sub>34</sub> Cl <sub>2</sub> O <sub>4</sub> Zr | C <sub>14</sub> H <sub>15</sub> ClO <sub>2</sub> Ti |
| Molecular weight (g/mol)                            | 524.61                                                            | 298.61                                              |
| Temperature (K)                                     | 100(2)                                                            | 293(2)                                              |
| Wavelength (Å)                                      | 0.71069                                                           | 0.71073                                             |
| Crystal system                                      | Monoclinic                                                        | Monoclinic                                          |
| Space group                                         | C2/c                                                              | P2 <sub>1</sub> /n                                  |
| <i>a</i> (pm)                                       | 2557.7(5)                                                         | 650.00(2)                                           |
| <i>b</i> (pm)                                       | 666.2(2)                                                          | 1486.00(5)                                          |
| <i>c</i> (pm)                                       | 1400.1(3)                                                         | 1397.90(5)                                          |
| <i>α</i> (°)                                        | 90.00                                                             | 90                                                  |
| <i>β</i> (°)                                        | 94.620(4)                                                         | 101.328(4)                                          |
| <i>γ</i> (°)                                        | 90.00                                                             | 90                                                  |
| Volume (Å <sup>3</sup> )                            | 2377.7(8)                                                         | 1.32393(8)                                          |
| <i>Z</i>                                            | 4                                                                 | 4                                                   |
| Calculated density (mg/m <sup>3</sup> )             | 1.465                                                             | 1.498                                               |
| Absorption coefficient <i>μ</i> (mm <sup>-1</sup> ) | 0.712                                                             | 0.838                                               |

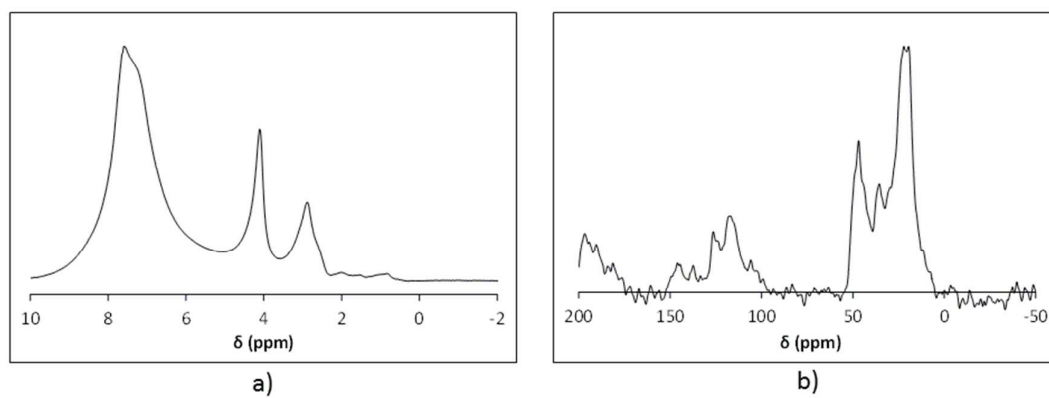
|                                                                              |                                                                    |                                                                    |
|------------------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| <b>F(000)</b>                                                                | 1088                                                               | 616                                                                |
| <b>Crystal size (mm)</b>                                                     | $0.20 \times 0.14 \times 0.12$                                     | $0.08 \times 0.06 \times 0.03$                                     |
| <b><math>\theta</math> range (°)</b>                                         | 2.92 a 20.89                                                       | 2.02 a 26.37                                                       |
| <b><i>hkl</i> ranges</b>                                                     | $-31 \leq h \leq 31$<br>$-5 \leq k \leq 8$<br>$-15 \leq l \leq 17$ | $-8 \leq h \leq 8$<br>$-18 \leq k \leq 18$<br>$-17 \leq l \leq 17$ |
| <b>Collected reflections</b>                                                 | 6807                                                               | 74651                                                              |
| <b>Independent reflections</b>                                               | 2424 [ $R_{\text{int}} = 0.0519$ ]                                 | 2711 [ $R_{\text{int}} = 0.1265$ ]                                 |
| <b>Completeness</b>                                                          | 99.5 % ( $\theta = 20.89^\circ$ )                                  | 100 % ( $\theta = 26.37^\circ$ )                                   |
| <b>Maximum and minimum transition</b>                                        | 1.000 and 0.820                                                    | 1 and 0.97588                                                      |
| <b>Refinement method</b>                                                     | Least squares on $F^2$                                             | Least squares on $F^2$                                             |
| <b>Data / Restraints / Parameters</b>                                        | 2424 / 0 / 136                                                     | 2711 / 0 / 178                                                     |
| <b>Goodness-of-fit on <math>F^2</math></b>                                   | 1.052                                                              | 1.009                                                              |
| <b>Final R indices [<math>I &gt; 2\sigma(I)</math>]</b>                      | $R_1 = 0.0531$<br>$wR_2 = 0.1307$                                  | $R_1 = 0.0547$<br>$wR_2 = 0.1343$                                  |
| <b>Final R indices (all data)</b>                                            | $R_1 = 0.0683$<br>$wR_2 = 0.1409$                                  | $R_1 = 0.1011$<br>$wR_2 = 0.1618$                                  |
| <b>Largest diffraction peak and hole (<math>e \cdot \text{\AA}^3</math>)</b> | 0.677 and -0.912                                                   | 0.845 and -0.207                                                   |

**Table S2. Data obtained by X-ray diffraction for materials KIT-6 and K4-K7.**

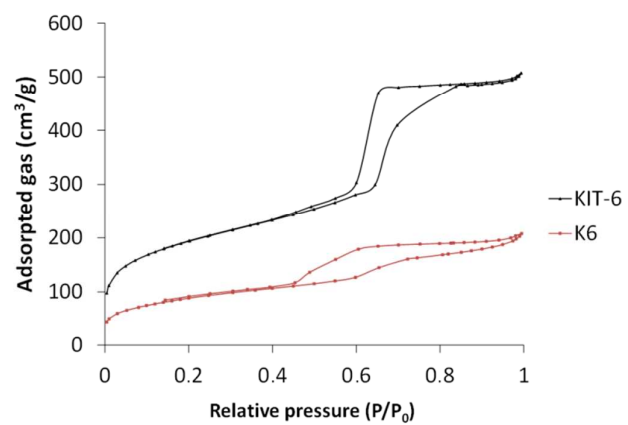
| <b>Material</b> | <b>(<i>hkl</i>)</b> | <b>2<math>\theta</math> (°)</b> | <b><math>d_{hkl}</math> (Å)</b> | <b><math>a_0</math> (Å)</b> |
|-----------------|---------------------|---------------------------------|---------------------------------|-----------------------------|
| KIT-6           | (211)               | 0.99                            | 89                              | 103.10                      |
|                 | (220)               | 1.65                            | -                               |                             |
|                 | (320)               | 1.91                            | 46                              |                             |
| <b>K4</b>       | (211)               | 1.01                            | 87                              | 100.71                      |
|                 | (220)               | 1.64                            | -                               |                             |
|                 | (320)               | 1.99                            | 44                              |                             |
| <b>K5</b>       | (211)               | 0.99                            | 89                              | 103.20                      |
|                 | (220)               | 1.62                            | -                               |                             |
|                 | (320)               | 1.98                            | -                               |                             |
| <b>K6</b>       | (211)               | 0.99                            | 89                              | 102.47                      |
|                 | (220)               | 1.66                            | -                               |                             |
|                 | (320)               | 1.94                            | -                               |                             |
| <b>K7</b>       | (211)               | 0.99                            | 89                              | 102.79                      |
|                 | (220)               | 1.64                            | -                               |                             |
|                 | (320)               | 1.94                            | -                               |                             |



**Figure S1. X-ray diffractograms of KIT-6 and K4.**



**Figure S2.  $^1\text{H}$  MAS NMR spectrum of K5 (a) and  $^{13}\text{C}$  CP MAS NMR spectrum of K4 (b).**



**Figure S3. Adsorption-desorption isotherms of KIT-6 and K6.**