

Electronic Supplementary Information

**Thorium(IV) trialkyl complexes of non-carbocyclic  
ligands as highly active isoprene polymerisation  
catalysts**

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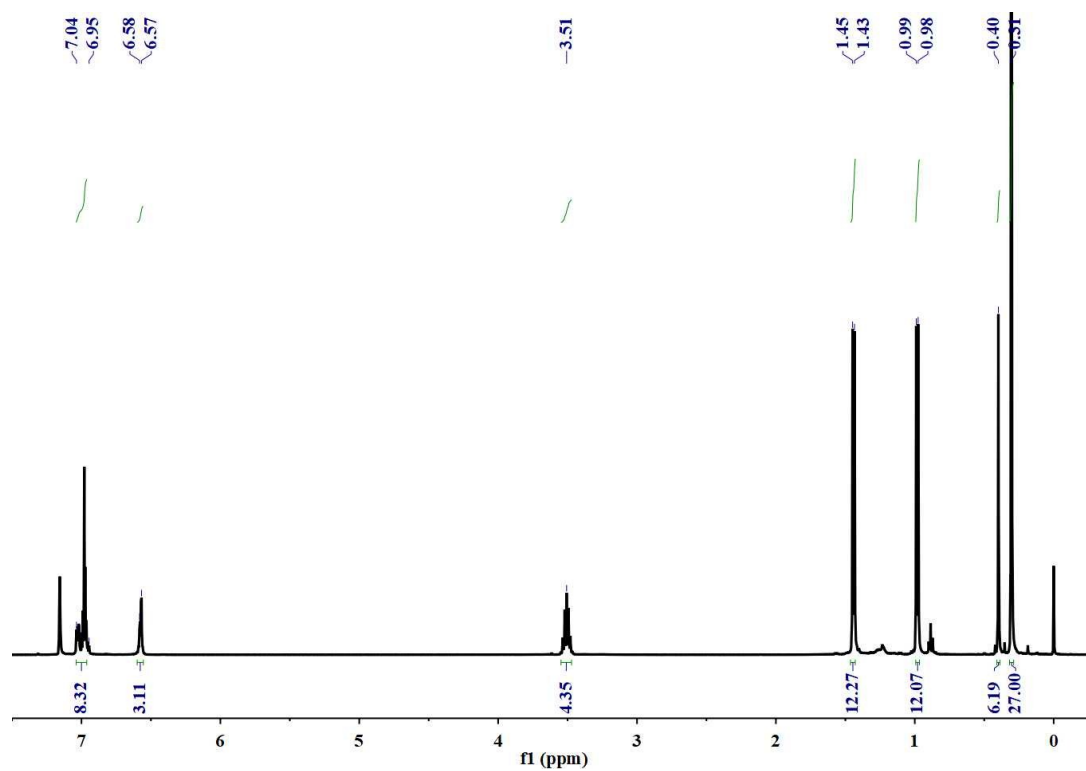


Figure S1.  $^1\text{H}$  NMR spectrum (400 MHz) of complex 1 in  $\text{C}_6\text{D}_6$  at 25 °C.

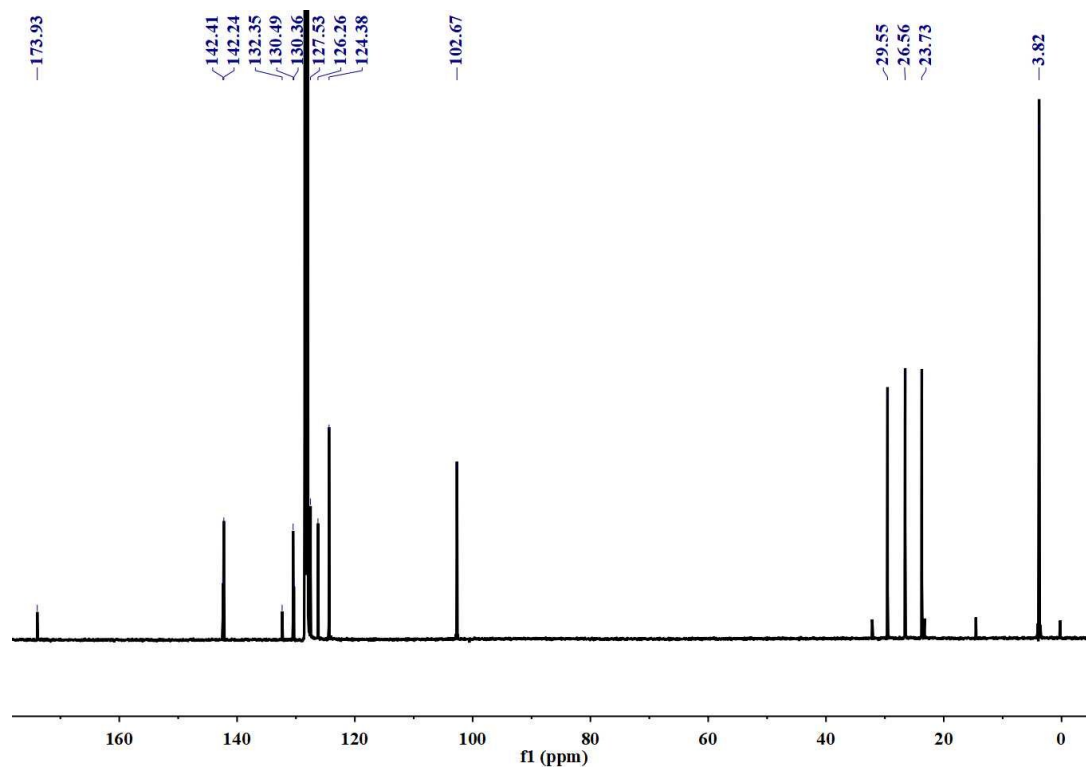
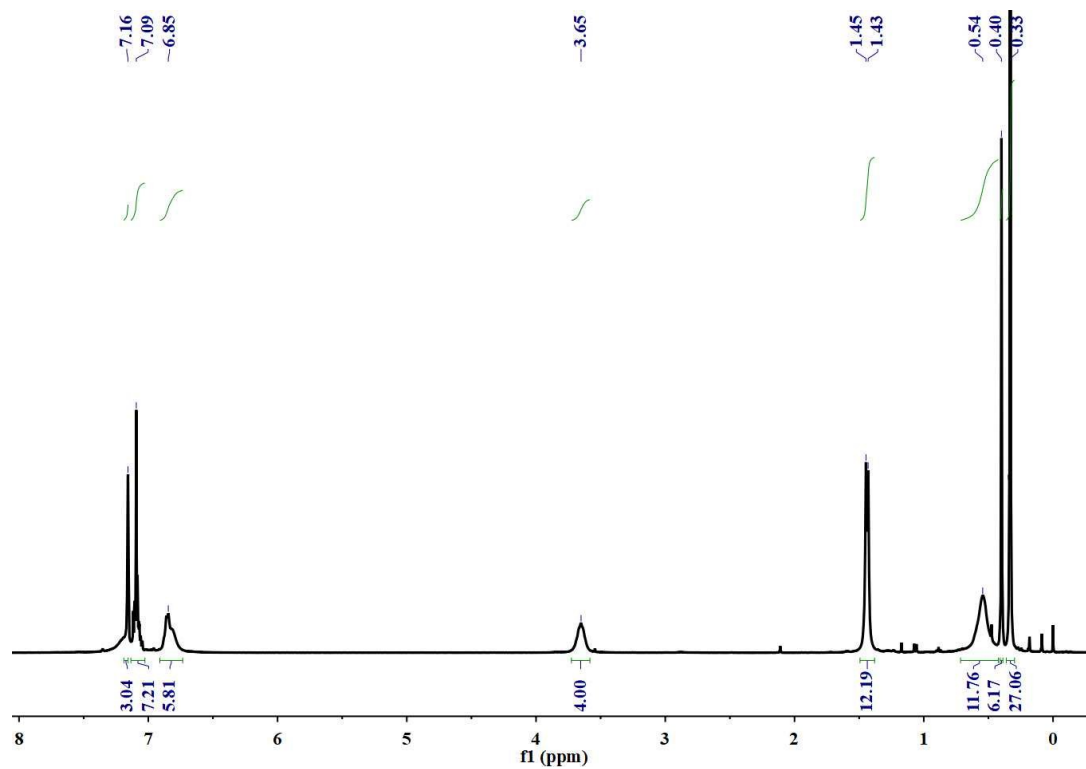
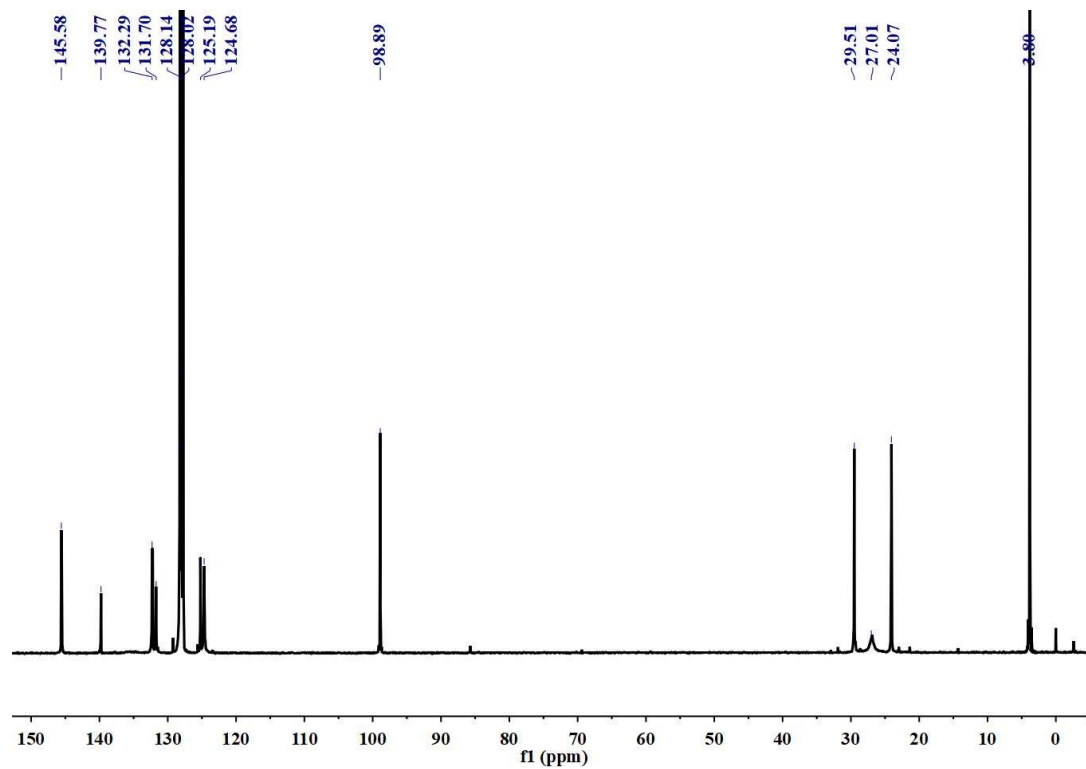


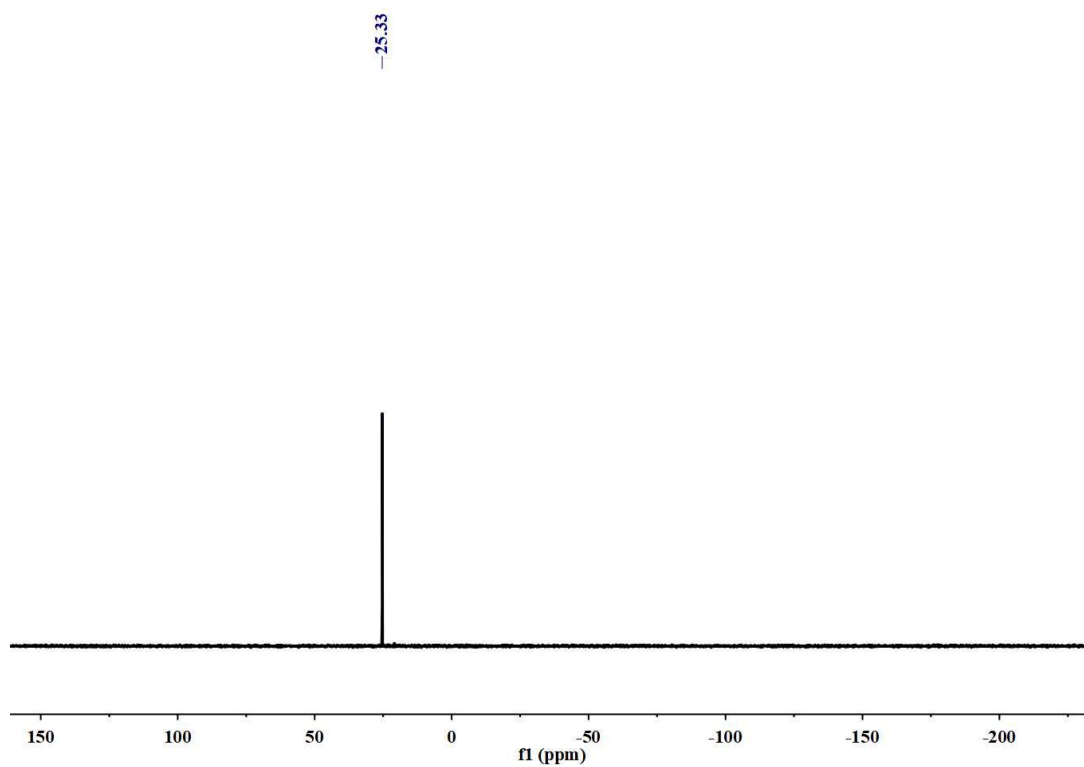
Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz) of complex 1 in  $\text{C}_6\text{D}_6$  at 25 °C.



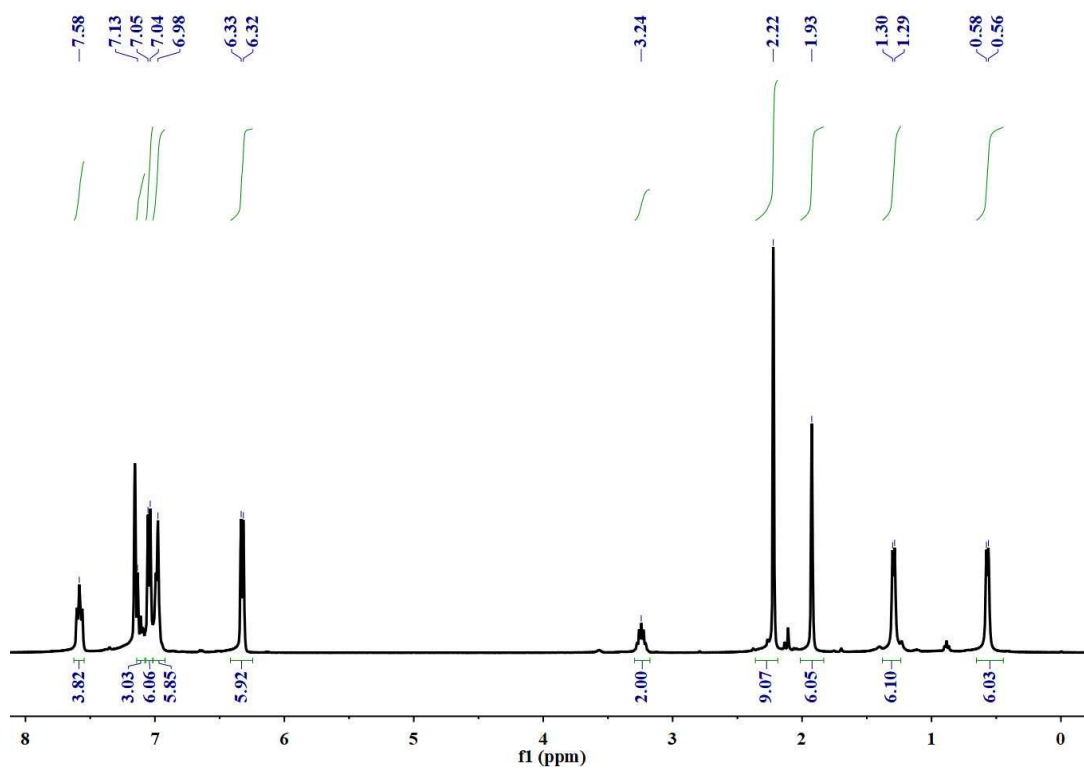
**Figure S3.**  $^1\text{H}$  NMR spectrum (400 MHz) of complex **2** in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ .



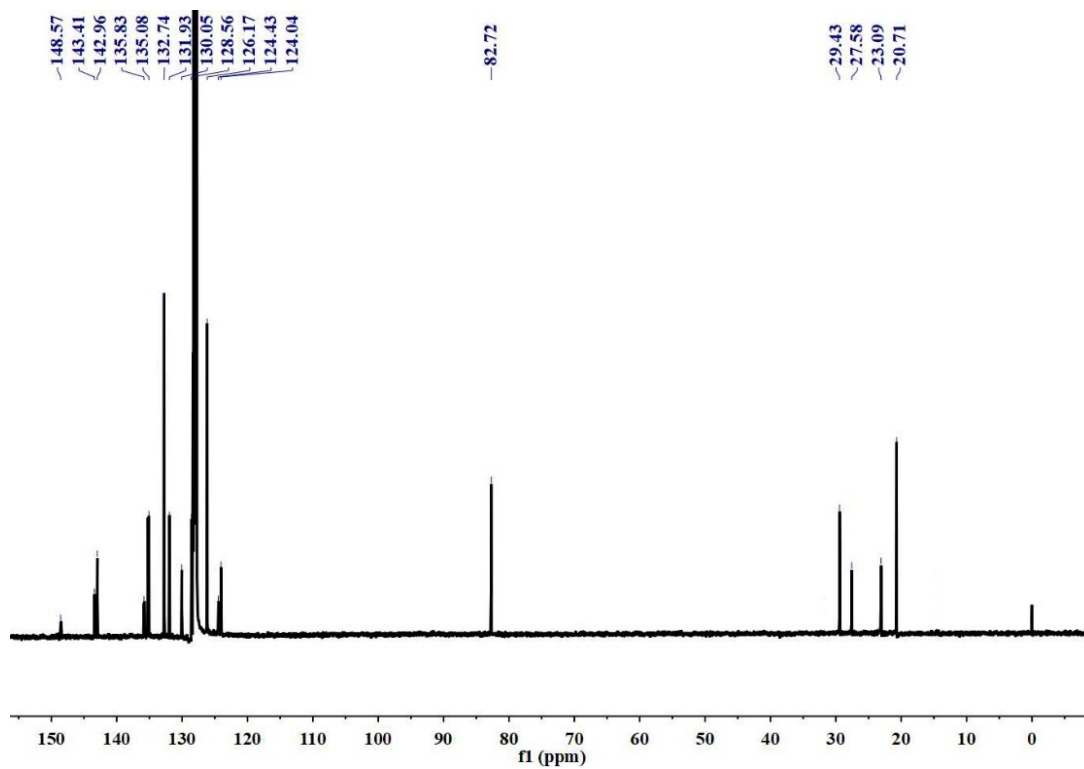
**Figure S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz) of complex **2** in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$ .



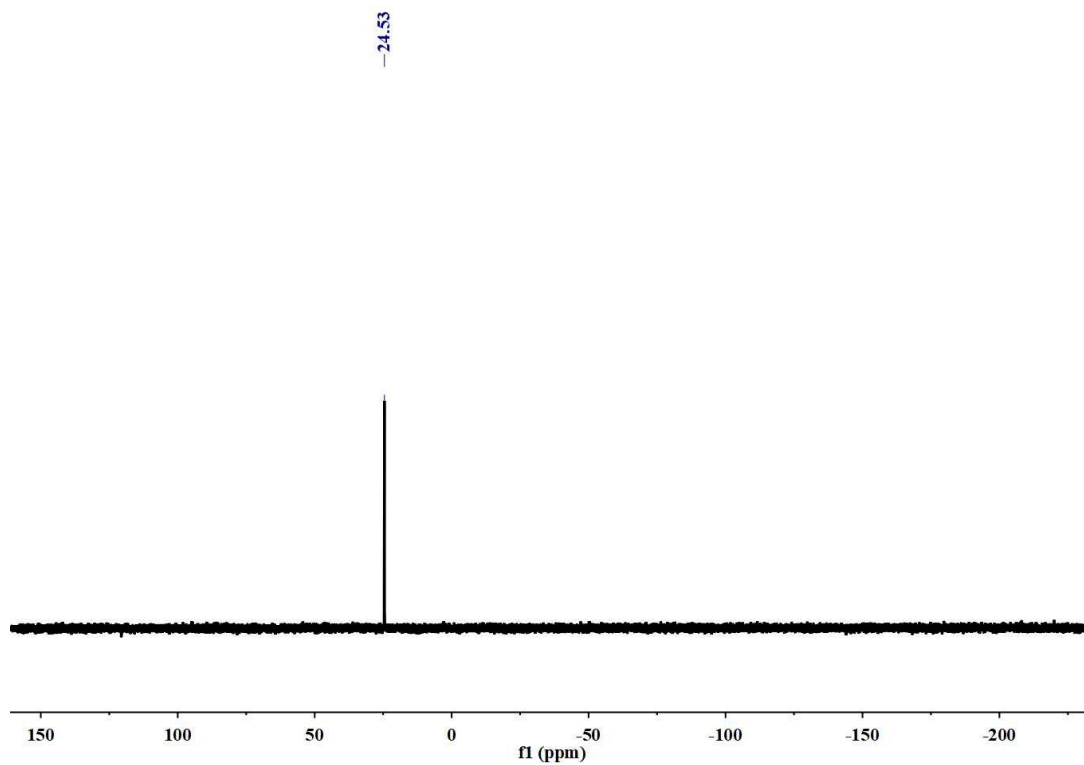
**Figure S5.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz) of complex **2** in  $\text{C}_6\text{D}_6$  at 25 °C.



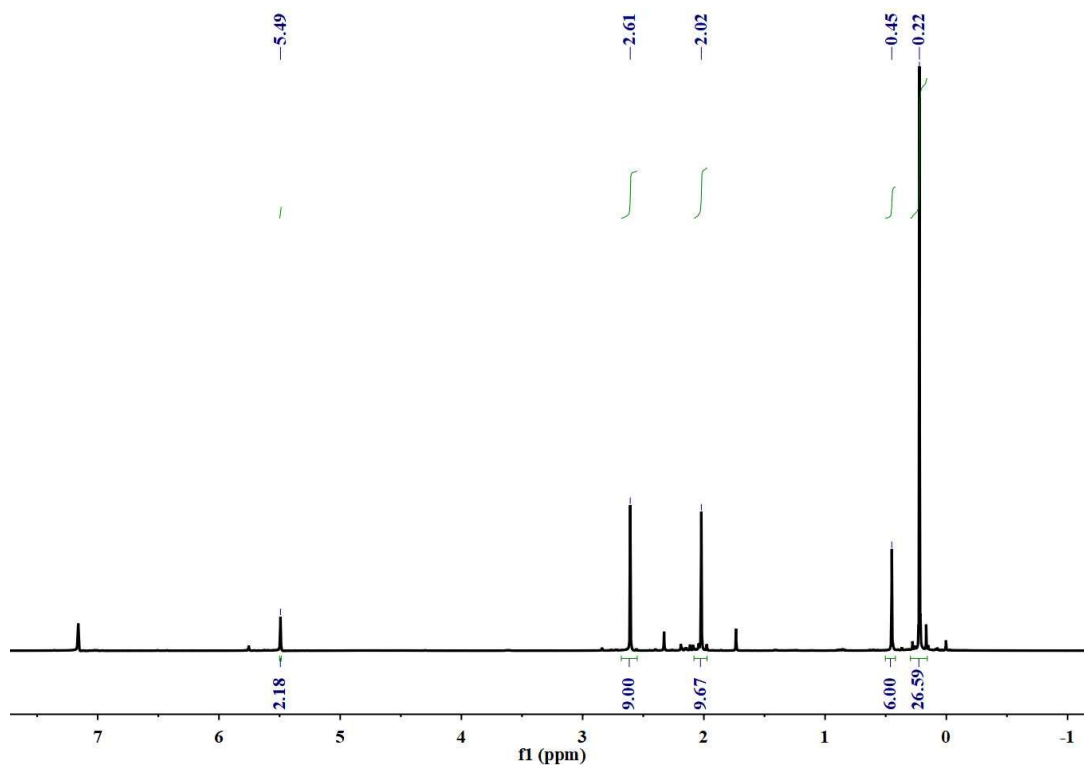
**Figure S6.**  $^1\text{H}$  NMR spectrum (400 MHz) of complex **3** in  $\text{C}_6\text{D}_6$  at 25 °C.



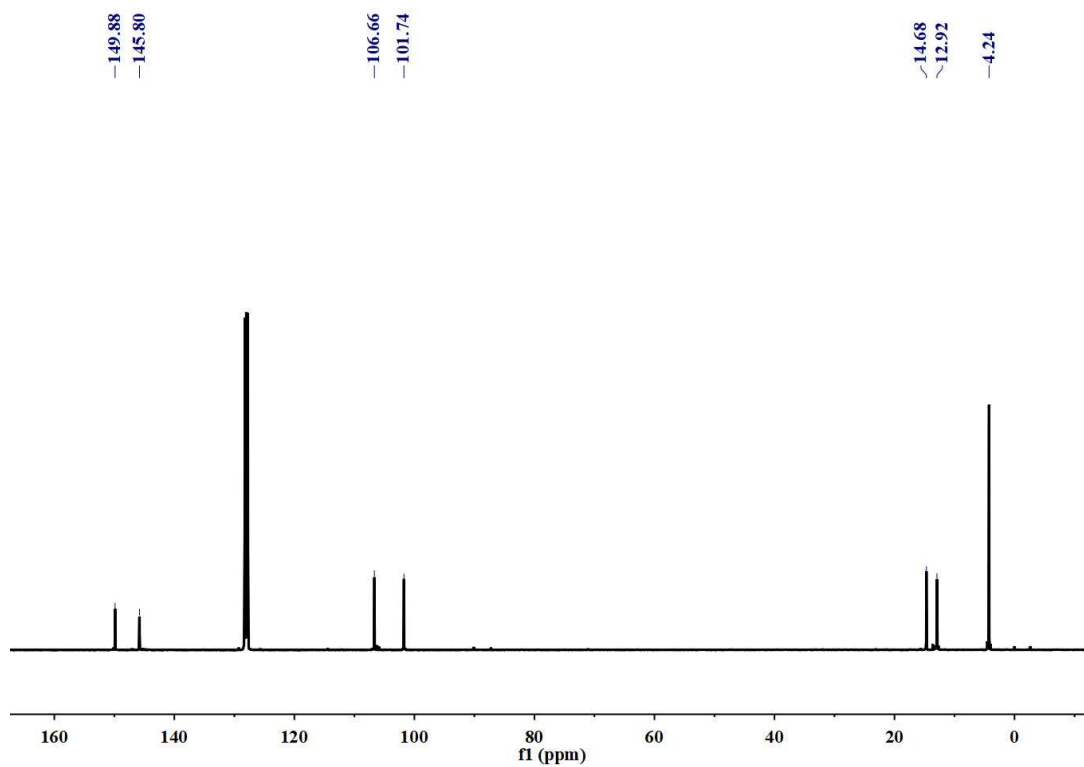
**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz) of complex **3** in  $\text{C}_6\text{D}_6$  at 25 °C.



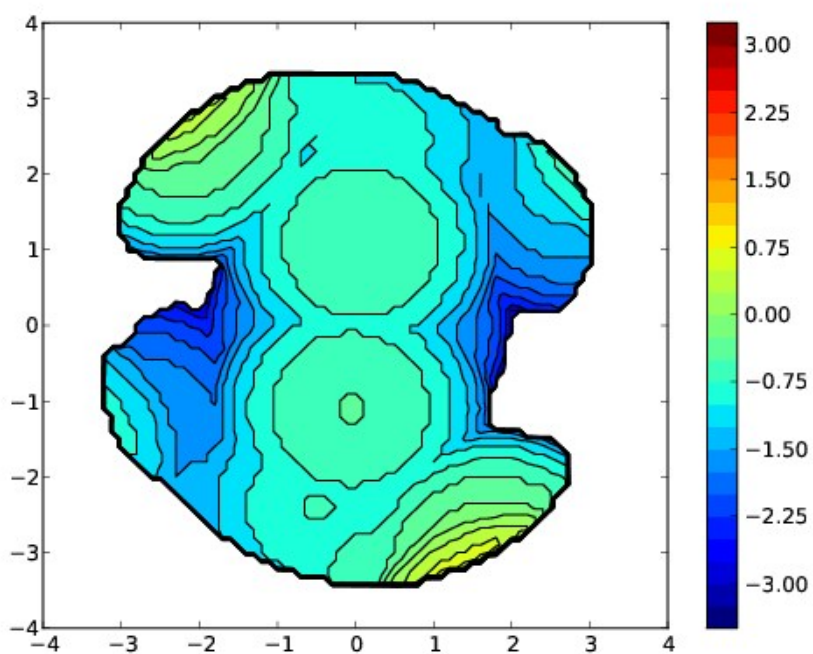
**Figure S8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162 MHz) of complex **3** in  $\text{C}_6\text{D}_6$  at 25 °C.



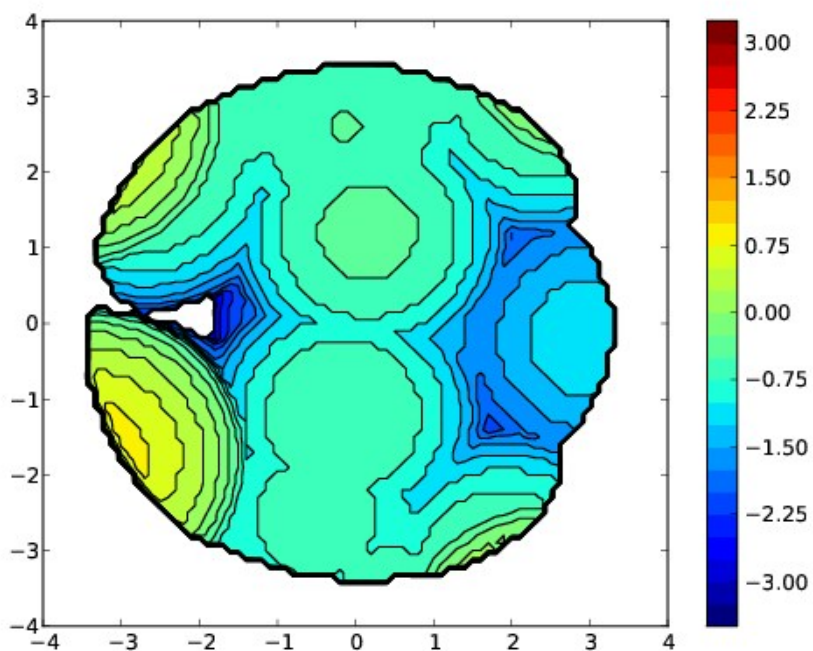
**Figure S9.**  $^1\text{H}$  NMR spectrum (400 MHz) of complex **4** in  $\text{C}_6\text{D}_6$  at 25 °C.



**Figure S10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz) of complex **4** in  $\text{C}_6\text{D}_6$  at 25 °C.



**Figure S11.** The steric map of complex 1



**Figure S12.** The steric map of complex 2

## Experimental details for the polymerization kinetics studies

The catalyst system of complex **1**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al<sup>i</sup>Bu<sub>3</sub> and complex **2**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al<sup>i</sup>Bu<sub>3</sub> were selected for investigation into the kinetics of the polymerization of isoprene.

Experimental details: Under a N<sub>2</sub> atmosphere at 25 °C, isoprene (0.34 g, 5 mmol) and a deuterated benzene solution (1.5 mL) of Al<sup>i</sup>Bu<sub>3</sub> (25 μmol) were added into a 5 mL flask containing a magnetic stir bar. A deuterated benzene solution (1 mL) of complex **1** (4.65 mg, 5 μmol) or complex **2** (5.12 mg, 5 μmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (9.2 mg, 10 μmol) was added quickly by an injector, the conversion of isoprene with time was monitored by <sup>1</sup>H NMR spectroscopy.