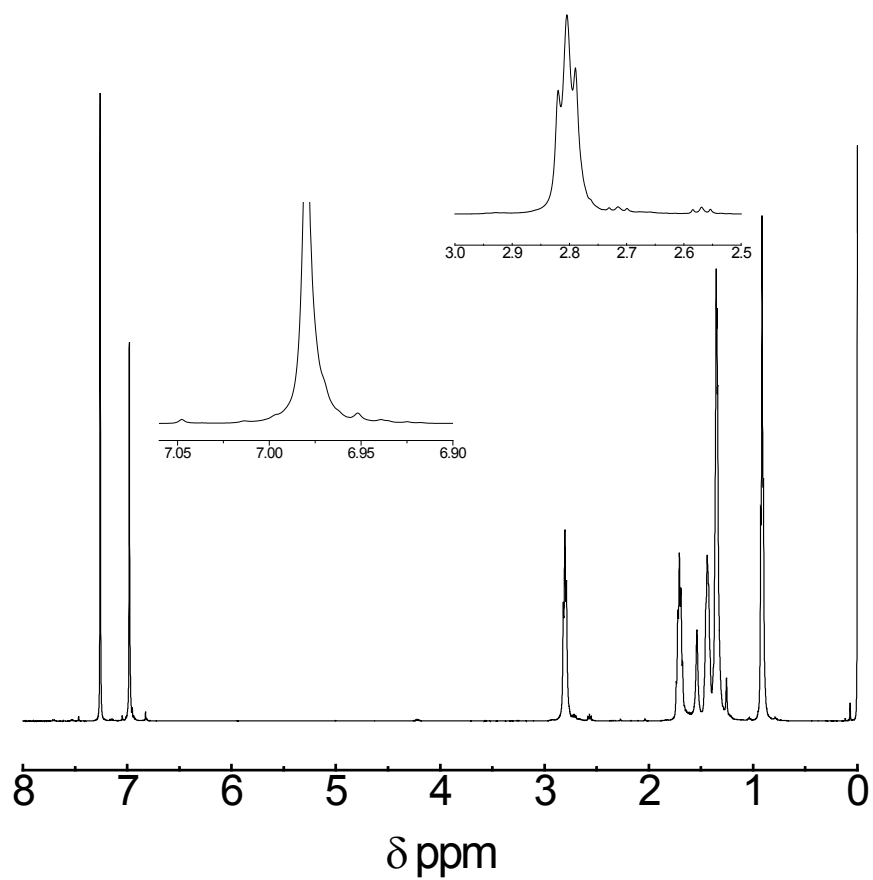


**Supporting Information for:**

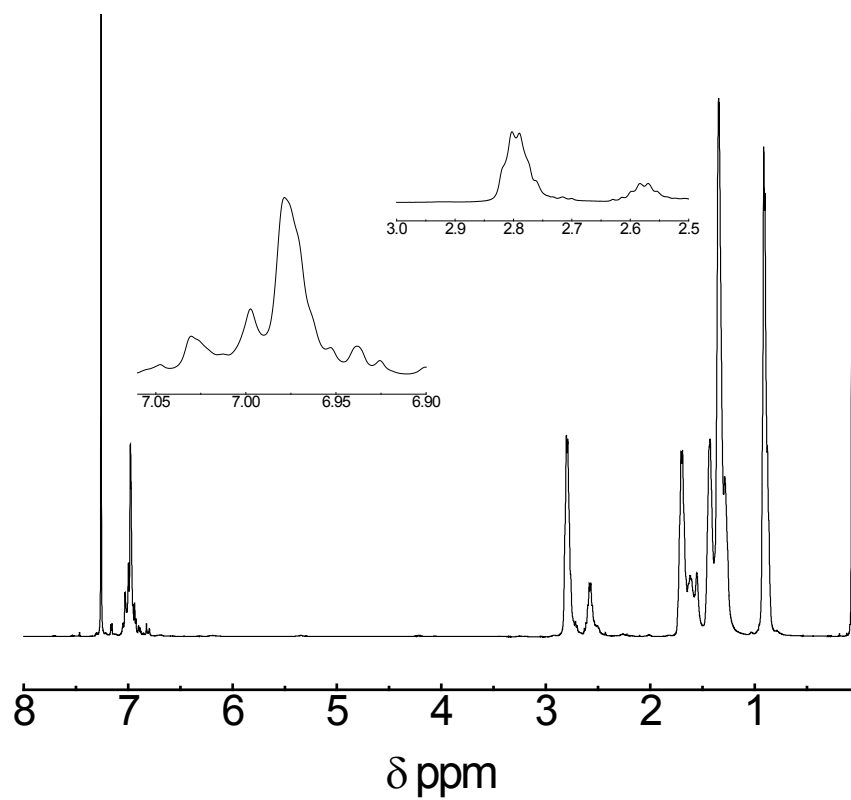
# Role of the Transition Metal in Grignard Metathesis Polymerization (GRIM) of 3-Hexylthiophene

*Mahesh P. Bhatt,<sup>a</sup> Harsha D. Magurudeniya,<sup>a</sup> Prakash Sista,<sup>a</sup> Elena E. Sheina,<sup>b</sup> Malika Jeffries-  
EL,<sup>c</sup> Benjamin G. Janesko,<sup>d\*</sup> Richard D. McCullough,<sup>e</sup> and Mihaela C. Stefan<sup>a,\*</sup>*

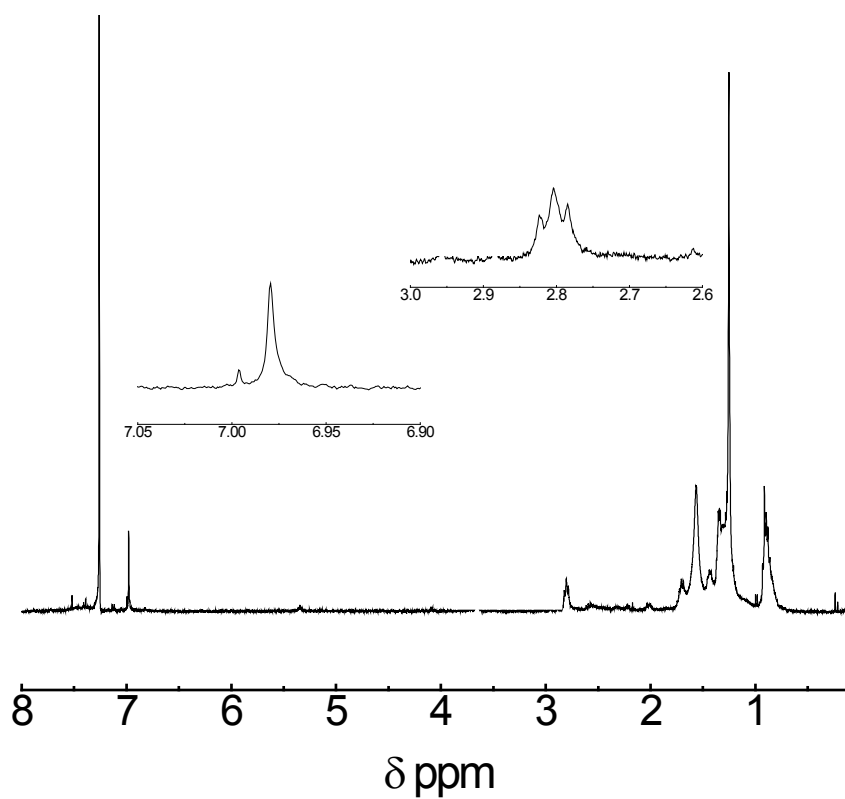
E-mail: [mci071000@utdallas.edu](mailto:mci071000@utdallas.edu)



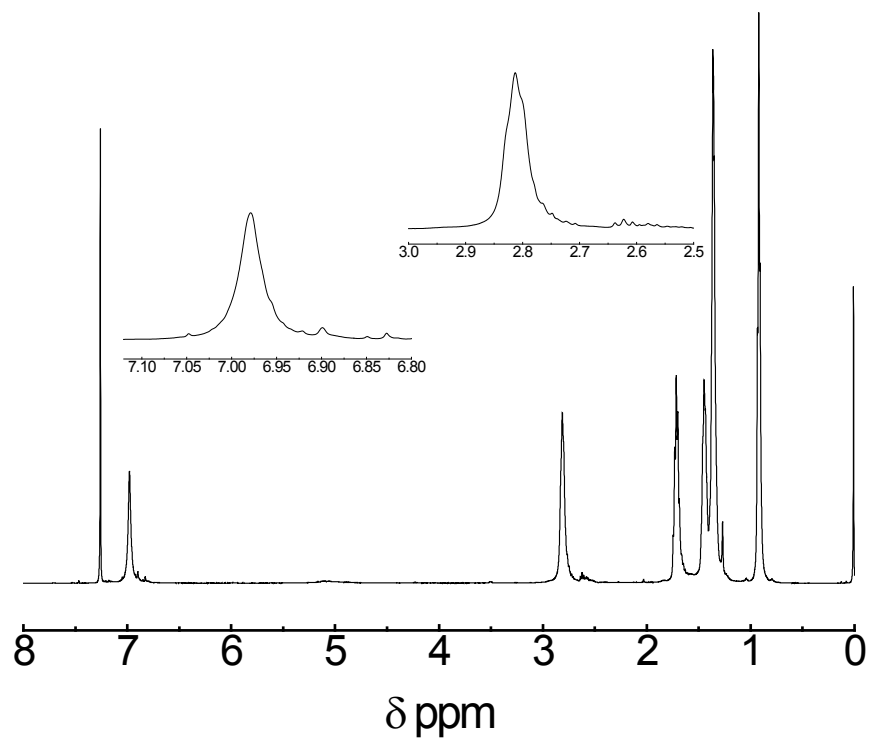
**Figure S1.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) synthesized by GRIM of 2,5-dibromo-3-hexylthiophene with Ni(dppe)Cl<sub>2</sub> as a catalyst.



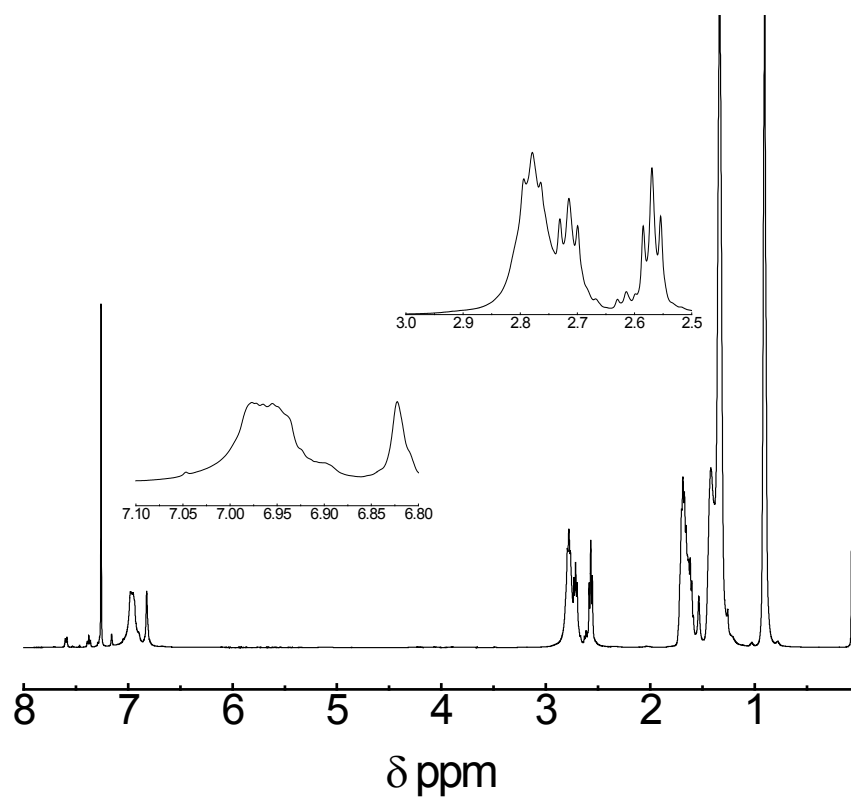
**Figure S2.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) synthesized by GRIM of 2,5-dibromo-3-hexylthiophene with Pd(dppe)Cl<sub>2</sub> as a catalyst.



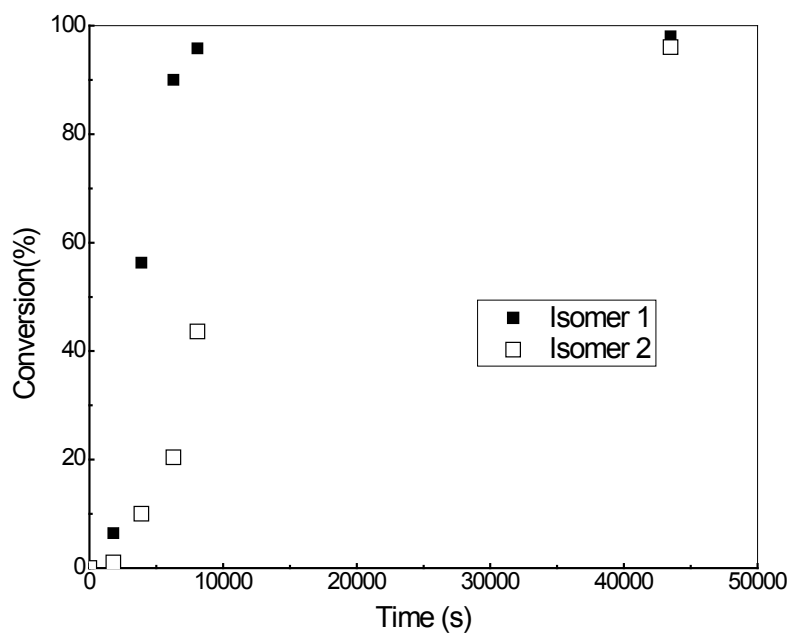
**Figure S3.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) synthesized by GRIM of 2,5-dibromo-3-hexylthiophene with Pt(dppe)Cl<sub>2</sub> as a catalyst.



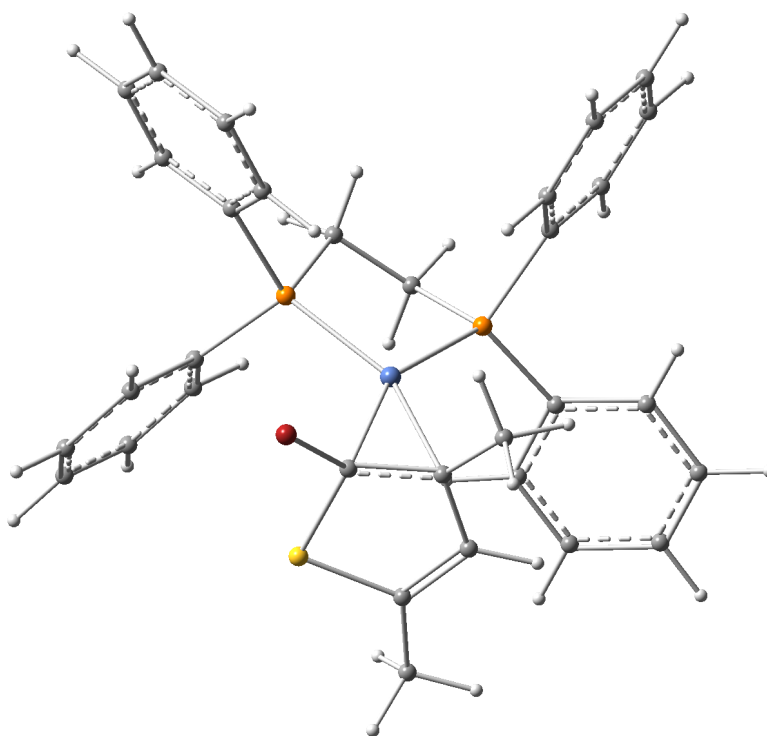
**Figure S4.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) synthesized by GRIM of 2-bromo-5-iodo-3-hexylthiophene with Ni(dppe)Cl<sub>2</sub> as a catalyst.



**Figure S5.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) synthesized by GRIM of 2-bromo-5-iodo-3-hexylthiophene with Pd(dppe)Cl<sub>2</sub> as a catalyst.

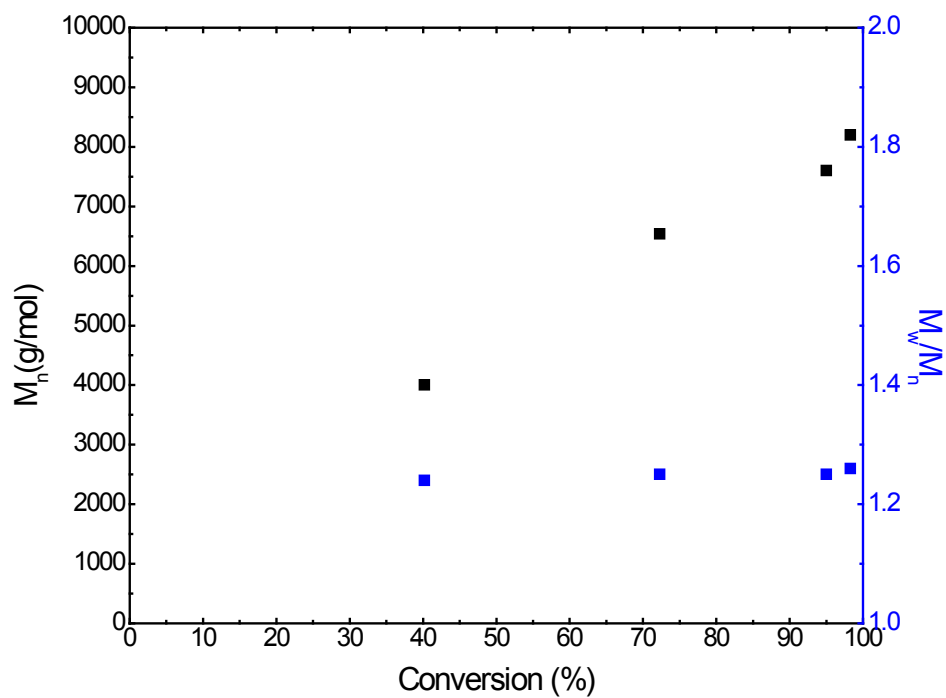


**Figure S6.** Conversion vs time plot for GRIM polymerization of 2,5-dibromo-3-hexylthiophene with Pd(dppe)Cl<sub>2</sub> as a catalyst. [DBHT]<sub>0</sub>=0.1 mol/L; [Pd(dppe)Cl<sub>2</sub>]<sub>0</sub>=0.0015 mol/L; temp=45 °C

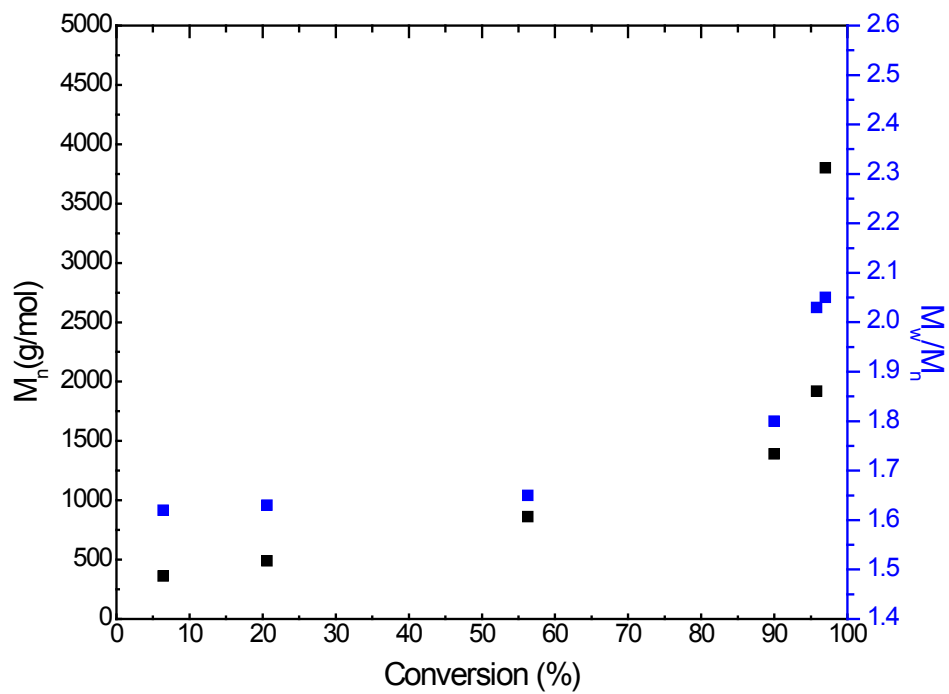


**Figure S7.** Calculated geometry of associated pair between Ni(0)(dppe) and the 2-bromo-(3,5)-dimethylthiophene model for the growing polythiophene chain. Spheres denote atoms with color code white(H), gray(C), yellow(S), orange(P),red(Br), blue(Ni).

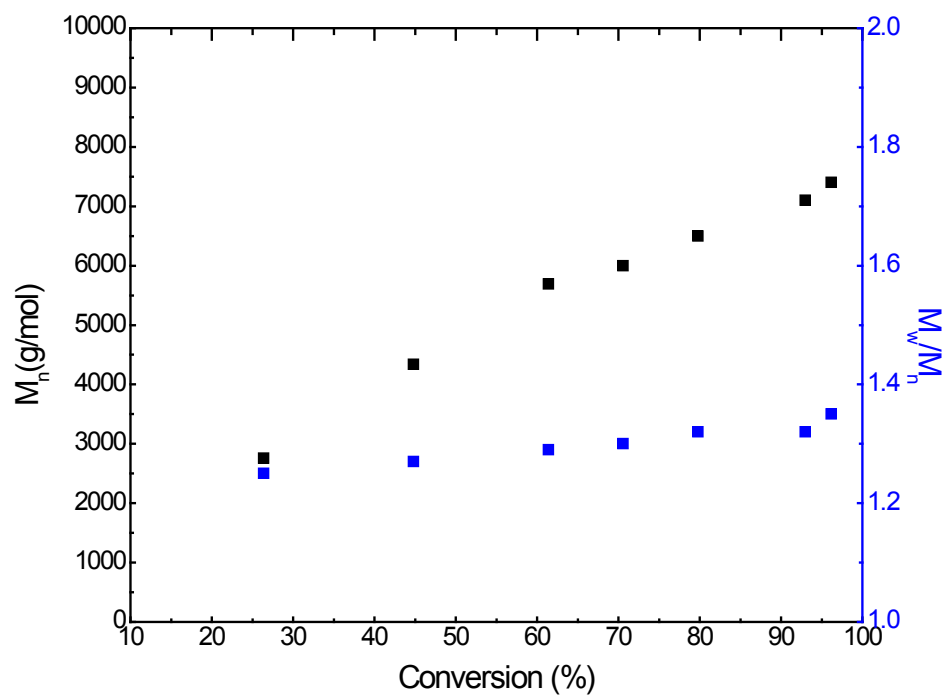




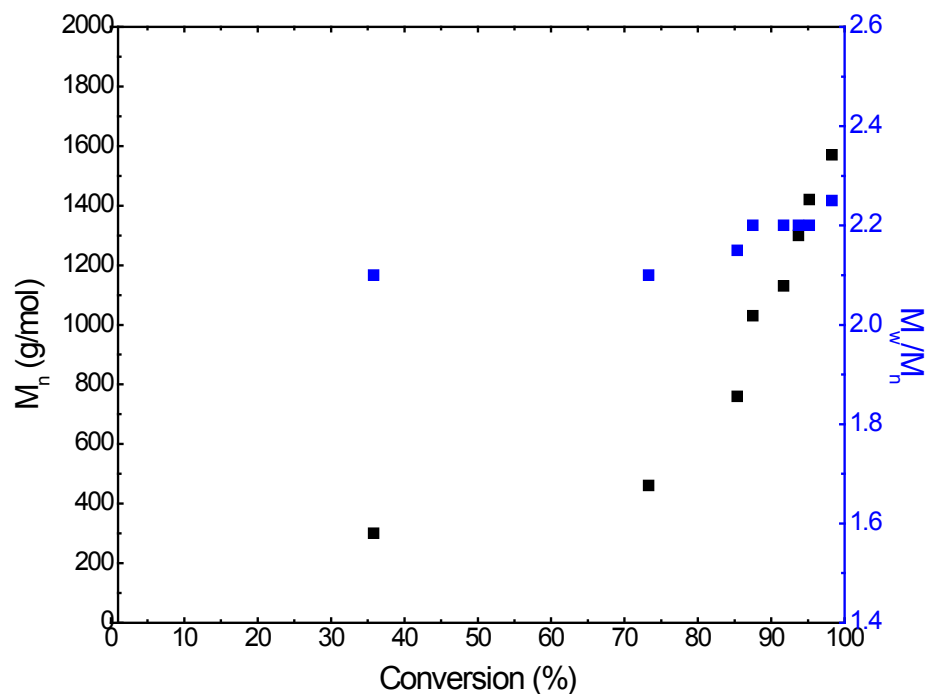
**Figure S8.** Molecular weight vs conversion and polydispersity index vs conversion plot GRIM polymerization of 2,5-dibromo-3-hexylthiophene.  $[\text{DBHT}]_0 = 0.1 \text{ mol/L}$ ;  $[\text{Ni}(\text{dppe})\text{Cl}_2]_0 = 0.0015 \text{ mol/L}$ ;  $\text{temp} = 23 \text{ }^\circ\text{C}$ .



**Figure S9.** Molecular weight vs conversion and polydispersity index vs conversion plot GRIM polymerization of 2,5-dibromo-3-hexylthiophene. [DBHT]<sub>0</sub>=0.1 mol/L; [Pd(dppe)Cl<sub>2</sub>]<sub>0</sub>=0.0015 mol/L; temp=45 °C.



**Figure S10.** Molecular weight vs conversion and polydispersity index vs conversion plot GRIM polymerization of 2-bromo-5-iodo-3-hexylthiophene.  $[IBHT]_0=0.1$  mol/L;  $[Ni(dppe)Cl_2]_0=0.0015$  mol/L; temp=23 °C.



**Figure S11.** Molecular weight vs conversion and polydispersity index vs conversion plot GRIM polymerization of 2-bromo-5-iodo-3-hexylthiophene.  $[IBHT]_0=0.1$  mol/L;  $[Pd(dppe)Cl_2]_0=0.0015$  mol/L; temp=45 °C.

**Table S1.** GRIM polymerization of DBHT using  $Pt(dppe)Cl_2$  catalyst<sup>a</sup>

Time (hrs)	Monomer conversion (%) <sup>a</sup>	$M_n$ (g/mol)	PDI
0	0	N/A	N/A
1	45.5	460	1.22
24	60	740	1.36
48	80.0	800	2.37

<sup>a</sup>Reaction conditions:  $[DBHT]_0=0.1$  mol/L;  $[Pd(dppe)Cl_2]_0=0.0015$  mol/L; temp=45 °C

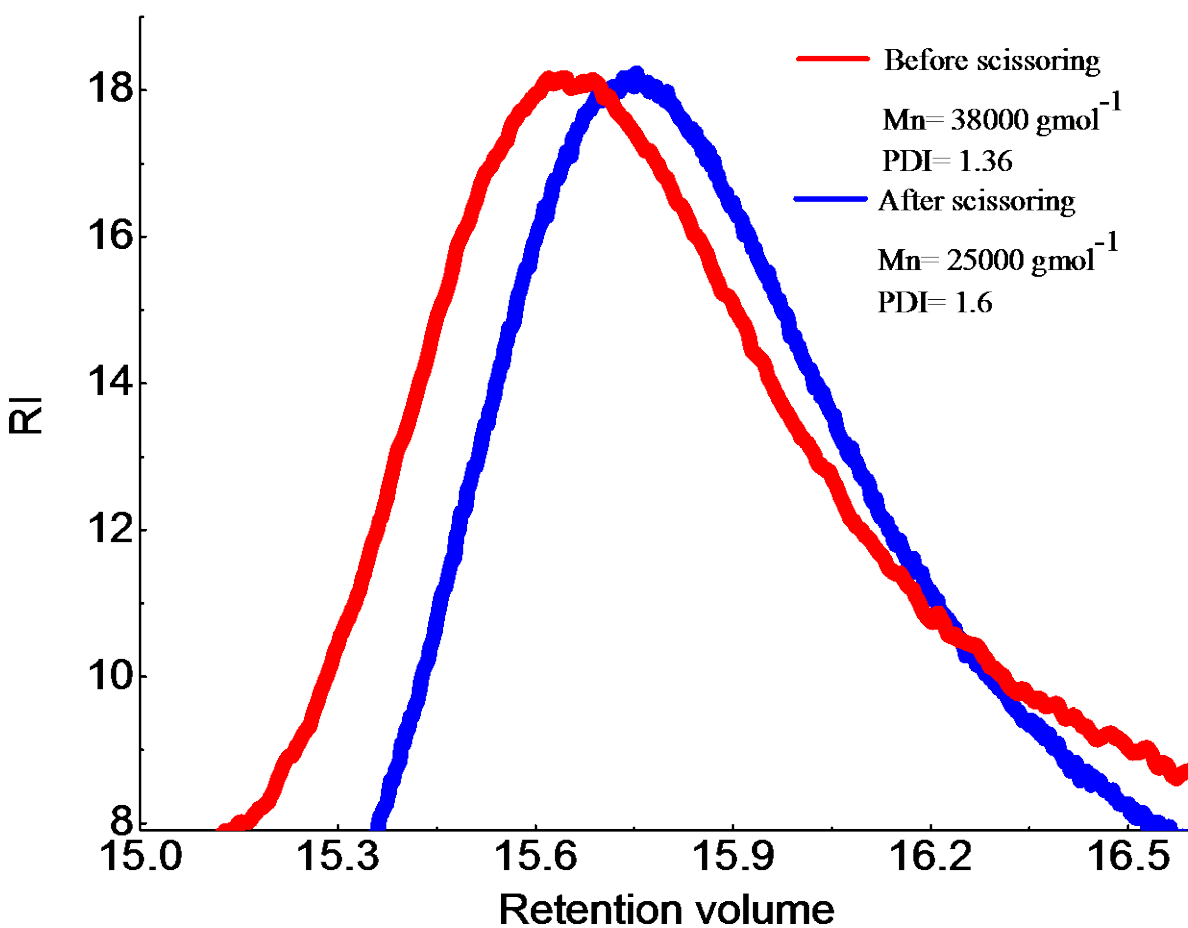
<sup>b</sup> Monomer conversion is calculated from the consumption of both isomers **1** and **2**

**Table S2.** GRIM polymerization of IBHT using Pt(dppe)Cl<sub>2</sub> catalyst<sup>a</sup>

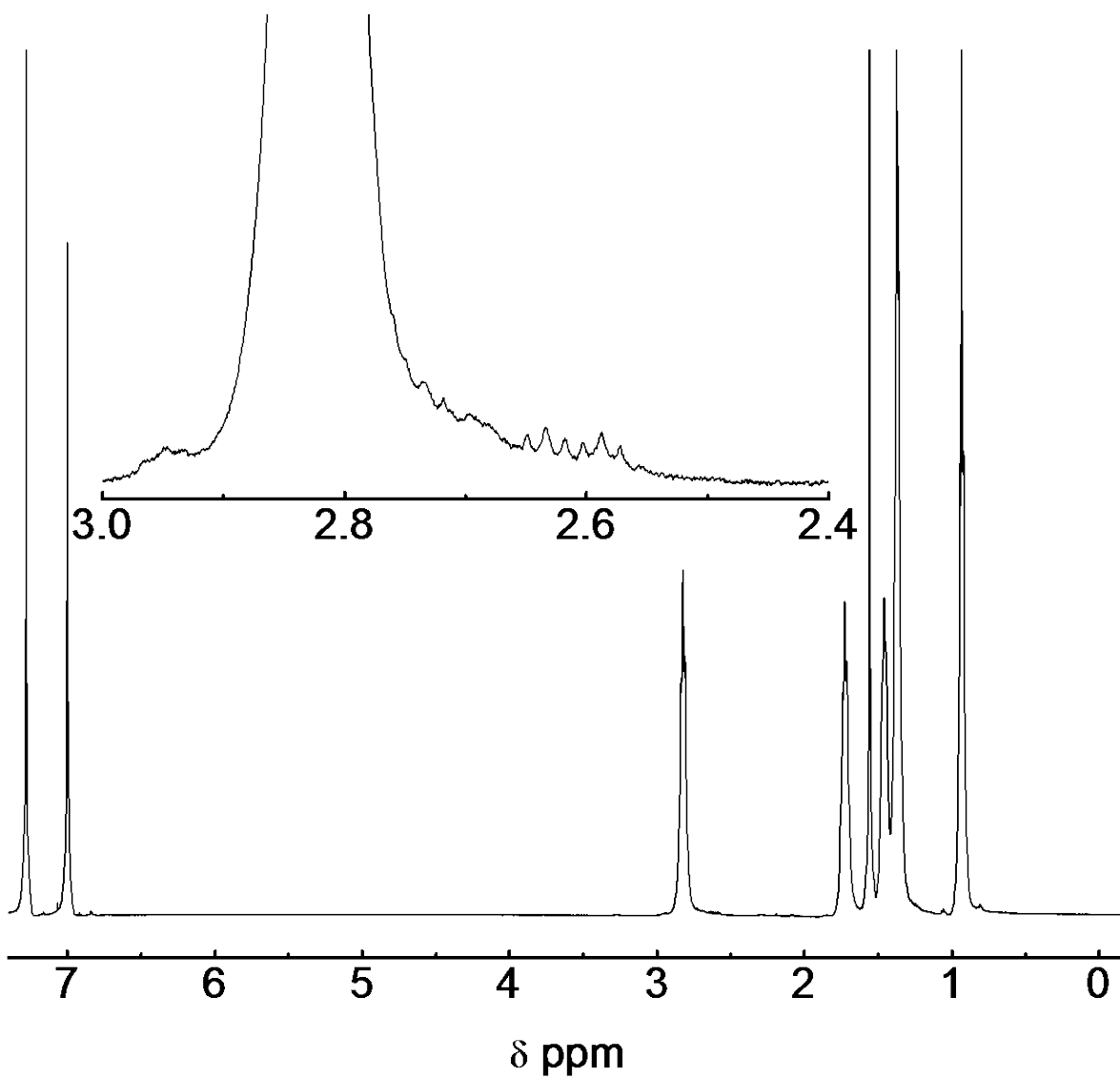
Time (hrs)	Monomer conversion (%) <sup>a</sup>	M <sub>n</sub> (g/mol)	PDI
0	0	N/A	N/A
1	43.7	1600	1.30
24	65.8	1640	1.48
48	83.1	1520	1.55

<sup>a</sup>Reaction conditions: [DBHT]<sub>0</sub>=0.1 mol/L; [Pt(dppe)Cl<sub>2</sub>]<sub>0</sub>=0.0015 mol/L; temp=45 °C

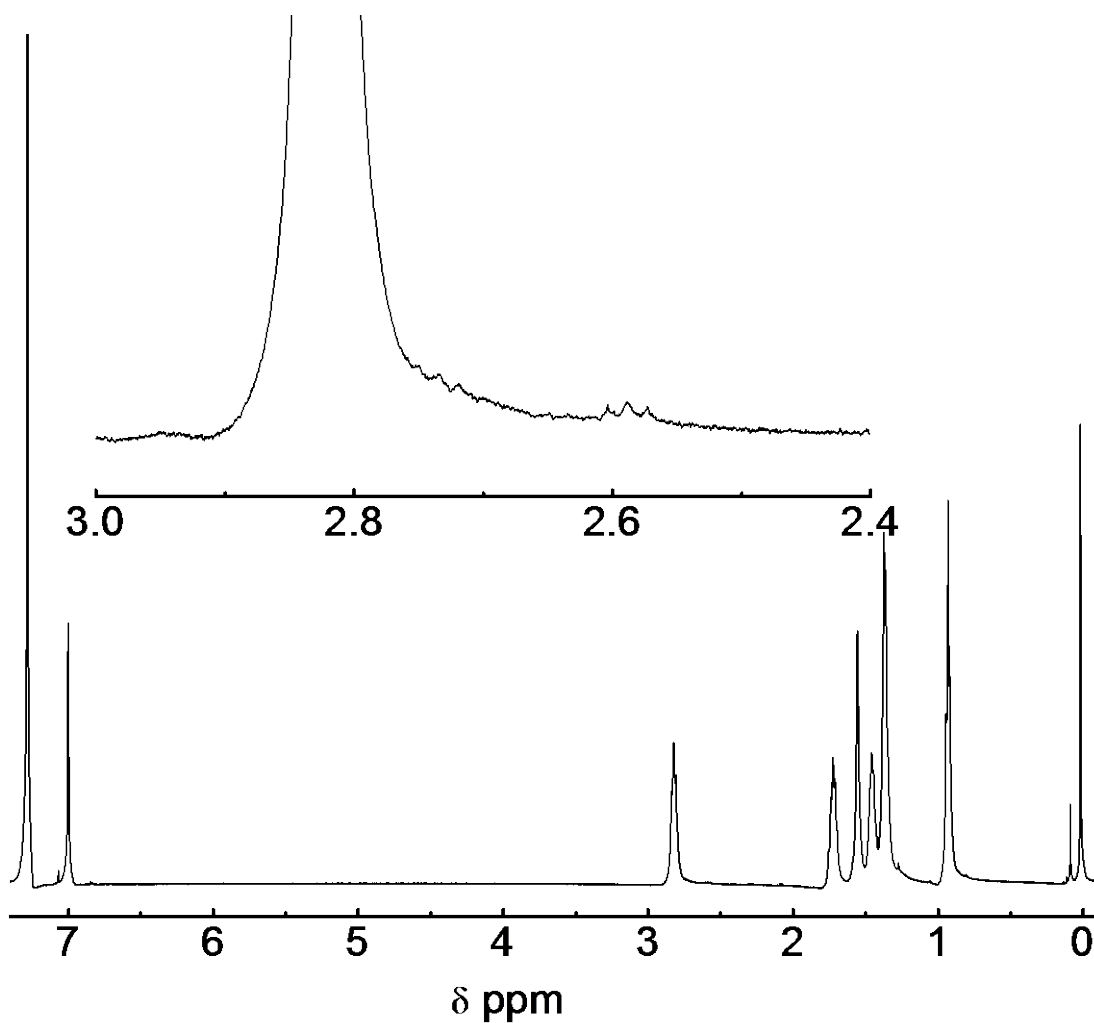
<sup>b</sup> Monomer conversion is calculated from the consumption of both isomers 1 and 2



**Figure S12.** SEC traces of poly(3-hexylthiophene): starting P3HT (red) and after scissoring experiment (blue)



**Figure S13.**  $^1\text{H}$  NMR spectrum of poly(3-hexylthiophene) before the scissoring experiment



**Figure S14.**  $^1\text{H}$  NMR spectrum of poly(3-hexylthiophene) after the scissoring experiment