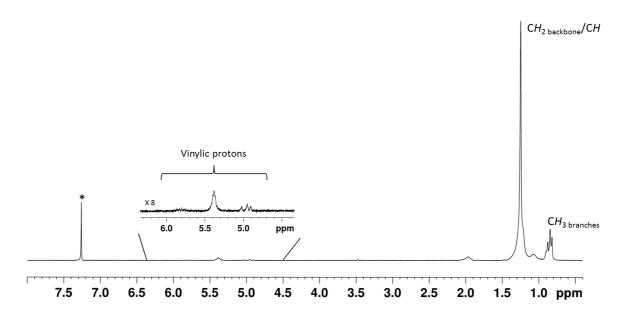
## Supplementary Material

Iminopyridine Ni(II) catalysts affording oily hyperbranched oligoethylenes and/or crystalline polyethylenes depending on the reaction conditions: possible role of in situ catalyst structure modifications

Ilaria D'Auria<sup>1</sup>, Zeinab Saki<sup>1</sup> and Claudio Pellecchia<sup>1,\*</sup>

<sup>1</sup>Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy

\* Correspondence: <a href="mailto:cpellecchia@unisa.it">cpellecchia@unisa.it</a>



**Figure S1.** <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 25°C) spectrum of oily fraction obtained in run 1, Table 1 (\* stands for residual solvent).

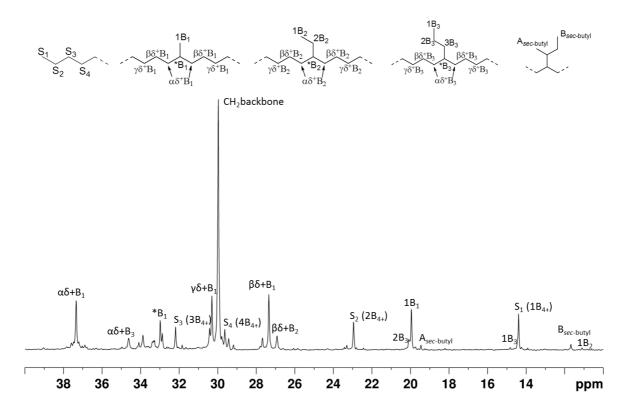
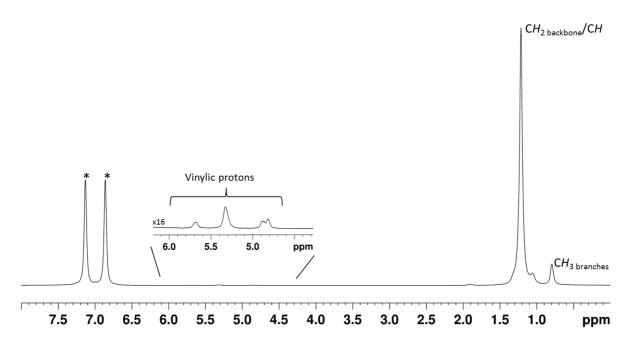
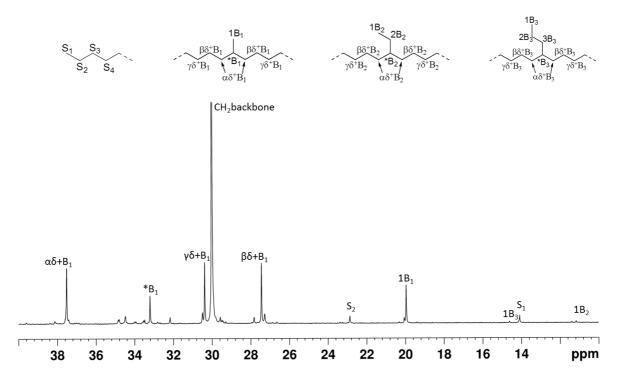


Figure S2. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz, 25°C) spectrum of oily fraction obtained in run 1, Table 1.



**Figure S3.**  $^{1}$ H-NMR ( $C_{6}$ D $_{4}$ Cl $_{2}$ , 600 MHz, 90 $^{\circ}$ C) spectrum of solid polymer obtained in run 1, Table 1 (\*\* stand for residual solvent).



 $\textbf{Figure S4.} \ ^{13}\text{C-NMR (C} \tiny{6}\text{D}_{4}\text{Cl}_{2}\text{, } 125 \ \text{MHz, } 90^{\circ}\text{C)} \ \text{spectrum of solid polymer obtained in run 1, Table 1.}$ 

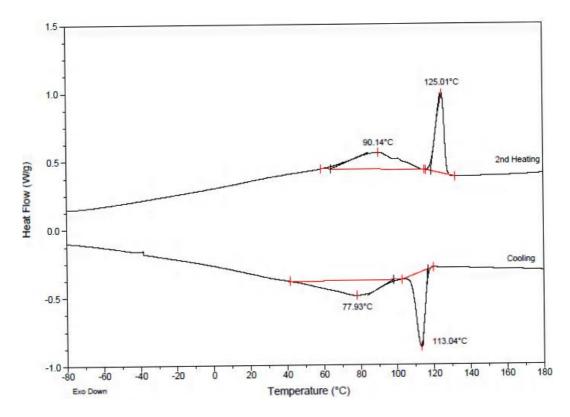
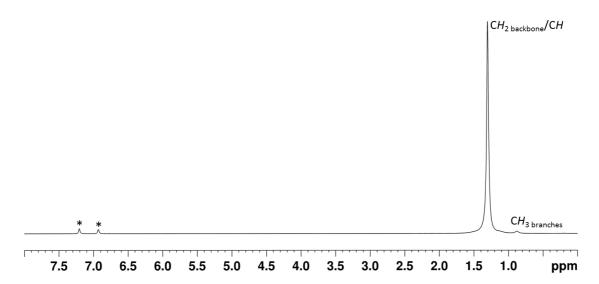
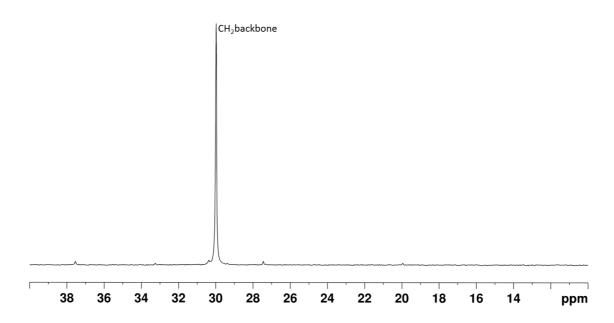


Figure S5. DSC thermogram of the solid polymer obtained in run 1, Table 1.



**Figure S6.**  $^{1}$ H-NMR ( $C_{6}D_{4}Cl_{2}$ , 600 MHz, 90°C) spectrum of the heptane-insoluble part of polymer obtained in run 1, Table 1 (\*\* stand for residual solvent).



**Figure S7**.  $^{13}$ C-NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 125 MHz, 90°C) spectrum of the heptane-insoluble part of polymer obtained in run 1, Table 1.

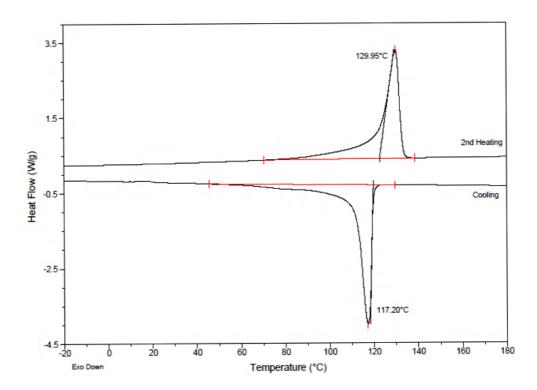


Figure S8. DSC thermogram of the heptane-insoluble fraction of polymer obtained in run 1, Table1.

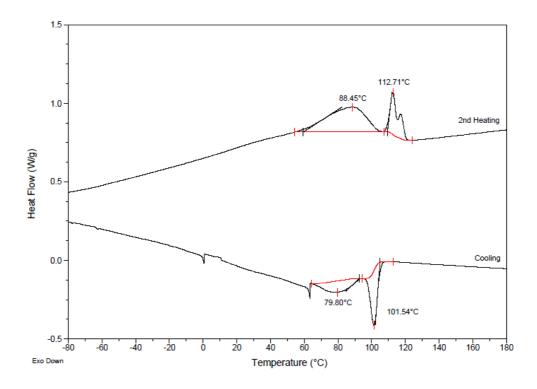
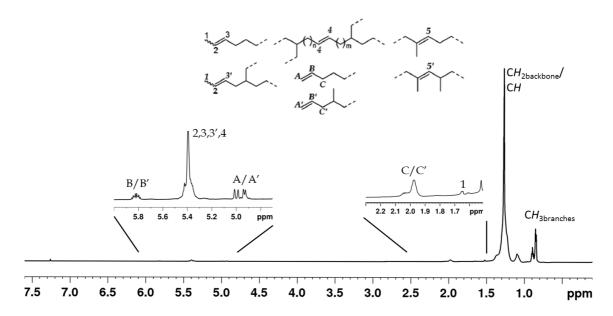
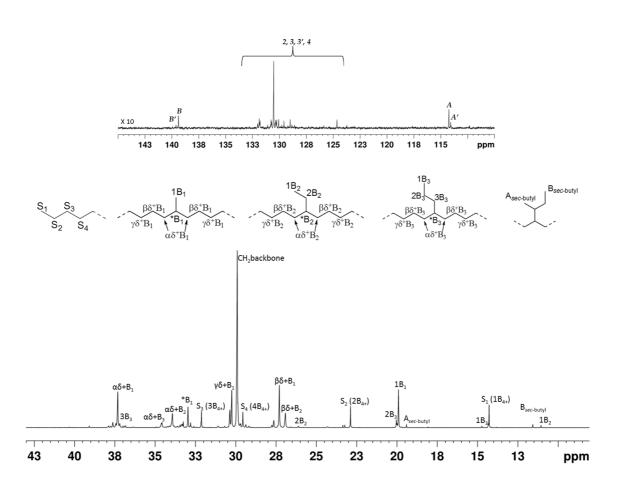


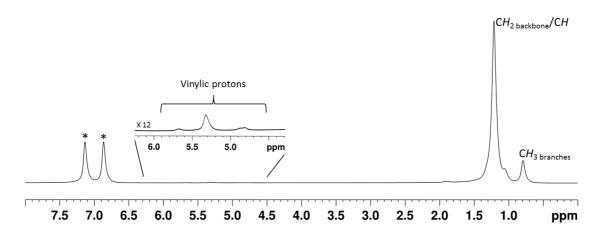
Figure S9. DSC thermogram of the heptane-soluble fraction of polymer obtained in run 1, Table1.



**Figure S10.**  $^{1}$ H-NMR (CDCl, 600 MHz, 20 $^{\circ}$ C) spectrum of a typical low MW oily polyethylene sample in Table 1.



**Figure S11.** <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz, 20°C) spectrum of a typical low MW oily polyethylene sample in Table 1.



**Figure S12.** <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 600 MHz, 90°C) spectrum of the polymer obtained in run 9, Table 1 (\*\* stand for residual solvent).

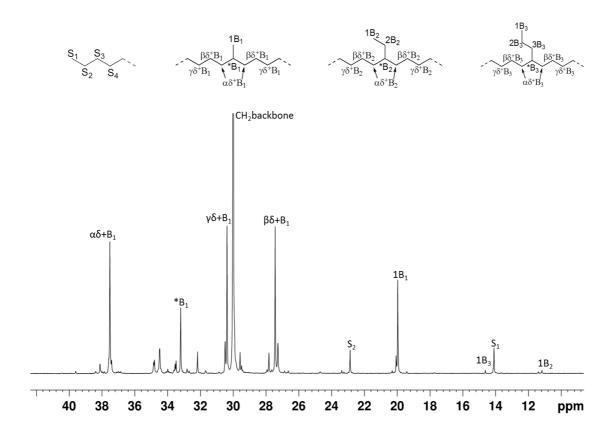
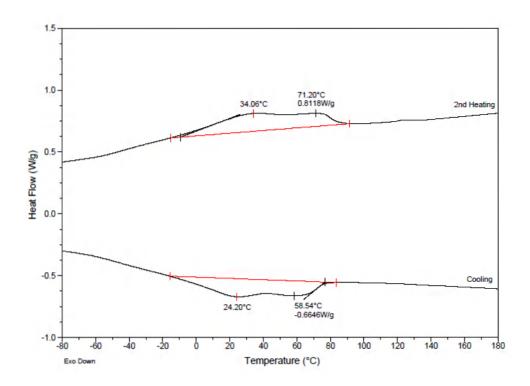
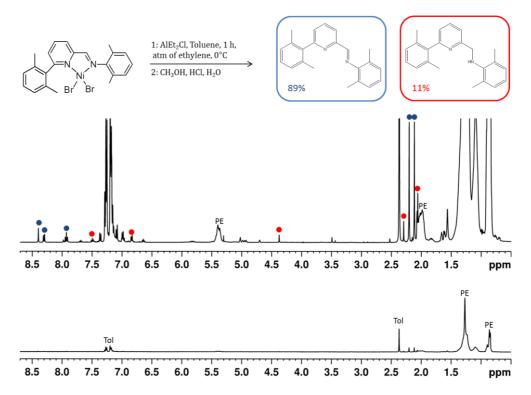


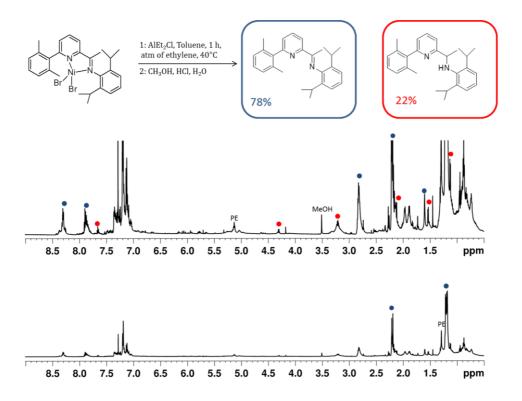
Figure S13. <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 125 MHz, 90°C) spectrum of the polymer obtained in run 9, Table 1.



**Figure S14**. DSC thermogram of the solid polymer obtained in run 9, Table 1.



**Figure S14.**<sup>1</sup>H –NMR (CDCl<sub>3</sub>, 400 MHz, 20 °C) spectra of the products of reaction between complex **3** and AlEt<sub>2</sub>Cl under ethylene pressure.



**Figure S15.**  $^{1}\text{H}$  –NMR (CDCl<sub>3</sub>, 400 MHz, 20  $^{\circ}\text{C}$ ) spectra of the products of reaction between complex 2 and AlEt<sub>2</sub>Cl under ethylene pressure.