Supplementary Material

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

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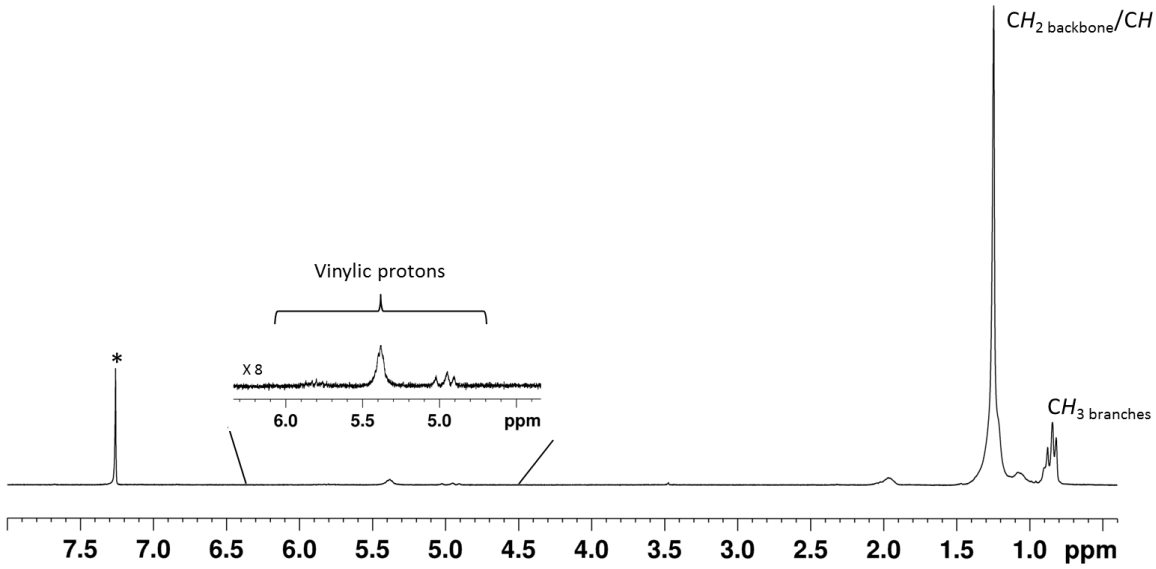

Figure S1. ^{1}H-NMR ($CDCl_3$, 400 MHz, 25°C) spectrum of oily fraction obtained in run 1, Table 1 (* stands for residual solvent).

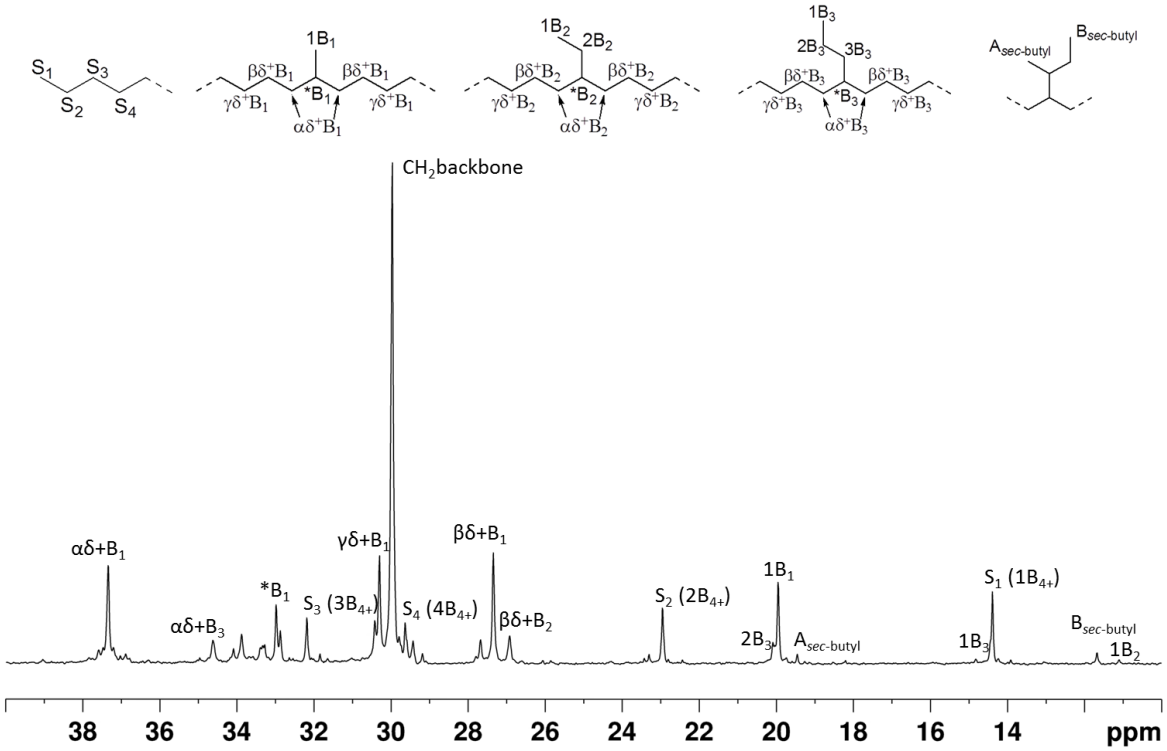

Figure S2. ^{13}C-NMR ($CDCl_3$, 100 MHz, 25°C) spectrum of oily fraction obtained in run 1, Table 1.

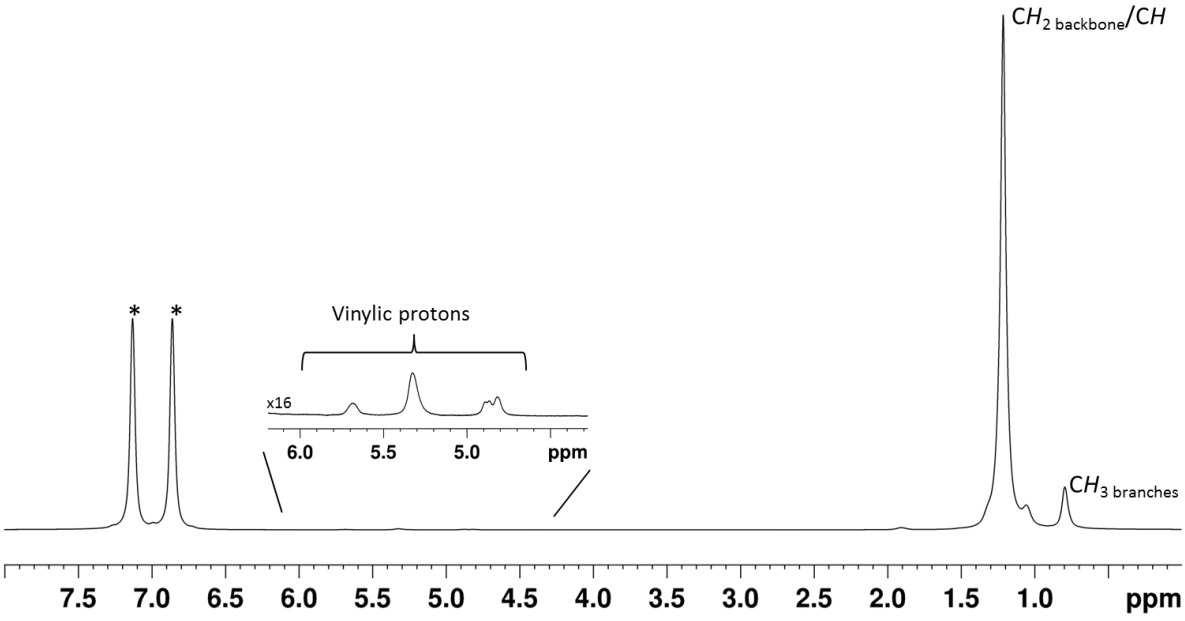

Figure S3. ^{1}H-NMR ($C_6D_4Cl_2$, 600 MHz, 90°C) spectrum of solid polymer obtained in run 1, Table 1 (** stand for residual solvent).

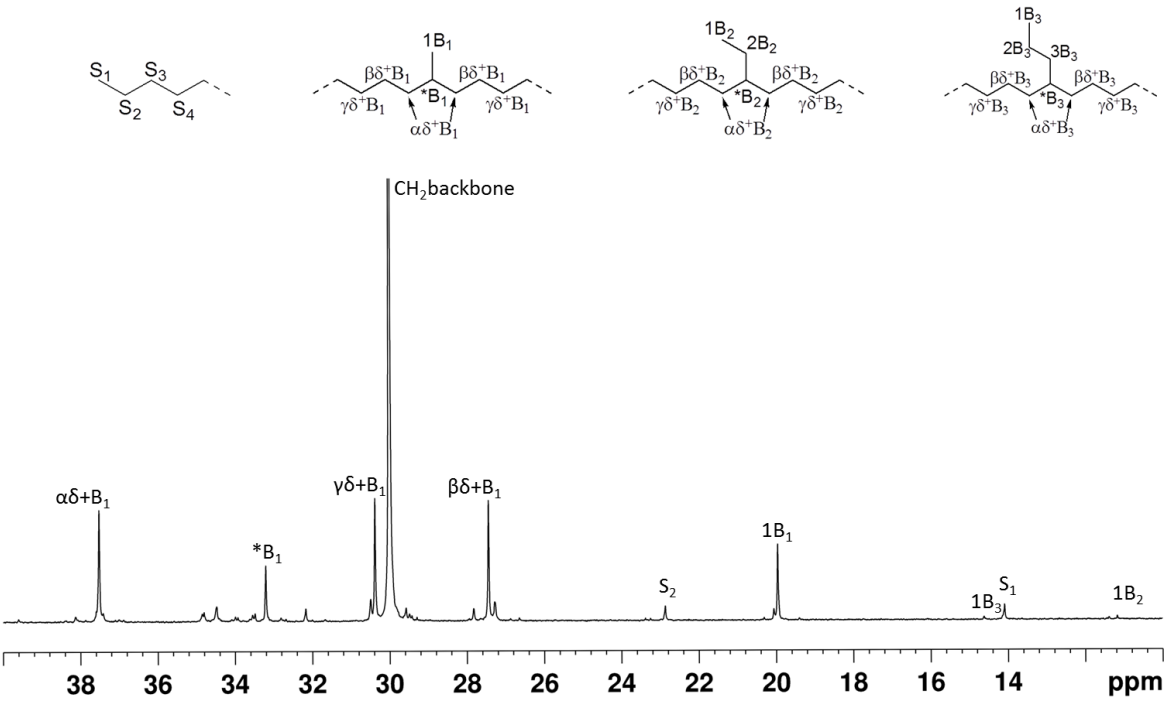

Figure S4. ^{13}C-NMR ($C_6D_4Cl_2$, 125 MHz, 90°C) spectrum of solid polymer obtained in run 1, Table 1.

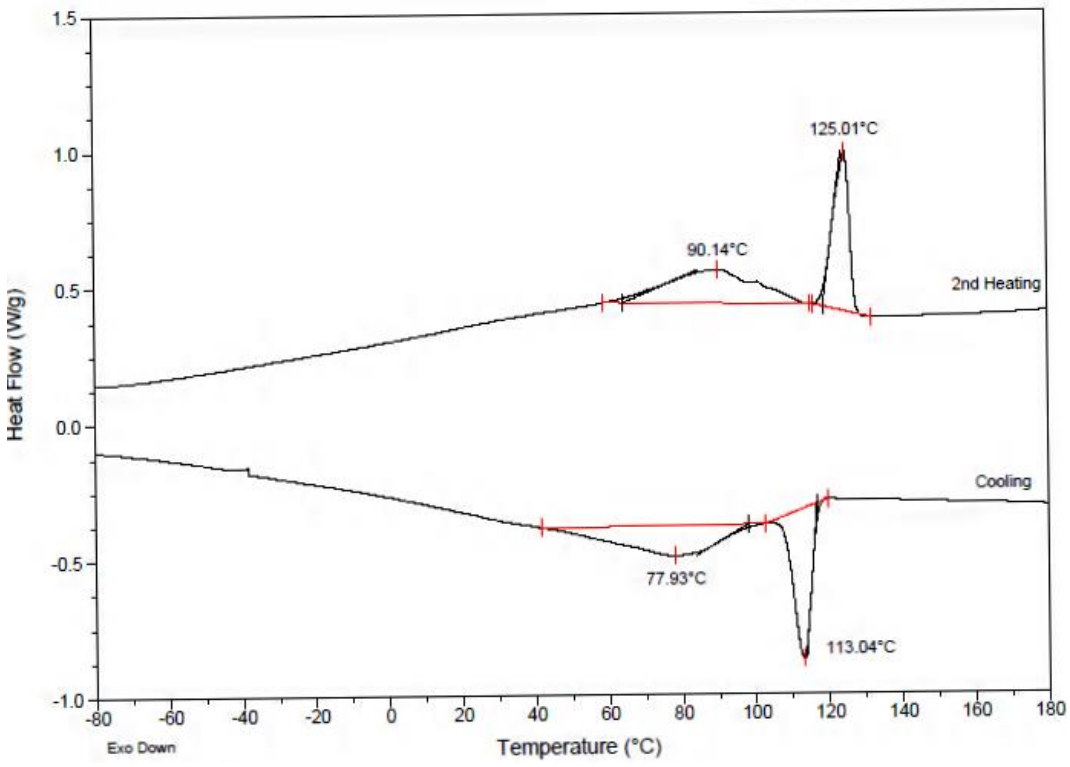

Figure S5. DSC thermogram of the solid polymer obtained in run 1, Table 1.

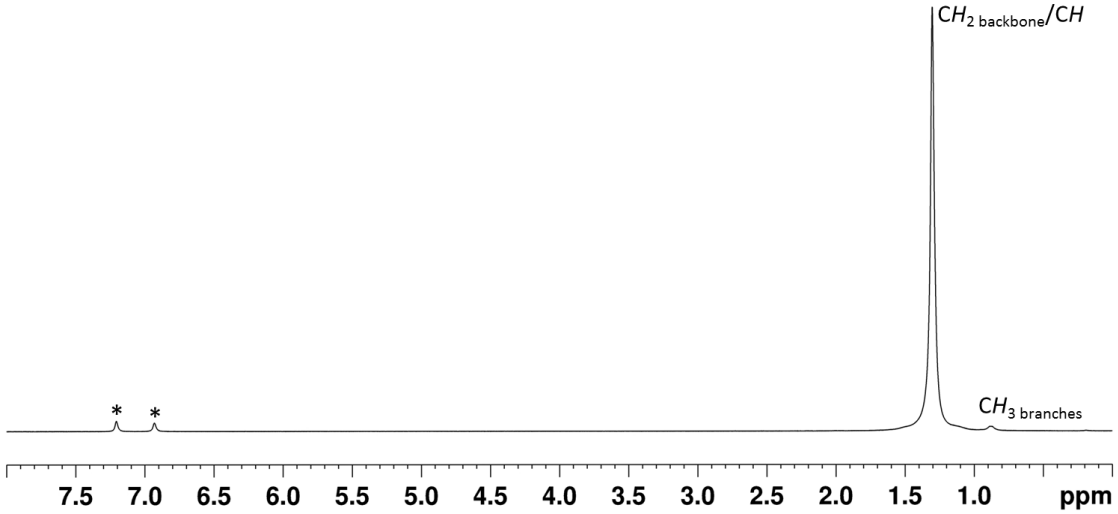

Figure S6. ^{1}H-NMR ($C_6D_4Cl_2$, 600 MHz, 90°C) spectrum of the heptane-insoluble part of polymer obtained in run 1, Table 1 (** stand for residual solvent).

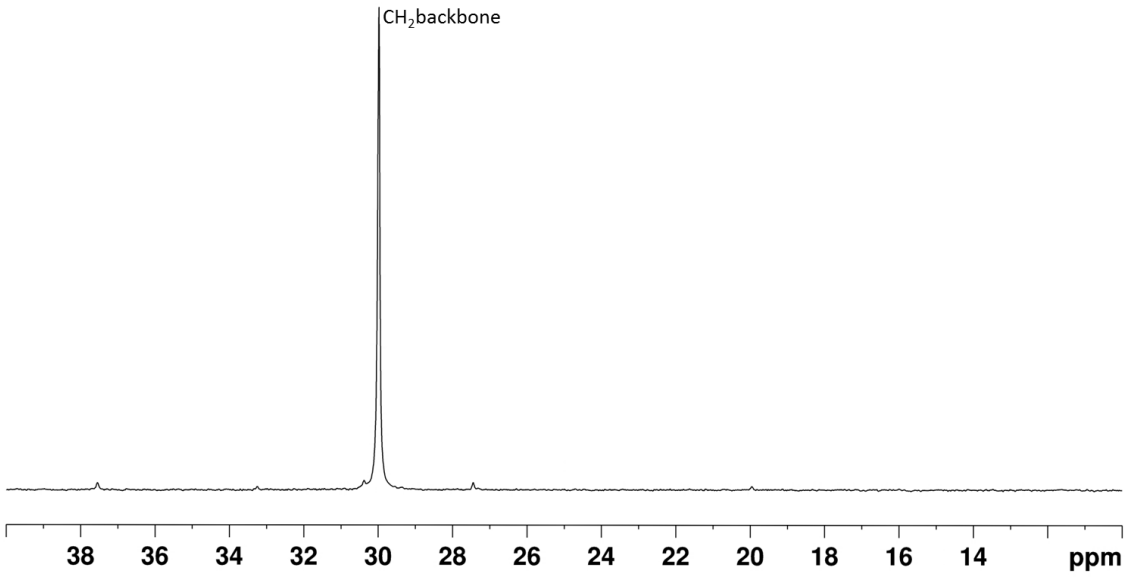

Figure S7. ^{13}C-NMR ($C_6D_4Cl_2$, 125 MHz, 90°C) spectrum of the heptane-insoluble part of polymer obtained in run 1, Table 1.

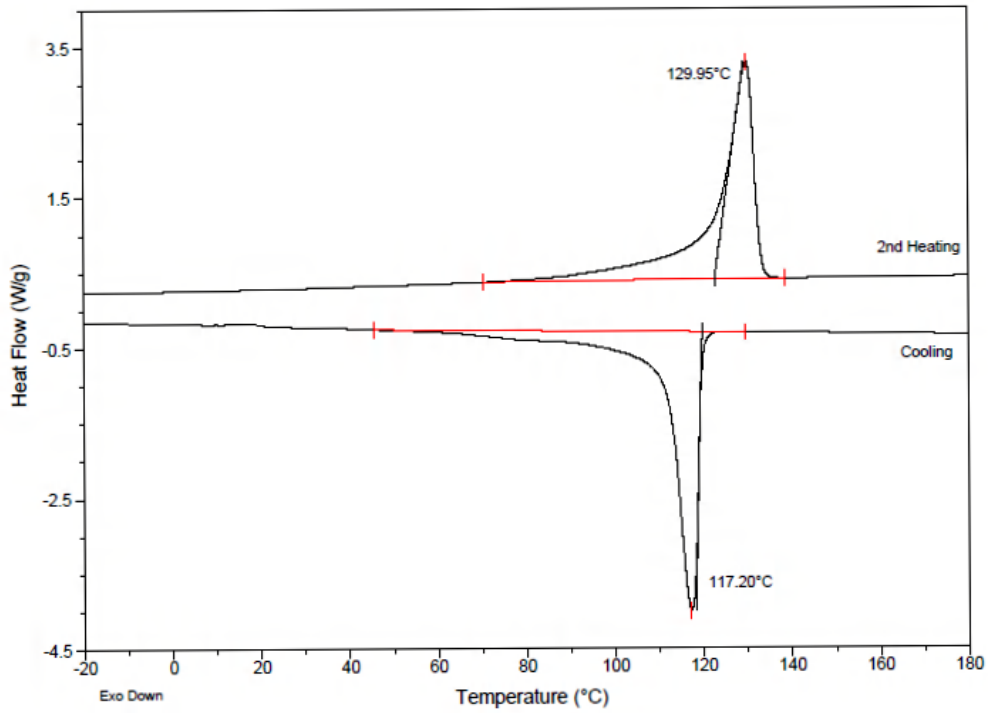

Figure S8. DSC thermogram of the heptane-insoluble fraction of polymer obtained in run 1, Table1.

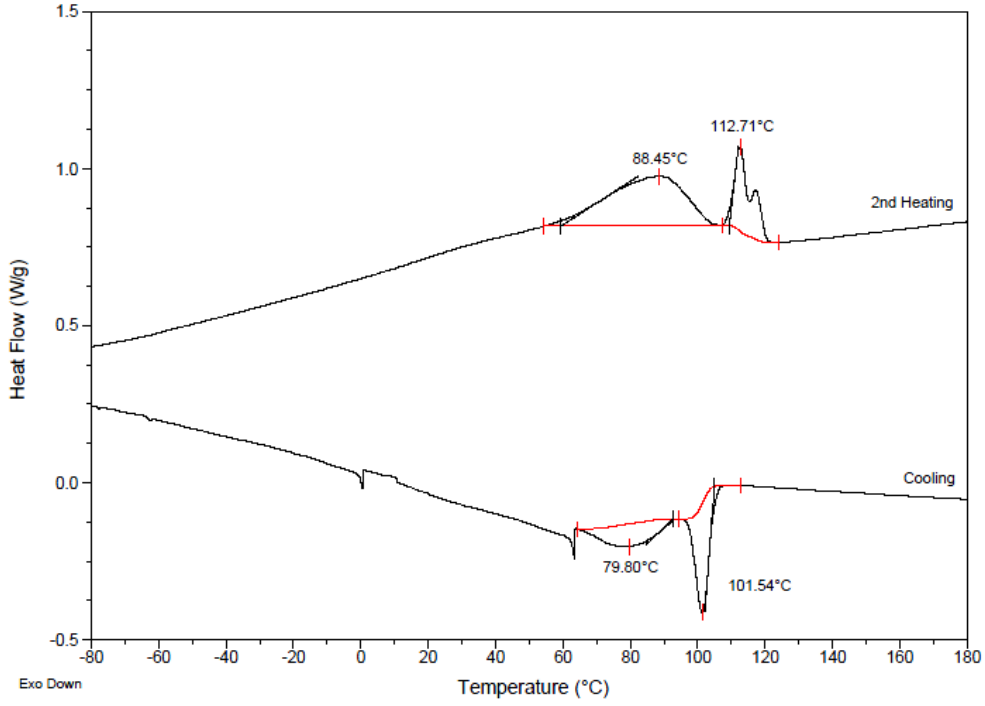

Figure S9. DSC thermogram of the heptane-soluble fraction of polymer obtained in run 1, Table1.

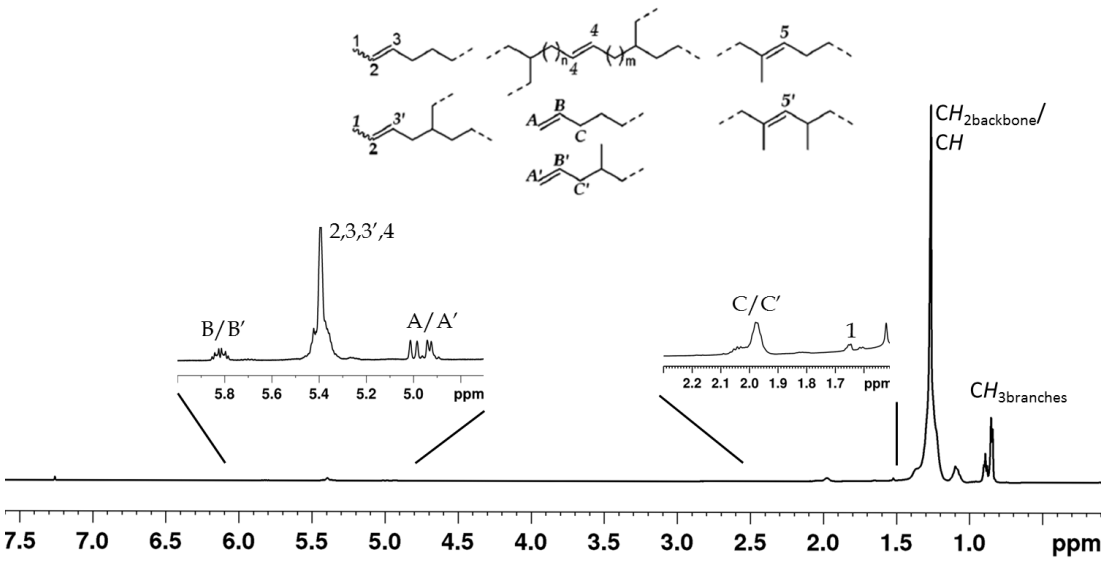

Figure S10. [1]H-NMR (CDCl, 600 MHz, 20°C) spectrum of a typical low MW oily polyethylene sample in Table 1.

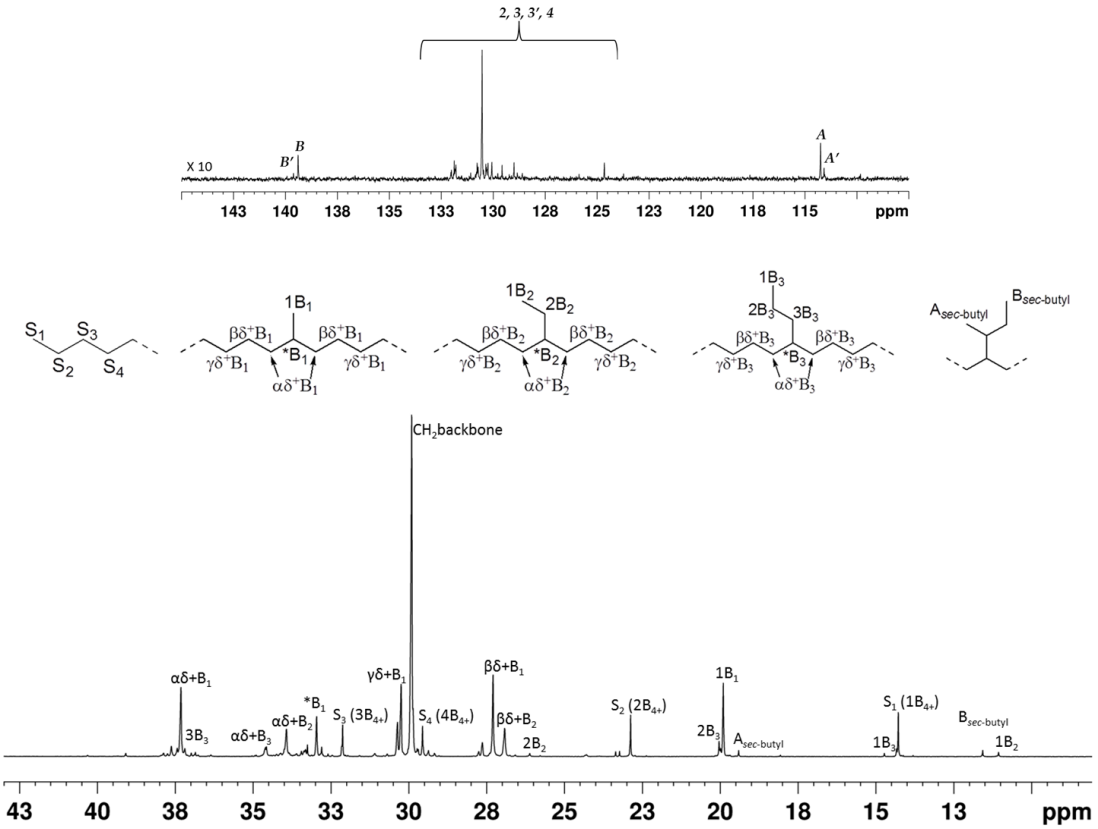

Figure S11. [13]C-NMR ($CDCl_3$, 125 MHz, 20°C) spectrum of a typical low MW oily polyethylene sample in Table 1.

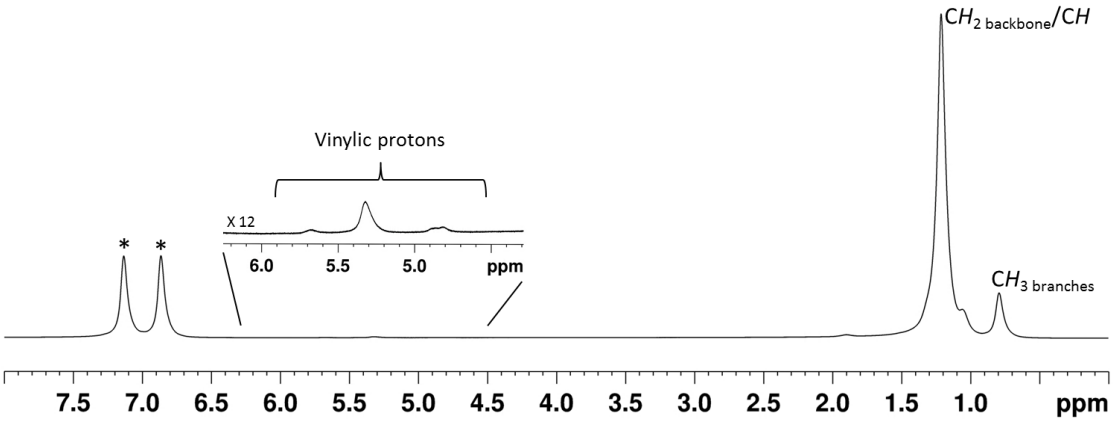

Figure S12. ^{1}H-NMR ($C_6D_4Cl_2$, 600 MHz, 90°C) spectrum of the polymer obtained in run 9, Table 1 (** stand for residual solvent).

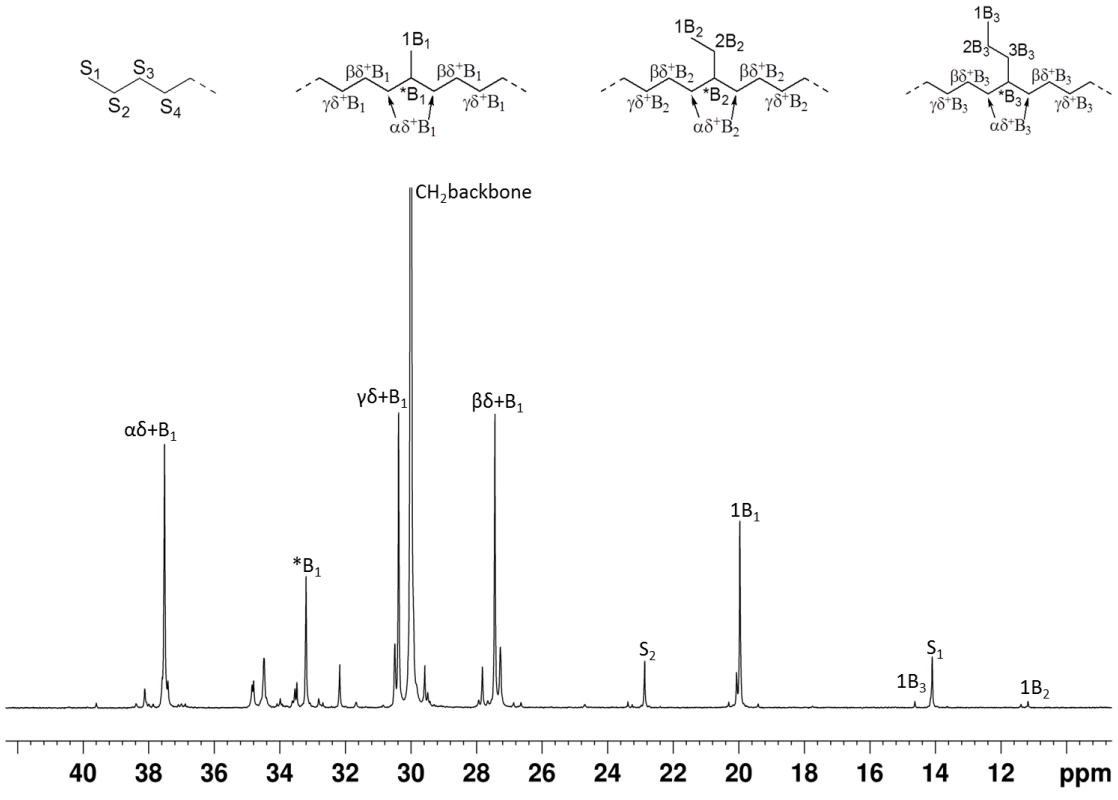

Figure S13. ^{13}C-NMR ($C_6D_4Cl_2$, 125 MHz, 90°C) spectrum of the polymer obtained in run 9, Table 1.

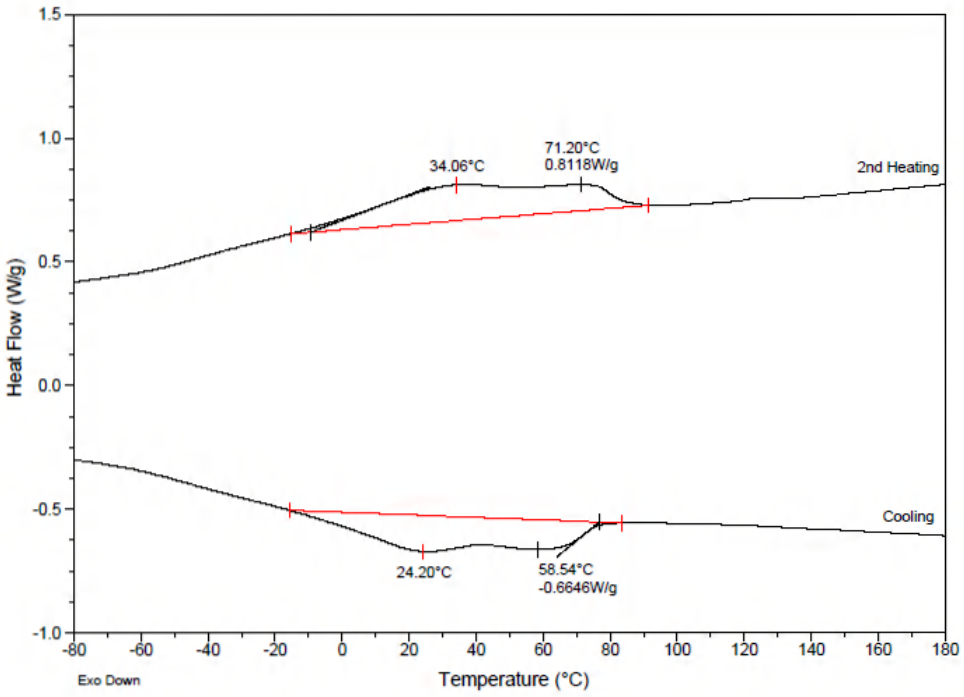

Figure S14. DSC thermogram of the solid polymer obtained in run 9, Table 1.

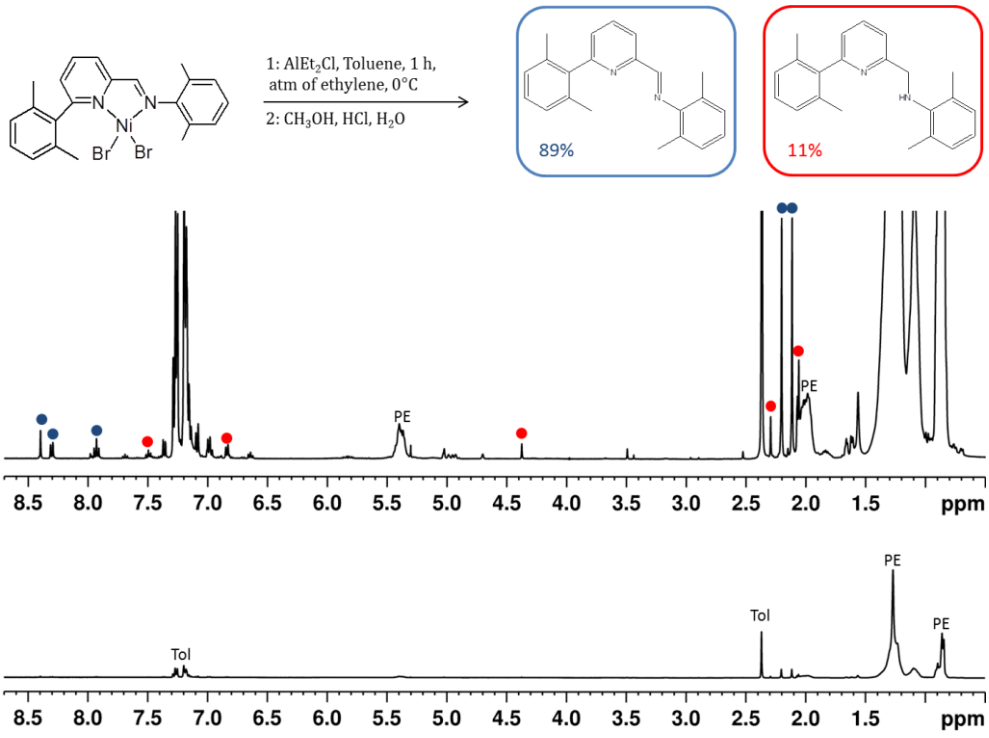

Figure S15. ^{1}H –NMR ($CDCl_3$, 400 MHz, 20 °C) spectra of the products of reaction between complex **3** and $AlEt_2Cl$ under ethylene pressure.

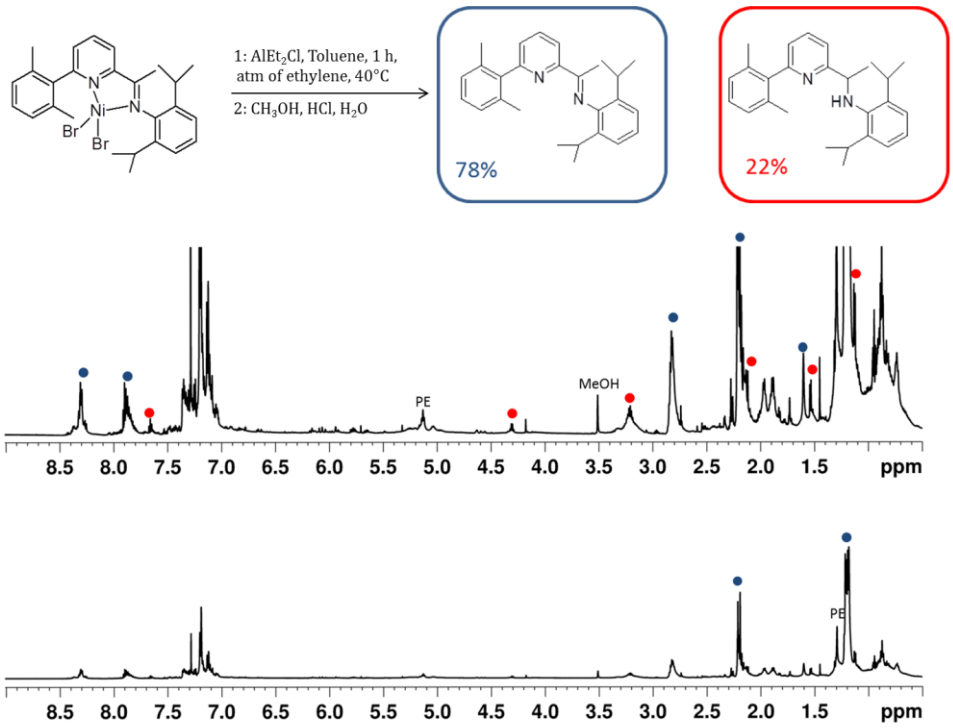

Figure S16. ^{1}H –NMR ($CDCl_3$, 400 MHz, 20 °C) spectra of the products of reaction between complex **2** and $AlEt_2Cl$ under ethylene pressure.

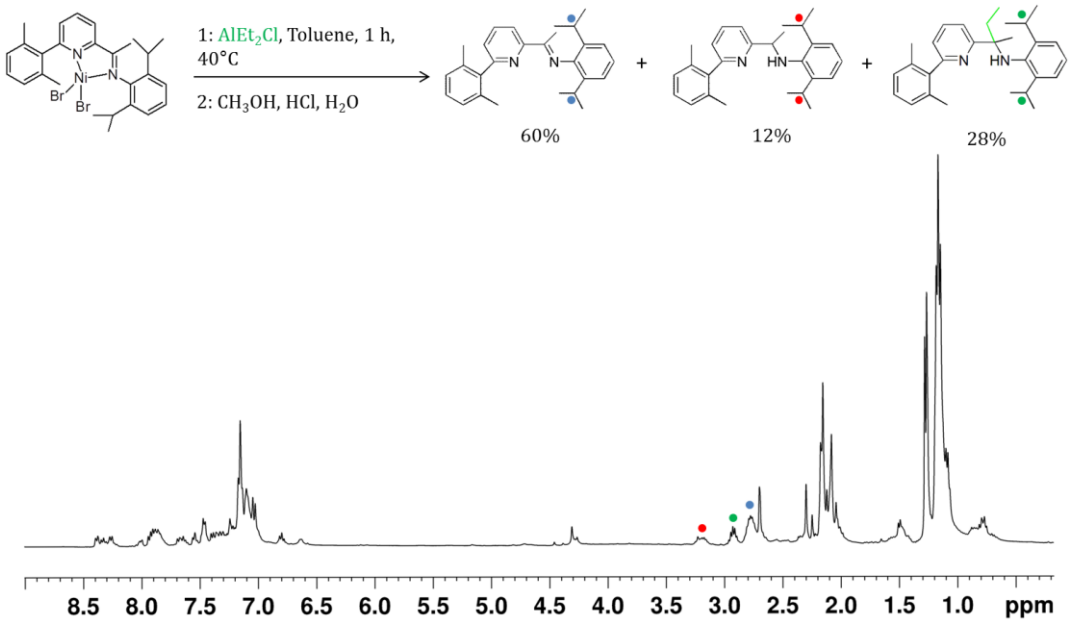

Figure S17. ^{1}H –NMR ($CDCl_3$, 400 MHz, 20 °C) spectrum of the products of reaction between complex **2** and $AlEt_2Cl$ under nitrogen atmosphere, without ethylene.