Supporting Information for

The Amido-Bridged Zirconocene's Reactivity and Catalytic Behavior for Ethylene Polymerization

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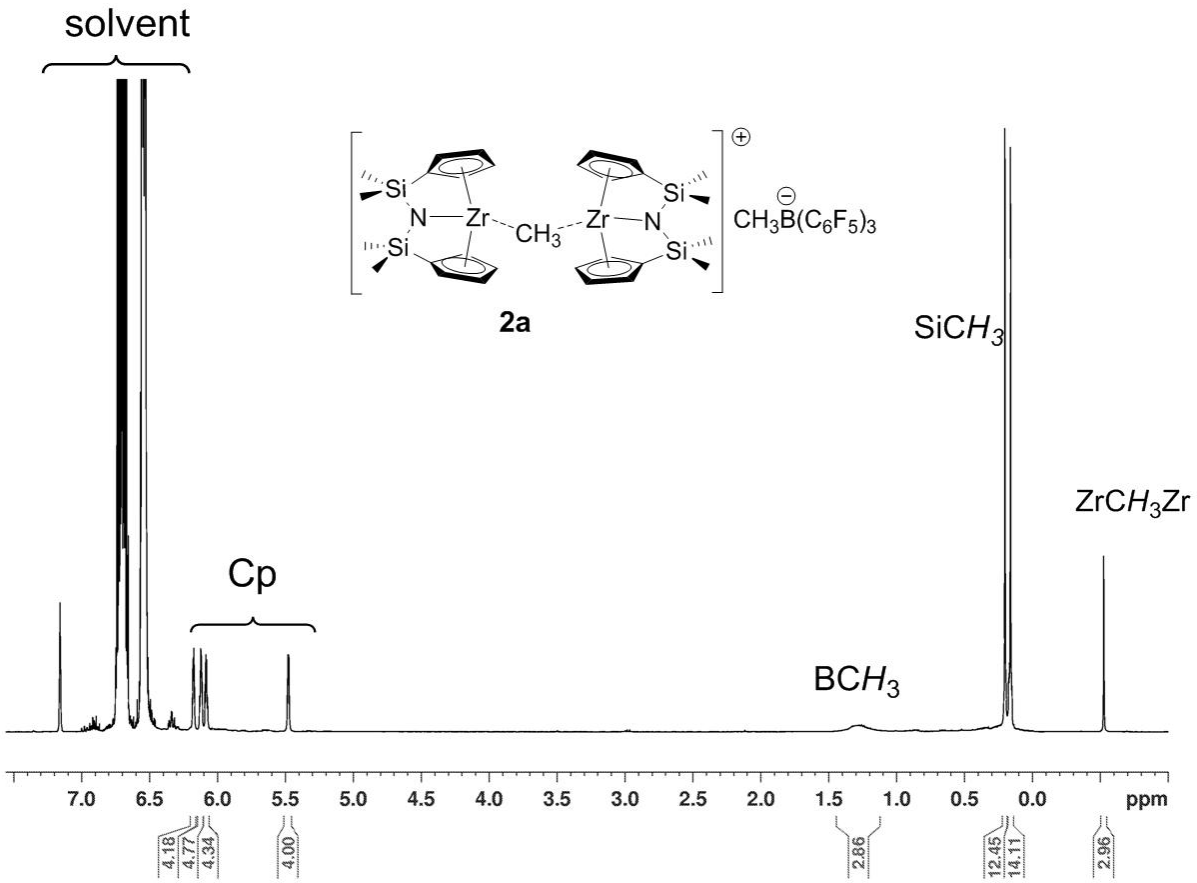

Fig. S1 ^{1}H NMR spectrum of **2a** ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

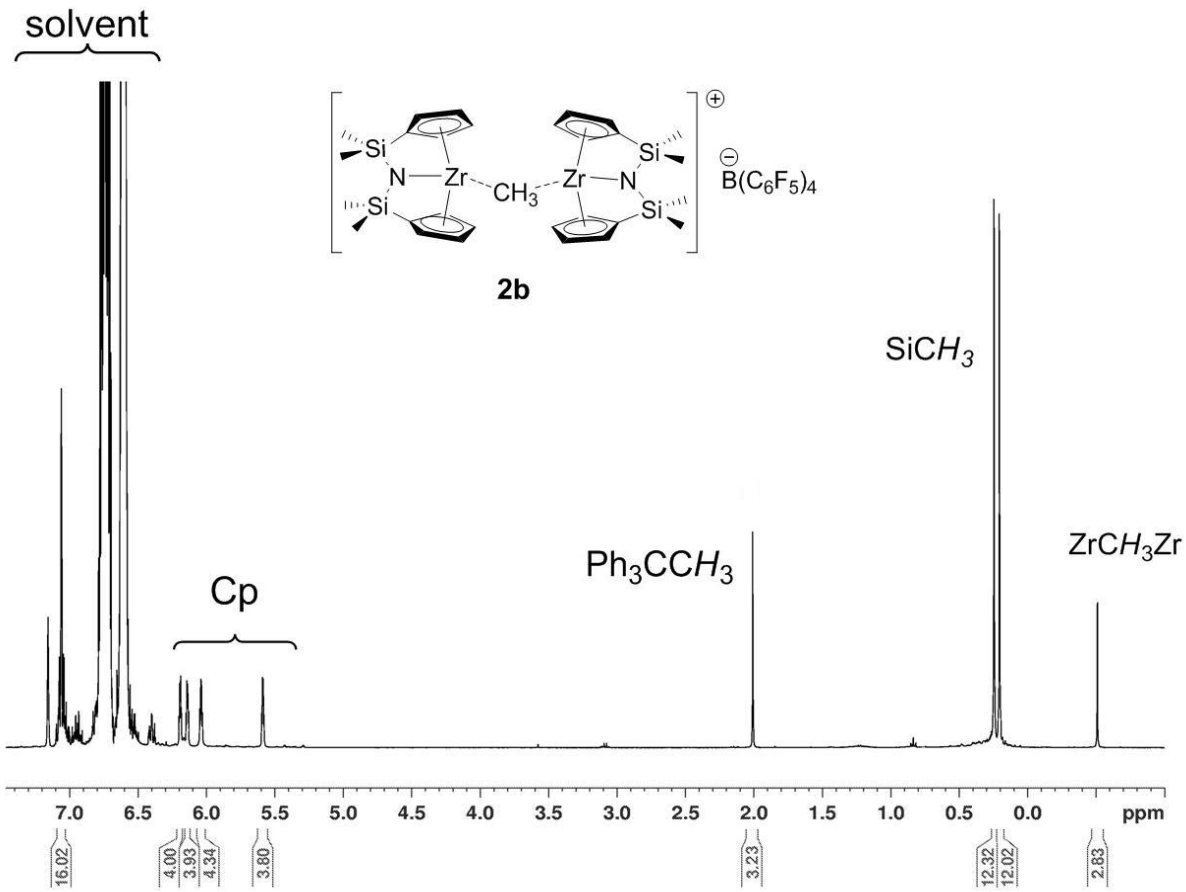

Fig. S2 ^{1}H NMR spectrum of **2b** ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

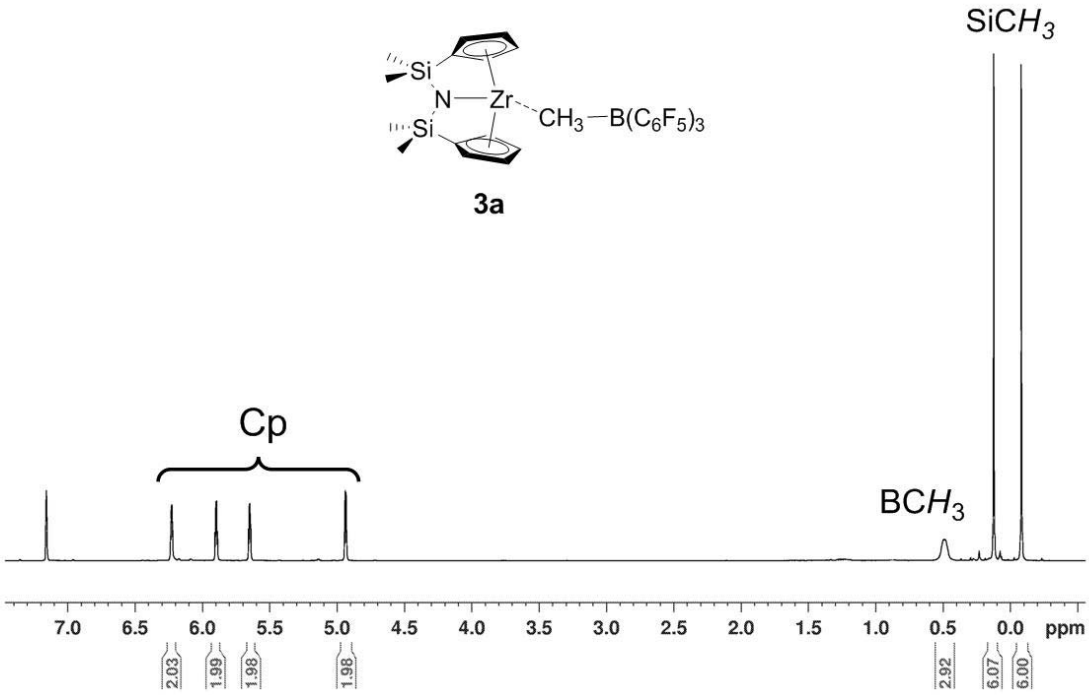

Fig. S3 ^{1}H NMR spectrum of **3a** ((400 MHz, C_6D_6, 298 K).

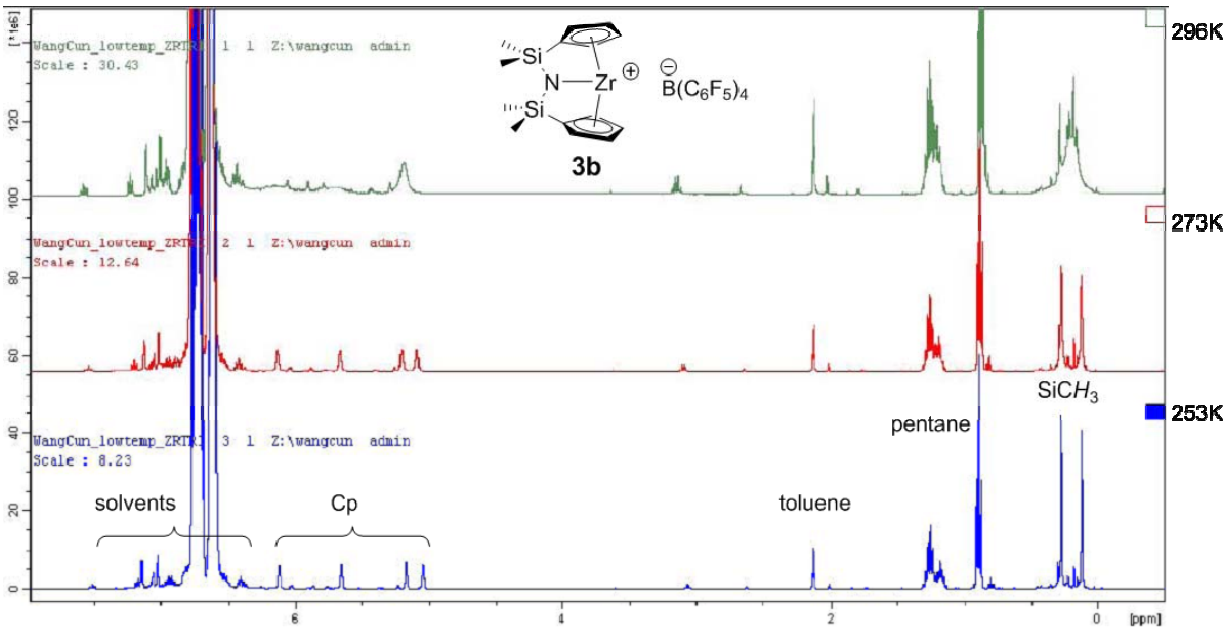

Fig. S4 Dynamic ^{1}H NMR spectra of **3b** ((400 MHz, $C_6D_5CD_3$/1,2-$C_6H_4F_2$).

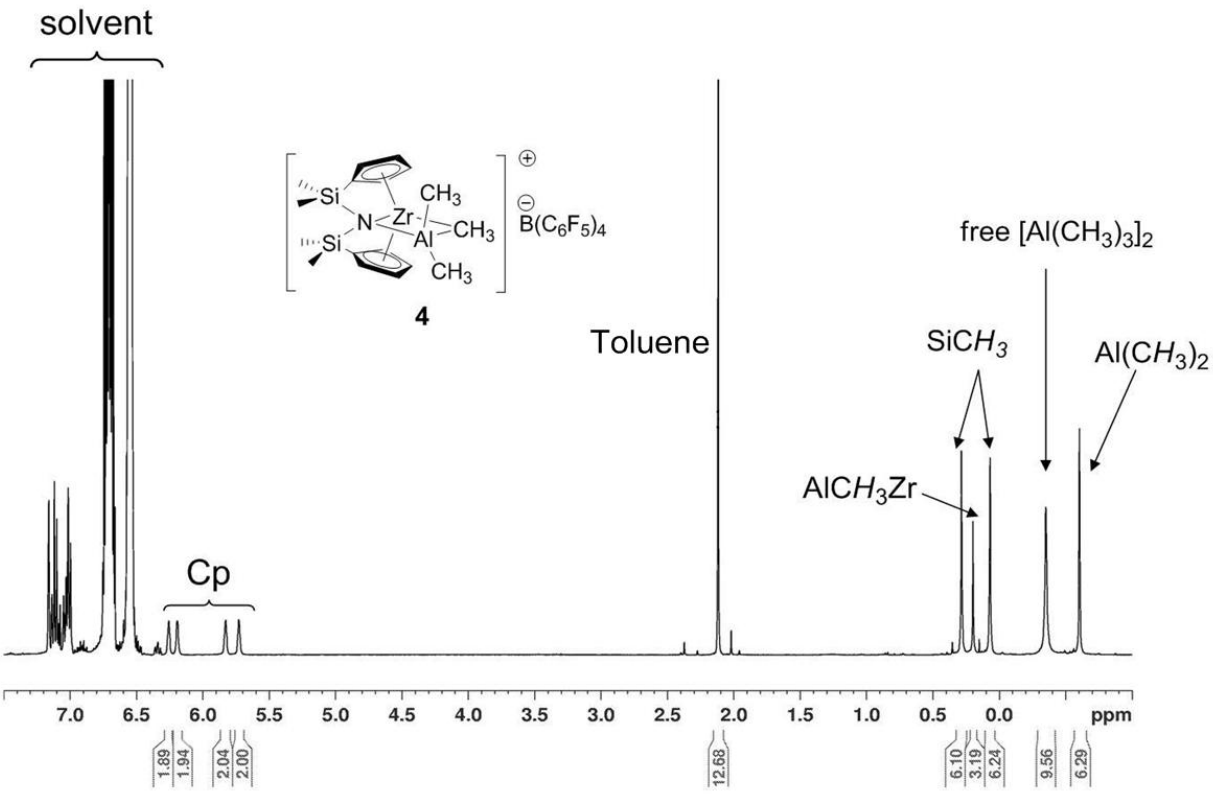

Fig. S5 ^{1}H NMR spectrum of **4** ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

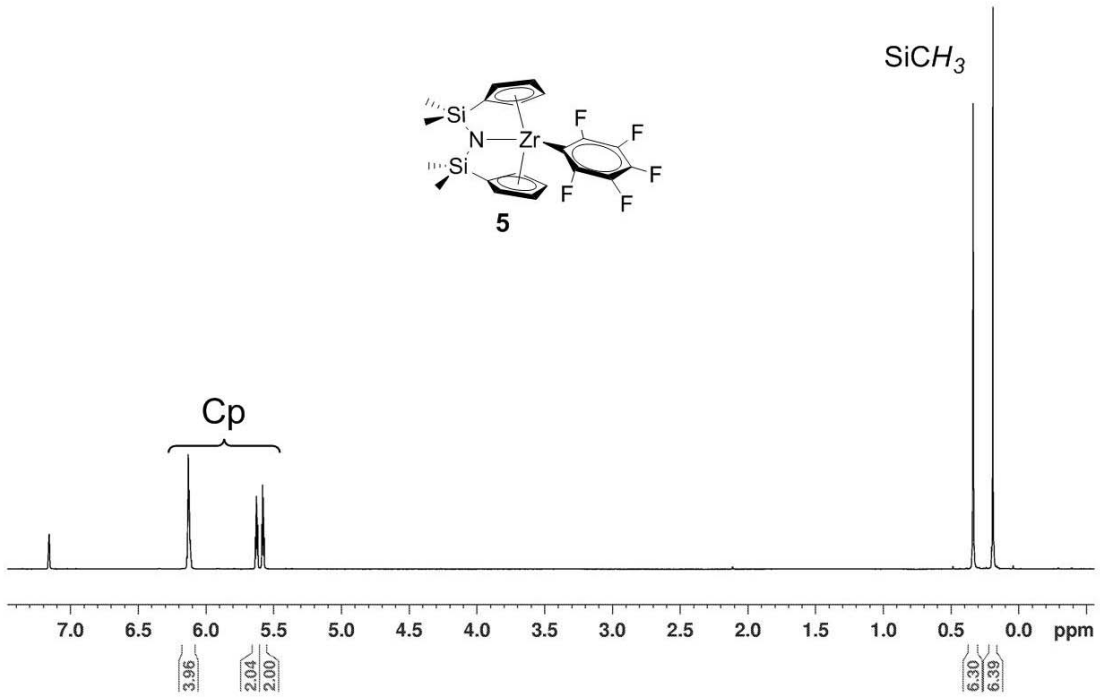

Fig. S6 ^{1}H NMR spectrum of **5** ((400 MHz, C_6D_6, 298 K).

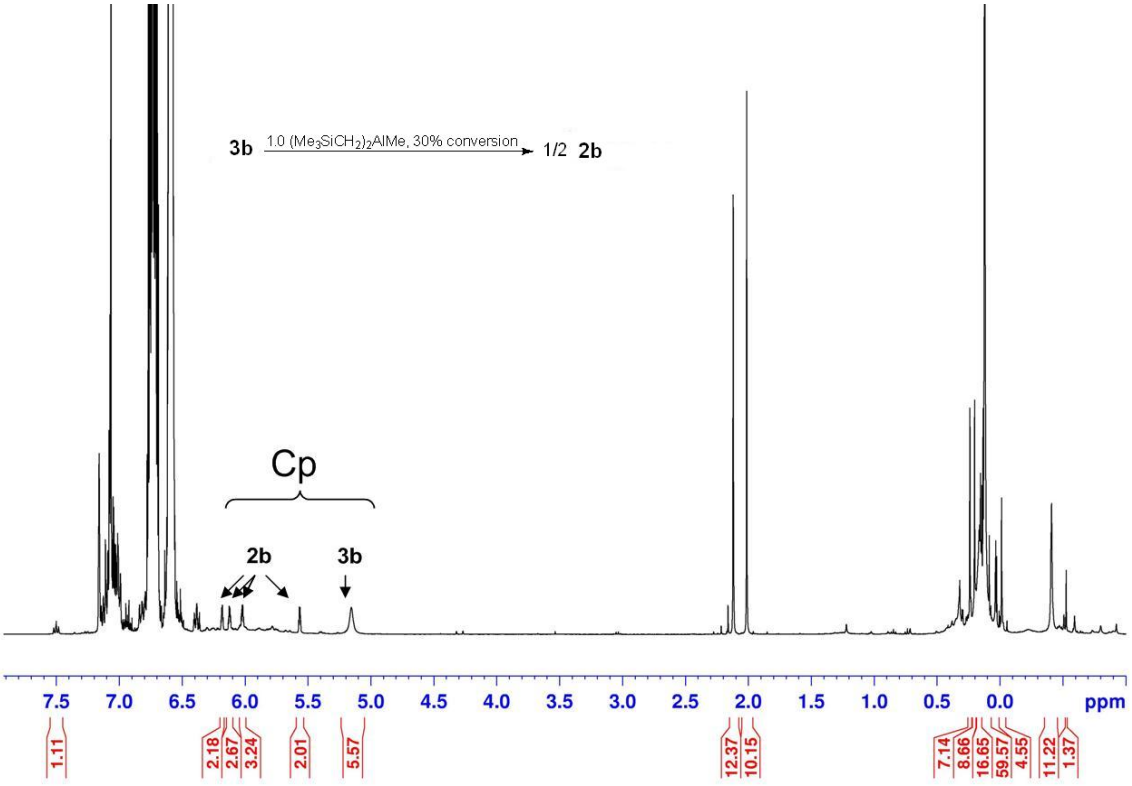

Fig. S7 ^{1}H NMR monitoring of the reaction of **3b** with 1 equiv of $(Me_3SiCH_2)_2AlMe$ in situ, about 30% conversion rate to **2b** was obtained ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

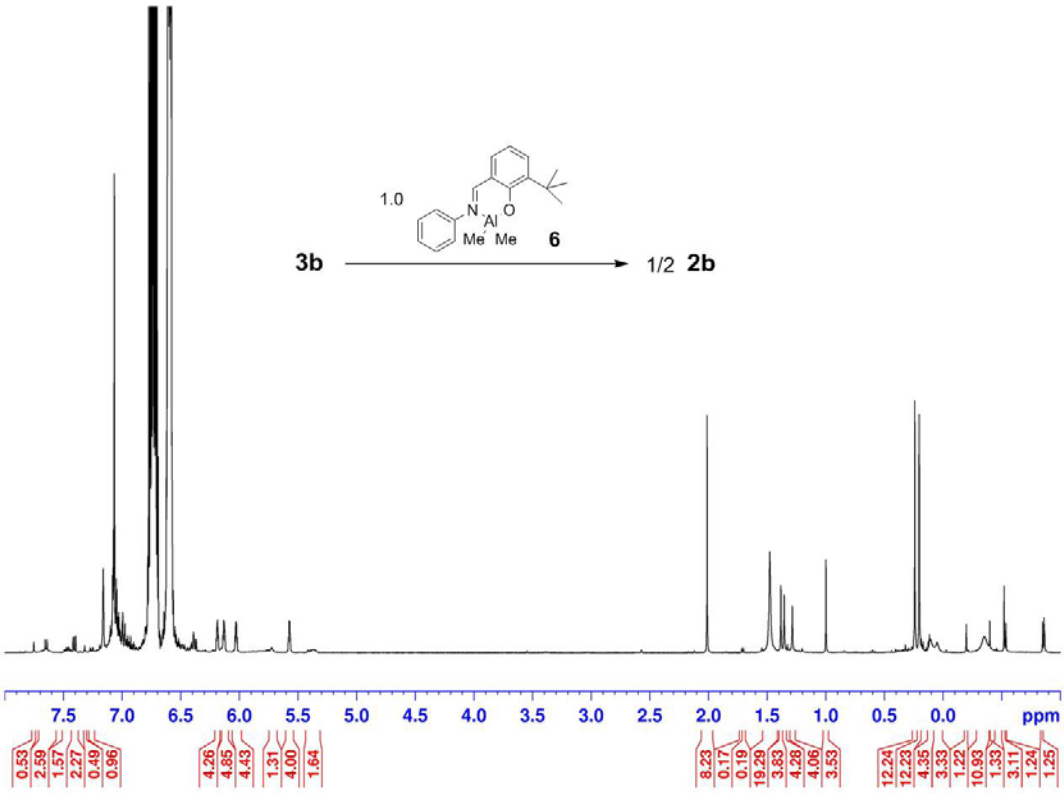

Fig. S8. ^{1}H NMR monitoring of the reaction of **3b** with 1 equiv of **6** ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

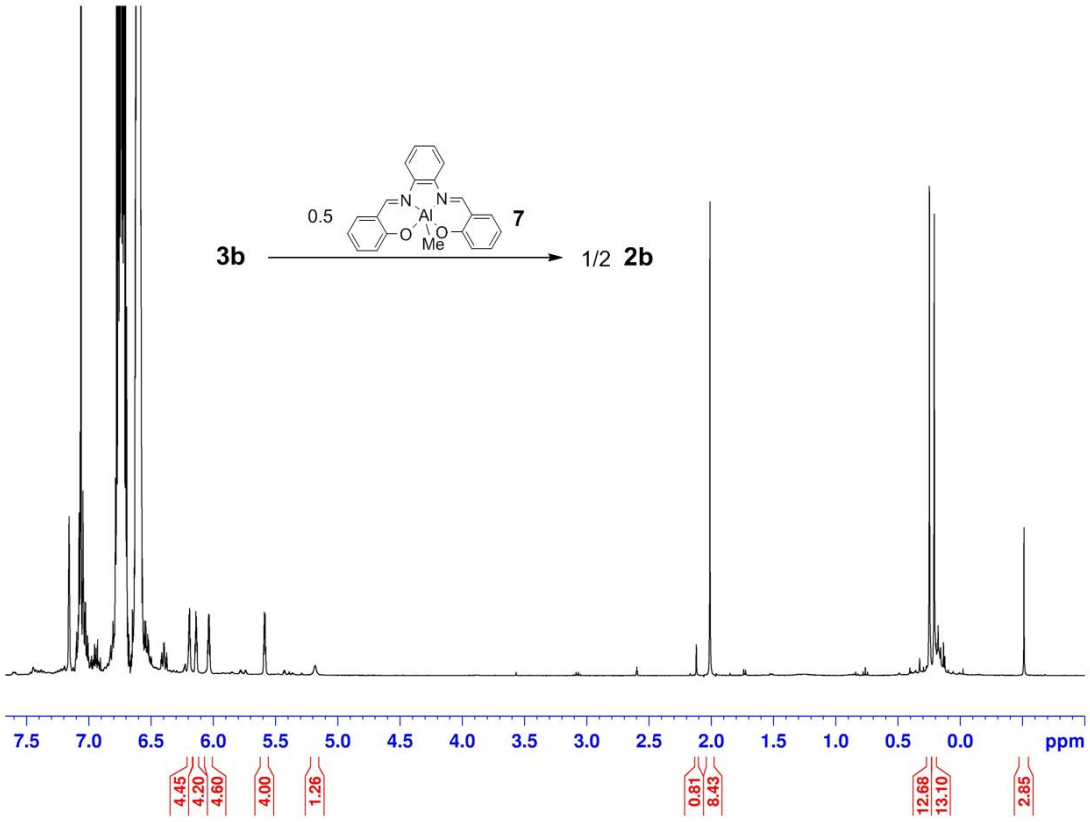

Fig. S9 ^{1}H NMR monitoring of the reaction of **3b** with half equiv of **7** ((400 MHz, C_6D_6/1,2-$C_6H_4F_2$, 298 K).

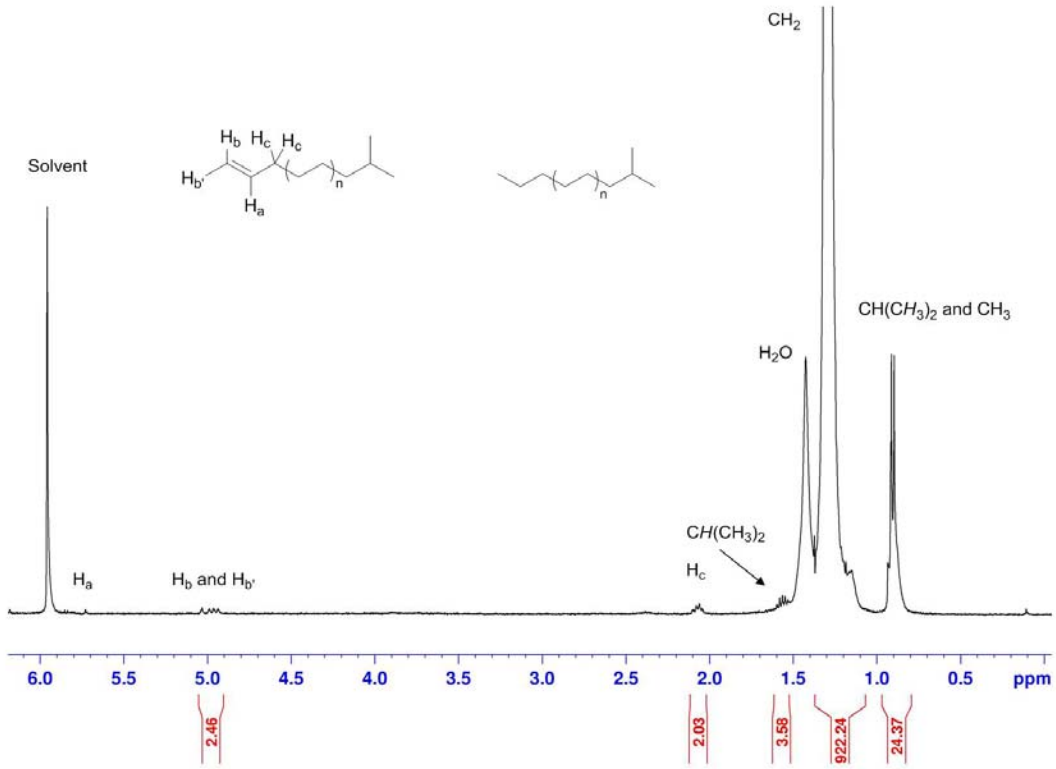

Fig. S10 ^{1}H NMR spectrum of polyethylene obtained by using **3a** and (*i*-Bu)$_3$Al (listed in Table 2, entry 2).

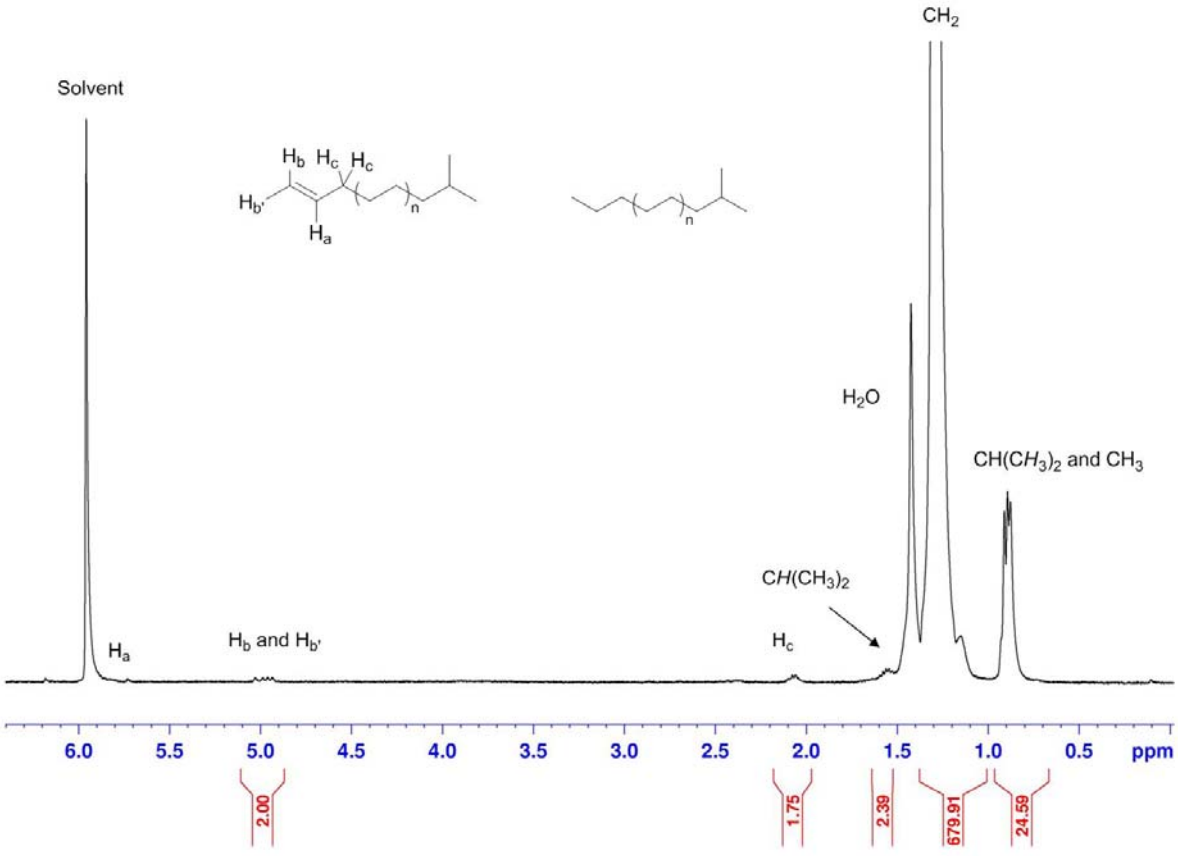

Fig. S11 ^{1}H NMR spectrum of polyethylene obtained by using **3b** and (*i*-Bu)$_3$Al (listed in Table 2, entry 2).

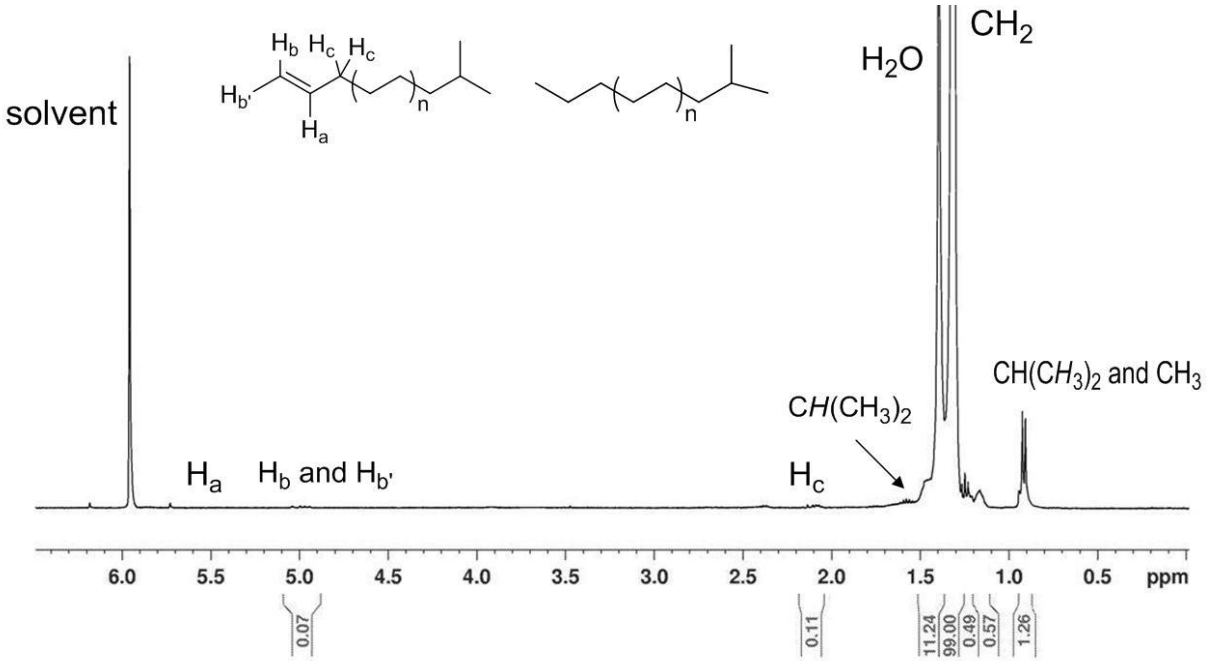

Fig. S12 ^{1}H NMR spectrum of polyethylene obtained by using **2a** and $(i\text{-Bu})_3$Al (listed in Table 2, entry 4).

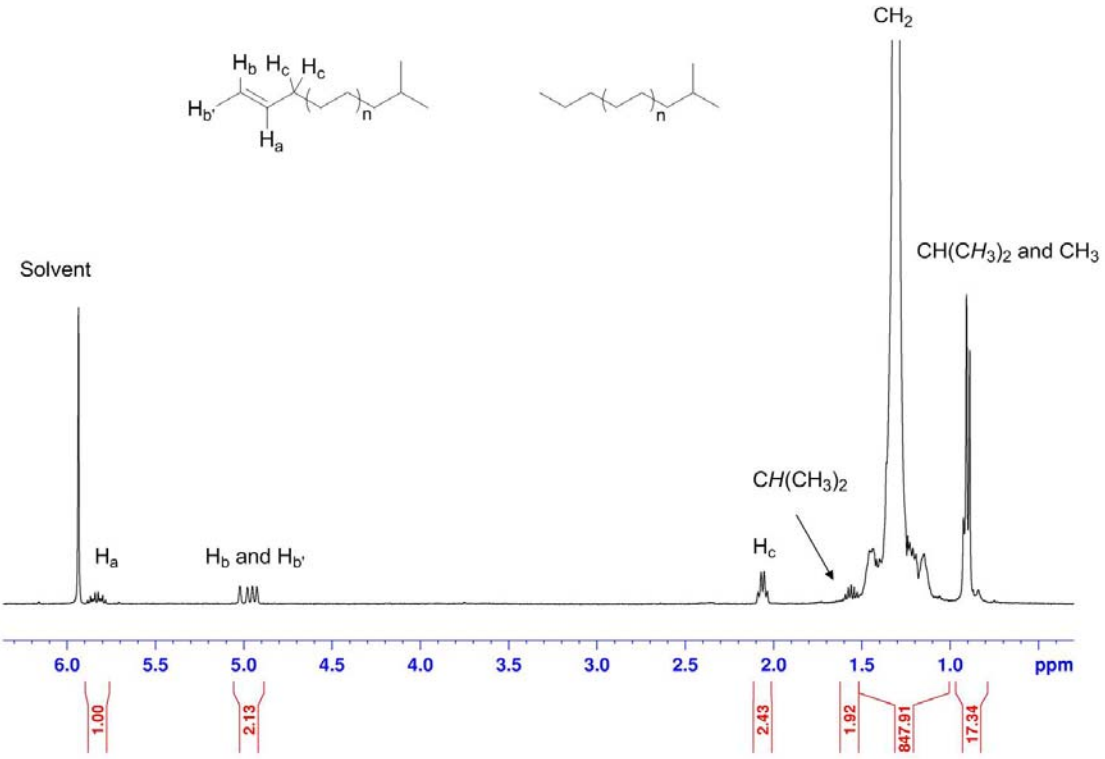

Fig. S13 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and $(i\text{-Bu})_3$Al (listed in Table 2, entry 5).

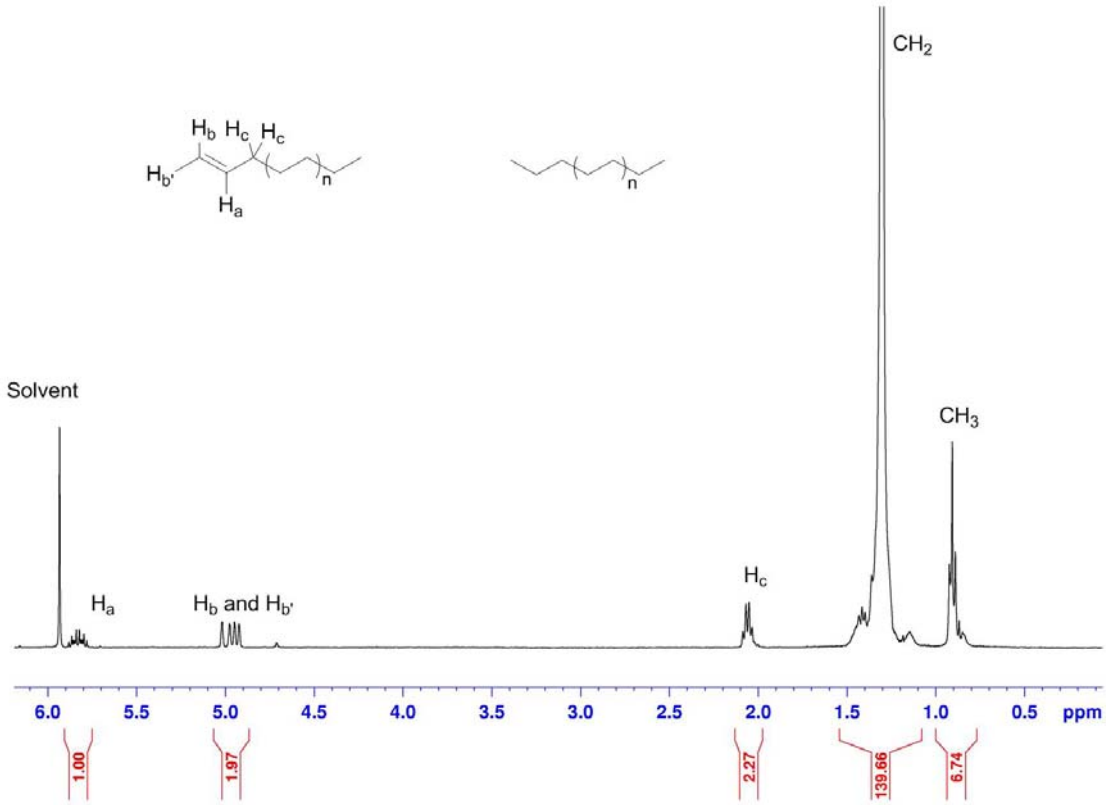

Fig. S14 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and Me_3Al (listed in Table 2, entry 6).

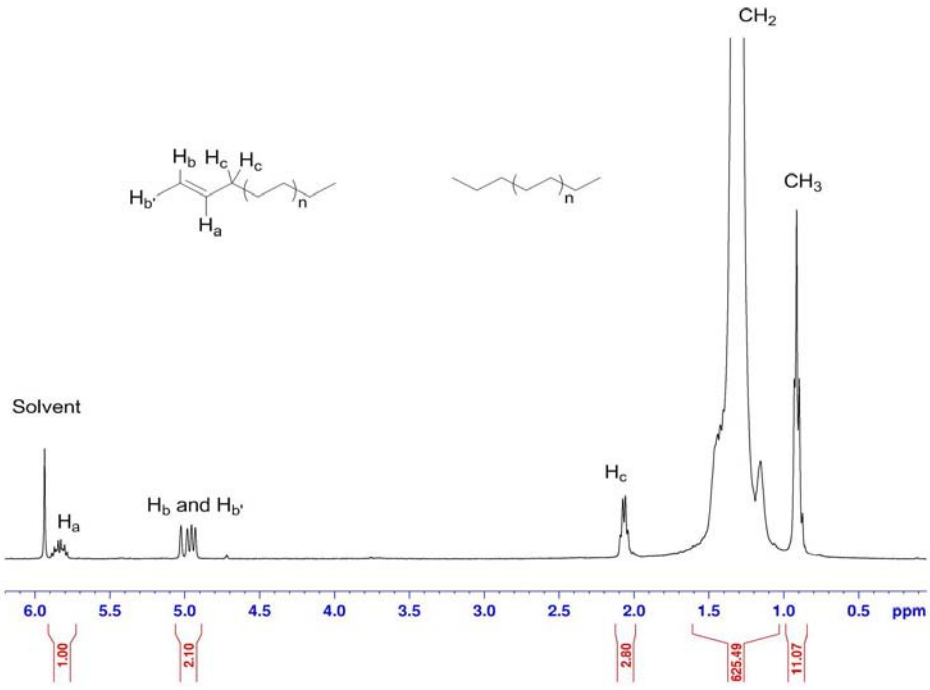

Fig. S15 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and Et_3Al (listed in Table 2, entry 7).

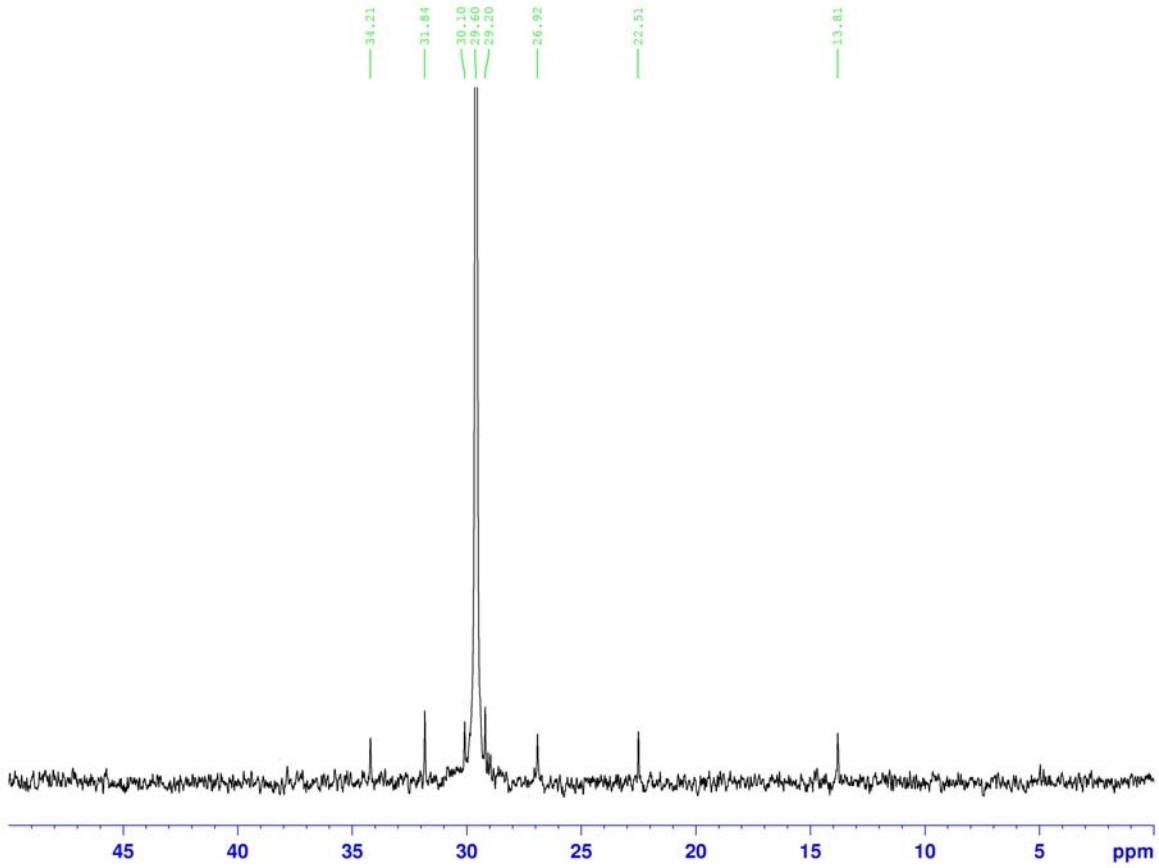

Fig. S16 ^{13}C NMR spectrum of polyethylene obtained by using **2b** and Et_3Al (listed in Table 2, entry 7).

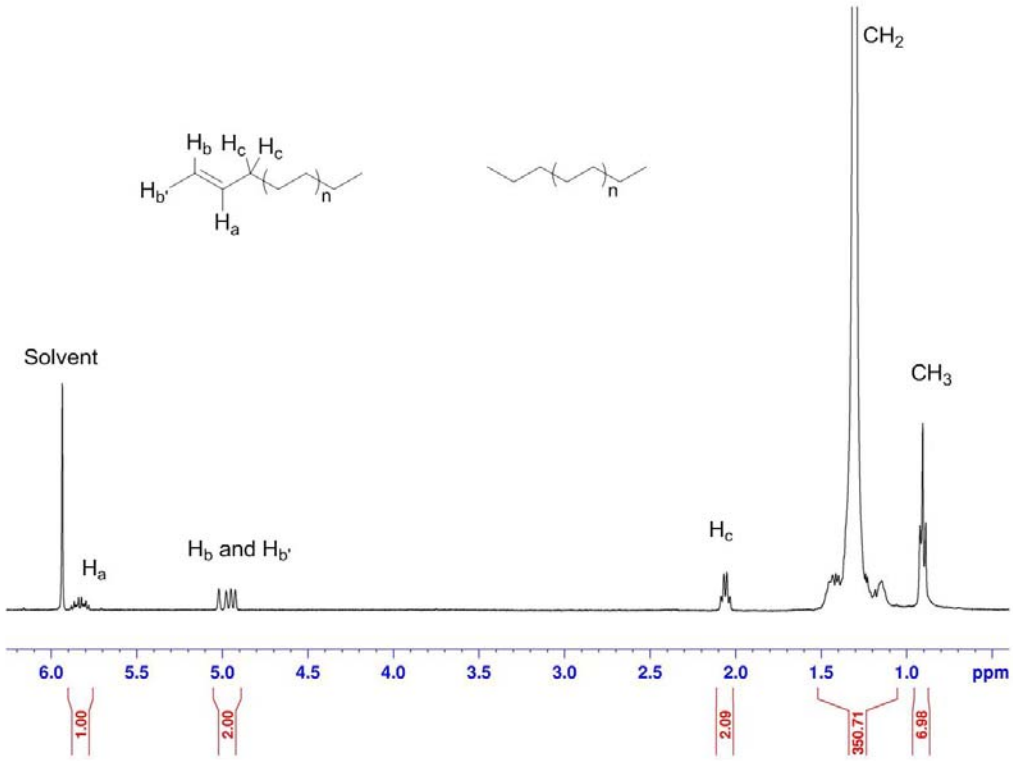

Fig. S17 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and Et_3Al (listed in Table 2, entry 8).

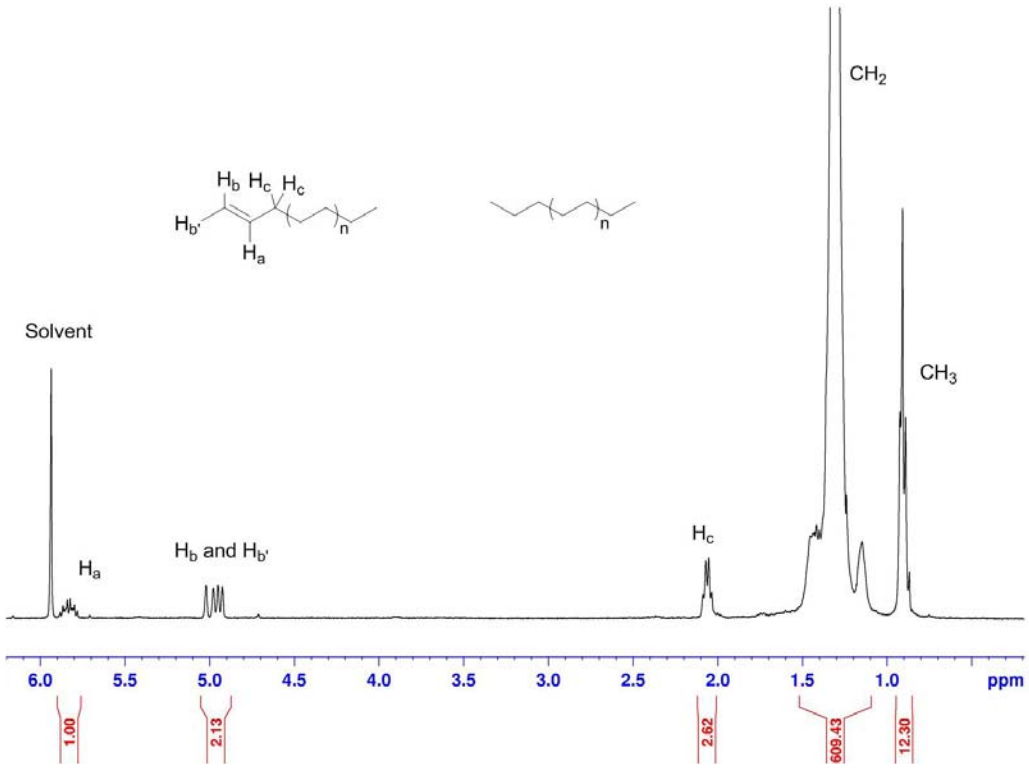

Fig. S18 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and Et_3Al (listed in Table 2, entry 9).

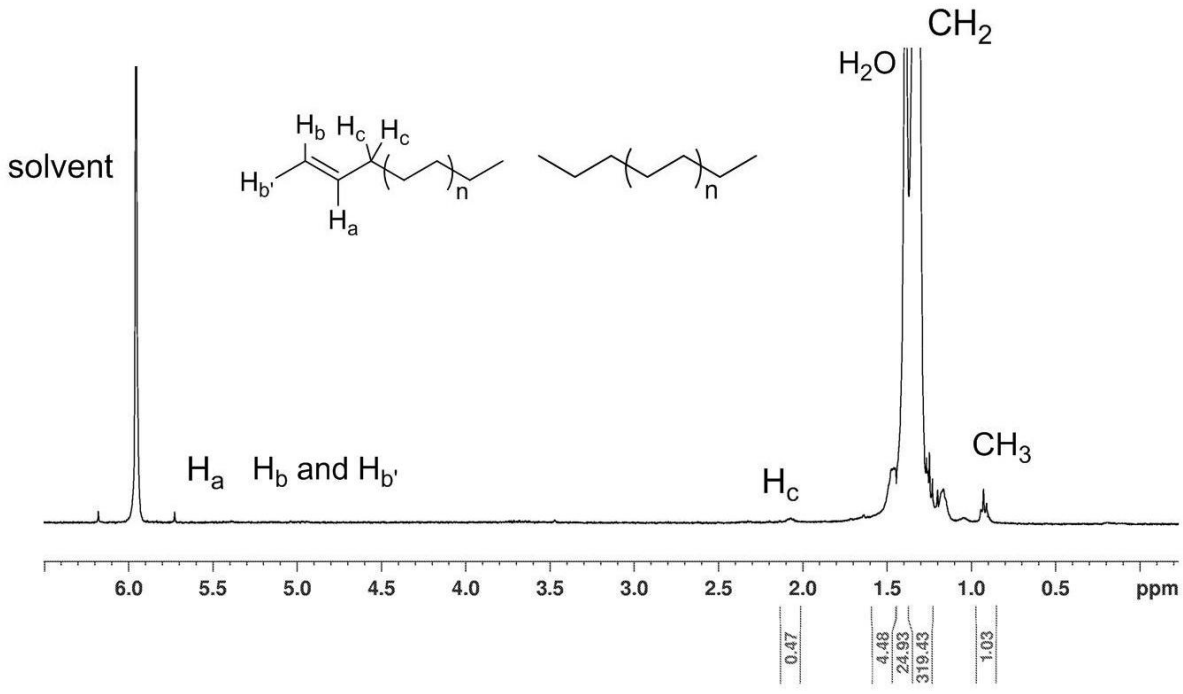

Fig. S19 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and $(Me_3SiCH_2)_3Al$ (listed in Table 2, entry10).

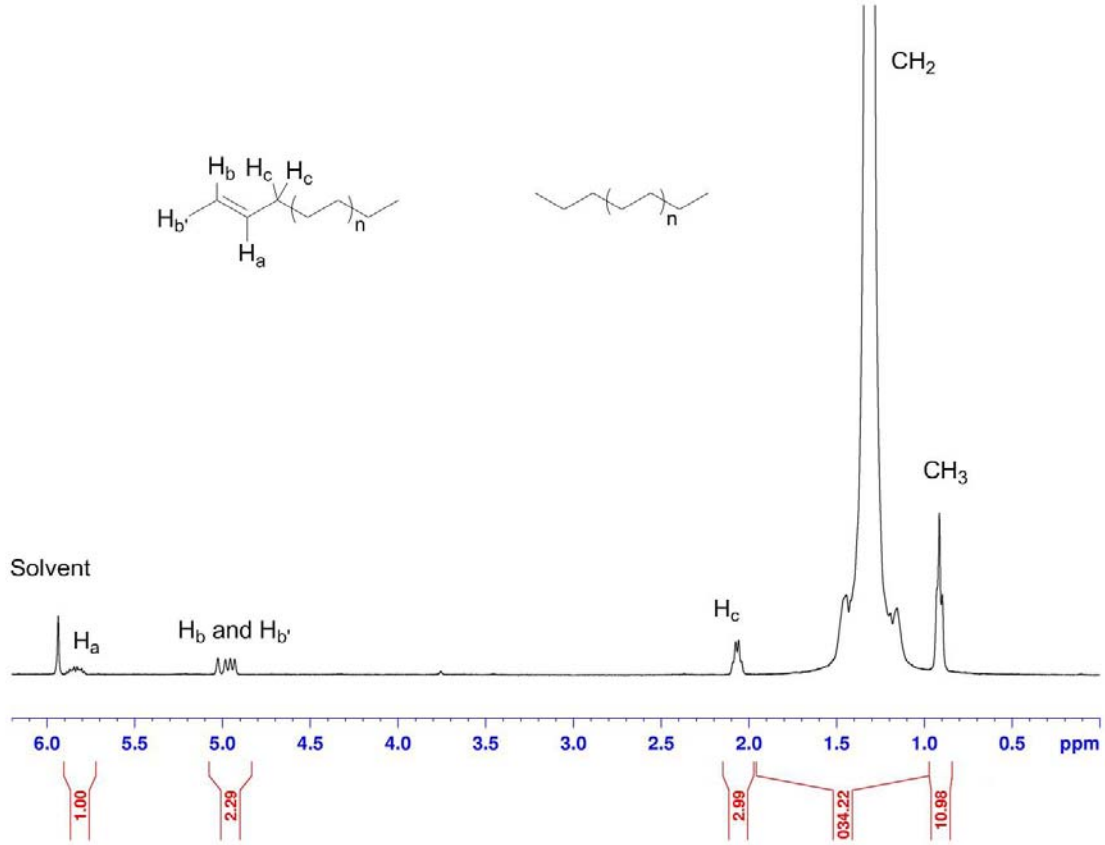

Fig. S20 ^{1}H NMR spectrum of polyethylene obtained by using **2b** and Me_3Al (listed in Table 2, entry11).

Determination of the content of 1-octene in copolymer: Usually the branch distributions in polymer can be determined by ^{13}C NMR anaylsis.[1] In our case that the product copolymer contains significant amounts of 1-octene, ^{1}H NMR spectroscopy is a much more convenient method by the integration of signals.[2] Since our product has low molecular weight and the end group signals can not be neglected, we calculated the content of 1-octene by a modification of the literature method.

$O = [I(CH_3) – 3•I(H_b) –3/2•I(H_c)]/3 = [34.97 – 3 –5.205]/3 = 8.92$

$E = [I(CH_2 \text{ and } CH) + I(H_d) + 5/2•I(H_a) + 2•I(H_c)– 13O]/4 = [176.43 + 5.18 + 6.96 + 9.6 – 115.98]/4 = 20.54$

$\text{Mol \% 1-octene} = 100O/(O + E) = 892/(8.92 + 20.54) = 30$

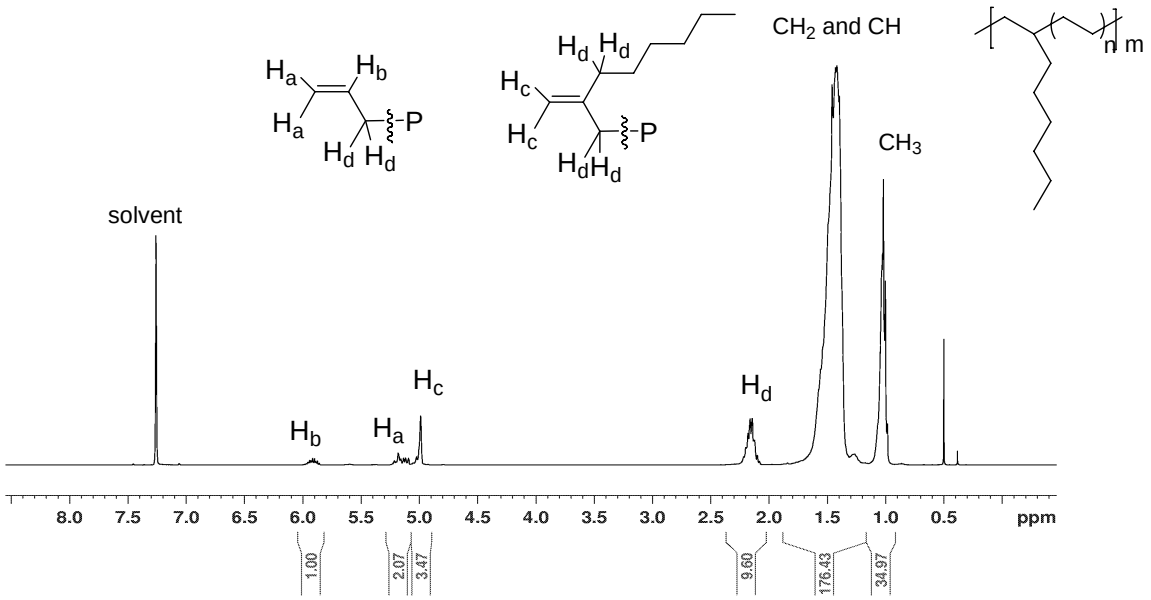

Fig. S21 ^{1}H NMR spectrum of the copolymer of ethylene with 1-octene using **1** and MAO (400 MHz, benzene-d_6, 298 K)

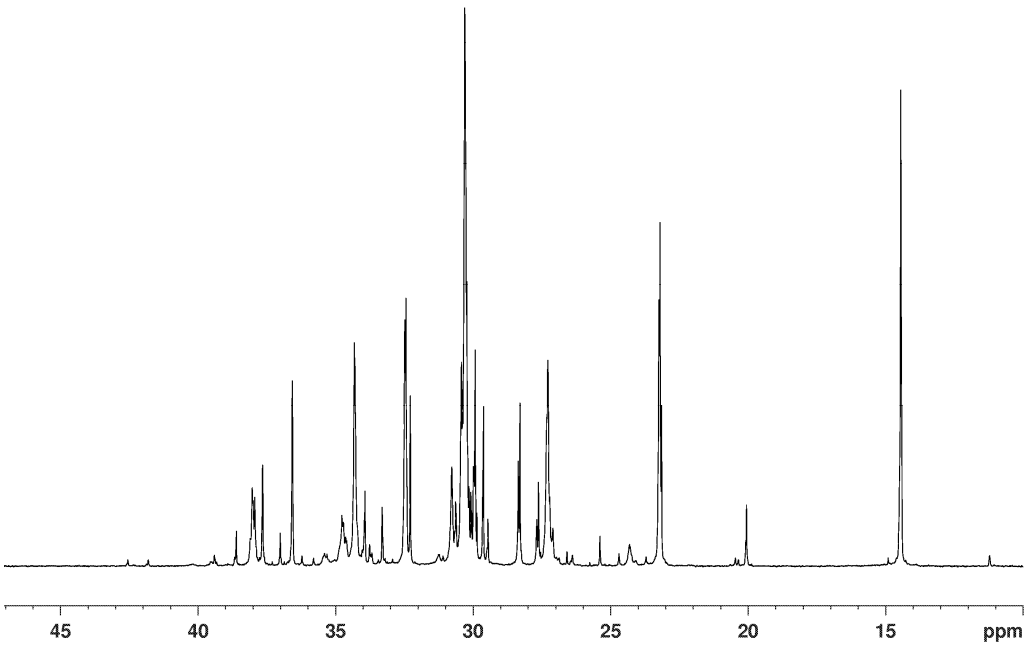

Fig. S22 ^{13}C NMR spectrum of the copolymer of ethylene with 1-octene using **1** and MAO (100 MHz, benzene-d_6, 298 K).

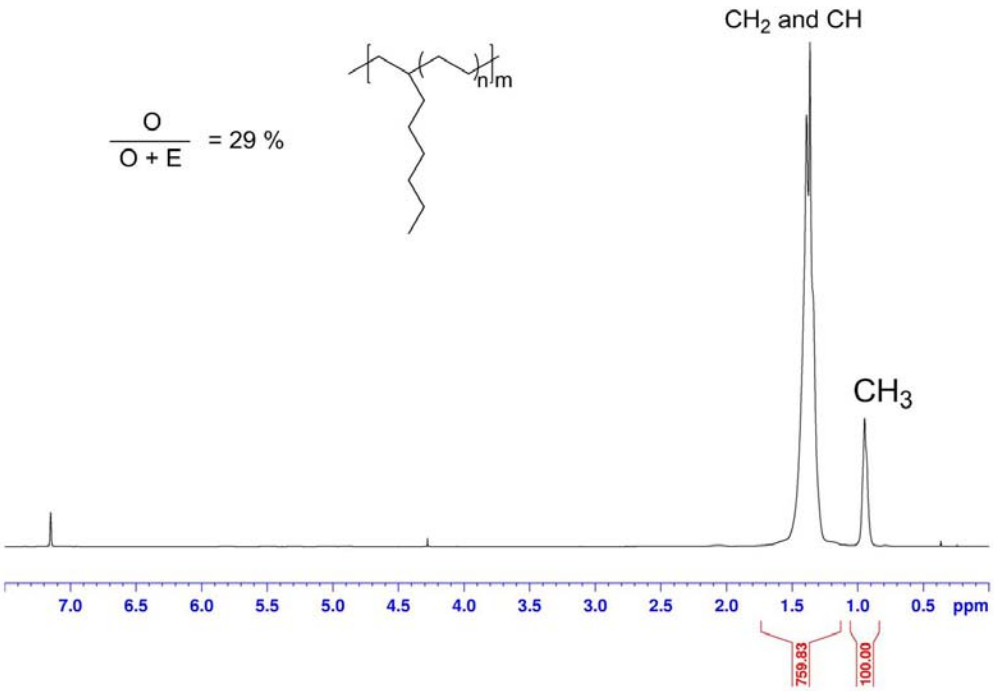

Fig. S23 ^{1}H NMR spectrum of the copolymer of ethylene with 1-octene using **2b** and Et_3Al (100 MHz, benzene-d_6, 298 K).

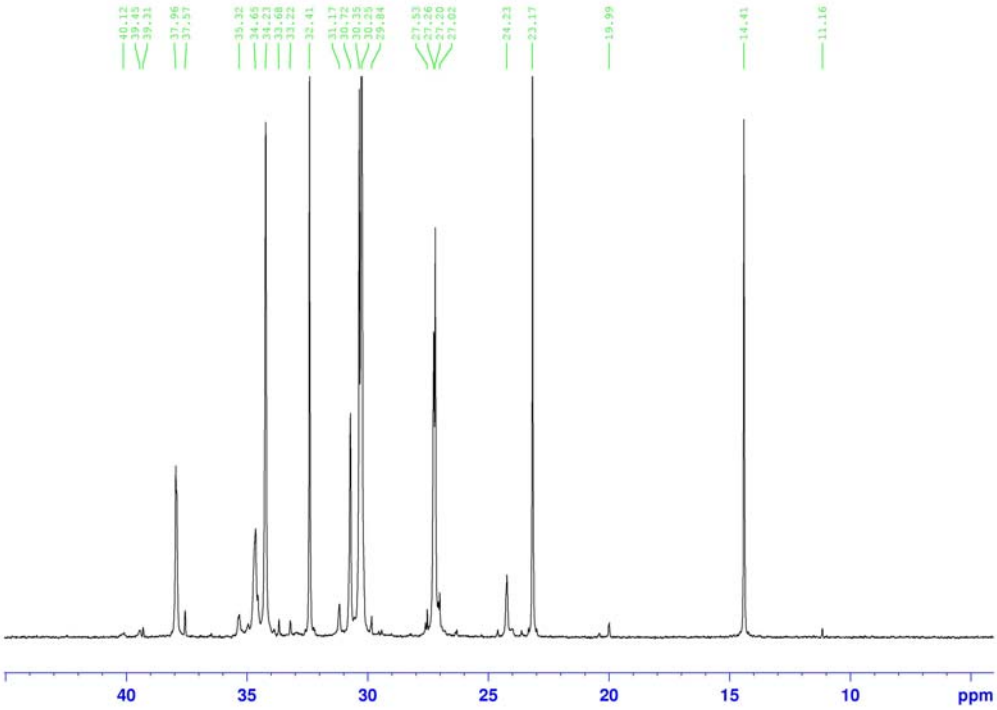

Fig. S24 ^{13}C NMR spectrum of the copolymer of ethylene with 1-octene using **2b** and Et_3Al (100 MHz, benzene-d_6, 298 K).

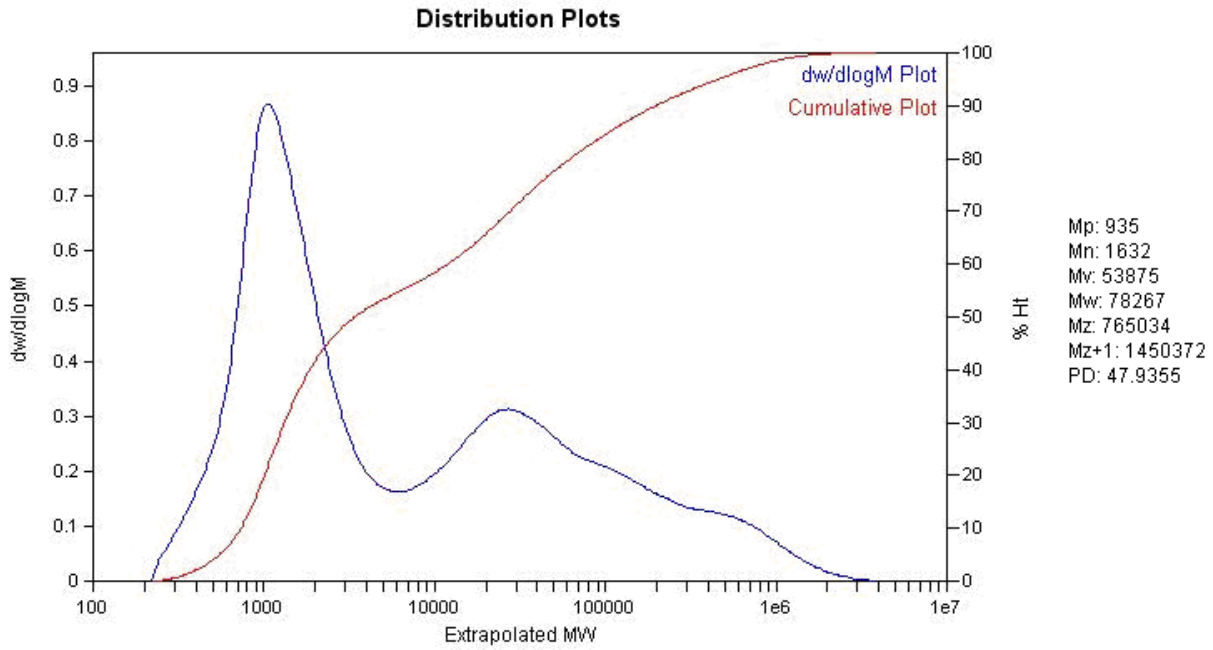

Fig. S25 GPC trace of the polyethylene (Table 2, entry 1).

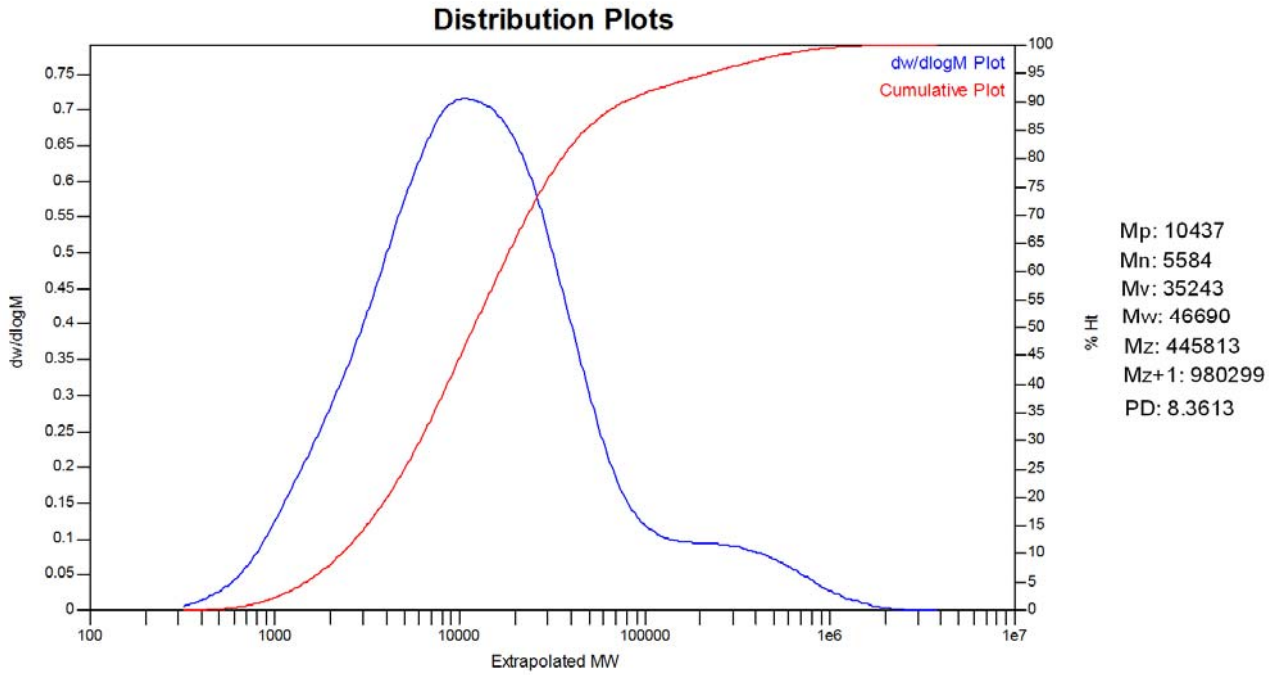

Fig. S26 GPC trace of the polyethylene (listed in Table 2, entry 2).

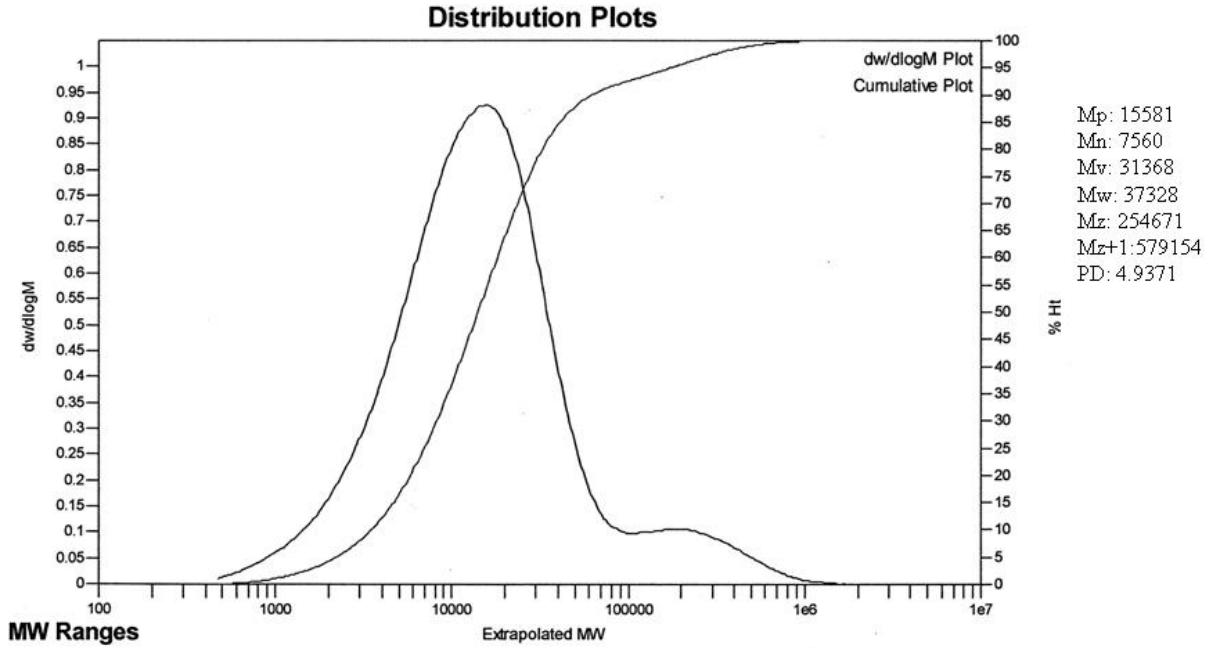

Fig. S27 GPC trace of the polyethylene (listed in Table 2, entry 3).

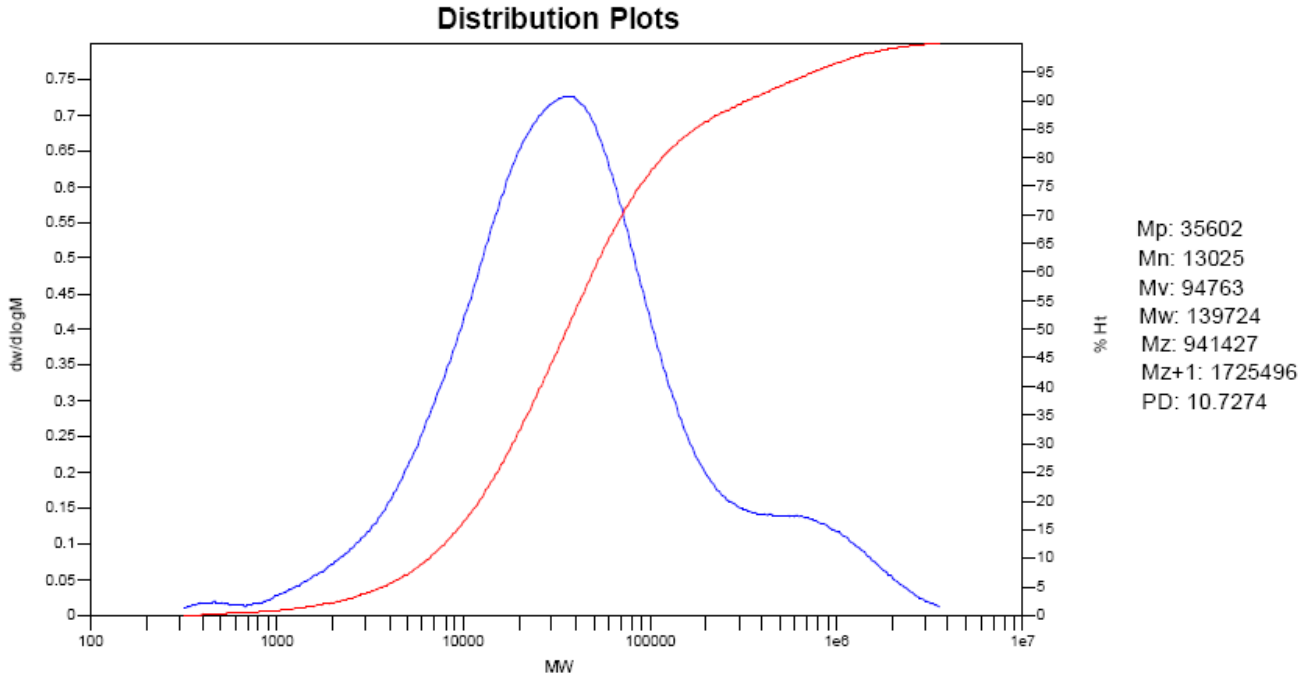

Fig. S28 GPC trace of the polyethylene (listed in Table 2, entry 4).

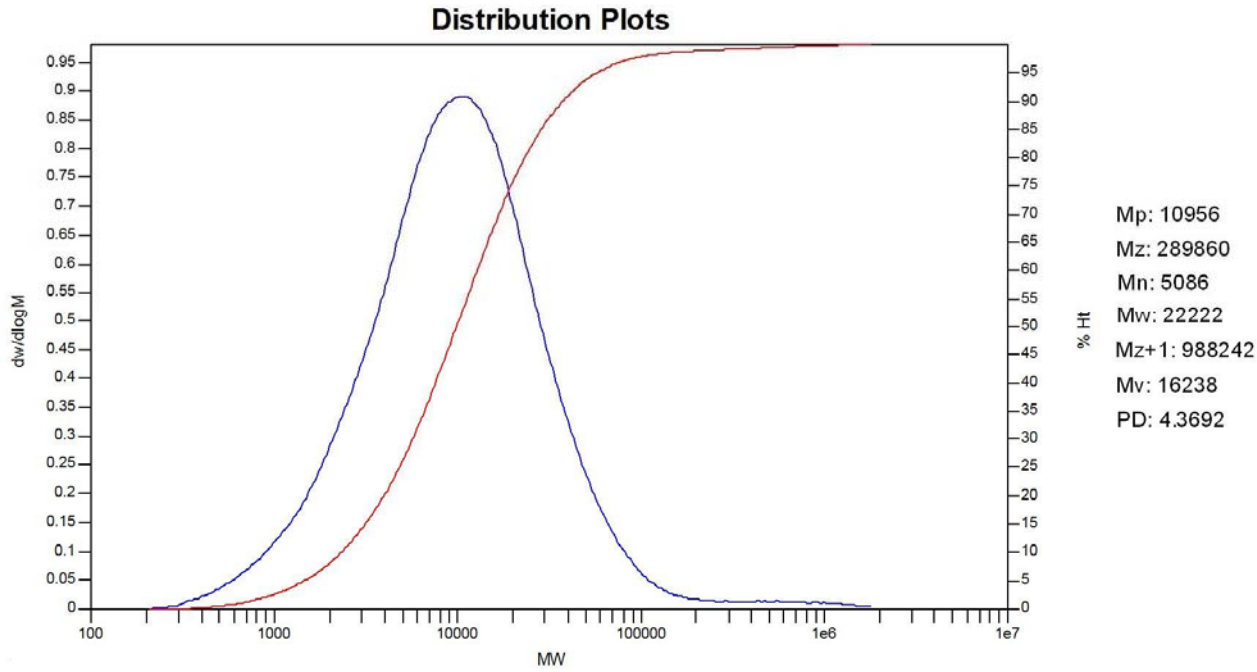

Fig. S29 GPC trace of the polyethylene (listed in Table 2, entry 5).

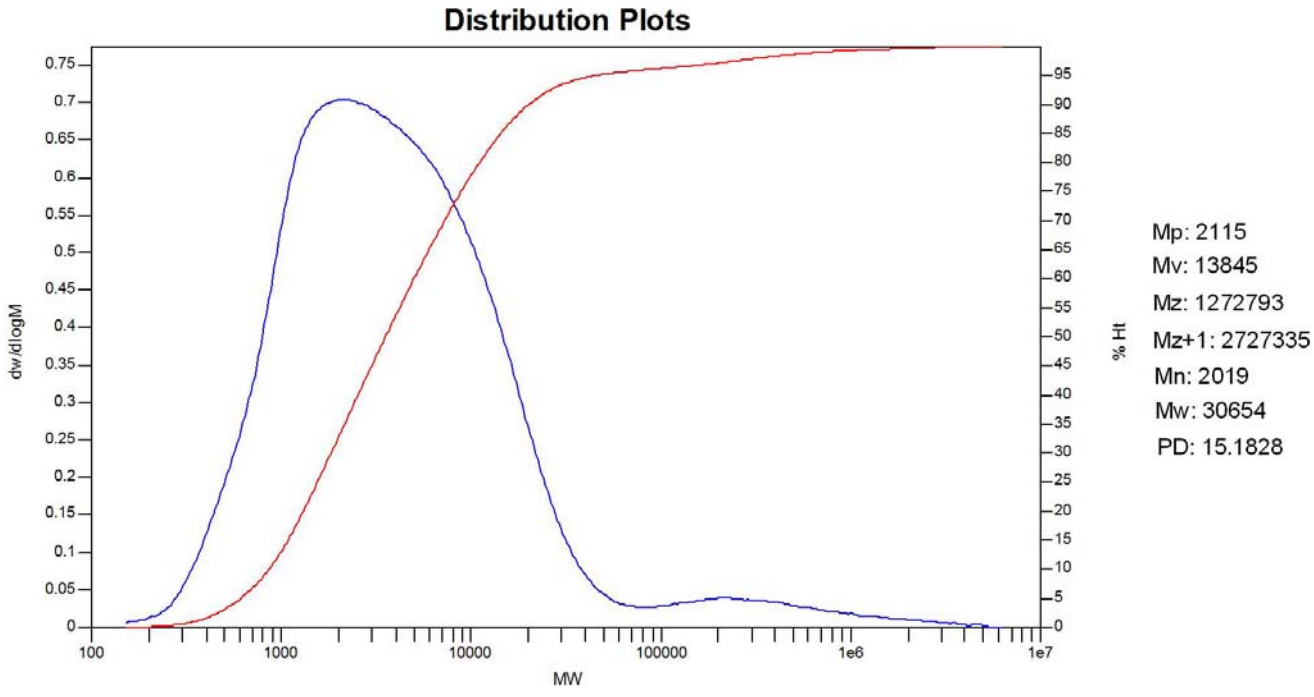

Fig. S30. GPC trace of the polyethylene (listed in Table 2, entry 6).

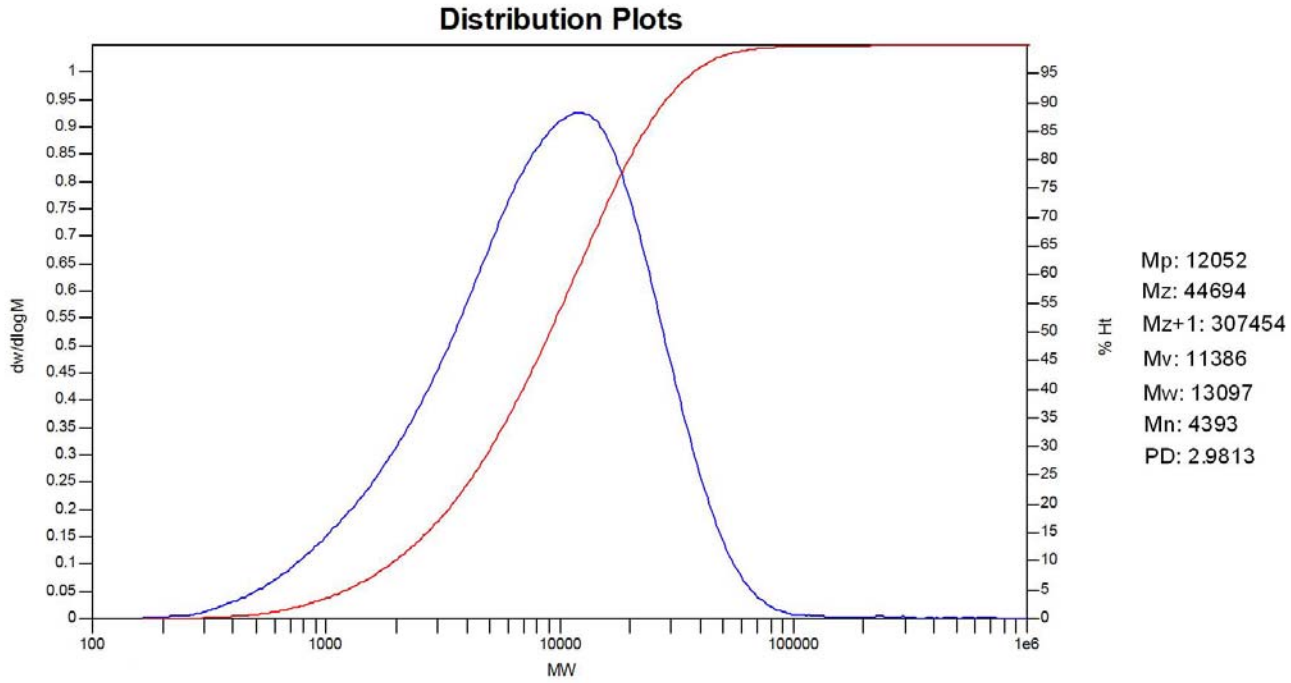

Fig. S31 GPC trace of the polyethylene (listed in Table 2, entry 7).

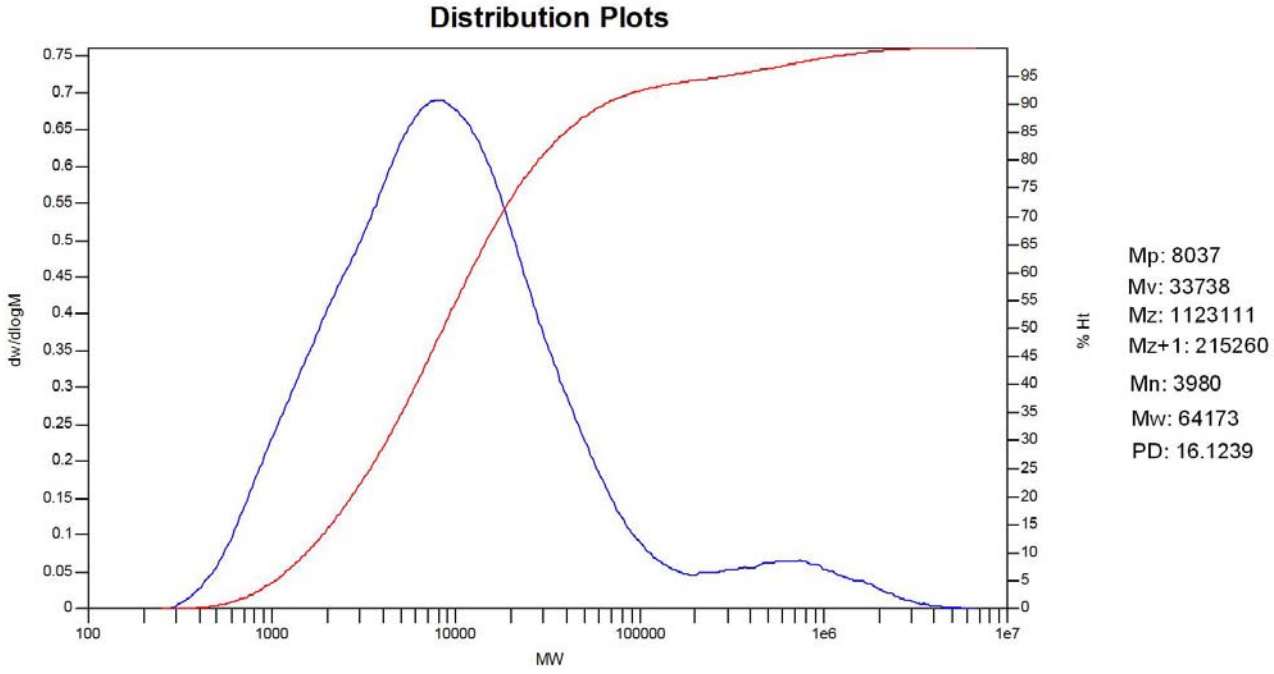

Fig. S32. GPC trace of the polyethylene (listed in Table 2, entry 8).

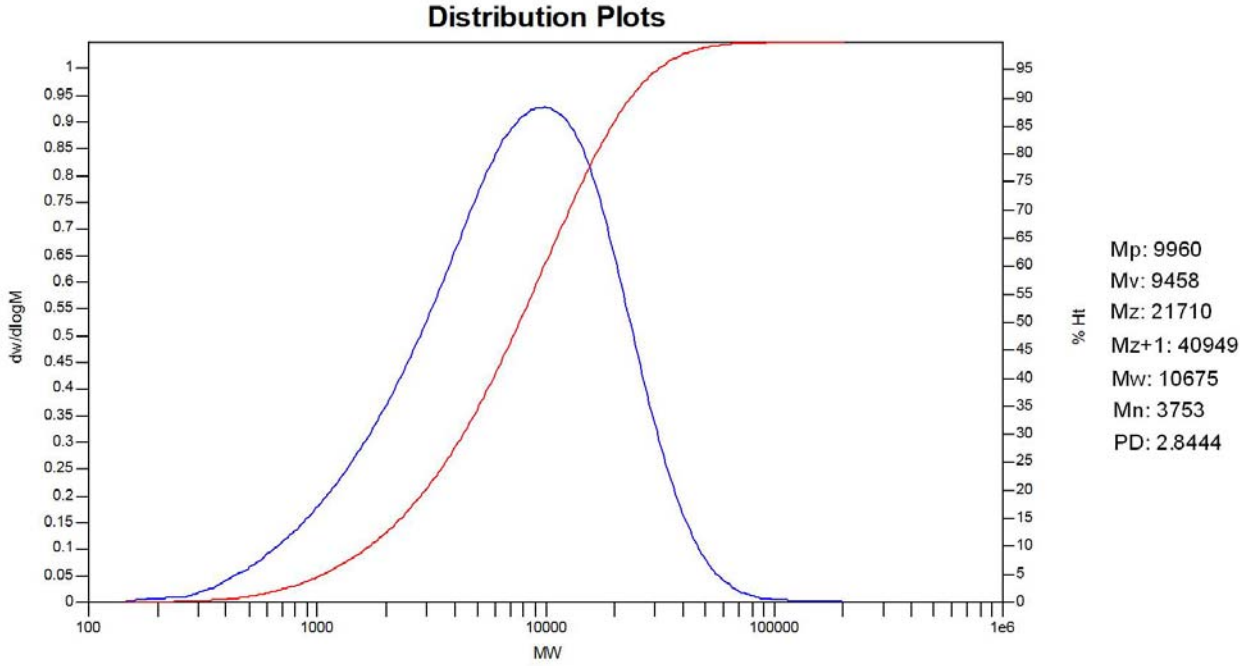

Fig. S33. GPC trace of the polyethylene (listed in Table 2, entry 9).

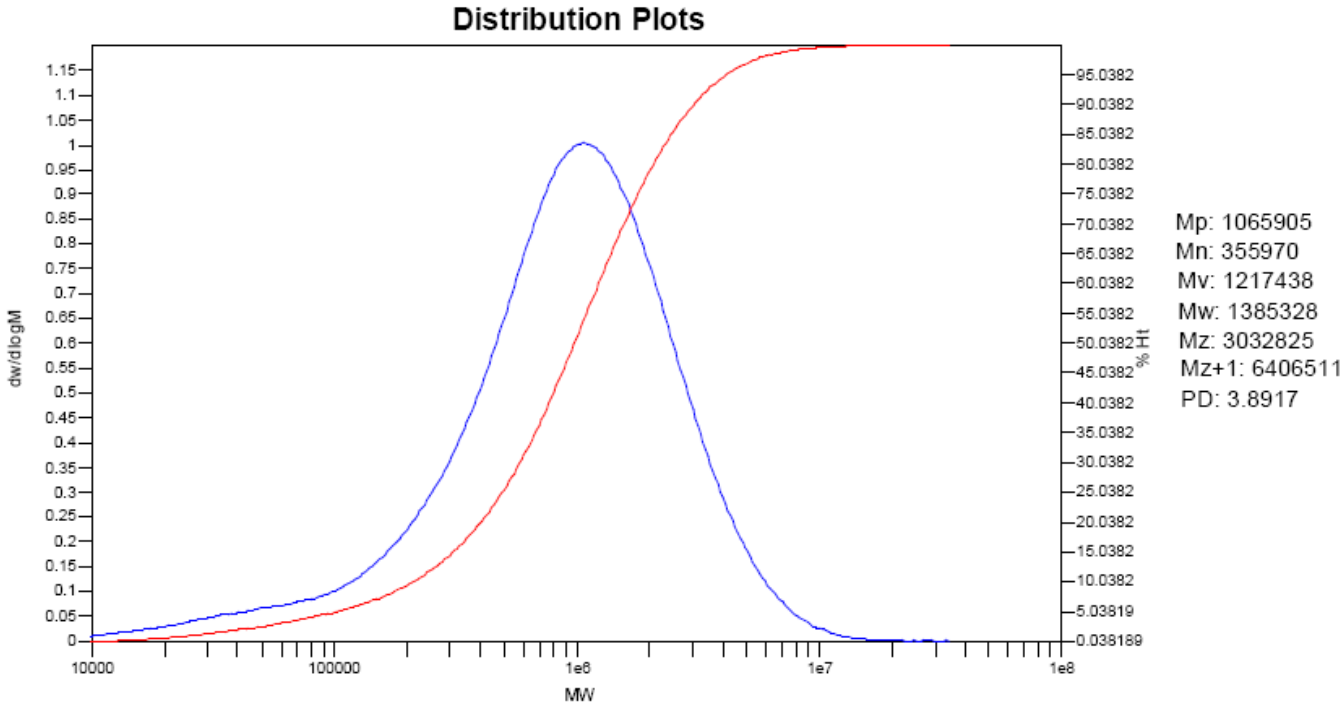

Fig. S34 GPC trace of the polyethylene (listed in Table 2, entry 10).

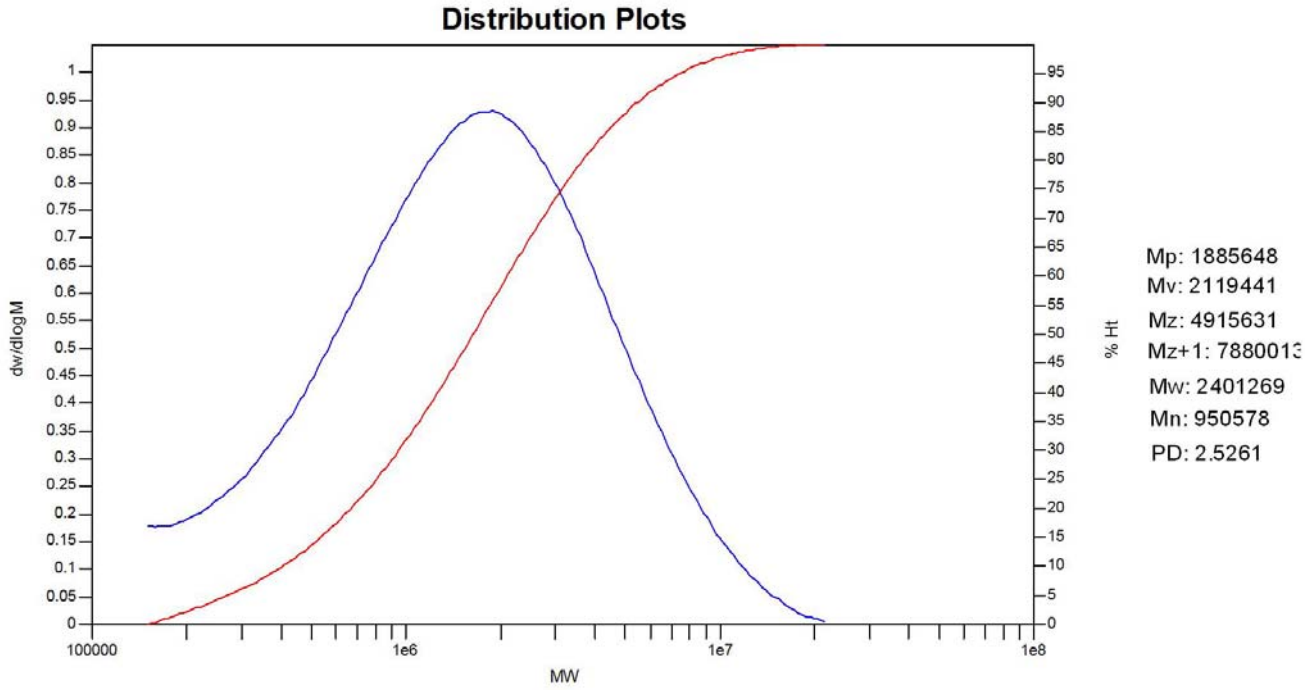

Fig. S35 GPC trace of the polyethylene (listed in Table 2, entry 11).

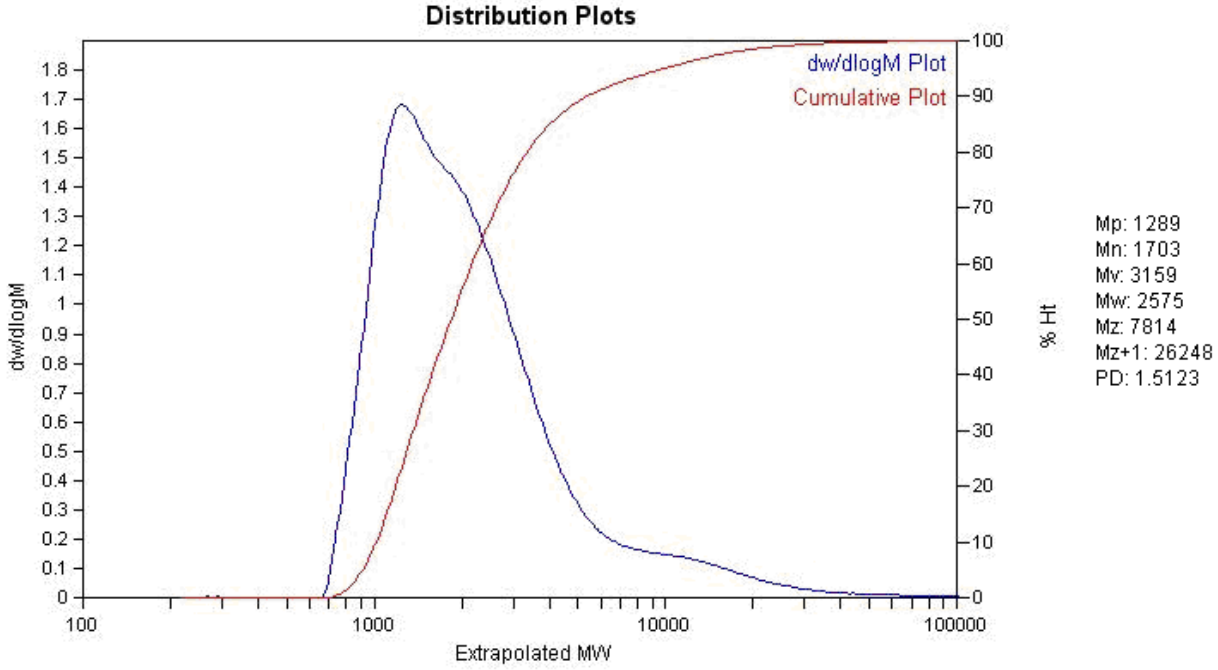

Fig. S36 GPC trace of the copolymer of ethylene with 1-octene using **1** and MAO.

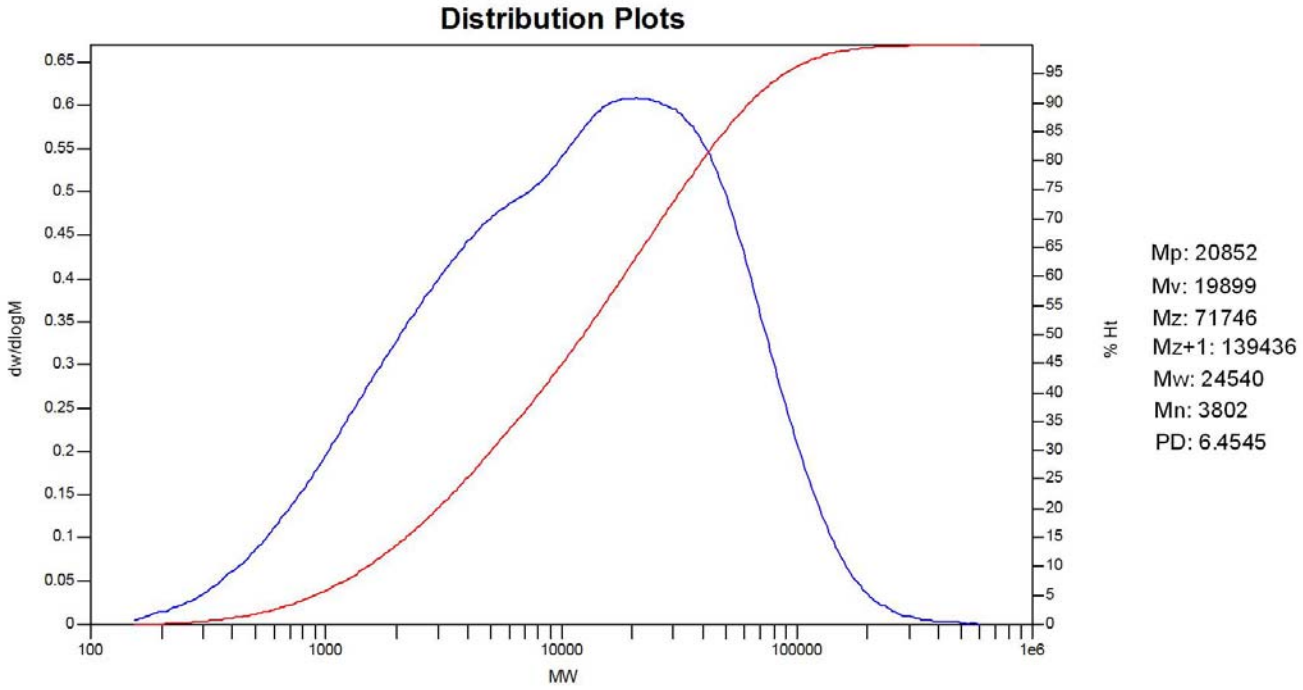

Fig. S37 GPC trace of the copolymer of ethylene with 1-octene using **2b** and Et_3Al.

1 (*a*) Pooter, M. De.; Smith, P. B.; Dohrer, K. K.; K. Bennett, K. F.; Meadows, M. D.; Smith, C. G. ; Schouwenaars, H. P.; Geerards, R. A. *J. Appl. Polym. Sci.* **1991**, *42*, 399. (*b*) Randall, J. C. *JMS-Rev. Macromol. Chem. Phys.* **1989**, C29 (2 & 3), 201. (*c*) Wang, W.-J.; Kolodka, E.; Zhu, S.; Hamielec, A. E. *J. Polym. Sci. A* **1999**, *37*, 2949. (*d*) Liu, W.; Ray III, D. G.; Rinaldi, P. L. *Macromolecules* **1999**, *32*, 3817.

2 Joe, D. J.; Wu, C. J.; Bok, T.; Lee, E. J.; Lee, C. H., Han, W.-S.; Kang, S. O.; Lee, B. Y. *Dalton Trans.* **2006**, 4056.