Electronic supplementary information

INFLUENCE OF DIETHYLZINC ON THE ETHYLENE POLYMERIZATION CATALYZED BY α-DIIMINE NICKEL(II) COMPLEXES

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Experimental section

All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean™ Gas Filters. Chlorobenzene was purified by following literature procedures [S1] and was stored over 4 Å molecular sieves. Pentane and tetrahydrofuran were distilled over Na/benzophenone ketyl. Diethylzinc solution (1.0M in hexanes) and diethylaluminum chloride solution (1.0M in hexanes) were purchased from Aldrich (296112 and 212806). 1,2-Dimethoxyethane complex of nickel(II) bromide was synthesized using the literature procedure [S2].

DSC studies of the resulting polyethylenes were performed with a DSC 204 F1 Phoenix differential scanning calorimeter («NETZSCH») in helium atmosphere. The analyses were performed at the heating rate of 10 °C/min in the temperature range from –80 to 160 °C. The heating cycle was run twice. In the first scan, the samples were heated and then cooled to –80 °C at the rate of –10 °C/min. In the second scan, the samples were reheated at the rate of 10 °C/min. The characteristic melting temperatures and the heat of fusion for PE are given according to the second heating for clear mechanical and thermal history of samples.

The ^{1}H NMR spectra of the polyethylenes obtained in runs 3–7, 9, and 11 (Table 1) in $CDCl_3/CCl_4$ solution and the ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of the ligands were recorded on a Bruker Ultrashield-400 spectrometer at room temperature. The residual solvent proton (^{1}H, $CHCl_3$ = 7.26) and carbon (^{13}C, $CDCl_3$ = 77.16) resonances were used as the reference values. The ^{1}H NMR spectra of the polyethylenes obtained in runs 1, 2, 8, and 10 (Table 1) were recorded on a Bruker Avance-400 spectrometer in *o*-dichlorobenzene (~5% solutions) at 110 °C due to their low solubility.

The molecular weight characteristics of the polyethylenes (weight average molecular mass (M_w), number average molecular mass (M_n), and molecular weight distribution (M_w/M_n)) were determined by gel permeation chromatography (GPC) at 135 °C on a Waters GPCV-2000 chromatograph equipped with two columns (PLgel, 5 μm and Mixed-C, 3007.5 mm) and a refractormer. 1,2,4-Trichlorobenzene served as an eluent, the elution rate was 1 mL·min^{-1}. The molecular masses of the polymers were determined from the universal calibration curve relative to the polystyrene standards with the narrow molecular weight distribution: for polystyrene ($K = 2.88\cdot10^{-4}$, $\alpha = 0.64$) and for PE ($K = 6.14\cdot10^{-4}$, $\alpha = 0.67$).

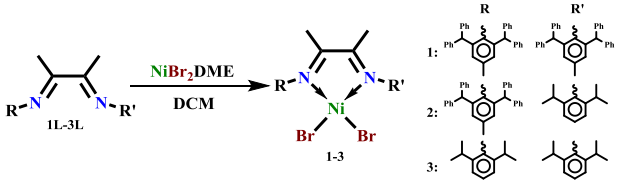
The branch density was calculated by the next formula: $BD = \frac{2I(0.6-1.0)}{3I(0.6-2.0)} \cdot 1000$, where allylic and vinylic protons were not observed due high molecular masses of the polymers; or $BD = \frac{2I(0.6-1.0)}{3Itotal} \cdot 1000$, where allylic and vinylic protons were observed.

Ethylene polymerization

The polymerization reactions were conducted in a 450 mL reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading the catalytic components. Before each experiment, the reactor was heated to 100 °C and then cooled under vacuum for 15 min to remove any residual moisture at room temperature. It was subsequently filled with ethylene, and then 20 mL of chlorobenzene was added under an ethylene flow. The reactor was heated to the desired temperature using a thermostat, after which the precatalyst was loaded into the reactor. The remaining precatalyst was washed from the reactor walls with additional 20 mL of chlorobenzene. The reactor was then evacuated to 80 mmHg, and the mixture was stirred at 400 rpm for 5 s, before being filled with ethylene. Once the temperature stabilized, the required amount of the cocatalyst (DEAC or a mixture of DEAC and DEZ) in hexanes was introduced, followed by the addition of 10 mL of chlorobenzene under an ethylene flow. The reactor was then pressurized with ethylene to a final pressure of 3 bar (non-excessive). The polymerization reactions were conducted at constant pressure and temperature for 30 min, after which the reaction was quenched mixture with 20 mL of isopropanol and 20 mL of 1M HCl. The resulting polymer was filtered off, washed with isopropanol, and dried in a vacuum oven at 60 °C to a constant weight.

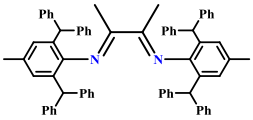
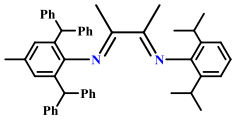
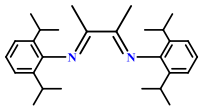
The ethylene polymerization experiments were conducted as part of a screening study to evaluate the influence of diethylzinc (DEZ) on the catalytic activity and polymer branching. Each polymerization run was performed once under identical conditions, following standard practice for initial screening studies. The observed trends across different DEZ concentrations were consistent with the literature data and internal control experiments. While single-run experiments provide valuable insights into the general trends, further studies involving multiple repetitions are planned to assess the reproducibility of specific data points, particularly at 75 and 150 equiv. of DEZ.

Synthesis of complexes 1–3 and ligands 1L–3L

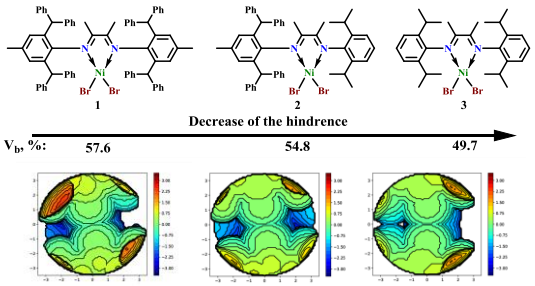


Scheme S1. General scheme for the synthesis of α-diimine Ni(II) complexes **1–3**

Ligands **1L** [S3], **2L** [S4], and **3L** [S5]**,** as well as complexes **1** [S6], **2** [S7], and **3** [S8], were prepared according to the published procedures.

1L		***N,N′*-(1,2-Dimethyl-1,2-ethanediylidene)bis[2,6-dibenzhydryl-4-methylbenzenamine]**	^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.11 (m, 24H), 7.08 – 7.02 (m, 8H), 7.00 – 6.92 (m, 8H), 6.64 (s, 4H), 5.15 (s, 4H), 2.14 (s, 6H),1.15 (s, 6H).	-
2L		***N*-(2,6-Dibenzhydryl-4-methylbenzenamine)-*N′*-(2,6-diisopropylbenzenamine)-(1,2-dimethyl-1,2-ethanediylidene)**	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 6.91 (m, 23H), 6.67 (s, 2H), 5.25 (s, 2H), 2.62 (hept, J = 6.7 Hz, 2H), 2.18 (s, 3H), 1.87 (d, J = 1.4 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.7 Hz, 6H), 0.87 (d, J = 1.4 Hz, 3H).	^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 168.0, 146.2, 145.7, 143.8, 142.6, 135.0, 131.8, 131.6, 129.9, 129.6, 128.9, 128.6, 128.2, 126.5, 126.2, 123.9, 123.1, 52.4, 28.3, 23.5, 23.3, 21.5, 16.9, 16.1.
3L		***N,N′*-(1,2-Dimethyl-1,2-ethanediylidene)bis[2,6-diisopropylbenzenamine]**	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.08 (m, 6H), 2.74 (hept, J = 7.1 Hz, 4H), 2.10 (s, 6H), 1.22 (d, *J* = 7.7 Hz, 12H), 1.19 (d, *J* = 7.7 Hz, 12H).	^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, JMOD) δ 168.3(-), 146.3(-), 135.2(-), 123.9(+), 123.1(+), 28.6(+), 23.1(+), 22.9(+), 16.7(+).

Steric maps of complexes 1–3



Scheme S2. Steric map of α-diimine Ni(II) complexes **1–3** from Sambvca 2.1 [S9].

Spectra of the ligands and polymers

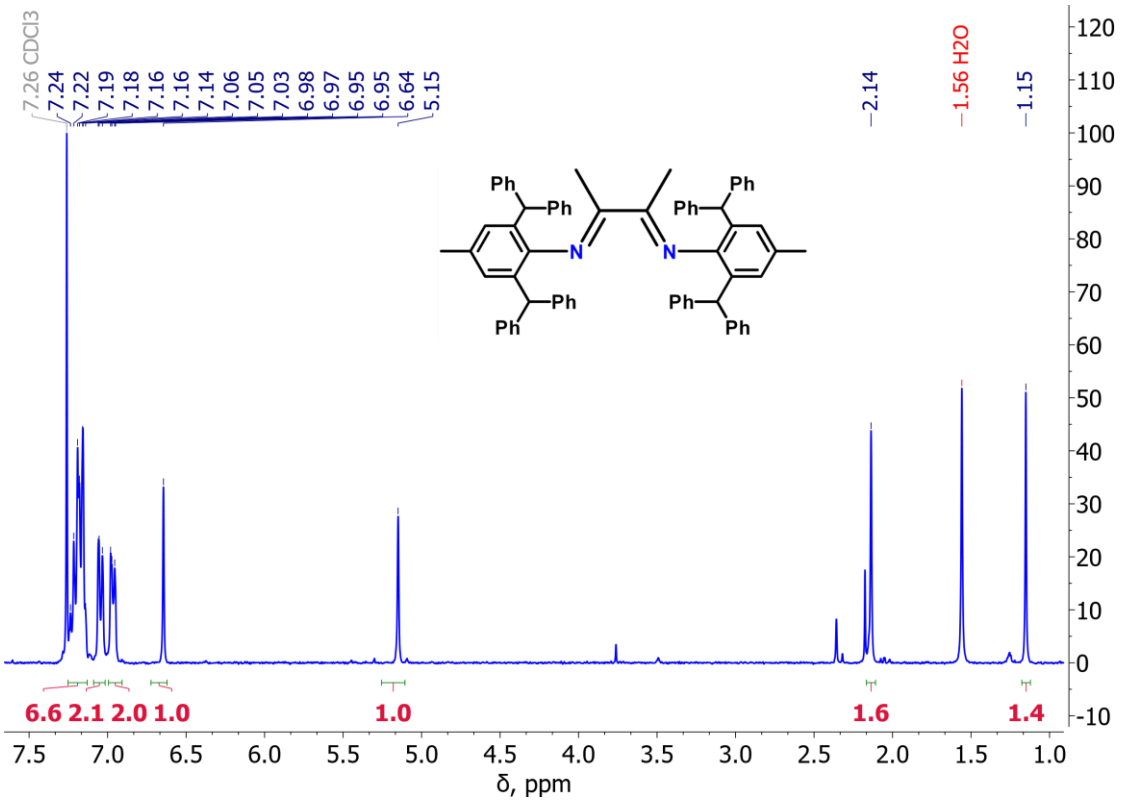


Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of *N,N′*-(1,2-dimethyl-1,2-ethanediylidene)-bis[2,6-dibenzhydryl-4-methylbenzenamine].

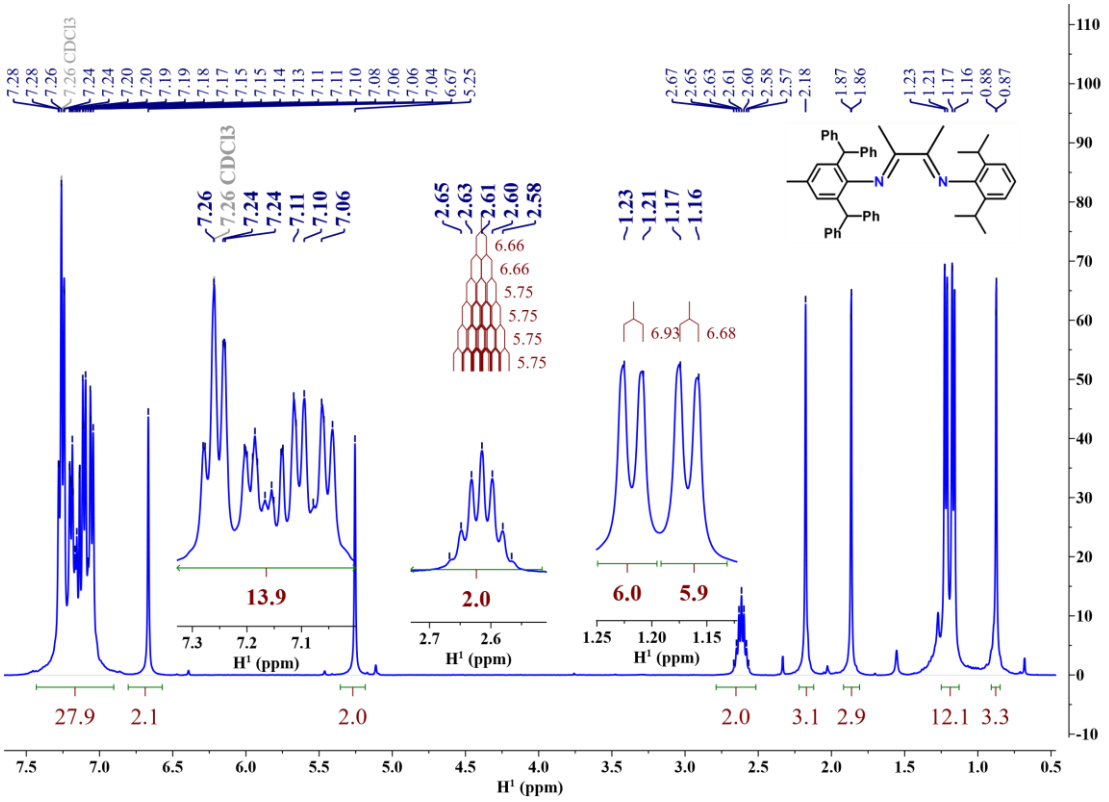


Figure S2. ^{1}H NMR spectrum ($CDCl_3$) of N^2-(2,6-dibenzhydryl-4-methylphenyl)-N^3-(2,6-diisopropylphenyl)butane-2,3-diimine.

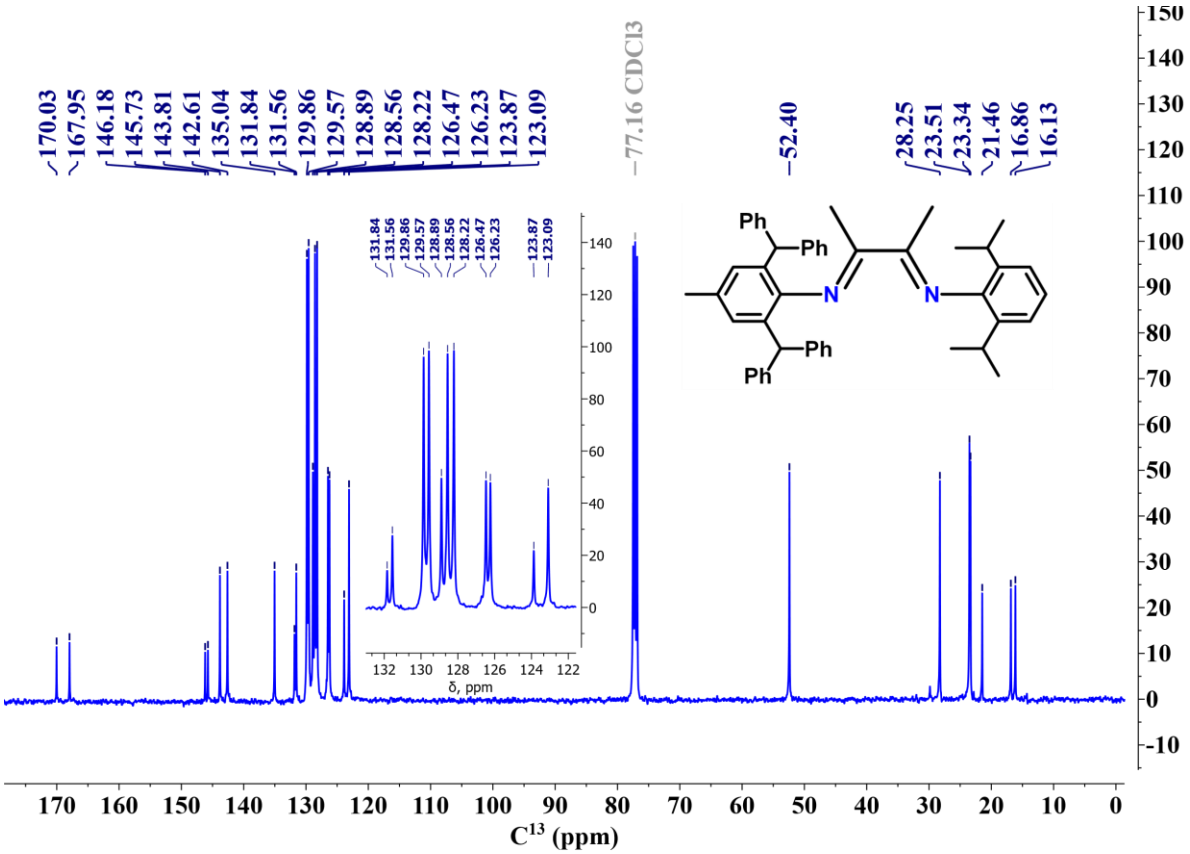


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of *N*^{2}-(2,6-dibenzhydryl-4-methylphenyl)-*N*^{3}-(2,6-diisopropylphenyl)butane-2,3-diimine.

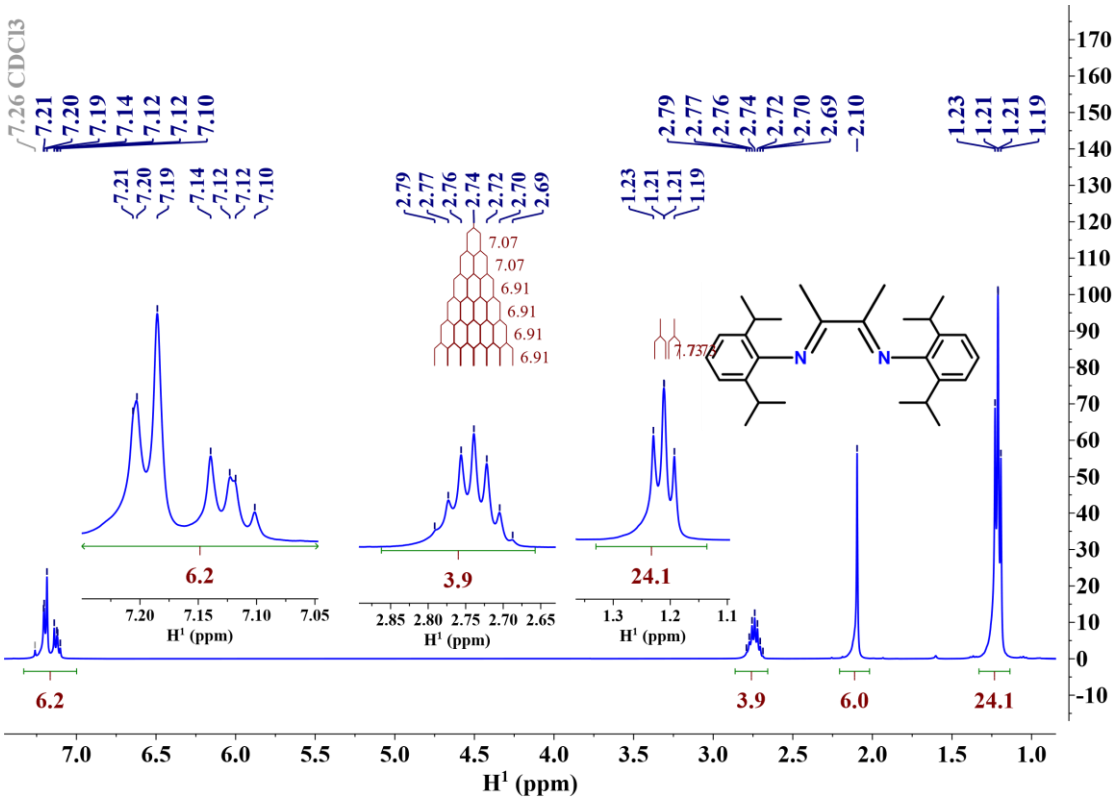


Figure S4. ^{1}H NMR spectrum ($CDCl_3$) of *N,N′*-(1,2-dimethyl-1,2-ethanediylidene)-bis[2,6-diisopropylbenzenamine].

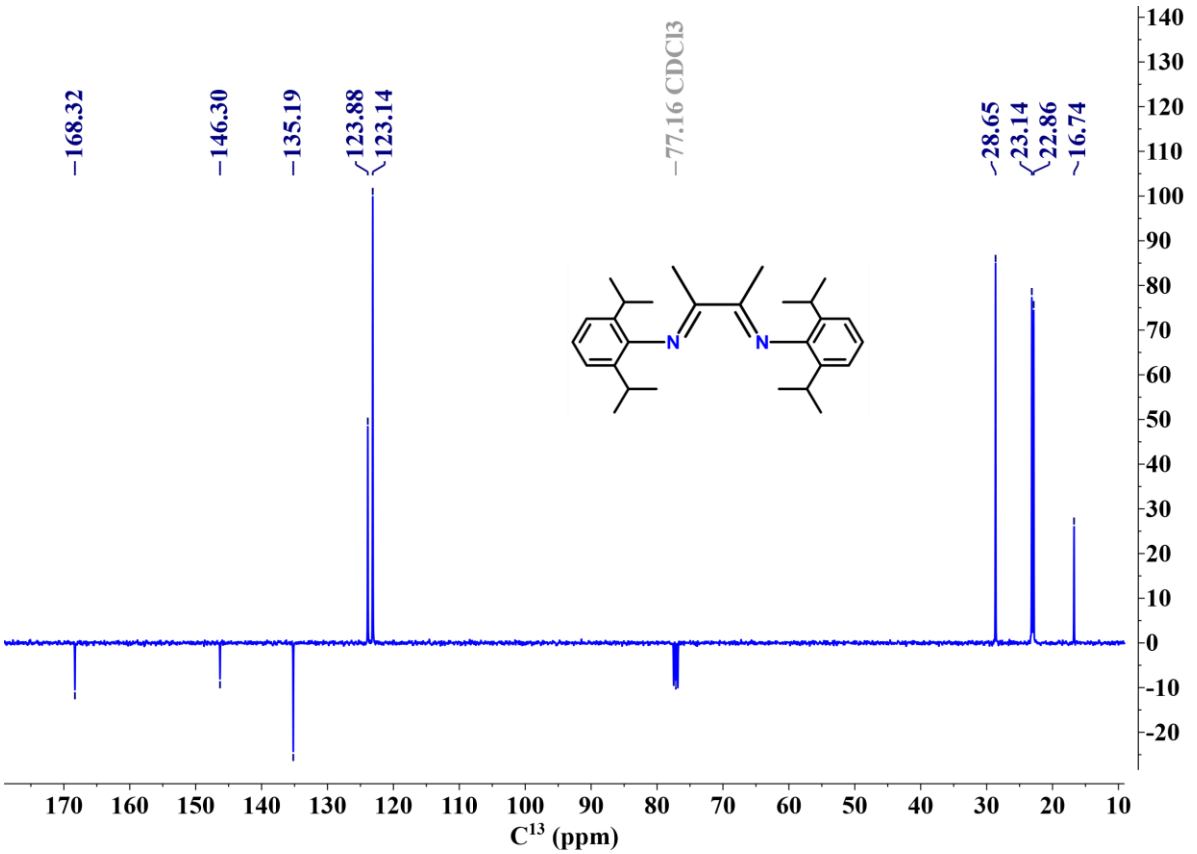


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of *N,N′*-(1,2-dimethyl-1,2-ethanediylidene)-bis[2,6-diisopropylbenzenamine].

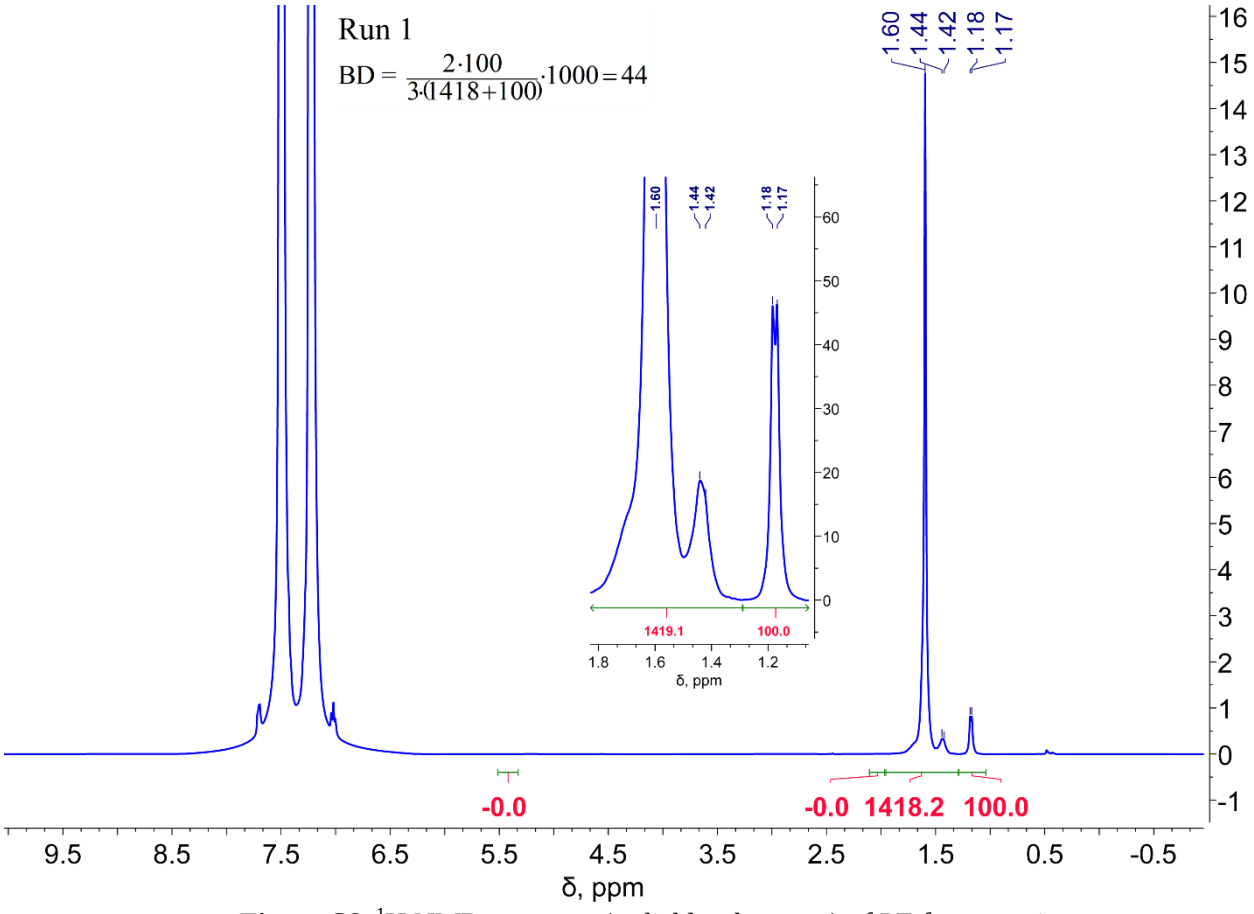


Figure S6. ^{1}H NMR spectrum (*o*-dichlorobenzene) of PE from run 1.

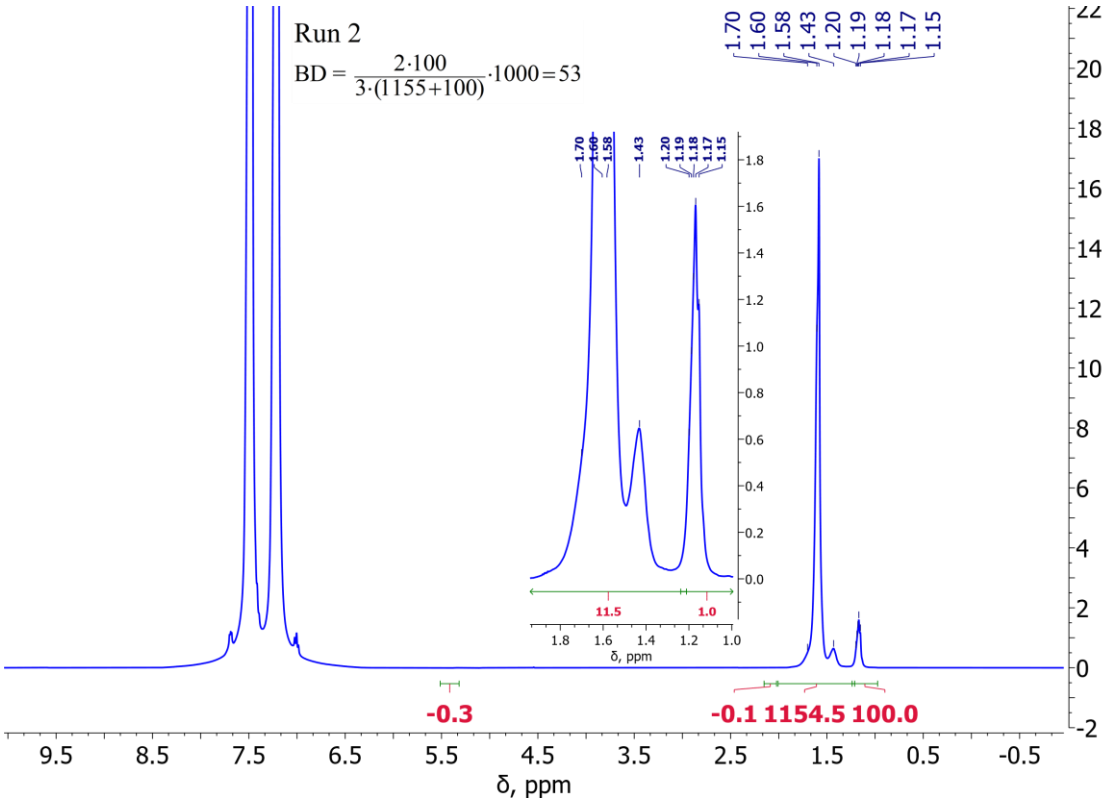


Figure S7. ^{1}H NMR spectrum (*o*-dichlorobenzene) of PE from run 2.

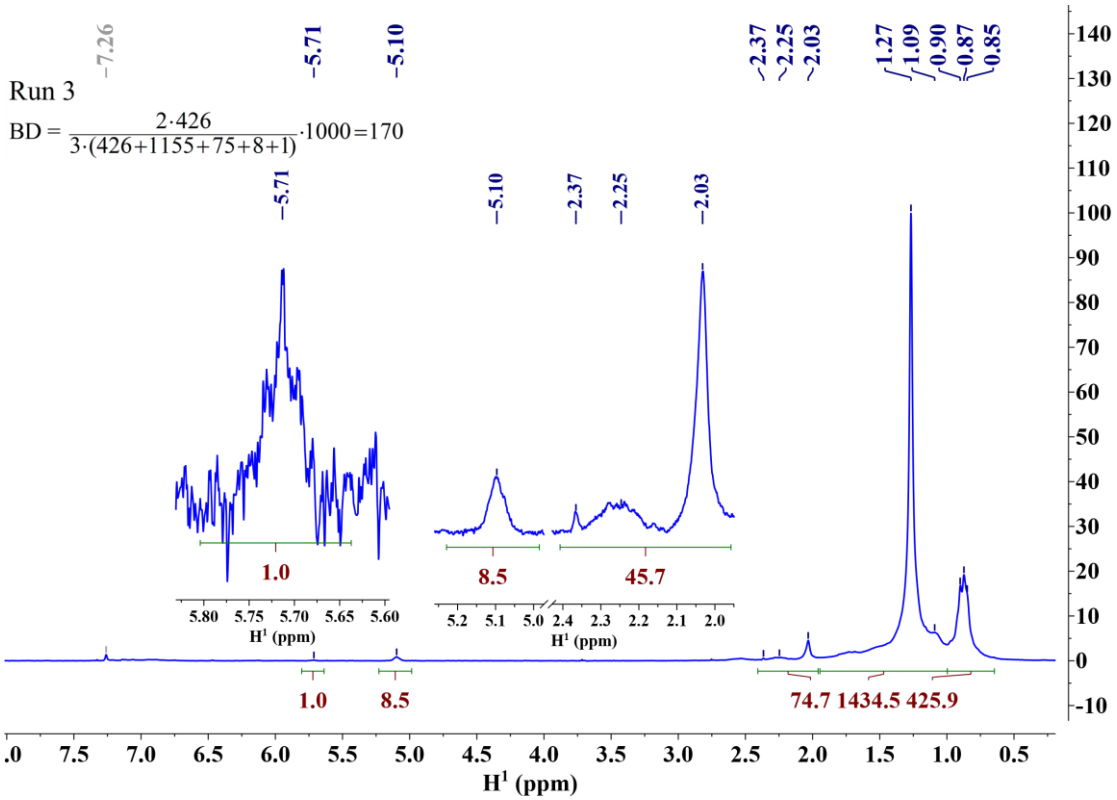


Figure S8. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 3.

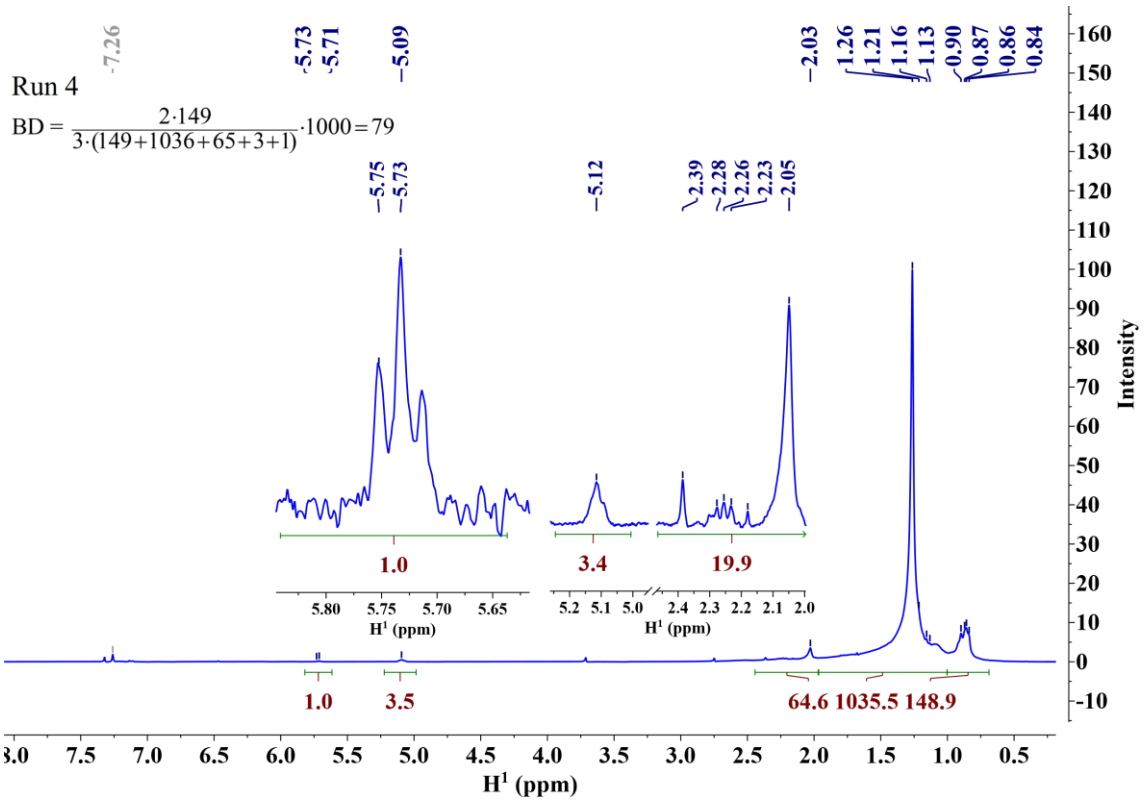


Figure S9. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 4.

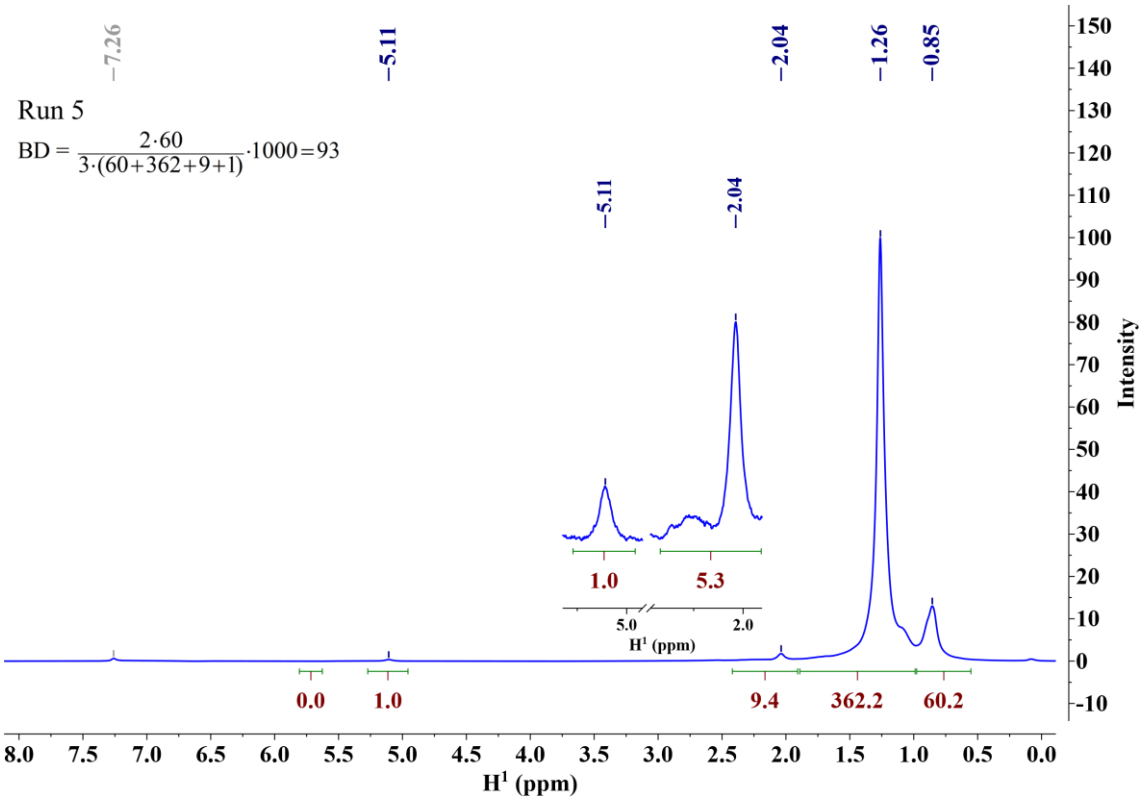


Figure S10. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 5.

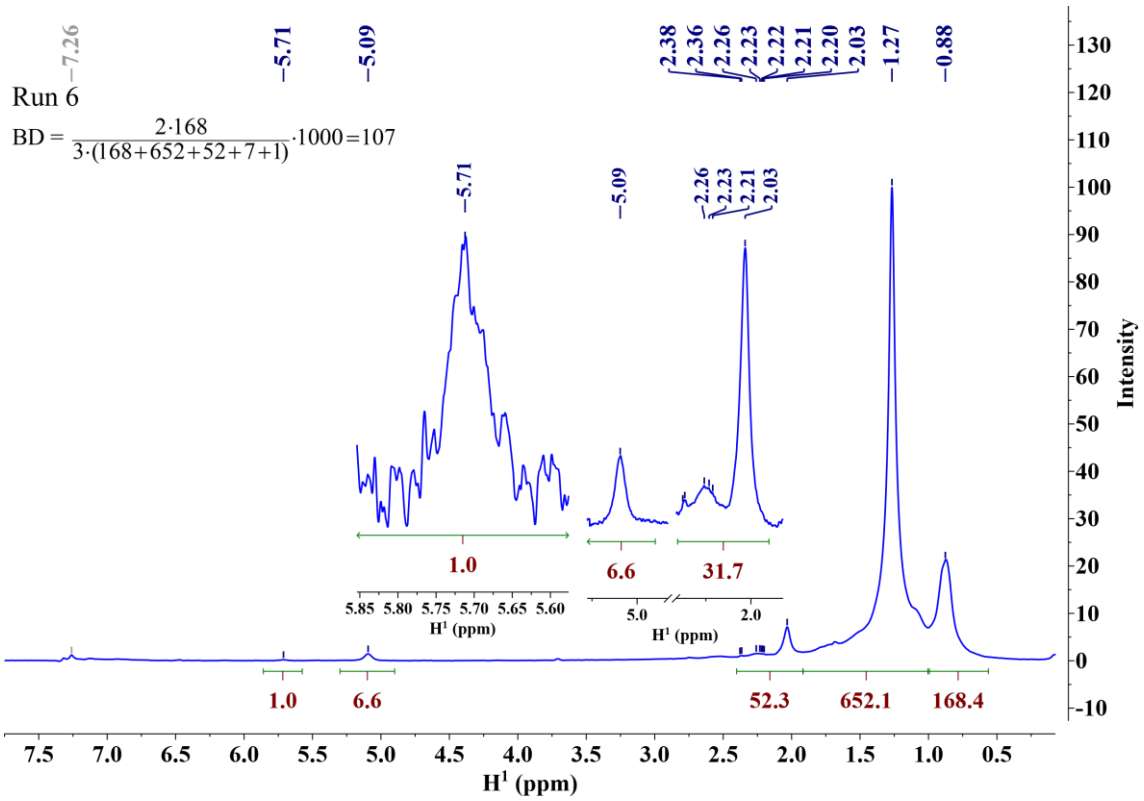


Figure S11. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 6.

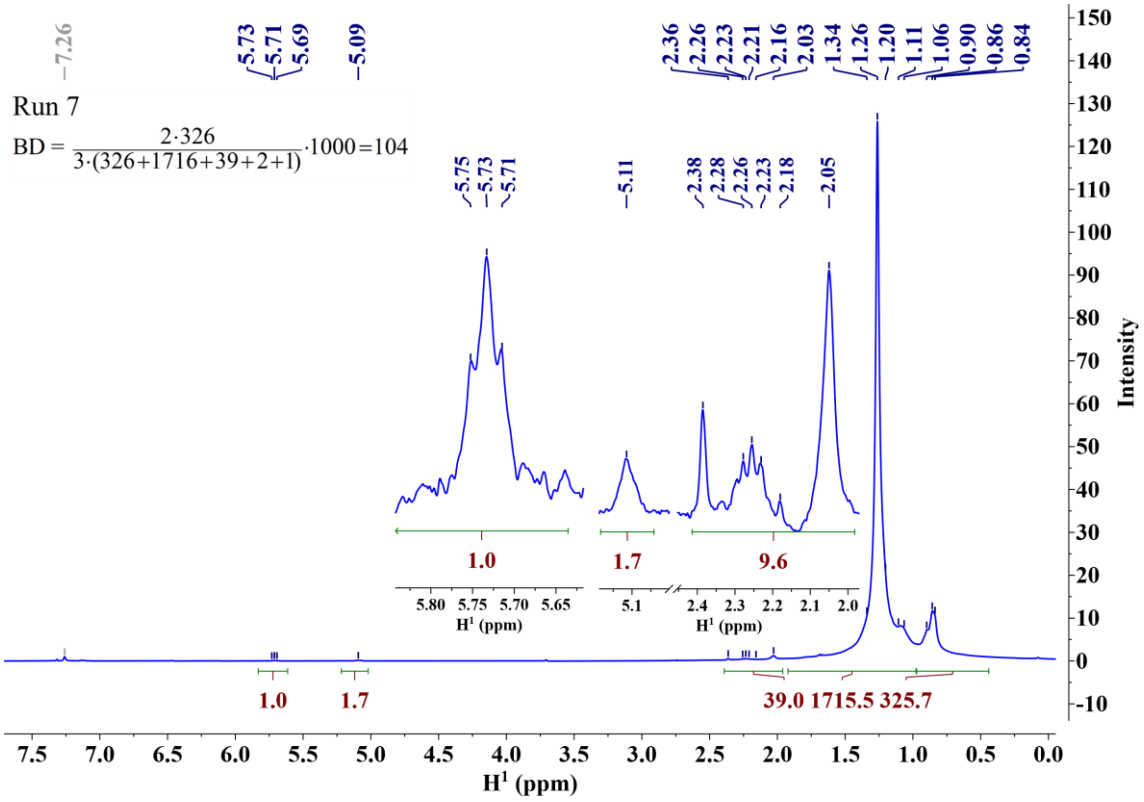


Figure S12. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 7.

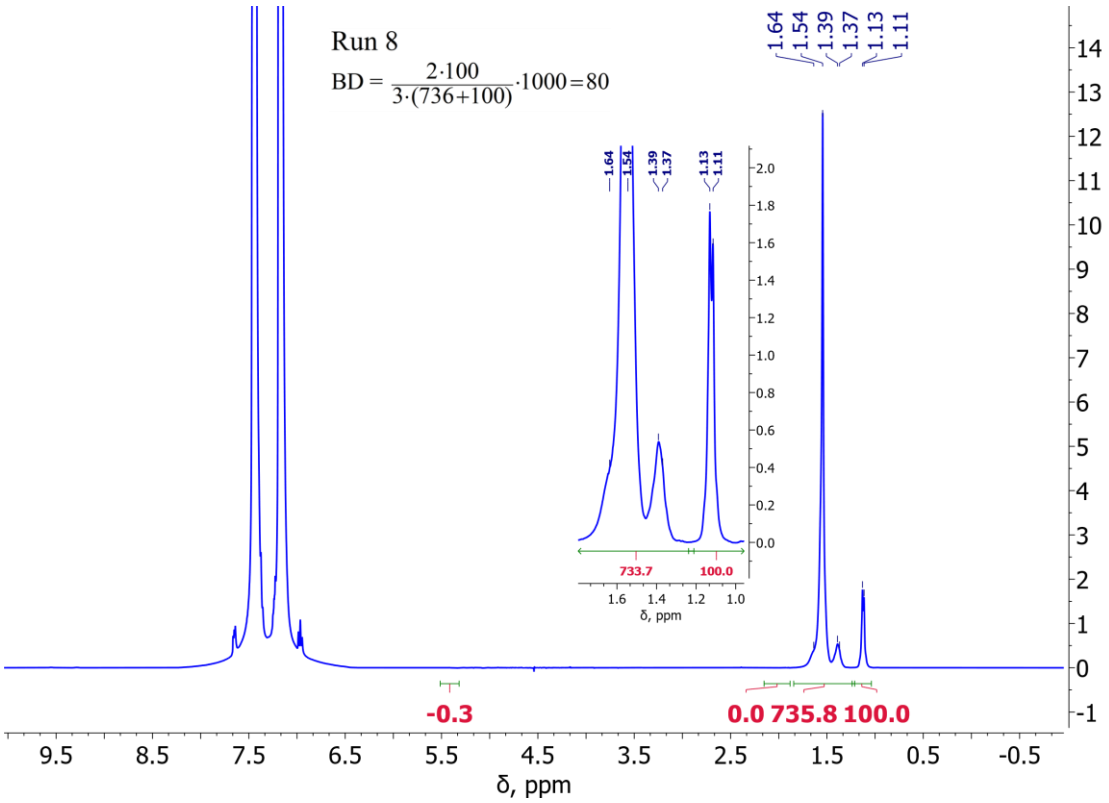


Figure S13. ^{1}H NMR spectrum (*o*-dichlorobenzene) of PE from run 8.

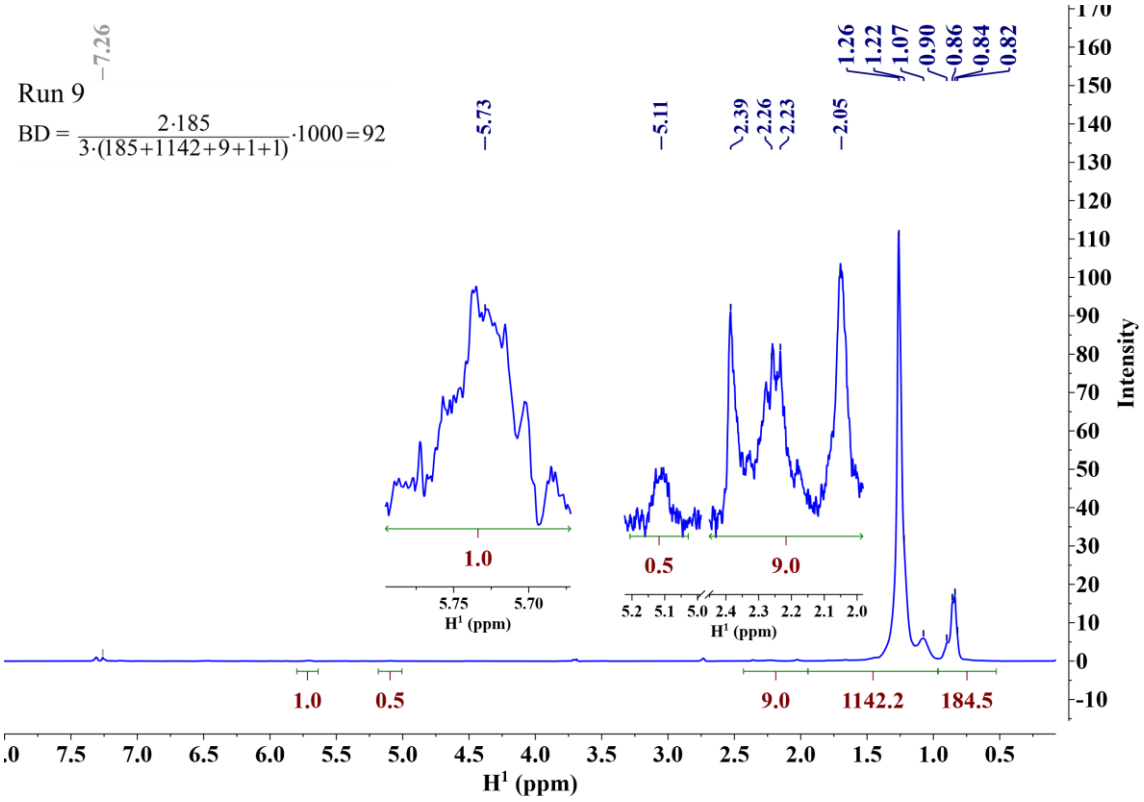


Figure S14. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 9.

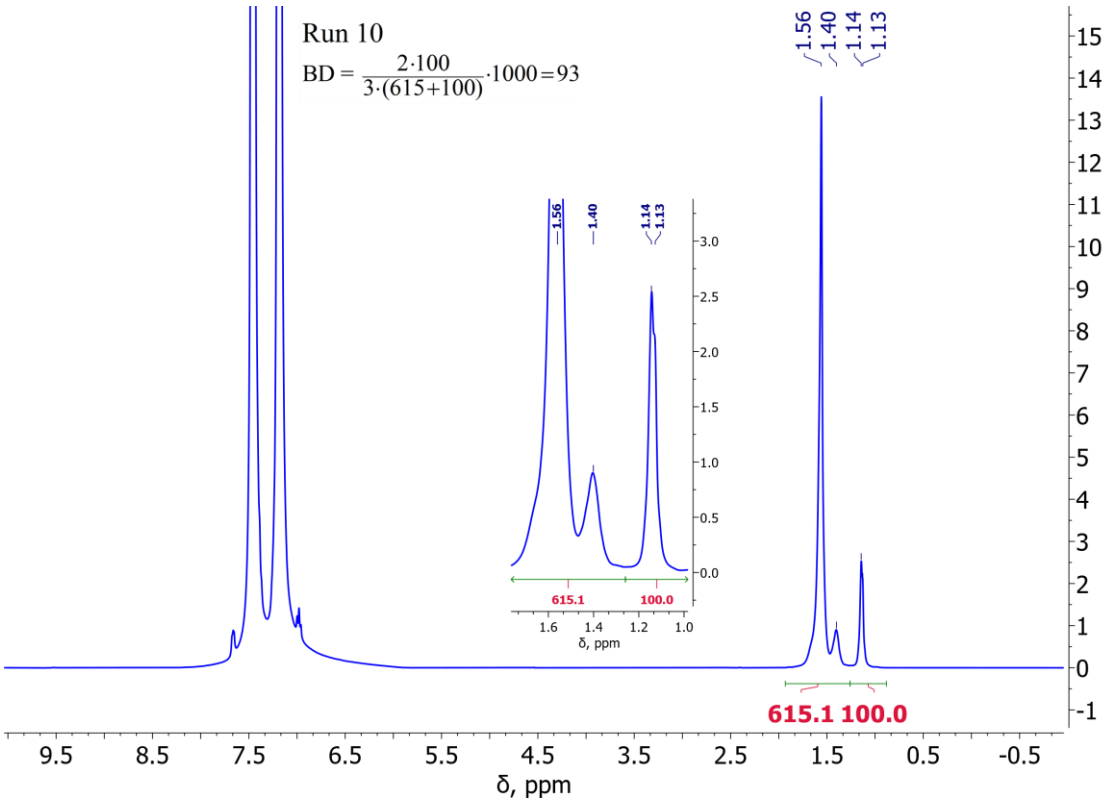


Figure S15. ^{1}H NMR spectrum (*o*-dichlorobenzene) of PE from run 10.

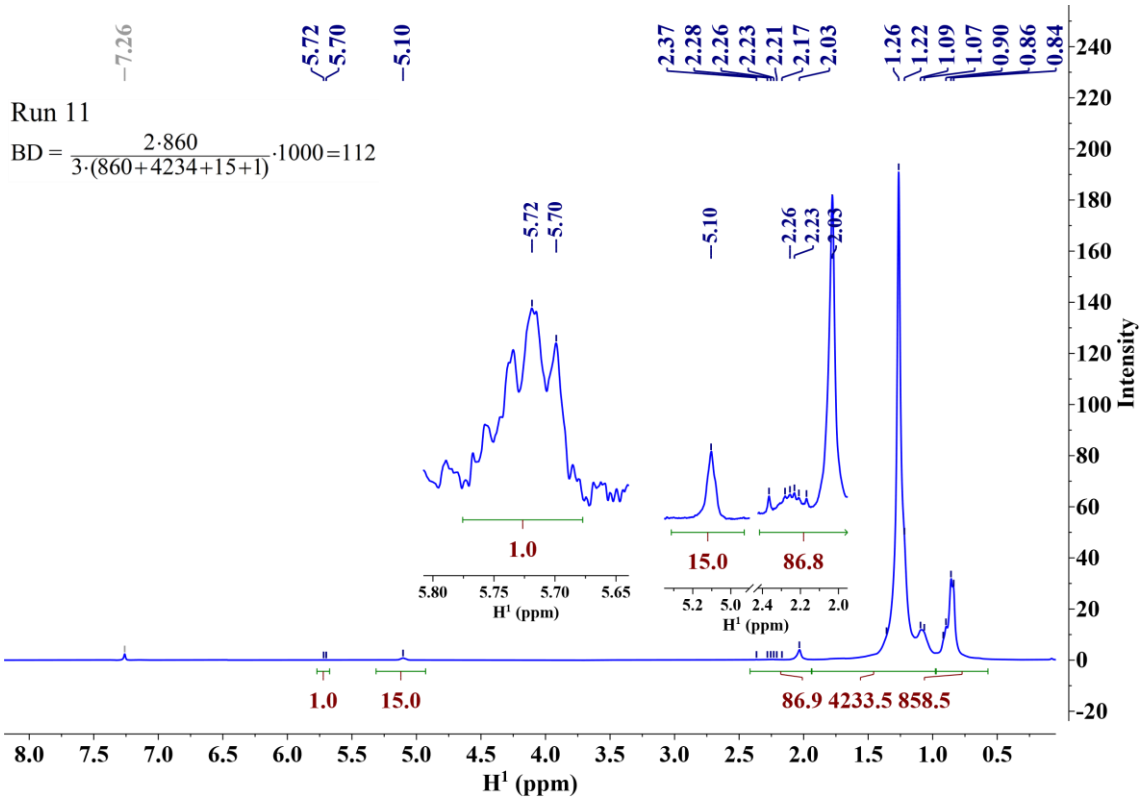


Figure S16. ^{1}H NMR spectrum ($CDCl_3/CCl_4$) of PE from run 11.

DSC data for the polymers

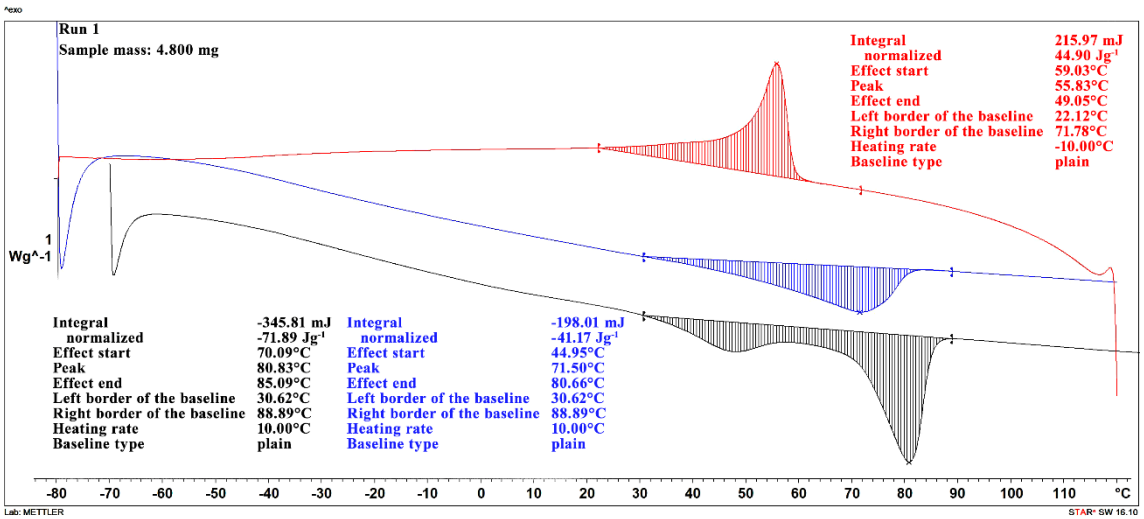


Figure S17. DSC curve of the polyethylene obtained in run 1 (Table 1).

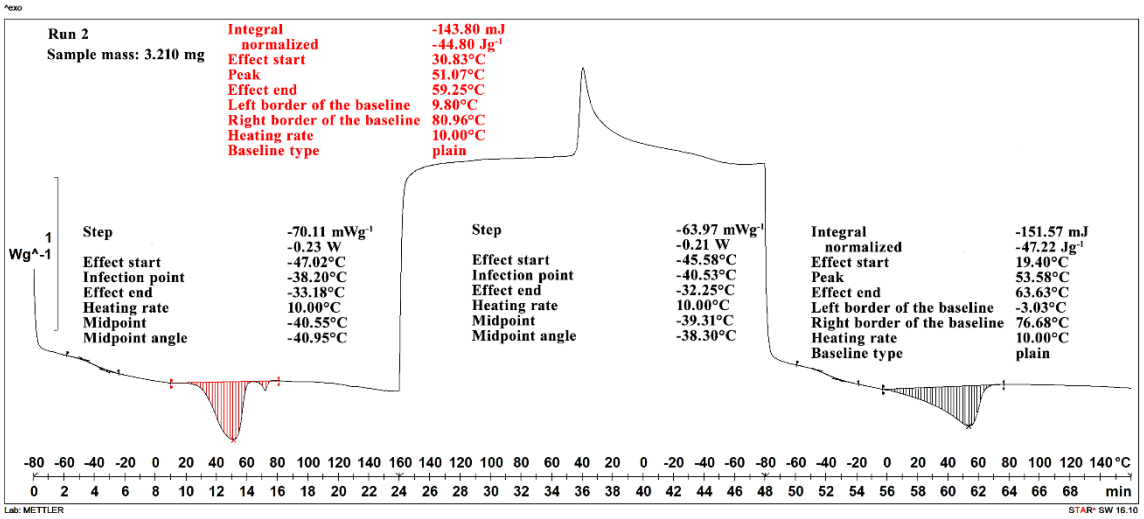


Figure S18. DSC curve of the polyethylene obtained in run 2 (Table 1).

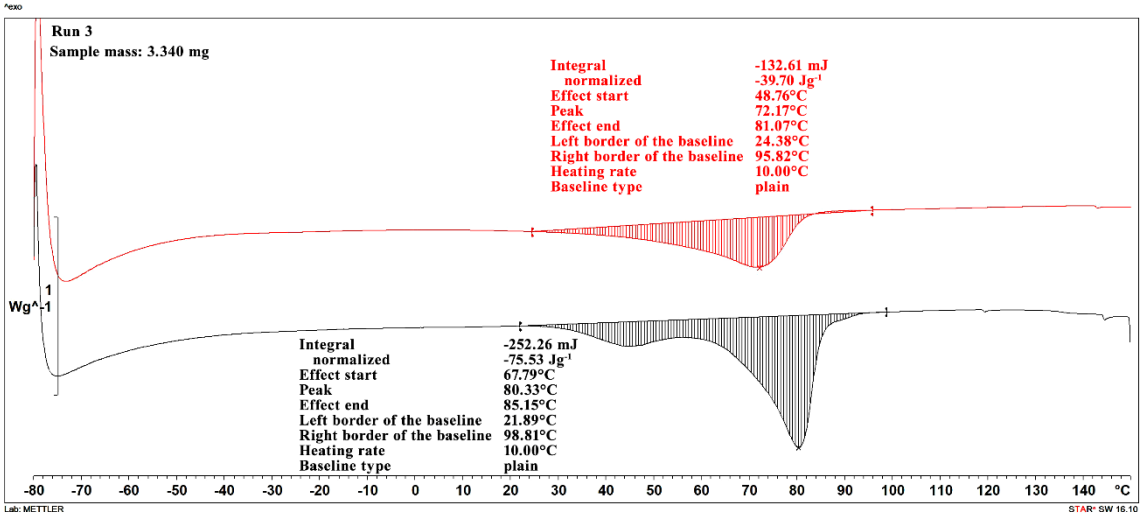


Figure S19. DSC curve of the polyethylene obtained in run 3 (Table 1).

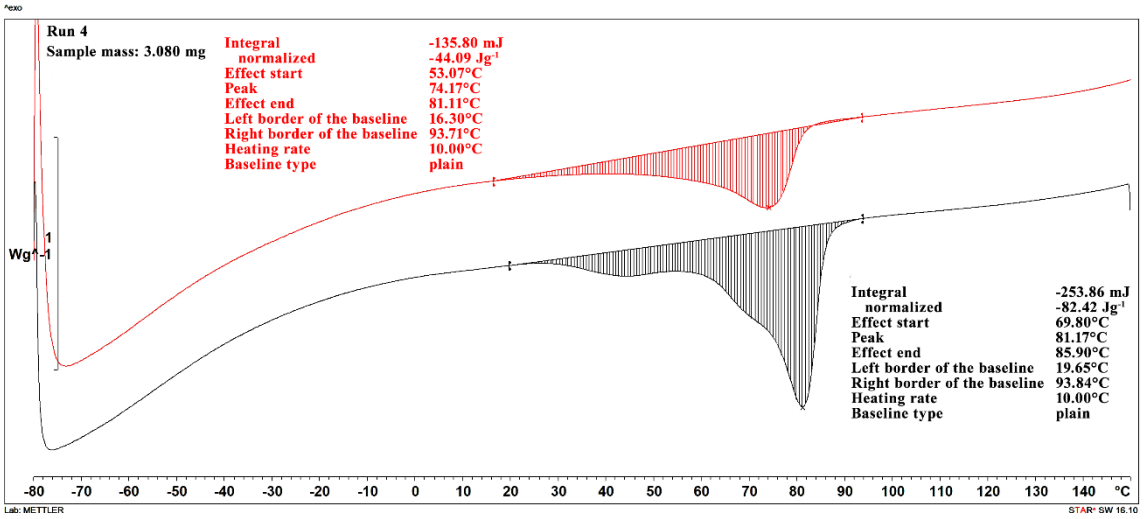


Figure S20. DSC curve of the polyethylene obtained in run 4 (Table 1).

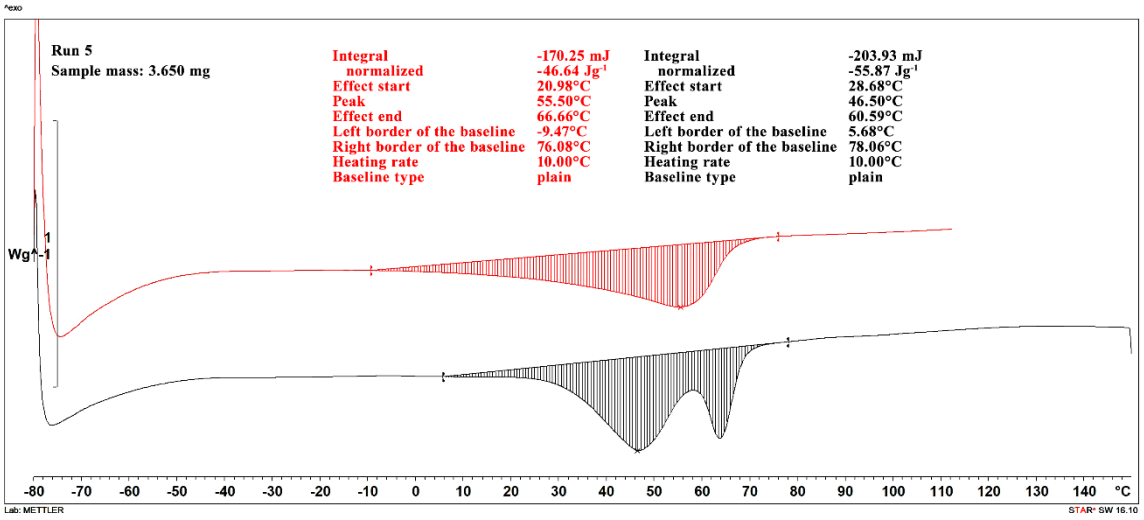


Figure S21. DSC curve of the polyethylene obtained in run 5 (Table 1).

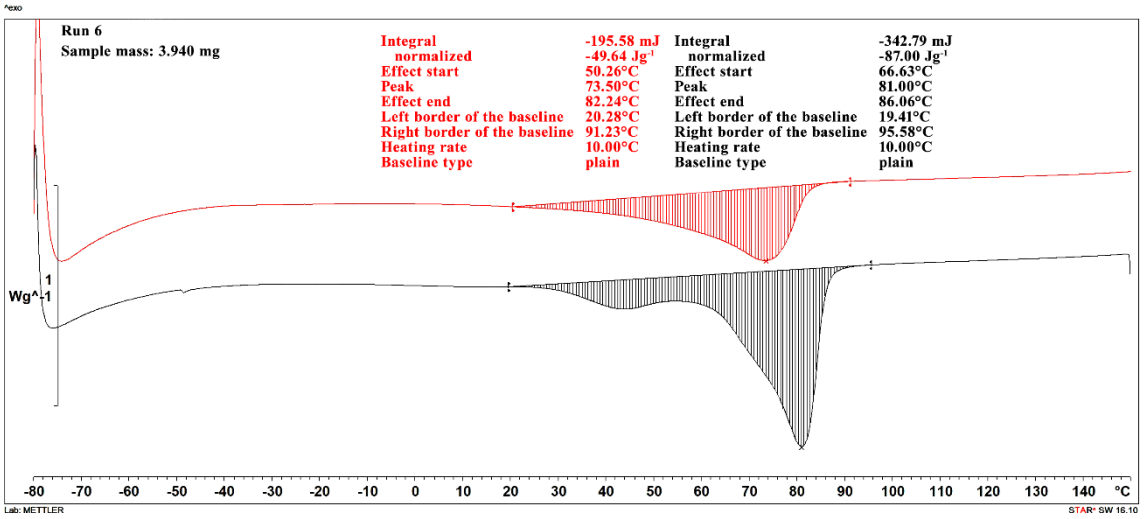


Figure S22. DSC curve of the polyethylene obtained in run 6 (Table 1).

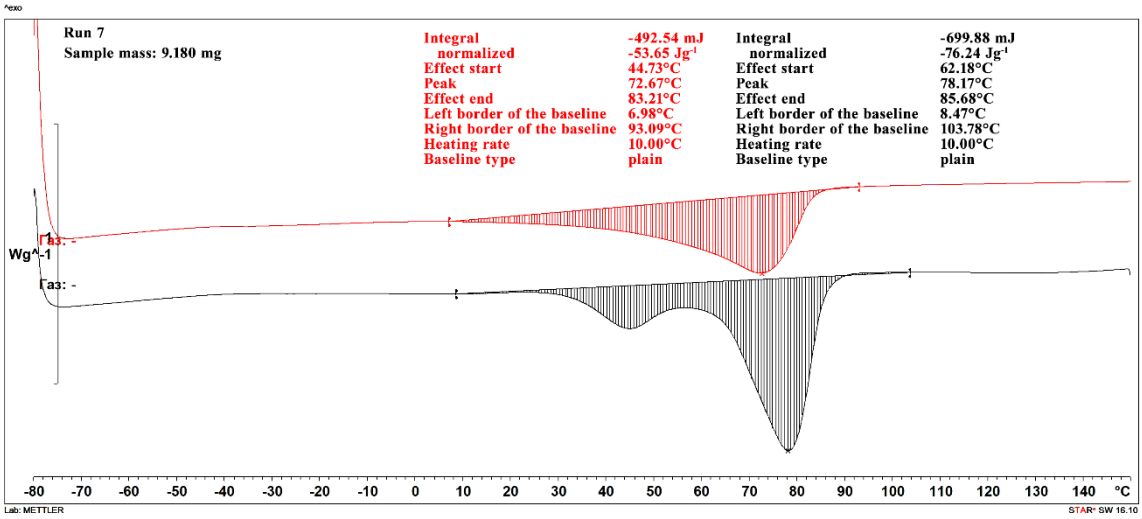


Figure S23. DSC curve of the polyethylene obtained in run 7 (Table 1).

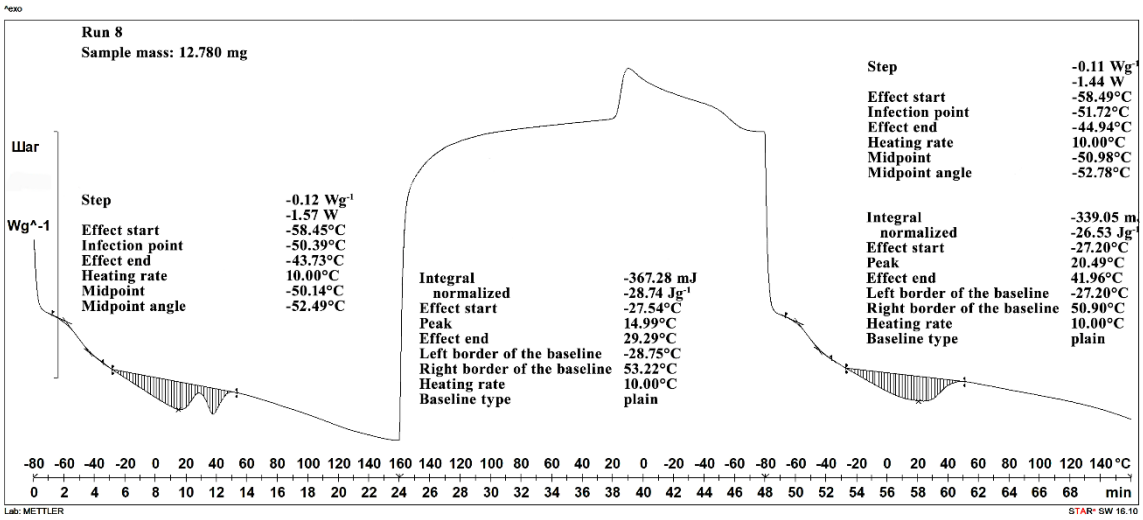


Figure S24. DSC curve of the polyethylene obtained in run 8 (Table 1).

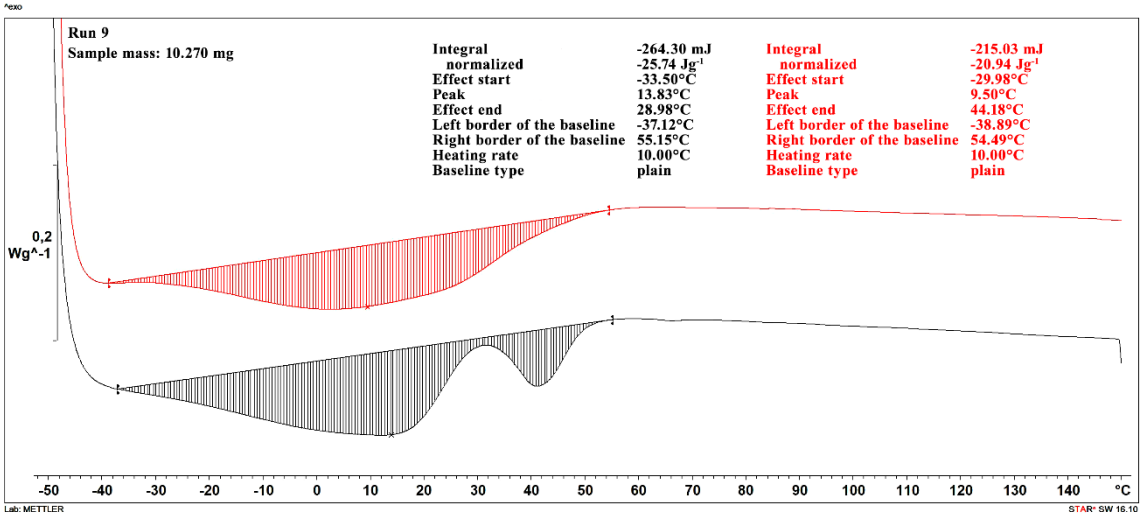


Figure S25. DSC curve of the polyethylene obtained in run 9 (Table 1).

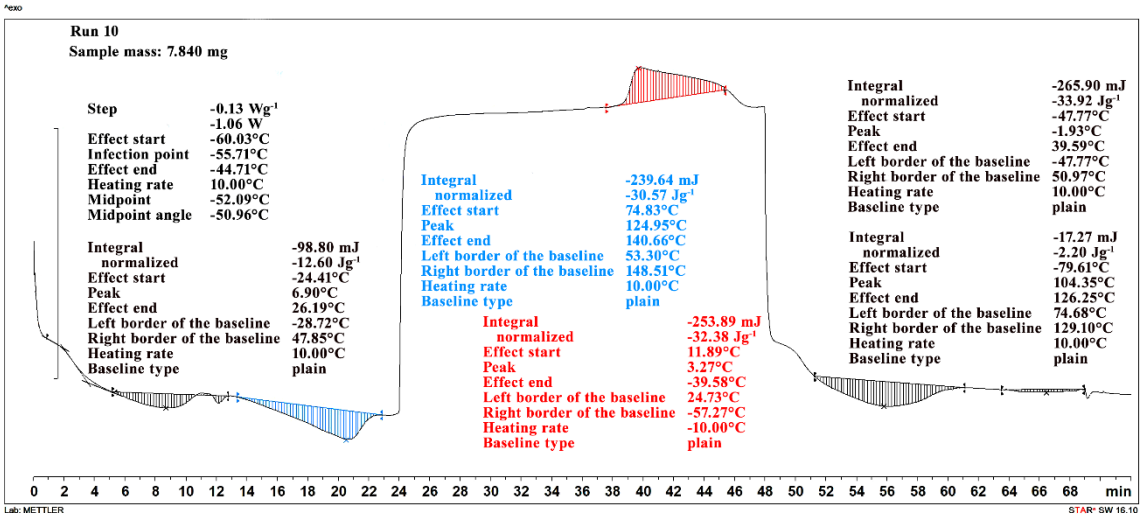


Figure S26. DSC curve of the polyethylene obtained in run 10 (Table 1).

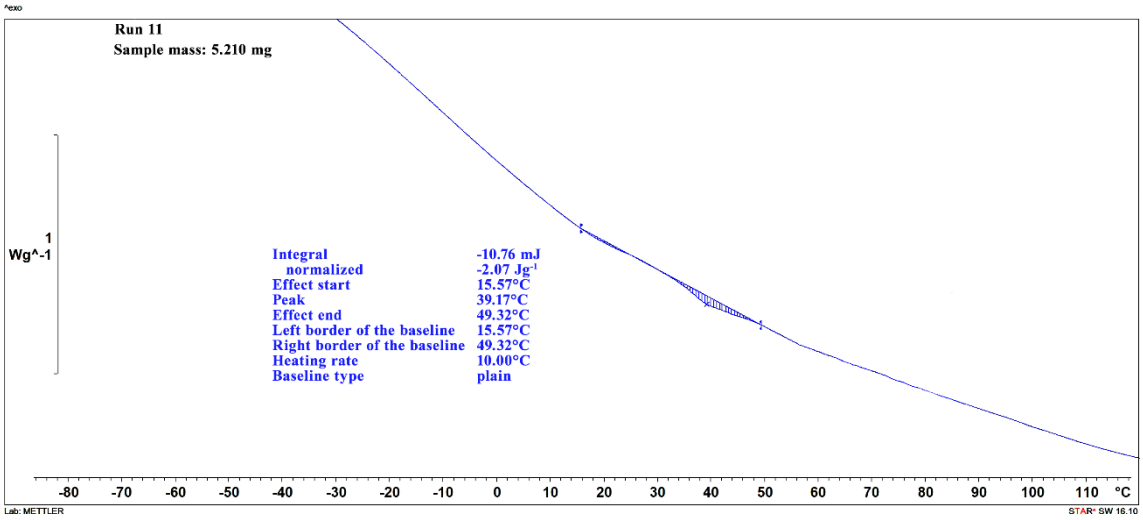


Figure S27. DSC curve of the polyethylene obtained in run 11 (Table 1).

GPC data for the polymers

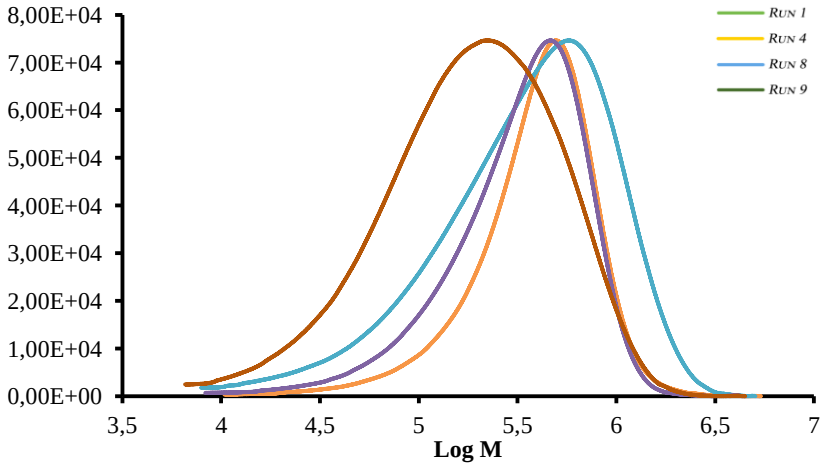


Figure S28. GPC curves of the PEs obtained in runs 1, 4, 8, and 9 (Table 1).

Run	M_n, g/mol	M_w, g/mol	M_w/M_n (PDI)
1	270629	474317	1.753
4	203564	408248	2.006
8	171871	517355	3.010
9	100215	279847	2.792

References

S1. W. L. F. Armarego, *Purification of Laboratory Chemicals, 8th ed.*, Butterworth-Heinemann, Oxford, **2017**.

S2. Z. Wang, Q. Liu, G. A. Solan, W.-H. Sun, *Coord. Chem. Rev.*, **2017**, *350*, 68–83. DOI: 10.1016/j.ccr.2017.06.003

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