

Supporting Information

Enhancing Thermal Stability and Living Fashion in α -Diimine-Nickel-Catalyzed (Co)polymerization of Ethylene and Polar Monomer by the Increasing Steric Bulk of Ligand Backbone

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1 Synthesis route and NMR spectroscopy of ligands

Scheme S1. Synthesis route of α -diimine nickel complexes

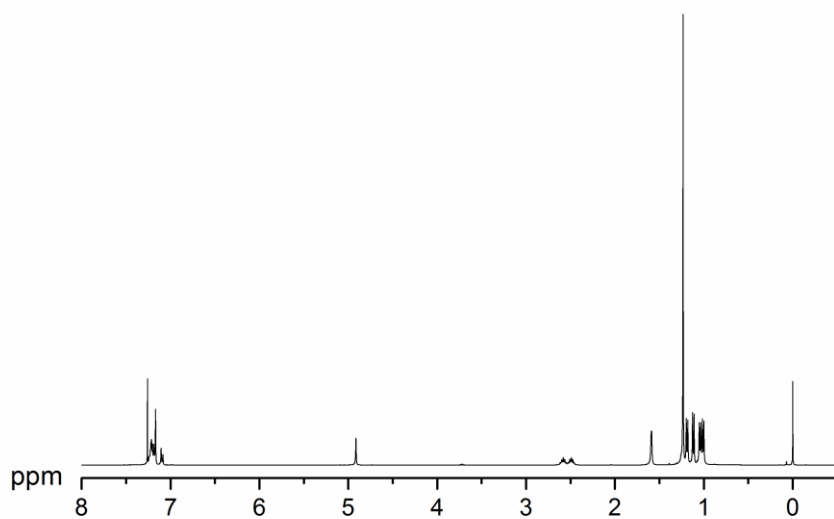
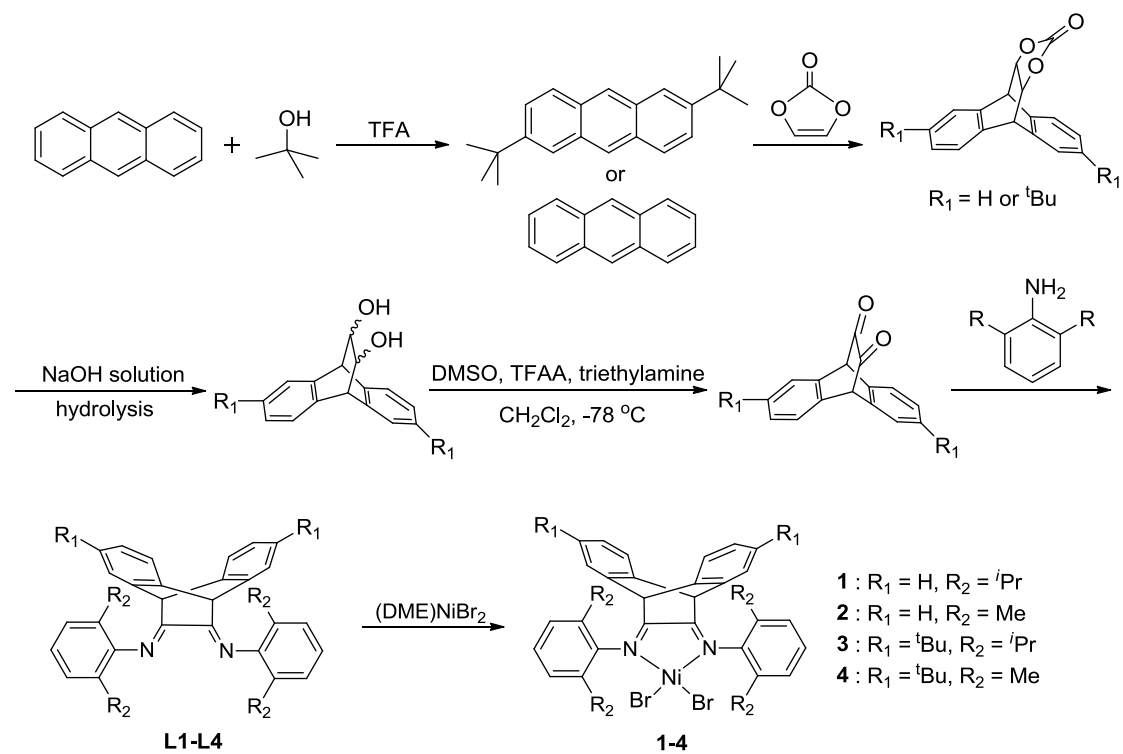


Figure S1. ^1H NMR spectrum of ligand **L3**.

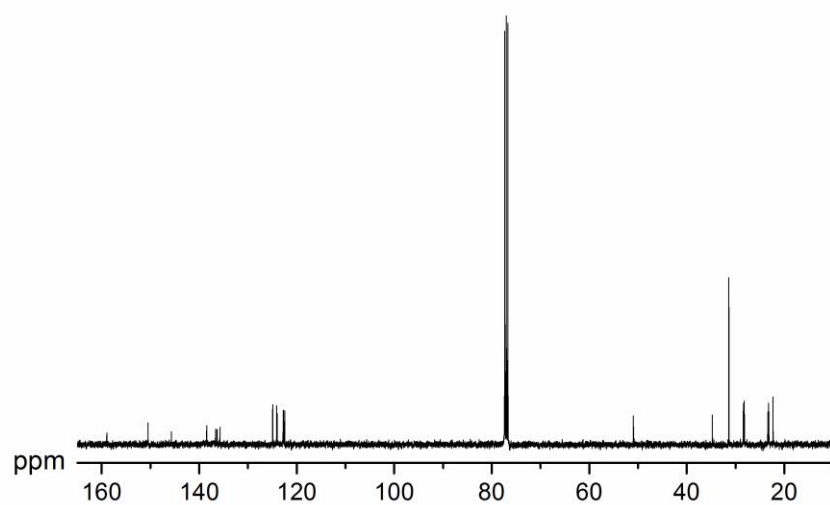


Figure S2. ^{13}C NMR spectrum of ligand **L3**.

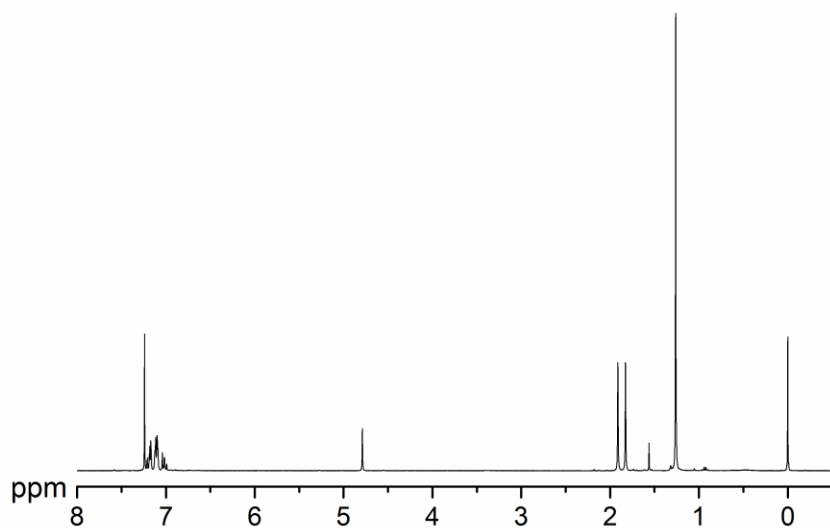


Figure S3. ^1H NMR spectrum of ligand **L4**.

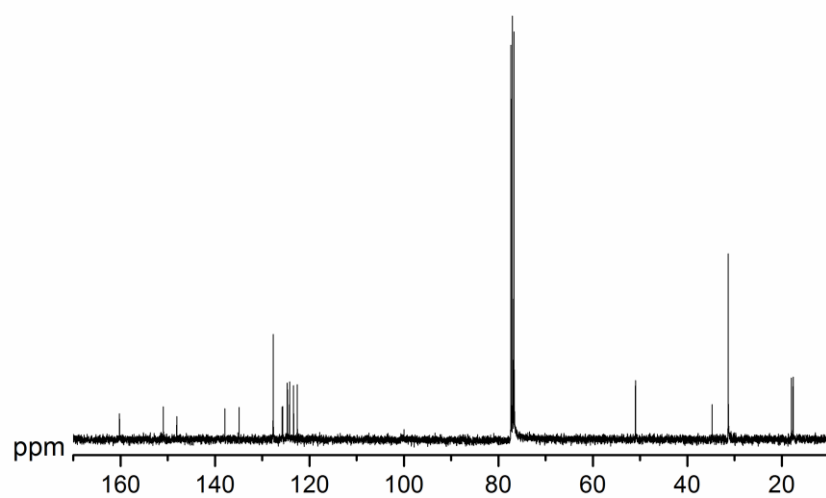


Figure S4. ^{13}C NMR spectrum of ligand L4.

2. Crystallographic data for nickel complexes 3 and 4

Table S1. Crystallographic data for the nickel complexes

	3	4
Empirical formula	C ₄₈ H ₆₀ Br ₂ N ₂ Ni	C ₄₀ H ₄₄ Br ₂ N ₂ Ni·CH ₂ Cl ₂
Formula weight	883.50	856.23
Crystal color	Red dark	Red dark
Crystal system	Trigonal	Triclinic
space group	R-3	P-1
a (Å)	26.8702(5)	16.4259(5)
b (Å)	26.8702(5)	17.1593(4)
c (Å)	35.7526(9)	17.2162(6)
α (deg)	90	76.750(3)
β (deg)	90	69.223(3)
γ (deg)	120	75.674(3)
Volume(Å ³)	22355.2(10)	4342.0(3)
Z	18	4
Calculated density (g/cm ³)	1.181	1.310
Absorption coefficient (mm ⁻¹)	2.662	4.137
F(000)	8280	1752
Crystal size (mm)	0.31 × 0.24 × 0.11	0.2 × 0.2 × 0.2
Theta range for data collection (deg)	3.117 to 66.926	2.691 to 67.226
Limiting indices	-26 ≤ h ≤ 31 -28 ≤ k ≤ 31 -33 ≤ l ≤ 42	-19 ≤ h ≤ 19 -11 ≤ k ≤ 20 -18 ≤ l ≤ 20
Max. and min. transmission	1.0000 and 0.69459	1.00000 and 0.71336
Data / restraints / parameters	8623 / 18 / 492	15263 / 0 / 916
Goodness-of-fit on F ²	1.023	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1214	R1 = 0.0457, wR2 = 0.1216
R indices (all data)	R1 = 0.0567, wR2 = 0.1320	R1 = 0.0537, wR2 = 0.1291
Largest diff. peak and hole (e/Å ³)	1.636 and -0.797	1.077 and -1.154

3. Characterization of selected polymer samples

Table S2. Ethylene living polymerization results at different times catalyzed by **1**/Et₂AlCl at 65 °C ^a

Entry	Time (min)	Yield (g)	Activity ^b	M_n^c (kg/mol)	PDI ^c
1	15	0.127	254	74	1.02
2	30	0.261	261	131	1.07
3	45	0.400	266	197	1.10
4	60	0.520	260	256	1.14

^a Conditions: 2 μmol of catalyst, Al/Ni = 600, 3 psig of ethylene pressure, 20 mL of toluene and 1 mL of CH₂Cl₂.

^b Activity in kg PE/(mol Ni·h).

^c Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

Table S3. Ethylene living polymerization results at different times catalyzed by **3**/AlEt₂Cl at 80 °C ^a

Entry	Time (min)	Yield (g)	Activity ^b	M_n^c (kg/mol)	PDI ^c
1	15	0.090	180	62	1.09
2	30	0.185	185	115	1.10
3	45	0.275	183	154	1.14
4	60	0.356	178	207	1.16

^a Conditions: 2 μmol of catalyst, Al/Ni = 600, 3 psig of ethylene pressure, 20 mL of toluene and 1 mL of CH₂Cl₂.

^b Activity in kg PE/(mol Ni·h).

^c Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

Table S4. Ethylene polymerization results with **3**/AlEt₂Cl at 100 °C

Entry	Time (min)	Yield (g)	TOF ^b	M_n^c (kg/mol)	PDI ^c
1	10	0.227	24.3	310	1.26
2	20	0.465	24.9	366	1.36
3	30	0.652	23.3	431	1.39
4	45	0.910	21.7	442	1.43
5	60	1.058	18.9	475	1.45

^a Conditions: 2 μmol of catalyst, Al/Ni = 600, 75 psig of ethylene pressure, 50 mL of toluene and 1 mL of CH₂Cl₂.

^b TOF in 10³ mol E/(mol Ni·h).

^c Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

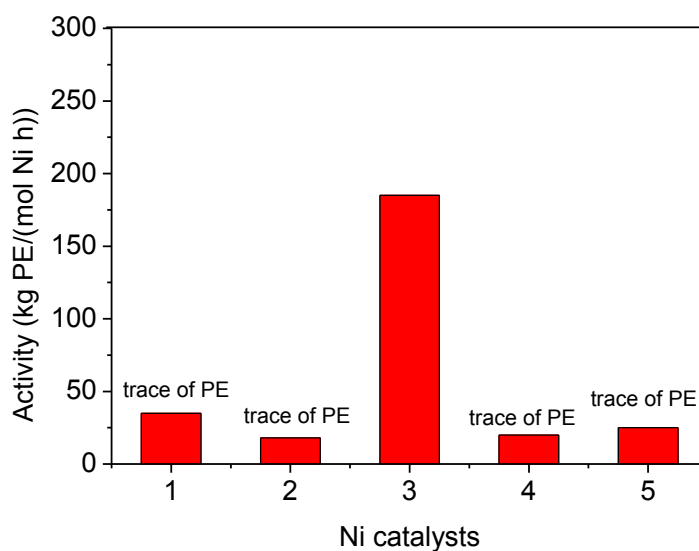


Figure S5. The comparison of ethylene polymerization activity with catalysts **1**, **2**, **3**, **4**, and **5** at high temperature of 80 °C (**5** is a conventional α -diimine nickel catalyst bearing the acenaphthene backbone).

Table S5. Branched chain distributions of PEs obtained by nickel catalysts **1-4**.

Entry	Catalyst	T(°C)	Branched chain (/1000C)						Branches (/1000C)
			Me	Et	Pr	Bu	Pe	Lg	
1	1	20	89	2	2	1	3	9	106
2	1	35	88	3	1	2	4	9	107
3	1	50	82	4	2	1	3	17	109
4	1	65	81	5	2	2	4	16	110
5	1	80							
6	2	-20	11	0	0	0	1	7	19
7	2	0	22	2	0	0	4	7	35
8	2	20	47	4	2	2	2	12	69
9	2	35	51	5	1	3	2	13	75
10	2	50							
11	3	20	90	2	1	1	1	7	102
12	3	35	90	3	2	1	1	7	104
13	3	50	86	3	2	2	2	10	105
14	3	65	83	4	1	2	2	13	105
15	3	80	82	4	2	2	3	15	108
16	4	0	20	1	0	0	1	4	26
17	4	20	31	3	1	1	1	7	44
18	4	35	39	4	2	2	2	9	58
19	4	50	55	6	3	3	2	14	83
20	4	65	61	9	3	4	3	19	99
21	4	80							

Determined by ¹³C NMR

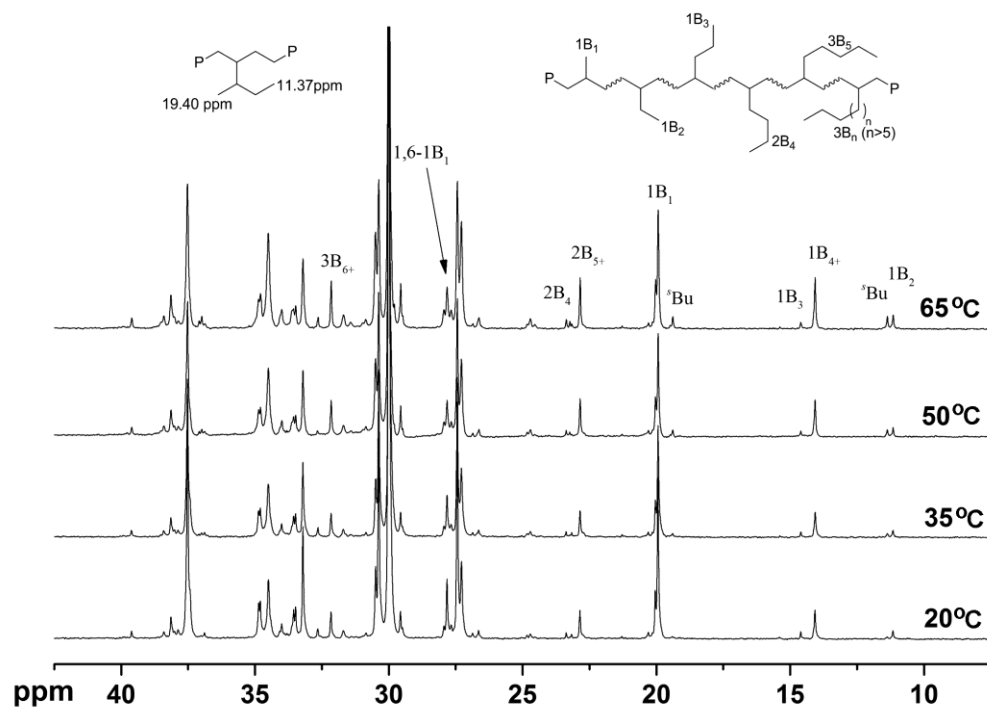


Figure S6. ^{13}C NMR spectra of PEs produced by **1**/ Et_2AlCl at different temperatures.

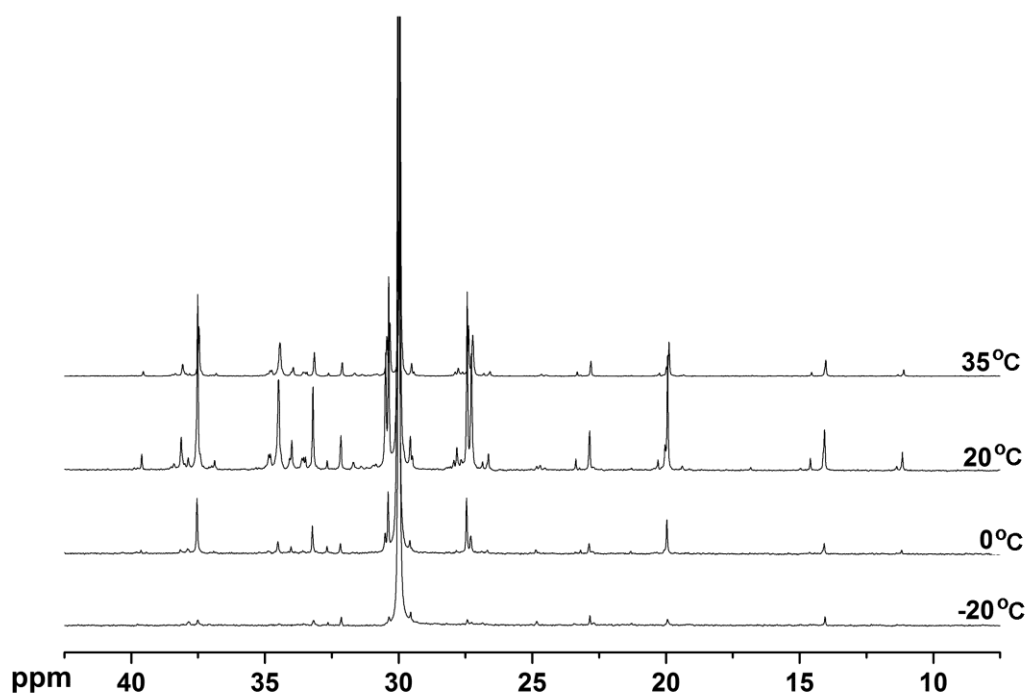


Figure S7. ^{13}C NMR spectra of PEs produced by **2**/ Et_2AlCl at different temperatures.

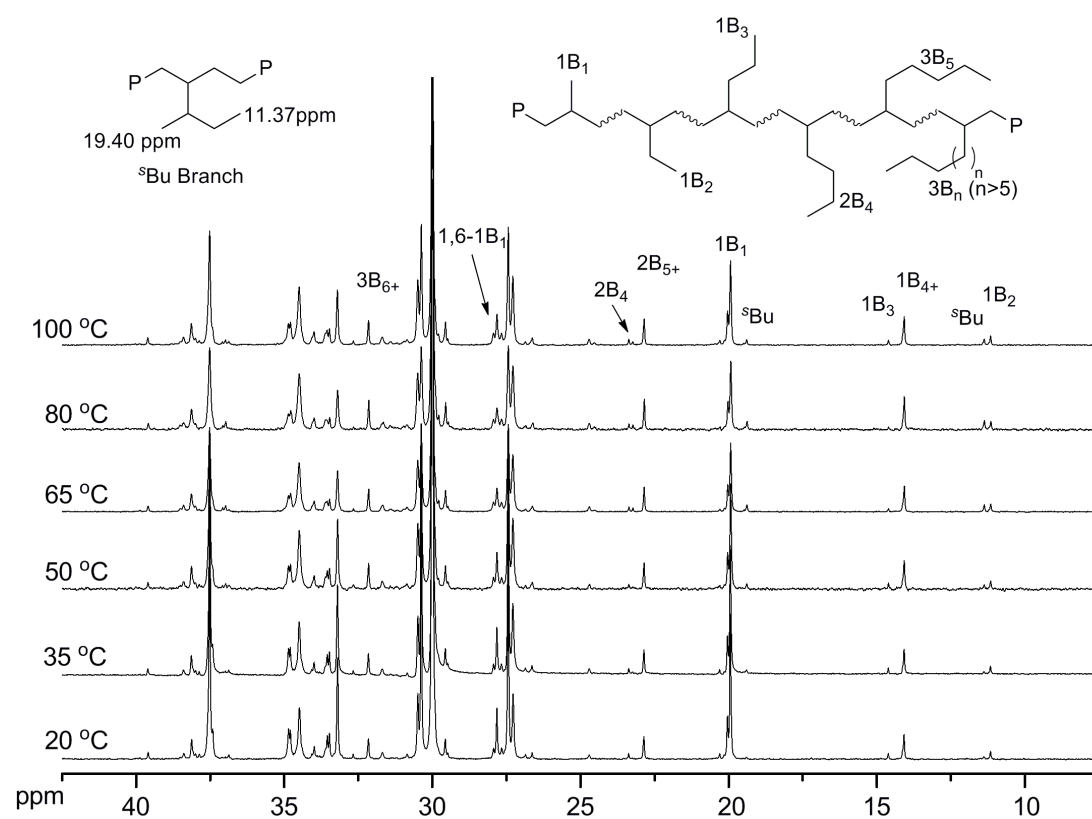


Figure S8. ^{13}C NMR spectra of PEs produced by $3/\text{Et}_2\text{AlCl}$ at different temperatures.

(3 psig of ethylene pressure for 20-80 °C, 75 psig of ethylene pressure for 100 °C)

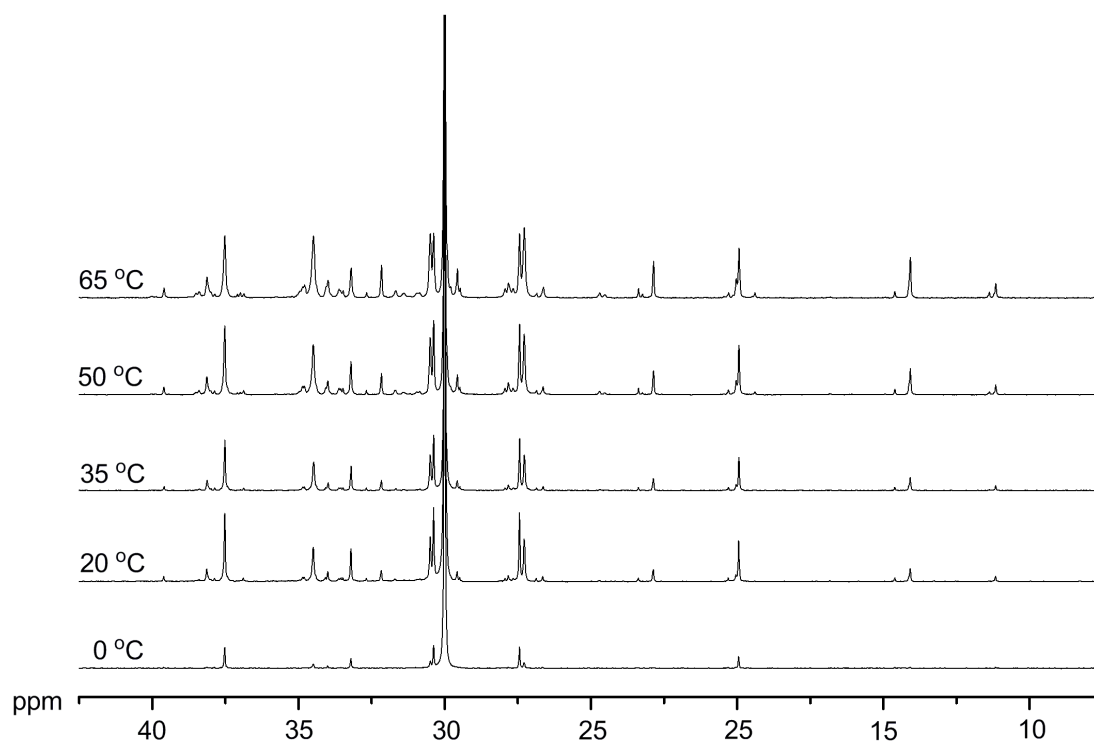


Figure S9. ^{13}C NMR spectra of PEs produced by **4**/ Et_2AlCl at different temperatures

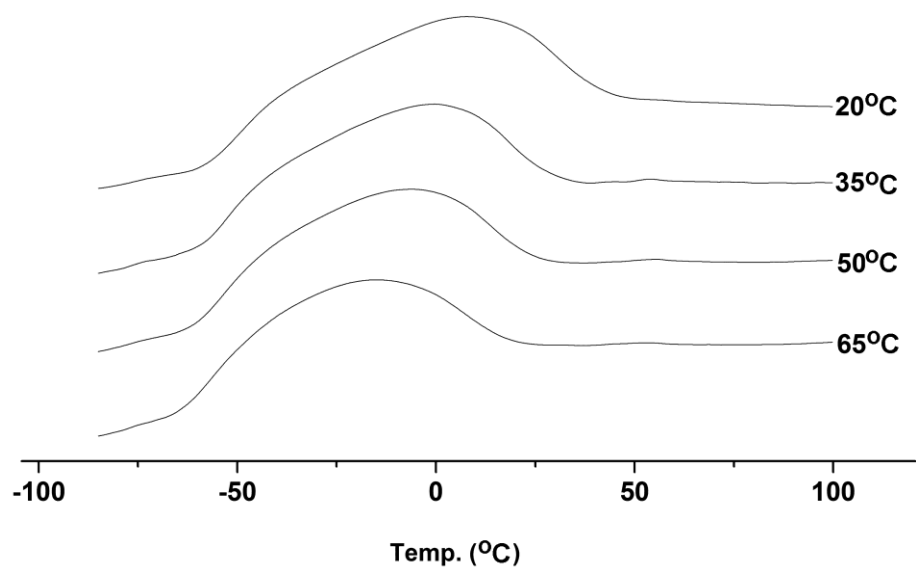


Figure S10. DSC curves of PEs produced by 1/Et₂AlCl at different temperatures.

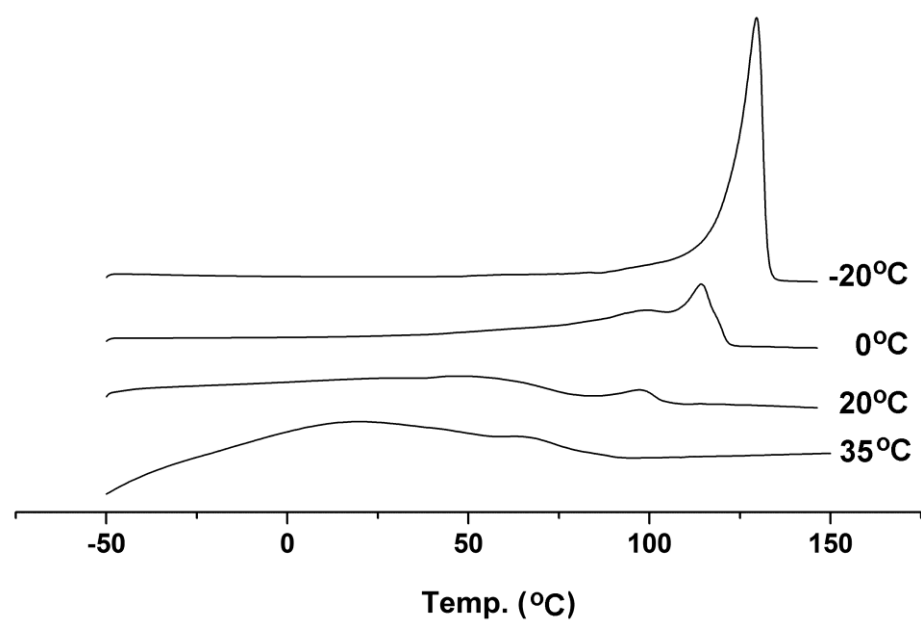


Figure S11. DSC curves of PEs produced by 2/Et₂AlCl at different temperatures.

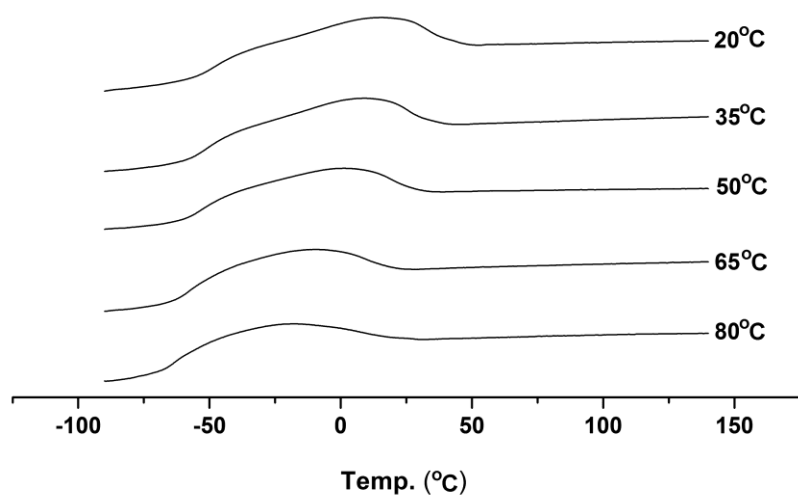


Figure S12. DSC curves of PEs produced by 3/Et₂AlCl at different temperatures.

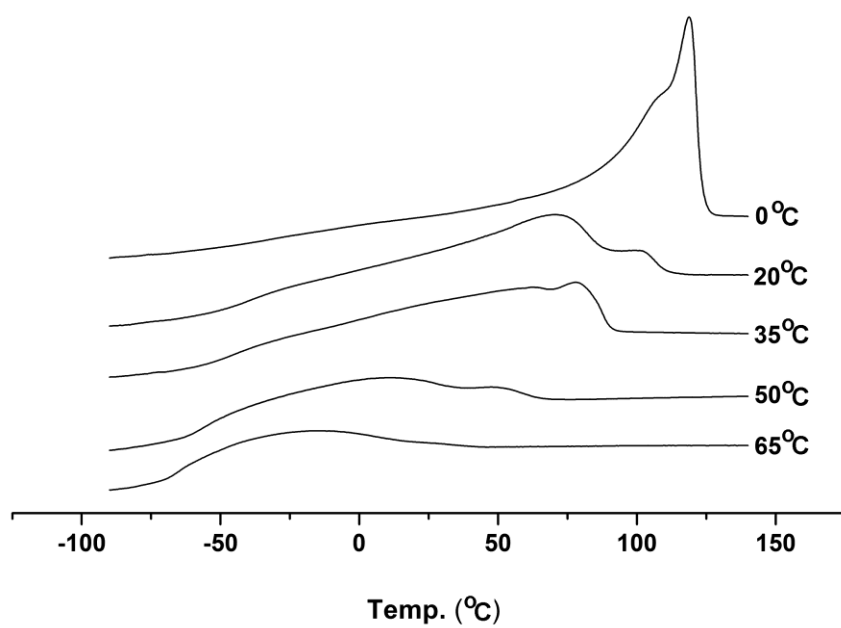


Figure S13. DSC curves of PEs produced by 4/Et₂AlCl at different temperatures.

Table S6. Living copolymerization of ethylene and methyl 10-undecenoate with **3**/AlEt₂Cl at 20 °C

Entry	Time (min)	Yield (g)	Activity kg copolymer/(mol Ni·h)	M_n^b (kg/mol)	PDI ^b
1	10	0.098	118	35	1.04
2	20	0.204	122	76	1.05
3	30	0.300	120	107	1.07
4	40	0.410	123	136	1.09

^a Conditions: 5 μmol of catalyst, Al/Ni = 1600, 3 psig of ethylene pressure, 20 mL of toluene and 1 mL of CH₂Cl₂.

^b Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

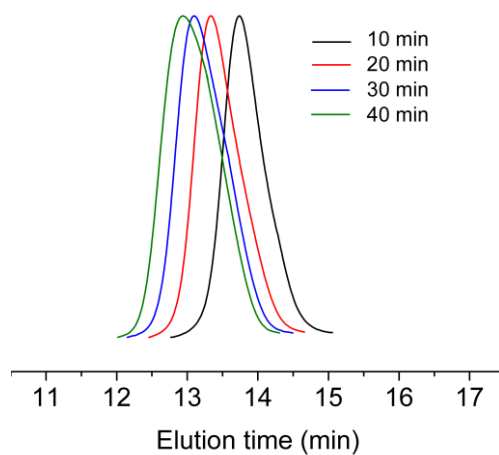


Figure S14. GPC traces of copolymers obtained by catalyst **3** at different times.

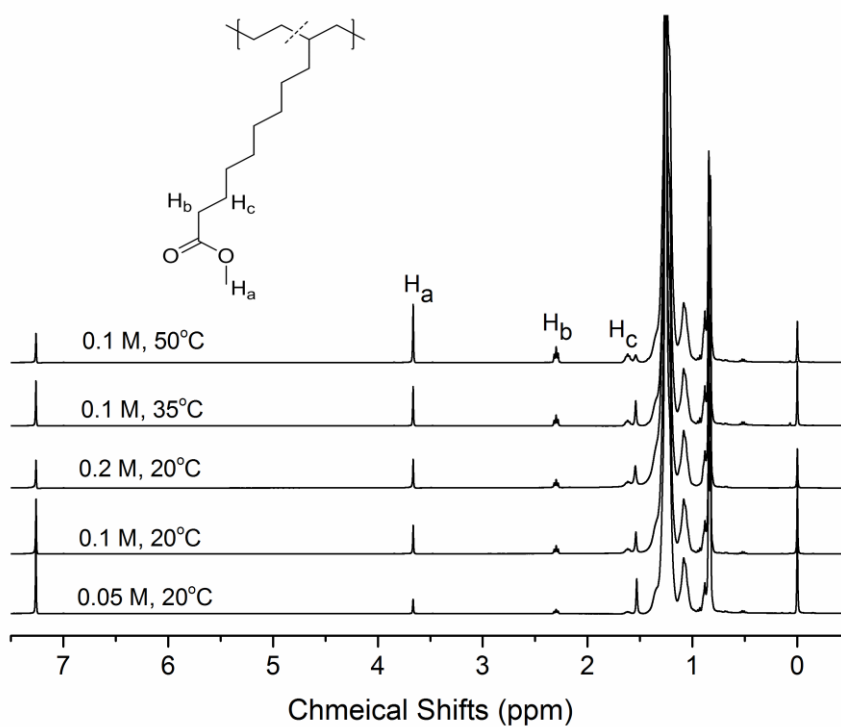


Figure S15. ^1H NMR spectra of copolymers obtained by catalyst **3** (entries 4-8 in Table 2).

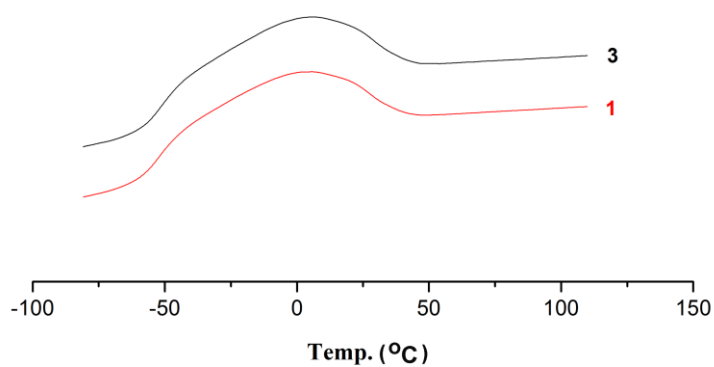


Figure S16. DSC curves of the copolymers of ethylene and methyl 10-undecenoate obtained catalyst **1** and **3** (entries 2 and 6 in Table 2).