Supporting information

Plastomeric-like polyethylenes achievable using thermally robust *N,N'*-nickel catalysts appended with electron withdrawing difluorobenzhydryl and nitro groups

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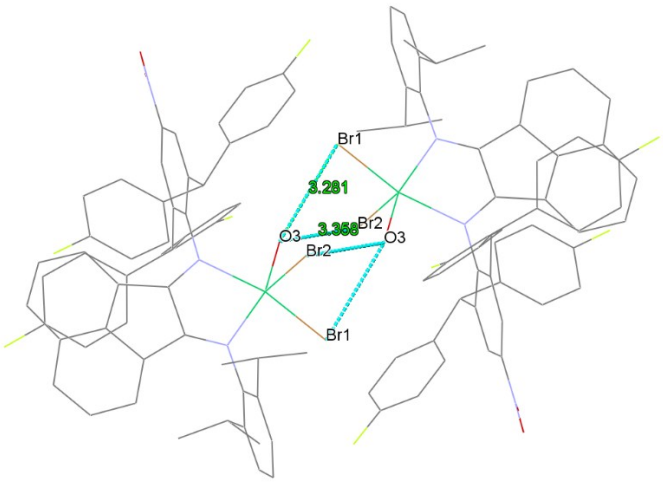


Figure S1. Dimerization of **Ni3**(OH_2) through OH···Br intermolecular hydrogen-bonding interactions.

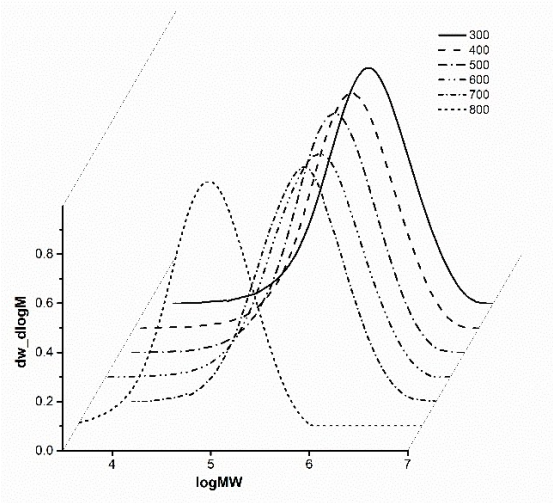


Figure S2. GPC curves of the polyethylenes obtained using **Ni1**/EASC at di□erent Al:Ni ratios (entries 1 – 6, Table 3).

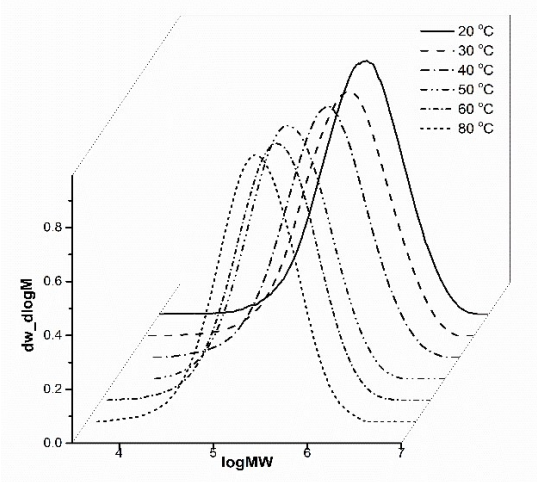


Figure S3. GPC curves of the polyethylenes obtained using **Ni1**/EASC at di□erent reaction temperatures (entries 4, 7 – 11, Table 3).

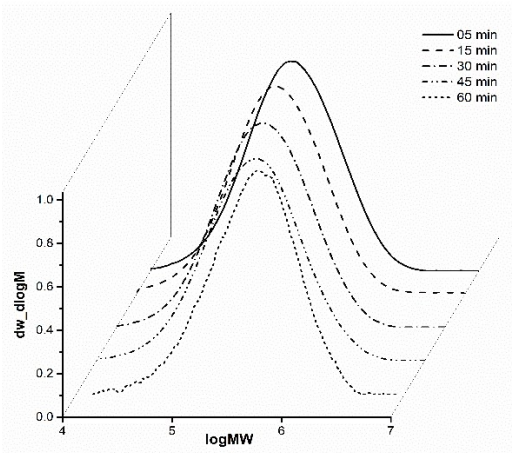


Figure S4. GPC curves of the polyethylenes obtained using **Ni1**/EASC over di□erent reaction times (entries 9 and 12 – 14, Table 3).

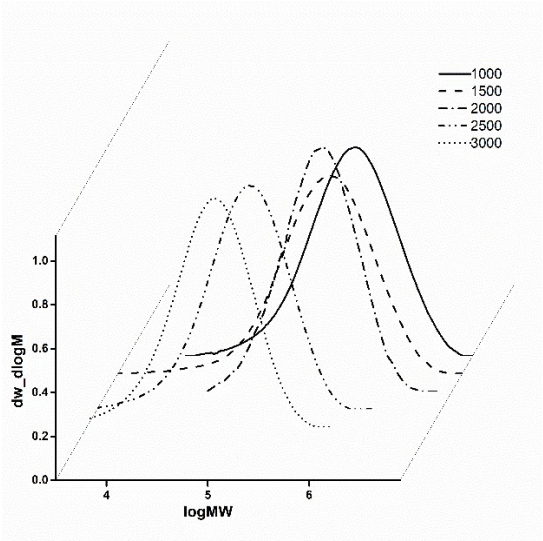


Figure S5. GPC curves of the polyethylenes obtained using **Ni1**/MAO at di□erent Al:Ni molar ratios (entries 1 – 5, Table 4).

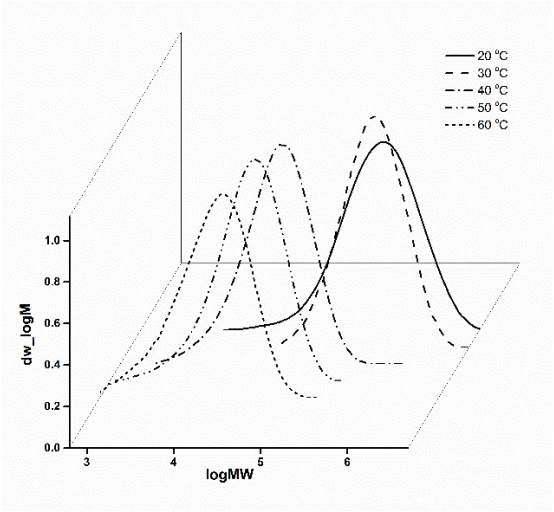


Figure S6. GPC curves of the polyethylenes obtained using **Ni1**/MAO at di□erent reaction temperatures (entries 3 and 6 – 9, Table 4).

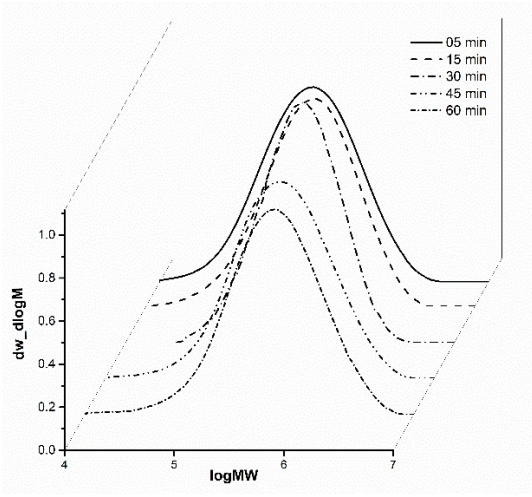


Figure S7. GPC curves of the polyethylenes obtained using **Ni1**/MAO at di erent reaction times (entries 3 and 10 – 12, Table 4).

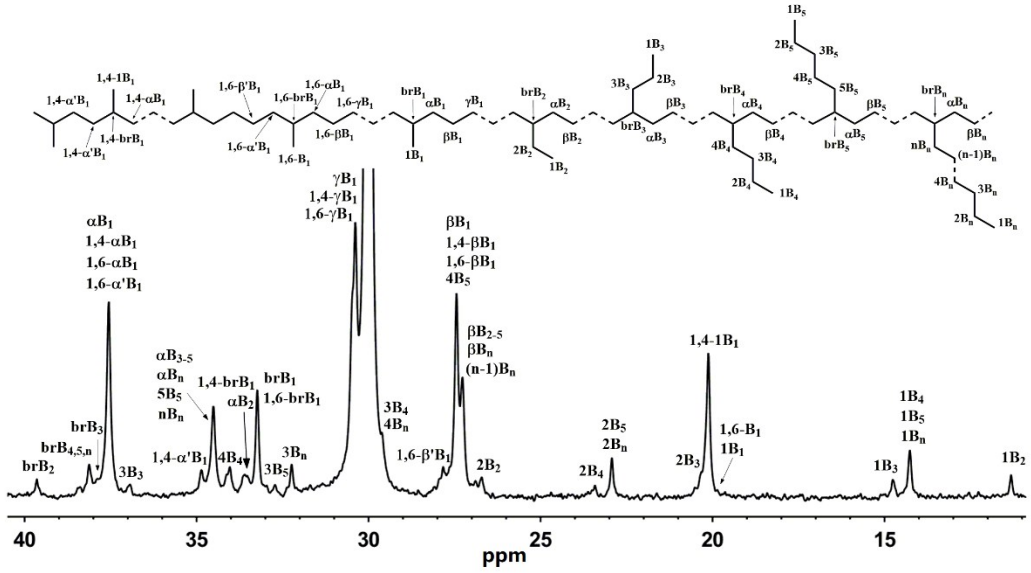


Figure S8. ^{13}C NMR spectrum of PE-50$_{E/Ni1}$ obtained using **Ni1**/EASC at 50 °C (entry 7, Table 3).

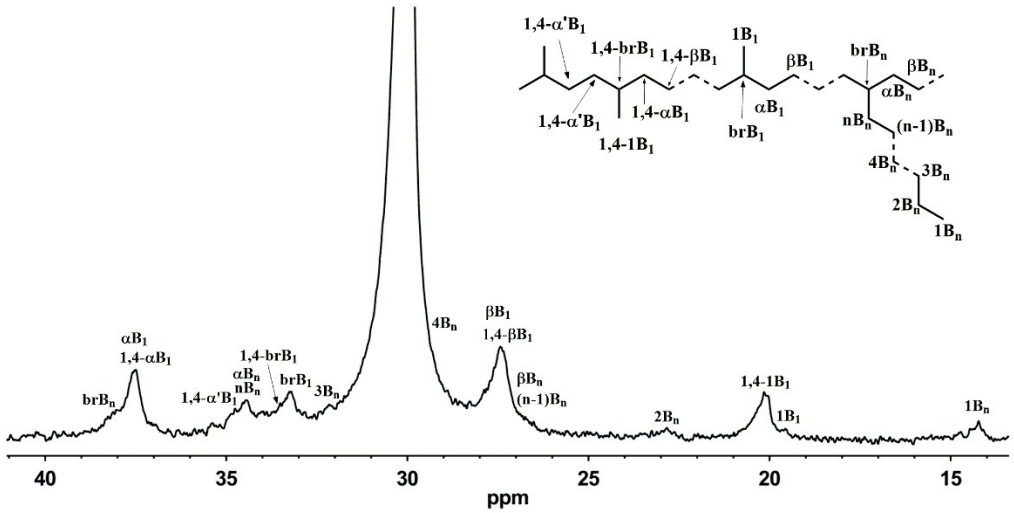
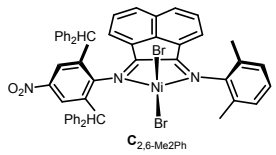
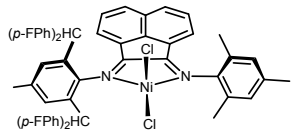
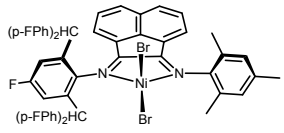
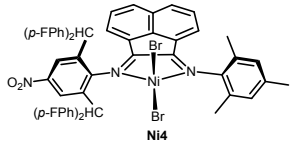


Figure S9. ^{13}C NMR spectrum of PE-60$_{M/Ni1}$ obtained using **Ni1**/MAO at 60 °C (entry 9, Table 4).

Table S1. Variation in the polyethylene properties as a function of the precatalyst structure; all polymerization runs performed with MAO activation[a]

Precatalyst	Temp /°C	Activity[b]	M_w[c]	M_w/M_n[c]
 $C_{2,6\text{-Me2Ph}}$	20	1.32	24.10	1.4
 $D_{Me/2,4,6\text{-Me3Ph}}$	30	8.73	4.33	1.8
 $D_{F/2,4,6\text{-Me3Ph}}$	30	12.48	4.81	2.1
 **Ni4**	30	5.12	8.21	3.0

[a] 10 atm C_2H_4; toluene as solvent and MAO as co-catalyst; [b] Values in units of 10^6 g (PE) mol^{-1} (Ni) h^{-1}; [c] Determined by GPC, M_w: 10^5 g mol^{-1}.

Table S2. Crystal data and structural refinements for **L3**, **Ni3** and **Ni4**.

	L3	**Ni3**(OH_2)	**Ni4**
Empirical formula	$C_{56}H_{43}F_4N_3O_2$	$C_{56}H_{45}Br_2F_4N_3NiO_3$	$C_{53}H_{37}Br_2F_4N_3NiO_2$
Formula weight	865.93	1102.48	1042.38
Temperature/K	173.15	173.15	173.15
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	11.3537(4)	11.3027(3)	14.652(3)
b/Å	23.9312(6)	32.3842(7)	32.546(7)
c/Å	17.2928(5)	15.9132(4)	10.810(2)
Alpha/°	90	90	90
Beta/°	105.819(3)	108.872(3)	95.61(3)
Gamm/°	90	90	90
Volume/Å^3	4520.6(2)	5511.6(3)	5130.0(18)
Z	4	4	4
D_{calcd}/(g/cm^{-3})	1.272	1.329	1.350
μ/mm^{-1}	0.089	1.858	1.991
F(000)	17628.0	2240.0	2104.0
Crystal size/mm^3	0.160 ×0.147 ×0.042	0.308 × 0.164 × 0.132	0.243 × 0.156 ×

			0.102
θ range (°)	2.982 to 63.074	2.982 to 63.12	2.502 to 54.934
Limiting indices	-16 ≤ h ≤ 16 -34 ≤ k ≤ 35 -25 ≤ l ≤ 25	-15 ≤ h ≤ 16 -45 ≤ k ≤ 47 -23 ≤ l ≤ 22	-18 ≤ h ≤ 19 -42 ≤ k ≤ 42 -14 ≤ l ≤ 14
No. of rflns collected	60972	92431	69720
No. unique rflns	14101	17353	11709
R_{int}	0.0798	0.1041	0.0691
No. of params	590	627	589
Completeness to θ	93.4	94.1	99.7
Goodness of fit on F^2	1.013	1.038	1.211
Final R indexes [I>=2σ (I)]	R_1 = 0.0715 wR_2 = 0.1279	R_1 = 0.0700 wR_2 = 0.1595	R_1 = 0.0772 wR_2 = 0.1558
Final R indexes (all data)	R_1 = 0.1588 wR_2 = 0.1562	R_1 = 0.1413 wR_2 = 0.1849	R_1 = 0.0840 wR_2 = 0.1614
Largest di□. peak and hole/(e Å^{-3})	0.32/-0.25	1.24/-0.68	1.21/-0.51