

Electronic Supplementary Information (ESI)

Electronic tuning of sterically encumbered 2-(arylimino)pyridine-nickel ethylene polymerization catalysts by *para*-group modification

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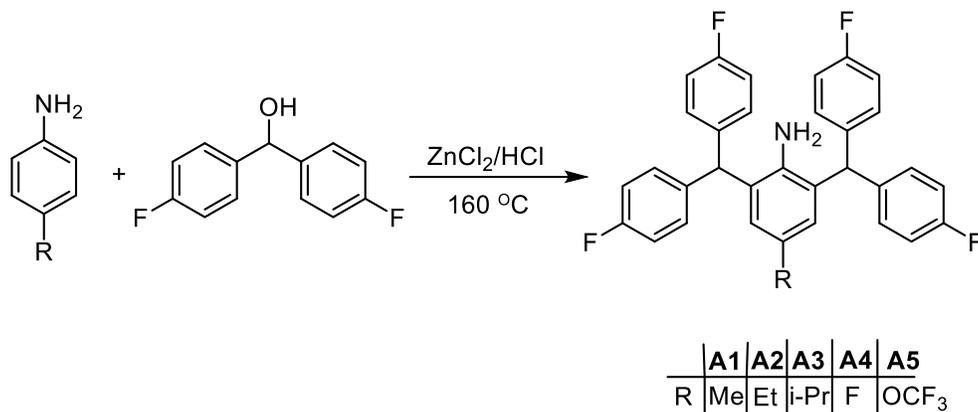
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Table S1 Crystal data and structure refinement for **Ni4'** and **Ni5**

1. Synthesis and characterization of anilines, 2,6-(CH(C₆H₄-*p*-F)₂)₂-4-RC₆H₂NH₂ (A1 – A5)



Scheme S1 Synthetic route to A1 – A5

(a) R = Me **A1**. Based on a Friedel-Crafts procedure,^[1,2] a round bottom flask (500 mL) was loaded with bis(4-fluorophenyl)methanol (12.55 g, 57 mmol) and 4-methylaniline (3.06 g, 28.62 mmol). The mixture was stirred at 160 °C for 20 min to form a homogeneous solution and then a catalytic amount of ZnCl₂ (0.59 g, 15 mol%) in a 36-38% in HCl (3 mL) added dropwise. The reaction mixture was further stirred for 4 h. After cooling to room temperature, the resulting solid was dissolved in dichloromethane (250 mL) and the solution filtered. The filtrate was washed with a saturated aqueous solution of NH₄Cl (55 mL) followed by a saturated solution of NaCl (2 x 55 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure. The sticky residue was dissolved in a minimum amount dichloromethane and methanol (55 mL) added to induce precipitation. After filtration **A1** was afforded as a white solid (8.28 g, 55%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 6.93-7.01 (m, 16H), 6.30 (s, 2H), 5.37 (s, 2H), 3.32 (s, 2H), 2.00 (s, 3H).

(b) R = Et **A2**. By employing a similar method as outlined for the preparation of **A1**, **A2** was obtained as a white solid (5.60 g, 56%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 6.93-7.01 (m, 16H), 6.30 (s, 2H), 5.37 (s, 2H), 3.32 (s, 2H), 2.00 (s, 3H).

(c) R = i-Pr **A3**. By employing a similar method as outlined for the preparation of **A1**, **A3** was obtained as a white solid (6.25 g, 48%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 6.90-7.03 (m, 16H), 6.37 (s, 2H), 5.39 (s, 2H), 2.52-2.57 (m, 1H), 0.94 (d, *J* = 8.0 Hz, 6H).

(d) R = F **A4**. By employing a similar method as outlined for the preparation of **A1**, **A4** was obtained as a white solid (5.2 g, 55%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 6.72-7.04 (m, 16H), 6.38 (s, 1H), 6.28 (s, 1H), 5.39 (s, 1H), 5.07 (s, 1H), 3.20 (s, 2H).

(e) R = OCF₃ **A5**. By employing a similar method as outlined for the preparation of **A1**, **A5** was obtained as a white solid (7.6 g, 53%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.21 (m, 16H), 6.64 (s, 2H), 5.60 (s, 2H), 3.65 (s, 2H).

2. GPC curves for the polyethylenes produced using Ni/MMAO

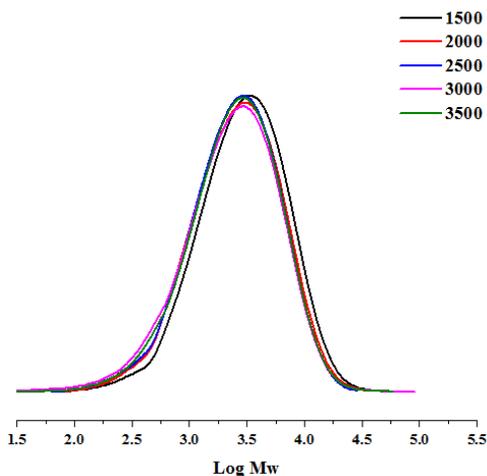


Figure S1 GPC curves for the polyethylene produced using Ni1/MMAO at different Al:Ni molar ratios (runs 1 – 5, Table 4).

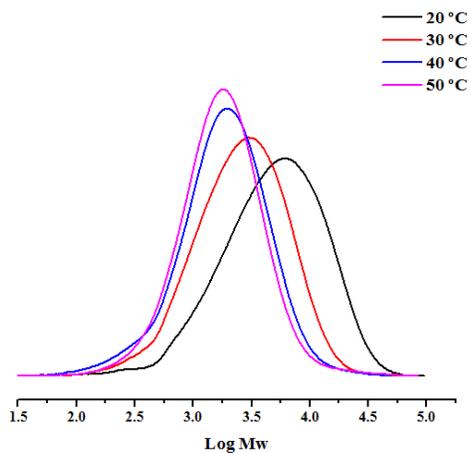


Figure S2 GPC curves for the polyethylene produced using Ni1/MMAO at different reaction temperatures (runs 2, 6 – 8, Table 4).

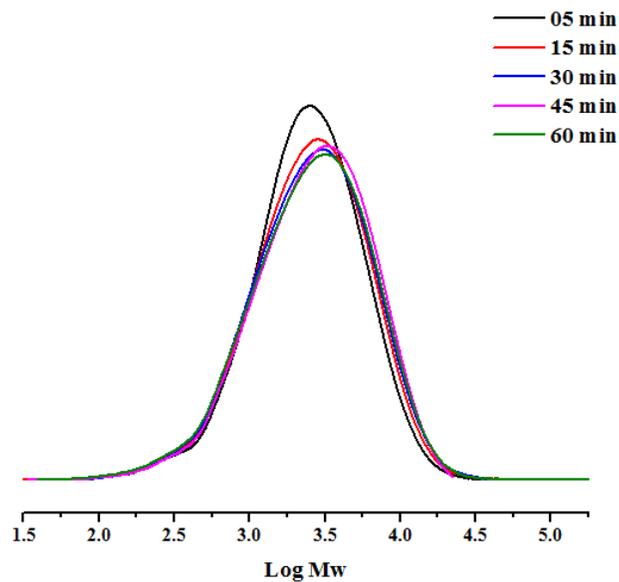


Figure S3 GPC curves for the polyethylene produced using Ni1/MMAO at different reaction times (runs 2, 9 – 12, Table 4).

Figure S5 ^{13}C NMR spectrum of the polyethylene sample produced using Ni1/EtAlCl₂ at 20 °C (run 7, Table 3), including an inset of the alkenic region and a segment of the assigned polymer backbone; recorded at 100 °C in *d*-C₂D₂Cl₄.

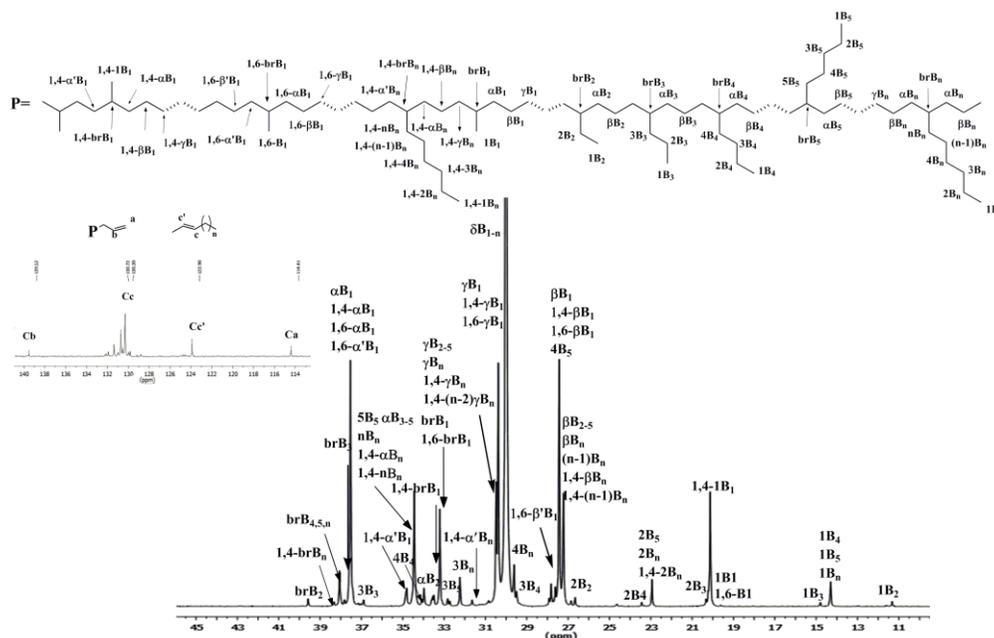


Figure S6 ^{13}C NMR spectrum of the polyethylene sample produced using Ni1/EtAlCl₂ at 50 °C (run 9, Table 3), including an inset of the alkenic region and a segment of the assigned polymer backbone; recorded at 100 °C in *d*-C₂D₂Cl₄.

4. ^1H and ^{13}C NMR spectra of the polyethylene obtained using Ni1/MMAO at 30 °C (run 6, Table 3).

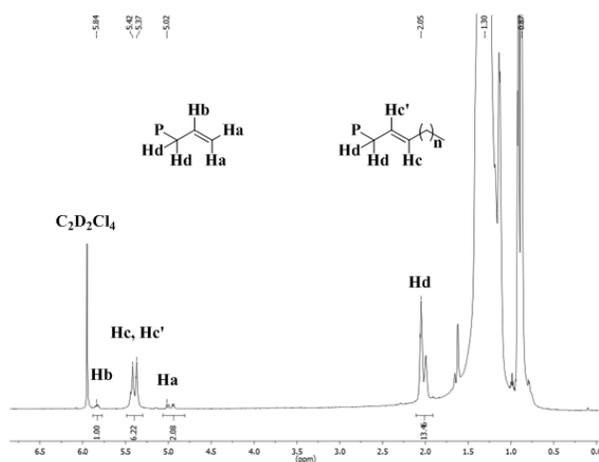


Figure S9 ^{19}F NMR spectrum of L1 (recorded in CDCl_3 at room temperature).

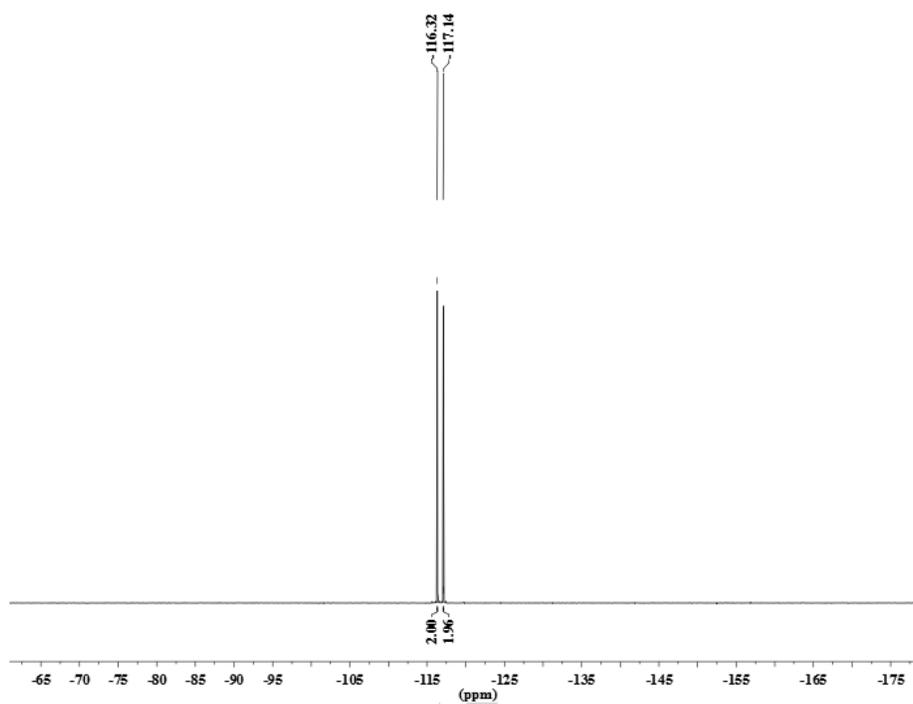


Figure S10 ^{19}F NMR spectrum of L2 (recorded in CDCl_3 at room temperature).

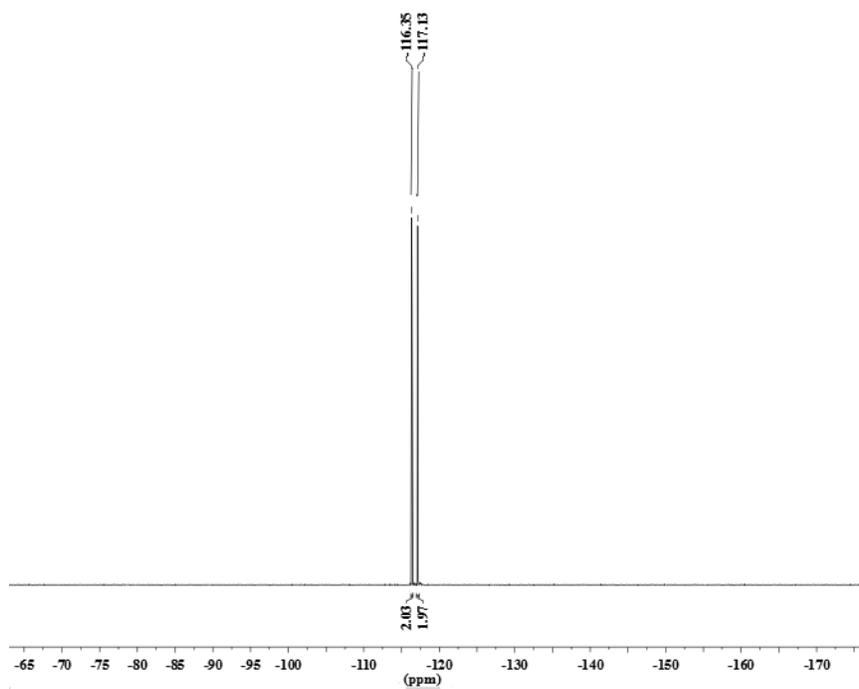


Figure S11 ^{19}F NMR spectrum of L3 (recorded in CDCl_3 at room temperature).

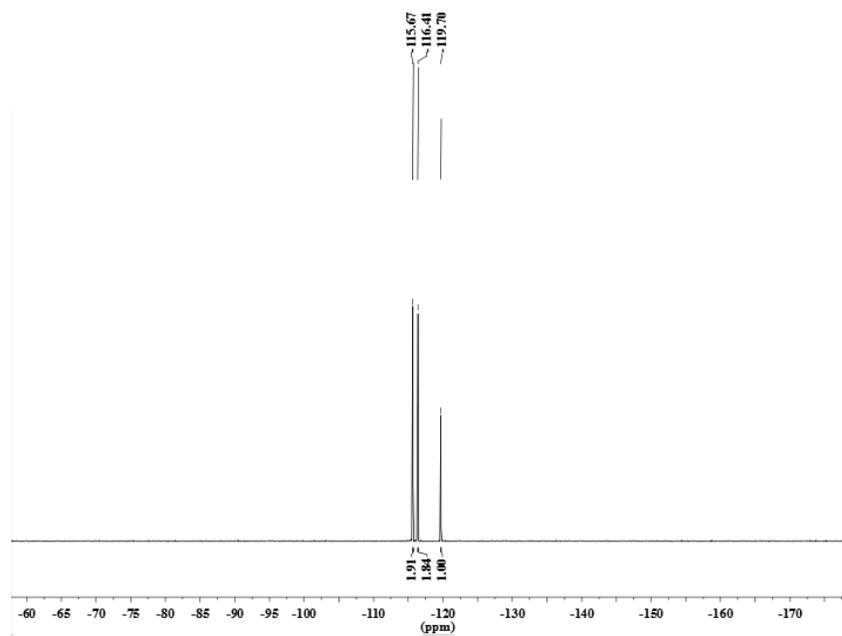


Figure S12 ^{19}F NMR spectrum of L4 (recorded in CDCl_3 at room temperature).

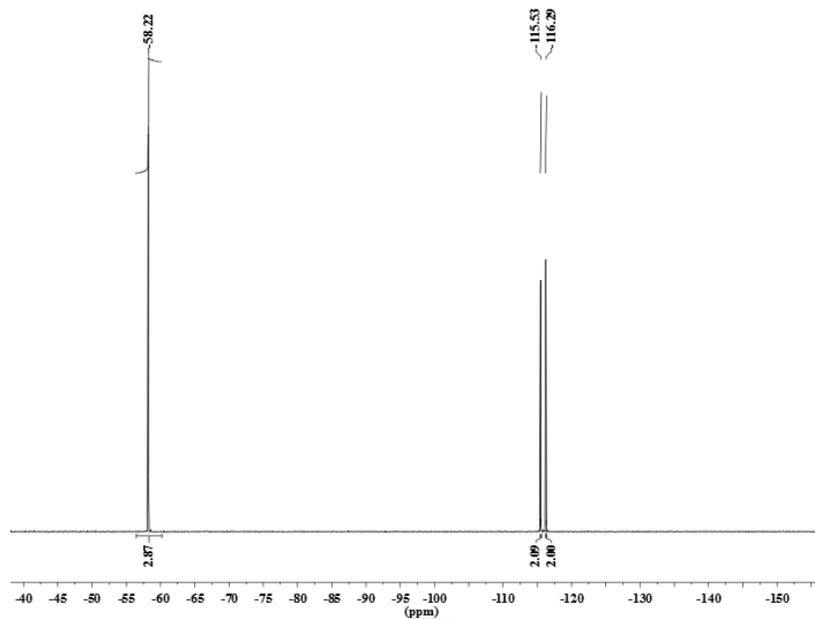


Figure S13 ^{19}F NMR spectrum of L5 (recorded in CDCl_3 at room temperature).

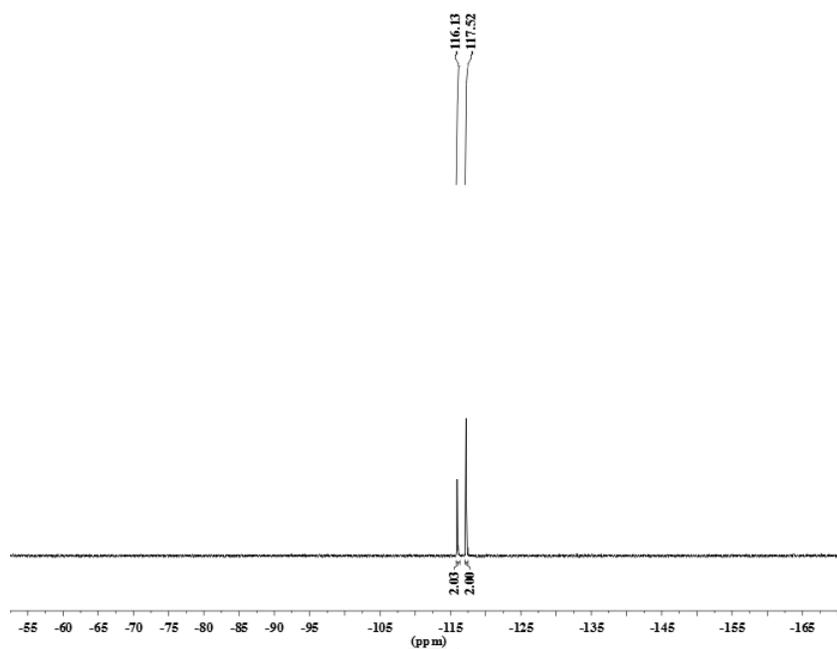


Figure S14 ^{19}F NMR spectrum of Ni1 (recorded in CDCl_3 at room temperature).

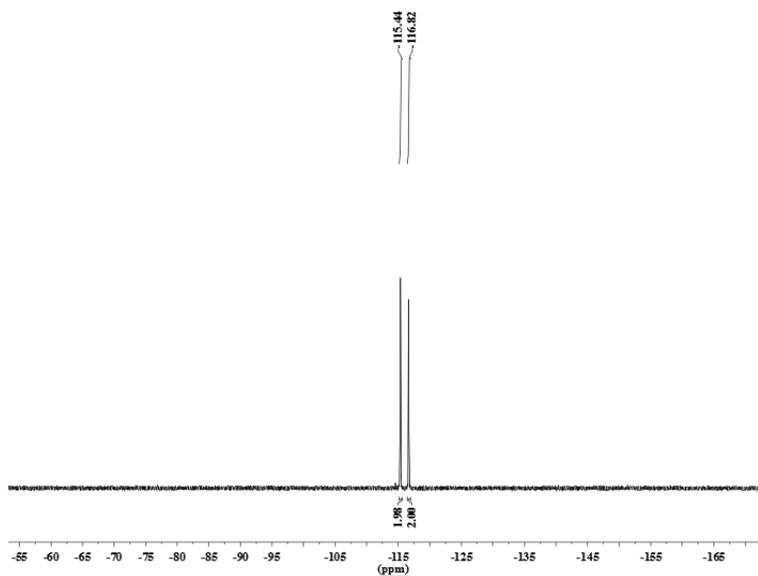


Figure S15 ^{19}F NMR spectrum of Ni2 (recorded in CDCl_3 at room temperature).

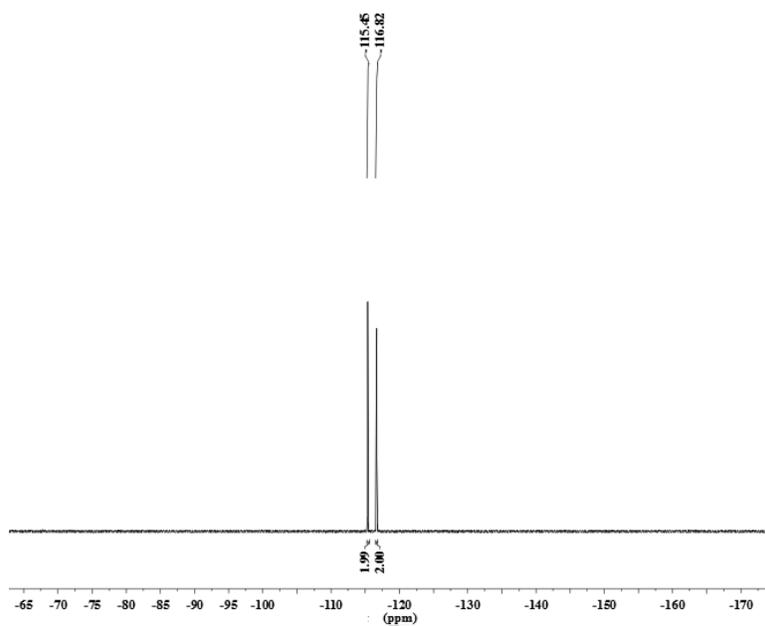


Figure S16 ^{19}F NMR spectrum of Ni3 (recorded in CDCl_3 at room temperature).

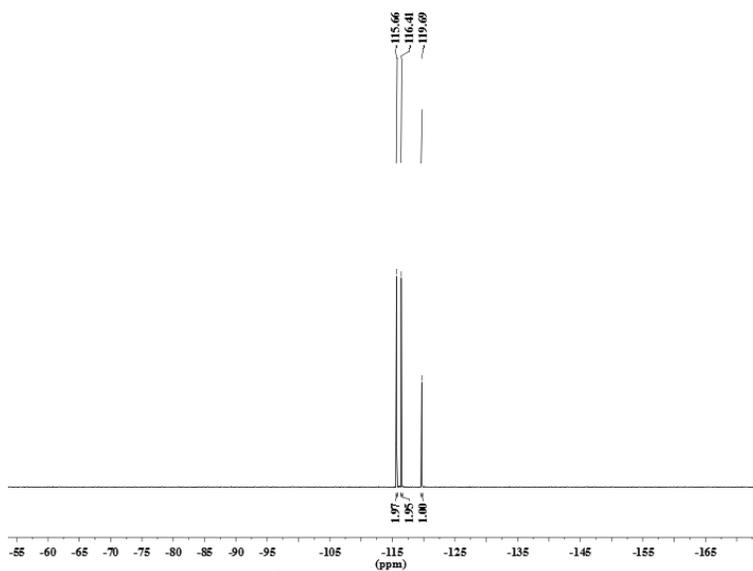


Figure S17 ^{19}F NMR spectrum of Ni4 (recorded in CDCl_3 at room temperature).

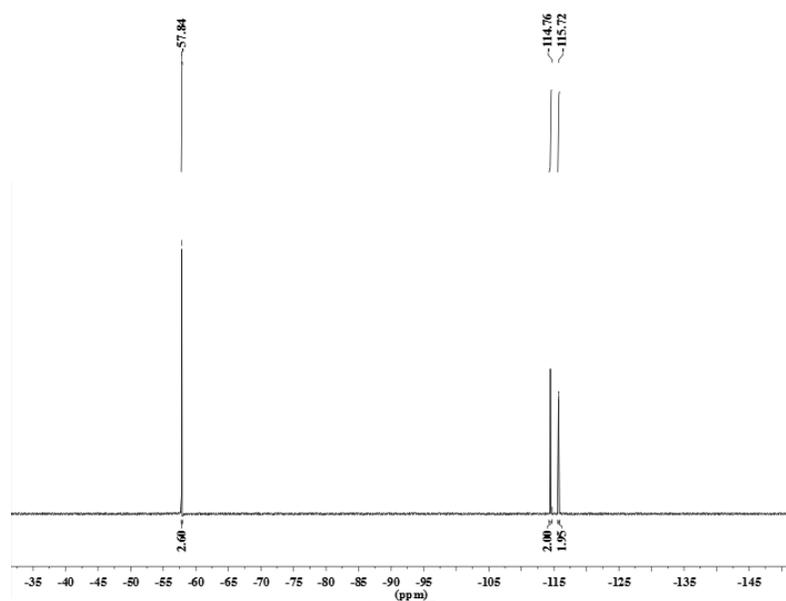


Figure S18 ^{19}F NMR spectrum of Ni5 (recorded in CDCl_3 at room temperature).

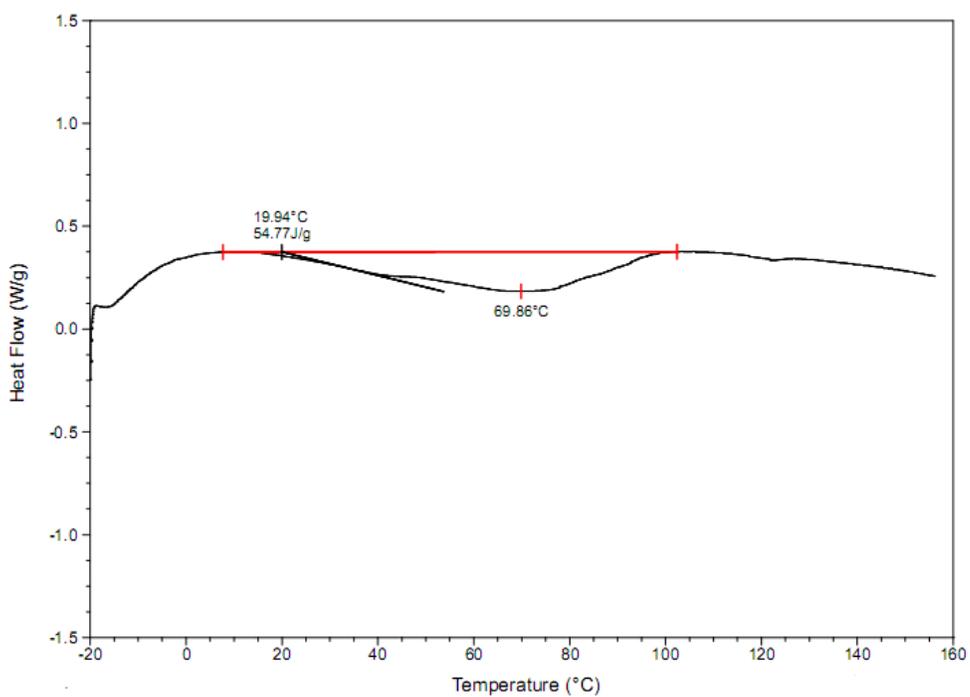


Figure S19 DSC curve Ni/MMAO (recorded at room temperature).

Table S1 Crystal data and structure refinement for Ni4' and Ni5

	Ni4'	Ni5
Identification code	2215182	2215183
Empirical formula	BrC ₃₉ F ₅ N ₂ Ni _{0.5}	Br ₂ C ₄₀ F ₇ N ₂ NiO
Formula weight	700.68	875.95
Temperature/K	169.98(11)	169.99(11)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	11.1117(4)	10.2966(4)
b/Å	13.3208(4)	10.7584(4)
c/Å	13.5631(4)	16.8828(5)
α /°	113.925(3)	103.165(3)
β /°	90.490(3)	100.812(3)
γ /°	106.159(3)	96.110(3)
Volume/Å ³	1745.64(11)	1766.82(11)
Z	2	2
$\rho_{\text{calc}}/\text{cm}^3$	1.333	1.647
μ/mm^{-1}	2.351	4.086
F(000)	684.0	846.0
Crystal size/mm ³	0.35 × 0.2 × 0.05	0.15 × 0.05 × 0.02
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	7.2 to 151.232	5.51 to 150.7
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -20 ≤ l ≤ 19
Reflections collected	22774	21981
Independent reflections	6900 [R _{int} = 0.0553, R _{sigma} = 0.0517]	6956 [R _{int} = 0.0631, R _{sigma} = 0.0587]
Data/restraints/parameters	6900/0/430	6956/0/478
Goodness-of-fit on F ²	1.037	1.044
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0785, wR ₂ = 0.2231	R ₁ = 0.0596, wR ₂ = 0.1704
Final R indexes [all data]	R ₁ = 0.0886, wR ₂ = 0.2342	R ₁ = 0.0673, wR ₂ = 0.1791
Largest diff. peak/hole / e Å ⁻³	1.52/-1.31	1.52/-1.15

6. References

- 1 Meiries, S.; Speck, K.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P. S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin and S. P., Nolan, [Pd(IPr^{*OMe})(acac)Cl]: Tuning the N-Heterocyclic Carbene in Catalytic C–N Bond Formation. *Organometallics*, **2012**, *32*, 330-339.
- 2 Zada, M.; Guo, L.; Zhang, R.; Zhang, W.; Ma, Y.; Solan, G. A.; Sun, Y.; Sun, W.-H. Moderately branched ultra-high molecular weight polyethylene by using N,N'-nickel catalysts adorned with sterically hindered dibenzocycloheptyl groups. *Appl. Organomet. Chem.* **2019**, *33*, e4749.