Supplementary Materials

Thermally stable and highly efficient *N,N,N*-cobalt olefin polymerization catalysts affixed with *N*-2,4-bis(dibenzosuberyl)-6-fluorophenyl groups

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X-Ray diffraction analysis

The single crystal X-ray diffraction studies on **Co1** and **Co2** were performed on a Rigaku Saturn 724+ CCD diffractometer (Rigaku, Tokyo, Japan) using graphite-monochromated Mo-Kα radiations (λ = 0.71073 Å). The cell parameters were obtained by global refinement of the positions of all collected reflections. The intensities were corrected for Lorentz polarization effects and an empirical absorption was made. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All hydrogen atoms were placed in calculated positions and the structural solution of each complex and refinement were performed using SHELXT-97 [72,73]. All the hydrogen atoms have been omitted in the ORTEP diagrams of the corresponding complexes for clarity. The details of crystal data and refinement parameters are provided in the Table S1.

Table S1. Details of the crystal data and structure refinement parameters for **Co1** and **Co2**

	Co1	**Co2**
CCDC No.	2214375	2214376
Empirical formula	$C_{53}H_{46}Cl_2CoFN_3$	$C_{55}H_{50}Cl_2CoFN_3$
Formula weight	873.76	901.81
Temperature (K)	170.00(10)	170.00(10)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	17.1521(10)	16.5451(4)
b (Å)	16.0737(9)	16.4409(3)
c (Å)	16.0822(10)	18.3798(4)
α (°)	90	90
β (°)	106.800(7)	112.856(3)
γ (°)	90	90
Volume (Å^3)	4244.6(5)	4607.1(2)
Z	4	4
D_{calcd} (g/cm^3)	1.367	1.300
μ (mm^{-1})	0.576	0.533
F (000)	1820.0	1884.0
Crystal size (mm^3)	0.198 × 0.178 × 0.041	0.372 × 0.223 × 0.111
θ range (°)	6.942 to 61.574	6.814 to 49.998
Limiting indexes	$-24 \le h \le 23$, $-13 \le k \le 22$, $-15 \le l \le 22$	$-19 \le h \le 19$, $-18 \le k \le 19$, $-20 \le l \le 21$
No. of rflns collected	38454	51108
No. of unique rflns [R(int)]	11754 (0.0922)	8098 (0.0242)
Completeness to θ (%)	0.884	0.997
Data/restraints/parameters	11754/0/545	20691/0/1167
Goodness of fit on F^2	0.957	1.038
Final R indexes [$I > = 2\sigma$ (I)]	$R_1 = 0.0594$, $wR_2 = 0.1193$	$R_1 = 0.0269$, $wR_2 = 0.0652$
R indexes (all data)	$R_1 = 0.1365$, $wR_2 = 0.1425$	$R_1 = 0.0299$, $wR_2 = 0.0664$
Largest diff. peak and hole (e Å^{-3})	0.92/-0.41	0.23/-0.26

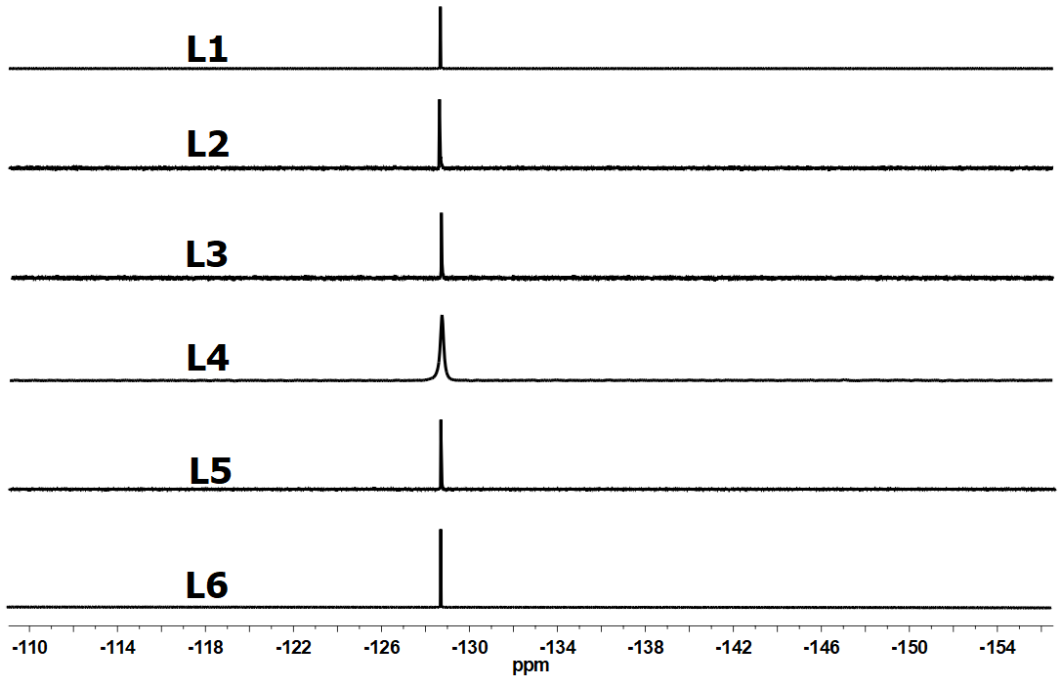

Figure S1. ^{19}F NMR spectra of **L1–L6**; recorded in $CDCl_3$ at ambient temperature.

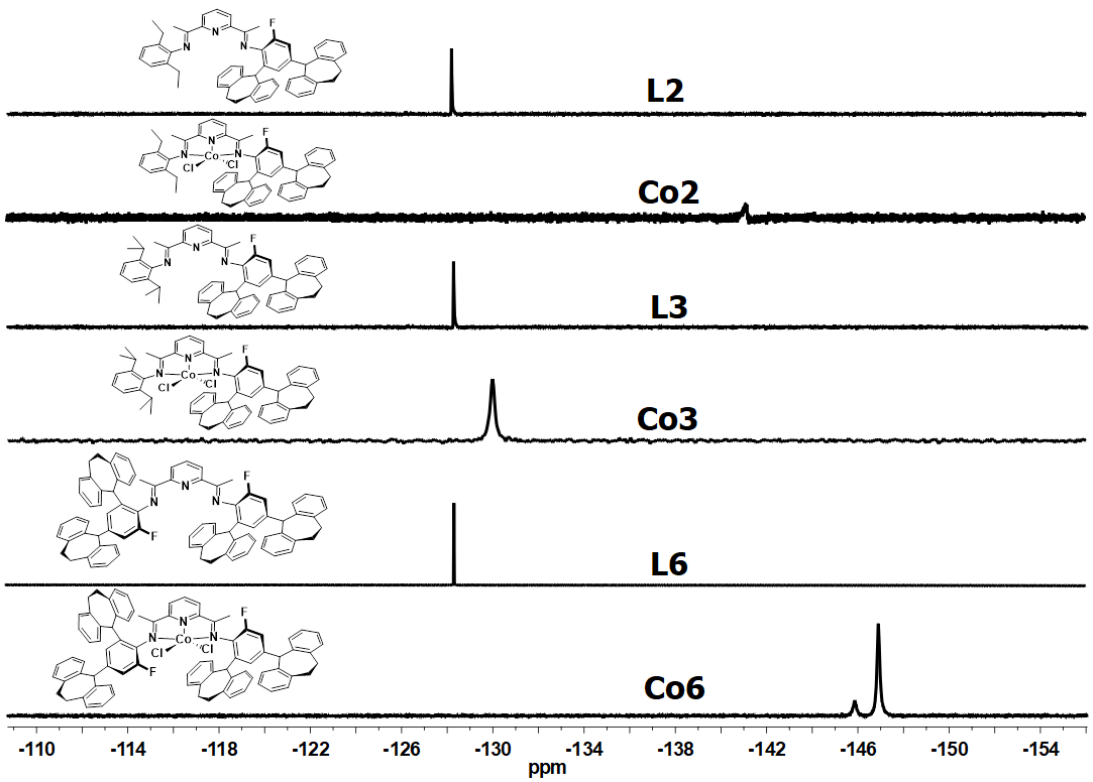

Figure S2. ^{19}F NMR spectra of **L2**, **L3** and **L6** along with those for their corresponding complexes **Co2**, **Co3** and **Co6**; recorded in $CDCl_3$ at ambient temperature.

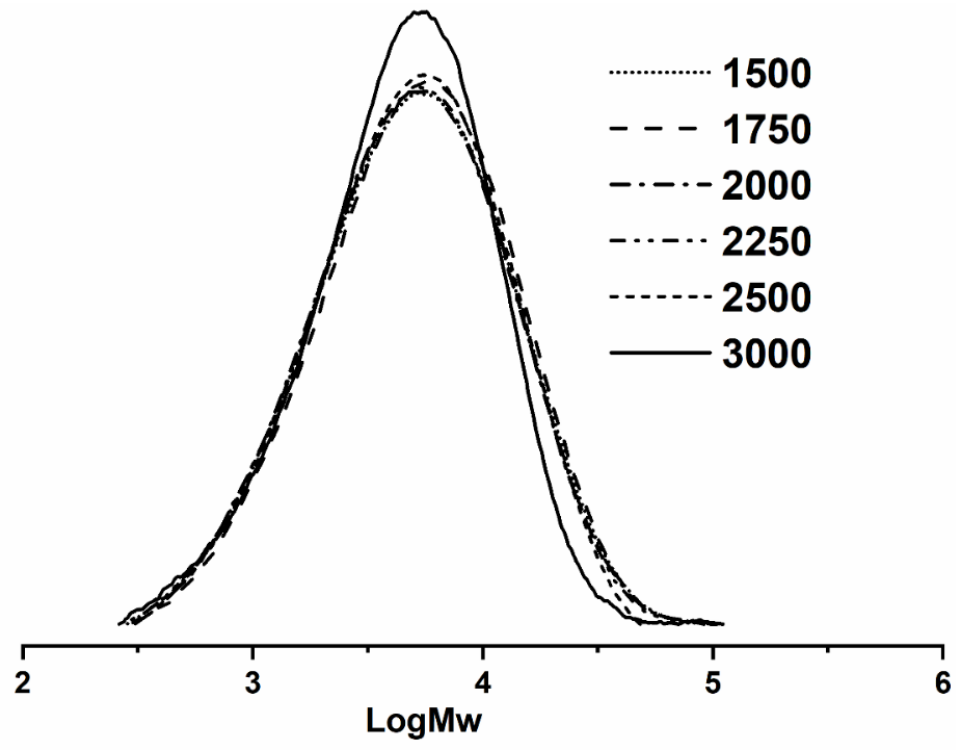

Figure S3. GPC curves showing log M_w for the polyethylene produced using **Co1**/MAO as a function of Al:Co molar ratio (runs 5, 8–12, Table 2).

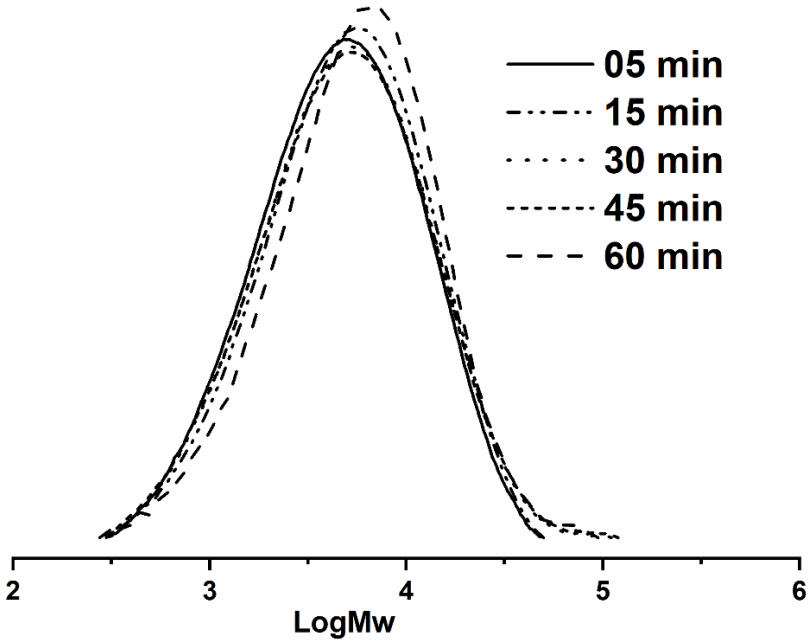

Figure S4. GPC curves showing log M_w for the polyethylene produced using **Co1**/MAO as a function of reaction time (runs 5, 13–16, Table 2).

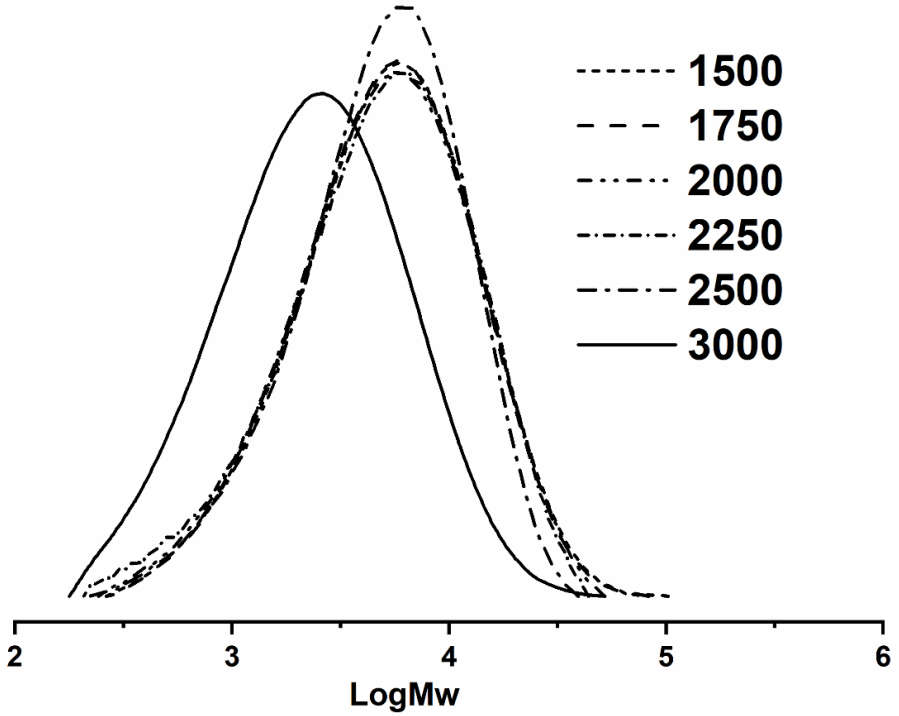

Figure S5. GPC curves showing log M_w for the polyethylene produced using **Co1**/MMAO as a function of Al:Co molar ratio (runs 5, 8–12, Table 3).

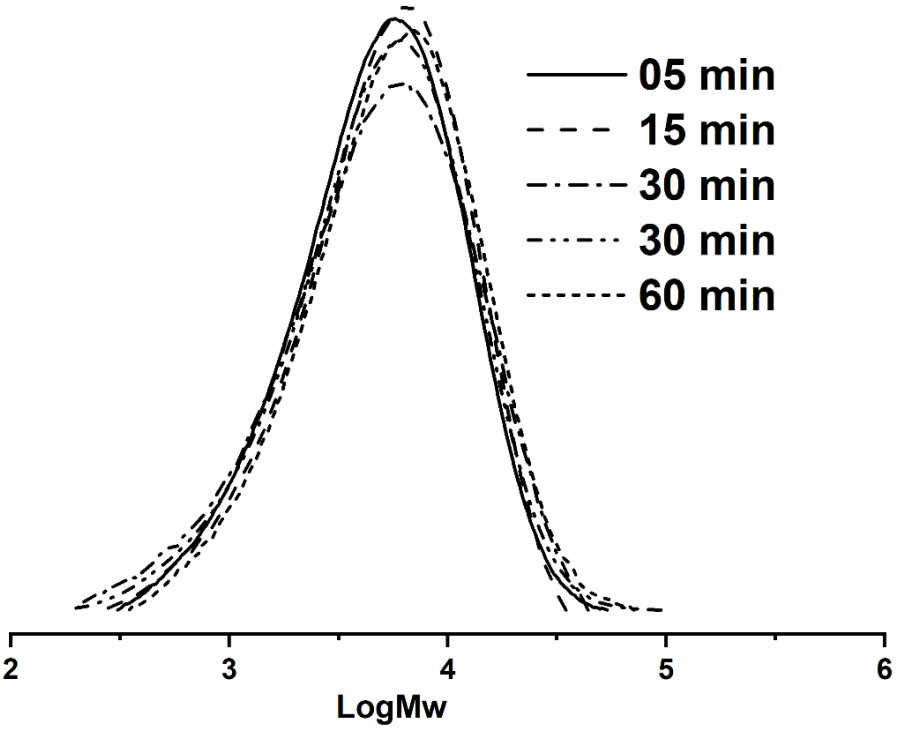

Figure S6. GPC curves showing log M_w for the polyethylene produced using **Co1**/MMAO as a function of reaction time runs 10, 13–16, Table 3).

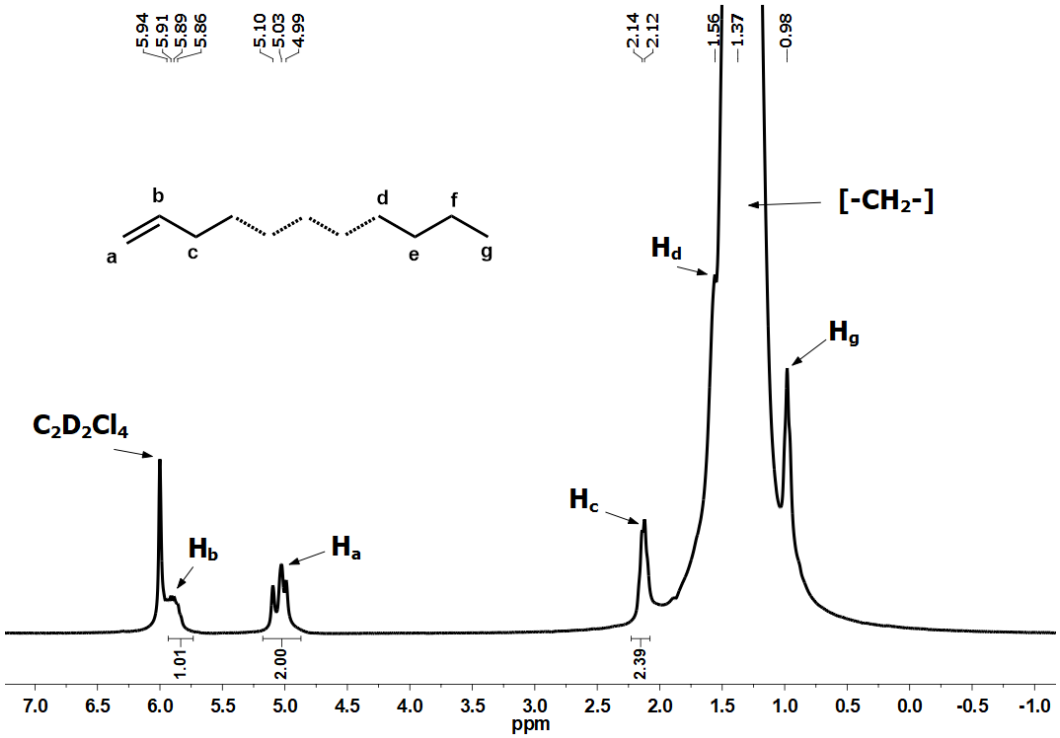

Figure S7. [1]H NMR spectrum of the polyethylene produced using **Co1**/MMAO (run 10, Table 3); recorded in $C_2D_2Cl_4$ at 100 °C.

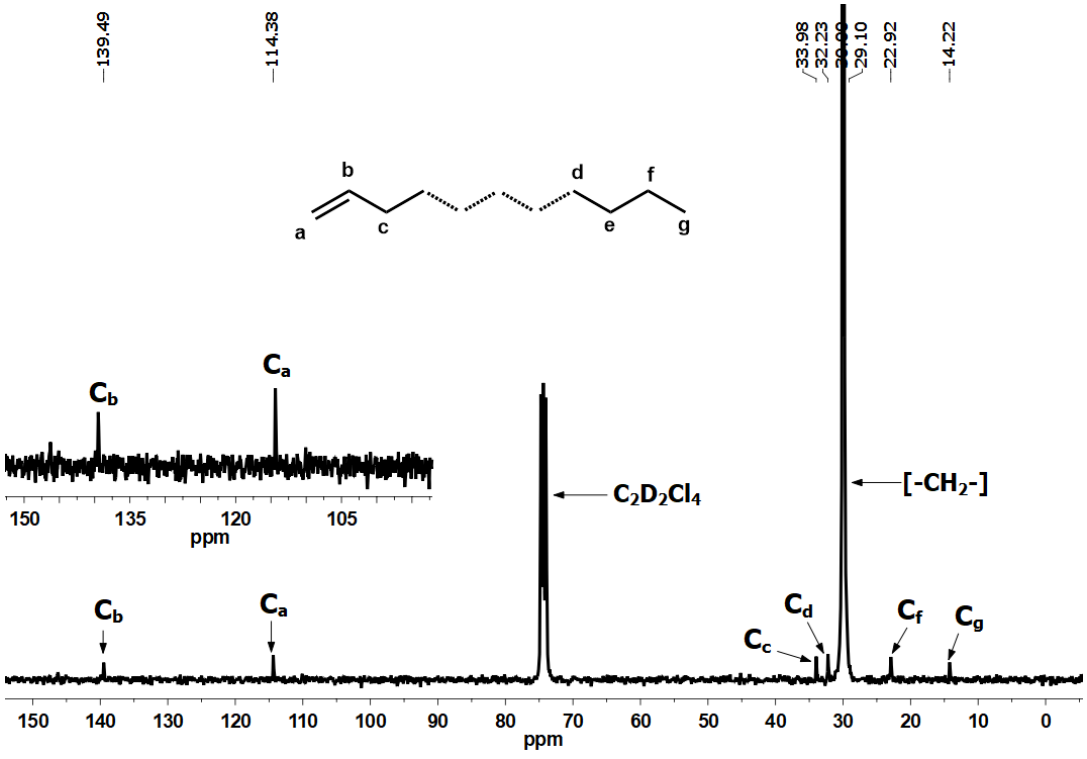

Figure S8. [13]C NMR spectrum of the polyethylene produced using **Co1**/MMAO (run 10, Table 3; recorded in deuterated $C_2D_2Cl_4$ at 100 °C.