Supporting information
for

Bis-cycloheptyl-fused bis(imino)pyridine-cobalt catalysts for PE wax formation: positive effects of fluoride substitution on catalytic performance and thermal stability

Qiuyue Zhang,[†,‡] Ningning Wu,[†] Junfeng Xiang,[†] Gregory A. Solan,*[,†,§] Hongyi Suo,[†,‡] Yanping Ma,*[,†] Tongling Liang[†] and Wen-Hua Sun*[,†,‡,#]

[†] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail. whsun@iccas.ac.cn; Fax: +86-10-62618239; Tel: +86-10-62557955.
[‡] CAS Research/Education Center for Excellence in Molecular Sciences and International School, University of Chinese Academy of Sciences, Beijing 100049, China.
[§] Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK. E-mail: gas8@leicester.ac.uk. Tel: +44-116-2522096.
[#] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

Table of Contents

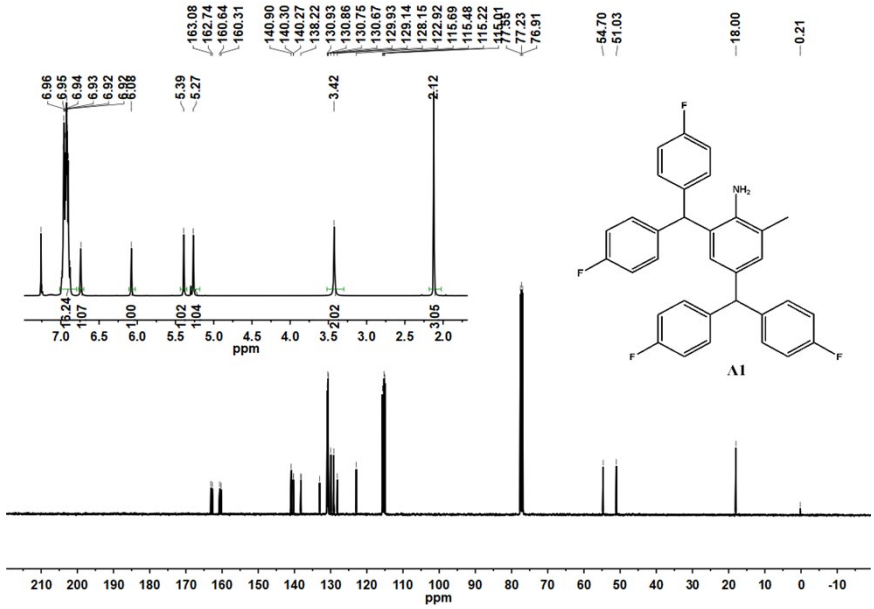
1. **NMR data for the anilines, A1 – A7** S2
2. **Figure S1** ^{19}F NMR spectra of **Co1**, **Co2**, **Co3**, **Co4**, **Co6** and **Co7**; recorded in $CDCl_3$ at ambient temperature. S6
3. **Figure S2** (a) GPC traces for the polymers obtained using **Co5**/MMAO at various temperatures; (b) Plot of activity and M_w versus temperature for the catalyst and polyethylene, respectively (entries 1 − 6, Table 4). S6
4. **Figure S3** (a) GPC traces for the polymers obtained using **Co5**/MMAO at various Al:Co molar ratios; (b) Plot of activity and M_w versus Al:Co molar ratio for the catalyst and polyethylene, respectively (entries 4, 7 − 10, Table 4). S7
5. **Figure S4** (a) GPC traces for the polymers obtained using **Co5**/MMAO at various run imes; (b) Plot of activity and M_w versus time for the catalyst and polyethylene, respectively (entries 4, 11 − 14, Table 4). S7
6. **Figure S5** Comparison of the catalytic activities and molecular weight of the polyethylenes generated using **Co1** – **Co7** and **Co**$_{mes}$; MMAO used as co-catalyst in each case. S7
7. **Figure S6** ^{1}H NMR spectrum of the polyethylene obtained using **Co4**/MAO at 60 °C; recorded at 100 °C in 1,1,2,2-tetrachloroethane-d_2 (entry 5, Table 3). S8
8. **Figure S7** ^{1}H NMR spectrum of the polyethylene obtained using **Co5'**/MAO at 60 °C; recorded at 100 °C in 1,1,2,2-tetrachloroethane-d_2 (entry 7, Table 3). S8
9. **Table S1** Crystal data and structure refinements for **Co4**, **Co5**, **Co5'** and **Co5''**. S9
10. **References** S10

NMR data for the anilines, A1 – A7

Compounds **A1** – **A7** were synthesized based on related literature procedures.[1]

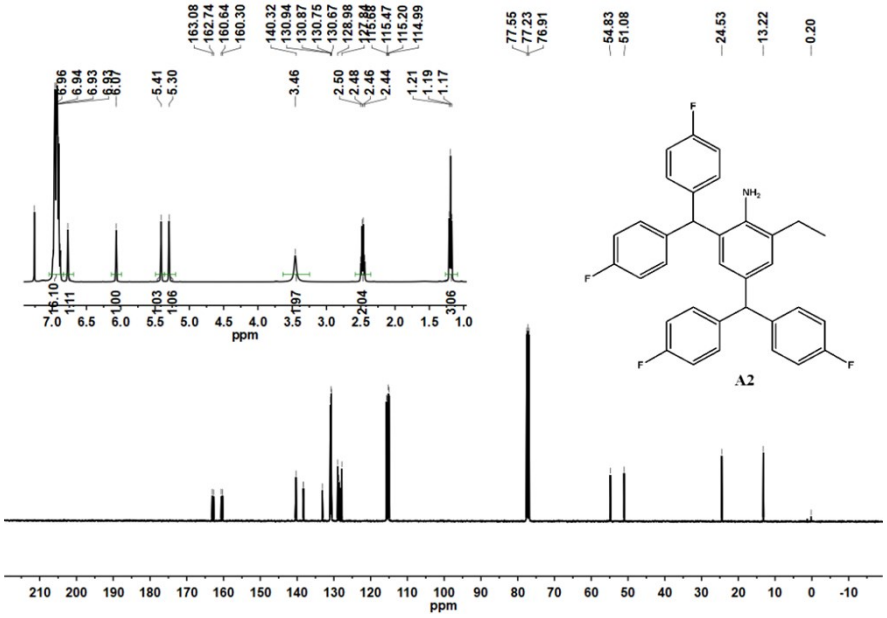
(a) ^{1}H and ^{13}C NMR spectroscopic data for **A1** − **A7**

2-Methyl-4,6-bis{di(*p*-fluorophenyl)methyl}aniline (**A1**, Yield: 59%)



Compound **A1**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.98−6.88 (m, 16H), 6.74 (s, 1H, aryl-H), 6.08 (s, 1H, aryl-H), 5.39 (s, 1H, CH(*p*-FPh)$_2$), 5.27 (s, 1H, CH(*p*-FPh)$_2$), 3.42 (s, 2H, NH_2), 2.12 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.08, 162.74, 160.64, 160.31, 140.90, 140.30, 140.27, 138.22, 138.19, 133.05, 130.93, 130.86, 130.75, 130.67, 129.93, 129.14, 128.15, 122.92, 115.69, 115.48, 115.22, 115.01, 54.70, 51.03, 18.00.

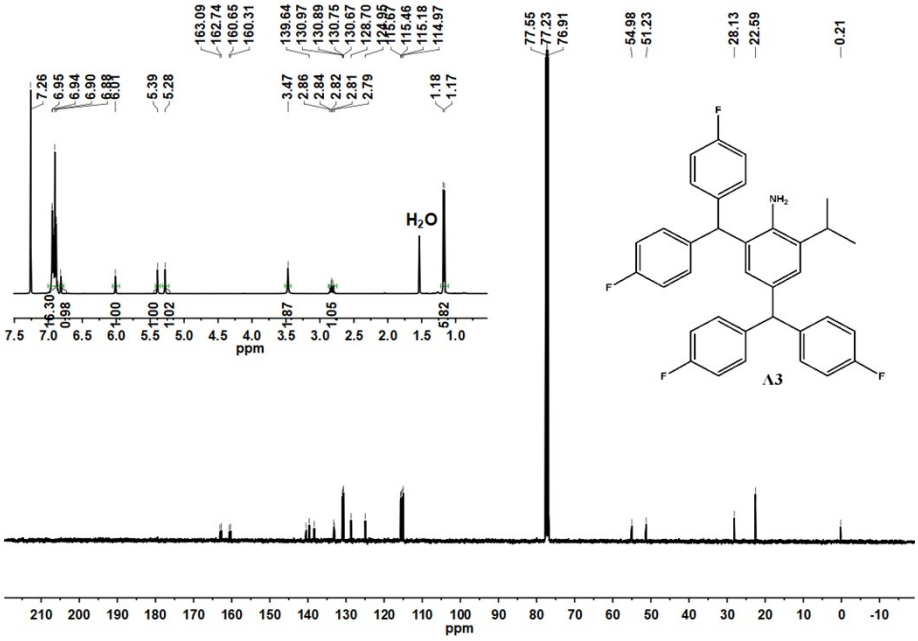
2-Ethyl-4,6-bis{di(*p*-fluorophenyl)methyl}aniline (**A2**, Yield: 73%)



Compound **A2**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.99−6.88 (m, 16H), 6.77 (s, 1H, aryl-H), 6.07 (s, 1H, aryl-H), 5.41 (s, 1H, CH(*p*-FPh)$_2$), 5.30 (s, 1H, CH(*p*-FPh)$_2$), 3.46 (s, 2H, NH_2), 2.47 (q, J = 8 Hz, 2H, CH_2CH$_3$), 1.19 (t, J = 8 Hz, 3H, CH$_2$CH_3). ^{13}C NMR (100 MHz,

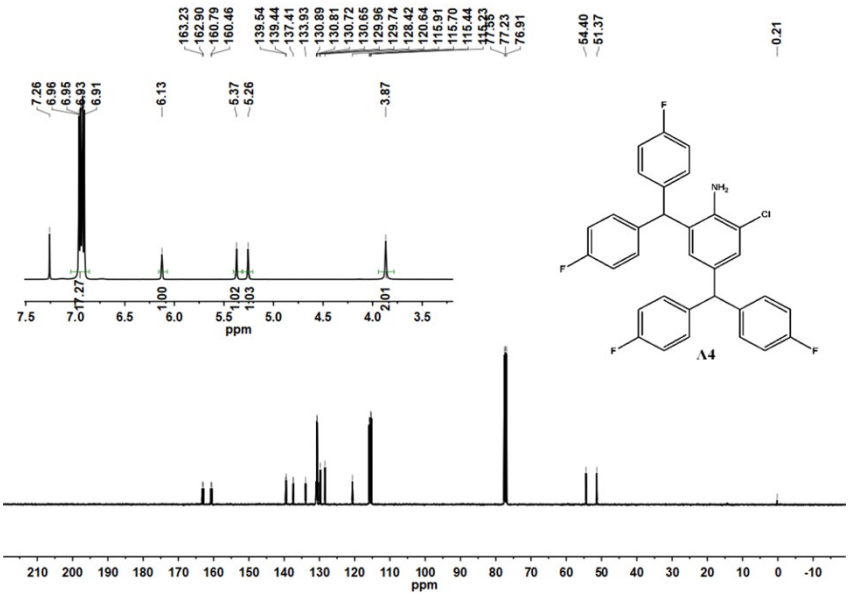
$CDCl_3$, TMS): δ 163.08, 162.74, 160.64, 160.30, 140.38, 140.35, 140.32, 138.30, 138.27, 133.13, 130.94, 130.87, 130.75, 130.67, 128.98, 128.66, 128.42, 127.84, 115.68, 115.47, 115.20, 114.99, 54.87, 51.08, 24.53, 13.22.

2-Isopropyl-4,6-bis{di(*p*-fluorophenyl)methyl}aniline (**A3**, Yield: 82%)



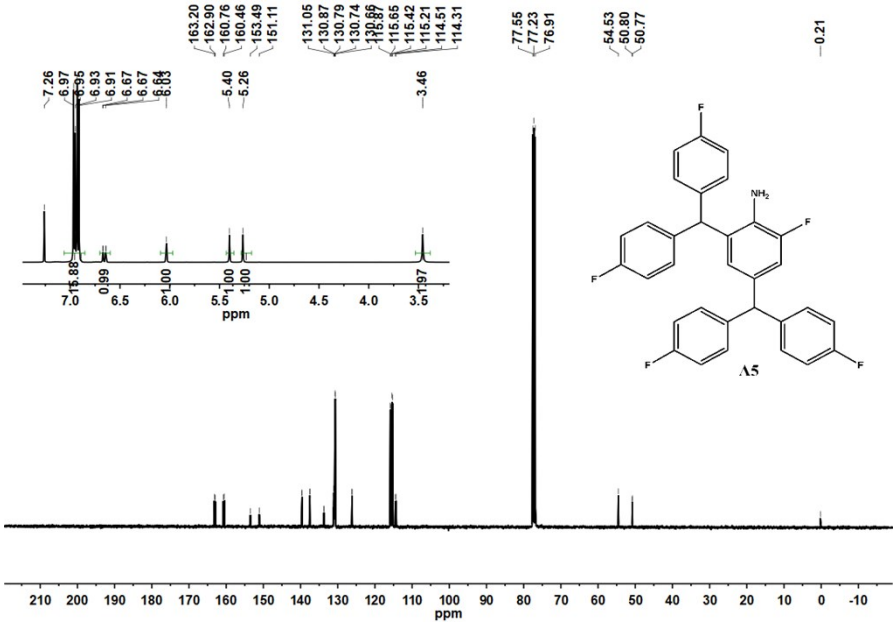
Compound **A3**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.95−6.86 (m, 16H), 6.82 (s, 1H, aryl-H), 6.01 (s, 1H, aryl-H), 5.39 (s, 1H, CH(*p*-FPh)$_2$), 5.28 (s, 1H, CH(*p*-FPh)$_2$), 3.47 (s, 2H, NH_2), 2.82 (m, 1H, C*H*$(CH_3)_2$), 1.17 (d, J = 4 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.09, 162.74, 160.65, 160.31, 140.46, 139.64, 138.34, 133.21, 133.07, 130.97, 130.89, 130.75, 130.67, 128.70, 128.64, 124.95, 115.67, 115.46, 115.18, 114.97, 54.98, 51.23, 28.13, 22.59.

2-Chloro-4,6-bis{di(*p*-fluorophenyl)methyl}aniline (**A4**, Yield: 65%)



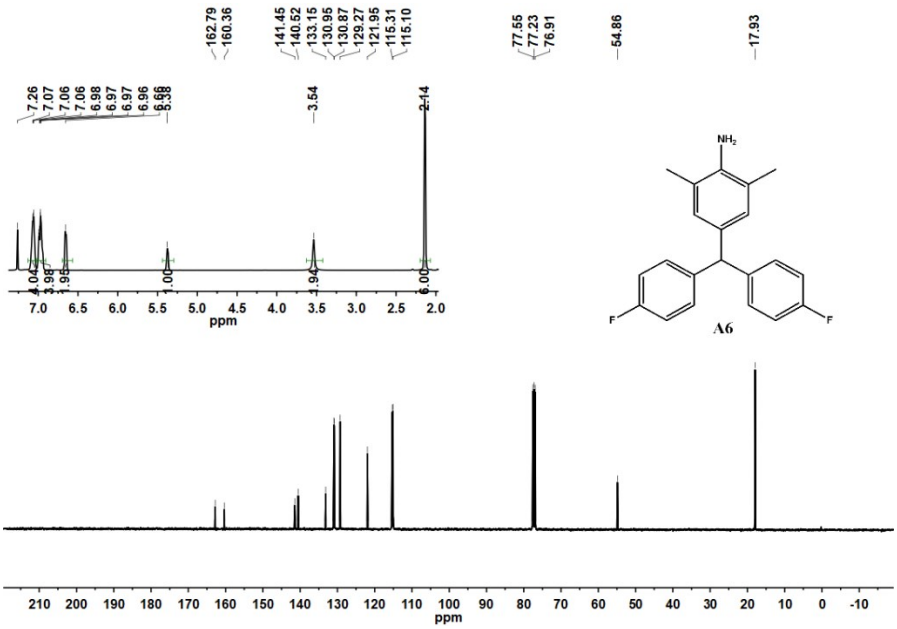
Compound **A4**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.96−6.91 (m, 17H), 6.13 (s, 1H), 5.37 (s, 1H, CH(*p*-FPh)$_2$), 5.26 (s, 1H, CH(*p*-FPh)$_2$), 3.87 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.23, 162.90, 160.79, 160.46, 139.54, 139.44, 137.41, 133.93, 130.89, 130.81, 130.72, 130.65, 129.96, 129.74, 128.42, 120.64, 115.91, 115.70, 115.44, 115.23, 54.40, 51.37.

2-Fluoro-4,6-bis{di(*p*-fluorophenyl)methyl}aniline (**A5**, Yield: 80%)



Compound **A5**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.97−6.91 (m, 16H), 6.65 (d, J = 6 Hz, 1H), 6.03 (s, 1H, aryl-F), 5.40 (s, 1H, CH(*p*-FPh)$_2$), 5.26 (s, 1H, CH(*p*-FPh)$_2$), 3.46 (s, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.20, 162.90, 160.76, 160.46, 153.49, 151.11, 131.05, 130.87, 130.79, 130.74, 130.66, 115.87, 115.65, 115.42, 115.21, 114.51, 114.31, 54.53, 50.80, 50.77.

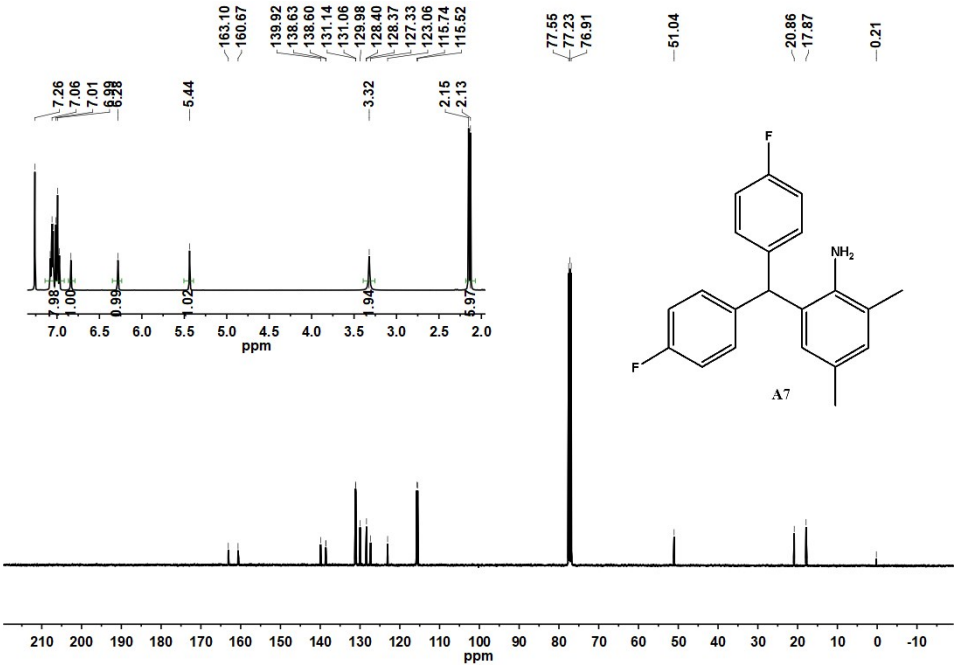
2,6-Dimethyl-4-{di(*p*-fluorophenyl)methyl}aniline (**A6**, Yield:69%)



Compound **A6**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.07−6.95 (m, 8H), 6.66 (s, 2H, aryl-

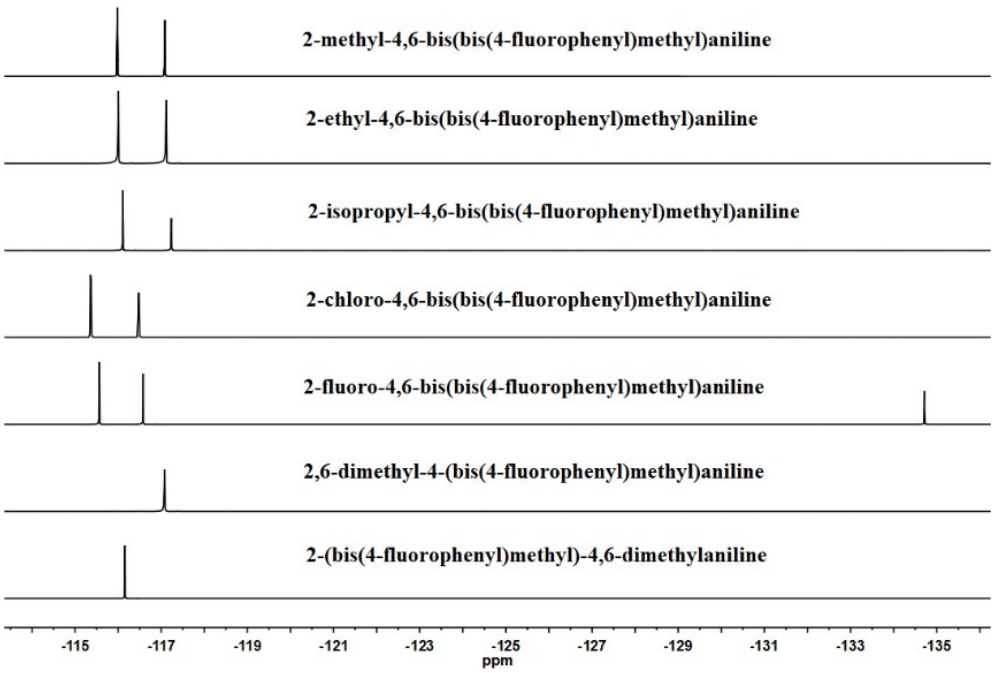
H), 5.38 (s, 1H, CH(*p*-FPh)$_2$), 3.54 (s, 2H, NH_2), 2.14 (s, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 162.79, 160.36, 141.45, 140.52, 133.15, 130.95, 130.87, 129.27, 121.95, 115.31, 115.10, 54.86, 17.93.

2,4-Dimethyl-6-{di(*p*-fluorophenyl)methyl}aniline (**A7**, Yield:65%)



Compound **A7**. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.08−6.97 (m, 8H), 6.84 (s, 1H, aryl-H), 6.28 (s, 1H, aryl-H), 5.44 (s, 1H, CH(*p*-FPh)$_2$), 3.32 (s, 2H, NH_2), 2.15 (s, 3H, CH_3), 2.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.10, 160.67, 139.92, 138.63, 138.60, 131.14, 131.06, 129.98, 128.40, 128.37, 127.33, 123.06, 115.74, 115.52, 51.04, 20.86, 17.87.

(b) ^{19}F NMR spectroscopic data for **A1** − **A7**



A1: ^{19}F NMR (470 MHz, $CDCl_3$): δ –115.98, –117.08.

A2: ^{19}F NMR (470 MHz, $CDCl_3$): δ –116.01, –117.12.
A3: ^{19}F NMR (470 MHz, $CDCl_3$): δ –116.11, –117.23.
A4: ^{19}F NMR (470 MHz, $CDCl_3$): δ –115.36, –115.37, –116.47, –116.48.
A5: ^{19}F NMR (470 MHz, $CDCl_3$): δ –115.56, –115.58, –134.72.
A6: ^{19}F NMR (470 MHz, $CDCl_3$): δ –117.08.
A7: ^{19}F NMR (470 MHz, $CDCl_3$): δ –116.16.

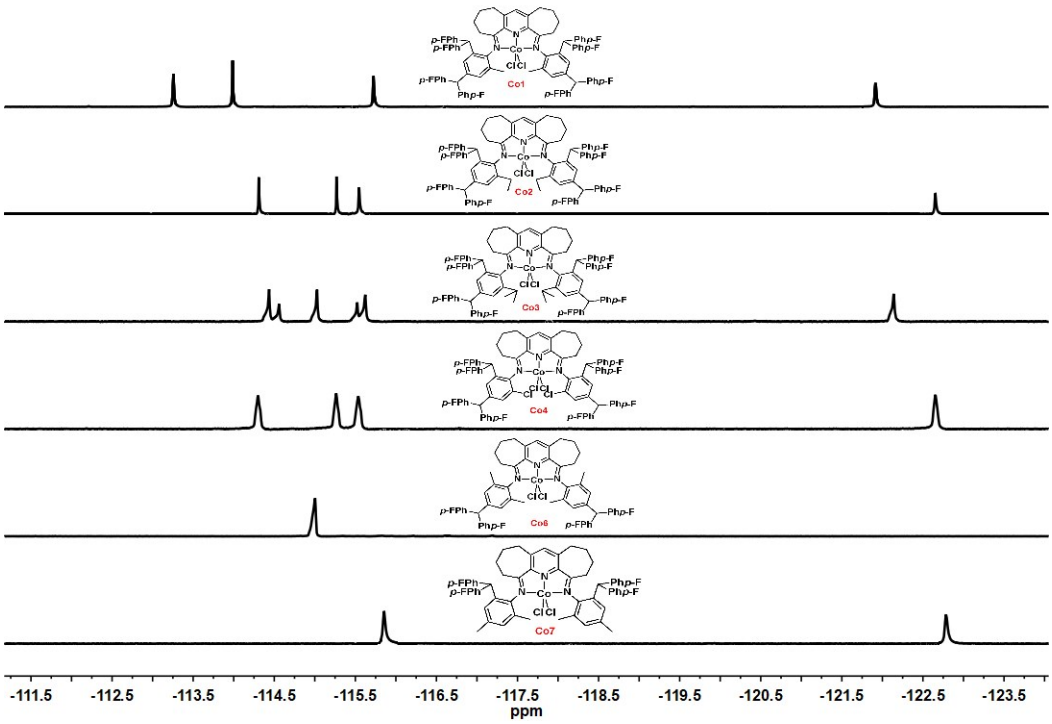


Figure S1. ^{19}F NMR spectra of **Co1**, **Co2**, **Co3**, **Co4**, **Co6** and **Co7**; recorded in $CDCl_3$ at ambient temperature.

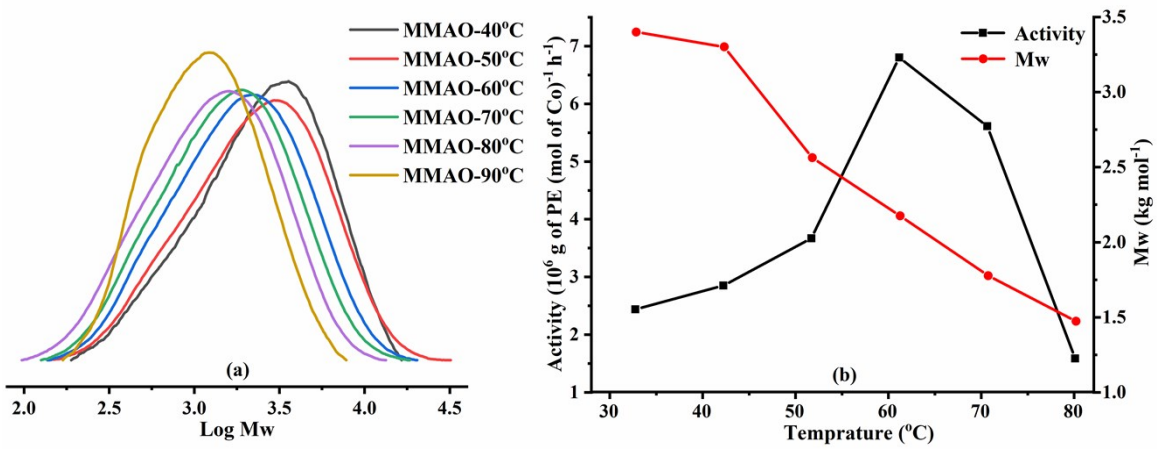


Figure S2. (a) GPC traces for the polymers obtained using **Co5**/MMAO at various temperatures; (b) Plot of activity and M_w versus temperature for the catalyst and polyethylene, respectively (entries 1 − 6, Table 4).

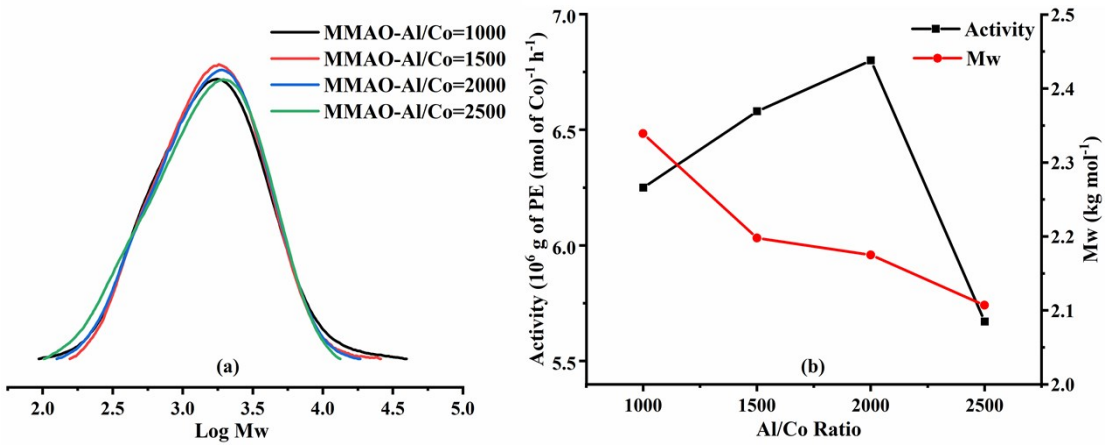


Figure S3. (a) GPC traces for the polymers obtained using **Co5**/MMAO at various Al:Co molar ratios; (b) Plot of activity and M_w versus Al:Co molar ratio for the catalyst and polyethylene, respectively (entries 4, 7 − 10, Table 4).

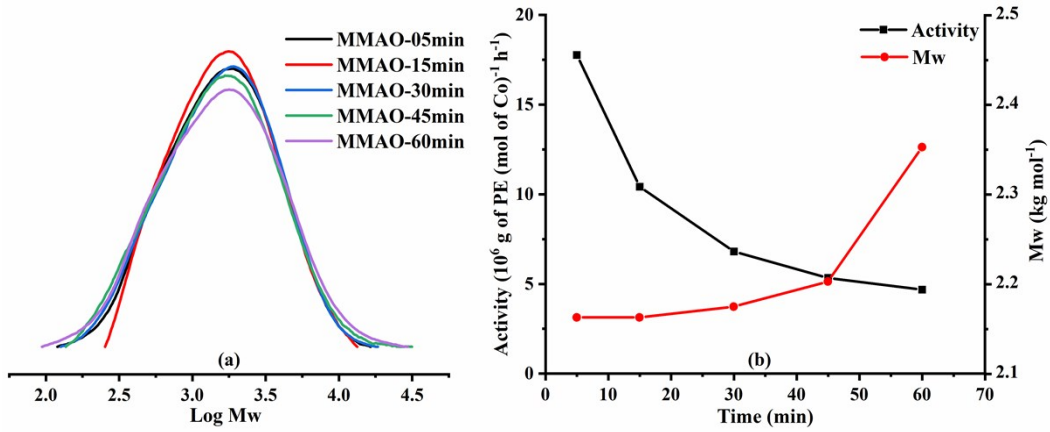


Figure S4. (a) GPC traces for the polymers obtained using **Co5**/MMAO at various times; (b) Plot of activity and M_w versus time for the catalyst and polyethylene, respectively (entries 4, 11 − 14, Table 4).

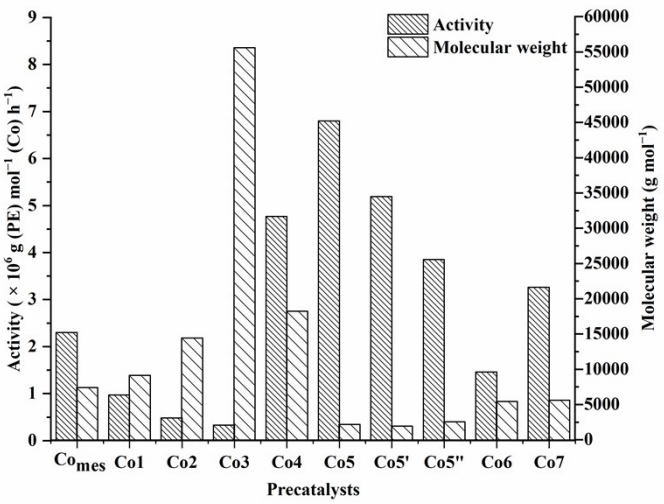


Figure S5. Comparison of the catalytic activities and molecular weight of the polyethylenes generated using **Co1** – **Co7** and **Co**$_{mes}$; MMAO used as co-catalyst in each case.

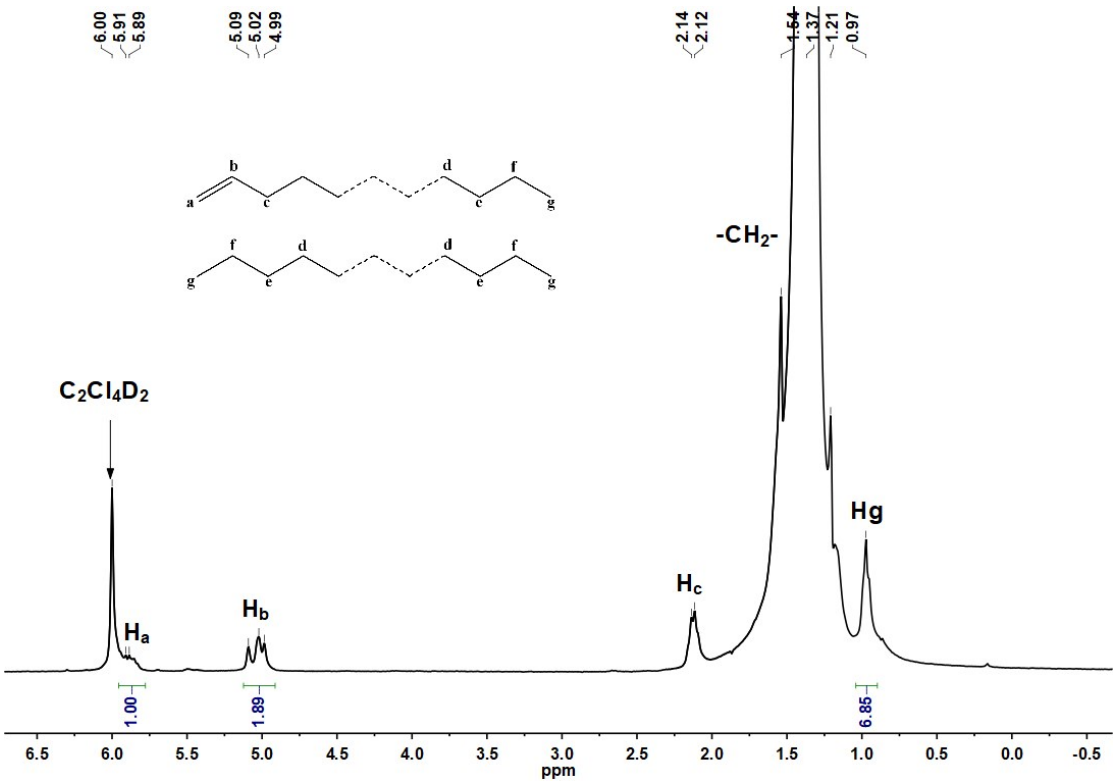


Figure S6. ^{1}H NMR spectrum of the polyethylene obtained using **Co4**/MAO at 60 °C; recorded at 100 °C in 1,1,2,2-tetrachloroethane-d_2 (entry 5, Table 3).

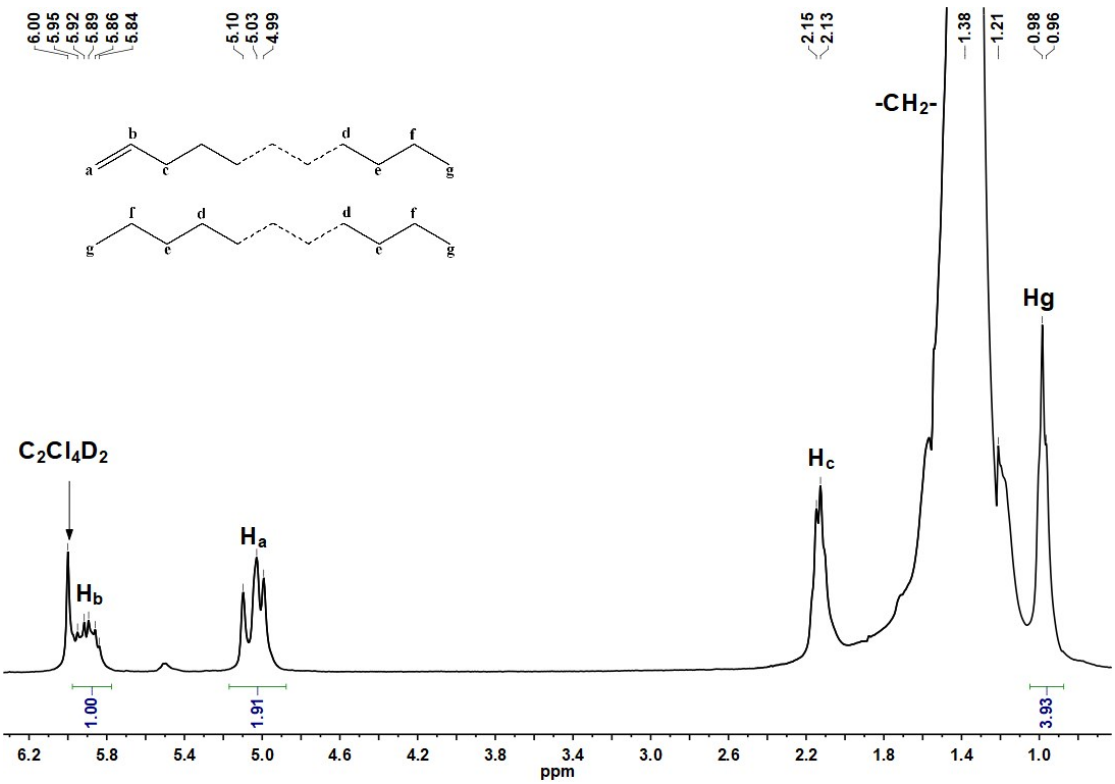


Figure S7. ^{1}H NMR spectrum of the polyethylene obtained using **Co5'**/MAO at 60 °C; recorded at 100 °C in 1,1,2,2-tetrachloroethane-d_2 (entry 7, Table 3).

Table S1. Crystal data and structure refinements for **Co4, Co5, Co5'** and **Co5''**

	Co4	**Co5**	**Co5'**	**Co5''**
CCDC Number	1998230	1998231	1998232	1998233
Empirical formula	$2(C_{79}H_{57}C_{l4}CoF_8N_3)$	$2(C_{79}H_{57}Cl_2CoF_{10}N_3)$ $\cdot C_4H_{10}O$	$C_{81}H_{60}ClCoF_{10}N_3O_2$	$C_{79}H_{65}Cl_2CoF_2N_3\cdot$ $C_4H_8O\cdot CH_2Cl_2$
Formula weight	2802.01	2810.32	1391.70	1381.20
Temperature/K	169.99(10)	169.99(12)	169.99(11)	169.99(12)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1
a/Å	16.65280(10)	15.6079(2)	18.5816(3)	10.4294(4)
b/Å	25.4947(2)	28.3387(4)	27.4361(2)	18.2182(7)
c/Å	35.8638(2)	33.8316(5)	16.5226(3)	20.3353(7)
α/°	90	90	90	65.813(4)
β/°	97.8590(10)	92.5730(10)	116.265(2)	76.760(4)
γ/°	90	90	90	81.879(3)
Volume/$Å^3$	15083.25(17)	14948.9(4)	7553.7(2)	3426.0(2)
Z	4	4	4	2
ρ_{calc}g/cm^3	1.234	1.249	1.224	1.339
μ/mm^{-1}	3.607	3.043	2.704	3.840
F(000)	5752.0	5792.0	2868.0	1442.0
Crystal size/mm^3	0.225 × 0.145 × 0.078	0.38 × 0.27 × 0.15	0.519 × 0.256 × 0.089	0.25 × 0.15 × 0.05
2Θ range for data collection/°	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
Index ranges	4.974 to 151.166	5.23 to 151.272	5.304 to 151.278	4.852 to 151.946
Reflections collected	$-20 \le h \le 20$, $-31 \le k \le 27$, $-44 \le l \le 44$	$-19 \le h \le 19$, $-35 \le k \le 34$, $-36 \le l \le 42$	$-19 \le h \le 21$, $-34 \le k \le 34$, $-20 \le l \le 20$	$-12 \le h \le 13$, $-22 \le k \le 22$, $-25 \le l \le 24$
Independent reflections	108973	109151	48495	47515
Data/restraints/parameters	30074 [R_{int} = 0.0477, R_{sigma} = 0.0424]	29571 [R_{int} = 0.0524, R_{sigma} = 0.0422]	14476 [R_{int} = 0.0501, R_{sigma} = 0.0349]	13523 [R_{int} = 0.0813, R_{sigma} = 0.0759]
Goodness-of-fit on F^2	30074/169/1748	29571/0/1758	14476/867/1173	13523/0/858
Final R indexes [I>=2σ (I)]	1.016	1.031	1.049	1.238
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1476	R_1 = 0.0919, wR_2 = 0.2534	R_1 = 0.1101, wR_2 = 0.2728	R_1 = 0.1134, wR_2 = 0.3074
Largest diff. peak/hole / e $Å^{-3}$	R_1 = 0.0747, wR_2 = 0.1607	R_1 = 0.1127, wR_2 = 0.2680	R_1 = 0.1508, wR_2 = 0.3026	R_1 = 0.1370, wR_2 = 0.3290
Flack parameter	0.41/-0.34	1.22/-0.72	0.55/-0.39	2.16/-1.50

References

1 (a) S. Meiries, K. Speck, B. D. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2013, **32**, 330–339; (b) P. Shaw, A. R. Kennedy and D. J. Nelson, *Dalton Trans.*, 2016, **45**, 11772–11780.