Supplementary Information for

Bis(imino)pyridines fused with 6- and 7-membered carbocylic rings as

N,N,N-scaffolds for cobalt ethylene polymerization catalysts

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1. Experimental Section

1.1 General considerations

All manipulations involving air- and moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was heated to reflux over sodium and distilled under nitrogen prior to use. The NMR spectra were recorded with a Bruker DMX 500 MHz instrument at ambient temperature using TMS as internal standard. The melting points of the polyethylenes were measured from the fourth scanning run on a PerkinElmer TA-Q2000 differential scanning calorimeter under a nitrogen atmosphere. A sample of about 5.0 mg was heated to 160 °C at a rate of 20 °C min⁻¹, maintained for 2 min at 160 °C to remove the thermal history and then cooled to -40 °C at a rate of 20 °C min⁻¹. The ¹³C NMR spectra of the polyethylenes were recorded with a Bruker DMX 300 MHz instrument at 135 °C in 1,1,2,2-tetrachloroethane- d_2 with TMS as internal standard.

1.2 Synthesis and characterization of 6,7,8,9,10-pentaahydrocyclohepta[b]-quinoline (1)

Based on previous work,¹ (2-aminophenyl)methanol (123.0 g, 1.0 mol), cycloheptanol (136.8 g, 1.2 mol), *t*-BuOK (134.4 g, 1.2 mol) and [*fac*-PNN]RuH(PPh₃)(CO) (380 mg, 0.5 mmol, 0.05 mol%) in a mixture of THF (100 mL) and toluene (500 mL) were stirred and heated to reflux under an atmosphere of nitrogen. After stirring for 72 h at this temperature, the resultant solution was cooled to room temperature and water (300 mL) added. The mixture was stirred for 0.5 h at room temperature and then extracted with ethyl acetate (2 × 400 mL). The combined organic layers were washed with water (2 × 100 mL) and dried over anhydrous MgSO₄. Evaporation of the solvent gave a red oil (180.0 g) which was dissolved in dichloromethane (100 mL) and hexane (300 mL) introduced. After cooling the mixture to 0 °C the resulting precipitate was filtered affording **1** as a pale yellow solid (148.0 g, 74%). Mp: 94 – 95 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 3.24 – 3.18 (m, 2H), 2.96 – 2.92 (m, 2H), 1.91 – 1.87 (m, 2H), 1.82 – 1.73 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 164.85, 146.44, 136.67, 134.73, 128.62, 127.53, 127.04, 126.98, 125.90, 40.24, 35.62, 32.41, 29.03, 27.19. FT-IR (cm⁻¹): 2918 (m), 2849 (w), 1604 (w), 1562 (w), 1491 (m), 1451 (w), 1417 (w), 1340 (w), 1308 (w), 1258 (w), 1194 (w), 1149 (w), 1125 (w), 1095 (w), 1015 (w), 957 (m), 926 (m), 852 (w), 838 (w), 787 (s) 747 (s), 704 (w). Anal. Calcd for C₁₄H₁₅N (197.28): C, 85.24; H, 7.66; N, 7.10. Found: C, 84.92; H, 7.63; N, 7.09%.

1.3 Synthesis and characterization of 1,2,3,4,6,7,8,9,10-nonahydrocyclohepta[b]-quinoline (2)

Based on the procedure described by Vierhapper and Eliel,² a stainless steel 1 L autoclave, equipped with a magnetic stir bar, was charged with **1** (145.0 g, 0.73 mol), 10% Pd/C (14.5 g) and 2,2,2-trifluoroacetic acid (500 mL). The autoclave was purged using three cycles of pressurization/venting with hydrogen (10 bar) and then pressurized and maintained at 40 bar hydrogen. The contents of the autoclave was stirred and heated to 80 °C for 24 h. After cooling to room temperature, the pressure was slowly released and the reaction mixture filtered through a plug of silica gel. The mixture was made basic with a 10% aqueous NaOH solution and then extracted with CH₂Cl₂ (3×400 mL). The combined organic layers were washed with water (2×100 mL) and dried over anhydrous MgSO₄. Evaporation of the solvent gave **2** as a white solid (118.0 g, 80%). Mp: 45 - 46 °C.¹H NMR (500 MHz, CDCl₃) δ 7.08 (s, 1H), 3.01 – 2.95 (m, 2H), 2.87 (t, J = 6.4 Hz, 2H), 2.69 (q, J = 6.9, 6.4 Hz, 4H), 1.85 (dq, J = 11.5, 5.9 Hz, 4H), 1.77 (dt, J = 11.8, 6.3 Hz, 2H), 1.66 (ddt, J = 22.1, 10.7, 5.4 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 159.83, 152.84, 137.86, 135.38, 129.47, 77.33, 77.31, 77.08, 76.82, 38.38, 34.82, 32.52, 31.47, 28.20, 28.18, 26.70, 23.20, 22.77. FT-IR (cm⁻¹): 2914 (s), 2846 (m), 1715 (w), 1598 (w), 1568 (w), 1490 (w), 1453 (s), 1355 (w), 1253 (w), 1194 (w), 1162 (w), 1128 (w), 1072 (w), 1015 (w), 957 (m), 868 (w), 825 (w), 790 (w), 742 (w), 716 (w). Anal. Calcd for C₁₄H₁₉N (201.31): C, 83.53; H, 9.51; N, 6.90. Found: C, 83.52; H, 9.63; N, 6.89%.

1.4 Synthesis and characterization of 1,2,3,7,8,9,10-heptahydrocyclohepta[b]-quinoline-4,6-dione (3)³

A mixture of **2** (60.0 g, 0.30 mol) and freshly distilled benzaldehyde (318.0 g. 3.00 mol, 10 eq) in acetic anhydride (240.0 g, 2.40 mol, 8 eq) was stirred and heated to reflux under an atmosphere of nitrogen for 72 h (monitored by TLC). Benzaldehyde, acetic anhydride and acetic acid were then removed by distillation under reduced pressure to give a dark oil and this residue was directly used in the next step. A solution of the residue (150 g) in CH₂Cl₂ (1000 mL) was treated with a mixture of ozone and oxygen at - 60 °C until the reaction was complete (monitored by TLC analysis). The solution was then purged by bubbling nitrogen to remove any residual ozone. Me₂S (20 mL) was added and the mixture stirred for 0.5 h at -35 °C and then at room temperature overnight. The solution was washed with water (100 mL), 5% aqueous NaOH (100 mL), dried over anhydrous Na₂SO₄ and concentrated to give a dark red oil, which was purified by chromatography on silica gel with EtOAc/MeOH = 100:1 as eluent. The title compound **3** was obtained as a light yellow powder (10.5 g, 15%). Mp: 95 - 96 °C ¹H NMR (500 MHz, CDCl₃) δ 7.50 (s, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.89 (t, *J* = 6.1 Hz, 2H), 2.78 (t, *J* = 6.1 Hz, 2H), 2.74 (m, t, *J* = 6.1 Hz, 2H), 2.17 (p, *J* = 6.4 Hz, 2H), 1.93-1.82 (m, 4H).¹³C NMR (125 MHz, CDCl₃) δ 204.50, 195.61, 155.57, 147.04, 142.49, 138.81, 138.69, 40.48, 39.71, 30.96, 29.11, 25.17, 22.49, 21.67. FT-IR (cm⁻¹): 2956 (w), 2918 (m), 2859 (w), 1692 (s,v_{C=O}), 1586 (m), 1541 (w), 1447 (m), 1405 (w), 1355 (w), 1312 (w), 1259 (w), 1204 (m), 1152 (m), 1129 (m), 1051 (w), 1002 (w), 932 (m), 832 (w), 806 (w), 776 (w), 708 (w). Anal. Calcd for C₁₄H₁₅NO₂ (228.29): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.32; H, 6.63; N, 6.09%.

1.5 Synthesis and characterization of 4,6-di(arylimino)-1,2,3,7,8,9,10-heptahydrocyclohepta[b]quinoline-cobalt(II) chloride, Co1 - Co5

(a) Aryl = 2,6-dimethylphenyl (Co1). A suspension of 3 (0.23 g, 1.0 mmol), 2,6-dimethylaniline (0.49 g, 4.0 mmol) and $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mol) in glacial acetic acid (15 mL) was stirred and heated to reflux for 12 h. On cooling to room temperature, an excess of diethyl ether was added to induce precipitation. The precipitate was collected by filtration and then dissolved in methanol (10 ml) and the solution concentrated on the rotary evaporator. The product was then re-precipitated with diethyl ether and the resulting solid collected by filtration and dried under reduced pressure to give Co1 as a brown powder (0.45 g,

79%). ¹H NMR (400 MHz, CDCl₃) δ 36.17 (1H, Py-*H*_p), 28.19 (2H, Ar_{Hep}-*H*_m), 24.06 (2H, Ar_{Hex}-*H*_m), 14.15 (2H, N=C_{Hep}-C*H*₂), 11.79 (2H, N=C_{Hex}-C*H*₂), 7.62 (4H, C*H*_{2Hep} and Hex), 2.73 (2H, C*H*_{2Hep}), 2.45 (2H, C*H*_{2Hex}), 1.20 (2H, C*H*_{2Hep}), -11.28 (1H, Ar_{Hep}-*H*_p), -12.01 (1H, Ar_{Hex}-*H*_p), -25.31 (6H, Ar-C*H*_{3Hex}), -28.16 (6H, Ar-C*H*_{3Hex}). FT-IR (cm⁻¹): 2927 (w), 2863 (w), 1618 (m, *v*_{C=N}), 1586 (w), 1561 (w), 1467 (s), 1377 (w), 1257 (w), 1233 (w), 1202 (w), 1167 (w), 1093 (w), 1034 (w), 948 (w), 924 (w), 835 (w), 772 (s), 689 (w). Anal. Calcd for C₃₀H₃₃Cl₂N₃Co (565.14): C, 63.72, H, 5.88, N, 7.43. Found: C, 63.64, H, 5.92, N, 7.42%.

(b) Aryl = 2,6-diethylphenyl (**Co2**). By using the same procedure as that described for the synthesis of **Co1**, **Co2** was obtained as a brown powder (0.48 g, 77%). ¹H NMR (400 MHz, CDCl₃) δ 42.45 (1H, Py- H_p), 32.77 (2H, Ar_{Hep}- H_m), 29.30 (2H, Ar_{Hex}- H_m), 15.92 (2H, N=C_{Hep}-CH₂), 13.36 (2H, N=C_{Hex}-CH₂), 9.27 (2H, CH_{2Hep}), 8.21 (2H, CH_{2Hex}), 2.60 (2H, CH_{2Hep}), 2.27 (2H, CH_{2Hex}), 1.27 (2H, CH_{2Hep}), -9.93 (1H, Ar_{Hep}- H_p), -10.99 (1H, Ar_{Hex}- H_p), -18.90 (6H, CH₂- Me_{Hep}), -19.10 (6H, CH₂- Me_{Hex}), -34.93 (4H, Ar-CH_{2Hep}), -39.45 (2H, Ar-CH_{2Hex}), -46.91 (2H, Ar-CH_{2Hex}). FT-IR (cm⁻¹): 2956 (w), 2861 (w), 1614 (m, $v_{C=N}$), 1583 (w), 1465(w), 1358 (s), 1325 (w), 1242 (w), 1186 (w), 1102 (w), 1052 (w), 945 (w), 803 (w), 771 (s), 695 (w). Anal. Calcd for C₃₄H₄₁Cl₂N₃Co (621.56): C, 65.70, H, 6.65, N, 6.76. Found: C, 65.64, H, 6.76, N, 6.63%.

(c) Aryl = 2,6-diisopropylphenyl (**Co3**). By using the same procedure as that described for the synthesis of **Co1**, **Co3** was obtained as a brown powder (0.42 g, 62%). ¹H NMR (400 MHz, CDCl₃) δ 52.32 (1H, Py- H_p), 38.83 (2H, Ar_{Hep}- H_m), 36.47 (2H, Ar_{Hex}- H_m), 18.71 (2H, N=C_{Hep}-CH₂), 15.53 (2H, N=C_{Hex}-CH₂), 11.26 (2H, CH_{2Hep}), 10.06 (2H, CH_{2Hex}), 5.38 (2H, CH_{2Hep}), 3.57 (2H, CH_{2Hex}), 1.20 (2H, CH_{2Hep}), -8.24 (1H, Ar_{Hep}- H_p), -9.11 (1H, Ar_{Hex}- H_p), -16.70 (12H, *i*Pr- Me_{Hep}), -17.52 (6H, *i*Pr- Me_{Hex}), -21.68 (6H, *i*Pr- Me_{Hex}), -79.74 (2H, *i*Pr-CH_{Hep}), -86.58 (2H, *i*Pr-CH_{Hex}). FT-IR (cm⁻¹): 2961 (w), 2866 (w), 1620 (m, $v_{C=N}$), 1584 (w), 1470 (w), 1439 (s), 1360 (w), 1327 (w), 1251 (w), 1185 (w), 1104 (w), 1059 (w), 965 (w), 937 (w) 803 (w), 777 (s), 753 (w). Anal. Calcd for C₃₈H₄₉Cl₂N₃Co (676.26): C, 67.35, H, 7.29, N, 6.20. Found: C, 67.24, H, 7.36, N, 6.13%.

(d) Aryl = mesityl (**Co4**). By using the same procedure as that described for the synthesis of **Co1**, **Co4** was obtained as a brown powder (0.47 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ 35.48 (1H, Py-*H*_p), 27.98 (2H, Ar_{Hep}-*H*_m), 24.03 (2H, Ar_{Hex}-*H*_m), 19.43 (2H, N=C_{Hep}-C*H*₂), 15.23 (2H, N=C_{Hex}-C*H*₂), 13.77 (2H, C*H*_{2Hep}), 2.30 (6H, C*H*_{2Hep} and Hex), 1.62 (2H, C*H*_{2Hep}), -4.93 (3H, Ar-C*H*_{3Hep}), -16.87 (3H, Ar-C*H*_{3Hex}), -24.77 (6H, Ar-C*H*_{3Hep}), -27.54 (6H, Ar-C*H*_{3Hex}). FT-IR (cm⁻¹): 3011 (w), 2917 (w), 2858 (w), 1624 (m, $v_{C=N}$), 1537 (w), 1481 (m), 1430 (s), 1371 (w), 1313 (w), 1288 (w), 1223 (w), 1162 (w), 1038 (w), 1014 (w), 965 (w), 857 (m), 738 (m), 714 (s). Anal. Calcd for C₃₂H₃₇Cl₂N₃Co (593.50): C, 64.76, H, 6.28, N, 7.08. Found: C, 64.64, H, 6.36, N, 7.13%.

(e) Aryl = 2,6-diethyl-4-methylphenyl (**Co5**). By using the same procedure as that described for the synthesis of **Co1**, **Co5** was obtained as a brown powder (0.45 g, 77%).¹H NMR (400 MHz, CDCl₃) δ 43.13 (1H, Py- H_p), 33.08 (2H, Ar_{Hep}- H_m), 29.71 (2H, Ar_{Hex}- H_m), 16.05 (2H, N=C_{Hep}-CH₂), 13.49 (2H, N=C_{Hex}-CH₂), 9.43 (2H, CH_{2Hep}), 8.35 (2H, CH_{2Hex}), 2.86 (2H, CH_{2Hep}), 2.39 (2H, CH_{2Hex}), 1.34 (2H, CH_{2Hep}), -4.07 (3H, Ar-CH_{3Hep}), -15.99 (3H, Ar-CH_{3Hex}), -19.06 (6H, CH₂- Me_{Hep}) -19.27 (6H, CH₂- Me_{Hex}), -35.02 (4H, Ar-CH_{2Hep}), -39.68 (2H, Ar-CH_{2Hex}), -47.18 (2H, Ar-CH_{2Hex}), FT-IR (cm⁻¹): 3011 (w), 2917 (w), 2857 (w), 1620 (m, $v_{C=N}$), 1537 (w), 1430 (s), 1370 (w), 1313 (w), 1288 (w), 1223 (w), 1162 (w), 1038 (w), 1014 (w), 965 (w), 857 (w), 737 (m), 714 (s). Anal. Calcd for C₃₅H₄₃Cl₂N₃Co (649.61): C, 66.56, H, 6.98, N, 6.47. Found: C, 66.44, H, 7.02, N, 6.33%.



Figure S1. ¹H NMR spectrum of 6,7,8,9,10-pentahydrocyclohepta[*b*]quinoline (1); recorded in CDCl₃ (500 MHz) at room temperature.



Figure S2. ¹³C NMR spectrum of 6,7,8,9,10-pentahydrocyclohepta[*b*]quinoline (1); recorded in CDCl₃ (500 MHz) at room temperature.



Figure S3. ¹H NMR spectrum of 1,2,3,4,6,7,8,9,10-nonahydrocyclohepta[*b*]quinoline (**2**); recorded in CDCl₃ (500 MHz) at room temperature.



Figure S4. ¹³C NMR spectrum of 1,2,3,4,6,7,8,9,10-nonahydrocyclohepta[*b*]quinoline (**2**); recorded in CDCl₃ (500 MHz) at room temperature.



Figure S5. ¹H NMR spectrum of 1,2,3,7,8,9,10-heptahydrocyclohepta[*b*]quinoline-4,6-dione (**3**); recorded in CDCl₃ (500 MHz) at room temperature.



Figure S6. ¹³C NMR spectrum of 1,2,3,7,8,9,10-heptahydrocyclohepta[*b*]quinoline-4,6-dione (**3**); recorded in CDCl₃ (500 MHz) at room temperature.

3. The ¹H NMR spectra of complexes Co1 – Co5



Figure S7. ¹H NMR spectrum of Co1; recorded in CDCl₃ (400 MHz) at room temperature.



Figure S8. ¹H NMR spectrum of Co2; recorded in CDCl₃ (400 MHz) at room temperature.



Figure S9. ¹H NMR spectrum of Co3; recorded in CDCl₃ (400 MHz) at room temperature.



Figure S10. ¹H NMR spectrum of Co4; recorded in CDCl₃ (400 MHz) at room temperature.



Figure S11. ¹H NMR spectrum of Co5; recorded in CDCl₃ (400 MHz) at room temperature.

4. NMR spectra of selected polyethylenes



Figure S12. ¹³C NMR spectrum of the polyethylene obtained using Co4/MMAO at 40 °C (entry 8, Table 3); recorded in 1,1,2,2-tetrachloroethane- d_2 (δ C 73.7) at 100 °C.



Figure S13. ¹H NMR spectrum of the polyethylene obtained using Co4/MMAO at 40 °C (entry 8, Table 3); recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C.



Figure S14. ¹H NMR spectrum of the polyethylene obtained using Co4/MMAO at an Al/Co ratio = 1000 (entry 1, Table 3); recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C.



Figure S15. ¹H NMR spectrum of the polyethylene obtained using Co4/MMAO at an Al/Co ratio = 1500 (entry 3, Table 3); recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C.



Figure S16. ¹H NMR spectrum of the polyethylene obtained using Co4/MMAO at an Al/Co ratio = 2000 (entry 5, Table 3); recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C.



Figure S17. ¹H NMR spectra of the polyethylene obtained with Co4/MMAO at different ratios of Al/Co (entries 1, 3 and 5, Table 3) (recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C).

5. GPC curves of selected polyethylenes



Figure S18. GPC curves for the polyethylenes obtained using Co4/MMAO with various Al/Co ratios (at 30 $^{\circ}$ C and under 10 atm of C₂H₄) (entries 1 – 6, Table 3).



Figure S19. GPC curves of the polyethylenes obtained using Co4/MMAO at different reaction temperatures (10 atm of C_2H_4 , Al/Co ratio = 2000 and 30 minute run time) (entries 4 and 7 – 10, Table 3).



Figure S20. GPC curves of the polyethylenes obtained using Co4/MMAO at different reaction times (10 atm of C_2H_4 , Al/Co ratio = 2000, 40 °C and 30 minute run time).

6. X-Ray crystallographic studies



Figure S21. OLEX2 representations of **Co1**. Thermal ellipsoids are shown at 30% probability while hydrogen atoms have been omitted for clarity.



Figure S22. OLEX2 representations of Co3. Thermal ellipsoids are shown at 30% probability while hydrogen atoms have been omitted for clarity.



Figure S23. OLEX2 representations of Co4. Thermal ellipsoids are shown at 30% probability while hydrogen atoms have been omitted for clarity.

Identification code	Co1	Co3	Co4
Empirical formula	C ₃₀ H ₃₃ Cl ₂ N ₃ Co	C ₃₈ H ₄₉ Cl ₂ N ₃ Co	C ₃₂ H ₃₇ Cl ₂ N ₃ Co
Formula weight	565.46	677.67	593.47
Temperature/K	173.15	173.15	173.15
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Fdd2	$P2_1/n$	C2/c
a/Å	13.273(3)	10.061(2)	24.045(5)
b/Å	46.113(9)	24.985(5)	8.9623(18)
c/Å	9.1517(18)	14.220(3)	13.812(3)
α/°	90	90	90
β/°	90	95.30(3)	91.99(3)
$\gamma/^{\circ}$	90	90	90
Volume/Å ³	5601.4(19)	3559.3(12)	2974.7(11)
Z	8	4	4
$\rho_{calc}g/cm^3$	1.3433	1.2646	1.325
µ/mm ⁻¹	0.827	0.662	0.782
F(000)	2373.8	1439.0	1244.0
Crystal size/mm ³	$0.51 \times 0.31 \times 0.02$	$0.891\times 0.431\times 0.091$	$0.161\times0.154\times0.047$
Radiation	Mo Kα (λ = 0.71073) Mo K α (λ = 0.71073)	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/°	5.48 to 54.82	3.3 to 54.96	3.39 to 50.394
	$-17 \le h \le 17$,	$-13 \le h \le 13$,	$-28 \le h \le 28,$
Index ranges	$-59 \le k \le 59$,	$-32 \le k \le 32,$	$-10 \le k \le 10$,
	$-11 \le l \le 11$	$-18 \le l \le 18$	$-16 \le l \le 16$
Reflections collected	17831	38806	16643
Independent reflections	3189 [R_{int} = 0.0755,	$8134 [R_{int} = 0.0410,$	2666 [R_{int} = 0.0783, R_{sigma} =
	$R_{sigma} = 0.0428$]	$R_{sigma} = 0.0285$]	0.0414]
Data/restraints/parameters	3189/172/225	8134/0/405	2666/121/208
Goodness-of-fit on F ²	1.050	1.036	1.191
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0598,$	$R_1 = 0.0602,$	$R_1 = 0.0838,$

Table S1 Crystal data and structure refinement for Co1, Co3 and Co4

	$wR_2 = 0.1418$	$wR_2 = 0.1446$	$wR_2 = 0.2098$
Final D indovas [all data]	$R_1 = 0.0628$,	$R_1 = 0.0625$,	$R_1 = 0.0899,$
Final K indexes [all data]	$wR_2 = 0.1442$	$wR_2 = 0.1462$	$wR_2 = 0.2133$
Largest diff. peak/hole / e Å ⁻³	0.44/-0.46	1.62/-0.50	1.03/-0.32

7. Comparison of the polymerization data for (A_{mesityl})CoCl₂/MAO, (B_{mesityl})CoCl₂/MAO, (C_{mesityl})CoCl₂/MAO (D_{mesityl})CoCl₂/MAO and Co4/MAO [(E_{mesityl})CoCl₂/MAO] under comparable conditions



Table S2. Polymerization screening using $[(A_{mesityl})CoCl_2/MAO (re-screened in the Sun lab at 10 atm)]^a$

Run	Al/Co	$T(^{o}C)$	t (min)	Yield of	Activity ^b	$M_{ m w}{}^c$	D^{c}	$T_{\rm m} ({}^{\rm o}{\rm C})^d$
				polymer (g)				
1	1500	30	30	5.6	3.73	3.1	2.3	123.6
2	1500	40	30	6.8	4.53	2.4	2.0	122.1

^a Conditions: 3.0 µmol of cobalt precatalyst; 100 mL toluene, 10 atm C₂H₄.

^b Values in units of 10⁶ g(PE) mol⁻¹ (Co) h⁻¹.

^c Determined by GPC, and $M_{\rm w}$ in kg mol⁻¹.

^d Determined by DSC

Table S3. Polymeriza	tion screening us	sing [(B _{mesityl})	CoCl ₂ /MAO	(re-screened	in the S	Sun lab	at 10	atm)] ^a
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Run	Al/Co	T (°C)	t (min)	Yield of	Yield of	Total	$M_{ m w}{}^c$	Ðc	$T_{\rm m} (^{\rm o}{\rm C})^d$
				oligomer (g)	polymer (g)	activity ^b			
1	1500	30	30	0.584	2.89	2.32	45.6	2.9	126.5
2	1500	40	30	0.438	3.05	2.33	33.3	2.9	126.8

^a Conditions: 3.0 µmol of cobalt precatalyst; 100 mL toluene, 10 atm C₂H₄.

 $^{\rm b}$ Values in units of 10 $^{\rm 6}$ g(PE) mol^{-1} (Co) h^{-1}.

^c Determined by GPC, and $M_{\rm w}$ in kg mol⁻¹.

^d Determined by DSC

Table S4. Polymerization screening using [(C_{mesityl})CoCl₂/MAO]^a

Run	Al/Co	T (°C)	t (min)	Activity ^b	$M_{ m w}{}^c$	D^c	$T_{\rm m} (^{\rm o}{\rm C})^d$
1	1800	30	30	2.82	6.1	2.6	129.2
2	1800	40	30	3.69	4.6	2.1	126.3

^a Conditions: 3.0 µmol of cobalt precatalyst; 100 mL toluene, 10 atm C₂H₄.

^b Values in units of 10⁶ g(PE) mol⁻¹ (Co) h⁻¹.

^{*c*} Determined by GPC, and $M_{\rm w}$ in kg mol⁻¹.

^d Determined by DSC

Run	Al/Co	T (°C)	t (min)	Yield (g)	Activity ^b	$M_{ m w}{}^c$	D^c	T _m
								$(^{\circ}C)^{d}$
1	1500	30	30	4.33	2.89	422.7	2.7	135.0
2	1500	40	30	2.90	1.93	151.2	4.4	135.5

Table S5. Polymerization screening using [(D_{mesityl})CoCl₂/MAO]^a

^a Conditions: 3.0 µmol of cobalt precatalyst; 100 mL toluene, 10 atm C₂H₄.

^b Values in units of 10⁶ g(PE) mol⁻¹ (Co) h⁻¹.

^{*c*} Determined by GPC, and $M_{\rm w}$ in kg mol⁻¹.

^d Determined by DSC

Table S6. Polymerization screening using Co4/MAO [(Emesityl)CoCl₂/MAO]^a

Run	Al/Co	T (°C)	t (min)	Yield (g)	Activity ^b	$M_{ m w}{}^c$	D^c	T _m
								$(^{\circ}C)^{d}$
1	1500	30	30	5.92	3.95	1.63	1.71	121.2
2	1500	40	30	7.55	5.03	1.53	1.62	121.8

^a Conditions: 3.0 µmol of cobalt precatalyst; 100 mL toluene, 10 atm C₂H₄.

^b Values in units of 10⁶ g(PE) mol⁻¹ (Co) h⁻¹.

^{*c*} Determined by GPC, and $M_{\rm w}$ in kg mol⁻¹.

^d Determined by DSC

8. References

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