Supporting information

for

Activity and Thermal Stability of Cobalt(II)-Based Olefin Polymerization Catalysts Adorned with Sterically Hindered Dibenzocycloheptyl Groups

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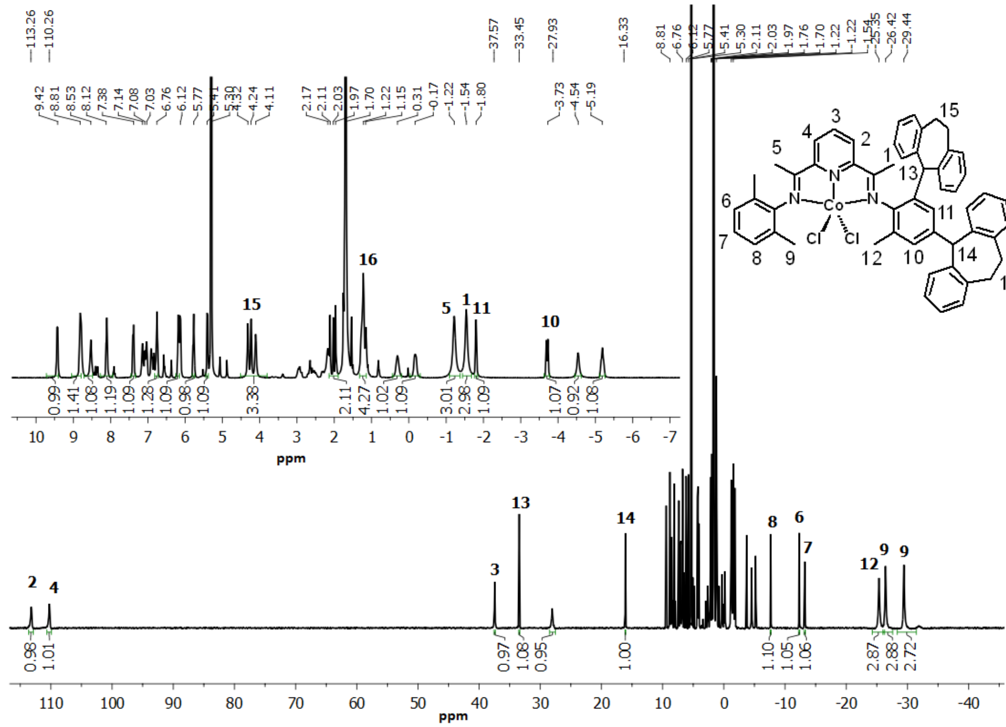

Figure S1 [1]H NMR spectrum of **Co1** in CD_2Cl_2 at room temperature.

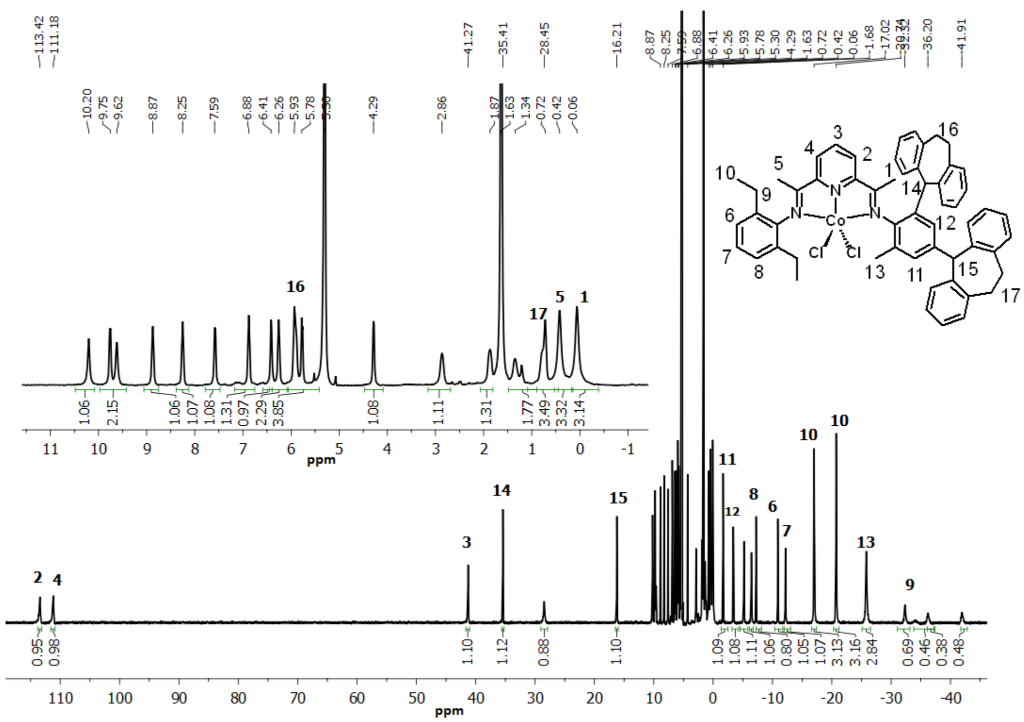

Figure S2 [1]H NMR spectrum of **Co2** in CD_2Cl_2 at room temperature.

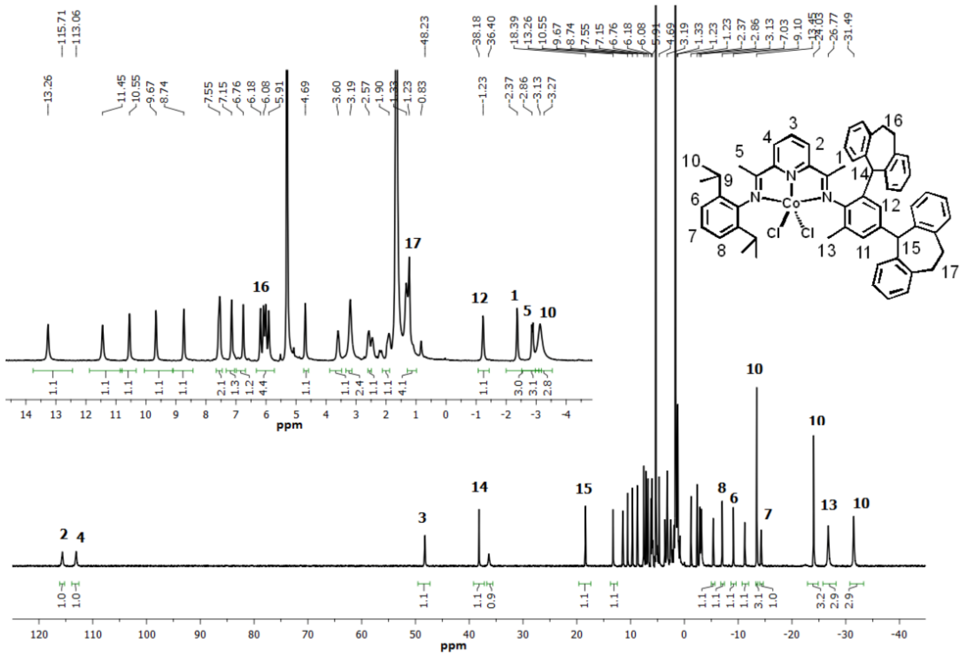

Figure S3 ^{1}H NMR spectrum of **Co3** in CD_2Cl_2 at room temperature.

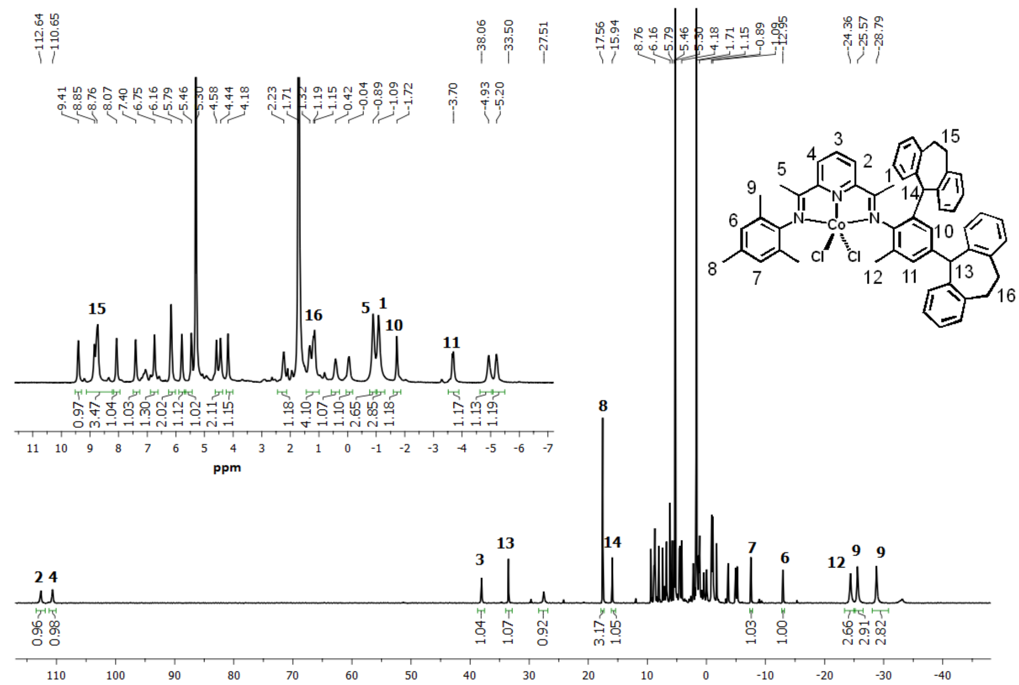

Figure S4 ^{1}H NMR spectrum of **Co4** in CD_2Cl_2 at room temperature.

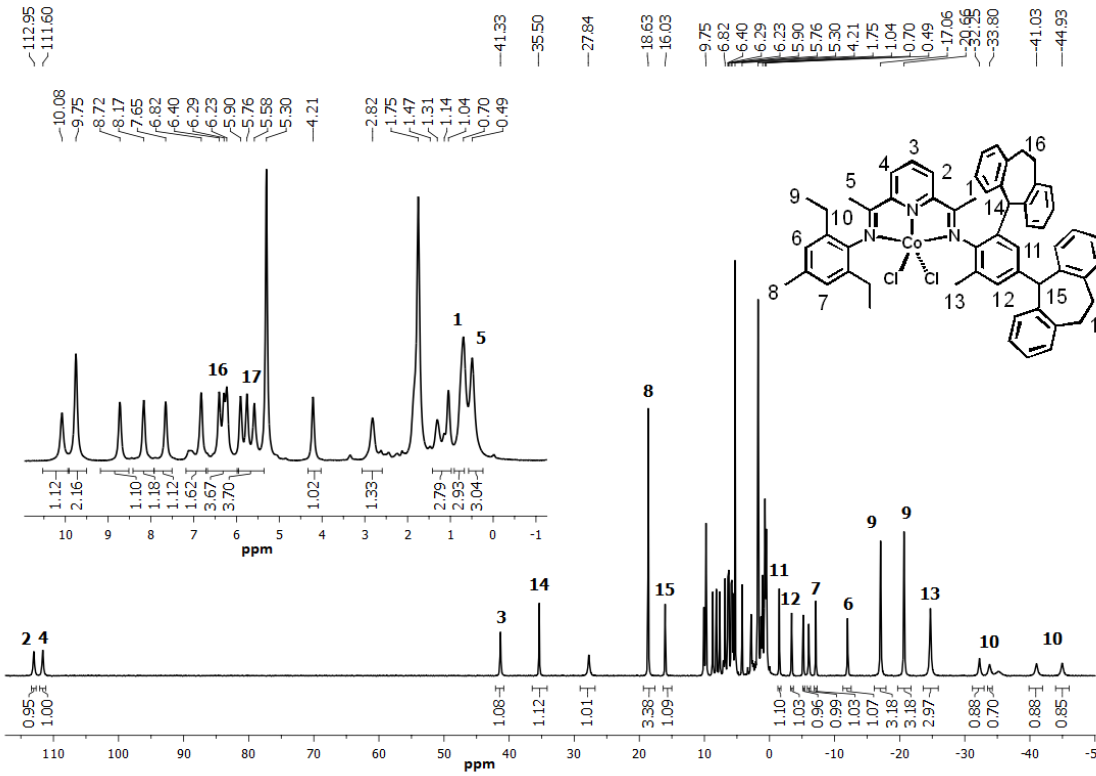

Figure S5 ^{1}H NMR spectrum of **Co5** in CD_2Cl_2 at room temperature.

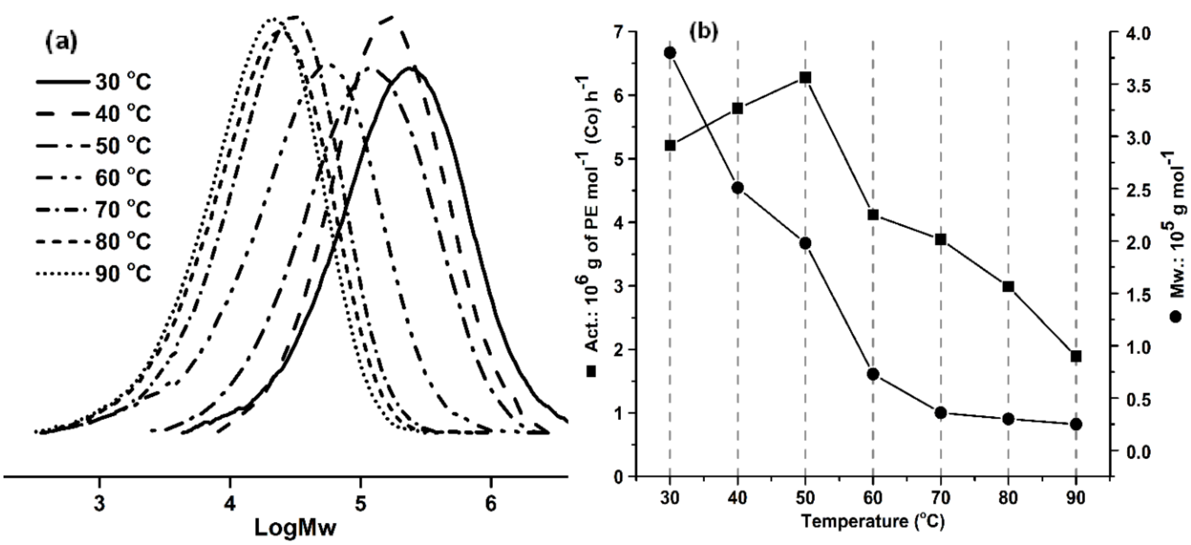

Figure S6 GPC curves of the obtained polyethylene (**a**); activity and M_w as a function of reaction temperature (**b**) for the **Co1**/MMAO system (Table 5, entries 1 – 7).

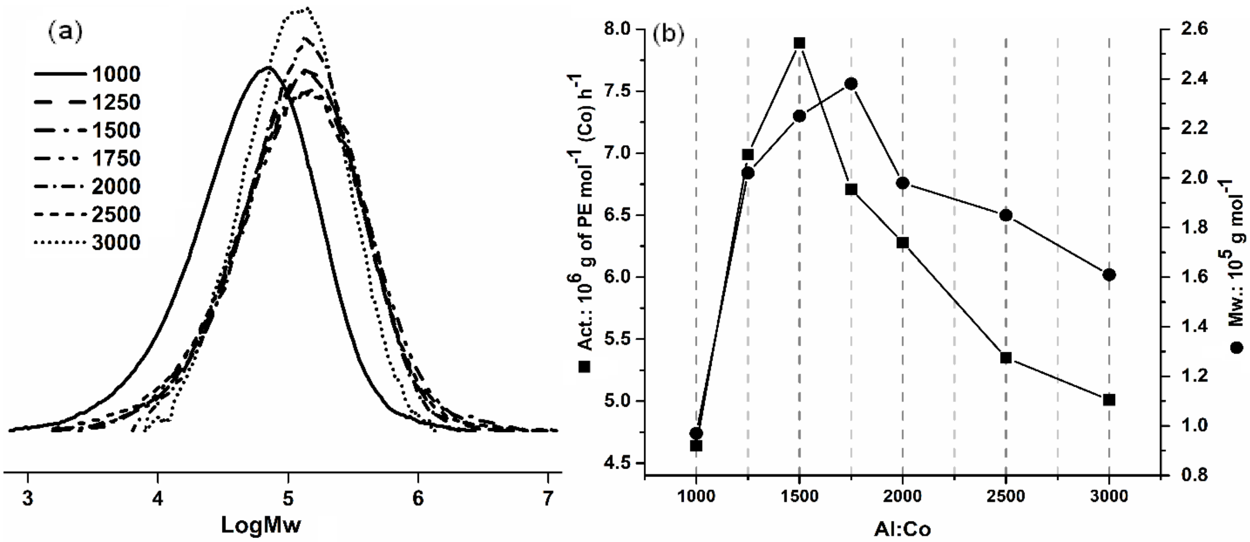

Figure S7 GPC curves of the obtained polyethylene (**a**); activity and M_w as a function of Al/Co ratio (**b**) for the **Co1**/MMAO system (Table 5, entries 3 and 8 – 13).

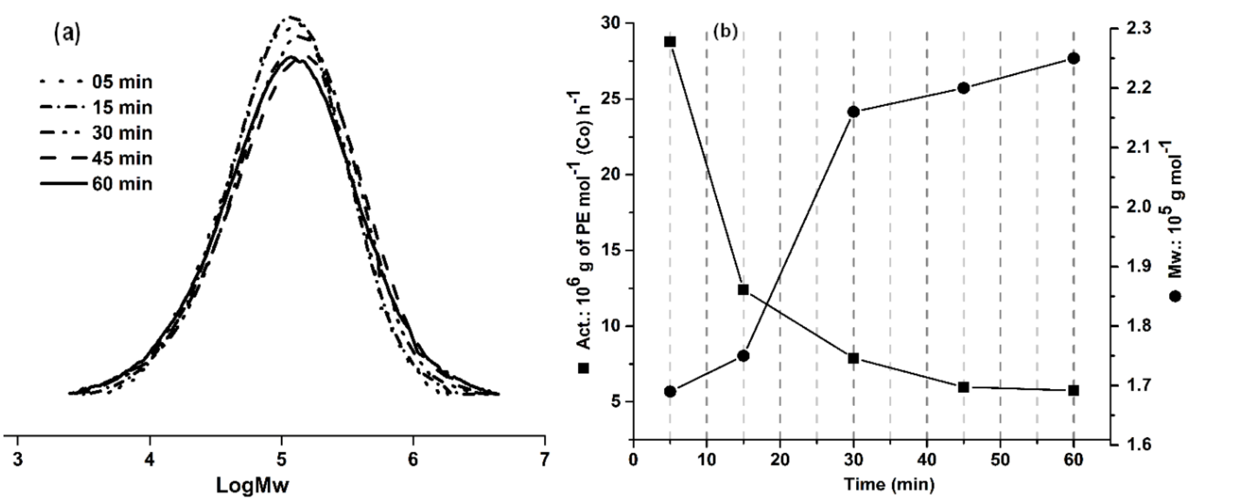

Figure S8 GPC curves of the obtained polyethylene (**a**); activity and M_w as a function of run time (**b**) for the **Co1**/MMAO system (Table 5, entries 10 and 14 – 17).

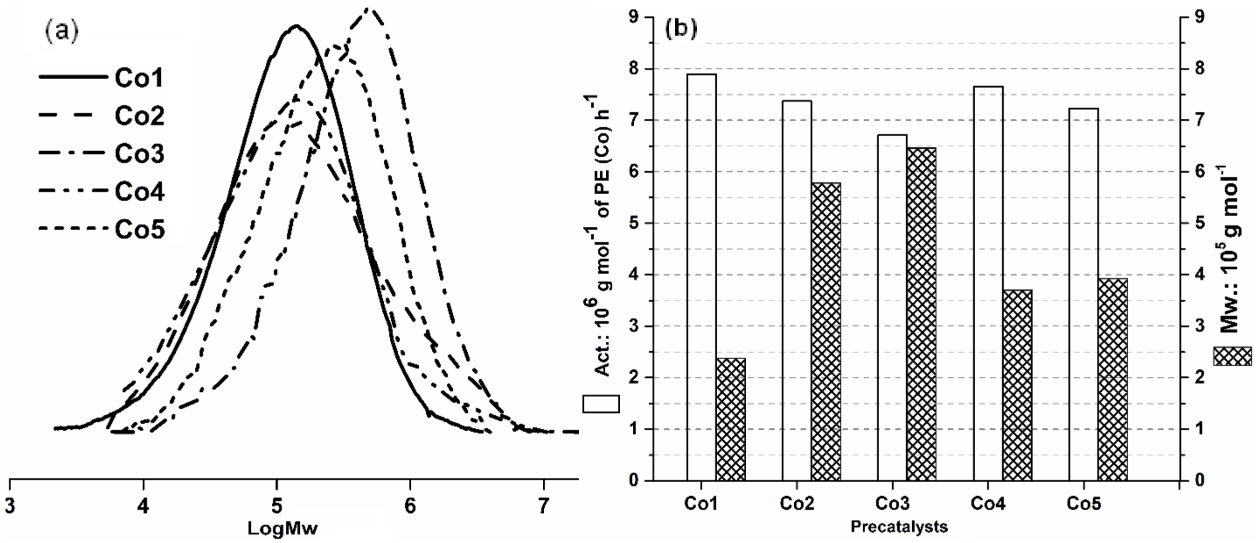

Figure S9 GPC curves of the obtained polyethylene (**a**); activity and M_w for different precatalysts (**b**) at the optimized reaction conditions with MMAO as cocatalyst (Table 6, entries 1 – 5).

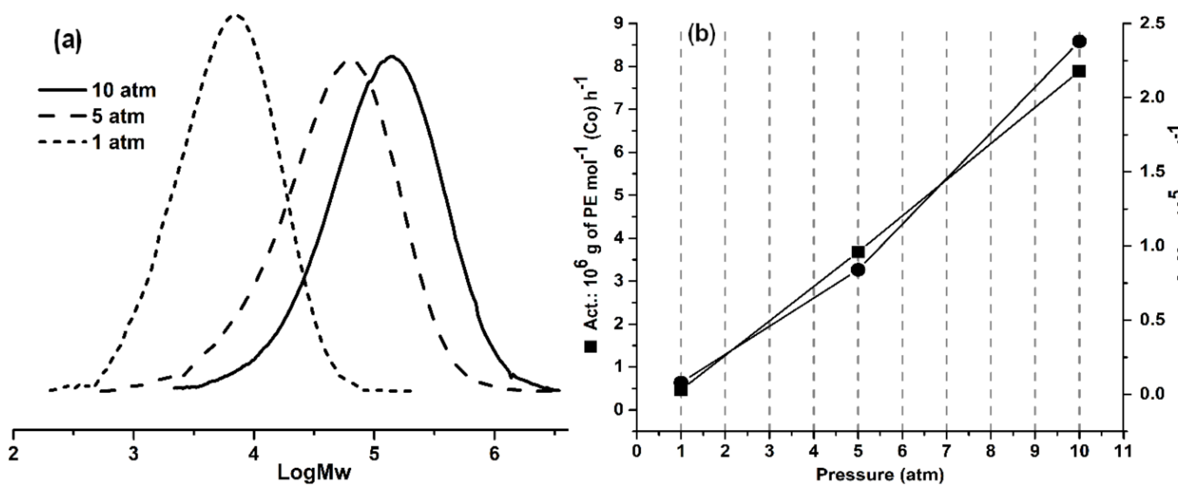

Figure S10 GPC curves of the obtained polyethylene (**a**); activity and M_w as a function of ethylene pressure (**b**) at the optimized reaction conditions for the **Co1**/MMAO system (Table 5, entries 10, 18 and 19).

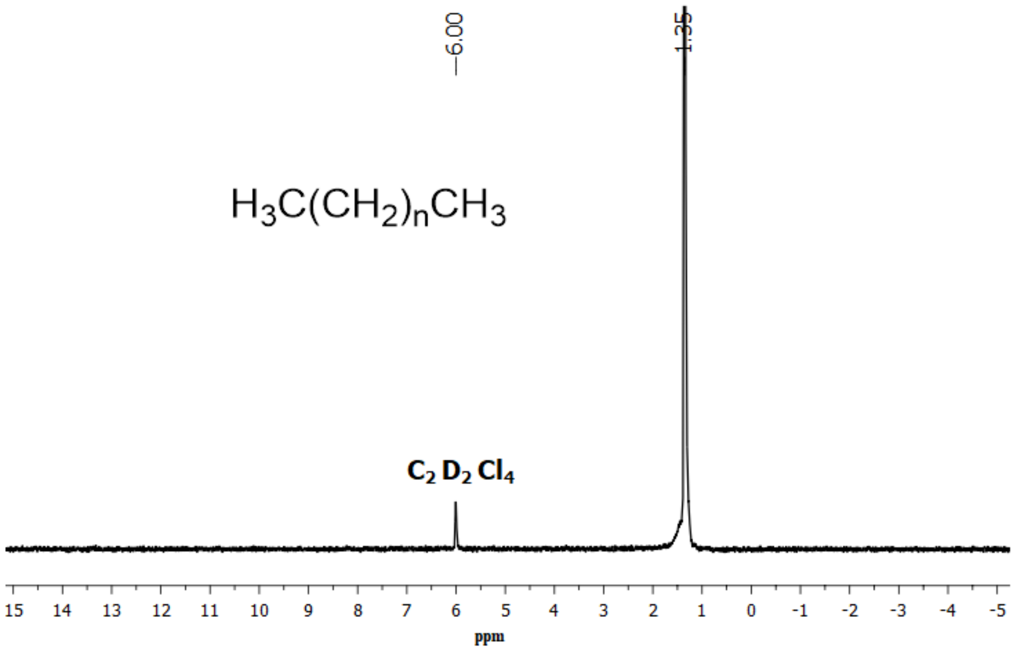

Figure S11 The ^{1}H NMR spectrum of the polyethylene obtained with **Co1**/MMAO (Table 5, entry 10).

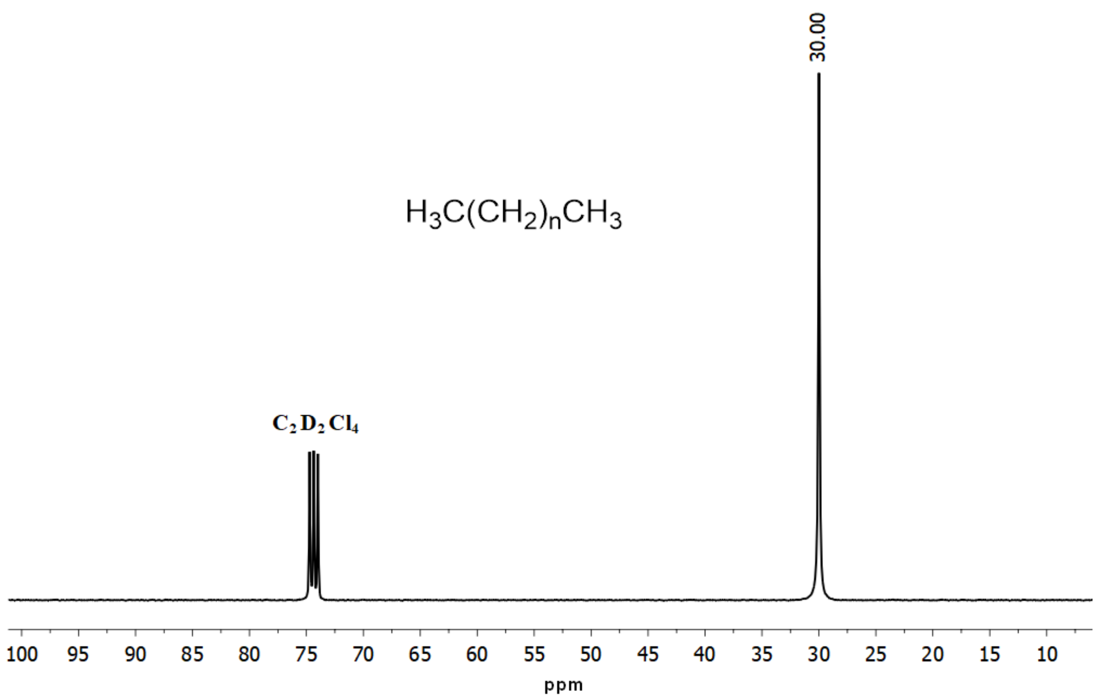

Figure S12 The ^{13}C NMR spectrum of the polyethylene obtained with **Co1**/MMAO (Table 5, entry 10).

Table S1 The selected bond lengths (Å) and angles (º) for the *B* molecules of **Co3** and **Co4**

	Co3	**Co4**
	Molecule B	*Molecule B*
Bond Lengths (Å)		
Co(1)–N(1)	2.062(4)	2.059(7)
Co(1)–N(2)	2.216(4)	2.177(7)
Co(1)–N(3)	2.230(5)	2. 212(7)
Co(1)–Cl(1)	2.2572(16)	2.265(2)
Co(1)–Cl(2)	2.2957(16)	2.298(2)
N(2)–C(10)	1.441(7)	1.437(10)
N(3)–C(47)	1.448(8)	1.435(12)
N(1)–C(3)	1.349(7)	1.335(13)
N(1)–C(7)	1.320(7)	1.317(12)
N(2)–C(8)	1.288(7)	1.272(10)
N(3)–C(2)	1.295(8)	1.289(12)
Bond Angles (º)		
N(1)–Co(1)–N(2)	73.47(17)	74.40(3)
N(1)–Co(1)–N(3)	74.46(18)	74.40(3)
N(2)–Co(1)–N(3)	141.15(17)	142.70(3)
N(1)–Co(1)–Cl(1)	154.04(13)	150.70(2)
N(2)–Co(1)–Cl(1)	99.00(12)	98.34(17)
N(3)–Co(1)–Cl(1)	100.26(15)	98.90(2)
N(2)–Co(1)–Cl(2)	102.35(12)	100.44(18)
N(3)–Co(1)–Cl(2)	101.25(15)	102.23(19)
Cl(1)–Co(1)–Cl(2)	111.86(6)	114.16(9)
N(1)–Co(1)–Cl(2)	94.08(13)	95.10(2)
C(10)–N(2)–Co(1)	124.20(3)	125.40(5)
C(47)–N(3)–Co(1)	125.20(4)	123.70(6)