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Supporting Information

Influence of N−H Functionality on Activating O,N,N-Titanium Complexes and Controlling Polyethylene Molecular Weights and Distributions

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Figure S1. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**. ……..…S4

Figure S2. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**.……..…S4

Figure S3. ^{1}H-^{13}C HSQC (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**……..S5

Figure S4. SEC curves of polymers obtained using **1-TiCl$_3$** at different ethylene pressures (Table 1 runs 2−5). ….....S5

Figure S5. Stacked ^{1}H NMR (400 MHz, in C_6D_6, at 20 °C) spectra of reactions of **1-TiCl$_3$** with 5 or 20 equiv of *d*-MAO in C_6D_6 ……...S6

Figure S6. Stacked ^{1}H NMR (400 MHz, in C_6D_6, at 20 °C) spectra of reactions of **1-TiCl$_2$** with 5 or 20 equiv of *d*-MAO in C_6D_6 ……...S6

Figure S7. SEC curves of polymers obtained by **1-TiCl$_3$** (blue) and **1-TiCl$_2$** (red) with pre-activation by 200 equiv of *d*-MAO at 20 atm of ethylene (Table 2 runs 8 and 9) …S7

Figure S8. FT-IR (4000–500 cm^{-1}) spectrum of polymer obtained in Table 1 run 2. Fourier transform infrared (FT-IR) spectrum (solid sample, 10 mg, 20 °C) was obtained on a Bruker Tensor II FT-IR spectrometer in attenuated total reflection mode at a 4 cm^{-1} resolution and reported in the frequency of absorption…….S7

Figure S9. SEC curves of polymers obtained using **1-TiCl$_3$** with pre-activation by 200 equiv of $AlEt_3$ (black) or Al^iBu_3 (red) in Table 2 runs 6 and 7. ……..…S8

Figure S10. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-b**...…….…S8

Figure S11. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-c**…….....S9

Figure S12. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-L**.….....…S9

Figure S13. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-L**.....…..S10

Figure S14. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-TiCl$_3$**.....…S10

Figure S15. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-TiCl$_3$**.……S11

Figure S16. SEC curves of poly (ethylene-*co*-1-octene)s prepared by different Ti complexes (Table 3 runs 1−3) ……...……S11

Figure S17. DSC thermogram of poly(ethylene-*co*-1-octene) copolymer sample produced in Table 3 run 1 ……..……S12

Figure S18. DSC thermogram of poly(ethylene-*co*-1-octene) copolymer sample produced in Table 3 run 3 ……..……S12

Figure S19. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of polymer obtained in Table 3 run 1 in $C_2D_2Cl_4$ at 120 °C. ……..……S13

Figure S20. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of polymer obtained in Table 3 run 3 in $C_2D_2Cl_4$ at 120 °C. ……..……S13

Figure S21. SEC curves of polymers prepared in the copolymerizations by **1-TiCl$_3$** and **1-TiCl$_2$** with pre-activation (Table 3 runs 4 and 5). ...…….S14

Figure S22. DSC thermogram of polymer prepared in the copolymerization by **1-TiCl$_3$** with pre-activation (Table 3 run 4). ……..S14
Figure S23. DSC thermogram of polymer prepared in the copolymerization by **1-TiCl$_2$** with pre-activation (Table 3 run 5). ……S15
Figure S24. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of polymer obtained in the copolymerization by **1-TiCl$_3$** with pre-activation (Table 3 run 4). ……...S15
Figure S25. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of polymer obtained in the copolymerization by **1-TiCl$_2$** with pre-activation (Table 3 run 5). …….S16

Table S1. Crystal Data and Structure Refinement for Metal Complexes ..…...……S17

Table S2. Selected Bond Distances (Å) and Angles (deg) for **1-TiCl$_3$** ……....…S18

Table S3. Selected Bond Distances (Å) and Angles (deg) for **2-TiCl$_3$** ……..……S18

Table S4. Selected Bond Distances (Å) and Angles (deg) for **1-TiCl$_{1.84}$Me$_{0.16}$** …..S19

Table S5. Selected Bond Distances (Å) and Angles (deg) for **1-TiCl$_{1.30}$Me$_{0.70}$** ……S19

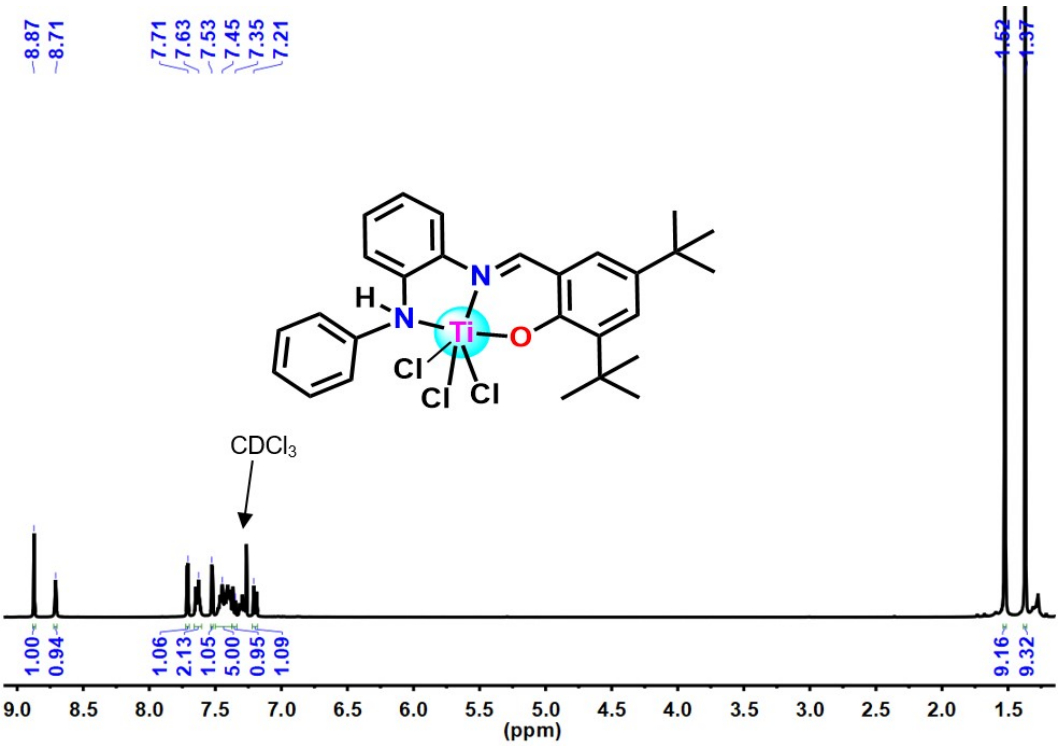


Figure S1. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**.

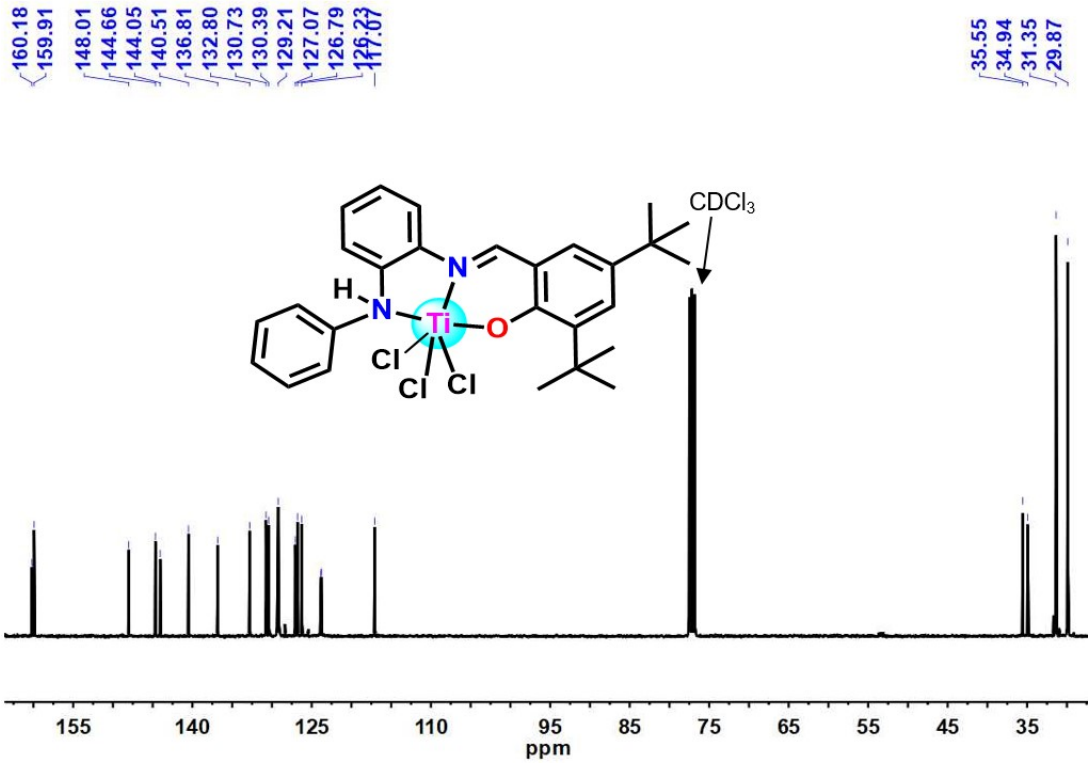


Figure S2. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**.

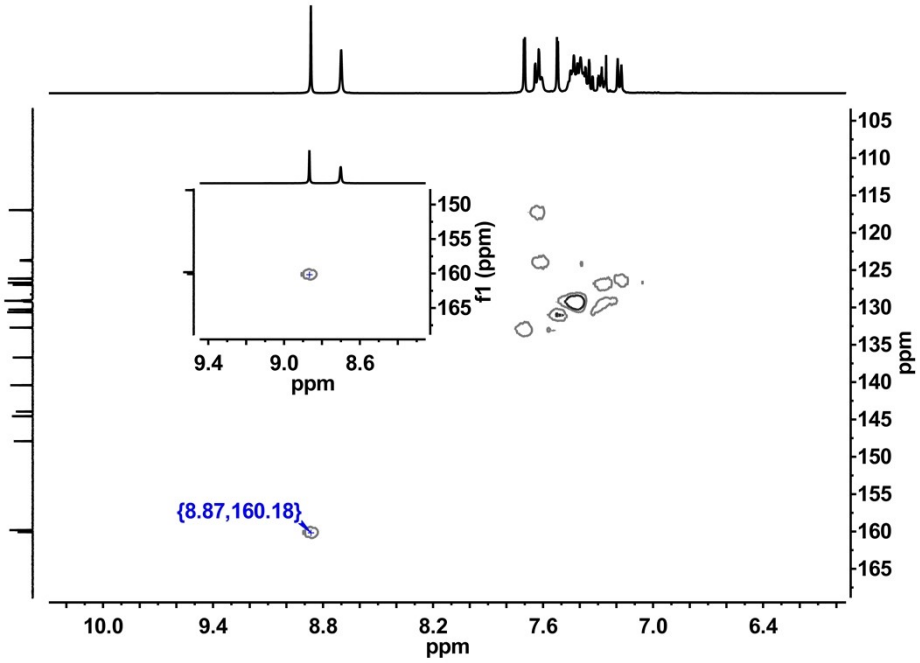
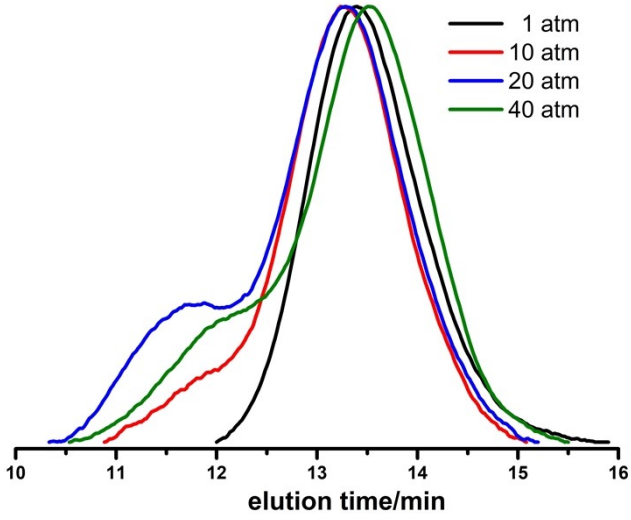


Figure S3. ^{1}H-^{13}C HSQC (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, in $CDCl_3$, at 20 °C) spectrum of **1-TiCl$_3$**.



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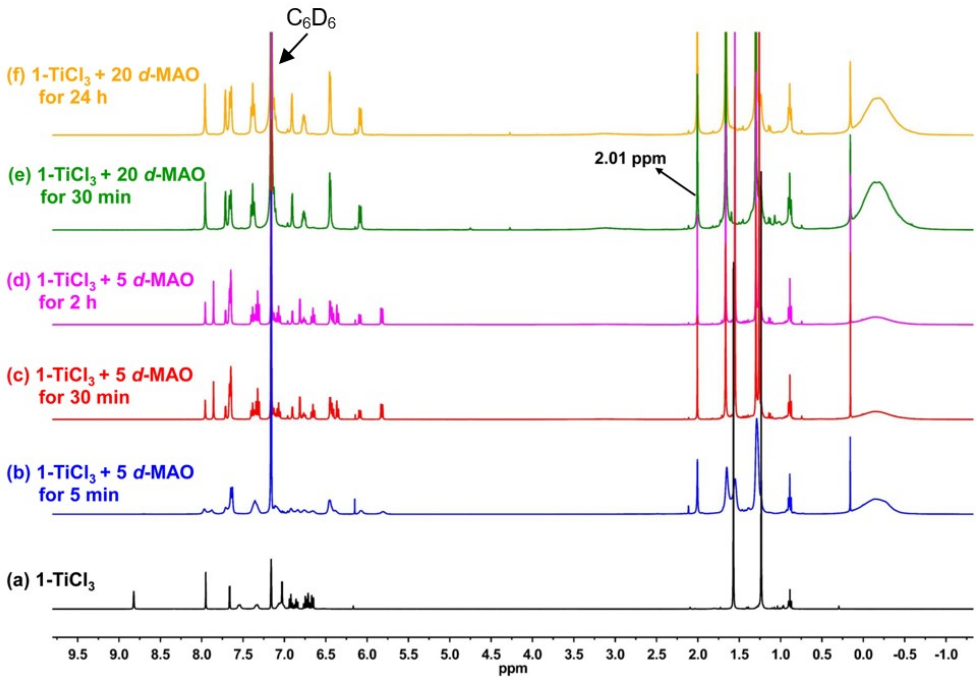


Figure S5. Stacked ^{1}H NMR (400 MHz, in C_6D_6, at 20 °C) spectra of reactions of **1-TiCl$_3$** with 5 or 20 equiv of *d*-MAO.

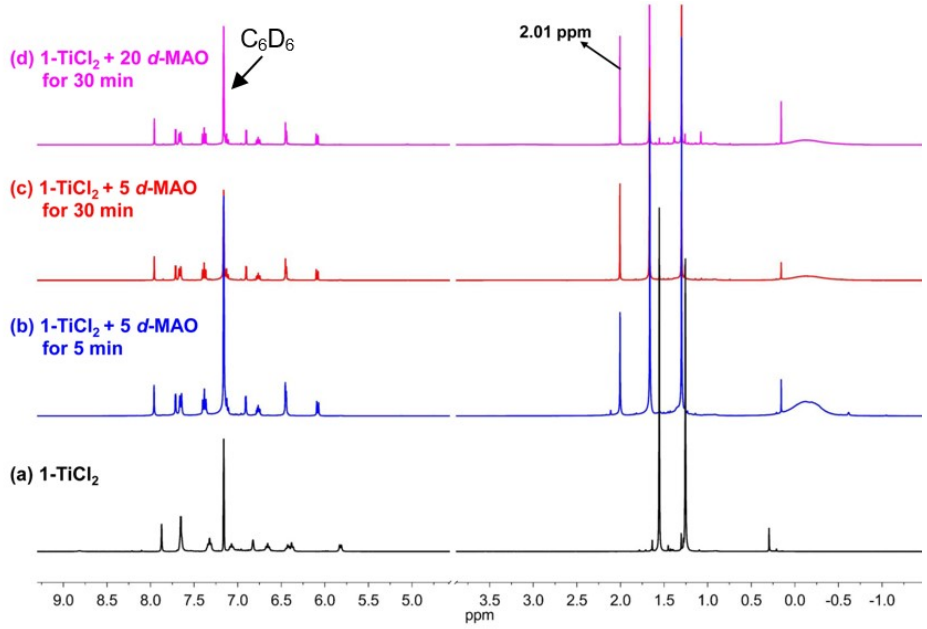


Figure S6. Stacked ^{1}H NMR (400 MHz, in C_6D_6, at 20 °C) spectra of the reaction mixtures of **1-TiCl$_2$** with 5 or 20 equiv of *d*-MAO.

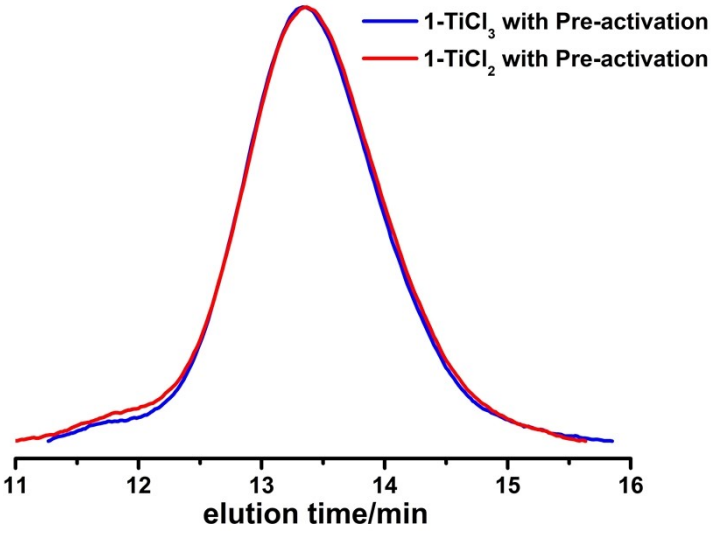
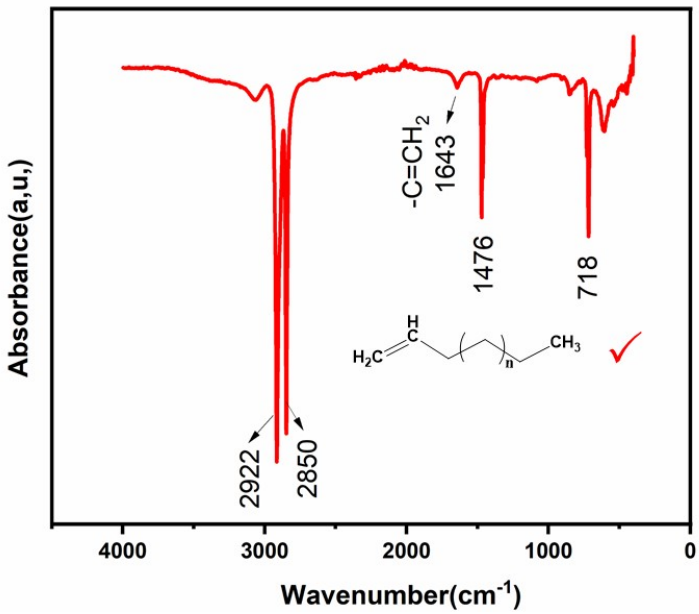


Figure S7. SEC curves of polymers obtained using **1-TiCl$_3$** (blue) and **1-TiCl$_2$** (red) with pre-activation by 200 equiv of *d*-MAO at 20 atm of ethylene (Table 2 runs 8 and 9).



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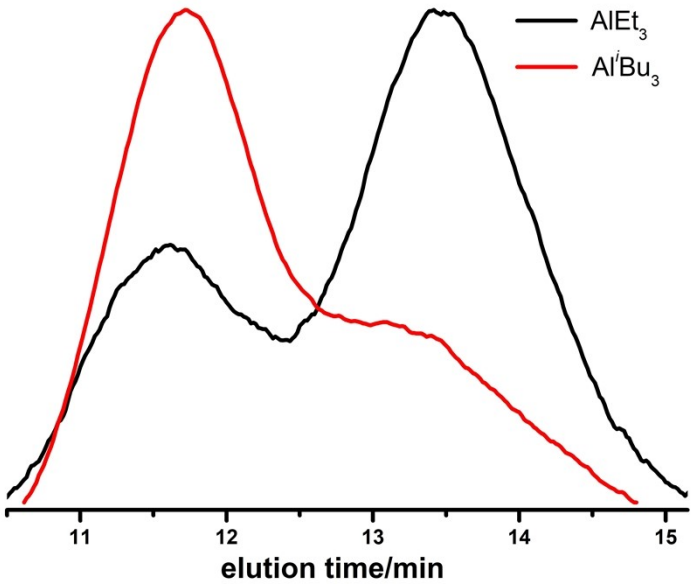

Figure S9. SEC curves of polymers obtained using **1-TiCl$_3$** with pre-activation by 200 equiv of $AlEt_3$ (black) or Al^iBu_3 (red) in Table 2 runs 6 and 7.

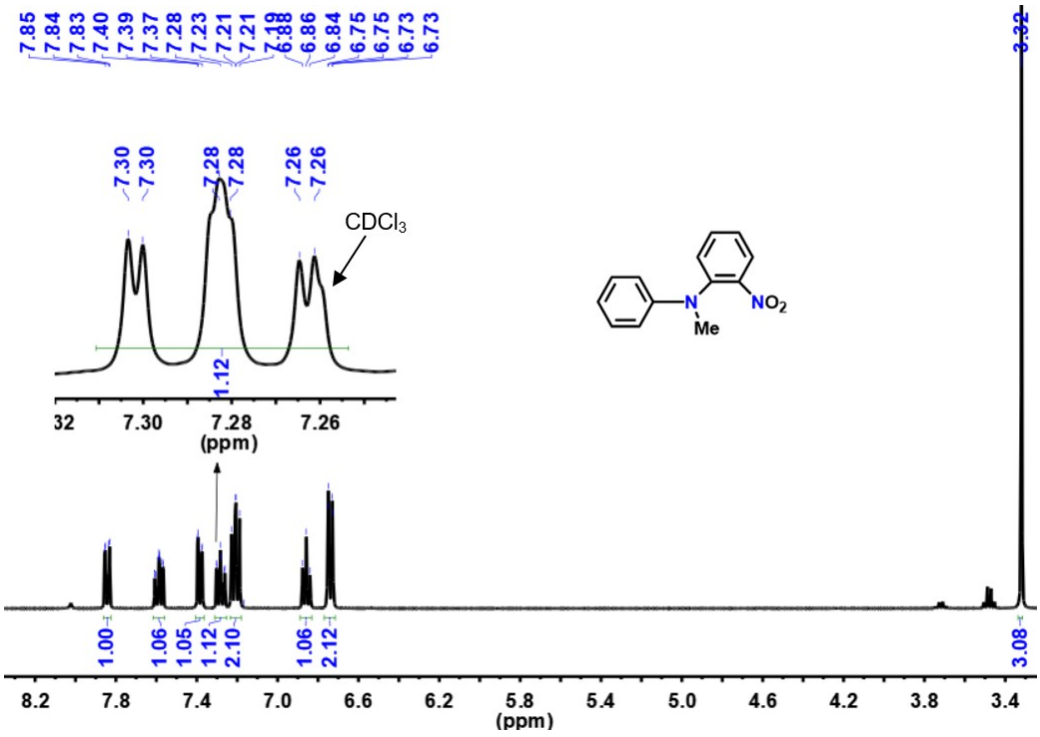

Figure S10. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-b**.

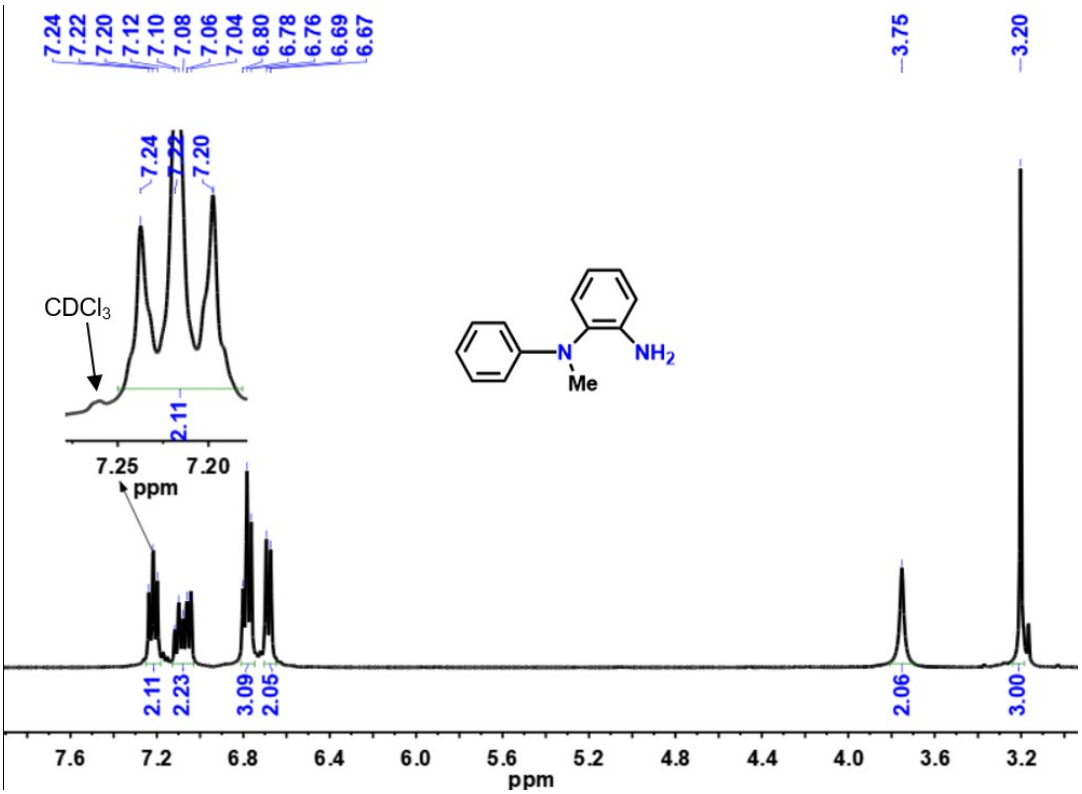

Figure S11. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-c**.

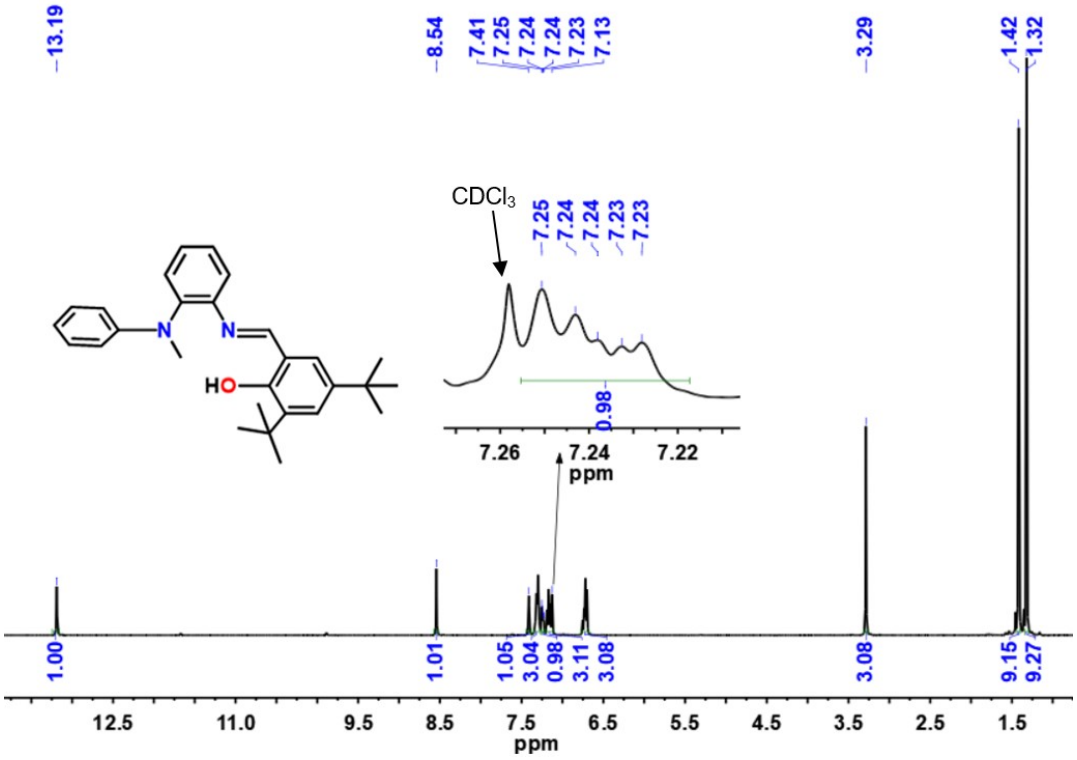

Figure S12. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-L**.

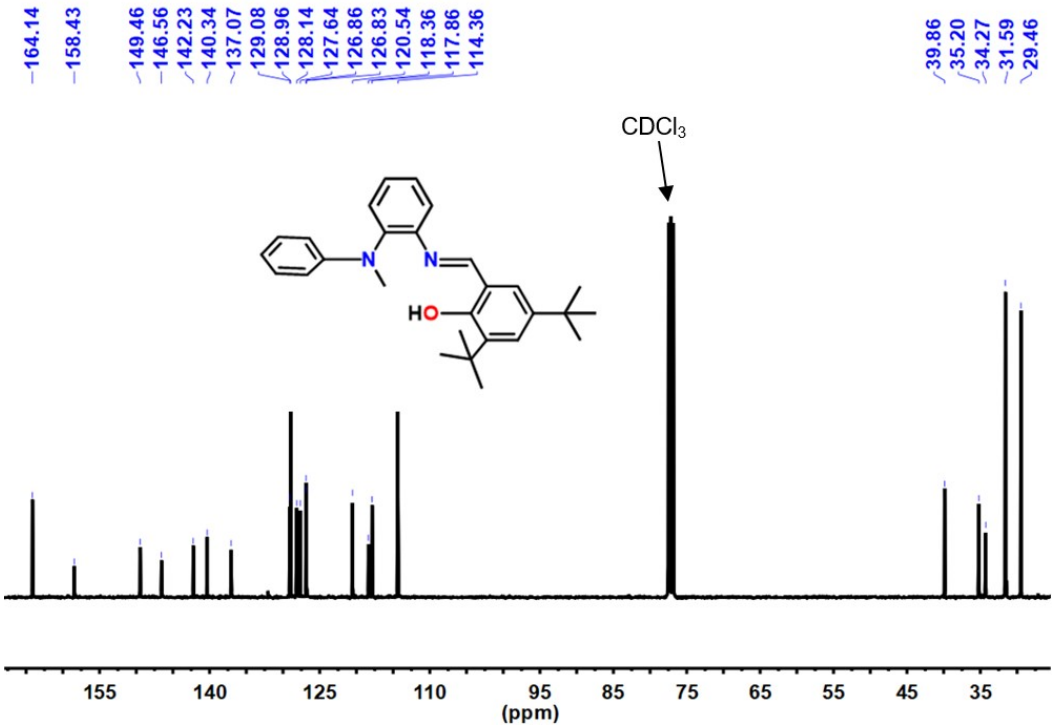

Figure S13. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-L**.

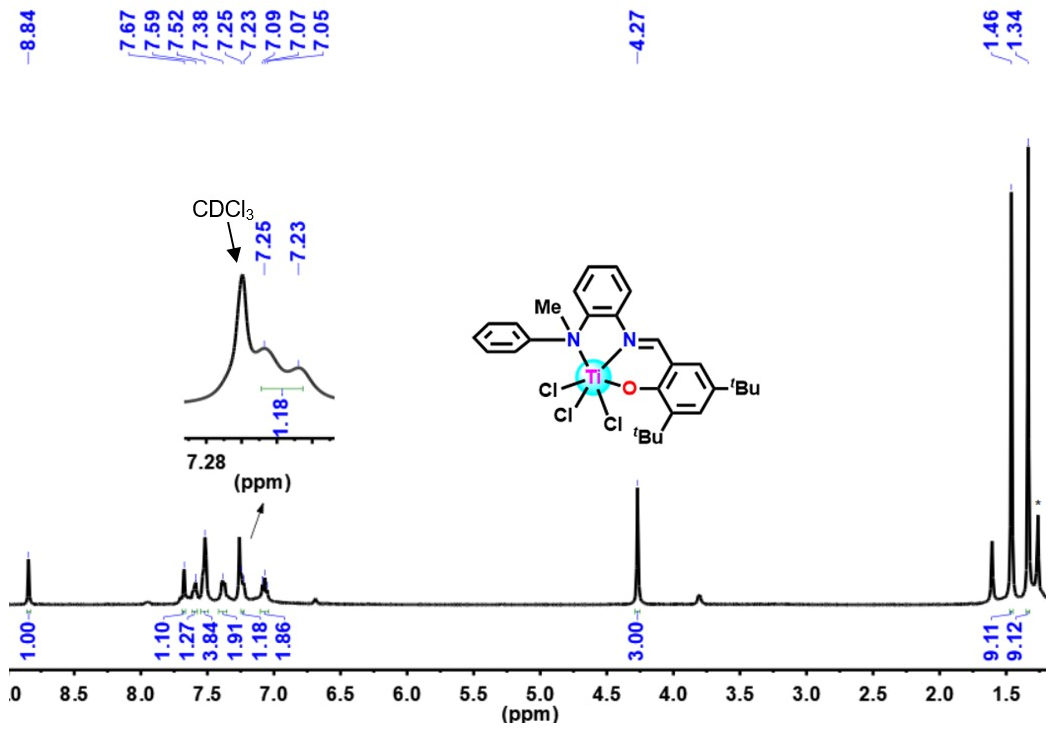

Figure S14. ^{1}H NMR (400 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-TiCl$_3$**.

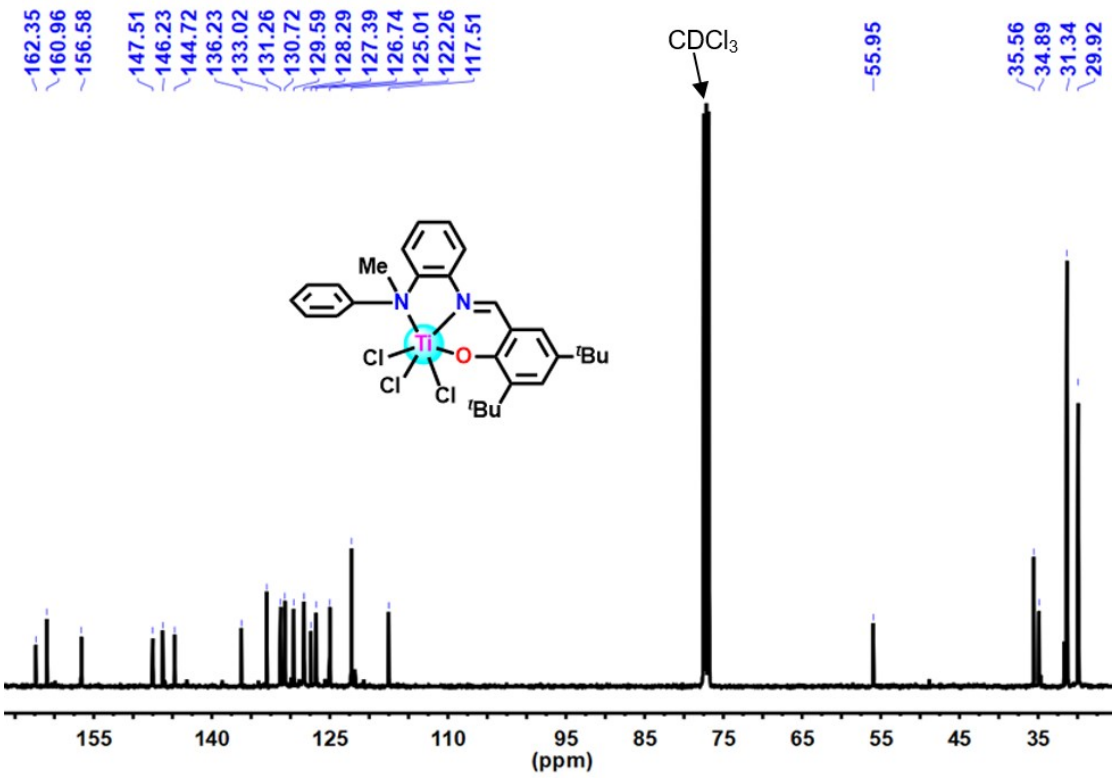

Figure S15. ^{13}C NMR (100 MHz, in $CDCl_3$, at 20 °C) spectrum of **2-TiCl$_3$**.

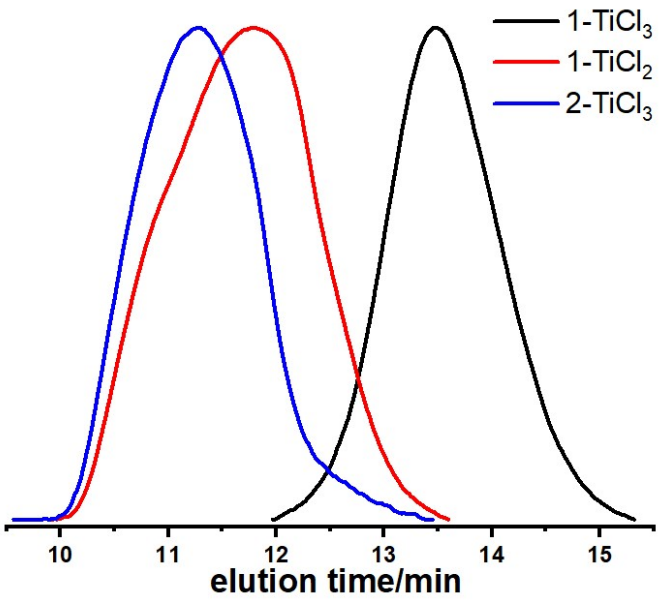

Figure S16. SEC curves of poly(ethylene-*co*-1-octene)s prepared using different Ti complexes (Table 3 runs 1-3).

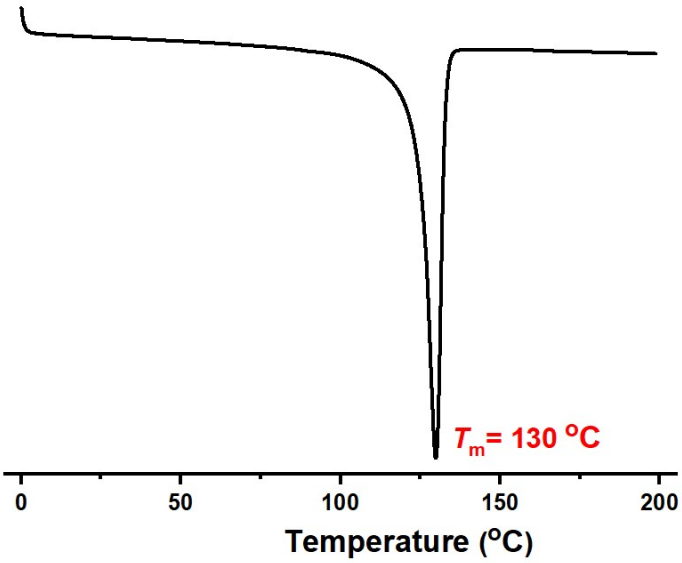

Figure S17. DSC thermogram of a poly(ethylene-*co*-1-octene) copolymer sample produced in Table 3 run 1.

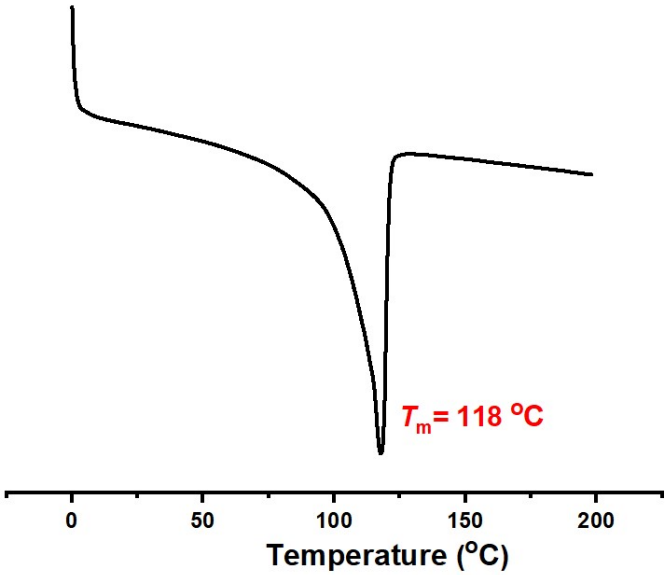

Figure S18. DSC thermogram of a poly(ethylene-*co*-1-octene) copolymer sample produced in Table 3 run 3.

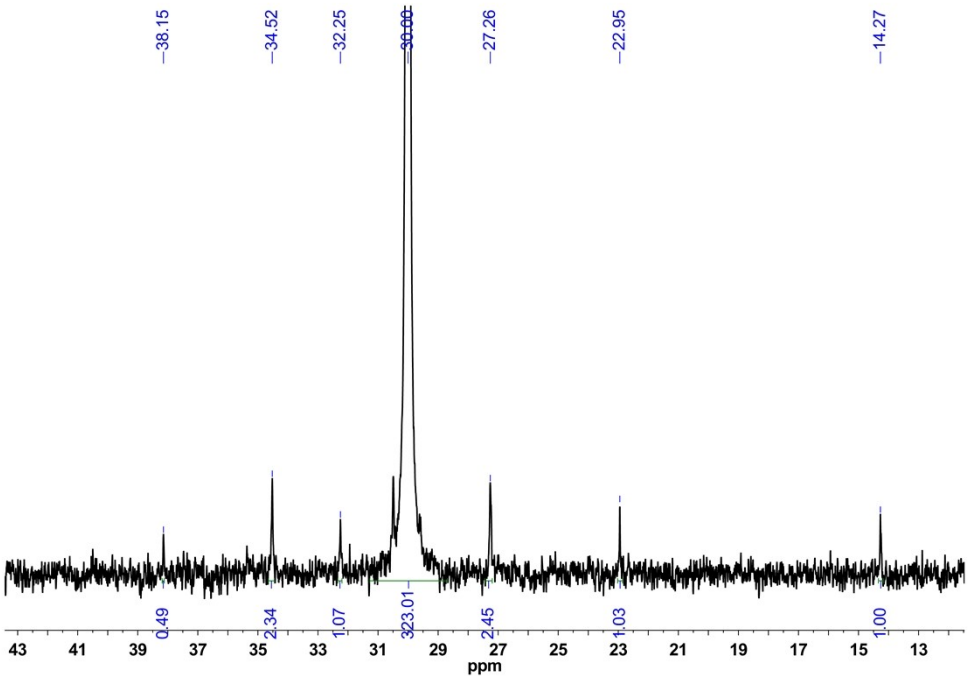

Figure S19. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of the polymer obtained in Table 3 run 1.

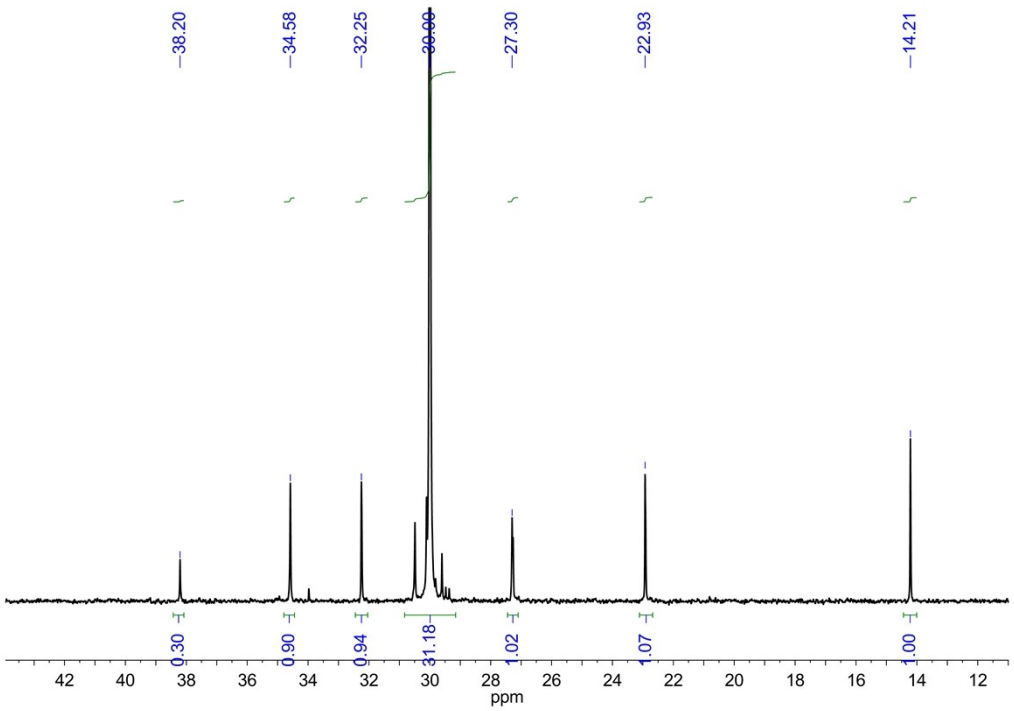

Figure S20. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of the polymer obtained in Table 3 run 3.

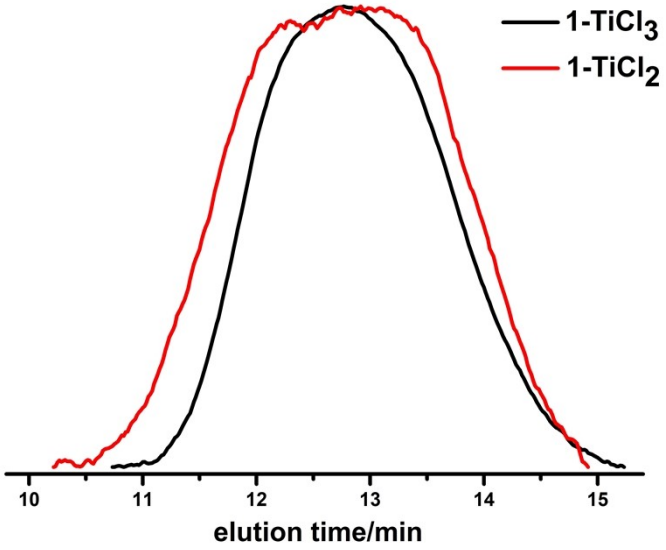

Figure S21. SEC curves of the polymers prepared in the copolymerizations using **1-$TiCl_3$** and **1-$TiCl_2$** with pre-activation (Table 3 runs 4 and 5).

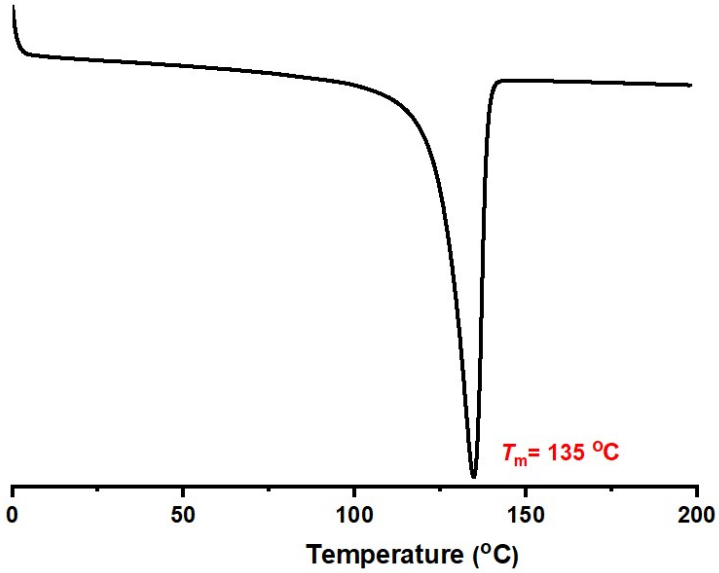

Figure S22. DSC thermogram of the polymer prepared in the copolymerization using **1-$TiCl_3$** with pre-activation (Table 3 run 4).

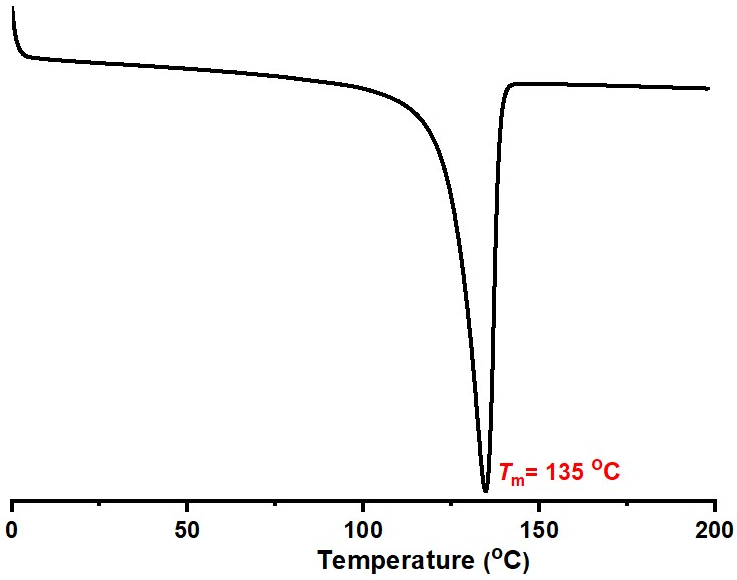

Figure S23. DSC thermogram of the polymer prepared in the copolymerization using **1-TiCl$_2$** with pre-activation (Table 3 run 5).

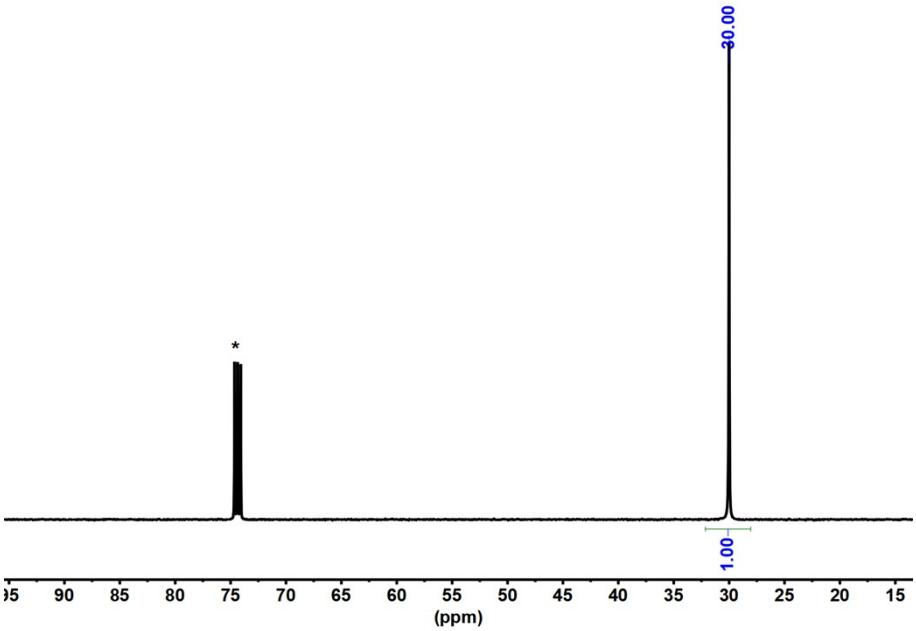

Figure S24. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of the polymer obtained in the copolymerization using **1-TiCl$_3$** with pre-activation (Table 3 run 4).

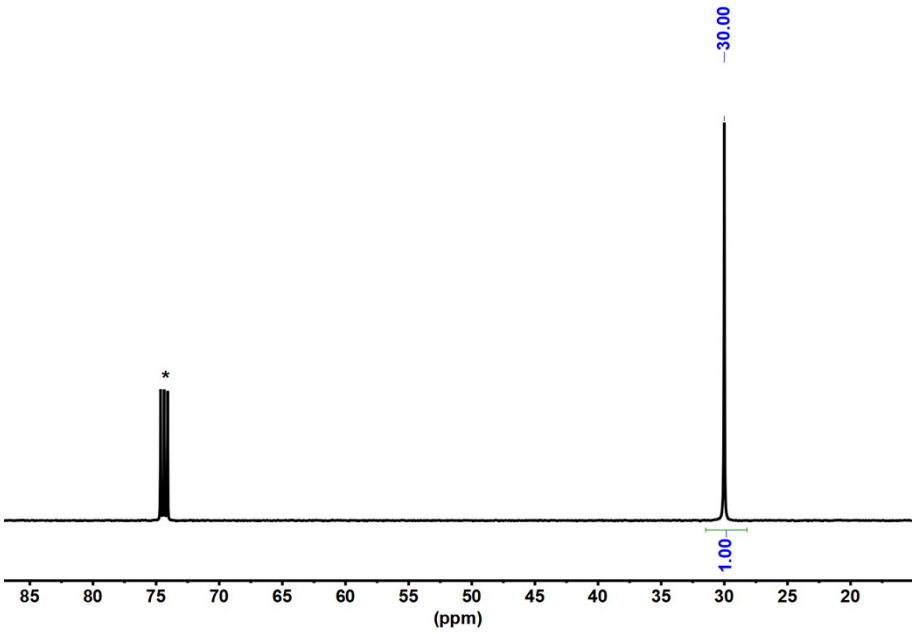

Figure S25. ^{13}C NMR (100 MHz, in $C_2D_2Cl_4$, at 120 °C) spectrum of the polymer obtained in the copolymerization using **1-TiCl$_2$** with pre-activation (Table 3 run 5).

Table S1. Crystal Data and Structure Refinement for Metal Complexes.

Complex	**1-$TiCl_3$**	**2-$TiCl_3$**	**1-$TiCl_{1.84}Me_{0.16}$**	**1-$TiCl_{1.30}Me_{0.70}$**
Empirical formula	$C_{27}H_{31}Cl_3N_2OTi$	$C_{28}H_{33}Cl_3N_2OTi$	$C_{27.16}H_{30.49}Cl_{1.84}N_2OTi$	$C_{27.7}H_{32.1}Cl_{1.3}N_2OTi$
Formula weight	553.79	567.80	513.96	503.04
Temperature / K	193.00	193.0	193.00	193.00
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	$P2_1/c$	$P2_1/n$	$P2_1/n$
a / Å, b / Å, c / Å	12.2892(6), 17.0825(8), 26.1980(13)	16.1090(7), 37.3013(12), 20.2183(7)	9.3489(5), 16.2196(7), 16.7518(8)	9.3909(4), 16.2313(7), 16.8292(5)
α/°, β/°, γ/°	90, 90, 90	90, 112.596(2), 90	90, 93.897(2), 90	90 94.109(2) 90
Volume / $Å^3$	5499.8(5)	11216.3(7)	2534.3(2)	2558.62(17)
Z	8	4	4	4
ρ_{calc} / mg mm^{-3}	1.338	1.126	1.347	1.306
μ / mm^{-1}	3.683	3.175	0.554	2.858
F(000)	2304.0	3952.0	1075.0	1058.0
Crystal size / mm^3	0.13 × 0.12 × 0.1	0.13 × 0.12 × 0.1	0.13 × 0.12 × 0.1	0.13 × 0.12 × 0.1
Radiation / Å	Ga-Kα (λ = 1.34139)	Ga-Kα (λ = 1.34139)	Mo-Kα (λ = 0.71073)	Ga-Kα (λ = 1.34139)
2Θ range for data collection	5.87 to 114.002°	4.606 to 107.814°	4.854 to 54.932°	6.59 to 120.368°
Index ranges	-15 ⩽ h ⩽ 15, -21 ⩽ k ⩽ 20, -32 ⩽ l ⩽ 32	-19⩽h⩽19, -44⩽k⩽44, -22⩽l⩽24	-12 ⩽ h ⩽ 10, -21 ⩽ k ⩽ 20, -21 ⩽ l ⩽ 21	-11 ⩽ h ⩽ 6, -18 ⩽ k ⩽ 20, -20 ⩽ l ⩽ 21
Reflections collected	39965	64768	22960	19735
Independent reflections	5624 [R(int) = 0.0622]	2025 [R(int) = 0.0998]	5778 [R(int) = 0.0605]	5589 [R(int) = 0.0723]
Data/restraints/parameters	5624/0/313	20505/36/1045	5778/0/307	5589/0/307
Goodness-of-fit on F^2	1.036	1.065	1.051	1.019
Final R indexes [$I>2\sigma(I)$]	R1 = 0.0370, wR2 = 0.0908	R_1 = 0.0778, wR_2 = 0.1796	R_1 = 0.0465, wR_2 = 0.1082	R_1 = 0.0554, wR_2 = 0.1183
Final R indexes [all data]	R_1 = 0.0529, wR_2 = 0.0981	R_1 = 0.1688, wR_2 = 0.2173	R_1 = 0.0651, wR_2 = 0.1203	R_1 = 0.1071, wR_2 = 0.1417
Largest diff. peak/hole / e $Å^{-3}$	0.47 / -0.35	0.41 / -0.66	0.31 / -0.34	0.40 / -0.34

Table S2. Selected Bond Distances (Å) and Angles (deg) for **1**-$TiCl_3$.

Distances			
Ti1–Cl1	2.3205(6)	Ti1–O1	1.7883(14)
Ti1–Cl2	2.2558(6)	Ti1–N2	2.1743(17)
Ti1–Cl3	2.3400(7)	Ti1–N1	2.2922(18)
Angles			
Cl1–Ti1–Cl3	163.47(3)	O1–Ti1–N1	156.99(7)
Cl2–Ti1–Cl1	93.60(2)	N2–Ti1–Cl1	83.59(5)
Cl2–Ti1–Cl3	95.03(3)	N2–Ti1–Cl2	170.54(5)
Cl2–Ti1–N1	96.58(5)	N2–Ti1–Cl3	85.61(5)
O1–Ti1–Cl1	99.88(5)	N2–Ti1–N1	74.22(6)
O1–Ti1–Cl2	105.32(5)	N1–Ti1–Cl1	85.45(5)
O1–Ti1–Cl3	91.40(5)	N1–Ti1–Cl3	79.58(5)
O1–Ti1–N2	84.08(6)		

Table S3. Selected Bond Distances (Å) and Angles (deg) for **2**-$TiCl_3$.

Distances			
Ti1–Cl3	2.3260(19)	Ti1–O1	1.792(4)
Ti1–Cl2	2.279(2)	Ti1–N2	2.379(5)
Ti1–Cl1	2.289(2)	Ti1–N1	2.129(5)
Angles			
Cl3–Ti1–N2	88.02(13)	O1–Ti1–Cl2	103.19(14)
Cl1–Ti1–Cl3	170.74(9)	O1–Ti1–N1	84.68(18)
Cl1–Ti1–N2	85.78(13)	O1–Ti1–N2	159.40(18)
Cl2–Ti1–Cl3	91.49(8)	N1–Ti1–Cl3	83.60(13)
Cl2–Ti1–Cl1	96.10(9)	N1–Ti1–Cl2	170.66(16)
Cl2–Ti1–N2	97.22(13)	N1–Ti1–Cl1	88.14(13)
O1–Ti1–Cl3	88.68(13)	N1–Ti1–N2	74.74(18)
O1–Ti1–Cl1	94.72(13)		

Table S4. Selected Bond Distances (Å) and Angles (deg) for **1-TiCl$_{1.84}$Me$_{0.16}$**.

Distances			
Ti1–Cl1	2.2448(8)	Ti1–N1	1.9468(18)
Ti1–Cl2	2.2469(7)	Ti1–C2A	2.2469(7)
Ti1–O1	1.8327(15)	Ti1–C1A	2.2448(8)
Ti1–N2	2.1698(18)		
Angles			
Cl1–Ti1–Cl2	108.86(3)	N2–Ti1–C2A	114.78(5)
O1–Ti1–Cl1	94.90(5)	N2–Ti1–C1A	136.36(5)
O1–Ti1–Cl2	97.37(5)	N1–Ti1–C11	97.48(6)
O1–Ti1–N2	80.20(7)	N1–Ti1–Cl2	99.23(6)
O1–Ti1–N1	154.81(8)	N1–Ti1–N2	75.70(7)
O1–Ti1–C2A	97.37(5)	N1–Ti1–C2A	99.23(6)
O1–Ti1–C1A	94.90(5)	N1–Ti1–C1A	97.48(6)
N2–Ti1–Cl1	136.36(5)	C1A–Ti1–C2A	108.86(3)
N2–Ti1–Cl2	114.78(5)		

Table S5. Selected Bond Distances (Å) and Angles (deg) for **1-TiCl$_{1.30}$Me$_{0.70}$**.

Distances			
Ti1–Cl1	2.2539(11)	Ti1–Cl2A	2.2606(16)
Ti1–O1	1.835(2)	Ti1–C2A	2.2606(16)
Ti1–N2	2.173(2)	Ti1–C1A	2.2539(11)
Ti1–N1	1.952(2)		
Angles			
Cl1–Ti1–Cl2A	106.55(5)	N2–Ti1–C2A	115.02(8)
O1–Ti1–Cl1	95.36(7)	N2–Ti1–C1A	138.43(7)
O1–Ti1–N2	80.66(9)	N1–Ti1–Cl1	98.13(8)
O1–Ti1–N1	155.78(10)	N1–Ti1–N2	75.89(9)
O1–Ti1–Cl2A	96.38(8)	N1–Ti1–Cl2A	98.91(9)
O1–Ti1–C2A	96.38(8)	N1–Ti1–C2A	98.91(9)
O1–Ti1–C1A	95.36(7)	N1–Ti1–C1A	98.13(8)
N2–Ti1–Cl1	138.43(7)	C1A–Ti1–C2A	106.55(5)
N2–Ti1–Cl2A	115.02(8)		