Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Polymerization of α-olefins and their copolymerization with ethylene by half-sandwich scandium catalysts with an *N*-heterocyclic carbene ligand

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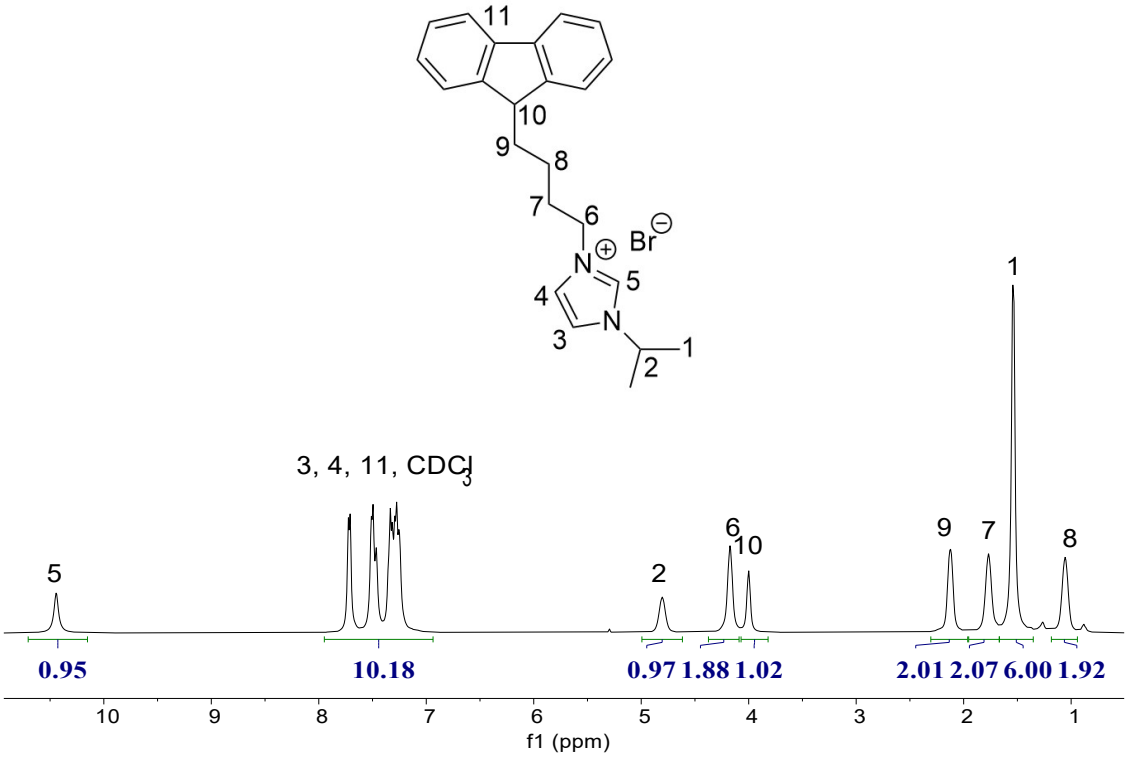

Fig. S1 ^{1}H-NMR spectrum of {Fluorenyl-H-$(CH_2)_4$-NHC-H}Br.

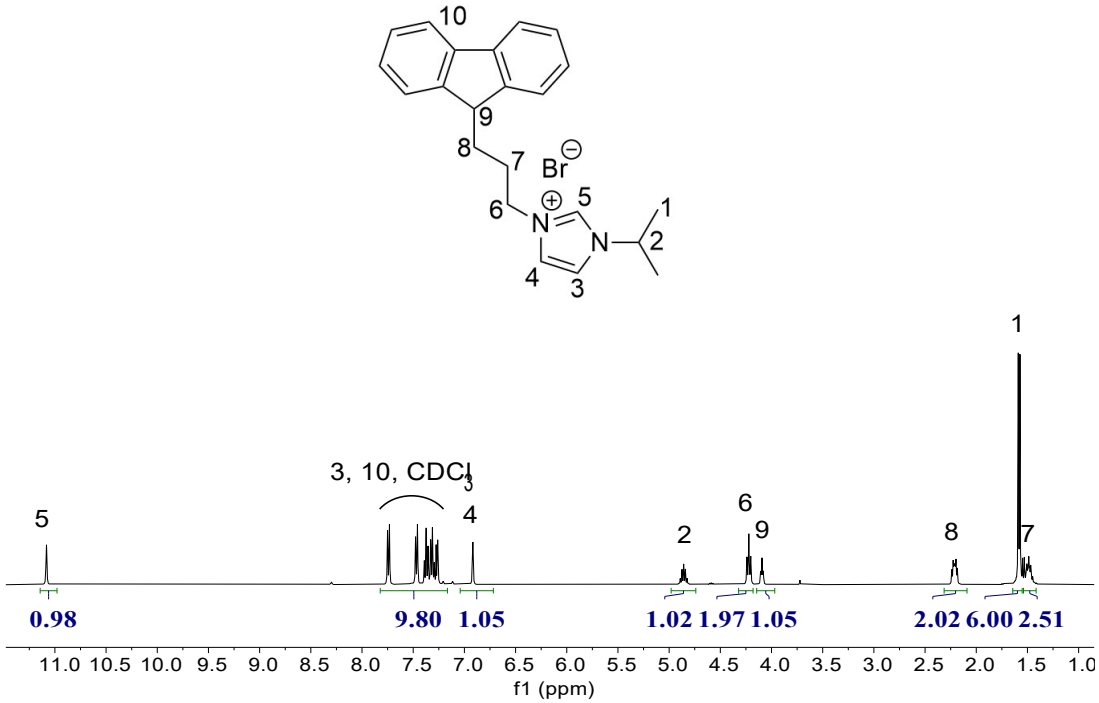

Fig. S2 ^{1}H-NMR spectrum of {Fluorenyl-H-$(CH_2)_3$-NHC-H}Br.

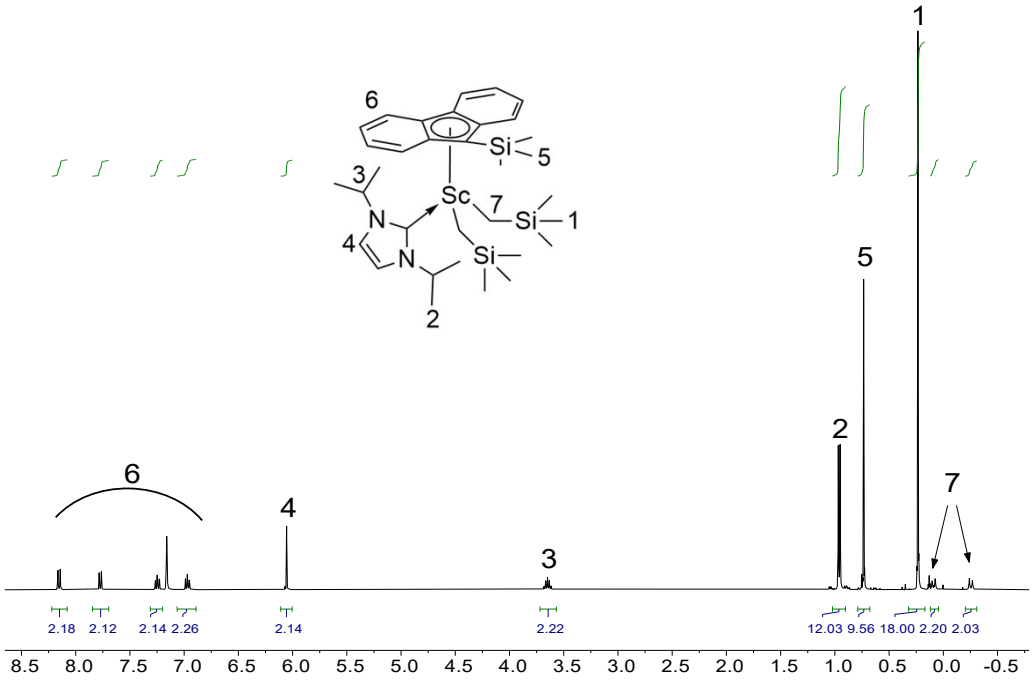

Fig. S3 ^{1}H-NMR spectrum of scandium complex **2**.

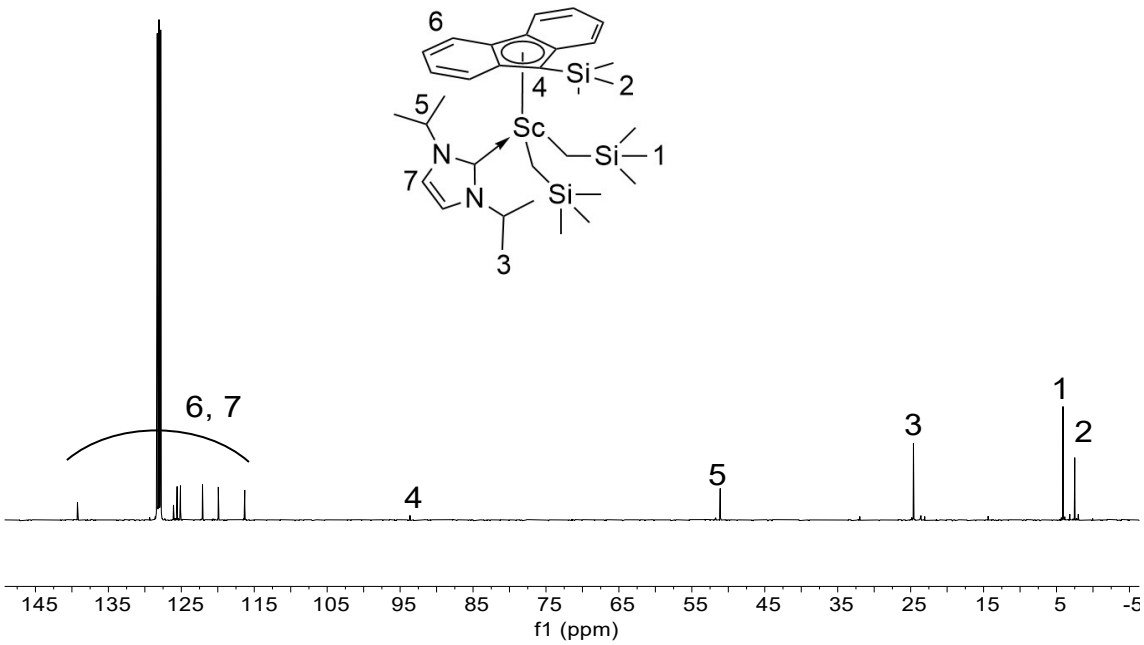

Fig. S4 ^{13}C-NMR spectrum of scandium complex **2.**

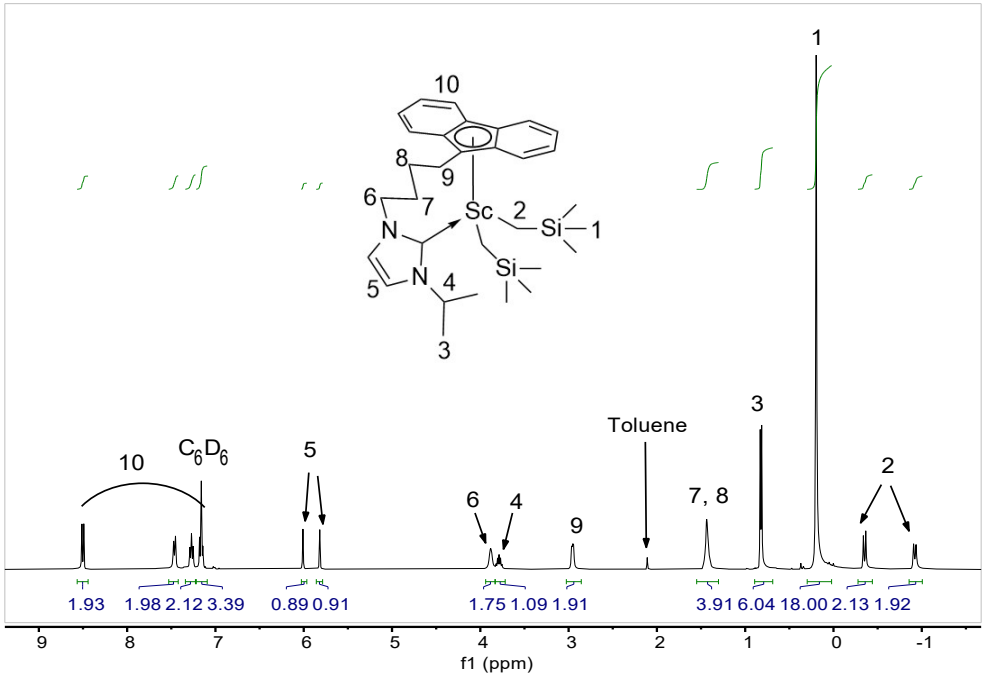

Fig. S5. ^{1}H-NMR spectrum of scandium complex **3a.**

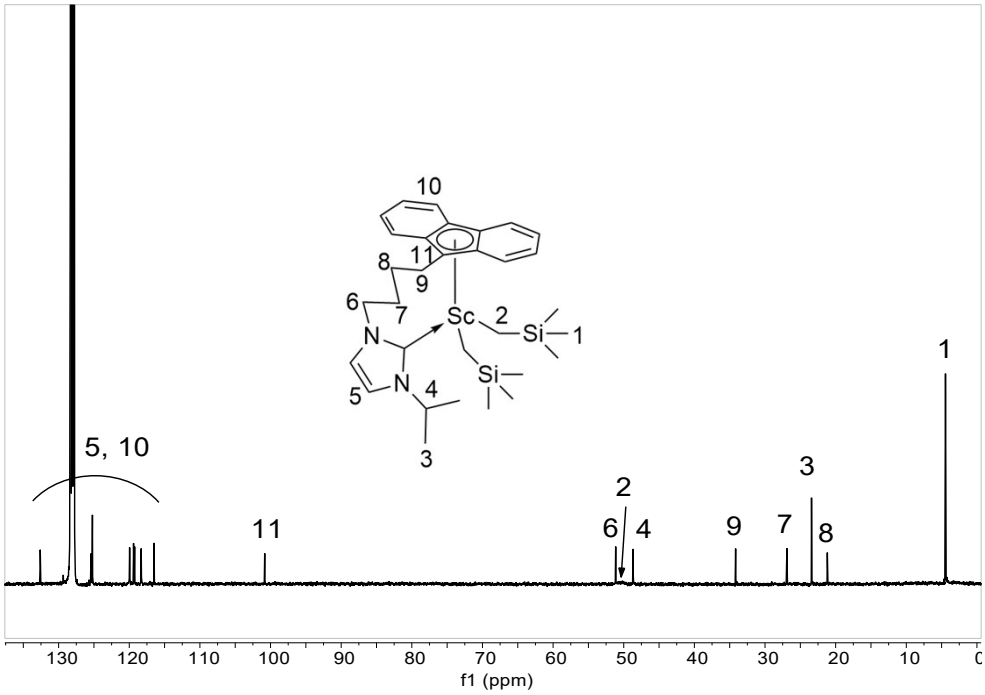

Fig. S6 ^{13}C-NMR spectrum of scandium complex **3a.**

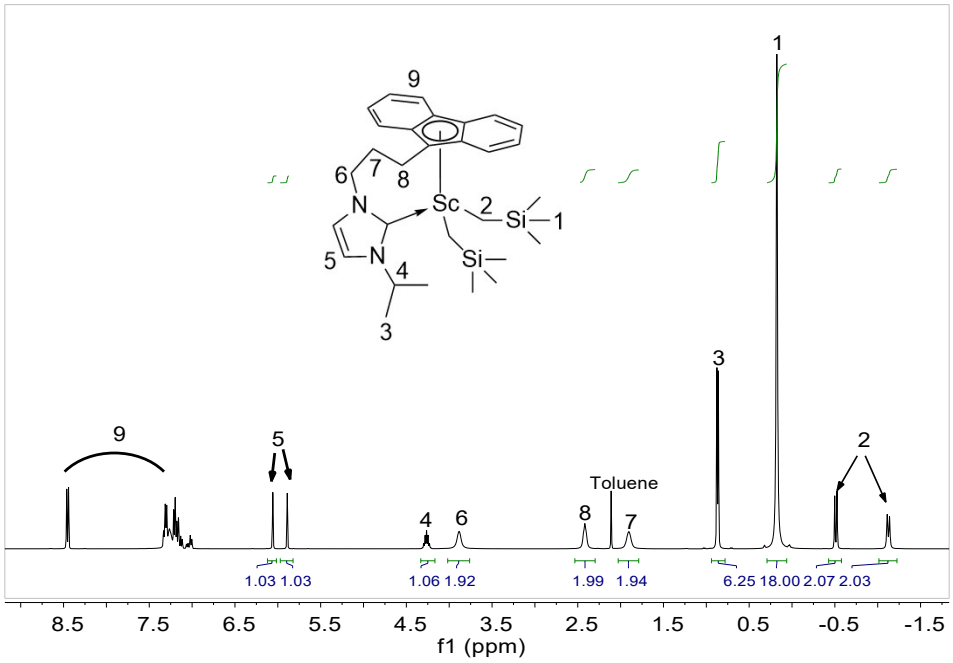

Fig. S7 ^{1}H-NMR spectrum of scandium complex **3b.**

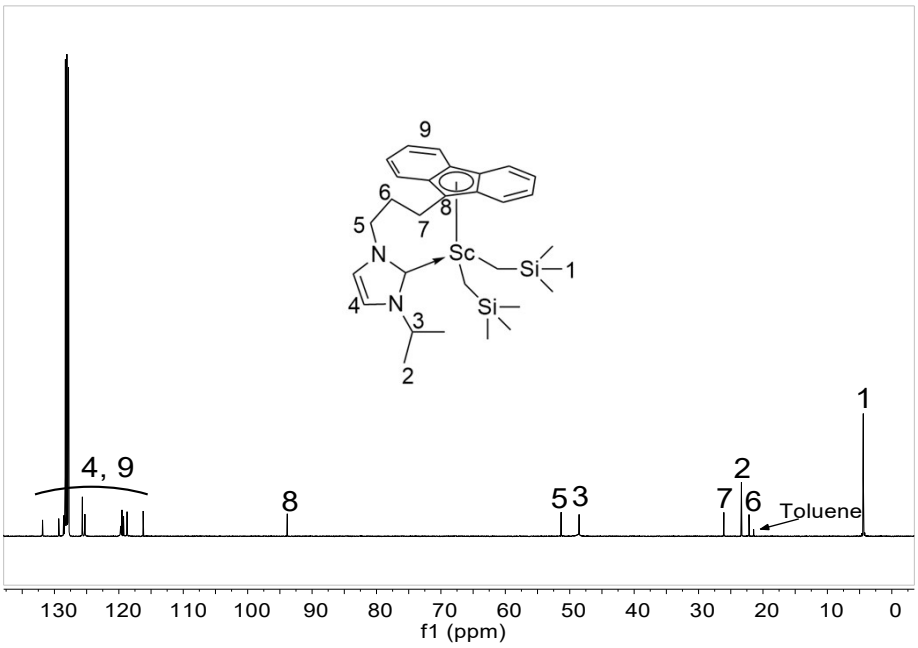

Fig. S8 ^{13}C-NMR spectrum of scandium complex **3b.**

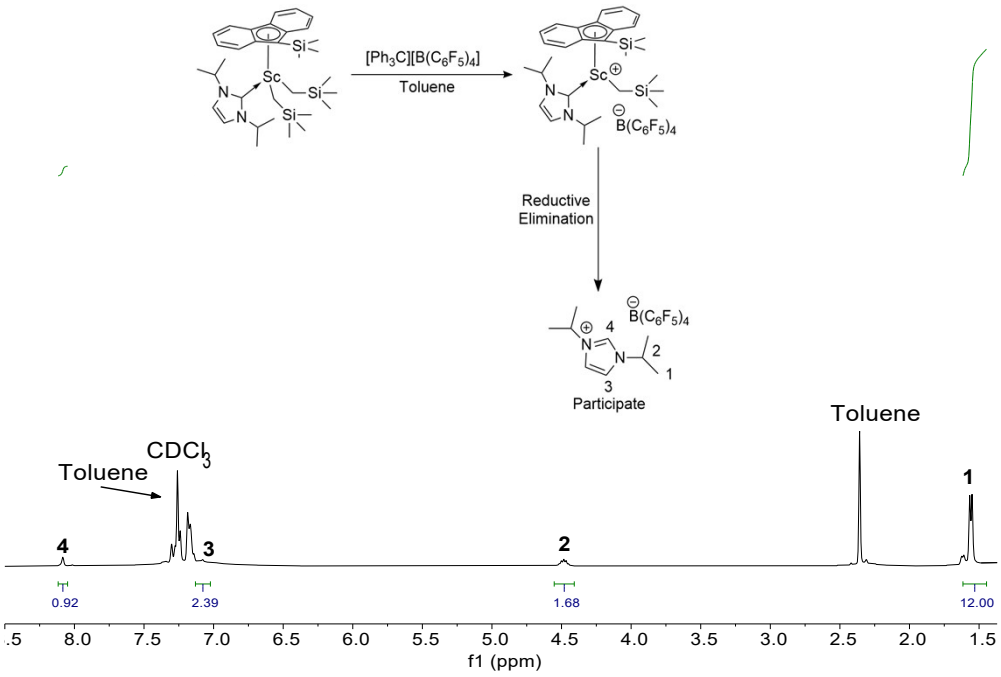

Fig. S9 ^{1}H-NMR spectrum of the precipitate. (In a glovebox, 5 mL toluene solution of $[Ph_3C][B(C_6F_5)_4]$ (46.1mg, 50μmol) was added to 10mL toluene solution of **2** (30.5mg, 50μmol) at room temperature and stirred for 1h. The participate was filtered and washed by toluene and 1-hexene. Then the participate was dried and dissolved in $CDCl_3$ for ^{1}H-NMR analysis. ^{1}H-NMR spectrum referred to: J. M. Farrell, J. A. Hatnean and D. W. Stephan, *J. Am. Chem. Soc.* 2012, **134**, 15728−15731.)

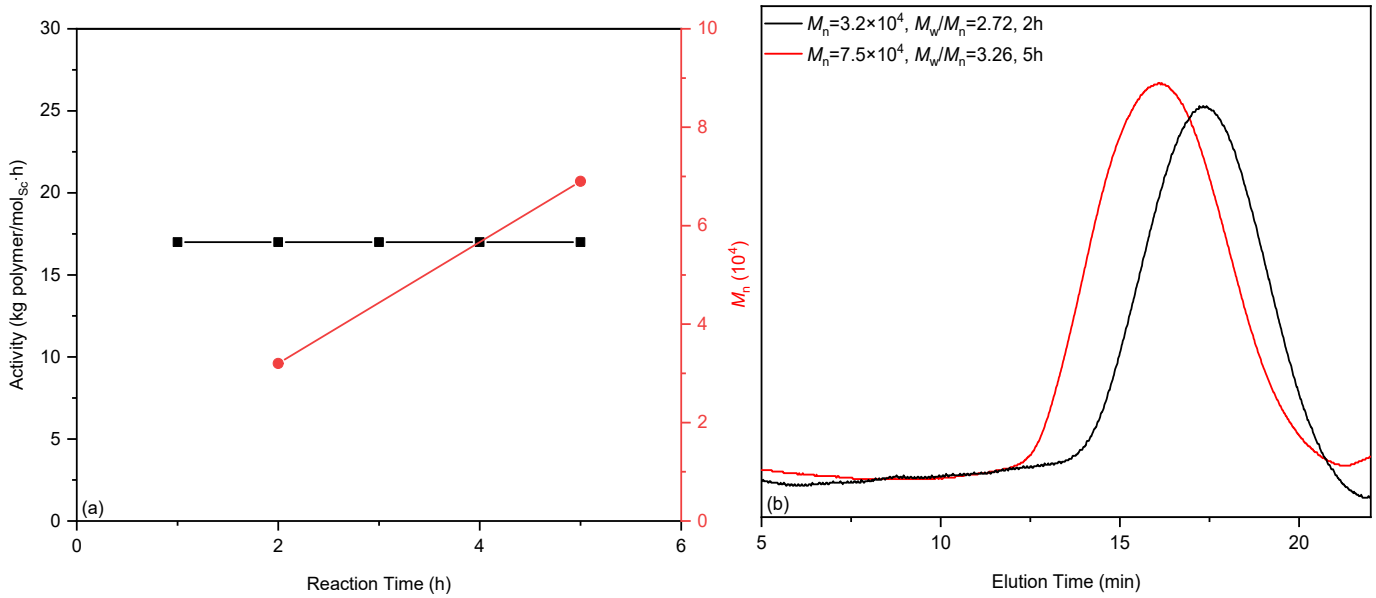

Fig. S10 Polymerization activity and molecular weight of polymer products before the 3rd addition and after the final reaction. (In a glovebox, 2 mmol 1-hexene was added to 12 mL toluene solution of **3b** (5.3 mg, 10 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) every 1 h for a total of five additions. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product before the 3rd addition and after the final reaction.)

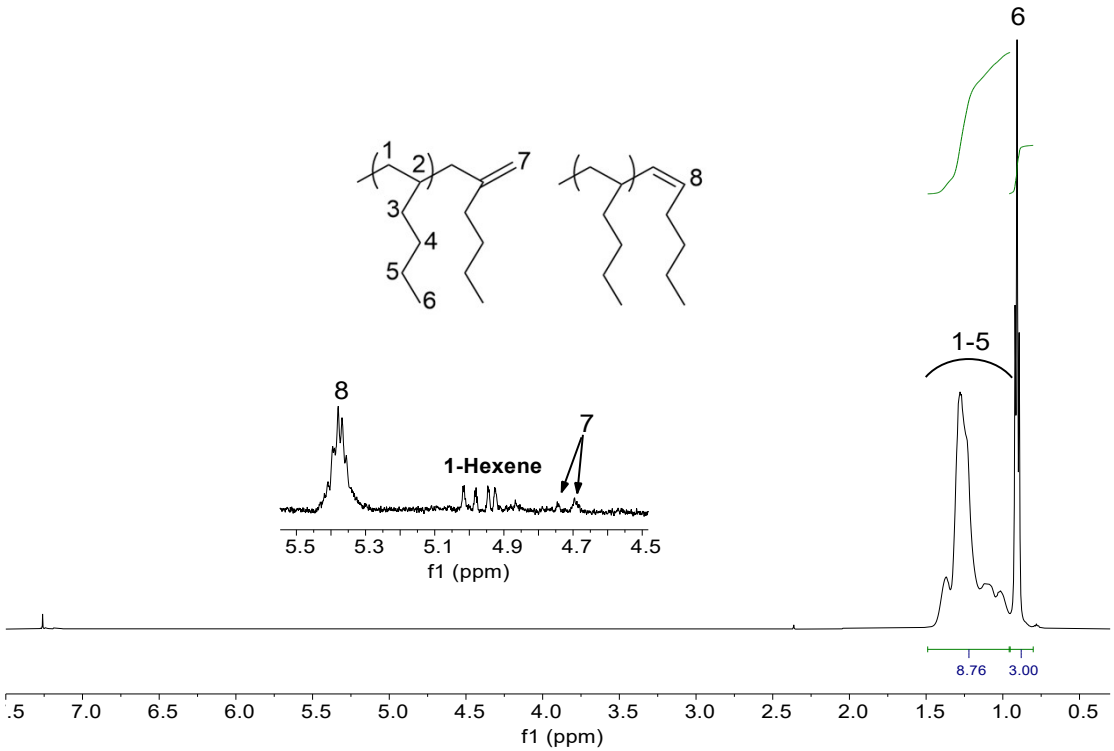

Fig. S11 ^{1}H-NMR spectrum of a 1-hexene homopolymer prepared by **3c** at 25 °C.

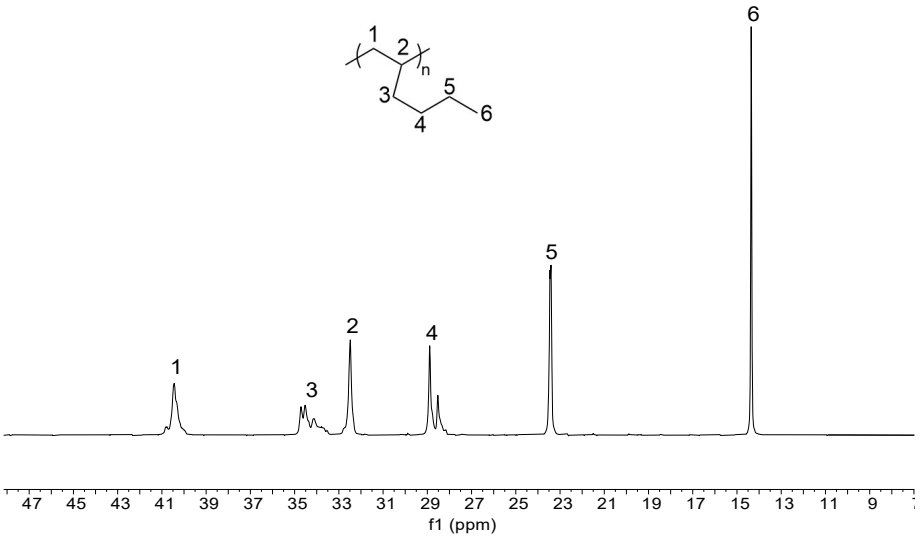

Fig. S12 ^{13}C-NMR spectrum of a 1-hexene homopolymer prepared by complex **3b** at 25 °C.

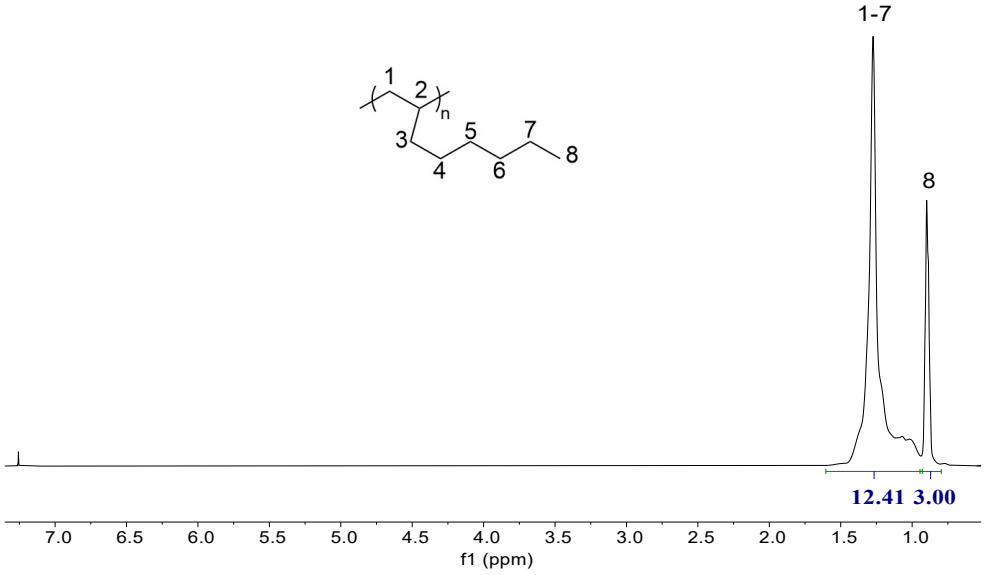

Fig. S13 ^{1}H-NMR spectrum of a 1-octene homopolymer prepared by **3b** at 25 °C.

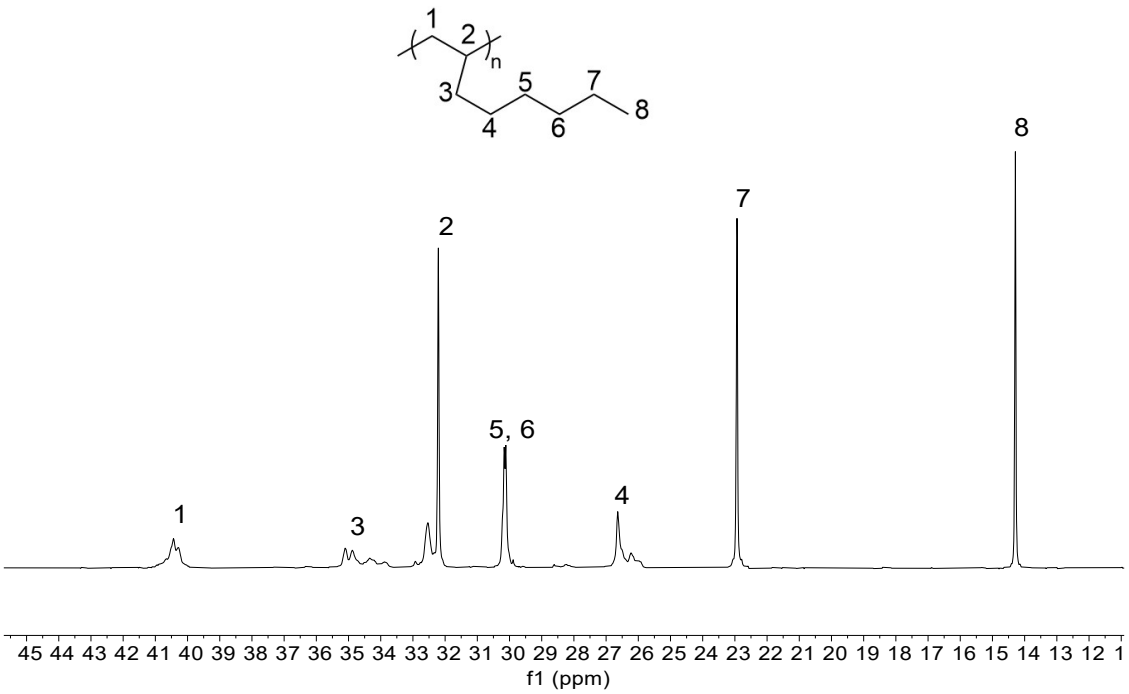

Fig. S14 ^{13}C-NMR spectrum of a 1-octene homopolymer prepared by **3b** at 25 °C.

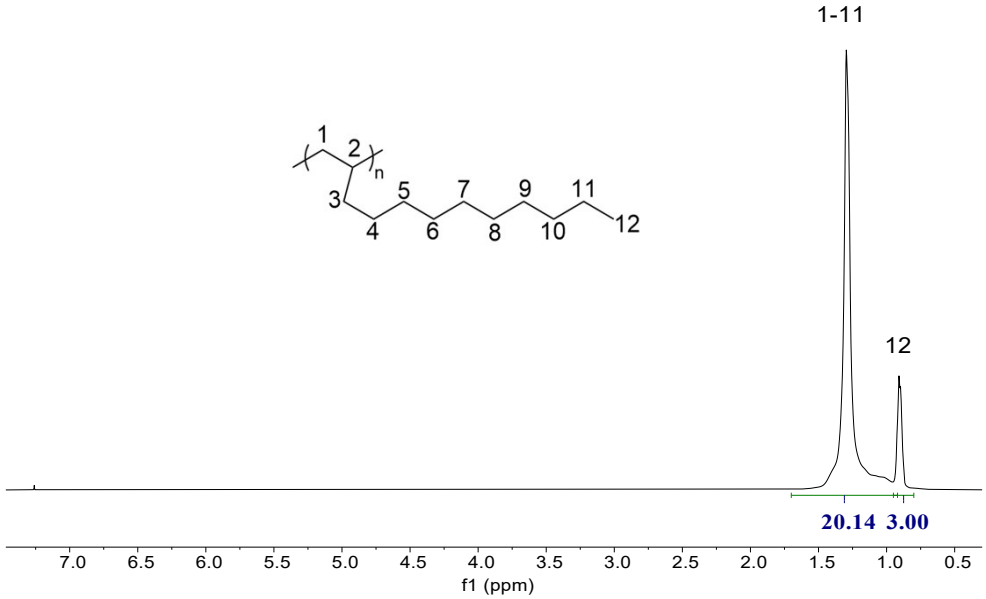

Fig. S15 ^{1}H-NMR spectrum of a 1-dodecene homopolymer prepared by **3b** at 25 °C.

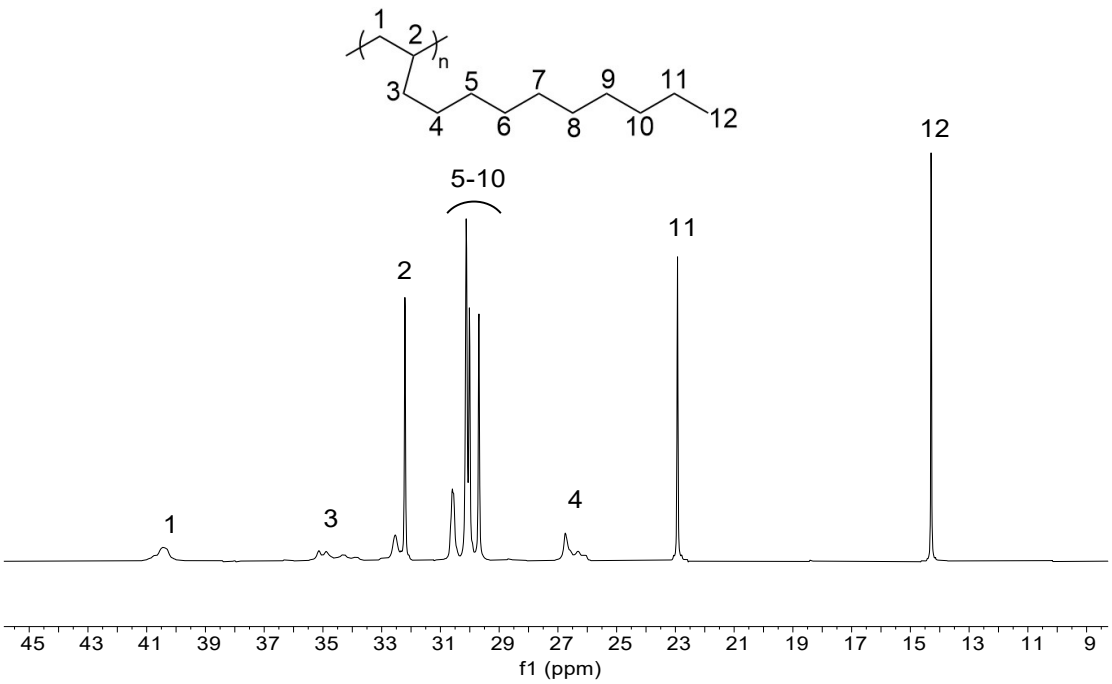

Fig. S16 ^{13}C-NMR spectrum of a 1-dodecene homopolymer prepared by complex **3b** at 25 °C.

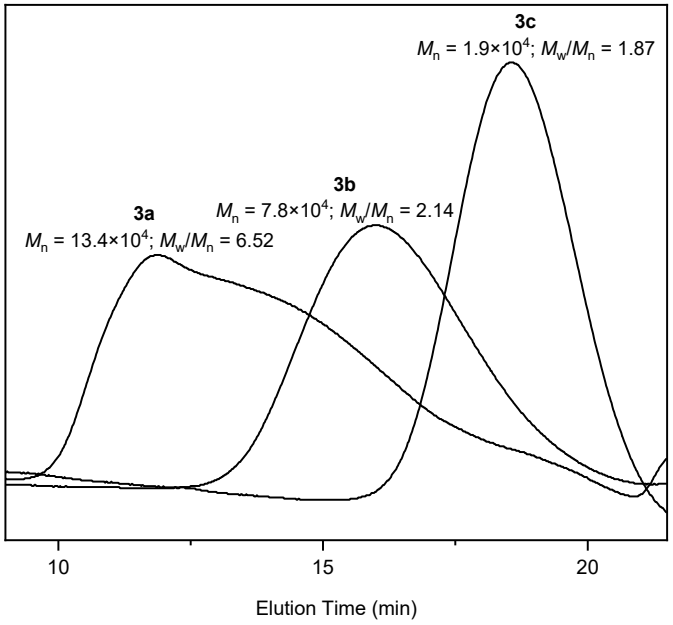

Fig. S17 GPC curves of 1-hexene homopolymers prepared by complexes **3a**, **3b** and **3c** at 25 °C.

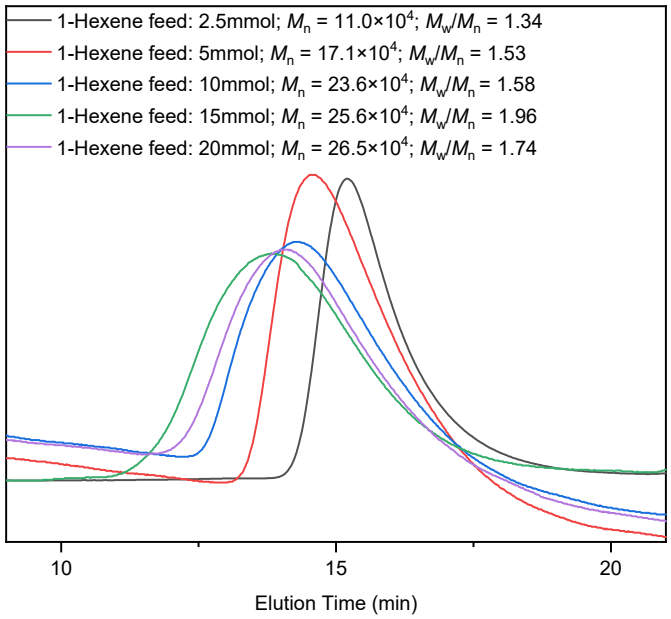

Fig. S18 GPC curves of 1-hexene homopolymers prepared by **1** at -30 °C.

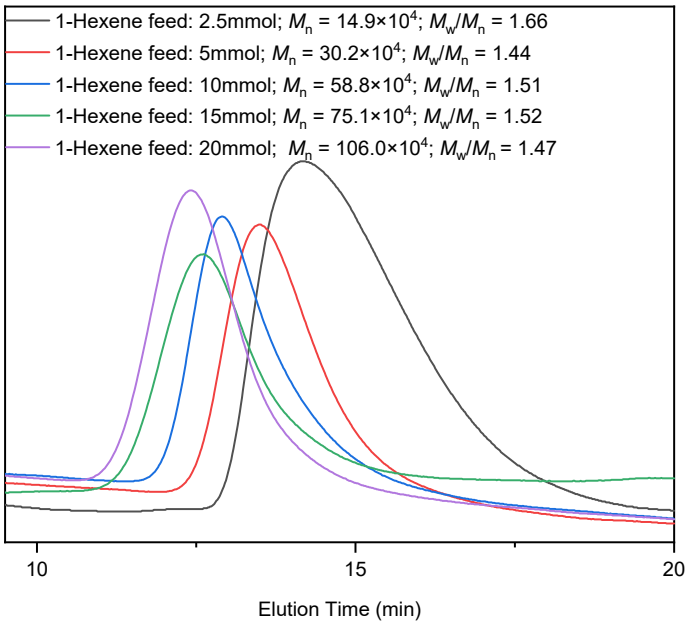

Fig. S19 GPC curves of 1-hexene homopolymers prepared by **2** at -30 °C.

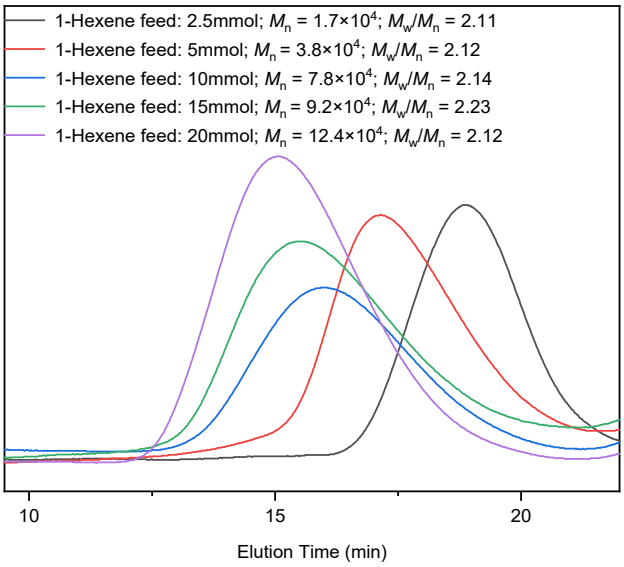

Fig. S20 GPC curves of 1-hexene homopolymers prepared by **3b** at 25 °C.

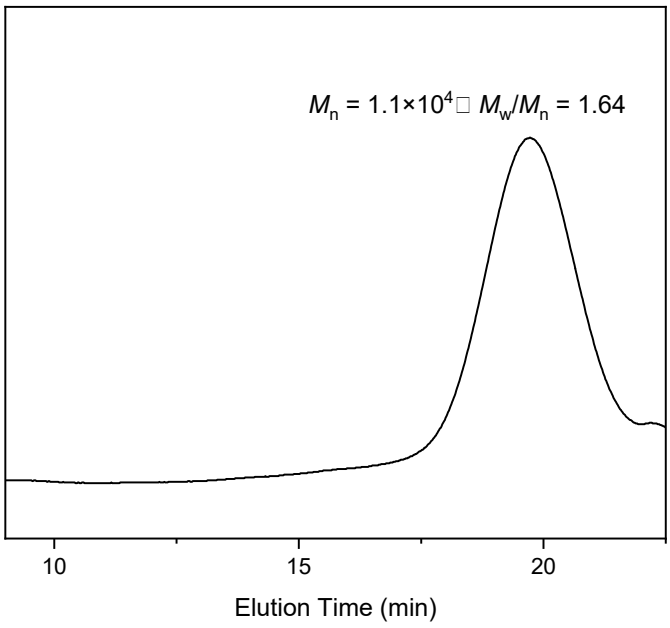

Fig. S21 GPC curves of 1-hexene homopolymers prepared by **3b** at 80 °C.

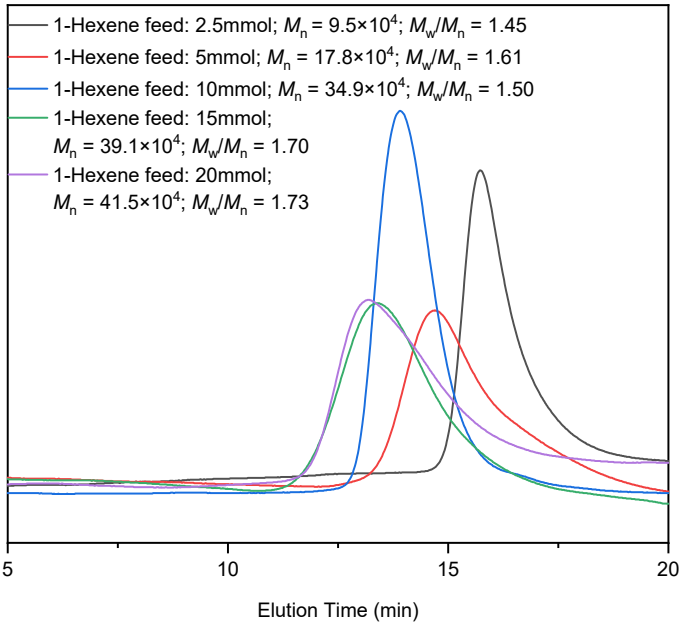

Fig. S22 GPC curves of 1-hexene homopolymers prepared by **3b** at -30 °C.

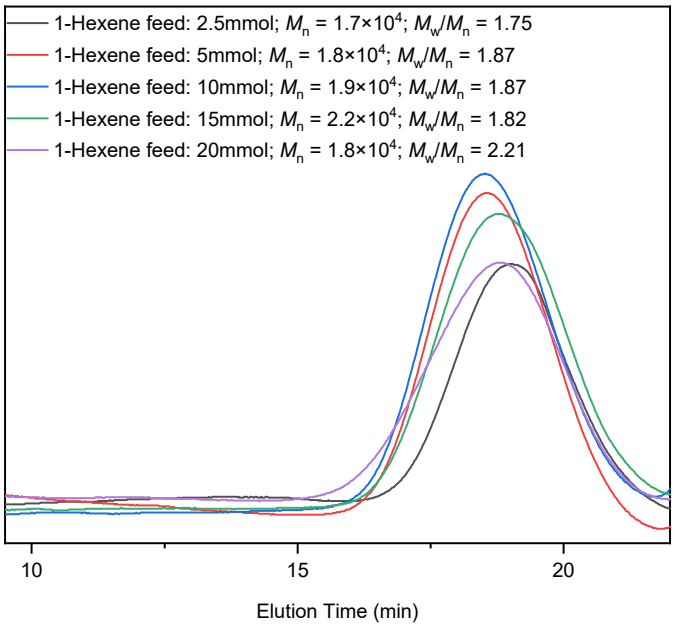

Fig. S23 GPC curves of 1-hexene homopolymers prepared by **3a** at 25 °C.

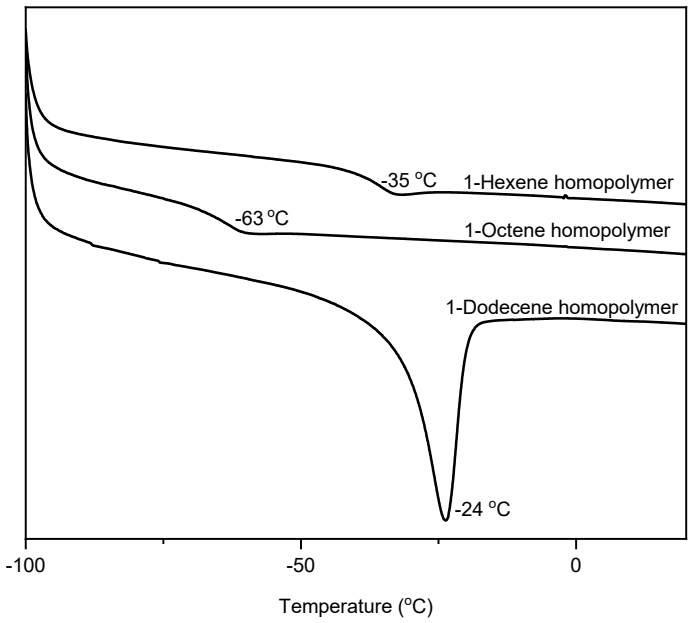

Fig. S24 DSC curves of 1-hexene, 1-octene and 1-dodecene homopolymers prepared by **3b**.

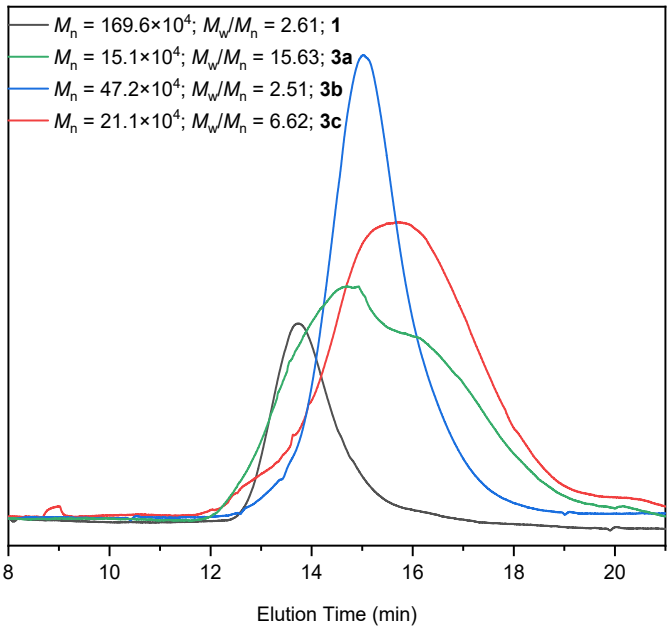

Fig. S25 GPC curves of ethylene homopolymers prepared by **1, 3a, 3b** and **3c**.

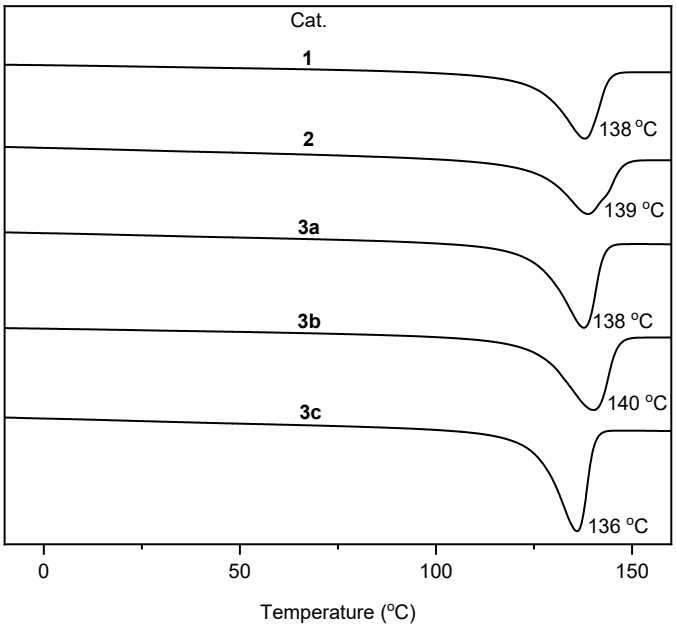

Fig. S26 DSC curves of ethylene homopolymers prepared by **1**, **2, 3a, 3b** and **3c**.

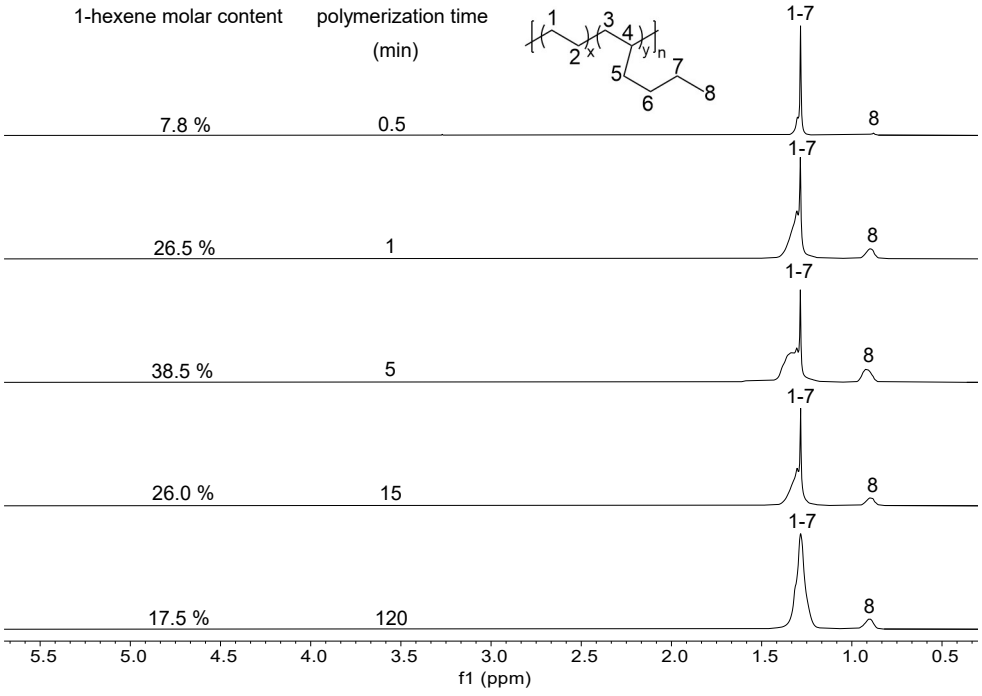

Fig. S27 ^{1}H-NMR spectra of 1-hexene-ethylene copolymers prepared by **3b** with different polymerization time.

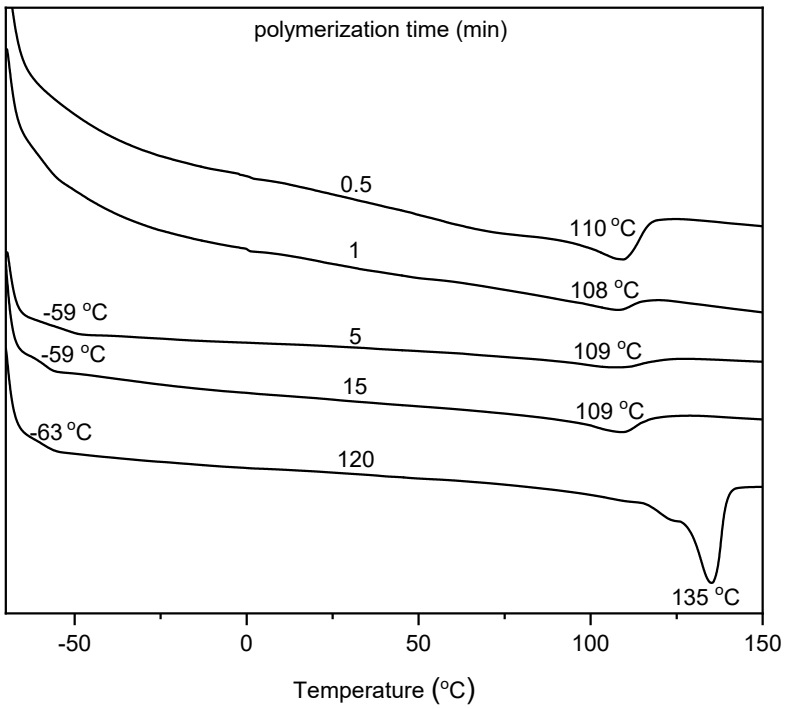

Fig. S28 DSC curves of 1-hexene-ethylene copolymers prepared by **3b** with different polymerization time.

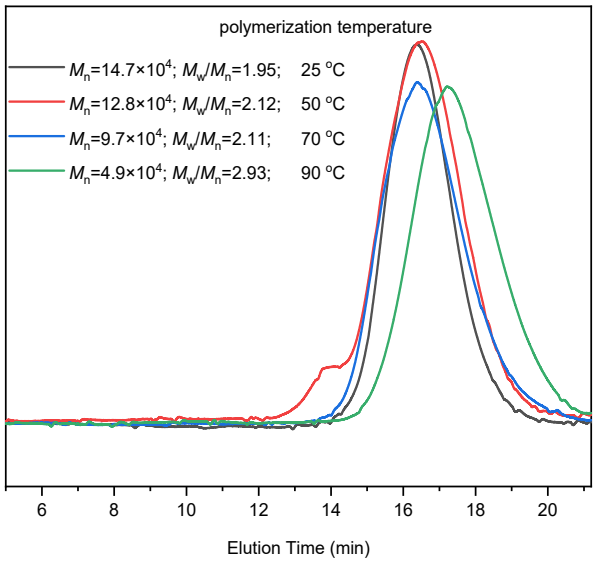

Fig. S29 GPC curves of 1-hexene-ethylene copolymers prepared by **3b** at different temperature.

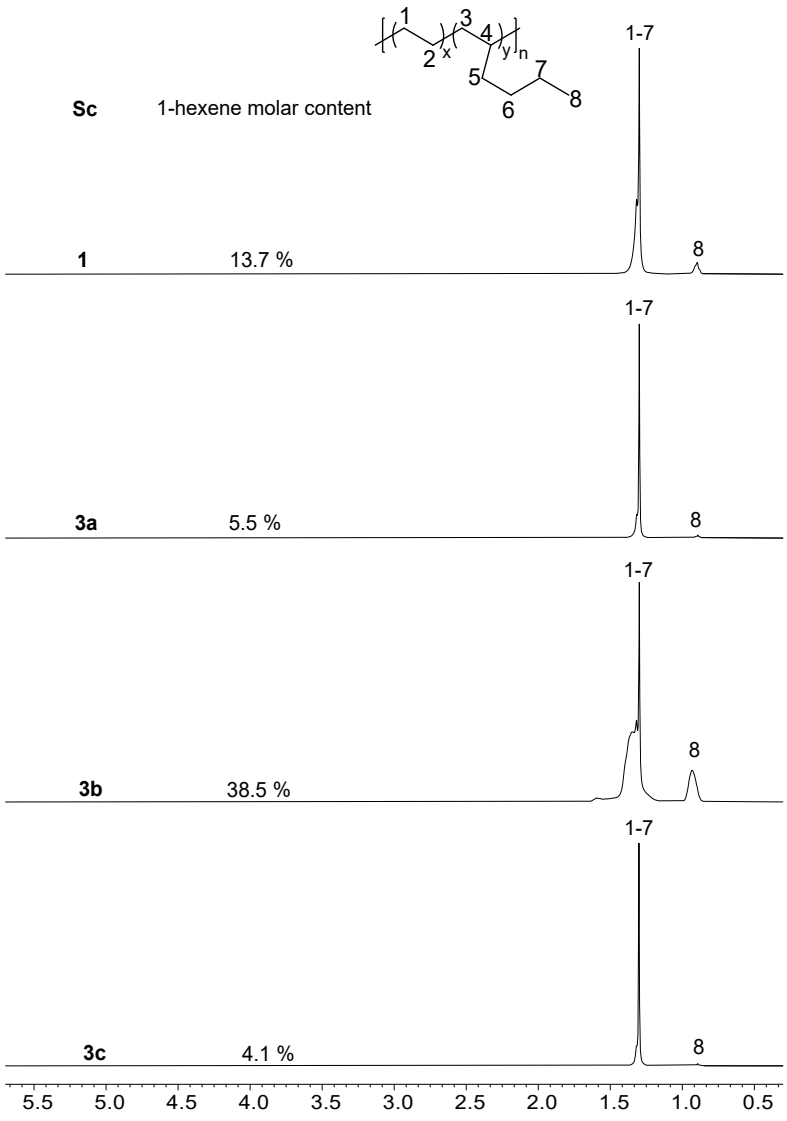

Fig. S30 ^{1}H-NMR spectra of 1-hexene-ethylene copolymers prepared by complex **1**, **3a**, **3b** and **3c**.

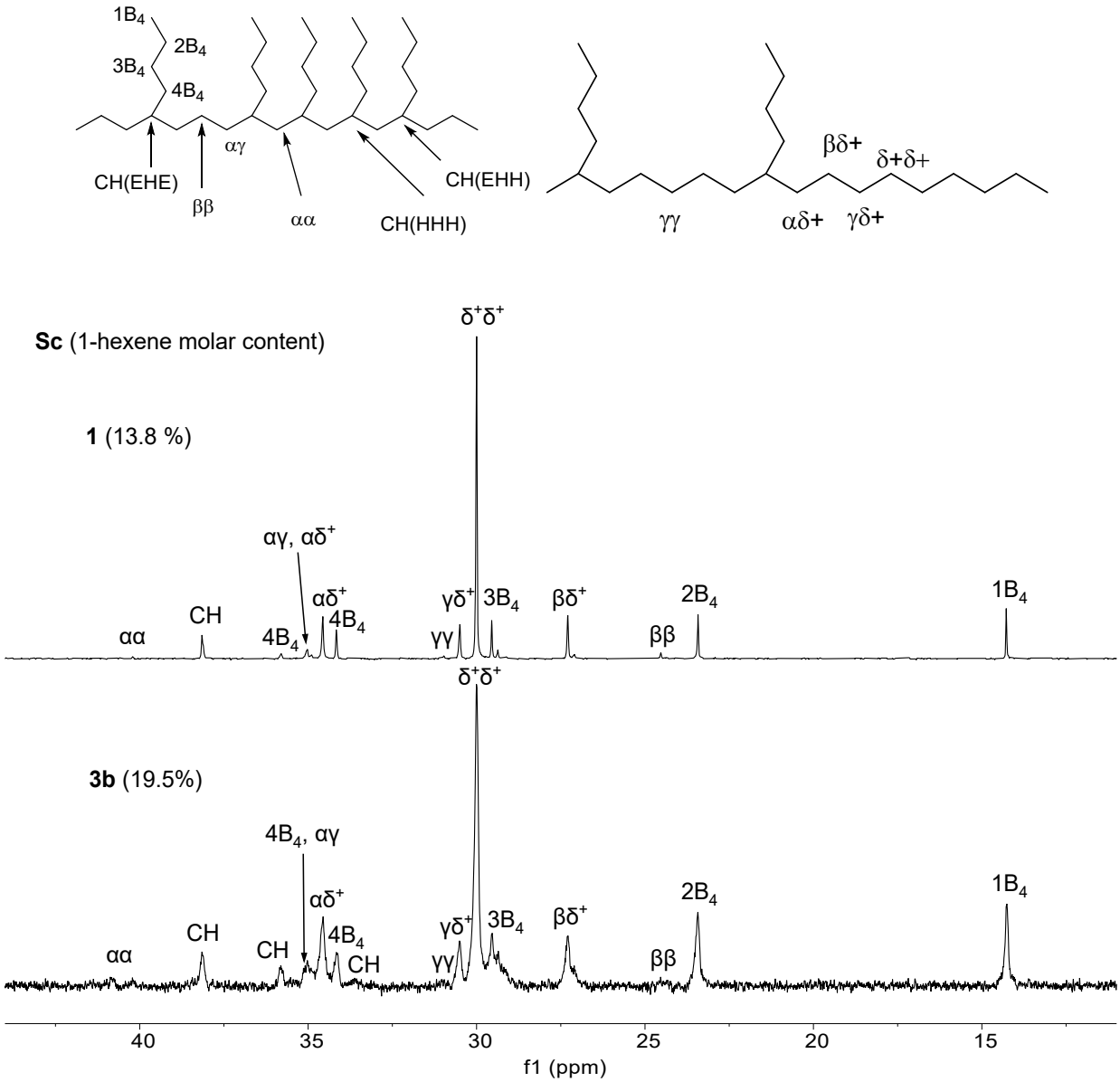

Fig. S31 ^{13}C-NMR spectra of 1-hexene-ethylene copolymers prepared by **1** and **3b.**

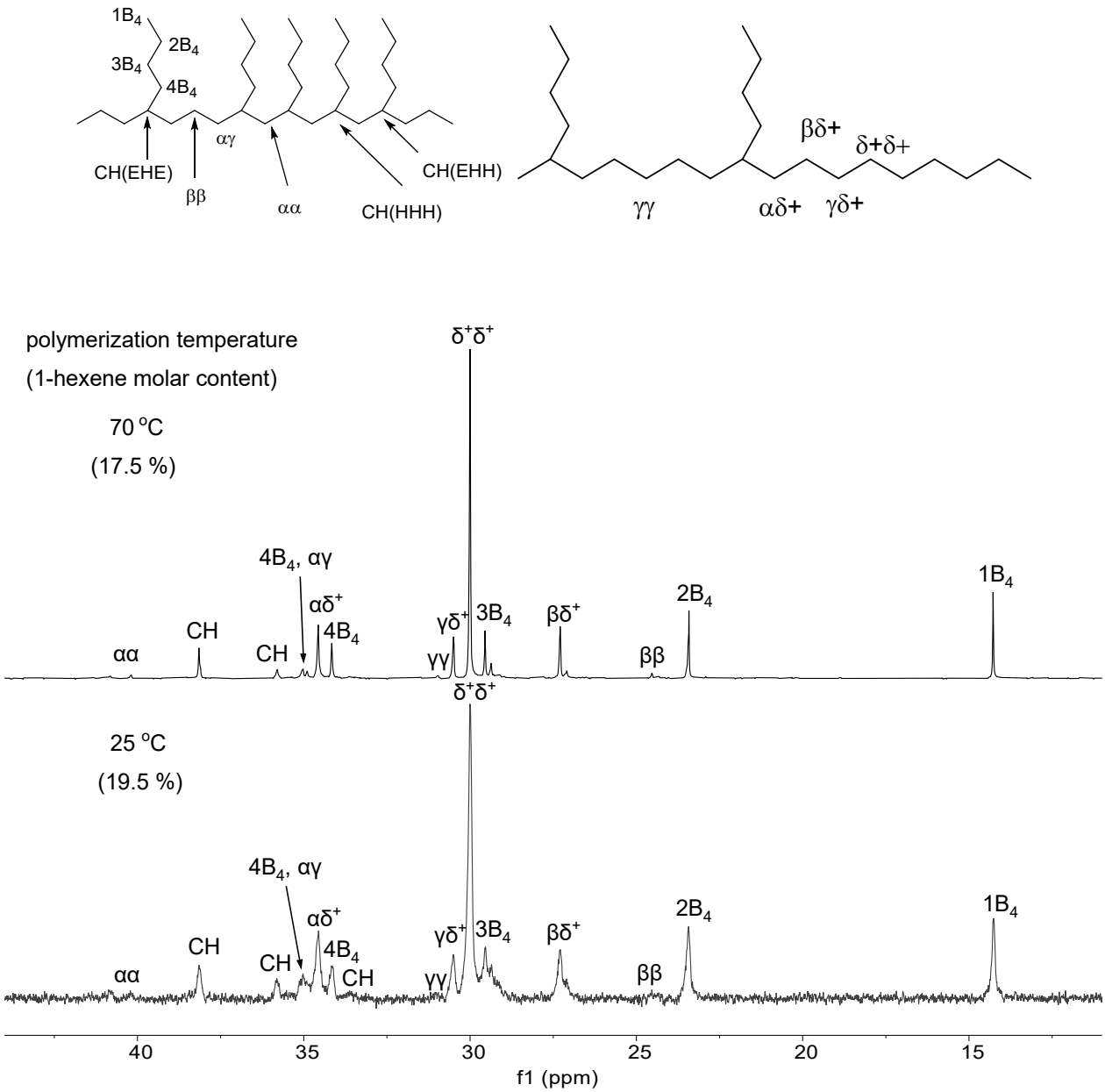

Fig. S32 ^{13}C-NMR spectra of 1-hexene-ethylene copolymers prepared by **3b** at different temperature.

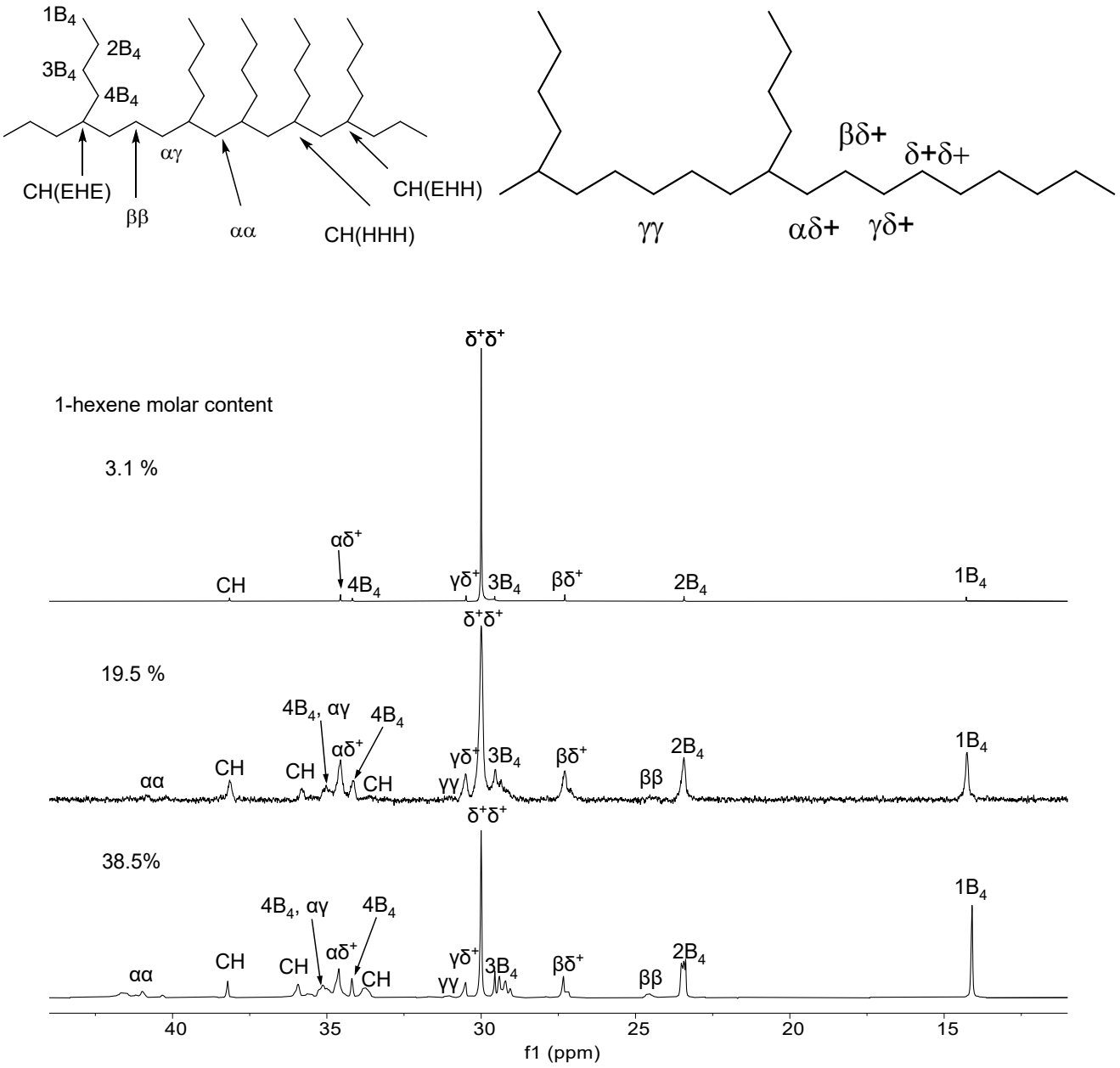

Fig. S33 ^{13}C-NMR spectra of 1-hexene-ethylene copolymers prepared by **3b.**

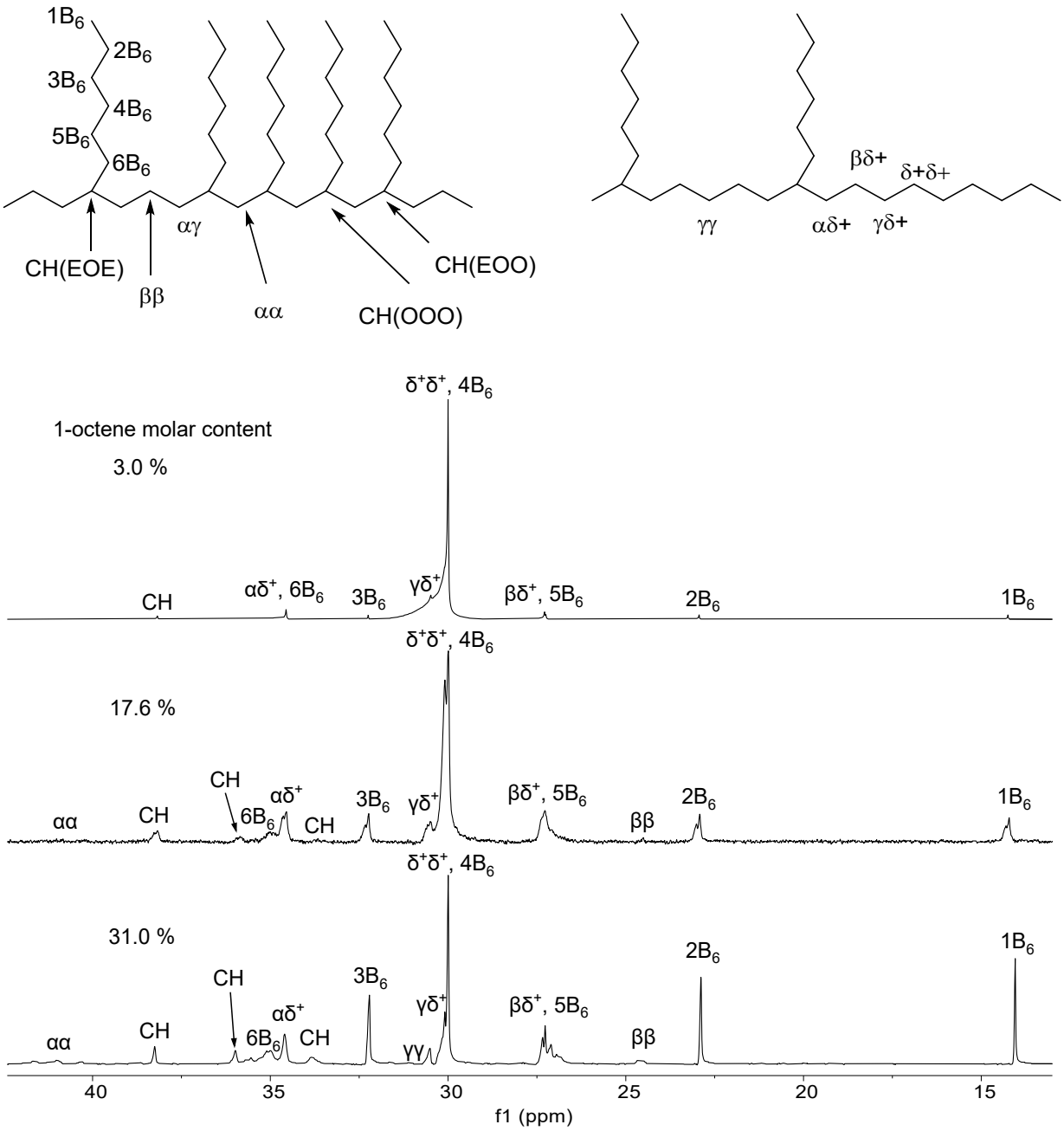

Fig. S34 ^{13}C-NMR spectra of 1-octene-ethylene copolymers prepared by **3b.**

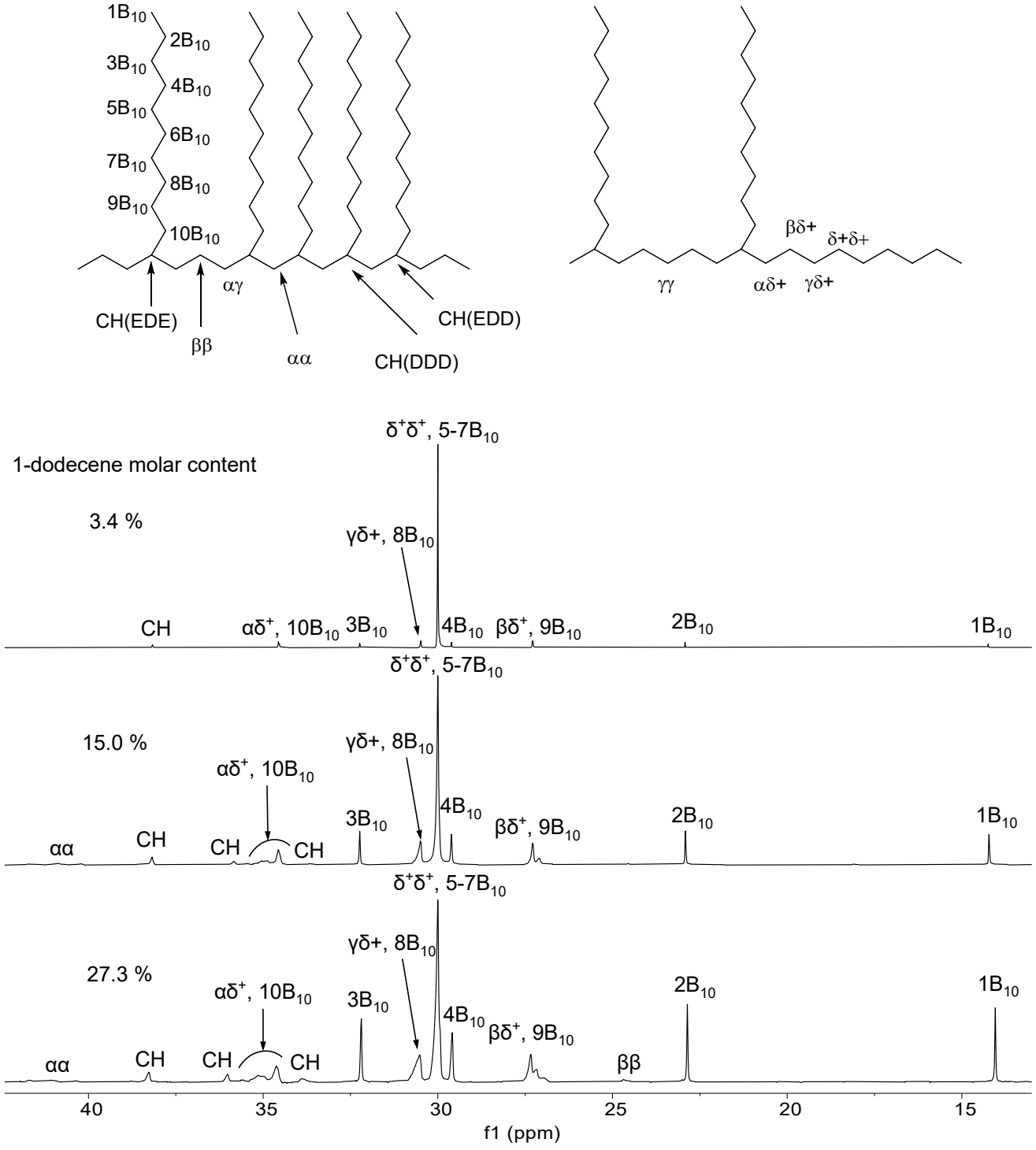

Fig. S35 ^{13}C-NMR spectra of 1-dodecene-ethylene copolymers prepared by **3b.**

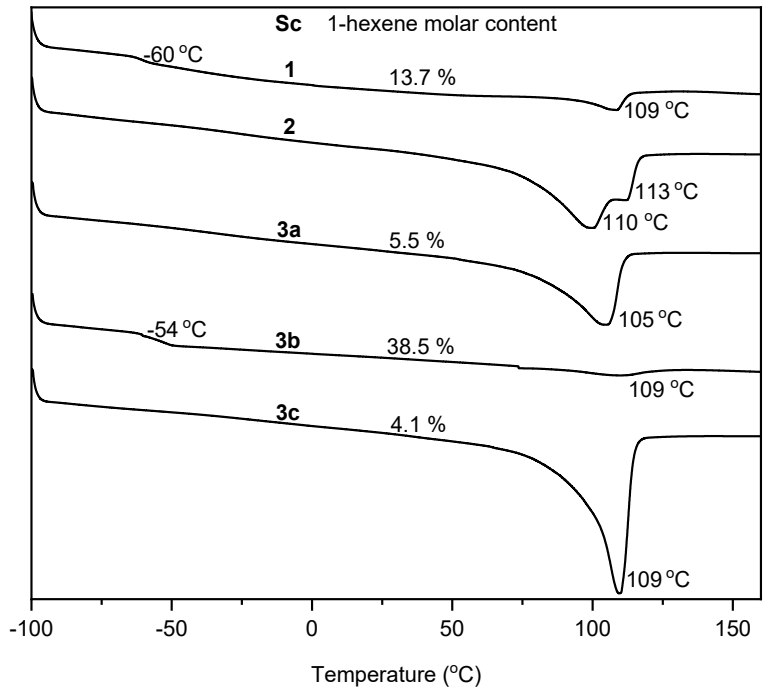

Fig. S36 DSC curves of 1-hexene-ethylene copolymers prepared by **1**, **2**, **3a**, **3b**, **3c**.

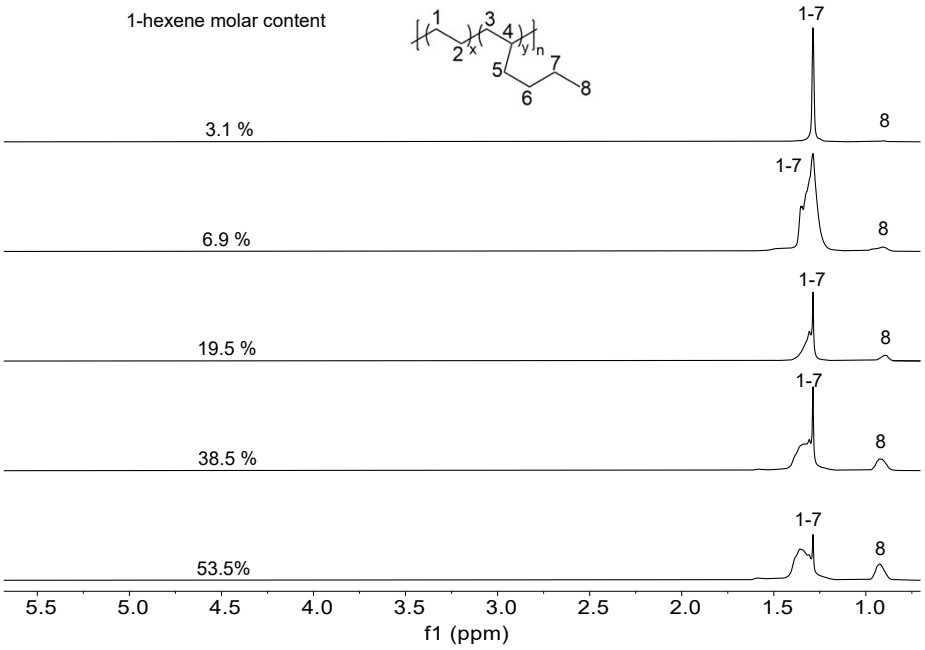

Fig. S37 ^{1}H-NMR spectra of 1-hexene-ethylene copolymers prepared by **3b** with different 1-hexene content.

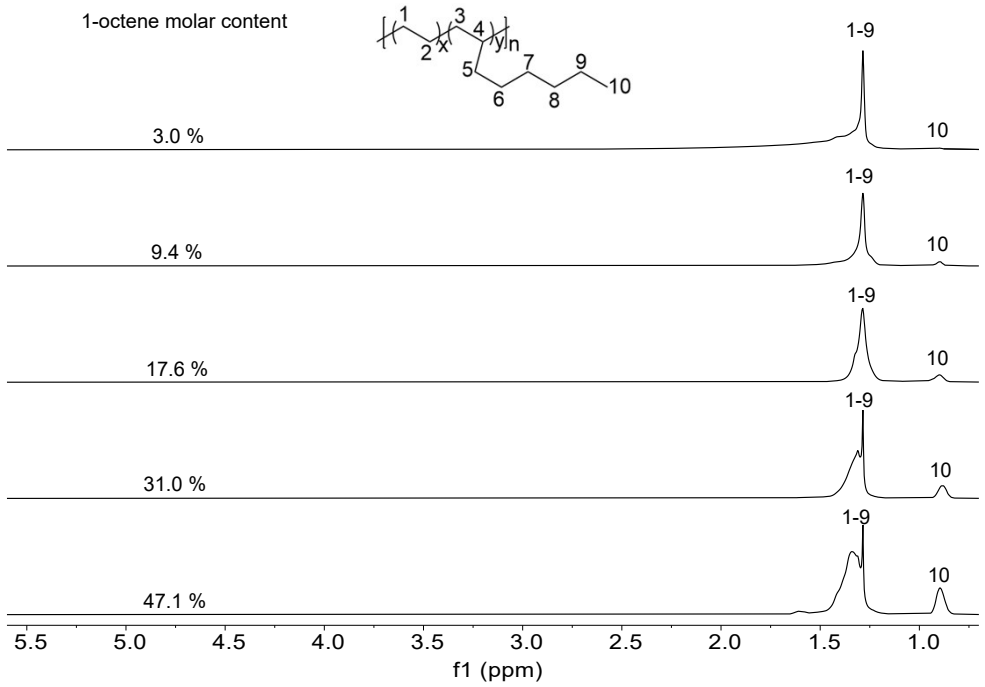

Fig. S38 ^{1}H-NMR spectra of 1-octene-ethylene copolymers prepared by **3b** with different 1-octene content.

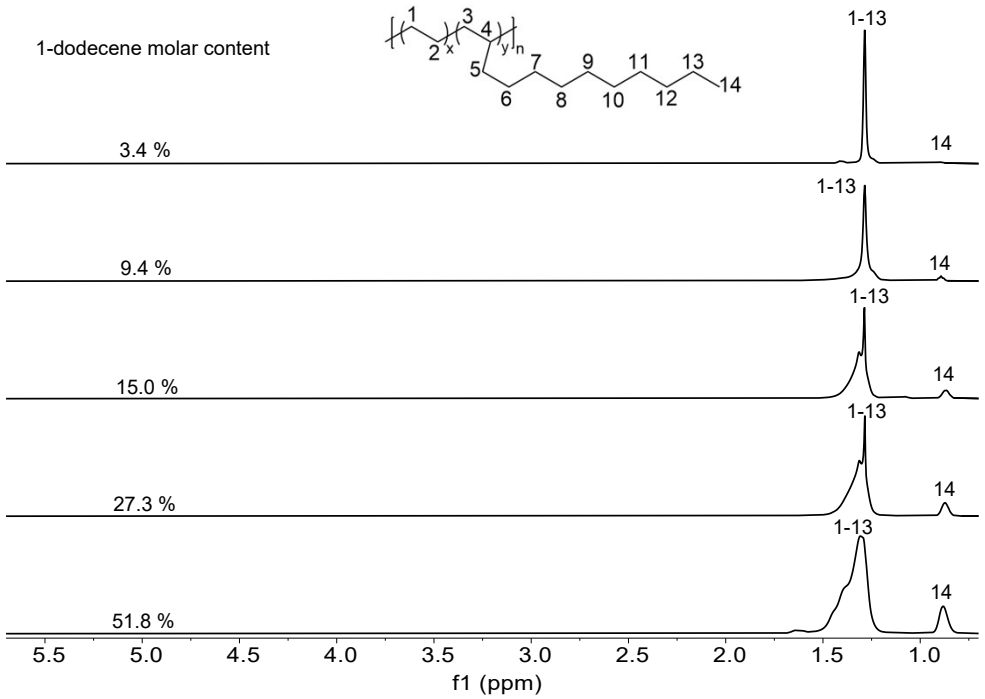

Fig. S39 ^{1}H-NMR spectra of 1-dodecene-ethylene copolymers prepared by **3b** with different 1-dodecene content.

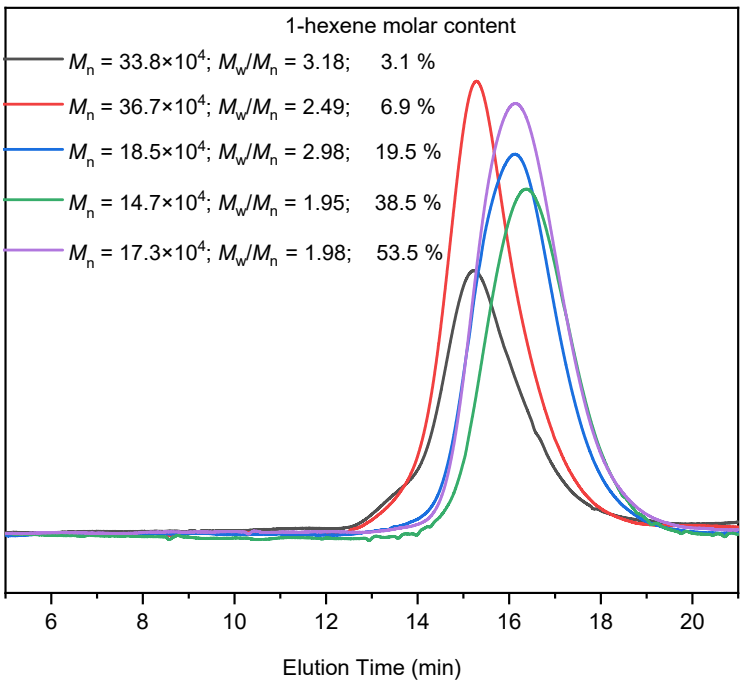

Fig. S40 GPC curves of 1-hexene-ethylene copolymers prepared by **3b** different 1-hexene content.

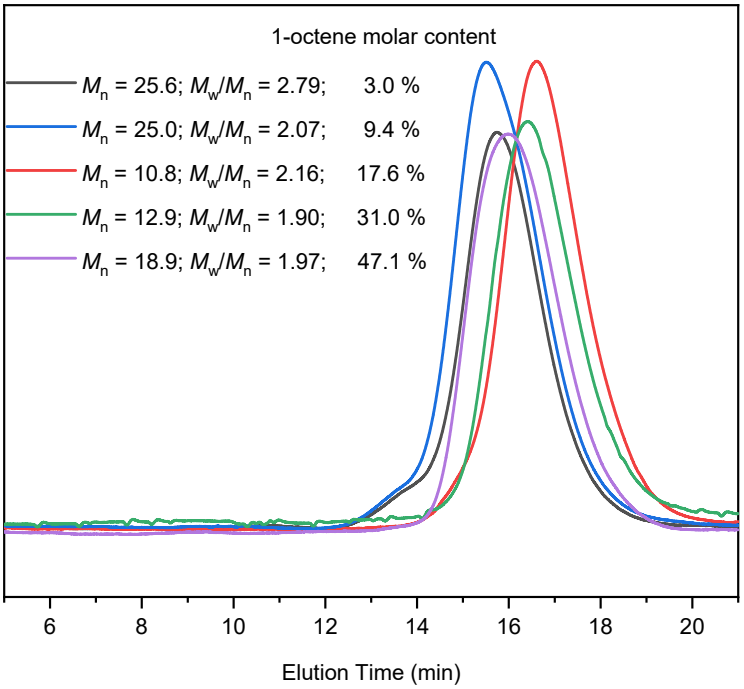

Fig. S41 GPC curves of 1-octene-ethylene copolymers prepared by **3b** with different 1-octene content.

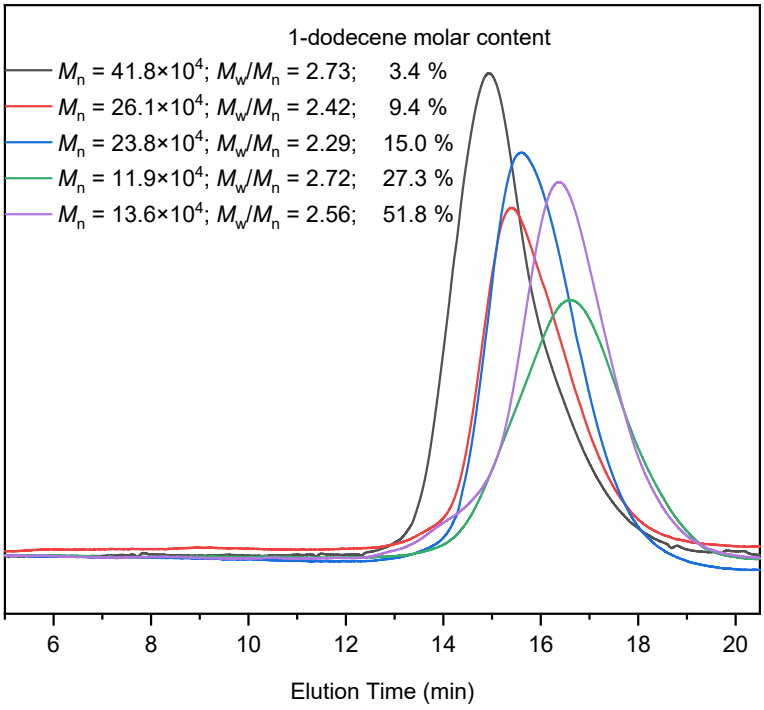

Fig. S42 GPC curves of 1-dodecene-ethylene copolymers prepared by **3b** with different 1-dodecene content.

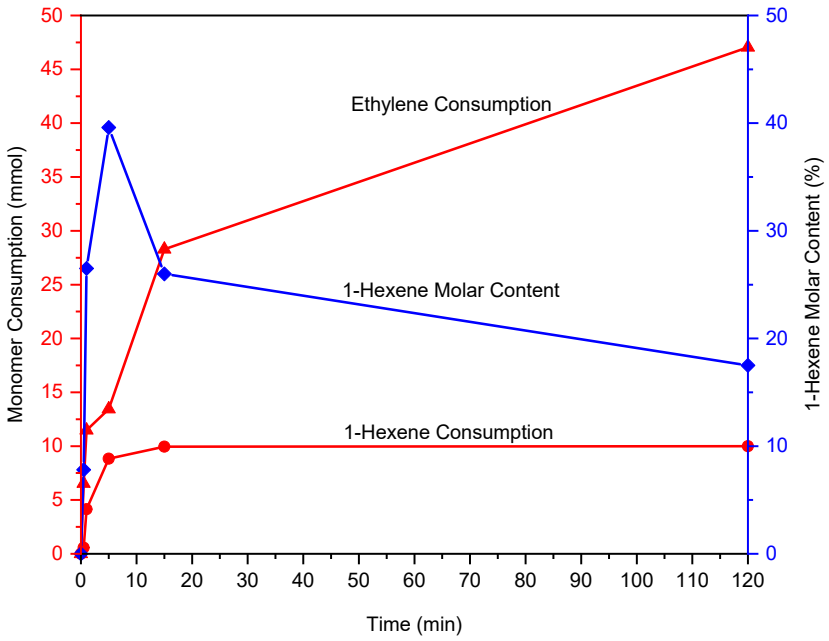

Fig. S43 Plot of ethylene consumption (solid triangle), 1-hexene consumption (solid circle) and 1-hexene molar content (solid diamond) as a function of polymerization time.

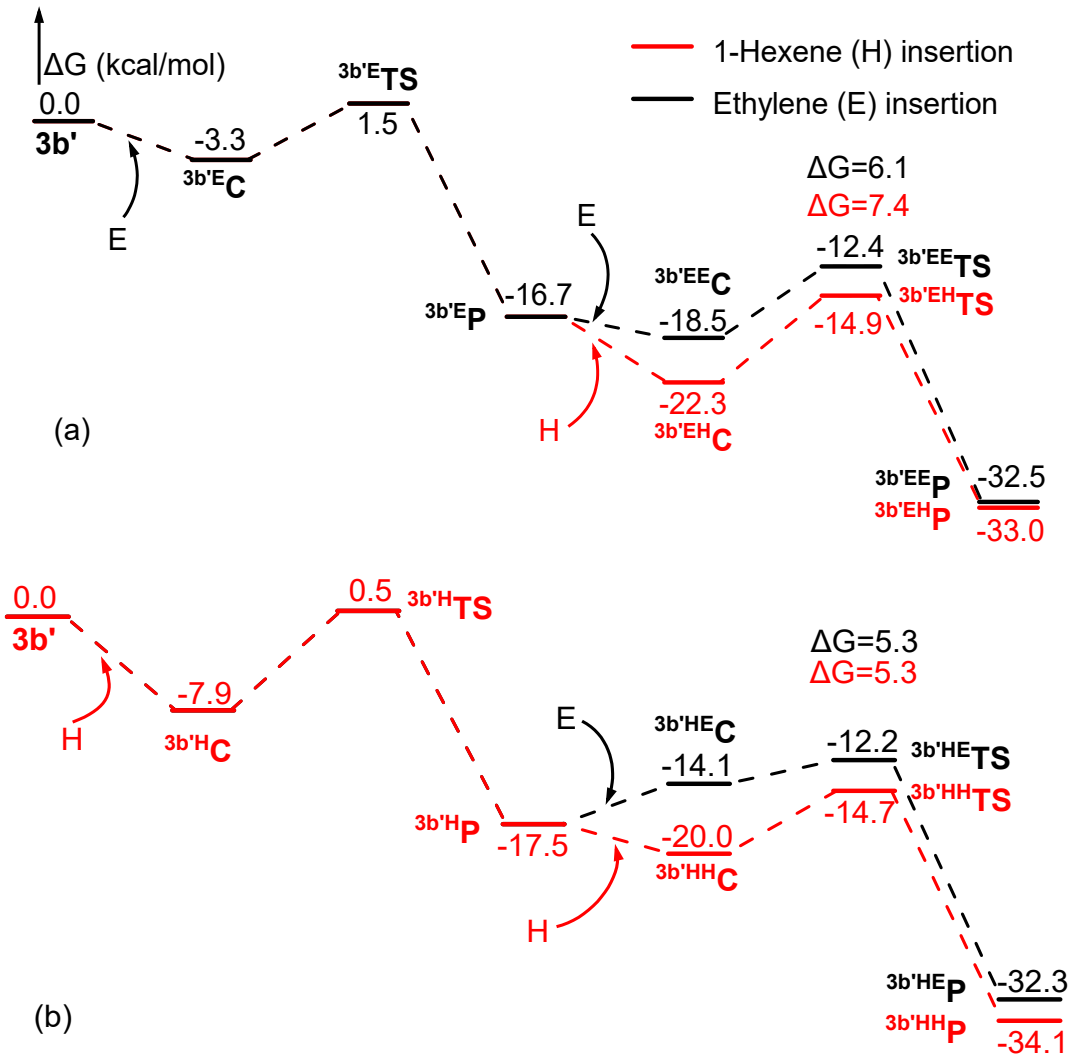

Fig. S44 Computed energy profiles for1-hexene or ethylene insertion after an ethylene insertion into Sc-C bond (a) and1-hexene or ethylene insertion after an 1-hexene insertion into Sc-C bond (b).

Table S1 Crystal data, data collection and processing parameters for complexes **2**, **3a** and **3b**

	2	**3a**	**3b**
Formula	C33 H55 N2 Sc Si3	C31 H47 N2 Sc Si2	C30 H45 N2 Sc Si2
Mw	609.02	548.84	534.82
Crystal system	monoclinic	monoclinic	tetragonal
Space group	$P1_{21/n1}$	$P1_{21/c1}$	$P\text{-}4_{21c}$
a[Å]	11.6387(8)	10.3315(8)	17.6502(16)
b[Å]	17.0971(12)	17.5787(12)	17.6502(16)
c[Å]	19.0816(12)	18.0108(13)	20.387(3)
α[°]	90	90	90
β[°]	93.598(2)	99.520(2)	90
γ[°]	90	90	90
V[Å^3]	3789.5(4)	3226.0(4)	6351.2(14)
Z	4	4	8
ρ_{calcd} [Mg/m^3]	1.067	1.130	1.119
μ [mm^{-1}]	0.311	0.323	0.327
F (000)	1320	1184	2304
θ range [°]	2.45 to 27.68	2.310 to 26.020	2.307 to 27.546
no. of reflns collected	55814	34148	30781
no. of indep reflns	6450	4605	6518
GOF	1.187	1.037	1.267
R [I >2σ (I)]	0.0858	0.0486	0.0609
*R*w	0.1517	0.1137	0.1212

Table S2 Polymerization of 1-hexene by scandium complexes[a]

Run	Cat.	1-hexene (mmol)	T (°C)	t (min)	Yield (%)	Activity[b]	M_n[c](10^4)	M_w/M_n[c]
1	**1**	2.5	-30	30	99	42	11.0	1.34
2	**1**	5	-30	30	93	78	17.1	1.53
3	**1**	10	-30	120	95	40	23.6	1.58
4	**1**	15	-30	120	97	61	25.6	1.96
5	**1**	20	-30	120	95	80	26.5	1.74
6	**2**	2.5	-30	30	99	42	14.9	1.66
7	**2**	5	-30	30	98	82	30.2	1.44
8	**2**	10	-30	120	99	42	58.8	1.51
9	**2**	15	-30	120	90	89	75.1	1.52
10	**2**	20	-30	120	85	71	106.0	1.47
11	**3b**	2.5	25	5	99	252	1.7	2.11
12	**3b**	5	25	5	94	477	3.8	2.12
13	**3b**	10	25	5	95	960	7.8	2.14
14	**3b**	15	25	30	99	250	9.2	2.23
15	**3b**	20	25	30	92	328	12.4	2.12
16	**3b**	2.5	-30	120	99	11	9.5	1.45
17	**3b**	5	-30	120	97	20	17.8	1.61
18	**3b**	10	-30	120	94	39	34.9	1.50
19	**3b**	15	-30	120	91	63	39.1	1.70
20	**3b**	20	-30	120	90	76	40.5	1.73
21	**3c**	2.5	25	120	95	10	1.7	1.75
22	**3c**	5	25	120	92	19	1.8	1.87
23	**3c**	10	25	180	90	25	1.9	1.87
24	**3c**	15	25	720	95	10	2.2	1.82
25	**3c**	20	25	720	95	13	1.8	2.21

[a] Condition: [**Sc**] (10 μmol), $[Ph_3C][B(C_6F_5)_4]$ (10 μmol), monomer concentration (0.83 mol/L). [b] Given in kg polymer $mol^{-1}_{Sc}\cdot h^{-1}$. [c] Determined by GPC.

Table S3 Polymerization of ethylene by scandium complexes [a]

Run	Cat	T (°C)	Yield (g)	Activity[b]	M_n[c](10^4)	M_w/M_n[c]	T_m[d] (°C)
1	**1**	-30	1.18	1416	169.6	2.61	138
2	**2**	-30	0.29	348	n.d.[e]	n.d.	139
3	**3a**	25	0.32	384	15.1	15.63	138
4	**3b**	25	0.95	1140	47.2	2.51	140
5	**3c**	25	0.45	540	21.1	6.62	136

[a] Condition: [**Sc**] (10 μmol), $[Ph_3C][B(C_6F_5)_4]$ (10 μmol), toluene (30 mL), time (5 min), ethylene (0.1 MPa). [b] Given in kg polymer $mol^{-1}_{Sc}\cdot h^{-1}$. [c] Determined by GPC. [d] Determined by DSC. [e] not determined because of the very low solubility in organic solvents.