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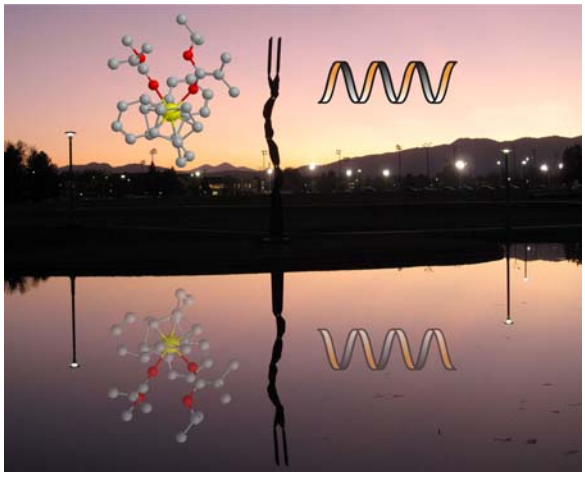

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Synthesis, characterization, and catalytic behaviours of β-carbonylenamine-derived [O⁻NS]TiCl$_3$ complexes in ethylene homo- and copolymerization†

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A series of [O⁻NS]TiCl$_3$ complexes **5a–l** derived from β-carbonylenamine were synthesized and characterized. In the presence of modified methylaluminoxane (MMAO), complexes **1**, **5a–i** and **5l** are highly active for ethylene polymerization and copolymerization of ethylene with 1-hexene, CPE and NBE. Up to 5.12×10^6 g mol^{-1} h^{-1} atm^{-1} of activity for the copolymerization of ethylene with 1-hexene is achieved with a 28.9 mol% incorporation ratio.

Introduction

Development of effective catalysts for olefin polymerization and copolymerization is of great interest in both basic research and industrial applications since the discovery of the Ziegler–Natta catalyst.[1-3] Recently, considerably attention has been paid to single-site non-metallocene catalysts due to their elegant capability to catalyze the olefin polymerization and the copolymerization of ethylene with α-olefins[4] or cycloolefins[5,6] allowing access to previously inaccessible polymers.[7]

In our studies on the design and synthesis of olefin polymerization catalysts,[8] we reported salicylaldiminato-derived [O⁻NX]TiCl$_3$ (Fig. 1) complexes and their applications in olefin polymerization in the presence of MMAO. Generally, it is found that [O⁻NX]TiCl$_3$/MMAO are highly active for ethylene polymerization and for the copolymerization of ethylene/α-alkenes and ethylene/cycloalkenes such as norbornene and dicyclopentadiene.[8b–f] For such catalysts, steric hindrance around titanium proves crucial for the copolymerization performance.[8b–e] For instance, when X group was changed from –SPh to –SMe, the copolymerization activity of ethylene/norbornene increased 10 times. We also developed a simple one pot method for the screening of new titanium catalyst. This method allows us to combine β-carbonylenamines with TiCl$_4$(THF)$_2$ *in situ* for direct activity evaluation. By this strategy, titanium complex **1** (Fig. 2) was synthesized and proved to be highly active toward ethylene polymerization.[8g] Based on these results, the newly-designed β-carbonylenamines-derived titanium complexes **5a–l** were synthesized very recently. Further studies show that such complexes exhibit better copolymerization capability than the corresponding salicylaldehyde-derived complexes, especially in the copolymerization of ethylene with cycloolefins. In this paper, we will report the synthesis, characterization of the complexes as well as their polymerization behaviours upon activation with MMAO in detail.

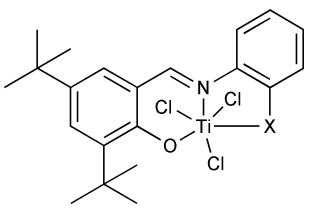

Fig. 1 Salicylaldiminato-derived [O⁻NX]TiCl$_3$.

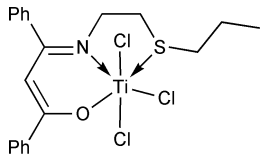

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Fig. 2 β-Carbonylenamine-derived complex **1**.

Results and discussion

Synthesis of [O⁻NS]TiCl$_3$ 5a–l

The desired β-carbonylenamine **4a–l** were readily available from the corresponding 1,3-diketones. Under the reaction conditions without optimization, as shown in Table 1, **4a–l** could be prepared in moderate to good yields by treatment of diketones with amines in the presence of catalytic amount of 4-methylbenzenesulfonic acid (TsOH) in toluene.

Complexes **5a–l** were synthesized in two ways (Scheme 1). One is to prepare the titanium complexes by the reaction of β-carbonylenamine with TiCl$_4$ directly in the absence of base. 1.2 equiv. of TiCl$_4$ was mixed with 1.0 equiv. of the corresponding enamine in toluene at −78 °C. The resulting mixture was warmed to room temperature. After stirring for the desired time, the pure complex was obtained in high yield by removal of the solvent, the excess amount of TiCl$_4$ and the produced HCl *in vacuo* (method

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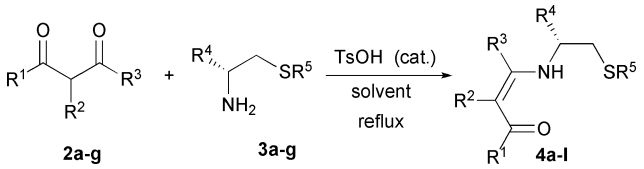
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra along with X-ray crystallographic data. CCDC reference numbers 734045 and 734047. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b910868h

Table 1 Synthesis of β-carbonylenamine **4a–l**[a]



2, 3, 4	R^1	R^2	R^3	R^4	R^5	Yield (%)[b]
2a, **3a**, **4a**	Ph	H	Ph	H	Me	77
2a, **3b**, **4b**	Ph	H	Ph	H	^{i}Pr	50
2a, **3c**, **4c**	Ph	H	Ph	H	^{n}C$_8$H$_{17}$	55
2a, **3d**, **4d**	Ph	H	Ph	H	^{n}C$_{18}$H$_{37}$	61
2a, **3e**, **4e**	Ph	H	Ph	H	Ph	77
2b, **3f**, **4f**	Ph	H	Me	H	^{n}Pr	75
2c, **3f**, **4g**	Ph	H	*p*-CF$_3$C$_6$H$_4$	H	^{n}Pr	67
2d, **3f**, **4h**	*p*-CH$_3$C$_6$H$_4$	H	*p*-CH$_3$C$_6$H$_4$	H	^{n}Pr	77
2e, **3f**, **4i**	*p*-OCH$_3$C$_6$H$_4$	H	*p*-OCH$_3$C$_6$H$_4$	H	^{n}Pr	78
2f, **3f**, **4j**	Ph	Bn	Ph	H	^{n}Pr	37
2g, **3f**, **4k**	Ph	Me	Ph	H	^{n}Pr	41
2a, **3g**, **4l**	Ph	H	Ph	^{i}Pr	^{n}Pr	32

[a] Reaction conditions: 1,3-dione **2** (12.0 mmol), amine **3** (11.0 mmol), toluene (25 mL), 4-methylbenzenesulfonic acid hydrate (0.062 g, 0.33 mmol), refluxing for 3 d. [b] Isolated yield.

A in Scheme 1). Of the complexes shown in Scheme 1, **5a**, **5c–d** and **5f–i** were prepared by this method. The second one is by the deprotonation of β-carbonylenamine with KH, followed by the treatment with $TiCl_4$ (method B in Scheme 1). Complexes **5b**, **5e** and **5j–5l** were prepared in moderate yields by method B.

Characterization of β-carbonylenamines 4a-l and complexes 5a–l

The structures of the compounds **4a–e** and **4h–l** that are derived from the symmetric diketones were well-characterized by ^{1}H, ^{13}C NMR, MS, elemental analysis, and IR. The ^{13}C NMR spectra of β-carbonylenamines **4a–i** and **4l** display a signal at around δ 188 ppm, which is assigned to be C=O group. Substituents at R^2 position (**4j** and **4k**) cause downfield chemical shift of carbonyl group to *ca.* 196 ppm. In the case that 1-phenylbutane-1,3-dione was employed for the preparation of enamine, noticeably, only one product **4f** was isolated but it was difficult to determine the structure by ^{1}H NMR and ^{13}C NMR since both carbonyl groups might react with amine. Fortunately, crystal of a similar enamine **4m** suitable for X-ray analysis,[9] which is made from the same diketone as **4f** used, were developed from ethanol. As shown in Fig. 3, X-ray crystallographic analysis shows clearly that **4m** was the product that acetyl group of **2b** reacted with amine. In the molecular structure of **4m**, H–N1–C7–C8–C9–O1 form a six member ring *via* an intramolecular hydrogen bond between H and O1. The C9–O1 bond length is 1.254(4) Å, much shorter than the typical C–O single bond. C7–N1 bond length is 1.351(5) Å, showing clearly that the C–N bond is a single bond. Thus, **4m** exists in β-carbonylenamine form. Combining these results together with the fact that ^{13}C NMR signals of the carbonyl group and N–C=C unit in **4m** are similar to the correspondent in **4f** (188.93 *vs.* 187.66 and 163.21 ppm *vs.* 164.14 ppm), the structure of **4f** was determined. The diarylketone **2c** reacted with amine **3f** affording a mixture with a ratio of 1/2, which could not be separated by column chromatography. Fortunately, the mixture of enamines could be used for the preparation of complex **5g**

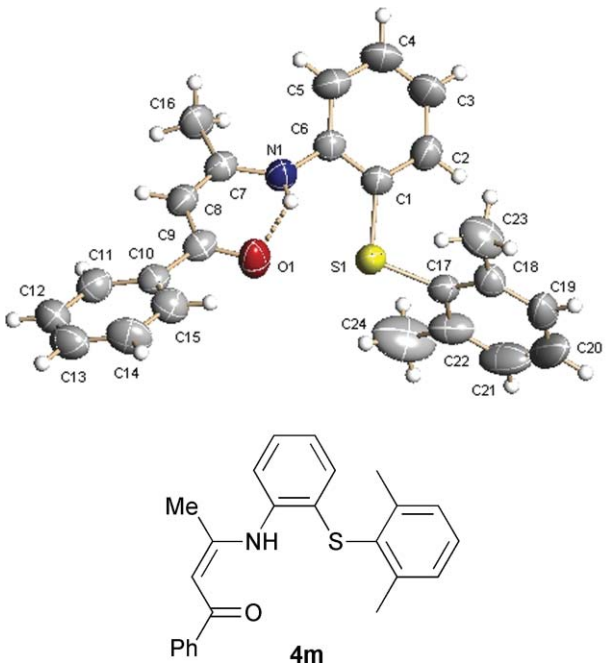
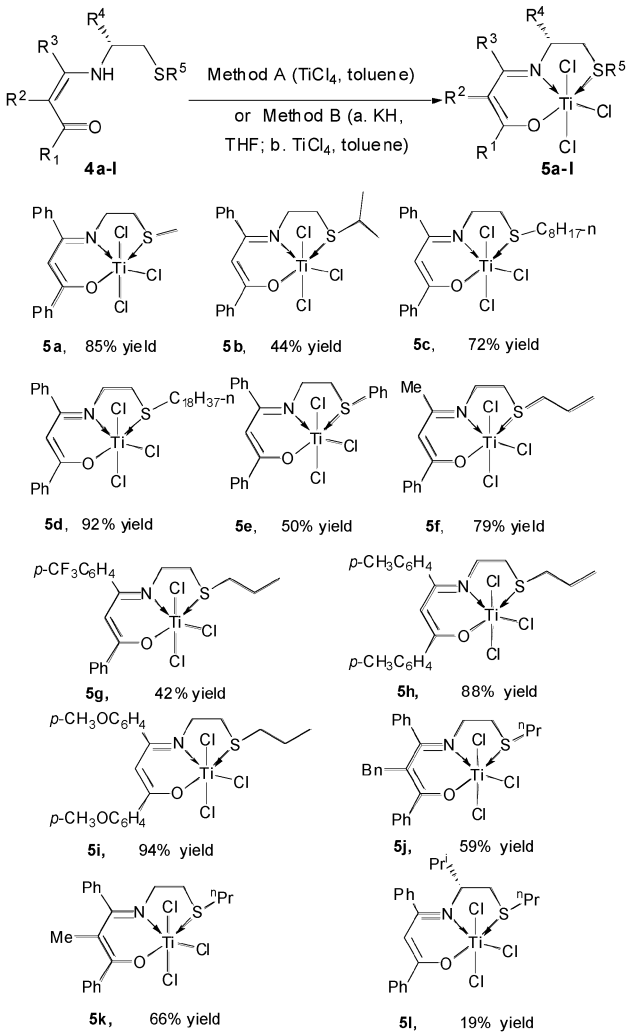


Fig. 3 The molecular structure of **4m**. Selected bond lengths (Å) and angles (°): S1–C1, 1.763(4); O1–C9, 1.254(4); N1–C7, 1.351(5); N1–C6, 1.420(5); C7–C8, 1.362(5); C8–C9, 1.419(5); C1–S1–C17, 105.91(19); C7–N1–C6, 130.2(4); C1–S1–C17, 105.91(19).

and its purification was performed readily by recrystallization in toluene.[10]

The structures of the complexes **5a–l** were also well-characterized by ^{1}H, ^{13}C NMR, elemental analysis, and IR. From ^{13}C NMR analysis of titanium complexes **5**, the chemical shift higher than 180 ppm was disappeared and two signals at around 170 ppm were observed, suggesting no carbonyl group in the complexes. This observation is consistent with the X-ray study of **5b**.[9] As shown in Fig. 4, X-ray crystallographic analysis of **5b**



Method A: -78 ºC to r.t, toluene, 1.2 equiv. $TiCl_4$; **5a**, **5c-5d** and **5f-5i** were prepared by method A. Method B: (a) -78 ºC to r.t, THF, 1.2 equiv. KH; (b) -78 ºC to r.t, toluene, 1.2 equiv. $TiCl_4$. **5b**, **5e**, **5j-5l** were prepared by method B.

Scheme 1 Synthesis of complexes **5a–l**.

revealed that the ligand coordinated titanium atom with enolate oxygen, imine nitrogen, and sulfur atom. C9–O1 and C7–N1 bond lengths are 1.330(3) Å and 1.309(4) Å, respectively. The geometry around titanium atom is a distorted octahedral with three chlorine ligands in a *mer* disposition. Of which, the bond angles of Cl1–Ti–Cl3, Cl2–Ti–Cl3, and Cl1–Ti–Cl2 are 165.43(4), 93.68(4), and 93.26(4)°, respectively. This geometry is favorable for the olefin coordination and insertion. The sulfur atom in **5b** is sp^3-hybridized, with S1–C2 being roughly perpendicular to the S1-containing five-membered ring. The Ti–S1 bond length is 2.6413(10) Å, which is longer than that in **1** (2.5953 Å)[8g] as well as those in salicylaldiminato-derived $[O^-NS]TiCl_3$ complexes.[8c] Crystal data and details of data collection and structure refinements were given in Table 2.

Ethylene homopolymerization

Upon activation with MMAO (MMAO/Ti = 1000/1) in toluene, complexes **5a–l** were investigated for ethylene polymerization. As

Table 2 The crystal data and details of data collections for **4m** and **5b**[a]

Data	**4m**	**5b**
Formula	$C_{24}H_{23}NOS$	$C_{20}H_{22}Cl_3NOSTi$
FW	373.49	478.70
Crystal size/mm	$0.369 \times 0.278 \times 0.125$	$0.486 \times 0.092 \times 0.070$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P21/c$
a/Å	21.6646(19)	7.0434(10)
b/Å	8.0100(7)	11.2130(15)
c/Å	24.360(2)	28.939(4)
α/°	90	90
β/°	106.432(2)	96.423(3)
γ/°	90	90
V/Å^3	4054.6(6)	2271.2(5)
Z	8	4
D_c/Mg m^{-3}	1.224	1.400
μ/mm^{-1}	0.173	0.832
θ_{max}/°	27.50	27.00
Reflections collected/unique	23 753/9119 [$R_{int} = 0.1314$]	13 122/4923 [$R_{int} = 0.0548$]
Goodness-of-fit on F^2	0.881	0.921
Final R indices [$I > 2(I)$]	$R_1 = 0.0654$, w$R_2 = 0.1749$	$R_1 = 0.0503$, w$R_2 = 0.0842$
R indices (all data)	$R_1 = 0.1590$, w$R_2 = 0.1931$	$R_1 = 0.0846$, w$R_2 = 0.0928$

[a] Data collections for compounds were performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The SADABS absorption correction was applied. The structure were solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program.

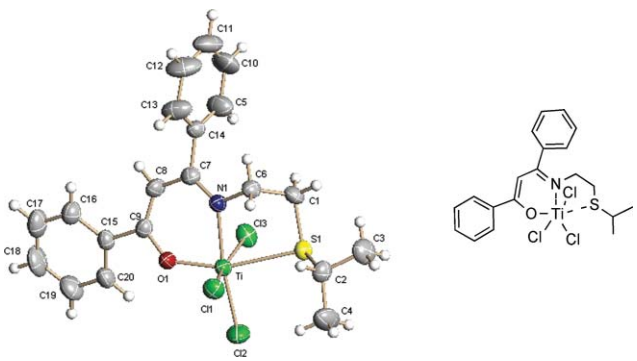


Fig. 4 The molecular structure of **5b**. Selected bond lengths (Å) and angles (°): S1–C1, 1.806(3); O1–C9, 1.330(3); N1–C7, 1.309(4); N1–C6, 1.468(4); C7–C8, 1.429(4); C8–C9, 1.351(4); Ti–O1, 1.827(2); Ti–N1, 2.148(2); Ti–Cl2, 2.2720(10); Ti–Cl1, 2.2902(10); Ti–Cl3, 2.3293(9); Ti–S1, 2.6413(10); C1–S1–C2, 101.97(15); C7–N1–C6, 119.9(3); O1–Ti–N1, 84.12(9); O1–Ti–Cl2, 103.24(7); O1–Ti–Cl1, 98.92(7); N1–Ti–Cl1, 87.72(7); O1–Ti–Cl3, 91.93(7); Cl1–Ti–Cl3, 165.43(4); Cl2–Ti–Cl1, 93.26(4); Cl2–Ti1–Cl3, 93.68(4); S1–C1–C6–N1, –59.7(3); C14–C7–C8–C9, –176.5(3); N1–C7–C8–C9, 5.7(5); S1–C1–C6–N1, –59.7(3).

shown in Table 3, the structure of the complexes influenced the ethylene polymerization behaviours including both the catalytic activity and the molecular weight of the resulting polyethylene. Complexes **1** and **5a–d** gave similar activities and molecular weights, suggesting that the steric hindrance of substituent R^5 on sulfur atom has almost no effect on the behaviours of ethylene

Table 3 Ethylene polymerization using complexes **5**

Entry[a]	Cat.	PE/g	Activity[b]	M_w[c,d]	M_w/M_n[c]
1	**5a**	0.83	1.66	12.7	2.03
2	**1**[8g]	0.99	1.98	10.4	2.75
3	**5b**	0.84	1.68	12.6	3.05
4	**5c**	0.86	1.72	11.1	2.65
5	**5d**	0.88	1.76	12.7	2.91
6	**5e**	0.51	1.02	33.6	2.14
7	**5f**	0.63	1.26	14.9	2.82
8	**5g**	0.73	1.46	22.2	2.19
9	**5h**	0.94	1.88	14.8	2.62
10	**5i**	0.95	1.90	29.6	2.12
11	**5j**	Trace	—	—	—
12	**5k**	Trace	—	—	—
13	**5l**	0.53	1.06	16.2	2.10
14[e]	**5a**	1.72	0.57	10.1	2.75

[a] 50 mL toluene, 3 μmol of cat., MMAO/Ti = 1000, 30 °C, 1 atm ethylene, 10 min. [b] 10^6 g mol^{-1} Ti h^{-1} atm^{-1}. [c] Determined by GPC. [d] 10^4 g mol^{-1}. [e] 60 min.

polymerization (entries 1–5), which is similar to the corresponding salicylaldiminato-derived catalysts.[8f] Replacement of alkyl group with phenyl group on sulfur atom increased the molecular weight but decreased the activity slightly (entries 1–5 *vs.* entry 6). The catalytic activity was decreased from 1.98 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} to 1.26 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} when the substituent R^3 was changed from phenyl group to methyl group (entry 2 *vs.* 7). The activity of **5g** with an electron-withdrawing group *p*-$CF_3C_6H_4$ at R^3 position is slightly lower than that of **1** (entry 2 *vs.* 8). Similar catalytic activities were observed for **1**, **5h** and **5i**, showing substituent effects at R^1 and R^3 positions are weak (entry 2 *vs.* entries 9, 10). Noticeably, substitution of hydrogen atom with methyl or benzyl group at R^2 position resulted in loss of activity (entry 2 *vs.* 11, 12). The reason is not clear. GPC studies showed that the molecular weight distribution ranged from 2.03 to 3.05, similar to those of PE produced by a single site catalyst. Catalytic activity decreased slightly when the polymerization time was prolonged to 1 hour, probably due to the wrapping of catalytic species by precipitated polyethylene (entry 14).

Ethylene copolymerization with α-olefins

The performance of a catalyst for copolymerization of ethylene with α-olefin is very important. Using complex **1** as a model catalyst, we investigated the copolymerization between ethylene and α-olefins. As shown in Table 4, positive comonomer effects were observed. For example, **1** catalyzed ethylene polymerization at 30 °C with 1000 Al/Ti ratio in an activity of 1.98 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} (entry 2, Table 3). However, under the same polymerization conditions with complex **1** as a catalyst, the activity of ethylene/hexene copolymerization was over 5.00 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} (entry 10, Table 4). The polymerization temperature influenced the activity, molecular weight as well as incorporation ratio of monomer (entry 1–3). For instance, the copolymerization activity was 0.88 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} at 0 °C. Raising the temperature from 0 to 25 °C increased the activity to 4.34 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} and decreased the M_w from 58.6 × 10^4 g mol^{-1} to 11.8 × 10^4 g mol^{-1}. The 1-hexene incorporation ratio was also increased from 7.2 mol% to 11.1 mol% (entry 1 *vs.* 2).[11] Further enhancing the temperature to 50 °C resulted in a decrease of activity and an increase of 1-hexene incorporation ratio (entry 2 *vs.* 3). The catalyst performance was Al/Ti molar ratio-dependent. High activity could be achieved with 500 Al/Ti molar ratio. Increasing the Al/Ti molar ratio from 500 to 2000 further improved activity obviously and increased the 1-hexene incorporation but decreased the molecular weight (entries 2 and 4–6). With increasing the amount of comonomer feed, the copolymerization activity almost maintained while the content of 1-hexene in the copolymer increased rapidly (entries 2, 7–9). Besides 1-hexene, other α-olefins such as 1-octene, 1-dodecene, and 1-octadecene could be incorporated easily in the polyethylene backbone with high activity (entries 11–13). It is worthy to note that complex **1** exhibited much higher copolymerization capability than the corresponding salicylaldehyde-derived imine titanium complex **6** (Fig. 5), probably due to the much more open space around titanium atom in **1** than in **6** (entry 14 *vs.* 2 and 15 *vs.* 9). As shown in Table 4, for example, **6**/MMAO promoted the copolymerization of ethylene/1-hexene in an activity of 1.98 × 10^6 g mol^{-1} of Ti h^{-1} atm^{-1} with 10.5 mol% 1-hexene incorporation ratio. However, when **1** was employed instead of **6**, the activity and 1-hexene incorporation ratio were increased to 4.44 × 10^6 g mol^{-1} Ti h^{-1} atm^{-1} and 23.6 mol%, respectively, under the same polymerization conditions (entry 9 *vs.* 15).

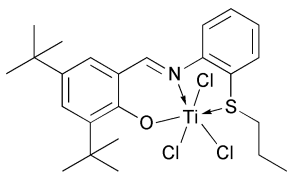


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Fig. 5 Salicylaldehyde-derived imine titanium complex **6**.

Ethylene copolymerization with cycloolefins

Ethylene/cycloolefin copolymerization might lead to important high performance polymer materials with many unique properties. Complexes **1** and **5a–b** prove to catalyze the copolymerization of ethylene with cycloolefins very efficiently. Both cyclopentene (CPE) and norbornene (NBE) are suitable comonomers upon activation with MMAO. As shown in Table 5, at the same initial concentration of CPE and the same scale of complex **1**, diluting **1** with toluene increased both the yield and M_w of the polymer but the insertion ratio of CPE decreased obviously (entries 1–3). Enhancing the initial concentration of CPE improved the incorporation ratio of monomer (entries 3–6). For instance, the CPE incorporation ratio doubled when the concentration of CPE was increased from 2.0 M to 5.0 M, reaching 26.0 mol% (entry 3 *vs.* 6).[12] Complexes **5a** and **5b** also exhibited good activity toward the copolymerization of ethylene/CPE with good comonomer incorporation ratio (entries 8–9). Comparing with **1**, both **5a** and **5b** gave the copolymers under the same polymerization conditions with higher molecular weight (entry 3 *vs.* entries 8 and 9). Similar to the aforementioned copolymerization of ethylene with 1-hexene, complex **1** is obviously superior to salicylaldehyde-derived imine titanium complex **6** for the ethylene/CPE copolymerization. Under the same conditions, **1** showed much higher activity and much better comonomer incorporation than **6** (entry 3 *vs.* 10).

Table 4 Ethylene copolymerization with α-olefins

Entry[a]	Comonomer/mmol	Polymer/g	Activity[a]	M_w[c,d]	M_w/M_n[c]	Incorporation ratio (mol%)[e]
1[f]	1-Hexene (12)	0.44	0.88	58.6	1.85	7.2
2	1-Hexene (12)	2.17	4.34	11.8	2.22	11.1
3[g]	1-Hexene (12)	1.42	2.84	10.4	2.10	16.7
4[h]	1-Hexene (12)	1.44	2.88	21.8	2.05	13.2
5[i]	1-Hexene (12)	2.01	4.02	11.7	2.15	14.2
6[j]	1-Hexene (12)	2.11	4.22	8.6	2.01	17.1
7	1-Hexene (6)	2.20	4.40	11.2	2.20	8.6
8	1-Hexene (24)	2.47	4.94	15.7	2.22	18.0
9	1-Hexene (36)	2.22	4.44	15.2	2.20	23.6
10[k]	1-Hexene (36)	2.56	5.12	10.3	1.94	28.9
11	1-Octene (12)	1.59	3.18	18.8	2.06	10.0
12	1-Dodecene (12)	1.80	3.60	19.6	2.11	7.2
13	1-Octadecene (12)	2.02	4.04	21.4	2.13	5.5
14[l]	1-Hexene (12)	0.88	1.76	18.3	2.06	6.5
15[l]	1-Hexene (36)	0.99	1.98	21.5	1.83	10.5

[a] Toluene (50 mL), 3 μmol of **1**, 1 atm of ethylene, 25 °C, MMAO/Ti = 1000, 10 min. [b] Activity, 10^6 g mol^{-1} h^{-1} atm^{-1}. [c] Determined by GPC. [d] 10^4 g mol^{-1}. [e] Determined by ^{13}C NMR. [f] 0 °C. [g] 50 °C. [h] MMAO/Ti = 500. [i] MMAO/Ti = 1500. [j] MMAO/Ti = 2000. [k] 30 °C. [l] 3 μmol of **6**.

Table 5 Copolymerization of ethylene with cyclopentene and norbornene[a]

Entry	Cat.	Comonomer/mmol	C[b]	Polymer/g	Activity[c]	M_w[d,e]	M_w/M_n[d]	Incorporation ratio[f] (mol%)
1	**1**	CPE (25)	2.0	0.56	0.93	4.1	1.74	24.0
2	**1**	CPE (50)	2.0	0.68	1.13	5.6	1.70	21.1
3	**1**	CPE(100)	2.0	0.97	1.62	7.2	1.57	12.8
4	**1**	CPE(100)	3.0	0.77	1.28	3.4	1.77	17.3
5	**1**	CPE(100)	4.0	0.65	1.08	5.5	1.77	21.3
6	**1**	CPE(100)	5.0	0.53	0.88	4.9	1.62	26.0
7[g]	**1**	CPE(50)	3.3	1.20	3.00	5.4	2.11	29.7
8	**5a**	CPE(100)	2.0	0.97	1.62	10.1	2.08	7.2
9	**5b**	CPE(100)	2.0	0.83	1.38	11.1	2.13	5.5
10	**6**	CPE(100)	2.0	0.59	0.98	10.1	1.84	4.3
11[h]	**1**	NBE(4)	0.08	1.14	22.80	24.4	2.10	11.2
12[h]	**1**	NBE(6)	0.12	0.70	14.00	42.8	1.85	26.0
13[h]	**1**	NBE(8)	0.16	0.65	13.00	44.8	1.91	30.6
14[h]	**1**	NBE(10)	0.20	0.37	7.40	23.1	1.55	39.7
15[h]	**1**	NBE(20)	0.40	0.28	5.60	15.8	1.60	44.2
16[h]	**1**	NBE(30)	0.60	0.17	3.40	11.9	1.75	45.6
17[h]	**6**	NBE(20)	0.40	0.97	19.40	31.3	1.70	29.8

[a] Toluene (50 mL), 12 μmol of cat., 30 °C, MMAO/Ti = 1000, 1 atm of ethylene, 30 min. [b] Concentration of the comonomer, mol L^{-1}. [c] 10^5 g mol^{-1} Ti h^{-1} atm^{-1}. [d] Determined by GPC. [e] 10^4 g mol^{-1}. [f] Determined by ^{13}C NMR. [g] 20 min. [h] 3 μmol cat., 10 min.

Since the performance of complex **1** for the copolymerization of ethylene with CPE is better than complexes **5a** and **5b**, **1** was chosen as a catalyst to investigate the ethylene/norbornene copolymerization. As shown in Table 5, both the incorporation ratio and the activity depended on the initial concentration of norbornene. With an increasing feed of norbornene from 4 to 30 mmol, the copolymerization activity was decreased strongly but the molar incorporation ratio was increased to 45.6% at 1 atm of ethylene atmosphere (entries 11–16).[13] When 4 mmol of NBE (0.08 M) was used, an activity of 2.28×10^6 g mol^{-1} Ti h^{-1} atm^{-1} and an incorporation of 11.2 mol% were obtained. With the increase of the initial concentration of NBE, the molecular weight of the copolymer increased first and then decreased. The highest molecular weight was obtained when the concentration was 0.16 mol L^{-1} (entry 13). Remarkably, 0.16 M of NBE concentration in the case of complex **1** gave a similar incorporation ratio to that when 0.40 M of NBE concentration was employed using complex **6** as a catalyst (entry 15 *vs.* 17, Table 5). This result suggested that compound **1** promote the copolymerization of ethylene with NBE more efficient than **6**.

Conclusions

The titanium complexes derived from β-carbonylenamine were prepared and characterized. In the presence of MMAO, these titanium complexes showed high activity toward ethylene polymerization. α-Alkene and cycloalkenes such as CPE and NBE proved to incorporate into polyethylene backbone efficiently with an activity of up to 5.12×10^6 g mol^{-1} Ti h^{-1} atm^{-1}, affording copolymers with tunable contents of the comonomer. By changing the comonomer initial concentration and polymerization conditions, the high incorporation ratios of CPE and NBE could be achieved with up to 29.7 mol% and 45.6 mol%, respectively. Higher activity and better incorporation capability of β-carbonylenamine derived [O$^-$NS]TiCl$_3$ complexes than that of the corresponding salicylaldiminato-derived complex **6** were demonstrated.

Experimental

General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz or 400 MHz spectrometer with TMS as the internal standard. Mass spectra were obtained using a HP5959A spectrometer. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). M_n, M_w, and M_w/M_n values of polymers were determined with a Waters Alliance GPC 2000 series at 135 °C (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 0.92 mL min^{-1}). ^{13}C NMR data of polymer was obtained using *o*-dichlorobenzene-d_4 as a solvent at 110 °C. X-Ray crystallographic data were collected using a Bruker AXSD8 X-Ray diffractometer. Toluene, THF, and hexane were distilled over sodium/benzophenone ketyl prior to use. Dichloromethane was distilled over CaH_2. Modified methylaluminoxane (MMAO) was purchased from Akzo Chemical as a 1.9 M toluene solution. Polymerization-grade ethylene was purified before use. The complex **1**[8g] and **6**[8f] were prepared according to the literature methods reported.

The synthesis of the new compounds

(*Z*)-3-(2-(methylthio)ethylamino)-1,3-diphenylprop-2-en-1-one (4a). To a solution of 1,3-diphenylpropane-1,3-dione (**2a**, 2.71 g, 12.0 mmol) and 2-(methylthio)ethanamine (**3a**, 1.00 g, 11.0 mmol) in toluene (25 mL) was added 4-methylbenzenesulfonic acid hydrate (0.062 g, 0.33 mmol) at room temperature. The flask was equipped with a water separator. After refluxing for 3 d, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give yellow solid. Yield: 2.53 g (77%). M.p.: 72–76 °C;^{1}H NMR (300 MHz, $CDCl_3$): δ 11.47 (s, 1 H), 7.91–7.88 (m, 2 H), 7.48–7.36 (m, 8 H), 5.79 (s, 1 H), 3.44 (ABd, J = 6.9 Hz, 1 H), 3.40 (ABd, J = 6.9 Hz, 1 H), 2.63 (t, J = 6.9 Hz, 2 H), 2.00 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.62, 166.39, 140.07, 135.47, 130.77, 129.50, 128.57, 128.15, 127.72, 127.07, 93.87, 43.63, 34.91, 15.46. IR (KBr) ν (cm^{-1}): 3058, 2915, 1595, 1583, 1569, 1480, 1331, 1295, 1225, 1143, 1057, 1025, 749, 692; MS (EI): m/z = 297 (M$^+$); HRMS: 297 ($C_{18}H_{19}NOS$).

(*Z*)-1,3-diphenyl-3-(2-(isopropylthio)ethylamino)prop-2-en-1-one (4b). The same procedure as that for the preparation of **4a**. Yield: 3.20 g (50%). M.p: 66–71 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.45 (brs, 1 H), 7.91–7.88 (m, 2H), 7.47–7.37 (m, 8 H), 5.78 (s, 1 H), 3.42 (ABd, J = 6.9 Hz, 1 H), 3.37 (ABd, J = 6.6 Hz, 1 H), 2.81–2.76 (m, 1 H), 2.66 (t, J = 7.5 Hz, 2 H), 1.18 (d, J = 6.3 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.59, 166.34, 140.07, 135.41, 130.76, 129.50, 128.57, 128.16, 127.68, 127.03, 93.83, 44.60, 34.87, 31.11, 23.26. IR (KBr) ν (cm^{-1}): 3060, 2980, 1595, 1579, 1554, 1480, 1443, 1340, 1299, 1224, 1201, 1141, 1057, 747, 707, 691. $C_{20}H_{23}NOS$ (325.47): calcd C 73.81, H 7.12, N 4.30. Found: C 73.58, H 6.94, N 4.19. MS (ESI): m/z = 326 (M + H$^+$).

(*Z*)-3-(2-(octylthio)ethylamino)-1,3-diphenylprop-2-en-1-one (4c). The same procedure as that for the preparation of **4a**. Yield: 1.15 g (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.46 (s, 1 H), 7.91–7.88 (m, 2 H), 7.48–7.36 (m, 8 H), 5.78 (s, 1 H), 3.43 (ABd, J = 7.2 Hz, 1 H), 3.38 (ABd, J = 6.6 Hz, 1 H), 2.64 (t, J = 7.5 Hz, 2 H), 2.38 (t, J = 7.2 Hz, 2 H), 1.50–1.43 (m, 2 H), 1.43–1.25 (m, 12 H), 0.88 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.58, 166.37, 140.06, 135.44, 130.76, 129.49, 128.57, 128.15, 127.71, 127.06, 93.83, 44.32, 32.69, 32.08, 31.76, 29.57, 29.15, 29.12, 28.80, 22.62, 14.08. IR (KBr) ν (cm^{-1}): 3060, 2925, 2854, 1595, 1584, 1570, 1480, 1331, 1295, 1225, 1143, 1057, 1025, 748, 691, 612. $C_{25}H_{33}NOS$ (395.6): calcd C 75.90, H 8.41, N 3.54. Found C 76.10, H 8.50, N 3.36. MS (ESI) (m/z): 396 (M + H$^+$).

(*Z*)-3-(2-(octadecylthio)ethylamino)-1,3-diphenylprop-2-en-1-one (4d). The same procedure as that for the preparation of **4a**. Yield: 0.61 g (61%). M.p: 42–44 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 11.46 (brs, 1 H), 7.91–7.88 (m, 2 H), 7.47–7.37 (m, 8 H), 5.78 (1 H), 3.43 (ABd, J = 6.6 Hz, 1 H), 3.38 (ABd, J = 6.9 Hz, 1 H), 2.63 (t, J = 6.9 Hz, 2 H), 2.37 (t, J = 6.9 Hz, 2 H), 1.50-1.43 (m, 2 H), 1.40-1.20 (m, 30 H), 0.88 (t, J = 6.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): 188.59, 166.38, 140.06, 135.44, 130.77, 129.49, 128.56, 128.16, 127.71, 127.06, 93.83, 44.31, 32.69, 32.08, 31.89, 30.92, 29.67, 29.63, 29.57, 29.50, 29.34, 29.18, 28.81, 22.66, 14.11. IR (KBr) ν (cm^{-1}): 3061, 2923, 2852, 2386, 1596, 1584, 1570, 1517, 1480, 1329, 1295, 1223, 1143, 1055, 1025, 748. $C_{35}H_{53}NOS$ (535.87): calcd C 78.45, H 9.97, N 2.61. Found C 78.31, H 9.67, N 2.49. MS (EI) (m/z): 535 (M$^+$).

(*Z*)-1,3-diphenyl-3-(2-(phenylthio)ethylamino)prop-2-en-1-one (4e). The same procedure as that for the preparation of **4a**. Yield: 1.80 g (77%). M.p: 50–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.48 (s, 1 H), 7.90 (dd, J = 1.5 Hz, 7.5 Hz, 2 H), 7.44-7.18 (m, 13 H), 5.78 (s, 1 H), 3.45-3.38 (m, 2 H), 3.02-2.98 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.75, 166.29, 140.04, 135.27, 134.65, 130.84, 129.73, 129.50, 129.01, 128.62, 128.19, 127.66, 127.09, 126.44, 94.10, 43.58, 34.44. IR (KBr) ν (cm^{-1}): 3058, 2987, 1595, 1569, 1480, 1331, 1296, 1057, 1025, 743, 691. $C_{23}H_{21}NOS$ (359.48): calcd C 76.85, H 5.89, N 3.90. Found C 76.62, H 5.99, N 3.70. MS (ESI) (m/z): 360 (M + H$^+$).

(*Z*)-1-phenyl-3-(2-(propylthio)ethylamino)but-2-en-1-one (4f). The same procedure as that for the preparation of **4a**. Yield: 2.47 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.52 (s, 1 H), 7.87–7.85 (m, 2 H), 7.41–7.35 (m, 3 H), 5.69 (s, 1 H), 3.54 (ABd, J = 6.6 Hz, 1 H), 3.49 (ABd, J = 7.2 Hz, 1 H), 2.74 (t, J = 6.9 Hz, 2 H), 2.55 (t, J = 7.2 Hz, 2 H), 2.09 (s, 3 H), 1.66–1.59 (m, 2 H), 0.99 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.66, 164.14, 140.08, 130.28, 127.93, 126.70, 92.24, 43.02, 34.23, 32.01, 22.77, 19.29, 13.22. IR (KBr) ν (cm^{-1}): 3059, 2961, 2927, 2870, 1602, 1584, 1552, 1521, 1441, 1322, 1294, 1229, 1085, 1064, 1027, 738. $C_{15}H_{21}NOS$ (263.40): calcd C 68.40, H 8.04, N 5.32. Found C 68.51, H 7.79, N 5.41. MS (EI) (m/z): 263 (M$^+$).

(*Z*)-3-(2-(propylthio)ethylamino)-1,3-di-*p*-tolylprop-2-en-1-one (4h). The same procedure as that for the preparation of **4a**. Yield: 1.06 g (77%). M.p: 64–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.41 (s, 1 H), 7.79 (d, J = 8.1 Hz, 2 H), 7.31–7.18 (m, 6 H), 5.76 (s, 1 H), 3.40 (q, J = 6.6 Hz, 2 H), 2.62 (t, J = 6.9 Hz, 2 H), 2.41-2.34 (m, 8 H), 1.54–1.47 (m, 2 H), 0.92 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.36, 166.31, 141.01, 139.55, 137.48, 132.66, 129.17, 128.84, 127.66, 127.07, 93.68, 44.31, 34.04, 32.61, 22.87, 21.39, 21.30, 13.34. IR (KBr) ν (cm^{-1}): 2960, 2920, 2869, 1590, 1582, 1561, 1509, 1488, 1329, 1301, 1228, 1180, 1142, 1063,

1018, 824, 772. $C_{22}H_{27}NOS$ (353.52): calcd C 74.74, H 7.70, N 3.96. Found C 74.20, H 8.00, N 3.93. MS (EI) (*m*/*z*): 353 (M^+).

(*Z*)-1,3-bis(4-methoxyphenyl)-3-(2-(propylthio)ethylamino) prop-2-en-1-one (4i). The same procedure as that for the preparation of **4a**. Yield: 1.87 g (78%). M.p: 50–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.35 (s, 1 H), 7.90–7.87 (m, 2 H), 7.39–7.36 (m, 2 H), 6.98–6.88 (m, 4 H), 5.74 (s, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 3.41 (q, J = 6.6 Hz, 2 H), 2.63 (t, J = 6.3 Hz, 2 H), 2.38 (t, J = 7.2 Hz, 2 H), 1.55-1.48 (m, 2 H), 0.93 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.56, 165.80, 161.71, 160.44, 132.88, 129.22, 128.88, 127.91, 113.86, 113.30, 93.44, 55.31, 55.26, 44.33, 34.05, 32.63, 22.86, 13.35. IR (KBr) ν (cm^{-1}): 2959, 2933, 2836, 1592, 1567, 1510, 1490, 1461, 1441, 1332, 1292, 1251, 1228, 1172, 1143, 1063, 1029, 841, 782. $C_{22}H_{27}NO3S$ (385.52): calcd C 68.54, H 7.06, N 3.63. Found C 68.30, H 7.36, N 3.63. MS (EI) (*m*/*z*): 385 (M^+).

(*Z*)-2-benzyl-1,3-diphenyl-3-(2-(propylthio)ethylamino) prop-2-en-1-one (4j). The same procedure as that for the preparation of **4a**. Yield: 0.90 g (37%). M.p: 59–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.46 (s, 1 H), 7.33–7.21 (m, 8 H), 7.09–7.00 (m, 5 H), 6.71–6.68 (m, 2 H), 3.35 (s, 2 H), 3.16 (q, J = 6.6 Hz, 2 H), 2.58 (t, J = 6.9 Hz, 2 H), 2.31 (t, J = 7.2 Hz, 2 H), 1.52–1.45 (m, 2 H), 0.91 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.15, 167.38, 143.20, 142.90, 133.82, 128.68, 128.40, 127.76, 127.75, 127.61, 127.51, 126.44, 125.00, 102.85, 44.55, 35.42, 34.02, 32.46, 22.90, 13.36. IR (KBr) ν (cm^{-1}): 3058, 3024, 2960, 2929, 2870, 1590, 1585, 1493, 1443, 1321, 1288, 1225, 1158, 1073, 1027, 781, 755, 699. MS (EI) (*m*/*z*): 415 (M^+). HRMS: 415 ($C_{27}H_{29}NOS$).

(*Z*)-2-methyl-1,3-diphenyl-3-(2-(propylthio)ethylamino) prop-2-en-1-one (4k). The same procedure as that for the preparation of **4a**. Yield: 0.92 g (41%). M.p: 48–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.19 (s, 1 H), 7.52–7.29 (m, 10 H), 3.17 (q, J = 7.2 Hz, 2 H), 2.57 (t, J = 6.9 Hz, 2 H), 2.31 (t, J = 6.9 Hz, 2 H), 1.52–1.45 (m, 5 H), 0.91 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.21, 166.07, 142.97, 134.92, 128.89, 128.73, 128.71, 127.78, 127.50, 127.00, 98.33, 44.60, 34.02, 32.60, 22.90, 17.42, 13.33. IR (KBr) ν (cm^{-1}): 3057, 2960, 2929, 2870, 1585, 1569, 1550, 1466, 1442, 1320, 1284, 1157, 1002, 987, 783, 703. $C_{21}H_{25}NOS$ (339.49): calcd C 74.29, H 7.42, N 4.13. Found C 74.01, H 7.52, N 4.05. MS (EI) (*m*/*z*): 339 (M^+).

(*R*,*Z*)-3-(3-methyl-1-(propylthio)butan-2-ylamino)-1,3-diphenylprop-2-en-1-one (4l). The same procedure as that for the preparation of **4a**. Yield: 1.50 g (32%). M.p: 58–67 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.51 (d, J = 10.5 Hz, 1 H), 7.97–7.89 (m, 2 H), 7.48–7.37 (m, 8 H), 5.77 (s, 1 H), 3.45–3.36 (m, 1 H), 2.71–2.59 (m, 2 H), 2.30 (t, J = 6.9 Hz, 2 H), 2.02–1.92 (m, 2 H), 1.56–1.44 (m, 2 H), 1.00 (d, J = 6.6 Hz, 3 H), 0.90 (t, J = 6.6 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.26, 167.24, 140.14, 135.85, 130.68, 129.23, 128.33, 128.13, 127.04, 93.84, 59.32, 36.25, 34.85, 31.61, 31.54, 22.79, 19.77, 16.82, 13.41. IR (KBr) ν (cm^{-1}): 3060, 2960, 2930, 2872, 1584, 1569, 1478, 1443, 1333, 1303, 1224, 1143, 1055, 1025, 749, 702, 692. $C_{23}H_{29}NOS$ (367.55): calcd C 75.16, H 7.95, N 3.81. Found C 74.62, H 8.13, N 3.88. MS (EI) (*m*/*z*): 367 (M^+).

[(1*Z*,3*Z*)-1,3-diphenyl-3-(2-(methylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5a as an example for method A). To a solution of $TiCl_4$ (0.51 g, 2.7 mmol) in toluene (7 mL) at −78 °C was added dropwise a solution of (*Z*)-3-(2-(methylthio)ethylamino)-1,3-diphenyl prop-2-en-1-one (**4a**) (0.66 g, 2.2 mmol) in toluene (7 mL) over 15 min. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. After removing the solvent under reduced pressure, the brown-red solid was collected and dried *in vacuo* to give the desired pure complex. Yield: 0.85 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.82 (m, 2 H), 7.53–7.40 (m, 6 H), 7.32–7.30 (m, 2 H), 6.39 (s, 1 H), 4.18–4.01 (m, 2 H), 3.26 (t, J = 10 Hz, 1 H), 2.78 (s, 3 H), 2.69 (d, J = 11.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.86, 169.89, 137.64, 132.06, 129.86, 129.38, 128.94, 127.17, 125.90, 109.54, 56.86, 38.09, 22.40. IR (KBr) ν (cm^{-1}): 3292, 1600, 1587, 1572, 1501, 1480, 1449, 1440, 1410, 1282, 1237, 1078, 1062, 1020, 834, 779, 770, 702, 687. $C_{18}H_{18}Cl_3NOSTi$ (450.63): calcd C 47.98, H 4.03, N 3.11. Found C 47.82, H 4.04, N 3.03.

[(1*Z*,3*Z*)-1,3-diphenyl-3-(2-(isopropylthio)ethylimino) prop-1-en-1-olate]Ti(IV)Cl_3 (5b as an example for method B). To a suspension of potassium hydride (KH) (0.21 g, 5.3 mmol) in tetrahydrofuran (THF) (20 mL) was added a solution of **4b** (1.40 g, 4.4 mmol) in THF (10 mL) at −78 °C. The resulting suspension was warmed to room temperature and stirred for 3 h. After removal of the solvent under vacuum, CH_2Cl_2 (20 mL) was added to the residue to give a yellow solution. It was then added dropwise to a solution of $TiCl_4$ (1.00 g, 5.3 mmol) in CH_2Cl_2 (30 mL) at room temperature, and the mixture was stirred for 16 h. The solid was filtered off and washed with CH_2Cl_2 (10 mL). The combined organic solutions were concentrated under vacuum to about 5 mL and then kept it at −30 °C for few a days. The solid was collected to afford **5b** as red-brown crystals. Yield: 0.90 g (44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, J = 6.9 Hz, 2 H), 7.52–7.39 (m, 8 H), 6.40 (s, 1 H), 4.05 (d, J = 13.5 Hz, 2 H), 3.74–3.70 (m, 1 H), 3.16–2.85 (m, 2 H), 1.74–1.38 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.72, 169.72, 137.65, 132.14, 131.99, 129.80, 129.34, 128.93, 127.19, 125.84, 109.53, 57.32, 42.16, 34.71, 23.35, 21.68. IR (KBr) ν (cm^{-1}): 2966, 1603, 1588, 1571, 1502, 1480, 1449, 1404, 1284, 1236, 1062, 1024, 1003, 833, 780, 769, 701, 639. $C_{20}H_{22}Cl_3NOSTi$ (478.69): calcd C 50.18, H 4.63, N 2.93. Found C 50.45, H 4.57, N 2.77.

[(1*Z*,3*Z*)-1,3-diphenyl-3-(2-(octylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5c). The same procedure as that for the preparation of **5a**. Yield: 0.83 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 6.9 Hz, 2 H), 7.52–7.29 (m, 8 H), 6.39 (s, 1 H), 4.13–4.04 (m, 2 H), 3.45–3.43 (m, 1 H), 3.24–3.17 (m, 1 H), 2.98–2.96 (m, 1 H), 2.73 (d, J = 6.0 Hz, 1 H), 1.95–1.85 (m, 2 H), 1.53–1.46 (m, 2 H), 1.31–1.28 (m, 8 H), 0.88 (t, J = 5.7 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.72, 169.81, 137.64, 132.11, 132.00, 129.80, 129.34, 128.90, 127.15, 125.89, 109.47, 57.31, 39.71, 36.40, 31.73, 29.08, 29.06, 28.88, 28.18, 22.61, 14.08. IR (KBr) ν (cm^{-1}): 3220, 2954, 2925, 2853, 1686, 1602, 1591, 1573, 1506, 1487, 1450, 1442, 1285, 1238, 1077, 1062, 1591, 1573, 1506, 1487, 1450, 1285, 1238, 1077, 1062, 1025, 834, 778, 771, 693. $C_{25}H_{32}Cl_3NOSTi$ (547.07): calcd C 54.71, H 5.88, N 2.55. Found C 54.21, H 5.49, N 2.44.

[(1*Z*,3*Z*)-1,3-diphenyl-3-(2-(octadecylthio)ethylimino) prop-1-en-1-olate]Ti(IV)Cl_3 (5d). The same procedure as that for the preparation of **5a**. Yield: 0.51 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 6.3 Hz, 2 H), 7.52–7.29 (m, 8 H), 6.39 (s, 1 H), 4.17–4.04 (m, 2 H), 3.45 (t, J = 14.4 Hz, 1 H), 3.20

(t, $J = 9.9$ Hz, 1 H), 3.00–2.96 (m, 1 H), 2.73 (d, $J = 6.3$ Hz, 1 H), 1.94–1.82 (m, 2 H), 1.52–1.26 (m, 32 H), 0.88 (t, $J = 6.9$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.71, 169.81, 137.64, 132.12, 131.99, 129.79, 129.33, 128.90, 127.14, 125.82, 109.46, 57.29, 39.72, 36.40, 31.91, 29.69, 29.64, 29.63, 29.54, 29.43, 29.35, 29.12, 28.88, 28.19, 22.68, 14.11. IR (KBr) ν (cm^{-1}): 3200, 2920, 2850, 1603, 1591, 1573, 1507, 1488, 1450, 1285, 1238, 1077, 1062, 1025, 833, 779, 771, 702. $C_{35}H_{52}Cl_3NOSTi$ (689.08): calcd C 61.00, H 7.61, N 2.03. Found C 60.59, H 7.46, N 1.83.

[(1*Z*,3*Z*)-1,3-diphenyl-3-(2-(phenylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5e). The same procedure as that for the preparation of **5b**. Yield: (0.31 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, toluene): δ 7.81–7.16 (m, 18 H), 6.40 (s, 1 H), 4.25 (s, 2 H), 3.49 (t, $J = 4.8$ Hz, 2 H), 2.35 (s, 1.7 H). ^{13}C NMR (100 MHz, $CDCl_3$, toluene): δ 171.01, 170.11, 137.49, 132.81, 132.06, 131.95, 129.92, 129.40, 129.31, 129.02, 128.93, 128.49, 128.20, 127.45, 127.16, 125.86, 125.28, 109.61, 57.50, 35.04, 21.45. IR (KBr) ν (cm^{-1}): 3212, 1686, 1588, 1572, 1501, 1483, 1450, 1440, 1282, 1236, 1062, 1026, 766, 742, 698, 687. $C_{23}H_{20}Cl_3NOSTi$(510.98): calcd C 53.88, H 3.93, N 2.73. Found C 53.68, H 4.19, N 2.20.

[(1*Z*,3*E*)-1-phenyl-3-(2-(propylthio)ethylimino)but-1-en-1-olate]Ti(IV)Cl_3 (5f). The same procedure as that for the preparation of **5a**. Yield: 1.32 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, $J = 7.6$ Hz, 2 H), 7.49–7.41 (m, 3 H), 6.34 (m, 1 H), 4.20 (d, $J = 4.2$ Hz, 2 H), 3.42–3.33 (d, 2 H), 2.97–2.91 (d, 2 H), 2.31 (s, 3 H), 1.97–1.93 (m, 2 H), 1.15 (t, $J = 7.6$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.07, 169.02, 132.06, 131.81, 128.96, 128.92, 126.98, 110.10, 55.07, 41.44, 35.93, 23.79, 21.74, 13.53. IR (KBr) ν (cm^{-1}): 2964, 1598, 1575, 1504, 1487, 1447, 1408, 1336, 1274, 1243, 1183, 1101, 1075, 1028, 924, 769, 688. $C_{15}H_{20}Cl_3NOSTi$ (416.62): calcd C 43.24, H 4.84, N 3.36. Found C 42.79, H 5.08, N 3.44.

[(1*Z*,3*Z*)-1-phenyl-3-(2-(propylthio)ethylimino)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-olate]Ti(IV)Cl_3 (5g). The same procedure as that for **5a** but using the crude product of diketone **2c** and amine **3f**. The pure **5g** was isolated by recrystallization from toluene. Yield: 0.20 g (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84–7.79 (m, 4 H), 7.52–7.40 (m, 5 H), 6.32 (s, 1 H), 4.15–3.96 (m, 2 H), 3.44–3.42 (m, 1 H), 3.22 (t, $J = 10.2$ Hz, 2 H), 2.98–2.96 (m, 1 H), 2.75 (d, $J = 13.2$ Hz, 1 H), 2.00–1.90 (m, 2 H), 1.14 (t, $J = 8.7$ Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.54, 169.19, 141.15, 132.33, 132.17, 131.89, 131.84, 129.00, 127.24, 126.49, 126.18 (q, $J = 271$ Hz), 108.50, 57.30, 41.62, 36.34, 21.75, 13.54. ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.34. IR (KBr) ν (cm^{-1}): 3309, 2967, 2937, 1599, 1577, 1515, 1502, 1488, 1455, 1406, 1322, 1159, 1125, 1106, 1072, 1016, 847, 773. $C_{21}H_{21}Cl_3F_3NOSTi$ (546.68): calcd C 46.14, H 3.87, N 2.56. Found C 46.56, H 4.28, N 2.59.

[(1*Z*,3*Z*)-3-(2-(propylthio)ethylimino)-1,3-di-*p*-tolylprop-1-en-1-olate]Ti(IV)Cl_3 (5h). The same procedure as that for the preparation of **5a** was used. Yield: 1.0 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, $J = 7.2$ Hz, 2 H), 7.32–7.15 (m, 6 H), 6.35 (s, 1 H), 4.13–4.03 (m, 2 H), 3.42 (brs, 1 H), 3.19–3.15 (m, 1 H), 2.94 (brs, 1 H), 2.73 (brs, 1 H), 2.42 (s, 3 H), 2.38 (s, 3 H), 1.96–1.91 (m, 2 H), 1.13 (t, $J = 7.5$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.02, 169.89, 142.79, 140.03, 134.69, 129.86, 129.61, 129.30, 127.14, 125.87, 109.19, 57.31, 41.46, 36.42, 21.75, 21.62, 21.36, 13.52. IR (KBr) ν (cm^{-1}): 3212, 2923, 1607, 1588, 1567, 1482, 1452, 1408, 1337, 1284, 1236, 1186, 1120, 1060, 1018, 843, 810. $C_{22}H_{26}Cl_3NOSTi$ (506.74): calcd C 52.14, H 5.17, N 2.76. Found C 51.50, H 5.22, N 3.23.

[(1*Z*,3*Z*)-1,3-bis(4-methoxyphenyl)-3-(2-(propylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5i). The same procedure as that for the preparation of **5a** was used. Yield: 1.31 g (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, $J = 8.4$ Hz, 2 H), 7.23 (d, $J = 8.4$ Hz, 2 H), 7.00 (d, $J = 8.4$ Hz, 2 H), 6.90 (d, $J = 8.4$ Hz, 2 H), 6.30 (s, 1 H), 4.09 (brs, 2 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 3.41 (brs, 1 H), 3.19 (brs, 1 H), 2.96 (s, 1 H), 2.75 (d, 1 H), 1.96–1.91 (m, 2 H), 1.12 (t, $J = 7.5$ Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.77, 162.61, 155.81, 153.58, 122.71, 122.19, 121.19, 120.74, 117.50, 107.56, 107.32, 101.59, 50.29, 48.51, 48.47, 34.49, 29.53, 14.78, 6.54. IR (KBr) ν (cm^{-1}): 3202, 2839, 1669, 1603, 1589, 1566, 1508, 1478, 1438, 1420, 1336, 1302, 1258, 1240, 1175, 1124, 1060, 1026, 917, 846, 811, 784. $C_{22}H_{26}Cl_3NO_3STi$ (538.74): calcd C 49.05, H 4.86, N 2.60. Found C 48.32, H 5.03, N 3.26.

[(1*Z*,3*E*)-2-benzyl-1,3-diphenyl-3-(2-(propylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5j). The same procedure as that for the preparation of **5b**. Yield: 0.73 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–6.59 (m, 15 H), 3.98 (brs, 1 H), 3.83–3.71 (m, 2 H), 3.50–3.40 (m, 2 H), 3.06 (brs, 1 H), 2.92 (brs, 1 H), 2.62 (brs, 1 H), 1.94–1.87 (m, 2 H), 1.11 (t, $J = 7.6$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.35, 171.90, 139.57, 135.89, 134.16, 130.37, 129.01, 128.64, 128.46, 128.30, 128.28, 128.05, 126.19, 125.70, 119.88, 57.93, 41.58, 37.03, 35.59, 21.75, 13.53. IR (KBr) ν (cm^{-1}): 2961, 2928, 1599, 1566, 1495, 1468, 1442, 1328, 1262, 1157, 1141, 1072, 811, 699. $C_{27}H_{28}Cl_3NOSTi$ (568.81): calcd C 57.01, H 4.96, N 2.46. Found C 56.70, H 5.02, N 2.23.

[(1*Z*,3*E*)-2-methyl-1,3-diphenyl-3-(2-(propylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl_3 (5k). The same procedure as that for the preparation of **5b**. Yield: 0.75 g (66%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.42 (m, 8 H), 7.19 (d, $J = 6.4$ Hz, 2 H), 4.05–3.90 (m, 2 H), 3.40 (brs, 1 H), 3.12 (brs, 1 H), 2.90 (brs, 1 H), 2.66 (brs, 1 H), 1.96–1.87 (m, 2 H), 1.80 (s, 3 H), 1.11 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.42, 170.12, 137.20, 134.24, 130.35, 129.63, 129.36, 128.97, 128.29, 125.31, 117.55, 58.18, 41.47, 35.84, 21.74, 19.58, 13.52. IR (KBr) ν (cm^{-1}): 3220, 2963, 1583, 1570, 1502, 1474, 1440, 1330, 1158, 1073, 1018, 799, 783, 700. $C_{21}H_{24}Cl_3NOSTi$ (492.71): calcd C 51.19, H 4.91, N 2.84. Found C 51.71, H 5.01, 2.56.

[(1*Z*,3*Z*)-3-((*R*)-3-methyl-1-(propylthio)butan-2-ylimino)-1,3-diphenylprop-1-en-1-olate]Ti(IV)Cl_3 (5l). The same procedure as that for the preparation of **5b**. Yield: 0.2 g (19%).^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, $J = 7.2$ Hz, 2 H), 7.54–7.21 (m, 8 H), 6.36 (s, 1 H), 4.04 (d, $J = 9.3$ Hz, 2 H), 3.48 (m, 2 H), 3.25 (brs, 1 H), 2.93 (brs, 1 H), 2.54 (brs, 1 H), 1.90–1.86 (m, 2 H), 1.12 (t, $J = 7.2$ Hz, 3 H), 0.76 (d, $J = 5.7$ Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.63, 170.00, 139.58, 132.06, 129.56, 129.38, 129.02, 128.86, 127.21, 126.79, 124.51, 109.79, 73.68, 44.07, 40.28, 33.25, 22.21, 20.10, 19.61, 13.51. IR (KBr) ν (cm^{-1}): 3309, 2963, 1587, 1569, 1467, 1332, 1282, 1231, 1125, 1063, 1024, 1000, 762, 703, 683. $C_{23}H_{28}Cl_3NOSTi$ (520.77): calcd C 53.05, H 5.42, N 2.69. Found C 53.19, H 5.33, N 2.65.

Typical procedure for ethylene polymerization. (Using complex 5b as a representative example.)

Under 1 atm ethylene atmosphere, to a solution of MMAO (1.6 mL, 1.9 M in toluene) in toluene (50 mL, saturated with ethylene) was added a solution of complex **5b** (3 μmol, 3 μmol mL^{-1} in toluene) at 30 °C. The polymerization was carried out for 10 min and then quenched with concentrated HCl in ethanol (400 mL, HCl/EtOH, 1 : 20, v/v). The precipitated polymer was collected, washed with ethanol, and then dried overnight in a vacuum oven at 50 °C to constant weight.

Typical procedure for ethylene copolymerization

Under 1 atm ethylene atmosphere, to a solution of MMAO (1.6 mL, 1.9 M in toluene) and the desired amount of comonomer in toluene (50 mL, saturated with ethylene) was added a solution of complex **1** (3 μmol, 3 μmol mL^{-1} in toluene) at 30 °C. The polymerization was carried out for 10 min and then quenched with concentrated HCl in ethanol (400 mL, HCl/EtOH, 1 : 20, v/v). The precipitated polymer was collected, washed with ethanol, and then dried overnight in a vacuum oven at 50 °C to constant weight.

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