One-Pot Screening of Titanium Catalysts for Ethylene Polymerization

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A simple and practical one-step method for the screening of new titanium catalysts for olefin polymerization has been developed, which allows to combine ligands such as enamine and salicylaldehyde-derived imines with $TiCl_4(THF)_2$ *in situ* for direct activity evaluation. By this strategy, β-carbonylenamine made $TiCl_4(THF)_2$, a highly active and single-site-like catalyst for ethylene polymerization and copolymerization. A rationale involving a newly formed titanium complex that was characterized by X-ray analysis is discussed.

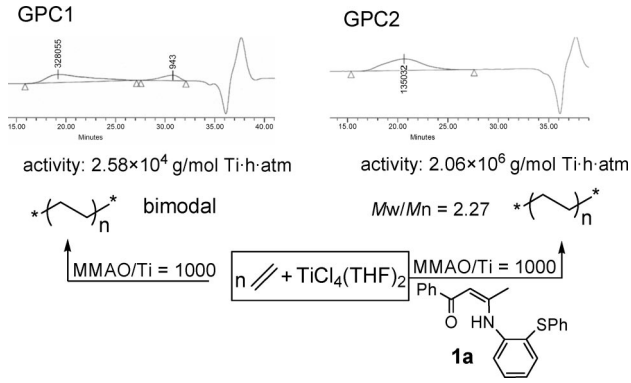
Introduction

$TiCl_4$ is one of the key components of heterogeneous Ziegler−Natta catalysts for olefin polymerization.[1,2] Under homogeneous conditions, $TiCl_4(THF)_2$ could also promote ethylene polymerization upon activation with modified methylaluminoxane (MMAO) but gave bimodal polyethylene with low activity (2.58×10^4 g/mol Ti·h·atm). Under the same polymerization conditions, unexpectedly, we found that $TiCl_4(THF)_2$, *in situ* mixed with enamine **1a**,[3−5] became highly active to give polyethylene with a narrow molecular distribution, and the activity was as high as 2.06×10^6 g/mol Ti·h·atm (Scheme 1). Thus, this provides a useful method for the discovery of new olefin polymerization catalysts.[6] In this paper, we report the results in detail.

Results and Discussion

Initially, it was found that polyethylene was obtained with high activity (entry 1, Table 1) by addition of an *in situ* mixed solution of $TiCl_4(THF)_2$ and enamine **1a** to MMAO (Al/Ti = 2000:1) in toluene under an ethylene atmosphere. To further improve the activity, several polymerization conditions were screened, and the results are summarized in Table 1. The Al/Ti ratio proved to influence the activity slightly (entries 1−4, Table 1). Under the screened conditions, the optimal ratio is 1000:1. At 0 °C, the polymerization of ethylene proceeded well to give polyethylene with high activity and narrow PDI ($M_w/M_n = 1.33$,

Scheme 1. $TiCl_4(THF)_2$-Catalyzed Ethylene Polymerization in the Presence and in the Absence of 1a



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(1) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979; pp 587−598.

(2) For recent reviews on the catalysts of olefin polymerization, see:(a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534. (d) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (e) Yoshida, Y.; Matsui, S.; Fujita, T. *J. Organomet. Chem.* **2005**, *690*, 4382. (f) Furuyama, R.; Saito, J.; Ishii, S.; Makio, H.; Mitani, M.; Tanaka, H.; Fujita, T. *J. Organomet. Chem.* **2005**, *690*, 4398. (g) Bianchini, C.; Giambastiani, G.; Rios, I. G.; Mantovani, G.; Meli, A.; Segarra, A. M. *Coord. Chem. Rev.* **2006**, *250*, 1391. (h) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.

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(4) For [O−NX] complexes as catalysts for olefin polymerization, see: (a) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706. (b) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Chem. Commun.* **2000**, 379. (c) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017. (d) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Chem Commun.* **2001**, 2120. (e) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M. *Organometallics* **2002**, *21*, 662. (f) Groysman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Inorg. Chim. Acta* **2003**, *345*, 137. (g) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200. (h) Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062. (i) Gendler, S.; Groysman, S.; Goldschmidt, Z.; Shuster, M.; Kol, M. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1136.

(5) For β-enaminoketonato metal complexes as olefin polymerization catalysts, see: (a) Guan, Z.; Marshall, W. J. *Organometallics* **2002**, *21*, 3580. (b) Li, X.; Dai, K.; Ye, W.-P.; Pan, L.; Li, Y. *Organometallics* **2004**, *23*, 1223. (c) Tang, L.; Hu, T.; Bo, Y.; Li, Y.; Hu, N. *J. Organomet. Chem.* **2005**, *690*, 3125. (d) Tang, L.; Duan, Y.; Pan, L.; Li, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 1681. (e) Zhang, L.; Brookhart, M.; White, P. S. *Organometallics* **2006**, *25*, 1868.

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Table 1. Optimization of Al/Ti Ratio and Polymerization Temperature[a]

entry	Al/Ti	T (°C)[b]	PE (g)	activity[c]	M_w[d,e]	M_w/M_n[e]
1	2000:1	30	0.76	1.52	15.7	2.51
2	1500:1	30	0.89	1.78	21.0	2.49
3	1000:1	30	1.03	2.06	20.7	2.27
4	500:1	30	0.66	1.32	38.8	2.09
5	1000:1	0	0.85	1.70	53.2	1.33
6	1000:1	50	0.50	1.00	18.5	2.70
7	1000:1	70	0.42	0.84	14.3	2.58

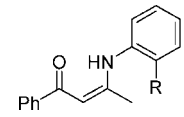
[a] Conditions: 50 mL of toluene; $TiCl_4(THF)_2$/**1a** = 1:1 = 3 μmol; cocatalyst, MMAO (1.9 mmol/mL in toluene); 10 min; 1 atm ethylene pressure. [b] Temperature of the oil bath. [c] 10^6 g/mol Ti·h·atm. [d] 10^4 g/mol. [e] Determined by GPC.

entry 5).[7] Increasing the temperature to 30 °C (entry 3 vs 5, Table 1), the activity reached 2.06×10^6 g PE/mol Ti·h·atm. Further raising the temperature lowered the activity greatly (entries 6 and 7, Table 1). The high-temperature GPC analysis revealed that the M_w of the polyethylene was temperature- and Al/Ti ratio-dependent. The molecular weight distribution ranged from 1.33 to 2.70, similar to those of PE produced by a single-site catalyst.[8] ^{13}C NMR analysis of the polyethylene showed that the polymer is highly linear polyethylene without branches.[7] This result was also consistent with the analysis of differential scanning calorimetry (T_m values 126−136 °C).

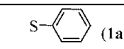
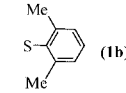
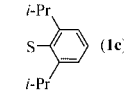
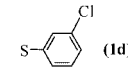
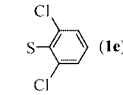
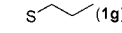
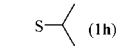
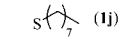
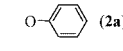
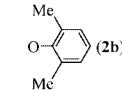
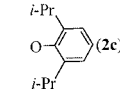
Encouraged by the aforementioned results, we first examined various *ortho*-substituted aniline-derived enamines **1a**−**j** and **2a**−**c** under the optimal conditions. As shown in Table 2, the *ortho* substituents on aniline strongly influenced the activity. Increasing the steric hindrance of the *ortho* substituents resulted in a significant decrease of catalytic activities (entries 1−3, 7−9, and 11−13) but an increase of the molecular weight of the polyethylene. For example, *n*-propyl-substituted enamine **1g** gave high activity (1.98×10^6 g/mol·h·atm, entry 7) and isopropyl-substituted enamine **1h** decreased to 0.86×10^6 g/mol·h·atm (entry 8). For bulky *tert*-butyl-substituted enamine **1i**, the lowest activity was observed (0.08×10^6 g/mol Ti·h·atm, entry 9). Compared with [O⁻NS]-enamines **1a**−**c**, the corresponding [O⁻NO]-enamines **2a**−**c** gave lower activities (entry 1 vs 11, 2 vs 12, 3 vs 13). When the phenylthio group of **1a** was replaced with a perfluorophenylthio group (**1f**), the activity was almost the same, and the resulting polymer became insoluble in 1,2,4-trichlorobenzene even at 135 °C, probably due to its high molecular weight (entry 1 vs 6, Table 2). Substitution of the phenylthio group of **1a** with a chlorine atom decreased the activity greatly (entries 4 and 5).

To further understand the relationship between the activity and structure, several other enamines with different structures were screened, and the results are summarized in Scheme 2.

Table 2. One-Pot Ethylene Polymerization Using Ligands 1a−j and 2a−c upon Activation with MMAO[a]



1a-1j
2a-2c

entry	R (L)	PE (g)	activity[b]	Mw[c,d]	Mw/Mn[d]
1	 (**1a**)	1.03	2.06	20.7	2.27
2	 (**1b**)	0.51	1.02	39.7	1.88
3	 (**1c**)	0.36	0.72	n.d[e]	n.d[e]
4	 (**1d**)	0.52	1.04	n.d[e]	n.d[e]
5	 (**1e**)	0.097	0.19	36.6	2.30
6	 (**1f**)	1.00	2.00	n.d[e]	n.d[e]
7	 (**1g**)	0.99	1.98	18.9	2.09
8	 (**1h**)	0.43	0.86	38.6	2.29
9	 (**1i**)	0.04	0.08	32.8[f]	2.56[f]
10	 (**1j**)	1.04	2.08	25.3	1.86
11	 (**2a**)	0.56	1.12	19.7	2.33
12	 (**2b**)	0.075	0.15	22.5	1.83
13	 (**2c**)	0.049	0.097	n.d[e]	n.d[e]

[a] Conditions: 50 mL of toluene; $TiCl_4(THF)_2$/ligand = 1:1 = 3 μmol; MMAO (1.6 mL, 1.9 mmol/mL in toluene); temperature of the oil bath 30 °C; 10 min; 1 atm of ethylene pressure. [b] 10^6 g/mol Ti·h·atm. [c] 10^4 g/mol. [d] Determined by GPC. [e] Not determined probably due to high molecular weights. [f] Bimodal; high molecular weight part.

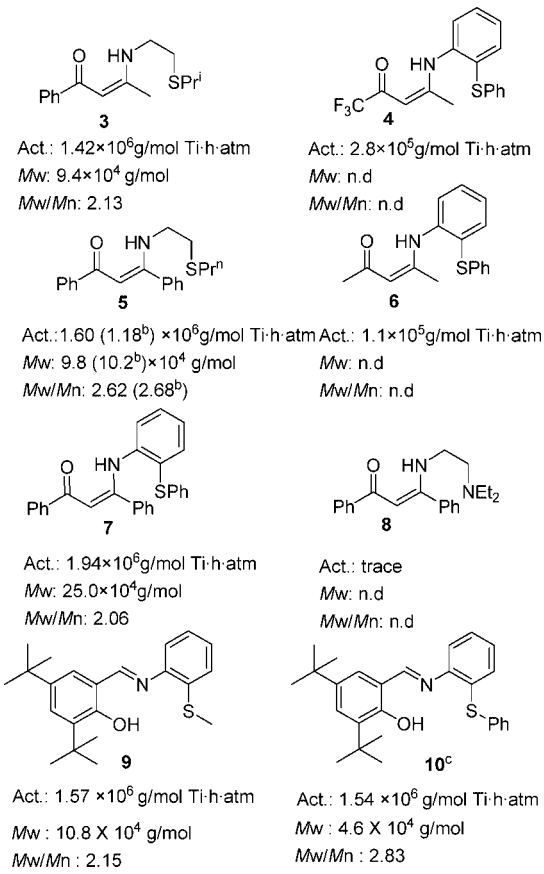
Compared with that of enamine **1a**, the activity of 2-(isopropylthio)ethanamine-derived enamine **3** decreased slightly. Replacement of the phenyl group of **1a** with a triflurometyl or methyl group (enanmines **4** and **6**) also reduced the activity greatly. 1,3-Diphenylpropane-1,3-dione- and 1-phenylbutane-1,3-dione-derived enamines gave similar results on ethylene polymerization (**7** in Scheme 2 vs **1a** in Table 2). Diamine-derived enamine **8** led to poor activity. Further studies showed that salicylaldehyde-derived imines[9] **9** and **10**[10] were also suitable ligands for this strategy (Scheme 2). For instance, the treatment of $TiCl_4(THF)_2$ with **9** and MMAO under ethylene atmosphere provided the desired polyethylene with

(6) For leading references on the development of screening strategies for the discovery of olefin polymerization catalyst, see:(a) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626. (b) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038. (c) Murphy, V.; Volpe, A. F.; Weinberg, W. H. *Curr. Opin. Chem. Biol.* **2003**, *7*, 427. (d) Boussie, T. R.; Diamond, G. M.; Goh, C.; Hall, K. A.; LaPointe, A. M.; Leclerc, M.; Lund, C.; Murphy, V.; Shoemaker, J. A. W.; Tracht, U.; Turner, H.; Zhang, J.; Uno, T.; Rosen, R. K.; Stevens, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 4306. (e) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 10798. (f) Adams, N.; Arts, H. J.; Bolton, P. D.; Cowell, D.; Dubberley, S. R.; Friederichs, N.; Grant, C. M.; Kranenburg, M.; Sealey, A. J.; Wang, B.; Wilson, P. J.; Cowley, A. R.; Mountford, P.; Schroder, M. *Chem. Commun.* **2004**, 434. (g) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 11037.

(7) For details, please see the Supporting Information.

(8) (a) Huang, B. T., Chen, W. *Metallocene Catalysts and Their Olefin Polymers*; Chemical Engineering Press: Beijing, 2000. (b) Ready, T. E.; Gurge, R.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 5236. (c) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347.

Scheme 2. Ligands Screened[a]



[a] Conditions: 50 mL of toluene; $TiCl_4(THF)_2$/ligand = 1:1 = 3 μmol; MMAO (1.6 mL, 1.9 mmol/mL); temperature of the oil bath 30 °C; 10 min; 1 atm of ethylene pressure. [b] 20 min. [c] 30 mL of toluene, 50 °C, 15 min.

high activity and narrow molecular distribution (PDI = 2.15) (Scheme 2).

$TiCl_4(THF)_2$ showed low activity toward ethylene polymerization, but the addition of enamine **1a** into the same system increased the activity from 2.58×10^4 to 2.06×10^6 g/mol Ti·h·atm. On the basis of these results, we are assuming that a new single-site catalyst was formed very quickly in the presence of enamine and MMAO. ^{1}H NMR (in $CDCl_3$) monitoring of the reaction of enamine **5** with $TiCl_4(THF)_2$ demonstrates this hypothesis clearly. As shown in Figure 1, after mixing **5** with $TiCl_4(THF)_2$ for 30 min and 1 h under room temperature, 51 and 61 mol % of **5**, respectively, were transformed into a new compound.[11] To determine the structure of this new-formed compound, we mixed enamine **5** with titanium tetrachloride at −78 °C and then warmed it to room temperature for 8 h, affording a pure complex in 97% yield (Scheme 3). ^{1}H NMR spectra of this complex proved virtually the same as that of the *in situ*-formed compound (Figure 1), indicating that the same compound was generated.

By ^{1}H and ^{13}C NMR analysis, the structure of the new-formed complex was assigned to be compound **11** (Scheme 3), which was further confirmed by an X-ray crystallographic analysis (Figure 2).[12] As shown in Figure 2, the X-ray analysis showed that the geometry at the titanium center could be described as a distorted octahedron with the three chlorine atoms in a *mer* disposition. Both Cl1 and Cl2 atoms are located *cis* to the Cl3 atom, which is favorable for the insertion of the monomer. Noticeably, the enamine was transformed to the imine form during the formation of the complex (Scheme 3).

Upon activation by MMAO, complex **11** proved to be a highly active catalyst for ethylene polymerization. The activity was comparable to that of the corresponding **5**/$TiCl_4(THF)_2$ mixture, as shown in Scheme 4. The GPC analysis revealed that the molecular weight and distributions of polyethylene produced by complex **11** were very similar to those of the corresponding "one-pot" method. These results, combined with the result of comparisons of **10** (in one pot) and complex **12** in Scheme 4, suggested that these two systems have the same catalytic species, disclosing the role of the enamine and the nature of the one-pot screening process.

Noticeably, the present screening method could also be used for the evaluation of the copolymerization of ethylene and α-olefin. Under the same conditions for ethylene polymerization, for example, an *in situ* mixture of enamine **5** and $TiCl_4(THF)_2$ could promote the copolymerization of ethylene with 1-hexene well (Table 3). Higher activities than that of ethylene polymerization were always observed, and the highest activity of 4.2×10^6 g/mol Ti·h·atm was obtained when the initial concentration of 1-hexene was 0.48 M (entry 2). With the increasing concentration of 1-hexene, both the molecular weight and the comonomer content of the resulting polymers improved significantly. For example, when the initial concentration of 1-hexene is 0.25 M, M_w of 12.6×10^4 g/mol and 21 mol % comonomer content were reached, which have been raised to 19.6×10^4 g/mol and 38 mol %, respectively, with a 3 times concentration of 1-hexene used.

Conclusion

Traditionally, the discovery of single-site catalysts involved a two-step process, including the time-consuming synthesis of pure metal complexes and their evaluation for olefin polymerization (strategy **a** in Scheme 5). Recently, Murphy and Gibson developed independently an elegant strategy of the synthesis of metal complex through the reaction of ligands with the prepared $M(CH_2Ph)_4$[6d] and $tolylCrCl_2(THF)_3$,[6b,g] respectively,

(9) For leading references on phenoxyimine-derived catalysts, see: (a) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1065. (b) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263. (c) Yoshida, Y.; Matsui, S.; Takagi, Y.; Mitani, M.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Fujita, T. *Chem. Lett.* **2000**, 1270. (d) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (e) Gibson, V. C.; Mastroianni, S.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.,* **2000**, 1969. (f) Bott, R. K. J. H.; David, L.; Schormann, M.; Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **2003**, *665*, 135. (g) Zhang, H.; Katao, S.; Nomura, K.; Huang, J. *Organometallics* **2007**, *26*, 5967.

(10) For [O⁻NX]$TiCl_3$ as olefin catalysts, see:(a) Hu, W.; Sun, X.; Wang, C.; Gao, Y.; Tang, Y.; Shi, L.; Xia, W.; Sun, J.; Dai, H.; Li, X.; Yao, X.; Wang, X. *Organometallics* **2004**, *23*, 1684. (b) Wang, C.; Sun, X.; Guo, Y.; Gao, Y.; Liu, B.; Ma, Z.; Xia, W.; Shi, L.; Tang, Y. *Macromol. Rapid Commun.* **2005**, *26*, 1609. (c) Wang, C.; Ma, Z.; Sun, X.; Gao, Y.; Guo, Y.; Tang, Y.; Shi, L. *Organometallics* **2006**, *25*, 3259. (d) Gao, M.; Wang, C.; Sun, X.; Qian, C.; Ma, Z.; Bu, S.; Tang, Y.; Xie, Z. *Macromol. Rapid Commun.* **2007**, *28*, 1511.

(11) In the polymerization conditions, MMAO can promote the formation of complex since MAO as well as alkylaluminium in MMAO is known as a base that is able to abstract the active hydrogen of alcohol; see: Marques, M. M.; Correia, S. G.; Ascenso, J. R.; Ribeiro, A. F. G.; GOMES, P. T.; Dias, A. R.; Foster, P.; Rausch, M. D.; Chien, J. C. W *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 2457.

(12) For details, please see the Supporting Information. CCDC 667769 (**11**) contains the supplementary crystallographic data. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk /data request/cif.

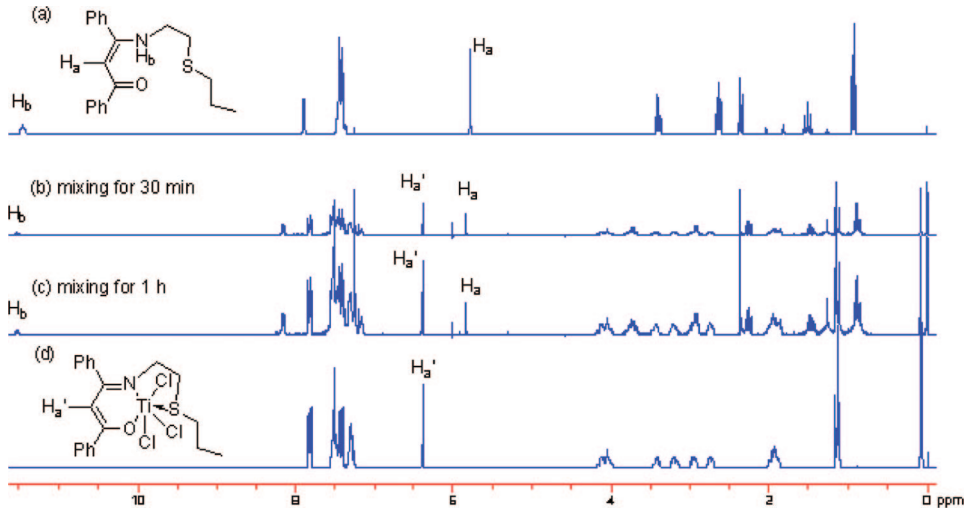
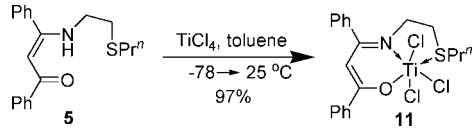


Figure 1. . ^{1}H NMR spectra of (a) ligand **5**, (b) mixing **5** with $TiCl_4(THF)_2$ for 30 min, (c) mixing **5** with $TiCl_4(THF)_2$ for 1 h, and (d) complex **11**.

Scheme 3. Synthesis of Titanium Complex 11



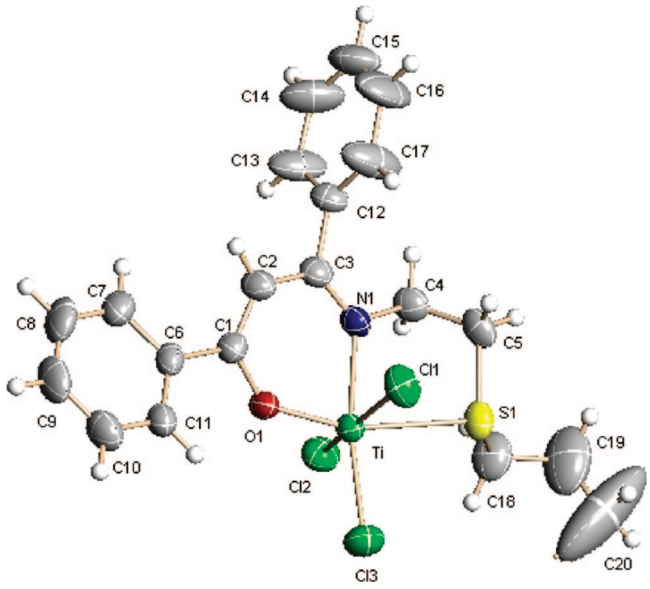
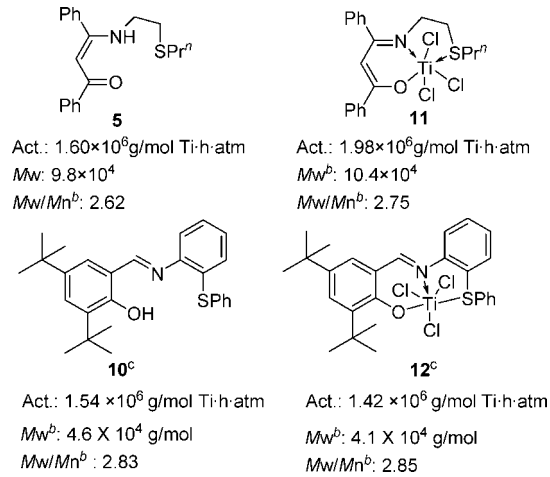


Figure 2. . Molecular structure of complex **11**. Selected bond lengths (Å) and angles (deg): Ti−O(1) = 1.823(2), Ti−N(1) = 2.155(3), Ti−Cl(3) = 2.2666(12), Ti−Cl(2) = 2.2881(13), Ti−Cl(1) = 2.3298(12), Ti−S(1) = 2.5953(12), N(1)−C(3) = 1.309(5), N(1)−C(4) = 1.478(4), O(1)−C(1) = 1.334(4), C(1)−C(2) = 1.347(5); O(1)−Ti−N(1) = 84.63(11), O(1)−Ti−Cl(3) = 105.18(9), O(1)−Ti−Cl(2)=97.37(10),O(1)−Ti−Cl(1)=92.45(9),O(1)−Ti−S(1) = 162.46(9), N(1)−Ti−Cl(2) = 86.85(9), N(1)−Ti−Cl(3) = 170.12(9), N(1)−Ti−Cl(1) = 84.00(9), Cl(3)−Ti−Cl(2) = 92.86(5), Cl(3)−Ti−Cl(1) = 94.33(5), Cl(2)−Ti−Cl(1) = 165.89(5).

followed by activity evaluation without the purification of the complex. In this paper, we have developed a simple and practical one-step method for the screening of new titanium catalysts for olefin polymerization (Scheme 5). This method allows combining ligands such as enamine and salicylaldehyde-derived imines with $TiCl_4(THF)_2$ *in situ* for direct activity evaluation.

Scheme 4. Comparison of the Ethylene Polymerization of Complexes 11 and 12 with the Corresponding One-Pot Approach[a]



[a] Conditions: 50 mL of toluene; cat. 3 μmol; Al/Ti 1000; oil bath temperature 30 °C; 10 min; 1 atm of ethylene pressure. [b] Determined by GPC. [c] 30 mL of toluene, oil bath temperature 50 °C, 15 min.

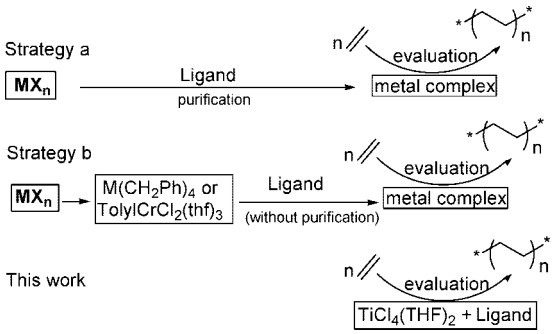
Table 3. Primary Results of Ethylene and 1-Hexene Copolymerization Using a One-Pot Approach[a]

entry	1-hexene (mmol)	T (°C)	t (min)	activity[b]	M_w[c,d]	M_w/M_n[d]	comonomer content (mol %)[e]
1	12	30	10	2.9	12.6	2.30	21
2	24	30	10	4.2	16.4	2.14	30
3	36	30	10	3.3	19.6	2.15	38
4	12	0	10	0.62	69.9	1.78	[f]
5	12	50	10	1.38	14.1	2.44	[f]
6	12	30	30	1.48	17.0	2.24	[f]
7[g]	12	30	10	2.39	35.4	1.98	[f]

[a] Conditions: toluene (50 mL); $TiCl_4(THF)_2$/**5** = 1:1 = 3 μmol; 1.6 mL of MMAO (1.9 mmol/mL); 1 atm of ethylene pressure. [b] 10^6 g/mol Ti·h·atm. [c] 10^4 g/mol. [d] Determined by GPC. [e] Determined by ^{13}C NMR at 110 °C in 1,2-dichlorobenzene-d_4. [f] Not determined. [g] $TiCl_4(THF)_2$/**1g** = 1:1 = 3 μmol.

By this strategy, β-carbonylenamine made $TiCl_4(THF)_2$, a highly active and single-site-like catalyst for ethylene polymerization.

Scheme 5. Strategies for the Discovery of Olefin Polymerization Catalysts



Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 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 (using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 0.92 mL/min). ^{13}C NMR data for polymers were obtained using *o*-dichlorobenzene-d_4 as the solvent at 110 °C. Transition melting temperatures of the polymers were determined by DSC with a Perkin-Elmer Pyris 1 differential scanning calorimeter, measured upon reheating the polymer sample to 200 °C at a heating rate of 10 °C/min. 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.

Synthesis of (*Z*)-1-Phenyl-3-(2-(phenylthio)phenylamino)-but-2-en-1-one (1a). To a solution of 1-phenylbutane-1,3-dione (3.24 g, 20.0 mmol) and 2-(phenylthio)benzenamine (3.84 g, 19.1 mmol) in ethanol (30 mL) were added a few drops of acetic acid at room temperature. After refluxing with stirring for 20 h, the resulting mixture was cooled to room temperature to afford a yellow solid, which could be used without further purification. Yield: 2.67 g (41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.93 (s, 1 H), 7.84−7.87 (m, 2 H), 7.47−7.15 (m, 12 H), 5.85 (s, 1 H), 1.97 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.84, 162.06, 139.94, 137.78, 133.95, 133.52, 132.55, 131.20, 130.83, 129.25, 128.16, 127.78, 127.22, 127.14, 126.99, 126.88, 94.32, 20.06. IR (KBr) ν 3060, 1597, 1574, 1546, 1317, 1287, 1271, 1060, 747, 732. Anal. Calcd $C_{22}H_{19}NOS$ (345.46): C 76.49, H 5.54, N 4.05. Found: C 76.64, H 5.63, N 3.77. MS (EI) (*m*/*z*): 345 (M^+).

Synthesis of (*Z*)-3-(2-(2, 6-Dimethylphenylthio)phenylamino)-1-phenylbut-2-en-1-one (1b). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.31 g, 1.9 mmol) and 2-(2,6-dimethylphenylthio)benzenamine (0.40 g, 1.7 mmol) were used. Yield: 0.47 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.84 (s, 1 H), 7.99−7.96 (m, 2 H), 7.46−7.43 (m, 3 H), 7.25−7.01 (m, 6 H), 6.44 (dd, J = 1.2 Hz, 7.8 Hz, 1 H), 5.99 (s, 1 H), 2.40 (s, 6 H), 2.06 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.93, 163.21, 144.06, 139.91, 136.21, 135.14, 130.83, 129.45, 129.17, 128.54, 128.15, 127.50, 127.15, 124.86, 124.76, 93.95, 21.68, 20.01. IR (KBr): ν 3420, 3060, 2920, 1599, 1577, 1317, 1284, 747. Anal. Calcd for $C_{24}H_{23}NOS$ (373.15): C 77.18, H 6.21, N 3.75. Found: C 77.44, H 6.18, N 3.34. MS (EI) (*m*/*z*): 373 (M^+).

Synthesis of (*Z*)-3-(2-(2,6-Diisopropylphenylthio)phenylamino)-1-phenylbut-2-en-1-one (1c). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1, 3-dione (0.19 g, 1.2 mmol) and 2-(2,6-diisopropylphenylthio)benzenamine (0.30 g, 1.1 mmol) were used. Yield: 0.32 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.82 (s, 1 H), 7.88−7.91 (m, 2 H), 7.48−7.43 (m, 4 H), 7.30−7.01 (m, 5 H), 6.39 (dd, J = 1.5 Hz, 7.5 Hz, 1 H), 6.02 (s, 1 H), 3.65−3.61 (m, 2 H), 2.08 (s, 3 H), 1.15 (s, 6 H), 1.12 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.98, 154.22, 139.96, 138.55, 130.87, 130.45, 128.22, 127.57, 127.50, 127.20, 126.78, 125.34, 124.55, 124.25, 93.90, 31.66, 24.17, 19.96. IR (KBr) ν 3060, 2980, 1597, 1575, 1461, 1319, 1284, 745. Anal. Calcd for $C_{28}H_{31}NOS$ (429.62): C 78.28, H 7.27, N 3.26. Found: C 78.29, H 7.51, N 3.07. MS (EI) (*m*/*z*): 430 (M^+).

Synthesis of (*Z*)-3-(2-(3-Chlorophenylthio)phenylamino)-1-phenylbut-2-en-1-one (1d). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.68 g, 4.2 mmol) and 2-(3-chlorophenylthio)benzenamine (1.00 g, 4.2 mmol) were used. The product was recrystallized from ethanol. Yield: 0.57 g (36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.95 (s, 1 H), 7.91−7.88 (m, 2 H), 7.47−7.15 (m, 11 H), 5.81 (s, 1 H), 1.95 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.00, 161.53, 139.83, 138.97, 136.57, 134.73, 132.99, 131.35, 130.89, 130.69, 130.08, 129.32, 128.44, 128.15, 127.39, 127.12, 126.99, 126.83, 94.59, 19.99. IR (KBr): ν 3060, 1594, 1574, 1552, 1458, 1315, 1278, 1271, 748. Anal. Calcd for $C_{22}H_{18}ClNOS$ (379.90): C 69.55, H 4.78, N 3.69. Found: C 69.60, H 4.64, N 3.43. MS (EI) (*m*/*z*): 379 (M^+).

Synthesis of (*Z*)-3-(2-(2,6-dichlorophenylthio)phenylamino)-1-phenylbut-2-en-1-one (1e). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.20 g, 1.2 mmol) and 2-(2,6-dichlorophenylthio)benzenamine (0.30 g, 1.1 mmol) were used. Yield: 0.34 g (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.81 (s, 1 H), 7.96 (d, J = 7.2 Hz, 1 H), 7.94 (d, J = 7.2 Hz, 1 H), 7.47−7.36 (m, 6 H), 7.30−7.10 (m, 3 H), 6.73−6.70 (m, 1 H), 5.96 (s, 1H), 2.01 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.00, 163.02, 141.70, 139.87, 136.02, 134.02, 130.86, 130.83, 130.29, 128.95, 128.17, 127.84, 127.57, 127.18, 126.83, 126.22, 94.16, 20.08. IR (KBr): ν 3420, 3060, 2920, 1600, 1578, 1553, 1317, 1283, 782, 750. Anal. Calcd for $C_{22}H_{17}Cl_2NOS$ (414.35): C 63.77, H 4.14, N 3.38. Found: C 63.54, H 4.04, N 3.20. MS (EI) (*m*/*z*): 414 (M^+).

Synthesis of (*Z*)-3-(2-(Perfluorophenylthio)phenylamino)-1-phenylbut-2-en-1-one (1f). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.89 g, 5.5 mmol) and 2-(perfluorophenylthio)benzenamine (1.46 g, 5.0 mmol) were used. Yield: 0.77 g (35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.86 (s, 1 H), 7.94−7.91 (m, 2 H), 7.46−7.42 (m, 3 H), 7.31−7.20 (m, 4 H), 5.95 (s, 1 H), 2.00 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.28, 162.20, 139.60, 138.08, 131.08, 130.53, 128.42, 128.25, 128.06, 127.61, 127.15, 94.40, 19.96. ^{19}F NMR (282 MHz, $CDCl_3$): δ −131.41 (d, J = 20.57 Hz, 2 F), −151.53 (t, J = 20.57 Hz, 1 F), −160.55 (t, J = 20.57 Hz, 2 F). IR (KBr): ν 3060, 1599, 1576, 1552, 1511, 1488, 1464, 1316, 1273, 1088, 980, 858, 751. Anal. Calcd for $C_{22}H_{14}F_5NOS$ (435.41): C 60.69, H 3.24, N 3.22. Found: C 60.64, H 3.28, N 3.04. MS (ESI) (*m*/*z*): 436 ($M + H^+$).

Synthesis of (*Z*)-1-Phenyl-3-(2-(propylthio)phenylamino) but-2-en-1-one (1g). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.90 g, 5.5 mmol) and 2-(propylthio)benzenamine (0.93 g, 5.5 mmol) were used. Yield: 1.70 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.86 (s,1 H), 7.96−7.94 (m, 2 H), 7.46−7.17 (m, 7 H), 5.94 (s, 1 H), 2.87 (t, J = 7.5 Hz, 2 H), 2.04 (s, 3 H), 1.71−1.64 (m, 2 H), 1.02 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.83, 162.45, 139.97, 137.53, 134.23, 130.83, 128.83, 128.17, 127.19, 126.85, 126.75, 125.89, 94.21, 34.64, 22.28, 20.23, 13.52. IR (KBr): ν 2962, 1598, 1574, 1548, 1317, 1280, 1195, 754. Anal. Calcd for $C_{19}H_{21}NOS$

(311.44): C 73.27, H 6.80, N 4.50. Found: C 73.20, H 6.81, N 4.23. MS (EI) (*m*/*z*): 311 (M^+).

Synthesis of (*Z*)-3-(2-(Isopropylthio)phenylamino)-1-phenylbut-2-en-1-one (1h). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (1.00 g, 6.0 mmol) and 2-(isopropylthio)benzenamine (1.00 g, 6.2 mmol) were used. The product was purified by column chromatography on silica gel to give a yellow oil. Yield: 0.48 g (26%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.94 (s, 1 H), 7.97−7.93 (m, 2 H), 7.49−7.42 (m, 4 H), 7.25−7.18 (m, 3H), 5.93 (s, 1 H), 3.41−3.37 (m, 1 H), 2.07 (s, 3 H), 1.30 (d, J = 6.9 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.67, 161.81, 139.95, 139.17, 132.57, 131.96, 130.75, 128.11, 127.10, 126.34, 126.20, 94.43, 37.50, 22.91, 20.34. IR (KBr): ν 2980, 1598, 1577, 1436, 1320, 1280, 1066, 758. Anal. Calcd for $C_{19}H_{21}NOS$ (311.44): C 73.27, H 6.80, N 4.50. Found: C 73.19, H 6.74, N 4.14. MS (EI) (*m*/*z*): 311 (M^+).

Synthesis of (*Z*)-3-(2-(*tert*-Butylthio)phenylamino)-1-phenylbut-2-en-1-one (1i). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (1.84 g, 11.3 mmol) and 2-(*tert*-butylthio)benzenamine (1.81 g, 10.0mmol) were used. Yield: 1.37 g (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.17 (s, 1 H), 7.98−7.94 (m, 2 H), 7.64 (dd, J = 1.2 Hz, 7.5 Hz, 1 H), 7.47−7.17 (m, 6 H), 5.93 (s, 1 H), 2.14 (s, 3 H), 1.32 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.53, 160.52, 143.05, 139.82, 130.80, 129.64, 128.16, 127.20, 125.20, 125.02, 95.17, 47.86, 30.84, 20.82. IR (KBr): ν 3060, 2980, 1596, 1577, 1555, 1280, 1456, 1321, 759. Anal. Calcd for $C_{20}H_{23}NOS$ (325.47): C 73.81, H 7.12, N 4.30. Found: C 73.73, H 7.07, N 3.95. MS (EI) (*m*/*z*): 325 (M^+).

Synthesis of (*Z*)-3-(2-(Octylthio)phenylamino)-1-phenylbut-2-en-1-one (1j). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.68 g, 4.2 mmol) and 2-(octylthio)benzenamine (1.00 g, 4.2 mmol) were used. The product was purified by column chromatography on silica gel to give a yellow oil. Yield: 0.48 g (30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.86 (s, 1 H), 8.00−7.90 (m, 2 H), 7.44−7.16 (m, 7 H), 5.94 (s, 1 H), 2.87 (t, J = 7.5 Hz, 2 H), 2.04 (s, 3 H), 1.67−1.62 (m, 2 H), 1.41−1.24 (m, 10 H), 0.86 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.79, 162.42, 139.94, 137.42, 134.35, 130.83, 128.65, 128.16, 127.18, 126.84, 126.71, 125.81, 94.19, 32.61, 31.75, 29.12, 28.90, 28.85, 22.61, 20.23, 14.08. IR (KBr): ν 3060, 2953, 2926, 2854, 1599, 1577, 1553, 1464, 1317, 1281, 1064, 746, 688. Anal. Calcd for $C_{24}H_{31}NOS$ (381.57): C 75.54, H 8.19, N 3.67. Found: C 75.51, H 8.08, N 3.53. MS (ESI) (*m*/*z*): 382 ($M + H^+$).

Synthesis of (*Z*)-3-(2-Phenoxyphenylamino)-1-phenylbut-2-en-1-one (2a). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (1.75 g, 10.8 mmol) and 2-phenoxybenzenamine (2 g, 10.8 mmol) were used. Yield: 2.03 g (57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.83 (s, 1 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.85 (d, J = 7.5 Hz, 1 H), 7.43−7.00 (m, 12 H), 5.87 (s, 1 H), 2.15 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.70, 162.48, 156.58, 151.33, 140.07, 130.73, 130.05, 129.72, 128.15, 127.06, 127.01, 126.90, 123.61, 123.44, 119.22, 118.80, 94.46, 20.30. IR (KBr): ν 3060, 2940, 1599, 1576, 1553, 1489, 1318, 1283, 747, 689. MS (ESI) (*m*/*z*): 330 ($M + H^+$). HRMS (MALDI/DHB): 330 ($C_{22}H_{20}NO_2^+$).

Synthesis of (*Z*)-3-(2-(2,6-Dimethylphenoxy)phenylamino)--1-phenylbut-2-en-1-one (2b). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (0.76 g, 4.7 mmol) and 2-(2,6-dimethylphenoxy)benzenamine (1.00 g, 4.7 mmol) were used. Yield: 1.51 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.02 (s, 1 H), 7.94−7.91 (m, 2 H), 7.45−7.40 (m, 3 H), 7.29−7.26 (m, 1 H), 7.10−6.98 (m, 5 H), 6.44 (dd, J = 1.5, 7.8 Hz, 1 H), 5.96 (s, 1 H), 2.24 (s, 3 H), 2.15 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.74, 162.70, 151.30, 151.04, 140.09, 131.19, 130.70, 128.97, 128.14, 127.34, 127.07, 126.89, 126.42, 125.23, 121.28, 113.42, 94.42, 20.48, 16.31. IR (KBr): ν 3060, 1603, 1576, 1552, 1477, 1323, 1282, 1187, 760. Anal. Calcd for $C_{24}H_{23}NO_2$ (357.44): C 80.64, H 6.49, N 3.92. Found: C 80.59, H 6.37, N 3.70. MS (ESI) (*m*/*z*): 358 ($M + H^+$).

Synthesis of (*Z*)-3-(2-(2,6-Diisopropylphenoxy)phenylamino)--1-phenylbut-2-en-1-one (2c). The same procedure as that for the preparation of **1a** was used. 1-Phenylbutane-1,3-dione (2.11 g, 13.0 mmol) and 2-(2,6-diisopropylphenoxy)benzenamine (3.50 g, 13.0 mmol) were used. Yield: 3.74 g (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.98 (s, 1 H), 7.94−7.90 (m, 2 H), 7.43−7.19 (m, 7 H), 7.04−6.96 (m, 2 H), 6.44 (dd, J = 1.5, 8.4 Hz, 1 H), 5.95 (s, 1 H), 3.02−2.93 (m, 2 H), 2.20 (s, 3 H), 1.20 (d, J = 7.2 Hz, 6 H), 1.09 (d, J = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.61, 162.81, 153.07, 148.55, 141.52, 140.26, 130.66, 128.16, 127.22, 127.07, 126.92, 126.83, 125.96, 124.35, 121.24, 113.77, 94.20, 27.13, 24.24, 22.37, 20.33. IR (KBr): ν 3060, 2961, 1606, 1576, 1558, 1476, 1322, 1282, 1218, 760, 742, 705. Anal. Calcd for $C_{28}H_{31}NO_2$ (413.24): C 81.32, H 7.56, N 3.39. Found: C 81.31, H 7.44, N 3.30. MS (ESI) (*m*/*z*): 414 ($M + H^+$).

Synthesis of (*Z*)-3-(2-(Isopropylthio)ethylamino)-1-phenylbut-2-en-1-one (3). To a solution of 1-phenylbutane-1,3-dione (3.24 g, 20.0 mmol) and 2-(isopropylthio)ethanamine (2.38 g, 20.0 mmol) in xylene (30 mL) was added 4-methylbenzenesulfonic acid hydrate (0.11 g, 0.6 mmol) at room temperature. The flask was equipped with a water separator. After refluxing for 2 days, the solvent was removed by vaccum, and the residue was purified by column chromatography on silica gel to give a yellow oil. Yield: 0.60 g (11%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.51 (s, 1 H), 7.88−7.84 (m, 2 H), 7.39−7.36 (m, 3 H), 5.67 (s, 1 H), 3.48−3.41 (m, 2 H), 3.00−2.88 (m, 1 H), 2.71 (t, J = 7.2 Hz, 2 H), 2.02 (s, 3 H), 1.25 (d, J = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.61, 164.06, 140.07, 130.24, 127.89, 126.66, 92.19, 43.22, 35.04, 30.48, 23.21, 19.23. IR (KBr): ν 2960, 2918, 2860, 1601, 1550, 1443, 1294, 1085, 1065, 740, 675. MS (EI) (*m*/*z*): 264 ($M + H^+$). HRMS (MALDI/DHB): 264 ($C_{15}H_{21}NOS^+$).

Synthesis of (*Z*)-1,1,1-Trifluoro-4-(2-(phenylthio)phenylamino)pent-3-en-2-one (4). To a solution of 1,1,1-trifluoropentane-2,4-dione (0.99 g, 6.4 mmol) and 2-(phenylthio)benzenamine (1.92 g, 9.5 mmol) in dichloromethane (4 mL) were added 4 Å molecular sieves (0.40 g) at room temperature. After stirring for 3 days, the 4 Å molecular sieves were filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to give the product as an oil. Yield: 0.32 g (15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.35 (s, 1 H), 7.34−7.17 (m, 9 H), 5.44 (s, 1 H), 1.92 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.53, 167.93, 136.39, 134.25, 132.97, 132.34, 131.83, 129.41, 128.30, 128.09, 127.70, 127.25, 115.47, 90.81 (t, J = 5.4 Hz), 19.92. ^{19}F NMR (282 MHz, $CDCl_3$): δ −77.17 (s, 3 F). IR (KBr): ν 3155, 2925, 2852, 1620, 1590, 1565, 1467, 1439, 1428, 1292, 1241, 1062, 861, 753, 734. Anal. Calcd for $C_{17}H_{14}F_3NOS$ (337.36): C 60.52, H 4.18, N 4.15. Found: C 60.68, H 4.15, N 3.95. MS (ESI) (*m*/*z*): 338 ($M + H^+$).

Synthesis of (*Z*)-1,3-Diphenyl-3-(2-(propylthio)ethylamino)-prop-2-en-1-one (5). The same procedure as that for the preparation of **3** was used. 1,3-Diphenylpropane-1,3-dione (2.52 g, 11.2 mmol), 2-(propylthio)ethanamine (1.34 g, 11.2 mmol), and 4-methylbenzenesulfonic acid hydrate (0.064 g, 0.34 mmol) were used. Yield: 2.80 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.46 (s, 1 H), 7.91 (d, J = 7.8 Hz, 1 H), 7.88 (d, J = 7.2 Hz, 1 H), 7.47−7.39 (m, 8 H), 5.78 (s, 1 H), 3.43−3.36 (m, 2 H), 2.63 (t, J = 7.2 Hz, 2 H), 2.36 (t, J = 7.5 Hz, 2 H), 1.54−1.47 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.54, 166.34, 140.03, 135.38, 130.73, 129.46, 128.53, 128.12, 127.66, 127.01, 93.80, 44.24, 33.98, 32.56, 22.80, 13.34. IR (KBr): ν 3059, 2960, 2927, 2870, 1595, 1569, 1480, 1331, 1296, 1225, 1143, 1057, 749, 692. Anal. Calcd for C20H23NOS (325.47): C 73.81, H 7.12, N 4.30. Found: C 73.96, H 7.17, N 4.20. MS (ESI) (*m*/*z*): 326 ($M + H^+$).

Synthesis of (*Z*)-4-(2-(Phenylthio)phenylamino)pent-3-en-2-one (6). To a solution of pentane-2,4-dione (0.30 g, 3.0 mmol) and 2-(phenylthio)benzenamine (0.40 g, 2.0 mmol) in dichloromethane (10 mL) was added anhydrous magnesium sulfate (2.50 g) at room temperature. After stirring for 4 days, the magnesium sulfate was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to give the product as an oil. Yield: 0.39 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.34 (s, 1 H), 7.35−7.26 (m, 5 H), 7.19−7.11 (m, 4 H), 5.15 (s, 1 H), 2.09 (s, 3 H), 1.84 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.34, 159.95, 137.83, 133.68, 132.36, 131.14, 129.21, 128.92, 127.71, 127.17, 126.85, 126.66, 97.77, 29.15, 19.50. IR (KBr): ν 3450, 3058, 2960, 1575, 1500, 1355, 1275, 1186, 1024, 751. Anal. Calcd for $C_{17}H_{17}NOS$ (283.10): C 72.05, H 6.05, N 4.94. Found: C 72.10, H 6.02, N 4.78. MS (EI) (*m*/*z*): 283 (M^+).

Synthesis of (*Z*)-1,3-Diphenyl-3-(2-(phenylthio)phenylamino)prop-2-en-1-one (7). To a solution of 1,3-diphenylpropane-1,3-dione (2.24 g, 10.0 mmol) and 2-(phenylthio)benzenamine (2.01 g, 10.0 mmol) in xylene (30 mL) was added 4-methylbenzenesulfonic acid hydrate (0.57 g, 3 mmol) at room temperature. The flask was equipped with a water separator. After refluxing for 2 days, the solvent was removed by vaccum, and the residue was recrystallized from ethanol to give a yellow powder as the desired product. Yield: 2.18 g (53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.91 (s, 1 H), 7.98 (d, J = 5.4 Hz, 2 H), 7.45−7.18 (m, 14 H), 6.89 (s, 2 H), 6.42 (d, J = 6.6 Hz, 1 H), 6.08 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.59, 160.50, 139.94, 139.68, 135.87, 134.50, 132.95, 131.91, 131.31, 129.61, 129.12, 128.91, 128.44, 128.27, 128.03, 127.53, 127.41, 127.36, 124.90, 124.46, 97.92. IR (KBr): ν 3051, 1545, 1480, 1438, 1330, 1282, 1207, 1050, 1022, 781, 754, 686. Anal. Calcd for $C_{27}H_{21}NOS$ (407.53): C 79.57, H 5.19, N 3.44. Found: C 79.23, H 5.18, N 3.13. MS (EI) (*m*/*z*): 407 (M^+).

Synthesis of (Z)-3-(2-(Diethylamino)ethylamino)-1,3-diphenylprop-2-en-1-one (8). The same procedure as that for the preparation of **3** was used. 1,3-Diphenylpropane-1,3-dione (5.83 g, 26.0 mmol), *N*,*N*-diethylethane-1,2-diamine (3.00 g, 26.0 mmol), and 4-methylbenzenesulfonic acid hydrate (0.15 g, 0.78 mmol) were used. Yield: 1.85 g (22%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.33 (s, 1 H), 7.90−7.87 (m, 2 H), 7.47−7.36 (m, 8 H), 5.75 (s, 1 H), 3.30−3.24 (m, 2 H), 2.61−2.56 (m, 2 H), 2.51−2.44 (m, 4 H), 0.97 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.28, 166.60, 140.38, 135.79, 130.56, 129.35, 128.47, 128.11, 127.67, 127.00, 93.46, 53.13, 47.24, 43.12, 11.70. IR (KBr): ν 3060, 2968, 2933, 1596, 1583, 1569, 1481, 1330, 1057, 746, 693. Anal. Calcd for $C_{21}H_{26}N_2O$ (322.44): C 78.22, H 8.13, N 8.69. Found: C 78.56, H 7.85, N 8.43. MS (ESI) (*m*/*z*): 323 ($M + H^+$).

Synthesis of [(1*Z*,3*Z*)-1,3-Diphenyl-3-(2-(propylthio)ethylimino)prop-1-en-1-olate]Ti(IV)Cl$_3$ (11). To a solution of $TiCl_4$ (1.64 g, 8.7 mmol) in toluene (30 mL) at −78 °C was added dropwise a solution of ligand **5** (2.17 g, 6.7 mmol) in toluene (30 mL) over 15 min, and 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 complex **11**. Yield: 3.08 g (97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 2 H), 7.52−7.29 (m, 8 H), 6.39 (s, 1 H), 4.14−4.01 (m, 2 H), 3.48−3.38 (m, 1 H), 3.24−3.18 (m, 1 H), 3.00−2.91 (m, 1 H), 2.76−2.71 (m, 1 H), 1.99−1.89 (m, 2 H), 1.13 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.75, 169.78, 137.58, 132.01, 129.82, 129.34, 128.89, 127.14, 125.75, 109.51, 57.34, 41.49, 36.37, 21.76, 13.54. Anal. Calcd for $C_{20}H_{22}Cl_3NOSTi$ (478.69): C 50.18, H 4.63, N 2.93. Found: C 50.04, H 4.65, N 2.75.

Typical Procedure for Ethylene Polymerization by a One-Pot Approach. (using ligand **5** as a representative example). Under a 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 the *in situ* mixture of $Ti(THF)_2Cl_4$ and enamine **5** (0.30 mL, 10 μmol/mL in toluene, 1:1, molar ratio) 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 Polymerization. (using complex **11** as a representative example). Under a 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 **11** (3 μmol, 3 μmol/mL 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 and 1-Hexene Copolymerization by a One-Pot Approach. Under a 1 atm ethylene atmosphere, to a solution of MMAO (1.6 mL, 1.9 M in toluene) and the desired amount of 1-hexene in toluene (50 mL, saturated with ethylene) was added the *in situ* mixture of $Ti(THF)_2Cl_4$ and enamine **5** (0.30 mL, 10 μmol/mL in toluene, 1:1, molar ratio) 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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Supporting Information Available: ^{1}H NMR and ^{13}CNMR characterization data for all new compounds and the polymers, and X-ray crystallographic data in CIF format of complex **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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