

# SILICON-BRIDGED METALLOCENE CATALYST AND USE THEREOF

## TECHNICAL FIELD

The present invention belongs to the technical field of preparation of catalysts, and relates to a silicon-bridged metallocene catalyst and use thereof.

## BACKGROUND

Syndiotactic polypropylene has high transparency, good impact resistance, good room-temperature toughness, and other characteristics, and can be used in the fields of medical supplies, packaging materials, and sanitary products. Currently, various catalytic systems and processes for industrial production of the syndiotactic polypropylene have been successfully developed by many petrochemical companies (US 4892851, US 5155080, US 5225500, US 5428121, US 6713426, EP 0896022). A dimethyl-substituted carbon-bridged metallocene-fluorene type catalyst for preparation of the syndiotactic polypropylene was first synthesized by Ewen, et al. (*Journal of the American Chemical Society* **1988**, 110 (18), 6255-6256). However, polypropylene obtained by this type of catalyst generally has a lower molecular weight ( $M_w=3\times 10^4$ - $1.3\times 10^5$  g·mol<sup>-1</sup>).

In order to increase the molecular weight of the syndiotactic polypropylene, a diphenyl-substituted carbon-bridged metallocene-fluorene type catalyst has been used in a propylene polymerization reaction. Compared with the dimethyl-substituted carbon-bridged catalyst, the molecular weight of polypropylene obtained by the diphenyl-substituted carbon-bridged metallocene-fluorene type catalyst is increased ( $M_w=5.6\times 10^5$  g·mol<sup>-1</sup>), but catalytic activity is obviously decreased ( $6.82\times 10^4$  vs  $1.94\times 10^5$  g PP·(g Cat.)<sup>-1</sup>·h<sup>-1</sup>). A document (*Journal of Organometallic Chemistry* **1993**, 459 (1), 117-123) also reports that the molecular weight of polypropylene obtained by an Hf-coordinated metallocene-fluorene type catalyst is higher than that obtained by a same type of a Zr-coordinated catalyst ( $M_w=7.77\times 10^5$ ), but the activity is also obviously decreased ( $5.4\times 10^4$  g·(g Cat.)<sup>-1</sup>·h<sup>-1</sup>). However, an Hf-coordinated metallocene compound generally has a strong tendency to  $\beta$ -R migration, leading to an increased number of insertion error segments in the obtained syndiotactic polypropylene and a decrease in regularity of a polymer chain.

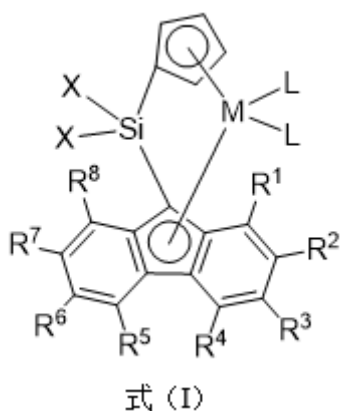
Silicon-bridged dual-indene type metallocene catalysts have been successfully used for production of polypropylene, especially for production of isotactic polypropylene. Compared with the carbon-bridged catalysts, the silicon-bridged catalysts have better stereoselectivity and regioselectivity. More importantly, compared with lower application temperatures (0°C-30°C) of many carbon-bridged catalysts, the silicon-bridged catalysts have good thermal stability and can maintain good activity, stereoregularity, regioregularity, and a molecular weight control ability at

industrial production temperatures, and their application temperatures can even reach 60°C-120°C. A document (*Journal of Organometallic Chemistry* **1996**, 509 (1), 63-71; *Journal of Molecular Catalysis A: Chemical* **1998**, 128 (1-3), 245-256; *Organometallics*, **2021**, 40, 4055-4065) reports that the silicon-bridged catalysts can be used for preparing the syndiotactic polypropylene with a higher molecular weight, but still have problems such as low activity and a poor syndiotactic control ability (*Macromolecular Symposia* **1995**, 89, 181-196; *Chemical Reviews* **2000**, 100 (4), 1253-1345). US6559089 discloses a silicon-bridged metallocene-fluorene type catalyst with multiple substituent modifications on a cyclopentadiene ring, but the catalyst can only be used for production of the isotactic polypropylene and cannot achieve production of the syndiotactic polypropylene.

In summary, there is still a need for a novel silicon-bridged metallocene compound to achieve highly active production of the syndiotactic polypropylene with a high molecular weight and high regularity at high industrial temperatures.

## SUMMARY

One objective of the present invention is to provide a silicon-bridged metallocene catalyst, which has a general structural formula of formula (I):



where M is a transition metal element of Group 4;

L is a monovalent anionic ligand;

X is unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, phenyl, or aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls;

R<sup>1</sup> and R<sup>8</sup> are independently selected from hydrogen, trifluoromethyl, phenyl, halogen, unsubstituted or substituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, and unsubstituted or substituted heteroaryl;

R<sup>2</sup>, R<sup>3</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently selected from hydrogen, trifluoromethyl, phenyl, naphthyl, anthryl, phenanthryl, halogen, unsubstituted or substituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl,

unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, unsubstituted or substituted aryl, and unsubstituted or substituted heteroaryl; and

R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen, trifluoromethyl, halogen, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, and silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls.

Further, M is zirconium or hafnium.

Further, L is halogen or unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl. Preferably, L is halogen or unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl.

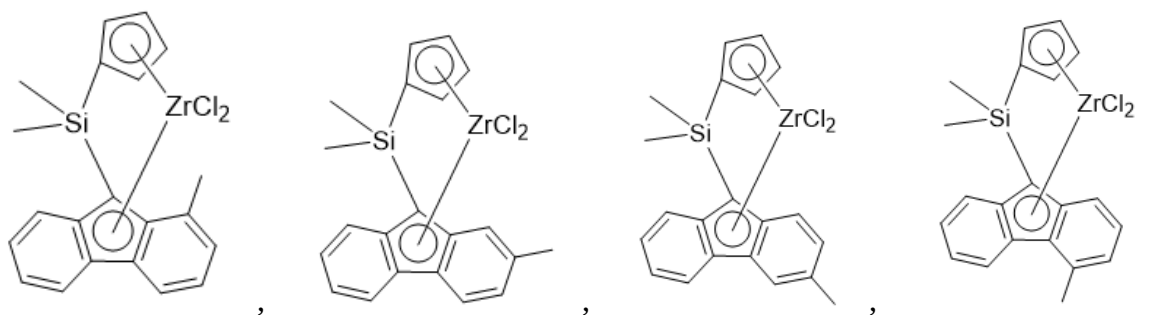
Further, X is unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl, phenyl, or aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyls. More preferably, X is methyl or phenyl.

Further, R<sup>1</sup> and R<sup>8</sup> are independently selected from hydrogen, trifluoromethyl, and unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl. More preferably, R<sup>1</sup> and R<sup>8</sup> are independently selected from hydrogen, trifluoromethyl, and unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl.

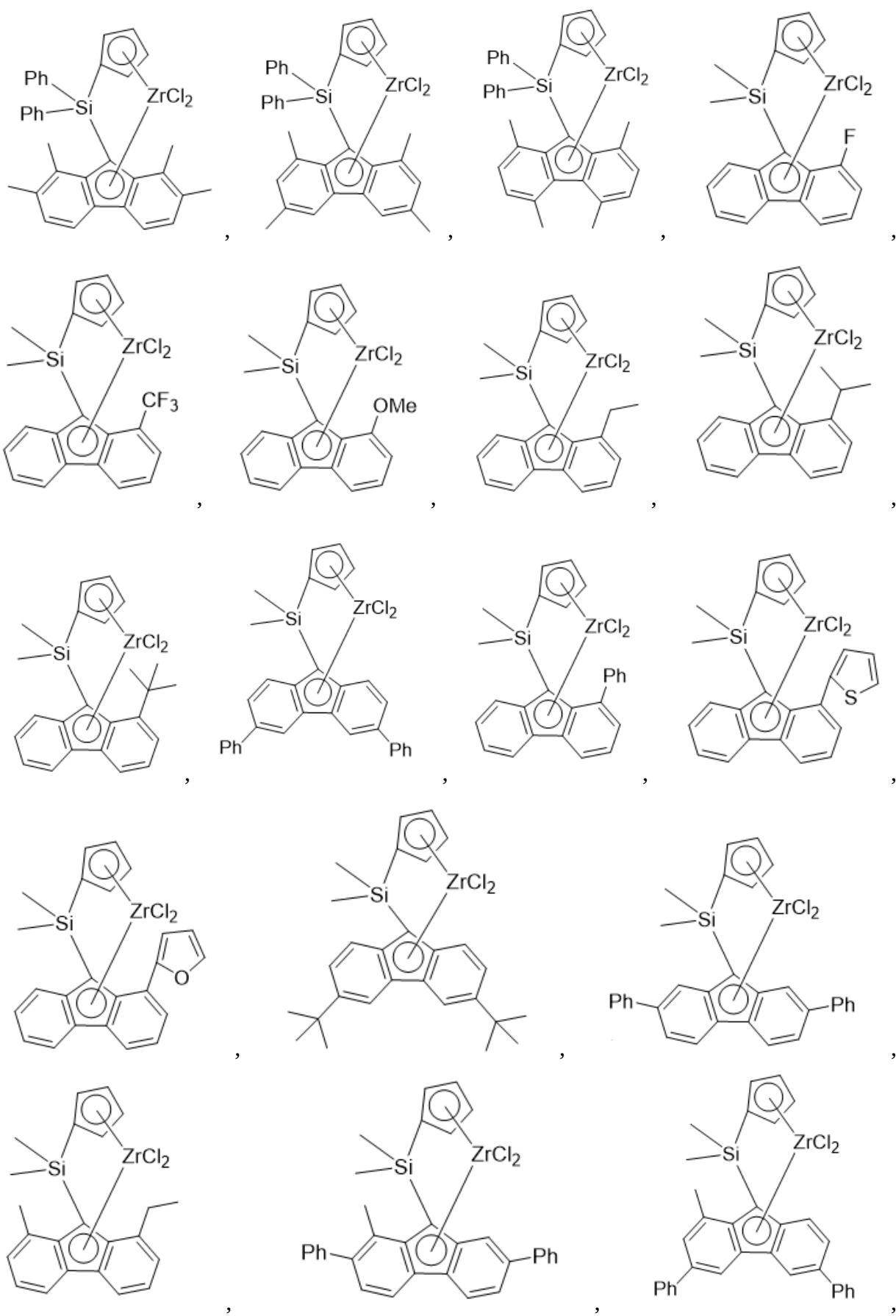
Further, R<sup>2</sup>, R<sup>3</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently selected from hydrogen, phenyl, naphthyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, and unsubstituted or substituted aryl. More preferably, R<sup>2</sup>, R<sup>3</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently selected from hydrogen, phenyl, unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyls, and aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyls.

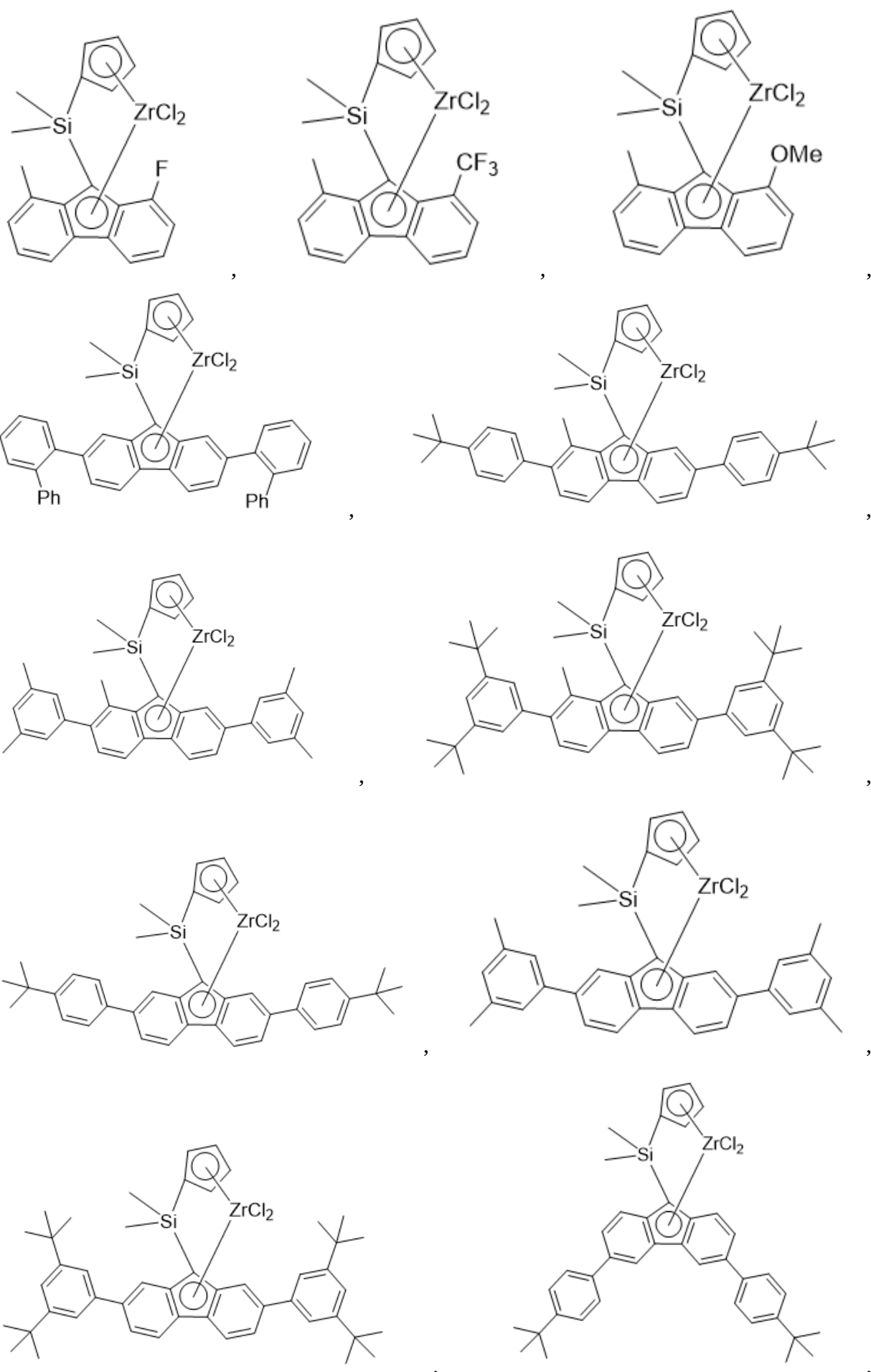
Further, R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen and unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl. More preferably, R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen and unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl.

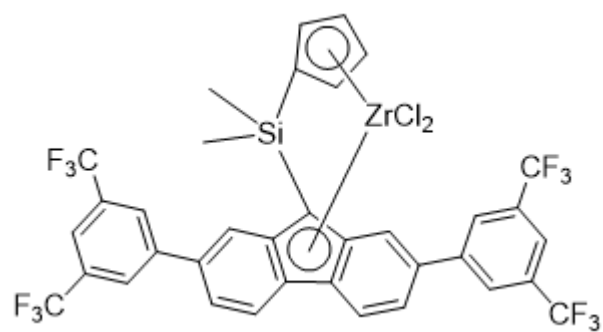
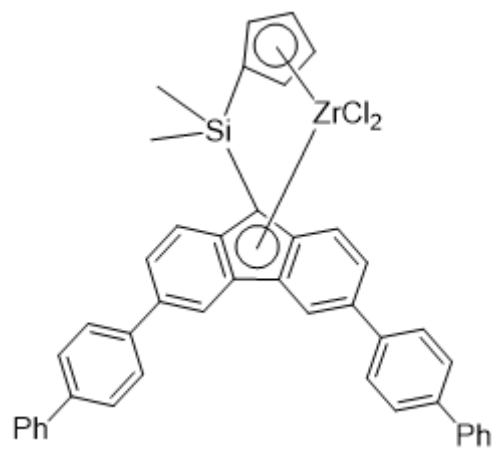
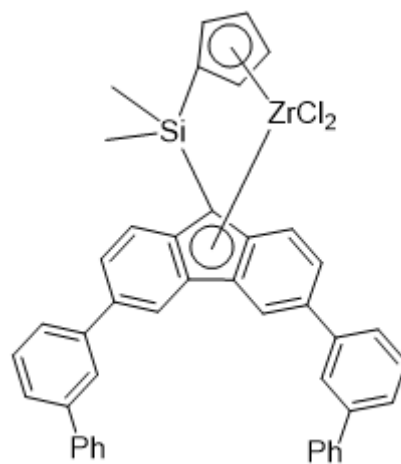
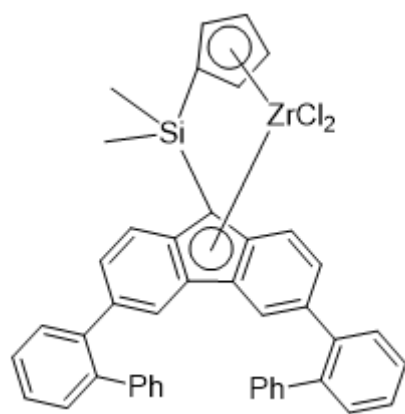
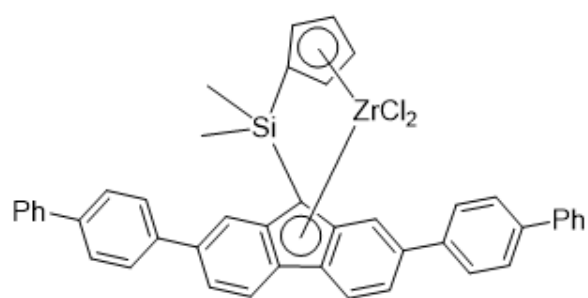
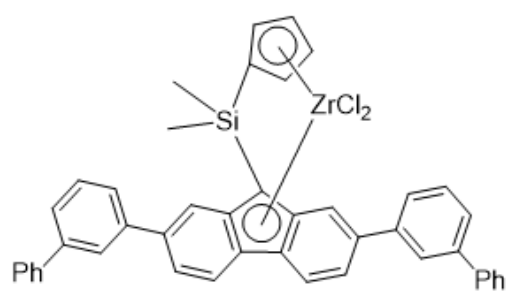
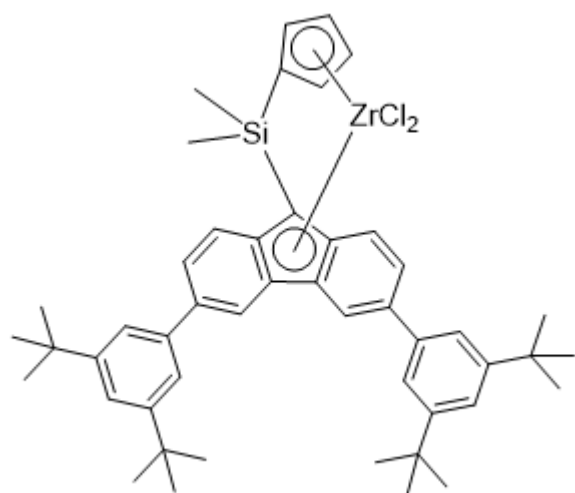
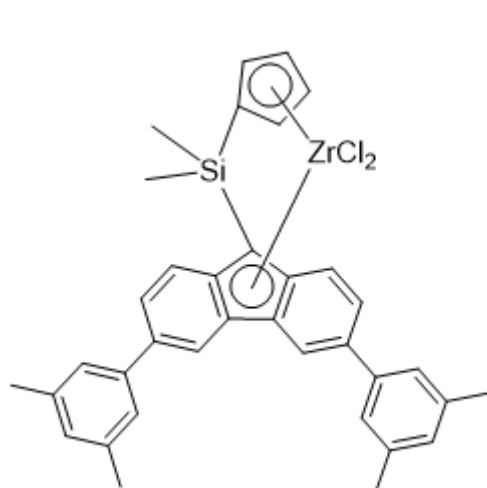
Further, preferred examples of the compound of formula (I) are as follows:

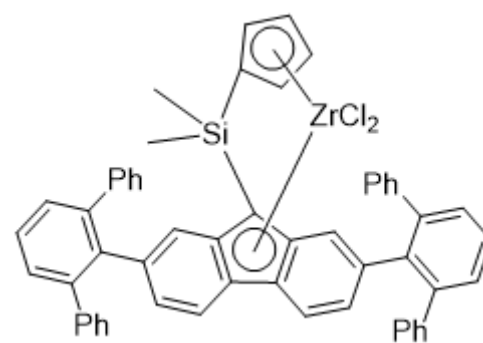
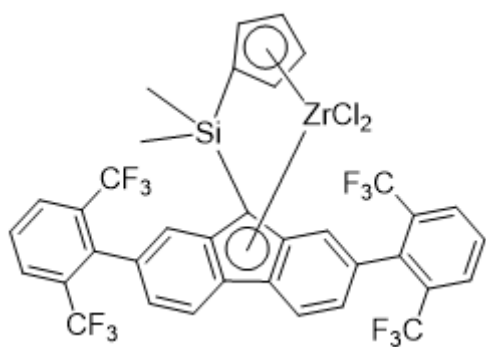
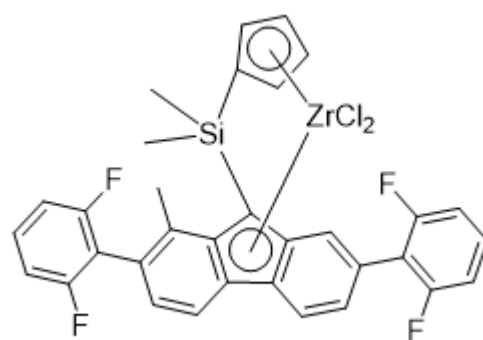
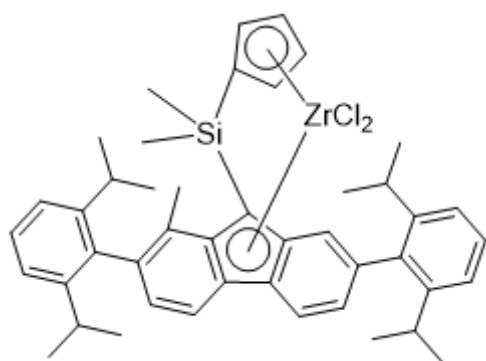
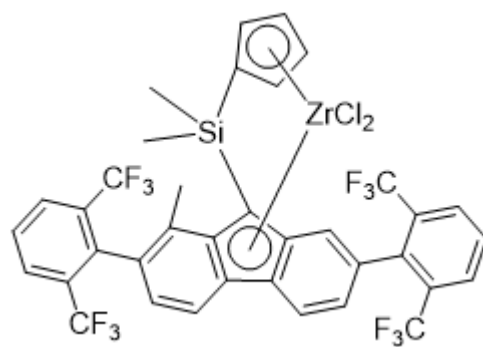
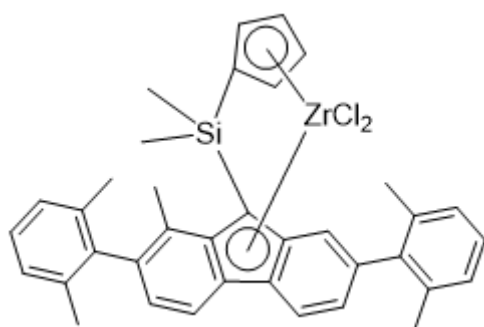
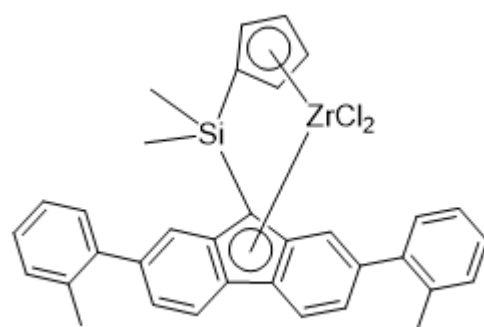
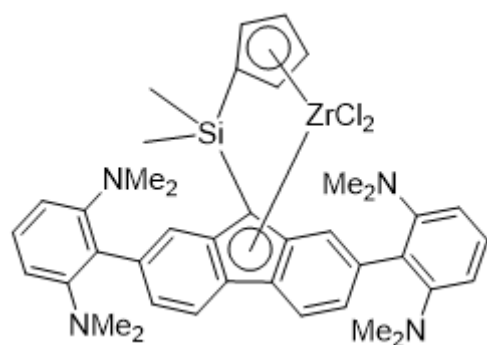
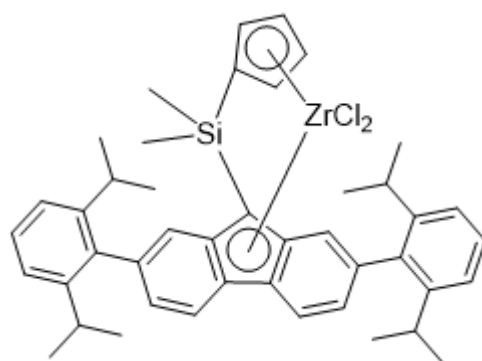
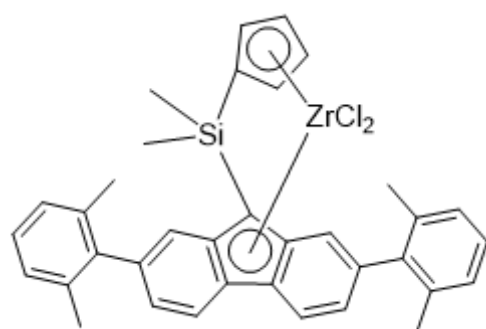


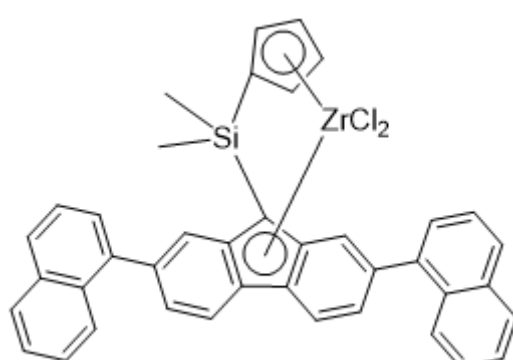
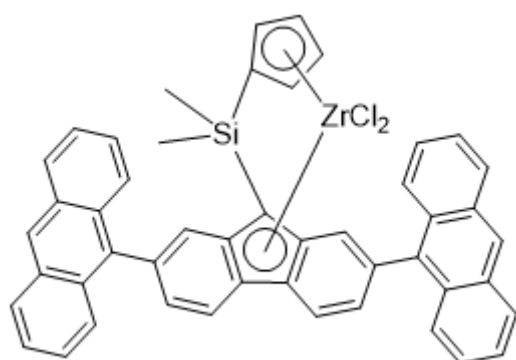
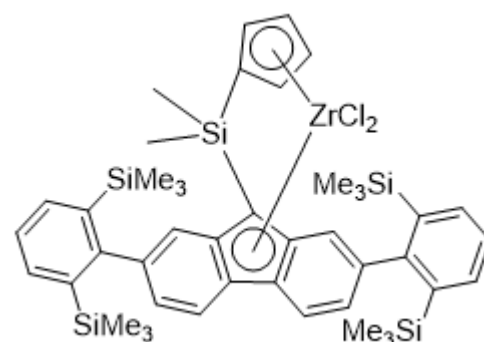
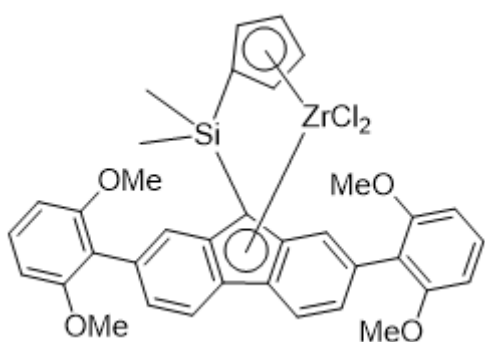
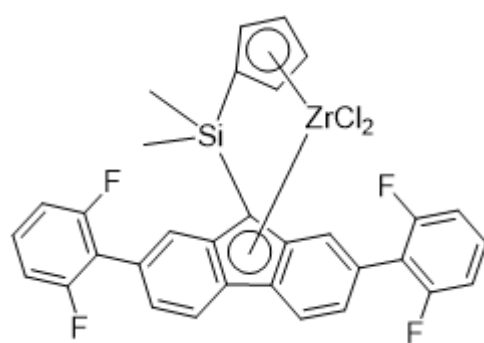
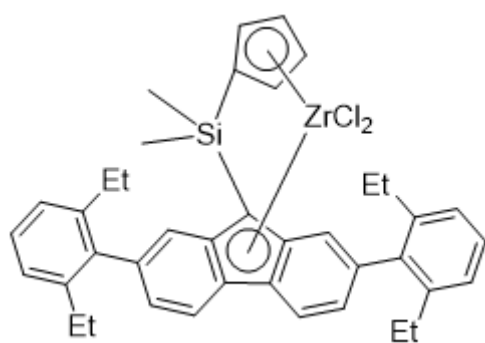
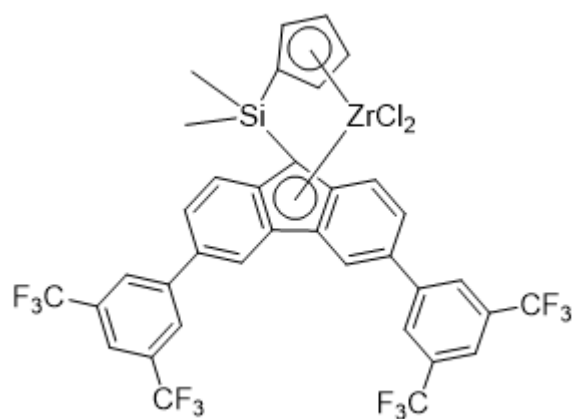
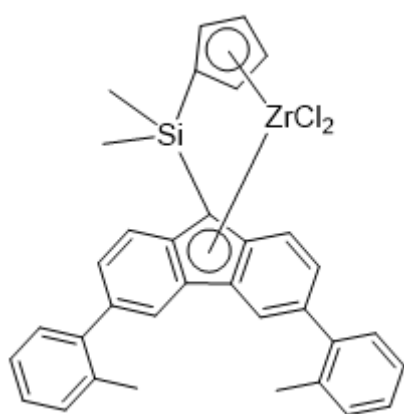


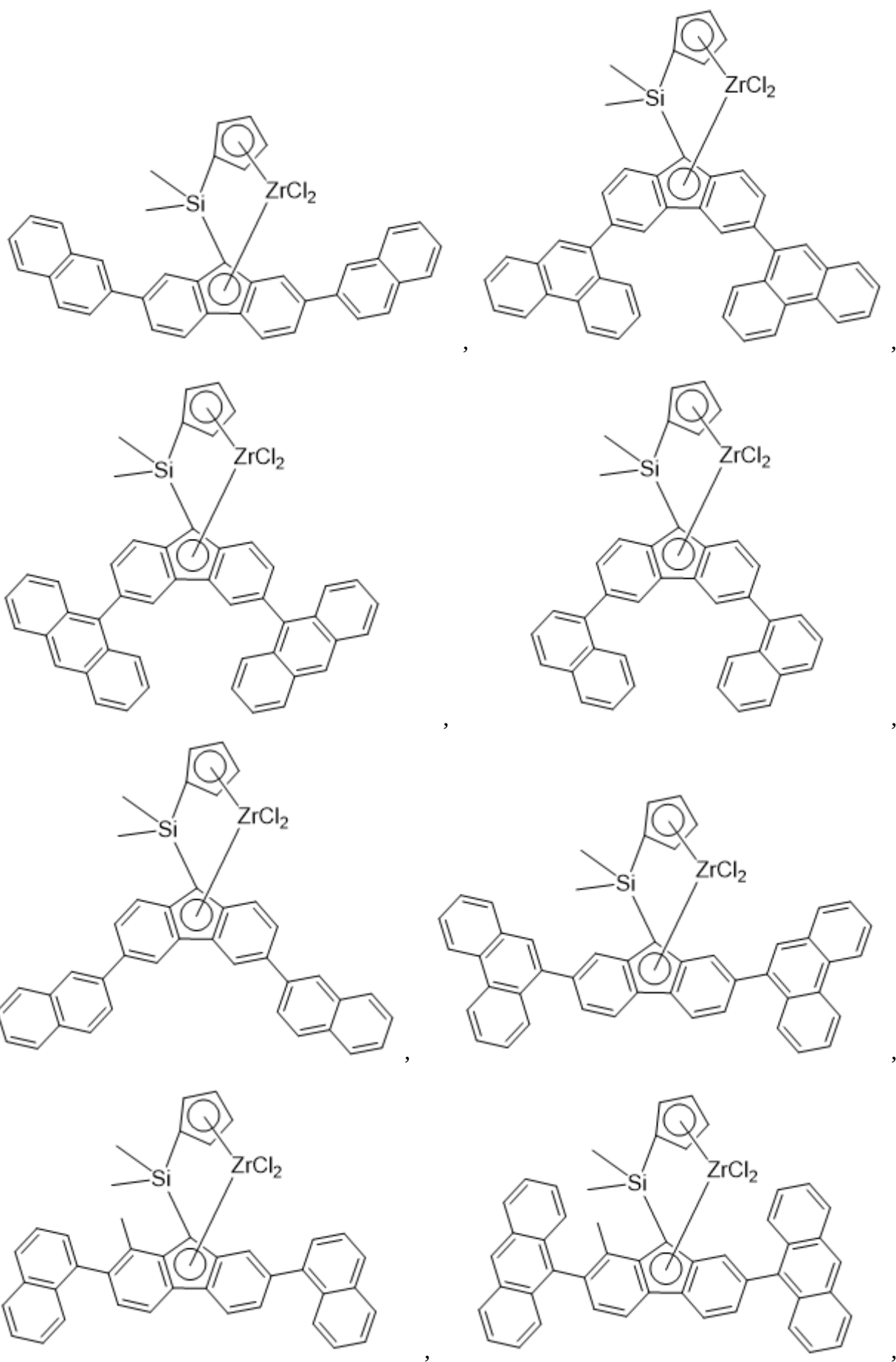


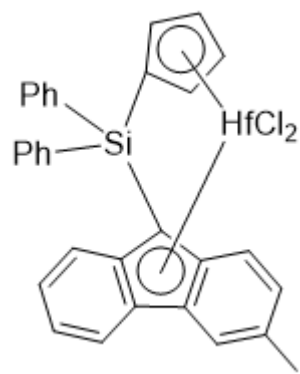
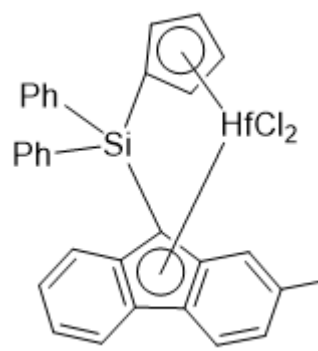
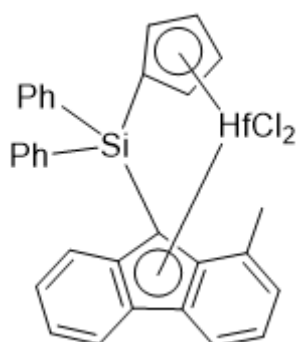
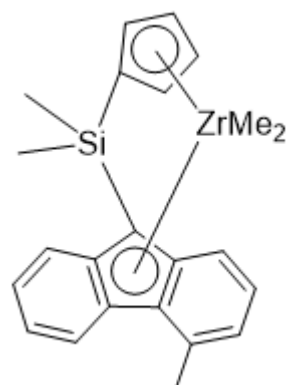
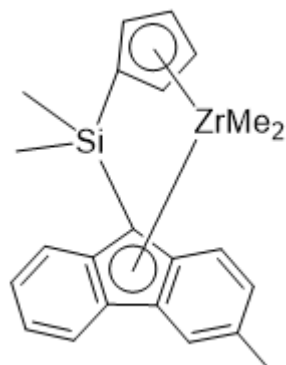
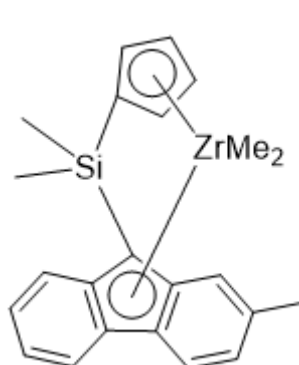
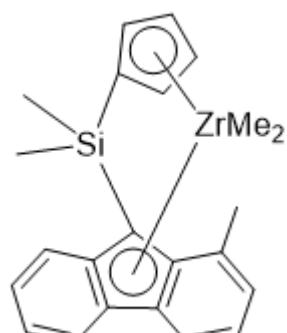
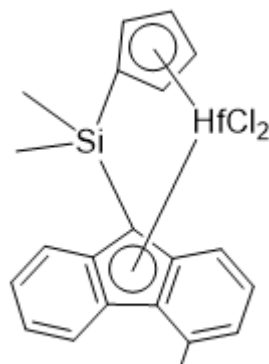
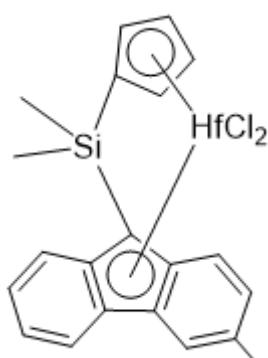
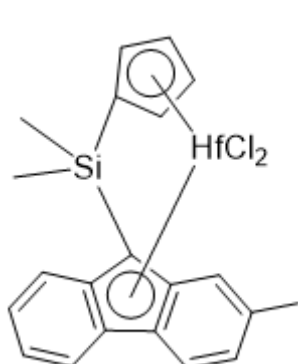
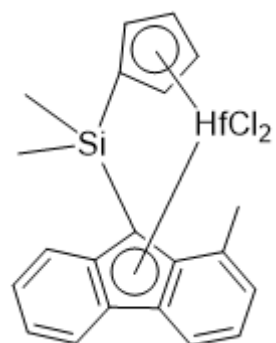
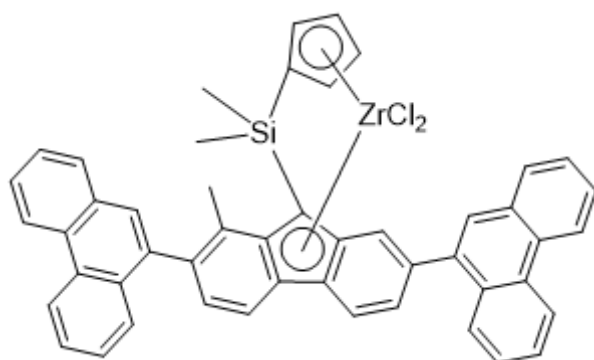


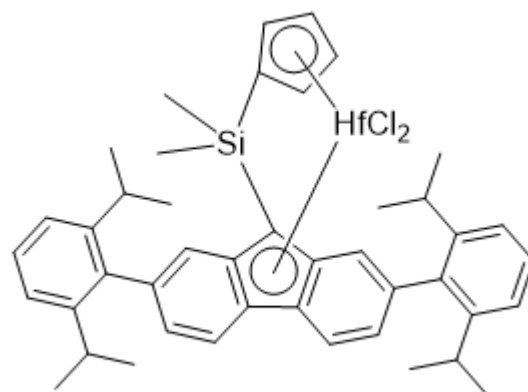
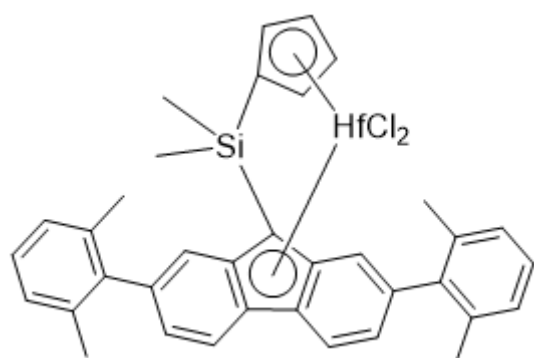
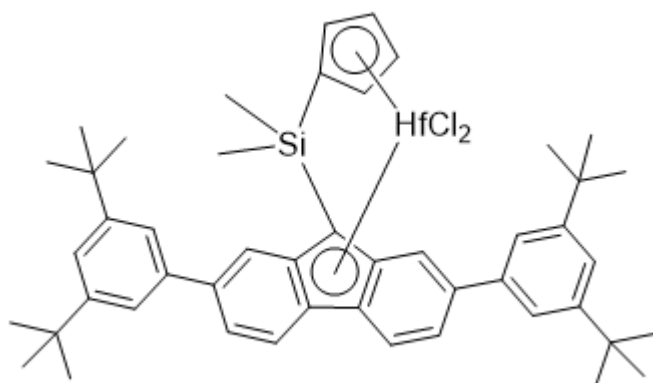
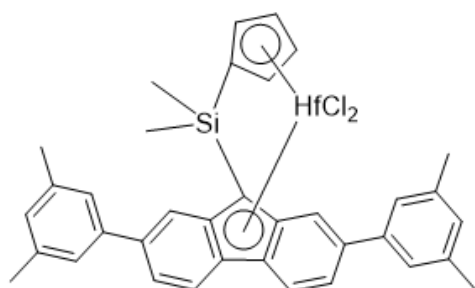
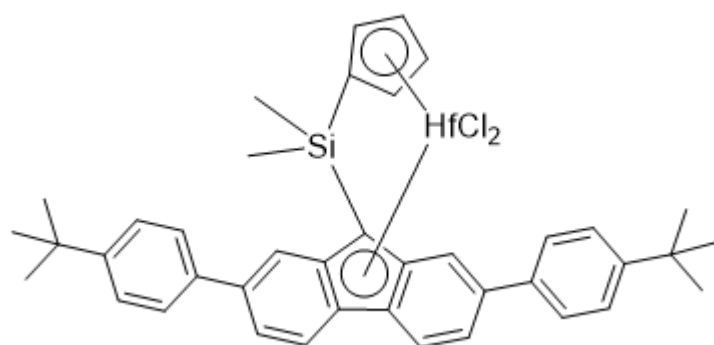
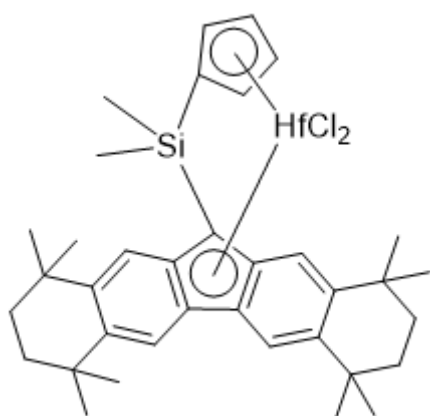
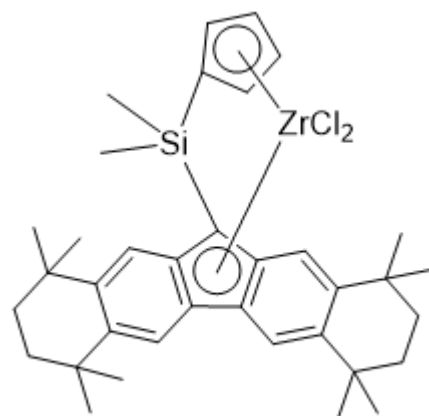
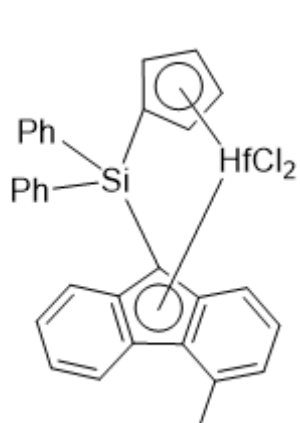


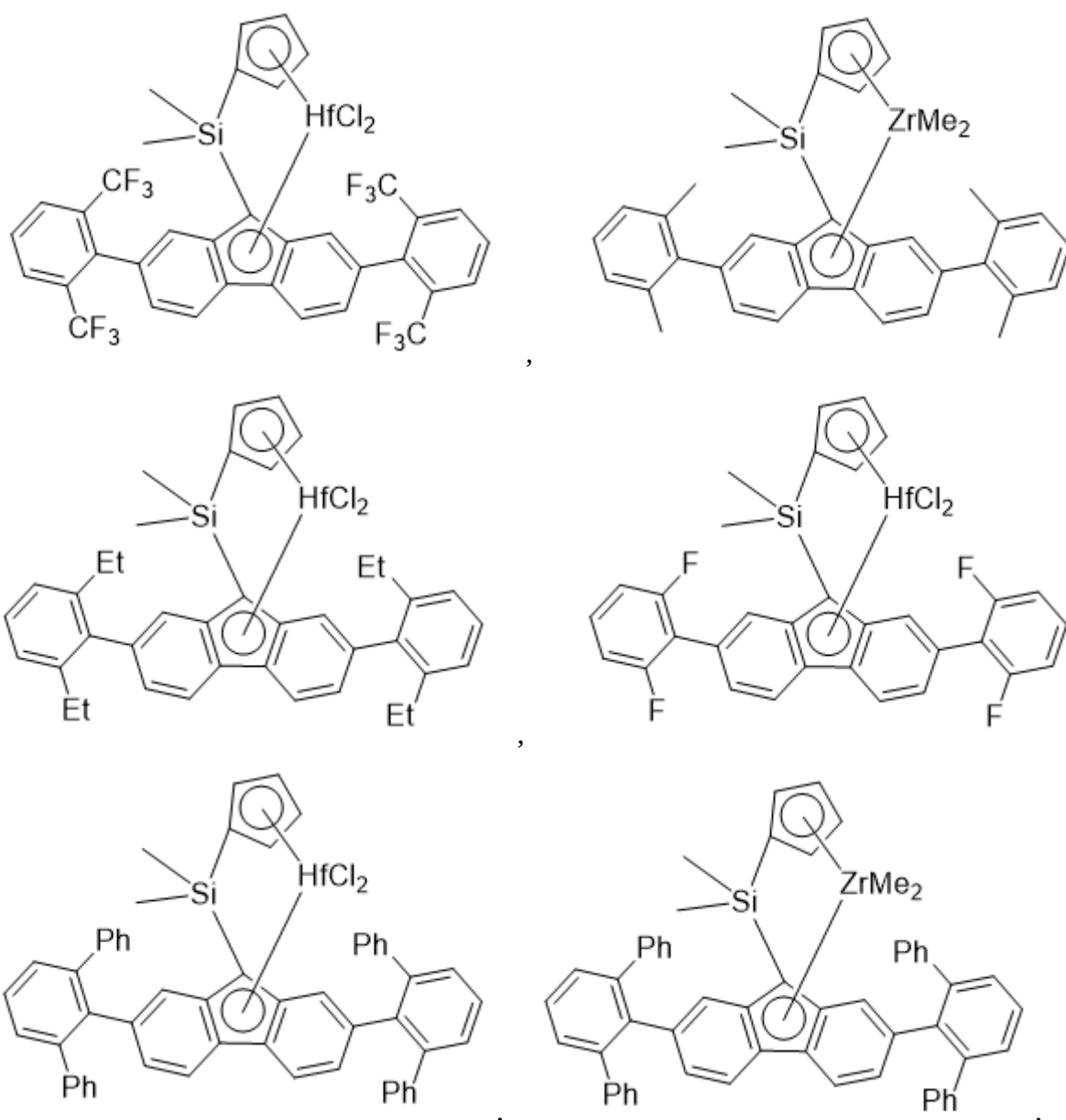












Another objective of the present invention is to provide use of the silicon-bridged metallocene catalyst in preparation of a catalytic system for olefin polymerization.

A third objective of the present invention is to provide a catalytic system for olefin polymerization, which includes an activator, an inert carrier, and the silicon-bridged metallocene catalyst having the structure of formula (I) above.

Further, the activator is selected from one or more of aluminoxane, alkylaluminum, and a borate.

Furthermore, the alkylaluminum activator suitable for the present invention is selected from one or more of trimethylaluminum, triethylaluminum, triisopropylaluminum, tri-n-propylaluminum, triisobutylaluminum, tri-n-butylaluminum, triisopentylaluminum, tri-n-pentylaluminum, triisohexylaluminum, tri-n-hexylaluminum, triiso-heptylaluminum, tri-n-heptylaluminum, triisooctylaluminum, tri-n-octylaluminum, triisononylaluminum, tri-n-nonylaluminum, triisodecylaluminum, and tri-n-decylaluminum.

Furthermore, the borate activator suitable for the present invention is selected from one or more of dimethylanilinium tetra(pentafluorophenyl)borate, diethylanilinium tetra(pentafluorophenyl)borate, dibutylanilinium tetra(pentafluorophenyl)borate, trimethylammonium tetra(pentafluorophenyl)borate, diethylammonium tetra(pentafluorophenyl)borate, and tributylammonium tetra(pentafluorophenyl)borate.

Furthermore, the aluminoxane activator suitable for the present invention is selected from one or more of methylaluminoxane, modified methylaluminoxane, triisobutyldialuminoxane, polyisobutylaluminoxane, tetraethyldialuminoxane, penta-isobutyltrialuminoxane, 1,3-dichloro-1,3-diethyldialuminoxane, and 1,3-dichloro-1,3-dimethyldialuminoxane.

Further, the inert carrier is selected from one or more of a silicon-containing inorganic porous carrier, an aluminum-containing inorganic porous carrier, a magnesium-containing inorganic porous carrier, and a high-molecular organic porous carrier. Preferably, a specific surface area of the carrier is not less than 20 m<sup>2</sup>/g.

Furthermore, the inert carrier suitable for the present invention is selected from one or more of silica, aluminum oxide, montmorillonite, magnesium chloride, a molecular sieve, cyclodextrin, polyethylene, polystyrene, polyvinyl alcohol, and a mesoporous silica gel fiber; and is preferably selected from one or more of the silica, the aluminum oxide, the montmorillonite, the magnesium chloride, and the molecular sieve.

Another objective of the present invention is to provide a method for preparing a propylene polymer, which includes the following steps:

- 1) adding the aforementioned catalytic system into a reactor;
- 2) introducing a propylene monomer into the reactor to be in contact with the catalytic system after the catalytic system is added; and
- 3) maintaining the propylene monomer under polymerization conditions to obtain a propylene polymer.

A propylene polymerization reaction of the present invention is carried out in a slurry or a gas phase, and the obtained propylene polymer has a weight-average molecular weight of 50,000-500,000 g/mol and a pentad syndiotacticity of 30%-90%.

## **DESCRIPTION OF THE EMBODIMENTS**

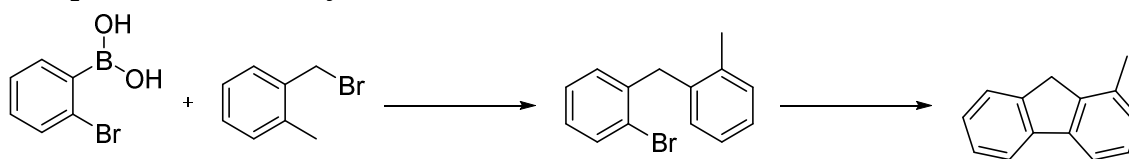
The present invention is described in detail below in combination with specific examples. The examples are implemented based on technical solutions of the present invention, and detailed embodiments and specific operation processes are provided, but the scope of protection of the present invention is not limited to the following examples.

In the following examples, unless otherwise specified, it is indicated that raw materials or treatment techniques are all conventional commercially available raw materials or conventional

treatment techniques in the art.

### Example 1

#### Preparation of 1-methylfluorene



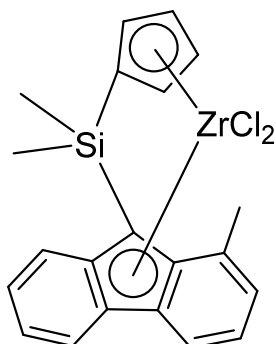
A 100 mL three-necked flask was taken, 433 mg of  $\text{Pd}(\text{PPh}_3)_4$  (0.38 mmol) and 3.98 g of  $\text{Na}_2\text{CO}_3$  (37.5 mmol) were added, nitrogen replacement was performed for three times, and then 1.51 g of 2-bromophenylboronic acid (7.50 mmol), 1.66 g of 2-methylbenzyl bromide (9.00 mmol), 40 mL of ethylene glycol dimethyl ether, 15 mL of water, and 3 mL of ethanol were added and heated to  $90^\circ\text{C}$  to carry out a reaction for 12 h. Cooling was performed to room temperature, followed by extraction with 25 mL of dichloroethane for 2 times. Organic phases were combined, washed with 10 mL of water for 2 times, and dried over anhydrous  $\text{MgSO}_4$ . Filtration was performed to remove the solvent to obtain 1-bromo-2-(2-methylbenzyl)benzene.

A 50 mL reaction flask was taken, 1.3 g of the 1-bromo-2-(2-methylbenzyl)benzene (5 mmol), 22.5 mg of  $\text{Pd}(\text{OAc})_2$  (0.1 mmol), 84.6 mg of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.2 mmol), and 0.69 g of  $\text{K}_2\text{CO}_3$  (5 mmol) were added, nitrogen replacement was performed for three times, and then 15 mL of N-methylpyrrolidone was added and heated to  $130^\circ\text{C}$  to carry out a reaction for 12 h. Cooling was performed to room temperature, followed by extraction with 10 mL of n-hexane for 2 times and washing with 10 mL of water for 2 times. Organic phases were collected, dried over anhydrous  $\text{MgSO}_4$ , and filtered. The solvent was removed to obtain 2.7 g of 1-methylfluorene.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.79 (d,  $J=7.5$  Hz, 1H), 7.65 (d,  $J=7.5$  Hz, 1H), 7.57 (d,  $J=7.4$  Hz, 1H), 7.38 (t,  $J=7.4$  Hz, 1H), 7.34–7.28 (m, 2H), 7.14 (d,  $J=7.4$  Hz, 1H), 3.80 (s, 2H), 2.44 (s, 3H).

### Example 2

#### Preparation of dimethyl(cyclopentadienyl)(1-methyl-9-fluorenyl)silylzirconium dichloride (catalyst 1)



A 100 mL Schlenk flask 1 was taken, the 1-methylfluorene (1 g, 5.05 mmol) was added,

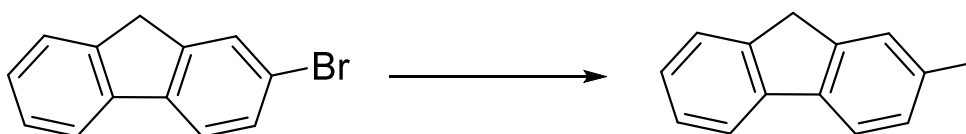
nitrogen replacement was performed for 3 times, 12 mL of toluene and 3.5 mL of tetrahydrofuran were added, and then n-BuLi (2.1 mL, 5.3 mmol) was slowly added at -40°C to carry out a reaction at 25°C for 3.5 h. Another 100 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 27 mL of toluene and dimethyldichlorosilane (3.9 g, 30.3 mmol) were added, and the solution in the flask 1 was added at -25°C to carry out a reaction at 25°C for 18 h. The reaction solvent was drained, supplemented with 5 mL of toluene, and then drained. 10 mL of toluene and 2.5 mL of tetrahydrofuran were added. Another 25 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 13.5 mL of tetrahydrofuran and cyclopentadiene (0.38 g, 5.05 mmol) were added, and then 2.1 mL of n-BuLi (5.3 mmol) was added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 3 h.

The reaction solvent was drained, 20 mL of toluene and 5 mL of ethyl ether were added, and then n-BuLi (4.1 mL, 10.4 mmol) was added at -40°C to carry out a reaction at 25°C for 20 h. ZrCl<sub>4</sub> (1.23 g, 5.15 mmol) was added at -75°C, first stirred in an ice bath at -20°C for 3 h, and then allowed to undergo a reaction at 25°C for 15 h. The reaction solvent was drained, 50 mL of toluene was added and heated to 75°C, and filtration was performed with diatomite under heat, followed by washing with 20 mL of toluene. A filtrate was crystallized at -40°C and filtered to obtain 0.3 g of an orange solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 8.15 (d, *J*=6.2 Hz, 1H), 8.02 (d, *J*=8.3 Hz, 1H), 7.79 (d, *J*=8.7 Hz, 1H), 7.61 (t, *J*=7.2 Hz, 1H), 7.52–7.47 (m, 1H), 7.34–7.29 (m, 1H), 7.15 (d, *J*=9.1 Hz, 1H), 6.72–6.68 (m, 1H), 6.51–6.47 (m, 1H), 5.82 (q, *J*=2.7 Hz, 1H), 5.69 (q, *J*=2.5 Hz, 1H), 2.59 (s, 3H), 1.21 (d, *J*=7.0 Hz, 6H).

### Example 3

#### Preparation of 2-methylfluorene



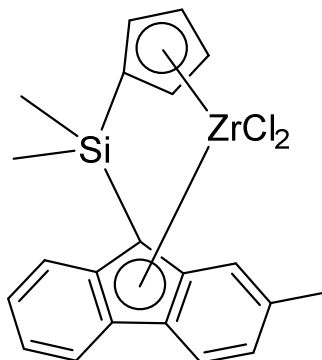
4.9 g of 2-bromofluorene (20 mmol) was weighed and added into a 100 mL three-necked flask, 0.22 g of (1,3-bis(diphenylphosphino)propane)nickel dichloride (0.4 mmol) was added, nitrogen replacement was performed for three times, and then 20 mL of ethyl ether was added. At 20-30°C, 7.51 mL of methylmagnesium bromide (24 mmol) was added dropwise and then allowed to undergo a reaction at 25°C, and the reaction was monitored by gas chromatography. After the reaction was completed, the reaction solution was added into 100 mL of water, 15 mL of a toluene solution was added for extraction for 2 times, and the solvent was removed to obtain 3.6 g of 2-methylfluorene with a gas chromatography (GC) purity of 98.1%.

<sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H),

7.56 (d,  $J = 7.4$  Hz, 1H), 7.42 – 7.37 (m, 2H), 7.31 (t,  $J = 7.4$  Hz, 1H), 7.22 (d,  $J = 6.9$  Hz, 1H), 3.89 (s, 2H), 2.47 (s, 3H).

#### Example 4

##### Preparation of dimethyl(cyclopentadienyl)(2-methyl-9-fluorenyl)silylzirconium dichloride (catalyst 2)



A 100 mL Schlenk flask 1 was taken, the 2-methylfluorene (3 g, 16.6 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (7 mL, 17.5 mmol) was added at -40°C to carry out a reaction at 25°C for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (12.9 g, 100 mmol) were added, and the solution in the flask 1 was added at -25°C to carry out a reaction at 25°C for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.10 g, 16.6 mmol) were added, and then n-BuLi (7 mL, 17.5 mmol) was slowly added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 6 h.

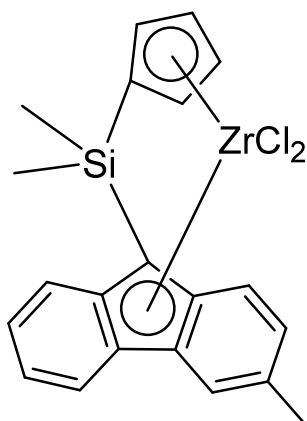
The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (13.6 mL, 34 mmol) was added at -45°C to carry out a reaction at 25°C for 20 h. ZrCl<sub>4</sub> (3.43 g, 14.6 mmol) was added at -75°C to carry out a reaction at 25°C for 20 h. The reaction solvent was drained, 250 mL of toluene was added, and filtration was performed with diatomite, followed by washing of the diatomite with 50 mL of toluene. A filtrate was collected to remove the solvent, n-hexane was added at -40°C and stirred for 30 min, and filtration was performed to obtain about 0.2 g of a red solid.

<sup>1</sup>H NMR (500 MHz, Chloroform-d)  $\delta$  8.07 (d,  $J = 8.3$  Hz, 1H), 8.01 (d,  $J=8.4$  Hz, 1H), 7.85 (t,  $J=6.5$  Hz, 1H), 7.78 (d,  $J=7.7$  Hz, 1H), 7.63 (t,  $J=7.6$  Hz, 1H), 7.53 (t,  $J=7.2$  Hz, 1H), 7.48 (d,  $J=8.9$  Hz, 2H), 6.61 (s, 2H), 5.75 (s, 2H), 2.42 (s, 3H), 1.15 (s, 6H).

#### Example 5

##### Preparation of dimethyl(cyclopentadienyl)(3-methyl-9-fluorenyl)silylzirconium

### dichloride (catalyst 3)



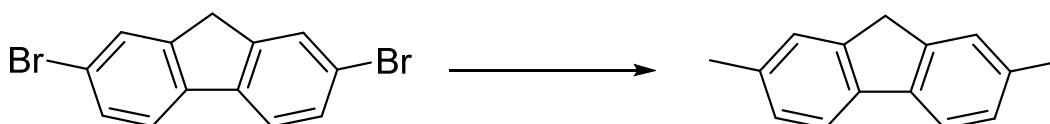
A 100 mL Schlenk flask 1 was taken, 3-methylfluorene (1 g, 5.05 mmol) was added, nitrogen replacement was performed for 3 times, 12 mL of toluene and 3.5 mL of tetrahydrofuran were added, and then n-BuLi (2.1 mL, 5.3 mmol) was slowly added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3.5 h. Another 100 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 27 mL of toluene and dimethyldichlorosilane (3.9 g, 30.3 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. The reaction solvent was drained, supplemented with 5 mL of toluene, and then drained. 10 mL of toluene and 2.5 mL of tetrahydrofuran were added. Another 25 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 13.5 mL of tetrahydrofuran and cyclopentadiene (0.38 g, 5.05 mmol) were added, and then 2.1 mL of n-BuLi (5.3 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained at  $35^{\circ}\text{C}$ , 20 mL of toluene and 5 mL of ethyl ether were added, and then n-BuLi (4.1 mL, 10.4 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{ZrCl}_4$  (1.23 g, 5.15 mmol) was added at  $-75^{\circ}\text{C}$ , first stirred in an ice bath at  $-20^{\circ}\text{C}$  for 3 h, and then transferred to a place to undergo a reaction at  $25^{\circ}\text{C}$  for 15 h. The reaction solvent was drained, 50 mL of toluene was added and heated to  $75^{\circ}\text{C}$ , and filtration was performed with diatomite under heat, followed by washing of the diatomite with 20 mL of toluene. A filtrate was collected, crystallized at  $-40^{\circ}\text{C}$ , and filtered to obtain 0.6 g of an orange solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  8.07 (d,  $J = 8.3$  Hz, 1H), 8.01 (d,  $J = 8.4$  Hz, 1H), 7.85 (t,  $J = 6.5$  Hz, 1H), 7.78 (d,  $J = 7.7$  Hz, 1H), 7.63 (t,  $J = 7.6$  Hz, 1H), 7.53 (t,  $J = 7.2$  Hz, 1H), 7.48 (d,  $J = 8.9$  Hz, 2H), 6.61 (s, 2H), 5.75 (s, 2H), 2.42 (s, 3H), 1.15 (s, 6H).

### Example 6

#### Preparation of 2,7-dimethylfluorene

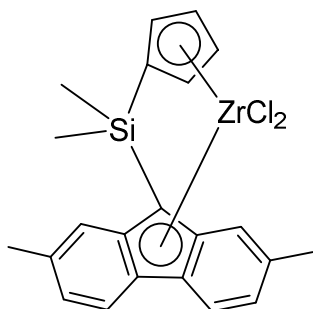


6.5 g of 2,7-dibromofluorene (20 mmol) was weighed and added into a 100 mL three-necked flask, 0.22 g of (1,3-bis(diphenylphosphino)propane)nickel dichloride (0.4 mmol) was added, nitrogen replacement was performed for three times, and then 20 mL of ethyl ether was added. At 20-30°C, 7.51 mL of methylmagnesium bromide (24 mmol) was added dropwise and then allowed to undergo a reaction at 25°C, and the reaction was monitored by gas chromatography. After the reaction was completed, the reaction solution was added into 100 mL of water, 15 mL of a toluene solution was added for extraction for 2 times, and the solvent was removed to obtain 3.88 g of 2,7-dimethylfluorene with a GC purity of 100%.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.65 (d,  $J$  = 7.6 Hz, 1H), 7.35 (s, 1H), 7.19 (d,  $J$  = 7.8 Hz, 1H), 3.84 (s, 1H), 2.45 (s, 3H).

### Example 7

#### Preparation of dimethyl(cyclopentadienyl)(2,7-dimethyl-9-fluorenyl)silylzirconium dichloride (catalyst 4)



A 100 mL Schlenk flask 1 was taken, the 2,7-dimethylfluorene (2.8 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then  $n\text{-BuLi}$  (6.05 mL, 15.1 mmol) was added at -40°C to carry out a reaction at 25°C for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at -25°C to carry out a reaction at 25°C for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then  $n\text{-BuLi}$  (6.05 mL, 15.1 mmol) was added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 3 h.

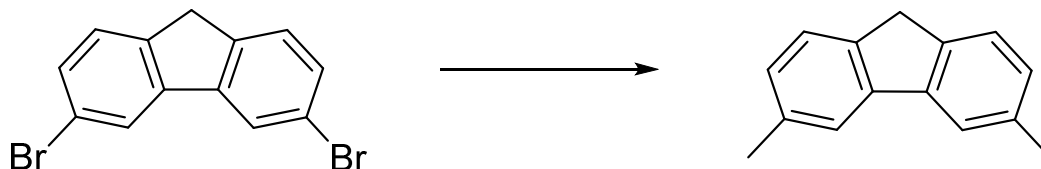
The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then  $n\text{-BuLi}$  (11.8 mL, 29.5 mmol) was added at -45°C to carry out a reaction at 25°C for 20 h.  $\text{ZrCl}_4$  (3.43 g, 14.6 mmol) was added at -75°C to carry out a reaction at 25°C for 3 h. The reaction solvent was drained, 100 mL of toluene was added and heated to 45°C, and filtration was performed with diatomite under heat, followed by washing of the diatomite with 20 mL of toluene

for 2 times. A filtrate was collected, crystallized at  $-20^{\circ}\text{C}$ , and filtered to obtain 0.35 g of an orange solid.

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J=8.5$  Hz, 2H), 7.45 (d,  $J=8.6$  Hz, 2H), 7.18 (d,  $J=7.1$  Hz, 2H), 6.62 (t,  $J=2.4$  Hz, 2H), 5.73 (t,  $J=2.4$  Hz, 2H), 2.41 (s, 6H), 1.13 (s, 6H).

### Example 8

#### Preparation of 3,6-dimethylfluorene

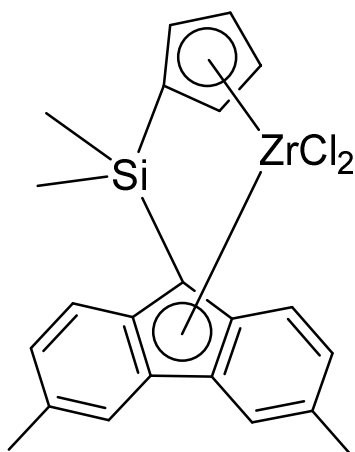


6.5 g of 3,6-dibromofluorene (20 mmol) was weighed and added into a 100 mL three-necked flask, 0.22 g of (1,3-bis(diphenylphosphino)propane)nickel dichloride (0.4 mmol) was added, nitrogen replacement was performed for three times, and then 20 mL of ethyl ether was added. At  $20-30^{\circ}\text{C}$ , 7.51 mL of methylmagnesium bromide (24 mmol) was added dropwise and then allowed to undergo a reaction at  $25^{\circ}\text{C}$ , and the reaction was monitored by gas chromatography. After the reaction was completed, the reaction solution was added into 100 mL of water, 15 mL of a toluene solution was added for extraction for 2 times, and the solvent was removed to obtain 3.9 g of 3,6-dimethylfluorene with a GC purity of 99.8%.

$^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.58 (s, 2H), 7.41 (d,  $J = 7.6$  Hz, 2H), 7.10 (d,  $J = 7.6$  Hz, 2H), 3.80 (s, 2H), 2.45 (s, 6H).

### Example 9

#### Preparation of dimethyl(cyclopentadienyl)(3,6-dimethyl-9-fluorenyl)silylzirconium dichloride (catalyst 5)



A 100 mL Schlenk flask 1 was taken, the 3,6-dimethylfluorene (2.8 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then *n*-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed

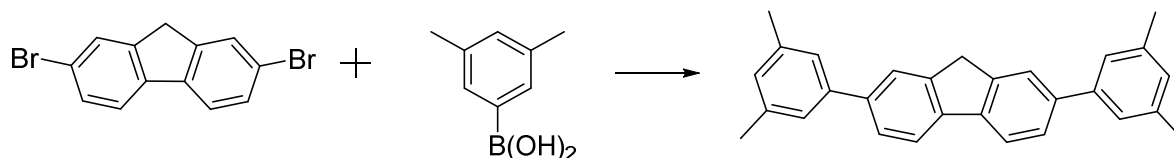
for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at -25°C to carry out a reaction at 25°C for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at -45°C to carry out a reaction at 25°C for 20 h. ZrCl<sub>4</sub> (3.43 g, 14.6 mmol) was added at -75°C to carry out a reaction at 25°C for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of n-hexane was added, and filtration and drying were performed to obtain 0.6 g of a yellow solid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (s, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.14 (dd, *J* = 8.7, 1.6 Hz, 2H), 6.59 (t, *J* = 2.4 Hz, 2H), 5.71 (t, *J* = 2.4 Hz, 2H), 2.61 (s, 6H), 1.11 (s, 6H).

#### Example 10

##### Preparation of 2,7-bis(3,5-dimethylphenyl)fluorene

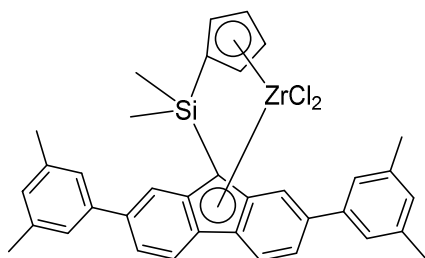


A 100 mL two-necked flask was taken, 2,7-dibromofluorene (3.24 g, 10 mmol), 3,5-dimethylphenylboronic acid (3.19 g, 21.27 mmol), tetrakis(triphenylphosphine)palladium (0.17 g, 0.147 mmol), and anhydrous sodium carbonate (3.20 g, 30.19 mmol) were sequentially added, and nitrogen replacement was performed for three times. 50 mL of ethanol and 4 mL of water were added for reflux for 24 h. After cooling, 250 mL of water and 100 mL of ethyl acetate were added for stratification. An organic phase was washed with water for two times and dried over anhydrous sodium sulfate to remove the solvent to obtain 3.18 g of a solid powder (with a high performance liquid chromatography (HPLC) purity of 98.85%).

<sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 7.84-7.01 (m, 12H), 4.01 (s, 2H), 2.41 (s, 12H).

#### Example 11

**Preparation of dimethyl(cyclopentadienyl)(2,7-bis(3,5-dimethylphenyl)-9-fluorenyl)silylzirconium dichloride (catalyst 6)**



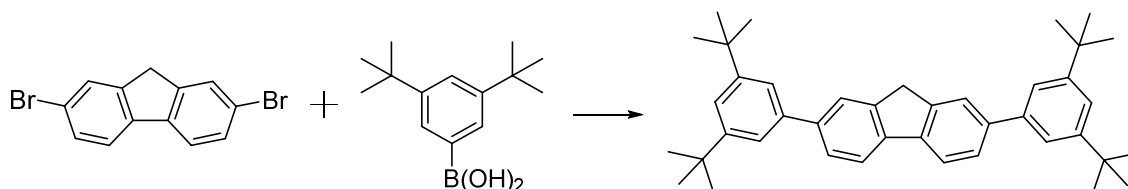
A 100 mL Schlenk flask 1 was taken, the 2,7-bis(3,5-dimethylphenyl)fluorene (5.4 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{ZrCl}_4$  (3.43 g, 14.6 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of n-hexane was added, and filtration and drying were performed to obtain 1.43 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.05 (m, 12H), 6.60 (t,  $J = 2.4$  Hz, 2H), 5.72 (t,  $J = 2.4$  Hz, 2H), 2.56 (s, 12H), 1.11 (s, 6H).

### Example 12

#### Preparation of 2,7-bis(3,5-di-tert-butylphenyl)fluorene



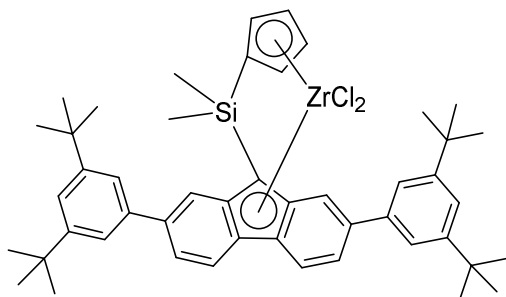
A 100 mL two-necked flask was taken, 2,7-dibromofluorene (3.24 g, 10 mmol), 3,5-di-tert-butylphenylboronic acid (5.00 g, 21.35 mmol), tetrakis(triphenylphosphine)palladium (0.13 g, 0.11 mmol), and anhydrous sodium carbonate (3.20 g, 30.19 mmol) were sequentially added, and nitrogen replacement was performed for three times. 50 mL of ethanol and 4 mL of water were added for reflux for 24 h. After cooling, 250 mL of water and 100 mL of ethyl acetate were added

for stratification. An organic phase was washed with water for two times and dried over anhydrous sodium sulfate to remove the solvent to obtain 4.08 g of a solid powder (with an HPLC purity of 98.32%).

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.89–7.43 (m, 12H), 4.05 (s, 2H), 1.41 (s, 36H).

### Example 13

#### Preparation of dimethyl(cyclopentadienyl)(2,7-bis(3,5-di-tert-butylphenyl)-9-fluorenyl)silylzirconium dichloride (catalyst 7)



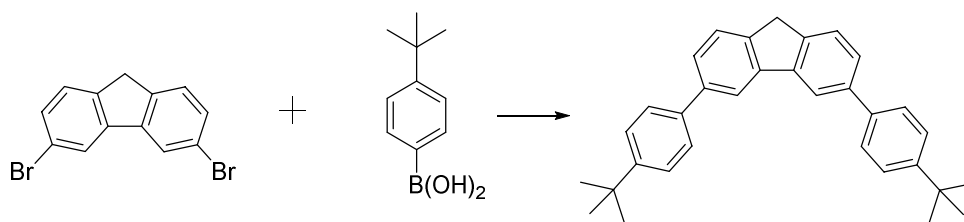
A 100 mL Schlenk flask 1 was taken, the 2,7-bis(3,5-di-tert-butylphenyl)fluorene (7.8 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then  $n\text{-BuLi}$  (6.05 mL, 15.1 mmol) was added at  $-40^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then  $n\text{-BuLi}$  (6.05 mL, 15.1 mmol) was added at  $-75^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^\circ\text{C}$  and stirred at  $25^\circ\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then  $n\text{-BuLi}$  (11.8 mL, 29.5 mmol) was added at  $-45^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 20 h.  $\text{ZrCl}_4$  (3.43 g, 14.6 mmol) was added at  $-75^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of  $n\text{-hexane}$  was added, and filtration and drying were performed to obtain 1.6 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91–7.45 (m, 12H), 6.60 (t,  $J = 2.4$  Hz, 2H), 5.72 (t,  $J = 2.4$  Hz, 2H), 2.55 (s, 36H), 1.11 (s, 6H).

### Example 14

#### 3,6-bis(4-tert-butylphenyl)fluorene

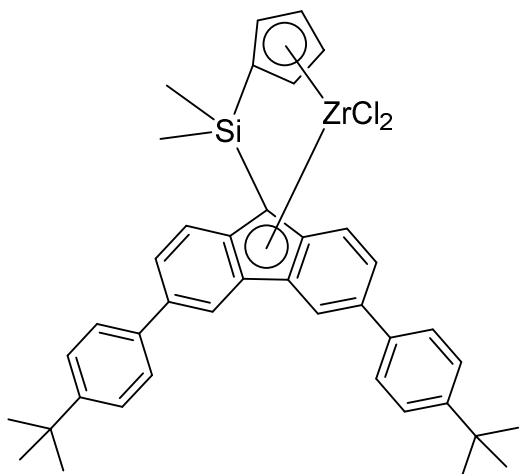


A 100 mL two-necked flask was taken, 3,6-dibromofluorene (3.24 g, 10 mmol), 4-tert-butylphenylboronic acid (3.76 g, 21.12 mmol), tetrakis(triphenylphosphine)palladium (0.13 g, 0.11 mmol), and anhydrous sodium carbonate (3.18 g, 30 mmol) were sequentially added, and nitrogen replacement was performed for three times. 50 mL of ethanol and 4 mL of water were added for reflux for 24 h. After cooling, 250 mL of water and 100 mL of ethyl acetate were added for stratification. An organic phase was washed with water for two times and dried over anhydrous sodium sulfate to remove the solvent to obtain 2.36 g of a solid powder (with an HPLC purity of 98.24%).

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.84-7.46 (m, 14H), 4.02 (s, 2H), 1.38 (s, 18H).

#### Example 15

**Preparation of dimethyl(cyclopentadienyl)(3,6-bis(4-tert-butylphenyl)-9-fluorenyl)silylzirconium dichloride (catalyst 8)**



A 100 mL Schlenk flask 1 was taken, the 3,6-bis(4-tert-butylphenyl)fluorene (6.2 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^\circ\text{C}$  to carry out a reaction at  $25^\circ\text{C}$  for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was

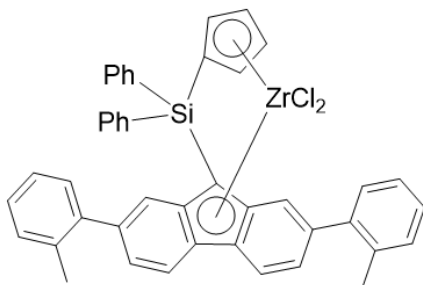
added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at -45°C to carry out a reaction at 25°C for 20 h. ZrCl<sub>4</sub> (3.43 g, 14.6 mmol) was added at -75°C to carry out a reaction at 25°C for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of n-hexane was added, and filtration and drying were performed to obtain 1.83 g of a yellow solid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86-7.48 (m, 14H), 6.61 (t, *J* = 2.4 Hz, 2H), 5.73 (t, *J* = 2.4 Hz, 2H), 2.53 (s, 18H), 1.09 (s, 6H).

### Example 16

**Preparation of diphenyl(cyclopentadienyl)(2,7-bis(2-methylphenyl)-9-fluorenyl)silylzirconium dichloride (catalyst 9)**



A 100 mL Schlenk flask 1 was taken, 2,7-bis(2-methylphenyl)fluorene (5.0 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at -40°C to carry out a reaction at 25°C for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (21.90 g, 86.5 mmol) were added, and the solution in the flask 1 was added at -25°C to carry out a reaction at 25°C for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at -75°C to carry out a reaction at 25°C for 2 h. Then, the solution in the flask 3 was added into the flask 2 at -45°C and stirred at 25°C for 3 h.

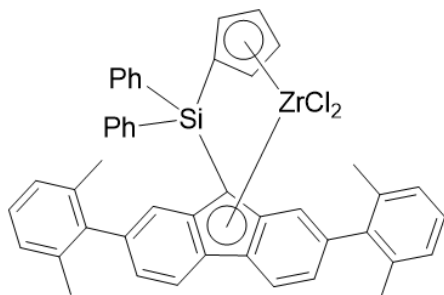
The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at -45°C to carry out a reaction at 25°C for 20 h. ZrCl<sub>4</sub> (3.43 g, 14.6 mmol) was added at -75°C to carry out a reaction at 25°C for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of n-hexane was added, and filtration and drying were

performed to obtain 2.48 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  8.26 -7.05 (m, 24H), 6.43 (s, 2H), 6.38 (s, 2H), 5.79 (s, 2H), 2.22 (s, 6H).

### Example 17

**Preparation of diphenyl(cyclopentadienyl)(2,7-bis(2,6-dimethylphenyl)-9-fluorenyl)silylzirconium dichloride (catalyst 10)**



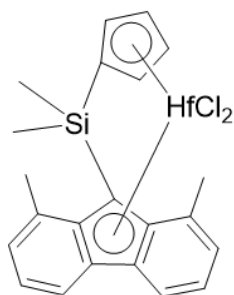
A 100 mL Schlenk flask 1 was taken, 2,7-bis(2,6-dimethylphenyl)fluorene (5.4 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then *n*-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and diphenyldichlorosilane (21.90 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then *n*-BuLi (6.05 mL, 15.1 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then *n*-BuLi (11.8 mL, 29.5 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h. ZrCl<sub>4</sub> (3.43 g, 14.6 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of *n*-hexane was added, and filtration and drying were performed to obtain 2.77 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  8.29-6.97 (m, 22H), 6.45 (s, 2H), 6.37 (s, 2H), 5.83 – 5.73 (m, 2H), 2.07 (s, 6H), 1.99 (s, 6H).

### Example 18

**Preparation of dimethyl(cyclopentadienyl)(1,8-dimethyl-9-fluorenyl)silylhafnium dichloride (catalyst 11)**



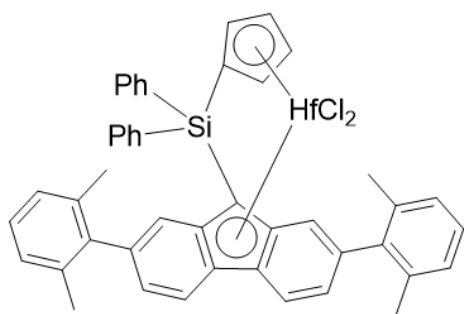
A 100 mL Schlenk flask 1 was taken, 1,8-dimethylfluorene (2.8 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{HfCl}_4$  (4.67 g, 14.6 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. The reaction solvent was drained, 100 mL of toluene was added and heated to  $45^{\circ}\text{C}$ , and filtration was performed with diatomite under heat, followed by washing of the diatomite with 20 mL of toluene for 2 times. A filtrate was collected, crystallized at  $-20^{\circ}\text{C}$ , and filtered to obtain 1.06 g of an orange solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.97- 6.64 (m, 8H), 5.74 (t,  $J=2.5$  Hz, 2H), 2.42 (s, 6H), 1.14(s, 6H).

### Example 19

**Preparation of diphenyl(cyclopentadienyl)(2,7-bis(2,6-dimethylphenyl)-9-fluorenyl)silylhafnium dichloride (catalyst 12)**



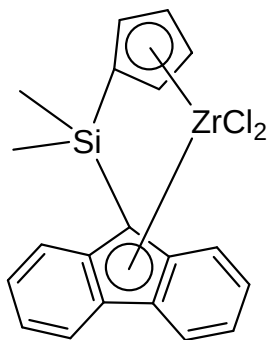
A 100 mL Schlenk flask 1 was taken, the 2,7-bis(3,5-dimethylphenyl)fluorene (5.4 g, 14.4 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (11.20 g, 86.5 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 24 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.002 g, 14.4 mmol) were added, and then n-BuLi (6.05 mL, 15.1 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{ZrCl}_4$  (3.43 g, 14.6 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, 40 mL of n-hexane was added, and filtration and drying were performed to obtain 1.43 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  8.31-6.98 (m, 22H), 6.54 (s, 2H), 6.43 (s, 2H), 5.85 – 5.75 (m, 2H), 2.09 (s, 6H), 1.88 (s, 6H).

### Comparative Example 1

**Preparation of dimethyl(cyclopentadienyl)(9-fluorenyl)silylzirconium dichloride (catalyst 13)**



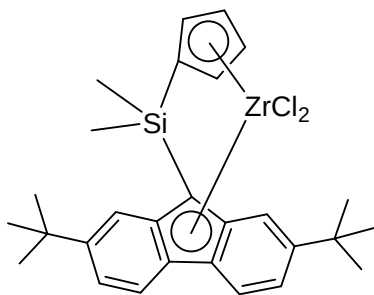
A 100 mL Schlenk flask 1 was taken, fluorene (2.8 g, 16.6 mmol) was added, nitrogen replacement was performed for 3 times, 35 mL of toluene and 5 mL of tetrahydrofuran were added, and then n-BuLi (7 mL, 17.5 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 40 mL of toluene and dimethyldichlorosilane (12.9 g, 100 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 35 mL of toluene, 5 mL of tetrahydrofuran, and cyclopentadiene (1.10 g, 16.6 mmol) were added, and then n-BuLi (7 mL, 17.5 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (13.6 mL, 34 mmol) was slowly added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{ZrCl}_4$  (3.96 g, 17.0 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h. The reaction solvent was drained, 100 mL of toluene was added at  $55^{\circ}\text{C}$ , and filtration was performed with diatomite under heat, followed by washing of the diatomite with 20 mL of toluene for 2 times. A filtrate was collected, crystallized at  $-40^{\circ}\text{C}$ , and filtered to obtain about 1.05 g of an orange solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  8.12 (d,  $J = 8.3$  Hz, 2H), 7.67 – 7.59 (m, 2H), 7.54 (d,  $J = 8.6$  Hz, 2H), 7.33 – 7.25 (m, 3H), 6.61 (t,  $J = 2.4$  Hz, 2H), 5.75 (t,  $J = 2.4$  Hz, 2H), 1.14 (s, 6H).

### Comparative Example 2

**Preparation of dimethyl(cyclopentadienyl)(2,7-di-tert-butyl-9-fluorenyl)silylzirconium dichloride (catalyst 14)**



A 100 mL Schlenk flask 1 was taken, 2,7-di-tert-butylfluorene (3 g, 10.8 mmol) was added, nitrogen replacement was performed for 3 times, 22 mL of toluene and 3 mL of tetrahydrofuran were added, and then n-BuLi (4.5 mL, 11.34 mmol) was added at  $-40^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. Another 250 mL Schlenk flask 2 was taken, nitrogen replacement was performed for 3 times, 30 mL of toluene and dimethyldichlorosilane (8.8 g, 64.8 mmol) were added, and the solution in the flask 1 was added at  $-25^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 18 h. The reaction solvent was drained, supplemented with 40 mL of toluene, and drained again. 40 mL of toluene was added. Another 100 mL Schlenk flask 3 was taken, nitrogen replacement was performed for 3 times, 22 mL of toluene, 3 mL of tetrahydrofuran, and cyclopentadiene (0.75 g, 10.8 mmol) were added, and then n-BuLi (4.5 mL, 11.34 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 2 h. Then, the solution in the flask 3 was added into the flask 2 at  $-45^{\circ}\text{C}$  and stirred at  $25^{\circ}\text{C}$  for 3 h.

The reaction solvent was drained, 30 mL of toluene and 7.5 mL of ethyl ether were added, and then n-BuLi (11.8 mL, 29.5 mmol) was added at  $-45^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 20 h.  $\text{ZrCl}_4$  (2.51 g, 10.8 mmol) was added at  $-75^{\circ}\text{C}$  to carry out a reaction at  $25^{\circ}\text{C}$  for 3 h. The reaction solvent was drained, followed by washing with toluene (150 mL) and filtration. A filtrate was concentrated to 40 mL, n-hexane was added, and filtration and drying were performed to obtain 1.01 g of a yellow solid.

$^1\text{H}$  NMR (500 MHz, Chloroform- $d$ )  $\delta$  7.99 (d,  $J=7.9$  Hz, 2H), 7.71 (dd,  $J=8.8$ , 1.7 Hz, 2H), 7.43 (s, 2H), 6.60 (t,  $J=2.4$  Hz, 2H), 5.66 (t,  $J=2.4$  Hz, 2H), 1.35 (s, 18H), 1.15 (s, 6H).

### Examples 20-38

#### Catalytic polymerization of propylene using the catalysts 1-12

150 mL of n-hexane, methylaluminoxane (MAO, a toluene solution with a mass fraction of 30%), and a catalyst-containing toluene solution (with a concentration of 0.5 g/L) were added into a 1 L reactor and stirred for 5 min, and 1.0 MPa propylene was introduced. After 1 h, ethanol (50 mL) was added to terminate a reaction. A polymer was washed with ethanol, filtered, and dried under vacuum to obtain polypropylene. Polymerization activity was calculated, and syndiotacticity (rrrr) of the polypropylene was calculated according to characterization by  $^{13}\text{C}$  nuclear magnetic resonance (NMR). A weight-average molecular weight ( $M_w$ ) and a molecular weight distribution (PDI) of the polypropylene were determined by gel permeation

chromatography (GPC). Polymerization data are listed in Table 1.

Table 1

| Example | Catalyst | Catalyst use amount/mL | MAO use amount/mL | Polymerization temperature/°C | Yield /g | Activity/g ·(g Cat.) <sup>-1</sup> | M <sub>w</sub> /g · mol <sup>-1</sup> | rrr / % | P DI |
|---------|----------|------------------------|-------------------|-------------------------------|----------|------------------------------------|---------------------------------------|---------|------|
| 20      | 1        | 4                      | 4                 | 15                            | 37.5     | 25000                              | 417000                                | 90      | 3.2  |
| 21      | 1        | 2                      | 2                 | 30                            | 67.2     | 56000                              | 125400                                | 87      | 3.6  |
| 22      | 1        | 4                      | 4                 | 45                            | 46.4     | 29000                              | 103500                                | 82      | 3.2  |
| 23      | 1        | 4                      | 4                 | 55                            | 23.1     | 21000                              | 69800                                 | 68      | 3.3  |
| 24      | 1        | 4                      | 4                 | 65                            | 10       | 14300                              | 39900                                 | 59      | 3.8  |
| 25      | 2        | 4                      | 4                 | 15                            | 20.2     | 10100                              | 100890                                | 85      | 4.4  |
| 26      | 2        | 4                      | 4                 | 30                            | 26.4     | 13200                              | 537400                                | 83      | 2.5  |
| 27      | 3        | 4                      | 4                 | 30                            | 21.4     | 10700                              | 189000                                | 81      | 3.1  |
| 28      | 4        | 4                      | 4                 | 15                            | 19.4     | 9700                               | 351500                                | 83      | 3.8  |
| 29      | 4        | 4                      | 4                 | 30                            | 22.3     | 11300                              | 230300                                | 70      | 3.2  |
| 30      | 4        | 4                      | 4                 | 45                            | 17.8     | 8900                               | 118700                                | 56      | 2.6  |
| 31      | 5        | 2                      | 3.5               | 30                            | 31.6     | 15800                              | 202000                                | 78      | 3.3  |
| 32      | 6        | 4                      | 4                 | 30                            | 28.2     | 14100                              | 386500                                | 79      | 2.9  |
| 33      | 7        | 4                      | 4                 | 30                            | 34.7     | 17350                              | 432100                                | 85      | 2.9  |
| 34      | 8        | 4                      | 4                 | 30                            | 23.6     | 11800                              | 158400                                | 72      | 3.1  |
| 35      | 9        | 4                      | 4                 | 30                            | 55.8     | 27900                              | 243900                                | 84      | 2.8  |
| 36      | 10       | 4                      | 4                 | 30                            | 61.3     | 30650                              | 252500                                | 86      | 2.7  |
| 37      | 11       | 4                      | 4                 | 30                            | 44.2     | 22100                              | 377400                                | 83      | 2.8  |
| 38      | 12       | 4                      | 4                 | 30                            | 47.1     | 23550                              | 282700                                | 86      | 3.0  |

### Comparative Examples 3-7 Catalytic polymerization of propylene using the catalysts 13-14

150 mL of n-hexane, MAO (a toluene solution with a mass fraction of 30%), and a catalyst-containing toluene solution (with a concentration of 1.0 g/L) were added into a 1 L reactor and stirred for 5 min, and 1.0 MPa propylene was introduced. After 1 h, ethanol (50 mL) was added to terminate a reaction. A polymer was washed with ethanol, filtered, and dried under vacuum to obtain polypropylene. Polymerization activity was calculated, and syndiotacticity (rrr) of the polypropylene was calculated according to characterization by <sup>13</sup>C NMR. A weight-average molecular weight (M<sub>w</sub>) and a molecular weight distribution (PDI) of the polypropylene were determined by GPC. Polymerization data are listed in Table 2.

Table 2

| Comparative Example | Catalyst | Catalyst use amount/mL | MAO use amount/mL | Polymerization temperature/°C | Yield/g | Activity/g·(g Cat.) <sup>-1</sup> | Mw/g·mol <sup>-1</sup> | rr<br>rr % | P<br>DI |
|---------------------|----------|------------------------|-------------------|-------------------------------|---------|-----------------------------------|------------------------|------------|---------|
| 3                   | 13       | 2                      | 3.5               | 30                            | 59      | 29500                             | 18900                  | 82         | 3.4     |
| 4                   | 14       | 2                      | 3                 | 30                            | 31.4    | 15700                             | 157300                 | 68         | 3.6     |
| 5                   | 14       | 2                      | 3                 | 45                            | 44      | 22000                             | 89600                  | 46         | 2.6     |
| 6                   | 14       | 2                      | 3                 | 65                            | 59.8    | 29900                             | 87200                  | 40         | 3.8     |
| 7                   | 14       | 2                      | 3                 | 75                            | 84.8    | 42400                             | 58700                  | 36         | 3.3     |

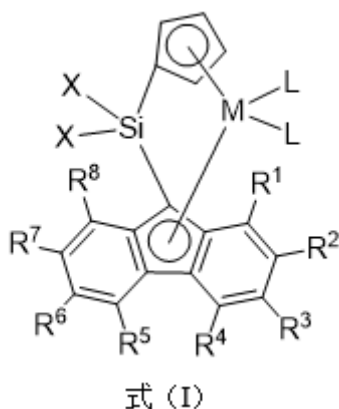
As can be seen from Table 1 and Table 2, the polypropylene obtained by the catalyst 13 has a lower weight-average molecular weight, and the presence of 1-methyl in the catalyst 1 not only increases the weight-average molecular weight of the obtained polypropylene, but also improves the polymerization activity. The presence of 2-methyl, 3-methyl, 2,7-dimethyl, and 3,5-dimethyl may also increase the weight-average molecular weight of the obtained polypropylene. Although the polypropylene obtained by the catalyst 14 has a higher weight-average molecular weight, the syndiotacticity of the polypropylene is significantly reduced. Due to the presence of 1-methyl, 2-methyl, 3-methyl, 2,7-dimethyl, and 3,5-dimethyl in the catalysts 1-5, the syndiotacticity of the obtained polypropylene is high and is even higher than that of the polypropylene obtained by the catalyst 13. Similarly, due to the presence of 2,7-diaryl in the catalyst 6, the catalyst 7, and the catalyst 8, the weight-average molecular weight of the obtained polypropylene is also much higher than that of the polypropylene obtained by the catalyst 13 and the catalyst 14. Meanwhile, the polypropylene obtained by the catalyst 6, the catalyst 7, and the catalyst 8 also possesses high syndiotacticity. When a bridge group is a diphenylsilicon bridge or a metal atom is hafnium, both the weight-average molecular weight and polymerization activity of the polypropylene obtained by the catalysts 9-12 are improved.

The above description of the examples is intended to facilitate understanding and application of the present invention by those of ordinary skill in the art. It is obvious that those skilled in the art can easily make various modifications to these examples and apply general principles described herein to other examples without inventive efforts. Therefore, the present invention is not limited to the above examples, and all improvements and modifications that are made by

those skilled in the art based on the revelation of the present invention without departing from the scope of the present invention shall fall within the scope of protection of the present invention.

## WHAT IS CLAIMED IS:

1. A silicon-bridged metallocene catalyst, having a general structural formula of formula (I):



wherein M is a transition metal element of Group 4;

L is a monovalent anionic ligand;

X is unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, phenyl, or aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls;

R<sup>1</sup> and R<sup>8</sup> are independently selected from hydrogen, trifluoromethyl, phenyl, halogen, unsubstituted or substituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, and unsubstituted or substituted heteroaryl;

R<sup>2</sup>, R<sup>3</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently selected from hydrogen, trifluoromethyl, phenyl, naphthyl, anthryl, phenanthryl, halogen, unsubstituted or substituted C<sub>5</sub>-C<sub>10</sub> cycloalkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, unsubstituted or substituted aryl, and unsubstituted or substituted heteroaryl; and

R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen, trifluoromethyl, halogen, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl, unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkoxy, amino containing 2 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls, and silyl containing 3 unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyls.

2. The silicon-bridged metallocene catalyst according to claim 1, wherein M is zirconium or hafnium.

3. The silicon-bridged metallocene catalyst according to claim 1, wherein L is halogen or unsubstituted or substituted C<sub>1</sub>-C<sub>10</sub> alkyl.

4. The silicon-bridged metallocene catalyst according to claim 1, wherein X is unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyl, phenyl, or aryl containing 1-3 unsubstituted or substituted C<sub>1</sub>-C<sub>6</sub> alkyls.

5. The silicon-bridged metallocene catalyst according to claim 1, wherein  $R^1$  and  $R^8$  are independently selected from hydrogen, trifluoromethyl, and unsubstituted or substituted  $C_1$ - $C_6$  alkyl;

$R^2$ ,  $R^3$ ,  $R^6$ , and  $R^7$  are independently selected from hydrogen, phenyl, naphthyl, unsubstituted or substituted  $C_1$ - $C_{10}$  alkyl, silyl containing 3 unsubstituted or substituted  $C_1$ - $C_{10}$  alkyls, aryl containing 1-3 unsubstituted or substituted  $C_1$ - $C_{10}$  alkyls, and unsubstituted or substituted aryl; and

$R^4$  and  $R^5$  are independently selected from hydrogen and unsubstituted or substituted  $C_1$ - $C_{10}$  alkyl.

6. Use of the silicon-bridged metallocene catalyst according to any one of claims 1-5 in preparation of a catalytic system for olefin polymerization.

7. A catalytic system for olefin polymerization, comprising an activator, an inert carrier, and the silicon-bridged metallocene catalyst according to any one of claims 1-5.

8. The catalytic system for olefin polymerization according to claim 7, wherein the activator is selected from one or more of aluminoxane, alkylaluminum, and a borate.

9. The catalytic system for olefin polymerization according to claim 7, wherein the inert carrier is selected from one or more of a silicon-containing inorganic porous carrier, an aluminum-containing inorganic porous carrier, a magnesium-containing inorganic porous carrier, and a high-molecular organic porous carrier.

10. A method for preparing a propylene polymer, comprising the following steps:

- 1) adding the catalytic system according to claim 7 into a reactor;
- 2) introducing a propylene monomer into the reactor to be in contact with the catalytic system after the catalytic system is added; and
- 3) maintaining the propylene monomer under polymerization conditions to obtain a propylene polymer.