

## SUPPORTING INFORMATION

### **Synthesis of Bis(oxazoline)-based Rare-earth Metal Complexes and Their Catalytic Performance in the Polymerization of Isoprene and Polar *ortho*-Methoxystyrene**

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**Figure S1**  $^1\text{H}$  NMR spectrum of **L1-H** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S2**  $^{13}\text{C}$  NMR spectrum of **L1-H** (100 MHz,  $\text{CDCl}_3$ , 25 °C)  
**Figure S3**  $^1\text{H}$  NMR spectrum of **1-Y** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
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**Figure S9**  $^1\text{H}$  NMR spectrum of **L2-H** (400 MHz,  $\text{CDCl}_3$ , 25 °C)  
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**Figure S11**  $^1\text{H}$  NMR spectrum of **2-Y** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
**Figure S12**  $^{13}\text{C}$  NMR spectrum of **2-Y** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
**Figure S13**  $^1\text{H}$  NMR spectrum of **2-Lu** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
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**Figure S15**  $^1\text{H}$  NMR spectrum of **2-Sc** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
**Figure S16**  $^{13}\text{C}$  NMR spectrum of **2-Sc** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
**Figure S17**  $^1\text{H}$  NMR spectrum of **1-Y** and **1-Y** + 1 equiv. TIBA (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  
**Figure S18**  $^1\text{H}$  NMR spectrum of atactic P(*o*MOS) catalyzed by **1-Y**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (400 MHz,  $\text{C}_2\text{Cl}_4\text{D}_2$ , 120 °C, Entry 3 in Table 2)  
**Figure S19**  $^{13}\text{C}$  NMR spectrum of atactic P(*o*MOS) catalyzed by **1-Y**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (100 MHz,  $\text{C}_2\text{Cl}_4\text{D}_2$ , 120 °C, Entry 3 in Table 2)  
**Figure S20** GPC curves of different polymerization time catalyzed by **1-Y**. time: 3min (a), 2.5min (b), 2min (c), 1.5min (d), and 1min (e)  
**Figure S21** GPC curves of different monomer feeds catalyzed by **1-Y**. [IP]/[**1-Y**]: 1500 (a), 1000 (b), 750 (c), 500 (d), and 300 (e)  
**Table S1** Summary of the crystallographic data for **1-Y**, **1-Lu** and **2-Sc**

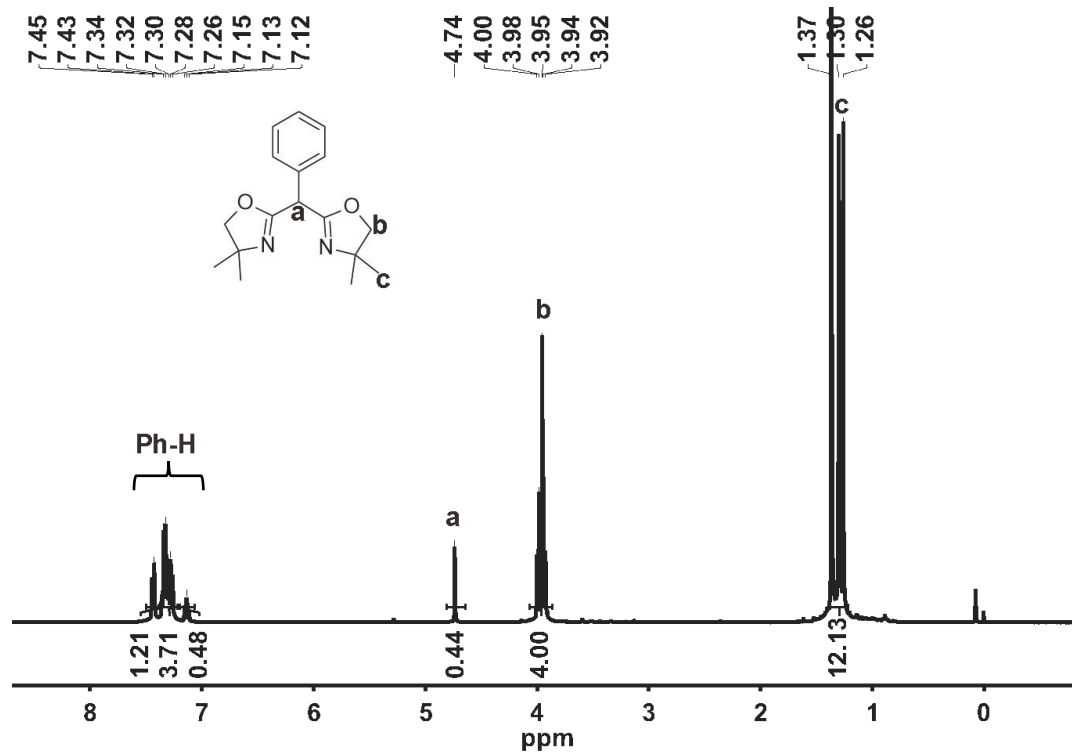


Figure S1  $^1\text{H}$  NMR spectrum of L1-H (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

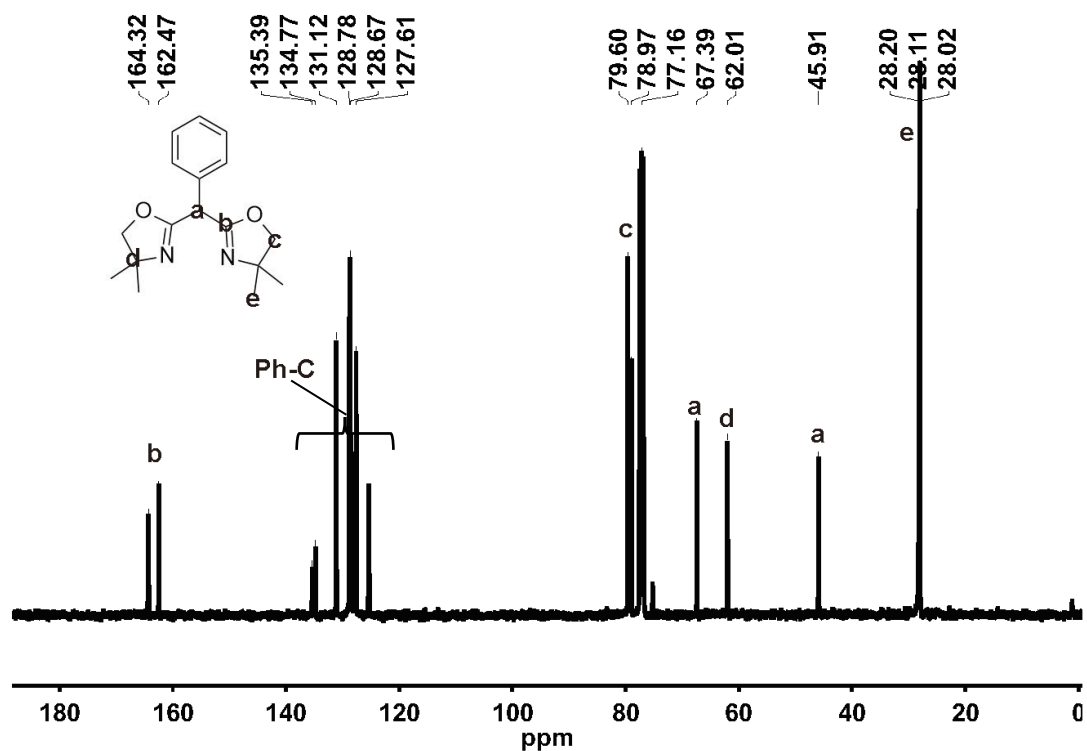


Figure S2  $^{13}\text{C}$  NMR spectrum of L1-H (100 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )

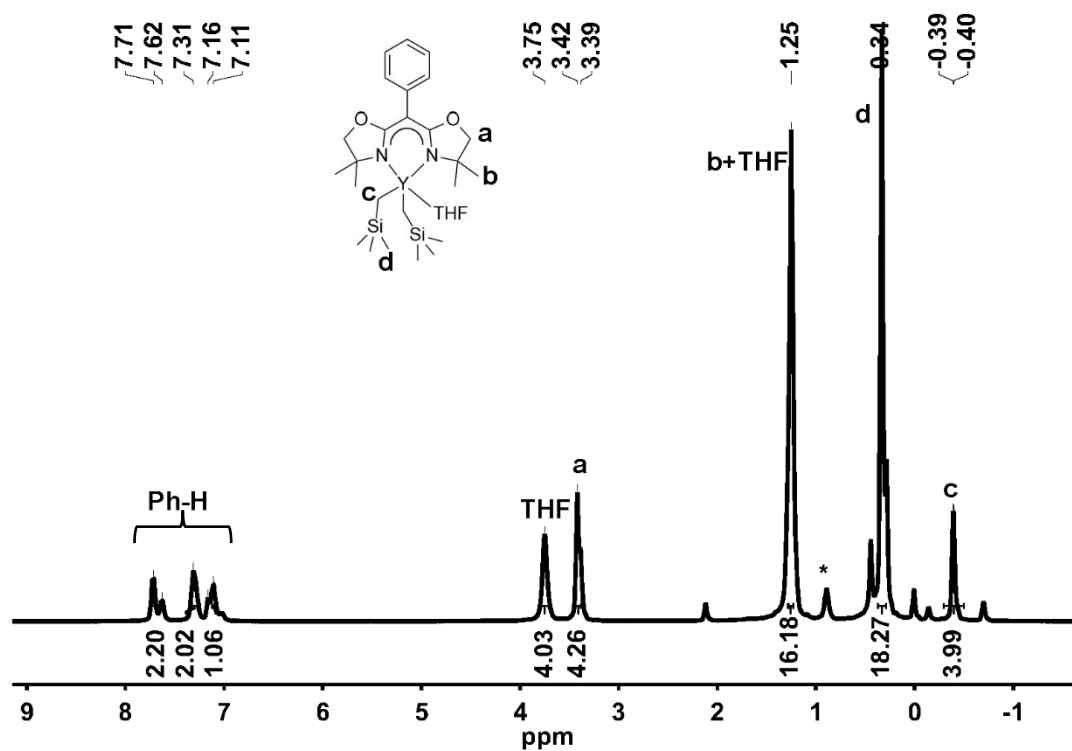


Figure S3  $^1\text{H}$  NMR spectrum of 1-Y (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ; \* *n*-hexane)

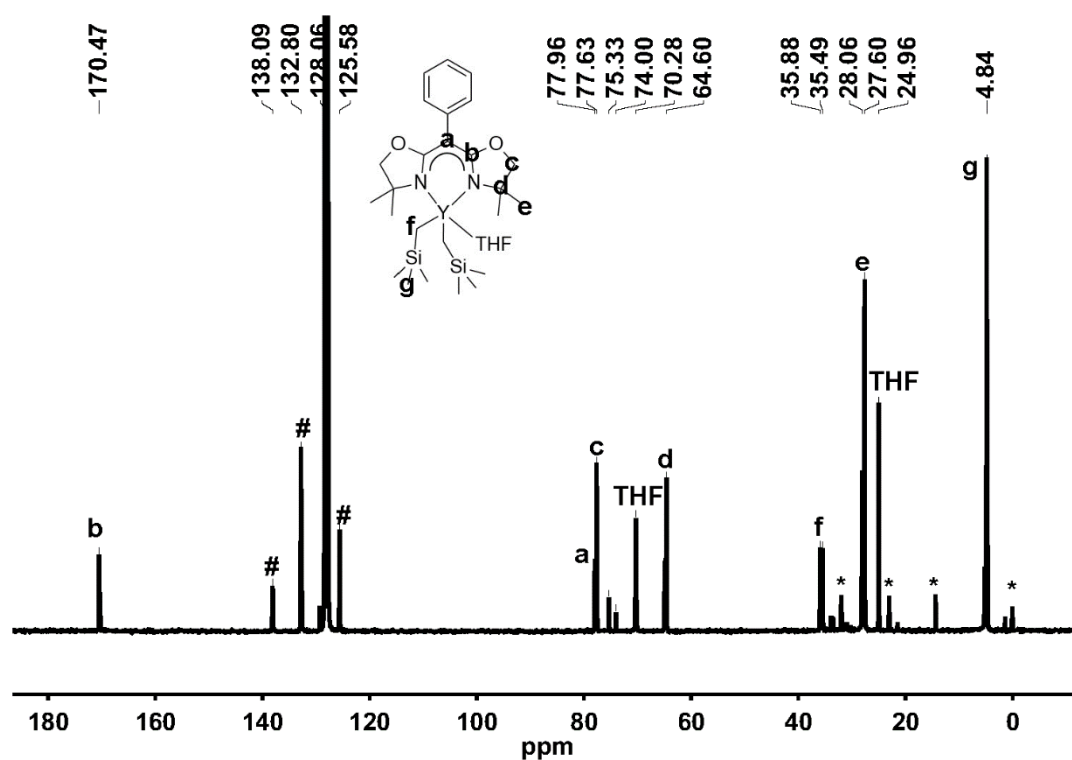


Figure S4  $^{13}\text{C}$  NMR spectrum of 1-Y (100 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ; \* *n*-hexane; # Ph-C)

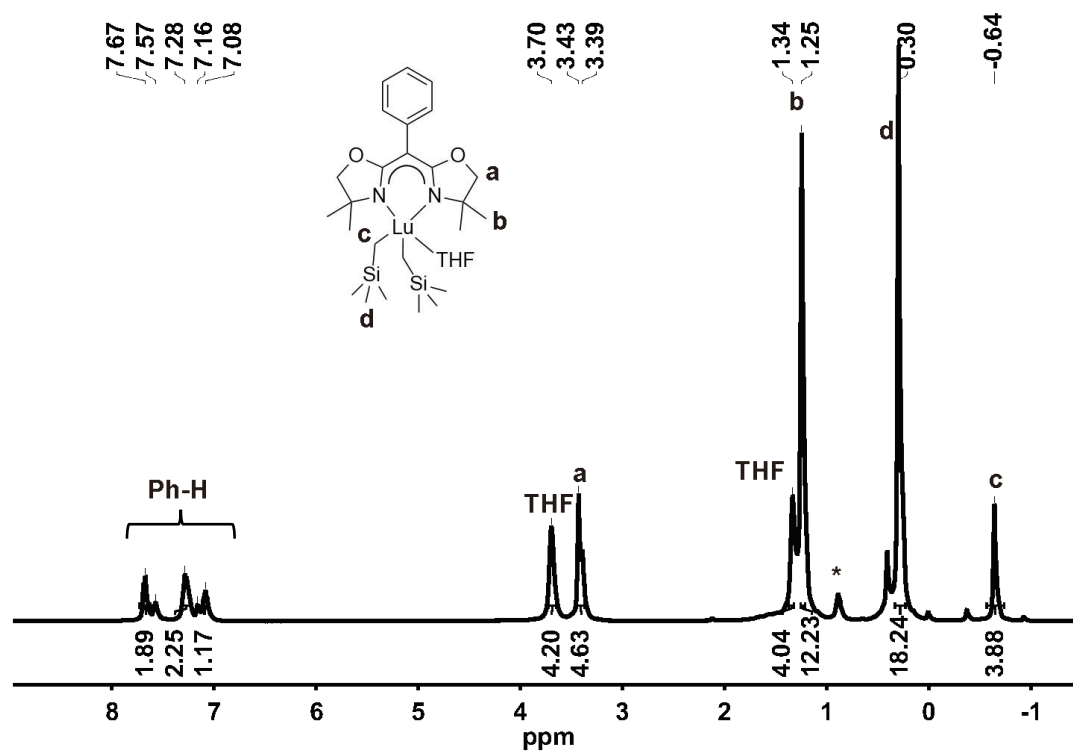


Figure S5  $^1\text{H}$  NMR spectrum of **1-Lu** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C; \* *n*-hexane)

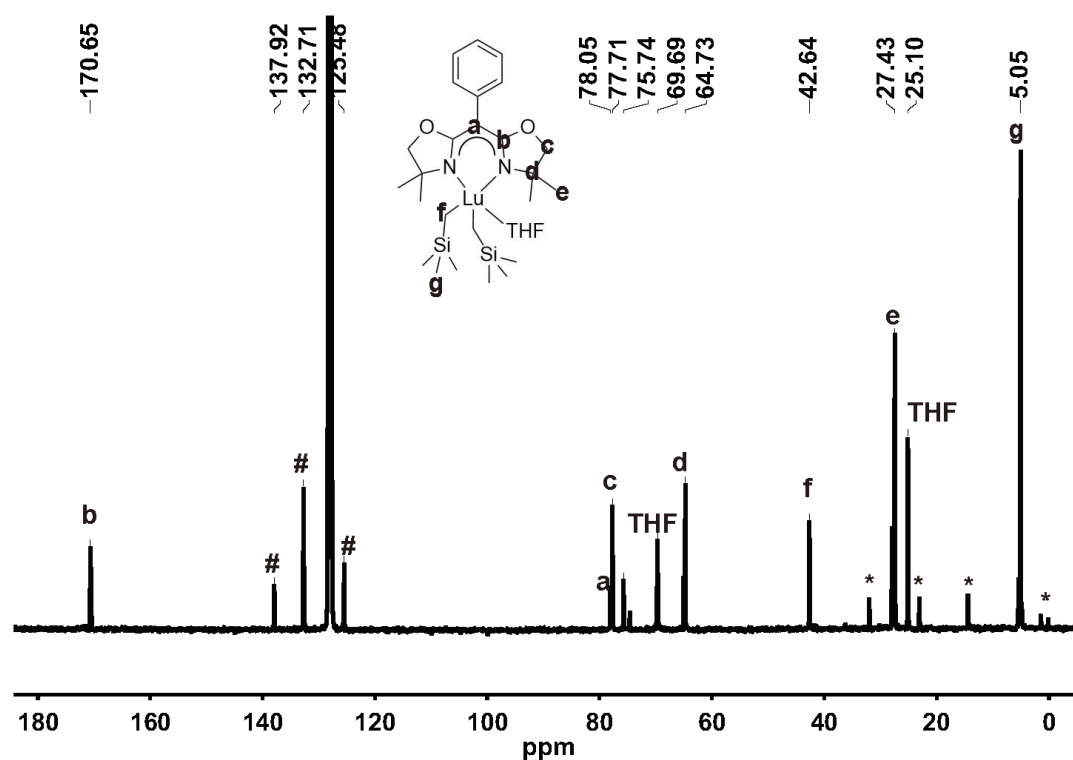


Figure S6  $^{13}\text{C}$  NMR spectrum of **1-Lu** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C; \* *n*-hexane; # Ph-C)

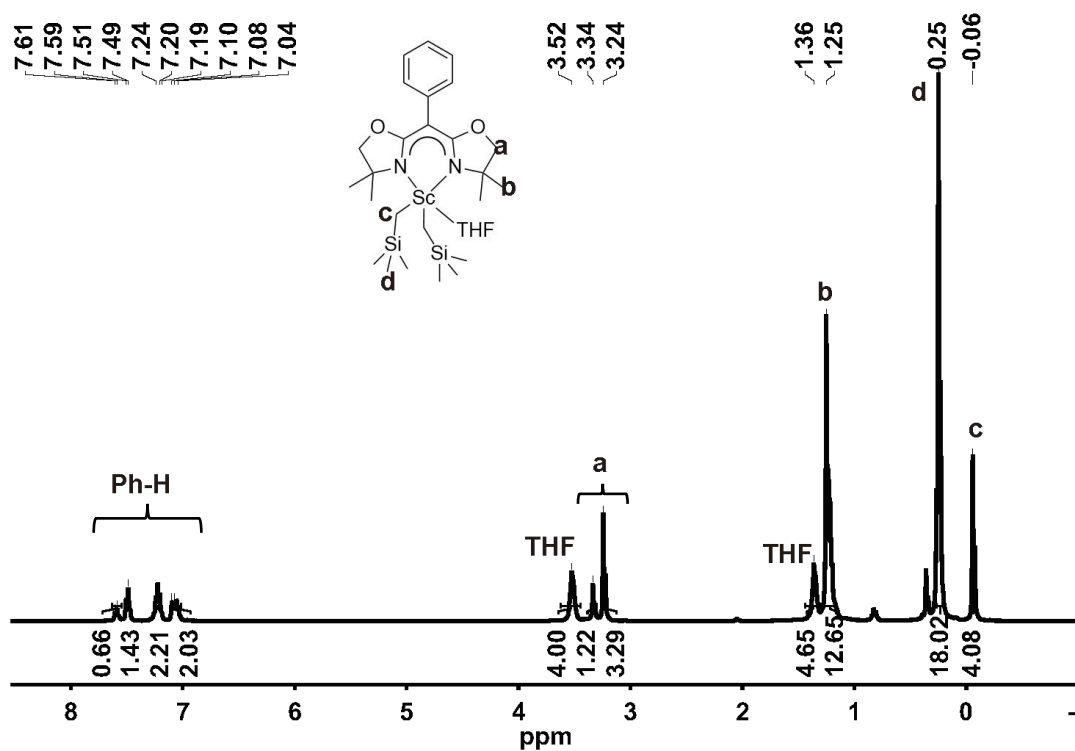


Figure S7  $^1\text{H}$  NMR spectrum of 1-Sc (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)

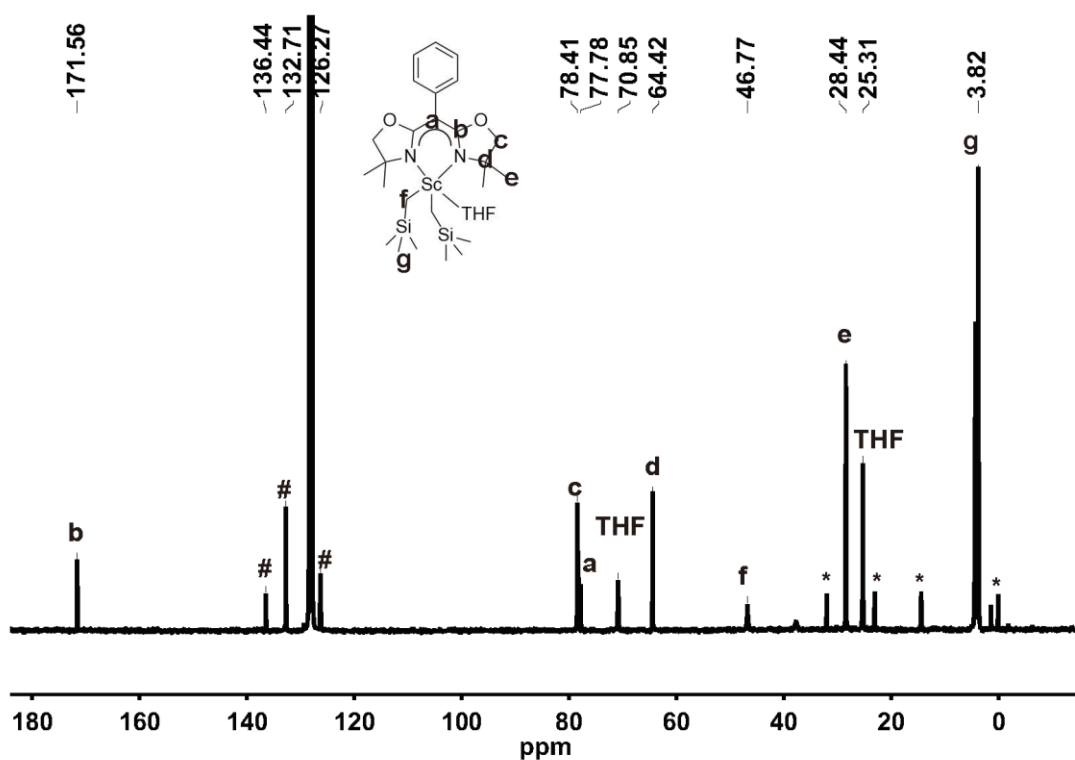


Figure S8  $^{13}\text{C}$  NMR spectrum of 1-Sc (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C; \**n*-hexane; # Ph-C)

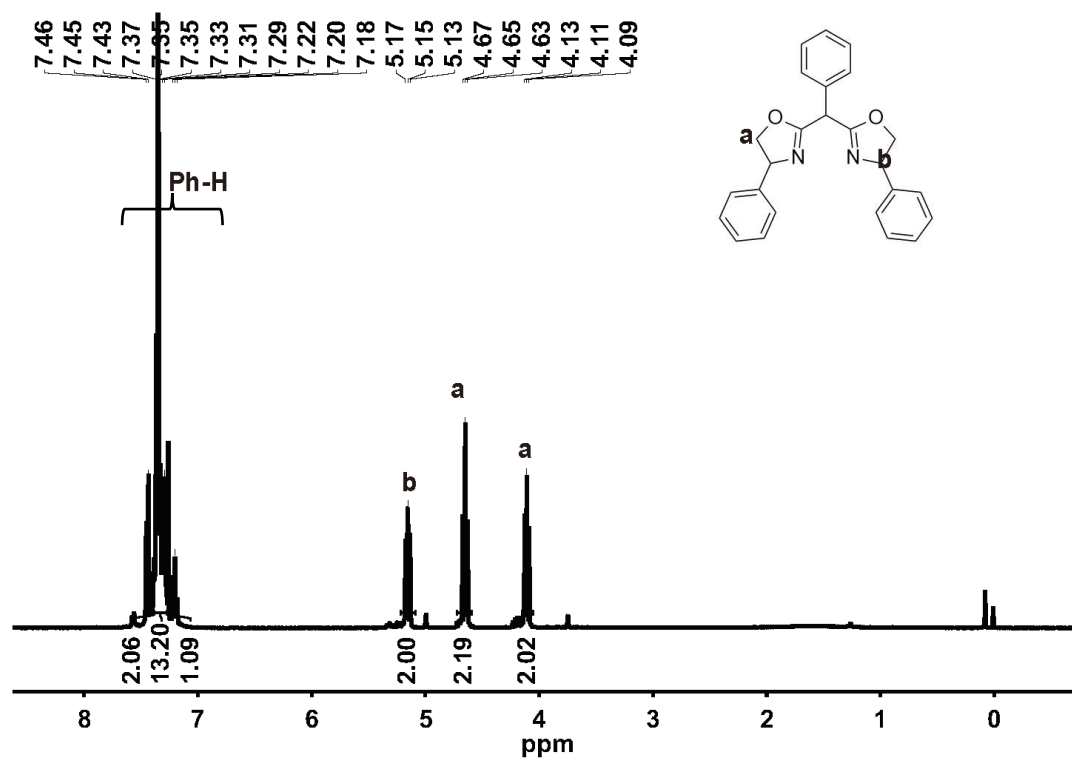


Figure S9  $^1\text{H}$  NMR spectrum of L2-H (400 MHz,  $\text{CDCl}_3$ , 25 °C)

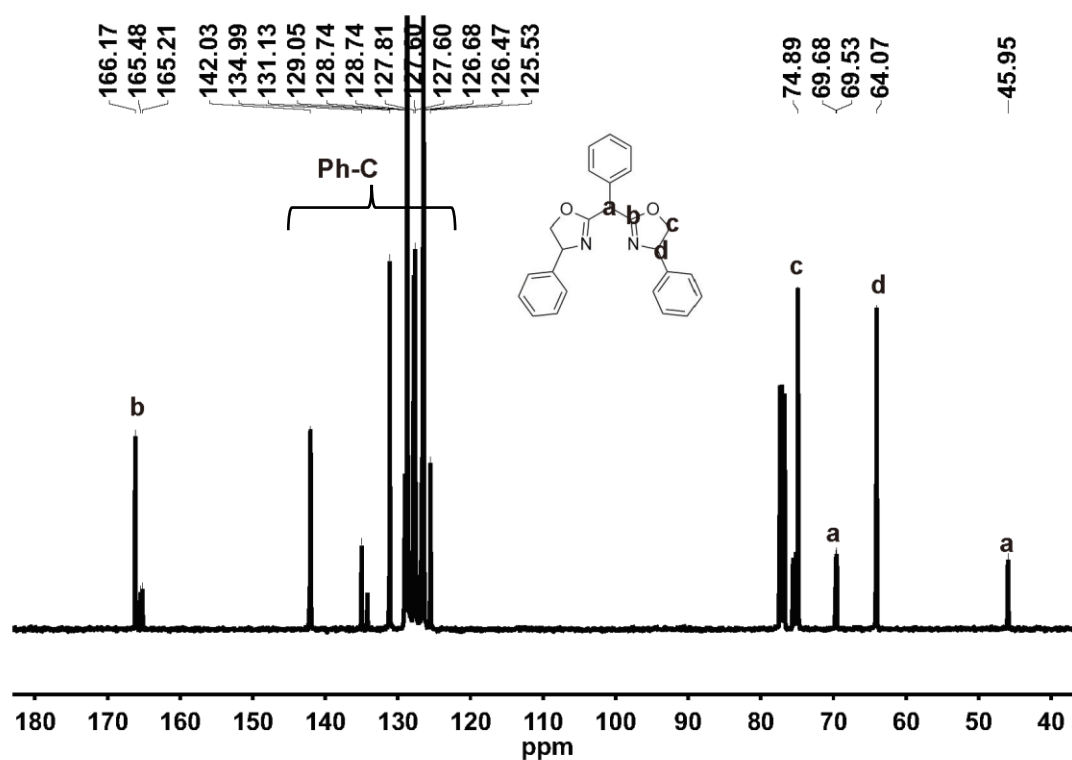


Figure S10  $^{13}\text{C}$  NMR spectrum of L2-H (100 MHz,  $\text{CDCl}_3$ , 25 °C)

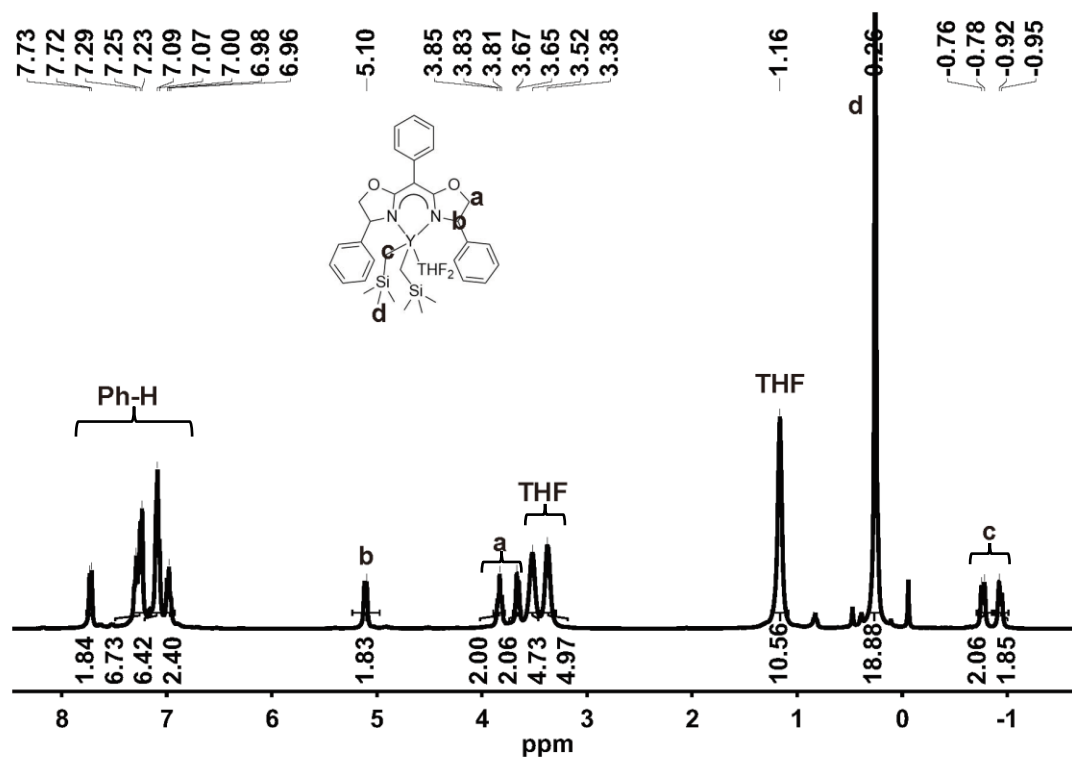


Figure S11  $^1\text{H}$  NMR spectrum of 2-Y (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)

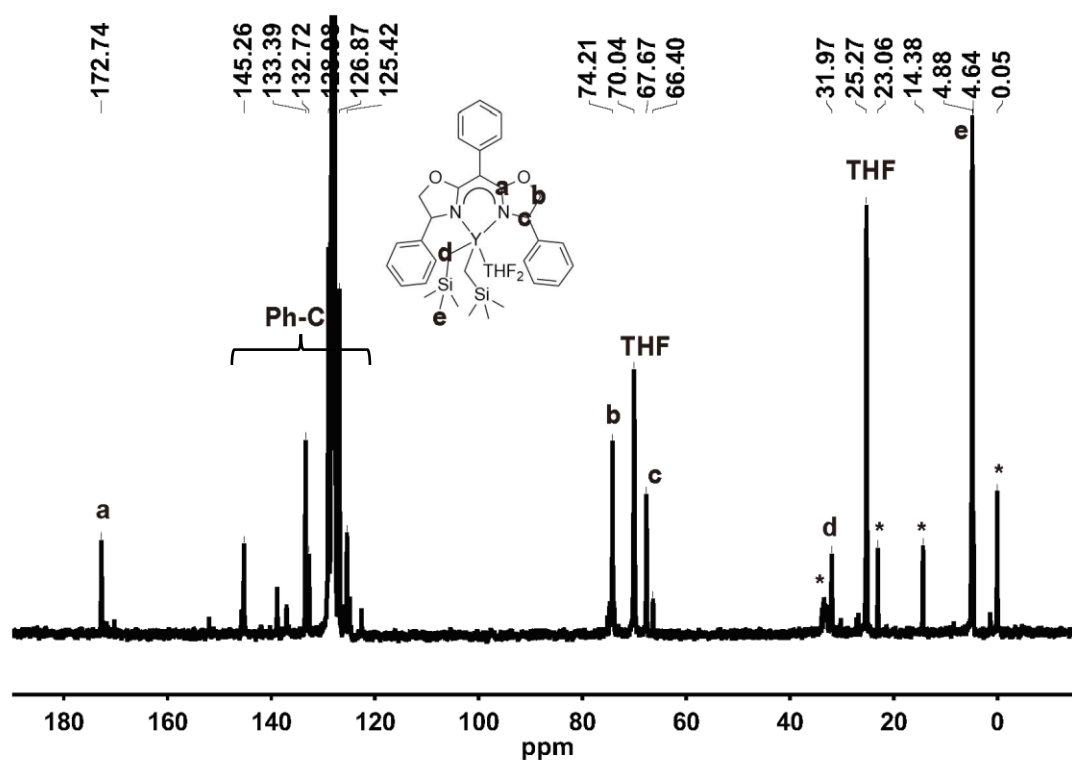


Figure S12  $^{13}\text{C}$  NMR spectrum of 2-Y (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C; \* *n*-hexane)



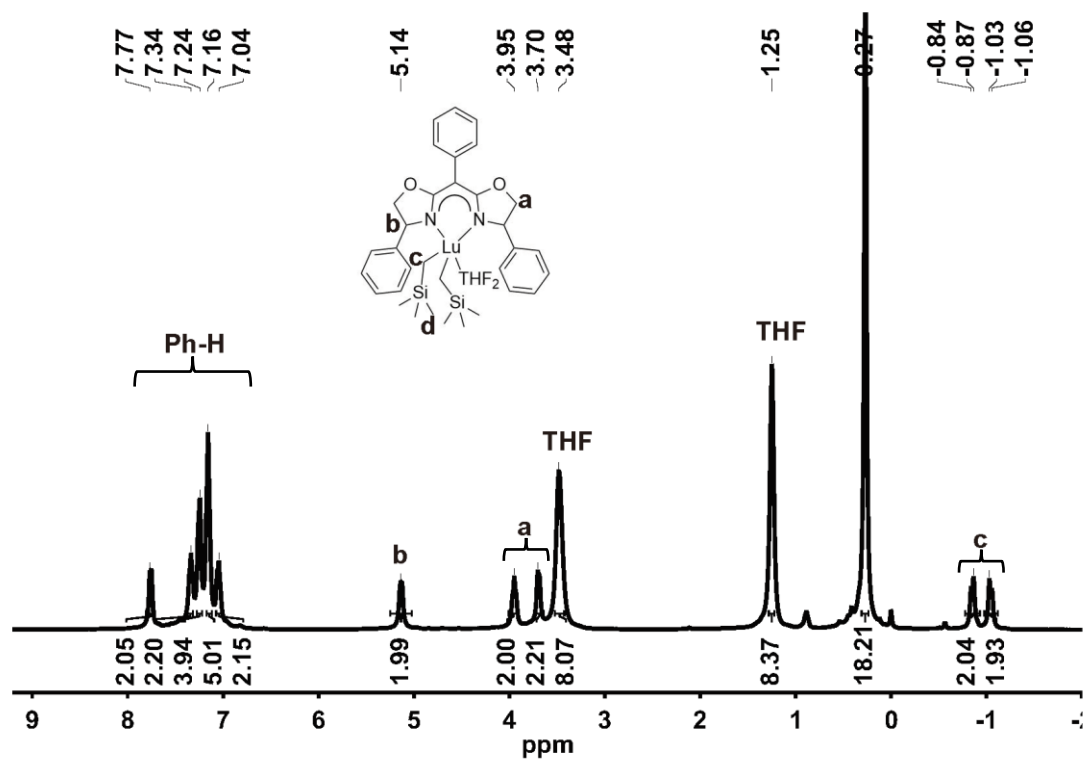


Figure S13  $^1\text{H}$  NMR spectrum of **2-Lu** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)

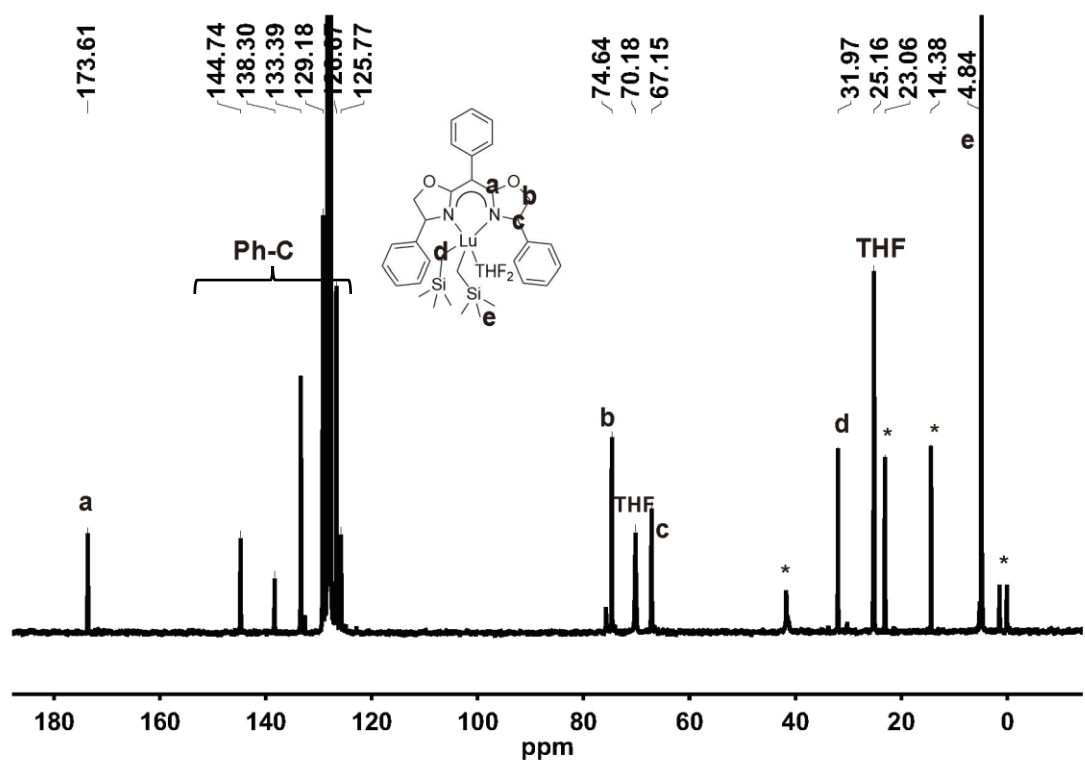


Figure S14  $^{13}\text{C}$  NMR spectrum of **2-Lu** (100 MHz,  $\text{C}_6\text{D}_6$ , 25 °C; \* *n*-hexane)

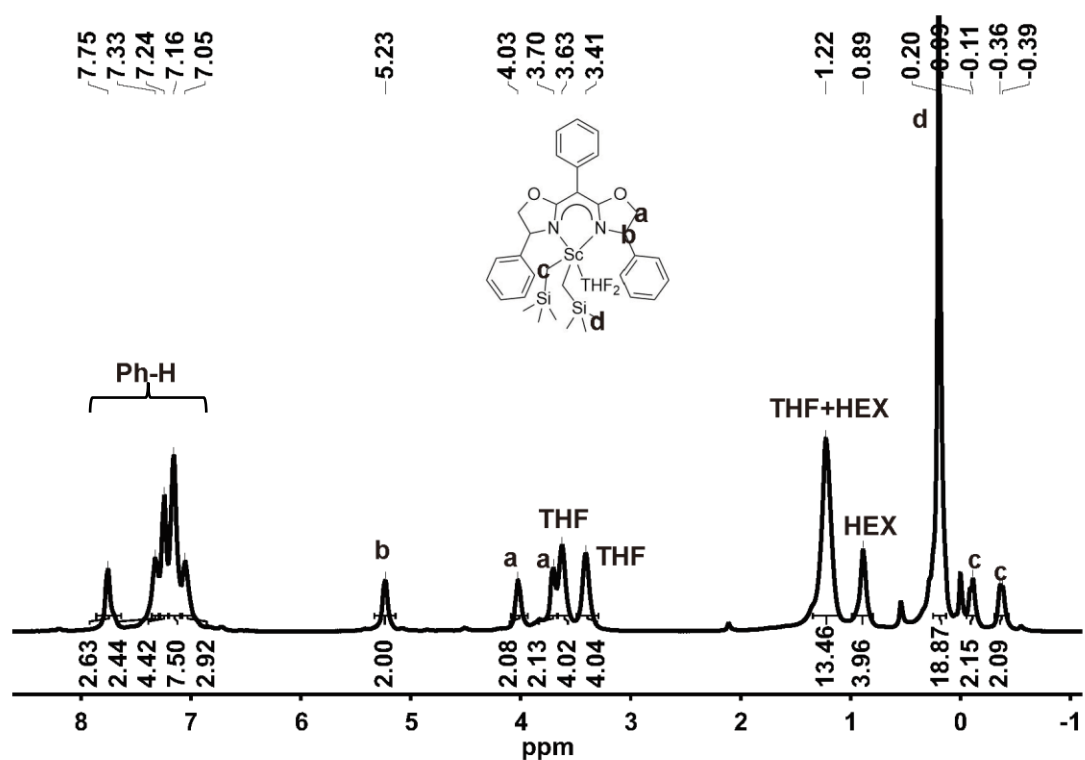


Figure S15  $^1\text{H}$  NMR spectrum of 2-Sc (400 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ )

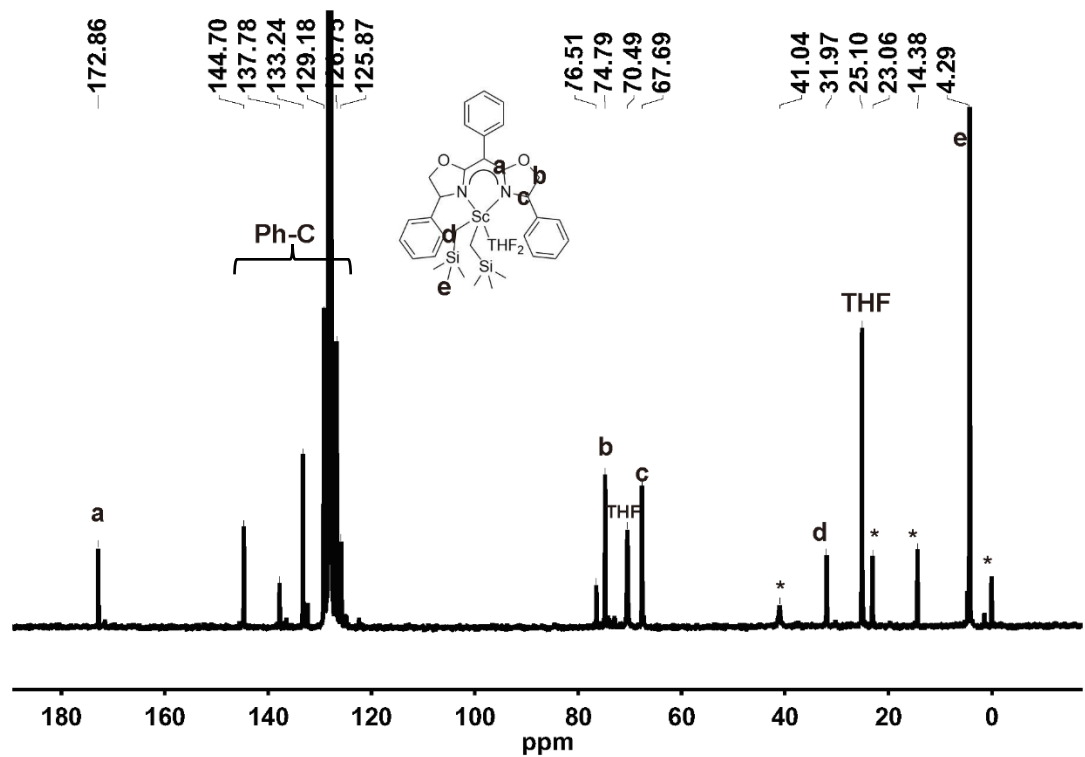
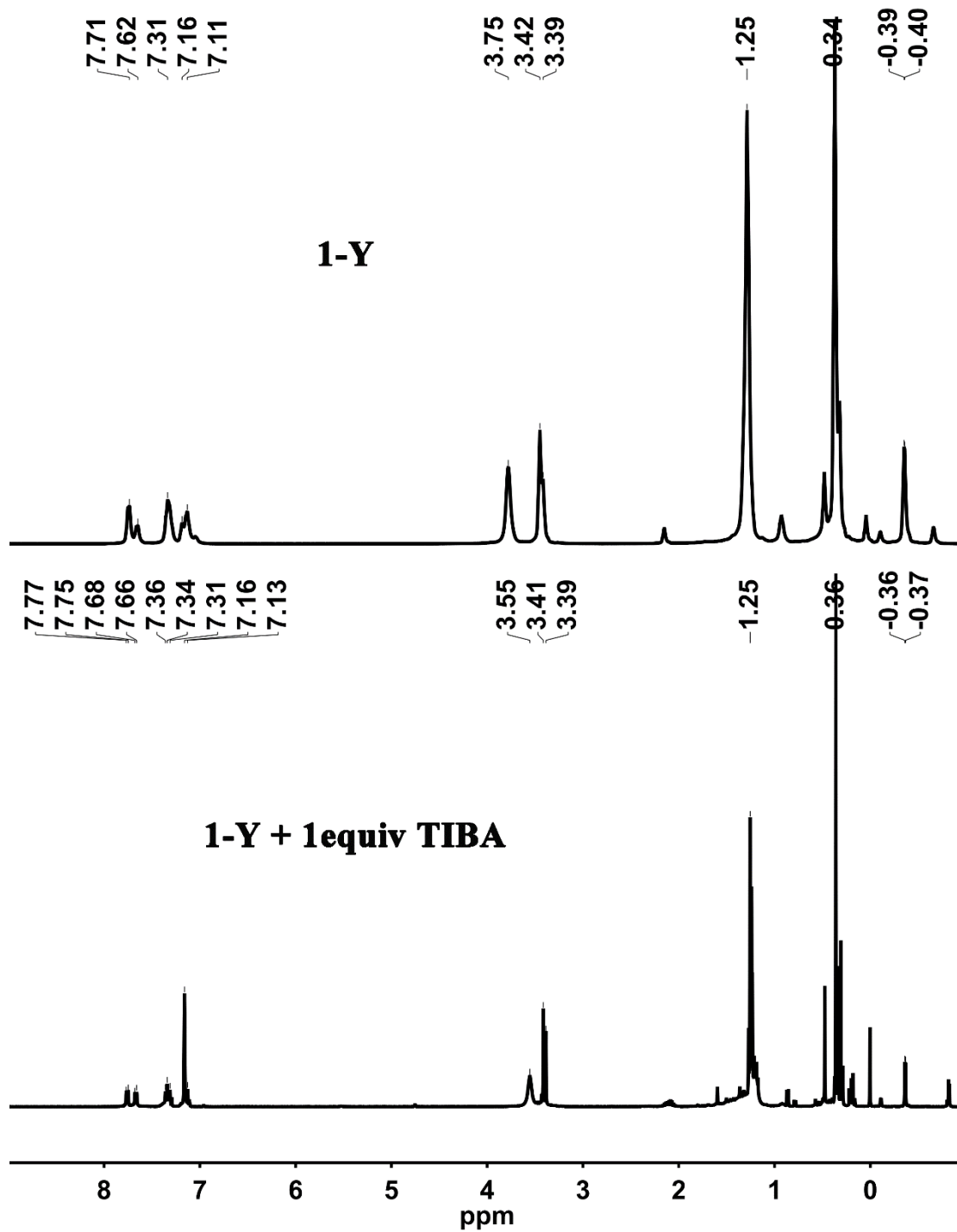
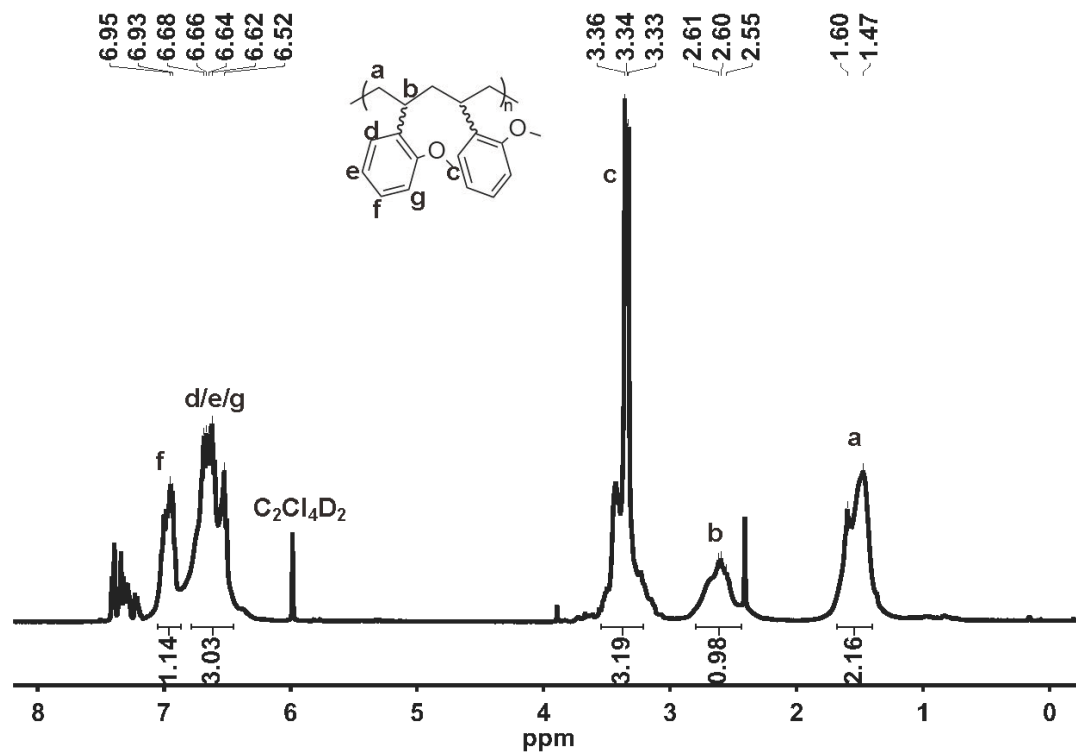


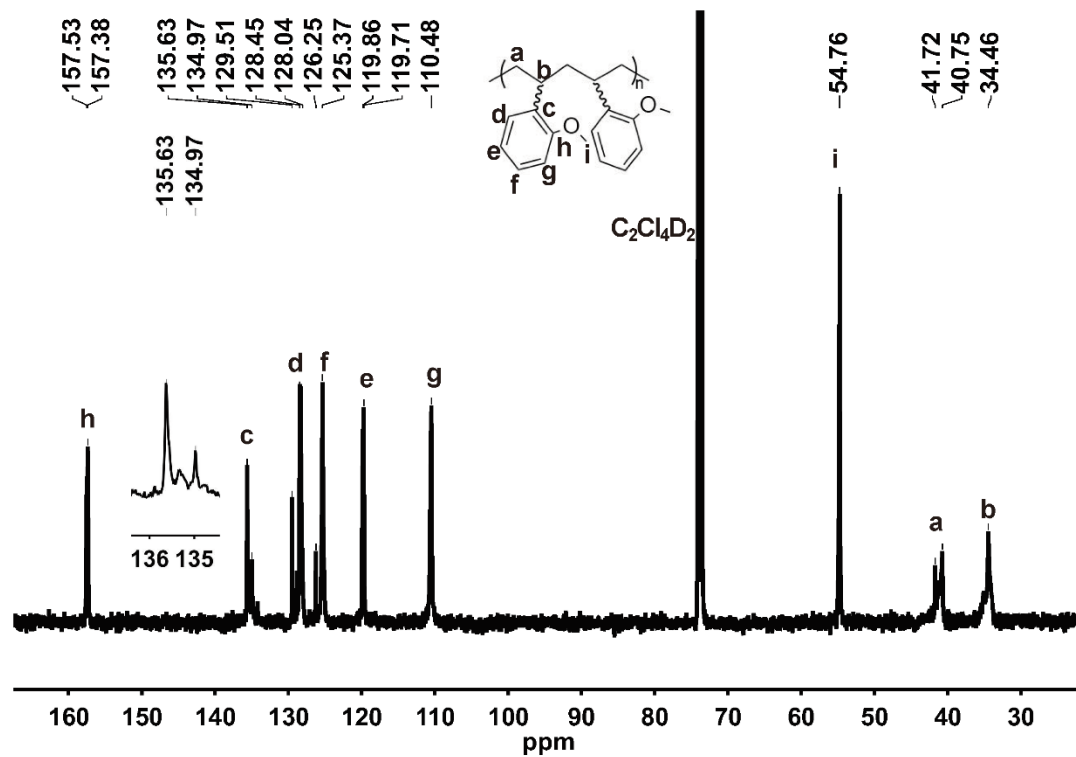
Figure S16  $^{13}\text{C}$  NMR spectrum of 2-Sc (100 MHz,  $\text{C}_6\text{D}_6$ , 25  $^\circ\text{C}$ ; \* *n*-hexane)



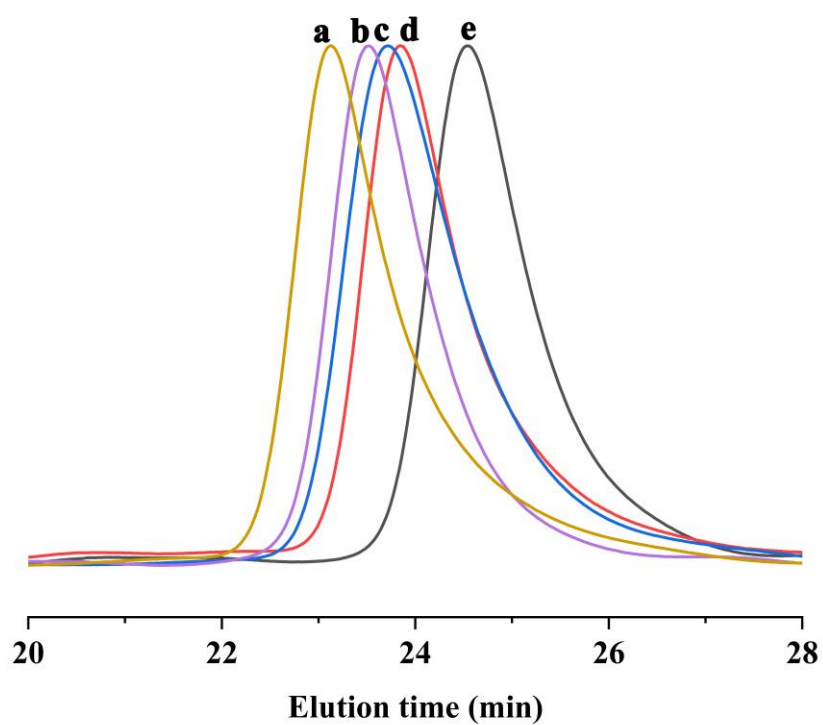
**Figure S17**  $^1\text{H}$  NMR spectrum of **1-Y** and **1-Y + 1 equiv TIBA** (400 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)



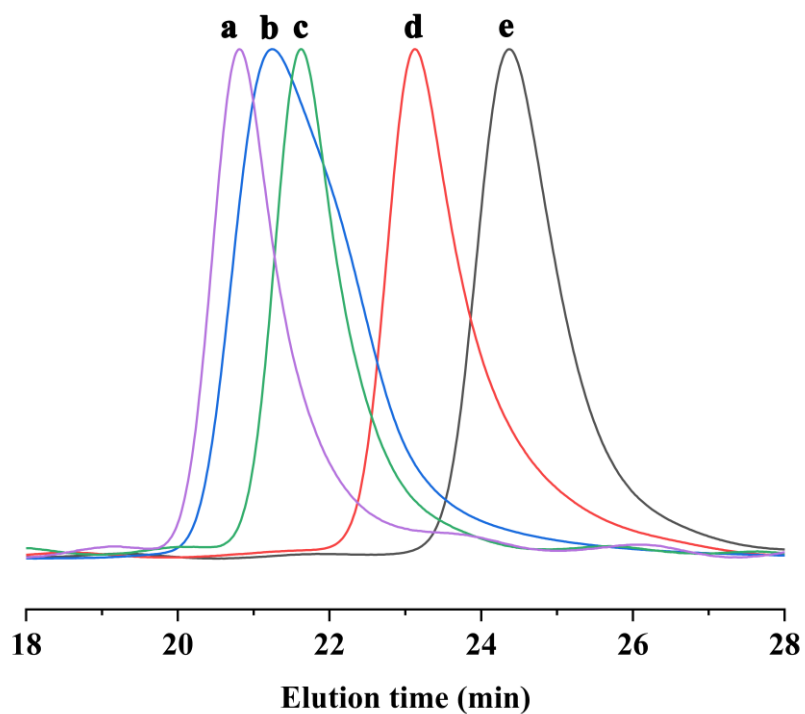
**Figure S18**  $^1\text{H}$  NMR spectrum of atactic P(oMOS) catalyzed by **1-Y**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (400 MHz, C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>, 120 °C, Entry 3 in Table 2)



**Figure S19**  $^{13}\text{C}$  NMR spectrum of atactic P(oMOS) catalyzed by **1-Y**/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/TIBA (100 MHz, C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>, 120 °C, Entry 3 in Table 2)



**Figure S20** GPC curves of different polymerization time catalyzed by **1-Y**. time: 3min (a), 2.5min (b), 2min (c), 1.5min (d), and 1min (e)



**Figure S21** GPC curves of different monomer feeds catalyzed by **1-Y**. [IP]/[**1-Y**]: 1500 (a), 1000 (b), 750 (c), 500 (d), and 300 (e)

**Table S1** Summary of the crystallographic data for **1-Y**, **1-Lu** and **2-Sc**

	<b>1-Y</b>	<b>1-Lu</b>	<b>2-Sc</b>
Empirical formula	C <sub>29</sub> H <sub>51</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>2</sub> Y	C <sub>29</sub> H <sub>51</sub> LuN <sub>2</sub> O <sub>3</sub> Si <sub>2</sub> Y	C <sub>41</sub> H <sub>55</sub> N <sub>2</sub> O <sub>2</sub> ScSi <sub>2</sub>
Formula weight	620.80	707.87	741.01
Temperature/K	150.00	150.00	150.00
Crystal system	triclinic	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (19)
<i>a</i> /Å	10.3675(12)	10.3467(4)	10.8048(16)
<i>b</i> /Å	11.7613(12)	11.7319(4)	12.4139(17)
<i>c</i> /Å	14.9863(10)	14.9386(5)	30.850(6)
$\alpha$ /°	92.529(3)	92.6780(10)	90
$\beta$ /°	100.532(3)	100.7490(10)	90
$\gamma$ /°	112.138(2)	112.1510(10)	90
Volume/Å <sup>3</sup>	1651.3(3)	1636.33(10)	4137.9(11)
<i>Z</i>	2	2	4
D <sub>c</sub> /Mg m <sup>-3</sup>	1.249	1.437	1.189
$\mu$ /mm <sup>-1</sup>	1.868	3.119	0.276
F(000)	660	726	1584
Crystal size/mm <sup>3</sup>	0.23×0.19×0.18	0.3×0.1×0.1	0.1×0.08×0.05
2 $\theta$ range for data collection/°	4.34 to 55.06	4.40 to 55.01	3.99 to 55.04
Index ranges	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -19 ≤ <i>l</i> ≤ 18	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -19 ≤ <i>l</i> ≤ 19	-14 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 15 -37 ≤ <i>l</i> ≤ 40
Reflections collected	55689	47958	46196
Independent reflections	7598 R <sub>int</sub> = 0.0988	7444 R(int) = 0.0483	9493 R(int) = 0.1436
Completeness to $\theta$ /°	25.242(99.9 %)	25.242(98.5 %)	25.242(100.0 %)
Data/Restraints/Parameters	7598/0/344	7444/0/344	9493/0/457
Goodness-of-fit on F <sup>2</sup>	1.033	0.963	1.025
Final R indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	R1 = 0.0319 wR2 = 0.0725	R1 = 0.0176 wR2 = 0.0521	R1 = 0.0612 wR2 = 0.1308
Final R indexes [all data]	R1 = 0.0454 wR2 = 0.0768	R1 = 0.0181 wR2 = 0.0524	R1 = 0.1082 wR2 = 0.1532
Largest peak/hole/eÅ <sup>-3</sup>	0.53/-0.41	0.86/-0.82	0.49/-0.29

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$