Supporting Information

for

2-(5-phenylpyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinolyliron chlorides as precatalyst for ethylene oligomerization

Jiahao Gao,[a] Yaling Fang,[b] Yanping Ma,[a] Liqun Jin,*[,b] Yizhou Wang,[a] Xinquan Hu,[b] Wenjuan Zhang,[c] *and* Wen-Hua Sun *[,a]

[a] *Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing,100190, China;*

[b] *State Key Laboratory of Green-Chemical Synthesis and Conversion Technology, the College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310032, China*

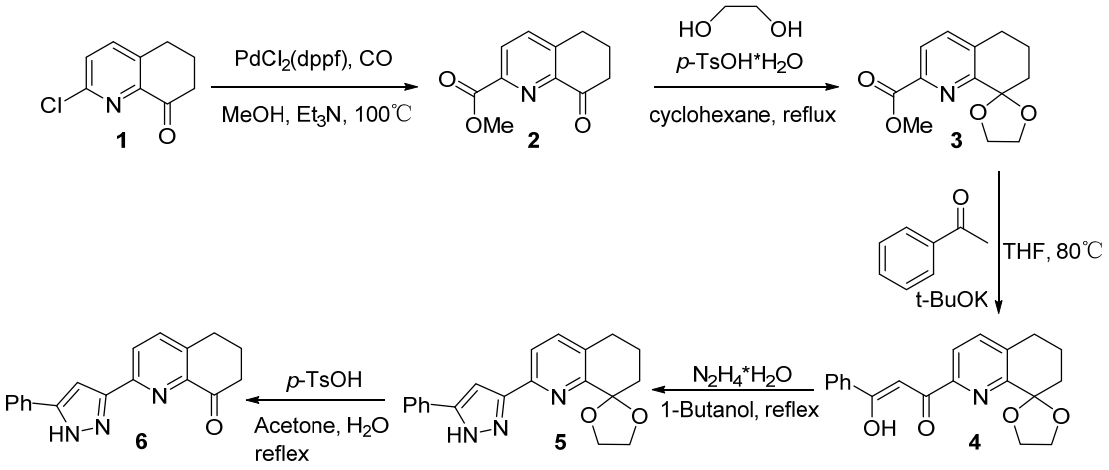
[c] *Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China*

Correspondence: liqunjin@zjut.edu.cn (L.J.); whsun@iccas.ac.cn (W.-H.S.); Tel.: +86-10-6255-7955 (W.-H.S.)

Table of Contents

1.	The additional experimental procedures of synthesizing 2-(5-phenyl-1H-pyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinoline (**6**)	S2
2.	The additional ethylene oligomerization results	S3
3.	The prepared chart of influencing factors for oligomerization result	S3
4.	The selected $^{1}H/^{13}C$ nuclear magnetic resonance spectrum of the compound	S7
5.	The FT-IR spectra of **Fe1**-**Fe6**	S10
6.	X-ray crystallographic studies	S13
7.	The selected GC spectrum by using **Fe4/MAO**	S14
8	Typical structures of methylaluminoxane (MAO)	S14
9	Possible reaction scheme of the alkylation and ion pair formation of iron complex and MAO	S14

1. The additional experimental procedures of systhesizing 2-(5-phenyl-1H-pyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinoline (6).



Scheme S1. Template synthetic route to 2-(5-phenyl-1H-pyrazol-3-yl)-5,6,7-dihydroquinolin-8-one.

Systhesis of 1-(6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolan]-2-yl)-3-hydroxy-3-phenylprop-2-en-1-one (4). Step 1: A 1 L autoclave was charged sequentially with 2-chlorotetrahydroquinolin-8-one (72.6 g, 0.4 mol), $PdCl_2$(dppf) (0.9 g, 0.01 mol), Et_3N (81 g, 0.8 mol), and 400 mL of methanol. After purged with N_2 for 5 min, the autoclave was then purged with CO and pressurized to 0.8 MPa. The autoclave was placed into oil bath at 100°C for 6 h. Then, the reaction mixture was cooled to room temperature, concentrated under reduced pressure, and purified by column chromatography (petroleum ether:ethyl acetate = 1:1) to afford **2** as a pale yellow solid (74.6 g, 91% yield).

Step 2: A 500 mL four-necked flask equipped with a Dean-Stark trap was charged with methyl 8-oxo-5,6,7,8-tetrahydroquinoline-2-carboxylate (18.45 g, 0.09 mol), *p*-toluenesulfonic acid (1.55 g, 0.009 mol), and cyclohexane. Upon reflux, ethylene glycol (6.70 g, 0.11 mol) was added dropwise over 10 min. After 5 h for reflux, the mixture was allowed to room temperature. The upper cyclohexane phase was separated and the lower oil phase was collected. After purified by column chromatography (petroleum ether:ethyl acetate = 10:1), **3** was obtained as a white solid (11.2 g, 90% yield).

Step 3: A 100 mL two-necked flask under N_2 was charged with *t*-BuOK (2.69 g, 0.024 mol), acetophenone (2.88 g, 0.024 mol), and THF (40 mL). A solution of methyl 6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolane]-2-carboxylate (**3**) (4.98 g, 0.02 mol) in THF was added dropwise. The mixture was stirred at 80 °C for 3 h, then quenched with water. Extraction with DCM (3 × 10 mL), drying over Mg_2SO_4, and concentration gave a crude orange solid. Purification by column chromatography (petroleum ether:ethyl acetate = 10:1) afforded **4** as a yellow solid (5.25 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.93(m, 3H), 7.64-7.40 (m, 3H), 4.61 (t, J = 6.8 Hz, 2H), 4.26 (t, J = 6.8 Hz, 2H), 2.87 (t, J = 6.2 Hz, 2H), 2.21-2.14 (m, 2H), 2.15-2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0, 184.7, 156.4, 150.4, 137.9, 136.5, 135.4, 132.4, 128.7, 127.1, 121.4, 106.0, 93.3, 66.4, 35.3, 28.9, 20.6.

Synthesis of 2-(5-Phenyl-1H-pyrazol-3-yl)-6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolane] (5) To a 50 mL round-bottom flask were added compound **4**, hydrazine hydrate (2.0 g, 0.04 mol), and 20 mL of *n*-butanol. The reaction mixture was refluxed for 3 h, then cooled to room temperature. The solvent was removed under vacuum to afford the crude product. Purification by column chromatography (petroleum ether:ethyl acetate = 10:1) yielded the desired compound **5** as a pale yellow solid (3.85 g, 86%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.87 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.21 (s, 1H), 4.53 (t, J = 6.4 Hz, 2H), 4.07 (t, J = 6.5 Hz, 2H), 2.77 (t, J = 6.4 Hz, 2H), 2.02-1.98 (m, 2H), 1.90-1.86 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.7, 138.1, 131.8, 129.3, 128.3, 125.7, 125.6, 119.4, 105.8, 101.1, 66.2, 35.8, 28.3, 20.9.

Synthesis of 2-(5-Phenyl-1H-pyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinoline (6) To a 100 mL round-bottom flask equipped with magnetic stirring were sequentially added 2-(5-phenyl-1H-pyrazol-3-yl)-6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolane] (**5**) (3.33 g, 0.01 mol), *p*-toluenesulfonic acid (0.344 g, 0.002 mol), 20 mL of acetone, and 20 mL of water. The reaction mixture was refluxed for 3 h. After concentration, the residue was extracted with 20 mL of DCM. Column chromatography purification (petroleum ether:ethyl acetate = 10:1) afforded the desired compound **6** as a pale yellow solid (2.39 g, 83%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (d, J = 7.5 Hz, 1H), 7.85-7.94 (m, 3H), 7.47-7.43 (m, 2H), 7.35 (d, J = 12.0 Hz, 1H), 7.24(s, 1H), 3.01 (t, J = 6.1 Hz, 2H), 2.73 (s, 2H), 2.11-2.06 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 196.6, 152.2, 147.7, 144.0, 143.2, 140.7, 139.6, 139.0, 129.5, 128.7, 128.0, 125.6, 123.3, 101.3, 28.7, 22.7.

2. The additional ethylene oligomerization results.

Table S1. Ethylene oligomerization by **Fe4** with different co-catalysts[a].

Entry	Cat	Co-catalyst	Oligomers [b] (wt.%)					Activity[c]	Wax[d]
			C4/ΣC	C6/ΣC	C8/ΣC	≥C10/ΣC	α-Olefin (%)		
1	**Fe4**	MAO	57.0	33.5	6.3	3.2	>90	2.70	-
2	**Fe4**	MMAO	97.2	2.7	0.1	-	>95	6.78	1.19
3[e]	-	MMAO	100	-	-	-	>99	0.09	-
4[e]	-	MAO	-	-	-	-	-	No	-
5[f]	**Fe4**	-	-	-	-	-	-	No	-

[a] Conditions: 2.0 μmol **Fe4**, Al:Fe = 1000, 100 mL toluene, and 10 atm ethylene, 20°C, 30 min. [b] Determined by GC. ΣC denotes the total amount of oligomers. [c] Activity for oligomer 10^5 g mol^{-1} (Fe) h^{-1}, [d] Activity for polyethylene wax: 10^5 g (PE) mol^{-1} (Fe) h^{-1}, [e] Oligomerization without catalyst, 2 mmol MAO. [f] Oligomerization without co-catalyst, 2.0 μmol **Fe4**.

3. The prepared chart of influencing factors for oligomerization reaction.

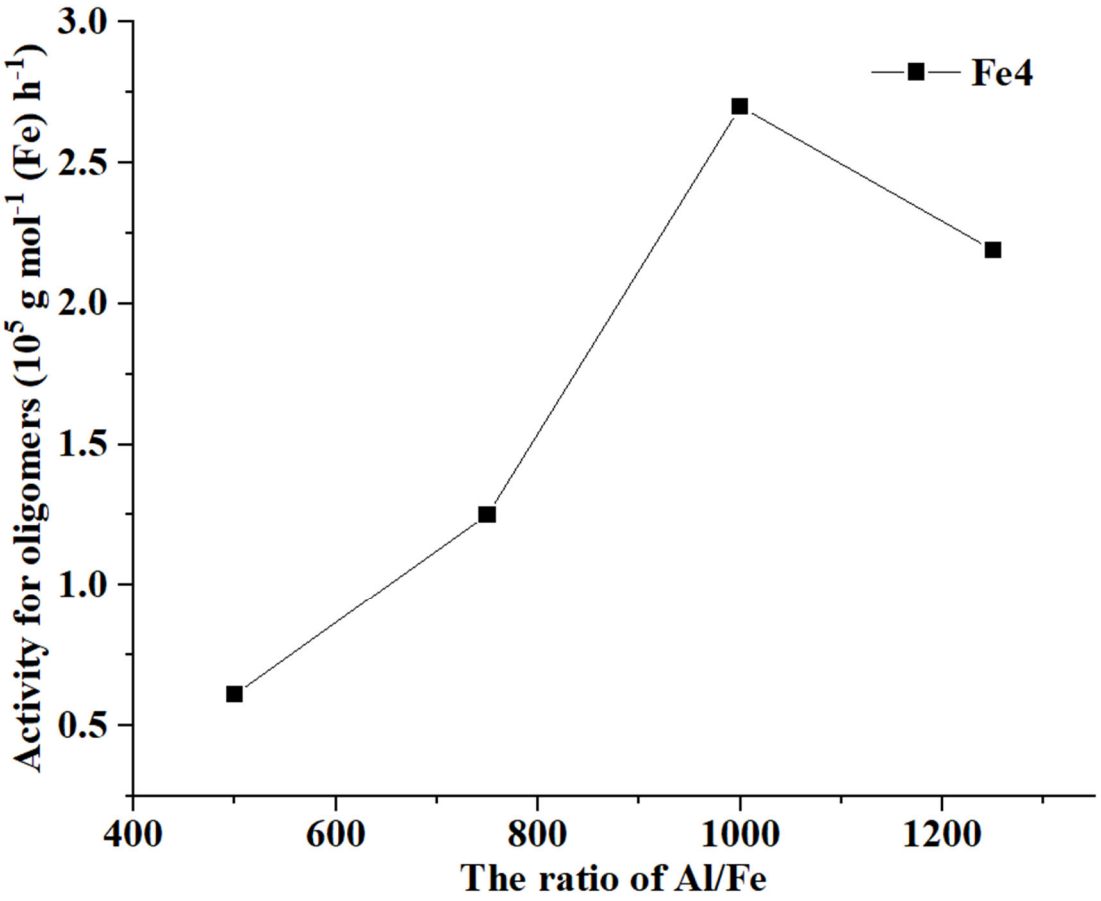


Figure S1. The influence of the proportion of co-catalysts on catalytic activity by using **Fe4**/MAO as catalyst (entry 1-4, **Table 3**).

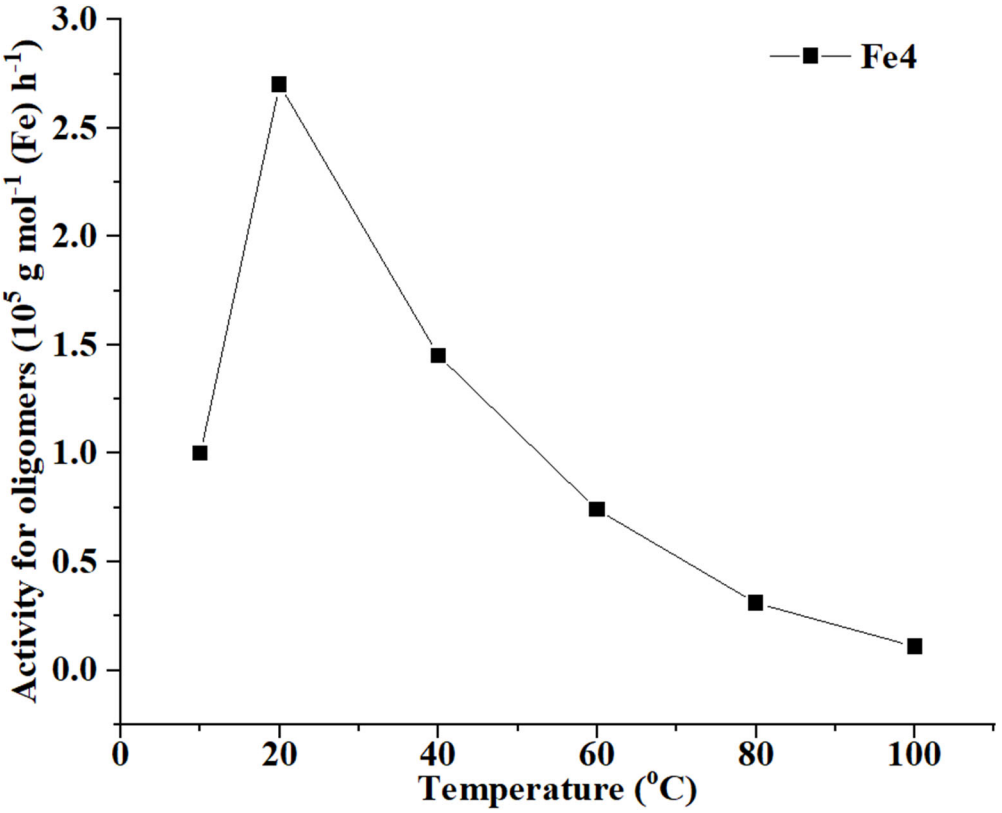


Figure S2. The influence of temperature on catalytic activity by using **Fe4**/MAO as catalyst (entry 2, 5-9, **Table 3**).

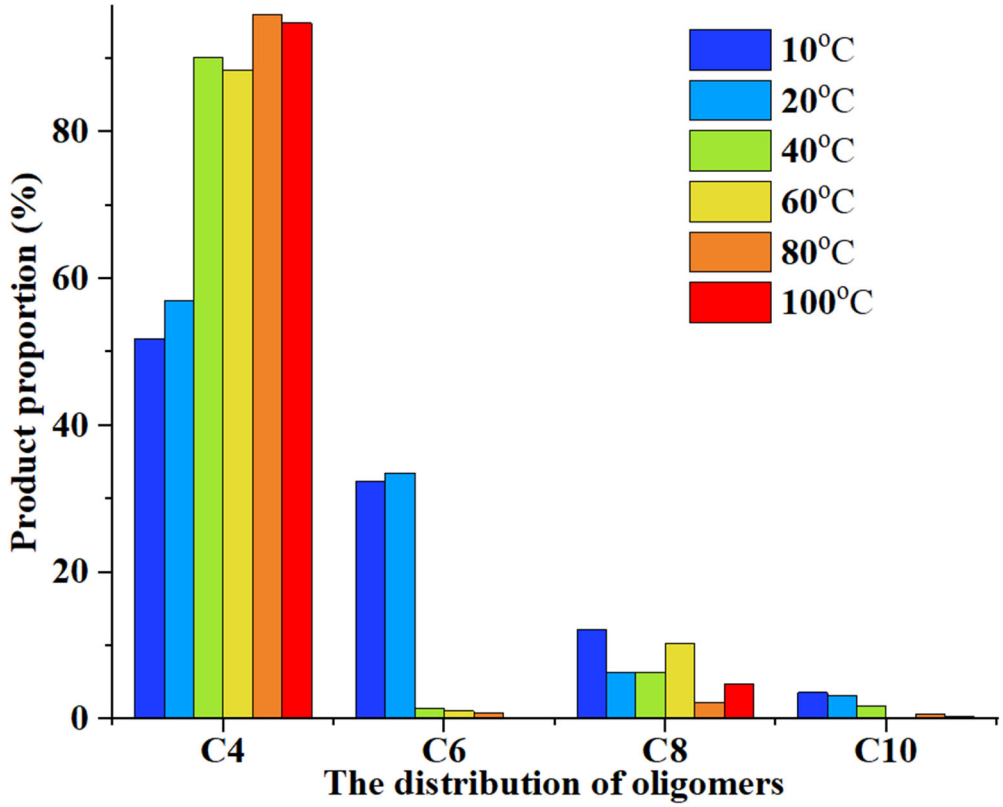


Figure S3. The influence of temperature on distribution of oligomer products by using **Fe4**/MAO as catalyst (entry 2, 5-9, **Table 3**).

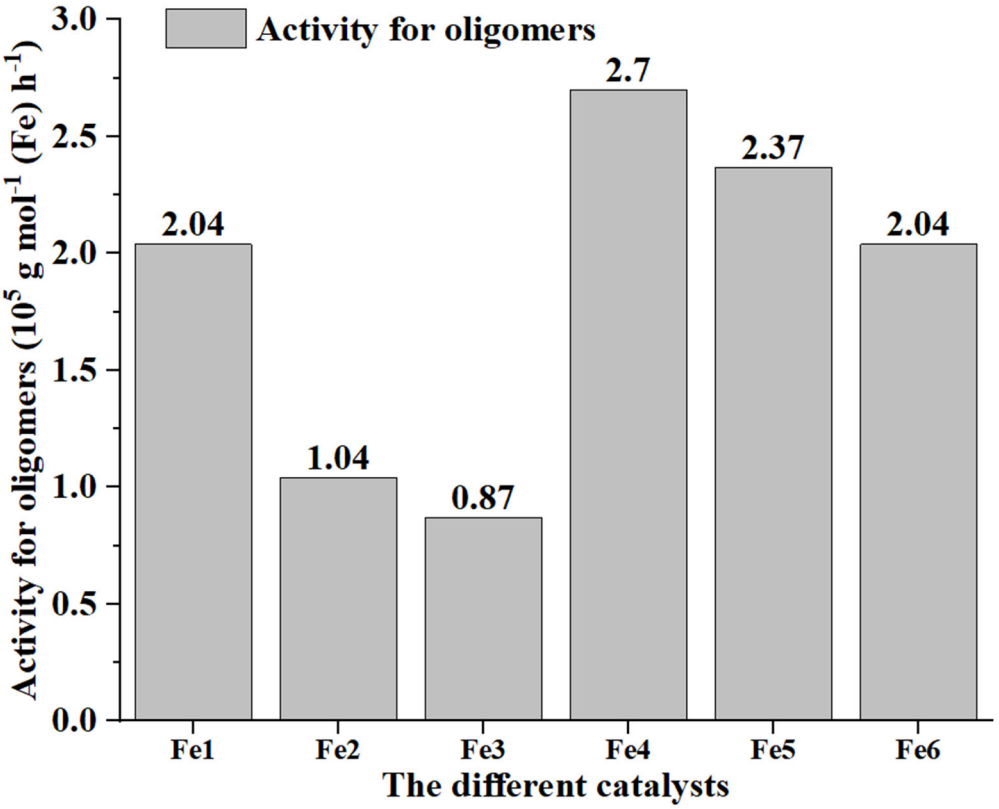


Figure S4. The influence of different catalysts on catalytic activity (entry 2, 13-17, **Table 3**).

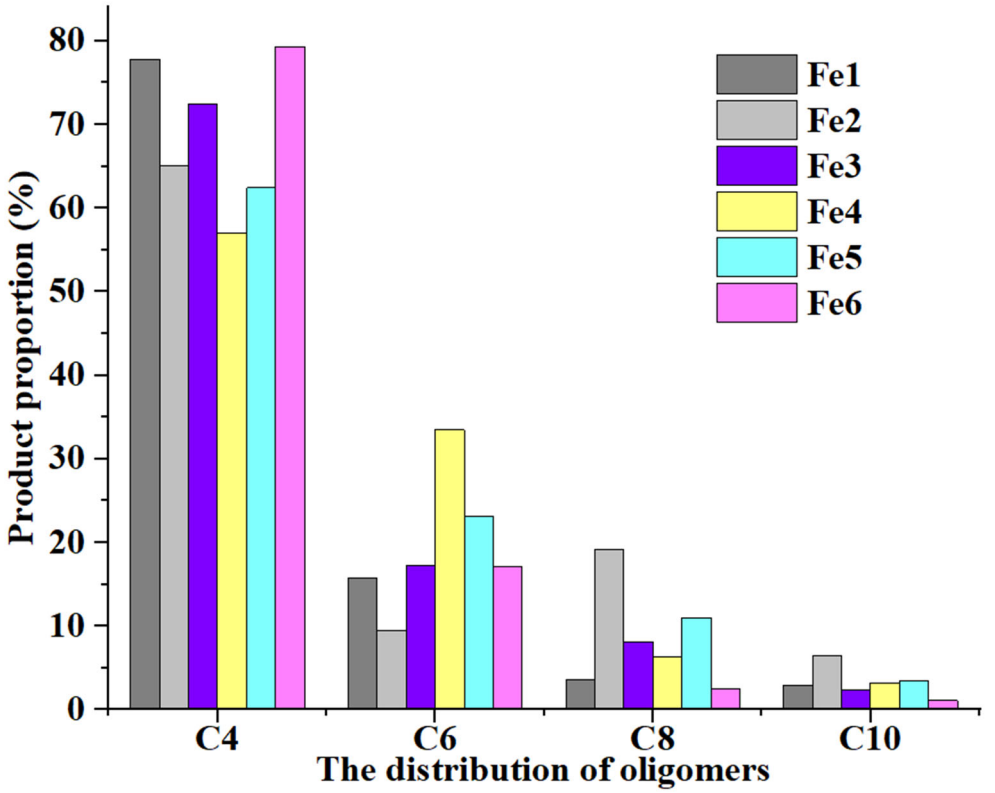


Figure S5. The influence of the different catalysts on distribution of oligomer products (entry 2, 13-17, **Table 3**).

4. The selected $^{1}H/^{13}C$ nuclear magnetic resonance spectrums of the compound.

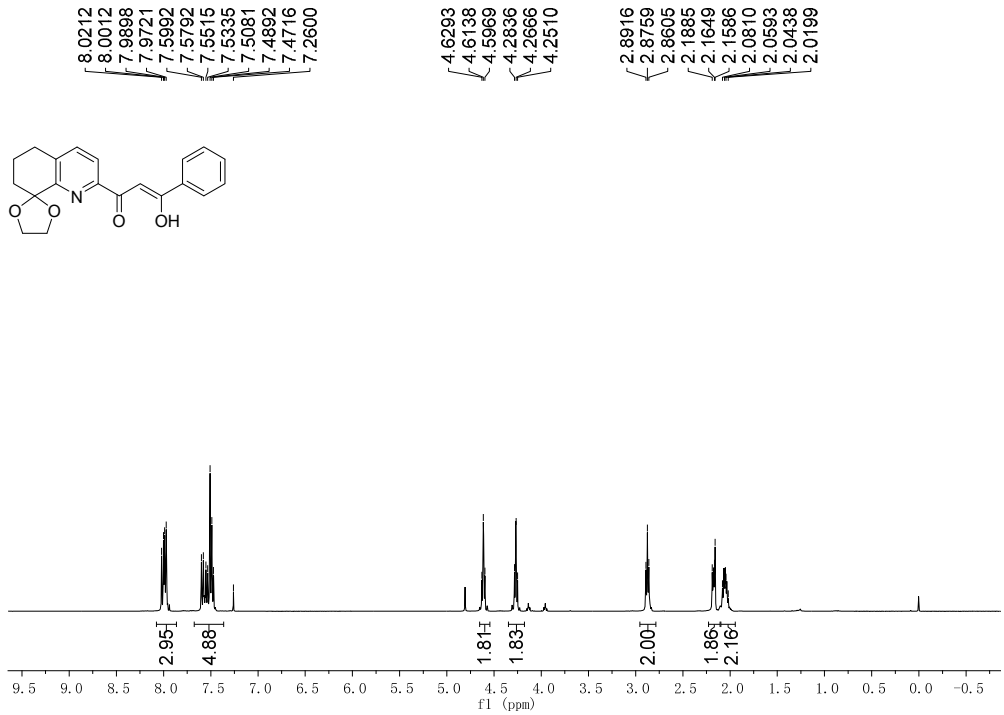


Figure S6. The ^{1}H NMR spectrum of 1-(6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolan]-2-yl)-3-hydroxy-3-phenylprop-2-en-1-one (**4**).

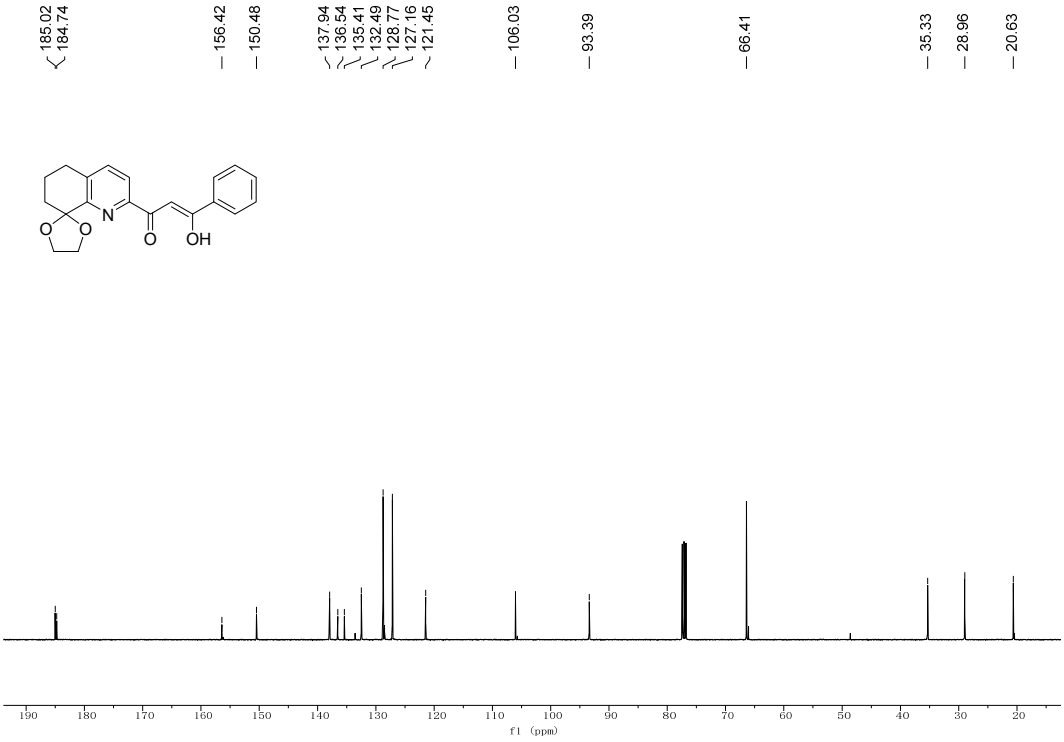


Figure S7. The ^{13}C NMR spectrum of 1-(6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolan]-2-yl)-3-hydroxy-3-phenylprop-2-en-1-one (**4**).

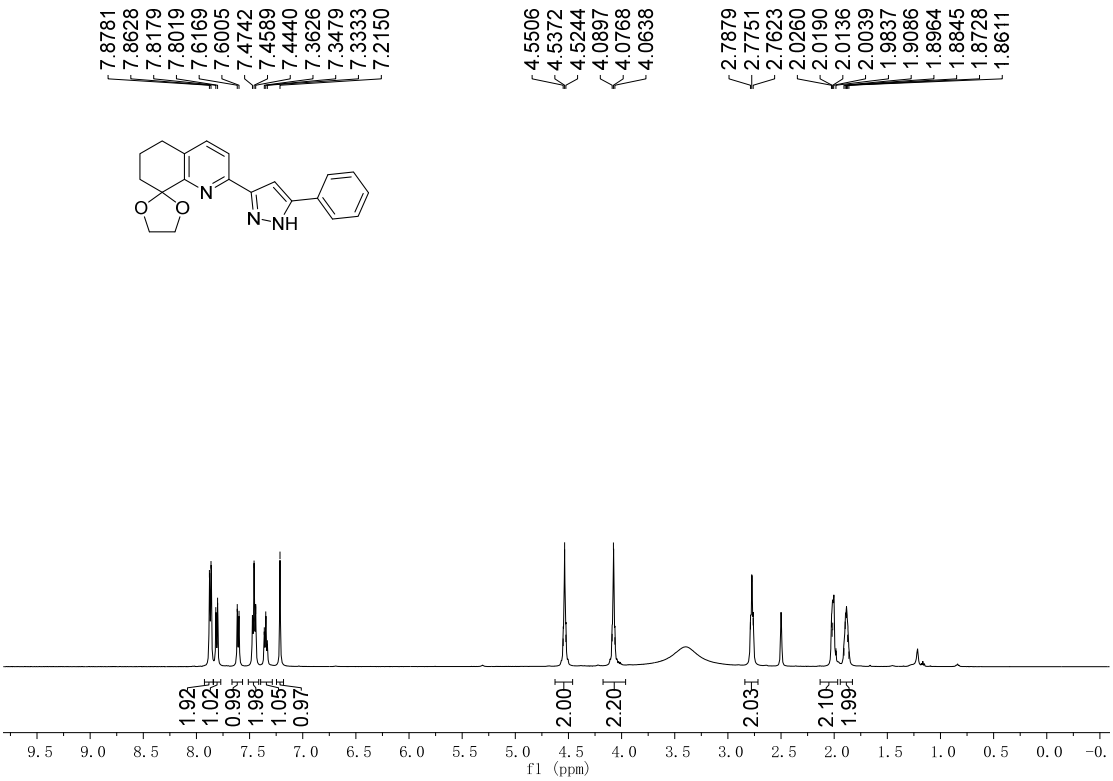


Figure S8. The ^{1}H NMR spectrum of 2-(5-phenyl-1H-pyrazol-3-yl)-6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolane] (**5**).

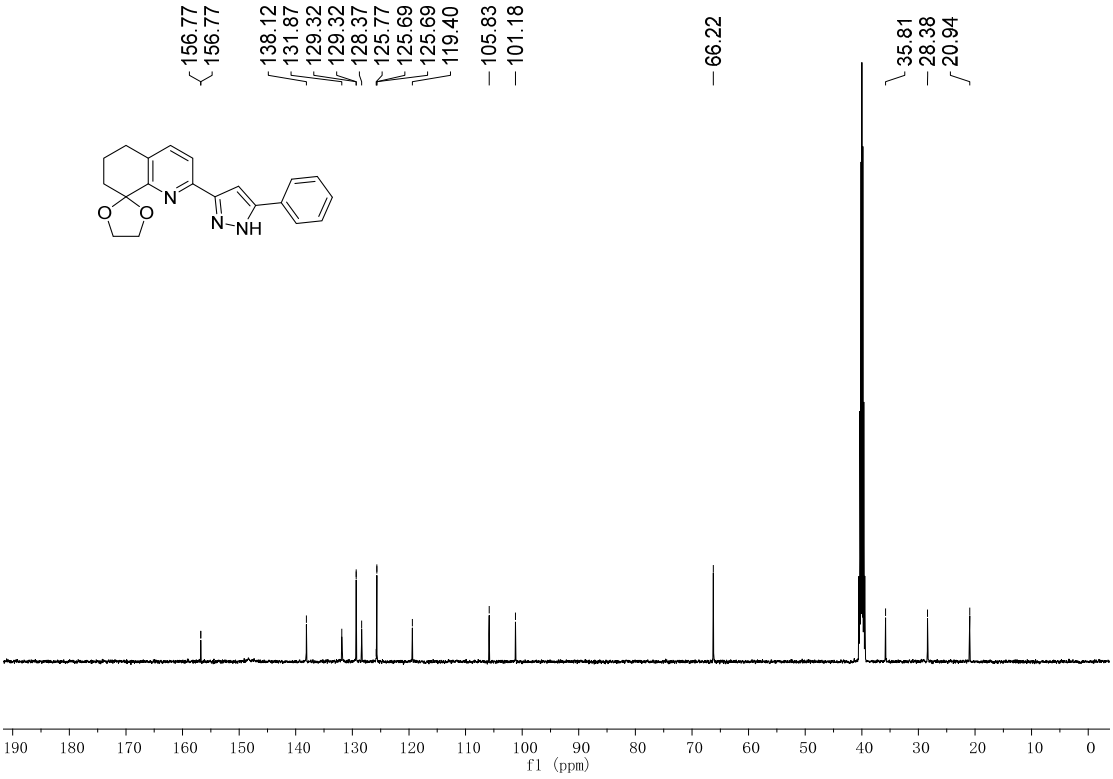


Figure S9. The ^{13}C NMR spectrum of 2-(5-phenyl-1H-pyrazol-3-yl)-6,7-dihydro-5H-spiro[quinoline-8,2'-[1,3]dioxolane] (**5**).

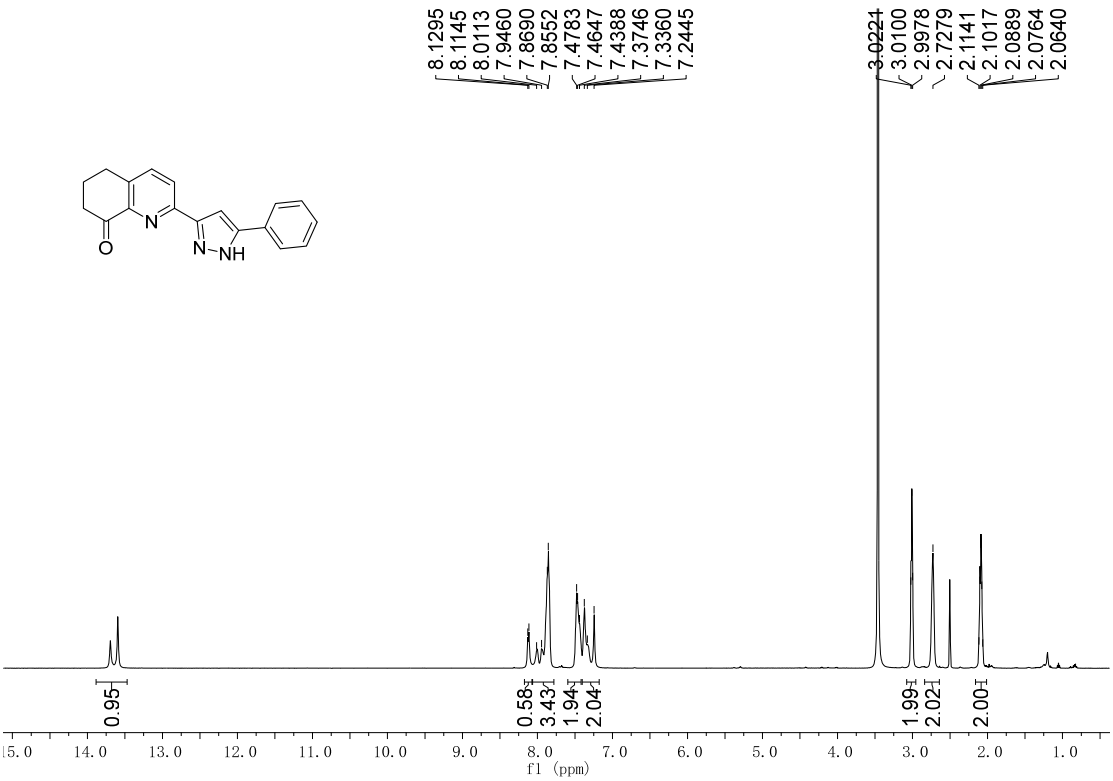


Figure S10. The ^{1}H NMR spectrum of 2-(5-phenyl-1H-pyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinoline (**6**).

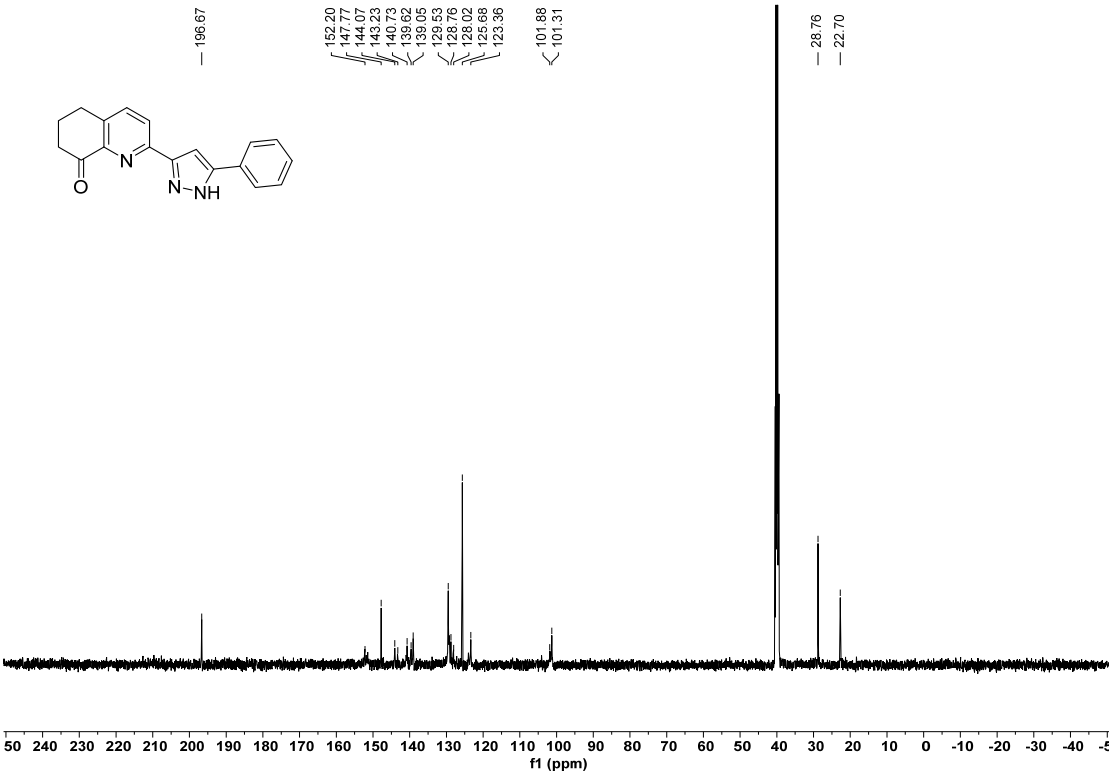


Figure S11. The ^{13}C NMR spectrum of 2-(5-phenyl-1H-pyrazol-3-yl)-8-arylimino-5,6,7-trihydroquinoline (**6**).

5. The FT-IR spectras of Fe1-Fe6.



Figure S12. The FT-IR spectra of **Fe1**.

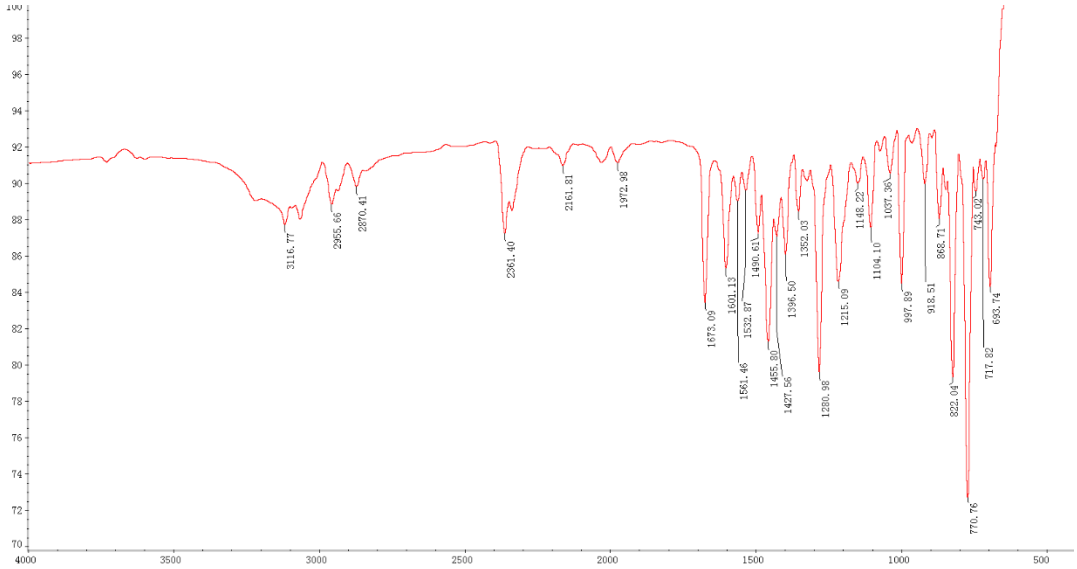


Figure S13. The FT-IR spectra of **Fe2**.

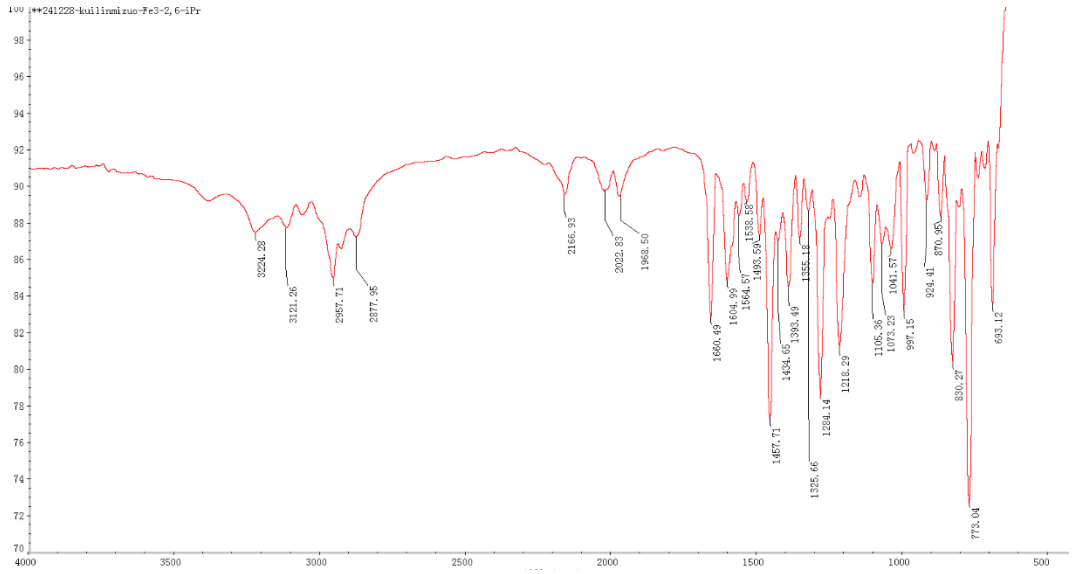


Figure S14. The FT-IR spectra of **Fe3**.

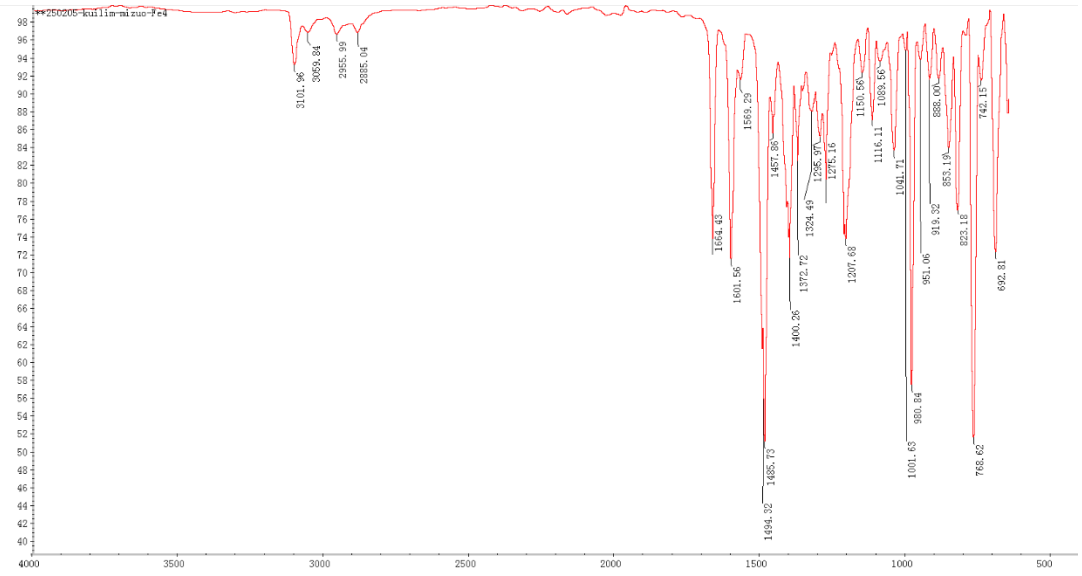


Figure S15. The FT-IR spectra of **Fe4**.

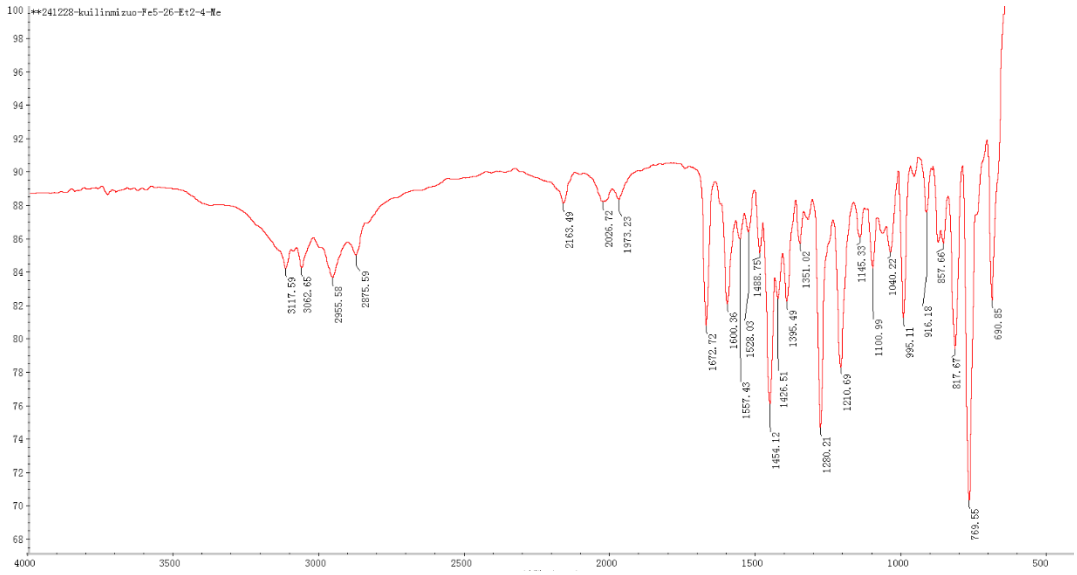


Figure S16. The FT-IR spectra of **Fe5**.

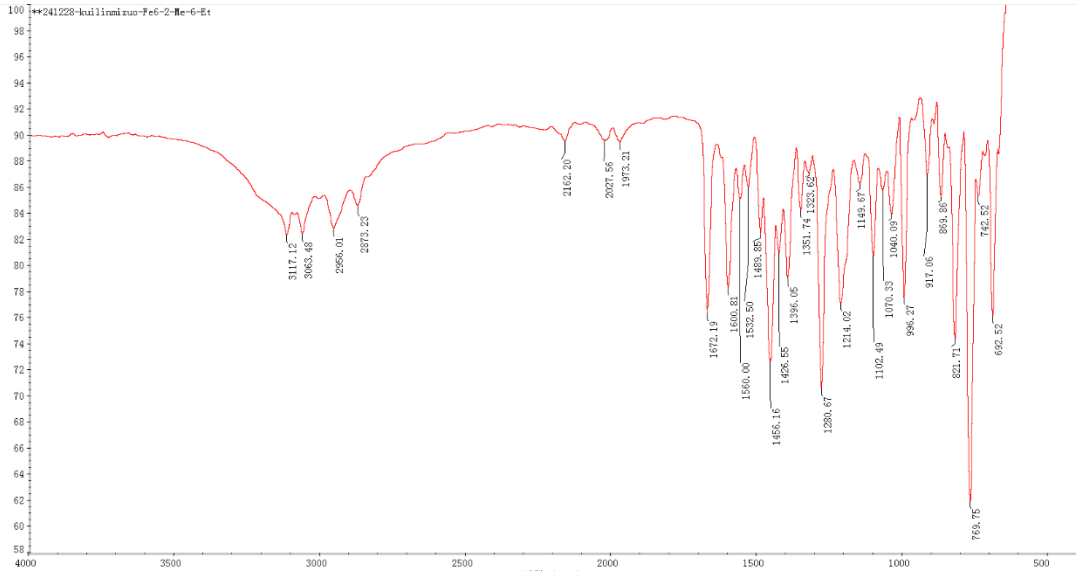


Figure S17. The FT-IR spectra of **Fe6**.

6. X-ray crystallographic studies

Table S2. Crystal Data and Structure Refinement Details for **Fe4**.

CCDC Number	2469522
Catalyst	**Fe4**·H_2O
Empirical formula	$C_{54}H_{54}Cl_4Fe_2N_8O$
Formula weight	1084.54
Temperature/K	170.1(4)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.28220(10)
b/Å	14.5415(2)
c/Å	19.1952(3)
α/°	90
β/°	97.9490(10)
γ/°	90
Volume/Å^3	2842.46(7)
Z	4
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	6.159
F(000)	1124.0
Crystal size/mm^3	0.25 × 0.18 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.654 to 155.022
Index ranges	$-13 \le h \le 9$, $-18 \le k \le 18$, $-24 \le l \le 24$
Reflections collected	19700
Independent reflections	5777 [R_{int} = 0.0331, R_{sigma} = 0.0300]
Data/restraints/parameters	5777/3/316
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1244
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1280
Largest diff. peak/hole / e Å^{-3}	0.80/-0.45

7. The selected GC chromatograms by using Fe4/MAO.

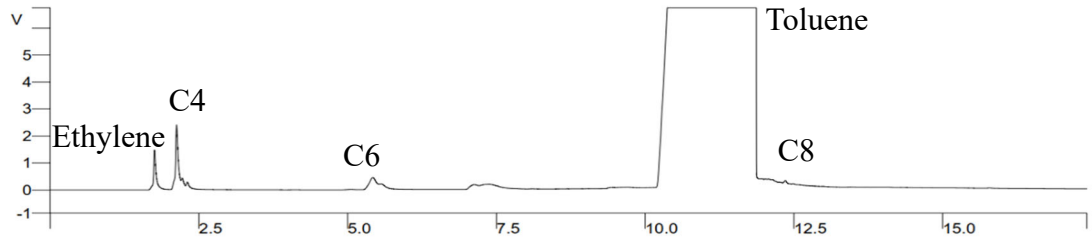


Figure S18. The examples of GC chromatograms by **Fe4/MAO** (entry 2, **Table 3**).

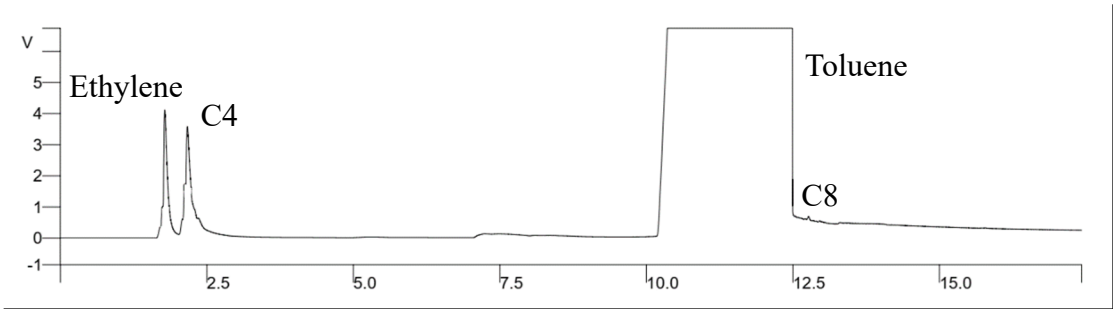
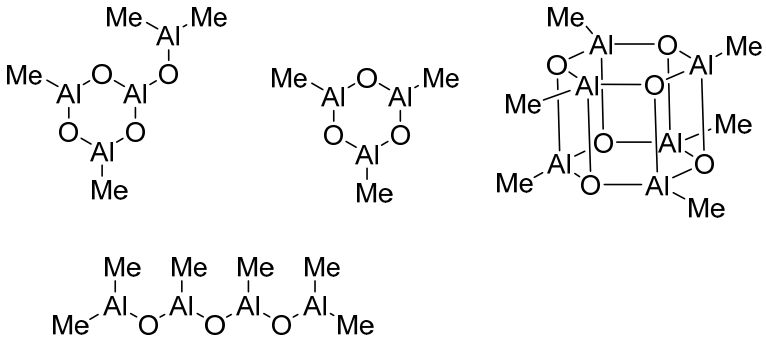


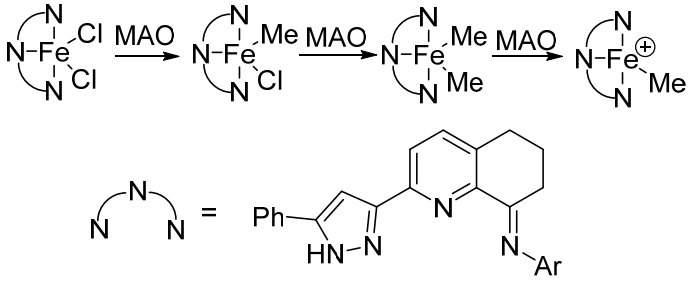
Figure S19. The examples of GC chromatograms by **Fe4/MAO** (entry 8, **Table 3**).

8. Typical structures of methylaluminoxane (MAO)



Scheme S2. Typical structures of methylaluminoxane (MAO).

9. Possible reaction scheme of the alkylation and ion pair formation of iron complex and MAO



Scheme S3. Possible reaction scheme of the alkylation and ion pair formation of iron complex and MAO