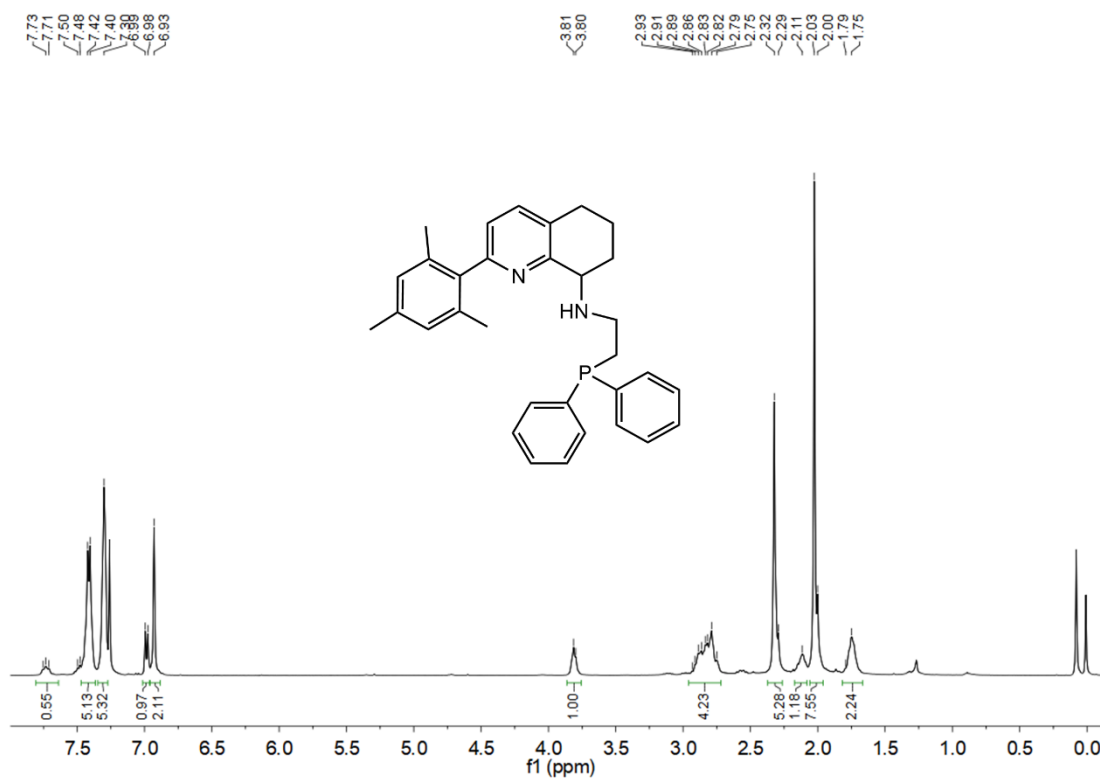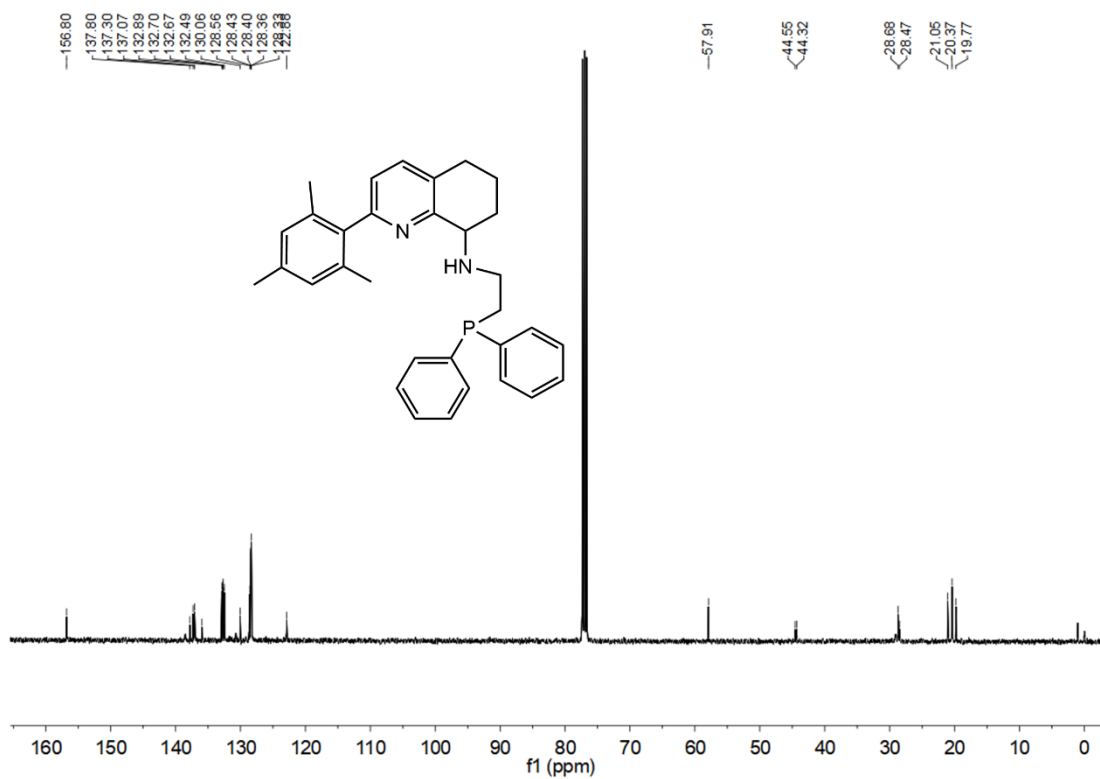Supporting information

of

N-(2-(Diphenylphosphino)ethyl)-2-alkyl-5,6,7,8-tetrahydroquinolin-8-amines iron(II) complexes: Structural diversity and the ring opening polymerization of ε-caprolactone

Yun Wang,[a,b,c] Wenjuan Zhang,*[a,b] Xing Wang,[b,c] Weiwei Zuo,*[a]   Xiaopan Xue,[b]

Yanping Ma,[a] Wen-Hua Sun*[c]

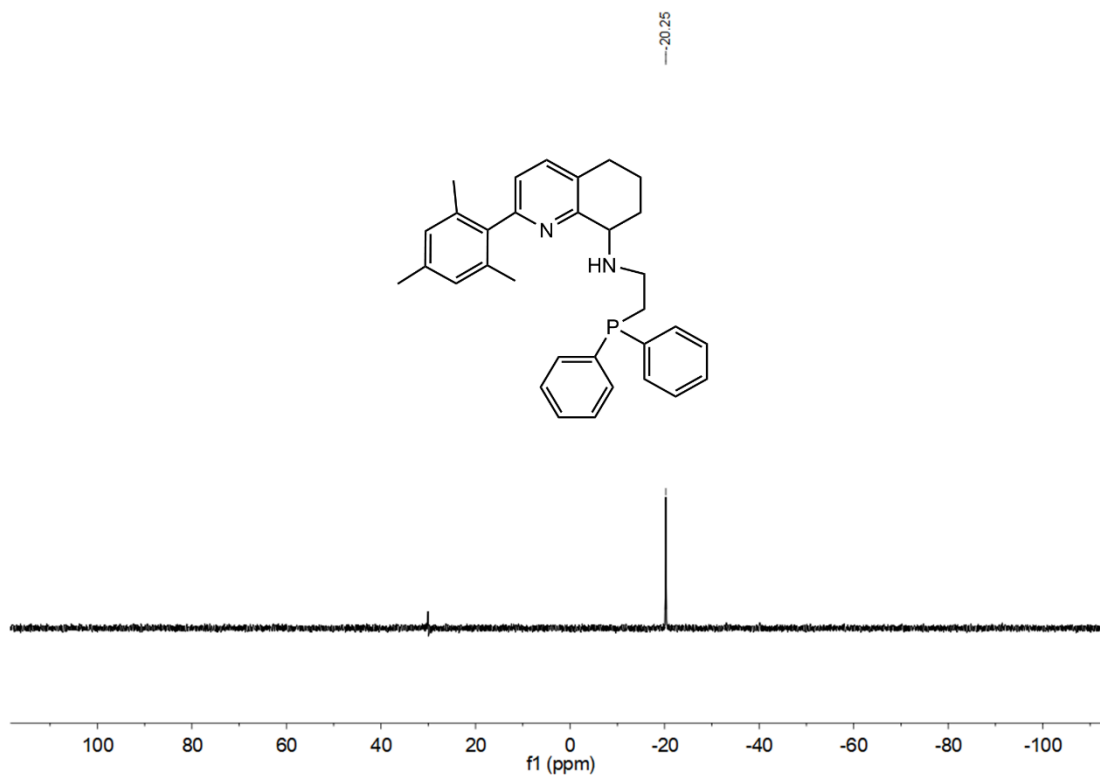**Fig. S1** ^{1}H NMR (CDCl$_3$, 25°C) spectrum of **L5**

Fig. S2 ^{13}C NMR (CDCl$_3$, 25°C) spectrum of **L5**

Fig. S3 ^{31}P NMR (CDCl$_3$, 25°C) spectrum of **L5**
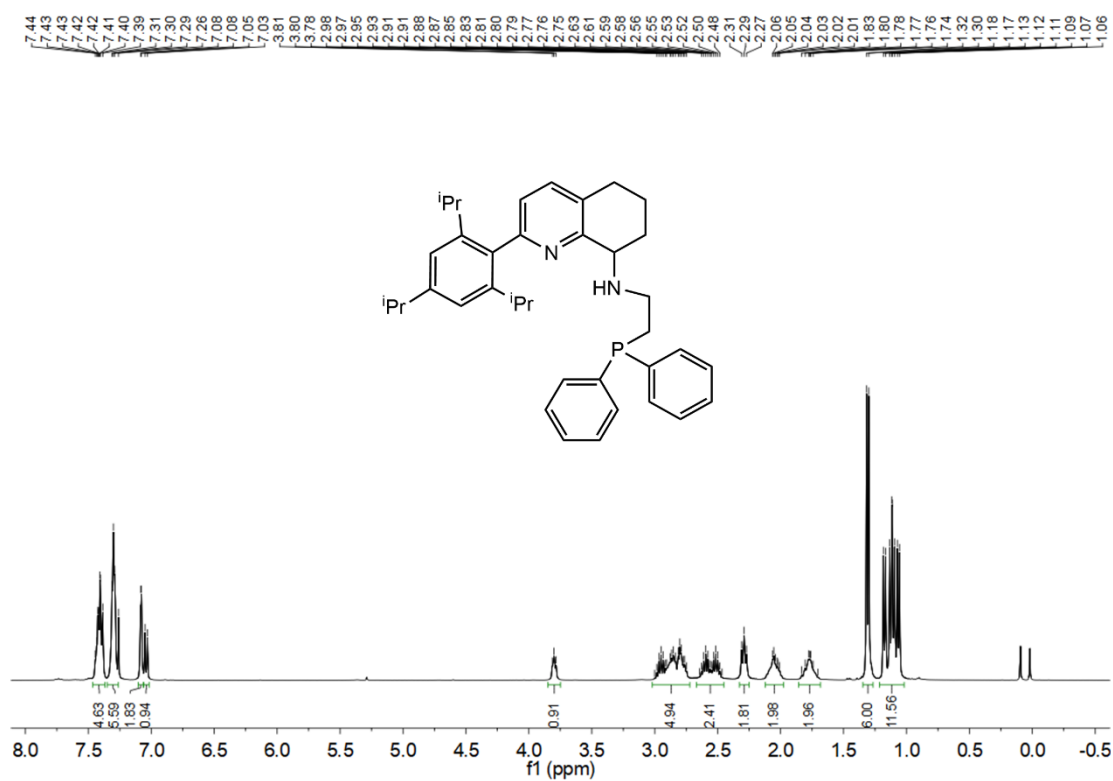
Fig. S4 ^{1}H NMR (CDCl$_3$, 25°C) spectrum of **L6**
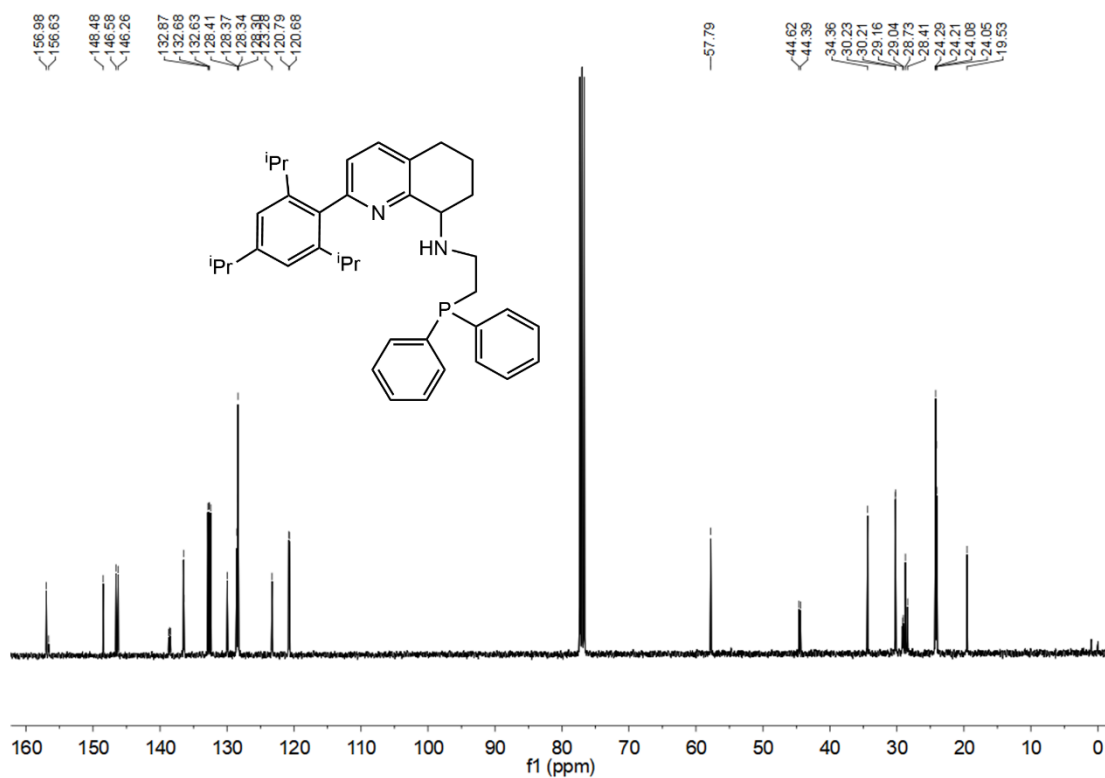
Fig. S5 ^{13}C NMR (CDCl$_3$, 25°C) spectrum of **L6**
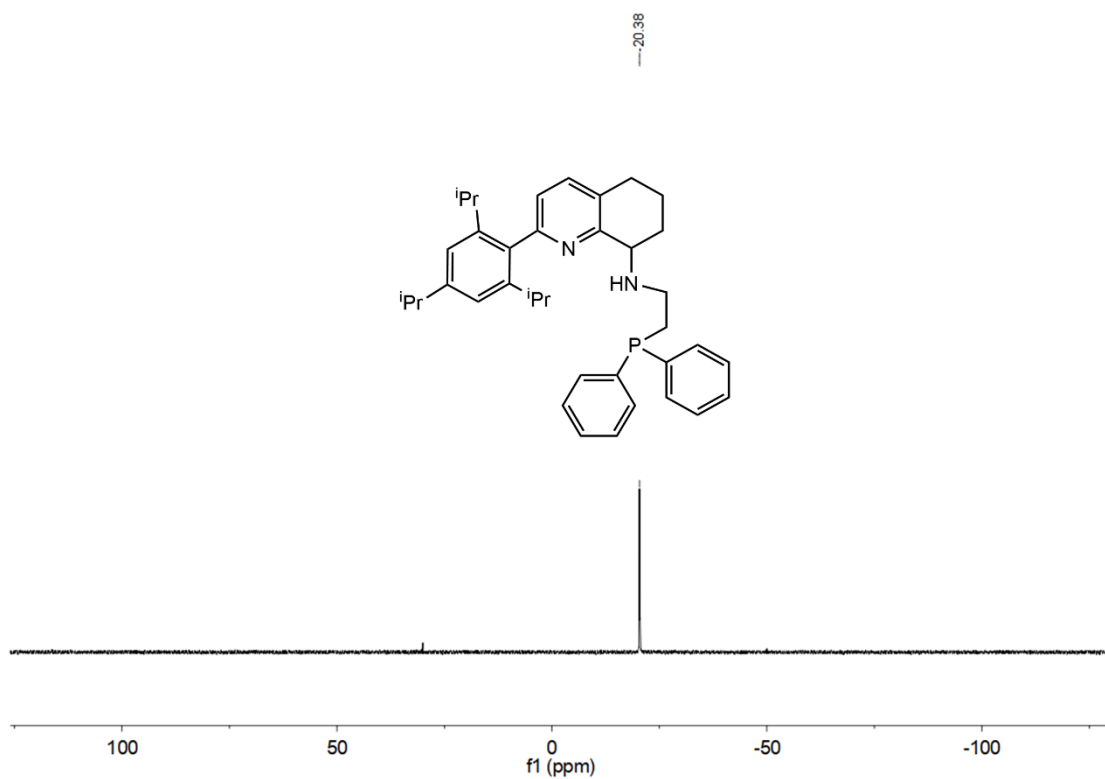
Fig. S6 ^{31}P NMR (CDCl$_3$, 25°C) spectrum of **L6**
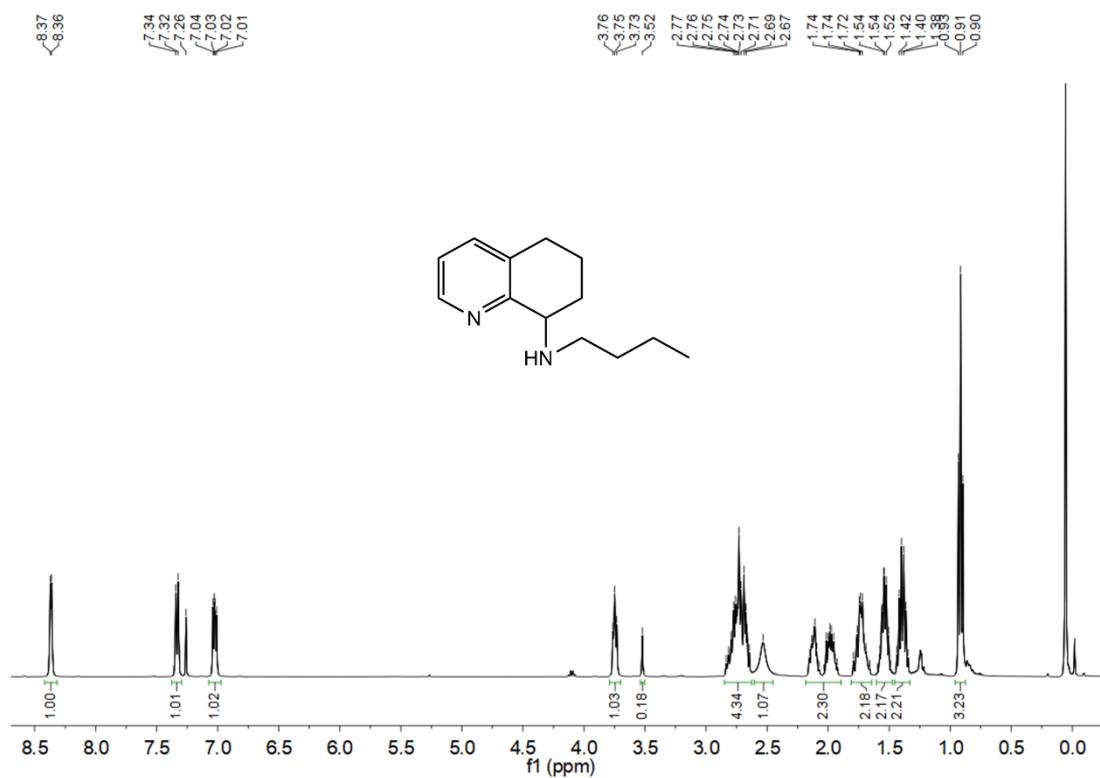
Fig. S7 ^{1}H NMR (CDCl$_3$, 25°C) spectrum of **L7**
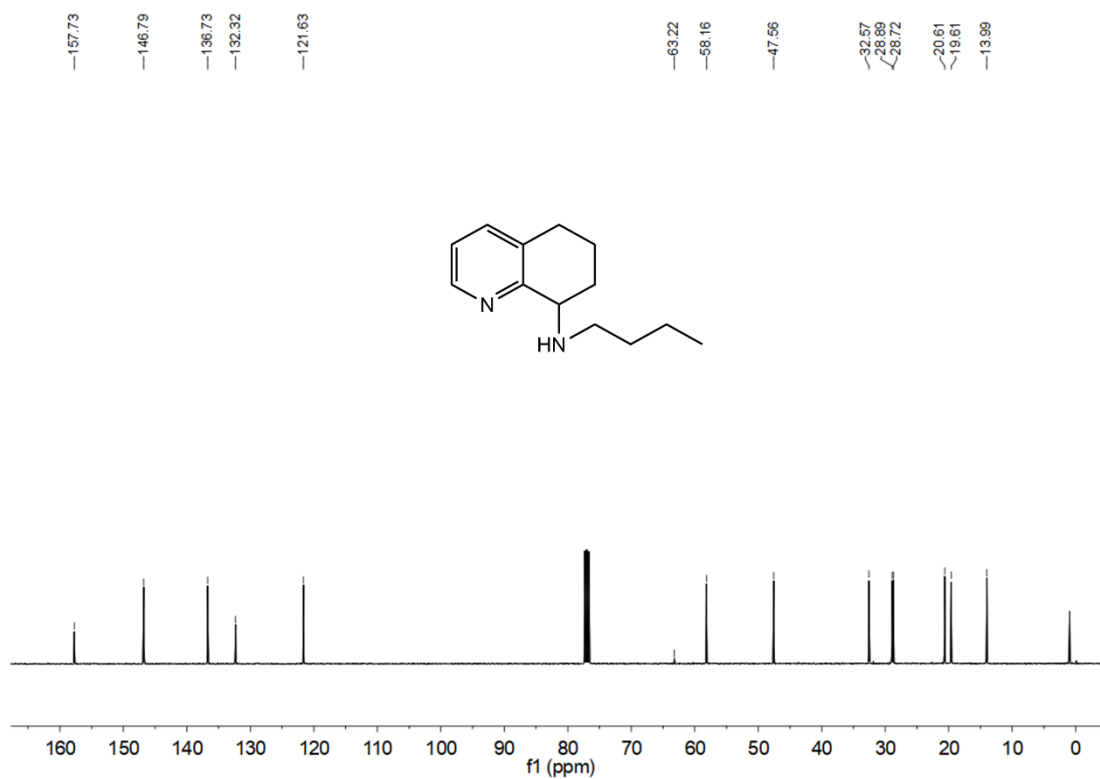
Fig. S8 ^{13}C NMR (CDCl$_3$, 25°C) spectrum of **L7**
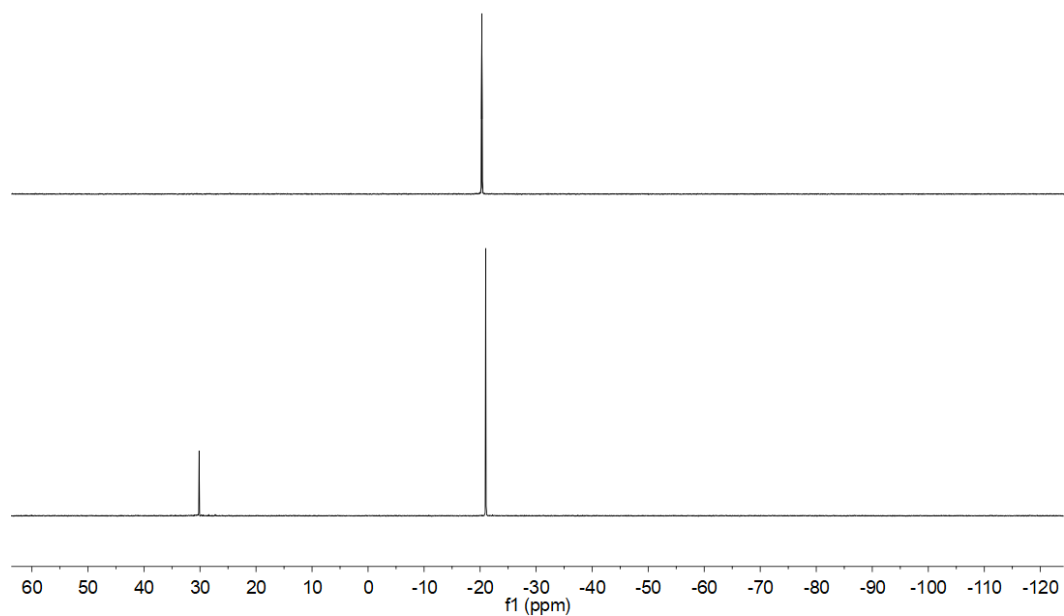
Fig. S9 The monitoring ^{31}P NMR spectra of **L4** in CDCl$_3$ (top) and **L4** in CDCl$_3$ (bottom, two weeks later)
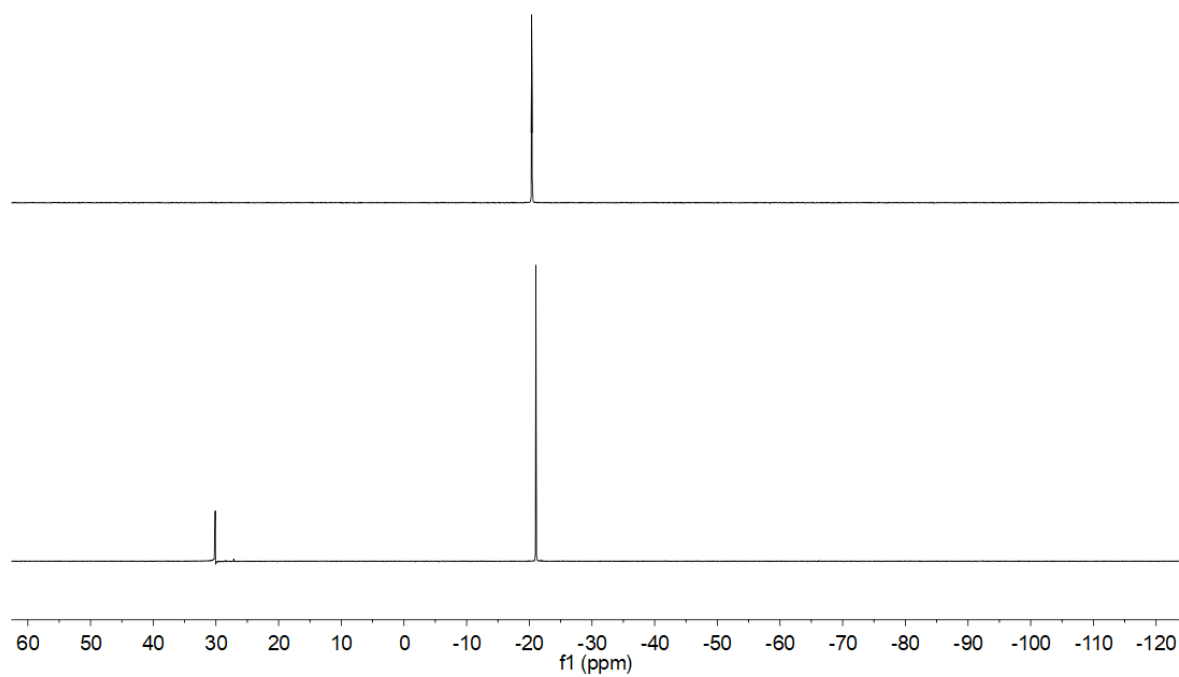
Fig. S10 The monitoring ^{31}P NMR spectra of **L1** in CDCl$_3$ (top) and **L1** in CDCl$_3$ (bottom, two weeks later)
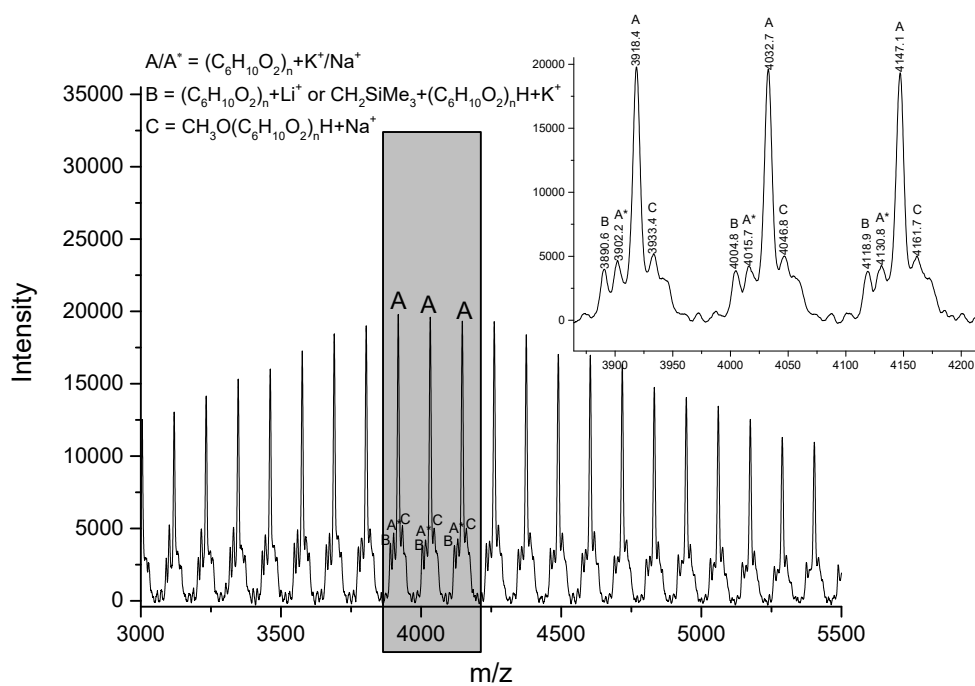
Fig. S11 MALDI-TOF mass spectrum of the PCL obtained using **Fe6** ([ε-CL]/[Fe] = 100:1, T = 30 °C, t = 10 min)
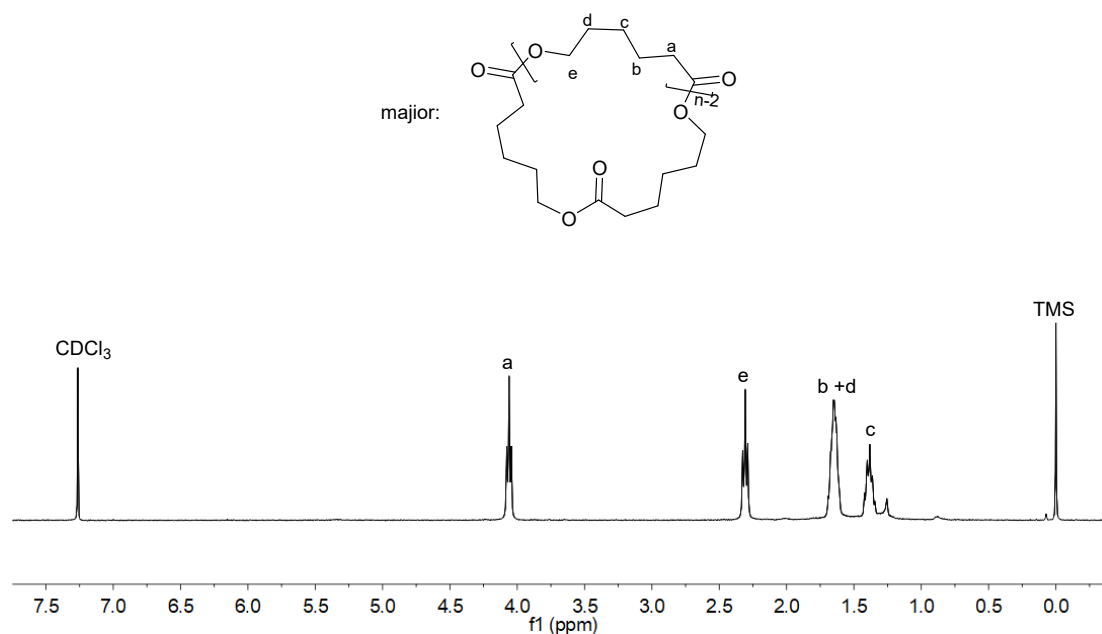
Fig. S12 ^{1}H NMR spectrum of the PCL obtained using **Fe6** ([ε-CL]/[Fe] = 100:1, T = 30 °C, t = 10 min)

A/A* = $CH_3O-(C_6H_{10}O_2)_nH+Na^+/K^+$

B = $(C_6H_{10}O_2)_n+K^+$ or $CH_3O-(C_6H_{10}O_2)_nH+Li^+$

C = $(C_6H_{10}O_2)_n+CH_2SiMe_3+K^++H$
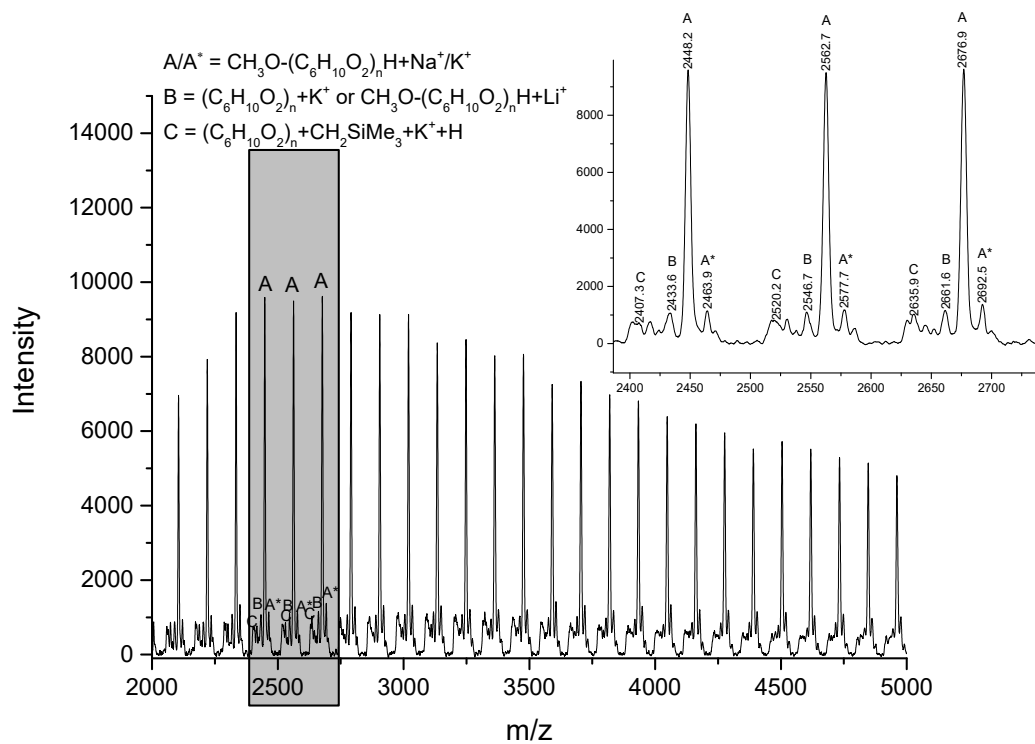
Fig. S13 MALDI-TOF mass spectrum of the PCL obtained using **Fe6** ($[\varepsilon$-CL]/[Fe] = 400:1, T = 30 °C, t = 10 min)
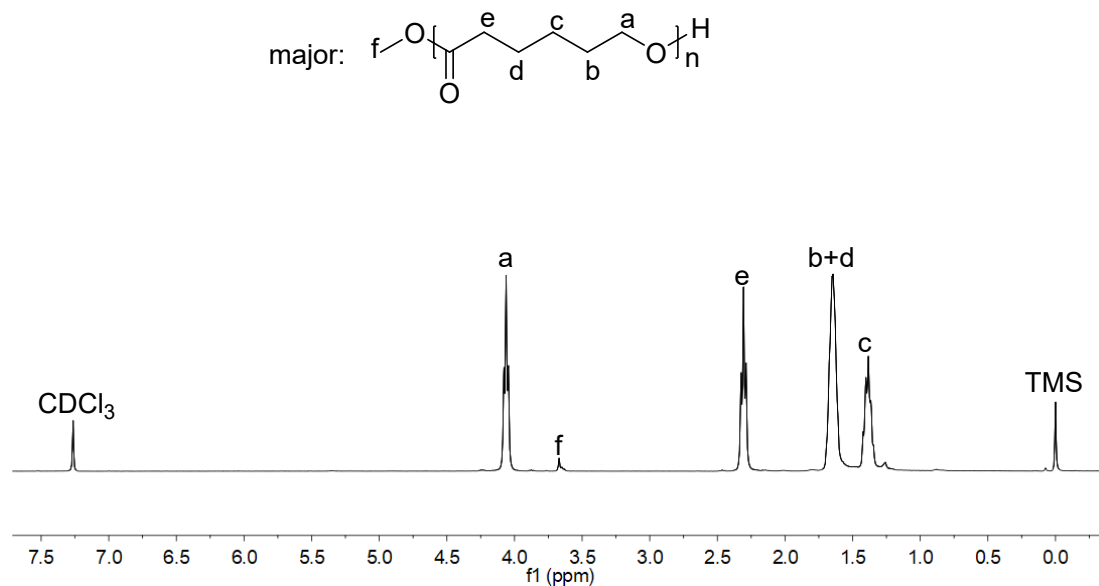
Fig. S14 ^{1}H NMR spectrum of the PCL obtained using **Fe6** ([ε-CL]/[Fe] = 400:1, T = 30 °C, t = 10 min
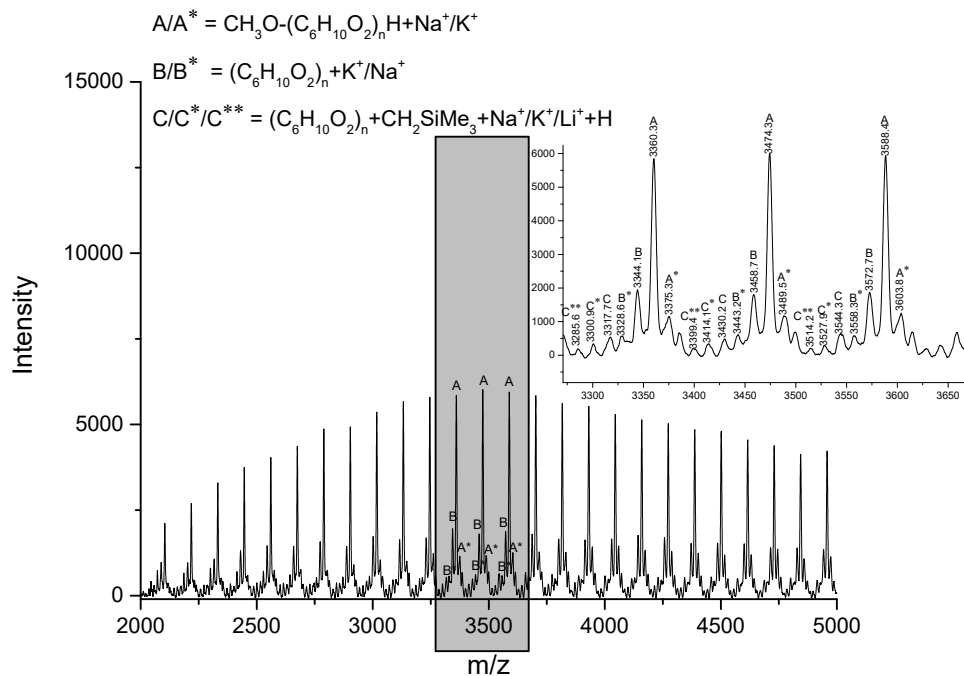
Fig. S15 MALDI-TOF mass spectrum of the PCL obtained using **Fe6** ([ε-CL]/[Fe] = 800:1, T = 30 °C, t = 10 min)
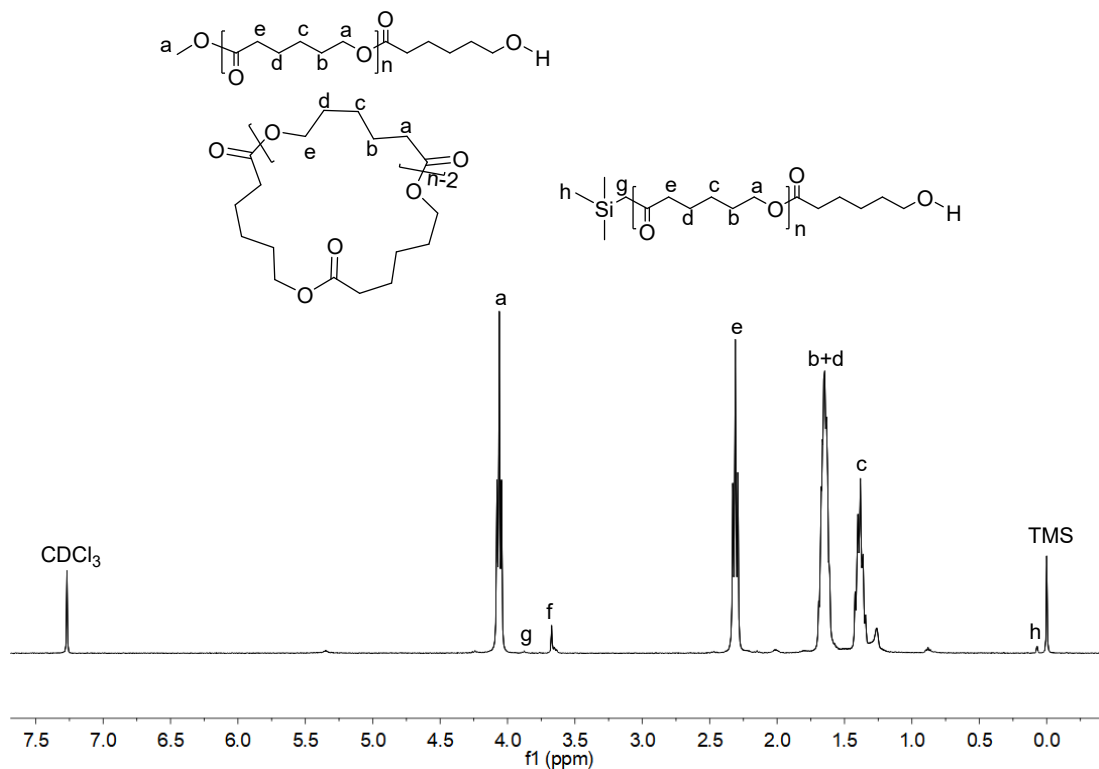
Fig. S16 ^{1}H NMR spectrum of the PCL obtained using **Fe6** ([ε-CL]/[Fe] = 800:1, T = 30 °C, t = 10 min)

Table S1 Crystal data and structure refinements for **Fe4'**

	Fe4'
empirical formula	$C_{23}H_{24}Cl_5Fe_{1.5}N_2OP$
formula weight	636.44
temperature/K	169.98(10)
crystal system	monoclinic
space group	$P2_1/n$
a/Å	12.0592(3)
b/Å	15.9546(4)
c/Å	13.9879(3)
α/°	90
β/°	94.627(2)
γ/°	90
volume/Å^3	2682.50(11)
Z	4
ρcalc/g cm^3	1.576
μ/mm^{-1}	11.901
F (000)	1292.0
crystal size/mm^3	0.2 × 0.12 × 0.1
radiation	CuKα (λ = 1.54184)

2θ range for data collection/°	8.422 to 154.838
index ranges	$-15 \le h \le 14$, $-19 \le k \le 20$, $-17 \le l \le 16$
reflections collected	22038
independent reflections	5463 [R_{int} = 0.0738, R_{sigma} = 0.0545]
data/restraints/parameters	5463/0/304
goodness-of-fit on F^2	1.043
final R indices [$I>=2\sigma$ (I)]	R_1 = 0.0537, wR_2 = 0.1424
final R indices [all data]	R_1 = 0.0636, wR_2 = 0.1502
largest diff. peak/hole/ e Å^{-3}	0.97/-0.67

Table S2 Selected bond lengths (Å) and angles (°) **Fe4'**

Bond length (Å)			
Fe1-N1	2.287(3)	P1-O1	1.501(2)
Fe1-N2	2.251(3)	N2-C8	1.479(4)
Fe1-O1	2.046(2)		
Bond angles (°)			
O1-Fe1-N1	91.68(9)	O1-P1-C11	111.20(14)
O1-Fe1-N2	91.37(9)	C8-N2-Fe1	106.34(18)
N2-Fe1-N1	73.44(9)	P1-O1-Fe1	127.93(13)

MW Averages

Mp: 386287	Mn: 260948	Mv: 403841	Mw: 432122
Mz: 639879	Mz+1: 836850	PD: 1.6560	
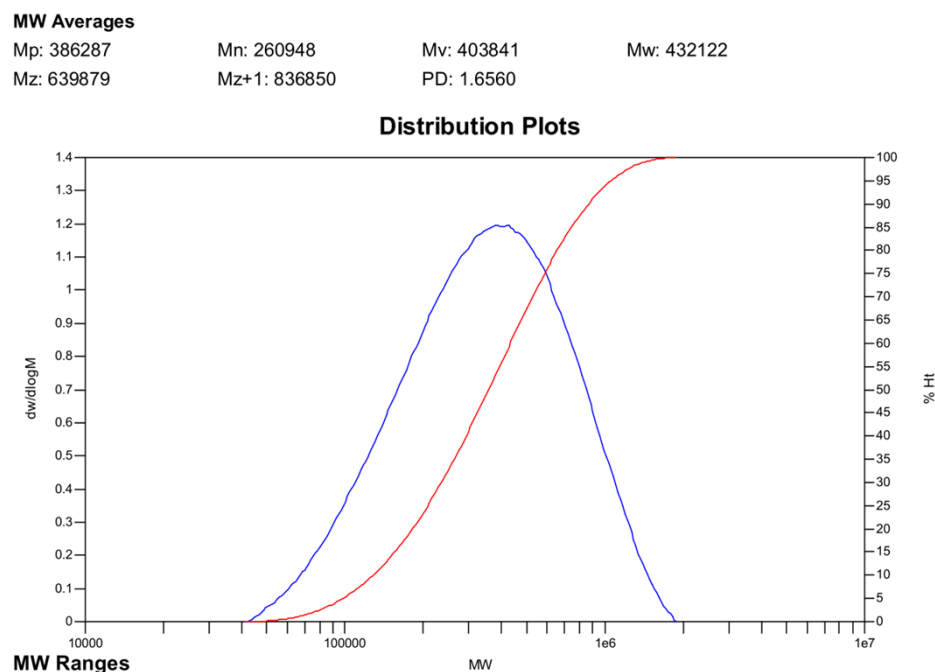
Fig. S17 The GPC spectra of high molecular PCL using **Fe6** ([ε-CL]/[Fe] = 1800:1, T = 90 ℃, t = 10 min)

MW Averages
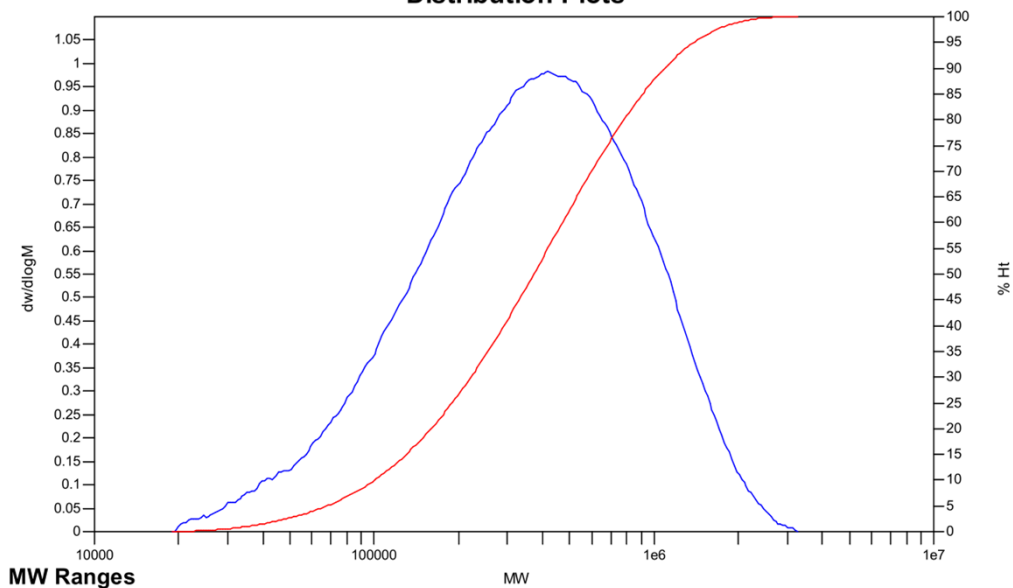
Mp: 386287   Mn: 239393   Mv: 411039   Mw: 443009

Mz: 672520   Mz+1: 879051   PD: 1.8506

Distribution Plots
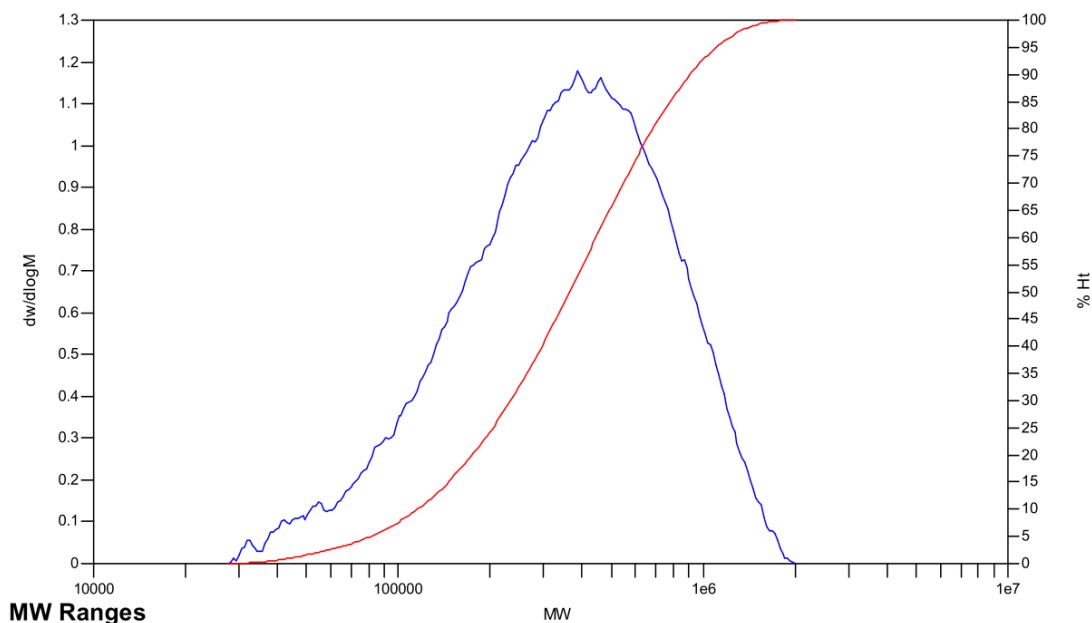
Fig. S18 The GPC spectra of high molecular PCL using **Fe6** ([ε-CL]/[Fe] = 2000:1, T = 90 °C, t = 10 min)

MW Averages

Mp: 418688   Mn: 219258   Mv: 449554   Mw: 496962

Mz: 865541   Mz+1: 1227595   PD: 2.2666

Distribution Plots

Fig. S19 The GPC spectra of high molecular PCL using **Fe4** ([ε-CL]/[Fe] = 1500:1, T = 90 °C, t = 10 min)

S12

MW Averages
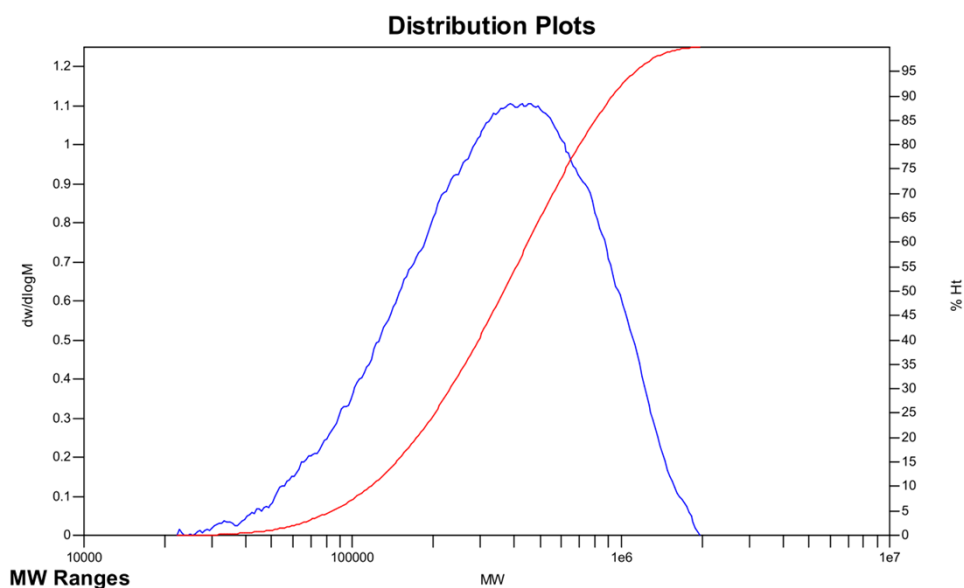
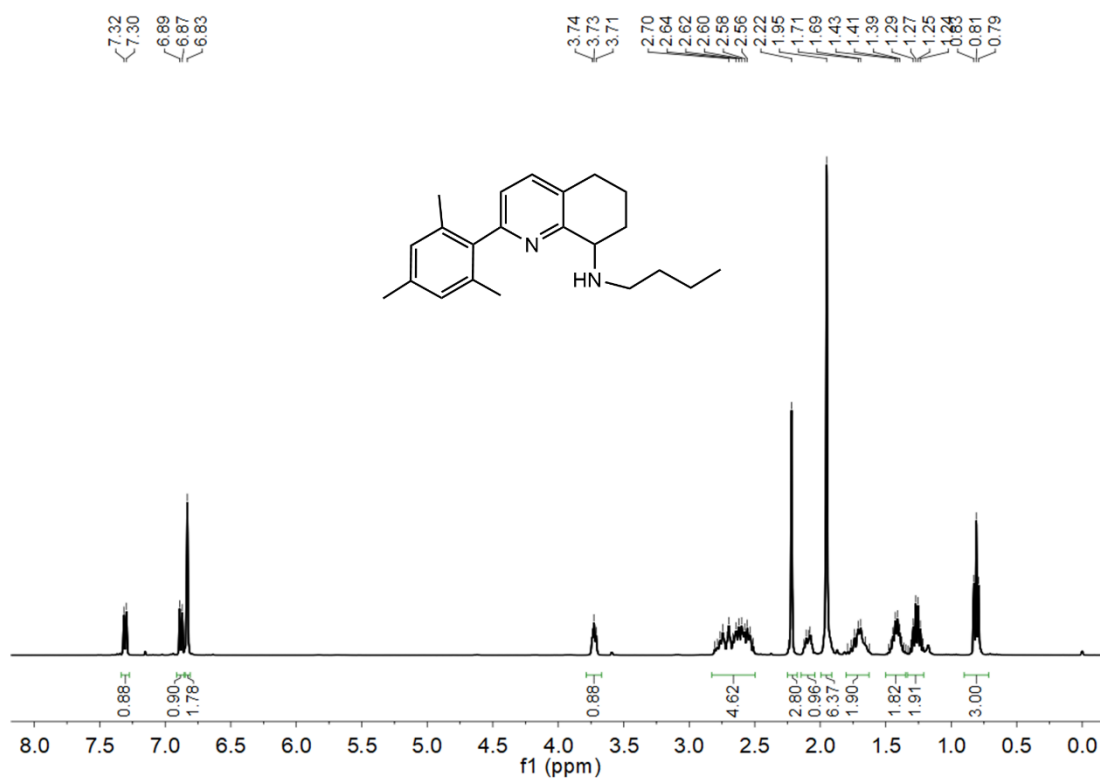|			
Mp: 386287	Mn: 243463	Mv: 416567	Mw: 449661
Mz: 688598	Mz+1: 901882	PD: 1.8469	

Fig. S20 The GPC spectra of high molecular PCL using **Fe5** ([ε-CL]/[Fe] = 1500:1, T = 90 °C, t = 10 min)

Fig. S21 ^{13}C NMR (CDCl$_3$, 25°C) spectrum of **L8**