ESI for

Design and Application of the Recyclable Poly (*L*-Proline-*co*-Piperidine) Catalyst for the Synthesis of Mesityl Oxide from Acetone

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Experimental

I. GC analysis

1. Equipment and conditions.

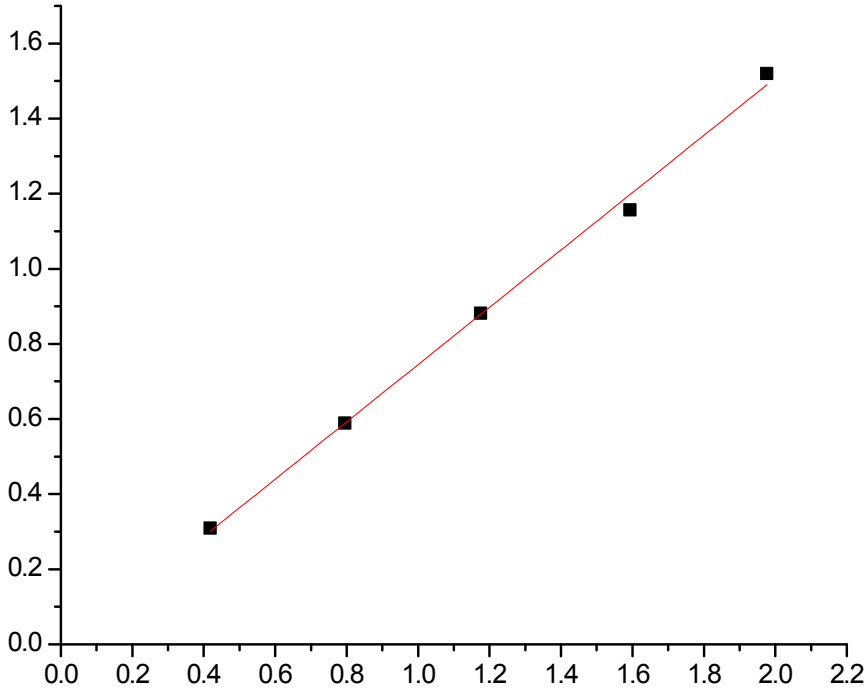
GC analysis of the reactions was performed by using a Agilent 6820 instrument with capillary HP-FFAP column (film thickness 0.3 μm, inside diameter 0.2 mm, column length 50 m) and a FID program were used in GC analysis; Velocities of the carrier gas (99.99% N_2), fuel gas (99.96% H_2) and auxiliary gas (air) were 30 mL/min, 30 mL/min and 300 ml/min respectively. The oven temperature was programmed at 60–270 ^oC (initial temperature 60 ^oC for 3 min, heating rate 30 ^oC/min to 270 ^oC and then kept for 5 min); Temperatures of the sample injector, detector and column were 250 ^oC, 270 ^oC and 90 ^oC respectively; The split ratio was 60:1 and the column pressure was 47 kPa; GC data was diposed with Zhida (Zhejiang Univ.) N2000 Chromatography workstation; GC yields were obtained using methyl benzoate as internal standard.

2. Internal standard curves for acetone, MO, DAA and IP

Acetone:

m_1/g[a]	m_2/g[b]	m_1/m_2(x)	c_1/%[c]	c_2/%[d]	c_1/c_2(y)	correction factor
0.2134	0.5105	0.41802	1.18395	3.82636	0.30942	1.3510
0.4054	0.5097	0.79537	2.60307	4.41942	0.58901	1.3504
0.6008	0.5114	1.17481	3.78782	4.29555	0.88180	1.3322
0.8036	0.5044	1.59318	4.93114	4.264	1.15646	1.3776
1.0098	0.5110	1.97612	6.41772	4.224	1.51934	1.3006

[a] Acteone weight; [b] Internal standard weight; [c] Content of acetone; [d] Content of internal standard.

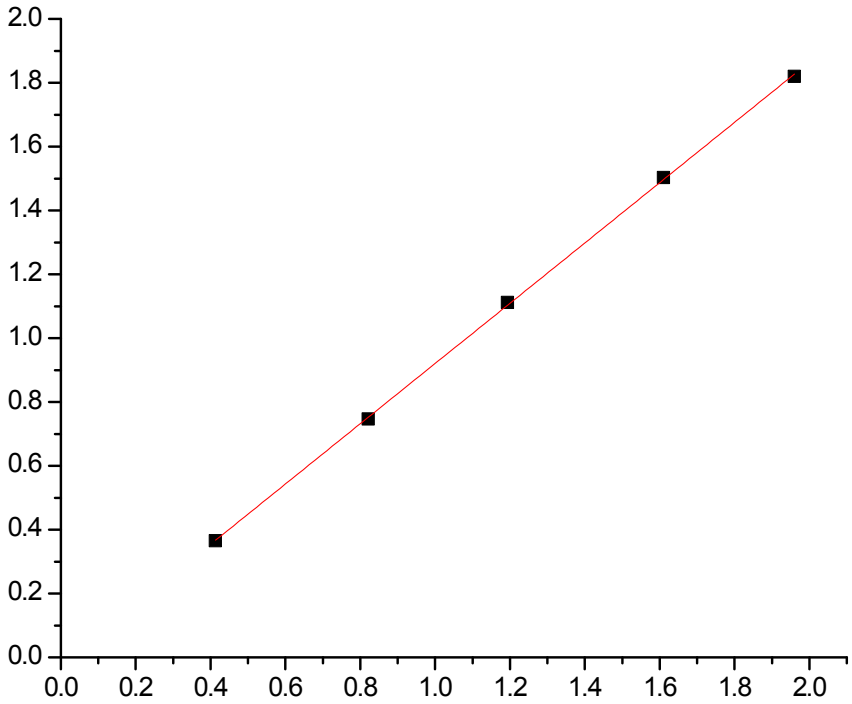


y=0.7630x-0.01791，R^2=0.9961

MO:

m_1/g[a]	m_2/g[b]	m_1/m_2(x)	c_1/%[c]	c_2/%[d]	c_1/c_2(y)	correction factor
0.2111	0.5105	0.4135	1.39848	3.82636	0.36549	1.1314
0.4186	0.5097	0.82127	3.29967	4.41942	0.74663	1.1000
0.6103	0.5114	1.19339	4.7729	4.29555	1.11113	1.0740
0.8125	0.5044	1.61082	6.4088	4.264	1.50300	1.0717
1.0016	0.5110	1.96007	7.68764	4.224	1.81999	1.0770

[a] MO weight; [b] Internal standard weight; [c] Content of MO; [d] Content of internal standard.

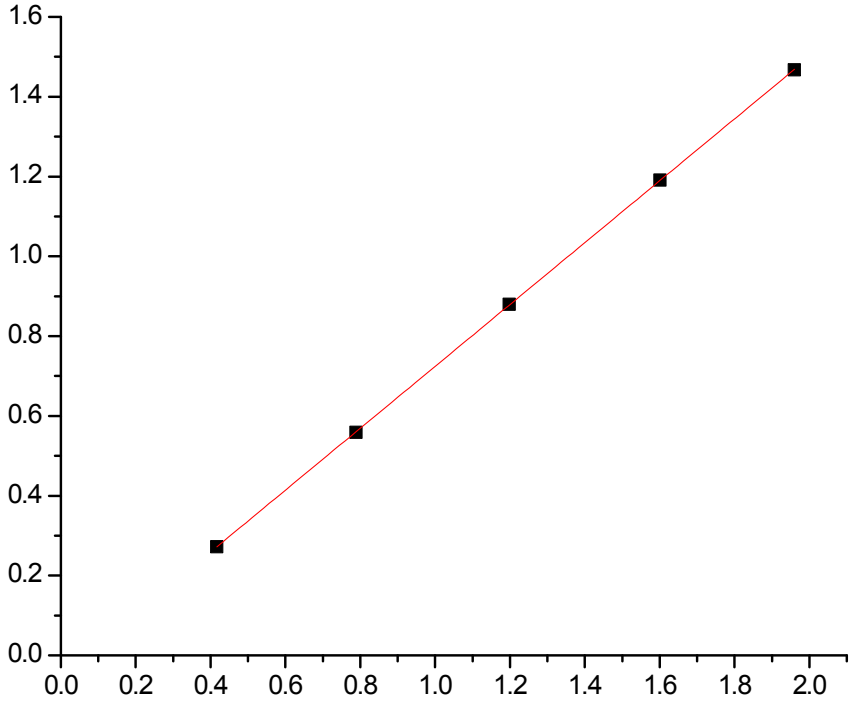


$y=0.9441x-0.02353$，$R^2=0.9998$

DAA:

m_1/g[a]	m_2/g[b]	m_1/m_2(x)	c_1/%[c]	c_2/%[d]	c_1/c_2(y)	correction factor
0.2128	0.5105	0.41685	1.04105	3.82636	0.27207	1.3521
0.4020	0.5097	0.78870	2.47092	4.41942	0.55911	1.4106
0.6130	0.5114	1.19867	3.7801	4.29555	0.88000	1.3621
0.8075	0.5044	1.60091	5.07765	4.264	1.19082	1.3444
1.0016	0.5110	1.96008	6.19802	4.224	1.46733	1.3358

[a] DAA weight; [b] Internal standard weight; [c] Content of DAA; [d] Content of internal standard.

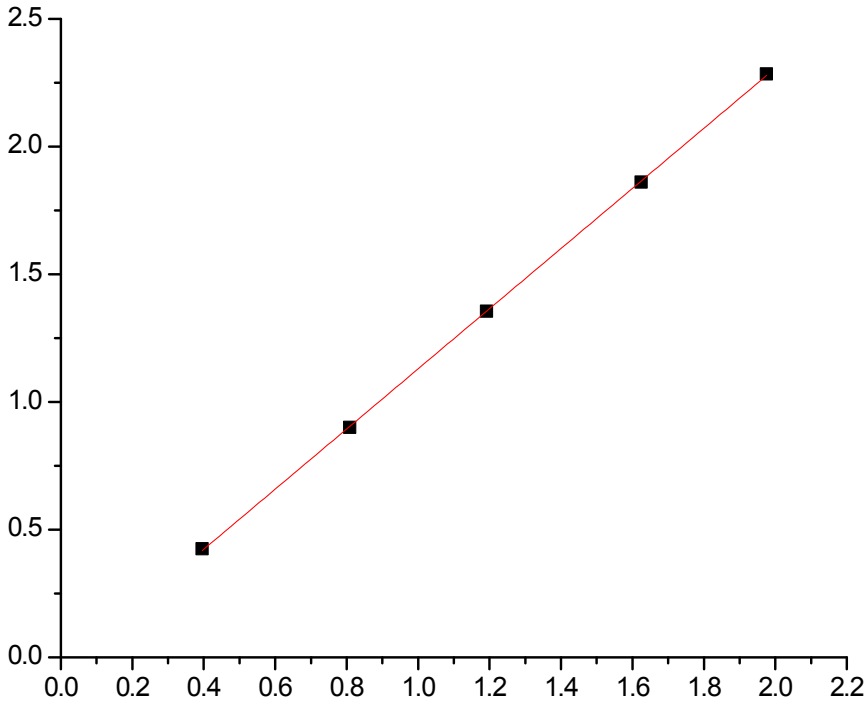


$y=0.7752x-0.05102$，$R^2=0.99999$

IP:

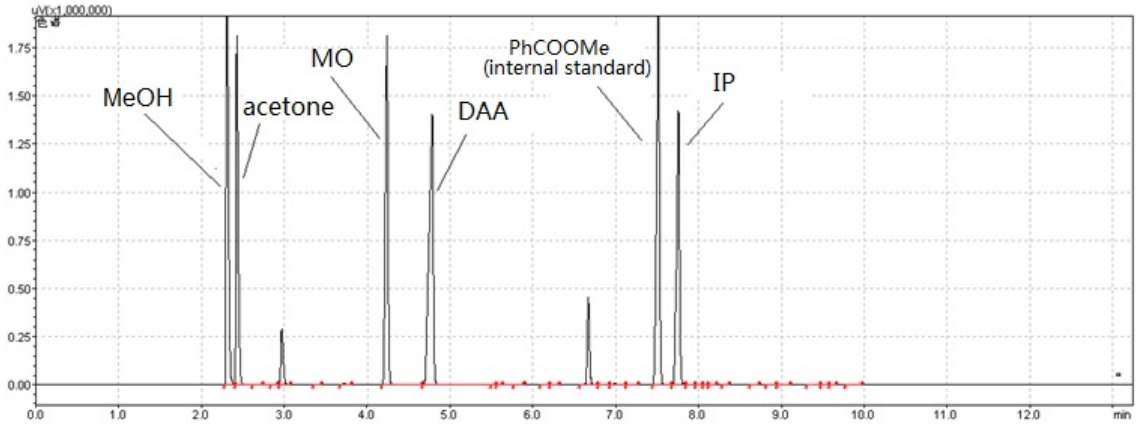
m_1/g[a]	m_2/g[b]	m_1/m_2(x)	c_1/%[c]	c_2/%[d]	c_1/c_2(y)	correction factor
0.2019	0.5105	0.39549	1.62322	3.82636	0.42422	0.9322
0.4125	0.5097	0.80930	3.97591	4.41942	0.89965	0.9000
0.6096	0.5114	1.19202	5.82001	4.29555	1.35489	0.8798
0.8195	0.5044	1.62470	7.9332	4.264	1.86051	0.8732
1.0093	0.5110	1.97515	9.64966	4.224	2.28448	0.8642

[a] IP weight; [b] Internal standard weight; [c] Content of IP; [d] Content of internal standard.



y=1.1776x-0.04754，R^2=0.9999

Internal standard analysis comparison GC spectra



II. Spectrophotography analysis for *L*-proline content

1. General

Reaction of *L*-proline with ninhydrin generated brown complex. Content of *L*-proline could be determined by standard curve of the absorption on 510 nm.

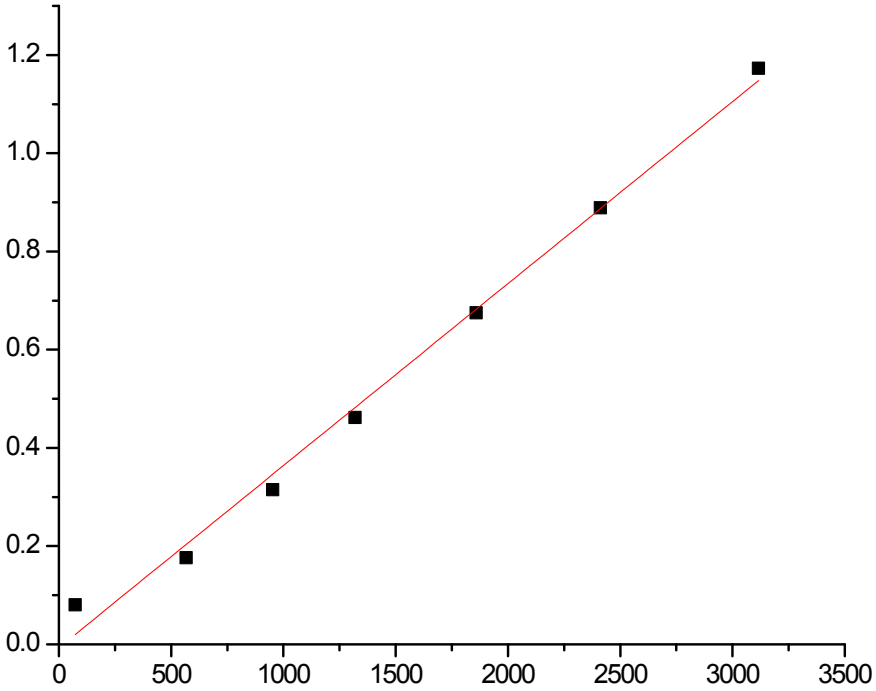
2. Procedure

Preparation of standard curve: *L*-proline standard solutions 0.0, 0.20, 0.40, 0.60, 0.80, 1.00 mL (0, 5, 10, 15, 20, 25 μg L-proline) were added to tubes with stoppers respectively and were all diluted with water to 1 mL. 0.25 mL formic and 1.0 mL ninhydrin-ethylene glycol monomethyl ether (EGME) solution were then added. The tubes were sealed with stoppers and heat in boiling water for 15 min and then removed to 70 ^{o}C thermostatic waterbath for 10 min. 15 mL of isopropanol was added and after keeping for 5 min, the absorbance was measured at 510 nm and standard curve was drawn accordingly.

Sample determinations: 5.0 g sample was dissolved by water and diluted to 100 mL with volumetric flask. 0.5-1.0 g of sample solution was removed to a tube and diluted to 1 mL. The absorbance was determined as above procedures and content of *L*-proline was calculated with the standard curve.

3. Standard curve

L-proline weight/g	L-concentration/ppm	A
0.5192	72.58	0.080
1.0800	567	0.176
1.8141	952.40	0.315
2.5144	1320.06	0.462
3.5395	1858.24	0.675
4.5932	2411.43	0.889
5.9352	3115.98	1.173



$y=3.7070\times10^{-4}x-0.00676$，$R^2=0.9918$

III. Table S1. Blank experimental results of co-catalyst[a]

run	Co-catalyst	X/%[b, c]
1	quinoline (**1**)	No reaction
2	pyridine (**2**)	No reaction
3	triethyl amine (**3**)	5.6
4	N-methyl pyrrolidone (**4**)	5.8
5	piperazine (**5**)	2.7
6	N,N-dimethyl piperazine (**6**)	3.0
7	piperidine (**7**)	2.3
8	N-methyl piperidine (**8**)	5.4

[a] Acetone (300g, 5.17 mmol) and co-catalyst (30g) were heated at different temperatures in autoclave for 4 h under N_2;

[b] Conversion ratio of acetone; [c] Determined by GC with methyl using benzoate as internal standard.

IV Effects of the catalyst dosage and reaction time

Table S2. Effects of the catalyst L-proline dosage[a]

Enrtry	Catalyst dosage (mol%)[b]	X/%[c]
1	1.7	22.8
2	3.4	30.5
3	5	37.9
4	6.7	38.5

[a] For detailed conditions see text, Table 2, entry 6; [b] Based on the amount of acetone; [c] Conversion ratio of acetone.

Table S3. Effects of the catalyst reaction time[a]

Enrtry	Time(h)	X/%[b]	S/%		
			MO	DAA	IP
1	4	37.9	67.0	8.7	3.3
2	8	38.5	66.5	7.1	4.0

[a] For detailed conditions see text, Table 2, entry 6; [b] Conversion ratio of acetone.

V Carbon mass balance calculation details

164.19 g of acetone, 16.42 g of *L*-proline and 5.47 g of piperidine were added into an 1 L high-pressure reaction kettle which was charged with N_2 and sealed. The reaction was performed at 90 ^{o}C for 4 h. The terminated reaction mixture was divided to be two layered. The water layer was extracted by ^{n}BuOH (25.0g ×2) , combined with the organic layer and sent to analysis. The analysis results were listed below.

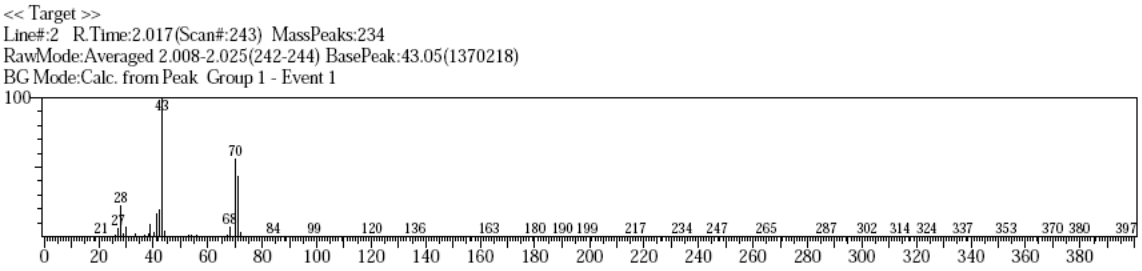
Carbon balance：			
1. Feedings	Carbon contained: 9.5283 mol		
1.1	（1）acetone	164.19	g
	（2）carbon contained	8.4925	mol
1.2	（1）*L*-proline	16.42	g
	（2）carbon contained	0.7139	mol
1.3	（1）piperidine	5.47	g

	（2）carbon contained	0.3219	mol
2. Discharge	Carbon contained: 9.4589		
2.1	（1）acetone	101.96	g
	（2）carbon contained	5.2738	mol
2.2	（1）MO	70.45	g
	（2）carbon contained	2.1566	mol
2.3	（1）DAA	10.84	g
	（2）carbon contained	0.2803	mol
2.4	（1）4-methylpent-4-en-2-one	4.69	g
	（2）carbon contained	0.1435	mol
2.5	（1）1,3,5-C_6H_3	1.41	g
	（2）carbon contained	0.0613	mol
2.6	（1）phorone	1.44	g
	（2）carbon contained	0.0617	mol
2.7	（1）Isophorone	1.63	g
	（2）carbon contained	0.1062	mol
2.8	（1）others	5.20	g
	（2）carbon contained	≈0.3696	mol
2.9	（1）*L*-proline	12.97	g
	（2）carbon contained	0.5640	mol
2.10	（1）pyrrolidine	2.13	g
	（2）carbon contained	0.12	mol
2.11	（1）piperidine	5.47	g
	（2）carbon contained	0.3219	mol

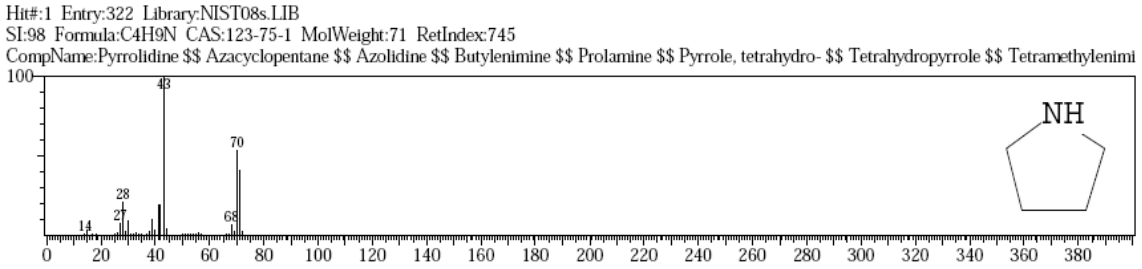
Carbon mass balance = 9.4589 / 9.5283 = 99.3 %.

VI. Mass spectra for *L*-proline decomposition

1. Mass spectra of the compound captured in reaction system



2. Standard spectra of pyrrolidine in library



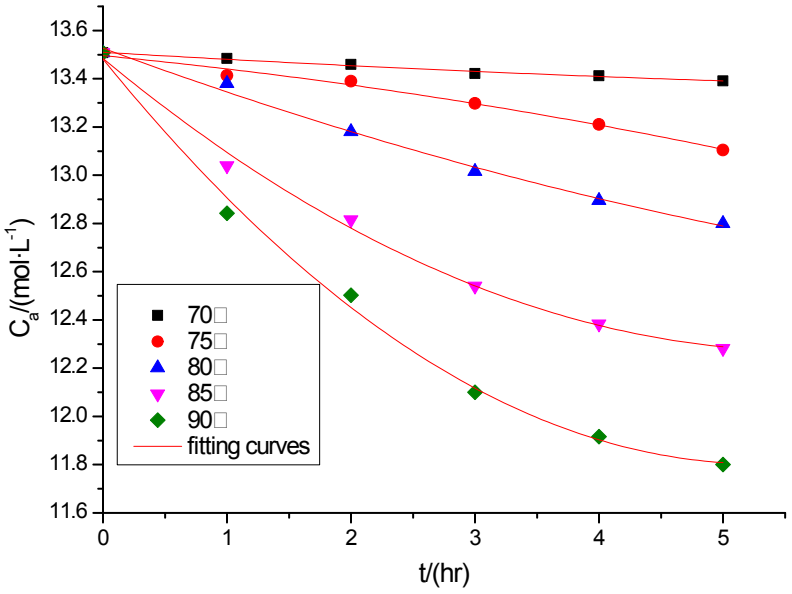
VII. Experimental Details for Dynamic Calculations

（1）*PNL* catalyzed condensation of acetone：

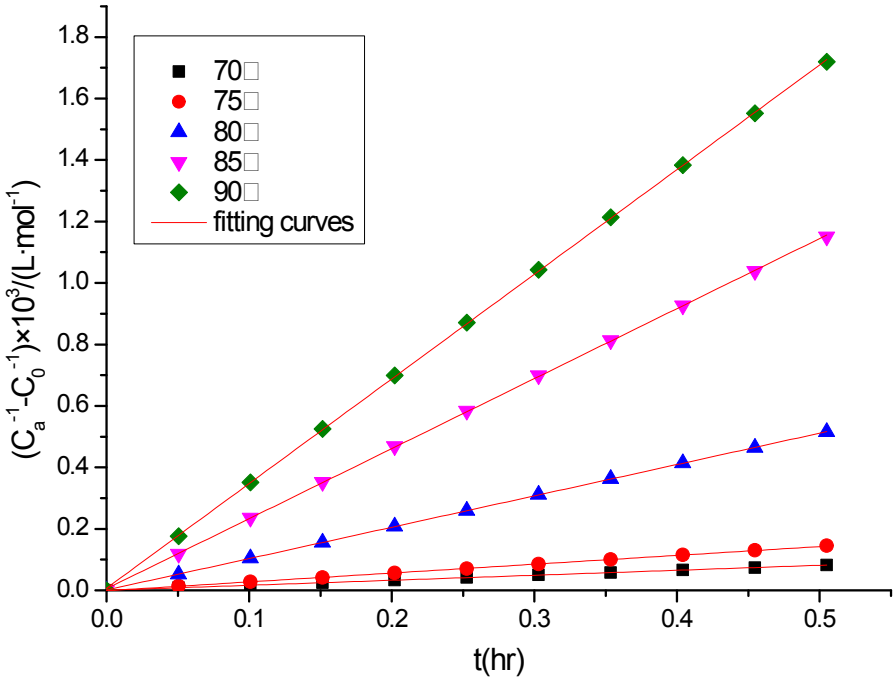
t/°C	t (h)	C_a/mol·L^{-1}
70	0	13.5072
	1	13.4837
	2	13.4592
	3	13.4218
	4	13.4122
	5	13.3914
75	0	13.5072
	1	13.4137
	2	13.3892
	3	13.2981
	4	13.2104
	5	13.1043
80	0	13.5072
	1	13.3804
	2	13.1805
	3	13.0155
	4	12.8953
	5	12.7994
85	0	13.5072

	1	13.0397
	2	12.8151
	3	12.5399
	4	12.3833
	5	12.2819
	0	13.5072
	1	12.8418
	2	12.5023
90		
	3	12.1008
	4	11.9167
	5	11.8003

According to the above data, the C_a-t curve should be:

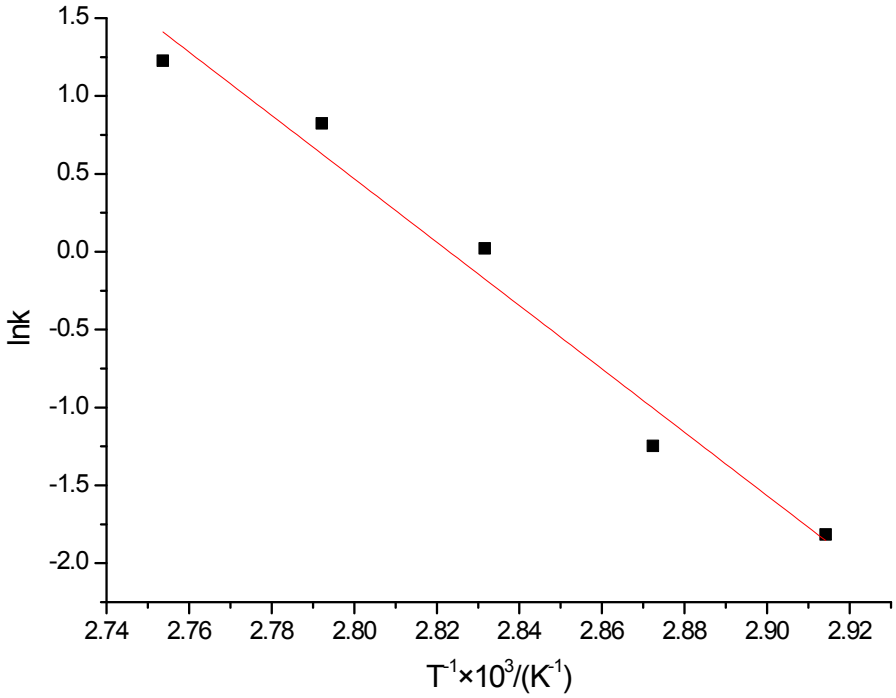


$(C_a^{-1}-C_0^{-1}) \times 10^3 \sim$ t curve was drawn accordingly:



According to the above results, reaction rate constants K at different temperatures were got, and the $\ln K \sim 1/T \times 10^3$ curve was drawn below:

t/°C	k	lnk	T/K	$T^{-1}\times10^3/K^{-1}$
70	0.16256	-1.81671	343.15	2.9142
75	0.28742	-1.24681	348.15	2.8723
80	1.02044	0.020234	353.15	2.8317
85	2.2787	0.823605	358.15	2.7921
90	3.40531	1.225336	363.15	2.7537



Conclutions：

The reaction was a second order reaction. The kinetic equation for the condensation of acetone catalyzed by L-proline alone was：

$$(-r_a) = 2.46\times10^{18}\exp(-169.17/RT)\, C_a^2$$

The activation energy $E_a$was 169.17kJ/mol.

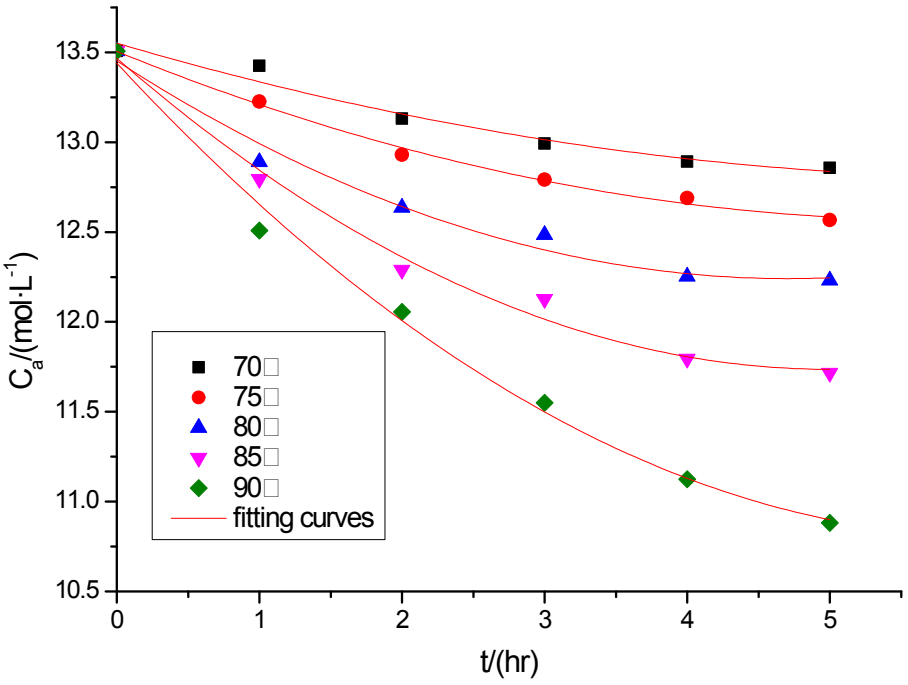
（2）*PNLD* catalyzed condensation of acetone

t/°C	t(h)	C_a/mol·L^{-1}
70	0	13.5072
	1	13.4254
	2	13.1307
	3	12.9918

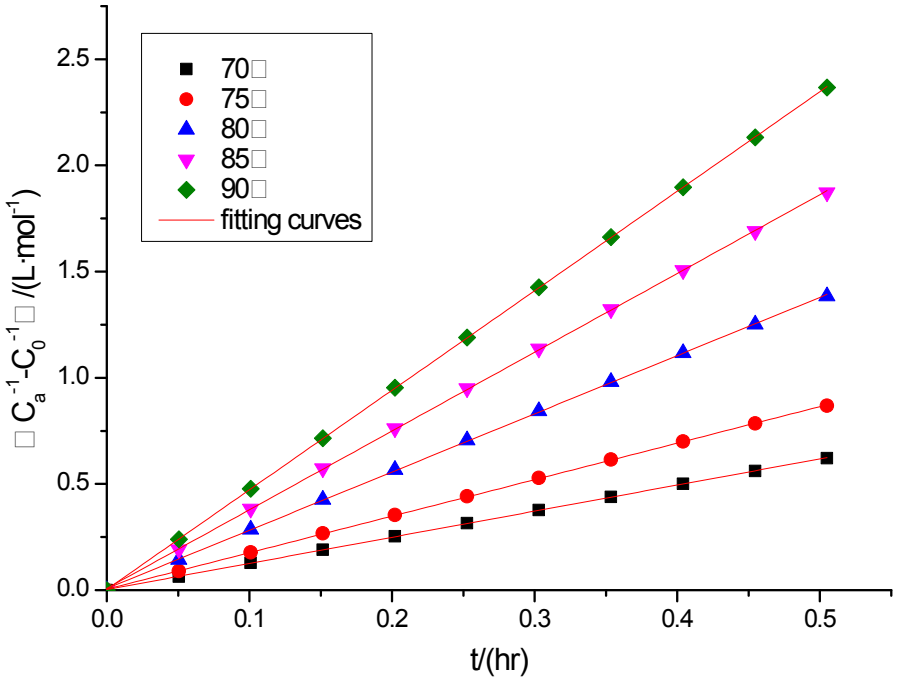
	4	12.8912
	5	12.8567
	0	13.5072
	1	13.2254
	2	12.9307
75	3	12.7918
	4	12.6891
	5	12.5671
	0	13.5072
	1	12.8902
	2	12.6355
80	3	12.4850
	4	12.2528
	5	12.2301
	0	13.5072
	1	12.7944
	2	12.2897
85	3	12.1274
	4	11.7946
	5	11.7161
	0	13.5072
90	1	12.5089

	2	12.0559
	3	11.5504
	4	11.1239
	5	10.8820

According to the above data, the C_a-t curve should be:

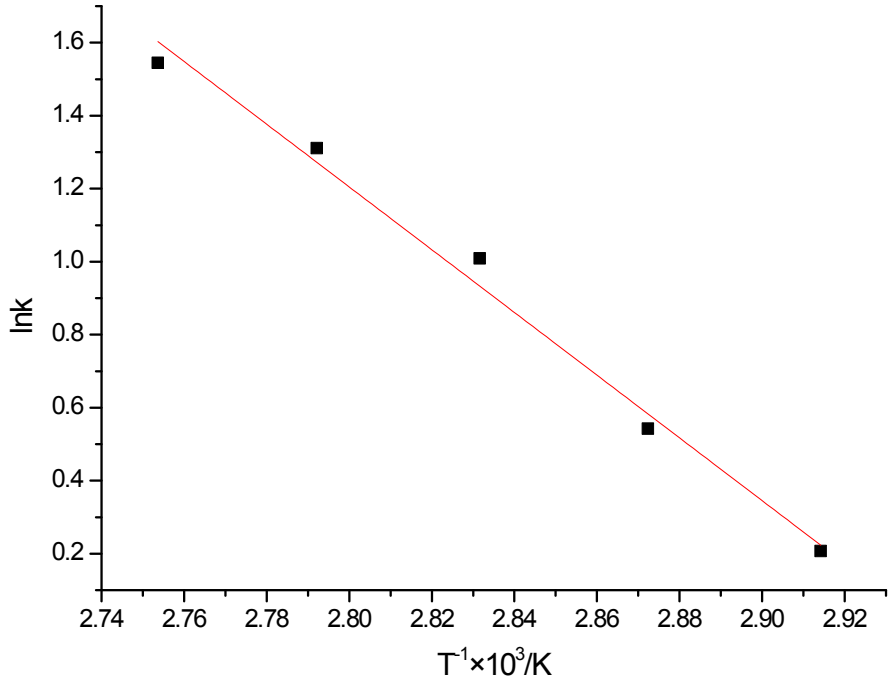


$(C_a^{-1}-C_0^{-1}) \times 10^3 \sim$ t curve was drawn accordingly:



According to the above results, reaction rate constants K at different temperatures were got, and the lnK~1/T×10^3 curve was drawn below:

t/°C	k	lnk	T/K	$T^{-1}\times10^3/K^{-1}$
50	1.2302	0.2072	323.15	3.0945
60	1.719	0.5422	333.15	3.0017
70	2.7423	1.0088	343.15	2.9142
75	3.7090	1.3108	348.15	2.8723
90	4.6863	1.5447	363.15	2.7537



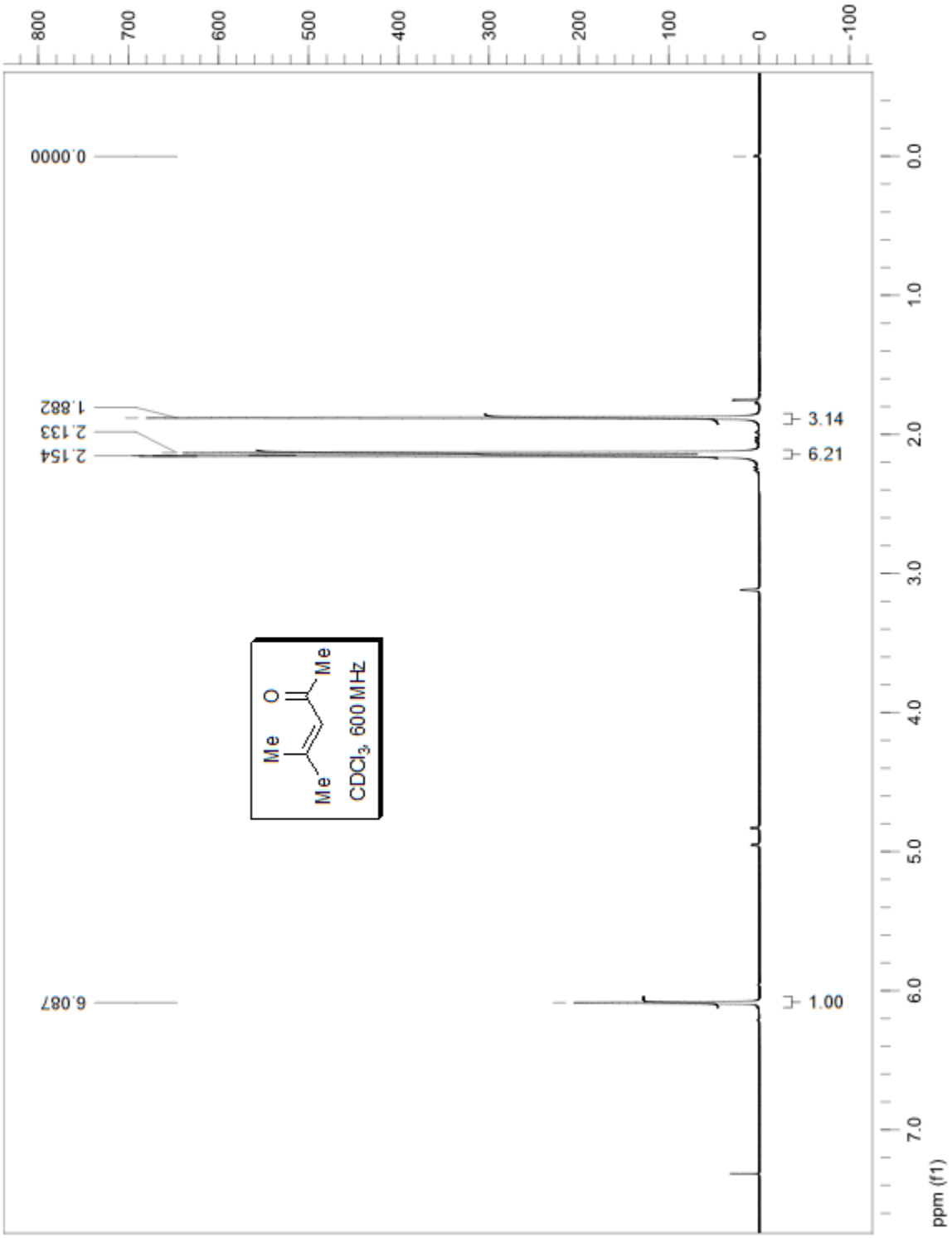
Conclutions：

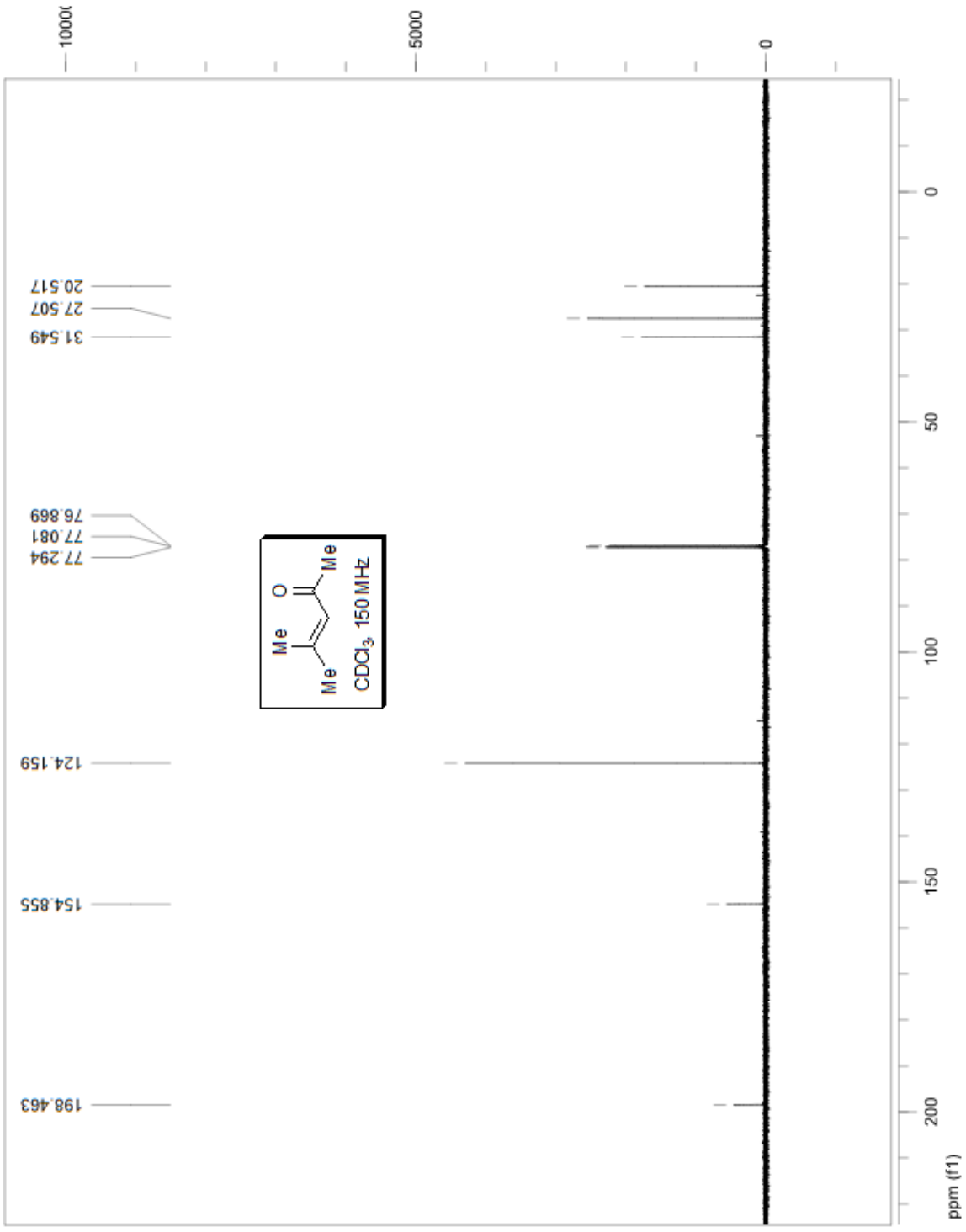
The reaction was a second order reaction. The kinetic equation for the condensation of acetone catalyzed by PNLD alone was：

$$(-r_a) = 2.61 \times 10^4 \exp(-71.45/RT)\, C_a^2$$

The activation energy E_a was 71.45 kJ /mol.

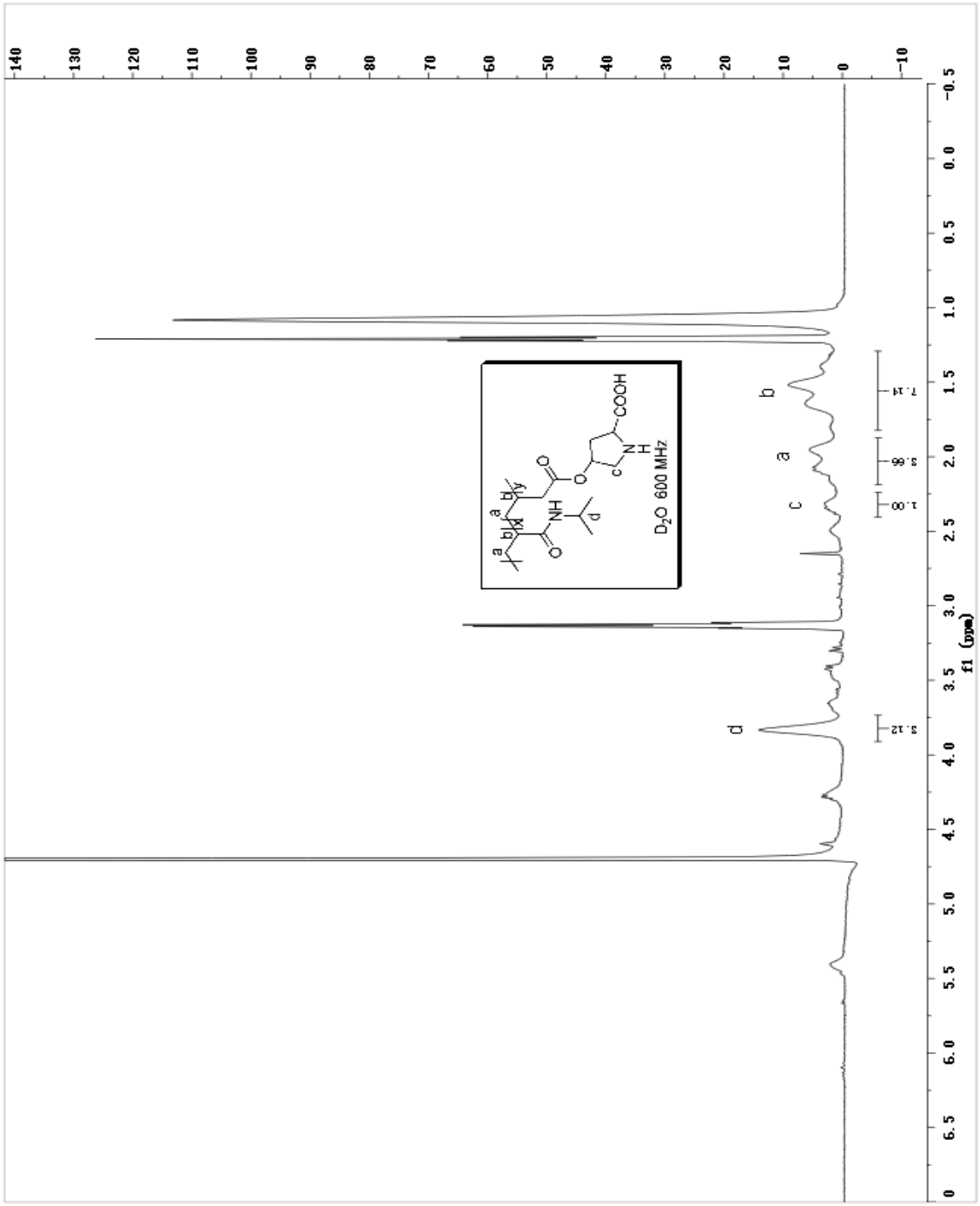
VIII. NMR Spectra of MO




198.463
154.855
124.159
77.294
77.081
76.869
31.549
27.507
20.517
Me
O
Me
Me
CDCl3, 150 MHz
ppm (f1)

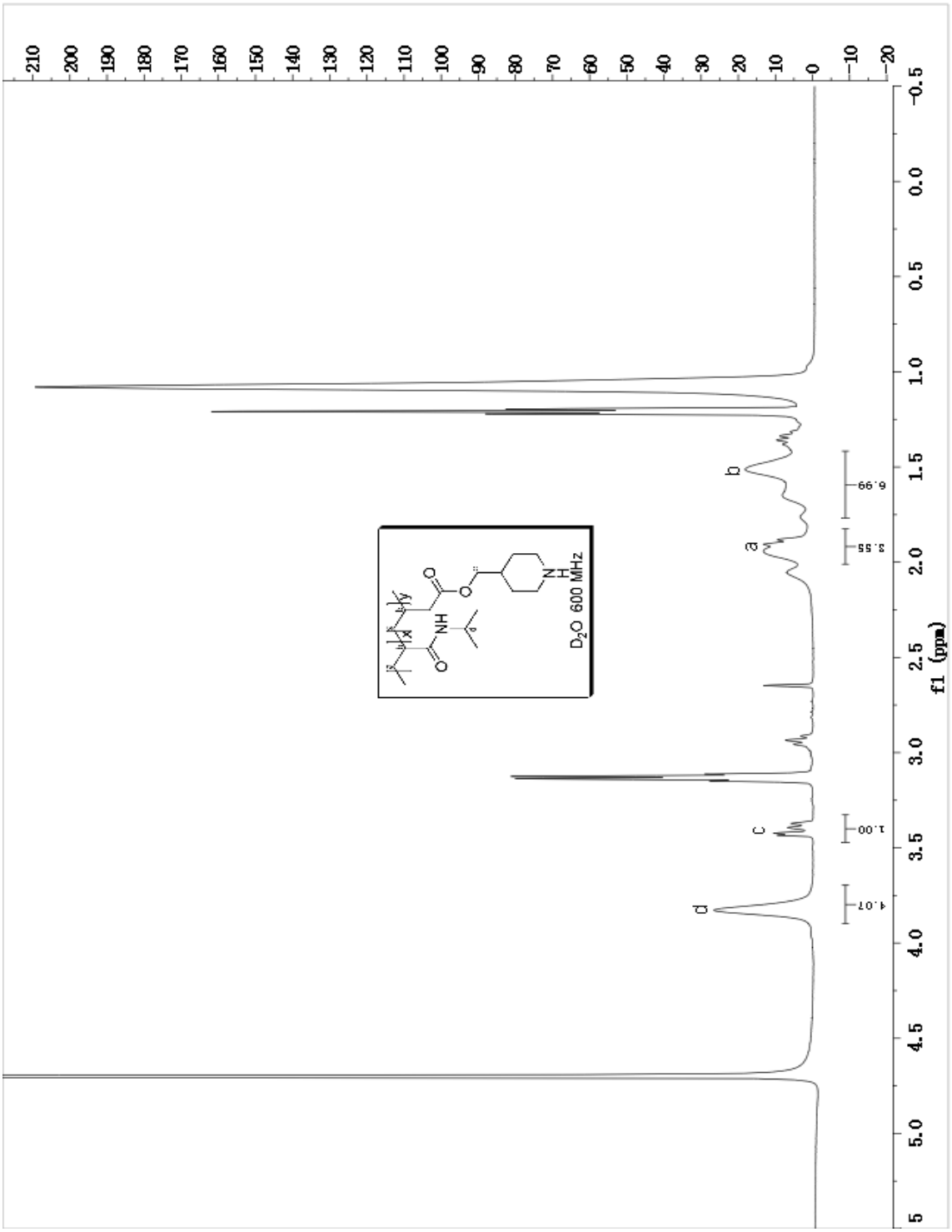
IX. ^{1}H NMR Spectra of PNL, PND and PNLD and Calculation of Catalyst Loadings and the Reaction TON and TOF

^{1}HNMR Spectra of PNL 7



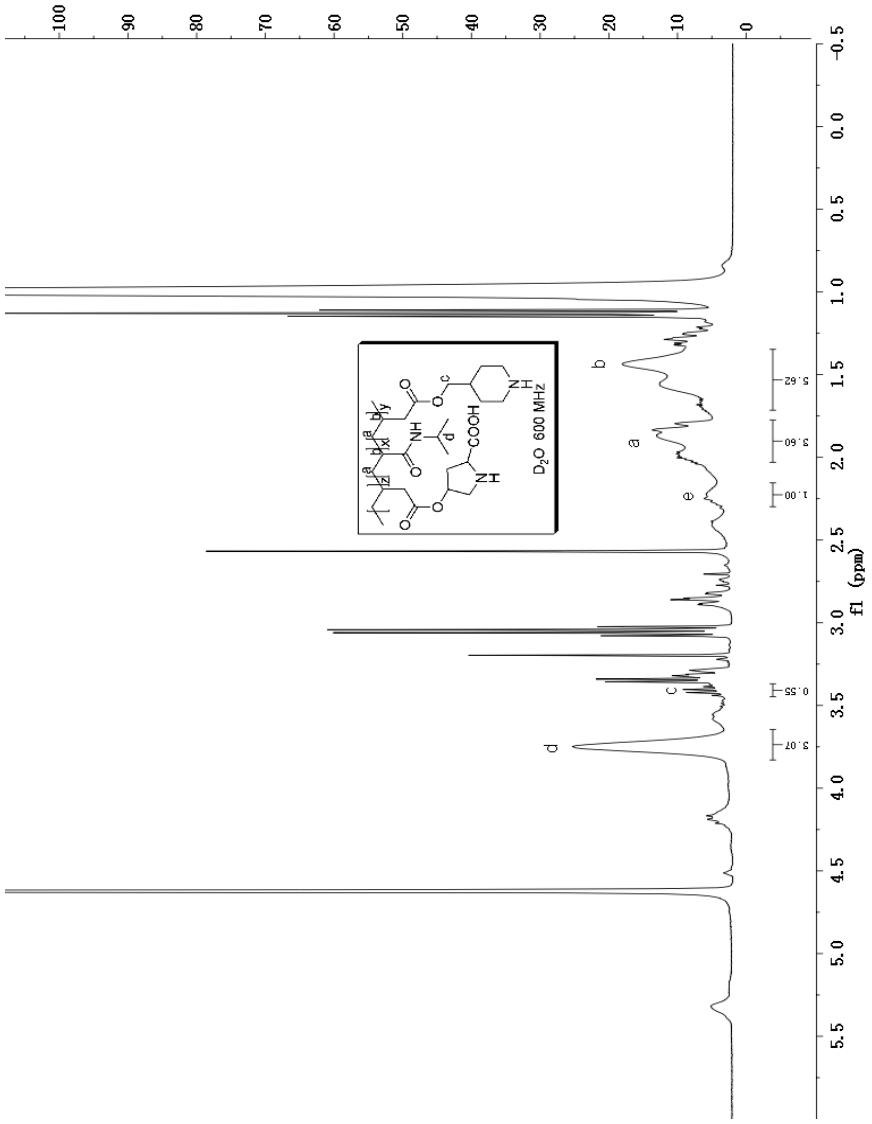
L-Proline loading = (c/2)/(d+c/2) = 13.8 mol/mol%

[1]HNMR Spectra of PND 8



Py loading = (c/2)/(d+c/2) = 10.9 mol/mol %

[1]HNMR Spectra of PNLD 9

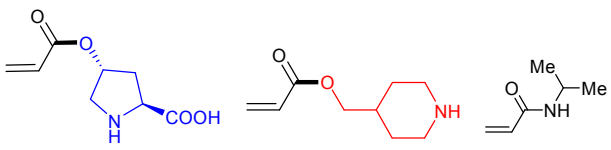


L-Proline loading = (e/2)/(e/2+d+c/2) = 12.9 (mol/mol %);

Py loading = (c/2)/(e/2+d+c/2) = 6.7 (mol/mol %);

N-isopropylacrylamide loading = 100-12.9-6.7 = 80.4 (mol/mol %);

The molecular weight of each component on PNLD **9** was shown below



M = 185.17 M = 169.22 M = 113..16

Therefore the molar concentrations (C) of each component on PNLD **9** were:

$C_{L\text{-Proline}} = 12.9 / (12.9* 185.17 + 6.7 * 169.22 + 80.4 * 113.16) = 1.02$ (mmol/g);

$C_{Py} = 6.7 / (12.9* 185.17 + 6.7 * 169.22 + 80.4 * 113.16) = 0.53$ (mmol/g);

For reaction in Table 5, entry 3 in the text:

The molar amount of catalyst *L*-proline on PNLD **9** was:

$M_{L\text{-Proline}} = 0.67 * 1.02 = 0.68$ (mmol);

The molar of MO generated was:

$M_{MO} = 60 * 0.241 * 0.744 = 10.76$ (mmol);

Therefore, TON and TOF were calculated as below:

TON = 10.76/0.68 = 15.8;

TOF = 15.8 / 4 = 4.0 (h^{-1});