Electronic supplementary information

Two heterotrimetallic organic frameworks constructed by a functionalized Schiff base ligand: syntheses, structures and visible photocatalytic activities for the degradation of chlorophenols

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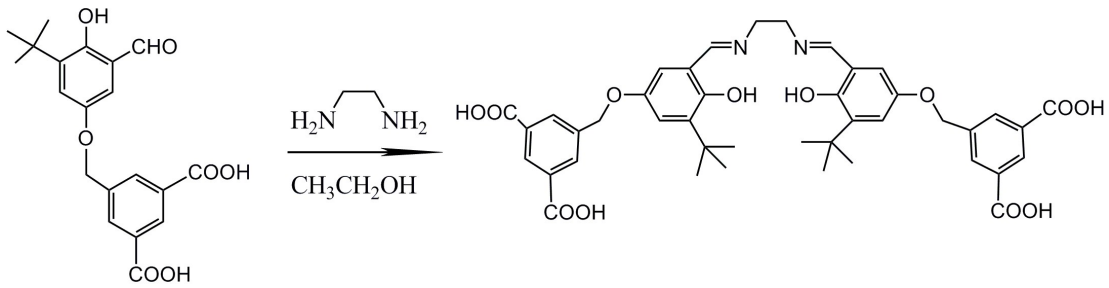
Experimental

Synthesis of H_6L. H_6L was synthesized by 3-tertiarybutyl-5-((3,5-carboxybenzyl) oxy)salicylidehyde (400 mg, 1 mmol) and ethylenediamine (30 mg, 0.5 mmol) in 100 mL of ethanol. The mixture was stirred for 4 h at room temperature, and then the yellow suspension was concentrated to 20 mL. The resulting yellow solid was filtered and washed with distilled water and dried in vacuum in 90% yield.



Scheme S1. Synthetic route of H_6L

Materials and instrumentation. All reagents and organic solvents were of analytical grade and used without further purification. FT-IR spectra were measured from KBr pellets in the range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric measurements (TGA) were performed on a Perkin-Elmer TG-7 analyzer heated from 20 to 600 ^{o}C at a ramp rate of 10 ^{o}C/min (Figure S1). The powder X-ray diffraction (PXRD) patterns were measured on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu-Kα radiation (λ = 0.154 nm). In the process of photocatalytic degradation, the concentrations of CPs were measured through a gas chromatograph which allocated with a capillary column (30 m long × 0.25 mm i.d., Wonda CAP 17) and an FID detector (GC 2014, Shimadzu, Japan). The variable-temperature magnetic susceptibility data were collected using a SQUID magnetometer (Quantum Design, MPMS-5) with an applied field of 1000 Oe. Inductively coupled plasma (ICP) analyses were conducted on a Leeman Laboratories Prodigy inductively coupled plasma−optical atomic emission spectrometry (ICP-AES) system. Scanning electron microscopy (SEM) imaging was performed on Hitachi SU8010. Energy dispersive X-ray Spectroscopy (EDS) analysis was conducted on EDAX.

Thermal analysis: The weight loss of **1**, corresponding to the DMF and water, is observed over the temperature range from 20 to 250 °C (Found: 16.02%, calcd: 15.99%). Thermogravimetric and elemental analyses demonstrate the presence of *ca.* one DMF and two water molecules in **1**. The weight loss of **2**, corresponding to the DMF and water, is observed over the temperature range from 20 to 250 °C (Found: 16.80%, calcd: 16.46%). Thermogravimetric and elemental analyses demonstrate the presence of *ca.* one DMF and two water molecules in **2**.

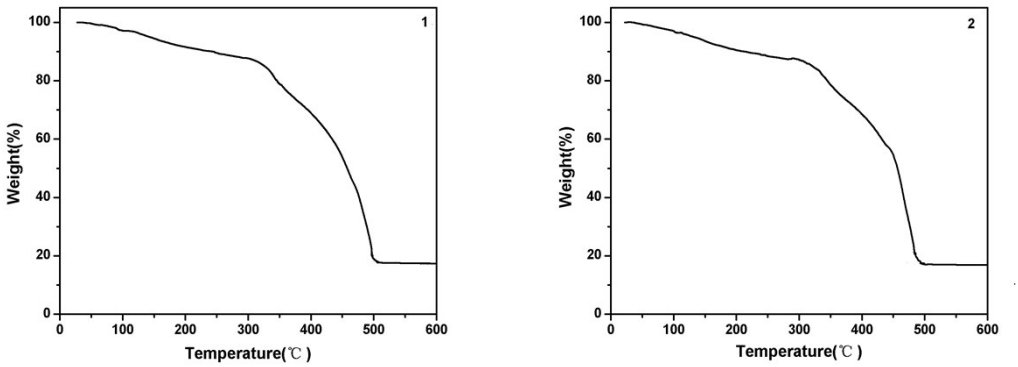
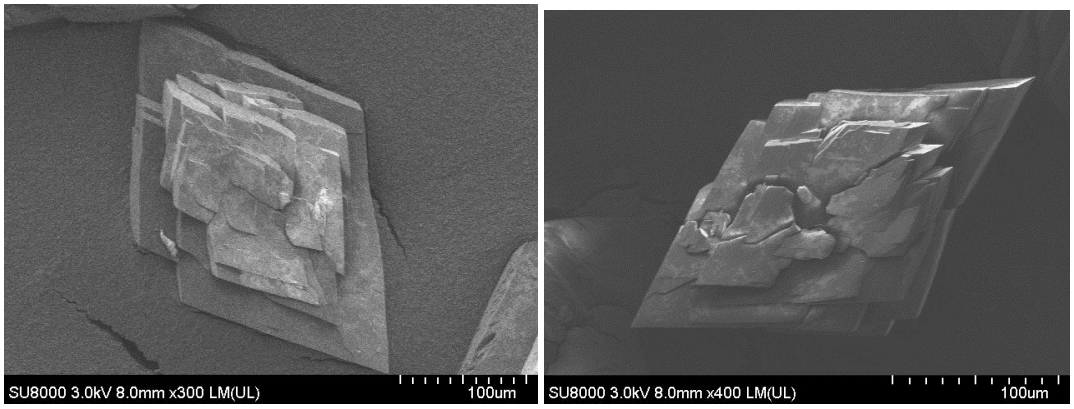
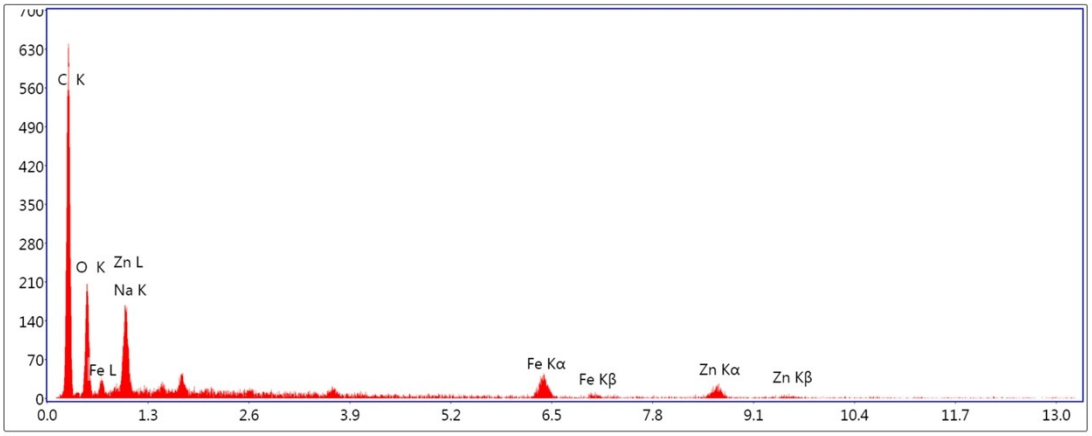


Fig. S1 Thermogravimetric curves of **1** and **2**.

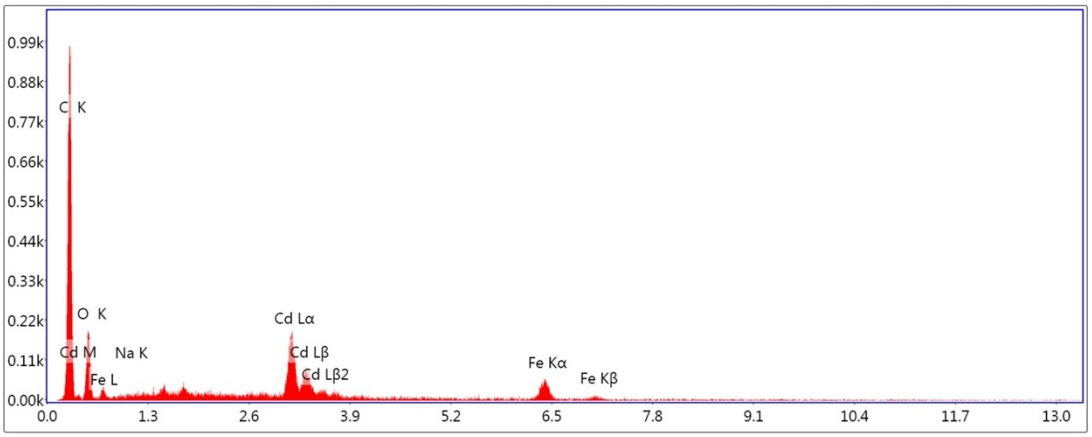


(a) (b)

Fig. S2 The SEM images of frameworks **1**(a) and **2**(b).



(a)



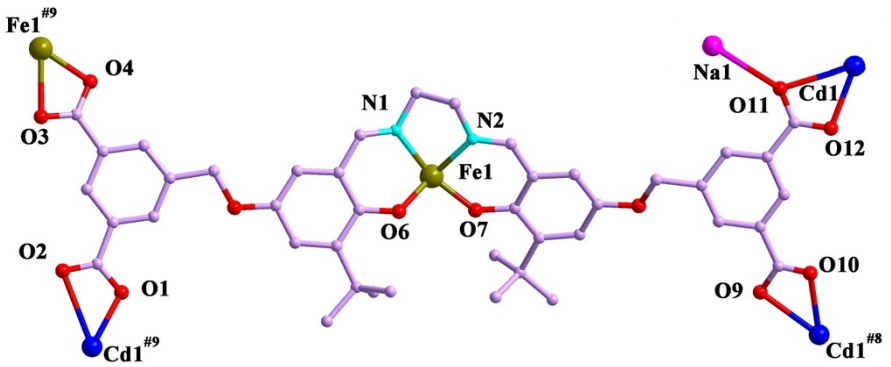
(b)

Fig. S3 The EDS analysis of the frameworks **1**(a) and **2**(b).

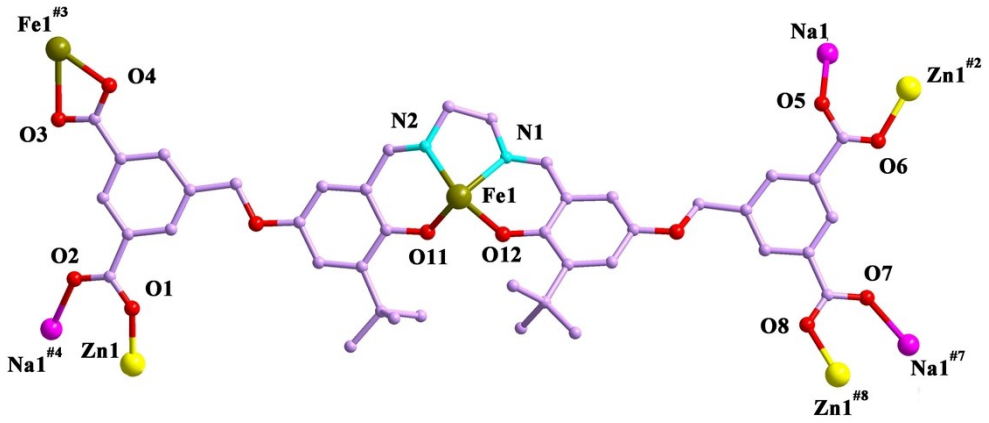
Table S1 The ICP analyses of the frameworks **1** and **2**.

1		**2**	
Element	Conc.(ug/mL)	Element	Conc.(ug/mL)
Fe	55.962	Fe	39.115
Cd	114.794	Zn	45.323
Na	11.932	Na	16.522

Coordination modes of L^{6-} anions in 1 and 2. From the structural description, we can see that both the internal [N_2O_2] pockets of L^{6-} anions in **1** and **2** are embedded by Fe(III) ions, while the external tetracarboxylate groups adopt different coordination modes (Fig. S2). For **1,** the external carboxylates of L^{6-} anion are ligated by one Fe(III), one Na(I) and three Cd(II) atoms, while they attach to one Fe(III), three Na(I) and three Zn(II) atoms in framework **2**.



(a)



(b)

Fig. S4 Coordination modes of L^{6-} anions in **1** (a) and **2** (b).

X-ray crystallography. Single-crystal X-ray data of compounds **1** and **2** were collected on an Oxford Diffraction Model Gemini R Ultra diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Direct methods were used to solve the structures on SHELXL-97 and all of the structures were refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX.[1-3] Absorption corrections were applied by using a multiscan technique. The disordered atoms in **1** (O2w) and **2** (O2w, O3w) were split into two sites with a total occupancy of 1. All non-hydrogen atoms were refined with anisotropic temperature parameters. The crystal samples of **1** and **2** show the relatively weak diffraction because of highly disordered solvents in the frameworks. During the refinement, SQUEEZE function in PLATON were applied.[4] The lattice molecules in **1** (one $(CH_3)_2NH^{2+}$ cation, four free water and four free DMF molecules) and **2** (two free water and two free DMF molecules) were demonstrated by the difference Fourier maps of original X-ray data, TGA data and elemental analyses. Selected distances and angles are listed in Tables S2 and S3.

Photocatalytic measurement. The photocatalytic degradation experiment was performed through a conventional process in aqueous solution. Crystals **1** or **2** (100 mg) and 30% H_2O_2 (2 mL, 15 mg·L^{-1}) were added into CP solutions (100 mL, 66 mg·L^{-1}), and their pH values were adjusted to different values with HCl (1 M). To

guarantee adsorption-desorption equilibrium between the photocatalyst and CP, the samples in tubular quartz reactor (100 mL) was stirred in the dark for 20 min. Then, the mixture was stirred under the irradiation of Hg lamp, which was used as the visible light source with a cutoff filter. At 20 min intervals, a series of 7 mL samples were taken out from the reaction system and separated by centrifugation to obtain the supernatant liquid. The photocatalytic decomposition separated samples were monitored by GC, and 2-pentanone was used as internal standard.

Notes and references

1. G. M. Sheldrick, *SHELXS-97 Programs for X-ray Crystal Structure Solution*, University of Goettingen, Germany, 1997.
2. G. M. Sheldrick, *SHELXL-97 Programs for X-ray Crystal Structure Refinement*; University of Goettingen, Germany, 1997.
3. L. J. Farrugia, *WINGX A Windows Program for Crystal Structure Analysis*, University of Glasgow, Glasgow, UK, 1988.
4. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.

Table S2 Selected bond distances (Å) and angles (°) for **1**.

Fe(1)-O(7)	1.874(4)	Cd(1)-O(1)$^{\#2}$	2.159(6)
Fe(1)-O(6)	1.891(4)	Cd(1)-O(12)	2.241(9)
Fe(1)-O(4)$^{\#1}$	2.029(4)	Cd(1)-O(10)$^{\#3}$	2.269(8)
Fe(1)-N(1)	2.097(5)	Cd(1)-O(9)$^{\#4}$	2.438(7)
Fe(1)-N(2)	2.118(5)	Cd(1)-O(13)	2.52(2)
Fe(1)-O(3)$^{\#1}$	2.305(5)	Cd(1)-O(13')	2.36(2)
Na(1)-O(11)	2.975(1)	Cd(1)-O(11)$^{\#3}$	2.645(7)
Na(1)-O(1W)	1.893(8)	Na(1)-O(2W')	2.73(2)
Na(1)-O(2W)	2.138(7)	O(7)-Fe(1)-O(6)	98.9(2)
N(1)-Fe(1)-N(2)	76.0(2)	O(7)-Fe(1)-O(4)$^{\#1}$	103.8(2)
O(7)-Fe(1)-O(3)$^{\#1}$	95.2(2)	O(6)-Fe(1)-O(4)$^{\#1}$	90.7(2)
O(6)-Fe(1)-O(3)$^{\#1}$	149.4(2)	O(7)-Fe(1)-N(1)	161.5 (2)

O(4)$^{\#1}$-Fe(1)-O(3)$^{\#1}$	59.6(2)	O(6)-Fe(1)-N(1)	86.3(2)
N(1)-Fe(1)-O(3)$^{\#1}$	88.7(2)	O(4)$^{\#1}$-Fe(1)-N(1)	93.8(2)
N(2)-Fe(1)-O(3)$^{\#1}$	88.9(2)	O(7)-Fe(1)-N(2)	86.0(2)
O(1)$^{\#2}$-Cd(1)-O(12)	158.6(3)	O(6)-Fe(1)-N(2)	118.7(2)
O(1$^{)\#2}$-Cd(1)-O(10)$^{\#3}$	111.9(3)	O(4)$^{\#1}$-Fe(1)-N(2)	147.4(2)
O(12)-Cd(1)-O(10)$^{\#3}$	89.2(4)	O(10)$^{\#3}$-Cd(1)-O(11)$^{\#3}$	84.8(3)
O(1)$^{\#2}$-Cd(1)-O(9)$^{\#4}$	89.6(3)	O(13')-Cd(1)-O(11)$^{\#3}$	103.0(1)
O(12)-Cd(1)-O(9)$^{\#4}$	102.0(4)	O(9)$^{\#4}$-Cd(1)-O(11)$^{\#3}$	130.6(3)
O(10)$^{\#3}$-Cd(1)-O(9)$^{\#4}$	49.9(3)	O(13)-Cd(1)-O(11)$^{\#3}$	123.7(8)
O(1)$^{\#2}$-Cd(1)-O(13)	84.2(6)	O(12)-Cd(1)-O(11)$^{\#3}$	52.1(3)
O(12)-Cd(1)-O(13)	79.9(6)	O(9)$^{\#4}$-Cd(1)-O(13)	81.3(1)
O(10)$^{\#3}$-Cd(1)-O(13)	126.5(1)	O(1$^{)\#2}$-Cd(1)-O(11)$^{\#3}$	130.6(3)
O(1W)-Na(1)-O(2W)	77.0(4)	O(1W)$^{\#3}$-Na(1)-O(2W)	103.0(4)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -x, y-1/2, -z-1/2 ; $^{\#2}$ x+1, y, z+1 ; $^{\#3}$ -x+1, -y+1, -z+1 ; $^{\#4}$ -x+1, y+1/2, -z+3/2.

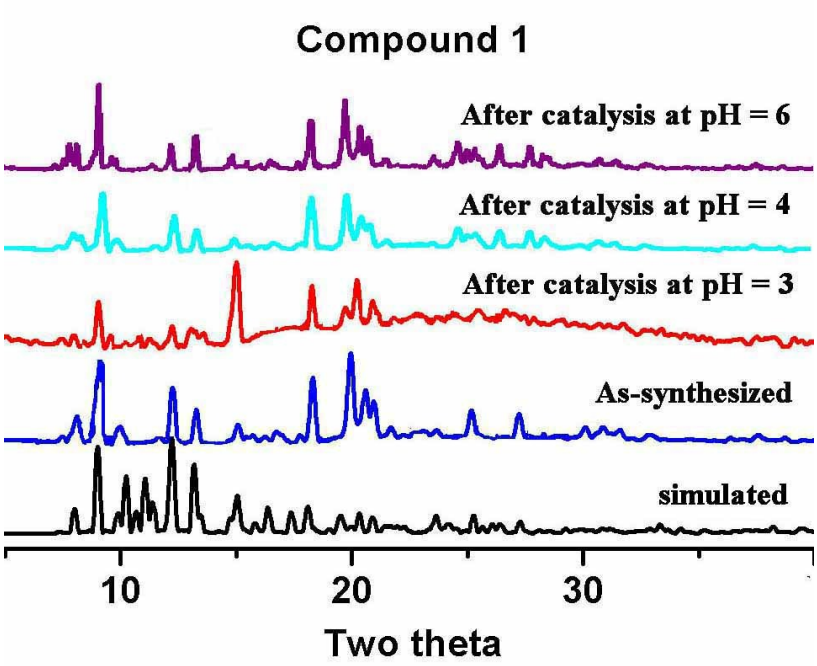
Table S3 Selected bond distances (Å) and angles (°) for **2**.

Na(1)-O(2W')	2.443(19)	Fe(1)-N(1)	2.114(5)
Na(1)-O(2W)	1.996(12)	Fe(1)-N(2)	2.091(6)
Na(1)-O(5)	1.972(11)	Fe(1)-O(3)$^{\#3}$	2.269(5)
Na(1)-O(2)$^{\#1}$	2.041(8)	Zn(1)-O(1)	1.900(6)
Na(1)-O(7)$^{\#2}$	2.061(10)	Zn(1)-O(6)$^{\#4}$	1.931(8)
Fe(1)-O(12)	1.868(5)	Zn(1)-O(8)$^{\#5}$	2.013(8)
Fe(1)-O(11)	1.900(4)	Zn(1)-O(1W)	2.063(10)
Fe(1)-O(4)$^{\#3}$	2.065(5)	O(12)-Fe(1)-O(11)	98.83(18)
O(2W)-Na(1)-O(5)	78.2(4)	O(12)-Fe(1)-O(4)$^{\#3}$	104.3 (2)
O(2W)-Na(1)-O(2)$^{\#1}$	75.3(4)	O(11)-Fe(1)-O(4)$^{\#3}$	90.74(18)
O(5)-Na(1)-O(2)$^{\#1}$	110.2(4)	O(12)-Fe(1)-N(2)	161. 43 (19)
O(2W)-Na(1)-O(7)$^{\#2}$	167.2(5)	O(11)-Fe(1)-N(2)	86.16(19)

O(5)-Na(1)-O(7)$^{\#2}$	99.3(4)	O(4)$^{\#3}$-Fe(1)-N(2)	93.4(2)
O(2)$^{\#1}$-Na(1)-O(7)$^{\#2}$	117.1(4)	O(12)-Fe(1)-N(1)	86.0(2)
O(1)-Zn(1)-O(6)$^{\#4}$	142.5(4)	O(11)-Fe(1)-N(1)	118.5(2)
O(1)-Zn(1)-O(8)$^{\#5}$	106.0(4)	O(4)$^{\#3}$-Fe(1)-N(1)	147.5 (2)
O(6)$^{\#4}$-Zn(1)-O(8)$^{\#5}$	103.9(4)	N(2)-Fe(1)-N(1)	76.0(2)
O(1)-Zn(1)-O(1W)	99.5(4)	O(12)-Fe(1)-O(3)$^{\#3}$	96.0(2)
O(6)$^{\#4}$-Zn(1)-O(1W)	97.8(4)	O(11)-Fe(1)-O(3)$^{\#3}$	150.14(17)
O(8)$^{\#5}$-Zn(1)-O(1W)	111.2(4)	O(4)$^{\#3}$-Fe(1)-O(3)$^{\#3}$	60.40(18)
N(1)-Fe(1)-O(3)$^{\#3}$	88.14(15)	N(2)-Fe(1)-O(3)$^{\#3}$	88.0(16)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ -x+2, y-1/2, -z+5/2 ; $^{\#2}$ x+1, y, z+1 ; $^{\#3}$ -x+1, y+1/2, -z+1/2 ; $^{\#4}$ x-1, y, z-1; $^{\#5}$ -x+1, y-1/2, -z+3/2.



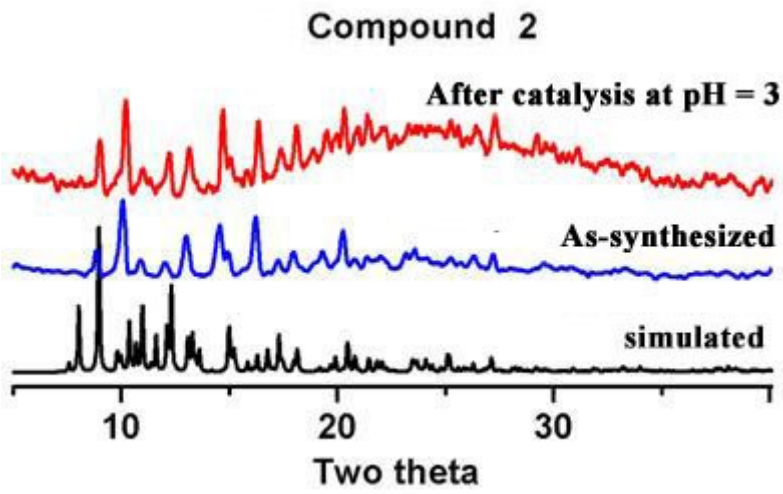


Figure S5. PXRD patterns for **1** and **2** after photodegradation of 4-CP.

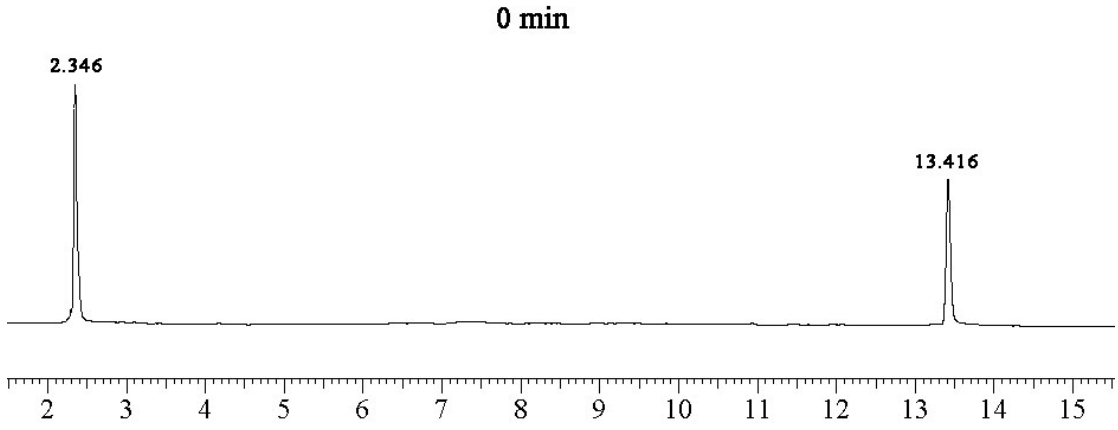
Table S4

PEAK LIST

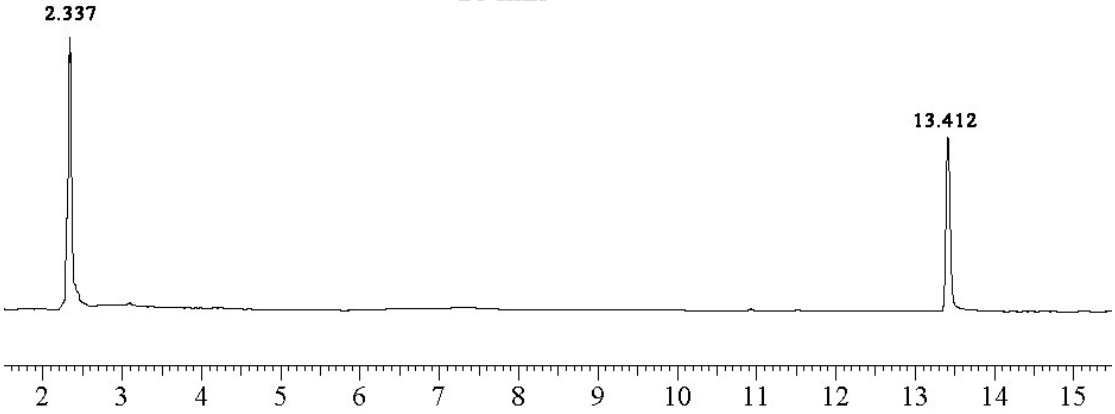
RT: 0.00-14.50

Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 4-CP)

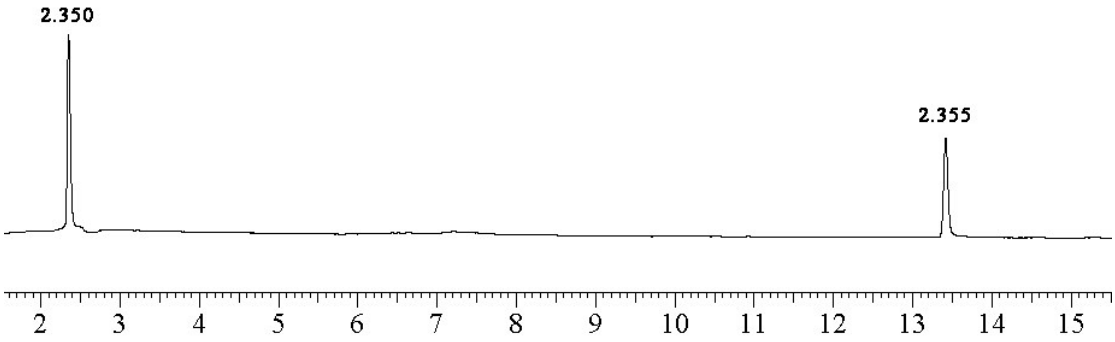
	0 min	20 min	40 min	60 min	80 min
Apex	2.346	2.377	2.350	2.355	2.352
	13.416	13. 412	13.415	13.413	13.421
Area	125625	153316	96131	124360	132630
	109527	130896	77300	99594	101682
Mass	0.0391 g				
	0.00782g				



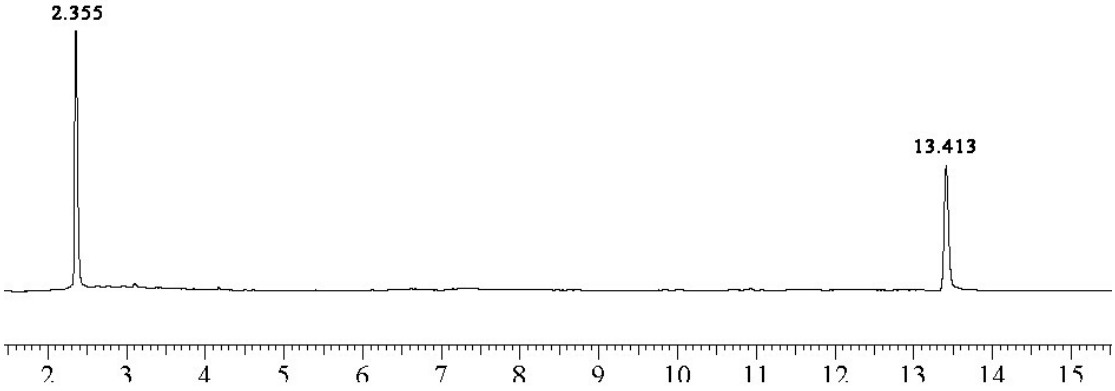
20 min

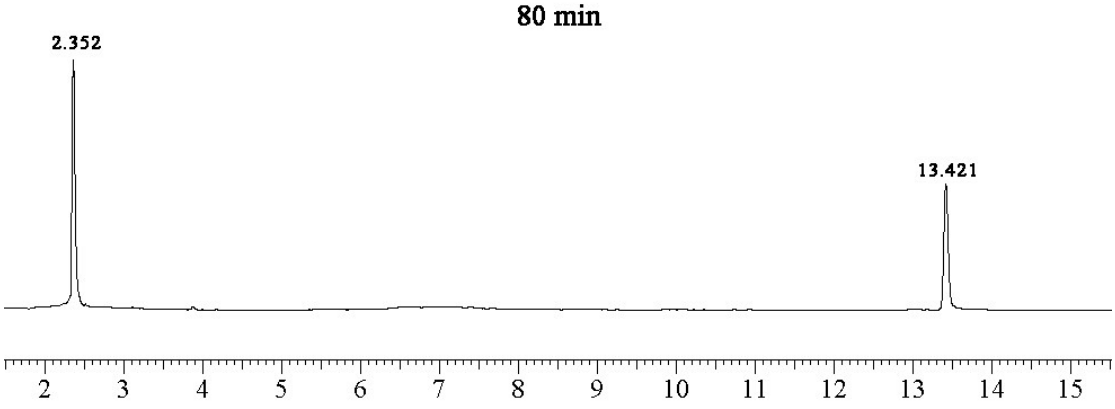


40 min



60 min

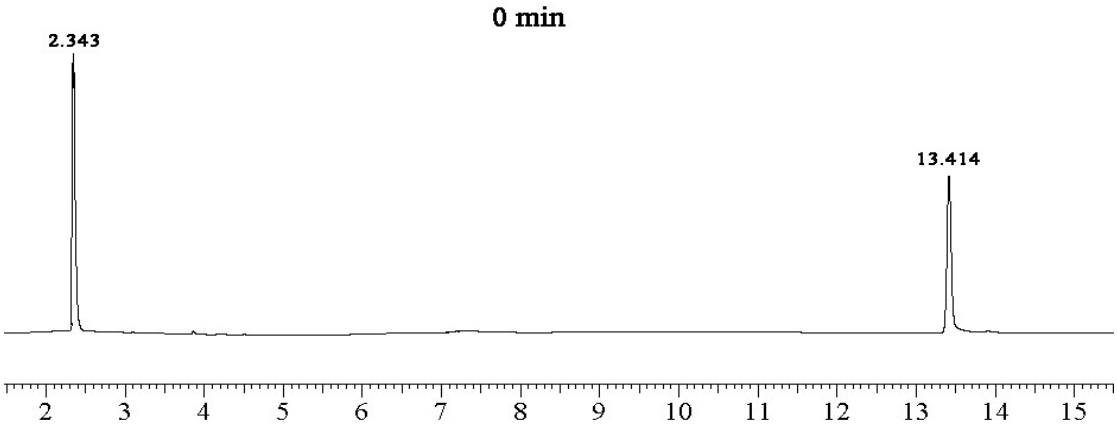


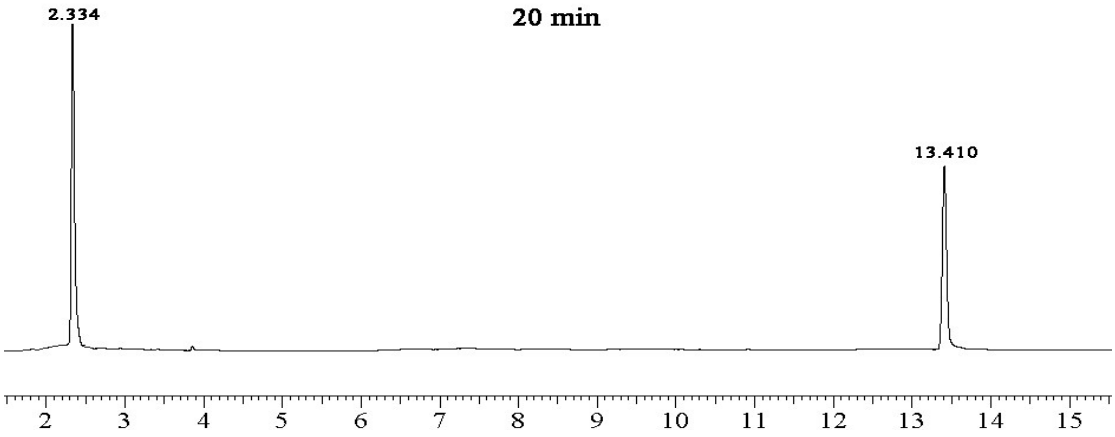


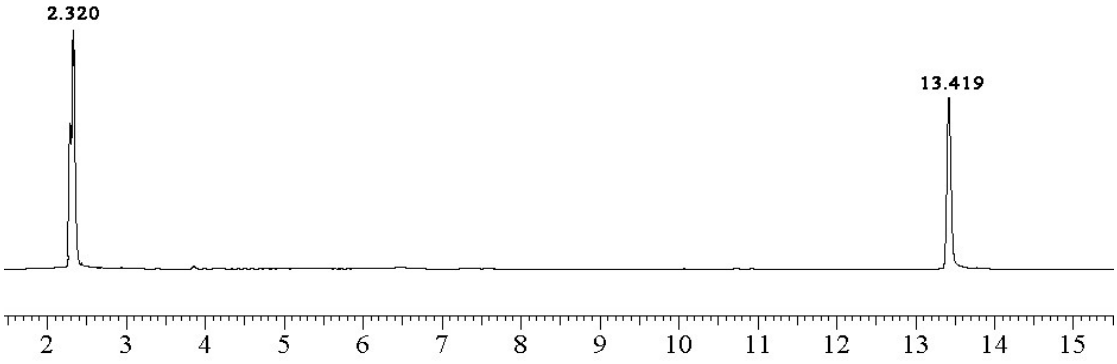
(a)

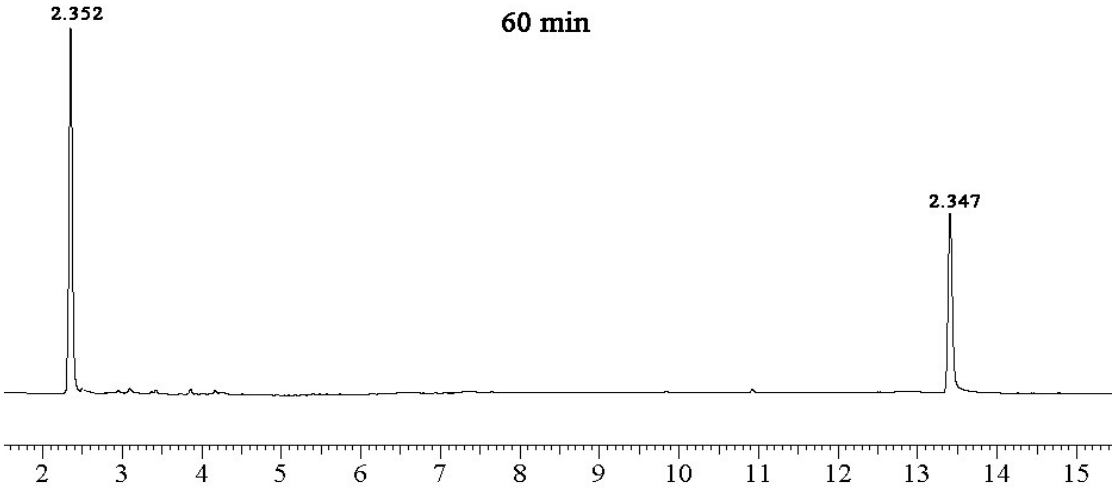
PEAK LIST
RT: 0.00-14.50
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 4-CP)

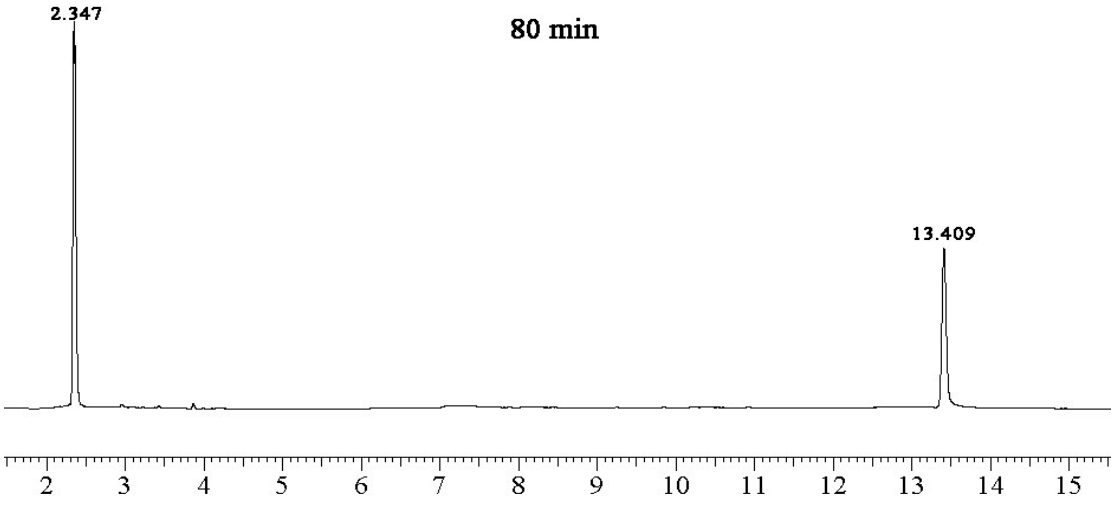
	0 min	20 min	40 min	60 min	80 min
Apex	2.343	2.334	2.320	2.352	2.347
	13.414	13.410	13.419	13.406	13.409
Area	156190	207482	177495	212136	202817
	133736	167772	136370	147843	130443
Mass	0.0340 g				
	0.00680 g				




2.334
20 min
13.410
2 3 4 5 6 7 8 9 10 11 12 13 14 15


40 min
2.320
13.419
2 3 4 5 6 7 8 9 10 11 12 13 14 15

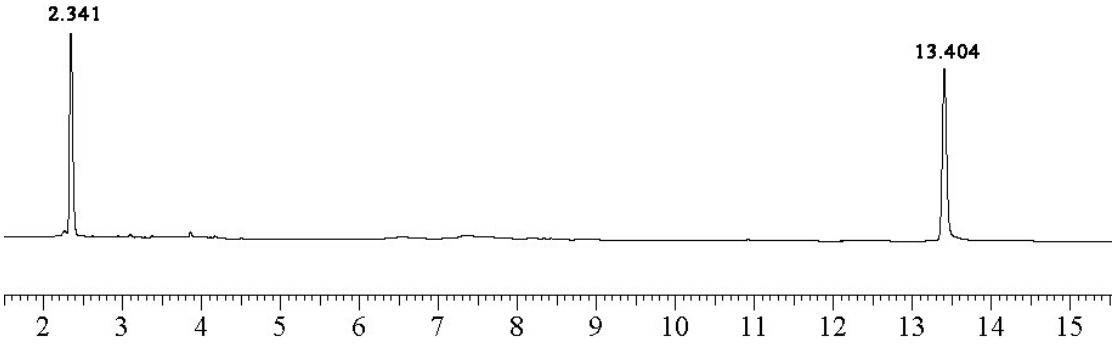

2.352
60 min
2.347
2 3 4 5 6 7 8 9 10 11 12 13 14 15

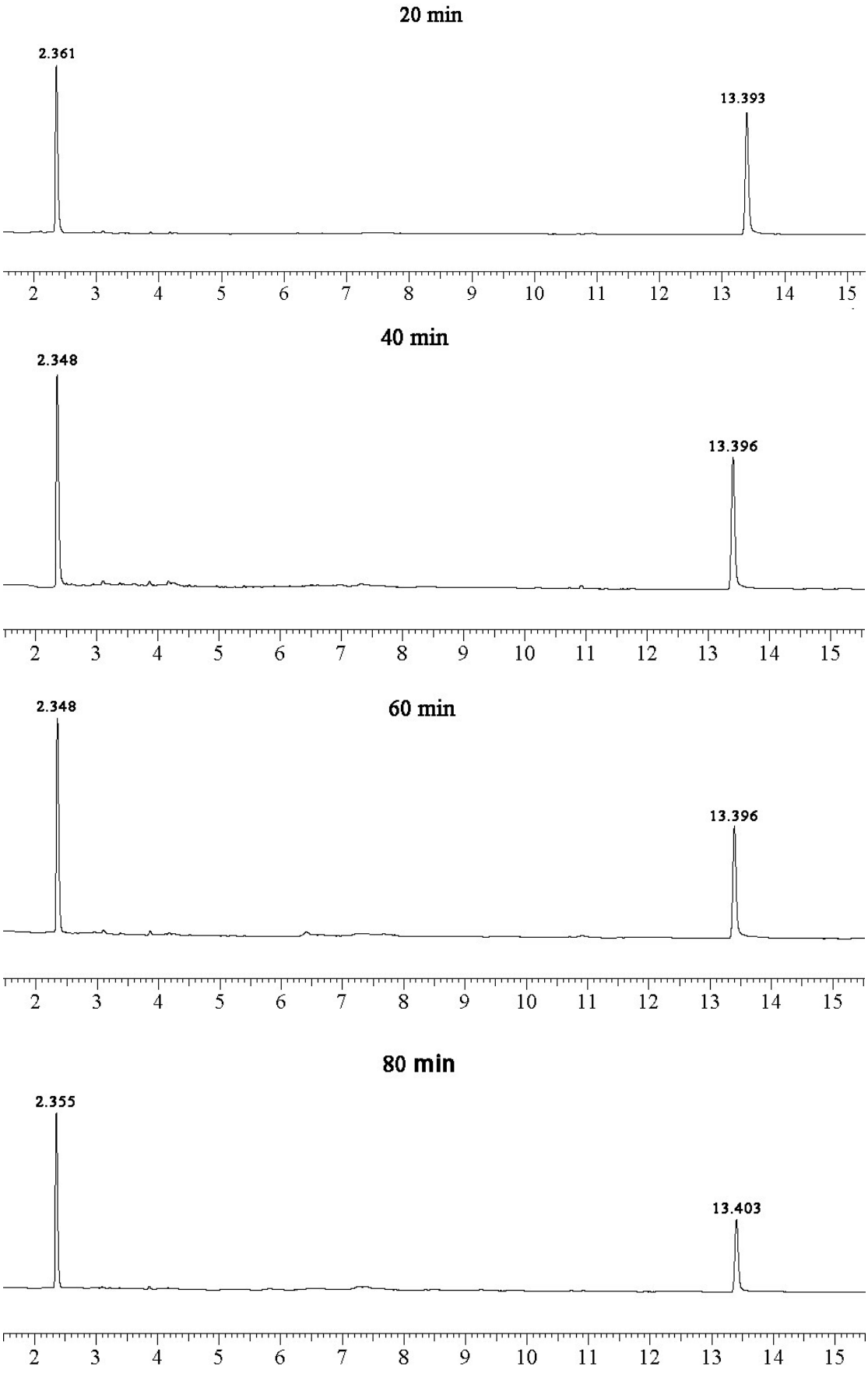


(b)

PEAK LIST
RT: 0.00-14.50
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 4-CP)

	0 min	20 min	40 min	60 min	80 min
Apex	2.341	2.361	2.347	2.348	2.355
	13.404	13.393	13.397	13.396	13.403
Area	102978	236822	144726	147739	109111
	132005	256290	138259	119128	72728
Mass	0.0368 g				
	0.00736 g				



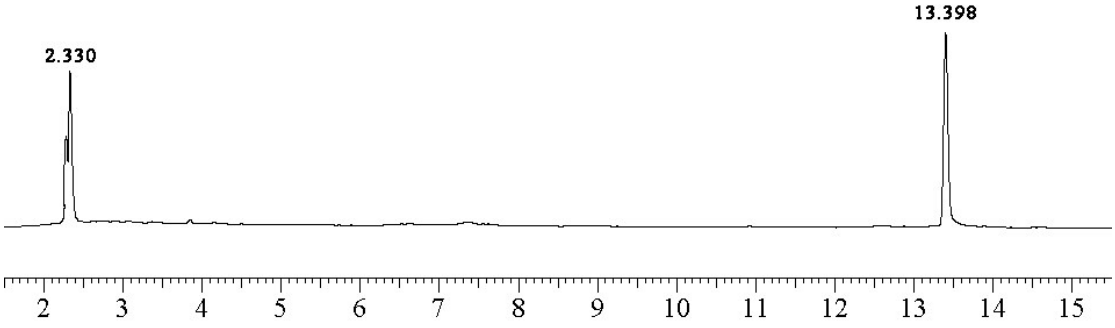

20 min
2.361
13.393
2 3 4 5 6 7 8 9 10 11 12 13 14 15
40 min
2.348
13.396
2 3 4 5 6 7 8 9 10 11 12 13 14 15
60 min
2.348
13.396
2 3 4 5 6 7 8 9 10 11 12 13 14 15
80 min
2.355
13.403
2 3 4 5 6 7 8 9 10 11 12 13 14 15

(c)

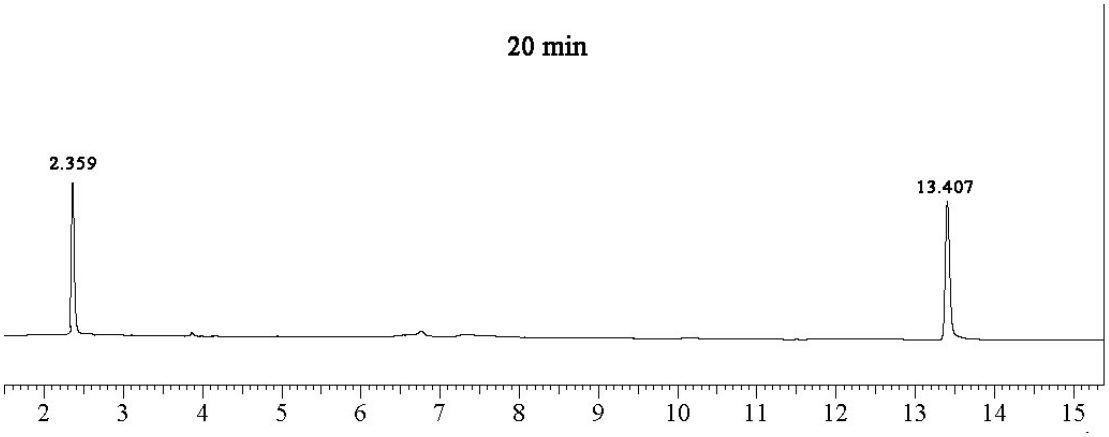
PEAK LIST
RT: 0.00-14.50
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 4-CP)

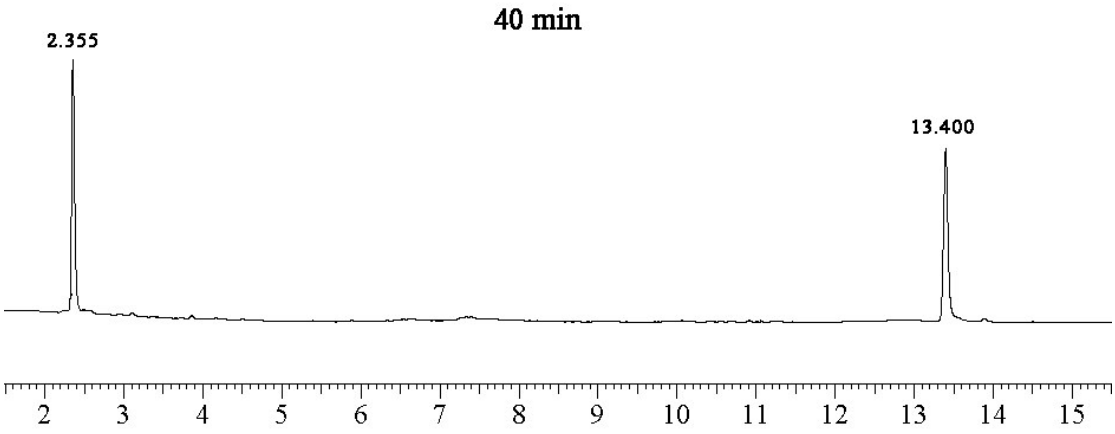
	0 min	20 min	40 min	60 min	80 min
Apex	2.330	2.359	2.355	2.346	2.337
	13.398	13.407	13.400	13.405	13.400
Area	73007	82701	59092	85043	128319
	152403.	120287	66576	87755	105198
Mass	0.0391g				
	0.00782g				

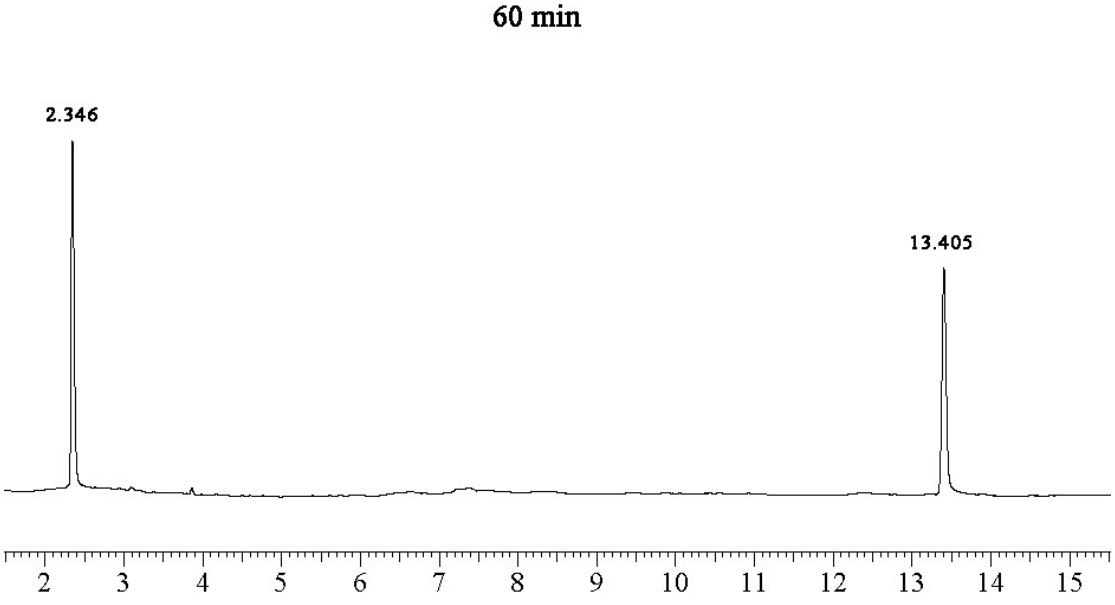
0 min

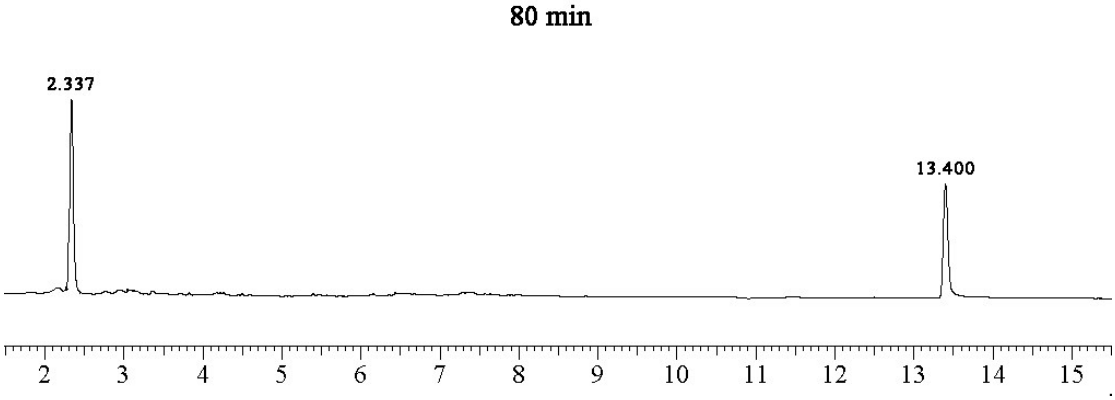


20 min









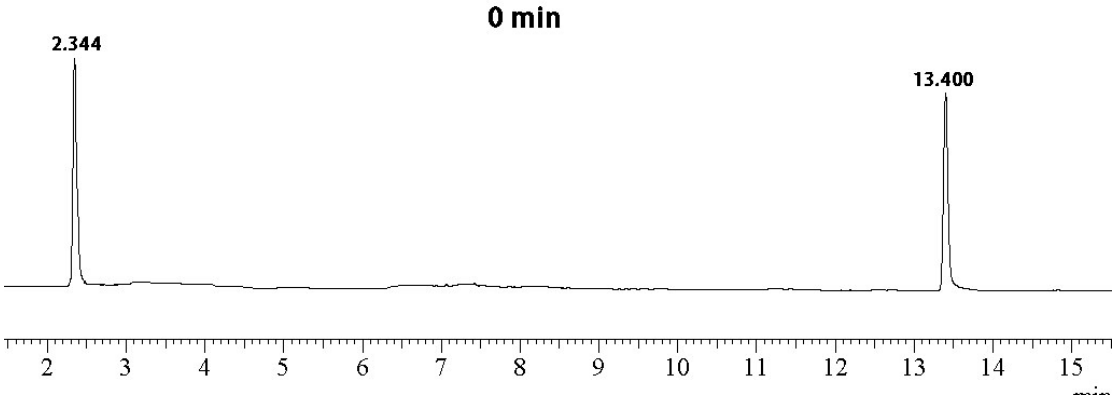
(d)

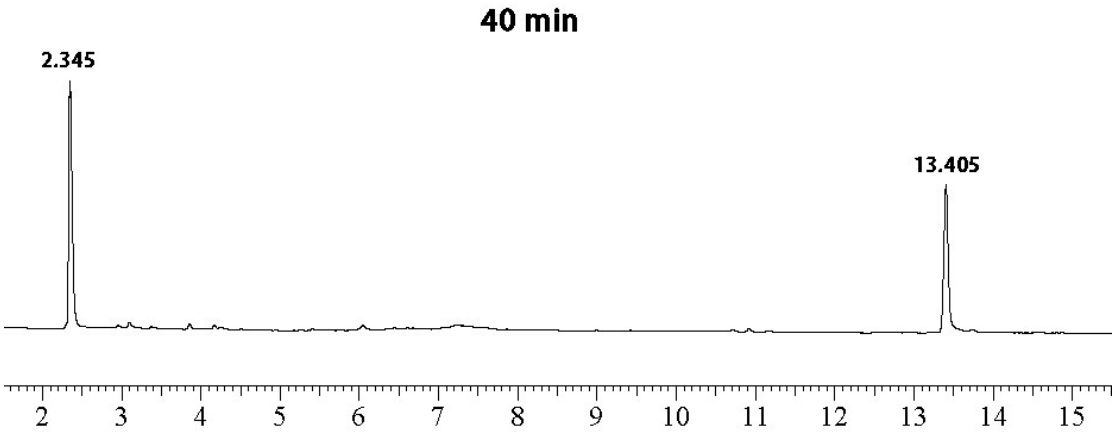
PEAK LIST

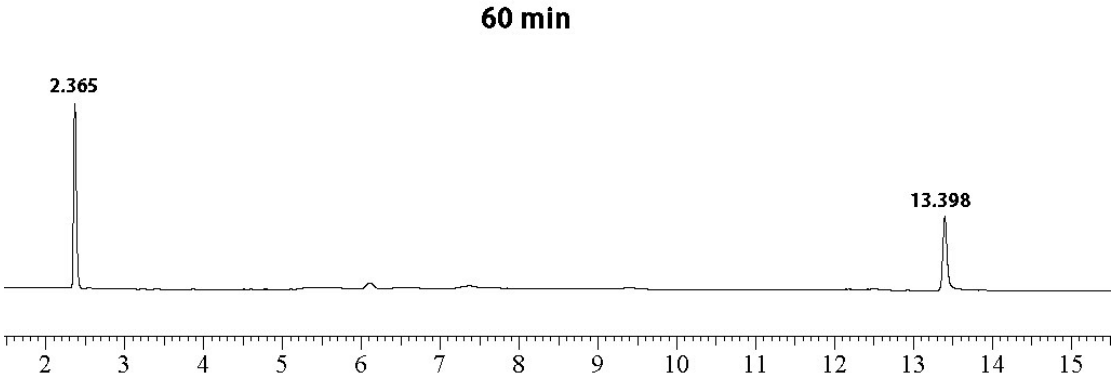
RT: 0.00-14.50

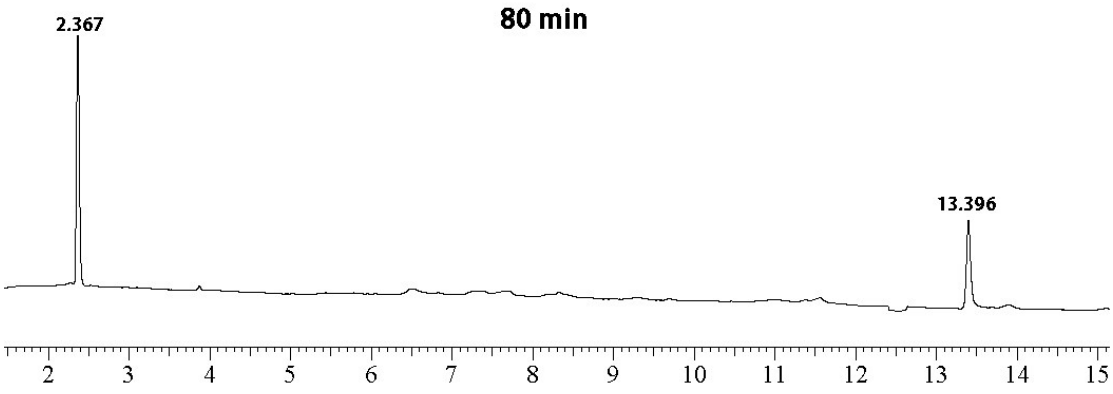
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 4-CP)

	0 min	20 min	40 min	60 min	80 min
Apex	2.344	2.349	2.345	2.365	2.367
	13.400	13.402	13.405	13.398	13.396
Area	158032	119609	136142	97401	66340
	176307.	113873	115046	64692	36134
Mass	0.0391g				
	0.00782g				









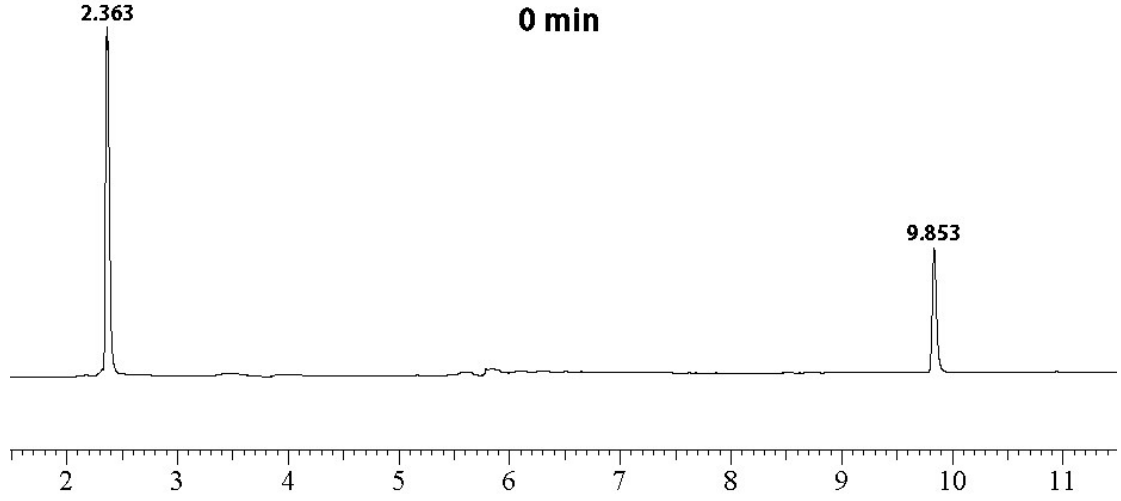
(e)

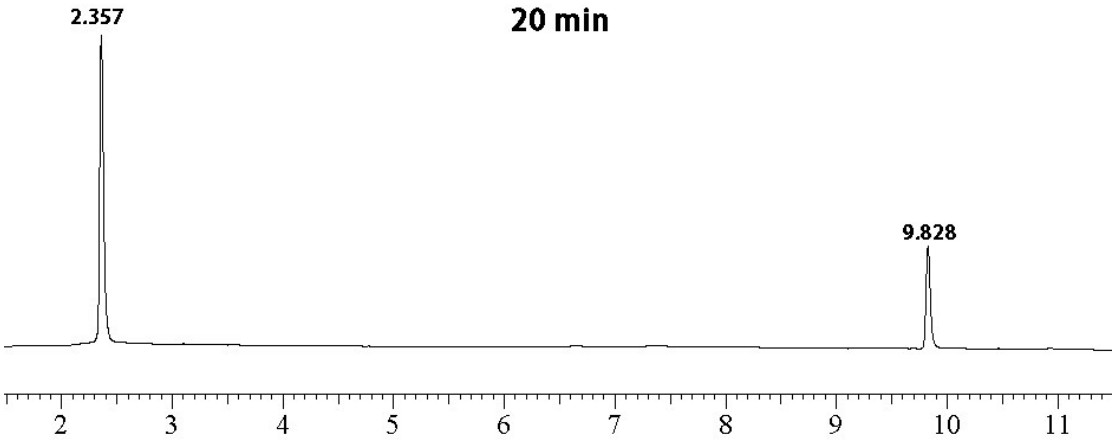
PEAK LIST

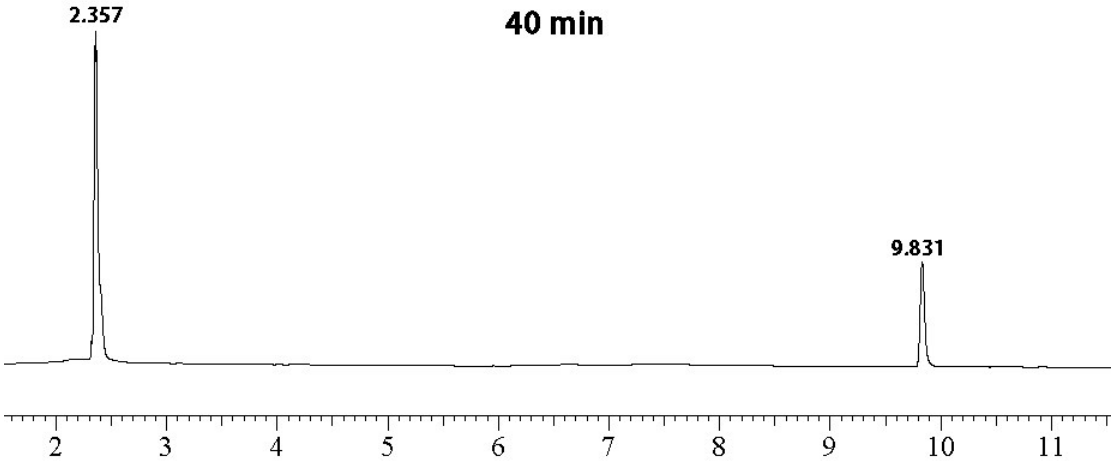
RT: 0.00-14.50

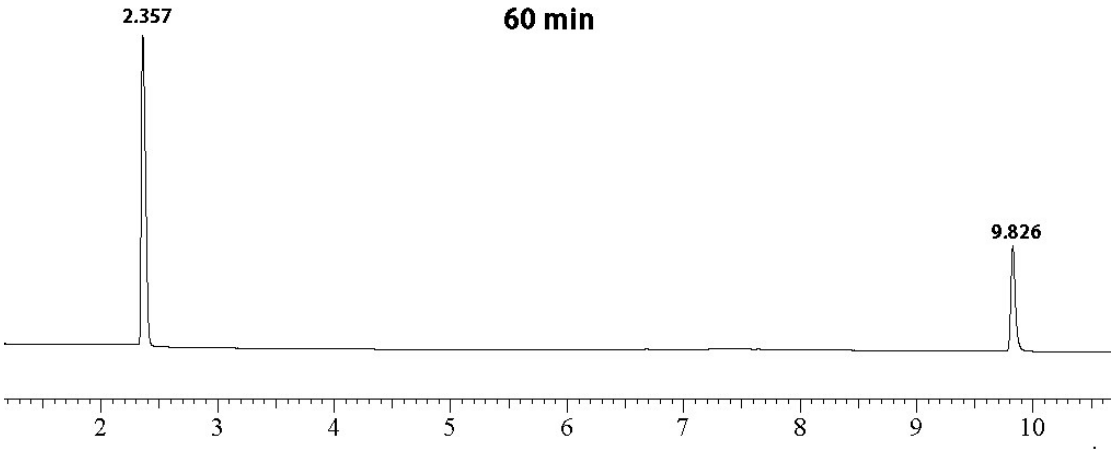
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 2,4-DCP)

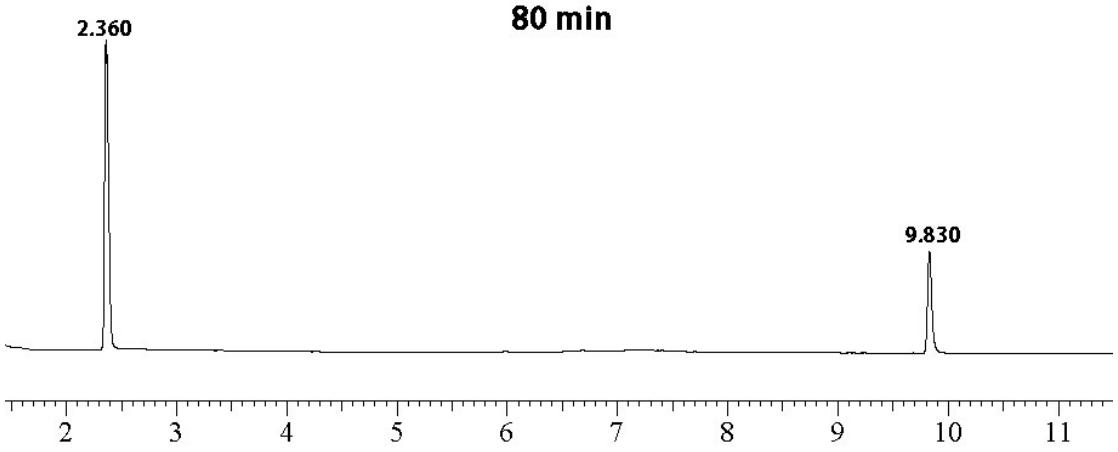
	0 min	20 min	40 min	60 min	80 min
Apex	2.363	2.357	2.357	2.357	2.360
	9.835	9.828	9.831	9.826	9.830
Area	152454	138425	148318	160711	143401
	63033	53465	55989	59854	52109
Mass	0.0328g				
	0.00656g				




20 min
2.357
9.828
2
3
4
5
6
7
8
9
10
11


40 min
2.357
9.831
2
3
4
5
6
7
8
9
10
11


60 min
2.357
9.826
2
3
4
5
6
7
8
9
10



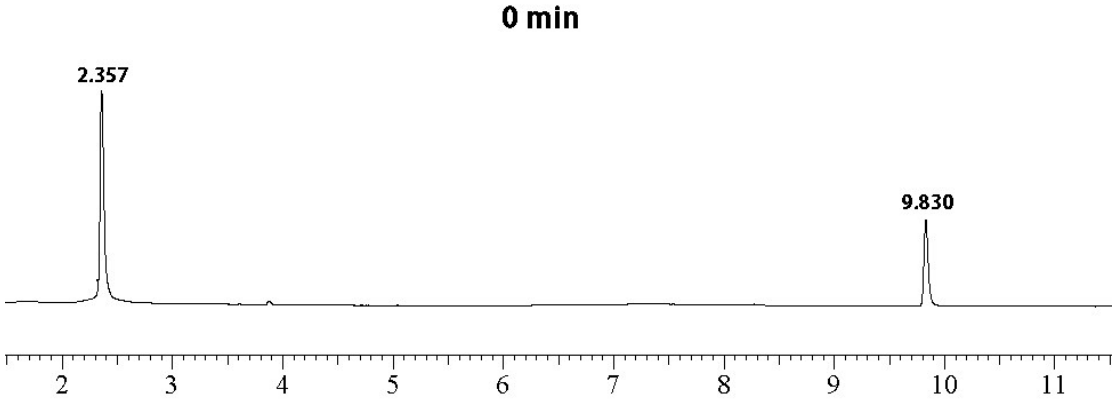
(f)

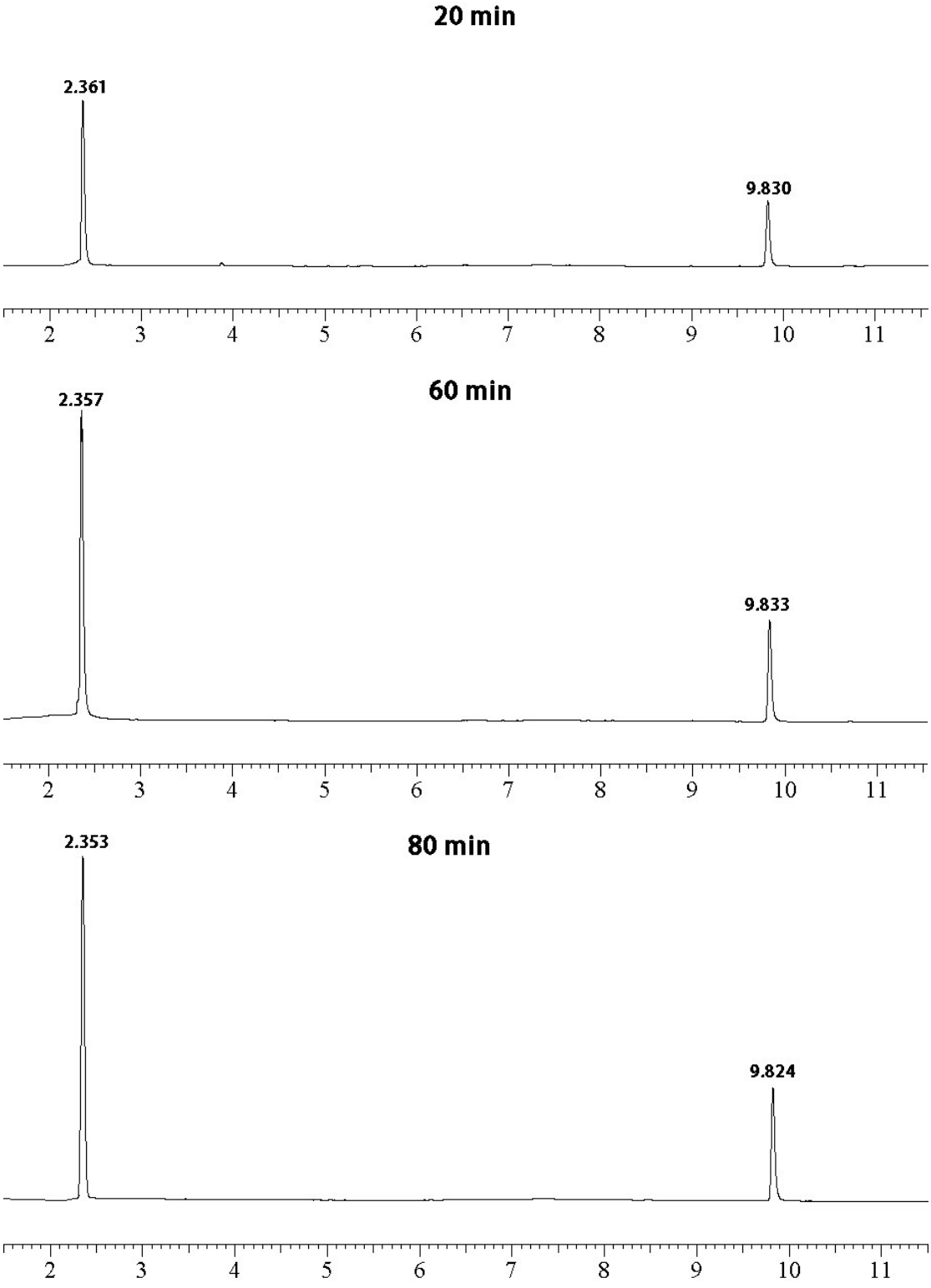
PEAK LIST

RT: 0.00-14.50

Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 2,4-DCP)

	0 min	20 min	40 min	60 min	80 min
Apex	2.357	2.361	2.366	2.357	2.353
	9.830	9.830	9.835	9.833	9.824
Area	88191	84551	69494	154975	200432
	46638	41554	31512	61931	69717
Mass	0.0286g				
	0.00572 g				





(g)

PEAK LIST

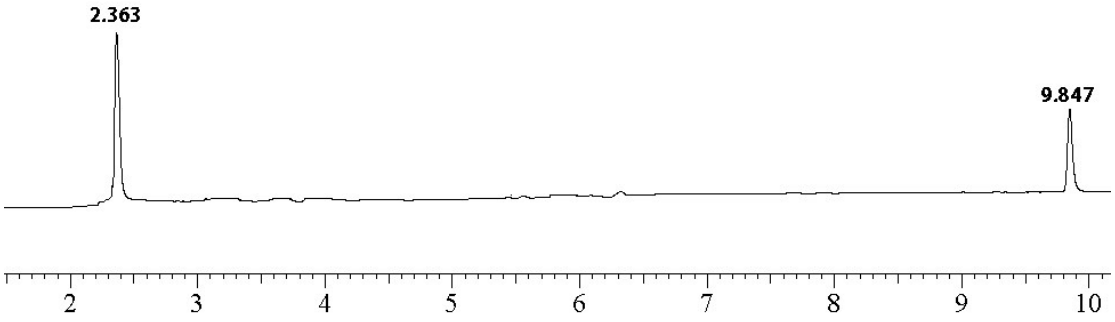
RT: 0.00-14.50

Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 2,4-DCP)

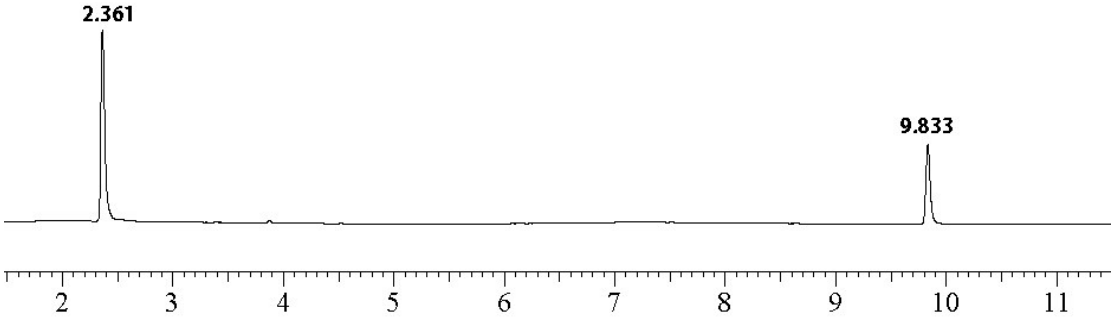
	0 min	20 min	40 min	60 min	80 min

Apex	2.363	2.361	2.367	2.360	2.362
	9.847	9.833	9.835	9.827	9.836
Area	81407	86120	163005	144246	163768
	46260	43257	71521	56596	57057
Mass	0.0307g				
	0.00614g				

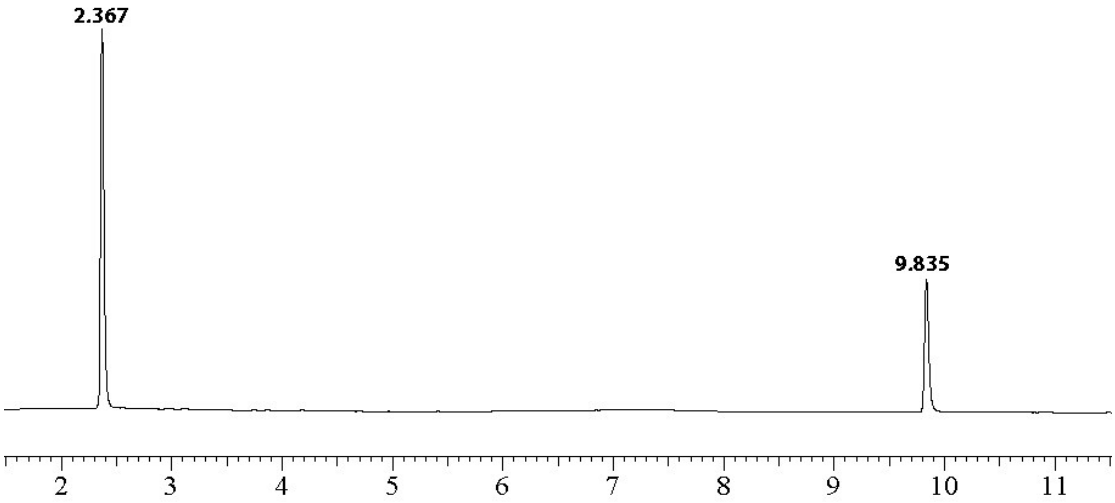
0 min

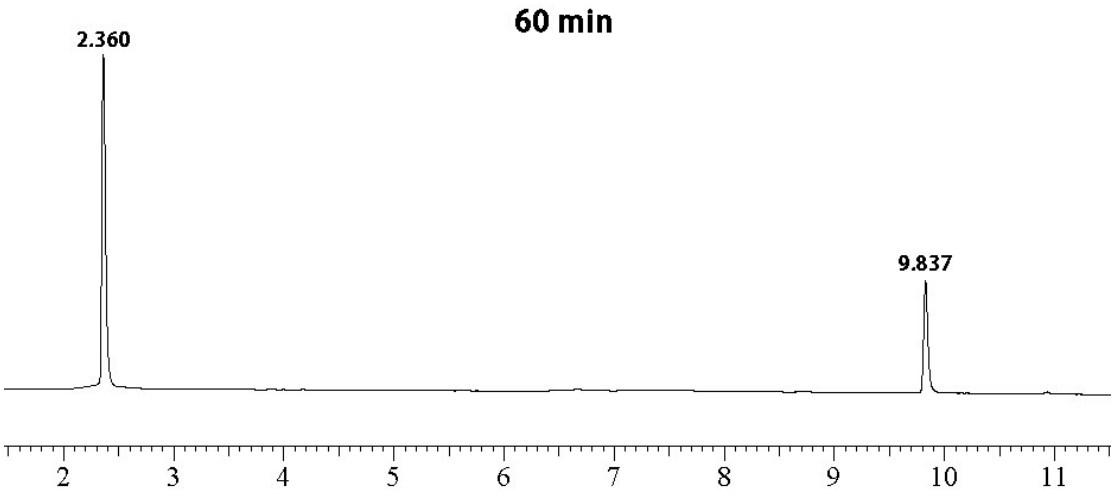


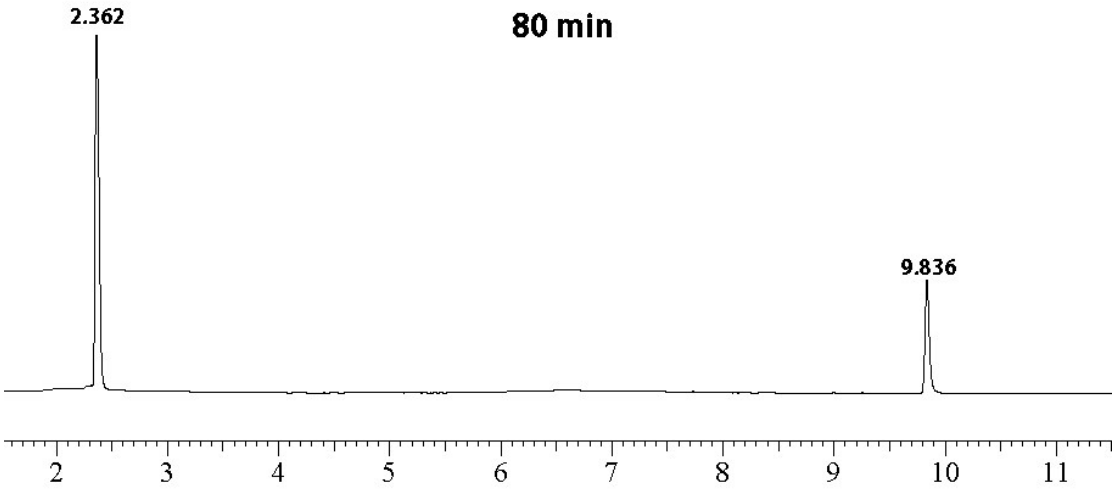
20 min



40 min







(h)

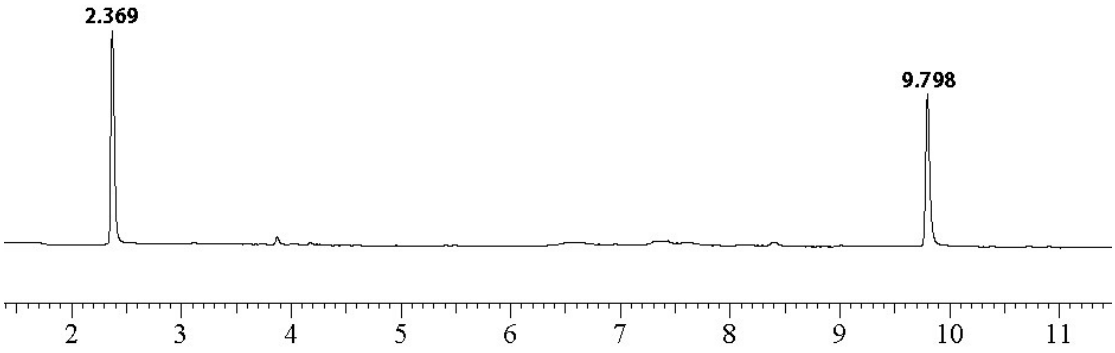
PEAK LIST

RT: 0.00-14.50

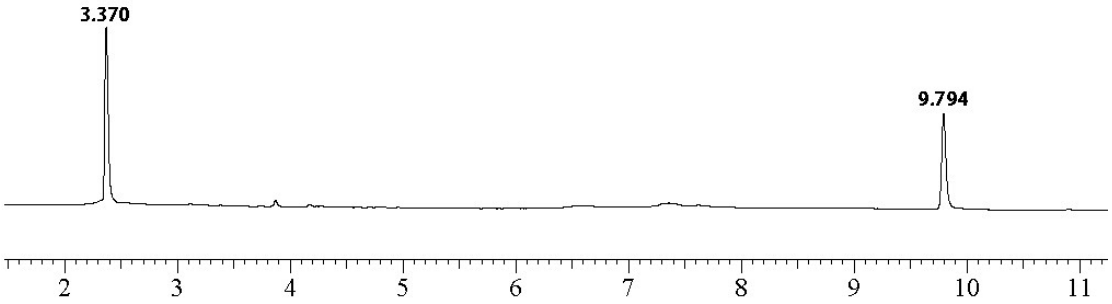
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 2,4-DCP)

	0 min	20 min	40 min	60 min	80 min
Apex	2.369	2.370	2.368	2.346	2.374
	9.798	9.794	9.796	9.800	9.802
Area	44382	37727	77548	83525	55488
	38329	26901	50686	51731	27227
Mass	0.0345g				
	0.00690 g				

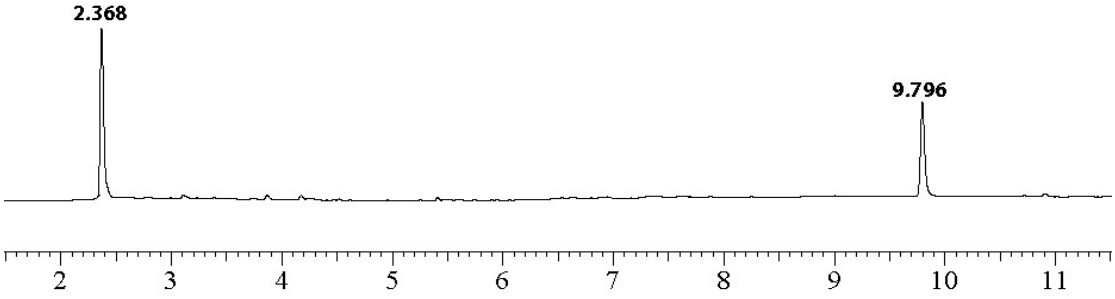
0 min



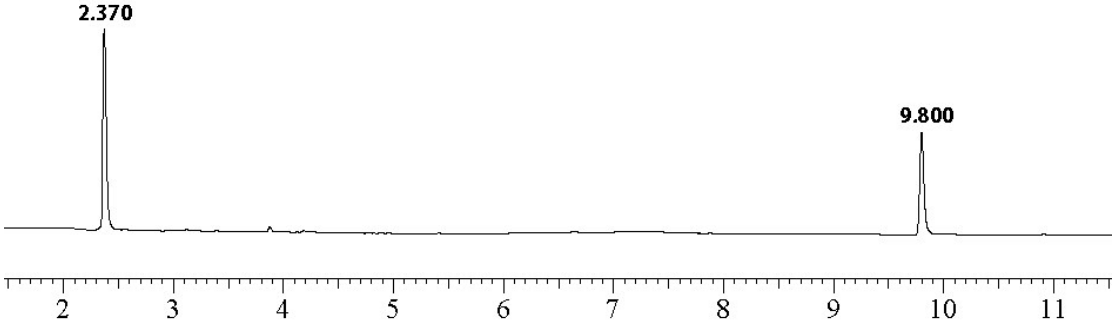
20 min

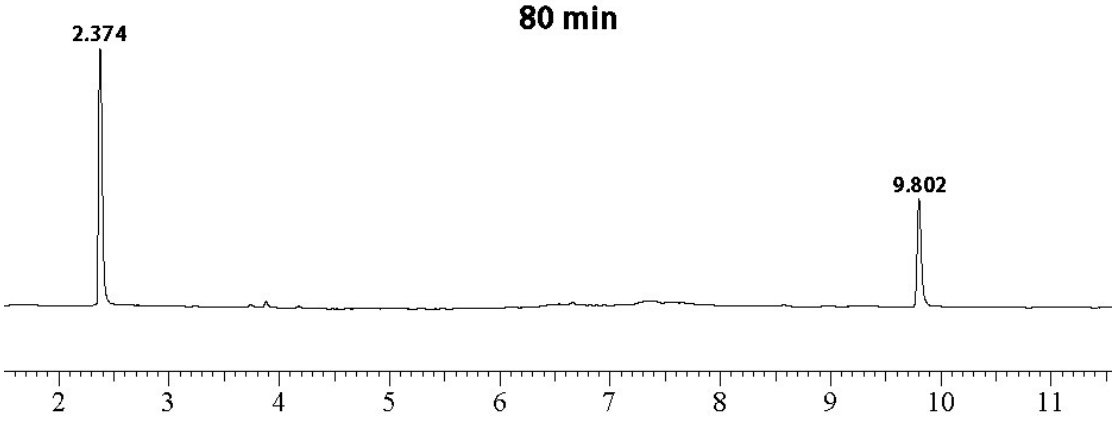


40 min



60 min

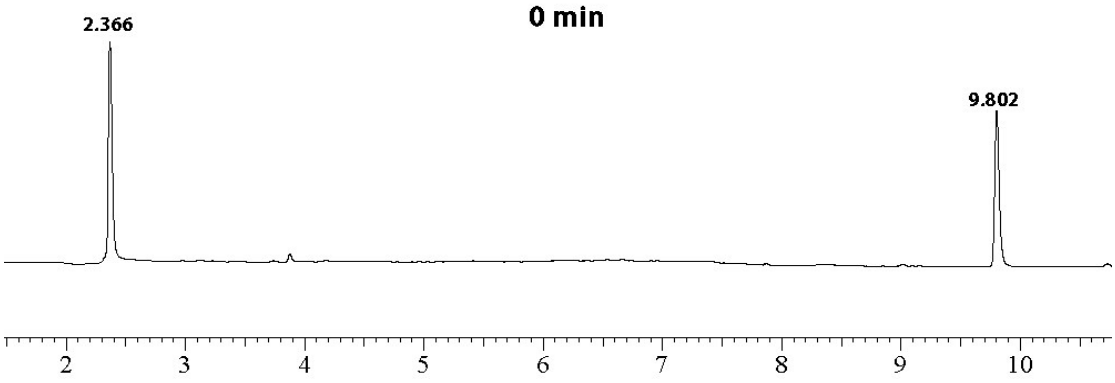


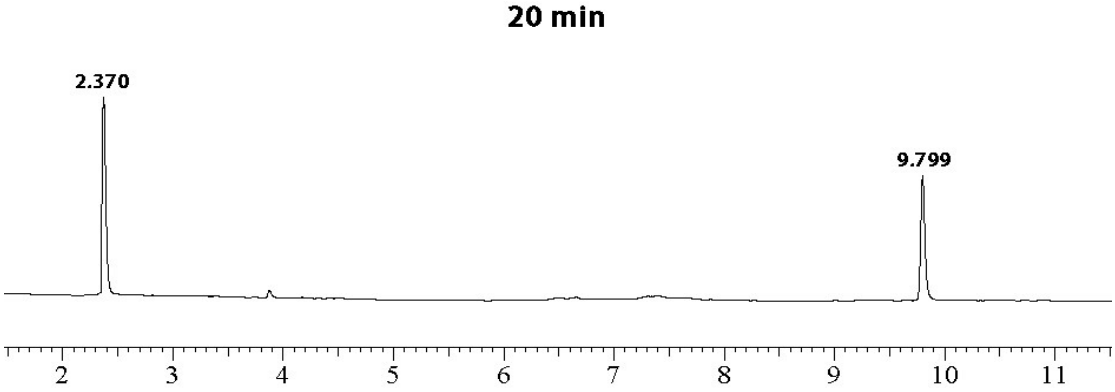


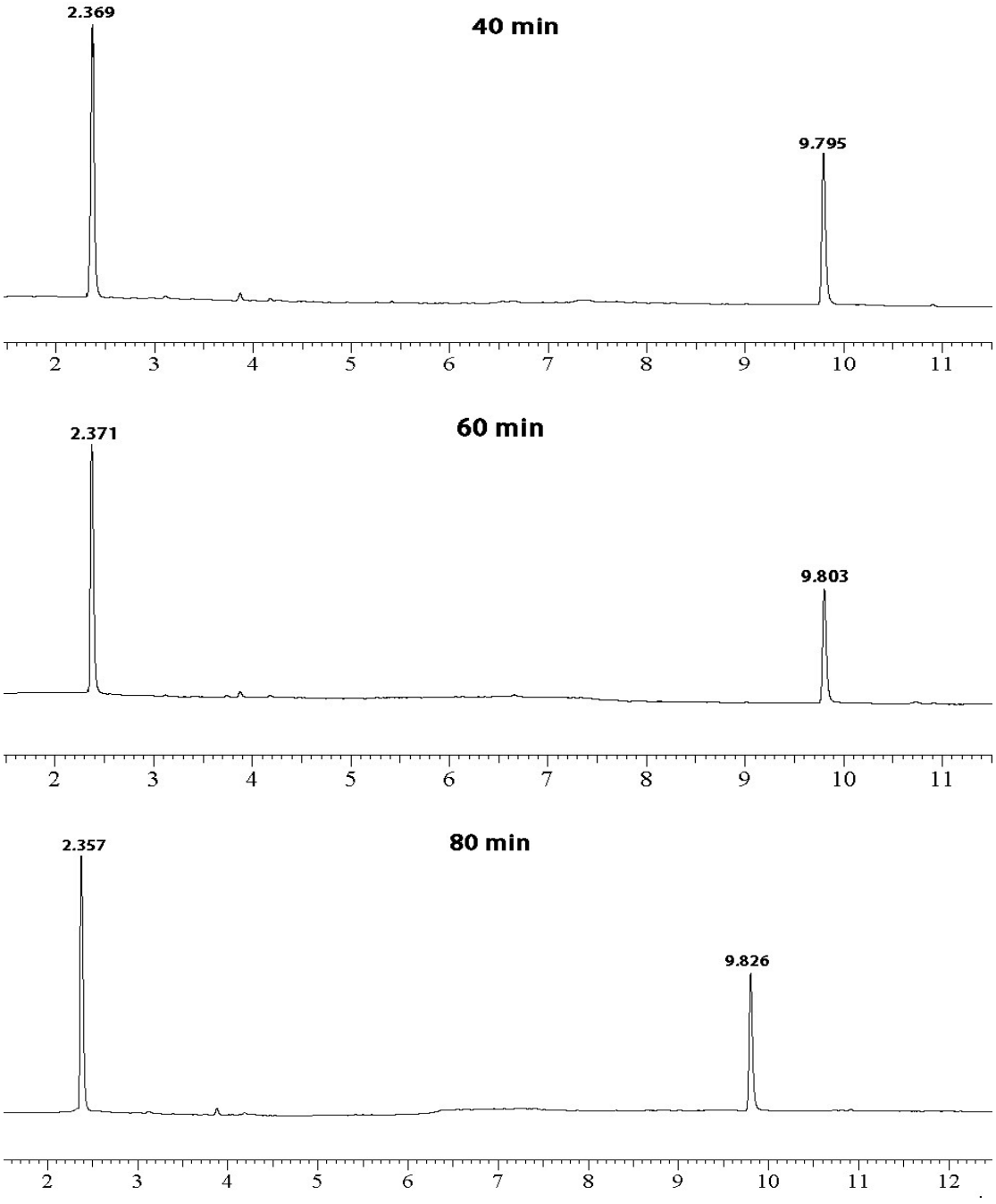
(i)

PEAK LIST
RT: 0.00-14.50
Number of measured peaks: 2 (the first peak is 2-pentanone, and the second peak is 2,4-DCP)

	0 min	20 min	40 min	60 min	80 min
Apex	2.366	2.370	2.369	2.371	2.357
	9.802	9.799	9.795	9.803	9.826
Area	52315	47464	90692	67242	160711
	45695	35639	56873	36314	59854
Mass	0.0302g				
	0.00606g				







(j)

Figure S6. (a)GC of blank experiment of 4-CP. (b) GC of 4-CP catalyzed by compound **2** at pH = 6. (c) GC of 4-CP catalyzed by compound **2** at pH = 4. (d) GC of 4-CP catalyzed by compound **2** at pH = 3. (e) GC of 4-CP catalyzed by compound **1** at pH = 3. (f)GC of blank experiment of 2,4-DCP. (g) GC of 2,4-DCP catalyzed by compound **2** at pH = 6. (h) GC of 2,4-DCP catalyzed by compound **2** at pH = 3. (i) GC of 4-CP catalyzed by compound **2** at pH = 4. (j) GC of 2,4-DCP catalyzed by compound **1** at pH = 4.