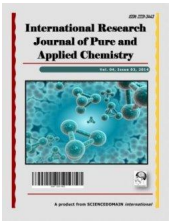

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Synthesis of Benzil by Air Oxidation of Benzoin and M(Salen) Catalyst

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Authors' contributions

This work was carried out in collaboration of all authors. Author YZ designed the study. All authors contributed in practical work and managed the analysis of the study. Author QS wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Bis salicylaldehyde ethylenediamine Schiff base (Salen) and its complexes with three metal ions (Co^{2+}, Ni^{2+}, Zn^{2+}) were prepared, and characterized by infrared spectroscopy(IR). Using air as oxygen source, the optimum reaction conditions for the catalytic oxidation of 0.05 mol benzoin by Co (Salen) were obtained by orthogonal test as follows: base KOH 2 g, catalyst 1.5 g, N, N-dimethylformamide(DMF) as solvent, reaction temperature 40 °C, reaction time 1 h. Under these conditions, the catalytic performances of different metal complexes were investigated. The catalytic activity of Co(Salen) was the best one, the yield of benzil was up to 93.6%, the number of Ni(Salen) and Zn(Salen) was 86.3% and 82.1%, respectively. The reused catalytic performance of M(Salen) complex was also studied. The catalytic activity of Co(Salen), Ni(Salen) and Zn(Salen) was stable after 4 times recycle, the yield of benzil was 71.4%, 63.3% and 57.4%, respectively, and it was easy for catalyst recycling. The oxidation product was certainly benzil with high purity according to the characterization results of melting point(MP), IR, high performance liquid chromatography(HPLC) and ^{1}H nuclear magnetic resonance(^{1}H NMR). Compared with the common synthetic method of benzil, this one has the advantages of friendly environment, low cost and easy operation. It is a simple and green way to synthesize benzoyl efficiently.

Keywords: Benzil; benzoin; M(Salen) catalyst; air oxidation; orthogonal experiment.

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1. INTRODUCTION

Benzil is an important organic intermediate and organic chemical raw material. It is synthesized by oxidation of benzoin and widely used in food, medicine, pesticide and other industries.

There are two methods for synthesizing benzil by oxidation of benzoin: One is non-catalytic oxidation. The benzil is prepared by oxidizing benzoin with an inorganic compound, or an organometallic compound, or a polymer, but there are problems such as large requirement of oxidant, intense reaction, large amount of by-products, serious pollution and so on. For example, Dip I et al. [1] reported that benzil was prepared from benzoin with ethyl acetate used as solvent, 40% trichloro isocyanuric acid(TCCA) as oxidant, the reaction time was as long as 24 h at room temperature, and the consumption of oxidant was greater.

The other is catalytic oxidation of benzil by using high efficiency catalyst and molecular oxygen or air as oxidant. This method has the advantages of low environmental pollution and conforms to the new concept of green chemistry and clean production. Tymonko SA et al. [2] reported the catalytic oxidation of benzoin to benzil by using air as oxidant, acetic acid aqueous solution as solvent, 40 mol% $Bi(NO_3)_2$ and 4 mol% $Cu(Ac)_2$ as catalyst, the reaction could be carried out for only 3 h, the reaction conditions were mild and the preparation of catalyst was simple, but it raised the cost due to large $Bi(NO_3)_2$ catalyst dosage. Shamim T et al. [3] reported that air as oxidant, toluene as solvent, Pd/SiO_2 as a catalyst to oxidize benzoin to benzil at 100°C, the reaction only needs 0.75 h, the reaction time was short, but the catalyst was expensive and the reaction cost was high, which is not conducive to the industrial production.

There are also studies that combines the use of a catalyst and an oxidant. Safari J et al. [4] used manganese(II) Schiff base complexes as catalyst in the presence of acetonitrile as solvent and H_2O_2 as oxidant, Maurya M R et al. [5] studied benzoin *oxidation* catalyzed by *cis*-dioxidomolybdenum(VI) complexes of tetradentate Mannich bases as catalyst, and organic dimethyl sulfoxide(DMSO) as oxidant. However, these oxidants are expensive compared to air used as oxidant, and the post-treatment is difficult.

Therefore, it is of great significance to develop a kind of catalyst with low environmental pollution, low cost and high reaction efficiency, which can selectively catalyze benzoin to benzil under mild conditions. Schiff bases are a very important class of nitrogen-containing ligands that work well with metal ions. Compared with mono Schiff base, the bis Schiff base contains more coordination sites and forms more stable complexes with metals, such as bis salicylaldehyde ethylenediamine(Salen) as ligand, which is often used to study the oxygen-carrying capacity and photothermal properties of complexes [6,7]. Xie KY et al. [8] developed a one-pot green synthesis of benzil catalyzed by M(Salen) (M=Co, Cu, Zn, Fe, Mn) from benzoin, the highest yield of 76.5% was obtained using Co(Salen) under 80% alcohol-water, 50 minutes and 70°C, and the other four catalysts were not as active as Co(Salen). Wu GC et al. [9] synthesized biomimeticcatalysts $Ln_2(H_2Salen)_3]\cdot(NO_3)_6]\cdot 3H_2O$ (Ln=Nd, Gd, Er), and found that the Nd-Salen, Gd-Salen and Er-Salen had a negative catalytic effect to benzil formation from benzoin oxidation.

In this paper, from the perspective of green chemistry, M(Salen) (M = Co, Ni, Zn), the bis salicylaldehyde ethylenediamine-metal complex was used as a catalyst to study the green synthesis of benzil from benzoin. Using air as the oxidant, so the input cost is reduced, and the reaction conditions are mild, the reaction process is green and environmentally friendly.

2. EXPERIMENTAL DETAILS

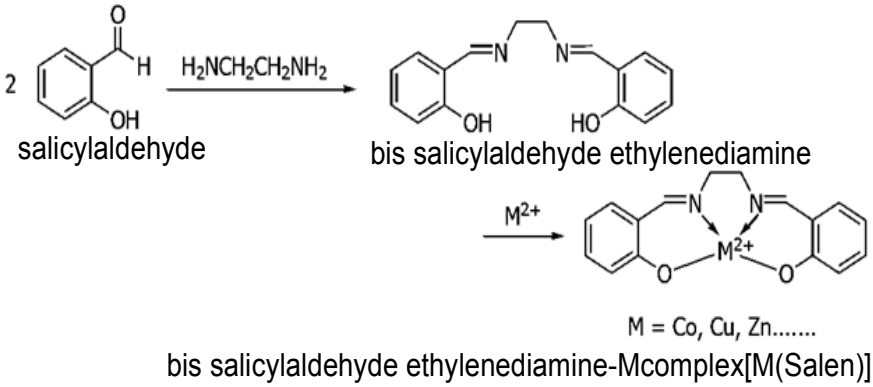
2.1 Reagents and Instruments

Reagents: benzoin(AR), salicylaldehyde(CP), ethylenediamine(AR), cobalt acetate(AR), zinc acetate(AR), nickel acetate(AR), potassium hydroxide(AR), anhydrous ethanol(AR), N, N-dimethylformamide(DMF, AR), dichloromethane (AR), anhydrous magnesium sulfate(AR), benzil(purity 98%).

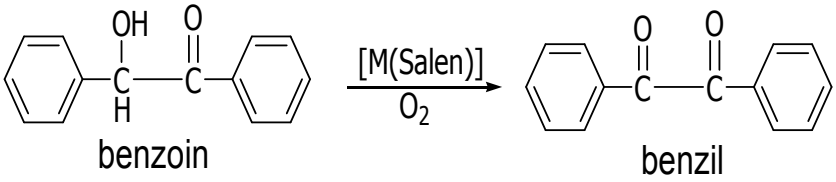
Instruments: Thermo Fisher NICOLET ISIO Fourier infrared spectrometer, Hitachi LC-2130 liquid chromatograph, WRS-1A melting point instrument, 78HW-1 digital thermostat magnetic stirrer, ZX98-1 rotary evaporator, Bruker Advance III HD 500MHz nuclear magnetic resonance instrument.

2.2 Synthesis of M(Salen) Catalyst

The synthesis of the M(Salen) complex catalyst is shown in the following scheme 1:



Scheme 1. Synthesis of M(Salen) catalyst



Scheme 2. Catalytic oxidation of benzoin

The process is as follows: 0.10 mol salicylaldehyde and 60 mL anhydrous ethanol were added to the three-necked flask, 0.05 mol ethylenediamine was further added under stirring, and the mixture was heated and refluxed for 1 h. Then, a 35 mL aqueous solution containing 0.05 mol $CoAc_2$ was dropped into the three-necked flask, and the solution was stirred at 75°C for 50 min. After cooling, suction filtration was carried out to obtain a dark red solid, which was washed and dried to give bis salicylaldehyde ethylenediamine-cobalt complex[Co(Salen)] [10].

Using the same method as above, Ni(Salen)(earth yellow solid), Zn(Salen)(light yellow solid) were prepared by the combination of $NiAc_2$, $ZnAc_2$ with bis salicylaldehyde ethylenediamine, respectively.

2.3 Catalytic Oxidation of Benzoin

The catalytic oxidation of benzoin by M(Salen) is shown in the following scheme 2:

A typical reaction is: 0.05 mol benzoin and 60 mL DMF were added to a three-necked flask equipped with a stirrer, reflux condenser and air duct. After dissolving, 1.5 g Co(Salen) catalyst and 2 g KOH were added, air was pumped in to oxidize benzoin. The solution was heated to 40°C in water bath, and the reaction process was tracked by thin layer chromatography (TLC). After the completion of the oxidation reaction, the mixture was cooled to room temperature, and the pH of the reaction solution was adjusted to 3-4. The mixture was poured into 150 mL water to precipitate a solid, which was filtered with suction and washed with water, then the yellow needle crystal benzil was obtained.

2.4 Recycling of M(Salen) Catalyst

The filtrate after the catalytic oxidation reaction of benzoin was extracted with CH_2Cl_2 in portions, and the extract was dried with anhydrous magnesium sulfate. The CH_2Cl_2 was recovered by rotary evaporator, and the residue was a DMF solution containing M(Salen) catalyst. A small amount of DMF was added, fresh benzoin and KOH were added to carry out the next batch of catalytic oxidation reaction, so that the M(Salen) catalyst was reused.

3. RESULTS AND DISCUSSION

3.1 Infrared Spectrum Analysis of M(Salen) Catalyst

The infrared spectrum of M(Salen) is shown in Fig. 1. The three catalysts all have absorption peaks caused by the vibration of the benzene

ring skeleton at 1600-1630 cm^{-1}, and by the stretching vibration of a bidentate chelating bond (two oxygen atoms coordinated with the surface M cation simultaneously) at 1340-1350 cm^{-1}. The absorption peak at 1150-1200 cm^{-1} and 1050-1090 cm^{-1} are caused by the C-N and C-O stretching vibration of the Salen ligand, the peak at 740-750 cm^{-1} corresponds to the out-of-plane bending vibration of C-H of the benzene ring. The above results indicated that three kinds of M(Salen) catalysts had been successfully prepared.

3.2 Orthogonal Experiment to Explore the Optimal Reaction Conditions for Catalytic Oxidation of Benzoin

Co(Salen) used as catalyst, a series orthogonal experiments with 5-factor and 4-level were designed to study the effect on benzoin catalytic oxidation to benzil. Reaction temperature(A), reaction time(B), base KOH amount(C), catalyst amount(D) and solvent type(E) were five factors, each factor had four levels. The factors and corresponding levels of $L_{16}(4^5)$ orthogonal experiment is listed in Table 1.

According to the design principle of orthogonal experiment, we designed the factor-level scheme of Table 2. The benzoin catalytic oxidation experiments were carried out according to the reaction conditions arranged in Table 2, and the yield of benzil was used as an experimental index.

From the yield data, we can obtain the data analysis in Table 3. From the mean value of each level labeled as K_i, the optimum levels of each factor can be judged. The maximum K_i value of each factor was: 77.6(K_2 of A), 79.4(K_2 of B), 81.1(K_2 of C), 79.1(K_3 of D) and 80.1(K_4 of E), respectively. So the optimal reaction conditions of the experiment obtained were as follows: the reaction temperature was 40 °C(the 2nd level), the reaction time was 1 h(the 2nd level), the amount of KOH was 2 g(the 2nd level), the amount of Co(Salen) catalyst was 1.5 g(the 3rd level) and the solvent was DMF(the 4th level). Excessive temperature, or excessive amounts of alkali, both can cause side reactions or partial decomposition of the product, hence the yield of benzil decreased.

The data of range labeled as R was 3(A), 5.4(B), 9.7(C), 6(D) and 9.1(E), respectively. This indicated that the amount of base(factor C) had the greatest influence on the catalytic oxidation of benzoin, followed by the solvent(factor E), then the amount of catalyst(factor D) and the reaction time(factor B), the reaction temperature(factor A) had the least influence on it. That is to say, the importance of each factor effect on benzoin catalytic oxidation to benzil was base amount > solvent type > catalyst amount > reaction time > reaction temperature.

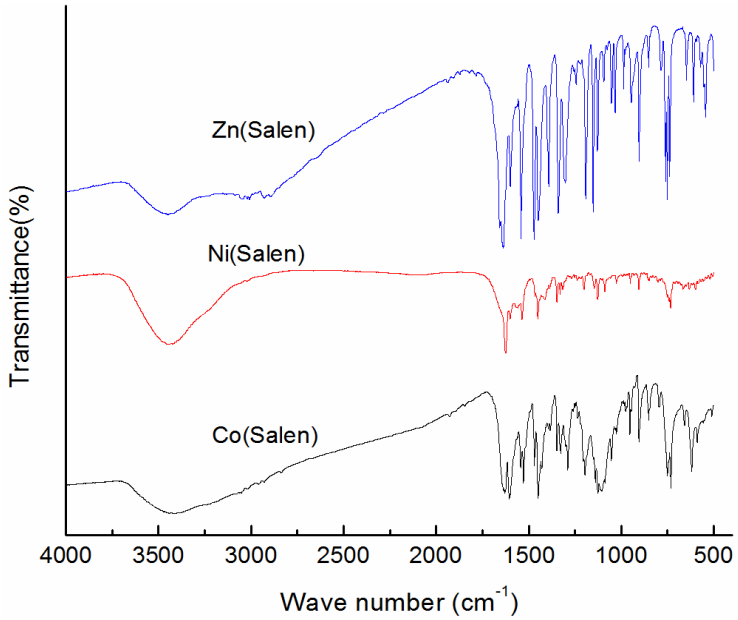


Fig. 1. IR spectrum of M(Salen)

Table 1. The factors and levels of this $L_{16}(4^5)$ orthogonal experiment

Level	Factor				
	A: Reaction temperature (°C)	B: Reaction time (h)	C: Base KOH amount (g)	D: Catalyst amount (g)	E: Solvent type
1	20	0.5	1	0.5	100% EtOH
2	40	1	2	1	80% EtOH
3	60	1.5	3	1.5	60% EtOH
4	80	2	4	2	DMF

Table 2. Factor-level scheme and experimental results of $L_{16}(4^5)$ orthogonal experiment

No.	Reaction temperature (°C)	Reaction time (h)	KOH amount (g)	Co(Salen) amount (g)	Solvent	Benzil yield (%)
1	20	0.5	1	0.5	100% EtOH	62.0
2	20	1	2	1	80% EtOH	87.9
3	20	1.5	3	1.5	60% EtOH	75.7
4	20	2	4	2	DMF	77.1
5	40	0.5	2	1.5	DMF	89.7
6	40	1	1	2	60% EtOH	72.4
7	40	1.5	4	0.5	80% EtOH	75.1
8	40	2	3	1	100% EtOH	73.2
9	60	0.5	3	2	80% EtOH	81.9
10	60	1	1	1.5	100% EtOH	78.0
11	60	1.5	4	1	DMF	74.1
12	60	2	2	0.5	60% EtOH	75.9
13	80	0.5	4	1	60% EtOH	74.9
14	80	1	3	0.5	DMF	79.3
15	80	1.5	2	2	100% EtOH	70.9
16	80	2	1	1.5	80% EtOH	73.1

Table 3. Analysis of orthogonal experimental results

Data analysis	A: Reaction temperature	B: Reaction time	C: Base KOH amount	D: Catalyst amount	E: Solvent type
K_1: Mean value of 1st level	75.7	77.1	71.4	73.1	71.0
K_2: Mean value of 2nd level	77.6	79.4	81.1	77.5	79.5
K_3: Mean value of 3rd level	77.5	74.0	77.5	79.1	74.7
K_4: Mean value of 4th level	74.6	74.8	75.3	75.6	80.1
R: Range	3	5.4	9.7	6	9.1

3.3 Catalytic Performance of Different M(Salen)

According to the optimal reaction conditions obtained above, we used Co(Salen), Ni(Salen) and Zn(Salen) as catalysts to carry out the oxidation reaction of benzoin. The yield of the obtained benzil is shown in Table 4. It can be seen that the catalytic effect of Co(Salen) was the best one, the yield of benzil was 93.6%. The yield of product obtained by catalytic oxidation using Ni(Salen) was in close proximity to that of Zn(Salen), and the value was 86.3% and 82.1%, respectively. Co, Ni and Zn are three metal elements of the same period, and the catalytic performance of the Salen complex formed by the three divalent cation decreased with the increase of the atomic number.

3.4 Recycling Performance of M(Salen) Catalyst

According to the above optimal reaction conditions, we used Co(Salen), Ni(Salen) and Zn(Salen) as catalysts to carry out the recovery and reuse performance studies. The yield of the obtained benzil is shown in Table 5.

It can be seen from Table 5 that with the increase of the number of the reuse of the catalyst, the catalytic activity gradually decreased, but when the catalyst was used for the fourth time, the benzil yield on Co(Salen), Ni(Salen) and Zn(Salen) catalysts was still maintained at 71.4%, 63.3% and 57.4%, respectively. The better recovery and reuse performance of M(Salen) can reduce the economic cost of the catalyst.

3.5 Characterization of the Benzil Product

The obtained product benzil was first determined by a melting point(MP) analyzer, and the melting range was 94.2-94.7°C, which was consistent with the theoretical melting point of benzil.

The product was further characterized by infrared spectroscopy(IR), high performance liquid chromatography(HPLC) and ^{1}H nuclear magnetic resonance(^{1}H NMR).

Fig. 2 is the infrared spectrum of benzil, which is similar to the standard spectrum in the infrared spectrometer's own database. The absorption peak at 3063 cm^{-1} corresponds to the C-H stretching vibration of the methylene group, the peak at 1659 cm^{-1} corresponds to the C = O stretching vibration of carbonyl group. The carbonyl group is conjugated with the benzene ring, so the absorption shifts to a low frequency(the normal absorption frequency of C=O is at 1740-1700cm^{-1}). 1593 cm^{-1}, the absorption peak at this position corresponds to the vibration of the benzene ring skeleton, the strong peak at 1211 cm^{-1} corresponds to the stretching vibration of C-C, and the peak at 718 cm^{-1} corresponds to the out-of - plane bending vibration of C-H on the benzene ring.

The qualitative analysis and purity of the obtained oxidation product benzil was carried out by HPLC using an Eclipse Plus C18 column, 70% methanol as the mobile phase, flow rate 1.0 mL/min, column temperature 35°C, detection wavelength 259 nm, and injection quantity 5 μL. The standard curve shown in Fig. 3 was obtained by taking the concentration of benzil standard solution series ($\times10^{-6}$) as 40, 80, 200, 400, 600, 800, 1000 mol/L. The regressive equation and correlation coefficient were Y = 266016+5991X and R^2 = 0.9916, respectively, indicating the standard curve in the range of 4×10^{-5}-1×10^{-3} mol/L had good linear relationship.

Then, the reaction product benzil 0.0105 g was weighed, and the solution was adjusted to 99.89×10^{-6} mol/L after dilution. The solution was sampled, the qualitative and the quantitative analyses were carried out based on the retention time and peak area respectively. The retention time of the product peak was found to be consistent with the retention time of the standard solution peak (t = 6.5 min), confirming that the product was indeed benzil. By substituting the peak area (Y = 857272) into the standard curve, the actual concentration of the oxidized product benzil was 98.69×10^{-6} mol/L, so the purity of the benzil product was $98.69\times10^{-6}/99.89\times10^{-6}$ = 98.80%.

The obtained oxidation product benzil was also characterized by ^{1}H NMR, and the result is shown in Fig. 4. The peak with a chemical shift of 7.99 - 7.50 ppm corresponds to hydrogen on the benzene ring. According to the peak area data, the ratio of three kinds of hydrogen is 2.10: 1.00: 2.19, which is close to 2: 1: 2 in accordance with the molecular formula of benzil, further confirming that the synthesis product was indeed benzil.

Table 4. Catalytic performances of different catalysts

Catalyst	Co(Salen)	Ni(Salen)	Zn(Salen)
Benzil yield (%)	93.6	86.3	82.1

**Reaction conditions: benzoin 0.05 mol, KOH 2 g, M(Salen) catalyst 1.5 g, DMF 60 mL, reaction temperature 40 °C, reaction time 1 h*

Table 5. The recovery and reuse performance of M(Salen) catalyst

Catalyst	Benzil yield (%)			
	1st used	2nd used	3rd used	4th used
Co(Salen)	93.6	81.1	77.8	71.4
Ni(Salen)	86.3	72.3	70.3	63.3
Zn(Salen)	82.1	69.8	63.7	57.4

**Reaction conditions: benzoin 0.05 mol, KOH 2 g, M(Salen) catalyst 1.5 g, DMF 60 mL, reaction temperature 40 °C, reaction time 1 h*

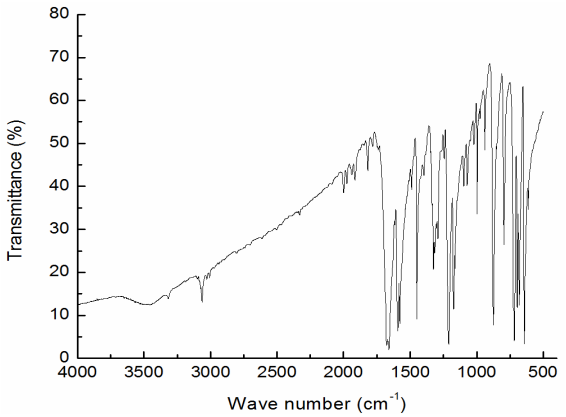


Fig. 2. IR spectrum of benzil

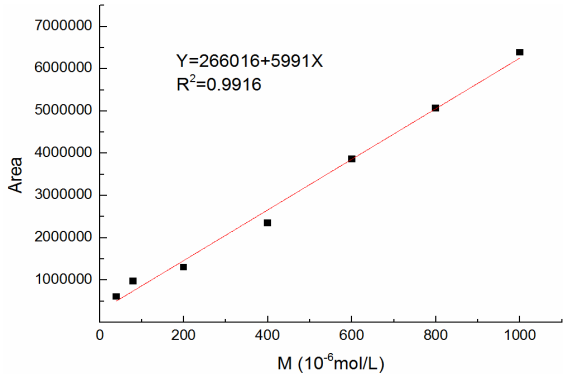


Fig. 3. LC standard curve of benzil

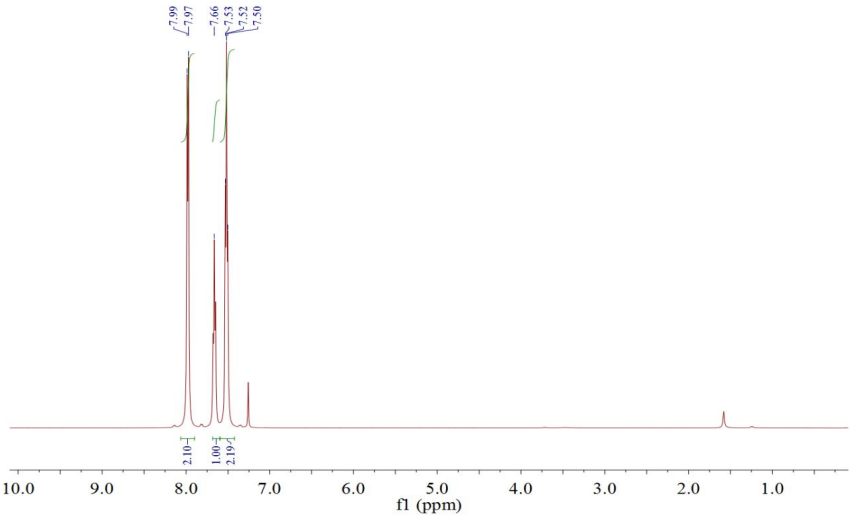


Fig. 4. ^{1}H NMR spectrum of benzil

4. CONCLUSION

We prepared M(Salen) complexes and used it for the air oxidation synthesis of benzil from benzoin. The experimental results showed that the M(Salen) complex has a good catalytic effect.

Orthogonal test method was carried out to investigate the optimum reaction conditions of

0.05 mol benzoin catalyzed by Co(Salen). The optimal reaction conditions were as follows: base KOH amount 2 g, catalyst amount 1.5 g, solvent DMF, reaction temperature 40°C, reaction time 1 h. The yield of benzil was as high as 93.6%, and the yield of the product catalyzed by Ni(Salen) and Zn(Salen) was also up to 86.3% and 82.1%, respectively.

The use of air as an oxidant reduces the input cost of reaction, and the reaction device is simple, the operation is also convenient. Meanwhile, the M(Salen) complex is easy to prepare, with the advantages as less dosage, high catalytic efficiency and convenient post-treatment. The recovered catalyst can be reused, reducing the production cost and meeting the requirements of green chemistry. After four cycles of use, the yield of benzil on the Co(Salen), Ni(Salen) and Zn(Salen) catalyst still reached 71.4%, 63.3% and 57.4%, respectively.

The oxidized product benzil was characterized by MP, IR, HPLC and ^{1}H NMR, all results of which proved the product was certainly high purity benzil. It was confirmed that M(Salen) complex catalyze the oxidation of benzoin to benzil was green and feasible.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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