

# Study on the Application of Beckmann Rearrangement in the Synthesis of Amides from Oximes

## ABSTRACT

In order to prepare amide under more moderate, environmental friendly environment with Beckmann rearrangement, we replaced the traditional liquid acid catalyst with Nafion perfluorinated sulfonic acid resin. We used diphenylketone oxime as for the substrate template, and carried out the experiments to explore the optimal conditions of the Beckmann rearrangement. We studied the influences of reaction temperature, reaction time, catalyst dosage, solvent kinds and volume on Beckmann rearrangement, and established the optimal reaction conditions were: diphenylketone oxime 2 g, solvent acetonitrile 20 mL, catalyst Nafion 0.4 g, reaction temperature 70 °C, reaction time 4 h. Under this condition, the conversion of diphenylketone oxime was 36.32%, benzanilide selectivity was 44.06%, and benzanilide yield was 16.00%. Melting point measurement, infrared spectrum, <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectrum test had been used to characterize the product. The reuse experiment of catalyst showed that Nafion had good recovery performance, and was a green and promising catalyst.

*Keywords: Beckmann rearrangement; diphenylketone oxime; Amide; Nafion.*

## 1. INTRODUCTION

Amide is a very important compound and also a very important functional group in organic chemistry and biochemistry. Such functional group is widely used in drugs, natural products and a large number of industrial materials such as polymers, detergents and lubricants. Beckmann rearrangement reaction [1], that is, oxime as the initial raw material to synthesize amide, has a long history. This classic reaction was first discovered by a German chemist named Beckmann in 1886 and has very important value in organic synthesis.  $\epsilon$ -caprolactam, the precursor of nylon-6 synthesis, is prepared through Beckmann rearrangement of cyclohexanone oxime.

The traditional Beckmann rearrangement method needs strong acid [2-6] as the catalyst, and it only can be carried out under stringent conditions. The equipment requirements are high level and the cost is expensive, the waste water generated is also a serious problem to the environment. Therefore, seeking for a moderate catalytic system and achieving Beckmann rearrangement under a more concise and environmentally friendly condition is the objective of many organic chemists [7-10].

We took diphenyl ketone as template substrate, obtained the corresponding ketoxime, and investigated the effect of catalyst kinds, solvent kinds, reaction temperature, reaction time, catalyst dosage, solvent volume (i.e. oxime concentration) on diphenylketone oxime Beckmann rearrangement, with melting point measurement, infrared spectrum (IR) and nuclear magnetic resonance (NMR) method for the qualitative methods, liquid chromatography for the quantitative method.

## 2. EXPERIMENTAL DETAILS

### 2.1 Reagents and instruments

Diphenyl ketone, hydroxylamine hydrochloride, Nafion™ NR50 perfluorinated sulfonic acid resin, Amberlyst®15 sulfonic acid resin, p-toluene sulfonic acid, amino sulfonic acid, polyphosphoric acid (PPA), acetonitrile, cyclohexane, dimethyl sulfoxide, methanol, ethanol.

42 78HW-1 digital display constant temperature magnetic stirrer, ZX98-1 rotary evaporator, LC2130  
 43 liquid chromatograph, WRR melting point instrument, NICOLET LS10 Fourier transform infrared  
 44 spectrometer, BRUKER AVANCE III nuclear magnetic resonance spectrometer.

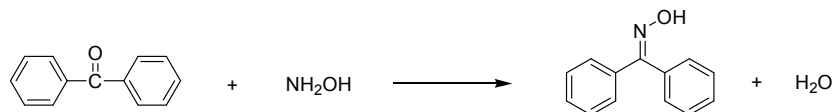
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## 46 2.2 preparation of diphenylketone oxime

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48 The equation for the formation of oxime from diphenyl ketone is shown as follows:

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**Scheme 1 Preparation of diphenylketone oxime**

54 In a 125 mL round bottom flask, dissolving 2.5 g diphenyl ketone and 1.5 g hydroxylamine  
 55 hydrochloride in 10 mL ethanol and 2 mL water, then adding 1.6 g sodium hydroxide. Magnetic  
 56 stirring, heating and refluxing for 2 h at 70 °C. Then transferring the solution into a beaker containing 8  
 57 mL concentrated hydrochloric acid and 50 mL water, so the diphenylketone oxime was precipitated  
 58 out as white powder crystals. After cooling, filtration and recrystallization with about 10 mL ethanol,  
 59 leaving a small amount of the dried products for melting point determination, the rest was used for the  
 60 next rearrangement reaction. Diphenylketone oxime was a colorless transparent needle crystal, the  
 61 literature value of melting point is 142.5 °C.

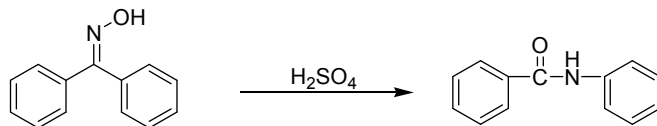
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## 63 2.3 Diphenylketone oxime rearrangement

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65 The Beckmann rearrangement equation of diphenylketone oxime is as follows:

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**Scheme 2 Rearrangement of diphenylketone oxime**

71 A typical rearrangement reaction was as follows: adding solvent (acetonitrile, 20 mL) to a 125 mL  
 72 round bottom flask, then adding the substrate oxime (diphenylketone oxime, 2 g) and solid catalyst  
 73 (Nafion, 0.4 g) respectively. Magnetic stirring and heating reflux for 2 h at 70 °C (thin layer  
 74 chromatography monitoring reaction progress, n-hexane: ethyl acetate =4:1). Keep stirring to cool  
 75 down. Filtrating out the solid catalyst, the solvent in the filtrate was recycled by the rotary evaporator  
 76 to get the crude product, with ethanol recrystallization, drying. The product benzanilide was white  
 77 needle crystal, the literature value of melting point is 163 °C.

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## 79 2.4 Liquid chromatography analysis

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81 Ultraviolet detector, the liquid chromatography conditions were as follows:

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83 Chromatographic column: C18, 250 mm×4.6 mm×5 μm, mobile phase: methanol/distilled water  
 84 =60:40 (V/V), detection wavelength: 254 nm, flow rate: 1.0 mL·min<sup>-1</sup>, column temperature: 30 °C,  
 85 injection volume: 20 μL.

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87 The oxime conversion is calculated by the amount of the oxime remaining after the reaction and the  
 88 amount before the reaction, the amide selectivity is calculated according to the amount of the product  
 89 and the amount of oxime conversion, the formula is as follows:

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$$91 \quad C = \frac{m_0 - m_1}{m_0} \times 100\%$$

$$S_I = \frac{m_2 * 197.24}{(m_0 - m_1) * 197.24} \times 100\%$$

In the formula, C: the conversion of oxime,  $S_I$ : the selectivity of amide.

$m_0$ ,  $m_1$ ,  $m_2$ : the amount of oxime before reaction, the residual oxime after reaction, and the amide formed.

197.24, 197.24: the molecular weight of diphenylketone oxime and benzanilide.

## 2.5 Melting point determination

Sample of 1-2 mm height, determining with melting point instrument.

## 2.6 Infrared spectrum analysis

Adding the dried sample 0.005 g into a mortar, then mixing with 0.005 g KBr powder, grinding, tablet compressing, scanning the sample.

## 2.7 Nuclear magnetic resonance test

500 M nuclear magnetic measurement, deuterium dimethylsulfoxide dissolved the samples.

## 3. RESULTS AND DISCUSSION

### 3.1 Standard curve of liquid chromatography

The peak data of standard samples were processed by Origin, the standard curve of benzanilide is shown in Fig. 1. The linear equation is  $Y=205034+51882X$ , correlation coefficient  $R=0.99885$ , indicating that there is a good linear relationship between the amide concentration and the chromatographic peak area in the range of measurement.

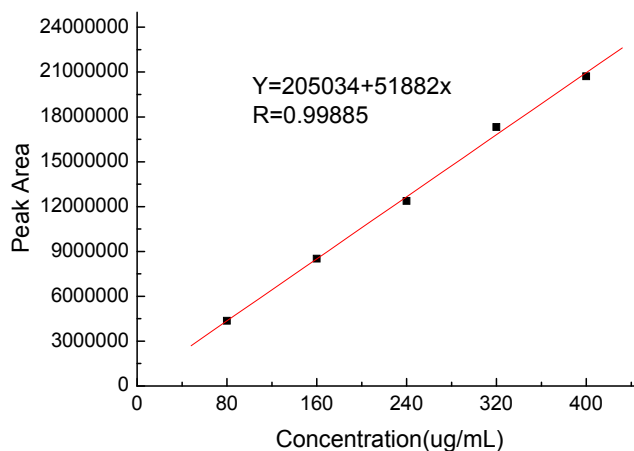


Fig. 1. The standard curve for liquid chromatography of benzanilide

Fig. 2 is the standard curve of diphenylketone oxime, the linear equation is  $Y=183614+48103X$ ,  $R=0.99847$ , indicating that in the measurement range, the oxime concentration is also in good linear relation with the peak area.

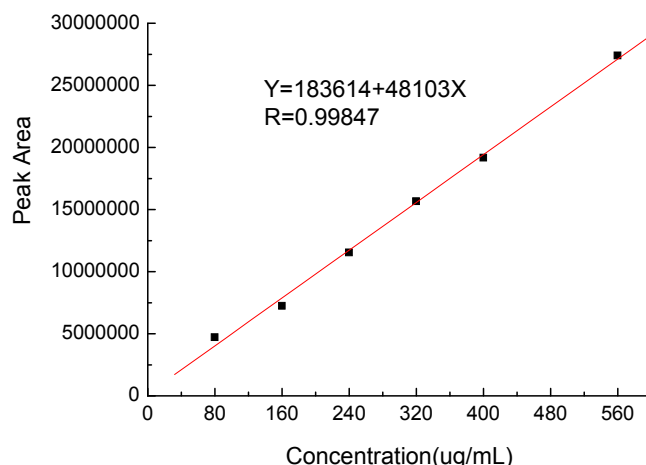


Fig. 2. The standard curve for liquid chromatography of diphenylketone oxime

### 3.2 Effects of different catalysts on Beckmann rearrangement

In order to investigate the effects of different catalysts on Beckmann rearrangement, we used with liquid acid polyphosphoric acid (PPA), and solid sulfonic acid p-toluene sulfonic acid, amino sulfonic acid, Amberlyst® 15 sulfonic acid resin, Nafion perfluorinated sulfonic acid resin as catalyst respectively for rearrangement reaction, the results are shown in table 1. The reaction with solid catalyst employed acetonitrile as the solvent. Considering the rearrangement is an exothermic reaction, the reaction temperature was selected at 70 °C, a bit lower than the boiling point 82 °C of acetonitrile.

As can be seen from table 1, the rearrangement reaction activity of different catalysts was not the same. In the rearrangement reaction of PPA as catalyst, the conversion of diphenylketone oxime reached 100%, the selectivity and the yield of benzanilide were also high. However, the disadvantages of liquid acid, such as strong corrosive, toxic, cannot be recycled, existed in the experiment. When the solid sulfonic acid used as catalyst, the yield of benzanilide was zero when catalyzed by amino sulfonic acid and p-toluene sulfonic acid, and these two catalysts were dissolved in the reaction liquid, cannot achieving the purpose of recycling the catalyst. Nafion and Amberlyst are sulfonic acid supported on resin, when they were used as catalysts, the diphenylketone oxime conversion, the selectivity and yield of benzanilide were all higher than the above two, and the activity of Nafion was better than that of Amberlyst. The reaction process was mild and safe, the recovery process of catalyst after the reaction was simple, the catalyst can be used repeatedly, so we selected Nafion perfluorinated sulfonic acid resin as catalyst.

Table 1. Effects of different catalysts on the Beckmann rearrangement of diphenylketone oxime

Catalyst	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
PPA <sup>a</sup>	100	68.69	68.69
Amino sulfonic acid <sup>b</sup>	1.53	0	0
P-toluene sulfonic acid <sup>b</sup>	2.54	0	0
Amberlyst-35 sulfonic acid resin <sup>b</sup>	2.96	36.75	1.09
Nafion(perfluoro sulfonic acid resin) <sup>b</sup>	16.44	43.26	7.11

\* Reaction conditions: diphenylketone oxime 2.0 g.

<sup>a</sup> liquid acid catalyst system: PPA 25 mL, solvent free, reaction temperature 100 °C, reaction time 0.5 h.

<sup>b</sup> solid catalyst system: catalyst 0.2 g, acetonitrile 20 mL, reaction temperature 70 °C, reaction time 2 h.

### 3.3 Effects of different solvents on Beckmann rearrangement

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165 In order to study the effects of different solvents on diphenylketone oxime Beckmann rearrangement,  
 166 we fixed the amount of diphenylketone oxime, Nafion catalyst dosage and reaction time, the results  
 167 are showed in table 2. The reaction temperatures were a bit lower than the boiling points of each  
 168 solvent.

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170 As can be seen from table 2, the solvent had a great influence on the Beckmann rearrangement of  
 171 diphenylketone oxime. A solvent with strong polarity usually had a higher conversion of  
 172 diphenylketone oxime. We can compare the reaction of acetonitrile and cyclohexane as the solvents,  
 173 the reaction temperature of these two was the same. While acetonitrile was used as solvent, the  
 174 conversion of diphenylketone oxime and the selectivity of benzanilide were relatively higher  
 175 compared to the other. This is probably due to the strong polarity of acetonitrile, which made it easier  
 176 for benzoaniline produced to be desorbed from Nafion and dissolved in solvents, thus improving the  
 177 conversion of diphenylketone oxime and the selectivity of benzanilide. The cyclohexane had very  
 178 weak polarity, so the conversion of diphenylketone oxime, the selectivity and yield of benzanilide were  
 179 the lowest. The same effect happened with DMSO and acetone used as solvents. Because we chose  
 180 the reaction temperature a little lower than the solvent's boiling point, the 130 °C of DMSO was too  
 181 high while the 45 °C of acetone was too low, the 70 °C of acetonitrile was the moderate reaction  
 182 temperature, so acetonitrile was selected as the solvent for the reaction.

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184 **Table 2. Effects of different solvents on the Beckmann rearrangement of diphenylketone oxime**

Solvent	Boiling point (°C)	Dielectric constant $\epsilon$	Reaction temperature (°C)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
Cyclohexane	81	2.02	70	4.06	22.05	0.90
Acetone	56	20.7	45	6.93	46.64	3.23
Acetonitrile	82	37.5	70	16.44	43.26	7.11
Dimethyl sulfone	189	48.9	130	13.31	49.85	6.63

185 \* Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, solvent 20 mL, reaction time 2 h.

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187 **3.4 Effects of reaction temperature on Beckmann rearrangement**

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189 Using acetonitrile as solvent, we investigated the effects of reaction temperature on the Beckmann  
 190 rearrangement of diphenylketone oxime catalyzed by Nafion, the results are shown in table 3.

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192 It can be seen from table 3, the reaction temperature affected the conversion of diphenylketone oxime  
 193 and the selectivity of benzanilide. At low temperature, the conversion of diphenylketone oxime was  
 194 very low, only 6.63% at 30 °C, and it increased with the increase of reaction temperature, the value  
 195 was 21.96% at 82 °C. But benzanilide selectivity decreased with reaction temperature increased, this  
 196 may be due to the high temperature increased the competition of oxime hydrolysis reaction compared  
 197 to the oxime rearrangement. The yield of benzanilide increased with the increase of reaction  
 198 temperature first, then leveled off, it reached highest at 70 °C. So we chose 70 °C for the  
 199 rearrangement reaction temperature, this not only ensured the diphenylketone oxime conversion and  
 200 benzanilide selectivity were higher, but also could receive the maximum benzanilide yield.

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202 **Table 3. Effects of reaction temperature on the Beckmann rearrangement of diphenylketone oxime**

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Reaction temperature (°C)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
30	6.63	77.90	5.16
50	8.50	63.88	5.43
70	16.44	43.26	7.11
82	21.96	30.23	6.64

204 \* Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, acetonitrile 20 mL, reaction time 2 h.

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206 **3.5 Effects of reaction time on Beckmann rearrangement**

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208 In order to further study the influence factors of Beckmann rearrangement, we investigated the effects  
 209 of reaction time on rearrangement reaction. The results are shown in table 4.

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 211 From table 4, it can be seen that the conversion of diphenylketoxime had tended to be the highest  
 212 when the reaction time was 4 h, and to be stable as the reaction time prolonged. During the reaction,  
 213 the selectivity of benzanilide decreased with time, possibly because of the polymerization reaction of  
 214 benzanilide with time prolonged. The yield of benzanilide reached the highest at 4 h, then decreased.  
 215 Therefore, we chose the reaction time of 4 h, which ensured that the conversion of diphenylketone  
 216 oxime was complete, the higher selectivity of amide was maintained, and the yield of benzanilide was  
 217 the largest.

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**Table 4. Effects of reaction time on the Beckmann rearrangement of diphenylketone oxime**

Reaction time (h)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
2	16.44	43.26	7.11
3	20.56	40.65	8.36
4	29.35	34.98	10.27
5	29.40	27.67	8.13
6	29.64	16.53	4.90

220 \* Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.2 g, acetonitrile 20 mL, reaction temperature 70 °C.

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### 3.6 Effects of catalyst dosage on Beckmann rearrangement

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**Table 5. Effects of catalyst dosage on the Beckmann rearrangement of diphenylketone oxime**

Nafion (g)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
0.2	29.35	34.98	10.27
0.3	32.75	38.87	12.73
0.4	36.32	44.06	16.00
0.5	39.21	36.68	14.38
0.6	40.09	30.24	12.12

234 \* Reaction conditions: diphenylketone oxime 2.0 g, acetonitrile 20 mL, reaction temperature 70 °C, reaction time  
 235 4 h.

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### 3.7 Effects of solvent volume on Beckmann rearrangement

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We fixed diphenylketone oxime amount and Nafion catalyst dosage to study the effects of diphenylketone oxime concentration on Beckmann rearrangement by changing solvent volume, the results are shown in table 6.

From table 6, it was known that in the range of oxime concentration investigated, the conversion of diphenylketone oxime first increased slowly and then decreased rapidly. This may be due to the higher concentration of reaction solution resulting in the difficulty in removing benzanilide from Nafion, thus reducing the content of amide in the reaction solution. The change of oxime concentration also affected the selectivity of benzoaniline. Along with increasing the volume of solvent, oxime concentration decreased, benzanilide selectivity increased. When the solvent volume was 20 mL, it reached 44.06%. Further increasing the solvent volume, the selectivity of benzanilide increased slowly. Higher yield of benzanilide can be obtained at the medium oxime concentration, while the

251 higher and lower oxime concentration all decreased the yield of amide. Therefore, the optimum  
 252 volume of the added acetonitrile was 20 mL.

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254 **Table 6. Effects of solvent volume on the Beckmann rearrangement of diphenylketone oxime**

Acetonitrile (mL)	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
10	34.98	9.06	3.17
15	36.01	30.89	11.12
20	36.32	44.06	16.00
25	20.78	50.65	10.53
30	13.30	59.57	7.92

255 \* Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.4 g, reaction temperature 70 °C, reaction time 4 h.

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### 257 3.8 Reuse performance of Nafion catalyst

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259 Perfluorinated sulfonic acid resin is granular solid, which can be separated by filtration from reaction  
 260 solution, and can be used for the reaction of the next batch by simple processing. Therefore, the  
 261 reuse performance of Nafion was investigated in this study, and the results are shown in table 7.

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263 From table 7, we can see that when Nafion was reused the first time, the conversion of  
 264 diphenylketone oxime and yield of benzanilide both dropped a little. As the numbers of reuse  
 265 increased, the conversion and yield decreased. The quality of sulfonic acid resin was lost in the  
 266 process of recycling and reuse, which may be the cause of the decrease in conversion and yield. In  
 267 general, Nafion catalyst can be recycled easily and can still be used again.

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269 **Table 7. The Beckmann rearrangement of diphenylketone oxime on the recycled Nafion**  
 270 **catalyst**

Catalyst	Conversion of diphenylketone oxime (%)	Selectivity of benzanilide (%)	Yield of benzanilide (%)
Fresh	36.32	44.06	16.00
First run recycled	34.67	45.87	15.90
Second run recycled	29.64	40.43	11.98
Third run recycled	25.87	38.98	10.08

271 \* Reaction conditions: diphenylketone oxime 2.0 g, Nafion 0.4 g, acetonitrile 20 mL, reaction temperature 70 °C,  
 272 reaction time 4 h.

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### 274 3.9 Characterization of benzanilide

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276 The benzanilide obtained was analyzed by melting point, IR and NMR, respectively.

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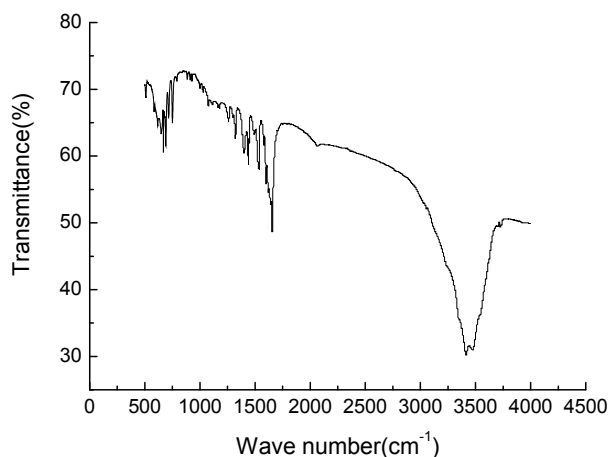
278 The melting point measurement showed that the mp of benzanilide was 161.7-162.3 °C, which was in  
 279 accordance with the literature value of 163 °C, indicating that the sample was pure.

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281 Fig. 3 is IR spectrogram of benzanilide. It can be seen that the absorption peak of 1655 cm<sup>-1</sup> and  
 282 1533 cm<sup>-1</sup>, which were assigned to the stretching vibration of C=O and the bending vibration of N-H in  
 283 amide. And the absorption peak of 3413 cm<sup>-1</sup> was the stretching vibration peak of N-H. The  
 284 absorption peak of 770-730 cm<sup>-1</sup> and 710-690 cm<sup>-1</sup> was the out-of-plane bending vibration peak of C-  
 285 H on the substituent benzene ring.

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**Fig. 3. IR spectrum of benzanilide**

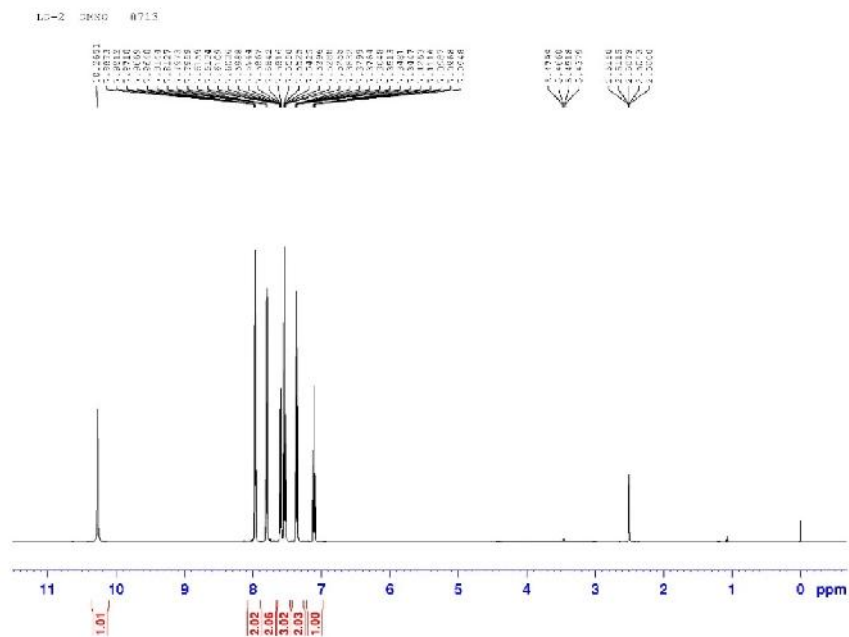
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290 The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrogram of benzanilide are shown in Fig. 4 and 5. Among them:

291  $^1\text{H}$  NMR (500MHz, DMSO):  $\delta$  10.27 (s, 1H, N-H), 7.97 (dt,  $J = 3.5, 2.3$  Hz, 2H, Ar-H), 7.81 (dd,  $J =$   
292 8.5, 1.0 Hz, 2H, Ar-H), 7.65-7.57 (m, 1H, Ar-H), 7.57-7.49 (m, 2H, Ar-H), 7.41-7.30 (m, 2H, Ar-H),  
293 7.17-7.04 (m, 1H, Ar-H).

294  $^{13}\text{C}$  NMR (126MHz, DMSO):  $\delta$ 165.5, 139.2, 135.0, 131.5, 128.5, 127.6, 123.6, 120.4 (the heptet of  
295 around 40 was the peak of solvent).



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**Fig. 4.  $^1\text{H}$  NMR spectrogram of benzanilide**



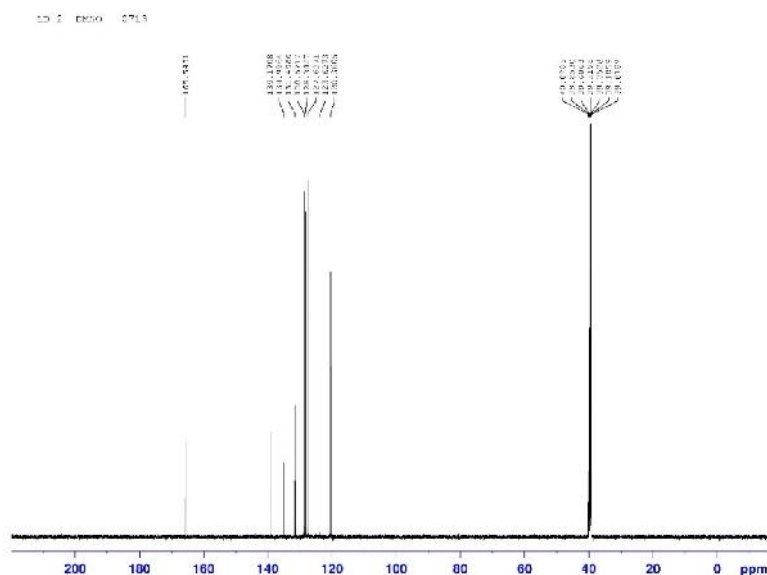


Fig. 5  $^{13}\text{C}$  NMR spectrogram of benzanilide

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Combined with identification of melting point determination, IR and NMR, it can be concluded that the product of Beckmann rearrangement was indeed benzanilide.

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#### 4. CONCLUSION

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In order to prepare amide in a more mild and friendly environment with Beckmann rearrangement reaction, we used Nafion perfluorinated sulfonic acid resin instead of the traditional liquid acid catalyst to study the optimal reaction conditions of Beckmann rearrangement with diphenylketone oxime as substrate template. And the reuse performance of the catalyst was also investigated. The following conclusions are obtained:

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(1) Compared with the other sulfonic acid catalysts, the Nafion Perfluorinated sulfonic acid resin had a relatively good effect on Beckmann rearrangement.

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(2) When the substrate diphenylketone oxime was in amount of 2 g, the optimal reaction conditions were as follows: reaction temperature 70 °C, reaction time 4 h, Nafion catalyst dosage 0.4 g, solvent acetonitrile volume 20 mL. Under this condition, the conversion of diphenylketone oxime was 36.32%, the selectivity of benzanilide was 44.06%, and the yield of benzanilide was 16.00%.

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(3) The Nafion Perfluorinated sulfonic acid resin catalyst can be easily separated from the solution and had no pollution to the environment. The reuse experiment showed that Nafion had a good recycling performance. It was a green and promising catalyst.

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