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#### Tetrahedron xxx (xxxx) xxx



# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# *o*-Phthalic Anhydride/Zn(OTf)<sub>2</sub> co-catalyzed Beckmann rearrangement under mild conditions

# Ze-Feng Xu<sup>a, b, \*</sup>, Teng Zhang<sup>a</sup>, Wenjun Hong<sup>a</sup>

<sup>a</sup> Department of Chemistry, Zhejiang Sci-Tech University, Xiasha West Higher Education District, Hangzhou, 310018, China <sup>b</sup> Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China

#### ARTICLE INFO

Article history: Received 16 March 2019 Received in revised form 17 April 2019 Accepted 23 April 2019 Available online xxx

*Keywords:* Beckmann rearrangement Oxime Amide Co-catalysis

# 1. Introduction

Oxime (1) could be converted to the corresponding amide (2) though Beckmann rearrangement, which was first discovered by the German chemist Ernst Otto Beckmann in 1886 [1], and is now the most important method to obtain  $\varepsilon$ -caprolactam which was used as the monomer of nylon in industry [2], and the reaction was also widely used in total synthesis of nature products and preparation of other bioactive molecules [3].

Traditionally, Beckmann rearrangement always occurred under very harsh conditions (strong acids and high temperatures) or in uneconomic manners (requirement of excess additives), additionally, oxime would be hydrolyzed giving ketone (**3**) in some cases [**4**]. These drawbacks limited its applications for oximes bearing sensitive groups. Organocatalysis is a powerful strategy in organic transformations with great compatibility. In 2002, Giacomelli group revealed that cyanuric chloride could promote the Beckmann rearrangement of both ketoximes and aldoximes under very mild conditions, producing amides and nitriles respectively [**5**]. From then on, many organic catalysts or promoters were developed for Beckmann rearrangement, for instance, bis(2-oxo-3-oxazolidinyl)

E-mail address: xuzefeng@zstu.edu.cn (Z.-F. Xu).

https://doi.org/10.1016/j.tet.2019.04.056 0040-4020/© 2019 Elsevier Ltd. All rights reserved.

#### ABSTRACT

*o*-Phthalic anhydride/ $Zn(OTf)_2$  co-catalyzed Beckmann rearrangement was developed, producing the corresponding amide in up to 99% yield with acid-sensitive functionalities tolerated well, and the scale of the reaction could be enlarged to 77 mmol and the excellent yield was maintained. A successive procedure was developed. Moreover, the reaction was carried out at rt under nearly neutral conditions, and the workup was concise. These features illustrated the potential of the protocol in amide synthesis. © 2019 Elsevier Ltd. All rights reserved.

> phosphinic chloride (BOP-Cl) [6], 2,2-dichloroimidazolidine-4,5dione (DCID) [7], cyclopropenium salt [8], cyanuric chloride [9], and so on [10]. Very recently, reported by Hall and coworkers, a true organocatalytic Beckmann rearrangement was achieved at rt employing 2-methoxycarbonylphenyl boronic acid/perfluoropinacol system, and a fully catalytic nonself-propagating mechanism was confirmed [11].

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Considering the significance of the Beckmann rearrangement in amide synthesis, developing of Beckmann rearrangement under mild conditions (room temperature, neutral conditions) with easily available and low-cost catalytic system and concise workup is still highly desirable. Thus, a cyclic anhydride **4** catalyzed Beckmann rearrangement was designed as depicted in Scheme 1. The oxygen atom of oxime would add to carbonyl in cyclic anhydride to produce intermediate **A**, which might fragment to cation **B** and acetate **C**. Re-combination of **B** and **C** would yield intermediate **D**, and if a recyclization of **D** occurs by addition of oxygen of the acid group to the carbonyl of the acetic acetimidic anhydride part, intermediate **E** might be generated after proton transfer. Elimination of **E** would then produce the desired amide **2** and rebirth cyclic anhydride **4** to close the catalytic cycle.

It's clear from the proposed catalytic cycle that the reaction conditions should be nearly neutral albeit catalytic amount of acid would be generated during the reaction. If such design could be realized, a very mild and low-cost catalytic system could be



<sup>\*</sup> Corresponding author. Department of Chemistry, Zhejiang Sci-Tech University, Xiasha West Higher Education District, Hangzhou, 310018, China.

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Scheme 1. Initial design of cyclic anhydride catalyzed Beckmann rearrangement.

established. The proposed transformation also features such challenge: for the formation of intermediate **A**, an active enough anhydride was required in order to facilitate the addition of hydroxyl of oxime to the carbonyl, however, such reactive anhydride may be deleterious to the formation of intermediate **E**. In order to resolve the contradiction, it's envisioned that the reactivity of the anhydride was necessary, and if the two carbonyls in **D** were located closely enough to each other, the generation of **E** should be possible.

With this consideration, several cyclic anhydrides were tested, and fortunately, after a series of screening of reaction conditions, such proposal was realized with the assistance of Lewis acid additive. So herein, we report our achievement on the mild Beckmann rearrangement employing *o*-phthalic anhydride/Zn(OTf)<sub>2</sub> catalytic system.

#### 2. Results and discussion

Our investigation was initiated with the evaluation of the influences of various cyclic anhydrides 4 on the Beckmann rearrangement of diphenylmethanone oxime (1a). Unfortunately, none of the tested anhydrides could promote the reaction even with 100 mol% dosages of 4 in refluxed CH<sub>3</sub>CN, and in each case, complex mixture was obtained and after purification, benzophenone (3a) was acquired (entries 1-5, Table 1). According to Kalkhambkar and coworkers [10f], equal-equivalent trifluoromethanesulfonic anhydride could promote Beckmann rearrangement easily at rt, signifying that the failure here might result from the low activities of the evaluated anhydrides. At this point, a variety of Lewis acids (such as triflates of Sc<sup>III</sup>, In<sup>III</sup>, Y<sup>III</sup>, Cu<sup>I</sup>, Cu<sup>II</sup>, Ag<sup>I</sup>, La<sup>III</sup>, Yb<sup>III</sup> and Zn<sup>II</sup>, Zn(OAc)<sub>2</sub>, ZnO, ZnCl<sub>2</sub>) were screened to promote the reactivity of the carbonyl in 4. However, no positive results were obtained for most of the tested Lewis acids, and **3a** was isolated as the major side product. Although only trace amount of amide **2a** was generated when the reaction was carried out with the addition of 20 mol% Zn(OTf)<sub>2</sub> and 100 mol% **4a** or **4b** after stirred at rt in CH<sub>3</sub>CN (entries 6–7, Table 1), the combinations of Zn(OTf)<sub>2</sub> and more rigid anhydrides provided much more dramatic results. When 20 ml% Zn(OTf)<sub>2</sub> and 100 mol% **4c** was used, still at rt, oxime **1a** transferred to the desired amide **2a** in 93% yield after 6 h (entry 8, Table 1). Replacement of 4c with Table 1

Optimization of the reactions.<sup>a</sup>



entry	4 (mol%)	LA (mol%)	solvent	time (h)	yield (%) <sup>b</sup>	note
1 <sup>c</sup>	<b>4a</b> (100)	_	CH₃CN	6	0	<b>3a</b> , complex
2 <sup>c</sup>	<b>4b</b> (100)	-	CH₃CN	6	0	<b>3a</b> , complex
3 <sup>c</sup>	<b>4c</b> (100)	_	CH <sub>3</sub> CN	6	0	<b>3a</b> , complex
4 <sup>c</sup>	<b>4d</b> (100)	_	CH <sub>3</sub> CN	6	0	<b>3a</b> , complex
5 <sup>c</sup>	<b>4e</b> (100)	-	CH <sub>3</sub> CN	6	0	<b>3a</b> , complex
6	<b>4a</b> (100)	Zn(OTf) <sub>2</sub> (20)	CH <sub>3</sub> CN	overnight	trace	<b>3a</b> , complex
7	<b>4b</b> (100)	Zn(OTf) <sub>2</sub> (20)	CH₃CN	overnight	trace	<b>3a</b> , complex
8	<b>4c</b> (100)	Zn(OTf)2 (20)	CH <sub>3</sub> CN	6	93	
9	<b>4d</b> (100)	Zn(OTf)2 (20)	CH <sub>3</sub> CN	6	63	3a
10	<b>4e</b> (100)	Zn(OTf)2 (20)	CH <sub>3</sub> CN	6	57	3a
11	<b>4c</b> (100)	Zn(OTf)2 (10)	CH <sub>3</sub> CN	6	32	1a remained
12	4c (50)	Zn(OTf) <sub>2</sub> (20)	CH <sub>3</sub> CN	6	99	
13	<b>4c</b> (20)	Zn(OTf) <sub>2</sub> (20)	CH <sub>3</sub> CN	6	85	
14	4c (10)	Zn(OTf) <sub>2</sub> (20)	CH <sub>3</sub> CN	6	88	
15	<b>4c</b> (10)	Zn(OTf) <sub>2</sub> (20)	DCE	6	45	3a
16	<b>4c</b> (10)	Zn(OTf)2 (20)	DCM	6	61	3a
17	<b>4c</b> (10)	Zn(OTf) <sub>2</sub> (20)	THF	6	50	3a
18	<b>4c</b> (10)	Zn(OTf) <sub>2</sub> (20)	toluene	6	27	3a

<sup>a</sup> Oxime **1** (1.0 mmol, 1.0 equiv), anhydride **4** and Lewis acid were dissolved in 1.0 mL CH<sub>3</sub>CN at rt under nitrogen atomesphere and stirred until the complete consumption of the oxime monitored by TLC analysis.

<sup>b</sup> Isolated yield.

<sup>c</sup> The reaction was carried in refluxed CH<sub>3</sub>CN.

more electron-deficient anhydride **4d** or rigid six-membered cyclic anhydride **4e** provided only 57–63% yields of **2a** (entries 9–10, Table 1), indicating that the electronic effect and the size of the ring in anhydride were both important for the reaction. Reducing the dosage of  $Zn(OTf)_2$  from 20 mol% to 10 mol% caused a sluggish reaction and remarkable decrease of the yield (32%, entry 11, Table 1). Actually, the amount of **4c** could be declined to 10 mol% and the yield of **2a** was reserved (88%, entry 14, Table 1). Although a quantitative yield was obtained when 50 mol% **4c** was utilized (entry 12, Table 1), the catalytic process (entry 14, Table 1) was selected for further investigation of solvent because of the convenience in workup, low cost and reagent efficiency. CH<sub>3</sub>CN was identified as the most effective among those tested solvents (27–61% yields, entries 15–18, Table 1).

As depicted in Scheme 2, the compatibility of the anhydride/ Zn(OTf)<sub>2</sub> catalytic system was evaluated under the optimized conditions by the Beckmann rearrangement of various oximes generated from corresponding ketones [12]. In general, the reaction was sensitive to the electronic effect of the oximes. For diaryl oximes, Beckmann rearrangement went very well and up to 99% yield was obtained. Electron-rich oximes reacted much faster than electron-deficient ones, for instance, dimethoxy substituted amide **2c** could be obtained in 99% yield within 20 min, whereas difluoroamide **2d** was generated in 97% yield after stirred overnight. The selectivity of the migration of phenyl and *p*-tolyl could not be controlled, and **2g** and **2g**' was produced as a 1:1 mixture in 84% total yield after 6 h. Aryl alkyl oximes were less reactive than diaryl oximes. *N*-phenylacetamide (**2h**) was produced in 71% yield after a

Please cite this article as: Z.-F. Xu et al., *o*-Phthalic Anhydride/Zn(OTf)<sub>2</sub> co-catalyzed Beckmann rearrangement under mild conditions, Tetrahedron, https://doi.org/10.1016/j.tet.2019.04.056

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Scheme 2. Reaction scope.

prolonged reaction time compared to **2a**; and the electron-rich *N*-(4-methoxyphenyl)acetamide (**2j**) was obtained in 81% yield after 6 h, which was also slower than the formation of **2c**. **2i** was produced in 91% yield. Disappointingly, 4-bromophenyl methyl oxime performed poorly, and after heated at 50 °C overnight, only 33% yield of *N*-(4-bromophenyl)acetamide (**2k**) was delivered. Steric substituent at the alkyl could not influence the reaction and amide **2l** was generated smoothly in 87% yield. Vinyl group could also migrate as well and *N*-vinyl acetamide **2m** was generated in 58% yield with the configuration retention of the carbon-carbon double bond. Heteroaryl, such as 1H-pyrrol-2-yl, was not compatible and no desired amide **2n** was obtained. Dialkyl oxime, such as camphor oxime (**1o**), was inert under the standard conditions, giving no desired corresponding amides (**2o**).

In order to protrude the advantage of the mild conditions, several acid-sensitive functionalities (such as silyloxy group, N-Boc and acetal moiety) were introduced into oximes (**1p-r**), which were then submitted to the standard conditions [13]. Gratifyingly, the tested acid-sensitive groups were all well compatible and the corresponding amides **2p-r** were obtained in excellent yields (91–99%) within 2 h, depicting the same accelerating influence of electron-donating groups on the reaction.



A scalable reaction was carried out with 77 mmol (15.2 g) **1a** as substrate under the catalysis of 10 mol% **4a** and only 10 mol% Zn(OTf)<sub>2</sub> (eq (1)). The workup of the reaction was very concise [14]

and 90% yield (69.3 mmol, 13.7 g) of amide 2a was obtained.

According to our observation, most of **2a** would precipitate as a white solid from the reaction mixture, it's envisioned that a successive operation for the synthesis of **2a** should be possible. So after the reaction of **1a** under standard conditions was completed, the mixture was filtrated quickly, and the precipitation was collected as product (washed with cold ethanol and no further purification was needed); and to the filtrate, containing catalysts and some amount of the dissolved product **2a**, a stirring bar and oxime **1a** was added to continue the reaction under nitrogen atmosphere. After the consumption of **1a**, the same operation was repeated. As depicted in Fig. 1, for the first cycle, the yield of **2a** was dissolved in the filtrate; the second and third cycles provided the desired **2a** in 81% and 79%





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yields respectively. As a whole, the developed successive procedure provided a relative green protocol for the synthesis of **2a**.



Several control experiments provided some insights into the mechanism. **4c** could not catalyze the Beckmann rearrangement at rt (eq (2)). When 20 mol% Zn(OTf)<sub>2</sub> was used as single catalyst, only trace amide **2a** was detected after stirred at rt overnight (eq (3)), indicating that Zn(OTf)<sub>2</sub> could not catalyze the reaction effectively at rt neither. Replacing **4c** and Zn(OTf)<sub>2</sub> with 10 mol% acetic anhydride under standard conditions could only produce **2b** in 15% yield, and it's reported that Tf<sub>2</sub>O could promote the rearrangement efficiently [10f]. These facts inferred that more reactive anhydrides (Ac<sub>2</sub>O, Tf<sub>2</sub>O) could promote Beckmann rearrangement, but **4c** was too stable to facilitate the reaction. Accordingly, the role of Zn(OTf)<sub>2</sub> might be to activate the anhydride functionality in **4c**.

# 3. Conclusion

A mild and easily handled Beckmann rearrangement was achieved employing the combination of rigid cyclic anhydride and Lewis acid. When *o*-phthalic anhydride and Zn(OTf)<sub>2</sub> were used as co-catalyst, Beckmann rearrangement of various oximes could produce the corresponding amide in up to 99% yield at rt under nearly neutral conditions and acid-sensitive functionalities were well compatible. Additionally, the reaction scale could be easily enlarged to 77 mmol and the efficiency was maintained, and also, a successive procedure was developed providing a promising protocol that could be utilized in large scale production of amide. In view of the appealing effect that combination of two low-effective catalysts produced a high effective catalytic system, the investigation of the detailed mechanism is still undergoing in our lab.

# 4. Experimental section

#### 4.1. General information

Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF254 pre-coated plates. Flash column chromatography was performed using 200–300 Mesh Silica Gel. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded using Brucker Avance IIDMX 400 MHz spectrometers. Chemical shift ( $\delta$ ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.00 ppm) or CDCl<sub>3</sub> (7.26 ppm) or DMSO-*d*<sub>6</sub> (2.50 ppm). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of CDCl<sub>3</sub> (77.00 ppm) or DMSO- $d_6$  (39.52 ppm). High resolution mass spectra (HRMS) were obtained by Center for Instrumental Analysis of Zhejiang Sci-Tech University and a Waters TOFMS GCT Premier instrument for HRMS. The results are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M<sup>+</sup>) or a suitable fragment ion.

# 4.2. General procedure for o-phthalic anhydride/Zn(OTf)<sub>2</sub> cocatalyzed Beckmann rearrangement

Oxime **1** (1.0 mmol, 1.0 equiv),  $Zn(OTf)_2$  (73.7 mg, 0.2 mmol, 0.2 equiv) and *o*-phthalic anhydride (15.0 mg, 0.1 mmol, 0.1 equiv) were dissolved in 1.0 mL CH<sub>3</sub>CN at rt under nitrogen atomesphere and stirred until the complete consumption of the oxime monitored by TLC analysis. The mixture was evaporated and the residue was purified on flash column chromatography with petroleum ether/ethyl acetate (5:1–2:1) as eluent to afford the desired amide **2**.

#### 4.3. Procedure for scalable reaction of 1a

Diphenyl oxime (**1a**) (15.2 g, 77 mmol, 1.0 equiv), Zn(OTf)2 (2.71 g, 7.7 mmol, 0.1 equiv) and o-phthalic anhydride (1.14 g, 7.7 mmol, 0.1 equiv) were dissolved in 150 mL CH<sub>3</sub>CN at rt under nitrogen atomesphere and stirred until the complete consumption of the oxime monitored by TLC analysis. The white precipitation was collected by filtration and the filtration was concentrated to 50 mL, and 1% NaOH solution was added, the mixture was extracted with ethyl acetate (20 mL) for tree times and the combined organic phase was washed with brine (20 mL), and then evaporated giving white slide. Recrystallization of the combined solid in ethanol providing pure N-phenylbenzamide (**2a**, 13.7 g, 69.3 mmol, 90% yield).

## 4.4. Analytical data of 2

## 4.4.1. N-phenylbenzamide (2a) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.27 (br, 1H), 7.98 (d, J = 7.3 Hz, 2H), 7.82 (d, J = 7.9 Hz, 2H), 7.64–7.47 (m, 3H), 7.37 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  166.05, 139.68, 135.49, 131.99, 129.07, 128.84, 128.13, 124.12, 120.84. HRMS (ESI) calcd for C<sub>13</sub>H<sub>12</sub>NO<sup>+</sup> 198.0919, found 198.0921.

# 4.4.2. 4-Methyl-N-(4-methylphenyl)benzamide (2b) [15]

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (br, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H), 2.38 (s, 3H).

# 4.4.3. 4-Methoxy-N-(4-methoxyphenyl)benzamide (2c) [7]

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.98 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 164.98, 162.22, 155.87, 132.87, 129.91, 127.55, 122.44, 114.14, 114.00, 55.84, 55.60. HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>NO<sup>+</sup> 258.1130, found 258.1136.

# 4.4.4. 4-Fluoro-N-(4-fluorophenyl)benzamide (2d) [10j]

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.32 (s, 1H), 8.04 (dd, J = 8.8, 5.6 Hz, 2H), 7.79 (dd, J = 8.8, 5.0 Hz, 2H), 7.37 (t, J = 8.8 Hz, 2H), 7.20 (t, J = 8.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 164.81, 164.56 (d, J = 249.0 Hz), 158.79 (d, J = 240.4 Hz), 135.88, 131.67, 130.82 (d, J = 9.0 Hz), 122.69 (d, J = 7.8 Hz), 115.84 (d, J = 15.1 Hz), 115.62 (d, J = 15.6 Hz). HRMS (ESI) calcd for C<sub>13</sub>H<sub>10</sub>F<sub>2</sub>NO<sup>+</sup> 234.0734, found

Please cite this article as: Z.-F. Xu et al., o-Phthalic Anhydride/Zn(OTf)<sub>2</sub> co-catalyzed Beckmann rearrangement under mild conditions, Tetrahedron, https://doi.org/10.1016/j.tet.2019.04.056

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234.0730.

## 4.4.5. 4-Chloro-N-(4-chlorophenyl)benzamide (2e) [16]

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, J = 8.7 Hz, 2H), 7.75 (s, 1H), 7.58 (d, *I* = 8.7 Hz, 2H), 7.48 (d, *I* = 8.7 Hz, 2H), 7.34 (d, *I* = 8.7 Hz, 2H).

4.4.6. 4-Bromo-N-(4-bromophenvl)benzamide (2f) [16] <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (s, 1H), 7.73 (d, I = 8.4 Hz, 2H),

7.63 (d, *J* = 8.7 Hz, 2H), 7.55–7.47 (m, 4H).

4.4.7. 4-Methyl-N-phenylbenzamide & N-(p-tolyl)benzamide (2g & **2g**′)

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.02 (br, 1H), 7.88–7.86 (m, 1H)), 7.79-7.77 (m, 1H), 7.67-7.65 (m, 1H), 7.54-7.52 (m, 2H), 7.48-7.44 (m, 1H), 7.38-7.34 (m, 1H), 7.28-7.25 (m, 1H), 7.18-7.14 (m, 1H),2.43&2.36 (3H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  165.98, 142.07, 138.06, 135.36, 134.90, 134.03, 131.96, 131.49, 129.36, 129.17, 128.82, 128.47, 127.06, 127.02, 124.25, 120.53, 120.37, 21.34, 20.79. HRMS (ESI) calcd for C<sub>14</sub>H<sub>14</sub>NO<sup>+</sup> 212.1075, found 2212.1083.

# 4.4.8. N-phenylacetamide (2h) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.92 (s, 1H), 7.59 (d, I = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 7.5 Hz, 1H), 2.05 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 168.73, 139.81, 129.10, 123.41, 119.44, 24.45. HRMS (ESI) calcd for C<sub>8</sub>H<sub>10</sub>NO<sup>+</sup> 136.0762, found 136.0762.

#### 4.4.9. N-(p-tolyl)acetamide (2i) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.82 (s, 1H), 7.46 (d, I = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H), 2.02 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 168.48, 137.30, 132.27, 129.47, 119.46, 24.38, 20.86.

# 4.4.10. N-(4-methoxyphenyl)acetamide (2j) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.77 (s, 1H), 7.49 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.71 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C NMR  $(101 \text{ MHz}, \text{DMSO-}d_6) \delta$  168.18, 155.47, 133.00, 120.99, 114.22, 55.56, 24.24. HRMS (ESI) calcd for C<sub>9</sub>H<sub>12</sub>NO<sup>+</sup> 166.0868, found 166.0868.

## 4.4.11. N-(4-bromophenyl)acetamide (2k) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.06 (s, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 2.04 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) & 168.92, 139.15, 131.92, 121.31, 114.94, 24.48. HRMS (ESI) calcd for C<sub>8</sub>H<sub>9</sub>BrNO<sup>+</sup> 213.9868, found 213.9870.

# 4.4.12. N,2-diphenylacetamide (21)

M.p.: 85–87 °C. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.18 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.45–7.13 (m, 7H), 7.04 (t, *J* = 7.3 Hz, 1H), 3.66 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  169.56, 139.72, 136.50, 129.57, 129.17 (s, 3H), 128.77, 126.98, 123.66, 119.58, 43.83. HRMS (ESI) calcd for C<sub>14</sub>H<sub>14</sub>NO<sup>+</sup> 212.1075, found 212.1082.

## 4.4.13. (E)-N-styrylacetamide (2m) [11]

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (br, 1H), 7.56 (dd, J = 14.5, 10.8 Hz, 1H), 7.39–7.26 (m, 4H), 7.21 (t, J = 7.0 Hz, 1H), 6.14 (d, J = 14.5 Hz, 1H), 2.16 (s, 3H).

# 4.4.14. N-(4-((Tert-butyldimethylsilyl)oxy)phenyl)acetamide (2p)

M.p.: 94–97 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (br, 1H), 7.37 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 2.17 (s, 3H), 1.01 (s, 9H), 0.21 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.23, 152.32, 131.56, 121.63, 120.25, 25.66, 24.31, 18.17, -4.48. HRMS (ESI) calcd for C14H23NNaO2Si<sup>+</sup> 288.1390, found 288.1392.

#### 4.4.15. Tert-butyl (4-acetamidophenyl)carbamate (2q) [11]

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  9.75 (s, 1H), 9.17 (s, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 1.96 (s, 3H), 1.42 (s, 9H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 167.76, 152.79, 134.71, 133.85, 119.43, 118.44, 78.75, 28.12, 23.79,

## 4.4.16. N-(Benzo[d] [1,3]dioxol-5-yl)acetamide (2r)

M.p.: 85–87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (s, 1H), 7.23 (s, 1H), 6.78 (ABd, J = 19.9, 8.3 Hz, 2H), 5.98 (s, 2H), 2.17 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.38, 147.75, 144.30, 132.10, 113.32, 107.99, 103.07, 101.23, 24.30. HRMS (ESI) calcd for C<sub>9</sub>H<sub>9</sub>NNaO<sup>+</sup><sub>3</sub> 202.0475. found 202.0472.

#### Acknowledgments

We are grateful for the support of this work by the National Natural Science Foundation of China (21801224), the Natural Science Foundation of Zhejiang Province (LQ18B020009), the Scientific Research Foundation of Zhejiang Sci-Tech University (16062193-Y).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.04.056.

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