

NOTE

### 铜催化醛肟脱水/贝克曼重排选择性可切换反应

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**摘要** 廉价金属铜,可催化醛肟的脱水反应,生成有机腈. 该反应在腈类溶剂中发生,并且使用二氧化锰作助催化剂,三苯基膦作配体. 如果使用水作溶剂,则会发生贝克曼重排,生成酰胺. 这种选择性随溶剂切换的有趣反应,为合成相关有用的有机化合物提供了简便方法,兼具学术与实用价值.

关键词 醛肟; 脱水; 贝克曼重排; 腈; 酰胺

### Copper-Catalyzed Selectivity-Switchable Dehydration/Beckmann Rearrangement Reactions of Aldoxime

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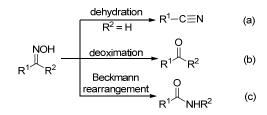
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**Abstract** It was found that, copper as a cheap metal, could well catalyze the dehydration reaction of aldoximes to organonitriles in nitrile solvent by using  $MnO_2$  as the co-catalyst and  $PPh_3$  as the ligand. In contrast, instead of organonitriles, the Cu-catalyzed reactions of the aldoximes in water led to amides, which were the products of the Beckmann rearrangements. These interesting selectivity-switchable reactions afford easy accesses to the related useful organic compounds and may be of both academic and practical values.

Keywords aldoxime; dehydration; Beckmann rearrangement; nitrile; amide

Oximes are easily accessible chemicals that can serve as the building blocks or ligands in synthetic organic chemistry with very broad application scopes. Despite their simple chemical structures, the reaction selectivities of oximes are complex and it may lead to three possible types of products in general (Scheme 1): the dehydration reaction of aldoximes can produce nitriles (path a), which are very useful intermediates in the industrial production of medicines, pesticides, materials, as well as fine chemicals; the oxidative deoximation reaction leads to the carbonyls (path b) and this method can be used in protection, characterization, and purification of carbonyl compounds as well as the synthesis of many important fine chemicals from the non-carbonyl starting materials, such as the pro-

duction of the spice *carvone* from *limonene*;<sup>[4]</sup> the Beckmann rearrangement of oximes gives a direct access to amides (path c), which are also very important building blocks in organic synthesis.<sup>[5]</sup>



**Scheme 1** Three typical reaction modes of oximes

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During our continuous investigations on green catalysis technologies, [6,7] we have reported a series of selective reactions of oximes as well as the related nitrogen-contained organic compounds.<sup>[7]</sup> Recently, it was unexpectedly found that catalyzed by Pd(OAc)2/MnO2, the dehydration reaction of aldoximes occurred in a nitrile solvent and led to the corresponding organonitriles.<sup>[7b]</sup> Control experiments as well as the X-ray photoelectron spectroscopy (XPS) studies demonstrated that the reaction proceeded through an interesting Pd/Mn relay catalysis mechanism. The method affords an efficient approach to synthesize organonitriles. However, as a noble metal, the price of Pd is expensive and it is dramatically increasing in recent two years (from ca. \$600/oz to \$1000/oz). Therefore, improving the protocol by using cheap metal catalysts (e.g. Cu, Fe, Co, Ni, etc.) is of good application values from the large-scale production viewpoint. [8] Recently, we investigated the copper-catalyzed reactions of aldoximes and found that the product selectivities were switchable by the reaction solvent.

#### 1 Results and discussion

Inspired by our previous work, [7b] 1 mmol of benzaldoxime 1a, 0.01 mmol of Cu(OAc)2 and 0.03 mmol of MnO<sub>2</sub> were initially heated in 2 mL [c(1a)=0.5 mol/L] of MeCN at 60 °C. The reaction was monitored by thin layer chromatography (TLC) and terminated after 96 h, affording the desired benzonitrile 2a in 88% GC yield (Table 1, Entry 1). Different from the Pd/Mn-catalyzed reaction, the Cu/Mn-catalyzed dehydration of aldoxime could be improved by adding PPh<sub>3</sub> ligand, and 2a could be produced in 98% GC yield in the case (Table 1, Entry 2). Control reactions demonstrated that MnO<sub>2</sub> additive was crucial for the transformation, otherwise, the product yield dropped dramatically (Table 1, Entries 3, 4). The isolated yield of 2a decreased to 80% due to the product volatility (Table 1, Entry 5 vs. Entry 2). It was then found that the reaction was obviously accelerated by using reduced amount of

**Table 1** Condition optimizations for the dehydration of benzaldoxime  $\mathbf{1a}$  to benzonitrile<sup>a</sup>

Entry	Ligand	Additive	$c^b/(\text{mol} \cdot \text{L}^{-1})$	t/h	Yield <sup>c</sup> /%
1	_	$MnO_2$	0.5	96	88 <sup>c</sup>
2	$PPh_3$	$MnO_2$	0.5	96	$98^d$
3	_	_	0.5	96	$33^d$
4	$PPh_3$	_	0.5	96	$37^{d}$
5	$PPh_3$	$MnO_2$	0.5	96	$80^c$
6	$PPh_3$	$MnO_2$	2.0	24	$93^{d}$
7	PPh <sub>3</sub>	$MnO_2$	2.0	24	76 <sup>c</sup>

<sup>&</sup>lt;sup>a</sup> The reactions were performed in 1 mmol of **1a** scale; <sup>b</sup> initial concentration of **1a**; <sup>c</sup> isolated yields based on **1a**; <sup>d</sup> GC yields.

solvent (0.5 mL), and **2a** could be produced in 93% GC yield (76% isolated yield) within 24 h (Table 1, Eentries 6, 7).

Under the optimized conditions, a series of aldoximes were employed to test the substrate scope of the reaction (Table 2). The reaction of electron-enriched aldoximes generally afforded higher product yield than the electron-deficient ones, while the later led to obviously more rapid reaction processes (Table 2, Entries  $1 \sim 8$  vs. Entries  $9 \sim 12$ ). The method was tolerant to substrate with active protons and (Z)-4-hydroxybenzaldehyde oxime ( $\mathbf{1g}$ ) bearing an phenolic hydroxyl could smoothly produce the corresponding organonitrile  $\mathbf{2g}$  in good yields (Table 2, Entries  $\mathbf{13}$ ,  $\mathbf{14}$ ).

**Table 2** Cu/Mn-catalyzed dehydration of aldoximes 1 to produce organonitriles  $2^a$ 

Entry	R	t/h	2	Yield <sup>c</sup> /%
1	Ph	96	2a	80 (98)
$2^b$	Ph	24	2a	76 (93)
3	$4-MeC_6H_4$	70	<b>2</b> b	92
$4^b$	$4-MeC_6H_4$	24	<b>2</b> b	87
5	$4-^{t}BuC_{6}H_{4}$	72	2c	75
$6^b$	$4-^{t}BuC_{6}H_{4}$	24	2c	73
7	4-MeOC <sub>6</sub> H <sub>4</sub>	70	2d	94
$8^b$	4-MeOC <sub>6</sub> H <sub>4</sub>	24	2d	81
9	$4-ClC_6H_4$	48	<b>2e</b>	74
$10^{b}$	$4-ClC_6H_4$	20	<b>2e</b>	73
11	4-BrC <sub>6</sub> H <sub>4</sub>	48	2f	76
$12^{b}$	4-BrC <sub>6</sub> H <sub>4</sub>	22	2f	78
13	$4\text{-HOC}_6\text{H}_4$	72	<b>2</b> g	90
14 <sup>b</sup>	$4\text{-HOC}_6\text{H}_4$	24	2g	87

<sup>&</sup>lt;sup>a</sup> The reactions were performed in 1 mmol of **1** scale and without special instruction, the initial concentration of **1** was 0.5 mol/L; <sup>b</sup> the initial concentration of **1** was 2.0 mol/L; <sup>c</sup> isolated yields based on **1a** outside the parenthesis, GC yields inside the parenthesis.

We then tried to further improve the method by using water as the green solvent. However, it was interesting that the reaction of benzaldoxime (1a) in aqueous solvent led to benzamide 3a instead of the expected benzonitrile 2a (Table 3, Entry 1). Clearly, a Beckmann rearrangement occurred instead of the dehydration reaction in this case. Further screenings demonstrated that neither MnO<sub>2</sub> nor PPh<sub>3</sub> was necessary for the reaction and the reaction of 1a with only 1 mol% Cu(OAc)<sub>2</sub> produced 2a in 78% yield (Table 3, Entry 3 vs. Entries 1, 2). MnO<sub>2</sub>, PPh<sub>3</sub> and their mixtures were all ineffective for the reaction (Table 3, Entries 4~6).

The Cu-catalyzed Beckmann rearrangement in water was then applied to a series of aldoxime substrates (Table 4). Bearing an electron-donation group, (Z)-4-methyl-

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**Table 3** Condition optimizations for the Cu-catalyzed Beckmann rearrangement of 1a to  $3a^a$ 

Entry	Catalyst <sup>b</sup>	Yield <sup>c</sup> /%	
1	Cu(OAc) <sub>2</sub> (1 mol%), MnO <sub>2</sub> (3 mol%), PPh <sub>3</sub> (4 mol%)	70	
2	Cu(OAc) <sub>2</sub> (1 mol%), MnO <sub>2</sub> (3 mol%)	62	
3	Cu(OAc) <sub>2</sub> (1 mol%)	78	
4	MnO <sub>2</sub> (3 mol%)	No reaction	
5	PPh <sub>3</sub> (4 mol%)	No reaction	
6	MnO <sub>2</sub> (3 mol%), PPh <sub>3</sub> (4 mol%)	No reaction	

<sup>&</sup>lt;sup>a</sup> 1 mmol of **1a** and 2 mL of water were employed; <sup>b</sup> values inside the parenthesis were the molar ratios vs. **1a**; <sup>c</sup> isolated yields based on **1a**.

**Table 4** Cu-catalyzed Beckmann rearrangement of aldoximes in water<sup>a</sup>

$$\begin{array}{c} \text{NOH} \\ \text{I} \\ \text{H} \end{array} \xrightarrow{\begin{array}{c} \text{Cu(OAc)}_2 \text{ (1 mol\%)} \\ \text{H}_2\text{O, 80 °C} \end{array}} \begin{array}{c} \text{O} \\ \text{NH}_2 \\ \text{3} \end{array}$$

Entry	R	t/d	3	Yield <sup>b</sup> /%
1	Ph	5	3a	78
2	$4-MeC_6H_4$	7	3b	70
3	$4-MeC_6H_4$	$3^c$	3b	68
4	$4-C1C_6H_4$	4	3c	65
5	$3-C1C_6H_4$	4	3d	100
6	4-BrC <sub>6</sub> H <sub>4</sub>	1	3e	80
7	$4-CF_3C_6H_4$	6	3f	55
8	$4-CF_3C_6H_4$	$2^c$	3f	60
9	(E)-PhCH=CH	4	3g	76

 $<sup>^</sup>a$  1 mmol of 1 and 2 mL of water were employed;  $^b$  Isolated yields based on 1;

benzaldehyde oxime (1b) as substrate required extended reaction time and produced the related amide 3b in a decreased yield (Table 4, Entry 2 vs. Entry 1). The reaction could be accelerated by using higher reaction temperature

at 100 °C (Table 4, Entry 3 vs. Entry 2). It was found that electron-deficient aldoxime substrates were more preferable and they led to the corresponding products  $3c\sim3f$  in moderate to quantitative yields in reduced reaction times (Table 4, Entries  $4\sim8$ ). The protocol was tolerant to C=C bond in substrate and the reaction with cinnamaldehyde oxime 1j as substrate afforded the desired amide 3g smoothly in 76% yield (Table 4, Entry 9).

On the basis of the literature reports<sup>[5,7b,9,10]</sup> as well as our previous works, a plausible mechanism for these selectivity switchable interesting reactions was proposed. As shown in Scheme 2, as proved by the control reactions in our previous works, [7b] in the presence of catalytic MnO<sub>2</sub>, the aldoximes 1 could be oxidized by air and led to the intermediate nitrile oxide 4. On the other hand, in nitrile solvent such as MeCN, the reaction of catalyst Cu(OAc)<sub>2</sub> with solvent (MeCN) first produced the metal complex 5 due to the strong ligating ability of the nitriles (path a).<sup>[9]</sup> Coupling of 5 with 4 led to the intermediate 6. Transfer of the oxygen from the nitrile oxide ligand to the acetonitrile ligand, probably via the Cu-O complex 7, [10] might lead to a new Cu-nitrile oxide complex 8, which then released the product 2 and by-product MeCNO species via coordinating with the high concentration solvent MeCN to regenerate the catalytic species 5. In contrast, under aqueous conditions (path b), Cu(OAc)<sub>2</sub> as a Lewis acid catalyst could coordinate with the substrate to produce the intermediate 9, in which, the N—O bond was activated and it could lead to the intermediate cation 10 and OH via a rearrangement. The reaction of 10 with OH produced amides 3 (Scheme 2). [5] Although these mechanisms remain to be fully clarified and alternative processes may also exist due to the complex reaction systems, Scheme 2 shall be the most likely mechanism on the basis of the experimental results and the literature reports.

#### 2 Conclusion

In conclusion, it was found that, copper as a cheap metal, could well catalyze the dehydration reaction of aldox-

Scheme 2 Possible mechanisms of the reactions

 $<sup>^</sup>c$  Reaction performed at 100  $\,^\circ \! \mathbb{C}$  .

imes to produce organonitriles in nitrile solvent in the presence of  $MnO_2$  and  $PPh_3$ . In contrast, the reaction in water led to amides, which were the products of the Beckmann rearrangement reactions. These selectivity-switchable reactions are interesting and are of both academic and practical values.

#### 3 Experimental

#### 3.1 General methods

Melting points were measured using a WRS-2A digital instrument. IR spectra were measured on a Bruker Tensor 27 Infrared spectrometer.  $^{1}$ H NMR and  $^{13}$ C NMR spectra were recorded on a Bruker Avance 600/400 instrument (600 or 400 MHz for  $^{1}$ H NMR and 150 or 100 MHz for  $^{13}$ C NMR spectroscopy). Chemical shifts for  $^{1}$ H NMR were referred to internal Me<sub>4</sub>Si.

Chemicals were purchased from reagent merchant with purities more than 98%. Solvents were analytical pure (AR) and directly used without any special treatment.

# 3.2 General procedure for the Cu/Mn-catalyzed dehydration of aldoximes

To a reaction tube, 1 mmol of aldoxime 1, 0.01 mmol of Cu(OAc)<sub>2</sub>, 0.03 mmol of MnO<sub>2</sub>, 0.04 mmol of PPh<sub>3</sub> and 0.5~2 mL of MeCN (see text) were added. The mixture was stirred at 60 °C in open air and the reaction was monitored by thin layer chromatography (TLC). After cooled to room temperature, the solvent was evaporated by vacuum and the residue was purified by preparation TLC (eluent: petroleum ether) to give the corresponding organonitriles 2.

Benzonitrile (**2a**):<sup>[7b]</sup> 82.5 mg, yield 80%. Oil; IR (film) v: 3067, 2260, 1491, 1447, 758 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 103 (M<sup>+</sup>, 100), 76 (22).

4-Methylbenzonitrile **(2b)**:<sup>[7b]</sup> 107.8 mg, yield 92%. Oil; IR (film) *v*: 3040, 2925, 2227, 1607, 1176, 817, 546 cm<sup>-1</sup>; MS (EI, 70 eV) *m/z* (%): 118 (11), 117 (M<sup>+</sup>, 100), 116 (63).

4-(*tert*-Butyl)benzonitrile (**2c**):<sup>[7b]</sup> 119.4 mg, yield 75%. Oil; IR (film) v: 3454, 2966, 2227, 1607, 1397, 1106, 837, 568 cm<sup>-1</sup>; MS (EI, 70 eV) *m/z* (%): 160 (4), 159 (M<sup>+</sup>, 21), 145 (12), 144 (100), 116 (60).

4-Methoxybenzonitrile (**2d**): 125.2 mg, yield 94%. White solid, m.p.  $55.2 \sim 56.6$  °C (lit.<sup>[7b]</sup>  $55 \sim 57$  °C); IR (film) v: 2216, 1603, 1509, 1259, 1174, 1023, 830, 680, 546 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 134 (11), 133 (M<sup>+</sup>, 100), 103 (46).

4-Chlorobenzonitrile (**2e**): 101.8 mg, yield 74%. White solid, m.p.  $92.9 \sim 93.7$  °C (lit. [7b]  $93 \sim 94$  °C); IR (KBr) v: 3453, 3091, 2224, 1591, 1482, 1088, 828, 542 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 139 (36), 137 (M<sup>+</sup>, 100), 102 (34).

4-Bromobenzonitrile (**2f**): 142.0 mg, yield 78%. White solid, m.p. 113.1 $\sim$ 113.7 °C (lit.<sup>[7b]</sup> 113 $\sim$ 114 °C); IR (KBr)  $\nu$ : 3272, 2222, 1474, 1065, 1010, 826, 542 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 183 (56), 181 (M<sup>+</sup>, 57), 102 (100).

4-Hydroxybenzonitrile (2g): 107.2 mg, yield 90%. Sol-

id, m.p.  $107.6 \sim 109.8$  °C (lit.<sup>[7b]</sup>  $107 \sim 109$  °C); IR (KBr) v: 2669, 2231, 1585, 1510, 1285, 1163, 838, 699, 545 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 120 (11), 119 (M<sup>+</sup>, 100), 91 (24).

## 3.3 General procedure for the Cu-catalyzed Beckmann rearrangement of aldoximes

To a reaction tube, 1 mmol of aldoxime 1, 0.01 mmol of  $Cu(OAc)_2$  and 2 mL of water were added. The mixture was stirred at 80 °C and the reaction was monitored by TLC. After cooled to room temperature, the solvent was evaporated by vacuum and the residue was purified by preparation TLC [eluent: V(petroleum ether): V(EtOAc)=1: 1] to give the corresponding amides 3.

Benzamide (**3a**): 94.5 mg, yield 78%. White solid, m.p.  $127.6 \sim 128.1$  °C (lit. [11]  $128 \sim 129$  °C); <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 7.39 (s, 1H), 7.45 $\sim$ 7.54 (m, 3H), 7.89 $\sim$ 7.91 (m, 2H), 8.00 (s, 1H); <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 127.4, 128.2, 131.2, 134.2, 167.9; IR (KBr)  $\nu$ : 3693, 2925, 1579, 1127, 963, 870, 693, 644 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 121 (M<sup>+</sup>, 68), 105 (90), 77 (100).

4-Methylbenzamide (**3b**): 94.6 mg, yield 70%. White solid, m.p.  $158.2 \sim 159.3$  °C (lit. [11]  $158 \sim 159$  °C); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.41 (s, 3H), 6.11 (br s, 2H), 7.25 (d, J=7.8 Hz, 2H), 7.72 (d, J=7.8 Hz, 2H); IR (KBr)  $\nu$ : 2956, 2925, 2853, 1670, 1615, 1567, 1460, 1412, 1395 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 135 (M<sup>+</sup>, 52), 119 (100).

4-Chlorobenzamide (**3c**): 101.1 mg, yield 65%. White solid, m.p. 172.4 $\sim$ 174.2 °C (lit.<sup>[11]</sup> 172 $\sim$ 174 °C); <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 7.47 (s, 1H), 7.53 (d, J= 8.4 Hz, 2H), 7.90 (d, J=8.4 Hz, 2H), 8.07 (s, 1H); <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 133.5, 134.6, 138.3, 141.3, 172.1; IR (KBr)  $\nu$ : 3370, 3180, 1664, 1624, 1410, 1392, 1092, 1017, 842, 788 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 155 (M<sup>+</sup>, 55), 139 (100), 111 (70).

3-Chlorobenzamide (**3d**): 155.5 mg, yield 100%. White solid, m.p. 132.6 $\sim$ 134.9 °C (lit. [11] 132 $\sim$ 134 °C); <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 7.45 (d, J=7.8 Hz, 1H), 7.52 $\sim$ 7.54 (m, 1H), 7.59 $\sim$ 7.61 (m, 1H), 7.85 (d, J=7.8 Hz, 2H), 7.92 (s, 1H); <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 131.4, 132.5, 135.4, 136.3, 138.4, 141.6, 171.7; IR (KBr)  $\nu$ : 3365, 3177, 2951, 2922, 2851, 1656, 1625, 1462, 1375, 1120 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 155 (M<sup>+</sup>, 68), 139 (100), 111 (49).

4-Bromobenzamide (**3e**): 160.1 mg, yield 80%. White solid, m.p.  $190.1 \sim 193.2$  °C (lit.<sup>[11]</sup> 190 °C); <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 7.46 (s, 1H), 7.67 (d, J=8.4 Hz, 2H), 7.82 (d, J=8.4 Hz, 2H), 8.07 (s, 1H); <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 125.0, 129.6, 131.2, 133.4, 166.9; IR (KBr)  $\nu$ : 3358, 3176, 1784, 1660, 1407, 1066, 842, 784, 650, 533, 448 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 200 (48), 199 (M<sup>+</sup>, 4), 198 (53), 184 (88), 182 (100).

4-(Trifluoromethyl)benzamide (**3f**): 113.5 mg, yield 60%. White solid, m.p.184.3 $\sim$ 185.1 °C (lit. [11] 183 $\sim$ 184 °C); <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 7.66 (s, 1H), 7.85 (d, J=7.8 Hz, 2H), 8.08 (d, J=8.4 Hz, 2H), 8.23 (s,

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1H); <sup>13</sup>C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 123.9 (d,  $J_{\text{C-F}}$ = 270.75 Hz), 125.2 (d,  $J_{\text{C-F}}$ = 3.75 Hz), 128.3, 131.1 (d,  $J_{\text{C-F}}$ = 31.65 Hz), 138.1, 166.7; IR (film)  $\nu$ : 3373, 3175, 1656, 1577, 1420, 1322, 1065, 859, 807, 661, 623, 536, 470 cm<sup>-1</sup>; MS (EI, 70 eV) m/z (%): 190 (6), 189 (M<sup>+</sup>, 66), 173 (100), 145 (95).

Cinnamamide (**3g**): 111.9 mg, yield 76%. White solid, m.p.  $147.4 \sim 148.9$  °C (lit.  $^{[11]}$   $148 \sim 151$  °C);  $^{1}$ H NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 6.64 (d, J=15.6 Hz, 1H), 7.16 (s, 1H), 7.38  $\sim$  7.41 (m, 1H), 7.42  $\sim$  7.46 (m, 3H), 7.57  $\sim$  7.61 (m, 3H);  $^{13}$ C NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 122.3, 127.5, 128.9, 129.4, 134.8, 139.1, 166.7; IR (film) v: 3362, 3168, 1662, 1605, 1397, 1114, 968, 853, 697, 526, 475 cm $^{-1}$ ; MS (EI, 70 eV) m/z (%): 148 (9), 147 (M $^+$ , 48), 146 (100), 131 (54).

**Supporting Information** <sup>1</sup>H NMR spectra of compounds **3**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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