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ARTICLE TYPE

Rearrangement of aldoximes to amides in water under air atmosphere catalyzed by water-soluble iridium complex $[Cp^*Ir(H_2O)_3][OTf]_2$†

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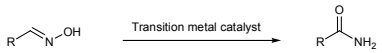
In the presence of water-soluble iridium complex $[Cp^*Ir(H_2O)_3][OTf]_2$, a variety of aldoximes, including aromatic, aliphatic, conjugated unsaturated and non-conjugated unsaturated aldoximes, were converted into the corresponding amides in water with good to excellent yields. Further, the one-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate *via* a tandem condensation/rearrangement reaction in water was also accomplished. Compared with the reported organometallic catalysts for the rearrangement of aldoximes to amides in water, the present catalyst exhibited some advantages such as phosphorus ligand-free, low catalyst loading, and operational convenience under air atmosphere.

Introduction

Amides are one of the most important functional groups of proteins, and are also widely utilized as key intermediates in the construction of numerous fine chemicals, natural products, peptides and polymers.[1] Typically, amides were synthesized by reactions of activated carboxylic acid derivatives, such as acid chlorides, anhydrides and esters, with amines.[2] However, these procedures suffer from use of toxic and expensive reagents, low tolerance to sensitive functional groups and the generation of a large amount of harmful by-products. As a result of it, in 2005 the American Chemical Society Green Chemistry Institute (comprising members from major pharmaceutical industries worldwide) voted 'amide formation avoiding poor atom economy reagents' as the top challenge for organic chemistry.[3]

The rearrangement of aldoximes to amides presents a complete atom-economical transformation and is accomplished using a variety of transition metal catalysts, such as Rh,[4] Ru,[5] Ir,[6] Au,[7] Pd,[8] Cu,[9] Zn[10] and In[10b] complexes or salts. However, these procedures have to be performed in organic solvents such as toluene. In recent years, much attention has been paid on the development of organic synthesis in water because water is cheap, safe and environmentally benign compared with traditional organic solvents. In 2007, Mizuno and co-workers reported the first example of the rearrangement of aldoximes to amides in water catalyzed by heterogeneous $Rh(OH)x/Al_2O_3$ (4 mol%).[11] However, this procedure required high reaction temperature (160 ^oC). Very recently, Cadierno and co-workers demonstrated the transformation of aldoximes to amides in water under nitrogen atmosphere catalyzed by homogeneous ruthenium complexes bearing water-soluble tris(dimethylamino)phosphine or tris(5-(2-aminothiazolyl))phosphine trihydrochloride as ligands (3-5 mol%).[12] From the standpoint of sustainable chemistry, the development of a new organometallic catalyst bearing non-phosphorus ligands with low catalyst loading for the rearrangement of aldoximes to amides in water under air atmosphere is highly desirable.

We have reported transition metal-catalyzed regioselective *N*-alkylation with alcohols for the preparation of 2-(*N*-alkylamino)azoles,[13a-d] 2-(*N*-alkylamino)quinazolines,[13e] *N,N'*-alkylarylureas and *N,N'*-dialkylureas.[13f] We have also demonstrated direct synthesis of *N*-alkylated amides from aldoximes and alcohols *via* tandem rearrangement/*N*-alkylation reaction catalyzed by Ru/Ir dual catalyst system,[14] Ir-catalyzed direct coupling of indoles with methanol to 3,3'-bisindoles (3,3'-BIM's)[15] and the *N*-alkylation of sulfonamides with alcohols in water catalyzed by water-soluble $[Cp^*Ir(6,6'-(OH)_2bpy)(H_2O)][OTf]_2$.[16] As part of a continuing interest in developing iridium-catalyzed reactions, herein we wish to describe our efforts towards the rearrangement of aldoximes to amides in water under air atmosphere catalyzed by water-soluble iridium complex. Further, the reaction mechanism was also investigated.



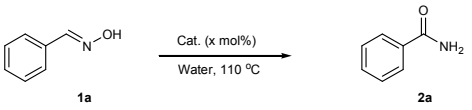
Scheme 1 Transition metal-catalyzed rearrangement of aldoximes to amides.

Results and discussion

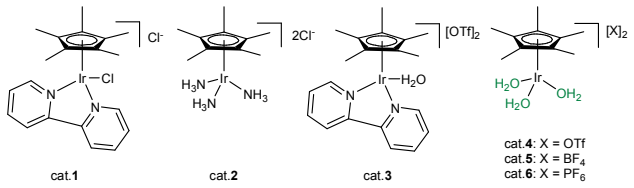
Initially, the rearrangement of benzaldoxime **1a** was chosen as a model in order to explore the feasibility of reaction. A range of water-soluble Cp*Ir complexes (Cp* = η^5-pentamethylcyclopentadienyl) (2 mol%) were assayed for their ability to catalyze this model reaction, including cationic

[Cp*Ir(bpy)Cl]Cl (bpy = 2,2'-bipyridine) (cat.**1**)[17] Cp*Ir complex bearing ammonia ligands $[Cp^*Ir(NH_3)_3][Cl]_2$ (cat.**2**),[18] Cp*Ir complex bearing one or more aqua ligands $[Cp^*Ir(bpy)(H_2O)][OTf]_2$ (cat.**3**)[19] and $[Cp^*Ir(H_2O)_3][OTf]_2$ (cat.**4**).[20] In the presence of cat.**1** and cat.**3**, reactions of **1a** (0.5 mmol) were carried out in water (1 ml) at 110 °C for 12h and no conversion was observed (Table 1, entry 1 and entry 3). Using cat.**2** as the catalyst, the product **2a** was obtained with 12% yield (Table 1, entry 2). To our delight, cat.**4** exhibited excellent reactivity for this rearrangement and this reaction afforded the product **2a** with 90% yield (Table 1, entry 4). The analogous complexes cat.**5** and cat.**6** bearing BF_4 and PF_6 as counteranions exhibited relatively low catalytic activities (Table 1, entries 5-6). When catalyst loading of cat.**4** was reduced to 1.5 mol%, the product **2a** could be obtained with 89% yield (Table 1, entry 7). Attempt to further reduce to the catalyst loading resulted in low yield (Table 1, entry 8).

Table 1 Rearrangement of benzaldoxime **1a** to benzamide **2a** [a]



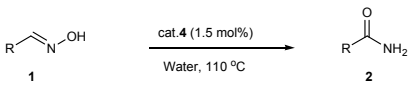
Entry	Cat.	x	Yield (%)[b]
1	cat.**1**	2.0	0
2	cat.**2**	2.0	12
3	cat.**3**	2.0	0
4	cat.**4**	2.0	90
5	cat.**5**	2.0	83
6	cat.**6**	2.0	60
7	**cat.4**	**1.5**	**89**
8	cat.**4**	1.0	76



[a] Reaction conditions: **1a** (0.5 mmol), catal. (x mol%), water (1 ml), 110 °C, 12h. [b] Isolated yield.

With the optimal reaction conditions in hand (Table 1, entry 7), the rearrangement of a variety of aromatic and aliphatic aldoximes was examined and the results are summarized in Table 2. Reactions of benzaldoximes bearing one or two electron-donating groups, such as methyl **1b**, isopropyl **1c**, *tert*-butyl **1d**, methoxy **1e** and dimethoxy **1f**, afforded the corresponding products **2b-f** with 82-93% yields (Table 2, entries 1-5). Similarly, transformations of benzaldoximes bearing one or two halide atoms, such as fluoro **1g-h**, chloro **1i-j**, dichloro **1k** and bromo **1l-m**, gave the desired products **2g-m** with 80-95% yields (Table 2, entries 6-12). The benzaldoximes bearing strong electron-withdrawing group, such as nitro **1n-o**, trifluoromethyl **1p** and trifluoromethoxy **1q**, were also proven to be suitable substrates, and the corresponding products **2n-q** were obtained with 82-86% yields (Table 2, entries 13-16). Furthermore, highly catalytic activities were also found in reactions of 2-naphthaldoxime **1r** and thiophene-2-aldoxime **1s** (Table 2, entries 17-18). In the case of aliphatic aldoximes, including 2-pentanaldoxime **1t**, 3-phenylpropanaldoxime **1u**, butylaldoxime **1v** and hexanaldoxime

Table 2 Reactions of a variety of aromatic and aliphatic aldoximes **1** to amides **2** [a]



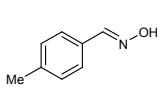
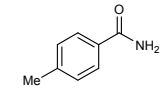
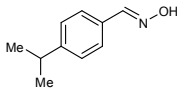
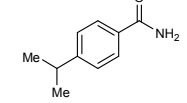
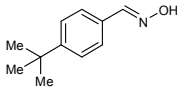
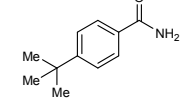
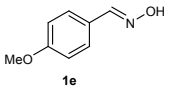
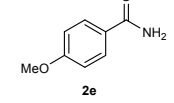
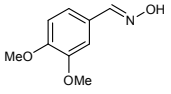
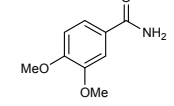
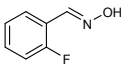
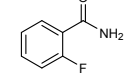
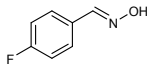
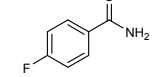
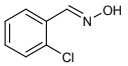
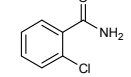
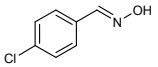
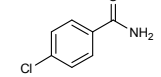
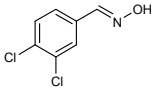
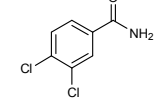
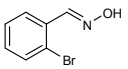
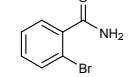
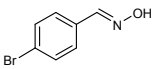
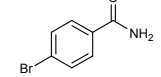
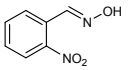
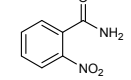
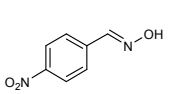
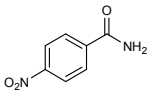
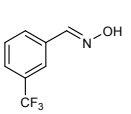
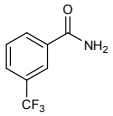
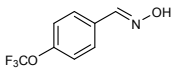
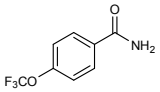
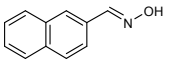
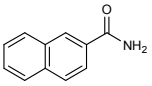
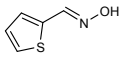
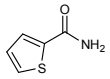
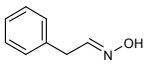
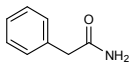
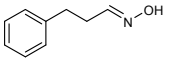
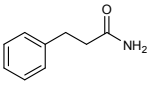
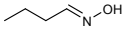
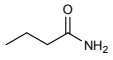
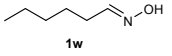
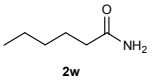
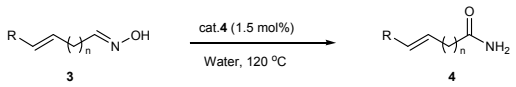
Entry	Aldoxime	Amide	Yield (%)[b]
1	 **1b**	 **2b**	93
2	 **1c**	 **2c**	92
3	 **1d**	 **2d**	83
4	 **1e**	 **2e**	82 [c]
5	 **1f**	 **2f**	92
6	 **1g**	 **2g**	83
7	 **1h**	 **2h**	95
8	 **1i**	 **2i**	88
9	 **1j**	 **2j**	93
10	 **1k**	 **2k**	81
11	 **1l**	 **2l**	80
12	 **1m**	 **2m**	90
13	 **1n**	 **2n**	82 [c]

Table 2 (Continued)

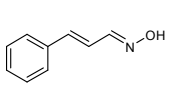
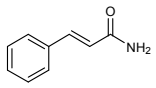
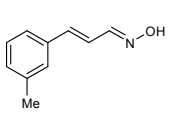
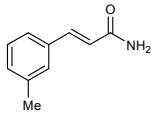
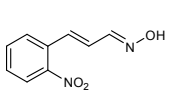
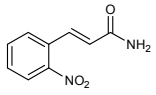
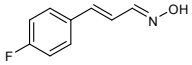
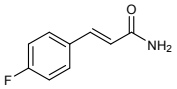
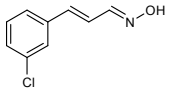
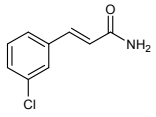
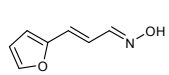
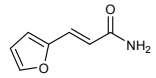
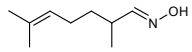
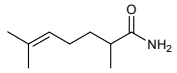
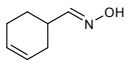
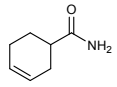
Entry	Aldoxime	Amide	Yield (%) [b]
14	 **1o**	 **2o**	86
15	 **1p**	 **2p**	84
16	 **1q**	 **2q**	83 [d]
17	 **1r**	 **2r**	80 [d]
18	 **1s**	 **2s**	90
19	 **1t**	 **2t**	92
20	 **1u**	 **2u**	82
21	 **1v**	 **2v**	80
22	 **1w**	 **2w**	78

[a] Reaction conditions: **1a** (0.5 mmol), cat.4 (1.5 mol%), water (1 ml), 110 °C, 12h. [b] Isolated yield. [c] 120 °C. [d] cat.**4** (2.5 mol%).

Table 3 Reactions of a variety of unsaturated aldoximes **3** to amides **4** [a]



3 **4**

Entry	Aldoxime	Amide	Yield (%) [b]
1	 **3a**	 **4a**	85
2	 **3b**	 **4b**	80
3	 **3c**	 **4c**	90
4	 **3d**	 **4d**	81
5	 **3e**	 **4e**	86
6	 **3f**	 **4f**	80 [c]
7	 **3g**	 **4g**	77 [c]
8	 **3h**	 **4h**	82 [c]

[a] Reaction conditions: **3** (0.5 mmol), cat.**4** (1.5 mol%), water (1 ml), 120 °C, 12h. [b] Isolated yield. [c] cat.**4** (2.5 mol%).

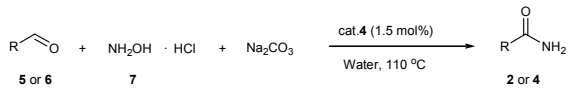
1w, the desired products **2t-w** could be obtained with 78-92% yields (Table 2, entries 19-22).

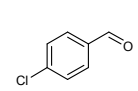
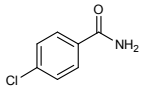
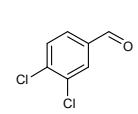
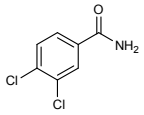
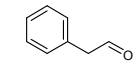
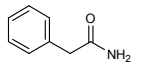
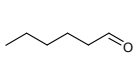
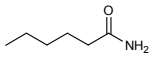
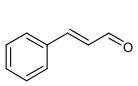
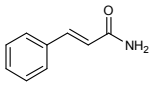
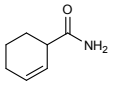
To expand further the scope of reaction, a series of unsaturated aldoximes were investigated. As shown in Table 3, *α,β*-unsaturated cinnamaldoxime **3a** was converted into the corresponding product **4a** with 85% yield (Table 3, entry 1). Reactions of cinnamaldoximes bearing an electron-donating group **3b** or strong electron-withdrawing group **3c** afforded the desired products **4b** and **4c** with 80% and 90% yields, respectively (Table 3, entries 2-3). When cinnamaldoximes bearing a halide atom **3d** and **3e** were used as substrates, the corresponding products **4d** and **4e** were obtained with 81% and 86% yields, respectively (Table 3, entries 4-5). The rearrangement was also applied to 3-(furan-2-yl)acrylamide **3f**, affording the desired product **4f** with 80% yield (Table 3, entry 6). Furthermore, non-conjugated unsaturated aldoximes **3g** and **3h** were examined and the desired products **4g** and **4h** were obtained with 77% and 82% yields, respectively (Table 3, entries 7-8).

The one-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate *via* a tandem condensation/rearrangement reaction in water was also investigated.[21] As shown in Table 4, in the presence of cat.**4**, reactions of a variety of aldehydes, including aromatic and aliphatic aldehydes **5** and unsaturated aldehydes **6**, afforded the desired products **2** and **4** with 71-86% yields.

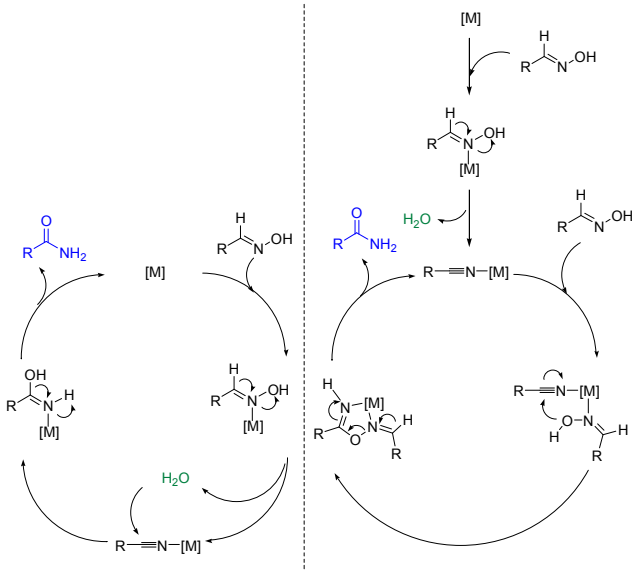
Two different reaction mechanisms for transition metal-catalyzed rearrangement of aldoximes to amides have been proposed.[22] The first mechanism involves the metal-promoted dehydration of aldoximes into metal-nitrile species, which are subsequently hydrated by water released in the previous step to give amides (Scheme 2, left). In the secondary mechanism, the metal-nitrile species, generated in the initial dehydration of aldoximes, are attacked by another coordinated aldoximes to give five-membered cyclic species, which decomposed to release amides with the regeneration of the metal coordinated nitriles as

Table 4 One-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate. [a]



Entry	Aldehyde	Amide	Yield (%) [b]
1	 **5j**	 **2j**	85
2	 **5k**	 **2k**	80
3	 **5t**	 **2t**	86
4	 **5w**	 **2w**	71
5	 **6a**	 **4a**	83 [c]
6	 **6h**	 **4h**	80 [d]

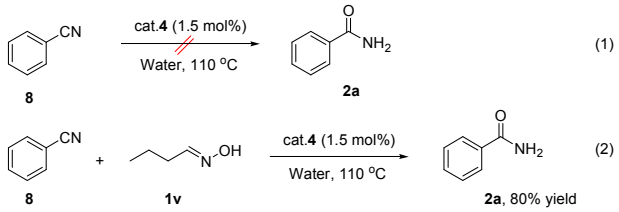
[a] Reaction conditions: **5** or **6** (0.5 mmol), **7** (1 equiv.), Na_2CO_3 (0.5 equiv.), water (1 ml), rt, 0.5 h. Then, cat.**4** (1.5 mol%) was added into the reactor, 110 °C, 12h. [b] Isolated yield. [c] cat.**4** (1.5 mol%), 120 °C. [d] cat.**4** (2.5 mol%), 120 °C.



Scheme 2. Two different reaction mechanisms.

catalytic species (Scheme 2, right).

To obtain the information about mechanism for this present reaction, several experiments were undertaken. The process of the rearrangement of benzaldoxime **1a** to benzamide **2a** (Table 1, entry 7) was monitored by ^{1}H NMR spectrum and none of benzonitrile as a by-product was detected. Further, in the presence of cat.**4** (1.5 mol%), the reaction of benzonitrile **8** was carried out in water at 110 °C for 12h and no conversion was observed [eqn (1)]. With the aid of butylaldoxime **1v**, the hydration of **8** proceeded for 12h under same conditions to give benzamide **2a** with 80% yield [eqn (2)]. Therefore, the rearrangement of aldoximes to amides in water catalyzed by water-soluble iridium complex $[Cp^*Ir(H_2O)_3][OTf]_2$ is in accord with the secondary mechanism.



Conclusion

We have demonstrated a general and highly efficient protocol for the rearrangement of aldoximes to amides in water under air atmosphere catalyzed by water-soluble iridium complex. In the presence of $[Cp^*Ir(H_2O)_3][OTf]_2$, a variety of aldoximes, including aromatic, aliphatic, conjugated unsaturated and non-conjugated unsaturated aldoximes, were converted into the corresponding amides with good to excellent yields. Further, the one-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate *via* a tandem condensation/rearrangement reaction in water was also accomplished. Compared with the reported organometallic catalysts for the rearrangement of aldoximes to amides in water, the present catalyst exhibited some advantages such as phosphorus ligand-free, low catalyst loading and operational convenience under air atmosphere.

Experimental Section

General Experimental Details. High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-Tof MS(Micro) spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$. Melting points were measured on a X-6 micro-melting apparatus. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a Bruker Avance III spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 2.50 ppm for DMSO-d_6. Coupling constants *J* values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz using a Bruker Avance III spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$ and 39.5 ppm for DMSO-d_6. ^{13}C NMR spectra were routinely run with broadband decoupling. All reactions were run under an atmosphere of air, unless otherwise

indicated. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates.

[Cp*Ir(bpy)Cl]Cl (cat.**1**),[23] $[Cp^*Ir(NH_3)_3][Cl]_2$ (cat.**2**),[18] $[Cp^*Ir(bpy)(H_2O)][OTf]_2$ (cat.**3**),[19] $[Cp^*Ir(H_2O)_3][OTf]_2$ (cat.**4**),[20a] $[Cp^*Ir(H_2O)_3][BF_4]_2$ (cat.**5**)[20a] and $[Cp^*Ir(H_2O)_3][PF_6]_2$ (cat.**6**)[20a] were synthesized according the previous reports.

General procedure for the rearrangement of aldoximes to amides in water catalyzed by $[Cp^*Ir(H_2O)_3][OTf]_2$. To an oven-dried, 25 ml Schlenk tube were added aldoximes (0.5 mmol), $[Cp^*Ir(H_2O)_3][OTf]_2$ (0.0075 mmol, 1.5 mol%) and H_2O (1 ml). The mixture of reaction was heated at 110 °C or 120 °C for 12h and allowed to cool to ambient temperature. The mixture of reaction was concentrated in *vacuo*, washed with hexanes, and isolated by simple filtration to afford the desired product.

Benzamide (2a).[5a] mp 128-129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H, ArH), 7.54 (t, *J* = 7.3 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 2H, ArH), 6.16 (br s, 1H, NH), 6.00 (br s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 133.3, 131.9, 128.6, 127.3.

4-methylbenzamide (2b).[5a] mp 159-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H, ArH), 7.25 (d, *J* = 7.9 Hz, 2H, ArH), 6.12 (br s, 1H, NH), 5.87 (br s, 1H, NH), 2.41 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 142.5, 130.4, 129.2, 127.3, 21.4.

4-isopropylbenzamide (2c).[24] mp 152-153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H, ArH), 7.30 (d, *J* = 8.2 Hz, 2H, ArH), 6.09 (br s, 1H, NH), 5.84 (br s, 1H, NH), 2.96 (heptet, *J* = 6.9 Hz, 1H , CH), 1.27 (d, *J* = 6.9 Hz, 6H , CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 153.2, 130.8, 127.5, 126.6, 34.1, 23.7.

4-(*tert*-butyl)benzamide (2d).[24] mp 173-174 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H, ArH), 7.47 (d, *J* = 8.0 Hz, 2H, ArH), 6.10 (br s, 1H, NH), 5.80 (br s, 1H, NH), 1.34 (s, 9H , CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 155.5, 130.4, 127.2, 125.5, 34.9, 31.1.

4-methoxybenzamide (2e).[12] mp 167-168 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.85-7.83 (m, 3H, ArH and NH), 7.19 (br s, 1H, NH), 6.97 (d, *J* = 8.3 Hz, 2H, ArH), 3.80 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.4, 161.5, 129.3, 126.5, 113.3, 55.3.

3,4-dimethoxybenzamide (2f).[25] mp 166-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.9 Hz, 1H, ArH), 7.34 (dd, *J* = 8.3 Hz and *J* = 1.9 Hz, 1H, ArH), 6.88 (d, *J* = 8.4 Hz, 1H, ArH), 6.09 (br s, 1H, NH), 5.84 (br s, 1H, NH), 3.94 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 152.1, 148.9, 125.8, 120.1, 110.7, 110.2, 56.0.

2-fluorobenzamide (2g).[12] mp 115-116 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69-7.64 (m, 3H, ArH and 2xNH), 7.54-7.50 (m,1H, ArH), 7.29-7.25 (m, 2H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 159.3 (d, $J_{C\text{-}F}$ = 247.7 Hz), 132.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 130.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 124.3 (d, $J_{C\text{-}F}$ = 2.6 Hz), 123.8 (d, $J_{C\text{-}F}$ = 14.0 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.5 Hz).

4-fluorobenzamide (2h).[12] mp 156-157 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 (br s, 1H, NH), 7.95-7.92 (m, 2H, ArH), 7.41 (br s, 1H, NH), 7.28 (t, *J* = 8.8 Hz, 2H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.8, 163.9 (d, $J_{C\text{-}F}$ = 246.8 Hz), 130.7(d, $J_{C\text{-}F}$ = 1.9 Hz), 130.0 (d, $J_{C\text{-}F}$ = 9.0 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.4 Hz).

2-chlorobenzamide (2i).[12] mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H, ArH), 7.44-7.34 (m, 3H, ArH), 6.38 (br s, 1H, NH), 6.12 (br s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 133.8, 131.7, 130.8, 130.5, 130.3, 127.1.

4-chlorobenzamide (2j).[12] mp 178-179 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (br s, 1H, NH), 7.88 (d, *J* = 8.4 Hz, 2H, ArH), 7.52 (d, *J* = 8.4 Hz, 2H, ArH), 7.48 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.8, 136.1, 133.0, 129.4, 128.3.

3,4-dichlorobenzamide (2k).[26] mp 138-139 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.15 (br s, 1H, NH), 8.10 (s, 1H, ArH), 7.84 (d, *J* = 8.2 Hz, 1H, ArH), 7.75 (d, *J* = 8.6 Hz, 1H, ArH), 7.62 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 134.6, 134.0, 131.2, 130.6, 129.4, 127.7.

2-bromobenzamide (2l).[27] mp 158-159 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88 (br s, 1H, NH), 7.64-7.58 (m, 2H, ArH), 7.41-7.34 (m, 3H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 169.0, 139.3, 132.7, 130.6, 128.5, 127.5, 118.6.

4-bromobenzamide (2m).[28] mp 190-191 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.06 (br s, 1H, NH), 7.81 (d, *J* = 8.1 Hz, 2H, ArH), 7.67 (d, *J* = 8.1 Hz, 2H, ArH), 7.48 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.9, 133.4, 131.2, 129.6, 125.0.

2-nitrobenzamide (2n).[5a] mp 175-176 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.15 (br s, 1H, NH), 7.99 (s, 1H, ArH), 7.76-7.67 (m, 4H, ArH and NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.2, 147.2, 133.3, 132.6, 130.6, 128.8, 123.9.

4-nitrobenzamide (2o).[12] mp 199-200 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.30 (br s, 3H, ArH and NH), 8.09 (s, 2H, ArH), 7.73 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.2, 149.1, 140.0, 128.9, 123.4.

3-(trifluoromethyl)benzamide (2p).[29] mp 120-121 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (br s, 1H, NH), 8.21 (s, 1H, ArH), 8.17 (d, *J* = 7.8 Hz, 1H, ArH), 7.90 (d, *J* = 7.8 Hz, 1H, ArH), 7.71 (t, *J* = 7.8 Hz, 1H, ArH), 7.64 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.3, 135.2, 131.4, 129.5, 129.1 (q, $J_{C\text{-}F}$ = 31.8 Hz), 127.7 (q, $J_{C\text{-}F}$ = 2.8 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.8 Hz), 124.0 (q, $J_{C\text{-}F}$ = 2.8 Hz).

4-(trifluoromethoxy)benzamide (2q).[12] mp 146-147 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.08 (br s, 1H, NH), 7.99 (d, *J* = 8.8 Hz, 2H, ArH), 7.51 (br s, 1H, NH), 7.45 (d, *J* = 8.3 Hz, 2H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.6, 150.3, 133.4, 129.7, 120.4, 119.9 (q, $J_{C\text{-}F}$ = 255.5 Hz).

2-naphthamide (2r).[30] mp 196-197 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.48 (s, 1H, ArH), 8.14 (br s, 1H, NH), 8.01-7.96 (m, 4H, ArH), 7.62-7.57 (m, 2H, ArH), 7.48 (br s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.0, 134.2, 132.1, 131.6, 128.9, 127.8, 127.8, 127.6, 126.6, 124.4.

Thiophene-2-carboxamide (2s).[12] mp 179-180 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.95 (br s, 1H, NH), 7.73 (s, 2H, ArH), 7.37 (br s, 1H, NH), 7.12 (s, 1H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.9, 140.3, 130.9, 128.7, 127.9.

2-phenylacetamide (2t).[31] mp 152-153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, J = 7.4 Hz, 2H, ArH), 7.32-7.26 (m, 3H, ArH), 5.47 (br s, 1H, NH), 5.37 (br s, 1H, NH), 3.60 (s, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 134.8, 129.4, 129.0, 127.4, 43.3.

3-phenylpropanamide (2u).[12] mp 99-100 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30-7.25 (m, 3H, ArH and NH), 7.21-7.15 (m, 3H, ArH), 6.78 (br s, 1H, NH), 2.79 (t, J = 7.7 Hz, 2H, CH_2), 2.34 (t, J = 7.5 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, DMSO-d_6) δ 173.4, 141.5, 128.2, 128.2, 125.8, 36.7, 30.9.

Butyramide (2v).[5a] mp 111-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (br s, 1H, NH), 5.54 (br s, 1H, NH), 2.21 (t, J = 7.6 Hz, 2H, CH_2), 1.67 (sext, J = 7.4 Hz, 2H, CH_2), 0.97 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 37.8, 18.9, 13.6.

Hexanamide (2w).[12] mp 95-96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (br s, 1H, NH), 5.49 (br s, 1H, NH), 2.22 (t, J = 7.6 Hz, 2H, CH_2), 1.67-1.61 (m, 2H, CH_2), 1.34-1.31 (m, 4H, CH_2), 0.90 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 35.9, 31.4, 25.2, 22.3, 13.9.

Cinnamamide (4a).[5a] mp 148-149 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.56-7.55 (m, 3H, ArH, NH, CH), 7.43-7.36 (m, 4H, ArH), 7.13 (br s, 1H, NH), 6.61 (d, J = 16.0 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.7, 139.2, 134.9, 129.5, 128.9, 127.6, 122.3.

(*E*)-3-(*m*-tolyl)acrylamide (4b).[32] mp 81-82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 15.6 Hz, 1H, CH), 7.33-7.31 (m, 2H, ArH), 7.28-7.25 (m, 1H, ArH), 7.18 (d, J = 7.2 Hz, 1H, ArH), 6.45 (d, J = 15.8 Hz, 1H, CH), 5.66 (br s, 2H, NH), 2.37 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 142.7, 138.5, 134.4, 130.8, 128.7, 128.6, 125.1, 119.2, 21.3.

(*E*)-3-(2-nitrophenyl)acrylamide (4c).[33] mp 168-169 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (d, J = 7.7 Hz, 1H, CH), 7.78 (s, 2H, ArH), 7.69-7.64 (m, 3H, ArH and NH), 7.29 (br s, 1H, NH), 6.61 (d, J = 15.5 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7, 148.3, 134.0, 133.7, 130.2, 129.9, 128.7, 127.1, 124.5.

(*E*)-3-(4-fluorophenyl)acrylamide (4d).[34] mp 130-131 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.62 (s, 2H, ArH), 7.53 (br s, 1H, NH), 7.41 (d, J = 15.6 Hz, 1H, CH), 7.24 (t, J = 7.1 Hz, 2H, ArH) 7.10 (br s, 1H, NH), 6.55 (d, J = 15.7 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.6, 162.6 (d, $J_{C\text{-}F}$ = 245.7 Hz), 137.9, 131.5, 129.7 (d, $J_{C\text{-}F}$ = 33.3 Hz), 122.2, 115.8 (d, $J_{C\text{-}F}$ = 21.8 Hz).

(*E*)-3-(3-chlorophenyl)acrylamide (4e).[35] mp 75-76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 15.8 Hz, 1H, CH), 7.50 (s, 1H, ArH), 7.38-7.29 (m, 3H, ArH), 6.46 (d, J = 15.7 Hz, 1H, CH), 5.78 (br s, 2H, 2xNH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 140.7, 136.3, 134.7, 130.0, 129.7, 127.4, 126.2, 121.2.

(*E*)-3-(furan-2-yl)acrylamide (4f).[36] mp 170-171 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (s, 1H, ArH), 7.57 (br s, 1H, NH), 7.21 (d, J = 16.0 Hz, 1H, CH), 7.08 (br s, 1H, NH), 6.75 (d, J = 2.6 Hz, 1H, ArH), 6.58 (s, 1H, ArH) 6.39 (d, J = 15.7 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.5, 150.9, 144.7, 126.6, 119.6, 113.6, 112.3.

2,6-dimethylhept-5-enamide (4g). mp 70-71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (br s, 1H, NH), 5.47 (br s, 1H, NH), 5.08 (s, 1H, CH), 2.28 (s, 1H, CH), 2.02 (s, 2H, CH_2), 1.69 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.42 (s, 2H, CH_2), 1.16 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 132.2, 123.7, 40.1, 34.2, 25.7, 25.7, 17.7, 17.7; HRMS-EI (70 eV) m/z calcd for $C_9H_{17}NONa$ $[M+Na]^+$ 178.1208, found 178.1201.

Cyclohex-3-enecarboxamide (4h).[37] mp 125-126 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.25 (br s, 1H, NH), 6.73 (br s, 1H, NH), 5.65 (br s, 2H, 2xCH), 2.30-2.26 (m, 1H, ArH), 2.05-1.93 (m, 4H, ArH), 1.78-1.76 (m, 1H, ArH), 1.51-1.42 (m, 1H, ArH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 177.1, 126.3, 125.9, 27.6, 25.4, 24.4.

The one-pot synthesis of amides from aldehydes, hydroxylamine hydrochloride and sodium carbonate catalyzed by $[Cp^*Ir(H_2O)_3][OTf]_2$. To an oven-dried 25 ml Schlenk tube were added aldehydes **5** or **6** (0.5 mmol), hydroxylamine hydrochloride **7** (1 equiv.), and Na_2CO_3 (0.5 equiv.) and H_2O (1 ml), and the mixture was started at room temperature for 0.5 h. Then, $[Cp^*Ir(H_2O)_3][OTf]_2$ (1.5 mol%) was added into the reactor, the reaction mixture was heated at 110 °C for another 12h and was allowed to cool to ambient temperature. The mixture of reaction was concentrated in *vacuo*, washed with hexanes, and isolated by simple filtration to afford the desired product.

The procedure for the hydration of benzonitrile 8 in water catalyzed by $[Cp^*Ir(H_2O)_3][OTf]_2$. To an oven-dried, 25 ml Schlenk tube were added benzonitrile **8** (0.5 mmol), $[Cp^*Ir(H_2O)_3][OTf]_2$ (1.5 mol%) and water (1 ml). The mixture of reaction was heated at 110 °C for 12h, and allowed to cool to ambient temperature. No conversion was observed from the ^{1}H NMR spectrum of the mixture.

The procedure for the hydration of benzonitrile 8 with the aid of butylaldoxime in water catalyzed by $[Cp^*Ir(H_2O)_3][OTf]_2$. To an oven-dried, 25 ml Schlenk tube were added benzonitrile **8** (0.5 mmol), butylaldoxime **1v** (2 equiv.), $[Cp^*Ir(H_2O)_3][OTf]_2$ (1.5 mol%) and water (1 ml). The mixture of reaction was heated at 110 °C for 12h, and allowed to cool to ambient temperature. The mixture of reaction was concentrated in *vacuo*, washed with hexanes, and isolated by simple filtration to afford the desired product.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Copies of the ^{1}H NMR and ^{13}C NMR spectra for all products. See DOI: 10.1039/b000000x/

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