Synthesis S. Verma et al. Special Topic

Zinc(II)-Catalyzed Synthesis of Secondary Amides from Ketones via Beckmann Rearrangement Using Hydroxylamine-*O*-sulfonic Acid in Aqueous Media

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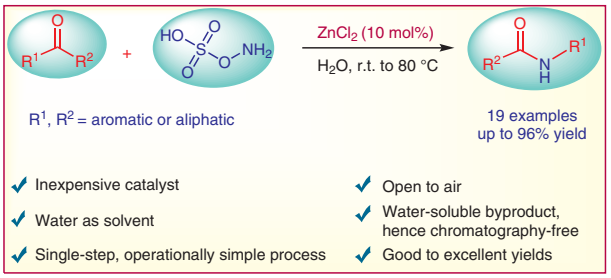

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Abstract A zinc(II)-catalyzed single-step protocol for the Beckmann rearrangement using hydroxylamine-*O*-sulfonic acid (HOSA) as the nitrogen source in water was developed. This direct method efficiently produces secondary amides under open atmosphere in a pure form after basic aqueous workup. It is environmentally benign and operationally simple.

Key words zinc(II) chloride, hydroxylamine-*O*-sulfonic acid (HOSA), ketones, Beckmann rearrangement, amides

Secondary amides play a pivotal role as a basic structural unit in numerous pharmaceuticals, bioactive natural products, polymers, dyes, and other functional materials (Figure 1).[1] They also serve as versatile building blocks for organic synthesis. For instance, the transformation of amides to different heterocyclic compounds is a well sought-after method for the preparation of medicinal agents and alkaloids.[2]

Conventionally, secondary amides are prepared from carboxylic acids and amines.[3] This trivial method typically requires the activation of the carboxylic acid functionality using a stoichiometric amount of reagents that eventually lead to a poor atom economy and release of a huge quantity of toxic waste. These serious limitations have severely impacted its industrial applications.[3a,e] Developing catalytic variations has led to substantial improvements, but with other limitations.[3c] In 1886, Beckmann and co-workers developed an altogether different approach, known as the Beckmann rearrangement, to prepare amides from ketones in two steps, using preformed oximes.[4] Nevertheless, the harsh reaction conditions (high temperature and strong acidic media) have largely precluded its application to sensitive substrates. Since then, tremendous advances have been made to surmount these shortcomings, leading to several interesting methods with relatively milder conditions from ketoximes (Scheme 1a).[5] Good progress has been made in recent years towards the development of direct methods using ketones instead of preformed ketoximes.[6] Nevertheless, these methods also suffer from some limitations, such as the use of toxic solvents, expensive reagents, or catalysts, high temperatures, and/or longer reaction

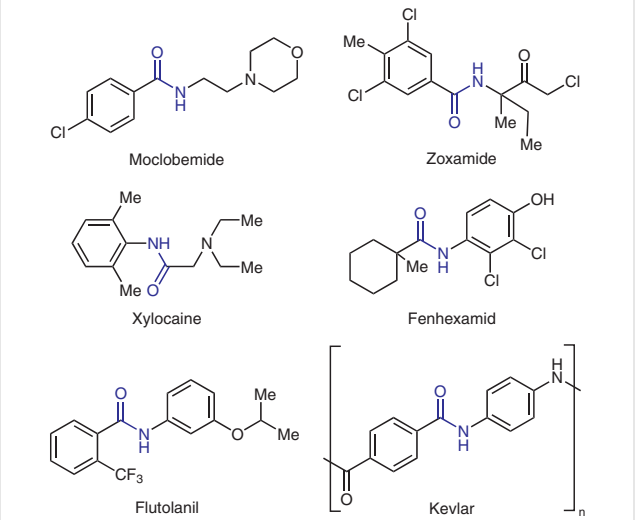

Figure 1 Examples of pharmacologically active molecules and polymers consisting of secondary amide functionalities

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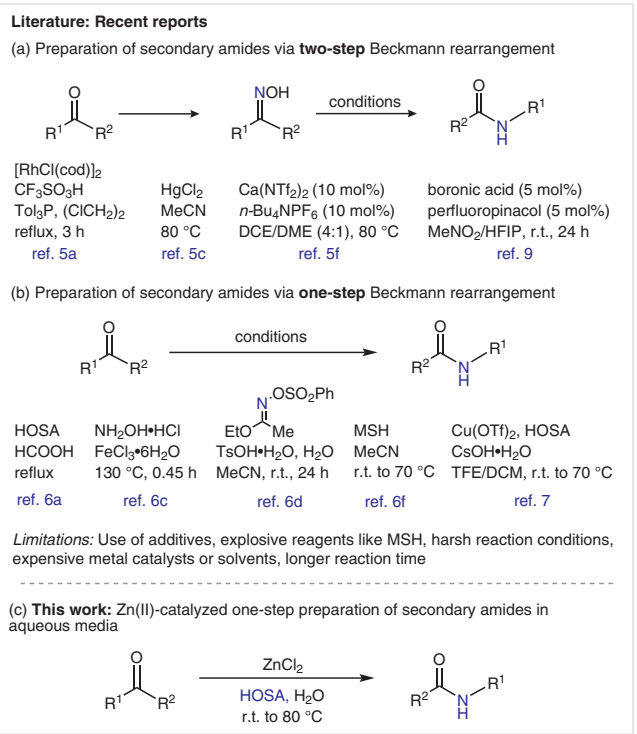
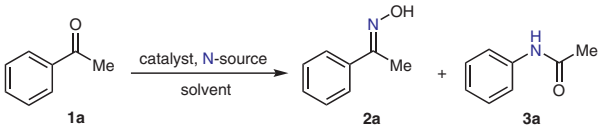
times (Scheme 1b). In 1979, Olah et al. synthesized secondary amides from ketones using commercially available hydroxylamine-*O*-sulfonic acid (HOSA), with formic acid as the solvent, at reflux temperature.[6a] This method was suitable only for cyclic ketones and required the use of strongly acidic solvent under reflux conditions. Recently, we reported a copper(II) triflate catalyzed single-step synthesis of secondary amides directly from ketones using hydroxylamine-*O*-sulfonic acid (HOSA) as the nitrogen source.[7] Although this provided several advantages over literature methods, it required the use of (a) expensive $Cu(OTf)_2$ catalyst, solvent (TFE), and additive (CsOH) and (b) column chromatography for purification. Therefore, an environmentally benign method, free from these limitations, is highly desired. Herein, we describe a Zn(II)-catalyzed synthesis of secondary amides from ketones using HOSA as the nitrogen source and water as the solvent (Scheme 1c). Much to our delight, the desired products could be obtained in pure form just after aqueous workup followed by a simple wash with *n*-hexane solvent, without requiring column chromatography.



Scheme 1 Preparation of secondary amides

We initiated the reaction conditions optimization studies by adopting acetophenone **1a** as a model substrate and hydroxylamine-*O*-sulfonic acid (HOSA) as the nitrogen source, as it is commercially available, water-soluble, and generates a non-interfering water-soluble byproduct (Table 1).[8] Initially, we screened solvents of varying polarity, such as 2,2,2-trifluoroethanol (TFE), acetonitrile, methanol, tetrahydrofuran, water, and ethanol without any catalyst at room temperature (entries 1–6).

Table 1 Optimization of Reaction Conditions[a]



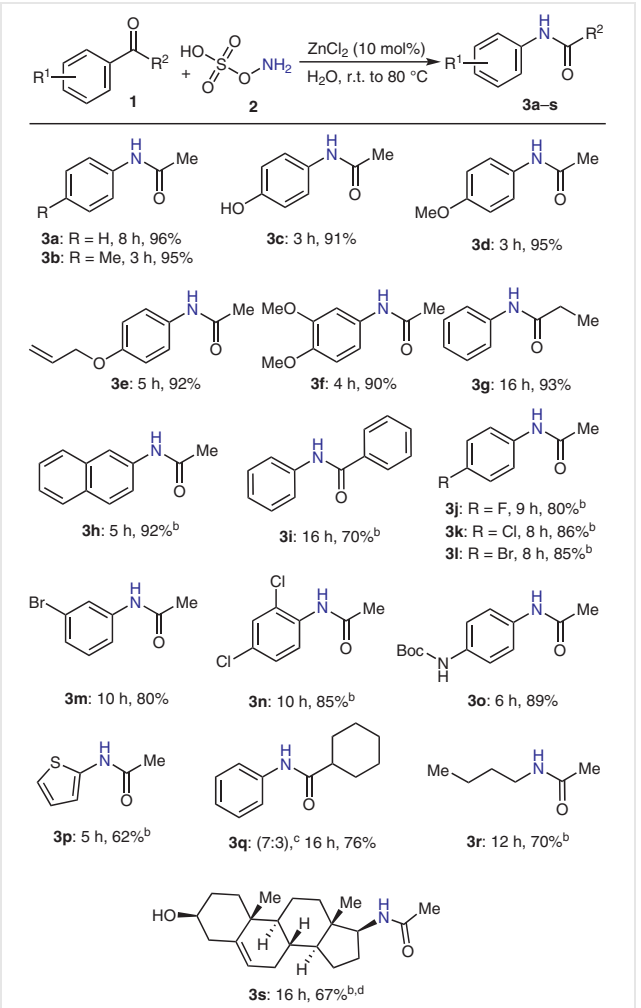
Entry	Solvent	Nitrogen source	Catalyst	Yield (%)[b]	
				2a	**3a**
1	TFE	HOSA	–	50	30
2	MeCN	HOSA	–	30	0
3	MeOH	HOSA	–	50	25
4	THF	HOSA	–	40	20
5	H_2O	HOSA	–	20	70
6	EtOH	HOSA	–	50	20
7	H_2O	HOSA	$FeSO_4$	10	70
8	H_2O	HOSA	$Fe(acac)_3$	10	65
9	H_2O	HOSA	$FeCl_2$	0	60
10	H_2O	HOSA	$Cu(OTf)_2$	10	80
11	H_2O	HOSA	$ZnCl_2$	0	96
12[c]	H_2O	HOSA	$ZnCl_2$	0	80
13[d]	H_2O	HOSA	$ZnCl_2$	10	80
14	H_2O	$NH_2OH{\cdot}HCl$	$ZnCl_2$	10	0
15[e]	H_2O	$NH_2OH{\cdot}HCl$	$ZnCl_2$	15	0

[a] Reaction conditions: **1a** (1.0 equiv), nitrogen source (1.5 equiv), catalyst (10 mol%), solvent (2 mL), r.t.
[b] Isolated yields.
[c] HOSA (1.0 equiv) was used.
[d] $ZnCl_2$ (5 mol%) was used.
[e] $NaHCO_3$ (2.0 equiv) was added at r.t.

To our delight, water proved to be the best choice, giving the desired product **3a** in 70% isolated yield (Table 1, entry 5). To further enhance the product yield, we screened commercially available inexpensive catalysts (entries 7–11). $ZnCl_2$ was observed to be the optimal catalyst that delivered the amide **3a** in an excellent yield of 96% (entry 11). It is worth mentioning that $ZnCl_2$ is cost-effective and readily accessible when compared to previously used expensive catalysts, and the reaction proceeds at room temperature, compared to an elevated/reflux temperature as in previous reports.[7] Attempts to reduce the loading of either HOSA or $ZnCl_2$ diminished the yield (entries 12 and 13). Furthermore, switching to another nitrogen source such as hydroxylamine hydrochloride did not provide any satisfactory result (entries 14 and 15). Remarkably, the product could be accessed in its pure form after a routine workup; column chromatographic purification was not needed.

With these optimized conditions in hand, we next investigated the substrate scope of the reaction (Scheme 2). Ketones with electron-donating substituents (e.g., Me, OH, OMe) at the *para* position of the aryl ring reacted smoothly at room temperature to furnish the corresponding secondary amides in excellent yields (**3b–d**). In a similar manner, the *para*-*O*-allyl substituted acetophenone afforded the desired product **3e** in 92% isolated yield. Gratifyingly, disubstituted acetophenones as well as propiophenone were also good substrates, providing the corresponding amides **3f** and **3g** in remarkable yields of 90% and 93%, respectively. In contrast, a naphthyl ketone and benzophenone required an elevated reaction temperature for the complete conversion to produce the corresponding products **3h** and **3i** in 92% and 70% isolated yields, respectively. We next examined electron-deficient ketones. Acetophenones substituted with electron-withdrawing groups on the aryl rings, such as Cl, F, and Br at *para* and *meta* positions, reacted smoothly at 80 °C to give the expected products **3j–m** in 80–86% yield. These conditions were suitable even for the conversion of a dihalo-substituted ketone (**3n**, 85% yield). The acid-sensitive *N*-Boc substrate also furnished the desired amide **3o** at room temperature without losing the Boc group. Pleasingly, a thienyl ketone was smoothly converted into the corresponding product **3p**. Cyclohexyl phenyl ketone was monitored under these reaction conditions, ending up producing a separable mixture of regiomers of **3q** (7:3), due to a competing migratory aptitude of the phenyl and cyclohexyl groups. The aliphatic acyclic ketone hexan-2-one could also be transformed into the corresponding amide **3r** at 80 °C. Gratifyingly, an encouraging result was obtained in the case of the complex ketone pregnenolone, which delivered the corresponding amide **3s** in a good yield.

In summary, we have developed an efficient and practical approach for the synthesis of secondary amides from ketones via the Beckmann rearrangement using HOSA as the nitrogen source in aqueous media. This single-step synthetic method is cost-effective, operationally simple, and environmentally benign.



Scheme 2 Substrate scope of the reaction. [a] *Reagents and conditions*: same as Table 1, entry 11, unless otherwise mentioned. [b] Reaction temperature 80 °C. [c] Ratio of separable regiomers; major isomer shown. [d] Reaction performed in H_2O/dioxane (2:1).

Reactions, unless otherwise stated, were carried out with magnetic stirring open to the atmosphere in oven-dried glassware. Reagents were used as received, unless otherwise noted. TLC was carried out on pre-coated plates (Merck silica gel 60, F_{254}) and was visualized with UV light and/or charring after dipping in PMA or $KMnO_4$ solution. The compounds were purified by triturating the crude reaction mixture under hexane. ^{1}H NMR spectra of samples in $CDCl_3$ or DMSO-d_6 as solvent were recorded at 400 MHz. Chemical shifts are reported relative to residual undeuterated solvent as an internal reference (^{1}H: δ = 7.26 for $CDCl_3$, δ = 2.50 for DMSO-d_6).

Secondary Amides from Ketones; General Procedure

To a stirring solution of $ZnCl_2$ (0.05 mmol, 10 mol%) in H_2O (2 mL) at r.t. in an open round-bottom flask, ketone **1** (0.5 mmol, 1.0 equiv) was added, followed by HOSA (1.5 equiv). The reaction mixture was stirred at the indicated temperature and for the duration indicated in Scheme 2. After completion, the reaction mixture was diluted with EtOAc (15 mL) and washed with sat. aq Na_2CO_3 (3 × 5 mL). The organic layer was washed with brine (5 mL) and dried over anhydrous Na_2SO_4. The crude product obtained after removal of all volatiles in vacuo was washed with *n*-hexane to remove some minor nonpolar impurities.

N-Phenylacetamide (3a)[9]

Yield: 65 mg (96%); white solid; mp 114–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (br s, 1 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.9 Hz, 2 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 2.16 (s, 3 H).

N-(*p*-Tolyl)acetamide (3b)[10]

Yield: 72 mg (95%); white solid; mp 150–152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.1 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H), 2.15 (s, 3 H).

***N*-(4-Hydroxyphenyl)acetamide (3c)**[9]

Yield: 68 mg (91%); brown solid; mp 169–171 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.66 (br s, 1 H), 9.16 (br s, 1 H), 7.34 (d, *J* = 8.6 Hz, 2 H), 6.68 (d, *J* = 8.6 Hz, 2 H), 1.98 (s, 3 H).

***N*-(4-Methoxyphenyl)acetamide (3d)**[9]

Yield: 78 mg (95%); white solid; mp 130–131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 3.78 (s, 3 H), 2.14 (s, 3 H).

***N*-[4-(Allyloxy)phenyl]acetamide (3e)**[11]

Yield: 88 mg (92%); white solid; mp 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1 H), 7.37 (d, *J* = 8.7 Hz, 2 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.03 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1 H), 5.39 (d, *J* = 17.2 Hz, 1 H), 5.27 (d, *J* = 10.6 Hz, 1 H), 4.49 (d, *J* = 5.0 Hz, 2 H), 2.12 (s, 3 H).

***N*-(3,4-Dimethoxyphenyl)acetamide (3f)**[13]

Yield: 88 mg (90%); white solid; mp 126–128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (br s, 1 H), 7.29 (s, 1 H), 6.86 (d, *J* = 8.7 Hz, 1 H), 6.78 (d, *J* = 8.5 Hz, 1 H), 3.84 (s, 6 H), 2.14 (s, 3 H).

***N*-Phenylpropionamide (3g)**[15]

Yield: 69 mg (93%); off white solid; mp 108–109 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.8 Hz, 2 H), 7.32 (t, *J* = 7.9 Hz, 2 H), 7.17 (br s, 1 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 2.39 (q, *J* = 7.6 Hz, 2 H), 1.25 (t, *J* = 7.6 Hz, 3 H).

***N*-(2-Naphthyl)acetamide (3h)**[10]

Yield: 85 mg (92%); brown solid; mp 133–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1 H), 7.90 (br s, 1 H), 7.77–7.73 (m, 3 H), 7.48–7.37 (m, 3 H), 2.21 (s, 3 H).

***N*-Phenylbenzamide (3i)**[9]

Yield: 69 mg (70%); white solid; mp 165–166 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.6 Hz, 2 H), 7.82 (br s, 1 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.4 Hz, 1 H).

***N*-(4-Fluorophenyl)acetamide (3j)**[9]

Yield: 61 mg (80%); Yellowish solid; mp 154–155 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (br s, 1 H), 7.46–7.43 (m, 2 H), 6.99 (t, *J* = 8.5 Hz, 2 H), 2.15 (s, 3 H).

***N*-(4-Chlorophenyl)acetamide (3k)**[12]

Yield: 72 mg (86%); white solid; mp 177–179 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 9.2 Hz, 2 H), 2.17 (s, 3 H).

***N*-(4-Bromophenyl)acetamide (3l)**[9]

Yield: 91 mg (85%); white solid; mp 167–170 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.39 (m, 5 H), 2.16 (s, 3 H).

***N*-(3-Bromophenyl)acetamide (3m)**[5c]

Yield: 86 mg (80%); white solid; mp 82–83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.47 (br s, 1 H), 7.40 (d, *J* = 7.9 Hz, 1 H), 7.24–7.14 (m, 2 H), 2.17 (s, 3 H).

***N*-(2,4-Dichlorophenyl)acetamide (3n)**[14]

Yield: 87 mg (85%); brown solid; mp 144–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.8 Hz, 1 H), 7.57 (br s, 1 H), 7.37 (s, 1 H), 7.24 (d, *J* = 8.9 Hz, 1 H), 2.23 (s, 3 H).

***tert*-Butyl (4-Acetamidophenyl)carbamate (3o)**[9]

Yield: 112 mg (89%); white solid; mp 159–161 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.9 Hz, 2 H), 7.30 (d, *J* = 8.7 Hz, 2 H), 7.16 (br s, 1 H), 6.45 (br s, 1 H), 2.15 (s, 3 H), 1.51 (s, 9 H).

***N*-(2-Thienyl)acetamide (3p)**[9]

Yield: 44 mg (62%); brown solid; mp 144–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (br s, 1 H), 6.88–6.82 (m, 1 H), 6.65 (d, *J* = 3.5 Hz, 1 H), 2.20 (s, 2 H).

***N*-Phenylcyclohexanecarboxamide (3q)**[9]

Yield: 78 mg (76%); white solid; mp 145–148 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.9 Hz, 2 H), 7.32–7.26 (m, 2 H), 7.08 (t, *J* = 7.3 Hz, 1 H), 2.29–2.16 (m, 1 H), 2.01–1.90 (m, 2 H), 1.89–1.77 (m, 2 H), 1.75–1.63 (m, 1 H), 1.61–1.47 (m, 2 H), 1.39–1.17 (m, 3 H).

***N*-Butylacetamide (3r)**[16]

Yield: 40 mg (70%); clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.46 (br s, 1 H), 3.14–3.09 (m, 2 H), 1.87 (s, 3 H), 1.44–1.33 (m, 2 H), 1.31–1.18 (m, 2 H), 0.82 (t, *J* = 7.3 Hz, 3 H).

***N*-[(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-Hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl]acetamide (3s)**[9]

Yield: 110 mg (67%); white solid; mp 230–232 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.38–5.32 (m, 1 H), 5.28 (d, *J* = 8.5 Hz, 1 H), 3.99–3.78 (m, 1 H), 3.59–3.46 (m, 1 H), 2.35–2.06 (m, 3 H), 2.03–1.95 (m, 1 H), 1.98 (s, 3 H), 1.90–1.78 (m, 2 H), 1.75–1.62 (m, 2 H), 1.61–1.16 (m, 9 H), 1.16–1.02 (m, 3 H), 1.01 (s, 3 H), 0.70 (s, 3 H).

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Supporting Information

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