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Letter

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Efficient and Selective Synthesis of (*E*)-Enamides via Ru(II)-Catalyzed Hydroamidation of Internal Alkynes

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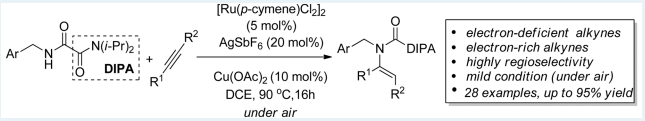
Supporting Information

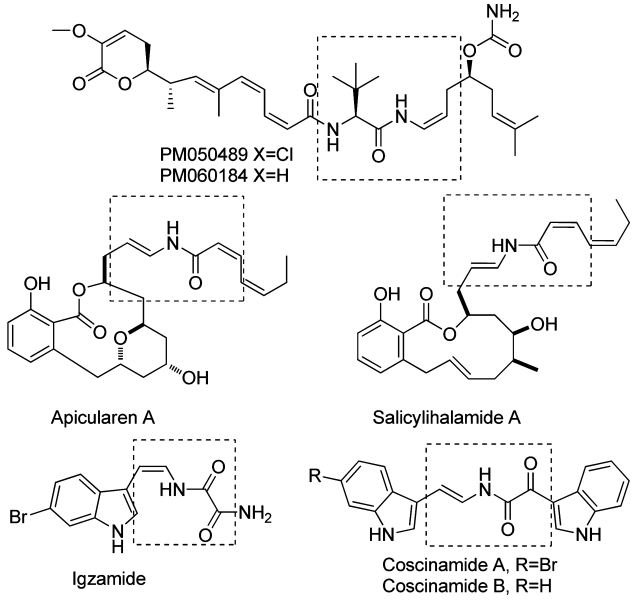
ABSTRACT: An efficient hydroamidation of benzylamides with internal alkynes catalyzed by Ru(II) has been developed. Various (*E*)-enamides were afforded in up to 95% yield for 28 examples. The protocol features excellent regio- and stereoselectivity, widely functional group tolerance, and easily accessible starting materials.



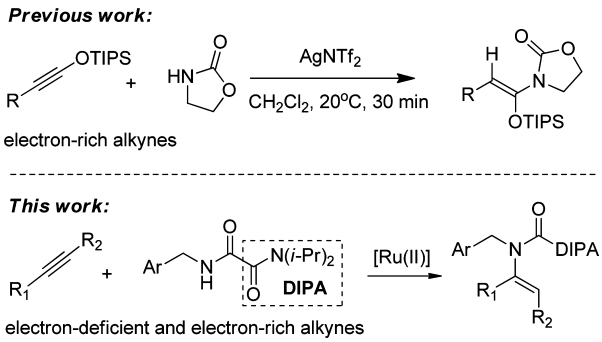
KEYWORDS: *hydroamidation, enamides, interanl alkynes, ruthenium, C−N formation*

The enamide moiety is a key functionality in numerous natural products[1] and pharmaceuticals with antibiotic,[2] antitumor,[3] cytotoxic,[4] anthelmintic,[5] and antifungal[6] activities (Chart 1). They also serves as important intermediates in organic reactions, such as [4 + 2]-cycloaddition,[7] cross-coupling reaction,[8] enantioselective addition,[9] or asymmetric hydrogenation.[10] Accordingly, much effort has been paid toward the development of new synthetic methods to build such a structure.[11] Considering the relatively harsh conditions, poor selectivity,[12] or the limited substrate scope[13] with the conventional procedures, the hydroamidation of alkynes has appeared as a promising method due to its mild reaction conditions and 100% atom economy in recent years.[14]

Chart 1. Biologically Active Natural Products Containing Enamide Motif



Scheme 1. Catalytic Hydroamidation of Alkynes



However, to the best of our knowledge, almost all protocols presented so far are restricted to terminal alkynes.[15] Only one example is applicable to internal alkynes with an amide, as reported by Kozmin and Sun,[16] in which silver-catalyzed hydroamidation of siloxy alkynes was successfully achieved (Scheme 1). However, this method is limited to an electron-rich alkyne. Therefore, it is still highly desirable to discover a new pathway to construct an enamide that displays the broad scope of internal alkynes, high regioselectivity, and efficiency. Herein, we present a novel hydroamidation of benzylamides with various alkynes catalyzed by Ru(II), affording the corresponding (*E*)-enamides in moderate to excellent yields, which featured excellent regio- and stereoselectivity, widely functional group tolerance, and easily accessible starting materials. To the best of our knowledge, this is the first example for the hydroamidation of electron-deficient internal alkynes (Scheme 1).

In our initial studies, the reaction of benzylamides **1a** with tolane **2a** was chosen as a model reaction to optimize various

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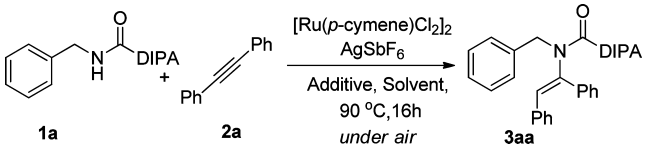
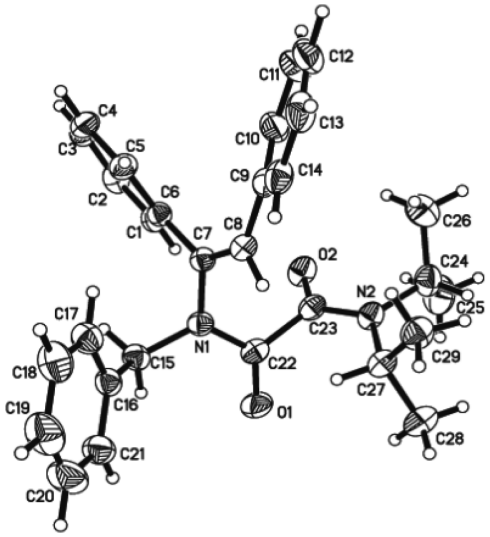
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	additive (equiv)	3aa (%)[b]
1	1,2-DCE	$Cu(OAc)_2$ (2)	81
2[c]	1,2-DCE	$Cu(OAc)_2$ (2)	n.r.
3[d]	1,2-DCE	$Cu(OAc)_2$ (2)	<5
4	1,2-DCE	——	<5
5	1,4-dioxane	$Cu(OAc)_2$ (2)	<5
6	PhMe	$Cu(OAc)_2$ (2)	<5
7	MeCN	$Cu(OAc)_2$ (2)	n.r.
8	DMF	$Cu(OAc)_2$ (2)	n.r.
9	*t*-AmOH	$Cu(OAc)_2$ (2)	n.r.
10	1,2-DCE	$Cu(OAc)_2$ (1)	85
11	1,2-DCE	$Cu(OAc)_2$ (10 mol %)	93(53)[e](82)[f]
12	1,2-DCE	KOAc (10 mol %)	77
13	1,2-DCE	NaOAc (10 mol %)	80
14	1,2-DCE	AcOH (10 mol %)	69
15	1,2-DCE	PivOH (10 mol %)	28

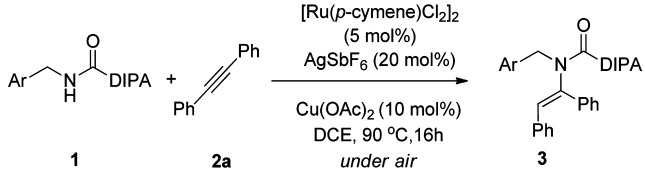
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), solvent (1.0 mL), 90 °C under air, 16 h. [b]Isolated yields. [c]Without [Ru(*p*-cymene)Cl_2]$_2$. [d]Without $AgSbF_6$. [e]3 mol % catalyst. [f]4 mol % catalyst.

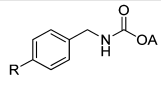
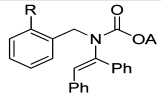
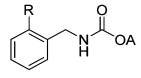
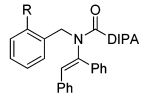
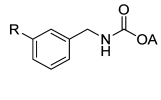
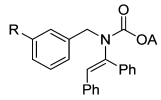
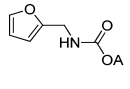
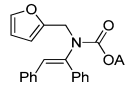
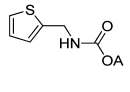
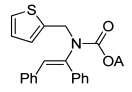
Chart 2. X-ray Molecular Structure of 3aa



reaction parameters (Table 1). The product of oxidative annulation of benzylamines with alkynes was not detected. However, the unexpected product **3aa** was obtained in 81% yield with [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %) and $AgSbF_6$ (20 mol %) as a cocatalyst (entry 1). The structure of the product **3aa** was confirmed by single-crystal X-ray diffraction (Chart 2). The desired product **3aa** could not be detected in the absence of [Ru(*p*-cymene)Cl_2]$_2$, $AgSbF_6$, or $Cu(OAc)_2$ (entries 2−4). With such an exciting preliminary result in hand, a systematic screening of reaction solvents was carried out (entries 5−9). Among the solvents examined, 1,2-DCE was proved to be the best choice. Moreover, we were pleased to find that decreasing the loading of $Cu(OAc)_2$ from stoichiometry to catalytic amounts (10 mol %) led to increasing the yield from 81% to

Table 2. Scope of benzylamides[a]



entry	substrate **1**	product **3**	yield (%)[b]
			
1	**1b**, R = Me	**3ba**, R = Me	80
2	**1c**, R = *t*-Bu	**3ca**, R = *t*-Bu	86
3	**1d**, R = OMe	**3da**, R=OMe	91
4	**1e**, R = Cl	**3ea**, R = Cl	88
5	**1f**, R = F	**3fa**, R = F	95
6	**1g**, R = NO_2	**3ga**, R = NO_2	91
7	**1h**, R = CF_3	**3ha**, R = CF_3	86
			
8	**1i**, R = Me	**3ia**, R = Me	57
9	**1j**, R = F	**3ja**, R = F	66
10	**1k**, R = CF_3	**3ka**, R = CF_3	58
			
11	**1l**, R = Me	**3la**, R = Me	91
12	**1m**, R = F	**3ma**, R = F	91
13	**1n**, R = Cl	**3na**, R = Cl	85
14	**1o**, R = CF_3	**3oa**, R = CF_3	86
			
15	**1p**	**3pa**	65
			
16	**1q**	**3qa**	47

[a]All reactions were carried out using benzylamide **1** (0.25 mmol), tolane **2a** (0.3 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), $Cu(OAc)_2$ (0.025 mmol) in 1,2-DCE (1.0 mL) at 90 °C under air for 16 h. [b]Isolated yields.

93% (entries 10−11). Besides, various additives, such as KOAc, NaOAc, HOAc, and PivOH, were screened. Lower yields were obtained in all cases (entries 12−15). Notably, reducing the catalyst loading to 3 mol % and 4 mol % significantly influences this reaction (entry 11).

With the optimized reaction conditions in hand, we first investigated the scope of benzylamides (Table 2). To our delight, a remarkably broad range of benzylamides was tolerated. Tolane **2a** could reacted efficiently with benzylamides **1** bearing either electron-donating or electron-withdrawing groups, delivering the targeted products in good to excellent yields. For instance, electron-donating groups, such as Me-, *tert*-

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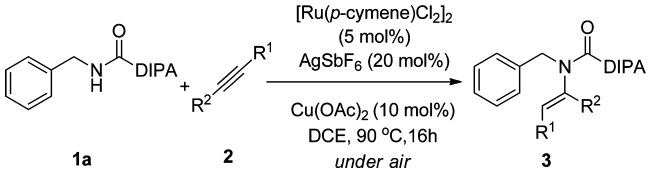
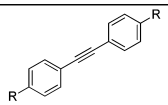
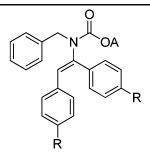
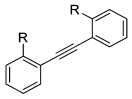
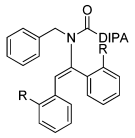
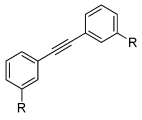
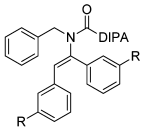
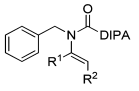
Table 3. Scope of Symmetrical and Unsymmetrical Alkynes[a]

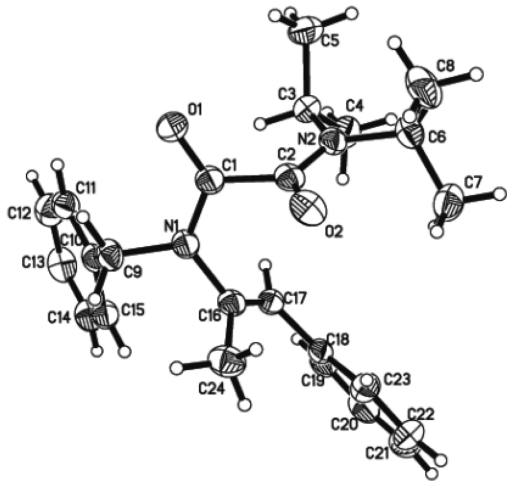


entry	substrate **2**	product **3**	yield (%)[b]
			
1	**2b**, R =Me	**3ab**, R=Me	82
2	**2c**, R = *t*-Bu	**3ac**, R = *t*-Bu	46
3	**2d**, R = F	**3ad**, R = F	85
4	**2e**, R = Cl	**3ae**, R = Cl	68
			
5	**2f**, R = F	**3af**, R = F	72
			
6	**2g**, R = Me	**3ag**, R = Me	69
7	**2h**, R = F	**3ah**, R = F	77
8	**2i**, R = Cl	**3ai**, R = Cl	55
			
9	**2j**, R^1 = Me, R^2 = Ph	**3aj**, R^1 = Me, R^2= Ph	80 (20:1)
10	**2k**, R^1 = Et, R^2 = Ph	**3ak**, R^1 = Et, R^2 = Ph	81 (10:1)
11	**2l**, R^1 = *n*-Bu, R^2 =Ph	**3al**, R^1 = *n*-Bu, R^2 = Ph	80 (8:1)

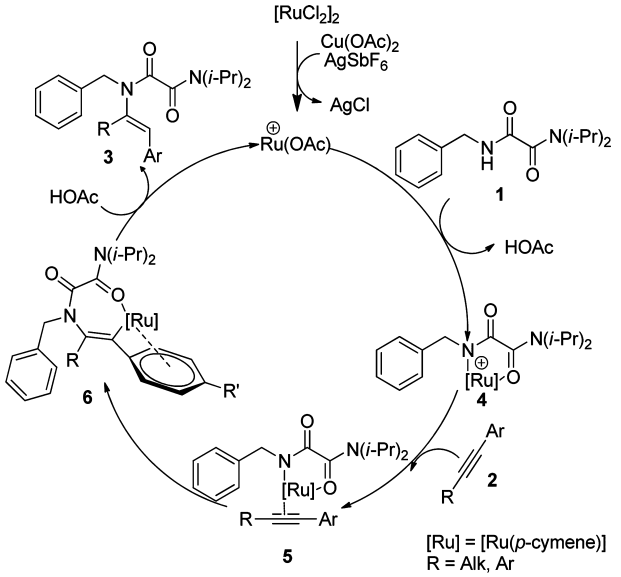
[a]All reactions were carried out using benzylamides **1a** (0.25 mmol), alkyne **2** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), $Cu(OAc)_2$ (0.025 mmol) and 1,2-DCE (1.0 mL) at 90 °C under air for 16 h. [b]Isolated yields.

Bu-, and MeO- (**1b−d**) promoted this transformation smoothly, yielding the hydroamidated products **3ba−da** in 80%, 86%, and 91% yields, respectively (entries 1−3). Likewise, electron-withdrawing groups, such as X- (Cl-, F-), NO_2-, and CF_3-substituted benzylamides **1e−h** also reacted efficiently with **2a**, giving trisubstituted alkenes **3ea−ha** in 88%, 95%, 91%, and 86% yields, respectively (entries 4−7). *ortho*-Me, -F, and -CF_3 benzylamines **1i, 1j**, and **1k** was less effective, probably due to the steric effect, giving the target, products **3ia, 3ja**, and **3ka** in moderate yields (entries 8−10). Furthermore, the reaction was tested with meta-substituted benzylamides **1l−1o**, producing enamide **3la−3oa** in excellent yields as well (entries 11−14). Moreover, heterocyclic substrates **1p** and **1q** were also successfully converted to the corresponding enamides **3pa** and **3qa** in 65% and 47% yields, respectively (entries 15 and 16). Other amides, such as *N*-benzylacetamide, methyl benzylcarbamate, N^1,N^1-diisopropyl-N^2-phenyloxalamide, N^1-butyl-N^2,N^2-diisopropyloxalamide, N^1-allyl-N^2,N^2-diisopropyloxalamide and the general amines, such as benzylamine, aniline, alkylamine, furan-2-ylmethanamine, and thiophen-2-ylmethanamine, had been examined under the standard reaction conditions. However, no desired product was obtained.

Chart 3. X-ray Structure of 3aj



Scheme 2. Plausible Reaction Mechanism



Subsequently, we further investigated the scope of alkynes (Table 3). Symmetrical para-substituted tolanes **2b−e** coupled with **1a** to form the target product **3ab−ae** smoothly (entries 1−4). Besides, 4,4′-COOEt-, CF_3-, and NO_2-substituted tolanes, which are electron-deficient alkynes, gave the corresponding products in 16%, 12% and 11% yields, respectively. Good yield was obtained for ortho- and meta-substituted tolanes (entries 5−8). Moreover, unsymmetrical alkynes such as 1-phenyl-1-propyne (**2j**), 1-phenyl-1-butyne (**2k**), and 1-phenyl-1-hexyne (**2l**) were also efficiently converted the products (**3aj−al**) in good yields with excellent regioselectivity (entries 9−11), which is probably due to the coordination of the aromatic ring from the alkynes with Ru atom. Furthermore, the configuration of **3aj** was confirmed by single-crystal X-ray diffraction (Chart 3). Dialkyl alkynes, such as 3-hexyne, ethynylbenzene, and trimethyl(phenylethynyl)-silane, were examined under the standard reaction conditions; however, no desired products were observed.

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On the basis of the obtained results and literatures,[17] the reaction mechanism was tentatively proposed and shown in Scheme 2. First, the active cationic $[Ru(OAc)]^+$ species was formed from $[RuCl_2(p\text{-cymene})]_2$ by the aid of $AgSbF_6$ and $Cu(OAc)_2$. Then, the coordination of oxygen atom from carbonyl group in benzylamide **1** with cationic $[Ru(OAc)]^+$ and the subsequent acetate-mediated deprotonation led to the intermediate cationic ruthenacycle **4** and released AcOH. Subsequently, the coordination of cationic ruthenacycle with alkyne afforded intermediate **5** and successively migratory insertion of alkyne furnished the seven-membered ruthenacycle **6.** Finally, protodemetalation of ruthenacycle **6** afforded the product **3** and regenerateed the active cationic $[Ru(OAc)]^+$ species for the next catalytic cycle. The excellent regioselectivity was obtained probably due to the coordination of the aromatic ring from the alkynes to Ru atom in the ruthenacycle **6**.

In summary, an efficient hydroamidation of internal alkynes with benzylamides catalyzed by Ru(II) has been achieved, affording the corresponding (*E*)-enamides in moderate to excellent yields. This is the first example of hydroamidation with electron-deficient and electron-rich internal alkynes. This protocol features excellent regio- and stereoselectivity, widely functional group tolerance, and easily accessible starting materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01791.

General procedures, relevant NMR spectra, X-ray structures, and catalytic experiments (PDF)
X-ray data (CIF)

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Notes

The authors declare no competing financial interest.

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