

# Ag- and Au-Catalyzed Addition of Alcohols to Ynimides: $\beta$ -Regioselective Carbonylation and Production of Oxazoles

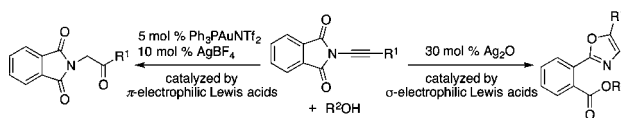
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## ABSTRACT



Metal-catalyzed reactions of ynimides with alcohols to afford  $\beta$ -ketoimides and oxazoles are demonstrated. The triple bond of ynamides is generally activated by mineral acids or metal salts to lead to the regioselective addition of nucleophiles at the  $\alpha$ -C-atom, because of the inherent electronic bias. In contrast, the two neighboring carbonyl groups of ynimides decrease the electron density of the triple bond and the nucleophiles attack the carbonyl C-atom.

Coinage metal catalysts such as silver<sup>1</sup> and gold<sup>2</sup> salts interact with the C–C triple bond of alkynes to allow the addition of various nucleophiles. For regioselective transformations, intramolecular reactions have generally been applied. In the case of intermolecular versions of the reaction with unsymmetrical internal alkynes, mixtures of regioisomers have been generated in most cases, accompanied by a Markovnikov type addition.<sup>3</sup> In contrast to such simple alkynes, the inherent electronic bias of ynamides<sup>4</sup> is perhaps

the feature needed to ensure the  $\alpha$ -regioselective addition of nucleophiles.<sup>5</sup> Therefore, not only has the utility of ynamides as the equivalent of ynamines been recognized in recent years, but also their usefulness in the regioselective functionalization of triple bonds in organic transformations has been significantly expanded (Scheme 1).

We have recently reported the Cu-catalyzed coupling of alkynyl(triaryl)bismuthonium salts with imides to furnish the first reliable synthetic method of ynimides.<sup>6a</sup> More recently, Davies has reported the first catalytic procedure for the synthesis of *N*-alkynylphthalimides directly from terminal alkynes.<sup>6c</sup> The electron-donating ability of the N-atom to the triple bond still present in ynimides allows for the  $\alpha$ -regioselective carbonylation with acidic water (see Supporting Information (SI)).

Compared with ynamides, the presence of two carbonyl groups on the N-atom of ynimides decreases the electron density of the triple bond, lowering the reactivity toward electrophiles and protons. Instead, the neighboring carbonyl carbons would become more electrophilic, as indicated by the facile dephthalimidation with various nucleophiles to give the free amino group. Thus, in the presence of an appropriate metal catalyst, nucleophiles should add to the neighboring carbonyl groups of ynimides, followed by

(1) For a review, see: Weibel, J.-M.; Blanc, A.; Pale, P. *Chem. Rev.* **2008**, *108*, 3149.

(2) For representative reviews, see: (a) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994. (b) Corma, A.; Leyva-Pérez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657. (c) Belmont, P.; Parker, E. *Eur. J. Org. Chem.* **2009**, 6075. (d) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395. (e) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. (f) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266. (g) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (h) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (i) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896.

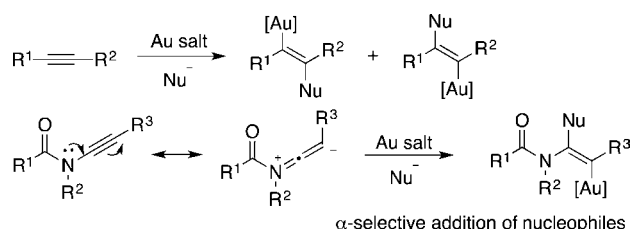
(3) For examples: (a) Santos, L. L.; Ruiz, V. R.; Sabater, M. J.; Corma, A. *Tetrahedron* **2008**, *64*, 7902. (b) Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729.

(4) For representative reviews, see: (a) Evano, G.; Jouvin, K.; Coste, A. *Synthesis* **2013**, *45*, 17. (b) Dekorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, *110*, 5064. (c) Evano, G.; Coste, A.; Louvin, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2840. (d) Mulder, J. A.; Kurtz, K. C. M.; Hsung, R. P. *Synlett* **2003**, 1379.

(5) For the Au-catalyzed  $\alpha$ -regioselective addition of nucleophiles to ynamides, see: (a) Davis, P. W.; Cremonesi, A.; Martin, N. *Chem. Commun.* **2011**, *47*, 379. (b) Li, C.; Zhang, L. *Org. Lett.* **2011**, *13*, 1738. (c) Kramer, S.; Dooleweerd, K.; Lindhardt, A. T.; Rorländer, M.; Skrydstrup, T. *Org. Lett.* **2009**, *11*, 4208. (d) Couty, S.; Meyer, C.; Cossy, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6726.

(6) (a) Sueda, T.; Oshima, A.; Teno, N. *Org. Lett.* **2011**, *13*, 3996. For a recent report for ynimides, see: (b) Souto, J. A.; Becker, P. B.; Iglesias, A.; Muñoz, K. *J. Am. Chem. Soc.* **2012**, *134*, 15505. (c) Alford, J. S.; Davies, M. L. *Org. Lett.* **2012**, *14*, 6020.

**Scheme 1.** Au Salt Catalyzed Markovnikov Addition toward Internal Alkynes



5-*endo*-dig cyclization and then ring cleavage. The  $\beta$ -regioselective carbonylation would be performed via the migration of the carbonyl oxygen to the  $\beta$ -C-atom of the ynimide (Scheme 2). Here, we describe the Ag- and Au-catalyzed addition of alcohols to ynimides to provide  $\beta$ -ketoimides and 2,5-disubstituted oxazole derivatives.

Our preliminary attempts were conducted with Ag- and Au-catalyzed reactions of *N*-(1-hexynyl)phthalimide (**1a**) with MeOH in CH<sub>2</sub>Cl<sub>2</sub> (Table 1). As expected,  $\beta$ -carbonylated compounds **2a** and **3a** (R = Me) were obtained and the corresponding  $\alpha$ -keto compound was not observed. In addition to  $\beta$ -carbonylated compounds, a small amount of methyl *ortho*-(2-oxazolyl)benzoate (**4a**, R = Me) was also obtained. The Ag salts were more reactive for this system than Au salts (Table 1, entries 1–2 vs 3–4), and the amount of MeOH affected the reaction time and distribution of products (Table 1, entries 4–8). By using a large excess of MeOH, only the  $\beta$ -carbonylation proceeded but a long reaction time was required (Table 1, entry 8). Gratifyingly, we found that the presence of both Ag and Au salts was crucial in terms of enhancing the reaction rate (Table 1, entry 8 vs 10) and for reducing the yield of side product **4a** (Table 1, entry 4 vs 9). Several alcohols were also tested for this transformation (Table 1, entries 11–15). Even bulky *tert*-BuOH was a good partner, but H<sub>2</sub>O was less effective.<sup>7</sup>

The regioselective  $\beta$ -carbonylations of various ynimides **1** and **5** were examined with 5 mol % of Ph<sub>3</sub>PAuNTf<sub>2</sub> and

**Table 1.** Screening Data for the Ag- and Au-Catalyzed  $\beta$ -Regioselective Carbonylation of Ynimide (**1a**)<sup>a</sup>

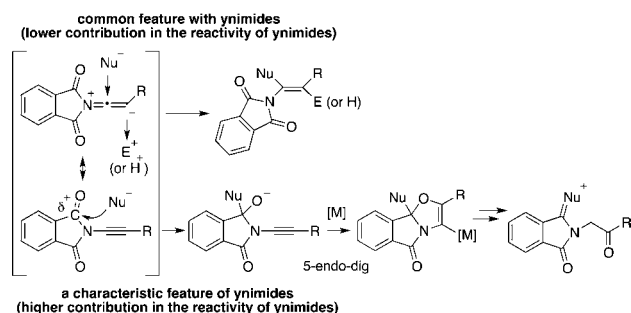
entry	R	ROH equiv	additive (mol %)	time (h)	yields, % <sup>b</sup>		
					<b>2a</b>	<b>3</b>	<b>4</b>
1	Me	2.5	AuCl (10)	24	27 <sup>c</sup>	0	0
2	Me	2.5	Ph <sub>3</sub> PAuNTf <sub>2</sub> (5)	24	14 <sup>d</sup>	12	6
3	Me	2.5	AgOTf (10)	24	81	0	10
4	Me	2.5	AgBF <sub>4</sub> (10)	6	68	21	9
5	Me	5.0	AgBF <sub>4</sub> (10)	5	49	41	6
6	Me	10	AgBF <sub>4</sub> (10)	4	45	51	4
7	Me	20	AgBF <sub>4</sub> (10)	24	31	64	1
8	Me	50	AgBF <sub>4</sub> (10)	24	13	85	0
9	Me	2.5	AgBF <sub>4</sub> (10)	0.5	62	37	0
10	Me	50	Ph <sub>3</sub> PAuNTf <sub>2</sub> (5) AgBF <sub>4</sub> (10)	0.5	10	90	0
11	H	2.5	AgBF <sub>4</sub> (10)	24	4 <sup>e</sup>	0	0
12	Et	2.5	AgBF <sub>4</sub> (10)	6	94	0	2
13	CF <sub>3</sub> CH <sub>2</sub>	2.5	AgBF <sub>4</sub> (10)	24	74	0	16
14	<i>i</i> -Pr	2.5	AgBF <sub>4</sub> (10)	24	99	0	1
15	<i>t</i> -Bu	2.5	AgBF <sub>4</sub> (10)	24	99	0	0

<sup>a</sup> **1a** (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). <sup>b</sup> Yields were determined by <sup>1</sup>H NMR on the crude reaction mixture using 1,2-dichloroethane as an internal standard. <sup>c</sup> 61% of **1a** was recovered. <sup>d</sup> 66% of **1a** was recovered. <sup>e</sup> 96% of **1a** was recovered.

10 mol % of AgBF<sub>4</sub> in MeOH at rt (Table 2). When the reaction was worked up with 1 M hydrochloric acid,  $\beta$ -ketoimides (**2** and **6**) were obtained in good to excellent yields and oxazoles (**4** and **18**) were not observed at all. For reasons that are yet unclear, terminal ynimides and ynimides bearing the TMS group led to inferior results. In these cases, a quantitative yield of phthalimide was observed in the <sup>1</sup>H NMR spectrum of the crude products.

Although there are still some ambiguities, we postulate a reaction mechanism for the complete regioselective  $\beta$ -carbonylation that includes the Ag salt mediated nucleophilic addition of MeOH toward the carbonyl group of ynimides (**1** → **8**),<sup>8</sup> followed by the Au-mediated 5-*endo*-dig cyclization (**8** → **10**),<sup>9</sup> protodeauration (**10** → **11**), and its ring cleavage (**11** → **12**) (Scheme 3). We speculate that intermediate **10** is not generated from the direct Au-mediated 5-*endo*-dig cyclization of ynimides followed by the addition of methanol since only ynamides bearing the *tert*-butyloxycarbonyl group on the N-atom were

**Scheme 2.** A Characteristic Feature of Ynimides

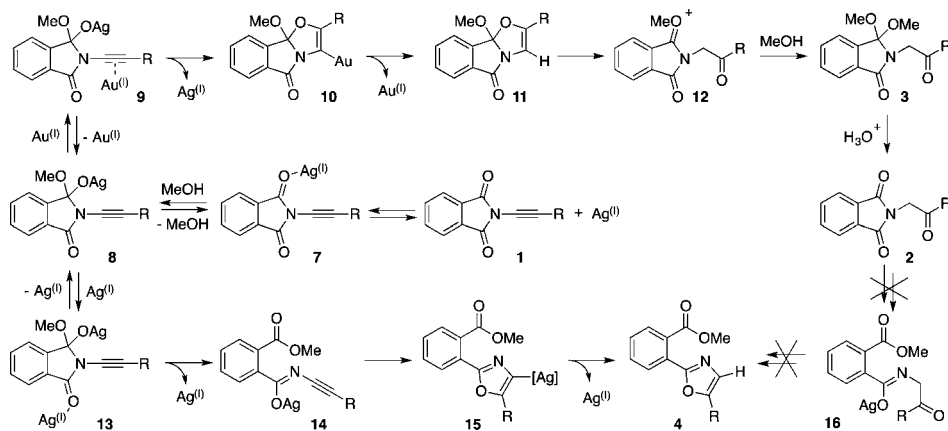


(7) MeOH adds to diphenylacetylene 2.5 times faster than H<sub>2</sub>O in the presence of Au<sup>(I)</sup> catalysts; see: Leyva, A.; Corma, A. *J. Org. Chem.* **2009**, *74*, 2067.

(8)  $\sigma$ -Coordination of Ag<sup>(I)</sup> is slightly preferred over  $\pi$ -coordination (see ref 9b), and this preference would cause the successful nucleophilic addition of alcohols to the carbonyl group of ynimides.

(9) The addition of silver salts generates cationic gold species, which leads to an increase in the  $\pi$ -Lewis acidity of gold catalysts and the reaction rate in many cases; see: (a) Leyva, A.; Corma, A. *J. Org. Chem.* **2009**, *74*, 2067. (b) Yamamoto, Y. *J. Org. Chem.* **2007**, *72*, 7817. (c) Muñoz, M. P.; Adrio, J.; Carretero, J. C.; Echavarren, A. M. *Organometallics* **2005**, *24*, 1293.

**Scheme 3.** Plausible Reaction Mechanism for the Production of  $\beta$ -Ketoimides and *ortho*-(2-Oxazoly)benzoates



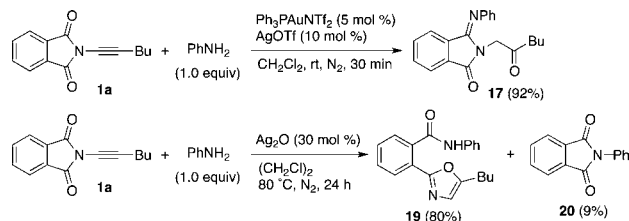
**Table 2.** Scope and Limitation for the Production of  $\beta$ -Ketoimides<sup>a</sup>

entry	ynimides		time (h)	product	yield <sup>b</sup> (%)
	R				
1	<b>1b</b>	H	2	<b>2b</b>	0
2	<b>1a</b>	Bu	1	<b>2a</b>	91
3	<b>1c</b>	<i>cyclo</i> -Pr	24	<b>2c</b>	69
4	<b>1d</b>	<i>tert</i> -Bu	1	<b>2d</b>	84
5	<b>1e</b>	Ph	1	<b>2e</b>	77
6	<b>1f</b>	TMS	1	<b>2f</b>	0
7	<b>5a</b>	Bu	1	<b>6a</b>	86
8	<b>5b</b>	<i>cyclo</i> -Pr	3	<b>6b</b>	89
9	<b>5c</b>	<i>tert</i> -Bu	3	<b>6c</b>	88
10	<b>5d</b>	Ph	1	<b>6d</b>	83

<sup>a</sup> **1** or **5** (0.1 mmol) in MeOH (2 mL). <sup>b</sup> Isolated yield.

cycloisomerized by Ag<sup>10</sup> or Au<sup>11</sup> salts. **3a** was easily converted to  $\beta$ -ketoimide **2a** by treatment with 1.0 M hydrochloric acid,<sup>12</sup> but **2a** and oxazole **4a** did not afford **3a** in the acidic methanol solution or under the optimized reaction conditions shown in Table 2. As shown in Scheme 4, only imine **17** was obtained in excellent isolated yield from the reaction of ynamide **1a** with 1.0 equiv of aniline in CH<sub>2</sub>Cl<sub>2</sub>.<sup>13</sup> These results indicate that  $\beta$ -ketoimides were produced

**Scheme 4.** Reaction with *Primary* Aromatic Amine



by a transfer of the carbonyl oxygen to the  $\beta$ -C-atom of ynamides, but were not produced by the metal-catalyzed *anti*-Markovnikov addition of MeOH.<sup>14</sup> The  $\pi$ -electrophilic Lewis acidity of the metal catalysts appears to play an important role in determining the final outcome. When the  $\pi$ -electrophilic Lewis acidity of metal catalysts is insufficient, cleavage of the ring of the intermediate **13** is required to give the *N*-alkynyl amide derivative **14**, which allows the formation of *o*-(2-oxazoly)benzoate **4** via voluntary 5-*endo*-dig cyclization.

The side product **4** is a noteworthy compound since oxazoles represent an important structural motif in bioactive and pharmacological molecules.<sup>15</sup> Furthermore, to our knowledge, the reports for the synthesis of *o*-(2-oxazoly)benzoates are rare.<sup>16</sup> Therefore, we investigated the selective formation of oxazole **4a** from ynamide **1a** (Table 3). The addition of Et<sub>3</sub>N for the purpose of decreasing the  $\pi$ -acidity enhanced the production of

(10) Istrate, F. M.; Buzas, A. K.; Jurberg, I. D.; Odabachian, Y.; Gagosz, F. *Org. Lett.* **2008**, *10*, 925.

(11) (a) Hashmi, A. S.; Salathé, R.; Frey, W. *Synlett* **2007**, 1763. (b) Buzas, A. K.; Istrate, F. M.; Gagosz, F. *Tetrahedron* **2009**, *65*, 1889 and also ref 10.

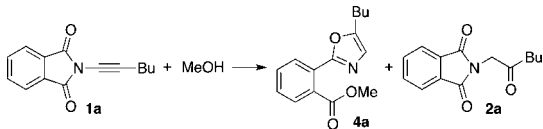
(12) Acetals are generally obtained in the Au-catalyzed reaction of alkynes in alcohols. For example, see: (a) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925. (b) Tales, J. H.; Brode, S.; Chabanas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1415. Also see refs 3b and 7.

(13) For a Au<sup>(I)</sup>-catalyzed hydroamination of ynamides giving rise to the Markovnikov products, see: Reference 5c.

(14) For examples of umpolung-type additions of nucleophiles to ynamides, see: (a) Koester, D. C.; Werz, D. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 7971. (b) Das, J. P.; Cheshik, H.; Marek, I. *Nat. Chem.* **2009**, *1*, 128. (c) Gourdet, B.; Lam, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 3802. (d) Gourdet, B.; Rudkin, M. E.; Watts, C. A.; Lam, H. W. *J. Org. Chem.* **2009**, *74*, 7849. (e) Fukudome, Y.; Naito, H.; Hata, T.; Urabe, H. *J. Am. Chem. Soc.* **2008**, *130*, 1820.

(15) Oxazoles are synthesized from the cyclization of *N*-propargyl-carboxamides by using a strong base, SiO<sub>2</sub>, CeCl<sub>3</sub>/NaI, FeCl<sub>3</sub>, and Au salts in recent organic transformations; see: Tran-Dubé, M.; Johnson, S.; McAlpine, I. *Tetrahedron Lett.* **2013**, *54*, 196 and references therein.

(16) Sakakibara, T.; Kume, T.; Ohyabu, T.; Hase, T. *Chem. Pharm. Bull.* **1989**, *37*, 1694.

**Table 3.** Screening Data for the Selective Formation of Oxazole<sup>a</sup>


entry	additive (equiv)	MeOH (equiv)	time (h)	yields, <sup>b</sup> %		
				4a	2a	1a <sup>c</sup>
1	AgBF <sub>4</sub> (0.1)	1.3	5	7	93	0
2	AgBF <sub>4</sub> (0.3), TFOH (1.0)	1.3	3	7	86	0
3	AgBF <sub>4</sub> (0.3), Ph <sub>3</sub> P (1.0)	1.3	24	0	0	100
4	AgBF <sub>4</sub> (0.3), Et <sub>3</sub> N (1.0)	1.3	24	73	1	20
5	AgBF <sub>4</sub> (0.3), Et <sub>3</sub> N (1.0)	1.3	24 <sup>d</sup>	66	1	21
6	Ag <sub>2</sub> O (0.3)	1.3	24	58	0	27
7	Ag <sub>2</sub> O (0.3)	2.5	24	93	0	0

<sup>a</sup> **1a** (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at rt under N<sub>2</sub>. <sup>b</sup> Yields were determined by <sup>1</sup>H NMR on the crude reaction mixture using 1,2-dichloroethane as an internal standard. <sup>c</sup> Recovered yield. <sup>d</sup> At 50 °C.

**4a** (Table 3, entry 4), while use of Ph<sub>3</sub>P in the reaction was not successful and the starting material **1a** was recovered quantitatively (Table 3, entry 3). Finally, Ag<sub>2</sub>O was found to be an effective catalyst and the use of 2.5 equiv of MeOH in CH<sub>2</sub>Cl<sub>2</sub> led to a high yield of **4a** (entry 7).

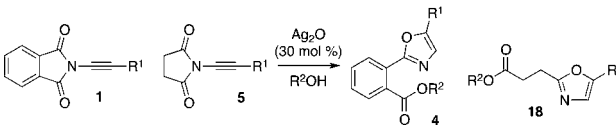
We also investigated the scope of the reaction with respect to ynimides and alcohols in the presence of 30 mol % of Ag<sub>2</sub>O (Table 4). Almost every *o*-(2-oxazolyl)benzoate **4** exhibited a strong luminescence on TLC plates under a UV lamp (254 nm). The reaction proceeded successfully to give simple *N*-alkynylphthalimides under the conditions of 2.5 equiv of MeOH at rt (Table 4, entries 1 and 2), whereas more sterically demanding and aromatic<sup>17</sup> substituted ynimides (Table 4, entries 3 and 4) and *N*-alkynylsuccinimides (Table 4, entries 5–8) required large amounts of MeOH and elevated temperatures to complete the reaction.  $\alpha$ - and  $\beta$ -Ketoimides were not observed in any of these reactions.

We were interested in applying this method to the use of amines as the nucleophile instead of alcohols. We observed that the reaction with aniline gave a mixture of the corresponding *ortho*-(2-oxazolyl)benzamide (**19**, 80% yield) and *N*-phenylphthalimide (**20**, 9% yield) (Scheme 4).

One might consider that oxazoles are generated via the mechanism (**2**→**16**→**4** in Scheme 3) of classical Robinson–Gabriel oxazoles formation from  $\beta$ -ketoamides.<sup>18</sup> However these conditions generally require strong Lewis or mineral acids. Furthermore,  $\beta$ -ketoimide **2a** did not give the corresponding oxazole **4a** in MeOH in the presence of 30 mol % of Ag<sub>2</sub>O at 80 °C. When the ynimide **1a** was employed in the presence of 5 mol % of Ph<sub>3</sub>PAuNTf<sub>2</sub> under standard reaction conditions C in Table 4, 73% of

(17) Similar reactivities are observed in Au<sup>(I)</sup>-catalyzed cycloisomerization of alkynes; see: Buzas, A. K.; Istrate, F. M.; Gagoxz, F. *Tetrahedron* **2009**, *65*, 1889.

(18) (a) Robinson, R. *J. Chem. Soc.* **1909**, 95, 2167. (b) Gabriel, S. *Ber.* **1910**, *43*, 1283. (c) Wasserman, H. H.; Vinick, F. J. *J. Org. Chem.* **1973**, *38*, 2407.

**Table 4.** Scope and Limitation for the Synthesis of Oxazoles<sup>a</sup>


entry	ynimide		conditions	time (h)	product (yield, <sup>b</sup> %)
	R <sup>1</sup>	R <sup>2</sup>			
1	<b>1a</b>	Bu	A	24	<b>4a</b> (79)
2	<b>1c</b>	<i>cyclo</i> -Pr	A	24	<b>4c</b> (86)
3	<b>1d</b>	<i>tert</i> -Bu	B	3	<b>4d</b> (98)
4	<b>1e</b>	Ph	B	1	<b>4e</b> (97)
5	<b>5a</b>	Bu	C	1	<b>18a</b> (87)
6	<b>5b</b>	<i>cyclo</i> -Pr	C	1	<b>18b</b> (66)
7	<b>5c</b>	<i>tert</i> -Bu	C	2	<b>18c</b> (66)
8	<b>5d</b>	Ph	C	1	<b>18d</b> (65)
9	<b>1a</b>	Bu	C	1	<b>4g</b> (91)
10	<b>1a</b>	Bu	CF <sub>3</sub> CH <sub>2</sub>	1	<b>4h</b> (90)
11	<b>1a</b>	Bu	<i>i</i> -Pr	1	<b>4i</b> (92)
12	<b>1a</b>	Bu	<i>tert</i> -Bu	24	<b>4j</b> (72)
13	<b>1a</b>	Bu	Ph	24	<b>4k</b> (0)
14	<b>1e</b>	Ph	<i>tert</i> -Bu	24	<b>4l</b> <sup>c</sup> (87)

<sup>a</sup> Conditions A: ynimide (0.1 mmol), R<sup>2</sup>OH (2.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at rt under N<sub>2</sub>. Conditions B: ynimide (0.1 mmol), R<sup>2</sup>OH (50 equiv) in (CH<sub>2</sub>Cl<sub>2</sub>)<sub>2</sub> (2 mL) at 80 °C under N<sub>2</sub>. Conditions C: ynimide (0.1 mmol) in R<sup>2</sup>OH (2 mL) at 80 °C under N<sub>2</sub>. <sup>b</sup> Isolated yields. <sup>c</sup> The structure was assigned by X-ray diffraction analysis; see SI.

oxazole **4a** and 5% of  $\beta$ -ketoimide **2a** were obtained. These results again suggest that the presence of the  $\pi$ -electrophilic Lewis acids leads to  $\beta$ -carbonylation of ynimides. Actually, representative  $\sigma$ -electrophilic Lewis acids such as CeCl<sub>3</sub> or MgCl<sub>2</sub> afforded the selective formation of **4a**. In contrast, Ag, Cu, and Au catalysts acted as a  $\sigma$ - and/or  $\pi$ -electrophilic catalysts<sup>9b</sup> to give **4a** and/or **2a** depending on their ligands and valence states (see SI).

In conclusion, we have demonstrated the first Ag- or Au-catalyzed reactions of ynimides with alcohols to give  $\beta$ -ketoimides and oxazoles. Although some mechanistic details are still unexplored, we believe these products are generated via the nucleophilic addition of alcohols to the carbonyl group of ynimides. This work also offers valuable insight into the chemistry of ynimides and would substantially broaden the field of *N*-substituted alkynes as building blocks in organic synthesis. Further studies with various nucleophiles are ongoing in our laboratory.

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**Supporting Information Available.** Additional results, experimental procedures including spectroscopic and analytical data of new compounds (PDF), and X-ray data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.