

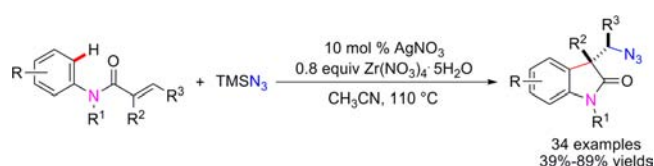
Silver-Catalyzed Carboazidation of  
ArylacrylamidesXiao-Hong Wei,<sup>†</sup> Ya-Min Li,<sup>†</sup> An-Xi Zhou,<sup>†</sup> Ting-Ting Yang,<sup>†</sup> and Shang-Dong Yang<sup>\*,†,‡</sup>

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## ABSTRACT



A novel and inexpensive method of nontoxic, silver-salt-catalyzed carboazidation of arylacrylamides to afford corresponding azide oxindoles is reported. This reaction system exhibits great functional group tolerance. All products form a crucial skeleton for the synthesis of various indole alkaloids.

Recent advances in transition-metal-catalyzed difunctionalization of alkenes have provided a powerful strategy for the synthesis of various organic compounds.<sup>1</sup> Metal-catalyzed carbon–hetero functionalization of arylacrylamides with various nucleophiles in particular has the potential to incite cyclization and promises a novel pathway for the synthesis of various functional oxindoles. For example, the Zhu, Liu, Zecchi, Lu, and Pan groups have independently developed some new methods of palladium-catalyzed oxidative carbo–hetero functionalization of arylacrylamides, which involve the following nucleophiles:

<sup>†</sup> Lanzhou University.<sup>‡</sup> Lanzhou Institute of Chemical Physics.

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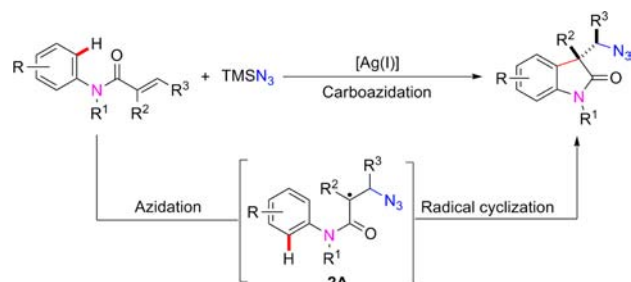
carbon, TsNH<sub>2</sub>, CF<sub>3</sub><sup>−</sup>, *t*-BuO<sub>2</sub>H, and DMF.<sup>2</sup> More recently, Li and co-workers reported a Fe-catalyzed oxidative 1,2-alkylarylation of arylacrylamides to synthesize a variety of alkoxyated oxindoles.<sup>3</sup> At present, the Zhu group has documented an excellent tandem protocol for the formation of quaternary oxindoles. Their method involves visible-light-promoted room-temperature decarboxylation.<sup>4</sup> In the past several years, we have focused our efforts on the development of new and efficient protocols for transition-metal-catalyzed C–P bond formation.<sup>5</sup> We have established a novel efficient protocol for the preparation of various diphenylphosphoryl oxindoles via silver-catalyzed difunctionalization of arylacrylamides by carbon–phosphorylation and a C–H functionalization cascade process as a result of our endeavors.<sup>5d</sup> All the evidence indicates that (a) this transformation involves a radical process and (b) that Ag-promoted generation of the phosphoryl radical is the key step. Inspired by these promising results as well as literature surveys, we hypothesized that the azide might

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# Scheme 1. Silver-Catalyzed Carboazidation of Arylacrylamides



prompt the silver salt to produce an azidyl radical, which in turn leads to the carboazidation of alkenes and follows C–C bond formation to afford corresponding azide oxindoles. After much effort, we were able to properly set up the Ag-catalyzed carboazidation of arylacrylamides (Scheme 1) and apply it to the synthesis of 3,3'-pyrrolidinylspirooxindole scaffolds such as the CR TH2 receptor antagonist.

Organic azides were extensive in many nitrogen-containing compounds. This versatile class of important core structures possesses unique reactivity and may easily be transformed into various organic functional groups.<sup>6</sup> In particular, the use of organic azides as powerful radical mediators provides a novel and concise pathway to the

synthesis of alkyl azides by radical addition to olefins or to the formation of the ubiquitous amino group by reduction.<sup>7</sup> The use of the azidyl radical can also be applied to Huisgen 1,3-dipolar cycloadditions or different variants of the Staudinger ligation.<sup>8</sup> The electrophilic character of the azidyl radical makes its reaction with olefins especially interesting.<sup>9</sup> The application of azidyl radicals to the functionalization of unactivated alkenes has seen advances over the past decades.<sup>10</sup> However, until now, transition-metal-catalyzed direct carboazidation by the addition of the azidyl radical to alkenes followed by the cascade carbon radical cyclization processes has never been reported and is highly desirable.

Table 1. Reaction Condition Screening<sup>a</sup>

entry	cat. (mol %)	additive (equiv)	yield <sup>b</sup> (%)
1	AgNO <sub>3</sub> (5)	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.5)	39
2	AgNO <sub>3</sub> (10)	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.5)	62
3	AgNO <sub>3</sub> (10)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O (0.5)	<10
4	AgNO <sub>3</sub> (10)	La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (0.5)	15
5	AgNO <sub>3</sub> (10)	Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (0.5)	17
6	AgNO <sub>3</sub> (10)	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.5)	15
7	AgNO <sub>3</sub> (10)	Ce(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.5)	<10
8	AgNO <sub>3</sub> (10)	NaNO <sub>3</sub> + H <sub>2</sub> O (0.5)	18
9	AgNO <sub>3</sub> (10)	NH <sub>4</sub> NO <sub>3</sub> (0.5)	55
10	AgNO <sub>3</sub> (10)	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O (0.5)	39
11	AgNO <sub>3</sub> (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (0.5)	71
12	AgNO <sub>3</sub> (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (0.8)	86
13	AgNO <sub>3</sub> (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	79
14	AgSbF <sub>6</sub> (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	17
15	AgBF <sub>4</sub> (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	23
16	AgOAc (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	N.R.
17	AgOTf (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	N.R.
18	Ag <sub>2</sub> O (10)	Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	N.R.
19		Zr(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O (1.0)	N.R.

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), catalyst (10 mol %), MeCN (2.0 mL), and additive (0.8 equiv) at 110 °C (oil-bath temperature) under argon atmosphere for 28 h. <sup>b</sup> Isolated yield.

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In an initial study, we chose the *N*-methyl-*N*-arylacrylamide **1a** as the model substrate to test different azide compounds in the presence of 5 mol % of AgNO<sub>3</sub> and 0.5 equiv of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in CH<sub>3</sub>CN at 110 °C. To our delight, this reaction works with TMSN<sub>3</sub> and affords the desired product **2a** in 39% yield (Table 1, entries 1). Encouraged by this result, we further optimized the reaction conditions. First, we increased loading of the silver catalyst to 10 mol %. As a result, the yield of **2a** improved to a rewarding 62% (Table 1, entries 2). Subsequently, we investigated different nitrates for their potential in this conversion in the presence of 10 mol % AgNO<sub>3</sub> in CH<sub>3</sub>CN at 110 °C. Results indicate that Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O is the best choice; the product of **2a** improves to 71% yield

(Table 1, entries 3–11). We further investigated the equivalents of  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ . The best yield of **2a** was obtained with an 0.8 equiv scale (Table 1, entries 12 and 13). We further examined other silver salts; results indicated that  $\text{AgNO}_3$  was the best choice (Table 1, entries 14–18). In addition, we noted that decreases in temperature cause correspondingly lower yields. Meanwhile, the control experiment revealed that use of only  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  fails to prompt the reaction (Table 1, entry 19).

Having established optimal reaction conditions (Table 1, entry 10), we further investigated the scope of arylacrylamides. As shown in Table 2, an examination of different *N*-protection groups revealed that methyl and benzyl were appropriate for the reaction (**2a** and **2c**), but tosyl and *N*-free arylacrylamide failed. Various substituted *N*-methylarylacrylamides worked very well, and the corresponding products were obtained in good-to-excellent yields regardless of electron-donating or electron-withdrawing groups on the *para*-position (**2d–l**). The arylacrylamides containing the *ortho*-position substituent groups exhibited a particularly distinct steric hindrance effect, and lower yields were observed as a result (**2m–s**); Substrates bearing *meta* substituents underwent carboazidation smoothly and readily converted to the product in a 72% yield with poor regioselectivity (**2t**). To our delight, the naphthalene acrylamide was also compatible with the transformation and successfully provided the product of **2t** in 43% lower yield. On the other hand, the tetrahydroquinoline derivative of acrylamide afforded tricyclic oxindole **2b** in 60% yield. Multisubstituted arylacrylamide was also well tolerated in this carboazidation process, affording the azide oxindoles with moderate yields (**2v** and **2w**). The *N*-methyl-*N*-phenylcyclohex-1-enecarboxamide was compatible with this transformation as well; the spiro-oxindole was obtained in 43% yield (**2ac**). It should be noted that different heterocyclic substrates such as pyridine, quinoline, and pyrimidine failed to detect any product as a result of lower reactivity. Furthermore, the evaluation of various substituent groups of alkenes were also performed. No reaction occurred in the case of monosubstituted olefins ( $\text{R}^2 = \text{H}$ ). A series of  $\alpha$ -substituted olefins bearing different functional groups, such as phenyl (**2x**), benzyl (**2y**), phthalimide (**2aa**), and ester (**2ab**), were tolerated well in this transformation and afforded the desired products in moderate-to-good yields besides the monosubstituent olefin ( $\text{R}^2 = \text{H}$ ). Moreover, we note that the synthesis of 3,4-dihydroquinolin-2(1*H*)-one derivatives is also possible under these reaction conditions (**2z**).

The spiro-4-pyrrolidinone skeleton exists in an extensive array of natural products and pharmaceuticals.<sup>11</sup> Thus, the development of simple and efficient ways to construct these compounds is highly desirable. Herein, products of **2ae** and **2af** can be easily transferred into a

**Table 2.** Silver-Catalyzed Carboazidation of Different Arylacrylamides<sup>a</sup>

entry	product	yield (%) <sup>b</sup>	entry	product	yield (%) <sup>b</sup>
2a		86%	2v		49%
2b		60%	2w		71%
2c		57%	2x		59%
2d		78%	2y		64%
2e		84%	2z		40%
2f		76%	2aa		40%
2g		75%	2ab		43%
2h		85%	2ac		43% trans:cis = 3.8:1
2i		89%	2ad		69% <sup>c</sup>
2j		78%	2ae		65% <sup>c</sup>
2k		78%	2af		67% <sup>c</sup>
2l		76%			
2m		42%			
2n		39%			
2o		57%			
2p		60%			
2q		53%			
2r		50%			
2s		50%			
2t		72% A:B = 1.83:1			
2u		48%			

<sup>a</sup> Reaction conditions: **1a–z** (0.3 mmol), catalyst (10 mol %), MeCN (2.0 mL), and additive (0.8 equiv) at 110 °C (oil-bath temperature), under argon atmosphere for 30 h. <sup>b</sup> Isolated yield. <sup>c</sup> 20 mol % catalyst was used.

spiro-4-pyrrolidinone skeleton **4** through use of the reported method,<sup>12</sup> which may then be used to synthesize horsfiline and CR TH2 receptor antagonist with further modification (Scheme 2).

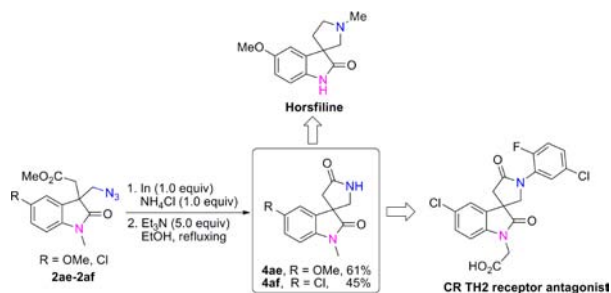
The detailed mechanism for this carboazidation of alkenes is indeed similar to our recent report on silver-catalyzed carbon–phosphorylation. Both mechanisms involve a radical process within which Ag-promoted

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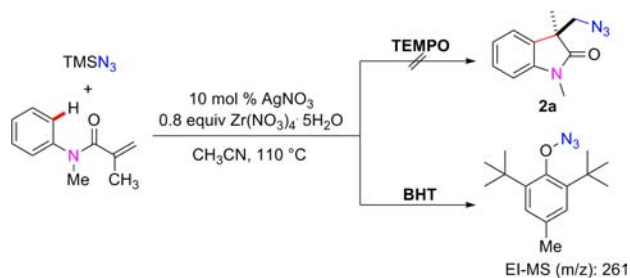


**Scheme 2.** Showing Utility of Our Protocol



generation of phosphoryl radical is the key step. In our carboazidation reaction of alkenes silver acts to arouse the azidyl radical. To certify this assumption and acquire straightforward proof, we performed chemical trapping of radicals. We used the well-known radical-trapping reagents TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and 2,6-di-*tert*-butyl-4-methylphenol.<sup>13</sup> Chemical trapping was carried out under standardized reaction conditions. As illustrated in Scheme 3, the addition of 1.0 equivalent of TEMPO or 2,6-di-*tert*-butyl-4-methylphenol under otherwise identical condition led to suppression of the carboazidation process. To our delight, 2,6-di-*tert*-butyl-4-methylphenol trapped the azidyl radical, and the product of 2-(azidoxy)-1,3-di-*tert*-butyl-5-methylbenzene was detected in the GC–MS.

**Scheme 3.** Radical-Trapping Experiment of Carboazidation

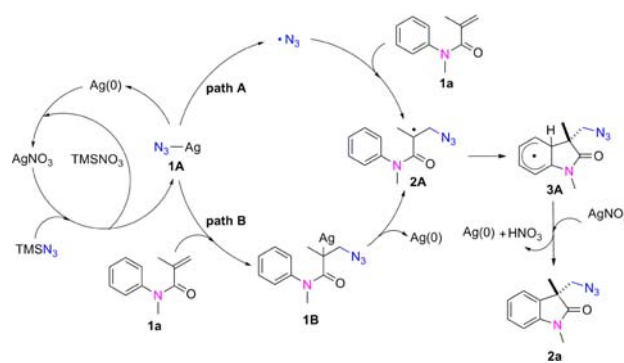


Based on the above experiments, we have outlined a tentative pathway for this transformation. Scheme 4 illustrates our proposed pathway. First,  $\text{TMSN}_3$  reacts with  $\text{AgNO}_3$  to form the intermediate  $\text{AgN}_3$  **1A** under the reaction conditions. Subsequently, the reaction may

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proceed by two different pathways: in path A,  $\text{AgN}_3$  **1A** first exhibits cleavage to generate the azidyl radical, which then reacts with alkene **1a** to produce the alkyl radical **2A**. Another possibility for the formation of alkyl radical **2A** involves the direct addition of **1A** to alkene **1a** to form  $\text{Ag(I)}$  species **1B**, which then transforms into the alkyl radical **2A** by oxidation (Scheme 4, path B). The resulting alkyl radical **2A** attacks the benzene ring and leads to the generation of the intermediate **3A** by intramolecular cyclization, which then passes by single electron transfer (SET) under the oxidation with  $\text{Ag(I)}$  to release the product along with  $\text{HNO}_3$  and  $\text{Ag(0)}$ . Finally, the  $\text{Ag(0)}$  is oxidized to  $\text{Ag(I)}$  in the presence of  $\text{HNO}_3$  and realizes catalytic cycling.

**Scheme 4.** Proposed Mechanism for Silver-Catalyzed Carboazidation of Alkenes



In conclusion, we have disclosed a highly efficient protocol of silver-catalyzed carboazidation of alkenes and a subsequent C–H functionalization cascade process that may be used to prepare various azide oxindoles. Our transformation employs inexpensive, nontoxic silver salt. Further application of this approach to other substrates is ongoing in our laboratory.

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**Supporting Information Available.** Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.