



## Catalytic alkenylation of $\gamma$ -substituted butenolides with cyclic *N*-sulfonylated imines in water leading to $\alpha$ -arylidene butenolide derivatives

Feng Li<sup>a</sup>, Jingjing Wang<sup>a,\*</sup>, Wenlong Pei<sup>b</sup>, Hai Ma<sup>c</sup>, Hong Li<sup>a</sup>, Mingyue Cui<sup>a</sup>, Shuxin Peng<sup>a</sup>, Shihui Wang<sup>a</sup>, Lantao Liu<sup>a,b,\*</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Shangqiu Normal University, 298 Wenhua Road, Shangqiu, Henan 476000, China

<sup>b</sup> College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450052, China

<sup>c</sup> Institute of Chinese Materia Medica, China Academy of Chinese Medical Sciences, Beijing 100700, China

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### ABSTRACT

An efficient Et<sub>3</sub>N-catalyzed alkenylation of  $\gamma$ -substituted deconjugated butenolides with cyclic *N*-sulfonylated imines in water is described. The reaction proceeds efficiently under mild reaction conditions to give  $\alpha$ -arylidene butenolide derivatives in high yield (82–96%).

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Water is an abundant, nontoxic, non-flammable, and environmentally friendly solvent [1]. In addition, water has unique and unusual physical and chemical properties, which can influence the selectivity and reactivity of reactions [2]. The use of water as a solvent for organic synthesis is regarded as an important subject in green chemistry [3]. In recent years, many organic reactions have been carried out in water under mild reaction conditions to improve synthetic efficiency [4]. However, the development of new reactions in water is still highly desirable.

Olefins are ubiquitous structural motifs found in a variety of biologically active molecules and serve as extremely versatile building blocks that can undergo various synthetically useful transformations [5]. Due to their synthetic significance, intense efforts have been made for the development of various methods to access structurally diverse families of substituted olefin derivatives [6]. However, new strategies for the facile synthesis of olefins are still being investigated, for example, the alkenylation of aldimines with carbon electrophiles. In this regard, the groups of Bestmann [7], Abdou [8], and Tian [9] reported the stereoselective

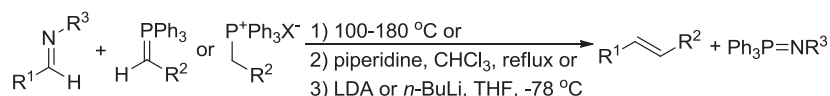
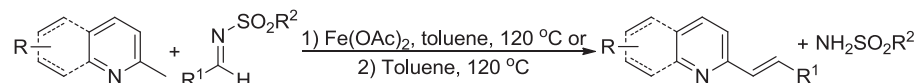
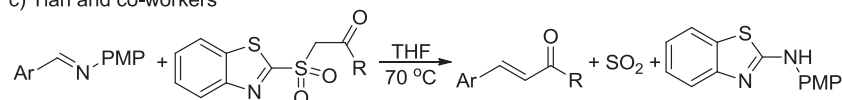
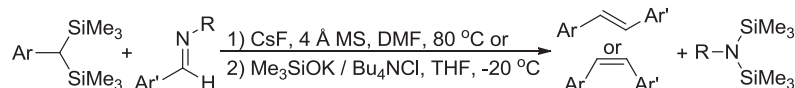
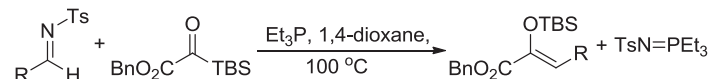
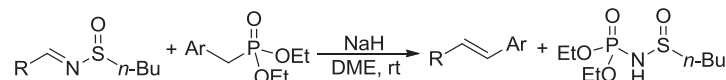
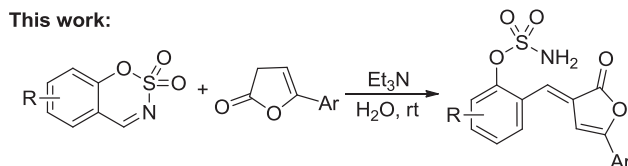
olefination of *N*-substituted imines with phosphonium ylides for the synthesis of 1,2-disubstituted alkenes (Scheme 1, a). In 2011, the groups of Huang [10], and Wang [11] developed the iron-catalyzed or catalyst-free direct alkenylation of azaarenes with *N*-sulfonyl aldimines via benzylic C–H bond activation to construct 2-alkenylated azaarenes (Scheme 1, b). In 2012, Tian and co-workers also described the olefination and vicinal difunctionalization of imines with  $\alpha$ -(benzothiazol-2-ylsulfonyl) carbonyl compounds in the absence of an external base to synthesize electron-deficient alkenes (Scheme 1, c) [12].

O'Shea and co-workers reported Peterson olefination reactions between bench-stable  $\alpha,\alpha$ -bis(trimethylsilyl)toluene reagents and *N*-substituted imines (Scheme 1, d) [13]. In 2016, Matsuya and co-workers disclosed the sequential 1,2-Brook/Wittig reaction of benzyl *tert*-butyldimethylsilyl glyoxylate with *N*-tosylimines for the preparation of silyl enol ethers (Scheme 1, e) [14]. Recently, Diesendruck and co-workers achieved the olefination of *N*-sulfonylimines with a Wittig-Horner reagent to give 1,2-diaryl-substituted alkenes (Scheme 1, f) [15].

Cyclic *N*-sulfonylated imines are readily accessible stable imines and have been utilized as versatile reagents in a wide range of organic reactions, including nucleophilic addition [16], annulation [17] and ring-expansion reactions [18]. Surprisingly, only one ring-opening reaction of cyclic *N*-sulfonylated imines has been

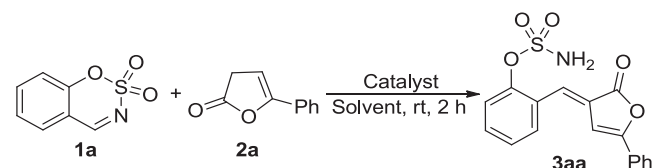
\* Corresponding authors at: College of Chemistry and Chemical Engineering, Shangqiu Normal University, 298 Wenhua Road, Shangqiu, Henan 476000, China (L. Liu).

E-mail addresses: [wangjingjing0918@163.com](mailto:wangjingjing0918@163.com) (J. Wang), [liult05@ccas.ac.cn](mailto:liult05@ccas.ac.cn) (L. Liu).

**Previous work:**a) Bestmann,<sup>7</sup> Abdou,<sup>8</sup> and Tian<sup>9</sup>b) Huang,<sup>10</sup> and Wang<sup>11</sup>c) Tian and co-workers<sup>12</sup>d) O'Shea and co-workers<sup>13</sup>e) Matsuya and co-workers<sup>14</sup>f) Diesendruck and co-workers<sup>15</sup>**This work:****Scheme 1.** Alkenylation of aldimines with various carbon electrophiles.

documented [19].  $\gamma$ -Substituted deconjugated butenolides have also emerged as versatile building blocks and are widely used in various catalytic strategies to construct the products of  $\gamma$ -addition [20]. In contrast to the well-studied  $\gamma$ -addition of deconjugated butenolides,  $\alpha$ -addition reactions have been far less exploited [21]. Herein, we report a triethylamine catalyzed alkenylation of  $\gamma$ -substituted deconjugated butenolides with cyclic *N*-sulfonylated imines in water under mild conditions *via* nucleophilic addition to the C=N double bond and subsequent cleavage of the C–N bond, which represents an efficient and atom-economical route to synthesize  $\alpha$ -arylidene butenolide derivatives.

Initially, benzo[e][1–3]oxathiazine 2,2-dioxide **1a** and  $\gamma$ -phenyl butenolide **2a** were chosen as model substrates to optimize the reaction conditions at room temperature (Table 1). Using Et<sub>3</sub>N (5 mol%) as the catalyst, the solvent effect was investigated. Using CH<sub>2</sub>Cl<sub>2</sub>, toluene, THF, and CH<sub>3</sub>CN as the solvent, product **3aa** was obtained in 65–82% yield (Entries 1–4). To our delight, the desired product **3aa** was obtained in 95% yield when H<sub>2</sub>O was used as the solvent (Entry 5). Subsequently, we examined the influence of different bases for the reaction in water. DABCO, DMAP and DBU were tested and afforded the desired product in 90–93% yield (Entries 6–8). In addition, when inorganic bases such as K<sub>2</sub>CO<sub>3</sub> and NaOH were used, the reactions were extremely sluggish with trace amounts of product formation (Entries 9 and 10). When the loading of Et<sub>3</sub>N was increased to 10 mol%, product **3aa** was obtained in 91% yield (Entry 11). Therefore, Et<sub>3</sub>N (5 mol%) as the catalyst and H<sub>2</sub>O as the solvent were the optimal conditions for

**Table 1**  
Reaction conditions screening.<sup>a</sup>

Entry	Catalyst	Solvent	Yield <b>3aa</b> (%) <sup>b</sup>
1	Et <sub>3</sub> N	CH <sub>2</sub> Cl <sub>2</sub>	82
2	Et <sub>3</sub> N	Toluene	65
3	Et <sub>3</sub> N	THF	78
4	Et <sub>3</sub> N	CH <sub>3</sub> CN	80
5	Et <sub>3</sub> N	H <sub>2</sub> O	95
6	DABCO	H <sub>2</sub> O	93
7	DMAP	H <sub>2</sub> O	92
8	DBU	H <sub>2</sub> O	90
9	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	Trace
10	NaOH	H <sub>2</sub> O	Trace
11 <sup>c</sup>	Et <sub>3</sub> N	H <sub>2</sub> O	91

<sup>a</sup> Reagents and conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (5 mol%), solvent (1.0 mL), rt, 2 h.

<sup>b</sup> Isolated yield.

<sup>c</sup> Catalyst (10 mol%).

the current transformation. Note, the structure of product **3aa** was identified by NMR spectroscopy and X-ray crystallographic analysis (Fig. 1) [22].

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