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PPh_3-Catalyzed [3 + 2] Spiroannulation of 1*C*,3*N*-Bisnucleophiles Derived from Secondary *β*-Ketoamides with *δ*-Acetoxy Allenoate: A Route to Functionalized Spiro *N*-Heterocyclic Derivatives

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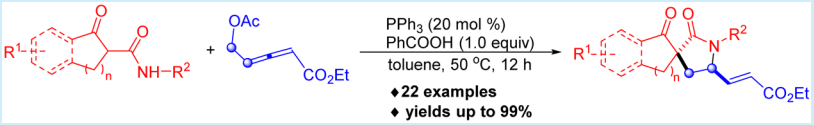
Supporting Information



ABSTRACT: A [3 + 2] annulation of *α*-substituted secondary *β*-ketoamides with *δ*-acetoxy-modified allenoate has been developed in the presence of phosphine catalyst. In this spiroannulation reaction, *β*-ketoamides were used as the bis-nucleophilic partner while the *γ*,*δ*-carbon of 5-acetoxypenta-2,3-dienoate participated as a C2 synthon, affording the desired functionalized five-membered *N*-heterocyclic derivatives in moderate to excellent yields and diastereoselectivities under mild conditions. Preliminary attempts on the asymmetric variant of this reaction have been also examined, giving the corresponding products with moderate ee values.

Five-membered *N*-heterocycles with quaternary stereocenters are valuable intermediates in organic synthesis, and they are also fundamental structural motifs in natural products and pharmaceuticals.[1] As its subunits, spirocyclic frameworks containing five-membered cyclic amides are frequently found in several biologically active molecules (Figure 1). Thus, the exploration of new synthetic approaches to directly construct this skeleton is highly desirable in the area of synthetic organic chemistry and medicinal chemistry.[2]

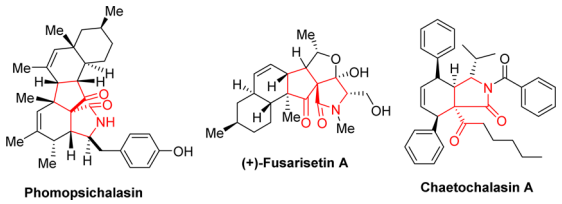
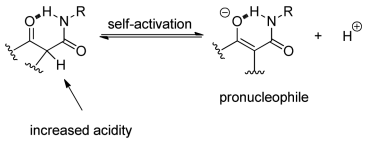


Figure 1. Selected examples of natural products with spiro-fused heterocyclic motifs.

The secondary *β*-ketoamide is one kind of 1,3-dicarbonyl compound and has been proven to be a promising class of pronucleophile for organocatalytic transformations such as Michael addition,[3] *α*-hydroxyamination,[4] *α*-arylation,[5] *α*-photoalkylation,[6] and spiroannulation.[7] The characteristic of secondary *β*-ketoamides is that they possess two distinct acidic protons, one is the C−H proton at *α*-position of dicarbonyl groups and another is the N−H proton at the secondary amide moiety (Scheme 1), the acidities of which can be regulated by modification of the electronic properties of the R substituent

Scheme 1. Characteristics of *β*-Ketoamides



on amide. Previous related reports revealed that the exceptional reactivity of these pronucleophiles is the consequence of self-activation, an intramolecular hydrogen bond between the acidic N−H proton and the ketone carbonyl group, and this hydrogen bond will increase the acidity of the *α*-proton in which the N−H proton is crucial to obtain high yields of nucleophilic addition products.[4]

During the past decades, the nucleophilic catalysis using allenoates as electrophilic reagents has emerged as a powerful synthetic tool to construct diversified carbo- and heterocycles.[8] Since the first example of phosphine-catalyzed annulation of unsubstituted butadienoate with electron-deficient olefins reported by Lu in 1995,[9] research on the potential reaction models based on different kinds of allenoates has been well-followed (Scheme 2). Typically, unsubstituted allenoates can

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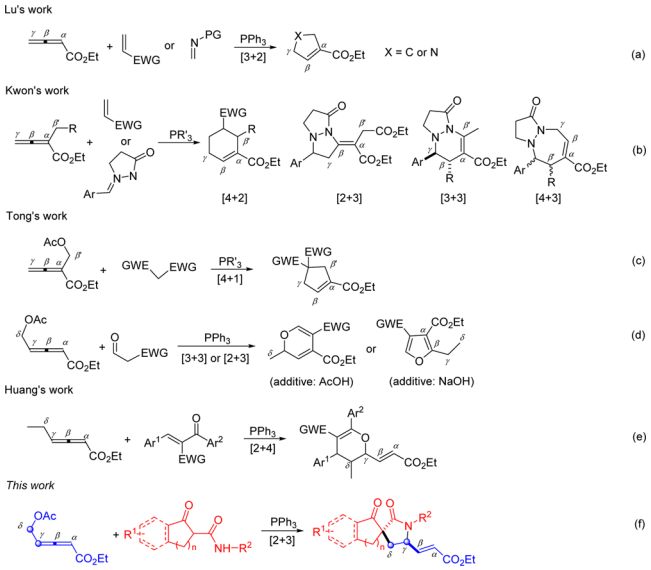
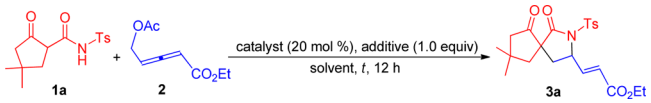
Scheme 2. Phosphine-Catalyzed Annulations Involved with Allenoates



offer their α,β,γ-olefinic carbons and function as one-, two-, or three-carbon synthons in the reactions with a variety of electrophilic coupling partners, undergoing [1 + 4],[10] [2 + 3],[11] and [3 + 2][12] annulations (Scheme 2, a). Other types of substituted allenoates and their reactiveness have also been extensively investigated. For example, the α,β,γ- and β'-carbons of α-substituted allenoates have been disclosed by Kwon and co-workers to play the role of two-[13] or three-[13c,14] or four-carbon[13c,15] synthons in the corresponding annulation cases (Scheme 2, b). Moreover, in 2010, Tong's group revealed that the installation of an acetate group at the β'-position of 2,3-butadienoate[16] could generate a novel [4 + 1][16a] annulation mode (Scheme 2, c). Successively, they also reported that δ-acetate modified allenoates could work as two- or three-carbon[17] units in producing the corresponding carbocycles (Scheme 2, d). Despite these significant achievements on the utilization of the internal C═C bond of allenoate in annulations, to the best of our knowledge, there are only scarce reports on phosphine-catalyzed annulations applying the δ-carbon to the formed cyclic motifs. In 2015, Huang's group reported a new strategy for which the δ-carbon atom of a γ-substituted allenoate[18] (Scheme 2, e) incorporated into a cyclic product as one of the endocyclic atoms through a reversible proton-transfer process between the zwitterionic intermediates.[18d] Herein, we wish to report the successful implementation of these tactics to provide a new pathway of phosphine-catalyzed [3 + 2] spiroannulation, using α-substituted secondary β-ketoamides **1** and the γ and δ sites of 5-acetoxypenta-2,3-dienoate **2** to selectively afford functionalized five-membered *N*-heterocyclic derivatives (Scheme 2, f).

On the basis of our previous work on nucleophilic phosphine catalysis, we initiated the investigation on the reaction of β-ketoamide **1a** and δ-acetoxy allenoate **2** in the presence of 20 mol % of PPh_3. A [3 + 2] annulation took place smoothly in toluene at 50 °C for 12 h, affording spiro-fused five-membered heterocyclic product **3a** in 37% isolated yield (Table 1, entry 1). Adding 1.0 equiv of Cs_2CO_3 did not improve the yield of **3a** (Table 1, entry 2). The examination of proton sources such as AcOH, H_2O, MeOH, and PhCOOH revealed that PhCOOH is the best additive, giving the desired product **3a** in 97% yield (Table 1, entries 3−6). Subsequently, various nucleophilic catalysts were

Table 1. Optimization of Reaction Conditions for the [3 + 2] Spiroannulation



entry[a]	cat. (mol %)	solvent	additive	temp (°C)	yield[b] (%)
1	PPh_3	toluene		50	37
2	PPh_3	toluene	Cs_2CO_3	50	28
3	PPh_3	toluene	AcOH	50	65
4	PPh_3	toluene	H_2O	50	65
5	PPh_3	toluene	MeOH	50	81
6	PPh_3	toluene	PhCOOH	50	97
7	DABCO	toluene	PhCOOH	50	33
8	DMAP	toluene	PhCOOH	50	52
9	$PMePh_2$	toluene	PhCOOH	50	82
10	PMe_2Ph	toluene	PhCOOH	50	78
11		toluene	PhCOOH	50	0
12	PPh_3	CH_3CN	PhCOOH	50	71
13	PPh_3	THF	PhCOOH	50	53
14	PPh_3	DCE	PhCOOH	50	66
15	PPh_3	toluene	PhCOOH	20	63

[a]All reactions were carried out with **1a** (0.1 mmol), **2** (0.2 mmol), catalyst (20 mol %), and PhCOOH (0.1 mmol) in solvent (3.0 mL) at 50 °C for 12 h. [b]Isolated yield by column chromatography; the diastereoisomers could not be separated by column chromatography.

examined, but no better result was obtained (Table 1, entries 7−10). The screening of solvent indicated that toluene was the optimal choice (Table 1, entries 12−14). Carrying out the reaction at room temperature did not favor the formation of **3a** (Table 1, entry 15). It should be noted that no reaction occurred in the absence of phosphine catalyst (Table 1, entry 11). Based on these experimental results, the best reaction condition was using PPh_3 (20 mol %) as catalyst, PhCOOH (1.0 equiv) as additive, and carrying out the reaction at 50 °C in toluene (3 mL) for 12 h.

With the optimized reaction conditions in hand, we then turned our attention toward the reaction scope and limitations, and the results are summarized in Scheme 3. All of the reactions proceeded smoothly under the optimal conditions, giving the desired products in moderate to high diastereoselectivities and excellent yields. Substrates **1b−d** having different ring sizes had little impact on the yield, but a larger cyclic ring resulted in lower dr value, giving the annulation products **3b**, **3c**, and **3d** in 94%, 95%, 99% yields along with 81:19, 70:30, and 60:40 dr values, respectively. As for substrates **1e−i** with different functional groups on the benzene ring of indanone and naphthalenone, the reactions also proceeded efficiently to afford the corresponding products **3e−i** in 87−99% yields along with 60:40−87:13 dr values. Gratifyingly, the reaction also tolerated straight chain β-ketoamide and heterocyclic aromatic ring. The use of **1j** and **1k** as substrates produced the desired products **3j** and **3k** in 99% yield along with 82:18 dr value and in 99% yield along with 88:12 dr value, respectively. The relative configuration of the major diastereoisomer of (*E*)-**3a** has been assigned by X-ray diffraction. Their ORTEP drawings and the CIF data are presented in the Supporting Information.

Using δ-acetoxy allenoate **2** as the substrate, we next examined its reaction with β-ketoamides bearing a distinct substituent on the *N* atom to elucidate the effect of the protecting group R (Scheme 4). Whether R was an alkyl- or an arylsulfonyl group, the reaction proceeded smoothly to give the corresponding

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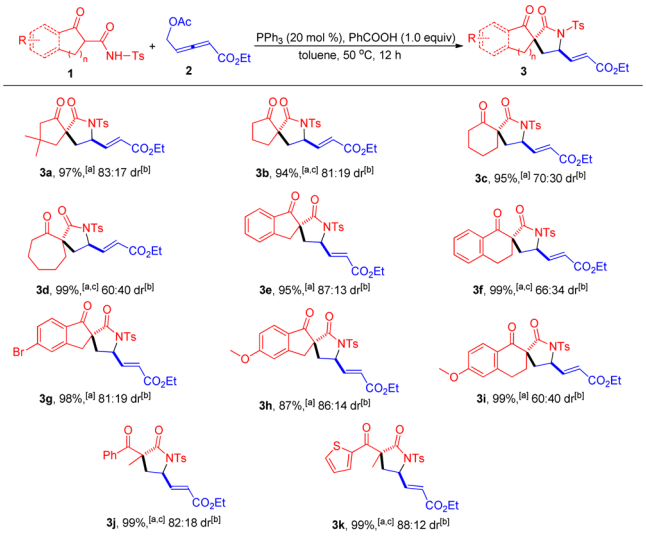
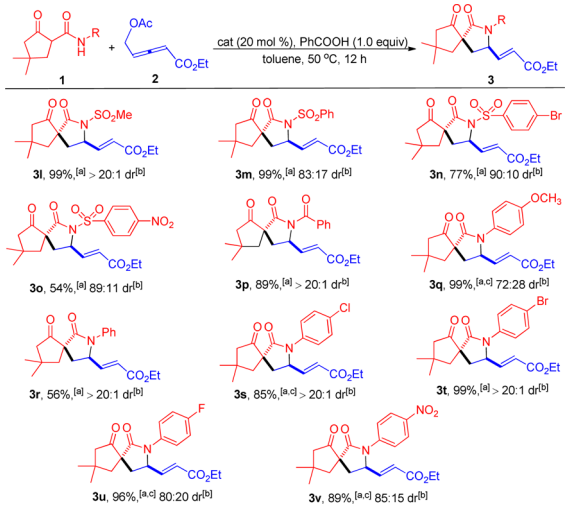
Scheme 3. Substrate Scope of the [3 + 2] Spiroannulation



[a]Isolated yield by column chromatography; the diastereoisomers could not be separated by column chromatography. [b]Determined by ^{1}H NMR spectroscopy of the isolated product. [c]The reaction was performed at 80 °C.

Scheme 4. Substrate Scope of β-Ketoamides with Different Functional Group at the N Atom

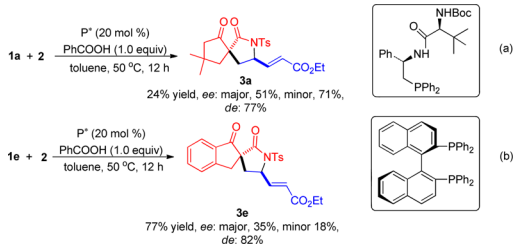


[a]Isolated yield by column chromatography; the diastereoisomers could not be separated by column chromatography. [b]Determined by ^{1}H NMR spectroscopy of the isolated product. [c]The reaction was performed at 80 °C.

annulation products **3l**–**o** in moderate to good yields (54–99%) with moderate to excellent dr values (83:17 to >20:1), respectively. Only in the case of **1o** was the adduct **3o** obtained in 54% yield along with 89:11 dr value, perhaps due to the strongly electron-withdrawing $-NO_2$ group. Substrate **1p** having a benzoyl amide group afforded the desired product **3p** in 89% yield and >20:1 dr value. To our delight, the reactions also tolerated substrates **1** with different aryl groups on the *N* atom, delivering the corresponding products **3q**–**w** in moderate to excellent yields (56–99%) and dr values (80:20 to >20:1). The structure of (*E*)-**3e** has also been assigned by X-ray diffraction.

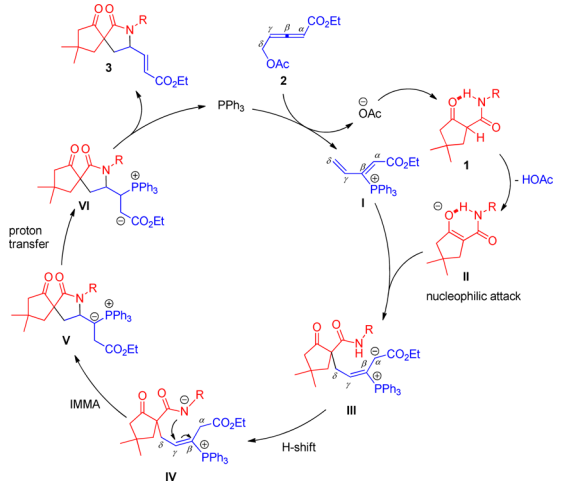
In view of the fact that chiral phosphines have been applied successfully in plenty of excellent asymmetric phosphine catalyzes, we extended our attention to explore the asymmetric variant of this [3 + 2] annulation of β-ketoamides with allenoate **2**. We found that the annulation catalyzed by chiral multifunctional phosphine derived from glycine produced **3a** in 24% yield and 51% ee of the major diastereoisomer along with 71% de. In addition, the use of chiral Binap in this annulation afforded **3e** in 77% yield and 35% ee of the major diastereoisomer along with 82% de (Scheme 5, see Schemes SI-I and SI-II for the more details).

Scheme 5. Chiral Phosphine-Catalyzed Asymmetric [3 + 2] Annulation of β-Ketoamides with Allenoate 2



According to our experimental results and the previously reported literature, a plausible mechanism for this [3 + 2] annulation has been outlined in Scheme 6. The reaction started

Scheme 6. Plausible Mechanism for the Formation of 3



with the formation of a zwitterionic intermediate **I**, generated by β-addition of phosphine into the allene moiety. Meanwhile, the detached acetate anion captured the α-proton of amide **1**, producing intermediate **II**, which underwent a nucleophilic attack onto the δ site of intermediate **I** to afford intermediate **III**. This intermediate could be transformed to intermediate **IV** via a proton shift from amide group. Then an intramolecular Michael addition (IMMA) took place to give another zwitterionic intermediate **V**, which underwent a [1,2]-proton transfer to afford intermediate **VI**. The elimination of phosphine furnished the final [3 + 2] annulation product **3**. Thus, we believe that the addition of PhCOOH may be beneficial to the two H-transfer processes.

In summary, we have disclosed a novel protocol of PPh_3-catalyzed [3 + 2] spiroannulation of 1*C*,3*N*-bisnucleophiles derived from α-substituted secondary β-ketoamides with δ-acetoxy-modified allenoate, giving the highly functionalized five-

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membered *N*-heterocyclic derivatives under mild conditions. A plausible mechanism has been proposed along with a preliminary asymmetric version. This finding provided a new way to synthesize a diversified spiro *N*-heterocycles from simple starting materials. Further investigations on an asymmetric version of this annulation and application of this new annulation reaction to the synthesis of biologically active substances are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00910.

Experimental procedure and characterization data for all compounds (PDF)
X-ray crystallographic data for **3a** (CIF)
X-ray crystallographic data for **3e** (CIF)

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Notes

The authors declare no competing financial interest.

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