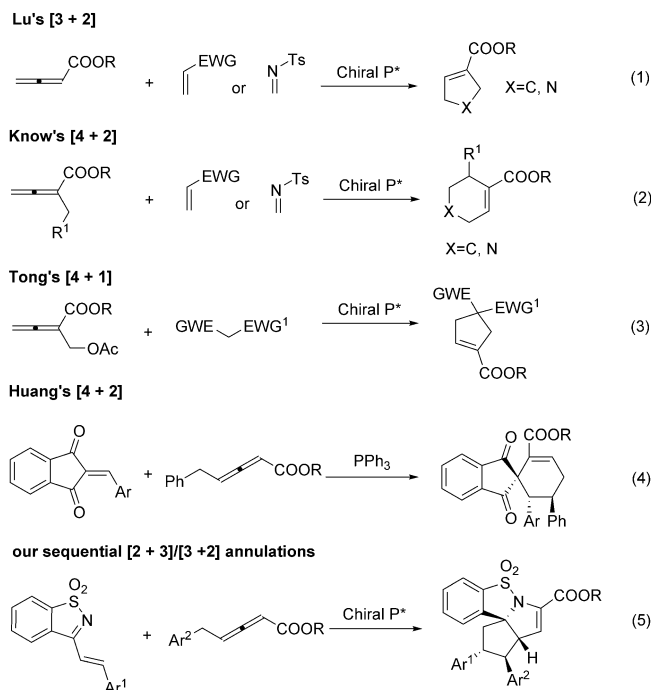# Bifunctional-Phosphine-Catalyzed Sequential Annulations of Allenoates and Ketimines: Construction of Functionalized Poly-heterocycle Rings

Erqing Li, Hongxing Jin, Penghao Jia, Xuelin Dong, and You Huang*

Abstract: *A highly stereoselective sequential annulation reaction between γ-substituted allenoates and ketimines was reported. By using bifunctional N-acyl aminophosphine catalysts, poly-heterocycle rings were obtained with high stereocontrol in good to excellent yields. The desired products have four contiguous stereogenic centers (one quaternary and three tertiary carbon centers), and only one isomer was obtained in all reactions.*

Sequential annulations are one of the most powerful methods for preparing structurally divergent polycyclic systems. Over the last decades, many chemists have devoted efforts to develop a highly efficient strategy to construct these polycyclic skeletons, which are widely found in natural products with significant biological properties.[1] In this field, the success is predominant at transition-metal-catalyzed intramolecular annulation reactions.[2] Nevertheless, such transition-metal-catalyzed reactions always rely on the use of non-commercially available or expensive ligands and has limited substrate scope, which severely restrict application in organic and pharmaceutical synthesis. Thus, developing a novel way to build the polycyclic systems in one step from readily available starting materials remains necessary.

Nucleophilic phosphine-catalyzed annulation reactions have been developed in laboratories worldwide.[3] Among them, Lu's [3+2] annulations demonstrated that phosphines are good catalysts for the construction of five-member carbocyclic and heterocyclic skeletons [Scheme 1, Eq. (1)].[4] Later, Kwon and co-workers developed the [4+2] annulations to build six-membered cyclic compounds [Scheme 1, Eq. (2)].[5] In 2010, Tong's group developed a [4+1] annulation reaction, which demonstrated that allenoates could work as 1,4-biselectrophiles and four-atom units [Scheme 1, Eq. (3)].[6] In 2013, Huang's group was first to develop phosphine-catalyzed [4+2] annulations with γ-benzyl allenoates [Scheme 1, Eq. (4)].[7] In 2003, Krische and co-workers developed the first intramolecular [3+2] annulations and applied it in total synthesis of (±)-Hirsutene.[8] Shortly

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Scheme 1. Phosphine-catalyzed domino annulation reaction of allenoates.

afterwards, phosphine-catalyzed intramolecular annulation reactions were developed by Tang, Kwon, and other groups.[9] Recently, our group developed a series of phosphine-catalyzed sequential annulation reactions to build the bicyclic compounds by intermolecular way.[10] No examples of asymmetric annulation reaction have been developed to build polycyclic compounds by intermolecular sequential annulations to date. This is because of the existence of some challenges: 1) Complex products are often formed in these reactions; 2) sequential chiral centers increase the difficulty in steric-control; and 3) multiple diastereoisomers are often obtained in these reactions. As part of our interest in asymmetric phosphine catalysis,[11] we aimed to design sequential annulation strategy for construction polycyclic compounds with high diastereoselectivity and enantioselectivity by selecting an appropriate chiral catalyst.
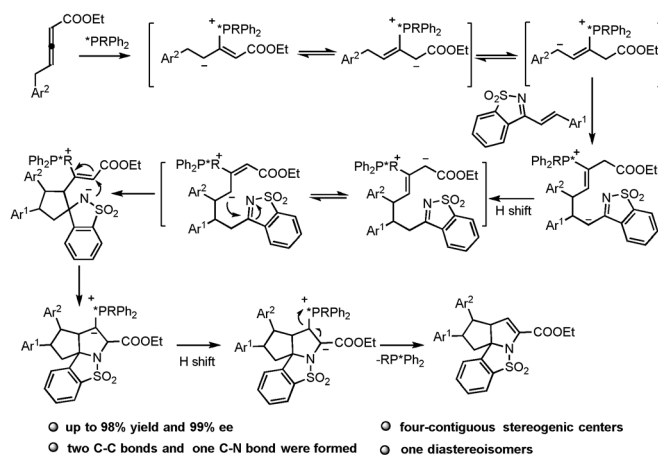
Poly-heterocyclic compounds containing dihydropyrrole skeleton represent an important structural motif featured in bioactive molecules and natural products.[12] For example, the alkaloid nakadomarin A,[1e–g,12c] the melodinus alkaloids isolated from either Apocynaceae or Kopsia species, Melo-

scine.[1h] Thus a lot of methods were developed to synthesize these compounds, including organic-catalyst-catalyzed annulation reactions.[13] To the best of our knowledge, synthesizing a chiral poly-heterocyclic skeleton through sequential annulation method by a chiral phosphine catalyst has been rarely reported.[14] Given the importance of these molecules, we designed chiral-phosphine-catalyzed sequential [2+3]/[3+2] annulation reaction between γ-benzyl allenoates and ketimines derived from saccharin. We envisaged that by the introduction of phenyl to allenoates could stabilize γ-methyene anion of allenoates, the normal Lu [3+2] reaction could be prevented. On the other hand, allenoates has multiple reactive sites. However, from previous experience, only two sites of allenoates could take part in the formation of chemical bonds in one reaction. We envisaged that more sites of allenates could take part in the formation of bonds by using suitable electrophilic reagent. In our previous work, γ-methyl substitution of allenoates could take part in the formation of chemical bonds with salicyl *N*-thiophosphinyl imines as the C2 synthon.[15] We wondered whether another nucleophilic addition could take place by using ketimines derived from saccharin after the first [2+3] cyclizations instead of normally regenerating catalyst to obtain products (Scheme 2). Herein,

○ up to 98% yield and 99% ee　　○ four-contiguous stereogenic centers
○ two C-C bonds and one C-N bond were formed　　○ one diastereoisomers

Scheme 2. Strategies for sequential annulations.

we document a novel phosphine-catalyzed sequential [2+3]/[3+2] annulation reaction between γ-benzyl substituted allenoates and ketimines derived from saccharin, leading to highly enantioselective construction of cyclopenta-[*b*]dihydropyrrole architectures. In this reaction, we successfully solved the problem of diastereoselectivity and stereoselectivity in this reaction, obtaining a series of poly-heterocyclic skeletons including four contiguous stereogenic centers with high diastereoselectivity and stereoselectivity.

Based on our previous work, we initiated the study by investigating the reaction between the 1-azadiene **1a** and γ-benzyl allenoates **2a** by using triphenylphosphine as the catalysts. To our delight, the reaction proceeded smoothly in chloroform at room temperature (Table 1, entry 1). The chiral phosphine **4a** derived from L-phenylalanine[16] as catalyst was used in the reaction, and the desired product **3a** was obtained

Table 1: Screening of catalysts and optimization of the reaction conditions.[a]
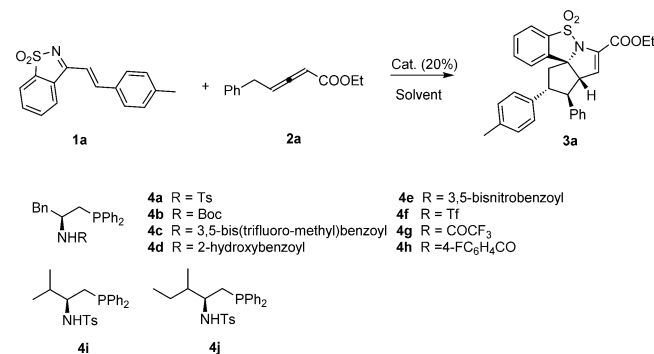
| Entry	Cat. [%]	Solvent	T [h]	Yield [%][b]	ee [%][c]
1	PPh₃	CHCl₃	1	82	–
2	**4a** (20)	CHCl₃	9	74	85
3[d]	**4a** (20)	CHCl₃	144	74	86
4	**4a** (20)	toluene	144	80	66
5	**4a** (20)	CH₂Cl₂	5	76	46
6	**4a** (20)	THF	3	99	51
7	**4a** (20)	CH₃CN	5	74	54.5
8	**4a** (20)	(CH₂Cl)₂	72	45	60
9	**4b** (20)	CHCl₃	9	57	59
10	**4c** (20)	CHCl₃	96	47	72
11	**4d** (20)	CHCl₃	22	78	50
12	**4e** (20)	CHCl₃	4	91	89
13	**4f** (20)	CHCl₃	96	trace	–
14	**4g (20)**	**CHCl₃**	**4**	**80**	**92.5**
15	**4h** (20)	CHCl₃	36	26	45
16	**4i** (20)	CHCl₃	3	66	−54
17	**4j** (20)	CHCl₃	4	83	48
18[e]	**4a** (20)	CHCl₃	9d	–	–
19	**4a** (10)	CHCl₃	9d	–	–

[a] All reactions were carried out using 0.05 mmol in a solvent (0.5 mL) at RT unless otherwise noted. The ratio of **1a**:**2a** was 1:2. [b] Yields of isolated products; no other isomers were detected by ¹H NMR.
[c] Determined by HPLC analysis on a chiral stationary phase. [d] Reaction at 0°C. [e] PhCOOH (20%) was added.

in 74% yield and 85% *ee* (Table 1, entry 2). Encouraged by this result, we screened various solvents and found that chloroform was the best solvent (Table 1, entries 3–8). Lowering the reaction temperature to 0°C, no better result was received (Table 1, entry 3). To optimize the reaction conditions, a series of chiral catalysts derived from α-amino acids were used, and the application of catalyst **4g** gave both high *ee* values (92.5%) and yield (80%; Table 1, entries 14 vs. 9–13, 15–17). Catalyst **4f** with the most acidic NH-functional group gave no desired product (Table 1, entry 13). Further studies suggested that adding the additive (PhCO₂H,) or decreasing the amount of catalysts inhibited the reaction (Table 1, entries 18, 19). It should be addressed that the sequential annulation reaction was completely regioselective and highly diastereoselective (only one isomer was detected in all reactions).

Having established the optimal conditions, we were first to explore the generality of this reaction with a variety of γ-substituted allenoates, and the results are shown in Table 2. The reaction was tolerant of a broad range of allenoates

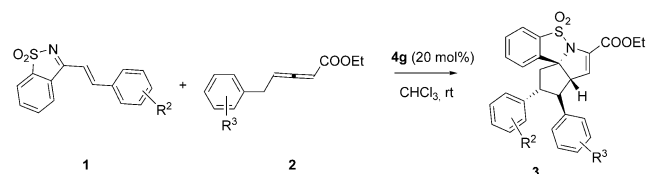**Table 2:** Enantioselective [2+3]/ [3+2] cycloadditions of γ-substituted allenoates **2** and ketimine **1a**.[a]
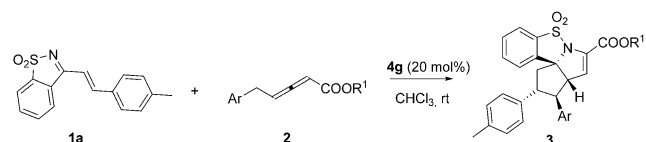
Entry	Ar	R^1	T [h]	Yield [%][b]	ee [%][c]
1	C$_6$H$_5$	Et	4	80	92.5
2	C$_6$H$_5$	Bn	18	59	91
3	4-MeC$_6$H$_4$	Et	4	98	90
4	4-OMeC$_6$H$_4$	Et	4	85	93
5	4-ClC$_6$H$_4$	Et	2	89	97
6	3-FC$_6$H$_4$	Et	4	70	88
7	3-OMeC$_6$H$_4$	Et	2	98	82
8	5-piperonyl	Et	4	95	81
9	2-MeC$_6$H$_4$	Et	24	73	87
10	2-FC$_6$H$_4$	Et	24	98	90
11	1-naphthyl	Et	4	93	90
12	2-naphthyl	Et	2	97	88

[a] All reactions were carried out using 0.05 mmol in a solvent (0.5 mL) at RT unless otherwise noted. The ratio of **1a**:**2a** was 1:2. [b] Yields of isolated products; no other isomers were detected by ^{1}H NMR. [c] Determined by HPLC analysis on a chiral stationary phase.

Table 3: Enantioselective [2+3]/ [3+2] cycloadditions of γ-substituted allenoates **2** and ketimine **1**.[a]

Entry	R^2	R^3	T [h]	Yield [%][b]	ee [%][c]
1	4-CN	H	4	85	99
2	2-Me	H	4	91	94
3	5-piperonyl	H	4	57	88
4	4-F	4-Cl	4	67	90
5	4-Cl	4-Cl	4	98	89
6	2.4-Cl$_2$	4-Cl	4	78	87
7	3,4-Me$_2$	4-Cl	4	90	96
8	3-Me	4-Cl	4	49	91
9	2-Br	4-Cl	4	66	90
10	2-F	4-Cl	4	51	84
11	2-Me	4-Cl	4	98	92
12	5-piperonyl	4-Cl	4	60	86
13	1-naphthyl	4-Cl	4	91	98
14	2-naphthyl	4-Cl	4	86	90
15	2-thienyl	4-Cl	4	48	92
16	2-furyl	4-Cl	4	90	90
17	4-CN	4-Cl	4	85	83
18	1-naphthyl	4-CN	4	53	91

[a] All reactions were carried out using 0.05 mmol in a solvent (0.5 mL) at RT unless otherwise noted. The ratio of **1a**:**2a** was 1:2. [b] Yields of isolated products; no other isomers were detected by ^{1}H NMR. [c] Determined by HPLC analysis on a chiral stationary phase.

derived from 3-aryl propionyl chloride, and those with either electron-withdrawing or electron-donating groups on an aromatic ring moiety resulted in high yields and *ee* values (Table 2). Allenoates with electron-withdrawing groups (such as 4-Cl, 3-F, 2-F) on the phenyl ring exhibited higher enantioselectivity (Table 2, entries 5, 6, 10), with 5-(4-chlorophenyl)penta-2, 3-dienoates giving highest enantioselectivity (table 2, entry 5). In contrast, strong electron-donating (5-(benzo[*d*][1,3]dioxol-5-yl)penta-2, 3-dienoate) lowered the enantioselectivity to 81% *ee* (Table 2, entry 8). The steric properties of the γ-benzyl allenoates **2** have a slight effect on the reaction, and reaction of benzyl 5-phenylpenta-2,3-dienoate gave similar enantioselectivity, albeit with lower yield (Table 2, entry 2). However, the positions of substituent at the aromatic ring have certain influence, and substituents at the *meta*-position resulted in low *ee* values (Table 2, entries 6–8). Furthermore, 1-naphthyl and 2-naphthyl allenoates also showed very high enantioselectivity (Table 2, entries 11, 12).

Next, we examined the scopes of the sequential annulation reaction with a series of 1-azadiene, and the results are shown in Table 3. The reactions were applicable to a wide range of ketimines bearing different aromatic groups, regardless of the steric and electronic properties of the substituents on the aromatic ring (Table 3, entries 1–13). Furthermore, a lower yield was obtained when the *meta*-substituent group was employed (Table 3, entry 8). 1-Naphthyl, 2-naphthyl, 2-furyl, and 2-thiophenyl-containing substrates were also examined, and the reaction could proceed smoothly to receive the desired products with high stereoselectivity (Table 3, entries 14–17). It should be noted that only one isomer was produced in all these reactions. The structure and stereochemistry of **3** were determined using a combination of NMR spectroscopy, HPLC, HRMS, and single-crystal X-ray analysis (**3a**).[17]

In summary, we have developed a novel chiral phosphine-catalyzed sequential annulation reaction between γ-benzyl allenoates and ketimines derived from saccharin. Highly stereoselectivity and yields could be obtained in most cases (up to 99% *ee* and up to 98% yield). It should be noted that we are first to report an asymmetrical intermolecular method to obtain poly-heterocyclic products by using chiral phosphine catalyst and the desired products gave four-contiguous stereogenic centers (one quaternary and three tertiary carbon), and only one isomer was obtained in all reactions. We are currently investigating the asymmetric synthesis of other heteroatom-containing ring systems by extending the strategy developed herein.

Experimental Section

Compound **1** (0.05 mmol) and **2** (0.1 mmol) in 0.5 mL CHCl$_3$ were added to a dry flask filled with nitrogen. Chiral bifunctional catalyst **4g** (0.01 mmol) was added. This solution was stirred at room temperature until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel column (60–120 mesh) using 10:1 petroleum ether–ethyl acetate solvent mixture as eluent to afford **3**.

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[17] CCDC 1431011 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
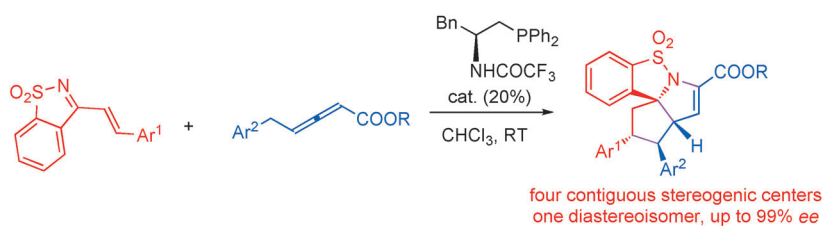
Communications

Organocatalysis

E. Li, H. Jin, P. Jia, X. Dong,
Y. Huang* ——————— ▪▪▪▪–▪▪▪▪

Bifunctional-Phosphine-Catalyzed
Sequential Annulations of Allenoates and
Ketimines: Construction of
Functionalized Poly-heterocycle Rings

four contiguous stereogenic centers
one diastereoisomer, up to 99% *ee*

A highly stereoselective sequential annulation reaction between γ-substituted allenoates and ketimines is presented. Using bifunctional *N*-acyl aminophosphine catalysts, poly-heterocycle rings were obtained in good to excellent yields. The desired products have four contiguous stereogenic centers (one quaternary and three tertiary carbon centers), and only one isomer was obtained in all reactions.