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Asymmetric Allylation/Retro-Claisen Cascade Reaction of 1,3-Diketones and 1-Hydroxyallylphenols/Aniline Catalyzed by an Iridium Complex

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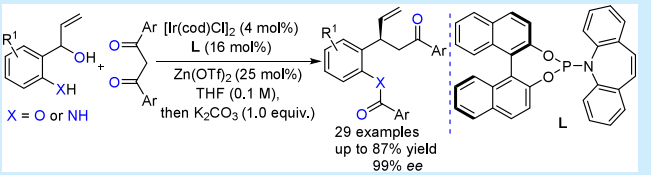
ABSTRACT: An asymmetric allylation/retro-Claisen cascade reaction of 1-hydroxyallylphenols/aniline with 1,3-diarylketones has been developed, and a series of chiral γ,δ-unsaturated 1,3-diaryl ketones could be produced in good to excellent yields (up to 87%) with outstanding enantioselectivities (up to 99% ee), thus providing convenient access to the synthesis of (−)-sugiresinol and calyxolane A analogues. Transformations of these chiral γ,δ-unsaturated 1,3-diaryl ketones into other derivatives have also been explored.



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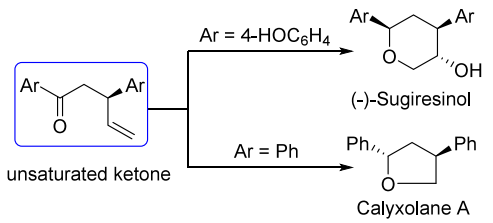
The chiral γ,δ-unsaturated 1,3-diaryl ketone substructure has been prevalent in bioactive natural products and pharmaceutical agents,[1] which also act as key synthetic building blocks employed in the concise enantioselective total synthesis of natural products (−)-sugiresinol[2] and calyxolane A[3] and their derivatives (Scheme 1). Given the

Scheme 1. Application of γ,δ-Unsaturated 1,3-Diaryl Ketones in the Synthesis of Natural Products



significance of the chiral γ,δ-unsaturated 1,3-diaryl ketones, a great deal of effort has been devoted to the development of methods for their preparation.[4−6] Those enantioselective methods mainly include (1) allylic alkylation of protected allylic alcohols with acyclic ketone enolates or enamines,[4] (2) decarboxylative allylic alkylation of allyl β-ketocarboxylates or β-ketoacids with allenes or alkynes,[5] and (3) asymmetric conjugate addition of vinyl metal salts to chalcone and others.[6]

1,3-Dicarbonyl compounds represent a privileged class of multipurpose synthons in organic chemistry, especially employed as nucleophiles in the form of an anion or an enol tautomer, and are applied in various carbon−carbon bond-forming reactions.[7,8] Among those reactions, the asymmetric allylic alkylation/retro-Claisen[8] cascade reactions have attracted the attention of synthetic chemists, and significant advances have been made. The method of allylation/ring expansion of 2-(1-hydroxyallyl)phenols[9] and cyclobutanone carboxamides has been developed to realize the synthesis of chiral medium-sized lactams or lactones (Scheme 2a).[7d] Asymmetric allylation/retro-Claisen cascade reaction of β-diketones with vinylethylene carbonate (VEC) has been achieved to access the key structural cores of the 3-hydroxymethyl pentenone unit (Scheme 2a).[7f]

Inspired by those prominent works[7d−f] and the reactivity of 1,3-diaryl ketones and 2-(1-hydroxyallyl)phenols, we surmised that if the asymmetric allylation/retro-Claisen cascade reaction between substituent 2-(1-hydroxyallyl)phenols and 1,3-diaryl ketones could be realized, and a series of chiral γ,δ-unsaturated 1,3-diaryl ketones with various structures could be available, thus making the synthesis of (−)-sugiresinol and calyxolane A analogues convenient. However, this envisioned asymmetric tandem reaction may encounter challenges. (1) The retro-Claisen reaction may be interrupted by intramolecular cyclization, yielding a hemiketal byproduct. (2) The failure of the retro-Claisen pathway could lead to dehydration of benzopyran derivatives as side products.

Here, we report the asymmetric allylation/retro-Claisen cascade reaction between substituent 2-(1-hydroxyallyl)-phenols/aniline and 1,3-diaryl ketones (Scheme 2b).

The reaction of 2-(1-hydroxyallyl)phenol **1a** and 1,3-diketone **2a** was selected as a model reaction (Table 1). After initial exploration in the presence of $[Ir(cod)Cl]_2$/**L1** and Lewis acid $Zn(OTf)_2$, the desired tandem reaction proceeded

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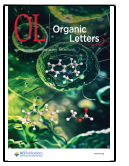

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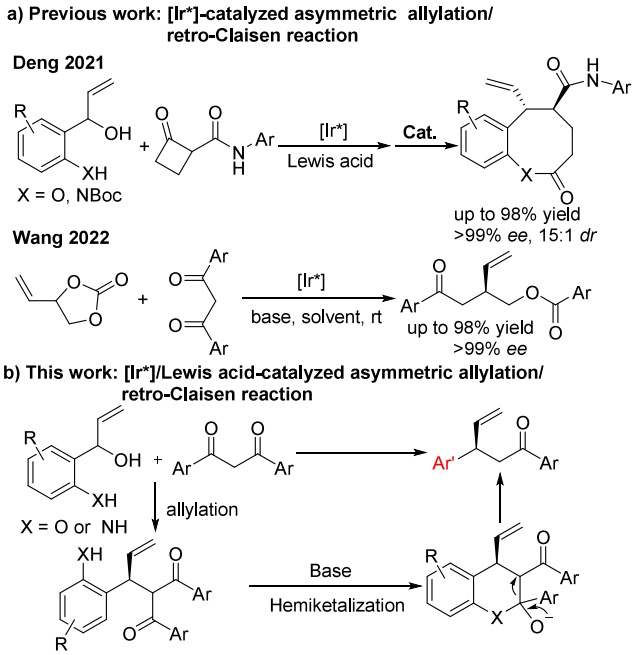
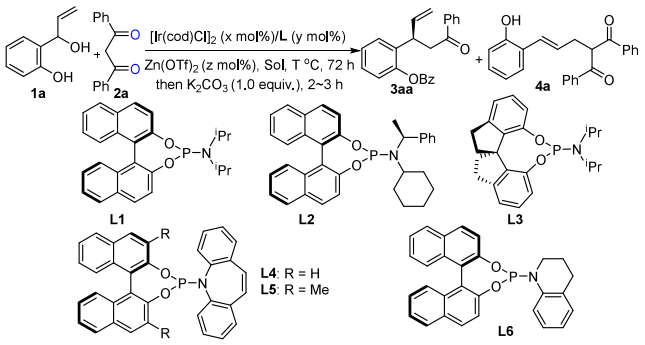
Scheme 2. Asymmetric Allylation/Retro-Claisen Cascade Reactions Involving 1,3-Dicarbonyl Compounds



smoothly to afford racemic product **3aa** in 25% yield (Table 1, entry 1). Along with the desired product **3aa**, the allylic substituent that was placed at the terminus of the allyl to form linear byproduct **4a** was also observed in 25% yield. In order to realize the stereoselectivity and control the amount of the byproduct, a series of ligands were screened (Table 1, entries 2−6). To our delight, when Carreira's ligand (*R*)-**L4**[10] was employed, target product **3aa** was afforded in up to 70% yield in 72% ee and gave only **4a** in 14% yield (Table 1, entry 4). Other ligands were also investigated, and no better performance was observed than that of **L4** (see the Supporting Information). The effect of the solvent on the reaction was evaluated (Table 1, entries 4, 7, and 8, and the Supporting Informationb), and it was demonstrated that THF was the best choice considering both the yield (85% yield) and the enantioselectivity (96% ee) (Table 1, entry 8). The effect of the ratio of central metal $[Ir(cod)Cl]_2$ to chiral ligand **L4** on the reaction was also studied (Table 1, entries 8−10), and the best result was observed when at a 1:4 ratio (Table 1, entry 8). Catalyst loading optimization demonstrated that the combination of 4 mol % $[Ir(cod)Cl]_2$ and 16 mol % ligand has shown the best catalytic efficiency (Table 1, entries 8 and 10−13). Other reaction parameters, including the amount of Lewis acid $Zn(OTf)_2$, the **1a**:**2a** ratio, the reaction concentration (Table 1, entries 17−20), and the reaction temperature (see the Supporting Information), were also investigated. The optimal reaction conditions were identified as the catalysis of $[Ir(cod)Cl]_2$ (4 mol %)/**L4** (16 mol %) and $Zn(OTf)_2$ (25 mol %) at a 2.5:1 **1a**:**2a** ratio with a THF as the solvent (0.1 mol/L) at −10 °C.

With the optimal conditions in hand, the accommodation of the 2-(1-hydroxyallyl)phenol substrate scope was evaluated (Scheme 3). When position 4 of the phenyl ring was with populated with Me, F, Cl, and Br substituents, the reaction proceeded smoothly and gave the desired products in moderate to good yields (48−84%) with good to excellent enantioselectivities (85−96% ee) (**3ba**−**3ea**, respectively).

Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	L	*x*/*y*	yield of **3aa** (%)[b]	ee (%)[c]	yield of **4a** (%)[b]
1	DCM	**L1**	4/16	25	0	25
2	DCM	**L2**	4/16	46	<5	19
3	DCM	**L3**	4/16	33	0	65
4	DCM	**L4**	4/16	70	72	14
5	DCM	**L5**	4/16	73	40	25
6	DCM	**L6**	4/16	40	<5	44
7	toluene	**L4**	4/16	90	84	<5
8	THF	**L4**	4/16	85	96	<5
9	THF	**L4**	4/12	76	90	23
10	THF	**L4**	4/20	73	86	25
11	THF	**L4**	2/8	55	71	35
12	THF	**L4**	3/12	70	88	25
13	THF	**L4**	5/20	85	96	10
14[d]	THF	**L4**	4/16	69	93	30
15[e]	THF	**L4**	4/16	84	94	12
16[f]	THF	**L4**	4/16	74	70	24
17[g]	THF	**L4**	4/16	22	83	<5
18[h]	THF	**L4**	4/16	79	96	<5
19[i]	THF	**L4**	4/16	76	89	<5
20[j]	THF	**L4**	4/16	54	91	<5

[a]The reactions were performed, unless indicated otherwise, on a 0.1 mmol scale using 0.1 mmol of **2a**, 0.25 mmol of **1a**, 4 mol % $[Ir(COD)Cl]_2$, 16 mol % **L4**, and 25 mol % $Zn(OTf)_2$ in 1.0 mL of a solvent at −10 °C for 72 h and then 1.0 equiv of K_2CO_3 for 2−3 h. [b]Isolated yields. [c]The ee value was determined by chiral HPLC analysis. [d]With 15 mol % $Zn(OTf)_2$. [e]With 20 mol % $Zn(OTf)_2$. [f]With 30 mol % $Zn(OTf)_2$. [g]With 1.0 equiv of **1a**. [h]With 2.0 equiv of **1a**. [i]With 0.5 mL of a solvent. [j]With 2.0 mL of a solvent.

When the Me was at position 3 or 5, the yield and enantioselectivity increased greatly (**3fa** or **3ga**, respectively). The same tendency was observed when substituent F shifts from position 4 to position 5 (**3ha**). On the contrary, the yield and enantioselectivity decreased when the Br was moved from position 4 to position 5 (**3ja**). Notably, the reaction of the 3,5-dihalogenated substrate proceeded smoothly to furnish **3ka** in moderate yield and good enantioselectivity. Upon introduction of a methyl group at the end of allyl to elongate the carbon chain, the reaction proceeded well to afford product **3la** in 49% yield with 87% ee. Most remarkably, the reaction was also suitable for 2-(1-hydroxyallyl)aniline, delivering allylation/retro-Claisen product **3ma** in 87% yield with excellent enantioselectivity (up to 97% ee).

The effect of the 1,3-diketones on the reaction has also been investigated and demonstrated that the reaction accommodated a broad range of substrates (Scheme 4). When the phenyl ring of the ketones was an electron-donating or electron-withdrawing substituent at the *para* position, the

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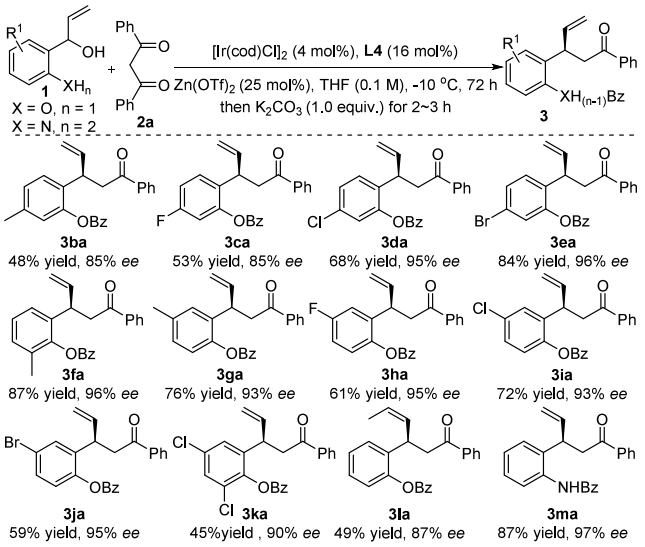
Scheme 3. 2-(1-Hydroxyallyl)phenol/Aniline Scope for the Reaction[a−c]

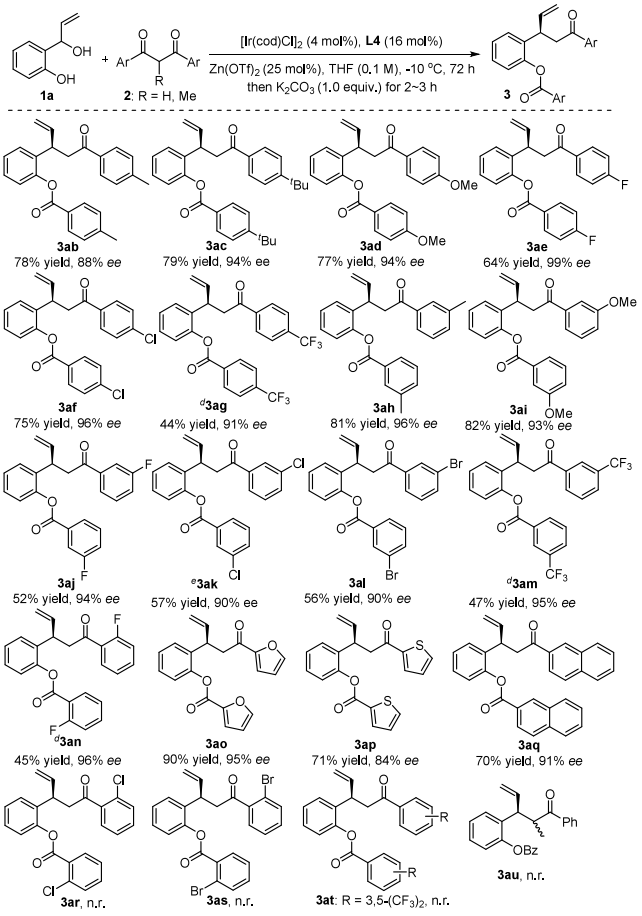


[a]The reactions were performed, unless indicated otherwise, on a 0.1 mmol scale using 0.1 mmol of **2a**, 0.25 mmol of **1a**, 4 mol % $[Ir(cod)Cl]_2$, 16 mol % **L4**, 25 mol % $Zn(OTf)_2$, and 1.0 mL of a solvent at −10 °C for 72 h and then 1.0 equiv of K_2CO_3 for 2−3 h. [b]Isolated yields. [c]The ee value was determined by chiral HPLC analysis.

reaction proceeded smoothly and afforded the desired products (**3ab**−**3af**) in good to excellent yields (64−79%) and excellent enantioselectivity (88−99% ee). However, introducing a strongly electron-withdrawing group (-CF_3) at the *para* position drastically reduced the reactivity, affording **3ag** in 44% yield, while maintaining excellent enantioselectivity (91% ee). When electron-donating groups moved from the *para* to *meta* position, the reactivity increased with almost better enantioselectivity (**3ah** and **3ai**). Relocation of electron-withdrawing groups (F and Cl) from the *para* to *meta* position resulted in marginally lower yields and enantioselectivities (**3aj** and **3ak**, respectively). In contrast, CF_3 at the *meta* position enhanced the yield slightly to 47% while maintaining good enantioselectivity (95% ee, **3am**). The substrate scope was further extended to heteroaromatic systems. Both thiophene- and furan-derived diketones (**3ao** and **3ap**, respectively) worked well and delivered the product in high yields with good enantioselectivities. 1,3-Di(naphthalen-1-yl)propane-1,3-dione was also suitable for this reaction, providing product **3aq** in 70% yield with 91% ee. Regretfully, when the substituent at the *ortho* position of the phenyl ring or with two strong electron-withdrawing substituents (-CF_3) at positions 3 and 5, the reaction did not take place, and no desired product (**3ar**, **3as**, or **3at**) was observed. When α-methyl-substituted 1,3-diketone **2u** was employed as the substrate, the reaction failed to proceed, which may be ascribed to steric hindrance.

To demonstrate the synthetic application of this method (Scheme 5), the reaction was scaled up to 2 mmol, which proceeded smoothly and provided product **3aa** in 75% yield with excellent enantioselectivity (96% ee) (Scheme 5a). **3aa** was treated with benzyl trimethylammonium hydroxide (Triton-B) to remove the benzoyl, followed by methylation of the phenolic hydroxyl group with MeI, which furnished ether product **5** in 69% yield with 94% ee (Scheme 5b). Hydrogenation of the double bond of **3aa** in the catalysis of

Scheme 4. Diarylketone Scope for the Reaction[a−c]



[a]The reactions were performed, unless indicated otherwise, on a 0.1 mmol scale using 0.1 mmol of **2a**, 0.25 mmol of **1a**, 4 mol % $[Ir(cod)Cl]_2$, 16 mol % **L4**, 25 mol % $Zn(OTf)_2$, and 1.0 mL of a solvent at −10 °C for 72 h and then 1.0 equiv of K_2CO_3 for 2−3 h. [b]Isolated yields. [c]The ee value was determined by chiral HPLC analysis. [d]At rt for 72 h. [e]At 0 °C for 72 h

Pd/C resulted in compound **6** in 79% yield and 98% ee. Reduction of the carbonyl group with $NaBH_4$ afforded alcohol **7** in 86% yield with 98% ee and 3:1 dr. Reaction with DNPH led to hydrazone **8** in 79% yield with 98% ee.

Crossover experiments between **1a** and **2a** and between **1a** and **2o** afforded expected products **3aa** and **3ao**, respectively, in good yields (73−89%) with consistently high enantioselectivity (93−95% ee), while no intermolecular crossover products (**9** or **10**) were detected in the system (Scheme 5c). These experimental results demonstrated that this allylation/retro-Claisen cascade reaction proceeded in an intramolecular manner. The absolute configuration of **5** was confirmed to be *R* by comparing its specific rotation with the reported value.[4c] Thus, the configurations of other products **3** are deduced by analogy.

A possible catalytic cycle for the formation of **3aa** was proposed (Scheme 6).[9a] The catalytically active iridium(I) species was formed *in situ* through ligand−metal coordination oxidative addition with **1a** with the assistance of Lewis acid, which generates key π-allyliridium intermediate **A**. The enol tautomer of dibenzoylmethane (**2a**) underwent an allylic alkylation reaction with intermediate **A** to form adduct **B** and regenerate the catalyst. In the presence of K_2CO_3, *in situ*-

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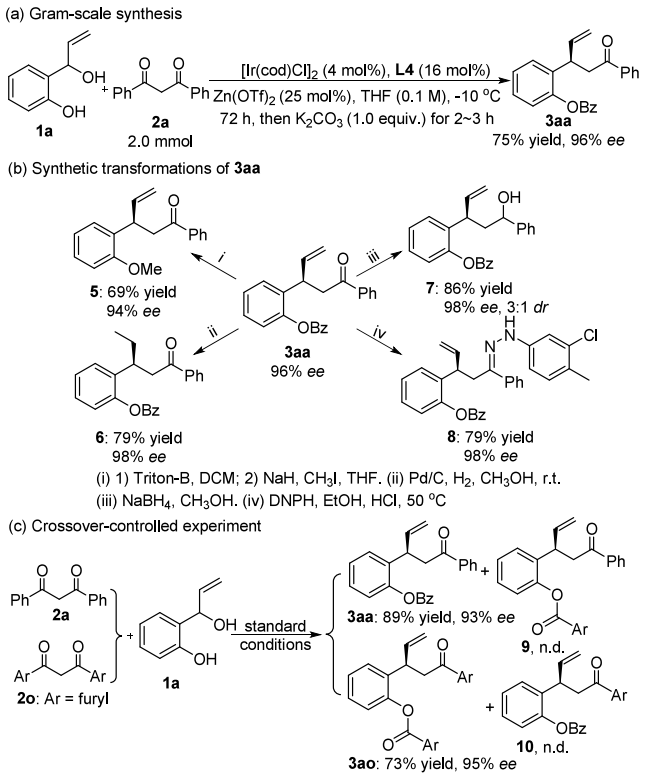
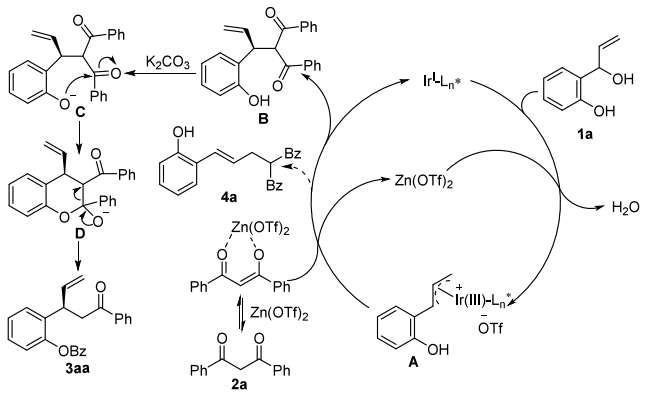
Scheme 5. Scale-up, Transformation Reactions, and Control Experiments



Scheme 6. Proposed Mechanism



formed phenolic anion **C** attacked the carbonyl group, triggering intramolecular hemiketalization to afford intermediate **D**, which then underwent a retro-Claisen reaction to afford product **3aa**.

In summary, an asymmetric allylation/retro-Claisen cascade reaction of 2-(1-hydroxyallyl)phenols/aniline and 1,3-diarylketones has been established, which enables the efficient construction of a series of chiral γ,δ-unsaturated 1,3-diaryl ketones and makes the synthesis of (−)-sugiresinol and calyxolane A analogues convenient.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c04493.

Experimental procedures and detailed characterization data of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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