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Ir/Zn Dual Catalysis: Enantioselective and Diastereodivergent α-Allylation of Unprotected α-Hydroxy Indanones

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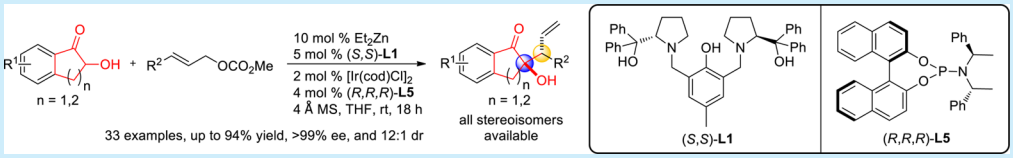
Supporting Information



ABSTRACT: A one-step enantioselective and diastereodivergent α-allylation of unprotected α-hydroxy indanones has been developed using an Ir/Zn dual catalyst system; no additional base is required. The cyclic tertiary α-hydroxyketones containing vicinal stereocenters can be synthesized with excellent enantioselectivity (up to >99% ee) and good diastereoselectivity (up to 12:1 dr). By a simple choice of the appropriate chiral metal catalyst combination, all four product stereoisomers could be obtained from the same starting materials and under identical conditions.

Cyclic α-hydroxyketones containing chiral tetrasubstituted stereocenters are significant structural motifs found in numerous bioactive natural products and potent medicines,[1] such as Syagrusin **1**,[1c] Asterogynin **2**,[1d] and MMP-9 inhibitor **3** (Figure 1).[1g] Accordingly, considerable efforts have been directed to their

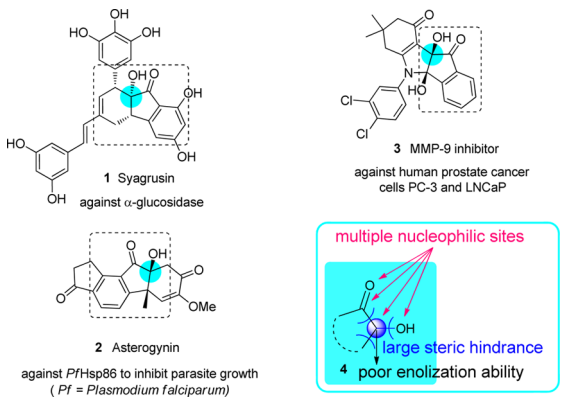
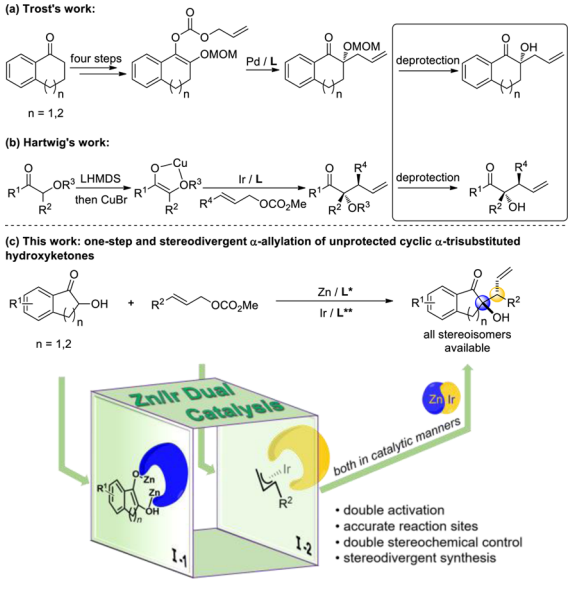


Figure 1. Representative examples of cyclic tertiary α-hydroxyketones and challenging nucleophiles.

stereoselective preparation, and a number of useful methodologies have been developed.[2] However, the preparation of optically active cyclic tertiary α-hydroxyketones from the unprotected cyclic α-trisubstituted hydroxyketones **4** remains to be exploited due to steric hindrance, multiple nucleophilic sites, and difficulty of the substrate to undergo enolization,[3] even though these types of substrates can be prepared with ease.[4]

Transition-metal-catalyzed asymmetric allylic alkylation (AAA) has become one of the most powerful methods for the construction of C−C bonds;[5] therefore, AAA of cyclic α-hydroxyketones is expected to provide access to tertiary α-hydroxyketones. In recent years, the Trost group has reported the synthesis of optically active tertiary α-hydroxyketones via a palladium-catalyzed decarboxylative asymmetric allylic alkylation from protected 1,2-endiol carbonates, which were synthesized in four steps (Scheme 1a).[6] To obtain the vicinal chiral stereocenters, Ir-catalyzed AAA of prochiral nucleophiles provides an effective and reliable method.[7,8] Accordingly, the Hartwig group reported Ir-catalyzed asymmetry allylic substitutions of acyclic α-alkoxy ketones over two successive steps using an equivalent of

Scheme 1. Synthesis of Tertiary α-Hydroxyketones via Asymmetric Allylic Alkylation



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the strong base LHMDS and an equivalent of CuBr as an additive (Scheme 1b).[7g] In order to provide the free tertiary alcohol, the products of both of the aforementioned reactions require removal of the protecting groups thus adding an extra step to the synthetic sequence. Considering atom economy and synthetic efficiency,[9] an AAA of unprotected α-hydroxy indanones, which are cheap and readily available synthons,[4] is greatly desired for the preparation of tertiary alcohols.

Recently, we have reported a number of dual catalyst systems for use in asymmetric allylic substitutions.[8g,10,11] Among these reactions, the AAA of simple acyclic α-hydroxyketones was achieved using a chiral Ir/Zn dual catalyst system;[8g] however, the AAA of α-trisubstituted hydroxyketones proved to be challenging under these conditions. By investigating the Zn catalyst and various reaction conditions, we developed a bimetallic dual catalysis for the efficient AAA of α-hydroxy indanones, providing cyclic tertiary α-hydroxyketones bearing vicinal stereocenters (Scheme 1c).

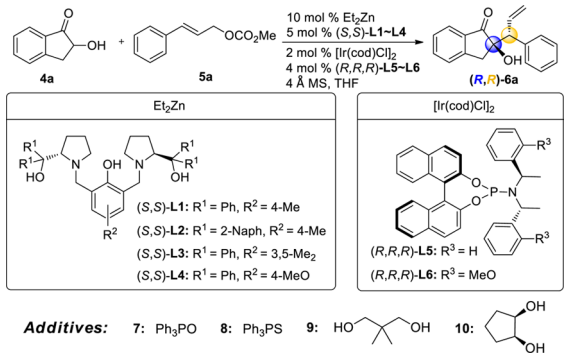
Initially, α-hydroxy indanone (**4a**) and cinnamyl methyl carbonate (**5a**) were selected as model substrates for the allylic substitution (Table 1). Predictably, none of the desired product (**6a**) was detected in the absence of the Zn catalyst (entry 1). Based on our previous findings,[8g] the Zn/ProPhenol complex with a ratio of 1:1 was selected as a catalyst and the reaction was carried out with 4 Å MS (entry 2). Unfortunately, the target compound was not generated under these conditions. We hypothesized that the α-hydroxy indanone could not be enolized due to the weak acidity of the α-hydrogen and large steric hindrance. Therefore, we adjusted the ratio of Et_2Zn and (*S*,*S*)-**L1** to 2:1 in order to generate a seven-membered ring consisting of a zinc enolate chelate rather than a former five-membered ring (entry 3).[8g,12] Both O atoms of the carbonyl and the hydroxyl groups separately coordinate with the two distinct Zn atoms providing stronger inductive effects, hence allowing for the substrate to be enolized more readily. Encouragingly, good catalytic activity, excellent enantioselectivity, and moderate diastereoselectivity were observed. Increasing the steric hindrance or changing the electron-donating groups of the ProPhenol (using **L2**, **L3**, or **L4**) reduced the reaction diastereoselectivity (entries 4–6);[12b] thus, the Zn/(*S*,*S*)-**L1** complex was chosen as the optimal Zn catalyst. A complicated ligand system consisting of an Ir complex provided no advatange to the reaction outcome but led to a lower yield (entry 7). Raising the temperature favored greater conversion; however, enantioselectivity was reduced (entries 8 and 9). Finally, the yield could be increased to 93% by prolonging the reaction time while also retaining acceptable diastereoselectivity and excellent enantioselectivity (entries 10 and 11). Adding a weak coordinating agent usually influences the performance of the Zn-ProPhenol catalyst[13] but did not benefit this reaction (entries 12–15).

After establishing the chemo- and stereoselective process for the α-allylation of α-hydroxy indanones, the substrate scope of the stereodivergent reaction was investigated (Scheme 2). All four stereoisomers of the indanone products could be prepared in high yields and with good enantio- and diastereoselectivity just by switching the combination of the two ligands with appropriate configurations. When an extra 20 mol % Ph_3PS was added as an additive, (*R*,*S*)-**6a** and (*S*,*R*)-**6a** could be obtained in 94% ee.[14]

Notably, a range of α-hydroxy indanones bearing either electron-donating or electron-withdrawing groups on the benzene ring, ranging from the 4- to 7-position, participated in the allylic substitutions to give the desired products (**6b**–**6k**) with high reactivities and excellent selectivities (Scheme 3). The absolute configuration of (*R*,*R*)-**6f** was determined by X-ray crystallographic analysis. In addition, α-hydroxy tetralone was also amenable to the reaction conditions and was converted into the product **6l** in 92% yield, and with 2:1 dr and 96% ee. Regrettably, simple 2-hydroxycyclopentanone did not afford the corresponding product under the same conditions.

Next, the scope of a series of cinnamyl carbonates was investigated (Table 2). Most products were obtained in high yields except for those bearing substituents at the ortho-position

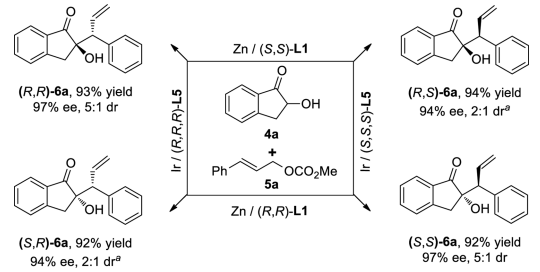
Table 1. Optimization of the Reaction Conditions[a]



entry	L(Zn)	L(Ir)	additive	yield (%)[b]	dr[c]	ee (%)[d]
1	–	(*R*,*R*,*R*)-**L5**	–	nr	–	–
2[e]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	trace	–	–
3	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	85	5:1	97
4	(*S*,*S*)-**L2**	(*R*,*R*,*R*)-**L5**	–	83	3:1	96
5	(*S*,*S*)-**L3**	(*R*,*R*,*R*)-**L5**	–	80	3:1	97
6	(*S*,*S*)-**L4**	(*R*,*R*,*R*)-**L5**	–	86	2:1	96
7	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L6**	–	80	5:1	97
8[f]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	64	5:1	97
9[g]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	96	5:1	95
10[h]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	**93**	**5:1**	**97**
11[i]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	–	93	5:1	97
12[h,j]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	**7**	91	4:1	96
13[h,j]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	**8**	90	4:1	94
14[h,j]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	**9**	94	5:1	95
15[h,j]	(*S*,*S*)-**L1**	(*R*,*R*,*R*)-**L5**	**10**	93	5:1	95

[a]Reaction conditions: **4a** (0.25 mmol, 1.0 equiv), **5a** (0.30 mmol, 1.2 equiv), Et_2Zn (10 mol %), (*S*,*S*)-**L1**–**L4** (5 mol %), $[Ir(cod)Cl]_2$ (2 mol %), (*R*,*R*,*R*)–**L5**–**L6** (4 mol %), rt, 12 h. [b]Isolated yield of all diastereoisomers. nr = no reaction. [c]Ratio of dr determined by ^1H NMR integration. [d]Determined by HPLC analysis using an AD-H column. [e]Et_2Zn (5 mol %), **L1** (5 mol %). [f]0 °C. [g]50 °C. [h]18 h. [i]24 h. [j]20 mol % additives.

Scheme 2. Construction of All Four Stereoisomers of 6a



[a]20 mol % Ph_3PS.

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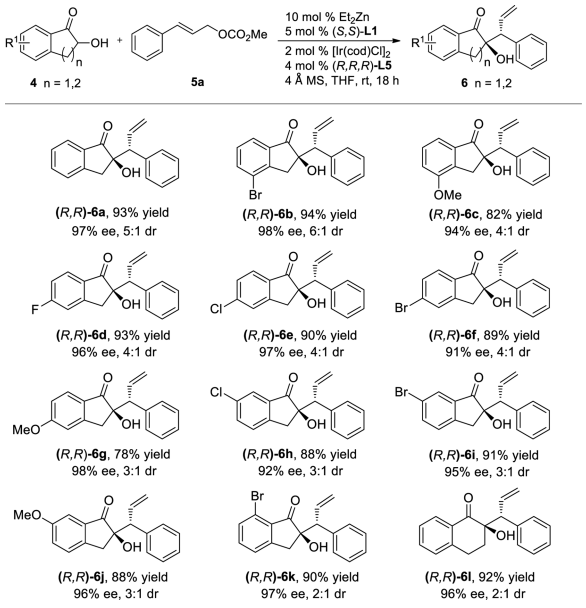
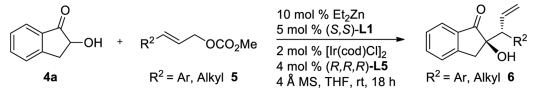
Scheme 3. Substrate Scope of α-Hydroxy Indanones[a]



[a]Reaction conditions, please see Table 1, entry 10.

Table 2. Substrate Scope of Allylic Carbonates[a]



entry	6	R^2	yield (%)	dr	ee (%)
1	(*R*,*R*)-**6m**	2-FC_6H_4	73	3:1	94
2	(*R*,*R*)-**6n**	3-FC_6H_4	88	3:1	91
3	(*R*,*R*)-**6o**	3-ClC_6H_4	90	3:1	96
4	(*R*,*R*)-**6p**	3-MeC_6H_4	94	6:1	99
5	(*R*,*R*)-**6q**	4-FC_6H_4	91	4:1	94
6	(*R*,*R*)-**6r**	4-ClC_6H_4	93	3:1	95
7	(*R*,*R*)-**6s**	4-BrC_6H_4	89	3:1	93
8	(*R*,*R*)-**6t**	4-$NO_2C_6H_4$	92	4:1	96
9	(*R*,*R*)-**6u**	4-$CF_3C_6H_4$	89	3:1	82
10	(*R*,*R*)-**6v**	4-MeC_6H_4	94	3:1	95
11	(*R*,*R*)-**6w**	4-$MeOC_6H_4$	85	4:1	97
12	(*R*,*R*)-**6x**	3,5-$Cl_2C_6H_3$	84	5:1	91
13	(*R*,*R*)-**6y**	2,4-$Me_2C_6H_3$	70	3:1	99
14	(*R*,*R*)-**6z**	2-naphthyl	88	5:1	96
15	(*R*,*S*)-**6aa**	2-furyl	90	3:1	87
16	(*R*,*R*)-**6ab**	3-(1-tosyl-indolyl)	87	12:1	91
17	(*R*,*S*)-**6ac**	*n*-propyl	86	4:1	>99
18	(*R*,*R*)-**6ad**	$BnOCH_2$	91	3:1	96

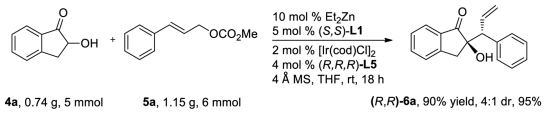
[a]Reaction conditions, please see Table 1, entry 10.

of the arene functionality. Furthermore, furyl- and alkyl-substituted allyl carbonates were successfully employed to furnish their desired products (**6aa**, **6ac**, and **6ad**). Additionally, the indolyl-substituted carbonate proved to be an excellent substrate for this reaction, providing product **6ab** with good reactivity, excellent enantioselectivity, and the highest observed diastereoselectivity (12:1 dr).

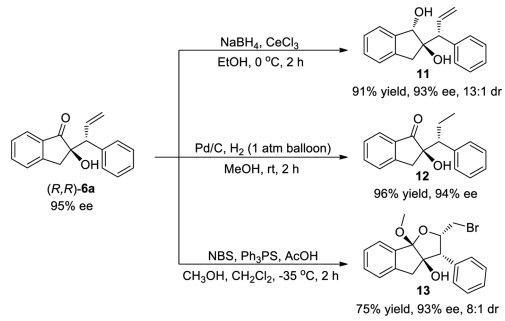
To examine the scalability of the catalyst system, a gram-scale synthesis of (*R*,*R*)-**6a** was carried out using the standard reaction conditions and comparable results were obtained (Scheme 4).

Furthermore, we conducted several synthetic transformations of the allylation product (*R*,*R*)-**6a** (Scheme 5). Reduction of the

Scheme 4. Preparatory Scale Experiment



Scheme 5. Derivatization of Product 6a



carbonyl group and hydrogenation of the olefin afforded compound **11** in 91% yield (93% ee, 13:1 dr) and **12** in 96% yield (94% ee), respectively. The terminal alkene functionality was also derivatized to give the tetrahydro-2*H*-indeno-[1,2-*b*]furan framework (**13**) in high yield with excellent stereoselectivity.

As previously described,[15] a possible explanation for the current transformation is illustrated in Figure 2. The α-hydroxy indanone

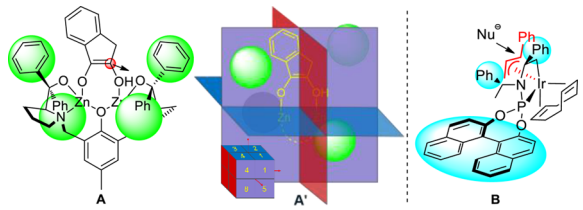


Figure 2. Model for explaining the origin of asymmetric induction.

serves as a bidentate ligand bridging the two zinc atoms (depicted as **A**) and is embedded tightly into the Zn−Ligand complex. Large, symmetrical steric hindrance is present in the second and fourth quadrants, and the phenyl group in the second quadrant partially blocks the underside of the enolate (Figure 2, **A′**). Therefore, the nucleophilic site most likely attacks the prochiral allyliridium intermediate **B** in the first quadrant. The stability of the structure and excellent stereomatching of the two prochiral intermediates ensure excellent stereoselectivity.

In summary, we have developed a mild, one-step Ir/Zn dual catalyst system for the stereodivergent α-allylation of unprotected cyclic α-hydroxy indanones. An array of chiral α-allyl-α-hydroxy indanones containing vicinal tetra- and trisubstituted stereocenters were synthesized in good yields and with excellent stereoselectivities. Furthermore, all four stereoisomers of the target compound can be prepared from the same starting materials and operation procedures using this dual catalyst system. Further exploration of stereodivergent bimetallic catalyst systems for challenging asymmetric transformations is ongoing in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02577.

Experimental procedures and spectral data for all new compounds (PDF)
Crystallographic data for **6f** (CIF)
Crystallographic data for **6l** (CIF)
Crystallographic data for **11a** (CIF)
Crystallographic data for **13** (CIF)

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Notes

The authors declare no competing financial interest.

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