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Asymmetric Intermolecular Rauhut–Currier Reaction for the Construction of 3,3-Disubstituted Oxindoles with Quaternary Stereogenic Centers

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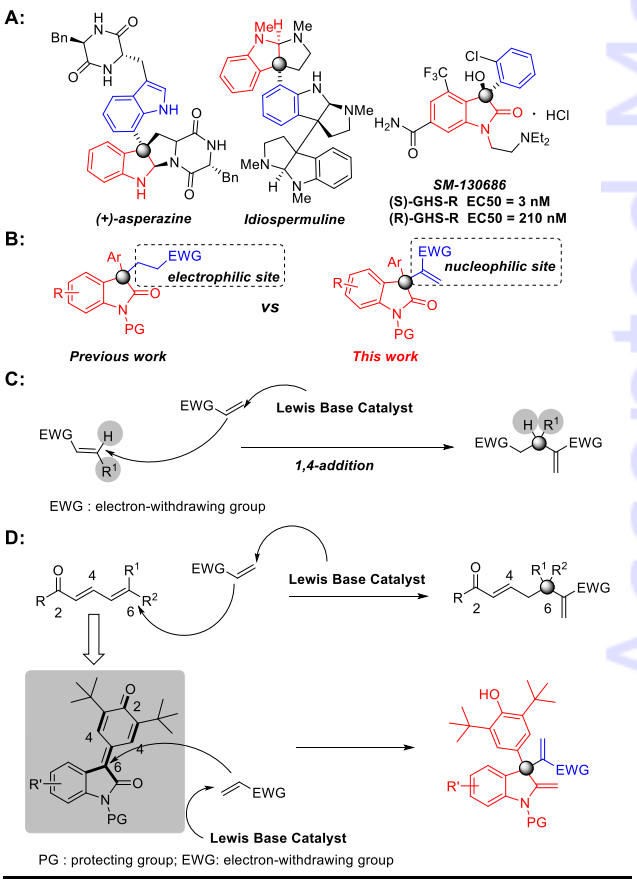
Abstract. A remote cross Rauhut–Currier reaction utilizing vinyl ketones and *para*-quinone methides derived from isatins was realized, which was successfully catalyzed using bifunctional phosphines, furnishing chiral 3,3-disubstituted oxindoles in excellent enantioselectivities and high yields. The mechanistic studies demonstrated the key role of the alkyl hydrogen of the vinyl ketones, which conceivably interacted with the *para*-quinone methide carbonyl group via the hydrogen bond, offering a new insight for the design of novel asymmetric reactions.

Keywords: Rauhut–Currier reaction; quaternary stereocenters; remote stereogenic center; asymmetric catalysis; organocatalysis

3-Arylindoles with quaternary stereogenic centers represent important structural units that exist in pharmaceutical compounds and biologically-active natural products, such as (+)-asperazine, idiospermuline and SM-130686 (Scheme 1A).[1] Therefore, the development of efficient synthetic methods for the construction of these molecules has sparked many research efforts in the past decades. Recently, a proof-of-concept study showed a powerful approach for preparing optically active molecules in which electrophiles were attached to 3-aryloxindoles. Moreover, the concept has been extended to many enantioselective variations for the construction of these valuable molecules, including the Mannich reactions,[2] Michael addition reactions,[3] S_N2 reactions and various cross-coupling reactions,[4] which use both organocatalysts and metal catalysts. Although many methods for preparing 3-aryloxindoles bearing electrophilic groups have been discovered, searching for new strategies for synthesizing 3-aryl oxindoles with nucleophilic groups is an attractive goal for obtaining diversely functionalized 3,3-disubstituted oxindoles (Scheme 1B).



Scheme 1. (A) Representative bioactive molecules; (B) 3,3-disubstituted oxindoles with electrophiles and nucleophiles; (C) intermolecular Rauhut–Currier reactions; (D) intermolecular remote Rauhut–Currier reactions.

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The intermolecular Rauhut–Currier reaction, known since 1963, uses two structurally diverse olefins for the production of fine chemicals, and has attracted considerable attention for the synthesis of valuable compounds.[5] In particular, the asymmetric Rauhut–Currier reaction stands out as a simple but efficient strategy for the construction of chiral carbon centers. Furthermore, various chiral Lewis base catalysts, including nucleophilic nitrogen, phosphine and sulfur donor atoms, have been successfully used for the asymmetric Rauhut–Currier reaction (Scheme 1C).[6] To the best of our knowledge, general methods for the formation of quaternary carbon centers with either the regular or asymmetric Rauhut–Currier reaction have yet to be developed, despite focused research reported in this area. This can be attributed to the lack of efficient selectivity control and the lower reaction activity of disubstituted alkenes. Therefore, novel methods should be investigated to resolve these challenging problems.

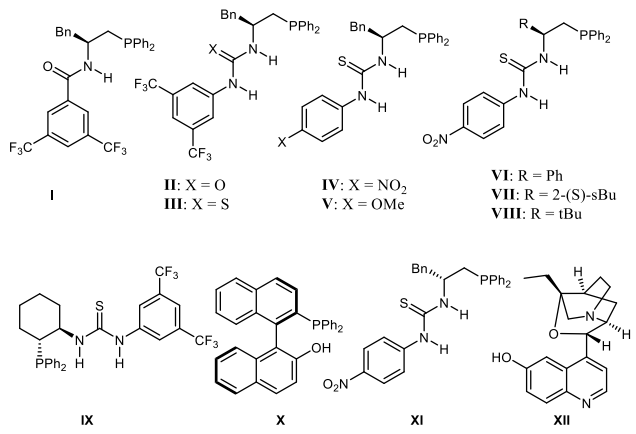
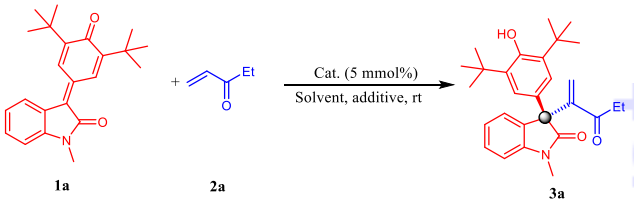


Figure 1. The catalysts screened in this study.

Remote enantiocontrol has emerged as an important field for the construction of remote chiral centers. However, the relatively low reactivity of 1,6-conjugate addition reactions is a major challenge for the remote enantiocontrol of these type of transformations.[7] The rational design of substrates and catalysts has helped, and at present, a variety of interesting substrates have been developed for the enantioselective construction of chiral products with remote stereogenic centers.[8] Meanwhile, *para*-quinone methide as an important synthon has been widely applied to prepare chiral functional products, since it was first reported by the groups of Fan and Jørgensen.[9] The realization of the remote cross Rauhut–Currier reaction is therefore an important development for the construction of chiral products (Scheme 1D). Considering this, the novel paraquinone methides derived from isatins reported in this paper were considered as promising substrates for the construction of chiral 3,3-disubstituted oxindoles using the challenging remote cross Rauhut–Currier reaction. Notably, anhydrous and anaerobic reaction conditions can be avoided, which have been essential for previous preparations of 3-aryloxindoles.[10] Herein we report the first asymmetric remote cross Rauhut–Currier reactions between vinyl ketones with widely available *para*-quinone methides derived from isatins using chiral Lewis base catalysts to yield variations of **3** with excellent enantioselectivities and yields.

Table 1. Screening conditions for the asymmetric remote cross Rauhut–Currier reaction.[a]



Entry	Cat.	Solvent	Time(h)	Yield(%)[b]	e.r.[c]
1	**I**	CH_2Cl_2	54	41	58:42
2	**II**	CH_2Cl_2	18	99	89:11
3	**III**	CH_2Cl_2	42	98	96:4
4	**IV**	CH_2Cl_2	54	98	95:5
5	**V**	CH_2Cl_2	60	37	67:33
6	**VI**	CH_2Cl_2	48	25	89:11
7	**VII**	CH_2Cl_2	54	17	63:37
8	**VIII**	CH_2Cl_2	48	Trace	-
9	**IX**	CH_2Cl_2	36	90	15:85
10	**X**	CH_2Cl_2	60	Trace	-
11	**XI**	CH_2Cl_2	54	95	5:95
12	**XII**	CH_2Cl_2	48	Trace	-
13	**III**	$CHCl_3$	30	96	95:5
14	**III**	Toluene	45	92	91:9
15	**III**	EtOAc	24	98	92:8
16	**III**	CH_3CN	80	71	69:31
17	**III**	Acetone	18	96	89:11
18	**III**	MeOH	24	44	60:40
19[d]	**III**	CH_2Cl_2	30	92	95:5
20[e]	**III**	CH_2Cl_2	54	79	74:26
21[f]	**III**	CH_2Cl_2	54	79	96:4
22[g]	**III**	CH_2Cl_2	96	47	92:8

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.05 mmol) and **2a** (0.10 mmol) catalyzed by a bifunctional chiral phosphine (5 mol%) in solvent at room temperature. [b] The isolated yield. [c] Determined by chiral HPLC analysis. [d] 2 equiv of H_2O was added. [e] 2 equiv of PhOH was added. [f] 20 mg 4 Å MS were added. [g] The reaction was performed at 0 °C.

Initially, the reaction between **1a** and **2a** catalyzed by bifunctional organophosphines was carried out in CH_2Cl_2 at room temperature. The reaction proceeded smoothly using catalyst **I**, and 41% yield was obtained by stirring for 54 h; however, low enantioselectivity was achieved (Table 1, entry 1). Informed by our previous work, in which H-bonding interactions were demonstrated to play a vital role in improving the enantioselectivities,[11] we investigated the influences of thiourea and urea with different groups derived from L-phenylalanine. Among the

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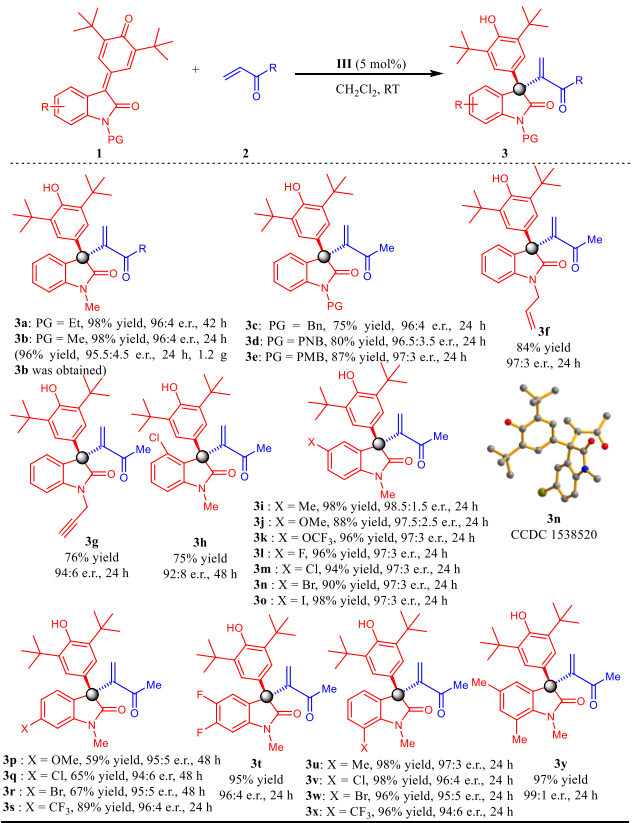
catalysts **I-V**, the thiourea catalyst **III** bearing 3,5-CF_3 groups was found to be the optimal one for this reaction (98% yield, 96:4 e.r.) Further examination of the chiral backbone with thiourea was performed to improve the enantioselectivity of the product, but no improvements in performance were found (Table 1, entries 6-10). The catalyst derived from D-phenylalanine was also examined, and excellent enantioselectivity with an opposite configuration was maintained (Table 1, entry 11). Meanwhile β-ICD was found to be unsuitable for this reaction (Table 1, entry 12). Other reaction parameters, including the solvent, additives and temperature, were investigated for the overall reaction optimization. Protic solvents and strong polar solvents exhibited certain detrimental effects on the enantioselectivities of the products (Table 1, entries 13-18). The additives were unfavorable for improving the ee values including H_2O, PhOH, 4 Å MS, however, trace water accelerated the reaction rate. Lowering the temperature slowed the reaction rate, and no higher ee values were obtained (Table 1, entry 19-22).

Table 2. Examples of vinyl ketones with *para*-quinone methides derived from isatins.[a]



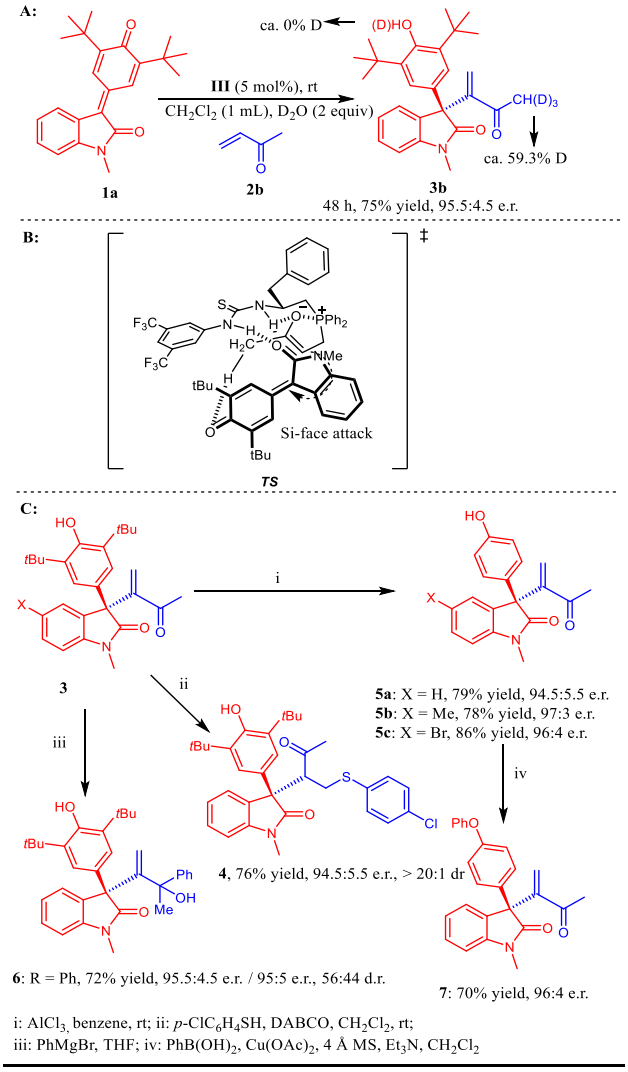
[a] Reactions were carried out under the optimized conditions as shown in Table 2. Yields of **3** were isolated yields. The e.r. was determined by chiral HPLC analysis. Supplementary crystallographic data for **3n** can be found in CCDC 1538520.[12] PNB, *p*-$NO_2C_6H_4$; PMB, *p*-$MeOC_6H_4$.

With the optimized conditions, we continued to explore the scope of the asymmetric remote cross Rauhut–Currier reaction (Table 2). Methyl vinyl ketone was first examined with **1a**, and the reaction proceeded faster compared to **2a**, which could be attributed to the steric influence of the ethyl group of **2a**. In particular, **3b** could be scaled up to a gram-level furnishing 1.2 g without the loss of enantioselectivity (95.5:4.5 e.r., 96% yield in 24 h). Investigations into the effects of different protecting groups on the nitrogen atom of **1**, including methyl, benzyl, *p*-methoxybenzyl (PMB), *p*-nitrobenzyl (PNB), allyl and propargyl groups, showed that the asymmetric reactions exhibited excellent stereoselectivities regardless of the electron-withdrawing or electron-donating nature of the groups. Furthermore, different substituents of **1** were also explored in detail. Regardless of the electronic and steric properties of the substituents on the benzene ring, all the reactions proceeded smoothly to afford the corresponding products with excellent enantioselectivities, Moderate yields were obtained with substituents on the 6 position of the benzene ring. The absolute configuration of **3n** was determined to be *R* by X-ray crystallographic analysis (see *SI*) and the other products were analogously determined.

To further test the potential of these asymmetric reactions using **1**, activated olefins were investigated (see *SI*). Remarkably, the methyl group in **1a** greatly improved the enantioselectivity and yield. However, replacing the methyl group with hydrogen, phenyl or phenoxy lowered the yield and enantioselectivity. To investigate the mechanism of the reaction, an isotope experiment was performed by adding D_2O (2 equiv) into the mixture (Scheme 2A). From the ^{1}H-NMR spectrum of the corresponding product **3b**, the methyl group of **2b** was 59.3% deuterated (see *SI*), while the hydroxyl group of **3b** remained undeuterated. Hence, it can be assumed that the methyl group of **2b** and trace water are key factors for controlling the stereoselectivity and increasing the yield of the remote cross Rauhut–Currier reaction. In addition, Yu and co-workers showed with theoretical calculations that H_2O can accelerate proton transfer in [3+2] cyclization.[13] A non-linear effect experiment that has been used for certain asymmetric reactions catalyzed by organophosphines was implemented to investigate the catalytic mechanism.[11] A general linear effect was observed using this experiment for **3b** catalyzed by **III** (see *SI*). According to these results and previous work, we tentatively proposed a possible transition state (***TS***) to explain the stereochemical results of the remote cross Rauhut–Currier reaction (Scheme 2B). Reaction of the organophosphine with methyl vinyl ketone forms a zwitterion by a synergistic action of its bifunctional groups. In addition to the interaction of the N-H bond of the phosphine and carbonyl group of **1a**, the H-bond (C-H-O) between the methyl group of **2b** and the other carbonyl group of **1a** simultaneously reduces the space between the two compounds. The electrophile **1a** might approach the zwitterion from

the *Si* face to minimize the steric repulsion of the catalyst.

To illustrate the utility of the method, some representative transformations were performed as shown in Scheme 2C. The *tert*-butyl group of **3** can be easily removed under mild conditions using $AlCl_3$ without the loss of enantioselectivity. Meanwhile, the cross-coupling reaction between **5a** and $PhB(OH)_2$ was carried out catalyzed by $Cu(OAc)_2$, the corresponding product was obtained in high yield. The transformation of **3b** with *p*-ClC_6H_4SH was performed under basic conditions, and gave the corresponding product **4** in high yield and excellent enantioselectivity. Finally, the reaction of RMgBr with the C=O group in **3** was attempted to prepare tertiary alcohols, and excellent results were obtained.



Scheme 2. (A) Isotope experiment; (B) possible transition state ***TS***; (C) representative transformations of **3**.

In summary, we have developed an asymmetric remote-cross-Rauhut–Currier reaction for the construction of quaternary stereocenters. Vinyl ketones efficiently reacted with various *para*-quinone methides derived from isatins with excellent enantioselectivities and yields catalyzed by **III** under mild conditions. Moreover, the mechanistic study revealed that the alkyl hydrogen of the vinyl ketone plays an important role in improving both the yield and the enantioselectivity. We anticipate that this method will be valuable for new reactions and synthetic strategies. Novel asymmetric reactions based on the *para*-quinone methides derived from isatins are currently under way in our lab.

Experimental Section

General procedure for the asymmetric intermolecular Rauhut–Currier reaction

To a solution of *para*-quinone methide **1** (0.05 mmol) in CH_2Cl_2 (1 mL), methyl vinyl ketone **2** (0.10 mmol) and catalyst (5 mol%) were sequentially added. The mixture was stirred at room temperature and monitored by TLC. The pure products (**3a-3y**) were obtained via flash chromatography (PE: EA = 4:1) as white solids.

Acknowledgements

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COMMUNICATION

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