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Visible-Light-Activated Rhodium Complex in Enantioselective Conjugate Addition of α-Amino Radicals with Michael Acceptors

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Abstract: We report an efficient enantioselective conjugate addition of photogenerated α-amino radicals to Michael acceptors catalyzed by newly prepared chiral-at-metal rhodium complex. This protocol exhibits that a single Rh(III) complex can serve not only as Lewis acid but also as photoredox catalyst to control the stereoselectivity during the bond formation.

Photochemistry has been recognized as a powerful tool in organic synthesis.[1] However, stereocontrol in a photochemical reaction still remains a long-standing challenge. Over the past decade, a number of novel catalytic systems have been developed to control the enantioselectivity in visible-light activated transformation.[2] Most of solutions relied on a dual catalytic system,[3] which is the combination of an achiral photoredox catalyst and a chiral co-catalyst such as chiral amine,[4] carbene,[5] hydrogen bonding catalyst[6] and Lewis acid.[7] A single chiral photocatalyst[8-13] is not only feasible to harvest visible light for activation of organic compounds, but also control the stereoselectivity during the chemical bond formation.

Recently, the chemistry of α-amino radicals has attracted a lot of attention in photochemical reactions. The utilization of these highly nucleophilic radical intermediates in photochemical transformations has been well established by several groups.[14] However, successful approaches of their enantioselective addition reactions are quite limited.[15-17] The Bach group realized a chiral hydrogen bonding-based thioxanthone catalyzed intramolecular conjugate addition of photochemically generated α-amino radical to a quinolone moiety.[15] The Meggers group developed a novel chiral-at-metal iridium complex[18] as a bifunctional photocatalysts to realize an efficient asymmetric 1,2-addition of the α-amino radicals to ketones.[16] Recently, the intermolecular conjugate addition of α-amino radicals were successfully achieved by the Yoon[17] and Melchiorre[10e] groups, respectively. The combination of transition metal photoredox catalysts with chiral Lewis acid catalysis or well-designed organocatalysts has enabled a highly enantioselective transformations, however with high catalyst loadings (Figure 1).

Despite these elegantly pioneering studies, the development of highly efficient and enantioselective transformations of photogenerated α-amino radicals is still desirable. Herein, we report our recent findings on a catalytic asymmetric conjugate addition of α-amino radicals generated from tertiary amines to Michael acceptors catalyzed by chiral-at-metal rhodium complex[19] under visible-light irradiation (Figure 1).

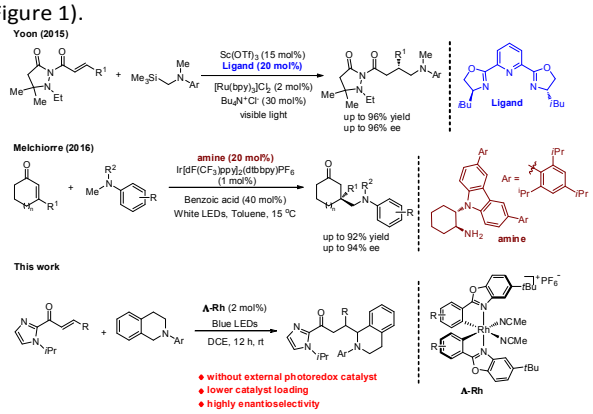

Figure 1. Previous protocols and this work on asymmetric intermolecular conjugate addition of photochemically generated α-amino radicals.

We initiated our investigation by irradiating a mixture of α, β-unsaturated 2-acyl imidazole (**1a**, 1 equiv.) and *N*-phenyltetrahydroisoquinoline (**2a**, 2 equiv.) in the presence of 2 mol% of chiral-at-metal complexes in degassed DCE with 20 W blue light emitting diodes. Chiral-at-metal iridium complex **Λ-Ir**[20], which is optimal catalyst in the enantioselective 1,2-addition of the photogenerated α-amino radicals to 2-

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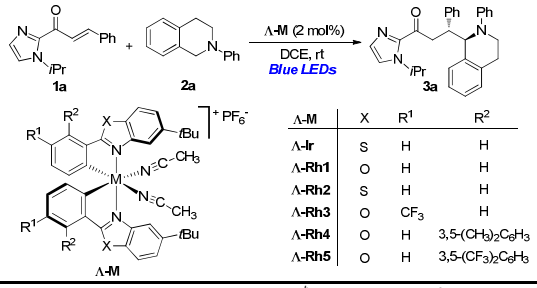
trifluoroacetyl imidazoles[16b], gave the desired product **3a** in 36% yield, but in racemic form (Table 1, entry 1). Pleasingly, employing chiral-at-metal rhodium complex **Λ-Rh1**[21] as catalyst, successful conversion to product was observed in 72% yield, 74:26 dr with 93% ee. Encouraged by these promising results, various chiral-at-metal Rh(III) complexes were examined. In general, all the reactions could proceed smoothly to give desired product in moderate to good yields and ee (Table 1, entries 3-6). Gratifyingly, a newly prepared catalyst **Λ-Rh5** turned out to be the most efficient one in terms of reactivity, diastero-, and enantioselectivity, resulting in **3a** in 90% yield with 83:17 dr, 95% ee (entry 6). Further optimization of reaction conditions disclosed that DCE functions as the optimal solvent (see Table S2 in the Supporting Information). Removal of **Λ-Rh5** from our standard protocol resulted in 20% yield of **3a** without selectivity (entry 7). Rigorous exclusion of light failed to produce even trace quantities of the desired product, confirming the photochemical nature of the reaction (entry 8). Under identical conditions, reducing the catalyst loading led to the diminished yield and ee (Table 1, entry 9).

Table 1. Optimization of reaction conditions[a]

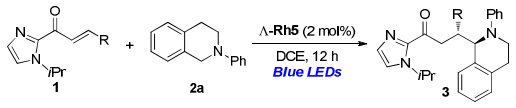


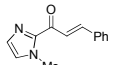
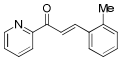
Entry	Catalyst	hν	d.r.[b]	Yield [%][c]	ee [%][d]
1	**Λ-Ir**	√	53:47	36	0
2	**Λ-Rh1**	√	74:26	72	93
3	**Λ-Rh2**	√	64:36	84	91
4	**Λ-Rh3**	√	75:25	67	50
5	**Λ-Rh4**	√	82:18	65	91
6	**Λ-Rh5**	√	83:17	90	95
7	none	√	50:50	20	-
8	**Λ-Rh5**	×	-	0	-
9[e]	**Λ-Rh5**	√	75:25	56	92

[a] Reaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 2 mol% of **Λ-M** in degassed 1,2-dichloroethane (DCE, 0.4 mL) at room temperature under irradiation with 20 W blue LEDs. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] NMR yield determined using 1,3,5-trimethoxybenzene as internal standard. [d] Determined by chiral HPLC analysis. [e] 1 mol% of **Λ-Rh5**.

With the optimized reaction conditions in hand (Table 1, entry 6), we first investigated the generality of Michael acceptors, α, β-unsaturated 2-acyl imidazoles and pyridine (Scheme 1). 2-Acyl imidazoles with either electron-donating or electron-withdrawing groups on phenyl ring had little effect on the selectivity, thus providing the desired products in good yields and excellent enantioselectivities with comparable diastereoselectivities (**3b-3h**). The Michael acceptor substrates with hetero-aromatic substituents worked well, affording **3i** and **3j** with 92-94% ee. When substrates with sterically hindered substitution such as 2-methyl aryl and 1-naphthyl were introduced, the reactions proceeded smoothly in good yields with satisfactory enantioselectivities (**3k-3l**). In addition to aromatic substituents, the aliphatic variants of α, β-unsaturated 2-acyl imidazoles (Me, CO_2Et) were also examined to deliver the corresponding products (**3n**, **3o**) with excellent ee, albeit with slightly diminished yields. Replacing of the *N*-isopropyl with *N*-methyl substituent didn't encumber the reaction (**3p**). Furthermore, α, β-unsaturated 2-acyl pyridine **1q** which could be coordinated to rhodium centre in bidentate fashion, afforded the desired adduct **3q** in 73% yield with 92% ee. The structure of the product was confirmed by an X-ray crystallographic analysis of the enantiopure major diastereomer **3k**.[22]

Table 2. The substrates scope of Michael acceptors[a]



Entry	**1**, R	**3**	d.r.[b]	Yield [%][c]	ee [%][d]
1	**1a**, C_6H_5	**3a**	83:17	90	95
2	**1b**, 4-Me-C_6H_4	**3b**	83:17	92	92
3	**1c**, 3-Me-C_6H_4	**3c**	82:18	87	91
4[e]	**1d**, 3-OMe-C_6H_4	**3d**	84:16	78	92
5	**1e**, 4-Cl-C_6H_4	**3e**	78:22	89	93
6	**1f**, 4-Br-C_6H_4	**3f**	84:16	91	94
7	**1g**, 4-NO_2-C_6H_4	**3g**	77:23	66	>99
8	**1h**, 4-CF_3-C_6H_4	**3h**	81:19	70	91
9	**1i**, 2-furyl	**3i**	58:42	80	94
10[e]	**1j**, 2-thienyl	**3j**	75:25	80	92
11	**1k**, 2-Me-C_6H_4	**3k**	80:20	81	93
12[e]	**1l**, 1-naphthyl	**3l**	76:24	87	92
13[e]	**1m**, 2-naphthyl	**3m**	80:20	90	93
14	**1n**, Me	**3n**	66:34	54	97
15	**1o**, CO_2Et	**3o**	52:48	55	92
16	 **1p**,	**3p**	84:16	91	91
17[e]	 **1q**,	**3q**	61:39	73	92

[a] Reaction conditions: 0.1 mmol of **1**, 0.2 mmol of **2a**, 2 mol% of **Λ-Rh5** in degassed DCE (0.4 mL) at room temperature under irradiation with 20 W blue LEDs. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of the isolated diastereoisomers. [d] Determined by chiral HPLC analysis. [e] 200 mol% of 2,6-lutidine was added as additive.

Next, we chose α, β-unsaturated 2-acyl imidazole **1k** for the evaluation of various of tetrahydroisoquinolines (Figure 2). The *N*-aryl tetrahydroisoquinolines with varying electronic nature reacted smoothly to yield the desired products in 74-86% yields with 92-96% ee (**3r-3u**). The diastereoselectivity was improved when the *ortho*-substituted *N*-arene substrate was introduced to the reaction (**3v**). The *N*-aryl isoquinoline

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derivatives, regardless of the electronic properties of the substituents, displayed excellent enantioselectivities (**3w**, **3x**). It should be note that *N*-Bn, Ts or Boc substituted isoquinolines were not suitable substrates for the title reaction.

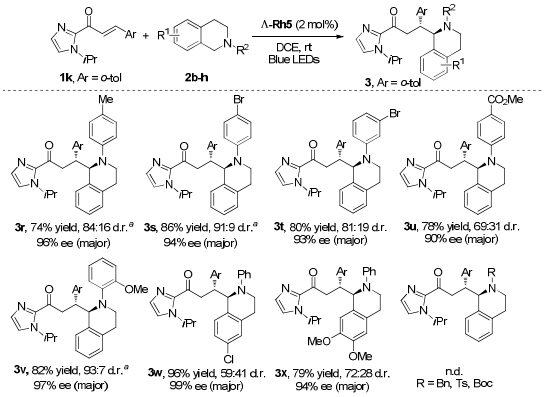
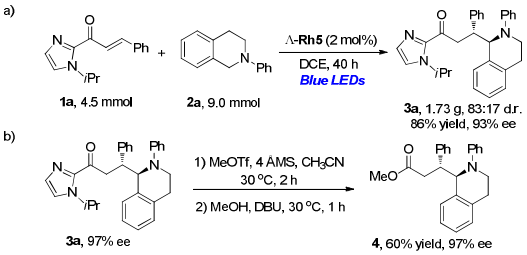


Figure 2. Substrates scope of tetrahydroisoquinolines **2**. [a] 200 mol% of 2,6-lutidine was added as additive.

To further verify practicality of the current method, synthesis of **3a** was executed on a 4.5 mmol scale (1.08 g, Scheme 1a). Under the optimal reaction conditions, the reaction proceeded with 86% yield and slight erosion of enantioselectivity was observed as compared to small-scale reaction (Table 2, entry 1). Moreover, the conversion of the imidazole moiety to useful synthetic building blocks were also investigated. It was found that the imidazole auxiliary could be easily converted to an ester without erosion of enantioselectivity (Scheme 1b).



Scheme 1. Gram-scale reaction of **1a** and product transformation.

The proposed mechanism is shown in Figure 3. Substrate **1** first coordinates with rhodium complex in bidentate fashion to generate intermediate **I**. Then, *N,O*-rhodium-coordinated α, β-unsaturated 2-acyl imidazoles complex (intermediate **I**) is photoexcited and reduced by tetrahydroisoquinoline **2**, thus generating an α-amino radical, which subsequently added to intermediate **I** to generate the secondary radical intermediate **II**. Intermediate **III** (rhodium enolate), which generated from intermediate **II** via single electron transfer (SET) process results in rhodium-coordinated product **IV** by protonation with H^+. The desired product is released by replacement of the coordinated product **IV** by **1a**.

A number of control experiments were conducted to support the proposed mechanism. First, the reaction could give the desired product in 20% yield without any catalyst

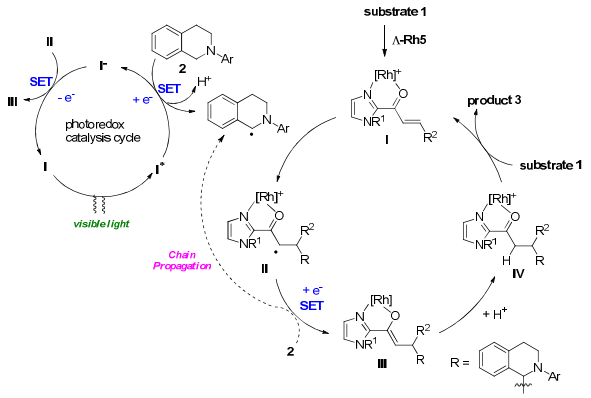


Figure 3. Proposed mechanism.

under the irradiation of a 20 W blue LEDs (Table 1, entry 7). Other Lewis acid catalysts such as $Sc(OTf)_3$ and $Gd(OTf)_3$ were introduced to the reaction instead of **Λ-Rh5**, resulting in sluggish transformations. These results indicate that **Λ-Rh5** acts not only as Lewis acid, but also likely promotes the formation of a complex with the substrate which can absorb the visible light. The results of Stern-Volmer plots reveal that the luminescence emission of **Λ-Rh5** or complex of **Λ-Rh5** with *N*-acylimidazole can be quenched by tetrahydroisoquinoline.[23] The reactions by using undegassed solvent or radical inhibitor TEMPO (2.0 eq.) result in a diminished yields and enantioselectivities of the desired product **3a**, which provide the evidence of a radical pathway. The deuterium labeling experiment gave the deuterated product in 25% yield, indicating that the reaction might go through the SET/protonation process. A quantum yield of >2 indicates that radical intermediate **II** might not only accept a single electron from the reduced photosensitizer $\mathbf{I}^-$, but also from substrate **2**, thus leading to a chain propagation cycle (see Supporting Information for more details).[24]

In conclusion, we have developed an efficient and practical catalytic enantioselective intermolecular Michael addition of photogenerated α-amino radicals with Michael acceptors catalyzed by newly prepared chiral-at-metal rhodium complex, affording desired adducts in good yields with excellent enantioselectivities. Moreover, this protocol demonstrates that *N,O*-rhodium-coordinated complex could serve not only as single visible-light-activated photoredox catalysis, but also as excellent chiral Lewis acid which accelerates the radical addition step and control the enantioselectivity during the bond formation.

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