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Visible Light Catalysis Assisted Site-Specific Functionalization of Amino Acid Derivatives by C−H Bond Activation without Oxidant: Cross-Coupling Hydrogen Evolution Reaction

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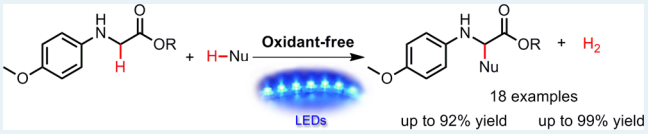
Supporting Information

ABSTRACT: Visible light catalysis assisted site-specific modification of α-amino acids by C−H bond functionalization without the use of any oxidant or base is described. Using $Ru(bpy)_3(PF_6)_2$ and $Co(dmgH)_2pyCl$ as a photosensitizer and a catalyst, respectively, a variety of glycine esters with β-keto esters or indole derivatives can be quantitatively converted into the desired cross-coupling products and hydrogen (H_2) in good to excellent yields under visible light irradiation. A mechanistic study reveals that the cascade electron transfer processes from glycine ester to the photoexcited $Ru(bpy)_3(PF_6)_2$ and then to $Co(dmgH)_2pyCl$ catalyst, together with the capture of protons delivered by substrates, are crucial for the cross-coupling hydrogen evolution reaction of secondary amines in organic solvents.



KEYWORDS: *amino acid derivatives, visible light catalysis, cross-coupling hydrogen evolution, photoinduced electron transfer, C−H bond activation*

INTRODUCTION

Developing efficient, atom- and step-economical methods for rapid access to α-amino acid derivatives is of great significance to realize their application in the synthesis of biologically active peptides. Direct and site-specific modification of α-amino acids takes advantage of the existing structure and provides a convenient way to generate large arrays of diverse amino acids. Over the years, there have been established effective methods to functionalize α-amino acid derivatives, such as functionalization of carbanions (performed by deprotonating with a strong base),[1−3] radicals (α-bromination by *N*-bromosuccinimide or UV photolysis in the presence of di-*tert*-butyl peroxide),[4−6] Claisen rearrangement,[7] metal-catalyzed alkynylation or arylation of amino acid derivatives,[8−10] and cross-dehydrogenative coupling (CDC) reactions.[11−17] However, all of the above reactions require an appropriate oxidant or base to help with the α-functionalization of amino acids, which lead to the known occurrence of radical mediated oxidations documented for biological systems, toxic waste byproducts, and low atom economy.[18] Direct site-specific modification of α-amino acids by C−H bond functionalization without any oxidant or base is to date, to the best of our knowledge, yet unknown.

It was not until recently that a new type of reaction, the cross-coupling hydrogen evolution reaction, appeared.[19] The reaction avoids the use of any sacrificial oxidants and achieves the desired cross-coupling product and hydrogen gas (H_2) in quantitative yields by taking advantage of visible light as an energy input, which is a more economical and environmentally benign strategy in comparison to the existing direct C−H bond activation.[19−24] Nevertheless, the efficient cross-coupling hydrogen evolution reaction has been hitherto limited to tertiary amines, with tetrahydroisoquinoline as the most frequently used substrate.[19,20] To accomplish the cross-coupling hydrogen evolution reaction of amino acids, for example, with glycine derivatives as substrates, one has to face the following challenges. (i) All of the cross-coupling hydrogen evolution reactions reported were performed in water or water-containing organic solvents, but the presence of water results in immediate decomposition of imine intermediates derived from secondary amines into amines and aldehydes. (ii) The relatively higher oxidation potential makes secondary amines harder to be oxidized than tertiary amines. (iii) The hydrogen atom adjacent to the nitrogen atom of secondary amines is more acidic than that of tertiary amine, thereby leading to lower stability of radical intermediates generated from secondary imines.

In the present work, we wish to report a new system based on visible light catalysis for the synthesis of amino acid derivatives in the absence of any sacrificial oxidant and base in homogeneous solution. Herein, $Ru(bpy)_3(PF_6)_2$ is employed as a photosensitizer to initiate cross-coupling of glycine derivatives with nucleophiles, and the earth-abundant molecular complex $Co(dmgH)_2pyCl$ (dmgH = dimethylglyoximate) is used as a catalyst to capture the electrons and protons eliminated from the C−H bonds of substrates (Scheme 1). Upon irradiation by

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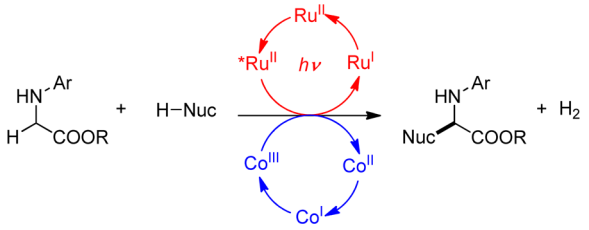
Scheme 1. Cross-Coupling Hydrogen Evolution Reaction of Glycine Esters and Nucleophiles in Anhydrous Organic Solvent

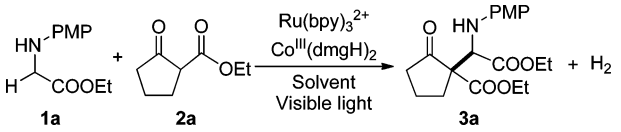


visible light, a variety of glycine esters with β-keto esters or indole derivatives could be quantitatively converted into the desired cross-coupling products and H_2 without the need for sacrificial oxidants or external bases in pure organic solvents. As no sacrificial oxidant is necessary, this method may be attractive for the formation of amino acids in proteins, as well as in other systems sensitive to the presence of oxidants.

RESULTS AND DISCUSSION

The photochemical reaction was carried out at room temperature. Initially, *N*-(4-methoxy)phenylglycine ethyl ester (**1a**) and ethyl 2-oxocyclopentanecarboxylate (**2a**) were used as model substrates for this type of cross-coupling hydrogen evolution reaction. After 5 mol % of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ and 10 mol % of $Co(dmgH)_2pyCl$ were added to an anhydrous CH_3CN solution containing **1a** and **2a**, the reaction mixture was deaerated by bubbling argon for 30 min and then irradiated by blue LEDs (λ_{max} 450 ± 10 nm) for 12 h. Gratifyingly, 35% of **1a** was consumed to yield 9% of the cross-coupling product **3a** and 27% of H_2 (Table 1, entry 1). In addition, the cross-coupling product **3a** and H_2 are the only products detected. Increasing the amount of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ resulted in an improvement of both conversion and the chemical yield of the reaction. When 10 mol % of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was used, the conversion increased to 52% and the yields of the cross-coupling product and H_2 approached 67% and 58%, respectively (Table 1, entries 2 and 3). On the other hand, 5 mol % of $Co(dmgH)_2pyCl$ was found to be sufficient for the cross-coupling reaction of glycine ester **1a** and β-keto ester **2a**: i.e., 88% and 80% yields of the cross-coupling product **3a** and H_2 could be obtained without any aid of sacrificial oxidant (Table 1, entries 2, 4, and 5). Other cobalt complexes, $Co(dmgH)_2Cl_2$ and $Co(dgmH)_2py_2$, were also used for the same transformation, yet inferior results were obtained (Figure 1 and Table 1, entries 6 and 7). Solvent screening indicated that CH_3CN was a more effective reaction medium than THF, DMF, and $CHCl_3$ (Table 1, entries 8–10). Addition of 1 drop of water greatly decreased the performance of the reaction (Table 1, entry 11). To ensure that the cross-coupling hydrogen evolution reaction was indeed occurring in the absence of water, $Ru(bpy)_3(PF_6)_2$ was employed to replace $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as the photosensitizer. To our surprise, the conversion of the reaction largely improved from 49% to 75% with no alteration of H_2 amounts (Table 1, entry 12). Prolonged irradiation (48 h) resulted in 100% conversion without any loss of the efficiency of the cross-coupling product and H_2 (Table 1, entry 13). Clearly, the cross-coupling reaction of glycine derivatives occurred in the absence of any oxidant, base, and water. Control experiments suggested that the conversion of **1a** was negligible when $Ru(bpy)_3(PF_6)_2$ or

Table 1. Optimization of the Reaction[a]



entry	solvent	T/h	conversion/%[b]	yield of **3a**/%[b]	dr[b]	yield of H_2/%[c]
1[d]	CH_3CN	12	35	9		27
2	CH_3CN	12	52	67	1:0.8	58
3[e]	CH_3CN	12	62	56	1:2.1	38
4[f]	CH_3CN	12	49	88	1:1.3	80
5[g]	CH_3CN	12	30	21	1:1.2	21
6[f,h]	CH_3CN	12	<5	trace		trace
7[f,i]	CH_3CN	12	27	44	1:1.4	70
8[f]	THF	12	37	trace		12
9[f]	DMF	12	50	trace		34
10[f]	$CHCl_3$	12	<5	trace		0
11[f,j]	CH_3CN	12	50	52	1:1.3	88
12[f,k]	CH_3CN	12	75	83	1:1.1	81
13[f,k]	CH_3CN	48	100	84	1:1.4	88
14[f,k,l]	CH_3CN	48		ND		ND
15[f,k,m]	CH_3CN	48	NR	NR		ND
16[f,k,n]	CH_3CN	48	NR	NR		ND

[a]Unless otherwise specified, the reaction was carried out with **1a** (0.1 mmol) and **2a** (0.2 mmol) in the presence of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (10 mol %) and $Co(dmgH)_2pyCl$ (10 mol %) in anhydrous solvent (4 mL) under 450 nm blue LED irradiation at room temperature. Abbreviations: PMP, 4-methoxyphenyl; ND, not detected; NR, no reaction. [b]The conversion, yield, and diastereomeric ratio were determined by ^1H NMR using diphenylacetonitrile as an internal standard. [c]Yields were detected by gas chromatography using pure methane as an internal standard based on **1a**. [d]5 mol % of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was used. [e]20 mol % of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was used. [f]5 mol % of $Co(dmgH)_2pyCl$ was used. [g]2.5 mol % of $Co(dmgH)_2pyCl$ was used. [h]5 mol % of $Co(dmgH)_2Cl_2$ was used instead of $Co(dmgH)_2pyCl$. [i]5 mol % of $Co(dmgH)_2py_2$ was used instead of $Co(dmgH)_2pyCl$. [j]A drop of water was added into the mixture. [k]10 mol % of $Ru(bpy)_3(PF_6)_2$ was used instead of $Ru(bpy)_3Cl_2{\cdot}6H_2O$. [l]$Co(dmgH)_2pyCl$ was absent from the reaction system. [m]$Ru(bpy)_3(PF_6)_2$ was absent from the reaction system. [n]The reaction was carried out in the dark.

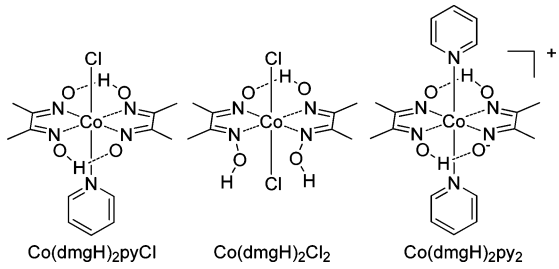


Figure 1. Structure of cobaloxime complexes.

$Co(dmgH)_2pyCl$ was absent from the reaction mixture, and no conversion of **1a** could be detected if the reaction was conducted in darkness (Table 1, entries 14–16). As a result, the site-specific modification of α-amino acids is achieved efficiently under optimal conditions: i.e., 10 mol % of $Ru(bpy)_3(PF_6)_2$, 5 mol % of $Co(dmgH)_2pyCl$, in anhydrous CH_3CN, under irradiation by blue LEDs (λ_{max} 450 ± 10 nm) at room temperature.

With the optimal conditions in hand, we explored the generality of the cross-coupling hydrogen evolution reaction on

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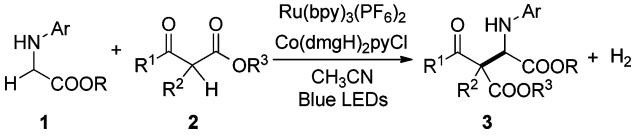
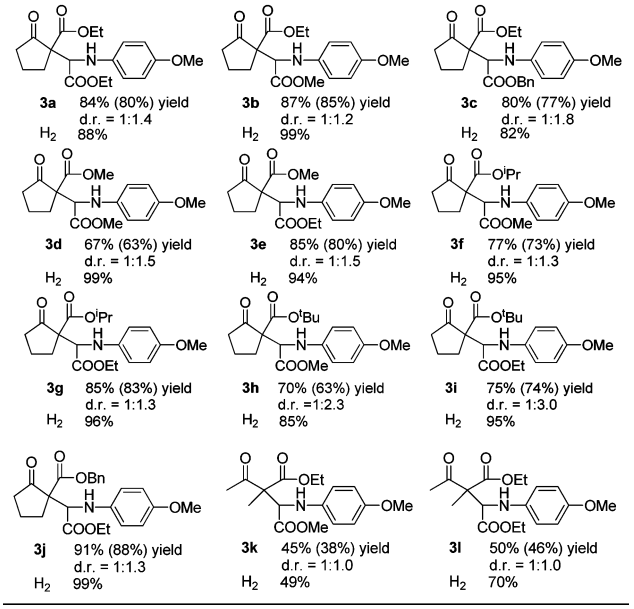
the scope of glycine esters and β-keto esters (Table 2). Secondary amines, glycines with different ester groups, could react with ethyl 2-oxocyclopentanecarboxylate (**2a**) smoothly to afford the corresponding cross-coupling products and H_2 in good to excellent yields (Table 2, **3a−c**). Note that the *p*-methoxyphenyl linked to the N atom of the glycine ester was essential to the reaction, while other functional groups (*p*-H, *p*-Cl, *p*-Br, *p*-NO_2) showed negligible efficiency (Table S1 in the Supporting Information). β-Keto esters with various substituents, on the other hand, had little effect on the outcome of the reaction; up to 91% and 99% yields of the cross-coupling product and H_2 were achieved, respectively (Table 2, **3d−j**). Intriguingly, acyclic β-keto esters were also suitable for the cross-coupling hydrogen evolution transformation. Moderate to good yields of the cross-coupling products and H_2 were obtained (Table 2, **3k,l**). Additionally, indoles with various substituents at different positions could also be introduced to the α-position of glycine esters with moderate to good yields of cross-coupling products and H_2 (Table 3). Halogen atoms were tolerated in our reaction system, albeit with somewhat lower product yields, which provides an opportunity for further functionalization.

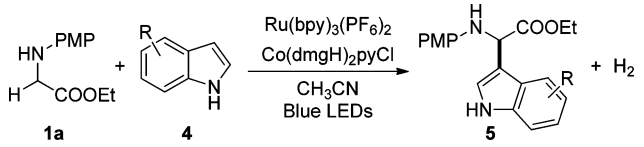
Table 2. Scope of the Substrates[a]

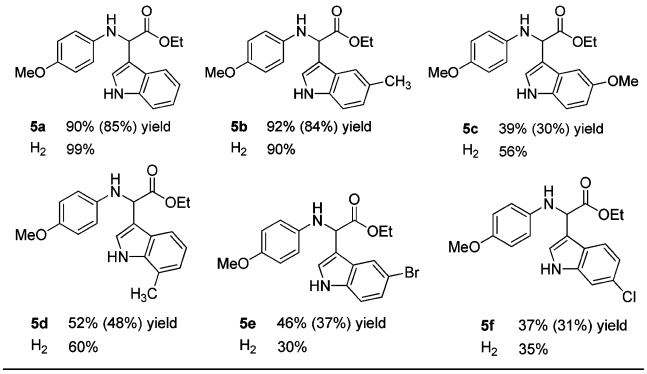




[a]Unless otherwise specified, the reaction was carried out with **1** (0.1 mmol) and **2** (0.2 mmol) in the presence of $Ru(bpy)_3(PF_6)_2$ (10 mol %) and $Co(dmgH)_2pyCl$ (5 mol %) in anhydrous CH_3CN (4 mL) under 450 nm blue LED irradiation at room temperature. All of the experiments were carried out at least three times, and the results are given by taking the average. The yields and diastereomeric ratios of coupling products were determined by ^1H NMR using diphenylacetonitrile or 1,3,5-trimethoxybenzene as an internal standard. Isolated yields are given in parentheses. Yields of hydrogen were detected by gas chromatography using pure methane as an internal standard based on **1**.

Table 3. Cross-Coupling Hydrogen Evolution Reaction between 1a and Indoles[a]





[a]Unless otherwise specified, the reaction was carried out with **1a** (0.1 mmol) and **4** (0.2 mmol) in the presence of $Ru(bpy)_3(PF_6)_2$ (10 mol %) and $Co(dmgH)_2pyCl$ (5 mol %) in anhydrous CH_3CN (4 mL) under 450 nm blue LED irradiation at room temperature. The yields of coupling products were determined by ^1H NMR using diphenylacetonitrile or 1,3,5-trimethoxybenzene as an internal standard. Isolated yields are given in parentheses. Yields of hydrogen were detected by gas chromatography using pure methane as an internal standard based on **1a**. PMP = 4-methoxyphenyl.

To shed light on the mechanism for this cross-coupling hydrogen evolution reaction, a flash photolysis study was carried out in degassed CH_3CN at room temperature. Upon laser excitation by 450 nm light, a strong negative bleach of the ground-state absorption of metal-to-ligand charge transfer (MLCT) state of $Ru(bpy)_3(PF_6)_2$ at ∼450 nm and a characteristic absorption at ∼350 nm ascribed to the reductive state of bipyridine of $Ru(bpy)_3(PF_6)_2$ were detected (Figure 2a).[25−27] When glycine ester **1a** was introduced into a solution of $Ru(bpy)_3(PF_6)_2$, a new absorption with a maximum at ∼520 nm that is characteristic of $Ru(bpy)_3^{+}$ [28,29] was detected in addition to the strong absorption of reductive state of bipyridine (Figure 2b). From the kinetics probed at 450 nm, we found that the lifetime of the ^{3}MLCT excited state of $Ru(bpy)_3(PF_6)_2$ changed from 550 to 311 ns when glycine ester **1a** was present in the reaction system (Figure 2c). A similar phenomenon was observed in an emission quenching study of $Ru(bpy)_3(PF_6)_2$ by glycine ester **1a** (Figure S1 in the Supporting Information). Monitoring the kinetics of absorption at 520 nm revealed the fast rise (247 ns) and slow decay (1683 ns) of the $Ru(bpy)_3^{+}$ intermediate (Figure 2d, blue line). All of the results suggested that the electron transfer from glycine ester **1a** to the excited ^{3}MLCT state of $Ru(bpy)_3(PF_6)_2$ took place, yielding the reduced $Ru(bpy)_3^{+}$ intermediate. The $Ru(bpy)_3^{+}$ intermediate was increased as a function of the concentration of glycine ester **1a** shown in Figure 2e, with the pseudo-first-order rate constant (K_{rise}) being 7.5×10^8 M^{-1} s^{-1}. Following the electron transfer, the $Ru(bpy)_3^{+}$ intermediate would interact with cobalt catalyst that is able to capture the electrons and protons delivered by the substrates. Indeed, with the addition of $Co(dmgH)_2pyCl$ into the mixture of $Ru(bpy)_3(PF_6)_2$ and **1a** in anhydrous CH_3CN solution, the

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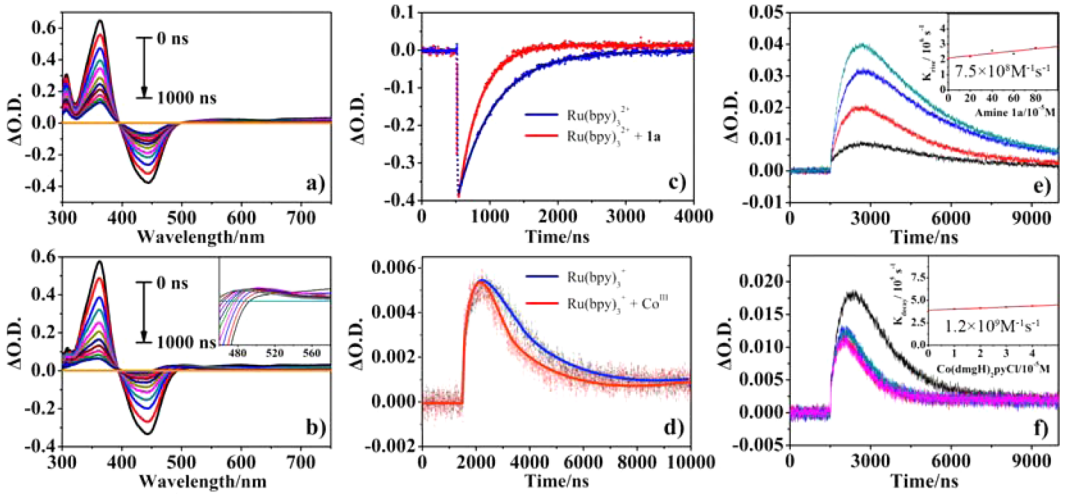
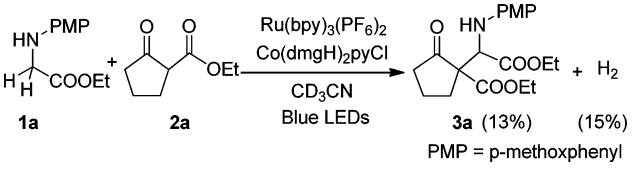


Figure 2. Nanosecond transient absorption (TA) spectra of (a) $Ru(bpy)_3(PF_6)_2$ (4×10^{-5} M) and (b) $Ru(bpy)_3(PF_6)_2$ (4×10^{-5} M) and glycine ester **1a** (1.6×10^{-4} M) in CH_3CN at the indicated delay times after 450 nm excitation. The inset shows the expanded view of the same TA spectra in the 460−560 nm region. (c) Comparison of the nanosecond TA kinetics of $Ru(bpy)_3(PF_6)_2$ (4×10^{-5} M) at 450 nm in the absence (blue line, λ_{ex} 450 nm) and presence of glycine ester **1a** (red line, λ_{ex} 450 nm). (d) Comparison of the formation and decay kinetics of the $Ru(bpy)_3^{+}$ intermediate at 520 nm in the absence (blue line) and presence (red line) of $Co(dmgH)_2pyCl$ (4×10^{-5} M) (red line) in CH_3CN solution (λ_{ex} 440 nm). (e) $Ru(bpy)_3^{+}$ intermediate absorption kinetics at 520 nm as a function of the concentration of glycine ester **1a** in CH_3CN (λ_{ex} 440 nm). The inset shows the plot of the pseudo-first-order rate constant (K_{rise}) for the formation of $Ru(bpy)_3^{+}$ intermediate. (f) $Ru(bpy)_3^{+}$ intermediate absorption kinetics at 520 nm in the presence of $Co(dmgH)_2pyCl$ in CH_3CN (λ_{ex} 440 nm). The inset shows the plot of the pseudo-first-order rate constant (K_{decay}) for electron transfer from the $Ru(bpy)_3^{+}$ intermediate to $Co(dmgH)_2pyCl$ vs $Co(dmgH)_2pyCl$.

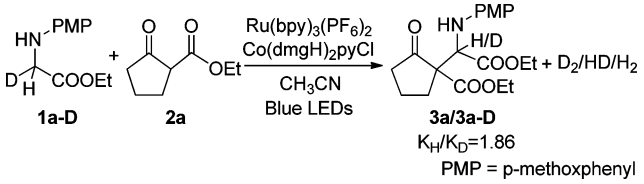
lifetime of reduced $Ru(bpy)_3^{+}$ decreased from 1683 to 1548 ns, which provided direct evidence for the electron transfer from the $Ru(bpy)_3^{+}$ intermediate to the $Co(dmgH)_2pyCl$ catalyst (Figure 2d, red line). In addition, the decay of the $Ru(bpy)_3^{+}$ intermediate moiety at 520 nm obeyed pseudo-first-order kinetics, with the rate constant being 1.2×10^9 M^{-1} s^{-1} (Figure 2f). As a result, $Ru(bpy)_3(PF_6)_2$ was recovered and the reduced $Co(dmgH)_2pyCl$ was formed. It is known that the reduced cobalt catalyst is able to capture the electrons and protons delivered by the amine radical cation to produce Co^{III}−H for H_2 evolution.[20,30,31]

In contrast to the cross-coupling hydrogen evolution reaction reported for tertiary amines, the current study for secondary amines was exclusively performed in anhydrous CH_3CN instead of water or a water-containing organic solvent. To identify the source of H_2 in this reaction, we designed a set of deuterium experiments. When CD_3CN was used instead of CH_3CN as the solvent, only H_2 and no D_2 was produced with no alteration of reaction efficiency throughout the reaction, in addition to the generation of cross-coupling product **3a** (Scheme 2). This finding confirmed that the source of H_2 was not from the solvent but the substrates in the system. When partially deuterated **1a-D** was used to react with β-keto ester **2a** under the same conditions, the ratio **3a**/**3a-D** (1.86) suggested that the dissociation of proton from glycine ester **1a** might be a rate-determining step for the cross-coupling hydrogen evolution process (Scheme 3). It should be pointed

Scheme 2. Deuterium Experiments

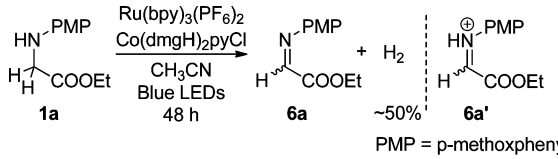


Scheme 3. Kinetic Isotope Effect



out that, when β-keto ester **2a** was absent from the system, secondary amine **1a** could evolve H_2 in a yield of 50% (Scheme 4). However, the presence of β-keto ester **2a** greatly improved

Scheme 4. Absence of Nucleophile



the yield of H_2 to 88% at an identical irradiation time (Table 1, entry 13), suggesting that the proton from β-keto ester **2a** also contributed to the H_2 evolution.

On the basis of these experimental results, a tentative mechanism taking β-keto esters as the nucleophiles was proposed (Scheme 5). Upon visible light irradiation of $Ru(bpy)_3^{2+}$ to its excited state $Ru(bpy)_3^{2+*}$, an electron transfer from **1** to $Ru(bpy)_3^{2+*}$ takes place, giving rise to an amine radical cation and reduced $Ru(bpy)_3^{+}$, the latter of which is further oxidized by $Co(dmgH)_2pyCl$ (Co^{III}) to regenerate $Ru(bpy)_3^{2+}$ and at the same time to yield the reduced Co^{II}. The amine radical cation subsequently releases an electron and/or proton to the reduced Co^{II} to afford the imine cation or imine and highly active Co^{I} species as well. The imine cation or imine is then captured by β-keto ester to give the cross-coupling

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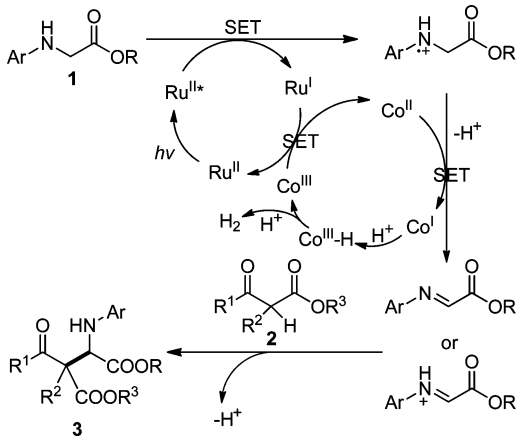
Scheme 5. Proposed Mechanism



product **3**. On the other hand, the Co^{I} species is reacted with protons delivered by the substrates to produce Co^{III}–H hydride. H_2 is generated by either protonation of Co^{III}–H hydride, H_2 elimination, and reduction of Co^{III} to Co^{II} or reduction of Co^{III}–H hydride to Co^{II}–H hydride followed by protonation to give H_2 and Co^{II}. The alternative involves a reaction between two Co^{III}–H hydrides to form H_2 and two molecules of Co^{II}.[32−35] In addition, the cobalt complexes may coordinate with β-keto ester **2** to activate the species[36] for a more effective cross-coupling reaction with imine and/or imine cation. On the whole, the cascade electron transfers from substrate **1** to the excited $Ru(bpy)_3^{2+}$* to produce $Ru(bpy)_3^{+}$ intermediate and then from the reduced $Ru(bpy)_3^{+}$ intermediate to $Co(dmgH)_2pyCl$ are believed to be responsible for the two catalytic cycles of efficient cross-coupling hydrogen evolution reactions in anhydrous solution.

CONCLUSION

In summary, we have established a new cross-coupling hydrogen evolution reaction for the synthesis of amino acid derivatives that involves coupling of glycine esters with β-keto esters or indole derivatives by visible light catalysis under oxidant-free and water-free conditions. Good to excellent yields of cross-coupling products are readily obtained in anhydrous solution under ambient conditions, and only H_2 is generated as a side product throughout the reaction. This is, to the best of our knowledge, the first example of direct site-specific modification of an α-amino acid by C–H bond functionalization without need for sacrificial oxidant or external base. The unique cross-coupling hydrogen evolution reaction is attractive because it not only expands the scope of substrates from tertiary amines to secondary amines but also realizes the cross-coupling hydrogen evolution transformation from working in water or water-containing solutions to organic solvents. A mechanistic study reveals that the cascade electron transfer processes from glycine ester to the photoexcited $Ru(bpy)_3(PF_6)_2$, and then to $Co(dmgH)_2pyCl$ catalyst, together with the capture of protons delivered by substrates, are crucial for the cross-coupling hydrogen evolution reaction in organic solvents. With the advantages of site specificity, mild conditions, and simple operation by visible light catalysis, the cross-coupling hydrogen evolution reaction presented should open the door to the formation of amino acids in proteins, as well as in other systems sensitive to the presence of oxidants, base, and/or water, which is being actively pursued in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00093.

Experimental procedures, methods, and product characterization (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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