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Combining Visible Light Catalysis and Transition Metal Catalysis for the Alkylation of Secondary Amines

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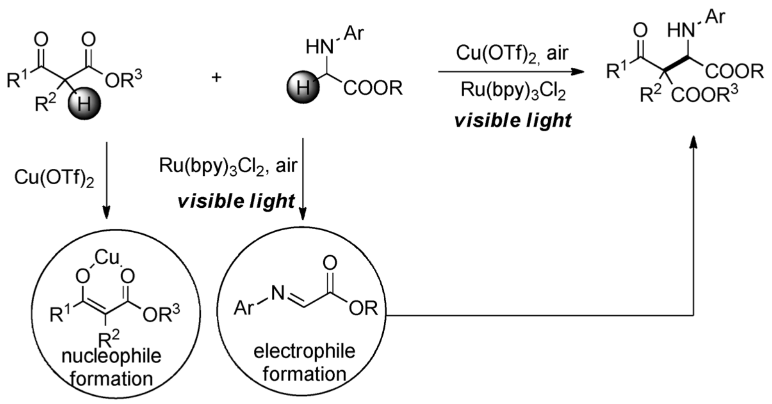
Abstract: By combining the visible-light catalyst, $Ru(bpy)_3Cl_2$, and transition metal salts, $Cu(OTf)_2$, we are able to functionalize secondary amines to form C_{sp3}–C_{sp3} bonds with β-keto esters efficiently by an aerobic oxidative coupling reaction under visible light irradiation at ambient conditions.

Keywords: alkylation; C–H activation; cross-coupling reactions; visible light catalysis

The design of synthetic approaches to functionalize secondary amines for the generation of large arrays of diverse α-amino acid derivatives is always an important concern of synthetic chemists.[1] Although the direct oxidative coupling of a substituted group at the α-position of tertiary amines has been extensively studied,[2,3] functionalization of secondary amines remains far behind. Only four successful examples of oxidative coupling reactions, to the best of our knowledge, were reported for the synthesis of amino acid derivatives.[4–7] In 2008, Li and co-workers developed the first example of an oxidative coupling reaction of secondary amines by an oxidative C–H/C–H coupling process.[4,5] The functionality, such as aryl, vinyl, and alkynyl, had been specifically anchored at the α-position of relatively unreactive glycine amines. Huang and Xie made use of a $Cu(OAc)_2$/pyrrolidine system to catalyze the oxidative reaction, but they found that the efficiency and selectivity of the reaction were poor.[6] Moreover, Wang and co-workers reported that a $Cu(OTf)_2$/chiral bisoxazoline ligand system was able to realize the oxidative cross-coupling reaction of *N*-substituted glycine esters and α-substituted β-keto esters with high yields and enantioselectivity.[7] Nevertheless, all of the reactions need a stoichiometric amount of oxidant (i.e., DDQ or *t*-BuOOH), and some of them were undertaken at high temperature.

To activate the C–H bond of secondary amines at the α-position, no matter by which of the approaches mentioned above, the following factors must be taken into consideration: (i) the relatively high oxidation potential that makes secondary amines difficult to be oxidized; (ii) the hydrogen atom connected to the nitrogen atom of secondary amines has some acidity, and therefore the cation radical intermediate generated from secondary amines is not as stable as that from tertiary amines, which may increase the possibility of by-product formation.

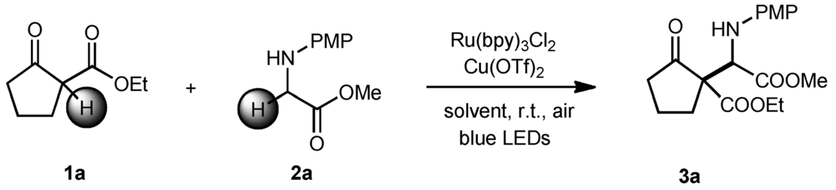
Very recently, Li and co-workers established a mild method for the α-indolylation of α-amino carbonyl compounds to build a C_{sp3}–C_{sp2} bond by using a visible-light catalysis strategy at elevated temperatures,[8] where molecular oxygen (O_2) was employed as a terminal oxidant. Rueping and co-workers, on the other hand, achieved an oxidative alkynylation of *N*-substituted tetrahydroisoquinolines by employing $[Ru(bpy)_2(dtbbpy)](PF_6)_2$ and $(MeCN)_4CuPF_6$ as the photosensitizer and metal catalyst, respectively.[9] Fu and co-workers developed the alkynylation of *N*-aryltetrahydroisoquinolines by merging Rose Bengal and CuI under visible light irradiation.[10] These appealing results inspired us to initiate the study of visible-light catalysis for the alkylation of secondary amines,[11] especially for the formation of a C_{sp3}–C_{sp3} bond of α-amino acid esters, which is more challengiung than that of a C_{sp3}–C_{sp2} or a C_{sp3}–C_{sp} bond. Since tertiary amines can be oxidized by O_2 under visible-light catalysis for the subsequent aza-Henry cross-coupling reaction,[12] we envisioned that secondary amino acid



Scheme 1. Combining visible-light catalysis and transition metal catalysis for the alkylation of secondary amines.

esters could be oxidized to generate iminium ions in the same way and, on the other hand, the aza-Henry reaction would be accelerated when transition metal salts are added to increase the nucleophilicity of β-keto esters (Scheme 1). As will be demonstrated later, the expectation was found to be indeed the case. The functionalization of secondary glycine esters has been achieved with enhanced efficiency and selectivity by

Table 1. Optimization of the reaction conditions.[a]



Entry	$Ru(bpy)_3^{2+}$	$Cu(OTf)_2$	Solvent	Time [h]	*dr*[b]	Yield [%][c]
1	1 mol%	–	CH_2Cl_2	24	–	<5
2	–	10 mol%	CH_2Cl_2	24	–	<5
3	1 mol%	10 mol%	CH_2Cl_2	24	1:1	30 (20)
4	1 mol%	10 mol%	THF	5	2:1	27 (18)
5	1 mol%	10 mol%	$CHCl_3$	6	3:2	42 (31)
6	1 mol%	10 mol%	toluene	12	2:1	50 (37)
7	1 mol%	10 mol%	DMSO	24	1:1	32 (23)
8	1 mol%	10 mol%	DMF	24	1:1	30 (22)
9	1 mol%	10 mol%	DCE	24	2:1	47 (35)
10	1 mol%	5 mol%	toluene	12	2:1	43 (34)
11	1 mol%	20 mol%	toluene	12	2:1	44 (32)
12	2 mol%	10 mol%	toluene	12	2:1	51 (37)
13	3 mol%	10 mol%	toluene	12	2:1	50 (37)
14	1 mol%	10 mol%	toluene	12	2:1	93 (86)[d]
15	1 mol%	–	toluene	12	2:1	30 (23)[d]
16	–	10 mol%	toluene	12	2:1	47 (36)[d]
17	1 mol%	10 mol%	toluene	12	2:1	NR[e]

[a] Unless otherwise specified, the reaction was carried out with **1a** (0.2 mmol) and **2a** (0.1 mmol) in the presence of $Ru(bpy)_3Cl_2$ and $Cu(OTf)_2$ in the solvent used (3 mL) under irradiation by blue LEDs at room temperature.

[b] The diastereomeric ratio (*dr*) was determined by ^1H NMR spectroscopy.

[c] Yields were measured by ^1H NMR spectroscopy using an internal standard, the isolated product yields are given in parentheses.

[d] The reaction was carried out with **1a** (0.1 mmol) and **2a** (0.2 mmol) and the yields is based on the consumption of **1a**.

[e] The reaction was carried out under an argon (Ar) atmosphere. DCE = 1,2-dichloroethane, PMP = *para*-methoxyphenyl, Tf = trifluoromethanesulfonyl and bpy = 2,2′-bipyridine, NR = no reaction.

the dual catalysis, visible-light catalysis and transition metal (copper) catalysis, giving rise to C_{sp3}–C_{sp3} cross-coupling products with moderate to excellent yields under ambient condition.

Initially, ethyl 2-oxocyclopentanecarboxylate (**1a**) and *N*-(4-methoxy)phenylglycine methyl ester (**2a**) were selected as the typical substrates for the photochemical reaction. When either $Ru(bpy)_3Cl_2$ or $Cu(OTf)_2$ was used, respectively, as the photocatalyst or the transition metal catalyst in CH_2Cl_2, only a trace of the desired cross-coupling product **3a** was obtained upon irradiation of the reaction mixture by blue LEDs ($\lambda = 450$ nm) for 24 h (Table 1, entries 1 and 2). However, the combination of $Ru(bpy)_3Cl_2$ and $Cu(OTf)_2$ in a one-pot reaction led to the formation of product **3a** in a yield of 30% under the same conditions (Table 1, entry 3). The evaluation of solvents suggested that toluene was the best solvent for the cross-coupling reaction, where a 50% yield of **3a** was obtained (Table 1, entries 3–9). Furthermore, the amounts of $Ru(bpy)_3Cl_2$ and $Cu(OTf)_2$ were carefully investigated and the results are summarized in Table 1. It is clear that 10 mol% of $Cu(OTf)_2$ showed the best result, more or less $Cu(OTf)_2$ resulted in decreases of the reaction yield and efficiency (Table, entries 6, 10 and 11). On the other hand, increasing the concentration of $Ru(bpy)_3Cl_2$ from 1 mol% to 3 mol% gave rise to almost the same yield of product **3a**, indicating that a small amount of $Ru(bpy)_3Cl_2$ (1 mol%) is sufficient for this reaction (Table 1, entries 12 and 13). Taken all together, we were delighted to see that combination of the visible light photocatalyst $Ru(bpy)_3Cl_2$ and the transition metal catalyst $Cu(OTf)_2$ is feasible to functionalize the secondary amino acid esters. When substrates **1a** and **2a** were irradiated by blue LEDs ($\lambda = 450$ nm) at ambient conditions for 12 h, the cross-coupling product **3a** could be achieved in 50% yield (Table 1, entry 6). Considering that the rate of the oxidative coupling reaction might depend on the amount of iminium ion intermediate, we modulated the ratio of **1a** and **2a** to increase the concentration of the iminium ion intermediate. As shown in Table 1, the yield of the coupling reaction was enhanced from 50% to 93% (entries 6 and 14) when the mole ratio of **1a**/**2a** was changed from 0.2/0.1 to 0.1/0.2, which further confirmed that the amount of iminium ion generated from amino acid esters is crucial for the reaction performance.

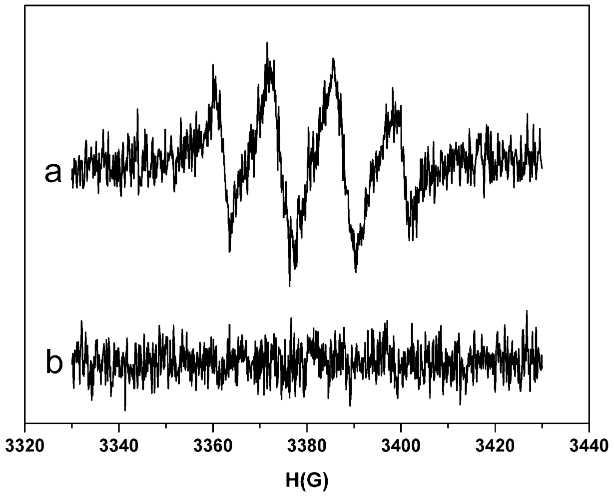
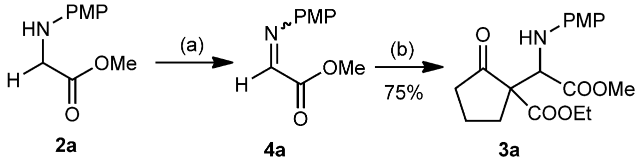


Figure 1. ESR spectrum of air-saturated toluene solution of a) **2a** (3.0×10^{-5} mol L^{-1}), $Ru(bpy)_3Cl_2$ (0.3×10^{-6} mol L^{-1}), and DMPO upon irradiation by blue LEDs for 30 s; b) **2a** (0.3×10^{-4} mol L^{-1}), $Ru(bpy)_3Cl_2\cdot(0.3\times10^{-6}$ mol L^{-1}), and TEMP upon irradiation for 30 s.

The cross-coupling reaction is an aerobic oxidative process because no photoproduct could be detected when the reaction was operated in an atmosphere of argon (Table 1, entry 17). Recent study has revealed that superoxide radical anion ($O_2^{-\bullet}$) is the real active species in the oxidative cross-coupling reaction of tertiary amines.[3a–d] To figure out the function of molecular oxygen in the oxidative reaction of glycine esters, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethyl-1-piperidine (TEMP) were employed to capture active species, $O_2^{-\bullet}$ and $^1O_2$, respectively, by electron spin resonance (ESR) spectroscopy.[13] It is evident that when the solution of DMPO, **2a** and $Ru(bpy)_3Cl_2$ in air-saturated toluene solution was irradiated with blue LED at 450 nm, a single radical was trapped (Figure 1a), the spectrum and hyperfine coupling constants of which are in line with the reported values for the adduct of $O_2^{-\bullet}$ with DMPO. By contrast, when TEMP, an $^1O_2$ scavenger, was used instead of DMPO in the same air-saturated solution, no signal was detected (Figure 1b). From these results, we infer that $O_2^{-\bullet}$ generated from molecular oxygen is the active species participating in the reaction of secondary amines.

It is of particular significance that upon irradiation of **2a** and $Ru(bpy)_3Cl_2$ in an air-saturated solution of toluene, the iminium intermediate **4a** could be isolated (Scheme 2). Strikingly, the obtained iminium intermediate **4a** can directly react with **1a** assisted by $Cu(OTf)_2$ to afford the desired product **3a** in an isolated yield of 75% within 2 h at room temperature (see the Supporting Information). These findings suggest that aerobic visible-light catalysis is responsible for the formation of an important iminium intermediate from glycine ester **2a**, and copper transition metal catalysis is helpful for the enhancement of the nucleophilicity of β-keto esters **1a** and the stabilization of the iminium intermediate **4a** as well.[14] As a result, secondary glycine ester **2a** and β-keto ester **1a** undergo the aerobic cross-coupling reaction quickly with suppression of competition from side reactions.

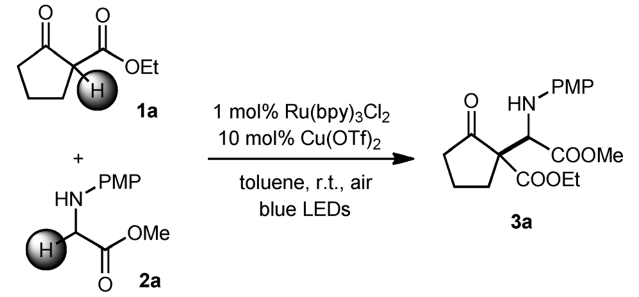
With this initial success, several copper salts were screened and $Cu(OTf)_2$ was found to be the most effi-



Scheme 2. The oxidation of *N*-PMP glycine ester (**2a**) by the dual catalysis.

cient transition metal catalyst for the alkylation of *N*-substituted gylcine ester (Table 2). As tabulated in Table 3, various β-keto esters and *N*-substituted glycine esters were studied under the optimized conditions, i.e., **1** (0.1 mmol) and **2** (0.2 mmol) in the presence of Ru(bpy)$_3$Cl$_2$ (0.001 mol) and Cu(OTf)$_2$ (0.01 mol) in air-saturated toluene solution (3 mL). For the reaction with ethyl 2-oxocyclopentanecarboxylate (**1a**), a series of *N*-substituted glycine esters, bearing electron-donating and electron-withdrawing groups on the 4-position of phenyl ring of **2**, was examined. All of them could be successfully transformed to their desired products **3** in the moderate to excellent yields (58–93%, Table 3, entries 1–5). Note that substrates **2** containing electron-donating groups on the phenyl ring showed better yields. For the reactions with *N*-(4-methoxy)phenyl-glycine ethyl ester (**2b**), β-keto esters also have a wide range of applicability. Substituted methyl, sterically bulky isopropyl, *tert*-butyl or benzyl groups showed good to excellent yields of 73–91% (Table 3, entries 6–9). Similar results were also observed for the reaction with **2a** (Table 3, entries 10 and 11), even for less reactive acyclic β-keto esters (Table 3, entries 12–14).

Table 2. Selection of copper catalyst.[a]



Entry	[Cu]	Solvent	*dr*[b]	Yield [%][c]
1	Cu(OTf)$_2$	toluene	2:1	93 (86)
2	CuBr	toluene	2:1	62 (50)
3	CuCl	toluene	3:2	70 (61)
4	CuI	toluene	3:1	48 (37)
5	Cu(OTf)	toluene	2:1	80 (71)
6	Cu(OAc)$_2$·H$_2$O	toluene	2:1	69 (62)

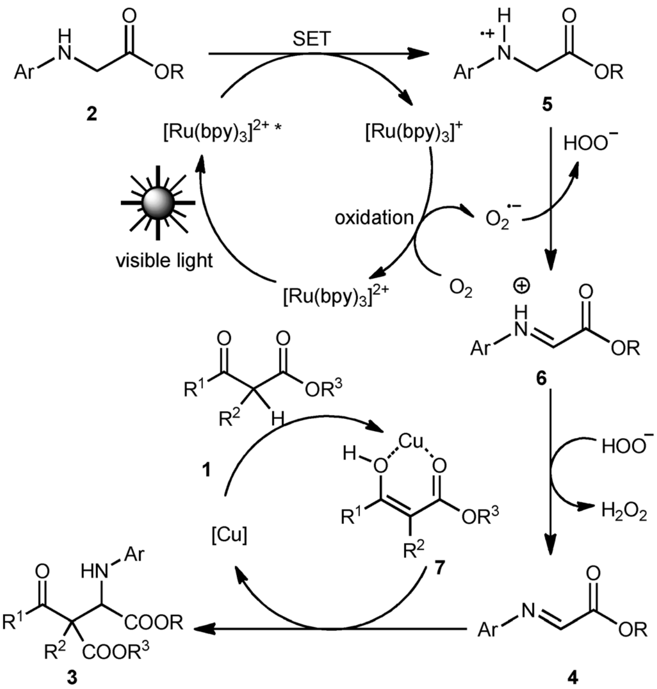
[a] Unless otherwise specified, the reaction was carried out with **1a** (0.1 mmol) and **2a** (0.2 mmol) in the presence of Ru(bpy)$_3$Cl$_2$ (0.001 mol) and Cu(OTf)$_2$ (0.01 mol) in the solvent (3 mL) under bule LEDs irradiation at room temperature.

[b] The diastereomeric ratio (*dr*) was determined by ^{1}H NMR spectroscopy.

[c] Yields were measured by ^{1}H NMR spectroscopy using an internal standard, the isolated product yields are given in parentheses.

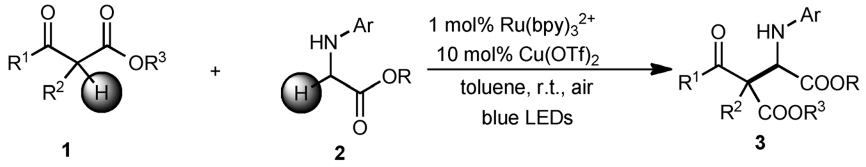
On the basis of the above results, we could speculate a plausible mechanism for the reaction as follows (Scheme 3): upon irradiation of [Ru(bpy)$_3$]$^{2+}$ by visible light, a single electron transfer from substrate **2** to the excited state of [Ru(bpy)$_3$]$^{2+}$ affords an aminyl cation radical **5** and reduced [Ru(bpy)$_3$]$^+$, the latter is regenerated by molecular oxygen, and at the same time to form an active species O$_2^{-\bullet}$ (supported by ESR experiments). Then aminyl cation radical **5** is further transformed to iminium ion **6** by interacting with the superoxide radical anion O$_2^{-\bullet}$. Subsequently, the HOO$^-$ ion generated *in situ* abstracts another hydrogen atom from iminium ion **6** to produce iminium intermediate **4**, as shown in Scheme 2. On the other hand, transition copper salts can coordinate with β-keto esters to increase their nucleophilicity.[15] And hence the generated strong nucleophilic species **7** attacks iminium intermediate **4** quickly to yield the C$_{sp3}$–C$_{sp3}$ cross-coupling product **3** and to release the copper salt for the next catalytic cycle.

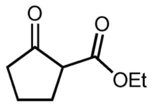
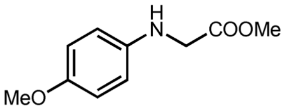
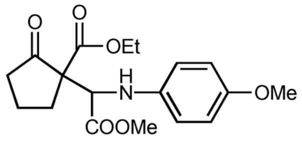
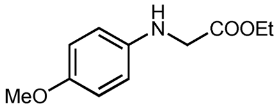
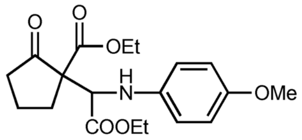
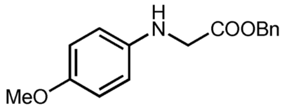
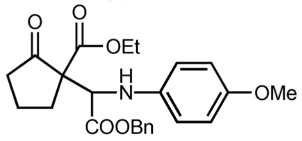
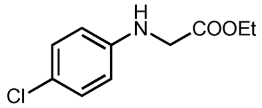
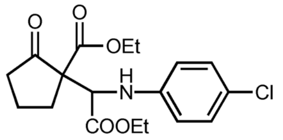
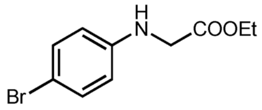
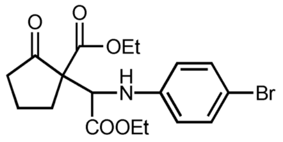
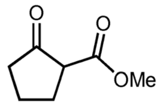
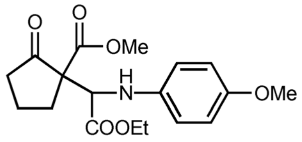
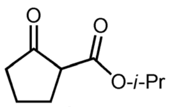
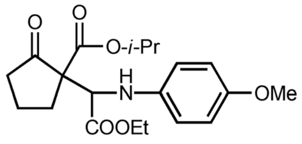
In summary, we have developed a dual catalytic system for the α-C–H functionalization of secondary amines. Taking advantage of visible-light catalysis and



Scheme 3. The proposed reaction mechanism.

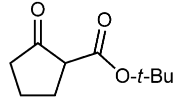
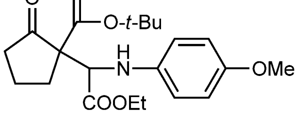
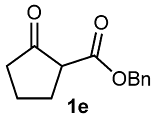
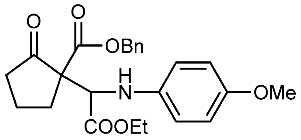
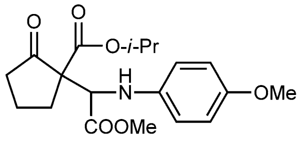
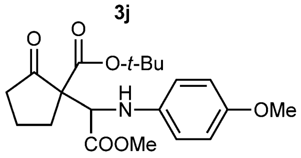
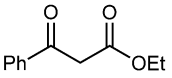
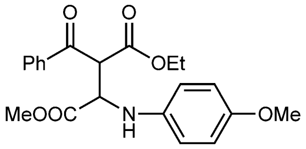
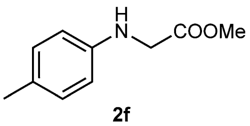
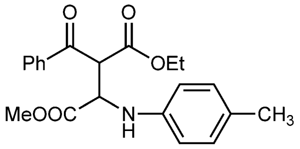
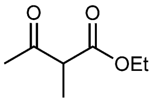
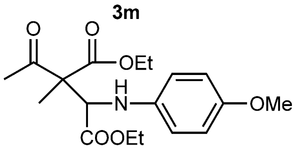
Table 3. Investigation of the scope of the procedure.[a]



Entry	1	2	Product	*dr*	Yield [%]
1	 **1a**	 **2a**	 **3a**	2:1	93 (86)
2	**1a**	 **2b**	 **3b**	2:1	82 (75)
3	**1a**	 **2c**	 **3c**	3:1	80 (72)
4	**1a**	 **2d**	 **3d**	2:1	67 (53)
5	**1a**	 **2e**	 **3e**	2:1	58 (43)
6	 **1b**	**2b**	 **3f**	2:1	73 (67)
7	 **1c**	**2b**	 **3g**	2:1	91 (80)

transition metal catalysis, the efficiency of the oxidative coupling reaction was improved greatly, i.e., from 30% for $Ru(bpy)_3Cl_2$ and 47% for $Cu(OTf)_2$, respectively, to 93% for a combination of the two catalysts under the optimal conditions. The reaction proceeds efficiently in the presence of molecular oxygen, thus avoiding usage of stoichiometric amounts of oxidant (e.g., DDQ or *t*-BuOOH). It is anticipated that this research line would provide an effective way to functionalize secondary amino acid esters under mild condition, which is actively under study in our group.

Table 3. (Continued)

Entry	1	2	Product	*dr*	Yield [%]
	1a	**2a**	**3a**		
8	 **1d**	**2b**	 **3h**	2:1	89 (80)
9	 **1e**	**2b**	 **3i**	2:1	80 (75)
10	**1c**	**2a**	 **3j**	3:1	91 (80)
11	**1d**	**2a**	 **3k**	3:1	75 (67)
12	 **1f**	**2b**	 **3l**	1:1	82 (75)
13	**1f**	 **2f**	 **3m**	1:1	81 (76)
14	 **1g**	**2b**	 **3n**	2:1	52 (30)

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[a] Unless otherwise specified, the reaction was carried out with **1** (0.1 mmol) and **2** (0.2 mmol) in the presence of $Ru(bpy)_3Cl_2$ (0.001 mol) and $Cu(OTf)_2$ (0.01 mol) in anhydrous toluene (3 mL) under blue LEDs irradiation at room temperature.

[b] The diastereomeric ratio (*dr*) was determined by ^1H NMR spectroscopy.

[c] Yields were measured by ^1H NMR spectroscopy using an internal standard, the isolated product yields are given in parentheses.

Experimental Section

For detailed experimental procedures, spectral data and characterization see the Supporting Information.

Experimental Procedure for the Alkylation of Secondary Amines

A 10-mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with β-keto ester **1** (0.1 mmol), *N*-arylglycine ester **2** (0.2 mmol), $Ru(bpy)_3Cl_2$ (0.001 mmol), $Cu(OTf)_2$ (0.01 mmol) and anhydrous toluene

(3 mL). The resulting mixture was irradiated by blue LEDs for 12 h. After the reaction was completed (monitored by TLC), the reaction mixture was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **3**.

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