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TBHP mediated oxidation of *N*-2-alkynylphenyl α-amino carbonyl compounds to oxalic amides using visible light photoredox catalysis and their application in the synthesis of 2-aryl indoles†

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A visible light promoted and TBHP mediated oxidative reaction of *N*-2-alkynylphenyl α-amino carbonyl compounds to *N*-2-alkynylphenyl oxalic amides was developed. In the presence of CuBr and photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$, the reaction proceeded smoothly to afford the corresponding oxalic amides under the irradiation of a 26 W compact fluorescence bulb at room temperature. Furthermore, *N*-2-alkynylphenyl oxalic amides could be subsequently transferred to 2-aryl indoles without an additional deacylation step through a favored 5-*endo*-dig *N*-cyclization process using $AgNO_3$ as catalyst.

The α-amino carbonyl is an important structural unit of many natural and synthetic compounds with diverse biological activities.[1,2] In biological systems, the peptide backbone is also constructed of α-amino carbonyl units.[3] For these reasons, the α-functionalization of α-amino carbonyl compounds represents an important transformation in organic chemistry.[4] Among these transformations, the oxidative cross dehydrogenative coupling (CDC)[5,6] of *N*-aryl α-amino carbonyl compounds such as glycine derivatives has attracted significant attention since the pioneering study of Zhao and Li in 2008.[6a] In 2010, Huang and coworkers developed a CDC reaction between α-amino acid derivatives and ketones under the cooperative catalysis of a copper salt and secondary amine.[6b] Recently, Wang reported an asymmetric CDC reaction of *N*-substituted glycine esters with α-substituted β-ketoesters by a chiral copper catalyst.[6c] More recently, Huang's group developed a CDC reaction between methylquinoline derivatives and *N*-aryl glycine to provide β-quinolinyl α-amino acid esters.[4m]

However, the CDC α-functionalization is not the predominant transformation of α-amino carbonyl during the radical-mediated protein damaging process in biological systems. In fact, the formation of α-carbon radicals of α-amino carbonyl units generally leads to the peptide backbone oxidations and fragmentations *via* oxalic acid derivatives and imine intermediates.[3] Recently, Huo reported an aerobic auto-oxidative of glycine derivatives to obtained oxalic acid derivatives using dioxygen.[7] Li and coworkers also demonstrated that visible light could promote the oxidation of *N*-aryl glycine ester to oxalic amide under dioxygen atmosphere with $Ru(bpy)_3Cl_2$ as photocatalyst.[6g] In the last half decade, visible light photoredox catalysis with transition metal complexes such as polypyridyl complexes of ruthenium has received much attention.[8] Although that molecular oxygen has also been used as oxidant in the photoredox-mediated oxidative organic reactions,[9] these reactions were often catalyzed by photocatalysts in combination with stoichiometric amounts of chemical oxidants such as $BrCCl_3$,[10] $K_2S_2O_8$,[11] $Co(acac)_3$,[12] *m*-dinitrobenzene (*m*-DNB)[13] and aryl diazonium salts.[14] Following our exploring process for the visible light promoted oxidative reaction,[15] we found that visible light could promote the chemoselective oxidation of *N*-2-alkynylphenyl glycine ester **1a** to the oxalic amide derivatives **2a** with stoichiometric oxidant *tert*-butyl hydroperoxide (TBHP) (Scheme 1).

Initially, we hoped to access 2,3-diacylated indole **3a** (Scheme 1) with *N*-2-alkynylphenyl glycine ester **1a** as substrate *via* activated imine intermediate **4a** followed by an intramolecular nucleophilic attack with the alkyne as reported by Patel.[16] Thus, the reaction was firstly carried out in DMSO with aqueous TBHP as oxidant. Disappointingly, no desired indole derivative **3a** was obtained. The oxalic derivative **2a**, an isomer of **3a**, was isolated in 3% yield along with the imine **4a** and 2-ethynylaniline **5a** as major products. To gain an insight into this type of oxidative reaction, we were

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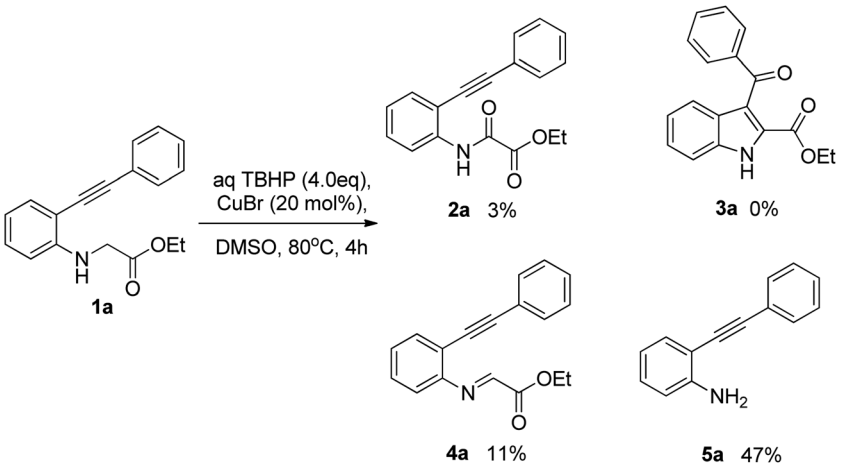
‡ These authors contributed equally to this work and should be considered joint first authors.

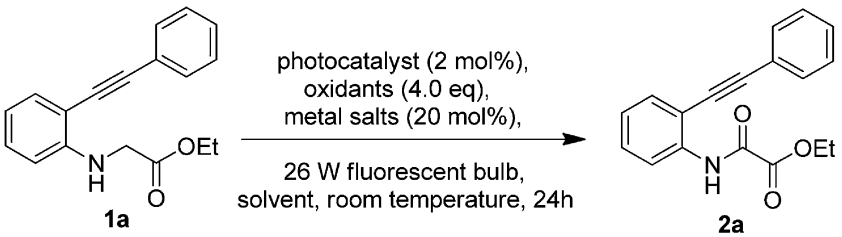


Scheme 1 Transformation of *N*-2-alkynylphenyl glycine ester **1a**.

encouraged to optimize the reaction parameters to promote the yield of oxalic acid derivative **2a** under more mild conditions using photocatalytic strategy.

We opted to investigate the photoredox transformation of module substrates *N*-2-alkynylphenyl glycine ester **1a** to oxalic amide **2a** (Table 1). The ruthium complex

Table 1 Reaction conditions evaluation[a]



Entry	Oxidants	Solvent	Photocatalyst 2% mol	Metal salts 20% mol	Yield[b] %
1	aq. TBHP	MeCN	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	4
2	aq. TBHP	DMSO	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	8
3	TBHP in decane	MeCN	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	35
4	TBHP in decane	DMSO	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	42
5	TBHP in decane	MeCN[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	40
6	TBHP in decane	DMSO[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	50
7	TBHP in decane	DMSO[c]	$Ru(phen)_3Cl_2$	CuBr	28
8	TBHP in decane	DMSO[c]	$Ir(ppy)_3$	CuBr	23
9	TBHP in decane	DMSO[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	$FeCl_3$	27
10	TBHP in decane	DMSO[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuI	31
11[d]	TBHP in decane	DMSO[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	41
12[e]	TBHP in decane	DMSO[c]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	35
13	Open air	MeCN	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	0
14	Open air	MeCN	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	—	0
15[f]	Open air	MeCN	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	—	0
16	TBHP in decane	DMSO/MeCN[g]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	57
17	$K_2S_2O_8$	DMSO/MeCN[g]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	7
18[h]	TBHP in decane	DMSO/MeCN[g]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	55
19	TBHP in decane	DMSO/MeCN[g]	—	CuBr	16
20[i]	TBHP in decane	DMSO/MeCN[g]	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	CuBr	5

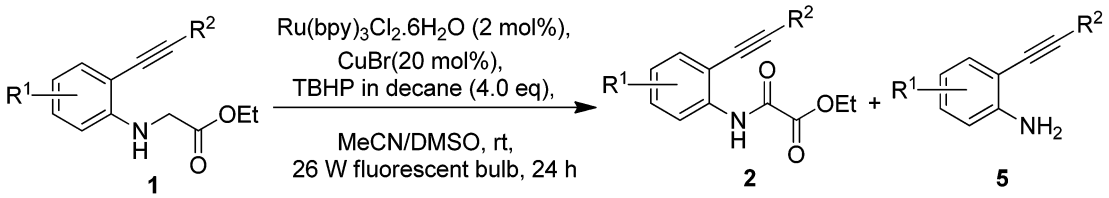
[a] Unless stated otherwise, the reaction was carried out with **1a** (0.5 mmol), oxidants (4.0 eq.), metal salts (20 mol%), and photocatalyst (2 mol%) in the indicated solvent (2 mL) and irradiated with 26 W compact fluorescent lamp for 24 h at room temperature. [b] Isolated yields. [c] Super dried solvents. [d] 10 mol% CuBr was used. [e] 40 mol% CuBr was used. [f] 1.1 eq. of K_2CO_3 was added to the reaction system. [g] Mixed solvents of super dried MeCN and DMSO ($V_{MeCN} : V_{DMSO} = 4 : 1$). [h] 3.0 eq. of TBHP was used. [i] Reaction was carried out in darkness.

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ and aqueous TBHP were chosen as the photocatalyst and oxidant respectively. When a solution of **1a**, aqueous TBHP and another 20 mol% of CuBr in MeCN was irradiated with a household 26 W compact fluorescent bulb in the presence of 2 mol% of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ for 24 hours, the desired oxalic derivative **3a** was obtained only in 4% isolated yield (Table 1, entry 1). When DMSO was used as solvent instead of MeCN in the reaction, the yield of **3a** slightly increased to 8% (Table 1, entry 2). Under the above conditions, 2-ethynylaniline (**5a**) was isolated as major product. Thus, we considered that water from aqueous TBHP solution had a significant influence on the reaction outcome because of the side hydrolysis reaction. Next, a 6 M solution of TBHP in decane was used as oxidant instead of aqueous TBHP. Fortunately, the change of oxidant resulted in significantly increased yield of **2a** to 35% and 42% in MeCN (Table 1, entry 3) and DMSO (Table 1, entry 4) respectively. Based on the above results, the reaction was then carried out in super dried solvent and led to slightly increased yield of **2a** in MeCN (40% yield, entry 5) and DMSO (50% yield, entry 6) respectively as we expected. In contrast, replacement of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ with the complex $Ru(phen)_3Cl_2$ or $Ir(ppy)_3$ resulted in decreased yield of **3a** (entries 7 and 8). Notably, replacement of CuBr with $FeCl_3$ or CuI provided **3a** in decreased yields respectively (27% and 31% yield, entries 9 and 10). Furthermore, it should be noted that when CuBr was reduced to 10% mol or increased to 40% mol, only 41% and 35% yield of **3a** were achieved respectively (entries 11 and 12). In contrast, no desired product was detected when the oxidation reaction was carried out under open air condition in MeCN with or without Cu salts (entries 13 and 14). Furthermore, when 1.1 eq. of K_2CO_3 was added to reaction system under open air condition, no transformation of the substrate was observed (entry 15). Interestingly, however, we found that a mixed solvents of MeCN and DMSO ($V_{MeCN} : V_{DMSO} = 4 : 1$) could slightly improve the yield of **3a** (57% yield, entry 16). Furthermore, when 4.0 eq. of $K_2S_2O_8$ was used as oxidant instead of TBHP, 100% conversion of substrate was observed, but only 7% yield of desired compound **3a** could be isolated with unidentified side products (entry 17). When 3.0 eq. of TBHP was used as oxidant, the desired compound **3a** was still obtained in 55% yield (entry 18). Finally, to verify the role of photocatalyst and visible light in this type of oxidation reaction, control experiments were conducted. As outlined in Table 1, the requirement of a photocatalyst and visible light was verified, as significantly decreased outcome of **3a** was observed without photocatalyst or visible light irradiation respectively (entries 19 and 20).

With the optimal oxidative conditions in hand, we next sought to determine the scope of *N*-2-alkynylphenyl glycine esters that can be employed in this photocatalytic oxidation protocol. As shown in Table 2, the scope of alkyne motif adjacent to the nitrogen atom was examined firstly. Generally, the electron-donating group on the phenyl ring of phenylacetylene motif decreased the oxidation efficiency. For example, when group R^2 was (4-methylphenyl)ethynyl (**2b**, 52% yield, Table 2, entry 2), (4-ethylphenyl)ethynyl (**2c**, 49% yield, entry 3) or (4-methoxylphenyl)ethynyl (**2d**, 46% yield, entry 4), yields of the desired compounds were slightly lower than the model substrate (**1a**, 57% yield, entry 1). When an electron-withdrawing fluorine atom was substituted on the phenyl ring of phenylethynyl motif, moderate yields of desired compounds (**2e**, 50% yield, entry 5; **2f**, 54% yield, entry 6) were achieved. Meanwhile, the optimized conditions could be applied to synthesize oxalic derivatives **2g** (43% yield, entry 7) and **2h** (41% yield, entry 8) that possessed *tert*-butylethynyl and 1-pentyl adjacent to the nitrogen atom respectively. At this point, we thought that substituent group R^1 that directly connected on the *N*-phenyl ring possibly had more obvious effect on the yields of target compounds. Thus, we next examined the scope of R^1. As outlined in Table 2, when the substituent at the *N*-phenyl ring was an electron-donating methyl group, a deleterious effect on overall reaction yield was observed (entries 9–13). Meanwhile, 2-ethynyl anilines **5**, the byproduct from imine hydrolysis reaction, could be isolated with increased yields. To further verify the influence of R^1, fluoro (R^1 = F, entries 14–16) and chloro (R^1 = Cl, entries 17 and 18) substituted substrates were chosen for the oxidation experiments. As we expected, the yields of target compounds **2n–2p** (R^1 = F, entries 14–16) increased obviously compared with corresponding methyl substituted substrates (R^1 = Me) due to the strong electron-withdrawing ability of fluorine atom. With respect to the chloro substrates (R^1 = Cl, entries 17 and 18), target compounds **2q–2r** were provided in 49% and 38% yields which slightly decreased from the corresponding fluoro substrates (**2j–2k**). In most cases as shown in Table 2, 2-ethynyl anilines **5** could be isolated as the main byproducts. Furthermore, the structure of compound **2q** was further established by X-ray diffraction study (Fig. 1).

To the best of our knowledge, the mechanism of TBHP mediated oxidation of α-amino carbonyl to oxalic derivatives was not clear. Based on our experimental results and previous available literature,[8,9] a plausible catalytic mechanism for the visible light mediated oxidation process was proposed. As shown in Scheme 2, visible light excited Ru complex ($*Ru(bpy)_3^{2+}$) was a strong reductant ($E_{1/2}^{*II/III} = -0.81$ V *vs.* SCE),[8a] which is oxidized by TBHP to generate $Ru(bpy)_3^{3+}$ through a single electron transfer (SET) process. Meanwhile, $Ru(bpy)_3^{3+}$, a powerful oxidant ($E_{1/2}^{III/II} = 1.29$ V *vs.* SCE),[8a] is able to oxidize substrate **1** to generate the corresponding amino radical cation **6** and $Ru(bpy)_3^{2+}$ to start a new photocatalytic cycle. The relatively acidic tertiary amine radical cation **6** is deprotonated by a strongly basic species –OH and then further oxidized by an SET process resulting in the reactive imine intermediate, which coordinates with Cu^+ to provide a more reactive intermediate **7**. At this point, the activated imine carbon of intermediate **7** accepts the nucleophilic attack from TBHP or *t*-BuOH and H_2O generated from the reaction system to give *N*-hybrid acetal peroxide **8** and byproduct aniline respectively. Intermediate **8** attends the second photocatalytic cycle and is then oxidized by $Ru(bpy)_3^{3+}$ to give amino radical cation **9**, which is deprotonated by basic species *t*-BuO^- or OH^- followed by

Table 2 Visible light promoted oxidation of *N*-2-alkynylphenyl glycine esters to oxalic amides[a]



Entry	R^1	R^2	Compounds **2**	Yield of **2**[b] (%)	Compounds **5**	Yield of **5**[b] (%)
1	H	Phenyl	**2a**	57	**5a**	11
2	H	4-Me phenyl	**2b**	52	**5b**	19
3	H	4-Et phenyl	**2c**	49	**5c**	18
4	H	4-MeO phenyl	**2d**	46	**5d**	7
5	H	4-F phenyl	**2e**	50	**5e**	15
6	H	2-F phenyl	**2f**	54	**5f**	14
7[c]	H	*t*-Butyl	**2g**	43	**5g**	—
8[c]	H	*n*-Propyl	**2h**	41	**5h**	—
9	4-Me	Phenyl	**2i**	33	**5i**	35
10	4-Me	4-Me phenyl	**2j**	37	**5j**	31
11	4-Me	4-MeO phenyl	**2k**	42	**5k**	28
12	4-Me	4-F phenyl	**2l**	39	**5l**	14
13	4-Me	2-F phenyl	**2m**	32	**5m**	23
14	4-F	Phenyl	**2n**	69	**5n**	5
15	4-F	4-Me phenyl	**2o**	55	**5o**	8
16	4-F	2-F phenyl	**2p**	56	**5p**	9
17	4-Cl	4-F phenyl	**2q**	49	**5q**	14
18	4-Cl	2-F phenyl	**2r**	38	**5r**	12

[a] Conditions: compounds **2** (1.0 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%), CuBr (20 mol%), TBHP (4.0 eq.) in solvent (4 mL). [b] Isolated yield. [c] Hydrolysis products **5** were not isolated.

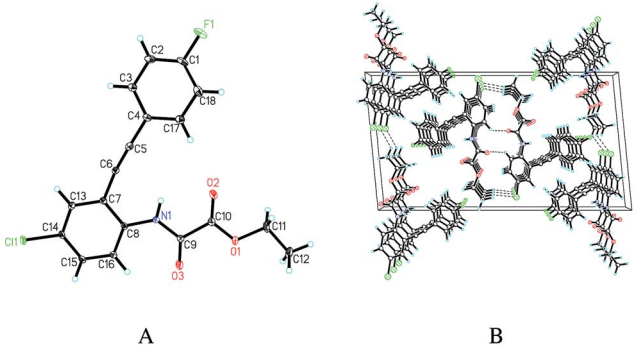
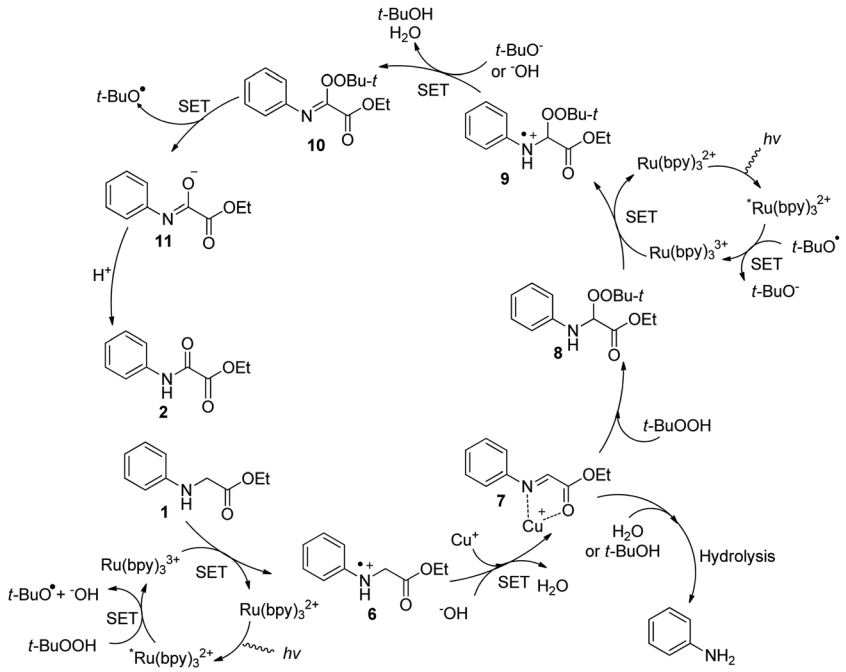


Fig. 1 X-ray derived ORTEP drawing (A) and hydrogen-bonded motif (B) of compound **2q**. Crystal data for compound **2q**: $C_{18}H_{13}ClFNO_3$, M = 345.74, monoclinic, a = 14.191(2) Å, b = 4.4973(7) Å, c = 25.988(4) Å, α = 90.00°, β = 95.570(2)°, γ = 90.00°, V = 1650.7(4) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.257 mm^{-1}, 15 559 reflections measured, 4056 independent reflections (R_{int} = 0.0691). The final R_1 values were 0.0596 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1059 ($I > 2\sigma(I)$). The final R_1 values were 0.0986 (all data). The final $wR(F^2)$ values were 0.1197 (all data). The goodness of fit on F^2 was 1.049.

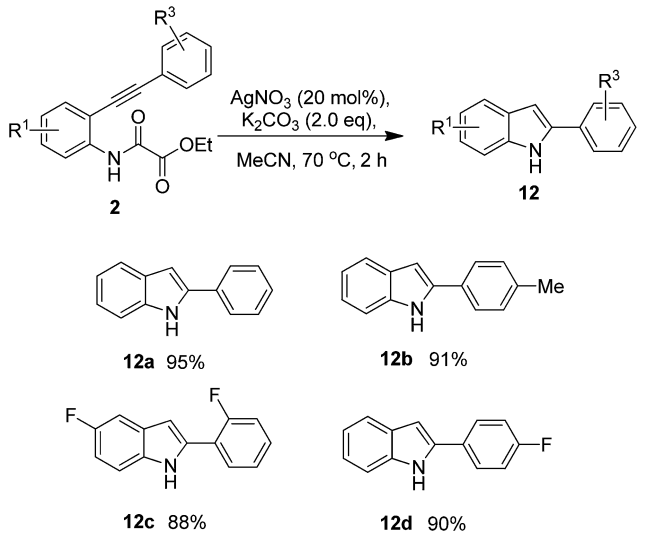
another SET process to give imine peroxide **10**. Intermediate **10** decomposes through a SET process to provide enolated anion **11**, which is finally protonated to afford the target compound **2**.

According to previous literature, the protocol for transition metal such as gold, palladium or copper catalyzed cycloisomerization of 2-alkynylaniline to indole derivatives was well established.[17] However, when the nitrogen atom of 2-alkynylaniline was acylated, the acylated 2-alkynylaniline carried two kind of nucleophiles, the *N* atom of amide and *O* atom of enolated amide. Thus, the heterocyclization could take place either through *O*- or *N*-ring closure processes.[18] With compounds **2** in hand, we next attempted to study the subsequent transformation of these oxalic amides. As shown in Scheme 3, when a solution of compound **2**, 20 mol% of $AgNO_3$ and 2.0 eq. of K_2CO_3 in MeCN was heated at 70 °C for 2 hours, the reaction proceeded through the favored 5-*endo*-dig *N*-cyclization process to provide 2-aryl indoles **12** in excellent isolated yield. Notably, no further step was needed to deacylate the *N* atom of indole. This transformation could be applied to synthesis of 3-aryl indole derivatives efficiently using cheap $AgNO_3$ as catalyst.

In conclusion, we have demonstrated a visible light promoted oxidation of *N*-2-alkynylphenyl glycine ester to oxalic amides with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ as photocatalyst and TBHP as oxidant respectively. The possible oxidation mechanism was also proposed. Furthermore, the *N*-2-alkynylphenyl oxalic amides can be used to synthesize 2-aryl indoles efficiently using $AgNO_3$ as catalyst without additional deacylation step.



Scheme 2 Possible mechanism.



Scheme 3 Transformation of oxalic amides **2** to 2-aryl indoles **12**.

Acknowledgements

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