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The Reaction of Tertiary Anilines with Maleimides under Visible Light Redox Catalysis

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Abstract: Tertiary anilines can be prompted to react with *N*-aryl- and *N*-benzylmaleimides to form tetrahydroquinoline products under photocatalysis using visible light irradiation, the ruthenium or iridium complexes $Ru(bpy)_3Cl_2$ or $Ir(ppy)_2(dtbbpy)PF_6$ as catalyst, and air as terminal oxidant.

Keywords: aerobic oxidation; maleimides; photocatalysis; tertiary anilines; tetrahydroquinolines

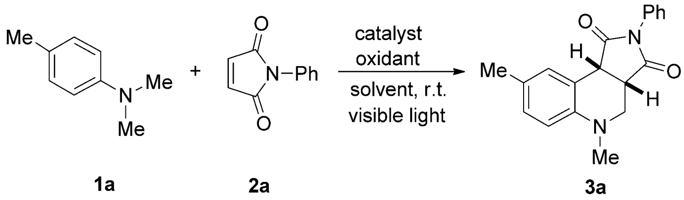
Photo-induced electron transfer (PET) has proved to be of great value in synthetic organic chemistry.[1] Many reported PET processes make use of tertiary amines as electron donors, because these molecules have low oxidation potentials. In this context, synthetic applications have been found for the single electron transfer (SET) reactions between tertiary amines and photo-excited electron accepters, which involve the addition of α-aminoalkyl radicals to alkenes as the key step.[1,2]

Recently PET reactions have rised to new prominence in organic synthesis, mostly due to the utilization of Ru(II) and Ir(III) polypyridyl complexes as photoredox catalyst to initiate organic reactions.[3] The advantages associated with Ru(II) and Ir(III) polypyridyl complexes not only allow the PET process to take place under visible light irradiation, but also raise greatly the photochemical efficiency. The synthetic potential of the so-called visible light photocatalysis or redox catalysis has been greatly demonstrated by the studies of MacMillan et al.,[4] Yoon et al.,[5] Stephenson et al.,[6] and others.[7,8] Ru(II) and Ir(III) polypyridyl complexes at their excited state can easily oxidize tertiary amines to generate α-aminoalkyl radicals, which can be further converted to the iminiums *via* a second SET process. While many current studies in this area deal with the chemistry of iminiums,[6d,f,7e–j,8a,c] recent works by Nishibayashi et al.,[9] Reiser et al.,[10] and MacMillan et al.[4d] reveal that thus formed α-aminoalkyl radicals are capable of reacting with electron deficient alkenes or arenes. In addition to these findings, we wish to report herein that $Ru(bpy)_3Cl_2$ or $Ir(ppy)_2(dtbbpy)PF_6$-mediated photoredox catalysis can effect the reaction of tertiary anilines with *N*-phenylmaleimide to form tetrahydroquinoline products. This transformation has recently been realized by using $CuCl_2$ as catalyst and air as oxidant.[11] The key steps for the formation of tetrahydroquinolines comprise the addition of α-aminoalkyl radicals to the double bond and the subsequent free radical cyclization. The present visible light-induced process constitutes a very effective protocol with a low loading level of catalyst.

We initiated this study by subjecting *N*,*N*,4-trimethylbenzenamine (**1a**) and *N*-phenylmaleimide (**2a**) to irradiation with two 40-W household fluorescent lamps as the light source. $Ru(bpy)_3Cl_2$ and $Ir(ppy)_2(dtbbpy)PF_6$ were employed as catalyst to prompt the reaction.

As shown in Table 1, when a mixture of 2.0 equiv. of **1a**, 1.0 equiv. of **2a**, and 5 mol% of $Ru(bpy)_3Cl_2$ in DMF was irradiated under an O_2 atmosphere, the tetrahydroquinoline product **3a** was generated in 52% yield after 24 h (Table 1, entry 1). The yield was raised to 75% by performing the reaction in air (Table 1, entry 2). On the other hand, the reaction did not take place as indicated by TLC analysis if the reaction was performed under an argon atmosphere (Table 1, entry 3). When the molar ratio of **1a** and **2a** was adjusted to 1:1 and 1:2, the yield of **3a** decreased considerably (Table 1, entries 7 and 8). It is interesting to see that the reaction was improved when the loading of $Ru(bpy)_3Cl_2$ was reduced to 3.5 mol% and 2 mol% (Table 1, entries 6 and 9). Using $Ir(ppy)_2(dtbbpy)PF_6$ as photocatalyst gave comparable results (Table 1, entries 10 and 11). The reaction was also performed in CH_3CN and CH_2Cl_2, but the results were less satsifactory. Control experiments show that

Table 1. Screening of the conditions for the reaction of **1a** and **2a**.[a]



Entry	Catalyst (mol%)	Oxidant	Solvent	Yield [%][b]
1	$Ru(bpy)_3Cl_2$ (5.0)	O_2	DMF	52
2	$Ru(bpy)_3Cl_2$ (5.0)	air	DMF	75
3	$Ru(bpy)_3Cl_2$ (5.0)	none[c]	DMF	N. D.[d]
4	$Ru(bpy)_3Cl_2$ (5.0)	air	CH_3CN	49
5	$Ru(bpy)_3Cl_2$ (5.0)	air	DCM	48
6	***$Ru(bpy)_3Cl_2$ (3.5)***	air	DMF	***83***
7	$Ru(bpy)_3Cl_2$ (3.5)	air	DMF	35[e]
8	$Ru(bpy)_3Cl_2$ (3.5)	air	DMF	50[f]
9	$Ru(bpy)_3Cl_2$ (2.0)	air	DMF	80
10	$Ir(ppy)_2(dtbbpy)PF_6$ (3.5)	air	DMF	84
11	$Ir(ppy)_2(dtbbpy)PF_6$ (3.5)	none[c]	DMF	N. D.[d]
12	none	air	DMF	N. D.[d]

[a] 0.5 mmol of **1a** and 0.25 mmol of **2a** were used unless otherwise specified. The reaction time was 12 h except for the cases of entries 1, 4 and 5 where the reaction time was 24 h.

[b] Isolated yield based on the compound used in lesser amount.

[c] The reaction was performed under a strict argon atmosphere.

[d] **3a** was not detected by TLC analysis.

[e] 0.25 mmol of **1a** and 0.25 mmol of **2a** were used.

[f] 0.25 mmol of **1a** and 0.5 mmol of **2a** were used.

the presence of photocatalyst is necessary for the desired reaction to proceed (Table 1, entry 12).

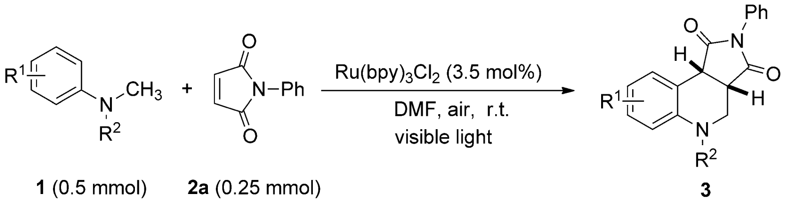
The optimized conditions (Table 1, entry 6) were then applied to the reaction of **2a** with variously substituted tertiary *N*-methylanilines, and the results are summarized in Table 2. *N,N*-Dimethylanilines incorporating methyl, methoxy, and halogen atoms on the phenyl ring reacted with **2a** to afford the corresponding tetrahydroquinolines **3** in good yields, except for **1j**. The reaction of compound **1g** with **2a** resulted in the formation of **3g-1** and **3g-2**, with **3g-1** being the major product. The preference for **3g-1** reflects the *ortho*-regioselectivity of free radical addition to aryl rings.[11,12] When **1h** and **1i** were used as substrate, the C–C coupling took place exclusively at the *N*-methyl carbon (Table 2, entries 8 and 9), consistent with the result reported by Miura et al.[11]

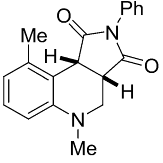
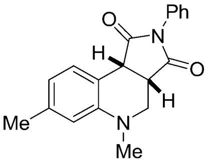
Besides compound **2a**, maleimides **2b**–**2g** reacted as well with **1a** as shown in Table 3. However, compound **1a** failed to react with the olefins shown in Figure 1 to deliver the tetrahydroquinoline products. In these cases, compound **1a** decomposed mostly under the reaction conditions. Performing the reaction at elevated temperature failed to render any improvement.

We believe that the formation of tetrahydroquinolines involves the addition of α-aminoalkyl radicals to the double bond and subsequent free radical cyclization as the key steps. It is generally accepted that the oxidative C–H functionalizations of tertiary amines under visible light photoredox catalysis are initiated by the single electron transfer between the photo-excited catalyst and amines, which would first generate α-aminoalkyl radicals. Besides this mechanism, competitive pathways might exist considering that singlet oxygen can be generated from quenching of the photo sensitizers by triplet molecular oxygen.[13] The reaction between singlet oxygen and amines may also generate α-aminoalkyl radicals. However, our control experiment indicates that singlet oxygen does not play an important role as the reaction proceeded rather slowly and with low yield under tetraphenylporphyrin (TPP)-sensitized conditions (Scheme 1).[14] Further evidence to support this scenario is provided by the fluorescence quenching experiments with $Ru(bpy)_3Cl_2$ (Figure 2). The Stern–Volmer studies show that *N,N*-dimethylaniline (**1b**) can efficiently quench the emission of $Ru(bpy)_3Cl_2$ in the presence of air.

To shed more light on the mechanistic details, we examined both inter- and intramolecular deuterium isotope effects, and the results are shown in Scheme 2. The $(k_H/k_D)_{inter}$ value for the reaction of **1b** was determined to be 4.0, larger than those expected for the oxidation of **1b** through electron/proton trans-

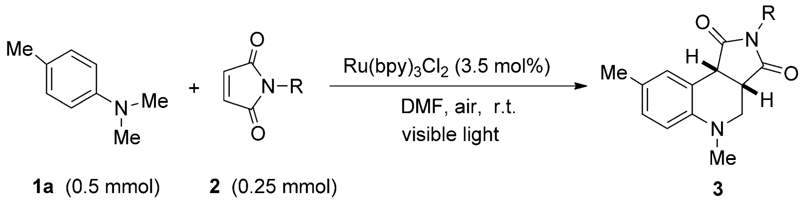
Table 2. The reaction of tertiary *N*-methylanilines with **2a**.



Entry	Amine (**1**)	Product(s) **3**/Yield [%][a]
1	**1a**, $R^1=4$-Me, $R^2=Me$	**3a**/83
2	**1b**, $R^1=H$, $R^2=Me$	**3b**/81
3	**1c**, $R^1=4$-MeO, $R^2=Me$	**3c**/62
4	**1d**, $R^1=4$-F, $R^2=Me$	**3d**/82
5	**1e**, $R^1=4$-Cl, $R^2=Me$	**3e**/72
6	**1f**, $R^1=4$-Br, $R^2=Me$	**3f**/67
7	**1g**, $R^1=3$-Me, $R^2=Me$	**3g-1**+**3g-2** (2:1)/89  **3g-1**  **3g-2**
8	**1h**, $R^1=4$-Me, $R^2=Bn$	**3h**/57
9	**1i**, $R^1=H$, $R^2=Et$	**3i**/80
10	**1j**, $R^1=H$, $R^2=Ph$	**3j**/20

[a] Isolated yield based on **2a**.

Table 3. The reaction of **1a** with *N*-substituted maleimides **2**



Entry	R	**2**	**3**/Yield [%][a]
1	$R=4$-Me-C_6H_4-	**2b**	**3ab**/66
2	$R=4$-MeO-C_6H_4-	**2c**	**3ac**/85
3	$R=4$-F-C_6H_4-	**2d**	**3ad**/98
4	$R=4$-Cl-C_6H_4-	**2e**	**3ae**/89
5	$R=4$-Br-C_6H_4-	**2f**	**3af**/80
6	$R=Bn$	**2g**	**3ag**/68

[a] Isolated yield.

fer process.[15] Therefore, in the present cases, the hydrogen atom transfer (HAT) mechanism cannot be ruled out for the formation of α-aminoalkyl radicals. Recently, Wu and co-workers reported a detailed study on the eosin Y bis(tetrabutylammonium salt) (TBA-eosin Y)-mediated photochemical cross dehydrogenative coupling of tetrahydroisoquinolines with nucleophiles.[8c] They proposed that besides the electron/proton transfer process, the α-amino radicals might form *via* hydrogen atom abstraction by the $HOO^•$ radical. This mechanism explains reasonably the observed intermolecular deuterium isotope effects in the present case.

On the basis of our experiments and the relevant literature, a mechanism is proposed for the reaction of **1** and **2** (Scheme 3). In this mechanism, the reaction is initiated by the single electron transfer from amine **1** to the photo-excited $Ru(bpy)_3Cl_2$, which re-

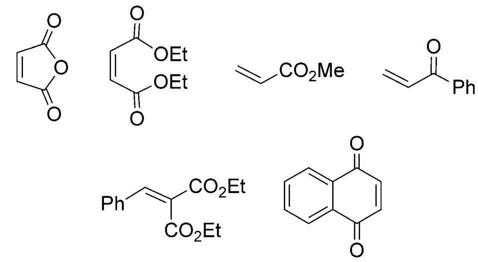


Figure 1. Olefins that failed to react with **1a** under the present conditions.

$$\mathbf{1b} + \mathbf{2a} \xrightarrow[\text{DMF, visible light, air, r.t., 60 h}]{\text{TPP (3.5 mol\%)}} \mathbf{3b}$$

yield: 16%

Scheme 1.

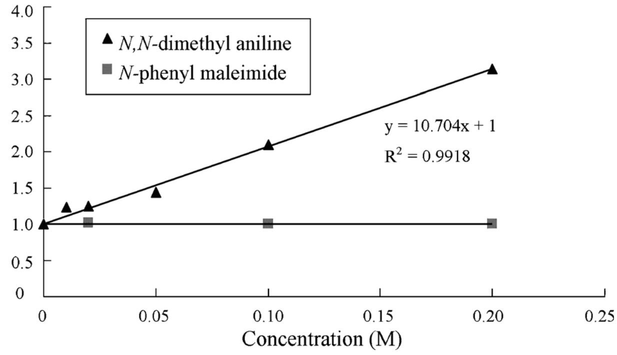
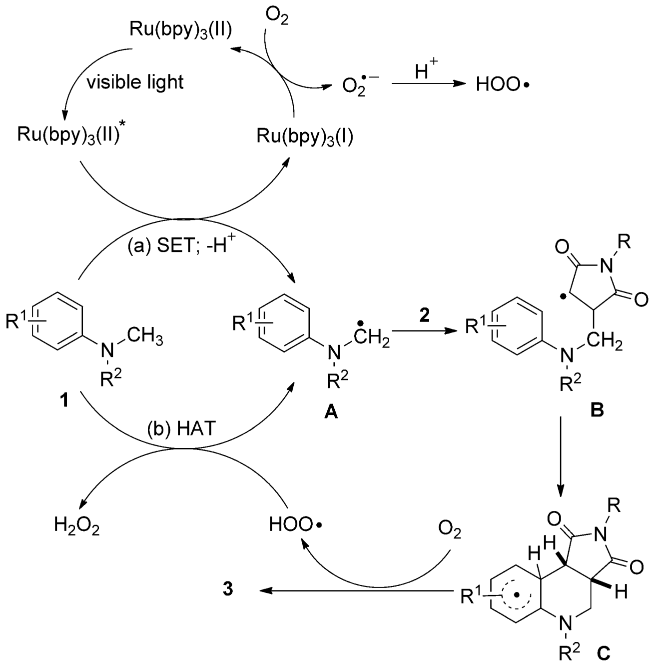


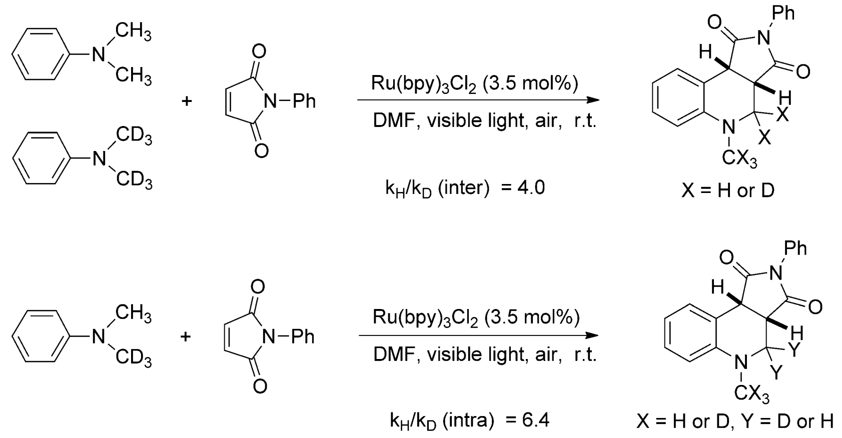
Figure 2. Emission quenching experiments with Ru(bpy)$_3$Cl$_2$ in the presence of air.



Scheme 3. Proposed reaction mechanism.

sults in the generation of α-aminoalkyl radical **A**. Ru(bpy)$_3$(II)* is reduced to Ru(bpy)$_3$(I) at the same time. **A** reacts with **2** to generate **B**, and the latter then undergoes cyclization to form radical **C**. **C** is converted to tetrahydroquinoline **3** following rapid oxidation by O_2. The catalyst Ru(bpy)$_3$(II) is regenerated from Ru(bpy)$_3$(I) *via* aerobic oxidation, with concomitant formation of superoxide radical anion.[6d,8c] The protonation of superoxide radical anion would generate the $HOO^{\bullet}$ radical. The HAT process between $HOO^{\bullet}$ and **1** opens another route to get access to **A**. $HOO^{\bullet}$ might be generated as well from the oxidation of radical **C** by O_2.

It should be noted that, in the works of Nishibayashi et al.[9] and Reiser et al.,[10] the photocatalyst was proposed to be recovered *via* the single electron oxidation of their reduced forms by the α-carbonyl radicals derived from the addition of α-aminoalkyl radicals to the α,β-unsaturated carbonyl compounds, as the reactions in their cases were conducted in the ab-



Scheme 2. Inter- and intramolecular deuterium isotope effects.

Table 4. Irradiation of **1k** and **2a** under an argon atmosphere.[a]

Entry	Catalyst	Reaction time [h]	Recovered S.M. [%][b]
1	$Ru(bpy)_3Cl_2$	12	80 (**2a**), 77 (**1k**))
2	$Ru(bpy)_3Cl_2$	48	trace
3	none	12	65 (**2a**), 35 (**1k**)
4	none	48	trace

[a] 2.0 equiv. of **1k** and 1.0 equiv. of **2a** were used.

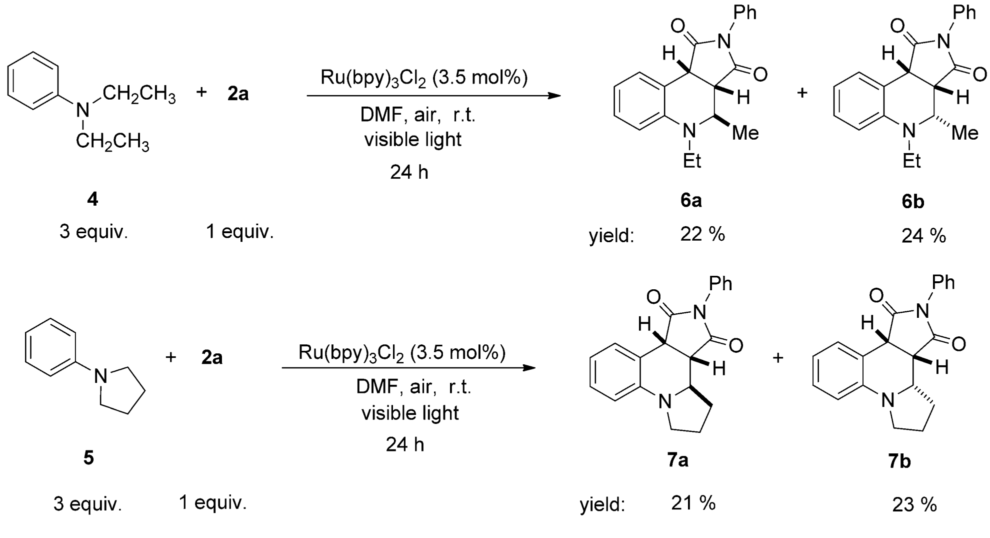
[b] Besides the recovered starting materials, a high polar complex mixture was detected after reaction.

sence of oxygen. However, the present reaction did not proceed in the absence of oxygen. We speculate that it is probably because the electron-withdrawing effect of the amido carbonyl group in intermediate **B** is not strong enough to render radical **B** to be reduced by $Ru(bpy)_3(I)$. To verify this hypothesis, an experiment was conducted with *N*,*N*,2,6-tetramethylaniline (**1k**) as the substrate. It was expected that if radical **B** could oxidize $Ru(bpy)_3(I)$, the simple addition product would form as the two *ortho*-methyl groups would prevent the cyclization step from competing with the redox process between **B** and $Ru(bpy)_3(I)$.[16] We found that under an argon atmosphere, **1k** did not react with **2a** to yield the addition product (Table 4). After 12 h of irradiation, most of the starting materials remained. Prolonging the reaction time to 48 h resulted in the disappearance of most **1k** and **2a**. Still, no addition product was detected. Control experiments showed that the loss of **1k** and **2a** was not caused by the $Ru(bpy)_3(II)$-mediated photochemical process, as the phenomenon was the same in the absence of $Ru(bpy)_3(II)$. These results provide evidence that intermediate **B** can not convert $Ru(bpy)_3(I)$ to $Ru(bpy)_3(II)$.

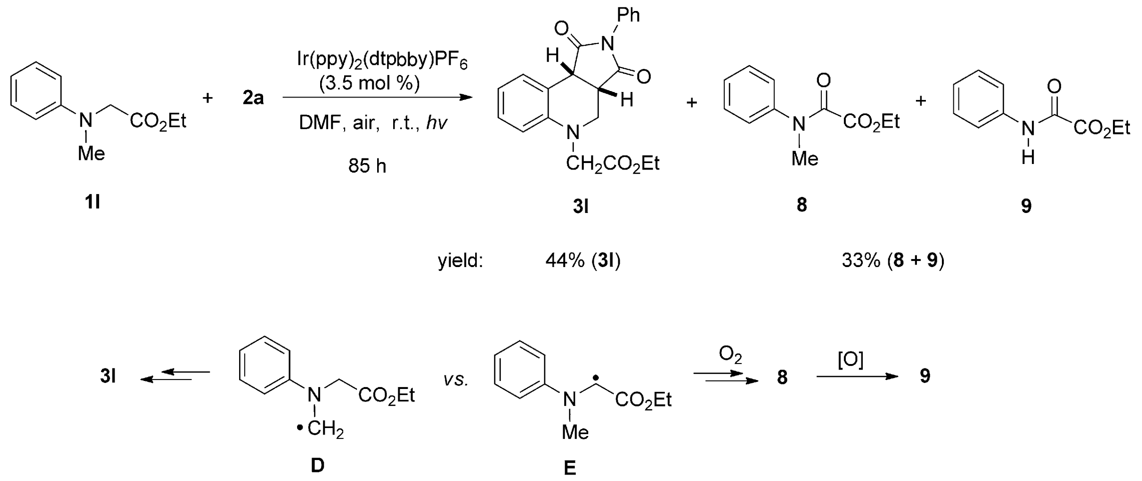
As shown in Table 2, the reaction of **1h** and **1i** with **2a** generated exclusively α-aminomethyl radicals resulting from deprotonation at the *N*-methyl group. It was of our interest to see if *N*,*N*-diethylaniline and other *N*-methyl-lacking tertiary anilines would undergo similar reaction under the present irradiation conditions. The work of Hirano and Miura et al. indicated that the $CuCl_2/O_2$ system failed to effect the reaction of *N*,*N*-diethylaniline with **1a**.[11] So next we chose *N*,*N*-diethylaniline (**4**) and 1-phenylpyrrolidine (**5**) as **2a**'s reaction partners. It turns out that both **4** and **5** can react with **2a** to generate the corresponding tetrahydroquinolines **6** and **7**, albeit in only moderate yields (Scheme 4) (3 equiv. of **4** and **5** were used to guarantee the complete conversion of **2a**). Both compounds **6** and **7** were obtained as roughly 1:1 diastereoisomers.

When compound **1l** was subjected to the reaction conditions, the expected reaction did not take place, with only the starting materials being recovered. To effect the reaction, $Ir(ppy)_2(dtbbpy)PF_6$, which is a more powerful oxidant as its excited state,[17] was used as photocatalyst under the otherwise same conditions. As expected, the reaction happened, generating tetrahydroquinoline product **3l** in yield of 44% (Scheme 5). Like the reaction of **1h** and **1i**, it was the *N*-methyl carbon that connected with the double bond of **2a** in the coupling step. Besides **3l**, a mixture of compounds **8** and **9** was also obtained. These two products might be from radical **E**, whose formation can be accounted for by the enhanced acidity of the *N*-methylene hydrogen and the captodative effect in **E**.

In summary, we have demonstrated that the $Ru(bpy)_3Cl_2$ or $Ir(ppy)_2(dtbbpy)PF_6$-mediated visible



Scheme 4.



Scheme 5.

light photochemistry provides an effective method for the preparation of tetrahydroquinoline compounds from tertiary anilines and *N*-arylmaleimides. This protocol is advantageous in terms of high catalytic efficiency and easy operation. This work serves as a new illustration that visible light photocatalysis will enhance the value of α-aminoalkyl radicals in organic synthesis.

Experimental Section

General Procedure for the Reactions of Tertiary Anilines (1) with Maleimides (2)

To a 10-mL round-bottom flask equipped with a drying tube (filled with $CaCl_2$) and magnetic stir bar were added tertiary anilines (**1**) (0.5 mmol, 2.0 equiv.), maleimides (**2**) (0.25 mmol, 1.0 equiv.), 0.035 equiv. of catalyst, and 3 mL of DMF. The solution was irradiated under stirring with two 40-W household fluorescent lamps (distance approx. 4 cm) at room temperature. After the reaction was complete (indicated by TLC), the reaction mixture was diluted with EtOAc (10 mL), and poured into saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (15 mL × 4) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was treated with silica gel chromatography to give products **3**. Compounds **3** could be further purified by recrystalization from CH_2Cl_2 and hexane.

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