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Reactivity and Mechanistic Insight into Visible-Light-Induced Aerobic Cross-Dehydrogenative Coupling Reaction by Organophotocatalysts

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Abstract: With visible-light irradiation, a mild, simple, and efficient metal-free photocatalytic system for the facile construction of sp^3–sp^3 C–C bonds between tertiary amines and activated C–H bonds has been achieved. Spectroscopic study and product analysis demonstrate for the first time that photoinduced electron transfer from *N*-aryl tetrahydroisoquinolines to eosin Y bis(tetrabutylammonium salt) (TBA-eosin Y) takes place to generate TBA-eosin Y radical anion, which can subsequently react with nucleophiles and molecular oxygen. More strikingly, electron spin resonance (ESR) measurements provide direct evidence for the formation of superoxide radical anions ($O_2^{-\bullet}$) rather than singlet oxygen ($^1O_2$) during visible-light irradiation. This active species is therefore believed to be responsible for the large rate of acceleration of the aerobic photocatalytic reactions.

Keywords: C–C coupling · C–H activation · electron transfer · molecular oxygen · photochemistry

Introduction

The development of efficient methods for the formation of C–C bonds is one of the fundamental challenges of organic synthesis. Transition-metal-catalyzed C–H bond activations and subsequent C–C bond formations have aroused much interest and have recently made great progress.[1] The cross-dehydrogenative coupling (CDC) reaction, a powerful tool to develop sustainable chemical processes, features the formation of C–C bonds directly from two different C–H bonds under oxidative conditions.[2] This straightforward reaction provides an alternative to the separate steps of prefunctionalization and defunctionalization that have traditionally been part of synthetic design. In 2003, Murahashi et al.[3] reported the first example of an aerobic catalytic method for C–C bond formation. Li et al.[4,5] have demonstrated that in the presence of metal catalysts such as copper or iron salts and oxidants such as hydrogen peroxide, oxygen, and *tert*-butylhydroperoxide, unfunctionalized sp^3 centers of C–H bonds can couple to other C–H bonds without preactivation. Very recently, Stephenson et al.[6] found an operationally simple method for the oxidative coupling of nitroalkanes by using visible-light photoredox catalysis. The reaction proceeds in high chemical yields by using Ir^{III} catalyst without the need for an external oxidant. Rueping et al.[7] combined photoredox catalysis and Lewis base catalysis to develop a dual catalytic system for the Mannich reaction. The two successful cases of CDC and Mannich reactions indicate that the visible-light-induced catalysis is an interesting subject even though the high cost and potential toxicity of Ru^{II} and Ir^{III} complexes as well as their limited availability are disadvantages of the metal-based methods. More importantly, the mechanism of the photocatalytic CDC and Mannich reactions has never been explored. Molecular oxygen (O_2) was found capable of facilitating the photoredox catalysis remarkably, but the active species of O_2 involved in the reaction mechanism remains elusive.

Particular interest in visible-light-initiated catalytic reactions[8,9] prompted us to study the typical CDC transformation of sp^3 C–H bonds adjacent to nitrogen by using organic photocatalysts. In this work, eosin Y, a famous organic dye, was used as a photocatalyst on account of its broad, high visible-light absorption and economic advantage over notable metal catalysts.[10] Moreover, the rich spectroscopic properties of eosin Y are expected to allow for the detection of the intermediate during irradiation.[11] With this system, we were able to achieve the oxidative coupling products of *N*-aryl tetrahydroisoquinolines with either nitroalkanes or dimethyl malonate and even acetone in good to excellent yields under mild conditions. Spectroscopic study and product analysis demonstrate for the first time that photoinduced electron transfer from *N*-aryl tetrahydroisoquinolines to eosin Y takes place to generate eosin Y radical anions, which can subsequently react with nitroalkanes and molecular oxygen. More strikingly, electron spin resonance (ESR)

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measurements provide direct evidence for the formation of superoxide radical anions ($O_2^{-\bullet}$) rather than singlet oxygen ($^1O_2$) during visible-light irradiation. This active species is therefore believed to be responsible for the large rate of acceleration of the aerobic photocatalytic reactions. As a result, a mild, simple, and efficient metal-free photocatalytic system for the facile construction of sp^3–sp^3 C–C bonds between tertiary amines and activated C–H bonds with the aid of molecular oxygen and visible light was established.

Results and Discussion

Our preliminary studies focused on the reaction of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) with nitromethane. Typically, a solution that contained **1a** and eosin Y (1 mol%) in degassed nitromethane was excited by a 500 W high-pressure Hanovia mercury lamp. A glass filter was used to cut off light below 450 nm, thus guaranteeing that only eosin Y was irradiated, whereas the substrates of **1a** and nitromethane were silent. To our delight, the desired CDC product was produced in 82% yield (26% conversion) as eosin Y disodium salt was irradiated for 24 h (Table 1, entry 1). The absence of eosin Y, however, resulted in negligible conversion of **1a** under the same conditions (entry 2). Moreover, no conversion could be observed when the reaction was conducted in the dark (entry 3). All of the results suggest that both light and eosin Y are essential for the reaction and eosin Y as a photocatalyst facilitates the C–C bond formation. Given that the poor solubility of eosin Y disodium salt in nitromethane was not good for the reaction, we changed the photocatalyst to organosoluble eosin Y bis(tetrabutylammonium salt) (TBA-eosin Y). As shown in entry 4 of Table 1, 92% conversion of **1a** and 86% yield of CDC product were obtained after 24 h irradiation. With 2 mol% TBA-eosin Y, complete conversion was observed in 20 h (entry 5). Strikingly, molecular oxygen was found to accelerate the reaction remarkably. In the presence of oxygen, 100% conversion of **1a** was achieved after just 4 h irradiation (entry 6). Keeping the initially irradiated sample in the dark under stirring for an additional 12 h caused a significant increase of the yield from 75 to 92% (entry 7). The system also worked well when oxygen was replaced by air, but much longer irradiation time was required (entry 8). To further confirm the participation of molecular oxygen, the aerobic reaction was investigated by means of oxygen-consumption experiments. It was noted that under the standard reaction conditions a full conversion of 0.2 mmol **1a** consumed approximately 0.15 mmol of oxygen as shown in Figure 1. Clearly, oxygen plays an important role in the oxidative coupling reaction. In addition, attempts to decrease the amount of nitromethane also led to the low yield of the CDC reaction (entry 9).

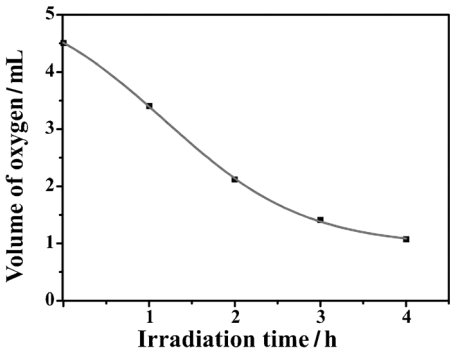
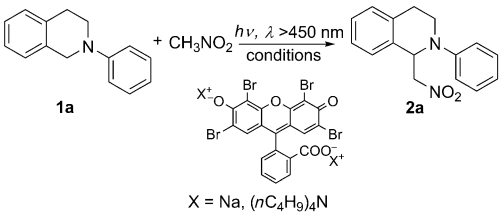


Figure 1. Oxygen uptake experiment: **1a** (0.2 mmol), TBA-eosin Y (0.004 mmol), CH_3NO_2 (10 mL). The sample was saturated with a stream of O_2 for 20 min and sealed in a Pyrex tube before irradiation. The amount of oxygen was determined by gas chromatograph analysis.

Table 1. Optimization of reaction conditions.



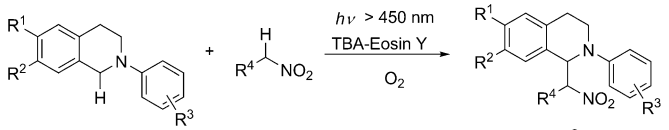
Entry	Conditions[a]	Irradiation time [h]	Conv. [%][b]	Yield [%][c]
1	eosin Y (1 mol%)	24	26	82
2	no catalyst	24	2	trace
3	no light, eosin Y (1 mol%)	–	0	0
4	TBA-eosin Y (1 mol%)	24	92	86
5	TBA-eosin Y (2 mol%)	20	100	88
6	TBA-eosin Y (2 mol%)[d]	4	100	75
7	TBA-eosin Y (2 mol%)[d]	**4**[e]	**100**	**92(86)**[f]
8	TBA-eosin Y (2 mol%) in air	5[e]	100	91
9	TBA-eosin Y (2 mol%), CH_3NO_2 (5 equiv), CH_3CN (10 mL)[d]	5[e]	100	34

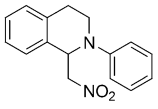
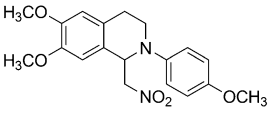
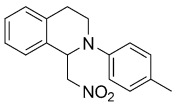
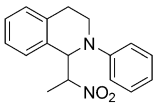
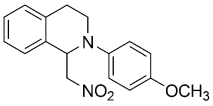
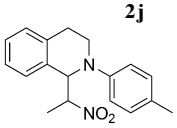
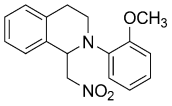
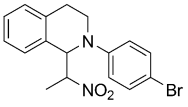
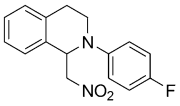
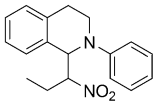
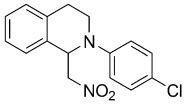
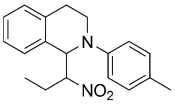
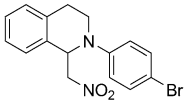
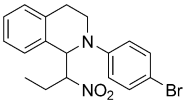
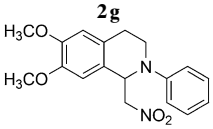
[a] Reaction conditions: **1a** (0.2 mmol), CH_3NO_2 (10 mL). The reaction was degassed with argon before irradiation unless indicated otherwise. [b] Conversion rates were determined by ^1H NMR spectroscopic analysis. [c] Yields were based on the conversion of **1a** and determined by ^1H NMR spectroscopy using an internal standard. [d] The solvent was saturated with oxygen before irradiation. [e] The irradiated sample was stirred in the dark at room temperature for 12 h. [f] Isolated yield after purification by chromatography on silica gel.

With this initial success, we screened the reaction scope with the aid of TBA-eosin Y and oxygen. As tabulated in Table 2, a series of substituted 1,2,3,4-tetrahydroisoquinoline derivatives were able to undergo the CDC reaction with nitromethane efficiently, thus resulting in the desired coupling products in good to excellent yields (Table 2, entries 1–9). The use of nitroethane as a nucleophile also gave the desired compounds in good yields (the ratios of the two diastereoisomers are 3:2) (entries 10–12), whereas the less efficient reaction of nitropropane may be due to the steric effect of the nucleophile (entries 13–15).

To shed light on the primary process of the photocatalytic CDC reaction, a flash-photolysis investigation was performed in a degassed CH_3CN solution at room temperature. Upon laser excitation by 532 nm light, a strong negative bleach of the ground-state absorption of TBA-eosin Y at ap-

Table 2. CDC reaction of nitroalkanes with tetrahydroisoquinolines using TBA-eosin Y as photocatalyst.[a]



Entry	Product	Yield [%][b]	Entry	Product	Yield [%][b]
1	 **2a**	86	9	 **2i**	79
2	 **2b**	84	10	 **2j**	76[c]
3	 **2c**	81	11	 **2k**	78[c]
4	 **2d**	75	12	 **2l**	64[c]
5	 **2e**	85	13	 **2m**	73[d]
6	 **2f**	77	14	 **2n**	60[d]
7	 **2g**	75	15	 **2o**	46[d]
8	 **2h**	84			

[a] Reaction conditions: **1** (0.2 mmol), TBA-eosin Y (0.004 mmol), nitroalkane (10 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield after column chromatography. [c] The ratios of the two diastereoisomers are 3:2. [d] The ratios of the two diastereoisomers are 7:4.

proximately 530 nm and characteristic absorptions at 580 nm were observed immediately, the decay of which throughout the absorption region and the recovery of the bleach occurs on the same timescale and can be thoroughly described by a monoexponential function with a lifetime of 16 μs, which is consistent with that of the triplet excited state of eosin Y derivatives in the literature.[11] Figure 2 displays the time-resolved absorption difference spectra for TBA-eosin Y and for TBA-eosin Y with **1a**, respectively. When **1a** was introduced into the solution of TBA-eosin Y, the absorptions were immediately replaced by a series of new absorptions with a maximum at 370 nm in addition to the strong triplet-state absorptions of TBA-eosin Y in the region of 500–650 nm. Following from spectroscopic studies of eosin Y derivatives,[11] the transient species that absorbed at 370 nm is ascribed to the reduced TBA-eosin Y radical anion. From the kinetics probed at 370 nm, a fast rise phase followed by a slow decay suggest that the photoinduced electron transfer from **1a** to the triplet state of TBA-eosin Y led to the formation and disappearance of the TBA-eosin Y radical anion. The rise grows quickly with the electron-transfer rate constant (k_{ET}) of $5.4\times10^4\,s^{-1}$ (18.2 μs), and the back charge recombination (k_{CR}) derived from the decay phase is rather slow with a lifetime of 410 μs ($2.4\times10^3\,s^{-1}$). Prolonged irradiation of the solution of TBA-eosin Y with **1a** in CH_3CN resulted in no permanent change, thereby indicating the TBA-eosin Y radical anion formed by the photoinduced electron transfer was quite stable.

It is known that eosin Y can react with molecular oxygen to generate either superoxide radical anion ($O_2^{-\bullet}$) or singlet oxygen ($^1O_2$).[12] To assess the generation ability of the active species of oxygen in the photocatalytic TBA-eosin Y system, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were employed as a probe to react with $O_2^{-\bullet}$ and $^1O_2$, respectively. The adducts can be easily detected by electron spin resonance (ESR) spectroscopy.[13] It is clearly shown in Figure 3 that when the solution of DMPO, TBA-eosin Y, and **1a** in air-saturated CH_3CN was irradiated with the laser at 532 nm, a single radical was trapped (Figure 3a), the spectrum and hyperfine coupling constants of which are in agreement with the reported values for the adduct of $O_2^{-\bullet}$ with DMPO.[13] By contrast, when TEMP, an $^1O_2$ scavenger, was used instead of DMPO in the same air-saturated solution, the nitroxide radical TEMPO was hardly detected (Fig-

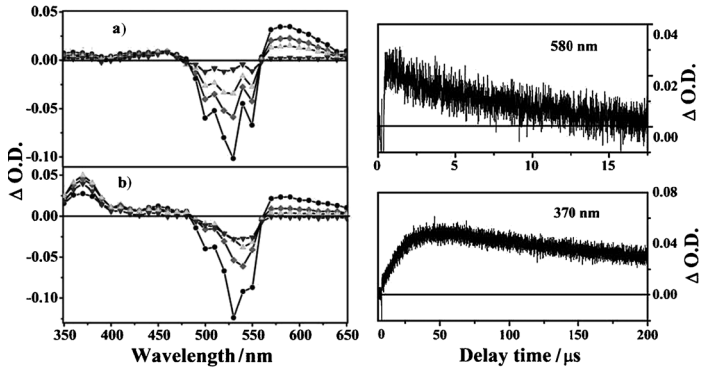


Figure 2. a) Transient absorption difference spectra of TBA-eosin Y in CH_3CN at room temperature; ●=0.46 μs, ◆=5.90 μs, ▲=11.35 μs, ▼=27.70 μs. b) Transient absorption difference spectra of TBA-eosin Y with **1a** (1.80×10^{-3} mol L^{-1}). [TBA-eosin Y] = 1.80×10^{-5} mol L^{-1}; λ_{ex} = 532 nm. ●=2.28 μs, ◆=15.90 μs, ▲=29.52 μs, ▼=111.24 μs.

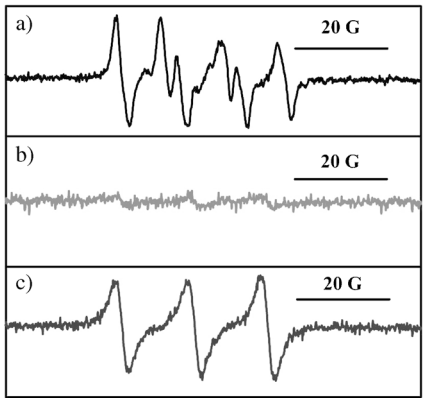
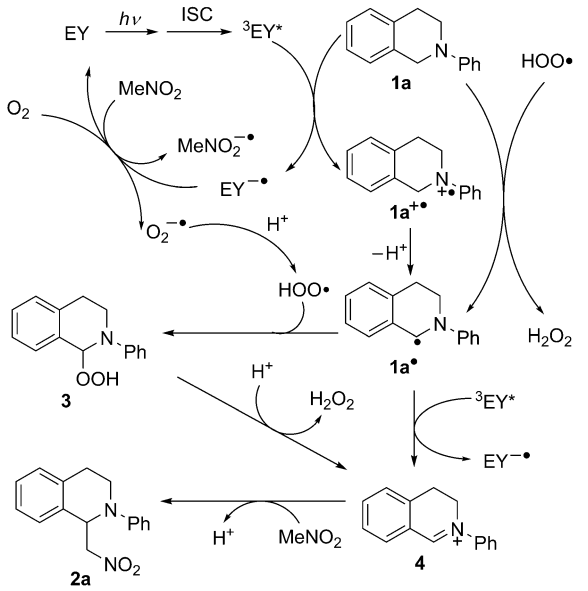


Figure 3. a) ESR spectrum of a solution of TBA-eosin Y (1.0×10^{-4} mol L^{-1}), **1a** (1.5×10^{-3} mol L^{-1}), and DMPO (2.0×10^{-2} mol L^{-1}) in air-saturated CH_3CN upon irradiation for 20 s. b) ESR spectrum of a solution of TBA-eosin Y (1.0×10^{-4} mol L^{-1}), **1a** (1.5×10^{-3} mol L^{-1}), and TEMP (0.12 mol L^{-1}) in air-saturated CH_3CN upon irradiation for 20 s. c) ESR spectrum of a solution of TBA-eosin Y (1.0×10^{-4} mol L^{-1}) and TEMP (0.12 mol L^{-1}) upon irradiation for 20 s in air-saturated CH_3CN.

ure 3b), whereas in the absence of **1a** this ESR signal was clearly observed (Figure 3c). Although triplet eosin Y has been reported to be an efficient sensitizer in the production of $^1O_2$ by an energy-transfer pathway,[14] the present case indicates that this pathway is highly suppressed by the effective electron transfer between triplet TBA-eosin Y and **1a** so that the generated radical anion of TBA-eosin Y can subsequently react with molecular oxygen to produce $O_2^{-\bullet}$ by an electron-transfer pathway.

On the basis of the above results, the aerobic CDC reaction can be rationalized in terms of the mechanism shown in Scheme 1. The photoinduced electron transfer from tetrahydroisoquinoline **1a** to the triplet TBA-eosin Y results in the formation of $\mathbf{1a}^{+\bullet}$ cation radical and TBA-eosin Y radical anion ($EY^{-\bullet}$). Subsequent electron transfer from $EY^{-\bullet}$ radical anion either to molecular oxygen or nitroalkane regenerates TBA-eosin Y, and at the same time produces superoxide radical anion ($O_2^{-\bullet}$) or radical anion of nitroalkane.[15] The generated $O_2^{-\bullet}$ radical anion may undergo protonation to populate $HOO^\bullet$ radical, which can further react with **1a** by means of hydrogen abstraction to afford $\mathbf{1a}^\bullet$ radical along with the formation of H_2O_2.[16] On the other hand, the fast deprotonation of $\mathbf{1a}^{+\bullet}$ radical cation furnishes $\mathbf{1a}^\bullet$ radical, which has a low oxidization barrier.[17] Once again, the photoinduced electron transfer from $\mathbf{1a}^\bullet$ radical to the triplet TBA-eosin Y produced iminium ion **4** and TBA-eosin Y radical anion ($EY^{-\bullet}$), respectively, which is similar to the reaction between α-amino radical and the $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) excited state reported by MacMillan et al.[17] The nucleophilic addition of the azinic acid tautomer of nitromethane to iminium **4** completes the reaction, thereby giving rise to 1-nitromethyltetrahydroisoquinoline **2a**. Because stirring the irradiated solution in the dark can further enhance the yield of product **2a**, a tetrahydroisoquinoline hydroperoxide intermediate **3** is likely involved in the coupling reaction. The transformation of hydroperoxide **3** to iminium **4** therefore results in the continuous production of **2a** and H_2O_2 in the dark.[18]

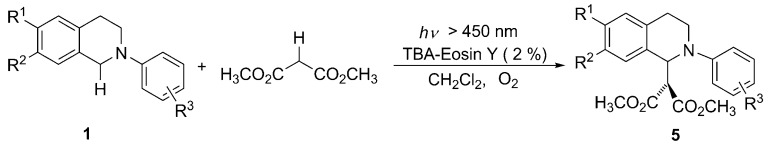


Scheme 1. Possible pathways for the aerobic photocatalytic CDC reactions.

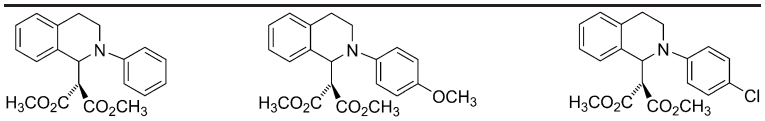
With the understanding of reaction mechanism, the present photocatalytic CDC method was further extended to the coupling of tetrahydroisoquinolines and dimethyl malonate (Table 3). Under visible-light irradiation, the *N*-phenyl tetrahydroisoquinoline derivatives **1** were treated smoothly with dimethyl malonate under an oxygen atmosphere to afford the desired products **5** in moderate to good yields. *N*-Aryl tetrahydroisoquinolines with an electron-withdrawing group located at the phenyl ring gave slightly better results.

Similarly, the photocatalytic aerobic CDC reaction was also applicable to the oxidative Mannich reaction between *N*-aryl tetrahydroisoquinolines **1** and acetone (Table 4). With a combination of organic photocatalyst TBA-eosin Y

Table 3. The CDC reaction of tetrahydroisoquinolines with malonate by organophotocatalyst.[a]

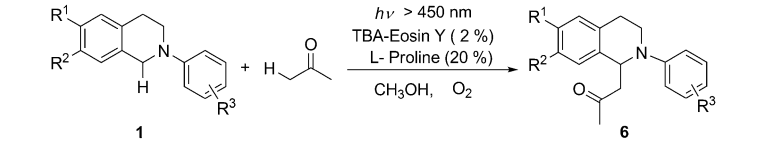


Product (yield [%])[b]

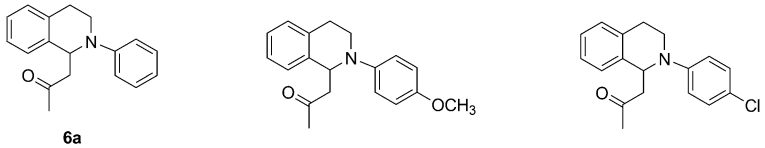


[a] Reaction conditions: **1** (0.2 mmol), TBA-eosin Y (0.004 mmol), dimethyl malonate (1.0 mmol), dissolved in CH_2Cl_2 (10 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield after column chromatography.

Table 4. The Mannich reaction of tetrahydroisoquinolines with acetone by organophotocatalyst.[a]



Product (yield [%])[b]



[a] Reaction conditions: **1** (0.2 mmol), TBA-eosin Y (0.004 mmol), L-proline (0.04 mmol), acetone (6 mL), CH_3OH (4 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield after column chromatography.

and cocatalyst L-proline, the reaction gave the desired amino ketones **6** in synthetically useful yields. Despite the fact that the yields are modest, the present system being performed by pure organocatalysts adds significantly to previous methodologies.[7,19]

Conclusion

In summary, we provide a simple and effective aerobic, metal-free catalytic CDC reaction for the direct C–C bond formation of *N*-aryl tetrahydroisoquinolines by means of visible-light irradiation. By combining organic photocatalyst TBA-eosin Y and the most economic oxidant molecular oxygen, the active participants in this coupling reaction have been broadened to nitroalkanes, dialkyl malonate derivatives, and even nonactivated simple ketones. Mechanistic studies demonstrate for the first time that photoinduced electron transfer from *N*-aryl tetrahydroisoquiline to the triplet TBA-eosin Y dominates the primary process of the oxidative coupling reaction. Subsequent electron transfer from TBA-eosin Y radical anion either to molecular oxygen or nitroalkane regenerates TBA-eosin Y, and at the same time produces a superoxide radical anion ($O_2^{-\bullet}$) or a radical anion of nitroalkane. The generated superoxide radical anion, a highly reactive species, can accelerate the reaction remarkably. Compared to the precious-metal-based CDC reaction and visible-light photoredox catalysis of recent years, systems by pure organophotocatalysts are still in high demand. More strikingly, the revelation of the mechanism of photocatalytic reactions is anticipated to be useful for designing more atom-economic and energy-efficient reactions.[20]

Experimental Section

General: ^{1}H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. Steady-state emission spectra were recorded using a Perkin–Elmer LS50B spectrofluorimeter. ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis before being purged with argon or oxygen for 30 min in the dark and illuminated directly in the cavity of the ESR spectrometer with a Nd:YAG laser (532 nm, 5–6 ns pulse width, 10 Hz repetition frequency, 10 mJ pulse energy). All reagents were weighed and handled in air, and backfilled under an inert atmosphere of argon at room temperature. Commercially available reagents and solvents were used without further purification. All the *N*-aryl tetrahydroisoquinolines **1** needed for CDC reactions were prepared by using the reported procedure[4c] and purified through column chromatography.

Oxygen uptake experiment: A 15 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with TBA-eosin Y (4.5 mg, 0.004 mmol), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), and CH_3NO_2 (10 mL). The mixture was bubbled with a stream of oxygen for 20 min. CH_4 (500 μL) was injected as internal standard for quantitative GC analysis. The tube was then sealed and irradiated by a 500 W high-pressure mercury lamp at ambient temperature, and a glass filter was employed to cut off light with wavelength below 450 nm. The residual oxygen molecular of the systems was measured using a GC-14B instrument (Shimadzu) with nitrogen as the carrier gas, molecular sieve 5 Å columns (30 m × 0.53 mm), and a thermal conductivity detector. The response factor for O_2/CH_4 was about 11.2 under experimental conditions, which was established by calibration with known amounts of O_2 and CH_4, and determined before and after a series of measurements.

General procedure for the CDC reaction of nitroalkanes with tetrahydroisoquinolines: A 15 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with TBA-eosin Y (4.5 mg, 0.004 mmol), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), and CH_3NO_2 (10 mL). The mixture was bubbled with a stream of oxygen for 20 min. The tube was then sealed and irradiated by a 500 W high-pressure mercury lamp at ambient temperature. A glass filter was employed to cut off light with wavelength below 450 nm. The progress of the reaction was monitored by thin-layer chromatography at regular intervals. Generally, the conversion was close to 100% after 4 h of irradiation. The irradiated sample was then stirred in the dark at the room temperature for 12 h. Upon removal of solvent under vacuum, the residue

was purified by flash chromatography on alkalescence silica gel to afford the corresponding products.

1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2a): ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.82 (dt, J=16.4, 4.9 Hz, 1H), 3.06–3.13 (m, 1H), 3.61–3.69 (m, 2H), 4.57 (dd, J=11.9, 6.6 Hz, 1H), 4.89 (dd, J=12.0, 8.0 Hz, 1H), 5.56 (t, J=8.0 Hz, 1H), 6.87 (t, J=7.3 Hz, 1H), 6.99 (d, J=8.2 Hz, 2H), 7.14 (d, J=7.2 Hz, 1H), 7.18–7.29 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=26.7, 42.3, 58.4, 79.0, 115.3, 119.7, 126.9, 127.2, 128.3, 129.4, 129.7, 133.2, 135.5, 148.6 ppm; EIMS: m/z (%): 268 (43) [M^+], 208 (100), 77 (5).

1-Nitromethyl-2-*p*-tolyl-1,2,3,4-tetrahydroisoquinoline (2b): ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.25 (s, 3H), 2.73 (dt, J=16.0, 4.0 Hz, 1H), 3.01–3.05 (m, 1H), 3.53–3.60 (m, 2H), 4.54 (dd, J=12.0, 6.4 Hz, 1H), 4.83 (dd, J=12.0 Hz, 8.0 Hz, 1H), 5.48 (t, J=8.0 Hz, 1H), 6.88 (d, J=8.6 Hz, 2H), 7.06 (d, J=8.6 Hz, 2H), 7.11–7.25 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.5, 26.4, 42.5, 58.6, 79.0, 116.1, 126.8, 127.2, 128.2, 129.3, 129.5, 130.2, 133.2, 135.6, 146.6 ppm; EIMS: m/z (%): 282 (60) [M^+], 222 (100), 118 (64), 91 (66), 77(12).

2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2c): ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.69 (dt, J=16.0, 4.0 Hz, 1H), 2.96–3.02 (m, 1H), 3.50–3.56 (m, 2H), 3.74 (s, 3H), 4.55 (dd, J=12, 5.8 Hz, 1H), 4.81 (dd, J=12, 8.6 Hz, 1H), 5.38 (dd, J=5.8, 8.6 Hz, 1H), 6.81 (d, J=9.0 Hz, 2H), 6.91 (d, J=9.0 Hz, 2H), 7.09–7.33 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.8, 43.1, 55.5, 58.9, 78.9, 114.7, 118.8, 126.6, 126.9, 127.9, 129.4, 132.9, 135.4, 143.0, 153.9 ppm; EIMS: m/z (%): 298 (73) [M^+], 239 (100), 223 (55), 115 (50), 91(12), 77 (18).

2-(2-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.71 (ddd, J=2.4, 3.8 Hz, 16.5 Hz, 1H), 2.94–2.98 (m, 1H), 3.44–3.61 (m, 2H), 3.82 (s, 3H), 4.53 (dd, J=5.2, 12.0 Hz, 1H), 4.82 (dd, J=8.0, 12.0 Hz, 1H), 5.50 (dd, J=8.3, 5.1 Hz, 1H), 6.81–6.88 (m, 3H), 6.98–7.05 (m, 1H), 7.12–7.30 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=27.1, 43.2, 56.0, 58.4, 79.4, 112.8, 121.3, 122.2, 124.3, 126.6, 129.7, 133.9, 135.6, 139.2, 153.4 ppm; EIMS: m/z (%): 298 (62) [M^+], 239 (95), 222 (100), 115 (33), 91(11), 77 (21).

2-(4-Fluorophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2e): ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.71 (dt, J=16.0, 4.4 Hz, 1H), 2.98–3.04 (m, 1H), 3.59 (dd, J=9.1, 4.4 Hz, 2H), 4.56 (dd, J=12.0, 5.8 Hz, 1H), 4.83 (dd, J=12.0, 8.6 Hz, 1H), 5.42 (dd, J=8.6, 5.8 Hz, 1H), 6.88–6.92 (m, 4H), 7.12–7.27 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.7, 29.7, 42.8, 58.7, 78.8, 115.8 (d, J(C,F)=22.2 Hz), 117.9 (d, J(C,F)=7.4 Hz), 126.7, 126.9, 128.1, 129.4, 132.5, 135.2, 145.3, 157.1 ppm (d, J-(C,F)=239.2 Hz); EIMS: m/z (%): 286 (63) [M^+], 227 (100), 115 (70), 95 (58), 91 (12), 77 (8); HRMS (EI): m/z calcd for $C_{16}H_{15}FN_2O_2$: 286.1118; found: 286.1117.

2-(4-Chlorophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2f): ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.76 (dt, J=4.4, 16.0 Hz, 1H), 3.05 (ddd, J=15.1, 8.4, 6.3 Hz, 1H), 3.46–3.73 (m, 2H), 4.55 (dd, J=6.3, 12.0 Hz, 1H), 4.82 (dd, J=8.0, 12.0 Hz, 1H), 5.47 (t, J=8.0 Hz, 1H), 6.88 (d, J=9.1 Hz, 2H), 7.10–7.26 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=26.3, 42.4, 58.4, 78.8, 116.7, 124.6, 127.0, 127.2, 128.4, 129.5, 132.7, 135.3, 147.3 ppm; EIMS: m/z (%): 302 (94) [M^+], 244 (100), 149 (64), 115 (72), 111 (50), 77 (14).

2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2g): ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.79 (dt, J=4.8, 16.0 Hz, 1H), 3.01–3.15 (m, 1H), 3.57–3.65 (m, 1H), 4.57 (dd, J=6.4, 12.0 Hz, 1H), 4.82 (dd, J=8.0, 12.0 Hz, 1H), 5.47 (t, J=8.0 Hz, 1H), 6.84 (d, J=9.1 Hz, 2H), 7.16–7.31 (m, 4H), 7.34 ppm (d, J=9.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=26.1, 42.0, 58.1, 78.6, 111.5, 116.7, 126.8, 126.9, 128.2, 129.2, 132.2, 132.4, 135.0, 147.5 ppm; EIMS: m/z (%): 348 (62), 346 (65) [M^+], 288 (100), 118 (99), 90 (25), 77 (12).

6,7-Dimethoxy-1-nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2h): ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.68 (dt, J=4.4, 16.0 Hz, 1H), 2.96–3.04 (m, 1H), 3.54–3.61 (m, 1H), 3.65–3.70 (m, 1H), 3.85 (s, 6H), 4.56 (dd, J=6.4, 12.0 Hz, 1H), 4.85 (dd, J=8.0, 12.0 Hz, 1H), 5.46 (t, J=8.0 Hz, 1H), 6.60 (s, 1H), 6.65 (s, 1H), 6.85 (t, J=8.0 Hz, 1H), 6.87 (d, J=8.0 Hz, 2H), 7.24–7.28 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=25.9, 42.2, 56.0, 56.2, 58.1, 78.9, 109.8, 111.9, 115.7, 119.7, 124.7, 127.6, 129.6, 147.9, 148.7, 148.9 ppm; EIMS: m/z (%): 328 (30) [M^+], 268 (100), 104 (15), 77 (36).

6,7-Dimethoxy-2-(4-methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (2i): ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.57 (dt, J=4.4, 16.0 Hz, 1H), 2.88–2.96 (m, 1H), 3.51–3.57 (m, 1H), 3.75 (s, 3H), 3.86 (s, 6H), 4.56 (dd, J=5.7, 12.0 Hz, 1H), 4.81 (dd, J=8.0, 12.0 Hz, 1H), 5.29 (dd, J=5.7 Hz, 8.6 Hz, 1H), 6.60 (s, 1H), 6.62 (s, 1H), 6.81 (d, J=8.0 Hz, 2H), 6.91 ppm (d, J=8.0 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$): δ=25.3, 43.4, 55.7, 56.0, 56.2, 58.9, 79.1, 109.6, 112.0, 114.8, 119.4, 124.6, 127.7, 143.3, 147.9, 148.9, 154.2 ppm; EIMS: m/z (%): 358 (78) [M^+], 298 (92), 296 (100), 282 (80), 254 (39), 149 (42), 77 (8).

1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2j): ^{1}H NMR (400 MHz, $CDCl_3$): δ=[1.53 (d, J=8.0 Hz), 1.69 (d, J=8.0 Hz), 3H], [2.83–2.94 (m), 2.99–3.09 (m), 2H], [3.51–3.61 (m), 3.80–3.86 (m), 2H], [4.84–4.92 (m), 5.01–5.08 (m), 1H], 5.22–5.26 (m, 1H), 6.79–6.84 (m, 1H), 6.97–7.01 (m, 2H), 7.08–7.29 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=(16.4, 17.4), (26.4, 26.7), (42.7, 43.5), (61.1, 62.7), (85.4, 88.9), (114.5, 115.4), (118.8, 119.3), 126.1, 126.6, 127.2, 128.2, 128.3, 128.7, 129.1, 129.3, 129.4, 129.6, 132.0, 133.8, 134.8, 135.6, 148.9, 49.2 ppm; EIMS: m/z (%): 282 (17) [M^+], 208 (100), 104 (46), 77 (55).

1-(1-Nitroethyl)-2-*p*-tolyl-1,2,3,4-tetrahydroisoquinoline (2k): ^{1}H NMR (400 MHz, $CDCl_3$): δ=[1.52 (d, J=6.8 Hz), 1.68 (d, J=6.8 Hz), 3H], [2.23 (s), 2.26 (s), 3H], [2.76–2.91 (m), 2.95–3.08 (m), 2H], [3.48–3.59 (m), 3.76–3.83 (m), 2H], [4.87 (dq, J=6.8, 13.6 Hz), 5.03 (dq, J=6.6, 13.3 Hz), 1H], 5.11–5.22 (m, 1H), 6.83–6.95 (m, 2H), 6.99–7.27 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=(16.4, 17.3), 20.3, (26.2, 26.5), (43.0, 43.9), (61.4, 62.9), (85.5, 88.9), (115.1, 116.0), 126.0, 126.5, 127.2, 128.1, 128.3, 128.8, 128.9, 129.1, 129.8, 129.9, 132.0, 133.8, 134.8, 135.7, 146.8, 147.1 ppm; EIMS: m/z (%): 296 (14) [M^+], 222 (100), 149 (38), 91 (31), 77 (10).

2-(4-Bromophenyl)-1-(1-nitroethyl)-1,2,3,4-tetrahydroisoquinoline (2l): ^{1}H NMR (400 MHz, $CDCl_3$): δ=[1.55 (d, J=8.0 Hz), 1.67 (d, J=8.0 Hz), 3H], [2.85–2.96 (m), 3.01–3.08 (m), 2H], [3.45–3.60 (m), 3.78–3.84 (m), 2H], [4.83–4.90 (m), 4.97–5.04 (m), 1H], 5.13–5.21 (m, 1H), 6.82–6.87 (m, 2H), 7.10–7.37 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=(16.8, 17.5), (26.4, 26.9), (43.0, 43.9), (61.3, 62.9), (85.6, 89.0), (116.3, 117.2), 126.5, 127.0, 127.2, 127.4, 128.5, 128.6, 128.9, 129.4, 129.6, 132.0, 132.2, 132.3, 132.7, 133.7, 134.7, 135.5, 148.1, 148.4 ppm; EIMS: m/z (%): 362 (8), 360 (8) [M^+], 314 (24), 312 (20), 288 (100), 206 (26), 129 (54), 115 (43), 91 (10), 77 (14).

1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (2m): ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91–0.96 (m, 3H), [1.77–1.89 (m), 2.04–2.16 (m), 2H], [2.83–2.93 (m), 3.02–3.11 (m) 2H], [3.48–3.69 (m), 3.81–3.88 (m), 2H], [4.64–4.70 (m), 4.83–4.89 (m), 1H], [5.12 (d, J=9.5 Hz), 5.23 (d, J=9.5 Hz), 1H], 6.76–6.83 (m, 1H), 6.92–7.00 (m, 2H), 7.13–7.29 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=10.7, (24.6, 25.0), (25.7, 26.8), (42.3, 43.5), (60.7, 62.2), (93.0, 96.1), (114.1, 115.8), (118.6, 119.4), 125.9, 126.6, 127.2, 128.2, 128.6, 128.7, 129.2, 129.3, 129.4, 132.6, 133.9, 134.7, 135.5, 149.0, 149.1 ppm; EIMS: m/z (%): 296 (36) [M^+], 209 (100), 115 (78), 104 (82), 77 (81).

1-(1-Nitropropyl)-2-*p*-tolyl-1,2,3,4-tetrahydroisoquinoline (2n): ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91–0.95 (m, 3H), [1.77–1.87 (m), 2.01–2.19 (m), 2H], 2.12 (s, 3H), [2.78–2.89 (m), 2.99–3.08 (m), 2H], [3.46–3.64 (m), 3.78–3.86 (m), 2H], [4.63–4.69 (m), 4.81–4.87 (m), 1H], [5.04 (d, J=12.0 Hz), 5.15 (d, J=12.0 Hz), 1H], 6.81–6.89 (m, 2H), 6.97–7.25 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=10.7, (20.2, 20.3), (24.6, 25.0), (25.5, 26.6), (42.5, 43.8), (60.9, 62.3), (93.1, 96.2), (114.7, 116.4), 125.8, 126.5, 127.2, 128.1, 128.6, 128.7, 128.9, 129.4, 129.7, 129.9, 132.5, 133.9, 134.7, 135.6, 146.9 ppm; EIMS: m/z (%): 310 (32) [M^+], 223 (100), 207 (34), 118 (57), 115 (52), 91 (84), 77 (12); HRMS (EI): m/z calcd for $C_{19}H_{22}N_2O_2$: 310.1681; found: 310.1684.

2-(4-Bromophenyl)-1-(1-nitropropyl)-1,2,3,4-tetrahydroisoquinoline (2o): ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.91–0.96 (m, 3H), [1.73–1.84 (m), 1.95–2.21 (m), 2H], [2.83–2.95 (m), 2.98–3.10 (m), 2H], [3.41–3.48 (m), 3.76–3.86 (m), 1H], [3.53–3.62 (m), 1H], [4.62–4.68 (m), 4.79–4.85 (m), 1H], [5.05 (d, J=12.0 Hz), 5.17 (d, J=12.0 Hz), 1H], [6.80 (d, J=9.1 Hz), 6.84 (d, J=9.1 Hz), 2H], 7.14–7.30 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=10.8, (24.9, 25.1), (25.8, 26.9), (42.6, 43.9), (60.8, 62.3), (93.1,

96.1), (93.1, 96.1), (110.7, 111.6), (115.8, 117.5), 126.2, 127.0, 127.3, 128.6, 128.8, 129.5, 132.1, 132.3, 132.4, 133.7, 134.6, 135.4, 148.2 ppm; EIMS: *m/z* (%): 376 (5) [M^+], 374 (6), 289 (67), 289 (67), 288 (100), 287 (74), 286 (76), 222 (33), 207(37), 184 (31), 182 (28), 115 (45), 103 (10), 77 (9); HRMS (EI): *m/z* calcd for $C_{18}H_{19}N_2O_2Br$: 374.0630; found: 374.0630.

General procedure for the photocatalytic CDC reaction of dimethyl malonate with tetrahydroisoquinolines: A 15 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with TBA-eosin Y (4.5 mg, 0.004 mmol), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), dimethyl malonate (132 mg, 1.0 mmol), and CH_2Cl_2 (10 mL). The mixture was bubbled with a stream of oxygen for 20 min. The tube was then sealed and irradiated by a 500 W high-pressure mercury lamp at ambient temperature. A glass filter was employed to cut off light with wavelength below 450 nm. After 4 h of irradiation, the sample was then stirred in the dark at the room temperature for 12 h and then concentrated under vacuum. Purification of the residue by flash column chromatography on silica gel gave the corresponding products.

Dimethyl 2-(1,2,3,4-tetrahydro-2-phenylisoquinolin-1-yl)malonate (5a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (dt, J = 16.5, 5.1 Hz, 1H), 3.07 (ddd, J = 15.6, 8.9, 6.3 Hz, 1H), 3.54 (s, 3H), 3.77–3.57 (m, 5H), 3.95 (d, J = 9.4 Hz, 1H), 5.70 (d, J = 9.4 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 7.31–7.06 ppm (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.22, 42.34, 52.70, 58.34, 59.28, 76.91, 77.23, 77.55, 115.36, 118.79, 126.21, 127.21, 127.80, 129.15, 129.27, 134.95, 135.83, 148.94, 167.57, 168.45 ppm; EIMS: *m/z* (%): 339 (47) [M^+], 209 (100), 193 (56), 115 (66), 77(74).

Dimethyl 2-[1,2,3,4-tetrahydro-2-(4-methoxyphenyl)isoquinolin-1-yl] malonate (5b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.75 (dt, J = 16.6, 4.4 Hz, 1H), 3.00 (ddd, J = 16.6, 10.2, 6.4 Hz, 1H), 3.52–3.70 (m, 2H), 3.61 (s, 3H), 3.64 (s, 3H), 3.73 (s, 3H), 3.96 (d, J = 9.4 Hz, 1H), 5.49 (d, J = 9.4 Hz, 1H), 6.82–6.69 (m, 2H), 6.99–6.86 (m, 2H), 7.23–7.06 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6, 43.1, 52.59, 52.63, 55.7, 59.3, 114.5, 118.4, 126.1, 127.2, 127.6, 129.3, 134.9, 135.5, 143.6, 153.4, 167.6, 168.4 ppm; EIMS: *m/z* (%): 369 (73) [M^+], 239 (100), 223 (81), 195 (28), 115 (63), 101 (74), 77 (17), 59 (53).

Dimethyl 2-[2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]malonate (5c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.90 (dt, J = 16.4, 5.4 Hz, 1H), 3.05 (ddd, J = 14.9, 8.6, 6.1 Hz, 1H), 3.61–3.50 (m, 4H), 3.72–3.62 (m, 4H), 3.91 (d, J = 9.5 Hz, 1H), 5.64 (d, J = 9.5 Hz, 1H), 6.99–6.78 (m, 2H), 7.24–7.09 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.2, 42.7, 52.8, 58.4, 59.3, 116.3, 123.5, 126.4, 127.2, 129.1, 134.8, 135.6, 147.5, 167.5, 168.4 ppm; EIMS *m/z* (%): 373 (77) [M^+], 242 (100), 138 (36), 115 (46); HRMS (EI): *m/z* calcd for $C_{20}H_{20}NO_4Cl$: 373.1081, found: 373.1081.

General procedure for the Mannich reaction of acetone with tetrahydroisoquinolines: A 15 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with TBA-eosin Y (4.5 mg, 0.004 mmol), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), L-proline (4.6 mg, 0.04 mmol), acetone (6 mL), and CH_3OH (4 mL). The mixture was bubbled with a stream of oxygen for 20 min. The tube was then sealed and irradiated by a 500 W high-pressure mercury lamp at ambient temperature. A glass filter was employed to cut off light with wavelength below 450 nm. After 4 h of irradiation, the sample was then stirred in the dark at the room temperature for 12 h. Upon removal of solvent under vacuum, the residue was purified by flash chromatography on silica gel to afford corresponding products.

1-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 3H), 2.82 (dt, J = 4.0, 16.0 Hz, 2H), 3.01–3.08 (m, 2H), 3.49–3.56 (m, 1H), 3.61–3.67 (m, 1H), 5.40 (t, J = 8.0 Hz, 1H), 6.77 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 7.11–7.27 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 31.1, 42.0, 50.2, 54.8, 114.7, 118.2, 126.4, 126.7, 126.8, 128.6, 129.3, 134.4, 138.3, 148.8, 207.2 ppm; EIMS: *m/z* (%): 265 (23) [M^+], 208 (100), 115 (32), 77 (43).

1-[2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]propan-2-one (6b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 2.70–2.79 (m, 2H), 2.96–3.04 (m, 2H), 3.42–3.56 (m, 2H), 3.74 (s, 3H), 5.24 (t, J = 8.0 Hz, 1H), 6.79–6.83 (m, 2H), 6.86–6.93 (m, 2H), 7.09–7.13 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.7, 30.8, 42.8, 49.9, 55.6, 55.9, 114.6, 118.4, 126.2, 126.6, 126.8, 128.9, 134.3, 138.2, 143.7, 153.3, 207.3 ppm; EIMS: *m/z* (%): 295 (46) [M^+], 239 (100), 223 (33), 115 (14).

1-[2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl]propan-2-one (6c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 3H), 2.78–2.85 (m, 2H), 3.00–3.07 (m, 2H), 3.47–3.62 (m, 2H), 5.34 (t, J = 8.0 Hz, 1H), 6.83–6.87 (m, 2H), 7.12–7.18 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 30.7, 41.8, 49.8, 54.4, 115.4, 122.6, 126.0, 126.4, 126.6, 128.3, 128.7, 133.8, 137.5, 147.1, 206.6 ppm; EIMS: *m/z* (%): 299 (46) [M^+], 242 (100), 227 (30), 138 (40), 115 (61), 111 (39), 77 (14).

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