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Platinum(II) Schiff Base Complexes as Photocatalysts for Visible-Light-Induced Cross-Dehydrogenative Coupling Reactions

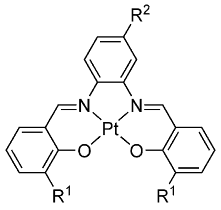
Deepak Prakash Shelar,[a] Ting-Ting Li,[a] Yong Chen,*[a] and Wen-Fu Fu[a, b]

Four phosphorescent platinum(II) Schiff base complexes are screened for application in visible-light-induced cross-dehydrogenative coupling (CDC) reactions. Preliminary studies show that, among the four platinum(II) complexes, **Pt3** is an efficient catalyst for CDC reactions with oxygen as an oxidant. Light irradiation ($\lambda > 420$ nm) on a mixture of the Pt^{II} complex, tertiary amine, and a variety of nucleophiles (nitroalkanes, ketones, or indoles) under aerobic conditions gives α-functionalized tertiary amines in good to excellent yields. The photoluminescence quenching experiment reveals that the CDC reaction is initiated by photoinduced electron transfer from *N*-phenyltetrahydroisoquinoline to the Pt^{II} complex. Further, electron spin resonance (ESR) measurements clearly indicate the formation of superoxide radical anions ($O_2^{\bullet-}$) rather than singlet oxygen ($^1O_2$) during the photocatalytic reaction.

Introduction

The development of C–C bond-forming reactions[1] is an important topic in organic chemistry. In particular, the cross-dehydrogenative coupling (CDC) reaction has attracted considerable interest among synthetic organic chemists, because it does not require substrate prefunctionalization, and thus, is atom economic.[2] Whereas organic peroxides such as *t*BuOOH are often used as the oxidant for CDC reactions,[3] molecular oxygen represents one environmentally friendly oxidant, which produces hydrogen peroxide and decomposes to form water.[2a,c] These advantages inspired the synthetic community to develop aerobic CDC reactions. Recently, the use of visible light to initiate a CDC reaction has attracted significant interest.[4] The groups of Macmillan,[5] Yoon,[6] Stephenson,[7] and others[8] have published seminal works on visible-light-promoted C–C bond-forming reactions catalyzed by ruthenium or iridium polypyridyl complexes. Specifically, the single electron transfer (SET) process of visible-light-active metal complexes can allow redox manipulation of organic molecules without the employment of stoichiometric quantities of redox reagents or the production of excess chemical waste. Platinum(II) complexes are well known for their long-lived excited states, high luminescence quantum yields, and good chemical stabilities, and thus, are promising for photochemical reactions.[9] Although some platinum(II) polypyridyl complexes have been applied as sensitizers for photo-oxidation reactions[10] and photocatalytic hydrogen evolution,[11] their use in CDC reactions is still in its infancy. Only very recently, Wu et al. reported an example of using a platinum terpyridyl complex for aerobic oxidative C–H bond functionalization.[12]

Platinum(II) Schiff base complexes can be synthesized easily from commercially available chemicals. They have been found to display broad visible-light absorption in the 400–550 nm region, and have a long-lived phosphorescence emission in solution.[13] Moreover, these complexes ligated by a tetradentate dianionic ligand framework are both thermally and photo stable. Enlightened by their intriguing photophysical properties, we envision that the robust platinum(II) Schiff base complexes (Figure 1) could be promising candidates for oxidative C–H functionalization. Herein, we screen the use of these complexes in CDC reactions, and find that **Pt3** is an efficient photocatalyst that is capable of catalyzing light-induced aerobic oxidative C–H functionalization reactions. ESR experiments reveal that the superoxide radical anion ($O_2^{\bullet-}$) is responsible for the facile transformation in the present system.



Pt1: $R^1 = R^2 = H$
Pt2: $R^1 = H$, $R^2 = Br$
Pt3: $R^1 = F$, $R^2 = H$
Pt4: $R^1 = OCH_3$, $R^2 = H$

Figure 1. Molecular structures of platinum(II) Schiff base complexes.

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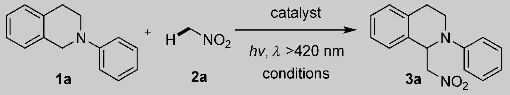
Results and Discussion

All of the complexes shown in Figure 1 were synthesized according to the previously reported procedure[13,14] and screened for their use in visible-light-induced CDC reactions. The results of the CDC reactions of **1a** with nitromethane using **Pt1**–**Pt4** as the visible light photoredox catalyst are summarized in Table 1. Gratifyingly, the desired product **3a** was obtained, and **Pt3** showed the best catalytic activity among all the catalysts, with a yield of 94% after 8 h irradiation under an oxygen atmosphere (Table 1, entries 1–4). Interestingly, the desired product **3a** was obtained in 8% yield in the absence of any catalyst (Table 1, entry 5). The control experiments showed that the reaction did not take place in the dark, and gave a trace amount of product **3a** in the absence of molecular oxygen (Table 1, entries 6, 7). Upon replacement of oxygen by air, the system also worked, but a slightly lower yield was obtained (Table 1, entry 8). For comparison, the well-known ruthenium and iridium polypyridyl complexes were also screened for CDC reactions under the same conditions, and the desired aza-Henry product **3a** was obtained in 96–98% yields (Table 1, entries 9 and 10). All the above results suggest that light irradiation and molecular oxygen are essential for the reaction, and in particular, the platinum complex **Pt3** as a photocatalyst facilitates the C–C bond formation. Consequently, the optimal reaction conditions include irradiation on nitromethane containing 1.5 mol% **Pt3** and **1a** under an oxygen atmosphere for 8 h.

Table 1. Optimization of CDC reaction of amine with nitromethane.



Entry	Conditions[a]	Conv. [%][b]	Yield [%][c]
1	**Pt1** (1.5 mol%)	37	29
2	**Pt2** (1.5 mol%)	46	32
3	**Pt3** (1.5 mol%)	100	94 (89)[d]
4	**Pt4** (1.5 mol%)	36	29
5	No catalyst	9	8
6	No light, **Pt3** (1.5 mol%)	0	0
7[e]	**Pt3** (1.5 mol%)	7	trace
8	**Pt3** (1.5 mol%) in air	76	63
9	$[Ru(bpy)_3]Cl_2$	100	98
10	$[Ir(ppy)_3]$	100	96

[a] Reaction conditions: **1a** (0.2 mmol), CH_3NO_2 (10 mL). The reaction was saturated with O_2 before irradiation unless indicated otherwise; reaction time of 8 h. [b] Conversions were determined by ^1H NMR spectroscopy of the crude product using 4,4′-dimethyl-2,2′-bipyridine as an internal standard based on **1a**. [c] Yields based on the amount of **1a** as determined by ^1H NMR spectroscopy. [d] Yield of isolated product based on recovered **1a**. [e] The reaction was deoxygenated.

With the optimal conditions in hand, we examined the scope of this visible-light-induced CDC reaction. In general, a variety of *N*-aryltetrahydroisoquinolines **1a–i** were subjected to the oxidative aza-Henry reaction, providing the desired coupling products **3a–i** in good to excellent yields (Table 2, entries 1–9). The presence of both electron-donating and electron-accepting groups on the phenyl ring had little influence on the product yields under the present reaction conditions. The use of nitroethane and nitropropane as a nucleophile in the oxidative aza-Henry reaction gave the desired products **3j–o** but with decreasing yields (Table 2, entries 10–15), which may be because of the steric effect of the nucleophiles. With acyclic 4-*N*,*N*-trimethylaniline employed as a substrate, a satisfactory yield of 72% for the desired product **3p** was obtained (Table 2, entry 16).

ESR experiments were performed to gain insight into the Pt-catalyzed CDC reaction mechanism. Whereas $^1O_2$ was found to play a key role in the photo-oxidation reactions photosensitized by platinum(II) complexes,[10a] $O_2^{\bullet-}$ was proposed recently as the active species in the CDC reaction photocatalyzed by a platinum(II) terpyridyl complex.[12] Thus, for determination of the actual active species of oxygen in the present system, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethyl-1-piperidine (TEMP) were used as $O_2^{\bullet-}$ and $^1O_2$ scavengers, respectively, in the ESR measurements. Initial effort was engaged in the detection of $^1O_2$. As shown in Figure 2a, irradiation of an air-saturated DMF solution of TEMP and **Pt3** by a 100 W mercury lamp ($\lambda > 420$ nm) generated the characteristic signal of $^1O_2$.[15] However, the nitroxide radical TEMPO was hardly detected upon addition of **1a** in the same air-saturated DMF solution (Figure 2b). Instead, the characteristic signal of $O_2^{\bullet-}$ attributed to the DMPO–$O_2^{\bullet-}$ adduct was observed upon irradiation of a solution of DMPO, **Pt3**, and **1a** by a 100 W mercury lamp ($\lambda > 420$ nm) (Figure 2c); the spectrum and the hyperfine coupling constants ($\alpha^N = 12.8$ G, $\alpha_\beta^H = 9.8$ G) were in agreement

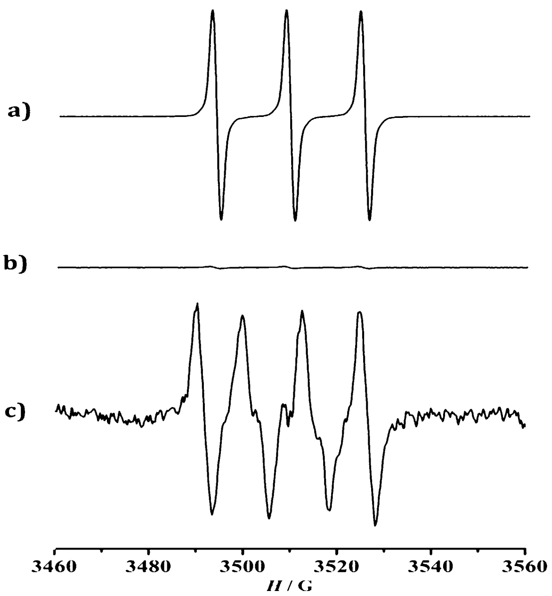
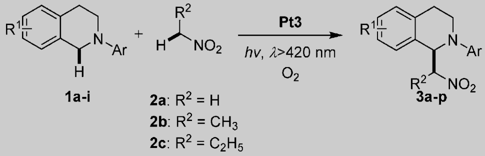
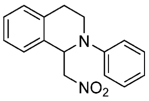
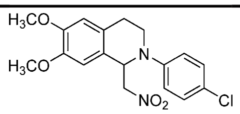
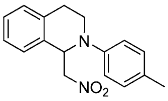
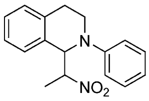
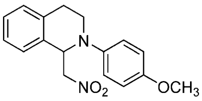
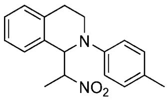
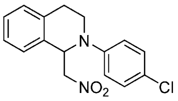
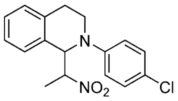
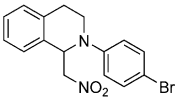
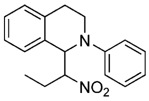
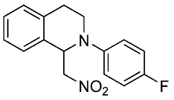
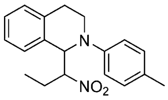
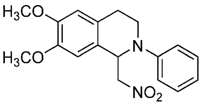
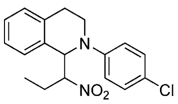
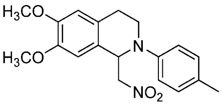
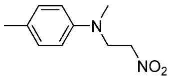


Figure 2. a) ESR spectrum of a solution in air-saturated DMF of **Pt3** (1.0×10^{-4} mol L^{-1}) and TEMP (2.0×10^{-2} mol L^{-1}) upon irradiation for 120 s. b) ESR spectrum of a solution in air-saturated DMF of **Pt3** (1.0×10^{-4} mol L^{-1}), **1a** (1.5×10^{-3} mol L^{-1}), and TEMP (2.0×10^{-2} mol L^{-1}) upon irradiation for 120 s. c) ESR spectrum of a solution in air-saturated DMF of **Pt3** (1.0×10^{-4} mol L^{-1}), **1a** (1.5×10^{-3} mol L^{-1}), and DMPO (2.0×10^{-2} mol L^{-1}) upon irradiation for 120 s. DMF = *N*,*N*-dimethylformamide.

Table 2. CDC reaction of tetrahydroisoquinolines with nitroalkanes using **Pt3** as photocatalyst.[a]



Entry	Product	Yield [%][b]	Entry	Product	Yield [%][b]
1		89	9		74
2		87	10		78
3		83	11		72
4		82	12		65
5		80	13		69
6		78	14		60
7		84	15		49
8		78	16		72

[a] Reaction conditions: **1** (0.2 mmol), **Pt3** (0.003 mmol), nitroalkane (10 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield of isolated product based on substrate **1**.

with the literature reports.[16] These observations imply that $O_2^{\bullet-}$ rather than $^1O_2$ was formed in the presence of *N*-phenyltetrahydroisoquinoline.

Then, the photoluminesence quenching of **Pt3** with the addition of *N*-phenyltetrahydroisoquinoline **1a** was performed to provide further information on the primary process of the reaction. As shown in Figure 3, upon addition of *N*-phenyltetrahydroisoquinoline **1a** to the solution of **Pt3** in degassed DMF, there was a drastic decrease in the emission intensity following a linear Stern–Volmer plot [Eq. (1)], in which I_0 is the emission intensity in the absence of quencher, I is the emission intensity in the presence of quencher, k_q is the quenching rate constant, τ_0 is the emission lifetime of **Pt3**, and [Q] is the concentration of the quencher. Analysis of the decay gave a quenching rate constant of $k_q = 3.07\times10^9\ s^{-1}\ M^{-1}$, suggesting that the intermolecular quenching was diffusion-controlled.

$$I_0/I = 1 + k_q\,\tau_0[Q] \qquad (1)$$

Evidently, *N*-phenyltetrahydroisoquinoline **1a** interacted with platinum(II) complex **Pt3** in the excited state. In light of the low energy of **Pt3** in the excited state with respect to that of **1a**, the energy transfer from the excited **Pt3** to **1a** is thermodynamically impossible. Therefore, photoinduced electron transfer should be responsible for the photoluminescence quenching. The free energy change (ΔG) of the electron transfer process was estimated by using the Rehm–Weller equation [Eq. (2)].

$$\Delta G^0 = E_{ox} - E_{red} - E_{00} - e^2/\varepsilon d < ZS > (2)$$

The ε value is high for polar solvents such as DMF, so the last term is negligible. According to previous reports, the oxidation potential E_{ox} of **1a** and the reduction potential E_{red} of **Pt3** are 0.82 and −1.10 V, respectively;[14] the E_{00} value (2.25 eV, Figure S1) of **Pt3** can be determined from the cross point of the absorption and emission spectra at 550 nm. Consequently, the negative ΔG of −0.33 eV confirms that the photoinduced electron transfer from **Pt3** to **1a** is thermodynamically favorable.

On the basis of the above results and literature reports,[17] the reaction mechanism for this photocatalytic CDC reaction is proposed, as shown in Scheme 1. We believe that visible light irradiation of **Pt3** generates the excited species **Pt3***, which is reductively quenched by **1a** through a single electron transfer (SET) process to form an aminyl radical cation **4** and radical anion $\mathbf{Pt3}^{\bullet-}$. The generated $\mathbf{Pt3}^{\bullet-}$ is subsequently quenched by molecular oxygen to furnish $O_2^{\bullet-}$ with concomitant recovery of the photocatalyst **Pt3**. Hydrogen abstraction of **4** by $O_2^{\bullet-}$ gives the iminium ion **5**, and subsequent deprotonation of the nucleophile, that is, CH_3NO_2, by the hydroperoxide anion HOO^- leads to hydrogen peroxide and the nucleophilic anion.[18] Finally, the iminium ion **5** undergoes nucleophilic addition to provide the desired product **3a**.

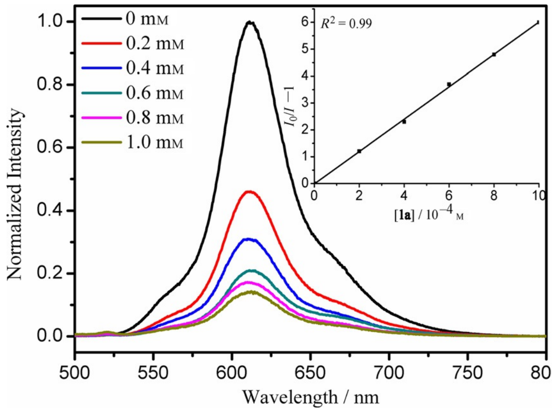
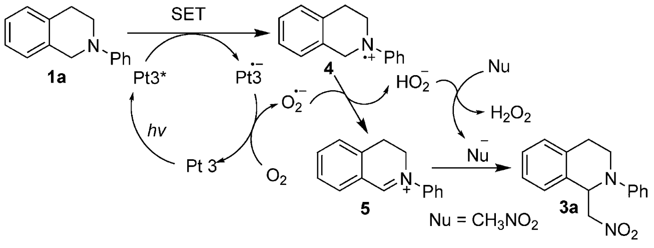


Figure 3. Luminescence spectra of **Pt3** (1.0×10^{-5} M) as a function of concentration of **1a** in degassed DMF with excitation at 450 nm. Inset is the Stern–Volmer plot of **Pt3** by **1a**.

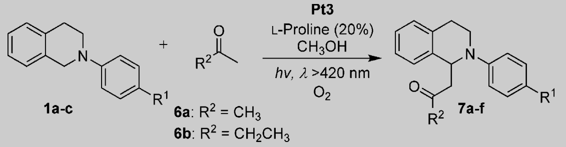


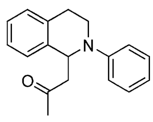
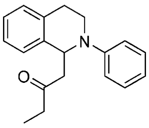
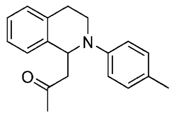
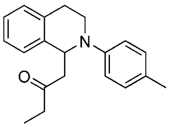
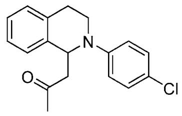
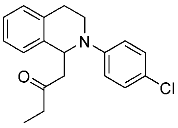
Scheme 1. Proposed reaction pathways for the aerobic photocatalytic CDC reaction.

The Mannich reaction is a fundamentally important C–C bond-forming reaction in organic synthesis, and is widely utilized in syntheses of nitrogen-containing drugs, natural products, and biologically active compounds.[19] Thus, in this work, the present photocatalytic CDC method was extended to the coupling of tetrahydroisoquinolines and acyclic ketones. If **Pt3** was used to catalyze the photochemical oxidative reaction of *N*-aryltetrahydroisoquinoline with acetone **6a** or methyl ethyl ketone **6b** in the presence of a cocatalyst, L-proline,[17b] under visible light irradiation in an oxygen atmosphere, the enantiopure Mannich-type product **7(a–f)** was obtained in moderate yield (Table 3).

Indoles and tetrahydroisoquinolines are naturally occurring heterocycles that are biologically active important pharmaceuticals,[20] and hence, the CDC methodology was also adopted for the coupling of tetrahydroisoquinolines with indoles. Initially, a solution of *N*-phenyltetrahydroisoquinoline **1a** and indole **8a** in DMF was irradiated with visible light under aerobic conditions using molecular oxygen as oxidant for 8 h. The desired product **9a** was obtained in moderate yield together with the formation of a byproduct amide **10** (Table S1, entry 1, Supporting Information). Upon performing the same reaction in the absence of indole **8a**, only amide **10** as a sole product was obtained in quantitative yield after 7 h (Table S1, entry 2). It has been reported that the introduction of $FeSO_4$ into this reaction system can efficiently prevent the formation of amide.[12] Indeed, the desired product **9a** can be obtained with an improved yield of 89% in the presence of $FeSO_4$ as an additive (Table S1, entry 3). Considering all these results, we determined the optimal reaction conditions, which include irradiation of a DMF solution of *N*-phenyltetrahydroisoquinoline and indole with platinum complex **Pt3** in the presence of $FeSO_4$ under an oxygen atmosphere for 8 h. For further investigation of the scope of this protocol, different *N*-aryltetrahydroisoquinolines and indole derivatives were subjected to these optimal reaction conditions and provided the desired indolyl tetrahydroisoquinolines in good yields (Table 4).

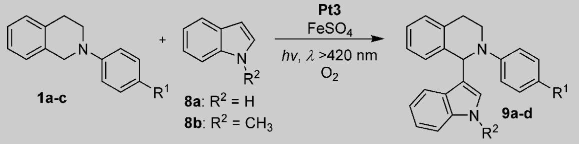
Table 3. The Mannich reaction of aryltetrahydroisoquinolines with ketone.[a]

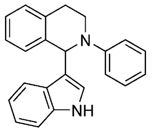
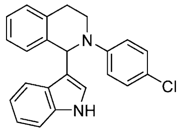
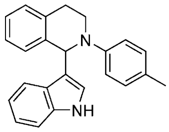
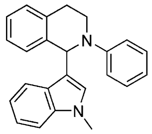


Product		Yield [%][b]	ee [%][c]	Product		Yield [%][b]	ee [%][c]
7a		63	99	**7d**		58	99
7b		66	99	**7e**		62	99
7c		64	99	**7f**		60	99

[a] Reaction conditions: **1** (0.2 mmol), **Pt3** (0.003 mmol), L-proline (0.04 mmol), ketone (6 mL), CH_3OH (4 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield of isolated product based on substrate **1**. [c] Determined by NMR spectroscopy.

Table 4. The CDC reaction of aryltetrahydroisoquinolines with indoles.[a]



Product		Yield [%][b]	Product		Yield [%][b]
9a		79	**9c**		68
9b		74	**9d**		76

[a] Reaction conditions: **1** (0.2 mmol), **Pt3** (0.003 mmol), indoles (0.4 mmol), $FeSO_4$ (0.4 mmol) dissolved in DMF (4 mL), irradiated at ambient temperature in the presence of oxygen. [b] Yield of isolated product based on substrate **1**.

Conclusion

In summary, we have synthesized four platinum(II) Schiff base complexes and examined their use in visible-light-induced CDC reactions. It was found that **Pt3** is the most efficient photocatalyst of the studied catalysts. Moreover, **Pt3** was used as the photocatalyst for the visible-light oxidative coupling reaction of tetrahydroisoquinoline with different nucleophiles such as nitroalkanes, ketones, and indoles. An ESR experiment provided evidence for the generation of $O_2^{\bullet-}$ under light irradiation. Further investigations on oxidative coupling reactions using platinum(II) complexes under visible light irradiation are underway in our laboratory.

Experimental Section

Electrospray Ionization (ESI) mass spectra were recorded on a Finnigan LCQ quadrupole ion trap mass spectrometer (samples were dissolved in HPLC-grade methanol). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Bruker Avance DPX 400 MHz instrument. UV/Vis absorption spectra were recorded on a PerkinElmer Lambda 19 UV/Vis spectrophotometer. Steady-state emission spectra were obtained on a SPEX 1681 Fluorolog-2 Model F111 fluorescence spectrophotometer equipped with a Hamamatsu R928 PMT detector. Melting points were determined with RY-1 Melting Point Apparatus. ESR spectra were recorded at room temperature with a Bruker ESP-300E spectrometer at 9.8 GHz, X-band with 100 Hz field modulation. Samples were injected quantitatively into specially made quartz capillaries for ESR analysis prior to purging with argon or oxygen for 30 min in the dark, and were illuminated directly in the cavity of the ESR spectrometer with a 100 W mercury lamp. Commercially available reagents and solvents were used without further purification unless indicated otherwise. The solvents used for spectral measurements were of HPLC grade. All the *N*-aryltetrahydroisoquinolines **1** needed for CDC reactions were prepared by following the reported procedure[21] and purified through column chromatography.

General procedure for the CDC reaction of nitroalkanes with tetrahydroisoquinolines

A mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), and **Pt3** (1.6 mg, 0.003 mmol) was dissolved in nitromethane (10 mL) in a 15 mL Pyrex tube equipped with a rubber septum and magnetic stirrer bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a 300 W Xe lamp at ambient temperature. A glass filter was employed to cut off light of wavelength below 420 nm. The progress of the reaction was monitored at regular intervals by thin-layer chromatography. After 8 h irradiation, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to afford the corresponding products.

General procedure for the Mannich reaction of acetone with tetrahydroisoquinolines

A mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), **Pt3** (1.6 mg, 0.003 mmol), and L-proline (4.6 mg, 0.04 mmol) was dissolved in a mixture of acetone (6 mL) and CH_3OH (4 mL) in a 15 mL Pyrex tube equipped with a rubber septum and magnetic stirrer bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a 300 W Xe lamp at ambient temperature. A glass filter was employed to cut off light of wavelength below 420 nm. After 8 h irradiation, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to afford the corresponding products.

General procedure for the CDC reaction of indoles with tetrahydroisoquinolines

A mixture of 2-phenyl-1,2,3,4-tetrahydroisoquinoline (42 mg, 0.2 mmol), **Pt3** (1.6 mg, 0.003 mmol), indole (0.4 mmol), and $FeSO_4$ (0.4 mmol) was dissolved in DMF (4 mL) in a 15 mL Pyrex tube equipped with a rubber septum and magnetic stirrer bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a 300 W Xe lamp at ambient temperature. A glass filter was employed to cut off light of wavelength below 420 nm. After 8 h irradiation, the solvent was removed under vacuum. Then, diethyl ether (25 mL) and water (25 mL) were added to the residue. The organic layer was extracted with diethyl ether (3×25 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel to afford the corresponding products.

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Keywords: aerobic reaction · C–C coupling · electron transfer · photochemistry · platinum

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