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A Highly Efficient and Selective Aerobic Cross-Dehydrogenative-Coupling Reaction Photocatalyzed by a Platinum(II) Terpyridyl Complex

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Abstract: Thanks to the superior redox potential of platinum(II) complex compared with that of $Ru(bpy)_3^{2+}$ in the excited state, an efficient and selective visible-light-induced CDC reaction has been developed by using a catalytic amount (0.25%) of **1**. With the aid of $FeSO_4$ (2 equiv), the corresponding amide could not be detected under visible-light irradiation ($\lambda = 450$ nm), but the desired cross-coupling product was exclusively obtained under ambient air conditions. A spectroscopic study and product analysis revealed that the CDC reaction is initiated by photoinduced electron-transfer from *N*-phenyltetrahydroisoquinoline to the complex. An EPR (electron paramagnetic resonance) experiment provides direct evidence on the generation of superoxide radical anion ($O_2^{-\bullet}$) rather than singlet oxygen ($^1O_2$) under irradiation of the reaction system, in contrast to that reported in the literature. Combined, the photoinduced electron-transfer and subsequent formation of superoxide radical anion ($O_2^{-\bullet}$) results in a clean and facile transformation.

Keywords: aerobic reaction · cross-coupling · platinum · radicals · visible-light catalysis

Introduction

The cross-dehydrogenative-coupling (CDC) reaction[1] is one of the most powerful tools to construct C–C bonds[2] directly from two different C–H bonds under oxidative conditions. Such a coupling makes the reaction more atom-economic and simpler because it avoids the prefunctionalization and defunctionalization that have been part of the traditional synthetic design. With the aid of a sacrificial oxidant, inorganic metal salts and organic oxidants have been successfully employed for the transformation in the past decade.[1–3] Recently, the use of visible light[4–7] to initiate a CDC reaction has appeared at the forefront. Stephenson et al.[8] took the lead in realizing the oxidative coupling of nitroalkanes and tetrahydroisoquinolines through visible-light catalysis. König,[9a] Tan,[9b] and our group[9c] developed the metal-free visible-light oxidative coupling of tetrahydroisoquinoline derivatives with various nucleophiles such as nitroalkanes, dialkyl malonates, dialkyl phophonates, and ketones, respectively. Significantly, molecular oxygen was found capable of facilitating the photoredox catalysis remarkably well, and the superoxide radical anion ($O_2^{-\bullet}$) has been demonstrated to be responsible for the large rate of acceleration of the aerobic photocatalytic reactions. Moreover, Rueping et al.[10] reported a dual catalytic system combining photoredox catalysis with Lewis base catalysis for the Mannich reaction. Rovis et al.[11] realized a catalytic asymmetric α-acylation of tertiary amines with aldehydes by combination of chiral N-heterocyclic carbene catalysis and photoredox catalysis. The group of Blechert and Wang[12] made use of mesoporous graphitic carbon nitride to construct C–C bonds of tertiary amines with nucleophiles under visible light. All of the studies indicate that the visible-light catalytic CDC reaction is an interesting subject, whereas a photocatalyst that can harness visible light to initiate a robust and efficient reaction has yet to be developed.

Thanks to visible-light absorption, long excited-state lifetime, high luminescent quantum yield, and good chemical stability, platinum(II) polypyridyl complexes[13–17] have been promising to initiate photochemical reactions.[18–19] With visible-light irradiation, for example, pyridine derivatives, 3,4-diarylpyrroles, and 3,4-diarylthiophenes have been successfully obtained,[18] respectively, in the absence of any oxidants. On the other hand, we have shown that platinum(II) polypyridyl complexes are ideal sensitizers for photooxidation by using molecular oxygen,[19] in which singlet oxygen ($^1O_2$) was generated upon irradiation of light in the visible region. Compared with the famous $Ru(bpy)_3^{2+}$ that is employed in visible-light catalysis,[20–22] the platinum(II) complex is still in its infancy.

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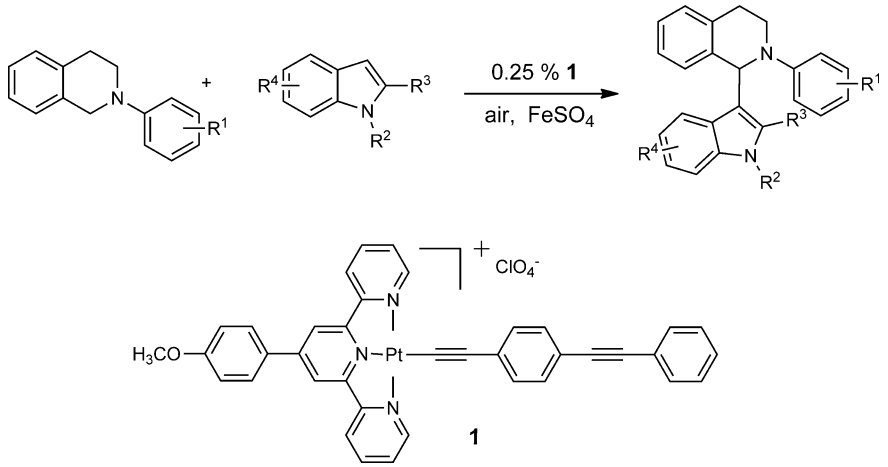


Scheme 1. Visible-light catalysis of indolation with tetrahydroisoquinolines by a platinum(II) complex **1**.

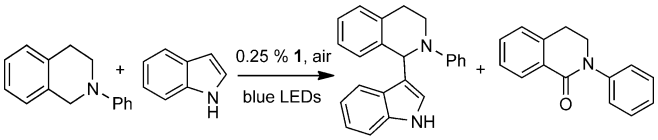
In the present work, we wish to report a highly efficient and selective visible-light-induced CDC reaction by using a catalytic amount (0.25 mol%) of a platinum(II) terpyridyl complex **1** (Scheme 1). With this system, we are able to obtain the desired coupling compounds of *N*-phenyltetrahydroisoquinolines and indoles within a short reaction time. Under ambient air conditions, the addition of $FeSO_4$ (2.0 equiv) improved the reaction selectivity remarkably, and the desired cross-coupling product was obtained exclusively. A spectroscopic study and product analysis reveal that the CDC reaction is initiated by photoinduced electron-transfer from *N*-phenyltetrahydroisoquinoline to the platinum(II) terpyridyl complex **1**. In contrast to the previous studies[19] on photosensitized oxidation by platinum(II) complexes, the EPR measurement demonstrates for the first time that superoxide radical anion ($O_2^{-\bullet}$) rather than singlet oxygen ($^1O_2$) was responsible for the facile transformation. The higher efficiency and selectivity is attributed to the superior redox potential of platinum(II) complex **1** compared with that of $Ru(bpy)_3^{2+}$[23] in the excited state.

Results and Discussion

Our initial study focused on the CDC coupling reaction of *N*-phenyltetrahydroisoquinoline with indole at room temperature. As *N*-phenyltetrahydroisoquinoline **2a** and indole **3a** were irradiated by blue LEDs ($\lambda = 450$ nm) at ambient conditions for 2 h, the desired product **4a** was obtained in a moderate yield accompanying with the formation of byproduct amide **5** (Table 1). Complete conversion of *N*-phenyltetrahydroisoquinoline was achieved in CH_3CN and DMF within 2 h irradiation. However, the conversion was rather low in either H_2O or a mixed solution of DMF and H_2O, even after a prolonged reaction time (Table 1, entries 1–4). It was noted that in the absence of indole **3a**, *N*-phenyltetrahydroisoquinoline was transformed into the corresponding amide **5** in a quantitative yield within 2 h (Table 1, entry 5), whereas in the presence of **3a** both the desired product **4a** and byproduct amide **5** were obtained similar to that observed in the literature.[3j,k,l]

Molecular oxygen[24–25] is crucial for this CDC reaction. When the reaction took place in an atmosphere of nitrogen, no photoproduct was observed (Table 1, entry 6). As mentioned above, the platinum(II) complex is an ideal photosensitizer for producing singlet oxygen ($^1O_2$).[19] However, the superoxide radical anion ($O_2^{-\bullet}$) was recently proposed as the active species in the CDC reaction.[9c] To make things clear, we studied the active species of oxygen in the reaction system of platinum(II) complex **1** by EPR, in which 2,2,6,6-tetramethyl-1-piperidine (TEMP) was used to capture $^1O_2$, and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a probe to trap $O_2^{-\bullet}$. As shown in Figure 1, irradiation of the DMF solution of TEMP and the platinum(II) complex **1** in air by blue LEDs resulted in the formation of characteristic signal of $^1O_2$, similar to our previous observation.[19] When *N*-phenyltetrahydroisoquinoline was added into the solution, however, the $^1O_2$ signal could not be detected. Instead, the characteristic signal of $O_2^{-\bullet}$ was clearly observed when DMPO was used as radical scavenger.

Table 1. Optimization of reaction conditions.[a]



2a **3a** **4a** **5**

	Conditions[a]	*t* [h]	Conv. [%][b]	**4a** [%][b]	**5** [%][b]
1	CH_3CN	2	100	45	47.6
2	H_2O	6	18	14.8	trace
3	DMF/H_2O	4	30	15	4.8
4	DMF	2	100	57	18
5[c]	DMF	2	100	–	100
6	DMF, in N_2	24	0	–	–
7	DMF, $FeSO_4$ (2.0 equiv)	4	100	93	–
8	CH_3CN, $FeSO_4$ (2.0 equiv)	4	100	65	28
9	DMF, $FeSO_4$ (1.1 equiv)	4	100	75	16
10	DMF, **3a** (1.2 equiv), $FeSO_4$ (2.0 equiv)	12	100	91	–
11[d]	DMF, **3a** (2.0 equiv), $FeSO_4$ (2.0 equiv)	6	100	93	–
12[e]	DMF, **3a** (2.0 equiv), $FeSO_4$ (2.0 equiv)	12	100	76	15

[a] Reaction conditions: *N*-phenyltetrahydroisoquinoline (0.1 mmol), **3a** (0.3 mmol), **1** (0.25 mol%), solvent (2 mL), ambient air, blue LEDs ($\lambda =$ 450 nm) irradiation. [b] Yields detected by NMR spectroscopy using an internal standard, 4-nitroacetophenone. [c] **3a** was not added. [d] **3a** (2.0 equiv) was used. [e] $[Ru(bpy)_3(PF_6)_2]\cdot 6H_2O$ (1 mol%) was used to replace **1** under the same conditions as entry 11.

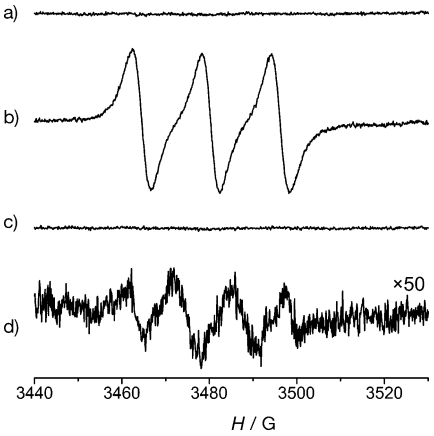


Figure 1. EPR measurement of a) a solution in DMF of platinum(II) complex **1** without *N*-phenyltetrahydroisoquinoline in the presence of DMPO (2.0×10^{-2} M); b) a solution in DMF of platinum(II) complex **1** without *N*-phenyltetrahydroisoquinoline in the presence of TEMP (2.0×10^{-2} M); c and d) a solution in DMF of *N*-phenyltetrahydroisoquinoline with the platinum(II) complex **1** (1.0×10^{-4} M) in the presence of c) TEMP (2.0×10^{-2} M) and d) DMPO (2.0×10^{-2} M).

To understand the primary process of the reaction, we examined the interaction between *N*-phenyltetrahydroisoquinoline and complex **1**. Platinum(II) complex **1** displays a broad visible-light absorption, assigned to a mixture of metal-to-ligand and ligand-to-ligand charge-transfer transitions,[26–27] ranging from 400 to 500 nm (Figure 2a). Excitation of the absorption resulted in moderately intense luminescence at λ_{max} 608 nm ($\tau=309$ ns) in degassed DMF solution at room temperature, which was readily quenched by *N*-phenyltetrahydroisoquinoline **2a** following the Stern–Volmer kinetics (Figure 2b). Evidently, *N*-phenyltetrahydroisoquinoline **2a** interacted with platinum(II) complex **1** in the excited state. Since the energy of singlet excited state of complex **1** is much lower than that of **2a**, the singlet energy-transfer from the excited complex **1** to **2a** is thermodynamically impossible. Therefore, the luminescence quenching is probably due to the photoinduced electron-transfer. Combining the electrochemical and spectroscopic studies, we estimated the free-energy change (ΔG) of the photoinduced electron-transfer process. According to the determined oxidation potential E_{ox} of **2a** (0.82 V), reduction potential E_{red} of complex **1** (−1.18 V), and the excited state energy E_{00} of complex **1** that was read from the cross-point of the absorption and luminescence spectra at 500 nm (2.48 V, Figure 2), the negative free energy change ($\Delta G=-0.48$ V) calculated by using the Rehm–Weller Equation (1) revealed that the photoinduced electron-transfer from complex **1** to **2a** is thermodynamically feasible. As compared with $Ru(bpy)_3^{2+}$, the platinum(II) complex **1** has a more positive redox potential ($E_{red}=-1.18$ V and −1.33 V, and $E_{00}=2.48$ V and 2.12 V for complex **1** and $Ru(bpy)_3^{2+}$, respectively).

$$\Delta G^0 = E_{ox}-E_{red}-E_{00} \quad (1)$$

On the basis of above results, we proposed a plausible reaction pathway shown in Scheme 2. Upon excitation of the

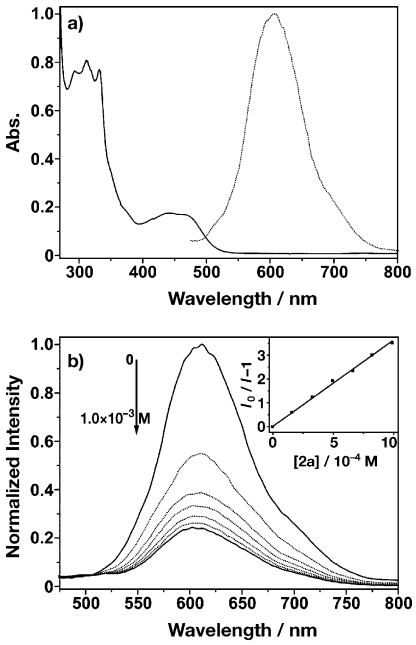
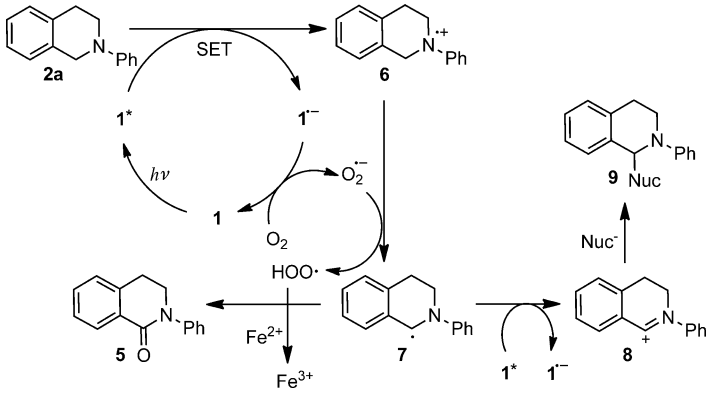


Figure 2. a) UV/Vis absorption and luminescence spectra of platinum(II) complex **1** (1.0×10^{-5} M) in DMF. b) Luminescence spectra of platinum(II) complex **1** (1.0×10^{-5} M) as a function of concentration of **2a** in degassed DMF with excitation at 450 nm. Inset is the Stern–Volmer plot of complex **1** by **2a**.



Scheme 2. A plausible reaction pathway.

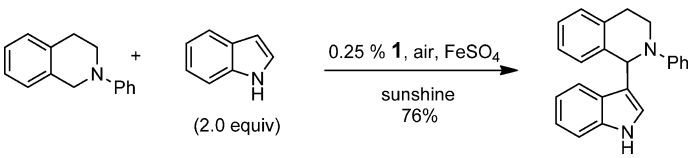
platinum(II) complex **1** at $\lambda=450$ nm, a single electron-transfer reduction[28] of the excited platinum(II) complex **1*** by **2a** takes place to generate radical cation **6** and one-electron-reduced radical **1**$^{-\bullet}$, which was subsequently quenched by oxygen to generate the superoxide radical anion ($O_2^{-\bullet}$) and the platinum(II) complex is recovered. Subsequently, hydrogen abstraction of **6** by $O_2^{-\bullet}$, generates a hydroperoxide free radical and intermediate **7**. There are two competitive reaction pathways: one is that **7** would lose one electron to give rise to a reactive intermediate iminium **8**, followed by nucleophile addition to give desired product **9**; whereas,

in the other pathway, the generated hydroperoxide free radical reacts directly with **7** to yield the byproduct amide **5**.

To further confirm the reaction mechanism, we introduced $FeSO_4$ to react with the hydroperoxide free radical generated from the reaction. It was encouraging to see that no amide was observed in the presence of the additive $FeSO_4$ (2 equiv). The selectivity of reaction was improved greatly and the yield of the desired product was excellent (Table 1, entry 7). An excess of $FeSO_4$ and indole were found to be necessary to obtain a good yield of the product (Table 1, entry 9). The absence of any components of reaction led to no or little formation of the desired product. Taking all these results together, we performed the CDC reaction under the optimized conditions: a DMF solution of *N*-phenyltetrahydroisoquinoline and indole (2 equiv) with the platinum(II) complex **1** (0.25%) in the presence of $FeSO_4$ (2 equiv) under an air atmosphere were irradiated by blue LEDs ($\lambda = 450$ nm) at room temperature. Strikingly, the performance of 0.25 mol% of platinum(II) complex **1** is much better than that of 1 mol% $Ru(bpy)_3^{2+}$ under the same conditions. In addition, the byproduct amide **5** could not be completely eliminated in the presence of $FeSO_4$ (2 equiv) when $Ru(bpy)_3^{2+}$ was used (Table 1, entry 12).

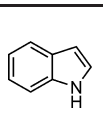
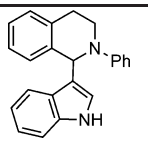
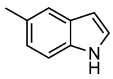
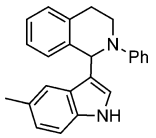
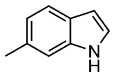
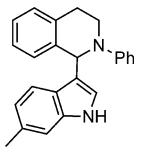
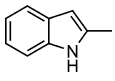
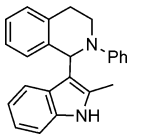
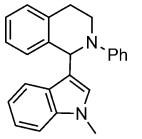
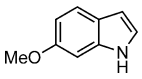
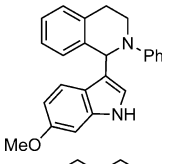
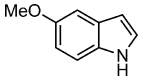
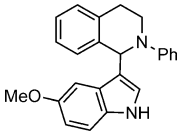
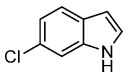
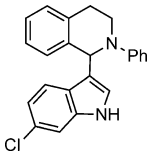
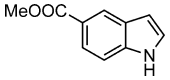
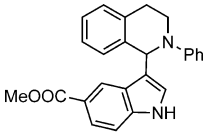
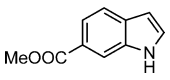
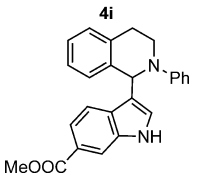
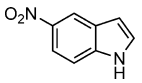
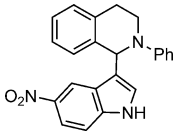
To extend the scope of reaction, we utilized different substituted indoles, and the representative results are listed in Table 2. Evidently, indoles with electron-donating groups worked well with **2a** giving the products in excellent yields (Table 2, entries 2–7). When electron-withdrawing groups were linked to indole, the reaction proceeded with slightly poor yields (Table 2, entry 11). This may be due to the electron-withdrawing groups having a great influence on the electron density of indole to reduce its nucleophilicity. With a prolonged reaction time, the steric hindrance does not seem to affect the yield of the reaction significantly (Table 2, entry 4).

Furthermore, we explored the variety of *N*-phenyltetrahydroisoquinolines. For both electron-withdrawing and electron-donating groups, the desired products could be obtained in excellent yields (Table 3). In spite of this, the reaction time is dependent on the linking groups; electron-donating groups need more time to achieve higher yields (Table 3, entries 1–3). Good to excellent yields were also obtained by using more nucleophilic substrates, such as nitroalkanes and malonate esters, to replace indoles (Table 4). Significantly, when the aerobic oxidative coupling was carried out under ambient sunlight, the combination of **2a** with **3a** could give rise to the desired product in 76% yield (Scheme 3). Clearly, the platinum(II) complex **1** is an ideal



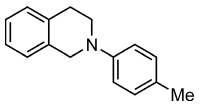
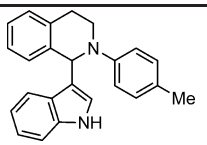
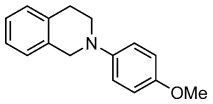
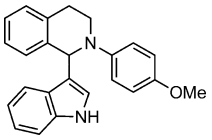
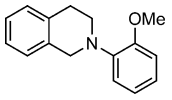
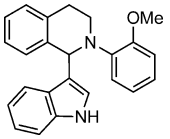
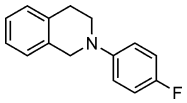
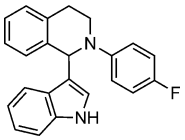
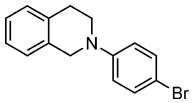
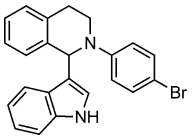
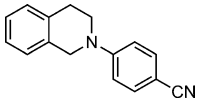
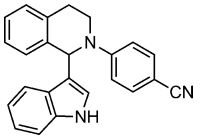
Scheme 3. Visible-light-driven aerobic CDC reaction under ambient sunshine irradiation.

Table 2. Scope of indoles for the indolation of **2a**.[a]

	3	Product 4		t [h]	Yield [%][b]
1		**3a**		**4a**	6	93 (81)
2		**3b**		**4b**	6	95 (76)
3		**3c**		**4c**	12	94 (80)
4		**3d**		**4d**	24	92 (74)
5		**3e**		**4e**	12	91 (78)
6		**3f**		**4f**	12	89 (75)
7		**3g**		**4g**	12	90 (76)
8		**3h**		**4h**	6	85 (68)
9		**3i**		**4i**	6	82 (63)
10		**3j**		**4j**	6	85 (67)
11		**3k**		**4k**	6	78 (56)

[a] Reaction conditions: *N*-phenyltetrahydroisoquinoline **2a** (0.1 mmol), indoles (0.2 mmol), $FeSO_4$ (0.2 mmol), platinum(II) complex **1** (0.25 mol%), DMF (2 mL), ambient air, blue LEDs irradiation. [b] Yields detected by NMR spectroscopy using an internal standard, 4-nitroacetophenone; the isolated product yields are given in parentheses.

Table 3. Varieties of tetrahydroisoquinoline derivatives.[a]

	2	Product 4		t [h]	Yield [%][b]
1		**2b**		**4l** 18	95 (75)
2		**2c**		**4m** 32	94 (78)
3		**2d**		**4n** 32	92 (72)
4		**2e**		**4o** 6	93 (78)
5		**2f**		**4p** 6	91 (77)
6		**2g**		**4q** 12	93 (71)

[a] Reaction conditions: Tetrahydroisoquinolines (0.1 mmol), **3a** (0.2 mmol), $FeSO_4$ (0.2 mmol), **1** (0.25 mol%), DMF (2 mL), ambient air, blue LEDs irradiation. [b] Yield detected by NMR spectroscopy using an internal standard, 4-nitroacetophenone; the isolated product yields are given in parentheses, the isolated product yield was lower because of some decomposition during the chromatography.

photocatalyst capable of using sunlight and air for the environmental benign CDC transformation.

Conclusion

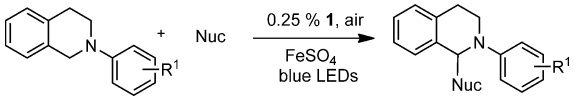
We have developed a visible-light-induced CDC reaction[29] by using a catalytic amount of platinum(II) complex **1** (0.25%). On account of its excellent photophysical and electrochemical characteristics, a small quantity of platinum(II) complex **1** can be employed as an efficient photocatalyst even under ambient sunshine irradiation. With the aid of additive $FeSO_4$ (2 equiv), the byproduct amide **5** that is generally observed in the CDC transformation has been completely eliminated, resulting in the formation of the cross-coupling product exclusively. Thanks to superior redox potential of platinum(II) complex **1** compared with that of $Ru(bpy)_3^{2+}$ in the excited state, the CDC transformation driven by complex **1** is more efficient and selective than the other reported photocatalytic systems. An EPR experiment provides direct evidence for the generation of superoxide radical anion under light irradiation. This is, to the best of our knowledge, the first example of the formation of a superoxide radical anion ($O_2^{-\bullet}$) by a platinum(II) complex. Further extension of visible-light catalytic systems by using powerful platinum(II) complexes is actively undergoing in our laboratory.

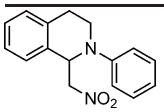
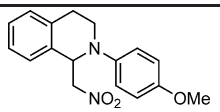
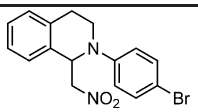
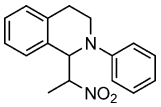
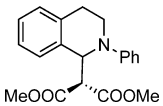
Experimental Section

General: ^1H NMR spectra were recorded by using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet); coupling constants (J) are in Hertz (Hz). ^{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. Commercially available reagents and solvents were used without further purification unless indicated otherwise. All of the *N*-aryl tetrahydroisoquinolines needed for CDC reactions were prepared by using the reported procedure and purified through column chromatography (300–400 mesh). Irradiation was performed by using blue LEDs (1 W, $\lambda = (450 \pm 10)$ nm, 145 Lm @700 mA).

General procedure for the synthesis of the photocatalyst: Complex **1** was prepared by the reaction of [Pt(trpy)Cl]Cl (trpy = 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine) with $HCCC_6H_4CCC_6H_5$-4 (2 equiv), which was synthesized by the literature method in the presence of catalyst CuI and trimethylamine under nitrogen in DMF at room temperature. Recrystallization of the crude product by diffusion of diethyl ether vapor into an acetonitrile solution gave complex **1** as orange crystals. ^1H NMR (400 MHz, DMSO): $\delta = 8.77$–8.48 (m, 6H), 8.28 (s, 2H), 7.95 (d, $J =$

Table 4. The visible-light-induced CDC reaction[a] of tetrahydroisoquinolines with other nucleophiles catalyzed by the platinum(II) complex **1**.



Product, Yield [%][b]		
 **4r** 90 (81)	 **4s** 96 (83)	 **4t** 92 (78)
 **4u** 81 (70)	 **4v** 95 (80)	

[a] Reaction conditions: Tetrahydroisoquinolines (0.1 mmol), nucleophile (0.3 mmol) was added, $FeSO_4$ (0.2 mmol), **1** (0.25 mol%), DMF (2 mL), ambient air, blue LEDs irradiation. [b] Yields detected by NMR spectroscopy using an internal standard, 4-nitroacetophenone; the isolated product yields are given in parentheses.

7.8, 2H), 7.59 (d, $J=19.4$, 4H), 7.46 (s, 3H), 7.37 (d, $J=7.6$, 2H), 7.26 (d, $J=7.5$, 2H), 7.10 (d, $J=7.7$, 2H), 3.87 ppm (s, 3H); IR: $\tilde{\nu}=2118\ cm^{-1}$; fluorescence (DMF): $\lambda_{ab}=450$; $\lambda_{em}=608$ nm; MS (FAB): m/z: 735 [M^+]; elemental analysis calcd for $C_{38}H_{26}ClN_3O_5Pt\cdot0.5H_2O$: C 54.07; H 3.22; N 4.98; O 10.42; found: C 53.84; H 2.94; N 4.81; P 10.38.

General procedure for the preparation of *N*-phenyltetrahydroisoquinolines: Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were put into a Schlenk-tube. The Schlenk-tube was evacuated and back filled with nitrogen. Next, 2-propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), Next, 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15.0 mmol), and iodobenzene (1.12 mL, 10.0 mmol) were added successively at room temperature. The reaction mixture was heated at 90°C for 24 h and then allowed to cool to room temperature. Diethyl ether (25 mL) and water (25 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2×25 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 using hexane/ethyl acetate (30:1) as eluent.

General procedure for the visible-light-induced CDC reaction: The tetrahydroquinoline derivatives (0.1 mmol, 1 equiv), indole derivatives (0.2 mmol, 2 equiv), $FeSO_4$ (0.2 mmol, 2 equiv), and platinum(II) complex **1** (0.00025 mmol, 0.0025 equiv) were dissolved in DMF (2 mL) in a 10 mL reaction tube equipped with magnetic stirring bar, and the resulting mixture was irradiated using blue LEDs under the ambient air condition. After the substrate was completely converted (monitored by TLC), the reaction mixture was evaporated under reduced pressure until DMF was gone. 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 sulphate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel by using hexane/ethyl acetate (20:1) as eluent.

1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4a): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.6$). ^{1}H NMR (400 MHz, acetone): $\delta=10.05$ (s, 1H), 7.56 (d, $J=8.0$, 1H), 7.37 (d, $J=7.6$, 2H), 7.28–7.12 (m, 5H), 7.07 (dd, $J=7.6$, 5.1, 3H), 6.94 (t, $J=7.5$, 1H), 6.79 (s, 1H), 6.69 (t, $J=7.0$, 1H), 6.28 (s, 1H), 3.65 (dd, $J=8.9$, 4.7, 2H), 3.16–2.99 (m, 1H), 2.93–2.84 ppm (m, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=150.8$, 139.0, 138.1, 136.4, 130.0, 129.6, 129.0, 127.6, 127.4, 126.5, 125.5, 122.3, 120.6, 119.8, 119.4, 118.6, 116.3, 112.3, 57.3, 42.9, 27.5 ppm; MS (EI, 70 eV): m/z (%): 324 (100) [M^+], 229, 218, 202, 93, 68.

1-(2-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4d): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.4$). ^{1}H NMR (400 MHz, acetone): $\delta=9.85$ (s, 1H), 7.20 (d, $J=8.2$, 2H), 7.18–7.01 (m, 8H), 6.92 (t, $J=7.5$, 1H), 6.82–6.71 (m, 2H), 6.07 (s, 1H), 3.69 (dt, $J=13.0$, 6.6, 1H), 3.66–3.54 (m, 1H), 3.06 (t, $J=5.9$, 2H), 2.14 ppm (s, 3H); ^{13}C NMR (100 MHz, acetone): $\delta=$ 152.1, 139.6, 136.5, 136.3, 134.6, 129.6, 129.4, 129.2, 127.0, 126.7, 121.1, 120.7, 120.0, 119.9, 119.6, 113.9, 111.2, 110.1, 57.7, 46.8, 28.9, 12.4 ppm; MS (EI, 70 eV): m/z (%): 338 (100) [M^+], 245, 218, 217, 209.

1-[4-(2-Methoxypropenyl)-1*H*-pyrrol-3-yl]-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4g): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.5$). ^{1}H NMR (400 MHz, acetone): $\delta=9.90$ (s, 1H), 7.41–7.33 (m, 1H), 7.28–7.13 (m, 6H), 7.08 (d, $J=8.1$, 2H), 6.96 (d, $J=2.3$, 1H), 6.77–6.64 (m, 3H), 6.25 (s, 1H), 3.63 (m, 5H), 3.08 (dt, $J=15.4$, 7.5, 1H), 2.91 ppm (dt, $J=16.2$, 4.7, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=154.7$, 151.1, 139.2, 136.4, 133.1, 130.0, 129.5, 129.0, 128.0, 127.4, 126.5, 126.1, 118.8, 118.7, 116.6, 112.8, 112.4, 102.6, 57.5, 55.8, 42.8, 27.9 ppm; MS (EI, 70 eV): m/z (%): 354 [M^+], 261 (100), 217, 206, 93.

1-(6-Chloro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4h): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.6$). ^{1}H NMR (400 MHz, acetone): $\delta=10.20$ (s, 1H), 7.49 (d, $J=8.5$, 1H), 7.40 (d, $J=1.5$, 1H), 7.36 (d, $J=5.6$, 1H), 7.25–7.13 (m, 5H), 7.07 (d, $J=8.0$, 2H), 6.94 (dd, $J=8.5$, 1.8, 1H), 6.82 (s, 1H), 6.71 (t, $J=7.2$, 1H), 6.26 (s, 1H), 3.68–3.57 (m, 2H), 3.13–3.01 (m, 1H), 2.88 ppm (dt, $J=16.3$, 4.7, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=150.9$, 138.7, 138.5, 136.4, 130.0, 129.7, 129.0, 127.8, 127.6, 126.6, 126.5, 126.3, 121.9, 120.2, 119.7, 119.0, 116.7, 112.1, 57.2, 43.1, 27.5 ppm; MS (EI, 70 eV): m/z (%): 358 [M^+], 264 (100), 253, 93.

1-(5-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4b): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.7$). ^{1}H NMR (400 MHz, acetone): $\delta=9.90$ (s, 1H), 7.35 (dd, $J=7.6$, 2.7, 2H), 7.27–7.12 (m, 6H), 7.07 (d, $J=7.9$, 2H), 6.91 (dd, $J=8.3$, 1.5, 1H), 6.73–6.66 (m, 2H), 6.23 (s, 1H), 3.66 (dt, $J=$ 10.2, 4.5, 2H), 3.07 (ddd, $J=15.4$, 8.9, 6.2, 1H), 2.88 (dt, $J=16.3$, 4.7, 1H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, acetone): $\delta=151.4$, 139.6, 137.0, 136.9, 130.4, 130.0, 129.5, 128.9, 128.3, 127.9, 126.9, 126.1, 124.4, 120.8, 119.5, 119.1, 117.0, 112.5, 57.8, 43.4, 28.0, 22.3 ppm; MS (EI, 70 eV): m/z (%): 338 (100) [M^+], 245, 232, 217, 121, 93; HRMS (ESI): m/z calcd for $C_{24}H_{23}N_2$: 339.18558 [$M+$H]; found: 339.18518.

1-(6-Methoxyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4f): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.5$). ^{1}H NMR (400 MHz, acetone): $\delta=$ 9.83 (s, 1H), 7.43–7.31 (m, 2H), 7.22–7.12 (m, 5H), 7.06 (d, $J=7.9$, 2H), 6.89 (d, $J=2.2$, 1H), 6.69 (t, $J=7.2$, 1H), 6.62 (ddd, $J=11.0$, 5.5, 1.6, 2H), 6.22 (s, 1H), 3.76 (s, 3H), 3.68–3.60 (m, 2H), 3.13–3.00 (m, 1H), 2.88 ppm (dt, $J=16.2$, 4.8, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=157.8$, 151.4, 139.5, 139.4, 136.9, 130.4, 130.0, 129.5, 127.9, 126.9, 124.7, 122.5, 121.7, 119.8, 119.1, 116.8, 110.5, 95.9, 57.9, 56.2, 43.4, 28.0 ppm; MS (EI): m/z (%): 354 [M^+], 261 (100), 246, 217, 206, 93; HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O$ [$M-$H]: 353.16484; found: 353.16548.

3-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1*H*-indole-5-carboxylic acid methyl ester (4i): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, $R_f=0.2$). ^{1}H NMR (400 MHz, acetone): $\delta=10.40$ (s, 1H), 8.41–8.31 (m, 1H), 7.77 (dd, $J=8.6$, 1.6, 1H), 7.43 (dd, $J=8.6$, 0.4, 1H), 7.38 (dd, $J=4.7$, 2.9, 1H), 7.24–7.14 (m, 5H), 7.14–7.06 (m, 2H), 6.89 (d, $J=1.4$, 1H), 6.77–6.67 (m, 1H), 6.32 (s, 1H), 3.81 (s, 3H), 3.65 (dd, $J=7.5$, 4.8, 2H), 3.08 (dt, $J=15.3$, 7.5, 1H), 2.90 ppm (dt, $J=16.3$, 4.7, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=168.3$, 150.9, 140.6, 138.7, 136.4, 130.0, 129.7, 129.0, 127.6, 127.3, 127.1, 126.6, 123.7, 123.6, 122.1, 120.9, 119.1, 117.0, 112.1, 57.2, 51.9, 43.23, 27.5 ppm; MS (EI): m/z (%) = 382.17 [M^+], 288 (100), 277, 229, 218, 93.

3-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1*H*-indole-6-carboxylic acid methyl ester (4j): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, $R_f=0.3$). ^{1}H NMR (400 MHz, acetone): $\delta=10.45$ (s, 1H), 8.11 (s, 1H), 7.61 (dt, $J=18.4$, 4.9, 2H), 7.39–7.33 (m, 1H), 7.23–7.14 (m, 5H), 7.07 (d, $J=8.0$, 2H), 7.02 (d, $J=1.9$, 1H), 6.71 (t, $J=7.2$, 1H), 6.30 (s, 1H), 3.85 (s, 3H), 3.63 (dd, $J=7.5$, 4.9, 2H), 3.07 (dt, $J=15.3$, 7.5, 1H), 2.92 ppm (t, $J=4.7$, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=167.3$, 150.0, 137.8, 136.4, 135.4, 130.0, 129.0, 128.7, 128.2, 128.0, 126.7, 125.7, 123.3, 119.7, 119.4, 119.0, 118.1, 115.8, 113.6, 56.3, 51.2, 42.2, 26.7 ppm; MS (EI): m/z (%): 382 [M^+], 289 (100), 277, 230, 218, 206, 93; HRMS (ESI): m/z calcd for $C_{25}H_{23}N_2O_2$ [$M+$H]: 383.17540; found: 383.17577.

1-(5-Nitro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4k): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, $R_f=0.2$). ^{1}H NMR (400 MHz, acetone) $\delta=10.76$ (s, 1H), 8.49 (d, $J=2.2$, 1H), 7.99 (dd, $J=9.0$, 2.3, 1H), 7.54 (d, $J=9.0$, 1H), 7.43–7.35 (m, 1H), 7.24–7.18 (m, 5H), 7.12 (d, $J=7.9$, 2H), 7.04 (s, 1H), 6.75 (t, $J=7.2$, 1H), 6.37 (s, 1H), 3.70–3.54 (m, 2H), 3.15–3.02 (m, 1H), 2.92 ppm (dd, $J=12.9$, 8.2, 1H); ^{13}C NMR (100 MHz, acetone): $\delta=150.0$, 141.3, 140.1, 137.3, 135.4, 129.1, 128.9, 128.3, 128.1, 126.8, 125.9, 125.8, 121.0, 118.7, 117.0, 116.8, 116.5, 111.7, 56.3, 42.5, 26.7 ppm; MS (EI): m/z (%): 369.14 (100) [M^+], 264, 217, 206, 104, 77.

1-(6-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4c): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, $R_f=0.5$). ^{1}H NMR (400 MHz, acetone): $\delta=9.88$ (s, 1H), 7.41 (d, $J=8.2$, 1H), 7.39–7.32 (m, 1H), 7.23–7.12 (m, 6H), 7.06 (d, $J=8.0$, 2H), 6.78 (d, $J=8.1$, 1H), 6.72–6.64 (m, 2H), 6.23 (s, 1H), 3.65 (dd, $J=8.9$, 4.7, 2H), 3.13–3.00 (m, 1H), 2.89 (dt, $J=16.2$, 4.8, 1H), 2.36 ppm (s, 3H); ^{13}C NMR (100 MHz, acetone): $\delta=150.9$, 139.1, 138.6, 136.4, 131.7, 130.0, 129.0, 127.4, 126.5, 125.6, 124.8, 121.6, 120.4, 119.3,

118.6, 116.3, 112.2, 112.1, 57.4, 43.0, 27.6, 21.8 ppm; MS (EI): *m/z* (%): 338.1 [M^+], 244 (100), 232, 217, 121, 93.

1-(1-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4e): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.4). ^{1}H NMR (400 MHz, acetone): δ = 7.57 (d, J = 8.0, 1H), 7.34 (dd, J = 21.6, 6.8, 2H), 7.23–7.10 (m, 6H), 7.06 (d, J = 8.1, 2H), 6.96 (t, J = 7.5, 1H), 6.73–6.66 (m, 2H), 6.26 (s, 1H), 3.69 (s, 3H), 3.68–3.58 (m, 2H), 3.06 (ddd, J = 15.1, 8.8, 5.9, 1H), 2.89 ppm (dt, J = 16.2, 4.8, 1H); ^{13}C NMR (100 MHz, acetone): δ = 150.7, 139.0, 138.5, 136.4, 130.0, 129.6, 129.6, 129.0, 128.0, 127.5, 126.6, 122.3, 120.8, 119.7, 118.5, 118.5, 116.2, 110.3, 57.1, 42.9, 32.8, 27.5 ppm; MS (EI): *m/z* (%): 338 [M^+], 245 (100), 232.

1-(1*H*-Indol-3-yl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (4p): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, R_f = 0.3). ^{1}H NMR (400 MHz, acetone): δ = 10.08 (s, 1H), 7.54 (d, J = 8.0, 1H), 7.44–7.34 (m, 2H), 7.34–7.26 (m, 2H), 7.22–7.13 (m, 3H), 7.11–7.05 (m, 1H), 7.05–6.99 (m, 2H), 6.99–6.90 (m, 1H), 6.84 (s, 1H), 6.26 (s, 1H), 3.74–3.55 (m, 2H), 3.08 (ddd, J = 14.6, 8.7, 5.8, 1H), 2.93 ppm (dt, J = 16.2, 5.0, 1H); ^{13}C NMR (100 MHz, acetone): δ = 150.4, 139.2, 138.6, 136.7, 133.1, 130.0, 129.4, 128.1, 127.9, 127.1, 125.9, 122.9, 121.0, 120.4, 119.4, 118.3, 112.9, 110.2, 57.7, 43.6, 28.1 ppm; MS (EI): *m/z* (%): 402 [M^+], 338, 245, 232 (100), 218; HRMS (ESI): *m/z* calcd for $C_{23}H_{20}N_2Br$: 403.08044 [M+H]; found: 403.08000.

1-(1*H*-Indol-3-yl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (4n): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, R_f = 0.3). ^{1}H NMR (400 MHz, acetone): δ = 9.93 (s, 1H), 7.27 (d, J = 8.1, 1H), 7.24–7.12 (m, 3H), 7.07 (d, J = 3.8, 2H), 7.01–6.93 (m, 2H), 6.88 (td, J = 7.8, 1.5, 1H), 6.78 (t, J = 7.5, 1H), 6.65 (qd, J = 7.8, 1.3, 3H), 6.16 (s, 1H), 3.88 (s, 3H), 3.53 (ddd, J = 12.6, 9.1, 5.5, 1H), 3.37 (dt, J = 12.5, 4.6, 1H), 3.04–2.90 ppm (m, 2H); ^{13}C NMR (100 MHz, acetone): δ = 155.0, 142.2, 140.3, 138.2, 136.4, 130.0, 129.6, 128.9, 127.3, 126.8, 126.3, 124.0, 123.3, 122.4, 122.0, 121.4, 119.9, 119.1, 113.4, 112.4, 57.9, 56.5, 45.2 ppm; MS (EI): *m/z* (%): 354.1 [M^+], 231 (100), 218, 123, 108, 80 ppm; HRMS (ESI): *m/z* calcd for $C_{24}H_{23}N_2O$: 355.18049 [M+H]; found: 355.18009.

1-(1*H*-Indol-3-yl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (4o): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.4). ^{1}H NMR (400 MHz, acetone): δ = 9.11 (s, 1H), 7.48 (d, J = 8.0, 1H), 7.35 (d, J = 8.2, 1H), 7.28 (d, J = 7.1, 1H), 7.24–6.99 (m, 7H), 6.95 (t, J = 7.5, 1H), 6.83–6.66 (m, 2H), 6.23 (s, 1H), 3.69–3.51 (m, 2H), 3.05 (dt, J = 14.9, 7.4, 1H), 2.92 ppm (dt, J = 16.4, 4.9, 1H); ^{13}C NMR (100 MHz, acetone) δ = 158.3 (d, J = 233.8 Hz), 148.0(d, J = 1.9 Hz), 138.9, 138.0, 136.1, 129.5, 129.0, 127.4, 126.5, 125.6, 122.3, 120.6, 119.8, 118.9 (d, J = 7.4 Hz), 118.9, 116.2 (d, J = 21.9 Hz), 116.0, 112.3, 58.2, 44.0, 27.7 ppm; MS (EI): *m/z* (%) = 342 (100) [M^+], 231, 218, 217, 111; HRMS (ESI): *m/z* calcd for $C_{23}H_{20}N_2F$: 343.16050 [M+H]; found: 343.15996 [M+H].

1-(1*H*-Indol-3-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (4m): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.4). ^{1}H NMR (400 MHz, acetone): δ = 9.98 (s, 1H), 7.45 (d, J = 8.0, 1H), 7.34 (d, J = 8.2, 1H), 7.23 (d, J = 7.4, 1H), 7.20–6.94 (m, 6H), 6.95–6.84 (m, 1H), 6.84–6.65 (m, 3H), 6.04 (s, 1H), 3.68 (s, 3H), 3.62–3.41 (m, 2H), 3.02 (ddd, J = 15.3, 9.3, 5.7, 1H), 2.94–2.80 ppm (m, 1H); ^{13}C NMR (100 MHz, acetone): δ = 154.3, 145.7, 139.2, 138.0, 136.2, 129.6, 129.1, 127.9, 127.2, 126.4, 125.7, 122.2, 120.9, 120.1, 119.6, 119.3, 115.2, 112.2, 58.7, 55.7, 44.8, 27.9 ppm; MS (EI): *m/z* (%): 354 [M^+], 230 (100), 218, 202, 123, 108.

1-(1*H*-Indol-3-yl)-2-(4-methyl-phenyl)-1,2,3,4-tetrahydroisoquinoline (4l): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.5). ^{1}H NMR (400 MHz, acetone): δ = 9.99 (s, 1H), 7.52 (d, J = 8.0, 1H), 7.33 (dd, J = 15.1, 7.2, 2H), 7.15 (dt, J = 7.1, 4.0, 3H), 7.06 (t, J = 7.6, 1H), 7.02–6.88 (m, 5H), 6.74 (d, J = 1.9, 1H), 6.19 (s, 1H), 3.59 (dd, J = 9.0, 4.7, 2H), 3.04 (ddd, J = 15.6, 8.8, 6.4, 1H), 2.86 (s, 1H), 2.18 ppm (s, 3H); ^{13}C NMR (100 MHz, acetone): δ = 149.4, 139.6, 138.6, 136.9, 130.9, 130.1, 129.6, 128.4, 128.3, 127.8, 126.9, 126.0, 122.8, 121.3, 120.2, 120.0, 117.7, 112.7, 58.1, 43.9, 27.9, 21.0 ppm; MS (EI): *m/z* (%): 338 [M^+], 231 (100), 218, 202, 115, 106; HRMS (ESI): *m/z* calcd for $C_{24}H_{21}N_2$ [M−H]; 337.16993; found: 337.16894.

1-(1*H*-Indol-3-yl)-2-(4-cyanophenyl)-1,2,3,4-tetrahydroisoquinoline (4q): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.3). ^{1}H NMR (400 MHz, acetone): δ = 11.13 (s, 1H), 8.41 (dd, J = 6.4, 2.8, 1H), 7.67 (d, J = 3.1, 1H), 7.60–7.54 (m, 1H), 7.53–7.43 (m, 3H), 7.38–7.25 (m, 5H), 6.65–6.58 (m, 2H), 6.36 (s, 1H), 3.50–3.39 (m, 2H), 2.99 ppm (t, J = 7.2, 2H); ^{13}C NMR (100 MHz, acetone): δ = 153.3, 138.9, 138.7, 136.7, 134.7, 129.8, 129.2, 128.4, 127.4, 125.7, 123.0, 121.2, 120.7, 120.5, 118.5, 114.7, 113.0, 99.4, 57.1, 43.4, 28.4 ppm; MS (EI): *m/z* (%): 349 [M^+], 230 (100), 218, 118; HRMS (ESI): *m/z* calcd for $C_{24}H_{20}N_3$: 350.16527 [M+H]; found: 350.16506 [M+H].

Dimethyl 2-(1,2,3,4-tetrahydro-2-phenylisoquinolin-1-yl)malonate (4v): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, R_f = 0.2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.06 (m, 7H), 6.98 (d, J = 8.1 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 5.70 (d, J = 9.4 Hz, 1H), 3.95 (d, J = 9.4 Hz, 1H), 3.77–3.57 (m, 5H), 3.54 (s, 3H), 3.07 (ddd, J = 15.6, 8.9, 6.3 Hz, 1H), 2.87 ppm (dt, J = 16.5, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.5, 167.6, 148.9, 135.8, 135.0, 129.3, 129.2, 127.8, 127.2, 126.2, 118.8, 115.4, 77.6, 77.2, 76.9, 59.3, 58.3, 52.7, 42.3, 26.2 ppm; MS (EI): *m/z* (%): 339 [M^+], 209 (100), 193, 115, 77.

1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4r): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.77 (dt, J = 16.4 Hz, 4.8 Hz, 1H), 3.03–3.11 (m, 1H), 3.56–3.63 (m, 2H), 4.54 (dd, J = 12.0 Hz, 6.8 Hz, 1H), 4.85 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 5.54 (t, J = 8.0 Hz, 1H), 6.84 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 8.2 Hz, 2H), 7.11–7.28 ppm (m, 7H); ^{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; MS (EI): *m/z* (%): 268 [M^+], 208 (100), 77.

2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (4s): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (dt, J = 16.0 Hz, 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 Hz, 5.8 Hz, 1H), 4.81 (dd, J = 12 Hz, 8.6 Hz, 1H), 5.38 (dd, J = 5.8 Hz, 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; MS (EI): *m/z* (%): 298 [M^+], 239 (100), 223, 115, 91, 77.

2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (4t): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 15:1, R_f = 0.4). ^{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; MS (EI): *m/z* (%): 346 [M^+] , 288 (100), 118, 90, 77.

1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4u): Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1, R_f = 0.6). ^{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 ppm (m, 6H); ^{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; MS (EI): *m/z* (%): 282 [M^+], 208 (100), 104, 77.

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