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以氢硅烷为氢源: 铱催化 *N*-杂环化合物的氢化

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摘要 发展了一种铱/氢硅烷/甲醇的催化体系, 不使用任何外加配体和碱的情况下, 实现了以喹啉化合物为代表的芳香杂环的选择性氢化, 得到了一系列 1,2,3,4-四氢喹啉及杂环类化合物. 该反应操作简单, 以廉价且稳定的氢硅烷为氢源, 避免了使用危险易发生爆炸的氢气. 同时, 该体系对溴、氯、氟、酯、羧酸、氰基和硝基等官能团具有良好的兼容性. 该催化体系为制备各种 1,2,3,4-四氢喹啉衍生物提供了一种方便、环保、实用的策略.
关键词 氢化; *N*-杂环化合物; 铱; 氢硅烷

Hydrosilanes as Hydrogen Source: Iridium-Catalyzed Hydrogenation of *N*-Heteroarenes

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Abstract A ligand- and base-free method for the catalytic synthesis of bioactive 1,2,3,4-tetrahydroquinolines via the homogeneous iridium-catalyzed hydrogenation of quinolines and related *N*-heteroarenes is reported. A catalytic reduction of *N*-heteroarenes employing low-cost and air-stable hydrosilane was demonstrated under mild conditions. This reaction is scalable and tolerable for sensitive functional groups, such as bromide, chloride, fluoride, ester, carboxylic acid, cyanogroup and nitro groups. This catalytic system provides a convenient, environmentally friendly and practical method to obtain a variety of 1,2,3,4-tetrahydroquinoline derivatives under mild reaction conditions.
Keywords hydrogenation; *N*-heteroarenes; iridium; hydrosilane

1 Introduction

Selective hydrogenation of unsaturated organic compounds has attracted considerable interest owing to their potential applications in preparation of attractive molecules, such as pharmaceuticals, and common chemical ingredients.[1-2] 1,2,3,4-Tetrahydroquinoline derivatives are important precursors for the synthesis of various bioactive compounds (Figure 1).[3-4] Therefore, the development of efficient strategies for the construction of tetrahydroquinoline derivatives has been the focus of research.[5] Direct hydrogenation of quinoline is one of the most effective methods to synthesize tetrahydroquinoline derivatives.[6]

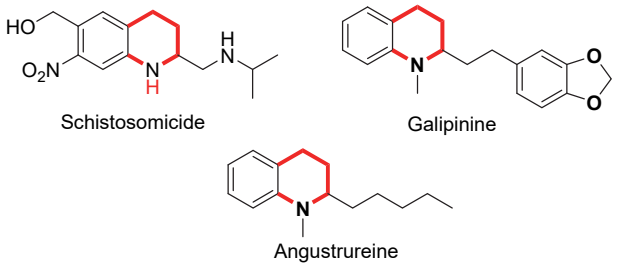

Figure 1 Examples of bioactive drugs and candidates bearing 1,2,3,4-tetrahydroquinoline moiety

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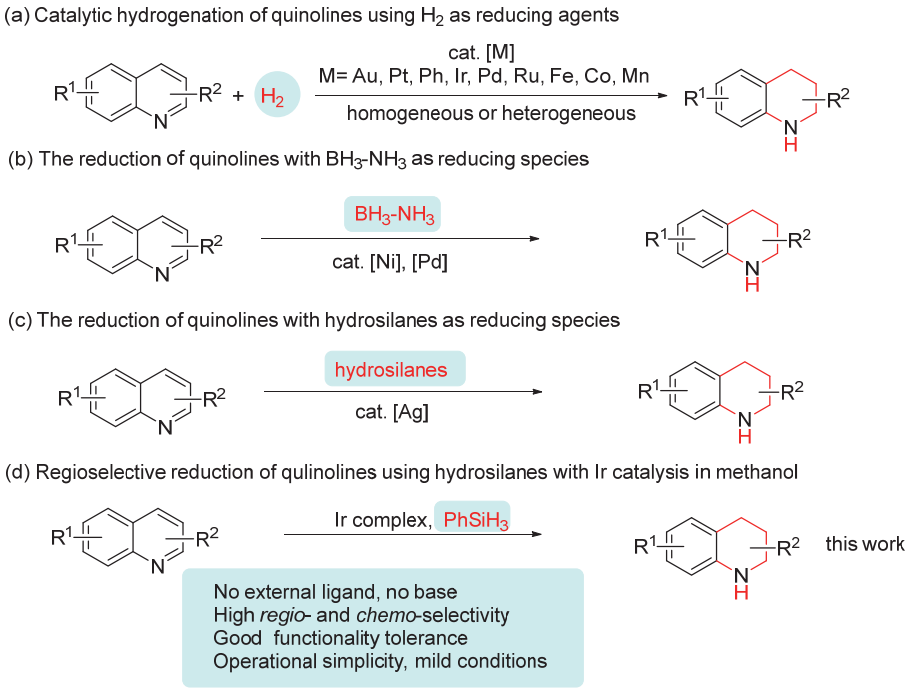
At present, transition metal-catalyzed hydrogenation of quinolones has been extensively reported, *e.g.* homogeneous or heterogeneous catalytic systems based on Au,[7] Pt,[8] Rh,[9] Ir,[10] Pd,[11] Ru,[12] Fe,[13] Co[14] and Mn[15] (Scheme 1a). These reactions usually proceed using hydrogen as the reductant, which is a highly flammable and explosive gas. In addition, the reactions also require special equipment and high temperature.[16] Due to these drawbacks, catalytic transfer hydrogenation has become a practical method because it is simple to operate and much safer than direct hydrogenation using hydrogen gas.[17] Stable organic reductant has been extensively studied over the past decades and has achieved great success for traditional unsaturated olefin, imines, and ketones.[18] Stable organic reductants have rarely been developed for hydrogenation of heterocycles. In particular, hantzsch ester, isopropanol and HCOOH were used as hydrogen sources for asymmetric hydrogenation of quinolines.[19] Swarts and Han described that inexpensive ammonia borane as the hydrogen source in catalytic reduction of quinolines and the formation of corresponding tetrahydroquinolines (Scheme 1b).[16c,20] Bi's group described a methodology using hydrosilanes as hydrogen source for the Ag-catalyzed reduction of quinolines and related *N*-heteroarenes (Scheme 1c).[21] Crabtree's group reported hydrosilylation of heterocycles catalyzed by $LiHBEt_3$ and $[Rh(nbd)(PPh_3)_2]PF_6$ forming tetrahydroquinoline and dihydroquinoline, respectively.[22] Compared with hydrosilanes, the stability of ammonia-borane as reducing agent has serious problems. In this work, we report a selective reduction of quinolines and related *N*-heteroarenes, which was enabled by using phenylsilane as reductant in methanol with Ir-catalysis. This strategy provides an operationally simple pathway to obtain a variety of 1,2,3,4-tetrahydroquinoline derivatives under mild reaction (Scheme 1d).

2 Results and discussion

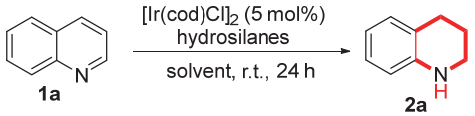
We began our research by using quinoline (**1a**) as a model substrate (Table 1). Initially, several silanes were tested in the presence of $[Ir(cod)Cl]_2$ (5 mol%) in MeOH at room temperature for 24 h. We found that polymethylhydrosiloxane (PMHs) could reduce the heterocycle of quinoline in methanol. The hydrogenated product was purified by column chromatography to give **2a** in 55% (Table 1, Entry 1). Other reducing reagents were screened as well, including $(EtO)_3SiH$, Et_3SiH, Ph_3SiH and Ph_2SiH_2, all of them could effectively allow the hydrogenation to proceed at room temperature to give **2a** in moderate yields (Table 1, Entries 2～5). $PhSiH_3$ gave a better result, leading to **2a** in 74% (Table 1, Entry 6).

Encouraged by the results, the optimization of the reaction media was further investigated. The reaction of $PhSiH_3$ in ethanol formed **2a** in a similar (71%, Entry 7). Other solvents, such as isopropanol and THF, were found to be unsatisfactory (Table 1, Entries 8, 9). The results demonstrated that the reaction media largely affected the successful conversion of quinoline. An isolated of **2a** was acquired in 68% when $PhSiH_3$ was loaded at 3.0 equiv. (Table 1, Entry 11), while increased to 71% at 5.0 equiv. (Table 1, Entry 10). However, both yields were slightly lower than that obtained from $PhSiH_3$ at 4.0 equiv. (74%, Entry 6). Therefore, changing the amount of reducing reagent could not effectively promote the hydrogenation reaction. However, increasing the reaction temperature to



Scheme 1 Reported examples of hydrogenation of quinolines

Table 1 Reduction of quinoline using hydrosilanes with iridium Catalysts



Entry[a]	[Si]—H (equiv.)	Solvent	*T*/℃	of **2a**[b]/%
1	PMHS (4.0)	MeOH	r.t.	55
2	$(EtO)_3SiH$ (4.0)	MeOH	r.t.	40
3	Et_3SiH (4.0)	MeOH	r.t.	59
4	Ph_3SiH (4.0)	MeOH	r.t.	61
5	Ph_2SiH_2 (4.0)	MeOH	r.t.	66
6	$PhSiH_3$ (4.0)	MeOH	r.t.	74
7	$PhSiH_3$ (4.0)	EtOH	r.t.	71
8	$PhSiH_3$ (4.0)	^{i}PrOH	r.t.	46
9	$PhSiH_3$ (4.0)	THF	r.t.	39
10	$PhSiH_3$ (5.0)	MeOH	r.t.	71
11	$PhSiH_3$ (3.0)	MeOH	r.t.	68
12	$PhSiH_3$ (2.0)	MeOH	r.t.	39
13	$PhSiH_3$ (4.0)	MeOH	45	94 (83)[c]

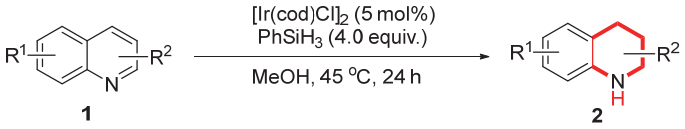
[a] Otherwise noted, all reactions were performed with **1a** (0.2 mmol), Ir complex (0.01 mmol), silane (4.0 equiv.), MeOH (2.5 mL), 24 h. [b] Isolated yield. [c] Hg(0) (100 equiv.) was added.

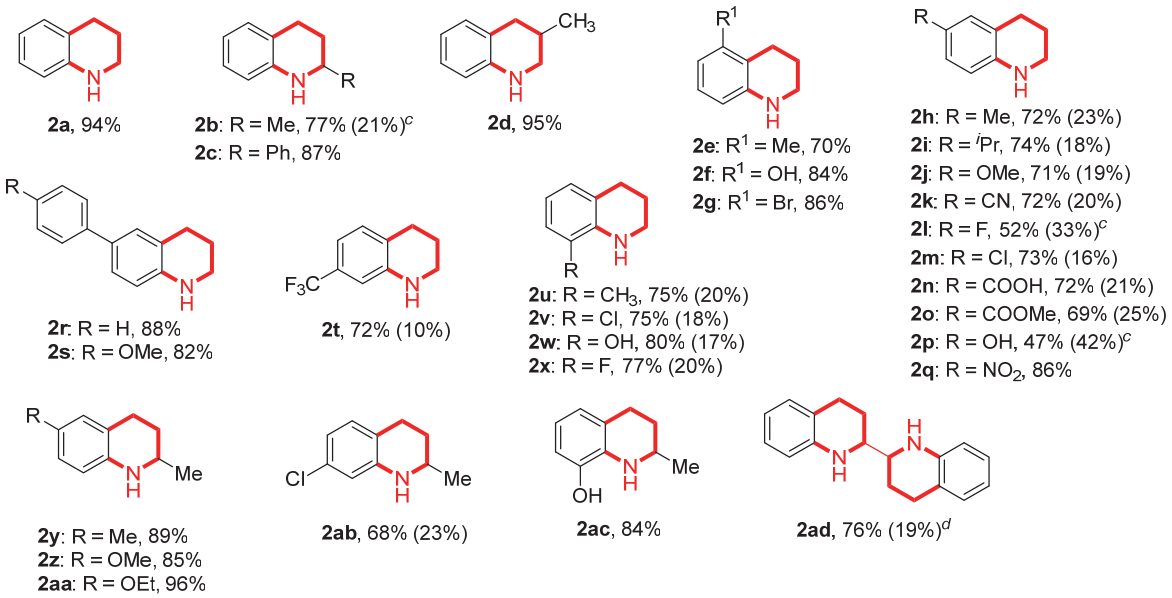
45 ℃ dramatically boosted the to 94% with the excellent selectivity maintained (Table 1, Entry 13).

With the optimal reaction conditions determined, the scope of quinolines was further evaluated. As shown in Table 2, three different methyl-substituted quinolines were estimated. The result suggested that the presence of methyl on C(2) resulted in a lower because of steric hindrance. A slightly higher (77%) was observed with the extended reaction time (36 h, Table 2, **2b**). Phenyl- substituted quinoline afforded the corresponding product **2c** in a better (87%). In contrast, C(3)-methyl quinolines, were successfully hydrogenated and **2d** was obtained in excellent (95%). However, the substitution of C(4)-methyl quinolines in the optimal conditions led to the recovery of starting material along with a trace amount of unidentified product. The electron-donating and electron- withdrawing groups on the aryl ring have good tolerance and the corresponding target products were given in good yields (Table 2, **2e**～**2g**).

In the case of 6-, 7- and 8-substituted quinolines, hydrogenation proceeded smoothly under the mild reaction conditions as well. For example, the substrates containing functional groups such as methoxy, ethoxy, fluoride, chloride, bromide, trifluoromethyl, and hydroxyl on the aryl ring were all well tolerated to give the corresponding products (Table 2, **2j**, **2l**, **2m**, **2s**, **2t**, **2v**, **2x**, **2ab**, **2ac**) in good yields. The chemoselectivity of the hydrogenation was also investigated over several quinolines bearing other reducible groups. The results showed that the $[Ir(cod)Cl]_2$/$PhSiH_3$/MeOH system selectively hydrogenated the heteroarene other than carboxyl and ester groups (Table 2, **2n**,

Table 2 Substrate scope of quinolines with substitution patterns[a,b]



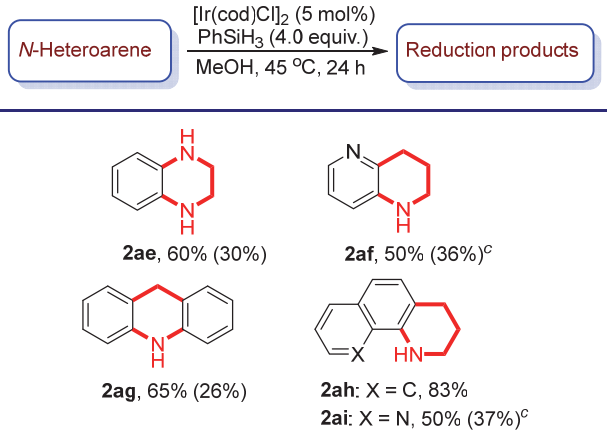


[a] All reactions were performed with substrate **1** (0.2 mmol), $[Ir(cod)Cl]_2$ (5 mol%), $PhSiH_3$ (4.0 equiv.), in MeOH (2.5 mL) at 45 ℃ for 24 h under N_2. [b] Isolated yields were given based on **1**, recovered substrates are given in parentheses. [c] 60 ℃ for 36 h. [d] $[Ir(cod)Cl]_2$ (10 mol%), 60 ℃ for 36 h.

2o). It is worth mentioning that highly sensitive cyano and nitro groups survived as well (Table 2, **2k**, **2q**). Interestingly, the 2,2'-biquinoline substrate reacted concurrently at both heterocyclic at 60 ℃ with 10 mol% of iridium and a longer reaction time to give the dual-hydrogenation product **2ad** in 76% as a mixture.

In addition, a series of other important *N*-heteroarenes were also tried (Table 3). After the screening of several different *N*-heteroarenes, it was turned out that the selective hydrogenation could be successfully applied for other aromatic heterocycles, such as quinoxaline (Table 3, **2ae**), naphthyridine (Table 3, **2af**), acridine (Table 3, **2ag**), benzo[*h*]quinoline (Table 3, **2ah**), and 1,10-phenanthroline (Table 3, **2ai**), which gave corresponding reduction products in moderate yields (50%～83%).

Table 3 Reduction of *N*-heteroarenes[a,b]



[a] Reaction conditions: substrate (0.2 mmol), $[Ir(cod)Cl]_2$ (5 mol%), $PhSiH_3$ (4.0 equiv.), in MeOH (2.5 mL) at 45 ℃ for 24 h under N_2. [b] Isolated yields, recovered substrates are given in parentheses. [c] 60 ℃ for 36 h.

Reaction profiles for the Ir-catalyzed hydrogenation of quinoline were investigated. The results suggested that hydrogenation of quinoline occurred very quickly, forming **2a** in 33% less than 1 min. When the time was extended to 2 h, leading to **2a** in 69% (Figure 2). We speculated that there is product inhibition during the reaction, so the of some substrates is low despite the longer reaction time. Ir-catalyzed hydrogenation of **1a** could proceed smoothly while introducing a mass of Hg(0) into the reaction system (Table 1, Entry 13), the experimental results show that it is highly likely to be a homogeneous catalytic system.[23] In addition, this catalytic system based on iridium catalysis can be carried out on a 10 mmol scale to give **2a** in 84% (Scheme 2, Eq. 1).

In order to get possible mechanism of the hydrogenation of quinoline, various control experiments were carried out. The regioselective hydrogenation of *N*-heteroarenes can be performed successfully upon addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2,2,6,6-tetramethyl-piperi-din-1-oxyl (TEMPO), confirming that the Ir-catalyzed reduction did not proceed via a radical mechanism (Scheme 2, Eqs. 2, 3).

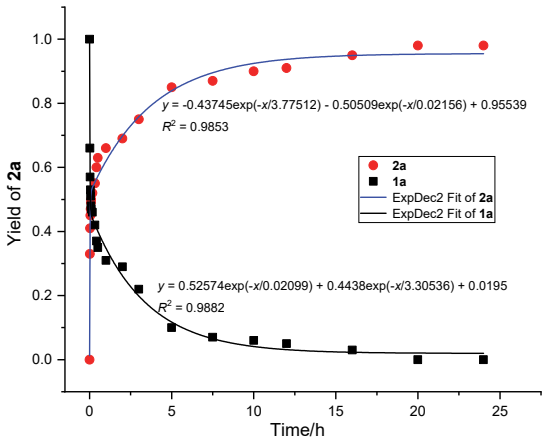
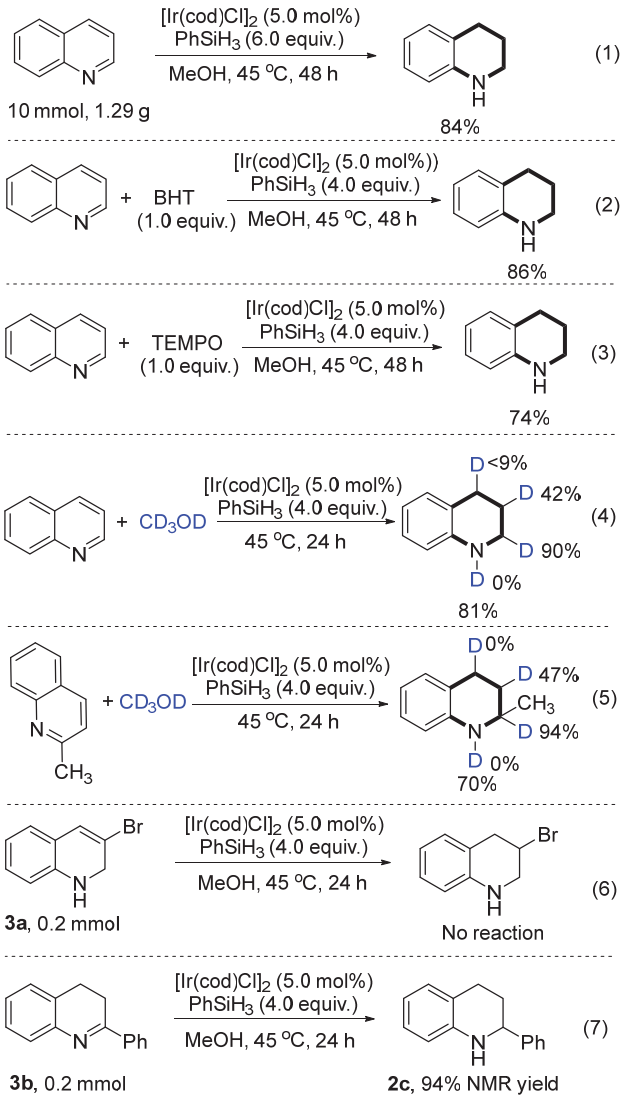


Figure 2 Reaction profile for iridium-catalyzed hydrogenation of quinoline



Scheme 2 Gram-scale reduction and control experiments

Then, the reduction of quinoline (**1a**) and 2-methylquinoline (**1b**) was performed in CD_3OD and deuterium was introduced mainly at the C(3) (42%, 47% deuterium,

respectively) and C(2) (90%, 94% deuterium, respectively) positions of 1,2,3,4-tetrahydroquinoline (Scheme 2, Eqs. 4, 5). The deuterium exchange was not observed at 1-position of the pyridine ring.

To further clarify the active hydrogenation pathway, the reductions of reaction intermediates **3a** and **3b** were conducted under the standard conditions (Scheme 2, Eqs. 6, 7). The reaction pathway is not a 1,2-hydride addition followed by a 3,4-hydride addition. Based on experimental results, it is shown that the quinoline may be reduced through a stepwise 1,4/1,2-addition of Ir—H species to quinolines.

3 Conclusions

In summary, we have developed an Ir-catalyzed selective reduction of quinolines and related derivatives by using stable hydrosilane as reductant in methanol without any ligand and base. The reaction proceeded in high regioselectivity and allowed for the scalable synthesis of 1,2,3,4-tetrahydroquinoline core moiety. The mild reaction conditions endow variously sensitive functional groups with good toleration. Further studies on the mechanism and enantioselective reduction of *N*-heteroarenes using hydrosilanes are undergoing.

4 Experimental section

4.1 General procedures

All reactions dealing with air or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm of 230～400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140～325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Chemical shifts (δ) are given relative to solvent: references for $CDCl_3$ were 7.26 (^{1}H NMR) and 77.00 (^{13}C NMR). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Quinoline derivatives were purchased or prepared according the known procedures.[24]

4.2 General procedure for Ir-catalyzed hydrogenation of quinoline derivatives

A mixture of quinoline derivatives (0.2 mmol) and $[Ir(cod)Cl]_2$ (5 mol%) was added to an oven dried high pressure tube under atmosphere of nitrogen. $PhSiH_3$ (4 equiv.) and MeOH (2.5 mL) were added by syringe. The reaction mixture was stirred at 45 ℃ for 24 h. After quenching with saturated NH_4Cl/H_2O (10 mL), the crude product was extracted with EtOAc (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum, the crude product was purified by column chromatography to afford the desired hydrogenation compound.

4.3 Gram-scale hydrogenation of **1a**

$[Ir(cod)Cl]_2$ (2.5 mol%) was added to an oven dried high pressure tube under atmosphere of nitrogen, and quinoline (10 mmol), $PhSiH_3$ (6 equiv.) and MeOH (100 mL) were added by syringe. The reaction mixture was stirred at 45 ℃ for 48 h. After quenched with NH_4Cl/H_2O (30 mL) and extracted with EtOAc (40 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to provide the hydrogenated product **2a**.

1,2,3,4-Tetrahydroquinoline (**2a**):[14c] 24.9 mg, 94% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99～6.93 (m, 2H), 6.61 (td, *J*=7.5, 0.9 Hz, 1H), 6.48 (d, *J*=7.8 Hz, 1H), 3.30 (t, *J*=5.48 Hz, 2H), 2.77 (t, *J*=6.4 Hz, 2H), 1.98～1.91 (m, 2H); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 144.9, 129.7, 126.9, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3. HRMS (ESI) calcd for $C_9H_{12}N$ $[M+H]^+$ 134.0964, found 134.0959.

2-Methyl-1,2,3,4-tetrahydroquinoline (**2b**):[14c] 22.6 mg, 77% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99～6.94 (m, 2H), 6.61 (td, *J*=7.4, 1.2 Hz, 1H), 6.48 (dd, *J*=8.3, 1.2 Hz, 1H), 3.70 (bs, NH), 3.45～3.37 (m, 1H), 2.90～2.80 (m,1H), 2.77～2.70 (m, 1H), 1.97～1.90 (m, 1H), 1.65～1.54 (m, 1H), 1.22 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 129.1, 126.5, 120.9, 116.8, 113.8, 46.9, 29.9, 26.4, 22.4. HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1123.

2-Phenyl-1,2,3,4-tetrahydroquinoline (**2c**):[14c] 36.3 mg, 87% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46～7.29 (m, 5H), 7.05 (t, *J*=7.4 Hz, 2H), 6.69 (td, *J*=7.4, 1.0 Hz, 1H), 6.57 (d, *J*=7.6 Hz, 1H), 4.47 (dd, *J*=9.3, 3.3 Hz, 1H), 4.07 (bs, NH), 3.02～2.90 (m, 1H), 2.77 (dt, *J*=16.3, 4.8 Hz,1H), 2.08～2.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 144.5, 129.1, 128.4, 127.2, 126.7, 126.4, 120.7, 116.9, 113.8, 56.0, 30.8, 26.2. HRMS (ESI) calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1277, found 210.1280.

3-Methyl-1,2,3,4-tetrahydroquinoline (**2d**):[14c] 28 mg, 95% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03～6.92 (m, 2H), 6.62 (td, *J*=7.4, 1.0 Hz, 1H), 6.50 (d, *J*=7.9 Hz, 1H), 3.28 (ddd, *J*=11.0, 3.7, 2.0 Hz, 1H), 2.91 (dd, *J*=10.8, 9.9 Hz, 1H), 2.79 (ddd, *J*=16.0, 4.8, 1.7 Hz, 1H), 2.45 (dd, *J*=16.0, 10.3 Hz, 1H), 2.13～1.98 (m, 1H), 1.06 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4, 129.7, 126.8, 121.3, 117.1, 113.9, 48.9, 35.6, 29.9, 27.3, 19.2. HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1119.

5-Methyl-1,2,3,4-tetrahydroquinoline (**2e**):[15c] 20.5 mg,

70% yield. Colorless oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.90 (t, J=7.7 Hz, 1H), 6.54 (d, J=7.4 Hz, 1H), 6.39 (d, J=8.0 Hz, 1H), 3.29～3.25 (m, 2H), 2.66 (t, J=6.6 Hz, 2H), 2.19 (s, 3H), 2.04～1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.8, 137.1, 125.9, 120.0, 118.7, 112.3, 41.4, 23.9, 22.3, 19.2. HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1123.

5-Hydroxyl-1,2,3,4-tetrahydroquinolin (**2f**):[20] 24.9 mg, 84% yield. White solid. m.p. 109～110 ℃, petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.84 (t, J=8.0 Hz, 1H), 6.12 (d, J=8.0 Hz, 2H), 4.39 (bs, NH), 3.29～3.24 (m, 2H), 2.66 (t, J=6.6 Hz, 2H), 2.01～1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.1, 146.3, 127.1, 108.3, 107.4, 103.9, 41.6, 21.9, 20.5. HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0913, found 150.0911.

5-Bromo-1,2,3,4-tetrahydroquinoline (**2g**):[20] 36.2 mg, 86% yield. Colorless oil, petroleum ether/EtOAc (V∶V=20∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.87 (dd, J=7.9, 1.3 Hz, 1H), 6.81 (t, J=7.8 Hz, 1H), 6.41 (dd, J=7.8, 1.3 Hz, 1H), 3.86 (bs, NH), 3.28～3.23 (m, 2H), 2.77 (t, J=6.6 Hz, 2H), 2.00～1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 127.4, 125.8, 120.5, 120.4, 112.9, 41.3, 27.4, 21.9. HRMS (ESI) calcd for $C_9H_{11}BrN$ $[M+H]^+$ 212.0069, found 212.0065.

6-Methyl-1,2,3,4-tetrahydroquinoline (**2h**):[14c] 21 mg, 72% yield. Colorless oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.80 (d, J=5.7 Hz, 2H), 6.44～6.41 (m, 1H), 3.31～3.27 (m, 2H), 2.75 (t, J=6.5 Hz, 2H), 2.22 (s, 3H), 1.98～1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.2, 129.9, 127.0, 126.1, 121.4, 114.3, 41.9, 26.7, 22.2, 20.2. HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1123.

6-Isopropyl-1,2,3,4-tetrahydroquinoline (**2i**):[15b] 25.9 mg, 74% yield. Yellow oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.91～6.81 (m, 2H), 6.46 (d, J=8.0 Hz, 1H), 3.34～3.25 (m, 2H), 2.78 (td, J=6.7, 2.3 Hz, 3H), 2.04～1.89 (m, 2H), 1.22 (d, J=7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 137.8, 127.6, 124.7, 121.5, 114.6, 42.3, 33.3, 29.8, 27.2, 24.4, 22.5. HRMS (ESI) calcd for $C_{12}H_{18}N$ $[M+H]^+$ 176.1437, found 176.1430.

6-Methoxy-1,2,3,4-tetrahydroquinolie (**2j**):[14c] 23 mg, 71% yield. Colorless oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.62～6.55 (m, 2H), 6.46 (d, J=8.5 Hz, 1H), 3.73 (s, 3H), 3.28～3.23 (m, 2H), 2.76 (t, J=6.5 Hz, 2H), 1.97～1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 138.7, 122.9, 115.4, 114.6, 112.7, 55.6, 42.1, 26.9, 22.2. HRMS (ESI) calcd for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1069.

6-Carbonitrile-1,2,3,4-tetrahydroquinoline (**2k**):[15c] 31.6 mg, 72% yield. Yellow oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (dd, J=10.4, 2.1 Hz, 2H), 6.38 (d, J=8.2 Hz, 1H), 4.42 (bs, NH), 3.40～3.30 (m, 2H), 2.72 (t, J=6.3 Hz, 2H), 1.96～1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.0, 132.9, 131.0, 120.7, 112.9, 97.3, 41.3, 26.5, 20.7. HRMS (ESI) calcd for $C_{10}H_{11}N_2$ $[M+H]^+$ 159.0917, found 159.0926.

6-Fluoro-1,2,3,4-tetrahydroquinoline (**2l**):[15b] 15.7 mg, 52% yield. Yellow oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.71～6.64 (m, 2H), 6.40 (dd, J=9.4, 4.9 Hz, 1H), 3.29～3.24 (m, 2H), 2.74 (t, J=6.5 Hz, 2H), 1.96～1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3 (d, J=234.5 Hz), 140.7 (d, J=1.0 Hz), 122.6 (d, J=6.7 Hz), 115.4 (d, J=21.6 Hz), 114.7 (d, J=7.6 Hz), 113.0 (d, J=22.4 Hz), 41.9, 26.8, 21.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ: −127.84. HRMS (ESI) calcd for $C_9H_{11}FN$ $[M+H]^+$ 152.0870, found 152.0870.

6-Chloro-1,2,3,4-tetrahydroquinoline (**2m**):[14c] 24.3 mg, 73% yield. Yellow oil, petroleum ether/EtOAc (V∶V=15∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.95～6.85 (m, 2H), 6.38 (d, J=8.3 Hz, 1H), 3.80 (bs, NH), 3.33～3.24 (m, 2H), 2.72 (t, J=6.4 Hz, 2H), 1.95～1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4, 129.2, 126.6, 122.9, 121.3, 115.2, 41.9, 26.9, 21.9. HRMS (ESI) calcd for $C_9H_{11}ClN$ $[M+H]^+$ 168.0575, found 168.0569.

1,2,3,4-Tetrahydroquinoline-6-carboxylic acid (**2n**):[14c] 25.6 mg, 72% yield. White solid, m.p. 170～172 ℃, petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J=7.5 Hz, 2H), 6.40 (d, J=8.7 Hz, 1H), 3.41～3.32 (m, 2H), 2.78 (t, J=6.3 Hz, 2H), 1.97～1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.58, 132.2, 130.1, 120.0, 116.5, 112.8, 41.9, 26.9, 21.4. HRMS (ESI) calcd for $C_{10}H_{12}NO_2$ $[M+H]^+$ 178.0863, found 178.0863.

6-Carboxylate-1,2,3,4-tetrahydroquinoline (**2o**):[14c] 26.2 mg, 69% yield. Colorless oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68～7.59 (m, 2H), 6.38 (d, J=8.9 Hz, 1H), 4.36 (bs, NH), 3.83 (s, 3H), 3.39～3.30 (m, 2H), 2.76 (t, J=6.3 Hz, 2H), 1.95～1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.4, 148.6, 131.1, 128.9, 119.7, 117.1, 112.4, 51.3, 41.5, 26.7, 21.2. HRMS (ESI) calcd for $C_{11}H_{14}NO_2$ $[M+Na]^+$ 214.0838, found 214.0837.

6-Hydroxyl-1,2,3,4-tetrahydroquinolin (**2p**):[14c] 13.9 mg, 47% yield. White solid, m.p. 159～160 ℃; petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.22 (s, 1H), 6.34～6.23 (m, 2H), 6.27～6.19 (m, 1H), 4.92 (bs, NH), 3.08～3.00 (m, 2H), 2.55 (t, J=6.5 Hz, 2H), 1.76～1.67 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 147.9, 138.2, 121.3, 115.6, 114.9, 113.6, 41.4, 26.8, 22.1. HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0913, found 150.0908.

6-Nitro-1,2,3,4-tetrahydroquinoline (**2q**):[25] 30.6 mg, 86% yield. Yellow solid, m.p. 160～162 ℃; petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39～7.24 (m, 2H), 6.36 (d, J=9.6 Hz,1H), 4.80 (bs, 1H), 3.41 (td, J=5.8, 2.6 Hz, 2H), 2.78 (t, J=6.3 Hz, 2H), 2.01～1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 137.2, 126.0, 124.4, 119.9, 112.3, 41.8, 26.9, 20.9. HRMS (ESI) calcd for $C_9H_{11}N_2O_2$ $[M+H]^+$ 179.0815, found 179.0814.

6-Phenyl-1,2,3,4-tetrahydroquinoline (**2r**):[26] 37 mg, 88% yield. Yellow oil; petroleum ether/EtOAc (*V*∶*V*=5∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.58～7.50 (m, 2H), 7.40 (dd, *J*=8.5, 7.0 Hz, 2H), 7.30～7.19 (m, 3H), 6.55 (d, *J*=7.9 Hz,1H), 3.83 (s, 1H), 3.38～3.29 (m, 2H), 2.84 (t, *J*=6.4 Hz, 2H), 2.02～1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 144.4, 141.6, 129.9, 128.7, 128.3, 126.4, 125.9, 125.6, 121.7, 114.6, 42.1, 27.2, 22.3. HRMS (ESI) calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1277, found 210.1276.

6-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline(**2s**):[26] 39.1 mg, 82% yield. Yellow oil; petroleum ether/EtOAc (*V*∶*V*=5∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.51～7.42 (m, 2H), 7.22～7.14 (m, 2H), 7.00～6.88 (m, 2H), 6.55 (dd, *J*=7.8, 0.8 Hz, 1H), 3.85 (s, 3H), 3.37～3.25 (m, 2H), 2.85 (t, *J*=6.4 Hz, 2H), 2.07～1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 158.3, 143.9, 134.4, 129.8, 127.9, 127.4, 125.3, 121.7, 114.6, 114.12, 55.4, 42.1, 27.2, 22.3. HRMS (ESI) calcd for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383, found 240.1382.

7-(Trifluoromethyl)-1,2,3,4-tetrahydroquinoline (**2t**):[27] 28.6 mg, 72% yield. Yellow oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.05～6.97 (m, 1H), 6.85～6.77 (m, 1H), 6.67 (s, 1H), 4.01 (bs, NH), 3.37～3.28 (m, 2H), 2.78 (t, *J*=6.4 Hz, 2H), 1.98～1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 144.9, 129.8, 129.2 (q, *J*=32.0 Hz), 124.9, 124.5(q, *J*=271.0 Hz), 113.1, 110.3, 41.8, 27.1, 21.6; ^{19}F NMR (377 MHz, chloroform-*d*) *δ*: －62.51. HRMS (ESI) calcd for $C_{10}H_{11}F_3N$ $[M+H]^+$ 202.0838, found 202.0842.

8-Methyl-1,2,3,4-tetrahydroquinoline (**2u**):[15b] 23 mg, 75% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.89 (t, *J*=9.0 Hz,2H), 6.61～6.55 (m, 1H), 3.66 (bs, NH), 3.42～3.37 (m, 2H), 2.81 (t, *J*=5.7 Hz, 2H), 2.10 (s, 3H), 2.00～1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 143.1, 128.3, 127.8, 121.6, 121.3, 116.8, 42.8, 27.7, 22.6, 17.6. HRMS (ESI) calcd for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1123.

8-Chloro-1,2,3,4-tetrahydroquinoline (**2v**):[14c] 24.7 mg, 75% yield. Yellow oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.07 (dd, *J*=7.9, 1.5 Hz, 1H), 6.86 (dd, *J*=7.5, 1.3 Hz, 1H), 6.51 (t, *J*=7.7 Hz, 1H), 4.42 (bs, 1H), 3.40 (t, *J*=5.6 Hz, 2H), 2.78 (t, *J*=6.4 Hz, 2H), 1.99～1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 140.9, 127.8, 126.9, 122.8, 118.2, 116.4, 41.9, 27.3, 21.8. HRMS (ESI) calcd for $C_9H_{11}ClN$ $[M+H]^+$ 168.0575, found 168.0573.

8-Hydroxyl-1,2,3,4-tetrahydroquinolin (**2w**):[10d] 23.7 mg, 80% yield. White soild, m.p. 120～122 ℃; petroleum ether/EtOAc (*V*∶*V*=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.57 (d, *J*=35.3 Hz, 3H), 4.46 (s, 2H), 3.31 (s, 2H), 2.78 (t, *J*=6.3 Hz, 2H), 2.03～1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 142.5, 133.6, 123.3, 121.9, 117.3, 112.5, 41.90, 26.7, 22.3. HRMS (ESI) calcd for $C_9H_{12}NO$ $[M+H]^+$ 150.0913, found 150.0912.

8-Fluoro-1,2,3,4-tetrahydroquinoline (**2x**):[14c] 23.2 mg, 77% yield. Yellow oil, petroleum ether/EtOAc (*V*∶*V*=30∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.79～6.67 (m, 2H), 6.47 (td, *J*=7.8, 5.3 Hz, 1H), 3.97 (s, 1H), 3.33～3.27 (m, 2H), 2.75 (t, *J*=6.4 Hz, 2H), 1.96～1.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 150.9 (d, *J*=237.0 Hz), 133.2 (d, *J*=12.2 Hz), 124.5(d, *J*=4.0 Hz), 123.6 (d, *J*=4.0 Hz), 115.5 (d, *J*=8.0 Hz), 112.1 (d, *J*=18 Hz), 41.3, 26.5, 21.8; ^{19}F NMR (377 MHz, $CDCl_3$) *δ*: －138.86. HRMS (ESI) calcd for $C_9H_{11}FN$ $[M+H]^+$ 152.0870, found 152.0867.

2,6-Dimethyl-1,2,3,4-tetrahydroquinoline (**2y**):[14c] 28.8 mg, 89% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.80 (d, *J*=7.4 Hz, 2H), 6.43 (d, *J*=8.2 Hz, 1H), 3.43～3.33 (m, 1H), 2.92～2.77 (m, 1H), 2.71 (ddd, *J*=16.4, 5.4, 3.3 Hz, 1H), 2.23 (s, 3H), 1.98～1.89 (m, 1H), 1.65～1.54 (m, 1H), 1.22 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 142.6, 129.9, 127.3, 126.4, 121.4, 114.4, 47.4, 30.5, 26.7, 22.7, 20.5. HRMS (ESI) calcd for $C_{11}H_{16}N$ $[M+H]^+$ 162.1277, found 162.1272.

6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (**2z**):[14c] 30.2 mg, 85% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.65～6.55 (m, 2H), 6.46 (d, *J*=8.3 Hz, 1H), 3.73 (s, 3H), 3.39～3.28 (m, 1H), 2.93～2.78 (m, 1H), 2.78～2.65 (m, 1H), 1.98～1.86 (m, 1H), 1.61～1.55 (m, 1H), 1.21 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 151.9, 139.0, 122.6, 115.4, 114.7, 112.9, 55.9, 47.6, 30.4, 27.0, 22.7. HRMS (ESI) calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1221.

6-Ethoxy-2-methyl-1,2,3,4-tetrahydroquinoline (**2aa**):[28] 36.9 mg, 96% yield. Colorless oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.64～6.55 (m, 2H), 6.44 (d, *J*=8.1 Hz, 1H), 3.94 (q, *J*=7.0 Hz, 2H), 3.40～3.26 (m, 1H), 2.92～2.77 (m, 1H), 2.70 (ddd, *J*=16.6, 5.4, 3.1 Hz, 1H), 1.98～1.85 (m, 1H), 1.63～1.52 (m, 1H), 1.37 (t, *J*=7.0 Hz, 3H), 1.20 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 150.9, 138.7, 122.3, 115.4, 115.1, 113.4, 63.9, 47.3, 30.1, 26.7, 22.4, 14.9. HRMS (ESI) calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1382.

7-Chloro-2-methyl-1,2,3,4-tetrahydroquinoline (**2ab**):[15b] 24.7 mg, 68% yield. Yellow oil, petroleum ether/EtOAc (*V*∶*V*=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.85 (d, *J*=8.0 Hz, 1H), 6.55 (dd, *J*=8.0, 2.1 Hz, 1H), 6.44 (d, *J*=2.1 Hz, 1H), 3.75 (bs, NH), 3.46～3.32 (m, 1H), 2.84～2.62 (m, 2H), 1.99～1.86 (m, 1H), 1.60～1.50 (m, 1H), 1.21 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 145.8, 132.0, 130.3, 119.4, 116.7, 113.4, 47.1, 29.9, 26.2, 22.6. HRMS (ESI) calcd for $C_{10}H_{13}ClN$ $[M+H]^+$ 182.0731, found 182.0734.

2-Methyl-8-hydroxyl-1,2,3,4-tetrahydroquinolin (**2ac**):[25] 27.4 mg, 84% yield. White soild, m.p. 79～81 ℃, petroleum ether/EtOAc (*V*∶*V*=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.56 (d, *J*=47.1 Hz, 3H), 4.45 (s, 2H), 3.35 (s, 1H), 2.79 (dd, *J*=35.0, 15.7 Hz, 2H), 1.93 (s, 1H), 1.61 (dd, *J*=13.0, 11.4 Hz, 1H), 1.25 (d, *J*=6.3 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 142.7, 133.5, 123.7, 121.7, 117.22, 112.7, 47.3, 30.2, 26.5, 22.5. HRMS (ESI) calcd for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1070, found 164.1067.

1,1',2,2',3,3',4,4'-Octahydro-2,2'-biquinoline (**2ad**):[14c] 26.8 mg, 76% yield. White soild, m.p. 132～133 ℃; petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.01 (t, J=7.8 Hz, 4H), 6.66 (t, J=7.8 Hz, 2H), 6.54 (d, J=7.8 Hz, 2H), 4.00 (bs, 2H), 3.49～3.39 (m, 2H), 2.98～2.75 (m, 4H), 2.00～1.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.8, 129.3, 127.0, 121.6, 117.4, 114.4, 55.4, 26.7, 23.1. HRMS (ESI) calcd for $C_{18}H_{21}N_2$ $[M+H]^+$ 265.1699, found 265.1700.

1,2,3,4-Tetrahydroquinoxaline (**2ae**):[14c] 15.8 mg, 60% yield. Colorless oil, petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.62～6.56 (m, 2H), 6.53～6.47 (m, 2H), 3.42 (bs, 4H+2NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 133.3, 118.4, 114.4, 40.9. HRMS (ESI) calcd for $C_8H_{11}N_2$ $[M+H]^+$ 135.0917, found 135.0917.

1,2,3,4-Tetrahydro-1,5-naphthyridine (**2af**):[14c] 13 mg, 50% yield. Yellow oil, petroleum ether/EtOAc (V∶V=2∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (dd, J=4.6, 1.2 Hz, 1H), 6.87 (dd, J=8.0, 4.7 Hz, 1H), 6.71 (dd, J=8.0, 1.4 Hz, 1H), 3.82 (bs, NH), 3.31～3.26 (m, 2H), 2.92 (t, J=6.5 Hz, 2H), 2.06～1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 140.5, 137.5, 121.4, 119.7, 41.0, 29.8, 21.3. HRMS (ESI) calcd for $C_8H_{11}N_2$ $[M+H]^+$ 135.0917, found 135.0917.

9,10-Dihydroacridine (**2ag**):[25] 23.8 mg, 65% yield. White solid, m.p. 168～170 ℃, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14～7.05 (m, 4H), 6.86 (td, J=7.4, 1.0 Hz, 2H), 6.67 (d, J=7.9 Hz, 2H), 5.96 (s,1H), 4.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.1, 128.6, 126.9, 120.6, 120.0, 113.4, 31.4. HRMS (ESI) calcd for $C_{13}H_{12}N$ $[M+H]^+$ 182.0964, found 182.0966.

1,2,3,4-Tetrahydrobenzo[*h*]quinolone (**2ah**):[14c] 30.6 mg, 83% yield. Yellow oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80～7.75 (m, 1H), 7.73～7.68 (m, 1H), 7.43 (dd, J=8.5, 1.3 Hz, 2H), 7.23～7.14 (m, 2H), 4.25 (bs, NH), 3.50 (t, J=5.4 Hz, 2H), 2.95 (t, J=6.4 Hz, 2H), 2.06 (dt, J=11.9, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.4, 133.4, 129.0, 128.9, 125.4, 125.2, 123.6, 119.9, 117.3, 116.2, 42.8, 27.9, 22.5. HRMS (ESI) calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1121, found 184.1124.

1,2,3,4-Tetrahydro-1,10-phenanthroline (**2ai**):[20] 18.4 mg, 50% yield. Yellow oil, petroleum ether/EtOAc (V∶V=10∶1); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (dd, J=4.2, 1.7 Hz, 1H), 8.01 (dd, J=8.3, 1.7 Hz, 1H), 7.29 (dd, J=8.3, 4.2 Hz, 1H), 7.16 (d, J=8.2 Hz, 1H), 6.98 (d, J=8.2 Hz, 1H), 5.93 (bs, NH), 3.56～3.50 (m, 2H), 2.92 (t, J=6.4 Hz, 2H), 2.10～2.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1, 140.8, 1;37.6, 136.0, 127.5, 120.7, 116.7, 113.2, 41.4, 27.2, 21.9. HRMS (ESI) calcd for $C_{12}H_{13}N_2$ $[M+H]^+$ 185.1073, found 185.1075.

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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