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Note

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DMSO/*t*-BuONa/O_2 mediated Aerobic Dehydrogenation of Saturated *N*-Heterocycles

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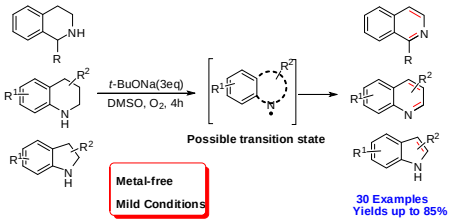
ABSTRACT:



Aromatic *N*-Heterocycles such as quinolines, isoquinolines and indolines are synthesized *via* a sodium *tert*-butoxide promoted oxidative dehydrogenation of the saturated heterocycles in DMSO solution. This reaction proceeds under mild reaction conditions and has a good functional group tolerance. Mechanistic studies suggest a radical pathway involving hydrogen abstraction of dimsyl radicals from the N-H bond or α-C-H of the substrates, and subsequent oxidation of the nitrogen or α-aminoalkyl radicals.

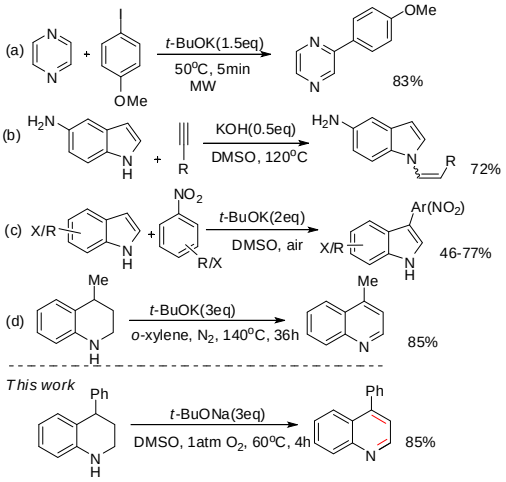
Dehydrogenation of saturated and partially saturated heterocycles is an efficient and atom-economic synthetic route for functionalized heterocyclic compounds with the advantage of avoiding the usually tedious multi-step procedures for regioselective introducing varied substituents at the preformed heterocycles. The dehydrogenation can be achieved either oxidatively with the help of a hydrogen acceptor (oxidative dehydrogenation, ODH),[1,2] or in an process with the evolution of hydrogen gas (acceptorless dehydrogenation, ADH).[3] Traditional ODH protocols[1] use stoichiometric amount of DDQ, *o*-Iodoxybenzoic acid (IBX), $KMnO_4$, metal oxide, *etc*. as oxidants and is not environmentally friendly by leaving a large amount of reduced oxidants as wastes. In contrary, the catalytic ODH reaction[2] proceeds with molecular oxygen as the hydrogen acceptor and water as the only by-product.

Quinolines are ubiquitous structural motifs found in many natural products[4] and pharmaceuticals[5]. The synthesis of diverse functionalized quinolines by the dehydrogenation of tetrahydroquinolines (THQ) has drawn much research interest in recent years. Catalytic ODH reactions of THQ have been realized by using metal complexes based on precious metals Ir, Ru, Rh, Pd[6] and non-precious metals Fe, Co, Ni, Cu, V, *etc*.,[7,8] and by using graphene oxide[9] as catalyst. Several metal co-catalyzed, redox-active compounds (*o*-quinones, azadicarboxylates, TEMPO) mediated ODH reactions[10] and photoredox catalyzed ODH reactions[11] have also been reported. At the

meantime, many ADH reactions of THQ have been developed using complexes of transition metals[12,13] (Ir, Ru, Co, Ni, Fe *etc.*), borane[14] or frustrated Lewis pair[15] as catalyst. Photoredox[16] and electrolytic[17] catalysis has also proved to be effective in carrying out ADH reactions. All these ODH and ADH reactions provided complementary approaches for the access of functionalized quinolines from THQ, but have their own respective limitations and shortcomings, such as the high cost of the metal complexes and the ligands, harsh reaction conditions of high reaction temperature or long reaction times, and limited tolerance to a wide range of functional groups. Therefore, it is highly important to further pursue new efficient dehydrogenation protocols of THQ with good functional group tolerance and proceeding under mild reaction conditions.

Strong bases such as potassium *tert*-butoxide and potassium hydroxide have shown great potential in metal-free C-C coupling of unreactive arenes with aryl halides[18,19] since Itami[19a] and his co-workers unexpectedly found in 2008 a coupling reaction of iodobenzene with pyrazine, only promoted by stoichiometric amount of *t*-BuOK(scheme 1a). Strong bases have also been found to be effective in N-H bond activation for C-N bond formation in addition reactions of amines to alkynes and olefins (scheme 1b).[20] Construction of C-C bond through cross dehydrogenative coupling reaction of sp^3 C-H or sp^2 C-H with nitrobenzene in the *t*-BuOK/DMSO/air system was reported as well(scheme 1c).[21] Very recently, a potassium *tert*-butoxide promoted ADH reaction of THQ was reported that proceeded in *o*-xylene solution at 140 °C (Scheme 1d).[22] We herein report a

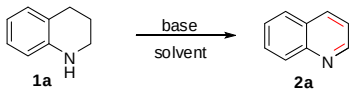
sodium *tert*-butoxide promoted dehydrogenation reaction of THQ, that, however, is different from the previously reported *t*-BuOK promoted reaction by proceeding *via* an ODH pathway under milder reaction conditions with tolerance of a diversity of functional groups.



Scheme 1: Base-promoted dehydrogenative C-C and C-N bond formation reactions

For our initial studies, 1, 2, 3, 4- tetrahydroquinoline(**1a**) was chosen as a substrate in a base/DMSO/O_2 system (Table 1). Control experiments (Table 1, entries 8-10) revealed that both oxygen and base are required for this reaction. Under the atmosphere of argon, the desired oxidative reaction did not proceed. Various bases such as Cs_2CO_3, KOH, CH_3ONa, NaH, *t*-BuOLi, *t*-BuOK and *t*-BuONa were screened for the optimization of reaction conditions (Table 1, entries 1-7). It was found that *t*-BuONa was the best base for promoting the dehydrogenation reactions. And stoichiometric base was needed for this reaction, while catalytic amount of base cannot lead to a complete conversion of the substrate (Table1, entry 11 and 12).

Table 1: Optimization of Reaction Conditions[a]



1a 2a

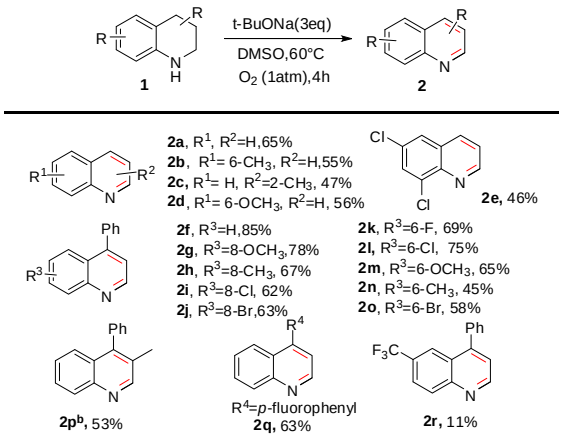
entry	base	solvent	T	yield[b]
1	Cs_2CO_3	DMSO	4h	trace
2	KOH	DMSO	4h	11
3	*t*-BuOLi	DMSO	4h	8
4	CH_3ONa	DMSO	4h	16
5	*t*-BuONa	DMSO	4h	65
6	*t*-BuOK	DMSO	4h	61
7	NaH	DMSO	4h	23
8[c]	*t*-BuONa	DMSO	12h	16
9[d]	*t*-BuONa	DMSO	12h	n.r.
10	--	DMSO	12h	n.r.
11[e]	*t*-BuONa	DMSO	12h	5
12[f]	*t*-BuONa	DMSO	12h	52
13	*t*-BuONa	DCM	12h	n.r.
14	*t*-BuONa	Toluene	12h	n.r.
15	*t*-BuONa	DMF	12h	32
16	*t*-BuONa	CH_3OH	12h	n.r.
17	*t*-BuONa	CH_3CN	12h	n.r.
18[g]	*t*-BuONa	DMSO	12h	53

[a]Unless otherwise noted, all reactions were performed with 0.6 mmol **1a**, 3eq *t*-BuONa, in 2.0 mL DMSO at 60 °C under 1 atm O_2, 4h; [b] isolated yields; [c] open air atmosphere; [d] Reaction performed under an argon atmosphere; [e] 0.2eq *t*-BuONa; [f] 2.2eq *t*-BuONa; [g] Reaction performed under 120 °C.

Other solvents such as DMF, DCM, CH_3CN, CH_3OH and toluene were also examined in the reaction (Table1, entries 13-18). Unfortunately, none of these solvents gave the product **2a** except DMF (Table 1, entry 16) giving 32% yield. Furthermore, no improvements were observed when the reaction was carried out by increasing reaction time and elevating reaction temperature (Table 1, entry 19). After extensive screening of various conditions, the best reaction conditions are set at carrying out the reaction with 3 equivalents of *t*-BuONa at 60 °C under 1 atm of oxygen (Table 1, entry5).

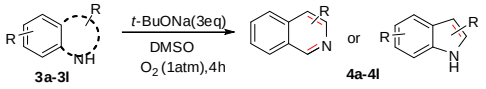
Under the optimized conditions, various substituted quinolines were generated from the corresponding THQ by this new method. The results in Table 2 confirmed that a broad range of substitution patterns on the tetrahydroquinoline were tolerated and the products were obtained in moderate to good yields. It is noteworthy that 4-phenyl-1,2,3,4-tetrahydroquinoline derivatives performed much well, giving the product **2f-2q** in 58%-85% yields, and 4-phenyl-1,2,3,4-tetrahydroquinoline exhibited the highest efficiency affording the desired **2f** in 85% yield. Besides, the compounds containing methyl group (**1b**, **1c**, **1n**, **1p**, respectively) gave lower yields. Fortunately, tetrahydroquinoline with strong electron-withdrawing group(-CF_3) also resulted in the desired product (**2r,** 11%).

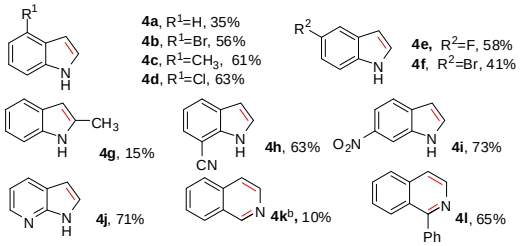
Table 2: Metal-free Aerobic Oxidation of 1,2,3,4-Tetrahydroquinoline to Quinoline[a]



[a] Reaction conditions: 0.2-0.6 mmol **1a-1r**, 3eq *t*-BuONa, in 2.0 mL DMSO at 60 °C under 1 atm O_2, 4h; [b] Room temperature.

Table 3: Dehydrogenation of other *N*-heterocyclic Derivatives





a) Reaction conditions: 0.4-0.6 mmol **3a**-**3l**, 3eq *t*-BuONa, in 2.0 mL DMSO under 1 atm O_2, 4h, 60 °C; b) 12h, 120 °C.

The above strategy was further applied for the synthesis of other *N*-heteroarene derivatives and the results are listed in Table 3. Treatment of indoline substrates under the standard conditions gave the products in 35-73% yields(Table 3, **4a**-**4j**). The results in Table 3 confirmed that a broad range of substitution patterns(CH_3, Br, Cl, F, NO_2, CN *etc*.) on the indoline were tolerated and the products were obtained in moderate yields. It is noteworthy that substrates with electron-withdrawing group(**4h**-**4j**) performed relative high yields. Under the reaction conditions, treatment of 1,2,3,4-tetrahydroisoquinoline yielded the product **4k** in 10% with most of the starting material remained. There was a dramatic increase in the yield when 1-phenyl-tetraisoquinoline **3l** was used as a substrate (Table 3, **4l**). From the above results, we can conclude that this mild condition oxidative dehydrogenation method has a large substrate scope. Substrates of *N*-heterocycles such as tetrahydroquinolines, indolines, and tetrahydroisoquinolines with either electro-withdrawing or electro-donating substituents worked well.

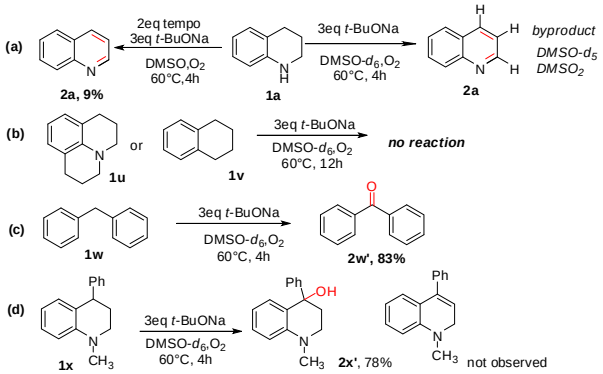
To gain insight into the reaction mechanism, we tested the effect of the free radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) on the reaction and found that the addition of two equivalents of TEMPO to the reaction mixture resulted in a drastic

inhibiting of the oxidation reaction, and only 9% yield of desired product was obtained (Scheme 2a). This result suggests that a radical intermediate may be involved during the transforming.

To get further evidence of the reaction mechanism, DMSO-d_6 was used as the solvent alternating the non-deuterated DMSO in the standard reaction (Scheme 2a). Then the reaction mixture was monitored at regular time interval by ^{1}H NMR. In the ^{1}H NMR(SI, Figure 1s(a)), the starting material(**1a**) was consumed and the product(**2a**) increase gradually. Significantly, the enlargement of integral peak area at δ=2.91ppm as the reaction time increases indicates the increasing amount of $CD_3SO_2CD_2H$ produced during the reaction (SI, Figure 1s(a)). $CD_3SO_2CD_2H$ was also confirmed by GC-MS(Retention time = 5.28 min, m/z: 99.0) of the reaction after 4 hours stirring(SI, Figure 3s). A proton exchanged DMSO-d_6, CD_3SOCD_2H was produced during the reaction as well(SI, Scheme 1s). Since intense quintet peaks at δ=39.6 ppm were observed by DEPT-135 NMR due to the C-D coupling of -CD_2H group, while -CD_3 group could not exhibited in DEPT-135 NMR spectrum(SI, Figure 2s(c)). The produced CD_3SOCD_2H was also confirmed by GC-MS results(SI, Figure 3s, Retention time = 4.73 min, m/z: 83.0). In addition, a broad peak shifted from 4.4 ppm to 3.57 ppm in regular time interval ^{1}H NMR due to the variation of concentration or pH value of the reaction system(SI, Figure 1s(b)). We propose that the broad peak is water produced during the reaction. To verify this hypothesis, after 4h stirring, 5 μl H_2O was added to the NMR tube

and measured ^{1}H NMR of the mixture again. The integral area at δ3.57 ppm increased and the chemical shift coincided with that of the mixture before adding water (SI, Figure 1s). According to the results of these spectra, we propose that DMSO-d_6 was oxidized into DMSO$_2$-d_6 by hydrogen peroxide, resulted in water molecules.

Furthermore，to verify whether the NH moiety in the substrate is a necessitate for the dehydrogenation, reactions of substrates **1u, 1v**, **1w** and **1x** were carried out under the standard conditions respectively. No reactions were found for substrates **1u** and **1v** (scheme 2b). When diphenylmethane (**1w**) was the substrate, benzophenone was isolated in 83% yield (scheme 2c). For the *N*-methyl tetrahydroquinoline **1x, 2x′** was isolated in 78% yield and the dehydrogenated product was not observed (Scheme 2d). These facts reveal that N-H is essential in the reaction and the dehydrogenation is probably initiated by the deprotonation of the N-H bond leading to a nitrogen radical rather than deprotonation at the benzyl C-H bond in the first step.



Scheme 2: Control Experiments

Additionally, EPR measurement shows that after mixing 1,2,3,4-tetrahydroquinoline and *t*-BuONa in DMSO at 1 atmosphere pressure of oxygen at room temperature, a radical signal was observed in situ (Figure 1). This EPR signal represents probably a nitrogen radical with a *g*-value of 2.0050 (A_N = 11.5 G). Under the same conditions, when either 1,2,3,4-tetrahydroquinoline or *t*-BuONa was absent, no EPR signal was detected (see SI, Figure 4s).

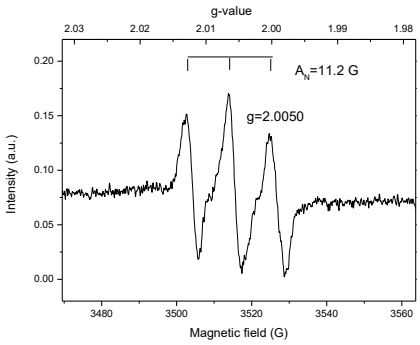
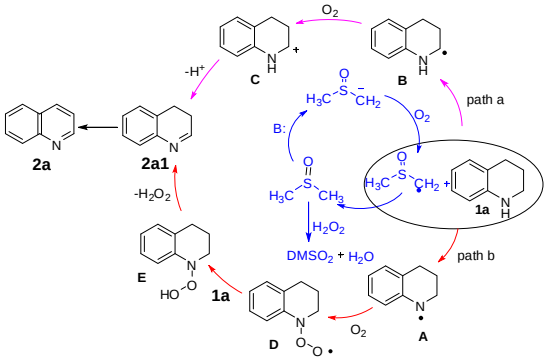


Figure 1: EPR spectrum of mixture of *t*-BuONa and 1,2,3,4-tetrahydroquinoline in DMSO solution at room temperature under 1 atm O_2.

Based on the above experimental results, two proposed mechanism pathways for the conversion of the tetrahydroquinoline (THQ) **1a** to quinoline **2a** are presented in Scheme 3. DMSO has a pK_a of 35 and *tert*-butanol as the conjugate acid of *t*-BuOK has a pK_a of 32.2 in DMSO solution.[23] As a consequence, DMSO can be partly deprotonated by sodium *tert*-butoxide to give dimsyl carbanions.[24] The dimsyl anions have been proposed to serve as electron donors in thermal single electron transfer (SET) reactions with such electron acceptors as iodobenzene[25] (half-wave reduction potential –1.81 V, SCE[26]), therefore, they may be oxidized by the molecular oxygen (half-wave reduction potential

–0.75 V, SCE)[27] to give dimsyl radicals. This kind of mechanism was also proposed by Haland [28] and Hawkins[29] with their coauthors. The dismyl radical may act as a hydrogen atom abstractor[30] from THQ at the N-H bond which has a rather low dissociation energy of∼85.9 kcal/mol[31,32] to lead the 1-tetrahydroquinolinyl radical **A**, or from THQ at the α-C-H bond[33] leading to the C-centered radical **B**. **A** may combine with oxygen to lead to the peroxy radical **D**, which also give dihydroquinoline by first abstracting a H atom from THQ to give the hydroperoxide **E** and subsequent elimination of hydrogen peroxide. Alternatively, As an aminoalkyl radical, **B** has a low oxidation potential of ∼–1.12 V (SCE),[33] which undergoes exothermic SET oxidation by oxygen to afford the carbocation **C**, which upon deprotonation give the 3,4-dihydroquinoline as a primary product. Isomerization of the 3,4-dihydroquinoline to the 1,2-dihydroquinoline[7b,11b,11c,13b] and subsequent oxidative dehydrogenation of the later following the same reaction sequence described above finally render the quinoline product.



Scheme 3: Proposed Reaction Mechanism

In summary, we have developed a metal-free protocol for oxidative dehydrogenation of 1,2,3,4-tetrahydroquinolines in the *t*-BuONa/DMSO/O_2 system.

This dehydrogenation proceeds under mild reaction conditions and has good functional group tolerance. Mechanistic studies including spin trap and isotope labeling experiments indicated a radical pathway, which was initiated by hydrogen abstraction from the N-H bond of the substrates by the dimsyl radicals derived from SET oxidation of the dimsyl anion. Further extension of the reaction scope to other *N*-heterocycles using this system and further mechanistic studies are currently under way.

EXPERIMENTAL SECTION

General Remarks:

All commercially available substrates were used as received. DMSO was dried over CaH_2, distilled under reduced pressure, and stored under an argon atmosphere over activated 4 Å molecular sieves in Teflon screwed Schlenk flasks before using. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometers and chemical shifts are given in parts per million (ppm) relative to standard tetramethylsilane (0.00 ppm for ^{1} H NMR) or residual solvent peaks for ^{13} C NMR. HR-MS was obtained using a Q-TOF instrument equipped with ESI source. GC-MS results were obtained by the Agilent 7000C GC/MSD system equipped with the HP-5MS (30m, 0.25mm, 0.25μm) column. The ESR Spectra were recorded on a Bruker E500 spectrometer at 20 °C. Standard column chromatography was performed on 200-300 mesh silica gel. using flash column chromatography techniques.

General Procedure for the Preparation of Quinoline and other *N*-heterocycles

To a disposable 13 mm×100 mm thick-walled tube were added sequentially *t*-BuONa and substrates **1a-1r and 3a-3l** (0.2-0.6 mmol), then dry DMSO (2 mL) was added to the mixture. The test tube was vacuumed， and purged for 5 minutes with O_2. The headspace was then filled with O_2 at a pressure of 1 atm. The mixture was allowed to stirred at 60 °C in oil bath for 4-18 h. After the stirring was stopped, the mixture was allowed to cool to room temperature. O_2 pressure was released and the resulting brown solution was washed with water and then extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and filtered through a short pad of celite. The filtrate was evaporated in vacuum, and the residue was purified by column chromatography.

Gram scale reaction for the Preparation of Quinoline

To a round-bottomed flask (100mL) were added sequentially *t*-BuONa (2.16 g, 22.6 mmol) and substrates **1a** (1.00g, 7.52mmol), then dry DMSO (25 mL) was added to the mixture. The flask was vacuumed， and purged with O_2. Repeat this three times. The mixture was allowed to stirred at 60 °C in oil bath for 4h. After the stirring was stopped, the mixture was allowed to cool to room temperature. The resulting brown solution was washed with water and then extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and filtered through a short pad of celite. The resultant residue was purified by flash column chromatography on silica gel (eluent: petroleum ether /EtOAc = 100:1-40:1, v/v) to afford **2a** as a yellow oil (504.7 mg, yield 52%) and the by-product **2a′** as a white solid (55.3 mg, yield 5%).

Characterization Data for Isolated Products

Quinoline(2a).[10e] Yellow oil (50.3 mg, yield 65%,; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v) ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91(dd, *J* = 8Hz, 1H), 8.11 (m, 2H), 7.79 (d, *J* = 8 Hz, 1H), 7.71 (m, 1H), 7.53 (t, *J* = 8 Hz, 1H), 7.34 (m, 1H). **^{13}C{H}** NMR (100 MHz, $CDCl_3$) δ 150.4, 148.2, 136.0, 129.4×2, 128.2, 127.7, 126.4, 121.0. **HRMS (ESI, m/z):** Calcd. for C_9H_7N: $[M+H]^+$= 130.0651; found: 130.0654.

3,4-dihydroquinolin-2(1H)-one (byproduct 2a′).[34] White solid (55.3 mg, yield 5%; eluent: petroleum ether /EtOAc = 10:1-1:1, v/v) ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.99 (t, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 2.98 (t, *J* = 6.8 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 172.4, 137.3, 127.8, 127.5, 123.6, 123.0, 115.6, 30.7, 25.3. **HRMS (ESI, m/z)**: Calcd. for C_9H_9NO: $[M+H]^+$ = 147.0684; found: 147.0686.

6-methylquinoline(2b).[10e] Yellow oil (47.2 mg, yield 55%; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81(m, 1H), 8.00 (m, 2H), 7.49 (m, 2H), 7.30 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.49 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 149.4, 146.8, 136.4, 135.4, 131.7, 129.0, 128.3, 126.6, 121.0, 21.5. **HRMS (ESI, m/z)**: Calcd. for $C_{10}H_9N$: $[M+H]^+$ = 144.0807; found: 144.0811.

2-methylquinolin(2c).[10e] Yellow oil (40.3 mg, yield 47%; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H),

7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.6, Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* =8.4 Hz, 1H), 2.74 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 158.9, 147.8, 136.1, 129.4, 128.6, 127.4, 126.4, 125.6, 122.0, 25.4. **HRMS (ESI, m/z)**: Calcd. for $C_{10}H_9N$: $[M+H]^+$ = 144.0807; found: 144.0809.

6-methoxyquinoline(2d).[10a] White solid (53.4 mg, yield 56%; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.93 (t, *J* = 9.2 Hz, 2H), 7.34-7.21 (m, 2H), 6.96 (s, 1H), 3.82 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 157.7, 147.9, 144.3, 134.8, 130.8, 129.3, 122.3, 121.3, 105.1, 55.5. **HRMS (ESI, m/z)**: Calcd. for $C_{10}H_9NO$: $[M+H]^+$ = 160.0757; found: 160.0759.

6,8-dichloroquinoline(2e).[35] White solid (27.2 mg, yield 46%; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.13 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.86 (d, *J* = 2.1 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 4.2 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 151.1, 143.1, 135.7, 134.8, 131.8, 130.3, 129.7, 125.7, 122.8. **HRMS (ESI, m/z)**: Calcd. for $C_9H_5Cl_2N$: $[M+H]^+$ = 197.9877; found: 197.9875.

4-phenylquinoline(2f). [10e] White solid (69.7 mg, yield 85%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.55-7.43 (m, 6H), 7.31 (d, *J* = 4.2 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 149.8, 148.7, 148.6,

138.0, 129.8, 129.5, 129.3, 128.5, 128.4, 126.8, 126.6, 125.9, 121.3. **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{11}N$: $[M+H]^+$ = 206.0969; found: 206.0964.

8-methoxy-4-phenylquinoline(2g).[36] White solid (73.3 mg, yield 78%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 4.4 Hz, 1H), 7.55-7.37 (m, 8H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.12 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 156.8, 150.5, 149.7, 141.4, 139.6, 130.9, 129.9×2, 129.4, 128.2, 123.4, 119.1, 109.1, 57.6. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_{13}NO$: $[M+H]^+$ = 236.1075; found: 236.1071.

8-methyl-4-phenylquinoline(2h).[10e] White solid (58.7 mg, yield 67%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v) ; **^{1}H NMR** (400 2MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 1H), 7.45-7.35 (m, 5H), 7.33-7.20 (m, 2H), 2.78 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 148.8, 148.7, 147.7, 138.5, 137.3, 129.6×2, 128.5, 128.3, 126.8, 126.3, 124.0, 121.2, 18.7. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_3N$: $[M+H]^+$ = 220.1126; found: 220.1129.

8-chloro-4-phenylquinoline(2i).[37] White solid (59.3 mg, yield 62%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 3.9 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.40-7.31 (m, 7H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 150.3, 149.2, 144.8, 137.5, 133.8, 129.5, 129.4, 128.7, 128.6, 128.2, 126.3, 125.1, 122.1. **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{10}ClN$: $[M+H]^+$=240.0580; found: 240.0574.

8-bromo-4-phenylquinoline(2j).[37] White solid (71.3 mg, yield 63%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.39-7.48 (m, 5H), 7.31 (d, *J* = 4.4 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 150.7, 149.2, 145.7, 137.6, 133.2, 129.5, 128.7×2, 128.3, 126.9, 126.0, 125.3, 122.2. **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{10}BrN$: $[M+H]^+$ =284.0075; found:284.0079.

6-fluoro-4-phenylquinoline(2k).[37] White solid (61.5 mg, yield 69%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.4 Hz, 1H), 8.07 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.47-7.34 (m, 7H), 7.24 (d, *J* = 4.4 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 160.7 (d, *J* = 246 Hz), 149.2×2, 148.1 (d, *J* = 5.6 Hz), 145.7, 132.3 (d, *J* = 9.1 Hz), 129.3, 128.8, 128.7, 127.6 (d, *J* = 9.7 Hz), 121.8, 119.6(d, *J* = 25.7 Hz), 109.2(d, *J* = 22.9 Hz). **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{10}FN$: $[M+H]^+$ = 224.0875; found: 224.0869.

6-chloro-4-phenylquinoline(2l).[37] White solid (71.7 mg, yield 69%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.50-7.36 (m, 5H), 7.27 (d, *J* = 4.4 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 150.0, 147.9, 146.9, 137.2, 132.7, 131.3, 130.3, 129.4, 128.8, 128.7, 127.5, 124.7,

122.0. **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{10}ClN$: $[M+H]^+$ = 240.0580; found: 240.0579.

6-methoxy-4-phenylquinoline(2m).[38] White solid (61.1 mg, yield 69%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 9.2 Hz, 1H), 7.57-7.46 (m, 5H), 7.39 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.28 (d, *J* = 4.4 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 157.9, 147.6, 147.1, 144.9, 138.4, 131.3, 129.3, 128.7, 128.4, 127.7, 121.8, 121.7, 103.7, 55.5. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_{13}NO$: $[M+H]^+$ = 236.1075; found:236.1072.

6-methyl-4-phenylquinoline(2n).[10e] White solid (40.3 mg, yield 46%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.4 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.57 (s, 1H), 7.48-7.36 (m, 6H), 7.18 (d, *J* = 4.4 Hz, 1H), 2.36 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 148.9, 148.0, 147.1, 138.2, 136.7, 131.7, 129.5, 129.4, 128.6, 128.4, 126.7, 124.6, 121.4, 21.8. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_3N$: $[M+H]^+$ = 220.1126; found: 220.1125.

6-bromo-4-phenylquinoline (2o).[38] White solid (49.2 mg, yield 58%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.3 Hz, 1H), 8.05 (d, *J* = 9.4 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.56-7.48 (m, 5H), 7.36 (d, *J* = 4.2 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 150.3, 147.7, 147.3,

137.3, 132.9, 131.6, 129.4, 128.8, 128.7, 128.0×2, 122.1, 120.9. **HRMS (ESI, m/z):** Calcd. for $C_{15}H_{10}BrN$: $[M+H]^+$= 284.0069; found: 284.0065.

3-methyl-4-phenylquinoline(2p).[10a] White solid (46.5 mg, yield 53%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.66-7.60 (m, 1H), 7.55-7.42 (m, 4H), 7.42-7.35 (m, 1H), 7.25-7.27 (m, 2H), 2.27 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 152.6, 146.8, 146.2, 136.8, 129.3, 129.2, 128.6, 128.2, 128.0, 127.9, 127.5, 126.4, 125.8, 17.57. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_3N$: $[M+H]^+$ = 220.1126; found: 220.1129.

4-(4-fluorophenyl)quinoline(2q).[39] White solid (56.2 mg, yield 63%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.4 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.42-7.30 (m, 3H), 7.18 (d, *J* = 4.4 Hz, 1H), 7.10 (t, *J* = 8.6 Hz, 2H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 162.9(d, *J* = 246.7 Hz), 149.8, 148.6, 147.3, 133.9 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 8.0 Hz), 129.9, 129.4, 126.8, 126.7, 125.6, 121.4, 115.6(d, *J* = 21.5 Hz). **HRMS (ESI, m/z)**: Calcd.. for $C_{15}H_{10}FN$: $[M+H]^+$= 224.0875; found: 224.0875.

4-phenyl-6-(trifluoromethyl)quinoline(2r).[38] White solid (18.0 mg, yield 11%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 4.4 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.25 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.61-7.27 (m, 6H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 152.0, 149.7, 149.6,

137.0, 131.2, 129.5, 129.0, 128.9, 128.4(q), 126.0, 125.3, 125.1, 124.0, 122.6, 122.4. **HRMS (ESI, m/z)**: Calcd. for $C_{16}H_{10}F_3N$: $[M+H]^+$= 274.0838; found: 274.0812.

benzophenone(2w′).[40] White solid (90.7 mg, yield 83%; eluent: petroleum ether /EtOAc = 100:1-40:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 196.8, 137.6, 132.4, 130.1, 128.3. **HRMS (ESI, m/z)**: Calcd. for $C_{13}H_{10}O$: $[M+H]^+$ = 183.0804; found: 180.0806.

methyl-4-phenyl-1,2,3,4-tetrahydroquinolin-4-ol(2x′).[41] White solid (79.8 mg, yield 78%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27-7.24 (m, 1H), 7.17 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 6.58 (t, J = 7.4 Hz, 1H), 3.46 (td, J = 11.3, 3.1 Hz, 1H), 3.11 (m, 1H), 2.97(s, 3H), 2.31-2.23 (m, 1H), 2.15-2.09 (m, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 148.0, 146.8, 129.2, 129.1, 127.8, 127.7, 126.7, 126.4, 116.5,111.5, 73.3, 47.6, 39.4, 39.2. **HRMS (ESI, m/z)**:Calcd. for $C_{16}H_{17}NO$: $[M+H]^+$ = 240.1383; found: 240.1385.

1H-indole(4a).[7b] Yellow oil (24.6 mg, yield 35%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.18-7.22 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.57 (s, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 135. 8, 127.9, 124.1, 122.0, 120.7, 119.8,

111.0, 102.7. **HRMS (ESI, m/z)**: Calcd. for C_8H_7N: $[M+H]^+$=118.0651; found: 118.0653.

4-bromo-1H-indole (4b).[42] White solid (65.6 mg, yield 48%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.34-7.13 (m, 3H), 7.06-7.01 (m, 1H), 6.59 (s, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 135.9, 128.6, 124.7, 122.9, 122.7, 114.7, 110.3, 102.9. **HRMS (ESI, m/z)**: Calcd. for C_8H_6BrN: $[M+H]^+$=195.9756; found: 195.9753.

4-methyl-1H-indole (4c).[22] Yellow oil (48.0 mg, yield 53%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.22-7.16 (m, 1H), 7.16-7.07 (m, 2H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.56 (s, 1H), 2.56 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 135.4,130.2, 127.7, 123.5, 122.1, 119.9, 108.6, 101.2, 18.8. **HRMS (ESI, m/z)**: Calcd. for C_9H_9N: $[M+H]^+$=132.0808; found: 132.0809.

4-chloro-1H-indole (4d).[43] Yellow oil (57.0 mg, yield 63%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.28-7.15 (m, 2H), 7.14-7.03 (m, 2H), 6.65 (s, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 136.4, 126.7, 126.0, 124.7, 122.6, 119.6, 109.7, 101.3. **HRMS (ESI, m/z)**: Calcd. for C_8H_6ClN: $[M+H]^+$=132.0808; found: 132.0809.

5-fluoro-1H-indole (4e).[42] White solid (47.0 mg, yield 58%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.32-7.26 (m, 2H), 7.26-7.22 (m, 1H), 6.95 (td, *J* = 9.1, 2.4 Hz, 1H), 6.54-6.48 (m, 1H). **^{13}C{H}**

NMR (100 MHz, $CDCl_3$) δ 159.3, 157.1, 132.2, 128.4, 128.0, 125.8, 111.6, 111.5, 110.6, 110.3, 105.6, 105.3, 102.9, 102.8. **HRMS (ESI, m/z)**: Calcd. for C_8H_6FN: $[M+H]^+$=136.0557; found: 136.0561.

5-bromo-1H-indole (4f).[17] White solid (48.0 mg, yield 41%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.76 (s, 1H), 7.29-7.12 (m, 3H), 6.48 (s, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 134.4, 129.6, 125.4, 124.8, 123.2, 113.0, 112.4, 102.3. **HRMS (ESI, m/z)**: Calcd. for C_8H_6BrN: $[M+H]^+$=195.9756; found: 195.9751.

2-methyl-1H-indole (4g).[17] White solid (11.8 mg, yield 15%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 6.9 Hz, 1H), 7.12-7.02 (m, 2H), 6.20 (s, 1H), 2.40 (s, 3H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 135.0, 132.6, 129.0, 120.9, 119.6×2, 110.2, 100.4, 13.7. **HRMS (ESI, m/z)**: Calcd. for C_9H_9N: $[M+H]^+$=132.0808; found: 132.0803.

1H-indole-7-carbonitrile (4h).[44] White solid (53.6 mg, yield 58%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 136.0, 128.8, 126.5, 126.2, 125.9, 119.7, 117.1, 103.7, 94.2. **HRMS (ESI, m/z)**: Calcd. for $C_9H_6N_2$: $[M+H]^+$=143.0604; found: 143.0602.

6-nitro-1H-indole (4i).[42] Yellow solid (71.0 mg, yield 65%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.41 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 6.68 (s, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 143.4, 134.3, 132.8, 130.0, 120.6, 115.4, 108.0, 103.7. **HRMS (ESI, m/z)**: Calcd. for $C_8H_6N_2O_2$: $[M+H]^+$=163.0502; found: 163.0506.

1H-pyrrolo[2,3-b]pyridine(4j).[45] White solid (50.3 mg, yield 63%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v) to afford **4j** as a; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.33 (d, *J* = 3.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.10 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.51 (d, *J* = 3.0 Hz, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 148.7, 142.8, 129.0, 125.0, 120.3, 115.9, 100.9. **HRMS (ESI, m/z)**: Calcd. for $C_7H_6N_2$: $[M+H]^+$=119.0604; found: 119.0608.

Isoquinolin(4k).[7b] Yellow oil (7.8 mg, yield 10%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.53 (d, *J* = 5.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72-7.66 (m, 1H), 7.65 (d, *J* = 5.8 Hz, 1H), 7.63-7.57 (m, 1H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 152.4, 142.7, 135.8, 130.5, 128.6, 127.7, 127.3, 126.5, 120.6. **HRMS (ESI, m/z)**: Calcd. for C_9H_7N: $[M+H]^+$ = 130.0651; found: 130.0652.

1-phenyl-isoquinoline(4l).[46] White solid (78.0 mg, yield 65%; eluent: petroleum ether /EtOAc = 40:1-10:1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.6 Hz,

1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.53-7.62 (m, 4H), 7.37-7.46 (m, 4H). **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ 160.7, 142.2, 139.5, 136.8, 129.9, 129.8, 128.5, 128.3, 127.5, 127.1, 126.9, 126.7, 119.9. **HRMS (ESI, m/z)**: Calcd. for $C_{15}H_{11}N$: $[M+H]^+$ = 206.0969; found: 206.0971.

ASSOCIATED CONTENT

Supporting Information

DMSO-d_6 experiment, EPR experiment, ^{1}H NMR and ^{13}C NMR of the products. This material is available free of charge via the internet at http://pubs.acs.org

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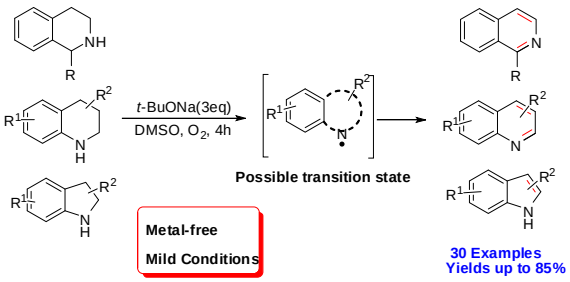

Aromatic *N*-Heterocycles such as quinolines, isoquinolines and indolines are synthesized *via* a sodium *tert*-butoxide promoted oxidative dehydrogenation of the saturated heterocycles in DMSO solution. This reaction proceeds under mild reaction conditions and has a good functional group tolerance. Mechanistic studies suggest a radical pathway involving hydrogen abstraction of dimsyl radicals from the N-H bond or α-C-H of the substrates, and subsequent oxidation of the nitrogen or α-aminoalkyl radicals.