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Metal-Ligand Cooperative Approach to Achieve Dehydrogenative Functionalization of Alcohols to Quinolines and Quinazolin-4(3H)-ones under Mild Aerobic Conditions

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Abstract. A simple metal-ligand cooperative approach for the dehydrogenative functionalization of alcohols to various substituted quinolines and quinazolin-4(3H)-ones under relatively mild reaction conditions (≤90°C) is reported. Simple and easy to prepare air stable Cu(II)-complexes featuring redox-active azo-aromatic scaffolds, 2-arylazo-(1,10-phenanthroline) ($\mathbf{L}^{1,2}$) are used as catalyst. Wide variety of substituted quinolines and quinazolin-4(3H)-ones were synthesized in moderate to good isolated yields via dehydrogenative coupling reactions of various inexpensive and easily available strarting materials under aerobic conditions. A few control experiments and deuterium labelling studies were carried out to understand the mechanism of the dehydrogenative coupling reactions which indicate that both copper and the coordinated azo-aromatic ligand participate in a cooperative manner during the catalytic cycle.

Introduction. Synthesis of nitrogen heterocycles has drawn considerable attention over the years because of their presence in a wide spectrum of natural and synthetic organic molecules.[1] Among them quinolines[2] and quinazolin-4(3H)-ones[3] are common structural motifs found in a large number of natural products and medicinally important compounds showing a broad range of bioactivities (Figure 1). Therefore, development of green, atom-economic synthetic approaches for the preparation of highly functionalized N-heterocycles such as quinolines and quinazolin-4(3H)-ones from inexpensive and easily available starting materials under relatively mild conditions is desirable.[4]

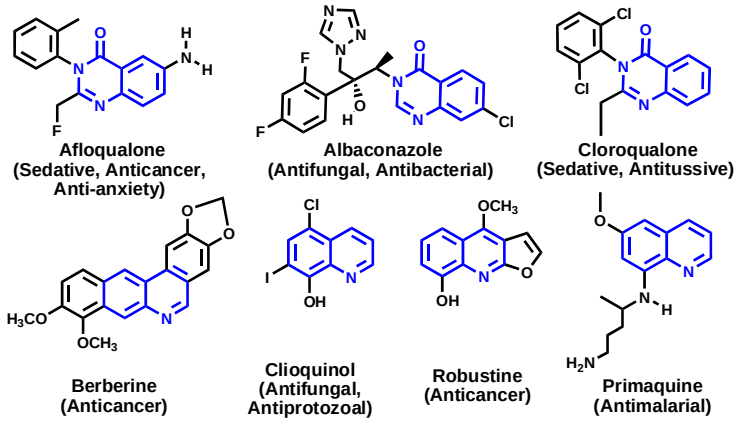


Figure 1. Selected examples of drugs containing quinoline and quinazolin-4(3H)-one moieties.

In recent times, the dehydrogenative functionalization of alcohols has emerged as an attractive atom economic and green synthetic route for the benign synthesis of various functionalized organic moleules including N-heterocycles.[5] In the last one decade, a significant progress have been achieved in designing new catalysts and synthetic strategies to attain efficient dehydrogenative functionalization of cheap and eco-friendly alcohols to numerous valuable products including N-heterocycles.[6-16] The groups of Crabtree,[6] Beller,[7] Kempe,[8a] Milstein,[9a] and Saito[10] independently reported Ru or Ir-catalyzed synthesis of pyrroles. Milstein,[9b] Kempe,[8b] Liu and Sun,[11] and co-workers reported Ir- and Ru-catalysed dehydrogenative synthesis of pyridines. Recently,

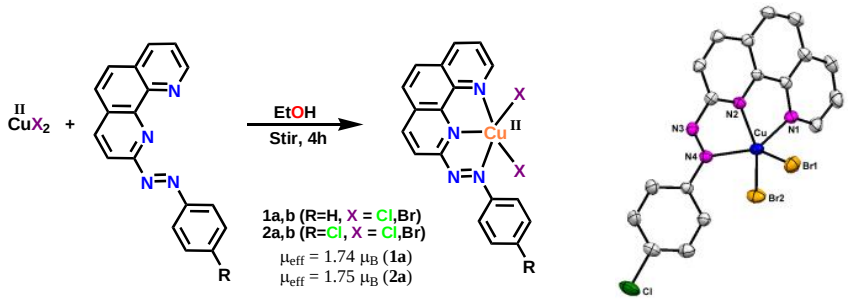
pyrimidines were also synthesized following the same dehydrogenative coupling approach.[8c] Dehydrogenative synthesis of quinolines were achieved by Shim,[12] Yus,[13] Verpoort,[14] Milstein,[9b] Liu and Sun[11] via a Ru-catalyzed indirect Friedlander synthesis. The groups of Zhou,[15] Li[16] and some others developed the synthesis of quinazolin-4(3H)-ones via Ru and Ir-catalyzed dehydrogenative coupling of 2-aminobenzamides and alcohols. Recently, Li and Lang reported Ru-catalyzed dehydrogenative synthesis of benzimidazoles and benzoxazoles.[17]

Despite, achieving tremendous advances on N-heterocycle synthesis via the straightforward dehydrogenative functionalization of alcohols, the catalyst mostly used are toxic and precious noble metals like Ru, Rh, and Ir.[6-17] Therefore, to make the dehydrogenative functionalization of alcohols more environment friendly and economically affordable these precious heavy metals ought to be replaced by non-precious, earth-abundant metals like Mn,[18] Fe,[19] Co,[20] Cu,[21] and Ni.[22] However, these metals tend to react by one electron pathway and the corresponding two electron redox events are mostly associated with high energy barrier and hence elevated temperature is almost always required.[23]

In this regard, the cooperative catalysis,[23] involving synergistic participation of both metal and ligands, offers an attractive alternative to achieve chemical transformations which are usually difficult to attain using first-row base metals under relatively mild conditions. Herein we report a simple copper catalyzed metal-ligand cooperative approach for dehydrogenative functionalization of alcohols to various substituted quinolines and quinazolin-4(3H)-ones under relatively mild aerial conditions. Well defined, air-stable and affordable copper(II)-complexes (**1a**,**b**, **2a**,**b**) of tridentate azo-aromatic ligands, 2-arylazo(1,10-phenanthroline) are used as catalysts. Azo-chromophores are redox active and known to participate as an electron sink[24,25] during dehydrogenation of alcohols. We envisioned that copper and the azo-aromatic scaffold

will participate in a synergistic manner and will allow us to carry out these dehydrogenative functionalization reactions under mild conditions (≤90°C).

Results and Discussion. Four Cu(II)-complexes, dichloro-(E)-2-(phenyldiazenyl)-1,10-phenanthroline-Cu(II) (**1a**), dibromo-(E)-2-(phenyldiazenyl)-1,10-phenanthroline-Cu(II) (**1b**), dichloro-(E)-2-((4-chlorophenyl)diazenyl)-1,10-phenanthroline-Cu(II) (**2a**) and dibromo-(E)-2-((4-chlorophenyl)diazenyl)-1,10-phenanthroline-Cu(II) (**2b**) of the tridentate azo-aromatic pincer, 2-arylazo-1,10-phenanthroline (**L**^{1,2}) were synthesized via stirring an equimolar mixture of CuX_2 (X = Cl, Br) and **L**^{1,2} in ethanol for four hours under air (Scheme 1). Characterization of the isolated complexes using available spectroscopic techniques including X-ray single crystal diffraction (of **2b**) reveals penta-coordinate geometry around the Cu(II)-center with the molecular formula of [$Cu^{II}LX_2$] (Scheme 1). X-ray structure of **2b**, unveils that two N-donor atoms N1(phen) and N4(azo) occupy the apical positions with a N1−Cu−N4 angle of 150.33(16)°. The N-N bond distance was found to be 1.264(6)Å indicating the presence of unreduced azo-chromophore.[24] The room temperature magnetic moment of these complexes are further in agreement with the Cu(II)-oxidation state.



Scheme 1. Synthesis of Cu(II)-complexes and crystal structure of **2b**.

Upon electrochemical analysis using Cyclic Voltammetry, the complexes **1a**,**b** and **2a**,**b** exhibited ligand centered irreversible one-electron reductions in CH_3CN at the potential range of -0.22 - -0.26V (See SI). The irreversibility may be due to the loss of a

chlorido (in case of complex **1a, 2a**) or bromido (in case of complex **1b**, **2b**) ligand upon reduction.

Electronic structure elucidation using DFT at B3LYP level revealed that the complex, $[Cu(L^{2a})Cl_2]$ (**2a**), is an open shell doublet species with a spin population of 0.51 on the Cu(II)-center and 0.10 spin population on the azo-aromatic scaffold (Figure 2). Molecular orbital analysis showed that the LUMOs are ligand centered; primarily localized on the azo-chromophore (see SI). This is indicative of the fact that the redox active azo-chromophore can act as an electron sink during the catalytic cycle.

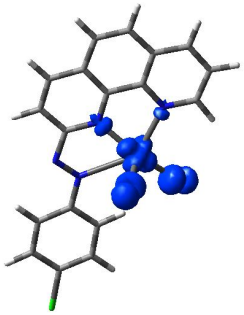


Figure 2. Spin density plot of **2a**.

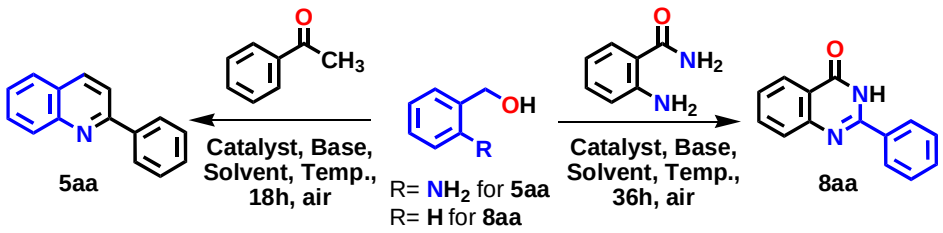
Intrigued by the characterization data, we began our study to synthesize quinolines via dehydrogenative coupling of primary alcohols with ketones using the complex **2a** as the catalyst. Initially, 2-aminobenzyl alcohol (**3a**) was reacted with acetophenone (**4a**) under various reaction conditions to find out the optimal reaction conditions for the synthesis of 2-phenylquinoline (**5aa**). Under aerial conditions, highest yield, 96% of **5aa** was obtained in toluene at 85°C with 1.0 mol% catalyst loading and 0.5 equiv. NaOH after 18h. Increasing the catalyst or base loading beyond the optimized condition does not improve the yield, however, upon lowering the yield decreases.

To further explore the potential of our catalyst, the possibility of dehydrogenative functionalization of alcohols to quinazolin-4(3H)-ones was also explored. To our delight, under the pre-optimized conditions (Table 1, entry 3), the dehydrogenative coupling of

2-aminobenzamide (**6a**) and benzylalcohol (**7a**) proceeds smoothly affording 66% of 2-phenylquinazolin-4(3H)-one (**8aa**). Slight modification of the reaction conditions by increasing the catalyst loading to 5.0 mol% and increasing the temperature to 90°C yielded the highest yield (95%) of **8aa** in 36h (Table 1, entry 12).

Other Cu(II)-salts, such as $CuCl_2.2H_2O$ and anhydrous $CuBr_2$ were found to be less effective/ineffective and yielded only a small amount of the desired products (Table 1, entries 17, 18). Very small or trace amount of the desired products were obtained in absence of the catalyst or base (Table 1, entries 19, 20). In presence of only NaOH, **5aa** and **8aa** were obtained in 19 and 16% and in presence of ligand and NaOH **5aa** and **8aa** were obtained in 22 and 18% respectively (Table 1, entries 20, 21). Even a 1:1 mixture of $CuCl_2.2H_2O$ and $\mathbf{L^2}$ was also found to be less effective than the pre-formed catalyst **2a**, affording **5aa** and **8aa** in 44 and 63% yields respectively (Table 1, entry 22). Reaction did not peoceed in absence of oxygen, under inert atmosphere **5aa** and **8aa** were obtained in trace amounts. However, under positive oxygen pressure we did not observe any noticeable change in yields of **5aa** and **8aa**.

Table 1. Optimization of the Reaction Conditions.[a-c]



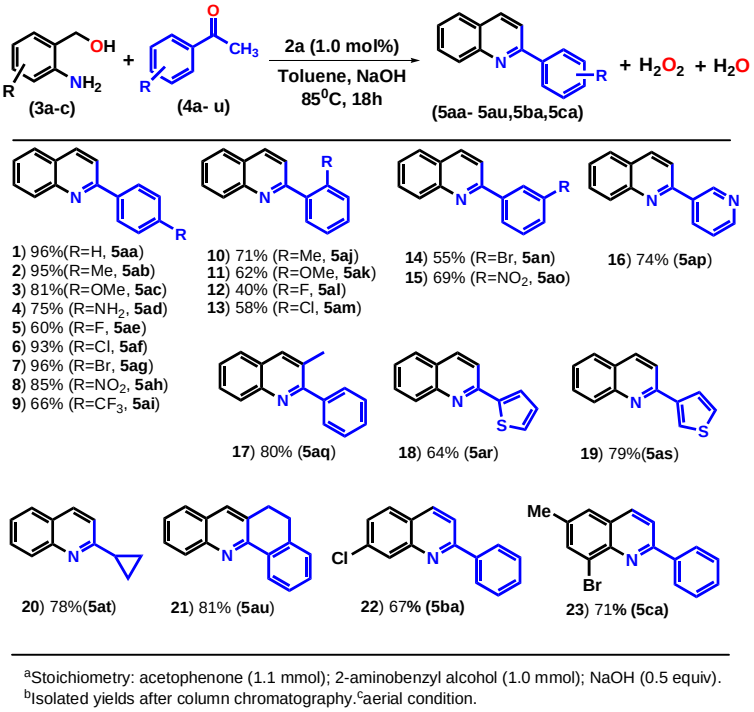
Entry	Catalyst (mol%)	Solvent	Base	Temp (°C)	Yield[b](%) (5aa)	(8aa)
1	**2a** (5.0 mol%)	Toluene	NaOH (1.0 equiv.)	40	80	56
2	**2a** (3.0 mol%)	Toluene	NaOH (0.5 equiv.)	60	92	63
3	**2a** (1.0 mol%)	Toluene	NaOH (0.5 equiv.)	85	96	66
4	**2a** (1.0 mol%)	Toluene	K_3PO_4 (0.5 equiv.)	85	30	35
5	**2a** (1.0 mol%)	Toluene	KOH (0.5 equiv.)	85	90	55
6	**2a** (1.0 mol%)	Toluene	NaO^tBu (0.5 equiv.)	85	94	63
7	**2a** (1.0 mol%)	Toluene	KO^tBu (0.5 equiv.)	85	95	64
8	**2a** (1.0 mol%)	ACN	NaOH (0.5 equiv.)	85	trace	trace
9	**2a** (1.0 mol%)	Ethanol	NaOH (0.5 equiv.)	85	NR	trace
10	**2a** (1.0 mol%)	THF	NaOH (0.5 equiv.)	85	70	54
11	**2a** (1.0 mol%)	Xylene	NaOH (0.5 equiv.)	85	95	65
12	**2a** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	90	95	95
13	**2a** (5.0 mol%)	Xylene	NaOH (0.7 equiv.)	90	94	94
14	**2b** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	90	93	91
15	**1a** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	90	90	88
16	**1b** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	90	88	85
17	$CuCl_2.2H_2O$ (5.0 mol%)	Toluene	NaOH (1.0 equiv.)	90	35	21
18	$CuBr_2$ (5.0 mol%)	Toluene	NaOH (1.0 equiv.)	90	33	20
19	-	Toluene	NaOH (0.7 equiv.)	90	22	18
20	**2a** (5.0 mol%)	Toluene	-	90	trace	trace
21	$\mathbf{L}^{1,2}$ (5.0 mol%)	Toluene	NaOH (1.0 equiv.)	90	19	16
22	$CuCl_2$+$\mathbf{L}^2$ (1:1) (5.0 mol%)	Toluene	NaOH (1.0 equiv.)	90	44	63
23[c]	**2a** (5.0 mol%)	Toluene	NaOH (0.7 equiv.)	90	trace	trace

[a]Stoichiometry: for quinoline: acetophenone (1.10 mmole); 2-aminobenzyl alcohol (1.0 mmole); for quinazolinone: 2-aminobenzamide (1.0 mmol); benzyl alcohol (1.10 mmol). [b]Isolated yields after column chromatography. [c]inert condition.

Having obtained the optimal conditions, we studied the substrate scope and the versatility of the dehydrogenative coupling reactions catalyzed by **2a**. Since catalyst **2a** was found to be more efficient compared to the others (Table 1, entries 14-16), substrate screening was carried out with the former. The catalyst was well tolerant towards a wide variety of substituted ketones (in case of quinolines) and substituted benzylalcohols (in

case of quinazolin-4(3H)-ones) bearing electron -donating, -withdrawing, heteroaryl functionalities under the optimized reaction conditions (Table 2 and Table 3).

Table 2. Dehydrogenative Coupling of Various Acetophenones with Various 2-Aminobenzyl Alcohols.[a-c]



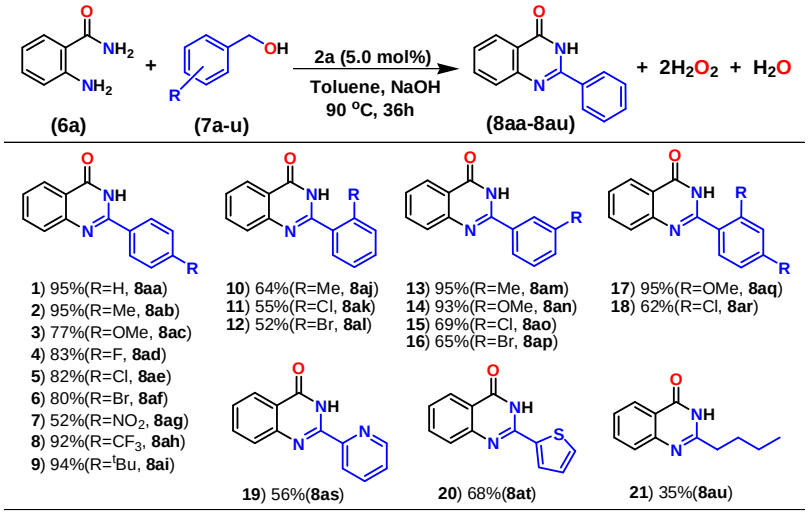
[a]Stoichiometry: acetophenone (1.1 mmol); 2-aminobenzyl alcohol (1.0 mmol); NaOH (0.5 equiv).
[b]Isolated yields after column chromatography.[c]aerial condition.

For example, acetophenones or benzylalcohols having electron donating -Me group at *para*- position produced the corresponding quinolines and quinazolin-4(3H)-ones in 95% isolated yields (Table 2, entry 2, and Table 3, entry 2). Strong electron withdrawing groups like NO_2, CF_3 were also found to be compatible affording the respective quinolines (Table 2, entries 8, 9) and quinazolin-4(3H)-ones (Table 3, entries 7, 8) in moderate to good yields. Reactions also proceed smoothly with heteroaryl alcohols (Table 2, entries 16, 18, 19 and Table 3, entries 19, 20). Long chain aliphatic alcohol also yielded the corresponding quinazolin-4(3H)-one, however in much lower yield and after a slightly long reaction time (Table 3, entry 21).

To further supplement the substrate scope, various substituted 2-aminobenzylalcohols (**3b**, **3c**) and 2-aminobenzamides (**6b-f**) were reacted separately under the optimized conditions. To

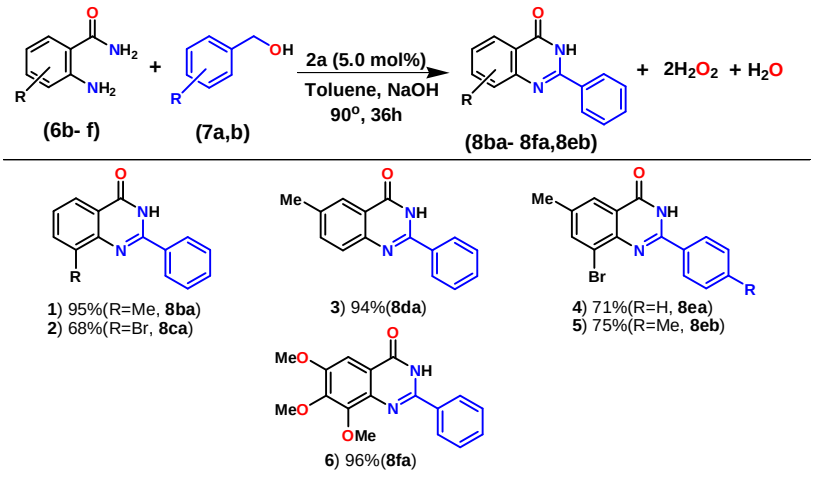
our pleasure, both electron donating and -withdrawing substitution on 2-aminobenzylalcohol and 2-aminobenzamides resulted in considerable high yield of quinolines (**5ba**, **5ca**) (67%-71%) and quinazolin-4(3H)-ones (**8ba-8fa**, **8eb**) (65-95%) respectively (Table 2, 4).

Table 3. Dehydrogenative Coupling of Various Benzylalcohols with 2-Aminobenzamide.[a-c]



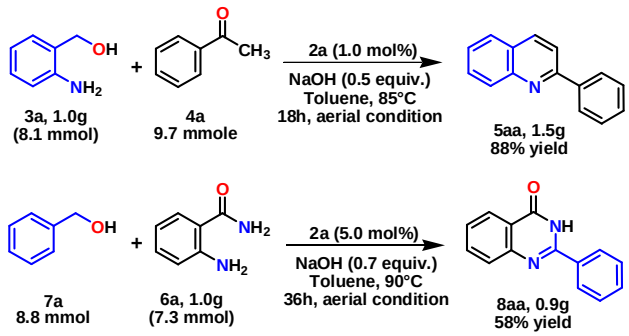
[a]Stoichiometry: 2-aminobenzamide (1.0 mmol); benzyl alcohol (1.1 mmol); NaOH (0.7equiv).
[b]Isolated yields after column chromatography.[c]aerial condition.

Table 4. Dehydrogenative Coupling of Various 2-Aminobenzamides with Various Benzyl Alcohols.[a-c]



[a]Stoichiometry: 2-aminobenzamide (1.0 mmol); benzyl alcohol (1.1 mmol); NaOH (0.7 equiv).
[b]Isolated yields after column chromatography.[c]aerial condition.

To further investigate the synthetic potential of our catalyst **2a** we performed "gram"-scale reaction of **3a** with **4a** and to our pleasure obtained **5aa** in 88% yield. **8aa** was also obtained in 58% yield upon "gram"-scale reaction of **3a** and **4a** (Scheme 2)**.**



Scheme 2. Gram-Scale synthesis of **5aa** and **8aa**.

Finally to unveil the reaction mechanism a series of control experiments were performed. Firstly, to check the purity of catalyst **2a**, inductively coupled plasma optical emission spectrometry (ICP-OES) was performed. Only 0.16 ppb of palladium and 1.8 ppb of iron was detected as trace metal impurities. No cobalt or nickel was detected. On carrying out the synthesis of 2-phenylquinoline (**5aa**) and 2-phenylquinazolin-4(3H)-one (**8aa**) with 100 ppb of palladium and copper seperately under the optimized conditions, **5aa** and **8aa** was obtained in 20 and 16% yields respectively, which is quite close to that obtained in presence of only NaOH. This experimental data clearly demonstrates that the complex **2a** plays an active role in the catalysis.

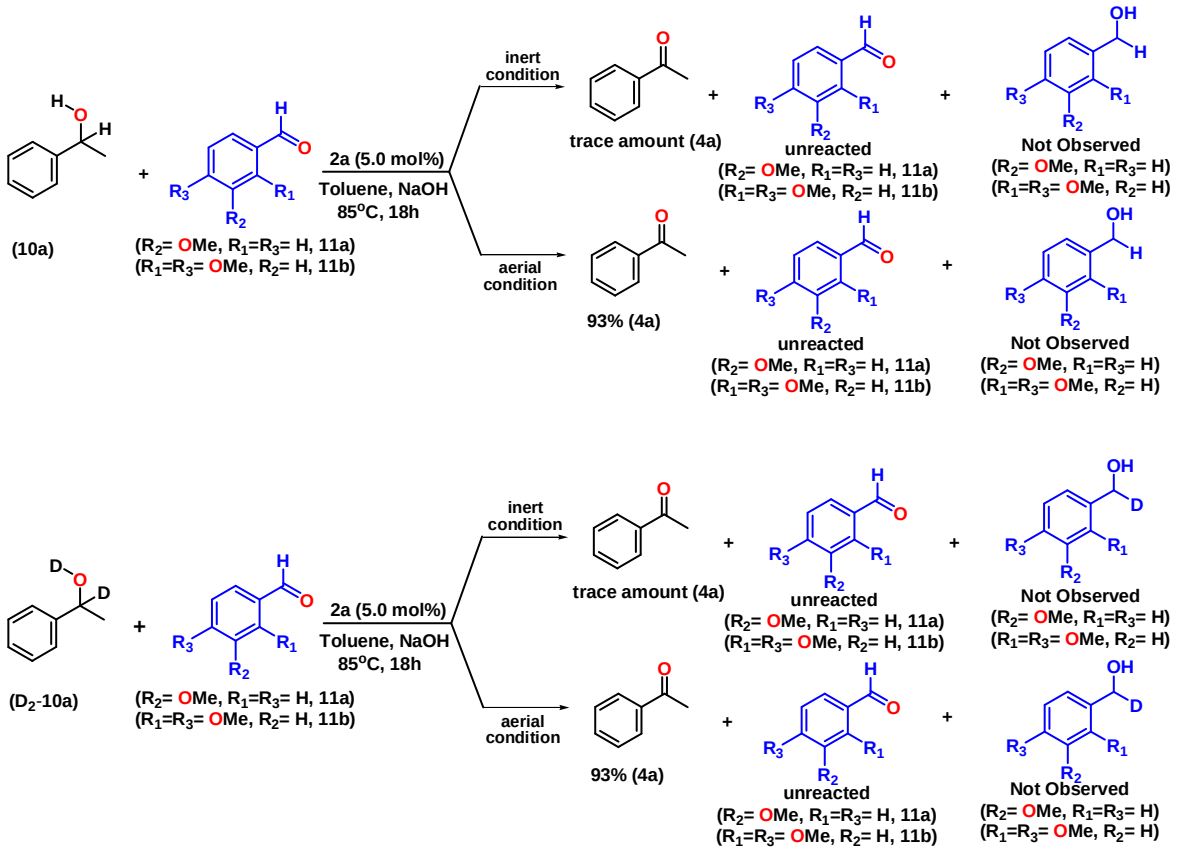
Since, our catalysts **1** or **2** undergoes ligand centered reduction and can produce azo-anion radical,[24,25] reactions were performed in presence of TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl). Contrary to our previous results,[24c] in presence of TEMPO, the yields of benzaldehyde (dehydrogenated product of benzylalcohol), **5aa**, and **8aa** remain almost unaltered indicating the non-involvement of any organic radicals during the present Cu-catalyzed dehydrogenation reactions.

Next to check the feasibility of $1e^-$ hydrogen atom transfer (HAT) vs. $2e^-$ hydride transfer pathway (involving a transient copper-hydride intermediate) the dehydrogenation of

cyclobutanol(radical clock substrate) was performed under the optimized conditions using **2a** as the catalyst. Formation of cyclobutanone as the dehydrogenated product indeed points to the involvement of the $2e^-$-hydride transfer process and rules out the possibility of HAT process involving ketyl radical intermediate as was also supported by the results obtained in presence of TEMPO (see SI).

Azo-aromatic ligands, even if does not form radical, can also act as an electron sink during a chemical reaction involving its azo/hydrazo redox couple.[24] Therefore, to investigate the possibility of the involvement of the azo-chromophore, 1-phenylethanol (**10a**) and deuterated 1-phenylethanol (D_2-**10a**) were subjected to dehydrogenation stoichiometrically under the optimized conditions in presence of argon. IR spectroscopic data of the reaction mixtures exhibit N-H stretching at 3029 and 3063 cm^{-1} and N-D stretching at 2079 and 2121 cm^{-1} indicating the active involvement of the coordinated azo-aromatic scaffold during dehydrogenation of **10a** and D_2-**10a** respectively (See SI).[24]

Next, to check whether H_2 evolution occurs during alcohol dehydrogenation, intermolecular hydrogen transfer reactions were carried out in a closed system using 4-methoxybenzaldehyde (**11a**) and 2,4- dimethoxybenzaldehyde (**11b**) (Scheme 3). Maintaining a closed system under both inert and aerobic conditions when dehydrogenation of 1-phenylethanol (**10a**) was carried out separately in presence of **11a** and **11b**, no hydrogenated products of the aldehydes (**11a** or **11b**) were obtained as shown in Scheme 3. On the other hand, H_2O_2 was detected spectrophotometrically under aerobic conditions (See Figure S4 in SI).[24c]

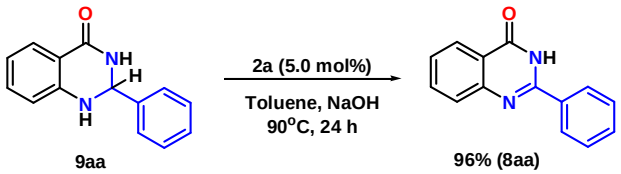


Scheme 3. Hydrogen transfer reactions.

A plausible mechanism for the present Cu-catalysed dehydrogenative synthesis of quinoline and quinazolin-4(3H)-ones via the dehydrogenative coupling of benzyl alcohols with ketones and 2-aminobenzamide respectively, is shown in Scheme 5. The reaction is believed to begin with the deprotonation of the primary alcohols followed by formation of the copper-alkoxy intermediate (**B**) which then undergoes dehydrogenation to produce the corresponding aldehydes.

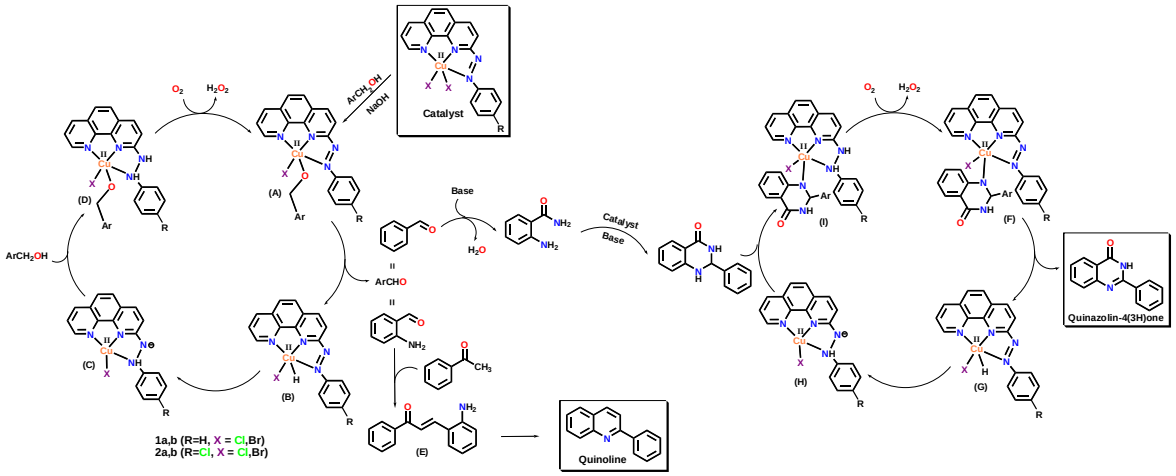
The dehydrogenation of alcohols from intermediate **A**, can proceed via hydride transfer to the copper center followed by hydrogen atom walking to the azo-chromophore[25] or direct hydride transfer to the azo-chromophore of the coordinated azo-aromatic ligands to form the intermediate **B**. The intermediate **B**, upon protonation, forms the intermediate **C** which further coordinates with second molecule of alcohol forming the dihydrazo intermediate **D. D** upon reaction with molecular oxygen forms H_2O_2 and

transforms back to **A**. The aldehydes, thus generated undergo NaOH mediated cross aldol condensation with ketones to form the intermediate **E** which in the subsequent steps produce quinoline via cyclodehydration reaction.



Scheme 4. Dehydrogenation of 2,3-dihydro-2-phenylquinazolin-4(1H)-one.

On the other hand, condensation of the in-situ formed aldehydes with 2-aminobenzamide produce the cyclic aminal **9aa** which then undergoes further dehydrogenation to afford quinazolin-4(3H)-one. Notably, the preformed cyclic aminal 2,3-dihydro-2-phenylquinazolin-4(1H)-one (**9aa**), when subjected to dehydrogenation under optimized reaction conditions for 24 hours afforded **8aa** in 96% yield (Scheme 4).



Scheme 5. Plausible mechanism for the dehydrogenative functionalization of alcohols to quinolines and quinazolin-4(3H)ones catalyzed by **2**.

Conclusion. In summary we have developed a simple and straightforward approach of dehydrogenative functionalization of environmentally benign alcohols to various substituted quinolines and quinazolin-4(3H)-ones under relatively mild (≤90°C) aerobic conditions using an

earth abundant and affordable copper complex of a tridentate azo-aromatic scaffold as catalyst. Variety of substituted quinolines and quinazolin-4(3H)-ones were synthesized in moderate to good isolated yields starting form various inexpensive and easily available starting precursors. Control experiments and mechanistic investigation indicate synergistic participation of both copper and azo-aryl ligand during this dehydrogenative coupling reactions which possibly allowed us to achieve these reactions under comparatively mild conditions (≤90°C). Our present result would possibly open up several other new aspects of metal-ligand cooperativity during catalysis which will probably enable us to achieve various other new chemical transformations using cheap and earth abundant base metal catalysts under relatively mild reaction conditions. Our work in this area is in progress and will be reported in due course.

Experimental Section.

General Information. Tetrahydrofuran(THF), xylene and toluene used in the reactions were refluxed and distilled over sodium/benzophenone maintaining an argon atmosphere and stored over 4 Å molecular sieves. All the other chemicals were purchased from commercial suppliers and were used without further purification. Merck 60 F254 silicagel plate (0.25 mm thickness) was used for performing analytical TLC and Merck 60 silica gel (60−120 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on Bruker DPX-300 (300 MHz), Bruker DPX-400 (400 MHz), and Bruker DPX-500 (500 MHz) spectrometers. For collecting microanalytical data (C, H, N), a Perkin Elmer 240C elemental analyzer was used. Jobin-Yvon ULTIMA 2 ICP optical emission spectrometer was used to carry out ICP-OES analysis.

Synthesis of Catalyst dichloro-(E)-2-(phenyldiazenyl)-1,10-phenanthroline-Cu(II) complex (1a). In a 100 mL round bottom flask, 100 mg (0.314 mmol) of the ligand, $\mathbf{L^1}$ was allowed to dissolve in ethanol and 53.5 mg (0.314 mmol) of $CuCl_2.2H_2O$ was added to it. Color of the resultant solution immediately changes from orange to deep red. Upon stirring the reaction mixture for four hours in a magnetic stirrer a red color precipitate was formed. The precipitate

was isolated by filtration of the reaction mixture and was purified by fractional crystallization with methanol/diethyl ether solvent mixture. Its yield and characterization data are as follows: Yield 92%. UV/Vis : $\lambda_{max/nm}$ (ε, $M^{-1}cm^{-1}$), 329(11,708), 385(10,987). IR (KBr cm^{-1}): 1638 (ν, C=N), 1352 (ν, N=N). μ_{eff} (RT): 1.74 μ_B. Elemental Analysis: $C_{18}H_{12}Cl_2CuN_4$: calcd: C, 51.63; H, 2.89; N, 13.38. Found: C, 51.54; H, 3.01; N, 13.45%.

Synthesis of Catalyst dibromo-(E)-2-(phenyldiazenyl)-1,10-phenanthroline-Cu(II) complex (1b). In a 100 mL round bottom flask, 100 mg (0.352 mmol) of the ligand, $\mathbf{L^1}$ was allowed to dissolve in ethanol. Then on addition of 78.6 mg (0.352 mmol) of anhydrous $CuBr_2$ the colour of the solution immediately changes from orange to deep red. Upon stirring the reaction mixture for four hours in a magnetic stirrer a red color precipitate was formed. The precipitate was isolated by filtration of the reaction mixture and was purified by fractional crystallization with methanol/diethyl ether solvent mixture. Its yield and characterization data are as follows: Yield 89%. UV/Vis : $\lambda_{max/nm}$ (ε, $M^{-1}cm^{-1}$), 323(15,288), 387(14,222). IR (KBr cm^{-1}): 1620 (ν, C=N), 1347 (ν, N=N). $C_{18}H_{12}Br_2CuN_4$: calcd: C, 42.59; H, 2.38; N, 11.04. Found: C, 42.51; H, 2.48; N, 11.10%.

Synthesis of Catalyst dichloro-(E)-2-((4-chlorophenyl)diazenyl)-1,10-phenanthroline-Cu(II) complex (**2a**).Catalyst **2a** was prepared following the same procedure as catalyst **1a**. Its yield and characterization data are as follows: Yield 92%. UV/Vis : $\lambda_{max/nm}$ (ε, $M^{-1}cm^{-1}$), 334(15,900), 389(19,100). IR (KBr cm^{-1}): 1623 (ν, C=N), 1345 (ν, N=N). μ_{eff}(RT): 1.75 μ_B. Elemental Analysis: $C_{18}H_{11}Cl_3CuN_4$: calcd: C, 47.70; H, 2.45; N, 12.36. Found: C, 47.61; H, 2.55; N, 12.48%.

Synthesis of Catalyst dibromo-(E)-2-((4-chlorophenyl)diazenyl)-1,10-phenanthroline-Cu(II) complex (2b). Catalyst **2b** was prepared following the same procedure as catalyst **1b**. Its yield and characterization data are as follows: Yield 90%. UV/Vis : $\lambda_{max/nm}$ (ε, $M^{-1}cm^{-1}$), 330(19,893), 390(23,095). IR (KBr cm^{-1}): 1609 (ν, C=N), 1340 (ν, N=N). Elemental Analysis: $C_{18}H_{11}Br_2ClCuN_4$: calcd: C, 39.88; H, 2.05; N, 10.33. Found: C, 39.79; H, 2.14; N, 10.39%.

Procedure for Dehydrogenative Coupling of 2-Aminobenzylalcohols and Acetophenones. Under aerial condition a mixture of catalyst **2a** (1.0 mol%), NaOH (0.5 equiv.), acetophenone (1.10 mmol) and 2-aminobenzylalcohol (1.0 mmol) were added to a 50.0 mL round bottom flask. Then 5.0 mL of toluene was added to it and the round bottom flask containing the reaction mixture was placed in an oil bath pre-heated at 85°C. The reaction was continued for 18h. After the reaction was completed, the resulting mixture was concentrated under vacuum and purified by column chromatography (silica gel). Eluent: petroleum ether/ethyl acetate (18 : 1)

Procedure for Dehydrogenative Coupling of Alcohols and 2-Aminobenzamides. A mixture of catalyst **2a** (4.0 mol%), NaOH (0.7 equiv.), alcohol (1.10 mmol) and 2-aminobenzamide (1.0 mmol) were added to a 50.0 mL round bottom flask. Then 5.0 mL of toluene was added to it and the round bottom flask containing the reaction mixture was placed in an oil bath pre-heated at 90°C. The reaction was continued for 36 h. After the reaction was completed, the resulting mixture was concentrated under vacuum and purified by flash column chromatography (silica gel). Eluent: petroleum ether/ethyl acetate (3:1).

Transfer Hydrogenation Reactions.

Under Inert Conditions. To an oven dried schlenk tube, 1-phenylethanol (**10a**) (1.0 mmol), 4-methoxybenzaldehyde (**11a**) (1.0 mmol) or 2,4-dimethoxybenzaldehyde (**11b**)(1.0 mmol) and NaOH (0.5 equiv.) were added under an argon atmosphere. Then the schlenk tube was evacuated, backfilled with argon, 3.0 mL of degassed toluene was added and sealed with a teflon screw cap. The reaction mixture was stirred in an oil bath at 85°C for 18h. After this the resultant mixture was concentrated and purified by column chromatography. Eluent: petroleum ether/dichloromethane (4:1). The dehydrogenated product of 1-phenylethanol was isolated in trace amount while no transfer hydrogenation was observed.

Under Aerial Conditions. Under air, to an oven dried schlenk tube, 1-phenylethanol (**10a**)(1.0 mmol),4-methoxybenzaldehyde (**11a**) (1.0 mmol) or 2,4-dimethoxybenzaldehyde (**11b**) (1.0 mmol) and NaOH (0.5 equiv.) were added. Then 3.0 mL of toluene was added and the schlenk

tube was sealed with a teflon screw cap. The reaction mixture was stirred in an oil bath at 85°C for 18h. After this the resultant mixture was concentrated and purified by column chromatography. Eluent: petroleum ether/dichloromethane (4:1). The dehydrogenated product of 1-phenylethanol was isolated in 93% yield. In this case also no hydrogenated products of **11a** or **11b** were obtained.

The same procedure as above was repeated with D_2-**10a** and same result as above was obtained.

Detection of Hydrogen Peroxide during the Catalytic Reactions.[23c] During catalytic alcohol oxidation reactions, production of H_2O_2 was detected spectrophotometrically monitoring the gradual development of the characteristic absorption band for I_3^- at 350 nm. 1-phenylethanol (1.0 mmol), KO^{t}Bu (0.1 mmol) and 3.0 mol% of catalyst **2a** in 5.0 mL of dry toluene was added in a 50 ml round bottom flask containing a stir bar and heated to 70°C for 4 h. 5.0 mL of distilled water was added to the reaction mixture, and the resultant solution was extracted three times with dichloromethane. To stop further oxidation of the alcohol, the separated aqueous layer thus obtained was then acidified with H_2SO_4 to pH 2. A 10% KI solution and a few drops of 3% ammonium molybdate solution were then added to it. The hydrogen peroxide produced during the catalytic cycle oxidises I^- to I_2, which reacts with excess I^- to form I_3^- according to the following chemical reactions: (i) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$; (ii) $I_2(aq) + I^- \rightarrow I_3^-$.

X-Ray Crystallography. We successfully obtained good quality single crystals, suitable for X-ray diffraction, of **2b** via slow evaporation of its methanol−diethyl ether solvent mixture. Single-crystal X-ray diffraction data of **2b** were collected with monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART Apex II diffractometer equipped with a CCD area detector. For data reduction the SAINT-NT software package was used.[26] With SADABS program, multiscan absorption correction was applied to all intensity data.[27] The structures were solved by a combination of direct methods with subsequent difference Fourier syntheses and refined by fullmatrix least-squares on F2 using the SHELX-2013 suite.[28] In all the cases, the non-hydrogen

atoms were treated anisotropically. The crystal data along with the refinement details are given in Table S1.

Computational Details. All the electronic structures were assigned by DFT calculations using the Gaussian 09 program[29] with B3LYP hybrid functional (G09/B3LYP).[30] Geometry optimizations were performed without imposing geometric constraints. Within the calculations the quasi-relativistic effective core pseudo potential proposed by Hay and Wadt, LANL2DZ pseudo potential,[31] and the corresponding optimized set of basis function has been employed for Cu. For carbon, hydrogen, nitrogen, and chlorine 6-31G* basis set[30] was used.

Characterisation Data of the Isolated Compounds.

2-phenylquinoline (5aa).[12,14a] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (96%, 197 mg). Mp: 82–84 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.24–8.16 (m, 4H), 7.90–7.82 (m, 2H), 7.76–7.71 (m, 1H), 7.57–7.44 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.5, 148.4, 139.8, 136.9, 129.8, 129.8, 129.4, 129.0, 127.7, 127.6, 127.3, 126.4, 119.1.

2-p-tolylquinoline (5ab).[12,14a] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (95%, 208 mg). Mp: 82–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.18 (t, J = 8.1 Hz, 2H), 8.08 (d, J = 8.1 Hz, 2H), 7.88–7.80 (m, 2H), 7.72 (t, J = 8.1 Hz, 1H), 7.51 (t, J = 8.1 Hz,1H), 7.34 (d, J = 7.5 Hz, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.5, 148.4, 139.5, 137.0, 136.8, 129.8, 129.7, 129.4, 128.6, 127.6, 127.2, 126.2, 119.0, 21.5.

2-(4-methoxyphenyl)quinoline (5ac).[12,14a,32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (81%, 81 mg). Mp: 122–124 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.19–8.13 (m, 4H), 7.82 (t, J = 9.0 Hz, 2H), 7.71 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 8.5 Hz, 2H), 3.9 (s, 3H). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$): δ (ppm) = 161.0, 157.1, 148.4, 136.8, 132.4, 129.7, 129.0, 128.8, 127.6, 127.1, 126.1, 118.7, 114.4, 55.5.

4-(quinolin-2-yl)benzenamine (5ad).[33] Eluent: petroleum ether/ethyl acetate (18 : 1). Yellow solid (75%, 165 mg). Mp: 192–193 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.11 (d, J = 8.7

Hz, 2H), 8.01 (d, *J* = 8 Hz, 2H), 7.76 (t, *J* = 8.7 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 8.7 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 3.85 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.2, 151.6, 148.1, 136.5, 130.7, 129.4, 129.0, 128.7, 127.4, 126.6, 125.5, 118.3, 115.0.

2-(4-fluorophenyl)quinoline (5ae).[12,32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (60%, 134 mg). Mp: 126–127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.23–8.14 (m, 4H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.26–7.18 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 163.7 (d, *J* = 293.1 Hz), 156.4, 148.4, 137.0, 136.0, 130.0, 129.8 (d, J = 10.5 Hz), 129.6, 129.5, 127.6, 127.2, 126.5, 118.8, 115.9 (d, *J* = 20.3 Hz).

2-(4-chlorophenyl)quinoline (5af).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (93%, 223 mg). Mp: 111–112 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.19–8.08 (m, 4H), 7.80–7.70 (m, 3H), 7.54–7.46 (m, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 155.9, 148.1, 137.9, 137.1, 135.6, 130.0, 129.6, 129.1, 128.9, 127.6, 127.3, 126.6, 118.6.

2-(4-bromophenyl)quinoline (5ag).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (96%, 273 mg). Mp: 117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.58–7.50 (m, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 156.0, 148.3, 138.5, 137.0, 132.0, 129.9, 129.8, 129.1, 127.6, 127.3, 126.6, 124.0, 118.5.

2-(4-nitrophenyl)quinoline (5ah).[12,14a] Eluent: petroleum ether/ethyl acetate (18 : 1). Brown solid (85%, 213 mg). Mp: 131–132 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.05 (t, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.71 (t, *J* = 7.1 Hz, 2H), 7.61(t, *J* = 7.1 Hz, 1H), 7.39 (t, *J* = 7.1 Hz, 1H), 6.73 (d, *J* = 10.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.2, 148.3, 147.9, 136.5, 129.8, 129.5, 129.3, 128.8, 127.4, 126.8, 125.6, 118.4, 115.2.

2-(4-(trifluoromethyl)phenyl)quinoline (5ai).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (66%, 180 mg). Mp: 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.26 (t, *J* = 7.3 Hz, 3H), 8.20 (d, *J* = 9.4 Hz, 1H), 7.85–7.82 (m, 2H), 7.79–7.73 (m, 3H), 7.56 (t, *J* = 7.3

Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 155.7, 148.4, 143.0, 137.2, 130.1, 130.0, 128.0, 127.9, 127.6, 127.5, 127.0, 125.9, 125.8, 118.8.

2-o-tolylquinoline (5aj).[12,14a] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (71%, 156 mg). Mp: 74–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.21 (t, *J* = 8.3 Hz, 2H), 7.86 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.78–7.73 (m, 1H), 7.59–7.53 (m, 3H), 7.36–7.35 (m, 3H), 2.46 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) =160.3, 147.9, 140.7, 136.1, 136.0, 130.9, 129.7, 129.6, 128.5, 127.5, 126.7, 126.4, 126.0, 122.4, 20.4.

2-(2-methoxyphenyl)quinoline (5ak).[14a] Eluent: petroleum ether/ethyl acetate (18 : 1). Yellow liquid (62%, 146 mg). ^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.22 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 7.5, 3 Hz, 2H), 7.82 (d, *J* = 7.3Hz, 1H), 7.74–7.69 (m, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.46–7.40 (m, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.2 (d, J = 6.7 Hz), 148.3, 135.1, 131.5, 130.4, 129.7, 129.6, 129.2, 127.4, 127.1, 126.2, 123.5, 121.3, 111.5, 55.6.

2-(2-fluorophenyl)quinoline (5al).[22c] Eluent: petroleum ether/ethyl acetate (18 : 1). Yellow liquid (40%, 89 mg). ^{1}H NMR (500 MHz, CDCl3): δ (ppm) = 8.22–8.18 (m, 2H), 8.10 (td, *J* = 7.5, 1.5 Hz, 1H), 7.90–7.84 (m, 2H), 7.76–7.73 (m, 1H), 7.58–7.54 (m, 1H), 7.46–7.41 (m, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23–7.19 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 160.9 (d, *J* = 247.5 Hz), 148.5, 136.3, 131.7, 130.9 (d, *J* = 8.8 Hz), 129.8 (d, *J* = 15.0 Hz), 128.1 (d, *J* = 12.5 Hz), 127.6, 127.4, 126.7, 124.8, 124.8, 122.6, 122.5, 116.4 (d, *J* = 22.5 Hz).

2-(2-chlorophenyl)quinoline (5am).[22c] Eluent: petroleum ether/ethyl acetate (18 :1). White solid (58%, 139 mg). Mp: 76–78 °C. ^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.20 (t, *J* = 9.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.77–7.70 (m, 3H), 7.59–7.50 (m, 2H), 7.43–7.36 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$): δ (ppm) = 157.4, 148.1, 139.6, 135.7, 132.4, 131.7, 130.1, 129.9, 129.7, 129.7, 127.6, 127.2, 127.2, 126.8, 122.8.

2-(3-bromophenyl)quinoline (5an).[32] Eluent: petroleumether/ethyl acetate (18 : 1). White solid (55%, 156 mg). Mp: 74–75 °C. ^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.36 (t, *J* = 1.7 Hz, 1H),

8.16 (t, *J* = 8.9 Hz, 2H), 8.04 (dt, *J* = 7.7 Hz, 1H), 7.80–7.70 (m,3H), 7.59–7.49 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) = 155.5, 148.2, 141.6, 137.0, 132.2, 130.6, 130.3, 129.9, 129.8, 127.5, 127.3, 126.7, 126.1, 123.2, 118.6.

2-(3-nitrophenyl)quinolone (5ao).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (69%, 173 mg). ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.99 (s, 1H), 8.50 (d, *J* = 5.34 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 10.0 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.65 (t, *J* = 8.6 Hz, 1H), 7.53 (t, *J* = 7.1 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, CDCl3): δ (ppm) = 154.4, 148.4, 148.2, 141.2, 137.5, 133.9, 130.2, 130.0, 129.8,127.6, 127.4, 127.1, 123.2, 122.4, 118.4.

2-(pyridin-3-yl)quinoline (5ap).[22c] Eluent: petroleum ether/ethyl acetate (18 : 1). Brown solid (74%, 153 mg). Mp: 65–67 °C.^{1}H NMR (500 MHz, CDCl3): δ (ppm) = 9.34 (s, 1H), 8.68 (d, *J* = 3.5 Hz, 1H), 8.49–8.47 (m, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.85–7.81 (m, 2H), 7.75-7.71 (m, 1H), 7.55–7.52 (m, 1H),7.44–7.41 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3): δ (ppm) = 154.6, 150.2, 148.8, 148.4, 137.2, 135.2, 135.0, 130.0, 129.8, 127.6, 127.4, 126.8, 123.7, 118.5.

3-methyl-2-phenylquinoline (5aq).[12,32] Eluent: petroleum ether/ethyl acetate (18 : 1). Pale-yellow oil (80%, 175 mg). ^{1}H NMR (500 MHz, CDCl3): δ (ppm) = 8.16 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.62–7.60 (m, 2H), 7.51–7.48 (m, 3H), 7.46–7.43 (m, 1H), 2.44 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3): δ (ppm) =160.6, 146.6, 141.0, 136.9, 129.4, 129.4, 129.0, 128.9, 128.4, 128.3, 127.7, 126.8, 126.5, 20.7.

2-(thiophen-2-yl)quinoline (5ar).[22c] Eluent: petroleum ether/ethyl acetate (18 : 1). Brown solid (64%, 135 mg). Mp: 131–132 °C. ^{1}H NMR (500 MHz, CDCl3): δ (ppm) = 8.10 (t, *J* = 9.0 Hz, 2H), 7.78–7.68 (m, 4H), 7.49–7.47 (m, 2H), 7.17–7.15 (m, 1H).$^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3): δ (ppm) =152.4, 148.1, 145.4, 136.6, 129.8, 129.3, 128.6, 128.1, 127.5, 127.2, 126.1, 125.9, 117.6.

2-(thiophen-3-yl)quinoline (5as).[22c] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (79%, 167 mg). Mp: 132–133°C.^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.17 (d, *J* = 8.0 Hz, 1H), 8.08–8.03 (m, 2H), 7.90 (d, *J* = 5.6 Hz, 1H), 7.72 (q, *J* = 8.0 Hz, 3H), 7.51–7.41 (m, 2H). ^{13}C{^{1}H} NMR (75MHz, CDCl3): δ (ppm) = 153.2, 148.2, 142.6, 136.6, 129.7, 129.4, 127.5, 127.1, 126.9, 126.4, 124.7, 119.0.

2-cyclopropylquinoline (5at).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). Pale-yellow oil (78%, 132 mg). ^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.00 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 2.28–2.19 (m, 1H), 1.17 (d, *J* = 3.4 Hz, 2H), 1.09 (d, *J* = 8.1 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl3): δ (ppm) = 163.4, 148.0, 135.8, 129.3, 128.6, 127.5, 126.7, 125.2, 119.3, 18.1, 10.3.

5,6-dihydrobenzo[c]acridine (5au).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (81%, 187 mg). Mp: 64–66 °C.^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.42 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.67 (s, 1H), 7.53–7.43 (m, 2H), 7.28–7.16 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 2.88 (d, *J* = 5.8 Hz, 2H), 2.80 (d, *J* = 5.3 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, CDCl3): δ (ppm) = 153.4, 147.6, 139.5, 134.7, 133.8, 130.6, 129.8, 129.4, 128.7, 128.0, 127.9, 127.4, 127.0, 126.1, 28.8, 28.4.

7-chloro-2-phenylquinoline (5ba).[32] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (67%, 161 mg). Mp: 108–109 °C. ^{1}H NMR (300 MHz, CDCl3): δ (ppm) = 8.19–8.14 (m, 3H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 9 Hz, 1H), 7.57–7.48 (m, 3H), 7.43 (dd, *J* = 8.7, 1.9 Hz, 1H) . ^{13}C{^{1}H} NMR (100 MHz, CDCl3): δ (ppm) = 158.1,148.6, 139.1, 136.5, 135.4, 129.7, 128.9, 128.7,127.6, 127.2, 125.5, 119.0.

8-bromo-6-methyl-2-phenylquinoline (5ca).[22c] Eluent: petroleum ether/ethyl acetate (18 : 1). White solid (71%, 212 mg). Mp: 81–82 °C. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) = 8.30–8.20 (m, 3H), 8.06 (t, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 3H), 2.39 (d, *J* = 9.0 Hz, 3H) .

2-phenylquinazolin-4(3H)-one (8aa).[22b,34,35] Eluent: petroleum ether/ethyl acetate (3:1). White solid (95%, 211 mg). Mp: 240−241 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 11.83 (s, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.28 (s, 2H), 7.86–7.81 (m, 2H), 7.60 (s, 3H), 7.52 (t, J = 8.0 Hz, 1H).

2-(p-tolyl)quinazolin-4(3H)-one (8ab).[34,35] Eluent: petroleum ether/ethyl acetate (3:1). White solid (95%, 224 mg). Mp: 244−246 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.43 (s, 1H), 8.14 (dd, J = 6.0, 3.0 Hz, 1H), 8.08 (d, J = 6.0 Hz, 2H), 7.85–7.80 (m, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.52–7.47 (m,1H), 7.34 (d, J = 9.0 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ (ppm) = 162.8, 152.8, 149.4, 142.0, 135.2, 130.4, 129.8, 128.2, 128.0, 127.0, 126.4, 121.4, 21.5.

2-(4-methoxyphenyl)quinazolin-4(3H)-one (8ac).[35] Eluent: petroleum ether/ethyl acetate (3:1). White solid (77%, 194 mg). Mp: 240−241 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.40 (s. 1H), 8.19 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ(ppm) = 162.2, 161.8, 151.9, 148.8, 134.5, 129.4, 127.2, 126.1,125.8, 124.8, 120.6, 114.0,55.4.

2-(4-fluorophenyl)quinazolin-4(3H)-one (8ad).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (83%, 199 mg). Mp: 258− 259 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.55 (s, 1H), 8.25–8.21 (m, 2H), 8.14 (d, J = 8.0, 1H), 7.82(t, J= 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.51(t, J= 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR(100 MHz,DMSO-d_6): δ (ppm) = 165.3, 162.5 (d, J = 244.0 Hz), 151.4, 148.6, 134.6, 130.4 (d, J = 36.0 Hz), 129.2 (d, J = 12.0 Hz), 127.4, 126.6, 125.8, 120.9, 115.6 (d, J = 88.0 Hz).

2-(4-chlorophenyl)quinazolin-4(3H)-one (8ae).[35] Eluent: petroleum ether/ethyl acetate (3:1). White solid (82%, 211mg). Mp: 294−296 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =12.60 (s, 1H), 8.21-8.15 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 1H).

2-(4-bromophenyl)quinazolin-4(3H)-one (8af).[35] Eluent: petroleum ether/ethyl acetate (3:1). White solid (80%, 241 mg). Mp: >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.59 (s, 1H), 8.15–8.10 (m, 3H), 7.83 (t, J = 8.0 Hz, 1H), 7.74 (t, J = 8.0, 2H), 7.53 (t, J = 8.0, 2H).

2-(4-nitrophenyl)quinazolin-4(3H)-one (8ag).[35] Eluent: petroleum ether/ethyl acetate (3:1). Brown solid (52%, 139 mg). Mp: >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.05 (s, 1H), 8.10–7.94 (m, 3H), 7.76–7.73 (m, 1H), 7.64–7.60 (m, 1H), 7.40 (d, J = 3.3 Hz, 1H), 6.65–6.61 (m, 2H).

2-(4-(trifluoromethyl)phenyl)quinazolin-4(3H)-one (8ah).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (92%, 267 mg). Mp: >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.72 (s, 1H), 8.34 (d, J = 9.0 Hz, 2H), 8.17 (dd, J= 6.2, 1.7 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.85 (dd, J = 6.0, 1.2 Hz, 1H), 7.79–7.76 (m, 1H), 7.59–7.54 (m,1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ (ppm) = 162.4, 151.4, 148.5, 135.0, 131.5, 131.0, 128.9, 127.8, 127.3, 126.1, 125.7 (d, J = 3.8 Hz), 121.3.

2-(4-*tert*-Butyl-phenyl)quinazolin-4(3H)-one (8ai).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (94%, 262 mg). Mp: 207−209 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.43 (s, 1H), 8.14–8.08 (m, 3H), 7.81 (t, J = 8.0 Hz,1H), 7.71 (d, J = 8.0 Hz,1H), 7.54–7.47 (m, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ (ppm) = 162.5, 154.6, 152.4, 149.0, 134.8, 130.0, 127.7, 127.6, 126.7, 126.0, 125.6, 121.0, 34.8, 31.0.

2-o-tolylquinazolin-4(3H)-one (8aj).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (64%, 151 mg). Mp: 222−224 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.44 (s, 1H), 8.16 (dd, J = 9.0, 3 Hz, 1H), 7.86–7.80 (m, 1H), 7.70 (d, J= 9.0 Hz, 1H), 7.56–7.47 (m, 2H), 7.42−7.40 (m,1H), 7.35–7.29 (m, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ (ppm) = 162.1, 154.6, 148.9, 136.3, 134.8, 134.3, 130.8, 130.2, 129.3,127.5, 127.0, 126.0, 126.0, 121.0, 19.7.

2-(2-chlorophenyl)quinazolin-4(3H)-one (8ak).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (55%, 141 mg). Mp: 194−196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.57 (s,

1H), 8.27 (d, *J* = 5.0 Hz, 1H), 7.82–7.79 (m, 3H), 7.54–7.42 (m, 4H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 162.4, 151.2, 149.2, 135.0, 133.0, 132.2, 132.1, 131.6, 130.7, 128.2, 127.6, 127.5, 126.7, 121.3.

2-(2-bromophenyl)quinazolin-4(3H)-one (8al).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (52%, 157 mg). Mp: 185−187 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.65 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.78–7.71 (m, 2H), 7.65–7.63 (m, 1H), 7.60–7.46 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ (ppm) = 161.6, 153.4, 148.6, 135.9, 134.7, 132.8, 131.8, 130.9, 127.8, 127.6, 127.2, 126.0, 121.3, 121.2 (d, *J* = 108.0 Hz).

2-m-tolylquinazolin-4(3H)-one (8am).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (95%, 224 mg). Mp: 210−211 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.45 (s, 1H),8.14 (d, *J*= 8.0 Hz, 1H), 8.00 (s, 1H), 7.95 (d, *J* = 8.0Hz, 1H), 7.82 (t, *J* = 8.0Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.51(t, *J* = 8.0Hz, 1H), 7.44–7.38 (m, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.2, 152.4, 148.8, 137.9, 134.6, 132.6, 132.0, 128.5, 128.3, 127.4, 126.5, 125.8, 124.9, 121.0, 21.0.

2-(3-methoxyphenyl)quinazolin-4(3H)-one (8an).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (93%, 235 mg). Mp: 210−212 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.52 (s, 1H), 8.16(d, *J* = 8.0Hz, 1H), 7.84 (t, *J* = 8.0Hz, 1H), 7.79–7.74 (m, 3H), 7.53 (t, *J* = 8.0Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0Hz, 1H) 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) = 162.4, 159.4, 152.2, 148.7, 134.8, 134.1, 129.9, 127.6, 126.8, 121.1, 120.2, 117.7, 112.6, 55.5.

2-(3-chlorophenyl)quinazolin-4(3H)-one (8ao).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (69%, 177 mg). Mp: 296−297 °C.^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.62 (s, 1H), 8.23 (s, 1H), 8.15 (t, *J* = 8.0 Hz, 2H), 7.86 (t, J= 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61–7.54 (m, 2H).

2-(3-bromophenyl)quinazolin-4(3H)-one (8ap).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (65%, 196 mg). Mp: 297−298 °C.^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.62

(s, 1H), 8.37 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.88–7.83 (m, 1H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.56–7.50 (m, 2H).

2-(2,4-dimethoxyphenyl)quinazolin-4(3H)-one (8aq).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (95%, 268 mg). Mp: 205−206 °C.^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 10.89 (s, 1H), 8.48 (d, *J* = 9.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.75–7.73 (m, 2H), 7.43–7.40 (m, 1H), 6.70–6.56 (m, 1H), 6.56 (s, 1H), 4.03 (s, 3H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ(ppm) = 163.9, 162.1, 159.3, 150.8, 149.7, 134.5, 133.1, 127.6, 126.4, 121.0, 112.7, 106.6, 98.9, 56.2, 55.7.

2-(2,4-dichlorophenyl)quinazolin-4(3H)-one (8ar).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (62%, 180 mg). Mp: 226−227 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 12.66 (s, 1H), 8.18 (d, *J* = 12 Hz, 1H), 7.89–7.81 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.61–7.55 (m, 2H), 7.59–7.51 (m, 1H).

2-(pyridin-2-yl)quinazolin-4(3H)-one (8as).[22b] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (56%, 125 mg). ^{1}H NMR(400 MHz, DMSO-d_6): δ (ppm) = 11.80 (s, 1H), 8.74 (d, *J* = 4.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.0Hz, 1H), 8.06 (t, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H).

2-(thiophen-2-yl)quinazolin-4(3H)-one (8at).[34] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (68%, 155 mg). Mp: 270−272 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.65 (s, 1H), 8.22 (d, *J* = 3.0 Hz, 1H), 8.12 (d, *J* = 6.0 Hz, 1H), 7.86 (d, *J* = 6.0, 1.0 Hz, 1H), 7.83–7.77 (m, 1H), 7.64 (d, *J* = 9.0, 1.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.23–7.21 (t, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ (ppm) = 161.8, 148.7, 147.8, 137.4, 134.7, 132.2, 129.4, 128.5, 127.0, 126.4, 126.0, 120.9.

2-butylquinazolin-4(3H)-one (8au).[34] Eluent: petroleum ether/ethyl acetate (3:1). White solid (35%, 71 mg). Mp: 108−109 °C.^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.15 (s, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.79–7.73 (m, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.47–7.42 (m, 1H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.75–1.65 (m, 2H), 1.40–1.30 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100

MHz, DMSO-d_6): δ (ppm) = 161.8, 157.5, 148.9, 134.2, 126.7, 125.8, 125.6, 120.7, 34.1, 28.8, 21.6, 13.6.

8-methyl-2-phenylquinazolin-4(3H)-one (8ba).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (95%, 224 mg). Mp: 246−248 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) = 12.45 (s, 1H), 8.14 (d, J = 6.0 Hz, 1H), 8.00 (s, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 6.0 Hz, 1H), 7.51 (t, J =6.0 Hz, 1H), 7.44−7.38 (m, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) = 161.5, 154.4, 148.7, 136.1, 134.5, 134.2, 130.5, 129.9, 129.1, 127.4, 126.6, 125.8, 125.7, 121.0, 19.6.

6-methyl-2-phenylquinazolin-4(3H)-one (8da).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (94%, 222 mg). Mp: 266−268 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.44 (s, 1H), 8.16 (dd, J = 6.0 Hz, 3H), 7.95 (s, 1H), 7.65 (s, 2H), 7.58− 7.51 (m, 3H), 2.46 (s, 3H).

8-bromo-2-phenylquinazolin-4(3H)-one (8ca).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (68%, 205 mg). Mp: 219−220 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.75 (s, 1H), 8.25 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 4.0 Hz, 2H), 7.62–7.56 (m, 3H), 7.41 (t, J = 8.0 Hz, 1H).

8-bromo-6-methyl-2-phenylquinazolin-4(3H)-one (8ea).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (71%, 224 mg). Mp: >300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) =12.64 (s, 1H), 8.22 (t, J = 7.5 Hz, 2H), 8.00 (d, J = 3 Hz, 1H), 7.93 (s, 1H), 7.60–7.52 (m, 3H), 2.43 (s, 3H).

8-bromo-6-methyl-2p-tolylquinazolin-4(3H)-one (8eb). Eluent: petroleum ether/ethyl acetate (3:1). White solid (75%, 247 mg). Mp: >290 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) =12.59 (s, 1H), 8.16 (d, J = 9.0 Hz, 2H), 8.00−7.93 (m, 2H), 7.37 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H) . ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) =161.8, 151.9, 144.1, 141.7, 138.8, 137.2, 129.6, 129.2, 127.7, 125.2, 122.1, 121.8, 21.0, 20.4.

6,7,8-trimethoxy-2-phenylquinazolin-4(3H)-one (8fa).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (96%, 300 mg). Mp: 273−275 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =

12.49 (s, 1H), 8.20−8.17 (m, 2H), 7.57−7.54 (m, 3H), 7.38 (s, 1H), 4.07(s, 3H), 3.90 (d, J = 9.5 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) = 161.7, 152.2, 149.6, 148.0, 147.2, 138.4, 132.9, 131.1, 128.6, 127.5, 117.1, 101.2, 62.1, 60.9, 56.0.

2,3-dihydro-2-phenylquinazolin-(1H)-one (9aa).[22b] Eluent: petroleum ether/ethyl acetate (3:1). White solid (87%, 195 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.26 (s, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.39–7.33 (m, 3H), 7.25–7.21 (m, 1H), 7.08 (s, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 5.74 (s, 1H).

ASSOCIATED CONTENT

Supporting Information. ORTEP, crytal data refinement parameters, FMO's, Cyclic voltammogram, UV-Vis spectra, IR spectra, CIF file, cartesian coordinates of the metal complex and the ^{1}H and ^{13}C NMR spectral data of all the synthesized compounds are provided in the Supporting Information. This material is available free of charge on the ACS Publications website.

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Notes

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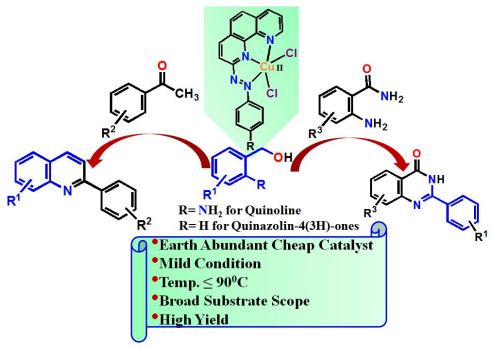
R= NH2 for Quinoline
R= H for Quinazolin-4(3H)-ones
Earth Abundant Cheap Catalyst
Mild Condition
Temp. ≤ 90°C
Broad Substrate Scope
High Yield