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ARTICLE TYPE

$CuSO_4$-D-glucose an inexpensive and eco-efficient catalytic system: direct access to diverse quinolines through modified Friedländer approach involving S_NAr/reduction/annulation cascade in one-pot

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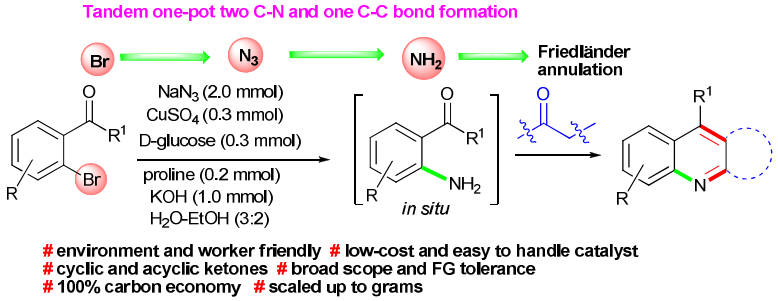

A highly efficient and scalable multicomponent domino reaction for the synthesis of functionalized/annulated quinolines is devised directly from 2-bromoaromatic aldehydes/ketones in H_2O-EtOH mixture for the first time. The key to this reaction is the use of an air-stable, eco-efficient and inexpensive $CuSO_4$-D-glucose catalyst system, which is able to catalyze multiple transformations in one-pot. The approach is carbon-economic and relies on sequential S_NAr/reduction/Friedländer annulation steps forming C–C and C–N bonds by cleavage of Csp^2–Br bond in a single synthetic operation. The reaction has a broad substrate scope and affords products in good to excellent yields.

Introduction

Generation of structural diversity and molecular complexity from easily available and inexpensive starting materials in operationally simple and pot, atom, and cost economic manner is one of the most promising challenges for synthetic chemists.[1] The core strategies to minimize the environmental impact of a reaction involves the use of greener solvents and recyclable eco-friendly catalysts.[1e,f] The copper-mediated transformations have emerged as a powerful method for the construction of C–C and C–heteroatom bonds because of its abundance, low-cost, and eco-efficient nature.[2]

Nitrogen-containing heterocycles are omnipresent in natural products and pharmaceutical substances. Consequently, the development of methods for the introduction of nitrogen in simple organic compounds is an intense focus of modern research. Quinolines[3] are present as a core structural unit in a wide range of pharmaceuticals and natural products.[4] They have been recognized as a privileged structure in the field of natural alkaloids, material and medicinal chemistry as well as in bio-organic/bio-organometallic processes.[5] Furthermore, they show antimalarial, tumoricidal, antimycobacterial, antimicrobial, anticonvulsant, anti-inflammatory, anticardiovascular, antifungal, and HIV-1 integrase inhibitory activities.[6] A number of quinoline derivatives have been successfully commercialized as drugs such as Singulair, Tafenoquine, Aldara, and hydroxychloroquine.[7] Also, they are valuable synthons for the preparation of materials with unique electronic and optical properties.[8]

Due to their vast applications, several strategies for the synthesis of quinolines have been reported.[9] The most common ones include Skraup,[10] Friedländer,[11] Pfitzinger,[12] Conrad-Limpach,[13] Combes[14] and Doebner-von Miller[15] synthesis. All these routes access the quinoline synthesis through inter/intramolecular annulation of aniline or its derivatives with carbonyl compounds. Friedländer reaction still being an "evergreen" method of choice, an array of conditional/structural modifications have been reported.[16] Nevertheless, many existing methods are inefficient and require multiple steps, highly functionalized substrates and complicated operational procedures producing large quantities of waste. Most relevant limitation is the use of the 2-aminobenzaldehyde as a substrate, which is highly prone to self condensation.[17] Therefore, 2-aminobenzylalcohols,[11b] 2-nitrobenzaldehyde,[11c] and 2-nitrobenzyl alcohols[16a] are frequently utilized as 2-aminobenzaldehyde counterpart.[17b] The privileged status of

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quinolines still demands the more economical and eco-efficient strategies for their synthesis.[9a,18]

To achieve this goal, two main approaches have been taken into consideration: 1) The development of suitable catalytic system and 2) the use of greener solvents instead of toxic organic solvents. The direct use of 2-bromoaromatic aldehydes/ketones with active methylene for the synthesis of quinolines has not been explored. Herein, we report an eco-efficient one-pot protocol for the direct synthesis of diverse quinolines from commercially available 2-bromoaromatic aldehydes/ketones as a mimic of 2-aminobenzaldehyde in the presence of inexpensive $CuSO_4$-D-glucose catalyst system in green water-ethanol solvent. This type of operationally simple and eco-friendly $CuSO_4$-D-glucose catalysed one-pot S_NAr/reduction/heteroannulation cascade for the synthesis of quinolines is not explored previously to the best of our knowledge.

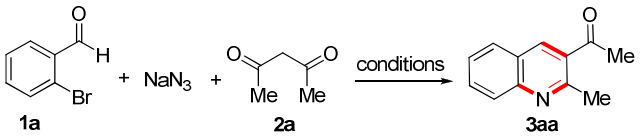
Results and discussion

With a view to construct quinoline framework, we selected 2-bromobenzaldehyde (**1a**) as a model substrate. In our initial study, the reaction of **1a** (1.0 mmol) with sodium azide (2.0 mmol) and acetyl acetone (**2a**, 1.1 mmol) in the presence of Cu_2O (0.3 mmol), proline (1.2 mmol) in DMSO at 90 ºC in the open atmosphere afforded the desired product 3-acetyl-2-methylquinoline **3aa** in 50% yield within 8 h (Table 1, entry 1). Encouraged by this result, we turned our attention to find the optimized reaction conditions by screening various catalysts, ligands and solvents. The results are listed in Table 1. The use of CuI (0.3 mmol) in place of Cu_2O in the above reaction afforded **3aa** in 55% yield (Table 1, entry 2). Change of the solvent from DMSO to PEG-400 could not offer the better result (Table 1, entry 3). Acetic acid in place of proline was also found to be ineffective (Table 1, entry 4). Next, we assumed that the use of base may improve the efficiency of this transformation.[19] Consequently, the use of K_2CO_3 in the above reaction furnished the desired product **3aa** in 62% yield (Table 1, entry 5). Further screening of other Cu salts such as $Cu(OAc)_2$ and $CuSO_4$ separately was found to be completely ineffective (Table 1, entries 6 and 7).

On the basis of above observations, we thought to generate Cu(I) *in situ* by the reduction of highly economical $CuSO_4$ salt. The use of sodium L-ascorbate with $CuSO_4$ noticeably increased the yield of **3aa** to 69% (Table 1, entry 8). The reaction did not proceed to completion when lesser amount of proline (0.2 equiv) was used under similar conditions (Table 1, entry 9). This may be due to dual role of proline as ligand and a proton source. Therefore, DMSO was replaced with ethanol to provide the direct proton source. Notably, the use of EtOH as a solvent in the presence of 0.2 equiv of proline increased the yield to 82% (Table 1, entry 10). We presume that this protocol undergoes copper-promoted Ullmann-type coupling of **1a** with NaN_3 followed by reduction to give 2-aminobenzaldehyde *in situ*. The subsequent reaction of 2-aminobenzaldehyde with acetyl acetone **2a** *via* Friedländer annulation afforded the desired quinoline **3aa**.

The success of this protocol prompted us to investigate about the use of reducing carbohydrate D-glucose. To our pleasure, the use of D-glucose in place of sodium L-ascorbate increased the yield to 87% (Table 1, entry 11).

Table 1 Optimization studies for the synthesis of quinoline **3aa**[a]



1a **2a** **3aa**

Entry	Catalyst (mmol)	Ligand (mmol) Base (mmol)	Solvent (5 mL)	Time (h)	Yield (%)[b]
1	Cu_2O (0.3)	Proline (1.2)	DMSO	8	50
2	CuI (0.3)	Proline (1.2)	DMSO	8	55
3	CuI (0.3)	Proline (1.2)	PEG-400	8	52
4	CuI (0.3)	Acetic acid (1.2)	DMSO	24	21
5	CuI (0.3)	Proline (1.2) + K_2CO_3 (1)	DMSO	8	62
6	$Cu(OAc)_2$ (0.3)	Proline (1.2) + K_2CO_3 (1)	DMSO	24	n.r.[c]
7	$CuSO_4$ (0.3)	Proline (1.2) + K_2CO_3 (1)	DMSO	24	n.r.[c]
8	$CuSO_4$ (0.3) + Na-L-ascorbate (0.3)	Proline (1.2) + K_2CO_3 (1)	DMSO	8	69
9	$CuSO_4$ (0.3) + Na-L-ascorbate (0.3)	Proline (0.2) + K_2CO_3 (1)	DMSO	24	21
10	$CuSO_4$ (0.3) + Na-L-ascorbate (0.3)	Proline (0.2) + K_2CO_3 (1)	EtOH	6	82
11	$CuSO_4$ (0.3) + D-Glucose (0.3)	Proline (0.2) + K_2CO_3 (1)	EtOH	5	87
12	$CuSO_4$ (0.3) + D-Glucose (0.3)	Proline (0.2) + K_2CO_3 (1)	H_2O	5	72
13	$CuSO_4$ (0.3) + D-Glucose (0.3)	Proline (0.2) + K_2CO_3 (1)	H_2O+ EtOH(3:2)	4	91
14	$CuSO_4$ (0.3) + D-Glucose (0.3)	Proline (0.2) + KOH (1)	H_2O+ EtOH(3:2)	3	95
15	$CuSO_4$ (0.1) + D-Glucose (0.1)	Proline (0.2) + KOH (1)	H_2O+ EtOH(3:2)	15	57
16	$CuSO_4$ (0.3) + D-Glucose (0.3)	Proline(0.2) + KOH (1)	PEG-400	5	-[d]

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.1 mmol), NaN_3 (2.0 mmol), $CuSO_4$ (0.3 mmol), D-glucose (0.3 mmol), proline (0.2 mmol), KOH (1 mmol), H_2O-EtOH (3:2, 5 mL), 90 ºC. [b] Isolated pure yields. [c] n.r. = no reaction. [d] Partial conversion with several overlapping spots.

In an attempt to find the green solvent, the above reaction was performed in water. Although the desired product **3aa** was obtained in 72% yield, the starting substrates were not completely soluble in water and remained unconsumed (Table 1, entry 12). We deemed to add ethanol to boost the worth of the reaction. After several attempt, the better result was obtained by carrying out the reaction in water-ethanol (3:2) mixture (Table 1, entry 13). We envisioned that the use of stronger base like KOH in place of K_2CO_3 may further improve the efficiency of the reaction by promoting dehydrative cyclization. As expected, the use of KOH increased the yield from 91% to 95% as well as reduced the reaction time from 4 h to 3 h (Table 1, entry 14). On lowering the catalytic loading, the conversion was drastically

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diminished (Table 1, entry 15). Finally, when the model reaction was carried out in PEG-400 at 90 °C, only partial conversion with several overlapping spots was observed (Table 1, entry 16). Thus, the optimum reaction conditions for the synthesis of quinoline **3aa** was achieved by employing **1a** (1 mmol), NaN_3 (2 mmol), **2a** (1.1 mmol), $CuSO_4$ (0.3 mmol), D-glucose (0.3 mmol), proline (0.2 mmol) and KOH (1 mmol) in water-ethanol (3:2) mixture at 90 °C.

Table 2 Reaction of 2-bromobenzaldehydes/2-bromobenzophenone with 1,3-diketones

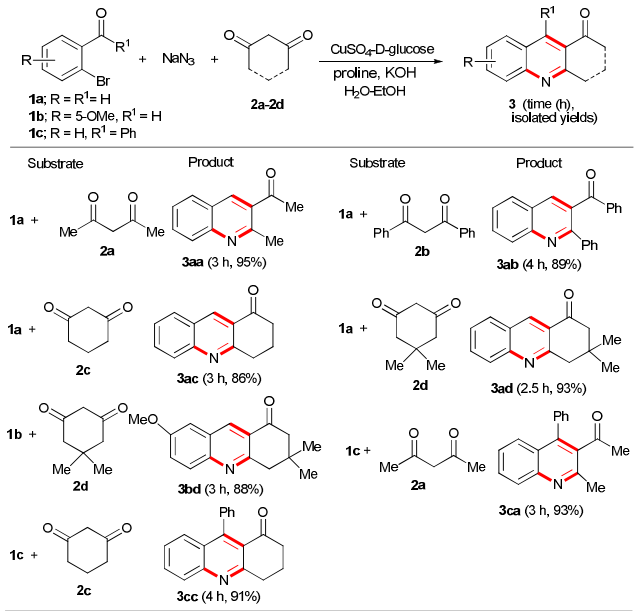
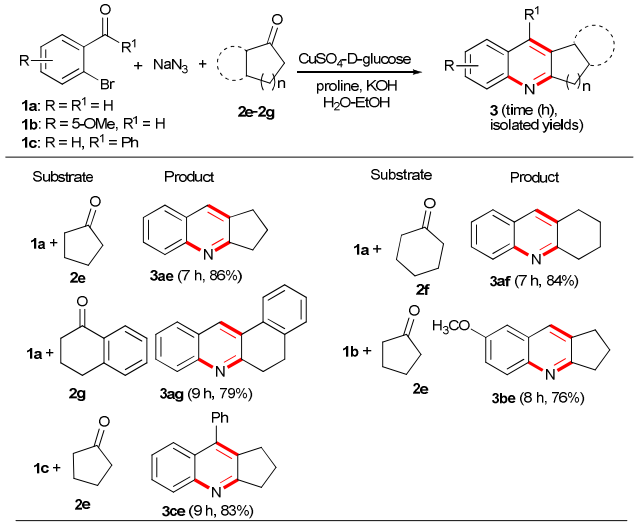


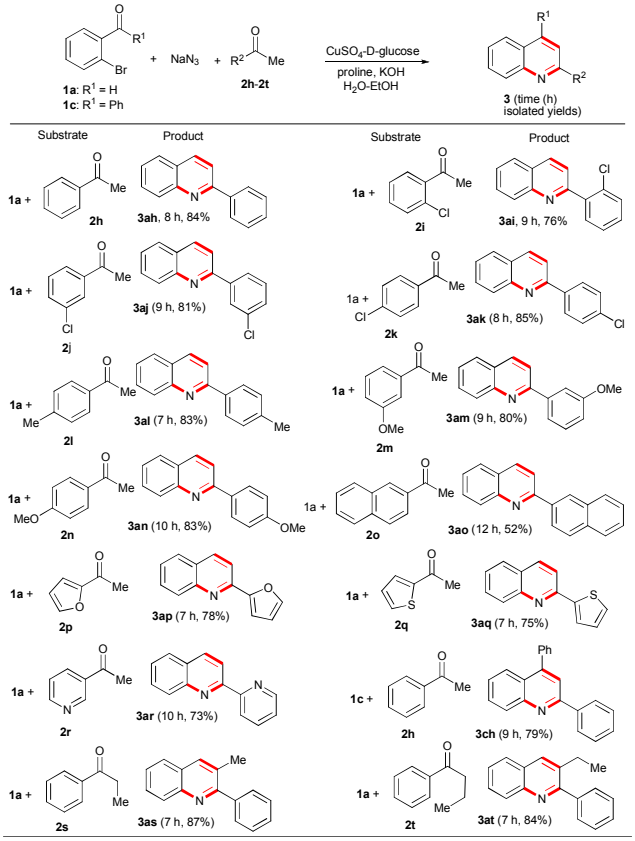
Table 3 Reaction of 2-bromobenzaldehydes/2-bromobenzophenone with cyclic ketones



Under the optimal reaction conditions, the protocol scope and generality for the direct construction of quinolines **3** was explored (Table 2). The one-pot cascade process serves as a general approach to access valuable substituted/annulated quinolines in excellent yields (86-95%) with a broad substrate scope. 2-Bromobenzaldehydes (**1a-b**) and 2-bromobenzophenone (**1c**) reacted smoothly with both acyclic (**2a-b**) and cyclic (**2c-d**) 1,3-diketones affording the corresponding quinolines **3** in excellent yields.

To illustrate the broad synthetic utility and generality of our developed one-pot domino methodology, we further treated 2-bromoaromatic aldehydes/ketone (**1a-c**) with various monocyclic and bicyclic ketones (**2e-g**) separately under the above optimized conditions. Both mono and bicyclic ketones were tolerated well and furnished the corresponding quinolines **3** in 76-86% yields (Table 3). Notably, the bicyclic ketone **2g** also worked efficiently and afforded the tetracyclic quinoline **3ag** in 79% yield. It seems that the ring size of the cyclic ketones has no effect on the tandem process.

Table 4 Reaction of 2-bromobenzaldehyde/2-bromobenzophenone with acyclic ketones



After the successful synthesis of 2,3-disubstituted/annulated quinolines, we turned our attention toward the synthesis of 2-substituted quinolines. Consequently, we utilized various acetophenones (**2h-o**) and heteroaromatic ketones (**2p-r**) under previously described one-pot optimized conditions. The workup of the reactions afforded the desired 2-substituted quinolines **3** in good yields. Notably, a series of substituted acetophenones such as *o*-Cl, *m*-Cl, *p*-Cl, *p*-Me, *m*-OMe, *p*-OMe groups on the phenyl ring are well tolerated and the corresponding 2-substituted quinolines (**3ah-3an**) are obtained in 76-85% yields (Table 4). The protocol worked nicely with both electron-donating and electron-withdrawing groups at *ortho*-, *meta*-, and *para*-positions of the phenyl ring. The bulky naphthyl ethanone (**2o**) also reacted under similar conditions to produce quinoline **3ao** in moderate yield. In addition, the reaction of propiophenone (**2s**) and

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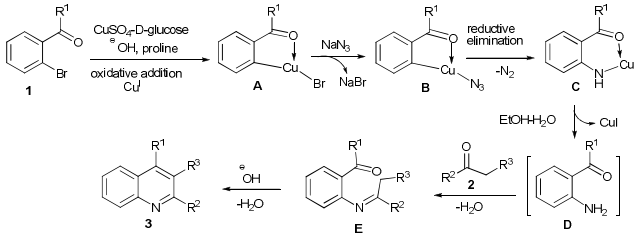
butyrophenone (**2t**) separately with 2-bromobenzaldeyde (**1a**) was successfully performed to afford the respective quinolines **3as** and **3at** in good yields. The structure of all the compounds showed full agreement with spectroscopic data and previous reports.[9a,20]

To demonstrate the usefulness of this novel one-pot domino protocol, a gram-scale experiment was carried out under the standard reaction conditions. The reaction of 2-bromobenzaldehyde **1a** (4 mL, 20 mmol) proceeded smoothly providing 6.76 g of product **3aa** (92%), which is comparable to the small scale experiment. Thus, this new methodology could be useful for the facile synthesis of quinoline scaffolds on an industrial scale. The use of inexpensive and easily prepared $CuSO_4$-D-glucose as an ideal catalytic system offers an attractive prospect in terms of industrial applications and sustainable developments.

Based on the entire experimental outcomes, a tentative mechanism is proposed in scheme 1. Initially, Cu(I) (generated *in situ* by the reduction of $CuSO_4$ in presence of D-glucose, base and proline) undergoes oxidative addition with substrate **1** to give copper complex **A**. The nucleophilic substitution of Br with sodium azide gives the azido Cu complex **B** followed by reductive elimination to give complex **C**, which readily converts to *ortho*-aminoaldehyde/ketone **D** under the reaction conditions. Intermediate **D** undergoes dehydrative coupling with ketone **2** to afford intermediate **E** followed by base-catalyzed dehydrative cyclocondensation to produce the desired quinoline **3**.



Scheme 1 Plausible mechanism for the synthesis of quinolines **3**.

Conclusions

In summary, we have successfully designed and developed an operationally simple, highly efficient one-pot practical and convenient method for the synthesis of diverse quinolines directly from 2-bromobenzaldehydes/2-bromobenzophenone. An inexpensive and easily prepared eco-efficient $CuSO_4$-D-glucose catalyst system and aqueous ethanol as the green solvent are the key features of this novel method with promising synthetic applications. The scope and diversity of the tolerated substrates in this work is rather much broad in comparison to the reported ones. The salient features of this domino protocol are its methodical simplicity, structural diversity, perfect carbon-economy, high product yields, readily available substrates and formation of three new bonds (one C─C and two C─N) and one ring in a single operation. In addition, the present one-pot process is amenable to gram scale synthesis. Further investigations for the synthetic utility of this catalyst system for the synthesis of different heterocyclic rings are currently underway in our laboratory.

Experimental section

General experimental details

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shift (δ) values are given in parts per million (ppm) with reference to tetramethylsilane (TMS) as the internal standard. Coupling constant (J) values are given in Hertz (Hz). The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. Melting points were determined with Buchi B-540 melting point apparatus and are uncorrected. Commercially obtained reagents were used after further purification when needed. All the reactions were monitored by TLC with silica gel coated plates. Column chromatography was carried out whenever needed, using silica gel of 100/200 mesh. Mixture of hexane/ethyl acetate in appropriate proportion (determined by TLC analysis) was used as eluent.

General procedure for the synthesis of compound 3

A mixture of 2-bromobenzaldehyde/2-bromoacetophenone **1** (1 mmol), NaN_3 (2 mmol) and cyclic/acyclic ketones **2** (1.1 mmol) in H_2O + EtOH (3:2, 5 mL) was placed in a 50 mL round bottom flask. To a stirring solution of above mixture added $CuSO_4$ (0.3 mmol), D-glucose (0.3 mmol), proline (0.2 mmol) and KOH (1 mmol). The reaction mixture was allowed to stir at 90 ºC for 3-10 h. After completion of reaction (monitored on TLC), solvent was removed under reduced pressure and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude residue thus obtained was purified by column chromatography to give the desired quinolines **3**.

3-Acetyl-2-methyl quinoline (3aa).[20a] Pale yellow solid, mp 74-75 ˚C; IR (KBr) cm^{-1}: 3053, 1788, 1624, 1579, 1456, 818; ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H, ArH), 8.05 (d, J = 8.4 Hz, 1H, ArH), 7.87-7.76 (m, 2H, ArH), 7.57-7.52 (m, 1H, ArH), 2.91 (s, 3H, $COCH_3$) 2.72 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 157.5, 138.2, 138.1, 131.6, 131.1, 128.5, 128.2, 126.6, 125.5, 29.2, 25.6.

Phenyl(2-phenylquinolin-3-yl)methanone (3ab).[20b] Yellow solid, mp 135-137 ºC; IR (KBr) cm^{-1}: 3163, 2960, 1756, 1684, 1562; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23-8.15 (m, 5H, ArH), 8.00 (d, J = 6.9 Hz, 1H, ArH), 7.89-7.81 (m, 2H, ArH), 7.75-7.70 (m, 1H, ArH), 7.55-7.43 (m, 6H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 157.3, 148.2, 139.6 (2C), 136.7, 132.4, 129.6, 129.2 (2C), 128.8 (3C), 128.6 (3C), 127.4 (2C), 127.1 (2C), 126.2, 118.9.

3,4-Dihydroacridin-1(2*H*)-one (3ac).[20a] White solid, mp 103-105 ºC; IR (KBr) cm^{-1}: 3463, 2926, 1737, 1452, 1230, 835; ^1H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H, ArH), 8.06 (d, J = 8.4 Hz, 1H, ArH), 7.94 (d, J = 8.1 Hz, 1H, ArH), 7.83-7.78 (m, 1H, ArH), 7.57 (t, J = 7.2 Hz, 1H, ArH), 3.34 (t, J = 6.0 Hz, 2H, CH_2), 2.82 (t, J = 6.0 Hz, 2H, CH_2), 2.32 (dd, J_1 = 6.0 Hz, J_2 = 12.6 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 161.9, 137.1, 132.3, 129.7, 128.4, 126.7, 126.6, 126.2, 39.0, 33.3, 21.7.

3,3-Dimethyl-3,4-dihydroacridin-1(2*H*)-one (3ad).[20a] White solid, mp 116-118 ºC; IR (KBr) cm^{-1}: 3062, 1768, 1594, 1488, 1231; ^1H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H, ArH), 8.06 (d, J = 8.7 Hz, 1H, ArH), 7.94 (d, J = 8.1 Hz, 1H, ArH), 7.82-7.77 (m, 1H, ArH), 7.57-7.52 (m, 1H, ArH), 3.20 (s, 2H, CH_2), 2.65 (s,

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2H, CH_2), 1.15 (s, 6H, 2xCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 160.7, 149.9, 136.4, 132.1, 129.7, 128.5, 126.6 (2C), 125.2, 52.4, 47.1, 32.7, 28.3(2C).

7-Methoxy-3,3-dimethyl-3,4-dihydroacridin-1(2*H*)-one (3bd).[20c] Yellow solid, mp 98-100 ºC; IR (KBr) cm^{-1}: 3062, 1768, 1594, 1488, 1231; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H, ArH), 7.97 (d, J = 9.0 Hz, 1H, ArH), 7.47-7.43 (m, 1H, ArH), 7.167 (s, 1H, ArH), 3.93 (s, 3H, OCH_3), 3.16 (s, 2H, CH_2), 2.63 (s, 2H, CH_2), 1.14 (s, 6H, 2xCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 158.2, 157.7, 146.1, 135.0, 129.8 (2C), 127.7, 125.3, 106.3, 55.6, 52.4, 46.7, 32.8, 28.3(2C).

3-Acetyl-2-methyl-4-phenyl quinoline (3ca).[20d] Yellow solid, mp 112-114 ºC; IR (KBr) cm^{-1}: 3053, 1788, 1624, 1579, 1456, 818; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H, ArH), 7.72-7.67 (m, 1H, ArH), 7.62 (d, J = 8.4 Hz, 1H, ArH), 7.49-7.44 (m, 3H, ArH), 7.42-7.34 (m, 3H, ArH), 2.70 (s, 3H, CH_3), 2.00 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 153.3, 147.3, 143.7, 135.0, 134.6, 129.9, 129.8 (2C), 128.8, 128.7, 128.5 (2C), 126.3, 126.0, 124.8, 31.8, 23.7.

9-Phenyl-3,4-dihydroacridin-1(2*H*)-one (3cc).[20d] Pale yellow solid, mp 153-156 ºC; IR (KBr) cm^{-1}: 3407, 3048, 2924, 1737, 1498, 1230, 749; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H, ArH), 7.78 (m, 1H, ArH), 7.50-7.37 (m, 5H, ArH), 7.19-7.16 (m, 2H, ArH), 3.40 (t, J = 6.3 Hz, 2H, CH_2), 2.72 (t, J = 6.3 Hz, 2H, CH_2), 2.29 (dd, J_1 = 6.6 Hz, J_2 = 12.6 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 162.2, 151.4, 148.5, 137.5, 131.7, 128.4 (2C), 128.1, 128.0 (2C), 127.9, 127.5 (2C), 126.4, 123.8, 40.6, 34.5, 21.3.

2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (3ae).[20a] White solid, mp 55-57 ºC; IR (KBr) cm^{-1}: 3053, 1646, 1562, 1212; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.67-7.64 (m, 1H, ArH), 7.60-7.55 (m, 1H, ArH), 7.43-7.38 (m, 1H, ArH), 3.14 (t, J = 7.5 Hz, 2H, CH_2), 3.02 (t, J = 7.2 Hz, 2H, CH_2), 2.19-2.11 (dd, J_1 = 7.5 Hz, J_2 = 15.0 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 147.2, 135.3, 130.0, 128.3, 128.2, 128.0, 127.1, 125.2, 34.3, 30.2, 23.3.

1,2,3,4-Tetrahydroacridine (3af).[20a,e] White solid, mp 85-87 ºC; IR (KBr) cm^{-1}: 3058, 1624, 1557, 1453, 1214; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.67-7.64 (m, 1H, ArH), 7.60-7.55 (m, 1H, ArH), 7.42-7.37 (m, 1H, ArH), 3.13 (t, J = 6.3 Hz, 2H, CH_2), 2.96 (t, J = 6.3 Hz, 2H, CH_2), 1.99-1.95 (m, 2H, CH_2), 1.88-1.84 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 146.4, 134.8, 130.8, 128.3, 128.1, 127.0, 126.7, 125.3, 33.4, 29.1, 23.1, 22.7.

5,6-Dihydrobenzo[*a*]acridine (3ag).[20f] Yellow solid, mp 63-65 ºC; IR (KBr) cm^{-1}: 3417, 2929, 1498, 1278, 1033, 789; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 7.5 Hz, 1H, ArH), 8.13 (d, J = 8.4 Hz, 1H, ArH),7.84 (s, 1H, ArH), 7.69-7.59 (m, 2H, ArH), 7.45-7.31 (m, 3H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 3.08-3.04 (m, 2H, CH_2), 2.97-2.93 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 147.5, 139.3, 134.6, 133.6, 130.4, 129.5, 129.3, 128.5, 127.8, 127.7, 127.2, 126.8, 126.0, 125.9, 28.7, 28.3.

7-Methoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (3be).[20g] White solid, mp 97-99 ºC; IR (KBr) cm^{-1}: 3407, 3048, 2924, 1595, 1498, 1230, 749; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 9.3 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.28-7.24 (m, 1H, ArH), 7.00 (d, J = 2.7 Hz, 1H, ArH), 3.90 (s, 3H, OCH_3), 3.24 (t, J =7.5 Hz, 2H, CH_2), 3.14-3.02 (m, 4H, 2xCH_2), 2.23-2.13 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 157.0, 143.3, 135.9, 129.7, 129.3, 128.2, 120.4, 105.5, 55.4, 34.2, 30.5, 23.6.

9-Phenyl-2,3-diydro-1-cyclopenta[*b*]quinoline (3ce).[20d] Yellow solid, mp 133-135 ºC; IR (KBr) cm^{-1}: 3053, 1625, 1586, 1230, 1033, 836; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H, ArH), 7.63 (m, 2H, ArH), 7.51-7.45 (m, 3H, ArH), 7.37-7.34 (m, 3H, ArH), 3.24 (t, J = 7.5 Hz, 2H, CH_2), 2.90 (t, J = 7.2 Hz, 2H, CH_2), 2.21-2.11 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 147.7, 142.8, 136.7, 133.6, 129.2 (2C), 128.6, 128.4, 128.2, 127.9 (2C), 126.2, 125.6, 125.5, 35.1, 30.3, 23.5.

2-Phenylquinoline (3ah).[20e,f] White solid, mp 85-87 ºC; IR (KBr) cm^{-1}: 3056, 1612, 1598, 1557, 1478; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21-8.14 (m, 3H, ArH), 7.88-7.80 (m, 2H, ArH), 7.74-7.69 (m, 1H, ArH), 7.55-7.43 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 148.2, 139.6, 129.6, 129.2 (2C), 128.8 (2C), 127.5 (2C), 127.4, 127.1, 126.2, 118.9.

2-(2-Chlorophenyl)quinoline (3ai).[9a] White solid, mp 72-75 ºC; IR (KBr) cm^{-1}: 3063, 1614, 1574, 1512, 1423; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20-8.17 (m, 2H, ArH), 8.13-8.08 (m, 2H, ArH), 7.81-7.69 (m, 2H, ArH), 7.54-7.45 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 148.1, 137.9, 136.9, 135.5, 129.9, 129.8, 128.9 (2C), 128.7 (2C), 127.4, 127.1, 126.4, 118.6.

2-(2-Chlorophenyl)quinoline (3aj).[20h] White solid, mp 65-67 ºC; IR (KBr) cm^{-1}: 3025, 2915, 1664, 1574, 1497, 1431, 815; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24-8.16 (m, 3H, ArH), 8.03-7.97 (m, 1H, ArH), 7.85-7.71 (m, 3H, ArH), 7.56-7.51 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 137.0, 134.9, 132.6, 130.8, 130.2, 129.9, 129.7, 129.3, 128.5, 127.7, 127.4, 126.6, 125.6, 118.6.

2-(4-Chlorophenyl)quinoline (3ak).[9a] White solid, mp 110-113 ºC; IR (KBr) cm^{-1}: 3065, 1610, 1553, 1525, 1412; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20-8.08 (m, 4H, ArH), 7.81-7.69 (m, 3H, ArH), 7.54-7.46 (3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 148.1, 138.0, 136.9, 135.5, 129.7, 129.6, 128.9 (2C), 128.7 (2C), 127.4, 127.1, 126.4, 118.4.

2-*p*-Tolylquinoline (3al).[20f] White solid, mp 80-82 ºC; IR (KBr) cm-^{1}: 3422, 2915, 1668, 1618, 1596, 1497, 815, 788; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H, ArH), 8.06 (d, J = 8.1 Hz, 2H, ArH), 7.83-7.68 (m, 3H, ArH), 7.49-7.47 (m, 1H, ArH), 7.32 (d, J = 7.8 Hz, 2H, ArH), 2.41 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 148.2, 139.3, 136.8, 136.5, 129.6 (2C), 129.4 (2C), 127.3 (3C), 127.0, 126.0, 118.7, 21.2.

2-(3-Methoxyphenyl)quinoline (3am).[20h] Yellow oil, IR (Neat) cm^{-1}: 3152, 1604, 1563, 1498; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H, ArH), 8.10 (d, J = 8.7 Hz, 1H, ArH), 7.78-7.65 (m, 5H, ArH), 7.47-7-35 (m, 2H, ArH), 6.99 (d, J = 8.1 Hz, 1H, ArH), 3.86 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 156.8, 148.0, 140.9, 136.5, 129.6, 129.5, 129.4, 127.3, 127.1, 126.1, 119.8, 118.8, 115.2, 112.6, 55.2.

2-(4-Methoxyphenyl)quinoline (3an).[20f] White solid, mp 117-120 ºC; IR (KBr) cm^{-1}: 3039, 2921, 2840, 1604, 1499, 1251, 1029, 818; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.11 (m, 4H, ArH), 7.80-7.75 (m, 2H, ArH), 7.71-7.65 (m, 1H, ArH), 7.49-7.44 (m, 1H, ArH), 7.03 (d, J = 8.7 Hz, 2H, ArH), 3.85 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 156.8, 148.2, 136.5, 132.1, 129.5, 129.4, 128.8, 127.3, 126.8, 125.8, 118.4, 114.1 (2C), 55.3.

2-(Naphthalen-2-yl)quinoline (3ao).[20f] White solid, mp 163-165

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ºC; IR (KBr) cm^{-1}: 3058, 1622, 1567, 1256; ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (s, 1H, ArH), 8.37 (d, J = 8.7 Hz, 1H, ArH), 8.22 (d, J = 8.4 Hz, 2H, ArH), 8.00-7.96 (m, 3H, ArH), 7.89-7.86 (m, 1H, ArH), 7.82 (d, J = 8.1 Hz, 1H, ArH), 7.75-7.70 (m, 1H, ArH), 7.53-7.49 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 148.3, 136.7, 133.8, 133.4, 129.6, 128.9, 128.7 (2C), 128.5, 127.6, 127.4, 127.2, 127.1, 126.6, 126.2 (2C), 125.0, 119.0.

2-(Furan-2-yl)quinoline (3ap).[20f] White solid, mp 90-92 ºC; IR (KBr) cm^{-1}: 3152, 1618, 1523, 1489; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15-8.12 (m, 2H, ArH), 7.81-7.61 (m, 4H, ArH), 7.47 (t, J = 7.5 Hz, 1H, ArH), 7.22-7.21 (m, 1H, ArH), 6.57 (bs, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 148.9, 148.0, 144.0, 136.6, 129.8, 129.3, 127.5, 127.1, 126.1, 117.4, 112.1, 110.0.

2-(Thiophen-2-yl)quinoline (3aq).[20f] White solid, mp 125-128 ºC; IR (KBr) cm^{-1}: 3101, 3054, 1624, 1578, 1223; ^1H NMR (300 MHz, $CDCl_3$) δ 8.11-8.06 (m, 2H, ArH), 7.77-7.65 (m, 4H, ArH), 7.48-7.43 (m, 2H, ArH), 7.15-7.12 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 148.0, 145.3, 136.5, 129.7, 129.2, 128.5, 128.0, 127.4, 127.1, 126.0, 125.7, 117.5.

2-(Pyridin-3-yl)quinoline (3ar).[20i] White solid, mp 93-95 ºC; IR (KBr) cm^{-1}: 3059, 2924, 1599, 1095, 787; ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 7.8 Hz, 1H, ArH), 8.25 (d, J = 8.7 Hz, 1H, ArH), 8.18 (d, J = 8.4 Hz, 1H, ArH), 7.86-7.71 (m, 4H, ArH), 7.56-7.47 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 150.0, 148.6, 148.2, 137.0 (2C), 134.8, 129.9, 129.6, 127.4, 127.2, 126.7 (2C), 118.4.

2,4-Diphenylquinoline (3ch).[16b] White solid, mp 112-115 ºC; IR (KBr) cm^{-1}: 3423, 3086, 2955, 1589, 1095, 846; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 4H, ArH), 7.67-7.56 (m, 4H, ArH), 7.51-7.38 (m 5H, ArH), 7.35-7.31 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 140.5, 137.5, 136.2, 136.0, 133.6, 133.0, 132.3, 131.8, 131.0, 130.0, 129.9, 129.0, 128.8, 128.5, 128.2, 128.1, 127.1, 119.4, 118.5, 118.5.

3-Methyl-2-phenylquinoline (3as).[20e,f] Yellow oil; IR (Neat) cm^{-1}: 3052, 1618, 1553, 1431, 1097, 756; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 1H, ArH), 7.96 (s, 1H, ArH), 7.74 (d, J = 8.1 Hz, 1H, ArH), 7.65-7.56 (m, 3H, ArH), 7.46-7.40 (m, 4H, ArH), 2.43 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ160.4, 146.5, 140.8, 136.6, 129.2, 129.0, 128.7 (2C), 128.6, 128.1 (2C), 128.0, 127.5, 126.6, 126.2, 20.5.

3-Ethyl-2-phenylquinoline (3at).[20j] Yellow oil. IR (Neat) cm^{-1}: 3048, 2924, 1595, 1432, 749; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H, ArH), 8.01 (s, 1H, ArH), 7.79 (d, J = 7.8 Hz, 1H, ArH), 7.66-7.61 (m, 1H, ArH), 7.54-7.52 (m, 2H, ArH), 7.48-7.41 (m, 4H, ArH), 2.81-2.73 (m, 2H, CH_2), 1.19 (t, J = 7.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 146.2, 140.8, 135.1, 134.8, 129.1, 128.7, 128.6, 128.1, 127.9, 127.6, 126.8, 126.2, 25.9, 14.6.

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Notes and references

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