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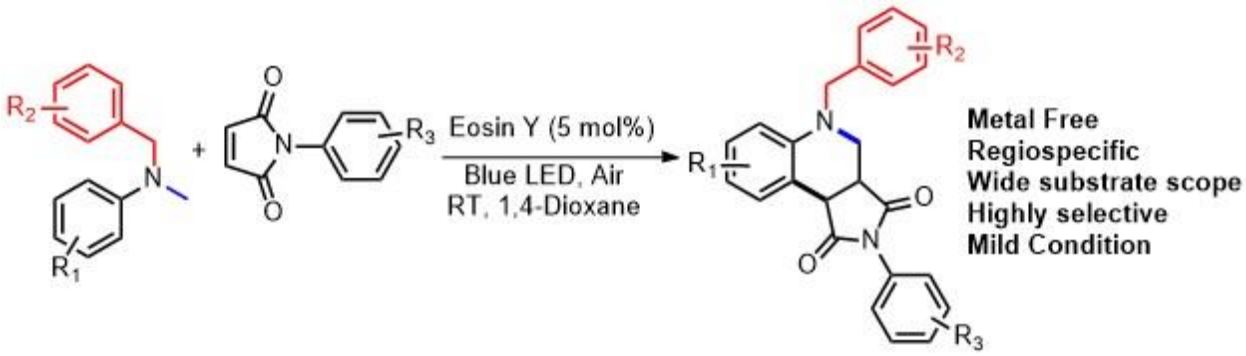

FULL PAPER

Visible Light-Induced *N*-methyl Activation of Unsymmetric Tertiary Amines

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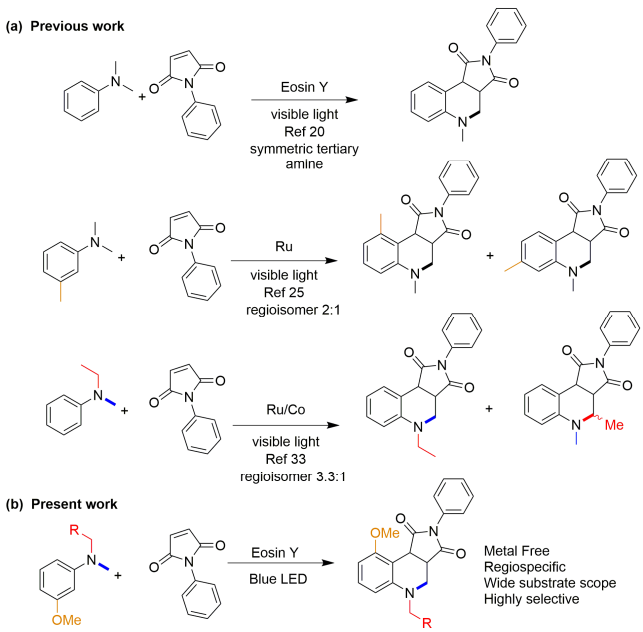
Dedicated to Professor Tien-Yau Luh on the Occasion of His 75th Birthday

Abstract: In the presence of methylene group, selective *N*-methyl activation of tertiary amines has been accomplished with the aid of visible light using organic photocatalyst under air. This protocol explores numerous aliphatic and aromatic substituted tetra-hydroquinoline analogues from various tertiary amines and maleimides. Furthermore, this approach was applied to activate the methyl group of *N*-methyl carbazole to generate the biologically active molecule.

Introduction

To develop a new synthetic methodology with good selectivity and high efficiency in a sustainable route for the small molecules and natural products, is always strengthening the organic synthetic utility.[1,2] The metal-free chemical transformations under thermal conditions contributed many achievements in developing sustainable synthetic route with a mild reaction condition. Of late, visible-light-induced photochemical reactions are becoming modish with atom economy, high selectivity and efficiency.[3,4] Along the line, metal-free organic photocatalyst mediated visible-light-induced chemical transformations are prominent with environmentally benign methodology. [5] For example, Eosin Y,[6,7] Rose Bengal,[8] salicylaldehyde, [9] 9-fluorenone[10] are in the rely on to enhance the sustainability of the visible light-mediated photochemical reactions and are promising photocatalysts in the near future.



Scheme 1: Previous reports on the synthesis of tetrahydroquinoline

Organic photocatalysts are in high demand for organic transformations. Representatively, Eosin Y is a well-known organic photocatalyst and economical alternative for transition metal catalyst in visible-light-driven organic reactions. Broadly, Eosin Y had been used in photocatalytic organic transformations due to its, easy access, typically inexpensive and productive photocatalytic performance.[11] It is noteworthy that a variety of reactive radical intermediates including α-aminoalkyl, [12,13,] arene,[14] azole,[15] perfluoroaryl[16] can be generated using the triplet excited Eosin Y[17,18]. These reactive intermediates are used in various visible light-mediated photocatalysis in particular oxidative cyclization,[19,20]C-H activation,[21,22]hydrogen atom transfer reactions,[6] dehydrogenative coupling.[23,24]

The amino radical cation is an interesting intermediate generated by single-electron oxidation of amines and this sole intermediate can produce lots of *α*-substituted amines.[12] Oxidative cyclization of the *α*-aminoalkyl radical with maleimide under visible light has been studied extensively in recent years.[19,25,26] Such extended literature, either dimethyl[20] or diethyl aniline was employed for the oxidative cyclization with maleimide to produce tetrahydroquinoline analogues. [27-31] Only few reports were contributed to *N*-methyl activation or unsymmetrical tertiary amine [26] in the propinquity of methylene group using metal photocatalyst $Ru(bpy)_3Cl_2$,[26] $CuCl_2$,[32] surface modified TiO_2 with NiO[33], relay catalyst $Ru(bpy)_3$ - $Co(dmgH)_2pyCl$[34] and Eosin Y [20] but dispirit with very limited examples, inadequate yield, selectivity and restrained with symmetric tertiary amines. In this account, we aspired to introduce a methylene group in unsymmetrical tertiary amines instead of a methyl in dimethylaniline to investigate the reaction conditions and mechanisms under photochemical pathway using organic photocatalyst. (Scheme 1).

Results and Discussion

We began our investigation with cyclization of **1a** (5.0 equiv.), **2a** (1.0 equiv.) using O_2, and air as an oxidant in 1,4-dioxane (**Table 1**). Fortunately, selective product **3aa** was obtained uniquely 22% and 20% yield under 10 W blue LEDs irradiation at room temperature for 24 h. (entry 1 and 2). **3aa**'s structure was further confirmed by the X-ray crystallography (CCDC: 2002654). With this propitious result, various organic photocatalysts such as Eosin Y, Rose Bengal in air were examined, surprisingly the yield was increased to 85% and 78% individually (entry 3 and 4). Unfortunately, there was no product formation without solvent (entry 5). The effect of solvent was also investigated with toluene, dichloromethane, dimethylformamide and tetrahydrofuran, however the major yield was obtained only in 1,4-dioxane (entry 6-9).

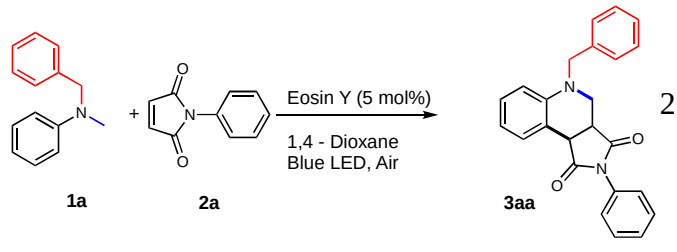
All the reactions were performed under 10 W blue LEDs irradiation at room temperature for 24 h, Isolated yields are given, [a] under O_2, [b] under air, [c] 5.0 mol%, [d] 4.0 mol%.

Entry	**1a**:**2a** (equiv.)	Solvent	Additive (10 mol%)	Product
1[a]	5:1	1,4-dioxane	-	22 %
2[b]	5:1	1,4-dioxane	-	20 %
3	5:1	1,4-dioxane	Eosin Y	85 %
4	5:1	1,4-dioxane	Rose Bengal	78 %
5	5:1	-	Eosin Y	N.R.
6	5:1	Toluene	Eosin Y	N.R.
7	5:1	DCM	Eosin Y	N.R.
8	5:1	DMF	Eosin Y	10 %
9	5:1	THF	Eosin Y	43 %
10	4:1	1,4-dioxane	Eosin Y	85 %
11	3:1	1,4-dioxane	Eosin Y	58 %
12	2:1	1,4-dioxane	Eosin Y	30 %
13	4:1	1,4-dioxane	Eosin Y[c]	85 %
14	4:1	1,4-dioxane	Eosin Y[d]	79 %

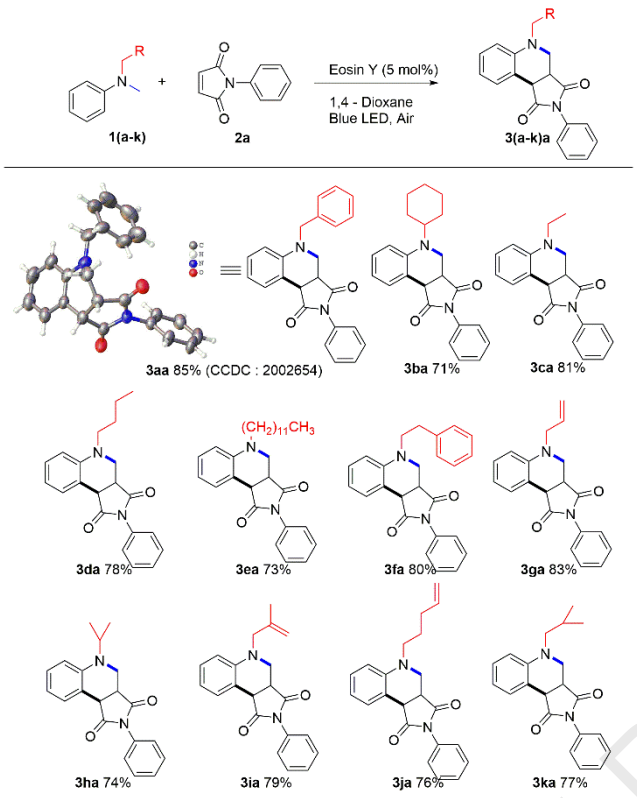
The equivalent of **1a** was lowered from 5.0 to 4.0 the yield was improved (entry 10), but it was dropped to 58% and 30% with 3.0 equiv. and 2.0 equiv. of **1a**, respectively. (entry 11 and 12). On altering the mol% of Eosin Y, there was no yield difference up to 5.0 mol% then it was reduced to 79% with 4.0 mol% of catalyst (entry 13 and 14). Finally, the standard reaction condition (Table 1, entry 13) was optimized in terms of **1a** (4.0 equiv.), **2a** (1.0 equiv.) and Eosin Y (5.0 mol%) in 1,4-dioxane under blue LEDs light for 24 h at room temperature.

Having successfully optimized reaction condition, we have focused on the scope of derivatives generality with electron donating, electron-withdrawing, alkyl and aryl groups. First and foremost, various methylene groups were introduced in aniline to get the variety of unsymmetric tertiary amines. Gratifyingly, the unsymmetric tertiary amines were synthesized from *N*-methyl aniline reacting with alkyl halide in the presence of K_2CO_3 at 50°C (See Supporting Information). The alkyl (benzyl, cyclohexyl, ethyl, n-butyl, dodecyl, phenethyl, isobutyl,) and alkenyl (allyl, 2-methyl allyl, 1-pentene) tertiary amines have been cyclized with (*N*)-phenyl maleimide (**2a**) and afford corresponding tetrahydroquinolines **3aa-3ka** in good yields 71% - 85% (Scheme 2). Among all alkyl tertiary amines, the benzyl substitution brought the highest yield 85%. All alkene substrates were well tolerated in standard reaction conditions and never observed the decomposition.

Table 1: **Optimization conditions for the cyclization of 1a with 2a**

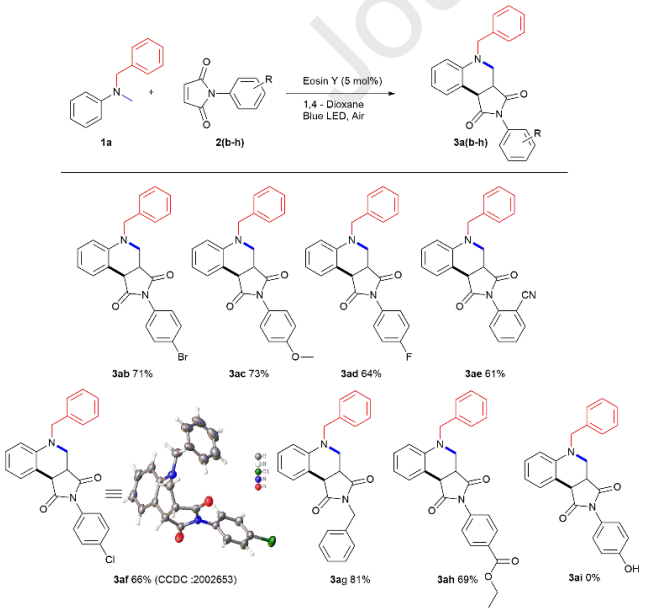


Scheme 2: Scope of alkyl substitution in unsymmetric tertiary amine



Reaction condition: All the reactions were performed with 1.2 mmol of **1a-k**, 0.3 mmol of **2**, Eosin Y (0.015 mmol), and 1.5 mL of 1,4-dioxane. The reactions were under 10 W blue LEDs irradiation at room temperature for 24 h. Isolated yields are given.

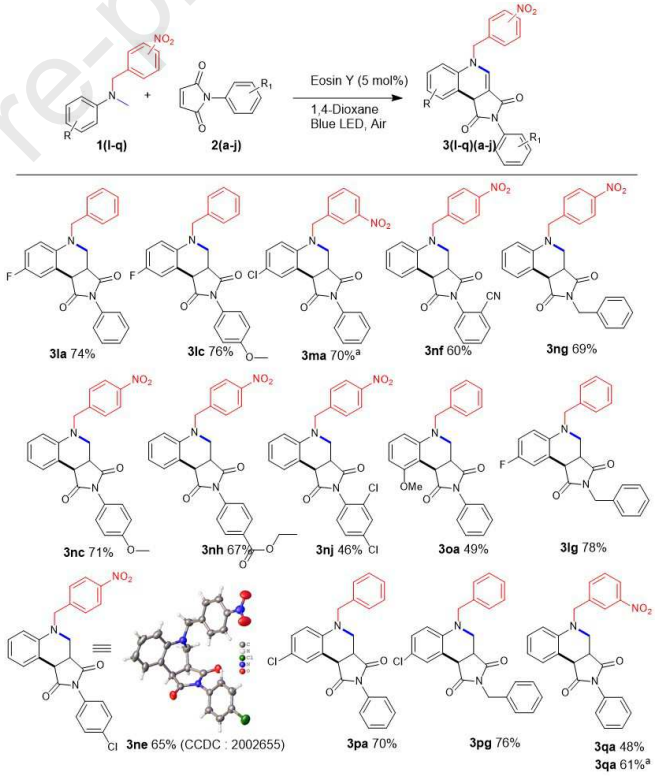
Scheme 3: Scope of *N*-substituted maleimide



Reaction condition: All the reactions were performed with 1.2 mmol of **1a**, 0.3 mmol of 2(**b-i**), Eosin Y (0.015 mmol) and 1.5 mL of 1,4-dioxane. The reactions were under 10 W blue LEDs irradiation at room temperature for 24 h. Isolated yields are given.

Further, the scope of the derivatives were explored by various *N*-phenyl maleimide (**2b-i**) analogues[35] (Scheme 3). The reaction of tertiary amine **1a** with numerous distinctive *N*-phenyl (4-bromo, 4-methoxy, 4-fluoro, 2-cyano, 4-chloro, 4-ethyl ester,) and *N*-benzyl maleimide proceeded smoothly to produce their respective tetrahydroquinoline **3ab-3ah** in good yield 61% - 81%. All electron-withdrawing substituents of maleimide afforded good yield except the 2-cyano (**3ae**) in 61% yield. The *N*-benzyl maleimide provided the highest yield of 81% (**3ag**) across this scope of derivatives and electron donating substituent methoxy phenyl maleimide gave 73% of yield (**3ac**). Hence, decisively the electron donating substituents at maleimide part favors the cyclization than electron-withdrawing substituent. To pursue the functional group tolerance, 4-phenyl ethyl ester and 4-phenyl hydroxy maleimide were used. Ethyl ester substituent afforded the desired product (**3ah**, 69%) whereas the hydroxyphenyl maleimide could not be produced desired product (**3ai**). **3af**'s structure was further confirmed by the X-ray crystallography (CCDC: 2002653).

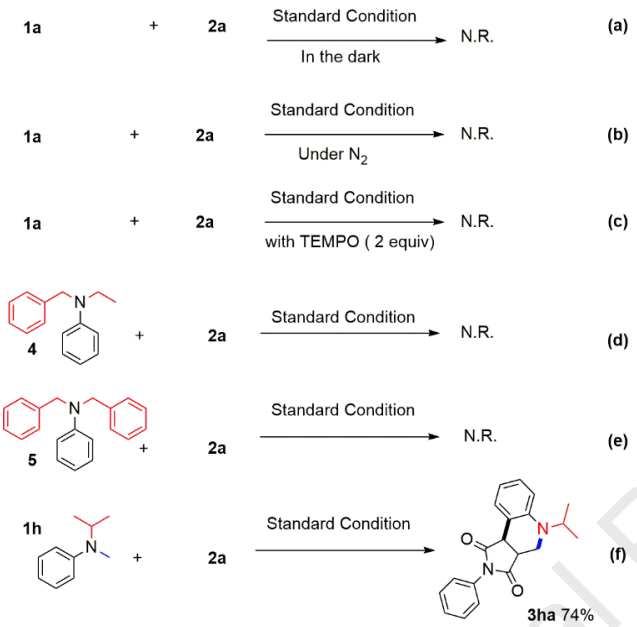
Scheme 4: Scope of phenyl and benzyl substitution of unsymmetric tertiary amine



Reaction condition: All the reactions were performed with 1.2 mmol of 1(**l-q**), 0.3 mmol of 2(**a-j**), Eosin Y (0.015 mmol) and 1.5 mL of 1,4-dioxane. The reactions were under 10 W blue LEDs irradiation at room temperature for 24 h. Isolated yields are given. [a] Reaction for 48 h.

Furthermore, the scope of phenyl- and benzyl- ring of tertiary amines were scrutinized as presented in Scheme 4. Introducing an electron-withdrawing (chloro-, fluoro-), electron-donating (methoxy-) functionalities in the phenyl ring and substitution of the *m*-, *p*- nitro group in benzyl ring of tertiary amines were reacted with various maleimides. The desired tetrahydroquinoline analogues **3ma**, **3nf**, **3ng**, **3nc**, **3nh**, **3ne** (CCDC: 2002655) and **3qa** were obtained in moderate to good yield except **3nj** (46%) which depends on the substituent at phenyl part of maleimide. Perhaps, the *m*-nitrobenzyl group

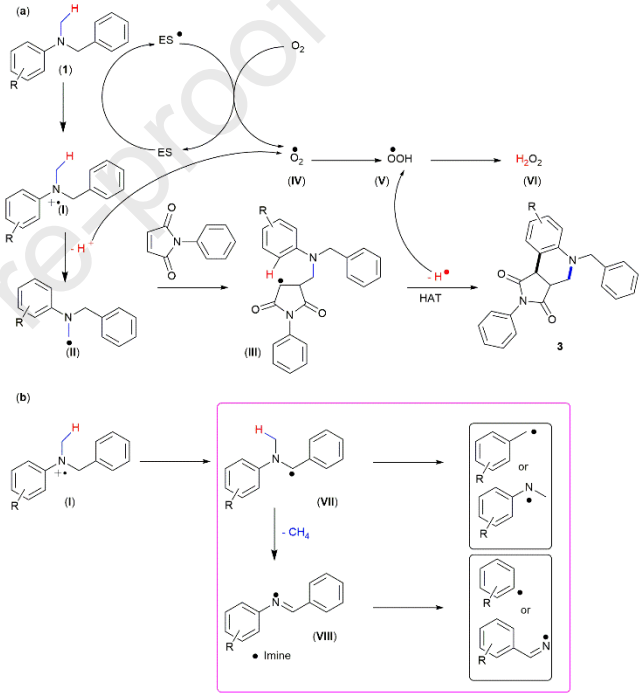
influenced the stability of tertiary amine radical; as a consequence, the rate of reaction was slower (48 h) than the *p*-nitrobenzyl substitution in the amine. The chloro- and fluoro-substituted phenyl tertiary amines afforded the desired product **3la**, **3lc**, **3lg**, **3pa** and **3pg** in good yield 68%-78%. Although the methoxy substituted phenyl tertiary amine gave corresponding tetrahydroquinoline (**3oa**) in lowered yield 49% but we did not observe the regioisomer.



Scheme 5: Control experiments

Generally, the benzyl radical is more stable than methylene radical nonetheless, surprisingly in all the situations we uniquely obtained methyl activated product. Hence, we keen to investigate mechanistic insight into the reaction. Furthermore, few control experiments were carried out to ensure the specificity and pathway of the reaction (Scheme 5). A set of experiments in dark (a) and in the presence of nitrogen (b) evidenced that the necessity of light and oxygen. Reaction with radical scavenger (c) TEMPO (2.0 equiv.) did not provide the desired product, perhaps the reaction undergoes in radical pathway. Dual methylene group substituted unsymmetric tertiary amines, *N*-benzyl *N*-ethyl aniline 4 and *N*, *N*-dibenzyl aniline 5 were reacted with (**2a**) in standard reaction condition but both the reactions (**d, e**) were not proceeded to yield respective tetrahydroquinoline. Excluding the methylene group, methine group substituted tertiary amine (**1h**) also utilized. Nevertheless, gratefully activated methyl group rather than the methine, merely yielded **3ha** in 74% yield (**f**). It indicates that the process specific for *N*-methyl activation. Then we analyzed the decomposition of tertiary amine **1a** in the reaction condition and found that the mass of imine (See Supporting Information Scheme S4).

Based on these findings and previous results, [19,33,26,34] a plausible mechanism for the cyclization is outline in Scheme 6. Upon irradiation of blue LEDs, tertiary amine **1** is oxidized by triplet excited state of Eosin Y through single electron transfer (SET). The radical cation (I) deprotonates and forms methylene radical (II). The reduced form of Eosin Y ($ES^{\bullet}$) oxidatively quenching with oxygen molecule present in the air and forms superoxide (IV). The superoxide associates with the proton which releases from (II) and produces peroxide radical (V). The methylene radical (II)–reacts with maleimide and produces the radical intermediate (III). Then the radical intermediate (III) is cyclized to give the desired product **3** by hydrogen atom transfer of peroxide radical (V) to hydrogen peroxide (VI). On the other hand, the radical cation (I) may form benzyl radical (VII). The benzyl radical may either decompose to imine radical (VIII) or a mixture of tolyl or *N*-methyl aniline radical. Imine radical (VIII) may also decompose into phenyl or phenylmethanimine radical. (See Supporting Information Scheme S4). Hence, the reactive species of methyl radical (II) can only produce tertiary tetrahydroquinoline **3**. Thus, the protocol exists as regiospecific and benzyl activated product was not obtained in this process. Since benzyl radical tends to form imine, it is one of the causes



that the reaction requires 4.0 equiv. of the tertiary amine.

Scheme 6: Plausible mechanism

Albeit tetrahydroquinoline core structure itself has several medicinal values viz antitumour[36] (Segolines A and B) antipsychotic, [37] and serotinin agonists, [38] furthermore we wish to illustrate the synthetic utility of the process excluding unsymmetric tertiary amine. Hence, in addition, the methyl group of *N*-methyl carbazole (**10**) has been activated and obtained biologically[39] significant carbazole-based compound **11** with

45% yield (Scheme 7).

Scheme 7: Synthetic application

Conclusion

In summary, we have effectively developed an adaptable methodology for selective activation of methyl group over the methylene group to synthesis tetrahydroquinoline from

unsymmetric tertiary amine and maleimide in a mild reaction condition under visible light using organic photocatalyst. The scope of derivatives proved by synthesizing variety of tetrahydroquinoline analogues and selectivity of the method has been demonstrated through various control experiments. The functional group tolerance of the process also investigated with various alkene, ester and hydroxy functionalized substrates. The imine formation has been identified during the reaction greatly supports to elucidate the mechanistic pathway and selectivity of the reaction.

Experimental Section

All chemicals were purchased from commercial vendors (Sigma Aldrich, Alfa Aesar, TCI, and matrix scientific) and used directly without further purification, unless otherwise noted. A well cleaned and oven dried glassware were used for the experiments. The reaction was monitored by Thin Layer Chromatography (TLC), purchased as pre-coated with silica gel 60 F254 from Merck. Column chromatography was carried out using the silica gel 60-120 mesh (purchased from Merck) with mixture of ethyl acetate/hexane or hexane as the eluent. ^{1}H NMR spectra were recorded on 400 MHz, JEOL NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C-NMR spectra were recorded on 100 MHz, JEOL NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The spectra were recorded and presented in chemical shifts (ppm) with tetramethylsilane (TMS) used as internal standard. Multiplicities were provided in s (singlet), d (doublet), dd (doublet of the doublets), t (triplet), q (quartet) and m (multiplet), coupling constants (*J*) were reported in Hz. All the HRMS (either ESI or EI mode) were recorded on JMS-700 spectrometer. Melting points (MP-2D) was determined from Fargo instruments.

General procedure for preparation of unsymmetric tertiary amines and its characterization data (1a-k): [40]

In a 100 mL round bottom flask, *N*-methyl aniline (10.0 mmol), dimethyl formamide (15 mL), potassium carbonate (25.0 mmol) and alkyl halide (15.0 mmol) were added and stirred at 60° C for four hours. The reaction mixture was quenched with ice water and extracted with ethyl acetate. Solvent was removed under reduced pressure. The crude product was purified by column chromatography (Eluent: Hexane).

General procedure for preparation of tetrahydroquinoline

In an 8.0 mL glass vial quipped with stir bar was added unsymmetric tertiary amine (1.2 mmol), dioxane (1.5 mL), maleimide (0.3 mmol), Eosin Y (0.015 mmol) and the solution was irradiated under four 10 W blue LEDs for 24h in ambient temperature. The reaction was stopped and solvent was removed under vacuum. The residue was dissolved in ethyl acetate and washed with water. Again, solvent was removed under vacuum. The crude product was purified by column chromatography using 60-200 silica gel (Eluent; Ethyl acetate:Hexane = 15:85).

5-benzyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3aa)

Title compound was synthesized according to the general procedure and obtain as yellow oil (85%) ;^{1}H-NMR (400 MHz, CDCl3) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.44 (td, *J* = 7.6, 1.8 Hz, 2H), 7.36 (t, *J* = 6.80 Hz, 1H), 7.29-7.21 (m, 8H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.47 (d, *J* = 15.6 Hz, 1H), 4.28-4.17 (m, 2H), 3.68 (dt, *J* = 11.7, 2.3 Hz, 1H), 3.57-3.53 (m, 1H), 3.27 (dq, *J* = 11.7, 2.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.6, 175.9, 147.6, 137.8, 132.1, 130.6, 129.1, 128..6, 127.5, 127.4, 126.4, 119.8, 118.9, 113.5, 55.4, 49.1, 44.2, 42.5; HRMS (ESI) calcd. for $C_{24}H_{20}N_2O_2Na$ $[M+Na]^+$: 391.1417, found for 391.1413.

5-cyclohexyl-2-pheny-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3ba)

Title compound was synthesized according to the general procedure and obtain as white solid (71%) m.p. 186 ℃ - 188 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47-7.39 (m, 3H), 7.35-7.31 (m, 1H), 7.25-7.18 (m, 3H), 6.83 (t, *J* = 12.00 Hz, 1H), 6.76 (d, *J* = 8.00 Hz, 1H), 4.10 (d, *J* = 12.00 Hz, 1H), 3.76 (dd, *J* = 4.00, 12.00 Hz, 1H), 3.55-3.51 (m, 1H), 3.46-3.43 (m, 1H), 2.93 (dd, *J* = 4.00, 12.00 Hz, 1H), 1.83-1.93 (m, 3H), 1.69 (d, *J* = 16.00 Hz, 1H), 1.57 (s, 3H), 1.12-1.37 (m, 4H).^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.0, 175.9, 148.2, 132.1, 131.0, 129.1, 128.6, 128.5, 126.4, 119.7, 118.9, 112.8, 55.4, 45.0, 42.8, 42.2, 31.3, 27.4, 26.3, 26.0, 25.8; HRMS (ESI) calcd. for $C_{23}H_{24}N_2O_2Na$ $[M+Na]^+$: 383.1730, found for 383.1730.

5-ethyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinolone-1,3(2*H*)-dione (3ca)

Title compound was synthesized according to the general procedure and obtain as white solid (81%) m.p. 214℃ - 216 ℃;^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 6.0 Hz, 1H), 7.43-7.39 (m, 2H), 7.35-7.32 (m, 1H), 7.25-7.16 (m, 3H), 6.86-6.82 (m, 1H), 6.76-6.74 (m, 1H), 4.12 (dd, *J* = 9.0, 2.2 Hz, 1H), 3.66-3.61 (m, 1H), 3.54-3.51 (m, 1H), 3.32-3.24 (m, 2H), 3.16-3.13 (m, 1H), 1.18-1.14 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.8, 175.9, 147.3, 132.0, 130.7, 129.1, 128.6, 128.5, 126.4, 119.0, 118.6, 112.6, 47.2, 44.7, 44.0, 42.4, 10.9; HRMS (ESI) calcd. for $C_{19}H_{19}N_2O_2$ $[M+H]^{+.}$ 307.1441, found for 307.1434.

5-butyl-2-phenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3da)

Title compound was synthesized according to the general procedure and obtain as brown oil (78%) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 1H), 7.46-7.32 (m, 3H), 7.28-7.17 (m, 3H), 6.89-6.82 (m, 1H), 6.75 (t, *J* = 10.0, Hz, 1H), 4.12 (t, *J* = 10.0 Hz, 1H), 3.65 (td, *J* = 11.8, 2.5 Hz, 1H), 3.54-3.50 (m, 1H), 3.32-3.04 (m, 3H), 1.62-1.52 (m, 2H), 1.40-1.25 (m, 2H), 0.97-0.82 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.8, 175.9, 147.6, 132.1, 130.7, 129.1, 128.6, 126.4, 119.0, 118.6, 112.6, 50.6, 48.3, 44.1, 42.4, 28.2, 20.4, 13.9; HRMS (m/z, ESI) calcd $[C_{21}H_{23}N_2O_2]^+$ $[M+H]^+$ 335.1754, observed 335.1749.

5-dodecyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ea)

Title compound was synthesized according to the general procedure and obtain as brown oil (73%) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 6.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.25-7.23 (m, 2H), 7.21-7.16 (m, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 9.6 Hz, 1H), 3.64 (dd, *J* = 11.4, 2.6 Hz, 1H), 3.52 (dt, *J* = 9.5, 3.5 Hz, 1H),

3.28-3.21 (m, 1H), 3.17 (dd, *J* = 11.8, 4.2 Hz, 1H), 3.11-3.04 (m, 1H), 1.35-1.23 (20H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.7, 175.8, 147.5, 131.9, 130.6, 128.9, 128.5, 128.4, 126.3, 118.9, 118.5, 112.5, 50.8, 48.2, 44.0, 42.3, 31.8, 30.9, 29.5, 29.4, 29.3, 27.2, 26.0, 22.6, 14.1, 0.9; HRMS (m/z, ESI) calcd $[C_{29}H_{39}N_2O_2]^+$ $[M+H]^+$ 447.3006, observed 447.3014.

5-phenethyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3fa)

Title compound was synthesized according to the general procedure and obtain as white solid (80%) m.p. 207 ℃ - 209 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 8.00 Hz, 1H), 7.43-7.38 (m, 1H), 7.36-7.19 (m, 10H), 6.89-6.81 (m, 2H), 4.10-4.15 (m, 1H), 3.71-3.66 (m, 1H), 3.56-3.41 (m, 3H), 3.27-3.22 (m, 1H), 2.94-2.86 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.4, 175.7, 146.7, 139.2, 131.9, 130.7, 128.9, 128.5, 128.4, 126.2, 119.1, 118.2, 112.4, 52.5,48.0, 43.7, 42.1, 32.2; HRMS (m/z, ESI) calcd $[C_{25}H_{22}N_2O_2Na]^+$ $[M+Na]^+$ 405.1573, observed 405.1566.

5-allyl-2-pheny-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3ga)

Title compound was synthesized according to the general procedure and obtain as white solid (83%) m.p. 205 ℃ - 207 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.52-7.47 (m, 1H), 7.44-7.29 (m, 3H), 7.25-7.12 (m, 3H), 6.89-6.71 (m, 2H), 5.90-5.78 (1H), 5.27-5.18 (m, 2H), 4.15-4.09 (m, 1H), 3.89-3.74 (m, 1H), 3.70-3.61 (m, 1H), 3.55-3.49 (m, 1H), 3.34-3.28 (m, 1H), 3.15-3.08 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.6, 175.7, 147.3, 133.1, 130.5, 129.5, 128.9, 128.4, 126.2, 122.3, 119.4, 118.6, 118.0, 113.0, 53.4, 47.6, 43.9, 42.3; HRMS (m/z, ESI) calcd $[C_{20}H_{18}N_2O_2Na]^+$ $[M+Na]^+$ 341.1260, observed 341.1257.

5-isopropyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3ha)

Title compound was synthesized according to the general procedure and obtain as white solid (74%) m.p. 200 ℃ - 202 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.32 (td, *J* = 6.6, 1.7 Hz, 2H), 7.26-7.22 (m, 1H), 7.17-7.09 (m, 3H), 6.77-6.70 (m, 2H), 4.01 (d, *J* = 9.6 Hz, 1H), 3.84 (q, *J* = 6.6 Hz, 1H), 3.62 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.46-3.42 (m, 1H), 2.78 (dd, *J* = 11.8, 4.2 Hz, 1H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.8, 175.8, 148.0, 132.0, 130.8, 128.9, 128.5, 128.4, 126.2, 119.5, 118.8, 112.6, 46.2, 44.5, 42.6, 40.6, 20.8, 16.2; HRMS (m/z, ESI) calcd $[C_{20}H_{20}N_2O_2Na]^+$ $[M+Na]^+$ 343.1417, observed 343.1420.

5-(2-methylally-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ia)

Title compound was synthesized according to the general procedure and obtain as brown oil(79%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.25-7.20 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.88 (td, *J* = 7.6, 1.8 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 4.91 (d, *J* = 16.4 Hz, 2H), 4.16-4.10 (m, 1H), 3.82 (d, *J* = 15.6 Hz, 1H), 3.67 (dt, *J* = 11.8, 2.8 Hz, 1H), 3.55-3.50 (m, 2H), 3.15 (td, *J* = 7.9, 4.2 Hz, 1H), 1.70 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.8, 175.9, 147.7, 141.1, 134.2, 132.1, 130.5, 129.1, 128.6, 126.4, 126.1, 122.4, 119.6, 118.6, 113.2, 113.0, 57.7, 48.4, 44.0, 42.4, 20.2.; HRMS (m/z, ESI) calcd $[C_{16}H_{14}NO]^+$ $[M+H]^+$ 333.1525, observed 333.1025

5-(pent-4-en-1-yl)-2-phenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3ja)

Title compound was synthesized according to the general procedure and obtain as yellow liquid (76%) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 1H), 7.44-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.25-7.17 (m, 3H), 6.85 (dd, *J* = 10.4, 4.0, 3.2 Hz, 1H), 6.74 (dd, *J* = 8.4, 3.2 Hz, 1H), 5.84-5.75 (m, 1H), 5.05-4.97 (m, 2H), 4.12 (q, *J* = 4.9 Hz, 1H), 3.65 (dq, *J* = 11.6, 2.6 Hz, 1H), 3.54-3.50 (m, 1H), 3.31-3.25 (1H), 3.19-3.05 (2H), 2.09 (m, 2H), 1.72-1.63 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.6, 175.7, 147.3, 137.7, 131.9, 130.6, 128.9, 128.5, 128.4, 126.2, 119.0, 118.5, 115.2, 112.4, 50.0, 48.2, 43.9, 42.2, 31.0, 25.1; HRMS (m/z, EI) calcd $[C_{22}H_{22}N_2O_2]^+$ $[M]^+$ 346.1681, observed 346.1682.

5-isobutyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ka)

Title compound was synthesized according to the general procedure and obtain as brown oil (77%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.43-7.32 (m, 3H), 7.25-7.17 (m, 3H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.13 (d, *J* = 9.6 Hz, 1H), 3.65 (dt, *J* = 11.6, 2.2 Hz, 1H), 3.52-3.49 (m, 1H), 3.22-3.10 (m, 2H), 2.69-2.63 (m, 1H), 1.97 (p, *J* = 6.4 Hz, 1H), 0.92-0.88 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.7, 175.8, 147.9, 131.9, 130.6, 129.0, 128.4, 126.2, 119.0, 118.6, 112.5, 59.2, 49.8, 44.1, 42.2, 26.7, 20.5, 20.3. HRMS (EI) calcd. for $C_{21}H_{22}N_2O_4$ $[M]^+$: 334.1681, found for 334.1673.

5-benzyl-2-(4-bromophenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3ab)

Title compound was synthesized according to the general procedure and obtain as brown oil (71%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57-7.50 (m, 3H), 7.26-7.11 (m, 8H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 15.2 Hz, 1H), 4.26-4.16 (m, 2H), 3.73-3.64 (m, 1H), 3.54-3.52 (m, 1H), 3.26-3.23 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.1, 175.4, 137.6, 132.2, 130.9, 130.5, 128.7, 128.6, 127.8, 127.4, 119.8, 118.7, 113.5, 55.3, 48.9, 44.2, 42.4; HRMS (m/z, EI) calcd $[C_{24}H_{19}BrN_2O_2]^+$ $[M]^+$ 446.0630, observed 446.0636.

5-benzyl-2-(4-methoxyphenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3ac)

Title compound was synthesized according to the general procedure and obtain as white solid (73%) m.p. 231 ℃ - 233 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 7.0 Hz, 1H), 7.29-7.10 (m, 10H), 6.98-6.93 (m, 1H), 6.89-6.85 (m, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 4.47 (dd, *J* = 15.0, 7.4 Hz, 1H), 4.27 (q, *J* = 7.7 Hz, 1H), 4.17 (t, *J* = 8.6 Hz 1H), 3.80 (s, 3H), 3.69-3.65 (m, 1H), 3.54-3.50 (m, 1H), 3.29-3.23 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.8, 176.1, 159.5, 147.6, 137.8, 130.6, 128.6, 127.6, 127.5, 127.4, 124.7, 119.8, 119.0, 114.4, 113.5, 55.5, 55.4, 49.1, 44.1, 42.4; HRMS (m/z, ESI) calcd $[C_{25}H_{22}N_2O_3Na]^+$ $[M+Na]^+$ 421.1522, observed 421.1525.

5-benzyl-2-(4-fluorophenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3ad)

Title compound was synthesized according to the general procedure and obtain as yellow liquid (64%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (t, *J* = 6.2 Hz, 1H), 7.21-7.14 (m, 7H), 7.08-7.03 (m, 3H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.0 Hz, 1H), 4.40 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.18 (dd, *J* = 15.2, 5.2 Hz, 1H), 4.13-4.09 (m, 1H), 3.59 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.48-3.44 (m,

1H), 3.21-3.15 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.4, 175.7, 147.5, 137.6, 130.5, 128.69, 128.62, 128.2, 128.1, 127.9, 127.4, 127.3, 119.8, 118.7, 116.2, 116.0, 113.5, 55.3, 49.0, 44.1, 42.4; HRMS (m/z, ESI) calcd $[C_{24}H_{19}FN_2O_2Na]^+$ [M+Na]$^+$ 409.1322, observed 409.1317.

(5-benzyl-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-2*H*-pyrrolo[3,4-*c*]quinolin-2-yl)benzonitrile (3ae)

Title compound was synthesized according to the general procedure and obtain as brown solid (61%) m.p. 172 ℃ - 174 ℃; ^{1}H-NMR (400 MHz, CDCl3): δ 7.69 (t, *J* = 52.00 Hz, 1H), 7.52-7.49 (m, 2H), 7.25-7.07 (m, 8H), 6.88-6.75 (m, 2H), 4.49-4.40 (m, 1H), 4.28 (s, 2H), 3.66-3.28 (m, 3H).^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.4, 174.9, 147.6, 137.7, 133.8, 130.6, 129.6, 129.1, 128.8, 128.6, 127.6, 127.4, 119.9, 113.5, 112.2, 55.4, 48.9, 44.4, 42.7; HRMS (m/z, ESI) calcd $[C_{25}H_{19}N_3O_2Na]^+$ [M+Na]$^+$ 416.1369, observed 416.1360.

5-benzyl-2-(4-chlorophenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinolone-1,3(2*H*)-dione (3af)

Title compound was synthesized according to the general procedure and obtain as white solid (66%) m.p. 217 ℃ - 219 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.51 (t, *J* = 5.6 Hz, 1H), 7.42-7.39 (m, 2H), 7.27-7.21 (m, 7H), 7.15-7.10 (m, 1H), 6.88 (t, *J* = 6.2 Hz, 1H), 6.74-6.71 (m, 1H), 4.45 (dd, *J* = 15.0, 4.6 Hz, 1H), 4.26-4.15 (m, 2H), 3.69-3.64 (m, 1H), 3.54-3.52 (m, 1H), 3.24 (dt, *J* = 8.2, 3.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.2, 175.5, 147.5, 137.5, 134.2, 130.4,129.2, 128.6, 128.5, 127.5, 127.4, 119.8, 118.7, 111.4, 55.2, 48.9, 44.1, 42.3; HRMS (m/z, EI) calcd $[C_{24}H_{19}N_2O_2Cl]^+$ [M]$^+$ 402.1135, observed 402.1136.

2,5-dibenzyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3ag)

Title compound was synthesized according to the general procedure and obtain as brown oil (81%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.31-7.21 (m, 8H), 7.12-7.07 (m, 3H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.66 (dd, *J* = 31.6, 14.4 Hz, 2H), 4.37 (d, *J* = 15.0 Hz, 1H), 4.18 (d, *J* = 15.0 Hz, 1H), 4.02 (d, *J* = 8.8 Hz, 1H), 3.55-3.51 (m, 1H), 3.36-3.33 (m, 1H), 3.13 (ddd, *J* = 11.6, 4.4, 1.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.9, 176.4, 147.4, 137.4, 135.5, 130.3, 128.59, 128.56, 128.53, 128.4, 127.8, 127.3, 127.1, 119.6, 118.8, 113.4, 55.4, 48.5, 43.8, 42.7, 42.2; HRMS (m/z, EI) calcd $[C_{25}H_{22}N_2O_2]^+$ [M]$^+$ 382.1681, observed 382.1689.

ethyl 4-(5-benzyl-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-2*H*-pyrrolo[3,4-*c*]quinolin-2-yl) benzoate (3ah)

Title compound was synthesized according to the general procedure and obtain as brown oil (69%); ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.51-7.49 (m, 1H), 7.44-7.32 (m, 3H), 7.35-7.17 (m, 3H), 6.85 (ddd, *J* = 10.4, 4.0, 3.2 Hz, 1H), 6.74 (dd, *J* = 8.4, 3.2 Hz, 1H), 5.83-5.76 (m, 1H), 5.05-4.97 (m, 2H), 4.12 (q, *J* = 4.8 Hz 1H), 3.65 (dq, *J* = 11.6, 2.8 Hz, 1H), 3.53-3.50 (m, 1H), 3.31-3.25 (m, 1H), 3.19-3.05 (m, 2H), 2.13-2.04 (m, 2H), 1.72-1.63 (m, 3H). ^{13}C-NMR (100 MHz, DMSO-d_6): δ 178.2, 176.4, 165.6, 148.1, 138.9, 136.9, 130.9, 130.4, 130.1, 128.9, 128.5, 127.7, 127.5, 127.4, 120.3, 119.4, 113.6, 61.5, 54.9, 49.9, 44.5, 42.7, 14.6; HRMS (m/z, EI) calcd $[C_{27}H_{24}N_2O_4]^+$ [M]$^+$ 440.1736, observed 440.1742.

5-benzyl-8-fluoro-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinolone-1,3(2*H*)-dione (3la)

Title compound was synthesized according to the general procedure and obtain as yellow liquid (74%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.49-7.44 (m, 2H), 7.41-7.36 (m, 1H), 7.33-7.23 (m, 8H), 6.83 (td, *J* = 8.5, 2.9 Hz, 1H), 6.67-6.62 (m, 1H), 4.42 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.23 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.17-4.11 (m, 1H), 3.68-3.64 (m, 1H), 3.54-3.50 (m, 1H), 3.24-3.19 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.3, 175.3, 144.0, 137.5, 132.0, 129.2, 128.7, 127.5, 127.4, 126.4, 120.6, 117.3, 117.1, 115.2, 115.0, 114.57, 114.50, 55.8, 49.6, 44.1, 42.6; HRMS (m/z, ESI) calcd $[C_{24}H_{19}N_2O_2FNa]^+$ [M+Na]$^+$ 409.1322, observed 409.1332.

5-benzyl-8-fluoro-2-(4-methoxyphenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3lc)

Title compound was synthesized according to the general procedure and obtain as white solid (76%) m.p. 224 ℃ - 226 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.14 (m, 8H), 6.95 (dd, *J* = 9.2, 2.4 Hz, 2H), 6.82 (td, *J* = 8.4, 3.1 Hz, 1H), 6.63 (q, *J* = 4.5 Hz, 1H), 4.39 (t, *J* = 14.2 Hz, 1H), 4.20 (t, *J* = 14.2 Hz, 1H), 4.12-4.06 (m, 1H), 3.81 (s, 3H), 3.63 (t, *J* = 11.4 Hz, 1H), 3.52-3.49 (m, 1H), 3.22-3.16 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.4, 175.4, 159.5,143.9, 137.4, 128.6, 127.5, 127.3, 124.5, 120.6, 120.5, 117.2, 116.9, 115.1, 114.8, 114.4, 55.7, 55.4, 49.5, 43.9, 42.4; HRMS (m/z, ESI) calcd $[C_{25}H_{21}N_2O_3FNa]^+$ [M+Na]$^+$ 439.1428, observed 439.1425.

8-chloro-5-(3-nitrobenzyl)-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ma)

Title compound was synthesized according to the general procedure and obtain as brown oil (70%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.50-7.02(m, 9H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 15.6 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 1H), 4.13 (d, *J* = 9.2 Hz, 1H), 3.67 (d, *J* = 12.0 Hz, 1H), 3.55 (s, 1H), 3.25 (d, *J* = 11.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.9, 174.8, 148.5, 147.4, 145.3, 139.6, 135.0, 133.2, 131.6, 130.4, 0130.2, 129.7, 129.2, 129.0, 128.8, 128.5, 128.3, 126.2, 125.4, 122.7, 122.1, 120.7, 114.5, 55.0, 49.2, 43.6, 42.0.; HRMS (m/z, ESI) calcd $[C_{24}H_{18}N_3O_4ClNa]^+$ [M+Na]$^+$ 470.0878, observed 470.0882.

2-(5-(4-nitrobenzyl)-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-2*H*-pyrrolo[3,4-*c*] quinolin-2-yl) benzonitrile (3nf)

Title compound was synthesized according to the general procedure and obtain as brown liquid (60%); ^{1}H-NMR (400 MHz, CDCl3): δ 8.07-8.04 (m, 2H), 8.15 (d, *J* = 8.00 Hz, 1H), 7.81-7.71 (m, 2H), 7.58-7.43 (m, 4H), 7.17-7.12 (m, 2H), 6.63 (dd, *J* = 8.00, 16.00 Hz, 1H), 4.59 (d, *J* = 16.00 Hz, 1H), 4.46-4.27 (m, 1H), 3.73 (d, *J* = 12.00 Hz, 2H), 3.37 (d, *J* = 8.00 Hz, 1H).^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.2,174.6, 147.2, 146.5, 145.4, 133.7, 133.6, 130.6, 130.4, 129.7, 129.4, 128.87, 128.81, 128.5, 128.0, 123.8, 113.4, 112.1, 55.1, 44.1, 42.5, 41.7.; HRMS (m/z, ESI) calcd $[C_{25}H_{18}N_4O_4Na]^+$ [M+Na]$^+$ 461.1220, observed 461.1217

2-benzyl-5-(4-nitrobenzyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3ng)

Title compound was synthesized according to the general procedure and obtain as brown oil (69%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.00 (dt, *J* = 6.5, 2.1 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H),

7.30-7.24 (m, 5H), 7.15-7.06 (m, 3H), 6.91-6.88 (m, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 4.74 (dd, *J* = 14.0, 2.4 Hz, 1H), 4.62 (dd, J = 14.0, 2.4 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 1H), 3.56 (d, *J* = 11.6 Hz, 1H), 3.41-3.38 (m, 1H), 3.22-3.14 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 178.0, 176.3, 147.1, 146.7, 145.3, 135.5, 130.6, 128.6, 128.5, 128.0, 127.8, 123.8, 120.4, 119.2, 113.2, 55.1, 49.3, 43.8, 42.9, 42.2.; HRMS (m/z, EI) calcd $[C_{25}H_{21}N_3O_4]^+$ $[M]^+$ 427.1532, observed 427.1534.

2-(4-methoxyphenyl)-5-(4-nitrobenzyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (**3nc**)

Title compound was synthesized according to the general procedure and obtain as brown oil (75%); ^{1}H-NMR (400 MHz, CDCl3): δ 8.14 (d, *J* = 8.00 Hz, 2H), 7.56 (d, *J* = 8.00 Hz, 1H), 7.41 (d, *J* = 8.00 Hz, 2H), 7.10-7.19 (m, 4H), 6.98 (d, *J* = 8.00 Hz, 1H), 6.94-6.87 (m, 1H), 6.57 (d, *J* = 8.00 Hz, 1H), 4.56 (d, *J* = 16.00 Hz, 1H), 4.34 (d, *J* = 16.00 Hz, 1H), 4.21 (d, *J* = 8.00 Hz, 1H), 3.83 (s, 3H), 3.70-3.72 (m, 1H), 3.57-3.59 (m, 1H), 3.32 (dd, *J* = 4.00, 12.00 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.6, 175.7, 159.5, 147.2, 146.6, 145.6, 130.7, 129.1, 128.6,127.8, 127.3, 124.4, 123.9, 120.4, 119.1, 114.4, 114.3,113.2, 55.4, 55.1, 49.5, 43.9, 42.2. HRMS (EI) calcd. for $C_{25}H_{21}N_3O_5$ $[M]^+$: 443.1481, found for 443.1473.

ethyl-4-(5-(4-nitrobenzyl)-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-2*H*-pyrrolo[3,4-*c*]quinolin-2-yl)benzoate (3nh)

Title compound was synthesized according to the general procedure and obtain brown oil (67%) ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16-8.08 (m, 4H), 7.56 (t, *J* = 6.6 Hz, 1H), 7.42-7.35 (m, 4H), 7.15-7.08 (m, 1H), 6.95-6.89 (m, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 4.56 (dd, *J* = 16.4, 6.6 Hz, 1H), 4.40-4.31 (m, 4H), 4.26-4.22 (m, 1H), 3.72-3.58 (m, 1H), 3.33-3.29 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.9, 175.1, 147.2, 146.6, 145.4, 135.6, 130.7, 130.3, 129.1, 128.7, 127.8, 125.8, 123.9, 120.5, 118.7, 113.3, 61.2, 555.0, 49.2, 44.0, 42.2, 14.2. HRMS (m/z, ESI) calcd $[C_{27}H_{23}N_3O_6Na]^+$ $[M+Na]^+$ 508.1479, observed 508.1475.

2-(2,4-dichlorophenyl)-5-(4-nitrobenzyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3nj)

Title compound was synthesized according to the general procedure and obtain as brown oil (46%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.14 (td, *J* = 6.2, 2.1 Hz, 2H), 7.56-7.30 (m, 6H), 7.21-7.08 (m, 1H), 6.94-6.87 (m, 1H), 6.57 (dd, *J* = 28.6, 8.6 Hz, 1H), 4.55 (dd, *J* = 16.4, 8.8 Hz, 1H), 4.40-4.25 (m, 2H), 3.75-3.60 (m, 2H), 3.38-3.31 (1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.5, 174.7, 147.3, 146.6, 146.4, 145.6, 136.4, 130.8, 130.6, 130.5, 128.9, 128.3, 128.0, 124.0, 120.6, 120.2, 117.8, 113.4, 55.6, 49.2, 44.0, 42.6HRMS. HRMS (m/z, EI) calcd $[C_{24}H_{17}N_3O_4Cl_2]^+$ $[M]^+$ 481.0596, observed 481.0604.

5-benzyl-7-methoxy-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c] quinoline-1,3(2H)-dione (3oa)

Title compound was synthesized according to the general procedure and obtain as brown oil (49%); ^{1}H-NMR (400 MHz, CDCl3): δ 7.46-7.35 (m, 3H), 7.31-7.17 (m, 8H), 6.55-6.40 (m, 1H), 6.36-6.21 (m, 1H), 4.50-4.33 (m, 1H), 4.28-4.20 (m, 1H), 3.69 (s, 3H), 3.53-3.46 (m, 1H), 4.00-3.90 (m, 1H), 3.26 (dd, *J* = 4.00, 12.00 Hz, 1H), 3.07 (dd, *J* = 4.00, 12.00 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177., 176.1, 137.7, 137.6, 132.0, 131.2, 129.0, 128.9, 128.7, 128.6, 128.5, 127.5, 127.4, 127.3, 126.3, 111.1, 106.7, 104.4, 103.6, 100.3, 55.5, 55.1, 48.8, 43.8, 41.7.; HRMS (m/z, ESI) calcd $[C_{25}H_{22}N_2O_3]^+$ $[M+H]^+$ 398.1630, observed 398.1640

2,5-dibenzyl-8-fluoro-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3lg)

Title compound was synthesized according to the general procedure and obtain as yellow liquid (78%); ^{1}H-NMR (400 MHz, CDCl3): δ 7.33 (dd, *J* = 4.00, 8.00 Hz, 1H), 7.29-7.21 (m, 8H), 7.06-7.04 (m, 2H), 4.75-4.62 (m, 2H), 4.33 (dd, *J* = 8.00, 14.00 Hz, 1H), 4.14 (dd, *J* = 8.00, 16.00 Hz, 1H), 3.96 (d, *J* = 8.00 Hz, 1H), 3.51 (dd, *J* = 4.00, 10.00 Hz, 1H), 3.28-3.35 (m, 1H), 3.06-3.12 (m, 1H).). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.7, 175.8, 157.7, 155.3, 143.9, 137.2, 135.4, 128.6, 128.5, 127.9, 127.3, 127.2, 120.58, 120.51, 117.0, 116.8, 114.9, 114.7, 114.4, 114.3, 55.8, 49.0, 43.6, 42.9, 42.2. HRMS (m/z, ESI) calcd $[C_{25}H21FN2O2]^+$ $[M+Na]^+$ 423.1479, observed 423.1487

2-(4-chlorophenyl)-5-(4-nitrobenzyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ne)

Title compound was synthesized according to the general procedure and obtain as yellow oil (65%); ^{1}H-NMR (400 MHz, CDCl3): δ 8.13 (d, *J* = 8.00 Hz, 2H), 7.55 (d, *J* = 8.00 Hz, 1H), 7.39 (d, *J* = 12.00 Hz, 2H), 7.28-7.24 (m, 2H), 7.15-7.10 (m, 3H), 6.92 (t, *J* = 8.00 Hz, 1H), 6.57 (d, *J* = 8.00 Hz, 1H), 4.56 (d, *J* = 16.00 Hz, 1H), 4.35 (d, *J* = 16.00 Hz, 1H), 4.23 (d, *J* = 12.00 Hz, 1H), 3.70 (dd, *J* = 0.00, 10.00 Hz, 1H), 3.60-3.58 (m, 1H), 3.29 (dd, *J* = -52.00, 40.00 Hz, 1H). 177.3, 175.5, 147.4, 146.6, 145.5, 130.8, 128.8, 128.1, 128.0, 127.8, 124.0, 120.6, 118.9, 116.4, 116.2, 113.4, 55.2, 49.4, 44.0, 42.3. HRMS (EI) calcd. for $C_{24}H_{18}N_3O_4Cl$ $[M]^+$: 447.0986, found for 447.0994.

5-benzyl-8-chloro-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3pa)

Title compound was synthesized according to the general procedure and obtain as brown liquid (68%); ^{1}H-NMR (400 MHz, CDCl3): δ 7.51-7.35 (m, 5H), 7.29-7.19 (m, 6H), 7.07-7.03 (m, 1H), 6.66-6.59 (m, 1H), 4.41 (dd, *J* = 8.00, 16.00 Hz, 1H), 4.27 (dd, *J* = 12.00, 16.00 Hz, 1H), 4.15-4.06 (m, 1H), 3.70-3.53 (m, 2H), 3.29-3.23 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.0, 175.1, 146.0, 137.1, 130.0, 129.9, 129.1, 129.0, 128.6, 128.4, 127.4, 127.2, 126.2, 124.5, 120.2, 114.6, 55.5, 48.9, 43.8, 42.1. HRMS (EI) calcd. for $C_{24}H_{19}N_2O_2Cl$ $[M]^+$: 402.1135, found for 402.1136.

2,5-dibenzyl-8-choro-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3pg)

Title compound was synthesized according to the general procedure and obtain as yellow brown oil (76%); ^{1}H-NMR (400 MHz, CDCl3): δ 7.41-7.18 (m, 11H), 7.00 (s, 1H), 6.65-6.51 (m, 1H), 4.67-4.54 (m, 4H), 4.21 (dd, *J* = 16.00, 60.00 Hz, 1H), 3.92-3.68 (m, 1H), 3.45 (dd, *J* = 12.00, 24.00 Hz, 1H), 3.03 (dd, *J* = 12.00, 44.00 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.6, 175.8, 146.0, 135.4, 130.0, 129.8, 128.6, 128.3, 127.9, 127.8, 127.4, 127.2, 124.4, 114.7, 55.5, 48.5, 43.5, 42.9, 41.9. HRMS (EI) calcd. for $C_{25}H_{21}N_2O_2Cl$ $[M]^+$; 416.1292, found for 416.1300.

5-(3-nitrobenzyl-2-phenyl)-3a,4,5,9b-tetrahydro-1*H*-pyrrolo[3,4-*c*] quinoline-1,3(2*H*)-dione (3qa)

Title compound was synthesized according to the general procedure and obtain as brown oil (61%); ^{1}H-NMR (400 MHz, CDCl3): δ 8.05-8.01 (m, 2H), 7.51-7.49 (m, 2H), 7.40-7.27 (m, 6H), 7.07-7.03 (m, 1H), 6.86-6.82 (m, 1H), 6.61-6.52 (m, 1H), 4.48 (d, *J* = 16.00 Hz, 1H), 4.25-4.14 (m, 2H), 3.64 (d, *J* = 12.00 Hz, 1H), 3.52-3.43 (m, 1H), 3.24-3.20 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 177.3, 175.5, 146.7, 140.1, 133.3, 130.7, 129.8, 129.6, 129.1, 128.6, 126.2, 122.5, 122.3, 122.2, 120.5, 119.3, 119.2, 113.2, 112.3, 55.0, 49.3, 43.9, 42.2. HRMS (ESI) calcd. for $C_{24}H_{19}N_3O_4Na$ $[M+Na]^+$; 436.1267, found for 436.1277.

5-phenyl-6a,7-dihydropyrrolo[3',4':4,5]pyrido[3,2,1-*jk*]carbazole-4,6(3b*H*,5*H*)-dione (11) Title compound was synthesized according to the general procedure and obtain as white solid (45 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.61-7.60 (m, 1H), 7.41-7.39 (m, 4H), 7.20-7.14 (m, 4H), 4.80 (d, *J* = 5.6 Hz, 2H), 4.57 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.6, 174.6, 140.7, 132.6, 129.4, 128.9, 127.4, 126.3, 122.8, 120.8, 119.6, 109.9, 71.3, 49.2.

***N*-cyclohexyl-*N*-methylaniline (1b)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26-7.21 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.71-6.67 (m, 1H), 3.58 (tt, *J* = 11.4, 3.4 Hz, 1H), 2.79 (s, 3H), 1.87-1.67 (m, 5H), 1.51-1.31 (m, 4H), 1.15 (qt, *J* = 12.7, 3.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.1, 129.0, 116.1, 113.1, 58.0, 31.1, 30.0, 26.1, 25.9.

***N*-Methyl-*N*-undecylaniline (1e)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.24-7.19 (m, 2H), 6.69-6.64 (m, 3H), 3.29 (t, *J* = 7.6 Hz, 2H), 2.91 (s, 3H), 1.57-1.54 (m, 2H), 1.30-1.25 (16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.3, 129.1, 115.7, 112.0, 52.8, 38.2, 31.9, 29.65, 29.62, 29.5, 29.3, 27.1, 26.6, 22.6, 14.1.

***N*-Allyl-*N*-methylaniline (1g)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 6.81-6.75 (m, 3H), 5.96-5.86 (m, 1H), 5.31-5.20 (m, 2H), 3.99-3.97 (m, 2H), 3.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.4, 133.7, 129.0, 116.3, 116.0, 112.3, 55.1, 37.8.

***N*-isopropyl-*N*-methylaniline (1h)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27-7.23 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.72 (td, *J* = 7.2, 0.8 Hz, 1H), 4.12 (t, *J* = 6.8 Hz, 1H), 2.75 (s, 3H), 1.19 (d, *J* = 6.4 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.1, 129.0, 116.3, 113.2, 48.8, 29.7, 19.2.

***N*-methyl-*N*-(2-methylallyl)aniline (1i)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 8.0 Hz, 2H), 6.73-6.71 (m, 3H), 4.88-4.84 (m, 2H), 3.83 (s, 2H), 2.98 (s, 3H), 1.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.5, 141.3, 128.9, 116.1, 116.0, 111.8, 110.8, 58.7, 50.6, 42.2, 38.1, 20.9, 19.9.

***N*-methyl-*N*-(pent-4-en-1-yl)aniline (1j)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 7.8 Hz, 2H), 6.69-6.43 (m, 3H), 5.85-5.81 (m, 1H), 5.04-4.96 (m, 2H), 3.50-3.28 (2H), 3.11-2.90 (m, 3H), 2.10-2.06 (2H), 1.69-1.64 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.2, 138.1, 129.1, 115.8, 114.9, 112.0, 52.1, 38.2, 31.1, 25.7.

***N*-isobutyl-*N*-methylaniline (1k)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27-7.21 (m, 2H), 6.68 (t, *J* = 8.8 Hz, 3H), 3.14-3.09 (2H), 2.99-2.93 (m, 3H), 2.12-2.03 (m, 1H), 0.94 (td, J = 12.3, 6.6 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 149.5, 129.0, 115.5, 11.7, 60.8, 39.3, 27.3, 20.4.

***N*-benzyl-*N*-ethylaniline (4)**

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.16 (m, 8H), 6.71 (m, 3H), 4.53 (s, 2H), 3.48 (q, *J* = 7.0 Hz, 2H), 1.21 (td, *J* = 7.1, 1.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.4, 139.2, 129.1, 12.5, 126.7, 126.5, 115.9, 112.0, 53.8, 45.0, 12.0. HRMS (m/z, ESI) calcd $[C_{23}H_{16}N_2O_2]^+$ $[M+H]^+$ 352.1212, observed 352.1011

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1. Bhojgude, S. S.; Bhunia, A.; Biju, A. T. *Acc. Chem. Res.* **2016,** *49*, 1658-1670.
2. Sun, C. L.; Shi, Z. J. *Chem Rev.* **2014,** *114*, 9219-9280.
3. Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. *Acc. Chem. Res.* **2016,** *49*, 1566-1577.
4. Staveness, D.; Bosque, I.; Stephenson, C. R. J. *Acc. Chem. Res.* **2016,** *49*, 2295-2306.
5. Majek, M.; Jacobi Von Wangelin, A. *Acc. Chem. Res.* **2016,** *49*, 2316-2327.
6. Fan, X. Z.; Rong, J. W.; Wu, H. L.; Zhou, Q.; Deng, H. P.; Da Tan, J.; Xue, C. W.; Wu, L. Z.; Tao, H. R.; Wu, J. *Angew. Chem. Int. Ed.* **2018,** *57*, 8514-8518.
7. Du, K.; Wang, S.-C.; Basha, R. S.; Lee, C.-F. *Adv. Syn. Cat.* **2019,** *361*, 1597-1605.
8. Zhang, Y.; Riemer, D.; Schilling, W.; Kollmann, J.; Das, S. *ACS Catal.* **2018,** *8*, 6659-6664.
9. Zhuang, Y. J.; Qu, J. P.; Kang, Y. B. *J. Org. Chem.* **2020,** *85*, 4386-4397.
10. Schilling, W.; Riemer, D.; Zhang, Y.; Hatami, N.; Das, S. *ACS Catal.* **2018,** *8*, 5425-5430.
11. Hari, D. P.; König, B. *Chem. Comm.* **2014,** *50*, 6688-6699.
12. Nakajima, K.; Miyake, Y.; Nishibayashi, Y. *Acc. Chem. Res.* **2016,** *49*, 1946-1956.
13. Hwang, J. Y.; Ji, A. Y.; Lee, S. H.; Kang, E. J. *Org. Lett.* **2020,** *22*, 16-21.
14. Kundu, D.; Ahammed, S.; Ranu, B. C. *Org. Lett.* **2014,** *16*, 1814-1817.
15. Maity, P.; Kundu, D.; Ranu, B. C. *Eur. J. Org. Chem.* **2015,** *2015*, 1727-1734.
16. Arora, A.; Weaver, J. D. *Acc. Chem. Res.* **2016,** *49*, 2273-2283.
17. Srivastava, V.; Singh, P. P. *Rsc Adv* **2017,** *7*, 31377-31392.
18. Hari, D. P.; Konig, B. *Chem. Comm.* **2014,** *50*, 6688-6699.
19. Hsu, C. W.; Sundén, H. *Org. Lett.* **2018,** *20*, 2051-2054.
20. Liang, Z. W.; Xu, S.; Tian, W. Y.; Zhang, R. H. *Beilstein J. Org. Chem.* **2015,** *11*, 425-430.
21. Yu, J.; Zhang, L.; Yana, G. *Adv. Syn. Cat.* **2012,** *354*, 2625-2628.
22. Xiao, T.; Dong, X.; Tang, Y.; Zhou, L. *Adv. Syn. Cat.* **2012,** *354*, 3195-3199.

23. Zhong, J. J.; Meng, Q. Y.; Liu, B.; Li, X. B.; Gao, X. W.; Lei, T.; Wu, C. J.; Li, Z. J.; Tung, C. H.; Wu, L. Z. *Org. Lett.* **2014,** *16*, 1988-1991.
24. Konig, D. P. H.; Burkhard. *Org. Lett.* **2011,** *13*, 3852-3855.
25. Guo, J. T.; Yang, D. C.; Guan, Z.; He, Y. H. *J. Org. Chem.* **2017,** *82*, 1888-1894.
26. Ju, X.; Li, D.; Li, W.; Yu, W.; Bian, F. *Adv. Syn. Cat.* **2012,** *354*, 3561-3567.
27. Nicholls, T. P.; Constable, G. E.; Robertson, J. C.; Gardiner, M. G.; Bissember, A. C. *ACS Catal.* **2016,** *6*, 451-457.
28. Huang, P.; Wang, P.; Wang, S.; Tang, S.; Lei, A. *Green Chem.* **2018,** *20*, 4870-4874.
29. Firoozi, S.; Hosseini-Sarvari, M.; Koohgard, M. *Green Chem.* **2018,** *20*, 5540-5549.
30. Sakai, N.; Matsumoto, S.; Ogiwara, Y. *Tetrahedron Lett.* **2016,** *57*, 5449-5452.
31. Song, Z.; Antonchick, A. P. *Tetrahedron* **2016,** *72*, 7715-7721.
32. Nishino, M.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2011,** *76*, 6447-6451.
33. Tang, J.; Grampp, G.; Liu, Y.; Wang, B. X.; Tao, F. F.; Wang, L. J.; Liang, X. Z.; Xiao, H. Q.; Shen, Y. M. *J. Org. Chem.* **2015,** *80*, 2724-2732.
34. Yang, X. L.; Guo, J. D.; Lei, T.; Chen, B.; Tung, C. H.; Wu, L. Z. *Org. Lett.* **2018,** *20*, 2916-2920.
35. Xu, W.-L.; Tang, L.; Ge, C.-Y.; Chen, J.; Zhou, L. *Adv. Syn. Cat.* **2019,** *361*, 2268-2273.
36. Rudi, A.; Kashman, Y. *J. Org. Chem.* **1989,** *54*, 5331-5337.
37. Shapiro, H. S. *United States Patent* **1984,** *4,440,768*.
38. Mitchell, I. S.; Lee, T.; Chen, W.; Cacciola, J. *United States Patent* **2004,** *6,777,406*.
39. Katritzky, A. R.; Zhang, G.; Qi, M.; Xie, L. *Tetrahedron Lett.* **1997,** *38*, 6959-6960.
40. Xu, W. L.; Tang, L.; Ge, C. Y.; Chen, J.; Zhou, L. *Adv. Syn. Cat.* **2019,** *361*, 2268-2273.

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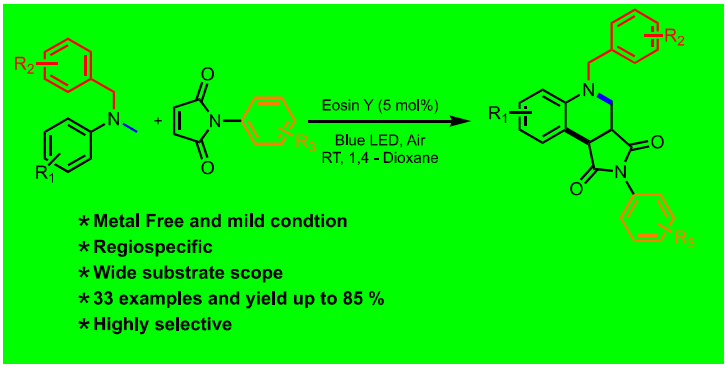

A metal free regioselective methodology has been developed for the synthesizing of various tetrahydroquinoline through photocatalytic pathway in presence of visible light and air. The regioselectivity of the method was evidenced with diverse control experiments.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: