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Research article

7-Hydroxy-4-phenyl-1, 2-dihydroquinoline derivatives: synthesis via one-pot, three-component reaction and structure elucidation

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ABSTRACT

We have developed a new and facile one pot three component protocol catalyzed by ammonium acetate for construction of new functionalized 7-hydroxy-4-phenyl-1,2-dihydroquinoline derivatives. A variety of quinoline derivatives were obtained in good to excellent yield from inexpensive reagents and catalyst in mild reaction conditions that provide atom economy and cost efficacy. Various spectroscopic techniques like FTIR, ^{1}HNMR and ^{13}CNMR were employed to study their structure while mass of the synthesized compounds were confirmed through MALDI-TOF-MS and EI mass spectrometry.

1. Introduction

In recent years one pot multicomponent reactions attracted great attention due to simplicity, atom economy, and greater efficiency with less wastage of products during separation due to reduced number of intermediate purification steps that increase the yield of target products. These reactions may proceed through one step protocol or by many successive steps with generation of diversity of heterocyclic compounds in one pot [1, 2]. Multicomponent one pot reactions due to their efficiency and effectiveness provide a prevailing platform to access sustainable, complexity as well as diversity oriented synthesis of heterocyclic compounds from simple and inexpensive starting materials [3, 4, 5, 6, 7, 8, 9, 10]. Quinoline derivatives are heterocyclic compounds that are used as selective and potent drugs against many diseases. They show excellent antiviral activity against dengue virus [11], zika virus [12], avian influenza virus [13] and now in recent pandemic conditions against COVID-19 [14, 15, 16, 17]. They also possess pharmacological properties such as anti-inflammatory [18, 19, 20], antimalarial [21, 22, 23, 24, 25], anti-cancer [26, 27, 28, 29, 30, 31], anti-hypertension [32], anti-bacterial [33, 34, 35, 36, 37], anti-tubercular [38, 39, 40, 41, 42, 43], anti-fungal [33, 44, 45, 46, 47], anti-urease [48], anti-Alzheimer [49], anti-diabetic [50] and anti-oxidant [51, 52, 53]. Quinoline moiety is a vital part of various natural and pharmacologically active compounds exhibiting a wide-range of biological activities [54, 55, 56]. Owing to their vital role in medicinal agents and natural products, quinolines have become important synthetic targets for chemists. A diverse range of one pot multicomponent protocols including both catalytic and non-catalytic synthetic methods have been developed that use diverse starting materials to construct the quinoline ring with virtually boundless combinations of functionality [10, 57, 58, 59, 60, 61, 62, 63]. L-proline as catalyst was reported for the synthesis of 4-phenyl quinoline derivatives from anilines but reaction time was 8–12h [58] so we use ammonium acetate as catalyst in one pot protocol which reduced the reaction time to 20min- 90min. Ammonium acetate is used as catalyst as well as reagent in synthesis of a wide range of heterocyclic compounds [64, 65]. In this paper we report a quick one pot, three component facile reaction of malononitrile, 3-aminophenol and substituted aldehydes for the synthesis of quinoline derivatives catalyzed by ammonium acetate.

2. Results and discussion

Our study instigated with optimization of reaction conditions by choosing benzaldehyd (**1a**) malononitrile (**2**) and 3-amino phenol (**4**) as model substrates in the absence and presence of different catalysts. The results are summarized and enlisted in Table 1. Surprisingly we got 4-phenyl-1,2-dihydroquinoline products instead of 4-phenyl quinoline derivatives as confirmed by EIMS and ^{1}HNMR. At the beginning we tried to obtain product without using any catalyst and to our delight 35% of product was separated in 1 h at reflux temperature (entry 1 Table 1). Intermediate **3** was not obtained by the reaction of **1a** and **2** but after

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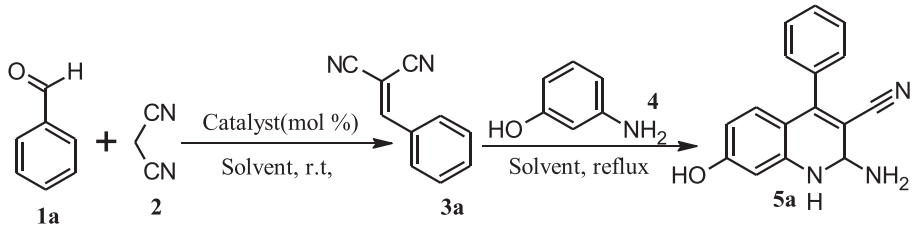
Table 1. Optimization of reaction conditions.[a]

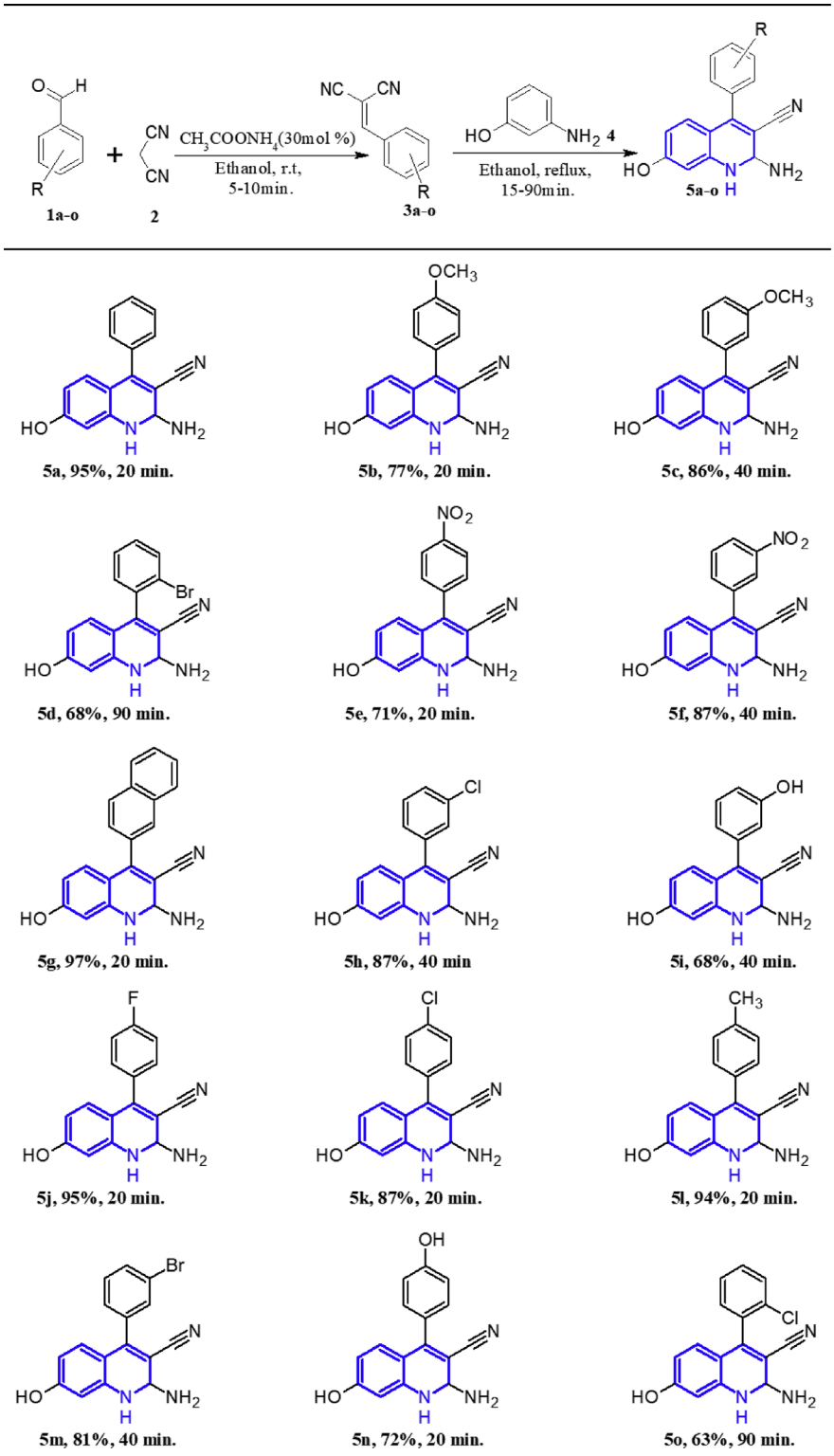


Entry	Catalyst	Catalyst amount mol%	Solvent	Time	Yield %[b]
1[c]	-	-	Ethanol	1h	35
2	K_2CO_3	20	Ethanol: Water (4:1)	1h	43 (40)[d]
3	Et_3N	10	Ethanol	2h	50 (46)[d]
4	Et_3N	20	Ethanol	2h	50 (46)[d]
5	L-Proline	20	Ethanol	12h	NR[e]
6	CH_3COONH_4	10	Ethanol	1h	65
7	$(NH_4)_2CO_3$	20	Ethanol: Water (4:1)	1h	40
8	NH_4Cl	20	Ethanol: Water (4:1)	8h	NR
9	CH_3COONH_4	20	Ethanol	40min	76
10	CH_3COONH_4	25	Ethanol	30min	87
11	**CH_3COONH_4**	**30**	**Ethanol**	**20min**	**95**[f]
12	CH_3COONH_4	35	Ethanol	20min	95
13	CH_3COONH_4	30	Water	2h	NR
14	CH_3COONH_4	30	Methanol	2h	NR
15	CH_3COONH_4	30	n-Propanol	2h	20[g]
16	CH_3COONH_4	30	n-Butanol	2h	15[g]
17	CH_3COONH_4	30	DCM	40min	45
18	CH_3COONH_4	30	Ethanol: Water (1:1)	1h	60

[a] Reaction conditions: **1a** (2mmol), **2** (2mmol), catalyst, Solvent (5mL) Stirred at room temperature then added **4** (2mmol), Solvent (5mL) and refluxed.
[b] Isolated yield in hot reaction mixture.
[c] Without any catalyst.
[d] In parentheses is the isolated yield through one step reaction.
[e] NR stands for no reaction.
[f] Most suitable reaction conditions.
[g] Product was isolated after cooling the reaction mixture at room temperature.

addition of **4**, at first intermediate **3** was produced at room temperature then on reflux it yielded the product **5a**, and from these results it was concluded that catalyst is necessary and 3-aminophenol itself acted as catalyst for the reaction. So to increase the yield we tried different catalyst and recorded results in Table 1 and found that 25 mol% of K_2CO_3 in ethanol and water (4:1) solvent system yielded 43% of product **5a** when reaction was proceeded through two steps that is firstly **1a** allowed to react with **2** at room temperature and then solution of **4** was added at reflux temperature while 40% yield was obtained when all reactants were added together (one step multicomponent protocol) (entry 2 Table 1). Next we used Et_3N 10 mol% and 20 mol% (Table 1 entry 3 and 4) but the yield was not exceeded from 50% and 46% through two steps and one step reaction respectively. With L. proline (Table 1 entry 5) reaction was not accomplished and reactants **1a** and **2** remains as such even after 12 h of stirring. As from above results it was clear that adding all reactants together decrease the yield to some extent and it may be due to the involvement of **4** as catalyst in the production of benzylidenemalononitrile (**3a**), we further investigated other catalyst only through two steps reactions. We tried different ammonium salts (Table 1 entries 6–8) as catalyst and amazingly got 65% yield of product with ammonium acetate in 1 h at reflux temperature. Then we used different quantities of ammonium acetate and best result was obtained with 30 ml% of ammonium acetate (Table 1 entry 11) which was 95% yield of product in just 20 min (5min stirring at room temperature (step 1) and 15 min stirring at reflux temperature (step 2)). After the selection of appropriate catalyst we further investigated different solvents for reaction (Table1 entries 13–18) Reaction was not proceeded in water that might be due to the insolubility of **1a** and **4** in water while in methanol inspite the solubility of reactants **1a** did not react with **2** to yield solid product rather slight change in color occurred which when monitored with TLC showed a third component in reaction medium beside **1a** and **2** but when **4** was added in reaction mixture no product was separated at all. Ethanol was found to be the most suitable solvent for reaction as product separated during heating and no further purification was required except washing the product with hot ethanol.

With optimized reaction conditions (Table 1 entry 11) in hand we further evaluated the scope and generality of substrates for this one pot reaction and results are enlisted in Figure 1. A variety of aldehydes, non-substituted (**1a**, **1g**) and substituted with electron withdrawing groups such as NO_2 (**1e**, **1f**), Cl (**1h**, **1k**), Br (**1d**, **1m**), F (**1J**) and electron donating groups like OCH_3 (**1b**, **1c**), CH_3 (**1l**, **1o**) and OH (**1i**, **1n**) reacted smoothly with 3-amino phenol (**4**) and malononitrile (**2**) and furnished the corresponding 4-phenyl quinoline derivatives in good to excellent yield (63–97%) under mild reaction conditions. Non-substituted aldehydes **1a** and **1g** produced the required products **5a** and **5g** in highest yields which are 95% and 97% respectively in just 20 min (1st step in 5minuts and second step in15 min). Substitution on aldehydes effected the time of completion of reaction for example non substituted and *para* substituted aldehydes converted into products in 20 min. while *meta* substituted aldehydes took 40 min. for completion of reaction and for *ortho* substituted aldehydes longest time was required to convert the reactants into desired product (90 min.). Beside the effect on time of



[a]Reaction conditions: 1(5.0 mmol), 2(5.0mmol), 4(5.0 mmol), ammonium acetate(30mol %), ethanol (20ml), reaction proceeded firstly at room temperature then at reflux temperature.[b]Isolated yields, [c] Reaction completion time

Figure 1. Substrate scope for synthesis of 7-hydroxy-4-phenyl quinoline derivatives (**5a-o**).[a,b,c]

reaction *ortho* substitution on aldehydes irrespective of activating or deactivating group also decreased the yield of corresponding quinoline derivatives **5** as compared to *meta* and *para* substitution. This effect may be aroused due to steric hindrance of groups present at *ortho* position. Methoxy (OCH_3) group at *meta* position of aldehyde (**1c**) produced excellent yield of product **5c** (86%) as compared to *para* methoxy benzaldehyde (**1b**) which 77% converted into product **5b** while *ortho* methoxy benzaldehyde did not produced the desired product at all.

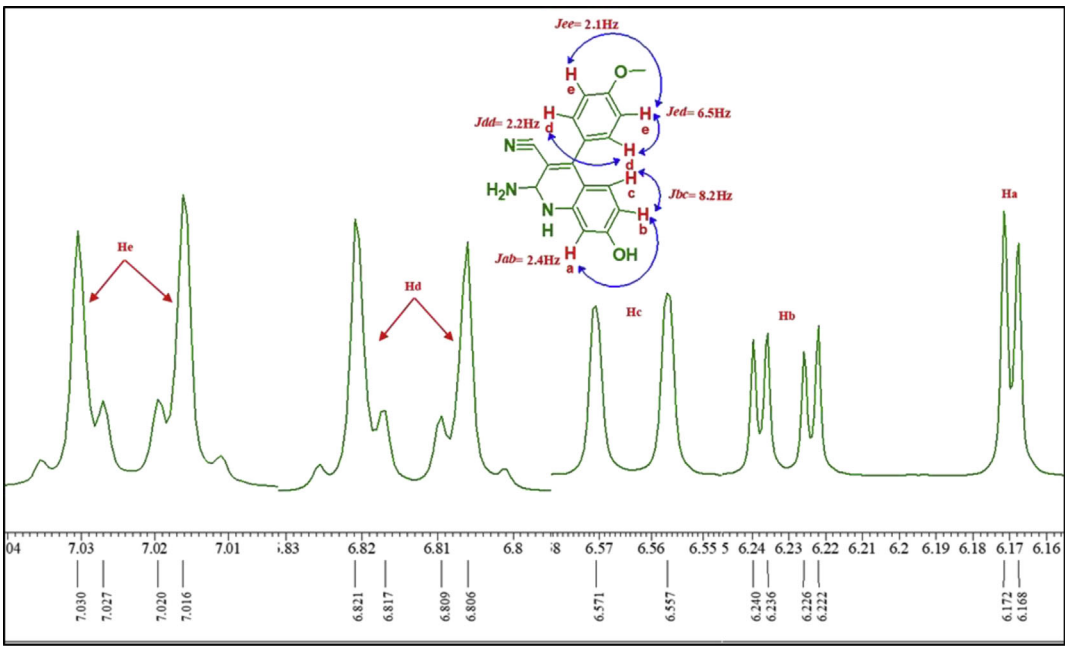


Figure 2. Elaborated ^{1}HNMR spectra of **5b** to explain coupling constants.

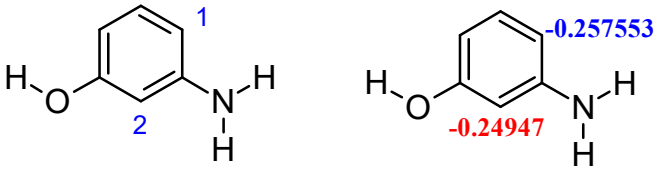


Figure 3. The NPA charges at the MP2/6–31*G (d, p) level [58].

Methyl group showed an opposite effect than that of OCH_3 as its presence at *para* position gave excellent yield (94%) of **5l**. NO_2 group at *meta* position of **1** furnished the product **5f** in 87% yield while para nitro group produced lesser yield (71%) of product. Halogen groups (F, Cl, and Br) produced 95%, 87% and 81% of required products irrespective of the position of substituents while OH at para position resulted in higher yield (72%) of products as compared OH at *meta* position (68%). Some aldehydes did not yielded the products, for example *para* dimethyl amino

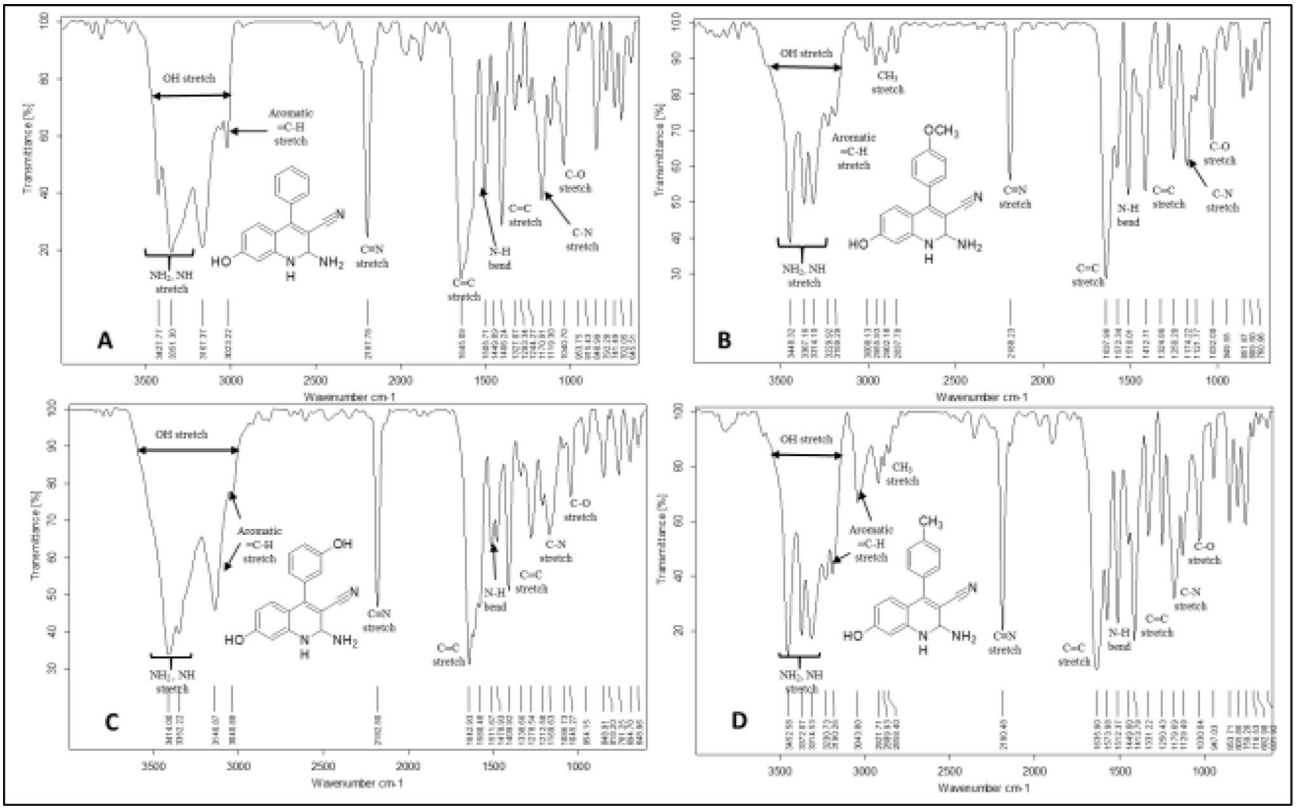


Figure 4. FTIR spectra of A) 5a B) 5b C) 5i D) 5l.

benzaldehyde only furnished the intermediate **3** and did not converted into product **5**, similarly heterocyclic aldehydes like 2-pyridine aldehyde, furfural aldehyde did not reacted to produce the corresponding products.

2.1. Rigioselectivity of reaction

This multicomponent one pot protocol furnished 2-amino-7-hydroxy-4-aryl-1,2-dihydroquinoline-3-carbonitrile derivatives confirmed by NMR studies as represented in elaborated ^{1}HNMR spectra of **5b** (Figure 2) that clearly indicated that Hb showed a doublet peak due to coupling with *ortho* Hc with 8.2 Hz coupling constant while Hb showed doublet of doublet ($J = 8.2, 2.4$Hz)) as it has one *ortho* (Hc) and one *meta* (Ha) neighboring proton. Ha coupled with Hb which is at its meta position and showed a doublet with $J = 2.4$ Hz. Hd and He coupled with their *ortho* as well as meta protons giving doublet of doublet with coupling constant 6.7, 2.2 Hz and 6.5, 2.1 Hz respectively. These studies showed that Michael addition take place at position 1 of 3-aminophenol which is more reactive than position 2 (Figure 3) and thus the product obtained was more stable in accordance with Ali Khalafi-Nezhad et al. who explained it on the basis of NPA charges calculations (Figure 3), thermodynamics and steric hindrance [58]. They also explained the oxidation process in 3-carbonitrile derivatives which helped to aromatize the product but in our case we obtained 1,2-dihydroquinoline derivatives instead of 1,4-dihydroquinoline derivatives so aromatization did not take place in products we obtained as reported in Figure 1.

2.2. FTIR study for structure elucidation of *5a-o*

FTIR spectra of all synthesized compounds were recorded in 4000 cm^{-1} to 600 cm^{-1} domain and all spectra have prominent peaks characteristic of synthesized quinoline derivatives such as NH_2, NH, OH, C≡N, C=C, C–N and C–O peaks in the vibrational range of 3500–1000 cm^{-1} (Figures S1–S15). NH_2 and NH peaks appear in the range of 3500–3300cm^{-1} while C≡N showed peaks in the region of 2200–2100cm^{-1} and OH peaks appear as broadened NH_2 peak from 3500-3000cm^{-1} in all spectra of compounds 5a-o. In exemplary spectra of **5a, 5b, 5i and 5l** (Figure 4) C≡N stretching vibration appears as sharp and strong peak at 2197.78, 2188.23, 2182.20 and 2190.48 cm^{-1} respectively. NH_2 vibrations appear as strong double peaks (asymmetric and symmetric stretch) in all spectra while NH vibration overlapped by NH_2 vibration in **5a** and is not visible while it is visible in **5b** and **5l** and in **5i** broad two OH groups peak overlapped it as well. Sp^3 CH stretching

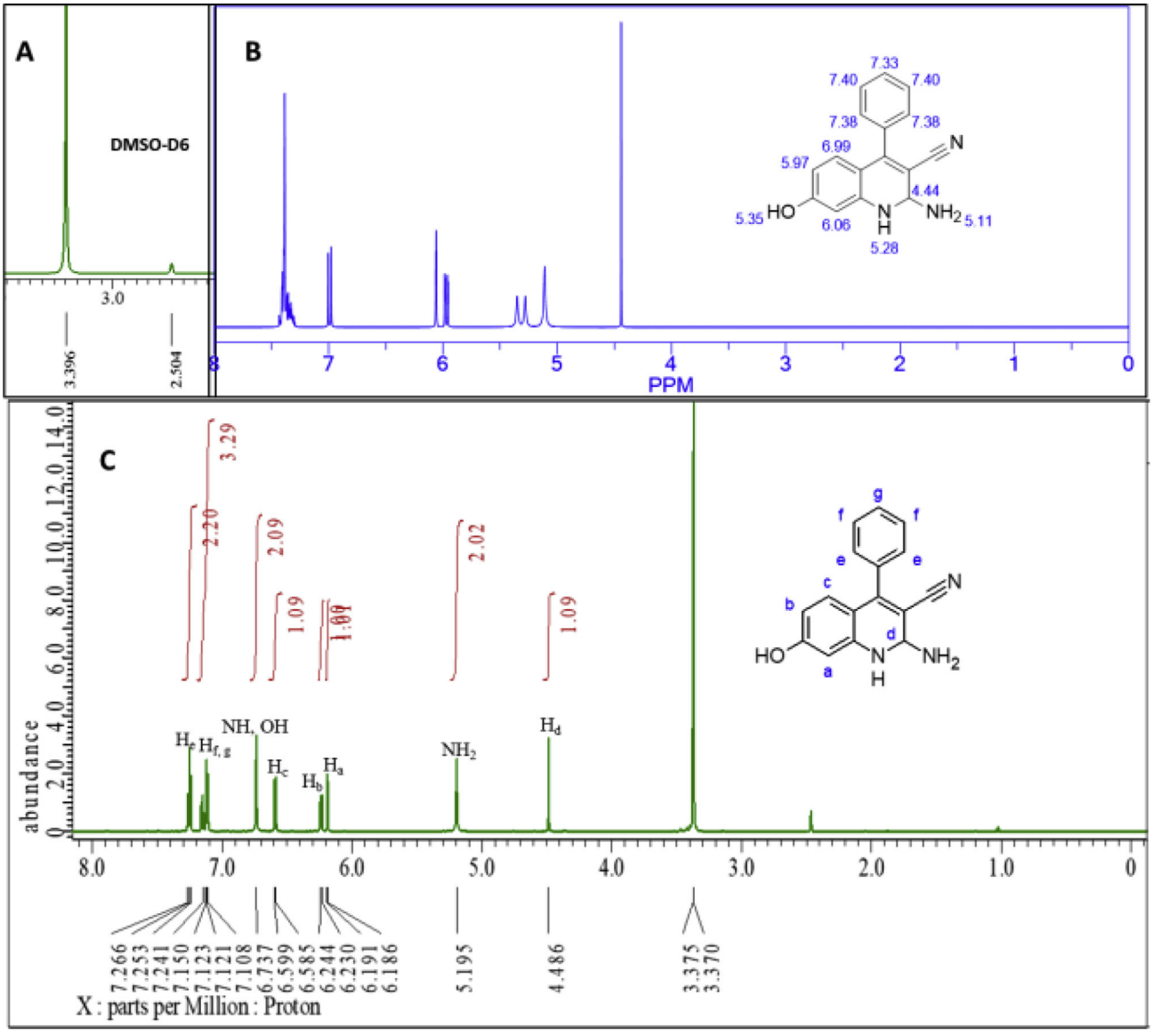


Figure 5. ^{1}HNMR spectra of A) DMSO-D6 B) **5a** theoretical C) **5a** experimental.

signals can also be clearly seen in spectra of **5b** and **5l**. Strong stretching band in the region of 1650–1400 cm^{-1} are assigned to C=C groups of aromatic ring of reported compounds. All these peaks are in accordance with the proposed structure of reported compounds.

2.3. NMR study for structure elucidation of *5a-o*

In ^{1}HNMR and ^{13}CNMR spectra of all synthesized compounds (**5a-5o**) all required signals conforming the respective proton and carbon nuclei of suggested structures are observed at agreeing chemical shifts (ppm) values which helped in unambiguous characterization of 7-hydroxy-4-phenyl-1,2-dihydroquinoline derivatives (Figures S16–S30). Experimental spectra are almost in accordance with theoretical spectra obtained by using Chem draw ultra 12.0. Exemplary ^{1}HNMR of **5a** (Figure 5C) allows us to identify different proton's chemical shift values, for example, signal at 4.49 ppm (s) is assigned to CH attached to NH_2 while overlapped singlet peak of two protons at 5.20 ppm is of NH_2, peaks originating due to H_a, H_b and H_c are observed at 6.19 ppm (d, J =

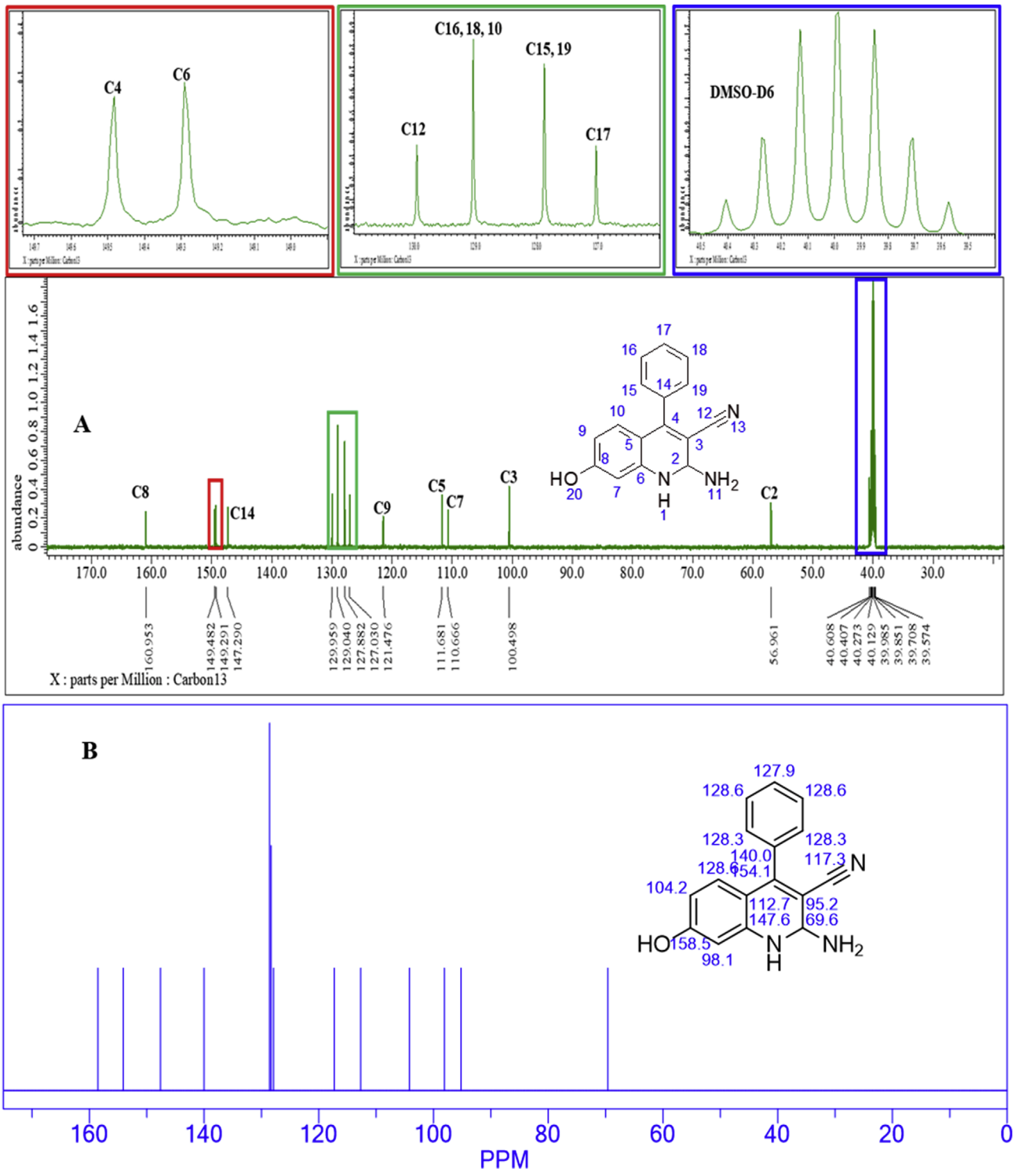


Figure 6. ^{13}CNMR spectra of **5a** A) experimental B) Theoretical.

Table 2. Observed peaks in MALDI-TOF-MS spectra of **5a-o**.

Compound	$[M + H]^+$	$M^{+\cdot}$	$[M-H]^+$	$[M-H_2]^+$	$[M-H-H_2]^+$
5a	-	-	262.22	261.24	260.22
5b	-	293.68	292.67	291.66	-
5c	294.63	-	292.63	291.64	-
5d	342.53	341.21	340.61	-	338.87
5e	-	-	307.84	306.61	-
5f	-	-	307.30	306.10	305.06
5g	-	-	312.05	311.04	310.02
5h	-	297.07	296.03	295.05	294.02
5i	-	-	278.13	-	276.18
5j	-	-	280.09	279.07	278.04
5k	-	297.64	296.62	-	294.62
5l	-	-	276.35	275.09	274.90
5m	-	341.07	340.49	-	338.86
5n	-	-	278.94	277.49	-
5o	-	-	296.48	-	-

2.7 Hz), 6.24 ppm (dd, J = 8.2, 2.1 Hz) and 6.59 ppm (d, J = 8.2 Hz) respectively and aromatic protons of Ar produce signals in the range of 7.25 ppm (t, J = 7.6 Hz, 2H) and 7.16–7.11ppm (m, 3H). NH, and OH signal appear at 6.71ppm as singlet strong peak of two protons. Experimental ^{1}HNMR spectra is almost in accordance with predicted ^{1}HNMR spectra (Figure 5B) that confirms the formation of our required products.

Similarly ^{13}CNMR of 5a (Figure 6A) showed distinct resonances all corresponding to respective carbon nuclei. Carbon bonded to NH_2 group resonated at 56.96 ppm while the signals of carbon atom attached with nitrile group is evident at 100.68 ppm and aromatic carbon attached to OH group appear at 160.95 ppm. In addition quaternary carbon C10 attached to nitrogen of pyridine ring resonate at 149.29 ppm. Carbon of nitrile group appear at 129.96 ppm. All other carbon nuclei also appear in aromatic region which are in accordance with predicted ^{13}CNMR of **5a** (Figure 6B). ^{13}CNMR of all other 1,2-dihydroquinoline derivatives showed same trend of peaks which confirms the formation of our desired products (Figures S31–S45).

2.4. MALDI-TOF-MS and EI-MS study

Mass of the synthesized compounds were determined by EI-MS using electron ionization (Figures S61–S63) and MALDI-TOF-MS by using

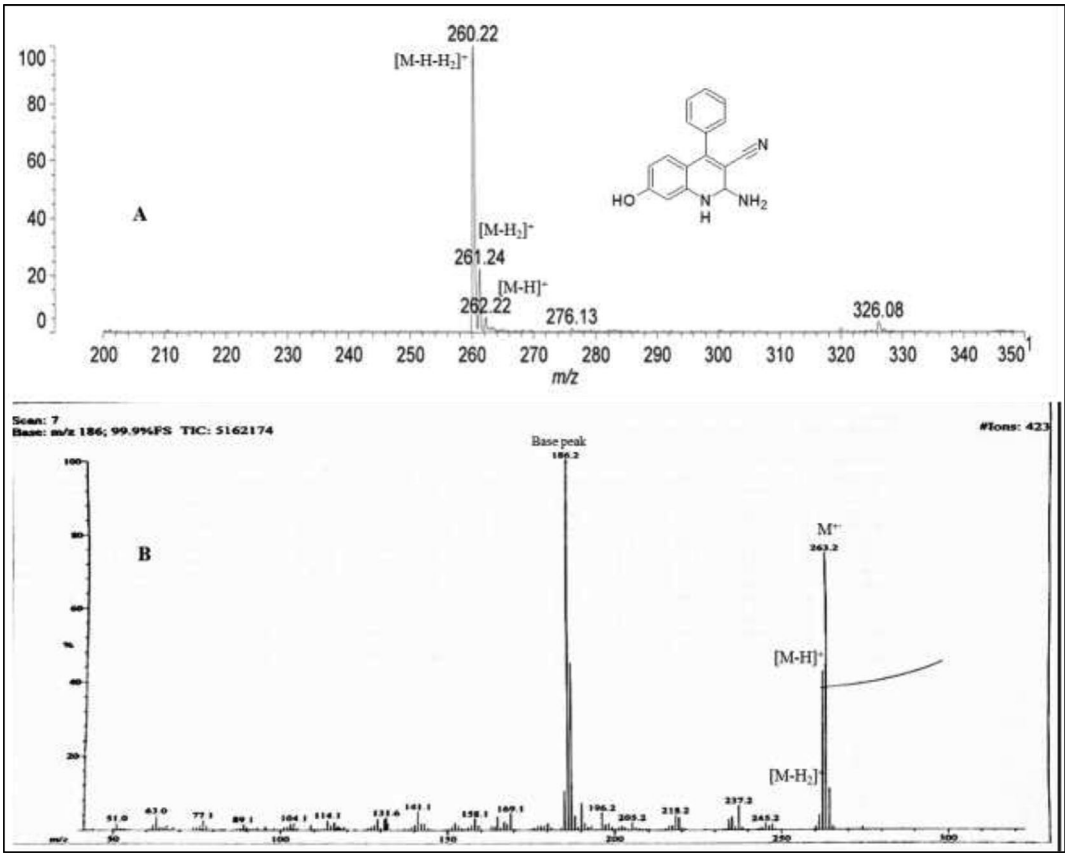
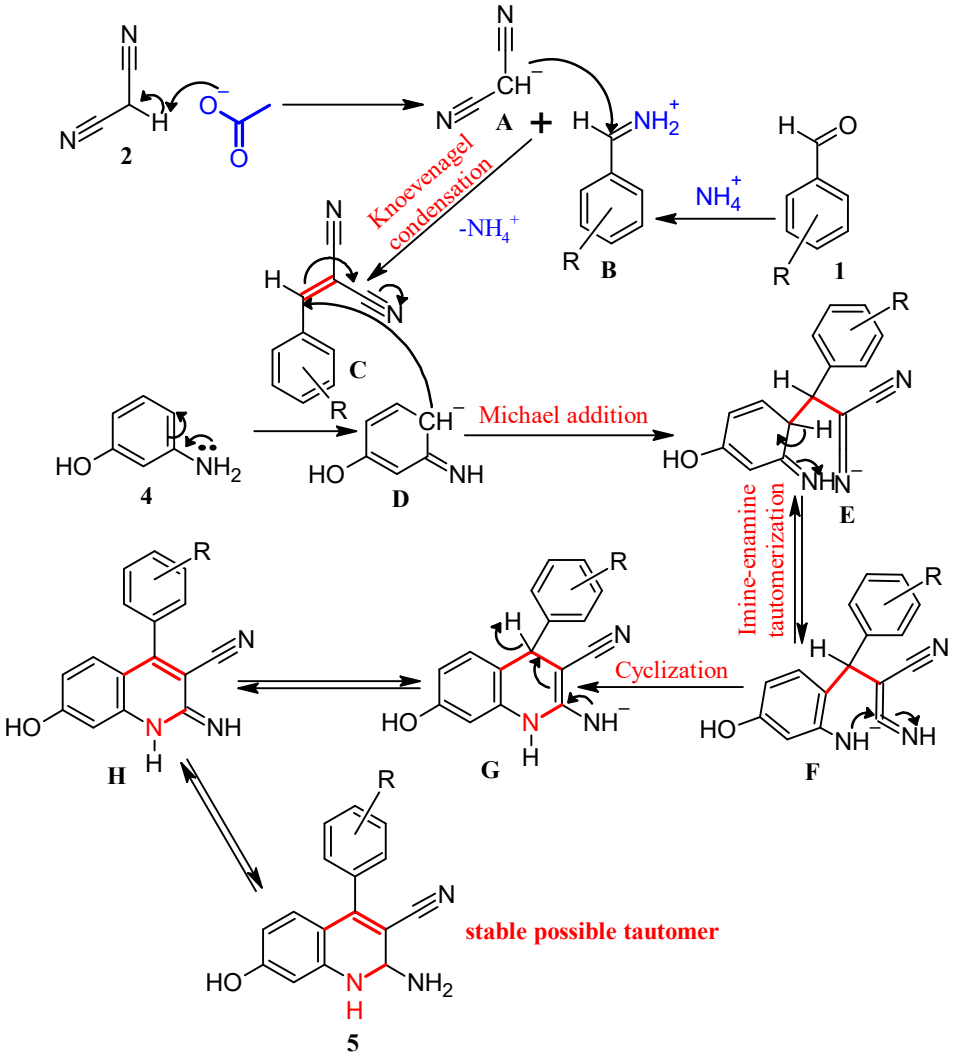


Figure 7. Mass spectra of **5a** A) MALDI-TOF-MS B) EI-MS.

Alpha-Cyano-4-hydroxycinnamic acid (α-CHCA) as matrix in positive ion, reflectron mode (Figures S46–S60). MALDI-TOF uses soft ionization method to generate ions and is well known as a high throughput technique [66]. Previously it was mostly used for compounds with higher molecular weight but now a days it is also employed for compounds with low molecular weight with great success [67, 68]. Surprisingly $[M\text{-}H]^+$ and $M^{+\cdot}$ peaks were observed in almost all investigated compounds instead of $[M+H]^+$ peaks which are observed only in **5c** (Figure S48) and **5d** (Figure S49) spectra, this indicated that these type of compounds produce $[M\text{-}H]^+$, $[M\text{-}H\text{-}H_2]^+$, $[M\text{-}H_2]^+$ and $M^{+\cdot}$ positive ions by this soft ionization technique (Table 2). $[M\text{-}H]^+$ peak is observed in all spectra which may appear due to; a) transfer of hydrogen atom from radical cation of analyte or b) by hydride removal from neutral molecule of analyte, or c) removal of H_2 from protonated molecule of analyte [69, 70, 71, 72] All these three mechanisms may occur simultaneously or not depending on the structure of analyte molecule [73]. $M^{+\cdot}$ observed in spectra of **5b, 5d, 5h, 5k** and **5m** (Figures S47, S49, S53, S56 and S58) may be due to photoionization process. $[M\text{-}H\text{-}H_2]^+$ appeared as strongest peak in almost all spectra which produced due to removal of H_2 molecule from [M-H] ion similarly $[M\text{-}H_2]^+$ peak is also observed in many compounds due to H_2 molecule from $M^{+\cdot}$ molecular ion. In exemplary MALDI spectra of **5a** (Figure 7A) $[M\text{-}H]^+$ peak appear at 262.22 and most intense peak is $[M\text{-}H\text{-}H_2]^+$ at 260.22 m/z while peak observed at 261.24 m/z is due to the removal of hydrogen molecule from positive molecular ion ($M^{+\cdot}$) of **5a**. Similarly EI-MS spectra of some selected compound like **5a**, **5b** and **5f** were recorded in positive ion mode using JEOL-600H-1 mass spectrometer which confirmed the results obtained from MALDI-TOF spectra and molecular mass of synthesized compounds. EI-MS spectrum of **5a** (Figure 7B) showed molecular ion ($M^{+\cdot}$) peak at 263.2 m/z with 74.5% abundance while $[M\text{-}H]^+$ and $[M\text{-}H_2]$ peaks were also observed at 262.2 and 261.2 with 42.6% and 4.2% abundance respectively and confirmed the formation of **5a**.

2.5. Proposed mechanism

Based on the experimental results and previous literature [65, 74, 75] a proposed mechanism of the reaction was shown in Scheme 1. According to proposed mechanism acetate ion facilitate the removal of H from **2** to yield **A** while ammonium ion catalyzed the formation of iminium ion (**B**) which due to higher reactivity than carbonyl group expedite the Knoevenagel condensation between **A** and **B** followed by elimination of ammonium ion to yield benzylidenemalononitrile (**C**). Then **C** through Michael addition with intermediate **D** produced **E** which by imine-enamine rearrangement and cyclization yielded **F** and **G** respectively. Intermediate **G** may exist in three possible forms that are **G**, **H** and **5** out of which **5** (7-hydroxy-4-phenyl-1,2-dihydro quinoline derivatives) is most stable as predicted by spectroscopic data.



Scheme 1. Proposed mechanism for the synthesis of compound 5.

3. Conclusion

In conclusion, we successfully synthesized 7-hydroxy-4-phenyl-1,2-dihydroquinoline derivatives (5a-o) by a convenient one pot, three component protocol in 63–97% yield. The reaction proceed though Knoevenagel condensation, Michael addition, rearrangement and cyclization. Notably, this protocol proceeded without the use of toxic solvents, co-catalysts, precious metals, inert atmosphere and harsh reaction conditions. This one pot atom economic method eliminates the wastage of products and exhibits wide range of functional group tolerance with high substrate scope under mild reaction conditions with excellent yield of corresponding products as high as 97%. Furthermore, structure of all synthesized compounds were elucidated by various techniques including FTIR, ^{1}HNMR, ^{13}CNMR, MALDI-TOF-MS and EI-MS which confirmed that the obtained products are 7-hydroxy-1,2-dihydroquinoline derivatives instead of 7-hydroxy quinolines. Further applicability of this protocol to a wide variety of substrates and bio screening of these compounds are in progress in our laboratory.

4. Experimental

4.1. General information

All reagents were commercially available which were used without further purification. Melting points were recorded by open capillary method on Stuart SMP10 and are uncorrected. Silica gel plates were used to monitor the progress of reaction and purity of compounds by thin layer chromatography technique using ethanol: n-hexane (1: 1), acetone: n-hexane (1:1) and acetone: n-hexane (7:3) solvent system which were visualized under UV. FTIR spectra were recorded on Bruker Tensor 27 FTIR spectrophotometer using KBr discs. ^{1}HNMR and ^{13}CNMR spectra were recorded on JEOL DELTA2 NMR spectrophotometer operating at 600 MHz and Bruker DMZ NMR spectrophotometer operating at 300 MHz H1NMR data are reported as: chemical shift (multiplicity, coupling constant (Hz)). Multiplicity is represented as: s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra were recorded by MALDI-TOF-MS technique on Shimadzu Biotech Axima Performance mass spectrometer using Alpha-Cyano-4- hydroxycinnamic acid (α-CHCA) as matrix in positive ion, reflectron mode. EI-MS spectra were recorded in positive ion mode using JEOL-600H-1 mass spectrometer.

4.2. General procedure for the synthesis of 7-hydroxy-4-phenylquinoline derivatives (5a-o)

To a solution of malononitrile **2** (0.33g, 5.0mmol) and ammonium acetate (0.116g, 30 mol %) in 10ml ethanol, appropriate benzaldehyde **1** (5.0 mmol) was added and stirred at room temperature for 5–10 min. Intermediate benzylidenemalononitrile **3** was obtained as solid product. Then the temperature of the reaction mixture was increased to 70 °C which helped in dissolving **3** in ethanol. After getting clear solution of reaction mixture, solution of 3-amino phenol (0.545g, 5.0 mmol) in 10mL ethanol was added in it and refluxed for 15–90 min. The solid thus obtained was filtered and washed with hot ethanol to obtain highly pure corresponding product **5a-o** in up to 97% yield.

4.2.1. 2-amino-7-hydroxy-4-phenyl-1, 2-dihydroquinoline-3-carbonitrile (5a)

Light yellow solid, Yield: 95%, m.p: 235–237 °C, Rf: 0.69 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3427.77, 3351.30 (NH_2, NH stretch), 3167.37, 3023.22 (Ar CH), 2197.78 (C≡N), 1645.09 (C=C), 1505.71 (NH_2 bend) 1406.24 (C=C), 1170.91 (C–N), 1040.70 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.25 (t, J = 7.6 Hz, 2H, He), 7.15–7.11 (m, 3H, Hf, Hg), 6.74 (s, 2H, NH, OH), 6.59 (d, J = 8.2 Hz, 1H, Hc), 6.24 (d, J = 8.2 Hz, 1H, Hb), 6.19 (d, J = 2.7 Hz, 1H, Ha), 5.19 (s, 2H, NH_2), 4.49 (s, 1H, Hd), ^{13}C-NMR (151 MHz, DMSO-D6) δ 160.9 (C8), 149.5 (C4), 149.3 (C6), 147.3 (C14), 129.9 (C12), 129.0 (C16, C18, C10), 127.9 (C15, C19), 127.0 (C17), 121.5 (C9), 111.7 (C5), 110.6 (C7), 100.5 (C3), 56.97 (C2), MALDI-TOF-MS m/z: $[M\text{-}H]^{+}$, required for $C_{16}H_{12}N_3O^{+}$: 262.097, found: 262.22, EI-MS m/z: $M^{+\cdot}$ required for $C_{16}H_{13}N_3O^{+\cdot}$: 263.11, found: 263.2.

4.2.2. 2-amino-7-hydroxy-4-(4-methoxyphenyl)-1, 2-dihydroquinoline-3-carbonitrile (5b)

yellow solid, Yield: 77%, m.p: 218–221 °C, Rf: 0.56 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3448.31, 3367.16, 3314.10 (NH_2, NH stretch), 3229.92, 3189.29, 3008.13 (Ar CH), 2955.93, 2902.18, 2837.78 (OCH_3), 2188.23 (C≡N), 1637.96 (C=C), 1510.01 (NH_2 bend), 1412.71 (C=C), 1174.22 (C–N), 1032.00 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.02 (dd, J = 6.5, 2.1 Hz, 2H, He), 6.81 (dd, J = 6.7, 2.2 Hz, 2H, Hf), 6.69 (s, 2H, NH, OH), 6.56 (d, J = 8.2 Hz, 1H, Hc), 6.23 (dd, J = 8.2, 2.4 Hz, 1H, Hb), 6.17 (d, J = 2.4 Hz, 1H, Ha), 5.18 (s, 2H, NH_2), 4.43 (s, 1H, Hd), 3.67 (s, 3H, OCH_3), ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.7 (C8), 158.3 (C17), 149.3 (C4), 149.1 (C6), 139.3 (C14), 129.9 (C12), 128.8 (C15, C19), 121.4 (C9), 114.3 (C16, C18), 111.6 (C5), 110.9 (C7), 100.4 (C3), 57.2 (C2), 55.5 (C21, OCH_3), MALDI-TOF-MS m/z: $[M\text{-}H]^{+}$, required for $C_{17}H_{14}N_3O_2^{+}$: 292.11, found: 292.67, EI-MS m/z: $M^{+\cdot}$ required for $C_{17}H_{15}N_3O_2^{+\cdot}$: 293.12, found: 293.2.

4.2.3. 2-amino-7-hydroxy-4-(3-methoxyphenyl)-1, 2-dihydroquinoline-3-carbonitrile (5c)

Dark yellow solid, Yield: 86%, m.p: 196–198 °C, Rf: 0.67 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3462.98, 3376.91, 3337.02 (NH_2, NH stretch), 3243.98, 3201.22, 3050.12, 3009.30 (Ar CH), 2964.27, 2935.25, 2841.80 (OCH_3), 2192.16 (C≡N), 1638.71(C=C), 1512.98(NH_2 bend), 1407.58 (C=C), 1172.63 (C–N),1044.69 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.19–7.17 (m, 1H, Hf), 6.75–6.72 (m, 3H, NH, OH, He), 6.69–6.68 (m, 2H, He, Hg), 6.63 (d, J = 8.6 Hz, 1H, Hc), 6.25 (dd, J = 8.2, 2.1 Hz, 1H, Hb), 6.19 (d, J = 2.4 Hz, 1H, Ha), 5.20 (s, 2H, NH_2), 4.46 (s, 1H, Hd), 3.68 (s, 3H, OCH_3), ^{13}C-NMR (151 MHz, DMSO-D6) δ 161.0 (C18), 159.8 (C8), 149.4 (C4), 149.3 (C6), 148.9 (C14), 130.1 (C16), 129.9 (C10), 121.4 (C9), 120.1 (C15), 114.0 (C12), 111.9 (C17), 111.6 (C5, C19), 110.5 (C7), 100.5 (C3), 56.8 (C2), 55.5 (C21, OCH_3), MALDI-TOF-MS m/z: $[M\text{-}H]^{+}$, required for $C_{17}H_{14}N_3O_2^{+}$: 292.11, found: 292.63.

4.2.4. 2-amino-4-(2-bromophenyl)-7-hydroxy-1, 2-dihydroquinoline-3-carbonitrile (5d)

Light yellow solid, Yield: 68%, m.p: 194–196 °C, Rf: 0.61 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3462.01, 3376.59, 3336.67 (NH_2, NH stretch), 3231.58, 3186.68, 3066.43 (Ar CH), 2192.36 (C≡N), 1640.01 (C=C), 1512.39 (NH_2 bend), 1413.84 (C=C), 1173.91 (C–N), 1126.20 (C–Br), 1036.38 (C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 7.56 (d, J = 7.5 Hz, 1H, Hh), 7.30–7.11 (m, 3H, He, Hf, Hg), 6.88 (s, 2H, NH, OH), 6.63 (d, J = 7.5 Hz, 1H, Hc), 6.32 (d, J = 7.7 Hz, 2H, Hb, Ha), 5.20 (d, J = 43.3 Hz, 3H, NH_2, Hd) ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.1 (C8), 149.5 (C4, C6), 145.5 (C14), 133.2 (C18), 131.4 (C12), 129.2 (C16, C10), 129.1 (C17), 128.8 (C19), 122.8 (C15), 121.0 (C9), 111.8 (C5), 109.6 (C7), 100.6 (C3), 55.9 (C2), MALDI-TOF-MS m/z: $[M\text{-}H]^{+}$, required for $C_{16}H_{11}BrN_3O^{+}$: 340.00, found: 340.61.

4.2.5. 2-amino-7-hydroxy-4-(4-nitrophenyl)-1, 2-dihydroquinoline-3-carbonitrile (5e)

Dark yellow solid, Yield: 71%, m.p: 193–195 °C, Rf: 0.63 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3478.58, 3432.99, 3385.93, 3339.23 (NH_2, NH stretch), 3248.52 (Ar CH), 2189.38 (C≡N), 1643.38 (C=C), 1514.16 (NH_2 bend), 1412.26 (C=C), 1345.29 (NO_2 stretch), 1173.83 (C–N), 1042.81 (C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 8.18 (d, J = 8.5 Hz, 2H, Hf), 7.43 (d, J = 8.7 Hz, 2H, He), 6.94 (s, 2H, NH, OH), 6.63 (d, J = 8.3 Hz, 1H, Hc), 6.31–6.25 (m, 2H, Hb, Ha), 5.31 (s, 2H, NH_2), 4.75 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.0 (C8), 154.7 (C17), 149.7 (C4), 149.4 (C6), 146.7 (C14), 129.9 (C12), 129.1 (C15, C19), 124.4 (C16, C18), 121.0 (C9), 111.7 (C5), 109.0 (C7), 100.5

(C3), 55.7 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{11}N_4O_3^+$: 307.08, found: 307.84.

4.2.6. 2-amino-7-hydroxy-4-(3-nitrophenyl)-1, 2-dihydroquinoline-3-carbonitrile (5f)

yellow solid, Yield: 87%, m.p: 207–209 °C, Rf: 0.61 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3447.78, 3366.62, 3314.86 (NH_2, NH stretch), 3229.61, 3186.51, 3051.97 (Ar CH), 2188.95 (C≡N), 1635.69 (C=C), 1510.91 (NH_2 bend), 1412.96 (C=C), 1327.31(NO_2 stretch), 1170.93 (C–N), 1031.31 (C–O), 1H-NMR (600 MHz, DMSO-D6) δ 8.04 (dq, J = 7.9, 1.3 Hz, 1H, Hg), 7.95 (t, J = 2.1 Hz, 1H, Hh), 7.62–7.57 (m, 2H, He, Hf), 6.92 (s, 2H, NH, OH), 6.62 (d, J = 8.6 Hz, 1H, Hc), 6.26 (dd, J = 8.2, 2.1 Hz, 1H, Hb), 6.22 (d, J = 2.4 Hz, 1H, Ha), 5.28 (s, 2H, NH_2), 4.77 (s, 1H, Hd) ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.1 (C8), 149.6 (C4), 149.5 (C6), 148.4 (C18), 134.7 (C14), 130.7 (C12), 129.9 (C15), 122.2 (C17,C19), 121.1 (C9), 111.8 (C5), 109.3 (C7), 100.5 (C3), 56.0 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{11}N_4O_3^+$: 307.08, found: 307.30, EI-MS m/z: $M^{+\cdot}$ required for $C_{16}H_{12}N_4O_3^{+\cdot}$: 308.09, found: 308.2.

4.2.7. 2-Amino-7-hydroxy-4-(naphthalen-2-yl)-1, 2-dihydroquinoline-3-carbonitrile (5g)

Light yellow solid, Yield: 97%, m.p: 261–264 °C, Rf: 0.74 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3448.28,3367.07, 3315.09 (NH_2, NH stretch), 3231.40, 3187.34, 3051.81 (Ar CH), 2189.06 (C≡N), 1636.56 (C=C), 1510.36, 1413.02 (C=C), 1170.80 (C–N), 1032.29 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.85 (d, J = 7.9 Hz, 1H, Hf), 7.81 (t, J = 7.9 Hz, 2H, Hg), 7.70 (s, 1H, Hi), 7.45 (ddd, J = 13.2, 7.9, 1.4 Hz, 2H, Hh), 7.21 (dd, J = 8.6, 1.7 Hz, 1H, He), 6.82 (s, 2H, NH, OH), 6.61 (d, J = 8.9 Hz, 1H, Hc), 6.24 (td, J = 4.5, 2.2 Hz, 2H, Hb, a), 5.23 (s, 2H, NH_2), 4.68 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.8 (C8), 149.4 (C4), 149.3 (C6), 144.4 (C14), 133.3 (C10), 132.5 (C17), 130.1 (C22), 128.9 (C18), 128.1 (C21), 128.0 (C15), 126.7 (19), 126.5 (C20), 126.2 (C23), 125.9 (C12), 121.4 (C9), 111.7 (C5), 110.2 (C7), 100.5 (C3), 56.8 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{20}H_{14}N_3O^+$: 312.11, found: 312.05.

4.2.8. 2-Amino-4-(3-chlorophenyl)-7-hydroxy-1, 2-dihydroquinoline-3-carbonitrile (5h)

Off white solid, Yield: 87%, m.p: 222–224 °C, Rf: 0.56 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3811.32, 3459.81, 3378.02, 3333.69, 3233.16 (NH_2, NH stretch), 3189.23, 3072.58 (Ar CH), 2193.38 (C≡N), 1638.68 (C=C), 1512.55 (NH_2 bend), 1413.54 (C=C), 1177.27 (C–N), 1126.90(C–Cl),1035.16 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.28 (t, J = 7.9 Hz, 1H, Hf), 7.21 (dq, J = 7.9, 1.0 Hz, 1H, Hg), 7.15 (t, J = 1.9 Hz, 1H, He), 7.11–7.10 (m, 1H, Hh), 6.85 (s, 2H, NH, OH), 6.63 (d, J = 8.2 Hz, 1H, Hc), 6.28 (dd, J = 8.4, 2.2 Hz, 1H, Hb), 6.23 (d, J = 2.1 Hz, 1H, Ha), 5.25 (s, 2H, NH_2), 4.57 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.0 (C8), 149.7 (C4), 149.5 (C6), 149.4 (C14), 133.6 (C16), 131.0 (C18), 129.9 (C12), 127.5 (17), 127.0 (C15), 126.6 (C19), 121.2 (C9), 111.7 (C5), 109.7 (C7), 100.4 (C3), 56.2 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{11}ClN_3O^+$: 296.06, found: 296.03.

4.2.9. 2-Amino-7-hydroxy-4-(3-hydroxyphenyl)-1, 2-dihydroquinoline-3-carbonitrile (5i)

Light yellow solid, Yield: 68%, m.p: 209–212 °C, Rf: 0.54 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3414.00, 3352.22 (NH_2, NH stretch), 3140.87, 3040.87 (Ar CH), 2182.80 (C≡N), 1642.93 (C=C), 1511.67 (NH_2 bend), 1409.92 (C=C), 1169.63 (C–N), 1045.27 (C–O), 1H-NMR (600 MHz, DMSO-D6) δ 7.05 (t, J = 7.7 Hz, 1H, Hf), 6.73 (s, 2H, NH, OH), 6.63–6.56 (m, 3H, Hg, Hh, He), 6.52 (d, J = 1.7 Hz, 1H, Hc), 6.27 (dd, J = 8.2, 2.1 Hz, 1H, Hb), 6.21 (d, J = 2.1 Hz, 1H, Ha), 5.18 (s, 2H, NH_2), 4.40 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.9 (C8), 160.8 (C16), 149.4 (C4), 149.1 (C6), 148.7 (C14), 129.8 (C10, C18), 121.4 (C12), 118.5 (C9), 114.5 (C17), 114.0 (C15), 111.5 (C5), 110.7 (C7), 100.4 (C3), 56.9 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{12}N_3O_2^+$: 278.09, found: 278.13.

4.2.10. 2-Amino-4-(4-fluorophenyl)-7-hydroxy-1, 2-dihydroquinoline-3-carbonitrile (5j)

White solid, Yield: 95%, m.p: 220–222 °C, Rf: 0.67 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3450.28, 3368.22, 3317.72 (NH_2, NH stretch), 3232.34, 3189.07, 3048.76 (Ar CH), 2189.18 (C≡N), 1637.19 (C=C), 1509.74 (NH_2 bend), 1414.27 (C=C), 1230.27(C–F), 1181.41 (C–N), 1030.44 (C–O), ^{1}H-NMR (600 MHz, DMSO-D6) δ 7.17 (td, J = 6.0, 2.7 Hz, 2H, Hf), 7.08–7.05 (m, 2H, He), 6.79 (s, 2H, NH_2), 6.60 (d, J = 8.2 Hz, 1H, Hc), 6.29 (dd, J = 8.2, 2.4 Hz, 1H, Hb), 6.26 (d, J = 2.4 Hz, 1H, Ha), 5.21 (s, 2H, NH_2), 4.55 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 163.0–159.7 (C17(C–F) J = 242.65), 160.8 (C8), 149.4 (C4), 149.3 (C6), 143.4 (C14), 129.9 (C15), 129.7 (C19), 129.6 (C12), 121.3 (C9), 115.8 (C16), 115.5 (C18), 111.7 (C5), 110.4 (C7), 100.4 (C3), 56.8 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{11}FN_3O^+$: 280.09, found: 280.09.

4.2.11. 2-Amino-4-(4-chlorophenyl)-7-hydroxy-1, 2-dihydroquinoline-3-carbonitrile (5k)

Light yellow solid, Yield: 80%, m.p: 226–229 °C, Rf: 0.71 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3447.77, 3367.73,3313.88 (NH_2, NH stretch), 3231.93, 3186.42, 3042.10 (Ar CH), 2189.89 (C≡N), 1636.50 (C=C), 1514.28 (NH_2 bend), 1414.33 (C=C), 1131.58 (C–N), 1092.97(C–Cl), 1026.00 (C–O), 1H-NMR (300 MHz, DMSO-D6) δ 7.35 (d, J = 8.1 Hz, 2H, Hf), 7.18 (d, J = 8.3 Hz, 2H, He), 6.83 (s, 2H, NH, OH), 6.62 (d, J = 8.3 Hz, 1H, Hc), 6.31–6.25 (m, 2H, Hb, Ha), 5.26 (s, 2H, NH_2), 4.57 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.9 (C8), 149.4 (C4, C6), 146.2 (C14), 131.6 (C12), 129.9 (C17), 129.7 (C16, C18, C10), 128.9 (C15, C19), 121.3 (C9), 111.7 (C5), 110.0 (C7), 100.5 (C3), 56.5 (C2), MALDI-TOF-MS m/z: $[M + H]^+$, required for $C_{16}H_{11}ClN_3O^+$: 296.06, found: 296.62.

4.2.12. 2-Amino-7-hydroxy-4-(4-methylphenyl)-1, 2-dihydroquinoline-3-carbonitrile (5l)

Off white solid, Yield: 94%, m.p: 242–244 °C, Rf: 0.45 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3452.58, 3372.07, 3314.53 (NH_2, NH stretch), 3230.73, 3190.26, 3043.80 (Ar CH), 2921.71(C≡N), 2889.92, 2858.39 (CH_3 stretch), 2190.48 (C≡N), 1635.90 (C=C), 1512.37 (NH_2 bend), 1413.79 (C=C), 1179.69 (C–N), 1030.04 (C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 7.07 (dd, J = 15.3, 8.1 Hz, 4H, He, Hf), 6.77 (s, 2H, NH, OH), 6.62 (d, J = 8.1 Hz, 1H, Hc), 6.31–6.24 (m, 2H, Hb, Ha), 5.23 (s, 2H, NH_2), 4.49 (s, 1H, Hd), 2.24 (s, 3H, CH_3), ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.8 (C8), 149.4 (C4), 149.1 (C6), 144.2 (C14), 136.0 (C17), 129.9 (C12), 129.5 (C16, C18), 127.7 (C15, C19), 121.4 (C9), 111.6 (C5), 110.8 (C7), 100.5 (C3), 57.1 (C2), 21.1 (C21, CH_3), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{17}H_{14}N_3O^+$: 276.11, found: 276.35.

4.2.13. 2-Amino-4-(3-bromophenyl)-7-hydroxy-1, 2-dihydroquinoline-3-carbonitrile (5m)

Light yellow solid, Yield: 81%, m.p: 224–227 °C, Rf: 0.59 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3462.01, 3376.59, 3336.67 (NH_2, NH stretch), 3231.58, 3186.67, 3066.43 (Ar CH), 2192.36 (C≡N), 1640.01 (C=C), 1512.39 (NH_2 bend), 1413.84 (C=C), 1173.91 (C–N), 1126.20 (C–Br), 1036.38(C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 7.39 (d, J = 7.9 Hz, 1H, Hg), 7.31–7.24 (m, 2H, Hf, He), 7.19 (s, 1H, Hh), 6.86 (s, 2H, NH, OH), 6.65 (d, J = 8.5 Hz, 1H, Hc), 6.32–6.28 (m, 1H, Hb), 6.24 (d, J = 2.1 Hz, 1H, Ha), 5.28 (s, 2H, NH_2), 4.58 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.0 (C8), 150.0 (C4), 149.5 (C6), 149.4 (C14), 131.3 (C12), 130.4 (C16), 129.9 (C17, C15), 127.0 (C18), 122.3 (C19), 121.2 (C9), 111.7 (C5), 109.7 (C7), 100.4 (C3), 56.3 (C2), MALDI-TOF-MS m/z: $[M-H]^+$, required for $C_{16}H_{11}BrN_3O^+$: 340.00, found: 340.49.

4.2.14. 2-Amino-7-hydroxy-4-(4-hydroxyphenyl)-1, 2-dihydroquinoline-3-carbonitrile (5n)

Yellow solid, Yield: 72%, m.p: 259–261 °C, Rf: 0.59 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3454.62, 3395.25, 3326.41 (NH_2, NH stretch), 3201.42, 3047.74 (Ar CH), 2182.64 (C≡N), 1649.34 (C=C), 1510.77 (NH_2 bend), 1399.76 (C=C), 1168.89(C–N), 1036.80 (C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 6.95 (d, J = 8.5 Hz, 2H, Hf), 6.68 (d, J = 8.3 Hz, 5H, He, 2OH, NH), 6.61 (d, J = 8.3 Hz, 1H, Hc), 6.27 (dd, J = 8.2, 2.2 Hz, 1H, Hb), 6.20 (d, J = 2.1 Hz, 1H, Ha), 5.19 (s, 2H, NH_2), 4.41 (s, 1H, Hd) ^{13}C-NMR (75 MHz, DMSO-D6) δ 160.7 (C8), 156.3 (C17), 149.3 (C4), 149.0 (C6), 137.7 (C14), 129.9 (C12), 128.8 (C15, C19), 121.5 (C9), 115.6 (C16, C18), 111.5 (C5), 111.2 (C7), 100.4 (C3), 57.4 (C2), MALDI-TOF-MS m/z: $[M\text{-}H]^+$, required for $C_{16}H_{12}N_3O_2^+$: 278.09, found: 278.94.

4.2.15. 2-Amino-7-hydroxy-4-(2-chlorolphenyl) -1, 2-dihydroquinoline-3-carbonitrile (5o)

Off white solid, Yield: 63%, m.p: 196–198 °C, Rf: 0.61 (Acetone: n-hexane (7:3)), FTIR (KBr disc, cm^{-1}): 3476.84, 3378.07 (NH_2, NH stretch), 3220.45, 3166.05, 3050.89 (Ar CH), 2182.15 (C≡N), 1649.04 (C=C), 1511.60 (NH_2 bend), 1401.46 (C=C), 1178.57 (C–N), 1124.76 (C–Cl), 1039.45 (C–O), ^{1}H-NMR (300 MHz, DMSO-D6) δ 7.39 (d, J = 7.5 Hz, 1H, Hh), 7.29–7.17 (m, 3H, He, Hf, Hg), 6.87 (s, 2H, NH, OH), 6.62 (d, J = 8.1 Hz, 1H, Hc), 6.30 (d, J = 9.6 Hz, 2H, Hb, Ha), 5.27 (s, 2H, NH_2), 5.10 (s, 1H, Hd), ^{13}C-NMR (75 MHz, DMSO-D6) δ 161.2 (C8), 149.5 (C4), 149.5 (C6), 143.7 (C14), 132.3 (C12), 131.1 (C15), 130.1 (C17), 129.3 (C16), 128.8 (C19), 128.2 (C18), 121.1 (C9), 111.7 (C5), 109.4 (C7), 100.6 (C3), 55.6 (C2), MALDI-TOF-MS m/z: $[M\text{-}H]^+$, required for $C_{16}H_{11}ClN_3O^+$: 296.06, found: 296.05.

Declarations

Author contribution statement

Rukhsana Tabassum: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Muhammad Ashfaq: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Hiroyuki Oku: Analyzed and interpreted the data.

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