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Synthesis, spectral characterization and photophysical studies of tetrahydroquinolines

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ABSTRACT

A metal-free, ultrasound-assisted, fast synthesis of fluorescent *N*-Boc-protected 1,2,3,4–tetrahydroquinolines **9a-p** is described through carbanion-induced ring transformation of 6-aryl-2*H*-pyran-2-ones **7** with *tert*–butyl 3-oxopiperidine-1-carboxylate **8** under basic condition. The reaction products **9a-p** were isolated in high yields. Our synthetic approach is flexible for introducing electron-withdrawing and electron-donating groups. All the synthesized 1,2,3,4–tetrahydroquinolines **9a-p** showed blue fluorescence in the range of 422–470 nm. Based on the optical behavior of compounds **9a–p**, we calculated stokes shift, quantum yield and optical band gap which are highly influenced by the substituents in the ring.

1. Introduction

Nitrogen atom containing heterocyclic compounds represents a core functioning unit in medicine, agrochemicals, biological and material chemistry [1–3]. Among them, 1,2,3,4-tetrahydroquinolines constitutes an attractive and unique class of heterocyclic compounds. They are isolated from variety of natural sources [4,5]. 1,2,3,4-Tetrahydroquinolines-based compounds are greatly targeted by several researchers due their availability in most of the biologically active natural products such as martinelline, martinellic acid, angustureine, cuspareine, galipeine, galipinine, benzastatins (C and D) and 5-alkyl-1,2,3,4-tetrahydroquinolines (Fig. 1) [6]. Whereas apart from the biological activity, a great effort has been directed towards the total synthesis of these privileged scaffolds [7]. Moreover, fluorescent compounds play a major role in the detection of microorganisms through imaging technique [8]. Additionally, natural and synthetically derived 1,2,3,4–tetrahydroquinoline skeleton played prominent role as chemotherapeutic agent such as anti-HIV agent, anticancer activity, antimicrobial activity, antileishmanial activity, antioxidant, antithrombotic, active antagonist against asthma, antitubercular agent, anti-hyperlipidemic agent, anti-alzheimer agent, anti-diabetic agent and anti-fertility agent [9,10].

Tailor made fluorescent tetrahydroquinoline dyes acts as a promising candidate as a metal free organic sensitizer for TiO_2 based dye sensitized solar cell due to its suitable photo response in the visible region [11]. Being good H-donor, tetrahydroquinoline compounds acts as a thermal stabilizer to improve the thermal stability of fuels [12], fluorescent dyes [13], molecular glasses [14], hole transporting materials used for electrophotography [15] and OLED [16]. Since tetrahydroquinoline-based compounds have broadened its mark in various fields of research, several methods have been developed for their synthesis over the years.

Various metal-catalyzed intermolecular and intramolecular cyclization approaches have been successfully employed to construct the functionalized 1,2,3,4-tetrahydroquinolines [17–20]. The synthesis of 1,2,3,4-tetrahydroquinolines has been successfully achieved by the partial hydrogenation of quinolines using different transition metal catalysts such as ruthenium [21], iron [22], cobalt [23], nickel [24], palladium [25] and gold catalyst [26] with suitable hydrogen sources [26]. Besides this metal-catalyzed synthesis, Povarov reactions triggered by various acid catalysts involving [4 + 2] cycloaddition reaction have been used as alternate route to access similar systems [27]. In 2017, Palacios and co-workers illustrated an example of Povarov reaction for the synthesis of phosphino- or phosphine sulfide-1,2,3,4-tetrahydroquinolines involving multicomponent reaction of 2-phosphinoaniline or 2-phosphine sulfide-aniline, styrenes and aldehydes [28]. Recently, Reyes and co-authors employed helical dications (known as

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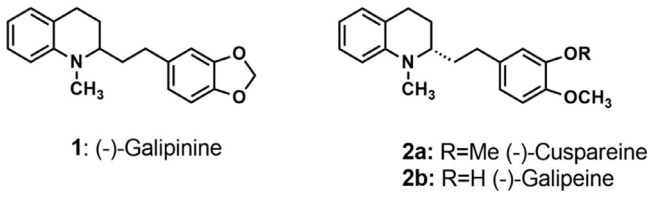


Fig. 1. Naturally occurring alkaloids **1** and **2** containing tetrahydroquinoline moiety.

helquats) as catalyst in the synthesis of diastereomeric 1,2,3,4-tetrahydroquinolines by Povarov reaction of *N*-arylimine and 2,3-dihydrofuran [29].

Stereoselective synthesis of 1,2,3,4-tetrahydroquinolines was developed by Mori et al. via C–H bond functionalization of benzylidene malonate using chiral phosphoric acid as catalyst [30]. Very recently, Chen and co-workers described a three-component cascade reaction to prepare similar systems involving 2-alkenyl aniline, aldehydes and ethyl cyanoacetate in the presence of 1,8-diazabicyclo[5.4.0]undec–7-ene (DBU) through Knoevenagel condensation followed by aza-Michael–Michael addition [31]. Das and coworkers demonstrated the synthesis of tetrahydroquinoline-embedded bridged benzothiaoxazepine-1,1-dioxides by intramolecular Friedel-Crafts epoxide-arene (IFCEA) cyclization of *N*-aryl-2-fluorobenzenesulfonamides followed by NaH-mediated cycloetherification reaction [32]. El-Badry et al. employed microwave-assisted base mediated preparation of tetrahydroquinoline derivatives in the presence of tetrabutylammonium benzoate as a catalyst [33]. Gomez et al. found an eco-friendly method for the synthesis of tetrahydroquinoline *via* aza Diels-Alder reaction of substituted aldehydes, aromatic amines and anise oil in chloride/zinc chloride (deep eutectic solvents) via Povarov reaction [34]. On the other hand, 3,3,4,4-tetrafluoro-1,2,3,4-tetrahydroquinolines were prepared from *N*-(3-methyl–bromo–2,2,3,3-tetrafluoropropyl)anilines by irradiating blue light emitting diodes in the presence of $[Ir(ppy)_3]$ [35]. In 2017, the synthesis of THQ from *N,N*-dimethylanilines and maleimides was also achieved by using chlorophyll as a photosensitizer in a visible light mediated redox reaction [36]. Pratap and coworkers reported the synthesis of functionalized quinolines using 2*H*-pyran-2-ones as the key precursor [37].

In spite of all the metal associated reactions shows considerable break through but having few disadvantages such as require harsh reaction condition, associated with poor yield, involved multistep process, expensive reagents, require inert atmosphere and difficulties in workup process. Thus, it is necessary to find an alternate pathway towards the synthesis of 1,2,3,4-tetrahydroquinolines functionalized with electron donor and acceptor functionalities.

2*H*-pyran-2-ones have emerged as versatile scaffolds owing to their unique reactivity towards several nucleophiles generating diverse array of valuable molecules [38]. This methodology marked considerable attention as it provides an alternate pathway for the synthesis of functionalised benzenes [39–44] and heterocyclic compounds [45–47] which are associated with versatile applications in medicinal and material chemistry. Recently, we have already developed the synthesis of functionalized 2-tetralones [48], diarylmethanes [49], tetrahydroisoquinolines [50], allylbenzenes [51], *meta*- and *para*-terphenyls [52,53] under mild reaction conditions.

In recent years, use of ultrasound radiation in organic synthesis is a powerful green technique, widely used in number of synthetic transformation as an alternate source of energy [54]. In sonochemistry, the high intensity of ultrasound waves causes cavitation effect which implies formation, expansion and collapse of bubbles in a liquid medium subjected under ultra-sonication [55,56]. This effect increases the pressure and temperature of the surrounding medium thereby enhancing the reaction rates and product yields of a chemical reaction. Sono-chemistry is associated with various advantages such as shorter reaction time, non-toxic, low waste generation, high efficiency and excellent selectivity in comparison to existing traditional methods.

Since our on-going interest is in ultrasound and lactone chemistry, herein we report an ultrasound-assisted synthesis and photophysical behavior of 1,2,3,4-tetrahydroquinolines through ring transformation of 2*H*-pyran-2-ones **7** with *tert*–butyl 3-oxopiperidine-1-carboxylate **8** under basic reaction condition.

2. Experimental section

2.1. Materials and instrumental methods

^1H NMR and ^{13}C NMR spectra were studied on AV-400 Bruker using $CDCl_3$ as the solvent and TMS as an internal standard, the operating frequency ranges 400 and 100 MHz, respectively. Chemical composition was confirmed by Elementar VarioMICRO Select 15,162,036 analyser. The molecular weights of the compounds (*m/z*) were analysed using Shimadzu GC-mass spectrometer-QP2020. Melting points were analysed on REMI DDMS 2545 melting point apparatus in an open capillary tube. Infrared spectra were recorded using Thermo Scientific Nicolet Nexus 470FT-IR spectrometer. The UV–Vis spectra of the compounds were recorded on a Perkin Elmer Lambda 35. The emission spectra were recorded on a Varian cary eclipse fluorescence. All the chemicals and solvents were purchased from Avra Synthesis Pvt. Ltd. Used without further purification. The reactions were monitored by thin-layer chromatography (TLC) that was performed on Merck KgaA pre-coated sheets of silica gel 60. Column chromatography was carried out with neutral alumina (100–125 mesh) obtained from Avra synthesis. Eluting solvents are indicated in the text.

2.2. Synthesis

2.2.1. General procedure for the synthesis of ethyl 2-cyano-3,3-dimethylsulfanylacrylate **3** [42]

To an ice-cold solution of sodium methoxide, freshly prepared *in situ* by dissolving sodium metal (3.44 g, 150.0 mmol) in absolute MeOH (40 mL) at 0 °C, was added ethyl cyano acetate (11.3 mL, 100.0 mmol) dropwise over a period of 15 min. The white-coloured precipitate obtained was further stirred vigorously for another 15 min followed by the drop-wise addition of carbon disulfide (6.4 mL, 100.0 mmol) at 20 °C to give a yellow-colored liquid. Next, dimethyl sulfate (23.6 mL, 248 mmol) was added slowly over a period of 30 min. The yellow semi-solid material obtained was stirred for another 15 min and excess MeOH was removed under reduced pressure. Finally, the resulting reaction mixture was poured into the beaker containing crushed ice with constant stirring and the precipitate obtained was filtered, washed with cold water, dried and recrystallized from EtOAc/hexane (1:4) to give yellow crystalline compound **3** in 90% yield.

2.2.2. General procedure for the synthesis of 6-Aryl-4-methylsulfanyl-2-oxo-2H-pyran-3-carbonitriles **5** [57]

To the round bottom flask containing ethyl 2-cyano-3,3-dimethylsulfanylacrylate **3** (2.17 g, 10.0 mmol, 1.0 equiv) in dry DMSO, was added aryl ketones **4** (12 mmol, 1.2 equiv) and powdered KOH (0.84 g, 15 mmol, 1.5 equiv) and the resulting mixture was stirred at room temperature for 14–18 h. On completion of the reaction, the reaction mixture was poured into the ice-cold water with constant stirring. The residue obtained was then filtered and purified by silica gel column chromatography using chloroform as an eluent.

2.2.3. General procedure for the synthesis of 6-aryl-4-amino-2-oxo-2H-pyran-3-carbonitriles ***7*** *[57]*

A mixture of 6-aryl-4-methylsulfanyl-2-oxo-2*H*-pyran-3-carbonitrile **5** (1.0 mmol, 1.0 equiv) and secondary amine **4** (1.2 mmol, 1.2 equiv) was refluxed in MeOH for 6–8 h. Thin layer chromatography was used to check the progress of the reaction. Upon completion, the reaction mixture was cooled to room temperature, filtered and the solid residue was rinsed with MeOH (2 × 5 mL) to provide products **7**.

2.2.4. General procedure for the synthesis of N–tert–butyloxycarbonyl-protected tetrahydroquinolines ***9a-p*** *and* ***11***

To the solution of 6-aryl-4-amino-2*H*-pyran-2-ones **7** or 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[h]chromene-3-carbonitrile **10** (1.0 mmol, 1.0 equiv) in DMF (3 mL) was added *N-Boc*-3-piperidone (1.2 mmol, 1.2 equiv) and powdered KOH (1.2 mmol). The reaction mixture was irradiated in an ultrasonic bath maintaining the minimum frequency of 40 KHz at room temperature for 40–70 min. The temperature of the ultrasonic water bath was maintained at room temperature by replacing the water at mild hot condition. Thin layer chromatography was used to check the progress of the reaction. The reaction mixture was poured into ice cold water and neutralised by adding dilute HCl. The resultant organic layer was extracted with EtOAc. After that, the organic layer collectively dried over anhydrous sodium sulfate and concentrated under vacuum and the crude products were purified by column chromatography using the solvent EtOAc:hexane (1:49) passed through neutral alumina. Finally, the isolated products were characterized as 8-aryl-6-substituted-1,2,3,4-tetrahydroquinoline-5-carbonitriles **9a-q** and **11** by their spectroscopic analysis.

2.2.4.1. Tert–butyl 5-cyano-8-phenyl-6-(4-phenylpiperazin-1-yl)–3,4-dihydroquinoline-1(2H)- carboxylate ***9a***. Colourless solid; yield: 85%; mp: 150–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.53–1.16 (m, 9H, 3CH_3), 1.32–1.66 (m, 1H, CH_2), 1.68–1.93 (m, 1H, CH_2), 1.99–2.39 (m, 1H, CH_2), 2.45–2.77 (m, 1H, CH_2), 2.86–3.13 (m, 1H, CH_2), 3.17–3.47 (m, 8H, 4NCH_2), 3.98–4.56 (m, 1H, CH_2), 6.76–6.82 (m, 1H, ArH), 6.84 (s, 1H, ArH), 6.91 (d, J = 8.0 Hz, 2H, ArH), 7.22 (t, J = 8.0 Hz, 3H, ArH), 7.25–7.47 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 24.0, 26.1, 27.5, 43.0, 50.0, 51.9, 80.7, 104.7, 116.4, 116.8, 118.4, 120.1, 127.9, 128.1, 128.8, 129.2, 131.9, 139.3, 140.7, 142.8, 151.2, 153.4 ppm; IR (KBr): 2206 cm^{-1} (CN), 1693 cm^{-1} (C=O), 1547 cm^{-1} (C=C), 1214 cm^{-1} (C–N), 1061 cm^{-1} (C–O); MS (EI): m/z = 495 [M + 1]$^+$; Anal. for $C_{31}H_{34}N_4O_2$: C, 75.28; H, 6.93; N, 11.33; Found C, 75.09; H, 6.82; N, 11.16%.

2.2.4.2. Tert–butyl 5-cyano-8-phenyl-6-(piperidin-1-yl)–3,4-dihydroquinoline-1(2H)-carboxylate ***9b***. Colourless solid; yield: 83%; mp: 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (s, 9H, 3CH_3), 1.45–1.57 (m, 2H, CH_2), 1.62–1.80 (m, 5H, 2CH_2 + CH), 2.00–2.35 (m, 1H, CH_2), 2.49–2.80 (m, 1H, CH_2), 2.88–3.24 (m, 6H, 3 NCH_2), 3.90–4.43 (m, 1H, CH_2), 6.78 (s, 1H, ArH), 7.21–7.40 (m, 5H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 24.1, 26.0, 26.2, 27.5, 42.9, 53.5, 80.5, 104.4, 117.0, 118.5, 127.9, 128.7, 131.0, 139.5, 140.4, 142.6, 153.5, 154.9 ppm; IR (KBr): 2206 cm^{-1} (CN), 1688 cm^{-1} (C=O), 1569 cm^{-1} (C=C), 1059 cm^{-1} (C–O), 1222 cm^{-1} (C–N); MS (EI): m/z = 418 [M + 1]$^+$; Anal. for $C_{26}H_{31}N_3O_2$: C, 74.79; H, 7.48; N, 10.06. Found C, 74.38; H, 7.32; N, 10.27%

2.2.4.3. Tert–butyl 5-cyano-6-morpholino-8-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate ***9c***. Colourless solid; yield: 78%; mp: 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (s, 9H, CH_3), 1.70–1.92 (m, 1H, CH_2), 1.96–2.42 (m, 1H, CH_2), 2.46–2.721 (m, 2H, CH_2), 2.74–2.94 (m, 1H, CH_2), 2.96–3.27 (m, 4H, 2 OCH_2), 3.29–3.59 (m, 1H, CH_2), 3.84 (s, 4H, NCH_2), 6.79 (s, 1H, ArH), 7.14–7.23 (m, 2H, ArH), 7.24–7.44 (m, 3H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 27.5, 28.5, 42.9, 52.2, 67.0, 80.7, 104.6, 116.8, 118.3, 127.8, 128.1, 128.5, 128.6, 128.8, 153.4, 154.2, 154.5 ppm; IR (KBr): 2208 cm^{-1} (CN), 1684 cm^{-1} (C=O), 1509 cm^{-1} (C=C), 1214 cm^{-1} (C–N), 1059 cm^{-1} (C–O),; MS (EI): m/z = 421 [M + 1]$^+$; Anal. for $C_{25}H_{29}N_3O_3$: C, 71.57; H, 6.97; N, 10.02; Found C, 71.23; H, 6.78; N, 9.91%

2.2.4.4. Tert–butyl 8-(4-chlorophenyl)–5-cyano-6-(piperidin-1-yl)–3,4-dihydroquinoline-1(2H)-carboxylate ***9d***. Colourless solid; yield: 89%; mp: 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (m, 9H, 3 CH_3), 1.47–1.55 (m, 2H, CH_2), 1.61–1.90 (m, 5H, 2 CH_2 + CH), 1.91–2.33 (m, 1H, CH_2), 2.45–2.78 (m, 1H, CH_2), 2.92–3.22 (m, 6H, 3 NCH_2), 3.97–4.48 (m, 1H, CH_2), 6.72 (s, 1H, ArH), 7.21–7.38 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.8, 24.1, 26.2, 27.6, 27.8, 43.1, 53.5, 80.7, 104.9, 116.9, 118.1, 128.4, 128.9, 129.2, 130.9, 133.9, 140.4, 153.4, 155.0 ppm; IR (KBr): 2203 cm^{-1} (CN), 1692 cm^{-1} (C=O), 1522 cm^{-1} (C=C), 1214 cm^{-1} (C–N), 1061 cm^{-1} (C–O); MS (EI): m/z = 453 [M + 1]$^+$, 455 [M + 3]$^+$; Anal. for $C_{26}H_{30}ClN_3O_2$: C, 69.09; H, 6.69; Cl, 7.84; N, 9.30. Found C, 69.19; H, 6.31; N, 9.06%.

2.2.4.5. Tert–butyl 8-(4-chlorophenyl)–5-cyano-6-morpholino-3,4-dihydroquinoline-1(2H)-carboxylate ***9e***. Colourless solid; yield: 82%; mp: 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–1.15 (m, 9H, CH_3), 1.16–1.24 (m, 1H, CH_2), 1.51–1.92 (m, 2H, CH_2), 2.02–2.39 (m, 1H, CH_2), 2.55–2.86 (m, 1H, CH_2), 2.92–3.30 (m, 4H, NCH_2), 3.83 (t, J = 4.0 Hz, 4H, OCH_2), 3.97–4.53(m, 1H, CH_2), 6.74 (s, 1H, ArH), 7.22–7.43 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.8, 26.1, 27.6, 29.3, 29.6, 43.2, 44.5, 52.1, 66.9, 80.9, 105.1, 116.6, 117.9, 118.2, 129.2, 131.9, 133.3, 137.3, 140.7, 153.4 ppm; IR (KBr): 2214 cm^{-1} (CN), 1692 cm^{-1} (C=O), 1588 cm^{-1} (C=C), 1212 cm^{-1} (C–N), 1061 cm^{-1} (C–O); MS (EI): m/z = 455 [M + 1]$^+$, 457 [M + 3]$^+$; Anal. for $C_{25}H_{28}ClN_3O_3$: C, 66.14; H, 6.22; N, 9.26; Found C, 65.87; H, 6.01; N, 9.53%.

2.2.4.6. Tert–butyl 8-(4-chlorophenyl)–5-cyano-6-(4-phenylpiperazin-1-yl)–3,4-dihydroquinoline-1(2H)-carboxylate ***9f***. Colourless solid; yield: 89%; mp: 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 9H, CH_3), 1.60–1.95 (m, 2H, CH_2), 1.99–2.40 (m, 1H, CH_2), 2.45–2.79 (m, 1H, CH_2), 2.92–3.14 (m, 1H, CH_2), 3.17–3.44 (m, 8H, NCH_2), 4.05–4.65 (m, 1H, CH_2), 6.78 (s, 1H, ArH), 6.83(t, 1H, J = 8.0 Hz, ArH), 6.91 (d, 2H, J = 8.0 Hz, ArH), 7.19–7.38 (m, 6H, ArH) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.8, 26.1, 27.6, 43.2, 49.6, 51.8, 51.9, 80.8, 104.1, 108.2, 116.5, 116.6, 118.1, 120.2, 122.9, 129.2, 130.9, 131.7, 133.9, 140.5, 140.3, 151.2, 153.4 ppm; IR (KBr): 2238 cm^{-1} (CN), 1733 cm^{-1} (C=O), 1542 cm^{-1} (C=C), 1216 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 530 [M + 1]$^+$, 532 [M + 3]$^+$; Anal. for $C_{31}H_{33}ClN_4O_2$: C, 70.37; H, 6.29; Cl, 6.70; N, 10.59. Found C, 70.02; H, 6.15; N, 10.26%.

2.2.4.7. Tert–butyl 8-(4-bromophenyl)–5-cyano-6-(piperidin-1-yl)–3,4-dihydroquinoline-1(2H)-carboxylate ***9 g***. Colourless solid; 81%; mp: 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–1.18 (m, 9H, CH_3), 1.45–1.60 (m, 2H, CH_2), 1.62–1.89 (m, 5H, CH_2), 2.02–2.34 (m, 1H, CH_2), 2.46–2.84 (m, 1H, CH_2), 2.85–3.24 (m, 6H, NCH_2), 3.95–4.49 (m, 1H, CH_2), 6.72 (s, 1H, ArH), 7.08–7.33 (m, 2H, ArH), 7.47 (s, 2H, ArH) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.8, 24.1, 26.0, 26.2, 27.6, 43.1, 53.5, 80.8, 104.9, 107.2, 115.7, 116.9, 118.0, 122.05, 129.4, 129.5, 131.8, 140.3, 155.0 ppm; IR (KBr): 2214 cm^{-1} (CN), 1692 cm^{-1} (C=O); 1590 cm^{-1} (C=C), 1221 cm^{-1} (C–N), 1056 cm^{-1} (C–O); MS (EI): m/z = 497 [M + 1]$^+$, 499 [M + 3]$^+$; Anal.for $C_{26}H_{30}BrN_3O_2$: C, 62.90; H, 6.09; Br, 16.10; N, 8.46. Found C, 62.72; H, 5.92; N, 8.15%.

2.2.4.8. Tert–butyl 8-(4-bromophenyl)-5-cyano-6-(4-phenylpiperazin-1-yl)-3,4-dihydroquinoline-1(2H)-carboxylate ***9h***. Colourless solid; yield: 84%; mp: 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–1.11 (m, 9H, CH_3), 1.43 (s, 2H, CH_2), 1.69–1.95 (m, 1H, CH_2), 1.99–2.29 (m, 1H, CH_2), 2.43–2.75 (m, 1H, CH_2), 3.11–3.46 (m, 8H, NCH_2), 3.79–4.49 (m, 1H, CH_2), 6.78 (s, 1H, ArH), 6.82 (t, J = 8.0 Hz, 1H, ArH), 6.91 (d, J = 8.0 Hz, 2H, ArH), 7.22 (t, J = 8.0 Hz, 4H, ArH), 7.41–7.59 (m, 2H, ArH) ppm;^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.8, 26.1, 27.6, 28.4, 43.05, 49.6, 51.9, 80.9, 116.5, 116.7, 118.2, 120.2, 123.5, 125.3, 129.2, 129.5, 130.3, 131.7, 131.9, 140.7, 151.1, 153.5 ppm IR (KBr): 2219 cm^{-1} (CN), 1694 cm^{-1} (C=O); 1507 cm^{-1} (C=C), 1222 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 575 [M + 1]$^+$, 577 [M + 3]$^+$; Anal. for $C_{31}H_{33}BrN_4O_2$: C, 64.92; H, 5.80; N, 9.77. Found C, 64.66; H, 5.71; N, 9.51%.

2.2.4.9. Tert–butyl 5-cyano-8-(3,4-dichlorophenyl)-6-(4-phenylpiperazin-1-yl)-3,4-dihydroquinoline-1(2H)-carboxylate ***9i***. Colourless solid; yield: 81%; mp: 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 9H, CH_3), 1.61 (s, 1H, CH_2), 1.69–2.18 (m, 2H, CH_2), 2.69–3.12 (m, 2H, CH_2), 3.14–3.46 (m, 8H, NCH_2), 3.73–4.45 (m, 1H, CH_2), 6.64 (s, 1H, ArH), 6.82 (t, J = 8.0 Hz, 1H, ArH), 6.90 (d, J = 8.0 Hz, 2H, ArH), 7.11–7.47 (m, 5H, ArH) ppm;^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.7, 26.2, 27.8, 44.6, 49.6, 51.9, 80.7, 106.0, 107.9, 116.4, 116.5, 118.3, 120.2, 127.1, 128.2 129.2, 133.8, 136.9, 140.5, 143.7, 151.2, 153.5 ppm; IR (KBr): 2215 cm^{-1} (CN), 1691 cm^{-1} (C=O); 1586 cm^{-1} (C=C), 1232 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 565 [M + 1]$^+$; Anal. for $C_{31}H_{32}Cl_2N_4O_2$**:** C, 66.07; H, 5.72; N, 9.94; Found C, 66.29; H, 5.35; N, 10.13%.

2.2.4.10. Tert–butyl 5-cyano-6-(piperidin-1-yl)−8-(p-tolyl)−3,4-dihydroquinoline-1(2H)-carboxylate **9j**. Colourless solid; yield: 69%; mp: 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.74–1.08 (m, 9H, CH_3), 1.46–1.58 (m, 2H, CH_2), 1.63–1.75 (m, 4H, NCH_2), 1.76–1.86 (m, 2H, CH_2), 2.06–2.17 (m, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.52–2.66 (m, 1H, CH_2), 2.94–3.17 (m, 4H, NCH_2), 3.52–3.77 (m, 1H, CH_2), 4.01–4.40 (m, 1H, CH_2), 6.77 (s, 1H, ArH), 7.09–7.18 (m, 2H, ArH), 7.21–7.31 (m, 2H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 21.1, 24.0, 24.1, 26.2, 27.5, 42.9, 53.5, 68.0, 80.5, 104.2, 117.1, 118.3, 127.7, 129.3, 131.0, 136.6, 137.8, 140.4, 142.6, 153.6, 154.9 ppm; IR (KBr): 2214 cm^{-1} (CN), 1691 cm^{-1} (C=O); 1586 cm^{-1} (C=C), 1232 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 433 [M + 1]$^+$; Anal. for $C_{27}H_{33}N_3O_2$: C, 75.14; H, 7.71; N, 9.74; Found C, 74.85; H, 8.11; N, 9.53%.

2.2.4.11. Tert–butyl 5-cyano-7-methyl-8-phenyl-6-(piperidin-1-yl)−3,4-dihydroquinoline-1(2H)-carboxylate ***9k***. Colourless solid; yield: 72%; mp: 177–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 9H, 3CH_3), 1.45–1.84 (m, 2H, CH_2), 1.91–2.19 (m, 6H, CH_2), 2.96 (m, 3H, CH_3), 3.14 (s, 2H, CH_2), 3.56–3.92 (m, 6H, 3NCH_2), 6.78 (s, 1H, ArH), 7.22–7.36 (m, 3H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 16.6, 23.7, 25.5, 27.8, 31.6, 44.6, 50.6, 67.8, 80.6, 109.7, 117.0, 127.8, 129.2, 133.0, 133.4, 134.2, 135.5, 136.0, 136.5, 143.7, 150.6, 152.7 ppm; IR (KBr): 2214 cm^{-1} (CN), 1692 cm^{-1} (C=O); 1591 cm^{-1} (C=C), 1232 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 467 [M + 1]$^+$; Anal. for $C_{27}H_{32}ClN_3O_2$: C, 69.59; H, 7.05; N, 9.02. Found C, 69.19; H, 6.88; N, 8.91%.

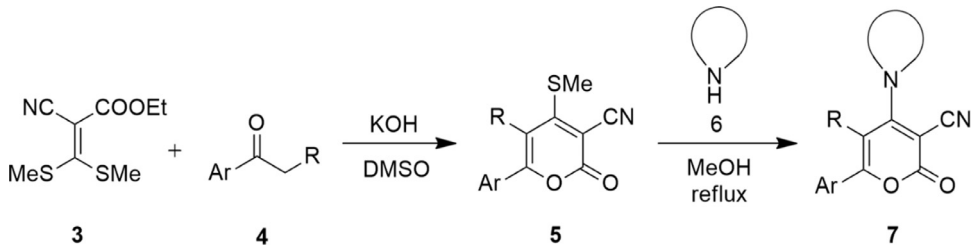
2.2.4.12. Tert–butyl 5-cyano-8-(naphthalen-2-yl)−6-(piperidin-1-yl)−3,4-dihydroquinoline-1(2H)-carboxylate ***9l***. Colourless solid; yield: 68%; mp: 172–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39–1.00 (m, 9H, CH_3), 1.47–1.59 (m, 2H, CH_2), 1.64–1.93 (m, 5H, CH_2), 1.98–2.41 (m, 1H, CH_2), 2.46–2.88 (m, 1H, CH_2), 2.89–3.38 (m, 6H, NCH_2), 3.91–4.66 (m, 1H, CH_2), 6.90 (s, 1H, ArH), 7.42 (d, J = 8.0 Hz, 3H, ArH), 7.67–7.88 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 24.1, 26.1, 26.2, 27.4, 43.1, 53.5, 80.5, 104.6, 117.1, 118.7, 125.8, 126.4, 127.0, 127.6, 128.0, 128.1, 128.2, 131.2, 132.7, 133.5, 137.2, 140.4, 142.6, 155.0 ppm; IR (KBr): 2213 cm^{-1} (CN), 1692 cm^{-1} (C=O), 1591 cm^{-1} (C=C), 1243 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 468 [M + 1]$^+$; Anal. for $C_{30}H_{33}N_3O_2$**:** C, 77.06; H, 7.11; N, 8.99; Found C, 77.43; H, 6.99; N, 8.76%.

2.2.4.13. Tert–butyl 5-cyano-8-(naphthalen-1-yl)−6-(piperidin-1-yl)−3,4-dihydroquinoline-1(2H)-carboxylate ***9m***. Colourless solid; yield: 76%; mp: 175–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.41–1.11 (m, 9H, CH_3), 1.40–1.59 (m, 2H, CH_2), 1.61–1.94 (m, 5H, CH_2), 2.02–2.38 (m, 1H, CH_2), 2.43–2.79 (m, 1H, CH_2), 2.88–3.29 (m, 6H, NCH_2), 3.61–4.35 (m, 1H, CH_2), 6.69–7.01 (m, 1H, ArH), 7.21–7.67 (m, 5H, ArH), 7.68–7.97 (m, 2H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 24.1, 26.2, 27.6, 43.7, 53.4, 79.2, 104.4, 107.4, 109.9, 114.7, 117.3, 119.3, 121.7, 125.0, 125.7, 126.4,127.3, 127.9, 128.5, 132.4, 139.9, 142.7, 155.3 ppm; IR (KBr): 2214 cm^{-1} (CN), 1690 cm^{-1} (C=O), 1589 cm^{-1} (C=C), 1233 cm^{-1} (C–N), 1048 cm^{-1} (C–O); MS (EI): m/z = 468 [M + 1]$^+$; Anal. for $C_{30}H_{33}N_3O_2$: C, 77.06; H, 7.11; N, 8.99; Found C, 77.27; H, 7.03; N, 8.75%.

2.2.4.14. Tert–butyl 5-cyano-8-(naphthalen-2-yl)−6-(4-phenylpiperazin-1-yl)−3,4-dihydroquinoline-1(2H)-carboxylate ***9n***. Colourless solid; yield: 73%; mp: 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.61–0.98 (m, 9H, CH_3), 1.50 (s, 2H, CH_2), 1.74–2.06 (m, 1H, CH_2), 2.14–2.86 (m, 2H, CH_2), 3.17–3.50 (m, 8H, NCH_2), 3.97–4.62 (m, 1H, CH_2), 6.82 (t, J = 8.0 Hz, 1H, ArH), 6.87–7.03 (m, 3H, ArH), 7.22 (t, J = 8.0 Hz, 2H, ArH), 7.36–7.52 (m, 3H, ArH), 7.70–7.89 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 26.2, 27.4, 28.5, 49.6, 51.9, 80.7,104.7, 116.5, 116.8, 118.7, 120.1, 125.8, 126.5, 126.6, 127.7, 127.8, 128.1, 128.4, 129.2, 132.1, 132.8, 133.5, 142.8, 145.8, 151.2, 153.5 ppm; IR (KBr): 2206 cm^{-1} (CN), 1692 cm^{-1} (C=O), 1591 cm^{-1} (C=C), 1232 cm^{-1} (C–N), 1050 cm^{-1} (C–O); MS (EI): m/z = 545 [M + 1]$^+$; Anal. for $C_{35}H_{36}N_4O_2$: C, 77.18; H, 6.66; N, 10.29;. Found C, 77.09; H, 6.29; N, 10.04%

2.2.4.15. Tert–butyl-8-([1,1′-biphenyl]−4-yl)−5-cyano-6-(piperidin-1-yl)−3,4-dihydroquinoline-1(2H)-carboxylate ***9o***. Colourless solid; yield: 75%; mp: 212–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79–1.19 (m, 9H, CH_3), 1.46–1.61 (m, 2H, CH_2), 1.62–1.89 (m, 5H, CH_2), 2.02–2.39(m, 1H, CH_2), 2.49–2.78 (m, 1H, CH_2), 2.90–3.24 (m, 6H, NCH_2),4.26– 4.59(m, 1H, CH_2), 6.83 (s, 1H, ArH), 7.26–7.33 (m, 1H, ArH), 7.33–7.47 (m, 4H, ArH), 7.48–7.65 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 24.1, 26.1, 26.2, 27.5, 43.1, 53.5, 80.7, 104.0, 117.0, 118.3, 127.0, 127.4, 127.5, 128.3, 128.9, 131.0, 131.1, 131.05, 140.9, 142.2, 153.6, 154.9 ppm; IR (KBr): 2209 cm^{-1} (CN), 1715 cm^{-1} (C=O), 1589 cm^{-1} (C=C), 1233 cm^{-1} (C–N), 1049 cm^{-1} (C–O); MS (EI): m/z = 494 [M + 1]$^+$; Anal. for $C_{32}H_{35}N_3O_2$: C, 77.86; H, 7.15; N, 8.51. Found C, 77.53; H, 7.01; N, 8.19%

2.2.4.16. Tert–butyl 8-([1,1′-biphenyl]−4-yl)−5-cyano-6-morpholino-3,4-dihydroquinoline-1(2H)-carboxylate ***9p***. Colourless solid; yield: 75%; mp: 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.74–1.15 (m, 9H, CH_3), 1.15–1.52 (m, 1H, CH_2), 1.63–1.95 (m, 1H, CH_2), 2.06–2.36 (m, 1H, CH_2), 2.38–2.90 (m, 1H, CH_2), 2.91–3.35 (m, 5H, NCH_2), 3.83 (s, 4H, OCH_2), 3.94–4.67 (m, 1H, CH_2), 6.84 (s, 1H, ArH), 7.25–7.33 (m, 1H, ArH), 7.34–7.47 (m, 4H, ArH), 7.48–7.67 (m, 4H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 23.9, 26.1, 27.5, 43.1, 52.2, 67.1, 80.2, 104.8, 116.8, 118.1, 127.0, 127.5, 128.2, 128.9, 132.0, 138.3, 140.5, 140.7, 141.0, 142.4, 153.4 ppm; IR (KBr): 2214 cm^{-1} (CN), 1692 cm^{-1} (C=O), 1602 cm^{-1} (C=C), 1262 cm^{-1} (C–N), 1061 cm^{-1} (C–O); MS (EI): m/z = 496 [M + 1]$^+$; Anal. for $C_{31}H_{33}N_3O_3$: C, 75.13; H, 6.71; N, 8.48; Found C, 74.97; H, 6.31; N, 8.21%.



Scheme 1. Synthesis of 6-aryl-4-amino-2*H*-pyran-2-ones **7** starting from ketene dithioacetal **3**.

2.2.4.17. Tert–butyl-5-cyano-6-(piperidin-1-yl)-3,4,7,8-tetrahydronaphtho[2,1-h]quinoline-1(2H)-carboxylate ***11***. Colourless solid; yield: 76%; mp: 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 9H, CH_3), 1.17 (s, 1H, CH_2), 1.54–1.70 (m, 4H, CH_2), 1.71–1.87 (m, 2H, CH_2), 2.08–2.31 (m, 2H, CH_2), 2.44–2.64 (m, 2H, CH_2), 2.65–2.76 (m, 1H, CH_2), 2.80–3.32 (m, 6H, CH_2), 3.59 (s, 1H, CH_2), 4.16–4.49 (m, 1H, CH_2), 7.05–7.16 (m, 2H, ArH), 7.20–7.25 (m, 1H, ArH), 7.47–7.58 (m, 1H, ArH) ppm; ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 24.0, 24.2, 24.7, 25.8, 27.5, 29.5, 42.8, 52.1, 80.5, 106.5, 117.8, 125.1, 126.9, 127.6, 128.1, 132.3, 134.2, 135.7, 136.7, 137.9, 138.5, 150.9, 153.3 ppm; MS (EI): *m/z* = 444 $[M + 1]^+$; IR (KBr): 2214 cm^{-1} (CN), 1691 cm^{-1} (C=O), 1565 cm^{-1} (C=C), 1218 cm^{-1} (C–N), 1061 cm^{-1} (C–O); Anal. for $C_{28}H_{33}N_3O_2$: C, 75.81; H, 7.50; N, 9.47; Found C, 75.43; H, 7.15; N, 9.31%.

3. Results and discussions

3.1. Synthesis of compounds ***9a-p*** *and* ***11***

With the comprehensive literature framework, we describe an alternate approach for synthesizing functionalized *N-Boc* protected tetrahyroquinoline derivatives **9** using 6-aryl-4-amino-2*H*-pyran-2-ones **7** as starting material. The synthesis of parent precursors **7** was achieved in two chemical steps (Scheme 1) [57]. In first step, ethyl 2-cyano-3,3-dimethylsulfanylacrylate **3** [42] was treated with functionalized aryl ketones **4** in the presence of KOH in DMSO to form 2-pyranones **5** in 57–73% yields [58]. In the second step, the synthesized 2-pyranones **5** were reacted with cyclic amines **6** in methanol at reflux temperature to form 6-aryl-4-amino-2*H*-pyran-2-ones **7** in 71–85% [57, 58]. The synthon **3** was ultimately prepared by reacting ethyl cyanoacetate with carbon disulfide (CS_2) followed by methylation in methanol under alkaline condition in 84% yield [42]. Furthermore, the functionalized *N-Boc* protected tetrahyroquinoline derivatives **9** was successfully synthesized through ring transformation of 6-aryl-4-amino-2*H*-pyran-2-ones **7** with commercially available *tert*–Butyl 3-oxopiperidine-1-carboxylate **8** in an ultrasonic bath in the presence of KOH (1.2 equiv) and minimum amount of DMF. Overall, the ultrasound-assisted method is a hands-on method and also an economical pathway for the preparation of the desired product with high yields and less time-consuming.

In order to find the optimized reaction condition, various solvents and bases were screened by taking 2-oxo-6-phenyl-4-(4-phenylpiperazin-1-yl)-2*H*-pyran-3-carbonitrile **7a** (1.0 equiv) and *tert*–butyl 3-oxopiperidine-1-carboxylate (1.2 equiv) **8** as model substrates and the results are shown in Table 1. At first, we performed the reaction of 2-oxo-6-phenyl-4-(4-phenylpiperazin-1-yl)-2*H*-pyran-3-carbonitrile **7a** with *tert*–butyl 3-oxopiperidine-1-carboxylate **8** in the presence of KOH as a base in DMF and the desired product **9a** was isolated in 74% yield (Table 1, entry 1). With these preliminary results, we started monitoring the formation of required product **9a** in the presence of NaOH which gave 64% yield (Table 1, entry 2). Reaction performed using K_2CO_3 as base resulted in poor product **9a** yield (Table 1, entry 3). The product formation is observed in the presence of KO^{t}Bu and desired product was isolated in 59% (Table 1, entry 4). However, the reaction failed in the case of Et_3N and the reactants were recovered completely (Table 1, entry 5).

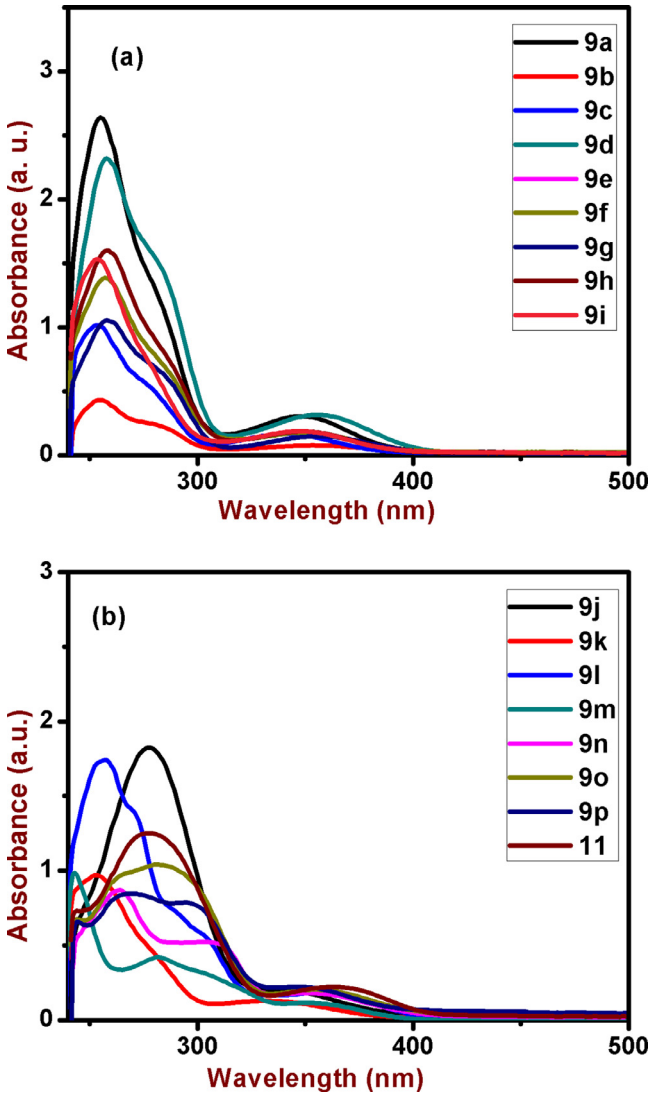
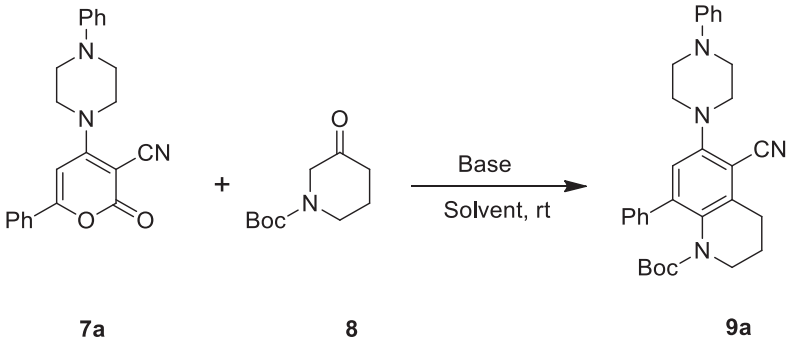


Fig. 2. UV–Vis spectra of compounds in chloroform (a) **9a-i**; (b) **9j-p** and **11**.

Moreover, the progress of the reaction was further monitored using various solvents based on their polarity. We began the ring transformation reaction of **7a** and **8** in DMF using KOH and the desired product **9a** was obtained in 74% yield (Table 1, entry 1). Later, the same reaction was performed in DMSO as a solvent and reac-

Table 1
Screening of base and solvent for the ring transformation reaction of 2-oxo-6-phenyl-4-(4-phenylpiperazin-1-yl)-2*H*-pyran-3-carbonitrile **7a** with *N*-Boc 3-piperidone **8** to **9a**.



7a **8** **9a**

Entry	Base	Solvent	Time	Yield (%)
1	KOH	DMF	10 h	74
2	NaOH	DMF	10 h	64
3	K_2CO_3	DMF	10 h	10
4	KO^{t}Bu	DMF	10 h	59
5	Et_3N	DMF	10 h	–
6	KOH	DMSO	10 h	66
7	KOH	MeCN	10 h	traces
8	KOH	Et_2O	10 h	–
9	KOH	MeOH	10 h	–
10	KOH	$CHCl_3$	10 h	–
11[a]	KOH	DMF	45 min	85

[a] Reaction was performed in an ultrasonic bath at room temperature.

tion product **9a** was formed in 66% (Table 1, entry 6). However, the course of reaction was found quite similar in both DMF and DMSO. Furthermore, the course of the reaction was analysed in MeCN and reaction could not proceed (Table 1, entry 7). Additionally, the ring reaction was unsuccessful when Et_2O, MeOH and $CHCl_3$ were used as solvents (Table 1, entries 8–10). After getting the optimized condition, it was found that the KOH and DMF are the suitable base and solvent for the ring transformation of lactone **7a** (1.0 equiv) with *tert*–butyl 3-oxopiperidine-1-carboxylate (1.2 equiv) **8** to desired product **9a** was found the best conventional reaction condition**.**

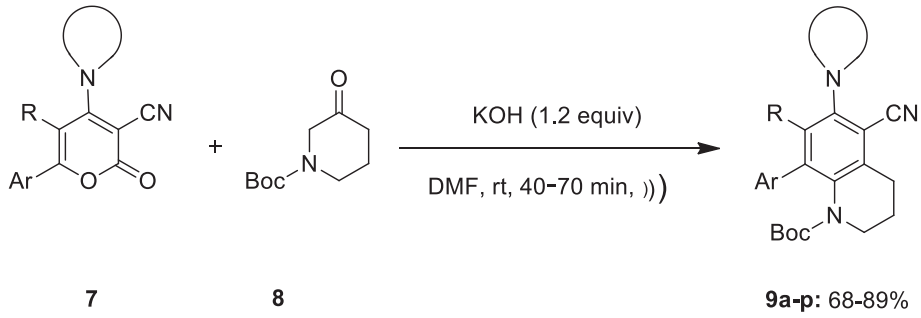
Based on the observed results, ring transformation of lactone **7** with *tert*–butyl–3-oxopiperidine-1-carboxylate (1.2 equiv) **8** in the presence of KOH (1.2 equiv) in DMF at room temperature for 10 h shows good yield of desired product **9a**. In this regard, the only limitation was prolonged reaction timing. Therefore, we subsequently concentrate on reducing the time of the reaction. Among the other methods, sonication is an alternate technique to achieve the chemical reactions. Sonication is advantageous over the conventional reaction conditions due significant decrease in reaction time by increasing in the reactivity. Moreover, it provides minimum or no adverse impact on our environment and considered as a green chemistry laboratory technique. It works by the principle of cavitation involving the growth, oscillation and bubble collapse by acoustic field. Chemical reactivity increases by ultrasound by the formation and the collapse of the cavitation bubbles in a liquid medium [59]. Cavitation is better attained at lower temperatures when there is a constant ultrasonic power of the generator. When the temperature increases, the vapor pressure of the solvent raises and hence the cavitation bubbles are filled with more solvent vapor that tends to collapse less violently. This ultimately leads to less sonication effects. Dissolved gas bubbles can act as nuclei for cavitation favoring the ultra-sonication process [60].

Thus, we thought to utilize this green technique in our ring transformation reaction. Next, fresh reaction mixture of 6-aryl-2-oxo-4-(*sec*.amino)-2*H*-pyran-3-carbonitrile **7a** and *tert*–butyl–3-oxopiperidine-1-carboxylate (1.2 equiv) **8** in the presence of KOH in DMF was subjected to ultrasound irradiation in an ultrasonic bath at room temperature. As expected, the reaction time was reduced to 45 min and the anticipated product **9a** was obtained in 85% yield (Table 1, entry 11).

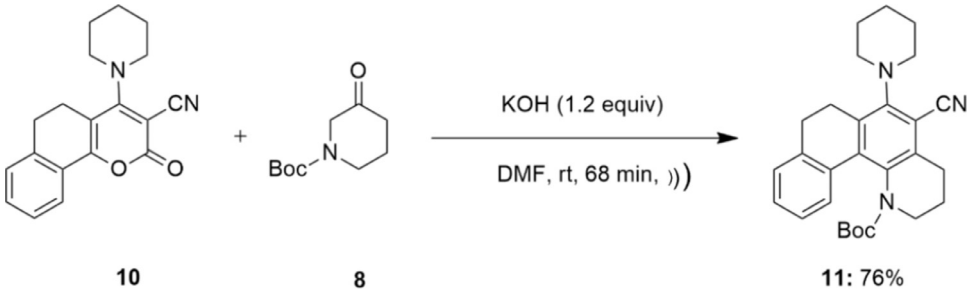
With this optimum reaction condition (Table 1, entry 11), we have synthesized *N*–*tert*–butyloxycarbonyl-protected tetrahydroquinoline derivatives **9a–q** in good yield by treating 6-aryl-2-oxo-4-(*sec*.amino)-2*H*-pyran-3-carbonitriles **7** with *tert*–butyl 3-oxopiperidine-1-carboxylate (1.2 equiv) **8** in the presence of powdered KOH (1.2 equiv) in DMF at room temperature under ultrasound irradiation condition for 40–70 min (Table 2, entries 1–16). Interestingly, the precursor 6-aryl-4-amino-2*H*-pyran-2-ones **7** showed versatility towards the ring transformation reaction and both electron-donating and withdrawing groups were successfully tolerated under given reaction conditions. Initially, we performed the ring transformation of simple 6-phenyl-2-oxo-4-(*sec*.amino)-2*H*-pyran-3-carbonitriles **7a–7c** containing different cyclic secondary amines such as ***N*-**phenylpiperazine, piperidine and morpholine and the desired ring transformed products **9a-c** were isolated in 78–85% yields (Table 2, entry 1–3).

Later, the feasibility of the ring transformation was analyzed with the 6-aryl-4-amino-2*H*-pyran-2-ones **7d–7i** bearing electron-withdrawing groups in the phenyl ring. The ring transformed products **9d–9i** were obtained in excellent yields (Table 2, entries 4–9). Furthermore, we explored the feasibility of the desired product in the presence of electron donating groups in **7j** and **7k**. It was observed that the yields of **9j** and **9 K** slightly reduced when compared to the precursors bearing electron withdrawing groups (Table 2, entries 10 and 11). In the same way, bulky 6-naphthyl-4-amino-2*H*-pyran-2-ones have been participated in the ring transformation reaction and corresponding ring transformed products **9l-n** were obtained in moderate yields (Table 2, entries 12–14). Similarly, the scope of the reaction was expanded with 6-biphenyl-4-amino-2*H*-pyran-ones (Table 2, entries 15 and16) and the reaction products were obtained in good

Table 2
Synthesis of *N*–*tert*–butyloxycarbonyl-protected tetrahydroquinoline **9** through ring transformation of 6-aryl-4-amino-2*H*-pyran-2-ones **7** with *tert*–butyl 3-oxopiperidine-1-carboxylate **8**.



Entry	9	Ar	R	amine	Time (min)	Yield (%)
1	**9a**	C_6H_5	H	*N*-phenylpiperazin-1-yl	45	85
2	**9b**	C_6H_5	H	piperidin-1-yl	40	83
3	**9c**	C_6H_5	H	morpholin-1-yl	45	78
4	**9d**	4-ClC_6H_4	H	piperidin-1-yl	48	89
5	**9e**	4-ClC_6H_4	H	morpholin-1-yl	48	82
6	**9f**	4-ClC_6H_4	H	*N*-phenylpiperazin-1-yl	50	89
7	**9 g**	4-BrC_6H_4	H	piperidin-1-yl	40	81
8	**9h**	4-BrC_6H_4	H	*N*-phenylpiperazin-1-yl	41	84
9	**9i**	3,4–ClC_6H_4	H	*N*-phenylpiperazin-1-yl	45	81
10	**9j**	4-MeC_6H_4	H	piperidin-1-yl	52	69
11	**9k**	4-ClC_6H_5	Me	piperidin-1-yl	44	72
12	**9l**	1-Naphthyl	H	piperidin-1-yl	65	68
13	**9m**	2-Naphthyl	H	piperidin-1-yl	48	76
14	**9n**	2-Naphthyl	H	*N*-phenylpiperazin-1-yl	70	73
15	**9o**	4-biphenyl	H	piperidin-1-yl	57	75
16	**9p**	4-biphenyl	H	morpholin-1-yl	66	75



Scheme 2. The ring transformation of 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[h]chromene-3-carbonitrile **10** with *N*-Boc-3-piperidone **8** to corresponding ring transformed product **11**.

yields. Finally, our efforts were directed to explore the possibility of the nucleophile **8** with 2-oxo-4-(piperidin-1-yl)-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile **10**. The ring transformation reaction was performed under same reaction and condition and corresponding ring transformed product **11** was isolated in 76% yield (Scheme 2). All the synthesized compounds **9a**-**p** and **11** were characterized by their spectroscopic analysis.

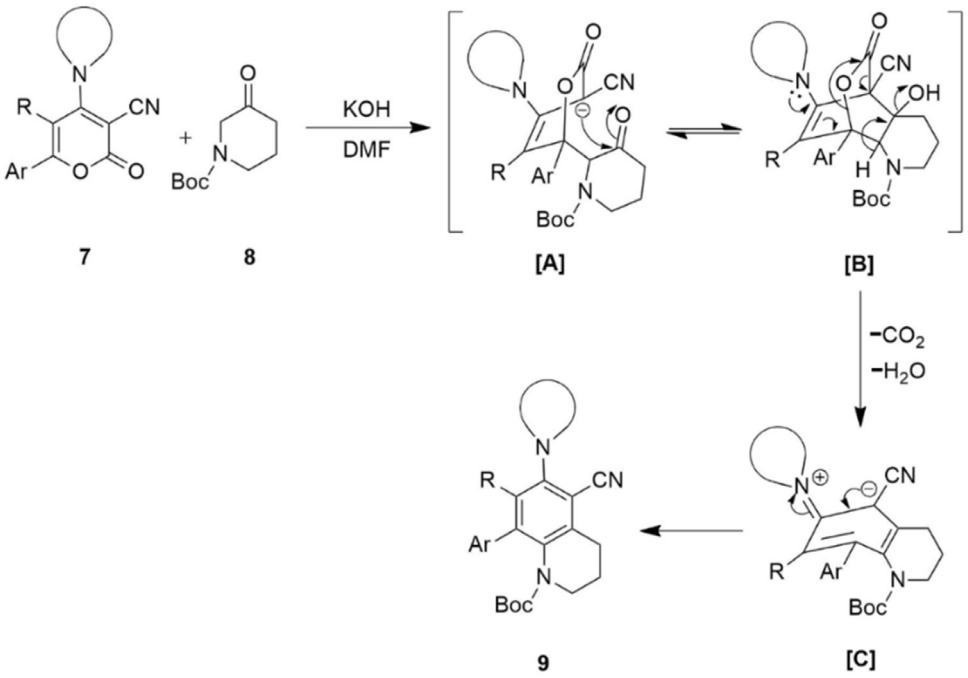
Based on the reported literature [48], the possible mechanistic pathway for the ring transformation of 6-aryl-2*H*-pyran- 2-ones **8** to *N*–*tert*–butyloxycarbonyl protected tetrahydroquinolines **9** is illustrated in Scheme 3. Initially, the presence of base could trigger the anion generation of *tert*–Butyl 3-oxopiperidine-1-carboxylate which attacks the C-6 position of 6-aryl-2*H*-pyran-2-ones through the Michael addition and gives intermediate **[A]**. Immediately, the bicyclic intermediate **[B]** was formed by the intramolecular cyclization of intermediate **[A]** involving the C-3 position of pyran ring and the carbonyl functionality. Further, bicyclic intermediate provides intermediate **[C]** by decarboxylation and dehydration. Finally, intermediate **[C]** undergoes aromatization to afford the *N*-Boc protected 1,2,3,4-tetrahydroquinolines.

*3.2. Photophysical properties of compounds **9a-p** and **11***

Generally, quinolines and quinolones are excellent fluorescent compounds, suitable for various applications such as the fluorescent probe for bio-imaging [8], solar cells [11] and OLED [16]. Interestingly, the entire synthesized *N*–*tert*–butyloxycarbonyl-protected tetrahydroquinolines **9** and **11** exhibit blue emission under UV lamp in a solution state.

In this regard, the optical properties of the synthesized compounds **9a–p** were studied by recording the absorption and emission spectra in the solution of concentration ~10^{-5} M in $CHCl_3$. The relative quantum yield of all the compounds were determined using quinine sulfate in 0.1 M H_2SO_4 ($\phi = 0.54$) and the optical band gap was also calculated using UV-DRS spectra using the formula $E_g = 1242/\lambda_{max}$ [61]. Moreover, the stokes shift of all the synthesized compounds were also calculated.

In UV–Vis absorption all the compounds **9a–p** shows two major peaks, the peak appears in the shorter wavelength region between 243 and 293 nm corresponds to $\pi-\pi^*$ electronic transition due to the chromophores corresponding to aromatic π system (Fig. 3a and



Scheme 3. Plausible mechanism for the synthesis of tetrahydroquinoline **9** via ring transformation reaction of 6-aryl-2*H*-pyran-2-ones **7** cyclic ketone **8** as carbanion source.

Fig. 3b). The longer wavelength absorption peak at 334–361 nm appears due to the electronic transition corresponds probably due to internal charge transfer from tertiary amino group and nitrogen atom in the ring (Fig. 3a and Fig. 3b).

While comparing the emission spectra of the tetrahydroquinolines **9a**–**9p**, the maximum emission wavelength appears between 435 and 470 nm (Fig. 3). In the simple phenyl substituted compounds **9a**–**9c,** emission wavelength was obtained in between 422 and 461 nm (Fig. 3a). Meanwhile, few blue fluorescing tetrahydroquinolines **9d**–**9i** bearing electron withdrawing substituents in the phenyl ring showed the emission wavelength in between 440 and 470 nm (Fig. 3a). Similarly, the tetrahydroquinolines **9d**–**9i** bearing electron donating moieties **9j** and **9k** exhibit the emission in the range of 427–438 nm (Fig. 3b).

Notably, slight blue shift was observed when the simple phenyl is replaced with naphthyl or biphenyl rings in the products **9l-p** (Fig. 3b).

Furthermore, our efforts were directed towards photophysical studies by UV–Vis and fluorescence spectroscopy. The UV–Vis absorption spectrum of benzochromene based tetrahydroquinoline **11** shows strong absorption peak at 247 nm attributed to π-π^* transition and weak absorption band appears around 349 nm due to the n-π^* transition. The fluorescence spectrum of compound **11** shows emission maxima at 466 nm and exhibits large stokes shift due to the presence of bulky group and intramolecular charge transfer (ICT).

The optical band gap of compounds **9a**-**p** and **11** were calculated using the formula $E_g = 1242/\lambda_{max}$ [61] longest wavelength from UV-DRS measurements which explains the band structure and nature of conducting material, modified by tuning the functionalities in an organic compounds. The band gap of the compounds **9a–p** and **11** ranging between 3.01–3.29 eV are detail is summarized in Table 4. It was observed that the compounds **9l** and **9j** exhibit lower band gap of 3.01 eV and 3.04 eV. Based on the results, it was observed that the optical band gap of the synthesized compounds may be highly influenced by the amine functionality at the C-6 position and the aryl substrates at C-8 position of the 1,2,3,4-tetrahydroquinolines. Finally, the quantum yields

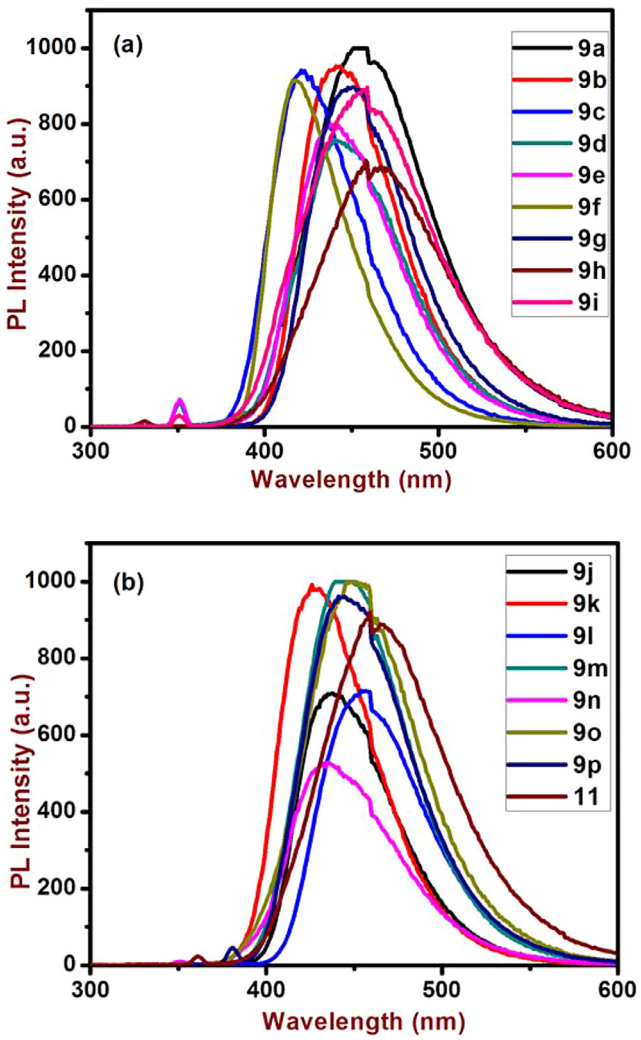
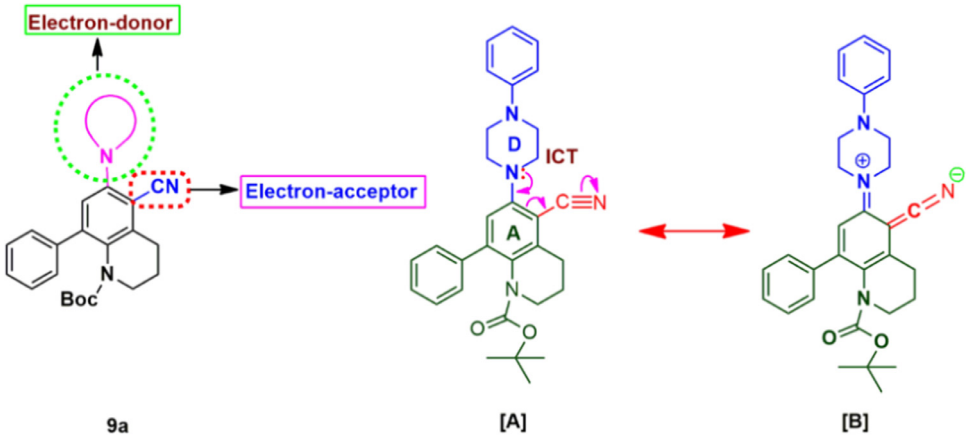


Fig. 3. Fluorescence spectra of compounds in chloroform (a) **9a-i**; (b) **9j-p** and **11**.



Scheme 4. Donor/acceptor based tetrahydroquinoline molecule.

of compounds **9a–p** were calculated by using quinine sulfate in 0.1 M H_2SO_4 (ϕ = 0.54). All the synthesized compounds exhibit the quantum yield in the range from 0.19 to 0.74. Interestingly, compounds **9a, 9f, 9h, 9l, 9m** and **9o** exhibited better quantum yield compare to quinine sulfate while compound **9f** showed the best quantum yield (ϕ = 0.74).

Likewise, the stokes shift values were also calculated for all the compounds **9a-q** and obtained in the range of 5387 to 7112 cm^{-1} due to internal charge transfer between the donor and acceptor part of the molecule. Based on the results we found few molecules such as **9a, 9h, 9j** and **9o** shows comparatively large stokes shift. Among that, the molecule **9a** bearing *N*-phenylpiperazine at C-6 position showed slightly red shifted in the emission spectrum due to the intramolecular charge transfer associated with extended π-electron conjugation in the *N*-phenylpiperazine. Moreover, **9h** exhibits higher emission wavelength comparatively to all the molecules due to the bulky bromo group substituted in the phenyl ring when compared to **9i** substituted with methyl group. Interestingly, the molecule **9o** possessing piperidine in C-6 position and biphenyl group in C-8 position shows slight red shift in the emission region which is attributed to the intramolecular charge transfer between piperidine and cyano group, also exhibits a greater influence in the rigidity in the molecule.

We carried out the solvatochromic response of compound **9a** with various solvents possessing different polarity index which investigates the effect of solvent and solute interaction on excited state. Tetrahydroquinoline **9a** shows good solvatochromic shift based on the increasing polarity of the solvents for toluene (λ_{max}, UV = 332 nm and λ_{max}, PL = 440 nm) to chloroform (λ_{max}, UV = 348 nm and λ_{max}, PL = 461 nm) to THF (λ_{max}, UV = 349 nm and λ_{max}, PL = 470 nm) to acetonitrile (λ_{max}, UV = 357 nm and λ_{max}, PL = 489 nm). The maximum shift was observed for DMSO (λ_{max}, UV = 365 nm and λ_{max}, PL = 493 nm) and DMF (λ_{max}, UV = 385 nm and λ_{max}, PL = 496 nm) as given in Fig. 4a and b, Table 4.

These experimental results confirm the π-conjugated tetrahydroquinolines shows positive solvatochromic effect, as the polarity of the solvent increases the peak is shifting to the red end of the fluorescence spectrum due to the intramolecular charge transfer process. This positive solvatochromic effect is favored only when the excited-state of the molecule acquire greater dipole moment is related to its ground state as from non-polar solvent to polar solvent [62,64].

A possible mechanism of fluorescence involves internal charge transfer (ICT) in the compound 9a is given in Scheme 4. In tetrahydroquinoline molecules, the central core unit is attached to electron rich (amino group) in C-6 position and strong electron withdrawing group (CN group) in C-5 position which makes them suitable for internal charge transfer (ICT). During the photo excitation, the lone pair of electron of amine functionality is usually transfer

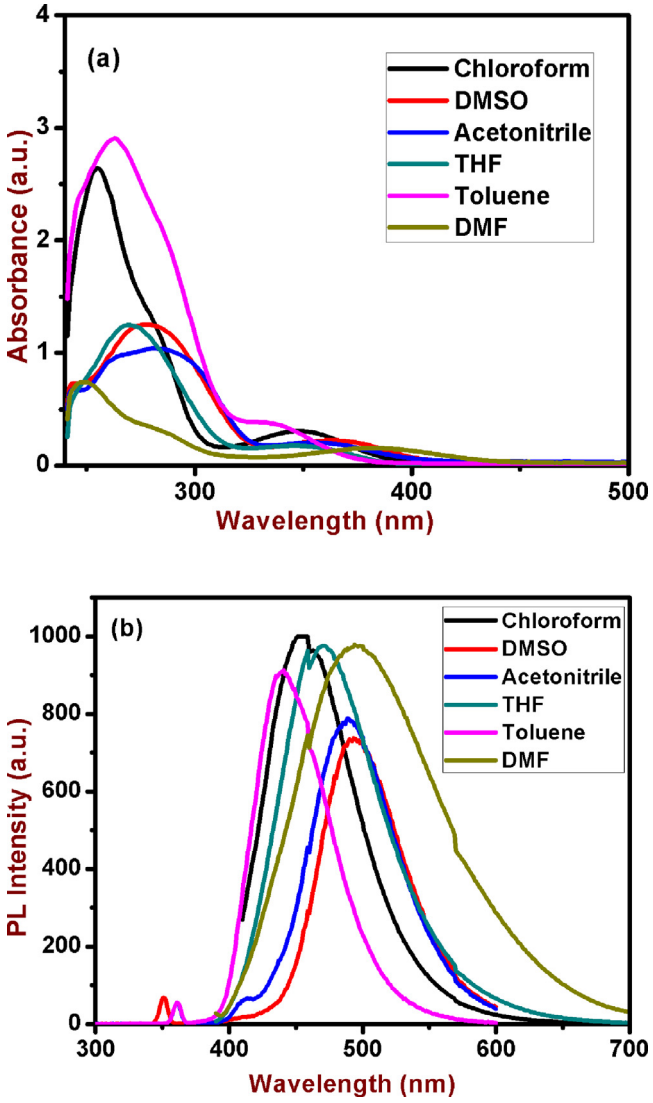


Fig. 4. (a) UV–Vis spectra of compound **9a** in different solvents; (b) PL spectra of compound **9a** in different solvents.

Table 3
Different photophysical parameters of compounds **9a**–**p** and **11**.

Entry	Compound	λ_{max} (abs) (nm)	λ_{max} (em) (nm)	E_{op} (eV)	Φ	$\Delta\bar{\upsilon}$ (cm^{-1})
1	**9a**	255, 348	461	3.11	0.58	7027
2	**9b**	255, 354	444	3.25	0.48	5726
3	**9c**	253, 338	422	3.28	0.45	5889
4	**9d**	258, 355	442	3.11	0.19	5387
5	**9e**	256, 349	440	3.21	0.46	5926
6	**9f**	257, 350	466	3.08	0.74	7112
7	**9 g**	258, 355	449	3.29	0.47	5739
8	**9h**	258, 351	470	3.18	0.69	7213
9	**9i**	254, 349	460	3.25	0.51	6914
10	**9j**	277, 343	438	3.04	0.47	6324
11	**9k**	253, 334	427	3.25	0.52	6521
12	**9l**	256, 361	456	3.01	0.57	5819
13	**9m**	243, 356	446	3.16	0.66	5719
14	**9n**	263, 352	435	3.18	0.22	5420
15	**9o**	247, 349	466	3.18	0.58	7148
16	**9p**	282, 356	451	3.09	0.40	5917
17	**9q**	293, 348	443	3.18	0.34	6163

Table 4
Absorbance and emission maxima of the compound **9a** in various solvents.

Entry	Solvents	λ_{max}, UV (nm)	λ_{max}, PL (nm)
1	Toluene	262,332	440
2	Chloroform	255, 348	461
3	THF	269, 348	470
4	Acetonitrile	283, 357	489
5	DMSO	279, 365	493
6	DMF	249, 385	496

to the benzene ring of the molecule containing electron withdrawing group in the excited state [62,63] (Scheme 4).

4. Conclusion

In conclusion, we have developed an ultrasound-assisted rapid synthesis of *N*–*tert*–butyloxycarbonyl protected tetrahydroquinolines **9** via carbanion induced ring transformation reaction of 6-aryl-2*H*-pyran-2-ones **7** with *tert*–butyl 3-oxopiperidine-1-carboxylate **8** under mild reaction conditions. Our methodology is associated with notable advantages such as easy work-up procedure, environmental friendly conditions, and shorter reaction time and offers the flexibility of introducing electronic donating and withdrawing groups in tetrahydroquinoline systems. Our synthetic approach offers a possibly alternative to the conventional transition metal–catalyzed cross-coupling reactions. Additionally, the photophysical behavior of the synthesized molecules was studied by using UV–Vis and fluorescence spectroscopy. All the synthesized compounds **9** and **11** exhibit blue fluorescence in the range 435–470 nm. The donor-acceptor based tetrahydroquinolines substituted with bulky groups can be designated as tunable ICT molecules possessing considerable changes in their photophysical behavior. Moreover, the other photophysical parameters such as optical band gap, quantum yield and stokes shift were calculated. The fluorescent compounds **9** and **11** might be the strong candidates in the future for developing new Organic Light Emitting Devices (OLED). Further investigations about this ring transformation approach and its application in our research group are currently in progress (Table 3 and Fig. 4).

Author statement

C. Subashini: Synthesis of all the compounds, recorded spectral data and recorded UV, fluorescence and prepared manuscript and supporting information.

L. John Kennedy: Supported in analysing of photophysical parameters of synthesizing compounds.

Fateh V. Singh: Supervision, proposal of work, arranging of chemicals, reviewing and editing of the manuscript.

Declaration of Competing Interest

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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129365.

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