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ORIGINAL ARTICLE

Synthesis of Green/Blue Light Emitting Quinolines by Aza-D-A Reaction Using $InCl_3$ Catalyst

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Abstract

An efficient $InCl_3$-catalyzed sequential reaction of aromatic amines, aromatic aldehydes and functionalized alkynes leading to the formation of new quinoline derivatives exhibiting significant fluorescence activities is described. The photophysical investigations of quinolines were carried out by absorption and photoluminescence measurements. One particular compound 4 **h** having maximum intensity, emitting green colour ($\Phi = 0.78$) with average life time of 6.20 ns was the best amongst the tested compounds**.** The presence of the amino group at the 4-aryl substituent of the quinoline backbone played an important role in executing the Povarov cyclization successfully and enhancing the flourescence properties of the newly synthesized quinolines.

Keywords 2-Ethynylaniline · Quinolines · Life time · Photophysical properties · Povarov reaction

Introduction

Quinolines constitute an important class of *N*-based heterocyclic aromatic compounds occurred as natural products and synthetic complex organic molecules [1–4]. They are well known for exhibiting broad spectrum of biological activities like antitumor, antimalarial, antibacterial, antifungal, antiparasitic and insecticidal, antiviral, anti-inflammatory, antiplatelet and other activities [5–8]. The most well-known and significant quinoline alkaloids are chloroquinine and hydroxychloroquine as antimalarial drugs recently associated with the treatment of the pandemic SARS-CoV-2 [9] and camptothecin an anticancer drug [10, 11] development respectively, (Fig. 1). In addition to bioactivity, quinolines scaffolds also show luminescent properties with potential applications in organic solar cells (OSCs), organic light emitting diodes (OLEDs), biomolecular markers, molecular probes and switches [12–14]. Moreover, quinoline-based dyes such as ethyl red iodide and pinacyanol (Fig. 1) have been used since the beginning of the nineteenth century in photographic plates [15] The diverse applications of quinolines as functional materials is related to its excellent mechanical properties and high quantum yields, making ideal materials in the electron transport [16] and presenting essential characteristics for their subsequent use in OLEDs [17]. Hence, a significant advance in luminescence efficiency and brightness in OLEDs is observed when conjugated organic compounds contain quinoline moeties [18] Povarov reaction (aza Diel-Alder reaction) [19] remains one of the most efficient methods affording highly substituted and densely functionalized quinoline frameworks. Povarov reaction involves [4 + 2] cycloaddition reaction of *N*-aryl imines with electron-rich dienophiles via activation of a terminal alkyne C-H bond and complexation of C-C multiple bonds to facilitate C-N and C-C bond formation, which are key intermediates for the construction of quinolines [20]. Recently, many metal salts like CuCl/AuCl [21] $AuCl_3$/CuBr [22], $Yb(OTf)_3$ [23], $Fe(OTf)_3$ [24], $Cu(OTf)_2$ [25], $Zn(OTf)_2$ [26], AgNTf [27], $NbCl_5$ [28] are explored as effective Lewis acid catalytic system for quinoline synthesis though Povarov started with $BF_3.OEt_2$ in his original work [19]. Thus, the development of simple and efficient protocols for quinolines containing unique substituent from readily available starting materials is of great interest to organic chemists.

Rajkumar Romeshkumar Singh and Thokchom Prasanta Singh contributed equally to this work.

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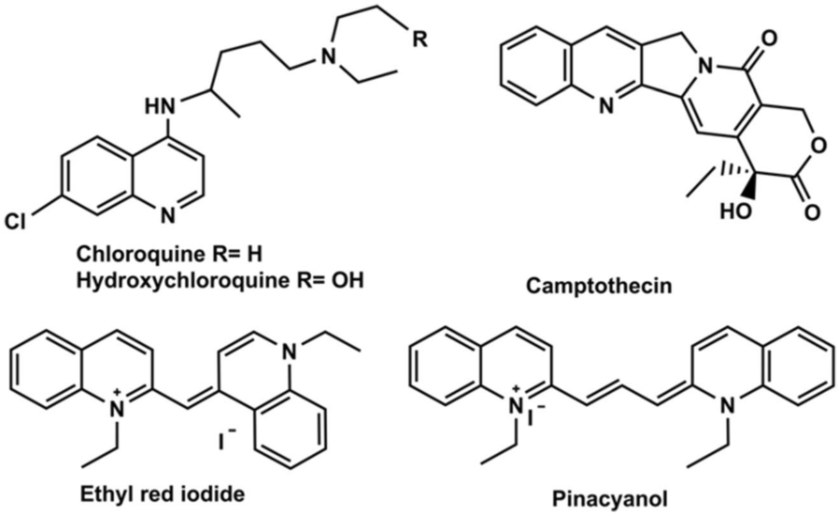


Fig. 1 Biological and fluorescent actives Quinolines

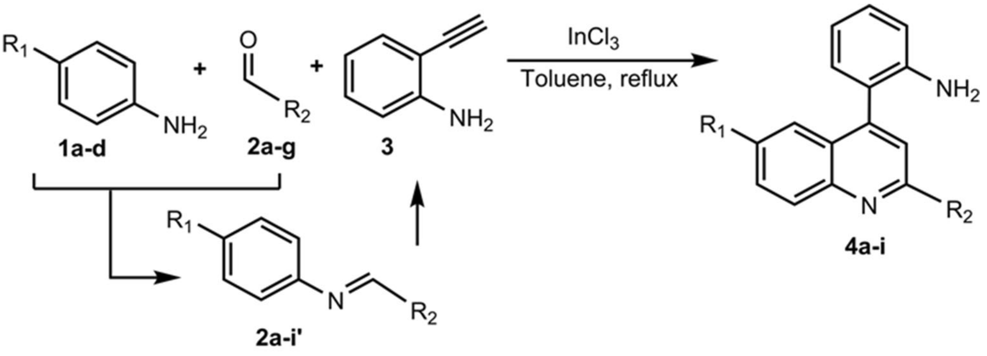
Indium trichloride ($InCl_3$) has been widely used in organic transformations for the construction of complex heterocycles [29–31]. In continuation of our efforts on exploring the catalytic potential of $InCl_3$ for the synthesis of novel *N*-heterocycles [32–34], we herein report the $InCl_3$-mediated efficient synthesis and the optical characterization of new 2,4-disubstituted quinoline derivatives having potential application as dyes in organic electronic devices (Scheme 1).

Materials and Methods

Reagents and Instruments

All reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. For compounds **(4a-i)** ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker spectrometer using $CDCl_3$ whereas ^1H NMR (400 MHz) spectrum for compound **4b** was recorded on FT-NMR spectrometer using $CDCl_3$. Chemical shifts δ are in parts per million (ppm) with $CDCl_3$ as solvent and are relative to tetramethylsilane (TMS) as the internal reference. Data are reported as follows: chemical shift, multiplicity(s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet) and coupling constants (*J*) in Hertz. The FT-IR spectra were recorded on a FT-IR spectrometer (KBr). Gas chromatography-electron impact mass spectrometry (GC-EIMS) spectra were measured on a Varian spectrometer using ionization by fast atom bombardment (FAB). Melting points were determined on a "*Veego*" capillary melting point apparatus and are uncorrected. All the luminescence spectra and quantum yield were recorded using *Horiba Fluoromax 4 Spectrophotometer*. Samples were dissolved in different solvents and 2 mL of each solution was put in a 3 mL quartz cuvette and it was mounted on the sample holder. All the measurements were carried out at room temperature. For quantum yield measurement, the above cuvette containing sample solutions was put inside an integrated sphere and the measurement of both emission and excitations were recorded in the form of emission spectra only.

For the lifetime measurements, time-correlated single photon count (TCSPC) technique was used with the help of *Horiba DeltaFlex* instrument. 2 mL of solution which contain



Where R_1**= H,** ***p*****-OMe,** ***p*****-Cl &** ***p*****-Me**
R_2**= Ph,** ***p*****-Me-Ph,** ***p*****-Cl-Ph,** ***p*****-Br-Ph, Thienyl,** ***p*****-OMe-Ph, &** ***p***$\textbf{-NO}_2$

Scheme 1 Quinoline synthesis by Povarov reaction using $InCl_3$

sample was put in a quartz cuvette and it was mounted on the sample holder.

General Procedure for the Preparation of 4a-f

An equimolar mixture of aromatic amines **1** (1.0 mmol) and aromatic aldehydes **2** (1.0 mmol) in presence of 10 mol% of $InCl_3$ were refluxed in 5 mL of toluene. Then after refluxing for 1 h (as indicated by TLC), 2-ethynylaniline **3** (1.0 mmol) was added to reaction pot and refluxed the system for another 23 h. Then, the completions of the reactions were monitored by UV-lamp (giving distinct blue/green colouration). The reaction mixture was brought to room temperature and extracted with ethylacetate (2 × 10 mL). The organic layer containing the quinoline was dried over anhydrous Na_2SO_4 and then evaporated. The crude residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:5) as eluent to afford pure product **4a-i** in good yields.

Characterization Data of the Isolated Compounds 4a-I

1. 2-(2-Phenylquinolin-4-Yl)Aniline (4a): The crude substance purified by gravity column chromatography(ethyl acetate/n-hexane 1:2).

White solid, yield 0.21 g (70%), m.p. 173-175 °C; R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2), FTIR V: 3389, 3020(N-H); 2929, 2854(aromatic = C-H stretching); 1903, 1614(aromatic = C-H bending), 1519(C=C); 1093, 806 (mono-substituted ring C-H) cm^{-1}, ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 3.59 (s, 2H, NH_2), 6.93–6.85 (m, 3H. Ar. =CH), 7.04–7.00 (m, 2H, Ar. = CH), 7.21–7.19 (m, 1H, Ar. =CH), 7.0–7.04(d, 2H, Ar. =CH, *J*: 6.4 Hz), 8.12 (d, 3H, *J*: 7.2 Hz), ^{13}C NMR (100 MHz, $CHCl_3$-*d*) δ (ppm): 103.7 (Ar. CH), 114.2 (Ar, CH), 115.7 (Ar, CH), 118.5 (Ar. CH), 120.0 (Ar. CH), 122.1(Ar. CH), 123.6 (Ar. CH), 126.4(Ar. CH), 128.6 (Ar. CH), 129.6 (Ar. CH), 130.6 (Ar. CH), 131.4 (Ar. CH), 132.2 (Ar. CH), 138.8 (Ar. CH), 144.8 (Ar. CH), 145.1 (Ar. CH), 154.6 (Ar. CH), 157.8 (Ar. CH), ESI-MS: $[M + H]^+$ m/z: 297; Chemical Formula: $C_{21}H_{16}N_2$.

2. 2-(6-Methoxy-2-(*p*-Tolyl)Quinolin-4-Yl)Aniline (4b): The crude substance purified by gravity column chromatography(ethyl acetate/n-hexane 1:2).

White solid, yield 0.24 g (73%), m.p. 156-158 °C; R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2), FTIR V: 3375, 3025(N-H), 2909, 2867 (aromatic = C-H), 1903, 1617 (aromatic = C-H), 1511 (C=C), 1097, 810 (mono-substituted ring C-H), ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 2.42(s, 3H,=CH_3), 3.78(s, 3H, =OCH_3), 6.95–6.85(m, 3H, Ar. =CH), 7.21(d, 1H, Ar. =CH, *J*: 7.6 Hz), 7.30 (t, Ar. =CH, *J*: 8.0 Hz), 7.40–7.37(m, 2H, Ar. =CH), 7.82(s, 1H, AR. =CH), 8.14–8.04 (dd, 3H, Ar. = CH, *J*: 9.2, 8.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): 21.3 (CH_3), 55.5 (OCH_3), 103.7 (Ar. CH), 115.7 (Ar. CH), 118.5 (Ar. CH), 120.3 (Ar. CH), 122.1 (Ar. CH), 123.5 (Ar. CH), 126.6 (ar. CH), 127.1 (Ar. CH), 129.6 (Ar. CH), 130.6 (Ar. CH), 131.6 (Ar. CH), 136.7 (Ar. CH), 139.1 (Ar. CH), 143.8 (Ar. CH), 144.9 (Ar. CH), 145.1 (Ar. CH), 155.0 (Ar. CH), 157.8 (Ar. CH), ESI-MS: $[M + H]^+$ m/z: 341; Chemical Formula: $C_{23}H_{20}N_2O$.

3. 2-(2-(4-Chlorophenyl)-6-Methoxyquinolin-4-Yl)Aniline (4c): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.26 g (74%), m.p. 174-176 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3382 (NH_2), 3035, 2809, 2859 (Aromatic = CH), 1900, 1615, 1515 (C=C), 1082, 815,600 (mono-substituted aromatic ring C-Cl), ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 3.80(s, 3H, CH_3), 6.87(d, 1H, Ar. =CH, *J*: 5.2 Hz), 6.96–6.1(m, 2H, Ar. =CH), 7.21–7.19 (m, 1H, Ar. =CH), 8.13–8.08 (m, 3H, Ar. = CH), 7.33–7.30(m, 1H, Ar. =CH), 7.41–7.39(m, 1H, Ar. =CH), 7.47(d, 2H, Ar. = CH, *J*: 6 Hz, 2H), 7.80(s, 1H, Ar. =CH), ^{13}C NMR(400 MHZ,$CDCl_3$): 55.5 (OCH_3), 103.7 (Ar. CH), 113.6 (Ar. CH), 113.7 (Ar. CH), 118.5 (Ar. CH), 120.06 (Ar. CH), 122.46 (Ar. CH), 126.8 (Ar. CH), 128.5 (Ar. CH), 128.9 (Ar. CH), 129.7 (Ar. CH), 130.5 (Ar. CH), 131.6 (Ar. CH), 133.2 (Ar. CH), 135.2 (Ar. CH), 137.9 (Ar. CH), 143.7 (Ar. CH), 145.4 (Ar. CH), 158.1 (Ar. CH), ESI-MS: $[M + H]^+$ m/z 361; Chemical Formula: $C_{22}H_{17}ClN_2O$.

4. 2-(2-(4-Bromophenyl)-6-Methoxyquinolin-4-Yl)Aniline (4d): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.30 g (75%) m.p. 108-110 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3435 (NH_2), 3318, 3205, 3063, 2916 (aromatic = C-H), 2354, 1917, 1626, 1583 (C=C), 1492, 1305, 1091, 1014, 823 (mono-substituted aromatic ring CH) cm^{-1},^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 3.81(s, 1H, OCH_3), 6.99–6.88(m, 3H, Ar. -CH), 7.35–7.19(m, 2H, Ar. =CH), 7.51–7.41(m, 3H, Ar. =CH), 7.74(s, 1H, Ar. =CH), 8.14(d, 2H, Ar. =CH, *J:* 8.4 Hz), 8.37(s,1H, Ar. =CH), ^{13}C NMR (100 MHz, $CHCl_3$-*d*) δ (ppm): 55.3 (OCH_3), 103.61 (Ar. CH), 115.7 (Ar. CH), 118.6 (Ar. CH), 120.0 (Ar. CH), 122.5 (Ar. CH), 123.3 (Ar. CH), 123.6 (Ar. CH), 126.9 (Ar. CH), 128.8 (Ar. CH), 129.7 (Ar. CH), 130.5 (Ar. CH), 131.6 (Ar. CH), 131.9 (Ar. CH), 143.7 (Ar. CH), 145.5 (ar. CH), 144.8 (Ar. CH), ESI-MS: $[M + H]^+$ m/z: 405; Chemical Formula: $C_{22}H_{17}BrN_2O$.

5. 2-(6-Chloro-2-(Thiophen-2-Yl)Quinolin-4-Yl)Aniline (4e): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Table 1 Optimization of reaction conditions for the synthesis of 2,4-disubstituted quinoline derivative (**4a**)[a]

Entry	Catalyst	Mol (%) of catalyst	Solvent	Reaction condition	Time (h)	Yield[b] (%)
1.	$InCl_3$	5	Toluene	Reflux	24	65
2.	$InCl_3$	10	Toluene	Reflux	24	70
3.	$InCl_3$	15	Toluene	Reflux	24	70
4.	$InCl_3$	10	CH_3CN	Reflux	24	55
5.	$InCl_3$	10	DCM	Reflux	24	50
6.	$InCl_3$	10	EtOH	Reflux	24	45
7.	$InCl_3$	10	THF	Reflux	24	40
8.	$InCl_3$	10	H_2O	Reflux	48	NR
9.	$InCl_3$	10	No solvent	100 °C	48	NR
10.	$InCl_3$	10	CH_3NO_2	Reflux	24	50
11.	$InBr_3$	10	Toluene	Reflux	24	50
12.	$AlCl_3$	10	Toluene	Reflux	24	42
13.	$FeCl_3$	10	Toluene	Reflux	24	34
14.	$CuCl_2$	10	Toluene	Reflux	24	45
15.	$Cu(OTf)_2$	10	Toluene	Reflux	24	Multi-spots
16.	CAN	10	Toluene	Reflux	24	48
17.	I_2	10	Toluene	Reflux	24	45
18.	TFA	10	Toluene	Reflux	24	30
19.	*p*-TsOH	10	Toluene	Reflux	24	35
20.	BF_3OEt_3	10	Toluene	Reflux	24	38

[a] All the reactions were performed with aniline **1a** (1.0 mmol), benzaldehyde **2a** (1.0 mmol) and 2-ethynylaniline **3** (1.0 mmol). [b] Isolated yields NR- No reaction.

Brown solid substance, yield 0.24 g (72%) m.p. 145-147 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3489 (NH_2), 3020, 2939, 2874 (aromatic = C-H), 1963, 1654, 1530 (C=C), 1083, 906,708 (mono-substituted C aromatic ring C-Cl) cm^{-1}; ^1H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm): 6.51(s, 1H, Ar. =CH); 7.03(t, 1H, *J*: 4.8 Hz), 7.46–7.19(m, 5H, Ar. =CH), 7.59 (s, 1H, Ar. =CH), 7.62 (d, 1 h, *J*: 7.2 Hz), 7.78 (d, 1H, *J*: 8.4 Hz), 7.98 (d, 1H, *J*: 8.4 Hz), ^{13}C NMR (100 MHz, $CHCl_3$-H) δ (ppm): 98.9 (Ar. CH), 119.4 (Ar. CH), 123.7 (Ar. CH), 125.2 (Ar. CH), 127.9 (Ar. CH), 128.2 (Ar. CH), 129.5 (Ar. CH), 129.9 (Ar. CH), 129.9 (Ar. CH), 130.1 (Ar. CH), 138.6 (Ar. CH), 145.6 (Ar. CH), 147.4 (Ar. CH), 125.5 (Ar. CH), 152.9 (Ar. CH), MS: $[M+H]^+$ m/z 337. Chemical Formula: $C_{19}H_{13}ClN_2S$.

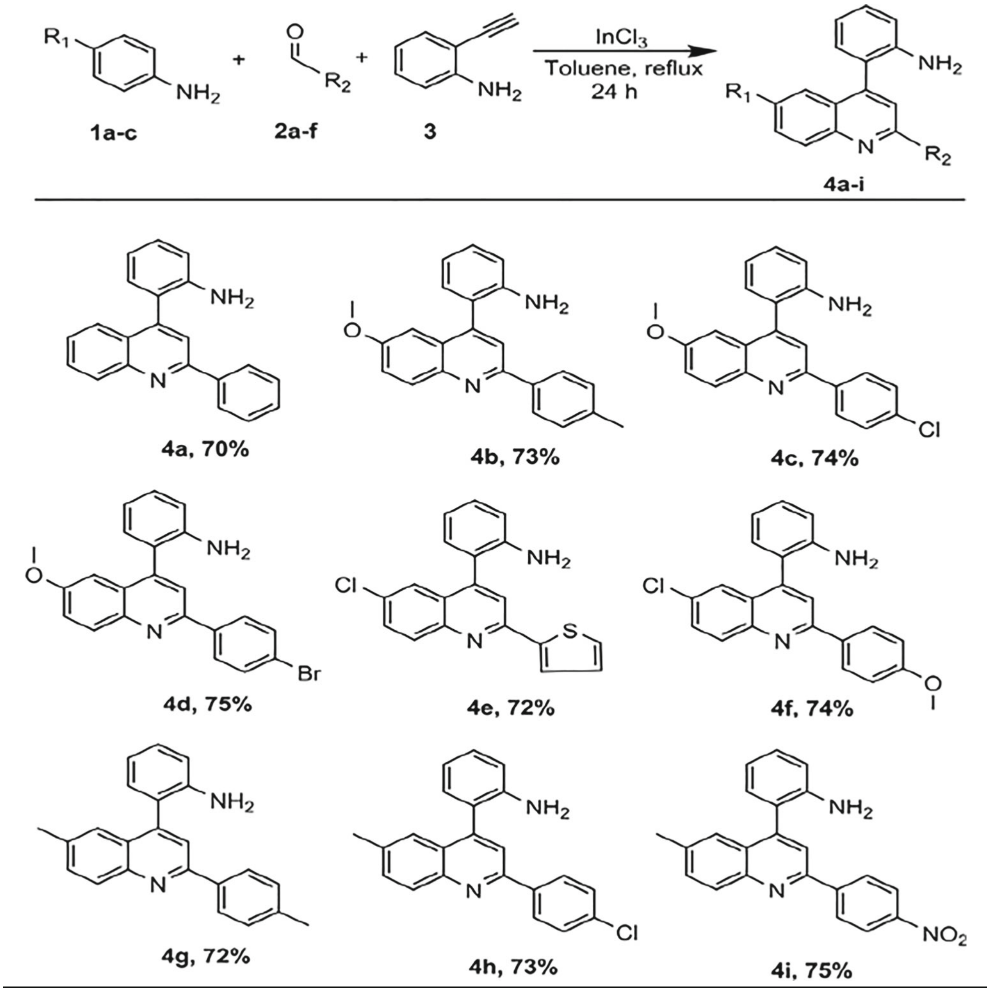
6. 2-(6-Chloro-2-(4-Methoxyphenyl)Quinolin-4-Yl)Aniline (4f): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.26 g (74%) m.p. 138-140 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3484 (NH_2), 3023, 2932 (aromatic = C-H), 2865, 1960, 1657, 1596 (C=C), 1068, 907,760 (mono-substituted aromatic ring C-H) cm^{-1}; ^1H NMR (400 MHz, CHCl3-*d*): δ (ppm): 3.55(s, 2H, NH_2), 3.86(s, 3H, OCH_3), 6.94–6.85(m, 3H, Ar. =CH), 7.15 (d, 1H, Ar. =CH, *J*: 7.2 Hz), 7.33–7.25(m, 2H, Ar. =CH), 7.63 (d, 2H, Ar. =CH, *J*: 10 Hz), 7.84 (s, 1H, Ar. =CH), 8.12(t, 3H, Ar. =CH, *J*: 4.8 Hz); ^{13}C NMR (100 MHz, $CHCl_3$-H) δ (ppm): 55.4(OCH_3), 114.3 (Ar. CH), 115.8 (Ar. CH), 118.6 (Ar. CH), 120.4 (Ar. CH), 122.6 (Ar. CH), 124.6 (Ar.CH), 126.2 (Ar.CH), 128.9(Ar.CH), 130.0 (Ar.CH), 130.6(Ar.CH), 130.7 (Ar.CH), 132.0 (Ar.CH), 143.7 (Ar.CH), 145.8 (Ar.CH), 147.3 (Ar.CH), 157.1 (Ar.CH), 161.1 (Ar.CH); ESI-MS: $[M+H]^+$ m/z 361. Chemical Formula: $C_{22}H_{17}ClN_2O$.

7. 2-(6-Methyl-2-(*p*-Tolyl)Quinolin-4-Yl)Aniline (4 g): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.23 g (72%) m.p. 145-147 °C, R_f: 0.70 (SiO2, ethyl acetate/n-hexane 1:2). FTIR V: 3474 (NH_2), 3013, 2899 (aromatic = C-H), 2854, 1990, 1657, 1526 (C=C), 1078, 879,731 (mono-substituted aromatic ring C-H) cm^{-1}; ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 2.38(s, 3H, CH_3), 2.49(s, 3H, CH_3), 3.49(s, 2H, NH_2), 6.95(d, 1H, Ar. =CH, *J*: 8.8 Hz), 6.87–6.63(m, 3H, Ar. =CH), 7.11(d, 1H, *J*: 7.6 Hz), 7.26–7.18(m, 1H, Ar. =CH), 7.33(s, 1H, Ar. =CH), 7.47(d, 1H, Ar. =CH, *J*: 8.4 Hz), 7.71(s, 1H, Ar. =CH), 8.07–8.01(dd, 3H, *J*: 8.4, 8.8), ^{13}C NMR (100 MHz, $CHCl_3$-H) δ (ppm): 21.3 (CH_3), 21.8 (CH_3), 115.6 (Ar. CH), 118.4(Ar. CH), 120.1 (Ar. CH), 123.7 (Ar. CH), 124.4 (Ar. CH), 125.7 (Ar. CH), 127.3(Ar. CH), 129.5 (Ar. CH), 129.8(Ar. CH), 130.6 (Ar. CH), 132.1 (Ar. CH),

Table 2 Synthesis of various 2,4-disubstituted quinoline derivatives using Povarov reaction.[a]



[a] Reactions condition: Aromatic amines (1.0 mmol), aromatic aldehydes (1.0 mmol), and 2-ethynylaniline (1.0 mmol) in the presence of 10 mol% of $InCl_3$ in 5 mL of toluene under reflux conditions.

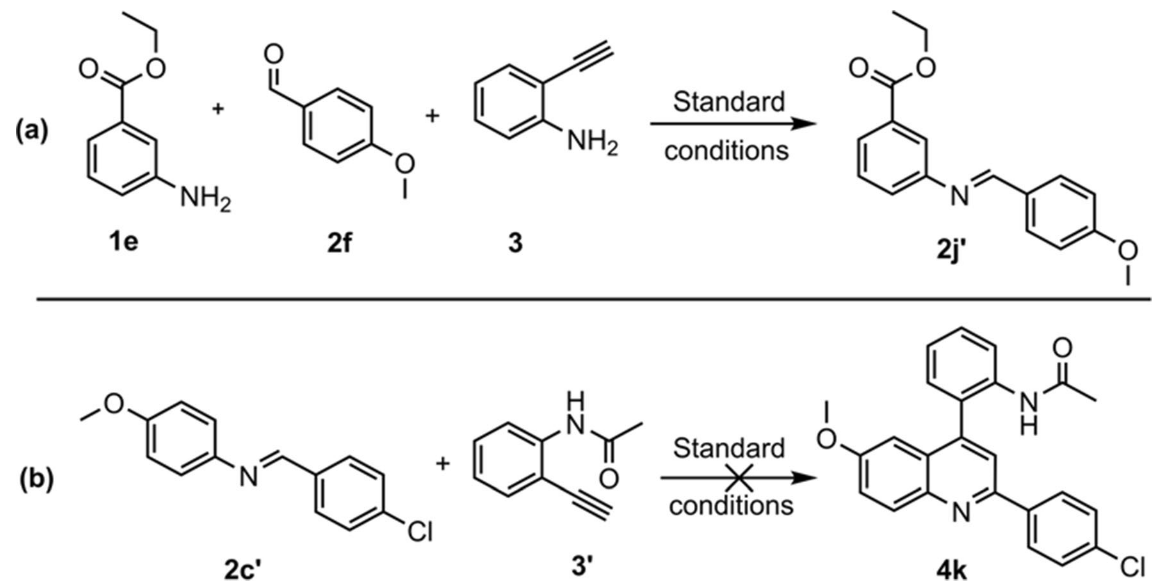
136.4 (Ar. CH), 143.9 (Ar. CH), 145.8 (Ar. CH), 147.4 (Ar. CH); ESI-MS: $[M + H]^+$ m/z 325. Chemical Formula: $C_{23}H_{20}N_2$.

8. 2-(2-(4-Chlorophenyl)-6-Methylquinolin-4-Yl)Aniline (4 H): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.25 g (73%) m.p. 96-98 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3474 (NH_2), 3005, 2945 (aromatic = C-H), 2867, 1970, 1661, 1546 (C=C), 1078, 900, 872(mono-substituted aromatic ring C-H) cm^{-1}; ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 2.45(s, 3H, CH_3), 3.52(s, 2H, NH_2), 6.94–6.85(m, 2H, Ar. =CH), 7.18–7.16(m, 1H, Ar. =CH), 7.25(s, 1H, Ar. =CH), 7.34–7.30(m, 2H, Ar. =CH), 7.47(t, 1H, Ar. =CH, *J*: 8.8 Hz), 7.58–7.55 (m, 1H, Ar. =CH), 7.8 (s, 1H, Ar. =CH), 8.11 (d, 3H, Ar. =CH, *J*: 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 20.8 (CH_3), 115.7 (Ar. CH), 118.5 (Ar. CH), 119.8 (Ar. CH), 123.4 (Ar. CH), 124.4(Ar. CH), 125.8 (Ar. CH), 128.7 (Ar. CH), 129.0 (Ar. CH), 129.6 (Ar. CH), 129.9 (Ar. CH), 130.6 (Ar. CH), 132.3 (Ar. CH), 135.4 (Ar. CH), 136.9 (Ar. CH), 137.9 (Ar. CH), 143.8 (Ar. CH), 146.2 (Ar. CH), 147.3 (Ar. CH), 155.1 (Ar. CH); ESI-MS: $[M + H]^+$ m/z 345. Chemical Formula: $C_{22}H_{17}ClN_2$.

9. 2-(6-Methyl-2-(4-Nitrophenyl)Quinolin-4-Yl)Aniline (4i): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brown solid substance, yield 0.26 g (75%) m.p. 167-169 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V: 3494 (NH_2), 3028, 2938 (aromatic = C-H), 2877, 1950, 1650, 1536 (C=C), 1068, 877,721 (mono-substituted aromatic ring C-H) cm^{-1}; ^1H NMR (400 MHz, $CHCl_3$-*d*): δ (ppm): 2.50(s, 3H, CH_3), 3.57(s, 2H, NH_2),



Scheme 2 Controlled experiment to established the effect of amino group in this Povarov reaction.

6.98–6.90(m, 2H, Ar. =CH), 7.20(d, 2H, *J*: 7.6), 7.26(s, 1H, Ar. =CH), 7.37(t, 1H, Ar. =CH, *J*: 8.0 Hz), 7.45(s, 1H, Ar. =CH), 7.72–7.62(m, 1H, Ar. =CH), 7.89 (s, 1H, Ar. =CH), 8.16 (d, 1 h, *J*: 8.4 Hz), 8.55 (d, 1H, *J*: 7.6 Hz), 9.07(s, 1H, Ar. =CH); ^{13}C NMR (100 MHz, $CDCl_3$): 21.8 (CH_3), 115.7 (Ar. CH), 118.5 (Ar. CH), 119.8 (Ar. CH), 123.4 (Ar. CH), 124.4 (Ar. CH), 125.8 (Ar. CH), 128.7 (Ar. CH), 129.0 (Ar. CH), 129.6 (Ar. CH), 129.9 (Ar. CH), 130.6 (Ar. CH), 132.3 (Ar. CH), 135.4 (Ar. CH), 137.0 (Ar. CH), 138.0 (Ar. CH), 143.8 (Ar. CH), 146.2 (Ar. CH), 147.3 (Ar. CH), 155.1 (Ar. CH); ESI-MS: $[M+H]^+$ m/z 356. Chemical Formula: $C_{22}H_{17}N_3O_2$.

10. Ethyl (*E*)-3-((4-Methoxybenzylidene)Amino)Benzoate (2j’): The crude substance purified by gravity column chromatography (ethyl acetate/n-hexane 1:2).

Brownish solid substance, yield 0.26 g (92%) m.p. 58-62 °C, R_f: 0.70 (SiO_2, ethyl acetate/n-hexane 1:2). FTIR V:

Scheme 3 Proposed mechanism for the synthesis of Quinoline **4a**

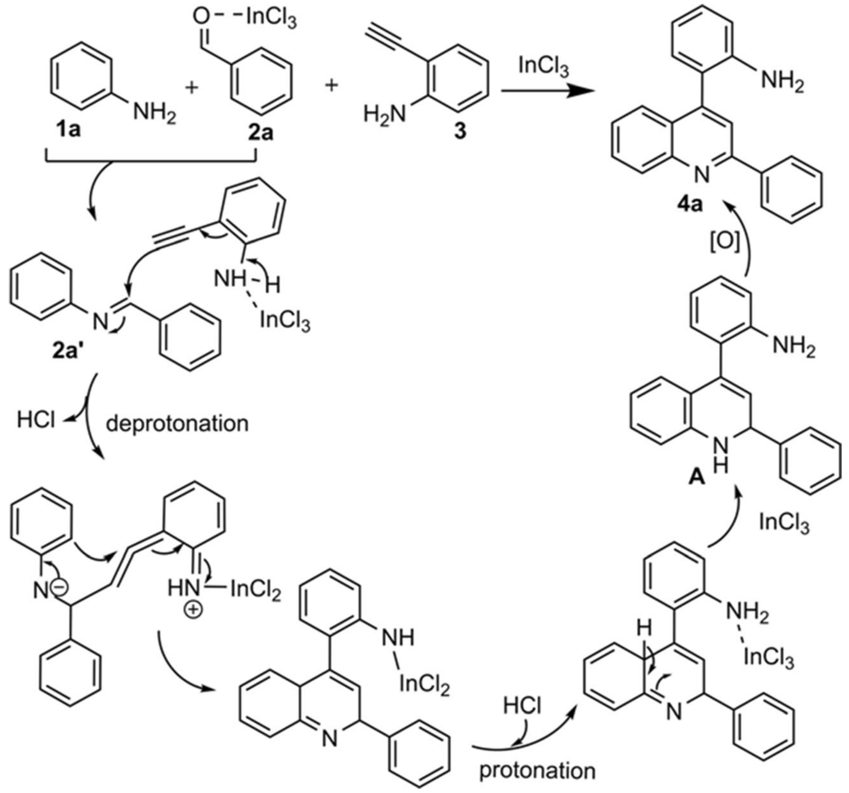


Table 3 Maximum absorption wavelength (λ_{max}) for quinoline derivatives

Sl. No.	Compounds	Chloroform		Acetonitrile		Methanol	
		Peaks (nm)	λ_{max} (nm)	Peaks (nm)	λ_{max}(nm)	Peaks (nm)	λ_{max}(nm)
1.	**4a**	249, 319	249	250, 318	250	281, 319	281
2.	**4b**	250, 387	250	264, 383	264	263, 385	263
3.	**4c**	264, 333	333	260, 319	318	268, 322	322
4.	**4d**	262, 372	262	268, 351	268	264, 348	264
5.	**4e**	267, 337	267	268, 332	268	267, 332	267
6.	**4f**	265, 348	265	271, 342	271	270, 344	270
7.	**4 g**	262, 347	262	279, 342	279	280,345	280
8.	**4 h**	260, 380	260	260, 384	260	260, 379	260
9.	**4i**	260, 343	260	261, 326	261	260, 324	260

3067 (aromatic = C-H), 2987, 1705, 1612(C=N), 1413, 1365, 870 (monosubstituted aromatic ring C-H) cm^{-1}; ^{1}H NMR (400 MHz, $CHCl_3$-*d*) δ (ppm): 1.37 (t, 3H, $-CH_3$, *J*: 6.8 Hz), 3.82(s, 3H, OCH_3), 4.37–4.31(dd, 2H, *J*: 7.2, 7.2 Hz), 6.79–6.77 (m, 2H, Ar. = CH), 6.88 (d, 1H, *J*: 8.8 Hz), 7.19 (s, 1H, Ar. =CH), 7.22 (d, 1H, *J*: 4.0 Hz), 7.26 (t, 1H, *J*: 6.4 Hz), 7.33 (d, 1H, *J*: 5.6 Hz), 7.38 (d, 1H, *J*: 7.6 Hz), 8.52 (s, 1H, Ar. = CH), 13C NMR-APT (100 MHz, CHCl3-d) δ (ppm): 14.3 (CH_3), 55.3 (OCH_3), 60.9 ($-CH_2-$), 117.1 (Ar. CH), 114.1 (Ar. CH), 113.5 (Ar. CH), 114.3 (Ar. CH), 118.6 (Ar. CH), 128.0 (Ar. CH), 129.2 (Ar. CH), 130.9 (Ar. CH), 131.3 (Ar. CH), 148.1 (Ar. CH), 158.9 (Ar. CH), 167.0 (C=N); ESI-MS: $[M + H]^+$ m/z 284. Chemical Formula: $C_{17}H_{17}NO_3$.

Results and Discussion

Initially, a mixture of aniline **1a** (1.0 mmol), benzaldehyde **2a** (1.0 mmol) and 2-ethynylaniline **3** (1.0 mmol) with $InCl_3$ (5 mol%) were refluxed for 24 h in 5 mL of toluene, (*E*)-*N*-(2-ethynylphenyl)-1-phenylmethanimine and traces of unreacted aniline were isolated instead of our target compound quinolines. Then, we modified the reaction in a stepwise controlled method so that aniline **1a** (1.0 mmol) and benzaldehyde **2a** (1.0 mmol) were allowed to react in refluxing toluene in presence of 5 mol% of $InCl_3$ for 1 h showing the characteristic formation of imine (as indicated by TLC) and 2-ethynylaniline **3** (1.0 mmol) was added to reaction pot and refluxed the system for another 23 h. The product 2-(2-phenylquinolin-4-yl)aniline **4a** was obtained in 65% yield (Table 1, entry 1), the structure of **4a** was deduced from its elemental analysis and spectral data (^{1}H and ^{13}C NMR, IR). To our delight, the desired product **4a** was obtained in 70% yield when we increased the catalytic loading to 10 mol% (entry 2). However, no increase in yield was observed on further increasing the catalyst beyond 10 mol% (entry 3). Inspired by this result, we next screened the effect of solvent on the reaction by using 10 mol% of $InCl_3$ as standard catalyst loading. For scrutinizing the suitable solvent system, similar reactions (entries 4–8) were conducted in various solvent systems such as CH_3CN, DCM, EtOH, THF and CH_3NO_2 under reflux conditions. It was noted that the shortest reaction time and the best yield were obtained in toluene (entry 2) under reflux condition. Interestingly, the same reaction did not proceed and provide low yield when it was carried out in water and solvent free condition even after prolonging the reaction duration (Table 1, entries 9–10).

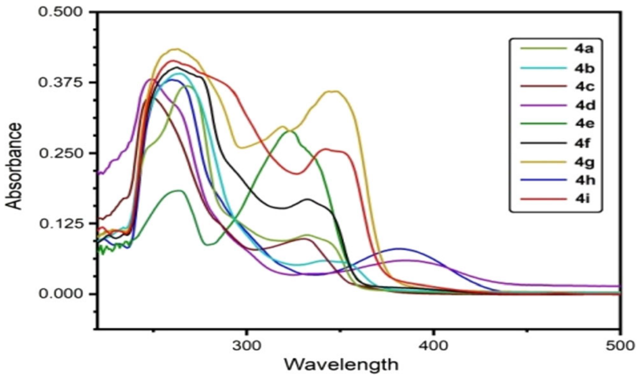


Fig. 2 UV-Vis absorption of quinoline derivatives (**4a-i**) in CH_3Cl

To examine the efficacy of $InCl_3$ extensive comparative studies with several catalytic systems have been investigated. Thus, several reactions were scrutinized in the presence of catalysts like $InBr_3$, $AlCl_3$, $FeCl_3$, $Cu(OTf)_2$, $CuCl_2$, CAN, I_2, TFA, *p*-TsOH and BF_3OEt_3, respectively (Table 1, entries 11–20). All the tested acids gaive lower yields than that of $InCl_3$, however, in the case of $Cu(OTf)_2$, a mixture of compounds are observed. Lewis acids showed better activity as compared to those of Bronsted acids and amongst the tested Lewis acids $InCl_3$ was the best catalyst in this Povarov reaction (Table 1). Hence, the optimized reaction condition for the formation of **4a** was established with 10 mol% of $InCl_3$ in toluene under refluxing for 24 h using aniline **1a** (1.0 mmol), benzaldehyde **2a** (1.0 mmol) and 2-ethynylaniline 3 (1.0 mmol) (entry 2).

With this optimized reaction condition in our hand, its substrate scope and generality was examined (Table 2). Amines with electron-donating substituents such as methoxy and methyl react with aldehydes having different substituents such as methoxy, methyl, chloro, bromo and nitro in presence of 2-ethynylaniline to give moderate yields (72–75%). Again, *p*-chloroaniline react with *p*-methoxybenzaldehyde or thienyl-2-carbaldehyde along with 2-ethynylaniline to give the corresponding quinolines in comparable yields with other products. However, the best yields were obtained when amines having the electron-donating groups coupled with aldehydes having electron-withdrawing substituents such as in **4d** and **4i** (75% yield). Thus, a small library of highly functionalized quinolines with potentials of exhibiting strong luminescence properties under UV lamp was established. We were curious to find out the role of amino group which is *ortho* to enyne moiety.

To understand the role of amino group, an experiment for ethyl 3-aminobenzoate **1e** (1.0 mmol), *p*-methylbenzaldehyde **2f** (1.0 mmol) and 2-ethynylaniline **3** (1.0 mmol) were subjected to establish optimized reaction condition (Table 1, entry 2). The intermediate Schiff base **2j'** was obtained instead of expected quinoline, probably due to the reduction in the electron density on ortho to the ester carbon as well as steric hindrance between the amino group and bulky acetate. Thus, less chances for the formation of quinoline.

In another experiment, the –NH_2 of ethynylaniline was acylated with acetic anhydride and allowed to react with isolated Schiff base **2c'** using the established protocol. Again, the reaction mixture gives multi-spot as observed by TLC, indicating that the amino group must be involved in the cycloaddition reaction between the Schiff base and 2-ethynylaniline as shown in Scheme 2. Taking into consideration of the above two observations, we propose the plausible reaction mechanism of this Povarov reaction to get quinoline via oxidation. Here, the Schiff base **2a'** undergo [4 + 2] Povarov cycloaddition reaction with 2-ethynylaniline initiated from amino group. The cyclized dihydroquinoline **A** is obtained with the departure of the $InCl_3$ catalyst and restoration of the catalytic cycle. Then dihydroquinoline **A** undergoes a spontaneous oxidation to give the final quinoline **4a** (Scheme 3).

Photophysical Properties

In this study, we examine the absorption, emission, life time and fluorescence quantum yields of the quinolines. The photophysical characteristics were investigated in CH_3CN, $CHCl_3$ and CH_3OH solutions. The data of UV-Vis absorption

Table 4 Photophysical data obtained from fluorescence emission of quinoline derivatives

Sl. No.	Compounds	λ_{em}	$\Delta\lambda st$	Parameters	Average Life-Time (τ_{av})	Quantum Yield Φfx	CIE Coordinate
1.	**4a**	454	90	(a) $\tau_1 = 1.366$ (b) $\tau_2 = 5.494$ (c) $\chi^2 = 0.999$	2.745 ns	0.01	X = 0.214 Y = 0.200
2.	**4b**	438	100	(a) $\tau_1 = 1.681$ (b) $\tau_2 = 4.733$ (c) $\chi^2 = 0.999$	1.805 ns	0.01	X = 0.160 Y = 0.095
3.	**4c**	490	94	(a) $\tau_1 = 2.704$ (b) $\tau_2 = 10.742$ (c) $\chi^2 = 0.999$	3.313 ns	0.09	X = 0.259 Y = 0.510
4.	**4d**	491	95	(a) $\tau_1 = 3.700$ (b) $\tau_2 = 7.510$ (c) $\chi^2 = 0.999$	4.177 ns	0.20	X = 0.266 Y = 0.550
5.	**4e**	492	95	(a) $\tau_1 = 4.307$ (b) $\tau_2 = 7.409$ (c) $\chi^2 = 0.999$	7.266 ns	0.09	X = 0.323 Y = 0.042
6.	**4f**	488	108	(a) $\tau_1 = 2.304$ (b) $\tau_2 = 12.175$ (c) $\chi^2 = 0.999$	3.435 ns	0.04	X = 0.223 Y = 0.604
7.	**4 g**	480	99	(a) $\tau_1 = 1.861$ (b) $\tau_2 = 8.341$ (c) $\chi^2 = 0.999$	5.598 ns	0.02	X = 0.125 Y = 0.112
8.	**4 h**	496	77	(a) $\tau_1 = 2.488$ (b) $\tau_2 = 8.322$ (c) $\chi^2 = 0.999$	6.204 ns	0.78	X = 0.245 Y = 0.525
9.	**4i**	472	92	(a) $\tau_1 = 2.314$ (b) $\tau_2 = 10.852$ (c) $\chi^2 = 0.999$	3.210 ns	0.16	X = 0.165 Y = 0.181

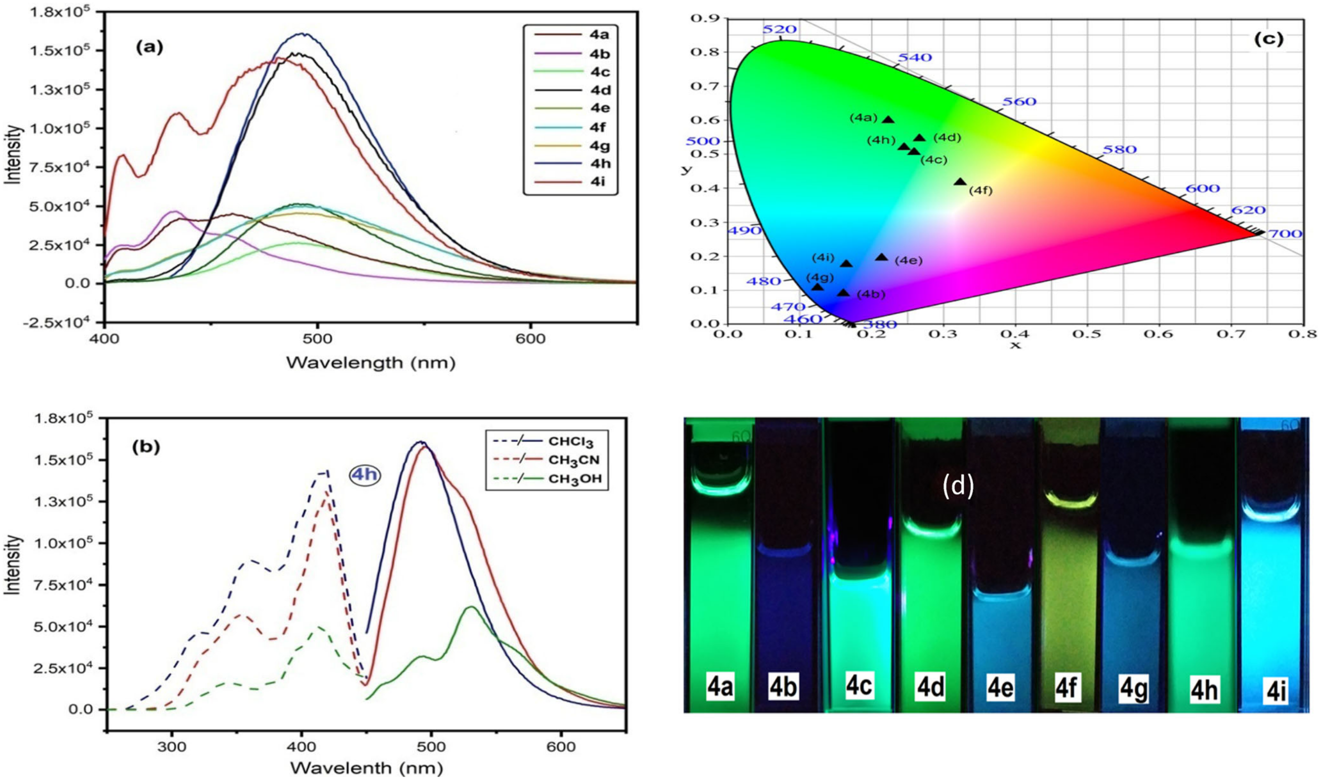
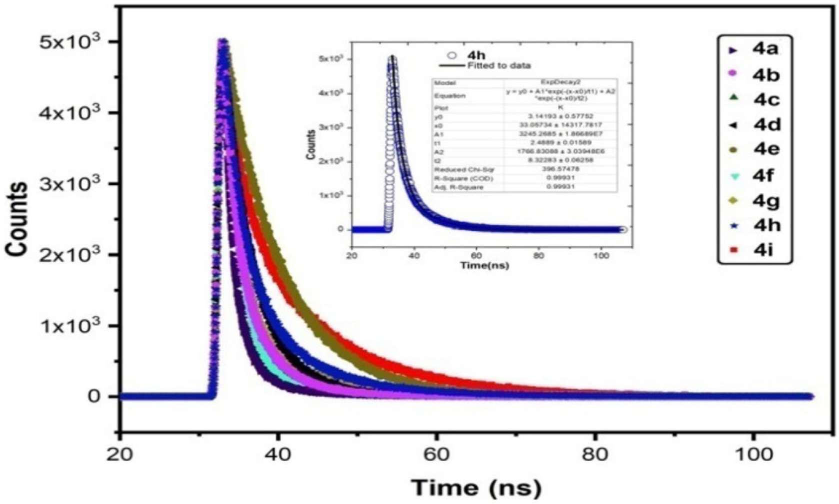


Fig. 3 **a** Fluorescence emission of quinoline derivatives (**4a**–**i**) in $CHCl_3$ (**b**), Emission (solid line) and absorption (dotted line) spectra of compound **4 h** in each solvent ($CHCl_3$, CH_3CN, CH_3OH) (**c**), Photograph taken under UV light (365 nm) in $CHCl_3$ solution. **d** Chromaticity diagram showing the CIE coordinates of the compounds **4a-i**

are summarized in Table 3 in 10^{-3} mol. L^{-1} in CH_3CN, $CHCl_3$ and CH_3OH solutions.

The nature of the substituents were examined taking **4a** as reference compound, it was found that all the compounds exhibit red shifts. The highest shift occurred in 2-position thienyl substituted **4e**, as expected (18 nm). The absorption spectra of the 2,4-disubstituted quinoline derivatives in $CHCl_3$ are characterized by strong absorption peaks centred at 249–267 nm and 319–387 nm probably due to π-π* and n-π* transitions. Bands located at 319–387 nm range can be assigned to the possible intermolecular charge transfer transition (ICT) [35]. On changing the polarity to polar solvents like CH_3CN and CH_3OH, most of the compounds experience red shift and blue shift respectively for π-π* and n-π* peaks. The λ_{max} changes by 31 nm from acetonitrile to methanol for **4a** (Table 3). It can be attributed to possible protonation of quinolines in methanol. However, the compound **4c** showed blue shift in both the transitions in CH_3CN from $CHCl_3$. In all the

Fig. 4 Fluorescence lifetime decays of quinolines (**4a**–**i**)



Model	ExpDecay2
Equation	y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2)
Plot	K
y0	3.14193 ± 0.57752
x0	33.05734 ± 14317.7817
A1	3245.2685 ± 1.86689E7
t1	2.4889 ± 0.01589
A2	1766.83088 ± 3.03948E6
t2	8.32283 ± 0.06258
Reduced Chi-Sqr	396.57478
R-Square (COD)	0.99931
Adj. R-Square	0.99931

compounds the change in λ_{max} due to substituent's nature seems to be less pronounced. This can be attributed due to the strong influence of amino group at *o*-position of the aryl substituent at position 4, no significant alteration was observed by changing the substituents on the phenyl ring in position 2 as well as at position 6 of quinolines (Fig. 2). All the compounds showed λ_{max} in π-π* transition however, compound **4c** is the exception with λ_{max} 323 nm (n-π* transition) having methoxy and chloro as substituents in all the solvents (absorption spectra in CH_3CN and CH_3OH are enclosed in SI). The absorption spectra of chloroform solutions (10^{-3} mol.L^{-1}) of 2,4-disubstituted quinoline derivatives are depicted in Fig. 2.

The fluorescence and excitation spectra were measured with a *Horiba Fluoromax 4 Spectrophotometer*. All measurements were done repeatedly and reproducible results were obtained. All the solutions were excited at around 338–419 nm with an excitation and emission slit width of 2 nm. As in absorption, the solvent polarity affects the fluorescence properties of quinolines. The Stokes shift data, given by the difference between the maximum peak of absorption and emission spectra which is estimated from the intersection of the absorption and emission spectra, is observed in Table 4 for $CHCl_3$ solution. Most of the compounds showed a similar pattern in the shift around 472–496 nm whereas **4a** (454 nm) and **4b** (438 nm) as expected show the shift at lower wavelength. The larger Stoke's shift values of 77–108 can be attributed to the ICT transitions and electron-substituent properties that exist in these compounds. They showed green to blue emission under UV-lamp (365 nm) except **4f** with yellowish colour (Fig. 3c) and *Commission Internationale de L'Eclairage* (CIE) colour coordinates of the compounds are summarized in Table 4 (also in Fig. 3d).

When the difference in fluorescence intensity was analyzed in $CHCl_3$, compounds **4d**, **4 h** and **4i** presented greater intensity, with **4 h** being the highest one (Fig. 3a). On changing the polarity of the solvents, the shifts pattern are drastically affected with low intensity observing in polar-protic solvent CH_3OH (**S3**) than polar aprotic solvent CH_3CN (**S4**). Whereas, compounds **4d**, **4 h** and **4i** remain with greater intensity than other in both the polar solvents like in $CHCl_3$. The intensity of peaks decreased significantly owing to the hydrogen-bonding interaction between $-NH_2$ group of **4a-i** and protic-solvent in CH_3OH along with polarity effect, but no such hydrogen-bonding with CH_3CN having only polar effect where $CHCl_3$ has none of the effect (Fig. 3d).

The fluorescence quantum yields (φ) of all the compounds in $CHCl_3$ solution are also summarized in Table 4. The higher φ values were obtained in three compounds i.e., 0.78, 0.20, and 0.16 for **4 h**, **4d**, and **4i** respectively. And, for other compounds φ values ranges between 0.01–0.09 in $CHCl_3$ solution. The CH_3CN solution exhibits lower values due to its polarity (0.75, 0.18, and 0.15 for **4 h**, **4d**, and **4i**). The lower φ values (0.54, 0.05, and 0.01 for **4 h**, **4d**, and **4i**) in CH_3OH solution is due to its higher polarity.

Average Lifetime

Average lifetime (τav) measurements for all the newly synthesized compounds have been carried out. It was found that **4e** (7.266 ns) has highest lifetime followed by **4 h** (6.20 ns), **4 g** (5.60 ns), **4d** (4.18 ns), **4f** (3.44 ns), **4c** (3.313 ns), **4i** (3.21 ns), **4a** (2.75 ns) and **4b** (1.81 ns) (Fig. 4). The average lifetime signifies that species with higher τav is likely to persist for longer period in the excited state. Thus, compounds **4e**, **4 h**, **4 g** and **4d** can be explored for potential candidates in fluorescence imaging.

Conclusion

In summary, $InCl_3$-catalyzed [4 + 2] cycloaddition reaction giving novel quinoline derivatives having an amino group at the 4-aryl substituent is presented. To the best of our knowledge, the use of 2-ethynylaniline in Povarov reaction is not reported till now except our work. All the newly synthesized quinolines gave intense green/blue fluorescence with large Stokes shifts. Some of the compounds also have good quantum yield as well as reasonable life time. Studies expanding this novel modular approach to enhance molecular diversity with better yields and more detailed photophysical investigations are currently underway for their photonic applications.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-020-02647-3.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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