Synthesis of Green/Blue Light Emitting Quinolines by Aza-D-A Reaction Using InCl₃ Catalyst

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Abstract
An efficient InCl₃-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 4ₕ having maximum intensity, emitting green colour (Φ = 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 fluorescence 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 occurring 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 chloroquine 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 moieties [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] AuCl₃/CuBr [22], Yb(OTf)₃ [23], Fe(OTf)₃ [24], Cu(OTf)₂ [25], Zn(OTf)₂ [26], AgNTf₂[27], NbCl₃ [28] are explored as effective Lewis acid catalytic system for quinoline synthesis though Povarov started with BF₃·OEt₂ 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.
Indium trichloride (InCl₃) 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 InCl₃ for the synthesis of novel N-heterocycles [32–34], we herein report the InCl₃-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 ¹³C NMR (100 MHz) spectra were recorded on Bruker spectrometer using CDCl₃ whereas ¹H NMR (400 MHz) spectrum for compound 4b was recorded on FT-NMR spectrometer using CDCl₃. Chemical shifts δ are in parts per million (ppm) with CDCl₃ 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 excitation and emissions 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

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**Scheme 1** Quinoline synthesis by Povarov reaction using InCl₃

1a-d + 2a-g + 3 → 4a-i

Where R₁ = H, p-OMe, p-Cl & p-Me
R₂ = Ph, p-Me-Ph, p-Cl-Ph, p-Br-Ph, Thiényl, p-OMe-Ph, & p-NO₂
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 InCl₃ 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 ethyl acetate (2 × 10 mL). The organic layer containing the quinoline was dried over anhydrous Na₂SO₄ 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; Rₛ: 0.70 (SiO₂, ethyl acetate/n-hexane 1:2); FTIR V: 3389, 3020(N-H); 13C NMR (400 MHz, CDCl₃): 55.5 (OCH₃), 103.7 (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), 122.1 (Ar. CH), 123.6 (Ar. CH), 126.4 (Ar. CH), 128.6 (Ar. CH), 131.9 (Ar. CH), 143.8 (Ar. CH), 144.9 (Ar. CH), ESI-MS: [M + H]+ m/z: 341; Chemical Formula: C₁₂H₁₃N₂O.

2. 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; Rₛ: 0.70 (SiO₂, ethyl acetate/n-hexane 1:2); FTIR V: 3345 (NH₂), 3205, 2929 (Aromatic = CH), 1900, 1615, 1515 (C=C), 1082, 815,600 (mono-substituted aromatic ring C-Cl), 1H NMR (400 MHz, CDCl₃-d): δ (ppm): 3.81(s, 3H, OCH₃), 6.99–6.88(m, 3H, Ar. -CH), 7.35–7.19(m, 2H, Ar. =CH, CH₃), 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), 13C NMR (100 MHz, CHCl₃-d): δ (ppm): 21.3 (CH₃), 55.3 (OCH₃), 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), 13C NMR (100 MHz, CHCl₃-d): δ (ppm): 55.3 (OCH₃), 103.6 (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), 128.6 (Ar. CH), 131.9 (Ar. CH), 143.7 (Ar. CH), 144.7 (Ar. CH), 151.9 (Ar. CH), ESI-MS: [M + H]+ m/z: 405; Chemical Formula: C₂₂H₁₇BrN₂O.

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, Rₛ: 0.70 (SiO₂, ethyl acetate/n-hexane 1:2); FTIR V: 3382 (NH₂), 3035, 2809, 2859 (Aromatic = CH), 1900, 1615, 1515 (C=C), 1082, 815,600 (mono-substituted aromatic ring C-Cl), 1H NMR (400 MHz, CHCl₃-d): δ (ppm): 3.80(s, 3H, CH₃), 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), 13C NMR (400 MHz, CDCl₃): 55.5 (OCH₃), 103.7 (Ar. CH), 113.6 (Ar. CH), 113.7 (Ar. CH), 118.5 (Ar. CH), 120.0 (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), 143.7 (Ar. CH), 144.5 (Ar. CH), 151.9 (Ar. CH), ESI-MS: [M + H]+ m/z: 361; Chemical Formula: C₂₂H₁₇ClN₂O.

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 0.26 g (74%), m.p. 174–176 °C, Rₛ: 0.70 (SiO₂, ethyl acetate/n-hexane 1:2); FTIR V: 3382 (NH₂), 3035, 2809, 2859 (Aromatic = CH), 1900, 1615, 1515 (C=C), 1082, 815,600 (mono-substituted aromatic ring C-Cl), 1H NMR (400 MHz, CHCl₃-d): δ (ppm): 3.81(s, 1H, OCH₃), 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), 13C NMR (100 MHz, CHCl₃-d): δ (ppm): 55.3 (OCH₃), 103.6 (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: C₂₂H₁₇BrN₂O.
Brown solid substance, yield 0.24 g (72%) m.p. 145-147 °C, Rf: 0.70 (SiO2, ethyl acetate/n-hexane 1:2). FTIR V: 3489 (NH2), 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, CHCl₃-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, 1H, J: 7.2 Hz), 7.78 (d, 1H, J: 8.4 Hz), 7.98 (d, 1H, J: 8.4 Hz), 13CN M R (100 MHz, CHCl₃-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), 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: C₁⁹H₁₃ClN₂S.

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, Rf: 0.70 (SiO2, ethyl acetate/n-hexane 1:2). FTIR V: 3484 (NH2), 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, NH₂), 3.86(s, 3H, OCH₃), 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); 13C NMR (100 MHz, CHCl₃-H) δ (ppm): 55.4(OCH₃), 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), 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: C₂₂H₁₇ClN₂O.

7. 2-(6-Methyl-2-(p-Tolyl)Quinolin-4-Yl)Aniline (4g): 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, Rf: 0.70 (SiO2, ethyl acetate/n-hexane 1:2). FTIR V: 3474 (NH2), 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, CHCl₃-d) δ (ppm): 2.38(s, 3H, CH₃), 2.49(s, 3H, CH₃), 3.49(s, 2H, NH₂), 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), 13C NMR (100 MHz, CHCl₃-H) δ (ppm): 21.3 (CH₃), 21.8 (CH₃), 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 1 Optimization of reaction conditions for the synthesis of 2,4-disubstituted quinoline derivative (4a)³

| Entry | Catalyst | Mol (%) of catalyst | Solvent | Reaction condition | Time (h) | Yield (%) |
|-------|----------|---------------------|---------|-------------------|---------|-----------|
| 1.    | InCl₃    | 5                   | Toluene | Reflux            | 24      | 65        |
| 2.    | InCl₃    | 10                  | Toluene | Reflux            | 24      | 70        |
| 3.    | InCl₃    | 15                  | Toluene | Reflux            | 24      | 70        |
| 4.    | InCl₃    | 10                  | CH₂CN   | Reflux            | 24      | 55        |
| 5.    | InCl₃    | 10                  | DCM     | Reflux            | 24      | 50        |
| 6.    | InCl₃    | 10                  | EtOH    | Reflux            | 24      | 45        |
| 7.    | InCl₃    | 10                  | THF     | Reflux            | 24      | 40        |
| 8.    | InCl₃    | 10                  | H₂O     | Reflux            | 48      | NR        |
| 9.    | InCl₃    | 10                  | No solvent | 100 °C  | 48      | NR        |
| 10.   | InCl₃    | 10                  | CH₂NO₂  | Reflux            | 24      | 50        |
| 11.   | InBr₃    | 10                  | Toluene | Reflux            | 24      | 50        |
| 12.   | AlCl₃    | 10                  | Toluene | Reflux            | 24      | 42        |
| 13.   | FeCl₃    | 10                  | Toluene | Reflux            | 24      | 34        |
| 14.   | CuCl₂    | 10                  | Toluene | Reflux            | 24      | 45        |
| 15.   | Cu(O Tf)₂| 10                  | Toluene | Reflux            | 24      | Multi-spots |
| 16.   | CAN      | 10                  | Toluene | Reflux            | 24      | 48        |
| 17.   | I₂       | 10                  | Toluene | Reflux            | 24      | 45        |
| 18.   | TFA      | 10                  | Toluene | Reflux            | 24      | 30        |
| 19.   | p-TsOH   | 10                  | Toluene | Reflux            | 24      | 35        |
| 20.   | BF₃OEt₃ | 10                  | Toluene | Reflux            | 24      | 38        |

These 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.
Table 2  Synthesis of various 2,4-disubstituted quinoline derivatives using Povarov reaction.4

| R1          | R2          | InCl3  | Toluene, reflux | 24 h | R1 | R2 | 3               | InCl3  | Toluene, reflux | 24 h |
|-------------|-------------|--------|-----------------|------|----|----|-----------------|--------|-----------------|------|
| 1a-c        | 2a-f        |        |                 |      |    |    |                 |        |                 |      |

73.6 (Ar. CH), 143.9 (Ar. CH), 145.8 (Ar. CH), 147.4 (Ar. CH); ESI-MS: [M + H]+ m/z 325. Chemical Formula: C23H20N2.

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, Rf: 0.70 (Silica gel, ethyl acetate/n-hexane 1:2). FTIR V: 3474 (NH2), 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, CDCl3-d): δ (ppm): 2.45(s, 3H, CH3), 3.52(s, 2H, NH2), 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); 13C NMR (100 MHz, CDCl3): 20.8 (CH3), 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: C22H17ClN2.

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, Rf: 0.70 (Silica gel, ethyl acetate/n-hexane 1:2). FTIR V: 3494 (NH2), 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, CDCl3-d): δ (ppm): 2.50(s, 3H, CH3), 3.57(s, 2H, NH2),
6.98–6.90 (m, 2H, Ar. =CH), 7.20 (d, 2H, J: 7.6), 7.45 (s, 1H, Ar. =CH), 7.72–7.62 (m, 1H, Ar. =CH), 7.89 (s, 1H, Ar. =CH); ESI-MS: [M + H]+ m/z 356. Chemical Formula: C_{22}H_{17}N_{3}O_{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, Rf 0.70 (SiO₂, ethyl acetate/n-hexane 1:2). FTIR ν:

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

Scheme 3  Proposed mechanism for the synthesis of Quinoline 4a.
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 InCl₃ (5 mol%) were refluxed for 24 h in 5 mL of toluene, (E)-N-(2-ethynylphenyl)-1-phenylmethylamine 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 InCl₃ 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 refuxed 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 (¹H and ¹³C 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 InCl₃ as standard catalyst loading. For scrutinizing the suitable solvent system, similar reactions (entries 4–8) were conducted in various solvent systems such as CH₃CN, DCM, EtOH, THF and CH₃NO₂ 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). To examine the efficacy of InCl₃ extensive comparative studies with several catalytic systems have been investigated. Thus, several reactions were scrutinized in the presence of catalysts like InBr₃, AlCl₃, FeCl₃, Cu(OTf)₂, CuCl₂, CAN, I₂, TFA, p-TsOH and BF₃OEt₂, respectively (Table 1, entries 11–20). All the tested acids gave lower yields than that of InCl₃, 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 InCl₃ 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 InCl₃ in toluene under refluxing for 24 h using aniline 1a (1.0 mmol),

Table 3 Maximum absorption wavelength (λₘₐₓ) for quinoline derivatives

| Sl. No. | Compounds | Chloroform | Acetonitrile | Methanol |
|---------|-----------|------------|-------------|----------|
|         |           | Peaks (nm) | λₘₐₓ (nm)   | Peaks (nm) | λₘₐₓ (nm)   | Peaks (nm) | λₘₐₓ (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.      | 4g        | 262, 347   | 262         | 279, 342  | 279         | 280, 345   | 280       |
| 8.      | 4h        | 260, 343   | 260         | 260, 384  | 260         | 260, 379   | 260       |
| 9.      | 4i        | 260, 343   | 260         | 261, 326  | 261         | 260, 324   | 260       |

Fig. 2 UV-Vis absorption of quinoline derivatives (4a-i) in CH₂Cl₂
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 –NH2 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 cycloadition 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 InCl3 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 CH3CN, CHCl3 and CH3OH solutions. The data of UV-Vis absorption

| Sl. No. | Compounds | λem | ΔΛst | Parameters | Average Life-Time (τav) | Quantum Yield Φfx | CIE Coordinate |
|--------|-----------|-----|------|------------|------------------------|------------------|---------------|
| 1.     | 4a        | 454 | 90   | (a) τ1 = 1.366  
(b) τ2 = 5.494  
(c) X2 = 0.999 | 2.745 ns | 0.01 | X = 0.214  
Y = 0.200 |
| 2.     | 4b        | 438 | 100  | (a) τ1 = 1.681  
(b) τ2 = 4.733  
(c) X2 = 0.999 | 1.805 ns | 0.01 | X = 0.160  
Y = 0.095 |
| 3.     | 4c        | 490 | 94   | (a) τ1 = 2.704  
(b) τ2 = 10.742 
(c) X2 = 0.999 | 3.313 ns | 0.09 | X = 0.259  
Y = 0.510 |
| 4.     | 4d        | 491 | 95   | (a) τ1 = 3.700  
(b) τ2 = 7.510  
(c) X2 = 0.999 | 4.177 ns | 0.20 | X = 0.266  
Y = 0.550 |
| 5.     | 4e        | 492 | 95   | (a) τ1 = 4.307  
(b) τ2 = 7.409  
(c) X2 = 0.999 | 7.266 ns | 0.09 | X = 0.323  
Y = 0.042 |
| 6.     | 4f        | 488 | 108  | (a) τ1 = 2.304  
(b) τ2 = 12.175 
(c) X2 = 0.999 | 3.435 ns | 0.04 | X = 0.223  
Y = 0.604 |
| 7.     | 4g        | 480 | 99   | (a) τ1 = 1.861  
(b) τ2 = 8.341  
(c) X2 = 0.999 | 5.598 ns | 0.02 | X = 0.125  
Y = 0.112 |
| 8.     | 4h        | 496 | 77   | (a) τ1 = 2.488  
(b) τ2 = 8.322  
(c) X2 = 0.999 | 6.204 ns | 0.78 | X = 0.245  
Y = 0.525 |
| 9.     | 4i        | 472 | 92   | (a) τ1 = 2.314  
(b) τ2 = 10.852 
(c) X2 = 0.999 | 3.210 ns | 0.16 | X = 0.165  
Y = 0.181 |
are summarized in Table 3 in $10^{-3}$ mol. L$^{-1}$ in CH$_3$CN, CHCl$_3$ and CH$_3$OH 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 $\pi-\pi^*$ and $n-\pi^*$ 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$_3$CN and CH$_3$OH, most of the compounds experience red shift and blue shift respectively for $\pi-\pi^*$ and $n-\pi^*$ peaks. The $\lambda_{\text{max}}$ 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$_3$CN from CHCl$_3$.

Fig. 3  a Fluorescence emission of quinoline derivatives (4a–i) in CHCl$_3$ (b). Emission (solid line) and absorption (dotted line) spectra of compound 4h in each solvent (CHCl$_3$, CH$_3$CN, CH$_3$OH) (c). Photograph taken under UV light (365 nm) in CHCl$_3$ solution. d Chromaticity diagram showing the CIE coordinates of the compounds 4a–i.
compounds the change in $\lambda_{\text{max}}$ 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 $\lambda_{\text{max}}$ in $\pi-\pi^*$ transition however, compound 4c is the exception with $\lambda_{\text{max}}$ 323 nm (n-$\pi^*$ transition) having methoxy and chloro as substituents in all the solvents (absorption spectra in CH$_3$CN and CH$_3$OH 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, 4h and 4i presented greater intensity, with 4h 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$_3$OH (S3) than polar aprotic solvent CH$_3$CN (S4). Whereas, compounds 4d, 4h 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$_3$OH along with polarity effect, but no such hydrogen-bonding with CH$_3$CN having only polar effect where CHCl$_3$ has none of the effect (Fig. 3d).

The fluorescence quantum yields (\(\varphi\)) of all the compounds in CHCl$_3$ solution are also summarized in Table 4. The higher \(\varphi\) values were obtained in three compounds i.e., 0.78, 0.20, and 0.16 for 4h, 4d, and 4i respectively. And, for other compounds \(\varphi\) values ranges between 0.01–0.09 in CHCl$_3$ solution. The CH$_3$CN solution exhibits lower values due to its polarity (0.75, 0.18, and 0.15 for 4h, 4d, and 4i). The lower \(\varphi\) values (0.54, 0.05, and 0.01 for 4h, 4d, and 4i) in CH$_3$OH solution is due to its higher polarity.

### Average Lifetime

Average lifetime ($\tau_{av}$) measurements for all the newly synthesized compounds have been carried out. It was found that 4e (7.266 ns) has highest lifetime followed by 4h (6.20 ns), 4g (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 $\tau_{av}$ is likely to persist for longer period in the excited state. Thus, compounds 4e, 4h, 4g 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.

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### Compliance with Ethical Standards

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

### Supplementary Information

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