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Synthesis, characterization and electronic effects investigations of new 5,7-disubstituted tris(8-quinolinolate)Al(III) complexes

Saleh N. Al-Busafi*, FakhrEldin O. Suliman, Zaid R. Al-Alawi

Department of Chemistry, College of Science, Sultan Qaboos University, Box 36, Al-Khodh 123, Oman

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ABSTRACT

Eight 5,7-diaryl-8-hydroxyquinoline ligands were synthesized and characterized by ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry. The electron-donating and electron-withdrawing aryl groups were attached to the 5- and 7-positions of the quinolinolate ring via Suzuki coupling reaction. The aluminum complexes of these ligands exhibited successful tuning in the emission color, covering a large segment of the visible spectrum.

1. Introduction

8-Hydroxyquinoline (8-HQ), one of the most popular and versatile organic reagents, and its derivatives have found a great variety of applications ranging from pharmacological and pharmaceutical agents [1] to electron carriers in organic light-emitting diodes (OLEDs) [2] and fluorescent chemosensors for metal ions [3]. 8-hydroxyquinoline has bactericidal activity of comparable potency against non-replicating and replicating *Mycobacterium tuberculosis* (Mtb) [4], and *Staphylococcus aureus* [5]. Moreover, many substituted 8-HQ exhibit greater activity against bacterial strains and fungal strains than do the parent compounds, but moderate activity compared with standard drugs [6,7].

It has been almost more than two decades since tris(8-hydroxyquinoline)aluminum (III) [AlQ_3] was introduced as an electron-transporting material in organic light-emitting diodes (OLEDs) [8]. Nowadays, OLEDs are gradually replacing liquid crystal displays (LCD) as the most important full-color flat panel display technology. In order to improve the efficiency of MQ_3 (M = metal ion) complexes, researchers have centered their efforts on two major aspects: changing the chelated metal ion and modifying the structure of the chelating ligands [9–12]. Concerning the chelating ligands, it has been predicted that electron-donating substituents in the C-5 or C-7 positions of the quinoline skeleton cause a red-shift of the complex emission, while a blue-shift is expected when electron-withdrawing groups are attached in the same positions. In this regard, blue-shifted absorbance/luminescence bands were recorded for 8-hydroxy-5-piperidinylquinolinesulfonamide complexes of aluminum [9]. A successful tuning in the emission color of AlQ_3 was achieved by attachment of electron-donating (EDG) or electron-withdrawing (EWG) aryl groups to the 5-position of the quinolinolate ligand [13].

Sensing metal ions by fluorescent chemosensors is highly applicable to a wide range of technologies and has currently been studied intensively [14]. A chemosensor having a bipodal thiocarbamate scaffold attached to histidine moieties senses Hg^{2+} with a remarkable selectivity [15]. Azathia crown ethers carrying pyrene pendant as receptor molecules showed promising results as metal sensor systems for Cu^{2+}, Zn^{2+}, and Cd^{2+} [16]. Aluminum (III) ion exists widely in the environment due to acid rain and human activities. Its toxicity to the environment and to humans is well documented [17]. Therefore, detection of Al^{3+} is crucial to control its concentration levels in the biosphere, hence its impact on human health. In this regard, 2-hydroxy-1-naphthaldehyde was used as a highly sensitive and selective fluorescent sensor for Al^{3+} in EtOH–H_2O solution [18]. The fluorescent reagent sodium 4-(2,5-diphenyl-1H-pyrrol-1-yl)benzoate (TriPP-COONa) showed good detection limit (27 μg L^{-1}) for detecting aluminum ion in water samples [19]. An efficient fluorescent Al^{3+} receptor, 1-[[(2-

* Corresponding author. Tel.: +968 24142305; fax: +968 24141469.
E-mail address: saleh1@squ.edu.om (S.N. Al-Busafi).

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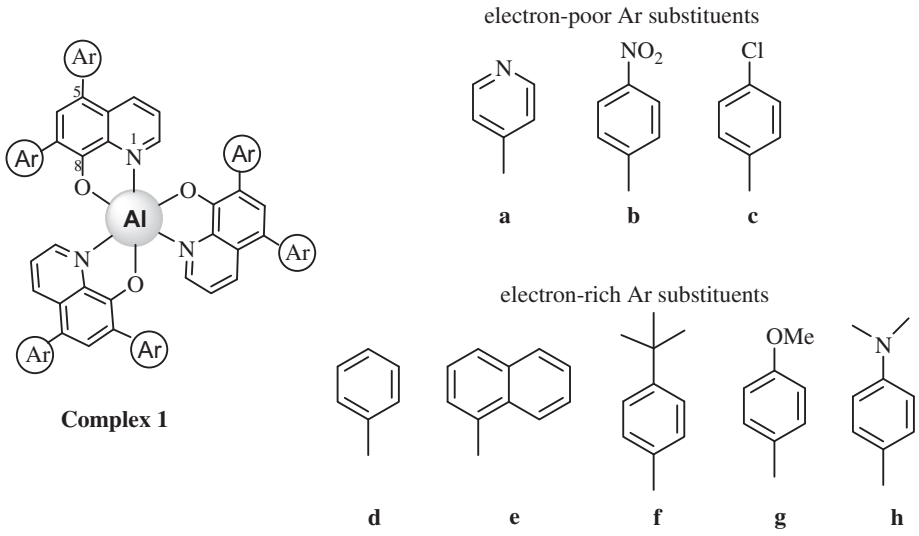


Fig. 1. Structure of AlQ_3 complexes **1a**–**h** with electron-rich and electron-poor aromatic moieties.

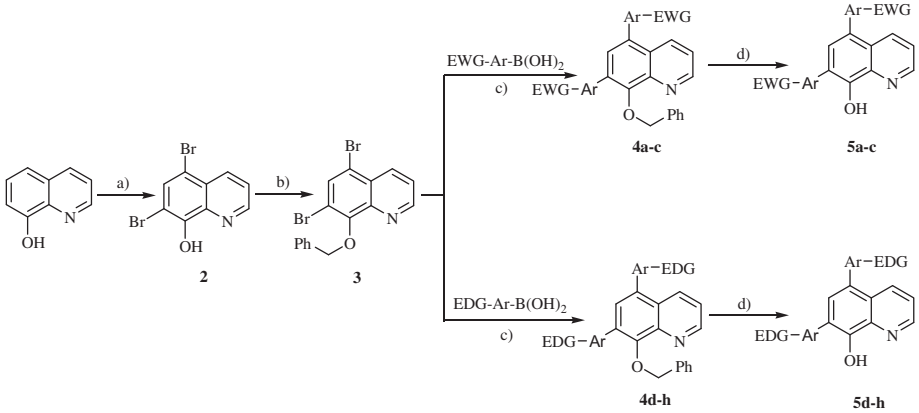
furanylmethyl)imino]methyl]-2-naphthol exhibited high selectivity and affinity towards Al^{3+} [20]. Owing to their chelating ability toward a great number of metal ions, 8-HQ and its derivatives have found many applications in the chemosensing field [21]. 8-Hydroxyquinoline was used to detect Al^{3+} in soil extracts with fluorometric detection limit of $\sim 1 \times 10^{-8}$ *M* (0.3 ppb) Al [22]. Moderate selectivity for Al^{3+} over other metal ions with detection limit reaching $<10^{-7}$ *M* under weak acidic conditions was reported for 8-hydroxyquinoline-carbaldehyde Schiff-base [23].

Nevertheless, there is a need for more research to achieve higher selectivity and sensitivity to detect Al^{3+} over other metal ions. Our approach concentrates on increasing the chelating properties of 8-HQ derivative ligands to enhance the fluorescent output of the produced AlQ_3 complexes and consequently increase the quantum yield and shifting the color to red regions by introducing electron-withdrawing and electron-donating phenyl moieties at the C5 and C7 positions of 8-HQ [24]. In this paper, we report the synthesis, spectroscopic identification, and photophysical behavior of eight AlQ_3 complexes **1a**–**h** in which the phenyl groups at C5 and C7 of the ligands are substituted either with electron-withdrawing groups **a**–**c** or with electron-donating groups **d**–**h** (Fig. 1).

2. Results and discussion

2.1. Synthesis

The eight ligands were prepared starting from 8-hydroxy quinoline following previously published method [25]. Dibromination of 8-HQ at C-5 and C-7 was performed satisfactorily using the published method with some modifications in which the concentrated sulfuric acid was replaced with acetic acid and the reaction was performed at room temperature to give compound **2** in 75.4% yield. The hydroxyl group in **2** was protected smoothly by the stable benzyl (Bn) group prior to the Pd-catalyzed coupling reactions to yield intermediate **3** in 54.0%. Compounds **4a**–**h** were prepared by coupling intermediate **3** with a suitable arylboronic acid using Suzuki cross-coupling reaction. Hence, the electron-rich EDG arenes and electron-poor EWG arenes were, respectively, attached to 8-benzyloxy-5,7-dibromoquinoline **3** in 50–89% yield. Deprotection of the benzyl group was achieved by catalytic transfer hydrogenation (CTH) using cyclohexa-1,4-diene and Pd/C catalyst in absolute ethanol to give ligands **5a**–**h** in 50–90% yield (Scheme 1). The final AlQ_3 complexes **1a**–**h** were prepared by reacting the ligands **5a**–**h** with $AlCl_3 \cdot 6H_2O$ in methanol. All the



Scheme 1. Synthesis of compounds **5a**–**h**; reaction conditions: a) Br_2, AcOH, RT, 20 min; b) Bn-Cl, K_2CO_3, KI, acetone, reflux, 16 h; c) $[Pd(pph_3)_4]$ (6%), Na_2CO_3, benzene, H_2O, EtOH, reflux, 24 h; d) 1,4-cyclohexadiene, Pd–C (10%), EtOH, reflux, 5 h.

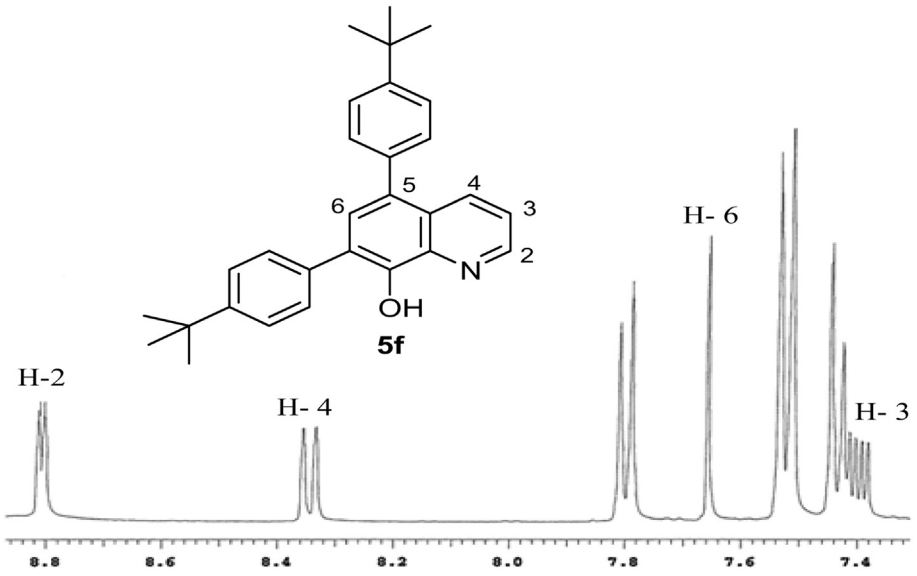


Fig. 2. ^{1}H NMR of **5f**.

synthesized complexes are new except **1d** which was prepared before by Hay et al. [25].

The prepared ligands **5a**–**h** exhibit a distinctive ^{1}H NMR coupling pattern for the protons 2, 3, 4, and 6 while protons that belong to the substituted phenyl groups at C-5 and C-7 varies from one ligand to another. In this regard, proton 2 appears as doublet of doublet, shifted down field by N-atom of the pyridine ring. The *J* values range from 1.0 to 1.4 Hz due to *meta*-coupling with H-4 and 4.0 to 4.5 Hz due to *ortho*-coupling with H-3. Proton 4 appears as doublet of doublet with *J* values varies from 1.0 to 1.4 Hz due to *meta*-coupling with H-2 and 8.0 to 8.4 Hz due to *ortho*-coupling with H-3. Proton 3 appears up-field as doublet of doublet and proton 6 as singlet (Fig. 2).

2.2. Spectroscopic properties

The complexes **1a**–**h** were studied by using UV–visible and fluorescence spectroscopies and the resulting photophysical data are summarized in Table 1. For the series, the π–π^* absorption maxima of the complexes shifted to lower energies relative to the transition of the parent AlQ_3 ($\lambda_{max} = 388$ nm), most likely due to the extension in the conjugation of the quinoline chromophore. The fluorescence maximum of 5,7-diphenyl-8-hydroxyquinoline **1d** exhibited a red shift of 15 nm compared to the parent 8-hydroxyquinoline complex. As expected, the introduction of two aryl groups at C-5 and C-7 to the 8-HQ system results in a higher degree of conjugation and hence lowers the π–π^* transition energies for the complexes. Such result also supported by high oscillating strength for the extended chromophores in complexes **1a**–**h** ($\varepsilon = 2.6 \times 10^4$–$8.9 \times 10^4$ M^{-1} cm^{-1}) relative to the parent complex AlQ_3 ($\varepsilon = 7.6 \times 10^3$ M^{-1} cm^{-1}).

Examination of the data in Table 1 and fluorescence spectra in Fig. 3 reveals successful emission color tuning in complexes **1a**–**h** arbitrated by the aryl electronic spacers at C-5 and C-7 of the quinolinolate ring system. Almost direct correlation can be observed between the photophysical properties and the electronic nature of the attached aryl substituents. It is clear from Fig. 3 that the emission shifts systematically from blue to green, yellow, and red depending on the electronic nature of the modulator group. We believe that aluminum complex in which the quinolinolate chromophore is attached to two electronic effectors at C-5 and C-7 would exhibit amplified emission tuning compared to the C-5 substituted quinolinolate chromophores. The emission maxima of complexes **1a**–**h** span over 63 nm between 503 and 567 nm, covering a significant portion of the visible light spectrum. The

Table 1
Photophysical properties[a] recorded for AlQ_3 and complexes **1a**–**h** in methanol at 23 °C.

Complex	$\lambda_{max}^{abs}(\varepsilon)$[b]	λ_F [nm]	ϕ_F[c]	τ_F[ns]
AlQ_3	388 (7.6×10^3)	520	0.171	15.38
1a	390 (8.9×10^4)	503	0.960	8.17
1b	398 (5.5×10^4)	527	0.950	7.90
1c	400 (5.7×10^4)	531	0.950	7.60
1d	401 (5.7×10^4)	535	0.930	7.45
1e	394 (2.6×10^4)	540	0.910	5.39
1f	408 (4.6×10^4)	542	0.440	5.07
1g	398 (6.0×10^4)	543	0.260	2.86
1h	410 (4.5×10^4)	567	0.189	1.23

[a] λ_{max}^{abs} = absorption maximum, λ_F = fluorescence maximum, ϕ_F = fluorescence quantum yield, τ_F = fluorescence lifetime.
[b] Unite are [nm](M^{-1} cm^{-1}).
[c] Determined by using quinine sulfate (in 0.05 M H_2SO_4) as a standard.

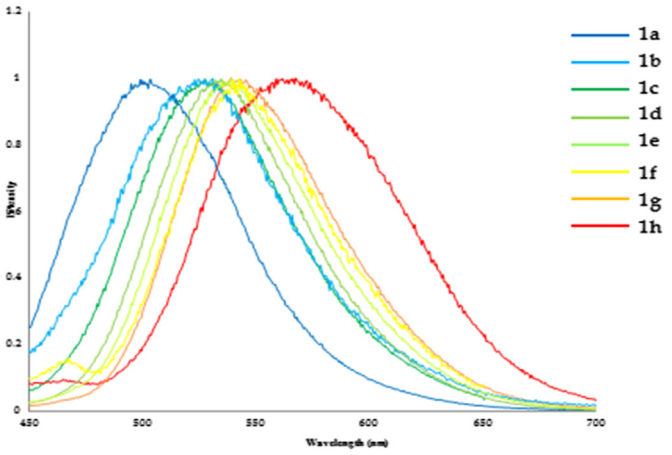


Fig. 3. Emission spectra of complexes **1a**–**h**.

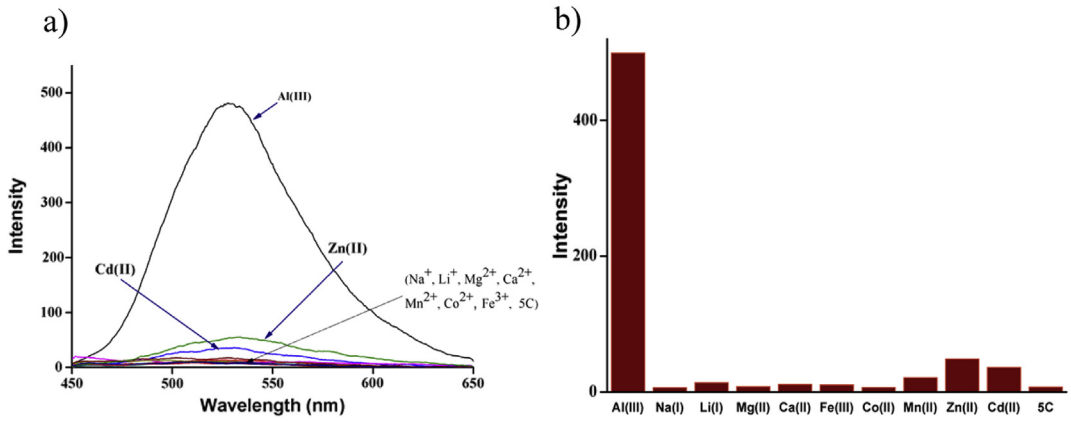


Fig. 4. a) Emission spectra of complexes formed between **5c** and Al^{3+}, Na^{+}, Li^{+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, $Zn^{2+}$and Cd^{2+} ions; b) Bar graph showing the change of emission intensity of **5c** at 531 nm when treated with various metal ions (max: 400 nm).

fluorescence of aluminum complex of 5,7-diphenyl-8-hydroxy quinoline **1d** (aryl substituent) is the reference of the series with $\lambda_F = 535$ nm since all the other ligands have either EW aryl groups **1a**–**c** or ED aryl groups **1e**–**h**. Hence, substitution of EW aryl groups at positions 5 and 7 of the quinoline ring shifted the fluorescence maximum wavelength from 4 to 32 nm towards blue (hypsochromic shift) relative to 5,7-diphenyl-8-hydroxyquinoline **1d** as in compounds **1a**–**c**. On the other hand, substitution of ED aryl groups at positions 5 and 7 of the quinoline ring shifted the fluorescence maximum wavelength from 5 to 32 nm towards red (bathochromic shift) compared to 5,7-diphenyl-8-hydroxyquino line **1d** as in compounds **1e**–**h**.

Furthermore, close inspection of the data in Table 1 reveals that the fluorescence quantum yield (ϕ_F) and lifetime (τ_F) of complexes **1a**–**h** depend on the electronic properties of the substituted aryl moieties connected to C-5 and C-7 of 8-HQ. For instance, the fluorescence quantum yield of the eight complexes has increased significantly relative to the parent 8-HQ from 11% in the case of **1h** to 462% for **1a**. In addition, the fluorescence quantum yield and lifetime decrease when the aryl groups are substituted with electron-donating groups for complexes **1e**–**h**, whereas electron-withdrawing entities as in complexes **1a**–**c** lead to an increase in both the fluorescence quantum yield and lifetime when compared with non-substituted aryl group (complex **1d**).

To examine the detection selectivity of the prepared ligands towards Al^{3+}, the response of ions such as Na^{+}, Li^{+}, Mg^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Mn^{2+}, $Zn^{2+}$and Cd^{2+} was investigated for compound **5c**. The results are shown in Fig. 4. **5c** itself exhibits weak fluorescence in methanol. However, treatment with Al^{3+} (10 μM) resulted in a significant increase in fluorescence intensify at 531 nm upon excitation at 400 nm. No such effect was observed when other ions (100 μM) were used. Therefore, **5c** and possibly the other ligands exhibit selectivity for Al^{3+} over other metal ions. In addition, using **5c**, we obtained a detection limit for Al^{3+} of 0.11 ppb.

3. Conclusion

In summary, starting from 8-hydroxyquinoline, we have synthesized a series of 5,7-disubstituted tris(8-quinolinolate) aluminum (III) complexes containing EW/ED groups connected via aryl spacer groups. We have demonstrated that the emission color and fluorescence quantum yield of the produced complexes influenced by the electronic environment of the aryl substituents. The spectroscopic measurements of the new AlQ_3 complexes demonstrate clearly the possibility of tuning their emission color by connecting the quinolinolate ligands with selected substituted aryl moieties at C-5 and C-7. Ligand **5c** shows high sensitivity towards Al^{3+} in the presence of interference ions.

4. Experimental

4.1. General

Melting points were determined using Gallen-Kamp melting point apparatus. NMR analysis (^1H and ^{13}C) were performed on a Varian400 (VNMRS-400 MHz) spectrometer using $CDCl_3$ solution (referenced internally to Me_4Si): *J* values are given in Hertz. IR spectra were obtained with a Nicolet model Magna 560 spectrometer; absorption bands are recorded in wave number (cm^{-1}). TLC was performed on dry silica gel plates and developed by using hexane/ethyl acetate mixture as the eluent. Mass spectra were obtained using Quattro Ultima Pt tandem quadruple mass spectrometer (Waters Corp. MA, USA) instrument. UV–Vis spectra were performed on Varian CARY 50 spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence spectrophotometer.

All reagents and solvents were purchased from Sigma–Aldrich and were used without further purification.

4.2. Synthesis of 5,7-dibromo-8-hydroxyquinoline (*2*)

A solution of bromine (8.79 g, 55.2 mmol) in acetic acid (25 mL) was added over 5 min with stirring to a solution of 8-hydroxyquinoline (4.00 g, 27.6 mmol) in acetic acid (25 mL). After stirring at room temperature for further 15 min, 300 mL of cold water was added to the mixture followed by 2 g of sodium metabisulfite. The crude product was filtered and recrystallized from ethanol to give the title compound as white solid (6.30 g, 75.4%), Mp: 198.2–199.4 °C. IR (KBr) ν_{max} in cm^{-1}: 3325, 3080, 1581 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26 (s, 1H), 7.58 (dd, $J = 4.3$, $J = 8.6$ Hz, 1H), 7.92 (s, 1H), 8.46 (dd, $J = 1.4$, $J = 8.6$ Hz, 1H), 8.81 (dd, $J = 1.4$, $J = 4.3$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 105.60, 110.54, 123.42, 127.70, 134.23, 136.52, 139.04, 149.62, 150.09. ESI-MS $(M)^+$ calcd for $C_9H_5Br_2NO$:302.95, found:302.74.

4.3. Synthesis of 8-benzyloxy-5,7-dibromoquinoline (*3*)

A mixture of 5,7-dibromo-8-hydroxyquinoline (**2**) (5.00 g, 16.5 mmol), benzyl chloride (2.50 g, 19.8 mmol), potassium carbonate (3.70 g, 26.7 mmol) and potassium iodide (0.13 g,

0.78 mmol) in acetone (60 mL) was refluxed under N_2 for 10 h. The reaction mixture was poured into ice water, filtered and washed with water. The crude product was recrystallized from ethanol/water and dried under vacuum to yield white to green solid (3.5 g, 54.0%), Mp.: 114.5–116.5 °C. IR (KBr) ν_{max} in cm^{-1}: 3100, 1574, 1366. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.98 (dd, $J = 1.2$, $J = 4.1$ Hz, 1H), 8.47 (dd, $J = 1.2$, $J = 8.5$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.5 (dd, $J = 4.1$, $J = 8.5$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 7.25–7.36 (m, 5H), 5.43 (s, 2H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 151.06, 122.3, 136.40, 128.75, 122.90, 134, 117.20, 152.73, 137.41, 116.70, 144.31, 128.47 (2C), 129.08, 128.60 (2C). ESI-MS $(M)^+$ calcd for $C_{16}H_{11}Br_2NO$: 393.10, found: 393.12.

4.4. General procedure for the synthesis of compounds **4a–h**

A mixture of 8-benzyloxy-5,7-dibromoquinoline (**3**) (3.00 g, 7.63 mmol), substituted phenylboronic acid (2.2 equiv), benzene (30 mL), ethanol (12 mL), water (22 mL) and sodium carbonate (3.70 g, 30.3 mmol) was degassed under nitrogen for 30 min. To the mixture was added $Pd(PPh_3)_4$ (0.53 g, 0.46 mmol) and the reaction was refluxed under nitrogen for 24 h.

4.4.1. Synthesis of 5,7-bis(pyridin-4-yl)-8-benzyloxyquinoline (**4a**)

The specific amount of chemical used is: 4-Pyridinylboronic acid (2.06 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give 4a (1.70 g, 55.6%) as a yellow powder. Mp.: 204.0–205.8 °C. IR (KBr) ν_{max} in cm^{-1}: 3009, 2950, 1594, 1352, 745. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.53 (s, 2H), 7.07 (m, 2H), 7.19 (m, 2H), 7.35–7.42 (m, 5H), 7.52 (m, 1H), 7.65 (s, 1H), 7.67 (m, 2H), 8.11 (dd, $J = 1.2$, $J = 8.3$ Hz, 1H), 8.74 (m, 2H), 8.98 (dd, $J = 1.2$, 4.0 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 74.05, 116.53, 121.83, 124.80 (2C), 126.65, 127.69, 128.15 (2C), 128.34 (2C), 128.65 (2C), 129.89, 131.21, 133.96, 134.73, 137.16, 143.66, 145.83, 149.61, 150.14 (2C), 150.24 (2C), 152.72. ESI-MS $(M + H)^+$ calcd for $C_{26}H_{19}N_3O$: 389.15, found: 390.28.

4.4.2. Synthesis of 5,7-bis(p-nitrophenyl)-8-benzyloxyquinoline (**4b**)

The specific amount of chemical used is: 4-nitrophenyl boronic acid (2.23 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4b** (2.63 g, 82.5%) as a tan powder. Mp.: 162.1–163.8 °C. IR (KBr) ν_{max} in cm^{-1}: 3010, 2977, 1595, 1346, 845. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.54 (s, 2H), 7.08 (m, 5H), 7.44 (dd, $J = 4.4$, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.67 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 8.08 (dd, $J = 1.6$, $J = 8.8$ Hz, 1H), 8.20 (m, 2H), 8.35 (d, $J = 8.4$ Hz, 2H), 9.00 (dd, $J = 1.6$, $J = 4.4$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 76.57, 116.49, 121.89, 122.30, 123.23, 123.86 (2C), 126.84, 128.09–128.52 (5C), 128.66 (2C), 128.78 (2C), 130.82 (2C), 131.42, 134.24, 137.13, 144.43, 144.62, 145.46, 150.06, 150.37, 152.78. ESI-MS $(M + H)^+$ calcd for $C_{28}H_{19}N_3O_5$: 477.47, found: 477.85.

4.4.3. Synthesis of 5,7-bis(p-chlorophenyl)-8-benzyloxyquinoline (**4c**)

The specific amount of chemical used is: 4-chloro-phenyl boronic acid (2.63 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4c** (1.80 g, 50.2%) as an orange powder. Mp.: 119.1–121.2 °C. IR (KBr) ν_{max} in cm^{-1}: 3009, 2967, 1637, 1343, 787. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.23 (s, 2H), 7.20 (m, 5H), 7.36 (m, 1H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.44 (s, 1H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 8.19 (dd, $J = 1.6$, $J = 8.6$ Hz, 1H), 9.03 (dd, $J = 1.6$, $J = 4.4$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 76.21, 121.40, 127.35, 127.79, 128.05 (2C), 128.30 (2C), 128.55 (2C), 128.76 (2C), 129.18, 131.25 (2C), 131.34 (2C), 132.77, 133.45, 133.84, 134.18, 134.78, 136.40, 137.13, 137.47, 143.53, 149.92, 151.31. ESI-MS $(M + H)^+$ calcd for $C_{28}H_{19}Cl_2NO$: 456.36, found: 456.29.

4.4.4. Synthesis of 5,7-diphenyl-8-benzyloxyquinoline (**4d**)

The specific amount of chemical used is: Phenylboronic acid (2.47 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4d** (2.37 g, 80.1%) as a brown solid. Mp.: 122.5–122.8 °C. IR (KBr) ν_{max} in cm^{-1}: 3019, 1353, 1210, 1073. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.18 (s, 2H), 7.40 (dd, $J = 4.0$, $J = 8.0$ Hz, 1H), 7.43–7.45 (m, 5H), 7.50 (m, 6H), 7.55 (s, 1H), 7.68 (m, 4H), 8.27 (dd, $J = 2.0$, $J = 8.0$ Hz, 1H), 9.02 (dd, $J = 4.0$, $J = 2.0$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 76.34, 121.09, 127.29, 127.39, 127.61, 128.00 (2C), 128.14 (2C), 128.50 (4C), 129.70, 129.72, 129.97 (2C), 130.13 (2C), 133.92, 134.48, 135.95, 137.45, 138.14, 139.22, 143.60, 149.75, 151.11. ESI-MS $(M + H)^+$ calcd for $C_{28}H_{21}NO$: 387.47, found: 388.04.

4.4.5. Synthesis of 5,7-dinaphthyl-8-benzyloxyquinoline (**4e**)

The specific amount of chemical used is: 1-naphthalene boronic acid (2.89 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4e** (2.49 g, 67.0%) as brown solid. Mp.: 179.1–182.2 °C. IR (KBr) ν_{max} in cm^{-1}: 3010, 2870, 1590, 1219, 1095, 776. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.24 (s, 2H), 6.87–7.14 (m, 5H), 7.38–7.88 (m, 14H), 7.64 (s, 1H), 7.31 (m, 1H), 7.94 (dd, $J = 1.8$, $J = 8.0$ Hz 1H), 9.07 (dd, $J = 1.8$, $J = 4.1$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 76.76, 121.91, 125.77, 125.26–128.19, 126.48, 128.89, 127.37, 127.81–128.38 (6C), 135.08, 135.08, 137.53, 143.36, 149.88. ESI-MS $(M + H)^+$ calcd for $C_{36}H_{25}NO$: 487.59, found: 488.37.

4.4.6. Synthesis of 5,7-bis(p-tert-butylphenyl)-8-benzyloxyquinoline (**4f**)

The specific amount of chemical used is: 4-*tert*-butylphenylboronic acid (2.99 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4f** (3.40 g, 89.2%) as an orange powder. Mp.: 149.0–149.2 °C. IR (KBr) ν_{max} in cm^{-1}: 3010, 2830, 1637, 1368, 756. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.40 (s, 9H), 1.41 (s, 9H), 5.18 (s, 2H), 7.18–7.21 (m, 5H), 7.37 (dd, $J = 4.0$, $J = 8.4$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.58 (s, 1H), 7.61 (d, $J = 8.4$ Hz, 2H), 8.32 (dd, $J = 1.6$, $J = 8.4$ Hz, 1H), 9.01 (dd, $J = 1.6$, $J = 4.0$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 31.45 (6C), 34.63, 34.67, 76.47, 120.84, 125.03 (2C), 125.41 (2C), 127.27, 127.54, 127.91 (2C), 128.61 (2C), 129.68 (2C), 129.81 (2C), 133.92, 134.63 (2c), 135.27, 135.82, 136.34, 137.63, 143.70, 149.63, 150.30, 150.48, 151.14. ESI-MS $(M + H)^+$ calcd for $C_{36}H_{37}NO$: 499.69, found: 500.30.

4.4.7. Synthesis of 5,7-bis(p-methoxyphenyl)-8-benzyloxyquinoline (**4g**)

The specific amount of chemical used is: 4-methoxy phenylboronic acid (2.55 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4g** (2.40 g, 70.3%) as a pale yellow solid. Mp.: 147.1–147.9 °C. IR (KBr) ν_{max} in cm^{-1}: 3019, 1609, 1351, 1026, 723, ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.87 (s, 3H), 3.89 (s, 3H), 5.17 (s, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 8.8$ Hz, 2H), 7.24–7.30 (m, 5H), 7.36 (dd, $J = 4.4$, $J = 8.4$ Hz, 1H) 7.42 (d, $J = 8.8$ Hz, 2H), 7.53 (s, 1H), 7.66 (d, $J = 8.8$ Hz, 2H), 8.27 (dd, $J = 1.8$, $J = 8.4$ Hz, 1H), 9.01 (dd, $J = 1.8$, $J = 4.4$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 55.34, 55.43, 76.13, 113.95 (2C), 114.05 (2C), 120.84, 127.22, 128.03 (2C), 128.54 (2C), 129.59, 129.62, 130.56, 131.14, 131.20 (2C), 134.52 (2C), 134.86, 135.63, 137.61, 141.73, 149.70, 150.70, 159.04, 159.17. ESI-MS $(M + H)^+$ calcd for $C_{30}H_{25}NO_3$: 447.52, found: 448.38.

*4.4.8. Synthesis of 5,7-bis(p-dimethylaminophenyl)-8-benzyloxy quinoline (**4h**)*

The specific amount of chemical used is: 4-(dimethylamino) phenylboronic acid (2.77 g, 16.8 mmol). The crude product was extracted with benzene, recrystallized from ethanol, and dried under vacuum to give **4h** (1.98 g, 54.7%) as light yellow powder. Mp.: 159.1–159.6 °C. IR (KBr) ν_{max} in cm^{-1}: 3012, 2967, 1521, 1086. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.013 (s, 6H), 3.014 (s, 6H), 5.48 (s, 2H), 6.79–6.87 (m, 4H), 7.31 (dd, $J = 4.0$, $J = 8.0$ Hz, 1H), 7.06–7.24 (m, 5 H), 7.56 (s, 1H), 7.66 (m, 4H), 8.31 (dd, $J = 2.0$, $J = 8.0$ Hz, 1H), 8.96 (dd, $J = 2.0$, $J = 4.0$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 40.53 (2C), 40.62 (2C), 75.75, 112.23 (2C), 112.33 (2C), 121.20, 126.71, 127.35 (2C), 127.46–128.31 (5C), 128.05, 130.91–130.60 (4C), 132.87, 134.64, 137.19, 140.62, 148.99, 149.77, 153.12 (2C). ESI-MS $(M + H)^+$ calcd for $C_{32}H_{31}N_3O$: 473.61, found: 474.41.

*4.5. General procedure for the synthesis of compounds **5a–h***

A mixture of compound 4–11, Pd/C (10 wt%), cyclohexa-1,4-diene, and absolute ethanol was refluxed under N_2 for 5 h. The mixture was filtered, and ethanol was evaporated under vacuum.

4.5.1. Synthesis of 5,7-bis(pyridin-4-yl)-8-hydroxyquinoline (5a)

The specific amount of chemicals used are: 5,7-bis(pyridin-4-yl)-8-benzyloxyquinoline (11) (1.01 g, 2.57 mmol), Pd/C (0.79 g), cyclohexa-1,4-diene (1.84 g, 22.8 mmol), and ethanol (25.0 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5a (0.512 g, 61.2%) as orange solid. Mp.: p134.6–134.9 °C. IR (KBr) ν_{max} in cm^{-1}: 3409, 1508, 1334, 1257. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, $J = 8.0$ Hz, 2H), 7.77 (s, 1H), 7.78 (dd, $J = 4.4$, 8.8 Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 6.8$ Hz, 2H), 8.64 (dd, $J = 1.2$, 8.6 Hz, 1H), 8.86 (d, $J = 6.8$ Hz, 2H), 8.99 (dd, $J = 1.2$, 4.4 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 111.92, 122.88, 125.51, 126.51, 126.98 (4C), 131.02, 133.89, 135.94, 136.14, 143.71 (4C), 147.16, 153.90, 154.40. ESI-MS $(M + H)^+$ calcd for $C_{16}H_{13}N_3O$: 299.33, found: 300.02.

4.5.2. Synthesis of 5,7-bis(p-nitrophenyl)-8-hydroxyquinoline (5b)

The specific amount of chemicals used are: 5,7-bis(p-nitrophenyl)-8-benzyloxyquinoline (10) (1.02 g, 2.09 mmol), Pd/C (0.64 g), cyclohexa-1,4-diene (1.50 g, 18.6 mmol), and ethanol (20.4 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5b (0.50 g, 61.7%) as brown solid. Mp.: 122.2–122.5 °C. IR (KBr) ν_{max} in cm^{-1}: 3468, 3061, 1482, 1230. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.81 (m, 2H), 7.21 (m, 2H), 7.34 (m, 1H), 7.38 (m, 2H), 7.62 (s, 1H), 7.68 (m, 2H), 8.30 (m, 1H), 8.95 (d, $J = 2.8$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 115.0 (2C), 121.89, 128.35, 128.64 (2C), 128.72 (2C), 130.42, 130.78 (2C), 131.95, 134.13, 138.01, 138.28, 1441.01, 144.66, 148.27, 148.91, 150.28. ESI-MS $(M + H)^+$ calcd for $C_{21}H_{13}N_3O_5$: 387.35, found: 388.18.

4.5.3. Synthesis of 5,7-bis(p-chlorophenyl)-8-hydroxyquinoline (5c)

The specific amount of chemicals used are: 5,7-bis(*p*-chlorophenyl)-8-benzyloxyquinoline (9) (1.01 g, 2.19 mmol), Pd/C (0.67 g), cyclohexa-1,4-diene (1.57 g, 19.5 mmol), and ethanol (21.4 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5c (0.720 g, 89.7%) as yellow crystals. Mp.: 168.1–168.5 °C. IR (KBr) ν_{max} in cm^{-1}: 3415, 1538, 1381. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (m, 1H), 7.44 (m, 2H), 7.53 (m, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 7.2$ Hz, 2H), 7.83 (s, 1H), 8.90 (d, $J = 8.0$ Hz, 1H), 9.03 (m, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 120.35, 128.52, 128.69 (2C), 129.10 (2C), 129.85, 130.11 (2C), 131.22 (2C), 132.77, 133.59, 134.05, 134.43, 134.69, 141.70, 141.84, 144.81 (2C), 144.93. ESI-MS $(M)^+$ calcd for $C_{21}H_{13}Cl_2NO$: 366.24, found: 366.18.

4.5.4. Synthesis of 5,7-diphenyl-8-hydroxyquinoline (5d)

The specific amount of chemicals used are: 5,7-diphenyl-8-benzyloxyquinoline (4) (1.0 g, 2.58 mmol), Pd/C (0.794 g), cyclohexa-1,4-diene (1.85 g, 23.0 mmol), and ethanol (25.2 mL). The crude product was filtered and recrystallized from ethanol/water and dried under vacuum to give 5d (0.511 g, 66.7%) as light yellow crystals. Mp.: 136.1–136.5 °C. IR (KBr) ν_{max} in cm^{-1}: 3315, 3033, 1638, 1371. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39–7.43 (m. 2H), 7.47 (dd, $J = 4.0$, 8.8 Hz, 1H), 7.49–7.55 (m, 6H), 7.67 (s, 1H), 7.89 (m, 2H), 8.31 (dd, $J = 1.6$, 8.8 Hz, 1H), 8.83 (dd, $J = 1.6$, 4.0 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 121.68, 122.25, 125.88, 127.33, 127.36, 128.45 (2C), 128.58 (2C), 129.42 (2C), 129.97, 130.14, 130.72, 134.62, 137.60, 138.69, 139.30, 147.91, 148.23. ESI-MS $(M + H)^+$ calcd for $C_{21}H_{15}NO$: 297.35, found: 298.06.

4.5.5. Synthesis of 5,7-dinaphthyl-8-hydroxyquinoline (5e)

The specific amount of chemicals used are: 5,7-dinaphthyl-8-benzyloxyquinoline (8) (1.01 g, 2.05 mmol), Pd/C (0.63 g), cyclohexa-1,4-diene (1.47 g, 18.2 mmol), and ethanol (20.0 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5e (0.57 g, 70.2%) as gold crystals. Mp.: 202.2–203.6 °C. IR (KBr) ν_{max} in cm^{-1}: 3433, 3046, 1631, 1193. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.46–7.62 (m, 7H), 7.91–7.96 (m, 7H), 7.34 (m, 1H), 7.64 (s, 1H), 7.84 (m, 1H), 8.86 (d, $J = 4.1$ Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 121.80, 126.02, 128.03–128.55 (24C), 135.23, 148.09, 149.00. ESI-MS $(M)^+$ calcd for $C_{29}H_{19}NO$: 397.47, found: 397.99.

4.5.6. Synthesis of 5,7-bis(p-tert-butylphenyl)-8-hydroxyquinoline (5f)

The specific amount of chemicals used are: 5,7-bis(*p*-tert-butylphenyl)-8-benzyloxyquinoline (6) (1.50 g, 3.00 mmol), Pd/C (0.92 g), cyclohexa-1,4-diene (2.15 g, 26.6 mmol), and ethanol (22.0 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5f (0.670 g, 65.1%) as linen crystals. Mp.: 138.6–139.8 °C. IR (KBr) ν_{max} in cm^{-1}: 3489, 2954, 1637, 1361. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.39 (s, 9H), 1.41 (s, 9H), 7.39 (dd, $J = 4.4$, 8.4 Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.52 (m, 4H), 7.66 (s, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 8.35 (dd, $J = 1.2$, 8.4 Hz, 1H), 8.81 (dd, $J = 1.2$, 4.4 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 31.37 (3C), 31.43 (3C), 34.60, 34.63, 121.40, 122.13, 125.38 (2C), 125.43 (2C), 125.80, 128.97 (2C), 129.75 (2C), 129.89, 130.54, 134.63, 134.77, 136.34, 138.70, 147.75, 147.92, 150.13, 150.22. ESI-MS $(M + H)^+$ calcd for $C_{29}H_{31}NO$: 409.56, found: 410.23.

4.5.7. Synthesis of 5,7-bis(p-methoxyphenyl)-8-hydroxyquinoline (5g)

The specific amount of chemicals used are: 5,7-bis(*p*-methoxyphenyl)-8-benzyloxyquinoline (5) (1.0 g, 2.23 mmol), Pd/C (0.70 g), cyclohexa-1,4-diene (1.60 g, 20.0 mmol), and ethanol (22.0 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give 5g (0.689 g, 54.0%) as orange crystals. Mp.: 118.2–119.3 °C. IR (KBr) ν_{max} in cm^{-1}: 3352, 3015, 1635, 1266. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.87 (s, 3H), 3.89 (s, 3H), 7.03 (d, $J = 8.8$ Hz, 2H), 7.05 (d, $J = 8.8$ Hz, 2H), 7.37 (dd, $J = 4.0$, 8.4 Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.58 (s, 1H), 7.80 (d, $J = 8.8$ Hz, 2H), 8.27 (dd, $J = 1.2$, 8.4 Hz, 1H), 8.78 (dd, $J = 1.2$, 4.0 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 55.34, 55.39, 113.90 (2C), 113.97 (2C), 121.34, 121.89, 125.76, 129.64, 129.99, 130.29, 130.50 (2C), 131.13 (2C), 131.70, 134.63, 138.70, 147.62, 147.78, 158.89, 158.99. ESI-MS $(M)^+$ calcd for $C_{23}H_{19}NO_3$: 357.40, found: 357.40.

4.5.8. Synthesis of 5,7-bis(p-dimethylaminophenyl)-8-hydroxyquinoline (5h)

The specific amount of chemicals used are: 5,7-bis(*p*-dimethylaminophenyl)-8-benzyloxyquinoline (7) (0.30 g, 0.63 mmol), Pd/C (0.79 g), cyclohexa-1,4-diene (1.85 g, 23.0 mmol), and ethanol (15.0 mL). The crude product was recrystallized from ethanol/water and dried under vacuum to give **5h** (0.12 g, 50.2%) as yellow crystals. Mp.: 176.2–177.8 °C. IR (KBr) ν_{max} in cm^{-1}: 3332, 2954, 1520, 1353. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.02 (s, 12H), 6.84 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 2H), 7.25 (s, 1H), 7.32 (d, $J = 8.8$ Hz, 2H), 7.38 (dd, $J = 4.0$, 8.8 Hz, 1H), 7.40 (d, $J = 7.8$ Hz, 2H), 8.34 (dd, $J = 1.6$, 8.8 Hz, 1H), 8.76 (dd, $J = 1.6$, 4.0 Hz, 1H). δ_C (100.4 MHz, $CDCl_3$): δ (ppm) 40.60 (4C), 109.46 (2C), 112.42 (2C), 121.45, 126.98, 127.38 (2C), 127.79, 130.76 (4C), 131.2, 135.01, 138.36, 147.47, 149.75 (2C), 150.92. ESI-MS $(M + H)^+$ calcd for $C_{25}H_{25}N_3O$: 383.49, found: 384.14.

4.6. General method for the preparation of the aluminum complexes

The stock solution of $AlCl_3 \cdot 6H_2O$ was prepared by dissolving (0.0604 g, 0.4530 mmol) of $AlCl_3$ in 25.00 mL of water. The stock solutions of ligands were prepared by taking 15.00 mg of compound **5a**, 19.40 mg of compound **5b**, 18.31 mg of compound **5c**, 15.00 mg of compound **5d**, 20.00 mg of compound **5e**, 20.50 mg of compound **5f**, 18.00 mg of compound **5g**, and 19.00 mg of compound **5h**, and dissolved in 25 mL of methanol in separate volumetric flasks. The final concentration of all the stock solutions including $AlCl_3 \cdot 6H_2O$ was 1.00×10^{-2} M. The complexes **1a**–**h** were prepared by mixing appropriate volumes of the ligands with the respective volume of aluminum chloride in 5.00 mL volumetric flasks then the volume was completed with methanol to the mark. The final concentration of all complexes was 2.0×10^{-5} M.

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