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Synthesis of 4-(2-arylvinyl)-8-hydroxyquinolines via anhydrous Heck coupling reaction and the PL properties of their Al complexes

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ABSTRACT

Anhydrous Heck coupling between **2** and eight different arylvinyl compounds using 3 mol% of $PdCl_2/2PPh_3$ catalyst system occurs selectively at position-4 of **2** affording 4-(2-arylvinyl)-8-tosyloxyquinolines **3** in good to high yields. The tosyloxy protecting group showed high stability under anhydrous coupling conditions. Deprotection of the resulting 4-arylvinyl-8-tosyloxyquinolines produced 4-(2-arylvinyl)-8-hydroxyquinolines **4** in high yields. The aluminium complexes of the resulting 8-hydroxyquinolines have been synthesized and their photoluminescence (PL) properties have been studied. One of the complexes with a 2,4,6-trimethoxystyryl substituent at position-4 of the quinolate shows higher relative PL quantum yield than the other complexes due to the minimization of the cis–trans photoisomerization in solution.

1. Introduction

Arylvinylquinolines such as styrylquinolines and pyridylvinylquinolines are important quinoline classes due to their biological potency as LTD_4 receptor antagonists.[1,2] 2-Styrylquinolines derivatives are also promising antiviral agents because they inhibit HIV integrase (an enzyme that integrates genetic material from the virus into target cell) both in vitro and in vivo and are devoid of cellular toxicity.[3–9] Both 4- and 2-(2-arylvinyl)-8-hydroxyquinoline derivatives can also act as chelating agents, which co-ordinate with divalent metal ions such as Zn(II) and Mg(II)[9] and trivalent metal ions such as Al(III)[10,11] and can, therefore, be used for the production of many important metal complexes.

2-Arylvinylquinolines are usually prepared by condensation reactions between methylquinolines and suitable aromatic aldehydes. The condensation reactions may result in the formation of mixture of isomers (*E* and *Z*) of the target 2-arylvinylquinoline and the condensations are often accompanied by long reaction time and low yields.[1–15]

Recently, Dabiri et al.[16] have developed a one-pot synthesis of 2-(2-arylvinyl)quinolines bearing different groups at position-3. They used a Friedländer reaction of a 2-aminoalkylketone and a methylketone followed by Knoevenagel condensation with an aromatic aldehyde. The reactions were performed in the presence of 1-methylimidazolium trifluoroacetate.

The Heck coupling reaction is one of the most important reactions for C–C bond formation.[17–32] The reaction is usually used to couple olefins to unsaturated halides or triflates. The coupling is stereoselective giving the trans isomer predominantly. The wide variety of palladium catalyst systems and the high stereoselectivity of the resulting products in Heck coupling enable us to study it as an alternative for the production of 4-(2-arylvinyl)quinolines. Several protecting groups such as OMe, OTBS or OTDS have been used to protect hydroxyl groups during a Heck coupling.[28–32] Tosyloxy group has been used as a leaving group[33] and it has not so far been used as a protecting group for hydroxyls during Heck coupling reactions of unsaturated halides and olefins.

In this work, we have used a commercially available $PdCl_2/2PPh_3$ catalyst system and 4-bromo-8-tosyloxyquinoline **2** as the substrate in Heck couplings with arylvinyl compounds to produce 4-(2-arylvinyl)-8-tosyloxyquinolines **3** in good to high yields. The tosyloxy protecting group was very stable under the coupling conditions. Subsequent alkaline hydrolysis[34,35] of the coupling products **3** gave 4-(2-arylvinyl)-8-hydroxyquinoline derivatives **4** in high yields.

The aluminium complexes of the resulting 4-(2-arylvinyl)-8-hydroxyquinolines (complexes **5**) have also been synthesized and their PL properties have been studied.

Aluminium and zinc metal complexes of 2-styryl-8-hydroxyquinolines with 4-methyl, 4-chloro and 4-methoxy substituents on the styryl group are generally red shifted (λ_{PL} 513–576 nm) from the parent aluminium tris(8-hydroxyquiniline) (Alq_3, λ_{PL}=509 nm), they are significantly more thermally stable and more soluble in common organic solvents than the parent Alq_3 and zinc

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bis(8-hydroxyquinoline) (Znq_2). Moreover, the Al complexes showed PL quantum yields ranging from 0.007 to 0.133 (the PL quantum yield for Alq_3 is 0.171).[10] Compared with the unsubstituted Alq_3, Al complexes with 2-arylvinyl substituents at position-4 (complexes **5a**–**h**) show large red shifts (56–88 nm) in the PL emission and are less soluble in common organic solvents.

On the other hand, it has earlier been observed that metal complexes of styryl-substituted ligands undergo cis–trans photoisomerization in fluids at room temperature. Such phenomena cause a quenching for the PL emission. For example, cyclometalated platinum complexes of phenylpyridine ligands bearing styryl moieties at position-4 showed cis–trans photoisomerization in solution under sunlight. The cis–trans photoisomerization caused weak PL emission intensities and lower PL quantum yields (1×10^{-4} to 2×10^{-3}) compared to their parent complex (Φ_{PL}=0.15).[36] Also the iridium complex of phenylpyridine ligand with styryl substituent at position-4 of the phenylpyridine ligand showed very week emission and low PL quantum yield (Φ=0.0005) than its hydrogenated derivatives (Φ=0.54). The low PL intensity and PL quantum yield at room temperature is attributed to the quenching property of the *trans*-styryl moiety.[37]

In this research, the quench of PL emission caused by cis–trans photoisomerization in the synthesized Al tris{4-(2-arylvinyl)-8-hydroxyquinolines (**5a**–**h**) can be minimized by adding substituents to 2- and 6-positions of the styryl group (complex **5f**).

2. Results and discussion

4-Bromo-8-tosyloxyquinoline **2** was prepared in a high yield (93%) by treating a stirred solution of 4-hydroxy-8-tosyloxyquinoline[34,35] with phosphorus oxybromide at 90–95 °C.

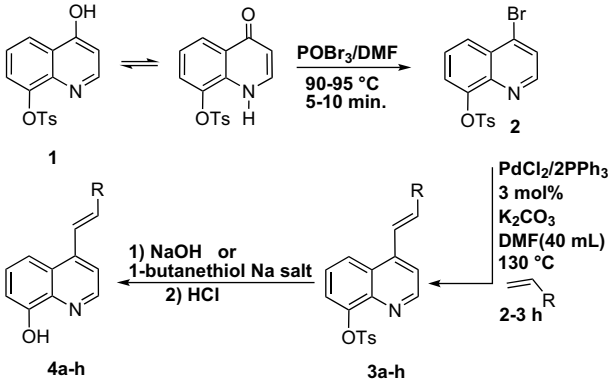
We investigated the Heck coupling between **2** and styrene and found that the coupling proceeded efficiently with complete conversion at 130 °C in dry DMF by using 3 mol % of commercially available $PdCl_2/2PPh_3$ catalyst and with K_2CO_3 as the base. The coupling was completed in 2–3 h. Organic bases such as triethylamine and diisopropylamine extended the coupling time (6–10 h) and reduced the yield noticeably (30–50%). Addition of water to the reaction mixture caused a cleavage of the tosyl group either from the substrate **2** or from the products **3**. Apparently, the use of anhydrous coupling conditions during Heck coupling is a prerequisite for efficient production of 4-(2-arylvinyl)-8-tosyloxyquinolines **3** from **2.**

The coupling went smoothly under this anhydrous Heck reaction conditions with all the arylvinyl compounds to give desired coupling products **3** in good to high yields (67–86%) except for 4-(2-(pyridin-4-yl)vinyl)-8-tosyloxyquinoline **3g** and 4-(2-(pyridin-2-yl)vinyl)-8-tosyloxyquinoline **3h**, the yields of the coupling were 37 and 20%, respectively. We also observed that if the catalyst loading was increased from 3 mol % to 10 mol % the coupling yields of 4-(2-(pyridin-4-yl)vinyl)-8-tosyloxyquinoline **3g** and 4-(2-(pyridin-2-yl)vinyl)-8-tosyloxyquinoline **3h** were increased from 37 and 20% to 98 and 90%, respectively.

It is also worth mentioning that the tosyloxy group was stable to oxidative addition even at a high catalyst loading (10 mol %) of $PdCl_2/2PPh_3$ used to couple the slowly reacting vinylpyridines and **2**.

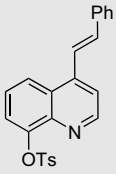
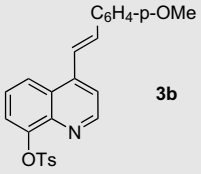
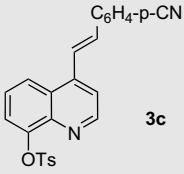
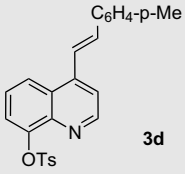
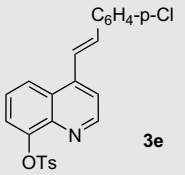
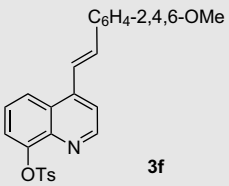
4-(2-Arylvinyl)-8-tosyloxyquinolines **3** were purified by flash chromatography on silica gel and they were efficiently hydrolyzed by using sodium hydroxide[34,35] to give 4-(2-arylvinyl)-8-hydroxyquinolines **4** in high yields. During the attempted alkaline hydrolysis of **3c** we observed a simultaneous complete hydrolysis of the cyano group.[38] The hydrolysis method for **3c** was refined and it was finally determined that sodium 1-butanethiolate selectively removed the tosyloxy group to give **4c** in high yield (94%).[34,39]

The overall synthetic route for the production of (*E*)-4-(2-arylvinyl)-8-tosyloxyquinolines (**3a**–**h**) and (*E*)-4-(2-arylvinyl)-8-hydroxyquinolines (**4a**–**h**) is described in Scheme 1 and the 4-(2-arylvinyl)-8-tosyloxyquinolines produced by Heck coupling and their yields are shown in Table 1.



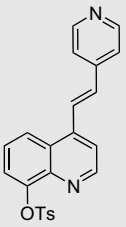
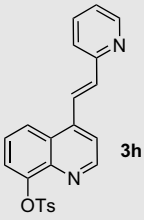
Scheme 1.

Table 1
The (*E*)-4-(2-arylvinyl)-8-tosyloxyquinolines produced by Heck coupling and their yields

R	Quinoline coupling product[a]	Yield %
Ph	 **3a**	70
C_6H_4-p-OMe	 **3b**	69
C_6H_4-p-CN	 **3c**	83
C_6H_4-p-Me	 **3d**	67
C_6H_4-p-Cl	 **3e**	70
C_6H_4-2,4,6-OMe[b]	 **3f**	86

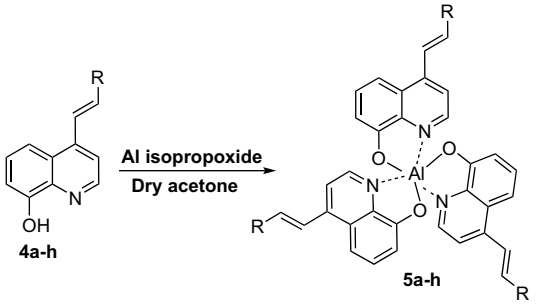
(*continued on next page*)

Table 1 (*continued*)

R	Quinoline coupling product[a]	Yield %
	 **3g**	(37) 98[c]
	 **3h**	(20) 90[c]

[a] ^{1}H NMR spectroscopy showed that the *E* isomer formed selectively.
[b] See Experimental procedure for preparation.
[c] Using $PdCl_2$ (10 mol %) and PPh_3 (20 mol %).

Aluminium complexes (**5a–h**) were prepared by refluxing the ligands (**4a–h**) and aluminium isopropoxide either in anhydrous acetone or methanol for 24 h under nitrogen atmosphere. The synthetic route for Al tris{4-(2-arylvinyl)-8-hydroxyquinoline} is described in Scheme 2.



Scheme 2.

The UV–vis spectra of all complexes (**5**) (Fig. 1) show two absorption bands, a strong band in the UV region ranging from 300 to 353 nm and another weaker band in the visible region ranging from 414 to 445 nm. However, the UV–vis spectrum of **5f** has the both bands in the visible region (at 371 and 414 nm).

PL emission wavelengths of the aluminium complexes **5a–h** were generally strongly red shifted (56–88 nm) compared with the PL emission of parent Alq_3 (λ=509 nm).[10] The strong red shift can be attributed to an extension of the π system caused by the styryl moiety.[10,11,36,37,40]

We have also studied how different substituents in the styryl moiety affect the emission wavelength of Al complexes. We observed that an electron-withdrawing chloro substituent on the phenyl ring causes a slightly red shifted (7 nm) PL emission compared with **5a** (λ=583 nm) while an electron-donating methyl (**5d**), methoxy (**5b**) and trimethoxy (**5f**) substituents cause a blue shift (4, 12 and 17 nm, respectively) compared with **5a**.

Aluminium complexes **5g** and **5h** are also red shifted (88 and 83 nm, respectively) compared with the parent Alq_3 due to the extension of conjugation.[10,11,36,37,40]

In general, the PL emission intensities of series **5a–h** in solution (chloroform) at room temperature are low and their relative PL

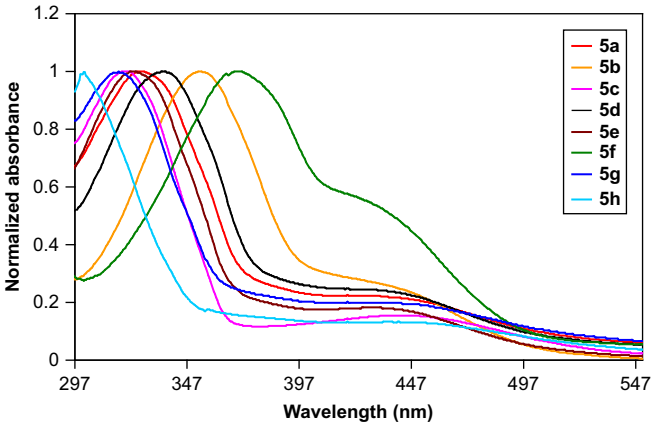


Figure 1. Normalized absorption spectra of complexes **5a–h**.

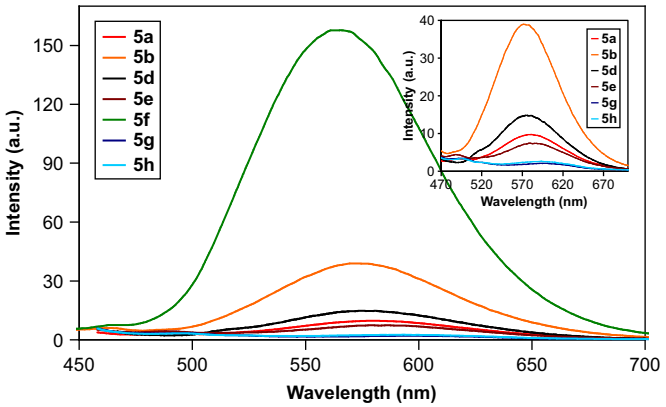


Figure 2. The PL emission spectra for complexes **5a–h**.

quantum yields are also low compared to the PL intensity and quantum yield of the parent Alq_3 (Fig. 2). The weak PL intensity may be attributed to the quenching of PL, which results from cis–trans isomerization. Related phenomena have also been observed by other groups for other metal complexes with styryl substituents.[36,37,40]

Minimizing the aptitude for cis–trans photoisomerization by introducing MeO groups to the 2- and 6- positions of the phenyl ring in the styryl group (complex **5f**) enhances the PL intensity and the relative photoluminescence quantum yield noticeably but the quantum yield is still lower than the PL quantum yield of the parent Alq_3.[41,42]

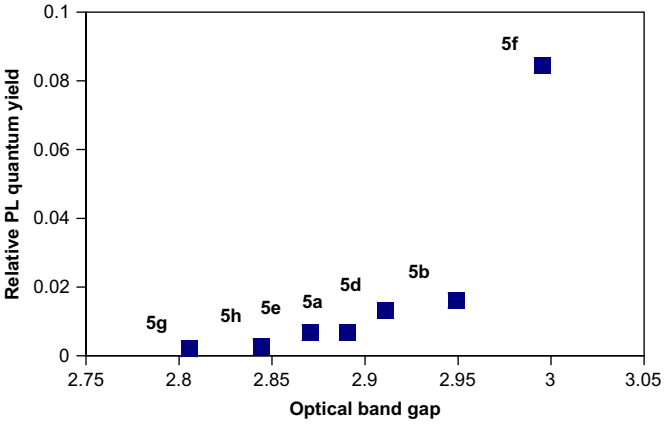


Figure 3. Optical band gap versus relative PL quantum yield of series **5a–h**, the PL quantum yields are relative to Alq_3, which has a quantum yield of **1**.

Table 2
The photophysical properties of complexes **5a–h**

Complex	$\lambda_{ex}(\varepsilon)$[a]	λ_{em}[b]	Φ_{PL}[c]	Optical band gap[d]
5a	429 (1.7×10^4)	583	0.0069	2.89
5b	421 (2.7×10^4)	571	0.016	2.95
5c	445 (1.1×10^4)	Nd[e]	Nd[e]	2.79
5d	426 (1.4×10^4)	579	0.013	2.92
5e	432 (1.2×10^4)	590	0.0067	2.87
5f	414 (3.2×10^4)	566	0.085	2.99
5g	442 (8.5×10^3)	597	0.0017	2.81
5h	436 (6.5×10^3)	593	0.0027	2.84

[a] Absorption maximum (nm) and molar absorptivity ($L\,mol^{-1}\,cm^{-1}$) in brackets.
[b] Photoluminescence emission maximum (nm) of 20 μM of sample in chloroform.
[c] Relative PL quantum yield calculated from the relation used by Velapoldi et al. and giving a quantum yield of 1.00 to Alq_3.[43]
[d] Estimated from the UV–vis spectra by using $E=hC/\nu$.
[e] Not detected.

Figure 3 shows the relationship between the optical band gap and the calculated relative PL quantum yields[43] of the synthesized complexes **5a**,**b**,**d–h**. Complex **5f** shows a clear deviation from the other complexes, which indicates that the relative PL quantum yield can be enhanced considerably by minimizing cis–trans photoisomerization in solution.

The photophysical properties of the aluminium complexes **5** are shown in Table 2.

3. Conclusion

Anhydrous Heck coupling conditions using a commercially available catalyst $PdCl_2/2PPh_3$ have been successfully applied to the synthesis of a series of 4-(2-arylvinyl)-8-tosyloxyquinolines. The tosyloxy group at position-8 was highly stable to oxidative addition during anhydrous Heck coupling. The 4-(2-arylvinyl)-8-hydroxyquinolines could be obtained easily and in high yields either by alkaline hydrolysis or by the treatment of 4-(2-arylvinyl)-8-tosyloxyquinolines with sulfur nucleophiles such as 1-butanthiol sodium salt.

Aluminium complexes of the 4-(2-aryvinyl)-8-hydroxyquinolines can be obtained by reaction of aluminium isopropoxide and the 4-(2-aryvinyl)-8-hydroxyquinoline in anhydrous acetone or methanol. The PL emission wavelengths of the Alq_3 derivatives are generally red shifted compared to the emission wavelength of parent Alq_3 (56–80 nm) due to the extension of conjugation. Alq_3 derivatives with 4-(2-arylvinyl) substituents have weak PL emission intensities in solution at room temperature, which can partly be attributed to quenching of PL emission caused by cis–trans photoisomerization. Relative PL quantum yields of the aluminium complexes of the 4-arylvinyl-8-tosyloxyquinolines are lower when compared with the quantum yield of the parent Alq_3.

Minimizing the cis–trans photoisomerization by introducing substituents at the 2- and 6- positions of the phenyl ring in the styryl group (e.g., **5f**) enhances the PL intensity and the relative PL quantum yield.

4. Experimental

4.1. General

Commercially available solvents and reagents were used without any further purification. The solvents were dried with molecular sieves. Flash chromatography was executed by using silica gel with 0.04–0.063 mm particle size purchased from Merck (Finland). NaH used in the preparation of 2,4,6-trimethoxystyrene was purchased from Merck (Finland). Compound **1** was prepared from the commercially available xanthurenic acid according to earlier reported procedures.[34,35]

4.2. Synthesis of 4-bromo-8-tosyloxyquinoline (2)

$POBr_3$ (0.65 g, 2.27 mmol) was added to a stirred solution of 4-hydroxy-8-tosyloxyquinoline **1**[34,35] (1.00 g, 3.17 mmol) in DMF (30 mL) at 90 °C. Temperature rose spontaneously to 95 °C and stirring was continued for 10 min at 95 °C. The reaction mixture was poured into water and neutralized with Na_2CO_3. The precipitate was collected by filtration, washed with water and recrystallized from ethanol/$CHCl_3$ mixture to give **2** as white crystals (1.11 g, 93%). Mp: 148–149 °C; IR (KBr): ν 1174, 1374, 1489, 1583, 3073 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 7.36–7.41 (d, J=8.2 Hz, 2H), 7.57–7.61 (d, J=8.2 Hz, 1H), 7.69–7.81 (m, 3H), 7.94–7.96 (d, J=4.8 Hz, 1H), 8.05–8.09 (d, J=8.5 Hz, 1H), 8.60–8.63 (d, J=4.3 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.99, 124.08, 126.61, 127.25, 128.80, 129.23 (3C), 130.77 (2C), 132.91, 133.79, 142.42, 145.70, 146.47, 151.65. HRMS $(M+H)^+$ calcd for $C_{16}H_{13}NO_3SBr$: 377.9800, found: 377.9815.

4.3. General procedures for the synthesis of 4-(2-arylvinyl)-8-tosyloxyquinolines (3a–h) via Heck coupling

4-Bromo-8-tosyloxyquinoline **2** was dissolved in anhydrous DMF (40 mL), $PdCl_2$ (3 mol %), PPh_3 (6 mol %), anhydrous K_2CO_3 (1 equiv) and 2 equiv of the arylvinyl compound were added to the stirred DMF solution at 130 °C. The reaction mixture was stirred at 130 °C for 2.5–3 h under nitrogen atmosphere. DMF was then evaporated under vacuum and the product was purified by flash chromatography using the appropriate solvent.

*4.3.1. (E)-4-Styryl-8-tosyloxyquinoline (**3a**)*

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.07 mL of styrene were used to prepare the title compound. Eluent used for flash chromatography was EtOAc/*n*-hexane (2:3) to afford **3a** (151.4 mg, 71%) as white crystals. Mp: 151–152 °C; IR (KBr): ν 1179, 1378, 1497, 1584, 1625, 3040 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.37 (s, 3H), 7.39–7.59 (m, 8H), 7.80–7.84 (d, J=7.6 Hz, 5H), 8.00–8.08 (d, J=15.8 Hz, 1H), 8.47–8.51 (d, J=8.5 Hz, 1H), 8.77–8.79 (d, J=4.5 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.98, 118.28, 122.79, 124.55, 126.77, 128.17, 128.46, 129.20 (3C), 129.64 (2C), 129.66, 130.68 (2C), 133.28, 136.63, 137.11, 142.39, 143.23, 145.94, 146.24, 151.41. HRMS $(M+H)^+$ calcd for $C_{24}H_{20}NO_3S$: 402.1164, found: 402.1136.

*4.3.2. (E)-4-(4-Methoxystyryl)-8-tosyloxyquinoline (**3b**)*

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.14 mL of *p*-methoxystyrene were used to prepare the title compound. Flash chromatography using acetone/*n*-hexane (3.5:6.5) afforded compound **3b** as yellowish crystals (157.8 mg, 69%). Mp: 142–143 °C; IR (KBr): ν 1177, 1376, 1507, 1707, 2835, 2923, 2960, 3034 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.85 (s, 3H), 6.92–6.96 (d, J=8.8 Hz, 2H), 7.23–7.28 (m, 3H), 7.40–7.61 (m, 6H), 7.86–7.90 (d, J=8.3 Hz, 2H), 8.13 (d, J=7.8 Hz, 1H), 8.73–8.75 (d, J=4.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.07, 55.79, 114.74 (2C), 117.72, 120.33, 122.61, 122.70, 125.91, 128.23, 129.00 (2C), 129.16 (2C), 129.48, 129.83 (2C), 133.63, 135.62, 142.55, 143.38, 145.38, 146.30, 150.85, 160.74. HRMS $(M+Na)^+$ calcd for $C_{25}H_{21}NO_4NaS$: 454.1089, found: 454.1103.

*4.3.3. (E)-4-(4-Cyanostyryl)-8-tosyloxyquinoline (**3c**)*

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.14 mL of 4-cyanostyrene were used to prepare the title compound. The product was purified using EtOAc/*n*-hexane (1:1) as eluent affording (187.6 mg, 83%) of white needles. Mp:

181–182 °C; IR (KBr): ν 1172, 1340, 1504, 2220, 2925, 3331 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.35 (s, 3H), 7.36–7.40 (d, J=7.5 Hz, 2H), 7.47–7.50 (d, J=8.1 Hz, 1H), 7.57–7.65 (m, 2H), 7.77–7.88 (m, 5H), 7.96–8.00 (m, 2H), 8.16 (d, J=16.2 Hz, 1H), 8.46–8.50 (d, J=9.2 Hz, 1H), 8.78–8.80 (d, J=4.8 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.96, 111.56, 118.69, 119.71, 122.91, 124.57, 126.58, 126.97, 128.06, 129.08, 129.18 (3C), 130.68 (2C), 133.22, 133.48 (2C), 134.83, 141.68, 142.37, 142.54, 145.91, 146.24, 151.43. HRMS $(M+H)^+$ calcd for $C_{25}H_{19}N_2O_3S$: 427.1116, found: 427.1111.

4.3.4. (E)-4-(4-Methylstyryl)-8-tosyloxyquinoline (**3d**)

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.14 mL of 4-methylstyrene were used to prepare the title compound. The product was purified using acetone/*n*-hexane (1:2) as eluent giving (147 mg, 67%) as white solid. Mp: 184–185 °C; IR (KBr): ν 1177, 1376, 1585, 1630, 3037 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 2.40 (s, 3H), 7.25–7.29 (d, J=8.3 Hz, 2H), 7.41–7.45 (d, J=8.6 Hz, 2H), 7.51–7.65 (m, 3H), 7.69–7.76 (m, 2H), 7.82–7.89 (m, 3H), 7.97–8.05 (d, J=16.2, 1H), 8.49–8.53 (d, J=8.3 Hz, 2H), 8.78–8.80 (d, J=5.1 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{25}H_{22}NO_3S$: 416.1320, found: 416.1316.

4.3.5. (E)-4-(4-Chlorostyryl)-8-tosyloxyquinoline (**3e**)

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.13 mL of 4-chlorostyrene were used to prepare the title compound. The product was purified by flash chromatography using acetone/*n*-hexane (1:2) as eluent affording (161.6 mg, 70%) as a white powder. Mp: 144–145 °C; IR (KBr): ν 1178, 1373, 1586, 1626, 3038 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.40 (s, 3H), 7.40–7.45 (d, J=8.3 Hz, 2H), 7.50–7.65 (m, 5H), 7.82–7.90 (m, 5H), 8.06–8.14 (d, J=16.2, 1H), 8.50–8.54 (d, J=8.3 Hz, 1H), 8.81–8.83 (d, J=4.7 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 22.02, 118.32, 123.00, 123.69, 125.00, 126.85, 128.14, 129.23 (2C), 129.67 (2C), 130.18 (2C), 130.72 (2C), 133.30, 134.20, 135.29, 136.12, 142.43, 143.04, 145.96, 146.28, 151.44. HRMS $(M+H)^+$ calcd for $C_{24}H_{19}NO_3SCl$: 436.0774, found: 436.0774.

4.3.6. (E)-4-(2,4,6-Trimethoxystyryl)-8-tosyloxyquinoline (**3f**)

The following amounts of chemicals were used to prepare the title compound: 4-bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.14 mL of 2,4,6-trimethoxystyrene,[44] which was prepared in 98% yield as yellowish oil by stirring methyltriphenylphosphonium bromide (1.365 g, 3.8 mmol) and NaH (0.15 g, 3.75 mmol) in THF for 2 h at room temperature followed by the addition of 2,4,6-trimethoxybenzaldehyde (0.5 g, 2.5 mmol), reflux for 2 h and flash chromatography using an acetone and *n*-hexane mixture (1:2). The title compound **3f** was purified by flash chromatography using EtOAc/*n*-hexane (1:2) as eluent affording (224.1 mg, 86%) of **3f** as bright yellow powder. Mp: 133–134 °C; IR (KBr): ν 1166, 1201, 1605, 2837, 2938 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 3.82 (s, 3H), 3.89 (s, 6H), 6.31 (s, 2H), 7.36–7.64 (m, 6H), 7.79–7.82 (d, J=7.9 Hz, 2H), 8.10–8.17 (m, 2H), 8.70–8.72 (d, J=4.9 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.96, 56.24, 56.83 (2C), 91.80, 107.04, 117.50, 122.20, 122.49, 124.00, 126.32, 127.61, 128.08, 129.19 (2C), 130.64 (2C), 133.28, 142.30, 145.28, 146.00, 146.20, 151.50, 160.72 (3C), 162.42. HRMS $(M+H)^+$ calcd for $C_{27}H_{26}NO_6S$: 492.1481, found: 492.1485.

4.3.7. (E)-4-(2-(Pyridin-4-yl)vinyl)-8-tosyloxyquinoline (**3g**)

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.11 mL 4-vinylpyridine were the amounts of chemicals used to prepare the title compound. Acetone/*n*-hexane mixture (3:2) was used as eluent to purify the product by flash chromatography, which was obtained as a white powder (78.9 mg, 37%). Using $PdCl_2$ (10 mol %) and PPh_3 (20 mol %) under same reaction condition afforded the title compound **3g** (209.1 mg, 98%). Mp: 160–161 °C; IR (KBr): ν 1177, 1348, 1588, 3045 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 7.37–7.41 (d, J=8.1 Hz, 2H), 7.49–7.88 (m, 8H), 8.25–8.33 (d, J=15.2 Hz, 1H), 8.47–8.51 (d, J=8.1 Hz, 1H), 8.60–8.63 (d, J=5.5 Hz, 2H), 8.80–8.82 (d, J=5.2 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 22.06, 118.94, 122.53, 122.55, 124.56, 127.07, 127.59, 128.03, 129.20 (3C), 130.69 (2C), 133.22, 134.14, 142.37 (2C), 144.15, 145.93, 146.27, 151.01 (2C), 151.56. HRMS $(M+H)^+$ calcd for $C_{23}H_{19}N_2O_3S$: 403.1116, found: 403.1104.

4.3.8. (E)-4-(2-(Pyridin-2-yl)vinyl)-8-tosyloxyquinoline (**3h**)

4-Bromo-8-tosyloxyquinoline **2** (200 mg, 0.53 mmol), $PdCl_2$ (2.82 mg, 0.016 mmol), PPh_3 (8.35 mg, 0.03 mmol), K_2CO_3 (73.32 mg, 0.53 mmol) and 0.11 mL 2-vinylpyridine were used to prepare the title compound. The product was purified using acetone/*n*-hexane (1:2) as eluent in flash chromatography giving the title compound as a white powder (42.7 mg, 20%). Using $PdCl_2$ (10 mol %) and PPh_3 (20 mol %) under same previous conditions increased the yield to 192 mg, 90%. Mp: 127–128 °C; IR (KBr): ν 1180, 1377, 1584, 3042 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 7.34–7.90 (m, 11H), 8.31–8.41 (m, 2H), 8.64–8.66 (d, J=4.1 Hz, 1H), 8.80–8.83 (d, J=4.6 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.96, 118.9, 122.87, 124.10, 124.30, 124.35, 126.16, 127.16, 128.09 (2C), 129.20 (2C), 130.69, 133.24, 136.08, 137.9, 142.35, 142.41, 146.00, 146.25, 150.61, 151.50, 154.86. HRMS $(M+H)^+$ calcd for $C_{23}H_{19}N_2O_3S$: 403.1116, found: 403.1131.

4.4. General procedure for synthesis of 4-(2-arylvinyl)-8-hydroxyquinoline (4a, 4b and 4d–h)

4-(2-Arylvinyl)-8-tosyloxyquinolines **3a**,**b** and **d**–**h** were dissolved in ethanol (25 mL) and NaOH (1 M, 5 equiv) was then added. The mixture was refluxed for 1 h, then more water was added and the mixture was neutralized with HCl (1 M). The precipitate formed was filtered, washed with water and dried in an oven at 50 °C for 3 h.

4.4.1. (E)-4-Styrylquinolin-8-ol (**4a**)

4-Styryl-8-tosyloxyquinoline **3a** (0.5 g, 1.25 mmol) and NaOH (1 M, 6.23 mL, 6.23 mmol) were used to prepare the title compound. The product was collected and recrystallized from a $CHCl_3$/EtOH mixture giving a reddish powder (0.3 g, 99%). Mp: 180–181 °C; IR (KBr): ν 1508, 1566, 1624, 3051, 3312 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.19–7.26 (t, J=7.0 Hz, 1H), 7.32–7.54 (m, 5H), 7.62–7.83 (m, 5H), 8.74–8.77 (d, J=4.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 110.12, 114.12, 118.00, 123.19, 127.04, 127.57 (2C), 127.98, 129.32 (3C), 135.61, 136.86, 139.24, 143.58, 147.86, 152.96. HRMS $(M+H)^+$ calcd for $C_{17}H_{14}NO$: 248.1075, found: 248.1028.

4.4.2. (E)-4-(4-Methoxystyryl)quinolin-8-ol (**4b**)

4-(4-Methoxystyryl)-8-tosyloxyquinoline **3b** (1.0 g, 2.32 mmol) and NaOH (1 M, 11.6 mL, 11.6 mmol) were used to prepare the title compound. The product was collected by filtration and recrystallized from a $CHCl_3$/EtOH mixture to give a reddish brown powder (0.58 g, 91%). Mp: 172–173 °C (lit.[11] 163–165 °C); IR (KBr): ν 1250, 1570, 1605, 3022, 3326 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 3.8 (s, 3H), 6.94–6.98 (d, J=8.8 Hz, 2H), 7.18–7.28 (m, 2H), 7.49–7.71 (m, 6H), 8.71–8.74 (d, J=4.4 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 56.06, 111.75, 114.67, 115.08 (2C), 117.43, 120.78, 127.44, 128.08, 129.87 (2C), 129.94, 135.50, 139.94, 143.46, 148.42, 154.31, 160.69. HRMS $(M+H)^+$ calcd for $C_{18}H_{16}NO_2$: 278.1181, found: 278.1176.

*4.4.3. (E)-4-(4-Methylstyryl)quinolin-8-ol (**4d**)*

4-(4-Methylstyryl)-8-tosyloxyquinoline **3d** (200 mg, 0.48 mmol) and (1 M, 2.4 mL, 2.4 mmol) NaOH were used to prepare the title compound. The precipitate formed was collected and recrystallized from EtOH/$CHCl_3$ mixture to give the product **4d** as a yellow powder (124.5 mg, 99%). Mp: 154–155 °C; IR (KBr): ν 1401, 1508, 1561, 1623, 3048, 3325 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 2.36 (s, 3H), 7.12–7.15 (d, J=7.7 Hz, 1H), 7.25–7.29 (d, J=8.1 Hz, 2H), 7.47–7.61 (m, 2H), 7.72–7.67 (d, J=7.7 Hz, 2H), 7.89–8.03 (m, 3H), 8.81–8.84 (d, J=4.5 Hz, 1H), 9.80 (br, OH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 21.83, 111.83, 114.69, 117.76, 122.29, 127.49, 128.35 (2C), 130.29 (2C), 134.56, 135.80, 139.28, 139.96, 143.29, 148.49, 154.38 (2C). HRMS $(M+H)^+$ calcd for $C_{18}H_{16}NO$: 262.1232, found: 262.1237.

*4.4.4. (E)-4-(4-Chlorostyryl)quinolin-8-ol (**4e**)*

4-(4-Chlorostyryl)-8-tosyloxyquinoline **3e** (0.5 g, 1.15 mmol) was refluxed with NaOH (1 M, 5.75 mL, 5.75 mmol). The precipitate formed was collected by filtration and recrystallized from $CHCl_3$/EtOH giving the title compound as a yellowish powder (0.3 g, 94%). Mp: 142–143 °C; IR (KBr): ν 1213, 1404, 1562, 1629, 3272 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 7.13–7.16 (d, J=7.9 Hz, 1H), 7.48–7.64 (m, 4H), 7.87–8.12 (m, 5H), 8.84–8.86 (d, J=4.3 Hz, 1H), 9.82 (br, OH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 111.94, 114.74, 118.04, 124.35, 127.50, 128.35, 128.67 (2C), 130.08 (2C), 134.01, 134.50, 136.27, 139.97, 142.94, 148.47, 154.41. HRMS $(M+H)^+$ calcd for $C_{17}H_{13}NOCl$: 282.0686, found: 282.0694.

*4.4.5. (E)-4-(2,4,6-Trimethoxystyryl)quinolin-8-ol (**4f**)*

4-(2,4,6-Trimethoxystyryl)-8-tosyloxyquinoline **3f** (0.5 g, 1 mmol) was reacted with NaOH (1 M, 5.1 mL, 5.1 mmol). The precipitate formed was recrystallized from EtOH/$CHCl_3$ mixture to give the title compound as a yellow powder (0.34 g, 99%). Mp: 159–160 °C; IR (KBr): ν 1209, 1509, 1606, 2836, 2937, 3004, 3307 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 3.84 (s, 3H), 3.91 (s, 6H), 6.33 (s, 2H), 7.07–7.10 (d, J=7.9 Hz, 1H), 7.46–7.50 (t, J=7.5 Hz, 1H), 7.59–7.68 (m, 3H), 8.05–8.13 (d, J=16.8 Hz, 1H), 8.74–8.77 (d, J=4.7 Hz, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 56.26, 56.86, 91.86, 107.16, 111.65, 113.99, 116.94, 123.14, 126.80, 127.40, 128.19, 139.84, 145.29, 148.00, 154.46, 160.65 (3C), 162.25. HRMS $(M+H)^+$ calcd for $C_{20}H_{20}NO_4$: 338.1392, found: 338.1394.

*4.4.6. (E)-4-(2-(Pyridin-4-yl)vinyl)quinolin-8-ol (**4g**)*

4-(2-(Pyridin-4-yl)vinyl)-8-tosyloxyquinoline **3g** (200 mg, 0.5 mmol) was refluxed with NaOH (1 M, 2.5 mL, 2.5 mmol). The precipitate formed was recrystallized from a chloroform/ethanol mixture giving the title compound as a brown powder (113.5 mg, 92%). Mp: 174–175 °C; IR (KBr): ν 1507, 1592, 3030, 3307 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 7.09–7.12 (d, J=7.6 Hz, 1H), 7.44–7.56 (m, 2H), 7.74–7.92 (m, 4H), 8.22–8.30 (d, J=16.6 Hz, 1H), 8.59–8.61 (d, J=4.7 Hz, 2H), 8.82–8.83 (d, J=4.3 Hz, 1H), 9.86 (br, OH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 112.23, 114.68, 118.66, 122.48 (2C), 127.44, 128.25, 128.58, 133.36, 139.95, 142.26, 144.32, 148.59, 151.02 (2C), 154.45. HRMS $(M+H)^+$ calcd for $C_{16}H_{13}N_2O$: 249.1028, found: 249.1029.

*4.4.7. (E)-4-(2-(Pyridin-2-yl)vinyl)quinolin-8-ol (**4h**)*

4-(2-(Pyridin-2-yl)vinyl)-8-tosyloxyquinoline **3h** (200 mg, 0.5 mmol) was refluxed with NaOH (1 M, 2.5 mL, 2.5 mmol). The precipitate collected was recrystallized from EtOH/$CHCl_3$ to give the title compound as a brownish powder (116 mg, 94%). Mp: 129–130 °C; IR (KBr): ν 1508, 1587, 3055, 3313 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 7.07–7.08 (d, J=7.8 Hz, 1H), 7.31–7.87 (m, 7H), 8.32–8.40 (d, J=15.6 Hz, 1H), 8.62–8.64 (d, J=3.9 Hz, 1H), 8.80–8.82 (d, J=4.4 Hz, 1H), 9.84 (br, OH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 112.02, 114.31, 118.49, 124.22 (2C), 126.96, 127.50, 128.81, 135.26, 138.04, 139.93, 142.27, 148.55, 150.60, 154.53, 155.01. HRMS $(M+H)^+$ calcd for $C_{16}H_{13}N_2O$: 249.1028, found: 249.1029.

4.5. Cleavage of tosyl group by 1-butanthiol sodium salt: synthesis of (*E*)-4-(4-cyanostyryl)quinolin-8-ol (4c)

NaH (47.3 mg, 1.97 mmol) in a 60% oil dispersion was washed with *n*-pentane (4 mL), and then 1-butanthiol (0.2 mL, 1.97 mmol) was added. The mixture was stirred at room temperature for 10 min and 4-(4-cyanostyryl)-8-tosyloxyquinoline **3c** (280 mg, 0.66 mmol) in *tert*-amyl alcohol was then added and the whole mixture was refluxed for 1 h. After cooling, water was added to the mixture to dissolve the deep red precipitate formed and the mixture was neutralized with HCl (1 M). The precipitate formed was collected by filtration and recrystallization from EtOH gave a yellow powder (168.1 mg, 94%). Mp: 210–211 °C; IR (KBr): ν 1508, 1599, 2216, 3288 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 7.09–7.13 (d, J=6.5 Hz, 1H), 7.44–7.7.66 (m, 2H), 7.85–8.24 (m, 7H), 8.81–8.83 (d, J=4.3 Hz, 1H), 9.86 (br, 1H). ^{13}C NMR (50 MHz, DMSO-d_6): δ 111.41, 112.10, 114.00, 118.34, 119.88, 127.26, 127.46, 128.49, 129.00 (2C), 133.49 (2C), 134.08, 139.95, 141.86, 142.45, 148.82, 154.42. HRMS $(M+H)^+$ calcd for $C_{18}H_{13}N_2O$: 273.1028, found: 273.1038.

4.6. General procedure for the preparation of aluminium complexes (5a–h)

4-(2-Arylvinyl)-8-hydroxyquinolines (**4a**–**h**) were refluxed with aluminium isopropoxide in dry acetone or methanol for 24 h. The reaction mixture was then concentrated and the precipitate was filtered and washed with acetone.

*4.6.1. Al tris(4-styryl-8-hydroxyquinoline) (**5a**)*

4-(Styryl)-8-hydroxyquinoline **4a** (200 mg, 0.81 mmol) and aluminium isopropoxide (55 mg, 0.27 mmol) gave the title compound as an orange powder (167 mg, 81%). ^1H NMR (200 MHz, DMSO-d_6): δ 6.76–6.80 (d, J=8.1 Hz, 1H), 6.92–6.96 (d, J=7.4 Hz, 2H), 7.33–8.05 (m, 31H), 8.55–8.58 (d, J=4.7 Hz, 1H), 8.69–8.72 (d, J=4.1 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{51}H_{37}N_3O_3Al$: 766.2650, found: 766.2662.

*4.6.2. Al tris{4-(4-methoxystyryl)-8-hydroxyquinoline} (**5b**)[11]*

4-(4-Methoxystyryl)-8-hydroxyquinoline **4b** (150 mg, 0.54 mmol) and Al isopropoxide (36.9 mg, 0.18 mmol) gave the title compound (131 mg, 85%) as an orange powder. ^1H NMR (200 MHz, DMSO-d_6): δ 3.38 (s, 9H), 6.77–6.81 (d, J=7.4 Hz, 1H), 6.92–7.03 (m, 8H), 7.32–7.34 (d, J=5.4 Hz, 1H), 7.47–7.98 (m, 21H), 8.54–8.57 (d, J=4.7 Hz, 1H), 8.67–8.70 (d, J=5.4 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{54}H_{43}N_3O_6Al$: 856.2967, found: 856.2967.

*4.6.3. Al tris{4-(4-cyanostyryl)-8-hydroxyquinoline} (**5c**)*

4-(4-Cyanostyryl)-8-hydroxyquinoline **4c** (200 mg, 0.74 mmol) and Al isopropoxide (50 mg, 0.25 mmol) gave the title compound as a deep orange powder (178.9 mg, 87%). ^1H NMR (200 MHz, DMSO-d_6): δ 6.77 (d, J=6.20 Hz, 1H), 6.92–6.95 (d, J=5.2 Hz, 2H), 7.38–8.24 (m, 28H), 8.57–8.59 (m, 1H), 8.70–8.72 (m, 1H). HRMS $(M+H)^+$ calcd for $C_{54}H_{34}N_6O_3Al$: 841.2508, found: 841.2522.

*4.6.4. Al tris{4-(4-methylstyryl)-8-hydroxyquinoline} (**5d**)*

4-(4-Methylstyryl)-8-hydroxyquinoline **4d** (200 mg, 0.77 mmol) and Al isopropoxide (52 mg, 0.26 mmol) gave the title complex as an orange powder (162.8 mg, 79%). ^1H NMR (200 MHz, DMSO-d_6): δ 2.35 (s, 9H), 6.79–6.82 (d, J=7.5 Hz, 1H), 6.94–6.97 (d, J=6.2 Hz, 2H), 7.25–7.36 (m, 7H), 7.54–7.74 (m, 16H), 7.92–8.02 (m, 5H), 8.56–8.58 (d, J=4.4 Hz, 1H), 8.70–8.8.72 (d, J=5.0 Hz, 1H). HRMS $(M+Na)^+$ calcd for $C_{54}H_{42}N_3O_3NaAl$: 830.2939, found: 830.2921.

*4.6.5. Al tris{4-(4-chlorostyryl)-8-hydroxyquinoline} (**5e**)*

4-(4-Chlorostyryl)-8-hydroxyquinoline **5d** (200 mg, 0.71 mmol) and Al isopropoxide (48 mg, 0.24 mmol) gave the title compound as an

orange powder (173 mg, 84%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.79–6.83 (d, J=6.9 Hz, 1H), 6.95–6.99 (d, J=6.6 Hz, 2H), 7.73–8.12 (m, 26H), 8.59–8.61 (d, J=4.4 Hz, 1H), 8.72–8.75 (d, J=4.1 Hz, 1H). HRMS $(M+Na)^+$ calcd for $C_{51}H_{33}N_3O_3NaAlCl_3$: 890.1301, found: 890.1318.

*4.6.6. Al tris{4-(2,4,6-trimethoxystyrene)-8-hydroxyquinoline} (**5f**)*

4-(2,4,6-Trimethoxystyryl)-8-hydroxyquinoline **4f** (200 mg, 0.59 mmol) and Al isopropoxide (40 mg, 0.20 mmol) gave the title complex as a yellow powder (176 mg, 86%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.85–3.91 (m, 27H), 6.16–6.18 (m, 6H), 7.07–7.15 (t, J=7.6, 8.1 Hz, 3H), 7.27–7.78 (m, 13H), 8.07–8.20 (m, 3H), 8.75–8.78 (t, J=4.1 Hz, J=4.6 Hz, 2H). HRMS $(M+H)^+$ calcd for $C_{60}H_{55}N_3O_{12}Al$: 1036.3601, found: 1036.3623.

*4.6.7. Al tris{4-(2-(pyridin-4-yl)vinyl)quinolin-8-ol} (**5g**)*

4-(4-Vinylpyridinyl)-8-tosyloxyquinoline **5g** (200 mg, 0.81 mmol) and Al isopropoxide (55 mg, 0.27 mmol) gave the title compound as a deep orange powder (171 mg, 83%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.80–6.83 (d, J=7.1 Hz, 1H), 6.97–7.22 (d, J=7.1 Hz, 2H), 7.41–7.92 (m, 19H), 8.03–8.06 (d, J=4.8 Hz, 1H), 8.21–8.33 (m, 3H), 8.62–8.64 (m, 6H), 8.76–8.78 (d, J=4.6 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{48}H_{34}N_6O_3Al$: 769.2508, found: 769.2511.

*4.6.8. Al tris{4-(2-(pyridin-2-yl)vinyl)quinolin-8-ol} (**5h**)*

4-(2-Vinylpyridinyl)-8-hydroxyquinoline **4h** (200 mg, 0.81 mmol) and Al isopropoxide (55 mg, 0.27 mmol) gave the title compound as an orange powder (161 mg, 78%). ^{1}H NMR (200 MHz, DMSO-d_6): δ 6.82–6.85 (d, J=6.46 Hz, 1H), 6.99–7.02 (d, J=7.2 Hz, 2H), 7.36–7.95 (m, 20H), 7.97–7.99 (d, J=4.9 Hz, 1H), 8.08–8.09 (d, J=5.7, 1H), 8.32–8.43 (m, 3H), 8.62–8.69 (m, 4H), 8.77–8.79 (d, J=4.9 Hz, 1H). HRMS $(M+H)^+$ calcd for $C_{48}H_{34}N_6O_3Al$: 769.2508, found: 769.2519.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.028.

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