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2,4-Diarylquinolines: synthesis, absorption and emission properties

Adewale O. Adeloye and Malose J. Mphahlele*

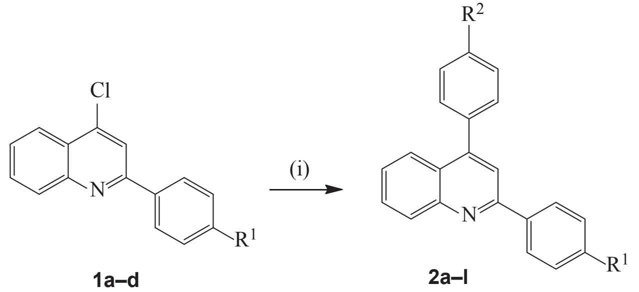
Department of Chemistry, College of Science, Engineering and Technology, University of South Africa, PO Box 392, Pretoria 0003, South Africa

The absorption and emission spectra of series of 2,4-diarylquinolines prepared *via* palladium catalysed Suzuki–Miyaura cross-coupling of 2-aryl-4-chloroquinolines with arylboronic acids were measured in solution to understand the influence of substituents on intramolecular charge transfer.

Keywords: 2-aryl-4-chloroquinolines, Suzuki–Miyaura cross-coupling, 2,4-diarylquinolines, photophysical properties

Polysubstituted quinolines in which the quinoline framework is linked to an aryl substituent directly or *via* a π-conjugated spacer to comprise a donor-π-acceptor system continue to attract considerable attention as fluorophores. Polyarylquinolines serve as emitting chromophores due to their inherent fluorescent properties,[1,2] and this scaffold serves as an electron-acceptor unit in carbazole–quinoline and phenothiazine–quinoline copolymers and oligomers found to exhibit intramolecular charge transfer (ICT).[3] Moreover, polyarylquinoline–based compounds constitute an important component in optoelectronic materials[4,5] and this moiety also constitutes a π-conjugated bridge in nonlinear optical polymers.[6] Similarly, quinolines are also interesting ligands for transition metal complexes for the development of organic electroluminescent diodes (OLEDs).[7,8] More thermally stable and mechanically robust nonlinear optical polymers with donor-acceptor architectures incorporating quinoline units as a π-conjugated bridge have been prepared previously and their photophysical properties investigated.[3,7] Preliminary absorption and photoluminescence properties of 5,7-diphenylquinoline and 2,5,7-triphenylquinolines in chloroform (2.5 mol L^{-1}) have previously been reported.[8] The absorption spectra of a series of 2-(hetero)aryl-substituted 4-phenylquinolines in dichloromethane have revealed that 2-substitution of the quinoline core only exerts a bathochromic effect if the donor capacity is strong enough to generate co-planarity to comprise a push–pull system.[1] We required quinoline derivatives substituted with aryl substituents at the 2- and 4-positions to comprise the requisite donor-π-acceptor system and to probe their absorption and fluorescence properties in solvents of different polarities. Arylated quinolines were previously prepared by classic reactions, such as the Skraup, Doebner–Miller, Conrad–Limpach, Friedländer, and Pfitzinger syntheses.[9] Moreover, a three-component approach involving a coupling-cycloisomerisation reaction of aldehydes, terminal alkynes and amines to afford aryl-substituted quinolines has been reported.[10,11] Treatment of 4-chloro-2-arylquinolines with arylmagnesium halides in the presence of nickel(II) chloride as a catalyst in 2-methyltetrahydrofuran afforded the corresponding cross-coupling products in good yields.[12] Our approach to the 2,4-diarylquinolines involves the use of the 2-aryl-4-chloroquinolines as substrates for palladium-catalysed Suzuki cross-coupling with arylboronic acids as coupling partners. The 2,4-diarylquinolines **2** used in this investigation as models for the absorption and emission property studies were prepared by subjecting substrates **1a–d** to arylboronic acids (1.2 equiv.) in the presence of the Pd(PPh$_3$)$_4$–PCy$_3$ catalyst complex as the Pd(0) source and potassium carbonate as a base in dioxane–water mixture (3 : 1, v/v) under reflux, based on the literature precedent (Table 1).[13] The 18-electron, Pd(0)(PPh$_3$)$_4$ dissociates in solution to form a stable 16-electron SPd(0)(PPh$_3$)$_3$ which, in turn, produces the 14-electron Pd(0)(PPh$_3$)$_2$ as follows: Pd(0)(PPh$_3$)$_4$ $\rightleftharpoons$ SPd(0)(PPh$_3$)$_2$+PPh$_3$, (K$_1$/[PPh$_3$] >> 1); where S is the solvent}.[14] The extra PPh$_3$ generated from this dissociation has been found to inhibit the oxidative addition step particularly when the palladium(0) complex is generated from Pd(0)(PPh$_3$)$_4$.[14] Tricyclohexylphosphine (PCy$_3$) in this case counteracts the inhibitory effect of PPh$_3$ by coordinating to palladium of either the 16- or 14-electron Pd(0) species thereby increasing the electron density of the metal and speeding up the oxidative addition step. Some of the compounds prepared in this investigation have been prepared previously *via* methods such as the Friedlander synthesis[15] or tandem addition–cyclisation–oxidation reactions of imines with alkynes.[11] However, the compounds previously reported have either been described as oils[10,16] or with no melting point values included.[15] Despite these anomalies, the spectroscopic data of compounds **2a–l** represent a close fit that are fully consistent with the assigned structures.

Table 1 Suzuki cross-coupling of the 2-aryl-4-chloroquinolines with arylboronic acids.



1a–d **2a–l**

Compd	R^1	R^2	Yield **2**/%
2a	H	H	40
2b	F	H	74
2c	Cl	H	53
2d	OMe	H	62
2e	H	F	52
2f	F	F	48
2g	Cl	F	51
2h	OMe	F	63
2i	H	OMe	47
2j	F	OMe	54
2k	Cl	OMe	61
2l	OMe	OMe	48

Reagents and conditions: (i) 4-R^{2}C$_6$H$_4$B(OH)$_2$ (1.2 equiv.), Pd(Ph$_3$)$_4$, PCy$_3$, dioxane–water (3 : 1, v/v), reflux, 18 h.

Polysubstituted quinolines **2a–l** comprise an electron-deficient quinoline framework as an electron-acceptor linked directly to the 4-substituted aryl ring to comprise a donor-π-acceptor system. A quinoline moiety is known to act only as an acceptor in the ICT,[17] which occurs through space interaction or orbital overlap between donor and acceptor groups.[18,19] The lone pair electrons of nitrogen are in an orbital which is orthogonal

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* Correspondent. E-mail: mphahmj@unisa.ac.za

to the π-ring system and this makes it is difficult for N-1 to become a donor through a resonance effect. As a prelude to compounds with photophysical properties, we determined the absorption and fluorescence properties of compounds **2a–l** in solvents of medium (chloroform) and high polarity (methanol).

The electronic absorption spectra of compounds **2a–l** were acquired in chloroform ($CHCl_3$) at room temperature (Fig. 1a–c and Table 2). Both the absorption maxima and wavelength within each series are influenced by the variation of substituents on the *para* position of the 4-aryl- and the 2-aryl-groups. The high energy intense absorption maxima are located in the UV region λ 260–284 nm with lower intensity and broad bands observed in the near visible region λ 316–336 nm (ε in the order of 10^3 dm^3 mol^{-1} cm^{-1}). The bands are assigned to the π–π* transitions and the intermolecular donor-acceptor charge transfer absorption[20]. For the 2-aryl-4-phenylquinolines **2a–d**, the presence of a 4-(halogenophenyl) ring at the 2-position leads to an increased molar extinction coefficient over those for the 2-phenyl- and 2-(4-methoxyphenyl)-substituted derivatives and the trend is as follows: **2c** > **2b** > **2a** > **2d** (Fig. 1a). Although the methoxyphenyl derivative **2d** has the lowest molar extinction coefficient, it absorbs at a relatively higher wavelength (λ 277 nm) than the other compounds. The reverse in trend for the molar extinction coefficient is observed for the 4-(4-fluorophenyl) derivatives, **2e** > **2f** > **2g** > **2h**, with the methoxyphenyl derivative **2h** absorbing at higher wavelength at λ 275 nm (Fig. 1b). A combination of the 2-phenyl- and 4-(4-fluorophenyl)-groups on the electron deficient quinoline framework of **2e** leads to the highest molar extinction coefficient of all of the compounds. Increased broadening and molar extinction coefficients compared to **2d** and **2h** are observed for compound **2l** bearing the 4-methoxyphenyl-group at both positions 2- and 4- (Fig. 1c). The molar extinction coefficient and the absorption wavelength are enhanced and red-shifted by λ *ca* 24 nm for **2l** (Fig. 1c). This observation is consistent with a recent study on the distinct photophysical properties observed in 2,4-diphenylquinoline.[21] The increase in the wavelength for **2l** clearly indicates that the methoxy substituent plays a role in determining the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).[22]

The fluorescence emission spectra of compounds **2a–l** in less polar chloroform (dashed lines) and more polar protic methanol (solid lines) at excitation wavelength, $\lambda_{ex} = 370$ nm, show similar patterns and are characterised by single intense emission bands (Fig. 2a–c). These compounds yield blue to green emission and the maximal emission peaks are mainly located in the region $\lambda_{em} = 410–520$ nm. Intense emission maxima are observed for all the compounds in chloroform and methanol; however, within each series the emission wavelengths are influenced by the variation of substituents on the *para* position of the 4-aryl- and the 2-aryl-groups. Since the π,π* state is much more polarisable than the ground state, a change in polarity of the medium has been previously found to cause measurable displacements of the π–π* transition towards the red bands.[23] Methanol is expected to form strong solute–solvent interaction through intermolecular hydrogen bonds with N-1 and, in turn, make the quinoline framework more electron-deficient. A combination of such interaction and the strongly electron withdrawing effect of the 2-(4-chlorophenyl)-group in compound **2c** (see **2c′** in Fig. 2a) would result in a less pronounced ICT due to the π–π* transition and therefore reduced emission intensity. The moderately and strongly donating 4-fluoro- and 4-methoxy-groups, respectively, in compounds **2b** and **2d**, on the other hand, are expected to increase the π-electron delocalisation into the quinoline ring leading to increased emission maxima. Reduced intensity and the blue shift for the emission band of compound **2d** in methanol (see **2d′** in Fig. 2a) are presumably the result of additional hydrogen bonding between the solvent and the methoxy group, which would, in our view, diminish its propensity for electron donation to the aromatic ring.

Compounds **2e–h** with a moderately electron donating 4-fluorophenyl-group at the 4-position of the quinoline moiety exhibited increased emission intensities in chloroform and the emission wavelengths are influenced by the substituent on the *para* position of the 2-aryl-group (Fig. 2b). However, compound **2e** emits at a shorter wavelength compared to the other compounds, with reduced emission intensity resulting from the envisioned methanol–quinoline interaction (see **2e′** in Fig. 2b). The 2-(4-chlorophenyl)-group in compound **2g** is expected to reduce the electron density of the quinoline ring and presumably its capacity to participate in hydrogen bonding with methanol. This, in turn, would cause the moderately donating 4-(4-fluorophenyl)-group to release electrons through the resonance effect, hence exhibiting increased intensity in both solvents. The presence of the electron releasing 4-fluorophenyl- unit at the 2- or the 4-positions in **2f** or 2-(4-fluorophenyl)- and 4-(4-methoxyphenyl)-groups in **2h** leads to an increased π–π* transition in both solvents and then shifts the emission wavelength in methanol to the red. All the 4-(4-methoxyphenyl)-substituted derivatives **2i–k** exhibit increased emission intensities due to an increased π–π* transition, however, their emission wavelengths seem to be influenced by the substituent on the 2-aryl-group (Fig. 2c). As in the case of **2e** in methanol above (see **2e′** in Fig. 2b), the 2-phenyl-derivative **2i** emits at relatively lower wavelength ($\lambda_{em.}$ *ca* 410 nm) in methanol presumably due to hydrogen bonding between the solvent and N-1 (see **2i′** in Fig. 2c). Increased emission intensity in this case is due to the propensity of the 4-(4-methoxyphenyl)-group for π-electron donation into the quinoline ring, which leads to an increased π–π* transition. The emission band for the 2-(4-chlorophenyl)-substituted derivative in methanol (see **2k′**), on the other hand, is shifted to relatively longer emission wavelength. The additional undesired red-shifted emission band of reduced intensity exhibited for **2l** in methanol is presumably due to the re-absorption of light emitted and/or molecular excited state interaction with a ground state molecule, leading to a partial transfer of charge in the molecule.[24]

The absorption and fluorescent properties of compounds **2a–l** showed a strong correlation with the substituent on the *para* position of the 2- and 4-phenyl groups. The solvent-dependent emission characteristics of compounds **2a–l** may result from

Table 2 The absorption and emission data for compounds **2a–l**

2	λ_{max} (nm)	Molar extinction coefficient (ε) × 10^3 dm^3 mol^{-1} cm^{-1}	Emission wavelength, λ_{em}/nm $CHCl_3$	Emission wavelength, λ_{em}/nm CH_3OH
2a	261; 327	47.52; 9.24	477	499
2b	261; 327	54.36; 11.10	439	459
2c	266; 327	60.38; 13.78	430	458
2d	277; 336	30.47; 10.09	459	438
2e	260; 316	81.85; 17.69	437	419
2f	262; 316	57.94; 12.25	452	520
2g	268; 313	53.38; 14.01	478	439
2h	275; 336	43.24; 14.76	463	491
2i	260; 316	52.76; 16.58	459	409
2j	260; 316	44.62; 14.39	438	453
2k	265; 316	51.22; 16.71	447	494
2l	284; 334	46.05; 18.61	455	449

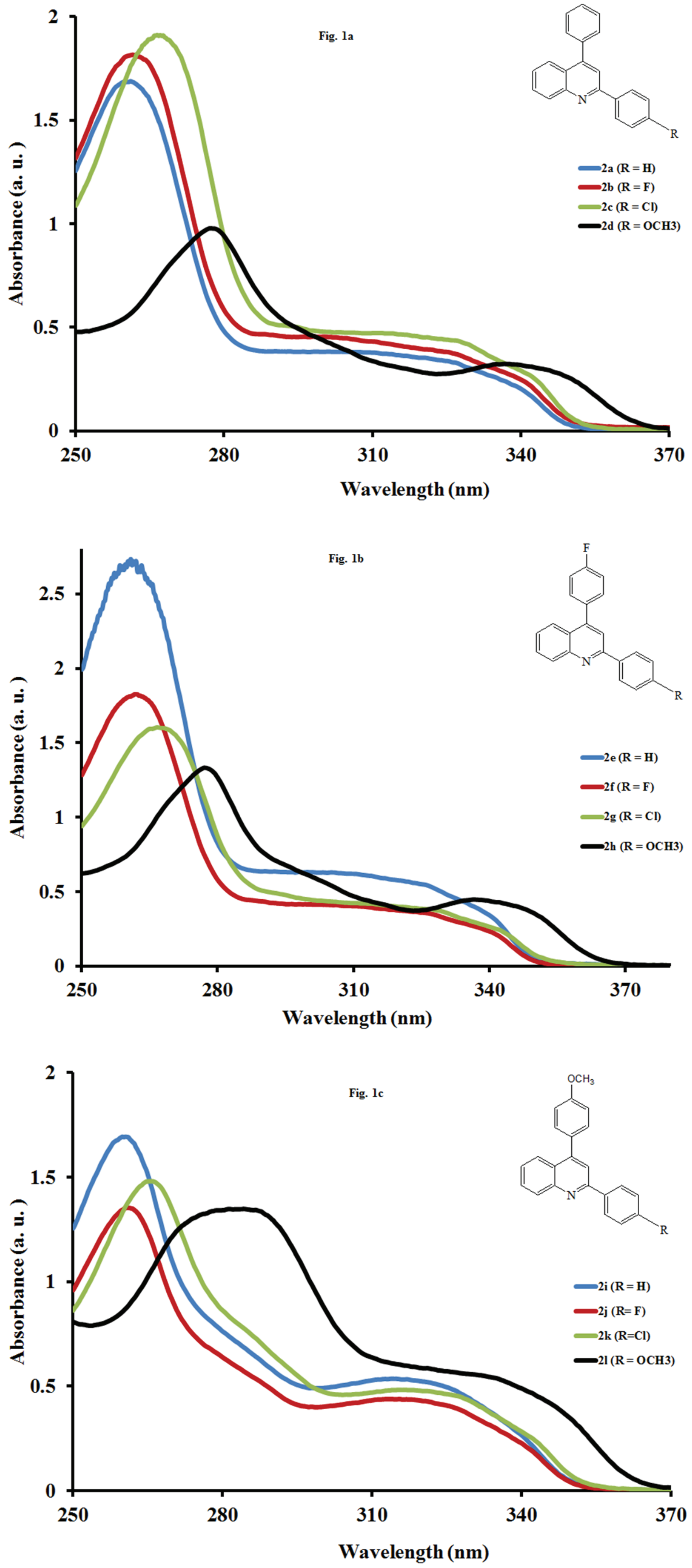

Fig. 1 UV-Vis spectra of 2-aryl-4-phenylquinolines in $CHCl_3$ (1.0×10^{-3} mol L^{-1}). (a) **2a–d**; (b) **2e–h**; and (c) **2i–l**.

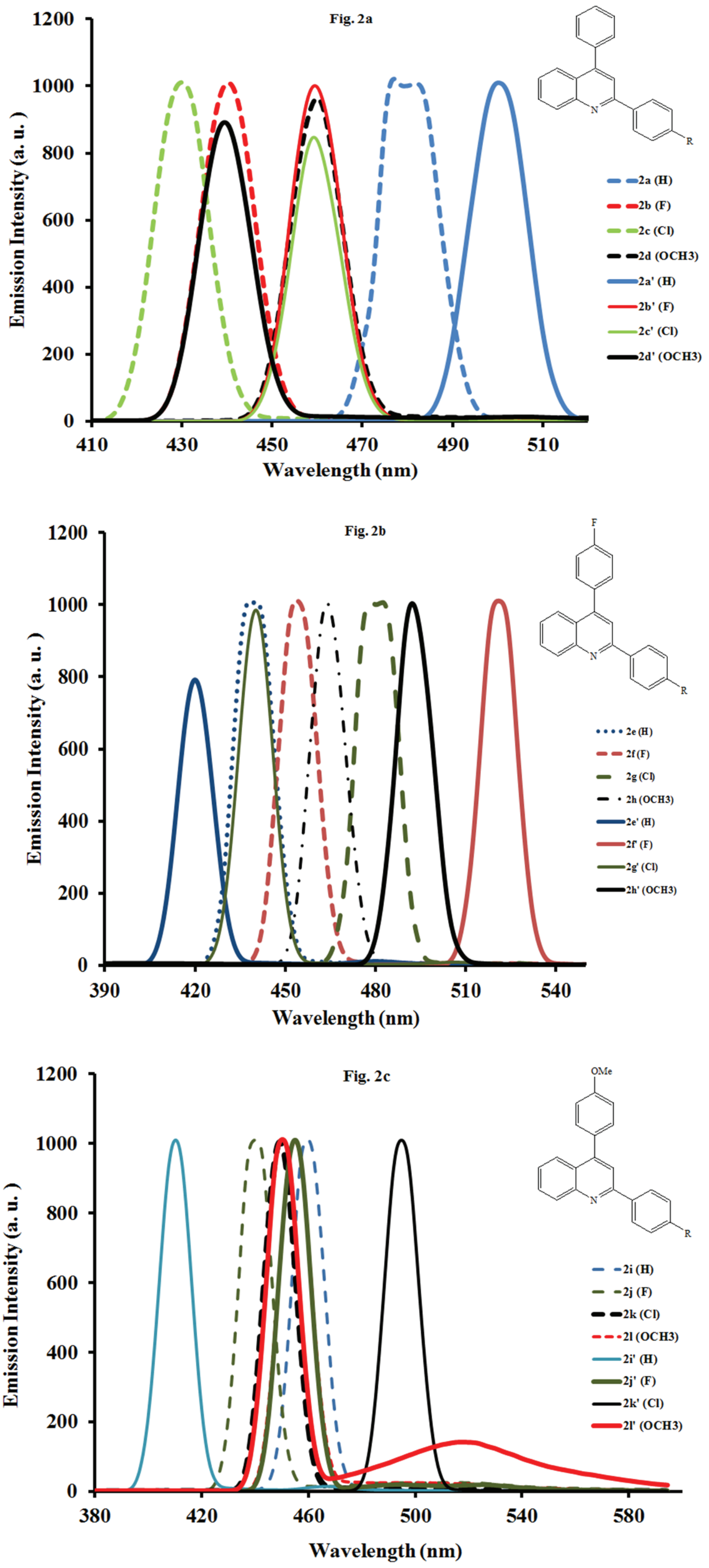

Fig. 2 Fluorescence emission spectra (λ_{ex} = 370 nm) in $CHCl_3$ (dashed lines) and MeOH (solid lines) at room temperature (conc. = 1.0×10^{-3} mol L^{-1}). (a) of **2a–d;** (b) **2e–h**; and (c) **2i–l**.

the dipolar interaction with the polar solvent thus suggesting the ICT character of the emission state, in which the HOMOs and LUMOs are localised on the aryl rings and the quinoline-based moiety, respectively. The 2,4-diarylquinolines **2a–l** are suitable candidates for potential application as organic light-emitting diode materials, either as a single component or as ligands for further synthesis of metal complexes (*e.g.*, with iridium, palladium, platinum, *etc.*). This is because polyarylsubstituted quinolines have been metallated with iridium to form cyclometallated iridium complexes with potential application in OLEDs,[4,5,7] or novel red-emitting electrophosphorescent devices.[2]

Experimental

Melting points were recorded on a thermocouple digital melting point apparatus and are uncorrected. IR spectra were recorded as powders using a Bruker VERTEX 70 FT-IR spectrometer with a diamond ATR (attenuated total reflectance) accessory by using the thin-film method. The UV-Vis spectra were recorded on a Cecil CE 9500 (9000 Series) UV-Vis spectrometer while emission spectra were taken using a PerkinElmer LS 55 fluorescence spectrometer. For column chromatography, Merck kieselgel 60 (0.063–0.200 mm) was used as stationary phase. NMR spectra were obtained as $CDCl_3$ solutions using Varian Mercury 300 MHz NMR spectrometer and the chemical shifts are quoted relative to the solvent peaks. Low- and high-resolution mass spectra were recorded at an ionisation potential of 70 eV using Micromass Autospec-TOF (double focusing high resolution) instrument. The synthesis and analytical data of compounds **1a–d** have been described previously.[25]

Suzuki-Miyaura cross-coupling of **1** *with arylboronic acids; general procedure*

2-Aryl-4-chloroquinoline **1** (1 equiv.), arylboronic acid (1.2 equiv.), $Pd(PPh_3)_4$ (5 mol% of **1**), PCy_3 (10 mol% of **1**), K_2CO_3 (2 equiv.) and 3 : 1 dioxane–water (*ca* 5 mL mmol^{-1} of **1**) were added to a two-necked flask equipped with a stirrer bar, rubber septum and a condenser. The mixture was flushed for 20 minutes with argon gas and a balloon filled with argon gas was connected to the top of the condenser. The mixture was heated with stirring at 80–90 °C under argon atmosphere for 18 h and then allowed to cool to room temperature. The cooled mixture was poured into ice-cold water and the product was taken-up into chloroform. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and then evaporated under reduced pressure. The residue was purified by column chromatography over silica gel to afford the 2,4-diarylquinoline **2**. The following products were prepared in this fashion:

2,4-Diphenylquinoline (**2a**): A mixture of **1a** (0.50 g, 2.09 mmol), phenylboronic acid (0.31 g, 2.50 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), PCy_3 (0.06 g, 0.21 mmol) and K_2CO_3 (0.58 g, 4.17 mmol) in dioxane–water (15 mL) afforded **2a** as a white solid (0.23 g, 40%), m.p. 107–109 °C (lit. 109 °C,[1] 99–101 °C[10]); R_f ($CHCl_3$) 0.38; ν_{max}/cm^{-1} (ATR): 588, 699, 765, 872, 1356, 1405, 1444, 1488, 1544, 1588; δ_H (300 MHz, $CDCl_3$): 7.46–7.55 (m, 9H), 7.73 (t, J = 7.2 Hz, 1H), 7.82 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 7.5 Hz, 2H), 8.25 (d, J = 8.4 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 119.4, 125.6, 125.8, 126.3, 127.6, 128.4, 128.6, 128.8, 129.3, 129.5, 129.6, 130.1, 138.4, 139.7, 148.8, 149.2, 156.9; *m/z* 282 (100 MH$^+$); HRMS (ES): MH$^+$, found 282.1289. $C_{21}H_{16}N^+$ requires 282.1283.

2-(4-Fluorophenyl)-4-phenylquinoline (**2b**): A mixture of **1b** (0.50 g, 1.94 mmol), phenylboronic acid (0.28 g, 2.33 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), PCy_3 (0.05 g, 0.19 mmol) and K_2CO_3 (0.54 g, 3.88 mmol) in dioxane–water (15 mL) afforded **2b** as a white solid (0.43 g, 74%), m.p. 83–85 °C (lit. [10] 68–69 °C); R_f ($CHCl_3$) 0.44; ν_{max}/cm^{-1} (ATR): 528, 701, 727, 755, 769, 806, 831, 999, 1098, 1355, 1419, 1488, 1547, 1585; δ_H (300 MHz, $CDCl_3$): 7.20 (t, J = 7.8 Hz, 2H), 7.45–7.54 (m, 6H), 7.72 (d, J = 7.8 Hz, 1H), 7.76 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 8.17–8.23 (m, 3H); δ_C (75 MHz, $CDCl_3$): 115.8 (d, $^2J_{CF}$ = 21.3), 118.9, 125.7, 126.4, 128.5, 128.6, 129.4, 129.5 (d, $^3J_{CF}$ = 4.8 Hz), 129.6, 130.0, 135.8 (d, $^4J_{CF}$ = 3.2 Hz), 138.3, 148.7, 149.3, 155.8, 163.8 (d, $^1J_{CF}$ = 247 Hz); *m/z* 300 (100 MH$^+$); HRMS (ES): MH$^+$, found 300.1191. $C_{21}H_{15}NF^+$ requires 300.1189.

2-(4-Chlorophenyl)-4-phenylquinoline (**2c**): A mixture of **1c** (0.50 g, 1.82 mmol), phenylboronic acid (0.27 g, 2.19 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), PCy_3 (0.05 g, 0.19 mmol) and K_2CO_3 (0.50 g, 3.64 mmol) in dioxane–water (15 mL) afforded **2c** as a white solid (0.30 g, 53%), m.p. 101–103 °C (lit.[1] 103 °C); R_f ($CHCl_3$) 0.30; ν_{max}/cm^{-1} (ATR): 485, 539, 602, 742, 756, 963, 1093, 1355, 1415, 1485, 1544, 1590; δ_H (300 MHz, $CDCl_3$): 7.45 (m, 8H), 7.72 (d, J = 7.5 Hz, 1H), 7.77 (s, 1H), 7.90 (d, J = 7.5 Hz, 1H), 8.15 (d, J = 7.5 Hz, 2H), 8.21 (d, J = 7.5 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 118.9, 125.7, 125.8, 126.5, 128.5, 128.6, 128.8, 129.0, 129.5, 129.7, 130.1, 135.6, 138.0, 138.2, 148.7, 149.4, 155.5; *m/z* 316 (100 MH$^+$); HRMS (ES): MH$^+$, found 316.0897. $C_{21}H_{15}N^{35}Cl^+$ requires 316.0893.

2-(4-Methoxyphenyl)-4-phenylquinoline (**2d**): A mixture of **1d** (0.30 g, 1.09 mmol), phenylboronic acid (0.16 g, 1.31 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.06 mmol), PCy_3 (0.03 g, 0.11 mmol) and K_2CO_3 (0.30 g, 2.19 mmol) in dioxane–water (15 mL) afforded **2d** as a white solid (0.21 g, 62%), m.p. 73–75 °C (lit. 76 °C,[1] oil[10]); R_f ($CHCl_3$) 0.60; ν_{max}/cm^{-1} (ATR): 543, 750, 823, 1025, 1171, 1250, 1518, 1575; δ_H (300 MHz, $CDCl_3$): 3.87 (s, 3H), 7.05 (d, J = 9.3 Hz, 2H), 7.44 (t, J = 7.5 Hz, 1H), 7.52–7.58 (m, 5H), 7.72 (t, J = 7.5 Hz, 1H), 7.78 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 8.10–8.25 (m, 3H); δ_C (75 MHz, $CDCl_3$): 55.3, 114.1, 114.2, 118.8, 125.5, 125.9, 128.3, 128.5, 128.8, 129.4, 129.5, 129.8, 132.1, 138.4, 148.7, 148.9, 156.3, 160.7; *m/z* 312 (100 MH$^+$); HRMS (ES): MH$^+$, found 312.1397. $C_{22}H_{16}NO^+$ requires 312.1388.

4-(4-Fluorophenyl)-2-phenylquinoline (**2e**): A mixture of **1a** (0.50 g, 2.09 mmol), 4-fluorophenylboronic acid (0.35 g, 2.51 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol), PCy_3 (0.06 g, 0.21 mmol) and K_2CO_3 (0.58 g, 4.17 mmol) in dioxane–water (15 mL) afforded **2e** as a white solid (0.13 g, 52%), m.p. 82–83 °C; R_f ($CHCl_3$) 0.29; ν_{max}/cm^{-1} (ATR): 696, 763, 838, 1156, 1222, 1491, 1542, 1607; δ_H (300 MHz, $CDCl_3$): 7.25 (t, J = 7.5 Hz, 2H), 7.47–7.56 (m, 6H), 7.74 (t, J = 7.5 Hz, 1H), 7.79 (s, 1H), 7.86 (d, J = 7.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 2H), 8.25 (d, J = 7.5 Hz, 1H), δ_C (75 MHz, $CDCl_3$): δ 115.6 (d, $^2J_{CF}$ = 21.3 Hz), 119.3, 125.3, 125.6, 126.4, 127.5, 128.8, 129.4, 129.6, 130.2, 131.2 (d, $^3J_{CF}$ = 8.3 Hz), 134.3 (d, $^4J_{CF}$ = 3.5 Hz), 139.5, 147.9, 148.8, 156.8, 162.8 (d, $^1J_{CF}$ = 246.7 Hz); *m/z* 300 (100 MH$^+$); HRMS (ES): MH$^+$, found 300.1186. $C_{21}H_{15}NF^+$ requires 300.1189.

2,4-Bis(4-fluorophenyl)quinoline (**2f**): A mixture of **1b** (0.50 g, 1.94 mmol), 4-fluorophenylboronic acid (0.33 g, 2.33 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), PCy_3 (0.05 g, 0.19 mmol) and K_2CO_3 (0.54 g, 3.88 mmol) in dioxane–water (15 mL) afforded **2f** as a flaky yellow solid (0.29 g, 48%), m.p. 103–105 °C; R_f ($CHCl_3$) 0.62; ν_{max}/cm^{-1} (ATR): 762, 838, 1157, 1223, 1354, 1493, 1599; δ_H (300 MHz, $CDCl_3$): 7.19–7.29 (m, 4H), 7.48–7.57 (m, 3H), 7.75 (s, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.86 (d, J = 9.0 Hz, 1H), 8.18–8.25 (m, 3H); δ_C (75 MHz, $CDCl_3$): 115.8 (d, $^2J_{CF}$ = 21.3 Hz), 115.7 (d, $^2J_{CF}$ = 21.6 Hz), 118.9, 125.3, 125.6, 126.5, 129.4 (d, $^3J_{CF}$ = 8.3 Hz), 129.6, 130.1, 131.2 (d, $^3J_{CF}$ = 8.0 Hz), 134.2 (d, $^4J_{CF}$ = 3.1 Hz), 135.6 (d, $^4J_{CF}$ = 3.1 Hz), 148.2, 148.7, 155.7, 162.9 (d, $^1J_{CF}$ = 243.5 Hz), 163.8 (d, $^1J_{CF}$ = 247.6 Hz); *m/z* 318 (100 MH$^+$); HRMS (ES): MH$^+$, found 318.1096. $C_{21}H_{14}NF_2^+$ requires 318.1094.

2-(4-Chlorophenyl)-4-(4-fluorophenyl)quinoline (**2g**): A mixture of **1c** (0.50 g, 1.82 mmol), 4-fluorophenylboronic acid (0.31 g, 2.18 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), PCy_3 (0.05 g, 0.18 mmol) and K_2CO_3 (0.50 g, 3.64 mmol) in dioxane–water (15 mL) afforded **2g** as a white solid (0.31 g, 51%), m.p. 96–98 °C; R_f ($CHCl_3$) 0.47; ν_{max}/cm^{-1} (ATR): 553, 718, 806, 829, 1013, 1090, 1156, 1221, 1501, 1597; δ_H (300 MHz, $CDCl_3$): 7.26 (t, J = 8.4 Hz, Hz, 2H), 7.48–7.56 (m, 5H), 7.74 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 9.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 115.7 (d, $^2J_{CF}$ = 21.3 Hz), 118.9, 125.4, 126.7, 128.6, 128.8, 128.9, 129.8, 130.1, 131.2 (d, $^3J_{CF}$ = 8.0 Hz), 134.1 (d, $^4J_{CF}$ = 3.5 Hz), 135.6, 137.8, 148.3, 148.7, 155.4, 162.9 (d, $^1J_{CF}$ = 246.8 Hz); *m/z* 334 (100 MH$^+$); HRMS (ES): MH$^+$, found 334.0804. $C_{21}H_{14}NF^{35}Cl^+$ requires 334.0799.

4-(4-Fluorophenyl)-2-(4-methoxyphenyl)quinoline (**2h**): A mixture of **1d** (0.50 g, 1.85 mmol), 4-fluorophenylboronic acid (0.31 g, 2.22 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.09 mmol), PCy_3 (0.05 g, 0.18 mmol) and K_2CO_3 (0.51 g, 3.70 mmol) in dioxane–water (15 mL) afforded **2h** as a cream white solid (0.38 g, 62%), m.p. 117–120 °C; R_f ($CHCl_3$) 0.54; ν_{max}/cm^{-1} (ATR): 713, 750, 823, 1025, 1326, 1544, 1575, 1604; δ_H (300 MHz, $CDCl_3$): 3.88 (s, 3H), 7.04 (d, J = 9.3 Hz, 2H), 7.24 (t, J = 7.8 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.74 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 9.0 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 55.4, 114.2, 115.6 (d, $^2J_{CF}$ = 21.3 Hz), 118.9, 125.3, 125.4, 126.1, 128.9, 129.5, 129.9, 131.2 (d, $^3J_{CF}$ = 8.3 Hz), 132.0, 134.4 (d, $^4J_{CF}$ = 3.1 Hz), 147.9, 148.8, 156.4, 160.8, 162.9 (d, $^1J_{CF}$ = 246.4 Hz); m/z 330 (100 MH^+); HRMS (ES): MH^+, found 330.1297. $C_{22}H_{17}NOF^+$ requires 330.1294.

4-(4-Methoxyphenyl)-2-phenylquinoline (**2i**): A mixture of **1a** (0.25 g, 1.04 mmol), phenylboronic acid (0.19 g, 1.25 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol), PCy_3 (0.03 g, 0.10 mmol) and K_2CO_3 (0.29 g, 2.09 mmol) in dioxane–water (15 mL) afforded **2i** as a pale yellow solid (0.15 g, 47%), m.p. 99–100 °C (lit.[16,26] oil); R_f ($CHCl_3$) 0.58; ν_{max}/cm^{-1} (ATR): 584, 676, 686, 718, 767, 1026, 1169, 1181, 1286, 1490, 1502, 1592, 1607; δ_H (300 MHz, $CDCl_3$): 3.90 (s, 3H), 7.07 (d, J = 8.7 Hz, 2H), 7.56–7.44 (m, 6H), 7.73 (t, J = 8.4 Hz, 1H), 7.80 (s, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.7 Hz, 2H), 8.26 (d, J = 8.7 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 55.4, 114.0, 119.3, 125.6, 125.9, 126.2, 127.5, 128.8, 129.2, 129.4, 130.1, 130.6, 130.8, 139.7, 148.8, 148.9, 156.9, 159.8; m/z 312 (100 MH^+); HRMS (ES): MH^+, found 312.1385. $C_{22}H_{18}NO^+$ requires 312.1388.

2-(4-Fluorophenyl)-4-(4-methoxyphenyl)quinoline (**2j**): A mixture of **1b** (0.25 g, 0.97 mmol), phenylboronic acid (0.18 g, 1.16 mmol), $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol), PCy_3 (0.03 g, 0.10 mmol) and K_2CO_3 (0.27 g, 1.94 mmol) in dioxane–water (15 mL) afforded **2j** as a white solid (0.19 g, 54%), m.p. 89–91 °C (lit.[16] orange oil); R_f ($CHCl_3$) 0.56; ν_{max}/cm^{-1}: 576, 767, 830, 1023, 1155, 1493, 1592; δ_H (300 MHz, $CDCl_3$): 3.91 (s, 3H), 7.08 (d, J = 9.0 Hz, 2H), 7.20 (t, J = 9.0 Hz, 2H), 7.49 (d, J = 7.5 Hz, 3H), 7.71 (d, J = 7.5 Hz, 1H), 7.74 (s, 1H), 7.95 (d, J = 9.3 Hz, 1H), 8.16–8.24 (m, 3H), δ_C (75 MHz, $CDCl_3$): 55.3, 114.0, 115.7 (d, $^2J_{CF}$ = 21.4 Hz), 118.8, 125.6, 125.8, 126.2, 129.3, 129.4 (d, $^3J_{CF}$ = 8.3 Hz), 129.9, 130.5, 130.7, 135.8 (d, $^4J_{CF}$ = 3.1 Hz), 148.8, 148.9, 155.7, 159.8, 163.7 (d, $^1J_{CF}$ = 247.3 Hz); m/z 330 (100 MH^+); HRMS (ES): MH^+, found 330.1298. $C_{22}H_{17}NOF^+$ requires 330.1294.

2-(4-Chlorophenyl)-4-(4-methoxyphenyl)quinoline (**2k**): A mixture of **1c** (0.25 g, 0.97 mmol), phenylboronic acid (0.17 g, 1.09 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.05 mmol), PCy_3 (0.03 g, 0.09 mmol) and K_2CO_3 (0.25 g, 1.82 mmol) in dioxane–water (15 mL) afforded **2k** as a white solid (0.21 g, 61%), m.p. 94–97 °C; R_f ($CHCl_3$) 0.49; ν_{max}/cm^{-1} (ATR): 718, 823, 1090, 1177, 1244, 1488, 1589; δ_H (300 MHz, $CDCl_3$): 3.90 (s, 3H), 7.07 (d, J = 9.3 Hz, 2H), 7.45–7.51 (m, 5H), 7.71 (d, J = 6.0 Hz, 1H), 7.74 (s, 1H), 7.94 (d, J = 9.3 Hz, 1H), 8.13 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 7.5 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 55.4, 114.1, 118.8, 125.7, 125.9, 126.4, 128.8, 129.0, 129.6, 130.0, 130.5, 130.8, 135.5, 138.1, 148.8, 149.1, 155.5, 159.9; m/z 346 (100 MH^+); HRMS (ES): MH^+, found 346.1000. $C_{22}H_{17}NO^{35}Cl^+$ requires 346.0999.

2,4-Bis(4-methoxyphenyl)quinoline (**2l**): A mixture of **1d** (0.40 g, 1.48 mmol), phenylboronic acid (0.27 g, 1.78 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.07 mmol), PCy_3 (0.04 g, 0.15 mmol) and K_2CO_3 (0.41 g, 2.96 mmol) in dioxane–water (15 mL) afforded **2l** as a white solid (0.24 g, 48%), m.p. 84–87 °C (lit.[16] orange oil); R_f ($CHCl_3$) 0.49; ν_{max}/cm^{-1} (ATR): 782, 830, 1027, 1178, 1234, 1247, 1307, 1496, 1511, 1605; δ_H (300 MHz, $CDCl_3$): 3.86 (s, 3H), 3.89 (s, 3H), 6.72 (d, J = 3.3 Hz, 1H), 7.09–7.06 (m, 3H), 7.43 (d, J = 7.8 Hz, 1H), 7.49 (s, 1H), 7.51 (d, J = 3.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.76 (d, J = 3.0 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 8.15 (dd, J = 3.0 Hz, 9.3 Hz, 2H), 8.24 (d, J = 9.3 Hz, 1H); δ_C (75 MHz, $CDCl_3$): 55.2, 55.3, 113.9, 114.1, 114.6, 116.1, 118.9, 125.6, 125.8, 128.9, 129.4, 129.6, 130.7, 148.7, 148.8, 156.5, 159.7, 160.7; m/z 342 (100 MH^+); HRMS (ES): MH^+, found 342.1494. $C_{23}H_{20}NO_2^+$ requires 342.1494.

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