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ONO Pincer type Pd(II) complexes: Synthesis, crystal structure and catalytic activity towards C-2 arylation of quinoline scaffolds

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ABSTRACT

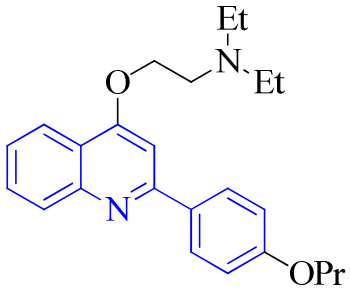
Four new palladium(II) complexes featuring ONO pincer type hydrazone ligands were synthesized and characterized by spectroscopic and single-crystal XRD analysis. These complexes showed excellent catalytic activity towards Suzuki-Miyaura cross coupling reaction of 2-chloroquinoline derivatives with various aryl boronic acids. The main advantages over previous methodologies include low catalyst loading, less problematic reaction media (H_2O-DMF (80:20%)) and a lower reaction temperature of 60 °C for optimal performance.

INTRODUCTION

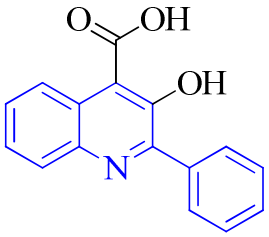
Nitrogen based heterocycles are important constituents in a large number of biologically active compounds.[1] Among which quinoline scaffolds play a vital role. Several quinolines and their derivatives are currently in use as antibacterial, antifungal, analgesics, antituberculosis, antimalarial, anti-inflammatory, anticancer, antibiotic and anti-HIV drugs.[2] In addition, quinoline analogues are valuable synthons for the preparation of nano and mesostructures with enhanced electronic and photonic properties.[3] Despite the numerous pharmacological activities and related synthetic methods,[4] the development of new, facile and eco-friendly synthetic approaches to 2-substituted quinolines using mild conditions are desirable and subject of ongoing research. 2-Arylated quinoline and their derivatives have proven significant *in vivo* activities against *Leishmaniadonovani* and are in preclinical development.[5] Likewise, a few other 2-aryl quinolines display significant antiviral activity in HIV-infected cells.[6]

Within the efforts to realize 2-substituted quinolines, most established routines require elevated reaction temperatures, prolonged reaction times, excess amounts of various reagents, including toxic compounds and harsh reaction conditions[7] which are unsuitable for sensitive substrates and thus constitute a challenge in targeted syntheses. Palladium catalyzed Suzuki-Miyaura cross-coupling (SMC) reactions were tried as an alternative, but unfortunately, nitrogen containing heterocycles are problematic substrates for SMC reactions[8] because of a tendency to bind with the metal ion and thus deactivates the catalyst.

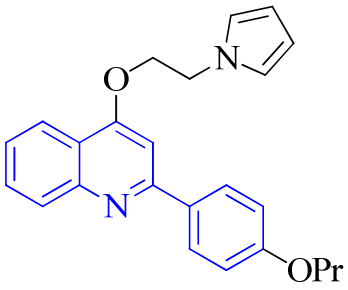
However, catalysts like $[PdCl_2(PPh_3)_2]$ and $Pd(OAc)_2/D^tBPF$ (D^tBPF = 1,1′-bis(ditert-butylphosphino)ferrocene) were reported to offer improved results compared to the Pd-L catalysts with electron-rich, bulky, monodentate phosphine ligands such as P^tBu_3 and PCy_2- (biphenyl), but requiring a high catalyst loading (5 mol %).[8 (c),9]



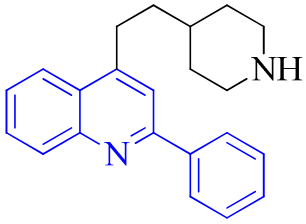
Diethyl-{2-[2-(4-propoxy-phenyl)-quinolin -4-yloxy]-ethyl}-amine



3-Hydroxy-2-phenyl-quinoline -4-carboxylic acid



2-(4-Propoxy-phenyl)-4-(2-pyrrol-1-yl-ethoxy) -quinoline



2-Phenyl-4-(2-piperidin-4-yl-ethyl) -quinoline

Figure1. Biologically active 2-phenylquinoline derivatives

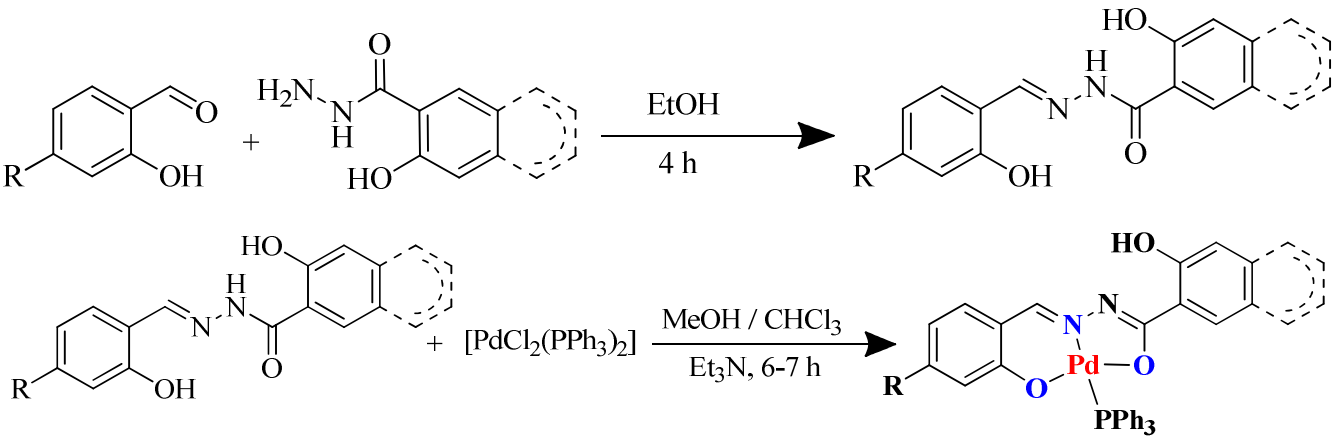
Currently, our group is actively pursuing research on the synthesis and biological applications of hydrazone based transition metal complexes with pincer type geometry.[10] More recently, we turned our attention to evaluate hydrazone based pincer type palladium complexes as catalysts for the SMC reaction.[11] Synthesis of transition metal pincer type complexes with high stability and catalytic activity has been a most productive area of homogeneous catalysis and coordination chemistry.[12,13] The remarkable equilibrium between stability and reactivity of the pincer complexes can be controlled by precise ligand design and subsequent co-operative construction of metal complexes.[13] As a result, research on the development of pincer ligands possessing CCC, CNC, PNP, SNS, NNN, NCN and SCS donor atoms got much attention.[14] However, studies on ONO pincer ligands and corresponding complexes are scanty in the literature. A recent review on Ru, Ir, W, Ta, Re, Pb, Fe and Sb complexes containing ONO pincer ligand moiety highlighted their importance as catalysts in various organic reactions.[13a, 15] In our previous study, we reported for the first time, the catalytic potential of[11] ONO pincer analogous palladium complexes for SMC of challenging aryl chlorides with various aryl boronic acids bearing activating as well as deactivating substituents.

In this manuscript, we describe the synthesis of four new palladium(II) complexes (**1** – **4**) bearing ONO pincer type ligands and their catalytic activity towards SMC reaction of 2-chlroroquinoline derivatives with substituted aryl boronic acids. To the best of our insight, this is the first study on the utility of the

titled complexes as catalysts in SMC reactions of 2-chlroroquinoline derivatives with substituted aryl boronic acids in H_2O-DMF system to synthesis a library of 2-arylquinolines.

RESULTS AND DISCUSSIONS

Direct reactions of palladium precursor $[PdCl_2(PPh_3)_2]$ with the pincer type ligands H_3L1–H_3L4 (where, H_3L is pincer type ligand derived from the condensation of salicylaldehyde with salicylichydrazide (H_3L1) or 3-hydroxynaphthoic acid hydrazide(H_3L2), and 4-methoxysalicylaldehyde with salicylichydrazide (H_3L3) or 3-hydroxynaphthoic acid hydrazide (H_3L4)) yielded complexes **1**–**4** of the type $[Pd(HL)(PPh_3)]$ as depicted in **Scheme 1**.



Where R = H or OCH_3

Scheme 1. Synthesis of ligands and their respective Pd(II) complexes.

IR spectra of the four complexes were compared with corresponding free ligands. The absorption due to free OH groups of the ligands observed respectively, at 3719, 3614, 3610 and 3640 cm^{-1}. A strong band observed at 3185, 3260, 3181, and 3249 cm^{-1} indicated the presence of a N−H functional group in the free ligands. Intense C=O absorption bands were found at 1618, 1641, 1624, and 1623 cm^{-1} in the spectrum of the free ligands. All four ligands exhibited a very sharp band at 1555, 1572, 1556, and 1556 attributed to the C=N group. In the IR spectra of the complexes discussed here, non-existence of a strong band from free OH indicated the deprotonation of phenolic oxygen and its coordination to the palladium(II) ion. The N−H and C=O stretching vibrations were missing thus proving that the ligands underwent enolisation followed by deprotonation prior to coordination with the palladium(II) ion.[16a] In addition, a new band occurred due to the C=N−N=C group at 1494, 1472, 1488, and 1473 cm^{-1}, respectively. The absorption related to a C−O group was identified as a new sharp band at 1255, 1299, 1222 and 1303 cm^{-1} in for complexes **1** - **4**. The IR spectral features unambiguously prove that the pincer type ligands H_3L1, H_3L2, H_3L3, and H_3L4 were coordinated to palladium(II) ion via the phenolate oxygen, the azomethine nitrogen and the imidolate oxygen in complexes **1**−**4.**[16b]

^1H NMR spectra of them were recorded in order to study the exact coordination mode of the pincer type ligand in the palladium complexes **1**−**4**. None displayed any signal due to a N−H proton and thus indicated that the oxygen is coordinated to the palladium ion in the imidolate form. Sharp singlet observed in the spectra of complexes **1**–**4** at 8.61, 9.15, 8.20, and 9.39 ppm, respectively were assigned to the azomethine proton of the pincer ligand. The non-involvement of OH groups, despite their presence in the phenyl/naphthyl ring of the corresponding pincer type ligands in coordination with

palladium ion is confirmed by the singlet resonances at 6.38, 5.77, 5.36, and 5.40 ppm, respectively. However, in the spectra of complexes **3,** and **4** a sharp singlet at 3.81 and 3.42 ppm, respectively confirmed the presence of a methoxy group. Aromatic protons present in complexes **1**–**4** were identified in the region of 8.34 to 6.98 ppm.[17] Similarly, the ^{13}C NMR resonance of the complexes showed downfield signals at 159.2, 159.3, 159.2, and 157.8 ppm, respectively, owing to the imidolate carbon (N=C–O) involved in coordination. The azomethine carbon of the complexes **1**–**4** gave signals at 151.5, 151.6, 151.5, and 148.5, respectively. Signals featuring in the region of 143.8–105.1 and at 55.2/51.4 ppm have been assigned to aromatic and methoxy carbons present in complexes **1**–**4**.[17]

The molecular structure of complexes **1**–**4** were determined by single-crystal X-ray diffraction to study the exact coordination mode of the pincer type ligands with palladium ion. Selected bond angles and bond distances are gathered in Table 1 in the ESI. The ORTEP diagrams provided in Figure 2–5 shows pincer type ligands coordinated to the palladium ion via the phenolate oxygen, azomethine nitrogen and deprotonated imidole oxygen. Complex **1** crystallized in the triclinic system, but the other three were primitive monoclinic with space groups P-1, $P2_1/a$, $P2_1/c$ and $P2_1/c$, respectively. The Pd(II) ion adopts a distorted square-planar geometry in all four structures by accommodating the ligand as a binegative tridentate ONO donor and the fourth site is occupied by a triphenylphosphine. The bite angles of O(1)– Pd(1)–O(2) in **1**–**4** are 174.29(8), 174.30(13), 174.37(6), and 173.74(15), respectively. Similarly, angles N(1)–Pd(1)–P(1) are 174.77(7), 173.09(9), 179.17(5), and 172.74(13). Unit cell packing diagrams of complexes **1**–**4** are provided in ESI. The observed bond lengths and bite angles are very similar to those observed in other palladium(II) complexes.[18] Relevant data concerning data collection and details of the structure refinements are summarized Table 2 in the electronic supplementary information (ESI). Based on ^{1}H, ^{13}C NMR and single-crystal XRD data, the pincer type hydrazone ligand is coordinated to the palladium ion in a tridentate fashion by replacing both chloride ions and the triphenylphospine from the starting precursor.

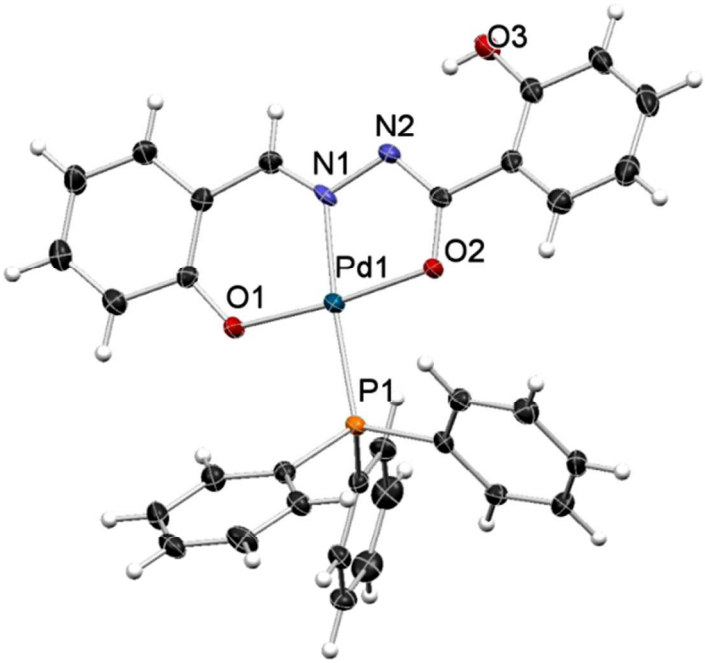


Figure 2. ORTEP diagram of complex **1** with thermal ellipsoids at the 50% probability level.

(Catalyst 1)

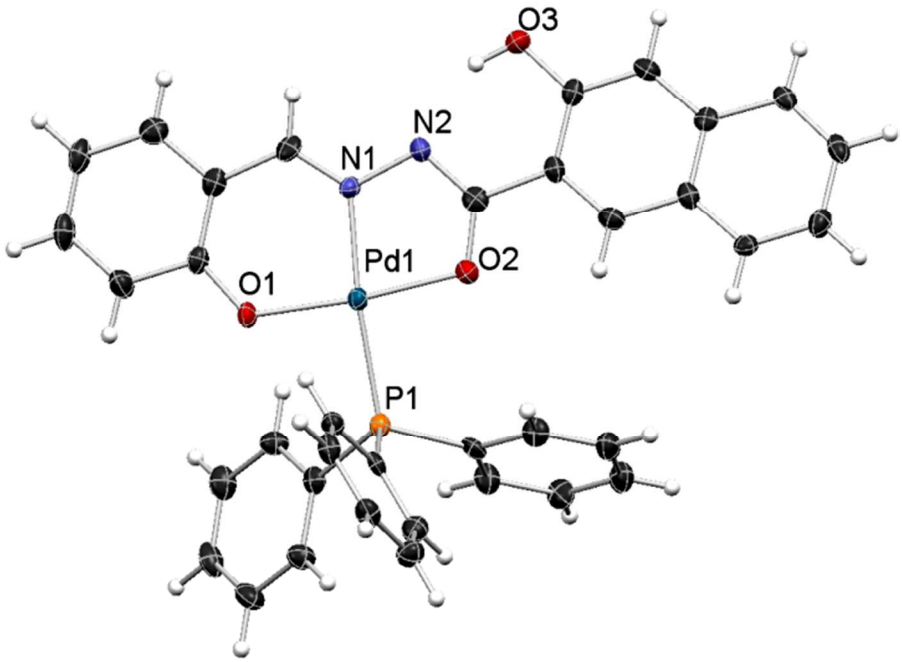


Figure 3. ORTEP diagram of complex **2** with thermal ellipsoids at the 50% probability level.

(Catalyst 2)

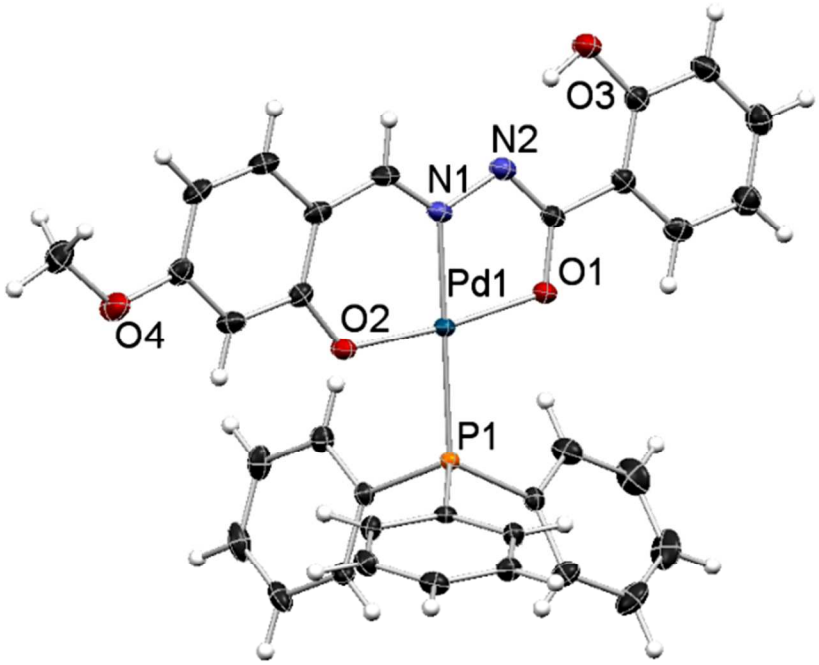


Figure 4. ORTEP diagram of complex **3** with thermal ellipsoids at the 50% probability level.

(Catalyst 3)

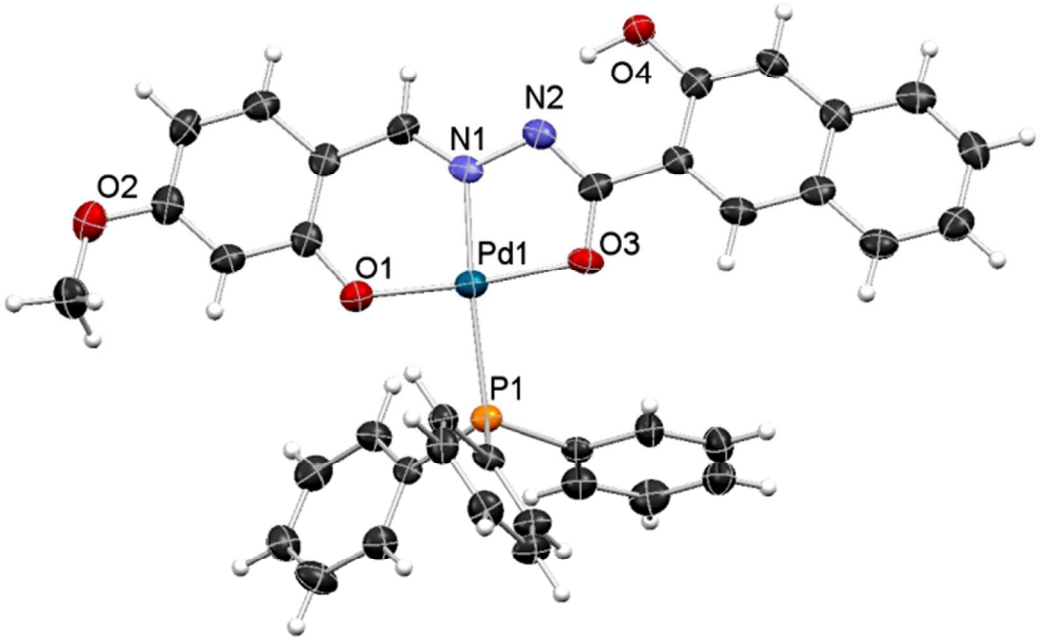
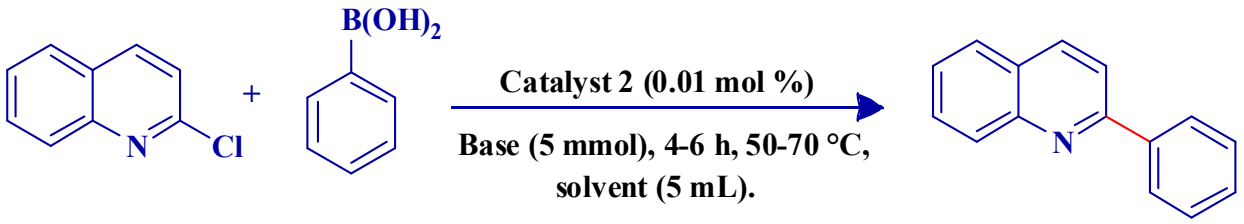


Figure 5. ORTEP diagram of complex **4** with thermal ellipsoids at the 50% probability level. (Catalyst 4)

Table 1. Optimization of reaction conditions



Entry	Catalyst	Base	Solvent	Yield (%)
1	Catalyst 2	No base	H_2O	No reaction
2	Catalyst 2	No base	H_2O / DMF	19
3	Catalyst 2	KOH	H_2O / DMF	90
4	Catalyst 2	K_2CO_3	H_2O / DMF	85
5	Catalyst 2	NaOH	H_2O / DMF	84
6	Catalyst 2	Na_2CO_3	H_2O / DMF	79
7	Catalyst 2	CH_3COONa	H_2O / DMF	52
8	Catalyst 2	Et_3N	H_2O / DMF	45
9	Catalyst 2	Pyridine	H_2O / DMF	39
10	Catalyst 2	KOH	H_2O / DCM	40
11	Catalyst 2	KOH	H_2O / toluene	41
12	Catalyst 2	KOH	H_2O / $CHCl_3$	43
13	Catalyst 2	KOH	H_2O / DMF	90
14	Catalyst 2	KOH	H_2O / CH_3CN	72
15	Catalyst 2	KOH	H_2O / THF	61
16	Catalyst 2	KOH	H_2O / DMSO	82
17	Catalyst 2	KOH	H_2O / EtOAc	55
18	Catalyst 2	KOH	H_2O / benzene	53
19	Catalyst 2	KOH	H_2O / DMF (10 %)	80
20	Catalyst 2	KOH	H_2O / DMF (20 %)	90
21	Catalyst 2	KOH	H_2O / DMF (30 %)	83
22	Catalyst 2	KOH	H_2O / DMF (40 %)	76
23	Catalyst 2	KOH	H_2O / DMF (50 %)	70
24	Catalyst 1	KOH	H_2O / DMF (20 %)	85
25	Catalyst 2	KOH	H_2O / DMF (20 %)	90
26	Catalyst 3	KOH	H_2O / DMF (20 %)	79

27	**Catalyst 4**	**KOH**	**H_2O / DMF (20 %)**	**96**

Catalysis

Catalytic activity of the complexes 1–4 were investigated towards SMC reactions of 2-chloroquinoline derivatives with different substituted aryl boronic acids. Reaction conditions were optimized by utilizing 2-chloroquinoline and phenylboronic acid as model substrates in aqueous–organic media and the results are summarized in Table 1.

Initially, the catalytic reaction was studied with various bases such as KOH, NaOH, K_2CO_3, $NaHCO_3$, Na_2CO_3, CH_3COONa, Et_3N, and pyridine, where KOH provided a coupled product of 90% isolated yield. No reaction was observed in neat water, because of catalyst insolubility (Table 1, entry 1). This problem was circumvented by adding organic solvents to help dissolve the catalyst in the reaction media. A 80:20% mixture of H_2O-DMF was found to be most effective for the titled coupling reaction. A comparative catalytic study was carried out involving all the four catalysts towards the chosen SMC reaction. Catalysts **2** and **4** performed better than the other two which may be related to a napthyl unit in the coordinated pincer ligand. In particular catalyst **4** with a methoxy substituent in the salicylaldehyde part, is more effective than catalyst **2**, which is composed of non-substituted salicylaldehyde in its molecular architecture. The role of triphenylphosphine ligand in the catalysts **1**–**4** is to help in activating C–Cl bonds in quinolines.[19]

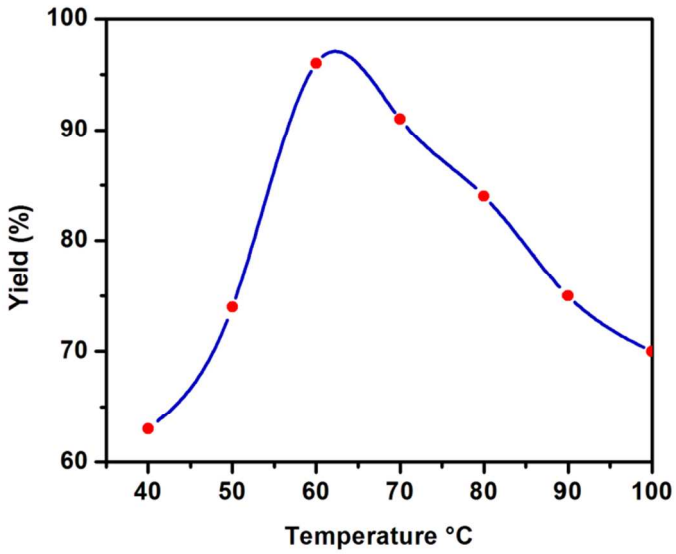


Figure 6. Effect of temperature on the SMC reaction.

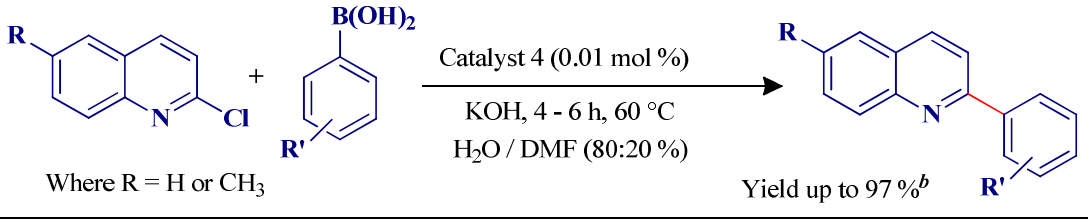
In addition, the effect of temperature on this coupling reaction was investigated by using 2-chloroquinoline (3 mmol), phenylboronic acid (4 mmol), KOH (5 mmol), catalyst **4** (0.01 mol %) in H_2O-DMF (80:20%) and the isolated yield of coupled products were illustrated in Figure 6. A distinct optimum was reached at 60 °C.

To further explore the scope and application of the reaction, we studied the reaction of various aryl boronic acids with 2-chloroquinoline derivatives under the optimized conditions mentioned above. Aryl boronic acids featuring an electron- donating group such as $–CH_3$, $–OCH_3$, $t–(CH_3)_3C–$, –OH, and $–NR_2$ furnished the reaction smoothly and afforded 65–92% of the coupled products over a period of 4–6 h (Table 2 entries 1c, 1f, 1k, 2c, 2f and 2k). Interestingly, sterically hindered aryl boronic acids afforded a 82–90% yield (Table 2 entries 1b, 1d, 1e, 1g, 1h, 1i, 2b, 2d, 2e, 2g, 2h and 2i). Similarly, boronic acids bearing moderate electron with drawing groups such as Br and $–COCH_3$ efficiently underwent the coupling reaction, to afford the products in 74–90% (Table 2 entries 1j, 1l, 2j and 2l). Not even a trace of neither homocoupling of aryl boronic acids nor coupling with –OH and –Br groups of the substrates were observed (Table 2, entry 1g, 1j, 2g, and 2j). This offers an opportunity to conduct further cross-coupling reactions by exploiting the halogenated positions available on selective boronic acids (Table 2, entry 1j and 2j).

Catalyst loading tests of complex **4** revealed best performance for 0.01 mol%. Reducing catalyst stacking from 0.01–0.0001 mol% under optimized conditions resulted in low yield as reported earlier.[20] On the other hand, use of 0.0001 mol% catalyst resulted in high turnover number (Table 3).

Reusability of the selected catalyst **4**, 0.01 mol% was screened and the trend of the isolated yield is summarized in Figure 7. A 20 mL round bottom flask was charged with 2-chloroquinoline (3.0 mmol) and phenylboronic acid (4 mmol), KOH (5 mmol) in H_2O-DMF (80:20%). To this reaction mixture was added catalyst **4** (0.01 mol%) and heated to 60 °C. After completion of the reaction, the mixture was extracted with ethyl acetate and the organic layer was subjected to column chromatography to separate the catalyst and product using silica gel and petroleum ether/ ethyl acetate (90/10%) as an eluent. The recovered catalyst was washed with distilled water, dried and utilized for the next cycle under same reaction conditions. The identity of the recovered catalyst was confirmed by R_f value (0.54) and melting point of the original catalyst 219-221 °C. The first cycle afforded 96% of the corresponding coupled product, but yield decreased steadily in subsequent cycles (Figure 7).

Table 2. SMC reaction of 2-chloroquinolines with substituted phenylboronic acids using complex **4** as catalyst[a]



Where R = H or CH_3

Yield up to 97 %[b]

1a 4 h, **96%** TON = 9600 TOF = 2400	1b 5 h, **84%** TON = 8400 TOF = 1680	1c 5 h, **90%** TON = 9000 TOF = 1800	1d 6 h, **82%** TON = 8200 TOF = 1366
1e 5 h, **89%** TON = 8900 TOF = 1780	1f 6 h, **81%** TON = 8100 TOF = 1350	1g 6 h, **90%** TON = 9000 TOF = 1500	1h 6 h, **79%** TON = 7900 TOF = 1316
1i 6 h, **80%** TON = 8000 TOF = 1333	1j 5 h, **87%** TON = 8700 TOF = 1740	1k 6h, **65%** TON = 6500 TOF = 1083	1l 5 h, **74%** TON = 7400 TOF = 1480
2a 4 h, **97%** TON = 9700 TOF = 2425	2b 5 h, **87%** TON = 8700 TOF = 1740	2c 5 h, **92%** TON = 9200 TOF = 1840	2d 6 h, **86%** TON = 8600 TOF = 1433
2e 5 h, **90%** TON = 9000 TOF = 1800	2f 6 h, **82%** TON = 8200 TOF = 1366	2g 5 h, **91%** TON = 9100 TOF = 1820	2h 6 h, **83%** TON = 8300 TOF = 1383
2i 5 h, **89%** TON = 8900 TOF = 1780	2j 5 h, **90%** TON = 9000 TOF = 1800	2k 6h, **69%** TON = 6900 TOF = 1150	2l 6 h, **78%** TON = 7800 TOF = 1300

[a]=Reaction conditions: 2-chloroquinoline or 6-methyl-2-chloroquinoline (3.0 mmol), aryl boronic acid (4.0 mmol), 0.01 mol % of complex **4**, KOH (5.0 mmol), H_2O (4 mL), and DMF (1 mL) stirred for 4–6 h at 60 °C.

[b]=Isolated yield after column chromatography, TON =Turnover number = ratio of moles of product formed to moles of catalyst used, TOF = Turnover frequency = TON/h.

Table 3. Low catalyst loading on SMC reaction

Entry	Mol %	Isolated yield %	TON
1	0.01	96	9,600
2	0.001	92	92,000
3	0.0001	85	850,000

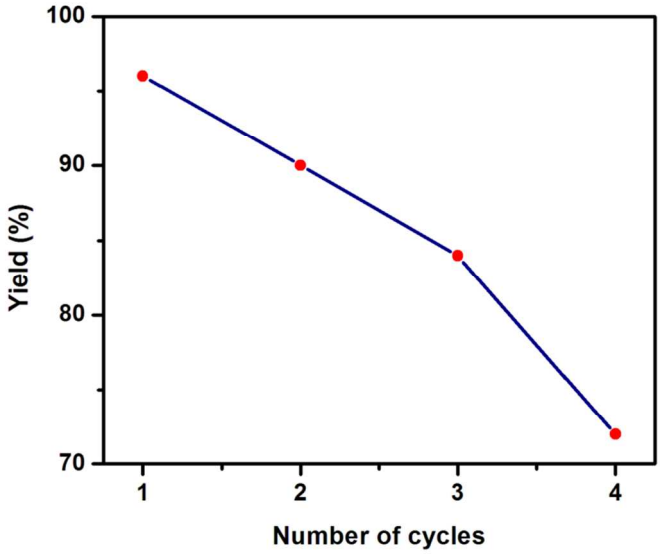


Figure 7. Reusability of catalyst **4**

Very recently, P. T. Perumal *et al*[21] reported a $SnCl_2.2H_2O$ mediated synthesis of 2–substituted quinolines in ethanol via A^3- coupling followed by reductive cyclization in 89% yield. Advantageously, we herein demonstrated that SMC of aryl boronic acids with 2-chloroquinolines

catalyzed by new ONO pincer type palladium(II) complex led to similar 2-arylquinolines in an excellent yield up to 97% in H_2O-DMF over a period of 4–6 h with low catalyst loading (0.01 mol %).

CONCLUSIONS

Herein, we portrayed the synthesis of four new palladium complexes bearing ONO pincer type ligands along with thorough characterization using IR, ^1H and ^{13}C NMR and single-crystal XRD techniques. These complexes showed strong performance in the Suzuki–Miyaura coupling reaction between 2-chloroquinoline scaffolds and aryl boronic acids with low catalyst loading in H_2O-DMF (80:20%) at moderate temperature. We feel that the present palladium catalyzed methodology offers a simple and straight forward route to synthesize a series of biologically important 2-arylquinolines possessing both activating and deactivating groups in excellent yields.

EXPERIMENTAL SECTION

All chemicals utilized for the synthesis of ligands and their complexes were obtained from Sigma-Aldrich, India. Solvents were purified and dried according to standard procedures.[22] Elemental analysis (C, H and N) was performed on a Vario EL III Elemental analyzer instrument. IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet Avatar Model FT-IR spectrophotometer. Melting points were determined with a Lab India instrument.^1H and ^{13}C NMR spectra were recorded in deuterated $CHCl_3$ as solvent on BRUKER 400 and 100 MHZ instruments, respectively.

Synthesis of ligands

Pincer type ligands H_3L were synthesized by condensing equimolar amounts of salicylaldheyde or 4-methoxy salicylaldheyde with salicylhydrazide (H_3L1 and H_3L3) or 3-hydroxy-2-naphthoic acid hydrazide (H_3L2 and H_3L34) in ethanol according to literature method (Scheme 1).The reaction mixture was then refluxed on a water-bath for 4 h and poured into crushed ice. The corresponding solid pincer type ligand formed was filtered, washed several times with distilled water and recrystallized from ethanol in 80–90% yield. The purity of the ligands were checked by various analytical techniques and is in accordance with literature reports.[23]

General method for the synthesis of the palladium complexes

To a warm methanolic solution (20–30 mL) of appropriate ligands (1 equiv.) were added a chloroform solution of $[PdCl_2(PPh_3)_2]$ (1 equiv.) followed by two drops of triethylamine. The reaction mixture was refluxed 6–7 h and kept at room temperature for crystallization. Needle like

reddish brown crystals suitable for X-ray studies were obtained on slow evaporation over 45–60 days.

[Pd(HL1)(PPh_3)] (complex **1)** Yield 71%. M.p. 207–210 °C. Elemental analysis (%) calculated for $C_{32}H_{25}N_2O_3PPd$; C, 61.70; H, 4.05; N, 4.50. Found (%); C, 61.68; H, 4.03; N, 4.46. UV-visible (solvent: DMSO, nm): 296, 313, 372, and 400. Selected IR bands (KBr, ν in cm^{-1}): 3322, 1596, 1494, and 1255. ^1H NMR ($CDCl_3$, δ ppm) 8.61 (s, 1H), 8.34 (d, J = 9.2 Hz, 2H), 8.20 (d, J = 8 Hz, 2H), 7.56 (t, J = 9.8 Hz, 2H), 7.42–7.48 (m, 9H), 7.31–7.41 (m, 4H), 7.28 (d, J = 6.8 Hz, 2H), 6.38 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm) 159.2, 151.5, 143.8, 141.55, 140.3, 137.7, 135.5, 133.7, 132.3, 131.4, 129.3, 128.1, 127.2, 126.5, 126.1, 125.4, 125.1, 124.8, 113.3, 110.0.

[Pd(HL2)(PPh_3)] (complex **2)** Yield 69%. M.p. 215–218 °C. Elemental analysis (%) calculated for $C_{36}H_{27}N_2O_3PPd$; C, 64.25; H, 4.04; N, 4.16. Found (%); C, 64.23; H, 4.02; N, 4.14. UV-visible (solvent: DMSO, nm): 298, 316, 371, and 400. Selected IR bands (KBr, ν in cm^{-1}): 3322,1593, 1472 and 1299. ^1H NMR ($CDCl_3$, δ ppm) 9.15 (s, 1H), 8.10 (s, 3H), 7.80–7.84 (m, 6H),7.57 (t, J = 7.8 Hz, 5H), 7.48 (t, J = 9.6 Hz, 7H), 7.31 (t, J = 2.6 Hz, 4H), 5.77 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm) 159.3, 151.6, 143.2, 141.7, 137.6, 132.7, 132.6, 132.0, 130.9, 128.5, 128.0, 127.4, 126.3, 126.1, 125.8, 125.1, 124.9, 123.5, 119.8, 114.3, 110.7.

[Pd(HL3)(PPh_3)] (complex **3)** Yield 76%. M.p. 212–214 °C. Elemental analysis (%) calculated for $C_{33}H_{27}N_2O_4PPd$; C, 60.70; H, 4.17; N, 4.29. Found (%); C, 60.68; H, 4.15; N, 4.26.UV-visible (solvent: DMSO, nm): 299, 316, 360, and 391. Selected IR bands (KBr, ν in cm^{-1}): 3416, 1597, 1488, and 1222. ^1H NMR ($CDCl_3$, δ ppm) 8.20 (s, 1H), 7.81 (d, J = 7.6 Hz, 4H), 7.53–7.56 (m, 3H), 7.48 (t, J = 9.8 Hz, 4H), 7.28–7.39(m, 8H), 6.98 (d, J = 8.4 Hz, 3H), 5.36 (s, 1H), 3.81 (s, 3H). ^{13}C NMR ($CDCl_3$, δ ppm) 159.2, 151.5, 143.6, 141.7, 139.4, 137.3, 133.5, 133.1, 132.3, 131.6, 129.4, 128.9, 128.5, 126.5, 126.4, 125.6, 125.3, 124.4, 123.0, 113.6, 110.7, 51.4.

Pd(HL4)(PPh_3)] (complex **4)** Yield 74%. M.p. 219–221 °C. Elemental analysis (%) calculated for $C_{37}H_{29}N_2O_4PPd$; C, 63.21; H, 4.16; N, 3.98. Found (%);C, 63.20; H, 4.14; N, 3.94. UV-visible (solvent: DMSO, nm): 291, 319, 372, and 401. Selected IR bands (KBr, ν in cm^{-1}): 3416, 1593, 1473, and 1303. ^1H NMR ($CDCl_3$, δ ppm) 9.39 (s, 1H), 8.09 (s, 5H), 7.96 (t, J = 11.6 Hz, 3H), 7.65 (t, J = 8.0 Hz, 4H), 7.59 (d, J = 8.0 Hz, 5H), 7.39–750 (m, 4H), 7.37 (d, J = 8.0 Hz, 3H), 5.40 (s, 1H), 3.42 (s, 3H). ^{13}C NMR ($CDCl_3$, δ ppm) 157.8, 148.5, 143.1, 141.9, 141.8, 136.1, 134.8, 131.1, 129.3, 128.6, 128.1, 127.5, 126.9, 126.5, 126.4, 125.5, 124.6, 123.1, 122.7, 118.6, 105.1, 55.2.

Single crystal X-ray diffraction studies

Data collection: single-crystal X-ray diffraction data of complexes 1–4 were collected on Bruker APEX II single crystal X-ray diffractometer. The data was integrated and scaled using SAINT / SADABS from within the APEX2 software package by Bruker (Version 2.1-4). Indexing and unit cell refinement indicated complex 1 is triclinic and all other complexes were primitive monoclinic, with space groups $P\bar{1}$, $P2_1/a$, $P2_1/c$ and $P2_1/c$, respectively. Solution by direct methods (SHELXS, SIR97)[24] produced complete heavy atom phasing models consistent with the proposed structures. The structures were completed by difference Fourier synthesis with SHELXL97.[25,26] Scattering factors are from Waasmair and Kirfel.[27] Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Angstrom. Isotropic thermal parameters Ueq were fixed such that they were 1.2Ueq of their parent atom Ueq for CH's and 1.5Ueq of their parent atom Ueq in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

Catalysis

General procedure for Suzuki-Miyaura C–C coupling reaction and recycling of the catalyst-4

A 20 mL round bottom flask was charged with 2-chloroquinoline (3 mmol), phenylboronic acid (4 mmol) and KOH (5 mmol) in H_2O-DMF (80:20%). Then, the catalyst **4** (0.01 mol %) was added to this mixture and stirred at 60 °C. The progress of the SMC reaction was monitored by thin layer chromatography (petroleum ether/ ethyl acetate (90-10%)) and the Rf value of the product was measured to be 0.61. After completion of the reaction, the mixture was solvent diluted with ethyl acetate and dried over anhydrous Na_2SO_4. Solvent was evaporated under vacuo and the residue was purified by column chromatography using petroleum ether/ EtOAc as eluent to afford 2-phenylquinoline as a pale yellow solid. The product was washed with distilled water to remove inorganic base. The identity of the product was confirmed by ^1H and ^{13}C NMR data.

NMR spectral data of coupled products as listed in Table 3.

^1H and ^{13}C NMR spectra were recorded in deuterated $CHCl_3$ and DMSO as solvent on BRUKER 400 and 100 MHZ instruments, respectively. The signals corresponding to various protons of the coupled products are assigned by comparison with reported data.[28]

Entry **1a:** 2-phenylquinoline: Elemental analysis (%) calculated for $C_{15}H_{11}N$; C, 87.77; H, 5.40; N, 6.82. Found (%); C, 87.72; H, 5.38; N, 6.81. ^1H NMR δ (ppm): 7.96 (d, J = 8 Hz, 2H), 7.85–7.91(m, 3H), 7.74 (d, J = 7.6 Hz, 1H), 7.32–7.37 (m, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.26 (d, J =

9.6 Hz, 1H) 7.16–7.18 (m, 1H). ^{13}C NMR: δ (ppm): 157.8, 149.1, 143.1, 140.9, 139.3, 133.7, 130.4, 129.5, 128.3, 128.1, 127.7.

Entry **1b:** 2-*o*-tolylquinoline: Elemental analysis (%) calculated for $C_{16}H_{13}N$; C, 87.64; H, 5.98; N, 6.39. Found (%); C, 87.61; H, 5.95; N, 6.38. ^{1}H NMR δ (ppm): 7.93 (d, *J* = 8 Hz, 1H), 7.81–7.86(m, 1H), 7.63(d, *J* = 7.2 Hz, 2H), 7.34–7.37 (m, 1H), 7.29–7.33 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR: δ (ppm): 156.7, 148.9, 143.2, 141.0, 139.5, 137.9, 130.3, 129.6, 129.0, 128.8, 128.5, 126.8, 126.6, 125.3, 125.2, 21.3.

Entry **1c:** 2-*p*-tolylquinoline: Elemental analysis (%) calculated for $C_{16}H_{13}N$; C, 87.64; H, 5.98; N, 6.39. Found (%); C, 87.62; H, 5.96; N, 6.37. ^{1}H NMR δ (ppm): 7.92 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8 Hz, 1H), 7.25–7.38 (m, 1H), 7.10–7.23 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 2.43 (s, 3H). ^{13}C NMR: δ (ppm): 158.2, 150.8, 144.2, 140.1, 138.8, 133.3, 130.2, 129.3, 127.9, 127.7, 125.4, 125.1, 124.9, 120.7, 21.6.

Entry **1d:** 2-(2,3-dimethyl-phenyl)-quinoline: Elemental analysis (%) calculated for $C_{17}H_{15}N$; C, 87.52; H, 6.48; N, 6.00. Found (%); C, 87.50; H, 6.46; N, 5.98. ^{1}H NMR δ (ppm): 8.05 (d, *J* = 9.2 Hz, 1H),7.91 (q, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8 Hz, 1H), 7.40–7.48 (m, 1H), 7.35–7.39 (m, 1H), 7.27–7.34 (m, 1H), 7.19–7.23 (m, 2H), 2.93 (s, 3H), 2.76 (s, 3H). ^{13}C NMR: δ (ppm): 156.8, 150.4, 142.0, 140.8, 139.1, 138.8, 133.7, 133.4, 130.3, 129.8, 128.9, 128.7, 128.2, 127.7, 125.5, 125.2, 24.4, 21.1.

Entry **1e:** 2-(2-methoxy-phenyl)-quinoline: Elemental analysis (%) calculated for $C_{16}H_{13}NO$; C, 81.68; H, 5.57; N, 5.95. Found (%); C, 81.67; H, 5.55; N, 5.93. ^{1}H NMR δ (ppm): 7.97 (d, *J* = 8.4 Hz, 1H), 7.82–7.88 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 6.2 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.30–7.38 (m, 1H), 7.10–7.19 (m, 1H), 2.90 (s, 3H). ^{13}C NMR: δ (ppm): 158.3, 150.9, 142.2, 140.1, 139.6, 128.8, 133.5, 131.8, 130.1, 129.2, 128.9, 128.5, 127.8, 127.7, 127.3, 51.4.

Entry **1f:** 2-(4-*tert*-butyl-phenyl)-quinoline: Elemental analysis (%) calculated for $C_{19}H_{19}N$; C, 87.31; H, 7.33; N, 5.36. Found (%); C, 87.30; H, 7.32; N, 5.34. ^{1}H NMR δ (ppm): 7.91 (s, 2H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 9.6 Hz, 1H), 7.31–7.21 (m, 2H), 7.0 (m, 1H), 1.55 (s, 9H). ^{13}C NMR: δ (ppm): 157.0, 148.8, 143.1, 141.4, 140.3, 137.4, 135.4, 129.5, 128.7, 128.2, 127.5, 126.8, 126.3, 125.9, 125.3, 124.1, 34.6, 29.6.

Entry **1g:** 3-quinolin-2-yl-phenol: Elemental analysis (%) calculated for $C_{15}H_{11}NO$; C, 81.43; H, 5.01; N, 6.33. Found (%); C, 81.42; H, 4.99; N, 6.29. ^{1}H NMR δ (ppm): 7.89–7.98 (m,1H), 7.87 (s, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 2.4, 2.4 Hz, 1H), 7.34 (t, *J* = 8 Hz, 3H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.10–7.21 (m, 1H), 7.08 (s, 1H). ^{13}C NMR: δ (ppm): 161.6, 159.1, 148.7, 143.9, 141.3, 140.5, 138.2, 134.7, 134.1, 129.7, 129.6, 128.3, 128.2, 127.0, 126.9, 125.1, 124.5.

Entry **1h:** 2-naphthalen-2-yl-quinoline: Elemental analysis (%) calculated for $C_{19}H_{13}N$; C, 89.38; H, 5.13; N, 5.49. Found (%); C, 89.35; H, 5.11; N, 5.45. ^{1}H NMR δ (ppm): 7.83–7.90 (m, 3H), 7.65 (d, *J* = 11.2 Hz, 1H), 7.50 (d, *J* = 2 Hz, 1H), 7.34 (dd, *J* = 1.6, 8 Hz, 1H), 7.25–7.30 (m, 1H), 7.24 (d, *J* = 1.6 Hz, 2H), 7.20 (t, *J* = 1.4 Hz, 3H), 7.10–7.19 (m, 1H). ^{13}C NMR: δ (ppm): 155.0, 148.8, 141.1, 140.4, 140.2, 139.5, 136.3, 133.8, 130.3, 129.9, 128.8, 128.6, 128.5, 127.7, 126.5, 125.4, 124.5, 124.0, 119.8, 118.9.

Entry **1i:** 2-biphenyl-4-yl-quinoline: Elemental analysis (%) calculated for $C_{21}H_{15}N$; C, 89.65; H, 5.37; N, 4.98. Found (%); C, 89.62; H, 5.34; N, 4.95. ^{1}H NMR δ (ppm): 7.91–7.94 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 12 Hz, 1H), 7.31–7.37 (m, 3H) 7.28 (d, *J* = 2.8 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 3H), 6.99 (d, *J* = 8 Hz, 2H). ^{13}C NMR: δ (ppm): 155.0, 147.9, 143.0, 142.7, 139.6, 137.1, 137.0, 129.3, 129.0, 127.9, 126.8, 125.8, 125.1, 119.5, 116.7.

Entry **1j:** 2-(4-bromo-phenyl)-quinoline: Elemental analysis (%) calculated for $C_{15}H_{10}BrN$; C, 63.40; H, 3.55; N, 4.93. Found (%); C, 63.38; H, 3.54; N, 4.91. ^{1}H NMR δ (ppm): 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 10.4 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.20–7.23 (m, 2H) 7.07–7.19 (m, 2H), 6.94 (s, 2H). ^{13}C NMR: δ (ppm): 157.0, 147.6, 142.6, 140.2, 139.2, 137.4, 135.9, 130.3, 128.5, 127.5, 126.1, 125.6, 124.3, 119.4, 116.5, 89.1.

Entry **1k:** dimethyl-(4-quinolin-2-yl-phenyl)-amine: Elemental analysis (%) calculated for $C_{17}H_{16}N_2$; C, 82.22; H, 6.49; N, 11.28. Found (%); C, 82.20; H, 6.47; N, 11.25. ^{1}H NMR δ (ppm): 7.96 (d, *J* = 8 Hz, 1H), 7.83–7.87 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.32–7.38 (m, 3H), 7.20–7.27 (m, 1H) 7.14 (d, *J* = 8.8 Hz, 2H), 2.83 (s, 6H). ^{13}C NMR: δ (ppm): 156.5, 149.1, 143.4, 141.5, 141.3, 138.2, 133.5, 131.0, 130.2, 128.4, 128.1, 127.5, 127.1, 126.6, 125.5, 125.3, 124.3, 122.6, 37.8.

Entry **1l:** 1-(4-quinolin-2-yl-phenyl)-ethanone: Elemental analysis (%) calculated for $C_{17}H_{13}NO$; C, 82.57; H, 5.30; N, 5.66. Found (%); C, 82.56; H, 5.27; N, 5.65. ^{1}H NMR δ (ppm): 7.91 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 8 Hz, 1H), 7.30–7.37 (m, 1H), 7.25 (d, *J* = 5.6 Hz, 1H), 7.14–7.20 (m, 1H), 6.95 (d, *J* = 12.4 Hz, 2H), 2.92 (s, 3H). ^{13}C NMR: δ (ppm): 169.6, 159.3, 143.9, 143.5, 141.7, 141.1, 138.0, 134.1, 134.0, 132.8, 130.3, 128.5, 128.3, 127.7, 127.5, 126.1, 29.0.

Entry **2a:** 6-methyl-2-phenyl-quinoline: Elemental analysis (%) calculated for $C_{16}H_{13}N$; C, 87.64; H, 5.98; N, 6.39. Found (%); C, 87.61; H, 5.95; N, 6.37. ^{1}H NMR δ (ppm): 7.82 (s, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 2 Hz, 2H), 7.57 (t, *J* = 2 Hz, 1H), 7.49–7.55 (m, 3H), 7.37–7.48 (m, 1H), 2.49 (s, 3H). ^{13}C NMR: δ (ppm): 161.2, 148.1, 147.2, 135.7, 135.3, 129.4, 128.3, 128.1, 127.1, 126.4, 123.1, 122.0, 29.0.

Entry **2b:** 6-methyl-2-*o*-tolyl-quinoline: Elemental analysis (%) calculated for $C_{17}H_{15}N$; C, 87.52; H, 6.48; N, 6.00. Found (%); C, 87.50; H, 6.45; N, 5.98. ^{1}H NMR δ (ppm): 8.50 (s, 1H), 7.93–8.10 (m, 5H), 7.66 (d, *J* = 2 Hz, 2H), 7.50–7.57 (m, 1H), 3.35 (s, 3H) 2.51 (s, 3H). ^{13}C NMR: δ (ppm): 160.3, 147.7, 147.4, 135.5, 134.9, 131.9, 128.3, 127.9, 126.9, 122.7, 121.9, 120.9, 120.1, 26.9, 19.8.

Entry **2c:** 6-methyl-2-*p*-tolyl-quinoline: Elemental analysis (%) calculated for $C_{17}H_{15}N$; C, 87.52; H, 6.48; N, 6.00. Found (%); C, 87.50; H, 6.45; N, 5.97. ^{1}H NMR δ (ppm): 8.17 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 2H), 3.66 (s, 3H), 2.56 (s, 3H). ^{13}C NMR: δ (ppm): 160.2, 147.9, 147.7, 136.0, 135.2, 133.1, 129.2, 128.6, 128.1, 127.0, 124.2, 121.8, 121.2, 121.1, 112.8, 21.9, 19.4.

Entry **2d:** 2-(2,3-dimethyl-phenyl)-6-methyl-quinoline: Elemental analysis (%) calculated for $C_{18}H_{17}N$; C, 87.41; H, 6.93; N, 5.66. Found (%); C, 87.39; H, 6.91; N, 5.62. ^{1}H NMR δ (ppm): 8.20 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.43–7.46 (m, 2H), 3.96 (s, 3H), 3.91 (s, 3H), 2.50 (s, 3H). ^{13}C NMR: δ (ppm): 160.4, 147.9, 135.6, 134.2, 128.3, 128.0, 127.4, 127.0, 122.9, 122.0, 119.5, 119.4, 111.8, 106.3, 26.8, 19.5, 16.2.

Entry **2e:** 2-(2-methoxy-phenyl)-6-methyl-quinoline: Elemental analysis (%) calculated for $C_{17}H_{15}NO$; C, 81.90; H, 6.06; N, 5.62. Found (%); C, 81.88; H, 6.04; N, 5.59. ^{1}H NMR δ (ppm): 8.71 (s, 1H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.74–7.46 (m, 1H), 7.20–7.26 (m, 1H) 2.71 (s, 3H), 1.83 (s, 3H). ^{13}C NMR: δ (ppm): 160.4, 149.5, 146.4, 135.8, 134.4, 131.1, 129.4, 129.1, 128.8, 128.4, 128.2, 127.9, 127.4, 125.8, 12.9, 120.8, 119.5, 119.4, 111.1, 53.5, 25.1

Entry **2f:** 2-(4-*tert*-butyl-phenyl)-6-methyl-quinoline: Elemental analysis (%) calculated for $C_{20}H_{21}N$; C, 87.23; H, 7.69; N, 5.09. Found (%); C, 87.21; H, 7.66; N, 5.07. ^{1}H NMR δ (ppm): 8.24 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.39 (d, *J* = 3.6 Hz, 2H), 7.61 (t, *J* = 6.4 Hz, 1H), 7.40–7.49 (m, 2H), 7.26–7.38 (m, 1H), 2.35 (s, 3H), 1.49 (s, 9H). ^{13}C NMR: δ (ppm):161.4, 147.4, 143.9, 139.7, 137.7, 136.5, 131.6, 130.8, 129.3, 129.1, 128.6, 128.3, 127.9, 127.7, 127.5, 126.8, 126.7, 125.3, 123.1, 120.8, 120.4, 119.1, 110.7, 106.5, 31.6, 32.4, 23.4.

Entry **2g:** 3-(6-methyl-quinolin-2-yl)-phenol: Elemental analysis (%) calculated for $C_{16}H_{13}NO$; C, 81.68; H, 5.57; N, 5.95. Found (%); C, 81.65; H, 5.54 N, 5.92. ^{1}H NMR δ (ppm): 8.26 (s, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.68 (t, *J* = 12.4 Hz, 1H), 7.58–7.62 (m, 1H), 7.50–7.56 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 11.6 Hz, 1H), 7.37 (s, 1H), 5.31 (s, 1H), 2.50 (s, 3H). ^{13}C NMR: δ (ppm): 158.9, 149.5, 147.1, 138.1, 135.3, 130.1, 129.6, 126.6, 126.3, 123.6, 123.1, 120.7, 119.4, 118.5, 112.8, 25.8.

Entry **2h:** 6-methyl-2-naphthalen-2-yl-quinoline: Elemental analysis (%) calculated for $C_{20}H_{15}N$; C, 89.19; H, 5.61; N, 5.20. Found (%); C, 89.17; H, 5.59; N, 5.18. ^{1}H NMR δ (ppm): 8.20 (s, 1H), 7.95 (d, *J* = 6.4 Hz, 4H), 7.59 (d, *J* = 6 Hz, 1H), 7.50 (d, *J* = 2 Hz, 1H), 7.46 (t, *J* = 6 Hz, 2H), 7.42–7.46 (m, 1H), 7.30-7.40 (m, 1H), 2.64 (s, 3H). ^{13}C NMR: δ (ppm): 160.4, 147.8, 147.6, 136.3, 135.9, 133.6, 129.3, 127.9, 127.7, 127.0, 125.7, 121.6, 121.3, 121.0,111.9, 23.1.

Entry **2i:** 2-biphenyl-4-yl-6-methyl-quinoline: Elemental analysis (%) calculated for $C_{22}H_{17}N$; C, 89.46; H, 5.80; N, 4.74. Found (%); C, 89.45; H, 5.78; N, 4.71. ^{1}H NMR δ (ppm): 8.07 (s, 2H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.76 (t, *J* = 9 Hz, 1H), 7.68 (d, *J* = 6.4 Hz, 3H), 7.64 (d, *J* = 5.6 Hz, 1H), 7.43 (t, *J* = 9 Hz, 2H), 7.21–7.37 (m, 1H), 2.50 (s, 3H). ^{13}C NMR: δ (ppm): 160.9, 147.9, 146.8, 135.2, 133.9, 128.6, 127.8, 127.3, 126.4, 123.2, 122.0, 120.2, 119.4, 117.4, 109.9, 108.3, 31.1.

Entry **2j:** 2-(4-bromo-phenyl)-6-methyl-quinoline: Elemental analysis (%) calculated for $C_{16}H_{12}BrN$; C, 64.45; H, 4.06; N, 4.70. Found (%); C, 64.41; H, 4.03; N, 4.68. ^{1}H NMR δ (ppm): 7.71 (d, *J* = 7.6 Hz, 2H), 7.60 (s, 1H), 7.41–7.52 (m, 2H), 7.38 (t, *J* = 3 Hz, 1H), 7.31 (s, 2H), 7.21–7.28 (m, 1H), 2.35 (s, 3H). ^{13}C NMR: δ (ppm): 152.7, 141.1, 136.8, 130.9, 128.5, 124.8, 124.1, 123.2, 122.4, 119.1, 117.0, 116.4, 26.4.

Entry **2k:** dimethyl-[4-(6-methyl-quinolin-2-yl)-phenyl]-amine: Elemental analysis (%) calculated for $C_{18}H_{18}N_2$; C, 82.41; H, 6.92; N, 10.68. Found (%); C, 82.39; H, 6.89; N, 10.66. ^{1}H NMR δ (ppm): 7.79 (d, *J* = 12.8 Hz, 2H), 7.51 (t, *J* = 12.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 6.8 Hz, 1H), 7.29–7.34 (m, 2H), 6.92–7.15 (m, 1H), 2.96m (s, 6H), 2.34 (s, 3H). ^{13}C NMR: δ (ppm): 158.3, 141.9, 137.0, 133.5, 130.8, 128.2, 123.2, 122.4, 120.8, 119.8, 118.7, 115.4, 36.7, 29.4.

Entry **2l:** 1-[4-(6-methyl-quinolin-2-yl)-phenyl]-ethanone: Elemental analysis (%) calculated for $C_{18}H_{15}NO$; C, 82.73; H, 5.79; N, 5.36. Found (%); C, 82.71; H, 5.76; N, 5.32. ^{1}H NMR δ (ppm): 8.01 (d, *J* = 11.2 Hz, 2H), 7.96 (d, *J* = 12.2 Hz, 2H), 7.74 (d, *J* = 14.4 Hz, 2H), 7.52 (t, *J* = 10.4 Hz, 2H), 7.30–7.43 (m, 1H), 3.31 (s, 3H), 2.84 (s, 3H). ^{13}C NMR: δ (ppm): 170.9, 158.3, 140.5, 136.7, 135.4, 133.1, 129.0, 128.8, 125.6, 124.6, 124.1, 123.7, 121.0, 114.8, 29.3, 24.2.

ACKNOWLEDGMENT

Mr. Vignesh Arumugam thanks the University Grants Commission (UGC), New Delhi, India, for the award of Junior Research Fellowship (JRF) under UGC-BSR RFSMS.

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