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FULL PAPER

# Cp*Rh(III)-Catalyzed Sterically Controlled C(sp$^3$)-H Selective Mono- and Diarylation of 8-Methylquinolines with Organoborons

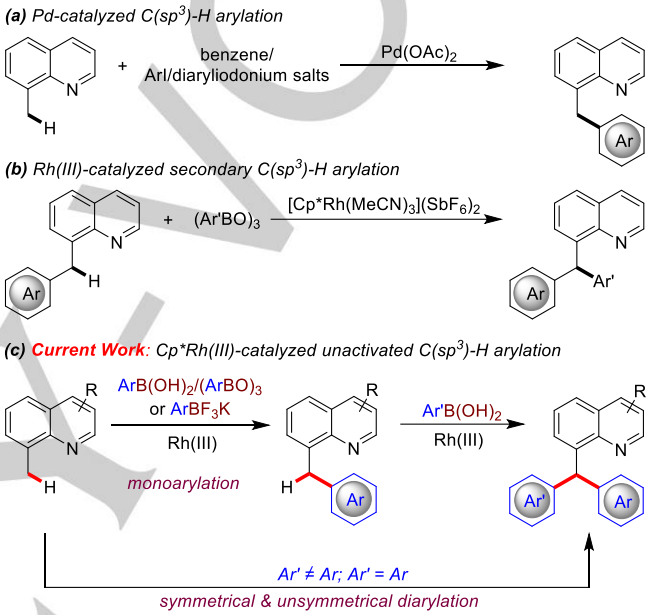
Rakesh Kumar,[a] Diksha Parmar,[a] Shiv Shankar Gupta,[a] Devesh Chandra,[a] Ankit Kumar Dhiman[a] and Upendra Sharma*[a]

**Abstract:** Herein Rh(III)-catalyzed selective mono-arylation and diarylation (symmetrical and unsymmetrical) of 8-methylquinolines with organoboron reagents is disclosed. The selective monoarylation of primary C(sp$^3$)-H bond is achieved by using the 7-substituted 8-methylquinolines or by changing the quantity of aryl boronic acids. The method is also applicable for the arylation of 2-ethylpyridine, and heteroarylation with thiophene-2-ylboronic acid. Symmetrical and unsymmetrical diarylation of 8-methylquinolines has been carried out in one-pot and sequential manner, respectively. Late-stage mono-arylation of oxime derivative and gram-scale synthesis of mono-arylated product has also been carried out. The mechanistic study revealed that the current reaction is first order with respect to both reactants and a five-membered rhodacycle intermediate may be involved in the catalytic cycle.

## Introduction

TM-catalyzed C-H bond activation leading to C-C bond construction has been largely applied for the synthesis of various natural products and other organic molecules, because of its notable potential in terms of step-economy and chemoselectivity.[1] In the past two decades, tremendous efforts have been made for the C(sp$^2$)-H bond functionalization using Rh(III)-catalyst due to its high efficiency and selectivity.[2] Although Rh(III)-catalyst has been explored widely for the functionalization of C(sp$^2$)-H bond,[3] it's application in less reactive C(sp$^3$)-H bond activation is still at its initial stage of development.[4] Recently, efforts have been made for Rh(III)-catalyzed alkylation,[5] alkenylation,[6] amination,[7] acylation,[8] aminocarbonylation,[9] borylation,[10] and arylation[11] of the C(sp$^3$)-H bonds, particularly of the 8-methylquinolines owing to the easy formation of the five-membered rhodacycle intermediate.

The C(sp$^3$)-arylation has great significance for the construction of important bioactive molecules[12] and the early examples mostly include the Pd-catalyzed arylation of primary C(sp$^3$)-H bond with diaryliodonium salts, aryl halides and benzene (Scheme 1a).[13] Although, the organoboron reagents have been utilized for the C(sp$^2$)-H functionalization of heterocyclic compounds,[14] their use in Rh(III)-catalyzed construction of the C(sp$^3$)-C(sp$^2$) bonds is limited.[15] Homocoupling of organoboron reagents always remains a challenge mainly in C(sp$^3$)-H bond functionalization. In a recent report, the Rh(II)/*N*-Heterocyclic Carbene-catalyzed diarylation of the 8-methylquinoline with bromobenzene has been disclosed by Chang group.[16] Similarly, Glorius group also reported the Rh(III)-catalyzed arylation of 2-alkylpyridines and diarylmethanes with triarylboroxine (Scheme 1b).[11a] However, these methods are either not applied or not applicable for the selective mono-arylation of 8-methylquinolines as the mixture of mono and diarylated products were obtained in the case of 2-ethylpyridines. During the compilation of current work, Ghosh *et. al* reported the Rh-catalyzed C(sp$^3$)-H activation of 8-methyl quinolines followed by functionalization with diazo compounds but this method is only applicable for the introduction of naphthol/phenol moieties.[17]




**Scheme 1.** TM-Catalyzed C(sp$^3$)-H Arylation

In continuation of our interest in C(sp$^3$)-H bond activation/functionalization of 8-methylquinolines[18] herein, we unveiled the first Rh(III)-catalyzed highly selective mono-arylation of the 8-methylquinolines with bench stable arylboronic acids. The chemoselectivity is sterically controlled in case of C7-substituted-8-methylquinolines whereas, in the case of 8-methylquinolines without C7-substituent, the mono- or symmetrical di-arylation is achieved by controlling the amount of arylboronic acids. Additionally, the current method is also applicable for the selective unsymmetrical diarylation of 8-methyl quinolines (Scheme 1c).

## Results and Discussion

Initially, 7-chloro-8-methyl quinoline (**1a**) was reacted with 4-amylphenylboronic acid (**2a,** 2 equiv) using $[RhCp^*Cl_2]_2$/$AgSbF_6$, $Ag_2CO_3$ and DCE at 100 °C for 24 h to get the product (**3a**) in 37% yield (Table 1, entry 2). Different additives were screened and yield increases to 52% with $Cu(OTf)_2$ (Table 1, entry 3). Eliminating $AgSbF_6$ and using only $Cu(OTf)_2$ as an additive also gave the product (**3a**) in 53% yield (Table 1, entry 4). Further, optimization of reaction conditions afforded product (**3a**) in 62% yield with AgOTf (10 mol%) as an additive and **2a** (2.5 equiv) (Table 1, entry 5). Moreover, using triflic anhydride (10 mol%) as an additive and **2a** (2.5 equiv) afforded **3a** in 76% yield (Table 1, entry 1). The solvent screening revealed that DCE gave the highest yield of the desired product (Table 1, entries 1, 6-8). Using $Ag_2CO_3$, $MnO_2$ or CuO as an oxidant instead of $Ag_2O$ did not

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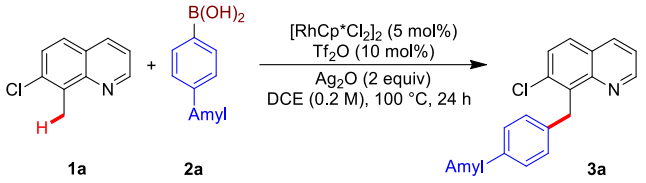
prove fruitful (Table 1, entry 9, 14-15). Control reactions without triflic anhydride or $Ag_2O$ provided traces of product (Table 1, entries 10-11). The lower yield of the product was obtained at room temperature (Table 1, entries 12). Replacing $[RhCp^*Cl_2]_2$ with Co-catalyst not proved fruitful for current arylation reaction (Table 1, entries 13). After detailed optimization (Table S1),[19] the reaction conditions were finalized, and the reaction of 7-chloro-8-methyl quinoline (**1**, 0.1 mmol) with 4-amylphenylboronic acid (**2a**, 0.25 mmol) using $[RhCp^*Cl_2]_2$ (5 mol%), $Tf_2O$ (10 mol%), $Ag_2O$ (2 equiv) in DCE (0.2 M) at 100 °C for 24 h under inert atmosphere afforded 68% of the isolated product (Table 1, entry 1).

**Table 1.** Optimization study[a]



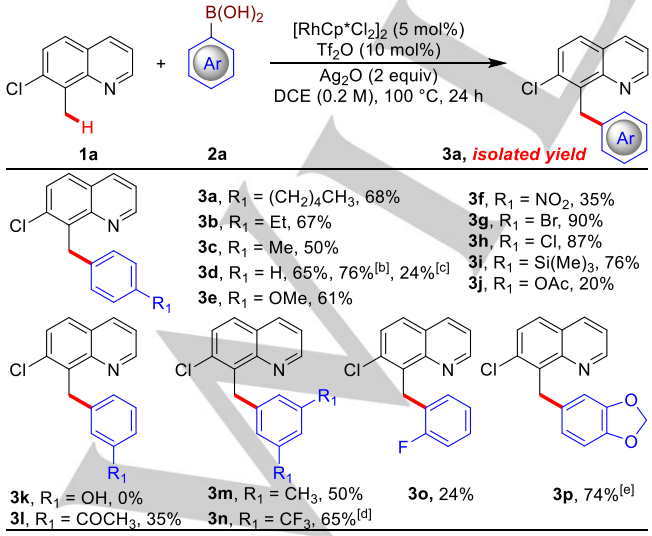

1a 2a 3a

| Sr. No. | variation from Standard Condition | yield (%)[b] |
|---|---|---|
| 1[d] | - | 76 (68)[c] |
| 2[e] | $AgSbF_6$ in place of $Tf_2O$ | 37 |
| 3[e,f] | $AgSbF_6$ + $Cu(OTf)_2$ in place of $Tf_2O$ | 52 |
| 4[f] | $Cu(OTf)_2$ in place of $Tf_2O$ | 53 |
| 5[d,g] | AgOTf in place of $Tf_2O$ | 62 |
| 6 | DME in place of DCE | 54 |
| 7 | TFE in place of DCE | 36 |
| 8 | 1,4 dioxane in place of DCE | 35 |
| 9 | $Ag_2CO_3$ in place of $Ag_2O$ | 56 |
| 10 | Without $Tf_2O$ | <5 |
| 11 | Without $Ag_2O$ | <5 |
| 12 | At rt | 56 |
| 13 | $CoCp^*COI_2$/ AgOTf | nd |
| 14 | $MnO_2$ instead of $Ag_2O$ | 10 |
| 15 | CuO instead of $Ag_2O$ | nd |

[a] reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), inert atmosphere. [b] Yield based on NMR analysis of crude reaction mixture using tetrachloroethane as an internal standard. [c] Isolated yield in parentheses, [d] 2.5 equiv of **2,** [e] $AgSbF_6$ (20 mol%), [f] $Cu(OTf)_2$ (20 mol%), [g] AgOTf (10 mol%). nd: not detected.

After having the optimized conditions in hand, the substrate scope was examined by reacting different phenylboronic acids with **1a** (Table 2).

**Table 2.** Substrate scope with arylboronic acids[a]

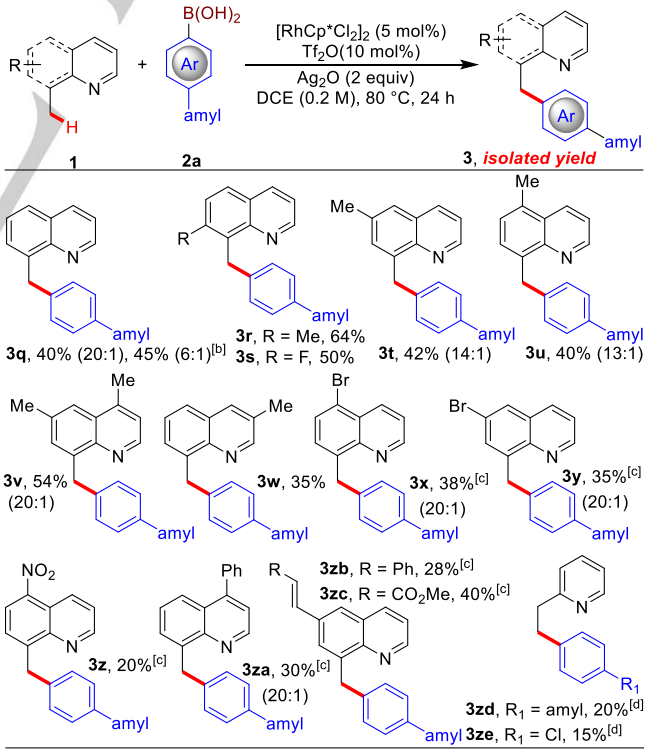



[a] reaction conditions: **1** (0.30 mmol), **2** (0.75 mmol), [RhCp*Cl2] (5 mol%), $Tf_2O$ (10 mol%), $Ag_2O$ (2 equiv), DCE (0.2 M), 100 °C, 24 h, under inert atmosphere. [b] $(PhBO)_3$ as arylating source. [c] $PhBF_3^-K^+$ as arylating source. [d] **2n** (1.2 equiv) at 80 °C. [e] Use of AgOTf instead of $Tf_2O$.

Various *para*-substituted phenylboronic acids with electron-withdrawing and electron-donating groups gave the desired monoarylated products in moderate to excellent yields (Table 2, **3a**-**j**). Among them, the halogen-substituted phenylboronic acids provided the desired products in highest yields (Table 2, **3g**-**h**, 87-90%). However, only 20% yield of the product was observed with (4-acetoxyphenyl)boronic acid (Table 2, **3j**). Similarly, the *meta*-substituted phenylboronic acids also afforded the desired monoarylated product in 35-65% yields (Table 2, **3l**-**n**). The reaction of **1a** with 3,5-trifluoromethyl phenylboronic acid provided a mixture of mono and diarylated product under the developed reaction conditions. When the reaction was carried at 80°C with a decreased quantity of 3,5-trifluoromethyl phenylboronic acid (1.2 equiv), the only monoarylated product was obtained in 65% yield (**3n**). No product was obtained in the case of (3-hydroxyphenyl)boronic acid (**3k**). The *ortho*-substituted phenylboronic acid provided the desired product in low yield this may be due to the steric hindrance (**3o**). Benzo[*d*][1,3]dioxol-5-ylboronic acid also reacted successfully with **1a** to afford the desired monoarylated product in 74% yield (**3p**). Further, other arylation source such as triphenylboroxine and potassium phenyltrifluoroborate were also found compatible under the developed reaction conditions (Table 2, entry **3d**).

After studying the substrate scope concerning arylboronic acids, different 8-methyl quinoline derivatives were reacted with **2a** (Table 3). In contrast to 7-substituted 8-methyl quinoline, the reaction of 8-methylquinolines with 4-amylphenylboronic acid (**2a**) (2.5 equiv) at 100 ℃ provided the mixture of mono and diarylated product (6:1) in 45% yield (Table 3, entry **3q**). Complete selectivity for mono-arylation in the case of 7-substituted 8-methyl quinoline might be due to steric hindrance of the substituent at the C7 position (Table 2).

**Table 3.** Substrate scope with 8-methylquinolines[a]




[a] reaction conditions: **1** (0.30 mmol), **2** (0.60 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $Tf_2O$ (10 mol%), $Ag_2O$ (2 equiv), DCE (0.2 M), 80 °C, 24 h under inert atmosphere. [b] **2** (2.5 equiv) at 100 °C. [c] Use **2** (1.2 equiv). [d] Use of AgOTf instead of $Tf_2O$. In parenthesis ratio of mono and diarylated product.

To get selectively the mono-arylated product, the reaction conditions were optimized further and at 80 ℃ with 2.0 equiv of **2a**, the monoarylated product was obtained in 20:1 selectivity with

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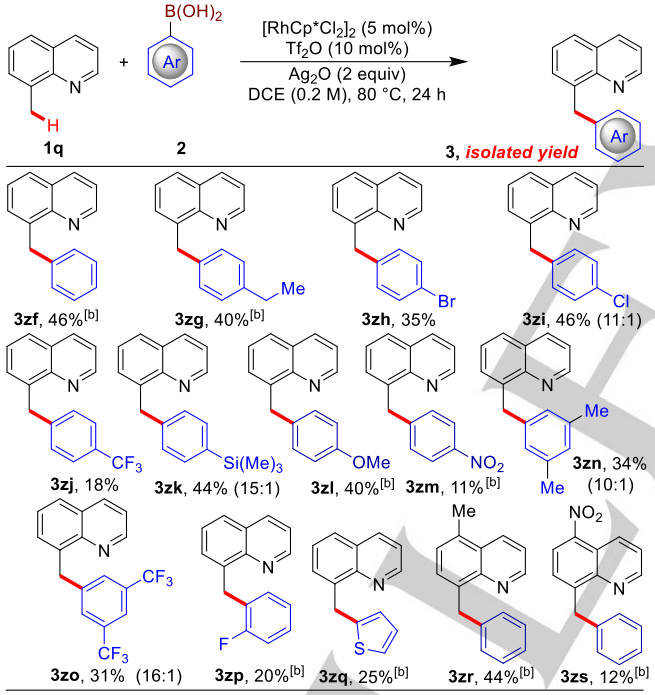
a minor decrease in yield (**3q**). Next, different substituted 8-methylquinolines were reacted with **2a** (2.0 equiv) at 80 ℃ of reaction temperature. Methyl substituent at C7, C6, C5, C4, and C3 position of 8-methylquinolines were well tolerated under the reoptimized condition and afforded the desired monoarylated products with high selectivity (**3r, 3t-v**, 40-64%, 13:1-20:1). The halogen-substituted 8-methylquinoline also afforded the monoarylated products in moderate yield (**3s**, **3x-y**). 5-Nitro-8-methylquinoline and 4-phenyl-8-methylquinoline also reacted successfully with **2a** and gave the desired monoarylated products in 20% and 40% yields, respectively (**3z** & **3za**). Further, olefin substituents at C6 of 8-methylquinolines also gave the products in good yields (**3zb-zc**). Other substrates such as 2-ethyl pyridine also found compatible under present reaction conditions affording the mono-arylated products with complete chemoselectivity albeit in low yields (**3zd-ze**).[11a]

Next, 8-methylquinoline (**1q**) was also reacted with different substituted phenylboronic acids (Table 4). Different functional groups at the *ortho*, *meta* or *para* position of phenylboronic acid were well tolerated and provided the desired mono-arylated products with high selectivity in moderate yields (**3ze-zp**). The reaction of 8-methylquinoline with thiophene-2-ylboronic acid also gave the product (**3zq**) in 25% yield. Further, the 5-substituted 8-methylquinolines with electronically different groups afforded the desired products (**3zr-3zs**) in moderate yield.

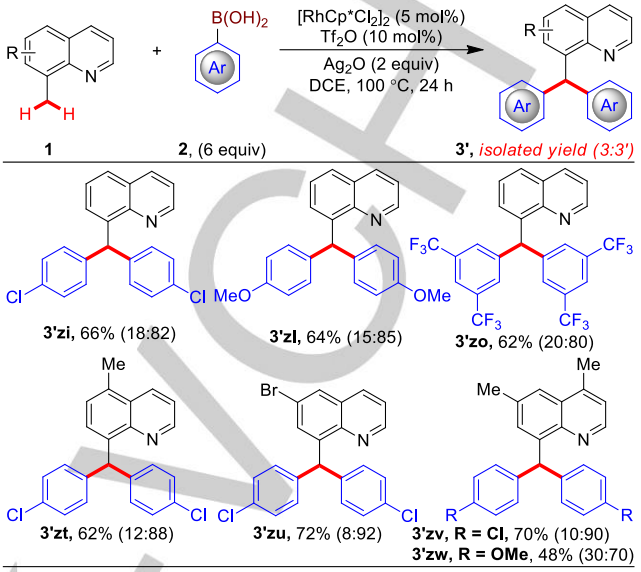
**Table 4.** Substrate scope with arylboronic acids[a]




[a] reaction conditions: **1q** (0.30 mmol), **2** (0.36 mmol), [RhCp*Cl$_2$]$_2$ (5 mol%), triflic anhydride (10 mol%), Ag$_2$O (2 equiv), DCE (0.2 M), 80 °C, 24 h under inert atmosphere. [b] **2** (2 equiv). In parenthesis ratio of mono and diarylated product.

Further to extend the scope of the current reaction, symmetrical as well as unsymmetrical double arylation of C(sp$^3$)-H bond of 8-methyquinoline was carried out (Table 5 and 6). Firstly, one-pot symmetrical double arylation was attempted (Table 5). We were pleased to note that the chemoselectivity can be switched towards the symmetrical diarylated product by reacting 8-methyl quinolines with an increased quantity of arylboronic acids (6 equiv) under same reaction conditions as applied for monoarylation (Table 5). Various *meta*- and *para*-substituted arylboronic acids were reacted with 8-methyl quinoline to afford diarylated products in good yield and chemoselectivity (**3'zi, 3'zl** & **3'zo**). Substituted 8-methylquinolines also reacted successfully to give the diarylated product along with the formation of the minor monoarylated product (**3'zt-3'zw**). The phenyboronic acids substituted at *para*-position with electron-donating groups and *meta*-position with electron-withdrawing groups favour the product formation.

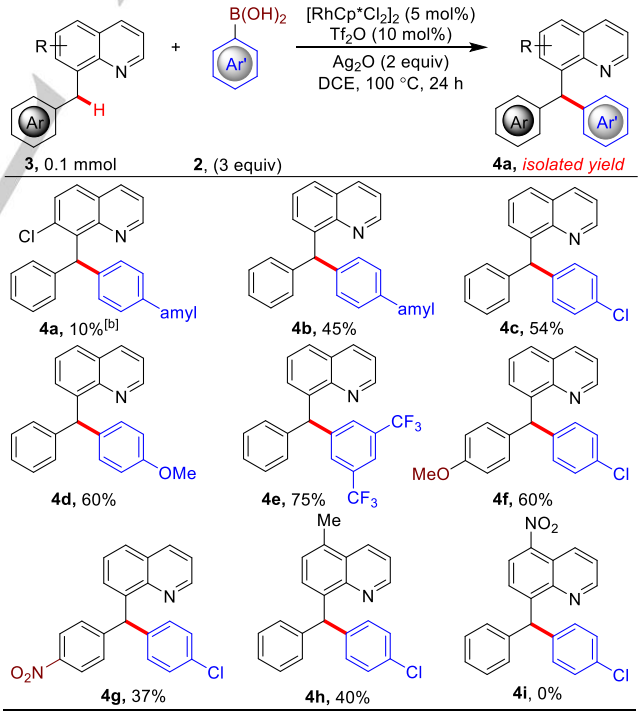
**Table 5.** Substrate scope for symmetrical diarylation[a]




[a] reaction conditions: **1** (0.30 mmol), **2** (1.80 mmol), [RhCp*Cl$_2$]$_2$ (5 mol%), Tf$_2$O (10 mol%), Ag$_2$O (2 equiv), DCE (0.2 M), 100 °C, 24 h under inert atmosphere.

The unsymmetrical diarylation was achieved by reacting mono-arylated products (**3**) with different arylboronic acids (3 equiv) (Table 6).

**Table 6.** Substrate scope for unsymmetrical diarylation[a]




[a] reaction conditions: **1** (0.30 mmol), **2** (0.9 mmol), [RhCp*Cl$_2$]$_2$ (5 mol%), Tf$_2$O (10 mol%), Ag$_2$O (2 equiv), DCE (0.2 M), 100 °C, 24 h under inert atmosphere. [b] NMR yield using TCE as an internal standard.

In the case of 7-substituted 8-methylquinolines very low yield of double arylated product (**4a**) was observed, which further confirmed that the high chemoselectivity for the monoarylation is sterically controlled. The unsymmetrical diarylated products (**4b-d**) were obtained in 45-60% yields when 8-benzylquinoline (**3zf**)

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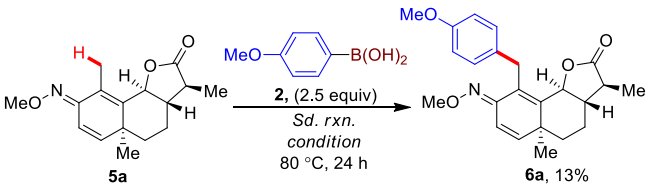
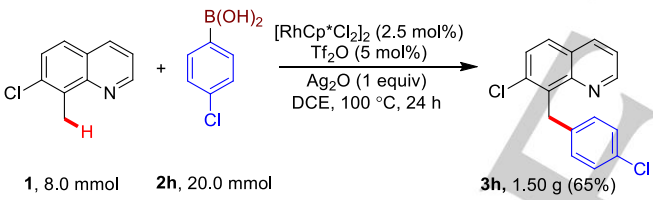
was reacted with 4-substituted phenylboronic acids (**2**) under the optimized reaction conditions. The 3,5-trifluoromethylphenylboronic acid was also well compatible under the developed reaction condition (**4e**). Further, the effect of the electronic nature of substituents on *para*-position of benzyl and 5-position of the quinoline ring of 8-benzylquinoline was studied. The reaction of 4-chlorophenylbornoic acid with 8-(4-methoxybenzyl)quinoline (**3zl**) afforded the diarylated product (**4f**) in higher yield whereas reaction with 8-(4-nitrobenzyl)quinoline (**3zm**) provided a lower yield (**4g**) as compared to **4c**. No reaction was observed in the case of 5-nitro-8-benzylquinoline (**4i**) whereas 5-methyl-8-benzylquinoline reacted successfully to afford 40% of the corresponding diarylated product (**4h**). These reactions indicated that electron-donating group on *para*-position of a benzyl ring and 5-position of quinoline ring of **3zf** favour the unsymmetrical diarylated product formation (**4**).

Furthermore, late-stage arylation of the oxime derivative of santonin (**5a**) was carried out with 4-methoxyphenylboronic acid (Scheme 2). Complete regioselectivity was observed for monoarylation with a very low yield of corresponding monoarylated product (**6a**).



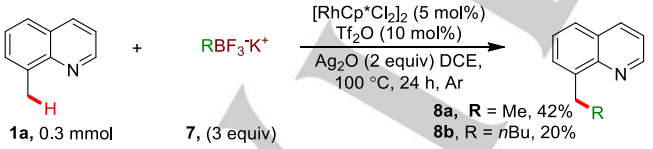

**Scheme 2.** Late-stage C($sp^3$)-H arylation

Subsequently, scalability of the developed protocol was demonstrated by synthesizing **3h** up to 1.50 g from reaction of **1a** with **2h** (Scheme 3).



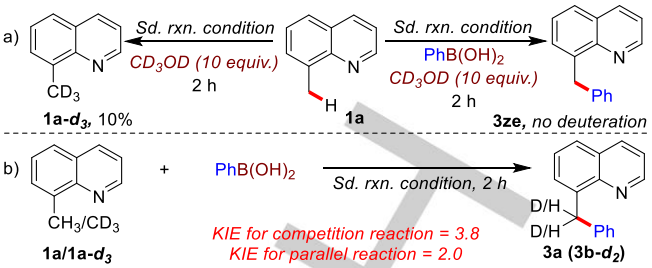

**Scheme 3.** Gram scale reaction

Current reaction conditions are also applicable for C($sp^3$)-alkylation of 8-methylquinoline (Scheme 4). The reaction of 8-methyl quinoline with $MeBF_3K$ and $nBuBF_3K$ salt provided the methylated and alkylated product (**8a-b**) in 42% and 20% yields, respectively (Scheme 4), while the aliphatic boronic acids failed to provide the desired products.



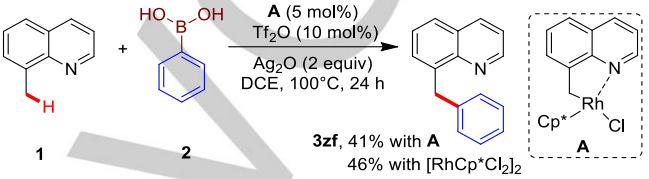

**Scheme 4:** Alkylation of primary C($sp^3$)-H bond.

Various experiments were carried out to understand the reaction mechanism (Scheme S1-S5).[19] Under arylation condition 10% *d*-incorporation was observed in the absence of phenylboronic acid (**2d**) whereas no *d*-incorporation was observed in the presence of **2d**, signifying that C-H activation step is slower than the subsequent steps (Scheme 5a). The C-H bond cleavage might be the rate-determining step as revealed by the KIE value for the competition and parallel experiments (Scheme 5b).




**Scheme 5**. Deuterium labelling experiments

Next, a five-membered rhodacycle (**A**) was synthesized[6d] and applied as a catalyst to afford 41% of the arylated product (Scheme 6). This experiment confirms that rhodacycle (**A**) is an intermediate in the catalytic cycle of the developed reaction.




**Scheme 6.** Intermediate study

Further, a kinetic study was also performed to demonstrate the order of the reaction by initial rate method at room temperature, which revealed an overall second-order reaction, first order with respect to 7-chloro-8-methylquinoline as well as 4-amylphenylboronic acid (Figure 1). Therefore, the rate of the monoarylation reaction depends upon the concentration of both the reactants.

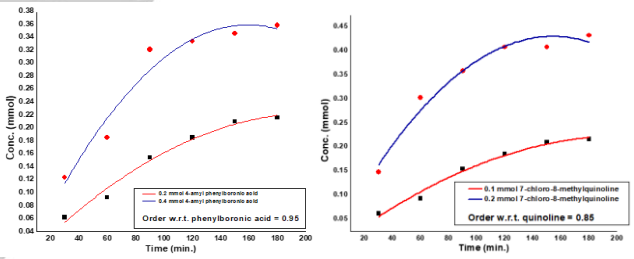
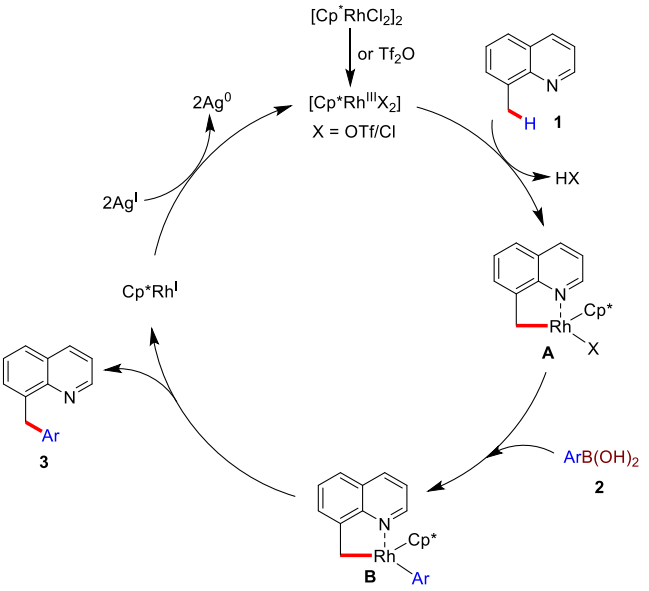



**Figure 1.** Kinetic study




**Scheme 7.** Plausible mechanistic cycle

A catalytic cycle was proposed on the basis of preliminary experiments and literature reports (Scheme 7).[11a] Initially, Rh(III)-precursor in the presence of $AgSbF_6$ or $AgOTf/Tf_2O$ is converted into active Rh-species which react with 8-methyquinoline to form rhodacycle **A**. Rhodacycle **A** undergo ligand exchange with aryl organoboron reagent to give **B** which on reductive elimination provided the desired arylated product along with Rh(I) species. Active catalytic species is regenerated from Rh(I) species in the presence of oxidant to continue the catalytic cycle.

## Conclusion

In summary, we have disclosed a Cp*Rh(III)-catalyzed regioselective and chemoselective C-H arylation of 8-methylquinolines with organoboron reagents through C($sp^3$)-H activation. In addition to the selective mono-functionalization, one-step symmetrical and two-step unsymmetrical diarylation of C($sp^3$)-H has also been carried out. Further, the developed method is also applicable for the arylation of oxime derivative and 2-ethylpyridine. The kinetic study revealed an overall second-order reaction for the monoarylation. The developed protocol is also applicable for the gram-scale synthesis of arylated products.

## Experimental Section

**Reagent information**. Unless otherwise stated, all reactions were carried out under inert atmosphere in screw cap reaction vials. Solvents were bought from Aldrich in sure-seal bottle and used as such. Chemicals were bought from Sigma Aldrich, Alfa-aesar and TCI. For column chromatography, silica gel (230-400 mesh) and C-18 reverse silica from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254).

**Analytical information**. The melting points were recorded on a Bronsted Electro thermal 9100. All isolated compounds are characterized by 1H NMR, 13C NMR, LC-MS and IR. In addition, all the compounds are further characterized by HRMS. Mass spectra were recorded on Water Q-ToF-Micro Micromass, high-resolution 6560 Ion Mobility Q-TOF LC/MS (Agilent, Santa Clara,USA) and maXis Impact mass spectrometers. Copies of 1H, 13C NMR can be found in the NMR supporting information. IR was analyzed by Shimadzu IR Prestige-21with ZnSe Single reflection ATR accessory. Nuclear magnetic resonance spectra were recorded either on a Bruker-Avance 600 or 300 MHz instrument. All 1H NMR experiments are reported in units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26) in the deuterated solvents. All 13C NMR spectra were reported in ppm relative to deuterated chloroform (77.16) and all were obtained with 1H decoupling. Optimization studies were done by NMR by using TCE as internal standard.

**Preparation of starting materials.** Substituted 8-methyl quinolines **1w**, **1zb** and **1zc** were synthesized according to the literature procedure,[20] compound **1r**, **1s**, **1t**, **1u, 1x, 1y** and **1z** were synthesized according to the literature procedure,[7a] compound **1za** was synthesized according to the literature procedure,[21] and all other substituted 8-methyl quinolines were used from commercially available sources. The compound **5a** was synthesized according to the literature procedure.[22]

**General procedure for the functionalization of 7-chloro-8-methyl quinolines with arylboronic acids and characterization data.** To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 7-chloro-8-methylquinoline (0.3 mmol), arylboronic acid (0.75 mmol), $[RhCp^*Cl_2]_2$ (5 mol %) and $Ag_2O$ (2.0 equiv) were added under argon atmosphere, followed by the addition of dichloroethane (1.5 mL) and triflic anhydride (10 mol%). The subsequent reaction mixture was stirred at 100 °C for 24 h. On completion of reaction, the solvent was evaporated under reduced pressure to get the crude reaction mixture. The crude mixture was purified by flash chromatography using silica gel (230−400 mesh size) and *n*-hexane: EtOAc as the eluent.

**Characterization Data** *7-chloro-8-(4-pentylbenzyl)quinoline (Table 2, Entry 3**a**)*. Yellow solid, yield = 66.1 mg (68%). Mp = 40-42 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.98-8.99 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.39-7.41 (m, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.84 (s, 2H), 2.50-2.53 (m, 2H), 1.53-1.58 (m, 2H), 1.27-1.31 (m, 4H), 0.86-0.88 (m, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 150.6, 147.8, 140.4, 137.7, 137.5, 136.2, 135.4, 128.9, 128.5, 128.3, 127.2, 127.1, 121.1, 35.7, 33.2, 31.7, 31.3, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2922, 2855, 2338, 1948, 1913, 1605, 1587, 1510, 1489, 1308, 1234, 1117, 1038, 1020, 928, 856, 827, 808, 795, 764, 602, 496. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{21}H_{23}ClN$, 324.1514; found 324.1510.

*7-chloro-8-(4-ethylbenzyl)quinoline (Table 2, Entry **3b**)*. Yellow liquid, yield = 56.6 mg (67%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ)*: 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.39 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 4.87 (s, 2H), 2.56-2.63 (m, 2H), 1.18-1.23 (m, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 150.6, 147.7, 141.7, 137.7, 137.6, 136.2, 135.4, 128.9, 128.4, 127.7, 127.19, 127.1, 121.1, 33.2, 28.5, 15.6. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2963, 2336, 1605, 1589, 1512, 1489, 1422, 1362, 1314, 1125, 1040, 953, 928, 851, 829, 808, 795, 660, 627, 602, 534, 473. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{17}ClN$, 282.1044; found 282.1041.

*7-chloro-8-(4-methylbenzyl)quinoline (Table 2, Entry 3**c**)*. Yellow solid, yield = 40.2 mg (50%). Mp = 73-76 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ)*: 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 2.26 (s, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 150.6, 147.7, 137.7, 137.3, 136.2, 135.4, 135.3, 129.0, 128.9, 128.5, 127.2, 127.1, 121.1, 33.2, 21.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2961, 2932, 2855, 2338, 1892, 1605, 1589, 1512, 1489, 1447, 1422, 1362, 1310, 1125, 1105, 1040, 976, 926, 851, 826, 808, 793, 750, 660, 627, 602, 519. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{15}ClN$, 268.0888; found 268.0881.

*8-benzyl-7-chloroquinoline (Table 2, Entry **3d**)*. White solid, yield = 49.5 mg (65%). Mp = 66-68 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.22-7.24 (m, 2H), 7.14-7.16 (m, 1H) 4.90 (s, 2H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 150.6, 147.7, 140.4, 137.4, 136.2, 135.5, 129.0, 128.4, 128.2, 127.2, 127.2, 125.9, 121.1, 33.6. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3059, 3026, 2976, 2941, 2328, 1601, 1589, 1489, 1452, 1422, 1368, 1312, 1169, 1121, 1032, 935, 907, 822, 783, 758, 708, 694, 665, 602, 577, 517, 476. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}ClN$, 254.0731; found, 254.0736.

*7-chloro-8-(4-methoxybenzyl)quinoline (Table 2, Entry **3e**)*. Yellow solid, yield = 52 mg (61%). Mp = 79-80 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.81 (s, 2H), 3.73 (s, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 157.8, 150.6, 147.6, 137.8, 136.2, 135.3, 132.5, 130.0, 128.5, 127.2, 127.1, 121.1, 113.6, 55.3, 32.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3007, 2839, 2336, 1607, 1508, 1487, 1296, 1234, 1179, 1121, 1032, 930, 827, 816, 795, 752, 598, 523. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0837; found 284.0830.

*7-chloro-8-(4-nitrobenzyl)quinoline (Table 2, Entry **3f**)*. Yellow solid, yield = 31.3 mg (35%). Mp = 100-112 ℃. Isolated from flash chromatography (6% EtOAc/n-hexane). $^1$H NMR (300 MHz, CDCl3, *δ*): 8.97 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.43-7.48 (m, 3H), 4.94 (s, 2H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 150.9, 148.3, 147.5, 146.5, 136.5, 135.9, 135.6, 129.8, 128.5, 128.0, 127.3, 123.5, 121.5, 33.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3057, 2924, 2855, 2336, 1597, 1520, 1489, 1341, 1314, 1261, 1171, 1111, 930, 854, 831, 810, 756, 716, 691, 669, 596, 482. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{12}ClN_2O_2$, 299.0582; found 299.0586.

*8-(4-bromobenzyl)-7-chloroquinoline (Table 2, Entry **3g**)*. White solid, yield = 89.8 mg (90%). Mp = 99-101 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, CDCl3, *δ*): 8.97 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.30-7.35 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 150.7, 147.6, 139.4, 136.9, 136.3, 135.4, 131.3, 130.9, 128.5, 127.5, 127.3, 121.3, 119.8, 33.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3048, 2963, 2943, 2924, 2851, 1605, 1585,

1483, 1422, 1260, 1123, 1101, 1067, 1042, 1009, 932, 835, 827, 802, 777, 592, 517, 492. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{12}BrClN$, 331.9836; found 331.9836.

*7-chloro-8-(4-chlorobenzyl)quinoline (Table 2, Entry **3h**)*. White solid, yield = 75.2 mg (87%). Mp = 80–82 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, CDCl3, *δ*): 8.97 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.19 (m, 2H), 4.83 (s, 2H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 150.7, 147.6, 138.9, 137.0, 136.3, 135.4, 131.7, 130.4, 128.4, 128.3, 127.5, 127.2, 121.2, 33.0. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3028, 2936, 2336, 1929, 1595, 1487, 1360, 1179, 1126, 1088, 1042, 1015, 934, 829, 802, 494. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{12}Cl_2N$, 288.0341; found 288.0345.

*7-chloro-8-(4-(trimethylsilyl)benzyl)quinoline (Table 2, Entry **3i**)*. White sticky, yield = 74.3 mg (76%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ*): 9.00 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.38-7.45 (m, 5H), 4.92 (s, 2H), 0.26 (s, 9H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, *δ*): 150.6, 147.8, 141.0, 137.4, 136.2, 135.5, 133.4, 128.5, 128.4, 127.2, 121.1, 33.6, -0.9. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3012, 2949, 2326, 1597, 1489, 1247, 1107, 931, 835, 823, 800, 790, 765, 731, 640, 592, 489. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{19}H_{21}ClNSi$, 326.1126; found 326.1121.

*4-((7-chloroquinolin-8-yl)methyl)phenyl acetate (Table 2, Entry **3j**)*. Yellow solid, yield = 18.7 mg (20%). Mp = 154-156 ℃. Isolated from flash chromatography (10% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ*): 8.97 (dd, *J* = 3.9, 1.8 Hz, 1H), 8.13 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 2H), 2.24 (s, 3H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, *δ*): 169.7, 150.6, 148.9, 147.7, 138.0, 137.3, 136.3, 135.4, 130.1, 128.5, 127.3, 127.3, 121.2, 121.2, 33.0, 21.3. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3053, 2924, 2336, 1746, 1595, 1506, 1489, 1373, 1227, 1192, 1171, 1016, 920, 835, 797, 764, 627, 598, 525, 507, 473, 428. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{18}H_{15}ClNO_2$, 312.0786; found 312.0780.

*1-(3-((7-chloroquinolin-8-yl)methyl)phenyl)ethanone (Table 2, Entry **3l**)*. White solid, yield = 31.1 mg (35%). Mp = 86-88 ℃. Isolated from flash chromatography (10% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ*): 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.01 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.42 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.26 – 7.31 (d, *J* = 7.8 Hz, 1H) 4.91 (s, 2H), 2.53 (s, 3H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 198.5, 150.7, 147.6, 141.0, 137.3, 136.8, 136.4, 135.5, 133.8, 129.2, 128.5, 127.6, 127.3, 126.1, 121.3, 33.5, 26.8. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3063, 3028, 2920, 2851, 2336, 1672, 1603, 1584, 1489, 1358, 1269, 1125, 1082, 1040, 835, 812, 797, 600, 590, 478. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{18}H_{15}ClNO$, 296.0837; found 296.0832.

*7-chloro-8-(3,5-dimethylbenzyl)quinoline (Table 2, Entry **3m**)*. White solid, yield = 42.3 mg (50%). Mp = 76-78 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, CDCl3, *δ*): 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.93 (s, 2H), 6.79 (s, 1H), 4.82 (s, 2H), 2.23 (s, 6H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 150.6, 147.8, 140.1, 137.6, 136.2, 135.6, 128.5, 127.7, 127.2, 127.1, 126.8, 121.1, 33.5, 21.5. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 2916, 2851, 2336, 1599, 1487, 1422, 1360, 1314, 1121, 1040, 920, 843, 827, 799, 698, 592. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{18}H_{17}ClN$, 282.1044; found 282.1041.

*8-(3,5-bis(trifluoromethyl)benzyl)-7-chloroquinoline (Table 2, Entry **3n**)*. Use of (3,5-bis(trifluoromethyl)phenyl)boronic acid (1.2 equiv) at 80 ℃. White solid, yield = 76.0 mg (65%). Mp = 124-126 ℃. Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, CDCl3, *δ*): 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.87 (s, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.66 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.95 (s, 2H). $^{13}$C{$^1$H} NMR (75 MHz, CDCl3, *δ*): 150.9, 147.4, 143.0, 136.5, 135.6, 135.5, 131.37 (q, $J_{CF}$ = 33.0 Hz), 129.46 (d, $J_{CF}$ = 3.8 Hz), 128.4, 128.1, 127.4, 123.64 (d, $J_{CF}$ = 270.8 Hz), 121.5, 120.03-120.24 (m), 33.45. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3032, 2997, 2940, 2334, 1607, 1489, 1377, 1283, 1157, 1115, 947, 895, 829, 800, 683. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{18}H_{11}ClF_6N$, 390.0479; found 390.0475.

*7-chloro-8-(2-fluorobenzyl)quinoline (Table 2, Entry **3o**)*. White sticky, yield = 19.6 mg (24%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ*): 8.94 (dd, *J* = 4.2, 2.1 Hz, 1H), 8.16 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.42 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.02-7.15 (m, 2H), 6.83-6.88 (m, 1H), 6.66-6.71(m, 1H), 4.89 (s, 2H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, *δ*): 161.17 (d, *J* = 243.8 Hz), 150.8, 148.0, 136.3, 136.04, 136.03, 129.79 (d, *J* = 4.5 Hz), 128.5, 127.6, 127.38 (d, *J* = 7.5 Hz), 127.11, 127.10 (d, *J* = 15.0 Hz), 123.80 (d, *J* = 3.0 Hz), 121.3, 115.06 (d, *J* = 21.8 Hz), 26.40 (d, *J* = 3.8 Hz). IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3032, 2997, 2957, 2926, 2326, 1967, 1902, 1603, 1483, 1449, 1422, 1223, 1126, 1092, 1055, 1038, 953, 930, 860, 827, 814, 758, 449. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{16}H_{12}ClFN$, 272.0637; found 272.0639.

*8-(benzo[d][1,3]dioxol-5-ylmethyl)quinoline (Table 2, Entry **3p**)*. Use of AgOTf (10 mol%) instead of $Tf_2O$. Yellow solid, yield = 66.1 mg (74%). Mp = 85–86 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 7.8, 4.2 Hz, 1H), 6.86 (s, 1H), 6.83-6.85 (m, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 2H), 4.78 (s, 2H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 150.7, 147.6, 147.4, 145.7, 137.5, 136.3, 135.4, 134.2, 128.5, 127.3, 127.2, 122.0, 121.2, 109.7, 108.1, 100.8, 33.2. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 2922, 2904, 2852, 2335, 1602, 1485, 1438, 1423, 1363, 1247, 1232, 1035, 792, 609, 474. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{17}H_{13}ClNO_2$, 298.0629; found 298.0624.

**General procedure for the arylation of 8-methyl quinolines with arylboronic acid and characterization data.** To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, arylboronic acid (0.6 mmol or 0.36 mmol), $[RhCp^*Cl_2]_2$ (5 mol %) and $Ag_2O$ (2 equiv) were added under argon atmosphere, followed by the addition of 8-methylquinoline (0.3 mmol), dichloroethane (1.5 mL) and triflic anhydride (10 mol%). The subsequent reaction mixture was stirred at 80 °C for 24 h. On completion of reaction, the solvent was evaporated under reduced pressure to get the crude reaction mixture. The crude mixture was purified by flash chromatography using silica gel (230-400 mesh size) and *n*-hexane: EtOAc as the eluent.

*8-(4-pentylbenzyl)quinoline (Table 3, Entry **3q**)*. Colourless liquid, yield = 34.7 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14-8.16 (m, 1H), 7.69 (t, *J* = 4.8 Hz, 1H), 7.45 (d, *J* = 5.4 Hz, 2H), 7.41 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.69 (s, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.60-1.65 (m, 2H), 1.33-1.37 (m, 4H), 0.91-0.93 (m, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 149.6, 146.9, 140.6, 140.5, 138.5, 136.4, 129.5, 129.3, 128.5, 128.5, 126.5, 126.3, 121.1, 36.5, 35.7, 31.7, 31.4, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3005, 2926, 2855, 2336, 1595, 1512, 1497, 1466, 1369, 1319, 1074, 1022, 818, 789, 754, 606. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{21}H_{24}N$, 290.1903; found 290.1905.

*7-methyl-8-(4-pentylbenzyl)quinoline (Table 3, Entry **3r**)*. Yellow liquid, yield = 58.3 mg (64%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.94-8.95 (m, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33-7.36 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 4.78 (s, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 1.54-1.59 (m, 2H), 1.28-1.34 (m, 4H), 0.87-0.90 (m, 3H). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$, *δ*): 149.8, 147.6, 140.1, 138.3, 138.1, 137.2, 136.1, 130.1, 128.5, 128.3, 126.9, 125.9, 120.2, 35.6, 32.3, 31.7, 31.3, 22.7, 20.6, 14.1. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 3005, 2955, 2926, 2855, 2336, 1614, 1503, 1460, 1362, 1317, 1070, 1020, 829, 797, 658, 610. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{22}H_{26}N$, 304.2060; found 304.2058.

*7-fluoro-8-(4-pentylbenzyl)quinoline (Table 3, Entry **3s**)*. Use 4-amylboronic acid (2.5 equiv) at 100 ℃. Yellow liquid, yield = 46.1 mg (50%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.68 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.32-7.37 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.66 (d, *J* = 1.8 Hz, 2H), 2.52 (t, *J* = 7.8 Hz, 2H), 1.53-1.58 (m, 2H), 1.27-1.33 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$, *δ*): 160.87 (d, $J_{CF}$ = 246.0 Hz), 150.6, 147.78 (d, $J_{CF}$ = 10.5 Hz), 140.5, 138.1, 136.3, 128.8, 128.36, 127.61 (d, $J_{CF}$ = 10.5 Hz), 125.66, 124.67 (d, *J* = 15.0 Hz), 120.24, 120.23, 117.13 (d, *J* = 27.0 Hz), 35.7, 31.7, 31.3, 28.8, 28.8, 22.7, 14.1. IR (ZnSe) $\nu_{max}$ (cm$^{-1}$): 2926, 2855, 2349, 2326, 1620, 1501, 1462, 1431, 1364, 1319, 1248, 1217, 1065, 993, 829, 797, 773, 746, 694, 664, 611, 534, 500, 457. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{21}H_{23}FN$, 308.1809; found 308.1832.

*6-methyl-8-(4-pentylbenzyl)quinoline (Table 3, Entry **3t**)*. Yellow liquid, yield = 38.2 mg (42%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.90 – 8.91 (m, 1H), 8.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.44 (s, 1H), 7.36-7.38 (m, 1H), 7.29 (s, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.62 (s, 2H), 2.55-2.58 (m, 2H), 2.46 (s, 3H), 1.58-1.63 (m, 2H), 1.31-1.34 (m, 4H), 0.88-0.90 (m, 3H). $^{13}$C{$^1$H}

NMR (150 MHz, $CDCl_3$, *δ*): 148.8, 145.5, 140.5, 140.1, 138.7, 136.3, 135.7, 131.9, 129.3, 128.6, 128.5, 125.2, 121.1, 36.4, 35.7, 31.7, 31.4, 22.7, 21.8, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2855, 2328, 1597, 1512, 1493, 1454, 1369, 1115, 1036, 862, 804, 781, 611, 536. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{26}N$, 304.2060; found 304.2054.

*5-methyl-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3u****)*. Brown liquid, yield = 36.4 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.97 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 7.42-7.44 (m, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 4.62 (s, 2H), 2.65 (s, 3H), 2.55-2.58 (m, 2H), 1.58-1.62 (m, 2H), 1.38-1.24 (m, 4H), 0.88-0.90 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.1, 147.1, 140.5, 138.8, 138.5, 132.8, 132.7, 129.3, 129.2, 128.5, 127.8, 127.0, 120.7, 36.5, 35.7, 31.7, 31.4, 22.7, 18.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2855, 2326, 1599, 1501, 1468, 1356, 1022, 824, 812, 787, 557. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{26}N$, 304.2060; found 304.2056.

*4,6-dimethyl-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3v****)*. Colourless liquid, yield = 51.4 mg (54%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.77 (d, *J* = 4.5 Hz, 1H), 7.63 (s, 1H), 7.28 (s, 1H), 7.20-7.24 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 2H), 2.68 (s, 3H), 2.57 (t, 7.8 Hz, 2H), 2.49 (s, 3H), 1.56-1.66 (m, 2H), 1.31-1.35 (m, 4H), 0.88-0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 148.4, 145.2, 143.6, 140.6, 140.4, 138.9, 135.8, 131.5, 129.3, 128.5, 128.5, 122.0, 121.2, 36.7, 35.7, 31.7, 31.3, 22.7, 22.1, 19.1, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2855, 2326, 1595, 1510, 1501, 1433, 1377, 1022, 856, 841, 829, 800, 519. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{28}N$, 318.2216; found 318.2211.

*3-methyl-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3w****)*. Yellow liquid, yield = 31.9 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.81 (d, *J* = 2.1 Hz, 1H), 7.90 (dd, *J* = 2.4 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.33-7.42 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.63 (s, 2H), 2.52-2.58 (m, 5H), 1.56-1.61 (m, 2H), 1.29-1.33 (m, 4H), 0.86-0.90 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 151.6, 145.3, 140.5, 140.4, 138.7, 135.1, 130.4, 129.3, 128.6, 128.5, 128.4, 126.6, 125.7, 36.5, 35.7, 31.8, 31.4, 22.7, 18.8, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2855, 1605, 1512, 1491, 1466, 1373, 1076, 961, 881, 804, 766, 611. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{26}N$, 304.2060; found 304.2055.

*5-bromo-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3x****)*. Use 4-amylboronic acid (1.2 equiv). Yellow solid, yield = 42.0 mg (38%). Mp = 42-45 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.55 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.61 (s, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.55-1.65 (m, 2H), 1.30-1.35 (m, 4H), 0.88-0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 150.2, 147.6, 140.9, 140.8, 138.0, 135.8, 130.3, 129.9, 129.3, 128.6, 127.7, 122.2, 119.9, 36.4, 35.7, 31.7, 31.3, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2926, 2855, 2336, 1591, 1564, 1512, 1491, 1460, 1383, 1346, 1207, 1146, 1034, 920, 907, 856, 822, 806, 789. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{21}H_{23}BrN$, 368.1008; found 368.1002.

*6-bromo-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3y****)*. Use 4-amylboronic acid (1.2 equiv). Colourless liquid, yield = 38.7 mg (35%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.96 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.83 (s, 1H), 7.51 (s, 1H), 7.42 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.61 (s, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.56-1.65 (m, 2H), 1.30-1.35 (m, 4H), 0.87-0.91 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.9, 145.6, 143.1, 140.9, 137.7, 135.4, 132.8, 129.7, 129.3, 128.7, 128.3, 122.0, 120.6, 36.2, 35.7, 31.7, 31.3, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2926, 2855, 1589, 1570, 1512, 1487, 1466, 1425, 1360, 1319, 1234, 1182, 1115, 1090, 1030, 1022, 864, 845, 802, 781, 725, 648, 606, 594, 559, 530, 503, 488, 461. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{21}H_{23}BrN$, 368.1008; found 368.1011.

*5-nitro-8-(4-pentylbenzyl)quinoline (Table 3, Entry* ***3z****)*. Use 4-amylboronic acid (1.2 equiv). Yellow solid, yield = 20.1 mg (20%). Mp = 101-103 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 9.03-9.08 (m, 2H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.65 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.71 (s, 2H), 2.54-2.60 (m, 2H), 1.55-1.65 (m, 2H), 1.29-1.34 (m, 4H), 0.86-0.91 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 150.6, 149.2, 146.5, 144.1, 141.3, 137.0, 132.3, 129.4, 128.8, 127.5, 124.8, 123.9, 121.4, 37.2, 35.7, 31.7, 31.3, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2953, 2922, 2855, 2326, 1595, 1518, 1499, 1400, 1323, 1153, 1119, 835, 795, 737. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{21}H_{23}N_2O_2$, 335.1754; found 335.1748.

*8-(4-pentylbenzyl)-4-phenylquinoline (Table 3, Entry* ***3za****)*. Use 4-amylboronic acid (1.2 equiv). Sticky yellow liquid, yield = 32.9 mg (30%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 9.00 (d, *J* = 4.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.49-7.55 (m, 5H), 7.45 (d, *J* = 6.6 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.34-7.36 (m, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 4.71 (s, 2H), 2.55-2.60 (m, 2H), 1.56-1.66 (m, 2H), 1.32-1.35 (m, 4H), 0.88-0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.0, 148.8, 147.3, 140.9, 140.6, 138.7, 138.7, 129.7, 129.5, 129.4, 128.6, 128.5, 128.4, 127.0, 126.5, 124.4, 121.4, 36.9, 35.7, 31.8, 31.4, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2926, 2855, 1566, 1508, 1489, 1464, 1445, 1431, 1395, 1350, 1275, 1182, 1115, 1074, 849, 812, 764, 700, 600, 577, 556, 544, 519, 488, 446. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{28}N$, 366.2216; found 366.2216.

*(E)-8-(4-pentylbenzyl)-6-styrylquinoline (Table 3, Entry* ***3zb****)*. Use 4-amylboronic acid (1.2 equiv). Yellow liquid, yield = 32.9 mg (28%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.92 (d, *J* = 3.6 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.71 (s, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.36-7.42 (m, 3H), 7.26-7.31 (m, 3H), 7.11-7.19 (m, 4H), 4.68 (s, 2H), 2.56-2.61 (m, 2H), 1.57-1.67 (m, 2H), 1.32-1.36 (m, 4H), 0.87-0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.4, 146.9, 140.8, 140.6, 138.5, 137.3, 136.3, 135.4, 130.1, 129.3, 128.92, 128.87, 128.6, 128.3, 128.0, 127.6, 126.8, 124.4, 121.5, 36.6, 35.7, 31.7, 31.4, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3022, 2955, 2926, 2855, 1589, 1491, 1375, 1117, 959, 881, 835, 783, 746, 691, 556, 480. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{29}H_{30}N$, 392.2373; found 392.2370.

*(E)-methyl 3-(8-(4-pentylbenzyl)quinolin-6-yl)acrylate (Table 3, Entry* ***3zc****)*. Use 4-amylboronic acid (1.2 equiv). Yellow liquid, yield = 44.8 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ)*: 8.97 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.75-7.80 (m, 2H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.45 (d, *J* = 16.2 Hz, 1H), 4.63 (s, 2H), 3.81 (s, 3H), 2.55-2.60 (m, 2H), 1.55 – 1.65 (m, 2H), 1.29-1.34 (m, 4H), 0.86-0.91 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 167.4, 150.6, 147.8, 144.4, 141.6, 140.8, 138.0, 136.8, 132.4, 129.3, 128.6, 128.5, 127.7, 127.4, 121.9, 118.9, 51.9, 36.5, 35.7, 31.7, 31.3, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3009, 2951, 2926, 2855, 1707, 1632, 1587, 1514, 1493, 1433, 1310, 1285, 1256, 1192, 1165, 1126, 1038, 1018, 1001, 980, 930, 885, 856, 835, 804, 785, 773, 729, 561, 484, 436. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{25}H_{28}NO_2$, 374.2115; found 374.2118.

*2-(4-pentylphenethyl)pyridine (Table 3, Entry* ***3zd****)*. Use AgOTf (10 mol%) instead of $Tf_2O$. Yellow liquid, yield = 15.2 mg (20%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.56 (d, *J* = 4.2 Hz, 1H), 7.57 (td, *J* = 7.2, 1.8 Hz, 1H), 7.08-7.13 (m, 6H), 3.07-3.09 (m, 2H), 3.00-3.03 (m, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.57-1.62 (m, 2H), 1.29-1.33 (m, 4H), 0.88-0.90 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 161.6, 149.4, 140.7, 138.9, 136.4, 128.5, 128.5, 123.1, 121.3, 40.5, 35.8, 35.7, 31.7, 31.4, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2855, 2326, 1589, 1514, 1474, 1435, 814, 746, 556. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{24}N$, 254.1903; found 254.1903.

*2-(4-chlorophenethyl)pyridine (Table 3, Entry* ***3ze****)*. Use AgOTf (10 mol%) instead of $Tf_2O$. Brown liquid, yield = 9.8 mg (15%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.56 (d, *J* = 4.2 Hz, 1H), 7.56 (td, *J* = 7.8, 1.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.09-7.13 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 1H), 3.01-3.08 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 160.9, 149.5, 140.1, 136.5, 131.8, 130.0, 128.6, 123.2, 121.4, 40.1, 35.4. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3011, 2924, 2855, 2326, 1591, 1568, 1491, 1474, 1433, 1092, 1015, 816, 748, 627, 523, 490, 403. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{13}H_{13}ClN$, 218.0721; found 218.0731.

*8-benzylquinoline (Table 4, Entry* ***3zf****)*.[23] White solid, yield = 30.2 mg (46%). Mp = 50-52 ℃. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15-8.16 (m, 1H), 7.69 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.41-7.47 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.28-7.30 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H) 4.70 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.6, 146.8, 141.5, 140.3, 136.4, 129.6, 129.5, 128.5, 128.4, 126.5, 126.4, 126.0, 121.1, 36.9. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3028, 2961, 2924, 1599, 1574, 1491, 1391, 1360, 1314, 1260, 1153, 1080, 1028, 872, 810, 787, 758, 700, 606, 571, 515, 438. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{14}N$, 220.1121; found 220.1120.

*7-chloro-8-(4-ethylbenzyl)quinoline (Table 4, Entry* ***3zg****)*. Yellow liquid, yield = 29.7 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.98-8.99 (m, 1H), 8.14-8.16 (m,

1H), 7.68-7.69 (m, 1H), 7.44-7.46 (m, 2H), 7.41 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.67 (s, 2H), 2.61-2.65 (m, 2H), 1.23 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.6, 146.9, 141.8, 140.6, 138.6, 136.4, 129.5, 129.4, 128.5, 128.0, 126.5, 126.3, 121.1, 36.5, 28.6, 15.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2963, 2326, 1597, 1512, 1497, 1369, 1319, 1246, 1074, 1022, 851, 818, 789, 758, 604, 534. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{18}N$, 248.1434; found 248.1434.

*8-(4-bromobenzyl)quinoline (Table 4, Entry* ***3zh****)*.[13e] Use arylboronic acid (1.2 equiv). White solid, yield = 31.3 mg (35%). Mp = 45-46 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.41-7.47 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.63 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.8, 146.7, 140.6, 139.6, 136.4, 131.5, 131.2, 129.6, 128.6, 126.7, 126.5, 121.3, 119.8, 36.4. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3041, 2929, 1595, 1573, 1485, 1435, 1404, 1388, 1361, 1070, 1010, 850, 819, 796, 761, 655, 617, 590, 472, 439. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}BrN$, 298.0226; found 298.0229.

*8-(4-chlorobenzyl)quinoline (Table 4, Entry* ***3zi****)*.[11b] Use arylboronic acid (1.2 equiv). White solid, yield = 35.0 mg (46%). Mp = 50–52 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (300 MHz, $CDCl_3$, *δ):* 8.96 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14-8.17 (m, 1H), 7.71 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.40-7.49 (m, 3H), 7.21-7.28 (m, 4H), 4.65 (s, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.7, 146.8, 140.1, 139.8, 136.4, 131.8, 130.8, 129.6, 128.6, 128.5, 126.7, 126.5, 121.2, 36.4. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3003, 2951, 2920, 2853, 2336, 1595, 1576, 1491, 1393, 1090, 1074, 1016, 800, 787, 758, 727, 694, 665, 598, 550, 517, 476, 434. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}ClN$, 254.0731; found 254.0734.

*8-(4-(trifluoromethyl)benzyl)quinoline (Table 4, Entry* ***3zj****)*.[13e] Use arylboronic acid (1.2 equiv). White solid, yield = 15.5 mg (18%), Mp = 53-55 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.96 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.72-7.73 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.46-7.49 (m, 2H), 7.42-7.44 (m, 3H), 4.73 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.8, 146.8, 145.8, 139.2, 136.5, 129.7, 129.6, 128.7, 128.3 (q, $J_{CF}$ = 31.5 Hz), 126.9, 126.5, 121.3, 125.30-125.37 (q, $J_{CF}$ = 4.5 Hz), 124.64 (q, $J_{CF}$ = 270 Hz), 36.9. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3046, 2934, 2334, 1614, 1499, 1418, 1319, 1161, 1126, 1107, 1063, 1016, 953, 854, 824, 806, 791, 764, 750, 739, 698, 658, 598, 513. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{13}F_3N$, 288.0995; found 288.0991.

*8-(4-(trimethylsilyl)benzyl)quinoline (Table 4, Entry* ***3zk****)*. Use arylboronic acid (1.2 equiv). Brown solid, yield = 38.5 mg (44%). Mp = 92–94 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.68-7.70 (m, 1H), 7.45-7.46 (m, 4H), 7.42 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.70 (s, 2H), 0.26 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.7, 146.9, 142.1, 140.2, 137.5, 136.4, 133.6, 129.6, 128.9, 128.5, 126.5, 126.4, 121.1, 36.9, -0.91. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2953, 2911, 2336, 1595, 1497, 1396, 1260, 1248, 1105, 835, 816, 791, 758, 727, 696, 665, 635, 613, 588, 519, 478, 440. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{22}NSi$, 292.1516; found 292.1511.

*8-(4-methoxybenzyl)quinoline (Table 4, Entry* ***3zl****)*. Yellow liquid, yield = 29.9 mg (40%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ*): 8.96-8.97 (m, 1H), 8.14-8.16 (m, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.40-7.46 (m, 3H), 7.24-7.26 (m, 2H), 6.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 4.63 (s, 2H), 3.78 (d, *J* = 1.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 157.9, 149.5, 146.7, 140.6, 136.3, 133.4, 130.3, 129.4, 128.4, 126.4, 126.2, 121.0, 113.8, 55.2, 36.0. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3001, 2907, 2833, 2326, 1611, 1508, 1497, 1464, 1439, 1300, 1242, 1175, 1105, 1034, 816, 791, 760, 746, 725, 602, 525. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{16}NO$, 250.1226; found 250.1223.

*8-(4-nitrobenzyl)quinoline (Table 4, Entry* ***3zm****)*. Yellow solid, yield = 8.7 mg (11%). Mp = 85-87 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.93 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.08-8.11 (m, 2H), 7.74-7.75 (m, 1H), 7.47-7.51 (m, 2H), 7.45-7.46 (m, 2H), 7.43 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.75 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.9, 149.7, 146.6, 146.4, 138.4, 136.5, 130.0, 129.9, 128.7, 127.3, 126.5, 123.7, 121.4, 37.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2926, 1595, 1497, 1339, 1107, 851, 806, 716, 592, 515 HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}N_2O_2$, 265.0972; found 265.0972.

*8-(3,5-dimethylbenzyl)quinoline (Table 4, Entry* ***3zn****)*.[13e] Use arylboronic acid (1.2 equiv). White solid, yield = 25.2 mg (34%). Mp = 80-82 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.98 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.68-7.69 (m, 1H), 7.41-7.46 (m, 3H), 6.94 (s, 2H), 6.85 (s, 1H), 4.62 (s, 2H), 2.27 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.6, 146.9, 141.3, 140.5, 137.9, 136.4, 129.6, 128.5, 127.7, 127.4, 126.5, 126.3, 121.1, 36.6, 21.5. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3019, 2965, 2916, 2851, 1595, 1497, 1431, 1319, 1069, 851, 827, 793, 758, 727, 692, 588. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{18}N$, 248.1434; found 248.1433.

*8-(3,5-bis(trifluoromethyl)benzyl)quinoline (Table 4, Entry* ***3zo****)*. Use arylboronic acid (1.2 equiv). White solid, yield = 33.1 mg (31%). Mp = 49-50 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ):* 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.83 (s, 2H), 7.76 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.69 (s, 1H), 7.49-7.53 (m, 2H), 7.43 (dd, *J* = 7.8, 4.2 Hz, 1H), 4.77 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.9, 146.6, 144.2, 138.2, 136.5, 131.46 (q, $J_{CF}$ = 33.0 Hz), 129.7, 128.8, 129.5 (q, $J_{CF}$ = 4.5 Hz), 127.4, 126.6, 123.62 (d, $J_{CF}$ = 271.5 Hz), 121.5, 120.04 – 120.15 (m), 37.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3055, 2924, 2326, 1501, 1375, 1273, 1175, 1128, 1113, 1103, 1072, 1053, 1028, 891, 870, 841, 827, 793, 758, 702. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{12}F_6N$, 356.0868; found 356.0861.

*8-(2-fluorobenzyl)quinoline (Table 4, Entry* ***3zp****)*. Colourless liquid, yield = 14.2 mg (20%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ*): 8.98 (d, *J* = 3.6 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.41-7.46 (m, 3H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.18-7.21 (m, 1H), 7.06-7.09 (m, 1H), 7.02-7.05 (m, 1H) 4.74 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 161.45 (d, $J_{CF}$ = 244.5 Hz), 149.6, 146.9, 138.8, 136.4, 131.9 (d, $J_{CF}$ = 4.5 Hz), 129.3, 128.5, 128.22 (d, $J_{CF}$ = 16.5 Hz), 127.85 (d, $J_{CF}$ = 9.0 Hz), 126.6, 126.5, 124.05 (d, *J* = 3.0 Hz), 121.15, 115.33 (d, $J_{CF}$ = 22.5 Hz), 29.91 (d, $J_{CF}$ = 4.5 Hz). IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3040, 2326, 1584, 1489, 1454, 1369, 1319, 1225, 1094, 1032, 827, 791, 772, 750, 696, 583, 496, 447. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}FN$, 238.1032; found 238.1029.

*8-(thiophen-2-ylmethyl)quinoline (Table 4, Entry* ***3zq****)*. Transparent crystalline solid, yield = 16.9 mg (25%). Mp = 71-73 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57 (d, *J* = 6.6 Hz, 1H), 7.48 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.42 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.12-7.13 (m, 1H), 6.92-6.93 (m, 2H), 4.87 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.7, 146.5, 144.2, 139.5, 136.4, 129.3, 128.5, 126.8, 126.8, 126.6, 125.6, 123.9, 121.3, 31.25. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 1591, 1497, 1427, 1393, 1366, 1072, 826, 799, 760, 745, 700, 642, 613, 577, 513, 440. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{12}NS$, 226.0685; found 226.0685.

*8-benzyl-5-methylquinoline (Table 4, Entry* ***3zr****)*. Yellow liquid, yield = 30.8 mg (44%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). 8.98 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.31-7.33 (m, 2H), 7.25-7.30 (m, 3H), 7.18-7.21 (m, 2H), 4.66 (s, 3H), 2.66 (s, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.1, 147.1, 141.8, 138.3, 132.9, 132.7, 129.8, 129.5, 129.2, 128.4, 126.9, 125.9, 120.7, 36.9, 18.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3024, 2920, 2326, 1601, 1580, 1493, 1470, 1452, 1356, 1346, 1315, 1150, 1072, 1030, 1003, 968, 847, 816, 802, 785, 770, 750, 725, 698, 687, 619, 594, 552, 503, 473. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{16}N$, 234.1277; found 234.1277.

*8-benzyl-5-nitroquinoline (Table 4, Entry* ***3zs****)*. Yellow solid, yield = 9.5 mg (12%). M.pt. = 69-71 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). 9.07 (dd, *J* = 4.2, 1.8 Hz, 1H), 9.05 (dd, *J* = 9.0, 1.8 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.30-7.32 (m, 4H), 7.22-7.25 (m, 1H), 4.75 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 150.7, 148.8, 146.4, 144.1, 139.9, 132.3, 129.5, 128.8, 127.6, 126.6, 124.7, 123.9, 121.4, 37.6. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2924, 2853, 1518, 1489, 1398, 1317, 1263, 1234, 1153, 864, 835, 802, 766, 739, 708, 698, 575, 503. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{13}N_2O_2$, 265.0972; found 265.0972.

**General procedure for the symmetrical diarylation of 8-methylquinoline with arylboronic acids and characterization data.** To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, phenylboronic acid (6 equiv), $[RhCp^*Cl_2]_2$ (5 mol %) and $Ag_2O$ (2 equiv) were added under argon atmosphere, followed by the addition of 8-methylquinoline (0.3 mmol), dichloroethane (1.5 mL) and triflic anhydride (10 mol%). The subsequent reaction mixture was stirred at 100 °C for 24 h. On completion of reaction, the solvent was evaporated under reduced pressure to get the crude reaction mixture. The crude mixture was purified either by flash chromatography using silica gel (230-400 mesh size) and

*n*-hexane: EtOAc as the eluent or by column chromatography using reverse silica C-18 and $H_2O$: MeOH as eluent.

*8-(bis(4-chlorophenyl)methyl)quinoline (Table 5, Entry **3'zi**)*. White solid, yield = 72.1 mg (66%). Mp = 147-149 °C. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ)*: 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.45-7.50 (m, 1H), 7.39 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.22-7.26 (m, 5H), 7.07 (d, *J* = 8.7 Hz, 4H), 7.01 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 150.0, 146.3, 142.7, 142.0, 136.4, 132.2, 131.0, 130.2, 128.6, 127.2, 126.3, 121.4, 49.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3040, 2999, 1950, 1898, 1886, 1595, 1487, 1466, 1402, 1385, 1090, 1074, 1011, 854, 820, 787, 766, 754, 694, 681, 615, 538, 519, 494, 444. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{16}Cl_2N$, 364.0654; found 364.0654.

*8-(bis(4-methoxyphenyl)methyl)quinoline (Table 5, Entry **3'zl**)*. Transparent Crystalline solid, yield = 68.2 mg (64%). Mp = 131-133 °C. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.88 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.12-8.14 (m, 1H), 7.69-7.71 (m, 1H), 7.45-7.48 (m, 1H), 7.36 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.33 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.07-7.09 (m, 4H), 6.98 (s, 1H), 6.79-6.82 (m, 4H), 3.77 (s, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 157.9, 149.8, 146.5, 143.5, 137.1, 136.3, 130.6, 130.3, 128.5, 126.5, 126.2, 121.1, 113.7, 55.3, 48.5. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3055, 3003, 2963, 2833, 1607, 1582, 1506, 1495, 1302, 1246, 1173, 1107, 1030, 835, 816, 797, 773, 760, 577, 515. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{24}H_{22}NO_2$, 356.1645; found 356.1645.

*8-(bis(3,5-bis(trifluoromethyl)phenyl)methyl)quinoline (Table 5, Entry **3'zo**)*. White solid, yield = 105.5 mg (62%). Mp = 118-120 °C. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.21 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.84 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.79 (s, 2H), 7.61 (s, 4H), 7.55 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.46 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.32 (s, 1H), 7.22 (dd, *J* = 7.2, 1.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 150.3, 145.8, 145.3, 139.4, 136.7, 131.09 (q, $J_{CF}$ = 33.0 Hz), 130.0, 129.59 (q, $J_{CF}$ = 3.0 Hz), 128.9, 128.4, 126.5, 123.34 (d, $J_{CF}$ = 273.0 Hz), 122.0, 121.18-121.29 (m), 49.81. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2322, 1501, 1371, 1273, 1167, 1119, 1109, 1084, 899, 799, 704, 681. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{14}F_{12}N$, 568.0929; found 568.0930.

8-(bis(4-chlorophenyl)methyl)-5-methylquinoline *(Table 5, Entry **3'zt**)*. Light yellow solid, yield = 70.4 mg (62%). Mp = 139-142 °C. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.90 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 7.46 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 4H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.01 (s, 1H), 2.68 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 148.9, 145.5, 142.5, 139.4, 133.8, 133.6, 132.1, 130.9, 130.4, 128.4, 127.9, 126.9, 120.8, 48.9, 18.6. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2326, 1599, 1487, 1086, 1011, 818, 791, 768, 602, 583, 498. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{18}Cl_2N$, 378.0811; found 378.0810.

*8-(bis(4-chlorophenyl)methyl)-6-bromoquinoline (Table 5, Entry **3'zu**)*. White solid, yield = 95.7 mg (72%). Mp = 178-179 °C. Isolated from reverse silica C-18 (20% $H_2O$/MeOH). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.25-7.27 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 4H), 6.96 (s, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 150.2, 144.8, 144.4, 141.8, 135.4, 133.4, 132.5, 130.9, 129.7, 129.2, 128.7, 122.3, 120.4, 49.0. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2920, 2851, 2326, 1593, 1487, 1433, 1402, 1371, 1088, 1011, 864, 833, 822, 804, 795, 756, 725, 683, 646, 519, 500, 478, 415. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{15}BrCl_2N$, 441.9759; found 441.9757.

*8-(bis(4-chlorophenyl)methyl)-4,6-dimethylquinoline (Table 5, Entry **3'zv**)*. Pale yellow solid, yield = 82.4 mg (70%). Mp = 174-176 °C. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.64 (d, *J* = 4.2 Hz, 1H), 7.68-7.69 (m, 1H), 7.21-7.24 (m, 4H), 7.17-7.18 (m, 1H), 7.05-7.07 (m, 5H), 7.00 (s, 1H), 2.67 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 148.7, 144.5, 143.7, 142.9, 142.0, 135.6, 132.1, 132.0, 131.0, 128.6, 128.5, 122.3, 122.1, 49.2, 22.3, 19.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2920, 2851, 2326, 1593, 1487, 1433, 1402, 1371, 1088, 1011, 864, 833, 822, 804, 795, 756, 725, 683, 646, 519, 500, 478, 415. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{24}H_{20}Cl_2N$, 392.0967; found 392.0964.

8-(bis(4-methoxyphenyl)methyl)-4,6-dimethylquinoline *(Table 5, Entry **3'zw**)*. Yellow solid, yield = 55.2 mg (48%). Mp = 182-185 °C. Isolated from flash chromatography (4% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.67 (d, *J* = 4.2 Hz, 1H), 7.65 (s, 1H), 7.20-7.15 (m, 1H), 7.17 (d, *J* = 4.2 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 4H), 6.97 (s, 1H), 6.80 (d, *J* = 9.0 Hz, 4H), 3.77 (s, 6H), 2.67 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 157.8, 148.4, 143.4, 140.8, 137.2, 135.6, 132.3, 132.2, 130.6, 128.5, 122.0, 121.5, 113.6, 55.3, 48.6, 22.3, 19.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3007, 2922, 2830, 1607, 1508, 1452, 1439, 1244, 1169, 1036, 833, 814, 584, 517. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}NO_2$, 384.1958; found 384.1960.

**General procedure for the secondary C(sp$^3$)-H bond arylation of 8-benzylquinoline with arylboronic acids and characterization data.** To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-benzylquinoline (0.3 mmol), arylboronic acid (3 equiv), $[RhCp^*Cl_2]_2$ (5 mol %) and $Ag_2O$ (2 equiv) were added under argon atmosphere, followed by the addition of dichloroethane (1.5 mL) and triflic anhydride (10 mol%). The subsequent reaction mixture was stirred at 100 °C for 24 h. On completion of reaction, the solvent was evaporated under reduced pressure to get the crude reaction mixture. The crude mixture was purified either by flash chromatography using silica gel (230-400 mesh size) and *n*-hexane: EtOAc as the eluent or by column chromatography using reverse silica C-18 and $H_2O$: MeOH as eluent.

*8-((4-pentylphenyl)(phenyl)methyl)quinoline (Table 6, Entry **4b**)*. Yellow liquid, yield = 49.3 mg (45%). Isolated from flash chromatography (1% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ)*: 8.89 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.70 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.45-7.50 (m, 1H), 7.34-7.38 (m, 3H), 7.24-7.29 (m, 2H), 7.16-7.20 (m, 3H), 7.09 (s, 5H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.56-1.66 (m, 2H), 1.30-1.35 (m, 4H), 0.87-0.92 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.8, 146.5, 144.9, 143.2, 141.7, 140.7, 136.3, 130.5, 129.8, 129.6, 128.5, 128.3, 128.2, 126.6, 126.3, 126.0, 121.1, 49.7, 35.7, 31.8, 31.2, 22.7, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2926, 2855, 2336, 1597, 1510, 1495, 1466, 1450, 1366, 1186, 1078, 820, 793, 758, 727, 698, 610. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{28}N$, 366.2216; found 366.2208.

*8-((4-chlorophenyl)(phenyl)methyl)quinoline (Table 6, Entry **4c**)*. White solid, yield = 69.3 mg (70%). Mp = 149-151 °C. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (300 MHz, $CDCl_3$, *δ)*: 8.88 (dd, *J* = 3.9, 1.5 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.73 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.21-7.31 (m, 6H), 7.15-7.18 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*): 149.9, 146.4, 144.1, 143.2, 142.5, 136.4, 131.9, 131.1, 130.4, 129.7, 128.6, 128.4, 126.9, 126.4, 126.3, 121.3, 49.6. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3065, 3028, 3001, 1597, 1485, 1173, 1086, 1011, 824, 800, 783, 754, 729, 700, 694, 606, 486. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{17}ClN$, 330.1044; found 330.1044.

*8-((4-methoxyphenyl)(phenyl)methyl)quinoline (Table 6, Entry **4d**)*. White solid, yield = 58.6 mg (60%). Mp = 163-167 °C. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.88 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.37 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.32 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.24-7.27 (m, 2H), 7.19 (d, 7.2 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 158.0, 149.8, 146.5, 145.0, 143.2, 136.7, 136.3, 130.7, 130.4, 129.7, 128.5, 128.3, 126.6, 126.2, 126.1, 121.2, 113.7, 55.3, 49.3. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3030, 2957, 1609, 1582, 1508, 1493, 1441, 1302, 1248, 1173, 1109, 1026, 1011, 839, 818, 795, 787, 766, 756, 733, 704, 662, 631, 608, 581, 513, 420. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{20}NO$, 326.1539; found 326.1545.

*8-((3,5-bis(trifluoromethyl)phenyl)(phenyl)methyl)quinoline (Table 6, Entry **4e**)*. Yellow liquid, yield = 97.1 mg (75%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.88 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16-8.18 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.64-7.65 (m, 2H), 7.50-7.53 (m, 1H), 7.41 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.33 (td, *J* = 7.8, 2.4 Hz, 2H), 7.27-7.30 (m, 2H), 7.22 (d, *J* = 4.2 Hz, 1H), 7.15-7.17 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 150.1, 147.3, 146.1, 142.6, 141.1, 136.5, 131.45 (q, $J_{CF}$ = 33 Hz), 131.3, 130.3, 129.71-129.75 (m), 129.7, 128.8, 128.7, 127.5, 127.0, 126.4, 123.57 (q, $J_{CF}$ = 270 Hz), 121.6, 120.38-120.45 (m), 50.03. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2326, 1497, 1371, 1275, 1167, 1125, 1109, 1078, 941, 899, 849, 795, 783, 762, 727, 700, 681, 669. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{24}H_{16}F_6N$, 432.1181; found 432.1183.

*8-((4-chlorophenyl)(4-methoxyphenyl)methyl)quinoline (Table 6, Entry **4f**)*. Yellow solid, yield = 64.8 mg (60%). Mp = 117-119 °C. Isolated from reverse silica C-18 (20% $H_2O$/MeOH). $^1$H NMR (600 MHz, $CDCl_3$, *δ)*: 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.8, 7.2 Hz, 1H), 7.38 (dd, *J* = 7.8, 4.2 Hz, 1H), 7.28-7.30 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05-7.07 (m, 4H), 6.98 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, *δ*):

158.1, 149.9, 146.3, 143.6, 142.7, 136.4, 136.2, 131.8, 131.0, 130.7, 130.3, 128.6, 128.4, 126.9, 126.3, 121.4, 113.8, 55.3, 48.8. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2953, 2920, 2851, 1709, 1508, 1491, 1460, 1369, 1300, 1246, 1173, 1155, 1132, 1105, 1090, 1072, 1026, 1015, 795, 773, 758, 719, 619, 577, 538, 463, 446, 422. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{19}ClNO$, 360.1150; found 360.1151.

*8-((4-chlorophenyl)(4-nitrophenyl)methyl)quinoline (Table 6, Entry **4g**)*. yellow sticky, yield = 41.6 mg (37%). Isolated from reverse silica C-18 (20% $H_2O$/MeOH). 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.10-8.12 (m, 2H), 7.78 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.49 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.41 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.27-7.31 (m, 4H), 7.23 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.11 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 152.0, 150.1, 146.6, 146.1, 141.5, 141.0, 136.5, 132.7, 131.1, 130.4, 130.2, 128.9, 128.7, 127.6, 126.3, 123.7, 121.6, 49.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2924, 2853, 2326, 1597, 1516, 1489, 1342, 1089, 1012, 821, 790, 518. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{16}Cl\ N_2O_2$, 375.0895; found 375.0894.

*8-((4-chlorophenyl)(phenyl)methyl)-5-methylquinoline (Table 6, Entry **4h**)*. White solid, yield = 41.3 mg (40%). Mp = 116-118 ℃. Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 8.87 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.41 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.24-7.28 (m, 2H), 7.19-7.22 (m, 3H), 7.14-7.17 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 1H), 2.67 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 149.3, 146.6, 144.3, 143.4, 140.5, 133.5, 132.7, 131.8, 131.1, 130.0, 129.8, 129.7, 128.4, 128.2, 126.7, 126.3, 120.9, 49.6, 18.8. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 3026, 2920, 2851, 1740, 1599, 1487, 1086, 1011, 827, 797, 779, 733, 698, 577. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{19}ClN$, 344.1201; found 344.1203.

*(3S,3aS,5aS,9bS,E)-9-(4-methoxybenzyl)-8-(methoxyimino)-3,5a-dimethyl-3a,4,5,5a,8,9b-hexahydronaphtho[1,2-b]furan-2(3H)-one (Scheme 2, Entry **6a**)*. Use of 4-methoxyphenylboronic acid (2.5 equiv.) at 80 ℃. Yellow solid, yield = 14.9 mg (13%). Mp = 122-125 ℃. Isolated from flash chromatography (10% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, $CDCl_3$, *δ)*: 7.16 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 9.6 Hz, 1H), 6.74-6.76 (m, 2H), 5.97 (d, *J* = 10.2 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.19 (d, *J* = 14.4 Hz, 1H), 4.00 (d, *J* = 14.4 Hz, 1H), 3.90 (s, 3H), 3.75 (s, 3H), 2.23-2.29 (m, 1H), 1.92-1.95 (m, 1H), 1.72-1.75 (m, 1H), 1.59-1.63 (m, 2H), 1.46-1.51 (m, 1H), 1.26 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, *δ*): 177.9, 157.4, 148.9, 145.0, 139.5, 134.5, 129.6, 126.6, 113.3, 113.2, 82.1, 62.2, 55.3, 53.2, 41.1, 41.0, 38.8, 29.2, 25.9, 24.1, 12.7. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2934, 2324, 1773, 1508, 1240, 1157, 1057, 1032, 984, 893, 874, 802, 523. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{23}H_{28}NO_4$, 382.2013; found 382.2016.

*8-ethylquinoline (Scheme 4, Entry **8a**)*.[23] Use of $MeBF_3K$ (3 equiv.) instead of boronic acid salt at 100 ℃. Colourless liquid, yield = 28.8 mg (61%). Isolated from flash chromatography (3% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, CDCl3, *δ*): 8.94-8.95 (m, 1H), 8.15 (dd, *J* = 7.8 Hz, 1H), 7.67 (dd, *J* = 7.8 Hz, 1H), 7.58 (dd, *J* = 7.2 Hz, 1H), 7.46-7.48 (m, 1H), 7.36-7.38 (m, 1H), 3.31-3.34 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl3, *δ*): 149.3, 146.9, 143.0, 136.5, 128.5, 128.0, 126.5, 125.9, 120.9, 24.7, 15.1. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2953, 2924, 2853, 1742, 1462, 1377, 1283, 1244, 1163, 1098, 1034, 802. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{11}H_{12}N$, 158.0964; found, 158.0964.

*8-pentylquinoline (Scheme 4, Entry **8b**)*.[24] Use of *n*$BuBF_3K$ (3 equiv.) instead of boronic acid salt at 100 ℃. Yellow liquid, yield = 6.0 mg (10%). Isolated from flash chromatography (5% EtOAc/*n*-hexane). $^1H$ NMR (600 MHz, CDCl3, *δ*): 8.94 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.45-7.48 (m, 1H), 7.38 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.27 (t, *J* = 7.8 Hz, 2H), 1.77-1.82 (m, 2H), 1.36-1.46 (m, 4H), 0.89-0.91 (m, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl3, *δ*): 149.4, 147.1, 141.9, 136.5, 128.8, 128.6, 126.4, 125.9, 120.9, 32.1, 31.5, 30.5, 22.8, 14.2. IR (ZnSe) $\nu_{max}$ ($cm^{-1}$): 2955, 2924, 2857, 1597, 1499, 1466, 1366, 1261, 1163, 1078, 1026, 966, 826, 793, 758, 729. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}N$, 200.1434; found, 200.1433.

**Gram scale reaction (Scheme 3)** To an oven-dried Schlenk-flask (100 ml) charged with a spin vane magnetic stir-bar, 7-chloro-8-methylquinoline (8.0 mmol, 1.42 g), 4-chlorophenylboronic acid (20.0 mmol, 3.13 g), $[RhCp^*Cl_2]_2$ (2.5 mol%, 123.62 mg) and $Ag_2O$ (1 equiv, 1.85 g) were added under argon atmosphere, followed by the addition of dichloroethane (40 mL) and triflic anhydride (5 mol%, 67.2 µl). The subsequent reaction mixture was stirred at 100 °C for 24 h. Solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using silica gel (230−400 mesh size) and 3% EtOAc: *n*-hexane as the eluent. Product **3h** was isolated (1.50 g, 65%).

**Synthesis of 1a-$d_3$**[5d] To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 8-methylquinoline (1a) (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $CD_3COOD$ (1 equiv.) and $Cu(OAc)_2$ (2 equiv.) were added in $D_2O$ (1 mL) under air at room temperature subsequent reaction mixture was stir at 100 ℃ for 20 h. The reaction mixture was extracted with EtOAc and the organic layer was dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the crude mixture was purified by flash chromatography using silica gel (230-400 mesh size) and *n*-hexane: EtOAc as eluent and 97%-D of 1a-$d_3$ was obtained.

**Rhodacycle synthesis A** Rhodacycle intermediate **A** synthesised according to the literature procedure.[6a] Yellow solid, $^1H$ NMR (600 MHz, CDCl3, *δ*): 8.94 (dd, *J* = 5.4, 1.2 Hz, 1H), 8.09 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.62 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.42-7.47 (m, 2H), 7.36 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.95-3.98 (m, 1H), 3.68-3.71 (m, 1H), 1.62 (s, 15H). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl3, *δ*): 153.7, 151.8, 151.5, 136.7, 130.1, 128.8, 128.1, 123.1, 122.1, 93.99, 93.95, 33.8, 33.7, 9.3.

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### Notes

The authors declare no competing financial interest.

**Keywords:** Rhodium catalyst, arylation, di-arylation, 8-methyl quinolines and organoboron reagents.

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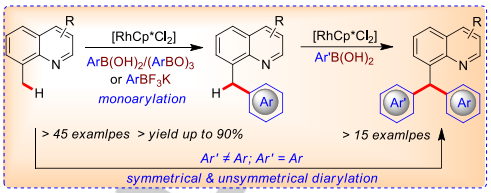
FULL PAPER

*R. Kumar, D. Parmar, S. S. Gupta, D. Chandra, A. K. Dhiman and U. Sharma**

# Cp*Rh(III)-Catalyzed Sterically Controlled C(sp$^3$)-H Selective Mono- and Diarylation of 8-Methylquinolines with Organoborons




***Arylation:*** *Monoarylation of C(sp$^3$)-H of 8-methylquinolines is disclosed along with symmetrical and unsymmetrical diarylation of 8-methylquinolines in one-pot and sequential manner, respectively. Order of reaction with respect to each reactant is first order.*