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# Direct alkenylation of alkylazaarenes with aldehydes through C($sp^3$)–H functionalization under catalytic $InCl_3$ activation

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ABSTRACT

Under the influence of $InCl_3$ as a Lewis acid catalyst, a methodology on the C($sp^3$)–H functionalization of alkylazaarenes has been demonstrated through the activation of benzylic C–H bonds towards their addition reaction with the appropriate electrophiles. This methodology was chiefly applied in the direct alkenylation of primary and secondary benzylic C–H bonds of alkylazaarenes with aldehydes. A variety of alkenyl products were afforded in generally good yields including the starting alkenyl intermediate used in the synthesis of montelukast and other related molecules.

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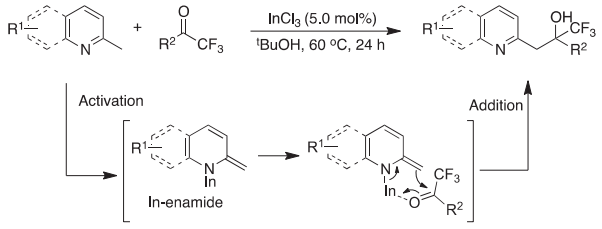
## 1. Introduction

The prevalent of the azaarene moiety among molecules in a diverse field of applications ensures that it occupies an important position in organic synthesis.[1] Unsurprisingly, a considerable degree of attention has been focused on the development of synthetic approaches towards various azaarene compounds.[2]

Since the direct functionalization of the azaarene core is traditionally cumbersome, an alternative approach that flourished during the last few years is the C($sp^3$)–H functionalization of alkylazaarenes.[3] These recent developments also represent advances in the often imposing research on the direct functionalization of C($sp^3$)–H bonds.[4]

Among the predominant recent examples are the catalytic methodologies based on the C–H addition strategy.[5] In the presence of an electrophilic species, the C–H addition is thought to proceed through a characteristically nucleophilic enamide form of the appropriate alkylazaarenes. Under either a Lewis acid or Bronsted acid catalysis, the generation of this reactive enamide intermediate is generally proposed as a consequence of the catalytic benzylic C–H activation on the substrate.[6]

Previously, we reported an In-catalyzed methodology for the C($sp^3$)–H functionalization of 2-methylazaarenes with trifluoromethyl ketones (Scheme 1).[7]




**Scheme 1.** In-catalyzed C($sp^3$)–H functionalization of 2-methylazaarenes with trifluoromethyl ketones.

Similarly, upon the C($sp^3$)–H activation effect of the Lewis acid catalyst, a reactive intermediate in the form of an In-enamide species was proposed. This is believed to be a key in the successful benzylic C–H addition to the electrophilic carbonyl carbon of trifluoromethyl ketones.

Such catalytic applicability of trivalent indium for the activation of chemical reactions is desirable due to their inherent lure of being inexpensive, low toxic and high tolerance.[8,9] However, the potential of Lewis acidic trivalent indium for this class of C($sp^3$)–H functionalization is still underdeveloped.

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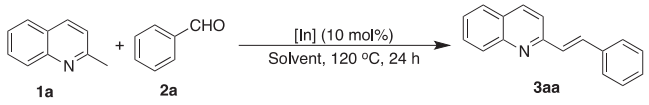
Therefore, synchronizing with our interest in the development of economical and benign metal-catalyzed organic reactions, we subsequently envisioned a further development on In-catalyzed C($sp^3$)–H functionalization of alkylazaarenes through addition reaction with electrophiles.

## 2. Results and discussion

Through the cleavage of two C($sp^3$)–H bonds of alkylazaarenes, synthesis of alkenyl products under neutral condensation conditions with aldehydes was considered.

Henceforth, we began by the reaction between quinaldine **1a** and benzaldehyde **2a** in which the incorporation of 10 mol % $InCl_3$ was found to be vital in enriching yield of **3aa** (Table 1, entries 1 and 2).[10] This set of observations formed the basis to validate the activation role of catalytic $InCl_3$ against several existing reports on catalyst-free procedures for this class of C($sp^3$)–H functionalization.[11] It is also noteworthy that only a single isomer of **3aa** as the *(E)*-styrylquinoline was identified upon $^1$H NMR analysis of the crude reaction mixture.

**Table 1**
Screening of conditions for the In-catalyzed C($sp^3$)–H alkenylation of **1a** with **2a**[a]




| Entry | [In] | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | — | $H_2O$ | 30 |
| 2 | $InCl_3$ | $H_2O$ | 68 |
| 3 | $InCl_3$ | $^t$BuOH | 76 |
| 4 | $InCl_3$ | DCM | 80 |
| 5 | $InCl_3$ | DCE | 73 |
| 6 | $InCl_3$ | Toluene | 82 |
| 7 | $InCl_3$ | THF | 88 |
| 8 | $InBr_3$ | THF | 69 |
| 9 | $In(OTf)_3$ | THF | 30 |
| 10 | $In(CF_3CO_2)_3$ | THF | 64 |

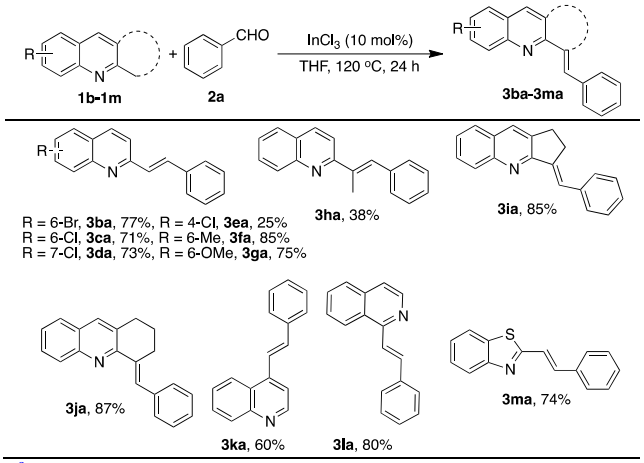
[a] General reaction conditions: **1a** (0.5 mmol), **2a** (2.0 equiv), [In] (10 mol %), Solvent (0.3 mL), 120 °C, 24 h.
[b] Isolated yield.

After a series of attempts using several different solvents, the reaction yield was subsequently further improved with the isolation of **3aa** in 88% yield (entry 7). The applicability of trivalent indium was also concluded with $InCl_3$ deemed as the best among other In sources screened (entries 8–10).

Utilizing the catalytic influence of $InCl_3$ in THF as the general reaction conditions, the C($sp^3$)–H alkenylation of various alkylazaarenes with **2a** was next demonstrated (Scheme 2).

We started off with the synthesis of several 2-styrylquinolines (**3ba**–**3ga**) from differently substituted quinaldines.[12] Reasonably good yields were obtained in all cases except in the example using 4-chloroquinaldine whereby only 25% yield of the **3ea** was isolated.

The alkenylation of a higher order alkyl-substituted azaarene was next attempted through the functionalization of secondary benzylic C–H bonds of 2-ethylquinoline (**1h**) with **2a** from which **3ha** was obtained in 38% yield. Despite the modest yield from our maiden attempt, studies with several other substrates bearing similar secondary C($sp^3$)–H bonds were also considered. Gratifyingly, with 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**1i**) and 1,2,3,4-tetrahydroacridine (**1j**), the corresponding alkenyl products **3ia** and **3ja** were sumptuously yielded in 85% and 87%, respectively. However, other attempts with substrates possessing larger aliphatic ring sizes (7- and 8-membered) as well as 2-(but-3-en-1-yl)quinoline




[a] General reaction conditions: **1b-1m** (0.5 mmol), **2a** (2.0 equiv.), $InCl_3$ (10 mol%), THF (0.3 mL), 120 °C, 24 h.

**Scheme 2.** Scope of alkylazaarenes[a].

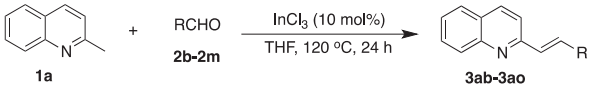
and 2-phenethylquinoline were disappointingly found to be unreactive with only the starting materials being recovered.

Besides 2-alkyl substituted quinolines, the functionalization of a methyl group at the 4-position of the quinoline core was also feasible. This was illustrated with our successful attempt using lepidine in which a satisfactory 60% yield of **3ka** was obtained.

Additionally, **3la** and **3ma** were also easily synthesized from the corresponding 1-methylisoquinoline (**1l**) and 2-methylbenzo[*d*]thiazole (**1m**) in 80% and 74% yields, respectively. However, attempts with 3-methylisoquinoline, 2-picoline and 2,6-lutidine were unsuccessful. Presumably, this could be attributed to the severe aromaticity disruption on these substrates en route to the generation of the respective In-enamide intermediates. An attempt with 2-methylquinoxaline also failed due to substrate decomposition.

Scope of aldehydes for this In-catalyzed C($sp^3$)–H functionalization was next tested (Table 2).

**Table 2**
Scope of aldehydes[a]




| Entry | Aldehyde, *R* | Product | Yield (%)[b] |
|---|---|---|---|
| 1 | **2b**, 4-Br$C_6H_4$ | **3ab** | 82 |
| 2 | **2c**, 4-Cl$C_6H_4$ | **3ac** | 84 |
| 3 | **2d**, 4-F$C_6H_4$ | **3ad** | 83 |
| 4 | **2e**, 4-$F_3C$$C_6H_4$ | **3ae** | 80 |
| 5 | **2f**, 4-Ph$C_6H_4$ | **3af** | 80 |
| 6 | **2g**, 4-Me$C_6H_4$ | **3ag** | 70 |
| 7 | **2h**, 4-OMe$C_6H_4$ | **3ah** | 60 |
| 8 | **2i**, 2-pyridyl | **3ai** | 75 |
| 9 | **2j**, 3-pyridyl | **3aj** | 83 |
| 10 | **2k**, 4-pyridyl | **3ak** | 80 |
| 11 | **2l**, 2-furyl | **3al** | 85 |
| 12 | **2m**, 2-thienyl | **3am** | 82 |
| 13 | **2n**, (*E*)-PhCH=CH | **3an** | 60 |
| 14 | **2o**, $(CH_3)_3C$ | **3ao** | 20 |

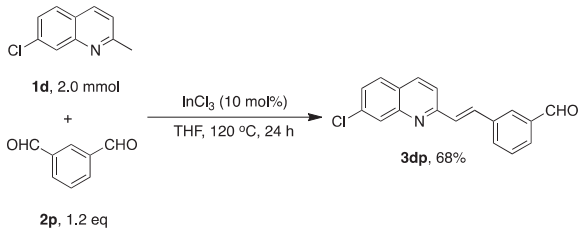
[a] General reaction conditions: **1a** (0.5 mmol), **2b**–**2o** (2.0 equiv), $InCl_3$ (10 mol %), THF (0.3 mL), 120 °C, 24 h.
[b] Isolated yield.

Generally, with various substituted benzaldehydes, good yields ranging from 60% to 84% of the corresponding 2-styrylquinolines

were obtained (entries 1–7). Pyridinecarboxaldehydes **2i**, **2j**, and **2k** were also compatible with the isolation of the respective polynitrogen-containing alkenyl products in 75%, 83% and 80% yields (entries 8–10). Other heteroaromatic aldehydes as **2l** and **2m** also furnished the intended product in high yields (entries 11 and 12).

Comparatively, a slightly lower reactivity of cinnamaldehyde **2n** was observed as indicated by the moderate 60% yield of **3an** (entry 13). However, with the aliphatic aldehyde **2o**, a severely diminished reactivity was evident with merely 20% yield of **3ao** was obtainable (entry 14).

The synthetic utility of this In-catalyzed C($sp^3$)–H functionalization methodology was also demonstrated (Scheme 3).




**Scheme 3.** Preparation of **3dp**.

From a 2.0 mmol scaled reaction in the presence of 1.2 equiv **2p**, the intended product **3dp** was obtained in a good yield of 68%. Synthetically, **3dp** is an important starting intermediate towards montelukast and other related molecules.[13]

We next attempted the synthesis of several other alkenyl products based on the secondary benzylic C–H functionalization. On the additional ground related to the importance of **1i**,[14] the application of this In-catalyzed methodology involving **1i** with several aldehydes was initiated (Fig. 1).

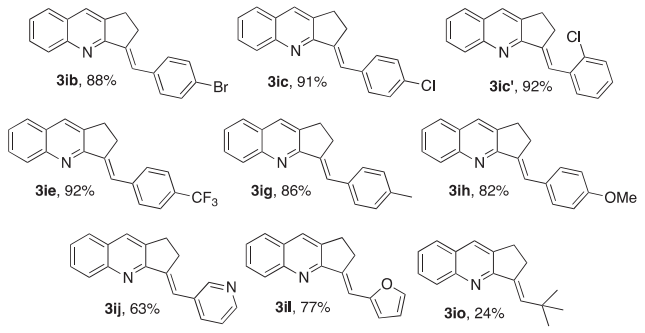


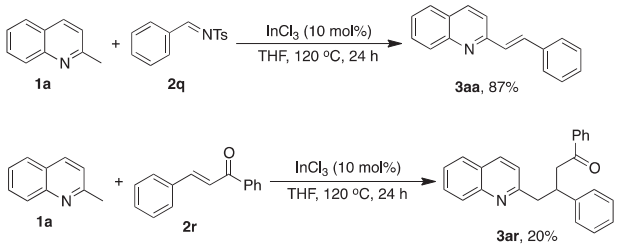

**Fig. 1.** In-catalyzed C($sp^3$)–H alkenylation of **1i** with various aldehydes under the general reaction conditions of **1i** (0.5 mmol), aldehydes (2.0 equiv), $InCl_3$ (10 mol %), THF (0.3 mL), 120 °C, 24 h.

High yields of the intended products were obtained from the reaction with substituted benzaldehydes (82%–92%). 2-Substituted benzaldehyde as 2-chlorobenzaldehyde also exemplified no effect on the reaction efficiency as an excellent 92% yield of **3ic′** was obtained. However, other aldehydes tested exhibited lower reactivity with **2o** noticeably affording only 24% yield of **3io**.

Under the general reaction conditions, the C($sp^3$)–H functionalization with other electrophiles were also attempted (Scheme 4).

**2q** was firstly tested as a representative C=N electrophile from which **3aa** was obtained in essentially the same efficiency as the analogous reaction between **1a** and **2a**.

However, with **2r** as a potential C=C electrophile, only 20% of the intended **3ar** was isolated. Nonetheless, this observation




**Scheme 4.** In-catalyzed C($sp^3$)–H functionalization of **1a** with C=N and C=C electrophiles.

proved to be significant as no intended product was formed when the reaction was conducted in the absence of $InCl_3$. Furthermore, despite its low yielding, the In-catalyzed protocol exhibited only a single C($sp^3$)–H bond cleavage and no addition to the carbonyl of **2r**.

The unreactive nature of ketones was also observed in the cases of our attempts with acetophenone and benzophenone. The electrophilic C=C of *trans*-β-nitrostyrene was also insusceptible towards the C–H addition.

## 3. Conclusion

In conclusion, an In-catalyzed C($sp^3$)–H functionalization of alkylazaarenes with the appropriate electrophiles through the benzylic C–H addition was successfully developed. Under the catalytic C($sp^3$)–H activation effect of $InCl_3$ Lewis acid, the synthesis of various alkenyl products was described as the C($sp^3$)–H alkenylation of alkylazaarenes with aldehydes. A similar strategy using representative electrophilic C=N and C=C was also successfully demonstrated.

## 4. Experimental section

### 4.1. General

All commercially available chemicals and anhydrous solvents were used directly upon purchase from suppliers. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plates (0.2 mm thickness) and visualized using UV radiation on Spectroline Model ENF-24061/F 254 nm. Flash chromatography was performed using Merck silica gel 60 with AR grade solvents. Melting points were determined using OptiMelt automated melting point system and are uncorrected. IR spectra were recorded using Perkin–Elmer Paragon 1000 FTIR spectrophotometer on KBr plates. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX 400 spectrophotometer. Chemical shifts for $^1H$ and $^{13}C$ NMR are reported as $\delta$ in units of parts per million (ppm) downfield from $SiMe_4$ and relative to the residual signal of $CDCl_3$. Multiplicities are reported based on apparent multiplicities and coupling constants ($J$ values) are reported in unit of Hertz (Hz). Elemental analysis was performed on vario MICRO CUBE CHNS. Mass spectroscopy was performed using Water Q-Tof Permies Mass Spectrometer.

### 4.2. Synthesis of alkylazaarenes 1h–j

*4.2.1. 2-Ethylquinoline (**1h**).* To an oven-dried RBF equipped with a magnetic stir bar, quinaldine (5.0 mmol) and anhydrous ether (5 mL) were added under an atmosphere of nitrogen. The mixture was subsequently cooled to 0 °C prior to the dropwise addition of *n*-BuLi (1.2 equiv). The resulting reaction mixture was then stirred at rt for 2 h followed by the dropwise addition of iodomethane (2.0 equiv). After stirring for a further 5 h at rt, water (5 mL) was

slowly poured to the reaction mixture and the crude product was extracted using EtOAc (3×10 mL). The combined organic layer was then dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (hexane/EtOAc) then afforded **1h** as a yellow oil in 81% yield. **1h** is a known compound.[6n]

*4.2.2. 2,3-Dihydro-1H-cyclopenta[b]quinoline (**1i**) and 1,2,3,4-tetrahydroacridine (**1j**).* To an oven-dried RBF equipped with a magnetic stir bar, 2-nitrobenzaldehyde (5.0 mmol) was dissolved in EtOH (15 mL). Iron powder (4.0 equiv) and 0.1 N HCl (5.0 mol %, 2.5 mL) were next added after which the resulting mixture was then stirred at 95 °C for 40 min. Upon cooling, cyclopentanone or cyclohexanone (1.0 equiv) was added followed by the portionwise addition of powdered KOH (1.2 equiv). Heating was continued at 95 °C for another 30 min. The reaction mixture was then filtered through a pad of Celite with the resulting filtrate subsequently washed with water and extracted using dichloromethane (3×10 mL). The combined organic layers were further washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (hexane/EtOAc) then afforded **1i** or **1j** as yellow solid in 87% or 90% yield, respectively. **1i** and **1j** are known compounds.[15]

### 4.3. General procedure for $InCl_3$-catalyzed C($sp^3$)–H functionalization

To a screw-capped reaction vial equipped with a magnetic stir bar, $InCl_3$ (10 mol %), alkylazaarene (0.5 mmol), aldehyde (2.0 equiv) and THF (0.3 mL) were sequentially added. The resulting reaction vial was then placed into a preheated oil bath at 120 °C with vigorous stirring. After 24 h, the reaction vial was taken out of the oil bath and allowed to cool to room temperature. The reaction mixture was next concentrated under reduced pressure and the remaining residue was purified by silica gel chromatography (hexane/EtOAc) to afford the desired product.

*4.3.1. (E)-2-Styrylquinoline (**3aa**).*[10] White solid (88%, 101.8 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.41–7.35 (m, 1H), 7.39–7.44 (m, 3H), 7.50 (t, $J$=7.5 Hz, 1H), 7.64–7.73 (m, 5H), 7.79 (d, $J$=8.0 Hz, 1H), 8.08, (d, $J$=9.0 Hz, 1H), 8.14 (d, $J$=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.3, 126.2, 127.3, 127.4, 127.5, 128.7, 128.8, 129.1, 129.2, 129.8, 134.5, 136.4, 136.6, 148.3, 156.0; Elemental Anal. calcd (%) for $C_{17}H_{13}N$: C 88.28, H 5.67, N 6.06; found: C 87.90, H 5.70, N 6.02.

*4.3.2. (E)-6-Bromo-2-styrylquinoline (**3ba**).*[10] White solid (77%, 119.4 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.32–7. 43 (m, 4H), 7.63–7.73 (m, 4H), 7.77 (dd, $J$=2.0, 9.0 Hz, 1H), 7.93–7.95 (m, 2H), 8.04 (d, $J$=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.9, 120.3, 127.4, 128.4, 128.6, 128.9, 129.6, 130.9, 133.2, 135.0, 135.3, 136.4, 146.9, 156.4; HRMS (ESI) calcd for $C_{17}H_{13}BrN$ [M+H]: 310.0231, found: 310.0231.

*4.3.3. (E)-6-Chloro-2-styrylquinoline (**3ca**).*[10] White solid (71%, 94.4 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.32–7.43 (m, 4H), 7.63–7.72 (m, 5H), 7.77 (d, $J$=2.0 Hz, 1H), 8.01 (d, $J$=9.0 Hz, 1H), 8.05 (d, $J$=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 120.3, 126.2, 127.3, 127.9, 128.6, 128.8, 128.9, 130.7, 130.8, 131.8, 134.9, 135.4, 136.4, 146.7, 156.3; HRMS (ESI) calcd for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0736.

*4.3.4. (E)-7-Chloro-2-styrylquinoline (**3da**).*[10] White solid (73%, 97.0 mg); $R_f$ (20% *EtOAc/hexane*) 0.61; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.32–7.46 (m, 5H), 7.65 (d, $J$=8.5 Hz, 3H), 7.70–7.74 (m, 2H), 8.08–8.11 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.6, 119.7, 125.7, 127.1, 127.4, 128.2, 128.5, 128.7, 128.9, 135.2, 135.5, 136.1, 136.3, 148.7, 156.9; HRMS (ESI) calcd for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0737.

*4.3.5. (E)-4-Chloro-2-styrylquinoline (**3ea**).*[16] Light yellow solid (25%, 33.7 mg); $R_f$ (20% *EtOAc/hexane*) 0.57; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.31–7.36 (m, 2H), 7.39–7.43 (m, 2H), 7.56–7.60 (m, 1H), 7.63–7.70 (m, 3H), 7.73–7.77 (m, 2H), 8.90 (d, $J$=8.5 Hz, 1H), 8.17–8.20 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.3, 124.0, 125.5, 127.1, 127.4, 128.0, 128.9, 129.0, 129.6, 130.7, 135.4, 136.2, 142.7, 149.1, 156.0; HRMS (ESI) calcd for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0737.

*4.3.6. (E)-6-Methyl-2-styrylquinoline (**3fa**).*[10] White solid (85%, 104.3 mg); $R_f$ (20% *EtOAc/hexane*) 0.43; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.32–7.34 (m, 1H), 2.54 (s, 3H), 7.38–7.42 (m, 3H), 7.53–7.55 (m, 2H), 7.63–7.68 (m, 4H), 7.97 (d, $J$=8.0 Hz, 1H), 8.04 (d, $J$=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.6, 119.3, 126.5, 127.2, 127.4, 128.5, 128.8, 128.9, 129.2, 132.0, 133.9, 135.7, 136.1, 136.7, 146.9, 155.2; Elemental Anal. calcd (%) for $C_{18}H_{15}N$: C 88.13, H 6.16, N 5.71; found: C 87.99, H 6.18, N 5.71.

*4.3.7. (E)-6-Methoxy-2-styrylquinoline (**3ga**).*[10] White solid (75%, 98.1 mg); $R_f$ (20% *EtOAc/hexane*) 0.34; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.94 (s, 3H), 7.07 (d, $J$=3.0 Hz, 1H), 7.31–7.42 (m, 5H), 7.60–7.65 (m, 4H), 7.98 (d, $J$=9.0 Hz, 1H), 8.03 (d, $J$=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.6, 105.3, 119.6, 122.3, 127.1, 128.3, 128.8, 129.1, 130.7, 133.2, 135.1, 136.7, 144.3, 153.7, 157.7; HRMS (ESI) calcd for $C_{18}H_{16}NO$ [M+H]: 262.1232, found: 262.1225.

*4.3.8. (E)-2-(1-Phenylprop-1-en-2-yl)quinoline (**3ha**).*[17] White solid (38%, 46.0 mg); $R_f$ (20% *EtOAc/hexane*) 0.52; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.54 (d, $J$=1.0 Hz, 3H), 7.31 (t, $J$=7.5 Hz, 1H), 7.43 (t, $J$=7.5 Hz, 2H), 7.49–7.53 (m, 4H), 7.70–7.74 (m, 1H), 7.76 (d, $J$=8.5 Hz, 1H), 7.81 (dd, $J_1$=8.0 Hz, $J_2$=1.5 Hz, 1H), 8.14 (d, $J$=8.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.1, 118.7, 126.1, 127.0, 127.1, 127.3, 128.2, 129.46, 129.48, 129.6, 131.7, 136.1, 137.7, 137.9, 147.8, 160.1; HRMS (ESI) calcd for $C_{18}H_{16}N$ [M+H]: 246.1282, found: 246.1284.

*4.3.9. (E)-3-Benzylidene-2,3-dihydro-1H-cyclopenta[b]quinoline (**3ia**).* Light yellow solid (85%, 109.8 mg); mp 138–140 °C; $R_f$ (20% *EtOAc/hexane*) 0.54; $\nu_{max}$ (KBr) 3047, 2880, 1604, 1565, 1496, 1444, 1404, 1277, 1239, 1199, 1148, 957, 911, 877, 859, 726 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.21–3.25 (m, 4H), 7.28–7.32 (m, 1H), 7.41–7.47 (m, 3H), 7.62–7.67 (m, 3H), 7.72 (d, $J$=8.0 Hz, 1H), 7.83–7.84 (m, 1H), 7.93 (s, 1H), 8.12 (d, $J$=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 27.9, 29.1, 124.8, 125.8, 127.38, 127.4, 128.3, 128.5, 128.8, 129.2, 129.5, 131.3, 137.0, 137.5, 140.8, 148.3, 162.2; HRMS (ESI) calcd for $C_{19}H_{16}N$ [M+H]: 258.1282, found: 258.1284.

*4.3.10. (E)-4-Benzylidene-1,2,3,4-tetrahydroacridine (**3ja**).* Yellow solid (87%, 117.5 mg); mp 105–107 °C; $R_f$ (20% *EtOAc/hexane*) 0.60; $\nu_{max}$ (KBr) 3049, 2947, 2871, 1584, 1489, 1442, 1409, 1309, 1253, 1161, 911, 855, 749 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.90–1.96 (m, 2H), 3.00–3.05 (m, 4H), 7.29 (t, $J$=7.0 Hz, 1H), 7.39–7.47 (m, 3H), 7.51–7.53 (m, 2H), 7.62–7.66 (m, 1H), 7.71 (d, $J$=8.0 Hz, 1H), 7.84 (s, 1H), 8.09 (d, $J$=8.5 Hz, 1H), 8.24 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 23.1, 28.5, 30.3, 125.9, 126.7, 127.0, 127.7, 128.1, 128.7, 129.3, 129.4, 129.9, 131.4, 134.7, 135.9, 137.9, 147.2, 154.4; HRMS (ESI) calcd for $C_{20}H_{18}N$ [M+H]: 272.1439, found: 272.1441.

*4.3.11. (E)-4-Styrylquinoline (**3ka**).*[17] Light yellow solid (60%, 68.9 mg); $R_f$ (20% *EtOAc/hexane*) 0.23; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.31–7.38 (m, 2H), 7.41–7.45 (m, 2H), 7.57–7.64 (m, 4H), 7.71–7.75

(m, 1H), 7.81 (d, *J*=16.5 Hz, 1H), 8.15 (d, *J*=8.5 Hz, 1H), 8.21 (d, *J*=8.5 Hz, 1H), 8.90 (d, *J*=3.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 117.1, 122.9, 123.5, 126.5, 127.1, 128.8, 128.9, 129.3, 130.2, 135.1, 136.6, 142.9, 148.7, 150.2; HRMS (ESI) calcd for $C_{17}H_{14}N$ [M+H]: 232.1126, found: 232.1127.

*4.3.12. (E)-1-Styrylisoquinoline (**3la**).*[10] Light yellow solid (80%, 92.0 mg); $R_f$ (20% *EtOAc/hexane*) 0.40; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.32–7.36 (m, 1H), 7.41–7.44 (m, 2H), 7.54 (d, *J*=5.5 Hz, 1H), 7.58–7.72 (m, 4H), 7.80 (d, *J*=8.5 Hz, 1H), 8.01 (s, 2H), 8.37 (d, *J*=8.0 Hz, 1H), 8.57 (d, *J*=5.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.9, 122.8, 124.4, 126.7, 127.1, 127.2, 127.4, 128.5, 128.7, 129.8, 135.8, 136.6, 136.9, 142.4, 154.4; HRMS (ESI) calcd for $C_{17}H_{14}N$ [M+H]: 232.1126, found: 232.1120.

*4.3.13. (E)-2-Styrylbenzo[d]thiazole (**3ma**).* [18] Yellow solid (74%, 88.4 mg); $R_f$ (20% *EtOAc/hexane*) 0.54; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.34–7.43 (m, 5H), 7.45–7.50 (m, 1H), 7.51–7.59 (m, 3H), 7.86 (d, *J*=8.0 Hz, 1H), 8.01 (d, *J*=8.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 121.5, 122.1, 123.0, 125.4, 126.3, 127.4, 129.0, 129.4, 134.4, 135.4, 137.7, 153.9, 167.0; HRMS (ESI) calcd for $C_{15}H_{12}NS$ [M+H]: 238.0690, found: 238.0689.

*4.3.14. (E)-2-(4-Bromostyryl)quinoline (**3ab**).*[10] Light yellow solid (82%, 127.2 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J*=16.5 Hz, 1H), 7.45–7.51 (m, 5H), 7.58–7.62 (m, 2H), 7.70 (t, *J*=7.5 Hz, 1H), 7.76 (d, *J*=8.0 Hz, 1H), 8.08 (d, *J*=8.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.4, 122.6, 126.3, 127.4, 127.5, 128.7, 129.3, 129.7, 129.9, 132.0, 133.1, 135.5, 136.5, 148.3, 155.6; HRMS (ESI) calcd for $C_{17}H_{13}BrN$ [M+H]: 310.0231, found: 310.0234.

*4.3.15. (E)-2-(4-Chlorostyryl)quinoline (**3ac**).*[10] White solid (84%, 111.7 mg); $R_f$ (20% *EtOAc/hexane*) 0.43; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35–7.39 (m, 3H), 7.51 (t, *J*=7.5 Hz, 1H), 7.57 (d, *J*=9.0 Hz, 2H), 7.63–7.67 (m, 2H), 7.71 (t, *J*=7.5 Hz, 1H), 7.79 (d, *J*=8.0 Hz, 1H), 8.08 (d, *J*=8.5 Hz, 1H), 8.14 (d, *J*=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.4, 126.3, 127.4, 127.6, 128.4, 129.0, 129.3, 129.6, 129.9, 133.1, 134.3, 135.1, 136.5, 148.3, 155.6; HRMS (ESI) calcd for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0730.

*4.3.16. (E)-2-(4-Fluorostyryl)quinoline (**3ad**).*[10] White solid (83%, 103.5 mg); $R_f$ (20% *EtOAc/hexane*) 0.40; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.09 (t, *J*=8.5 Hz, 2H), 7.32 (d, *J*=16.0 Hz, 1H), 7.50 (t, *J*=7.0 Hz, 1H), 7.59–7.79 (m, 6H), 8.10 (dd, $J_1$=8.5 Hz, $J_2$=19.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 115.9 (d, *J*=22.0 Hz), 119.3, 126.2, 127.4, 128.8 (d, *J*=2.5 Hz), 127.5, 128.9 (d, *J*=8.0 Hz), 129.2, 129.8, 132.8 (d, *J*=3.5 Hz), 133.2, 136.4, 148.3, 155.8, 163.0 (d, *J*=249.0 Hz); HRMS (ESI) calcd for $C_{17}H_{13}FN$ [M+H]: 250.1042, found: 250.1029.

*4.3.17. (E)-2-(4-(Trifluoromethyl)styryl)quinoline (**3ae**).*[10] White solid (80%, 119.7 mg); $R_f$ (20% *EtOAc/hexane*) 0.40; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.46–7.55 (m, 2H), 7.65–7.75 (m, 7H), 7.81 (d, *J*=8.0 Hz, 1H), 8.09 (d, *J*=8.5 Hz, 1H), 8.17 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.5, 124.1 (q, *J*=272.0 Hz), 125.8 (q, *J*=3.5 Hz), 126.6, 127.3, 127.6, 129.3, 130.0, 130.2 (q, *J*=32.5 Hz), 131.4, 132.7, 136.6, 140.01, 140.02, 148.3, 155.2; HRMS (ESI) calcd for $C_{18}H_{13}F_3N$ [M+H]: 300.1000, found: 300.0988.

*4.3.18. (E)-2-(2-([1,1′-Biphenyl]-4-yl)vinyl)quinoline (**3af**).*[10] Light yellow solid (80%, 123.2 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35–7.39 (m, 1H), 7.44–7.53 (m, 4H), 7.64–7.81 (m, 10H), 8.09 (d, *J*=8.5 Hz, 1H), 8.14 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.3, 126.2, 127.0, 127.4, 127.47, 127.53, 127.7, 128.8, 128.9, 129.0, 129.2, 129.8, 134.0, 135.6, 136.4, 140.5, 141.4, 148.3, 156.0; HRMS (ESI) calcd for $C_{23}H_{18}N$ [M+H]: 308.1439, found: 308.1442.

*4.3.19. (E)-2-(4-Methylstyryl)quinoline (**3ag**).*[10] White solid (70%, 86.0 mg); $R_f$ (20% *EtOAc/hexane*) 0.52; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.22 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=16.5 Hz, 1H), 7.49 (t, *J*=7.5 Hz, 1H), 7.55 (d, *J*=8.0 Hz, 2H), 7.65–7.72 (m, 3H), 7.78 (d, *J*=8.0 Hz, 1H), 8.07 (d, *J*=8.5 Hz, 1H), 8.12 (d, *J*=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.4, 119.2, 126.1, 127.2, 127.3, 127.5, 128.1, 129.2, 129.6, 129.7, 133.8, 134.4, 136.3, 138.8, 148.3, 156.2; Elemental Anal. calcd (%) for $C_{18}H_{15}N$: C 88.13, H 6.16, N 5.71; found: C 87.92, H 6.20, N 5.72.

*4.3.20. (E)-2-(4-Methoxystyryl)quinoline (**3ah**).*[10] Yellow solid (60%, 78.8 mg); $R_f$ (20% *EtOAc/hexane*) 0.36; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.94 (d, *J*=9.0 Hz, 2H), 7.28 (d, *J*=17.0 Hz, 1H), 7.48 (t, *J*=7.5 Hz, 1H), 7.57–7.72 (m, 5H), 7.77 (d, *J*=8.0 Hz, 1H), 8.06 (d, *J*=8.5 Hz, 1H), 8.11 (d, *J*=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.3, 119.2, 126.0, 126.9, 127.3, 127.5, 128.7, 129.1, 129.4, 129.7, 134.1, 136.3, 148.3, 156.4, 160.2; HRMS (ESI) calcd for $C_{18}H_{16}NO$ [M+H]: 262.1232, found: 262.1222.

*4.3.21. (E)-2-(2-(Pyridin-2-yl)vinyl)quinoline (**3ai**).*[10] Light yellow solid (75%, 87.3 mg); $R_f$ (20% *EtOAc/hexane*) 0.17; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.21 (ddd, $J_1$=7.0 Hz, $J_2$=5.0 Hz, $J_3$=1.0 Hz, 1H); 7.51 (t, *J*=7.5 Hz, 1H), 7.58 (d, *J*=8.0 Hz, 1H), 7.67–7.74 (m, 3H), 7.79–7. 88 (m, 3H), 8.10 (d, *J*=9.0 Hz, 1H), 8.15 (d, *J*=8.5 Hz, 1H), 8.65–8.66 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 120.3, 122.78, 122.8, 126.4, 127.5, 127.6, 129.4, 129.8, 132.6, 133.7, 136.5, 136.6, 148.3, 149.8, 155.1, 155.3; HRMS (ESI) calcd for $C_{16}H_{13}N_2$ [M+H]: 233.1078, found: 233.1075.

*4.3.22. (E)-2-(2-(Pyridin-3-yl)vinyl)quinoline (**3aj**).*[10] Light yellow solid (83%, 96.4 mg); $R_f$ (20% *EtOAc/hexane*) 0.36; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, $J_1$=5.0 Hz, $J_2$=8.0 Hz 1H), 7.42 (d, *J*=16.5 Hz, 1H), 7.50 (t, *J*=7.5 Hz, 1H), 7.61–7.78 (m, 4H), 7.92 (d, *J*=8.0 Hz, 1H), 8.10 (dd, $J_1$=8.5 Hz, $J_2$=12.0 Hz, 2H), 8.54 (s, 1H), 8.83 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.4, 123.7, 126.5, 127.52, 127.55, 129.3, 129.9, 130.6, 130.9, 132.3, 133.3, 136.6, 148.2, 149.2, 149.4, 155.2; HRMS (ESI) calcd for $C_{16}H_{13}N_2$ [M+H]: 233.1078, found: 233.1075.

*4.3.23. (E)-2-(2-(Pyridin-4-yl)vinyl)quinoline (**3ak**).*[10] Yellow solid (80%, 93.1 mg); $R_f$ (50% *EtOAc/hexane*) 0.23; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.48–7.83 (m, 8H), 8.10 (d, *J*=9.0 Hz, 1H), 8.18 (d, *J*=9.0 Hz, 1H), 8.64 (d, *J*=5.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.6, 121.4, 126.8, 127.6, 127.7, 129.4, 130.0, 131.5, 133.3, 136.7, 143.8, 149.7, 150.4, 154.7; HRMS (ESI) calcd for $C_{16}H_{13}N_2$ [M+H]: 233.1078, found: 233.1078.

*4.3.24. (E)-2-(2-(Furan-2-yl)vinyl)quinoline (**3al**).*[10] Brown solid (85%, 94.4 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): δ 6.47 (dd, $J_1$=3.0 Hz, $J_2$=1.5 Hz, 1H), 6.55 (d, *J*=3.5 Hz, 1H), 7.28 (d, *J*=16.5 Hz, 1H), 7.46–7.58 (m, 4H), 7.69 (t, *J*=7.5 Hz, 1H), 7.77 (d, *J*=8.0 Hz, 1H), 8.06 (d, *J*=8.5 Hz, 1H), 8.10 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 111.1, 112.0, 119.9, 121.7, 126.0, 126.8, 127.3, 127.5, 129.2, 129.7, 136.3, 143.2, 148.3, 152.8, 155.6; HRMS (ESI) calcd for $C_{15}H_{12}NO$ [M+H]: 222.0919, found: 222.0914.

*4.3.25. (E)-2-(2-(Thiophen-2-yl)vinyl)quinoline (**3am**).*[10] Yellow solid (82%, 97.2 mg); $R_f$ (20% *EtOAc/hexane*) 0.53; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.05 (dd, $J_1$=5.0 Hz, $J_2$=3.5 Hz, 1H), 7.19–7.24 (m, 2H), 7.29 (d, *J*=5.0 Hz, 1H), 7.47–7.51 (m, 1H), 7.58 (d, *J*=9.0 Hz, 1H), 7.68–7.72 (m, 1H), 7.77 (d, *J*=8.5 Hz, 1H), 7.85 (d, *J*=16.0 Hz, 1H), 8.06 (d, *J*=8.5 Hz, 1H), 8.11 (d, *J*=9.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$):

δ 119.4, 126.0, 126.1, 127.3, 127.5, 127.8, 128.1, 128.2, 129.1, 129.7, 136.3, 142.1, 148.3, 155.5; HRMS (ESI) calcd for $C_{15}H_{12}NS$ [M+H]: 238.0690, found: 238.0685.

*4.3.26. 2-((1E,3E)-4-Phenylbuta-1,3-dien-1-yl)quinoline (**3an**).*[10] Yellow solid (60%, 77.0 mg); $R_f$ (20% *EtOAc/hexane*) 0.51; $^1$H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, *J*=15.5 Hz, 1H), 6.95 (d, *J*=15.5 Hz, 1H), 7.07 (dd, $J_1$=15.5 Hz, $J_2$=11.0 Hz, 1H), 7.26–7.29 (m, 1H), 7.36 (t, *J*=7.5 Hz, 2H), 7.46–7.59 (m, 5H), 7.69 (t, *J*=8.0 Hz, 1H), 7.77 (d, *J*=8.0 Hz, 1H), 8.05 (d, *J*=8.5 Hz, 1H), 8.10 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.5, 126.1, 126.8, 127.3, 127.5, 128.2, 128.6, 128.8, 129.2, 129.7, 132.9, 134.9, 136.0, 136.2, 137.0, 148.4, 156.0; HRMS (ESI) calcd for $C_{19}H_{16}N$ [M+H]: 258.1282, found: 258.1272.

*4.3.27. (E)-2-(3,3-Dimethylbut-1-en-1-yl)quinoline (**3ao**).*[6c] Light yellow oil (20%, 21.2 mg); $R_f$ (20% *EtOAc/hexane*) 0.60; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 9H), 6.66 (d, *J*=16.5 Hz, 1H), 6.83 (d, *J*=16.5 Hz, 1H), 7.46–7.48 (m, 1H), 7.57 (d, *J*=8.5 Hz, 1H), 7.65–7.67 (m, 1H), 7.74–7.76 (m, 1H), 8.05 (t, *J*=9.5 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 29.5, 33.9, 118.6, 125.6, 126.5, 127.2, 127.4, 129.1, 129.5, 136.2, 148.1, 148.3, 156.9; HRMS (ESI) calcd for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1437.

*4.3.28. (E)-3-(2-(7-Chloroquinolin-2-yl)vinyl)benzaldehyde (**3dp**).*[10] Yellow solid (68%, 402 mg); $R_f$ (20% *EtOAc/hexane*) 0.36; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.42–7.47 (m, 2H), 7.58 (t, *J*=8.0 Hz, 1H), 7.62 (d, *J*=8.5 Hz, 1H), 7.72 (d, *J*=9.0 Hz, 1H), 7.78 (d, *J*=16.5 Hz, 1H), 7.84 (d, *J*=7.5 Hz, 1H), 7.88 (d, *J*=7.5 Hz, 1H), 8.08–8.13 (m, 3H), 10.07 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 120.0, 125.9, 127.4, 128.2, 128.3, 128.7, 129.6, 129.8, 130.2, 133.0, 133.5, 135.8, 136.4, 137.0, 137.4, 148.7, 156.2, 192.1; HRMS (ESI) calcd for $C_{18}H_{13}ClNO$ [M+1]: 294.0685, found: 294.0681.

*4.3.29. (E)-3-(4-Bromobenzylidene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ib**).* Yellow solid (88%, 147.9 mg); mp 191–193 °C; $R_f$ (20% *EtOAc/hexane*) 0.54; $\nu_{max}$ (KBr) 3087, 2915, 1599, 1564, 1487, 1426, 1406, 1275, 1153, 1135, 1073, 1005, 893, 824, 759 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.18–3.22 (m, 4H), 7.45–7.48 (m, 3H), 7.52–7.54 (m, 2H), 7.65 (t, *J*=7.5 Hz, 1H), 7.72–7.74 (m, 2H), 7.96 (s, 1H), 8.10 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.1, 121.3, 123.5, 126.0, 127.5, 128.4, 128.9, 129.3, 130.9, 131.4, 131.7, 136.4, 137.0, 141.6, 148.4, 161.9; HRMS (ESI) calcd for $C_{19}H_{15}BrN$ [M+H]: 336.0388, found: 336.0389.

*4.3.30. (E)-3-(4-Chlorobenzylidene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ic**).* Yellow solid (91%, 132.6 mg); mp 142–144 °C; $R_f$ (20% *EtOAc/hexane*) 0.51; $\nu_{max}$ (KBr) 3042, 2915, 1603, 1563, 1497, 1489, 1428, 1406, 1272, 1134, 1095, 1011, 895, 829, 749 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.17–3.25 (m, 4H), 7.35–7.38 (m, 2H), 7.44–7.48 (m, 1H), 7.53 (d, *J*=8.5 Hz, 2H), 7.63–7.67 (m, 1H), 7.71–7.76 (m, 2H), 7.94 (s, 1H), 8.10 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.0, 123.5, 125.9, 127.5, 128.4, 128.7, 128.9, 129.2, 130.6, 131.4, 133.1, 136.0, 136.9, 141.4, 148.3, 161.9; HRMS (ESI) calcd for $C_{19}H_{15}ClN$ [M+H]: 292.0893, found: 292.0892.

*4.3.31. (E)-3-(2-Chlorobenzylidene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ic′**).* Yellow solid (92%, 133.7 mg); mp 142–144 °C; $R_f$ (20% *EtOAc/hexane*) 0.51; $\nu_{max}$ (KBr) 3048, 2880, 1630, 1554, 1500, 1604, 1438, 1408, 1240, 1152, 1037, 946, 880, 832, 734 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.10–3.18 (m, 4H), 7.20–7.24 (m, 1H), 7.27–7.31 (m, 1H), 7.44–7.47 (m, 2H), 7.59–7.61 (m, 1H), 7.63–7.67 (m, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.92 (s, 1H), 8.06–8.07 (m, 1H), 8.14 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.0, 121.2, 126.0, 126.4, 127.4, 128.41, 128.43, 128.8, 129.46, 129.53, 129.8, 131.3, 134.7, 136.0, 137.0, 143.1, 148.4, 161.7; HRMS (ESI) calcd for $C_{19}H_{15}ClN$ [M+H]: 292.0893, found: 292.0891.

*4.3.32. (E)-3-(4-(Trifluoromethyl)benzylidene)-2,3-dihydro-1H-cyclopenta[b]quinoline (**3ie**).* Yellow solid (92%, 150.4 mg); mp 156–159 °C; $R_f$ (20% *EtOAc/hexane*) 0.53; $\nu_{max}$ (KBr) 3067, 2930, 1614, 1565, 1498, 1445, 1412, 1327, 1246, 1116, 1071, 1013, 897, 833, 756 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, br s, 4H), 7.45–7.49 (m, 1H), 7.62–7.72 (m, 6H), 7.81 (s, 1H), 7.93 (m, 1H), 8.11 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.8, 29.1, 123.1, 124.2 (q, *J*=272.0 Hz), 125.4 (q, *J*=4.0 Hz), 126.1, 127.5, 128.5, 128.7, 129.0, 129.3, 129.4, 131.5, 137.0, 140.9, 143.4, 148.3, 161.5; HRMS (ESI) calcd for $C_{20}H_{15}F_3N$ [M+H]: 326.1156, found: 326.1157.

*4.3.33. (E)-3-(4-Methylbenzylidene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ig**).* Yellow solid (86%, 116.5 mg); mp 164–166 °C; $R_f$ (20% *EtOAc/hexane*) 0.57; $\nu_{max}$ (KBr) 3033, 2919, 2858, 1596, 1561, 1510, 1496, 1403, 1275, 1153, 1134, 894, 806, 754 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.22 (s, br s, 4H), 7.23 (d, *J*=8.0 Hz, 2H), 7.44–7.46 (m, 1H), 7.53 (d, *J*=8.0 Hz, 2H), 7.64–7.65 (m, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.81 (s, 1H), 7.92 (s, 1H), 8.11 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.4, 27.9, 29.0, 124.8, 125.7, 127.4, 128.2, 128.7, 129.1, 129.3, 129.5, 131.2, 134.7, 137.0, 137.4, 139.7, 148.3, 162.4; HRMS (ESI) calcd for $C_{20}H_{18}N$ [M+H]: 272.1439, found: 272.1434.

*4.3.34. (E)-3-(4-Methoxybenzylidene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ih**).* Yellow solid (82%, 117.6 mg); mp 129–130 °C; $R_f$ (20% *EtOAc/hexane*) 0.46; $\nu_{max}$ (KBr) 3076, 2924, 2838, 1597, 1564, 1509, 1428, 1304, 1249, 1173, 1027, 894, 831, 755 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.22 (s, br s, 4H), 3.85 (s, 3H), 6.95–6.97 (m, 2H), 7.44–7.46 (m, 1H), 7.58 (d, *J*=9.0 Hz, 2H), 7.61–7.64 (m, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.78 (s, 1H), 7.92 (s, 1H), 8.09 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.0, 55.3, 114.1, 124.5, 125.6, 127.4, 128.2, 128.7, 129.1, 130.4, 130.9, 131.2, 136.9, 138.3, 148.3, 159.0, 162.6; HRMS (ESI) calcd for $C_{20}H_{18}NO$ [M+H]: 288.1388, found: 288.1387.

*4.3.35. (E)-3-(Pyridin-3-ylmethylene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3ij**).* Yellow solid (63%, 81.4 mg); mp 132–135 °C; $R_f$ (50% *EtOAc/hexane*) 0.29; $\nu_{max}$ (KBr) 3058, 2919, 1604, 1582, 1565, 1497, 1419, 1313, 1273, 1220, 1151, 1129, 1021, 943, 891, 740 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.19–3.25 (m, 4H), 7.33 (s, br s, 1H), 7.44–7.48 (m, 1H), 7.63–7.67 (m, 1H), 7.71–7.56 (m, 2H), 7.86 (d, *J*=8.0 Hz, 1H), 7.95 (s, 1H), 8.10 (d, *J*=8.5 Hz, 1H), 8.52 (s, br s, 1H), 8.90 (s, br s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.8, 29.1, 120.9, 126.1, 127.5, 128.4, 129.0, 129.3, 131.5, 135.7, 136.9, 143.2, 147.9, 148.3, 150.7, 161.4; HRMS (ESI) calcd for $C_{18}H_{15}N_2$ [M+H]: 259.1235, found: 259.1239.

*4.3.36. (E)-3-(Furan-2-ylmethylene)-2,3-dihydro-1H-cyclopenta[b] quinoline (**3il**).* Yellow solid (77%, 95.6 mg). Mp 147–150 °C; $R_f$ (20% *EtOAc/hexane*) 0.51; $\nu_{max}$ (KBr) 3076, 2927, 1598, 1560, 1481, 1404, 1275, 1135, 1021, 931, 878, 735 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 3.21 (s, br s, 4H), 6.49–6.53 (m, 2H), 7.41–7.45 (m, 1H), 7.51–7.52 (m, 1H), 7.60–7.65 (m, 2H), 7.69 (d, *J*=8.0 Hz, 1H), 7.90 (s, 1H), 8.06 (d, *J*=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 27.5, 28.7, 111.3, 111.9, 112.2, 125.7, 127.4, 128.2, 128.8, 129.1, 131.1, 137.7, 138.9, 142.8, 148.3, 154.0, 161.7; HRMS (ESI) calcd for $C_{17}H_{14}NO$ [M+H]: 248.1075, found: 248.1074.

*4.3.37. (E)-3-(2,2-Dimethylpropylidene)-2,3-dihydro-1H-cyclopenta [b]quinoline (**3io**).* Yellow solid (24%, 28.9 mg); mp 112–114 °C; $R_f$ (20% *EtOAc/hexane*) 0.63; $\nu_{max}$ (KBr) 3059, 2985, 2945, 1652, 1608, 1564, 1496, 1402, 1360, 1265, 1231, 1199, 1134, 954, 884, 756 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H), 3.01–3.05 (m, 2H), 3.11–3.14 (m, 2H), 6.95–6.96 (m, 1H), 7.39–7.43 (m, 1H), 7.58–7.62

(m, 1H), 7.69 (d, $J$=8.5 Hz, 1H), 7.89 (s, 1H), 8.04 (d, $J$=8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 26.8, 27.7, 30.3, 33.4, 125.4, 127.3, 128.1, 128.5, 129.2, 131.1, 136.2, 136.9, 137.0, 148.2, 162.8; HRMS (ESI) calcd for $C_{17}H_{20}N$ [M+H]: 238.1595, found: 238.1595.

*4.3.38. 1,3-Diphenyl-4-(quinolin-2-yl)butan-1-one (**3ar**).*[19] Light yellow solid (20%, 35.2 mg): $R_f$ (20% *EtOAc/hexane*) 0.29; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.32–3.49 (m, 4H), 4.05–4.11 (m, 1H), 7.11–7.29 (m, 6H), 7.31–7.36 (m, 2H), 7.39–7.49 (m, 2H), 7.61–7.65 (m, 1H), 7.71 (d, $J$=8.0 Hz, 1H), 7.82–7.84 (m, 2H), 7.95–7.99 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 41.4, 44.4, 45.8, 121.9, 125.8, 126.5, 126.8, 127.5, 127.6, 128.0, 128.38, 128.43, 128.9, 129.2, 132.8, 136.0, 137.2, 144.1, 147.9, 160.4, 198.7; HRMS (ESI) Calcd for $C_{25}H_{22}NO$ [M+H]: 352.1701, found: 352.1703.

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## Supplementary data

Supplementary data (copies of $^1$H and $^{13}$C NMR spectra of all new compounds) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.03.004.

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