Visible-Light-Mediated Minisci C–H Alkylation of Heteroarenes with Unactivated Alkyl Halides Using O₂ as an Oxidant

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1. General Information

Reagents were purchased from commercial sources and were used as received. $^1$H and $^{13}$C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, $\lambda_{max} = 470$ nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

Figure S1 Photograph of the Photocatalytic reactor used for reactions conducted under blue LED irradiation.
2. Preparation of photocatalyst Ir[dF(CF$_3$)$_2$ppy]$_2$(dtbbpy)PF$_6$

The photocatalyst was synthesized according to literature report.[1] The spectral data of the photocatalyst is consistent with the literature data. The other photocatalysts (Eosin Y, Fluorescein, [Ru(bpy)$_3$]Cl$_2$6H$_2$O, Ru(bpy)$_3$(PF$_6$)$_2$, Ir(ppy)$_3$ and Mes-Acr) are commercially available.

3. Preparation of 3R-Bromo-5R-cholestane

3R-Bromo-5R-cholestane was synthesized according to literature report.[2] The spectral data is consistent with the literature data.

4. Investigation of the Key Reaction Parameters.

Table S1: Screening of different silanes$^a$

| entry | silanes   | yield (%)$^b$ |
|-------|-----------|--------------|
| 1     | TTMS      | 82           |
| 2     | Ph$_3$SiH | NR           |
| 3     | Et$_3$SiH | NR           |
| 5     | Cl$_3$SiH | NR           |

$^a$General conditions: 1 (0.2 mmol), 2 (0.4 mmol), Ir[dF(CF$_3$)$_2$ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol), Silane (0.4 mmol), TFA (0.4 mmol) and acetone (2 mL) under O$_2$ atmosphere. $^b$Isolated yield. NR = no reaction.

Table S2: Screening of photocatalysts$^a$

| entry | photocatalyst | yield (%)$^b$ |
|-------|---------------|--------------|
| 1     | Ir[dF(CF$_3$)$_2$ppy]$_2$(dtbbpy)PF$_6$ | 82           |
| 2     | Ir(ppy)$_3$   | trace        |
| 3     | [Ru(bpy)$_3$]Cl$_2$6H$_2$O | NR           |
| 4     | [Ru(bpy)$_3$](PF$_6$)$_2$ | NR           |
| 5     | Fluorescein   | trace$^c$    |

$^a$General conditions: 1 (0.2 mmol), 2 (0.4 mmol), 36 W blue LED, r.t. 24 h.
General conditions: 1 (0.2 mmol), 2 (0.4 mmol), photocatalyst (0.002 mmol), TTMS (0.4 mmol), TFA (0.4 mmol) and acetone (2 mL) under O₂ atmosphere. NR = no reaction.

Table S3: Screening of different solvents

| entry | solvent | yield (%)<sup>b</sup> |
|-------|---------|----------------------|
| 1     | acetone | 82                   |
| 2     | MeOH    | 52                   |
| 3     | dioxane | 20                   |
| 4     | DMF     | 23                   |
| 5     | CH₃CN   | 68                   |

*General conditions: 1 (0.2 mmol), 2 (0.4 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.002 mmol), TTMS (0.4 mmol), TFA (0.4 mmol) and Solvent (2 mL) under O₂ atmosphere. Isolated yield.

Table S4: Screening of the amount of TFA

| entry | x eq. TFA | yield (%)<sup>b</sup> |
|-------|-----------|----------------------|
| 1     | 0         | 28                   |
| 2     | 1         | 74                   |
| 3     | 2         | 82                   |
| 4     | 4         | 81                   |

*General conditions: 1 (0.2 mmol), 2 (0.4 mmol), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (0.002 mmol), TTMS (0.4 mmol), TFA (0.2x mmol) and acetone (2 mL) under O₂ atmosphere. Isolated yield.

Table S5: Screening of the amount of bromocyclohexane and TTMS

| entry | x eq. 2 | y eq. TTMS | yield (%)<sup>b</sup> |
|-------|---------|------------|----------------------|
| 1     | 2       | 2          | 82                   |
| 2     | 1.5     | 2          | 71                   |
General conditions: 1 (0.2 mmol), 2 (0.2x mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol), TTMS (0.2y mmol), TFA (0.4 mmol) and acetone (2 mL) under O$_2$ atmosphere.\(^b\) Isolated yield.

5. Investigation of the mechanism.

5.1 TEMPO and BHT were used as radical scavengers.

**Scheme S1**
To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.24 mg, 0.002 mmol, 1 mol %), 1 (0.2 mmol, 1.0 equiv), TTMS (123 μL, 0.4 mmol, 2.0 equiv), 2 (0.4 mmol, 2.0 equiv), TEMPO (78.1 mg, 0.5 mmol, 2.5 equiv) or BHT (110 mg, 0.5 mmol, 2.5 equiv), TFA (30 μL, 0.4 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixture was degassed by bubbling with O$_2$ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The corresponding alkylated product 3 was not observed based on $^1$H NMR analysis.

5.2 Benzy l acrylate 48 was used as radical scavengers.

**Scheme S2**
To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.24 mg, 0.002 mmol, 1 mol %), 1 (0.2 mmol, 1.0 equiv), TTMS (123 μL, 0.4 mmol, 2.0 equiv), 2 (0.4 mmol, 2.0 equiv), benzy l acrylate 48 (1.0 mmol, 5.0 equiv), TFA (30 μL, 0.6 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixture was degassed by bubbling with O$_2$ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the acetone. The reaction mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the acetone. The mixture was diluted with 10 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the
desired products 3 and 49. The corresponding product of cyclohexyl radical trapping, benzyl 3-cyclohexylpropanoate 50 can be observed by HR-MS (positive mode ESI).

Figure S2 HR-ESI mass spectra of benzyl 3-cyclohexylpropanoate (50)
5.3 Radical clock experiment.

Scheme S3

To a 10 mL glass vial was added Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (3.36 mg, 0.003 mmol, 1 mol %), 1 (0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), bromoalkane (0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The reaction mixture was degassed by bubbling with O₂ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the acetone. The mixture was diluted with 10 mL of aqueous 1 M NaHCO₃ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na₂SO₄, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.4 Light/dark experiment.

Eight standard reaction mixtures in 10 mL glass vials were charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2.24 mg, 0.002 mmol, 1 mol %), 1 (0.2 mmol, 1.0 equiv), TTMS (123 μL, 0.4 mmol, 2.0 equiv), 2 (0.4 mmol, 2.0 equiv), TFA (30 μL, 0.4 mmol, 2.0 equiv) and 2.0 mL of acetone. The reaction mixtures were degassed by bubbling with O₂ for 15 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature. After 2 h, the Blue LED was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 2 h. Then, one vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining six reaction mixtures. After an additional 2 h of irradiation, the Blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 2 h. Then, a vial was removed for analysis, and the Blue LED was turned back on to irradiate the remaining four reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 2 h, then, a vial was removed for analysis and the Blue LED was turned back on to
irradiate the remaining two reaction mixtures. After 2 h, the Blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 2 h, and then it was analyzed. The yield was determined by $^1$H NMR spectroscopy using dibromomethane as the internal standard.

**Figure S3 Light/dark experiment.**

6. Experimental Procedures and Product Characterization

6.1 General Procedure for the alkylation of N-heteroarenes.
To a 10 mL glass vial was added Ir[($\text{CF}_3$)ppy)$_2$(dtbbpy)PF$_6$ (3.36 mg, 0.003 mmol, 1 mol %), heteroarene (0.3 mmol, 1.0 equiv), TTMS (185 μL, 0.6 mmol, 2.0 equiv), bromoalkane (0.6 mmol, 2.0 equiv), TFA (45 μL, 0.6 mmol, 2.0 equiv) and 3.0 mL of acetone. The reaction mixture was degassed by bubbling with O$_2$ for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuo to remove the acetone. The mixture was diluted with 10 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

6.2. Product Characterization

2-cyclohexyl-4-methylquinoline (3).

According to the general procedure. The spectral Data is consistent with the literature data.$^{[3]}$
Yellow oil (55.4 mg, 82%).
$R_f$ 0.40 (Petroleum ether/EtOAc, 40/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.4$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.16 (s, 1H), 3.02 – 2.80 (m, 1H), 2.67 (s, 3H), 2.01 (d, $J = 12.0$ Hz, 2H), 1.89 (d, $J = 12.8$ Hz, 2H), 1.79 (d, $J = 12.4$ Hz, 1H), 1.62 (ddd, $J = 24.8, 12.4, 2.4$ Hz, 2H), 1.46 (dd, $J = 25.2, 12.4$ Hz, 2H), 1.40 – 1.30 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 147.7, 144.4, 129.5,
129.0, 127.1, 125.5, 123.7, 120.3, 47.7, 32.9, 26.7, 26.2, 19.0.
HRMS (ESI) calcd for C_{16}H_{20}N [M + H]^+ 226.1590, found 226.1595.

4-methyl-2-propylquinoline (4).

According to the general procedure. Yellow oil (27.8 mg, 50%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.04 (d, \( J = 8.4 \) Hz, 1H), 7.95 (dd, \( J = 8.4, 0.8 \) Hz, 1H), 7.67 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.50 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.15 (s, 1H), 2.96 – 2.84 (m, 2H), 2.68 (d, \( J = 0.8 \) Hz, 3H), 1.83 (dq, \( J = 14.8, 7.6 \) Hz, 2H), 1.02 (t, \( J = 7.6 \) Hz, 3H).
\(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.7, 147.8, 144.4, 129.4, 129.2, 126.9, 125.6, 123.7, 122.3, 41.3, 23.5, 18.9, 14.2.
HRMS (ESI) calcd for C_{13}H_{16}N [M + H]^+ 186.1277, 186.1280.

2-butyl-4-methylquinoline (5).

According to the general procedure. The spectral Data is consistent with the literature data.\(^4\)
Yellow oil (36.4 mg, 61%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.04 (d, \( J = 8.4 \) Hz, 1H), 7.94 (dd, \( J = 8.4, 0.8 \) Hz, 1H), 7.67 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.50 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.14 (s, 1H), 2.98 – 2.85 (m, 2H), 2.67 (d, \( J = 0.8 \) Hz, 3H), 1.83 – 1.71 (m, 2H), 1.43 (dt, \( J = 14.8, 7.2 \) Hz, 2H), 0.96 (t, \( J = 7.2 \) Hz, 3H).
\(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.9, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.1, 32.4, 22.9, 18.8, 14.1.
HRMS (ESI) calcd for C_{14}H_{18}N [M + H]^+ 200.1434, found 200.1438.

2-hexyl-4-methylquinoline (6).
According to the general procedure. Yellow oil (57.2 mg, 84%).
$R_f$ 0.40 (Petroleum ether/EtOAc, 40/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.14 (s, 1H), 2.96 – 2.86 (m, 2H), 2.67 (s, 3H), 1.86 – 1.71 (m, 2H), 1.50 – 1.20 (m, 6H), 0.88 (t, $J = 6.0$ Hz, 3H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 147.8, 144.3, 129.4, 129.1, 126.9, 125.5, 123.7, 122.2, 39.4, 31.9, 30.2, 29.4, 22.7, 18.8, 14.2.

HRMS (ESI) calcd for C$_{16}$H$_{22}$N [M + H]$^+$ 228.1747, found 228.1748.

2-dodecyl-4-methylquinoline (7).

According to the general procedure. Yellow oil (42.0 mg, 45%).
$R_f$ 0.50 (Petroleum ether/EtOAc, 40/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.72 – 7.64 (m, 1H), 7.55 – 7.47 (m, 1H), 7.15 (s, 1H), 3.00 – 2.84 (m, 2H), 2.68 (s, 3H), 1.79 (dt, $J = 15.6$, 7.6 Hz, 2H), 1.42 – 1.19 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.8, 147.3, 129.4, 129.1, 126.9, 125.7, 123.7, 122.2, 119.8, 39.2, 32.0, 30.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 22.6, 18.9, 14.2.

HRMS (ESI) calcd for C$_{22}$H$_{34}$N [M + H]$^+$ 312.2686, found 312.2689.

2-(but-3-yn-1-yl)-4-methylquinoline (8).

According to the general procedure. Yellow oil (43.9 mg, 75%).
$R_f$ 0.30 (Petroleum ether/EtOAc, 20/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.72 – 7.64 (m, 1H), 7.55 – 7.47 (m, 1H), 7.15 (s, 1H), 3.00 – 2.84 (m, 2H), 2.68 (s, 3H), 1.79 (dt, $J = 15.6$, 7.6 Hz, 2H), 1.42 – 1.19 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H). $^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.1, 147.9, 144.6, 129.6, 129.3, 127.1, 125.8, 123.8, 122.3, 83.9, 69.0, 37.8, 18.9, 18.6.

HRMS (ESI) calcd for C$_{14}$H$_{14}$N [M + H]$^+$ 196.1121, found 196.1126.

4-methyl-2-(pent-4-en-1-yl)quinoline (9).
According to the general procedure. Yellow oil (51.3 mg, 81%).

\( R_f \) 0.40 (Petroleum ether/EtOAc, 40/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 8.4 \) Hz, 1H), 7.85 (d, \( J = 8.4 \) Hz, 1H), 7.57 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.40 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.04 (s, 1H), 5.77 (ddt, \( J = 16.8, 10.0, 6.4 \) Hz, 1H), 5.01 – 4.83 (m, 2H), 2.91 – 2.79 (m, 2H), 2.58 (s, 3H), 2.08 (dd, \( J = 14.4, 7.6 \) Hz, 2H), 1.81 (dt, \( J = 15.2, 7.6 \) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.5, 147.8, 144.4, 138.6, 129.4, 129.2, 126.9, 125.6, 123.7, 122.2, 115.0, 38.7, 33.7, 29.3, 18.8.

HRMS (ESI) calcd for C\(_{15}\)H\(_{18}\)N \([\text{M + H}]^+\) 212.1434, found 212.1436.

ethyl 3-(4-methylquinolin-2-yl)propanoate (10).

According to the general procedure. The spectral Data is consistent with the literature data.[5]

Yellow oil (40.8 mg, 56%).

\( R_f \) 0.40 (Petroleum ether/EtOAc, 7/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (d, \( J = 8.4 \) Hz, 1H), 7.95 (dd, \( J = 8.4, 0.8 \) Hz, 1H), 7.67 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.50 (ddd, \( J = 8.4, 6.8, 1.2 \) Hz, 1H), 7.17 (s, 1H), 4.14 (q, \( J = 7.2 \) Hz, 2H), 3.25 (t, \( J = 7.6 \) Hz, 2H), 2.90 (t, \( J = 7.6 \) Hz, 2H), 2.67 (s, 3H), 1.24 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 173.3, 160.3, 147.8, 144.5, 138.6, 129.5, 129.2, 127.0, 125.7, 123.7, 60.5, 33.6, 33.4, 18.8, 14.4.

HRMS (ESI) calcd for C\(_{15}\)H\(_{18}\)NO\(_2\) \([\text{M + H}]^+\) 244.1332, found 244.1334.

2-(2-(1,3-dioxolan-2-yl)ethyl)-4-methylquinoline (11).

According to the general procedure. Yellow oil (32.1 mg, 44%).
R$_f$ 0.30 (Petroleum ether/EtOAc, 7/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.67 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.50 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.17 (s, 1H), 5.00 (t, $J = 4.8$ Hz, 1H), 4.04 – 3.97 (m, 2H), 3.91 – 3.84 (m, 2H), 3.13 – 3.02 (m, 2H), 2.67 (d, $J = 0.8$ Hz, 3H), 2.26 – 2.16 (m, 2H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.6, 147.7, 144.7, 129.4, 129.3, 127.0, 125.7, 123.7, 122.3, 104.0, 65.1, 33.8, 33.3, 18.8.
HRMS (ESI) calcd for C$_{15}$H$_{18}$NO [M + H]$^+$ 244.1332, found 244.1336.

4-methyl-2-(2-phenoxyethyl)quinoline (12).

According to the general procedure. Yellow oil (35.5 mg, 45%).
R$_f$ 0.40 (Petroleum ether/EtOAc, 7/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 8.4$ Hz, 1H), 7.96 (dd, $J = 8.4$, 0.8 Hz, 1H), 7.69 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.52 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.34 – 7.21 (m, 3H), 7.00 – 6.88 (m, 3H), 4.45 (t, $J = 6.8$ Hz, 2H), 3.41 (t, $J = 6.8$ Hz, 2H), 2.69 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.0, 158.9, 147.8, 144.7, 129.5, 129.4, 129.3, 127.1, 125.9, 122.9, 120.9, 114.8, 67.3, 38.8, 18.9.
HRMS (ESI) calcd for C$_{18}$H$_{18}$NO [M + H]$^+$ 264.1383, found 264.1388.

4-methyl-2-phenethylquinoline (13).

According to the general procedure. Yellow oil (57.8 mg, 78%).
R$_f$ 0.40 (Petroleum ether/EtOAc, 20/1).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.68 (t, $J = 7.2$ Hz, 1H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.33 – 7.22 (m, 4H), 7.23 – 7.16 (m, 1H), 7.09 (s, 1H), 3.29 – 3.20 (m, 2H), 3.18 – 3.09 (m, 2H), 2.65 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.6, 147.8, 144.5, 141.8, 129.4, 129.3, 128.6, 128.5, 127.0, 126.1, 125.7, 123.8, 122.4, 41.0, 36.0, 18.8.
HRMS (ESI) calcd for C$_{18}$H$_{18}$N [M + H]$^+$ 248.1434, found 248.1436.

4-methyl-2-(2-phenoxyethyl)quinoline (14).
According to the *general procedure*. Yellow oil (59.4 mg, 85%).
$R_f$ 0.30 (Petroleum ether/EtOAc, 20/1).

$^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J$ = 8.4 Hz, 1H), 7.92 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.68 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.50 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 7.05 (s, 1H), 4.29 (s, 2H), 2.59 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.0, 147.7, 144.8, 139.5, 129.6, 129.3, 128.7, 127.0, 126.6, 125.9, 123.7, 122.3, 45.6, 18.8.

HRMS (ESI) calcd for C$_{17}$H$_{16}$N [M + H]$^+$ 234.1277, found 234.1278.

2-cyclopropyl-4-methylquinoline (15).

According to the *general procedure*. The spectral Data is consistent with the literature data.[4]

Yellow oil (32.4 mg, 59%).
$R_f$ 0.40 (Petroleum ether/EtOAc, 40/1).

$^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 8.4 Hz, 1H), 7.90 (d, $J$ = 8.4 Hz, 1H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 1H), 6.98 (s, 1H), 2.64 (s, 3H), 2.26 – 2.11 (m, 1H), 1.16 – 1.02 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2, 147.9, 143.9, 129.3, 129.1, 126.9, 125.1, 123.7, 119.9, 18.8, 18.1, 10.1.

HRMS (ESI) calcd for C$_{13}$H$_{14}$N [M + H]$^+$ 184.1121, found 184.1122.

2-cyclobutyl-4-methylquinoline (16).

According to the *general procedure*. The spectral Data is consistent with the literature data.[5]

Yellow oil (39.6 mg, 67%).
$R_f$ 0.40 (Petroleum ether/EtOAc, 40/1).

$^{1}H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.53 – 7.44 (m, 1H), 7.19 (s, 1H), 3.83 (p, $J$ = 8.8 Hz, 1H), 2.67 (s, 3H), 2.50 – 2.35 (m, 4H), 2.21 – 2.05 (m, 1H), 2.00 – 1.87 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.8, 147.7, 144.2, 129.6, 129.0, 127.0, 125.5, 123.6, 120.3, 42.8, 28.3, 18.9, 18.5.
HRMS (ESI) calcd for C_{14}H_{16}N [M + H]^+ 198.1277, found 198.1279.

2-cyclopentyl-4-methylquinoline (17).

![17]

According to the *general procedure*. The spectral Data is consistent with the literature data.\(^3\) Yellow oil (45.6 mg, 72%).

\(R_f\) 0.40 (Petroleum ether/EtOAc, 40/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.4\) Hz, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 7.70 – 7.61 (m, 1H), 7.52 – 7.44 (m, 1H), 7.17 (s, 1H), 3.41 – 3.27 (m, 1H), 2.67 (s, 3H), 2.17 (ddd, \(J = 10.8, 9.2, 2.4\) Hz, 2H), 1.97 – 1.81 (m, 4H), 1.81 – 1.66 (m, 2H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.0, 147.6, 144.2, 129.5, 129.0, 127.1, 125.4, 123.6, 120.7, 48.9, 33.7, 26.1, 18.9.

HRMS (ESI) calcd for C_{15}H_{18}N [M + H]^+ 212.1434, found 212.1436.

2-cycloheptyl-4-methylquinoline (18).

![18]

According to the *general procedure*. Yellow oil (55.9 mg, 78%).

\(R_f\) 0.40 (Petroleum ether/EtOAc, 40/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.4\) Hz, 1H), 7.92 (dd, \(J = 8.4, 0.8\) Hz, 1H), 7.65 (ddd, \(J = 8.4, 6.8, 1.2\) Hz, 1H), 7.47 (ddd, \(J = 8.4, 6.8, 1.2\) Hz, 1H), 7.13 (s, 1H), 3.03 (tt, \(J = 10.4, 3.6\) Hz, 1H), 2.66 (s, 3H), 2.12 – 1.98 (m, 2H), 1.93 – 1.52 (m, 10H).\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.2, 147.6, 144.5, 129.5, 129.0, 127.0, 125.4, 123.6, 120.4, 49.7, 35.2, 28.0, 27.6, 18.9.

HRMS (ESI) calcd for C_{17}H_{22}N [M + H]^+ 240.1747, found 240.1750.

2-(adamantan-2-yl)-4-methylquinoline (19).

![19]

According to the *general procedure*. The spectral Data is consistent with the literature data.\(^5\) White solid (49.9 mg, 60%). M.p. = 89 – 90 °C.

\(R_f\) 0.80 (Petroleum ether/EtOAc, 40/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 8.4\) Hz, 1H), 7.95 (dd, \(J = 8.4, 0.8\) Hz, 1H), 7.66 (ddd, \(J =
8.4, 6.8, 1.2 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.28 (d, J = 8.8 Hz, 1H), 3.20 (s, 1H), 2.78 (s, 2H), 2.69 (s, 3H), 2.07 – 1.94 (m, 7H), 1.81 (s, 3H), 1.63 (d, J = 12.4 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.2, 147.8, 143.5, 129.9, 128.7, 126.6, 125.4, 123.6, 120.6, 50.5, 39.3, 38.0, 32.7, 31.0, 28.2, 28.1, 19.0.

HRMS (ESI) calcd for C$_{20}$H$_{24}$N [M + H]$^+$ 278.1903, found 278.1906.

tert-butyl 3-(4-methylquinolin-2-yl)azetidine-1-carboxylate (20).

According to the general procedure. The spectral Data is consistent with the literature data.$^{[4]}$

Yellow oil (41.1 mg, 46%). $R_f$ 0.20 (Petroleum ether/EtOAc, 10/1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.70 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.55 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.28 (s, 1H), 4.39 (t, J = 8.8 Hz, 2H), 4.28 (dd, J = 8.4, 6.0 Hz, 2H), 4.01 (tt, J = 8.8, 6.0 Hz, 1H), 2.72 (s, 3H), 1.48 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.1, 156.7, 147.6, 145.4, 129.7, 129.5, 127.3, 126.2, 123.8, 120.1, 79.7, 54.6, 35.9, 28.6, 19.0.

HRMS (ESI) calcd for C$_{18}$H$_{23}$N$_2$O$_2$ [M + H]$^+$ 299.1754, found 299.1759.

tert-butyl 4-(4-methylquinolin-2-yl)piperidine-1-carboxylate (21).

According to the general procedure. The spectral Data is consistent with the literature data.$^{[4]}$

Yellow oil (44.0 mg, 45%). $R_f$ 0.20 (Petroleum ether/EtOAc, 20/1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.54 – 7.47 (m, 1H), 7.14 (s, 1H), 4.28 (s, 2H), 3.71 (t, J = 6.0 Hz, 1H), 3.01 (tt, J = 12.0, 3.6 Hz, 1H), 2.68 (s, 3H), 2.43 (t, J = 6.0 Hz, 1H), 1.97 (d, J = 12.0 Hz, 2H), 1.84 (td, J = 12.4, 4.0 Hz, 2H), 1.49 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.4, 155.0, 147.7, 144.8, 129.6, 129.3, 127.3, 126.2, 123.8, 120.1, 79.5, 45.6, 44.4, 31.7, 28.6, 19.0.

HRMS (ESI) calcd for C$_{20}$H$_{27}$N$_2$O$_2$ [M + H]$^+$ 327.2067, 327.2072.

4-methyl-2-(tetrahydro-2H-pyran-4-yl)quinoline (22).
According to the general procedure. The spectral Data is consistent with the literature data.\[^{[3]}\]
White solid (44.9 mg, 66%). M.p. = 107 – 108 °C.
R\(_f\) 0.20 (Petroleum ether/EtOAc, 20/1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.4\) Hz, 1H), 7.94 (d, \(J = 8.4\) Hz, 1H), 7.67 (t, \(J = 7.6\) Hz, 1H), 7.50 (t, \(J = 7.6\) Hz, 1H), 7.17 (s, 1H), 4.12 (dd, \(J = 11.2, 3.6\) Hz, 2H), 3.59 (td, \(J = 11.6, 1.6\) Hz, 2H), 3.12 (tt, \(J = 11.6, 3.6\) Hz, 1H), 2.69 (s, 3H), 2.14 – 1.85 (m, 4H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 164.3, 147.7, 144.8, 129.6, 129.2, 127.2, 125.8, 123.7, 120.0, 68.2, 44.5, 32.4, 19.0.
HRMS (ESI) calcd for C\(_{15}\)H\(_{18}\)NO [M + H]\(^+\) 228.1383, found 228.1386.

2-isopropyl-4-methylquinoline (23).

According to the general procedure. The spectral Data is consistent with the literature data.\[^{[5]}\]
Yellow oil (52.7 mg, 95%).
R\(_f\) 0.40 (Petroleum ether/EtOAc, 40/1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 (d, \(J = 8.4\) Hz, 1H), 7.94 (d, \(J = 8.4\) Hz, 1H), 7.52 – 7.44 (m, 1H), 7.18 (s, 1H), 3.30 – 3.11 (m, 1H), 2.68 (s, 3H), 1.39 (d, \(J = 6.8\) Hz, 6H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.8, 147.6, 144.5, 129.6, 129.1, 127.1, 125.8, 123.7, 119.9, 37.4, 22.7, 19.0.
HRMS (ESI) calcd for C\(_{13}\)H\(_{16}\)N [M + H]\(^+\) 186.1277, found 186.1280.

(S)-2-(sec-butyl)-4-methylquinoline (24).

According to the general procedure. The spectral Data is consistent with the literature data.\[^{[4]}\]
Yellow oil (44.2 mg, 74%).
R\(_f\) 0.50 (Petroleum ether/EtOAc, 40/1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 (d, \(J = 8.4\) Hz, 1H), 7.94 (d, \(J = 8.4\) Hz, 1H), 7.66 (t, \(J = 7.6\) Hz, 1H), 7.49 (t, \(J = 7.6\) Hz, 1H), 7.13 (s, 1H), 3.06 – 2.87 (m, 1H), 2.68 (s, 3H), 1.92 – 1.77 (m, 1H), 1.76 – 1.63 (m, 1H), 1.35 (d, \(J = 7.2\) Hz, 3H), 0.89 (t, \(J = 7.2\) Hz, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.8, 147.8, 144.3, 129.7, 129.0, 127.2, 125.5, 123.7, 120.3, 44.7, 30.1, 20.5, 18.9, 12.4.
HRMS (ESI) calcd for C\(_{14}\)H\(_{18}\)N [M + H]\(^+\) 200.1434, found 200.1436.

2-(tert-butyl)-4-methylquinoline (25).
According to the *general procedure*. The spectral Data is consistent with the literature data.\(^{[5]}\)

**2-(adamantan-1-yl)-4-methylquinoline (26).**

![Structure of 2-(adamantan-1-yl)-4-methylquinoline](image)

White solid (73.9 mg, 89%). M.p. = 105 – 106 °C.

\( \text{R}_f \) 0.40 (Petroleum ether/EtOAc, 100/1).

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 8.06 (d, \( J = 7.2 \text{ Hz}, 1 \text{H} \)), 7.93 (d, \( J = 8.4 \text{ Hz}, 1 \text{H} \)), 7.65 (t, \( J = 7.6 \text{ Hz}, 1 \text{H} \)), 7.48 (t, \( J = 7.6 \text{ Hz}, 1 \text{H} \)), 7.32 (s, 1H), 2.68 (s, 3H), 2.19 – 2.05 (m, 9H), 1.82 (s, 6H).

\(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 168.8, 148.0, 136.4, 129.3, 129.1, 127.6, 127.1, 125.7, 119.7, 41.9, 39.7, 37.0, 29.0, 19.1.

**HRMS (ESI)** calcd for C\(_{20}\)H\(_{24}\)N [M + H]^+ 278.1903, found 278.1906.

**2-cyclohexylquinoline (27).**

![Structure of 2-cyclohexylquinoline](image)

Yellow oil (28.5 mg, 45%).

\( \text{R}_f \) 0.50 (Petroleum ether/EtOAc, 60/1).

\(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 8.07 (dd, \( J = 12.4, 8.4 \text{ Hz}, 2 \text{H} \)), 7.77 (d, \( J = 8.4 \text{ Hz}, 1 \text{H} \)), 7.67 (t, \( J = 7.6 \text{ Hz}, 1 \text{H} \)), 7.47 (t, \( J = 7.6 \text{ Hz}, 1 \text{H} \)), 7.33 (d, \( J = 8.4 \text{ Hz}, 1 \text{H} \)), 2.93 (tt, \( J = 12.0, 3.2 \text{ Hz}, 1 \text{H} \)), 2.03 (d, \( J = 12.4 \text{ Hz}, 2 \text{H} \)), 1.90 (d, \( J = 12.8 \text{ Hz}, 2 \text{H} \)), 1.79 (d, \( J = 12.8 \text{ Hz}, 1 \text{H} \)), 1.63 (dd, \( J = 12.4, 3.2 \text{ Hz}, 2 \text{H} \)), 1.48 (ddd, \( J = 15.6, 12.8, 6.4 \text{ Hz}, 2 \text{H} \)), 1.40 – 1.30 (m, 1H).

\(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 167.0, 148.0, 136.4, 129.3, 129.1, 127.6, 127.1, 125.7, 119.7, 47.8, 33.0, 26.7, 26.3.

**HRMS (ESI)** calcd for C\(_{16}\)H\(_{18}\)N [M + H]^+ 212.1434, found 212.1436.
4-chloro-2-cyclohexylquinoline (28).

According to the general procedure. The spectral Data is consistent with the literature data.\[^3\]
Yellow oil (61.7 mg, 84%).
$R_t$ 0.70 (Petroleum ether/EtOAc, 20/1).
$^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 8.16 (dd, $J = 8.4$, 0.8 Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.72 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.56 (ddd, $J = 8.4$, 6.8, 1.2 Hz, 1H), 7.42 (s, 1H), 2.89 (tt, $J = 12.0$, 3.2 Hz, 1H), 2.02 (dd, $J = 13.2$, 1.6 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.79 (ddd, $J = 12.8$, 4.8, 2.4 Hz, 1H), 1.60 (ddd, $J = 24.8$, 12.4, 2.8 Hz, 2H), 1.53 – 1.39 (m, 2H), 1.38 – 1.28 (m, 1H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 166.9, 148.8, 142.7, 130.3, 129.4, 126.7, 125.2, 124.0, 119.9, 47.5, 32.8, 26.5, 26.1.
HRMS (ESI) calcd for C\textsubscript{15}H\textsubscript{17}ClN [M + H]$^+$ 246.1044, found 246.1048.

4-bromo-2-cyclohexylquinoline (29).

According to the general procedure. The spectral Data is consistent with the literature data.\[^3\]
Yellow oil (35.5 mg, 41%).
$R_t$ 0.70 (Petroleum ether/EtOAc, 20/1).
$^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 8.13 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.72 (t, $J = 7.6$ Hz, 1H), 7.63 (s, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 2.88 (tt, $J = 12.0$, 3.2 Hz, 1H), 2.02 (d, $J = 12.8$ Hz, 2H), 1.95 – 1.85 (m, 2H), 1.79 (d, $J = 12.8$ Hz, 1H), 1.61 (ddd, $J = 24.8$, 12.4, 2.8 Hz, 2H), 1.52 – 1.39 (m, 2H), 1.39 – 1.29 (m, 1H). $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 166.9, 148.6, 134.3, 130.4, 129.5, 127.0, 126.6, 126.6, 123.8, 47.4, 32.8, 26.6, 26.1.
HRMS (ESI) calcd for C\textsubscript{15}H\textsubscript{17}BrN [M + H]$^+$ 290.0539, found 290.0542.

4-cyclohexyl-2-methylquinoline (30).

According to the general procedure. The spectral Data is consistent with the literature data.\[^3\]
Yellow oil (54.7 mg, 81%).
$R_t$ 0.30 (Petroleum ether/EtOAc, 20/1).
**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.07 – 7.98 (m, 2H), 7.63 (dd, $J = 8.4, 6.8, 1.2$ Hz, 1H), 7.47 (dd, $J = 8.4, 6.8, 1.2$ Hz, 1H), 7.15 (s, 1H), 3.36 – 3.20 (m, 1H), 2.71 (s, 3H), 2.10 – 1.78 (m, 5H), 1.63 – 1.44 (m, 4H), 1.40 – 1.21 (m, 1H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 158.9, 153.4, 148.2, 129.5, 128.9, 125.3, 125.2, 122.9, 118.4, 38.8, 33.6, 27.0, 26.4, 25.6.

**HRMS** (ESI) calcd for C$_{16}$H$_{20}$N [M + H]$^+$ 226.1590, found 226.1593.

methyl 1-cyclohexylisoquinoline-4-carboxylate (31).

According to the *general procedure*. Colorless oil (65.4 mg, 81%).

$R_f$ 0.60 (Petroleum ether/EtOAc, 20/1).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 9.11 (s, 1H), 8.96 (d, $J = 8.4$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 3.99 (s, 3H), 3.59 (t, $J = 11.2$ Hz, 1H), 1.94 (t, $J = 11.2$ Hz, 4H), 1.89 – 1.75 (m, 3H), 1.59 – 1.45 (m, 2H), 1.44 – 1.33 (m, 1H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 170.8, 167.4, 146.0, 134.4, 131.3, 127.2, 126.0, 125.8, 125.1, 118.7, 52.2, 42.2, 32.6, 26.8, 26.2.

**HRMS** (ESI) calcd for C$_{17}$H$_{20}$NO$_2$ [M + H]$^+$ 270.1489, found 270.1492.

4-cyclohexyl-2,6-dimethylpyridine (32).

According to the *general procedure*. The spectral Data is consistent with the literature data.$^{[3]}$

Yellow oil (28.4 mg, 50%).

$R_f$ 0.30 (Petroleum ether/EtOAc, 7/1).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 6.80 (s, 2H), 2.50 (s, 6H), 2.45 – 2.37 (m, 1H), 1.84 (d, $J = 8.4$ Hz, 4H), 1.75 (d, $J = 12.4$ Hz, 2H), 1.38 (t, $J = 10.8$ Hz, 4H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 157.6, 157.5, 119.2, 44.0, 33.7, 26.7, 26.1, 24.4.

**HRMS** (ESI) calcd for C$_{13}$H$_{20}$N [M + H]$^+$ 190.1590, found 190.1593.

2,6-dicyclohexylnicotinonitrile (33).

According to the *general procedure*. Colorless oil (32.2 mg, 40%).

$R_f$ 0.70 (Petroleum ether/EtOAc, 20/1).
**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.73 (m, 1H), 7.08 – 6.99 (m, 1H), 3.19 – 2.97 (m, 1H), 2.71 (tt, $J = 11.6, 3.2$ Hz, 1H), 1.96 – 1.79 (m, 7H), 1.72 (ddd, $J = 25.6, 12.8, 3.2$ Hz, 4H), 1.54 – 1.31 (m, 6H), 1.28 (d, $J = 6.8$ Hz, 3H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 170.2, 168.4, 140.5, 118.2, 117.9, 104.9, 46.9, 44.9, 32.6, 32.0, 26.4, 26.3, 26.1, 25.9.

**HRMS** (ESI) calcd for C$_{18}$H$_{25}$N$_2$ [M + H]$^+$ 269.2012, found 269.2015.

1-cyclohexylphthalazine (34).

![1-cyclohexylphthalazine](34)

According to the general procedure. Yellow oil (29.3 mg, 46%).

$R_f$ 0.50 (CH$_2$Cl$_2$/MeOH, 40/1).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 9.41 (s, 1H), 8.17 (d, $J = 7.6$ Hz, 1H), 7.90 (ddd, $J = 14.4, 8.4, 7.2$ Hz, 3H), 3.63 – 3.39 (m, 1H), 2.09 – 2.01 (m, 2H), 1.99 – 1.93 (m, 3H), 1.86 – 1.79 (m, 2H), 1.62 – 1.46 (m, 2H), 1.46 – 1.37 (m, 1H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 132.4, 131.8, 127.3, 125.1, 123.6, 40.8, 32.4, 27.0, 26.2.

**HRMS** (ESI) calcd for C$_{14}$H$_{17}$N$_2$ [M + H]$^+$ 213.1386, found 213.1389.

2-chloro-4-cyclohexylquinazoline (35).

![2-chloro-4-cyclohexylquinazoline](35)

According to the general procedure. Colorless oil (41.3 mg, 56%).

$R_f$ 0.70 (Petroleum ether/EtOAc, 20/1).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.89 (t, $J = 7.6$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 3.53 (t, $J = 11.6$ Hz, 1H), 2.01 – 1.90 (m, 4H), 1.89 – 1.77 (m, 3H), 1.54 – 1.45 (m, 2H), 1.44 – 1.35 (m, 1H). **13C NMR** (100 MHz, CDCl$_3$) $\delta$ 179.2, 157.6, 152.2, 134.6, 128.6, 127.7, 124.6, 121.8, 41.8, 32.0, 26.5, 25.9.

**HRMS** (ESI) calcd for C$_{14}$H$_{16}$ClN$_2$ [M + H]$^+$ 247.0997, found 247.0999.

6-chloro-7-cyclohexylimidazo[1,2-b]pyridazine (36).

![6-chloro-7-cyclohexylimidazo[1,2-b]pyridazine](36)

According to the general procedure. The spectral Data is consistent with the literature data.[3]

Yellow oil (33.8 mg, 48%).

$R_f$ 0.70 (Petroleum ether/EtOAc, 3/1).

**1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 1.2$ Hz, 1H), 7.72 (d, $J = 1.2$ Hz, 1H), 6.86 (s, 1H), 3.42 –
3.27 (m, 1H), 2.13 – 2.04 (m, 2H), 1.96 – 1.87 (m, 2H), 1.82 (d, \( J = 17.2 \) Hz, 2H), 1.55 – 1.50 (m, 3H), 1.32 (ddd, \( J = 12.4, 8.0, 3.6 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 148.2, 147.5, 138.1, 133.3, 117.4, 114.7, 38.9, 32.2, 26.4, 26.1. HRMS (ESI) calcd for C\(_{12}\)H\(_{15}\)ClN\(_3\) [M + H]\(^+\) 236.0949, found 236.0951.

2-cyclohexylbenzo[d]thiazole (37).

According to the general procedure. The spectral Data is consistent with the literature data.[3] Yellow oil (28.6 mg, 44%). 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.97 (d, \( J = 8.0 \) Hz, 1H), 7.84 (d, \( J = 8.0 \) Hz, 1H), 7.48 – 7.40 (m, 1H), 7.37 – 7.29 (m, 1H), 3.11 (tt, \( J = 11.6, 3.6 \) Hz, 1H), 2.21 (dd, \( J = 13.2, 2.0 \) Hz, 2H), 1.94 – 1.84 (m, 2H), 1.77 (ddd, \( J = 12.4, 4.8, 2.4 \) Hz, 1H), 1.64 (ddd, \( J = 24.8, 12.4, 3.2 \) Hz, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.28 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 177.8, 153.2, 134.7, 125.9, 124.6, 122.7, 121.7, 43.6, 33.6, 26.2, 25.9. 

HRMS (ESI) calcd for C\(_{13}\)H\(_{16}\)NS [M + H]\(^+\) 218.0998, found 218.1001.

2-cyclohexyl-4,7-dimethyl-1,10-phenanthroline (38).

According to the general procedure. White solid (40.9 mg, 47%). M.p. = 62 – 63 \(^{\circ}\)C. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.06 (d, \( J = 4.4 \) Hz, 1H), 7.96 (q, \( J = 9.2 \) Hz, 2H), 7.40 (d, \( J = 4.4 \) Hz, 1H), 7.38 (s, 1H), 3.27 (tt, \( J = 12.0, 3.2 \) Hz, 1H), 2.76 (d, \( J = 4.4 \) Hz, 6H), 2.08 (d, \( J = 12.4 \) Hz, 2H), 1.86 (d, \( J = 12.8 \) Hz, 2H), 1.65 – 1.53 (m, 3H), 1.50 – 1.42 (m, 2H), 1.39 – 1.31 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 150.0, 146.3, 145.6, 144.4, 144.3, 128.1, 126.6, 123.8, 122.2, 121.7, 121.1, 48.0, 33.6, 26.6, 26.3, 19.5, 19.3. 

HRMS (ESI) calcd for C\(_{20}\)H\(_{23}\)N\(_2\) [M + H]\(^+\) 291.1856, found 291.1858.

2-cyclohexyl-3,4,7,8-tetramethyl-1,10-phenanthroline (39).

According to the general procedure. White solid (63.9 mg, 67%). M.p. = 89 – 90 \(^{\circ}\)C. 

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.95 (s, 1H), 7.99 (dd, \( J = 22.8, 9.6 \) Hz, 2H), 3.17 (tt, \( J = 11.2, 3.6 \) Hz,
1H), 2.68 (s, 6H), 2.51 (s, 6H), 2.04 – 1.84 (m, 7H), 1.44 (td, $J = 12.8, 6.4$ Hz, 2H), 1.33 (dd, $J = 12.8, 3.2$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6, 151.3, 144.5, 143.4, 142.2, 141.4, 130.2, 128.9, 127.2, 125.6, 122.7, 120.9, 44.2, 31.8, 27.0, 26.0, 17.6, 15.4, 15.2, 14.8.

**HRMS (ESI)** calcd for C$_{22}$H$_{27}$N$_2$ [M + H]$^+$ 319.2169, found 319.2173.

2-cyclohexyl-4,7-diphenyl-1,10-phenanthroline (40).

According to the general procedure. White solid (72.0 mg, 58%). M.p. = 103 – 104 °C. $R_f$ 0.50 (CH$_2$Cl$_2$/MeOH, 80/1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.27 (d, $J = 4.4$ Hz, 1H), 7.84 – 7.76 (m, 2H), 7.57 – 7.50 (m, 12H), 3.41 (tt, $J = 12.0, 3.2$ Hz, 1H), 2.19 (d, $J = 12.4$ Hz, 2H), 1.94 – 1.87 (m, 2H), 1.84 (s, 1H), 1.66 (dd, $J = 12.4, 3.2$ Hz, 2H), 1.57 – 1.50 (m, 2H), 1.40 – 1.33 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.2, 149.9, 148.9, 148.5, 146.9, 146.2, 138.7, 138.3, 129.9, 129.8, 128.7, 128.6, 128.5, 128.4, 126.7, 125.2, 124.2, 123.3, 123.1, 121.3, 48.1, 33.6, 26.6, 26.3.

**HRMS (ESI)** calcd for C$_{30}$H$_{27}$N$_2$ [M + H]$^+$ 415.2169, found 415.2173.

(1S)-(2-isopropyl-6-methoxyquinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (41).

According to the general procedure. The spectral Data is consistent with the literature data.$^{[6]}$

White solid (73.6 mg, 67%). M.p. = 144 – 145 °C.

$R_f$ 0.50 (CH$_2$Cl$_2$/MeOH, 20/1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, $J = 9.2$ Hz, 1H), 7.52 (s, 1H), 7.21 (dd, $J = 9.2, 2.8$ Hz, 1H), 7.09 (d, $J = 2.8$ Hz, 1H), 5.75 (d, $J = 2.8$ Hz, 1H), 5.67 (ddd, $J = 17.6, 10.4, 7.6$ Hz, 1H), 4.94 (t, $J = 14.0$ Hz, 2H), 3.79 (s, 3H), 3.72 (t, $J = 6.4$ Hz, 1H), 3.21 – 3.11 (m, 3H), 2.82 – 2.69 (m, 2H), 2.36 (s, 1H), 1.90 – 1.79 (m, 3H), 1.57 (t, $J = 10.0$ Hz, 1H), 1.48 – 1.40 (m, 1H), 1.34 (dd, $J = 6.8, 2.4$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.8, 157.4, 147.1, 143.7, 141.0, 131.2, 124.8, 121.3, 116.4, 115.2, 101.0, 71.0, 60.0, 56.7, 55.9, 43.6, 39.5, 37.2, 27.9, 27.0, 22.7, 20.6.

**HRMS (ESI)** calcd for C$_{23}$H$_{31}$N$_2$O$_2$ [M + H]$^+$ 367.2380, found 367.2383.

(1S)-(2-isopropylquinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (42a).
According to the general procedure. White solid (53.4 mg, 53%). M.p. = 168 – 169 °C. 
\( R_t \) 0.50 (CH\(_2\)Cl\(_2\)/MeOH, 20/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.03 (d, \( J = 8.4 \) Hz, 1H), 7.77 (d, \( J = 8.4 \) Hz, 1H), 7.60 (s, 1H), 7.57 (t, \( J = 7.6 \) Hz, 1H), 7.22 (t, \( J = 7.6 \) Hz, 1H), 6.14 – 5.94 (m, 1H), 5.84 (d, \( J = 3.2 \) Hz, 1H), 5.15 – 4.98 (m, 2H), 3.50 (dd, \( J = 12.0 \), 8.0 Hz, 1H), 3.23 (dp, \( J = 14.0 \), 6.8 Hz, 1H), 3.03 (dd, \( J = 9.2 \), 6.4 Hz, 1H), 2.91 (dd, \( J = 16.4 \), 6.8 Hz, 2H), 2.76 (dt, \( J = 13.2 \), 9.2 Hz, 1H), 2.24 (dd, \( J = 16.8 \), 8.2 Hz, 1H), 2.13 – 2.01 (m, 1H), 1.75 (s, 1H), 1.59 – 1.44 (m, 2H), 1.36 (d, \( J = 6.8 \) Hz, 6H), 1.13 – 1.00 (m, 1H). 

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.5, 149.0, 147.8, 140.2, 129.9, 128.9, 125.9, 124.3, 122.6, 116.4, 115.0, 71.3, 60.0, 50.1, 49.6, 39.9, 37.5, 28.4, 26.1, 22.7, 22.6, 20.4.

HRMS (ESI) calcd for C\(_{22}\)H\(_{29}\)N\(_2\)O \([\text{M + H}]^+\) 337.2274, found 337.2278.

(1S)-(2-(tert-butyl)quinolin-4-yl)((1S,4S)-5-vinylquinuclidin-2-yl)methanol (42b).

According to the general procedure. White solid (69.3 mg, 66%). M.p. = 172 – 173 °C. 
\( R_t \) 0.50 (CH\(_2\)Cl\(_2\)/MeOH, 20/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.06 (dd, \( J = 8.4 \), 0.8 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.65 (ddd, \( J = 8.4 \), 6.8, 1.3 Hz, 1H), 7.49 (ddd, \( J = 8.4 \), 6.8, 1.2 Hz, 1H), 7.36 (s, 1H), 5.99 (ddd, \( J = 17.2 \), 10.4, 6.8 Hz, 1H), 5.21 – 5.05 (m, 2H), 3.44 (dd, \( J = 13.2 \), 4.4 Hz, 1H), 3.20 – 3.10 (m, 1H), 3.10 – 2.85 (m, 5H), 2.31 (dd, \( J = 16.4 \), 8.0 Hz, 1H), 1.60 – 1.49 (m, 3H), 1.46 (s, 9H), 1.37 – 1.28 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.8, 147.8, 144.8, 140.7, 130.4, 128.7, 126.2, 125.7, 123.3, 118.8, 114.8, 56.0, 49.4, 47.8, 40.0, 38.1, 37.9, 30.2, 28.1, 28.0, 26.6.

HRMS (ESI) calcd for C\(_{23}\)H\(_{31}\)N\(_2\)O \([\text{M + H}]^+\) 351.2431, found 351.2432.

5-((1,4-diazepan-1-yl)sulfonyl)-1-isopropylisoquinoline (43).
According to the *general procedure*. The spectral Data is consistent with the literature data.[4]

Yellow oil (42.0 mg, 42%).

\( R_f \) 0.50 (CH\(_2\)Cl\(_2\)/MeOH, 20/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.63 (d, \( J = 6.0 \) Hz, 1H), 8.49 (d, \( J = 8.4 \) Hz, 1H), 8.35 – 8.26 (m, 2H), 7.66 (dd, \( J = 8.4, 7.6 \) Hz, 1H), 4.06 – 3.91 (m, 1H), 3.55 – 3.48 (m, 2H), 3.48 – 3.43 (m, 2H), 3.03 – 2.93 (m, 4H), 2.11 (s, 1H), 1.86 (dt, \( J = 12.0, 6.0 \) Hz, 2H), 1.45 (d, \( J = 6.8 \) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.3, 143.9, 135.3, 132.4, 130.4, 127.0, 125.3, 115.7, 51.2, 50.4, 47.8, 47.5, 31.6, 31.3, 22.4. HRMS (ESI) calcd for C\(_{17}\)H\(_{24}\)N\(_3\)O\(_2\)S [M + H]\(^+\) 334.1584, found 334.1587.

\((2\text{-chlorophenyl})(4\text{-chlorophenyl})(2\text{-isopropylpyrimidin-5-yl})\text{methanol (44).}\

According to the *general procedure*. Yellow oil (69.2 mg, 62%).

\( R_f \) 0.50 (CH\(_2\)Cl\(_2\)/MeOH, 80/1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.53 (s, 2H), 7.44 (dd, \( J = 8.0 \) Hz, 1H), 7.37 – 7.32 (m, 3H), 7.22 – 7.16 (m, 3H), 6.76 (dd, \( J = 8.0, 1.6 \) Hz, 1H), 4.42 (s, 1H), 3.30 – 3.19 (m, 1H), 1.37 (d, \( J = 6.8 \) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 174.6, 156.5, 142.6, 141.5, 135.2, 134.2, 132.9, 132.0, 130.8, 130.2, 128.9, 128.8, 127.1, 79.9, 37.4, 21.9, 21.8. HRMS (ESI) calcd for C\(_{20}\)H\(_{19}\)Cl\(_2\)N\(_2\)O [M + H]\(^+\) 373.0869, found 373.0873.

\(\text{ethyl 4-(8-chloro-2-isopropyl-5,6-dihydro-11\text{-}H\text{-}benzo[5,6]cyclohepta[1,2-\text{-}b]pyridin-11-ylidene)piperidine-1-carboxylate (45a).}\)
According to the general procedure. White solid (105.6 mg, 83%). M.p. = 99 – 100 °C.

$R_f$ 0.70 (CH$_2$Cl$_2$/MeOH, 80/1).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J$ = 8.0 Hz, 1H), 7.23 – 7.08 (m, 3H), 6.98 (d, $J$ = 8.0 Hz, 1H), 4.22 – 4.06 (m, 2H), 3.96 – 3.66 (m, 2H), 3.33 (ddd, $J$ = 16.4, 20.0, 5.6 Hz, 2H), 3.21 – 3.10 (m, 2H), 3.03 (dt, $J$ = 13.6, 6.8 Hz, 1H), 2.88 – 2.71 (m, 2H), 2.58 – 2.44 (m, 1H), 2.44 – 2.25 (m, 3H), 1.29 – 1.22 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.4, 155.8, 155.6, 140.0, 138.2, 138.1, 137.4, 134.6, 132.8, 130.7, 128.9, 126.1, 118.5, 61.4, 45.0, 36.0, 31.9, 31.5, 31.0, 30.7, 23.5, 22.2, 14.8.

HRMS (ESI) calcd for C$_{25}$H$_{30}$ClN$_2$O$_2$ [M + H]$^+$ 425.1990, found 425.1993.

**ethyl 4-(8-chloro-2-cyclohexyl-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (45b).**

According to the general procedure. White solid (58.5 mg, 42%). M.p. = 105 – 106 °C.

$R_f$ 0.30 (CH$_2$Cl$_2$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J$ = 8.0 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.95 (d, $J$ = 8.0 Hz, 1H), 4.14 (q, $J$ = 7.2 Hz, 2H), 3.83 (s, 2H), 3.43 – 3.22 (m, 2H), 3.10 (t, $J$ = 9.6 Hz, 2H), 2.88 – 2.73 (m, 2H), 2.68 (t, $J$ = 11.6 Hz, 1H), 2.49 (s, 1H), 2.34 (ddd, $J$ = 9.2, 4.5 Hz, 3H), 1.85 (ddd, $J$ = 46.4, 28.8, 11.6 Hz, 6H), 1.44 – 1.34 (m, 3H), 1.26 (t, $J$ = 7.2 Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.7, 155.9, 155.7, 140.1, 138.3, 138.1, 137.4, 134.7, 132.9, 130.7, 130.3, 128.9, 126.2, 118.9, 61.4, 46.2, 45.0, 34.0, 32.5, 31.9, 31.5, 31.1, 30.8, 26.8, 26.6, 26.2, 14.8.

HRMS (ESI) calcd for C$_{28}$H$_{34}$ClN$_2$O$_2$ [M + H]$^+$ 465.2303, found 465.2307.

**ethyl 4-(2-(tert-butyl)-8-chloro-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (45c).**
According to the general procedure. White solid (80.2 mg, 61%). M.p. = 102 – 103 °C. 

\[ R_f \] 0.50 (CH\textsubscript{2}Cl\textsubscript{2}).

**\textsuperscript{1}H NMR** (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.30 (d, \( J = 8.0 \) Hz, 1H), 7.18 (s, 1H), 7.16 – 7.07 (m, 3H), 4.15 (q, \( J = 7.2 \) Hz, 2H), 3.77 – 3.56 (m, 3H), 3.42 – 3.36 (m, 2H), 3.32 – 3.18 (m, 1H), 2.89 – 2.68 (m, 2H), 2.61 (d, \( J = 4.8 \) Hz, 1H), 2.45 – 2.31 (m, 1H), 2.30 – 2.15 (m, 2H), 1.31 (s, 9H), 1.27 (d, \( J = 7.2 \) Hz, 3H). **\textsuperscript{13}C NMR** (100 MHz, CDCl\textsubscript{3}) \( \delta \) 166.0, 155.7, 154.7, 140.4, 139.0, 137.24, 134.7, 132.7, 130.5, 129.7, 128.5, 126.1, 117.2, 62.9, 61.5, 45.4, 37.3, 31.8, 31.7, 30.8, 30.3, 15.2, 14.9.

**HRMS** (ESI) calcd for C\textsubscript{26}H\textsubscript{32}Cl\textsubscript{2}N\textsubscript{2}O\textsubscript{2} \([\text{M + H}]^{+}\) 439.2147, found 439.2149.

2-((tert-butyl)-5,7-dichloro-4-(4-fluorophenoxy)quinoline (46a).

![46a](image)

According to the general procedure. White solid (82.8 mg, 76%). M.p. = 86 – 87 °C. 

\[ R_f \] 0.50 (Petroleum ether/EtOAc, 40/1).

**\textsuperscript{1}H NMR** (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.99 (d, \( J = 2.0 \) Hz, 1H), 7.50 (d, \( J = 2.0 \) Hz, 1H), 7.20 – 7.02 (m, 4H), 6.76 (s, 1H), 1.30 (s, 9H). **\textsuperscript{13}C NMR** (100 MHz, CDCl\textsubscript{3}) \( \delta \) 172.3, 162.1, 159.8 (d, \( J = 244 \) Hz), 151.2, 150.8, 134.71, 129.8, 128.8, 128.0, 121.8, 121.7, 117.2, 116.9, 116.8, 104.9, 38.4, 29.8.

**HRMS** (ESI) calcd for C\textsubscript{19}H\textsubscript{17}Cl\textsubscript{2}FNO \([\text{M + H}]^{+}\) 364.0666, found 364.0671.

5,7-dichloro-2-cyclohexyl-4-(4-fluorophenoxy)quinoline (46b).

![46b](image)
According to the general procedure. The spectral data is consistent with the literature data.[7]
White solid (80.5 mg, 69%). M.p. = 92 – 93 °C.
\( R_f \) 0.60 (Petroleum ether/EtOAc, 40/1).

\[ ^1H \text{NMR} \quad (400 \text{ MHz, CDCl}_3) \delta 7.95 (d, J = 2.0 \text{ Hz, 1H}), 7.49 (d, J = 2.0 \text{ Hz, 1H}), 7.20 – 7.06 (m, 4H), 6.52 (s, 1H), 2.68 (tt, J = 11.6, 3.2 Hz, 1H), 1.85 (dd, J = 23.2, 12.4 Hz, 4H), 1.72 (d, J = 12.4 Hz, 1H), 1.40 (ddd, J = 15.6, 9.6, 2.8 Hz, 4H), 1.26 (ddd, J = 12.0, 5.6, 3.2 Hz, 1H).

\[ ^13C \text{NMR} \quad (100 \text{ MHz, CDCl}_3) \delta 169.7, 162.45, 159.0 (d, J = 244 \text{ Hz}), 151.5, 150.5, 134.9, 130.0, 128.7, 127.6, 122.1, 122.0, 117.2, 117.1, 117.0, 105.8, 47.4, 32.5, 26.4, 26.0.

HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)Cl\(_2\)FNO \([\text{M} + \text{H}]^+\) 390.0822, found 390.0824.

2-((3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-4-methylquinoline (47).

According to the general procedure. Steride (0.2 mmol) and lepidine (0.4 mmol) \( \text{Ir[}dF(CF}_3\text{ppy})\_2(\text{dtbbpy})\text{PF}_6 \) (2.24 mg, 0.002 mmol, 1 mol %), TTMS (123 \( \mu \text{L}, 0.4 \text{ mmol, 2.0 equiv}), TFA (30 \( \mu \text{L}, 0.4 \text{ mmol, 2.0 equiv}) and 2.0 mL of acetone.
White solid (72.8 mg, 71%). M.p. = 180 – 181 °C.
\( R_f \) 0.68 (Petroleum ether/EtOAc, 40/1).

\[ ^1H \text{NMR} \quad (400 \text{ MHz, CDCl}_3) \delta 8.04 (d, J = 8.4 \text{ Hz, 1H}), 7.93 (d, J = 8.4 \text{ Hz, 1H}), 7.66 (t, J = 7.2 \text{ Hz, 1H}), 7.48 (t, J = 7.2 \text{ Hz, 1H}), 7.18 (s, 1H), 3.00 – 2.84 (m, 1H), 2.68 (s, 3H), 2.02 – 1.95 (m, 1H), 1.90 – 1.78 (m, 4H), 1.68 (d, J = 11.6 Hz, 2H), 1.63 – 1.51 (m, 4H), 1.39 – 1.21 (m, 9H), 1.13 (ddd, J = 18.8, 9.6, 4.0 Hz, 7H), 1.01 (ddd, J = 12.4, 9.6 Hz, 3H), 0.97 – 0.90 (m, 7H), 0.87 (dd, J = 6.8, 1.6 Hz, 6H), 0.67 (s, 3H).

\[ ^13C \text{NMR} \quad (100 \text{ MHz, CDCl}_3) \delta 166.4, 147.8, 144.3, 129.6, 129.0, 127.2, 125.5, 123.7, 120.3, 56.7, 56.4, 54.7, 48.1, 46.9, 42.8, 40.2, 39.7, 38.8, 36.3, 36.0, 35.9, 35.7, 35.1, 32.3, 29.0, 28.5, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.2, 19.0, 18.8, 12.8, 12.2.

HRMS (ESI) calcd for C\(_{37}\)H\(_{56}\)N \([\text{M} + \text{H}]^+\) 514.4407, found 514.4412.

benzyl 3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)propanoate (49).

According to the general procedure. Colorless oil.
\( R_f \) 0.60 (Petroleum ether/EtOAc, 200/1).

\[ ^1H \text{NMR} \quad (400 \text{ MHz, CDCl}_3) \delta 7.39 – 7.35 (m, 4H), 5.12 (s, 2H), 2.46 – 2.32 (m, 2H), 1.19 – 1.07 (m, 2H), 0.17 (s, 27H).

\[ ^13C \text{NMR} \quad (100 \text{ MHz, CDCl}_3) \delta 174.7, 136.2, 128.7, 128.4, 128.3, 66.4, 33.3, 2.9, 1.2.

HRMS (ESI) calcd for C\(_{19}\)H\(_{42}\)NO\(_2\)Si\(_4\) \([\text{M} + \text{NH}_4]^+\) 428.2287, found 428.2283.
2-(cyclopentylmethyl)-4-methylquinoline and 2-(hex-5-en-1-yl)-4-methylquinoline (52).

According to the general procedure. The spectral Data is consistent with the literature data.[5]

Yellow oil (56.0 mg, 83%).

\[ R_f \ 0.35 \ \text{(Petroleum ether/EtOAc, 20/1).} \]

\[^1\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta 8.05 (d, J = 8.4 \text{ Hz}, 1H), 7.94 (d, J = 7.6 \text{ Hz}, 1H), 7.72 – 7.63 (m, 1H), 7.55 – 7.44 (m, 1H), 7.13 (s, 1H), 5.81 (ddt, J = 16.8, 10.0, 6.8 \text{ Hz}, 0.05H), 5.04 – 4.92 (m, 0.1H), 2.93 (d, J = 7.6 \text{ Hz}, 2H), 2.67 (s, 3H), 2.43 – 2.28 (m, 1H), 1.87 – 1.61 (m, 4H), 1.60 – 1.46 (m, 2H), 1.33 – 1.24 (m, 2H). \[^{13}\text{C NMR}\ (100 \text{ MHz, CDCl}_3) \delta 162.4, 147.8, 144.1, 129.5, 129.1, 126.9, 125.5, 123.7, 122.6, 45.2, 40.9, 32.7, 25.1, 18.9. \]

\[^{HRMS}\ (\text{ESI})\ \text{calcd for C}_{16}\text{H}_{20}\text{N}[\text{M} + \text{H}]^+ 226.1590, \text{found 226.1593.} \]

2-(but-3-en-1-yl)-4-methylquinoline (54).

\[^{1}\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta 8.04 (d, J = 8.4 \text{ Hz}, 1H), 7.95 (d, J = 8.4 \text{ Hz}, 1H), 7.68 (dd, J = 8.4, 6.8 \text{ Hz}, 1H), 7.51 (dd, J = 8.4, 6.8 \text{ Hz}, 1H), 7.15 (s, 1H), 5.93 (ddt, J = 16.8, 10.4, 6.4 \text{ Hz}, 1H), 5.09 (dd, J = 16.8, 1.2 \text{ Hz}, 1H), 4.99 (d, J = 10.4 \text{ Hz}, 1H), 3.10 – 2.97 (m, 2H), 2.68 (s, 3H), 2.58 (td, J = 7.6, 1.2 \text{ Hz}, 2H). \[^{13}\text{C NMR}\ (100 \text{ MHz, CDCl}_3) \delta 161.8, 147.8, 144.4, 137.9, 129.4, 129.2, 127.0, 125.6, 123.76, 122.3, 115.3, 38.6, 34.0, 18.9. \]

\[^{HRMS}\ (\text{ESI})\ \text{calcd for C}_{14}\text{H}_{16}\text{N}[\text{M} + \text{H}]^+ 198.1277, \text{found 198.1279.} \]

2-(cyclobutylmethyl)-4-methylquinoline and 4-methyl-2-(pent-4-en-1-yl)quinoline (56).

\[^{1}\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta 8.05 (d, J = 8.4 \text{ Hz}, 1H), 7.94 (d, J = 7.6 \text{ Hz}, 1H), 7.72 – 7.63 (m, 1H), 7.55 – 7.44 (m, 1H), 7.13 (s, 1H), 5.81 (ddt, J = 16.8, 10.0, 6.8 \text{ Hz}, 0.05H), 5.04 – 4.92 (m, 0.1H), 2.93 (d, J = 7.6 \text{ Hz}, 2H), 2.67 (s, 3H), 2.43 – 2.28 (m, 1H), 1.87 – 1.61 (m, 4H), 1.60 – 1.46 (m, 2H), 1.33 – 1.24 (m, 2H). \[^{13}\text{C NMR}\ (100 \text{ MHz, CDCl}_3) \delta 162.4, 147.8, 144.1, 129.5, 129.1, 126.9, 125.5, 123.7, 122.6, 45.2, 40.9, 32.7, 25.1, 18.9. \]

\[^{HRMS}\ (\text{ESI})\ \text{calcd for C}_{16}\text{H}_{20}\text{N}[\text{M} + \text{H}]^+ 226.1590, \text{found 226.1593.} \]

2-(but-3-en-1-yl)-4-methylquinoline (54).

According to the general procedure. The spectral Data is consistent with the literature data.[5]

Yellow oil (26.6 mg, 45%).

\[ R_f \ 0.40 \ \text{(Petroleum ether/EtOAc, 40/1).} \]

\[^{1}\text{H NMR}\ (400 \text{ MHz, CDCl}_3) \delta 8.04 (d, J = 8.4 \text{ Hz}, 1H), 7.95 (d, J = 8.4 \text{ Hz}, 1H), 7.68 (dd, J = 8.4, 6.8 \text{ Hz}, 1H), 7.51 (dd, J = 8.4, 6.8 \text{ Hz}, 1H), 7.15 (s, 1H), 5.93 (ddt, J = 16.8, 10.4, 6.4 \text{ Hz}, 1H), 5.09 (dd, J = 16.8, 1.2 \text{ Hz}, 1H), 4.99 (d, J = 10.4 \text{ Hz}, 1H), 3.10 – 2.97 (m, 2H), 2.68 (s, 3H), 2.58 (td, J = 7.6, 1.2 \text{ Hz}, 2H). \[^{13}\text{C NMR}\ (100 \text{ MHz, CDCl}_3) \delta 161.8, 147.8, 144.4, 137.9, 129.4, 129.2, 127.0, 125.6, 123.76, 122.3, 115.3, 38.6, 34.0, 18.9. \]

\[^{HRMS}\ (\text{ESI})\ \text{calcd for C}_{14}\text{H}_{16}\text{N}[\text{M} + \text{H}]^+ 198.1277, \text{found 198.1279.} \]

2-(cyclobutylmethyl)-4-methylquinoline and 4-methyl-2-(pent-4-en-1-yl)quinoline (56).

According to the general procedure. The spectral Data is consistent with the literature data.[5]

Yellow oil (26.6 mg, 42%).

\[ R_f \ 0.40 \ \text{(Petroleum ether/EtOAc, 40/1).} \]
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 8.4 Hz, 1H), 7.94 (dd, $J$ = 8.4, 0.8 Hz, 1H), 7.66 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.08 (s, 1H), 5.87 (ddt, $J$ = 16.8, 10.4, 6.8 Hz, 0.08H), 5.11 – 4.93 (m, 0.16H), 3.02 (d, $J$ = 7.6 Hz, 2H), 2.81 (dt, $J$ = 15.6, 7.6 Hz, 1H), 2.66 (s, 3H), 2.12 – 2.00 (m, 2H), 1.95 – 1.77 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.5, 147.8, 144.2, 129.5, 129.1, 126.9, 125.5, 123.7, 122.3, 46.1, 36.4, 28.5, 18.9, 18.7.

HRMS (ESI) calcd for C$_{15}$H$_{18}$N [M + H]$^+$ 212.1434, found 212.1436.

7. Gram-scale Reaction

![Scheme S4](image)

To an oven dried Schlenk tube was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (67.3 mg, 0.06 mmol, 1 mol %), lepidine (0.8 mL, 6.0 mmol, 1.0 equiv), TTMS (3.7 mL, 12 mmol, 2.0 equiv), bromoalkane (2.6 g, 12 mmol, 2.0 equiv), TFA (0.9 mL, 12 mmol, 2.0 equiv) and 60 mL of acetone. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The reaction mixture was concentrated in vacuum to remove the acetone. The mixture was diluted with 60 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. After purification by flash column chromatography on silica gel, the product was obtained in 77% yield.

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NMR Spectra

\[ ^1H \text{ NMR spectrum of compound 3} \]

\[ ^13C \text{ NMR spectrum of compound 3} \]
$^1$H NMR spectrum of compound 4

$^{13}$C NMR spectrum of compound 4
$^1$H NMR spectrum of compound 5

$^{13}$C NMR spectrum of compound 5
$^1$H NMR spectrum of compound 6

$^{13}$C NMR spectrum of compound 6
$^1$H NMR spectrum of compound 7

$^{13}$C NMR spectrum of compound 7
$^1$H NMR spectrum of compound 8

$^{13}$C NMR spectrum of compound 8
$^1$H NMR spectrum of compound 9

$^{13}$C NMR spectrum of compound 9
$^1$H NMR spectrum of compound 10

$^{13}$C NMR spectrum of compound 10
$^1$H NMR spectrum of compound 11

$^{13}$C NMR spectrum of compound 11
$^1$H NMR spectrum of compound 12

$^{13}$C NMR spectrum of compound 12
$^1$H NMR spectrum of compound 13

$^{13}$C NMR spectrum of compound 13
$^1$H NMR spectrum of compound 14

$^{13}$C NMR spectrum of compound 14
$^{1}H$ NMR spectrum of compound 15

$^{13}C$ NMR spectrum of compound 15
$^1$H NMR spectrum of compound 16

$^{13}$C NMR spectrum of compound 16
$^1$H NMR spectrum of compound 17

$^{13}$C NMR spectrum of compound 17
$^1$H NMR spectrum of compound 18

$^{13}$C NMR spectrum of compound 18
$^1$H NMR spectrum of compound 19

$^{13}$C NMR spectrum of compound 19
H NMR spectrum of compound 21

\[
\text{\textsuperscript{13}C NMR spectrum of compound 21}
\]
$^1$H NMR spectrum of compound **22**

$^{13}$C NMR spectrum of compound **22**
$^1$H NMR spectrum of compound 23

$^{13}$C NMR spectrum of compound 23
$^1$H NMR spectrum of compound 24

$^{13}$C NMR spectrum of compound 24
$^1$H NMR spectrum of compound 25

$^{13}$C NMR spectrum of compound 25
$^1$H NMR spectrum of compound 26

$^{13}$C NMR spectrum of compound 26
$^1$H NMR spectrum of compound 27

$^{13}$C NMR spectrum of compound 27
$^1$H NMR spectrum of compound 28

$^{13}$C NMR spectrum of compound 28
$^1$H NMR spectrum of compound 29

$^{13}$C NMR spectrum of compound 29
$\text{H NMR spectrum of compound 30}$

$\text{C NMR spectrum of compound 30}$
$^1$H NMR spectrum of compound 31

$^{13}$C NMR spectrum of compound 31
$^1$H NMR spectrum of compound 32

$^{13}$C NMR spectrum of compound 32
$^{1}H$ NMR spectrum of compound 33

$^{13}C$ NMR spectrum of compound 33
$^{1}H$ NMR spectrum of compound 34

$^{13}C$ NMR spectrum of compound 34
$^{1}$$H$ NMR spectrum of compound 35

$^{13}$$C$ NMR spectrum of compound 35
$^1$H NMR spectrum of compound 36

[Image of H NMR spectrum]

$^{13}$C NMR spectrum of compound 36

[Image of C NMR spectrum]
$^1$H NMR spectrum of compound 37

$^{13}$C NMR spectrum of compound 37
$^1$H NMR spectrum of compound 38

$^{13}$C NMR spectrum of compound 38
$^1$H NMR spectrum of compound 39

$^{13}$C NMR spectrum of compound 39
$^1$H NMR spectrum of compound 41

$^{13}$C NMR spectrum of compound 41
$^1$H NMR spectrum of compound 42a

$^{13}$C NMR spectrum of compound 42a
$^1$H NMR spectrum of compound 42b

$^{13}$C NMR spectrum of compound 42b
$^1$H NMR spectrum of compound 43

$^{13}$C NMR spectrum of compound 43
$^1$H NMR spectrum of compound 44

$^{13}$C NMR spectrum of compound 44
$^1$H NMR spectrum of compound 45a

$^{13}$C NMR spectrum of compound 45a
$^1$H NMR spectrum of compound 45b

$^{13}$C NMR spectrum of compound 45b
$^1$H NMR spectrum of compound 45c

$^{13}$C NMR spectrum of compound 45c
$^1$H NMR spectrum of compound 46a

$^{13}$C NMR spectrum of compound 46a
$^1$H NMR spectrum of compound 46b

$^{13}$C NMR spectrum of compound 46b
\(^1\)H NMR spectrum of compound 47

\(^{13}\)C NMR spectrum of compound 47
$^1\text{H NMR spectrum of compound 49}$

$^{13}\text{C NMR spectrum of compound 49}$
