Electronic Supplementary Information (ESI)

Metal-Free Oxidative Isocyanides Insertion with Aromatic Aldehydes to Aroylated N-heterocycles

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1. General information

Reactions were monitored by using thin-layer chromatography (TLC) on commercial silica gel plates (GF254). Visualization of the developed plates was performed under UV lights (254 nm). Flash column chromatography was performed on silica gel (200-300 mesh). $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV300, 400 and 500 MHz spectrometers. Chemical shifts ($\delta$) were reported in ppm referenced to the CDCl$_3$ residual peak ($\delta$ 7.26) or the DMSO-d$_6$ residual peak ($\delta$ 2.50) for $^1$H NMR. Chemical shifts of $^{13}$C NMR were reported relative to CDCl$_3$ ($\delta$ 77.0) or D$_6$-DMSO ($\delta$ 39.5). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, $J$, was reported in Hertz unit (Hz). Melting points (mp) were taken on a MEL-TEMP® apparatus and were uncorrected. High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer.

2. Synthesis of isocyanides

2.1 Synthesis of phenyl isocyanides 1a-1w

The isocyanide 1a was prepared according to the reported method.\textsuperscript{1}

\begin{center}
\begin{align*}
\text{S1} & \xrightarrow{\text{Pd(II) (cat.)}} \text{S2} & \xrightarrow{\text{HCOCH(OH)2}} \text{S3} & \xrightarrow{\text{POCl3}} \text{1a} \\
\end{align*}
\end{center}

4-Methyl-2-(phenyl)phenyl isocyanide (1a). To an oven-dried three necked flask, 2-bromo-4-methylaniline S1 (925 mg, 5 mmol), phenylboronic acid (732 mg, 6 mmol), aqueous solution of K$_2$CO$_3$ (2M, 11 mL) and DME (10 mL) were added under a gentle stream of Ar, and the mixture was stirred for 30 min at room temperature under Ar atmosphere. PdCl$_2$(PPh$_3$)$_2$ (70 mg, 0.10 mmol) was subsequently added at room temperature, and the mixture was stirred overnight at 80 °C under Ar. The reaction mixture was cooled to room temperature and diluted with EtOAc. The organic layer was washed with water and dried over Na$_2$SO$_4$. After removing the volatiles in vacuo, the residue was subjected to column chromatography on silica gel (petroleum ether/EtOAc = 4 : 1) to afford 4-methyl-2-phenylaniline S2 (788 mg, 86% yield).

Acetic formic anhydride (0.89 mL) was added dropwise to a stirred solution of S2 (788 mg, 4.30 mmol) in THF (8 mL) at 0 °C, and then the mixture was stirred for 2 h.
at room temperature. The mixture was quenched by a saturated aqueous solution of NaHCO₃ and extracted with EtOAc three times. The extract was dried over Na₂SO₄ and concentrated to give formamide S₃ as a pale yellow oil. This material was used for the subsequent dehydration without further purification.

To an oven-dried three-necked flask equipped with a dropping funnel, THF (8 mL), NEt₃ (4.3 mL) and the whole amount of S₃ obtained above were added under Ar atmosphere and cooled to 0 °C. POCl₃ (0.7 mL) in 2 mL of THF was added dropwise, and the mixture was stirred for 2 h at 0 °C until the addition was complete. The mixture was slowly quenched at 0 °C by a saturated aqueous solution of NaHCO₃ and stirred for 1 h at room temperature. The mixture was extracted with EtOAc three times, dried over Na₂SO₄ and evaporated under reduced pressure. The residues were purified by column chromatography (petroleum ether/EtOAc = 30 : 1) to give 1a as a pale yellow solid (811 mg, 84% yield).

1b-1w were prepared according to the procedure described for 1a.

2.2 Synthesis of vinyl isocyanides 4a-4e

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{O} & \quad \text{CN} \quad \text{CO}_2\text{Me} \\
\text{S4} & \quad \text{S5} \\
\text{rt, 2h} & \quad \text{NaH, THF} \\
\text{Ph} & \quad \text{MeO}_2\text{C} \quad \text{NHCHO} \\
\text{S6} & \quad \text{POCl}_3 \quad \text{Et}_3\text{N, THF} \\
\text{0 °C, 2h} & \quad \text{Ph} \quad \text{MeO}_2\text{C} \quad \text{NC} \\
\text{S6} & \quad \text{S4} \\
\text{S6} & \quad \text{4a}
\end{align*}
\]

To a mixture of benzophenone S₄ (0.91 g, 5 mmol) and methyl isocyanoacetate S₅ (0.5 g, 5 mmol) in THF (5 mL), a suspension of NaH (60% in oil) (0.24 g, 6 mmol) in THF (5 ml) was added dropwise at room temperature for 2 h. After the reaction was completed (as judged by TLC analysis), the solvent was removed under reduced pressure and the residue was extracted with CH₂Cl₂ three times and the extract was washed with H₂O, dried over Na₂SO₄ and concentrated under reduced pressure. The material S₆ was used for the subsequent dehydration without further purification.

To an oven-dried three-necked flask equipped with a dropping funnel, THF (10 mL), NEt₃ (5 mL) and the whole amount of S₆ obtained above were added under Ar atmosphere and cooled to 0 °C. POCl₃ (0.8 mL) in 2 mL of THF was added dropwise, and the mixture was stirred for 2 h at 0 °C until the addition was complete. The mixture was slowly quenched by a saturated aqueous solution of NaHCO₃ at 0 °C and stirred for 1 h at room temperature. The mixture was extracted with EtOAc three times, dried over Na₂SO₄ and evaporated under reduced pressure. The residues were purified by column chromatography (petroleum ether/EtOAc = 30 : 1) to give 4a as a white solid.
4b-4e were prepared according to the procedure described for 4a.

3. Synthesis of material 6

![Chemical reaction diagram](image)

A 100 mL round-bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with a solution of 2-formylphenylboronic acid (950 mg, 5 mmol) and allyl bromide (0.5 mL, 6 mmol) in THF (25 mL). Then PdCl$_2$(PPh$_3$)$_2$ (88 mg, 0.125 mmol) and aq. Na$_2$CO$_3$ (1M, 10 mmol) solution was added. The reaction mixture was heated at reflux for 3-4 h. The reaction mixture was quenched with H$_2$O and extracted with CH$_2$Cl$_2$ three times. The combined organic layers were washed with H$_2$O, dried over MgSO$_4$, and concentrated in vacuo. The residues were purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the desired product 6 (82% yield) as a pale yellow oil.

4. General procedure and product characterization

4.1 General procedure

Typical procedure for PIDA-mediated oxidative phenyl isocyanides insertion with aromatic aldehydes to 6-aroylated phenanthridines 3a-3w.

![Chemical reaction diagram](image)

A oven-dried sealed tube was equipped with a magnetic stir bar and was charged with a mixture of 2-isocyanobiphenyl (0.2 mmol), aldehyde (1.2 mmol) and TMSN$_3$ (0.5 mmol) in CH$_2$Cl$_2$ (1.0 mL). Then (diacetoxyiodo)benzene (PIDA) (0.5 mmol) was dissolved in CH$_2$Cl$_2$ (1.0 mL) and added dropwise to the reaction mixture for 10
minutes at 50 °C. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and CH₂Cl₂ (20 mL) was added to the solution and washed with water (20 ml x 3), dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the targeted product 3a-3w.

Typical procedure for PIDA-mediated oxidative vinyl isocyanides insertion with aromatic aldehydes to 1-arylated isoquinolines 5a-5e.

A oven-dried sealed tube was equipped with a magnetic stir bar and was charged with a mixture of vinyl isocyanide (0.2 mmol), aldehyde (1.2 mmol), K₂CO₃ (0.4 mmol) and TMSN₃ (0.5 mmol) in CH₂Cl₂ (1.0 mL). Then (diacetoxyiodo)benzene (PIDA) (0.5 mmol) was dissolved in CH₂Cl₂ (1.0 mL) and added dropwise to the reaction mixture for 10 minutes at 50 °C. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and CH₂Cl₂ (20 mL) was added to the solution and washed with water (20 ml x 3), dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the targeted product 5a-5e.

Typical procedure for PIDA-mediated oxidative phenyl isocyanide insertion with aromatic aldehyde bearing ortho terminal alkene 6 to phenanthridine derivative 7.

A oven-dried sealed tube was equipped with a magnetic stir bar and was charged with a mixture of 2-isocyanobiphenyl 1a (0.2 mmol), aldehyde 6 (1.2 mmol) and TMSN₃ (0.5 mmol) in CH₂Cl₂ (1.0 mL). Then (diacetoxyiodo)benzene (PIDA) (0.5 mmol)
was dissolved in CH$_2$Cl$_2$ (1.0 mL) and added dropwise to the reaction mixture for 10 minutes at 50 °C. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and CH$_2$Cl$_2$ (20 mL) was added to the solution and washed with water (20 ml x 3), dried over Na$_2$SO$_4$, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the targeted product 7.

4.2 Product characterization

(2-methylphenanthridin-6-yl)(phenyl)methanone (3a) $^4$

![Image of (2-methylphenanthridin-6-yl)(phenyl)methanone (3a)]

Yield: 74%. Mp 171-173 °C. Pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.70 (d, $J = 8.4$ Hz, 1H), 8.44 (s, 1H), 8.16-8.09 (m, 2H), 8.04 (d, $J = 8.0$ Hz, 2H), 7.88 (t, $J = 7.2$ Hz, 1H), 7.67-7.60 (m, 3H), 7.48 (t, $J = 7.2$ Hz, 2H), 2.68 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 194.9, 156.4, 140.9, 138.3, 136.3, 133.8, 133.0, 131.0, 130.8, 130.4, 128.5, 127.6, 127.2, 124.3, 124.0, 122.2, 121.7, 22.1; HRMS (ESI): Exact mass calcd for C$_{21}$H$_{15}$NO [M+H]$^+$, 298.1193; Found: 298.1190.

(2-methylphenanthridin-6-yl)(p-tolyl)methanone (3b) $^{4a}$

![Image of (2-methylphenanthridin-6-yl)(p-tolyl)methanone (3b)]

Yield: 66%. Mp 170-172 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.70 (d, $J = 8.4$ Hz, 1H), 8.43 (s, 1H), 8.11 (t, $J = 7.2$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.87 (t, $J = 7.6$ Hz, 1H), 7.66-7.60 (m, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 2.67 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 194.6, 156.8, 144.9, 141.0, 138.2, 133.9, 133.0, 130.9, 129.3, 127.6, 127.3, 124.3, 123.9, 122.2, 121.7, 22.1, 21.8; HRMS (ESI): Exact mass calcd for C$_{22}$H$_{17}$NO [M+H]$^+$, 312.1383; Found: 312.1385.
(4-ethylphenyl)(2-methylphenanthridin-6-yl)methanone (3c)

Yield: 63%. Mp 129-131 °C. Yellow solid. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.70 (d, \(J = 8.0\) Hz, 1H), 8.43 (s, 1H), 8.12 (t, \(J = 8.0\) Hz, 2H), 7.96 (d, \(J = 7.6\) Hz, 2H), 7.87 (t, \(J = 7.6\) Hz, 1H), 7.66-7.60 (m, 2H), 7.28 (d, \(J = 7.6\) Hz, 2H), 2.75-2.69 (m, 2H), 2.67 (s, 3H), 1.26 (t, \(J = 7.2\) Hz, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)): \(\delta\) 197.5, 157.2, 141.3, 140.2, 138.3, 137.0, 133.2, 132.4, 132.0, 131.8, 130.7, 130.6, 127.6, 127.4, 125.4, 124.5, 124.1, 122.2, 121.6, 29.1, 22.1, 15.1; HRMS (ESI): Exact mass calcd for C\(_{23}\)H\(_{19}\)NO \([M+H]\)^{+}, 326.1539; Found: 326.1539.

(4-methoxyphenyl)(2-methylphenanthridin-6-yl)methanone (3d) \(^{4a}\)

Yield: 76%. Mp 142-144 °C. White solid. \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.70 (d, \(J = 8.0\) Hz, 1H), 8.43 (s, 1H), 8.12 (t, \(J = 5.6\) Hz, 2H), 8.01 (t, \(J = 7.6\) Hz, 2H), 7.87 (t, \(J = 7.6\) Hz, 1H), 7.65-7.60 (m, 2H), 6.94 (d, \(J = 7.6\) Hz, 2H), 3.87 (s, 3H), 2.67 (s, 3H); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)): \(\delta\) 193.6, 164.4, 157.1, 141.1, 138.2, 133.3, 133.1, 131.0, 130.9, 130.4, 129.5, 127.6, 127.5, 124.4, 124.0, 122.3, 121.8, 113.9, 55.6, 22.2; HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{17}\)NO\(_2\) \([M+H]\)^{+}, 328.1332; Found: 328.1331.

(4-fluorophenyl)(2-methylphenanthridin-6-yl)methanone (3e) \(^{4a}\)

Yield: 49%. Mp 188-190 °C. White solid. \(^{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.71 (d, \(J =
8.1 Hz, 1H), 8.44 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.14-8.09 (m, 3H), 7.92-7.87 (m, 1H), 7.70-7.62 (m, 2H), 7.17 (t, J = 8.7 Hz, 2H), 2.69 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 193.2, 168.0, 164.6, 155.9, 140.9, 138.6, 133.7, 133.6, 133.1, 132.8, 132.7, 131.1, 130.9, 130.4, 127.7, 127.2, 124.4, 123.9, 122.3, 121.8, 115.9, 115.6, 22.2; HRMS (ESI): Exact mass calcld for C$_{21}$H$_{14}$FNO $[M+H]^+$, 316.1132; Found: 316.1129.

(4-chlorophenyl)(2-methylphenanthridin-6-yl)methanone (3f) $^{4a}$

![Chemical structure of (4-chlorophenyl)(2-methylphenanthridin-6-yl)methanone](image)

Yield: 45%. Mp 216-218 °C. White solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.72 (d, J = 8.4 Hz, 1H), 8.45 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.04-8.00 (m, 2H), 7.93-7.88 (m, 1H), 7.71-7.62 (m, 2H), 7.49-7.45 (m, 2H), 7.31 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 193.5, 155.6, 140.8, 140.4, 138.7, 134.7, 133.1, 132.3, 131.1, 131.0, 130.4, 128.9, 127.8, 127.2, 124.5, 123.9, 122.3, 121.8, 22.2.

(2-methylphenanthridin-6-yl)(4-(trifluoromethyl)phenyl)methanone (3g)

![Chemical structure of (2-methylphenanthridin-6-yl)(4-(trifluoromethyl)phenyl)methanone](image)

Yield: 13%. Pale yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.75 (d, J = 8.4 Hz, 1H), 8.47 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.4 Hz, 1H), 7.96-7.91 (m, 1H), 7.79-7.63 (m, 4H), 2.71 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 193.5, 154.9, 140.8, 139.3, 139.0, 133.2, 131.2, 131.0, 130.5, 129.2, 127.9, 127.1, 125.5, 125.4, 124.6, 123.9, 122.4, 121.8, 22.2; HRMS (ESI): Exact mass calcld for C$_{22}$H$_{14}$F$_3$NO $[M+H]^+$, 366.1025; Found: 366.1029.

(2-methylphenanthridin-6-yl)(o-tolyl)methanone (3h) $^{4a}$
Yield: 50%. Mp 126-128 °C. White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.70 (d, \(J = 6.8\) Hz, 1H), 8.42 (s, 1H), 8.25 (d, \(J = 8.0\) Hz, 1H), 8.05 (d, \(J = 8.4\) Hz, 1H), 7.88 (t, \(J = 7.2\) Hz, 1H), 7.67 (t, \(J = 8.0\) Hz, 1H), 7.58 (d, \(J = 8.4\) Hz, 1H), 7.52 (d, \(J = 7.6\) Hz, 1H), 7.45 (t, \(J = 7.6\) Hz, 1H), 7.35 (d, \(J = 7.2\) Hz, 1H), 7.18 (t, \(J = 7.6\) Hz, 1H), 2.66 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.5, 157.2, 141.3, 140.2, 138.3, 137.0, 133.2, 132.4, 132.0, 131.8, 130.7, 130.6, 127.6, 127.4, 125.4, 124.5, 124.1, 122.2, 121.6, 21.9, 21.4; HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{17}\)NO \([\text{M+H}]^+\), 312.1385; Found: 312.1384.

\((2\text{-}(\text{tert-butyl})\text{phenyl})(2\text{-methylphenanthridin-6-yl})\text{methanone (3i)}\)

Yield: 35%. Pale yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 9.04 (d, \(J = 8.4\) Hz, 1H), 8.72 (d, \(J = 8.4\) Hz, 1H), 8.41 (s, 1H), 7.99-7.77 (m, 3H), 7.66 (d, \(J = 8.1\) Hz, 1H), 7.56-7.53 (m, 1H), 7.47-7.42 (m, 1H), 7.20 (d, \(J = 4.5\) Hz, 2H), 2.66 (s, 3H), 1.50 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 201.5, 154.3, 149.1, 140.9, 140.8, 139.3, 133.2, 131.2, 130.6, 129.4, 128.9, 128.1, 127.6, 127.5, 124.9, 124.6, 124.5, 122.1, 121.6, 36.4, 32.3, 22.2; HRMS (ESI): Exact mass calcd for C\(_{25}\)H\(_{23}\)NO \([\text{M+H}]^+\), 354.1852; Found: 354.1859.

\((2,6\text{-dimethylphenyl})(2\text{-methylphenanthridin-6-yl})\text{methanone (3j)}\)

Yield: 51%. Mp 101-103 °C. White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.05 (d, \(J = 8.4\) Hz, 1H), 8.68 (d, \(J = 8.4\) Hz, 1H), 8.36 (s, 1H), 7.93 (d, \(J = 8.4\) Hz, 1H), 7.87 (t, \(J = 8.4\) Hz, 1H), 7.60 (t, \(J = 7.6\) Hz, 1H), 7.52 (d, \(J = 8.4\) Hz, 1H), 7.50 (t, \(J = 7.2\) Hz, 1H), 7.47 (t, \(J = 7.2\) Hz, 1H), 7.45 (t, \(J = 7.2\) Hz, 1H), 7.43 (t, \(J = 7.2\) Hz, 1H), 7.37 (d, \(J = 8.4\) Hz, 1H), 7.35 (d, \(J = 8.4\) Hz, 1H), 7.21 (t, \(J = 7.2\) Hz, 1H), 2.66 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.5, 157.2, 141.3, 140.2, 138.3, 137.0, 133.2, 132.4, 132.0, 131.8, 130.7, 130.6, 127.6, 127.4, 125.4, 124.5, 124.1, 122.2, 121.6, 21.9, 21.4; HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{17}\)NO \([\text{M+H}]^+\), 312.1385; Found: 312.1384.
= 7.6 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 2.62 (s, 3H), 2.22 (s, 6H); 13C NMR (100 MHz, CDCl3): δ 202.4, 153.8, 142.2, 141.5, 139.6, 135.2, 133.7, 131.6, 130.7, 128.9, 128.3, 127.9, 127.7, 125.4, 124.0, 122.4, 121.8, 22.3, 20.0; HRMS (ESI): Exact mass calcd for C23H19NO [M+H]+, 326.1539; Found: 326.1540.

(2-methylphenanthridin-6-yl)(m-tolyl)methanone (3k) 4a

Yield: 42%. Mp 124-126 °C. Yellow solid. 1H NMR (400 MHz, CDCl3): δ 8.71 (d, J = 8.4 Hz, 1H), 8.44 (s, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.87 (t, J = 7.6 Hz, 2H), 7.80 (t, J = 7.6 Hz, 1H), 7.66-7.64 (m, 2H), 7.43 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 2.68 (s, 3H), 2.38 (s, 3H); 13C NMR (125 MHz, CDCl3): δ 195.2, 156.8, 141.0, 138.4, 138.3, 136.4, 134.8, 133.0, 131.1, 131.0, 130.8, 130.4, 128.5, 127.6, 127.3, 124.3, 124.0, 122.3, 121.8, 22.1, 21.3; HRMS (ESI): Exact mass calcd for C22H17NO [M+H]+, 312.1383; Found: 312.1384.

(3-methoxyphenyl)(2-methylphenanthridin-6-yl)methanone (3l)

Yield: 52%. Mp 148-150 °C. White solid. 1H NMR (400 MHz, CDCl3): δ 8.70 (d, J = 8.0 Hz, 1H), 8.43 (s, 1H), 8.12 (t, J = 8.0 Hz, 2H), 7.87 (t, J = 7.2 Hz, 1H), 7.67-7.60 (m, 3H), 7.50 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.17(d, J = 8.0 Hz, 1H), 3.85 (s, 3H), 2.67 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 194.7, 160.2, 156.8, 141.5, 138.5, 138.3, 133.4, 131.1, 130.8, 129.7, 127.8, 127.6, 124.7, 124.3, 124.2, 122.5, 120.8, 114.9, 55.7, 22.2; HRMS (ESI): Exact mass calcd for C22H17NO2 [M+H]+, 328.1332; Found: 328.1332.

(8-(tert-butyl)-2-methylphenanthridin-6-yl)(4-methoxyphenyl)methanone (3m)
Yield: 47%. Mp 128-130 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.62 (d, $J = 8.4$ Hz, 1H), 8.39 (s, 1H), 8.08 (d, $J = 8.8$ Hz, 2H), 8.03 (d, $J = 7.6$ Hz, 2H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 2H), 3.87 (s, 3H), 2.66 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.8, 164.2, 156.9, 150.7, 140.8, 138.0, 133.2, 130.9, 130.4, 130.2, 129.6, 129.4, 124.3, 124.0, 122.8, 122.0, 121.6, 113.8, 55.5, 35.0, 31.1, 22.1; HRMS (ESI): Exact mass calcd for C$_{26}$H$_{25}$NO$_2$ [M+H]$^+$, 384.1958; Found: 384.1960.

(8-methoxy-2-methylphenanthridin-6-yl)(4-methoxyphenyl)methanone (3n)

Yield: 62%. Mp 185-187 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.59 (d, $J = 8.8$ Hz, 1H), 8.33 (s, 1H), 8.08-8.01 (m, 3H), 7.55-7.48 (m, 3H), 6.95 (d, $J = 8.0$ Hz, 2H), 3.88 (s, 6H), 2.65 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.6, 164.2, 158.8, 155.6, 140.2, 138.3, 133.3, 132.2, 130.2, 129.8, 129.4, 127.5, 125.3, 124.5, 123.8, 122.2, 121.2, 113.8, 106.7 55.5, 22.1; HRMS (ESI): Exact mass calcd for C$_{23}$H$_{19}$NO$_3$ [M+H]$^+$, 358.1438; Found: 358.1436.

(8-(benzyloxy)-2-methylphenanthridin-6-yl)(4-methoxyphenyl)methanone (3o)
NOMe

Yield: 76%. Mp 189-191 °C. White solid. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.61 (d, \( J = 8.8 \) Hz, 1H), 8.34 (s, 1H), 8.07 (d, \( J = 8.4 \) Hz, 1H), 8.01 (d, \( J = 7.6 \) Hz, 2H), 7.61 (s, 1H), 7.55 (t, \( J = 8.4 \) Hz, 2H), 7.43 (d, \( J = 7.2 \) Hz, 2H), 7.38-7.31 (m, 3H), 6.95 (d, \( J = 7.6 \) Hz, 2H), 5.12 (s, 2H), 3.89 (s, 3H), 2.65 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 193.7, 164.5, 158.3, 156.1, 140.8, 138.4, 136.7, 133.4, 130.7, 130.1, 130.0, 128.8, 128.3, 128.0, 127.9, 125.6, 124.8, 124.1, 122.6, 121.4, 114.1, 108.9, 70.8, 55.7, 22.2; HRMS (ESI): Exact mass calcd for C\(_{29}\)H\(_{23}\)NO\(_3\) [M+H]\(^+\), 434.1751; Found: 434.1752.

\((8\text{-fluoro-2-methylphenanthridin-6-yl})(4\text{-methoxyphenyl})\text{methanone (3p)}\)

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OMe

Yield: 87%. Mp 176-178 °C. Yellow solid. \( ^1 \)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.70-8.67 (m, 1H), 8.36 (s, 1H), 8.10 (d, \( J = 8.4 \) Hz, 1H), 8.03 (d, \( J = 8.0 \) Hz, 2H), 7.83 (d, \( J = 9.6 \) Hz, 1H), 7.61 (t, \( J = 8.0 \) Hz, 2H), 6.96 (d, \( J = 7.6 \) Hz, 2H), 3.89 (s, 3H), 2.67 (s, 3H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 192.6, 164.4, 162.8, 160.3, 155.7, 140.8, 138.7, 133.2, 130.6, 130.5, 129.8, 129.6, 125.2, 124.7, 124.6, 124.1, 121.4, 120.2, 119.9, 113.9, 112.1, 111.9, 55.4, 21.9; HRMS (ESI): Exact mass calcd for C\(_{22}\)H\(_{18}\)FNO\(_2\) [M+H]\(^+\), 346.1238; Found: 346.1240.

\((4\text{-methoxyphenyl})(2\text{-methyl-8-}(\text{trifluoromethyl})\text{phenanthridin-6-yl})\text{methanone (3q)}\)
Yield: 62%. Mp 201-203 °C. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.81 (d, $J$ = 8.8 Hz, 1H), 8.49 (s, 1H), 8.44 (s, 1H), 8.14 (d, $J$ = 8.4 Hz, 1H), 8.05 (d, $J$ = 8.4 Hz, 3H), 7.69 (t, $J$ = 8.4 Hz, 1H), 6.97 (t, $J$ = 7.6 Hz, 2H), 3.89 (s, 3H), 2.69 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 192.6, 164.6, 156.3, 141.6, 139.2, 133.5, 132.1, 130.7, 129.2, 126.8, 126.7, 125.1, 125.0, 123.5, 123.4, 122.2, 114.0, 55.7, 22.2; HRMS (ESI): Exact mass calcd for C$_{23}$H$_{16}$F$_3$NO$_2$ [M+H]$^+$, 396.1206; Found: 396.1206.

(2,7-dimethylphenanthridin-6-yl)(4-methoxyphenyl)methanone (3r) and (2,9-dimethyl-phenanthridin-6-yl)(4-methoxyphenyl)methanone (3r')

Yield: 3r = 36%, 3r' = 20%. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.61 (d, $J$ = 8.4 Hz, 0.64H), 8.45 (s, 0.36H), 8.42 (s, 1H), 8.09-7.94 (m, 3H), 7.75 (t, $J$ = 7.2 Hz, 0.64H), 7.58 (d, $J$ = 6.0 Hz, 1H), 7.46 (d, $J$ = 7.2 Hz, 1H), 6.94 (t, $J$ = 7.2 Hz, 2H), 3.87 (s, 3H), 2.65 (s, 4H), 2.54 (s, 1.8H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 195.2, 164.8, 164.7, 157.7, 141.3, 138.2, 136.7, 134.7, 133.6, 133.3, 131.1, 131.0, 130.9, 130.5, 130.3, 129.7, 127.8, 124.9, 122.4, 122.3, 122.1, 120.9, 114.5, 114.4, 55.9, 32.0, 24.1, 23.0, 22.4, 22.3.

(4-methoxyphenyl)(10-methylphenanthridin-6-yl)methanone (3s)
Yield: 44%. Mp 143-145 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.68 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.95 (t, $J = 7.2$ Hz, 3H), 7.69 (d, $J = 7.2$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 2H), 3.86 (s, 3H), 3.18 (s, 3H), 2.67 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 193.9, 164.3, 158.1, 142.6, 136.9, 135.5, 135.0, 133.0, 130.7, 129.8, 129.7, 126.9, 126.4, 126.0, 125.8, 125.5, 113.9, 55.4, 26.7, 22.3; HRMS (ESI): Exact mass calcd for C$_{22}$H$_{17}$NO$_2$ [M+H]$^+$, 342.1489; Found: 342.1487.

(4-methoxyphenyl)(phenanthridin-6-yl)methanone (3t)

Yield: 66%. Mp 162-164 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.72 (d, $J = 8.0$ Hz, 1H), 8.65 (d, $J = 7.6$ Hz, 1H), 8.22 (t, $J = 7.6$ Hz, 1H), 8.12(d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.89 (t, $J = 7.6$ Hz, 1H), 7.81-7.74 (m, 2H), 7.66 (t, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 193.4, 164.3, 158.0, 142.7, 133.3, 133.2, 131.2, 130.6, 129.2, 129.0, 128.0, 127.7, 127.4, 124.4, 123.8, 122.2, 122.1, 113.9, 55.5; HRMS (ESI): Exact mass calcd for C$_{21}$H$_{15}$NO$_2$ [M+H]$^+$, 314.1176; Found: 314.1179.

(4-methoxyphenyl)(3-methylphenanthridin-6-yl)methanone (3u)

Yield: 62%. Mp 143-145 °C. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.66 (d, $J$
= 8.4 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 7.6 Hz, 3H), 7.86 (t, J = 7.6 Hz, 1H), 7.63-7.57 (m, 2H), 6.94 (d, J = 8.0 Hz, 2H), 3.87 (s, 3H), 2.60 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.5, 164.3, 157.9, 142.8, 139.3, 133.3, 133.2, 131.1, 130.1, 129.7, 129.3, 127.4, 127.2, 123.5, 122.1, 122.0, 121.9, 113.8, 55.5, 21.5; HRMS (ESI): Exact mass calcd for C$_{22}$H$_{17}$NO$_2$ [M+H]$^+$, 328.1332; Found: 328.1334.

(3-chlorophenanthridin-6-yl)(4-methoxyphenyl)methanone (3v)

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{O} & \quad \text{CO} \\
\text{OMe} & \quad \text{Me}
\end{align*}
\]

Yield: 75%. Mp 162-164 ºC. Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.65 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.8 Hz, 1H), 8.22 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 2H), 7.90 (t, J = 7.2 Hz, 1H), 7.72-7.65 (m, 2H), 6.95 (d, J = 7.6 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.0, 164.8, 159.4, 143.9, 135.1, 133.3, 131.7, 130.1, 129.7, 128.7, 128.1, 128.0, 124.2, 123.7, 123.2, 122.4, 114.2, 55.7; HRMS (ESI): Exact mass calcd for C$_{21}$H$_{14}$ClNO$_2$ [M+H]$^+$, 348.0784; Found: 348.0786.

(4-methoxyphenyl)(2-(trifluoromethyl)phenanthridin-6-yl)methanone (3w)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{N} \\
\text{O} & \quad \text{CO} \\
\text{OMe} & \quad \text{Me}
\end{align*}
\]

Yield: 81%. Mp 184-186 ºC. White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.92 (s, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.00-7.95 (m, 4H), 7.73 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 192.9, 164.6, 160.2, 144.2, 133.1, 133.0, 131.9, 131.5, 128.8, 127.8, 125.0, 124.0, 122.3, 120.0, 119.9, 114.0, 55.6; HRMS (ESI): Exact mass calcd for C$_{22}$H$_{14}$F$_3$NO$_2$ [M+H]$^+$, 382.1049; Found: 382.1050.

methyl 1-(4-methoxybenzoyl)-4-phenylisoquinoline-3-carboxylate (5a)
methyl 1-(4-methoxybenzoyl)-7-methyl-4-(p-tolyl)isoquinoline-3-carboxylate (5b)

Yield: 48%. Mp 165-167 °C. White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.24-8.20 (m, 1H), 8.10-8.04 (m, 2H), 7.76-7.66 (m, 3H), 7.55 (t, \(J = 5.7\) Hz, 3H), 7.46-7.41 (m, 2H), 7.02-6.97 (m, 2H), 3.90 (s, 3H), 3.69 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 192.5, 167.2, 164.4, 156.5, 140.6, 136.4, 135.6, 134.9, 133.4, 131.2, 129.7, 129.3, 129.2, 128.3, 126.8, 126.5, 126.4, 113.9, 55.6, 52.5; HRMS (ESI): Exact mass calcd for C\(_{25}\)H\(_{19}\)NO\(_4\) [M+H]^+, 398.1392; Found: 398.1394.

methyl 1-(4-methoxybenzoyl)-7-methyl-4-(p-tolyl)isoquinoline-3-carboxylate (5b)

Yield: 46%. Mp 132-134 °C. Pale yellow Solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.07-8.03 (m, 2H), 7.97 (s, 1H), 7.66 (d, \(J = 8.7\) Hz, 1H), 7.51 (d, \(J = 8.7\) Hz, 1H), 7.36-7.28 (m, 4H), 6.98 (t, \(J = 8.7\) Hz, 2H), 3.88 (s, 3H), 3.71 (s, 3H), 2.49 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 192.7, 167.3, 164.3, 155.5, 139.8, 139.6, 137.9, 135.1, 134.8, 133.4, 132.7, 129.5, 129.3, 129.0, 126.8, 126.7, 125.1, 113.9, 55.6, 52.4, 21.9, 21.4; HRMS (ESI): Exact mass calcd for C\(_{27}\)H\(_{23}\)NO\(_4\) [M+H]^+, 426.1705; Found: 426.1715.

Methyl 7-fluoro-4-(4-fluorophenyl)-1-(4-methoxybenzoyl)isoquinoline-3-carboxylate (5c)

Yield: 42%. Mp 148-150 °C. White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.09-8.05
(m, 2H), 7.92 (d, \( J = 9.6 \) Hz, 1H), 7.72 (t, \( J = 5.4 \) Hz, 1H), 7.52-7.45 (m, 1H), 7.41-
7.36 (m, 2H), 7.27-7.22 (m, 2H), 7.00 (d, \( J = 5.1 \) Hz, 2H), 3.90 (s, 3H), 3.71 (s, 3H);
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 191.7, 166.8, 164.5, 163.8, 161.2, 160.5, 155.5, 140.2,
140.1, 134.2, 133.7, 133.5, 131.4, 131.3, 131.1, 129.7, 129.6, 128.9, 127.9, 127.7,
122.1, 121.7, 115.8, 115.5, 113.9, 110.5, 110.2, 55.6, 52.6; HRMS (ESI): Exact mass calcd for
\( \text{C}_{25}\text{H}_{17}\text{F}_{2}\text{NO}_{4}\) [M+H]^+ 434.1204; Found: 434.1205.

**methyl 7-chloro-4-(4-chlorophenyl)-1-(4-methoxybenzoyl)isoquinoline-3-
carboxylate(5d)**

\[
\begin{align*}
\text{Cl} & \quad \text{NMeO}^2 \quad \text{CO} \quad \text{OMe} \\
\text{Cl} & \\
\text{MeO}_2\text{C} & \\
\text{O} & \\
\text{OMe} &
\end{align*}
\]

Yield: 61%. Mp 137-138 °C. Pale yellow solid. \( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.27 (s, 1H),
8.04 (t, \( J = 3.0 \) Hz, 2H), 7.64 (t, \( J = 3.3 \) Hz, 2H), 7.56-7.52 (m, 2H), 7.36-7.32
(m, 2H), 7.02-6.98 (m, 2H), 3.92 (s, 3H), 3.73 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \)
191.6, 166.6, 164.5, 155.6, 140.5, 135.8, 134.8, 134.7, 133.9, 133.5, 132.4, 130.9,
128.9, 128.8, 128.3, 127.2, 125.5, 114.0, 55.6, 52.7; HRMS (ESI): Exact mass calcd for
\( \text{C}_{25}\text{H}_{17}\text{Cl}_{2}\text{NO}_{4}\) [M+H]^+ 466.0613, Found: 466.0618; [M+2+H]^+, 468.0305, Found:
468.0309; [M+4+H]^+, 470.0125, Found: 470.0122.

**methyl 1-(4-methoxybenzoyl)-4-methylisoquinoline-3-carboxylate (5e)**

\[
\begin{align*}
\text{MeO}_2\text{C} & \\
\text{N} & \\
\text{O} & \\
\text{OMe} &
\end{align*}
\]

Yield: 41%. Mp 130-132 °C. Pale yellow solid. \( ^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.25-
8.14 (m, 2H), 8.00-7.95 (m, 2H), 7.86-7.80 (m, 1H), 7.70-7.64 (m, 1H), 6.97-6.92 (m,
2H), 3.98 (s, 3H), 3.88 (s, 3H), 2.93 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 192.6,
167.7, 164.2, 155.0, 140.3, 136.6, 133.4, 131.1, 130.9, 129.4, 129.0, 126.9, 126.3,
124.5, 113.8, 55.5, 52.7, 14.6; HRMS (ESI): Exact mass calcd for \( \text{C}_{20}\text{H}_{17}\text{NO}_{4}\) [M+H]^+,
336.1236; Found: 336.1233.

**2-((2-methylphenanthridin-6-yl)methyl)-2,3-dihydro-1H-inden-1-one (7)**

17
Yield: 48%. mp 172-174 °C. yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J = 8.0 Hz, 1H), 8.42 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.69 (t, J = 7.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 8.8 Hz, 2H), 7.39 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 3.34 (t, J = 6.8 Hz, 2H), 3.11 (t, J = 7.2 Hz, 2H), 2.66 (s, 3H), 2.10-2.02 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 197.6, 156.9, 143.3, 141.0, 138.5, 136.5, 133.0, 132.4, 131.3, 130.9, 130.8, 130.5, 127.8, 127.2, 125.9, 124.4, 123.9, 122.2, 121.7, 51.1, 31.5, 30.6, 22.1; HRMS (ESI): Exact mass calcd for C₂₄H₁₉NO [M+H]⁺, 338.1501; Found: 338.1502.

5. Free-Radical inhibition experiment

An oven-dried sealed tube was equipped with a magnetic stir bar and was charged with a mixture of 2-isocyanobiphenyl 1a (0.2 mmol), benzaldehyde 2a (1.2 mmol), TEMPO (0.5 mmol) and TMSN₃ (0.5 mmol) in CH₂Cl₂ (1.0 mL). Then (diacetoxyiodo)benzene (PIDA) (0.5 mmol) was dissolved in CH₂Cl₂ (1.0 mL) and added dropwise to the reaction mixture for 10 minutes at 50 °C. After stirring for 5 minutes, the reaction was monitored by TLC analyst and almost no the targeted product 3a was observed along with a great material 1a remained.
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7. Copies of $^1$H NMR and $^{13}$C NMR spectra
