Electronic Supporting Information

Copper-catalyzed C2 alkenylation of pyridine-N-oxides with alkynes

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1. General information

Unless otherwise noted, all reactions were performed under an argon atmosphere (purity ≥ 99.999%) using standard Schlenk-type tubes on a dual-manifold Schlenk line. Various reagents were purchased from commercial sources and used without further purification. All the solvents were refluxed with CaH₂ for 12 h, then distilled, further degassed by bubbling with argon for 20 min at room temperature, and stored with activated 4 Å molecular sieves. Isolated yields were determined after purification of the crude product by column chromatography with 10 ~ 40 μm silica gel. Literature methods[1] were used to synthesize IMesCuCl, SIMesCuCl, IPrCuCl, SIPrCuCl and ICyCuCl.

¹H NMR and ¹³C NMR spectra were recorded on Bruker Advance III HD 500 spectrometer with complete proton decoupling. All NMR data were obtained in CDCl₃ at ambient temperature. High-resolution mass spectrometric (HRMS) were recorded on a solariX-70FT-MS. X-ray crystallographic analysis was carried out by Bruker APEII CCD.

2. General procedure for alkenylation of pyridine-N-oxides

![Chemical Reaction Diagram]

To an oven-dried Schlenk tube were added IPrCuCl (24.4 mg, 0.05 mmol), NaOt-Bu (4.8 mg, 0.05 mmol) and alkyne 2 (1.0 mmol, if the alkyne is solid). The tube was evacuated and backfilled with argon for three times. Under argon atmosphere, 0.5 mL toluene was syringed into the reaction tube by a disposable syringe. The reaction mixture was stirred at room temperature for 30 minutes, and then used a microliter syringe to add triethoxysilane (1.5 mmol) into the reaction tube. After stirring for 10 minutes, pyridine-N-oxide 1 (0.5 mmol) and toluene (0.5 mL) was syringed into the tube by a microliter syringe. The resultant mixture was stirred at 80 °C for 48 hours. After cooling to room temperature, an ethanol solution of sodium hydroxide was added into the system to quench the reaction. The combined organic layers were concentrated in vacuo and purified by chromatography on silica gel using ethyl acetate/petroleum ether as the eluent to give products 3.
3. Characterization data

3.1 Characterization of the catalysts

[1,3-Bis[2,6-diisopropylphenyl]imidazol-2-ylidene]copper(I) chloride (IPrCuCl)\(^1\):

\[
\begin{array}{c}
\text{Cl} \\
\text{Cu} \\
\text{N} \\
i-\text{Pr} \\
i-\text{Pr}
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.49 (t, \(J = 7.8\) Hz, 2H), 7.31 – 7.29 (m, 4H), 7.13 (s, 2H), 2.60 – 2.53 (m, 4H), 1.30 (d, \(J = 6.9\) Hz, 12H), 1.23 (d, \(J = 6.9\) Hz, 12H).

[1,3-Bis[2,6-(diisopropylphenyl)imidazolidin-2-ylidene]copper(I) chloride (SIPrCuCl)\(^1\):

\[
\begin{array}{c}
\text{Cl} \\
\text{Cu} \\
\text{N} \\
i-\text{Pr} \\
i-\text{Pr}
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40 (t, \(J = 7.8\) Hz, 2H), 7.29 – 7.20 (m, 4H), 4.02 (s, 4H), 3.07 (dt, \(J = 13.8, 6.9\) Hz, 4H), 1.38 – 1.34 (m, 24H).

[1,3-Bismesitylimidazol-2-ylidene]copper(I) chloride (IMesCuCl)\(^1\):

\[
\begin{array}{c}
\text{Cl} \\
\text{Cu} \\
\text{N} \\
\text{Me} \\
\text{Me}
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.05 (s, 2H), 7.00 (s, 4H), 2.35 (s, 6H), 2.11 (s, 12H).

[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]copper(I) chloride (SIMesCuCl)\(^1\):

\[
\begin{array}{c}
\text{Cl} \\
\text{Cu} \\
\text{N} \\
\text{Me} \\
\text{Me}
\end{array}
\]

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.95 (s, 4H), 3.95 (s, 4H), 2.31 – 2.30 (m, 18H).
[1,3-dicyclohexylimidazol-2-ylidene]copper(I) chloride (ICyCuCl) \(^{[1]}\);

\[
\begin{array}{c}
\text{N} \\
\text{Cu} \\
\text{Cl}
\end{array}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 6.93 (s, 2H), 4.30 (tt, \(J = 12.0, 3.6\) Hz, 2H), 2.08 (d, \(J = 11.7\) Hz, 4H), 1.89 (d, \(J = 13.7\) Hz, 4H), 1.76 (d, \(J = 13.2\) Hz, 2H), 1.65 (qd, \(J = 12.5, 3.2\) Hz, 4H), 1.50 – 1.41 (m, 4H), 1.23 (ddd, \(J = 13.0, 10.1, 3.4\) Hz, 2H).

### 3.2 Characterization of the aryl acetylenes

1,2-di-p-tolylethyne (2b) \(^{[2]}\):

\[
\begin{array}{c}
\text{Me} \\
\text{C} \\
\text{Me}
\end{array}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.1\) Hz, 4H), 7.15 (d, \(J = 7.9\) Hz, 4H), 2.37 (s, 6H).

1,2-bis(4-chlorophenyl)ethyne (2c) \(^{[2]}\):

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{Cl}
\end{array}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.52 – 7.41 (m, 4H), 7.36 – 7.30 (m, 4H).

1,2-bis(4-bromophenyl)ethyne (2d) \(^{[2]}\):

\[
\begin{array}{c}
\text{Br} \\
\text{C} \\
\text{Br}
\end{array}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 8.3\) Hz, 4H), 7.38 (d, \(J = 8.3\) Hz, 4H).

1,2-di(thiophen-2-yl)ethyne (2e) \(^{[2]}\):

\[
\begin{array}{c}
\text{S} \\
\text{C} \\
\text{S}
\end{array}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.31 (d, \(J = 5.1\) Hz, 2H), 7.29 (d, \(J = 3.6\) Hz, 2H), 7.02 (dd, \(J = 5.1, 3.7\) Hz, 2H).
3.3 Characterization of the 2-alkenylpyridines

*(E)-2-(1,2-diphenylvinyl)-6-methylpyridine (3aa):*

![Chemical Structure Image]

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.89 (s, 1H), 7.43 – 7.34 (m, 4H), 7.27 – 7.23 (m, 2H), 7.13 – 7.09 (m, 3H), 7.07 – 7.04 (m, 2H), 7.02 (d, $J$ = 7.6 Hz, 1H), 6.70 (d, $J$ = 7.8 Hz, 1H), 2.64 (s, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 158.04, 157.87, 140.55, 139.38, 136.94, 136.41, 130.62, 130.28, 130.01, 128.90, 127.80, 127.46, 127.04, 121.61, 119.62, 24.82. **HRMS (ESI):** $m/z$ [M + H]$^+$ calcd for C$_{20}$H$_{18}$N:272.1439, found 272.1435.

*(E)-2-(1,2-diphenylvinyl)-6-phenylpyridine (3ba):*

![Chemical Structure Image]

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 8.19 – 8.14 (m, 3H), 7.63 (d, $J$ = 5.0 Hz, 1H), 7.52 (d, $J$ = 7.7 Hz, 2H), 7.44 (dt, $J$ = 17.7, 8.7 Hz, 4H), 7.15 (t, $J$ = 6.1 Hz, 3H), 7.13 – 7.11 (m, 4H), 7.10 (s, 1H), 6.89 (d, $J$ = 7.4 Hz, 1H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 158.11, 157.87, 140.55, 139.38, 136.94, 136.41, 130.62, 130.28, 130.01, 128.90, 127.80, 127.46, 127.04, 121.61, 119.62, 24.82. **HRMS (ESI):** $m/z$ [M + H]$^+$ calcd for C$_{25}$H$_{20}$N:334.1596, found 334.1605.

*(E)-2-(1,2-diphenylvinyl)-5-methylpyridine (3ca):*

![Chemical Structure Image]

**$^1$H NMR** (500 MHz, CDCl$_3$) δ 8.49 (dd, $J$ = 4.7, 1.0 Hz, 1H), 7.48 (dd, $J$ = 7.6, 0.8 Hz, 1H), 7.24 – 7.19 (m, 5H), 7.19 – 7.16 (m, 5H), 7.15 – 7.13 (m, 1H), 6.80 (s, 1H), 2.14 (s, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 160.85, 146.81, 141.77, 139.09, 138.65, 136.98, 131.96, 131.81, 129.85, 129.71, 128.47, 128.08, 127.47, 127.23, 122.40, 19.81. **HRMS (ESI):** $m/z$ [M + H]$^+$ calcd for C$_{20}$H$_{18}$N:272.1439, found 272.1442.
(E)-2-(1,2-diphenylvinyl)-4-methylpyridine (3da):

\[
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array}
\]

\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 8.52 (d, \( J = 4.9 \) Hz, 1H), 7.81 (s, 1H), 7.43 – 7.37 (m, 3H), 7.25 (dt, \( J = 4.0, 2.2 \) Hz, 2H), 7.14 – 7.09 (m, 3H), 7.06 – 7.02 (m, 2H), 6.98 (d, \( J = 4.8 \) Hz, 1H), 6.79 (s, 1H), 2.23 (s, 3H). 

\( ^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \): 158.81, 149.03, 147.38, 140.61, 139.29, 136.87, 130.87, 130.28, 129.01, 127.91, 127.59, 127.18, 123.39, 123.01, 21.14. 

HRMS (ESI): \( m/z \) [M + H]\(^+\) calcd for C\(_{20}\)H\(_{18}\)N: 272.1434, found 272.1431.

(E)-2-(1,2-diphenylvinyl)-4,6-dimethylpyridine (3ea):

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array}
\]

\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.86 (s, 1H), 7.38 (q, \( J = 6.9 \) Hz, 3H), 7.26 – 7.23 (m, 2H), 7.11 – 7.08 (m, 3H), 7.05 – 7.01 (m, 2H), 6.86 (s, 1H), 6.53 (s, 1H), 2.59 (s, 3H), 2.16 (s, 3H). 

\( ^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \): 158.00, 157.64, 147.32, 140.67, 139.44, 137.02, 130.60, 130.30, 129.98, 128.85, 127.75, 127.40, 126.92, 122.63, 120.66, 24.62, 20.92. 

HRMS (ESI): \( m/z \) [M + H]\(^+\) calcd for C\(_{21}\)H\(_{20}\)N: 286.1596, found 286.1606.

(E)-6-(1,2-diphenylvinyl)-2,3-dimethylpyridine (3fa):

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array}
\]

\( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \): 7.86 (s, 1H), 7.36 (ddt, \( J = 9.0, 5.3, 3.5 \) Hz, 3H), 7.26 – 7.20 (m, 3H), 7.09 (dd, \( J = 6.0, 3.9 \) Hz, 3H), 7.06 – 7.03 (m, 2H), 6.64 (d, \( J = 7.8 \) Hz, 1H), 2.58 (s, 3H), 2.26 (s, 3H). 

\( ^{13}\text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \): 156.54, 155.53, 140.52, 139.49, 137.18, 137.08, 130.26, 129.90, 129.88, 129.61, 128.81, 127.74, 127.35, 126.82, 120.07, 23.00, 18.85. 

HRMS (ESI): \( m/z \) [M + H]\(^+\) calcd for C\(_{21}\)H\(_{20}\)N: 286.1596, found 286.1588.
(E)-4-chloro-6-(1,2-diphenylvinyl)-2,3-dimethylpyridine (3ga):

![Chemical Structure]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.89 (s, 1H), 7.44 – 7.35 (m, 3H), 7.23 (dd, $J$ = 7.6, 1.6 Hz, 2H), 7.14 – 7.08 (m, 3H), 7.03 (dd, $J$ = 6.8, 2.8 Hz, 2H), 6.73 (s, 1H), 2.63 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.95, 155.96, 144.19, 139.43, 138.70, 136.68, 130.80, 130.16, 129.99, 129.06, 128.02, 127.83, 127.68, 127.18, 120.77, 24.04, 15.41. HRMS (ESI): $m$/z [M + H]$^+$ calcd for C$_{21}$H$_{19}$ClN: 320.1206, found 320.1212.

(E)-2-(1,2-diphenylvinyl)-5,6,7,8-tetrahydroquinoline (3ha):

![Chemical Structure]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.72 (s, 1H), 7.30 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 7.06 (d, $J$ = 8.0 Hz, 1H), 7.02 – 6.96 (m, 3H), 6.96 – 6.91 (m, 2H), 6.54 (d, $J$ = 8.0 Hz, 1H), 2.92 (t, $J$ = 6.5 Hz, 2H), 2.63 (t, $J$ = 6.3 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.74 – 1.67 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 156.77, 155.76, 140.56, 139.47, 137.03, 136.76, 130.77, 130.22, 129.89, 129.78, 128.77, 127.69, 127.32, 126.80, 119.90, 32.91, 28.49, 23.15, 22.75. HRMS (ESI): $m$/z [M + H]$^+$ calcd for C$_{23}$H$_{22}$N: 312.1752, found 312.1760.

(E)-2-(1,2-diphenylvinyl)quinoline (3ia):

![Chemical Structure]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (dd, $J$ = 8.5, 1.1 Hz, 1H), 7.96 (t, $J$ = 4.3 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.35 (m, 3H), 7.30 (dd, $J$ = 7.6, 1.9 Hz, 2H), 7.15 – 7.09 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.25, 148.08, 141.10, 139.32, 136.92, 136.09, 132.62, 130.49, 130.30, 129.75, 129.74, 129.13, 128.03, 127.81, 127.54, 127.49, 127.35, 126.29, 120.95. HRMS (ESI): $m$/z [M + Na]$^+$ calcd for C$_{23}$H$_{17}$NNa: 330.1259, found 330.1254.
(E)-2-(1,2-di-p-tolylvinyl)-6-methylpyridine (3ab):

![Chemical structure image]

**1H NMR** (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.03 – 6.90 (m, 5H), 6.72 (d, J = 7.9 Hz, 1H), 2.64 (s, 3H), 2.42 (s, 3H), 2.27 (s, 3H).**13C NMR** (126 MHz, CDCl₃) δ 158.49, 157.80, 139.69, 137.05, 136.86, 136.56, 136.35, 134.28, 130.43, 130.17, 129.68, 128.61, 121.39, 119.53, 24.88, 21.38, 21.24. **HRMS (ESI):** m/z [M + H]+= calcd for C₂₂H₂₂N: 300.1752, found 300.1757.

(E)-2-(1,2-bis(4-chlorophenyl)vinyl)-6-methylpyridine (3ac):

![Chemical structure image]

**1H NMR** (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.03 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 6.68 (d, J = 7.8 Hz, 1H), 2.62 (s, 3H). **13C NMR** (126 MHz, CDCl₃) δ 158.07, 157.29, 140.00, 137.34, 136.49, 135.12, 133.63, 132.92, 131.65, 131.06, 129.79, 129.26, 128.16, 121.95, 119.48 , 24.77. **HRMS (ESI):** m/z [M + H]+= calcd for C₂₀H₁₆Cl₂N: 340.0660, found 340.0654.

(E)-2-(1,2-bis(4-bromophenyl)vinyl)-6-methylpyridine (3ad):

![Chemical structure image]

**1H NMR** (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.55 – 7.50 (m, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.12 – 7.09 (m, 2H), 7.05 (d, J = 7.5 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.69 (d, J = 7.8 Hz, 1H), 2.62 (s, 3H). **13C NMR** (126 MHz, CDCl₃) δ 158.15, 157.29, 140.20, 137.86, 136.55, 135.60, 132.26, 132.00, 131.39, 131.18, 129.88, 122.03, 121.87, 121.29, 119.56, 24.78. **HRMS (ESI):** m/z [M + H]+= calcd for C₂₀H₁₆Br₂N: 427.9649, found 427.9650.
(Z)-2-(1,2-di(thiophen-2-yl)vinyl)-6-methylpyridine (3ae): 

![Chemical Structure]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.40 (s, 1H), 7.56 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.23 – 7.15 (m, 3H), 7.03 (dd, $J = 3.4, 1.2$ Hz, 1H), 7.02 – 6.98 (m, 1H), 6.94 (dd, $J = 5.1, 3.7$ Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 2.62 (s, 3H).  $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.68, 156.64, 140.55, 138.46, 136.67, 131.20, 129.68, 129.01, 128.36, 127.98, 127.72, 127.14, 126.28, 121.54, 118.95, 24.76. HRMS (ESI): $m/z$ [M + H]$^+$ calcd for C$_{16}$H$_{14}$NS$_2$: 284.0568, found 284.0559.

(E)-2-methyl-6-(oct-4-en-4-yl)pyridine (3af): 

![Chemical Structure]

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.48 (t, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 7.9$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.20 (t, $J = 7.3$ Hz, 1H), 2.59 (t, $J = 7.8$ Hz, 2H), 2.53 (s, 3H), 2.22 (q, $J = 7.3$ Hz, 2H), 1.50 (h, $J = 7.4$ Hz, 2H), 1.44 – 1.38 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H), 0.90 (d, $J = 7.2$ Hz, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 159.53, 157.35, 139.91, 136.31, 131.75, 120.64, 117.31, 30.78, 30.38, 24.75, 22.86, 22.11, 14.16, 14.09. HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for C$_{14}$H$_{21}$NNa: 226.1572, found 226.1567.

(E)-2-(dec-5-en-5-yl)-6-methylpyridine (3ag): 

![Chemical Structure]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (t, $J = 7.7$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 6.95 (d, $J = 7.5$ Hz, 1H), 6.20 (t, $J = 7.3$ Hz, 1H), 2.60 (t, $J = 7.3$ Hz, 2H), 2.53 (s, 3H), 2.24 (q, $J = 7.4$ Hz, 2H), 1.47 – 1.31 (m, 8H), 0.94 – 0.87 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.51, 157.34, 153.18, 136.31, 131.72, 120.62, 117.27, 31.86, 31.18, 28.34, 28.04, 24.73, 22.79, 22.58, 14.00, 13.96. HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for C$_{16}$H$_{25}$NNa: 254.1588, found 254.1580.
\((E)-2\text{-methyl-6-(1-phenylprop-1-en-1-yl)pyridine (3ah)}:\)

\[
\text{Me} \quad \text{H} \quad \text{Me} \quad \text{Ph}
\]

\(^{1}\text{H NMR} (500 \text{ MHz, } \text{CDCl}_3) \delta 7.43 - 7.37 (\text{m, } 2\text{H}), 7.37 - 7.31 (\text{m, } 2\text{H}), 7.25 - 7.19 (\text{m, } 2\text{H}), 7.04 (\text{q, } J = 7.2 \text{ Hz, } 1\text{H}), 6.96 (\text{d, } J = 7.6 \text{ Hz, } 1\text{H}), 6.60 (\text{d, } J = 7.8 \text{ Hz, } 1\text{H}), 2.59 (\text{s, } 3\text{H}), 1.76 (\text{d, } J = 7.2 \text{ Hz, } 3\text{H}).\]

\(^{13}\text{C NMR} (126 \text{ MHz, } \text{CDCl}_3) \delta 157.85, 157.66, 141.55, 138.96, 136.30, 130.06, 128.32, 127.85, 126.95, 121.08, 119.05, 24.79, 15.40. \]

\text{HRMS (ESI): } m/z [\text{M+H}]^+ \text{ calcd for } \text{C}_{15}\text{H}_{16}\text{N}: 210.1283, \text{ found 210.1293.}

\((E)-2\text{-methyl-6-(1-phenylprop-1-en-2-yl)pyridine (3ai)}:\)

\[
\text{Me} \quad \text{H} \quad \text{Me} \quad \text{Ph}
\]

\(^{1}\text{H NMR} (500 \text{ MHz, } \text{CDCl}_3) \delta 7.57 (\text{t, } J = 7.7 \text{ Hz, } 1\text{H}), 7.47 (\text{d, } J = 1.5 \text{ Hz, } 1\text{H}), 7.44 - 7.40 (\text{m, } 2\text{H}), 7.38 (\text{t, } J = 7.7 \text{ Hz, } 2\text{H}), 7.32 (\text{d, } J = 7.8 \text{ Hz, } 1\text{H}), 7.26 (\text{s, } 1\text{H}), 7.05 (\text{d, } J = 7.6 \text{ Hz, } 1\text{H}), 2.60 (\text{s, } 3\text{H}), 2.35 (\text{d, } J = 1.4 \text{ Hz, } 3\text{H}).\]

\(^{13}\text{C NMR} (126 \text{ MHz, } \text{CDCl}_3) \delta 159.31, 157.55, 138.14, 136.57, 129.93, 129.37, 128.08, 126.68, 121.38, 117.17, 24.77, 15.95. \]

\text{HRMS (ESI): } m/z [\text{M+H}]^+ \text{ calcd for } \text{C}_{15}\text{H}_{16}\text{N}: 210.1283, \text{ found 210.1293.}

\((E)-2\text{-}(1,2\text{-bis(4-chlorophenyl)vinyl)quinoline (3ic)}:\)

\[
\text{H} \quad \text{Cl} \quad \text{Cl} \quad \text{Ph}
\]

\(^{1}\text{H NMR} (500 \text{ MHz, } \text{CDCl}_3) \delta 8.14 (\text{d, } J = 8.6 \text{ Hz, } 1\text{H}), 8.01 (\text{d, } J = 8.6 \text{ Hz, } 1\text{H}), 7.86 (\text{s, } 1\text{H}), 7.80 - 7.69 (\text{m, } 2\text{H}), 7.54 - 7.49 (\text{m, } 1\text{H}), 7.41 - 7.36 (\text{m, } 2\text{H}), 7.24 - 7.19 (\text{m, } 2\text{H}), 7.18 - 7.12 (\text{m, } 2\text{H}), 7.07 (\text{dd, } J = 19.8, 8.5 \text{ Hz, } 3\text{H}).\]

\(^{13}\text{C NMR} (126 \text{ MHz, } \text{CDCl}_3) \delta 158.37, 147.93, 140.48, 137.20, 136.21, 135.00, 133.89, 133.34, 131.75, 131.63, 131.26, 129.82, 129.61, 129.38, 128.31, 127.41, 127.29, 126.44, 120.52. \]

\text{HRMS (ESI): } m/z [\text{M+H}]^+ \text{ calcd for } \text{C}_{23}\text{H}_{16}\text{Cl}_{2}\text{N}: 376.0660, \text{ found 376.0652.}
(E)-2-(1-phenylprop-1-en-1-yl)quinoline (3i):  

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \quad \text{Me} \\
\end{align*}
\]

\[^1\text{H NMR}\ (500\ MHz, \text{CDCl}_3) \ \delta \ 8.16\ (d, J = 8.5\ Hz, 1\text{H}), 7.98\ (d, J = 8.6\ Hz, 1\text{H}), 7.75\ (dd, J = 16.8, 7.6\ Hz, 2\text{H}), 7.53 - 7.43\ (m, 3\text{H}), 7.40\ (d, J = 7.1\ Hz, 1\text{H}), 7.32\ (d, J = 7.7\ Hz, 2\text{H}), 7.15\ (d, J = 7.3\ Hz, 1\text{H}), 7.07\ (d, J = 8.6\ Hz, 1\text{H}), 1.91\ (d, J = 7.2\ Hz, 3\text{H}). \]

\[^{13}\text{C NMR}\ (126\ MHz, \text{CDCl}_3) \ \delta \ 159.00, 147.86, 142.06, 138.63, 135.82, 130.13, 129.97, 129.48, 129.40, 128.40, 127.30, 127.16, 127.03, 125.85, 120.75, 15.71. \]

HRMS (ESI): \( m/\zeta \ [M + H]^+ \) calcd for C\textsubscript{18}H\textsubscript{16}N: 246.1283, found 246.1275.

(E)-2-(1-phenylprop-1-en-2-yl)quinoline (3ii):  

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{H} & \quad \text{Ph} \\
\end{align*}
\]

\[^1\text{H NMR}\ (500\ MHz, \text{CDCl}_3) \ \delta \ 8.17 - 8.10\ (m, 2\text{H}), 7.81\ (d, J = 8.1\ Hz, 1\text{H}), 7.76\ (d, J = 8.6\ Hz, 1\text{H}), 7.71\ (t, J = 7.7\ Hz, 1\text{H}), 7.50\ (t, J = 5.9\ Hz, 4\text{H}), 7.42\ (t, J = 7.5\ Hz, 2\text{H}), 7.30\ (t, J = 7.3\ Hz, 1\text{H}), 2.53\ (s, 3\text{H}). \]

\[^{13}\text{C NMR}\ (126\ MHz, \text{CDCl}_3) \ \delta \ 160.13, 147.79, 137.90, 137.67, 136.15, 131.74, 129.61, 129.49, 129.46, 128.24, 127.35, 127.12, 127.05, 126.10, 118.73, 16.12. \]

HRMS (ESI): \( m/\zeta \ [M + H]^+ \) calcd for C\textsubscript{18}H\textsubscript{16}N: 246.1283, found 246.1275.

(E)-4-chloro-6-(1,2-di-p-tolyvinyl)-2,3-dimethylpyridine (3gb):  

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

\[^1\text{H NMR}\ (500\ MHz, \text{CDCl}_3) \ \delta \ 7.82\ (s, 1\text{H}), 7.20\ (d, J = 7.8\ Hz, 2\text{H}), 7.12 - 7.08\ (m, 2\text{H}), 6.94\ (d, J = 1.6\ Hz, 4\text{H}), 6.73\ (s, 1\text{H}), 2.62\ (d, J = 2.1\ Hz, 3\text{H}), 2.41\ (s, 3\text{H}), 2.33\ (d, J = 2.0\ Hz, 3\text{H}), 2.25\ (d, J = 2.2\ Hz, 3\text{H}). \]

\[^{13}\text{C NMR}\ (126\ MHz, \text{CDCl}_3) \ \delta \ 157.84, 156.41, 144.16, 138.54, 137.24, 137.01, 135.82, 134.00, 130.60, 130.01, 129.95, 129.80, 128.61, 127.72, 120.64, 24.03, 21.36, 21.20, 15.39. \]

HRMS (ESI): \( m/\zeta \ [M + H]^+ \) calcd for C\textsubscript{23}H\textsubscript{23}ClN: 348.1519, found 348.1510.
(E)-6-(1,2-bis(4-bromophenyl)vinyl)-4-chloro-2,3-dimethylpyridine (3gd):

\[
\text{Cl} \quad \text{Me} \quad \text{N} \quad \text{Br} \quad \text{Cl} \quad \text{Me}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.78 (s, 1H), 7.61 – 7.44 (m, 2H), 7.27 (dt, \(J = 4.7, 2.7\) Hz, 2H), 7.15 – 7.01 (m, 2H), 6.89 (d, \(J = 8.5\) Hz, 2H), 6.71 (s, 1H), 2.62 (s, 3H), 2.35 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 158.26, 155.20, 144.35, 139.10, 137.24, 135.35, 132.43, 131.89, 131.37, 131.23, 130.09, 128.59, 122.11, 121.47, 120.74, 23.99, 15.45. HRMS (ESI): \(m/z\) [M + H]\(^+\) calcd for C\(_{21}\)H\(_{17}\)Br\(_2\)ClN: 477.9396, found 477.9430.

(Z)-4-chloro-6-(1,2-di(thiophen-2-yl)vinyl)-2,3-dimethylpyridine (3ge):

\[
\text{Me} \quad \text{N} \quad \text{S} \quad \text{Me} \quad \text{Cl} \quad \text{Me}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 8.37 (s, 1H), 7.57 (d, \(J = 5.1\) Hz, 1H), 7.23 – 7.21 (m, 1H), 7.19 (d, \(J = 5.0\) Hz, 1H), 7.16 (d, \(J = 3.6\) Hz, 1H), 7.02 (d, \(J = 3.4\) Hz, 1H), 6.94 (t, \(J = 4.5\) Hz, 1H), 6.83 (s, 1H), 2.62 (s, 3H), 2.33 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 157.78, 154.68, 144.46, 140.33, 137.68, 131.35, 129.12, 128.62, 128.56, 128.11, 127.98, 127.94, 127.37, 126.32, 120.14, 24.01, 15.44. HRMS (ESI): \(m/z\) [M + H]\(^+\) calcd for C\(_{17}\)H\(_{15}\)ClNS\(_2\): 332.0334, found 332.0344.

(E)-4-chloro-2,3-dimethyl-6-(1-phenylprop-1-en-1-yl)pyridine (3gh):

\[
\text{Cl} \quad \text{Me} \quad \text{N} \quad \text{Ph} \quad \text{Me} \quad \text{H}
\]

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 7.41 (t, \(J = 7.4\) Hz, 2H), 7.35 (d, \(J = 7.4\) Hz, 1H), 7.23 – 7.12 (m, 2H), 7.02 (d, \(J = 7.2\) Hz, 1H), 6.63 (s, 1H), 2.58 (s, 3H), 2.31 (s, 3H), 1.74 (d, \(J = 7.2\) Hz, 3H).

\(^{13}\text{C NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 157.79, 155.79, 144.10, 140.54, 138.30, 129.99, 128.47, 128.25, 127.45, 127.18, 120.25, 24.00, 15.42, 15.33. HRMS (ESI): \(m/z\) [M + H]\(^+\) calcd for C\(_{16}\)H\(_{17}\)ClN: 258.1050, found 258.1059.
(E)-6-(1,2-diphenylvinyl)-2,2'-bipyridine (3ja):

\[
\begin{align*}
\text{\textsuperscript{1}H NMR} & \ (500 \text{ MHz, CDCl}_3) \ \delta \ 8.69 \ (\text{ddd}, \ J = 4.8, 1.8, 0.9 \text{ Hz}, \ 1\text{H}), \ 8.61 \ (\text{dt}, \ J = 8.0, 0.9 \text{ Hz}, \ 1\text{H}), \\
& \ 8.30 \ (\text{dd}, \ J = 7.8, 0.9 \text{ Hz}, \ 1\text{H}), \ 8.08 \ (\text{s}, \ 1\text{H}), \ 7.85 \ (\text{td}, \ J = 7.7, \ 1.8 \text{ Hz}, \ 1\text{H}), \ 7.67 \ (\text{t}, \ J = 7.8 \text{ Hz}, \ 1\text{H}), \\
& \ 7.47 - 7.37 \ (\text{m}, \ 3\text{H}), \ 7.37 - 7.28 \ (\text{m}, \ 3\text{H}), \ 7.18 - 7.06 \ (\text{m}, \ 5\text{H}), \ 6.97 \ (\text{dd}, \ J = 7.8, 0.9 \text{ Hz}, \ 1\text{H}). \\
\text{\textsuperscript{13}C NMR} & \ (126 \text{ MHz, CDCl}_3) \ \delta \ 157.79, \ 156.39, \ 155.22, \ 149.05, \ 140.47, \ 139.18, \ 137.24, \ 136.89, \ 136.85, \ 130.86, \ 130.30, \ 130.04, \ 128.99, \ 127.93, \ 127.58, \ 127.23, \ 123.71, \ 121.27, \ 119.25. \\
\text{HRMS (ESI):} & \ m/z \ [\text{M + H}]^+ \ \text{calcd for C}_{24}\text{H}_{19}\text{N}_{2}: \ 335.1548, \ \text{found} \ 335.1561.
\end{align*}
\]

4. Further functionalization reactions

**Synthesis of 2-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-6-methyl pyridine**

![Reaction Scheme](attachment:reaction_scheme.png)

To an oven-dried Schlenk tube equipped with a magnetic stir bar, IMesCuCl (0.06 mmol, 24.3 mg), NaOBu' (0.06 mmol, 5.8 mg), 3aa (0.3 mmol, 81.4 mg) and B\textsubscript{2}Pin\textsubscript{2} (0.45 mmol, 114.3 mg) were added. The tube was evacuated and backfilled with argon (this process was repeated three times). Under argon atmosphere, dioxane (1.5 mL) and tert-butanol (0.45 mmol, 42 \text{$\mu$L}) were added into the tube. The resulting mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the organic phases were concentrated in vacuo and purified by column chromatography to obtain the product 4 (64 mg, 53%) as a white solid. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.63 – 7.58 (m, 2H), 7.24 (d, J = 7.4 Hz, 3H), 7.19 – 7.06 (m, 5H), 7.00 – 6.95 (m, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 4.53 (d, J = 12.5 Hz, 1H), 3.66 (d, J = 12.5 Hz, 1H), 2.41 (s, 3H), 0.90 (d, J = 7.8 Hz, 12H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 161.78, 157.46, 144.03, 141.00, 135.91, 129.23, 128.78, 128.08, 127.89, 126.34, 125.10, 120.22, 119.59, 83.18, 56.27, 24.57, 24.42, 24.19. HRMS (ESI): m/z [M + H]\textsuperscript{+} calcd for C\textsubscript{26}H\textsubscript{18}BNO\textsubscript{2}: 400.2442, found 400.2483.
Synthesis of 2-(1,2-diphenylethyl)-6-methylpyridine:

To an oven-dried Schlenk tube equipped with a magnetic stir bar, IMesCuCl (0.06 mmol, 24.3 mg), NaOBu′ (0.3 mmol, 28.8 mg), 3aa (0.3 mmol, 81.4 mg) and B₂Pin₂ (0.45 mmol, 114.3 mg) were added. The tube was evacuated and backfilled with argon (this process was repeated three times). Under argon atmosphere, dioxane (1.5 mL) and tert-butanol (3.0 mmol, 286 μL) were added into the tube. The resulting mixture was stirred at 100 °C for 48 h. After cooling to room temperature, the organic phases were concentrated in vacuo and purified by column chromatography to obtain the product 5 (73.7 mg, 90%) as a transparent oily. **1H NMR** (500 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.22 (dd, J = 10.4, 4.8 Hz, 2H), 7.15 – 7.11 (m, 3H), 7.09 – 7.03 (m, 3H), 6.88 (d, J = 7.7 Hz, 2H), 4.33 (t, J = 7.8 Hz, 1H), 3.63 (dd, J = 13.7, 7.8 Hz, 1H), 3.30 (dd, J = 13.7, 7.8 Hz, 1H), 2.53 (s, 3H). **13C NMR** (126 MHz, CDCl₃) δ 162.34, 157.78, 143.63, 140.67, 136.43, 129.20, 128.34, 128.31, 128.04, 126.37, 125.80, 120.81, 119.86, 55.52, 41.64, 24.75.

5. X-Ray data of the compound 3aa

CCDC 2144539 (3aa) contains the supplementary crystallographic data for this paper. These
data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

6. References

