

Electronic Supporting Information

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

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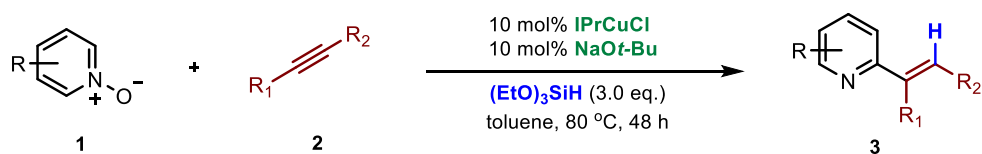
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1. General information

Unless otherwise noted, all reactions were performed under an argon atmosphere (purity \geq 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 CaH_2 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 ^{13}C NMR spectra were recorded on Bruker Advance III HD 500 spectrometer with complete proton decoupling. All NMR data were obtained in CDCl_3 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

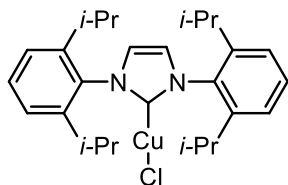


To an oven-dried Schlenk tube were added IPrCuCl (24.4 mg, 0.05 mmol), NaOt-Bu (4.8 mg, 0.05 mmol) and alkyne **2** (1.0 mmol, if the alkyne is solid). The tube was evacuated and backfilled with argon for three times. Under argon atmosphere, 0.5 mL toluene was syringed into the reaction tube by a disposable 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

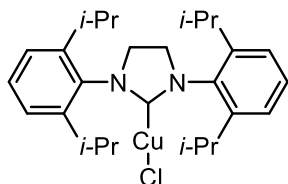
3.1 Characterization of the catalysts

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



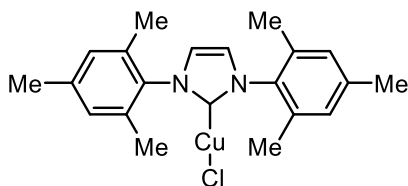
¹H NMR (500 MHz, CDCl₃) δ 7.49 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.29 (m, 4H), 7.13 (s, 2H), 2.60 – 2.53 (m, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H).

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



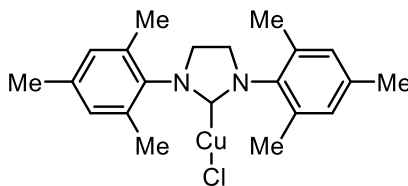
¹H NMR (500 MHz, CDCl₃) δ 7.40 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.20 (m, 4H), 4.02 (s, 4H), 3.07 (dt, *J* = 13.8, 6.9 Hz, 4H), 1.38 – 1.34 (m, 24H).

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



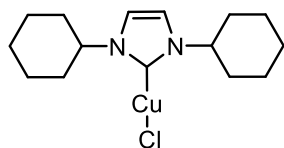
¹H NMR (500 MHz, CDCl₃) δ 7.05 (s, 2H), 7.00 (s, 4H), 2.35 (s, 6H), 2.11 (s, 12H).

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



¹H NMR (500 MHz, CDCl₃) δ 6.95 (s, 4H), 3.95 (s, 4H), 2.31 – 2.30 (m, 18H).

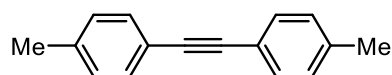
[1,3-dicyclohexylimidazol-2-ylidene]copper(I) chloride (ICyCuCl) ^[1]:



¹H NMR (500 MHz, CDCl₃) δ 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).

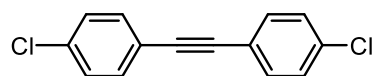
3.2 Characterization of the aryl acetylenes

1,2-di-*p*-tolylethyne (2b) ^[2]:



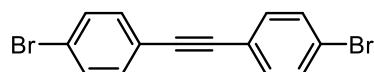
¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.1 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 4H), 2.37 (s, 6H).

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



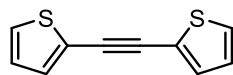
¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.41 (m, 4H), 7.36 – 7.30 (m, 4H).

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



¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 8.3 Hz, 4H), 7.38 (d, *J* = 8.3 Hz, 4H).

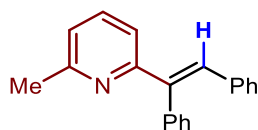
1,2-di(thiophen-2-yl)ethyne (2e) ^[2]:



¹H NMR (500 MHz, CDCl₃) δ 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).

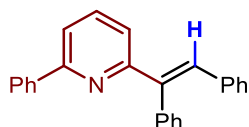
3.3 Characterization of the 2-alkenylpyridines

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



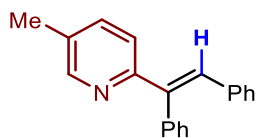
¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.43 – 7.34 (m, 4H), 7.27 – 7.23 (m, 2H), 7.13 – 7.09 (m, 3H), 7.07 – 7.04 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 2.64 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.04, 157.87, 140.55, 139.38, 136.94, 136.41, 130.62, 130.28, 130.01, 128.90, 127.80, 127.46, 127.04, 121.61, 119.62, 24.82. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₈N:272.1439, found 272.1435.

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



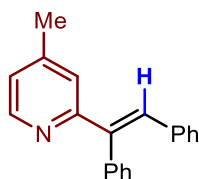
¹H NMR (500 MHz, CDCl₃) δ 8.19 – 8.14 (m, 3H), 7.63 (d, *J* = 5.0 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.44 (dt, *J* = 17.7, 8.7 Hz, 4H), 7.15 (t, *J* = 6.1 Hz, 3H), 7.13 – 7.11 (m, 4H), 7.10 (s, 1H), 6.89 (d, *J* = 7.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 158.11, 156.31, 140.45, 139.53, 139.29, 130.95, 130.31, 130.07, 128.98, 128.68, 127.89, 127.52, 127.17, 127.10, 120.79, 118.58. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₂₀N :334.1596, found 334.1605.

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



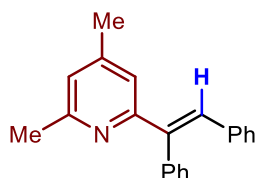
¹H NMR (500 MHz, CDCl₃) δ 8.49 (dd, *J* = 4.7, 1.0 Hz, 1H), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.24 – 7.19 (m, 5H), 7.19 – 7.16 (m, 5H), 7.15 – 7.13 (m, 1H), 6.80 (s, 1H), 2.14 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 160.85, 146.81, 141.77, 139.09, 138.65, 136.98, 131.96, 131.81, 129.85, 129.71, 128.47, 128.08, 127.47, 127.23, 122.40, 19.81. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₈N:272.1439, found 272.1442.

(E)-2-(1,2-diphenylvinyl)-4-methylpyridine (3da):



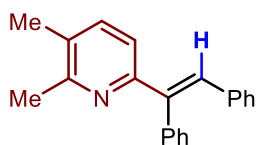
¹H NMR (500 MHz, CDCl₃) δ 8.52 (d, *J* = 4.9 Hz, 1H), 7.81 (s, 1H), 7.43 – 7.37 (m, 3H), 7.25 (dt, *J* = 4.0, 2.2 Hz, 2H), 7.14 – 7.09 (m, 3H), 7.06 – 7.02 (m, 2H), 6.98 (d, *J* = 4.8 Hz, 1H), 6.79 (s, 1H), 2.23 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 158.81, 149.03, 147.38, 140.61, 139.29, 136.87, 130.87, 130.28, 130.01, 129.01, 127.91, 127.59, 127.18, 123.39, 123.01, 21.14. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₁₈N: 272.1434, found 272.1431.

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



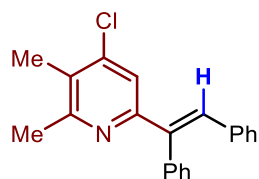
¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.38 (q, *J* = 6.9 Hz, 3H), 7.26 – 7.23 (m, 2H), 7.11 – 7.08 (m, 3H), 7.05 – 7.01 (m, 2H), 6.86 (s, 1H), 6.53 (s, 1H), 2.59 (s, 3H), 2.16 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 158.00, 157.64, 147.32, 140.67, 139.44, 137.02, 130.60, 130.30, 129.98, 128.85, 127.75, 127.40, 126.92, 122.63, 120.66, 24.62, 20.92. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for C₂₁H₂₀N: 286.1596, found 286.1606.

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



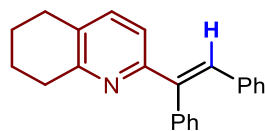
¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.36 (ddt, *J* = 9.0, 5.3, 3.5 Hz, 3H), 7.26 – 7.20 (m, 3H), 7.09 (dd, *J* = 6.0, 3.9 Hz, 3H), 7.06 – 7.03 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 2.58 (s, 3H), 2.26 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 156.54, 155.53, 140.52, 139.49, 137.18, 137.08, 130.26, 129.90, 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 C₂₁H₂₀N: 286.1596, found 286.1588.

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



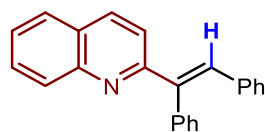
¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.44 – 7.35 (m, 3H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.14 – 7.08 (m, 3H), 7.03 (dd, *J* = 6.8, 2.8 Hz, 2H), 6.73 (s, 1H), 2.63 (s, 3H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.95, 155.96, 144.19, 139.43, 138.70, 136.68, 130.80, 130.16, 129.99, 129.06, 128.02, 127.83, 127.68, 127.18, 120.77, 24.04, 15.41. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₁H₁₉ClN:320.1206, found 320.1212.

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



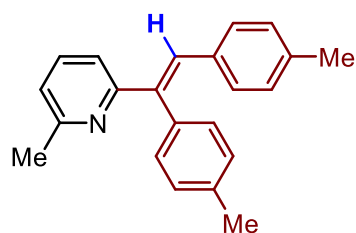
¹H NMR (500 MHz, CDCl₃) δ 7.72 (s, 1H), 7.30 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.02 – 6.96 (m, 3H), 6.96 – 6.91 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.63 (t, *J* = 6.3 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.74 – 1.67 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 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 C₂₃H₂₂N :312.1752, found 312.1760.

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



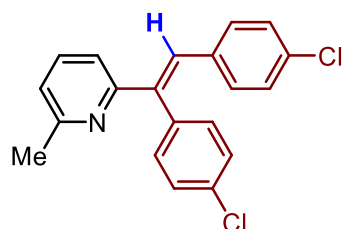
¹H NMR (500 MHz, CDCl₃) δ 8.17 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.96 (t, *J* = 4.3 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.35 (m, 3H), 7.30 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.15 – 7.09 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 159.25, 148.08, 141.10, 139.32, 136.92, 136.09, 132.62, 130.49, 130.30, 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 C₂₃H₁₇NNa: 330.1259, found 330.1254.

(E)-2-(1,2-di-p-tolylvinyl)-6-methylpyridine (3ab):



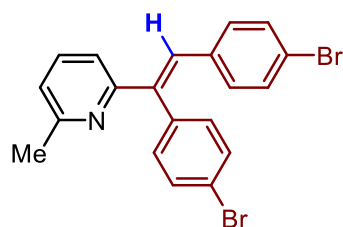
¹H NMR (500 MHz, CDCl₃) δ 7.84 (s, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.90 (m, 5H), 6.72 (d, *J* = 7.9 Hz, 1H), 2.64 (s, 3H), 2.42 (s, 3H), 2.27 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.49, 157.80, 139.69, 137.05, 136.86, 136.56, 136.35, 134.28, 130.43, 130.17, 130.01, 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):



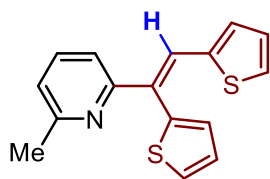
¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.18 – 7.14 (m, 2H), 7.12 – 7.08 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 2.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.07, 157.29, 140.00, 137.34, 136.49, 135.12, 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):



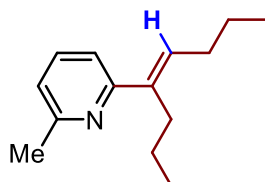
¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.55 – 7.50 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.12 – 7.09 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 2.62 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.15, 157.29, 140.20, 137.86, 136.55, 135.60, 132.26, 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):



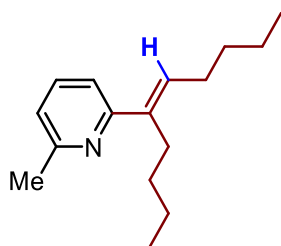
¹H NMR (500 MHz, CDCl₃) δ 8.40 (s, 1H), 7.56 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.03 (dd, *J* = 3.4, 1.2 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.94 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 2.62 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 157.68, 156.64, 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 C₁₆H₁₄NS₂: 284.0568, found 284.0559.

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



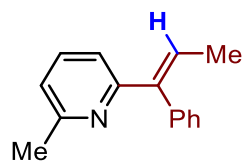
¹H NMR (500 MHz, Chloroform-*d*) δ 7.48 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.20 (t, *J* = 7.3 Hz, 1H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.53 (s, 3H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.50 (h, *J* = 7.4 Hz, 2H), 1.44 – 1.38 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 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 C₁₄H₂₁NNa: 226.1572, found 226.1567.

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



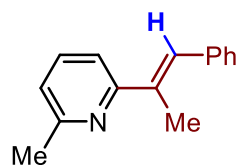
¹H NMR (500 MHz, CDCl₃) δ 7.48 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.20 (t, *J* = 7.3 Hz, 1H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.53 (s, 3H), 2.24 (q, *J* = 7.4 Hz, 2H), 1.47 – 1.31 (m, 8H), 0.94 – 0.87 (m, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.51, 157.34, 153.18, 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 C₁₆H₂₅NNa: 254.1588, found 254.1580.

(E)-2-methyl-6-(1-phenylprop-1-en-1-yl)pyridine (3ah):



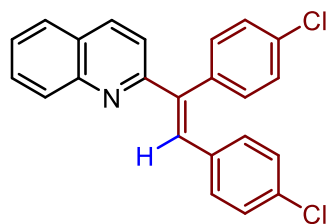
¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 7.25 – 7.19 (m, 2H), 7.04 (q, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 2.59 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 157.85, 157.66, 141.55, 138.96, 136.30, 130.06, 128.32, 127.85, 126.95, 121.08, 119.05, 24.79, 15.40. **HRMS** (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₆N: 210.1283, found 210.1293.

(E)-2-methyl-6-(1-phenylprop-1-en-2-yl)pyridine (3ai):



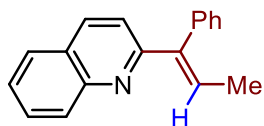
¹H NMR (500 MHz, CDCl₃) δ 7.57 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 1.5 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.60 (s, 3H), 2.35 (d, *J* = 1.4 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.31, 157.55, 138.14, 136.57, 129.93, 129.37, 128.08, 126.68, 121.38, 117.17, 24.77, 15.95. **HRMS** (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₆N: 210.1283, found 210.1293.

(E)-2-(1,2-bis(4-chlorophenyl)vinyl)quinoline (3ic):



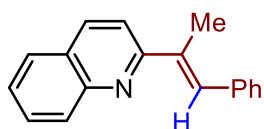
¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.86 (s, 1H), 7.80 – 7.69 (m, 2H), 7.54 – 7.49 (m, 1H), 7.41 – 7.36 (m, 2H), 7.24 – 7.19 (m, 2H), 7.18 – 7.12 (m, 2H), 7.07 (dd, *J* = 19.8, 8.5 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 158.37, 147.93, 140.48, 137.20, 136.21, 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. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for C₂₃H₁₆Cl₂N: 376.0660, found 376.0652.

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



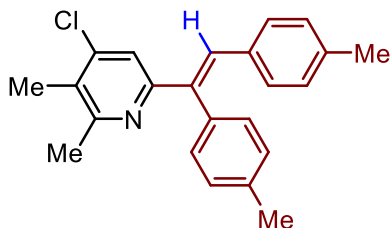
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.6$ Hz, 1H), 7.75 (dd, $J = 16.8, 7.6$ Hz, 2H), 7.53 – 7.43 (m, 3H), 7.40 (d, $J = 7.1$ Hz, 1H), 7.32 (d, $J = 7.7$ Hz, 2H), 7.15 (d, $J = 7.3$ Hz, 1H), 7.07 (d, $J = 8.6$ Hz, 1H), 1.91 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 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/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{16}\text{N}$: 246.1283, found 246.1275.

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



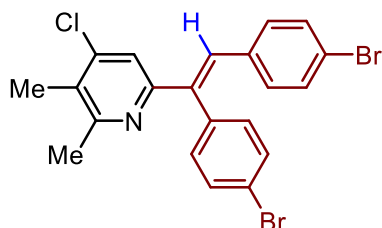
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.17 – 8.10 (m, 2H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.76 (d, $J = 8.6$ Hz, 1H), 7.71 (t, $J = 7.7$ Hz, 1H), 7.50 (t, $J = 5.9$ Hz, 4H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 2.53 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.13, 147.79, 137.90, 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/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{16}\text{N}$: 246.1283, found 246.1275.

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



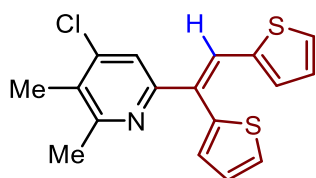
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 (s, 1H), 7.20 (d, $J = 7.8$ Hz, 2H), 7.12 – 7.08 (m, 2H), 6.94 (d, $J = 1.6$ Hz, 4H), 6.73 (s, 1H), 2.62 (d, $J = 2.1$ Hz, 3H), 2.41 (s, 3H), 2.33 (d, $J = 2.0$ Hz, 3H), 2.25 (d, $J = 2.2$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 157.84, 156.41, 144.16, 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/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{ClN}$: 348.1519, found 348.1510.

(E)-6-(1,2-bis(4-bromophenyl)vinyl)-2,3-dimethylpyridine (3gd) :



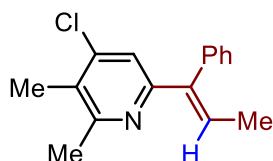
¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 1H), 7.61 – 7.44 (m, 2H), 7.27 (dt, *J* = 4.7, 2.7 Hz, 2H), 7.15 – 7.01 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.71 (s, 1H), 2.62 (s, 3H), 2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.26, 155.20, 144.35, 139.10, 137.24, 135.35, 132.43, 131.89, 131.37, 131.23, 130.09, 128.59, 122.11, 121.47, 120.74, 23.99, 15.45. HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₁H₁₇Br₂ClN :477.9396, found 477.9430.

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



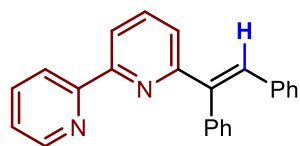
¹H NMR (500 MHz, CDCl₃) δ 8.37 (s, 1H), 7.57 (d, *J* = 5.1 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.02 (d, *J* = 3.4 Hz, 1H), 6.94 (t, *J* = 4.5 Hz, 1H), 6.83 (s, 1H), 2.62 (s, 3H), 2.33 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.78, 154.68, 144.46, 140.33, 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 C₁₇H₁₅ClNS₂ :332.0334, found 332.0344.

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



¹H NMR (500 MHz, CDCl₃) δ 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). ¹³C NMR (500 MHz, CDCl₃) δ 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 C₁₆H₁₇ClN :258.1050, found 258.1059.

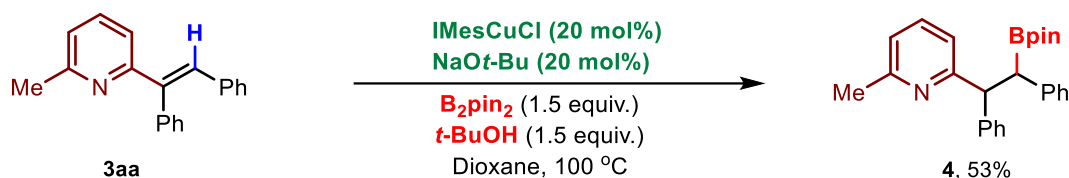
(E)-6-(1,2-diphenylvinyl)-2,2'-bipyridine (3ja):



$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.69 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H), 8.61 (dt, $J = 8.0, 0.9$ Hz, 1H), 8.30 (dd, $J = 7.8, 0.9$ Hz, 1H), 8.08 (s, 1H), 7.85 (td, $J = 7.7, 1.8$ Hz, 1H), 7.67 (t, $J = 7.8$ Hz, 1H), 7.47 – 7.37 (m, 3H), 7.37 – 7.28 (m, 3H), 7.18 – 7.06 (m, 5H), 6.97 (dd, $J = 7.8, 0.9$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 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, 122.37, 121.27, 119.25. **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2$: 335.1548, found 335.1561.

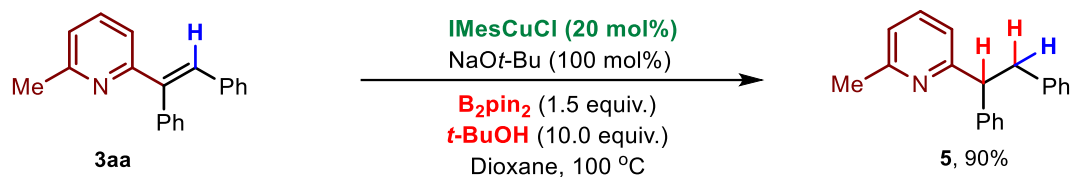
4. Further functionalization reactions

(E)-6-(1,2-diphenylprop-1-en-1-yl)-2,2'-bipyridine



To an oven-dried Schlenk tube equipped with a magnetic stir bar, IMesCuCl (0.06 mmol, 24.3 mg), NaOBu^t (0.06 mmol, 5.8 mg), **3aa** (0.3 mmol, 81.4 mg) and B_2Pin_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 μL) were added into the tube. The resulting mixture was stirred at 100 $^\circ\text{C}$ 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. $^1\text{H NMR}$ (500 MHz, CDCl_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). $^{13}\text{C NMR}$ (126 MHz, CDCl_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 $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{31}\text{BNO}_2$: 400.2442, found 400.2483.

(E)-2-(1,2-diphenylvinyl)-6-methylpyridine



To an oven-dried Schlenk tube equipped with a magnetic stir bar, **IMesCuCl** (0.06 mmol, 24.3mg), **NaOBu^t** (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 μ 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 **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. References

- [1]. O. Santoro, A. Collado, A. M. Slawin, S. P. Nolan, C. S. Cazin, *Chem. Commun.*, 2013, **49**, 10483.
- [2]. M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth, P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199.

