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General Methods. All solvents were distilled before use. 4-chloro-2-trimethylsilylpyridine 1, 3-chloro-2-trimethylsilylpyridine 2, 2-chloro-2-trimethylsilylpyridine 22 and 4-methyl-2-trimethylsilylpyridine 23 were prepared by lithiation-silylation of 4-chloropyridine and 4-methylpyridine respectively using the BuLi-LiDMAE reagent. Ag2O was dried overnight under vacuum before use. All other reagents and catalysts were commercially available and used as such. 1H and 13C NMR spectra were performed on Bruker spectrometers at 200 or 400 MHz (1H) and 50 or 100 MHz (13C) in CDCl3 using TMS as reference. GC experiments were performed on a Shimadzu chromatograph fitted with a 15m capillary column. GC-MS spectra with electronic impact were performed on a Shimadzu QP 2010 apparatus. High resolution mass spectra were performed on a Bruker microTOF-Q. Column Chromatography was performed on silica gel (70–230 mesh).

General procedure for cross-coupling reactions
To a suspension of the aryl halide (0.5 mmol) and Ag2O (1 mmol) in degassed DMF (5 mL) under argon were added the trimethylsilylpyridine (1 mmol), PdCl2(PPh3)2 (0.025 mmol) and TBAF (0.05 mmol, 0.05 mL of a 1M solution in THF). The resulting suspension was stirred at 90°C for 3h. After cooling, the reaction medium was diluted with EtOAc (5 mL), filtered, and concentrated. Column chromatography using Cyclohexane-AcOEt as eluent afforded products.

**1a,** Yield, 70%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.29 (dd, $J$ = 5.3, 1.9 Hz, 1H), 7.40 (ddd, $J$ = 8.8, 5.0, 0.9 Hz, 1H), 7.74 (dd, $J$ = 1.9, 0.6 Hz, 1H), 8.28 (dt, $J$ = 7.9, 1.9 Hz, 1H), 8.59 (s, 1H), 8.61 (d, $J$ = 0.6 Hz, 1H), 8.67 (dd, $J$ = 5.0, 1.9 Hz, 1H), 9.13 (d, $J$ = 5.0, 1.9 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 120.8, 123.0, 123.6, 133.6, 134.3, 145.0, 148.2, 150.5, 150.8, 156.3. FTIR (KBr): 3043, 2923, 1724, 1572, 1542, 1413, 1102, 804. MS (EI): m/z (%): 190 [M+] (100), 164 (22).

**1b,** Yield, 85%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.36 (dd, $J$ = 5.3, 1.9 Hz, 1H), 7.76 (d, $J$ = 1.9 Hz, 1H), 8.64 (d, $J$ = 5.4 Hz, 1H), 8.29 (d, $J$ = 8.2 Hz, 1H), 9.30 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 120.8, 123.8, 131.3, 145.3, 151.2, 153.5, 155.1, 159.1. FTIR (KBr): 3045, 2923, 1564, 1376, 1185, 1056, 821. MS (EI): m/z (%): 191 [M+] (85), 113 (100). HRMS (ESI (M+H+)): calcd. for C$_9$H$_6$ClN$_3$ 192.0323, found 192.0330.

**1c,** Yield, 62%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.30 (dd, $J$ = 5.3, 1.9 Hz, 1H), 7.57 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.74 (td, $J$ = 8.2, 1.6 Hz, 1H), 8.14 (d, $J$ = 8.5 Hz, 1H), 8.64 (d, $J$ = 5.7 Hz, 1H), 8.71 (d, $J$ = 2.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 121.1, 123.8, 131.3, 145.3, 151.2, 153.5, 155.1, 159.1, 160. FTIR (KBr): 3039, 1573, 1329, 1121, 966, 753. MS (EI): m/z (%): 240 [M+] (100), 205 (20). HRMS (ESI (M+H+)): calcd. for C$_{14}$H$_9$ClN$_2$ 241.0527, found 241.0530.

**1e,** Yield, 52%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.10-7.16 (m, 2H), 7.43 (dd, $J$ = 5.0, 0.9 Hz, 1H), 7.59 (dd, $J$ = 3.5, 1.0 Hz, 1H), 7.65 (dd, $J$ = 1.9, 0.6 Hz, 1H), 8.45 (dd, $J$ = 5.3, 0.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 118.5, 118.9, 122.0, 124.4, 125.0, 125.3, 128.1, 128.4, 150.3. FTIR (KBr): 3073, 2924, 1568, 1538, 1383, 1089, 819, 699. MS (EI): m/z (%): 195 [M+] (100), 160 (25).

**1f,** Yield, 25%. $^1$H NMR (250 MHz, CD$_3$OD) $\delta$: 2.30 (s, 3 H), 7.27 - 7.37 (m, 4 H), 7.48 (dd, $J$ = 5.48, 1.98 Hz, 1H), 7.57 (d, $J$ = 1.98 Hz, 1H), 8.55 (d, $J$ = 5.48 Hz, 1H). $^{13}$C NMR (62.5 MHz, CD$_3$OD) $\delta$: 23.3, 122.0, 124.4, 126.0, 129.0, 129.5, 130.9, 135.8.

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139.1, 144.1, 150.0, 161.45 ppm. FTIR (KBr): 3050, 1567, 1540, 1149, 1353, 1114, 1087, 824, 723. LCMS (ESI): 206 (60), 204 (M+H+) (100), 157 (15). HRMS (ESI (M+H+)) : calcd. for C12H10ClN 204.0502, found 204.0497.

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\text{N} \quad \text{Cl} \quad \text{CN}
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1g, Yield, 80%. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm: 7.34 (dd, \(J=5.33, 1.98\) Hz, 1 H), 7.56 - 7.66 (m, 1 H), 7.68 - 7.78 (m, 2 H), 8.22 (, dt, \(J=7.92, 1.60\) Hz, 1 H), 8.33 (t, \(J=1.45\) Hz, 1 H), 8.57 - 8.68 (m, 1 H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \(\delta\) ppm: 113.2, 118.5, 121.0, 123.4, 129.7, 130.8, 131.0, 132.9, 139.2, 145.3, 150.8, 156.4 ppm. FTIR (KBr): 3050, 2227, 1573, 1549, 1458, 1367, 1058, 910, 873. LCMS (ESI): 217 (40), 215 (M+H+) (100). HRMS (ESI (M+H+)) : calcd. for C12H7ClN2 215.0376, found 215.0371.

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\text{N} \quad \text{Cl} \quad \text{COCH}_3
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1h, Yield, 59%. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm: 2.70 (s, 3 H), 7.31 (dd, \(J=5.33, 1.98\) Hz, 1 H), 7.61 (t, \(J=7.77\) Hz, 1 H), 7.82 (d, \(J=1.37\) Hz, 1 H), 8.05 (dt, \(J=7.77, 1.45\) Hz, 1 H), 8.21 (ddd, \(J=7.80, 1.17, 1.14\) Hz, 1 H), 8.57 (t, \(J=1.52\) Hz, 1 H), 8.62 (d, \(J=5.33\) Hz, 1 H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \(\delta\) ppm: 26.8, 121.1, 122.9, 126.8, 129.2, 131.5, 137.7, 138.5, 145.1, 150.5, 157.8, 197.9. FTIR (KBr): 3100, 1674, 1571, 1554, 1458, 1360, 1300, 1245, 802. LCMS (ESI): 234 (60), 232 (M+H+) (100). HRMS (ESI (M+H+)) : calcd. for C13H10ClNO 232.0529, found 232.0530.

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\text{N} \quad \text{Cl} \quad \text{Ac}
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1i, Yield, 60%. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm: 2.67 (s, 3 H), 7.32 (dd, \(J=5.33, 1.83\) Hz, 1 H), 7.80 (d, \(J=1.37\) Hz, 1 H), 8.09 (brs, 4 H),, 8.63 (d, \(J=5.33\) Hz, 1 H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \(\delta\) ppm: 26.8, 121.4, 123.1, 127.2, 128.9, 137.6, 142.2, 145.0, 150.7, 157.6, 197.7. FTIR (KBr): 3060, 1672, 1567, 1548, 1355, 1266, 967, 822. LCMS (ESI): 234 (60), 232 (M+H+) (100), 157 (14).

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1j, Yield, 27%. \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm: 7.29 - 7.36 (m, 1 H), 7.67 - 7.84 (m, 3 H), 8.11 (d, \(J=8.07\) Hz, 2 H), 8.63 (dd, \(J=5.25, 0.53\) Hz, 1 H). \(^{13}\)C NMR (62.5 MHz, CDCl\(_3\)) \(\delta\) ppm: 121.2, 123.1, 125.8, 127.3, 131.1, 131.7, 141.4, 145.1, 150.7, 157.3 ppm. NMR (235 MHz, CDCl\(_3\)) \(\delta\) C = 121.2, 123.1, 124.5, 124.7 (d, \(J_{CF} = 272\) Hz), 125.8, 126.5 (d, \(J_{CF} = 5\) Hz), 127.3, 131.5 (q, \(2J_{CF} = 33\) Hz), 141.4, 145.1, 150.7, 157.3 ppm. NMR (235 MHz, CDCl\(_3\)) \(\delta\) F = -62.65. FTIR (KBr): 2985, 1674, 1549, 1329, 1167, 1104, 1245, 849, 827. LCMS (ESI): 260 (50), 258 (M+H+) (100). HRMS (ESI (M+H+)) : calcd. for C11H10ClF3N 258.0219, found 258.0215.

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**1k**, Yield, 86%. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm: 7.37 (dd, $J$ = 5.25, 1.90 Hz, 1H), 7.78 - 7.87 (m, 1H), 8.14 - 8.24 (m, 2H), 8.30 - 8.43 (m, 2H), 8.61 - 8.71 (m, 1H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ ppm: 121.6, 123.8, 124.1, 127.8, 143.9, 145.2, 148.5, 150.9, 156.3. LCMS (ESI): 237 (55), 235 (M+H$^+$) (100). HRMS(ESI (M+H$^+$)): calcd. for C$_{11}$H$_7$ClN$_2$O$_2$ 235.0274, found 235.0266.

**4a**, Yield, 43%. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm: $\delta$ = 9.18 (m, 1H), 8.65 (m, 1H), 8.58 (d, $J$ = 5.0, Hz, 1H), 8.31 (ddd, $J$ = 8.2, 4.1, 1.9 Hz, 1H), 7.57 (m, 1H), 7.40 (dd, $J$ = 4.9, 3.7 Hz, 1H), 7.12 (d, $J$ = 5.1 Hz, 1H), 2.44 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ ppm: 21.2, 121.6, 123.5, 123.8, 134.4, 148.1, 148.2, 149.3, 149.7, 150.0, 154.7. FTIR (KBr): 2918, 1602, 1545, 1379, 1207, 988, 829. MS (EI) ; m/z (%): 170 [ M+] (100), 144 (29).

**4b**, Yield, 46%. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm: 9.31 (s, 2H), 9.25 (s, 1H), 8.60 (d, $J$ = 5.0, Hz, 1H), 7.57 (m, 1H), 7.17 (d, $J$ = 5.0, Hz, 1H), 2.46 (s, 3H). $^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ ppm: 21.2, 121.5, 124.5, 132.5, 148.4, 150.1, 151.8, 155.0, 158.5. FTIR (KBr): 2924, 2854, 1725, 1605, 1464, 14136, 1190, 1023, 869, 807. MS (EI) ; m/z (%): 171 [ M+] (97), 93 (100).

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