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Supporting Information

Synthesis of Heteroarylated Pyridines via a Double C–H Bond Functionalization using Palladium-catalyzed 1,4-Migration Combined with Direct Arylation

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1 General

Pd(OAc)₂ (98%) was purchased from Aldrich. DMA (99+%) extra pure was purchased from ACROS. KOPiv (95%), the 1,2-dihalobenzenes, the pyridineboronic acid derivatives, dppb and dppf were purchased from Doug Discovery. These compounds were not purified before use. All reagents were weighed and handled in air. All reactions were carried out under an inert atmosphere with standard Schlenk techniques. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Low-resolution mass spectra were measured on a Shimadzu GCMS-QP2010 SE. High-resolution mass spectra were measured on a Bruker MaXis 4G spectrometer. Melting points were determined with a Kofler hot bench system. Chromatography purifications were performed using a CombiFlash NextGen 300 with Buchi FlashPure cartridges containing 40 μm irregular silica.

2 Preparation of the PdCl(C₃H₅)(dppb) catalyst:^[16]

An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ³¹P NMR (162 MHz, CDCl₃) δ = 19.3 (s).

3 General procedures for the preparation of 3- or 4-(2-bromoaryl)pyridines 1a-1p and 5-(2bromophenyl)pyrimidine 1q:

As a typical experiment, a mixture of 1-bromo-2-iodobenzene derivative (4 mmol), pyridineboronic or pyrimidineboronic acid derivative (2 mmol), K_2CO_3 (0.552 g, 4 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol) and dppf (55.4 mg, 0.1 mmol) in DMA (5 mL) was stirred at 100 °C for 16 h. After being allowed to cool to room temperature, the resulting mixture was extracted with Et₂O (3 × 10 mL). The combined organic phase was dried over MgSO₄, filtrated, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (heptane/EtOAc 5/1) to give the (2-bromoaryl)pyridines or (2-bromoaryl)pyrimidines **1a-1q**.

4-(2-Bromophenyl)pyridine (1a)^[12]

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1a** was isolated in 74% (0.346 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.77 (bs, 2H), 7.68 (dd, J = 7.7, 1.0 Hz, 1H), 7.43-7.36 (m, 3H), 7.32-7.23 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 149.3, 148.8, 139.8, 133.5, 130.7, 129.9, 127.7, 124.7, 121.7. LRMS calcd for [M]⁺ C₁₁H₈BrN 235, found: 235.

4-(2-Bromo-4-methylphenyl)pyridine (1b)

From 3-bromo-4-iodotoluene (1.188 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1b** was isolated in 76% (0.377 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 5.3 Hz, 2H), 7.46 (s, 1H), 7.27 (d, J = 5.3 Hz, 2H), 7.17-7.10 (m, 2H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ149.4, 148.7, 140.2, 136.8, 133.9, 130.5, 128.5, 124.4, 121.4, 20.8. LRMS calcd for [M]⁺ C₁₂H₁₀BrN 249, found: 249.

4-(2-Bromo-4-fluorophenyl)pyridine (1c)

From 2-bromo-4-fluoroiodobenzene (1.204 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1c** was isolated in 62% (0.312 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, J = 6.1 Hz, 2H), 7.40 (dd, J = 8.2, 2.5 Hz, 1H), 7.28 (d, J = 6.1 Hz, 2H), 7.25 (dd, J = 8.5, 6.0 Hz, 1H), 7.09 (td, J = 6.9, 2.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 162.2 (d, J = 252.7 Hz), 149.6, 147.7, 136.1 (d, J = 3.6 Hz), 131.7

(d, J = 8.5 Hz), 124.3, 122.0 (d, J = 9.6 Hz), 120.6 (d, J = 24.4 Hz), 114.9 (d, J = 21.2 Hz).

¹⁹F NMR (376 MHz, CDCl₃): *δ*-111.2.

LRMS calcd for $[M]^+$ C₁₁H₇BrFN 251, found: 251.

4-(2-Bromo-4-chlorophenyl)pyridine (1d)

From 2-bromo-4-chloroiodobenzene (1.270 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1d** was isolated in 71% (0.380 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, J = 6.1 Hz, 2H), 7.66-7.60 (m, 1H), 7.35-7.28 (m, 1H), 7.28-7.21 (m, 2H), 7.21-7.13 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 149.7, 147.4, 138.3, 135.0, 133.0, 131.4, 128.0, 124.1, 122.2. LRMS calcd for [M]⁺ C₁₁H₇BrClN 267, found: 267.

4-(2-Bromo-4-(trifluoromethyl)phenyl)pyridine (1e)

From 2-bromo-1-iodo-4-(trifluoromethyl)benzene (1.404 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1e** was isolated in 75% (0.453 g) yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, J = 6.0 Hz, 2H), 7.96 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 6.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): v 149.9, 147.4, 143.5, 132.0 (q, J = 33.4 Hz), 131.1, 130.4 (q, J = 3.8 Hz), 124.6 (q, J = 3.8 Hz), 123.8, 123.0 (q, J = 273.0 Hz), 122.2. ¹⁹F NMR (376 MHz, CDCl₃): δ -62.8.

LRMS calcd for $[M]^+$ C₁₂H₇BrF₃N 301, found: 301.

4-(2-Bromo-4-(trifluoromethoxy)phenyl)pyridine (1f)

From 2-bromo-1-iodo-4-(trifluoromethoxy)benzene (1.468 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1f** was isolated in 71% (0.451 g) yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.69-8.59 (m, 2H), 7.57-7.50 (m, 1H), 7.33-7.19 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 149.1, 147.3, 138.6, 131.5, 125.8, 124.1, 122.2, 120.4 (q, *J* = 258.8 Hz), 120.0. ¹⁹F NMR (376 MHz, CDCl₃): δ -57.9.

LRMS calcd for $[M]^+$ C₁₂H₇BrF₃NO 317, found: 317.

Methyl 3-bromo-4-(4yridine-4-yl)benzoate (1g)

From methyl 3-bromo-4-iodobenzoate (1.364 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1g** was isolated in 76% (0.444 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.66 (d, *J* = 6.1 Hz, 2H), 8.32 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.34 (d, *J* = 8.0, Hz, 1H), 7.31 (d, *J* = 6.1 Hz, 2H), 3.92 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 165.3, 149.8, 147.7, 144.1, 134.5, 131.6, 130.7, 128.7, 123.9, 121.8, 52.5.

LRMS calcd for $[M]^+$ C₁₃H₁₀BrNO₂ 291, found: 290.

4-(2-Bromo-5-methylphenyl)pyridine (1h)

From 1-bromo-2-iodo-4-methylbenzene (1.188 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1h** was isolated in 64% (0.317 g) yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, *J* = 5.3 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.31 (d, *J* = 5.3 Hz, 2H), 7.09 (s, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 149.5, 148.8, 139.5, 137.7, 133.2, 131.5, 130.7, 124.3, 118.3, 20.9. LRMS calcd for [M]⁺ C₁₂H₁₀BrN 249, found: 249.

4-(2-Bromo-5-fluorophenyl)pyridine (1i)

From 2-bromo-5-fluoroiodobenzene (1.204 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1i** was isolated in 62% (0.312 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, *J* = 6.1 Hz, 2H), 7.62-7.56 (m, 1H), 7.28 (d, *J* = 6.1 Hz, 2H), 7.03-6.91 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 161.9 (d, J = 248.8 Hz), 149.7, 147.5, 141.4 (d, J = 7.8 Hz), 134.8 (d, J = 8.0 Hz), 123.9, 117.8 (d, J = 23.5 Hz), 117.0 (d, J = 22.3 Hz), 116.0 (d, J = 3.4 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ -114.1.

LRMS calcd for $[M]^+$ C₁₁H₇BrFN 251, found: 251.

4-(2-Bromo-6-fluorophenyl)pyridine (1j)

From 2-bromo-6-fluoroiodobenzene (1.204 g, 4 mmol) and 4-pyridineboronic acid (0.246 g, 2 mmol), **1j** was isolated in 60% (0.302 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.68 (d, J = 6.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 1H), 7.26-7.17 (m, 3H), 7.10 (t, J = 8.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 159.6 (d, *J* = 250.9 Hz), 149.7, 142.4, 130.7 (d, *J* = 9.0 Hz), 128.9 (d, *J* = 3.7 Hz), 128.3 (d, *J* = 18.2 Hz), 125.0, 123.2 (d, *J* = 2.9 Hz), 115.1 (d, *J* = 22.6 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ-109.8. LRMS calcd for $[M]^+$ C₁₁H₇BrFN 251, found: 251.

4-(2-Bromophenyl)-2-fluoropyridine (1k)

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and (2-fluoropyridin-4-yl)boronic acid (0.282 g, 2 mmol), **1k** was isolated in 50% (0.252 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 5.1 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.41 (ddd, J = 7.8, 7.0, 1.3 Hz, 1H), 7.34-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.00-6.98 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 163.5 (dd, J = 238.5, 3.1 Hz), 153.9 (m), 147.3 (d, J = 15.5 Hz), 138.7, 133.5, 130.6, 130.3, 127.8, 122.3 (d, J = 4.0 Hz), 121.4 (d, J = 3.4 Hz), 110.8 (d, J = 36.9 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ-67.6.

LRMS calcd for [M]⁺ C₁₁H₇BrFN 251, found: 251.

3-(2-Bromophenyl)pyridine (11)^[22]

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and 3-pyridineboronic acid (0.246 g, 2 mmol), **11** was isolated in 77% (0.360 g) yield as a purple oil.

¹H NMR (400 MHz, CDCl₃): δ 8.66 (d, J = 2.3 Hz, 1H), 8.60 (dd, J = 5.0 1.7 Hz, 1H), 7.73 (dt, J = 7.9, 2.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.3 Hz, 1H), 7.40-7.27 (m, 3H), 7.22 (dd, J = 7.3, 1.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): *δ* 149.9, 148.7, 138.9, 136.8, 136.7, 133.3, 131.2, 129.6, 127.7, 122.8, 122.7.

LRMS calcd for $[M]^+$ C₁₁H₈BrN 233, found: 233.

5-(2-Bromophenyl)-2-methoxypyridine (1m)

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol), (6-methoxypyridin-3-yl)boronic acid (0.306 g, 2 mmol), **1m** was isolated in 85% (0.449 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.20 (dd, J = 3.5, 0.8 Hz, 1H), 7.70-7.64 (m, 2H), 7.37 (td, J = 7.4, 1.2 Hz, 1H), 7.31 (dd, J = 7.5, 1.8 Hz, 1H), 7.22 (td, J = 8.0, 1.8 Hz, 1H), 6.80 (dd, J = 8.5, 0.8 Hz, 1H), 3.99 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 163.5, 146.9, 139.8, 139.1, 133.3, 131.3, 130.0, 129.1, 127.6, 123.2, 110.0, 53.5.

LRMS calcd for $[M]^+$ C₁₂H₁₀BrNO 263, found: 263.

5-(2-Bromophenyl)-2-fluoropyridine (1n)

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and (6-fluoropyridin-3-yl)boronic acid (0.282 g, 2 mmol), **1n** was isolated in 70% (0.353 g) yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 2.5 Hz, 1H), 7.85 (td, *J* = 5.6, 2.5 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.24 (td, *J* = 7.4, 2.1 Hz, 1H), 6.98 (ddd, *J* = 8.4, 3.0, 0.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 163.0 (d, *J* = 250.0 Hz), 147.8 (d, *J* = 15.0 Hz), 142.1 (d, *J* = 8.0 Hz), 137.8, 134.6 (d, *J* = 4.7 Hz), 133.4, 131.2, 129.8, 127.8, 122.8, 108.7 (d, *J* = 37.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -69.1.

LRMS calcd for $[M]^+$ C₁₁H₇BrFN 251, found: 251.

3-(2-Bromophenyl)-2-methoxypyridine (10)

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol), (2-methoxypyridin-3-yl)boronic acid (0.306 g, 2 mmol), **10** was isolated in 61% (0.322 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.24 (dd, J = 5.0, 2.0 Hz, 1H), 7.65 (dd, J = 8.0, 1.2 Hz, 1H), 7.46 (dd, J = 7.2, 2.0 Hz, 1H), 7.32 (td, J = 7.5, 1.2 Hz, 1H), 7.27 (dd, J = 7.5, 2.0 Hz, 1H), 7.18 (td, J = 7.5, 2.0 Hz, 1H), 6.93 (dd, J = 57.2, 5.0 Hz, 1H), 3.94 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 160.9, 146.7, 139.3, 138.1, 132.8, 131.5, 129.3, 127.3, 124.4, 124.1, 116.5, 53.6.

LRMS calcd for $[M]^+$ C₁₂H₁₀BrNO 263, found: 263.

3-(2-Bromophenyl)-2-fluoropyridine (1p)

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and (2-fluoropyridin-3-yl)boronic acid (0.282 g, 2 mmol), **1p** was isolated in 78% (0.393 g) yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.20 (bs, 1H), 7.71-7.57 (m, 2H), 7.36-7.15 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 160.2 (d, J = 250.9 Hz), 147.4 (d, J = 14.3 Hz), 142.0 (d, J = 4.1 Hz), 135.0 (d, J = 4.2 Hz), 133.0, 131.4, 130.1, 127.5, 123.4, 123.3 (d, J = 31.2 Hz), 121.2 (d, J = 4.3 Hz).

¹⁹F NMR (376 MHz, CDCl₃): *δ*-68.2.

LRMS calcd for $[M]^+$ C₁₁H₇BrFN 251, found: 251.

5-(2-Bromophenyl)pyrimidine (1q)^[23]

From 1-bromo-2-iodobenzene (1.134 g, 4 mmol) and pyrimidin-5-ylboronic acid (0.248 g, 2 mmol) at 70 °C, **1q** was isolated in 70% (0.329 g) yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 9.27 (s, 1H), 8.86 (s, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38-7.31 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 156.8, 135.5, 134.7, 133.6, 131.1, 130.5, 128.1, 122.7. LRMS calcd for [M]⁺ C₁₀H₇BrN₂ 234, found: 234.

4 General procedure for the preparation of arylated arylpyridines 2a-35a:

As a typical experiment, the reaction of the (2-bromoaryl)pyridine derivative **1a-1p** (1 mmol), heteroarene (2 mmol) and KOPiv (0.280 g, 2 mmol) at 150 °C during 16 h in DMA (4 mL) in the presence of PdCl(C_3H_5)(dppb) (12.2 mg, 0.02 mmol) under argon affords the coupling product after evaporation of the solvent and purification on silica gel. The **a**:**b** ratios were determined by ¹H NMR and GC/MS analysis of the crude mixtures.

2-Isopropyl-4-methyl-5-(4-phenylpyridin-3-yl)thiazole (2a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-isopropyl-4-methylthiazole (0.282 g, 2 mmol), **2a** was isolated in 63% (0.185 g) yield as a yellow solid: mp 64-66 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.64-8.62 (m, 2H), 7.39-7.34 (m, 1H), 7.34-7.27 (m, 3H), 7.21-7.14 (m, 2H), 3.20 (sept., J = 7.1 Hz, 1H), 1.98 (s, 3H), 1.33 (d, J = 7.1 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): *δ* 177.4, 151.9, 149.9, 149.3, 149.2, 138.1, 128.7, 128.5, 128.4, 126.8, 125.3, 124.4, 33.3, 23.1, 15.5.

HRMS calcd for [M+H]⁺ C₁₈H₁₉N₂S 295.1264, found: 295.1266.

One fraction containing product **2b** was also analysed by ¹³C NMR (100 MHz, CDCl₃): \Box 176.7, 150.2, 148.8, 148.1, 139.6, 132.3, 130.4, 129.9, 33.2, 23.2, 15.6.

2-Isobutyl-5-(4-phenylpyridin-3-yl)thiazole (3a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-isobutylthiazole (0.282 g, 2 mmol), **3a** was isolated in 72% (0.212 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.74 (s, 1H), 8.60 (d, *J* = 5.0 Hz, 1H), 7.46 (s, 1H), 7.39-7.32 (m, 3H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.24-7.20 (m, 2H), 2.76 (d, *J* = 7.1 Hz, 2H), 2.07-1.93 (m, 1H), 0.93 (d, *J* = 7.1 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): *δ* 171.8, 150.2, 149.0, 148.7, 141.3, 137.9, 133.1, 129.0, 128.6, 128.5, 126.4, 124.7, 42.2, 29.7, 22.2.

HRMS calcd for $[M+H]^+$ C₁₈H₁₉N₂S 295.1264, found: 295.1266.

3-(5-Methylthiophen-2-yl)-4-phenylpyridine (4a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **4a** was isolated in 78% (0.196 g) yield as a yellow solid: mp 68-70 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.74 (s, 1H), 8.54 (d, *J* = 5.0 Hz, 1H), 7.39-7.34 (m, 3H), 7.30-7.24 (m, 3H), 6.60 (d, *J* = 3.5 Hz, 1H), 6.58 (dq, *J* = 3.5, 1.1 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 150.1, 148.0, 147.8, 141.6, 138.6, 136.3, 129.6, 129.0, 128.4, 128.3, 127.7, 125.6, 125.0, 15.3.

HRMS calcd for [M+H]⁺ C₁₆H₁₄NS 252.0842, found: 252.0844.

3-(5-Chlorothiophen-2-yl)-4-phenylpyridine (5a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-chlorothiophene (0.237 g, 2 mmol), **5a** was isolated in 54% (0.147 g) yield as a brown solid: mp 176-178 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.71 (s, 1H), 8.59 (d, J = 5.0 Hz, 1H), 7.43-7.34 (m, 3H), 7.31 (d, J = 5.1 Hz, 1H), 7.30-7.24 (m, 2H), 6.76 (d, J = 3.5 Hz, 1H), 6.65 (d, J = 3.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): *δ* 149.6, 148.7, 148.2, 137.9, 137.3, 131.5, 129.0, 128.7, 128.6, 128.5, 127.0, 126.4, 125.1.

HRMS calcd for [M+H]⁺ C₁₅H₁₁ClNS 272.0295, found: 272.0295.

1-(5-(4-Phenylpyridin-3-yl)thiophen-2-yl)ethan-1-one (6a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-acetylthiophene (0.252 g, 2 mmol), **6a** was isolated in 60% (0.167 g) yield as a yellow solid: mp 112-114 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.76 (s, 1H), 8.63 (d, *J* = 5.0 Hz, 1H), 7.48 (d, *J* = 3.9 Hz, 1H), 7.38-7.30 (m, 4H), 7.25-7.20 (m, 2H), 6.76 (d, *J* = 3.9 Hz, 1H), 2.49 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 190.4, 150.3, 149.5, 148.6, 147.4, 145.0, 137.8, 132.4, 128.9, 128.8, 128.7, 128.4, 125.0, 26.6.

HRMS calcd for [M+H]⁺ C₁₇H₁₄NOS 280.0791, found: 280.0794.

Ethyl 5-(4-phenylpyridin-3-yl)thiophene-2-carboxylate (7a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and ethyl thiophene-2-carboxylate (0.312 g, 2 mmol), **7a** was isolated in 64% (0.198 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): *δ* 8.76 (bs, 1H), 8.64 (bs, 1H), 7.58 (d, *J* = 3.9 Hz, 1H), 7.39-7.30 (m, 4H), 7.26-7.20 (m, 2H), 6.72 (d, *J* = 3.9 Hz, 1H), 4.31 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 162.0, 150.3, 149.3, 148.7, 145.7, 137.9, 134.6, 133.3, 128.9, 128.7, 128.6, 128.5, 125.0, 61.2, 14.3.

HRMS calcd for [M+H]⁺ C₁₈H₁₆NO₂S 310.0896, found: 310.0899.

Cyclopropyl(5-(4-phenylpyridin-3-yl)thiophen-2-yl)methanone (8a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and cyclopropyl(thiophen-2-yl)methanone (0.304 g, 2 mmol), **8a** was isolated in 62% (0.189 g) yield as a yellow solid: mp 108-110 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1H), 8.63 (s, 1H), 7.60 (d, *J* = 3.9 Hz, 1H), 7.39-7.31 (m, 4H), 7.27-7.21 (m, 2H), 6.78 (d, *J* = 3.9 Hz, 1H), 2.49-2.39 (m, 1H), 1.27-1.17 (m, 2H), 1.04-0.95 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): *δ* 192.6, 149.9, 149.0, 148.9, 146.5, 145.6, 137.7, 131.4, 129.0, 128.9, 128.8, 128.7, 125.2, 17.9, 11.5.

HRMS calcd for [M+H]⁺ C₁₉H₁₆NOS 306.0947, found: 306.0948.

3-(5-(2-Methyl-1,3-dioxolan-2-yl)thiophen-2-yl)-4-phenylpyridine (9a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-methyl-2-(thiophen-2-yl)-1,3dioxolane (0.340 g, 2 mmol), **9a** was isolated in 68% (0.220 g) yield as a yellow solid: mp 88-90 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.76 (s, 1H), 8.58 (s, 1H), 7.40-7.30 (m, 4H), 7.28-7.22 (m, 2H), 6.85 (d, J = 3.9 Hz, 1H), 6.66 (d, J = 3.9 Hz, 1H), 4.07-3.83 (m, 4H), 1.70 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 149.3, 149.2, 149.1, 147.1, 138.1, 137.8, 129.0, 128.6, 128.5, 127.8, 125.2, 124.3, 107.0, 64.9, 27.3.

HRMS calcd for [M+H]⁺ C₁₉H₁₈NO₂S 324.1053, found: 324.1057.

2-(5-(4-Phenylpyridin-3-yl)thiophen-2-yl)acetonitrile (10a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-(thiophen-2-yl)acetonitrile (0.246 g, 2 mmol), **10a** was isolated in 62% (0.171 g) yield as a purple oil.

¹H NMR (400 MHz, CDCl₃): δ 8.73 (s, 1H), 8.59 (d, J = 5.0 Hz, 1H), 7.40-7.32 (m, 3H), 7.28 (d, J = 5.0 Hz, 1H), 7.27-7.22 (m, 2H), 6.90 (d, J = 3.7 Hz, 1H), 6.71 (d, J = 3.7 Hz, 1H), 3.83 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 149.1, 148.0, 139.8, 138.2, 132.1, 129.0, 128.6, 128.5, 128.4, 127.7, 127.4, 124.8, 116.6, 18.7.

HRMS calcd for [M+H]⁺ C₁₇H₁₃N₂S 277.0794, found: 277.0795.

3-(3-Methylbenzo[*b*]thiophen-2-yl)-4-phenylpyridine (11a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 3-methylbenzo[*b*]thiophene (0.296 g, 2 mmol), **11a** was isolated in 66% (0.199 g) yield as a yellow solid: mp 200-202 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.72 (bs, 1H), 8.69 (d, J = 5.1 Hz, 1H), 7.78 (d, J = 7.1 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 5.1 Hz, 1H), 7.39-7.30 (m, 2H), 7.28-7.22 (m, 5H), 1.93 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 152.4, 149.7, 149.6, 140.2, 139.8, 138.3, 133.2, 130.2, 128.7, 128.6, 128.5, 128.2, 124.5, 124.3, 124.1, 122.2, 122.1, 12.2.

HRMS calcd for $[M+H]^+$ C₂₀H₁₆NS 302.0998, found: 302.0999.

3-(5-Butylfuran-2-yl)-4-phenylpyridine (12a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 2-butylfuran (0.248 g, 2 mmol), **12a** was isolated in 91% (0.252 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.97 (s, 1H), 8.48 (d, J = 5.0 Hz, 1H), 7.44-7.36 (m, 3H), 7.30-7.24 (m, 2H), 7.17 (d, J = 5.0 Hz, 1H), 5.87 (d, J = 3.3 Hz, 1H), 5.73 (d, J = 3.3 Hz, 1H), 2.55 (t, J =

7.6 Hz, 2H), 1.50 (quint., J = 7.6 Hz, 2H), 1.31 (sext., J = 7.6 Hz, 2H), 0.89 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 157.0, 148.1, 147.7, 147.3, 146.1, 139.5, 128.5, 128.3, 128.2, 125.7, 124.9, 111.1, 106.8, 30.0, 27.7, 22.2, 13.8.

HRMS calcd for [M+H]⁺ C₁₉H₂₀NO 278.1539, found: 278.1539.

1-(5-(4-Phenylpyridin-3-yl)furan-2-yl)butan-1-one (13a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 1-furan-2-ylbutan-1-one (0.276 g, 2 mmol), **13a** was isolated in 78% (0.227 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 9.05 (s, 1H), 8.62 (d, *J* = 5.0 Hz, 1H), 7.47-7.38 (m, 3H), 7.30-7.23 (m, 3H), 7.05 (d, *J* = 3.7 Hz, 1H), 6.07 (d, *J* = 3.7 Hz, 1H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.62 (sext., *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 189.8, 153.5, 152.4, 149.6, 149.0, 147.6, 138.8, 128.7, 128.6, 128.3, 125.0, 124.3, 117.5, 112.2, 40.2, 17.6, 13.9.

HRMS calcd for [M+H]⁺ C₁₉H₁₈NO₂ 292.1332, found: 292.1335.

3-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)-4-phenylpyridine (14a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (0.300 g, 2 mmol), **14a** was isolated in 76% (0.230 g) yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.80 (bs, 1H), 8.56 (bs, 1H), 7.39-7.28 (m, 4H), 7.28-7.20 (m, 2H), 2.53 (dd, J = 16.0, 5.2 Hz, 1H), 2.37-2.22 (m, 2H), 2.14-2.00 (m, 1H), 1.94-1.76 (m, 2H), 1.56 (s, 3H), 1.41-1.26 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 150.8, 150.7, 148.3, 148.0, 143.5, 139.2, 128.4, 128.3, 127.9, 126.4, 124.6, 118.8, 118.5, 31.3, 31.2, 29.6, 21.4, 20.0, 8.5.

HRMS calcd for $[M+H]^+$ C₂₁H₂₂NO 304.1618, found: 304.1616.

1-(1-Ethyl-5-(4-phenylpyridin-3-yl)-1H-pyrrol-2-yl)ethan-1-one (15a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 1-(1-ethylpyrrol-2-yl)ethan-1-one (0.274 g, 2 mmol), **15a** was isolated in 50% (0.145 g) yield as a yellow solid: mp 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.71 (d, J = 5.1 Hz, 1H), 8.61 (s, 1H), 7.42 (d, J = 5.1 Hz, 1H), 7.32-7.24 (m, 3H), 7.21-7.14 (m, 2H), 7.00 (d, J = 4.0 Hz, 1H), 6.13 (d, J = 4.0 Hz, 1H), 3.96-3.76 (m, 2H), 2.44 (s, 3H), 0.93 (t, J = 7.0 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 188.0, 151.9, 150.3, 149.2, 137.8, 137.1, 130.3, 128.7, 128.6, 128.4, 126.4, 124.1, 120.3, 111.5, 41.2, 27.5, 16.1.

HRMS calcd for [M+H]⁺ C₁₉H₁₉N₂O 291.1492, found: 291.1495.

3-(1,2-Dimethylimidazol-5-yl)-4-phenylpyridine (16a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and 1,2-dimethylimidazole (0.192 g, 2 mmol), **16a** was isolated in 48% (0.119 g) yield as a purple solid: mp 166-168 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.70 (d, J = 5.1 Hz, 1H), 8.61 (s, 1H), 7.43 (d, J = 5.1, Hz, 1H), 7.37-7.30 (m, 3H), 7.25-7.20 (m, 2H), 7.05 (s, 1H), 2.75 (s, 3H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 152.3, 150.4, 148.4, 146.0, 138.1, 129.2, 128.8, 128.7, 128.4, 126.8, 124.2, 124.0, 30.6, 13.3.

HRMS calcd for [M+H]⁺ C₁₆H₁₆N₃ 250.1339, found: 250.1341.

3-(4-Phenylpyridin-3-yl)imidazo[1,2-*a*]pyridine (17a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and imidazo[1,2-*a*]pyridine (0.236 g, 2 mmol), **17a** was isolated in 62% (0.168 g) yield as a brown solid: mp 170-172 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.81-8.71 (m, 2H), 7.70 (s, 1H), 7.58 (d, J = 9.1 Hz, 1H), 7.49 (d, J = 5.0 Hz, 1H), 7.36 (d, J = 6.9 Hz, 1H), 7.24-7.11 (m, 5H), 7.06 (dd, J = 9.1, 6.7 Hz, 1H), 6.46 (dd, J = 6.9, 1.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 152.3, 150.4, 148.4, 146.0, 137.8, 134.1, 128.8, 128.7, 127.5, 124.5, 124.4, 123.2, 123.1, 121.5, 117.8, 112.0.

HRMS calcd for [M+H]⁺ C₁₈H₁₄N₃ 272.1183, found: 272.1182.

3-(4-Phenylpyridin-3-yl)imidazo[1,2-c]pyrimidine (18a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and imidazo[1,2-c]pyrimidine (0.238 g, 2 mmol), **18a** was isolated in 80% (0.218 g) yield as a brown solid: mp 184-186 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.92 (s, 1H), 8.71 (d, J = 5.1, Hz, 1H), 8.06 (dd, J = 4.4, 1.6, Hz, 1H), 7.91 (dd, J = 9.1, 1.6, Hz, 1H), 7.62 (s, 1H), 7.45 (d, J = 5.0 Hz, 1H), 7.25-7.10 (m, 5H), 6.95 (dd, J = 9.1, 4.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): *δ* 151.2, 149.8, 149.6, 142.6, 139.5, 138.7, 134.5, 128.4, 128.3, 127.8, 125.7, 125.2, 124.6, 122.9, 116.8.

HRMS calcd for [M+H]⁺ C₁₇H₁₃N₄ 273.1135, found: 273.1138.

3-(4-Phenylpyridin-3-yl)imidazo[1,2-*b*]pyridazine (19a)

From 4-(2-bromophenyl)pyridine **1a** (0.234 g, 1 mmol) and imidazo[1,2-*b*]pyridazine (0.238 g, 2 mmol), **19a** was isolated in 76% (0.207 g) yield as a brown solid: mp 182-184 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.91 (s, 1H), 8.72 (d, J = 5.0 Hz, 1H), 8.05 (dd, J = 4.4, 1.7 Hz, 1H), 7.91 (dd, J = 9.2, 1.7 Hz, 1H), 7.63 (s, 1H), 7.45 (d, J = 5.1 Hz, 1H), 7.24-7.09 (m, 5H), 6.95 (dd, J = 9.2, 4.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): *δ* 151.4, 150.1, 149.4, 142.6, 139.5, 138.8, 134.6, 128.3, 128.2, 127.8, 125.7, 125.3, 124.5, 122.8, 116.7.

HRMS calcd for [M+H]⁺ C₁₇H₁₃N₄ 273.1135, found: 273.1137.

3-(5-Methylthiophen-2-yl)-4-(*p***-tolyl)pyridine (20a)**

From 4-(2-bromo-4-methylphenyl)pyridine **1b** (0.248 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **20a** was isolated in 78% (0.207 g) yield as a yellow solid: mp 100-102 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.71 (s, 1H), 8.51 (d, J = 5.0 Hz, 1H), 7.23 (d, J = 5.0 Hz, 1H), 7.17-7.14 (m, 4H), 6.61 (d, J = 3.5 Hz, 1H), 6.58 (d, J = 3.5 Hz, 1H), 2.43 (d, J = 1.0 Hz, 3H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 150.5, 148.2, 147.7, 141.3, 138.1, 136.7, 135.8, 129.4, 129.1, 128.9, 127.5, 125.5, 124.9, 21.3, 15.3.

HRMS calcd for [M+H]⁺ C₁₇H₁₆NS 266.0998, found: 266.1001.

3-(5-Butylfuran-2-yl)-4-(*p***-tolyl)pyridine (21a)**

From 4-(2-bromo-4-methylphenyl)pyridine **1b** (0.248 g, 1 mmol) and 2-butylfuran (0.248 g, 2 mmol), **21a** was isolated in 76% (0.221 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.94 (s, 1H), 8.46 (d, J = 5.0 Hz, 1H), 7.21 (d, J = 7.7 Hz, 2H),

7.19-7.14 (m, 3H), 5.87 (d, J = 3.3 Hz, 1H), 5.76 (d, J = 3.3 Hz, 1H), 2.56 (t, J = 7.6 Hz, 2H), 2.41

(s, 3H), 1.50 (quint., *J* = 7.6 Hz, 2H), 1.32 (sext., *J* = 7.6 Hz, 2H), 0.90 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 156.8, 148.4, 148.0, 147.6, 146.0, 137.9, 136.6, 129.2, 128.2,

125.7, 124.9, 110.9, 106.7, 30.1, 27.7, 22.2, 21.3, 13.8.

HRMS calcd for [M+H]⁺ C₂₀H₂₂NO 292.1996, found: 292.1700.

4-(4-Fluorophenyl)-3-(5-methylthiophen-2-yl)pyridine (22a)

From 4-(2-bromo-4-fluorophenyl)pyridine **1c** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **22a** was isolated in 71% (0.191 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.72 (s, 1H), 8.53 (d, *J* = 5.0 Hz, 1H), 7.28-7.19 (m, 3H), 7.04 (t, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 3.3 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 162.8 (d, J = 248.1 Hz), 150.6, 148.4, 146.6, 141.6, 136.3, 134.7 (d, J = 3.4 Hz), 130.8 (d, J = 18.2 Hz), 129.5, 127.6, 125.6, 124.7, 115.5 (d, J = 21.6 Hz), 15.2. ¹⁹F NMR (376 MHz, CDCl₃): δ-113.4.

HRMS calcd for [M+H]⁺ C₁₆H₁₃FNS 270.0742, found: 270.0750.

4-(4-Chlorophenyl)-3-(5-methylthiophen-2-yl)pyridine (23a)

From 4-(2-bromo-4-chlorophenyl)pyridine **1d** (0.267 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **23a** was isolated in 51% (0.145 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.72 (s, 1H), 8.55 (d, *J* = 5.0 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.23-7.19 (m, 3H), 6.60 (s, 2H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 150.7, 148.5, 146.4, 141.7, 137.2, 136.1, 134.4, 130.4, 129.4, 128.7, 127.8, 125.7, 124.5, 15.3.

HRMS calcd for [M+H]⁺ C₁₆H₁₃ClNS 286.0452, found: 286.0454.

3-(5-Methylthiophen-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridine (24a)

From 4-(2-bromo-4-(trifluoromethyl)phenyl)pyridine **1e** (0.302 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **24a** was isolated in 73% (0.233 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.76 (s, 1H), 8.57 (d, J = 5.0 Hz, 1H), 7.62 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 5.0 Hz, 1H), 6.60 (d, J = 3.3 Hz, 1H), 6.57 (d, J = 3.3 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 150.8, 148.5, 146.1, 142.4, 141.9, 135.7, 130.3 (q, *J* = 32.6 Hz), 129.4, 129.3, 127.9, 125.8, 125.4 (q, *J* = 3.7 Hz), 124.4, 124.1 (q, *J* = 273.5 Hz), 15.2.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.6.

HRMS calcd for $[M+H]^+ C_{17}H_{13}F_3NS$ 320.0637, found: 320.0634.

3-(5-Methylthiophen-2-yl)-4-(4-(trifluoromethoxy)phenyl)pyridine (25a)

From 4-(2-bromo-4-(trifluoromethoxy)phenyl)pyridine **1f** (0.239 g, 1 mmol) and 2methylthiophene (0.196 g, 2 mmol), **25a** was isolated in 61% (0.204 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.74 (s, 1H), 8.56 (d, *J* = 5.0 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 5.0 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.60 (s, 2H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): *δ* 150.7, 149.2, 148.5, 146.2, 141.8, 137.3, 136.0, 130.6, 129.4, 127.8, 125.6, 124.5, 120.8, 120.3 (q, *J* = 257.6 Hz), 15.2.

¹⁹F NMR (376 MHz, CDCl₃): δ-57.8.

HRMS calcd for [M+H]⁺ C₁₇H₁₃F₃NOS 336.0586, found: 336.0587.

3-(5-Methylthiophen-2-yl)-4-(*m*-tolyl)pyridine (27a)

From 4-(2-bromo-5-methylphenyl)pyridine **1h** (0.248 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **27a** was isolated in 71% (0.188 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.72 (s, 1H), 8.52 (bs, 1H), 7.28-7.14 (m, 3H), 7.11 (s, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 150.5, 148.2, 147.7, 141.3, 138.7, 138.1, 136.6, 129.6, 129.4, 128.9, 128.2, 127.6, 126.1, 125.5, 124.8, 21.4, 15.3.

HRMS calcd for $[M+H]^+$ C₁₇H₁₆NS 266.0998, found: 266.1001.

4-(3-Fluorophenyl)-3-(5-methylthiophen-2-yl)pyridine (28a)

From 4-(2-bromo-5-fluorophenyl)pyridine **1i** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **28a** was isolated in 74% (0.199 g) yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃): δ 8.74 (s, 1H), 8.54 (d, J = 5.0 Hz, 1H), 7.36-7.28 (m, 1H), 7.22 (d, J = 5.0 Hz, 1H), 7.09-7.02 (m, 2H), 6.98 (d, J = 9.0 Hz, 1H), 6.63-6.57 (m, 2H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 162.6 (d, J = 246.4 Hz), 150.7, 148.4, 146.2 (d, J = 2.1 Hz), 141.7,

140.9 (d, *J* = 7.8 Hz), 135.9, 130.0 (d, *J* = 8.3 Hz), 129.3, 127.7, 125.6, 124.8 (d, *J* = 3.0 Hz), 124.5, 116.1 (d, *J* = 22.3 Hz), 115.1 (d, *J* = 21.1 Hz), 15.3.

¹⁹F NMR (376 MHz, CDCl₃): *δ*-112.6.

HRMS calcd for [M+H]⁺ C₁₆H₁₃FNS 270.0747, found: 270.0747.

4-(2-Fluorophenyl)-3-(5-methylthiophen-2-yl)pyridine (29a)

From 4-(2-Bromo-6-fluorophenyl)pyridine **1j** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **29a** was isolated in 76% (0.204 g) yield as a white solid: mp 110-112 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.79 (s, 1H), 8.54 (bs, 1H), 7.42-7.34 (m, 1H), 7.28-7.14 (m, 3H), 7.06 (t, J = 8.5 Hz, 1H), 6.62 (d, J = 3.3 Hz, 1H), 6.58 (d, J = 3.3 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 159.5 (d, J = 248.2 Hz), 150.1, 149.5, 147.0, 141.5 (d, J = 7.6 Hz), 136.3, 131.2 (d, J = 3.1 Hz), 130.4 (d, J = 8.0 Hz), 127.0, 126.5 (d, J = 15.7 Hz), 125.6, 125.3, 124.3 (d, J = 3.6 Hz), 115.9 (d, J = 21.8 Hz), 15.3.

¹⁹F NMR (376 MHz, CDCl₃): δ -114.6.

HRMS calcd for [M+H]⁺ C₁₆H₁₃FNS 270.0747, found: 270.0749.

2-Fluoro-5-(5-methylthiophen-2-yl)-4-phenylpyridine (30a)

From 4-(2-bromophenyl)-2-fluoropyridine **1k** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **30a** was isolated in 41% (0.110 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.31 (s, 1H), 7.40-7.31 (m, 5H), 6.92 (d, J = 2.2 Hz, 1H), 6.57 (d, J = 3.3 Hz, 1H), 6.54 (d, J = 3.3 Hz, 1H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 163.0 (d, J = 240.1 Hz), 153.3 (d, J = 8.2 Hz), 148.3 (d, J = 15.3 Hz), 141.4, 137.8 (d, J = 2.7 Hz), 135.3, 128.8, 128.7, 128.5, 127.8 (d, J = 5.0 Hz), 127.7, 125.5, 110.0 (d, J = 27.5 Hz), 15.3.

¹⁹F NMR (376 MHz, CDCl₃): δ -70.8.

HRMS calcd for [M+H]⁺ C₁₆H₁₃FNS 270.0747, found: 270.0749.

6-Fluoro-2-(5-methylthiophen-2-yl)-3-phenylpyridine (33a)

From 5-(2-bromophenyl)-2-fluoropyridine **1n** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **33a** was isolated in 41% (0.110 g) yield as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.59 (t, J = 8.1 Hz, 1H), 7.46-7.39 (m, 3H), 7.35-7.28 (m, 2H), 6.77 (dd, J = 8.1, 3.5 Hz, 1H), 6.46 (s, 2H), 2.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.6 (d, J = 238.6 Hz), 148.7 (d, J = 14.1 Hz), 143.9 (d, J = 7.8 Hz), 143.2, 140.1, 139.1, 131.5 (d, J = 4.6 Hz), 129.3, 129.1, 128.9, 128.1, 125.9, 106.1 (d, J = 37.8 Hz), 15.3.

¹⁹F NMR (376 MHz, CDCl₃): δ-69.2.

HRMS calcd for [M+H]⁺ C₁₆H₁₃FNS 270.0747, found: 270.0747.

2-Methoxy-4-(5-methylthiophen-2-yl)-3-phenylpyridine (34a)

From 3-(2-bromophenyl)-2-methoxypyridine **10** (0.264 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **34a** was isolated in 75% (0.211 g) yield as a white solid: mp 136-138 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 5.4 Hz, 1H), 7.41-7.34 (m, 3H), 7.25-7.20 (m, 2H), 7.11 (d, J = 5.4 Hz, 1H),), 6.55 (d, J = 3.3 Hz, 1H), 6.51 (d, J = 3.3 Hz, 1H), 3.89 (s, 3H), 2.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 162.3, 145.4, 142.8, 142.2, 138.0, 135.7, 130.6, 128.5, 128.4, 127.6, 125.5, 121.6, 117.0, 53.9, 15.2.

HRMS calcd for [M+H]⁺ C₁₇H₁₆NOS 282.0947, found: 282.0948.

2-Fluoro-4-(5-methylthiophen-2-yl)-3-phenylpyridine (35a)

From 3-(2-bromophenyl)-2-fluoropyridine **1p** (0.252 g, 1 mmol) and 2-methylthiophene (0.196 g, 2 mmol), **35a** was isolated in 78% (0.210 g) yield as a white solid: mp 130-132 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, J = 5.3 Hz, 1H), 7.44-7.39 (m, 3H), 7.37 (d, J = 5.3 Hz, 1H), 7.31-7.24 (m, 2H), 6.63 (d, J = 3.3 Hz, 1H), 6.54 (d, J = 3.3 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.8 (d, J = 235.9 Hz), 146.1 (d, J = 8.1 Hz), 145.7 (d, J = 5.0 Hz), 143.4, 136.5 (d, J = 4.6 Hz), 132.8 (d, J = 2.5 Hz), 130.3, 129.3, 128.7, 128.5, 125.9, 121.0 (d, J = 3.8 Hz), 120.6 (d, J = 33.1 Hz), 15.3.

¹⁹F NMR (376 MHz, CDCl₃): δ -68.5.

HRMS calcd for $[M+H]^+$ C₁₆H₁₃FNS 270.0747, found: 270.0750.

5 References

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[23] J. Ruch, A. Aubin, G. Erbland, A. Fortunato, J.-P. Goddard, *Chem. Commun.* **2016**, *52*, 2326-2329.

6 NMR Spectra for all Products 4-(2-Bromophenyl)pyridine (1a)



4-(2-Bromo-4-methylphenyl)pyridine (1b)



4-(2-Bromo-4-fluorophenyl)pyridine (1c)







4-(2-Bromo-4-chlorophenyl)pyridine (1d)





4-(2-Bromo-4-(trifluoromethyl)phenyl)pyridine (1e)









4-(2-Bromo-4-(trifluoromethoxy)phenyl)pyridine (1f)







Methyl 3-bromo-4-(pyridin-4-yl)benzoate (1g)



4-(2-Bromo-5-methylphenyl)pyridine (1h)



4-(2-Bromo-5-fluorophenyl)pyridine (1i)









4-(2-Bromo-6-fluorophenyl)pyridine (1j)







4-(2-Bromophenyl)-2-fluoropyridine (1k)








3-(2-Bromophenyl)pyridine (11)





5-(2-Bromophenyl)-2-methoxypyridine (1m)



5-(2-Bromophenyl)-2-fluoropyridine (1n)





3-(2-Bromophenyl)-2-methoxypyridine (10)





3-(2-Bromophenyl)-2-fluoropyridine (1p)





5-(2-Bromophenyl)pyrimidine (1q)



Arylated 4-arylpyridines 2a-35a:

2-Isopropyl-4-methyl-5-(4-phenylpyridin-3-yl)thiazole (2a)



2-Isobutyl-5-(4-phenylpyridin-3-yl)thiazole (3a)



3-(5-Methylthiophen-2-yl)-4-phenylpyridine (4a)



3-(5-Chlorothiophen-2-yl)-4-phenylpyridine (5a)



1-(5-(4-Phenylpyridin-3-yl)thiophen-2-yl)ethan-1-one (6a)



Ethyl 5-(4-phenylpyridin-3-yl)thiophene-2-carboxylate (7a)



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Cyclopropyl(5-(4-phenylpyridin-3-yl)thiophen-2-yl)methanone (8a)



3-(5-(2-Methyl-1,3-dioxolan-2-yl)thiophen-2-yl)-4-phenylpyridine (9a)



2-(5-(4-Phenylpyridin-3-yl)thiophen-2-yl)acetonitrile (10a)







3-(5-Butylfuran-2-yl)-4-phenylpyridine (12a)





1-(5-(4-Phenylpyridin-3-yl)furan-2-yl)butan-1-one (13a)







3-(3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran-2-yl)-4-phenylpyridine (14a)

1-(1-Ethyl-5-(4-phenylpyridin-3-yl)-1H-pyrrol-2-yl)ethan-1-one (15a)



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3-(1,2-Dimethylimidazol-5-yl)-4-phenylpyridine (16a)







3-(4-Phenylpyridin-3-yl)imidazo[1,2-*c*]pyrimidine (18a)



3-(4-Phenylpyridin-3-yl)imidazo[1,2-b]pyridazine (19a)



3-(5-Methylthiophen-2-yl)-4-(p-tolyl)pyridine (20a)



3-(5-Butylfuran-2-yl)-4-(p-tolyl)pyridine (21a)



4-(4-Fluorophenyl)-3-(5-methylthiophen-2-yl)pyridine (22a)







4-(4-Chlorophenyl)-3-(5-methylthiophen-2-yl)pyridine (23a)



3-(5-Methylthiophen-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridine (24a)







3-(5-Methylthiophen-2-yl)-4-(4-(trifluoromethoxy)phenyl)pyridine (25a)




3-(5-Methylthiophen-2-yl)-4-(*m*-tolyl)pyridine (27a)



4-(3-Fluorophenyl)-3-(5-methylthiophen-2-yl)pyridine (28a)













2-Fluoro-5-(5-methylthiophen-2-yl)-4-phenylpyridine (30a)





6-Fluoro-2-(5-methylthiophen-2-yl)-3-phenylpyridine (33a)





2-Methoxy-4-(5-methylthiophen-2-yl)-3-phenylpyridine (34a)





2-Fluoro-4-(5-methylthiophen-2-yl)-3-phenylpyridine (35a)





