

Supplementary Data

One-Pot Gold(I)-Catalyzed Synthesis of 2-Pyridonyl Alcohols

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General

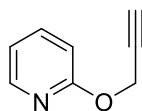
All chemical reagents and solvents were purchased from Merck, Acros and Sigma-Aldrich and used without any purification. Solvents were dried with 3 Å molecular sieve activated and used analytical grade. Varian 400 MHz Mercury and Agilent 400 MHz NMR Magnet were used for ^1H , ^{19}F and ^{13}C NMR spectra. Abi-Sciex 4600 Triple-Quadropol TOF was used for HRMS results. Thin Layer chromatography (TLC) purchased from Merck was used to monitorize all reactions. Silica gel 60 purchased from Merck was used for column chromatography.

General procedure for 2-propagloxy pyridine derivatives

2-hydroxypyridine (5.26 mmol, 1 eq.), Ag_2CO_3 (5.78 mmol, 1.1 eq.) and 60 mL acetonitrile were placed in a single necked 100 ml flask. The reaction was stirred at 50 °C for 2 hours. Then propargyl bromide (1.05 mmol, 2 eq.) was added and stirred for 4 hours at 50 °C. The reaction was cooled to room temperature and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate=20:1).

General procedure for 2-(but-3-yn-1-yloxy)pyridine derivatives

2-hydroxypyridine (5.26 mmol, 1 eq.), Ph_3P (5.79 mmol, 1.1 eq.) and 3-butyn-1-ol (5.79 mmol, 1.1 eq.) were placed in a single necked 100 ml flask. It was dissolved by adding 30 mL of anhydrous THF and the flask was cooled to 0 °C with an ice bath. DIAD solution (5.79 mmol, 1.1 eq.) dissolved in 20 mL anhydrous THF was slowly added and stirred 1 hour at 0 °C. The flask was taken to the oil bath at 50 °C and stirred at this temperature for 6 hours. The reaction was cooled to room temperature and the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate=20:1).



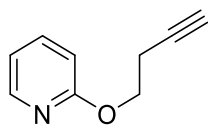
2-(prop-2-yn-1-yloxy)pyridine (1a)

Yield: 45%

^1H NMR (400 MHz, CDCl_3) δ 8.16 (dd, $J = 5.1, 1.9$ Hz, 1H), 7.63 – 7.53 (m, 1H), 6.94 – 6.86 (m, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 4.97 (d, $J = 2.4$ Hz, 2H), 2.48 (t, $J = 2.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.39 (s), 146.80 (s), 138.90 (s), 117.54 (s), 111.33 (s), 79.37 (s), 74.33 (s), 53.33 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_8\text{H}_7\text{NO}+\text{H}]^+$: 134.0600, found: 134.0601.



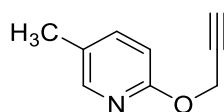
2-(but-3-yn-1-yloxy)pyridine (1b)

Yield: 44%

^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, $J = 5.1, 1.5$ Hz, 1H), 7.60 – 7.51 (m, 1H), 6.86 (ddd, $J = 7.1, 5.1, 0.9$ Hz, 1H), 6.75 (d, $J = 8.4$ Hz, 1H), 4.42 (t, $J = 6.9$ Hz, 2H), 2.67 (td, $J = 6.9, 2.7$ Hz, 2H), 2.02 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.38 (s), 146.88 (s), 138.76 (s), 117.05 (s), 111.30 (s), 81.01 (s), 69.73 (s), 63.68 (s), 19.39 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_9\text{NO}+\text{H}]^+$: 148.0757, found: 148.0762.



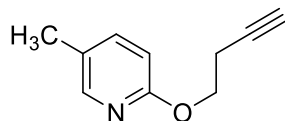
5-methyl-2-(prop-2-yn-1-yloxy)pyridine (1aa)

Yield: 40%

^1H NMR (400 MHz, CDCl_3) δ 7.95 (dd, $J = 1.5, 0.6$ Hz, 1H), 7.40 (dd, $J = 8.4, 2.3$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 4.94 (d, $J = 2.4$ Hz, 2H), 2.46 (t, $J = 2.4$ Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.70 (s), 146.19 (s), 139.96 (s), 126.55 (s), 110.67 (s), 79.57 (s), 74.20 (s), 53.29 (s), 17.53 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_9\text{NO} + \text{H}]^+$: 148.0757, found: 148.0757.



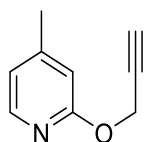
2-(but-3-yn-1-yloxy)-5-methylpyridine (1ba)

Yield: 36%

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 2.2$ Hz, 1H), 7.38 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.66 (d, $J = 8.4$ Hz, 1H), 4.39 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.16 (s, 3H), 2.01 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.68 (s), 146.26 (s), 139.87 (s), 126.01 (s), 110.63 (s), 81.11 (s), 69.67 (s), 63.68 (s), 19.44 (s), 17.54 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_{10}\text{H}_{11}\text{NO} + \text{H}]^+$: 162.0913, found: 162.0912.



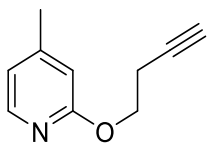
4-methyl-2-(prop-2-yn-1-yloxy)pyridine (1ab)

Yield: 52%

^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 5.2$ Hz, 1H), 6.74 (d, $J = 5.2$ Hz, 1H), 6.61 (s, 1H), 4.96 (d, $J = 2.4$ Hz, 2H), 2.46 (t, $J = 2.4$ Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.79 (s), 150.33 (s), 146.35 (s), 119.16 (s), 111.39 (s), 79.56 (s), 74.20 (s), 53.29 (s), 21.06 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_9\text{NO}+\text{H}]^+$: 148.0757, found: 148.0755.



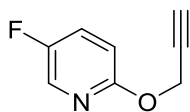
2-(but-3-yn-1-yloxy)-4-methylpyridine (1bb)

Yield: 40%

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 5.2$ Hz, 1H), 6.69 (d, $J = 5.2$ Hz, 1H), 6.57 (s, 1H), 4.40 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.27 (s, 3H), 2.01 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.57 (s), 149.99 (s), 146.27 (s), 118.53 (s), 111.21 (s), 80.97 (s), 69.55 (s), 63.50 (s), 20.90 (s), 19.32 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_{10}\text{H}_{11}\text{NO}+\text{H}]^+$: 162.0913, found: 162.0907.



5-fluoro-2-(prop-2-yn-1-yloxy)pyridine (1ac)

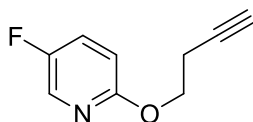
Yield: 77%

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 3.0$ Hz, 1H), 7.35 (ddd, $J = 9.0, 7.6, 3.0$ Hz, 1H), 6.77 (dd, $J = 9.0, 3.6$ Hz, 1H), 4.93 (d, $J = 2.4$ Hz, 2H), 2.47 (t, $J = 2.4$ Hz, 1H).

^{19}F NMR (376 MHz, CDCl_3) δ -138.37 (dd, $J = 7.5, 3.5$ Hz).

^{13}C NMR (101 MHz, CDCl_3) δ 158.56 (s), 155.88 (d, $J = 246.2$ Hz), 133.22 (d, $J = 26.3$ Hz), 126.94 (d, $J = 21.4$ Hz), 111.96 (d, $J = 4.7$ Hz), 79.18 (s), 74.44 (d, $J = 2.1$ Hz), 53.91 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_6\text{NOF} + \text{H}]^+$: 152.0506, found: 152.0501.



2-(but-3-yn-1-yloxy)-5-fluoropyridine (1bc)

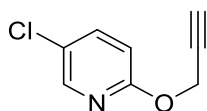
Yield: 46%

^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 3.1$ Hz, 1H), 7.33 (ddd, $J = 9.0, 7.6, 3.1$ Hz, 1H), 6.73 (dd, $J = 9.0, 3.6$ Hz, 1H), 4.39 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.02 (t, $J = 2.7$ Hz, 1H).

^{19}F NMR (376 MHz, CDCl_3) δ -139.11 (dd, $J = 7.6, 3.6$ Hz).

^{13}C NMR (101 MHz, CDCl_3) δ 159.44 (s), 155.46 (d, $J = 245.6$ Hz), 133.05 (d, $J = 26.0$ Hz), 126.65 (d, $J = 21.3$ Hz), 111.74 (d, $J = 4.7$ Hz), 80.75 (s), 69.64 (s), 64.10 (s), 19.21 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_8\text{NOF} + \text{H}]^+$: 166.0663, found: 166.0665.



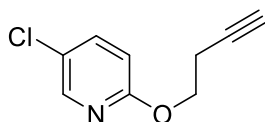
5-chloro-2-(prop-2-yn-1-yloxy)pyridine (1ad)

Yield: 89%

^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 2.6$ Hz, 1H), 7.55 (dd, $J = 8.8, 2.6$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 1H), 4.94 (d, $J = 2.4$ Hz, 2H), 2.48 (t, $J = 2.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 160.87 (s), 145.15 (s), 138.90 (s), 125.02 (s), 112.33 (s), 78.96 (s), 74.61 (s), 53.87 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_6\text{ClNO} + \text{H}]^+$: 168.0211, found: 168.0206.



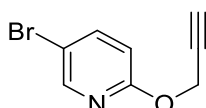
2-(but-3-yn-1-yloxy)-5-chloropyridine (1bd)

Yield: 63%

^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 2.6$ Hz, 1H), 7.51 (dd, $J = 8.8, 2.7$ Hz, 1H), 6.71 (d, $J = 8.8$ Hz, 1H), 4.39 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.02 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.82 (s), 145.16 (s), 138.73 (s), 124.42 (s), 112.29 (s), 80.77 (s), 69.87 (s), 64.19 (s), 19.29 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_8\text{ClNO}+\text{H}]^+$: 182.0367, found: 182.0369.



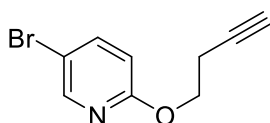
5-bromo-2-(prop-2-yn-1-yloxy)pyridine (1ae)

Yield: 81%

^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 2.4$ Hz, 1H), 7.67 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.72 (d, $J = 8.8$ Hz, 1H), 4.94 (d, $J = 2.4$ Hz, 2H), 2.48 (t, $J = 2.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.27 (s), 147.49 (s), 141.52 (s), 112.96 (s), 112.69 (s), 78.92 (s), 74.65 (s), 53.83 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_6\text{BrNO}+\text{H}]^+$: 211.9706, found: 211.9697.



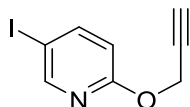
5-bromo-2-(but-3-yn-1-yloxy)pyridine (1ae)

Yield: 54%

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 2.5$ Hz, 1H), 7.64 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.68 (d, $J = 8.8$ Hz, 1H), 4.39 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.02 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.23 (s), 147.53 (s), 141.34 (s), 112.95 (s), 112.10 (s), 80.76 (s), 69.88 (s), 64.17 (s), 19.29 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_8\text{BrNO}+\text{H}]^+$: 225.9862, found: 225.9864.



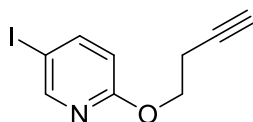
5-iodo-2-(prop-2-yn-1-yloxy)pyridine (1af)

Yield: 79%

^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, $J = 2.2$ Hz, 1H), 7.81 (dd, $J = 8.7, 2.3$ Hz, 1H), 6.65 (d, $J = 8.7$ Hz, 1H), 4.93 (d, $J = 2.4$ Hz, 2H), 2.48 (t, $J = 2.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.84 (s), 152.70 (s), 146.77 (s), 113.70 (s), 83.24 (s), 78.90 (s), 74.67 (s), 53.71 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_6\text{INO}+\text{H}]^+$: 259.9567, found: 259.9557.



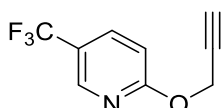
2-(but-3-yn-1-yloxy)-5-iodopyridine (1bf)

Yield: 56%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.30 (d, $J = 2.3$ Hz, 1H), 7.78 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.60 (d, $J = 8.7$ Hz, 1H), 4.38 (t, $J = 6.9$ Hz, 2H), 2.66 (td, $J = 6.9, 2.7$ Hz, 2H), 2.02 (t, $J = 2.7$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.77 (s), 152.74 (s), 146.58 (s), 113.71 (s), 82.57 (s), 80.76 (s), 69.89 (s), 64.05 (s), 19.27 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_8\text{INO} + \text{H}]^+$: 273.9723, found: 273.9728.



2-(prop-2-yn-1-yloxy)-5-(trifluoromethyl)pyridine (1ag)

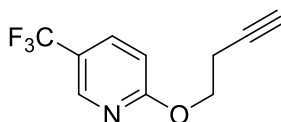
Yield: 70%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.49 – 8.44 (m, 1H), 7.80 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.89 (d, $J = 8.7$ Hz, 1H), 5.03 (d, $J = 2.4$ Hz, 2H), 2.50 (t, $J = 2.4$ Hz, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.66 (s).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.51 (d, $J = 0.8$ Hz), 144.94 (q, $J = 4.5$ Hz), 136.12 (q, $J = 3.1$ Hz), 123.99 (d, $J = 271.3$ Hz), 120.94 (dd, $J = 66.4, 33.1$ Hz), 111.54 (s), 78.60 (s), 74.88 (s), 54.15 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_6\text{F}_3\text{NO} + \text{H}]^+$: 202.0474, found: 202.0472.



2-(but-3-yn-1-yloxy)-5-(trifluoromethyl)pyridine (1bg)

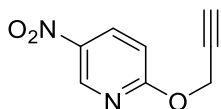
Yield: 55%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 – 8.31 (m, 1H), 7.78 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 4.49 (t, $J = 6.8$ Hz, 2H), 2.70 (td, $J = 6.8, 2.7$ Hz, 2H), 2.03 (t, $J = 2.7$ Hz, 1H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.60 (s).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.45 (s), 145.32 – 144.12 (m), 135.93 (td, $J = 3.9, 2.9$ Hz), 124.08 (d, $J = 270.2$ Hz), 120.38 (d, $J = 33.5$ Hz), 111.51 (s), 81.54 – 79.52 (m), 70.00 (s), 64.49 (s), 19.27 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_{10}\text{H}_8\text{F}_3\text{NO} + \text{H}]^+$: 216.0631, found: 216.0620.



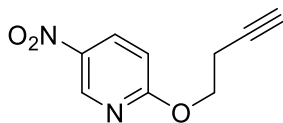
5-nitro-2-(prop-2-yn-1-yloxy)pyridine (1ah)

Yield: 81%

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.09 – 9.07 (m, 1H), 8.39 (dd, $J = 9.1, 2.8$ Hz, 1H), 6.90 (dd, $J = 9.1, 0.5$ Hz, 1H), 5.07 (d, $J = 2.4$ Hz, 2H), 2.53 (t, $J = 2.4$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.66 (s), 144.67 (s), 140.09 (s), 134.37 (s), 111.61 (s), 77.94 (s), 75.40 (s), 55.00 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_8H_6N_2O_3+H]^+$: 179.0451, found: 179.0451.



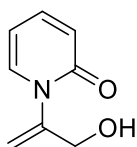
2-(but-3-yn-1-yloxy)-5-nitropyridine (1bh)

Yield: 53%

1H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, $J = 2.8$ Hz, 1H), 8.36 (dd, $J = 9.1, 2.8$ Hz, 1H), 6.86 (d, $J = 9.1$ Hz, 1H), 4.55 (t, $J = 6.8$ Hz, 2H), 2.71 (td, $J = 6.8, 2.7$ Hz, 2H), 2.04 (t, $J = 2.7$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.70 (s), 144.85 (s), 139.77 (s), 134.19 (s), 111.56 (s), 80.18 (s), 70.23 (s), 65.36 (s), 19.23 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_9H_8N_2O_3+H]^+$: 193.0608, found: 193.0609.



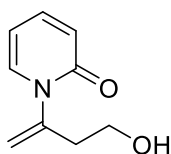
1-(3-hydroxyprop-1-en-2-yl)pyridin-2(1H)-one (2a)

Yield: 98%

1H NMR (400 MHz, $CDCl_3$) δ 7.41 (ddd, $J = 9.0, 6.6, 2.0$ Hz, 1H), 7.27 (dd, $J = 6.8, 2.0$ Hz, 1H), 6.58 (d, $J = 9.2$ Hz, 1H), 6.26 (t, $J = 6.7$ Hz, 1H), 5.58 (s, 1H), 5.30 (s, 1H), 4.33 (s, 2H), 3.67 (br. s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.05 (s), 150.57 (s), 140.91 (s), 138.16 (s), 121.17 (s), 115.53 (s), 106.97 (s), 63.12 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_8H_9NO_2+H]^+$: 152.0706, found: 152.0709.



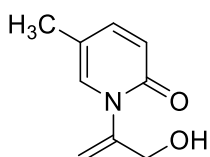
1-(4-hydroxybut-1-en-2-yl)pyridin-2(1H)-one (2b)

Yield: 96%

1H NMR (400 MHz, $CDCl_3$) δ 7.38 (ddd, $J = 8.9, 6.7, 2.0$ Hz, 1H), 7.22 (dd, $J = 6.8, 1.8$ Hz, 1H), 6.56 (d, $J = 9.2$ Hz, 1H), 6.24 (td, $J = 6.7, 0.9$ Hz, 1H), 5.43 (s, 1H), 5.21 (s, 1H), 3.61 (t, $J = 5.7$ Hz, 2H), 3.43 (br. s, 1H), 2.62 (t, $J = 5.6$ Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.84 (s), 146.33 (s), 140.62 (s), 137.66 (s), 121.18 (s), 117.48 (s), 106.78 (s), 58.80 (s), 38.50 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_9H_{11}NO_2+H]^+$: 166.0863, found: 166.0864.



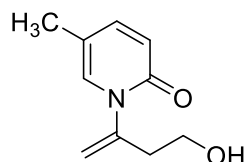
1-(3-hydroxyprop-1-en-2-yl)-5-methylpyridin-2(1H)-one (2aa)

Yield: 98%

^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.14 (m, 1H), 7.01 (d, $J = 1.0$ Hz, 1H), 6.49 (d, $J = 9.3$ Hz, 1H), 5.52 (s, 1H), 5.25 (d, $J = 0.7$ Hz, 1H), 4.57 (s, 1H), 4.29 (d, $J = 2.3$ Hz, 2H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.32 (s), 150.80 (s), 143.48 (s), 135.50 (s), 120.76 (s), 115.95 (s), 115.29 (s), 63.37 (s), 17.04 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_{11}\text{NO}_2+\text{H}]^+$: 166.0863, found: 166.0864.



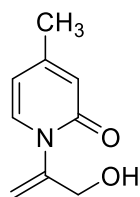
1-(4-hydroxybut-1-en-2-yl)-5-methylpyridin-2(1H)-one (2ba)

Yield: 98%

^1H NMR (400 MHz, CDCl_3) δ 7.24 (dd, $J = 9.3, 2.4$ Hz, 1H), 6.97 (d, $J = 0.9$ Hz, 1H), 6.51 (d, $J = 9.3$ Hz, 1H), 5.42 (s, 1H), 5.20 (s, 1H), 4.11 (s, 1H), 3.61 (t, $J = 5.6$ Hz, 2H), 2.60 (t, $J = 5.6$ Hz, 2H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.10 (s), 146.39 (s), 143.21 (s), 134.90 (s), 120.82 (s), 117.41 (s), 115.86 (s), 58.90 (s), 38.78 (s), 17.02 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_{10}\text{H}_{13}\text{NO}_2+\text{H}]^+$: 180.1019, found: 180.1018.



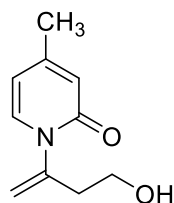
1-(3-hydroxyprop-1-en-2-yl)-4-methylpyridin-2(1H)-one (2ab)

Yield: 96%

^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, $J = 7.0$ Hz, 1H), 6.35 (s, 1H), 6.08 (dd, $J = 7.0, 1.8$ Hz, 1H), 5.52 (s, 1H), 5.24 (d, $J = 0.4$ Hz, 1H), 4.34 (s, 1H), 4.29 (d, $J = 0.5$ Hz, 2H), 2.19 (d, $J = 0.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.01 (s), 152.83 (s), 150.54 (s), 136.96 (s), 119.43 (s), 115.33 (s), 109.52 (s), 63.34 (s), 21.40 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_{11}\text{NO}_2+\text{H}]^+$: 166.0863, found: 166.0862.



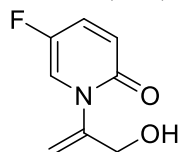
1-(4-hydroxybut-1-en-2-yl)-4-methylpyridin-2(1H)-one (2bb)

Yield: 97%

^1H NMR (400 MHz, CDCl_3) δ 7.09 (d, $J = 6.9$ Hz, 1H), 6.37 (s, 1H), 6.09 (dd, $J = 6.9, 1.8$ Hz, 1H), 5.43 (s, 1H), 5.20 (s, 1H), 3.61 (t, $J = 5.6$ Hz, 2H), 3.21 (s, 1H), 2.60 (t, $J = 5.6$ Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.87 (s), 152.54 (s), 146.13 (s), 136.41 (s), 119.48 (s), 117.58 (s), 109.38 (s), 58.86 (s), 38.75 (s), 21.43 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_{10}H_{13}NO_2+H]^+$: 180.1019, found: 180.1018.



5-fluoro-1-(3-hydroxyprop-1-en-2-yl)pyridin-2(1H)-one (2ac)

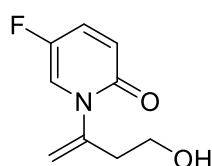
Yield: 95%

1H NMR (400 MHz, $CDCl_3$) δ 7.35 (ddd, $J = 10.0, 6.8, 3.2$ Hz, 1H), 7.21 (t, $J = 3.5$ Hz, 1H), 6.53 (dd, $J = 10.0, 5.2$ Hz, 1H), 5.57 (s, 1H), 5.30 (s, 1H), 4.32 (s, 2H), 4.28 (s, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -148.39 (dd, $J = 10.5, 5.3$ Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01 (s), 150.13 (s), 147.84 (d, $J = 233.8$ Hz), 132.67 (d, $J = 24.0$ Hz), 123.71 (d, $J = 37.2$ Hz), 121.84 (d, $J = 7.3$ Hz), 115.69 (s), 62.84 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_8H_8NO_2F+H]^+$: 170.0612, found: 170.0614.



5-fluoro-1-(4-hydroxybut-1-en-2-yl)pyridin-2(1H)-one (2bc)

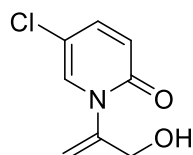
Yield: 73%

1H NMR (400 MHz, $CDCl_3$) δ 7.35 (ddd, $J = 10.1, 6.8, 3.3$ Hz, 1H), 7.17 (t, $J = 3.5$ Hz, 1H), 6.56 (dd, $J = 10.0, 5.2$ Hz, 1H), 5.47 (s, 1H), 5.26 (s, 1H), 3.69 (s, 1H), 3.64 (t, $J = 5.6$ Hz, 2H), 2.64 (t, $J = 5.2$ Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -148.28 – -148.34 (m).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.76 (s), 147.55 (d, $J = 234.0$ Hz), 145.94 (s), 132.30 (d, $J = 23.9$ Hz), 123.03 (d, $J = 36.7$ Hz), 121.84 (d, $J = 7.2$ Hz), 117.82 (s), 58.78 (s), 38.16 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_9H_{10}NO_2F+H]^+$: 184.0768, found: 184.0773.



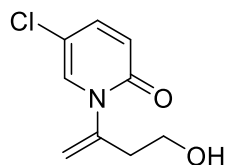
5-chloro-1-(3-hydroxyprop-1-en-2-yl)pyridin-2(1H)-one (2ad)

Yield: 98%

1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 6.51 (d, $J = 9.6$ Hz, 1H), 5.57 (d, $J = 0.8$ Hz, 1H), 5.29 (d, $J = 0.9$ Hz, 1H), 4.31 (d, $J = 0.7$ Hz, 2H), 4.14 (br. s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.26 (s), 149.82 (s), 141.69 (s), 135.70 (s), 121.90 (s), 115.71 (s), 113.33 (s), 62.60 (s).

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_8H_8ClNO_2+H]^+$: 186.0316, found: 186.0309.



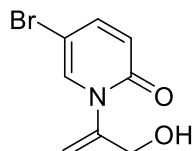
5-chloro-1-(4-hydroxybut-1-en-2-yl)pyridin-2(1H)-one (2bd)

Yield: 81%

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.25 (m, 2H), 6.55 (d, $J = 9.7$ Hz, 1H), 5.47 (s, 1H), 5.26 (s, 1H), 3.63 (t, $J = 5.6$ Hz, 2H), 3.24 (br. s, 1H), 2.63 (t, $J = 5.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.25 (s), 145.88 (s), 141.52 (s), 135.16 (s), 122.08 (s), 118.07 (s), 113.24 (s), 58.80 (s), 38.28 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_{10}\text{ClNO}_2+\text{H}]^+$: 200.0473, found: 200.0479.



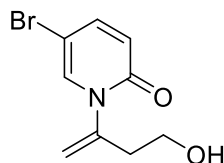
5-bromo-1-(3-hydroxyprop-1-en-2-yl)pyridin-2(1H)-one (2ae)

Yield: 92%

^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.35 (m, 2H), 6.47 (d, $J = 9.4$ Hz, 1H), 5.57 (d, $J = 0.7$ Hz, 1H), 5.30 (d, $J = 0.9$ Hz, 1H), 4.31 (d, $J = 0.7$ Hz, 2H), 3.85 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.37 (s), 149.84 (s), 143.78 (s), 137.89 (s), 122.32 (s), 115.86 (s), 98.97 (s), 62.77 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_8\text{BrNO}_2+\text{H}]^+$: 229.9811, found: 229.9818.



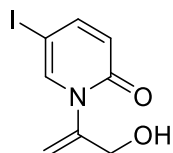
5-bromo-1-(4-hydroxybut-1-en-2-yl)pyridin-2(1H)-one (2be)

Yield: 77%

^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, $J = 9.7, 2.7$ Hz, 1H), 7.36 (d, $J = 2.6$ Hz, 1H), 6.50 (d, $J = 9.7$ Hz, 1H), 5.47 (s, 1H), 5.26 (s, 1H), 3.64 (t, $J = 5.6$ Hz, 2H), 3.34 (s, 1H), 2.63 (t, $J = 5.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.29 (s), 145.88 (s), 143.57 (s), 137.40 (s), 122.48 (s), 118.07 (s), 98.80 (s), 58.85 (s), 38.37 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_{10}\text{BrNO}_2+\text{H}]^+$: 243.9968, found: 243.9970.



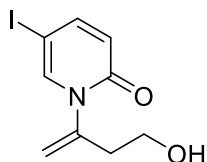
1-(3-hydroxyprop-1-en-2-yl)-5-iodopyridin-2(1H)-one (2af)

Yield: 98%

^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.36 (m, 2H), 6.39 (dd, $J = 8.9, 1.2$ Hz, 1H), 5.57 (d, $J = 0.5$ Hz, 1H), 5.31 (d, $J = 0.8$ Hz, 1H), 4.31 (d, $J = 0.3$ Hz, 2H), 3.37 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.46 (s), 149.78 (s), 148.17 (s), 142.70 (s), 122.96 (s), 116.01 (s), 65.47 (s), 62.96 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_8\text{H}_8\text{INO}_2+\text{H}]^+$: 277.9673, found: 277.9674.



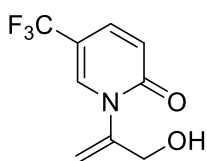
1-(4-hydroxybut-1-en-2-yl)-5-iodopyridin-2(1H)-one (2bf)

Yield: 92%

^1H NMR (400 MHz, CDCl_3) δ 7.48 (dd, $J = 9.5, 2.5$ Hz, 1H), 7.45 (d, $J = 2.4$ Hz, 1H), 6.40 (d, $J = 9.5$ Hz, 1H), 5.45 (s, 1H), 5.24 (s, 1H), 3.63 (t, $J = 5.6$ Hz, 2H), 3.34 (s, 1H), 2.62 (t, $J = 5.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.29 (s), 147.92 (s), 145.79 (s), 142.30 (s), 123.03 (s), 117.95 (s), 65.24 (s), 58.82 (s), 38.36 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_{10}\text{INO}_2+\text{H}]^+$: 291.9829, found: 291.9821.



1-(3-hydroxyprop-1-en-2-yl)-5-(trifluoromethyl)pyridin-2(1H)-one (2ag)

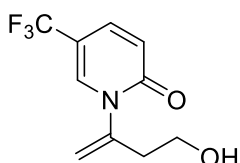
Yield: 90%

^1H NMR (400 MHz, CDCl_3) δ 7.65 (s, 1H), 7.50 (dd, $J = 9.6, 2.7$ Hz, 1H), 6.60 (d, $J = 9.6$ Hz, 1H), 5.61 (d, $J = 0.9$ Hz, 1H), 5.32 (d, $J = 1.0$ Hz, 1H), 4.34 (d, $J = 0.7$ Hz, 2H), 3.66 (s, 1H).

^{19}F NMR (376 MHz, CDCl_3) δ -62.56 (s).

^{13}C NMR (101 MHz, CDCl_3) δ 162.14 (s), 149.64 (s), 137.89 (q, $J = 5.1$ Hz), 136.30 (d, $J = 2.1$ Hz), 123.19 (q, $J = 270.0$ Hz), 121.78 (d, $J = 0.9$ Hz), 115.98 (d, $J = 2.7$ Hz), 110.49 (q, $J = 35.2$ Hz), 62.42 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_9\text{H}_8\text{F}_3\text{NO}_2+\text{H}]^+$: 220.0580, found: 220.0585.



1-(4-hydroxybut-1-en-2-yl)-5-(trifluoromethyl)pyridin-2(1H)-one (2bg)

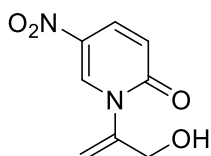
Yield: 59%

^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.51 (dd, $J = 9.6, 2.7$ Hz, 1H), 6.64 (d, $J = 9.6$ Hz, 1H), 5.51 (d, $J = 0.8$ Hz, 1H), 5.29 (s, 1H), 3.66 (t, $J = 5.7$ Hz, 2H), 2.96 (s, 1H), 2.68 (t, $J = 5.6$ Hz, 2H).

^{19}F NMR (376 MHz, CDCl_3) δ -62.50 (s).

^{13}C NMR (101 MHz, CDCl_3) δ 162.15 (s), 146.12 (s), 137.37 (q, $J = 5.5$ Hz), 136.07 (d, $J = 2.1$ Hz), 123.22 (q, $J = 270.1$ Hz), 121.96 (s), 118.12 (s), 110.36 (q, $J = 35.0$ Hz), 58.92 (s), 38.03 (s).

HRMS (ESI): m/z $[\text{M}+\text{H}^+]$ calcd for $[\text{C}_{10}\text{H}_{10}\text{F}_3\text{NO}_2+\text{H}]^+$: 234.0736, found: 234.0739.



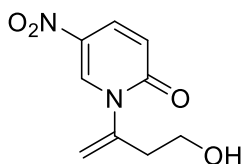
1-(3-hydroxyprop-1-en-2-yl)-5-nitropyridin-2(1H)-one (2ah)

Yield: 66%

^1H NMR (400 MHz, DMSO- d_6) δ 8.67 (d, J = 2.9 Hz, 1H), 8.18 (dd, J = 10.1, 3.0 Hz, 1H), 6.51 (d, J = 10.1 Hz, 1H), 5.59 (s, 1H), 5.45 (s, 1H), 5.29 (s, 1H), 4.19 (s, 2H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 160.29 (s), 148.77 (s), 141.80 (s), 133.87 (s), 129.88 (s), 118.83 (s), 114.84 (s), 60.23 (s).

HRMS (ESI): m/z [$\text{M}+\text{H}^+$] calcd for [$\text{C}_8\text{H}_8\text{N}_2\text{O}_4+\text{H}$] $^+$: 197.0557, found: 197.0562.



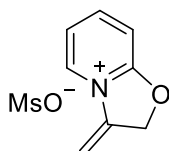
1-(4-hydroxybut-1-en-2-yl)-5-nitropyridin-2(1H)-one (2bh)

Yield: 69%

^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, J = 2.6 Hz, 1H), 8.13 (dd, J = 10.1, 3.0 Hz, 1H), 6.56 (d, J = 10.1 Hz, 1H), 5.54 (s, 1H), 5.34 (s, 1H), 3.70 (s, 2H), 2.76 (s, 1H), 2.73 (t, J = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.63 (s), 146.24 (s), 139.71 (s), 134.01 (s), 131.16 (s), 120.09 (s), 118.22 (s), 59.10 (s), 37.36 (s).

HRMS (ESI): m/z [$\text{M}+\text{H}^+$] calcd for [$\text{C}_9\text{H}_{10}\text{N}_2\text{O}_4+\text{H}$] $^+$: 211.0713, found: 211.0720.



3-Methylidene-2,3-dihydro[1,3]oxazolo[3,2-a]pyridin-4-ium methanesulfonate

^1H NMR (400 MHz, D_2O) δ 8.66 (d, J = 6.6 Hz, 1H), 8.39 (ddd, J = 8.9, 7.4, 1.5 Hz, 1H), 7.52 (ddd, J = 8.9, 6.3, 2.6 Hz, 2H), 5.95 (dt, J = 5.1, 3.3 Hz, 1H), 5.64 (t, J = 3.0 Hz, 2H), 5.52 (dt, J = 5.4, 2.8 Hz, 1H), 2.74 (s, 3H).

^{13}C NMR (101 MHz, D_2O) δ 162.02 (s), 149.66 (s), 137.50 (s), 130.85 (s), 119.23 (s), 111.43 (s), 98.77 (s), 73.23 (s), 38.27 (s).

