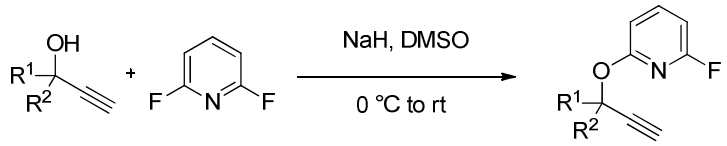
# 2-Propynyloxy-6-Fluoropyridines as a Us Synthetic Platform to Access Valuable Heterocyclic Compounds - Divergence in Reactivity Between Au Catalysis, Ag Catalysis, and Thermal Conditions

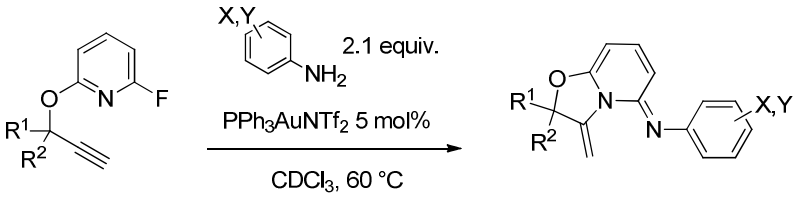
# *1. General procedures*

## General procedure 2.1:




To a round-bottomed flask were added, in the following order, dimethylsulfoxide (0.8 M compared to pyridine), propargyl alcohol (1.2 equiv.) and difluoropyridine (1.0 equiv.). Sodium hydride (1.2 equiv.) was then added portionwise over 30 minutes. The reaction was then put under nitrogen and stirred at room temperature under nitrogen atmosphere until completion was indicated by TLC analysis. The excess reagents were then quenched with water. The mixture was extracted three times with diethyl ether. The organic phases were combined and washed with water and brine and then dried over magnesium sulfate. The solvent was evaporated under reduced pressure. The crude was then purified by silica gel chromatography (98 : 2 petroleum ether : ethyl acetate)

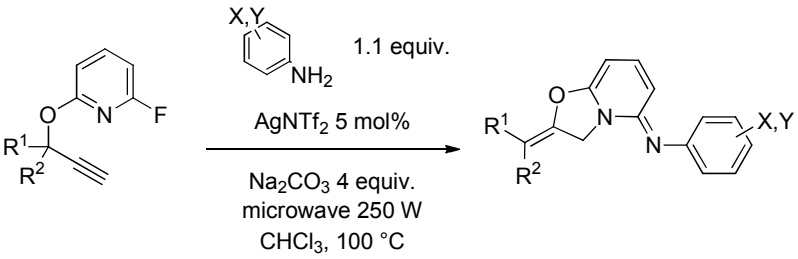
## General procedure 2.2:




To a NMR tube containing 0.1 mmol of fluoropropynyloxypyridine in deuterated chloroform were added 0.21 mmol (2.1 equiv.) of aniline and 0.005 mmol (5 mol%) of gold catalyst ($PPh_3AuNTf_2$).

The NMR tube was then heated to 60 °C in an oil bath. After $^1H$ NMR showed no starting material remaining, the reaction mixture was filtered on a pad of silica and washed with ethyl acetate. The crude was then purified by silica gel chromatography (95 : 5 petroleum ether : ethyl acetate) leading to the pure compound.

## General procedure 2.3:

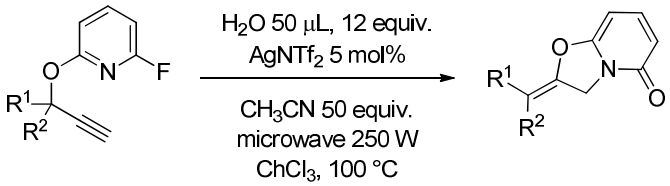


To a microwave vial (from 2 mL to 5 mL) were added 0.1 mmol of fluoropropynyloxypyridine, 0.11 mmol (1.1 equiv.) of aniline, 0.4 mmol (4.0 equiv.) of sodium carbonate, 2.5 mL of chloroform and 0.01 equiv. (10 mol%) of silver salt ($AgNTf_2$).

The vial was then heated for 2 hours at 100 °C in the microwave.

The reaction mixture was then filtered on a pad of silica and washed with ethyl acetate. The crude was then purified by silica gel chromatography (90 : 10 petroleum ether : ethyl acetate) leading to the pure compound.

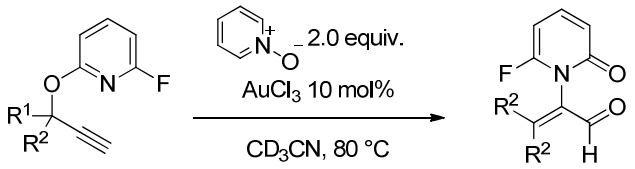
## General procedure 2.4:




To a microwave vial (from 2 mL to 5 mL) were added 0.1 mmol of fluoropropynyloxypyridine, 0.05 mL of water (27.5 equiv.) and 0.05 mL (12 equiv.) of acetonitrile, 2.5 mL of chloroform and 0.01 mmol (10 mol%) of silver salt ($AgNTf_2$). The vial was then heated for 1 hour at 100 °C in the microwave.

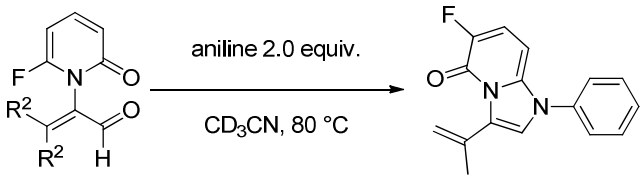
The reaction mixture was then filtered on a pad of silica washed with dichloromethane : methanol (95 : 5). The crude was then purified by silica gel chromatography (99 : 1 dichloromethane:methanol) leading to the pure compound.

## General procedure 2.5:



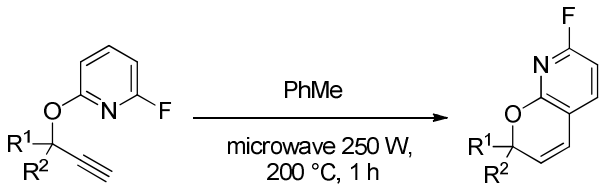

To a NMR tube was added 0.1mmol of fluoropropynyloxypyridine followed by 0.2 mmol of pyridine oxide in 0.5 mL deuterated acetonitrile. Gold trichloride (10 mol%) was then added to the reaction mixture and the tube was heated to reflux in an oil bath. The reaction is monitored by $^1H$ NMR. When no starting material remains, the reaction mixture is filtered through a pad of silica with ethyl acetate as the eluent. The crude product was then purified by silica gel chromatography (60 : 40 petroleum ether : ethyl acetate) leading to the pure aldehyde (notably unstable).

## General procedure 2.6:



To a NMR tube were added 1 equiv. of the aldehyde, anilin (2 equiv.) and deuterated acetonitrile (500 µL). The reaction mixture was heated to reflux and the reaction was followed by NMR. When no aldehyde remained, the crude was purified by silica gel chromatography (99 : 1 dichloromethane : methanol) leading to the pure compound.

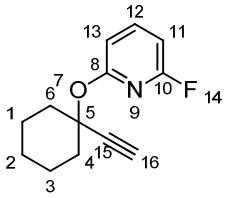
## General procedure 2.7:




In a microwave vial (from 2 mL to 5 mL), 0.1 mmol of fluoropropynyloxypyridine was dissolved in 2.0 mL of toluene. The vial was sealed and heated in the microwave to 200 °C for 2 hours. The solvent was then evaporated and the product purified by silica gel chromatography using petroleum ether : ethyl acetate as the eluent (90 : 10).

# *2. Preparation of propynyloxy-6-fluoropyridines*

| **2-((1-Ethynylcyclohexyl)oxy)-6-fluoropyridine (2.53)** | $C_{13}H_{14}FNO$ | **MW = 219.3 g.mol$^{-1}$** |
|---|---|---|



**Procedure :** see general procedure 2.1

**Product:** colorless oil.

**Yield:** 60%.

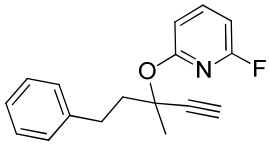
**$^{1}$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69 (q app, *J* = 8.0 Hz, 1H, **H12**), 6.76 (qd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H, **H13**), 6.54 (qd, *J* = 8.0 Hz, *J* = 2.8 Hz, 1H, **H11**), 2.64 (s, 1H, **H16**), 2.37-2.30 (m, 2H, **H4 and H6**), 2.10-2.02 (m, 2H, **H4 and H6**), 1.78-1.56 (m, 5H, **H1, H2 and H3**), 1.47-1.36 (m, 1H, **H3**).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ (ppm) 161.6 (d, *J* = 238.2 Hz, **C10**), 161.4 (d, *J* = 14.3 Hz, **C8**), 142.3 (d, *J* = 7.9 Hz, **C12**), 108.8 (d, *J* = 5.1 Hz, **C13**), 100.9 (d, *J* = 35.8 Hz, **C11**), 84.2 (**C15**), 76.3 (**C16**), 75.2 (**C5**), 37.6 (2C, **C6 and C6**), 25.2 (**C2**), 22.6 (2C, **C1 and C3**).

**HRMS:** $C_{13}H_{14}FNO$ [M+Na$^{+}$]; was submitted twice with no result .

**IR** ($CCl_4$): ν ($cm^{-1}$) 3312, 2939, 2863, 1612, 1439, 1329, 1230.

| **2-fluoro-6-[(3-methyl-5-phenylpent-1-yn-3-yl)oxy]pyridine (2.60)** | $C_{17}H_{16}FNO$ | **MW = 269.3 g.mol$^{-1}$** |
|---|---|---|



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 64 % (m = 516 mg, n = 1.92 mmol)

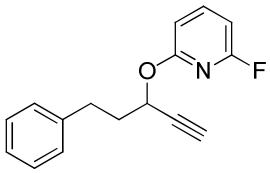
**$^{1}$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.66 (dd, *J* = 7.9 Hz, *J* = 8.1 Hz, 1H), 7.33-7.29 (m, 2H), 7.26-7.19 (m, 3H), 6.71 (dd, *J* = 1.0 Hz, *J* = 7.9 Hz, 1H), 6.53 (dd, *J* = 2.7 Hz, *J* = 7.8 Hz, 1H), 3.00-2.87 (m, 2H), 2.63 (s, 1H), 2.44 (ddd, *J* = 5.8 Hz, *J* = 11.4 Hz, *J* = 13.5 Hz, 1H), 2.29 (ddd, *J* = 5.6 Hz, *J* = 11.7 Hz, *J* = 13.6 Hz, 1H), 1.91 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 161.5 (d, *J* = 238 Hz), 142.4 (d, *J* = 10.5 Hz), 141.7, 128.5 (3C), 125.9 (2C), 108.9 (d, *J* = 21.6 Hz), 101.3, 100.9 (d, *J* = 19.3 Hz), 84.1, 75.7, 74.4 (d, *J* = 11.5 Hz), 44.2, 30.6, 27.0.

**HRMS:** $C_{17}H_{16}FNO$ [M$^{+}$]; calculated: 269.1216, found 269.1219.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3311, 3029, 2939, 1614, 1575, 1441, 1327, 1232, 1171, 1089, 1017.

**2-fluoro-6-[(5-phenylpent-1-yn-3-yl)oxy]pyridine (2.62)** $C_{16}H_{14}FNO$ **MW = 255.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 72 % (m = 551 mg, n = 2.16 mmol)

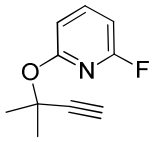
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69 (q app, *J* = 8.0 Hz, 1H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 3H), 6.67 (dd, *J* = 1.3 Hz, *J* = 8.0 Hz, 1H), 6.52 (dd, *J* = 2.5 Hz, *J* = 7.7 Hz, 1H), 5.63 (dt, *J* = 2.0 Hz, *J* = 6.5 Hz, 1H), 2.90 (t, *J* = 8.0 Hz, 2H), 2.50 (d, *J* = 2.0 Hz, 1H), 2.34-2.19 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 162.0 (d, *J* = 239.9 Hz), 161.5 (d, *J* = 13.3 Hz), 142.9 (d, *J* = 7.9 Hz), 141.0, 128.6, 128.5, 126.2, 107.6, 107.5, 101.1, 100.8, 81.8, 73.9, 65.1, 36.6, 31.3.

**HRMS:** $C_{16}H_{14}FNO$ [$M^+$]; calculated: 255.1059; found: 255.1069.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2940, 1656, 1567, 1537, 1480, 1242, 1165.

**2-fluoro-6-[(2-methylbut-3-yn-2-yl)oxy]pyridine (2.64)** $C_{10}H_{10}FNO$ **MW = 179.2 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** volatile colorless oil

**Yield:** 57 % (m = 304 mg, n = 1.7 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.61 (q app, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 1.1 Hz, *J* = 8.0 Hz, 1H), 6.46 (dd, *J* = 2.7 Hz, *J* = 8.0 Hz, 1H), 2.51 (s, 1H), 1.78 (s, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 161.2 (d, *J* = 238.3 Hz), 161.2 (d, *J* = 14.2 Hz), 142.3, 108.6 (d, *J* = 9.6 Hz), 100.6 (d, *J* = 13.4 Hz), 85.1, 73.0 (d, *J* = 6.6 Hz), 72.6, 29.5 (2C).

**HRMS:** $C_{10}H_{10}FNO$ [$M^+$]; calculated: 179.0746, found 179.0741.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3310, 2940, 2870, 1608, 1577, 1439, 1328, 1233, 1140, 1047, 1013.

**2,4-difluoro-6-[(2-methylbut-3-yn-2-yl)oxy]pyridine (2.66)** $C_{10}H_9F_2NO$ **MW = 197.2 g.mol$^{-1}$**

**Procedure:** see general procedure 2.1 replacing 2,6-difluoropyridine by 2,3,6-trifluoropyridine

**Product:** volatile colorless oil

**Yield:** 21 % (m = 125 mg, n = 0.063 mmol)

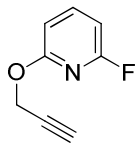
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.42 (dt, *J* = 6.4 Hz, *J* = 8.6 Hz, 1H), 6.45 (ddd, *J* = 2.1 Hz, *J* = 3.5 Hz, *J* = 8.5 Hz, 1H), 2.54 (s, 1H), 1.87 (s, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 155.5 (d, *J* = 238.0 Hz), 145.3 (dd, *J* = 6.4 Hz, *J* = 251.3 Hz), 127.4 (dd, *J* = 2.2 Hz, *J* = 19.3 Hz), 127.3 (dd, *J* = 2.0 Hz, *J* = 19.4 Hz), 100.6 (d, *J* = 40.2 Hz), 84.5, 74.2, 73.4, 29.6 (2C).

**HRMS:** $C_{10}H_9F_2NO$ [$M^+$]; calculated: 197.0652, not found.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3308, 2938, 2870, 1610, 1576, 1439, 1328, 1228, 1142, 1047.

**2-fluoro-6-(prop-2-yn-1-yloxy)pyridine (2.68)** $C_8H_6FNO$ **MW = 151.1 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** volatile colorless oil

**Yield:** 30 % (m = 135 mg, n = 0.89 mmol)

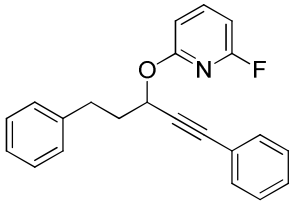
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.68 (dd, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 1.3 Hz, *J* = 8.0 Hz, 1H), 6.51 (dd, *J* = 2.4 Hz, *J* = 7.8 Hz, 1H), 4.94 (d, *J* = 2.4 Hz, 2H), 2.49 (t, *J* = 2.4 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 162.3 (d, *J* = 277.6 Hz), 160.9, 142.9 (d, *J* = 7.9 Hz), 107.4 (d, *J* = 5.1 Hz), 100.9 (d, *J* = 34.9 Hz), 78.5, 74.8, 54.1.

**HRMS:** $C_8H_6FNO$ [$M^+$]; calculated: 151.0433, found 151.0430.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3314, 2947, 2865, 1609, 1575, 1328, 1233, 1140, 1015.

**2-[(1,5-diphenylpent-1-yn-3-yl)oxy]-6-fluoropyridine (2.72)** $C_{22}H_{18}FNO$ **MW = 331.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 48 % (m = 475 mg, n = 1.44 mmol)

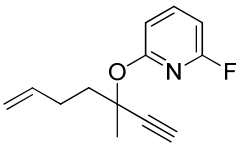
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.68 (q app, *J* = 8.1 Hz, 1H), 7.45-7.42 (m, 2H), 7.28-7.26 (m, 5H), 7.25-7.18 (m, 4H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.51 (dd, *J* = 2.5 Hz, *J* = 7.8 Hz, 1H), 2.96-2.90 (m, 2H), 2.41-2.25 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 162.0 (d, *J* = 239.6 Hz), 161.7 (d, *J* = 13.5 Hz), 142.8 (d, *J* = 7.9 Hz), 141.2, 132.0 (2C), 128.6, 128.5 (2C), 128.5 (2C), 128.3 (2C), 126.1, 122.5, 107.5 (d, *J* = 5.1 Hz), 100.7 (d, *J* = 35.2 Hz), 87.1, 85.7, 65.9, 36.8, 31.5.

**HRMS:** $C_{22}H_{18}FNO$ [$M^+$]; calculated: 331.1372, found 331.1386.

**IR ($CCl_4$):** ν ($cm^{-1}$) 2942, 1656, 1570, 1536, 1480, 1242, 1160.

**2-fluoro-6-[(3-methylhept-6-en-1-yn-3-yl)oxy]pyridine (2.100)** $C_{13}H_{14}FNO$ **MW = 219.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 47 % (m = 306 mg, n = 1.4 mmol)

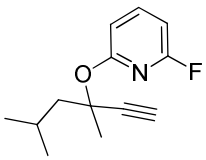
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.64 (q app, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 1.5 Hz, *J* = 8.1 Hz, 1H), 6.49 (dd, *J* = 2.7 Hz, *J* = 7.8 Hz, 1H), 5.86 (tdd, *J* = 6.4 Hz, *J* = 10.2 Hz, *J* = 16.8 Hz, 1H), 5.07 (dd, *J* = 1.7 Hz, *J* = 17.1 Hz, 1H), 4.98 (dd, *J* = 1.4 Hz, *J* = 10.2 Hz, 1H), 2.56 (s, 1H), 2.43-2.26 (m, 2H), 2.19 (ddd, *J* = 5.3 Hz, *J* = 11.0 Hz, *J* = 13.4 Hz, 1H), 2.04 (ddd, *J* = 5.1 Hz, *J* = 11.6 Hz, *J* = 13.5 Hz, 1H), 1.83 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 161.6 (d, *J* = 238.4 Hz), 161.4 (d, *J* = 14.3 Hz), 142.4 (d, *J* = 7.9 Hz), 137.9, 114.8, 108.8 (d, *J* = 5.2 Hz), 101.1 (d, *J* = 35.7 Hz), 84.2, 75.7, 74.3, 41.5, 28.6, 27.0.

**HRMS:** $C_{13}H_{14}FNO$ [$M^+$]; calculated: 219.1059, found 219.1056.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3309, 2942, 1650, 1570, 1536, 1480, 1159, 1012.

**2-[(3,5-dimethylhex-1-yn-3-yl)oxy]-6-fluoropyridine (2.104)** $C_{13}H_{16}FNO$ **MW = 221.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 43 % (m = 287 mg, n = 1.29 mmol)

**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.63 (q app, *J* = 8.1 Hz, 1H), 6.65 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 6.48 (dd, *J* = 2.8 Hz, *J* = 7.8 Hz, 1H), 2.55 (s, 1H), 2.11-1.99 (m, 2H), 1.88 (dd, *J* = 5.3 Hz, *J* = 13.8 Hz, 1H), 1.83 (s, 3H), 1.01 (dd, *J* = 6.5 Hz, *J* = 14.9 Hz, 6H).

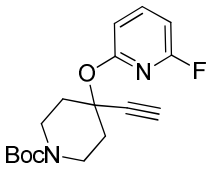
**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 161.5 (d, *J* = 238.1 Hz), 161.4 (d, *J* = 14.4 Hz), 142.2 (d, *J* = 7.9 Hz), 108.9 (d, *J* = 5.2 Hz), 100.8 (d, *J* = 25.8 Hz), 84.7, 76.2, 74.4, 50.4, 27.7, 25.0, 24.2, 24.0.

**HRMS:** $C_{13}H_{16}FNO$ [$M^+$]; calculated: 221.1216, found 221.1224. .

**IR** ($CCl_4$): ν ($cm^{-1}$) 3311, 2958, 2872, 1611, 1575, 1440, 1328, 1232, 1140, 1047, 1015.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3312, 2958, 2880, 1615, 1577, 1440, 1372, 1325, 1231, 1161, 1107, 1020.

**tert-butyl 4-ethynyl-4-[(6-fluoropyridin-2-yl)oxy]piperidine-1-carboxylate (2.106)** $C_{17}H_{21}FN_2O_3$ **MW = 320.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** white solid

**Yield:** 48 % (m = 464 mg, n = 1.45 mmol)

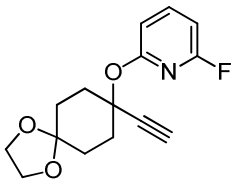
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.66 (q app, *J* = 8.1 Hz, 1H), 6.66 (dd, *J* = 1.3 Hz, *J* = 8.0 Hz, 1H), 6.51 (dd, *J* = 2.6 Hz, *J* = 8.0 Hz, 1H), 3.78-3.70 (m, 2H), 3.42 (ddd, *J* = 3.4 Hz, *J* = 9.0 Hz, *J* = 13.7 Hz, 2H), 2.62 (s, 1H), 2.36-2.31 (m, 2H), 2.13 (ddd, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 13.1 Hz, 2H), 1.46 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 161.2 (d, *J* = 240.0 Hz), 161.0 (d, *J* = 14.8 Hz), 154.7, 142.6 (d, *J* = 7.9 Hz), 108.9 (d, *J* = 5.2 Hz), 101.5, 101.2, 82.7, 79.8, 76.1 (2C), 74.3, 37.1 (2C), 28.5 (3C).

**HRMS:** $C_{17}H_{21}FN_2O_3$ [$M^+$]; calculated: 320.1536, found 320.1527.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3331, 2978, 2935, 1698, 1610, 1578, 1451, 1422, 326, 1246, 1231, 1176, 1149, 1038.

**2-({8-ethynyl-1,4-dioxaspiro[4.5]decan-8-yl}oxy)-6-fluoropyridine (2.108)** $C_{15}H_{16}FNO_3$ **MW = 277.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

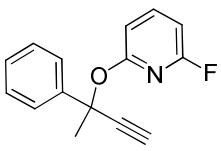
**Yield:** 69 % (m = 576 mg, n = 2.08 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.64 (q app, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 1.4 Hz, *J* = 8.0 Hz, 1H), 6.49 (dd, *J* = 2.7 Hz, *J* = 7.9 Hz, 1H), 3.95 (s, 4H), 2.58 (s, 1H), 2.40-2.34 (m, 4H), 1.82 (t, *J* = 6.3 Hz, 4H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 161.5 (d, *J* = 238.5 Hz), 161.3 (d, *J* = 24.3 Hz), 142.4 (d, *J* = 7.9 Hz), 108.9, 108.8, 107.7, 101.0 (d, *J* = 25.6 Hz), 83.5, 74.8 (d, *J* = 38.9 Hz), 64.5, 64.4, 35.0 (2C), 31.0 (2C).

**HRMS:** $C_{15}H_{16}FNO_3$ [$M^+$]; calculated: 277.1114, found: 277.1107.

**2-fluoro-6-[(2-phenylbut-3-yn-2-yl)oxy]pyridine (2.114)** C15H12FNO **MW = 241.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 35 % (m = 253 mg, n = 1.05 mmol)

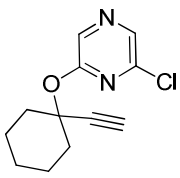
**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.65-7.62 (m, 2H), 7.52 (dd, *J* = 7.8 Hz, *J* = 8.1 Hz, 1H), 7.36-7.28 (m, 3H), 6.56 (dd, *J* = 1.7 Hz, *J* = 8.1 Hz, 1H), 6.42 (dd, *J* = 2.8 Hz, *J* = 7.8 Hz, 1H), 2.80 (s, 1H), 2.03 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 161.6 (d, *J* = 239.0 Hz), 160.6 (d, *J* = 14.6 Hz), 142.3 (d, *J* = 7.9 Hz), 142.1, 128.5 (2C), 128.0, 125.3 (2C), 108.0 (d, *J* = 5.0 Hz), 101.4 (d, 32.5 Hz), 83.0, 76.8, 76.7, 34.3.

**HRMS:** $C_{13}H_{12}FNO$ [$M^+$]; calculated: 241.6903, found 241.6910.

**IR ($CCl_4$):** ν($cm^{-1}$) 3308, 2941, 2860, 1637, 1478, 1084, 1012.

**2-[(1-ethynylcyclohexyl)oxy]-6-fluoropyrazine (2.119)** $C_{12}H_{13}ClN_2O$ **MW = 220.2 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1 replacing 2,6-difluoropyridine by 2,6-dichloropyrimidine

**Product:** colorless oil

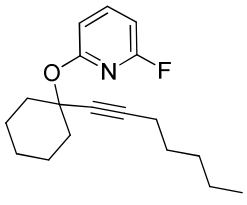
**Yield:** 12 % (m = 79 mg, n = 0.36 mmol)

**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 8.11 (dd, *J* = 0.9 Hz, *J* = 6.9 Hz, 2H), 2.60 (s, 1H), 2.32-2.24 (m, 2H), 2.04-1.95 (m, 2H), 1.72-1.48 (m, 5H), 1.40-1.30 (m, 1H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 157.8, 144.8, 135.8, 133.9, 83.0, 77.8, 76.0, 34.4 (2C), 25.1 (2C), 22.6.

**HRMS:** $C_{12}H_{13}ClN_2O$ [$M^+$]; calculated: 236.0716, found 236.0726.

**2-fluoro-6-{[1-(hept-1-yn-1-yl)cyclohexyl]oxy}pyridine (2.122)** $C_{18}H_{24}FNO$ **MW = 289.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 47 % (m = 407 mg, n = 1.41 mmol)

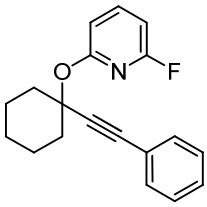
**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.62 (dd, 7.8 Hz, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 1.5 Hz, *J* = 8.0 Hz, 1H), 6.47 (dd, *J* = 2.8 Hz, *J* = 7.8 Hz, 1H), 2.26-2.18 (m, 4H), 1.99-1.92 (m, 2H), 1.72-1.51 (m, 4H), 1.49-1.42 (m, 2H), 1.39-1.20 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 161.7 (d, *J* = 237.7 Hz), 161.6 (d, *J* = 14.1 Hz), 142.0 (d, *J* = 8.0 Hz), 108.9 (d, *J* = 5.2 Hz), 100.7 (d, *J* = 36.1 Hz), 88.2, 80.5, 77.3, 38.1 (2C), 30.9, 28.3, 25.3, 22.9 (2C), 22.2, 18.8, 14.0.

**HRMS:** $C_{18}H_{24}FNO$ [$M^+$]; calculated: 289.1842, found 289.1847.

**IR ($CCl_4$):** ν ($cm^{-1}$) 2937, 2861, 1614, 1574, 1439, 1329, 1230, 1017.

**2-fluoro-6-{[1-(2-phenylethynyl)cyclohexyl]oxy}pyridine (2.124)** $C_{19}H_{18}FNO$ **MW = 295.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1

**Product:** colorless oil

**Yield:** 61 % (m = 540 mg, n = 1.83 mmol)

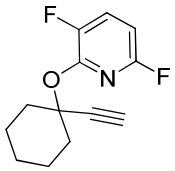
**$^1$H NMR** (400MHz, $CDCl_3$): δ (ppm) 7.65 (q app, *J* = 8.1 Hz, 1H), 7.42-7.40 (m, 2H), 7.31-7.28 (m, 3H), 6.79 (dd, *J* = 1.7 Hz, *J* = 7.9 Hz, 1H), 6.50 (dd, *J* = 2.8 Hz, *J* = 7.9 Hz, 1H), 2.41-2.37 (m, 2H), 2.11-2.04 (m, 2H), 1.81-1.56 (m, 5H), 1.46-1.36 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 161.6 (d, $^1J_{CF}$ = 237.9 Hz), 161.5 (d, $^2J_{CF}$ = 14.5 Hz), 160.5, 142.2 (d, $^3J_{CF}$ = 7.9 Hz), 131.7 (2C), 128.3 (2C), 128.2, 123.0, 108.9 (d, $^3J_{CF}$ = 5.2 Hz), 101.0, 100.7, 89.7, 87.3, 37.9 (2C), 25.3, 22.9.

**HRMS:** $C_{19}H_{18}FNO$ [$M^+$]; calculated: 295.1372, found 295.1358.

**IR ($CCl_4$):** ν ($cm^{-1}$) 3064, 2938, 2861, 1946, 1611, 1575, 1490, 1452, 1327, 1230, 1139.

**2-[(1-ethynylcyclohexyl)oxy]-3,6-difluoropyridine (2.165)** $C_{13}H_{13}F_2NO$ **MW = 237.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.1 replacing 2,6-difluoropyridine by 2,3,5-trifluoropyridine

**Product:** colorless oil

**Yield:** 40 % (m = 284 mg, n = 1.20 mmol)

**$^1$H NMR (400 MHz, $CDCl_3$):** *δ* (ppm) 7.41 (dt, *J* = 6.4 Hz, *J* = 8.7 Hz, 1H), 6.44 (ddd, *J* = 2.1 Hz, *J* = 3.5 Hz, *J* = 8.4 Hz, 1H), 2.60 (s, 1H), 2.37-2.29 (m, 2H), 2.10-2.05 (m, 2H), 1.76-1.61 (m, 4H), 1.59-1.51 (m, 1H), 1.43-1.34 (m, 1H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** *δ* (ppm) 155.5 (dd, *J* = 2.1 Hz, *J* = 237.4 Hz), 149.2 (dd, *J* = 13.1 Hz, *J* = 15.3 Hz), 145.5 (dd, *J* = 6.4 Hz, *J* = 251.2 Hz), 127.4 (dd, *J* = 9.0 Hz, *J* = 19.4 Hz), 100.6 (dd, *J* = 3.1 Hz, *J* = 40.3 Hz), 83.6, 77.9, 75.4, 37.7, 25.1, 22.6.

**HRMS:** $C_{13}H_{13}F_2NO$ [$M^+$]; calculated: 237.0965, found 237.0965.

**IR ($CCl_4$):** ν($cm^{-1}$) 3311, 2940, 2863, 1619, 1468, 1431, 1336, 1238, 1191, 1091, 1022.

# *3. Catalysis and preparation of the products*

- *Preparation of the aldehydes via gold catalysis*

**2-cyclohexylidene-2-(6-fluoro-2-oxo-1,2-dihydropyridin-1-yl)acetaldehyde (2.55)** $C_{13}H_{14}FNO_2$ **MW = 235.3 g.mol$^{-1}$**

**Procedure:** see general procedure 2.5

**Product:** colorless oil (product unstable that degrades rapidly when exposed to light or heat)

**Yield:** 47 % (m = 11.1 mg, n = 0.472 mmol)

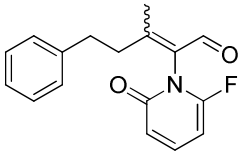
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 10.07 (s, 1H), 7.40 (ddd, *J* = 7.6 Hz, *J* = 9.0 Hz, *J* = 9.1 Hz, 1H), 6.40 (dd, *J* = 0.8 Hz, *J* = 9.3 Hz, 1H), 5.87 (ddd, *J* = 0.9 Hz, *J* = 4.4 Hz, *J* = 7.5 Hz, 1H), 3.00 (ddd, *J* = 4.3 Hz, *J* = 7.5 Hz, *J* = 13.6 Hz, 1H), 2.89 ( ddd, *J* = 4.3 Hz, *J* = 8.7 Hz, *J* = 13.8 Hz, 1H), 2.20-2.17 (m, 2H), 2.02-1.93 (m, 1H), 1.87-1.71 (m, 2H), 1.70-1.60 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 182.6, 166.5, 160.9 (d, *J* = 6.7 Hz), 155.2 (d, *J* = 267.4 Hz), 140.9 (d, *J* = 11.9 Hz), 126.6, 116.0 (d, *J* = 4.7 Hz), 86.9 (d, *J* = 20.8 Hz), 32.5, 29.6, 28.2, 27.5, 25.9.

**HRMS:** $C_{13}H_{14}FNO_2$ [$M^+$]; calculated: 235.1009, found 235.1009.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2949, 2923, 1690, 1617, 1533, 1435, 1380, 1138, 1059, 1030.

***(2Z)*-2-(6-fluoro-2-oxo-1,2-dihydropyridin-1-yl)-3-methyl-5-phenylpent-2-enal and *(2E)*-2-(6-fluoro-2-oxo-1,2-dihydropyridin-1-yl)-3-methyl-5-phenylpent-2-enal (2.61)** $C_{17}H_{16}FNO_2$ **MW = 285.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.5

**Product:** colorless oil (product unstable that degrades rapidly when exposed to light or heat)

**Yield:** 84 % (*Z*/*E* 1 : 1.4) (m = 24.0 mg, n = 0.0842 mmol)

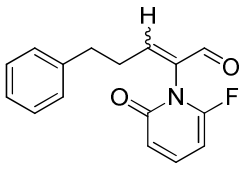
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 10.05 (s, 1H *E* isomer), 9.62 (s, 1H *Z* isomer), 7.41 (dd, *J* = 7.8 Hz, *J* = 9.2 Hz, *J* = 9.3 Hz, 1H both isomers), 7.33-7.28 (m, 3H), 7.26-7.20 (m, 7H), 7.10-7.08 (m, 2H), 6.44 (d, *J* = 9.4 Hz, 1H *Z* isomer), 6.41 (d, *J* = 9.3 Hz, 1H *E* isomer), 5.87 (d, *J* = 7.4 Hz, 1H *Z* isomer), 5.85 (d, *J* = 7.5 Hz, 1H *E* isomer), 3.26-3.19 (m, 1H *E* isomer), 3.09-2.71 (m, 7H), 2.46 (s, 3H *E* isomer), 1.90 (s, 3H *Z* isomer).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) *E* isomer: 182.7, 161.5, 160.5, 154.9, 141.0 (d, *J* = 11.8 Hz), 139.3, 130.3, 128.8 (2C), 128.6 (2C), 126.9, 116.1 (d, *J* = 1.6 Hz), 87.0 (d, *J* = 20.7 Hz), 35.0, 20.9. *Z* isomer: 183.6, 161.8, 160.6, 155.1 (d, *J* = 268.1 Hz), 141.1 (d, *J* = 11.9 Hz), 140.2, 129.3, 128.7 (2C), 128.2 (2C), 126.6, 116.1 (d, *J* = 1.8 Hz), 87.1 (d, *J* = 20.9 Hz), 38.2, 34.9, 32.9, 17.6.

**HRMS:** $C_{17}H_{16}FNO_2$ [$M^+$]; calculated: 285.1165, found 285.1158.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2928, 1693, 1619, 1536, 1533, 1433, 1292, 1263, 1137, 1032, 1013.

**2-(6-fluoro-2-oxo-1,2-dihydropyridin-1-yl)-5-phenylpent-2-enal (2.63)** $C_{16}H_{14}FNO_2$ **MW = 271.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.5

**Product:** colorless oil (product unstable that degrades rapidly when exposed to light or heat)

**Yield:** 40 % (m = 10.8 mg, n = 0.039 mmol)

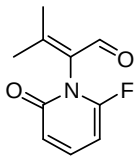
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 9.49 (s, 1H), 7.42 (ddd, *J* = 7.6 Hz, *J* = 9.0 Hz, *J* = 9.1 Hz, 1H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.19-7.17(m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.43 (dd, *J* = 0.8 Hz, *J* = 9.3 Hz, 1H), 5.88 (ddd, *J* = 0.8 Hz, *J* = 4.5 Hz, *J* = 7.5 Hz, 1H), 2.94-2.79 (m, 2H), 2.67 (dt, *J* = 6.9 Hz, *J* = 15.0 Hz, 1H), 2.54 (dt, *J* = 7.8 Hz, *J* = 15.5 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 186.3, 154.5, 141.2 (d, *J* = 11.6 Hz), 139.7, 141.2 (d, *J* = 11.6 Hz), 139.7, 134.5 (2C), 128.8, 128.4 (2C), 126.7, 116.1 (d, *J* = 4.7 Hz), 87.1 (d, *J* = 19.9 Hz), 33.4, 30.5.

**HRMS:** $C_{16}H_{14}FNO_2$ [$M^+$]; calculated: 271.1009, found 271.1008.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 3030, 1702, 1621, 1533, 1434, 1264, 1137

**2-(6-fluoro-2-oxo-1,2-dihydropyridin-1-yl)-3-methylbut-2-enal (2.65)** $C_{10}H_{10}FNO_2$ **MW = 195.2 g.mol$^{-1}$**



**Procedure:** see general procedure 2.5

**Product:** colorless oil (product unstable that degrades rapidly when exposed to light or heat)

**Yield:** 64 % (m = 12.5 mg, n = 0.0640 mmol)

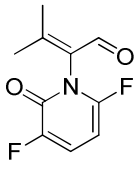
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 10.04 (s, 1H), 7.41 (ddd, *J* = 7.6 Hz, *J* = 8.9 Hz, *J* = 9.1 Hz, 1H), 6.42 (dd, *J* = 0.8 Hz, *J* = 9.1 Hz, 1H), 5.88 (ddd, *J* = 0.8 Hz, *J* = 4.4 Hz, *J* = 7.5 Hz, 1H), 2.46 (s, 3H), 1.90 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 183.1, 160.7, 159.6, 154.9 (d, *J* = 266.3 Hz), 141.0 (d, *J* = 11.6 Hz), 129.4, 116.1 (d, *J* = 4.6 Hz), 87.0 (d, *J* = 20.5 Hz), 22.7, 19.4.

**HRMS:** $C_{10}H_{10}FNO_2$ [$M^+$]; calculated: 195.0696, found 195.0698.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2959, 2927, 1693, 1620, 1536, 1433, 1373, 1294, 1263, 1138, 1070, 1032, 1015.

**2-(3,6-difluoro-2-oxo-1,2-dihydropyridin-1-yl)-3-methylbut-2-enal (2.67)** $C_{10}H_9F_2NO_2$ **MW = 213.2 g.mol$^{-1}$**



**Procedure:** see general procedure 2.5

**Product:** colorless oil (product unstable that degrades rapidly when exposed to light or heat)

**Yield:** 75 % (15.9 mg, n = 0.0749 mmol)

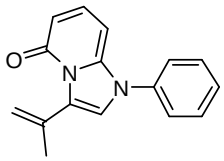
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 10.02 (s, 1H), 7.17 (ddd, *J* = 7.0 Hz, *J* = 8.7 Hz, *J* = 9.0 Hz, 1H), 5.78 (ddd, *J* = 3.4 Hz, *J* = 7.4 Hz, *J* = 8.2 Hz, 1H), 2.46 (s, 3H), 1.90 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 182.7, 160.5, 153.7 (dd, *J* = 4.6 Hz, *J* = 27.0 Hz), 150.6 (dd, *J* = 3.3 Hz, *J* = 264.0 Hz), 149.3 (dd, *J* = 5.4 Hz, *J* = 245.6 Hz), 129.0, 121.0 (dd, *J* = 11.1 Hz, *J* = 19.3 Hz), 84.2 (dd, *J* = 5.7 Hz, *J* = 23.7 Hz), 22.7, 19.5.

**HRMS:** $C_{10}H_9F_2NO_2$ [$M^+$]; calculated: 213.0601, found 213.0598.

**IR** ($CCl_4$): ν ($cm^{-1}$) 1707, 1692, 1641, 1571, 1554, 1427, 1371, 1297, 1256, 1239.

**1-phenyl-3-(prop-1-en-2-yl)-1H,5H-imidazo[1,2-a]pyridin-5-one (2.74)** $C_{16}H_{14}N_2O$ **MW = 250.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.6

**Product:** pale yellow oil

**Yield:** 35 %

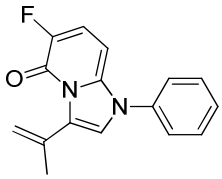
**$^1$H NMR (400 MHz, $CDCl_3$):** *δ* (ppm) 7.57-7.54 (m, 2H), 7.48-7.44 (m, 3H), 7.35 (t, *J* = 8.3 Hz, 1H), 6.90 (s, 1H), 6.12 (d, *J* = 7.5 Hz, 1H), 6.03 (d, *J* = 8.6 Hz, 1H), 5.25-5.23 (m, 1H), 5.20-5.19 (m, 1H), 2.31 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** *δ* (ppm) 158.7, 142.9, 137.7, 136.5, 135.6, 130.2 (2C), 129.3, 128.5, 124.6 (2C), 117.8, 117.5, 102.8, 83.9, 25.1.

**HRMS:** $C_{16}H_{14}N_2O$ [$M^+$]; calculated: 250.1106, found 250.1102.

**IR ($CCl_4$):** *ν* ($cm^{-1}$) 2961, 1671, 1574, 1525, 1503, 1421, 1296, 1161, 1073.

**6-fluoro-1-phenyl-3-(prop-1-en-2-yl)-1H,5H-imidazo[1,2-a]pyridin-5-one (2.75)** $C_{16}H_{13}FN_2O$ **MW = 268.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.6

**Product:** pale yellow oil

**Yield:** 36 %

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.58-7.54 (m, 2H), 7.48-7.45 (m, 3H), 7.33 (dd, *J* = 8.7 Hz, *J* = 10.7 Hz, 1H), 6.94 (s, 1H), 5.95 (dd, *J* = 2.7 Hz, *J* = 8.7 Hz, 1H), 5.28-5.26 (m, 1H), 5.22-5.21 (m, 1H), 2.32-2.31 (m, 3H).

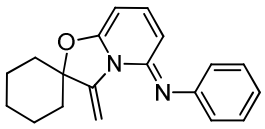
**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 143.0 (d, *J* = 226.0 Hz), 139.2, 136.3, 135.0, 130.3 (2C), 129.6 (d, *J* = 4.7 Hz), 128.6, 124.5 (2C), 124.4, 122.0 (d, *J* = 20.1 Hz), 118.5 (d, *J* = 16.6 Hz), 79.6 (d, *J* = 5.9 Hz), 77.3, 25.2.

**HRMS:** $C_{16}H_{13}FN_2O$ [$M^+$]; calculated: 268.1012, found 268.1004.

**IR ($CCl_4$):** ν ($cm^{-1}$) 2961, 1926, 1683, 1596, 1545, 1501, 1433, 1206.

- *<u>Preparation of the [1,3]oxazolopyridine-5-imines via gold catalysis</u>*

**3-methylidene-*N*-phenyl-3,5-dihydrospiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane]-5-imine (2.76)** $C_{19}H_{20}N_2O$ **MW = 292.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 97 % (m = 28.3 mg, n = 0.0968 mmol)

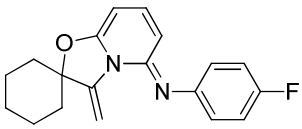
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.34 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.86 (s, 1H), 6.80 (dd, *J* = 7.6 Hz, *J* = 9.2 Hz, 1H), 5.98 (d, *J* = 9.2 Hz, 1H), 5.28 (d, *J* = 7.6 Hz, 1H), 4.78 (s, 1H), 2.11-2.03 (m, 2H), 1.88-1.59 (m, 8H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ (ppm) 156.0, 152.4, 150.7, 146.7, 136.3, 129.2 (2C), 122.1 (2C), 121.8, 105.2, 95.5, 87.5, 79.5, 37.3 (2C), 24.8, 21.8 (2C).

**HRMS:** $C_{19}H_{20}N_2O$ [$M^+$]; calculated: 292.1576, found: 292.1574.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3029, 2940, 2857, 1656, 1573, 1538.

***N*-(4-fluorophenyl)-3-methylidene-3,5-dihydrospiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane]-5-imine (2.85)** $C_{19}H_{19}FN_2O$ **MW = 310.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 79 % (m = 24.5 mg, n = 0.0790 mmol)

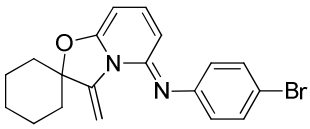
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.03-6.97 (m, 2H), 6.88-6.84 (m, 2H), 6.81 (s, 1H), 6.79 (dd, *J* = 7.1 Hz, *J* = 9.4 Hz, 1H), 5.92 (d, *J* = 9.4 Hz, 1H), 5.26 (d, *J* = 7.1 Hz, 1H), 5.75 (s, 1H), 2.03 (bd, *J* = 13.2 Hz, 2H), 1.83-1.71 (m, 5H), 1.68-1.59 (m, 2H), 1.40-1.30 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 158.5 (d, *J* = 237.7 Hz), 156.0, 153.0, 146.7, 136.6, 123.0 (2C), 122.9, 115.7 (d, *J* = 1.9 Hz, 2C), 104.9, 95.6, 87.6, 79.6, 37.3 (2C), 24.8, 21.8 (2C).

**HRMS:** $C_{19}H_{19}FN_2O$ [$M^+$]; calculated: 310.1481, found: 310.1478.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3032, 2945, 2856, 1650, 1573, 1535, 1241, 1153.

***N*-(4-bromophenyl)-3-methylidene-3,5-dihydrospiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane]-5-imine (2.86)** $C_{19}H_{19}BrN_2O$ **MW = 371.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 84 % (m = 31.1 mg, n = 0.084 mmol)

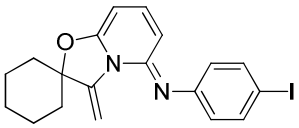
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.41-7.37 (m, 2H), 6.83-6.78 (m, 4H), 5.93 (dd, *J* = 0.8 Hz, *J* = 9.4 Hz, 1H), 5.29 (dd, *J* = 0.8 Hz, *J* = 7.2 Hz, 1H), 4.76 (d, *J* = 0.8 Hz, 1H), 2.03 (m, 2H), 1.83-1.59 (m, 7H), 1.40-1.29 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.0, 152.5, 149.7, 146.6, 136.9, 132.1 (2C), 123.9 (2C), 114.3, 104.8, 95.8, 87.7, 80.0, 37.3 (2C), 24.7, 21.8 (2C).

**HRMS:** $C_{19}H_{19}BrN_2O$ [$M^+$]; calculated: 370.0681, found: 370.0683.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2939, 1656, 1567, 1537, 1480, 1242, 1165.

**_N_-(4-iodophenyl)-3-methylidene-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane]-5-imine (2.87)** $C_{19}H_{19}IN_3O$ **MW = 418.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 95 % (m = 39.7 mg, n = 0.0949 mmol)

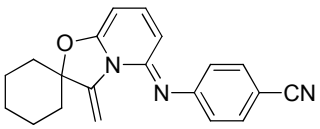
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.59-7.56 (m, 2H), 6.81 (dd, *J* = 7.1 Hz, *J* = 9.4 Hz, 1H), 6.77 (d, *J* = 0.9 Hz, 1H), 6.72-6.68 (m, 2H), 5.93 (dd, *J* = 0.9 Hz, *J* = 9.4 Hz, 1H), 5.29 (dd, *J* = 0.9 Hz, *J* = 7.1 Hz, 1H), 4.75 (d, *J* = 0.9 Hz, 1H), 2.04-2.01 (m, 2H), 1.83-1.58 (m, 7H), 1.37-1.25 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ 156.0, 152.4, 150.5, 146.6, 138.1 (2C), 136.9, 124.5 (2C), 104.8, 95.9, 87.7, 84.6, 80.0, 37.3 (2C), 24.7, 21.8 (2C).

**HRMS:** $C_{19}H_{19}IN_3O$ [$M^+$]; calculated: 418.0542, found: 418.0539.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2941, 2857, 1655, 1567, 1535, 1477, 1242, 1166, 1119.

**4-({3-methylidene-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane]-5-ylidene}amino)benzonitrile (2.88)** $C_{20}H_{19}N_3O$ **MW = 317.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 55 % (m = 16.1 mg, n = 0.0552 mmol)

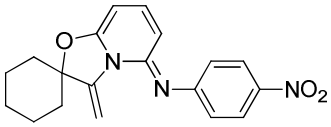
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.90 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 6.74 (s, 1H), 5.94 (d, *J* = 9.3 Hz, 1H), 5.39 (d, *J* = 7.3 Hz, 1H), 4.80 (s, 1H), 2.04 (bd, *J* = 13.2 Hz, 2H), 1.84-1.60 (m, 7H), 1.40-1.29 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ 156.1, 155.2, 152.1, 146.5, 138.0, 133.5 (2C), 122.8 (2C), 120.1, 104.3, 104.2, 96.7, 88.0, 81.2, 37.3 (2C), 24.7, 21.8 (2C).

**HRMS:** $C_{20}H_{19}N_3O$ [$M^+$]; calculated: 292.1576, found: 292.1577.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2941, 2225, 1656, 1566, 1534, 1497, 1246, 1166

**3-methylidene-*N*-(4-nitrophenyl)-3,5-dihydrospiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane]-5-imine (2.89)** $C_{19}H_{19}N_3O_3$ **MW = 337.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 45 % (m = 15.2 mg, n = 0.0449 mmol, 85% conversion)

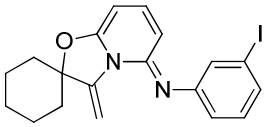
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.19-8.15 (m, 2H), 7.01-6.97 (m, 2H), 6.95 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 6.74 (d, *J* = 1.3 Hz, 1H), 6.01 (dd, *J* = 0.9 Hz, *J* = 9.3 Hz, 1H), 5.42 (dd, *J* = 0.8 Hz, *J* = 7.3 Hz, 1H), 4.82 (d, *J* = 1.2 Hz, 1H), 2.06-2.00 (m, 2H), 1.85-1.60 (m, 7H), 1.40-1.27 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 157.5, 156.2, 152.1, 146.5, 142.0, 138.5, 125.5 (2C), 122.1 (2C), 104.3, 97.1, 88.1, 81.9, 37.3 (2C), 24.7, 21.8 (2C).

**HRMS:** $C_{19}H_{19}N_3O_3$ [$M^+$]; calculated: 337.1426, found 337.1427.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2941, 1782, 1656, 1531, 1486, 1337, 1245, 1166, 1119.

***N*-(3-iodophenyl)-3-methylidene-3,5-dihydrospiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane]-5-imine (2.90)** $C_{19}H_{19}IN_2O$ **MW = 418.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 84 % (m = 35.1 mg, n = 0.0840 mmol)

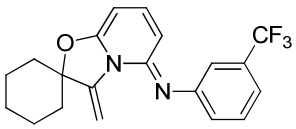
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.32-7.30 (m, 2H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.89 (ddd, *J* = 1.0 Hz, *J* = 1.7 Hz, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 7.1 Hz, 9.4 Hz, 1H), 6.76 (d, *J* = 1.0 Hz, 1H), 5.94 (dd, *J* = 0.7 Hz, *J* = 9.4 Hz, 1H), 5.30 (dd, *J* = 0.7 Hz, *J* = 7.1 Hz, 1H), 4.76 (d, *J* = 0.9 Hz, 1H), 2.03 (bd, *J* = 13.1 Hz, 2H), 1.83-1.58 (m, 7H), 1.40-1.29 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.0, 152.5, 152.2, 146.6, 137.1, 131.0, 130.7, 130.6, 121.6, 104.8, 96.0, 94.8, 87.7, 80.2, 37.3 (2C), 24.7, 21.8 (2C).

**HRMS:** $C_{19}H_{19}IN_2O$ [$M^+$]; calculated: 418.0542; found: 418.0539.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3025, 2942, 2850, 1656, 1563, 1538, 1240.

**_N_-(3-trifluoromethylphenyl)-3-methylidene-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane]-5-imine (2.91)** $C_{20}H_{19}F_3N_2O$ **MW = 360.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 75 % (m = 27.0 mg, n = 0.075 mmol)

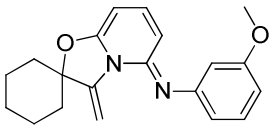
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.40 (t, *J* = 7.8 Hz, 1H); 7.23 (d, *J* = 7.9 Hz, 1H), 7.19 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 7.2 Hz, *J* = 9.4 Hz, 1H), 6.80 (s, 1H), 5.91 (d, *J* = 9.4 Hz, 1H), 5.33 (d, *J* = 7.2 Hz, 1H), 4.78 (s, 1H), 2.04 (bd, *J* = 13.2 Hz, 2H), 1.84-1.72 (m, 5H), 1.70-1.60 (m, 2H), 1.40-1.29 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 155.0, 151.7, 150.1, 145.5, 136.2, 130.5 (q, *J* = 31.5 Hz), 128.6, 124.7, 123.2 (q, *J* = 244.1 Hz), 117.9 (q, *J* = 3.7 Hz), 117.3 (q, *J* = 3.9 Hz), 103.5, 95.0, 86.7, 79.3, 36.2 (2C), 23.7, 20.8 (2C).

**HRMS:** $C_{20}H_{19}F_3N_2O$ [$M^+$]; calculated: 360.1449; found: 360.1431.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2941, 1656, 1572, 1537, 1326, 1168, 1130.

**N-(3-methoxyphenyl)-3-methylidene-3,5-dihydrospiro[[1,3]oxazolo[3,2-a]pyridine-2,1'-cyclohexane]-5-imine (2.92)** $C_{20}H_{22}N_2O_2$ **MW = 322.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 74 % (m = 23.8 mg, n = 0.0738 mmol)

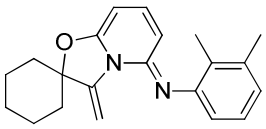
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.21 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 0.7 Hz, 1H), 6.78 (dd, *J* = 7.2 Hz, *J* = 9.4 Hz, 1H), 6.57 (ddd, *J* = 0.6 Hz, *J* = 2.4 Hz, *J* = 8.3 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.50 (t, *J* = 2.4 Hz, 1H), 5.98 (dd, *J* = 0.7 Hz, *J* = 9.4 Hz, 1H), 5.26 (dd, *J* = 0.7 Hz, *J* = 7.2 Hz, 1H), 4.75 (s, 1H), 3.80 (s, 3H), 2.04 (bd, *J* = 13.2 Hz, 2H), 1.83-1.69 (m, 5H), 1.70-1.59 (m, 2H), 1.40-1.30 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 160.7, 156.0, 152.4, 152.1, 146.6, 136.4, 129.9, 114.5, 107.9, 107.4, 105.3, 95.6, 87.6, 79.6, 55.2, 37.3 (2C), 24.8, 21.8 (2C).

**HRMS:** $C_{20}H_{22}N_2O_2$ [$M^+$]; calculated: 322.1681; found: 322.1683.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2940, 1656, 1574, 1537, 1478, 1156.

**_N_-(2,3-dimethylphenyl)-3-methylidene-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane]-5-imine (2.93)** $C_{21}H_{24}N_2O$ **MW = 320.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 80 % (m = 25.6 mg, n = 0.0799 mmol)

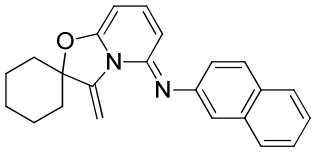
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.04 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 0.7 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.72 (dd, *J* = 7.1 Hz, *J* = 9.5 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.74 (dd, *J* = 0.9 Hz, *J* = 9.5 Hz, 1H), 5.21 (dd, *J* = 0.9 Hz, *J* = 7.1 Hz, 1H), 4.73 (d, *J* = 0.7 Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H), 2.06 (bd, *J* = 13.0 Hz, 2H), 1.84-1.72 (m, 5H), 1.71-1.59 (m, 2H), 1.41-1.32 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.0, 151.4, 149.0, 146.7, 137.5, 135.8, 128.3, 125.8, 123.7, 119.0, 105.5, 95.1, 87.5, 78.9, 37.3 (2C), 24.8, 21.9 (2C), 20.6, 13.8.

**HRMS:** $C_{21}H_{24}N_2O$ [$M^+$]; calculated: 320.1889; found: 320.1888.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2941, 1656, 1531, 1337, 1245, 1166.

**3-methylidene-_N_-(naphthalen-2-yl)-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane]-5-imine (2.95)** $C_{23}H_{22}N_2O$ **MW = 342.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 81 % (m = 27.8 mg, n = 0.0812 mmol)

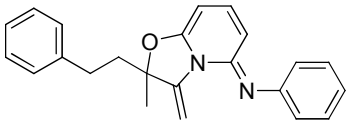
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.79 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.40 (ddd, *J* = 1.1 Hz, *J* = 6.9 Hz, *J* = 8.1 Hz, 1H), 7.34-7.30 (m, 2H), 7.16 (dd, *J* = 2.0 Hz, *J* = 8.6 Hz, 1H), 6.89 (s, 1H), 6.79 (dd, *J* = 7.2 Hz, *J* = 9.4 Hz, 1H), 6.00 (dd, *J* = 0.5 Hz, *J* = 9.4 Hz, 1H), 5.28 (d, *J* = 7.2 Hz, 1H), 4.78 (s, 1H), 2.07-2.04 (m, 2H), 1.84-1.57 (m, 7H), 1.40-1.30 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) 156.1, 152.7, 148.4, 146.7, 136.6, 134.9, 129.9, 128.9, 127.6, 126.9, 125.8, 123.9, 123.6, 117.4, 105.3, 95.7, 87.7, 79.8, 37.3 (2C), 24.8, 21.9 (2C).

**HRMS:** $C_{23}H_{22}N_2O$[$M^+$]; calculated: 342.1730; found: 342.1732.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2930, 2856, 1656, 1575, 1538, 1503, 1450, 1437, 1330, 1165, 1029.

**2-methyl-3-methylidene-*N*-phenyl-2-(2-phenylethyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.97)** $C_{23}H_{22}N_2O$ **MW = 342.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** pale yellow oil

**Yield:** 82 % (28.1 mg, n = 0.0822 mmol)

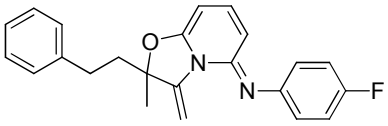
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.35-7.29 (m, 4H), 7.23-7.19 (m, 3H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 0.58 Hz, 1H), 6.79 (dd, *J* = 7.1 Hz, *J* = 9.4 Hz, 1H), 5.99 (d, *J* = 9.5 Hz, 1H), 5.26(d, *J* = 7.1 Hz, 1H), 4.81 (s, 1H), 2.80-2.68 (m, 2H), 2.23 (ddd, *J* = 6.2 Hz, *J* = 11.0 Hz, *J* = 14.4 Hz, 1H), 2.10 (ddd, *J* = 6.2 Hz, *J* = 10.8 Hz, *J* = 14.3 Hz, 1H), 1.65 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.1, 152.1, 150.4, 144.9, 141.0, 136.3, 129.3 (2C), 128.6 (2C), 128.4 (2C), 126.1, 122.1 (2C), 122.0, 105.4, 95.8, 88.2, 79.2, 43.3, 29.7, 27.5.

**HRMS:** $C_{23}H_{22}N_2O$ [$M^+$]; calculated: 342.1732, found 342.1724.

**IR** ($CCl_4$): $\nu$($cm^{-1}$) 3030, 1933, 1659, 1571, 1534, 1486, 1423, 1234, 1182, 1091, 1039.

***N*-(4-fluorophenyl)-2-methyl-3-methylidene-2-(2-phenylethyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.98)** $C_{23}H_{21}FN_2O$ **MW = 360.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** pale yellow oil

**Yield:** 81 % (m = 29.3 mg, n = 0.0814 mmol)

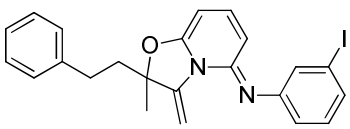
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 7.03-6.99 (m, 2H), 6.89-6.86 (m, 3H), 6.80 (dd, *J* = 7.2 Hz, *J* = 9.5 Hz, 1H), 5.95 (d, *J* = 9.5 Hz, 1H), 5.27 (d, *J* = 7.2 Hz, 1H), 4.81 (s, 1H), 2.74 (ddd, *J* = 6.0 Hz, *J* = 13.7 Hz, *J* = 17.0 Hz, 1H), 2.68 (ddd, *J* = 5.9 Hz, *J* = 13.5 Hz, *J* = 16.4 Hz, 1H), 2.23 (ddd, *J* = 6.4 Hz, *J* = 10.7 Hz, *J* = 14.3 Hz, 2H), 1.64 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.6 (d, *J* = 237.7 Hz), 156.2, 152.7, 146.6 (d, *J* = 2.6 Hz), 144.9, 141.0, 136.6, 128.4 (d, *J* = 17.1 Hz, 2C), 126.2 (2C), 123.1 (2C), 123.0, 115.8 (d, *J* = 21.9 Hz, 2C), 105.2, 95.9, 88.2, 79.3, 43.3, 29.7, 27.5.

**HRMS:** $C_{23}H_{21}FN_2O$ [$M^+$]; calculated: 360.1638, found 360.1643.

**IR** ($CCl_4$): $\nu$($cm^{-1}$) 3030, 1659, 1571, 1537, 1497, 1212, 1181, 1090, 1039.

**_N_-(3-iodophenyl)-2-methyl-3-methylidene-2-(2-phenylethyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.99)** $C_{23}H_{21}IN_2O$ **MW = 468.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** pale yellow oil

**Yield:** 55 % (m = 25.8 mg, n = 0.0552 mmol)

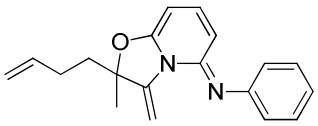
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.34-7.28 (m, 3H), 7.22-7.18 (m, 3H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.92-6.90 (m, 1H), 6.86-6.82 (m, 2H), 5.97 (d, *J* = 9.4 Hz, 1H), 5.31 (d, *J* = 7.1 Hz, 1H), 4.81 (d, *J* = 0.8 Hz, 1H), 2.76-2.65 (m, 2H), 2.23 (ddd, *J* = 6.8 Hz, *J* = 10.3 Hz, *J* = 14.3 Hz, 1H), 2.09 (ddd, *J* = 6.9 Hz, *J* = 10.0 Hz, *J* = 14.4 Hz, 2H), 1.64 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.1, 152.3, 152.1, 144.8, 140.9, 137.06, 131.0, 130.8, 130.8, 128.6 (2C), 128.4 (2C), 126.2, 121.6, 105.1, 96.3, 94.9, 88.3, 79.8, 43.3, 29.7, 27.5.

**HRMS:** $C_{23}H_{21}IN_2O$ [$M^+$]; calculated: 468.0699, found 468.0699.

**IR** ($CCl_4$)**:** *v*($cm^{-1}$) 3030, 2984, 1659, 1570, 1546, 1464, 1398, 1181, 1041.

**2-(but-3-en-1-yl)-2-methyl-3-methylidene-*N*-phenyl-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.101)** $C_{19}H_{20}N_2O$ **MW = 292.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 75 % (m = 21.8 mg, n = 0.0748 mmol)

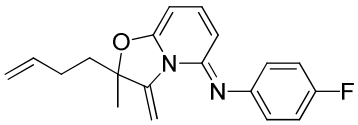
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.31 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 0.8 Hz, 1H), 6.76 (dd, *J* = 7.1 Hz, *J* = 9.5 Hz, 1H), 5.96 (d, *J* = 9.5 Hz, 1H), 5.81 (tdd, *J* = 6.5 Hz, *J* = 10.2 Hz, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 7.1 Hz, 1H), 5.04 (dd, *J* = 1.5 Hz, *J* = 17.2 Hz, 1H), 4.98 (dd, *J* = 1.5 Hz, *J* = 10.2 Hz, 1H), 4.74 (s, 1H), 2.21-2.14 (m, 2H), 1.99 (ddd, *J* = 6.3 Hz, *J* = 9.9 Hz, *J* = 14.3 Hz, 1H), 1.89 (ddd, *J* = 6.9 Hz, *J* = 9.5 Hz, *J* = 14.2 Hz, 1H), 1.61 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.1, 152.1, 150.6, 145.0, 137.3, 136.3, 129.2 (2C), 122.0 (2C), 121.9, 115.2, 105.4, 95.8, 88.1, 79.1, 40.6, 27.6, 27.4.

**HRMS:** $C_{19}H_{20}N_2O$ [$M^+$]; calculated: 292.1576, found 292.1577.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2984, 2931, 1659, 1572, 1538, 1485, 1365, 1264, 1233, 1186.

**2-(but-3-en-1-yl)-*N*-(4-fluorophenyl)-2-methyl-3-methylidene-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.102)** $C_{19}H_{19}FN_2O$ **MW = 310.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 85 % (m = 26.3 mg, n = 0.0848 mmol)

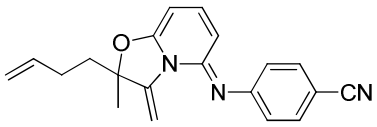
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.99 (t, *J* = 8.8 Hz, 2H), 6.86-6.83 (m, 3H), 6.78 (dd, *J* = 7.2 Hz, *J* = 9.5 Hz, 1H), 5.92 (dd, *J* = 0.8 Hz, *J* = 9.4 Hz, 1H), 5.80 (tdd, *J* = 6.5 Hz, *J* = 10.2 Hz, *J* = 16.8 Hz, 1H), 5.23 (dd; *J* = 0.9 Hz, *J* = 7.1 Hz, 1H), 5.03 (dd, *J* = 1.7 Hz, *J* = 17.2 Hz, 1H), 4.98 (dd, *J* = 1.4 Hz, *J* = 10.1 Hz, 1H), 4.74 (s, 1H), 2.19-2.13 (m, 2H), 1.98 (ddd, *J* = 6.4 Hz, *J* = 9.7 Hz, *J* = 14.6 Hz, 1H), 1.88 (ddd, *J* = 6.5 Hz, *J* = 12.5 Hz, *J* = 14.1 Hz, 1H), 1.60 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.5 (d, *J* = 237.8 Hz), 156.2, 152.6, 146.6 (d, *J* = 2.5 Hz), 145.0, 137.2, 136.5 (2C), 123.0 (d, *J* = 8.7 Hz), 115.8 (d, *J* = 21.9 Hz), 115.2 (2C), 105.1, 95.9, 88.2, 79.2, 40.6, 27.6, 27.4.

**HRMS:** $C_{19}H_{19}FN_2O$ [$M^+$]; calculated: 310.1481, found 310.1477.

**IR** ($CCl_4$): ν ($cm^{-1}$) 1658, 1570, 1542, 1497, 1212, 1186.

**4-{[2-(but-3-en-1-yl)-2-methyl-3-methylidene-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-ylidene]amino}benzonitrile (2.103)** $C_{20}H_{19}N_3O$ **MW = 317.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 84 % (m = 26.7 mg, n = 0.0843 mmol)

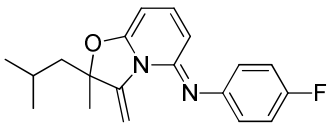
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.56 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 6.77 (d, *J* = 1.0 Hz, 1H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.79 (tdd, *J* = 6.5 Hz, *J* = 10.2 Hz, *J* = 13.4 Hz, 1H), 5.34 (d, *J* = 7.2 Hz, 1H), 5.03 (dd, *J* = 1.5 Hz, *J* = 10.2 Hz, 1H), 4.98 (dd, *J* = 1.5 Hz, *J* = 16.8 Hz, 1H), 4.79 (s, 1H), 2.17-2.12 (m, 2H), 2.04-1.96 (m, 1H), 1.92-1.84 (m, 1H), 1.61 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.3, 155.1, 151.8, 144.9, 137.9, 137.0, 133.5 (2C), 122.8 (2C), 120.1, 115.3, 104.5, 104.3, 96.9, 88.5, 80.8, 40.6, 27.6, 27.4.

**HRMS:** $C_{20}H_{19}N_3O$ [$M^+$]; calculated: 317.1528, found 317.1523.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2981, 1931, 2225, 1698, 1659, 1571, 1526, 1493, 1425, 1366, 1246, 1186, 1167, 1039.

**_N_-(4-fluorophenyl)-2-methyl-3-methylidene-2-(2-methylpropyl)-_2H,3H,5H-[1,3]_oxazolo_[3,2-a]_pyridin-5-imine (2.105)** $C_{19}H_{21}FN_2O$ **MW = 312.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 92 % (m = 28.7 mg, n = 0.0921 mmol)

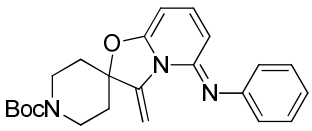
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.02-6.96 (m, 2H), 6.87-6.82 (m, 2H), 6.81 (s, 1H), 6.78 (dd, *J* = 7.2 Hz, *J* = 9.5 Hz, 1H), 5.91 (d, *J* = 9.5 Hz, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.71 (s, 1H), 1.91-1.70 (m, 3H), 1.57 (s, 3H), 0.95 (dd, *J* = 4.0 Hz, *J* = 6.4 Hz, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 158.6 (d, *J* = 237.6 Hz), 156.1, 152.7, 146.6, 145.9, 136.6, 123.0 (d, *J* = 7.7 Hz, 2C), 115.8 (d, *J* = 21.9 Hz, 2C), 104.9, 95.8, 88.9, 79.3, 49.6, 28.0, 24.2 (2C), 24.1.

**HRMS:** $C_{19}H_{21}FN_2O$ [$M^+$]; calculated: 312.1638, found: 312.1640.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2960, 1657, 1570, 1537, 1497, 1212, 1187, 1036.

***tert*-butyl 5-[phenylimino]-3-methylidene-3,5-dihydrospiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,4'-piperidine]-1'-carboxylate (2.107)** $C_{23}H_{26}FN_3O_3$ **MW = 393.5 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 39 % (m = 16.1 mg, n = 0.0393 mmol)

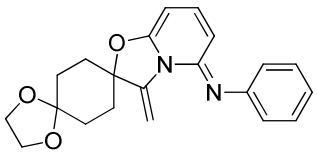
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.29 (t, *J* = 7.5 Hz, 2H), 6.99 (tt, *J* = 1.0 Hz, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 1.1 Hz, 1H), 6.76 (dd, *J* = 7.1 Hz, *J* = 9.5 Hz, 1H), 5.98 (d, *J* = 9.4 Hz, 1H), 5.26 (d, *J* = 7.1 Hz, 1H), 4.75 (s, 1H), 4.22-4.08 (m, 2H), 3.19-3.06 (m, 2H), 1.97 (d, *J* = 13.4 Hz, 2H), 1.84 (dt, *J* = 4.8 Hz, *J* = 13.4 Hz, 2H), 1.49 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 155.4, 154.7, 152.2, 150.4, 145.1, 136.1, 129.3, 122.1, 122.0, 105.9, 96.3, 85.3, 80.1, 79.7, 77.3, 36.6, 28.5.

**HRMS:** $C_{23}H_{26}FN_3O_3$ [$M^+$]; calculated: 411.1958, found 411.1964.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2979, 1698, 1657, 1569, 1533, 1421, 1365, 1235, 1168, 1012

**_N_-phenyl-3-methylidene-3,5-dihydrodispiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane-4',2''-_[1,3]_dioxolane]-5-imine (2.109)** $C_{21}H_{22}N_2O_3$ **MW = 350.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 73 % (m = 25.6 mg, n = 0.0731 mmol)

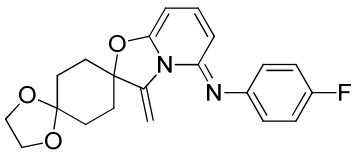
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.30 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 0.7 Hz, 1H), 6.76 (dd, *J* = 7.2 Hz, *J* = 9.4 Hz, 1H), 5.96 (d, *J* = 9.4 Hz, 1H), 5.25 (d, *J* = 7.1 Hz, 1H), 4.82 (s, 1H), 4.03-3.98 (m, 4H), 2.08-1.99 (m, 6H), 1.79-1.76 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 155.7, 152.3, 150.4, 145.2, 136.2, 129.2 (2C), 121.9 (2C), 121.9, 107.4, 105.4, 95.8, 86.3, 79.6, 64.5, 64.4, 35.0 (2C), 30.5 (2C).

**HRMS:** $C_{21}H_{22}N_2O_3$ [$M^+$]; calculated: 350.1630, found 350.1628.

**IR** ($CCl_4$): *ν*($cm^{-1}$) 2927, 2855, 1558, 1542, 1465, 1377, 1264.

**_N_-(4-fluorophenyl)-3-methylidene-3,5-dihydrodispiro[_[1,3]_oxazolo_[3,2-a]_pyridine-2,1'-cyclohexane-4',2''-[1,3]dioxolane]-5-imine (2.110)** $C_{21}H_{21}FN_2O_3$ **MW = 368.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 58 % (m = 21.4 mg, n = 0.0582 mmol)

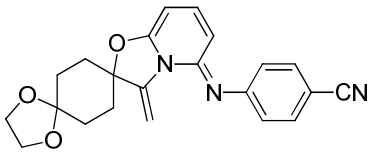
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.01-6.95 (m, 2H), 6.85-6.82 (m, 2H), 6.80 (d, *J* = 0.8 Hz, 1H), 6.78 (dd, *J* = 7.2 Hz, *J* = 9.5 Hz, 1H), 5.92 (dd, *J* = 0.6 Hz, *J* = 9.4 Hz, 1H), 5.26 (d, *J* = 7.1 Hz, 1H), 4.81 (d, *J* = 0.8 Hz, 1H), 4.03-3.96 (m, 4H), 2.07-1.99 (m, 6H), 1.78-1.76 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 158.5 (d, $^1J_{CF}$ = 237.8 Hz), 155.8, 152.9, 146.5 (d, *J* = 3.3 Hz), 145.3, 136.5, 123.0 (d, *J* = 7.7 Hz, 2C), 115.7 (d, *J* = 21.9 Hz, 2C), 107.5, 105.1, 95.9, 86.4, 79.8, 64.6, 64.4, 35.1 (2C), 30.6 (2C).

**HRMS:** $C_{21}H_{21}FN_2O_3$ [$M^+$]; calculated: 368.1536, found: 368.1527.

**IR** ($CCl_4$): ν ($cm^{-1}$) 2933, 1657, 1571, 1542, 1497, 1211, 1167, 1104.

**4-({3-methylidene-3,5-dihydrodispiro[*[1,3]*oxazolo*[3,2-a]*pyridine-2,1'-cyclohexane-4',2''-*[1,3]*dioxolane]-5-ylidene}amino)benzonitrile (2.111)** $C_{22}H_{21}N_3O_3$ **MW = 375.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** bright yellow oil

**Yield:** 66 % (m = 24.9 mg, n = 0.0663 mmol)

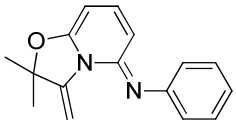
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.89 (dd, *J* = 7.3 Hz, *J* = 9.4 Hz, 1H), 6.75 (d, 1.2 Hz, 1H), 5.94 (dd, *J* = 0.7 Hz, *J* = 9.4 Hz, 1H), 5.38 (dd, *J* = 0.7 Hz, *J* = 7.3 Hz, 1H), 4.86 (d, *J* = 1.2 Hz, 1H), 4.03-3.96 (m, 4H), 2.08-2.00 (m, 6H), 1.80-1.76 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 155.9, 155.1, 152.0, 145.3, 137.9, 133.5 (2C), 122.8 (2C), 120.0, 107.3, 104.6, 104.3, 96.9, 86.8, 81.3, 64.6, 64.5, 35.2 (2C), 30.6 (2C).

**HRMS:** $C_{22}H_{21}N_3O_3$ [$M^+$]; calculated: 375.1583, found: 375.1595.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2953, 2931, 2225, 1658, 1563, 1533, 1497, 1492, 1245, 1165, 1104, 1036.

**2,2-dimethyl-3-methylidene-*N*-phenyl-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.112)** $C_{16}H_{16}N_2O$ **MW = 252.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** pale yellow oil

**Yield:** 94 % (m = 23.7 mg, n = 0.0940 mmol)

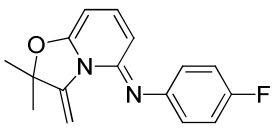
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.31 (d, *J* = 7.8 Hz, 2H), 7.00 (dd, *J* = 1.1 Hz, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 6.3 Hz, 2H), 6.80 (s, 1H), 6.67 (dd, *J* = 7.1 Hz, *J* = 9.5 Hz, 1H), 5.96 (d, *J* = 9.5 Hz, 1H), 5.22 (d, *J* = 7.1 Hz, 1H), 4.78 (s, 1H), 1.62 (s, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm) 155.7, 152.2, 150.5, 146.3, 136.3, 136.2, 129.2, 122.0, 121.8, 105.3, 95.3, 95.2, 86.0, 79.4, 79.3, 28.4 (2C).

**HRMS:** $C_{16}H_{16}N_2O$ [$M^+$]; calculated: 252.1263, found 252.1266.

**IR** ($CCl_4$): *v*($cm^{-1}$) 2956, 2927, 2856, 1659, 1570, 1538, 1484, 1463, 1186.

**_N_-(4-fluorophenyl)-2,2-dimethyl-3-methylidene-_2H,3H,5H-[1,3]_oxazolo_[3,2-a]_pyridin-5-imine (2.113)** $C_{16}H_{15}FN_2O$ **MW = 270.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.2

**Product:** pale yellow oil

**Yield:** 98 % (m = 26.4 mg, n = 0.0977 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.02-6.96 (m, 2H), 6.87-6.83 (m, 2H), 6.78 (dd, *J* = 7.1 Hz, *J* = 9.5 Hz, 1H), 6.77 (d, *J* = 1.1 Hz, 1H), 5.92 (dd, *J* = 0.8 Hz, *J* = 9.5 Hz, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.77 (d, *J* = 0.8 Hz, 1H), 1.61 (s, 6H).

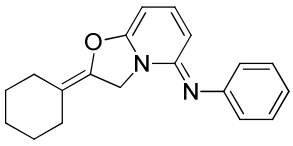
**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.5 (d, *J* = 237.8 Hz), 155.8, 152.8, 146.6 (d, *J* = 2.5 Hz), 146.4, 136.6, 123.0 (d, *J* = 5.6 Hz, 2C), 115.8 (d, *J* = 21.9 Hz, 2C), 105.1, 95.4, 86.1, 79.5, 28.4 (2C).

**HRMS:** $C_{16}H_{15}FN_2O$ [$M^+$]; calculated: 270.1168, found 270.1168.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2986, 1659, 1571, 1497, 1212, 1185.

- *Preparation of the [1,3]-oxazolopyridinimines via silver catalysis*

**2-cyclohexylidene-_N_-phenyl-_2H,3H,5H-[1,3]_oxazolo_[3,2-a]_pyridin-5-imine (2.83)** $C_{19}H_{20}N_2O$ **MW = 292.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 91 % (m = 26.6 mg, n = 0.0912 mmol)

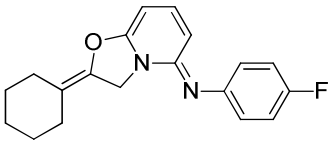
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 730-7.26 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.93-6.89 (m, 3H), 6.00 (d, *J* = 9.3 Hz, 1H), 5.34 (d, *J* = 7.2 Hz, 1H), 4.73 (bs, 2H), 2.34-2.29 (m, 2H), 2.07-2.03 (m, 2H), 1.58-1.54 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ (ppm) 156.1, 150.8, 150.8, 138.1, 137.4, 129.2 (2C), 122.8 (2C), 121.9, 114.2, 104.7, 79.8, 45.6, 29.1, 27.1, 26.8, 26.6, 26.2.

**HRMS:** $C_{19}H_{20}N_2O$ [$M^+$]; calculated: 292.1576; found: 292.1568.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2934, 1656, 1565, 1532, 1478, 1256, 1233, 1164.

**2-cyclohexylidene-*N*-(4-bromophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.135)** $C_{19}H_{19}FN_2O$ **MW = 310.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 98 % (m = 30.3 mg, n = 0.0979 mmol).

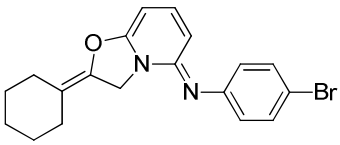
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.99-691 (m, 3H), 6.86-6.83 (m, 2H), 5.95 (d, *J* = 9.3 Hz, 1H), 5.35 (d, *J* = 7.1 Hz, 1H), 4.71 (s, 2H), 2.35-2.30 (m, 2H), 2.08-2.03 (m, 2H), 1.60-1.55 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 159.5 (d, *J* = 237.8 Hz), 156.2, 151.2, 138.3, 137.4, 123.7 (d, *J* = 7.7 Hz, 2C), 115.7 (d, *J* = 12.8 Hz, 2C), 114.4, 104.4, 80.0, 45.6, 29.1, 27.1, 26.8, 26.6, 26.5, 26.2.

**HRMS:** $C_{19}H_{19}FN_2O$ [$M^+$]; calculated: 310.1481; found: 310.1477.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2931, 2856, 1656, 1570, 1538, 1496, 1475, 1286, 1212, 1169.

**2-cyclohexylidene-*N*-(4-bromophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.136)** $C_{19}H_{19}BrN_2O$ **MW = 371.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 36 % (13.5 mg, n = 0.0364 mmol)

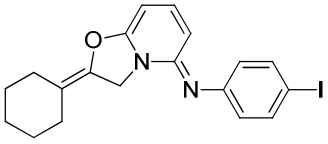
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.39-7.36 (m, 2H), 6.96 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 6.83-6.79 (m, 2H), 5.99 (dd, *J* = 0.7 Hz, *J* = 9.3 Hz, 1H), 5.39 (d, *J* = 7.1 Hz, 1H), 4.73 (s, 2H), 2.35-2.30 (m, 2H), 2.08-2.04 (m, 2H), 1.61-1.55 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.2, 150.9, 150.0, 138.6, 137.3, 132.2 (2C), 124.6 (2C), 114.5, 114.4, 104.3, 80.2, 45.6, 29.1, 27.1, 26.8, 26.6, 26.2.

**HRMS:** $C_{19}H_{19}BrN_2O$ [$M^+$]; calculated: 370.0681; found: 370.0684.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2933, 1656, 1567, 1534, 1475, 1263,1234, 1165.

**2-cyclohexylidene-*N*-(4-iodophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.137)** $C_{19}H_{19}IN_2O$ **MW = 418.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 50 % (m = 20.9 mg, n = 0.0500 mmol)

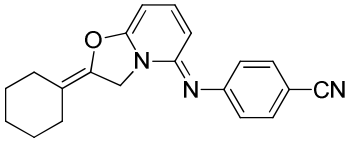
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.58-7.54 (m, 2H), 6.96 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 6.72-6.68 (m, 2H), 5.99 (dd, *J* = 0.6 Hz, *J* = 9.3 Hz, 1H), 5.39 (dd, *J* = 0.6 Hz, *J* = 7.3 Hz, 1H), 4.72 (s, 2H), 2.40-2.35 (m, 2H), 2.14-2.09 (m, 2H), 1.65-1.60 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.2, 150.9, 150.7, 138.6, 138.2 (2C), 137.3, 125.2 (2C), 114.5, 104.3, 84.7, 80.3, 45.7, 29.1, 27.1, 26.8, 26.6, 26.2.

**HRMS:** $C_{19}H_{19}IN_2O$ [$M^+$]; calculated: 418.0542; found: 418.0549.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2931, 2856, 1656, 1566, 1533, 1475, 1235, 1166.

**4-({2-cyclohexylidene-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-ylidene}amino)benzonitrile (2.138)** $C_{20}H_{19}N_3O$ **MW = 317.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 56 % (m = 17.7 mg, n = 0.0559 mmol).

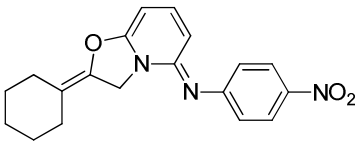
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.56-7.52 (m, 2H), 7.05 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 7.02-6.97 (m, 2H), 6.06 (dd, *J* = 0.6 Hz, *J* = 9.3 Hz, 1H), 5.49 (d, *J* = 7.3 Hz, 1H), 4.74 (s, 2H), 2.36-2.31 (m, 2H), 2.09-2.05 (m, 2H), 1.61-1.55 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.3, 155.6, 150.8, 139.6, 137.0, 133.5 (2C), 123.3 (2C), 120.1, 115.0, 104.1, 103.9, 81.6, 45.8, 29.1, 27.0, 26.7, 26.6, 26.1.

**HRMS:** $C_{20}H_{19}N_3O$ [$M^+$]; calculated: 317.1528; found: 317.1536.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2934, 2223, 1655, 1555, 1534, 1492, 1264, 1164.

**2-cyclohexylidene-*N*-(4-nitrophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.139)** $C_{19}H_{19}N_3O_3$ **MW = 337.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 60 % (m = 18.8 mg, n = 0.0598 mmol)

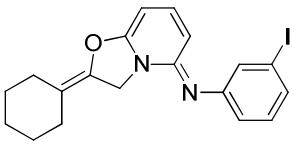
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.18-8.14 (m, 2H), 7.11 (dd, *J* = 7.4 Hz, *J* = 9.2 Hz, 1H), 7.01-6.98 (m, 2H), 6.15 (d, *J* = 9.2 Hz, 1H), 5.55 (d, *J* = 7.3 Hz, 1H), 4.78 (s, 2H), 2.37-2.33 (m, 2H), 2.10-2.06 (m, 2H), 1.61-1.57 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 158.0, 156.4, 150.9, 141.9, 140.0, 136.9, 125.5 (2C), 122.5 (2C), 115.2, 104.0, 82.3, 46.0, 29.2, 27.0, 26.7, 26.6, 26.1.

**HRMS:** $C_{19}H_{19}N_3O_3$ [$M^+$]; calculated: 337.1426; found: 337.1425.

**R** ($CCl_4$): *v* ($cm^{-1}$) 2927, 2855, 1732, 1655, 1563, 1555, 1465, 1334, 1289, 1110.

**2-cyclohexylidene-*N*-(3-iodophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.140)** $C_{19}H_{19}IN_2O$ **MW = 418.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 43 % (m = 18.0 mg, n = 0.0431 mmol)

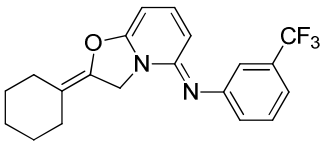
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.31-7.29 (m, 2H), 7.02-6.96 (m, 2H), 6.90-6.88 (m, 1H), 6.02 (d, *J* = 9.3 Hz, 1H), 5.40 (d, *J* = 7.3 Hz, 1H), 4.71 (s, 2H), 2.36-2.31 (m, 2H), 2.08-2.04 (m, 2H), 1.62-1.56 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.1, 152.5, 151.0, 138.7, 137.3, 131.7, 130.7 (2C), 122.2, 114.5, 104.4, 94.8, 80.5, 45.6, 29.1, 27.0, 26.8, 26.6, 26.2.

**HRMS:** $C_{19}H_{19}IN_2O$ [$M^+$]; calculated: 418.0542; found: 418.0538

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2932, 2856, 1656, 1566, 1531, 1463, 1286, 1231, 1170, 1112.

**2-cyclohexylidene-*N*-(3-trifluoromethylphenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.141)** $C_{20}H_{19}F_3N_2O$ **MW = 360.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 39 % (m = 14.6 mg, n = 0.0388 mmol).

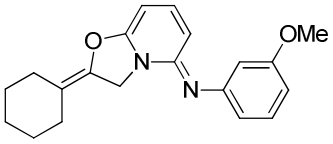
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.37 (t, *J* = 7.8 Hz, 1H), 7.23-7.19 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 7.3 Hz, *J* = 9.3 Hz, 1H), 5.99 (d, *J* = 9.3 Hz, 1H), 5.42 (d, *J* = 7.3 Hz, 1H), 4.74 (s, 2H), 2.37-2.32 (m, 2H), 2.10-2.05 (m, 2H), 1.62-1.55 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 156.2, 151.5, 151.2, 138.9, 137.2, 131.6 (q, *J* = 31.4 Hz), 129.6, 126.1, 125.4 (q, *J* = 270.6 Hz), 119.6 (q, *J* = 3.6 Hz), 118.3 (q, *J* = 3.8 Hz), 114.6, 104.1, 80.5, 45.7, 29.1, 27.0, 26.8, 26.5, 26.2.

**HRMS:** $C_{20}H_{19}F_3N_2O$ [$M^+$]; calculated: 376.1399; found: 376.1432.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2933, 2852, 1658, 1560, 1531, 1461, 1286, 1229, 1170.

**2-cyclohexylidene-*N*-(3-methoxyphenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.142)** $C_{20}H_{22}N_2O_2$ **MW = 322.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil rapidly turning dark green

**Yield:** 64 % (m = 20.7 mg, n = 0.0642 mmol).

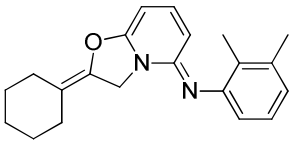
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.18 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 7.7 Hz, *J* = 8.8 Hz, 1H), 6.57-6.51 (m, 3H), 6.05 (d, *J* = 9.3 Hz, 1H), 5.37 (d, *J* = 7.2 Hz, 1H), 4.78-4.75 (bs, 2H), 3.78 (s, 3H), 2.35-2.29 (m, 2H), 2.07-2.03 (m, 2H), 1.58-1.54 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 158.4, 153.8, 148.5, 135.9, 135.1, 127.5, 112.9, 112.0, 105.8, 105.7 (2C), 102.5, 77.7, 52.9, 43.4, 26.8, 24.7, 24.5, 24.2, 23.9.

**HRMS:** $C_{20}H_{22}N_2O_2$ [$M^+$]; calculated: 322.1681; found: 322.1677.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2930, 1654, 1568, 1529, 1463, 1282, 1222, 1162, 1115.

**2-cyclohexylidene-*N*-(2,3-dimethylphenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.144)** $C_{21}H_{24}N_2O$ **MW = 320.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 46 % (14.8 mg, n = 0.0462 mmol)

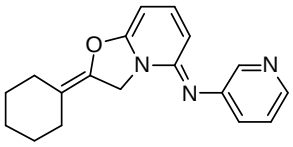
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.56 (m, 1H), 7.16-7.14 (m, 3H), 6.24 (d, *J* = 7.9 Hz, 1H), 5.99 (d, *J* = 8.8 Hz, 1H), 5.93 (s, 2H), 2.36-2.32 (m, 2H), 2.30 (s, 3H), 2.24-2.19 (m, 2H), 2.19 (s, 3H), 1.60-1.55 (m, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 155.5, 149.9, 144.1, 137.8, 134.1, 132.9, 129.0, 125.8, 124.2, 117.6, 101.9, 90.2, 49.7, 28.6, 28.2, 25.8, 25.6, 25.5, 24.8, 19.4, 13.4.

**HRMS:** $C_{21}H_{24}N_2O$ [$M^+$]; calculated: 320.1889; found: 320.1885.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2935, 1652, 1560, 1530, 1477, 1263, 1231, 1167.

| ***N*-{2-cyclohexylidene-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-ylidene}pyridin-3-amine (2.146)** | $C_{18}H_{19}N_3O$ | **MW = 293.4 g.mol$^{-1}$** |
|---|---|---|



**Procedure :** see general procedure 2.3

**Product:** brown oil.

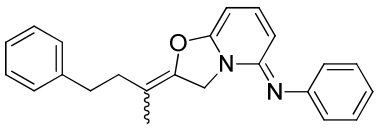
**Yield:** 50 % (m = 14.7 mg, n = 0.05 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.27 (d, *J* = 2.2 Hz, 1H), 8.24 (dd, *J* = 1.5 Hz, *J* = 4.7 Hz, 1H), 7.30-7.27 (m, 1H), 7.21 (dd, *J* = 4.7 Hz, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 7.4 Hz, *J* = 9.2 Hz, 1H), 6.02 (d, *J* = 9.2 Hz, 1H), 5.52 (d, *J* = 7.3 Hz, 1H), 2.35-2.29 (m, 2H), 2.08-2.04 (m, 2H), 1.60-1.54 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ (ppm) 156.3, 151.4, 145.7, 145.1, 143.5, 139.8, 136.9, 130.2, 123.9, 115.2, 103.8, 82.1, 46.0, 29.1, 27.0, 26.7, 26.6, 26.1.

**HRMS:** $C_{18}H_{19}N_3O$ [M+Na$^+$]; calculated: 293.3630; found:

| ***(2Z)*- and *(2E)*-*N*-phenyl-2-(4-phenylbutan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.149)** | $C_{23}H_{22}N_2O$ | **MW = 342.4 g.mol$^{-1}$** |
|---|---|---|



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 79 % (*Z*/*E* 1 : 1.6) (m = 27.1 mg, n = 0.0793 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* (ppm) 7.34-7.20 (m, 7H both isomers), 7.04-7.00 (m, 1H both isomers), 6.97-6.92 (m, 3H both isomers), 6.06 (d, *J* = 9.5 Hz, 1H *Z* isomer), 6.03 (d, *J* = 9.5 Hz, 1H *E* isomer), 5.40 (d, *J* = 7.2 Hz, 1H *Z* isomer), 5.39 (d, *J* = 7.1 Hz, 1H *E* isomer), 4.77 (s, 2H *Z* isomer), 4.60 (s, 2H *E* isomer), 2.82-2.76 (m, 2H both isomers), 2.57-2.54 (m, 2H *Z* isomer), 2.34-2.30 (m, 2H *E* isomer), 1.86 (s, 3H *E* isomer), 1.71 (s, 3H *Z* isomer).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* (ppm)

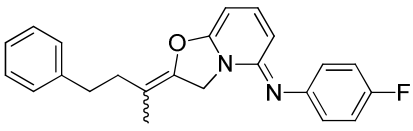
*E* isomer 155.8, 150.6, 150.3, 141.2, 141.0, 138.1, 129.2 (2C), 128.6 (2C), 128.4 (2C), 126.2, 122.7 (2C), 122.1, 109.5, 104.8, 79.9, 45.7, 35.0, 33.2, 14.2.

*Z* isomer 156.0, 150.7, 150.2, 141.5, 140.5, 138.2, 129.3 (2C), 128.5 (2C), 128.3 (2C), 126.0, 122.7 (2C), 122.1, 109.8, 104.8, 80.2, 46.1, 33.7, 32.2, 16.4.

**HRMS:** $C_{23}H_{22}N_2O$ [M$^+$]; calculated: 342.1732, found 342.1735.

**IR** ($CCl_4$): *v* (cm$^{-1}$) 3029, 2927, 2858, 1732, 1656, 1571, 1534, 1476, 1288, 1234, 1172, 1135, 1057, 1032.

***(2Z)- and (2E)-N*-(4-fluorophenyl)-2-(4-phenylbutan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.150)** $C_{23}H_{21}FN_2O$ **MW = 360.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 93 % (*Z/E* 1 : 1.2) (m = 33.5 mg, n = 0.0930 mmol)

The two isomers are partially separable and a 1:6 mixture is obtained.

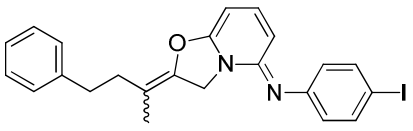
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.31-7.27 (m, 2H both isomers), 7.24-7.17 (m, 3H both isomers), 7.01-6.95 (m, 3H both isomers), 6.92-6.85 (m, 2H both isomers), 6.01 (d, *J* = 9.4 Hz, 1H *Z* isomer), 5.97 (d, *J* = 9.3 Hz, 1H *E* isomer), 5.44 (d, *J* = 7.2 Hz, 1H), 5.42 (d, *J* = 7.3 Hz, 1H *E* isomer), 4.80 (bs, 2H *Z* isomer), 4.61 (bs, 2H *E* isomer), 2.79-2.74 (m, 2H both isomers), 2.53 (t, *J* = 7.6 Hz, 2H *Z* isomer), 2.30 (t, *J* = 7.7 Hz, 2H *E* isomer), 1.83 (t, *J* = 2.1 Hz, 3H *E* isomer), 1.69-1.68 (m, 3H *Z* isomer).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) (only the *E* isomer is visible in 13C NMR) 156.0, 151.1 (2C), 141.0, 141.0, 138.8, 128.5 (2C), 128.5 (2C), 126.3, 124.0, 123.9, 116.0 (2C), 115.8 (2C), 110.0, 104.5, 46.0, 35.0, 33.6, 14.2.

**HRMS:** $C_{23}H_{21}FN_2O$ [$M^+$]; calculated: 360.1638, found 360.1627.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2927, 2856, 1657, 1570, 1537, 1497, 1212, 1171.

***(2Z)*- and *(2E)-N*-(4-iodophenyl)-2-(4-phenylbutan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.151)** $C_{23}H_{21}IN_2O$ **MW = 468.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 82 % (m = 38.4 mg, n = 0.0820 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.57-7.52 (m, 2H both isomers), 7.31-7.27 (m, 3H), 7.24-7.16 (m, 3H), 6.97-6.92 (m, 1H both isomers), 6.70-6.67 (m, 2H both isomers), 6.00 (d, *J* = 9.2 Hz, 1H *Z* isomer), 5.97 (d, *J* = 9.4 Hz, 1H *E* isomer), 5.38 (d, *J* = 7.2 Hz, 1H both isomers), 4.70-4.67 (bs, 2H *Z* isomer), 4.53-4.50 (bs, 1H *E* isomer), 2.79-2.73 (m, 2H *E* isomer +1 H *Z* isomer), 2.53 (t, *J* = 8.4 Hz, 2H *Z* isomer), 2.29 (t, *J* = 7.6 Hz, 2H *E* isomer), 1.83 (t, *J* = 2.0 Hz, 3H *E* isomer), 1.68-1.66 (m, 3H *Z* isomer).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm)

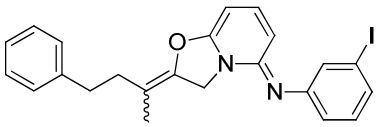
*E* isomer 155.9, 150.8, 150.6, 141.0, 141.0, 138.5, 138.2 (2C), 128.6 (2C), 128.4 (2C), 126.3, 125.2 (2C), 109.8, 104.5, 84.8, 80.3, 45.8, 35.0, 33.6, 14.2.

*Z* isomer 156.1, 150.9, 150.6, 141.5, 140.5, 138.6, 138.2 (2C), 128.4 (2C), 128.4 (2C), 126.1, 125.2 (2C), 110.0, 104.5, 84.8, 80.4, 46.1, 33.8, 32.3, 16.5.

**HRMS:** $C_{23}H_{21}IN_2O$ [$M^+$]; calculated: 468.0699, found 468.0684.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2927, 2857, 1656, 1563, 1534, 1475, 1289, 1235, 1167, 1135, 1054, 1034.

***(2Z)- and (2E)-N*-(3-iodophenyl)-2-(4-phenylbutan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.152)** $C_{23}H_{21}IN_2O$ **MW = 468.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 55 % (*Z/E* 1 : 1.3) (m = 25.6 mg, n = 0.0448 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.31-7.27 (m, 4H both isomers), 7.22-7.16 (m, 3H both isomers), 7.01-6.94 (m, 2H both isomers), 6.88-6.86 (m, 1H both isomers), 6.02 (d, *J* = 9.3 Hz, 1H *Z* isomer), 5.99 (d, *J* = 9.3 Hz, 1H *E* isomer), 5.39 (d, *J* = 7.2 Hz, 1H both isomers), 4.69-4.66 (bs, 2H Z isomer), 4.52-4.49 (m, 2H *E* isomer), 2.77 (t, *J* = 7.2 Hz, 2H *Z* isomer), 2.75 (t, *J* = 7.9 Hz, 2H *E* isomer), 2.28 (t, *J* = 7.8 Hz, 2H, *E* isomer), 2.53 (t, *J* = 7.3 Hz, 2H *Z* isomer), 1.84 (t, *J* = 2.1 Hz, 3H *E* isomer), 1.68-1.67 (m, 3H *Z* isomer).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm)

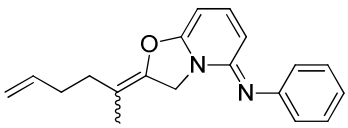
*E* isomer 156.0, 150.9, 141.5, 140.4, 138.8, 131.7, 130.8 (2C), 130.8, 128.4 (2C), 128.3, 126.1, 122.2 , 114.3, 110.1, 104.5, 94.8, 80.6, 46.1, 33.7, 32.3, 16.5.

*Z* isomer 155.9, 152.3, 150.8, 141.0, 141.0, 138.7, 131.7, 130.8 (2C), 130.7, 128.6, 128.4 (2C), 126.3, 122.2, 109.8, 104.5, 94.8, 80.5, 45.7, 35.1, 33.6, 14.2.

**HRMS:** $C_{23}H_{21}IN_2O$ [$M^+$]; calculated: 468.0699, found 468.0702.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2927, 1656, 1566, 1531, 1464, 1293, 1173, 1133, 1034.

***(2Z)*- and *(2E)*-2-(hex-5-en-2-ylidene)-*N*-phenyl-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.153)** $C_{19}H_{20}N_2O$ **MW = 292.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 47 % (*Z/E* 1 : 1.3) (m = 13.8 mg, n = 0.0822 mmol).

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.28 (t, *J* = 7.8 Hz, 2H both isomers), 6.98 (t, *J* = 7.4 Hz, 1H both isomers), 6.94-6.90 (m, 3H both isomers), 6.00 (d, *J* = 9.4 Hz, 1H both isomers), 5.88-5.73 (m, 1H both isomers), 5.36 (d, *J* = 7.2 Hz, 1H both isomers), 5.07 (dd, *J* = 1.6 Hz, *J* = 9.1 Hz, 1H major isomer), 5.03 (dd, *J* = 1.5 Hz, *J* = 9.0 Hz, 1H minor isomer), 4.99 (dd, *J* = 1.1 Hz, *J* = 10.1 Hz, 1H both isomers), 4.76-4.71 (m, 2H both isomers), 2.33-2.30 (m, 2H minor isomer), 2.23-2.18 (2H minor isomer + 2H major

isomer), 2.10-2.06 (2H major isomer), 1.80-1.78 (m, 3H major isomer), 1.67-1.65 (m, 3H minor isomer).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm)

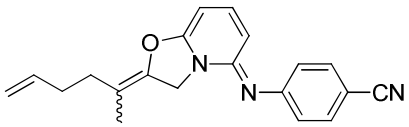
E isomer 156.0, 150.8, 140.9, 138.0, 137.3, 129.3 (2C), 122.7 (2C), 122.0, 115.8, 109.7, 104.9, 104.8, 79.8, 45.9, 32.4, 31.5, 14.1.

Z isomer 156.1, 150.7, 140.5, 138.0, 137.9, 129.3 (2C), 122.7 (2C), 122.0, 115.1, 109.7, 104.9, 104.8, 79.8, 46.0, 31.5, 29.7, 16.2.

**HRMS:** $C_{19}H_{20}N_2O$ [$M^+$]; calculated: 292.1576, found 292.1570.

**IR** ($CCl_4$): ν ($cm^{-1}$) 3076, 2926, 2857, 1656, 1567, 1530, 1288, 1264, 1235, 1166, 1124, 1057, 1032.

***(2Z)*- and 4-{[*(2E)*-2-(hex-5-en-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-ylidene]amino}benzonitrile (2.155)** $C_{20}H_{19}N_3O$ **MW = 317.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 45 % (*Z/E* 1 : 1.6 ) (m = 14.4 mg, n = 0.0454 mmol)

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.56-7.52 (m, 2H both isomers), 7.06 (dd, *J* = 7.4 Hz, *J* = 9.4 Hz, 1H both isomers), 7.00-6.97 (m, 2H both isomers), 6.06 (dd, *J* = 0.7 Hz, *J* = 9.3 Hz, 1H both isomers), 5.87-5.73 (m, 1H both isomers), 5.51 (dd, *J* = 0.8 Hz, *J* = 7.3 Hz, 1H both isomers), 5.05 (dddd, *J* = 1.5 Hz, *J* = 3.3 Hz, *J* = 6.2 Hz, *J* = 17.1 Hz, 1H both isomers), 4.99 (dddd, *J* = 1.1 Hz, *J* = 2.1 Hz, *J* = 4.6 Hz, *J* = 10.2 Hz, 1H both isomers), 4.75-4.71 (m, 2H both isomers), 2.34-2.30 (m, 2H *Z* isomer), 2.24-2.18 (m, 2H *E* isomer + 2H *Z* isomer), 2.10-2.06 (m, 2H *E* isomer), 1.79 (t, *J* = 2.16 Hz, 3H *E* isomer), 1.67 (t, *J* = 1.7 Hz, 3H *Z* isomer).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm)

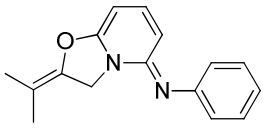
*E* isomer 156.0, 155.4, 150.7, 140.3, 139.5 (2C), 137.0, 133.5 (2C), 123.3 (2C), 120.0, 115.8, 104.0, 81.7, 46.0, 32.3, 31.3, 14.0.

*Z* isomer 156.1, 155.4, 150.7, 139.9, 139.5 (2C), 137.7, 133.5 (2C), 123.3 (2C), 115.1, 110.4, 104.1, 81.7, 46.1, 31.4, 29.6, 16.2.

**HRMS:** $C_{20}H_{19}N_3O$ [$M^+$]; calculated: 317.1528, not found (twice).

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2927, 2223, 1656, 1545, 1534, 1492, 1292, 1263, 1164, 1036.

***N*-phenyl-2-(propan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.162)** $C_{16}H_{16}N_2O$ **MW = 252.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 59 % (m = 14.8 mg, n = 0.0589 mmol)

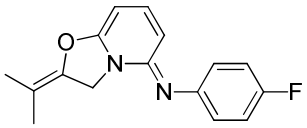
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.27 (d, *J* = 7.9 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.93-6.89 (m, 3H), 6.00 (d, *J* = 9.4 Hz, 1H), 5.34 (d, *J* = 7.2 Hz, 1H), 4.73-4.70 (m, 2H), 1.80-1.78 (m, 3H), 1.68-1.66 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.1, 150.8, 150.8, 140.0, 138.1, 129.3 (2C), 122.7 (2C), 122.0, 106.3, 104.8, 79.7, 45.9, 18.4, 16.4.

**HRMS:** $C_{16}H_{16}N_2O$ [$M^+$]; calculated: 252.1253, found 252.1248.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2923, 1656, 1573, 1532, 1489, 1285, 1211, 1161.

***N*-(4-fluorophenyl)-2-(propan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.163)** $C_{16}H_{15}FN_2O$ **MW = 270.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 78 % (m = 21.1 mg, n = 0.0781 mmol)

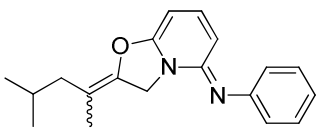
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.99-6.92 (m, 3H), 6.87-6.83 (m, 2H), 5.95 (dd, *J* = 0.8 Hz, *J* = 9.3 Hz, 1H), 5.37 (d, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 1.8 Hz, 2H), 1.78 (s, 3H), 1.67 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.4 (d, *J* = 238.7 Hz), 156.1, 151.2, 146.7 (d, *J* = 2.2 Hz), 139.9, 138.3, 123.7 (d, *J* = 8.7 Hz, 2C), 115.7 (d, *J* = 21.8 Hz, 2C), 106.5, 104.5, 79.3, 45.9, 18.4, 16.4.

**HRMS:** $C_{16}H_{15}FN_2O$ [$M^+$]; calculated: 270.1168, found 270.1168.

**IR** ($CCl_4$): *v*($cm^{-1}$) 2925, 1657, 1570, 1567, 1535, 1497, 1476, 1289, 1212, 1169, 1117.

***(2Z)*- and *(2E)*-2-(4-methylpentan-2-ylidene)-*N*-phenyl-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.156)** $C_{19}H_{20}N_3O$ **MW = 294.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 58 % (*Z/E* 1 : 1.6) (m = 17.0 mg, n = 0.0581 mmol)

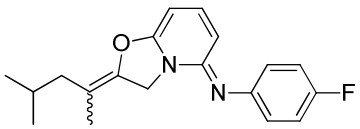
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.99-6.92 (m, 3H), 6.86-6.83 (m, 2H), 5.95 (d, *J* = 9.3 Hz, 1H), 5.37 (d, *J* = 7.2 Hz, 1H major isomer), 5.36 (d, *J* = 7.2 Hz, 1H minor isomer), 4.74-4.70 (bs, 2H), 2.10-2.07 (m, 2H minor isomer), 1.87-1.84 (m, 3H major isomer + 1H minor isomer), 1.76 (s, 3H major isomer), 1.64 (s, 3H minor isomer), 0.92-0.89 (m, 7H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) (only the *E* isomer can be described in $^{13}$C NMR) 156.0, 150.7, 149.6, 138.6, 138.1, 129.3 (2C), 122.9 (2C), 122.4, 111.8, 108.3, 104.9, 80.7, 64.5, 45.9, 34.7, 26.0, 23.5.

**HRMS:** $C_{19}H_{20}N_3O$ [$M^+$]; calculated: 294.1732, found 294.1721

**IR** ($CCl_4$): *v* ($cm^{-1}$) 3075, 2958, 2925, 2870, 1731, 1656, 1571, 1547, 1485, 1476, 1290, 1249, 1166, 1125, 1057, 1029. 1721

**_(2Z)_- and (2E)-N-(4-fluorophenyl)-2-(4-methylpentan-2-ylidene)-2H,3H,5H-[1,3]oxazolo_[3,2-a]_pyridin-5-imine (2.157)** $C_{19}H_{21}FN_2O$ **MW = 312.4 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 69 % (Z/E 1 : 1.5) (m = 21.5 mg, n = 0.0688 mmol)

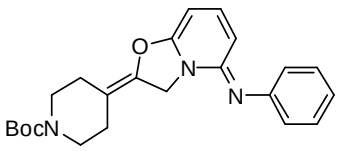
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.28 (t, *J* = 7.5 Hz, 2H major isomer), 7.28 (t, *J* = 6.4 Hz, 2H minor isomer), 6.98 (t, *J* = 7.7 Hz, 1H), 6.95-6.30 (m, 3H), 6.00 (d, *J* = 9.4 Hz, 1H), 5.36 (d, *J* = 7.2 Hz, 1H), 4.76-4.73 (bs, 2H), 2.10-2.07 (m, 2H minor isomer), 1.87-1.80 (2H major isomer + 1H minor isomer), 1.77-1.75 (m, 4H major isomer + 2H minor isomer), 1.66-1.64 (m, 2H major isomer), 0.94-0.89 (m, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) (only the major isomer can be described in $^{13}$C NMR) 158.6 (d, *J* = 237.6 Hz), 156.2 (d, *J* = 11.1 Hz), 151.3, 146.7, 143.9 (d, *J* = 25.7 Hz), 138.4, 123.8 (d, *J* = 5.7 Hz, 2C), 115.7 (d, *J* = 21.9 Hz, 2C), 110.1, 110.0, 104.5 (d, *J* = 6.8 Hz), 80.0, 79.9, 46.1, 42.1, 26.5, 22.4, 22.3, 16.6, 14.3.

**HRMS:** $C_{19}H_{21}FN_2O$ [$M^+$]; calculated: 312.1638, found 312.1644.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2958, 2925, 2870, 1656, 1574, 1547, 1495, 1475, 1290, 1212, 1169, 1125, 1057, 1030.

***tert*-butyl 4-[5-(phenylimino)-_2H,3H,5H-[1,3]_oxazolo_[3,2-a]_pyridin-2-ylidene]piperidine-1-carboxylate (2.158)** $C_{23}H_{27}N_3O_3$ **MW = 393.5 g.mol$^{-1}$**




**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 78 % (m = 30.6 mg, n = 0.0778 mmol)

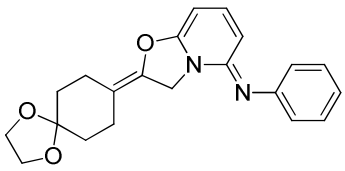
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.28 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.94 (dd, *J* = 7.2 Hz, *J* = 9.1 Hz, 1H), 6.91 (d, *J* = 7.1 Hz, 2H), 6.03 (d, *J* = 9.1 Hz, 1H), 5.39 (d, *J* = 7.2 Hz, 1H), 4.79 (s, 2H), 3.45 (t, *J* = 5.6 Hz, 4H), 2.43-2.38 (m, 2H), 2.14 (t, *J* = 5.4 Hz, 2H), 1.47 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 153.9, 152.9, 148.8, 148.6, 137.6, 136.2, 127.4 (3C), 120.8 (2C), 120.3, 108.0, 103.4, 78.0 (2C), 43.9 (2C), 26.7 (3C), 26.5, 24.2.

**HRMS:** $C_{23}H_{27}N_3O_3$ [$M^+$]; calculated: 393.2052, found 393.2056.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2928, 2856, 1698, 1659, 1571, 535, 1476, 1423, 1366, 1233, 1168, 1135, 1012.

**2-{1,4-dioxaspiro*[4.5]*decan-8-ylidene}-*N*-phenyl-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.159)** $C_{21}H_{22}N_2O_3$ **MW = 350.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 45 % (m = 15.8 mg, n = 0.0482 mmol)

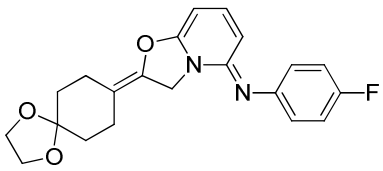
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.29 (t, *J* = 7.8 Hz, 2H), 7.02-6.92 (m, 4H), 6.03 (d, *J* = 9.3 Hz, 1H), 5.40 (d, *J* = 7.3 Hz, 1H), 4.80-4.78 (bs, 2H), 3.98 (s, 4H), 2.51 (t, *J* = 6.4 Hz, 2H), 2.24 (d, *J* = 6.3 Hz, 2H), 1.70 (d, *J* = 6.6 Hz, 4H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 155.9, 150.8, 149.8, 138.4, 138.1, 129.2 (2C), 122.8 (2C), 122.2, 111.5, 108.3, 104.8, 80.4, 64.4 (2C), 45.8, 34.6, 34.5, 25.9, 23.4.

**HRMS:** $C_{21}H_{22}N_2O_3$ [$M^+$]; calculated: 350.1630, found 350.1622.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2928, 1656, 1555, 1532, 1495, 1475, 1209, 1170, 1053.

**2-{1,4-dioxaspiro*[4.5]*decan-8-ylidene}-*N*-(4-fluorophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.160)** $C_{21}H_{21}FN_2O_3$ **MW = 368.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 66 % (m = 24.3 mg, n = 0.0660 mmol)

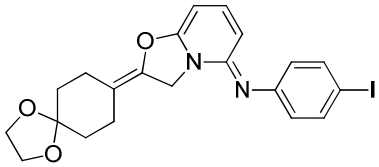
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 6.99-6.94 (m, 2H), 6.94 (dd, *J* = 7.2 Hz, *J* = 9.4 Hz, 1H), 6.85-6.82 (m, 2H), 5.96 (d, *J* = 9.3 Hz, 1H), 5.36 (d, *J* = 7.2 Hz, 1H), 4.75-4.73 (m, 2H), 3.98 (s, 4H), 2.50 (t, *J* = 6.4 Hz, 2H), 2.23 (t, *J* = 6.3 Hz, 2H), 1.71 (t, *J* = 6.5 Hz, 4H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.6 (d, *J* = 237.8 Hz), 156.0, 151.1, 138.3, 138.3, 123.7 (d, *J* = 8.7 Hz, 2C), 115.8 (d, *J* = 21.9 Hz, 2C), 111.5, 108.3, 104.7, 80.0, 64.5 (2C), 45.7, 34.8, 34.6, 26.1, 23.5 (2C).

**HRMS:** $C_{21}H_{21}FN_2O_3$ [$M^+$]; calculated: 368.1536, found 368.1546.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2929, 1656, 1570, 1537, 1497, 1475, 1212, 1170, 1092, 1056, 1035.

**2-{1,4-dioxaspiro*[4.5]*decan-8-ylidene}-*N*-(4-iodophenyl)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-imine (2.161)** $C_{21}H_{21}IN_2O_3$ **MW = 476.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.3

**Product:** pale yellow oil

**Yield:** 44 % (m = 20.9 mg, n = 0.0440 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.54 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 7.5 Hz, *J* = 9.1 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 2H), 5.99 (dd, *J* = 9.1 Hz, 1H), 5.39 (d, *J* = 7.3 Hz, 1H), 4.74-4.72 (bs, 2H), 3.97 (s, 4H), 2.49 (t, *J* = 6.3 Hz, 2H), 2.22 (t, *J* = 6.3 Hz, 2H), 1.70 (t, *J* = 6.3 Hz, 4H).

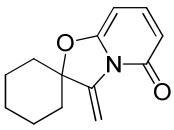
**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 155.9, 150.7, 150.4, 138.5, 138.1 (2C), 125.0 (2C), 111.6, 108.2, 104.5, 84.7, 80.4, 80.3, 64.4 (2C), 45.7, 34.7, 34.5, 26.0, 23.4.

**HRMS:** $C_{21}H_{21}IN_2O_3$ [$M^+$]; calculated: 476.0597, found 476.0598.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2954, 1656, 1567, 1533, 1475, 1289, 1244, 1229, 1168, 1133, 1093, 1054, 1036, 938.

- *Preparation of the oxazolopyridones*

**3-methylidene-3,5-dihydrospiro[[1,3]oxazolo[3,2-a]pyridine-2,1'-cyclohexane]-5-one (2.166)** $C_{13}H_{15}NO_2$ **MW = 217.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.4

**Product:** colorless oil

**Yield:** 80 % (m = 17.4 mg, n = 0.08 mmol)

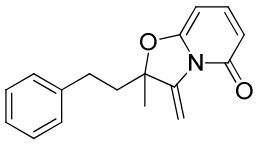
**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.25 (dd, *J* = 7.5 Hz, *J* = 9.2 Hz, 1H), 6.53 (s, 1H), 6.03 (d, *J* = 9.2 Hz, 1H), 5.58 (d, *J* = 7.5 Hz, 1H), 4.77 (s, 1H), 1.98-1.91 (m, 2H), 1.86-1.53 (m, 7H), 1.35-1.26 (m, 1H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 161.8, 156.0, 146.4, 141.6, 110.9, 96.8, 88.0, 83.3, 37.0, 24.6, 21.7.

**HRMS:** $C_{13}H_{15}NO_2$ [$M^+$]; calculated: 217.1103, found 217.1108.

**IR ($CCl_4$):** *v* ($cm^{-1}$) 2941, 2858, 1686, 1604, 1537, 1448, 1401, 1375, 1278, 1154, 1122.

**2-methyl-3-methylidene-2-(2-phenylethyl)-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.169)** $C_{17}H_{17}NO_2$ **MW = 267.3 g.mol$^{-1}$**



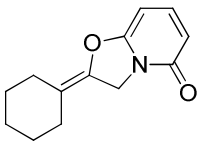
**Procedure:** see general procedure 2.4

**Product:** colorless oil

**Yield:** 75 % (m = 20.1 mg, n = 0.075 mmol)

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.57-7.55 (m, 1H), 7.51 (dd, *J* = 7.9 Hz, *J* = 8.9 Hz, 1H), 7.30-7.25 (m, 3H), 7.21-7.16 (m, 2H), 6.27 (dd, *J* = 0.6 Hz, *J* = 8.9 Hz, 1H), 6.23 (dd, *J* = 0.6 Hz, *J* = 7.9 Hz, 1H), 2.95-2.86 (m, 1H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.15-2.06 (m, 1H), 1.95-1.87 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H).

**2-cyclohexylidene-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-one (2.167)** $C_{13}H_{15}NO_2$ **MW = 217.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.4

**Product:** pale yellow oil

**Yield:** 98 % (*exo : endo* 20 : 1) (m = 21.3 mg, n = 0.0980 mmol) (only the major isomer is described)

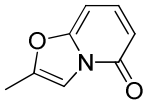
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.34 (dd, *J* = 7.6 Hz, *J* = 9.1 Hz, 1H), 6.11 (d, *J* = 9.1 Hz, 1H), 5.67 (d, *J* = 7.6 Hz, 1H), 4.76 (bs, 2H), 2.32-2.27 (bs, 2H), 2.04-1.99 (bs, 2H), 1.59-1.52 (bs, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 160.7, 155.9, 142.2, 136.7, 115.3, 110.8, 83.5, 44.9, 29.2, 27.0, 26.6, 26.5, 26.1.

**HRMS:** $C_{13}H_{15}NO_2$ [$M^+$]; calculated: 217.1103, found 217.1101.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2935, 2857, 1685, 1610, 1596, 1529, 1449, 1237, 1160, 1111, 1062.

**2-methyl-5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.174)** $C_8H_7NO_2$ **MW = 149.1 g.mol$^{-1}$**



**Procedure:** see general procedure 2.4

**Product:** volatile colorless oil

**Yield:** 45 % (m = 6.7 mg, n = 0.0450 mmol 50% conv)

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.54-7.52 (bs, 1H), 7.49 (t app, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 9.0 Hz, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 2.40 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 157.1, 153.5, 146.4, 139.2, 107.2, 106.7, 84.9, 11.5.

**HRMS:** $C_8H_7NO_2$ [$M^+$]; calculated: 149.0477, not found (submitted twice).

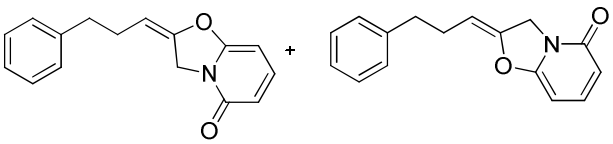
**IR** ($CCl_4$): $\nu$ ($cm^{-1}$) 2929, 1690, 1607, 1558, 1554, 1545, 1541, 1260, 1089.

| **(2E)- and (2Z)-2-(3-phenylpropylidene)-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.175 et 2.176)** | $C_{16}H_{15}NO_2$ | **MW = 253.3 g.mol$^{-1}$** |
|---|---|---|

**Procedure:** see general procedure 2.4

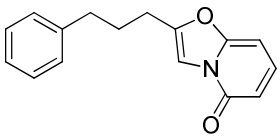
**Product:** pale yellow oil

**Yield:** 78 % (*exo*$_{Z:E:}$*endo* $1_{1:1}$ : 2) (m = 19.8 mg, n = 0.0782 mmol)



Major isomers:

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.38-7.33 (m, 1H both isomers), 7.32-7.26 (m, 2H both isomers), 7.23-7.16 (m, 3H both isomers), 6.13 (t app, *J* = 8.9 Hz, 1H both isomers), 5.71 (d, *J* = 7.5 Hz, 1H one isomer), 5.66 (d, *J* = 7.4 Hz, 1H one isomer), 5.32 (tt, *J* = 2.8 Hz, *J* = 8.1 Hz, 1H one isomer), 4.87 (tt, *J* = 2.1 Hz, *J* = 7.4 Hz, 1H one isomer), 4.75-4.72 (m, 2H one isomer), 4.59-4.54 (m, 2H one isomer), 2.76-2.68 (m, 2H both isomers), 2.59-2.50 (m, 2H one isomer), 2.32-2.29 (m, 2H one isomer).



Minor isomer:

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.56-7.54 (bs, 1H), 7.49 (dd, *J* = 8.1 Hz, *J* = 8.7 Hz, 1H), 7.32-7.26 (m, 2H), 7.23-7.16 (m, 3H), 6.25 (d, *J* = 8.9 Hz, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 2.76-2.68 (m, 4H), 2.05 (quintuplet app, *J* = 7.4Hz, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) (the mixture of isomers is described) 160.5, 157.1, 155.5, 155.4, 153.5, 150.0, 146.2, 144.9, 142.2, 142.1, 141.1, 140.7, 139.3, 128.6, 128.5, 128.5, 128.4, 126.4, 126.3, 126.2, 111.6, 111.3, 107.2, 106.5, 103.5, 103.3, 85.0 (1C isom + 1C normal), 83.7, 83.6, 46.0, 44.7, 35.5, 35.4, 34.9, 28.9, 28.1, 26.6, 25.1

for the mixture of isomers:

**HRMS:** $C_{16}H_{15}NO_2$ [$M^+$]; calculated: 253.1103, found 253.1096.

**IR** ($CCl_4$): $\nu$ ($cm^{-1}$) 2923, 1685, 1612, 1531, 1503, 1403, 1137, 1060, 1015.

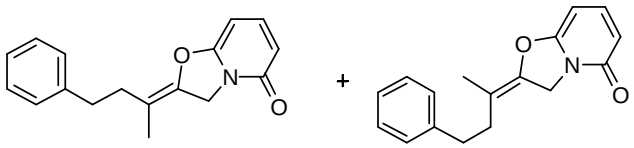
| **(2E)- and (2Z)-2-(4-phenylbutan-2-ylidene)-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-one and 2-(4-phenylbutan-2-yl)-5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.177 et 2.178)** | $C_{17}H_{17}NO_2$ | **MW = 267.3 g.mol$^{-1}$** |
|---|---|---|

**Procedure:** see general procedure 2.4

**Product:** pale yellow oil

**Yield:** 87 % (*exo*$_{Z:E:}$*:endo* $1_{1:1}$ : 0.2) (m = 23.2 mg, n = 0.0868 mmol)

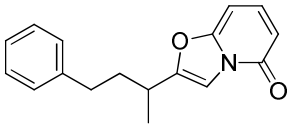
Major isomers:



**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.34 (dt, *J* = 7.8 Hz, *J* = 9.0 Hz, 1H both isomers), 6.13 (dd, *J* = 0.8, *J* = 9.0 Hz, 1H Z isomer), 6.10 (dd, *J* = 0.7 Hz, *J* = 9.1 Hz, 1H E isomer), 5.67 (d, *J* = 7.5 Hz, 1H both isomers), 4.75-4.72 (m, 2H E isomer), 4.49-4.46 (m, 2H Z isomer), 2.77-2.73 (m, 2H both isomers), 2.51 (t, *J* = 7.7 Hz, 2H Z isomer), 2.25 (t, *J* = 7.5 Hz, 2H E isomer), 1.83 (t, *J* = 2.2 Hz, 3H E isomer), 1.66 (t, *J* = 1.7 Hz, 3H Z isomer).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) E isomer: 160.5, 155.7, 142.2, 140.9, 140.6, 128.6 (2C), 128.4 (2C), 126.4 (2C), 110.9, 83.6, 45.0, 35.3, 33.4, 16.6. Z isomer: 160.6, 155.8, 142.2, 141.4, 139.9, 128.6 (2C), 128.4 (2C), 126.1 (2C), 110.8, 83.6, 45.3, 33.7, 32.3, 14.4.

Minor isomer:



**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.56-7.55 (m, 1H), 7.50 (dd, *J* = 8.0 Hz, *J* = 8.9 Hz, 1H), 7.30-7.26 (m, 2H), 7.22-7.14 (m, 3H), 6.26 (dd, *J* = 0.5 Hz, *J* = 9.0 Hz, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 2.90 (dt, *J* = 7.0 Hz, *J* = 7.2 Hz, 1H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.14-2.05 (m, 1H), 1.95-1.87 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H). **$^{13}$C NMR is impossible to get.**

for the mixture of isomers:

**HRMS:** $C_{17}H_{17}NO_2$ [$M^+$]; calculated: 267.1259, found 267.1251.

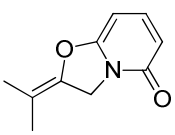
**IR** ($CCl_4$): *v* ($cm^{-1}$) 2928, 1682, 1610, 1530, 1497, 1406, 1160, 1133, 1063, 1031.

**2-(propan-2-ylidene)-*2H,3H,5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-one** and **2-(propan-2-yl)-*5H-[1,3]*oxazolo*[3,2-a]*pyridin-5-one (2.179 et 2.180)** $C_{10}H_{11}NO_2$ **MW = 177.2 g.mol$^{-1}$**

**Procedure:** see general procedure 2.4

**Product:** colorless oil

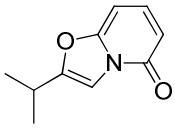
**Yield:** 98 % (*exo:endo* 10:1) (m = 17.4 mg, n = 0.0981 mmol)



Major isomer

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.35 (dd, *J* = 7.6 Hz, *J* = 9.1 Hz, 1H), 6.12 (d, *J* = 9.1 Hz, 1H), 5.69 (d, *J* = 7.5 Hz, 1H), 4.77-4.74 (m, 2H), 1.78-1.76 (m, 3H), 1.67-1.64 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 160.7, 155.9, 142.3, 139.2, 110.8, 107.5, 83.6, 45.2, 18.5, 16.5.



Minor isomer

**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.52 (m, 1H), 7.49 (dd, *J* = 8.0 Hz, *J* = 8.8 Hz, 1H), 6.24 (d, *J* = 8.9 Hz, 1H), 6.21 (d, *J* = 8.8 Hz, 1H), 2.99 (dqq, *J* = 1.2 Hz, *J* = 6.8 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 6H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ (ppm) 160.7, 155.9, 142.3, 107.0, 104.9, 85.0, 77.3, 26.3, 20.0 (2C).

for the mixture of the two isomers:

**HRMS:** $C_{10}H_{11}NO_2$ [$M^+$]; calculated: 177.0790, found 177.0794.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2920, 1680, 1614, 1601, 1532, 1474, 1406, 1235, 1159, 1114, 1063, 1031.

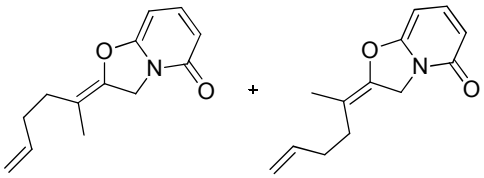
**(2E)- and (2Z)-2-(hex-5-en-2-ylidene)-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-one and 2-(hex-5-en-2-yl)-5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.181 et 2.182)** **$C_{13}H_{15}NO_2$** **MW = 217.3 g.mol$^{-1}$**

**Procedure:** see general procedure 2.4

**Product:** pale yellow oil

**Yield:** 83 % (*exo*$_{Z:E:}$*:endo* $1_{1:1}$ : 0.2) (m = 18.03 mg, n = 0.0831 mmol)

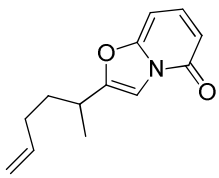
The product is obtained as a mixture of 3 isomers: the Z and E isomers and the regioisomer bearing the double bond inside the 5-membered ring cycle in a 1 : 1 : 0.2 ratio.



Major isomers:

**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.37 (dd, *J* = 7.6 Hz, *J* = 9.1 Hz, 1H both isomers), 6.14 (dd, *J* = 0.6 Hz, *J* = 9.2 Hz, 1H both isomers), 5.79 (m, 1H both isomers), 5.86-5.73 (d, *J* = 7.5 Hz, 1H both isomers), 5.09-4.96 (m, 2H both isomers), 4.80-4.75 (m, 2H both isomers), 2.33-2.29 (m, 2H E isomer), 2.24-2.18 (m, 2H Z isomer + 1H E isomer), 2.15-2.04 (m, 1H E isomer + 1H Z isomer), 1.90-1.86 (m, 1H Z isomer), 1.78 (t, *J* = 2.2 Hz, 3H E isomer), 1.67 (t, *J* = 1.7 Hz, 3H Z isomer).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 160.7 (2C), 155.9, 155.8, 142.3, 142.2, 139.7, 139.3, 137.8, 137.0, 116.0 (2C), 115.2 (2C), 110.9 (2C), 83.7, 83.7, 45.3, 45.2, 32.5, 31.4, 31.3, 29.7, 16.3, 14.1.



Minor isomer:

**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.55-7.54 (m, 1H), 7.51 (dd, *J* = 8.0 Hz, *J* = 8.9 Hz, 1H), 6.26 (d, *J* = 8.9 Hz, 1H), 6.23 (d, *J* = 7.9 Hz, 1H), 5.95-5.70 (m, 1H), 5.09-4.96 (m, 2H), 2.92 (q app, *J* = 6.4 Hz, 1H), 2.20-2.12 (m, 2H), 1.90-1.85 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 3H).

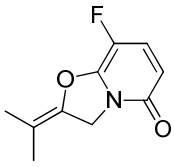
**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 160.7, 157.2, 140.2, 137.3, 115.7, 110.8, 107.1, 105.6, 85.1, 33.4, 30.9, 30.7, 17.9.

**8-fluoro-2-(propan-2-ylidene)-2H,3H,5H-[1,3]oxazolo[3,2-a]pyridin-5-one and 8-fluoro-2-(propan-2-yl)-5H-[1,3]oxazolo[3,2-a]pyridin-5-one (2.183 et 2.184)** $C_{10}H_{10}FNO_2$ **MW = 195.2 g.mol$^{-1}$**

**Procedure:** see general procedure 2.4

**Product:** pale yellow oil

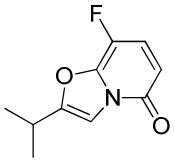
**Yield:** 99 % (*exo:endo* 15:1) (19.2 mg, n = 0.0989 mmol)



Major isomer:

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.35 (t app, *J* = 9.7 Hz, 1H), 6.01 (dd, *J* = 3.3 Hz, *J* = 9.9 Hz, 1H), 4.77 (bs, 2H), 1.81 (bs, 3H), 1.67 (bs, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 158.2, 143.4 (d, *J* = 22.3 Hz), 139.6, 133.3 (d, *J* = 18.1 Hz), 129.0 (d, *J* = 223.4 Hz), 109.9 (d, *J* = 4.1 Hz), 109.0, 45.8, 18.6, 16.5.



minor isomer:

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.22-7.16 (m, 2H), 5.86-5.81 (m, 1H), 2.84 (septuplet, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 6H). **$^{13}$C NMR is impossible to get.**

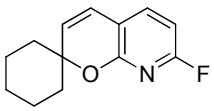
for the mixture of the two isomers:

**HRMS:** $C_{10}H_{10}FNO_2$ [$M^+$]; calculated: 195.0696, found 195.0702.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2920, 1703, 1625, 1603, 1545, 1537, 1471, 1285, 1230, 1153, 1112, 1056, 1001.

- *<u>Preparation of the pyranopyridines</u>*

**7'-fluorospiro[cyclohexane-1,2'-pyrano*[2,3-b]*pyridine] (2.185)** $C_{13}H_{14}FNO$ **MW = 219.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.7

**Product:** colorless oil

**Yield:** 70 % (m = 15.4 mg, n = 0.0702 mmol)

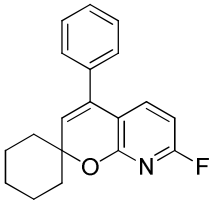
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.32 (t, *J* = 8.0 Hz, 1H), 6.40 (dd, *J* = 2.4 Hz, *J* = 7.9 Hz, 1H), 6.28 (d, *J* = 9.8 Hz, 1H), 5.63 (d, *J* = 9.8 Hz, 1H), 2.02-1.98 (m, 2H), 1.89-1.80 (m, 2H), 1.66-1.48 (m, 5H), 1.39-1.29 (m, 1H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ (ppm) 162.1 (d, *J* = 239.5 Hz), 158.9 (d, *J* = 15.2 Hz), 138.4 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 2.5 Hz), 120.5, 113.4 (d, *J* = 5.2 Hz), 101.0 (d, *J* = 35.9 Hz), 80.8, 36.9 (2C), 25.0, 21.0 (2C).

**HRMS:** $C_{13}H_{14}FNO$ [$M^+$]; calculated: 219.1059, found: 219.1049.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2938, 2866, 1643, 1596, 1582, 1464, 1420, 1308, 1214, 1168.

**7'-fluoro-4'-phenylspiro[cyclohexane-1,2'-pyrano*[2,3-b]*pyridine (2.188)** $C_{19}H_{18}FNO$ **MW = 295.4 g.mol$^{-1}$**



**Procedure:** see general procedure 2.7

**Product:** colorless oil

**Yield:** 60 % (m = 17.7 mg, n = 0.0599 mmol, 91% brsm)

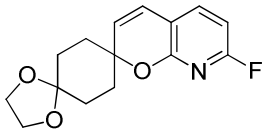
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.43-7.38 (m, 4H), 7.31-7.28 (m, 2H), 6.39 (dd, *J* = 2.6 Hz, *J* = 8.1 Hz, 1H), 5.63 (s, 1H), 2.07-2.03 (m, 2H), 1.93-1.83 (m, 2H), 1.70-1.51 (m, 4H), 1.44-1.35 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$): δ (ppm) 162.2 (d, *J* = 238.6 Hz), 159.3 (d, *J* = 24.2 Hz), 138.0 (d, *J* = 8.1 Hz), 137.3, 133.6, 128.7 (2C), 128.5 (2C), 128.3, 127.8, 114.5 (d, *J* = 5.2 Hz), 100.9 (d, *J* = 35.6 Hz), 80.3, 36.6 (2C), 25.1, 21.2 (2C).

**HRMS:** $C_{19}H_{18}FNO$ [$M^+$]; calculated: 295.1372; found: 295.1369.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2942, 2865, 1643, 1596, 1467, 1418, 1300, 1212.

**7''-fluorodispiro[1,3-dioxolane-2,1'-cyclohexane-4',2''-pyrano*[2,3-b]*pyridine] (2.189)** $C_{15}H_{16}FNO_3$ **MW = 277.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.7

**Product:** white solid

**Yield:** 65 % (m = 18.0 mg, n = 0.0649 mmol)

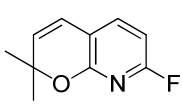
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.33 (t, *J* = 7.9 Hz, 1H), 6.41 (dd, *J* = 2.3 Hz, *J* = 7.9 Hz, 1H), 6.30 (d, *J* = 9.8 Hz, 1H), 5.57 (d, *J* = 9.8 Hz, 1H), 3.98-3.91 (m, 4H), 2.17-2.08 (m, 4H), 1.84-1.75 (m, 2H), 1.63-1.56 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$): δ (ppm) 162.2 (d, *J* = 230.0 Hz), 158.6 (d, *J* = 26.1 Hz), 138.6 (d, *J* = 8.3 Hz), 129.4 (d, *J* = 2.5 Hz), 121.1, 113.2 (d, *J* = 5.3 Hz), 108.0, 101.3 (d, *J* = 35.9 Hz), 79.6, 64.5, 64.3, 34.5 (2C), 29.5 (2C).

**HRMS:** $C_{15}H_{16}FNO_3$ [$M^+$]; calculated: 277.1114; found: 277.1111.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 2938, 2881, 1582, 1558, 1551, 1547, 1543, 1465, 1420, 1306, 1214, 1104, 1030.

**7-fluoro-2,2-dimethyl-*2H*-pyrano*[2,3-b]*pyridine (2.190)** $C_{10}H_{10}FNO$ **MW = 179.2 g.mol$^{-1}$**



**Procedure:** see general procedure 2.7

**Product:** colorless oil

**Yield:** 79 % (m = 14.2 mg, n = 0.0792 mmol)

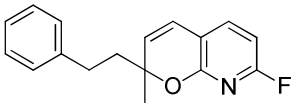
**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.33 (t app, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 2.4 Hz, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 9.8 Hz, 1H), 5.5ç (d, *J* = 9.8 Hz, 1H), 1.50 (s, 6H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$): δ (ppm) 162.1 (d, *J* = 239.5 Hz), 158.8 (d, *J* = 15.1 Hz), 138.4 (d, *J* = 8.2 Hz), 130.1 (d, *J* = 2.8 Hz), 120.1, 112.5 (d, *J* = 5.2 Hz), 101.1 (d, *J* = 36.0 Hz) 80.0, 28.8 (2C).

**HRMS:** $C_{10}H_{10}FNO$ [$M^+$]; calculated: 179.0646; found: 179.0646.

**IR** ($CCl_4$): *v* ($cm^{-1}$) 3049, 2983, 2930, 1647, 1596, 1583, 1467, 1419, 1375, 1311, 1289, 1264, 1199, 1115, 1028.

**7-fluoro-2-methyl-2-(2-phenylethyl)-*2H*-pyrano*[2,3-b]*pyridine (2.191)** $C_{17}H_{16}FNO$ **MW = 269.3 g.mol$^{-1}$**



**Procedure:** see general procedure 2.7

**Product:** colorless oil

**Yield:** 65 % (m = 17.6 mg, n = 0.0654 mmol)

**$^1$H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 7.9 Hz, 1H), 7.29-7.23 (m, 2H), 7.20-7.15 (m, 3H), 6.42 (dd, *J* = 2.4 Hz, *J* = 7.9 Hz, 1H), 6.37 (d, *J* = 9.9 Hz, 1H), 5.59 (d, *J* = 9.9 Hz, 1H), 2.81 (ddd, *J* = 5.3 Hz, *J* = 13.5 Hz, *J* = 18.6 Hz, 1H), 2.73 (ddd, *J* = 4.8 Hz, *J* = 13.5 Hz, *J* = 18.3 Hz, 1H), 2.15 (ddd, *J* = 5.4 Hz, *J* = 12.1 Hz, *J* = 13.8 Hz, 1H), 1.95 (ddd, *J* = 5.0 Hz, *J* = 12.2 Hz, *J* = 13.9Hz, 1H), 1.52 (s, 3H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 162.2 (d, *J* = 230.2 Hz), 159.0 (d, *J* = 16.3 Hz), 141.7, 138.6 (d, *J* = 8.3 Hz), 128.7 (d, *J* = 2.7 Hz), 128.5 (2C), 128.4 (2C), 126.0, 121.2, 112.4 (d, *J* = 5.2 Hz), 101.0 (d, *J* = 35.9 Hz), 82.4, 44.0, 30.4, 27.9.

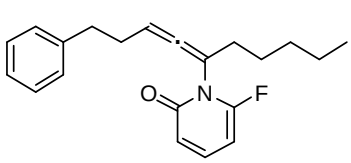
**HRMS:** $C_{17}H_{16}FNO$ [$M^+$]; calculated: 269.1216; found: 269.1218 .

**IR** ($CCl_4$): *v* ($cm^{-1}$) 3065, 2977, 2929, 1647, 1597, 1583, 1559, 1551, 1547, 1465, 1419, 1384, 1312, 1232, 1193, 1100, 1030.

- *Preparation of allenes*

Allenes could only be isolated in very little quantity as side products from various reactions. No isolated yields or procedure are therefore given for those compounds.

**6-fluoro-1-(1-phenyldeca-3,4-dien-5-yl)-1,2-dihydropyridin-2-one (2.71)** $C_{20}H_{24}FNO$ **MW = 313.4 g.mol$^{-1}$**



**Product:** colorless oil

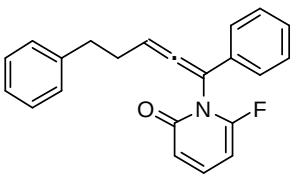
**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.40 (dd, *J* = 8.4 Hz, *J* = 9.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.17-7.15 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 9.3 Hz, 1H), 5.85 (dd, *J* = 4.4 Hz, *J* = 7.5 Hz, 1H), 2.90-2.76 (m, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.51 (dt, *J* = 6.9 Hz, *J* = 15.2 Hz, 1H), 2.44-2.34 (m, 1H), 1.67-1.60 (m, 2H), 1.34-1.25(m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 194.4, 160.8 (d, *J* = 6.4 Hz), 154.9 (d, *J* = 266.4 Hz), 144.1, 141.0 (d, *J* = 11.5 Hz), 140.1, 133.0, 128.7 (2C), 128.4 (2C), 126.5, 116.1 (d, *J* = 4.6 Hz), 87.9 (d, *J* = 20.5 Hz), 37.3, 33.8, 31.3, 30.4, 23.9, 22.5, 14.0.

**HRMS:** $C_{20}H_{24}FNO$ [$M^+$]; calculated: 313.1842, not found.

**IR ($CCl_4$):** ν (cm$^{-1}$) 2959, 2931, 2873, 1697, 1619, 1536, 1533, 1497, 1434, 1403, 1264, 1134, 1032.

**1-(1,5-diphenylpenta-1,2-dien-1-yl)-6-fluoro-1,2-dihydropyridin-2-one (2.73)** $C_{21}H_{18}FNO$ **MW = 319.4 g.mol$^{-1}$**



**Product:** colorless oil

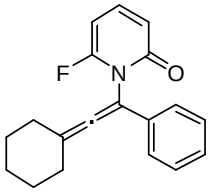
**$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta$ (ppm) 7.40 (dd, *J* = 8.4 Hz, *J* = 9.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.17-7.15 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 9.3 Hz, 1H), 5.85 (dd, *J* = 4.4 Hz, *J* = 7.5 Hz, 1H), 2.90-2.76 (m, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.51 (dt, *J* = 6.9 Hz, *J* = 15.2 Hz, 1H), 2.44-2.34 (m, 1H), 1.67-1.60 (m, 2H), 1.34-1.25(m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ (ppm) 191.0, 161.0 (d, *J* = 6.4 Hz), 155.1 (d, *J* = 267.2 Hz), 146.8, 141.1 (d, *J* = 11.7 Hz), 140.1, 136.9, 132.6, 132.5, 129.7 (2C), 128.7 (2C), 128.4 (4C), 126.6, 116.2, 116.1, 87.0 (d, *J* = 20.3 Hz), 33.8, 30.5.

**HRMS:** $C_{21}H_{18}FNO$ [$M^+$]; calculated: 319.1372, not found.

**IR ($CCl_4$):** ν (cm$^{-1}$) 3066, 3030, 1695, 1671, 1618, 1533, 1434, 1268, 1139.

**1-(2-cyclohexylidene-1-phenylethenyl)-6-fluoro-1,2-dihydropyridin-2-one (2.123)** $C_{19}H_{18}NFO$ **MW = 295.4 g.mol$^{-1}$**



**Product:** colorless oil

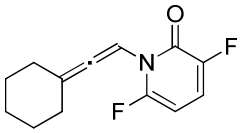
**$^{1}$H NMR** (400MHz, $CDCl_3$): δ (ppm) 7.41 (q, *J* = 8.9 Hz, 1H), 7.34-7.3à (m, 2H), 7.24-7.17 (m, 3H), 6.48 (d, *J* = 9.3 Hz, 1H), 5.90 (tdd, *J* = 1.0 Hz, *J* = 4.2 Hz, *J* = 7.5 Hz, 1H), 2.47-2.43 (m, 2H), 2.33-2.27 (m, 2H), 1.80-1.63 (m, 5H), 1.60-1.51 (m, 2H).

**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) δ (ppm) 196.9, 161.5 (d, $J_{CF}$ = 6.6 Hz), 156.1 (d, $J_{CF}$ = 266.3 Hz), 140.2 (d, $J_{CF}$ = 11.6 Hz), 133.5, 128.7 (2C), 127.5, 124.6 (d, $J_{CF}$ = 8.6 Hz, 2C), 116.3 (d, $J_{CF}$ = 4.7 Hz), 114.5, 102.7 (d, $J_{CF}$ = 2.2 Hz), 87.2, 86.9, 30.9, 27.4 (2C), 25.8 (2C). ).

**HRMS:** $C_{19}H_{18}NFO$ [$M^+$]; calculated: 295.1372, found 295.1371.

**IR ($CCl_4$):** ν ($cm^{-1}$) 2933, 2856, 1694, 1619, 1533, 1432, 1132

**1-(2-cyclohexylideneethenyl)-3,6-difluoro-1,2-dihydropyridin-2-one** $C_{13}H_{13}F_2NO$ **MW = 237.2 g.mol$^{-1}$**

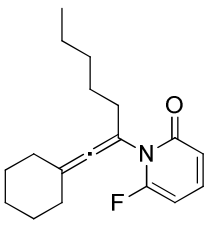


**Product:** colorless oil

**$^{1}$H NMR (400 MHz, $CDCl_3$):** *δ* (ppm) 7.07 (dt, *J* = 6.6 Hz, *J* = 8.5 Hz, 1H), 6.65-6.63 (m, 1H), 5.75 (ddd, *J* = 3.3 Hz, *J* = 5.3 Hz, *J* = 8.5 Hz, 1H), 2.29-2.20 (m, 4H), 1.68-1.60 (m, 4H), 1.57-1.54 (m, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** *δ* (ppm) 193.8, 153.0 (dd, *J* = 4.6 Hz, *J* = 27.2 Hz), 150.1 (dd, *J* = 2.7 Hz, *J* = 267.5 Hz), 147.4 (dd, *J* = 4.0 Hz, *J* = 242.8 Hz), 118.3 (dd, *J* = 11.1 Hz, *J* = 19.2 Hz), 112.2, 86.7 (d, *J* = 4.6 Hz), 83.6 (dd, *J* = 5.6 Hz, *J* = 23.7 Hz), 30.1 (2C), 25.6 (2C), 24.5.

**1-(1-cyclohexylidenehept-1-en-2-yl)-6-fluoro-1,2-dihydropyridin-2-one (2.123)** $C_{18}H_{24}FNO$ **MW = 289.4 g.mol$^{-1}$**



**Product:** colorless oil

**$^{1}$H NMR (400 MHz, $CDCl_3$):** *δ* (ppm) 7.29 (td, *J* = 7.6 Hz, 8.9 Hz, 1H), 6.35 (d, 9.3 Hz, 1H), 5.79 (ddd, *J* = 1.0 Hz, *J* = 4.4 Hz, *J* = 7.5 Hz, 1H), 2.32-2.24 (m, 4H), 2.18-2.12 (m, 2H), 1.70-1.28 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** *δ* (ppm) 195.2, 161.5 (d, *J* = 6.5 Hz), 155.9 (d, *J* = 266.2 Hz), 139.7 (d, *J* = 21.8 Hz), 116.0 (d, *J* = 4.6 Hz), 111.9, 101.8 (d, *J* = 1.7 Hz), 86.9 (d, *J* = 21.8 Hz), 31.7, 31.2 (2C), 31.1, 27.3 (2C), 26.5, 25.9, 22.6, 14.1.