Supporting Information

Alkynyl Triazenes as Fluoroalkyne Surrogates: Regioselective Access to 4-Fluoro-2-Pyridones by a Rh(III)-Catalyzed C-H Activation-Lossen Rearrangement-Wallach Reaction

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1. Materials and Methods:

All reactions were carried out under an atmosphere of dry nitrogen or nitrous oxide (purity: 99.999%, Messer Schweiz AG) using standard Schlenk and glovebox techniques in oven-dried glassware with magnetic stirring, unless otherwise indicated. Reagents and solvents were purchased from Aldrich, Acros, Alfa Aesar, Abcr, or TCI. Chemicals were used as obtained from the suppliers. Dry Et₂O, DCM, THF were obtained using a solvent purification system with an aluminum oxide column (Innovative Technologies). Falcon tubes used are 14 mL non-pyrogenic polypropylene round-bottomed tubes, (17 x 100 mm), purchased from Corning Science México S.A. De C.V.

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or basic alumina (Acros, Brockmann activity 1, 50-200 μm, 60A). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. For the purification of acid sensitive compounds, silicagel 230-400 mesh particle size (100 g) was deactivated prior to use by adding dichloromethane containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying of the silica at room temperature under oil pump vacuum overnight.

NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe and Bruker DRX600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; brs, broad singlet. Proton decoupled Carbon-13 nuclear magnetic resonance (¹³C NMR) data were acquired at 101 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to CDCl₃ (77.16 ppm).

Electrospray–ionisation HRMS data were acquired on a Q–Tof Ultima mass spectrometer (Waters) or an Agilent LC-MS TOF. High resolution mass are given in m/z. Data from the Lock–Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm⁻¹).
The reported alkynyl triazenes 2a, 2b, 2c, 2e, 2d, 2f and 2g were synthesized by reaction of lithium amides with N$_2$O and alkynyl Grignard reagents as described in the literature.$^{1,2}$ The spectra were in good agreement with the reported data.

The new alkynyl triazenes 2e and 2h were obtained in a similar fashion, and details are given below: 

Scheme S1: General procedure for the synthesis of alkynyl triazenes with nitrous oxide
General procedure for the synthesis of non-commercial alkynyl Grignard reagents:

Ethylmagnesium bromide (1 M, 1.0 eq.) was added to a solution of the respective alkyne in dry THF (1.5–2 M) under an atmosphere of N₂. The mixture was stirred at RT for 1 h and subsequently heated to 50 °C for 1 h. The solution was allowed to cool to RT, and it was then used for the triazene syntheses described below.

General Procedure for the synthesis of alkynyl triazenes with nitrous oxide:

The corresponding lithium amide (2 mmol, 1.0 eq.) was dissolved in THF (4 mL), and the resulting solution was stirred vigorously under an atmosphere of N₂O for 3 h at RT. A white precipitate formed. The N₂O atmosphere was then replaced by an atmosphere of dry N₂ and the corresponding Grignard reagent (1.5 eq.) in THF was added, resulting in formation of a yellow solution. The solution was stirred for 3 h at 50 °C. The mixture was quenched with water (20 mL), extracted with ethyl acetate (3 x 20 mL), and the unified organic phases were dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the product was obtained in sufficient purity or purified as stated below.

(E)-3,3-diisopropyl-1-(prop-1-ynyl)triaz-1-ene (2e):

The product was synthesized from lithium diisopropylamide (5.0 mmol, 531 mg, 1.0 eq.), N₂O and prop-1-ynylmagnesium bromide in THF (0.61 M, 13 mL, 1.5 eq.) according to the general procedure. After quenching, extraction, and removal of the solvent under reduced pressure, the crude product was purified by column chromatography.

Isolated as a yellow solid in 61 % yield (842 mg). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.47 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 7.1 Hz, 1H), 7.53 (dp, J = 16.2, 7.6, 6.5 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H), 5.21 (hept, J = 7.1 Hz, 1H), 4.08 (hept, J = 6.4 Hz, 1H), 1.42 (d, J = 6.6 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 133.4, 133.2, 129.4, 128.2, 127.4, 126.9, 126.3, 126.3, 125.5, 122.7, 99.0, 78.0, 50.5, 47.6, 23.6, 19.3; IR (ATR): ν 2976, 2933, 2183, 1506, 1455, 1412, 1356, 1297, 1258, 1248, 1216, 1156, 1129,
1095, 979, 800, 775, 563 cm$^{-1}$; **HRMS (ESI-TOF):** m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{22}$N$_3$+ 280.1808; Found 280.1811.

(\(E\))-3,3-diisopropyl-1-(prop-1-yn-1-yl)triaz-1-ene (2h):

The product was synthesized from lithium dimethylamide (5.5 mmol, 286 mg, 1.0 eq.), N$_2$O and prop-1-yn-1-ylmagnesium bromide in THF (0.64 M, 13 mL, 1.5 eq.) according to the general procedure.

Deviation from the general procedure: lithium dimethyl amide was stirred under N$_2$O-atmosphere for 22 h. Grignard reagents were stirred at RT for 2 h, then stirred at 50 °C for 2 h. After the addition of the Grignard reagent, the reaction was stirred at 50 °C for 4 h. After quenching, extraction, and removal of the solvent under reduced pressure, the crude product was purified by column chromatography.

Isolated as a colourless oil in 17% yield (131 mg). **$^1$H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.46 (s, 3H), 3.09 (s, 3H), 1.47 (tt, $J = 8.2$, 5.0 Hz, 1H), 0.85–0.78 (m, 2H), 0.76–0.69 (m, 2H); **$^{13}$C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 84.0, 80.1, 43.5, 36.3, 8.9, 0.3; **IR (ATR):** $\tilde{\nu}$ 2975, 2934, 1466, 1394, 1380, 1364, 1349, 1261, 1235, 1200, 1167, 1152, 1128, 1096, 1070, 1049, 1020, 915, 896, 866, 808, 584, 569, 538, 484 cm$^{-1}$. **HRMS (ESI-TOF):** m/z: [M + H]$^+$ Calcd for C$_7$H$_{12}$N$_3$+ 138.1026; Found 138.1021.
3. Preparation of Acrylamide Substrates

All acrylamide substrates were prepared based on reported procedure\textsuperscript{3,4}, as outlined in Scheme S2 or S3. All spectra were in good agreement with the reported data.

\textit{Scheme S2.}

**Step 1:** Two drops of DMF were added to a mixture of acrylic acid A1 (1.0 equiv.) and (COCl)\textsubscript{2} (1.1 equiv.) in DCM (0.1 M). The mixture was stirred at RT for 3 h. Volatiles were evaporated under reduced pressure to afford the crude acyl chloride. NH\textsubscript{3}OH.HCl (1.2 equiv.) and K\textsubscript{2}CO\textsubscript{3} (1.2 equiv.) were added, and the mixture was dissolved in 1:1 mixture of EtOAc and water (0.25 M) at 0 °C. The reaction was allowed to stir at this temperature and slowly warm up to RT over 16 h. Water (30 mL) and EtOAc (30 mL) were added, and the organic layer was separated. The aqueous layer was washed with EtOAc (30 x 2 mL). The organic layers were combined, dried with MgSO\textsubscript{4} and concentrated under reduced pressure to afford crude hydroxamic acid A2, which was directly used for the next step.

**Step 2:** A mixture of hydroxamic acid A2 (1.0 equiv.), pivalic anhydride (1.5 eq) and triethylamine (1.5 equiv.) in THF (0.2 M) was stirred at RT for 16 h. Water (30 mL) and EtOAc (30 mL) were added, and the organic layer was separated. The aqueous layer was washed with EtOAc (30 mL). The organic layers were combined, dried with MgSO\textsubscript{4} and concentrated under reduced pressure to afford the crude, which was then purified by column chromatography eluting with 0 % to 20 % EtOAc in pentane to give acrylamide product 1x.
Scheme S3.

**Step 1**: A mixture of ester A3 (1.0 equiv.), paraformaldehyde (1.5 eq) and K$_2$CO$_3$ (1.1 equiv.) in PhMe (0.3 M) was heated at 80 °C for 16 h. The mixture was cooled at room temperature, water (30 mL) and EtOAc (30 mL) were added, and the organic layer was separated. The aqueous layer was washed with EtOAc (30 mL). The organic layers were combined, dried with MgSO$_4$ and concentrated under reduced pressure to afford crude acrylic ester product A4, which was directly used for the next step.

**Step 2**: Crude acrylic ester A4 and LiOH (5.0 eq) were dissolved in THF/H$_2$O (1:1, 0.25 M). The reaction mixture was stirred at 80°C overnight. After cooling to RT, The aqueous phase was acidified with 2N HCl and extracted with EtOAc (30 mL x 2). The combined organic layers were dried over MgSO$_4$. The volatile compounds were removed under reduced pressure to afford crude acrylic acid A5, which was directly used for the next step.

**Step 3**: To a solution of crude acrylic acid A5 in DCM (0.2 M) was added pyridine (7.0 equiv.), EDCI (2 equiv.) and NH$_2$OPiv.TfOH$^5$ (1.2 eq) at 0°C. The mixture was stirred at 0°C and allowed to slowly warm up to RT overnight. The mixture was diluted with DCM (20 mL), washed with 2N HCl (20 mL), saturated aq. NaHCO$_3$ (20 mL) and brine (20 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give the crude, which was then purified by column chromatography eluting with 0 % to 20 % EtOAc in pentane to give acrylamide product 1x.
2-Benzyl-N-(pivaloyloxy)acrylamide (1a):
Prepared according to S2. Obtained as white solid in 74 % yield over 2 steps (1.79 g). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.93 (s, 1H), 7.35–7.30 (m, 2H), 7.23 (dd, } J = 9.2, 7.5 Hz, 3H), 5.93 (s, 1H), 5.37 (t, } J = 1.5 Hz, 1H), 3.67 (s, 2H), 1.31 (s, 9H).

2-Phenyl-N-(pivaloyloxy)acrylamide (1b):
Prepared according to S2. Obtained as white solid in 59 % yield over 2 steps (540 mg). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.79 (s, 1H), 7.49–7.43 (m, 2H), 7.43–7.35 (m, 3H), 6.20 (d, } J = 1.0 Hz, 1H), 5.77 (d, } J = 1.0 Hz, 1H), 1.34 (s, 9H).

N-(pivaloyloxy)-2-(4-(trifluoromethyl)phenyl)acrylamide (1c):
Prepared according to S3. Obtained as white solid in 26 % yield over 3 steps (244 mg). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.76 (s, 1H), 7.66 (d, } J = 8.3 Hz, 2H), 7.61 (d, } J = 8.3 Hz, 2H), 6.21 (s, 1H), 5.88 (s, 1H), 1.34 (s, 9H); ^{19}F NMR (376 MHz, CDCl}_{3}\delta (ppm) = -62.7.

N-(pivaloyloxy)-2-(p-toly)acrylamide (1d):
Prepared according to S3. Obtained as white solid in 24 % yield over 2 steps (336.5 mg). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.80 (s, 1H), 7.36 (d, } J = 8.1 Hz, 2H), 7.20 (d, } J = 7.9 Hz, 2H), 6.16 (s, 1H), 5.73 (d, } J = 1.0 Hz, 1H), 2.37 (s, 3H), 1.33 (s, 9H).

2-(4-Bromophenyl)-N-(pivaloyloxy)acrylamide (1e):
Prepared according to S3. Obtained as white solid in 16 % yield over 3 steps (1.18 g). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.78 (s, 1H), 7.56–7.49 (m, 2H), 7.38–7.32 (m, 2H), 6.14 (s, 1H), 5.79 (s, 1H), 1.34 (s, 9H).

N-(pivaloyloxy)-2-(2-(trifluoromethyl)phenyl)acrylamide (1f):
Prepared according to S3. Obtained as white solid in 59 % yield over 3 steps (309 mg). \[\text{^{1}H NMR (400 MHz, CDCl}_{3}\delta (ppm) = 8.59
(s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 6.61 (s, 1H), 5.69 (s, 1H), 1.30 (s, 9H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -58.3.

2-(Naphthalen-1-yl)-N-(pivaloyloxy)acrylamide (1g):

Prepared according to S3. Obtained as white solid in 7 % yield over 3 steps (440 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 8.48 (s, 1H), 7.96–7.87 (m, 3H), 7.59–7.44 (m, 4H), 6.82 (d, J = 1.6 Hz, 1H), 5.78 (d, J = 1.6 Hz, 1H), 1.26 (s, 9H).

N-(pivaloyloxy)methacrylamide (1h):

Prepared according to step 3 of S3. Obtained as colourless oil in 38 % yield (340 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 9.00 (s, 2H), 5.83 (t, J = 1.0 Hz, 1H), 5.53–5.44 (m, 1H), 1.99 (dd, J = 1.6, 1.0 Hz, 3H), 1.34 (s, 9H).

2-Cyclopentyl-N-(pivaloyloxy)acrylamide (1i):

Prepared according to S3. Obtained as colourless solid in 39 % yield over 3 steps (442 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 5.68 (d, J = 1.0 Hz, 1H), 5.40 (d, J = 1.7 Hz, 1H), 2.83 (dddd, J = 16.7, 8.9, 7.0, 3.8 Hz, 1H), 1.99–1.84 (m, 2H), 1.73–1.65 (m, 2H), 1.61 (tdq, J = 7.0, 4.9, 3.0, 2.1 Hz, 2H), 1.51–1.40 (m, 2H), 1.33 (s, 9H).

2-Methylene-N-(pivaloyloxy)pent-4-enamide (1j):

Prepared according to S3. Obtained as colourless solid in 13 % yield over 3 steps (160 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 5.92 (d, J = 0.9 Hz, 1H), 5.85 (ddtd, J = 16.2, 10.5, 6.6, 1.1 Hz, 1H), 5.49 (t, J = 1.5 Hz, 1H), 5.18 (dt, J = 6.5, 1.5 Hz, 1H), 5.15 (q, J = 1.4 Hz, 1H), 3.09 (dt, J = 6.8, 1.3 Hz, 1H), 1.32 (s, 9H).
4. Additional screening details to suppress Lossen rearrangement

![Chemical structure](image)

2.5 mol% [Cp*RhCl₂](2) 2 eq. Base
EtOH(0.3M), 23°C, 12 h

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a) at 80°C.

b) Instead of using [Cp*RhCl₂](2), 5 mol% Cp*Cot₂(CO) and 10 mol% AgOTf were used.
5. 4-Triazeny1-2-pyridone Formation

(E)-6-Benzyl-4-((3,3-diisopropyltriaz-1-en-1-yl)-3-phenylpyridin-2(1H)-one (3aa):

[Cp*RhCl₂]₂ (2.50 µmol, 1.5 mg, 5 mol% based on [Rh]), acrylamide 1a (0.12 mmol, 31.4 mg, 1.2 equiv.), triazene 2a (0.10 mmol, 22.9 mg, 1.0 equiv.) and NaOAc (0.20 mmol, 16.4 mg, 2.0 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of dry THF (0.2 mL) at RT. The mixture was stirred at RT for 1 h. After completion of the reaction, volatiles were evaporated. Crude was purified by silica gel chromatography eluting with pentane/EtOAc to afford the 4-triazeny1-2-pyridone product 3aa.

Obtained as light brown solid in 81 % yield (31.65 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.47–7.43 (m, 2H), 7.35–7.28 (m, 7H), 7.24–7.19 (m, 1H), 6.43 (s, 1H), 4.75 (m, J = 6.8 Hz, 1H), 4.01 (m, J = 6.6 Hz, 1H), 3.86 (s, 2H), 1.33 (d, J = 6.6 Hz, 6H), 1.07 (d, J = 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 165.1, 156.8, 144.5, 136.5, 134.9, 131.8, 129.5, 129.0, 127.4, 127.1, 126.5, 120.3, 97.9, 50.7, 48.0, 39.8, 23.7, 19.3; IR (ATR): ν 2974, 2929, 1621, 1600, 1496, 1467, 1454, 1398, 1366, 1334, 1252, 1212, 1159, 1128, 1102, 1035, 1004, 986, 721, 697 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]+ Calcd for C₂₄H₂₈N₄O⁺ 389.2336; Found 389.2334; Rf: 0.41 (EtOAc); m.p.: 232–234 °C.
6. General Procedure for the One-Pot Synthesis of 4-Fluoro-2-pyridones:

\[
\text{[Cp*RhCl}_2\text{]}_2 \ (3.75 \mu\text{mol}, 2.3 \text{ mg, 5 mol\% based on [Rh]}), \text{ acrylamide } 1x \ (0.18 \text{ mmol, 1.2 equiv.}), \text{ triazene } 2y \ (0.15 \text{ mmol, 1.0 equiv.}) \text{ and NaOAc (0.30 mmol, 24.6 mg, 2.0 equiv.) were weighed in a Falcon tube containing a magnetic stirring bar, followed by addition of dry THF (0.2 mL) at RT. The mixture was stirred at RT for 1 h. 0.3 mL of HF.pyridine was then added at RT, and the mixture was stirred at 60 °C in a preheated oil bath for 30 minutes. After completion of the reaction, the mixture was allowed to cool to RT, and quenched with excess calcium gluconate at 0 °C. EtOAc (5 mL) was added, followed by H}_2\text{O (8 mL). The two layers were rigourously stirred. The aqueous layer was then separated and rigorously washed with EtOAc (5 mL x 3). The organic layers were combined, dried over MgSO}_4\text{ and concentrated under reduced pressure (crude was analyzed by NMR to determine regiomeric ratio). Crude was purified by silica gel chromatography eluting with pentane/EtOAc to afford the 4-fluoro-2-pyridone product 5xy, which was subsequently washed with minimal amount of pentane (0.5 mL) if necessary.}

DCM was used as solvent for 5ib and 5jb.

Reactions for 5gb, 5hb, 5ib, and 5jb were carried out at 0.2 mmol scale.

3hh: 4 h reaction time. No HF.pyr treatment.
6-Benzyl-4-fluoro-3-phenylpyridin-2(1H)-one (5aa):

Obtained as pale yellow solid in 73 % yield (40.7 mg). **1H NMR** (400 MHz, CDCl₃) δ (ppm) = 12.92 (s, 1H), 7.54–7.50 (m, 2H), 7.39 (dd, J = 8.3, 6.8 Hz, 2H), 7.33–7.21 (m, 6H), 5.94 (d, J = 8.5 Hz, 1H), 3.84 (s, 2H); **13C NMR** (101 MHz, CDCl₃) δ (ppm) = 167.8 (d, J = 265.0 Hz), 165.9 (d, J_C-F = 12.9 Hz), 149.2 (d, J_C-F = 14.6 Hz), 135.8, 130.4 (d, J_C-F = 2.3 Hz), 130.0, 129.5, 129.0, 128.0, 127.9, 127.5, 113.4 (d, J_C-F = 10.3 Hz), 98.5 (d, J_C-F = 29.0 Hz), 39.2 (d, J_C-F = 2.3 Hz); **19F NMR** (376 MHz, CDCl₃) δ (ppm) = -98.1; **IR (ATR):** ν 2856, 2757, 1631, 1600, 1582, 1495, 1484, 1453, 1423, 1351, 1311, 1145, 1089, 1069, 1004, 987, 949, 791, 721, 697, 631, 513 cm⁻¹; **HRMS (ESI/QTOF) m/z:** [M + H]^+ Calcd for C₁₈H₁₅FNO 280.1132; Found 280.1133; **Rₐ:** 0.70 (EtOAc); **m.p.:** 207–209 °C.

4-Fluoro-3,6-diphenylpyridin-2(1H)-one (5ba):

Obtained as yellow solid in 80 % yield (21.1 mg). **1H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.77–7.73 (m, 2H), 7.64–7.60 (m, 2H), 7.53–7.42 (m, 5H), 7.38 (m, 1H), 6.51 (d, J = 8.9 Hz, 1H); **13C NMR** (101 MHz, CDCl₃) δ (ppm) = 167.7 (d, J = 255.5 Hz), 165.3 (d, J_C-F = 12.9 Hz), 146.7 (d, J_C-F = 14.8 Hz), 132.3 (d, J_C-F = 2.7 Hz), 130.5 (d, J_C-F = 2.5 Hz), 129.9, 129.4, 128.11, 128.05, 126.7, 114.2, 97.2 (d, J_C-F = 29.9 Hz); **19F NMR** (376 MHz, CDCl₃) δ (ppm) = -97.6; **IR (ATR):** ν 2924, 2854, 1627, 1598, 1576, 1503, 1443, 1395, 1347, 1330, 1310, 1267, 1188, 1057, 764, 692, 524 cm⁻¹; **HRMS (ESI/QTOF) m/z:** [M + H]^+ Calcd for C₁₇H₁₃FNO²⁺ 266.0976; Found 266.0983; **Rₐ:** 0.57 (pentane/EtOAc 1:1); **m.p.:** 250–253°C.

3-Cyclopropyl-4-fluoro-6-phenylpyridin-2(1H)-one (5bb):

Obtained as white solid in 81 % yield (18.5 mg). **1H NMR** (400 MHz, CDCl₃) δ (ppm) = 12.22 (s, 1H), 7.87–7.68 (m, 2H), 7.58–7.40 (m, 3H), 6.35 (d, J = 9.4 Hz, 1H), 1.88 (tt, J = 8.8, 5.5 Hz, 1H), 1.35–1.21 (m, 2H), 0.91–0.76 (m, 2H); **13C NMR** (101 MHz, CDCl₃) δ (ppm) = 168.80 (d, J_C-F = 260.8 Hz), 166.47 (d, J_C-F = 14.3 Hz), 144.46 (d, J_C-F = 14.8 Hz), 132.62 (d, J_C-F = 3.1 Hz), 130.33, 129.23, 126.62, 114.99 (d, J_C-F = 9.3 Hz), 97.01 (d, J_C-F = 29.8 Hz), 6.57 (d, J_C-F = 4.3 Hz), 5.04 (d, J_C-F = 2.8 Hz); **19F NMR** (376 MHz, CDCl₃) δ (ppm) = -102.9; **IR (ATR):** ν 3063, 3012, 2920, 2852, 1616, 1575,
1502, 1398, 1366, 1279, 1170, 1012, 919, 899, 880, 814, 760, 690, 555, 422 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₄H₁₃FNO⁺ 230.0976; Found 230.0979; Rᵣ: 0.59 (pentane/EtOAc 1:4); m.p.: 189–190 °C.

3-Cyclopropyl-4-fluoro-6-(4-(trifluoromethyl)phenyl)pyridin-2(1H)-one (5cb):

Obtained as yellow solid in 74 % yield (32.8 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.63 (s, 4H), 6.34 (d, J = 9.3 Hz, 1H), 1.87 (tt, J = 8.7, 5.5 Hz, 1H), 1.31–1.18 (m, 2H), 0.93–0.83 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 167.7 (d, Jₐₐ = 261.8 Hz), 165.6 (d, Jₐₐ = 14.2 Hz), 141.7 (d, Jₐₐ = 15.0 Hz), 132.0, 131.5, 128.9 (q, Jₐₐ = 30.9 Hz), 126.7 (q, Jₐₐ = 5.0 Hz), 123.6 (q, Jₐₐ = 273.8 Hz), 115.9 (d, Jₐₐ = 8.9 Hz), 100.5 (d, Jₐₐ = 30.4 Hz), 6.4 (d, Jₐₐ = 3.9 Hz), 4.9 (d, Jₐₐ = 2.5 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -62.9, -102.4; IR (ATR): ν 2923, 2853, 1630, 1610, 1322, 1260, 1166, 1116, 1093, 1067, 1014, 930, 879, 849, 803, 743, 702, 592, 556, 503 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₂F₄NO⁺ 298.0850; Found 298.0849; Rᵣ: 0.55 (pentane/EtOAc 4:1); m.p.: 192–195 °C.

3-Cyclopropyl-4-fluoro-6-(p-tolyl)pyridin-2(1H)-one (5db):

Obtained as pale yellow solid in 53 % yield (19.2 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.56 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 6.31 (d, J = 9.5 Hz, 1H), 2.42 (s, 3H), 1.87 (tt, J = 8.8, 5.5 Hz, 1H), 1.25 (dt, J = 6.1, 3.0 Hz, 2H), 0.90–0.82 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 168.9 (d, Jₐₐ = 260.6 Hz), 166.4 (d, Jₐₐ = 14.4 Hz), 144.5 (d, Jₐₐ = 14.8 Hz), 140.7, 130.0, 129.8, 129.8, 114.7 (d, Jₐₐ = 9.6 Hz), 96.5 (d, Jₐₐ = 30.0 Hz), 21.5, 6.5 (d, Jₐₐ = 4.0 Hz), 5.2 (d, Jₐₐ = 2.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -103.0; IR (ATR): ν 3015, 2923, 1626, 1519, 1394, 1367, 1353, 1229, 1192, 1168, 1090, 1070, 1014, 909, 878, 828, 798, 600, 541, 497, 419 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₅H₁₅FNO⁺ 244.1132; Found 244.1135; Rᵣ: 0.40 (pentane/EtOAc 1:4); m.p.: 214–215 °C.
6-(4-Bromophenyl)-3-cyclopropyl-4-fluoropyridin-2(1H)-one (5eb): Obtained as light brown solid in 64% yield (19.8 mg). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 11.78 (s, 1H), 7.61 (q, \(J = 8.7\) Hz, 4H), 6.32 (d, \(J = 9.3\) Hz, 1H), 1.88 (tt, \(J = 8.7, 5.5\) Hz, 1H), 1.32–1.20 (m, 2H), 0.97–0.82 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 168.8 (d, \(J_{C-F} = 260.7\) Hz), 166.4 (d, \(J_{C-F} = 14.3\) Hz), 144.4 (d, \(J_{C-F} = 14.6\) Hz), 132.6 (d, \(J_{C-F} = 3.0\) Hz), 130.35, 126.58, 115.0 (d, \(J_{C-F} = 9.2\) Hz), 97.0 (d, \(J_{C-F} = 29.9\) Hz), 6.4 (d, \(J_{C-F} = 4.1\) Hz), 5.1 (d, \(J_{C-F} = 2.6\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) (ppm) = -102.5; IR (ATR): \(\tilde{\nu}\) 3070, 3009, 2924, 2852, 1648, 1611, 1564, 1500, 1441, 1417, 1370, 1354, 1284, 1261, 1231, 1193, 1167, 1090, 1074, 1029, 1008, 876, 837, 817, 796, 564, 497 cm\(^{-1}\); HRMS (ESI/QTOF) m/z: [M + H\(^+\)] Calcd for C\(_{14}\)H\(_{12}\)BrFNO\(^+\) 308.0081; Found 308.0086; \(R_f\): 0.42 (pentane/EtOAc 7:3); m.p.: 201–208 °C (decomposed).

3-Cyclopropyl-4-fluoro-6-(2-(trifluoromethyl)phenyl)pyridin-2(1H)-one (5fb): Obtained as brown solid in 75% yield (33.2 mg). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 11.68 (s, 1H), 7.79 (d, \(J = 7.7\) Hz, 1H), 7.64 (dq, \(J = 15.2, 7.5\) Hz, 2H), 7.48 (d, \(J = 7.5\) Hz, 1H), 6.09 (d, \(J = 8.7\) Hz, 1H), 1.75 (td, \(J = 8.8, 4.4\) Hz, 1H), 1.06 (dt, \(J = 6.1, 3.0\) Hz, 2H), 0.71 (dt, \(J = 8.7, 3.2\) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 167.7 (d, \(J_{C-F} = 261.8\) Hz), 165.6 (d, \(J_{C-F} = 14.2\) Hz), 141.7 (d, \(J_{C-F} = 15.0\) Hz), 132.1, 132.0, 131.5, 130.1, 128.9 (q, \(J_{C-F} = 30.9\) Hz), 126.7 (q, \(J_{C-F} = 5.0\) Hz), 123.6 (q, \(J_{C-F} = 273.8\) Hz), 115.9 (d, \(J_{C-F} = 8.9\) Hz), 100.5 (d, \(J_{C-F} = 30.4\) Hz), 6.4 (d, \(J_{C-F} = 3.9\) Hz), 4.9 (d, \(J_{C-F} = 2.5\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) (ppm) = -57.6, -102.9; IR (ATR): \(\tilde{\nu}\) 3013, 2904, 1633, 1498, 1450, 1409, 1370, 1314, 1269, 1171, 1130, 1115, 1079, 1058, 1037, 879, 818, 768, 556 cm\(^{-1}\); HRMS (ESI/QTOF) m/z: [M + H\(^+\)] Calcd for C\(_{15}\)H\(_{12}\)BrFNO\(^+\) 298.0850; Found 298.0854; \(R_f\): 0.52 (pentane/EtOAc 7:3); m.p.: 185–188 °C.

3-Cyclopropyl-4-fluoro-6-(naphthalen-1-yl)pyridin-2(1H)-one (5gb): Obtained as white solid in 82% yield (45.9 mg). (0.2 mmol scale) \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 10.97 (s, 1H), 7.95 (ddt, \(J = 14.4, 7.0, 3.2\) Hz, 3H), 7.55 (dq, \(J = 6.9, 3.0, 2.2\) Hz, 4H), 6.24 (d, \(J = 8.7\) Hz, 1H), 1.78 (tt, \(J = 9.1, 5.5\) Hz, 1H),
1.15–0.98 (m, 2H), 0.81–0.68 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) = 168.1 (d, $J_{CF}$ = 261.9 Hz), 165.7 (d, $J_{CF}$ = 14.7 Hz), 143.4 (d, $J_{CF}$ = 15.0 Hz), 133.9, 131.18, 131.15, 130.6, 128.8, 127.43, 127.38, 126.7, 125.3, 124.7, 115.6 (d, $J_{CF}$ = 9.1 Hz), 100.6 (d, $J_{CF}$ = 29.7 Hz), 6.5 (d, $J_{CF}$ = 3.9 Hz), 5.1 (d, $J_{CF}$ = 3.0 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -103.0; IR (ATR): 3010, 1629, 1509, 1476, 1447, 1403, 1368, 1337, 1213, 1165, 1118, 1077, 100.6 (d, $J_{CF}$ = 29.7 Hz), 6.5 (d, $J_{CF}$ = 3.9 Hz), 5.1 (d, $J_{CF}$ = 3.0 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -102.7; IR (ATR): 2978, 2849, 1644, 1591, 1485, 1453, 1394, 1313, 1253, 1129, 1080, 1049, 896, 790, 639, 518 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{15}$FNO$^+$ 280.1132; Found 280.1134; R$_f$: 0.30 (pentane/EtOAc 7:3); m.p.: 169–172 °C.

3-Cyclopropyl-4-fluoro-6-methylpyridin-2(1H)-one (5hb):

![Chemical Structure Image]

Obtained as brown solid in 78 % yield (26.2 mg). (0.2 mmol scale) $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 5.86 (d, $J = 9.1$ Hz, 1H), 2.29 (s, 3H), 1.80 (tt, $J = 8.8, 5.5$ Hz, 1H), 1.10 (dt, $J = 6.0, 3.0$ Hz, 2H), 0.82 (dt, $J = 8.8, 3.1$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) = 168.9 (d, $J_{CF}$ = 261.7 Hz), 167.2 (d, $J_{CF}$ = 14.5 Hz), 143.6 (d, $J_{CF}$ = 15.1 Hz), 113.2 (d, $J_{CF}$ = 9.2 Hz), 98.4 (d, $J_{CF}$ = 28.6 Hz), 18.8 (d, $J_{CF}$ = 2.4 Hz), 6.1 (d, $J_{CF}$ = 3.4 Hz), 5.2 (d, $J_{CF}$ = 3.3 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -102.7; IR (ATR): 2978, 2849, 1644, 1591, 1485, 1453, 1394, 1313, 1253, 1129, 1080, 1049, 896, 790, 639, 518 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_9$H$_{11}$FNO$^+$ 168.0819; Found 168.0824; R$_f$: 0.64 (EtOAc); m.p.: 149–155 °C.

6-Cyclopentyl-3-cyclopropyl-4-fluoropyridin-2(1H)-one (5ib), 3-cyclopentyl-6-cyclopropyl-5-fluoropyridin-2(1H)-one (5ib'):

![Chemical Structure Image]

Obtained as light brown film in 55 % combined yield, mixture of inseparable isomers in 2:1 ratio (24.4 mg). (0.2 mmol scale) $^1$H NMR (400 MHz, CDCl$_3$, mixture of two isomers, ratio = 2:1) δ (ppm) = 11.06 (s, 1H), 6.59 (d, $J = 9.2$ Hz, 1H), 6.02 (d, $J = 9.4$ Hz, 1H), 3.14–3.05 (m, $J = 8.5$ Hz, 1H), 2.99–2.90 (m, $J = 8.5$ Hz, 1H), 2.19 (ddt, $J = 11.7, 7.8, 4.6$ Hz, 2H), 2.14–2.04 (m, 2H), 1.93–1.84 (m, 2H, overlapped with minor isomer), 1.83–1.71 (m, 3H, overlapped with minor isomer), 1.70–1.57 (m, 2H, overlapped with minor isomer), 1.14 (dt, $J = 6.2, 3.2$ Hz, 2H), 1.06 (dt, $J = 6.0, 3.0$ Hz, 2H), 1.04–0.96 (m, 2H), 0.86 (td, $J = 6.7, 4.5$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$, mixture of two isomers) δ (ppm) =
**5ib:** 171.7 (d, J<sub>CF</sub> = 270.3 Hz), 162.3 (d, J<sub>CF</sub> = 15.4 Hz), 152.9 (d, J<sub>CF</sub> = 13.5 Hz), 116.4 (d, J<sub>CF</sub> = 14.2 Hz), 103.63 (d, J<sub>CF</sub> = 26.8 Hz), 43.3 (d, J<sub>CF</sub> = 1.8 Hz), 32.4, 25.3, 6.2 (d, J<sub>CF</sub> = 3.3 Hz), 5.7 (d, J<sub>CF</sub> = 2.6 Hz). **5ib**: 172.4 (d, J<sub>CF</sub> = 273.7 Hz), 162.5 (d, J<sub>CF</sub> = 15.2 Hz), 156.1 (d, J<sub>CF</sub> = 13.5 Hz), 114.6 (d, J<sub>CF</sub> = 14.9 Hz), 103.57 (d, J<sub>CF</sub> = 26.3 Hz), 43.2, 32.9, 25.4, 7.3, 5.2; **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ (ppm) = -89.4; **IR (ATR):** ν 3208, 2958, 2874, 1627, 1573, 1444, 1362, 1226, 1077, 884, 821, 763, 550, 518 cm<sup>-1</sup>; **HRMS (ESI/QTOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>17</sub>FNO<sup>+</sup> 222.1289; Found 222.1286; **R<sub>t</sub>:** 0.29 (pentane/EtOAc 1:1); **m.p.:** 138–141 °C.

6-Allyl-3-cyclopropyl-4-fluoropyridin-2(1H)-one (5jb):

Obtained as brown solid in 61 % yield (23.4 mg). (0.2 mmol scale)

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 11.35 (s, 1H), 5.96–5.74 (m, 2H), 5.36–5.18 (m, 2H), 3.28 (d, J = 6.8 Hz, 2H), 1.81 (tt, J = 8.8, 5.5 Hz, 1H), 1.11 (dt, J = 6.1, 3.1 Hz, 2H), 0.88–0.77 (m, 2H); **13C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) = 168.8 (d, J<sub>CF</sub> = 261.9 Hz), 166.8 (d, J<sub>CF</sub> = 14.5 Hz), 145.2 (d, J<sub>CF</sub> = 14.3 Hz), 132.3, 119.7, 114.0 (d, J<sub>CF</sub> = 9.0 Hz), 97.9 (d, J<sub>CF</sub> = 29.3 Hz), 37.1, 6.2 (d, J<sub>CF</sub> = 3.6 Hz), 5.2 (d, J<sub>CF</sub> = 3.1 Hz); **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ (ppm) = -102.3; **IR (ATR):** ν 2961, 2855, 1631, 1588, 1485, 1426, 1386, 1368, 1327, 1239, 1176, 1129, 1077, 1050, 1025, 998, 921, 896, 800, 769, 684, 633, 583, 517 cm<sup>-1</sup>; **HRMS (ESI/QTOF) m/z:** [M + H]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>13</sub>FNO<sup>+</sup> 194.0976; Found 194.0976; **R<sub>t</sub>:** 0.32 (pentane/EtOAc 1:1); **m.p.:** 166–168 °C.

4-Fluoro-3-(4-fluorophenyl)-6-phenylpyridin-2(1H)-one (5bc):

Obtained as brown solid in 79 % yield (22.3 mg). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 11.46 (s, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.1 Hz, 2H), 7.50 (dt, J = 14.6, 7.1 Hz, 3H), 7.13 (t, J = 8.5 Hz, 2H), 6.50 (d, J = 9.0 Hz, 1H); **13C NMR** (101 MHz, CDCl<sub>3</sub>) δ (ppm) = 167.6 (d, J<sub>CF</sub> = 264.7 Hz), 165.1 (d, J<sub>CF</sub> = 12.4 Hz), 162.5 (d, J<sub>CF</sub> = 247.6 Hz), 146.6 (d, J<sub>CF</sub> = 14.8 Hz), 132.3 (d, J<sub>CF</sub> = 8.1 Hz), 131.0, 129.5, 126.6, 118.6, 116.1 (d, J<sub>CF</sub> = 21.8 Hz), 115.1 (d, J<sub>CF</sub> = 21.5 Hz), 113.3 (d, J<sub>CF</sub> = 10.4 Hz), 97.2 (d, J<sub>CF</sub> = 30.0 Hz); **IR (ATR):** ν 2923, 2854, 1638, 1627, 1601, 1592, 1512, 1388, 1334, 1300, 1268, 1237, 1189, 1160, 1103, 1090, 1059, 1032, 998, 837, 815, 764, 692, 559, 511 cm<sup>-1</sup>; **HRMS (ESI/QTOF) m/z:** [M + H]<sup>+</sup> Calcd for
C_{17}H_{12}F_{2}NO^+ 284.0881; Found 284.0883; R_f: 0.44 (pentane/EtOAc 1:1); m.p.: 274–277 °C.

4-Fluoro-3-(4-methoxyphenyl)-6-phenylpyridin-2(1H)-one (5bd):

Obtained as yellow solid in 65 % yield (19.2 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.79–7.69 (m, 2H), 7.63–7.55 (m, 2H), 7.54–7.45 (m, 3H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.49 (d, $J = 8.9$ Hz, 1H), 3.87 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) = 167.2 (d, $J_{C,F} = 263.0$ Hz), 164.9, 159.28, 145.6 (d, $J_{C,F} = 15.1$ Hz), 132.3, 131.5, 130.7, 129.4, 128.5 (d, $J_{C,F} = 113.2$ Hz), 126.3, 121.9, 113.5, 97.1 (d, $J_{C,F} = 30.3$ Hz), 132.3, 131.5, 130.7, 129.4, 128.5 (d, $J_{C,F} = 113.2$ Hz), 126.3, 121.9, 113.5, 97.1 (d, $J_{C,F} = 30.3$ Hz), 55.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -98.9; IR (ATR): $\tilde{\nu}$ 2959, 2922, 2852, 1538, 1608, 1574, 1513, 1442, 1392, 1294, 1253, 1181, 1091, 1059, 1031, 995, 913, 833, 799, 762, 740, 692, 566, 520 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{15}$FNO$_2$ 296.1081; Found 296.1076; R_f: 0.44 (pentane/EtOAc 1:1); m.p.: 274–277 °C.

4-Fluoro-3-(naphthalen-1-yl)-6-phenylpyridin-2(1H)-one (5be):

Obtained as light brown solid in 53 % yield (16.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 12.54 (s, 1H), 8.00–7.92 (m, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 7.7$ Hz, 2H), 7.61–7.49 (m, 3H), 7.49–7.43 (m, 1H), 7.05 (t, $J = 7.7$ Hz, 2H), 6.56 (d, $J = 8.1$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) = 168.5 (d, $J_{C,F} = 264.1$ Hz), 165.8 (d, $J_{C,F} = 13.5$ Hz), 147.9 (d, $J_{C,F} = 14.5$ Hz), 133.9, 132.1, 132.0 (d, $J_{C,F} = 2.9$ Hz), 132.01, 130.69, 129.15, 128.97, 128.54, 127.87, 126.68, 126.21, 125.96, 125.87, 125.52, 113.4 (d, $J_{C,F} = 12.5$ Hz), 96.7 (d, $J_{C,F} = 29.3$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ (ppm) = -94.1; IR (ATR): $\tilde{\nu}$ 3057, 2924, 2853, 1628, 1597, 1575, 1503, 1448, 1392, 1330, 1264, 1244, 1191, 1084, 963, 800, 774, 763, 735, 691, 587, 528, 509 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{21}$H$_{15}$FNO$^+$ 316.1132; Found 316.1133; R_f: 0.52 (pentane/EtOAc 1:1); m.p.: 225–227 °C.

4-Fluoro-3-methyl-6-phenylpyridin-2(1H)-one (5bf):

Obtained as light brown solid in 65 % yield (19.7 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) = 11.40 (s, 1H), 7.79–7.60 (m, 2H), 7.50 (dd, $J = 5.2$, 2.0 Hz, 3H), 6.37 (d, $J = 8.1$ Hz, 1H), 2.07 (s, 2H); $^{13}$C NMR
(101 MHz, CDCl₃) δ (ppm) = 168.2 (d, J_C-F = 260.9 Hz), 166.5 (d, J_C-F = 15.6 Hz), 144.7 (d, J_C-F = 14.3 Hz), 132.8 (d, J_C-F = 3.2 Hz), 130.5, 129.4, 126.5, 110.8 (d, J_C-F = 13.4 Hz), 96.9 (d, J_C-F = 29.7 Hz), 7.9 (d, J_C-F = 2.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -98.3; IR (ATR): ν 2929, 1620, 1596, 1500, 1454, 1401, 1373, 1332, 1273, 1204, 1119, 1072, 950, 911, 873, 815, 763, 735, 695, 656, 636, 557, 505, 474 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H⁺] Calcd for C₁₂H₁₁FNO⁺ 204.0819; Found 204.0824; Rᵣ: 0.52 (EtOAc).

3-Butyl-4-fluoro-6-phenylpyridin-2(1H)-one (5bg):

Obtained as yellow solid in 76 % yield (18.7 mg). ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.62 (s, 1H), 7.72 (dd, J = 6.7, 2.9 Hz, 2H), 7.49 (q, J = 2.9 Hz, 3H), 6.36 (d, J = 8.2 Hz, 1H), 2.57 (td, J = 7.6, 1.8 Hz, 2H), 1.56 (p, J = 8.0, 7.5 Hz, 2H), 1.39 (h, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 168.3 (d, J_C-F = 260.8 Hz), 166.6 (d, J_C-F = 15.8 Hz), 145.2 (d, J_C-F = 14.7 Hz), 132.8 (d, J_C-F = 3.1 Hz), 130.4, 129.3, 126.6, 115.2 (d, J_C-F = 13.4 Hz), 96.9 (d, J_C-F = 29.7 Hz), 30.4, 22.8, 22.6, 14.1; ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) = -100.8; IR (ATR): ν 2958, 2926, 2871, 2855, 1638, 1619, 1594, 1577, 1507, 1448, 1431, 1397, 1363, 1294, 1267, 1183, 1129, 1105, 1071, 1027, 917, 807, 759, 730, 689, 658, 569, 514 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H⁺] Calcd for C₁₅H₁₇FNO⁺ 246.1289; Found 246.1289; Rᵣ: 0.57 (pentane/EtOAc 1:1).

(E)-3-Cyclopropyl-4-(3,3-dimethyltriaz-1- en-1-yl)-6-methylpyridin-2(1H)-one (3hh):

Obtained as pale yellow solid in 59 % yield (39.2 mg). (0.3 mmol scale) ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 11.97 (s, 1H), 6.26 (d, J = 1.1 Hz, 1H), 3.53 (s, 3H), 3.21 (s, 3H), 2.33 (tt, J = 8.9, 5.6 Hz, 1H), 2.25 (s, 3H), 1.45 (dt, J = 5.7, 3.0 Hz, 2H), 0.79–0.71 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) = 166.7, 156.7, 140.7, 119.7, 97.6, 43.3, 36.4, 18.9, 8.5, 5.7; HRMS (ESI/QTOF) m/z: [M + H⁺] Calcd for C₁₁H₁₇N₄O⁺ 221.1397; Found 221.1400; Rᵣ: 0.42 (EtOAc).
7. Product Derivatizations:

**(E)-4-(3,3-Diisopropyltriaz-1-en-1-yl)-3,6-diphenylpyridin-2(1H)-one (3ba):**

**Gram scale synthesis:** [Cp*RhCl₂]₂ (75.0 µmol, 46.4 mg, 5 mol% based on [Rh]), acrylamide 1b (3.6 mmol, 890 mg, 1.2 equiv.), triazene 2a (3.0 mmol, 688 mg, 1.0 equiv.) and NaOAc (6.0 mmol, 492 mg, 2.0 equiv.) were weighed in a round-bottomed flask containing a magnetic stirring bar, followed by addition of dry THF (6.0 mL) at RT. The mixture was stirred at RT for 1 h. Volatiles were evaporated under reduced pressure, and the crude was directly purified by silica gel chromatography eluting with 20% to 50% EtOAc in pentane to afford 3ba as a light brown solid in 91% yield (1.02 g).

**¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.75–7.70 (m, 2H), 7.53 (dd, J = 8.2, 1.3 Hz, 2H), 7.46 (dd, J = 5.0, 2.0 Hz, 3H), 7.39–7.33 (m, 2H), 7.26 (dt, J = 14.7, 1.3 Hz, 1H), 6.90 (s, 1H), 4.81 (hept, J = 6.8 Hz, 1H), 4.05 (hept, J = 6.6 Hz, 1H), 1.38 (d, J = 6.6 Hz, 6H), 1.11 (d, J = 6.8 Hz, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ (ppm) = 165.0, 156.8, 143.6, 134.68, 134.4, 131.8, 129.8, 129.3, 127.1, 126.6, 126.3, 121.1, 97.0, 50.7, 48.1, 23.8, 19.3; **IR (ATR):** 2973, 2929, 1619, 1597, 1575, 1504, 1448, 1390, 1334, 1258, 1223, 1185, 1153, 1127, 1102, 1017, 766, 752, 695, 582 cm⁻¹; **HRMS (ESI/QTOF) m/z:** [M + H]+ Calcd for C₂₃H₂₇N₄O⁺ 375.2179; Found 375.2173; **Rf:** 0.61 (EtOAc); **m.p.:** 255–257 °C.

3,6-Diphenyl-4-(2,2,2-trifluoroethoxy)pyridin-2(1H)-one (6):

3ba (1.0 equiv., 24.3 mg, 0.065 mmol) was dissolved in 0.65 mL TFE, followed by addition of 0.1 mL TFA (20 equiv., 1.30 mmol). Mixture was stirred at 60 °C in a preheated oil bath for 18 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (10% to 50% EtOAc in pentane) to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a red solid in 90% yield (20.3 mg).

**¹H NMR** (400 MHz, CDCl₃) δ (ppm) = 7.80–7.69 (m, 2H), 7.56–7.51 (m, 2H), 7.50–7.38 (m, 5H), 7.37–7.31 (m, 1H), 6.35 (s, 1H), 4.32 (q, J = 8.1 Hz, 2H); **¹³C NMR** (101
MHz, CDCl$_3$) $\delta$ (ppm) = 164.9, 163.08, 146.8, 132.9, 131.6, 130.84, 130.7, 129.4, 127.9, 127.6, 126.7, 123.0 (q, $J_{C,F} = 278.3$ Hz), 115.4, 95.3, 66.4 (q, $J_{C,F} = 36.1$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ (ppm) = -73.8; IR (ATR): $\tilde{\nu}$ 2924, 2853, 1627, 1599, 1577, 1506, 1407, 1353, 1273, 1218, 1167, 1135, 989, 975, 762, 695 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{15}$F$_3$NO$_2^+$ 346.1049; Found 346.1048; $R_f$: 0.55 (pentane/EtOAc 1:1); m.p.: 212–216 °C (decomposed).

4-((1,1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3,6-diphenylpyridin-2(1H)-one (7):

3ba (1.0 equiv., 18.7 mg, 0.05 mmol) was dissolved in 5.0 mL HFIP, followed by addition of 11.5 µL TFA (3.0 equiv., 0.15 mmol). Mixture was stirred at 60 °C in a preheated oil bath for 16 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (10 % to 50 % EtOAc in pentane) to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a light brown solid in 70 % yield (14.5 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 11.99 (s, 1H), 7.82–7.64 (m, 2H), 7.55–7.34 (m, 8H), 6.33 (s, 1H), 4.86 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ (ppm) = 164.9, 161.7, 147.2, 132.6, 130.93, 130.7, 129.5, 128.0, 127.9, 126.7, 120.6 (q, $J_{C,F} = 285.6$ Hz), 117.5, 95.3, 74.1 (dt, $J_{C,F} = 67.7$, 33.7 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ (ppm) = -73.0; IR (ATR): $\tilde{\nu}$ 2925, 2854, 1632, 1600, 1577, 1505, 1371, 1291, 1265, 1230, 1199, 1134, 1108, 910, 756, 694 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{20}$H$_{14}$F$_3$NO$_2^+$ 414.0923; Found 414.0928; $R_f$: 0.73 (pentane/EtOAc 1:1); m.p.: 233–235 °C (decomposed).

4-Iodo-3,6-diphenylpyridin-2(1H)-one (8):

3ba (1.0 equiv., 120 mg, 0.32 mmol) was dissolved in 1.1 mL MeCN, followed by addition of TMSI (5 equiv., 0.22 mL, 1.60 mmol). Mixture was stirred at 80 °C in a preheated oil bath for 5 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (10 % to 50 % EtOAc in pentane) to provide the titled product, which was subsequently washed...
with minimal amount of pentane (0.5 mL) to give a light brown solid in 80 % yield (95.1 mg).

1H NMR (400 MHz, CDCl₃) δ (ppm) = 7.68 (d, J = 7.5 Hz, 2H), 7.49–7.38 (m, 6H), 7.37–7.32 (m, 2H), 7.09 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ (ppm) = 160.8, 144.6, 139.3, 136.6, 132.0, 131.9, 130.7, 130.0, 129.5, 128.3, 128.3, 126.6, 115.8; IR (ATR): ν = 3438, 1656, 1505, 1460, 1443, 1427, 1404, 1300, 1263, 1113, 985, 656, 560, 470 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₇H₁₃NO⁺ 374.0036; Found 374.0032; Rf: 0.35 (pentane/EtOAc 1:1).

3,6-Diphenyl-4-(trifluoromethyl)pyridin-2(1H)-one (9):

8 (1.0 equiv., 29 mg, 0.078 mmol), Na₃PO₄ (2.5 equiv., 31.8 mg, 0.194 mmol), CuCl (1.1 equiv., 8.5 mg, 0.085 mmol), 1,10-phenanthroline (1.1 equiv., 15.4 mg, 0.085 mmol), Na₂S₂O₃ (2.0 equiv., 24.6 mg, 0.155 mmol), were weighed into an oven-dried microwave tube. The tube was sealed, followed by addition of 0.39 mL DMSO. Mixture was stirred at 160 °C in a preheated oil bath for 24 h. After cooling to RT, crude mixture was partitioned between EtOAc (10 mL) and water (10 mL). The aqueous layer was washed with EtOAc (5 mL x 2). Organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure. The crude was purified using column chromatography (10 % to 40 % EtOAc in pentane to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a brown solid in 54 % yield (13.2 mg).

1H NMR (400 MHz, CDCl₃) δ (ppm) = 7.69 (d, J = 7.5 Hz, 2H), 7.49–7.42 (m, 4H), 7.40 (d, J = 7.4 Hz, 2H), 7.37–7.33 (m, 2H), 7.09 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ (ppm) = 160.3 (q, J_C-F = 36.4 Hz), 159.1, 139.4, 132.9, 130.39, 128.8, 128.3, 127.9, 126.1, 124.3, 123.2, 122.6, 120.2 (q, J_C-F = 274.9 Hz), 81.5; 19F NMR (376 MHz, CDCl₃) δ (ppm) = -59.4; IR (ATR): ν = 2924, 2854, 1637, 1619, 1450, 1356, 1262, 1239, 1185, 1138, 1097, 1034, 1006, 802, 766, 707, 697 cm⁻¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₈H₁₃F₃NO⁺ 316.0944; Found 316.0945; Rf: 0.50 (pentane/EtOAc 3:2).
(E)-4-(3,3-Diisopropyltriaz-1-en-1-yl)-3-phenylisoquinolin-1(2H)-one (13):

[Cp*RhCl₂]₂ (2.5 µmol, 1.5 mg, 5 mol% based on [Rh]), benzamide 12 (0.11 mmol, 24.3 mg, 1.1 equiv.), triazene 2a (0.1 mmol, 22.9 mg, 1.0 equiv.) and NaOAc (0.2 mmol, 16.4 mg, 2.0 equiv.) were weighed in a round-bottomed flask containing a magnetic stirring bar, followed by addition of dry THF (6.0 mL) at RT. The mixture was stirred at RT for 3 h. Volatiles were evaporated under reduced pressure, and the crude was directly purified by silica gel chromatography eluting with 20% to 50% EtOAc in pentane to afford 13 as a yellow solid in 89% yield (30.9 mg).

1H NMR (400 MHz, CDCl₃) δ (ppm) = δ 8.83 (s, 1H), 8.44 (dd, J = 8.0, 1.4 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.70 (ddd, J = 8.3, 7.0, 1.4 Hz, 1H), 7.53 (td, J = 7.5, 7.0, 1.2 Hz, 1H), 7.42–7.33 (m, 4H), 7.32–7.27 (m, 1H), 5.16 (s, 1H), 3.76 (s, 1H), 1.23 (s, 6H), 0.93 (s, 6H); 13C NMR (101 MHz, CDCl₃) δ (ppm) = 162.1, 136.4, 135.7, 132.5, 129.4, 129.1, 128.7, 128.0, 127.9, 127.7, 126.9, 125.4, 123.8, 48.6, 46.1, 23.8, 19.6; IR (ATR): ʋ 2973, 2931, 1643, 1606, 1487, 1468, 1447, 1419, 1365, 1348, 1258, 1223, 1153, 761, 696 ·¹; HRMS (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₂₁H₂₅N₄O⁺ 349.2023; Found 349.2022; Rf: 0.26 (pentane/EtOAc 1:1); m.p.: 172–176 °C.
4-(2,5-Dimethylphenyl)-3,6-diphenylpyridin-2(1H)-one (14): 

3ba (1.0 equiv., 24.3 mg, 0.065 mmol) was dissolved in 2.0 mL p-xylene, followed by addition of 0.2 mL TfOH and 0.1 mL THF (for solubilization). Mixture was stirred at 60 °C in a preheated oil bath for 12 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (10 % to 50 % EtOAc in pentane) to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a light brown solid in 88% yield (20.1 mg).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 7.79–7.74 (m, 2H), 7.46–7.39 (m, 3H), 7.23–7.14 (m, 5H), 6.95 (dq, $J$ = 4.9, 3.6, 2.5 Hz, 3H), 6.52 (s, 1H), 2.26 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ (ppm) = 163.9, 152.5, 143.8, 139.3, 135.1, 135.1, 133.3, 131.7, 130.8, 130.1, 129.8, 129.4, 128.8, 128.7, 127.4, 127.1, 126.4, 108.1, 21.0, 19.6; IR (ATR): $\tilde{\nu}$ 3012, 2921, 1628, 1597, 1575, 1536, 1502, 1442, 1350, 1257, 1008, 990, 915, 835, 809, 769, 753, 731, 694, 581, 562 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for C$_{25}$H$_{22}$NO$^+$ 352.1696; Found 352.1706; $R_f$: 0.38 (pentane/EtOAc 1:1).
N-(2-Oxo-3,6-diphenyl-1,2-dihydropyridin-4-yl)acetamide (15):

3ba (1.0 equiv., 24.3 mg, 0.065 mmol) was dissolved in 2.0 mL wet MeCN (spiked with 1 drop water), followed by addition of 0.2 mL TfOH. Mixture was stirred at 60 °C in a preheated oil bath for 12 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (EtOAc) to give a white solid in 55 % yield (10.9 mg)

$^1$H NMR (400 MHz, CD$_3$OD) δ (ppm) = 7.71 (d, $J$ = 7.2 Hz, 2H), 7.51 (tt, $J$ = 8.1, 6.0 Hz, 3H), 7.39 (d, $J$ = 7.6 Hz, 2H), 7.37–7.33 (m, 2H), 7.26 (t, $J$ = 7.5 Hz, 1H), 6.33 (s, 1H), 1.82 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) = 163.2, 151.0, 147.6, 145.3, 134.1, 133.2, 130.7, 130.0, 129.3, 129.2, 127.8, 126.4, 105.7, 94.5, 25.3; IR (ATR): $\tilde{\nu}$ 3051, 2923, 1606, 1578, 1501, 1441, 1376, 1349, 1261, 1179, 1038, 768, 696, 644, 574 cm$^{-1}$; HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcld for C$_{19}$H$_{16}$N$_2$O$_2$+ 304.1212; Found 304.1435; $R$: 0.15 (EtOAc).

2-Oxo-3,6-diphenyl-1,2-dihydropyridin-4-yl trifluoromethanesulfonate (16):

3ba (1.0 equiv., 24.3 mg, 0.065 mmol) was dissolved in 2.0 mL dry MeCN, followed by addition of 1.0 mL TfOH and 0.1 mL THF. Mixture was stirred at 60 °C in a preheated oil bath for 12 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (EtOAc) to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a light brown solid in 73 % yield (18.7 mg).

$^1$H NMR (400 MHz, CD$_3$OD) δ (ppm) = 7.69–7.66 (m, 2H), 7.51 (d, $J$ = 7.0 Hz, 3H), 7.47 (t, $J$ = 7.5 Hz, 2H), 7.37 (d, $J$ = 7.5 Hz, 2H), 7.34 (t, $J$ = 7.5 Hz, 1H), 6.34 (s, 1H); $^{13}$C NMR (101 MHz, CD$_3$OD) δ (ppm) = 165.2, 156.9, 146.6, 135.3, 135.1, 131.9, 131.0, 130.1, 128.4, 127.6, 121.7 (q, $J_{C-F}$ = 318.3 Hz), 107.1, 99.8; $^{19}$F NMR (376 MHz, CD$_3$OD) δ (ppm) = -80.1; IR (ATR): $\tilde{\nu}$ 1607, 1579, 1553, 1503, 1463, 1424, 1256, 1232, 1171, 1036, 836, 786, 765, 699, 638, 586, 530, 516, 421 cm$^{-1}$; $R$: 0.23 (EtOAc).
**Scheme S5.**

4-((1,1,3,3,3-Hexafluoropropan-2-yl)oxy)-3-phenylisoquinolin-1(2H)-one (17):

13 (1.0 equiv., 34.8 mg, 0.1 mmol) was dissolved in 5.0 mL HFIP, followed by addition of 0.1 mL TfOH. Mixture was stirred at 60 °C in a preheated oil bath for 12 h. After cooling to RT, volatiles were evaporated under reduced pressure, and the crude was purified using column chromatography (pentane/EtOAc 9:1) to provide the titled product, which was subsequently washed with minimal amount of pentane (0.5 mL) to give a yellow solid in 79 % yield (30.2 mg).

**1H NMR** (400 MHz, CDCl₃) δ (ppm) = δ 9.89 (s, 1H), 8.34 (dd, J = 8.3, 1.5 Hz, 1H), 7.60 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.54–7.40 (m, 5H), 7.36 (dt, J = 5.9, 1.5 Hz, 2H), 5.76 (m, 1H); **13C NMR** (101 MHz, CDCl₃) δ (ppm) = 161.5, 145.7, 139.7, 132.8, 132.0, 131.2, 128.6, 128.1, 126.4, 125.8, 124.9, 120.8 (d, J_{C-F} = 284.4 Hz), 120.2, 107.9, 72.2 (p, J_{C-F} = 33.5 Hz); **19F NMR** (376 MHz, CDCl₃) δ (ppm) = -73.1; **IR (ATR):** ʋ 2963, 2855, 1650, 1607, 1577, 1556, 1509, 1474, 1446, 1372, 1286, 1256, 1229, 1200, 1159, 1107, 1090, 906, 872, 773, 746, 703, 688, 524 -1; **HRMS (ESI/QTOF) m/z:** [M + H]⁺ Calcd for C₁₈H₁₁NxF₆O₂⁺ 388.0766; Found 388.0784; **Rf:** 0.32 (pentane/EtOAc 9:1).

4-Amino-3-phenylisoquinolin-1(2H)-one (18):
Reaction was carried out based on a published procedure.\textsuperscript{6} \textbf{13} (1.0 equiv., 34.8 mg, 0.1 mmol) was dissolved in 2.0 mL MeOH, followed by addition of 0.2 mL 1M aq. KOH solution. 300 mg Ni/Al alloy was added at RT, and the mixture was stirred at RT for 12 h. The reaction mixture was filtered through a pad of celite, followed by dilution with water (5.0 mL). The aqueous layer was washed with EtOAc (5.0 mL x 3), and the organic layers were combined, dried over MgSO\textsubscript{4}, filtered and concentrated. The crude was purified using column chromatography (EtOAc) to provide the titled product as a bright yellow solid in 49\% yield (11.56 mg).

\textbf{1H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) = \(\delta\) 8.49 (d, \(J = 8.0\) Hz, 1H), 8.44 (s, 1H), 7.79 (t, \(J = 7.6\) Hz, 1H), 7.75 (d, \(J = 8.1\) Hz, 1H), 7.58 (d, \(J = 7.1\) Hz, 3H), 7.55 (t, \(J = 7.5\) Hz, 2H), 7.47 (t, \(J = 7.5\) Hz, 1H), 3.48 (brs, 2H); \textbf{13C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) = 161.0, 133.7, 133.7, 132.9, 129.8, 129.3, 128.8, 128.4, 127.2, 125.8, 121.4, 121.3, 120.4; \textbf{IR (ATR)}: \(\tilde{\nu}\) 3060, 2923, 2853, 1642, 1605, 1552, 1487, 1467, 1447, 1429, 1366, 1313, 1261, 1242, 1154, 1031, 802, 763, 735, 698, 564 \textsuperscript{-1}; \textbf{HRMS (ESI/QTOF)} m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{15}H\textsubscript{13}N\textsubscript{2}O\textsuperscript{+} 237.1022; Found 237.1012; \(R\textsubscript{f}\): 0.22 (EtOAc).
8. The X-Ray Structures of 5aa and 13

Crystal data and structure refinement for 5aa.

Empirical formula \( \text{C}_{18}\text{H}_{14}\text{FNO} \)
Formula weight 279.30
Temperature 140.00(11) K
Wavelength 1.54184 Å
Crystal system Triclinic
Space group \( P-1 \)
Unit cell dimensions
\[
\begin{align*}
a & = 10.2367(3) \text{ Å} \\
b & = 11.4102(4) \text{ Å} \\
c & = 13.7829(5) \text{ Å}
\end{align*}
\]
Volume 1373.04(9) Å³
\( Z \) 4
Density (calculated) 1.351 Mg/m³
Absorption coefficient 0.758 mm⁻¹
\( F(000) \) 584
Crystal size 0.579 x 0.118 x 0.077 mm³
\( \Theta \) range for data collection 3.474 to 72.752°
Index ranges
\(-8 \leq h \leq 12, -14 \leq k \leq 11, -16 \leq l \leq 17\)
Reflections collected 9488
Independent reflections 5303 \([R_{int} = 0.0235]\)
Completeness to \( \theta = 67.684° \) 99.9 %
Absorption correction Gaussian
Max. and min. transmission 1.000 and 0.571
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 5303 / 0 / 492
Goodness-of-fit on \( F^2 \) 1.023
Final \( R \) indices \([I > 2\sigma (I)]\) \( R_1 = 0.0405, wR_2 = 0.1127 \)
\( R \) indices (all data) \( R_1 = 0.0443, wR_2 = 0.1177 \)
Extinction coefficient 0.0035(4)
Largest diff. peak and hole 0.228 and -0.197 eÅ⁻³
Crystal data and structure refinement for 13.

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<tr>
<td>a/Å</td>
<td>9.6626(11)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.1376(12)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.1294(15)</td>
</tr>
<tr>
<td>α/°</td>
<td>97.909(11)</td>
</tr>
<tr>
<td>β/°</td>
<td>105.084(11)</td>
</tr>
<tr>
<td>γ/°</td>
<td>114.113(11)</td>
</tr>
<tr>
<td>V/Å(^3)</td>
<td>923.2(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Z'</td>
<td>1</td>
</tr>
<tr>
<td>Wavelength/Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>θ_{min}^f</td>
<td>3.011</td>
</tr>
<tr>
<td>θ_{max}^f</td>
<td>29.392</td>
</tr>
<tr>
<td>Measured Refl.</td>
<td>6709</td>
</tr>
<tr>
<td>Independent Refl.</td>
<td>4264</td>
</tr>
<tr>
<td>Refractions with I &gt; 2(I)</td>
<td>3044</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0219</td>
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<tr>
<td>Parameters</td>
<td>331</td>
</tr>
<tr>
<td>Restraints</td>
<td>0</td>
</tr>
<tr>
<td>Largest Peak/e Å(^3)</td>
<td>0.427</td>
</tr>
<tr>
<td>Deepest Hole/e Å(^3)</td>
<td>-0.276</td>
</tr>
<tr>
<td>GooF</td>
<td>1.060</td>
</tr>
<tr>
<td>wR_{2} (all data)</td>
<td>0.1834</td>
</tr>
<tr>
<td>wR_{2}</td>
<td>0.1658</td>
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<tr>
<td>R_{1} (all data)</td>
<td>0.0974</td>
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<tr>
<td>R_{1}</td>
<td>0.0683</td>
</tr>
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</table>
9. $^1$H NMR Reaction Kinetics:

$\text{OPiv} \quad \text{Ph} \quad \text{N} \quad \text{N} \quad \text{Ph} \quad \text{Ph}$

$1b \text{ (1.2 eq.)} + 2a$  $\xrightarrow{2.5 \text{ mol}\% \ [\text{Cp}^*\text{RhCl}_2\text{]}}$  $3ba$

NaOAc, THF-$d_4$, 23 °C

$1b$  $2a$  $3ba$

93%

Conversion [%]

Time [minutes]
10. NMR Spectra:

\[ \text{NMR Spectra:} \]

\[ \text{\( ^1H \text{ NMR} \)} \]

\[ 400 \text{ MHz, CDCl}_3 \]

\[ \text{Chemical Shift (ppm)} \]

\[ \text{\( ^{13}C \text{ NMR} \)} \]

\[ 101 \text{ MHz, CDCl}_3 \]
$\equiv N - N$

2h

$^1H$ NMR
400 MHz, CDCl$_3$

\[ \text{ppm} \]

$\equiv N - N$

2h

$^{13}C$ NMR
101 MHz, CDCl$_3$

\[ \text{ppm} \]
1a
$^1$H NMR
400 MHz, CDCl$_3$

1b
$^1$H NMR
400 MHz, CDCl$_3$
$^{1}$H NMR
400 MHz, CDCl$_3$
$^{1}H$ NMR
400 MHz, CDCl$_3$

$^{13}C$ NMR
101 MHz, CDCl$_3$
**5aa**

**$^1$H NMR**

400 MHz, CDCl$_3$

* indicates minor regioisomer (1 : 33)

---

**$^{13}$C NMR**

101 MHz, CDCl$_3$
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
5db

$^1$H NMR
400 MHz, CDCl$_3$

Chemical Shift (ppm)

5db

$^{13}$C NMR
101 MHz, CDCl$_3$

Chemical Shift (ppm)
5dh
$^{19}$F NMR
376 MHz, CDCl$_3$

5eb
$^1$H NMR
400 MHz, CDCl$_3$
**13C NMR**

5eb

101 MHz, CDCl₃

Chemical Shift (ppm)

---

**19F NMR**

5eb

376 MHz, CDCl₃

Chemical Shift (ppm)
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
5hb
$^1$H NMR
400 MHz, CDCl$_3$

5hb
$^{13}$C NMR
101 MHz, CDCl$_3$
$5hb$

$^{19}F$ NMR
376 MHz, CDCl$_3$

$5ib$

$^1H$ NMR
400 MHz, CDCl$_3$

Minor isomer (indicated with *)
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
5bf
$^1$H NMR
400 MHz, CDCl$_3$

---

5bf
$^{13}$C NMR
101 MHz, CDCl$_3$
5bf
\(^{19}\text{F NMR}\)
376 MHz, CDCl\(_3\)

---

Chemical Shift (ppm)

---

5bg
\(^{1}\text{H NMR}\)
400 MHz, CDCl\(_3\)
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
$^1$H NMR
400 MHz, CDCl$_3$

$^{13}$C NMR
101 MHz, CDCl$_3$
$\text{\textsuperscript{19}F NMR}$

$376$ MHz, CDCl$_3$

$\text{\textsuperscript{1}H NMR}$

$400$ MHz, CDCl$_3$
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
9

$^1$H NMR
400 MHz, CDCl$_3$

Chemical Shift (ppm)

12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

160.84 159.72 158.27 132.87 128.28 127.94 126.84 124.38 123.17 122.63 118.82 116.09

13C NMR
101 MHz, CDCl$_3$

Chemical Shift (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30

S71
$^{19}$F NMR
376 MHz, CDCl$_3$

$^1$H NMR
400 MHz, CDCl$_3$
16
$^{19}$F NMR
376 MHz, CD$_3$OD

17
$^1$H NMR
400 MHz, CDCl$_3$
$^{13}$C NMR
101 MHz, CDCl$_3$

$^{19}$F NMR
376 MHz, CDCl$_3$
11. References:


