

Supporting Information for

Controlled Chemoselective Defluorination and Non-Defluorination for [5+1] Aromatic Annulation via Meisenheimer-Type Nitrogen Anion and Radical Intermediates

Jinlong Qian, Jinlong Zhang, Huameng Yang, Lei Kang, and Gaoxi Jiang*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Excellence in Molecular Synthesis, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P. R. China

E-mail: gxjiang@licp.cas.cn

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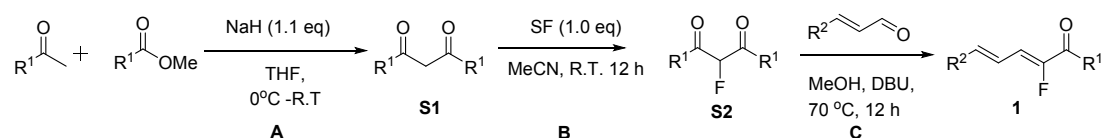
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1. General information

All reactions were run using flame-dried glassware and magnetic stirring. Chemicals and solvents were purchased from commercial suppliers and used as received. Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz, respectively. Fluorine (^{19}F NMR) nuclear magnetic resonance spectra were recorded at 377 MHz. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^1H NMR: $\text{CDCl}_3 = 7.27$ ppm, $\text{CD}_3\text{OD} = 4.87, 3.31$ ppm; for ^{13}C NMR: $\text{CDCl}_3 = 77.23$ ppm, $\text{CD}_3\text{OD} = 49.15$ ppm. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200-300 mesh). High resolution mass spectra (HRMS) were recorded on Bruker MicrOTOF-QII mass instrument (ESI). GC-MS were measured on the QP2010 SE instruments.

General procedures

General procedure A: Synthesis of 2-fluoro-1,3-diketone substrates **1**.^[1, 2]



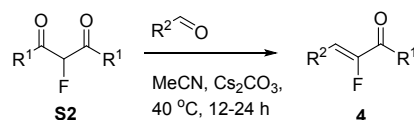
Step A: To a suspension of ketone (10 mmol) in THF (40 mL) was added NaH (0.8g, 20 mmol, 60%). After the reaction mixture was stirred at 0°C for about 1 h, the ester was added dropwise at the same temperature. Then the mixture was stirred at room temperature until TLC indicated the total consumption of the ketone. The reaction mixture was poured into ice-water (100 mL), acidified with aqueous HCl (3 M) to pH 2~3 and extracted with EtOAc (100 mL x 3). The combined organic layer was dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography to afford the pure 1,3-diketone (All the 1,3-diketones were obtained in the same process.)

Step B: The 1,3-diketone (5 mmol) was added to a solution of SelectfluorTM (1.77 g, 5 mmol) in CH_3CN (30 mL with 3mL water). After stirring at room temperature for 12 h, until TLC indicated the total consumption of the 1,3-diketone. The solvent was removed by rotary evaporation to provide raw products. The residue was then extracted with CH_2Cl_2 , dried over Na_2SO_4 . The solvent was removed under reduced pressure to yield corresponding 2-fluoro-1,3-diketones (All the products could be used for the next step without further purification).

Step C: The 2-fluoro-1,3-diketone (0.6 mmol) was added to a solution of cinnamyl aldehyde (0.5 mmol) and DBU (0.5 mmol) in CH_3CN (5 mL). After stirring at 70°C for 12 h, until TLC indicated the total consumption of the 2-fluoro-1,3-diketone. The solvent was removed by rotary evaporation to provide raw products. The

residue was then purified by silica gel flash chromatography using ethyl acetate/petroleum ether as eluent to give the expected product 2-fluoro-2,4-dien-1-one **1** in moderate yields (All the products **1** were not stable at room temperature, needs to be saved at -20 °C and in dark).

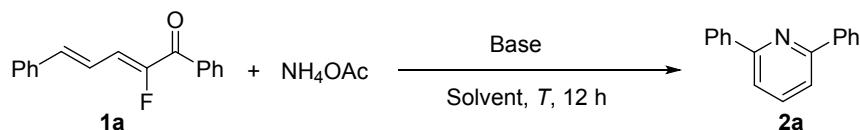
General procedure B: Synthesis of α -fluoro- α,β -unsaturated ketones **4**.^[1]



The 2-fluoro-1,3-diketone (0.6 mmol) was added to a solution of aldehyde (0.5 mmol) and Cs₂CO₃ (0.5 mmol) in CH₃CN (5 mL). After stirring at 40 °C for 12-24 h, until TLC indicated the total consumption of the 2-fluoro-1,3-diketone. The solvent was removed by rotary evaporation to provide raw products. The residue was then purified by silica gel flash chromatography using ethyl acetate/petroleum ether as eluent to give the expected product α -fluoro- α,β -unsaturated ketones **4** in moderate to excellent yields.

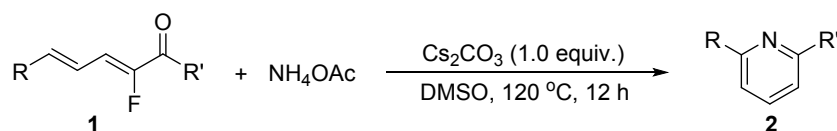
General procedure C: Base promote defluorination to synthesis of 2,6-disubstituted pyridine **2**. (Scheme 2)

Table 1. Optimization of the reaction conditions^[a]



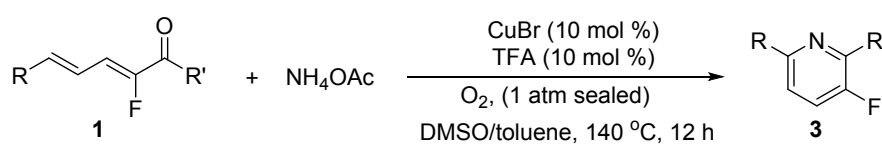
Entry	base	1a :Base:NH ₄ OAc	solvent	<i>T</i> [°C]	Yield [%]
1	Na ₂ CO ₃	1:1:5	DMSO	120	23
2	K ₂ CO ₃	1:1:5	DMSO	120	60
3	Cs ₂ CO ₃	1:1:5	DMSO	120	97 (93) ^b
4	NaOH	1:1:5	DMSO	120	77
5	Cs ₂ CO ₃	1:1.2:5	DMSO	120	90
6	Cs ₂ CO ₃	1:1:2	DMSO	120	66
7	Cs ₂ CO ₃	1:1:10	DMSO	120	93
8	Cs ₂ CO ₃	1:1:5	Toluene	120	52
9	Cs ₂ CO ₃	1:1:5	DMF	120	77
10	Cs ₂ CO ₃	1:1:5	MeCN	120	43
11	Cs ₂ CO ₃	1:1:5	DMSO	100	67
12	Cs ₂ CO ₃	1:1:5	DMSO	150	89
13 ^c	Cs ₂ CO ₃	1:1:5	DMSO	120	95

[a] **1a** (0.1 mmol), NH₄OAc, Cs₂CO₃, 12 h, solvent (1.0 mL). yields given by GC-MS using n-dodecane as an internal standard. [b] Yield of isolated products were given in the parentheses. [c] extended reaction time to 24 h.



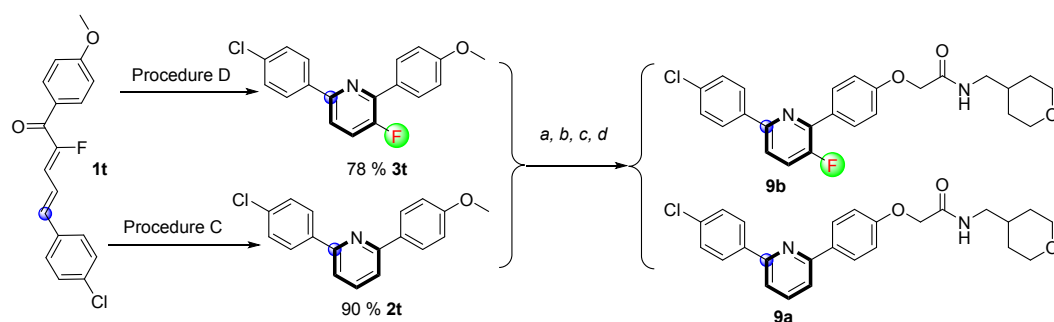
To a solution of 2-fluoro-2,4-dien-1-one **1** (0.1 mmol) and NH_4OAc (0.5 mmol) in DMSO (1 mL) was added Cs_2CO_3 (0.1 mmol) and stirred for 12 h at 120 °C. Upon consumption of 2-fluoro-2,4-dien-1-one **1** (monitored by TLC), the reaction mixture was extracted with EtOAc (5 mL x 3) and purified by silica gel flash chromatography to afford the 2,6-disubstituted pyridine **2a-r**. (All known compounds were compared with the literature).^[12]

General procedure D: Cu-catalyst aerobic dehydrogenative to synthesis of 3-fluoro-2,6-disubstituted pyridine **3**. (Scheme 3)



CuBr (10 mol %, 0.01 mmol), NH_4OAc (5.0 equiv, 0.5 mmol) and **1** (0.1 mmol) were added in a 10 mL Schlenk flask, after that the reaction tube have been degassed and placed with oxygen (1 atm) three times, then TFA (10 mol %, 0.01 mmol) and DMSO/toluene (1 mL, v/v = 5 %) were added under oxygen atmosphere. After stirring for 12 h under sealed tube conditions at 140 °C, the reaction mixture was concentrated and purified by silica gel flash chromatography to provide the expected 3-fluoro-2,6-disubstituted pyridine **3a-s**.

Procedure E: total synthesis of Blood lipid regulator **9a** and F-modified analogue **9b**.^[3]



a) BBr_3 , DCM, 0 °C-RT; b) K_2CO_3 , $\text{ClCH}_2\text{CO}_2\text{Et}$, DMF, RT; c) LiOH , MeOH, RT; d) (tetrahydro-2H-pyran-4-yl)methanamine, HOBT, EDCI, 4-ethylmorpholine, DMF, RT;

Procedure C: To a solution of (2Z,4E)-5-(4-chlorophenyl)-2-fluoro-1-(4-methoxyphenyl)penta-2,4-dien-1-one **1t** (5 mmol) and NH_4OAc (25 mmol) in DMSO (50 mL) was added Cs_2CO_3 (5 mmol) and stirred for 12 h at 120 °C. Upon consumption of (2Z,4E)-5-(4-chlorophenyl)-2-fluoro-1-(4-methoxyphenyl)penta-2,4-dien-1-one **1t** (monitored by TLC), the reaction mixture was extracted with EtOAc (50 mL x 3) and purified by silica gel flash chromatography to afford the product **2t**.

Procedure D: CuBr (10 mol %, 0.5 mmol), NH_4OAc (5.0 equiv, 25 mmol) and **1t** (5

mmol) were added in a 500 mL Schlenk flask, after that the reaction tube have been degassed and placed with oxygen (1 atm) three times, then TFA (10 mol %, 0.5 mmol) and DMSO/toluene (50 mL, v/v = 5 %) were added under oxygen atmosphere. After stirring for 12 h under sealed tube conditions at 140 °C, the reaction mixture was concentrated and purified by silica gel flash chromatography to provide the expected product **3t**.

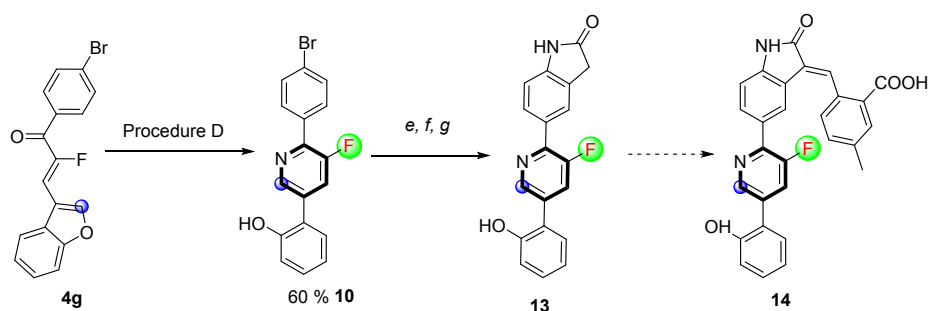
Step a: **2t/3t** dissolved in dichloromethane and the solution was cooled to 0 °C by ice-water bath. By use of a syringe a dichloromethane solution (1M) of 5 equivalents of BBr₃ per equivalent of methoxyl compound was added drop-wise under nitrogen. The ice bath was removed and reaction mixture stirred at RT for additional 2 hours under nitrogen. Reaction was quenched by addition of water and layers were separated. The water layer was washed two more times by use of dichloromethane. The water layer was neutralized to pH 7 by use of sodium bicarbonate and extracted by ethyl acetate. Collected extracts were dried over anhydrous MgSO₄ and solvent was removed. The crude products could be used for the next step without further purification.

Step b: To a solution of **6a/6b** (2 mmol) in DMF (10 ml), K₂CO₃ (0.6 g, 2.6 mmol) was added followed by the addition of ethyl 2-chloroacetate (0.32 g, 2.6 mmol) at room temperature and the reaction mixture was stirred at room temperature for 18 hours. The reaction mixture was poured into ice cold water. The water layer was extracted by ethyl acetate. Collected extracts were dried over anhydrous MgSO₄ and solvent was removed. The residue was then purified by silica gel flash chromatography using ethyl acetate/petroleum ether as eluent to give the expected product **7a/7b**.

Step c: To a solution of the product of step **b** (1.5 mmol) in a mixture of methanol (10 ml), THF (30 ml) and H₂O (10 ml), lithium hydroxide (0.13 g, 3.0 mmol) was added and the reaction mixture was stirred at ambient temperature for 4 hours. The solvents were evaporated under reduced pressure. The residue was dissolved in water and acidified with 1 N HCl. The water layer was extracted by ethyl acetate. Collected extracts were dried over anhydrous MgSO₄ and solvent was removed. The crude products **8a/8b** could be used for the next step without further purification.

Step d: To a solution of product of step **c** (1.00 mmol) in DMF (3 mL), (tetrahydro-2H-pyran-4-yl)methanamine (126 mg, 1.10 mmoles), HOBt (202 mg, 1.50 mmoles), EDC·HCl (230 mg, 1.20 mmoles) and N-ethyl morpholine (345 mg, 3.00 mmoles) were added and reaction mixture was stirred at room temperature for 20 hours under nitrogen atmosphere. The reaction mixture was poured into ice cold water. The water layer was extracted by ethyl acetate. Collected extracts were dried over anhydrous MgSO₄ and solvent was removed. The residue was then purified by silica gel flash chromatography using ethyl acetate/petroleum ether as eluent to give the expected product **9a/9b**.

Procedure F: total synthesis of F-modified AMPK receptor inhibitor 14.^[4,5,6]



e) CuI, NH₄OH, K₂CO₃, DMSO, 85 °C; f) acetic anhydride, DCM, RT; g) Pd(OAc)₂, AgOAc, ICH₂CO₂Et, TFA, 120 °C.

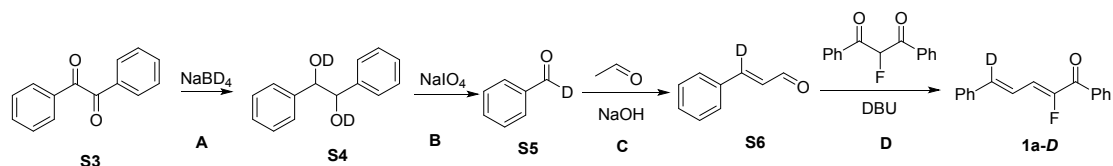
Procedure D: CuBr (10 mol %, 0.3 mmol), NH₄OAc (5.0 equiv, 15 mmol) and **4g** (3 mmol) were added in a 500 mL Schlenk flask, after that the reaction tube have been degassed and placed with oxygen (1 atm) three times, then TFA (10 mol %, 0.3 mmol) and DMSO/toluene (30 mL, v/v = 5 %) were added under oxygen atmosphere. After stirring for 12 h under sealed tube conditions at 140 °C, the reaction mixture was concentrated and purified by silica gel flash chromatography to provide the expected product **10**.

Step e: A mixture of **10** (1 mmol), aqueous ammonia (28%, 0.3 mL, 5.0 mmol), CuI (38 mg, 0.2 mmol) and K₂CO₃ (346 mg, 2.5 mmol) in 2 mL of DMSO was heated at 85 °C for 23 h. Then the cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by chromatography on silica gel with petroleum ether and ethyl acetate as eluent to provide the primary arylamine **11**.

Step f: Arylamine **11** (0.5 mmol; 1 equiv) was added to a round-bottom flask. The flask was purged with N₂ and CH₂Cl₂ (3 mL) was added. Ac₂O (1.2 mmol, 1.2 equiv) was added and the reaction was stirred at r.t. and monitored by TLC. Upon completion, the reaction mixture was washed with a saturated sodium carbonate solution, the organic layer was dried (MgSO₄), and the solvent was removed under reduced pressure. The crude product could be used for the next step without further purification.

Step g: A seal-tube (10 mL) initially fitted with a septum containing **12** (0.1 mmol), Pd(OAc)₂ (2.6 mg, 0.01 mmol, 10 mol%), and AgOAc (16.7 mg, 0.1 mmol) was evacuated and purged with N₂ three times. TFA (1.0 mL), and ethyl 2-iodoacetate (32 mg, 0.15 mmol) were added to the system and the reaction mixture was stirred at 120 °C for 24 h. The mixture was cooled to RT and filtered through a short Celite pad and washed with CH₂Cl₂ several times. The filtrate was concentrated under vacuum and purified on a silica gel column using petroleum ether/EtOAc as eluent to give the corresponding pure oxindole product **13**.

Procedure G: Synthesis of (2Z,4E)-2-fluoro-1,5-diphenylpenta-2,4-dien-1-one-5-d^[7,8]

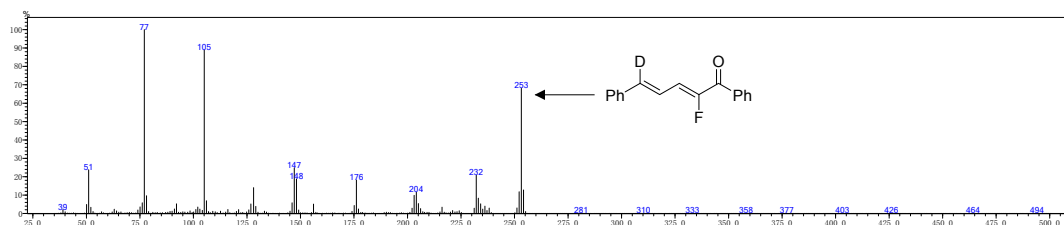


Step A: Following the similar procedure in literature with minor modification:^[7] firstly the Benzil (**S3**, 1.05g, 5 mmol) was dissolved in a mixture solvent, which containing dried THF (10 mL) and D₂O (0.5 mL). At 0 °C, NaBD₄ (250 mg, 6.2 mmol, >98% D isotopic purity) was added in portion-wise over one hour. The mixture was stirred until no **S3** left, monitored via TLC. After general workup, the reaction mixture was extracted with EtOAc, dried over Na₂SO₄, filtered and concentrated to give the product **S4** as a white solid in nearly quantitative yield, which was pure enough for the next step.

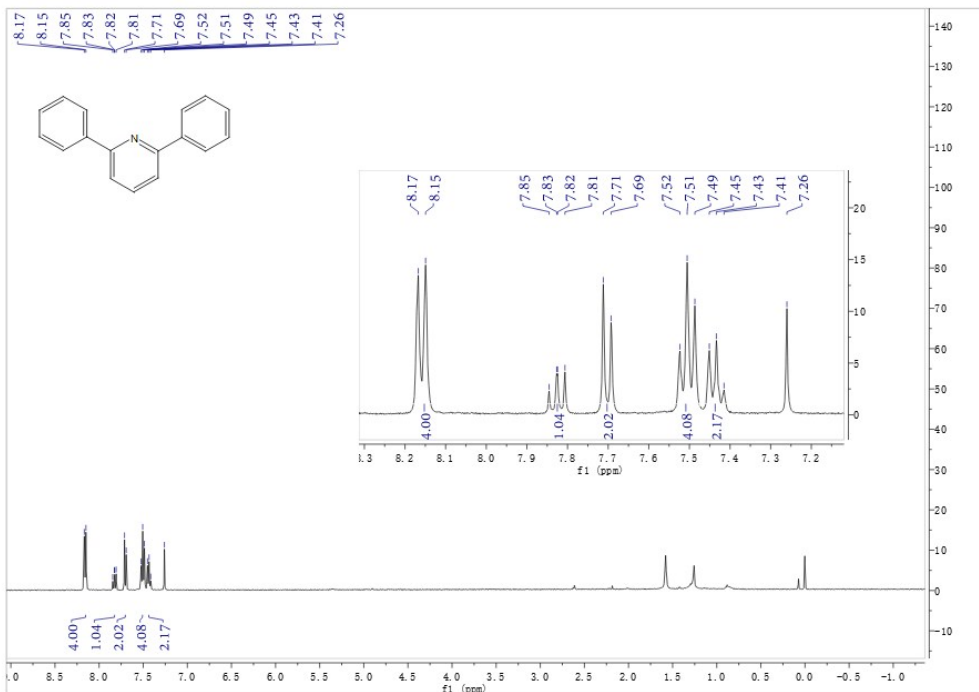
Step B: Following the similar procedure in literature with minor modification:^[8] The diol **S4** was oxidized with NaIO₄ in ethanol overnight at room temperature. After the reaction was complete (monitored by TLC), the mixture was treated with general workup. Deuteriobenzaldehyde **S5** was purified over silica gel.

Step C: To a solution of sodium hydroxide (0.12 g, 3 mmol) in a mixture of ethanol (8 mL) and water (24 mL) was added aldehyde (3 mmol). The mixture was stirred at 0 °C for 10 minutes. Then 40 percent acetaldehyde (0.66 g, 6 mmol) was added dropwise to the mixture over 3 h at the same temperature. Stirring was continued overnight at 0 °C. The resulting solution was extracted with DCM, the combined organic layer was washed with water and brine three times, and dried with anhydrous Na₂SO₄. The solution was concentrated and purified by flash chromatography on silica gel to give the pure **S6**.

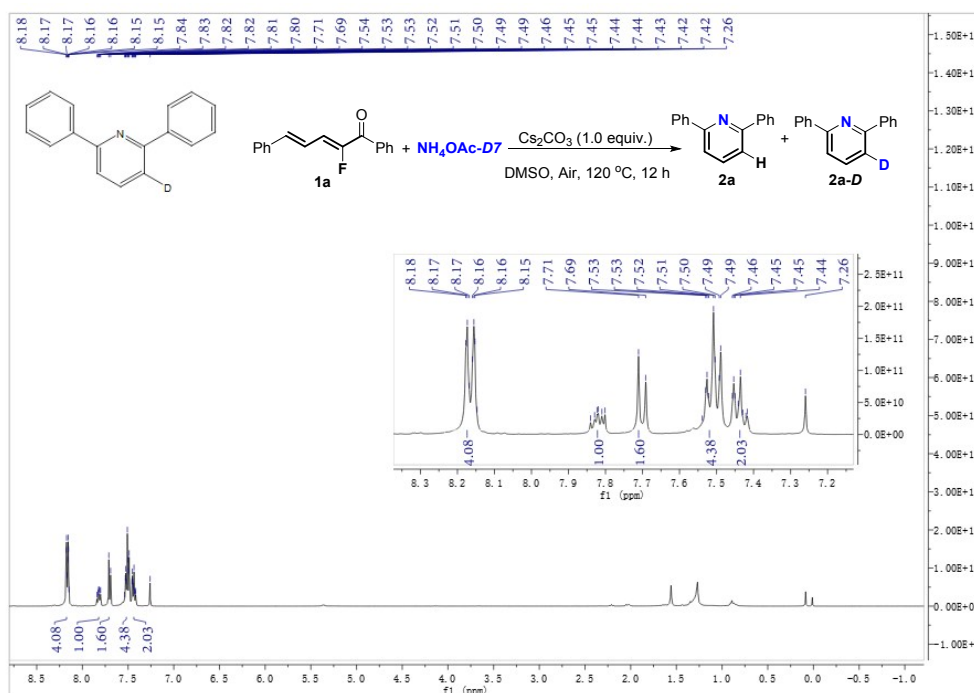
Step D: Following the similar procedure of **General procedure A, Step C**.



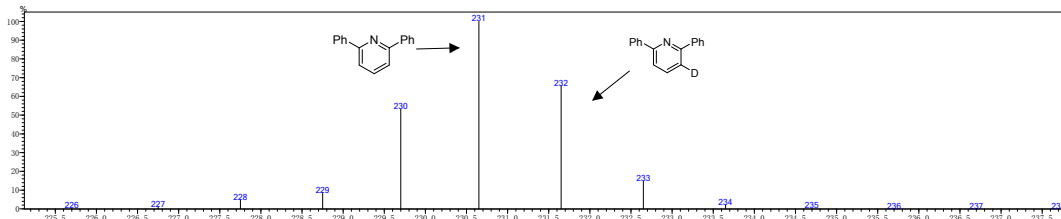
Deuterium labeled reaction result



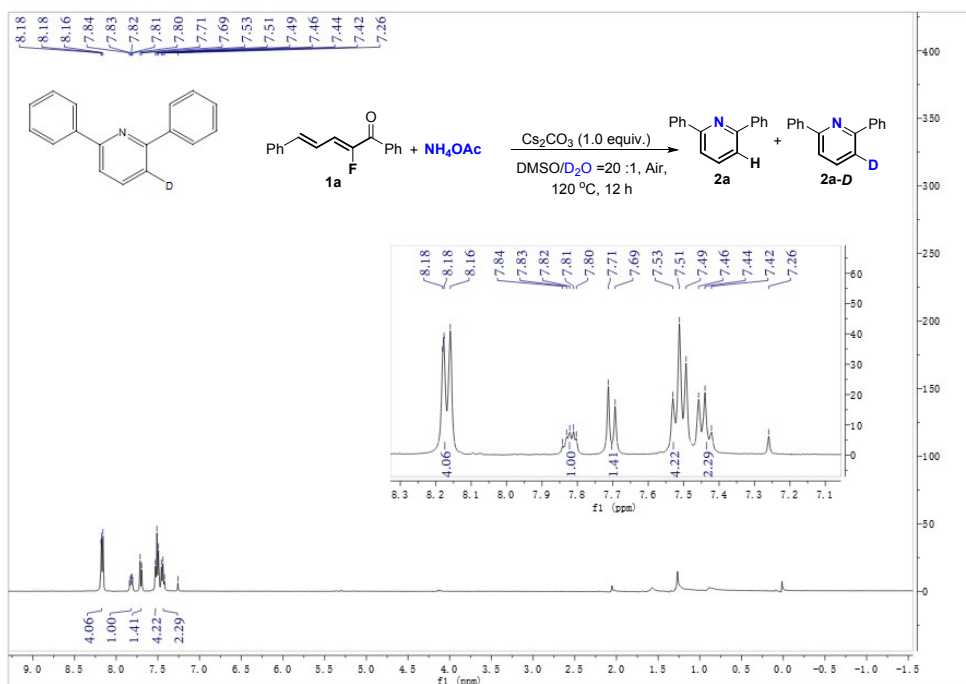
¹H-NMR of 2a



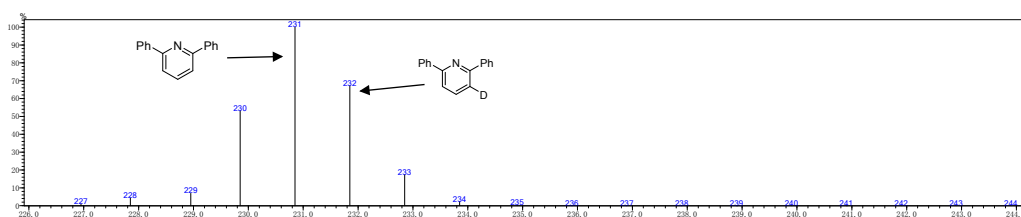
¹H-NMR of 2a/2a-D by using NH₄OAc-D₇ instead of NH₄OAc



GC-MS Spectrogram of 2a/2a-D by using NH₄OAc-D₇ instead of NH₄OAc



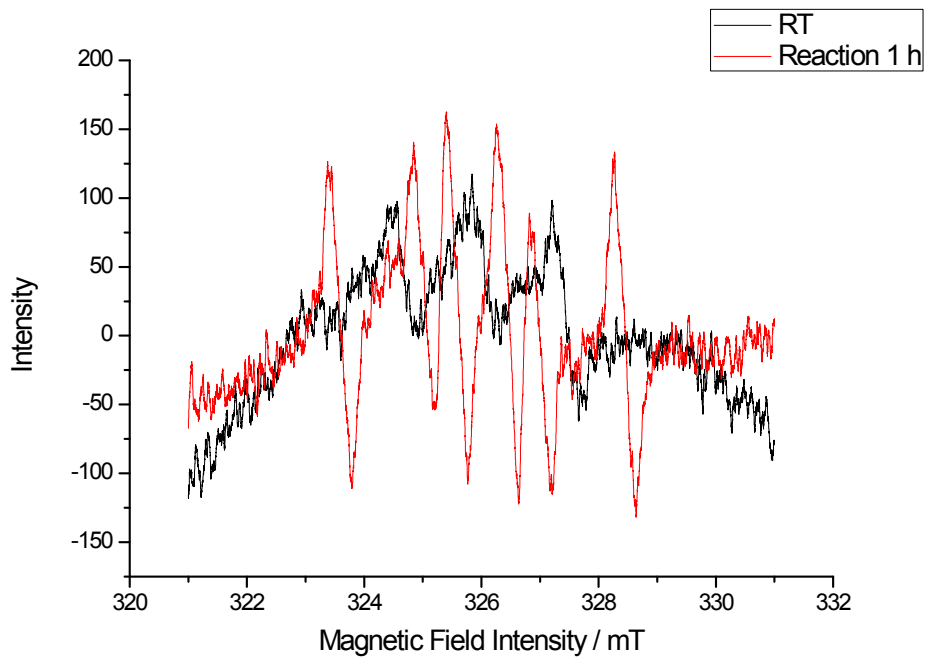
¹H-NMR of 2a/2a-D by using DMSO/D₂O = 20:1 as solvent



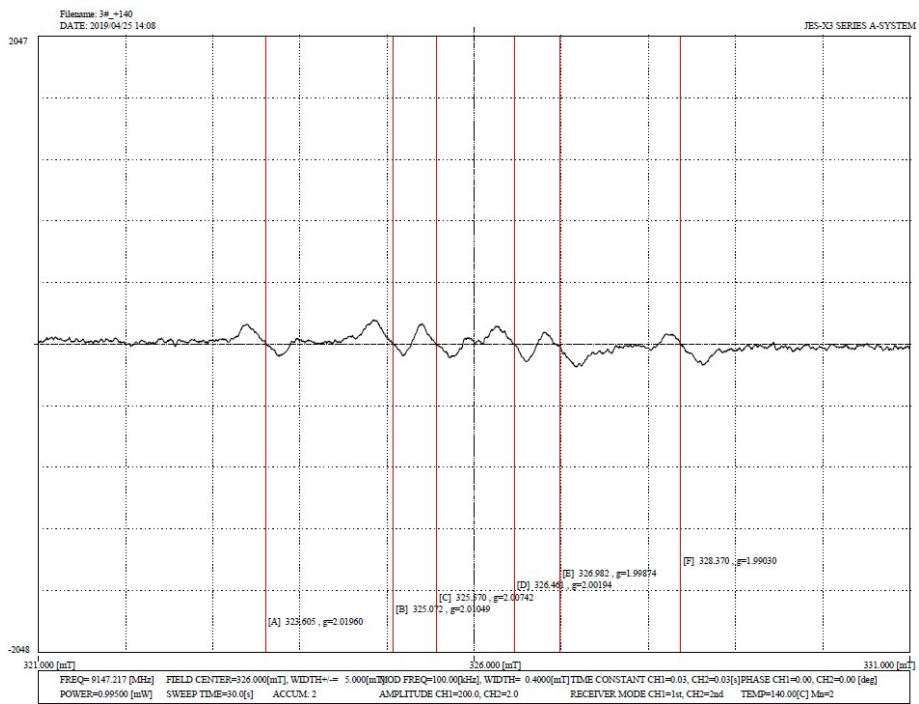
GC-MS Spectrogram of 2a/2a-D by using DMSO/D₂O = 20:1 as solvent

Procedure for Electron Paramagnetic Resonance (EPR)

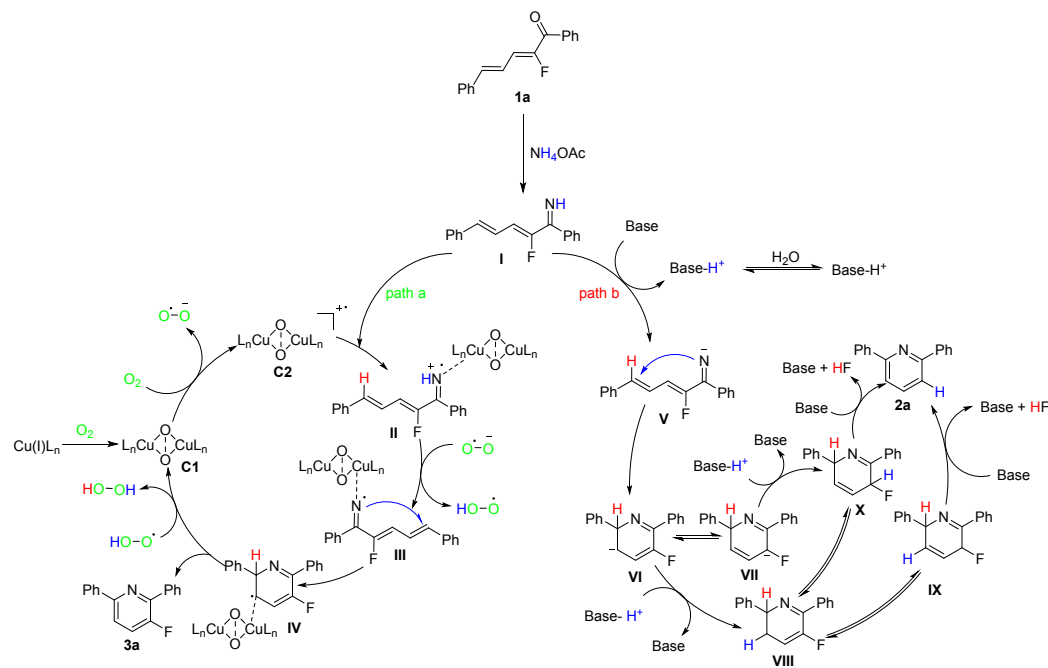
To a test tube, 0.1 mmol **1a**, 0.01 mmol CuBr and TFA, 0.5 mmol NH₄OAc, 1 mL DMSO/toluene (v/v = 5 %) and 10 μL DMPO were added. The result mixture was stirred at room temperature under oxygen atmosphere for 10 min, extract the reaction liquid for EPR testing. Then the reaction was stirred at 140 °C for 1 h, extract the reaction liquid for EPR testing.



The DMPO spin-trapping ESR spectra for $\cdot\text{O}_2^-$ in Cu-catalytic system.



The details of ESR spectra.



The proposed mechanism for the direct transformation.

Path a: On the basis of mechanistic studies results and literature survey, a plausible mechanism for the aerobic oxidative non-defluorinative [5+1] aromatic annulation is illustrated. The copper(I) salt was initially oxidized by dioxygen to form the more-active (μ - η^2 : η^2 -peroxy)dicopper(II) complex **C1**.^[9] Then, complex **C1** is oxidized by molecular oxygen, furnishing radical cation **C2** and superoxide radical anion ($\cdot\text{O}_2^-$), **C2** then oxidizes **I** via single-electron transfer (SET), producing amine radical cation **II**, followed by subsequent deprotonation and intramolecular cycloaddition forms intermediate **IV**,^[10, 11] which underwent hydrogen atom abstraction to give the corresponding 3-fluoropyridine product **3a**, regenerating **C1** for the catalytic cycle.

Path b: Imine anion **V** is deprotonated by base, which then occurred intramolecular cycloaddition reactions to produce **VI**. Intermediates **VI** could be transformed into **VII** or **VIII**, **VII** could be protonated by base- H^+ to produce intermediates **X**. **VIII** could also be produced **X** or **IX** by double bond migration reaction. At last, the product **2a** is generated from **IX** or **X** though defluorination reaction by base-promoted procedure. It should be mentioned that the base- H^+ species could be occurred hydrogen deuterium exchange process with water. As a result of the existence of isotope effect, which may lead to the low rate of deuterium labeled **2a** produced in the deuterium labeled reactions.

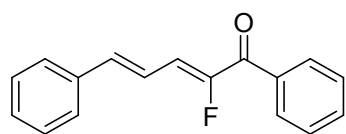
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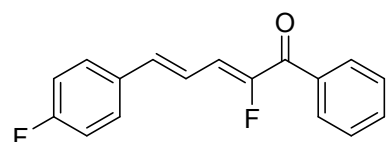
2. Experimental characterization data

(2Z,4E)-2-fluoro-1,5-diphenylpenta-2,4-dien-1-one (1a):



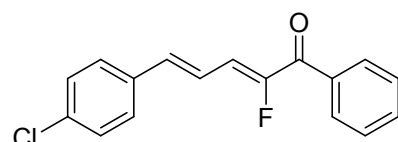
Yellow oil. 81.9 mg, 65 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (s, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.53 – 7.46 (m, 4H), 7.41 – 7.30 (m, 3H), 7.21 (dd, $J = 15.7, 11.3$ Hz, 1H), 6.90 (d, $J = 15.8$ Hz, 1H), 6.75 (dd, $J = 31.7, 11.3$ Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -123.03 (d, $J = 31.6$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.33, 154.03 (d, $J = 269.6$ Hz), 140.42, 136.25 (d, $J = 39.8$ Hz), 132.79, 129.40, 129.25, 129.21, 128.92, 128.50, 127.41, 122.24 (d, $J = 12.8$ Hz), 119.25. **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{14}\text{FO}$ [$\text{M}+\text{H}$]: 253.1029, found: 253.1031.

(2Z,4E)-2-fluoro-5-(4-fluorophenyl)-1-phenylpenta-2,4-dien-1-one (1b):



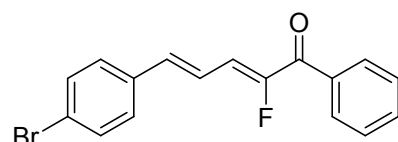
Yellow oil. 98.5 mg, 73 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.2$ Hz, 4H), 7.17 – 7.01 (m, 3H), 6.87 (d, $J = 15.8$ Hz, 1H), 6.74 (dd, $J = 31.6, 11.3$ Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -110.93, -122.97 (d, $J = 31.6$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.10 (d, $J = 27.6$ Hz), 163.30 (d, $J = 250.6$ Hz), 154.06 (d, $J = 269.7$ Hz), 138.95, 136.38, 132.82, 132.32, 129.22 (d, $J = 3.7$ Hz), 129.10 (d, $J = 8.3$ Hz), 128.49, 121.95, 119.02, 116.02 (d, $J = 21.9$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}$ [$\text{M}+\text{H}$]: 271.0934, found: 271.0935.

(2Z,4E)-2-fluoro-5-(4-chlorophenyl)-1-phenylpenta-2,4-dien-1-one (1c):



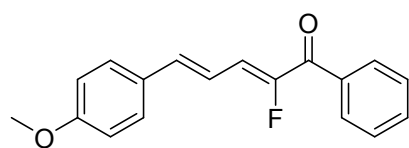
Yellow oil. 100.1 mg, 70 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.63 – 7.56 (m, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.17 (dd, $J = 15.6, 11.4$ Hz, 1H), 6.85 (d, $J = 15.7$ Hz, 1H), 6.74 (dd, $J = 31.5, 11.3$ Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.17. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.07 (d, $J = 27.2$ Hz), 154.26 (d, $J = 270.8$ Hz), 138.78, 136.31, 135.11, 134.56, 132.89, 129.25 (d, $J = 3.9$ Hz), 129.15, 128.51, 127.20, 121.62 (d, $J = 9.9$ Hz), 119.81 (d, $J = 3.0$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{13}\text{ClFO}$ [$\text{M}+\text{H}$]: 287.0639, found: 287.0637.

(2Z,4E)-2-fluoro-5-(4-bromophenyl)-1-phenylpenta-2,4-dien-1-one (1d):



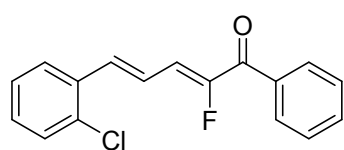
Yellow oil. 114.2 mg, 69 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.7$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.49 (dd, $J = 8.2, 6.2$ Hz, 4H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.19 (dd, $J = 15.8, 11.3$ Hz, 1H), 6.84 (d, $J = 15.7$ Hz, 1H), 6.74 (dd, $J = 31.5, 11.3$ Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.04 (d, $J = 31.4$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.18, 154.30 (d, $J = 272.3$ Hz), 138.79, 136.30, 134.99, 132.88, 132.10, 129.26, 128.73, 128.51, 123.40, 121.48 (d, $J = 9.5$ Hz), 119.90. **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{13}\text{BrFO}$ [$\text{M}+\text{H}$]: 331.0314, found: 331.0316.

(2Z,4E)-2-fluoro-5-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (1e):



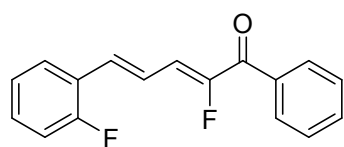
Yellow oil. 79.0 mg, 56 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.6$ Hz, 2H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.53 – 7.39 (m, 4H), 7.08 (dd, $J = 15.6$, 11.3 Hz, 1H), 6.96 – 6.83 (m, 3H), 6.75 (dd, $J = 31.7$, 11.3 Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -124.78 (d, $J = 31.8$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.03, 160.73, 153.58 (d, $J = 267.1$ Hz), 140.21, 136.67, 132.58, 129.17 (d, $J = 4.0$ Hz), 128.94, 128.43, 122.96 (d, $J = 8.6$ Hz), 117.19 (d, $J = 2.8$ Hz), 114.39, 55.40. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}_2$ [$\text{M}+\text{H}$]: 283.1134, found: 283.1135.

(2Z,4E)-2-fluoro-5-(2-chlorophenyl)-1-phenylpenta-2,4-dien-1-one (1f):



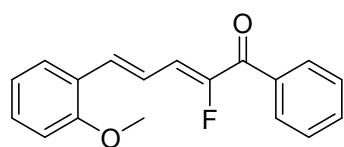
Yellow oil. 87.2 mg, 61 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 – 7.79 (m, 2H), 7.72 (d, $J = 5.9$ Hz, 1H), 7.61 (d, $J = 7.2$ Hz, 1H), 7.52 (d, $J = 6.4$ Hz, 2H), 7.43 – 7.36 (m, 1H), 7.26 (dd, $J = 30.1$, 16.5 Hz, 4H), 6.80 (dd, $J = 32.7$, 11.9 Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -121.72 (d, $J = 31.4$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.16 (d, $J = 29.1$ Hz), 174.39, 154.39 (d, $J = 272.1$ Hz), 136.30, 135.70 (d, $J = 3.8$ Hz), 134.11 (d, $J = 10.0$ Hz), 132.92, 130.13, 129.26 (d, $J = 4.0$ Hz), 128.56, 127.07 (d, $J = 14.3$ Hz), 121.88, 121.74, 121.51, 121.48. **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{13}\text{ClFO}$ [$\text{M}+\text{H}$]: 287.0639, found: 287.0641.

(2Z,4E)-2-fluoro-5-(2-fluorophenyl)-1-phenylpenta-2,4-dien-1-one (1g):



Yellow oil. 91.5 mg, 68 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (d, $J = 37.4$ Hz, 2H), 7.61 (s, 2H), 7.50 (s, 3H), 7.30 (d, $J = 10.8$ Hz, 2H), 7.14 – 7.04 (m, 2H), 6.86 – 6.67 (m, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -110.34 – -120.36 (m), -121.99 (d, $J = 31.5$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 191.30, 160.82 (d, $J = 253.3$ Hz), 154.28 (d, $J = 270.7$ Hz), 136.34, 134.55, 132.58 (d, $J = 57.4$ Hz), 130.66 (d, $J = 8.6$ Hz), 129.91 (d, $J = 9.4$ Hz), 129.24 (d, $J = 3.9$ Hz), 128.81, 128.52, 127.75, 124.47, 121.44, 116.07 (d, $J = 22.0$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}$ [$\text{M}+\text{H}$]: 271.0934, found: 271.0933.

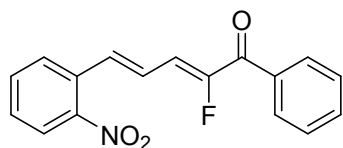
(2Z,4E)-2-fluoro-5-(2-methoxyphenyl)-1-phenylpenta-2,4-dien-1-one (1h):



Yellow oil. 70.5 mg, 50 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.6$ Hz, 2H), 7.64 – 7.56 (m, 2H), 7.49 (t, $J = 7.7$ Hz, 2H), 7.36 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.90 (d, $J = 8.3$ Hz, 1H), 6.85 – 6.71 (m, 1H), 3.88 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -124.22 (d, $J = 31.8$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 182.00 (d, $J = 25.8$ Hz), 152.28, 148.36 (d, $J = 267.5$ Hz), 131.38, 130.18 (d, $J = 4.4$ Hz), 127.26, 125.27, 123.86 (d, $J = 3.8$ Hz), 123.12, 122.17, 119.79, 118.23 (d, $J = 10.1$ Hz), 115.57, 114.40 (d, $J = 3.3$ Hz), 105.81, 50.23. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}_2$ [$\text{M}+\text{H}$]: 283.1134,

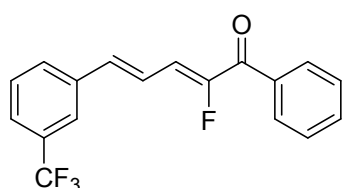
found: 283.1136.

(2Z,4E)-2-fluoro-5-(2-nitrophenyl)-1-phenylpenta-2,4-dien-1-one (1i):



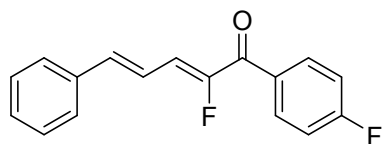
Yellow solid. m.p. 101-103 °C, 105.4 mg, 71 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.63 (q, *J* = 7.8, 7.1 Hz, 2H), 7.50 (t, *J* = 8.5 Hz, 3H), 7.40 (d, *J* = 15.7 Hz, 1H), 7.23 – 7.12 (m, 1H), 6.77 (dd, *J* = 31.3, 11.1 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -119.99 (d, *J* = 31.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 187.18, 154.81 (d, *J* = 272.6 Hz), 148.05, 136.01, 134.28, 133.41, 133.12, 131.58, 129.46, 129.26 (d, *J* = 3.8 Hz), 128.62, 128.49, 124.98, 123.93, 120.93. HRMS (ESI) calcd. for C₁₇H₁₃FNO₃ [M+H]: 298.0879, found: 298.0881.

(2Z,4E)-2-fluoro-5-(3-(trifluoromethyl)-1-phenylpenta-2,4-dien-1-one (1j):



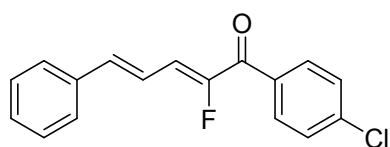
Yellow solid. m.p. 79-81 °C, 126.4 mg, 79 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.81 (m, 2H), 7.73 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 3H), 7.26 (ddd, *J* = 15.8, 11.3, 2.3 Hz, 1H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.77 (dd, *J* = 31.4, 11.3 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -62.90, -121.01 (d, *J* = 31.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 187.15, 154.65 (d, *J* = 272.1 Hz), 138.22, 136.84, 136.15, 133.01, 130.22, 129.41, 129.30, 129.27, 128.54, 125.66, 123.96, 120.96. HRMS (ESI) calcd. for C₁₈H₁₃F₄O [M+H]: 321.0903, found: 321.0904.

(2Z,4E)-2-fluoro-1-(4-fluorophenyl)-5-phenylpenta-2,4-dien-1-one (1k):



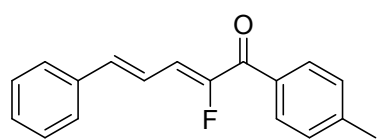
Yellow oil. 95.9 mg, 71 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (dd, *J* = 8.3, 5.4 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.36 (dd, *J* = 11.2, 7.0 Hz, 3H), 7.22 – 7.13 (m, 3H), 6.93 (d, *J* = 15.7 Hz, 1H), 6.79 (dd, *J* = 31.7, 11.3 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -100.31 – -108.68 (m), -122.74 (d, *J* = 31.7 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 185.23, 165.58 (d, *J* = 254.8 Hz), 154.10 (d, *J* = 270.6 Hz), 140.56, 136.03, 132.53, 132.39 – 131.37 (m), 129.44, 128.93, 127.41, 121.65, 119.13, 115.71 (d, *J* = 22.0 Hz). HRMS (ESI) calcd. for C₁₇H₁₃F₂O [M+H]: 271.0934, found: 271.0936.

(2Z,4E)-2-fluoro-1-(4-chlorophenyl)-5-phenylpenta-2,4-dien-1-one (1l):



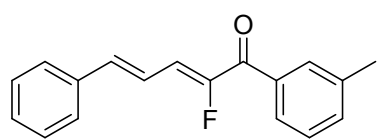
Yellow oil. 94.4 mg, 66 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 20.4, 7.7 Hz, 3H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.29 – 7.12 (m, 2H), 6.94 (d, *J* = 15.7 Hz, 1H), 6.78 (dd, *J* = 31.7, 11.3 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -123.17 (d, *J* = 31.6 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 185.78, 153.97 (d, *J* = 270.4 Hz), 140.78, 139.33, 135.98, 134.59, 130.72 (d, *J* = 4.7 Hz), 129.50, 128.94, 128.85, 127.44, 121.99, 119.11. HRMS (ESI) calcd. for C₁₇H₁₃ClFO [M+H]: 287.0639, found: 287.0641.

(2Z,4E)-2-fluoro-1-(p-tolyl)penta-5-phenylpenta-2,4-dien-1-one (1m):



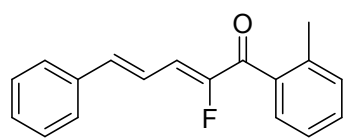
Yellow oil. 71.8 mg, 54 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.74 (m, 2H), 7.54 – 7.47 (m, 2H), 7.41 – 7.31 (m, 3H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.24 – 7.17 (m, 1H), 6.89 (d, $J = 15.8$ Hz, 1H), 6.75 (dd, $J = 31.8$, 11.3 Hz, 1H), 2.43 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.50 (d, $J = 31.7$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.63, 154.29 (d, $J = 273.2$ Hz), 143.74, 140.04, 136.13, 133.72, 129.45 (d, $J = 4.2$ Hz), 129.31, 129.19, 128.90, 128.43, 127.36, 126.44, 121.55 (d, $J = 12.2$ Hz), 119.35, 21.73. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}$ [$\text{M}+\text{H}$]: 267.1185, found: 267.1187.

(2Z,4E)-2-fluoro-5-phenyl-1-(m-tolyl)penta-2,4-dien-1-one (1n):



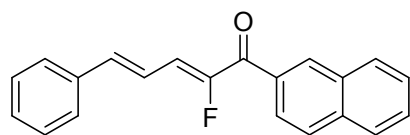
Yellow oil. 66.8 mg, 50 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (s, 2H), 7.51 (d, $J = 7.4$ Hz, 2H), 7.37 (t, $J = 6.5$ Hz, 5H), 7.23 (d, $J = 11.4$ Hz, 1H), 6.91 (d, $J = 15.8$ Hz, 1H), 6.75 (dd, $J = 31.6$, 11.3 Hz, 1H), 2.43 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.85 (d, $J = 31.6$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.41, 171.44, 154.07 (d, $J = 269.5$ Hz), 153.14, 140.28, 138.38 (d, $J = 8.0$ Hz), 134.61, 133.58, 130.60 (d, $J = 24.2$ Hz), 128.91, 128.31, 127.38, 126.38, 122.25 (d, $J = 10.3$ Hz), 119.32, 21.30. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}$ [$\text{M}+\text{H}$]: 267.1185, found: 267.1186.

(2Z,4E)-2-fluoro-5-phenyl-1-(o-tolyl)penta-2,4-dien-1-one (1o):



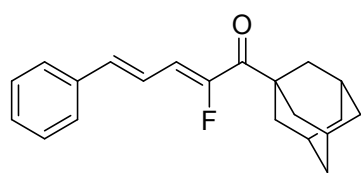
Yellow oil. 65.2 mg, 49 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.1$ Hz, 2H), 7.39 – 7.33 (m, 4H), 7.28 (d, $J = 8.8$ Hz, 2H), 7.23 – 7.17 (m, 1H), 7.08 (s, 1H), 6.85 (d, $J = 15.8$ Hz, 1H), 6.50 (dd, $J = 30.8$, 11.3 Hz, 1H), 2.38 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.39. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 190.21, 153.90 (d, $J = 267.5$ Hz), 140.94, 136.85, 135.91, 131.11, 130.72, 129.54, 128.93, 128.00, 127.45, 125.38, 124.12 (d, $J = 9.6$ Hz), 119.28, 19.54. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}$ [$\text{M}+\text{H}$]: 267.1185, found: 267.1186.

(2Z,4E)-2-fluoro-1-(naphthalen-2-yl)-5-phenylpenta-2,4-dien-1-one (1p):



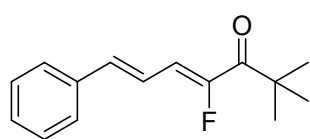
Yellow solid. m.p. 92-95 °C, 83.1 mg, 55 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.41 (s, 1H), 7.94 (dt, $J = 22.2$, 7.9 Hz, 4H), 7.60 (dt, $J = 19.2$, 7.2 Hz, 2H), 7.52 (d, $J = 7.4$ Hz, 2H), 7.37 (dt, $J = 11.4$, 7.0 Hz, 3H), 7.25 (t, $J = 13.6$ Hz, 1H), 6.92 (d, $J = 15.9$ Hz, 1H), 6.83 (dd, $J = 31.6$, 11.3 Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.41 (d, $J = 31.7$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 187.10, 154.32 (d, $J = 269.0$ Hz), 140.38, 136.08, 135.38, 133.65, 132.31, 130.81, 129.54, 129.40, 128.93, 128.57, 128.45, 127.87, 127.41, 126.96, 125.09, 122.14, 119.32. **HRMS** (ESI) calcd. for $\text{C}_{21}\text{H}_{16}\text{FO}$ [$\text{M}+\text{H}$]: 303.1185, found: 303.1187.

(2Z,4E)-1-((1S,3s)-adamantan-1-yl)-2-fluoro-5-phenylpenta-2,4-dien-1-one (1q):



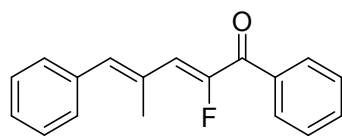
Yellow oil. 66.7 mg, 43 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 6.9$ Hz, 2H), 7.48 – 7.36 (m, 3H), 7.19 – 7.04 (m, 1H), 6.93 (dd, $J = 15.0, 10.7$ Hz, 1H), 6.87 – 6.69 (m, 1H), 2.12 (s, 3H), 2.03 (d, $J = 11.0$ Hz, 6H), 1.82 – 1.78 (m, 6H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -124.01. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.37 (d, $J = 29.6$ Hz), 155.75 (d, $J = 279.1$ Hz), 139.27, 136.35, 128.98, 128.81, 127.16, 119.21 (d, $J = 4.1$ Hz), 118.30 – 116.88 (m), 37.05, 36.64, 36.27, 27.96. **HRMS** (ESI) calcd. for $\text{C}_{21}\text{H}_{24}\text{FO}$ [$\text{M}+\text{H}$]: 311.1811, found: 311.1813.

(4Z,6E)-4-fluoro-2,2-dimethyl-7-phenylhepta-4,6-dien-3-one (1r):



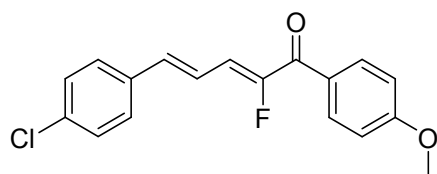
Yellow oil. 70.8 mg, 61 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 5.8$ Hz, 2H), 7.42 – 7.28 (m, 3H), 7.14 – 7.02 (m, 1H), 6.88 (d, $J = 16.0$ Hz, 1H), 6.77 (dd, $J = 31.3, 11.8$ Hz, 1H), 1.27 (s, 9H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -123.32. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 198.73, 155.16 (d, $J = 278.3$ Hz), 139.46, 136.31, 129.05, 128.85, 127.20, 119.18 (d, $J = 3.7$ Hz), 117.93 (d, $J = 9.4$ Hz), 42.85, 25.76. **HRMS** (ESI) calcd. for $\text{C}_{15}\text{H}_{18}\text{FO}$ [$\text{M}+\text{H}$]: 233.1342, found: 233.1344.

(2Z,4E)-2-fluoro-4-methyl-1,5-diphenylpenta-2,4-dien-1-one (1s):



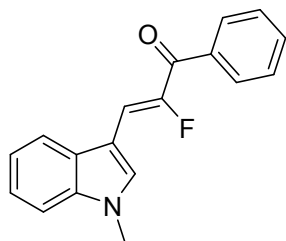
Yellow oil. 58.5 mg, 44 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 – 7.97 (m, 1H), 7.84 (d, $J = 7.7$ Hz, 2H), 7.49 (dt, $J = 9.2, 4.7$ Hz, 3H), 7.37 – 7.34 (m, 2H), 6.85 (d, $J = 15.3$ Hz, 1H), 6.63 (d, $J = 36.3$ Hz, 1H), 2.29 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -121.89 (d, $J = 36.2$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 185.80, 153.43 (d, $J = 271.9$ Hz), 138.67 (d, $J = 5.7$ Hz), 136.54, 132.60 (d, $J = 21.6$ Hz), 129.47, 129.30 (d, $J = 3.9$ Hz), 128.72, 128.45, 128.38, 127.86, 127.21, 125.64, 93.19, 16.68 (d, $J = 7.7$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{16}\text{FO}$ [$\text{M}+\text{H}$]: 267.1185, found: 267.1187.

(2Z,4E)-5-(4-chlorophenyl)-2-fluoro-1-(4-methoxyphenyl)penta-2,4-dien-1-one (1t):



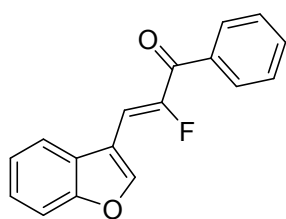
Yellow solid. m.p. 80-82 °C, 2.433 g, 77 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 – 7.87 (m, 2H), 7.45 – 7.29 (m, 4H), 7.14 (dd, $J = 15.7, 11.3$ Hz, 1H), 7.02 – 6.93 (m, 2H), 6.83 (d, $J = 15.8$ Hz, 1H), 6.75 (ddd, $J = 31.8, 11.4, 0.8$ Hz, 1H), 3.88 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -120.70. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 185.17 (d, $J = 26.9$ Hz), 163.61, 154.84 (d, $J = 272.7$ Hz), 138.08 (d, $J = 4.9$ Hz), 134.80 (d, $J = 18.3$ Hz), 131.85 (d, $J = 5.4$ Hz), 129.45, 129.10, 128.77, 128.42, 120.17 (d, $J = 10.4$ Hz), 119.91 (d, $J = 3.5$ Hz), 113.81, 55.54. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{ClFO}_2$ [$\text{M}+\text{H}$]: 317.0745, found: 317.0747.

(Z)-2-fluoro-3-(1-methyl-1H-indol-3-yl)-1-phenylprop-2-en-1-one (4d):



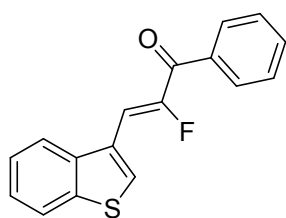
Yellow solid. m.p. 95-97 °C, 60.0 mg, 43 % yield. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.81 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.24 (dd, *J* = 9.7, 6.3 Hz, 2H), 3.89 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -122.30 (d, *J* = 37.7 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 187.30, 153.07 (d, *J* = 260.2 Hz), 137.39, 136.84, 133.40 (d, *J* = 14.6 Hz), 132.19, 129.15 (d, *J* = 3.6 Hz), 128.38, 127.51, 123.03, 121.20, 118.79, 115.02, 109.91, 107.12, 33.50. HRMS (ESI) calcd. for C₁₈H₁₅FNO [M+H]: 280.1138, found: 280.1139.

(Z)-3-(benzofuran-3-yl)-2-fluoro-1-phenylprop-2-en-1-one (4e):



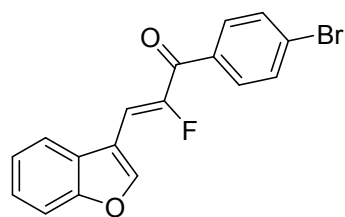
Yellow solid. m.p. 93-95 °C, 83.8 mg, 63 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 3.6 Hz, 1H), 7.98 – 7.89 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.59 – 7.49 (m, 3H), 7.35 (dt, *J* = 20.1, 7.4 Hz, 2H), 7.11 (dd, *J* = 37.2, 4.1 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -112.33 (d, *J* = 37.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 186.77 (d, *J* = 27.0 Hz), 155.26 (d, *J* = 270.3 Hz), 155.05, 147.95 (d, *J* = 14.9 Hz), 136.17, 133.06, 129.39 (d, *J* = 4.3 Hz), 128.58, 125.71, 125.41, 123.61, 119.75, 113.11, 111.87, 109.89 (d, *J* = 11.5 Hz). HRMS (ESI) calcd. for C₁₇H₁₂FO₂ [M+H]: 267.0821, found: 267.0823.

(Z)-3-(benzo[b]thiophen-3-yl)-2-fluoro-1-phenylprop-2-en-1-one (4f):

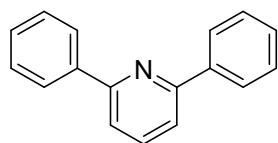


Brown solid. m.p. 76-78 °C, 105.8 mg, 75 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 1H), 7.98 – 7.86 (m, 3H), 7.86 – 7.77 (m, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 (qt, *J* = 8.0, 4.1 Hz, 2H), 7.29 (d, *J* = 29.6 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -116.94 (d, *J* = 35.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 187.43 (d, *J* = 30.1 Hz), 155.46 (d, *J* = 272.6 Hz), 139.23, 137.94, 136.28, 133.04, 131.26 (d, *J* = 16.2 Hz), 129.42 (d, *J* = 4.1 Hz), 128.82, 128.58, 126.23, 125.06 (d, *J* = 21.1 Hz), 122.92, 121.23, 111.23 (d, *J* = 8.7 Hz). HRMS (ESI) calcd. for C₁₇H₁₂FOS [M+H]: 283.0593, found: 283.0596.

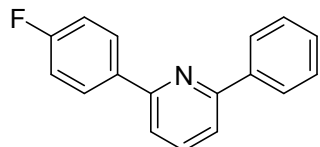
(Z)-3-(benzofuran-3-yl)-1-(4-bromophenyl)-2-fluoroprop-2-en-1-one (4g):



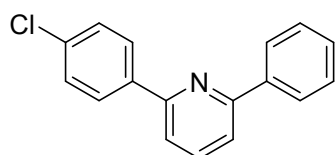
Yellow solid. m.p. 112-114 °C, 1.324 g, 77 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.12 (d, *J* = 37.2 Hz, 1H). ¹⁹F NMR (377 MHz, CDCl₃) δ -124.43 (d, *J* = 12.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 185.38 (d, *J* = 28.7 Hz), 155.15 (d, *J* = 270.6 Hz), 155.07, 148.16, 134.75, 131.91, 130.93 (d, *J* = 4.9 Hz), 128.29, 125.63, 125.49, 123.68, 119.74, 113.08, 111.89, 109.77 (d, *J* = 12.3 Hz). HRMS (ESI) calcd. for C₁₇H₁₁BrFO₂ [M+H]: 344.9926, found: 344.9928.

2,6-diphenylpyridine (2a):^[12a]

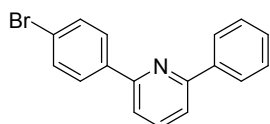
Buff solid. 21.0 mg, 93 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.21 – 8.10 (m, 4H), 7.82 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.47 – 7.40 (m, 2H).

2-(4-fluorophenyl)-6-phenylpyridine (2b):^[12a]

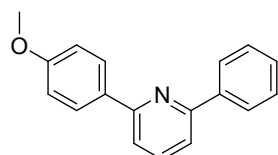
Yellow solid. 22.7 mg, 91 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.11 (m, 3H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 17.3, 7.8 Hz, 2H), 7.60 – 7.41 (m, 4H), 7.18 (t, *J* = 8.6 Hz, 2H).

2-(4-chlorophenyl)-6-phenylpyridine (2c):^[12a]

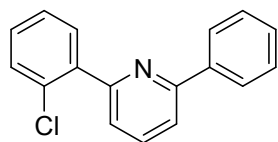
Yellow solid. 23.3 mg, 88 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.06 (m, 4H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.68 (dd, *J* = 17.7, 7.8 Hz, 2H), 7.55 – 7.41 (m, 5H).

2-(4-bromophenyl)-6-phenylpyridine (2d):^[12a]

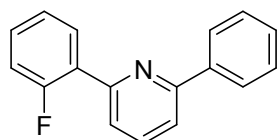
Yellow solid. 26.4 mg, 85 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (dt, *J* = 6.3, 1.3 Hz, 2H), 8.07 – 8.01 (m, 2H), 7.82 (dd, *J* = 8.3, 7.4 Hz, 1H), 7.69 (ddd, *J* = 18.9, 7.9, 1.0 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m, 1H).

2-(4-bromophenyl)-6-phenylpyridine (2e):^[12a]

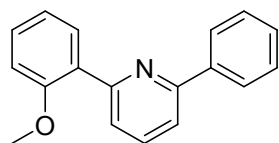
Yellow solid. 22.2 mg, 85 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.06 (m, 4H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.54 – 7.46 (m, 2H), 7.46 – 7.37 (m, 1H), 7.07 – 7.00 (m, 2H), 3.88 (s, 3H).

2-(2-chlorophenyl)-6-phenylpyridine (2f):^[12a]

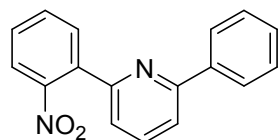
Yellow solid. 23.6 mg, 89 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.05 (m, 2H), 7.84 (t, *J* = 7.8 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.45 – 7.32 (m, 3H).

2-(2-fluorophenyl)-6-phenylpyridine (2g):^[12a]

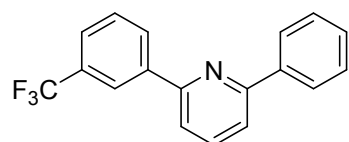
Yellow solid. 21.4 mg, 89 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (td, *J* = 7.9, 1.9 Hz, 1H), 8.15 – 8.09 (m, 2H), 7.87 – 7.75 (m, 2H), 7.72 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.47 – 7.35 (m, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.17 (ddd, *J* = 11.5, 8.2, 1.2 Hz, 1H).

2-(2-methoxyphenyl)-6-phenylpyridine (2h): ^[12a]

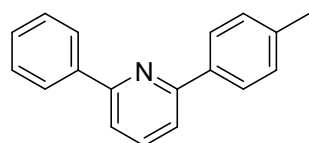
Yellow solid. 21.7 mg, 83 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.07 (m, 2H), 8.01 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.83 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.66 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.34 (m, 2H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H).

2-(2-nitrophenyl)-6-phenylpyridine (2i): ^[12a]

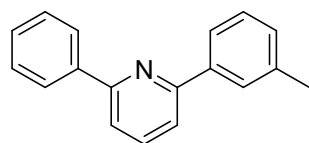
Yellow solid. 23.5 mg, 85 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.93 (m, 2H), 7.88 (t, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.60 (m, 2H), 7.55 (td, *J* = 7.7, 1.6 Hz, 1H), 7.52 – 7.38 (m, 4H).

2-phenyl-6-(3-(trifluoromethyl)phenyl)pyridine (2j): ^[12a]

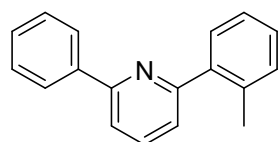
Yellow solid. 26.9 mg, 90 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.19 – 8.10 (m, 2H), 7.86 (td, *J* = 7.8, 0.9 Hz, 1H), 7.79 – 7.66 (m, 3H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.40 (m, 1H).

2-phenyl-6-(p-tolyl)pyridine (2m): ^[12a]

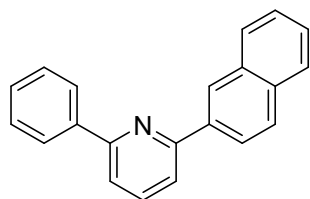
Yellow solid. 21.8 mg, 89 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.6 Hz, 2H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H).

2-phenyl-6-(m-tolyl)pyridine (2n): ^[12a]

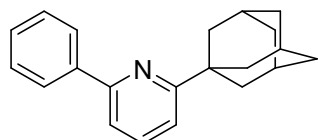
Yellow solid. 21.6 mg, 88 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 7.6 Hz, 2H), 7.98 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.34 (m, 3H), 2.46 (s, 3H).

2-phenyl-6-(o-tolyl)pyridine (2o): ^[12a]

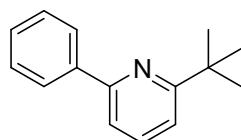
Yellow solid. 20.8 mg, 85 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.04 (m, 2H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.47 (td, *J* = 7.9, 6.0 Hz, 3H), 7.44 – 7.34 (m, 2H), 7.31 (d, *J* = 1.5 Hz, 3H), 2.49 (s, 3H).

2-(naphthalen-2-yl)-6-phenylpyridine (2p): ^{12a}

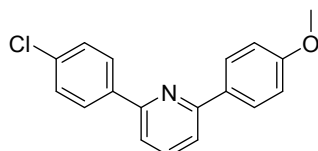
Yellow solid. 25.9 mg, 92 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.33 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 3H), 7.72 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 4H), 7.46 (d, *J* = 7.0 Hz, 1H).

2-((3r,5r,7r)-adamantan-1-yl)-6-phenylpyridine (2q):

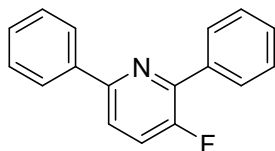
Yellow oil. 19.2 mg, 91 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 6H), 1.81 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 168.75, 155.50, 140.02, 136.76, 129.90, 128.57, 126.85, 117.16, 116.96, 42.00, 39.29, 36.94, 28.89. HRMS (ESI) calcd. for C₂₁H₂₄N [M+H]: 290.1909, found: 290.1910.

2-(tert-butyl)-6-phenylpyridine (2r): ^{12b}

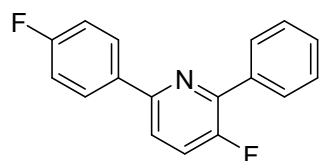
Yellow oil. 19.2 mg, 91 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.06 (m, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 5.6 Hz, 1H), 1.43 (s, 9H).

2-(4-chlorophenyl)-6-(4-methoxyphenyl)pyridine (2t):

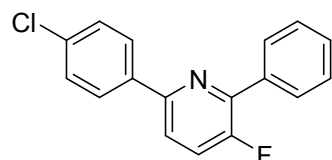
Yellow solid. 1.33 g, 90 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dq, *J* = 8.8, 1.9 Hz, 4H), 7.82 – 7.73 (m, 1H), 7.68 – 7.56 (m, 2H), 7.45 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.07 – 6.99 (m, 2H), 3.88 (d, *J* = 1.8 Hz, 3H).

3-fluoro-2,6-diphenylpyridine (3a):

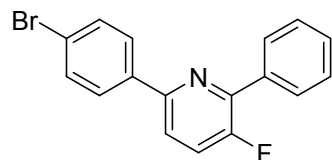
Pink oil. 19.9 mg, 80 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J* = 20.5, 7.7 Hz, 4H), 7.69 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.58 – 7.39 (m, 7H). ¹⁹F NMR (377 MHz, CDCl₃) δ -121.41 – -127.16 (m). ¹³C NMR (100 MHz, CDCl₃) δ 156.98 (d, *J* = 260.7 Hz), 152.85, 145.09, 138.53, 135.66, 129.24, 128.97, 128.91, 128.77, 128.44, 126.85, 124.94 (d, *J* = 21.5 Hz), 120.11 (d, *J* = 4.2 Hz). HRMS (ESI) calcd. for C₁₇H₁₃FN [M+H]: 250.1032, found: 250.1033.

3-fluoro-6-(4-fluorophenyl)-2-phenylpyridine (3b):

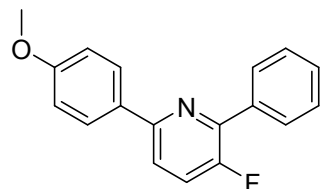
Pink oil. 20.0 mg, 75 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 – 8.00 (m, 4H), 7.62 (dd, $J = 8.5, 3.1$ Hz, 1H), 7.49 (dt, $J = 16.2, 9.4$ Hz, 4H), 7.15 (t, $J = 8.4$ Hz, 2H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -107.87 – -117.94 (m), -126.57 (dd, $J = 10.5, 2.8$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.49 (d, $J = 248.3$ Hz), 156.90 (d, $J = 260.7$ Hz), 151.88, 145.15, 135.54, 134.71, 129.31, 128.90 (d, $J = 6.1$ Hz), 128.64 (d, $J = 8.3$ Hz), 128.46, 125.01 (d, $J = 21.7$ Hz), 119.73 (d, $J = 4.3$ Hz), 115.65 (d, $J = 21.5$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_2\text{N}$ [$\text{M}+\text{H}$]: 268.0938, found: 268.0940.

6-(4-chlorophenyl)-3-fluoro-2-phenylpyridine (3c):

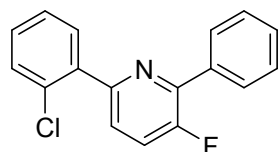
Pink oil. 20.4 mg, 72 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 – 8.07 (m, 2H), 8.05 – 7.98 (m, 2H), 7.67 (dd, $J = 8.5, 3.2$ Hz, 1H), 7.58 – 7.50 (m, 3H), 7.50 – 7.41 (m, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.89 (dd, $J = 10.7, 3.0$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.04 (d, $J = 261.2$ Hz), 151.65, 136.93, 135.04, 129.36, 128.93, 128.87, 128.48, 128.10, 125.05 (d, $J = 21.6$ Hz), 119.89 (d, $J = 4.4$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{ClFN}$ [$\text{M}+\text{H}$]: 284.0642, found: 284.0643.

6-(4-bromophenyl)-3-fluoro-2-phenylpyridine (3d):

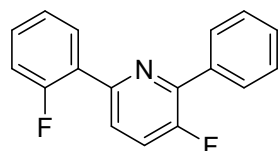
Pink oil. 24.3 mg, 74 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (dt, $J = 6.9, 1.4$ Hz, 2H), 7.98 – 7.92 (m, 2H), 7.66 (dd, $J = 8.6, 3.1$ Hz, 1H), 7.62 – 7.58 (m, 2H), 7.57 – 7.48 (m, 3H), 7.48 – 7.43 (m, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.72 (dt, $J = 10.3, 2.1$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.05 (d, $J = 261.3$ Hz), 137.35, 135.41, 131.87, 129.36, 128.89 (d, $J = 6.0$ Hz), 128.47, 128.38, 126.97, 125.04 (d, $J = 21.6$ Hz), 123.36, 122.25, 119.85 (d, $J = 4.4$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{BrFN}$ [$\text{M}+\text{H}$]: 328.0137, found: 328.0140.

3-fluoro-6-(4-methoxyphenyl)-2-phenylpyridine (3e):

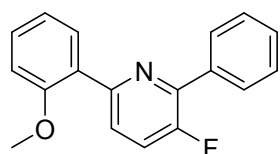
Pink oil. 22.6 mg, 81 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (d, $J = 7.6$ Hz, 2H), 8.03 (d, $J = 8.3$ Hz, 2H), 7.62 (dd, $J = 8.5, 3.3$ Hz, 1H), 7.48 (dt, $J = 25.3, 7.7$ Hz, 4H), 7.00 (d, $J = 8.3$ Hz, 2H), 3.87 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -127.66 (dd, $J = 10.8, 3.0$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.38, 156.59 (d, $J = 259.8$ Hz), 152.56, 144.81, 135.75 (d, $J = 5.9$ Hz), 131.26, 129.14, 128.92 (d, $J = 6.0$ Hz), 128.40, 128.12, 124.89 (d, $J = 21.7$ Hz), 119.32 (d, $J = 4.0$ Hz), 114.11, 55.40. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{FNO}$ [$\text{M}+\text{H}$]: 280.1138, found: 280.1140.

6-(2-chlorophenyl)-3-fluoro-2-phenylpyridine (3f):

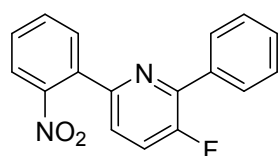
Pink oil. 23.2 mg, 82 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 – 8.02 (m, 2H), 7.68 (dd, $J = 7.3, 2.2$ Hz, 1H), 7.63 (dd, $J = 8.5, 3.4$ Hz, 1H), 7.59 – 7.53 (m, 1H), 7.53 – 7.41 (m, 4H), 7.36 (td, $J = 7.2, 1.8$ Hz, 2H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -121.93 – -138.21 (m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.76 (d, $J = 261.1$ Hz), 152.46, 145.41, 138.44, 135.29, 133.44, 131.78, 130.22, 129.67, 129.27, 128.94 (d, $J = 5.6$ Hz), 128.48, 127.05, 124.71 (d, $J = 4.4$ Hz), 124.11 (d, $J = 21.4$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{ClFN}$ [$\text{M}+\text{H}$]: 284.0642, found: 284.0643.

3-fluoro-6-(2-fluorophenyl)-2-phenylpyridine (3g):

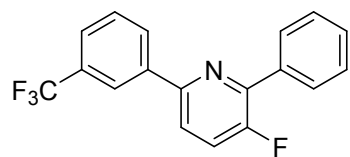
Pink oil. 20.0 mg, 75 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 (dd, $J = 21.9, 7.8$ Hz, 3H), 7.79 (d, $J = 8.6$ Hz, 1H), 7.50 (td, $J = 16.2, 15.3, 7.6$ Hz, 4H), 7.38 (q, $J = 6.9$ Hz, 1H), 7.27 (dd, $J = 12.8, 5.5$ Hz, 1H), 7.17 (dd, $J = 11.5, 8.2$ Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -114.15 – -118.40 (m), -121.93 – -128.21 (m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.57 (d, $J = 249.2$ Hz), 158.10, 147.13 (d, $J = 326.4$ Hz), 135.48, 131.20, 130.45, 130.37, 129.28, 128.90 (d, $J = 5.9$ Hz), 128.47, 124.57 (d, $J = 21.4$ Hz), 124.54 (d, $J = 3.2$ Hz), 124.38 (d, $J = 4.1$ Hz), 124.27 (d, $J = 4.4$ Hz), 116.23 (d, $J = 22.9$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_2\text{N}$ [$\text{M}+\text{H}$]: 268.0938, found: 268.0939.

3-fluoro-6-(2-methoxyphenyl)-2-phenylpyridine (3h):

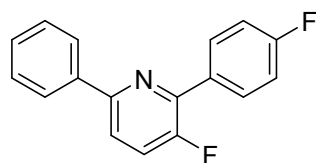
Pink oil. 20.9 mg, 75 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (dq, $J = 6.8, 1.6$ Hz, 2H), 7.95 (dt, $J = 7.6, 1.7$ Hz, 1H), 7.85 (ddd, $J = 8.6, 3.5, 1.2$ Hz, 1H), 7.53 – 7.35 (m, 5H), 7.15 – 7.07 (m, 1H), 7.01 (d, $J = 8.2$ Hz, 1H), 3.89 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.23. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.01, 156.46 (d, $J = 260.1$ Hz), 151.43 (d, $J = 4.7$ Hz), 144.93 (d, $J = 10.7$ Hz), 135.79 (d, $J = 5.6$ Hz), 131.40, 129.95, 128.97, 128.92, 128.86, 128.36, 125.02 (d, $J = 4.0$ Hz), 123.79 (d, $J = 21.0$ Hz), 121.11, 111.43, 55.63. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{FNO}$ [$\text{M}+\text{H}$]: 280.1138, found: 280.1139.

3-fluoro-6-(2-nitrophenyl)-2-phenylpyridine (3i):

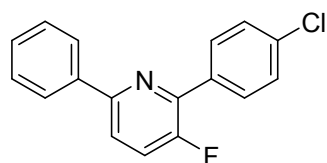
Pink oil. 25.0 mg, 85 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95 (dt, $J = 8.2, 1.7$ Hz, 2H), 7.89 – 7.84 (m, 1H), 7.68 – 7.63 (m, 2H), 7.63 – 7.51 (m, 2H), 7.51 – 7.39 (m, 4H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -124.37 (dq, $J = 10.5, 1.9$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.09 (d, $J = 262.1$ Hz), 150.67, 149.60, 145.90, 134.91, 134.26, 132.22, 130.92, 129.50, 129.28, 128.92 (d, $J = 6.0$ Hz), 128.52, 125.21 (d, $J = 21.7$ Hz), 124.45, 122.32 (d, $J = 4.7$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{FN}_2\text{O}_2$ [$\text{M}+\text{H}$]: 295.0883, found: 295.0885.

3-fluoro-2-phenyl-6-(3-(trifluoromethyl)phenyl)pyridine (3j):

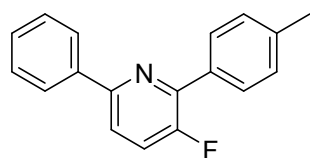
Pink oil. 24.7 mg, 78 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 (s, 1H), 8.26 (d, $J = 7.8$ Hz, 1H), 8.11 (d, $J = 7.6$ Hz, 2H), 7.73 (dd, $J = 8.5, 3.3$ Hz, 1H), 7.68 (d, $J = 7.5$ Hz, 1H), 7.60 (t, $J = 8.0$ Hz, 2H), 7.51 (dt, $J = 15.8, 7.3$ Hz, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -62.60, -114.67 – -130.95 (m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.27 (d, $J = 261.7$ Hz), 151.27, 145.59, 139.21, 137.80, 135.22, 130.05, 129.48, 129.27, 128.93 (d, $J = 6.2$ Hz), 128.53, 125.47, 125.18 (d, $J = 21.5$ Hz), 123.62, 120.23 (d, $J = 4.5$ Hz), 120.15 – 117.81 (m). **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{12}\text{F}_4\text{N}$ [$\text{M}+\text{H}$]: 318.0906, found: 318.0907.

3-fluoro-2-(4-fluorophenyl)-6-phenylpyridine (3k):

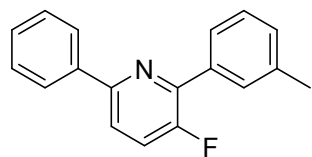
Pink oil. 17.9 mg, 67 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (ddt, $J = 6.9, 5.5, 1.4$ Hz, 2H), 8.05 (dt, $J = 6.4, 1.4$ Hz, 2H), 7.69 (dd, $J = 8.5, 3.2$ Hz, 1H), 7.60 – 7.41 (m, 4H), 7.19 (td, $J = 9.1, 2.8$ Hz, 2H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -112.07 – -112.25 (m), -122.98 – -133.35 (m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.44 (d, $J = 248.4$ Hz), 156.81 (d, $J = 260.7$ Hz), 152.89, 143.99, 138.40, 130.85, 130.85 (d, $J = 14.8$ Hz), 128.97, 128.79, 126.82, 125.03 (d, $J = 21.6$ Hz), 120.14, 115.42 (d, $J = 21.6$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_2\text{N}$ [$\text{M}+\text{H}$]: 268.0938, found: 268.0940.

2-(4-chlorophenyl)-3-fluoro-6-phenylpyridine (3l):

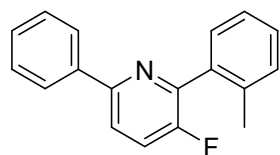
Pink oil. 21.2 mg, 75 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 – 8.00 (m, 4H), 7.70 (dd, $J = 8.6, 3.1$ Hz, 1H), 7.49 (dddd, $J = 18.0, 15.8, 10.0, 7.9$ Hz, 6H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -126.15 (d, $J = 11.0$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.94 (d, $J = 261.0$ Hz), 152.97, 143.78, 138.33, 135.33, 134.06, 130.22 (d, $J = 6.6$ Hz), 129.03, 128.80, 128.66, 126.82, 125.11 (d, $J = 21.4$ Hz), 120.43 (d, $J = 4.2$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{17}\text{H}_{12}\text{ClFN}$ [$\text{M}+\text{H}$]: 284.0642, found: 284.0644.

3-fluoro-6-phenyl-2-(p-tolyl)pyridine (3m):

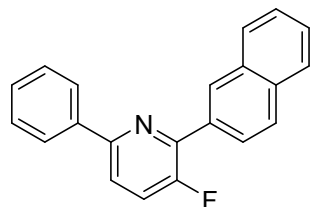
Pink oil. 18.9 mg, 72 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (ddd, $J = 14.6, 7.4, 3.5$ Hz, 4H), 7.69 – 7.62 (m, 1H), 7.52 – 7.45 (m, 3H), 7.43 – 7.40 (m, 1H), 7.31 (d, $J = 7.9$ Hz, 2H), 2.43 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -126.53 (dd, $J = 10.9, 3.0$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.90 (d, $J = 260.1$ Hz), 152.76, 139.28, 138.62, 137.41, 132.88, 129.17, 128.84, 128.78, 128.74, 126.84, 124.81 (d, $J = 21.3$ Hz), 119.74 (d, $J = 4.1$ Hz), 21.42. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{FN}$ [$\text{M}+\text{H}$]: 264.1189, found: 264.1190.

3-fluoro-6-phenyl-2-(m-tolyl)pyridine (3n):

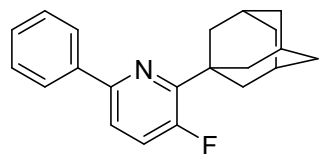
Pink oil. 16.1 mg, 61 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 – 8.03 (m, 2H), 7.95 – 7.87 (m, 2H), 7.68 (dd, $J = 8.5$, 3.1 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.41 (q, $J = 7.6$ Hz, 2H), 7.28 (s, 1H), 2.47 (s, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -124.02 – -134.05 (m). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.94 (d, $J = 260.8$ Hz), 152.89, 145.26, 138.60, 138.04, 135.52, 130.18, 130.00, 129.52 (d, $J = 5.2$ Hz), 128.85, 128.74, 126.87, 126.08 (d, $J = 6.4$ Hz), 124.84 (d, $J = 21.4$ Hz), 120.02 (d, $J = 4.0$ Hz), 21.63. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{FN}$ [$\text{M}+\text{H}$]: 264.1189, found: 264.1191.

3-fluoro-6-phenyl-2-(o-tolyl)pyridine (3o):

Pink oil. 15.6 mg, 59 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 (dt, $J = 6.2$, 1.4 Hz, 2H), 7.73 (dd, $J = 8.6$, 3.4 Hz, 1H), 7.54 (t, $J = 8.8$ Hz, 1H), 7.49 – 7.43 (m, 3H), 7.41 – 7.39 (m, 1H), 7.33 (tdd, $J = 9.2$, 7.1, 4.1 Hz, 3H), 2.35 (d, $J = 1.3$ Hz, 3H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.29 (d, $J = 9.1$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.33 (d, $J = 257.1$ Hz), 153.00, 147.70, 138.54, 136.85, 135.22, 130.49, 130.09, 128.90, 128.84, 128.75, 126.91, 125.67, 124.14 (d, $J = 21.1$ Hz), 120.36 (d, $J = 4.0$ Hz), 19.90. **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{15}\text{FN}$ [$\text{M}+\text{H}$]: 264.1189, found: 264.1190.

3-fluoro-2-(naphthalen-2-yl)-6-phenylpyridine (3p):

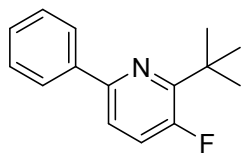
Off-white solid, m.p. 78-80 °C, 25.4 mg, 85 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.61 (s, 1H), 8.36 – 8.26 (m, 1H), 8.19 (d, $J = 7.3$ Hz, 1H), 8.11 (d, $J = 7.4$ Hz, 1H), 8.02 – 7.93 (m, 2H), 7.89 (d, $J = 4.9$ Hz, 1H), 7.84 (d, $J = 4.5$ Hz, 1H), 7.75 – 7.68 (m, 1H), 7.51 (q, $J = 7.0$ Hz, 4H), 7.44 (q, $J = 6.8$, 6.0 Hz, 1H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -125.92 (d, $J = 10.8$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 157.29 (d, $J = 261.0$ Hz), 156.87 (d, $J = 26.4$ Hz), 152.98 (d, $J = 4.8$ Hz), 144.94 (d, $J = 10.2$ Hz), 139.56, 138.57, 137.58, 136.84, 133.71 (d, $J = 8.0$ Hz), 133.40 (d, $J = 29.5$ Hz), 133.00 (d, $J = 5.8$ Hz), 129.00 (d, $J = 12.0$ Hz), 128.79 (d, $J = 4.7$ Hz), 128.38, 128.03, 127.70 (d, $J = 4.9$ Hz), 127.08, 126.91, 126.83, 126.43 (d, $J = 15.0$ Hz), 126.21 (dd, $J = 7.1$, 4.3 Hz), 125.04 (d, $J = 21.8$ Hz), 124.79, 120.16 (d, $J = 4.4$ Hz), 118.88 (d, $J = 17.5$ Hz). **HRMS** (ESI) calcd. for $\text{C}_{21}\text{H}_{15}\text{FN}$ [$\text{M}+\text{H}$]: 300.1189, found: 300.1191.

2-((3r,5r,7r)-adamantan-1-yl)-3-fluoro-6-phenylpyridine (3q):

Yellow oil. 9.5 mg, 31 % yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 7.9$ Hz, 2H), 7.62 – 7.54 (m, 1H), 7.50 – 7.41 (m, 2H), 7.41 – 7.28 (m, 2H), 2.20 (s, 6H), 2.13 (s, 3H), 1.82 (s, 6H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -122.72 (d, $J = 11.7$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.23 (d,

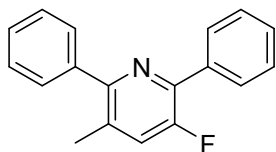
$J = 260.9$ Hz), 155.12, 151.09, 139.00, 128.63, 128.48, 126.61, 124.17 (d, $J = 22.0$ Hz), 118.37, 40.08 (d, $J = 3.4$ Hz), 37.01, 29.68, 28.83. **HRMS** (ESI) calcd. for $C_{21}H_{13}FN$ [$M+H$]: 308.1815, found: 308.1818.

2-(tert-butyl)-3-fluoro-6-phenylpyridine (3r):



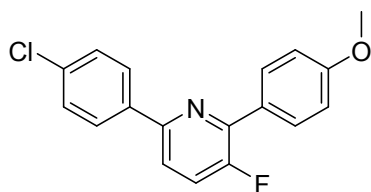
Yellow oil. 14.9 mg, 65 % yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.60 (dd, $J = 8.5, 3.0$ Hz, 1H), 7.45 (dd, $J = 8.3, 6.6$ Hz, 2H), 7.41 – 7.32 (m, 2H), 1.48 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -121.47 (d, $J = 11.5$ Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.88 (d, $J = 259.9$ Hz), 155.33 (d, $J = 11.2$ Hz), 150.77, 138.85, 128.70, 128.57, 126.62, 124.13 (d, $J = 22.0$ Hz), 118.75 (d, $J = 4.3$ Hz), 37.54 (d, $J = 5.4$ Hz), 28.76 (d, $J = 3.4$ Hz). **HRMS** (ESI) calcd. for $C_{15}H_{17}FN$ [$M+H$]: 230.1345, found: 230.1346.

3-fluoro-5-methyl-2,6-diphenylpyridine (3s):



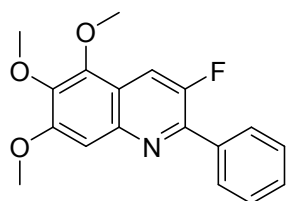
Pink oil. 17.1 mg, 65 % yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, $J = 7.5$ Hz, 2H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.43 (dt, $J = 24.9, 7.4$ Hz, 7H), 2.41 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -127.48 (d, $J = 11.5$ Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.40 (d, $J = 260.8$ Hz), 154.36, 139.97, 135.53, 134.66, 131.75, 129.21, 128.85, 128.74 (d, $J = 5.7$ Hz), 128.37, 128.15, 128.00, 126.20 (d, $J = 20.5$ Hz), 19.87. **HRMS** (ESI) calcd. for $C_{18}H_{15}FN$ [$M+H$]: 264.1189, found: 264.1191.

6-(4-chlorophenyl)-3-fluoro-2-(4-methoxyphenyl)pyridine (3t):



Yellow solid. m.p. 108-110 °C, 1.22 g, 78 % yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, $J = 8.4$ Hz, 2H), 8.01 (dd, $J = 8.6, 2.5$ Hz, 2H), 7.60 (dd, $J = 8.6, 2.9$ Hz, 1H), 7.50 (dd, $J = 10.8, 8.3$ Hz, 1H), 7.47 – 7.41 (m, 2H), 7.04 (dd, $J = 9.1, 2.6$ Hz, 2H), 3.89 (t, $J = 1.7$ Hz, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -120.36 – -136.66 (m). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.36 (d, $J = 253.6$ Hz), 155.51, 151.46, 144.93 (d, $J = 10.3$ Hz), 137.11, 134.95, 130.32, 128.87, 128.07, 124.82 (d, $J = 21.8$ Hz), 119.03, 113.90, 55.35. **HRMS** (ESI) calcd. for $C_{18}H_{14}ClFNO$ [$M+H$]: 314.0748, found: 314.0750.

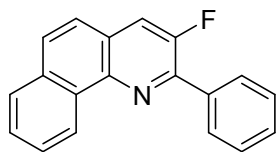
3-fluoro-5,6,7-trimethoxy-2-phenylquinoline (5a):



Yellow oil. 13.1 mg, 42 % yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 7.8$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.50 (q, $J = 9.6, 7.0$ Hz, 2H), 7.32 – 7.27 (m, 1H), 6.69 (d, $J = 8.7$ Hz, 1H), 4.06 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -76.03. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.18, 156.96 (d, $J = 210.8$ Hz), 141.84, 133.75, 130.20, 128.86, 128.51, 127.21, 116.63, 107.48, 99.16, 61.84, 61.18, 56.31. **HRMS** (ESI) calcd.

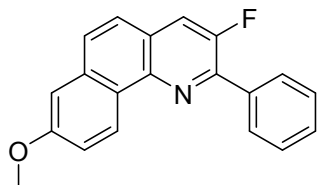
for C₁₈H₁₇FNO₃ [M+H]: 314.1192, found: 314.1194.

3-fluoro-2-phenylbenzo[h]quinoline (5b):



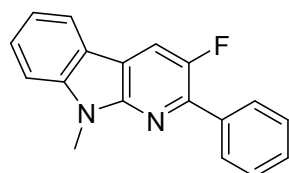
Yellow solid. m.p. 112-114 °C, 21.0 mg, 77 % yield. ¹H NMR (400 MHz, CDCl₃) δ 9.37 (d, *J* = 8.1 Hz, 1H), 8.28 (d, *J* = 7.6 Hz, 2H), 7.94 – 7.88 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 6.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 6.6 Hz, 2H). ¹⁹F NMR (377 MHz, CDCl₃) δ -125.10 (d, *J* = 11.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 156.17 (d, *J* = 261.0 Hz), 145.77 (d, *J* = 12.7 Hz), 142.81, 136.10, 133.25, 131.48, 129.49, 129.44, 129.38, 128.96, 128.55, 127.99 (d, *J* = 9.9 Hz), 127.35, 124.69, 124.28 (d, *J* = 3.0 Hz), 120.79 (d, *J* = 20.1 Hz). HRMS (ESI) calcd. for C₁₉H₁₃FN [M+H]: 274.1032, found: 274.1033.

3-fluoro-8-methoxy-2-phenylbenzo[h]quinoline (5c):



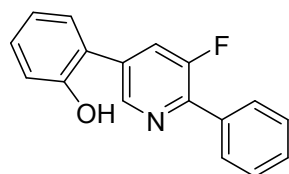
Yellow oil. 24.5 mg, 81 % yield. ¹H NMR (400 MHz, CDCl₃) δ 9.25 (d, *J* = 9.0 Hz, 1H), 8.26 (dt, *J* = 8.2, 1.6 Hz, 2H), 7.86 (d, *J* = 11.4 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.54 – 7.47 (m, 1H), 7.36 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.26 (d, *J* = 3.5 Hz, 1H), 3.99 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -126.52 (dd, *J* = 11.3, 1.9 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 159.52, 155.68 (d, *J* = 259.6 Hz), 145.85, 142.92, 136.18, 134.72, 129.41, 129.35, 128.50, 128.45, 126.42, 125.94, 125.54 (d, *J* = 5.1 Hz), 124.94 (d, *J* = 3.1 Hz), 120.74 (d, *J* = 19.9 Hz), 117.86, 107.90, 55.49. HRMS (ESI) calcd. for C₂₀H₁₅FNO [M+H]: 304.1138, found: 304.1139.

3-fluoro-9-methyl-2-phenyl-9H-pyrido[2,3-b]indole (5d):



Yellow solid. m.p. 90-92 °C, 21.8 mg, 79 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.6 Hz, 2H), 8.05 (dd, *J* = 19.1, 9.4 Hz, 2H), 7.53 (q, *J* = 8.6 Hz, 3H), 7.48 – 7.39 (m, 2H), 7.27 (dd, *J* = 13.0, 5.7 Hz, 1H), 3.99 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃) δ -135.49 (dd, *J* = 11.0, 1.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 153.20 (d, *J* = 246.8 Hz), 147.96, 141.76, 136.46, 129.10, 129.03, 128.78, 128.41, 127.21, 121.31, 119.76, 115.86 (d, *J* = 24.3 Hz), 109.27, 27.77. HRMS (ESI) calcd. for C₁₈H₁₄FN₂ [M+H]: 277.1141, found: 277.1743.

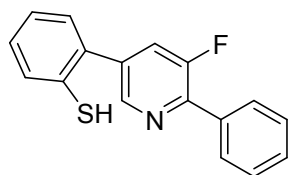
2-(5-fluoro-6-phenylpyridin-3-yl)phenol (5e):



Yellow solid. m.p. 82-84 °C, 18.0 mg, 68 % yield. ¹H NMR (400 MHz, CD₃OD) δ 8.70 (s, 1H), 7.98 – 7.87 (m, 3H), 7.49 (dt, *J* = 12.8, 7.0 Hz, 3H), 7.44 – 7.38 (m, 1H), 7.25 (td, *J* = 7.7, 1.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 2H). ¹⁹F NMR (377 MHz, CDCl₃) δ -121.61. ¹³C NMR (100 MHz, CD₃OD) δ 154.74, 154.42 (d, *J* = 260.1 Hz), 145.04 (d, *J* = 4.9 Hz), 143.39, 135.93, 134.92, 129.80 (d, *J* = 3.2 Hz), 128.88, 128.45, 128.39, 128.12, 124.64

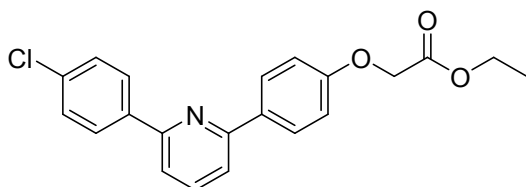
(d, $J = 21.2$ Hz), 122.67, 119.86, 115.81. **HRMS** (ESI) calcd. for $C_{17}H_{13}FNO$ [$M+H$]: 266.0981, found: 266.0983.

2-(5-fluoro-6-phenylpyridin-3-yl)benzenethiol (5f):



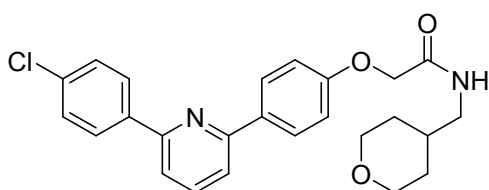
Yellow solid. m.p. 71-74 °C, 17.7 mg, 63 % yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, $J = 1.5$ Hz, 1H), 8.07 – 8.00 (m, 2H), 7.64 (dd, $J = 6.1, 3.0$ Hz, 1H), 7.50 (dt, $J = 14.6, 7.4$ Hz, 3H), 7.40 (dd, $J = 11.6, 1.7$ Hz, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -123.63 (dd, $J = 11.6, 1.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.73 (d, $J = 261.8$ Hz), 145.68 (d, $J = 4.7$ Hz), 145.00 (d, $J = 10.5$ Hz), 137.25, 135.77 (d, $J = 3.9$ Hz), 135.03, 134.97, 130.49, 130.35, 129.47 (d, $J = 10.5$ Hz), 128.84 (d, $J = 5.7$ Hz), 128.58, 128.17, 125.05 (d, $J = 21.3$ Hz), 122.25. **HRMS** (ESI) calcd. for $C_{17}H_{13}FNS$ [$M+H$]: 282.0753, found: 282.0754.

ethyl 2-(4-(6-(4-chlorophenyl)pyridin-2-yl)phenoxy)acetate (7a):



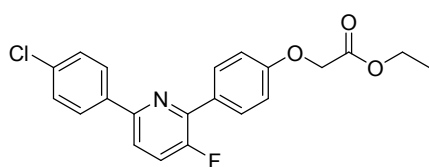
White solid. 667.9 mg, 91 % yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.10 (m, 4H), 7.82 (t, $J = 7.9$ Hz, 1H), 7.80 – 7.63 (m, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.5$ Hz, 2H), 4.74 (s, 2H), 4.34 (q, $J = 7.2$ Hz, 2H), 1.44 – 1.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.88, 158.91, 156.48, 155.60, 138.07, 137.66, 135.14, 133.11, 128.93, 128.44, 128.32, 118.33, 117.97, 114.95, 65.62, 61.56, 14.30.

2-(4-(6-(4-chlorophenyl)pyridin-2-yl)phenoxy)-N-((tetrahydro-2H-pyran-4-yl)methyl)acetamide (9a):



White solid. 357.5 mg, 82 % yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, $J = 16.8, 8.7$ Hz, 4H), 7.79 (t, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 5.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 8.8$ Hz, 2H), 6.69 (s, 1H), 4.57 (d, $J = 4.0$ Hz, 2H), 3.96 (d, $J = 12.5$ Hz, 2H), 3.36 (t, $J = 11.6$ Hz, 2H), 3.31 – 3.22 (m, 2H), 1.81 (d, $J = 5.0$ Hz, 1H), 1.60 (d, $J = 14.1$ Hz, 2H), 1.38 – 1.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.18, 158.03, 156.12, 155.63, 137.89, 137.66, 135.14, 133.55, 128.88, 128.58, 128.23, 118.28, 118.10, 114.86, 67.55, 44.70, 35.36, 30.59.

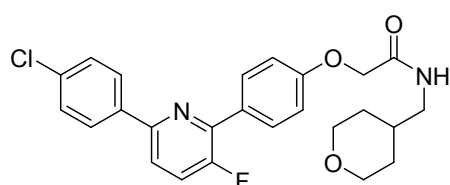
ethyl 2-(4-(6-(4-chlorophenyl)-3-fluoropyridin-2-yl)phenoxy)acetate (7b):



White solid. 622.9 mg, 87 % yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.59 (dd, $J = 8.6, 3.1$ Hz, 1H), 7.49 (dd, $J = 10.8, 8.5$ Hz, 1H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.03 (d, $J = 8.7$ Hz, 2H), 4.69 (s, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (377 MHz, CD_3OD) δ -127.93. ^{13}C

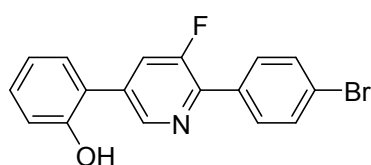
NMR (100 MHz, Chloroform-*d*) δ 168.73, 158.75, 156.82 (d, $J = 260.8$ Hz), 151.46, 144.61, 136.98, 134.97, 130.38 (d, $J = 6.9$ Hz), 129.07 (d, $J = 6.0$ Hz), 128.89, 128.06, 124.94 (d, $J = 21.6$ Hz), 119.34, 114.57, 65.43, 61.50, 14.20. **HRMS** (ESI) calcd. for $C_{21}H_{18}ClFNO_3$ [M+H]: 386.0959, found: 386.0951.

2-(4-(6-(4-chlorophenyl)-3-fluoropyridin-2-yl)phenoxy)-N-((tetrahydro-2H-pyran-4-yl)methyl)acetamide (9b):



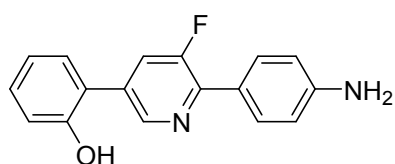
White solid. m.p. 100-103 °C, 340.5 mg, 75 % yield. **1H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 7.9$ Hz, 2H), 7.99 (d, $J = 8.6$ Hz, 2H), 7.63 (dd, $J = 8.5, 3.1$ Hz, 1H), 7.52 (dd, $J = 10.7, 8.6$ Hz, 1H), 7.44 (d, $J = 8.6$ Hz, 2H), 7.05 (d, $J = 8.9$ Hz, 2H), 6.69 (s, 1H), 4.58 (s, 2H), 3.96 (dd, $J = 11.1, 3.3$ Hz, 2H), 3.36 (t, $J = 11.7$ Hz, 2H), 3.27 (t, $J = 6.6$ Hz, 2H), 1.84 – 1.75 (m, 1H), 1.60 (d, $J = 12.9$ Hz, 2H), 1.35 (td, $J = 12.4, 4.1$ Hz, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -125.99. **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.11, 157.97, 156.84 (d, $J = 260.9$ Hz), 151.62, 144.39, 136.91, 135.08, 130.60 (d, $J = 6.4$ Hz), 129.62 (d, $J = 5.4$ Hz), 128.93, 128.06, 125.02 (d, $J = 20.9$ Hz), 119.57, 114.60, 67.52, 67.43, 44.69, 35.35, 30.58. **HRMS** (ESI) calcd. for $C_{21}H_{18}ClFNO_3$ [M+H]: 386.0959, found: 386.0951.

2-(6-(4-bromophenyl)-5-fluoropyridin-3-yl)phenol (10):



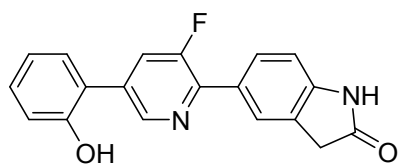
Yellow solid. m.p. 168-170 °C, 617.4 mg, 60 % yield. **1H NMR** (400 MHz, CD_3OD) δ 8.70 (s, 1H), 7.92 (d, $J = 12.6$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 7.7$ Hz, 1H), 7.24 (t, $J = 7.7$ Hz, 1H), 6.95 (dd, $J = 7.6, 3.9$ Hz, 2H). **^{19}F NMR** (377 MHz, $DMSO-d_6$) δ -124.27. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.01 (d, $J = 258.2$ Hz), 154.75, 145.23, 142.01, 136.24, 134.07, 131.32, 130.12 (d, $J = 5.9$ Hz), 129.82 (d, $J = 4.5$ Hz), 124.66 (d, $J = 21.4$ Hz), 123.11, 122.61, 119.88, 115.86. **HRMS** (ESI) calcd. for $C_{17}H_{12}BrFNO$ [M+H]: 344.0086, found: 344.0088.

2-(6-(4-aminophenyl)-5-fluoropyridin-3-yl)phenol (11):



Brown solid. m.p. 196-198 °C, 198.8 mg, 71 % yield. **1H NMR** (400 MHz, CD_3OD) δ 8.60 (s, 1H), 7.85 (dd, $J = 12.8, 1.8$ Hz, 1H), 7.70 (dd, $J = 8.6, 1.8$ Hz, 2H), 7.45 – 7.33 (m, 1H), 7.22 (td, $J = 7.7, 1.7$ Hz, 1H), 6.94 (t, $J = 7.2$ Hz, 2H), 6.84 – 6.73 (m, 2H). **^{19}F NMR** (377 MHz, CD_3OD) δ -126.45. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.59 (d, $J = 256.0$ Hz), 154.64, 149.20, 144.53 (d, $J = 4.4$ Hz), 144.14 (d, $J = 11.8$ Hz), 134.18, 129.72, 129.52, 129.47, 124.35 (d, $J = 21.7$ Hz), 123.80 (d, $J = 5.6$ Hz), 122.99, 119.84, 115.80, 114.31. **HRMS** (ESI) calcd. for $C_{17}H_{14}FN_2O$ [M+H]: 344.0086, found: 344.0088.

5-(3-fluoro-5-(2-hydroxyphenyl)pyridin-2-yl)indolin-2-one (13):



Brown solid. (thermal instability), 15.0 mg, 47 % yield. ¹H NMR (400 MHz, CD₃OD) δ 8.72 (s, 1H), 8.05 (dd, *J* = 11.1, 1.8 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.61 – 7.50 (m, 1H), 7.44 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.27 (td, *J* = 7.8, 1.7 Hz, 1H), 6.97 (t, *J* = 8.3 Hz, 2H), 3.72 (s, 2H). ¹⁹F NMR (377 MHz, CD₃OD) -124.10 (d, *J* = 11.2 Hz). ¹³C NMR (100 MHz, CD₃OD) δ 173.25, 159.12 (d, *J* = 190.1 Hz), 155.20 (d, *J* = 87.3 Hz), 144.17, 143.26 (d, *J* = 16.2 Hz), 137.40, 136.74, 134.86, 131.29, 131.03, 130.04, 129.90, 125.06 (d, *J* = 21.4 Hz), 123.03, 122.37, 119.93, 119.17, 115.85, 38.86. HRMS (ESI) calcd. for C₁₉H₁₄FN₂O₂ [M+H]: 321.1039, found: 321.1040.

3. Copies of ^1H , ^{19}F , ^{13}C NMR

