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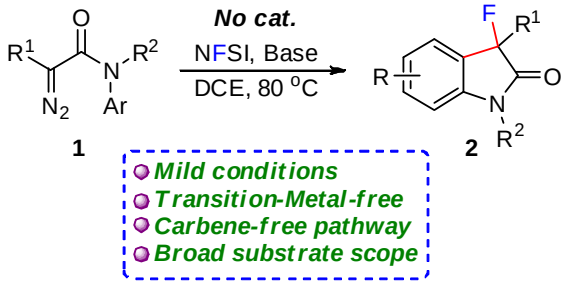
Transition Metal-Free Fluoroarylation of Diazoacetamides: A Complementary Approach to 3-Fluorooxindoles

Kuiyong Dong,[†] Bin Yan,[‡] Sailan Chang,[†] Yongjian Chi,[†] Lihua Qiu,[*,†] and Xinfang Xu[*,†]

[†] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China*

Email: xinfangxu@suda.edu.cn; qiulihua@suda.edu.cn

[‡] *Jinghua Anti-cancer Pharmaceutical Engineering Center, Nantong 226407, China*



ABSTRACT: An efficient transition metal-free fluoroarylation reaction of *N*-aryl diazoacetamides with NFSI (*N*-Fluorobenzenesulfonimide) is described. This reaction directly provides 3-fluorooxindole derivatives in yields of 67%~93% with high selectivity *via* a carbene-free process under mild reaction conditions.

Incorporation of fluorous functionalities into molecules is useful to modify the physical, chemical, and biological properties, which are pervasive in pharmaceuticals, agrochemicals, and material sciences.[1] Consequently, various efficient and direct fluorination approaches have been reported,[2] including palladium-catalyzed alkylaminofluorination disclosed by Hartwig;[3] alkene difunctionalization reported by Li and Rueping individually, such as aminofluorination,[4] phosphonofluorination,[5] azidofluorination,[6] and carbofluorination;[7] and more recently, a DBU-mediated deoxyfluorination of alcohols reported by Doyle and co-workers.[8] Among these fluorination methods, access to substituted oxindolefluorides, which are prevalent motifs in natural products and bio-active molecules, have attracted much attention;[9] and it was also found that fluorine atom at the 3-position of the oxindole ring played a

key role for enhancing the bioactivity (Figure 1).[10] For example, compound **A** (BMS 204352) is a promising agent for the treatment of stroke;[11a] compound **B** was reported as a potent and selective EP_3 receptor antagonist;[11b] compound **C** was tested as inhibitor of caspases-3 and -7 in apoptosis;[11c] and compound **D** showed potent therapeutic effect to CB_2-mediated disorders.[11d]

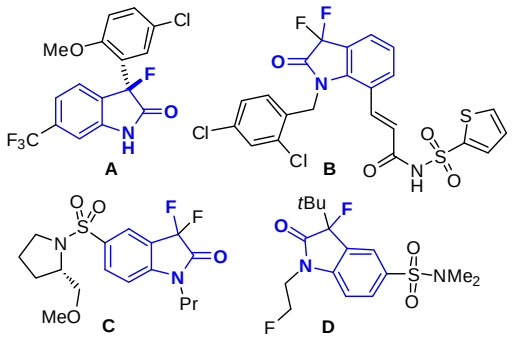
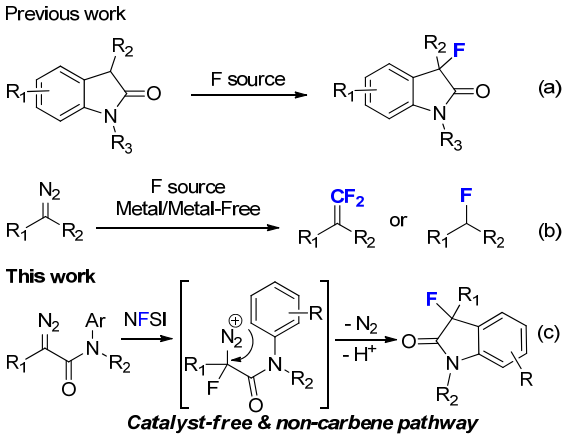


Figure 1. Examples of bioactive 3-fluorooxindole derivatives.

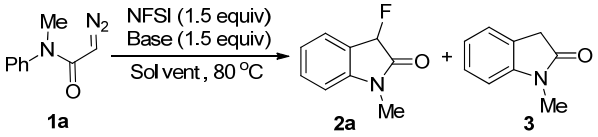
The reported works for the synthesis of these 3-fluorooxindole frameworks mostly rely on the further decoration of the existing 3-substituted oxindoles via a nucleophilic addition with fluoride reagent. Clearly, the diversity of these methods would be restricted to the existing oxindole derivatives (Scheme 1a).[12] Recently, attention has been attracted to the fluorination transformation with diazo compounds, which are versatile intermediates in organic synthesis and have commonly been employed as carbene precursors in transition-metal-catalyzed reactions.[13] In this context, the research groups of Hu,[14] Davies[15] and others[16] have intensively investigated the diverse fluorination reactions with different diazo compounds (Scheme 1b). It is known that the diazo compounds are amphiphilic reagents as the carbon atom bearing the diazo group is thus nucleophilic.[17] Based on this knowledge and inspired by these works, herein we wish to report a novel fluorination process of *N*-aryl diazoacetamides with NFSI (*N*-Fluorobenzenesulfonimide) under catalyst-free conditions to give the 3-fluorooxindoles in high to excellent yields *via* a carbene-free pathway (Scheme 1c).

Scheme 1. Approaches for the 3-Fluorooxindoles



Initially, the reaction of diazoacetamide (**1a**) with NFSI was carried out in DCE at 80 ℃ (Table 1). Interestingly, when the reaction was carried out in the absence of the catalyst, it gave the fluorinated product in 53% yield (entry 1) although long reaction time was needed. When Na_2CO_3 (1.5 eq) was applied, we envisioned that the base could promote the transformation,[18] and fortunately, the yield of **2a** was significantly improved to 72% (entry 2). With this result in hand, several bases were investigated, and NaOAc was determined to be the best with DCE as the solvent (entries 3-6). Various solvents were screened (entries 7-13), and only inferior results were obtained. The fluorine source was also crucial for this transformation, as using SelectFluor instead of NFSI only gave 32% yield (entry 14). Under the optimized conditions, the reaction could be carried out on gram-scale and the desired product **2a** was obtained in good yield (entry 15, 74% yields). Control reactions in the presence of $Cu(hfacac)_2$ or $Rh_2(OAc)_4$ were carried out, intramolecular aromatic substitution product **3** was obtained via carbene reaction in 63% and 81% yields respectively, and only 18% of desired product **2a** was obtained in the case of copper catalyst (entry 17).

Table 1. Optimization of Reaction Conditions[a]



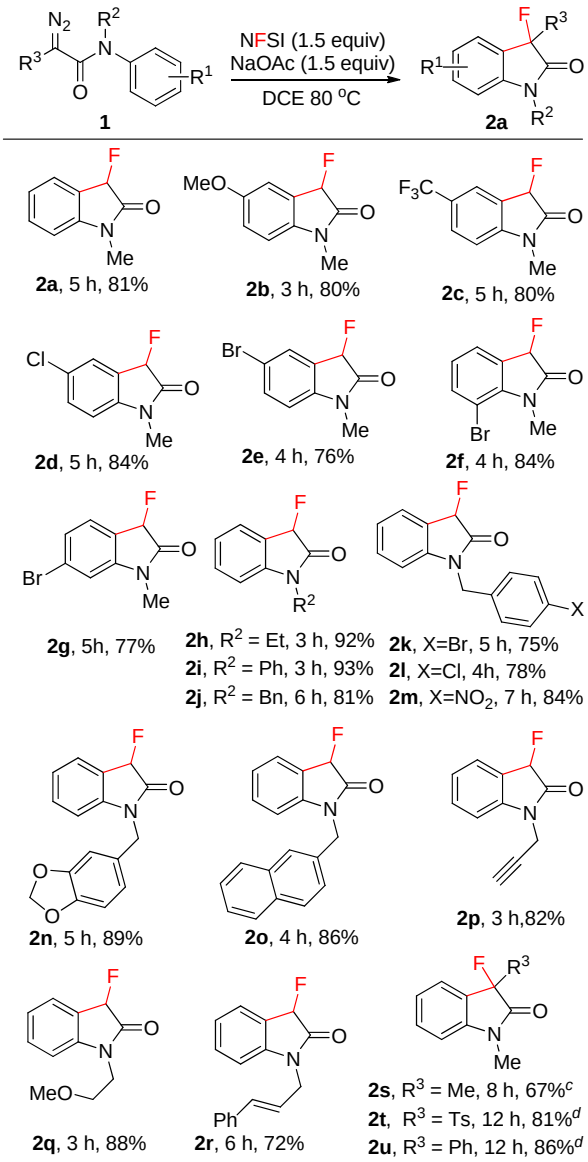
entry	base	solvent	time (h)	**2a** (%)[b]
1	-	DCE	16	53
2	Na_2CO_3	DCE	4	72
3	K_2CO_3	DCE	3	57
4	$NaHCO_3$	DCE	10	53

5	K_3PO_4	DCE	8	65
6	NaOAc	DCE	5	81
7	NaOAc	Toluene	4	49
8	NaOAc	DCM	4	73
9	NaOAc	$CHCl_3$	5	65
10	NaOAc	THF	2	41
11	NaOAc	TBME	8	74
12	NaOAc	PhCl	4	69
13	NaOAc	Dioxane	5	50
14[c]	NaOAc	DCE	12	32
15[d]	NaOAc	DCE	5	74
16[e]	-	DCE	5	18
17[f]	-	DCE	1	0

[a]To the reaction mixture of the base（0.3 mmol）and NFSI (0.3 mmol) in 1.0 mL of solvent, the solution of **1a** (0.2 mmol) in 1.0 mL of solvent was added *via* a syringe in 30 min. [b]Isolated yield after chromatography. [c]Using SelectFluor as the fluorine source. [d]The reaction was carried out on 6.0 mmol scale. [e]$Cu(hfacac)_2$ (5.0 mol%) was used as the catalyst and the major product is **3**. [f]$Rh_2(OAc)_4$ (1.0 mol%) was used as the catalyst.

With the optimized reaction conditions established, we evaluated the substrate scope of this protocol. As depicted in Scheme 2, the reaction exhibited a broad substrate generality, readily affording a variety of different 3-fluorooxindoles in good to high yields. Diazo compounds with electron-rich and deficient substitutions were uniformly fluorinated in 76-84% yield within a few hours (**2a-2e**). The diazoacetamides with *para*- or *meta*- and *ortho*-position substitutions on the aryl group had little effect, and all led to the corresponding products in comparable yields (**2e-2g**). Moreover, to extensively explore the substrates scope, diazoacetamides **1** with various R^2 groups were investigated and they all gave high yields (**2g-2r**, 72~93% yields). It should be noted that the reaction was highly selective，and diversified substitutions or functional groups were tolerated under this catalyst-free conditions. Compounds with benzyl (**2i-2o**, > 75% yields), propargyl (**2p**, 82% yield), ether (**2q**, 88% yield) and allyl groups (**2r**, 72% yield), were all untouched in this process. α-Substituted diazoacetamides **1** also performed well under these conditions, and the reaction of substrate **1s** can even occur at room temperature (**2s**, 67% yield) while higher reaction temperature was required to acquire 3-fluorooxindoles **2t** and **2u**.

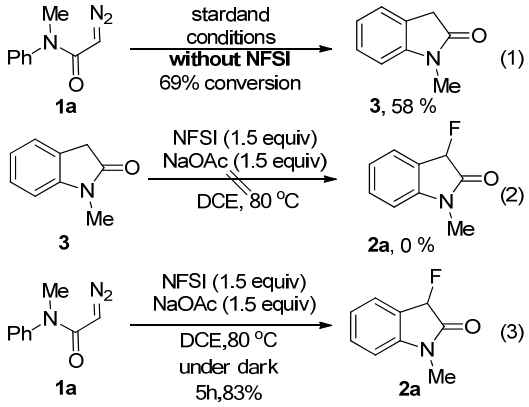
Scheme 2. Substrate Scope



[a]Reactions were carried out on a 0.2 mmol scale in 2.0 mL DCE at 80 °C. [b]To the reaction mixture of the NaOAc (0.3 mmol) and NFSI (0.3 mmol) in 1.0 mL DCE, **1a** (0.2 mmol) in 1.0 mL DCE was added via a syringe in 30 min. [c]Reaction was carried out at rt. [d]Reaction was carried out at 90 °C

To gain insight into the mechanism details, few control reactions were carried out. Reaction pathway of carbene intermediate was first excluded, cause no metal catalyst was used in this reaction, and the carbene transformation would prefer leading to the non-fluorinated product (Table 1, entries 16 and 17); the other control reaction in the absence of NFSI turned out slowly decomposition of the material to give 3a (Eq 1). The possibility via intermediate **3** could be ruled out, no fluorination product was detected under the standard conditions with **3** (Eq 2). Photolysis was also not the case since it gave the same results when the reaction was carried out in dark under the

same condition (Eq 3). It was also not the pathway to form the 3-halogenated oxindoles via α-halogenation of diazoacetamides **1** and followed by aromatic substitution, since all the α,α-disubstitute diazoacetamides (**1s**-**1u**), which couldn't go through this pathway all performed well under these conditions. Another Based on these observations, we proposed our reaction pathway (Scheme 1C). Initially, the nucleophilic carbon on the diazo group[17] was attacked by the F electrophile, followed by intramolecular addition with the aryl group, and releasing a molecule of N_2 synchronously to give the final ring-closed products.



In summary, we have developed a novel catalyst-free fluorination reaction for the synthesis of 3-fluorooxindoles with diazo compounds and NFSI under mild conditions.[27] The reaction showed high selectivity and broad substrate scope to give a variety of 3-fluorooxindoles in moderate to good yields. The mechanistic studies suggested that a carbene-free process fluorination pathway was involved. Under these conditions, many functional groups are all untouched in this process.

EXPERIMENTAL SECTION

General. All reactions were carried out under an atmosphere of nitrogen using oven-dried glassware. DCM, DCE and toluene were distilled prior to use and kept over activated 4 Å molecular sieves. TBME (*tert*-butyl methyl ether) and $CHCl_3$ were purchased from chemical company and used without further treatment. ^{1}H NMR (400 MHz), ^{19}F (376 M Hz) and ^{13}C NMR (100 MHz) were recorded on a NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F and ^{13}C NMR spectra were reported in ppm with the solvent signals as reference, and F NMR spectra were not proton decoupled. All coupling constants (*J* values) were reported in Hertz (Hz).

The peak information is described as: singlet(s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m) and composite (comp, for the overlapped signals). Column chromatography was performed on silica gel 300-400 mesh. High-resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer using electrospray ionization (ESI) techniques.

General Procedure for the Preparation of Diazoacetamides 1 (1a~1r).[20] To a 50-mL oven-dried flask with a magnetic stirring bar, substituted amines (3.8 mmol) and DIPEA (*N*,*N*-Diisopropylethylamine, 0.66 mL, 3.8 mmol) were dissolved in dry DCM (20.0 mL), and bromoacetyl bromide (0.34 mL, 3.8 mmol) was added slowly at 0 ^{o}C, then the reaction mixture was stirred at room temperature for 2-12 h. After the reaction was completed, DCM was removed under reduced pressure. The obtained crude 2-bromo-acetamides were directly used for the next step without further purification. The crude 2-bromo-acetamides and *N*,*N'*-ditosylhydrazine (3.2 g, 9.5 mmol) were dissolved in THF (20.0 mL), DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene, 2.7 mL, 18.0 mmol) was added slowly over 5 min at 0 ^{o}C, and the reaction mixture was stirred for 10-60 minutes until no more gas was generated from the reaction mixture. The reaction was quenched with saturated $NaHCO_3$ solution (30.0 mL), and the aqueous phase was extracted with ethyl acetate (20.0 mL×3). The combined organic phase was dried with anhydrous Na_2SO_4, the crude product was purified by column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 2:1) to give the pure diazoacetamides **1**.

Diazoacetamides **1s**,[21] **1t**[22] and **1u**[23] were prepared according to the reported references, and the characteristic data are consistent with the reported references.

General Procedure for the Synthesis of 2. To a 10-mL oven-dried vial with a magnetic stirring bar, NaOAc (24.6 mg, 0.3 mmol), NFSI (94.6 mg, 0.3 mol) and anhydrous DCE (1.0 mL), diazoacetamides **1** (0.2 mmol) in anhydrous DCE (1.0 mL) was added to the mixture under argon at 80 ^{o}C over 30 min *via* a syringe pump. After the diazo compound was consumed (monitored by thin layer chromatography), the resulting mixture was cooled to room temperature, and the crude reaction mixture was

purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 to 10:1) to give the pure products **2** in moderate to high yields.

3-Fluoro-1-methylindolin-2-one ***(2a).***[24] White solid, 26.7 mg, 81% yield (in 6.0 mmol scale: 732.6 mg, 74% yield); mp 63.2-64.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 (dd, *J* = 7.3, 0.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.66 (d, $J_{H\text{-}F}$ = 51.0 Hz, 1H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2 (d, *J* = 18.2 Hz), 144.8 (d, *J* = 5.3 Hz), 131.6 (d, *J* = 3.3 Hz), 126.1 (d, *J* = 1.2 Hz), 123.4 (d, *J* = 2.9 Hz), 122.8 (d, *J* = 16.2 Hz), 108.9 (d, *J* = 1.3 Hz), 85.6 (d, *J* = 188.2 Hz), 26.3; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -194.0 (d, $J_{H\text{-}F}$ = 51.0 Hz) HRMS (ESI) calculated for C_9H_8FNNaO $[M+Na]^+$: 188.0488, found 188.0488.

3-Fluoro-5-methoxy-1-methylindolin-2-one ***(2b).*** White solid, 31.1 mg, 80% yield; mp 81.9-83.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.08 (t, *J* = 1.8 Hz, 1H), 6.92 (dt, *J* = 8.5, 2.2 Hz, 1H), 6.74 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.64 (d, $J_{H\text{-}F}$ = 50.9 Hz, 1H), 3.80 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.9 (d, *J* = 18.2 Hz), 156.5 (d, *J* = 3.0 Hz), 138.1 (d, *J* = 5.2 Hz), 123.9 (d, *J* = 16.0 Hz), 116.0 (d, *J* = 3.2 Hz), 113.1 (d, *J* = 1.0 Hz), 109.4 (d, *J* = 1.2 Hz), 85.8 (d, *J* = 188.9 Hz), 56.0, 26.4; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.5 (d, $J_{H\text{-}F}$ = 50.9 Hz). HRMS (ESI) calculated for $C_{10}H_{10}FNNaO_2$ $[M+Na]^+$: 218.0593, found 218.0585.

3-Fluoro-1-methyl-5-(trifluoromethyl)indolin-2-one ***(2c).*** Yellow solid, 37.1 mg, 80% yield; mp 105.5-106.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.73 - 7.65 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 5.70 (d, $J_{H\text{-}F}$ = 50.7 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0 (d, *J* = 18.1 Hz), 147.8 (d, *J* = 4.1 Hz), 129.4 - 129.1 (m,1C), 125.8 (qd, *J* = 33.2, 2.9 Hz), 124.0 (q, *J* = 271.6 Hz), 123.5 - 123.3 (m, 1C), 123.2, 108.8 (d, *J* = 1.0 Hz), 84.7 (d, *J* = 190.5 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -61.9 (s), -194.5 (d, $J_{H\text{-}F}$ = 50.7 Hz). HRMS (ESI) calculated for $C_{10}H_7F_4NNaO$ $[M+Na]^+$: 256.0361, found 256.0364.

5-Chloro-3-fluoro-1-methylindolin-2-one ***(2d).*** White solid, 33.5 mg, 84% yield; mp 114.7-115.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 (s, 1H), 7.37 (dt, *J* = 8.3, 1.8 Hz, 1H), 6.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.64 (d, $J_{H\text{-}F}$ = 50.7 Hz, 1H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.7 (d, *J* = 18.1 Hz), 143.3 (d, *J* = 5.0 Hz), 131.5 (d, *J* = 3.1 Hz), 128.9 (d, *J* = 3.3 Hz), 126.6 (d, *J* = 1.1 Hz), 124.3 (d, *J* = 16.2 Hz), 109.9 (d, *J* = 1.2 Hz), 85.1 (d, *J* = 190.3 Hz), 26.5; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.5 (d, $J_{H\text{-}F}$ = 50.7 Hz). HRMS (ESI) calculated for $C_9H_7ClFNNaO$ $[M+Na]^+$: 222.0098, found 222.0089.

5-Bromo-3-fluoro-1-methylindolin-2-one ***(2e).*** White solid, 34.1 mg, 76% yield; mp 107.9-108.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 - 7.54 (m, 1H), 7.54 - 7.46

(m, 1H), 6.71 (d, J = 8.3 Hz, 1H), 5.63 (d, J_{H-F} = 50.7 Hz, 1H), 3.16 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.5 (d, J = 18.1 Hz), 143.8 (d, J = 5.0 Hz), 134.3 (d, J = 3.1 Hz), 129.3, 124.6 (d, J = 16.2 Hz), 115.9 (d, J = 3.3 Hz), 110.4, 85.0 (d, J = 190.4 Hz), 26.4; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.9 (d, J_{H-F} = 50.7 Hz). HRMS (ESI) calculated for $C_9H_7BrFNNaO$ $[M+Na]^+$: 265.9593, found 265.9590.

7-Bromo-3-fluoro-1-methylindolin-2-one ***(2f).*** White solid, 37.6 mg, 84% yield; mp 110.3-111.4 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 - 7.47 (m, 1H), 7.45 - 7.35 (m, 1H), 7.03 - 6.93 (m, 1H), 5.63 (d, J_{H-F} = 51.0 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.5 (d, J = 17.5 Hz), 142.1 (d, J = 5.0 Hz), 137.1 (d, J = 3.3 Hz), 125.8 (d, J = 16.0 Hz), 125.3 (d, J = 1.3 Hz), 124.6 (d, J = 2.9 Hz), 103.1 (d, J = 1.3 Hz), 84.8 (d, J = 188.7 Hz), 30.0; ^{19}F NMR (376 MHz, CDCl3) (δ, ppm) -192.2 (d, J_{H-F} = 51.0 Hz); HRMS (ESI) calculated for $C_9H_7BrFNNaO$ $[M+Na]^+$: 265.9593, found 265.9588.

6-Bromo-3-fluoro-1-methylindolin-2-one ***(2g).*** Yellow solid, 34.5 mg, 77% yield; mp 113.3-115.1 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.32 (dd, J = 7.9, 1.3 Hz, 1H), 7.26 (d, J = 6.2 Hz, 1H), 7.00 (s, 1H), 5.61 (d, J_{H-F} = 50.9 Hz, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0 (d, J = 18.1 Hz), 146.1 (d, J = 5.1 Hz), 127.4 (d, J = 1.0 Hz), 126.3 (d, J = 2.8 Hz), 125.5 (d, J = 4.0 Hz), 121.7 (d, J = 16.6 Hz), 112.6 (d, J = 1.3 Hz), 85.0 (d, J = 189.5 Hz), 26.5; ^{19}F NMR (376 MHz, CDCl3) (δ, ppm) -193.3 (d, J_{H-F} = 50.9 Hz); HRMS (ESI) calculated for $C_9H_7BrFNNaO$ $[M+Na]^+$: 265.9593, found 265.9591.

1-Ethyl-3-fluoroindolin-2-one ***(2h).*** Colorless oil, 33.1 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 (dd, J = 7.4, 0.6 Hz, 1H), 7.38 (dd, J = 11.1, 4.5 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 5.64 (d, J_{H-F} = 51.1 Hz, 1H), 3.72 (qd, J = 7.2, 0.9 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.3 (d, J = 18.0 Hz), 143.4 (d, J = 5.2 Hz), 130.9 (d, J = 3.3 Hz), 125.7 (d, J = 1.1 Hz), 122.6 (d, J = 2.8 Hz), 122.4, 108.4 (d, J = 1.3 Hz), 85.1 (d, J = 188.0 Hz), 34.3, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.5 (d, J_{H-F} = 51.1 Hz). HRMS (ESI) calculated for $C_{10}H_{10}FNNaO$ $[M+Na]^+$: 202.0644, found 202.0642.

3-Fluoro-1-phenylindolin-2-one ***(2i).*** Yellow solid, 44.6 mg, 93% yield; mp 106.5-108.4 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 - 7.50 (m, 3H), 7.47 – 7.38 (m, 3H), 7.33 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.84 (d, J_{H-F} = 51.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4 (d, J = 18.0 Hz), 144.9 (d, J = 5.0 Hz), 133.6, 131.5 (d, J = 3.3 Hz), 129.9, 128.6, 126.5 (d, J = 1.1 Hz), 126.4, 123.9 (d, J = 2.9 Hz), 122.7 (d, J = 16.2 Hz), 110.2 (d, J = 1.3 Hz), 85.7 (d, J = 188.7 Hz);^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -191.7 (d, J_{H-F} = 51.0 Hz); HRMS (ESI) calculated for $C_{14}H_{10}FNNaO$ $[M+Na]^+$: 250.0644, found 250.0636.

1-Benzyl-3-fluoroindolin-2-one ***(2j).*** Colorless oil, 39.2 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47 (d, J = 7.2 Hz, 1H), 7.37 - 7.22 (comp, 6H), 7.07 (t, J =

7.5 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.76 (d, J_{H-F} = 51.0 Hz, 1H), 4.87 (q, J = 15.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3 (d, J = 18.1 Hz), 144.0 (d, J = 5.1 Hz), 135.1, 131.5 (d, J = 3.3 Hz), 129.0, 128.0, 127.5, 126.3 (d, J = 1.1 Hz), 123.4 (d, J = 2.9 Hz), 122.9 (d, J = 16.3 Hz), 109.9 (d, J = 1.3 Hz), 85.6 (d, J = 188.4 Hz), 44.0; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.6 (d, J_{H-F} = 51.0 Hz); HRMS (ESI) calculated for $C_{15}H_{12}FNNaO$ $[M+Na]^+$: 264.0801, found 264.0793

1-(4-Bromobenzyl)-3-fluoroindolin-2-one ***(2k).*** White solid, 46.3 mg, 75% yield; mp 83.9-85.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52 - 7.40 (comp, 3H), 7.29 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 5.76 (d, J_{H-F} = 51.0 Hz, 1H), 4.82 (dd, J = 16 Hz ,J = 1.2 Hz ,2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3 (d, J = 18.1 Hz), 143.7 (d, J = 5.1 Hz), 134.1, 132.2, 131.6 (d, J = 3.3 Hz), 129.2, 126.4 (d, J = 1.1 Hz), 123.6 (d, J = 2.9 Hz), 122.9 (d, J = 16.4 Hz), 122.0, 109.7 (d, J = 1.3 Hz), 85.5 (d, J = 188.7 Hz), 43.4; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.4 (d, J_{H-F} = 51.0 Hz). HRMS (ESI) calculated for $C_{15}H_{11}BrFNNaO$ $[M+Na]^+$: 341.9906, found 341.9905.

1-(4-Chlorobenzyl)-3-fluoroindolin-2-one ***(2l).*** White solid, 42.8 mg, 78% yield; mp 78.3-79.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.48 (dd, J = 7.4, 0.6 Hz, 1H), 7.33 - 7.22 (comp, 5H), 7.10 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 5.76 (d, J_{H-F} = 51.0 Hz, 1H), 4.84 (dd, J = 16.8, 0.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3 (d, J = 18.1 Hz), 143.7 (d, J = 5.1 Hz), 134.0, 133.6, 131.6 (d, J = 3.4 Hz), 129.0 (d, J = 36.6 Hz), 126.4 (d, J = 1.2 Hz), 123.6 (d, J = 2.9 Hz), 122.9 (d, J = 16.4 Hz), 122.8, 109.8 (d, J = 1.4 Hz), 85.5 (d, J = 188.7 Hz), 43.4; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.5 (d, J_{H-F} = 51.0 Hz); HRMS (ESI) calculated for $C_{15}H_{11}ClFNNaO$ $[M+Na]^+$: 298.0411, found 298.0408.

3-Fluoro-1-(4-Nitrobenzyl)indolin-2-one ***(2m).*** Yellow solid, 47.8 mg, 84% yield; mp 157.0-157.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.17 (d, J = 8.7 Hz, 2H), 7.55 - 7.43 (comp, 3H), 7.30 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 5.79 (d, J_{H-F} = 50.9 Hz, 1H), 4.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3 (d, J = 18.2 Hz), 147.8, 143.3 (d, J = 5.1 Hz), 142.5, 131.7 (d, J = 3.3 Hz), 128.2, 126.6 (d, J = 1.1 Hz), 124.3, 123.9 (d, J = 2.9 Hz), 122.8 (d, J = 16.4 Hz), 109.5 (d, J = 1.3 Hz), 85.4 (d, J = 189.0 Hz), 43.3;^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.1 (d, J_{H-F} = 50.9 Hz); HRMS (ESI) calculated for $C_{15}H_{12}FN_2O_3$ $[M+H]^+$: 287.0832, found 287.0830.

1-(Benzo[d][1,3]dioxol-5-ylmethyl)-3-fluoroindolin-2-one ***(2n).*** White solid, 50.7 mg, 89% yield; mp 72.2-73.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.46 (dd, J = 7.4, 0.6 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.83 - 6.72 (comp, 4H), 5.93 (s, 2H), 5.74 (d, J_{H-F} = 51.0 Hz, 1H), 4.77 (dd, J = 15.6, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3 (d, J = 18.0 Hz), 148.3, 147.5, 143.9 (d, J = 5.1 Hz), 131.5 (d, J = 3.3 Hz), 128.9, 126.3 (d, J = 1.1 Hz), 123.5 (d, J = 2.9 Hz), 122.9 (d, J = 16.3 Hz), 121.1, 109.9 (d, J = 1.3 Hz), 108.6, 108.1, 101.3, 85.6 (d, J = 188.5 Hz),

43.8; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.7 (d, J_{H-F} = 51.0 Hz); HRMS (ESI) calculated for $C_{16}H_{12}FNNaO_3$ $[M+Na]^+$: 308.0699, found 308.0696.

*1-Fluoro-3-(Naphthalen-2-ylmethyl)-1H-inden-2(3H)-one (**2o**)*. White solid, 50.1 mg, 86% yield; mp 109.7-110.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.84 - 7.72 (comp, 4H), 7.51 - 7.36 (comp, 4H), 7.28 - 7.19 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.79 (d, J_{H-F} = 51.0 Hz, 1H), 5.02 (dd, *J* = 15.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.4 (d, *J* = 18.1 Hz), 144.0 (d, *J* = 5.1 Hz), 133.4, 133.0, 132.5, 131.5 (d, *J* = 3.3 Hz), 129.0, 127.9, 126.6, 126.4, 126.3, 126.3 (d, *J* = 1.1 Hz), 125.2, 123.5 (d, *J* = 2.9 Hz), 123.0, 122.8, 110.0 (d, *J* = 1.3 Hz), 85.7 (d, *J* = 188.5 Hz), 44.2;^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.4 (d, J_{H-F} = 51.0 Hz). HRMS (ESI) calculated for $C_{19}H_{14}FNNaO$ $[M+Na]^+$: 314.0957, found 314.0956.

*3-Fluoro-1-(prop-2-yn-1-yl)indolin-2-one (**2p**).* Yellow oil, 31.2 mg, 82% yield; ^{1}HNMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 5.71 (d, J_{H-F} = 50.9 Hz, 1H), 4.56 (dd, *J* = 17.7, 2.5 Hz, 1H), 4.40 (dd, *J* = 17.7, 2.5 Hz, 1H), 2.27 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 170.2 (d, *J* = 18.3 Hz), 142.9 (d, *J* = 5.1 Hz), 131.6 (d, *J* = 3.3 Hz), 126.3 (d, *J* = 1.1 Hz), 123.8 (d, *J* = 2.9 Hz), 122.8 (d, *J* = 16.5 Hz), 110.0 (d, *J* = 1.4 Hz), 85.5 (d, *J* = 189.5 Hz), 76.2, 73.0, 29.5; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.1 (d, J_{H-F} = 50.9 Hz); HRMS (ESI) calculated for $C_{11}H_8FNNaO$ $[M+Na]^+$: 212.0488, found 212.0479.

*3-Fluoro-1-(2-Methoxyethyl)indolin-2-one (**2q**).* Colorless oil, 37.1 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 5.66 (d, J_{H-F} = 51.1 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.84 - 3.73 (m, 1H), 3.66 – 3.56 (m, 2H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (d, *J* = 18.0 Hz), 144.6 (d, *J* = 5.1 Hz), 131.5 (d, *J* = 3.3 Hz), 126.1 (d, *J* = 1.2 Hz), 123.2 (d, *J* = 2.9 Hz), 122.8 (d, *J* = 16.2 Hz), 109.8 (d, *J* = 1.4 Hz), 85.6 (d, *J* = 188.1 Hz), 70.0, 59.1, 40.4; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -193.1 (d, J_{H-F} = 51.1 Hz); HRMS (ESI) calculated for $C_{11}H_{12}FNNaO_2$ $[M+Na]^+$: 232.0750, found 232.0751.

*1-Cinnamyl-3-fluoroindolin-2-one (**2r**).* White solid, 36.9 mg, 72% yield; mp 95.0-95.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (d, *J* = 7.2 Hz, 1H), 7.41 - 7.20 (comp, 6H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.23 - 6.11 (m, 1H), 5.73 (d, J_{H-F} = 51.0 Hz, 1H), 4.58 – 4.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.0 (d, *J* = 17.9 Hz), 144.1 (d, *J* = 5.1 Hz), 136.1, 133.8, 131.6 (d, *J* = 3.3 Hz), 128.8, 128.2, 126.6, 126.3 (d, *J* = 1.0 Hz), 123.4 (d, *J* = 2.9 Hz), 123.0 (d, *J* = 16.4 Hz), 122.2, 109.8, 85.6 (d, *J* = 188.6 Hz), 42.2;^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -192.9 (d, J_{H-F} = 51.0 Hz). HRMS (ESI) calculated for $C_{17}H_{14}FNNaO$ $[M+Na]^+$: 290.0957, found 290.0952.

*3-Fluoro-1,3-dimethylindolin-2-one (**2s**).*[25] Colorless oil, 24.0 mg, 67% yield; ^{1}H

NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.44 – 7.35 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.20 (s, 3H), 1.76 (d, J_{H-F} = 22.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 173.3 (d, J = 21.7 Hz), 143.7 (d, J = 5.1 Hz), 131.2 (d, J = 2.9 Hz), 127.4 (d, J = 18.6 Hz), 124.2 (d, J = 0.8 Hz), 123.4 (d, J = 2.6 Hz), 108.8 (d, J = 1.0 Hz), 91.0 (d, J = 183.8 Hz), 26.3, 21.3 (d, J = 29.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -152.7 (q, J_{H-F} = 22.1 Hz); HRMS (ESI) calculated for $C_{10}H_{10}FNNaO$ $[M+Na]^+$: 202.0644, found 202.0637.

*1-Fluoro-3-methyl-1-tosyl-1H-inden-2(3H)-one (**2t**).* White solid, 49.5 mg, 81% yield; mp 179.9-180.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.86 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 7.5 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.41 (d, J = 8.2 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 3.19 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.2 (d, J = 20.6 Hz), 146.7, 145.8 (d, J = 5.1 Hz), 133.8 (d, J = 2.6 Hz), 131.4, 130.2, 129.6, 128.0, 123.8 (d, J = 2.3 Hz), 117.3 (d, J = 17.5 Hz), 109.3, 100.5 (d, J = 238.6 Hz), 26.9, 22.0;^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -157.7 (s). HRMS (ESI) calculated for $C_{16}H_{15}FNO_3S$ $[M+H]^+$: 320.0757, found 320.0757

*3-Fluoro-1-methyl-3-phenylindolin-2-one (**2u**).*[26] Yellow solid, 41.5 mg, 86% yield; mp 85.7-87.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 - 7.32 (comp, 7H), 7.15 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.9 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.6 (d, J = 24.3 Hz), 144.9 (d, J = 5.4 Hz), 136.0 (d, J = 27.0 Hz), 131.7 (d, J = 3.0 Hz), 129.4 (d, J = 1.8 Hz), 128.7, 127.0 (d, J = 18.1 Hz), 126.3 (d, J = 0.6 Hz), 126.1 (d, J = 6.1 Hz), 123.7 (d, J = 2.7 Hz), 109.0 (d, J = 1.0 Hz), 93.3 (d, J = 187.7 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -152.9 (s); HRMS (ESI) calculated for $C_{15}H_{12}FNNaO$ $[M+Na]^+$: 264.0801, found 264.0803.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C and ^{19}F NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

Email: xinfangxu@suda.edu.cn; qiulihua@suda.edu.cn

Notes

The authors declare no competing financial interest.

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