Synthesis Z. Li et al. Paper

Efficient Monofluoroalkylation of Thiophenols or Phenols with α-Bromo-α-Fluoroketones under Mild Conditions

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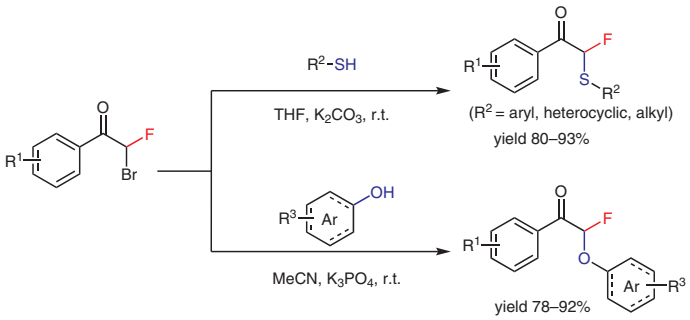

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Abstract An efficient nucleophilic substitution reaction between α-bromo-α-fluoroketones and thiophenols or phenols is reported for the synthesis of α-fluoro-β-ketosulfides or α-fluoro-β-ketone ethers in yields ranging from 78–93%. This method exhibits good functional group tolerance and a broad scope of nucleophilic substrates, including natural phenolic compounds.

Key words monofluoroalkyltion, nucleophilic substitution, α-bromo-α-fluoroketones, α-fluoro-β-ketosulfides, α-fluoro-β-ketone ethers

The incorporation of monofluoroalkyl groups into organic molecules is an active research area in organic synthesis since monofluorinated compounds have found wide applications as pharmaceuticals and agrochemicals.[1,2] Moreover, the introduction of fluoroalkyl groups containing sulfur or oxygen has attracted much attention as the presence of oxygen and sulfur would improve the lipophilicity of the parent molecules.[3,4] The -S(CF_n)- or -O(CF_n)- motif can be found in several pharmaceutical molecules,[5,6] for instance, sevoflurane, an inhalation anesthetic,[7] and fluticasone propionate, a synthetic glucocorticoid drug that is used for the treatment of certain allergic conditions (Figure 1).[8] Hence, the development of methods for the synthesis of compounds containing -S(CF_n)- or -O(CF_n)- motifs is highly desirable.

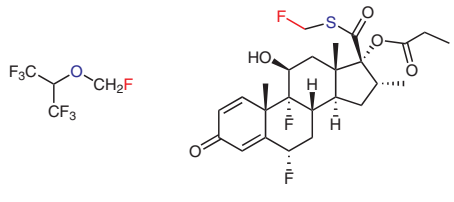
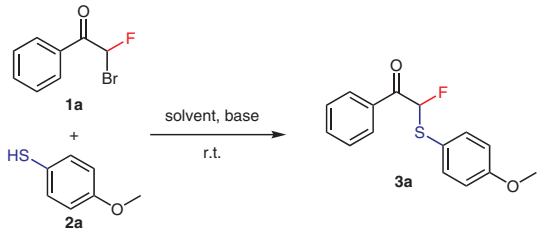


Figure 1 Examples of drugs containing -S(CHF)- and -O(CHF)- motifs

α-Fluoro-β-ketosulfides are useful intermediates in organic synthesis. Current methods employed for the preparation of such compounds have mainly involved fluorination reactions with Selectfluor,[9] HF[10] or NFSI (Scheme 1).[11]

Table 1 Optimization of the Reaction Conditions[a]



Entry	Base	Solvent	Yield (%)[c]
1[b]	–	EtOH	59
2	K_2CO_3	EtOH	75
3	K_2CO_3	MeCN	84
4	K_2CO_3	1,4-dioxane	81
5	K_2CO_3	THF	91
6	K_2CO_3	DMSO	31
7	AcONa	THF	78
8	AcOK	THF	80
9	K_3PO_4	THF	84
10	Na_2CO_3	THF	82

[a] Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), **2a** (0.22 mmol, 1.1 equiv), K_2CO_3 (0.22 mmol, 1.1 equiv), THF (2 mL), r.t., 1 h.
[b] Temp: 40 °C.
[c] Yield of isolated product.

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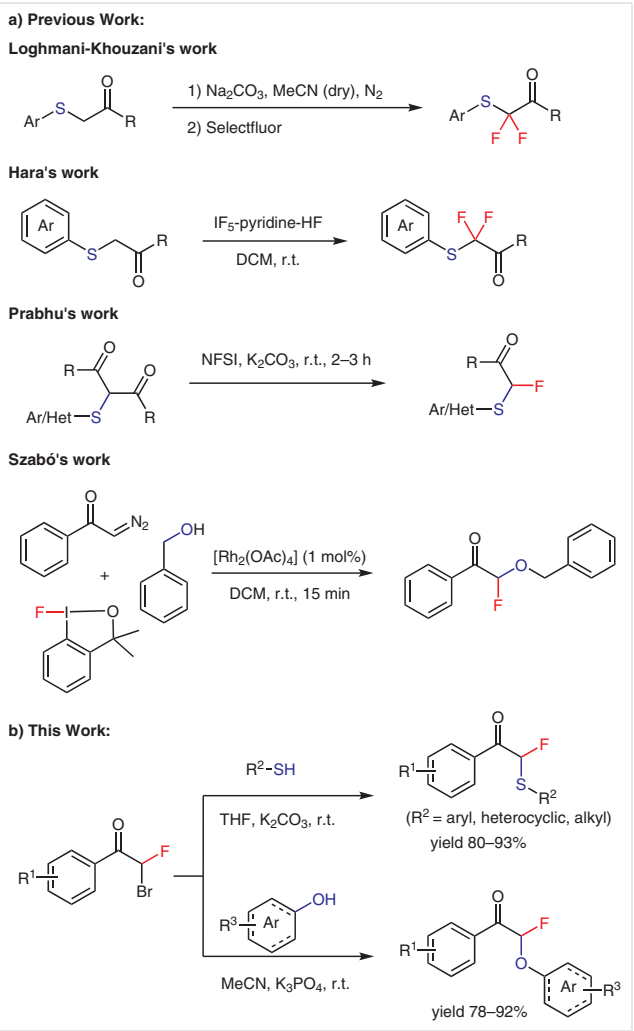
However, the above reactions might suffer from the lack of structure diversity due to the limited substrate scaffolds. In addition, Szabó's group disclosed the synthesis of α-fluoro-β-ketone ethers via rhodium-catalyzed geminal oxyfluorination of diazocarbonyl compounds with NFSI and alcohols (Scheme 1).[12] Accordingly, we assumed that the direct fluoroalkylation of thiophenol nucleophiles or their derivatives with α-fluoro-ketone agents would provide an efficient method for the synthesis of α-fluoro-β-ketosulfides.

Recently, our group disclosed a novel method for the preparation of monofluorinated reagents: α-bromo-α-fluoroketones, and reported an efficient coupling reaction between α-bromo-α-fluoroketones and arylboronic acids.[13] In continuation of our research on the application of α-bromo-α-fluoroketones in organic synthesis, we herein describe nucleophilic reactions of α-bromo-α-fluoroketones with thiophenols (thiols) or phenols for the synthesis of α-fluoro-β-ketosulfides or α-fluoro-β-ketone ethers under mild reaction conditions (Scheme 1).



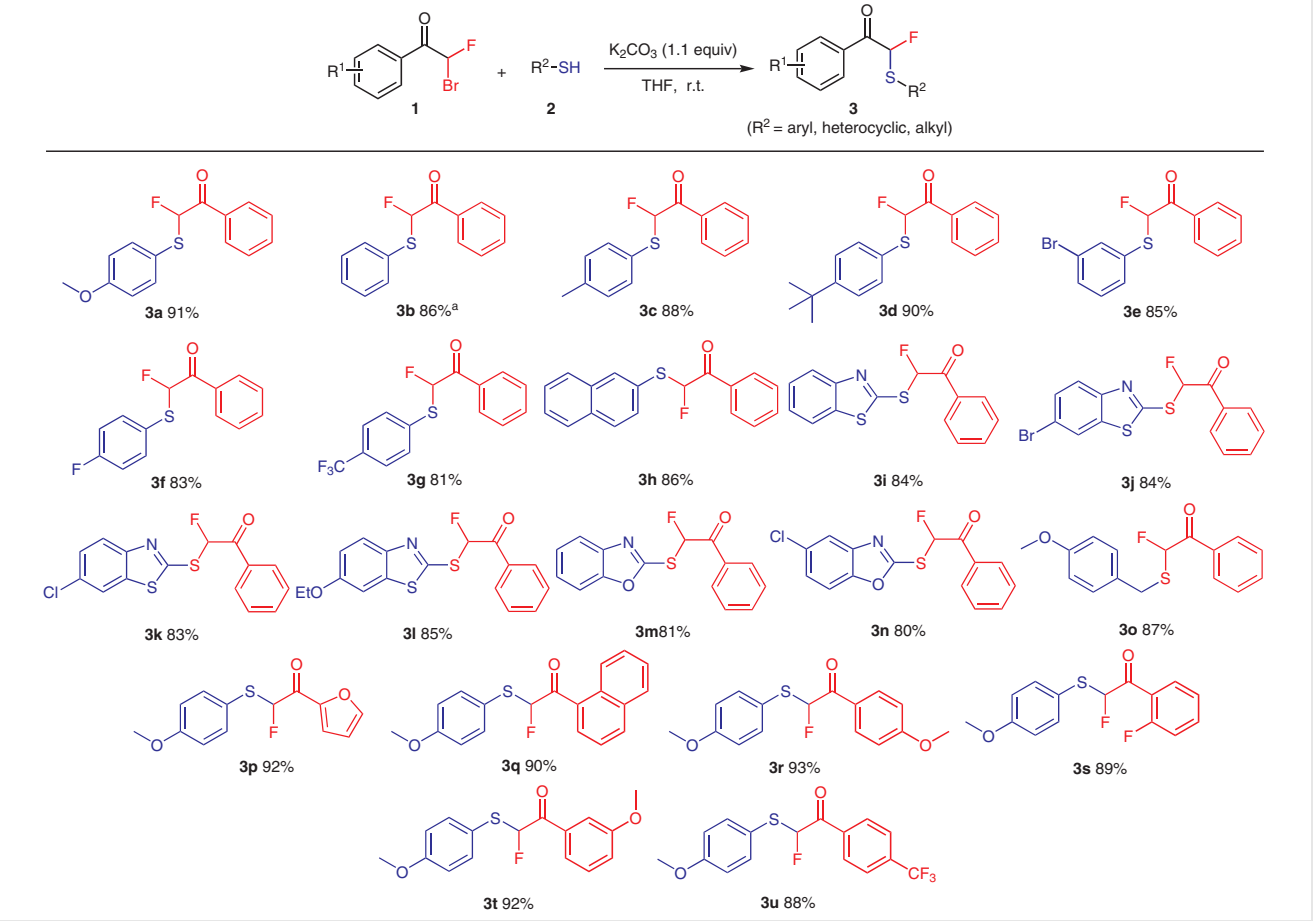
Scheme 1 Difunctionalization-based fluoroalkylation reactions

Initially, the reaction of α-bromo-α-fluorophenylethanone (**1a**) and *p*-methoxythiophenol (**2a**) was chosen as a model reaction using ethanol as the solvent at room temperature. The reaction afforded the desired product **3a** in 59% yield (Table 1, entry 1). The addition of K_2CO_3 to the reaction significantly improved the yield of **3a** to 75% (entry 2). Subsequent solvent screening showed that THF was superior to ethanol (entries 2–6). When other commonly used bases such as AcONa, AcOK, K_3PO_4 and Na_2CO_3 were employed, none of them were found to increase the yield of **3a** (entries 7–10). Ultimately, the optimized conditions for the synthesis of **3a** were determined as follows: α-bromo-α-phenylethanone (**1a**) (1.0 equiv), *p*-methoxythiophenol (**2a**) (1.1 equiv), K_2CO_3 (1.1 equiv), THF, room temperature (entry 5).

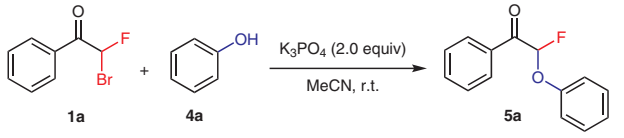
In order to explore the applications of this method in organic synthesis, various aryl thiophenol substrates containing aromatic rings such as benzene, naphthalene, benzoxazole and benzothiazole were tested. As shown in Scheme 2, electron-donating thiophenols reacted favorably (**3a–d**), though the electronic character of the thiophenol did not significantly affect the yields of the desired products (**3e–g**). The substrate scope could be extended to naphthyl and heteroaromatic thiophenols, which gave the desired products **3h,i–n** in high yields. Moreover, the reaction with *p*-methoxybenzyl mercaptan proceeded smoothly to afford product **3o** in 87% yield. Notably, *p*-methoxyphenylthiophenol showed excellent reactivity with various α-bromo-α-fluoroketones in this nucleophilic reaction, giving the desired products **3p–u** in yields of 88–93%.

To further examine the scope and limitations of this reaction, phenol (**4a**) was used as the nucleophilic substrate instead of thiophenol to react with **1a**. However, the yield of the desired product **5a** was unsatisfactory. Thus we optimized the reaction conditions by screening the base and solvent, and obtained product **5a** in a high yield of 83%. The optimized conditions were as follows: **1a** (1.0 equiv), **4a** (1.1 equiv), K_3PO_4 (2.0 equiv), MeCN, room temperature (Scheme 3).

Under the optimized conditions, a range of phenol nucleophiles was employed to explore the generality of the reaction (Scheme 4). Overall, phenols bearing electron-donating or electron-withdrawing groups were all compatible with the reaction conditions, delivering the desired products **5a–g** in yields of 79–89%. Furthermore, the naphthol (**5h**) and heterocyclic phenols (**5i,j**) also performed well under the reaction conditions. Interestingly, natural phenolic compounds such as guaiacol, combretastatin A-4 (CA4), eugenol, maltol and estrone reacted well to give the desired products **5k–r** in highly satisfactory yields, which showed that the process was suitable for late-stage oxofluorination. Similar to *p*-methoxyphenylthiophenol, *p*-methoxyphenol was a highly reactive substrate, giving the corresponding oxyfluorinated products **5s–x** in 87–91% yields. However,



Scheme 2 Scope of the synthesis of α-fluoro-β-ketosulfides. *Reagents and conditions*: **1a** (0.2 mmol, 1.0 equiv), sodium thiophenolate (0.22 mmol, 1.1 equiv), THF (2 mL), r.t., 1–2 h.



Scheme 3 The reaction of phenol and α-bromo-α-fluorophenylethanone

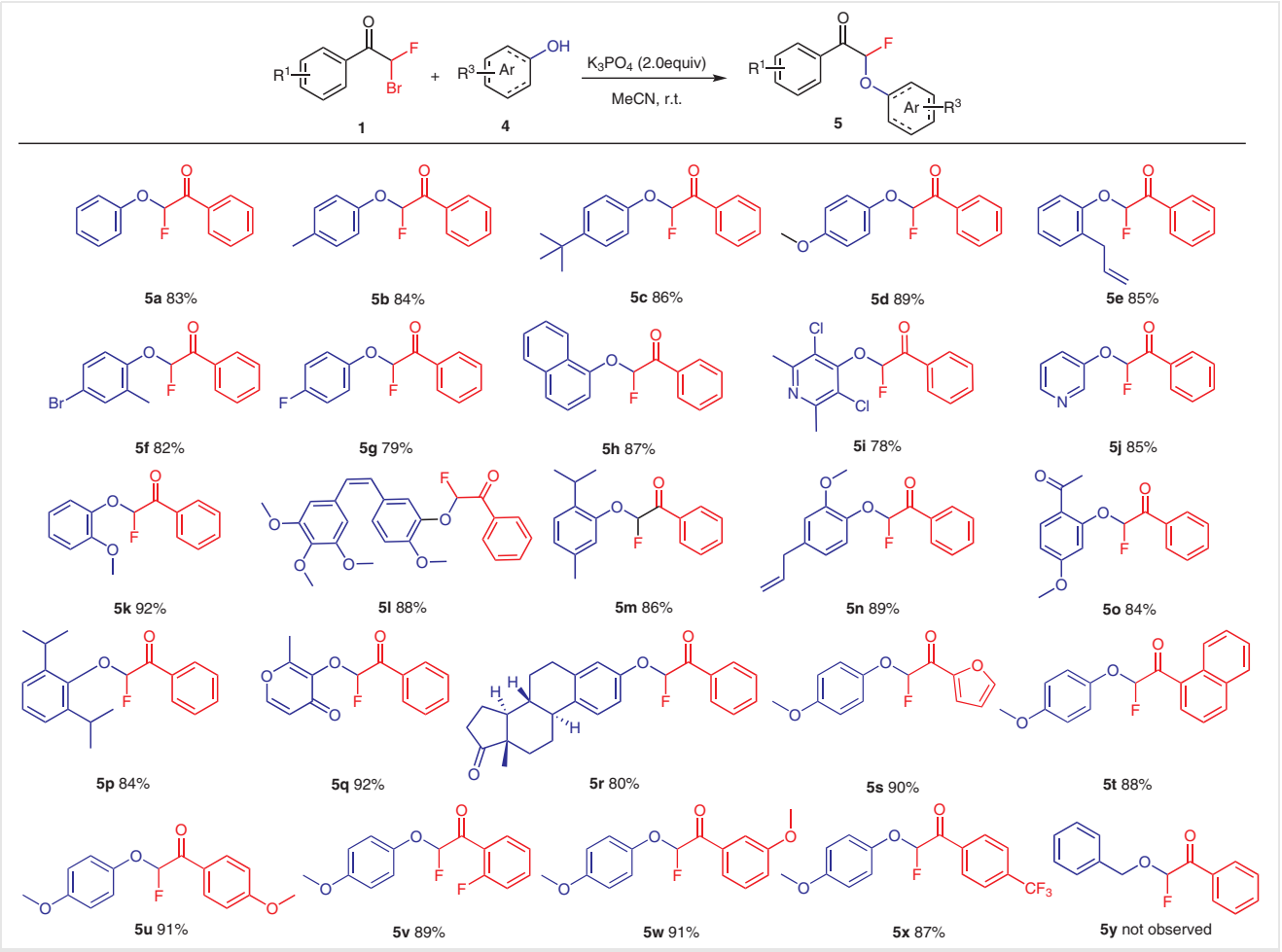
when benzyl alcohol was used as the substrate, the desired product **5y** was not obtained under the standard conditions.

In summary, we have developed an efficient approach for the synthesis of α-fluoro-β-ketosulfides and α-fluoro-β-ketone ethers via nucleophilic reactions of α-bromo-α-fluoroketones, respectively, with thiophenols (thiols) and phenols under mild conditions. This method exhibits good functional group tolerance and a broad scope of nucleophilic substrates, including natural phenolic compounds.

All reagents were commercially available and used without further purification unless indicated otherwise. Reactions were monitored by thin-layer chromatography (TLC) (CCIS/acrylic acid) using UV light for visualizing samples. Flash chromatography was performed with CCIS silica gel (200–300 mesh). Melting points were obtained using a SHANGHAI SHENGUANG, WRS-1C apparatus. NMR spectra were recorded on a Bruker Avance 500 (501 MHz for ^{1}H and 126 MHz for ^{13}C) equipped with a 5 mm inverse broadband probe head with z-gradients at 295.8 K and employing standard Bruker pulse programs. The samples were dissolved in 0.6 mL of $CDCl_3$ (99.8% D.TMS). Chemical shifts (δ) are referenced to the residual solvent signals (δ_H 7.26 for ^{1}H and δ_C 77.1 for ^{13}C in $CDCl_3$). ^{19}F NMR spectra were recorded on an Agilent MR 376 spectrometer. High-resolution mass spectrometry (HRMS) (compounds 3a–u and 5a–x) was performed by SolariX70 FT ICR-MS (Bruker, Switzerland) with an ESI ionization source.

α-Fluoro-β-ketosulfides 3a–u; General Procedure

A reaction tube containing a magnetic stir bar was charged with α-bromo-α-fluoroketone **1** (0.2 mmol, 1.0 equiv), sulfhydryl compound **2** (0.22 mmol, 1.1 equiv) and K_2CO_3 (0.22 mmol, 1.1 equiv). After THF (2.0 mL) had been added, the reaction tube was capped with a rubber stopper and the contents were stirred for 1–2 h at room temperature. The reaction mixture was then quenched with saturated aqueous



Scheme 4 Scope of the synthesis of α-fluoro-β-ketone ethers

NH_4Cl solution and extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE/EtOAc = 20:1 to 100:1) to give the α-fluoro-β-ketosulfide **3a–u**.

α-Fluoro-β-ketone Ethers 5a–x; General Procedure

A reaction tube containing a magnetic stir bar was charged with α-bromo-α-fluoroketone **1** (0.2 mmol, 1.0 equiv), phenol **4** (0.22 mmol, 1.1 equiv) and K_3PO_4 (0.4 mmol, 2.0 equiv). After CH_3CN (2.0 mL) had been added, the reaction tube was capped with a rubber stopper and the contents were stirred for 1–2 h at room temperature. The reaction mixture was then quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel (PE/EtOAc = 10:1 to 100:1) to give the α-fluoro-β-ketone ether **5a–x**.

2-Fluoro-2-[(4-methoxyphenyl)thio]-1-phenylethan-1-one (3a)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 50.3 mg (91%); white crystalline needles; mp 89.1–89.3 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.38 (d, *J* = 8.9 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 52.4 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.48 (d, *J* = 22.9 Hz), 161.24, 136.63 (d, *J* = 1.9 Hz), 134.31, 133.71, 129.24 (d, *J* = 1.3 Hz), 129.01, 120.19, 115.16, 98.55 (d, *J* = 233.3 Hz), 55.63.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –161.20 (d, *J* = 52.2 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}FO_2SNa$: 299.0512; found: 299.0516.

2-Fluoro-1-phenyl-2-(phenylthio)ethan-1-one (3b)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 42.4mg (86%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.7 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.53–7.45 (m, 4 H), 7.42–7.31 (m, 3 H), 6.79 (d, *J* = 53.2 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.14 (d, *J* = 22.8 Hz), 134.16, 133.66 (d, *J* = 2.1 Hz), 133.28, 130.34, 129.37, 129.09 (d, *J* = 1.6 Hz), 128.76, 98.51 (d, *J* = 233.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.33 (d, *J* = 53.6 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}FOSNa$: 269.0407; found: 269.0410.

2-Fluoro-1-phenyl-2-(*p*-tolylthio)ethan-1-one (3c)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 45.8 mg (88%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.02–7.98 (m, 2 H), 7.65–7.61 (m, 1 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.43–7.37 (m, 2 H), 7.17 (d, *J* = 7.8 Hz, 2 H), 6.77 (d, *J* = 53.0 Hz, 1 H), 2.37 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.18 (d, *J* = 23.1 Hz), 139.76, 134.03, 133.99 (d, *J* = 1.9 Hz), 130.12, 129.04 (d, *J* = 1.5 Hz), 128.72, 126.56, 98.60 (d, *J* = 234.0 Hz), 21.24.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –160.09 (d, *J* = 53.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}FOSNa$: 283.0563; found: 283.0567.

2-{[4-(*tert*-Butyl)phenyl]thio}-2-fluoro-1-phenylethan-1-one (3d)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 54.4 mg (90%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.7 Hz, 2 H), 7.64–7.59 (m, 1 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 7.46–7.42 (m, 2 H), 7.38–7.35 (m, 2 H), 6.74 (d, *J* = 53.5 Hz, 1 H), 1.32 (s, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.44 (d, *J* = 23.2 Hz), 152.81, 134.09, 133.61, 133.36, 129.14 (d, *J* = 1.7 Hz), 128.73, 126.91, 126.47, 99.06 (d, *J* = 234.1 Hz), 34.75, 31.20.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.13 (d, *J* = 52.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{19}FOSNa$: 325.1033; found: 325.1038.

2-[(3-Bromophenyl)thio]-2-fluoro-1-phenylethan-1-one (3e)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 55.3 mg (85%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 2 H), 7.67–7.59 (m, 2 H), 7.53–7.46 (m, 3 H), 7.43 (dt, *J* = 7.9, 1.3 Hz, 1 H), 7.22 (t, *J* = 7.9 Hz, 1 H), 6.80 (d, *J* = 53.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.81 (d, *J* = 22.7 Hz), 135.92 (d, *J* = 2.3 Hz), 134.35, 133.13, 132.47, 132.32, 132.06, 130.65, 129.08 (d, *J* = 1.8 Hz), 128.86, 122.88, 98.02 (d, *J* = 234.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.24 (d, *J* = 53.5 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{10}{}^{81}BrFOSNa$: 348.9492; found: 348.9499.

2-Fluoro-2-[(4-fluorophenyl)thio]-1-phenylethan-1-one (3f)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 43.9 mg (83%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.49 (t, *J* = 7.7 Hz, 2 H), 7.42–7.46 (m, 2 H), 7.02 (t, *J* = 8.6 Hz, 2 H), 6.76 (d, *J* = 52.3 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.90 (d, *J* = 23.0 Hz), 163.73 (d, *J* = 250.5 Hz), 136.55 (d, *J* = 8.5 Hz), 134.22, 133.25, 128.98 (d, *J* = 1.6 Hz), 128.81, 124.70, 116.55 (d, *J* = 22.2 Hz), 97.75 (d, *J* = 233.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.64, –160.91 (d, *J* = 52.0 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{10}F_2OSNa$: 287.0313; found: 287.0319.

2-Fluoro-1-phenyl-2-{[4-(trifluoromethyl)phenyl]thio}ethan-1-one (3g)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 50.9 mg (81%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.6 Hz, 2 H), 7.57–7.66 (m, 5 H), 7.49 (t, *J* = 7.7 Hz, 2 H), 6.86 (d, *J* = 52.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.59 (d, *J* = 22.7 Hz), 135.32, 134.39, 133.06, 132.98, 131.14 (q, *J* = 32.9 Hz), 129.07, 128.86, 126.14 (dd, *J* = 7.1, 3.4 Hz), 123.75 (q, *J* = 272.5 Hz), 98.56, 96.68.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.87, –159.40 (d, *J* = 52.0 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}F_4OSNa$: 337.0281; found: 337.0287.

2-Fluoro-2-(naphthalen-2-ylthio)-1-phenylethan-1-one (3h)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 51.0 mg (86%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.02–7.95 (m, 3 H), 7.87–7.74 (m, 3 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.56 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.54–7.51 (m, 2 H), 7.49 (t, *J* = 7.8 Hz, 2 H), 6.88 (d, *J* = 53.2 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.14 (d, *J* = 22.8 Hz), 134.19, 133.50, 133.32, 133.29, 133.25, 130.03, 129.13, 129.12, 128.79, 127.88, 127.83, 127.68, 127.19, 126.88, 98.70 (d, *J* = 234.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.25 (d, *J* = 53.6 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{13}FOSNa$: 319.0563; found: 319.0568.

2-(Benzo[*d*]thiazol-2-ylthio)-2-fluoro-1-phenylethan-1-one (3i)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 51.0 mg (84%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.7 Hz, 2 H), 8.02 (d, *J* = 8.2 Hz, 1 H), 7.95 (d, *J* = 51.5 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.68–7.61 (m,1 H), 7.51 (td, *J* = 8.0, 2.0 Hz, 3 H), 7.43–7.36 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.97 (d, *J* = 21.8 Hz), 160.38 (d, *J* = 3.1 Hz), 152.64, 136.18, 134.74, 132.70, 129.25 (d, *J* = 2.0 Hz), 129.01, 126.61, 125.38, 122.60, 121.35, 95.94 (d, *J* = 236.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –161.61 (d, *J* = 51.6 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}FNOS_2Na$: 326.0080; found: 326.0086.

2-[(6-Bromobenzo[*d*]thiazol-2-yl)thio]-2-fluoro-1-phenylethan-1-one (3j)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 64.2 mg (84%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.8 Hz, 2 H), 7.96 (d, *J* = 1.7 Hz, 1 H), 7.91 (d, *J* = 44.3 Hz, 1 H), 7.85 (d, *J* = 1.5 Hz, 1 H) 7.66 (t, *J* = 7.5 Hz, 1 H), 7.60 (dd, *J* = 8.7, 1.9 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.78 (d, *J* = 21.7 Hz), 161.22 (d, *J* = 3.1 Hz), 151.53, 137.70, 134.80, 132.66, 130.12, 129.26 (d, *J* = 1.9 Hz), 129.03, 123.86, 123.58, 119.01, 95.96 (d, *J* = 237.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –161.13 (d, *J* = 51.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_9{}^{81}BrFNOS_2Na$: 405.9164; found: 405.9166.

2-[(6-Chlorobenzo[*d*]thiazol-2-yl)thio]-2-fluoro-1-phenylethan-1-one (3k)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 56.1 mg (83%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.7 Hz, 2 H), 7.91 (d, *J* = 8.7 Hz, 1 H), 7.90 (d, *J* = 51.4 Hz, 1 H), 7.80 (d, *J* = 2.0 Hz, 1 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* =7.9 Hz, 2 H), 7.46 (dd, *J* = 8.7, 2.1 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.79 (d, *J* = 21.9 Hz), 161.09 (d, *J* = 3.1 Hz), 151.20, 137.27, 134.80, 132.65, 131.41, 129.26 (d, *J* = 1.9 Hz), 129.03, 127.41, 123.24, 120.96, 95.97 (d, *J* = 237.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –161.09 (d, *J* = 52.1 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_9{}^{35}ClFOSNa$: 359.9690; found: 359.9692.

2-[(6-Ethoxybenzo[*d*]thiazol-2-yl)thio]-2-fluoro-1-phenylethan-1-one (3l)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 59.1 mg (85%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.7 Hz, 2 H), 7.89 (d, *J* = 9.0 Hz, 1 H), 7.77 (d, *J* = 51.9 Hz, 1 H), 7.64 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 7.26 (d, *J* = 2.2 Hz, 1 H), 7.08 (dd, *J* = 9.0, 2.5 Hz, 1 H), 4.09 (q, *J* = 7.0 Hz, 2 H), 1.46 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.94 (d, *J* = 21.9 Hz), 157.26, 156.38 (d, *J* = 3.1 Hz), 147.25, 137.85, 134.67, 132.73, 129.24 (d, *J* = 1.7 Hz), 128.98, 123.21, 116.29, 104.57, 96.32 (d, *J* = 236.9 Hz), 64.21, 14.80.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –161.17 (d, *J* = 51.9 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}FNO_2S_2Na$: 370.0342; found: 370.0344.

2-(Benzo[*d*]oxazol-2-ylthio)-2-fluoro-1-phenylethan-1-one (3m)

Purified by flash column chromatography on silica gel (PE/EtOAc = 30:1).

Yield: 46.5 mg (81%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 7.7 Hz, 2 H), 7.87 (d, *J* = 51.3 Hz, 1 H), 7.71 (d, *J* = 7.5 Hz, 1 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.55–7.49 (m, 3 H), 7.34 (quin, *J* = 7.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.61 (d, *J* = 21.3 Hz), 160.00 (d, *J* = 4.0 Hz), 152.34, 141.42, 134.93, 132.54, 129.38 (d, *J* = 2.2 Hz), 129.08, 124.97, 124.89, 119.29, 110.40, 96.48 (d, *J* = 236.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –160.08 (d, *J* = 51.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}FNO_2SNa$: 310.0308; found: 310.0313.

2-[(5-Chlorobenzo[*d*]oxazol-2-yl)thio]-2-fluoro-1-phenylethan-1-one (3n)

Purified by flash column chromatography on silica gel (PE/EtOAc = 30:1).

Yield: 51.5 mg (80%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.1 Hz, 2 H), 7.85 (d, *J* = 51.1 Hz, 1 H), 7.70–7.65 (m, 2 H), 7.53 (t, *J* = 7.8 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 1 H), 7.30 (dd, *J* = 8.7, 2.1 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.46 (d, *J* = 21.4 Hz), 161.86 (d, *J* = 2.5 Hz), 150.84, 142.40, 135.07, 132.39, 130.51, 129.41 (d, *J* = 2.2 Hz), 129.13, 125.20, 119.28, 111.08, 96.51 (d, *J* = 237.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.61 (d, *J* = 51.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_9{}^{35}ClFNO_2SNa$: 343.9919; found: 343.9924.

2-Fluoro-2-[(4-methoxybenzyl)thio]-1-phenylethan-1-one (3o)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 50.5 mg (87%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 2 H), 7.60–7.53 (m, 1 H), 7.40 (t, *J* = 7.7 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 6.55 (d, *J* = 54.1 Hz, 1 H), 4.02 (dd, *J* = 13.1, 2.8 Hz, 1 H), 3.86 (d, *J* = 13.1 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.92 (d, *J* = 21.8 Hz), 159.22, 134.11, 133.04, 130.58, 128.95, 128.94, 128.94 (d, *J* =1.3 Hz), 128.66, 127.73, 114.22, 94.81 (d, *J* = 230.5 Hz), 55.35, 34.48.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –166.98 (d, *J* = 54.0 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}FO_2SNa$: 313.0669; found: 313.0666.

2-Fluoro-1-(furan-2-yl)-2-[(4-methoxyphenyl)thio]ethan-1-one (3p)

Purified by flash column chromatography on silica gel (PE/EtOAc = 50:1).

Yield: 49.0 mg (92%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.73 (s, 1 H), 7.54 (d, *J* = 3.6 Hz, 1 H), 7.10 (d, *J* = 9.0 Hz, 2 H), 6.87 (d, *J* = 8.9 Hz, 2 H), 6.62 (dd, *J* = 3.7, 1.7 Hz, 1 H), 6.14 (d, *J* = 60.7 Hz, 1 H), 3.78 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 177.60 (d, *J* = 29.8 Hz), 156.59, 149.97 (d, *J* = 3.0 Hz), 148.87, 148.51, 122.31 (d, *J* = 3.9 Hz), 119.01 (d, *J* = 1.6 Hz), 114.86, 112.74, 107.04 (d, *J* = 233.2 Hz), 55.65.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –162.86 (d, *J* = 52.4 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{11}FO_3SNa$: 289.0305; found: 289.0305.

2-Fluoro-2-[(4-methoxyphenyl)thio]-1-(naphthalen-1-yl)ethan-1-one (3q)

Purified by flash column chromatography on silica gel (PE/EtOAc = 50:1).

Yield: 58.8 mg (90%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 8.6 Hz, 1 H), 8.32 (d, *J* = 7.2 Hz, 1 H), 8.09 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.70–7.63 (m, 1 H), 7.62–7.52 (m, 2 H), 7.16–7.11 (m, 2 H), 6.92–6.85 (m, 2 H), 6.38 (d, *J* = 61.2 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 191.63 (d, *J* = 27.7 Hz), 156.54, 150.14 (d, *J* = 3.0 Hz), 134.68, 134.03, 131.23, 131.00 (d, *J* = 3.4 Hz), 129.52, 128.79, 128.77, 126.77, 125.61, 124.26, 119.02, 119.01, 114.87, 108.30 (d, *J* = 235.3 Hz), 55.67.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.98 (d, *J* = 52.1 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{15}FO_2SNa$: 349.0669; found: 349.0665.

2-Fluoro-1-(4-methoxyphenyl)-2-[(4-methoxyphenyl)thio]ethan-1-one (3r)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 57.0 mg (93%); white solid; mp 97.9–98.5 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.5 Hz, 2 H), 7.40 (d, *J* = 8.3 Hz, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.84 (d, *J* = 8.3 Hz, 2 H), 6.64 (d, *J* = 53.2 Hz, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.88 (d, *J* = 23.0 Hz), 164.23, 160.87, 136.21, 131.54, 131.53, 126.21 (d, *J* = 2.5 Hz), 120.49 (d, *J* = 2.5 Hz), 114.86, 113.97, 98.90 (d, *J* = 234.1 Hz), 55.58, 55.36.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –159.81 (d, *J* = 53.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}FO_3SNa$: 329.0618; found: 329.0616.

2-Fluoro-1-(2-fluorophenyl)-2-[(4-methoxyphenyl)thio]ethan-1-one (3s)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 52.4 mg (89%); light yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.72 (td, *J* = 7.5, 1.8 Hz, 1 H), 7.59 (qd, *J* = 7.1, 1.7 Hz, 1 H), 7.32–7.21 (m, 3 H), 7.17 (dd, *J* = 11.3, 8.4 Hz, 1 H), 6.82 (d, *J* = 9.0 Hz, 2 H), 6.79 (d, *J* = 50.8 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.08 (dd, *J* = 23.2, 5.0 Hz), 161.23 (d, *J* = 253.9 Hz), 161.02, 136.75, 135.58 (d, *J* = 9.2 Hz), 131.42, 124.91 (d, *J* = 3.2 Hz), 122.68 (d, *J* = 13.3 Hz), 118.97, 116.60 (d, *J* = 23.8 Hz), 114.76, 98.96 (dd, *J* = 231.8, 10.7 Hz), 55.37.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –106.55 (dt, *J* = 12.5, 5.7 Hz), –163.58 (dd, *J* = 50.2, 6.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}F_2O_2SNa$: 317.0418; found: 317.0419.

2-Fluoro-1-(3-methoxyphenyl)-2-[(4-methoxyphenyl)thio]ethan-1-one (3t)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 55.8 mg (92%); colorless oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 7.7 Hz, 1 H), 7.45 (t, *J* = 2.2 Hz, 1 H), 7.42–7.34 (m, 3 H), 7.15 (dd, *J* = 8.3, 2.6 Hz, 1 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.68 (d, *J* = 52.5 Hz, 1 H), 3.84 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.08 (d, *J* = 22.9 Hz), 161.01, 159.89, 136.41 (d, *J* = 2.1 Hz), 134.76, 129.75, 121.52, 120.65, 120.04, 114.92, 113.26, 98.38 (d, *J* = 233.2 Hz), 55.56, 55.40.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –160.81 (d, *J* = 52.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}FO_3SNa$: 329.0618; found: 329.0618.

2-Fluoro-2-[(4-methoxyphenyl)thio]-1-[4-(trifluoromethyl)phenyl]ethan-1-one (3u)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 121.2 mg (88%); white solid; mp 76.0–76.4 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 6.69 (d, *J* = 51.8 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.49 (d, *J* = 23.9 Hz), 161.19, 136.48 (d, *J* = 1.9 Hz), 136.32, 135.10 (q, *J* = 32.9 Hz), 129.39 (d, *J* = 1.4 Hz), 125.76 (q, *J* = 3.7 Hz), 123.48 (q, *J* = 274.0 Hz), 98.31 (d, *J* = 234.4 Hz), 55.38.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.27, –161.45 (d, *J* = 52.1 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{12}F_4O_2SNa$: 367.0386; found: 367.0384.

2-Fluoro-2-phenoxy-1-phenylethan-1-one (5a)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 38.2 mg (83%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.7 Hz, 2 H), 7.69–7.62 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.39 (t, *J* = 8.0 Hz, 2 H), 7.22–7.16 (m, 3 H), 6.37 (d, *J* = 60.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.77 (d, *J* = 28.2 Hz), 156.04 (d, *J* = 3.1 Hz), 134.39, 132.38 (d, *J* = 1.9 Hz), 130.00, 129.98, 128.76, 124.50, 117.32, 107.33 (d, *J* = 234.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –126.13 (d, *J* = 60.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}FO_2Na$: 253.0635; found: 253.0638.

2-Fluoro-1-phenyl-2-(*p*-tolyloxy)ethan-1-one (5b)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 41.0 mg (84%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.7 Hz, 2 H), 7.68–7.61 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 7.20–7.06 (m, 4 H), 6.33 (d, *J* = 60.8 Hz, 1 H), 2.35 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.90 (d, *J* = 28.5 Hz), 154.02 (d, *J* = 2.9 Hz), 134.34, 134.11, 132.43, 130.38, 129.98 (d, *J* = 2.1 Hz), 128.74, 117.29, 107.66 (d, *J* = 234.0 Hz), 20.69.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –125.85 (d, *J* = 60.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}FO_2Na$: 267.0792; found: 267.0795.

2-[4-(*tert*-Butyl)phenoxy]-2-fluoro-1-phenylethan-1-one (5c)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 49.2 mg (86%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.9 Hz, 2 H), 7.69–7.62 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 6.35 (d, *J* = 60.8 Hz, 1 H), 1.34 (s, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.88 (d, *J* = 28.5 Hz), 153.81 (d, *J* = 2.9 Hz), 147.42, 134.33, 132.43, 130.00 (d, *J* = 2.0 Hz), 128.73, 126.77, 116.84, 107.49 (d, *J* = 234.1 Hz), 34.39, 31.45.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –126.02 (d, *J* = 61.5 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{19}FO_2Na$: 309.1261; found: 309.1265.

2-Fluoro-2-(4-methoxyphenoxy)-1-phenylethan-1-one (5d)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 46.3 mg (89%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 7.8 Hz, 2 H), 7.68–7.61 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 7.13 (d, *J* = 9.1 Hz, 2 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 6.25 (d, *J* = 61.0 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.95 (d, *J* = 28.8 Hz), 156.54, 150.03 (d, *J* = 2.9 Hz), 134.34, 132.43, 129.97 (d, *J* = 1.6 Hz), 128.74, 118.92, 114.88, 108.31 (d, *J* = 234.0 Hz), 55.67.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –125.28 (d, *J* = 60.9 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}FO_3Na$: 283.0741; found: 283.0739.

2-(2-Allylphenoxy)-2-fluoro-1-phenylethan-1-one (5e)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 46.0 mg (85%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.8 Hz, 2 H), 7.69–7.62 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 7.33–7.21 (m, 3 H), 7.14 (td, *J* = 7.2, 1.7 Hz, 1 H), 6.32 (d, *J* = 60.3 Hz, 1 H), 5.86 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1 H), 4.98 (dq, *J* = 10.1, 1.6 Hz, 1 H), 4.92 (dq, *J* = 17.0, 1.7 Hz, 1 H), 3.40–3.28 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.94 (d, *J* = 29.2 Hz), 154.08 (d, *J* = 3.0 Hz), 136.08, 134.36, 132.35, 130.66, 130.23, 130.06 (d, *J* = 2.1 Hz), 128.71, 127.90, 124.52, 116.08, 115.62, 107.83 (d, *J* = 235.1 Hz), 34.26.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –124.71 (d, *J* = 60.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{15}FO_2Na$: 293.0948; found: 293.0948.

2-(4-Bromo-2-methylphenoxy)-2-fluoro-1-phenylethan-1-one (5f)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 52.0 mg (82%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.7 Hz, 2 H), 7.69–7.62 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 7.35 (d, *J* = 6.8 Hz, 2 H), 7.10 (d, *J* = 9.2 Hz, 1 H), 6.27 (d, *J* = 60.1 Hz, 1 H), 2.17 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.67 (d, *J* = 28.7 Hz), 153.56 (d, *J* = 3.0 Hz), 134.48, 134.08, 132.27 (d, *J* = 1.7 Hz), 130.80 (d, *J* = 1.8 Hz), 130.11, 129.92 (d, *J* = 2.2 Hz), 128.78, 117.33, 117.00, 107.60 (d, *J* = 236.1 Hz), 16.06.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –125.80 (d, *J* = 60.5 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}{}^{79}BrFO_2Na$: 344.9897; found: 344.9898.

2-Fluoro-2-(4-fluorophenoxy)-1-phenylethan-1-one (5g)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 39.2 mg (79%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 7.8 Hz, 2 H), 7.69–7.61 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.15 (dd, *J* = 9.1, 4.3 Hz, 2 H), 7.09–7.03 (m, 2 H), 6.28 (d, *J* = 60.6 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.59 (d, *J* = 28.2 Hz), 160.47, 158.53, 152.07 (t, *J* = 2.9 Hz), 134.46, 132.30, 129.94 (d, *J* = 2.2 Hz), 128.78, 119.15, 119.08, 116.58, 116.40, 107.87 (d, *J* = 235.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –118.53, –125.87 (d, *J* = 60.4 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{10}F_2O_2Na$: 271.0541; found: 271.0545.

2-Fluoro-2-(naphthalen-1-yloxy)-1-phenylethan-1-one (5h)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 48.8 mg (87%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 7.8 Hz, 2 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 8.2 Hz, 1 H), 7.71–7.64 (m, 2 H), 7.58–7.50 (m, 3 H), 7.51–7.43 (m, 2 H), 7.36 (d, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 60.0 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.83 (d, *J* = 28.6 Hz), 152.03 (d, *J* = 3.0 Hz), 134.68, 134.48, 132.49, 130.06 (d, *J* = 1.6 Hz), 128.85, 127.71, 126.92, 126.31, 125.69, 125.65, 124.32, 121.66, 110.12, 107.46 (d, *J* = 235.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –126.16 (d, *J* = 59.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{13}FO_2Na$: 303.0792; found: 303.0788.

2-[(3,5-Dichloro-2,6-dimethylpyridin-4-yl)oxy]-2-fluoro-1-phenylethan-1-one (5i)

Purified by flash column chromatography on silica gel (PE/EtOAc = 10:1).

Yield: 51.2 mg (78%); light yellow solid; mp 87.6–87.8 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 7.9 Hz, 2 H), 7.71–7.64 (m, 1 H), 7.55 (t, *J* = 7.7 Hz, 2 H), 6.25 (d, *J* = 58.9 Hz, 1 H), 2.62 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.92 (d, *J* = 27.6 Hz), 155.54, 154.04 (d, *J* = 1.4 Hz), 134.59, 131.84, 130.27 (d, *J* = 2.3 Hz), 128.79, 122.93, 109.20 (d, *J* = 243.8 Hz), 22.82.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –124.33 (d, *J* = 59.0 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}Cl_2FNO_2Na$: 350.0121; found: 350.0118.

2-Fluoro-1-phenyl-2-(pyridin-3-yloxy)ethan-1-one (5j)

Purified by flash column chromatography on silica gel (PE/EtOAc = 10:1).

Yield: 39.3 mg (85%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.55 (s, 1 H), 8.45 (d, *J* = 4.7 Hz, 1 H), 8.13 (d, *J* = 7.9 Hz, 2 H), 7.70–7.62 (m, 1 H), 7.52 (t, *J* = 7.7 Hz, 3 H), 7.34 (dd, *J* = 8.4, 4.7 Hz, 1 H), 6.36 (d, *J* = 59.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.08 (d, *J* = 27.5 Hz), 145.84, 140.21, 134.66, 132.12 (d, *J* = 1.7 Hz), 129.90 (d, *J* = 2.3 Hz), 128.87, 124.64, 124.63, 124.33, 107.06 (d, *J* = 237.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –126.59 (d, *J* = 59.1 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{10}FNO_2Na$: 254.0588; found: 254.0583.

2-Fluoro-2-(2-Methoxyphenoxy)-1-phenylethan-1-one (5k)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 47.9 mg (92%); white solid; mp 70.2–70.9 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 7.8 Hz, 2 H), 7.67–7.60 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.7 Hz, 1 H), 7.17 (t, *J* = 7.7 Hz, 1 H), 6.99–6.94 (m, 2 H), 6.34 (d, *J* = 60.8 Hz, 1 H), 3.85 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.17 (d, *J* = 27.3 Hz), 150.72, 144.54, 134.23, 132.65, 130.08 (d, *J* = 1.7 Hz), 128.65, 125.94, 121.09 (d, *J* = 5.2 Hz), 112.78, 107.80 (d, *J* = 234.2 Hz), 55.88.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –127.76 (d, *J* = 60.4 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}FO_3Na$: 283.0741; found: 283.0743.

2-Fluoro-2-[2-methoxy-5-(3,4,5-trimethoxystyryl)phenoxy]-1-phenylethan-1-one (5l)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 79.6 mg (88%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.8 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 2.1 Hz, 1 H), 7.09 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 6.54–6.44 (m, 4 H), 6.20 (d, *J* = 60.8 Hz, 1 H), 3.82 (d, *J* = 3.9 Hz, 6 H), 3.71 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.93 (d, *J* = 27.4 Hz), 153.10, 149.73, 144.00, 137.42 (d, *J* = 1.3 Hz), 134.24, 132.56, 130.34, 130.00 (d, *J* = 2.0 Hz), 129.83, 128.64, 126.66, 121.29, 112.33, 107.61 (d, *J* = 235.0 Hz), 105.98, 60.93, 55.97.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –127.63 (d, *J* = 60.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{25}FO_6Na$: 475.1527; found: 475.1522.

2-Fluoro-2-(2-isopropyl-5-methylphenoxy)-1-phenylethan-1-one (5m)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1). Yield: 49.2 mg (86%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 7.8 Hz, 2 H), 7.70–7.62 (m, 1 H), 7.53 (t, *J* = 7.7 Hz, 2 H), 7.19 (d, *J* = 7.8 Hz, 1 H), 7.08 (s, 1 H), 6.99 (d, *J* = 7.7 Hz, 1 H), 6.34 (d, *J* = 60.2 Hz, 1 H), 3.18 (sept, *J* = 6.9 Hz, 1 H), 2.39 (s, 3 H), 1.15 (dd, *J* = 11.9, 6.9 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.11 (d, *J* = 29.8 Hz), 153.43 (d, *J* = 3.1 Hz), 137.15, 135.50, 134.32, 132.39, 130.03 (d, *J* = 2.1 Hz), 128.70, 126.66, 125.29, 116.38, 108.10 (d, *J* = 234.6 Hz), 26.62, 22.95, 22.80, 21.16.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –124.06 (d, *J* = 60.4 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{19}FO_2Na$: 309.1261; found: 309.1263.

2-(4-Allyl-2-methoxyphenoxy)-2-fluoro-1-phenylethan-1-one (5n)

Purified by flash column chromatography on silica gel (PE/EtOAc = 50:1).

Yield: 53.4 mg (89%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 7.7 Hz, 2 H), 7.66–7.60 (m, 1 H), 7.51 (t, *J* = 7.7 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 6.82–6.75 (m, 2 H), 6.31 (d, *J* = 61.0 Hz, 1 H), 5.97 (ddt, *J* = 16.9, 10.4, 6.8 Hz, 1 H), 5.14–5.08 (m, 2 H), 3.84 (s, 3 H), 3.38 (d, *J* = 6.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.21 (d, *J* = 27.5 Hz), 150.53 (d, *J* = 1.8 Hz), 142.80, 138.10, 137.05, 134.19, 132.66, 130.07 (d, *J* = 1.8 Hz), 128.62, 121.08, 120.89, 116.19, 113.07, 107.90 (d, *J* = 234.1 Hz), 55.86, 39.97.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –127.85 (d, *J* = 60.4 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}FO_3Na$: 323.1054; found: 323.1056.

2-(2-Acetyl-5-methoxyphenoxy)-2-fluoro-1-phenylethan-1-one (5o)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 50.8 mg (84%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.8 Hz, 2 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 6.83 (d, *J* = 1.4 Hz, 1 H), 6.75 (dd, *J* = 8.8, 2.3 Hz, 1 H), 6.44 (d, *J* = 59.1 Hz, 1 H), 3.89 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.67, 188.10 (d, *J* = 28.0 Hz), 164.37, 156.66 (d, *J* = 3.0 Hz), 134.71, 132.83, 132.22, 129.84 (d, *J* = 2.3 Hz), 128.91, 122.24, 109.43, 106.74 (d, *J* = 236.9 Hz), 102.46, 55.83, 31.57.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –125.63 (d, *J* = 59.0 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{15}FO_4Na$: 325.0846; found: 325.0848.

2-(2,6-Diisopropylphenoxy)-2-fluoro-1-phenylethan-1-one (5p)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 52.8 mg (84%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.8 Hz, 2 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 2 H), 7.25–7.16 (m, 3 H), 5.87 (d, *J* = 59.3 Hz, 1 H), 3.41 (sept, *J* = 6.9 Hz, 2 H), 1.29 (d, *J* = 6.9 Hz, 6 H), 1.22 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 190.01 (d, *J* = 32.3 Hz), 151.29, 141.39 (d, *J* = 1.7 Hz), 134.30, 132.26 (d, *J* = 3.9 Hz), 130.23 (d, *J* = 2.4 Hz), 128.72, 126.41, 124.49, 112.66 (d, *J* = 236.1 Hz), 26.84, 23.81, 23.70.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –120.62 (d, *J* = 59.9 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{23}FO_2Na$: 337.1574; found: 337.1569.

3-(1-Fluoro-2-oxo-2-phenylethoxy)-2-methyl-4H-pyran-4-one (5q)

Purified by flash column chromatography on silica gel (PE/EtOAc = 30:1).

Yield: 48.2 mg (92%); light yellow solid; mp 130.0–130.6 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 7.6 Hz, 2 H), 7.71 (d, *J* = 5.7 Hz, 1 H), 7.66–7.59 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 6.95 (d, *J* = 62.4 Hz, 1 H), 6.45 (d, *J* = 5.7 Hz, 1 H), 2.38 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.50 (d, *J* = 22.3 Hz), 173.55, 161.62, 154.32, 140.58, 134.46, 132.85, 130.01, 128.80, 117.44, 103.72 (d, *J* = 233.8 Hz), 15.12.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –138.37 (d, *J* = 62.3 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}FO_4Na$: 285.0534; found: 285.0533.

(8*R*,9*S*,13*S*,14*S*)-3-(1-Fluoro-2-oxo-2-phenylethoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (5r)

Purified by flash column chromatography on silica gel (PE/EtOAc = 30:1).

Yield: 65.0 mg (80%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.7 Hz, 2 H), 7.67–7.60 (m, 1 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 7.28 (d, *J* = 8.6 Hz, 1 H), 6.97 (dt, *J* = 8.7, 2.8 Hz, 1 H), 6.92 (s, 1 H), 6.34 (d, *J* = 60.8 Hz, 1 H), 2.92 (dd, *J* = 9.8, 4.5 Hz, 2 H), 2.50 (dd, *J* = 19.0, 8.7 Hz, 1 H), 2.44–2.37 (m, 1 H), 2.27 (td, *J* = 10.8, 4.3 Hz, 1 H), 2.14 (dt, *J* = 18.5, 8.9 Hz, 1 H), 2.10–1.98 (m, 2 H), 2.00–1.93 (m, 1 H), 1.67–1.55 (m, 2 H), 1.57–1.39 (m, 4 H), 0.91 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 220.68, 188.82 (d, *J* = 28.3 Hz), 154.04 (d, *J* = 2.9 Hz), 138.58, 136.06, 134.35, 132.42, 129.95 (d, *J* = 1.6 Hz), 128.74, 126.87, 117.42 (d, *J* = 8.0 Hz), 114.67, 107.33 (d, *J* = 232.9 Hz), 50.42, 47.96, 44.06, 38.15, 35.86, 31.58, 29.57, 26.38, 25.87, 21.60, 13.86.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –126.02 (d, *J* = 59.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + NH_4]$^+$ calcd for $C_{26}H_{31}FO_3N$: 424.2282; found: 424.2283.

2-Fluoro-1-(furan-2-yl)-2-(4-methoxyphenoxy)ethan-1-one (5s)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 45.0 mg (90%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.64 (s, 1 H), 7.41 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 3.6 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.56 (dd, *J* = 3.7, 1.7 Hz, 1 H), 6.49 (d, *J* = 52.2 Hz, 1 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.44 (d, *J* = 25.9 Hz), 160.99, 149.45, 147.53, 136.59 (d, *J* =1.3 Hz), 120.55 (d, *J* = 4.6 Hz), 119.72, 114.84, 112.68, 98.20 (d, *J* = 233.8 Hz), 55.36.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –127.26 (d, *J* = 61.1 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{11}FO_4Na$: 273.0534; found: 273.0537.

2-Fluoro-2-(4-methoxyphenoxy)-1-(naphthalen-1-yl)ethan-1-one (5t)

Purified by flash column chromatography on silica gel (PE/EtOAc = 100:1).

Yield: 54.6 mg (88%); yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.30–8.24 (m, 1 H), 8.04 (d, *J* = 8.2 Hz, 1 H), 7.94 (d, *J* = 7.2 Hz, 1 H), 7.93–7.84 (m, 1 H), 7.57–7.51 (m, 2 H), 7.50 (dd, *J* = 8.2, 7.3 Hz, 1 H), 7.38–7.30 (m, 2 H), 6.82 (d, *J* = 52.2 Hz, 1 H), 6.84–6.77 (m, 2 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 192.16 (d, *J* = 23.3 Hz), 160.93, 136.44, 134.03, 133.98, 131.52, 130.70, 128.57, 128.35 (d, *J* = 1.6 Hz), 128.21, 126.78, 125.67, 124.15, 119.91, 114.82, 98.60 (d, *J* = 234.5 Hz), 55.40.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –123.82 (d, *J* = 61.2 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{15}FO_3Na$: 333.0897; found: 333.0893.

2-Fluoro-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (5u)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 42.8 mg (91%); light yellow solid; mp 77.6–77.8 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.7 Hz, 2 H), 7.12 (d, *J* = 9.0 Hz, 2 H), 6.98 (d, *J* = 9.0 Hz, 2 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 6.22 (d, *J* = 61.1 Hz, 1 H), 3.88 (s, 3 H), 3.79 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.52 (d, *J* = 28.5 Hz), 164.49, 156.45, 150.08 (d, *J* = 2.7 Hz), 132.45 (d, *J* = 1.8 Hz), 125.34, 118.88, 114.84, 114.04, 108.55 (d, *J* = 234.1 Hz), 55.66, 55.58.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –124.77 (d, *J* = 62.2 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}FO_4Na$: 313.0846; found: 313.0844.

2-Fluoro-1-(2-fluorophenyl)-2-(4-methoxyphenoxy)ethan-1-one (5v)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 49.5 mg (89%); light yellow oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.99 (t, *J* = 7.5 Hz, 1 H), 7.60 (q, *J* = 7.3 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 7.21–7.13 (m, 1 H), 7.10 (d, *J* = 9.3 Hz, 2 H), 6.86 (dd, *J* = 8.9, 1.7 Hz, 2 H), 6.39 (dd, *J* = 61.5, 2.7 Hz, 1 H), 3.78 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 187.56 (dd, *J* = 26.8, 3.7 Hz), 161.94 (d, *J* = 256.0 Hz), 156.51, 150.25 (d, *J* = 2.9 Hz), 136.04 (d, *J* = 9.4 Hz), 131.56, 124.91 (d, *J* = 3.4 Hz), 122.24 (d, *J* = 13.3 Hz), 118.97, 116.67 (d, *J* = 23.1 Hz), 114.80, 106.57 (dd, *J* = 231.3, 7.2 Hz), 55.65.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –108.80, –131.85 (dd, *J* = 61.6, 8.7 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}F_2O_3Na$: 301.0647; found: 301.0649.

2-Fluoro-2-(4-methoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-one (5w)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 52.8 mg (91%); colorless oil.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.6 Hz, 1 H), 7.66 (s, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.19 (dd, *J* = 8.0, 2.4 Hz, 1 H), 7.12 (d, *J* = 8.9 Hz, 2 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 6.25 (d, *J* = 60.9 Hz, 1 H), 3.86 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.75 (d, *J* = 28.4 Hz), 159.87, 156.59, 150.05 (d, *J* = 2.8 Hz), 133.72, 129.77, 122.67 (d, *J* = 2.5 Hz), 121.09, 118.98, 114.92, 113.89, 108.16 (d, *J* = 234.0 Hz), 55.70, 55.53.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –125.42 (d, *J* = 60.5 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}FO_4Na$: 313.0846; found: 313.0849.

2-Fluoro-2-(4-methoxyphenoxy)-1-[4-(trifluoromethyl)-phenyl]ethan-1-one (5x)

Purified by flash column chromatography on silica gel (PE/EtOAc = 20:1).

Yield: 114.2 mg (87%); light yellow solid; mp 74.2–74.5 °C.

^{1}H NMR (501 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.1 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.9 Hz, 2 H), 6.89 (d, *J* = 9.2 Hz, 2 H), 6.22 (d, *J* = 60.8 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.22 (d, *J* = 30.0 Hz), 156.77, 149.86 (d, *J* = 2.8 Hz), 135.38 (q, *J* = 32.9 Hz), 130.45 (d, *J* = 2.4 Hz), 125.73 (q, *J* = 3.6 Hz), 123.52 (q, *J* = 273.0 Hz), 118.91, 114.98, 108.66 (d, *J* = 234.1 Hz), 55.66.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.36, –124.22 (d, *J* = 60.8 Hz).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{12}F_4O_3Na$: 351.0615; found: 351.0613.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1395-4788.

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