Study on the selectivity in the electrophilic monofluorination of 2,3-allenoates with Selectfluor$^{\text{TM}}$: an efficient synthesis of 4-fluoro-2(5*H*)-furanones and 3-fluoro-4-oxo-2(*E*)-alkenoates†

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Different from the reaction of 2,3-allenoic acids with Selectfluor$^{\text{TM}}$, 4-fluoro-2(5*H*)-furanones and (*E*)-3-fluoro-4-oxo-2-alkenoates were highly selectively generated from 2,4-disubstituted 2,3-allenoates with Selectfluor$^{\text{TM}}$ under different conditions in moderate yields. The reaction of 2,4,4-trisubstituted 2,3-allenoates afforded the corresponding 4-fluoro-2(5*H*)-furanones highly selectively with up to 95% yield under different conditions. The scope of the substrates has been carefully explored. Due to the more readily availability of 2,3-allenoates as compared to 2,3-allenoic acids, new 4-fluoro-2(5*H*)-furanones were prepared. Based on the isolation and characterization of the minor fluorohydroxylation product *E*-**5m**, a mechanism has been proposed.

Introduction

Many fluorinated organic compounds have been identified as biologically active molecules,[1] probably due to the fact that the fluorine most closely resembles hydrogen in size among the atoms but is much more electronegative than oxygen.[2] Monofluorination has been usually conducted using the common but very dangerous and environmentally unfriendly fluorine gas. Considering this problem, chemists have developed a series of highly efficient and easily controlled electrophilic fluorination reagents such as DAST,[3] CF_3OF,[4] XeF_2,[5] *N*-fluoropyridinium triflate,[6] NFSI,[7] Selectfluor$^{\text{TM}}$,[8,9] *etc.* Among these reagents, Selectfluor$^{\text{TM}}$ has been proven to be a highly efficient fluorination reagent, and thus, has been widely used in organic synthesis.

In 2008, we reported that 4-fluoro-2(5*H*)-furanones could be synthesized conveniently by the cyclization of 2,3-allenoic acid in the presence of Selectfluor$^{\text{TM}}$.[8a] Recently, this type of fluorocyclization reaction using 4,5-allenoic acid and Selectfluor$^{\text{TM}}$ has also been reported by Zhao, Zhu, and their co-workers.[9] Since the acids are usually prepared from the hydrolysis of esters,[10] it is desirable to prepare lactones directly from 2,3-allenoates.[11a,b] In this paper, we wish to report our recent study on the reaction of 2,3-allenoates with Selectfluor$^{\text{TM}}$, which affords 4- fluoro-2(5*H*)-furanones and 3-fluoro-4-oxo-2(*E*)-alkenoates under different reaction conditions, respectively.[12]

Results and discussion

The initial experiment was carried out by using ethyl 2-methyl-4-phenyl-2,3-butadienoate **1a** and 1.2 equiv of Selectfluor$^{\text{TM}}$ **2** in MeCN at 80 °C (Table 1, entry 1). Interestingly, 4-fluoro-3-methyl-5-phenyl-2(5*H*)-furanone **4a** was formed together with an unknown product. However, from ^{1}H NMR and ^{13}C NMR, IR, MS and HRMS analysis, we identified this new product as ethyl 3-fluoro-2-methyl-4-oxo-4-phenyl-2(*E*)-butenoate **3a**.[13,14]

With the addition of Li_2CO_3,[13] the selectivity for the formation of **3a** was improved; however, the yield was still very low, indicating the difference of the reaction of 2,3-allenoates with PhSeCl and Selectfluor$^{\text{TM}}$ (Table 1, entry 2). Increasing the amount of Selectfluor$^{\text{TM}}$ could also improve the yield (Table 1, entry 3). Other bases such as Na_2CO_3, K_2CO_3, and Cs_2CO_3 are also unsuitable in this reaction (Table 1, entries 4–6). The carbonyl functionality formed in compound **3a** should have something to do with the trace amount of water in the commercially available MeCN or air, thus, the reaction was carried out under N_2 in anhydrous MeCN, which had been refluxed in the presence of calcium hydride for 10 h and distilled immediately before use, to afford *E*-**3a** in 26% yield with a selectivity of **3a**/**4a** as high as 98/2 (Table 1, entry 7). Encouraged by these results, a series of experiments were carried out by adding a fixed amount of water (Table 1, entries 8–9). The best results were given when 0.5 equiv of water was used to afford *E*-**3a** in 60% yield with the **3a**/**4a** ratio being 97/3 (Table 1, entry 8, Conditions A). In addition, it is interesting to observe that further increasing the amount of water led to almost exclusive formation of **4a** (Table 1, entries 10–13). When running the reaction with 1.7 equiv of Selectfluor$^{\text{TM}}$ in MeCN–H_2O = 2/1 at 80 °C, lactone **4a** was formed as the only product in 56% yield (Table 1, entry 14, Conditions B).

The configuration of the carbon–carbon double bond in *E*-**3a** was determined by ^{1}H–^{19}F HOESY analysis (heteronuclear Overhauser effect spectroscopy, see Fig. 1 and ESI†).

The scope of selective fluorination of 2,3-allenoates to form (*E*)-3-fluoro-4-oxo-2-butenoates **3** was then explored under Conditions A. Some typical results are summarized in Table 2. The R^1 group could be substituted phenyl group; R^2 could be alkyl or benzyl group.

However, the reaction could not be extended to 4-alkyl-substituted 2,3-allenoate **1k** (Scheme 1). The reaction of ethyl

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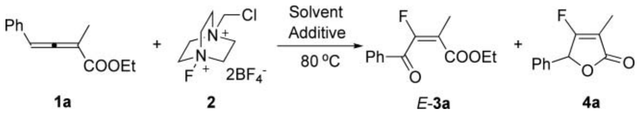
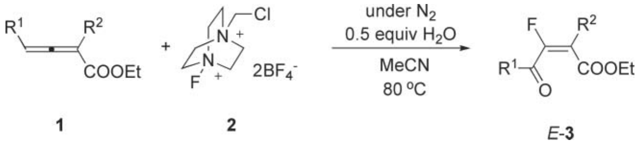
Table 1 Fluorination reaction of **1a** under different conditions



Entry	2[a]	Solvent	Additive (equiv)	Time/h	NMR Yield (%)[b] *E*-3a	NMR Yield (%)[b] 4a	Ratio (3a/4a)[b]	1a (%)[c]
1	1.2	MeCN	—	19.5	19	35	35/65	7
2	1.2	MeCN	Li_2CO_3 (2.0)	11.5	12.5	4.5	74/26	8
3	2.0	MeCN	Li_2CO_3 (2.0)	14	32	13	71/29	—
4	2.0	MeCN	Na_2CO_3 (2.0)	19.3	9	3	75/25	3.5
5	2.0	MeCN	K_2CO_3 (2.0)	19.3	10	—	87/13[d]	28
6	2.0	MeCN	Cs_2CO_3 (2.0)	19	Trace	Trace	—	33
7	3.0	MeCN[e]	—	9	26	—	98/2[d]	—
8	**3.0**	**MeCN**[e]	**H_2O (0.5)**	**10.5**	**60**	**1.6**	**97/3**	—
9	3.0	MeCN[e]	H_2O (1.0)	10	26	1.3	95/5	—
10	1.5	MeCN–H_2O = 5/1		12	—	54	1/99[d]	3
11	1.5	MeCN–H_2O = 3/1		11.5	—	50	1/99[d]	2
12	1.5	MeCN–H_2O = 2/1		11.5	—	57	1/99[d]	4
13	1.5	MeCN–H_2O = 1/1		10.5	—	44	1/99[d]	—
14	**1.7**	**MeCN/H_2O = 2/1**		**14.7**	—	**56**	**1/99**[d]	—

[a] Equivalents of **2**. [b] Determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethylbenzene as the internal standard. [c] **1a** recovered after the reaction. [d] Determined by ^{19}F NMR analysis. [e] The reaction was carried out under N_2; MeCN was refluxed in the presence of calcium hydride for 10 h and distilled immediately before use.

Table 2 Synthesis of (*E*)-3-fluoro-4-oxo-2-butenoates **3** from the reaction of 2,4-disubstituted 2,3-allenoates with Selectfluor™ under Conditions A[a]



Entry	1	R¹	R²	Time/h	Product	Yield (%)[b]	3/4[c]
1	**1a**	Ph	Me	10.5	*E*-**3a**	55	97/3
2	**1b**	Ph	Et	10	*E*-**3b**	56	98/2
3	**1c**	Ph	*n*-Pr	11	*E*-**3c**	53	98/2
4	**1d**	Ph	Bn	11.5	*E*-**3d**	45	98/2
5	**1e**	*p*-FC_6H_4	Me	10	*E*-**3e**	45	99/1
6	**1f**	*p*-ClC_6H_4	Me	10.5	*E*-**3f**	46	98/2
7	**1g**	*p*-BrC_6H_4	Me	12	*E*-**3g**	55	98/2
8	**1h**	*p*-BrC_6H_4	*n*-Pr	10.5	*E*-**3h**	46	98/2
9	**1i**	*p*-MeC_6H_4	Me	10	*E*-**3i**	43	98/2
10	**1j**	*p*-MeC_6H_4	Et	9.5	*E*-**3j**	39	98/2

[a] Conditions A: A solution of **1** (0.2–0.3 mmol), **2** (3 equiv), and water (0.5 equiv) was stirred in 2–3 mL of anhydrous MeCN under N_2 at 80 °C. [b] Isolated yield. [c] The ratio of **3**/**4** was determined by ^{19}F NMR spectra of crude products.

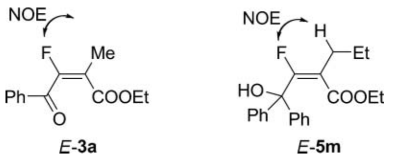
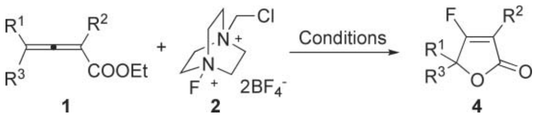


Fig. 1 ^1H–^{19}F HOESY analysis of *E*-**3a** and *E*-**5m**.

4-(2-chlorophenyl)-2-methyl-2,3-butadienoate (**1l**) afforded ketone *E*-**3l** together with lactone **4l** in a ratio of 87/13 (**3l**/**4l**) (Scheme 1).

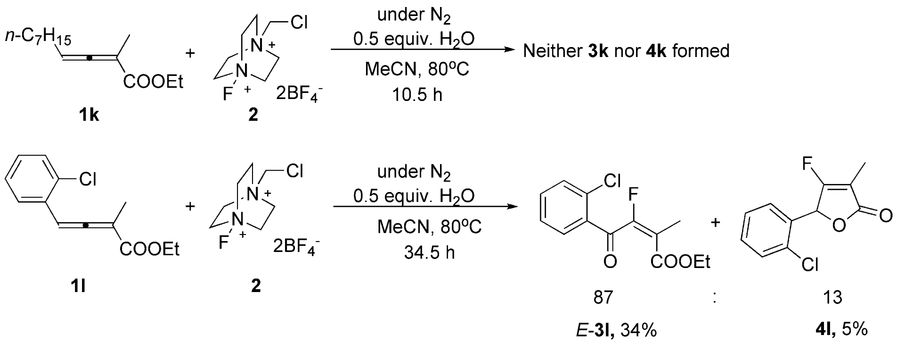
The fluorolactonization of 2,3-allenoates was also demonstrated under Conditions B (Table 3): When R² is ethyl or propyl, 2.5 equiv of Selectfluor™ were required to form the corresponding lactones (Table 3, entries 2 and 3). The reaction of fully substituted **1m** afforded **4m** under Conditions B in 86% yield together with the fluorohydroxylation product, *i.e.*, ethyl 3-fluoro-4-hydroxyl-4,4-diphenyl-2-propyl-2(*E*)-butenoate (**5m**) in 7% yield, indicating the existence of a **5m**-type intermediate for this type of transformation (Scheme 2). Treatment of **1m** with Selectfluor™ under Conditions A still led to the formation of lactone **4m** in 93% isolated yield together with *E*-**5m** in 5% isolated yield (Scheme 2). The configuration of the carbon–carbon double bond in *E*-**5m** was determined by ^1H-^{19}F HOESY analysis (see Fig. 1 and ESI†). Further screening led us to observe that **4m** could be afforded when **1m** was treated with just 1.2 equiv of Selectfluor™ in MeCN at 80 °C (Conditions C) in 90% isolated yield with a selectivity

Table 3 Synthesis of 4-fluoro-2(5*H*)-furanones **4** from the reaction of 2,3-allenoates with **2**

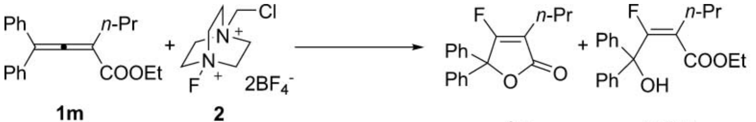


	1							
Entry	R^1	R^3	R^2	Conditions[a]	t/h	Yield (%)[b]	**4/3**[b]	**4/5**[b]
1	Ph	H	Me (**1a**)	B	14.7	51 (**4a**)	>99/1	—
2	Ph	H	Et (**1b**)	B[c]	23.5	50 (**4b**)	>99/1	—
3	Ph	H	*n*-Pr (**1c**)	B[c]	23.5	47 (**4c**)	>99/1	—
4	*p*-FC$_6$H$_4$	H	Me (**1e**)	B	26	60 (**4e**)	>99/1	—
5	*p*-BrC$_6$H$_4$	H	Me (**1g**)	B	21.5	42 (**4g**)	>99/1	—
6	*p*-MeC$_6$H$_4$	H	Me (**1i**)	B	21	64 (**4i**)	>99/1	—
7	Ph	Me	Me (**1n**)	C	5.3	80 (**4n**)	—	99/1
8	Ph	Ph	Me (**1o**)	C	5.5	93 (**4o**)	—	99/1
9	Ph	Et	Me (**1p**)	C	5.5	95 (**4p**)	—	98/2
10	Ph	Et	*n*-Pr (**1q**)	C	5	91 (**4q**)	—	99/1
11	Ph	Et	H (**1r**)	C	5	76 (**4r**)	—	98/2
12	-(CH$_2$)$_5$-		Me (**1s**)	C	11	30 (**4s**)	—	98/2
13	-(CH$_2$)$_5$-		Me (**1s**)	C[d]	10.8	42 (**4s**)	—	98/2

[a] Conditions B: A solution of **1** (0.2–0.4 mmol) and **2** (1.7 equiv) was stirred in 2–4 mL of MeCN–H$_2$O (2/1 (v/v)) at 80 °C; Conditions C: A solution of **1** (0.2 mmol) and **2** (1.2 equiv) was stirred in 2 mL of MeCN at 80 °C. [b] The ratios of **4/3** and **4/5** were determined by the ^{19}F NMR analysis of the crude products. [c] A quantity of 2.5 equiv of **2** was used. [d] MeNO$_2$ was used instead of MeCN.



Scheme 1



		4m	***E*-5m**
Conditions A	1.5 h	93%	5%
Conditions B	5 h	86%	7%
Conditions C	5.5 h	90%	-

Selectivity (**4m**/***E*-5m**): 98/2 by ^{19}F NMR analysis of the crude reaction mixture

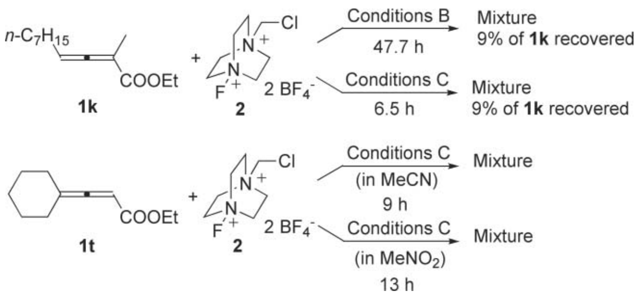
Scheme 2

of **4m/5m** being 98/2 as determined by ^{19}F NMR analysis of the crude reaction mixture (Scheme 2).

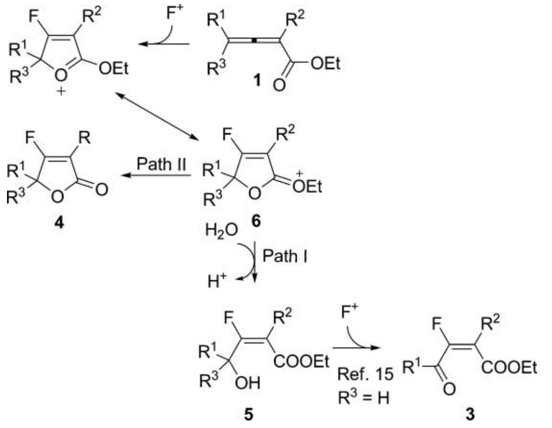
A series of 4,4-disubstituted 4-aryl 2,3-allenoates were then treated with Selectfluor™ under Conditions C. The corresponding 4-fluoro-2(5*H*)-furanones could also be afforded in excellent yields (Table 3, entries 7–11, Conditions C). MeNO$_2$ is more effective than MeCN leading the lactonization reaction of 2,4,4-trialkyl substituted ethyl 3-cyclohexylidene-2-methylacrylate (**1s**) to afford **4s** in relatively higher yields (Table 3, entries 12 and 13).

However, complicated products were observed when 2,4-disubstituted 2,3-allenoate **1k** was treated with Selectfluor™ under either Conditions B or Conditions C (Scheme 3). For 4,4-dialkyl substituted allenoate **1t**, either in MeCN or in MeNO$_2$, the corresponding lactone could not be afforded (Scheme 3).

A plausible mechanism was proposed for this reaction (Scheme 4): The relatively electron-rich carbon–carbon double bond of 2,3-allenoate firstly interacts with F$^+$ in Selectfluor™ to form cyclic intermediate **6**, which explains the *E*-stereoselectivity observed



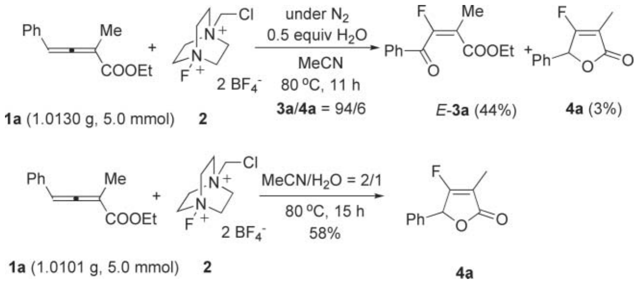
Scheme 3



Scheme 4

here. Hydroxylation at the 5-position would lead to the formation of fluorohydroxylation product **5**, which was confirmed by the isolation and characterization of *E*-**5m** (Scheme 2). If R^3 = H, subsequent oxidation by Selectfluor$^{TM 15}$ would form ketone **3** (Path I, Scheme 4). Corresponding dealkylation of intermediate **6** may lead to lactonization to form **4** (Path II, Scheme 4).

This reaction may easily be carried out with 5 mmol of ethyl 4-phenyl-2,3-butadienoate **1a** to afford **3a** and **4a**, respectively (Scheme 5).



Scheme 5

Conclusions

In conclusion, we have developed an efficient way to synthesize 3-fluoro-4-oxo-2(*E*)-alkenoates and 4-fluoro-2(5*H*)-furanones from the same starting materials 4-aryl-2-alkyl or benzyl-2,3-allenoates and Selectfluor™ in acetonitrile. The reaction of fully substituted 2,3-allenoates with Selectfluor™ afforded 4-fluoro-2(5*H*)-furanones highly selectively in excellent yields under Conditions A, B, and C. A mechanism has been proposed based on the isolation and characterization of the minor fluorohydroxylation product *E*-**5m**. Due to the readily availability of 2,3-allenoates and the formation of different types of monofluorinated products with functionalities for further elaboration under different conditions, this method shows more potential than that of 2,3-allenoic acids. Further studies in this area are being conducted in our laboratory.

Experimental section

1. Preparation of 3-fluoro-4-oxo-2(*E*)-butenoates (3a–j)

(1) Preparation of ethyl 3-fluoro-2-methyl-4-oxo-4-phenyl-2(*E*)-butenoate (3a). Typical procedure (Conditions A). Ethyl 2-methyl-4-phenyl-2,3-butadienoate (**1a**) (39.9 mg, 0.20 mmol) and 1 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) were added into a flame-dried Schlenk vessel, which was pre-evacuated and backfilled with nitrogen three times. Selectfluor™ (95%, 223.2 mg, 0.60 mmol) and another 1 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) were added sequentially under nitrogen. The resulting mixture was heated at 80 °C with a preheated oil bath. After 10.5 h, the reaction was complete as monitored by TLC. The reaction mixture was then quenched with 10 mL of H_2O, extracted with ether (40 mL + 2 × 10 mL), washed with 10 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and purification by chromatography (petroleum ether–ethyl acetate = 80 : 1) on silica gel afforded **3a** (25.8 mg, 55%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.66–7.58 (m, 1H), 7.53–7.45 (m, 2H), 3.99 (q, J = 7.2 Hz, 2H), 2.05 (d, J = 4.2 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.2 (d, J = 28.1 Hz), 166.1 (d, J = 17.4 Hz), 158.9 (d, J = 276.2), 134.6, 134.1, 129.2, 128.8, 114.9 (d, J = 16.9 Hz), 61.4, 13.4, 10.7 (d, J = 5.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –100.5; IR (neat) ν/cm^{-1} 3064, 2984, 2936, 1725, 1682, 1598, 1583, 1451, 1369, 1302, 1202, 1176, 1113, 1082, 1019; MS (70 eV, EI) m/z (%): 236 (M$^+$, 7.13), 105 (100); HRMS calcd for $C_{13}H_{13}O_3F$ (M$^+$): 236.0849. Found: 236.0842.

The following compounds were prepared according to this typical procedure.

(2) Ethyl 2-ethyl-3-fluoro-4-oxo-4-phenyl-2(*E*)-butenoate (3b). The reaction of **1b** (64.1 mg, 0.30 mmol) and Selectfluor™ (95%, 336.2 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) at 80 °C under nitrogen afforded **3b** (41.5 mg, 56%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H), 7.66–7.58 (m, 1H), 7.54–7.46 (m, 2H), 4.01 (q, J = 7.1 Hz, 2H), 2.53 (qd, J = 7.6 Hz and 3.6 Hz, 2H), 1.91 (t, J = 7.6 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.1 (d, J = 28.8 Hz), 165.9 (d, J = 16.5 Hz), 158.0 (d, J = 276.8 Hz), 134.7, 134.1, 129.2 (d, J = 2.0 Hz), 128.8, 121.5 (d, J = 15.4 Hz), 61.4, 19.2 (d, J = 4.4 Hz), 13.4, 12.8 (d, J = 2.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –104.5; IR (neat) ν/cm^{-1} 2981, 2940, 1727, 1683, 1598, 1582, 1450, 1369, 1309, 1276, 1256, 1201, 1176, 1122, 1024; MS (70 eV, EI) m/z (%): 250 (M$^+$, 6.31), 105 (100); HRMS calcd for $C_{14}H_{15}O_3F$ (M$^+$): 250.1005. Found: 250.1007.

(3) Ethyl 3-fluoro-4-oxo-4-phenyl-2-propyl-2(*E*)-butenoate (3c). The reaction of **1c** (70.2 mg, 0.31 mmol) and Selectfluor™ (95%, 339.3 mg, 0.91 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) at 80 °C under nitrogen afforded **3c** (42.8 mg, 53%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.65–7.58 (m, 1H), 7.54–7.46 (m, 2H), 4.00 (q, J = 7.2 Hz, 2H), 2.53–2.45 (m, 2H), 1.68–1.54 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.1 (d, J = 29.0 Hz), 166.0 (d, J = 16.6 Hz), 158.4 (d, J = 275.2 Hz), 134.7, 134.1, 129.2 (d, J = 1.4 Hz), 128.8, 120.1 (d, J = 16.0 Hz), 61.4, 27.5 (d, J = 3.4 Hz), 21.4 (d, J = 1.9 Hz), 13.8, 13.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ −103.9; IR (neat) ν/cm^{-1} 3065, 2966, 2936, 2875, 1728, 1682, 1598, 1582, 1451, 1369, 1305, 1275, 1229, 1200, 1177, 1124, 1033, 1002; MS (70 eV, EI) m/z (%): 264 (M$^+$, 10.02), 105 (100); HRMS calcd for $C_{15}H_{17}O_3F$ (M$^+$): 264.1162. Found: 264.1166.

(4) Ethyl 2-benzyl-3-fluoro-4-oxo-4-phenyl-2(*E*)-butenoate (3d). The reaction of **1d** (83.9 mg, 0.30 mmol) and Selectfluor™ (95%, 336.1 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3d** (42.1 mg, 45%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97–7.88 (m, 2H), 7.66–7.57 (m, 1H), 7.53–7.44 (m, 2H), 7.36–7.21 (m, 5H), 3.93 (q, J = 7.2 Hz, 2H), 3.85 (d, J = 3.6 Hz, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.9 (d, J = 28.4 Hz), 165.3 (d, J = 17.0 Hz), 159.2 (d, J = 278.6 Hz), 137.6 (d, J = 2.6 Hz), 134.5, 134.2, 129.2, 128.9, 128.7, 128.6, 126.7, 118.3 (d, J = 14.4 Hz), 61.5, 31.1 (d, J = 4.0 Hz), 13.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.3; IR (neat) ν/cm^{-1} 3084, 3064, 3030, 2983, 2937, 1724, 1682, 1598, 1582, 1495, 1451, 1370, 1310, 1276, 1203, 1182, 1103, 1037, 1022; MS (70 eV, EI) m/z (%): 312 (M$^+$, 4.06), 266 (100); HRMS calcd for $C_{19}H_{17}O_3F$ (M$^+$): 312.1162. Found: 312.1168.

(5) Ethyl 3-fluoro-4-(4′-fluorophenyl)-2-methyl-4-oxo-2(*E*)-butenoate (3e). The reaction of **1e** (65.8 mg, 0.30 mmol) and Selectfluor™ (95%, 335.6 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3e** (34.1 mg, 45%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.92 (m, 2H), 7.22–7.12 (m, 2H), 4.04 (q, J = 7.2 Hz, 2H), 2.05 (d, J = 4.5 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6 (d, J = 28.8 Hz), 166.3 (d, J = 256.1 Hz), 166.0 (d, J = 16.8 Hz), 158.6 (d, J = 276.5 Hz), 132.0 (dd, J = 9.8 Hz and 1.4 Hz), 131.1 (d, J = 3.2 Hz), 116.2 (d, J = 22.1 Hz), 115.2 (d, J = 16.0 Hz), 61.5, 13.5, 10.8 (d, J = 5.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.2, −102.7; IR (neat) ν/cm^{-1} 3078, 2985, 2937, 1727, 1683, 1600, 1507, 1446, 1413, 1370, 1306, 1240, 1202, 1155, 1114, 1082, 1018; MS (70 eV, EI) m/z (%): 254 (M$^+$, 6.93), 123 (100); HRMS calcd for $C_{13}H_{12}O_3F_2$ (M$^+$): 254.0755. Found: 254.0761.

(6) Ethyl 4-(4′-chlorophenyl)-3-fluoro-2-methyl-4-oxo-2(*E*)-butenoate (3f). The reaction of **1f** (71.4 mg, 0.30 mmol) and Selectfluor™ (95%, 335.4 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3f** (37.2 mg, 46%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–7.83 (m, 2H), 7.50–7.44 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 2.04 (d, J = 4.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9 (d, J = 29.0 Hz), 166.0 (d, J = 16.6 Hz), 158.4 (d, J = 276.3 Hz), 140.7, 133.0, 130.6 (d, J = 1.5 Hz), 129.2, 115.4 (d, J = 16.1 Hz), 61.5, 13.5, 10.8 (d, J = 4.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.7; IR (neat) ν/cm^{-1} 2984, 2937, 1728, 1682, 1589, 1572, 1488, 1445, 1402, 1369, 1304, 1203, 1173, 1113, 1015; MS (70 eV, EI) m/z (%): 272 (M$^+$(^{37}Cl), 2.93), 270 (M$^+$(^{35}Cl), 8.83), 139 (100); HRMS calcd for $C_{13}H_{12}O_3{}^{35}ClF$ (M$^+$): 270.0459. Found: 270.0453.

(7) Ethyl 4-(4′-bromophenyl)-3-fluoro-2-methyl-4-oxo-2(*E*)-butenoate (3g). The reaction of **1g** (83.8 mg, 0.30 mmol) and Selectfluor™ (95%, 335.5 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3g** (51.5 mg, 55%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 4.03 (q, J = 7.2 Hz, 2H), 2.04 (d, J = 4.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1 (d, J = 28.7 Hz), 166.0 (d, J = 15.9 Hz), 158.3 (d, J = 276.6 Hz), 133.4, 132.2, 130.6 (d, J = 1.0 Hz), 129.5, 115.5 (d, J = 16.0 Hz), 61.5, 13.5, 10.8 (d, J = 5.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.8; IR (neat) ν/cm^{-1} 3091, 2984, 2936, 2872, 1728, 1682, 1586, 1484, 1446, 1399, 1369, 1304, 1202,1173, 1112, 1069, 1012; MS (70 eV, EI) m/z (%): 316 (M$^+$(^{81}Br), 17.93), 314 (M$^+$(^{79}Br), 17.55), 185 (99.06), 183 (100); HRMS calcd for $C_{13}H_{12}O_3{}^{79}BrF$ (M$^+$): 313.9954. Found: 313.9952.

(8) Ethyl 4-(4′-bromophenyl)-3-fluoro-4-oxo-2-propyl-2(*E*)-butenoate (3h). The reaction of **1h** (91.1 mg, 0.29 mmol) and Selectfluor™ (95%, 330.6 mg, 0.89 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3h** (46.7 mg, 46%) (flash chromatography, eluent: petroleum ether–ethyl acetate = 100 : 1) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.73 (m, 2H), 7.67–7.60 (m, 2H), 4.05 (q, J = 7.2 Hz, 2H), 2.54–2.42 (m, 2H), 1.67–1.55 (m, 2H), 1.06 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0 (d, J = 30.0 Hz), 165.9 (d, J = 15.4 Hz), 157.8 (d, J = 275.0 Hz), 133.5, 132.2, 130.6 (d, J = 2.0 Hz), 129.4, 120.8 (d, J = 16.0 Hz), 61.5, 27.6 (d, J = 3.5 Hz), 21.3 (d, J = 2.2 Hz), 13.8, 13.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ 105.3; IR (neat) ν/cm^{-1} 2965, 2935, 2874, 1728, 1687, 1586, 1484, 1464, 1399, 1369, 1311, 1272, 1228, 1199, 1173, 1124, 1070, 1011; MS (70 eV, EI) m/z (%): 344 (M$^+$(^{81}Br), 20.01), 342 (M$^+$(^{79}Br), 20.23), 185 (98.06), 183 (100); HRMS calcd for $C_{15}H_{16}O_3{}^{79}BrF$ (M$^+$): 342.0267. Found: 342.0263.

(9) Ethyl 3-fluoro-2-methyl-4-(4′-methylphenyl)-4-oxo-2(*E*)-butenoate (3i). The reaction of **1i** (64.6 mg, 0.30 mmol) and Selectfluor™ (95%, 335.9 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3i** (32.4 mg, 43%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.31–7.26 (m, 2H), 3.99 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.04 (d, J = 4.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.8 (d, J = 28.2 Hz), 166.1 (d, J = 17.6 Hz), 159.3 (d, J = 277.2 Hz), 145.3, 132.2, 129.5, 129.4 (d, J = 1.2 Hz), 114.4 (d, J = 15.4 Hz), 61.4, 21.8, 13.4, 10.7 (d, J = 5.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ 99.9; IR (neat) ν/cm^{-1} 3033, 2984, 2934, 2872, 1727, 1681, 1606, 1574, 1446, 1410, 1369, 1299, 1202, 1177, 1113, 1081, 1019; MS (70 eV, EI) m/z (%): 250 (M$^+$, 8.05), 119 (100); HRMS calcd for $C_{14}H_{15}O_3F$ (M$^+$): 250.1005. Found: 250.1003.

(10) Ethyl 2-ethyl-3-fluoro-4-(4′-methylphenyl)-4-oxo-2(*E*)-butenoate (3j). The reaction of **1j** (69.3 mg, 0.30 mmol) and Selectfluor™ (95%, 336.0 mg, 0.90 mmol) in 3 mL of H_2O–MeCN (premixed, 0.9 μL mL^{-1}) at 80 °C under nitrogen afforded **3j** (30.7 mg, 39%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.31–7.25 (m, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.52 (qd, J = 7.4 Hz and 3.6 Hz, 2H), 2.42 (s, 3H), 1.18

(t, J = 7.4 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.7 (d, J = 29.0 Hz), 165.9 (d, J = 16.6 Hz), 158.3 (d, J = 276.2 Hz), 145.2, 132.2, 129.5, 129.4 (d, J = 1.0 Hz), 121.0 (d, J = 16.0 Hz), 61.3, 21.8, 19.1 (d, J = 4.5 Hz), 13.4, 12.8 (d, J = 2.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −103.9; IR (neat) ν/cm^{-1} 3033, 2981, 2939, 2879, 1727, 1681, 1606, 1574, 1462, 1369, 1317, 1277, 1256, 1177, 1120, 1061, 1025; MS (70 eV, EI) m/z (%): 264 (M^+, 6.53), 119 (100); HRMS calcd for $C_{15}H_{17}O_3F$ (M^+): 264.1162. Found: 264.1166.

2. Preparation of 4-fluoro-2(5*H*)-furanone (4a–i)

(1) Preparation of 4-fluoro-3-methyl-5-phenyl-2(5*H*)-furanone (4a). Typical procedure (Conditions B). A mixture of ethyl 2-methyl-4-phenyl-2,3-butadienoate (**1a**) (40.7 mg, 0.20 mmol) and Selectfluor™ (95%, 126.6 mg, 0.34 mmol) was stirred in a mixture of 1.4 mL of MeCN and 0.65 mL of water at 80 °C with a preheated oil bath. After 14.7 h, the reaction was complete as monitored by TLC. The reaction mixture was then quenched with 10 mL of H_2O, extracted with ether (40 mL + 2 × 10 mL), washed with 10 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and purification by chromatography (petroleum ether–ethyl acetate = 30 : 1) on silica gel afforded **4a**[8a] (19.9 mg, 51%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.38 (m, 3H), 7.36–7.30 (m, 2H), 5.79–5.75 (m, 1H), 1.88 (t, J = 1.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.0.

The following compounds were prepared according to this typical procedure.

(2) 3-Ethyl-4-fluoro-5-phenyl-2(5*H*)-furanone (4b). The reaction of **1b** (42.6 mg, 0.20 mmol) and Selectfluor™ (95%, 186.9 mg, 0.50 mmol) in a mixture of 1.3 mL of MeCN and 0.7 mL of H_2O at 80 °C afforded **4b** (20.3 mg, 50%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.39 (m, 3H), 7.36–7.27 (m, 2H), 5.77–5.73 (m, 1H), 2.35 (qt, $J_{H\text{-}H1}$ = 7.6 Hz, $J_{H\text{-}H2}$ = 1.2 Hz, $J_{H\text{-}F}$ = 1.2 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (d, J = 295.8 Hz), 171.2 (d, J = 22.0 Hz), 132.3 (d, J = 2.0 Hz), 129.9, 129.1, 126.6, 110.1 (d, J = 6.1 Hz), 77.5 (d, J = 22.5 Hz), 15.2 (d, J = 3.2 Hz), 11.7 (d, J = 2.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ 110.5; IR (neat) ν/cm^{-1} 3069, 3033, 2978, 2940, 2877, 1778, 1715, 1497, 1456, 1362, 1313, 1265, 1091, 1062, 1035, 1005; MS (70 eV, EI) m/z (%): 207 (M^+ + 1, 13.77), 206 (M^+, 100); HRMS calcd for $C_{12}H_{11}O_2F$ (M^+): 206.0743. Found: 206.0741.

(3) 4-Fluoro-5-phenyl-3-propyl-2(5*H*)-furanone (4c). The reaction of **1c** (46.5 mg, 0.20 mmol) and Selectfluor™ (95%, 187.3 mg, 0.50 mmol) in a mixture of 1.3 mL of MeCN and 0.7 mL of H_2O at 80 °C afforded **4c**[2] (20.8 mg, 47%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 3H), 7.35–7.30 (m, 2H), 5.78–5.74 (m, 1H), 2.34–2.26 (m, 2H), 1.70–1.57 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.0.

(4) 4-Fluoro-5-(4′-fluorophenyl)-3-methyl-2(5*H*)-furanone (4e). The reaction of **1e** (85.4 mg, 0.39 mmol) and Selectfluor™ (95%, 246.8 mg, 0.66 mmol) in a mixture of 2.7 mL of MeCN and 1.3 mL of H_2O at 80 °C afforded **4e** (48.6 mg, 60%) as a white solid: mp: 52.5–53.5 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.28 (m, 2H), 7.15–7.07 (m, 2H), 5.78–5.72 (m, 1H), 1.88 (t, $J_{H\text{-}H}$ = 2.0 Hz, $J_{H\text{-}F}$ = 2.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0 (d, J = 294.7 Hz), 171.3 (d, J = 21.4 Hz), 163.5 (d, J = 248.1 Hz), 128.7 (d, J = 7.7 Hz), 128.1 (t, J = 3.0 Hz), 116.2 (d, J = 21.7 Hz), 105.0 (d, J = 6.4 Hz), 77.1 (d, J = 23.1 Hz), 6.0 (d, J = 2.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.3, −110.9; IR (KBr) ν/cm^{-1} 2933, 1781, 1724, 1608, 1513, 1392, 1347, 1298, 1234, 1115, 1080, 1012; MS (70 eV, EI) m/z (%): 211 (M^+ + 1, 11.85), 210 (M^+, 90.78), 123 (100); Anal. Calcd. for $C_{11}H_8F_2O_2$: C, 62.86; H, 3.84. Found: C, 62.65; H, 3.81%.

(5) 5-(4′-Bromophenyl)-4-fluoro-3-methyl-2(5*H*)-furanone (4g). The reaction of **1g** (113.0 mg, 0.40 mmol) and Selectfluor™ (95%, 254.8 mg, 0.68 mmol) in a mixture of 2.7 mL of MeCN and 1.3 mL of H_2O at 80 °C afforded **4g** (45.3 mg, 42%) as a white solid: mp: 62.4–64.2 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (dt, J = 8.7 Hz and 2.1 Hz, 2H), 7.24–7.17 (m, 2H), 5.75–5.70 (m, 1H), 1.87 (t, $J_{H\text{-}H}$ = 2.0 Hz, $J_{H\text{-}F}$ = 2.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9 (d, J = 295.2 Hz), 171.3 (d, J = 21.6 Hz), 132.3, 131.3 (d, J = 1.9 Hz), 128.2, 124.1, 105.0 (d, J = 7.2 Hz), 77.0 (d, J = 22.4 Hz), 6.1 (d, J = 1.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.3; IR (KBr) ν/cm^{-1} 3067, 2965, 2930, 2863, 1778, 1716, 1590, 1489, 1411, 1390, 1345, 1300, 1198, 1114, 1069, 1009; MS (70 eV, EI) m/z (%): 272 (M^+(^{81}Br), 27.78), 270 (M^+(^{79}Br), 28.42), 191 (M^+ − Br, 100); Anal. Calcd. for $C_{11}H_8BrFO_2$: C, 48.74; H, 2.97. Found: C, 48.91; H, 2.88%.

(6) 4-Fluoro-3-methyl-5-(4′-methylphenyl)-2(5*H*)-furanone (4i). The reaction of **1i** (86.8 mg, 0.40 mmol) and Selectfluor™ (95%, 254.8 mg, 0.68 mmol) in a mixture of 2.7 mL of MeCN and 1.3 mL of H_2O at 80 °C afforded **4i** (52.6 mg, 64%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.18 (m, 4H), 5.75–5.70 (m, 1H), 2.36 (s, 3H), 1.87 (t, $J_{H\text{-}H}$ = 2.1 Hz, $J_{H\text{-}F}$ = 2.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3 (d, J = 294.8 Hz), 171.7 (d, J = 22.1 Hz), 139.9, 129.7, 129.1 (d, J = 2.8 Hz), 126.6, 104.7 (d, J = 6.3 Hz), 77.7 (d, J = 23.5 Hz), 21.2, 6.0 (d, J = 2.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.0; IR (neat) ν/cm^{-1} 2929, 1778, 1723, 1516, 1448, 1420, 1391, 1346, 1301, 1198, 1112, 1081, 1037, 1007; MS (70 eV, EI) m/z (%): 207 (M^+ + 1, 13.76), 206 (M^+, 100); HRMS calcd for $C_{12}H_{11}O_2F$ (M^+): 206.0743. Found: 206.0744.

3. Preparation of 4-fluoro-2(5*H*)-furanone (4m–s)

(1) 4-Fluoro-5,5-diphenyl-3-propyl-2(5*H*)-furanone (4m). Typical procedure (Conditions C). A mixture of ethyl 4,4-diphenyl-2-propyl-2,3-butadienoate (**1m**) (60.9 mg, 0.20 mmol) and Selectfluor™ (85.3 mg, 0.24 mmol) was stirred in 2 mL of MeCN at 80 °C with an oil bath. After 5.5 h, the reaction was complete as monitored by TLC. The reaction mixture was quenched with 10 mL of H_2O, extracted with ether (40 mL + 2 × 10 mL), washed with 10 mL of brine, and dried over Na_2SO_4. Filtration, evaporation, and purification by chromatography (petroleum ether–ethyl acetate = 30 : 1) on silica gel afforded 4-fluoro-5,5-diphenyl-3-propyl-2(5*H*)-furanone (**4m**)[8a] (52.8 mg, 90%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.35 (m, 10H), 2.31 (td, J = 7.5 Hz and 1.2 Hz, 2H), 1.72–1.58 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −106.2.

The formation of **4m** and *E*-**5m** under Conditions A:

The reaction of **1m** (0.6162 g, 2.01 mmol) and Selectfluor™ (95%, 2.2435 g, 6.02 mmol) in 20 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) at 80 °C under nitrogen afforded **4m** (0.5558 g, 93%) and *E*-**5m** (0.0375 g, 5%) (petroleum ether–ethyl acetate = 30 : 1 to 5 : 1) as a liquid.

4m: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.30 (m, 10H), 2.35–2.27 (m, 2H), 1.73-1.57 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).

E-**5m**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.30 (m, 10H), 4.25 (q, J = 7.1 Hz, 2H), 2.92 (d, J = 2.1 Hz, 1H), 1.98–1.89 (m, 2H), 1.34–1.15 (m, 5H), 0.65 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 167.6 (d, J = 5.0 Hz), 159.5 (d, J = 261.8 Hz), 142.7, 128.3, 127.5, 117.8 (d, J = 13.3 Hz), 80.7 (d, J = 30.4 Hz), 61.1, 28.6 (d, J = 3.2 Hz), 21.8 (d, J = 2.6 Hz), 14.2, 13.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.5; IR (neat) ν/cm^{-1} 3479, 3061, 3028, 2962, 2932, 2873, 1713, 1600, 1493, 1464, 1449, 1368, 1295, 1232, 1181, 1110, 1031; MS (ESI) m/z: 397 (M^+ + Na + MeOH), 365 (M^+ + Na), 360 (M^+ + NH_4), 325 (M^+ − OH); HRMS calcd for $C_{21}H_{23}FO_3Na$ (M^++Na): 365.1523. Found: 365.1536.

The formation of **4m** under Conditions B:

The reaction of **1m** (61.8 mg, 0.20 mmol) and Selectfluor™ (95%, 126.3 mg, 0.34 mmol) in a mixture of 1.3 mL of MeCN and 0.65 mL of H_2O at 80 °C afforded **4m** (51.6 mg, 86%) and *E*-**5m** (4.9 mg, 7%) (petroleum ether–ethyl acetate = 20 : 1 to 5 : 1) as a liquid.

4m: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.33 (m, 10H), 2.36–2.27 (m, 2H), 1.73–1.58 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

E-**5m**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.30 (m, 10H), 4.25 (q, J = 7.1 Hz, 2H), 2.91 (d, J = 2.1 Hz, 1H), 1.98–1.88 (m, 2H), 1.35–1.14 (m, 5H), 0.65 (t, J = 7.4 Hz, 3H).

The following compounds were prepared according to the Conditions C.

(2) 4-Fluoro-3,5-dimethyl-5-phenyl-2(5*H*)-furanone (4n). The reaction of **1n** (43.4 mg, 0.20 mmol) and Selectfluor™ (85.3 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4n**[8a] (33.0 mg, 80%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.31 (m, 5H), 1.90 (s, 3H), 1.81 (d, J = 1.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −111.2.

(3) 4-Fluoro-3-methyl-5,5-diphenyl-2(5*H*)-furanone (4o). The reaction of **1o** (55.8 mg, 0.20 mmol) and Selectfluor™ (85.3 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4o**[8a] (49.9 mg, 93%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.28 (m, 10H), 1.90 (d, J = 2.1 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −106.1.

(4) 5-Ethyl-4-fluoro-3-methyl-5-phenyl-2(5*H*)-furanone (4p). The reaction of **1p** (45.5 mg, 0.20 mmol) and Selectfluor™ (85.1 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4p**[8a] (41.5 mg, 95%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.32 (m, 5H), 2.33–2.20 (m, 1H), 2.19–2.06 (m, 1H), 1.80 (d, J = 2.4 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.3.

(5) 5-Ethyl-4-fluoro-5-phenyl-3-propyl-2(5*H*)-furanone (4q). The reaction of **1q** (52.4 mg, 0.20 mmol) and Selectfluor™ (85.4 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4q**[8a] (45.7 mg, 91%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.26 (m, 5H), 2.36–2.05 (m, 4H), 1.63–1.50 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.5.

(6) 5-Ethyl-4-fluoro-5-phenyl-2(5*H*)-furanone (4r). The reaction of **1r** (43.2 mg, 0.20 mmol) and Selectfluor™ (84.8 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4r** (31.4 mg, 76%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.32 (m, 5H), 5.53 (d, J = 1.5 Hz, 1H), 2.36–2.09 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 182.7 (d, J = 304.8 Hz), 169.0 (d, J = 23.4 Hz), 136.1 (d, J = 2.8 Hz), 128.8, 124.8, 124.7, 96.2 (d, J = 7.3 Hz), 86.6 (d, J = 18.6 Hz), 30.1 (d, J = 1.4 Hz), 7.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ −99.8; IR (neat) ν/cm^{-1} 3124, 3064, 2979, 2941, 2883, 1771, 1674, 1601, 1496, 1450, 1357, 1328, 1288, 1222, 1174, 1098; MS (70 eV, EI) m/z (%): 207 (M^+ + 1, 2.72), 206 (M^+, 20.54), 177 (100); HRMS calcd for $C_{12}H_{11}O_2F$ (M^+): 206.0743. Found: 206.0746.

(7) 4-Fluoro-3-methyl-1-oxaspiro[4.5]3-decen-2-one (4s). The reaction of (**1s**) (39.7 mg, 0.20 mmol) and Selectfluor™ (95%, 90.9 mg, 0.24 mmol) in 2 mL of MeCN at 80 °C afforded **4s**[8a] (11.2 mg, 30%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82–1.60 (m, 12H), 1.36–1.20 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.8.

The reaction of (**1s**) (37.8 mg, 0.19 mmol) and Selectfluor™ (95%, 88.5 mg, 0.24 mmol) in 2 mL of $MeNO_2$ at 80 °C afforded **4s**[8a] (14.9 mg, 42%) as a liquid.^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85–1.58 (m, 12H), 1.35–1.18 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −112.8.

4. Large scale reactions

(1) Ethyl 3-fluoro-2-methyl-4-oxo-4-phenyl-2(*E*)-butenoate (3a). Following Conditions A, a mixture of ethyl 2-methyl-4-phenyl-2,3-butadienoate (**1a**) (1.0130 g, 5.0 mmol), Selectfluor™ (95%, 5.5996 g, 15.0 mmol), and 50 mL of H_2O–MeCN (premixed, 0.9 µL mL^{-1}) were added into a flame-dried Schlenk vessel which was pre-evacuated and backfilled with nitrogen three times. The resulting mixture was then heated at 80 °C with an oil bath. After 11 h, the reaction was complete as monitored by TLC. The reaction mixture was quenched with 50 mL of H_2O, extracted with ether (100 mL + 2 × 25 mL), washed with 50 mL of brine, and dried over Na_2SO_4. Filtration, evaporation, and purification by chromatography (petroleum ether–ethyl acetate = 80 : 1 to 20 : 1) on silica gel afforded **3a** (0.5162 g, 44%) and **4a** (0.0323 g, 3%), respectively.

(2) 4-Fluoro-3-methyl-5-phenyl-2(5*H*)-furanone (4a). Following Conditions B, a mixture of ethyl 2-methyl-4-phenyl-2,3-butadienoate (**1a**) (1.0101 g, 5.0 mmol) and Selectfluor™ (95%, 3.1655 g, 8.5 mmol) were stirred in a mixture of 33.5 mL of MeCN and 16.5 mL of water at 80 °C in an oil bath. After 15 h, the reaction was complete as monitored by TLC. The reaction mixture was quenched with 50 mL of H_2O, extracted with ether (100 mL + 2 × 25 mL), washed with 50 mL of brine, and dried over Na_2SO_4. Filtration, evaporation, and purification by chromatography (petroleum ether–ethyl acetate = 30 : 1) on silica gel afforded **4a** (0.5532 g, 58%).

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