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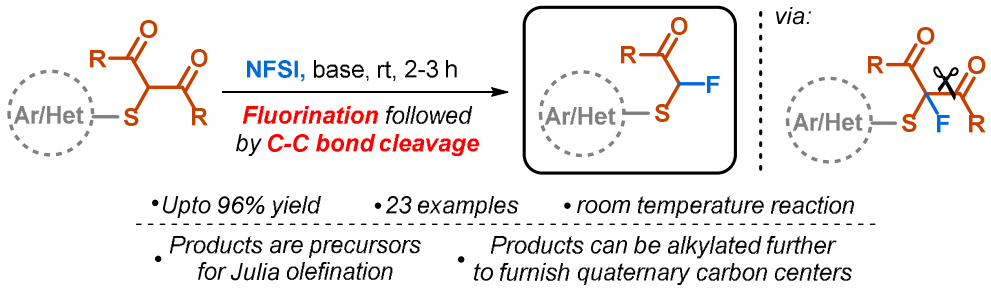
Sulfur Assisted Tandem Electrophilic Fluorinative Deacylation: Synthesis of *α*-Fluoro *β*-Ketosulfides

Begur Vasanthkumar Varun and Kandikere Ramaiah Prabhu*

Department of Organic Chemistry, Indian Institute of Science,
Bangalore 560 012, Karnataka, India.
prabhu@orgchem.iisc.ernet.in

ABSTRACT

A successful synthesis of *α*-fluoro-*β*-ketosulfides using electrophilic fluorination method has been reported for the first time. The reaction proceeds *via* an electrophilic fluorination of *α*-sulfenyl-*β*-diketones followed by an unexpected tandem deacylation. The resulting product, *α*-fluoro-*β*-ketosulfides, are easily oxidized to the corresponding *α*-fluoro-*β*-ketosulfones, which can be used for further useful olefination reactions.



Introduction

Incorporation of fluorine into organic molecules is an active research area in organic synthesis, because, fluorine containing organic compounds are found in biologically active compounds including pharmaceuticals and agrochemicals, and material science industries, agrochemistry and material science (Fig 1).[1,2]

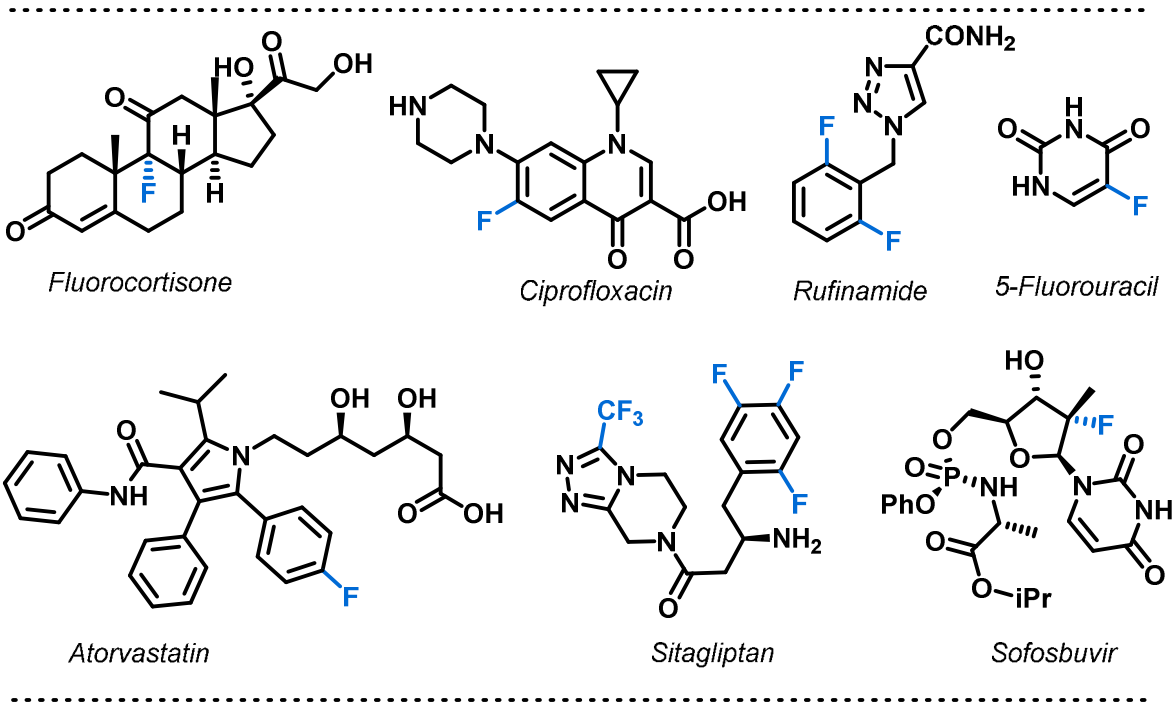
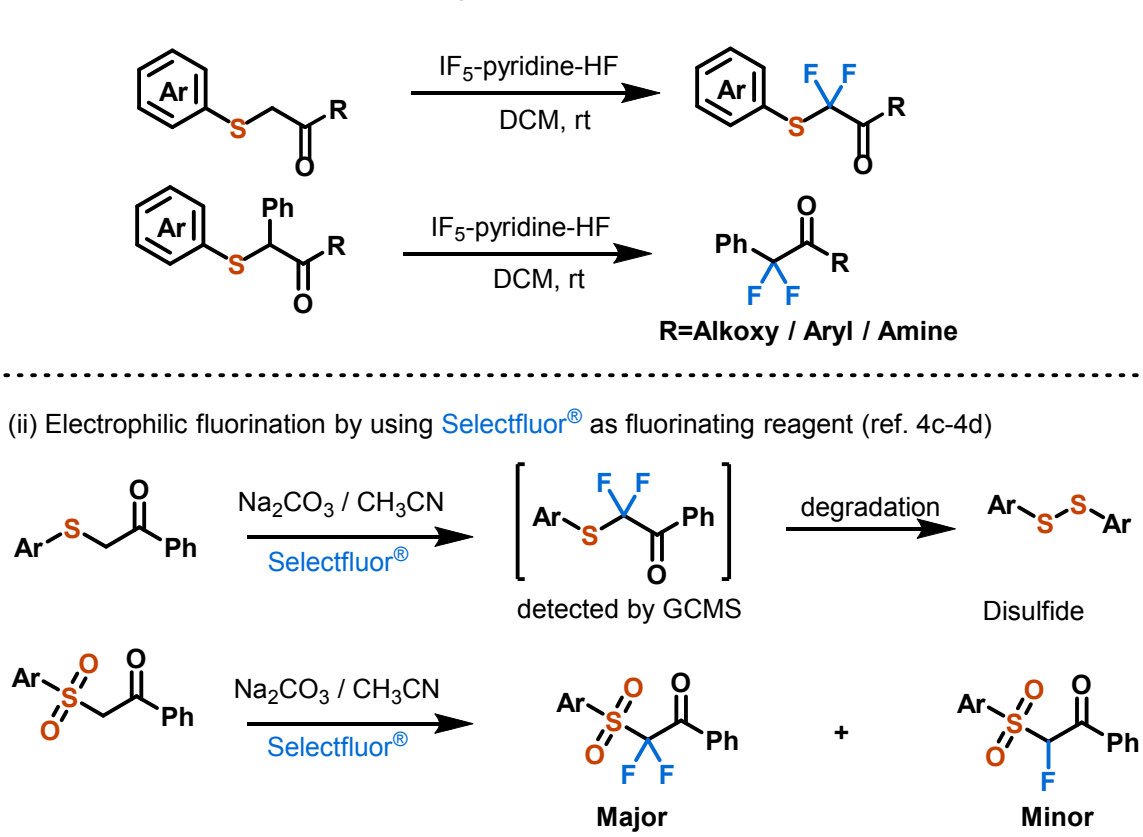


Fig 1: Examples of fluorine containing drug molecules

A plethora of methods are available in the literature for incorporation of fluorine into organic molecules to obtain a variety of structurally diverse molecular scaffolds.[3] However, controlled mono-electrophilic fluorination at α-position of an electron withdrawing group still remains a challenge in organic synthesis.[4] This problem becomes compounded when a sulfide group is present at α-position to an electron withdrawing moiety. Several attempts towards synthesizing α-fluoro-β-ketosulfides *via* electrophilic fluorination method by various groups, have resulted in the formation of undesired or over fluorinated products (Scheme 1).[4b-4d] This

is probably due to (i) the strong affinity between sulfur and fluorine to form S–F/S→F bond, which leads to undesired side reactions; and (ii) the presence of sulfur atom at α-position increases the acidity of α-C–H bond, and results in the rapid uncontrolled fluorination. The methods for the formation of α-fluoro-β-ketosulfides are limited to a few β-ketosulfide derivativess that bear the substitution at α-position.[4b]

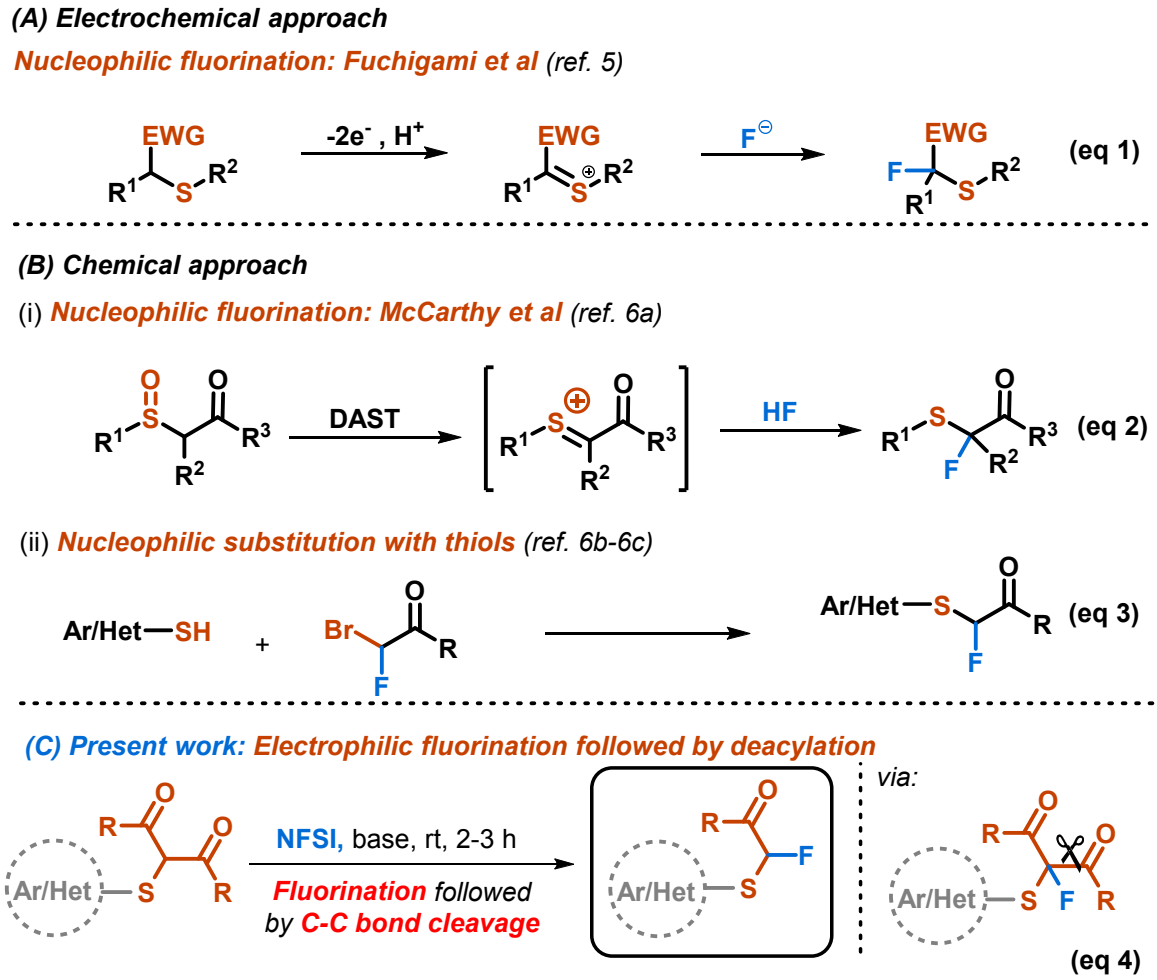


Scheme 1: Undesired/Uncontrolled electrophilic fluorination

In contrast to electrophilic fluorination, the controlled nucleophilic fluorination of β-ketosulfides could be successfully achieved by electrochemical methods (eq 1, Scheme 2).[5] The only chemical method known to obtain α-fluoro-β-ketosulfides is the nucleophilic fluorination of sulfoxide with DAST (diethyl amino sulfurtrifluoride) in the presence of catalytic amount of ZnI_2 (eq 2, Scheme 2).[6a] However, the nucleophilic substitution of α-

bromofluorocarbonyl compounds with thiols provides the expected α-fluoro-β-ketosulfides (eq 3, Scheme 2).[6b-6c]

On the other hand, several reports of deacylation of β-dicarbonyl compounds, such as classical acetoacetic ester synthesis, are well documented in the literature.[6d-6g] In recent years, the release of trifluro acetate group from the fluorinated β-dicarbonyl compounds shown as important reaction in organic synthesis.[6j-6k] When the α-position of β-dicarbonyl compounds is substituted with sulfides, the deacylation is relatively facile.[7] The deacylation of β-ketoesters is facile in the presence of nucleophilic base at ambient temperature.[7b] However, the deacylation of β-diketones, generally requires transition metal catalysts, and oxidants, and the reaction is performed at higher temperature.[7c-7d] A report for the electrophilic halogenative (+Cl and +Br) deacylation of non-sulfide bearing β-dicarbonyl compounds is known in the literature.[7e] Distinct from these reports, the present work involves an unexpected tandem deacylation of α-fluoro sulfenyl β-diketones in mild reaction conditions to synthesize α-fluoro-β-ketosulfides (eq 4, Scheme 2). To the best of our knowledge, till date, (i) a controlled fluorination leading to mono electrophilic fluorination of β-ketosulfides, and (ii) a successful synthesis of α-fluoro-β-ketosulfides *via* electrophilic fluorination method are unknown.



Scheme 2: Reaction development

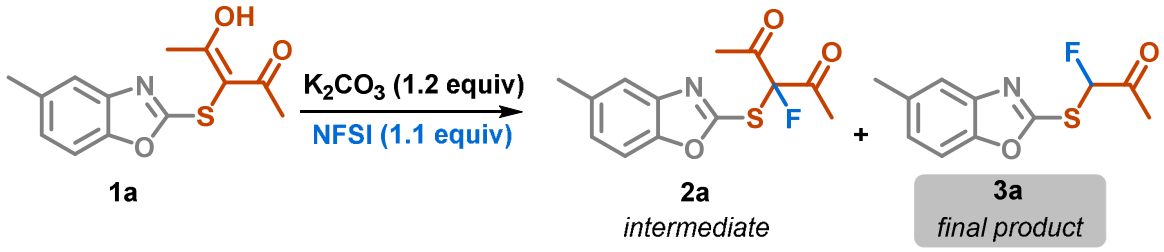
Results and Discussion

Optimization Studies

Initially, we performed a fluorination of α-sulfenyl-β-diketone (**1a**, 1 equiv) using NFSI (*N*-fluorobenzenesulfonimide, 1.1 equiv) as a fluorinating reagent and K_2CO_3 (1.2 equiv) as a base in CH_3CN (2 mL). The initial reaction furnished a mixture of fluorinated product **2a** and the corresponding deacylated product **3a** in 54 and 43%, respectively (determined by ^1H

NMR, Table 1, entry 1). Extending the reaction time to 1h led to the formation of **2a** and **3a** in 44 and 56%, respectively (entry 2).

Table 1: Screening studies [a] (*Standard conditions **A**)*



entry	solvent	time (h)[a]	^{1}H NMR yield (%) for crude reaction mixture [b]	
			2a	**3a**
1	CH_3CN	0.75	54	43
2	CH_3CN	1	44	56
3	CH_3CN	2	10	90 (96) [e]
4	THF	1	57	43
5	THF	2	nd	100
6	acetone	2	18	82
7	EtOAc	1	22	78 (92) [e]
8	**EtOAc**	**2**	**nd**	**100 (96)[e]**
9	DCM	2	50	50
10	toluene	2	41	51
11	MeOH	2	nd	nd
12	H_2O	2	nr	nr
13[c]	EtOAc	2	59	23
14[d]	EtOAc	2	nd	100

[a] Reaction conditions A: **1a** (0.1 mmol) and K_2CO_3 (1.2 equiv) in solvent (1 mL) were pre-stirred for 60-90 min, then NFSI (1.1 equiv) was added and the reaction mixture was stirred for the given time. [b] ^{1}H NMR yields (determined by using terephthaldehyde as internal standard). [c] Na_2CO_3 (1.2 equiv) [d] Cs_2CO_3 (1.2 equiv). [e] Values in the parentheses are isolated yields of **3a** after passing through silica gel column (**2a** converts to **3a** in the column)

Further extension to 2h led to the formation of a mixture of **2a** and **3a** in 10 and 90%, respectively (entry 3). On purification, we were able to isolate exclusively deacylated product **3a** in 96% isolated yield (entry 3), indicating that the fluorinated product **2a** underwent deacylation under the chromatographic conditions (see the Supporting Information, SI-3-SI-4). Further, reaction of **1a** using solvents such as THF and acetone resulted in the formation

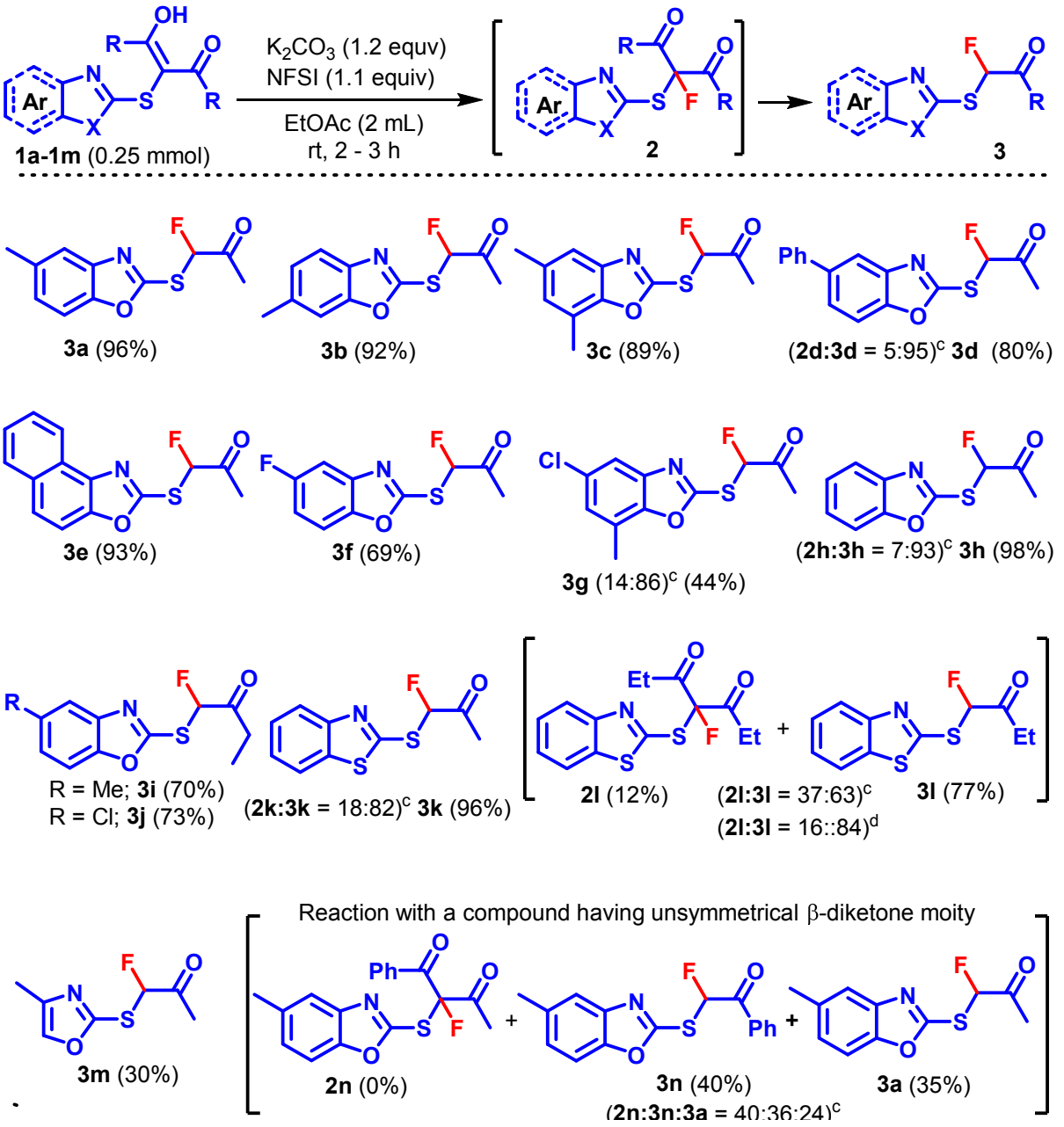
of a mixture of **2a** and **3a** (entries 4-6). The reaction of **1a** with NFSI in EtOAc (1h) furnished the products **2a** and **3a** in 22 and 78%, respectively (entry 7). Further, when the reaction was carried in EtOAc for 2h, it furnished exclusively deacylated product **3a** in almost quantitative yield (entry 8). Reactions with solvents such as CH_2Cl_2 and toluene led to a mixture of **2a** and **3a** (entries 9 and 10). Furthermore, the reaction in MeOH formed a complex mixture, whereas the reaction in H_2O was not successful (entries 11 and 12). The reaction performed using Na_2CO_3 gave **2a** and **3a** in 59 and 23%, respectively (entry 13), whereas the reaction using Cs_2CO_3 proceeded smoothly to furnish only **3a** in quantitative yield (entry 14).

Substrate scope

Under the established "*optimized reaction conditions A*" (entry 8, Table 1), the scope and limitations of this fluorinative deacylation reaction were explored (Scheme 3). As seen in Scheme 3, a variety of *α*-benzoxazole-2-sulfenyl acetylacetone derivatives bearing alkyl/aryl/halo substitution on benzoxazole ring (**1a-1g**) and unsubstituted *α*-benzoxazole-2-sulfenyl acetylactone (**1h**) underwent smooth electrophilic fluorination followed by deacetylation furnishing products **3a-3h** in moderate to excellent yields (96, 92, 89, 80, 93, 69, 44 and 98%, respectively). Further, a facile deacylation was observed even in the case of *α*-benzoxazole-2-sulfenyl-3,5-heptanediones (**1i** and **1j)** and the expected products **3i** and **3j** were obtained in good yields (70 and 73%, respectively). Under the optimal conditions, the benzothiazole derivative (**1k**) furnished the expected product **3k** in excellent yield (96%). However, *α*-benzothiazole-2-sulfenyl 3,5-heptanediones (**1l**) furnished an inseparable mixture of **2l** and **3l** in 12 and 77%, respectively (based on ^{1}H NMR ratio). The fluorinative deacylation reaction of *α*-oxazole-2-sulfenylacetylacetone (**1m**) furnished only 30% of the

desired product **3m** after column purification. The compound **1n**, which has the unsymmetrical diketone moiety, underwent fluorinative deacylation to give the mixture of

Scheme 3: Substrate scope [a, b, c, d]

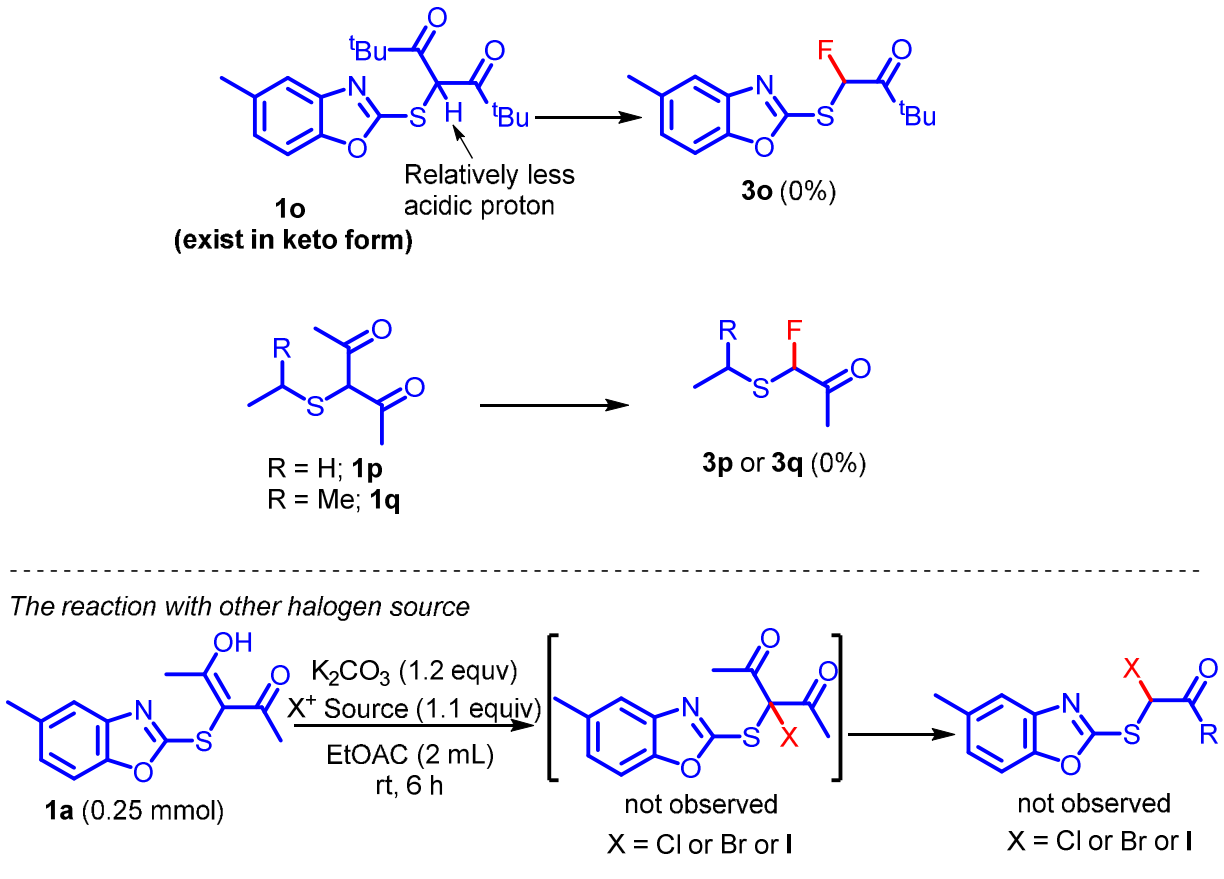


[a] Reaction Conditions: **1** (0.25 mmol) and K_2CO_3 (1.2 equiv), were pre-stirred for 60-90 minutes in EtOAc (2 mL), then NFSI (1.1 equiv) was added and reaction mixture was stirred at rt for further 2 - 3 h. [b] Values in the parentheses are isolated yields. [c] ^{1}H NMR ratio of products before column purification. [d] ^{1}H NMR ratio of products after column purification.

2n, 3n and **3a** in a ratio of 40:36:24. The compounds **3n** and **3a** were isolated in 40 and 35%, respectively, whereas the compound **2n** underwent deacylation on silica gel column. Hence, the increment in the isolated yields of **3n** and **3a** was observed.

The compound **1o**, which preferentially exists in diketone form (due to bulky carbonyl groups) bearing relatively less acidic proton,[7a] did not furnish the expected product **3o** and starting material was intact (based on ^{1}H NMR spectrum, Scheme 4). The starting materials **1p** and **1q** did not furnish the α-alkylthio-β-diketones (Scheme 4).[8a] Further, when the starting material **1a** was allowed to react with NCS/NBS/NIS instead of NFSI, the reaction produced complex inseparable mixture (Scheme 4).

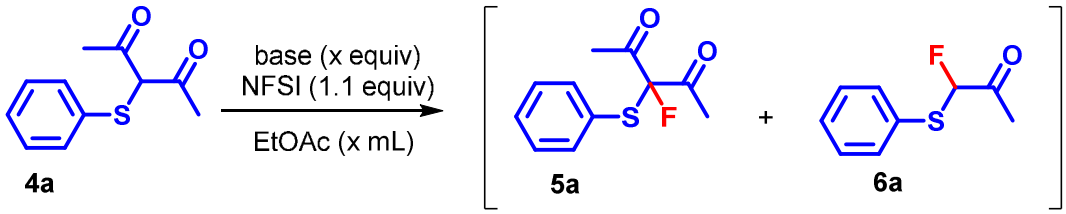
Scheme 4: Unsuccessful reaction under "*Optimized reaction condition A*"



Optimization for aryl-substituted sulfdes.

Under the "*optimized reaction conditions A*", 3-(phenylthio)pentane-2,4-dione **(4a)** did not undergo complete deacylation and instead furnished a mixture of non-deacylated and deacylated fluorine compounds. Therefore, further optimization study was under taken to enhance the deacylation process (entries 1-5, Table 2). During this optimization study, we found that increasing in the concentration of the reaction mixture (0.5 mmol of **4** in 2 mL of CH_3CN) in the presence of a strong base (Cs_2CO_3, 1.2 equiv) resulted in the complete deacylation (entry 5, *Optimized reaction condition B; Table 2*).

Table 2: Optimization for aryl substituted sulfides (6a-6i) (*Standard conditions **B**)*



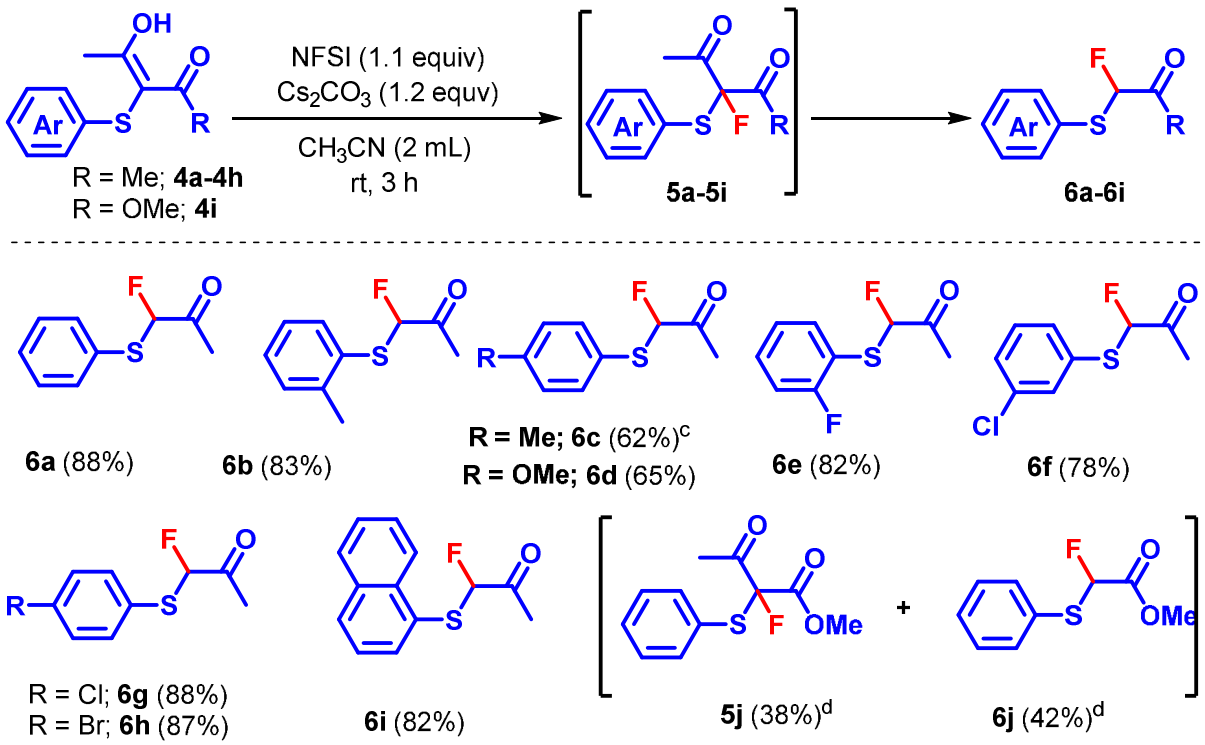
entry	**4a** (mmol)	solvent (mL)	base (equiv)	Conversion ratios in crude reaction mixture **5a : 6a**	Ratios after subjecting to column purification [c, d] **5a : 6a**
1	0.25	EtOAc (2.0)	K_2CO_3 (1.2)	68: 32	30:70 **5a** (19%); **6a** (60%)
2	0.5	EtOAc (4.0)	K_2CO_3 (3.0)	38: 62	8: 92 **5a** (6%); **6a** (82%)
3	0.5	EtOAc (2.0)	Cs_2CO_3 (1.2)	25: 75	7: 93 **5a** (5%); **6a** (91%)
4	0.25	CH_3CN (2.0)	K_2CO_3 (1.2)	34:66	-
5	**0.5**	**CH_3CN (2.0)**	**Cs_2CO_3 (1.2)**	**3:97**	**0:100** **5a** (0%); **6a** (88%)

[a] Reaction Conditions: **4a** (1 equiv) and Base (x equiv) were pre-stirred for 2 h, then NFSI (1.1 equiv) was added and the reaction mixture was stirred at room temperature for 3 h. [b] ^{1}H NMR ratio of products, [c] ^{1}H NMR ratio of products after silica gel column purification, [d] Values in the parenthesis are the isolated yield of inseparable mixture of products **5a** and **6a**. nd=not detected

Substrate Scope

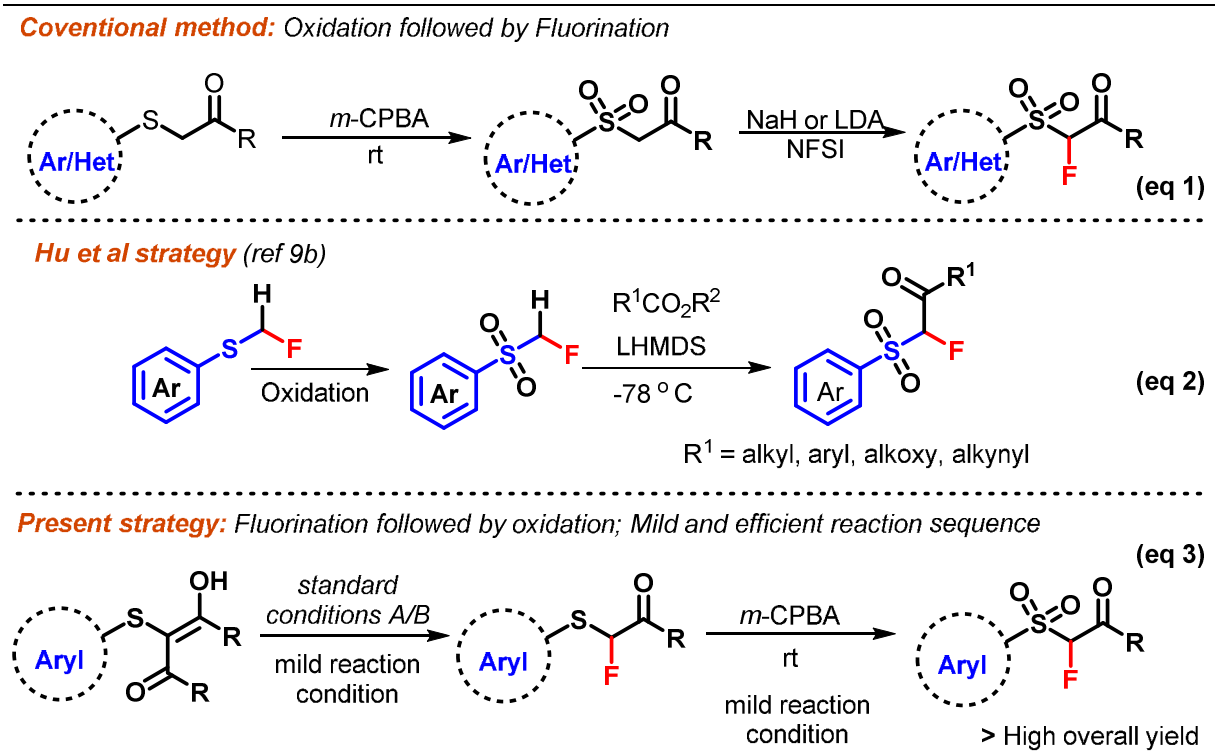
Under the *reaction conditions B*, *α*-thiophenyl acetyl acetone **4a** and its derivatives **4b-4h** underwent smooth reaction, which upon purification on a silica gel column furnished exclusively deacylated fluorine compounds **6a** (88%), **6b** (83%), **6c** (62%), **6d** (65%), **6e** (82%), **6f** (78%), **6g** (88%), **6h** (87%) and **6i** (82%) respectively (Scheme 5). The *α*-sulfenyl *β*-ketoester **4i** furnished the mixture of **5j** and **6j** in 38 and 42%, respectively (^{1}H NMR yield, see the Supporting information, SI-90 and 91). However, our attempt to isolate the **5j** and **6j** was not successful as the crude compound degraded on silica gel column.

Scheme 5: Substrate scope under the "*Optimized reaction condition B*" [a, b, c, d]



[a] Reaction conditions: 4 (0.5 mmol) and Cs_2CO_3 (1.2 equiv), were pre-stirred for 2 h in CH_3CN (2 mL), added NFSI (1.1 equiv) and reaction mixture was stirred at rt for further 3 h. [b] Values in the parentheses are Isolated yields. [c] Reaction time-6 h. [d] ^{1}H NMR yield (determined by using terephthaldehyde as internal standard; see SI-90 and 91) the compounds degraded during isolation

α-Fluoro-β-ketosulfones are important starting materials in Julia-Kocienski fluoro-olefination reaction for synthesizing fluoro-olefins.[6b-6c, 10] Further, the sulfones have great utility in organic synthesis as well as in pharmaceutical chemistry.[4b, 6b-6c, 9] The general reaction sequences used for the synthesis of α-fluoro-β-ketosulfones are cumbersome and have multiple problems (eq 1, Scheme 6).[6b-6c, 10a-10c] Hu et al, reported an alternate strategy, which avoids the over fluorination (eq 2, scheme 6).[9b]

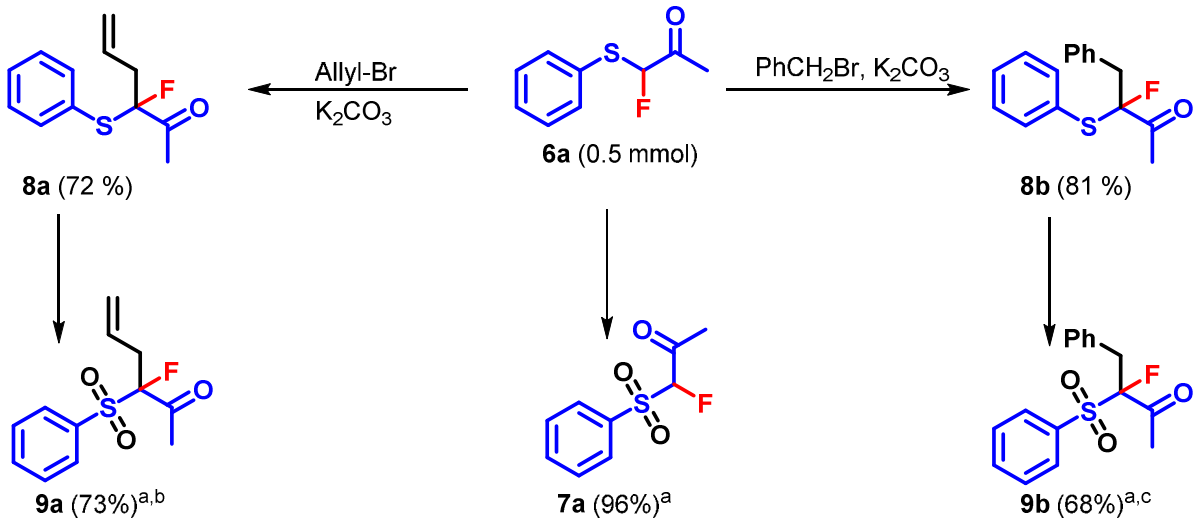


Scheme 6: Reaction development for the synthesis of fluorosulfones

To address these synthetic challenges, we thought that α-fluoro-β-ketosulfides would be suitable substrates for synthesizing α-fluoro-β-ketosulfones (eq 3, Scheme 6). Hence, the compound **6a** was chosen as the model substrate for the oxidation, and sulfones **7a**, **9a,** and **9b** were synthesized in good to excellent yields (96, 73 and 68%, respectively, Scheme 7) from the starting material **6a** under a mild reaction condition using *m*-CPBA as an oxidant.[8b] To demonstrate further synthetic utility, both allylation and benzylation of **6a** was performed,

in which only the products **8a** and **8b** were obtained from **6a** (see the Supporting Information, SI-95 and SI-99).

Scheme 7: Synthetic application [a, b, c, d]

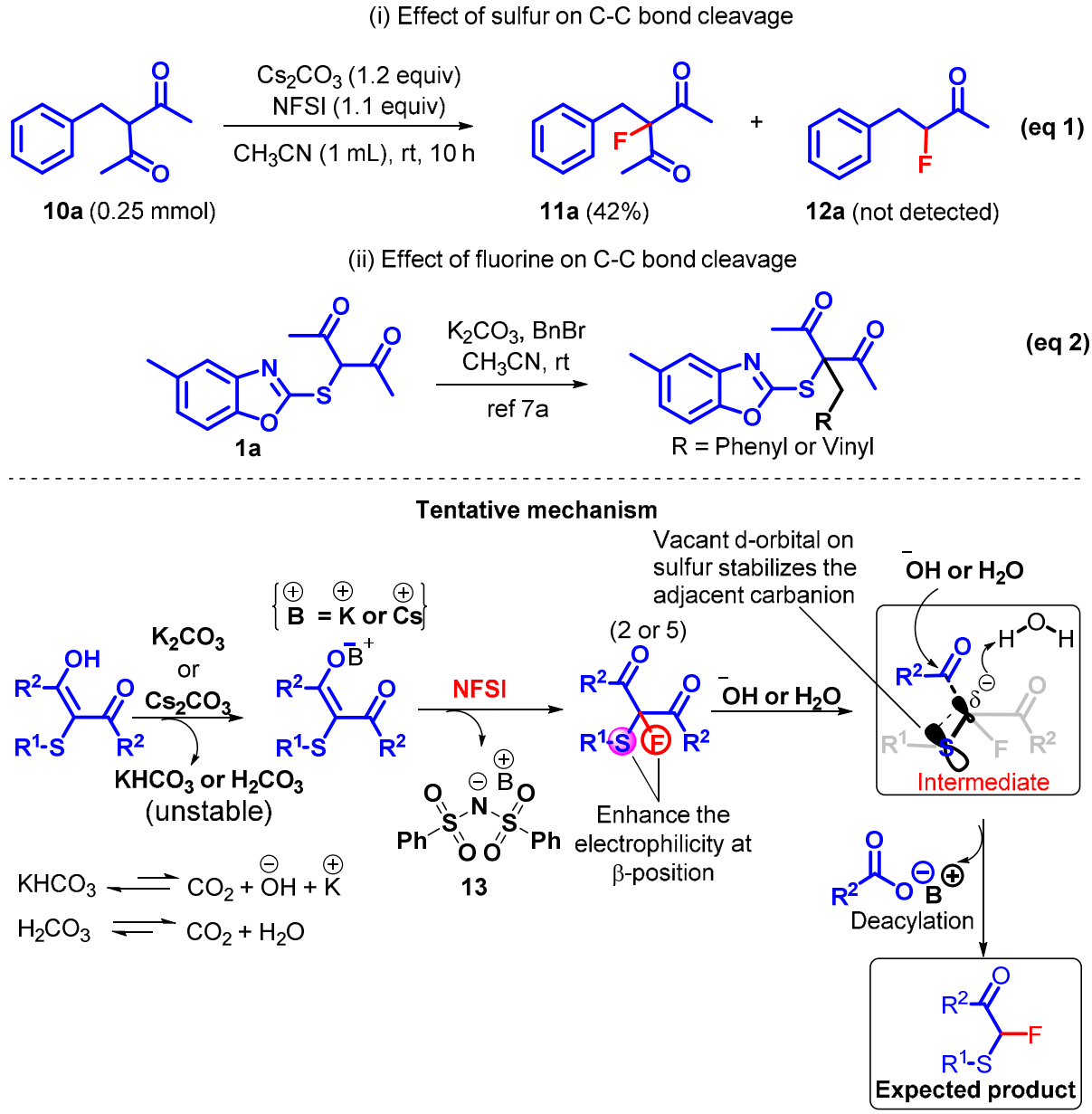


Reaction Conditions: [a] mCPBA (4 equiv), CH_2Cl_2 (5 mL), rt, 6 h, [b] **8a** (0.36 mmol), [c] **8b** (0.4 mmol), [d] Values in the parentheses are isolated yields.

Control experiments

To understand the effect of sulfur on deacylation reaction, the compound **10a** was fluorinated under "*optimized reaction condition B*", which furnished only the non-deacylated product **11a** in 42% yield (eq 1, Scheme 8, see SI-109 and SI-110). This result clearly indicates the necessity of sulfur moiety for deacylation of *α*-fluoro-*β*-diketones. Earlier, we reported a reaction in which the active methine position of **1a** is substituted (allylation and benzylation reactions) to form the non-deacylated products (eq 2, Scheme 8).[7a] This result clearly suggests the necessity of fluorine moiety for deacylation of *α*-sulfenyl *β*-diketones. Hence, these two results clearly indicate that the presence of both sulfur and fluorine at *α*-position of *β*-dicarbonyl is essential for facile deacylation. Based on these observations, a tentative mechanism has been proposed (Scheme 8). Fluorine being the most electronegative element, its substitution at *α*-position of *β*-dicarbonyl enhances the electrophilicity at of the carbonyl

carbons and thereby facilitating a even weak nucleophiles to attack carbonyl carbons.[11a-11b] On the other hand, the vacant d-orbital of sulfur stabilizes the adjacent carbanion[11b-11c] (Scheme 8) thereby favouring the deacylation.



Scheme 8: Establishment of mechanism

Therefore, the electronegativity factor as well as carbanion stabilization operate together causing the deacylation. Further, the residue that forms after the reaction has been

identified as the potassium/cesium salt of benzene sulfonimide and that of **4a** found to be cesium salt of benzene sulfonimide (compound **13**, determined by ^{1}H NMR in D_2O, Scheme 8). This indicates that the anion of benzene sulfonimide has probably no role in deacylation. Further, in addressing the substrate scope of the present work, the inherent instability of *α*-sulfenyl-*β*-dicarbonyl to undergo deacylation [7], limits the substrate scope as synthesizing the starting materials is cumbersome. Especially *α*-sulfenyl-*β*-ketoesters, are prone to undergo deacylation and decompose during isolation. However, we believe that the significance of the present fluorinative deacylation methodology and the application of *α*-fluoro *β*-ketosulfides would overcome the limitation of the substrate scope.

Conclusion

In conclusion, we have developed an unprecedented tandem electrophilic fluorinative deacylation method for synthesizing *α*-fluoro-*β*-keto sulfides under mild basic reaction conditions at room temperature. The unexpected deacylation upon fluorination of *α*-sulfenyl *β*-dicarbonyls is the salient feature of this method. The synthetic potential of the methodology has been demonstrated by synthesizing a series of sulfones which can be used for synthesizing fluro olefins.

Experimental Section

General experimental

All the reactions were carried out using commercially available AR grade solvents without further distillation. Unless otherwise noted, starting materials and solvents obtained from commercial suppliers were used without further purification. Reactions were monitored by using precoated silica TLC plates. Column chromatography was performed on Silica gel 100-200 mesh. Distilled petroleum ether was used for column chromatography. The starting

materials α-sulfenyl β-diketones (1a-1n) were prepared as described in the our earlier reports[7a, 12] and α-sulfenyl β-diketones (3a-3h) were prepared as described in the literature[13] with necessary modifications (see the given procedure and note 1). NMR spectra were recorded at 400 MHz, using either $CDCl_3$. For the spectra recorded in $CDCl_3$, TMS (tetramethylsilane) or residual $CHCl_3$ served as internal standard for ^1H NMR (0.00 ppm or 7.26) and solvent signal was used as reference signal for ^{13}C NMR (77.00 ppm). IR spectra were measured using a FT-IR spectrometer. Mass spectra were measured using Q-Tof (ESI-HRMS).

(A) Experimental procedures for the synthesis of the starting materials

(i) Typical experimental procedure for the synthesis of (E)-3-(ethylthio)-4-hydroxypent-3-en-2-one (1p) [13]

To a well-stirred, ice cold mixture of ethyl thiol (10 mmol) and α-chloro acetylacetone (10 mmol) was added pyridine slowly (11 mmol) for the period of 1 minute. The reaction mixture was stirred vigorously at room temperature for 12 h. Then the diethyl ether (15 mL) was added to the reaction mixture and crude compound was filtered through sintered funnel, and the filtrate containing crude compound was adsorbed on silica gel (100-200 mesh size) and purified on a silica gel column using EtOAc/Petroleum ether (2:98 – 5:95) as eluent to obtain the expected α-sulfenyl β-diketone **1p**.

(ii) Typical experimental procedure for the synthesis of (E)-4-hydroxy-3-(isopropylthio)pent-3-en-2-one (1q) [13]

To a well-stirred, ice cold mixture of isopropyl thiol (10 mmol) and α-chloro acetylacetone (10 mmol) was added pyridine slowly (11 mmol) for the period of 1 minute. The reaction mixture was stirred vigorously at room temperature for 12 h. After, the reaction mixture was

diluted with 3-4 mL of diethyl ether and directly transferred on silica gel column and purified using EtOAc/Petroleum ether (2:98 – 5:95) as eluent to obtain the expected α-sulfenyl β-diketone **1q**.

* We observed, the starting materials **1p** and **1q** are low boiling point liquids

(iii) General experimental procedure for the synthesis of starting materials (4a-4i) [13]

To a well-stirred, ice cold mixture of thiol (10 mmol) and α-chloro acetylacetone (10 mmol) was added pyridine slowly (11 mmol) for the period of 1 minute (please see the note 1). The reaction mixture was stirred vigorously at room temperature for 12 h. Then the diethyl ether (15 mL) was added to the reaction mixture and crude compound was filtered through sintered funnel, and the filtrate containing crude compound was adsorbed on silica gel (100-200 mesh size) and purified on a silica gel column using EtOAc/Petroleum ether (0:100 – 4:96) as eluent to obtain the expected α-sulfenyl β-diketone.

Note 1: When thiols are liquid no solvent used in the reaction. When thiols are solid, the reaction was performed in diethyl ether (15 mL) i.e., pyridine was added to the ice cold solution of thiol and α-chloro acetylacetone in diethyl ether.

(iv) Typical experimental procedure for the synthesis of starting material 4j [13]

To a well-stirred, ice cold mixture of thiophenol (10 mmol) and α-chloro methyl acetoacetate (10 mmol) was added pyridine slowly (11 mmol) for the period of 1 minute. The reaction mixture was stirred vigorously at room temperature for 12 h. Then the diethyl ether (15 mL) was added to the reaction mixture and crude compound was filtered through sintered funnel, and the filtrate containing crude compound was adsorbed on silica gel (100-200 mesh size) and purified on a silica gel column using EtOAc/Petroleum ether (0:100 – 5:95) as eluent to obtain the expected product **4j**.

(B) Experimental procedures for the synthesis of the products

(i) General experimental procedure for the synthesis of *α*-fluoro *β*-ketosulfides (3a-3n)

To a well-stirred, solution of *α*-sulfenyl *β*-diketone (**1**, 0.25 mmol) in EtOAc (2 mL) was added anhydrous K_2CO_3 (1.2 equiv). The reaction mixture was stirred at room temperature, till it turned into a white turbid heterogeneous reaction mixture (generally 60-90 min). The round bottom flask was then placed under the ice bath and NFSI (1.1 equiv) was added slowly to the cold reaction mixture. After 5 minutes of complete addition of NFSI, the ice bath was removed and stirring was continued at room temperature for 3 h. Then, the crude compound was filtered through sintered funnel and the residue was washed with EtoAc (5 mL x 2). The filtrate was adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (0:100 – 5:95) as the eluent to obtain the expected *α*-fluoro *β*-ketosulfides (3a-3n).

(ii) General experimental procedure for the synthesis of *α*-fluoro *β*-ketosulfides (6a-6i)

To a well-stirred, solution of *α*-sulfenyl *β*-diketone (**4**, 0.5 mmol) in CH_3CN (2.0 mL) was added anhydrous Cs_2CO_3 (1.2 equiv). The reaction mixture was stirred at room temperature until it turned into a white turbid heterogeneous reaction mixture (generally 2 h). The round bottom flask was then placed under the ice bath and NFSI (1.1 equiv) was added slowly to the cold reaction mixture. After 5 minutes of complete addition of NFSI, the ice bath was removed and stirring was continued at room temperature for 3 h. Then, the crude compound was filtered through sintered funnel and the residue was washed with EtOAc (5 mL x 2). The filtrate was adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (0:100 – 5:95) as the eluent to obtain the expected *α*-fluoro *β*-ketosulfides (6a-6i).

Note 2: For optimization studies, the following workup procedure was followed

The crude compound in EtOAc (10 mL) was taken in separating funnel, and then water (10 mL) was added and shaken well to form white turbid mixture. To this white turbid mixture, the brine solution was added (3-5 mL) to obtain a clear bilayer of organic and aqueous mixture. The organic layer was separated and the aqueous layer was washed with EtOAc (5 mL x 2). The combined organic fraction was dried over anhydrous Na_2SO_4 and ^1H NMR yield was determined by using terephthaldehyde as internal standard.

Note 3: Other than in the reaction medium, we observed the deacylation process on silica gel column also. Under the standard reaction condition, in some cases the complete mono deacyalation of fluorinated compound was not occurred. Therefore, retaining of small amount of non deacylated compounds i.e., *α*,*α*-fluoro sulfenyl *β*-diketones was observed after the work up (found by ^1H and ^{19}F NMR). However, such non deacylated fluorinated compounds (2 or 5) underwent deacylation on silica gel column during purification to give additional amount of expected product. As we observed, the *α*,*α*-fluoro sulfenyl *β*-diketones containing hetero aryl sulfenyl moity showed the high propensity to undergo deacylation. In these cases, irrespective of ratio of deacylated and non deacylated products obtained from the reaction media, the complete mono deacylated compounds were obtained after silica gel column chromatography. However, *α*,*α*-fluoro sulfenyl *β*-diketones containing aryl sulfenyl moity showed less propensity to undergo deacylation on silica gel column.

Note 4: As silica gel also influenced the deacylation process, 100-200 mesh sized silica gel columns with fixed size of 5 x 20 cm^2 was preferred for purification of all the crude compounds.

(iii) Typical experimental procedure for the synthesis of 1-fluoro-1-(phenylsulfonyl)propan-2-one (7a) [4d, 9c]

To a well-stirred, solution of 1-fluoro-1-(phenylthio)propan-2-one (**6a**, 0.5 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (55-70%, 4 equiv) at room temperature and the reaction mixture was stirred at room temperature for 6 h. Then, the saturated aqueous sodium sulfite solution was added to the reaction mixture and stirring was continued at room temperature for further 2 h. The crude compound was extracted into CH_2Cl_2 (10 mL x 3) and dried over anhydrous Na_2SO_4. The crude compound in CH_2Cl_2 was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (20:80-40:60) as eluent to obtain the 1-fluoro-1-(phenylsulfonyl)propan-2-one (**7a)** in 96% (104 mg) yield.

(iv) Typical experimental procedure for the synthesis of 3-fluoro-3-(phenylthio)hex-5-en-2-one (8a)

To a well-stirred, heterogeneous mixture of 1-fluoro-1-(phenylthio)propan-2-one (**6a**, 0.5 mmol) and anhydrous K_2CO_3 (4.0 equiv) in CH_3CN (4 mL) was added allyl bromide (6 equiv) at room temperature and the reaction mixture was refluxed for 24 h. Then, the crude compound was filtered through sintered funnel and the residue was washed with EtoAc (5 mL). The filtrate was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (0:100 – 2:98) as the eluent to obtain the allylated product **8a** in 72% (81 mg) yield.

Note 5: The ^{1}H NMR of the crude compound showed the presence of only allylated product **8a**.

(v) Typical experimental procedure for the synthesis of 3-fluoro-4-phenyl-3-(phenylthio)butan-2-one (8b)

To a well-stirred, heterogeneous mixture of 1-fluoro-1-(phenylthio)propan-2-one (**6a**, 0.5 mmol) and anhydrous K_2CO_3 (4.0 equiv) in CH_3CN (4 mL) was added benzyl bromide (2

equiv) at room temperature and the reaction mixture was refluxed for 24 h. Then, the crude compound was filtered through sintered funnel and the residue was washed with EtOAc (5 mL). The filtrate was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (0:100 – 2:98) as the eluent to obtain the benzylated product **8b** in 81% (112mg) yield.

Note 6: The ^{1}H NMR of the crude compound showed the presence of only the benzylated product **8b.**

(vi) Typical experimental procedure for the synthesis of 3-fluoro-3-(phenylsulfonyl)hex-5-en-2-one (9a) [4d, 9c]

To a well-stirred, solution of 1-fluoro-1-(phenylthio)propan-2-one (**8a**, 0.36 mmol) in CH_2Cl_2 (5 mL) was added mCPBA (55-70%, 4 equiv) at room temperature and the reaction mixture was stirred at room temperature for 6 h. Then, the saturated aqueous sodium sulfite solution was added to the reaction mixture and stirring was continued at room temperature for further 2 h. The crude compound was extracted into CH_2Cl_2 (10 mL x 3) and dried over anhydrous Na_2SO_4. The crude compound in CH_2Cl_2 was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column flash chromatography by using EtOAc/Petroleum ether (20:80-40:60) as eluent to obtain the α-fluoro-β-ketosulfone **9a** in 73% yield.

(vii) Typical experimental procedure for the synthesis of 3-fluoro-4-phenyl-3-(phenylsulfonyl)butan-2-one (9b) [4d, 9c]

To a well-stirred, solution of 1-fluoro-1-(phenylthio)propan-2-one (**8b**, 0.4 mmol) in CH_2Cl_2 (5 mL) was added mCPBA (55-70%, 4 equiv) at room temperature and the reaction mixture was stirred at room temperature for 6 h. Then, the saturated aqueous sodium sulfite solution was added to the reaction mixture and stirring was continued at room temperature for further

2 h. The crude compound was extracted into CH_2Cl_2 (10 mL x 3) and dried over anhydrous Na_2SO_4. The crude compound in CH_2Cl_2 was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column flash chromatography by using EtOAc/Petroleum ether (20:80-40:60) as eluent to obtain the *α*-fluoro-*β*-ketosulfone **9b** in 68% yield.

Note 7: For synthesis of sulfones mCPBA was dried under reduced pressure (4-5 h) before using in the reaction

(viii) Typical experimental procedure for the synthesis of 3-benzyl-3-fluoropentane-2,4-dione (11a)

To a well-stirred, solution of 3-benzylpentane-2,4-dione (**7a**, 0.25 mmol) in CH_3CN (1.5 mL) was added anhydrous Cs_2CO_3 (1.2 equiv). The reaction mixture was stirred at room temperature, until it turned into a white turbid heterogeneous reaction mixture (4-5 h). The round bottom flask was then placed under the ice bath and NFSI (1.1 equiv) was added slowly to the cold reaction mixture. After 5 minutes of complete addition of NFSI, the ice bath was removed and stirring was continued at room temperature for 8 h. Then, the crude compound was filtered through sintered funnel and the residue was washed with EtOAc (5 mL x 2). The filtrate was then adsorbed on silica gel (100-200 mesh size) and purified on silica gel (100-200 mesh size) column by using EtOAc/Petroleum ether (2:98-5:95) as the eluent to obtain only the non deacylated product **11a** in 42%.

Note 8: The ^{1}H NMR and ^{19}F NMR (single peak) of the crude compound showed only the presence of **11a**.

(ix) Potassium or Cesium salt of Benzene sulfonamide (13a or **13b):** The residue obtained after filtration of the crude reaction mixture of the fluorinative deacylation reaction of **1** or **4** under the respective optimized reaction conditions.

(C) Experimental data for starting materials

(*E*)-3-(Ethylthio)-4-hydroxypent-3-en-2-one (1p):[13] colourless liquid; **Yield**–66% (1.06 g); R_f (5% EtoAc/Pet ether) 0.6; **IR** (Neat, cm^{-1}): 1587, 1407, 1259, 1014; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 15.40 (brs, 1H), 2.54 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 6H), 1.22 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 197.5, 104.0, 30.4, 24.5, 14.1; **ESI-HRMS** *(m/z)*: Calculated for $C_7H_{12}O_2SNa$ (M + Na): 183.0456, found (M + Na): 183.0453.

(*E*)-4-Hydroxy-3-(isopropylthio)pent-3-en-2-one (1q):[13] Yellow liquid; **Yield**–24% (417 mg); R_f (5% EtoAc/Pet ether) 0.6; **IR** (Neat, cm^{-1}): 2360, 2335, 1628, 1446, 1180, 1128, 1020; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.86 (septet, *J* = 6.8 Hz, 1H), 2.42 (s, 6H), 1.22 (d, *J* = 2.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 197.9, 104.2, 39.6, 24.7, 24.6; **ESI-HRMS** *(m/z)*: Calculated for $C_8H_{14}O_2SNa$ (M + Na): 197.0612, found (M + Na): 197.0614.

(*E*)-4-Hydroxy-3-(phenylthio)pent-3-en-2-one (4a): [13,14,15] Yellow liquid; **Yield**–82% (1.7 g); R_f (Pet ether) 0.2; **IR** (Neat, cm^{-1}): 1582, 1477, 1404, 1255, 1081, 1018, 909; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 17.26 (brs, 1H), 7.29-7.25 (m, 2H), 7.13-7.08 (m, 3H), 2.35 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.3, 137.7, 129.2, 125.2, 124.6, 101.5, 24.3. **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{12}O_2SNa$ (M + Na): 231.0456, found (M + Na): 231.0459.

(*E*)-4-Hydroxy-3-(o-tolylthio)pent-3-en-2-one (4b): White solid; **Yield**–80% (1.78 g); **mp** – 67-69 °C R_f (Pet ether) 0.25; **IR** (KBr, cm^{-1}): 1573, 1458, 1386, 1255, 1044, 1003, 748; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.15-7.10 (m, 2H), 7.06-7.02 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.3, 136.5, 134.3, 130.3, 126.7, 124.7, 122.7, 100.7, 24.2, 19.6; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{14}O_2SNa$ (M + Na): 245.0612, found (M + Na): 245.0611.

(*E*)-4-Hydroxy-3-(p-tolylthio)pent-3-en-2-one (4c):[14,15] Low melting Yellow crystalline solid; **Yield**–82% (1.82 g); R_f (Pet ether) 0.25; **IR** (Neat, cm^{-1}): 1729, 1674, 1589, 1492, 1413, 1376, 1252, 1014; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.09 (d, J = 7.2 Hz, 2H), 6.99 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H), 2.34 (s, 6 H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.2, 135.1, 134.2, 129.9, 124.9, 102.1, 24.4, 20.8; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{14}O_2SNa$ (M + Na): 245.0612, found (M + Na): 245.0609.

(*E*)-4-Hydroxy-3-((4-methoxyphenyl)thio)pent-3-en-2-one (4d):[14,15] White crystalline solid; **mp** – 87-89 °C; **Yield**–72% (1.71 g); R_f (Pet ether) 0.3; **IR** (Neat, cm^{-1}): 1576, 1490, 1403, 1290, 1241, 1173, 1024; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.04 (d, J = 9.2 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 3.78 (s, 3 H), 2.36 (S, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.0, 157.9, 128.4, 126.9, 114.9, 103.0, 55.4, 24.4; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{14}O_3SNa$ (M + Na): 261.0561, found (M + Na): 261.0562.

(*E*)-3-((2-Fluorophenyl)thio)-4-hydroxypent-3-en-2-one (4e): Pale Yellow crystalline solid; **mp** – 54-56 °C; **Yield**–70% (1.58 g); R_f (Pet ether) 0.2; **IR** (KBr, cm^{-1}): 1585, 1544, 1394, 1343, 1265, 1194, 1133, 1057, 1012, 909, 850, 811; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.16-7.11 (m, 1 H), 7.09-7.03 (m, 2 H), 6.93 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 2.34 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.4, 159.3 (d, ^1J (CF) = 242 Hz), 126.82 (d, ^3J (CF) = 8 Hz), 126.13 (d, ^4J (CF) = 1 Hz), 124.91 (d, ^2J (CF) = 16 Hz), 124.75 (d, ^3J (CF) = 4 Hz), 115.69 (d, ^2J (CF) = 21 Hz), 99.7, 24.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -113.5; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{11}O_2FSNa$ (M + Na): 249.0361, found (M + Na): 249.0364.

(*E*)-3-((3-Chlorophenyl)thio)-4-hydroxypent-3-en-2-one (4f): Yellow liquid; **Yield**–78% (1.89 g); R_f (Pet ether) 0.2; **IR** (Neat, cm^{-1}): 1573, 1460, 1403, 1256, 1113, 1073, 1016, 910; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.20 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 7.04

(s, 1 H), 6.96 (d, J = 8.0 Hz, 1H), 2.33 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.3, 140.0, 135.3, 130.2, 125.4, 124.3, 122.6, 101.8, 24.3; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{11}O_2SClNa$ (M + Na): 265.0066, found (M + Na): 265.0064.

(*E*)-3-((4-Chlorophenyl)thio)-4-hydroxypent-3-en-2-one (4g):[15] White solid; **Yield**–83% (2.0 g); R_f (Pet ether) 0.25; **IR** (KBr, cm^{-1}): 1554, 1466, 1385, 1087, 1001, 907; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 17.27 (brs, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.3, 136.4, 131.1, 129.3, 125.9, 101.3, 24.3; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{11}O_2SClNa$ (M + Na): 265.0066, found (M + Na): 265.0065.

(*E*)-3-((4-Bromophenyl)thio)-4-hydroxypent-3-en-2-one (4h):[14,15] White crystalline solid; **Yield**–87% (2.5 g); R_f (Pet ether) 0.25; **IR** (KBr, cm^{-1}): 1548, 1465, 1379, 1244, 1079, 997, 905, 803; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, J = 8.4 Hz, 2H), 6.96 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 2.32 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.2, 137.0, 132.1, 126.1, 118.7, 101.1, 24.3; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{11}O_2SBrNa$ (M + Na): 308.9561, found (M + Na): 308.9562, (M +2 + Na): 310.9602.

(*E*)-4-Hydroxy-3-(naphthalen-1-ylthio)pent-3-en-2-one (4i): White solid; **Yield**–75% (1.93 g); **mp** – 92-94 °C; R_f (Pet ether) 0.25; **IR** (KBr, cm^{-1}): 1538, 1496, 1393, 1265, 1058, 1012, 905, 850, 810, 744; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.75 (m, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.48-7.39 (m, 3 H) 7.26-7.24 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.4, 135.3, 133.9, 131.5, 128.9, 127.8, 126.8, 125.4, 123.6, 121.8, 101.5, 24.4; **ESI-HRMS** *(m/z)*: Calculated for $C_{15}H_{14}O_2SNa$ (M + Na): 281.0612, found (M + Na): 281.0612.

(*E*)-4-Hydroxy-3-(phenylthio)pent-3-en-2-one (4j):[13] Brown liquid; **Yield**–40% (896 mg); R_f (5% EtOAc/Pet ether) 0.5; **IR** (Neat, cm^{-1}): 1633, 1589, 1441, 1338, 1254, 1070; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 13.80 (brs, 1H), 7.27-7.24 (m, 2H), 7.13-7.09 (m, 3H), 3.76 (s,

3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 185.2, 173.4, 137.8, 132.5, 128.9, 125.1, 125.0, 91.5, 52.7, 20.9; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{12}O_3SNa$ (M + Na): 247.0405, found (M + Na): 247.0403.

(D)Experimental data for the products (3a-3n)

1-Fluoro-1-((5-methylbenzo[d]oxazol-2-yl)thio)propan-2-one (3a): Colorless liquid; **Yield**–96% (57 mg); R_f (5% EtOAc/hexane) 0.25; **IR** (Neat, cm^{-1}): 1738, 1508, 1479, 1423, 1359, 1256, 1220, 1151, 1104, 1030; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.45 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.78 (d, ^2J (CH-F) = 50.4 Hz, 1H), 2.49 (d, ^4J (CH_3-F) = 3.2 Hz, 3H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.9 (d, ^2J (CF) = 25.0 Hz), 158.9, 150.4, 141.4, 134.7, 126.0, 119.2, 109.6, 97.1 (d, ^1J (CF) = 238.0 Hz), 26.3, 21.4; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.3; Calculated for $C_{11}H_{10}NO_2SFNa$ (M + Na): 262.0310, found (M + Na): 262.0315.

1-Fluoro-1-((6-methylbenzo[d]oxazol-2-yl)thio)propan-2-one (3b): White Solid; **Yield**–92% (55 mg); R_f (5% EtOAc/hexane) 0.25; **IR** (KBr, cm^{-1}): 1698, 1627, 1527, 1422, 1332, 1214; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.51 (d, J = 8.1 Hz, 1H), 7.29 (s, 1H), 7.14 (d, J = 8.2 Hz, 1H), 6.77 (d, ^2J (CH-F) = 50.5 Hz, 1H), 2.484 (d, ^4J (CH_3-F) = 3.2 Hz, 3H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.4 (d, ^2J (CF) = 25.4 Hz), 158.2, 152.5, 139.2, 135.5, 126.0, 118.6, 110.5, 97.1 (d, ^1J (CF) = 238.3 Hz), 26.3, 21.7; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.2; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{10}NO_2SFNa$ (M + Na): 262.0314, found (M + Na): 262.0312.

1-((5,7-Dimethylbenzo[d]oxazol-2-yl)thio)-1-fluoropropan-2-one (3c): white solid paste; **Yield**–89% (56 mg); R_f (5% EtOAc/hexane) 0.1; **IR** (KBr, cm^{-1}): 2924, 1732, 1633, 1511, 1151, 1116, 1018; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.25 (s, 1H), 6.92 (s, 1H), 6.78 (d,

^{2}J (CH-F) = 50.4 Hz, 1H), 2.486 (d, ^{4}J (CH_3-F) = 3.2 Hz, 3H), 2.44 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.9 (d, ^{2}J (CF) = 26.0 Hz), 158.5, 149.8, 141.1, 134.6, 127.2, 120.2, 116.5, 97.1 (d, ^{1}J (CF) = 238 Hz), 26.3, 21.3, 14.9; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.3; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{12}NO_2SFNa$ (M + Na): 276.0470, found (M + Na): 276.0468.

1-Fluoro-1-((5-phenylbenzo[d]oxazol-2-yl)thio)propan-2-one (3d): pale yellow gummy solid; **Yield**–80% (60 mg); R_f (5% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1737, 1507, 1466, 1419, 1359, 1258, 1141, 1105, 1023; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (s, 1H), 7.58 (d, *J*= 7.6 Hz, 2H), 7.52 (s, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.38-7.34 (m, 1H), 6.81 (d, ^{2}J (CH-F) = 50 Hz, 1H), 2.503 (d, ^{4}J (CH_3-F) = 3.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.8 (d, ^{2}J (CF) = 25.0 Hz), 159.8, 151.6, 141.9, 140.6, 138.7, 128.8, 127.4 (2 peaks), 124.4, 117.6, 110.2, 97.1 (d, ^{1}J (CF) = 238.0 Hz), 26.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.3; **HRESI-MS** *(m/z)*: Calculated for $C_{16}H_{12}NO_2FSNa$ (M + Na): 324.0471, found (M + Na): 324.0481.

1-Fluoro-1-(naphtho[1,2-d]oxazol-2-ylthio)propan-2-one (3e) : Yellow liquid; **Yield**–93% (60 mg); R_f (5% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1737, 1499, 1374, 1190, 1139, 1028; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.42 (d, *J* = 8.2 Hz, 1H), 7. 94 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.67-7.62 (m, 2H), 7.54 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.77 (d, ^{2}J (CH-F) = 52.0 Hz, 1H), 2.544 (d, ^{4}J (CH_3-F) = 3.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.0 (d, ^{2}J (CF) = 25.0 Hz), 156.94 (d, ^{3}J (CF) = 2.0 Hz), 149.8, 137.0, 131.1, 128.5, 127.2, 126.0, 125.71, 125.69, 122.1, 110.3, 97.3 (d, ^{1}J (CF) = 239.0 Hz), 26.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.1; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{10}NO_2FSNa$ (M + Na): 298.0316, found (M + Na): 298.0318.

1-Fluoro-1-((5-fluorobenzo[d]oxazol-2-yl)thio)propan-2-one (3f): white gummy solid; **Yield**–69% (42 mg); R_f (5% EtOAc/hexane) 0.1; **IR** (KBr, cm^{-1}): 1726, 1471, 1433, 1362, 1330, 1238, 1127, 1045, 951; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7. 42 (dd, J_1 = 9.0 Hz, J_2 = 4.4 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.04 (ddd, $J_1 = J_2$ = 9.0 Hz, J_3 = 2.0 Hz, 1H), 6.79 (d, ^2J (CH-F) = 50.0 Hz, 1H), 2.505 (d, ^4J (CH_3-F) = 3.2 Hz, 3H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.8 (d, ^2J (CF) = 25.0 Hz), 161.3 160.1 (d, ^1J (CF) = 233.0 Hz), 148.5, 142.1 (d, ^3J (CF) = 14.0 Hz), 112.46 (d, ^2J (CF) = 26.0 Hz), 110.57 (d, ^3J (CF) = 11.0 Hz), 105.87 (d, ^2J (CF) = 26.0 Hz), 97.0 (^1J (CF) = 239.0 Hz), 26.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -117.0, -162.5; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_7NO_2F_2SNa$ (M + Na): 266.0063, found (M + Na): 266.0063.

1-((5-Chloro-7-methylbenzo[d]oxazol-2-yl)thio)-1-fluoropropan-2-one (3g): pale yellow liqid; **Yield** – 44% (30 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1737, 1503, 1464, 1220, 1130, 1020; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.45 (s, 1H), 7.11 (s, 1H), 6.77 (d, ^2J (CH-F) = 50.4 Hz, 1H), 2.509 (d, ^4J (CH_3-F) = 3.6 Hz, 3H), 2.47 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.9 (d, ^2J (CF) = 26.0 Hz), 160.5, 150.1, 141.7, 130.1, 126.1, 122.0, 116.5, 97.0 (d, ^1J (CF) = 239 Hz), 26.4, 14.9; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.9; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_9NO_2FSClNa$ (M + Na): 295.9924, found (M + Na): 295.9925.

1-(Benzo[d]oxazol-2-ylthio)-1-fluoropropan-2-one (3h); Colorless liquid; **Yield**–98% (56 mg); R_f (5% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1778, 1735, 1509, 1481, 1452, 1359, 1135; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.66 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 1H), 7.49 (dd, J_1 = 5.8 Hz, J_2 = 2.0 Hz, 1H), 7.34 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 6.80 (d, ^2J (CH-F) = 50.4 Hz, 1H), 2.504 (d, ^4J (CH_3-F) = 3.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.9 (d, ^2J (CF) = 26.0 Hz), 159.2, 152.1, 141.3, 124.9, 124.8, 119.2, 110.3, 97.1 (d, ^1J (CF) = 238.0

Hz), 26.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -162.4; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_8NO_2FSNa$ (M + Na): 248.0157, found (M + Na): 248.0157.

1-Fluoro-1-((5-methylbenzo[d]oxazol-2-yl)thio)butan-2-one (3i): Colorless liquid; **Yield**–70% (45 mg); R_f (5% EtOAc/hexane) 0.3; **IR** (Neat, cm^{-1}): 1733, 1623, 1462, 1427, 1310, 1238, 1077; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.43 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.81 (d, ^2J (CH-F) = 50.8 Hz, 1H), 2.93-2.77 (m, 2H), 2.45 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 201.9 (d, ^2J (CF) = 24.0 Hz), 159.2, 150.4, 141.5, 134.7, 125.9, 119.1, 109.6, 97.0 (d, ^1J (CF) = 238.0 Hz), 32.2, 21.5, 7.08; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -163.6; Calculated for $C_{12}H_{12}NO_2FSNa$ (M + Na): 276.0470, found (M + Na): 276.0469.

1-((5-Chlorobenzo[d]oxazol-2-yl)thio)-1-fluorobutan-2-one (3j): Colorless liquid; **Yield**–73% (50 mg); R_f (5% EtOAc/hexane) 0.3; **IR** (Neat, cm^{-1}): 1735, 1504, 1450, 1140, 1019; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7. 62 (s, 1H), 7.40 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 6.82 (d, ^2J (CH-F) = 50.4 Hz, 1H), 2.96-2.97 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 201.80 (d, ^2J (CF) = 24.0 Hz), 161.3, 150.7, 142.3, 130.4, 125.1, 119.2, 110.9, 97.0 (d, ^1J (CF) = 239.0 Hz), 32.3, 7.0; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -163.9; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_9NO_2FSClNa$ (M + Na): 295.9924, found (M + Na): 296.0000.

1-(Benzo[d]thiazol-2-ylthio)-1-fluoropropan-2-one (3k): Colorless liquid; **Yield**–96% (58 mg); R_f (5% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1743, 1464, 1426, 1358, 1310, 1164; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, J = 8.1 Hz, J_2 = 2.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 8.0 Hz, 1H), 7.37 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 6.80 (d, ^2J (CH-F) = 50.4 Hz, 1H), 2.465 (d, ^4J (CH_3-F) = 3.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.0 (d, ^2J (CF) = 25.4 Hz), 159.5 (d, ^3J (CF) = 2.5 Hz), 152.5, 136.2, 126.5, 125.3, 122.4, 121.2, 97.2

(d, ^{1}J (CF) = 237.8 Hz), 26.3; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -161.8; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_8NOFS_2$ Na (M + Na): 263.9929, found (M + Na): 263.9928.

Mixture of 4-(benzo[d]thiazol-2-ylthio)-4-fluoroheptane-3,5-dione (2l) and 1-(benzo[d]thiazol-2-ylthio)-1-fluorobutan-2-one (3l): Colorless liquid; R_f (5% EtOAc/hexane) 0.2. **4-(Benzo[d]thiazol-2-ylthio)-4-fluoroheptane-3,5-dione (2l): Yield**–12% (9 mg); **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, J = 8.4 Hz, 0.19 H), 7.80 (d, J = 8.0 Hz, 0.19 H), 7.49-7.44 (m, 0.19 H), 7.37 (t, J = 8.0 Hz, 0.19 H), 3.03-2.70 (m, 0.76 H), 1.11 (t, J = 7.2 Hz, 1.14 H); **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -139.9; **ESI-HRMS** *(m/z)*: Calculated for $C_{14}H_{14}NO_2FS_2Na$ (M + Na): 334.0348, found (M + Na): 334.0348. **IR** (Neat, cm^{-1}) from the mixture of compounds (**2l** and **3l**): 1733, 1462, 1427, 1310, 1077.

1-(Benzo[d]thiazol-2-ylthio)-1-fluorobutan-2-one (3l) : Yield–77% (49 mg); R_f (5% EtOAc/hexane) 0.2; **^{1}H NMR** (400 MHz, $CDCl_3$): δ. (ppm) 7.93 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.49-7.44 (m, 1H), 7.37 (t, J = 8.0 Hz, 1H), 6.82 (d, ^{2}J (CH-F) = 50.8 Hz, 1H), 2.86-2.80 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 202.1 (d, ^{2}J (CF) = 24.0 Hz), 159.7, 152.6, 136.1, 126.5, 125.3, 122.4, 121.2, 97.2 (d, ^{1}J (CF) = 237.8 Hz), 32.2, 7.30; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -163.2; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{10}NOFS_2Na$ (M + Na): 278.0086, found (M + Na): 278.0086.

1-Fluoro-1-((4-methyloxazol-2-yl)thio)propan-2-one (3m): Colorless liquid; **Yield**–30% (14 mg); R_f (5% EtOAc/hexane) 0.1; **IR** (Neat, cm^{-1}): 1642, 1499, 1365, 1284, 1156, 1019; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.47 (s, 1H), 6.46 (d, ^{2}J (CH-F) = 50.8 Hz, 1H), 2.40 (d, ^{4}J (CH_3-F) = 3.2 Hz, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.76 (d, ^{2}J (CF) = 26.0 Hz), 153.5, 138.7, 137.7, 97.2 (d, ^{1}J (CF) = 239.0 Hz), 26.1, 11.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -161.2; Calculated for $C_7H_8NO_2FSNa$ (M + Na): 212.0157, found (M + Na): 212.0154.

2-Fluoro-2-((5-methylbenzo[d]oxazol-2-yl)thio)-1-phenylethan-1-one (3n): Colorless liquid; **Yield**–40% (30 mg); R_f (5% EtOAc / hexane) 0.4; **IR** (Neat, cm^{-1}): 1699, 1627, 1508, 1447, 1258, 1219, 1020; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J*= 7.6 Hz, 2H), 7.86 (d, ^2J (CH-F) = 51 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 (s, 1H), 7.38 (d, *J*= 8.4 Hz, 1H), 7.13 (d, *J*= 8.4 Hz, 1H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.60 (d, ^2J (CF) = 22.0 Hz), 159.8, 150.5, 141.5, 134.84 (d, ^3J (CF) = 12.0 Hz), 129.3, 129.3, 129.0, 125.9, 119.2, 109.7, 96.3 (d, ^1J (CF) = 235.0 Hz), 21.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -160.1; Calculated for $C_{16}H_{12}NO_2SFNa$ (M + Na): 324.0470, found (M + Na): 324.0473.

(E) Experimental data for the products (6a-6h)

1-Fluoro-1-(phenylthio)propan-2-one (6a):[5b] Colorless liquid; **Yield**–88% (81 mg); R_f (5% EtOAc/hexane) 0.5; **IR** (Neat, cm^{-1}): 1733, 1476, 1438, 1359, 1221, 1029; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.55-7.53 (m, 2H), 7.39-7.33 (m, 3H), 5.99 (d, ^2J (CH-F) = 52.4 Hz, 1H), 2.123 (d, ^4J (CH_3-F) = 2.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.22 (d, ^2J (CF) = 27.0 Hz), 133.855 (d, ^4J (CF) = 1.0 Hz), 129.3, 129.3, 129.2, 99.38 (d, ^1J (CF) = 235.0 Hz), 26.0. **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -158.7; **ESI-HRMS** *(m/z)*: Calculated for C_9H_9OFSNa (M + Na): 207.0256, found (M + Na): 207.0257.

1-Fluoro-1-(o-tolylthio)propan-2-one (6b): Colorless liquid; **Yield**–83% (77 mg); R_f (5% EtOAc/hexane) 0.4; **IR** (Neat, cm^{-1}); 1730, 1533, 1456, 1355, 1220, 1101, 1049. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.68 (d, 8 Hz, 1 H), 7.32-7.28 (m, 2H), 7.22-7.18 (m, 1H), 5.97 (d, ^2J (CH-F) = 53.2 Hz, 1H), 2.49 (s, 3H), 2.132 (d, ^4J (CH_3-F) = 2.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.76 (d, ^2J (CF) = 27.0 Hz), 141.60, 135.1, 130.8, 129.6, 128.9, 126.8, 99.09 (d, ^1J (CF) = 234.0 Hz), 25.9, 21.0; **^{19}F NMR** (377 MHz, $CDCl_3$): δ

(ppm) -158.4; **ESI-HRMS** *(m/z)*: Calculated for $C_{10}H_{11}OFSNa$ (M + Na): 221.0412, found (M + Na): 221.0420.

1-Fluoro-1-(p-tolylthio)propan-2-one (6c) : Colorless liquid; **Yield**: 62% (61 mg) **IR** (Neat, cm^{-1}): 1723, 1487, 1355, 1323, 1240, 1171, 1023, 955, 806, 724, 621; R_f (5% EtOAc/hexane) 0.5; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.41 (d, J = 8.0 Hz, 2 H), 7.16 (d, J_1 = 7.6 Hz, 2H), 5.95 (d, ^2J (CH-F) = 52.0 Hz, 1 H), 2.35 (s, 3 H), 2.107 (d, $^4J_1$ (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.54 (d, ^2J (CF) = 26.0 Hz), 139.88, 134.325 (d, ^4J (CF) = 1.0 Hz), 130.12, 125.34, 99.55 (d, ^1J (CF) = 234.0 Hz), 26.17, 21.20; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -159.0; **ESI-HRMS** *(m/z)*: Calculated for $C_{10}H_{11}OFSNa$ (M + Na): 221.0412, found (M + Na): 221.0410.

1-Fluoro-1-(4-methoxythio)propan-2-one (6d) : Pale yellow liquid; **Yield**: 65% (70 mg) **IR** (Neat, cm^{-1}): 1731, 1591, 1494, 1358, 1291, 1249, 1174, 1031; R_f (5% EtOAc/hexane) 0.3; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.46 (d, J = 8.8 Hz, 2 H), 7.87 (d, J = 8.8 Hz, 2 H), 5.90 (d, ^2J (CH-F) = 52 Hz, 1 H), 2.080 (d, ^4J (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.81 (d, ^2J (CF) = 27.0 Hz), 160.9, 136.5, 118.59, 114.9, 99.51 (d, ^1J (CF) = 234.0 Hz), 55.3, 26.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -159.7; **ESI-HRMS** *(m/z)*: Calculated for $C_{10}H_{11}O_2FSNa$ (M + Na): 237.0361, found (M + Na): 237.0361.

1-Fluoro-1-((2-fluorophenyl)thio)propan-2-one (6e): Colorless liquid; **Yield**–92% (92 mg); R_f (5% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1743, 1475, 1359, 1263, 1225, 1042; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.57 (dt, J_1 = 7.6 Hz, J_2 = 1.8 Hz, 2 H), 7.42-7.38 (m, 1 H), 7.18-7.12 (m, 2 H), 6.02 (d, ^2J (CH-F) = 51.6 Hz, 1 H), 2.23 (d, ^4J (CH_3-F) = 2.4 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.54 (d, ^2J (CF) = 25.0 Hz), 162.25 (d, ^1J (CF) = 248.0 Hz), 136.8, 132.0 (d, ^3J (CF) = 8.0 Hz), 124.87 (d, ^4J (CF) = 3.0 Hz), 116.3, 116.1, 115.82 (d, ^2J (CF) = 19.0 Hz), 98.09 (d, ^1J (CF) = 236.0 Hz), 25.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ

(ppm) -160.569 (d, ^{5}J (F-F coupling) = 1.35 Hz), -106.324 (d, ^{5}J (F-F coupling) = 1.36 Hz); **ESI-HRMS** *(m/z)*: Calculated for $C_9H_8OF_2SNa$ (M + Na): 225.0162, found (M + Na): 225.0162.

1-((3-Chlorophenyl)thio)-1-fluoropropan-2-one (6f): Colorless liquid; **Yield**–78% (85 mg); R_f (5% EtOAc/hexane) 0.25; **IR** (Neat, cm^{-1}): 1734, 1570, 1462, 1404, 1359, 1223, 1118, 1041; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.54-7.53 (m, 1 H), 7.42 (d, J = 7.6 Hz, 1 H), 7.37-7.36 (m, 1 H), 7.30 (d, J = 8 Hz, 1 H), 6.02 (d, ^{2}J (CH-F) = 52.4 Hz, 1 H), 2.181 (d, ^{4}J (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.82 (d, ^{2}J (CF) = 26.0 Hz), 134.9, 133.215 (d, ^{4}J (CF) = 1.0 Hz), 131.7, 131.3, 130.4, 129.6, 99.21 (d, ^{1}J (CF) = 236.0 Hz), 26.1; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -158.8; **ESI-HRMS** *(m/z)*: Calculated for $C_9H_8OFClSNa$ (M + Na): 240.9869, found (M + Na): 240.9866.

1-((4-Chlorophenyl)thio)-1-fluoropropan-2-one (6g): Pale yellow liquid; **Yield**–88% (96 mg); R_f (5% EtOAc/hexane) 0.5; **IR** (Neat, cm^{-1}): 1733, 1476, 1358, 1222, 1094; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.46 (d, J = 8.4 Hz, 2 H), 7.33 (d, J = 8.4 Hz, 2 H), 5.99 (d, ^{2}J (CH-F) = 52 Hz, 1 H), 2.144 (d, ^{4}J (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 198.88 (d, ^{2}J (CF) = 26.0 Hz), 136.0, 135.24 (d, ^{4}J (CF) = 2.0 Hz), 129.5, 127.5, 99.10 (d, ^{1}J (CF) = 235.0 Hz), 26.07; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -159.3; **ESI-HRMS** *(m/z)*: Calculated for $C_9H_8OFClSNa$ (M + Na): 240.9865, found (M + Na): 240.9866.

1-((4-Bromophenyl)thio)-1-fluoropropan-2-one (6h): Colorless yellow liquid; **Yield**–87% (75 mg); R_f (5% EtOAc/hexane) 0.4; ; **IR** (Neat, cm^{-1}): 2929, 1726, 1560, 1462, 1354, 1238, 1166, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.46 (dd, $J_1 = J_2$ = 7.6 Hz, 2 H), 7.46 (dd, J_1 = 8.4 Hz, J_2 = 2.0, 2 H), 5.99 (d, ^{2}J (CH-F) = 52 Hz, 1 H), 2.142 (d, ^{4}J (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.93 (d, ^{2}J (CF) = 26.0 Hz), 135.42 (d, ^{4}J (CF) = 2.0 Hz), 132.5, 128.2, 124.2, 99.02 (d, ^{1}J (CF) = 235.0 Hz), 26.1; **^{19}F NMR** (377 MHz,

$CDCl_3$): δ (ppm) -159.2; **ESI-HRMS** *(m/z)*: Calculated for $C_9H_8OFBrSNa$ (M + Na): 284.9362, found (M + Na): 284.9361.

1-Fluoro-1-(naphthalen-1-ylthio)propan-2-one (6i): Colorless liquid; **Yield**–82% (96 mg); R_f (3% EtOAc/hexane) 0.4; **IR** (Neat, cm^{-1}): 1737, 1586, 1499, 1420, 1357, 1223, 1040, 952; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.05 (s, 1H), 7.84-7.80 (m, 3 H), 7.57 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1 H), 7.54-7.50 (m, 2 H), 6.06 (d, ^2J (CH-F) = 52 Hz, 1H), 2.135 (d, ^4J (CH_3-F) = 2.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.37 (d, ^2J (CF) = 26.0 Hz), 133.67 (d, ^4J (CF) = 2.0 Hz), 133.4, 133.2, 133.265 (d, ^4J (CF) = 1.0 Hz), 129.1, 127.8, 127.7, 127.2, 126.9, 126.6, 99.76 (d, ^1J (CF) = 235.0 Hz), 26.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -158.5; **ESI-HRMS** *(m/z)*: Calculated for $C_{13}H_{11}OFSNa$ (M + Na): 257.0412, found (M + Na): 257.0414.

1-Fluoro-1-(phenylsulfonyl)propan-2-one (7a):[9b] Colorless liquid; **Yield**–96% (104 mg); R_f (30% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1739, 1448, 1335, 1214, 1153, 1076; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, J = 8.0 Hz, 2H), 7.73 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 5.50 (d, ^2J (CH-F) = 48.8 Hz, 1H), 2.323 (d, ^4J (CH_3-F) = 4.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 195.51 (d, ^2J (CF) = 21.0 Hz), 135.3, 134.7, 129.50, 129.47, 101.26 (d, ^1J (CF) = 233.0 Hz), 27.42; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -179.7; **ESI-HRMS** *(m/z)*: Calculated for $C_9H_9O_3FSNa$ (M + Na): 239.0154, found (M + Na): 239.0155.

3-Fluoro-3-(phenylthio)hex-5-en-2-one (8a): Colorless liquid; **Yield**–72% (81 mg), **Yield**–62% (based on recovery of starting material), R_f (5% EtOAc/hexane) 0.8; **IR** (Neat, cm^{-1}); 1728, 1642, 1434, 1355, 1099, 1021, 996; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.56-7.41 (m, 2H), 7.407-7.32 (m, 3H), 5.84-5.74 (m, 1H), 5.21 (s, 1H), 5.178 (d, J = 4.8 Hz, 1H), 2.95-2.76 (m, 2H), 1.853 (d, ^4J (CH_3-F) = 4.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 203.59 (d, ^2J (CF) = 33.0 Hz), 136.2, 129.8, 129.555 (d, ^3J (CF) = 3.0 Hz), 129.2, 128.1,

120.7, 108.09 (d, ^{1}J (CF) = 235.0 Hz), 41.10 (d, ^{2}J (CF) = 22.0 Hz), 27.1; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -136.3; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{13}OFSNa$ (M + Na): 247.0569, found (M + Na): 247.0568.

3-Fluoro-4-phenyl-3-(phenylthio)butan-2-one (8b): Colorless liquid; **Yield**–81% (112 mg), R_f (3% EtOAc/hexane) 0.5; **IR** (Neat, cm^{-1}); 1726, 1493, 1476, 1441, 1354, 1184, 1085, 1019; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, J = 7.2 Hz, 2H), 7.41-7.32 (m, 3H), 7.31-7.16 (m, 5H), 3.48 (dd, $^{3}J_1$ (CH-F) = 28.0 Hz, dd, $^{2}J_2$ (CH-H) = 14.0 Hz, 1H), 3.35 (dd, $^{3}J_1$ (CH-F) = 29 Hz, $^{2}J_2$ (CH-H) = 14.4 Hz, 1H), 1.60 (d, ^{4}J (CH_3-F) = 4.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 204.74 (d, ^{2}J (CF) = 34.0 Hz), 136.4, 133.4, 130.5, 129.7, 129.2, 128.4, 128.1, 127.4, 108.60 (d, ^{1}J (CF) = 237.0 Hz), 42.70 (d, ^{3}J (CF) = 22.0 Hz), 27.7; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -135.4; **ESI-HRMS** *(m/z)*: Calculated for $C_{16}H_{15}OFSNa$ (M + Na): 297.0725, found (M + Na): 297.0720.

3-Fluoro-3-(phenylsulfonyl)hex-5-en-2-one (9a): Colorless liquid; **Yield**–73% (67 mg); R_f (20% EtOAc/hexane) 0.2; **IR** (Neat, cm^{-1}): 1732, 1629, 1448, 1334, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, J = 8 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 5.55-5.45 (m, 1H), 5.14 (s, 1H), 5.112 (d, J = 2.8 Hz, 1H), 2.74-2.66 (m, 2H), 2.047 (d, ^{4}J (CH_3-F) = 5.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.80 (d, ^{2}J (CF) = 27.0 Hz), 135.2, 134.1, 130.4, 129.3, 126.955 (d, ^{3}J (CF) = 3.0 Hz), 122.4, 109.68 (d, ^{1}J (CF) = 233.0 Hz), 35.13 (d, ^{2}J (CF) = 20.0 Hz), 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -159.5; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{13}O_3FSNa$ (M + Na): 279.0467, found (M + Na): 279.0466.

3-Fluoro-4-phenyl-3-(phenylsulfonyl)butan-2-one (9b): White solid; **mp** – 78-80 °C; **Yield**–68% (83 mg); R_f (20% EtOAc/hexane) 0.5; **IR** (Neat, cm^{-1}): 1730, 1627, 1449, 1333, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.6 Hz,

1H), 7.63 (t, J = 8.0 Hz, 2H), 3.76 (dd, $^{3}J_{1}$ (CH-F) = 40.0 Hz, dd, $^{2}J_{2}$ (CH-H) = 14.2 Hz, 1H), 3.336 (dd, $^{3}J_{1}$ (CH-F) = 14.2 Hz, $^{2}J_{2}$ (CH-H) = 10.4 Hz, 1H), 1.74 (d, ^{4}J (CH_3-F) = 5.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 200.62 (d, ^{2}J (CF) = 28.0 Hz), 135.2, 134.4, 130.9, 130.5, 130.4, 129.3, 128.7, 127.8, 109.99 (d, ^{1}J (CF) = 234.0 Hz), 36.59 (d, ^{3}J (CF) = 18 Hz), 28.0; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -157.7; **ESI-HRMS** *(m/z)*: Calculated for $C_{16}H_{15}O_3FSNa$ (M + Na): 329.0624, found (M + Na): 329.0622.

3-Benzyl-3-fluoropentane-2,4-dione (11a): Colorless liquid; **Yield**–42% (22 mg); R_f (5% EtOAc/hexane) 0.5; **IR** (Neat, cm^{-1}): 1745, 1716, 1421, 1357, 1190, 1118, 759; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.31-7.25 (m, 3H), 7.18 (d, J = 7.2 Hz, 2H), 3.34 (d, ^{3}J (CH_2-F) = 25.6 Hz, 2H), 2.122 (d, ^{4}J (CH_3-F) = 5.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 201.67 (d, ^{2}J (CF) = 27.0 Hz), 132.9, 130.3, 128.5, 127.5, 106.26 (d, ^{1}J (CF) = 199.0 Hz), 40.21 (d, ^{2}J (CF) = 21.0 Hz), 26.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm) -164.8; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{13}O_2FNa$ (M + Na): 231.0797, found (M + Na): 231.0795.

Cesium salt of *bis*(phenylsulfonyl)amide (13b): White solid**; mp** – 208-210 °C; **Yield:** 99% (106 mg); **^{1}H NMR** (400 MHz, D_2O): δ (ppm) 7.59 (d, J = 8 Hz, 4H), 7.51 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 104.8, 132.3, 128.8, 126.0.

Experimental data for the minor compounds

3-Fluoro-3-(phenylthio)pentane-2,4-dione (5a): Yield–6% (8 mg: according to the ratio between **5a** and **6a** found by ^{1}H NMR); Only the distinguishable ^{1}H NMR and ^{13}C NMR peaks of **5a** are given. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.217 (d, ^{4}J (CH_3-F) = 3.2 Hz, 0.45 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 26.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm); - 136.9; **ESI-HRMS *(m/z)*:** Calculated for $C_{11}H_{11}O_2FSNa$ (M + Na): 249.0361, found (M + Na): 249.0363.

1-Fluoro-1-(phenylthio)propan-2-one (6a): Yield–91% (85 mg: according to the ratio between **5a** and **6a** found by ^{1}H NMR).

3-Fluoro-3-(*o*-tolylthio)pentane-2,4-dione (5b) : Yield–19% (23 mg: according to the ratio between 5b and 6b found by ^{1}H NMR); Only the distinguishable ^{1}H and ^{13}C NMR peaks of **5b** are given. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.49 (s, 0.95 H), 2.176 (d, ^{4}J (CF) = 1.8 Hz, 1.76H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 197.50 (d, ^{2}J (CH_3-F) = 29.0 Hz), 143.2, 131.0, 130.5, 126. 8, 126.0, 109.66 (d, ^{1}J (CF) = 244.0 Hz), 26.5, 21.1. **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm); - 136.8; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{13}O_2$ FSNa (M + Na): 263.0518, found (M + Na): 263.0516.

1-fluoro-1-(*o*-tolylthio)propan-2-one (6b): Yield–73% (72 mg: according to the ratio between **5b** and **6b** found by ^{1}H NMR).

3-Fluoro-3-(*p*-tolylthio)pentane-2,4-dione (5c) : Yield–26% (31 mg: according to the ratio between 5c and 6c found by ^{1}H NMR); Only the distinguishable ^{1}H and ^{13}C NMR peaks of **5c** are given. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.22 (d, ^{4}J (CH_3-F) = 3.6 Hz, 1.33 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 26.5; **ESI-HRMS** *(m/z)*: Calculated for $C_{12}H_{13}O_2$ FSNa (M + Na): 263.0518, found (M + Na): 263.0520.

1-Fluoro-1-(*p*-tolylthio)propan-2-one: Yield–70% (69.7 mg: according to the ratio between **5c** and **6c** found by ^{1}H NMR).

3-((4-Bromophenyl)thio)-3-fluoropentane-2,4-dione (5h): Yield–22% (34 mg: according to the ratio between 5h and 6h found by ^{1}H NMR); Only the distinguishable ^{1}H and ^{13}C NMR peaks of **5h** are given. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 2.24 (d, ^{4}J (CH_3-F) = 3.2 Hz, 2.40 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 26.4; **^{19}F NMR** (377 MHz, $CDCl_3$): δ (ppm); - 137.3; **ESI-HRMS** *(m/z)*: Calculated for $C_{11}H_{10}O_2FSBrNa$ (M + Na): 326.9467, found (M + Na): 326.9471.

1-((4-Bromophenyl)thio)-1-fluoropropan-2-one (6h): Yield–67% (87 mg: according to the ratio between **5h** and **6h** found by ^{1}H NMR).

AUTHOR INFORMATION

Corresponding Author

* E-mail: prabhu@orgchem.iisc.ernet.in

Notes

The authors declare no competing financial interest.

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Supporting Information Available. ^{1}H and ^{13}C Spectra for all compounds are available. This material is available free of charge *via* the Internet.

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