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Scope and limitations of the Julia–Kocienski reaction with fluorinated sulfonylesters

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ABSTRACT

The study of the Julia–Kocienski reaction between fluorinated arylsulfone and ketones is described. The corresponding fluoroalkenes were isolated in moderate to good yields from β- and δ-substituted cyclic ketones. From acyclic ketones and α-substituted cyclic ketones a decarbethoxylation reaction of the sulfonylesters occurred. This decarbethoxylation reaction opened a new route for the preparation of a variety of fluoroalkylsulfones as potential building blocks for the preparation of fluoroalkenes.

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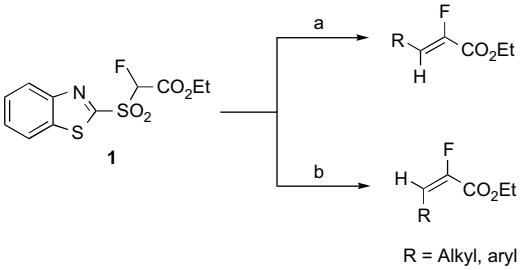
1. Introduction

It is well established that the fluorovinylic moiety plays an important role in the field of medicinal chemistry. It has been introduced onto nucleotides, carbohydrates, vitamins, prostaglandins, steroids, and peptides to improve their physiological stabilities or their biological activities.[1] Among the numerous methods for the preparation of fluoroolefins,[2] the HWE and Peterson reactions are the most common. However, these approaches are mostly efficient with reagents bearing electron-withdrawing groups. Thus, access to fluoroolefins containing an alkyl or functionalized alkyl chain still remains challenging and usually requires several steps.[3] Since the past decade, our laboratory is devoted to the development of new fluoroolefination reagents and, in 2002 we reported the first one-step synthesis of fluoroalkylidenes via the modified Julia reaction.[4] This approach has been adopted as a good alternative to the Wittig-type reactions. By this way *gem*-fluoroaryl alkenes,[5] α-fluoroacrylates,[6] α-fluoro-α,β-unsaturated amides,[7] nitriles,[8] and sulfones[9] have been prepared in good yields. However, this new fluoroolefination reaction has mainly been studied with aldehydes and only few examples using ketones were reported. In this paper, the scope and limitations of the modified Julia reaction between heteroaryl-fluorosulfones and ketones are reported.

2. Results and discussion

We previously showed the modified Julia reaction could be applied to the stereoselective synthesis of fluoroalkenoates from ethyl benzothiazolylfluorosulfonyl acetate **1**, aldehydes and DBU in the presence or absence of $MgBr_2$ (Scheme 1, path a or b).[6a]

The modified Julia reaction success depends on the nature of the aromatic ring of the starting sulfone and in this field, others π-deficient systems such as 1-phenyltetrazolyl-, bis-trifluoromethylphenyl-, and 2-pyrimidyl-sulfones were reported as good substrates for the preparation of alkenes.[10] To identify the most efficient aromatic moiety for the Julia–Kocienski reaction involving ketones, fluorosulfones **3** and **5** were prepared. These latter were obtained by the alkylation of 2-mercaptopyrimidine and 1-phenyltetrazole with ethyl bromofluoroacetate. Corresponding thioethers **2** and **4** were



Scheme 1. Stereoselective synthesis of fluoroalkenoates.

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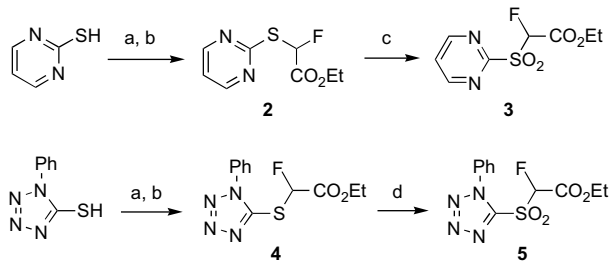


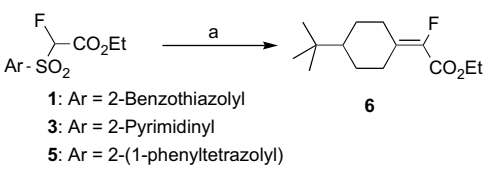
Scheme 2. Two-steps preparation of fluorosulfones **3**, **5**. (a) ^{t}BuOK, THF, 30 min at −17 °C. (b) $BrCHFCO_2Et$, THF, −17 °C to rt, 2 h, 81–82%. (c) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, H_2O_2, EtOH, 16 h at rt, 84%. (d) $NaIO_4$, $RuCl_3$ catalytic, MeCN, H_2O, 16 h at rt, 35%.

isolated in 81% and 82% yields, respectively. Oxidation of **2** into sulfones was realized in the presence of H_2O_2/Mo(VI), while **4** required stronger oxidant such as $NaIO_4$/Ru(III) (Scheme 2). Alternative synthesis of tetrazolylsulfones can be realized by direct electrophilic or electrolytic fluorination of 1-phenyltetrazolyl-sulfone and sulfide or by alkylation of the corresponding thiol.[5,6b,11]

The reactivity of sulfones **1**, **3**, and **5** was then evaluated in a model fluoroolefination reaction of 4-*tert*-butylcyclo-hexanone (Scheme 3). The reaction was realized from **1**, applying the experimental conditions used for aldehydes,[6a] and it was found that the reaction was slower. It required at least 6 h at room temperature to reach completion instead of the 2 h needed from aldehydes. Indeed, in the presence of DBU, the corresponding fluoroalkene **6** was formed in moderate to good yield from sulfones **1**, **3**, and **5**. Sulfones containing the pyrimidine and 1-phenyltetrazole displayed the same reactivity while benzothiazolylfluorosulfone **1** gave the best results.

The Julia–Kocienski olefination using ethyl benzothiazolyl-sulfonyl acetate **1** was extended to other ketones. The Barbier-type conditions were applied by following this scheme. DBU (1.4 equiv) was added to a mixture of fluorosulfone **1** (1 equiv) and ketones (1.2 equiv) in THF. Reactions were performed at room temperature for 6 h. Results are summarized in Table 1. From non-functionalized cyclic ketones such as cyclohexanone and cyclopentanone, corresponding fluoroalkenes **7** and **8** were obtained in moderate yields (Table 1, entries 1 and 2). Introduction of alkyl groups at the β-position of cyclic ketones did not affect the reaction efficiency. Indeed, from *cis*/*trans* 2-decalone, 3-methylcyclohexanone, and 3-methylcyclopentanone, fluorinated α,β-unsaturated esters **9**–**11** were isolated as a mixture of stereoisomers in 60–70% yield (Table 1, entries 3–5).

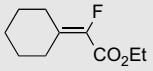
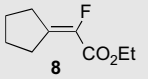
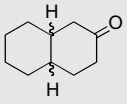
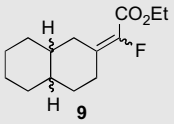
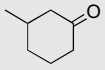
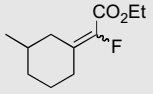
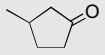
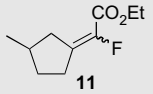
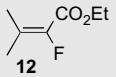
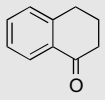
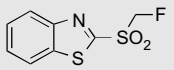
Attempts to increase the selectivity by changing the base (NaHMDS, ^{t}BuOK, 1,1,3,3-tetramethylguanidine) and the reaction temperature were unsuccessful. However, from linear ketones, such as 2-pentanone, traces of alkenes were formed, while from acetone, fluoroacrylate **12** was obtained after 12 h at 20 °C. In spite of a complete conversion of sulfone **1**, fluoroalkene **12** was isolated in low yield due to its high volatility (Table 1, entry 6). In contrast, from α-sterically hindered cyclic ketones, no olefination reaction was observed even after 24 h under stirring at 20 °C or under reflux. The cyclic α-substituted ketones such as α-tetralone, 2-methylcyclohexanone, and 2,6-dimethylcyclohexanone led to fluorosulfone **13** exclusively (Table 1, entry 7). The amount of sulfone **13** was limited to 10% when 1,1,3,3-tetramethylguanidine was used as



1: Ar = 2-Benzothiazolyl
3: Ar = 2-Pyrimidinyl
5: Ar = 2-(1-phenyltetrazolyl)

Scheme 3. Reactivity of sulfones **1**, **3**, and **5** in the Julia–Kocienski reaction. (a) 4-*tert*-Butylcyclohexanone, DBU, THF, 6 h at rt, 82% from **1**, 46% from **3**, 47% from **5**.

Table 1
Julia–Kocoenski reaction with sulfone **1** and ketones

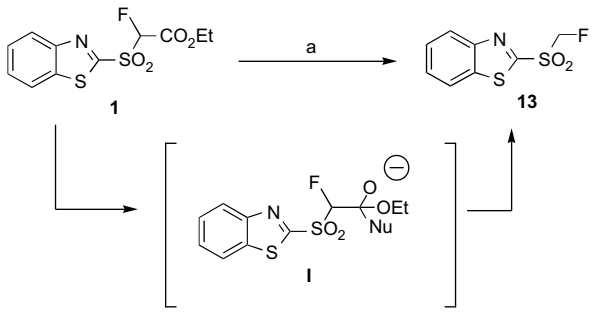
Entry	Ketone	Product	Yield %
1		 **7**	57[a]
2		 **8**	40[a]
3		 **9**	60[a]
4		 **10**	60[a]
5		 **11**	70[a]
6		 **12**	10[b]
7		 **13**	94[c]

[a] Isolated yield.
[b] Volatile compound.
[c] Conversion deducted by ^{19}F NMR.

base instead of DBU. However, this modification had no influence on the Julia–Kocienski reaction efficiency, and only traces of alkenes were detected. Attempts to optimize the fluoroolefination of bulky ketones by changing the base (NaHMDS, ^{t}BuOK, 1,1,3,3-tetramethylguanidine), the temperature, the order of addition of the reagents, the concentration or by introducing additives such as phase transfer agent (TBAB) or polar solvent (HMPA) already employed in the modified Julia reaction, were unsuccessful.[10e]

This competitive decarbethoxylation reaction has already been mentioned by Najera during the olefination of aldehydes with bis-trifluoromethylated arylsulfones.[12] This reaction observed from fluorosulfone **1** appeared attractive to prepare new halogeno- and alkyl-substituted fluoro-sulfones through the alkylation or halogenation of **1**. These reagents should be useful for the synthesis of fluoroalkylidenes or mono- and *gem*-difluoroalkenes. First, we concentrated our efforts on the optimization of the decarbethoxylation reaction of ethyl benzothiazolylsulfonyl acetate **1**. An overnight treatment of **1** with DBU in THF at room temperature afforded sulfone **13** in 30% yield. When ethyl acetate was used instead of THF, sulfone **13** was obtained in 47% yield. Increase of the reaction time did not improve the yield and we noticed the formation of non-identified products. These could be issued from the intermediate benzothiazolylfluoromethyl carbanion ($BTSO_2CHF^-$). The reaction was realized in presence of a catalytic amount of water (1%) to trap this anion. In this case, **13** was isolated in 77% yield and the reaction was easily scaled up to 2 g scale. Furthermore, similar results were observed either in THF or ethyl acetate (Scheme 4).

The decarbethoxylation reaction was explored from halogenated and alkylated fluorosulfones to prepare useful fluorinated modified Julia reagents. Alkylation reactions of sulfone **1** followed by a decarbethoxylation were then studied. Alkylation reactions were conducted from **1** under the Barbier-type conditions. DBU



Scheme 4. Synthesis of the decarbethoxylated sulfone **13**. (a) DBU, H_2O catalytic, AcOEt or THF, 16 h at rt, 77%.

(1.4 equiv) was added to a mixture of fluorosulfone **1** (1 equiv) and alkyl halide (1.4 equiv) in THF. Reactions were realized at room temperature over 1 h (Table 2 entries 1–4). From good alkylating reagent, such as methyl iodide, sulfone **14** was obtained in 92% yield. The reaction also worked with primary non-activated reagent. From ethyl iodide, **15** was isolated in 67% yield (Table 2, entries 1 and 2). However no alkylation was observed from the corresponding bromoalkane. In contrast, from activated bromoalkanes, such as benzyl bromide, corresponding sulfone **17** was isolated in excellent yield (93%). The alkylation reaction with allyl iodide afforded sulfone **16** in 63% yield (Table 2, entries 3 and 4). Introduction of a second fluorine atom was realized by using NFSI. However, the expected difluorosulfone **18** was accompanied with a by-product identified as the corresponding decarbethoxylated sulfone **23** by ^{19}F NMR analysis of the crude mixture. These sulfones were formed in a 2:3 ratio. The fluorination reaction of **1** was instantaneous and even by quenching the mixture after 5 min under stirring, sulfone **23** was still present in 20%. Additional experiments with 1,1,3,3-tetramethylguanidine prevented this decarbethoxylation and afforded ethyl benzothiazolylsulfonyl-difluoroacetate **18** in 70% yield without trace of **23** (Table 2, entry 5).

Having in hands α-substituted fluorinated sulfone esters **14**–**18**, the previous experimental conditions were applied to study their

Table 2
Alkylation or fluorination reactions of sulfone **1**

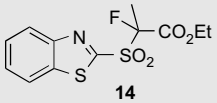
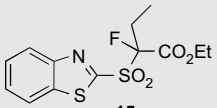
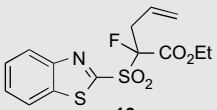
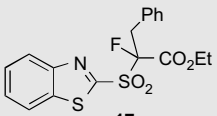
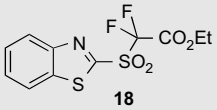
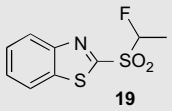
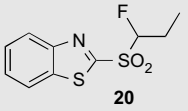
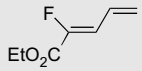
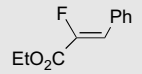
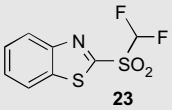
Entry	Electrophile	substituted sulfone	Yield %
1	CH_3I	 **14**	92
2	C_2H_5I	 **15**	67
3	$H_2C{=}CHCH_2I$	 **16**	63
4	$PhCH_2Br$	 **17**	93
5	NFSI	 **18**	70

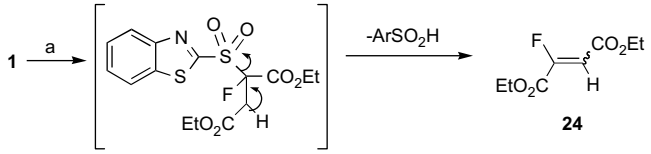
Table 3
Decarbethoxylation reactions of sulfones **14**–**18**

Entry	Starting sulfone	Product	Yield %
1	**14**	 **19**	51
2	**15**	 **20**	33
3	**16**	 **21** *Z*:*E* = 86:14[a]	27[13]
4	**17**	 **22** *Z*:*E* = 98:2[a]	68[6]
5	**18**	 **23**	63

[a] Determined by measurement of the $^3J_{HF}$ coupling constants.

decarbethoxylation (Table 3, entries 1–5). Sulfones **14** and **15** were treated overnight with DBU in THF in the presence of a catalytic amount of water. However, corresponding decarbethoxylated sulfones **19** and **20** were formed in less than 20% yield. Complete conversion of **14** and **15** was observed after 48 h under stirring at 50 °C. In these cases, **19** and **20** were isolated by flash chromatography in non-optimized 51% and 33% yields, respectively (Table 3, entries 1 and 2). This new approach combining alkylation and decarbethoxylation reactions of sulfone esters opened an alternative access to alkylated fluorosulfones, known as precursors of fluoroalkylidenes.[4] However, this method showed some limits since no trace of decarbethoxylated sulfones was detected from sulfones **16** and **17**. In these two cases, instead of the expected sulfones, fluoroalkenes **21** and **22** were isolated in 68 and 27% yield with a good *Z* selectivity (Table 3, entries 3 and 4). In contrast, from difluorinated ester **18** the decarbethoxylation was instantaneous at room temperature and difluoromethyl-benzothiazolylsulfone **23** was isolated in good yield (Table 3, entry 5).

The competitive desulfonylation reaction leading to fluoroalkenes **21** and **22**, observed from sulfones **16** and **17**, was due to the lability of the benzylic or allylic hydrogen atoms.[14] In addition, this desulfonylation reaction was easier and exclusive when the alkylation of **1** was attempted with ethyl bromoacetate (Scheme 5). The corresponding known fluorofumaric ester **24**[15] was obtained exclusively and isolated in 31% yield (*Z*/*E*=87:13).



Scheme 5. Desulfonation reaction. (a) DBU, $BrCH_2CO_2Et$ (1.1 equiv), THF, 20 °C, 1 h, 31%.

This decarbethoxylation reaction of fluorosulfones seems to be sensitive to the steric hindrance, the electrophilic character of the ester and the nature of the leaving group. From non-substituted sulfone ester **1**, the decarbethoxylation is efficient at room temperature, while from the corresponding alkylated sulfones longer reaction time and elevated temperature are required. Finally, the decarbethoxylation reaction was most efficient from difluorinated sulfone ester **18** in which the electrophilic character of the ester function is exalted by the introduction of a second fluorine atom. This experimental observation supports the evidence of the formation of the intermediate **I** suspected in the decarbethoxylation process.

3. Conclusion

In summary, we reported the limits and the scope of the Julia–Kocienski reaction from ethyl benzothiazolylfluorosulfonyl acetate **1** and ketones. The corresponding fluoroalkenes were obtained in moderate to good yields from β- and δ-substituted cyclic ketones but without any selectivity. In contrast, from acyclic ketones and α-substituted cyclic ketones, the modified Julia olefination reaction led to the decarbethoxylated sulfone **13** as the main reaction product in spite of several changes of reaction conditions. In addition, an efficient synthesis of sulfone **13** has also been developed starting from sulfone **1** via a decarbethoxylation reaction performed with DBU in THF or ethyl acetate in the presence of a catalytic amount of water. Finally, this new approach can be used to prepare new fluorinated alkylsulfones. We showed that sulfone **1** was easily alkylated and in some cases, the resulting sulfone could be decarbethoxylated to produce fluorosulfones that are important building blocks in the synthesis of fluoroalkenes.[4] The study of their reactivity in the modified Julia olefination reaction is under progress.

4. Experimental section

4.1. General

All commercially available reagents were bought from Aldrich and used as received. For anhydrous conditions the glassware was put in the oven at 120 °C the day before and cooled to room temperature under a continuous nitrogen flow. THF was dried at a solvent generator from 'Innovative Technologies Inc.', which uses an activated alumina column to remove water. HPLC grade ethyl acetate was used without further purification. Flash column chromatography was realized on silica gel 60 (40–63 μm) from Merck with air pressure and was detected by thin layer chromatography, on which the spots were visualized by UV-irradiation and/or $KMnO_4$ solution. NMR spectra were recorded on a 250 MHz or 400 MHz apparatus in deuterated solvent at 25 °C. ^{19}F NMR spectral lines are with respect to the internal references $CFCl_3$. All chemical shifts are reported in δ parts per million (ppm) and coupling constants are in hertz (Hz). High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

4.2. General procedure for the preparation of sulfides 2 and 4

In a 50 mL round bottom flask under N_2 were placed 2-mercaptoaryl (1.1 equiv) and dry THF (4 mL). The solution was cooled to −17 °C and a solution of ^{t}BuOK (1.3 equiv) in dry THF (3 mL) was slowly added. After 30 min stirring at −17 °C, ethyl bromofluoroacetate (1.0 equiv) was introduced dropwise. The resulting mixture was stirred at room temperature for 2 h, then quenched with a saturated NH_4Cl solution (10 mL) and extracted with CH_2Cl_2/Et_2O (1:1, 2×30 mL). Combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash silica gel chromatography to afford sulfides **2** and **4**.

4.2.1. Ethyl 2-fluoro-2-(2-pyrimidinylthio)acetate (2)

General procedure was followed with 2-mercaptopyrimidine (0.500 g, 2.67 mmol), ethyl bromofluoroacetate (0.31 mL, 2.43 mmol), ^{t}BuOK (0.350 g, 3.16 mmol). The purification by flash chromatography (pentane/AcOEt, 8:2) afforded **2** (0.442 g, 81%) as a colorless oil. ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.33 (t, 3H, $^3J_{HH}$=7.2 Hz), 4.33 (q, 2H, $^3J_{HH}$=7.1 Hz), 7.09 (d, 1H, $^1J_{FH}$=50.6 Hz), 7.12 (t, 1H, $^3J_{HH}$=4.9 Hz), 8.60 (d, 2H, $^3J_{HH}$=4.9 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −165.60 (d, 1F, $^1J_{FH}$=51.7 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.9, 62.7, 91.0 (d, $^1J_{CF}$=229.5 Hz), 118.2, 157.8, 165.9 (d, $^2J_{CF}$=27.0 Hz), 167.6, 177.6; MS (EI) *m/z* 217.1 (M+H, 30), 197.0 (100), 169.0 (5), 113.0 (6); HRMS (EI^+) *m/z* calcd for $[M+H]^+$ $C_8H_{10}FN_2O_2S$: 217.0447; found: 217.0435.

4.2.2. Ethyl 2-fluoro-2-(1-phenyl-5-tetrazolylthio)acetate (4)

General procedure was followed with 2-mercaptophenyl-tetrazole (0.500 g, 2.80 mmol), ethyl bromofluoroacetate (0.31 mL, 2.55 mmol), ^{t}BuOK (0.370 g, 3.31 mmol). The purification by chromatography (pentane/AcOEt, 8:2) afforded **4**[6b] (0.647 g, 82%) as a white solid (mp=47–49 °C). ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.34 (t, 3H, $^3J_{HH}$=7.2 Hz), 4.34 (q, 2H, $^3J_{HH}$=7.1 Hz), 6.96 (d, 1H, $^1J_{FH}$=50.5 Hz), 7.51–7.61 (m, 5H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −161.27 (d, 1F, $^1J_{FH}$=49.4 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.3, 63.9, 92.2 (d, $^1J_{CF}$=241.0 Hz), 124.6, 130.4, 131.2, 133.3, 150.2, 164.4 (d, $^2J_{CF}$=26.0 Hz); MS (EI) *m/z* 283.1 (M+H, 68), 240.1 (100), 161.0 (71), 150.0 (54), 118 (17); HRMS (EI^+) *m/z* calcd for $[M+H]^+$ $C_{11}H_{12}FN_4O_2S$: 283.0665; found: 283.0658.

4.3. Preparation of sulfones 3 and 5

4.3.1. Ethyl 2-fluoro-2-(2-pyrimidinylsulfonyl)acetate (3)

In a 25 mL round bottom flask under N_2 were placed $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.383 g, 0.31 mmol) and H_2O_2 (4.94 mL, 47.40 mmol, 30%). After cooling to 0 °C, a solution of sulfide **2** (0.342 g, 1.58 mmol) in EtOH (2.7 mL) was added dropwise. The mixture was stirred for 16 h at room temperature and quenched with H_2SO_4 (3 mL, 10%). EtOH was removed by evaporation and a NaCl (1 g, 17.10 mmol) was added. The resulting mixture was extracted with CH_2Cl_2/Et_2O (1:1, 3×20 mL). Combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. Purification of the crude mixture by flash silica gel chromatography (CH_2Cl_2) afforded **3** (0.330 g, 84%) as a colorless oil. ^1H NMR (250.13 MHz, $CDCl_3$) δ 1.24 (t, 3H, $^3J_{HH}$=7.2 Hz), 4.31 (q, 2H, $^3J_{HH}$=7.0 Hz), 6.28 (d, 1H, $^1J_{FH}$=47.1 Hz), 7.64 (t, 1H, $^3J_{HH}$=4.9 Hz), 8.94 (d, 2H, $^3J_{HH}$=4.9 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −185.13 (d, 1F, $^1J_{FH}$=46.9 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.2, 64.1, 94.8 (d, $^1J_{CF}$=232.7 Hz), 125.2, 159.4, 161.5 (d, $^2J_{CF}$=39.6 Hz), 163.8, 207.4; MS (EI) *m/z* 271.0 ($M+Na^+$, 100), 249.0 ($M+H^+$, 23), 197.0 (100), 169.0 (5), 113.0 (6); HRMS (EI^+) *m/z* calcd for $[M+H]^+$ $C_8H_{10}FN_2O_4S$: 249.0345; found: 249.0339.

4.3.2. Ethyl 2-fluoro-2-(1-phenyl-5-tetrazolylsulfonyl)acetate (5)

In a 25 mL round bottom flask were placed sulfide **4** (0.200 g, 0.71 mmol), MeCN (1.2 mL), and H_2O (2.4 mL). $NaIO_4$ (0.641 g, 2.99 mmol) and $RuCl_3\cdot 3H_2O$ (2.400 mg, 0.015 mmol) were introduced and the resulting mixture was stirred overnight, then hydrolyzed with H_2O (2.4 mL), and extracted with Et_2O (2×2.4 mL). Combined organic layers were washed with a saturated $NaHCO_3$ solution (2×2 mL) and brine (2×2 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (CH_2Cl_2/pentane, 8:2) to afford **5**[6b] (0.076 g, 35%) as a white solid (mp=85–88 °C).

^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.35 (t, 3H, $^3J_{HH}$=7.1 Hz), 4.40 (q, 2H, $^3J_{HH}$=7.2 Hz), 6.15 (d, 1H, $^1J_{FH}$=44.0 Hz), 7.60–7.64 (m, 5H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −180.01 (d, 1F, $^1J_{FH}$=47.1 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.8, 64.5, 97.1 (d, $^1J_{CF}$=238.0 Hz), 125.6, 129.6, 131.8, 132.5, 151.1, 158.9 (d, $^2J_{CF}$=23.0 Hz), 177.7; MS (EI) *m*/*z* 337.0 ($M+Na^+$, 100), 315.1 ($M+H^+$, 35), 176.0 (13), 117.1 (38); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{11}H_{12}FN_4O_4S$: 315.0563; found: 315.0564.

4.4. General procedure for the preparation of fluoroalkenes 7–11

In a 25 mL round bottom flask were placed sulfone **1** (0.200 g, 0.65 mmol, 1.0 equiv), ketone (0.79 mmol, 1.2 equiv), and dry THF (10 mL). DBU (0.17 mL, 1.12 mmol, 1.7 equiv) was added dropwise and the solution was stirred during 6 h at room temperature. The mixture was quenched with a saturated NH_4Cl solution (5 mL) and brine (2 mL), and then extracted with CH_2Cl_2 (2×30 mL). Combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography to afford corresponding fluoroalkenes **7**–**11**.

4.4.1. Ethyl 2-cyclohexylidene-2-fluoroacetate (*7*)

General procedure was followed with cyclohexanone (0.08 mL, 0.72 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **7** (0.070 g, 57%) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.26 (t, 3H, $^3J_{HH}$=7.1 Hz), 1.52–1.62 (m, 6H), 2.25–2.27 (m, 2H), 2.63–2.65 (m, 2H), 4.21 (q, 2H, $^3J_{HH}$=7.1 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −131.39 (s, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 27.0 (d, $^3J_{CF}$=1.4 Hz), 27.4, 27.5, 27.4, 27.8 (d, $^3J_{CF}$=2.3 Hz), 60.8, 136.3 (d, $^2J_{CF}$=12.0 Hz), 140.9 (d, $^1J_{CF}$=245.0 Hz), 161.6 (d, $^2J_{CF}$=35.0 Hz); MS (EI) *m*/*z* 186.1 (M, 68), 158.0 (100), 157.1 (35); HRMS (EI^+) *m*/*z* calcd for $[M]^+$ $C_{10}H_{15}FO_2$: 186.1056; found: 186.1054.

4.4.2. Ethyl 2-cyclopentylidene-2-fluoroacetate (*8*)

General procedure was followed with cyclopentanone (0.07 mL, 0.79 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **8** (0.045 g, 40 %) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.26 (t, 3H, $^3J_{HH}$=7.1 Hz), 1.56–1.74 (m, 4H), 2.43–2.48 (m, 2H), 2.60–2.66 (m, 2H), 4.20 (q, 2H, $^3J_{HH}$=7.1 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −126.27 (m, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.6, 25.9, 27.3, 30.8 (d, $^3J_{CF}$=2.9 Hz), 31.3 (d, $^3J_{CF}$=1.2 Hz), 61.2, 141.6 (d, $^2J_{CF}$=15.0 Hz), 141.8 (d, $^1J_{CF}$=244.0 Hz), 161.6 (d, $^2J_{CF}$=34.0 Hz); MS (EI) *m*/*z* 172.1 (M, 36), 144.1 (100); HRMS (EI^+) *m*/*z* calcd for $[M]^+$ $C_9H_{13}FO_2$: 172.0899; found: 172.0898.

4.4.3. Ethyl 2-fluoro-2-(2-decalinylidene) acetate (*9*)

General procedure was followed with 2-decalone (0.12 mL, 0.79 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **9** under a mixture of four stereoisomers (1/0.8/0.9/0.9, 0.094 g, 60%) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 0.99–1.79 (m, 15H), 1.96–3.62 (m, 4H), 4.00–4.35 (m, 2H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −129.90 (s, 1F), −131.15 (s, 1F), −131.46 (s, 1F), −131.57 (s, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 20.9, 22.5 (m), 24.4–29.2 (m), 31.5, 33.1 (m), 33.9 (m), 34.6 (m), 37.7 (m), 42.8, 44.0 (m), 60.3 (m), 135.3 (m), 139.7 (m), 143.4 (m), 161.8 (m), 171.0; MS (EI) *m*/*z* 240.2 (M, 41), 195.1 (52), 117.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M]^+$ $C_{14}H_{21}FO_2$: 240.1525; found: 240.1533.

4.4.4. Ethyl 2-fluoro-2-(3-methylcyclohexylidene)acetate (*10*)

General procedure was followed with 3-methylcyclohexanone (0.097 mL, 0.79 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **10** under a mixture of two stereoisomers (1/1, 0.070 g, 60%) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 0.94, 0.96 (d, 3H, $^3J_{HH}$=2.0 Hz), 1.00–1.23 (m, 1H), 1.32 (t, 3H, $^3J_{HH}$=7.0 Hz), 1.33–1.50 (m, 1H), 1.51–1.54 (m, 2H), 1.71–1.85 (m, 4H), 2.78–2.81 (m, 1H), 3.38–3.68 (m, 1H), 4.24 (q, 2H, $^3J_{HH}$=7.0 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −131.29 (m, 1F), −131.88 (m, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 22.1–26.4 (m), 27.0–28.1 (m), 32.3–33.4 (m), 34.3–35.6 (m), 60.8, 67.0, 135.7–135.9 (m), 141.0 (d, $^1J_{CF}$=246.0 Hz), 161.6 (d, $^2J_{CF}$=36.0 Hz); MS (EI) *m*/*z* 201.1 ($M+H^+$, 100), 173.1 (70), 153.1 (20), 130.2 (8); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{11}H_{18}FO_2$: 201.1291; found: 201.1287.

4.4.5. Ethyl 2-fluoro-2-(3-methylcyclopentylidene)acetate (*11*)

General procedure was followed with 3-methylcyclopentanone (0.085 mL, 0.79 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **11** as a mixture of two stereoisomers (1/1, 0.085 g, 70%) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 0.88–0.91 (d, 3H, $^3J_{HH}$=6.3 Hz), 1.29 (t, 3H, $^3J_{HH}$=7.1 Hz), 1.36–1.88 (m, 6H), 2.78–2.83 (m, 1H), 3.31–3.37 (m, 1H), 4.23 (q, 2H, $^3J_{HH}$=7.1 Hz); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −130.84 (m, 1F), −131.32 (m, 1F), −126.90, −126.91 (m, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 22.0, 25.9–26.4 (m), 27.0–27.3 (m), 33.4, 33.4, 33.7, 34.3–35.6 (m), 60.8, 135.7–135.8 (m), 141.0 (d, $^1J_{CF}$=246.0 Hz), 161.5 (d, $^2J_{CF}$=36.0 Hz); MS (EI) *m*/*z* 186.1 (100), 158.1 (70), 143.0 (52); HRMS (EI^+) *m*/*z* calcd for $[M]^+$ $C_{10}H_{15}FO_2$: 186.1055; found: 186.1050.

4.5. Preparation of sulfone 13

In a 250 mL round bottom flask were placed sulfone **1** (2 g, 6.59 mmol) and AcOEt (100 mL). DBU (1.30 mL, 9.23 mmol) and H_2O (0.4 mL) were added and the solution was stirred during 16 h at room temperature. The mixture was hydrolyzed with saturated NH_4Cl solution (20 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×50 mL). Combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography (pentane/AcOEt, 9:1) to afford **13** (1.182 g, 77%) as a white solid (mp=144–147 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 5.58 (d, 2H, $^1J_{FH}$=46.76 Hz), 7.64–7.69 (m, 2H), 8.04–8.07 (m, 1H), 8.25–8.29 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −210.87 (t, 1F, $^1J_{FH}$=46.83 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 91.0 (d, $^1J_{CF}$=223.27 Hz), 122.7, 126.1, 128.3, 128.9, 137.7, 153.1, 162.6, 178.2; MS (EI) *m*/*z* 231.9 ($M+H^+$, 100), 258.0 (10); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_8H_7FNO_2S_2$: 231.9902; found: 231.9911.

4.6. General procedure for the preparation of fluorosulfones 14–17

In a 50 mL round bottom flask under N_2 were placed sulfone **1** (1.0 equiv), halide (1.2–1.4 equiv), and THF (10 mL). DBU (1.4 equiv) was added dropwise and the solution was stirred 1 h at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (3 mL) and then extracted with CH_2Cl_2 (2×20 mL). Combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography to afford corresponding fluorinated sulfones **14**–**17**.

4.6.1. Ethyl 2-(2-benzothiazolylsulfonyl)-2-fluoropropanoate (*14*)

General procedure was followed with sulfone **1** (0.200 g, 0.66 mmol), CH_3I (0.05 mL, 0.79 mmol), and DBU (0.14 mL, 0.92 mmol). The purification by flash chromatography (pentane/AcOEt, 98:2) afforded **14** (0.193 g, 92%) as a white solid (mp=65–66 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.28 (t, 3H, $^3J_{HH}$=7.1 Hz), 2.16 (d, 3H, $^3J_{HH}$=21.3 Hz), 4.31–4.36 (m, 2H), 7.62–7.67 (m, 2H), 8.02–8.05 (m, 1H), 8.25–8.29 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −147.89 (q, 1F, $^3J_{FH}$=21.1 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.8,

17.8 (d, $^2J_{CF}$=20.7 Hz), 63.9, 96.7 (d, $^1J_{CF}$=234.9 Hz), 122.2, 126.0, 127.8, 128.6, 137.9, 152.6, 160.2 (d, $^2J_{CF}$=23.3 Hz); MS (EI) *m*/*z* 318.0 ($M+H^+$, 47), 200.0 (50), 182.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{12}H_{13}FNO_4S_2$: 318.0270; found: 318.0272.

*4.6.2. Ethyl 2-(2-benzothiazolylsulfonyl)-2-fluorobutanoate (**15**)*

General procedure was followed with sulfone **1** (0.200 g, 0.66 mmol), iodoethane (0.063 mL, 0.79 mmol), and DBU (0.14 mL, 0.92 mmol). The purification by flash chromatography (CH_2Cl_2/pentane, 95:5) afforded **15** (0.146 g, 67%) as a white solid (mp=62–63 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.07 (t, 3H, $^3J_{HH}$=8.0 Hz), 1.30 (t, 3H, $^3J_{HH}$=8.0 Hz), 2.53–2.72 (m, 2H), 4.34–4.40 (m, 2H), 7.63–7.68 (m, 2H), 8.02–8.05 (m, 1H), 8.26–8.28 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −158.68 (dd, 1F, $^3J_{FH}$=36.7 Hz, $^3J_{FH}$=36.7 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 6.9, 7.0, 13.9, 24.6 (d, $^2J_{CF}$=19.9 Hz), 63.8, 108.4 (d, $^1J_{CF}$=235.5 Hz), 122.2, 126.0, 127.8, 128.6, 137.9, 152.7, 160.9, 162.6 (d, $^2J_{CF}$=24.97 Hz); MS (EI) *m*/*z* 332.0 ($M+H^+$, 83), 199.9 (67), 181.9 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{13}H_{15}FNO_4S_2$: 332.0427; found: 332.0436.

*4.6.3. Ethyl 2-(2-benzothiazolylsulfonyl)-2-fluoro-4-pentenoate (**16**)*

General procedure was followed with sulfone **1** (0.250 g, 0.82 mmol), allyl iodide (0.083 mL, 0.91 mmol), and DBU (0.18 mL, 1.23 mmol). The purification by flash chromatography (pentane/AcOEt, 95:5) afforded **16** (0.177 g, 63%) as a white solid (mp=86–87 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.20 (t, 3H, $^3J_{HH}$=8.0 Hz), 3.18–3.35 (m, 2H), 4.28 (q, 2H, $^3J_{HH}$=8.0 Hz), 5.20–5.27 (m, 2H), 5.59–5.64 (m, 1H), 7.55–7.61 (m, 2H), 7.96–7.98 (m, 1H), 8.19–8.21 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −156.38 (dd, 1F, $^3J_{FH}$=36.7 Hz, $^3J_{FH}$=36.6 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.9, 35.3 (d, $^2J_{CF}$=19.2 Hz), 63.8, 106.8 (d, $^1J_{CF}$=236.8 Hz), 122.2, 122.7, 126.0, 126.7, 126.8, 127.9, 128.6, 137.9, 152.7, 160.7, 162.1 (d, $^2J_{CF}$=24.92 Hz); MS (EI) *m*/*z* 344.0 ($M+H^+$, 59), 199.9 (40), 181.9 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{14}H_{15}FNO_4S_2$: 344.0427; found: 344.0429.

*4.6.4. Ethyl 2-(2-benzothiazolylsulfonyl)-2-fluoro-3-phenylpropanoate (**17**)*

General procedure was followed with sulfone **1** (0.170 g, 0.56 mmol), benzyl bromide (0.093 mL, 0.79 mmol), and DBU (0.12 mL, 0.78 mol). The purification by flash chromatography (pentane/AcOEt, 95:5) afforded **17** (0.205 g, 93%) as a yellow oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.03 (t, 3H, $^3J_{HH}$=8.0 Hz), 3.67–3.98 (m, 2H), 4.06–4.16 (m, 2H), 7.11–7.20 (m, 5H), 7.49–7.57 (m, 2H), 7.91–7.93 (m, 1H), 8.13–8.17 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −154.85 (dd, 1F, $^3J_{FH}$=38.6 Hz, $^3J_{FH}$=38.5 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 36.7 (d, $^2J_{CF}$=18.8 Hz), 63.7, 107.2 (d, $^1J_{CF}$=238.3 Hz), 122.3, 125.9, 128.0, 128.1, 128.7, 128.9, 130.3, 130.6, 131.1, 137.9, 152.7, 160.7, 161.9 (d, $^2J_{CF}$=24.8 Hz), 171.1; MS (EI) *m*/*z* 394.1 ($M+H^+$, 73), 200.0 (22), 182.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{18}H_{17}FNO_4S_2$: 394.0583; found: 394.0598.

4.7. Preparation of difluorosulfone 18

In a 25 mL round bottom flask under N_2 were placed sulfone **1** (0.200 g, 0.66 mmol), NFSI (0.250 g, 0.79 mmol), and THF (10 mL). 1,1,3,3-Tetramethylguanidine (0.10 mL, 0.79 mmol) was added dropwise and the solution was stirred 5 min at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (3 mL) and then extracted with CH_2Cl_2 (2×20 mL). Combined organic layers were washed with $NaHCO_3$ (5 mL), brine (10 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography (pentane/AcOEt, 9:1) to afford difluorosulfone **18** (0.147 mg, 70%) as a white solid (mp=73–75 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.29 (t, 3H, $^3J_{HH}$=7.1 Hz), 4.40 (q, 2H, $^3J_{HH}$=7.1 Hz), 7.23–7.65 (m, 2H), 7.98–8.02 (m, 1H), 8.26–8.29 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −105.82 (s, 1F); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 65.6, 113.8 (t, $^1J_{CF}$=301.4 Hz), 122.3, 126.4, 128.2, 129.2, 138.3, 152.8, 157.5 (d, $^2J_{CF}$=31.5 Hz); MS (EI) *m*/*z* 322.0 ($M+H^+$, 77), 294.0 (100), 200.0 (62), 182.0 (49), 135.0 (8); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{11}H_{10}F_2NO_4S_2$: 322.0019; found: 322.0013.

4.8. General procedure for the formation of decarboxylated sulfones 19, 20 and esters 21, 22

In a 50 mL round bottom flask were placed sulfone **14**–**17** (1 equiv) and AcOEt (10 mL). DBU (1.7 equiv) and H_2O (catalytic amount) were introduced and the solution was stirred for 6–48 h at 50 °C or 70 °C according to the substrate. The reaction mixture was hydrolyzed with a saturated NH_4Cl solution (3 mL) and extracted with CH_2Cl_2 (2×30 mL). Combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography to afford compounds **19**–**22**.

*4.8.1. 2-(2-Fluoroethylsulfonyl)benzothiazole (**19**)*

General procedure was followed with sulfone **14** (0.184 g, 0.63 mmol), DBU (0.16 mL, 1.07 mmol), and H_2O (four drops) during 16 h at 50 °C. The purification by flash chromatography (CH_2Cl_2/pentane, 9:1) afforded **19** (0.073 g, 51%) as a white solid (mp=75–78 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.82 (dd, 3H, $^3J_{HH}$=6.4 Hz, $^3J_{HF}$=23.6 Hz), 5.75 (dq, 1H, $^3J_{HH}$=6.5 Hz, $^1J_{FH}$=41.4 Hz), 7.52–7.62 (m, 2H), 8.17–8.19 (m, 1H), 8.20–8.21 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −171.55 (dq, 1F, $^3J_{FH}$=23.0 Hz, $^1J_{FH}$=48.5 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.0 (d, $^2J_{CF}$=20.1 Hz), 99.4 (d, $^1J_{CF}$=219.5 Hz), 122.3, 125.7, 127.8, 128.4, 137.4, 152.8, 162.0; MS (EI) *m*/*z* 246.0 ($M+H^+$, 62), 200.0 (36), 182.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_9H_9FNO_2S_2$: 246.0059; found: 246.0047.

*4.8.2. 2-(2-Fluoropropylsulfonyl)benzothiazole (**20**)*

General procedure was followed with sulfone **15** (0.180 g, 0.54 mmol), DBU (0.14 mL, 0.92 mmol), and H_2O (four drops) during 48 h at 70 °C. The purification by flash chromatography (pentane/AcOEt, 95:5) afforded **20** (0.044 g, 33%) as a white solid (mp=100–101 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.16 (t, 3H, $^3J_{HH}$=7.5 Hz), 2.06–2.34 (m, 2H), 5.53 (ddd, 1H, $^3J_{HH}$=3.5 Hz, $^3J_{HH}$=9.3 Hz, $^1J_{HF}$=48.4 Hz), 7.53–7.61 (m, 2H), 7.95–7.97 (m, 1H), 8.18–8.20 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −179.14 (ddd, 1F, $^3J_{FH}$=16.3 Hz, $^3J_{FH}$=33.8 Hz, $^1J_{FH}$=48.6 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 8.8 (d, $^3J_{CF}$=3.7 Hz), 20.8 (d, $^2J_{CF}$=19.6 Hz), 103.2 (d, $^1J_{CF}$=222.1 Hz), 122.3, 125.8, 127.9, 128.3, 137.4, 152.8, 162.6; MS (EI) *m*/*z* 260.0 ($M+H^+$, 57), 200.0 (31), 182.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{10}H_{11}FNO_2S_2$: 260.0215; found: 260.0228.

*4.8.3. Ethyl 2-fluoro-2,4-pentadienoate (**21**)*

General procedure was followed with sulfone **16** (0.140 g, 0.41 mmol), DBU (0.10 mL, 0.69 mmol), and H_2O (six drops) during 48 h at 70 °C. The purification by flash chromatography (pentane/AcOEt, 95:5) afforded **21** under a mixture of two isomers (*Z*/*E*=86:14, 0.016 g, 27%) as a yellow oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.21–1.31 (m, 6H), 4.20–4.27 (m, 4H), 5.34–5.38 (m, 2H), 5.41–5.53 (m, 2H), 6.31–6.66 (m, 4H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −127.56 (d, 1F, $^3J_{FH}$=28.9 Hz, *Z*), −122.62 (d, 1F, $^3J_{FH}$=19.3 Hz, *E*); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 14.1, 29.7, 36.5, 61.7, 116.4, 127.5, 127.7, 128.6, 129.2, 129.3, 130.1, 146.0 (d, $^1J_{CF}$=268.0 Hz), 162.3 (d, $^2J_{CF}$=34.3 Hz).

*4.8.4. Ethyl 2-fluoro-3-phenylacrylate (**22**)*

General procedure was followed with sulfone **17** (0.180 g, 0.45 mmol), DBU (0.11 mL, 0.76 mmol), and H_2O (six drops) during 48 h at 70 °C. The purification by flash chromatography (pentane/

AcOEt, 95:5) afforded **21** under a mixture of two isomers (*Z*/*E*=98:2, 0.060 g, 68%) as a yellow oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 1.29 (t, 3H, $^3J_{HH}$=7.2 Hz), 4.26 (q, 2H, $^3J_{HH}$=7.2 Hz), 6.83 (d, 1H, $^3J_{HF}$=35.2 Hz), 7.25–7.33 (m, 3H), 7.54–7.56 (m, 2H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −125.29 (d, 1F, $^3J_{FH}$=35.2 Hz, *Z*), −117.17 (d, 1F, $^3J_{FH}$=21.9 Hz, *E*); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 13.0, 60.9, 116.4, 127.5, 127.7, 128.6, 128.7, 129.2, 129.3, 130.1, 130.2, 146.0 (d, $^1J_{CF}$=268.0 Hz), 162.3 (d, $^2J_{CF}$=34.3 Hz); MS (EI) *m*/*z* 194.0 ($M+H^+$, 100), 165.0 (37), 149.0 (34), 129 (17), 121 (17), 101 (33), 75 (18), 50 (11); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_{11}H_{12}FO_2$: 195.0821; found: 195.0819.

4.9. Preparation of difluorosulfone 23

In a 100 mL round bottom flask were placed sulfone **18** (0.616 mg, 1.92 mmol) and AcOEt (30 mL). DBU (0.40 mL, 2.68 mmol) and H_2O (15 drops) were added and the solution was stirred 16 h at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 (2×30 mL). Combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash silica gel chromatography (pentane/AcOEt, 9:1) to afford **23** (0.304 g, 63%) as a white solid (mp=133–135 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 6.51 (t, 1H, $^1J_{HF}$=52.8 Hz), 7.59–7.66 (m, 2H), 8.00–8.02 (m, 1H), 8.25–8.27 (m, 1H); ^{19}F NMR (235.35 MHz, $CDCl_3$) δ −121.36 (d, 1F, $^1J_{FH}$=53.4 Hz); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 113.4 (t, $^1J_{CF}$=288.1 Hz), 121.3, 125.2, 127.2, 128.0, 136.8, 151.9, 157.7; MS (EI) *m*/*z* 250.0 ($M+H^+$, 63), 200.0 (50), 182.0 (100); HRMS (EI^+) *m*/*z* calcd for $[M+H]^+$ $C_8H_6F_2NO_2S_2$: 249.9808; found: 249.9796.

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