Tetrahedron 70 (2014) 5632–5639

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Stereoselective formation of (*Z*)-2-fluoroalkenoates via Julia–Kocienski reaction of aldehydes with pyrimidinyl-fluorosulfones

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ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form 13 June 2014
Accepted 18 June 2014
Available online 24 June 2014

Keywords:
Fluoroalkenes
Julia–Kocienski reaction
Fluoroalkenoates
Selective synthesis

ABSTRACT

The selective synthesis of fluoroalkenoates is reported from a pyrimidinyl fluorosulfone. This sulfone allowed the preparation of *Z*-fluoroalkenoates with very high stereoselectivity from both aromatic and aliphatic aldehydes. The nature of the heterocycle on the course of the Julia–Kocienski reaction is discussed.

1. Introduction

The introduction of fluorine atoms onto bioactive compounds has been largely applied in the design of analogues of pheromones, herbicides, or drugs.[1] In this field, fluoroalkenoates are important building-blocks for the multi-steps synthesis of a large variety of biomolecules.[2] Fluoroalkenoates are prepared from aldehydes or ketones through the Wittig and related reactions,[3] Peterson reaction,[4] or Durst reaction.[5] For this one-step synthesis performed from aldehydes the Horner–Wadsworth–Emmons (HWE) reaction afforded mainly the *E*-alkenoates, while the *Z*-alkenoates were obtained as major products with the Peterson, Durst, and Wittig reactions. Alternatively, *Z*-alkenoates can be prepared in two steps from aldehydes, by isomerization of intermediate *E*-alkenoates in the presence of catalytic amount of iodine or bromine, or by addition of the dianionic form of diethyl 2-fluoro-phosphonoacetic acid followed by an esterification step. The acylation of an HWE reagent followed by the reduction of the intermediate phosphonoketoesters represents another possibility.[6]

Recently the modified Julia reaction has been introduced as a complementary method for the synthesis of fluoroalkenes.[7] This reaction presents some advantages, such as the preparation of both alkenoate isomers from the same reagent. However, as observed from the previous methods, this reaction also has limitations. Indeed, the selective preparation of *Z* or *E*-fluoroalkenoates is confined to aromatic aldehydes.[8] Despite great efforts in this field, while the synthesis of alkenoates from aromatic aldehydes and a large variety of heterocyclic fluorosulfones is selective, the control of the reaction is problematic with aliphatic aldehydes. Previous reports involving the synthesis of fluoroalkenoates through the Julia–Kocienski reaction (Table 1),[9] showed that from benzothiazolylsulfonyl acetates and aromatic aldehydes, the *E*-alkene was mainly obtained when the reaction was mediated by DBU, and the *Z*-alkene was produced as major isomer with DBU and $MgBr_2$.[8a,b]

In contrast, from bis-(CF_3)phenylsulfonyl acetates, *Z*-alkenes were obtained when the reaction was performed under phase-transfer condition.[8c] However, it is clear that the main limit of these reagents, as for the phosphorus containing reagents, is the control of the selectivity from aliphatic aldehydes. From nonanal, heptanal, and citronellal and the same fluorosulfones, a mixture of alkenoates is obtained (Table 1). In order to achieve selective formation of *Z*-alkenoates from both aliphatic and aromatic aldehydes, we initiated an investigation involving alternative fluorosulfonyl acetate derivatives in this reaction, with a focus on the role of the aromatic sulfone on the course of the reaction.

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http://dx.doi.org/10.1016/j.tet.2014.06.081
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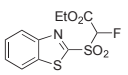
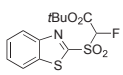
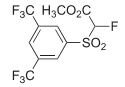
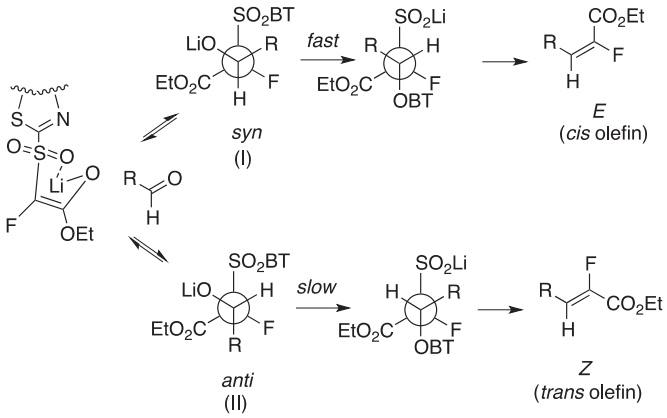
Table 1
Synthesis of fluoroalkenoates from arylsulfones

Base				
	DBU	DBU/$MgBr_2$	DBU	K_2CO_3 TBAB
Z/*E* *RCHO* (yield)	24/76[8b] *PhCHO* (70%) 24/76[8b] *Nonanal* (66%)	92/8[8b] *PhCHO* (71%) 88/12[8b] *Nonanal* (87%)	25/75[8a] *PhCHO* (78%) 17/83[8a] *Heptanal* (75%)	93/7[8c] *PhCHO* (95%) 43/57[8c] *Citronellal* (61%)

2. Results and discussion

The modified Julia reaction, originally developed with benzothiazolylsulfones, has been largely applied in total synthesis with other heterocyclic sulfones.[10] It has been already shown by Kocienski,[11] Charette,[12] Nájera,[13] and Zhu,[14] for example, that the nature of the heteroaryl sulfone modified the course of the reaction. In an early work, S. Julia suggested that the Smiles rearrangement is the limiting step, with the formation of the *cis*-olefin going through a fast Smiles rearrangement, and the formation of the *trans*-olefin going through a slow Smiles rearrangement (Scheme 1).[15] The π-deficient character of the heterocycle appears essential, and the Smiles rearrangement is possible and faster when the heterocycle presents a high π-deficient character.[15c]



Scheme 1. Mechanism of the Julia–Kocienski reaction.

In order to increase the rate of the Smiles rearrangement, we explored the reaction with sulfones containing more π-deficient heterocycles compared to benzothiazole. We should expect that with a pronounced π-deficient character of the heterocycle, the slow Smiles rearrangement will accelerate, possibly to the extent that the relative rate of the formation of the alcoholates (I) and (II) will reflect the stereoselectivity of the reaction. Given the reaction to the *anti*-alcoholate is thought to be favorable,[15c] this could then lead to an increase in *Z*-fluoroalkenoate selectivity.

Hence, more π-deficient heterocycles than benzothiazolyl ring were selected (based on the carbon NMR chemical shift of the C_2 carbon atom of the heterocycle), such as 5-(NO_2)-benzothiazolyl and pyrimidinyl heterocycles, and a less π-deficient, such as pyridinyl heterocycle (Fig. 1).[16]

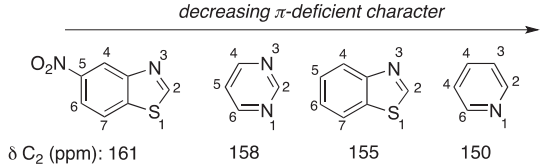
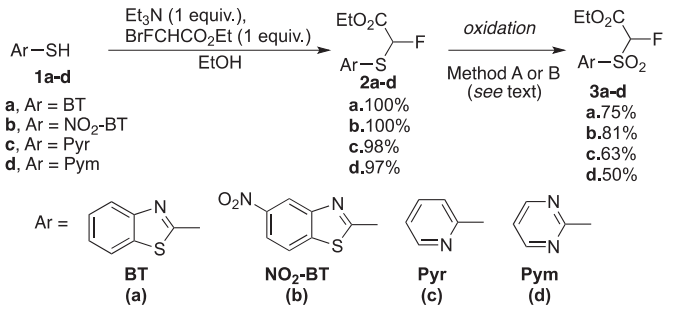


Fig. 1. Carbon NMR chemical shift.

The olefination reaction of both aromatic and aliphatic aldehydes was realized from these sulfones and the results were compared to those observed from the corresponding benzothiazolylsulfone. For a practical convenience, the study was realized with NaHMDS as base.[8b] The synthesis of fluorinated sulfones **3a**–**d**, was realized in two steps by alkylation of sulfanyl derivatives **1a**–**d** with ethyl bromofluoroacetate in the presence of triethylamine, followed by oxidation of the intermediate sulfide with hydrogen peroxide in the presence of catalytic amount of molybdate complex (Scheme 2, Method A).[8b] Although good yields were observed from benzothiazolyl-, pyridinyl,- and pyrimidinyl-sulfides **2a**, **2c**, **2d**, the oxidation step did not succeed from 5-nitro-benzothiazolyl-sulfides **2b**. For these substrates, corresponding sulfone **3b** was obtained after oxidation of **2b** in the presence of $NaIO_4$ and $RuCl_3$ (Scheme 2, Method B).[17]

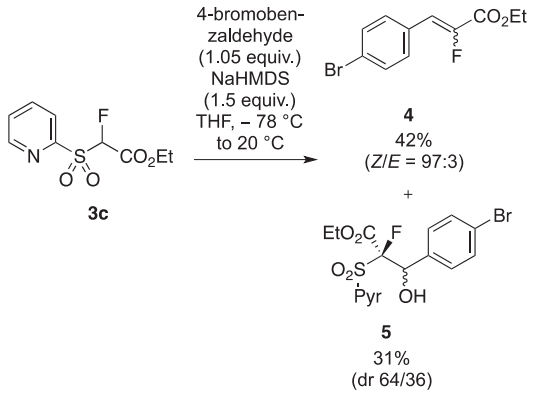


Scheme 2. Synthesis of fluorinated heteroaromatic sulfones.

In a preliminary experiment, the reactivity of the pyridinylsulfone reagents was investigated using our standard experimental conditions previously developed with sulfone **3a** (NaHMDS, THF, −78 °C to 20 °C).[8b]

While the reaction with the benzothiazolyl group (**3a**) afforded exclusively alkenes **4**, with **3c** the reaction did not reach completion after 4 h stirring from −78 °C to 20 °C (Scheme 3): a mixture of starting sulfone **3c**, corresponding fluoroalkenes **4**, and diastereoisomeric hydroxysulfones **5** was obtained in a 3:4:3 ratio. NMR analysis did not allow unambiguous assignment of the diastereomers **5**. Clearly, the formation of hydroxysulfones **5** indicated that the pyridinyl heterocycle is not electron deficient enough to ensure completion of the Smiles rearrangement, which confirms a report by S. Julia.[15c]

Then, the stereoselectivity of the olefination reaction was investigated using the more reactive benzothiazolylsulfone **3b** and pyrimidinylsulfone **3d**, and compared to sulfone **3a**, with aromatic aldehydes (Table 2). In all cases, alkenes **4**–**8** were exclusively obtained, and isolated in good yields (Table 2). From 4-bromobenzaldehyde and sulfone **3a**, the corresponding fluoroalkenes **4** were obtained in 72% yield in a *Z*/*E* ratio of 85:15. Gratifyingly, it was indeed observed that the selectivity depends on the nature of the heterocycle, with an increase up to 98:2 from sulfone **3b**, and the virtually exclusive formation of *Z*-alkene **4** from pyrimidinylsulfone **3d**. This observation was general, and from 2,5-dibromobenzaldehyde, thiophenecarboxaldehyde, and furfural, the corresponding fluoroalkenoates **6**, **7**, **8** were obtained in good yields



Scheme 3. Synthesis of fluoroalkenoates from pyridinylsulfone.

Table 2
Modified Julia reaction with aromatic aldehydes

Sulfone	Ar=BT **3a**		Ar=NO_2-BT **3b**		Ar=Pym **3d**	
Fluoroalkene	Yield[a] (%)	*Z*/*E*[b]	Yield[a] (%)	*Z*/*E*[b]	Yield[a] (%)	*Z*/*E*[b]
4	72	85:15	74	92:8	72	100:0
6	52	98:2	78	96:4	83	99:1
7	80	83:17	82	83:17	69	100:0
8	75	88:12	—	—	87	99:1

[a] Isolated yield.
[b] Determined by ^{19}F NMR of the crude.

and excellent selectivities (Table 2). Again, this selectivity increased from benzothiazolyl- to pyrimidinyl-sulfones **3a**, **3b**, **3d**.

Following the excellent stereoselectivity obtained from aromatic aldehydes this study was then extended to the more problematic aliphatic aldehydes (Table 3). As mentioned in the introduction, when benzothiazolyl-, tetrazolyl-, and bis(CF_3)-phenyl-sulfones were involved in the reaction, a mixture of fluoroalkenoates was obtained from aliphatic aldehydes (see Table 1). This was confirmed by the olefination reaction carried out with the standard benzothiazolysulfone **3a** and heptanal (Table 3), with a 1:1 mixture of isomeric alkenes **9** obtained. However, the influence of the nature of the heterocycle was again observed, and when the nitro-benzothiazolylsulfone **3b** was used, a significant increase in selectivity was observed, with *Z*-alkene **9** formed as major product (*Z*/*E*=74:26). This effect was even more pronounced using pyrimidinylsulfone **3d**, affording alkene **9** exclusively. This remarkably high selectivity with sulfone **3d** appeared general, and from nonanal, 10-undecenal, and citronellal, the corresponding alkenes **10**, **11**, **12** were obtained in good yields and in 99:1, 96:4, and 97:3 *Z*/*E* ratios, respectively. This selectivity was maintained with 3-phenylpropanal, while the yield dropped down up to 52%. From cyclohexycarbaldehyde, *Z*-isomer **14** was obtained as major product regardless the sulfone, with an excellent selectivity with sulfone **3d**. In addition, with a more complex aldehyde, such as

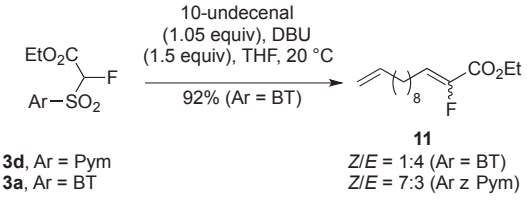
Table 3
Modified Julia reaction with aliphatic aldehydes

Sulfone	Ar=BT **3a**		Ar=NO_2-BT **3b**		Ar=Pym **3d**	
Fluoroalkene	Yield[a] (%)	*Z*/*E*[b]	Yield[a] (%)	*Z*/*E*[b]	Yield[a] (%)	*Z*/*E*[b]
9	50	53:47	60	74:26	84	100:0
10	81	46:54	92	84:16	73	99:1
11	66	43:57	82	85:15	79	96:4
12	49	55:45	—	—	81	97:3
13	40	69:31	—	—	52	97:3
14	62	71:29	60	88:12	60	99:1
15	57	33:67	—	—	72	95:5

[a] Isolated yield.
[b] Determined by ^{19}F NMR of the crude.

biocartol methyl ester, *Z*-alkene **15** was also obtained selectively, and in good yield.

As mentioned in Table 1, the use of DBU as base led to an increase in *E*-selectivity of the reaction, with a benzothiazolylsulfone reagent, and that the selectivity was reversed when $MgBr_2$ was added.[8b] An additional experiment was carried out by reacting pyrimidinyl- and benzothiazolylsulfone **3d** and **3a** with 10-undecenal in the presence of DBU instead of NaHMDS (Scheme 4). However, while with benzothiazolylsulfone **3a** alkenes were isolated in 92% yield after 3 h at 20 °C, from pyrimidinylsulfone **3d** the reaction did not reach completion, even after an overnight reaction. A different selectivity was obtained and from **3a**, the *E*-alkene **11** was the major product (*Z*/*E*=1:4), but from **3d** the *Z*-alkene was still obtained as the major isomer (*Z*/*E*=7:3). As expected, this ratio was increased when the reaction was carried out with DBU and $MgBr_2$: the reaction with **3d** reached completion after 2 h at 20 °C to afford **11**, but only in a 9:1 *Z*/*E* ratio. Hence, it is interesting to observe that the NaHMDS conditions lead to a higher ratio (96:4, Table 3) compared to the DBU and $MgBr_2$ conditions.



Scheme 4. Influence of the base.

These results obtained with pyrimidinylsulfone **3d** confirm the influence of the π-deficient character of the heterocyclic sulfone on the course of the reaction. In the present case, we presume that this electronic effect considerably enhances the rate of the Smiles rearrangement, and that the relative rate of formation of the intermediate alcoholates is reflected in the stereoselectivity of the reaction. To rule out fluoroalkene product isomerization, possibly catalyzed by the corresponding nucleophilic 2-hydroxypyrimidine byproduct, a control experiment was carried out in which a 1:1 mixture of *Z*/*E* alkene **9** was treated with 2-hydroxypyrimidine (1 equiv) in the presence of NaHMDS at −78 °C, and then at 20 °C. In this case, the ratio was maintained and no isomerization was observed, even after 18 h at 20 °C. Considering that the *retro*-addition reaction is thus negligible for aliphatic aldehydes, the high *Z*-stereoselectivity implies that the reaction proceeds via the *anti*-alcoholate (II), assuming an *anti* elimination is occurring. However, it was not possible to trap this intermediate alcoholate. Indeed, when adding AcOH to the reaction mixture at −78 °C after 10 min of stirring the corresponding alkenes were already obtained. Recently, another mechanism going through a *syn*-periplanar elimination was proposed, which cannot be excluded in the present case.[18]

3. Conclusion

In conclusion, the use of a pyrimidinylsulfone for the modified Julia reaction to 2-fluoroacrylates is shown to yield the *Z*-isomer in very high diastereomeric ratio, even when aliphatic aldehydes are employed as starting materials. The electron deficient nature of the pyrimidine ring appeared important to promote the formation of the *Z*-alkenes. Further research toward the use of pyrimidinyl fluorosulfone-based reagents for the selective synthesis of fluoroalkenes from aliphatic and aromatic aldehydes is underway.

4. Experimental section

All commercially available reagents were bought and used as received. For anhydrous conditions, the glassware was dried in the oven at 120 °C and cooled to room temperature under a continuous nitrogen flow. THF, CH_2Cl_2, Et_2O, and CH_3CN were dried at a solvent generator, which uses an activated alumina column to remove water. DMF and NEt_3 were distilled under CaH_2 or 4 Å molecular sieves. Flash column chromatography was realized on silica gel 60 (40–63 μm) with air pressure and were 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 line is with respect to the internal reference $CFCl_3$. 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. High-resolution mass data were recorded on a Micromass Q-TOF (Quadrupole Time-of-Flight) instrument with an electrospray source in the EI or ESI mode.

4.1. General procedure for the alkylation of thiol

Triethylamine (1 equiv) was added dropwise to a solution of sulfide (1 equiv) in EtOH (0.4 M) at 0 °C under N_2. After 10 min of stirring, ethyl bromofluoroacetate (1 equiv) was added to the resulting mixture and was stirred 3 h at 20 °C. The reaction mixture was quenched with HCl (1 N), then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure.

*4.1.1. Ethyl 2-fluoro-2-(5-nitrobenzothiazol-2-ylthio)acetate (**2b**).* General procedure was followed with 5-nitro-2-mercapto benzothiazole (1.00 g, 4.7 mmol) in EtOH (12.6 mL), followed by the addition of triethylamine (0.67 mL, 4.7 mmol) and ethyl bromofluoroacetate (0.53 mL, 4.7 mmol). The crude product was purified by flash silica gel chromatography (pentane/AcOEt, 80:20) to afford **2b** (1.49 g, 100%) as a yellow solid (mp 76–78 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, $^4J_{HH}$=2.2 Hz, $^5J_{HH}$=0.4 Hz, 1H), 8.26 (dd, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=2.2 Hz, 1H), 7.94 (dd, $^3J_{HH}$=8.8 Hz, $^5J_{HH}$=0.4 Hz, 1H), 7.02 (d, $^2J_{HF}$=50.4 Hz, 1H), 4.36 (q, $^3J_{HH}$=7.4 Hz, 2H), 1.35 (t, $^3J_{HH}$=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (d, $^2J_{CF}$=26.6 Hz), 164.5, 152.4, 147.1, 142.4, 121.7, 119.7, 117.8, 91.4 (d, $^1J_{CF}$=239.7 Hz), 63.4, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −161.9 (d, $^2J_{HF}$=50.4 Hz, 1F). HRMS (MS+) for $C_{11}H_{10}N_2O_4FS_2$ $(M+H)^+$ calcd 317.0066, found 317.0061.

*4.1.2. Ethyl 2-fluoro-2-(pyridin-2-ylthio)acetate (**2c**).*[19] General procedure was followed with 2-pyridinethiol (3.00 g, 27.0 mmol) in EtOH (72 mL), followed by the addition of triethylamine (3.77 mL, 27.0 mmol) and ethyl bromofluoroacetate (3.2 mL, 27.0 mmol). The crude product was purified by flash silica gel chromatography (pentane/AcOEt, 80:20) to afford **2c** (5.7 g, 98%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.52–8.53 (m, 1H), 7.60–7.64 (m, 1H), 7.07–7.31 (m, 2H), 7.11 (d, $^2J_{HF}$=51.6 Hz, 1H), 4.32–4.38 (m, 2H), 1.28–1.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (d, $^2J_{CF}$=27.9 Hz), 153.4, 149.0, 137.0, 123.3, 121.5, 90.8 (d, $^1J_{CF}$=230.6 Hz), 62.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −162.9 (d, $^2J_{HF}$=51.6 Hz, 1F).

*4.1.3. Ethyl 2-fluoro-2-(pyrimidin-2-ylthio)acetate (**2d**).*[20] General procedure was followed with 2-pyrimidinethiol (4.00 g, 35.7 mmol) in EtOH (95 mL), followed by the addition of triethylamine (5 mL, 35.7 mmol) and ethyl bromofluoroacetate (4.2 mL, 35.7 mmol). The sulfide **2d** was obtained without any further purification as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, $^3J_{HH}$=4.9 Hz, 2H), 7.12 (t, $^3J_{HH}$=4.9 Hz, 1H), 7.09 (d, $^2J_{HF}$=50.6 Hz, 1H), 4.33 (q, $^3J_{HH}$=7.2 Hz, 2H), 1.33 (t, $^3J_{HH}$=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 167.6, 165.9 (d, $^2J_{CF}$=27.0 Hz), 157.8, 118.2, 91.0 (d, $^1J_{CF}$=229.5 Hz), 62.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −165.6 (d, $^2J_{HF}$=50.6 Hz, 1F).

4.2. Ethyl 2-fluoro-2-(5-nitrobenzothiazol-2-ylsulfonyl)acetate (3b)

To a solution of sulfide **2b** (200 mg, 0.63 mmol, 1 equiv) in MeCN/H_2O (0.8 mL/2 mL), were added sodium periodate (22 mg, 2.91 mmol, 4.6 equiv) and ruthenium (III) chloride hydrate (1.3 mg, 0.06 mmol, 0.01 equiv). The resulting mixture was stirred at 20 °C and a white precipitate was formed. After 16 h of stirring, the precipitate was filtered and washed with CH_2Cl_2. The filtrate was diluted with CH_2Cl_2 and washed successively with a saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/AcOEt, 80:20) to afford the sulfone **3b** (179.0 mg, 81%) as a white solid (mp 113–115 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (dd, $^4J_{HH}$=2.2 Hz, $^5J_{HH}$=0.4 Hz, 1H), 8.52 (dd, $^3J_{HH}$=9.0 Hz, $^4J_{HH}$=2.2 Hz, 1H), 7.94 (dd, $^3J_{HH}$=9.0 Hz, $^5J_{HH}$=0.4 Hz, 1H), 6.07 (d, $^2J_{HF}$=47.3 Hz, 1H), 4.45–4.38 (m, 2H), 1.39 (t, $^3J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 159.7 (d, $^2J_{CF}$=23.3 Hz), 152.4, 147.9, 143.0, 123.4, 122.9, 121.5, 96.4 (d, $^1J_{CF}$=235.6 Hz), 64.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −180.8 (d, $^2J_{HF}$=47.3 Hz, 1F). MS (ESI+) *m*/*z* (%) 349.0 ($(M+H)^+$, 62), 321.0 (100), 303.0 (24). HRMS (MS+) for $C_{11}H_{10}N_2O_6FS_2$ $(M+H)^+$ calcd 348.9964, found 348.9980.

4.3. Ethyl 2-fluoro-2-(pyridin-2-ylsulfonyl)acetate (3c)

In a round bottom flask, under N_2, were placed $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (6.67 g, 5.4 mmol, 0.2 equiv) and H_2O_2 (85 mL,

810 mmol, 30 equiv). After cooling to 0 °C, a solution of sulfide **2c** (5.8 g, 27 mmol, 1 equiv) in EtOH (43 mL) was added dropwise. The mixture was stirred at 20 °C and quenched with H_2SO_4 (10%). EtOH was removed by evaporation and NaCl was added. The resulting mixture was extracted with CH_2Cl_2. Combined organic layers were washed with brine, with saturated aqueous Na_2SO_3, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford the sulfone **3c** (4.21 g, 63%) without any further purification as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74–8.72 (m, 1H), 8.10–8.07 (m, 1H), 7.98–7.94 (m, 1H), 7.59–7.55 (m, 1H), 6.02 (d, $^2J_{HF}$=47.6 Hz, 1H), 4.37–4.29 (m, 2H), 1.31–1.21 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $^2J_{CF}$=25.1 Hz), 154.0, 150.6, 138.4, 128.4, 124.6, 94.7 (d, $^1J_{CF}$=231.3 Hz), 63.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −184.5 (d, $^2J_{HF}$=47.6 Hz, 1F). MS (ESI+) *m*/*z* (%) 248.1 ($(M+H)^+$, 100), 220.1 (60), 202.0 (59). HRMS (MS+) for $C_9H_{11}NO_4FS$ $(M+H)^+$ calcd 248.0393; found 248.0403.

4.4. Ethyl 2-fluoro-2-(pyrimidin-2-ylsulfonyl)acetate (3d)[20]

In a round bottom flask, under N_2, were placed $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (8.82 g, 7.14 mmol) and H_2O_2 (112 mL, 1.07 mol, 30 equiv). After cooling to 0 °C, a solution of sulfide **2d** (7.07 g, 35.7 mmol) in EtOH (57 mL) was added dropwise. The mixture was stirred 48 h at 20 °C and quenched with H_2SO_4 (10%). EtOH was removed by evaporation and NaCl was added. The resulting mixture was extracted with CH_2Cl_2. Combined organic layers were washed with brine, with saturated aqueous Na_2SO_3, dried over $MgSO_4$, filtered, and evaporated under reduced pressure to afford the sulfone **3d** (4.43 g, 50%) without any further purification as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, $^3J_{HH}$=4.8 Hz, 2H), 7.64 (t, $^3J_{HH}$=4.8 Hz, 1H), 6.28 (d, $^2J_{HF}$=47.1 Hz, 1H), 4.31 (q, $^3J_{HH}$=7.1 Hz, 2H), 1.24 (t, $^3J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 163.8, 161.5 (d, $^2J_{CF}$=39.6 Hz), 159.4, 125.2, 94.8 (d, $^1J_{CF}$=232.7 Hz), 64.1, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −185.1 (d, $^2J_{HF}$=47.1 Hz, 1F).

4.5. General procedure for the formation of fluoroacrylates

NaHMDS 1 M in THF (1.5 equiv) was added dropwise to a solution of sulfone **3a**–**b**, **3d** (1 equiv) and aldehyde (1.05 equiv) in THF (0.04 M) at −78 °C under N_2. After 30 min of stirring, the resulting mixture was stirred for 2 h from −78 °C to 20 °C and then was quenched with a saturated solution of NH_4Cl and brine, then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by flash chromatography (pentane/AcOEt, 95:5).

*4.5.1. Ethyl 3-(4-bromophenyl)-2-fluoroacrylate (**4**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 4-bromobenzaldehyde (78 mg, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 100:0) was purified and afforded *Z*-fluoroalkene **4** (78.56 mg, 72%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), 4-bromobenzaldehyde (55.8 mg, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 92:8) afforded a mixture of fluoroalkene **4** (58.4 mg, 74%).

From sulfone **3a** (87.1 mg, 0.29 mmol), 4-bromobenzaldehyde (55.8 mg), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 85:15) afforded a mixture of fluoroalkene **4** (56.8 mg, 72%).

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.54 (m, 4H), 6.85 (d, $^3J_{HFtrans}$=33.9 Hz, 1H), 4.34 (q, $^3J_{HH}$=7.2 Hz, 2H), 1.37 (t, $^3J_{HH}$=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, $^2J_{CF}$=34.1 Hz), 147.4 (d, $^1J_{CF}$=269.0 Hz), 132.4, 131.7 (d, $^4J_{CF}$=8 Hz), 130.0 (d, $^3J_{CF}$=5.0 Hz), 124.0 (d, $^3J_{CF}$=4.8 Hz), 116.3 (d, $^2J_{CF}$=24.7 Hz), 62.1, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.9 (d, $^3J_{HFtrans}$=34 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.54 (m, 4H), 6.82 (d, $^3J_{HFcis}$=21.4 Hz, 1H), 4.26 (q, $^3J_{HH}$=7.2 Hz, 2H), 1.27 (t, $^3J_{HH}$=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, $^2J_{CF}$=37.0 Hz), 147.3 (d, $^1J_{CF}$=258.2 Hz), 132.5, 131.3 (d, $^4J_{CF}$=3.0 Hz), 131.3, 131.0, 129.9 (d, $^4J_{CF}$=9.3 Hz) 123.0, 120.5 (d, $^2J_{CF}$=26.9 Hz), 61.8, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.8 (d, $^3J_{HFcis}$=21.4 Hz, 1F).

*4.5.2. Ethyl 3-(2,5-dibromophenyl)-2-fluoroacrylate (**6**).* General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 2,5-dibromobenzaldehyde (111 mg, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 99:1) afforded a mixture of fluoroalkene **6** (116.8 mg, 83%) as a colorless oil.

From sulfone **3b** (91 mg, 0.26 mmol), 2,5-dibromobenzaldehyde (72.4 mg, 0.27 mmol), NaHMDS (290 μL, 0.29 mmol), and THF (6 mL). The crude product (*Z*/*E*: 96:4) afforded a mixture of fluoroalkene **6** (71.5 mg, 78%) as a white solid.

From sulfone **3a** (79 mg, 0.26 mmol), 2,5-dibromobenzaldehyde (72.4 mg, 0.27 mmol), NaHMDS (390 μL, 0.39 mmol), and THF (6 mL). The crude product (*Z*/*E*: 98:2) afforded a mixture of fluoroalkene **6** (47.9 mg, 52%) as a white solid.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, $^4J_{HH}$=2.3 Hz, 1H), 7.48 (d, $^3J_{HH}$=9.0 Hz, 1H), 7.33 (dd, $^3J_{HH}$=9.0 Hz, $^4J_{HH}$=2.3 Hz, 1H), 7.23 (d, $^3J_{HFtrans}$=33.3 Hz, 1H), 4.37 (q, $^3J_{HH}$=7.4 Hz, 2H), 1.39 (t, $^3J_{HH}$=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, $^2J_{CF}$=34.6 Hz), 136.6 (d, $^1J_{CF}$=272.3 Hz), 134.3, 133.9 (d, $^2J_{CF}$=13.9 Hz), 133.5, 132.7 (d, $^3J_{CF}$=4.2 Hz), 123.3, 121.5, 11.4 (d, $^4J_{CF}$=3.4 Hz), 62.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.6 (d, $^3J_{HFtrans}$=33.3 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $^4J_{HH}$=2.4 Hz, 1H), 7.44 (d, $^3J_{HH}$=8.5 Hz, 1H), 7.33–7.30 (m, 1H), 6.83 (d, $^3J_{HFcis}$=18.5 Hz, 1H), 4.19 (q, $^3J_{HH}$=7.4 Hz, 2H), 1.18 (t, $^3J_{HH}$=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, $^2J_{CF}$=34.6 Hz), 148.3 (d, $^1J_{CF}$=276.2 Hz), 134.3, 133.9 (d, $^2J_{CF}$=13.9 Hz), 133.5, 132.7 (d, $^3J_{CF}$=4.2 Hz), 123.3, 121.5, 11.4 (d, $^4J_{CF}$=3.4 Hz), 61.9, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.1 (d, $^3J_{HFcis}$=18.5 Hz, 1F). HRMS (MS+) for $C_{11}H_{10}O_2F^{79}Br_2Na$ $(M+Na)^+$ calcd 350.9032, found 350.9035.

*4.5.3. Ethyl 2-fluoro-3-(thiophen-2-yl)acrylate (**7**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 2-thiophenecarboxaldehyde (40 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 99:1) afforded a mixture of fluoroalkene **7** (69.7 mg, 87%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), 2-thiophene carboxaldehyde (28.2 μL, 0.30 mmol), NaHMDS (440 μL, 0.44 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 83:17) afforded a mixture of fluoroalkene **7** (47.4 mg, 82%) as a colorless oil.

From sulfone **3a** (87.1 mg, 0.29 mmol), 2-thiophene carboxaldehyde (28.2 μL, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 83:17) afforded a mixture of fluoroalkene **7** (46.7 mg, 80%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, $^3J_{HH}$=5.0 Hz, 1H), 7.35 (d, $^3J_{HH}$=3.7 Hz, 1H), 7.20 (d, $^3J_{HFtrans}$=34.2 Hz, 1H), 7.11–7.05 (m, 1H), 4.13 (q, $^3J_{HH}$=7.1 Hz, 2H), 1.19 (t, $^3J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, $^2J_{CF}$=32.9 Hz), 145.7 (d, $^1J_{CF}$=265.2 Hz), 134.6 (d, $^3J_{CF}$=5.8 Hz), 133.8 (d, $^3J_{CF}$=5.5 Hz), 131.5 (d, $^3J_{CF}$=4.8 Hz), 112.2 (d, $^2J_{CF}$=8.8 Hz), 62.1, 17.8, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.2 (d, $^3J_{HFtrans}$=34.2 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $^3J_{HH}$=5.1 Hz, 1H), 7.38–7.36 (m, 1H), 7.10 (d, $^3J_{HFcis}$=24.3 Hz, 1H), 7.11–7.05 (m, 1H), 4.18 (q, $^3J_{HH}$=7.1 Hz, 2H), 1.16 (t, $^3J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, $^2J_{CF}$=33.8 Hz), 144.4 (d, $^1J_{CF}$=253.6 Hz), 133.2 (d, $^3J_{CF}$=8.8 Hz), 131.2 (d, $^3J_{CF}$=4.7 Hz), 130.4 (d, $^3J_{CF}$=9.8 Hz), 127.1, 117.4 (d, $^2J_{CF}$=33.0 Hz),

62.0, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.9 (d, $^3J_{HFcis}$=24.3 Hz, 1F).

*4.5.4. Ethyl 2-fluoro-3-(furan-2-yl)acrylate (**8**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 2-furaldehyde (35 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 99:1) afforded a mixture of fluoroalkene **8** (49.5 mg, 87%) as a colorless oil.

From sulfone **3a** (121 mg, 0.40 mmol), 2-furaldehyde (35 μL, 0.42 mmol), NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 88:12) afforded a mixture of fluoroalkene **8** (55.2 mg, 75%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.51 (m, 1H), 6.94 (d, $^3J_{HFtrans}$=33.4 Hz, 1H), 6.86–6.84 (m, 1H), 6.52–6.51 (m, 1H), 4.32 (q, $^3J_{HH}$=7.1 Hz, 2H), 1.36 (t, $^3J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, $^2J_{CF}$=28.0 Hz), 147.1 (d, $^3J_{CF}$=4.3 Hz), 145.4 (d, $^1J_{CF}$=266.4 Hz), 144.5 (d, $^2J_{CF}$=3.9 Hz), 115.5 (d, $^3J_{CF}$=11.3 Hz), 112.8, 107.5 (d, $^3J_{CF}$=8.5 Hz), 62.0, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.6 (d, $^3J_{HFtrans}$=33.4 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.51 (m, 1H), 6.86–6.84 (m, 1H), 6.65 (d, $^3J_{HFcis}$=21.3 Hz, 1H), 6.52–6.51 (m, 1H), 4.32 (q, $^3J_{HH}$=7.1 Hz, 2H), 1.23 (t, $^3J_{HH}$=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $^2J_{CF}$=33.4 Hz), 146.3 (d, $^2J_{CF}$=10.4 Hz), 144.9 (d, $^1J_{CF}$=256.8 Hz), 144.3 (d, $^3J_{CF}$=4.7 Hz), 116.2 (d, $^3J_{CF}$=6.4 Hz), 112.8, 111.7 (d, $^2J_{CF}$=33.2 Hz), 61.8, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.8 (d, $^3J_{HFcis}$=21.3 Hz, 1F).

*4.5.5. Ethyl 2-fluoronon-2-enoate (**9**).* General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), heptanal (84 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 100:0) afforded *Z*-fluoroalkene **9** (67.7 mg, 84%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), heptanal (42.3 μL, 0.30 mmol), NaHMDS (440 μL, 0.44 mmol) in THF (6.6 mL). The crude product (*Z*/*E*: 74:26) afforded a mixture of fluoroalkene **9** (34.7 mg, 60%) as a colorless oil.

From sulfone **3a** (87.1 mg, 0.29 mmol), heptanal (42.3 μL, 0.30 mmol), NaHMDS (440 μL, 0.44 mmol) in THF (6.6 mL). The crude product (*Z*/*E*: 53:47) afforded a mixture of fluoroalkene **9** (34.7 mg, 50%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (dt, $^3J_{HFtrans}$=33.3 Hz, $^3J_{HH}$=7.0 Hz, 1H), 4.31–4.24 (m, 2H), 2.23 (dq, $^3J_{HH}$=7.4 Hz, $^4J_{HF}$=2.2 Hz, 2H), 1.45–1.41 (m, 2H), 1.39–1.23 (m, 9H), 0.89 (t, $^3J_{HH}$=6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, $^2J_{CF}$=35.5 Hz), 147.9 (d, $^1J_{CF}$=255.0 Hz), 146.9 (d, $^2J_{CF}$=11.9 Hz), 61.4, 31.5, 28.8, 28.3 (d, $^4J_{CF}$=1.8 Hz), 24.2 (d, $^3J_{CF}$=2.5 Hz), 22.5, 14.1, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.1 (dt, $^3J_{HFtrans}$=33.3 Hz, $^4J_{HF}$=2.2 Hz, 1F). *(E)-Isomer*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (dt, $^3J_{HFcis}$=21.8 Hz, $^3J_{HH}$=8.2 Hz, 1H), 4.31–4.24 (m, 2H), 2.50 (dq, $^3J_{HH}$=8.1 Hz, $^4J_{HF}$=1.6 Hz, 2H), 1.45–1.41 (m, 2H), 1.39–1.23 (m, 9H), 0.89 (t, $^3J_{HH}$=6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, $^2J_{CF}$=36.0 Hz), 146.9 (d, $^1J_{CF}$=250.0 Hz), 123.8 (d, $^2J_{CF}$=17.4 Hz), 61.2, 31.5, 29.2 (d, $^4J_{CF}$=2.0 Hz), 28.8, 25.4 (d, $^3J_{CF}$=5.0 Hz), 22.5, 14.1, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.8 (dt, $^3J_{HFcis}$=21.8 Hz, $^4J_{HF}$=1.6 Hz, 1F). HRMS (MS+) for $C_{11}H_{19}O_2FNa$ $(M+Na)^+$ calcd 225.1267, found 225.1264.

*4.5.6. Ethyl 2-fluoroundec-2-enoate (**10**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), nonanal (69 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 99:1) afforded a mixture of fluoroalkene **10** (67.3 mg, 73%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), nonanal (52 μL, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 84:16) afforded a mixture of fluoroalkene **10** (61 mg, 92%) as a colorless oil.

From sulfone **3a** (87.1 mg, 0.29 mmol), nonanal (52 μL, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 46:54) afforded a mixture of fluoroalkene **10** (53.6 mg, 81%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, $^3J_{HFtrans}$=33.5 Hz, $^3J_{HH}$=8.2 Hz, 1H) 4.20 (m, 2H), 2.18–2.48 (m, 2H) 1.14–1.39 (m, 15H), 0.80 (t, $^3J_{HH}$=10.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, $^2J_{CF}$=35.4 Hz), 147.3 (d, $^1J_{CF}$=248.6 Hz), 121.2 (d, $^2J_{CF}$=36.1 Hz), 61.8, 37.4, 32.2, 30.0, 29.6, 29.5, 28.7 (d, $^3J_{CF}$=1.7 Hz), 24.5 (d, $^4J_{CF}$=2.6 Hz), 22.9, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.1 (d, $^3J_{HFtrans}$=33.3 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dt, $^3J_{HFcis}$=21.2 Hz, $^3J_{HH}$=7.9 Hz, 1H), 4.20 (m, 2H), 2.18–2.48 (m, 2H) 1.14–1.39 (m, 15H), 0.80 (t, $^3J_{HH}$=10.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, $^2J_{CF}$=35.8 Hz), 142.1 (d, $^1J_{CF}$=235.2 Hz), 124.2 (d, $^2J_{CF}$=36.1 Hz), 61.8, 37.4, 32.2, 30.0, 29.6, 29.5, 28.7 (d, $^3J_{CF}$=1.7 Hz), 24.5 (d, $^4J_{CF}$=2.6 Hz), 22.9, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.8 (d, $^3J_{HFcis}$=21.5 Hz, 1F).

*4.5.7. Ethyl 2-fluorotrideca-2,4-dienoate (**11**).* General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 10-undecenal (84 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 96:4) afforded a mixture of fluoroalkene **11** (74.9 mg, 79%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), 10-undecenal (60 μL, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 85:15) afforded a mixture of fluoroalkene **11** (60.4 mg, 82%) as a colorless oil.

From sulfone **3a** (87.1 mg, 0.29 mmol), 10-undecenal (60 μL, 0.30 mmol), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 43:57) afforded a mixture of fluoroalkene **11** (48.8 mg, 66%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (dt, $^3J_{HFtrans}$=33.5 Hz, $^3J_{HH}$=7.7 Hz, 1H), 5.79 (ddt, $^3J_{HH}$=17.0 Hz, $^3J_{HH}$=13.4 Hz, $^3J_{HH}$=6.7 Hz, 1H), 4.98 (ddt, $^3J_{HH}$=17.0 Hz, $^3J_{HH}$=3.8 Hz, $^4J_{HH}$=1.5 Hz, 1H), 4.92 (ddt, $^3J_{HH}$=13.4 Hz, $^3J_{HH}$=3.8 Hz, $^4J_{HH}$=1.2 Hz, 1H), 4.26 (q, $^3J_{HH}$=7.2 Hz, 2H), 2.25–2.19 (m, 2H), 2.05–2.00 (m, 2H), 1.42–1.27 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, $^2J_{CF}$=32.2 Hz), 147.9 (d, $^1J_{CF}$=257.6 Hz), 139.1, 120.7 (d, $^2J_{CF}$=12.0 Hz), 114.1, 61.4, 33.7, 29.3, 29.2, 29.1, 29.0, 28.8, 28.2 (d, $^4J_{CF}$=1.8 Hz), 24.2 (d, $^3J_{CF}$=2.6 Hz), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.1 (dt, $^3J_{HFtrans}$=33.5 Hz, $^5J_{HF}$=2.0 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dt, $^3J_{HFcis}$=21.8 Hz, $^3J_{HH}$=8.2 Hz, 1H), 5.79 (ddt, $^3J_{HH}$=17.0 Hz, $^3J_{HH}$=13.4 Hz, $^3J_{HH}$=6.7 Hz, 1H), 4.92 (ddt, $^3J_{HH}$=13.4 Hz, $^3J_{HH}$=3.8 Hz, $^4J_{HH}$=1.2 Hz, 1H), 4.29 (q, $^3J_{HH}$=7.2 Hz, 2H), 2.52–2.46 (m, 2H), 2.05–2.00 (m, 2H), 1.42–1.27 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, $^2J_{CF}$=36.2 Hz), 146.9 (d, $^1J_{CF}$=248.7 Hz), 139.1, 123.8 (d, $^2J_{CF}$=17.9 Hz), 114.1, 61.2, 33.7, 29.3, 29.2, 29.1, 29.0, 28.8, 28.2 (d, $^4J_{CF}$=1.8 Hz), 25.4 (d, $^3J_{CF}$=5.4 Hz), 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.7 (dt, $^3J_{HFcis}$=21.8 Hz, $^5J_{HF}$=1.4 Hz, 1F). HRMS (MS+) for $C_{15}H_{25}O_2FNa$ $(M+Na)^+$ calcd 279.1736, found 279.1747.

*4.5.8. (S)-Ethyl 2-fluoro-5,9-dimethyldeca-2,8-dienoate (**12**).*[21] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), (*S*)-citronellal (76 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 97:3) afforded a mixture of fluoroalkene **12** (78.4 mg, 81%) as a colorless oil.

From sulfone **3a** (121 mg, 0.40 mmol), (*S*)-citronellal (76 μL, 0.42 mmol), NaHMDS (600 μL, 0.60 mmol), and THF (8.8 mL). The crude product (*Z*/*E*: 55:45) afforded a mixture of fluoroalkene **12** (47.5 mg, 49%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (dt, $^3J_{HFtrans}$=33.2 Hz, $^3J_{HH}$=7.6 Hz, 1H), 5.07 (t, $^3J_{HH}$=7.6 Hz, 1H), 4.26 (q, $^3J_{HH}$=7.0 Hz, 2H), 2.26–2.18 (m, 1H), 2.14–2.06 (m, 1H), 2.04–1.92 (m, 2H), 1.67 (s, 3H), 1.63–1.57 (m, 1H), 1.58 (s, 3H), 1.38–1.30 (m,

1H), 1.32 (t, $^{3}J_{HH}$=7.0 Hz, 3H), 1.24–1.15 (m, 1H), 0.91 (d, $^{3}J_{HH}$=6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $^{2}J_{CF}$=35.3 Hz), 148.4 (d, $^{1}J_{CF}$=253.8 Hz), 131.4, 124.3, 119.3 (d, $^{3}J_{CF}$=11.7 Hz), 61.4, 36.5, 32.2 (d, $^{4}J_{CF}$=1.7 Hz), 31.2 (d, $^{5}J_{CF}$=1.7 Hz), 25.6, 25.4, 19.4, 17.5, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −130.5 (d, $^{3}J_{HFtrans}$=33.2 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (dt, $^{3}J_{HFcis}$=22.1 Hz, $^{3}J_{HH}$=8.1 Hz, 1H), 5.07 (t, $^{3}J_{HH}$=7.6 Hz, 1H), 4.28 (q, $^{3}J_{HH}$=7.0 Hz, 2H), 2.55–2.36 (m, 2H), 2.06–1.91 (m, 2H), 1.67 (s, 3H), 1.63–1.57 (m, 1H), 1.58 (s, 3H), 1.38–1.30 (m, 1H), 1.33 (t, $^{3}J_{HH}$=7.0 Hz, 3H), 1.24–1.15 (m, 1H), 0.91 (d, $^{3}J_{HH}$=6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, $^{2}J_{CF}$=35.9 Hz), 147.3 (d, $^{1}J_{CF}$=248.9 Hz), 131.4, 124.4, 122.5 (d, $^{3}J_{CF}$=17.9 Hz), 61.2, 36.6, 32.9 (d, $^{4}J_{CF}$=1.7 Hz), 32.4 (d, $^{5}J_{CF}$=4.5 Hz), 25.6, 25.4, 19.4, 17.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ −121.4 (d, $^{3}J_{HFcis}$=22.1 Hz, 1F).

*4.5.9. Ethyl 2-fluoro-5-phenylpent-2-enoate (**13**).*[22] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), 3-phenylpropanal (55 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 97:3) afforded a mixture of fluoroalkene **13** (46 mg, 52%) as a colorless oil.

From sulfone **3a** (121 mg, 0.40 mmol), 3-phenylpropanal (55 μL, 0.42 mmol), NaHMDS (600 μL, 0.60 mmol), and THF (8.8 mL). The crude product (*Z*/*E*: 69:31) afforded a mixture of fluoroalkene **13** (35.8 mg, 40%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, $^{3}J_{HH}$=7.5 Hz, 2H), 7.25 (d, $^{3}J_{HH}$=7.5 Hz, 1H), 7.22 (d, $^{3}J_{HH}$=7.5 Hz, 2H), 6.17 (dt, $^{3}J_{HFtrans}$=33.3 Hz, $^{3}J_{HH}$=7.8 Hz, 1H), 4.29 (q, $^{3}J_{HH}$=7.1 Hz, 2H), 2.79 (t, $^{3}J_{HH}$=7.9 Hz, 2H), 2.59 (dtd, $^{3}J_{HH}$=7.9 Hz, $^{3}J_{HH}$=7.8 Hz, $^{4}J_{HF}$=1.9 Hz, 2H), 1.34 (t, $^{3}J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7 (d, $^{2}J_{CF}$=35.2 Hz), 148.1 (d, $^{1}J_{CF}$=254.9 Hz), 140.5, 128.4 (2C), 128.2 (2C), 126.2, 119.4 (d, $^{2}J_{CF}$=11.5 Hz), 61.4, 34.3 (d, $^{4}J_{CF}$=1.9 Hz), 25.8 (d, $^{3}J_{CF}$=2.4 Hz), 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −129.6 (dt, $^{3}J_{HFtrans}$=33.3 Hz, $^{4}J_{HF}$=1.9 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.21 (m, 5H), 5.95 (dt, $^{3}J_{HFcis}$=21.5 Hz, $^{3}J_{HH}$=8.2 Hz, 1H), 4.31 (q, $^{3}J_{HH}$=7.1 Hz, 2H), 2.90–2.77 (m, 4H), 1.36 (t, $^{3}J_{HH}$=7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $^{2}J_{CF}$=35.5 Hz), 147.3 (d, $^{1}J_{CF}$=250.7 Hz), 140.6, 128.4 (2C), 128.2 (2C), 126.1, 122.3 (d, $^{2}J_{CF}$=18.4 Hz), 61.3, 35.2 (d, $^{4}J_{CF}$=2.3 Hz), 27.1 (d, $^{3}J_{CF}$=5.0 Hz), 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ −121.7 (d, $^{3}J_{HFcis}$=21.5 Hz, 1F).

*4.5.10. Ethyl 3-cyclohexyl-2-fluoroacrylate (**14**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), cyclohexylcarboxaldehyde (84 μL, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 96:4) afforded a mixture of fluoroalkene **14** (74.9 mg, 79%) as a colorless oil.

From sulfone **3b** (100 mg, 0.29 mmol), cyclohexylcarboxaldehyde (36.5 μL), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 88:12) afforded a mixture of fluoroalkene **14** (34.4 mg, 60%) as a colorless oil.

From sulfone **3a** (87.1 mg, 0.29 mmol), cyclohexylcarboxaldehyde (36.5 μL), NaHMDS (320 μL, 0.32 mmol), and THF (6.6 mL). The crude product (*Z*/*E*: 71:29) afforded a mixture of fluoroalkene **14** (35.8 mg, 62%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, $^{3}J_{HFtrans}$=33.6 Hz, $^{3}J_{HH}$=9.6 Hz, 1H), 4.16–4.27 (m, 2H), 2.47–2.50 (m, 1H), 1.57–1.65 (m, 4H), 1.01–1.29 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, $^{2}J_{CF}$=36.1 Hz), 147.1 (d, $^{1}J_{CF}$=255.2 Hz), 129.0 (d, $^{2}J_{CF}$=15.3 Hz), 61.6, 34.1, 32.2, 26.0, 25.9, 25.7, 25.6, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.8 (d, $^{3}J_{HFtrans}$=33.9 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dd, $^{3}J_{HFcis}$=22.00 Hz, $^{3}J_{HH}$=10.4 Hz, 1H), 4.16–4.27 (m, 2H), 2.99–3.01 (m, 1H), 1.57–1.65 (m, 4H), 1.01–1.29 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, $^{2}J_{CF}$=36.2 Hz), 146.3 (d, $^{1}J_{CF}$=251.7 Hz), 125.8 (d, $^{2}J_{CF}$=11.2 Hz), 61.4, 34.8 (d, $^{3}J_{CF}$=4.6 Hz), 33.0, 26.0, 25.9, 25.7, 25.6, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.1 (d, $^{3}J_{HFcis}$=22.4 Hz, 1F).

*4.5.11. (1S,3S)-Methyl 3-(3-ethoxy-2-fluoro-3-oxoprop-1-enyl)-2,2-dimethylcyclopropane-carboxylate (**15**).*[8b] General procedure was followed with sulfone **3d** (100 mg, 0.40 mmol), biocartolmethylester (66 mg, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 95:5) afforded a mixture of fluoroalkene **15** (69.9 mg, 72%) as a colorless oil.

From sulfone **3a** (121 mg, 0.40 mmol), biocartolmethylester (66 mg, 0.42 mmol), and NaHMDS (600 μL, 0.60 mmol) in THF (8.8 mL). The crude product (*Z*/*E*: 33:67) afforded a mixture of fluoroalkene **15** (55.3 mg, 57%) as a colorless oil.

(Z)-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (dt, $^{3}J_{HFtrans}$=32.3 Hz, $^{3}J_{HH}$=10.5 Hz, 1H), 4.30–4.19 (m, 2H), 3.65 (s, 3H), 2.16 (dd, $^{2}J_{HH}$=10.5 Hz, $^{3}J_{HH}$=8.5 Hz, 1H), 1.88 (d, $^{3}J_{HH}$=8.5 Hz, 1H), 1.31–1.28 (m, 3H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 160.7 (d, $^{2}J_{CF}$=35.2 Hz), 149.7 (d, $^{1}J_{CF}$=255.2 Hz), 119.7 (d, $^{2}J_{CF}$=24.8 Hz), 61.7, 51.7, 33.0, 28.7, 29.0 (d, $^{3}J_{CF}$=7.4 Hz), 15.1 (2C), 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −132.5 (d, $^{3}J_{HFtrans}$=31.4 Hz, 1F). *(E)-Isomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dt, $^{3}J_{HFcis}$=20.9 Hz, $^{3}J_{HH}$=10.3 Hz, 1H), 4.30–4.19 (m, 2H), 3.58 (s, 3H), 2.77 (ddd, $^{2}J_{HH}$=10.0 Hz, $^{3}J_{HH}$=8.5 Hz, $^{3}J_{HH}$=1.3 Hz, 1H), 1.84 (d, $^{3}J_{HH}$=8.5 Hz, 1H), 1.31–1.28 (m, 3H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 161.6 (d, $^{2}J_{CF}$=34.6 Hz), 148.3 (d, $^{1}J_{CF}$=252.1 Hz), 116.3 (d, $^{2}J_{CF}$=7.5 Hz), 61.5, 51.7, 32.5, 28.6, 28.2 (d, $^{3}J_{CF}$=5.1 Hz), 14.9 (2C), 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.9 (d, $^{3}J_{HFcis}$=21.2 Hz, 1F).

Acknowledgements

The authors acknowledge the European Regional Development Fund (ERDF) for co-financing the ISCE-Chem project (No. 1907/4061) through the INTERREG IV A France (Channel)—England cross-border cooperation Programme.

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