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# A new synthesis of α-fluorovinylsulfones utilizing the Peterson olefination methodology

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**Abstract**

α-Fluoro-α-silyl-substituted sulfones **1** are readily prepared from fluoromethyl phenyl sulfone and the appropriate silyl chloride. The use of TBSCl improves both the stability and yield of **1**. Lithium derivatives **4** undergo a smooth Peterson olefination reaction with less-enolizable carbonyl compounds to give moderate to good yields of the expected α-fluorovinylsulfones **6**, in some cases with high *E*-stereoselectivity. One-pot reaction with **4** generated in situ from fluoromethyl phenyl sulfone in tetrahydrofuran (THF) also proceeds smoothly, particularly with aldehydes.


*Keywords:* α-Fluoro-α-silyl sulfone; Peterson olefination; Monofluorinated building block

## 1. Introduction

In the past few decades, interest in fluorinated compounds has increased significantly due to the unique influence of the fluorine substituent on the chemical, physical, and physiological properties of these compounds [1]. Functionalized fluoroolefins are particularly important, with current applications in the synthesis of biologically active materials such as peptide isosteres and enzyme inhibitors [2]. Several fluoroolefination methods have been reported (for reviews, see [3]), and monofluorinated vinylsulfones have been shown as an attractive approach toward a range of fluoroolefins [4–6]. Unsaturated sulfones themselves also have many synthetic applications [7]. The electron-withdrawing sulfonyl moiety is a useful functional group for further transformation, and removal of the sulfonyl group after completion of the procedure by reductive desulfonylation provides access to sulfur-free products [8]. Peterson olefination is a prominent method amongst the numerous reported techniques for the connective synthesis of alkenes [9–15]. This report describes a new preparation of fluorinated vinylsulfones by Peterson coupling between α-fluoro-α-silyl sulfone anions and less-enolizable carbonyl compounds.

## 2. Results and discussion

α-Fluoro-α-silyl sulfones **1–3** were readily prepared by deprotonation and subsequent silylation of fluoromethyl phenylsulfone. The use of TBSCl improved both the stability and yield of **1** (Table 1).

Treatment of **1** with 1 eq. of *n*-BuLi in tetrahydrofuran (THF) provided the lithiated sulfone **4**, which cleanly reacted with aldehydes to induce an aldol condensation. The so-formed β-oxidosilane intermediate **5** has been shown to undergo a *syn* β-elimination to form the corresponding α-fluorovinylsulfones (**6**, usually an *E*/*Z* mixture) under basic conditions (Table 2).

The stereochemistry of **6** was assigned by the hydrogen–fluorine vicinal coupling constants ($^3J_{HF}$). The 'butterfly' transition states with chelating control are well established [13,14], and the formation of a closed four-centered transition state could be assumed. Of the two configurations (**A** and **B**) of **5**, which have the *syn* alignment of alkoxide and silicon, **5A**, which would lead to the *E*-isomer, is preferable in terms of steric factor [16].

A partial separation of *E*- and *Z*-isomers was achieved by silica gel flash column chromatography to give a *Z*-major mixture of **6c** (*E*/*Z* = 1/20), which was isomerized to an *E*-major mixture (*E*/*Z* = 10/1) using catalytic amounts of thiophenol and AIBN in benzene under reflux, according to the Sato protocol (Scheme 1) [17].

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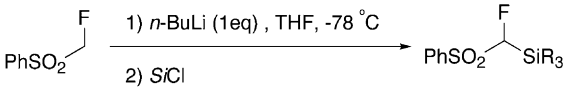
Table 1
Preparation of α-fluoro-α-silyl sulfones **1–3**

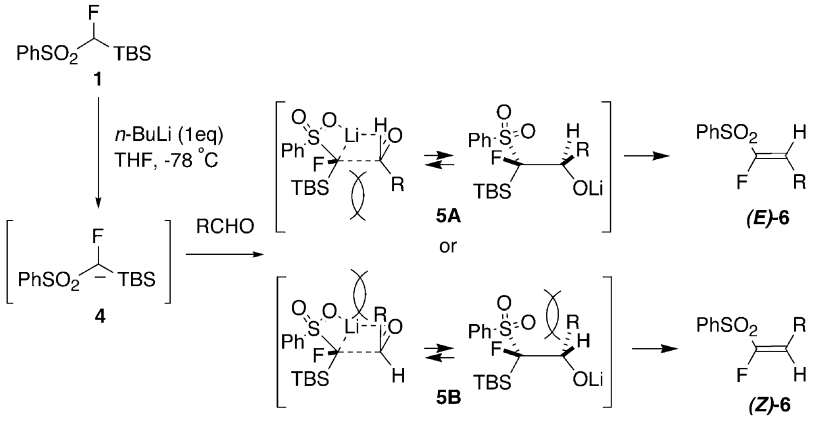



| *Si*Cl | Product | Yield (%) |
|---|---|---|
| TBSCl | **1** ($SiR_3$=TBS) | 68 |
| TMSCl | **2** ($SiR_3$=TMS) | 30 |
| DPMSCl | **3** ($SiR_3$=DPMS) | 18 |

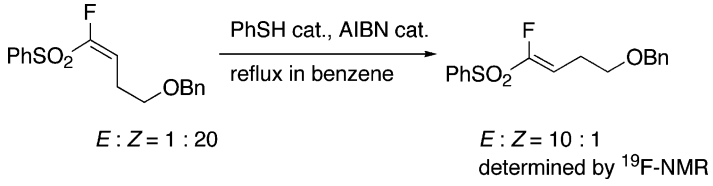
The aldol condensation of lithiofluoromethyl phenyl sulfone with benzaldehyde and the following acetylation afforded β-acetoxy-α-fluoro sulfone **7** in good yield (95%) as a 2:3 mixture of diastereomers (Scheme 2).

The configuration of the major isomer **7B** is characterized by an anti-alignment of the acetoxy group and fluorine atom, with a smaller hydrogen–fluorine vicinal coupling constant ($^3J_{HF} = 10.5$ Hz) than that ($^3J_{HF} = 26.0$ Hz) of minor isomer **7A** as shown above, which forms (*Z*)-**6a** through an anti β-elimination upon treatment with

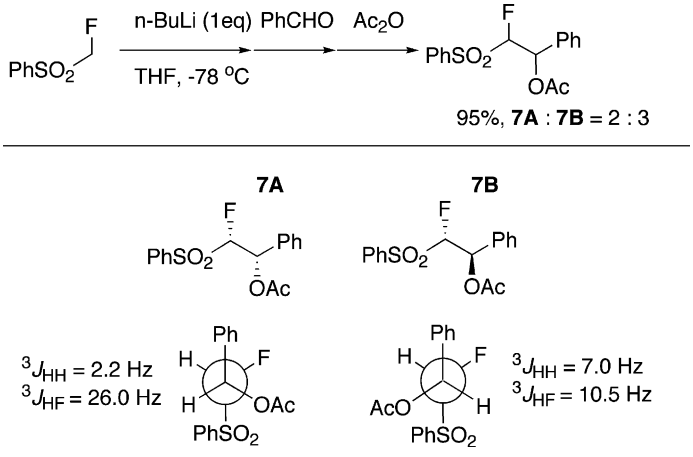
Table 2
α-Fluorovinylsulfonylation of aldehydes with **1**



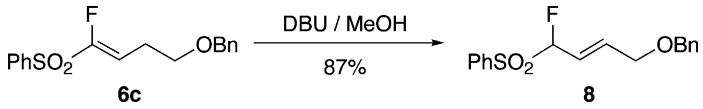

| RCHO | Product | Yield (%) | *E*:*Z* |
|---|---|---|---|
| PhCHO | **6a** | 65 | 7:1 |
| *i*PrCHO | **6b** | 54 | 4:1 |
| $BnOCH_2CH_2CHO$ | **6c** | 34 | 3.3:1 |




Scheme 1.




Scheme 2.



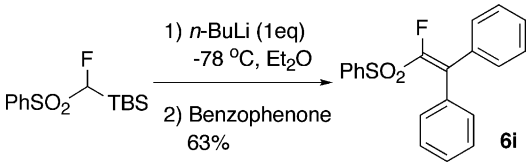

6c 8

Scheme 3.

1,8-diazabicyclo[5,4,0]undec-7-ene (DBU). However, it has been reported that allyl sulfones are more thermodynamically stable than the corresponding vinyl isomers [18]. Treatment of vinyl sulfone **6c** with DBU resulted in exclusive isomerization to allyl sulfone **8** (Scheme 3). This result suggests that the aldol–acylation–elimination sequence is not a general method to α-fluorovinylsulfone [4].

The authors then turned their attention toward one-pot synthesis of **4** as encouraged by the analogous Peterson olefination with α-silyl phosphorus stabilized carbanion generated in situ [13,15]. Fluoromethyl phenyl sulfone was treated with *n*-BuLi (2 eq.) in THF at −78 °C to afford *gem*-dianion, and the subsequent addition of TBSCl (1 eq.) was effective for the formation of **4** in pure form. At low temperature in THF, **4** readily underwent aldol condensation with aldehydes. The Peterson olefination reaction occurred exclusively to give the corresponding α-fluorovinylsulfones (**6**) in modest to good yields with *E*-stereoselectivity. The results are summarized in Table 3.

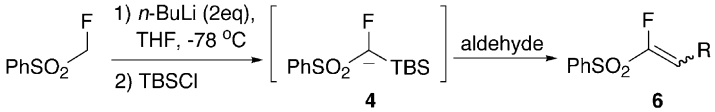
However, the reaction of **4** thus prepared with ketones was not effective (Table 4). In most cases, except cyclohexanone,




6i

Scheme 4.

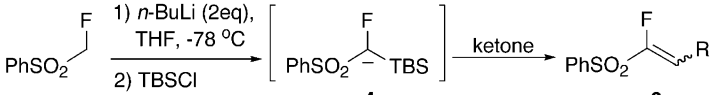
Table 3
One-pot preparation of α-fluorovinylsulfones **6** from aldehydes



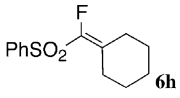
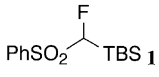

4 6

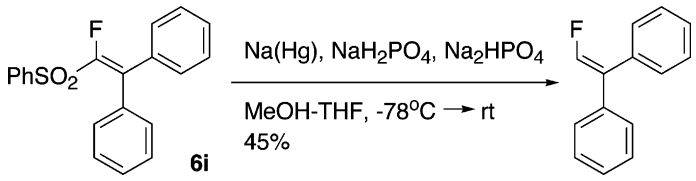
| Entry | Aldehyde | Product | Yield (%) (*E*:*Z*) |
|---|---|---|---|
| 1 | PhCHO | **6a** | 52 (3.3:1) |
| 2 | *i*PrCHO | **6b** | 41 (4:1) |
| 3 | $BnOCH_2CH_2CHO$ | **6c** | 42 (3.5:1) |
| 4 | $CH_3CH_2CH_2CHO$ | **6d** | 48 (7:1) |
| 5 | $CH_3(CH_2)_6CHO$ | **6e** | 44 (5:1) |
| 6 | $PhCH_2CH_2CHO$ | **6f** | 52 (9:1) |
| 7 | 2-Furaldehyde | **6g** | 36 (20:1) |

Table 4
Reaction of **4** with ketones




4 6

| Entry | Ketone | Product | Yield (%) |
|---|---|---|---|
| 1 | Cyclohexanone |  **6h** | 55 |
| 2 | Cycloheptanone | | |
| 3 | Benzophenone | | |
| 4 | Acetophenone |  **1** | 30–60 |
| 5 | 4-Heptanone | | |
| 6 | 2-Heptanone | | |
| 7 | 2-Heptanone with $CeCl_3$ | | |




Scheme 5.

the enolization of ketones overcame the aldol condensation to give α-silyl sulfone **1** as the main product. Interestingly, McCarthy demonstrated the one-pot Horner–Wittig reaction of diethyl 1-fluoro-1-(phenylsulfonyl)methane-phosphonate with ketones to afford the corresponding α-fluorovinylsulfones [5,6].

α-Fluorovinylsulfonylation of benzophenone by Peterson olefination was realized using a stepwise reaction in $Et_2O$. Treatment of **1** with 1 eq. of *n*-BuLi in $Et_2O$ provided the lithiated sulfone **4**, which cleanly reacted with less-enolizable ketones to induce a Peterson olefination reaction. The corresponding α-fluorovinylsulfone (**6i**) was obtained (Scheme 4).

Reductive removal of the phenylsulfonyl moiety from **6i** was readily achieved by treatment with sodium amalgam in the presence of $NaH_2PO_4$–$Na_2HPO_4$ (Scheme 5).

## 3. Conclusion

α-Fluorovinylsulfones **6** were stereospecifically prepared by the Peterson olefination of less-enolizable carbonyl compounds with α-fluoro-α-silyl sulfones prepared from fluoromethyl phenyl sulfone and the appropriate silyl chloride.

## 4. Experimental

All air- and moisture-sensitive reactions were carried out in flame-dried, argon-flushed, two-necked flasks sealed with rubber septa, and the dry solvents and reagents were introduced using a syringe. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Flash column chromatography was carried out on a Kanto Chemical silica gel 60N (spherical, neutral, 40–50 μm), and pre-coated Merck silica gel plates (Art5715 Kieselgel $60F_{254}$, 0.25 mm) were used for thin-layer chromatography (TLC). Unless mentioned otherwise, $^1H$, $^{13}C$ and $^{19}F$ nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a JEOL JNM-LA400 or JEOL JNM-LA300. Coupling constants were determined directly from $^1H$, $^{13}C$ and $^{19}F$ NMR spectra. Chemical shifts of $^{19}F$ NMR were given by $\delta$ relative to that of an external trifluoroacetic acid (TFA). Mass spectra were obtained on a JEOL JMS-700T or JEOL JMS-AX500 spectrometer. Infrared (IR) spectra were recorded on a JASCO FT/IR-700.

### 4.1. Typical procedure for the preparation of α-fluoro-α-silyl sulfones (*1*–*3*)

Under an Ar atmosphere, to a solution of fluoromethyl phenyl sulfone (1.74 g, 10.0 mmol) in THF (15 ml) was added *n*-BuLi (1.55 M solution in hexane; 6.9 ml, 11.0 mmol) at −78 °C. After 30 min stirring at this temperature, to the mixture was added dropwise a solution of *tert*-butyldimethylsilyl chloride (1.56 g, 10.0 mmol) in THF (6 ml). The reaction mixture was allowed to warm to room temperature and stirred overnight. A solution of pH 7.0 phosphate buffer (15 ml) was poured into the reaction mixture, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried ($Na_2SO_4$) and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography (10% EtOAc in hexane) to give **1** (1.97 g, 6.8 mmol; yield 68%).

#### 4.1.1. *tert*-Butyldimethylsilyl-fluoro-methyl phenyl sulfone (*1*)

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.30 (d, $^4J_{HF} = 1.2$ Hz, 3H), 0.38 (s, 3H), 0.98 (s, 9H), 5.19 (d, $^2J_{HF} = 47.1$ Hz, 1H), 7.53–7.58 (m, 2H), 7.63–7.67 (m, 1H), 7.92–7.94 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ −7.87 (d, $^3J_{CF} = 3.2$ Hz), −6.34 (d, $^3J_{CF} = 4.9$ Hz), 17.11, 26.20, 100.36 (d, $^1J_{CF} = 216.5$ Hz), 128.60, 129.09, 133.86, 138.51; $^{19}F$ NMR (283 MHz, $CDCl_3$) $\delta$ −7.04 (d, $^2J_{HF} = 47.1$ Hz); IR ($CH_2Cl_2$) *v* 3623, 3054, 2985, 2861, 1421, 1267, 1155, 1018, 896 $cm^{-1}$; MS (FAB) *m/z* 287 $[M-H]^-$; HRMS (FAB) Calcd for $C_{13}H_{20}O_2FSiS$ $[M-H]^-$: 287.0937. Found: 287.0954.

#### 4.1.2. Trimethylsilyl-fluoro-methyl phenyl sulfone (*2*)

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.30 (s, 9H), 5.08 (d, $^2J_{HF} = 46.8$ Hz, 1H), 7.45–7.50 (m, 2H), 7.54–7.59 (m, 1H), 7.84–7.86 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ −3.06, 101.11 (d, $^1J_{CF} = 217.2$ Hz), 128.26, 129.00, 133.76, 134.66; $^{19}F$ NMR (283 MHz, $CDCl_3$) $\delta$ −9.61 (d, $^2J_{HF} = 46.8$ Hz); IR ($CH_2Cl_2$) *v* 3623, 3055, 2985, 2835, 1444, 1421, 1267, 1155, 1016 $cm^{-1}$; MS (FAB) *m/z* 245 $[M-H]^-$; HRMS (FAB) Calcd for $C_{11}H_{13}O_2FSiS$ $[M-H]^-$: 245.0468. Found: 245.0464.

#### 4.1.3. Diphenylmethylsilyl-fluoro-methyl phenyl sulfone (*3*)

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.99 (s, 3H), 5.57 (d, $^2J_{HF} = 46.3$ Hz, 1H), 7.34–7.55 (m, 9H), 7.60–7.99 (m,

6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ −5.35 (d, $^3J_{CF}$ = 3.3 Hz), 100.88 (d, $^1J_{CF}$ = 218.9 Hz), 127.86, 128.02, 128.16, 128.60, 129.00, 129.81, 130.41, 130.51, 133.91, 135.07, 135.26, 135.28, 137.07, 138.20; $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −5.14 (d, $^2J_{HF}$ = 46.3 Hz); IR ($CH_2Cl_2$) $\nu$ 3070, 3054, 3027, 3012, 1427, 1326, 1153, 1118, 821, 798, 698 cm$^{-1}$; MS (FAB) *m/z* 369 [$M$−H]$^-$; HRMS (FAB) Calcd for $C_{20}H_{18}O_2FSiS$ [$M$−H]$^-$: 369.0780. Found: 369.0776.

### 4.2. One-pot procedure for the synthesis of α-fluorovinylsulfone (**6**)

Under an Ar atmosphere, to a solution of fluoromethyl phenyl sulfone in THF (2 ml) was added *n*-BuLi (1.55 M solution in hexane; 1.4 ml, 2.1 mmol) at −78 °C. After 30 min stirring at this temperature, to the mixture was added dropwise a solution of *tert*-butyldimethylsilyl chloride (0.151 g, 1.0 mmol) in THF (1 ml). The mixture was stirred for 60 min at this temperature, and then a solution of carbonyl compound (1.0 mmol) in THF (1 ml) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred overnight. A solution of pH 7.0 phosphate buffer was then poured into the reaction mixture, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to afford the crude product, which was then purified by flash column chromatography (10% EtOAc in hexane).

#### 4.2.1. 1-Fluoro-1-phenylsulfonyl-styrene (**6a**)

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.05 (d, $^3J_{HF}$ = 34.6 Hz, 1H), 7.31–7.70 (m, 8H), 7.85–8.01 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 115.45, 128.49, 128.86, 129.37, 130.05, 130.12, 130.31 (d, $^3J_{CF}$ = 2.5 Hz, C-3), 134.35, 137.31, 153.42 (d, $^1J_{CF}$ = 304.0 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −125.42 (d, $^3J_{HF}$ = 34.6 Hz); IR ($CH_2Cl_2$) $\nu$ 3624, 3055, 2985, 2835, 1423, 1267, 1163, 1018, 897 cm$^{-1}$; MS (EI) *m/z* 262 [$M^+$], HRMS (EI) Calcd for $C_{14}H_{11}O_2FS$: 262.0464. Found: 262.0438. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.90 (d, $^3J_{HF}$ = 21.9 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 118.92 (d, $^2J_{CF}$ = 19.0 Hz, C-2), 127.98, 128.63, 129.09, 129.29, 129.33, 129.75 (d, $^3J_{CF}$ = 2.5 Hz, C-3), 134.38, 137.79, 153.02 (d, $^1J_{CF}$ = 290.0 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −112.35 (d, $^3J_{HF}$ = 21.9 Hz).

#### 4.2.2. 1-Fluoro-1-phenylsulfonyl-3-methyl-but-1-ene (**6b**)

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.00–1.04 (m, 6H), 2.70 (m, 1H), 6.10 (dd, $^3J_{HH}$ = 9.8 Hz, $^3J_{HF}$ = 33.2 Hz, 1H), 7.50–7.56 (m, 2H), 7.61–7.67 (m, 1H), 7.88–7.93 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.75 (d, $^4J_{CF}$ = 1.7 Hz, C-4, C-5), 24.89 (d, $^3J_{CF}$ = 1.7 Hz, C-3), 124.50 (d, $^2J_{CF}$ = 6.6 Hz, C-2), 128.45, 129.32, 134.22, 137.52, 152.74 (d, $^1J_{CF}$ = 293.2 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −130.21 (d, $^3J_{HF}$ = 33.2 Hz); IR ($CH_2Cl_2$) $\nu$ 3626, 3055, 2985, 1423, 1333, 1267, 1151, 895 cm$^{-1}$; MS (EI) *m/z* 228 [$M^+$], HRMS (EI) Calcd for $C_{11}H_{13}O_2FS$: 228.0620. Found: 228.0625. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.53 (m, 1H), 5.62 (dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HF}$ = 22.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 22.81 (d, $^4J_{CF}$ = 2.4 Hz, C-4, C-5), 24.57 (d, $^3J_{CF}$ = 3.3 Hz, C-3), 126.87 (d, $^2J_{CF}$ = 9.9 Hz, C-2), 128.20, 129.34, 134.32, 138.45, 150.93 (d, $^1J_{CF}$ = 285.7 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −119.61 (d, $^3J_{HF}$ = 22.5 Hz).

#### 4.2.3. 4-Benzyloxy-1-fluoro-1-phenylsulfonyl-but-1-ene (**6c**)

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.45 (qd, $^4J_{HF}$ = 2.4 Hz, $^3J_{HH}$ = 7.6 Hz, 2H), 3.49 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 4.43 (s, 2H), 6.32 (dt, $^3J_{HH}$ = 7.6 Hz, $^3J_{HF}$ = 32.7 Hz, 1H), 7.18–7.29 (m, 5H), 7.41–7.51 (m, 2H), 7.54–7.64 (m, 1H), 7.82–7.98 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 25.04 (d, $^3J_{CF}$ = 2.5 Hz, C-3), 67.44, 72.90, 115.61 (d, $^2J_{CF}$ = 6.6 Hz, C-2), 127.53, 127.65, 128.26, 128.35, 128.45, 128.91, 129.29, 134.24, 137.38, 154.81 (d, $^1J_{CF}$ = 295.0 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −127.67 (d, $^3J_{HF}$ = 32.7 Hz); IR ($CH_2Cl_2$) $\nu$ 3626, 3055, 2985, 2866, 1421, 1263, 1167, 1018, 897 cm$^{-1}$; MS (FAB) *m/z* 319 [$M$ + H]$^+$, HRMS (FAB) Calcd for $C_{17}H_{16}O_3FS$ ($M$ + H)$^+$: 319.0795. Found: 319.0805. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.89–2.95 (m, 2H), 3.52–3.55 (m, 2H), 4.45 (s, 2H), 5.93 (dt, $^3J_{HH}$ = 8.1 Hz, $^3J_{HF}$ = 21.7 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 27.60 (C-3), 65.75, 67.47, 117.81 (d, $^2J_{CF}$ = 7.1 Hz, C-2), 151.11 (d, $^1J_{CF}$ = 270.3 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −115.95 (d, $^3J_{HF}$ = 21.7 Hz).

#### 4.2.4. 1-Fluoro-1-phenylsulfonyl-pent-1-ene (**6d**)

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.81–0.95 (m, 3H), 1.45 (sextet, $^3J_{HH}$ = 7.3 Hz, 2H), 2.17 (qd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HF}$ = 2.2 Hz, 2H), 6.23 (dt, $^3J_{HH}$ = 7.3 Hz, $^3J_{HF}$ = 32.7 Hz, 1H), 7.54 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.64 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.91 (d, $^3J_{HH}$ = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.31 (C-5), 21.21 (d, $^4J_{CF}$ = 1.6 Hz, C-4), 25.90 (d, $^3J_{CF}$ = 1.7 Hz, C-3), 118.28 (d, $^2J_{CF}$ = 7.4 Hz, C-2), 128.27, 129.23, 134.15, 137.48, 154.13 (d, $^1J_{CF}$ = 293.3 Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −129.79 (d, $^3J_{HF}$ = 32.7 Hz). IR ($CH_2Cl_2$) $\nu$ 3623, 3055, 2985, 2873, 1423, 1335, 1265, 1171, 897 cm$^{-1}$. MS (EI) *m/z* 228 [$M^+$]; HRMS (EI) Calcd for $C_{11}H_{13}O_2FS$: 228.0621. Found: 228.0600. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.60 (q, $^3J_{HH}$ = 8.5 Hz, 2H), 5.82 (dt, $^3J_{HH}$ = 8.5 Hz, $^3J_{HF}$ = 22.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 22.34 (d, $^4J_{CF}$ = 2.4 Hz, C-4), 26.07 (d, $^3J_{CF}$ = 3.3 Hz, C-3), 120.39 (d, $^2J_{CF}$ = 12.4 Hz, C-2), 128.05, 128.98, 134.24, 138.35, 152.15 (d, $^1J_{CF}$ = 271.1 Hz, C-1). $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −117.28 (d, $^3J_{HF}$ = 22.2 Hz).

*4.2.5. 1-Fluoro-1-phenylsulfonyl-non-1-ene (**6e**)*

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.82–1.45 (m, 13H), 2.19 (qd, $^3J_{HH} = 7.7$ Hz, $4J_{HF} = 2.2$ Hz, 2H), 6.24 (dt, $^3J_{HH} = 7.8$ Hz, $^3J_{HF} = 32.6$ Hz, 1H), 7.49–7.55 (m, 2H), 7.63–7.70 (m, 1H), 7.89–7.94 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 13.95 (C-9), 13.99 (C-8), 17.08 (C-7), 22.46 (C-6), 22.52 (C-5), 24.12 (d, $^4J_{CF} = 1.6$ Hz, C-4), 27.99 (d, $^3J_{CF} = 2.4$ Hz, C-3), 118.67 (d, $^2J_{CF} = 7.4$ Hz, C-2), 128.43, 129.29, 134.18, 137.63, 154.07 (d, $^1J_{CF} = 292.5$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −129.68 (d, $^3J_{HF} = 32.6$ Hz); IR ($CH_2Cl_2$) $\nu$ 2954, 2931, 2857, 1450, 1334, 1160, 782, 763, 728, 667 cm$^{-1}$; MS (FAB) *m/z* 285 $[M + H]^+$, HRMS (FAB) Calcd for $C_{15}H_{22}O_2FS$ $(M + H)^+$: 285.1325. Found: 285.1325. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.62 (q, $^3J_{HH} = 7.3$ Hz, 2H), 5.83 (dt, $^3J_{HH} = 8.4$ Hz, $^3J_{HF} = 22.3$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 24.35 (d, $^4J_{CF} = 3.0$ Hz, C-4), 28.93 (d, $^3J_{CF} = 5.8$ Hz, C-3), 120.76 (d, $^2J_{CF} = 13.7$ Hz, C-2), 128.21, 129.05, 134.28, 138.53, 151.95 (d, $^1J_{CF} = 270.7$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −117.40 (d, $^3J_{HF} = 22.3$ Hz).

*4.2.6. 1-Fluoro-1-phenylsulfonyl-4-phenyl-but-1-ene (**6f**)*

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.43 (qd, $^3J_{HH} = 7.6$ Hz, $^4J_{HF} = 2.2$ Hz, 2H), 2.66 (t, $^3J_{HH} = 7.6$ Hz, 2H), 6.16 (dt, $^3J_{HH} = 7.6$ Hz, $^3J_{HF} = 32.4$ Hz, 1H), 6.95–7.22 (m, 5H), 7.39–7.46 (m, 2H), 7.52–7.58 (m, 1H), 7.75–7.77 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 25.81 (d, $^4J_{CF} = 1.6$ Hz, C-4), 34.06 (d, $^3J_{CF} = 1.7$ Hz, C-3), 117.19 (d, $^2J_{CF} = 6.6$ Hz, C-2), 126.39, 128.23, 128.40, 128.53, 129.29, 134.20, 137.45, 139.84, 154.38 (d, $^1J_{CF} = 294.9$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −128.26 (d, $^3J_{HF} = 32.4$ Hz); IR ($CH_2Cl_2$) $\nu$ 3066, 3027, 2931, 1450, 1334, 1214, 1160, 1103, 767 cm$^{-1}$; MS (FAB) *m/z* 291 $[M + H]^+$, HRMS (FAB) Calcd for $C_{16}H_{16}O_2FS$ $(M + H)^+$: 291.0855. Found: 291.0866. *Isomer Z* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.69 (t, $^3J_{HH} = 8.6$ Hz, 2H), 2.90 (q, $^3J_{HH} = 8.6$ Hz, 2H), 5.75 (dt, $^3J_{HH} = 8.6$ Hz, $^3J_{HF} = 21.9$ Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 25.99 (C-4), 35.29 (d, $^3J_{CF} = 2.0$ Hz, C-3), 119.28 (d, $^2J_{CF} = 10.8$ Hz, C-2), 150.30 (d, $^1J_{CF} = 268.2$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −116.38 (d, $^3J_{HF} = 21.9$ Hz).

*4.2.7. 2-(2-Furyl)-1-fluoro-1-phenylsulfonylethylene (**6g**)*

*Isomer E*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.49 (dd, $^3J_{HH} = 1.7$, 3.3 Hz), 6.78 (d, $^3J_{HH} = 3.3$ Hz), 7.08 (d, $^3J_{HF} = 32.5$ Hz), 7.55–7.60 (m, 2H), 7.66–7.70 (m, 1H), 7.97–8.00 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 105.63 (d, $^4J_{CF} = 4.1$ Hz, C-4), 112.53, 115.96 (d, $^2J_{CF} = 9.1$ Hz, C-2), 128.59, 129.47, 134.42, 137.50, 145.04 (d, $^3J_{CF} = 4.1$ Hz, C-3), 145.09, 151.70 (d, $^1J_{CF} = 304.0$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −124.48 (d, $^3J_{HF} = 32.5$ Hz); IR ($CH_2Cl_2$) $\nu$ 3624, 3055, 2985, 1421, 1267, 1161, 1018, 897 cm$^{-1}$; MS (FAB) *m/z* 253 $[M + H]^+$, HRMS (FAB) Calcd for $C_{12}H_{10}O_3FS$ $(M + H)^+$: 253.0335. Found: 253.0354.

*4.2.8. (1-Fluoro-1-phenylsulfonyl-ethylidene)cyclohexane (**6h**)*

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.49–1.62 (m, 6H), 2.22–2.26 (m, 2H), 2.75–2.79 (m, 2H), 7.51–7.57 (m, 2H), 7.61–7.67 (m, 1H), 7.90–7.94 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 25.66, 26.86, 26.95, 27.23 (d, $^3J_{CF} = 1.6$ Hz, C-3), 27.84 (d, $^3J_{CF} = 8.2$ Hz, C-7), 127.88, 129.20, 133.69 (d, $^2J_{CF} = 8.2$ Hz, C-2), 133.89, 139.43, 145.89 (d, $^1J_{CF} = 276.7$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −125.97 (s, 1.0F); IR ($CH_2Cl_2$) $\nu$ 3624, 3055, 2985, 2834, 1421, 1267, 1159, 1018, 897 cm$^{-1}$; MS *m/z* 255 $[M + H]^+$, HRMS (FAB) Calcd for $C_{13}H_{16}O_2FS$ $(M + H)^+$: 255.0855. Found: 255.0861.

*4.3. Stepwise procedure for synthesis of 2,2-diphenyl-1-fluoro-1-phenylsulfonyl-ethylene (**6i**)*

Under an Ar atmosphere, to a solution of **1** (0.343 g, 1.2 mmol) in diethyl ether (5 ml) was added *n*-BuLi (2.66 M solution in hexane; 0.49 ml, 1.3 mmol) at −78 °C. After 30 min stirring at this temperature, a solution of benzophenone (0.238 g, 1.2 mmol) in diethyl ether (2 ml) was added dropwise to the mixture. The reaction mixture was allowed to warm to room temperature and stirred overnight. A solution of pH 7.0 phosphate buffer (5 ml) was poured into the reaction mixture, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, and dried ($MgSO_4$) and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography (5% EtOAc in hexane) to give **6i** (0.256 g, 0.75 mmol; yield 63%).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.11–7.22 (m, 6H), 7.24–7.35 (m, 4H), 7.38–7.43 (m, 2H), 7.50–7.56 (m, 1H), 7.73–7.76 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 126.48, 127.19, 127.46, 128.05, 128.26, 128.40, 128.91, 129.33, 129.60, 129.66, 130.10 (d, $^3J_{CF} = 3.3$ Hz), 133.92 (d, $^2J_{CF} = 4.1$ Hz, C-2), 150.62 (d, $^1J_{CF} = 297.4$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −117.55 (s, 1.0F); IR ($CH_2Cl_2$) $\nu$ 3624, 3055, 2985, 2835, 1423, 1265, 1018, 897 cm$^{-1}$; MS (FAB) *m/z* 339 $[M + H]^+$, HRMS (FAB) Calcd for $C_{20}H_{16}O_2FS$ $(M + H)^+$: 339.0855. Found: 339.0860.

*4.4. Typical procedure for aldol condensation of lithiofluoromethyl phenyl sulfone with aldehydes*

Under an Ar atmosphere, to a solution of fluoromethyl phenyl sulfone in THF (5 ml) was added *n*-BuLi (2.44 M in hexane; 0.82 ml, 2.0 mmol) at −78°C. After 30 min stirring at this temperature, to the mixture was added dropwise a solution of benzaldehyde (0.212 g, 2.0 mmol) in THF (3 ml). The reaction mixture was allowed to warm to −20 °C and stirred for 4 h, after which acetic anhydride (0.24 ml, 2.5 mmol) was dropped into the mixture. The reaction mixture was allowed to warm to room temperature

and stirred overnight. Water was poured into the reaction mixture, and the aqueous layer was extracted with $Et_2O$. The combined organic extracts were dried ($Na_2SO_4$) and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography (10% EtOAc in hexane) to give 2-acetoxy-2-phenyl-1-fluoro-1-phenylsulfonylethane (0.611 g, 1.9 mmol; yield 95%) as a 2:3 mixture of diastereomers.

*Diastereomer A*: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.86 (s, 3H), 5.26 (dd, $^2J_{HF} = 45.1$ Hz, $^3J_{HH} = 2.2$ Hz, 1H), 6.49 (dd, $^3J_{HF} = 26.0$ Hz, $^3J_{HH} = 2.2$ Hz, 1H), 7.29–7.38 (m, 5H), 7.49–7.58 (m, 2H), 7.63–7.70 (m, 1H), 7.87 (d, $^3J_{HH} = 7.9$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.32, 70.00 (d, $^2J_{CF} = 15.7$ Hz), 102.17 (d, $^1J_{CF} = 232.1$ Hz), 127.10, 127.92, 128.66, 129.14, 129.19, 134.43, 134.57, 136.22, 168.55; $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −192.77 (dd, $^2J_{HF} = 45.1$ Hz, $^3J_{HF} = 26.0$ Hz). IR ($CH_2Cl_2$) $\nu$ 3055, 1736, 1699, 1267, 1018 cm$^{-1}$. MS (EI) *m/z* 262 [$M^+$]; HRMS (EI) Calcd for $C_{14}H_{11}O_2FS$: 262.0464. Found: 262.0437. *Diastereomer B* (*diagnostic peaks only*): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.13 (s, 3H), 5.39 (dd, $^2J_{HF} = 46.4$ Hz, $^3J_{HH} = 7.0$ Hz, 1H), 6.28 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{HF} = 11.0$ Hz, 1H), 7.32–7.38 (m, 5H), 7.56 (t, $^3J_{HH} = 7.6$ Hz, 2H), 7.69 (t, $^3J_{HH} = 7.6$ Hz, 1H), 7.91 (d, $^3J_{HH} = 7.6$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.82, 70.66 (d, $^2J_{CF} = 24.8$ Hz), 100.56 (d, $^1J_{CF} = 223.0$ Hz), 128.07, 128.57, 129.23, 129.42, 129.62, 133.70, 134.73, 135.40, 168.77; $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −183.54 (dd, $^2J_{HF} = 46.4$ Hz, $^3J_{HF} = 11.0$ Hz).

### 4.5. Typical procedure for isomerization to allylsulfones with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU)

Under an Ar atmosphere, to a solution of **6c** (0.262 g, 0.82 mmol) in methanol (3 ml) was added DBU (0.149 g, 0.98 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After removing the solvents, a solution of sat $NH_4Cl$ aq (3 ml) was poured into the reaction mixture, and the aqueous layer was extracted with $Et_2O$. The combined organic extracts were washed with brine, and dried ($Na_2SO_4$) and evaporated under reduced pressure to afford the crude product, which was then purified by flash column chromatography (10% EtOAc in hexane) to give 4-benzyloxy-1-fluoro-1-phenylsulfonyl-2-butene **8** (0.227 g, 0.71 mmol; yield 87%).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.07–4.10 (m, 2H), 4.52 (s, 2H), 5.58 (ddd, $^2J_{HF} = 47.0$ Hz, $^3J_{HH} = 6.1$ Hz, $^4J_{HH} = 1.2$ Hz, 1H), 5.95 (dddt, $^3J_{HF} = 16.1$ Hz, $^3J_{HH} = 6.1$, 16.1 Hz, $^4J_{HH} = 1.7$ Hz, 1H), 6.12–6.16 (m, 1H), 7.29–7.38 (m, 5H), 7.58 (t, $^3J_{HH} = 7.8$ Hz, 2H), 7.70 (t, $^3J_{HH} = 7.8$ Hz, 1H), 7.93 (d, $^3J_{HH} = 7.8$ Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 68.75, 72.57, 100.66 (d, $^1J_{CF} = 218.1$ Hz, C-1), 117.97 (d, $^2J_{CF} = 19.0$ Hz, C-2), 127.67, 127.83, 128.47, 129.15, 129.84, 134.64, 134.93, 137.68, 138.21 (d, $^3J_{CF} = 9.1$ Hz, C-3); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −175.40 (d, $^2J_{HF} = 47.0$ Hz, $^3J_{HF} = 16.1$ Hz). IR ($CH_2Cl_2$) $\nu$ 3055, 1699, 1421, 1267, 1018 cm$^{-1}$. MS (EI) *m/z* 320 [$M^+$]; HRMS (EI) Calcd for $C_{17}H_{17}O_3FS$: 320.0882. Found: 320.0886.

### 4.6. Typical procedure for reductive desulfonylation

A 0.188 g weight of **6i** (0.56 mmol) was dissolved in methanol–THF (1:2, 6 ml) under an Ar atmosphere. After addition of anhydrous sodium hydrogen phosphate (0.202 g, 1.7 mmol) and anhydrous disodium hydrogen phosphate (0.340 g, 2.2 mmol), the reaction mixture was cooled to −78 °C. A 5% sodium amalgam (0.640 g, 1.4 mmol) was added in several portions with vigorous stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was then decanted from the solid residue, which was extracted with diethyl ether and pentane. The combined organic extracts were dried ($Na_2SO_4$) and evaporated under reduced pressure to afford the crude product, which was purified by flash column chromatography (hexane) to give 2,2-diphenyl-1-fluoroethylene (0.0491 g, 0.25 mmol; yield 45%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.96 (d, $^2J_{HF} = 83.4$ Hz, 1H), 7.23–7.25 (m, 2H), 7.29–7.39 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 126.22 (d, $^2J_{CF} = 5.8$ Hz, C-2), 127.75, 127.79, 128.14, 128.19, 128.49, 128.64, 128.68, 129.72, 129.76, 135.12, 136.94, 137.03, 145.76 (d, $^1J_{CF} = 267.7$ Hz, C-1); $^{19}$F NMR (283 MHz, $CDCl_3$) $\delta$ −128.93 (d, $^2J_{HF} = 83.4$ Hz, 1.0F); IR ($CH_2Cl_2$) $\nu$ 3626, 3055, 2985, 2835, 1421, 1267, 897 cm$^{-1}$; MS (EI) *m/z* 198 [$M^+$], HRMS (EI) Calcd for $C_{14}H_{11}F$: 198.0845. Found: 198.0853.

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