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PAPER

Synthesis of fluorinated pseudopeptides: metal mediated reversal of stereochemistry in diastereoselective addition of organometallic reagents to *N*-(*tert*-butanesulfinyl)-α-fluoroenimines†

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The addition reaction of organometallic reagents to *N*-(*tert*-butanesulfinyl)-α-fluoroenimines was studied. Depending of the nature of the organometallic species (Grignard reagents or zincate complexes), we were able to control the configuration of the newly created stereogenic centers in high yields with good to high diastereomeric ratios. The chiral β-fluoro allylamines are key synthons toward the synthesis of fluorinated pseudopeptides bearing a fluoroolefin moiety as a peptide bond mimic.

Introduction

Fluorine chemistry has generated a high amount of interest over recent decades. Indeed, the introduction of fluorine atom(s) into a molecule often increases the therapeutic profile of potential biological agents, explaining why nowadays more than 20% of pharmaceutical agents and 40% of agrochemical compounds in the market feature at least one fluorine atom on their structure.[1] In addition, fluorinated compounds are extensively used as materials and studied due to environmental concerns.[2] We are interested in the synthesis of fluorinated pseudopeptides bearing a fluoroolefin as a peptide bond mimic. The fluoroolefin moiety possesses steric and electronic similarities with the amide bond, allowing the use of the fluoroolefin as an effective mimic (Fig. 1).[3]

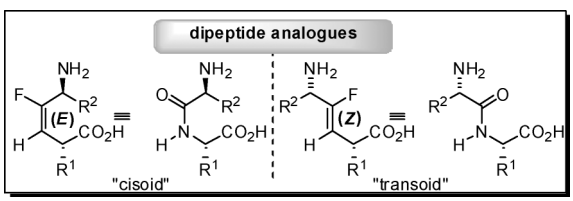

Fig. 1 Fluorinated pseudopeptides.

Moreover, used as a peptide bond mimic, the fluoroolefin is more stable than an olefin—isomerisation and conjugation with the acid moiety being disfavoured by the fluorine atom—and more resistant to enzymatic degradation compared to the peptidic bond. Recently, we reported the synthesis of some fluorinated pseudopeptides synthesized through a diastereoselective reductive amination reaction on α-fluoroenone[4] and also by organometallic addition onto α-fluoroenimine.[5] In this latter case, Grignard reagents provided higher yields and better diastereoselectivities than organolithium reagents. Herein, we report complementary results obtained with other organometallic species, especially organozincates that appeared highly efficient in the reaction and revealed a different stereochemical outcome. There are very few reports of diastereoselective addition of organozincates to imines containing a chiral auxiliary at the nitrogen atom.[6,7] This is the first report of such "ate" complex addition to α-fluoroenimines, providing an interesting option for the synthesis of fluorinated pseudopeptides.

Results and discussion

In order to synthesize the fluorinated pseudopeptide targets, we developed a methodology involving the diastereoselective addition of different organometallic species onto α-fluoroenimines bearing a *tert*-butanesulfinyl chiral auxiliary. Two model substrates **5** and **6** have been synthesised for this purpose from *p*-anisaldehyde **1** and 3-{[*tert*-butyl(diphenyl)silyl]oxy}propanal **2** in a four-step synthesis sequence. It involved a stereoselective olefination reaction leading to the corresponding *Z*-α-fluoroacrylates **3** and **4**,[8] a reduction of the ester moiety into an alcohol followed by oxidation into an aldehyde, and then a condensation of the (*S*)-*tert*-butanesulfinamide to end up with α-fluoroenimines **5** and **6** (Scheme 1).

The aldehyde **2** is obtained from propan-1,3-diol by a monoprotection with TBDPS-Cl and oxidation of the alcohol with IBX. It has to be noted that the α-fluoroenimine **6** is the precursor of the Gly analog part in the fluorinated pseudodipeptides (Scheme 2).

As reported in our previous paper, Grignard reagents are efficient organometallic compounds for addition onto imines with good diastereoselectivities.[5] Organolithiated reagents are also efficient for the addition reaction, albeit with a quite poor stereodifferentiation. In addition, organozinc reagents were tested

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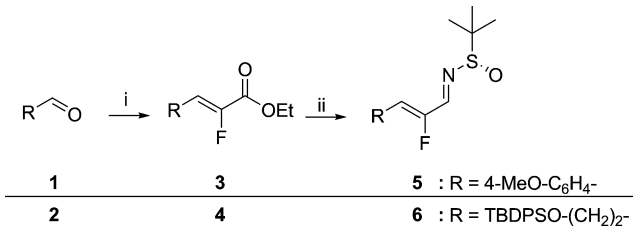
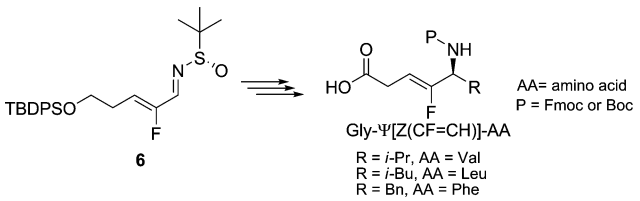
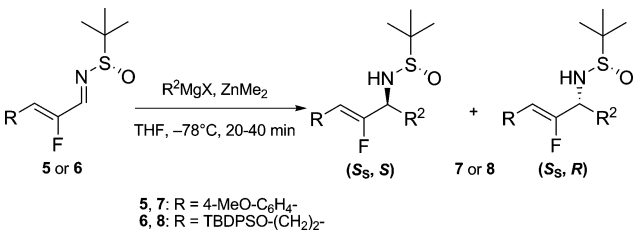


Scheme 1 Synthesis of compounds **5** and **6**. Reagents and conditions: (i) Br_2FCCO_2Et, $ZnEt_2$, DCM, 25 °C, 38–60%; (ii) (a) $LiAlH_4$, THF, 0 °C, 90–98%; b) IBX, AcOEt, reflux, 97–98%; (c) (*S*)-NH_2SOt-Bu, Ti(O*i*-Pr)$_4$, THF, reflux, 89–96%.



Scheme 2 Further transformation of **6** into fluorinated pseudopeptides.

at different temperatures but failed to give addition product. We then decided to investigate "ate" zinc complexes in organometallic additions to α-fluoroenimines **5** and **6** (Scheme 3).



Scheme 3 Diastereoselective addition of triorganozincates onto α-fluoroenimines **5** and **6**.

The active zinc(II) ate complexes are more reactive than usual organozinc reagents and are also less basic and more nucleophilic than Grignard reagents. In 2008, Guijarro, Yus and co-workers described the efficient diastereoselective addition of triorganozincates to *N*-(*tert*-butanesulfinyl)imines.[7a–b] The triorganozincates were generated by addition of a solution of Grignard reagent to a solution of dialkylzinc reagent. The biggest alkyl group was transferred to the imine regardless of its initial position on the Grignard or organozinc reagent. As the kinetics of transfer of the methyl group proved to be very slow, the organozincates were generated using either of the two following procedures: (i) methyl Grignard (MeMgBr) + dialkylzinc species—with the possibility of transferring both alkyl groups of the dialkyl zinc used,[7c] (ii) dimethylzinc ($ZnMe_2$) + various Grignard or organolithium compounds. At low temperature, the triorganozincate species proved to be much more reactive than Grignard or organolithium reagents, except in the case of aryl transfer for which the aryldialkylzincate seems not to be formed. We tried the experimental procedure (ii) with α-fluoroenimines **5** and **6**. Results are presented in Table 1 and are compared with results obtained with Grignard or organolithium reagents as indicated in parentheses.

Table 1 Diastereoselective addition of triorganozincates ($ZnMe_2$ + R_2MgX) *versus* Grignard or organolithium reagents to α-fluoroenimines **5** and **6**

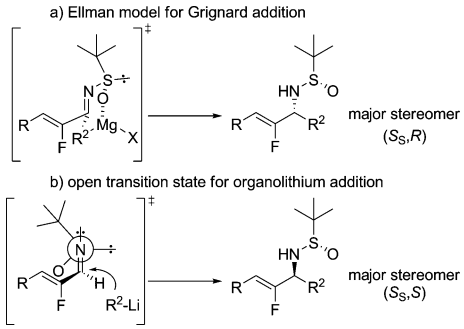
Entry	Substrate	R^2MgX	Product	Yield (%)[a,b]	Dr[c,d]
1	**5**	PhMgBr	**7a**	0 (95)	nd (10/90)
2	**5**	MeMgBr	**7b**	10[e] (82)[f]	nd (6/94)[f]
3	**5**	*i*-PrMgCl	**7c**	82 (60) (98)[g]	94/6 (30/70) (60/40)[g]
4	**5**	*i*-BuMgBr	**7d**[h]	82 (27)	98/2 (30/70)
5	**5**	$PhCH_2MgCl$	**7e**	91 (94)	81/19 (30/70)
6	**5**	AllylMgBr	**7f**	95 (72) 95[i]	59/41 (4/96) 64/36[i]
7	**5**	VinylMgBr	**7g**	95 (95)	90/10 (33/67)
8	**6**	PhMgBr	**8a**	0 (90)	nd (14/86)
9	**6**	MeMgBr	**8b**	0 (90)[f]	nd (10/90)[f]
10	**6**	*i*-PrMgCl	**8c**[h]	63 (41) (91)[g]	93/7 (49/51) (67/33)[g]
11	**6**	*i*-BuMgBr	**8d**[h]	75 (36)	98/2 (30/70)
12	**6**	$PhCH_2MgCl$	**8e**	96 (90)	84/16 (43/57)
13	**6**	AllylMgBr	**8f**	74 (91)	67/33 (8/92)
14	**6**	VinylMgBr	**8g**	98 (98)	91/9 (35/65)

[a] Yield of silica gel chromatographed analytically pure compounds. [b] In parentheses, yield of products obtained when using organomagnesium reagents. [c] Diastereomeric ratios were determined by ^{19}F NMR of the crude reaction mixtures. [d] In parentheses, dr measured from reactions run with an organomagnesium reagent alone. [e] Conversion of substrate determined by ^{19}F NMR after 10 h of reaction. [f] Reaction carried out with 1.1 eq. of $AlMe_3$ as additive. [g] Results obtained with *i*-PrLi. [h] Along with methylated product (entry 4: **7b** 11%; entry 10: **8b** 7%; entry 11: **8b** 17% (% of isolated yield)). [i] Results obtained in a catalytic version of the reaction using 0.25 eq. of $ZnMe_2$ and 1.7 eq. of Grignard.

As already mentioned earlier in the text, the reaction run with phenylmagnesium bromide and dimethylzinc did not proceed (Table 1, entries 1 and 8). Alkyl transfer was slowly achieved in the reaction with trimethylzincate, with only 10% conversion after 10 h (Table 1, entry 2). For other triorganozincates, most of the reactions gave better yields compared to Grignard reagents. Indeed, the yields were largely improved with zincates using *i*-PrMgCl and *i*-BuMgCl with both enimines **5** and **6** (Table 1, entries 3–4 and 10–11) albeit still lower than reactions run with *i*-propyllithium. It is worth noting that the use of these alkylmagnesium reagents alone generated mainly the β-hydride transfer to the imine moiety leading to the imine reduction products. The zincate complexes proved to be more efficient since no reduction product was observed. Also, in a few cases, we nevertheless observed a methyl group transfer onto the imine instead of the bulkier group of the triorganozincate. This side-reaction (methyl group transfer) occurred with bulky Grignard reagents such as *i*-BuMgBr or *i*-PrMgCl always in minor proportions compared to the desired product (Table 1, entries 4, 10–11, see footnote *h*).

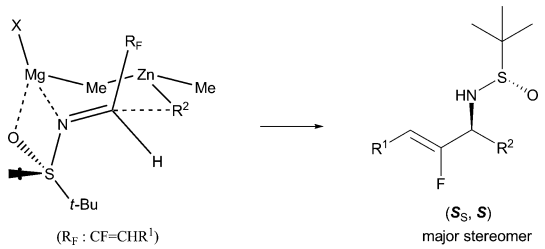
Based on the X-ray crystallography of the minor diastereomer of **7b**[4] establishing the *S* configuration for the stereogenic carbon center formed with methyl Grignard (addition on the *Re*-face), we assumed that all other Grignard reagents added in the same way, on the *Re*-face of the imine. By comparison of NMR data obtained with the products of the Grignard additions, we noticed a reversal of stereochemistry from Grignard reagents to organolithium reagents or organozincates, clearly demonstrating that transition states of the addition processes are different and dependent on

the nucleophilic species. It has been proposed that with Grignard reagents in noncoordinating solvents, a Zimmerman–Traxler chelated transition state is involved, whereas with organolithium reagents in coordinating solvents an open transition state gives the product with opposite stereochemistry (Scheme 4).[9]



Scheme 4 Transition state proposed with Grignard and organolithum reagents.

In the case of addition of bulky Grignard reagents such as benzyl, *i*-propyl or *i*-butyl groups, the diastereoselectivity observed is moderate probably due to steric hindrance within the six-membered ring transition state that causes competition with the open transition state (Table 1, entries 3–5, 10–12). The results are more surprising for the addition of vinyl Grignard giving a poor stereoselectivity with no evidence of a steric problem (Table 1, entries 7, 14). Nevertheless, the use of triorganozincates largely improved diastereomeric ratios, except for allyl Grignard for which the stereoselectivity is better using the Grignard alone (Table 1, entries 6, 13). In the chelated transition state, the Grignard reagent attacks the imine on the *Re* face whereas the organolithium compound attacks the *Si* face of the imine in the open transition state. As the configuration of the stereogenic center of the major diastereomer is the same using either organolithiums or zincates, the same open transition state seemed to be generated during the reaction with these two organometallic species. But in terms of stereoselectivity, zincates proved to be much more efficient than organolithium reagents certainly due to a different transition state, more rigid, more constrained and so more "stereo-inducing" than the open transition state. Based on the transition state proposed by Ishihara and co-workers,[10] the facial selectivity for zincate addition to *N*-sulfinyl α-fluoro-α,β-unsaturated aldimines can be rationalised by the transition-state assembly shown in Scheme 5. The Me_2R^2ZnMgX reagent coordinates to the aldimine at the MgX^+ moiety through a six-membered ring chair-conformation with concomitant tetracoordination of magnesium with the sulfinyl oxygen on the opposite face of the bulky *tert*-butyl group that shields the *Re* face of the imine.[6a] The coordination activates



Scheme 5 Proposed transition state with organozincates.

the substrate and places favorably the zincate $[Me_2ZnR^2]^-$ for the addition reaction on the *Si* face of the imine. We assume that the fluorine atom does not play any role, apart from the activation of the imine, in the stereodifferentiation process.

During the triorganozincate addition, the release of the corresponding adduct is concomitant to the regeneration of Me_2Zn, allowing the promotion of a catalytic cycle as described by Guijarro, Yus and co-workers.[7b] We then try the catalytic version of the reaction with the combination $ZnMe_2$ (0.25 eq.)/allylMgBr (1.7 eq.) on substrate **5**. We obtained similar results, 95% yield with a slight increase of the diastereomeric ratio (64/36 instead of 59/41 (Table 1, entry 6)). Next, products **8** have been employed in the synthesis of fluorinated pseudopeptides (see Scheme 2) through simple experimental protocols already reported by us.[4]

Conclusion

We have developed efficient triorganozincate additions to α-fluoroenimines bearing a chiral auxiliary. The stereodifferentiation is very good as well as the yields. The reversal of stereoselectivity can be planned by the choice of appropriate organometallic species. We have proposed a different transition state with zincates to explain the higher stereoselectivity observed compared to organomagnesium and organolithium reagents. This methodology is currently applied to the synthesis of new fluorinated pseudopeptides.

Experimental section

General

All organometallic reagents were commercially available and purchased from Aldrich or Acros company. Reactions with organometallics were carried out under argon atmosphere. THF was distilled prior to use from sodium benzophenone ketyl under nitrogen atmosphere and dichloromethane from CaH_2. TLC were performed on Merck 60F-250 silica gel plates, using UV light as a visualizing agent and an ethanolic solution of phosphomolybdic acid and heat as developing agent. Flash column chromatography purifications were carried out using silica gel (70–230 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR ($CFCl_3$ as internal reference) were recorded at 300.13, 75.47 and 282.40 MHz, respectively on a Bruker DXP 300. Abbreviations used for peak multiplicity are s: singulet, b: broad singulet, d: doublet, t: triplet, q: quadruplet, m: multiplet. *J* was used to indicate coupling constant in Hertz. IR spectra were recorded on a Perkin–Elmer 500 FT-IR spectrometer. Absorption bands are reported in cm^{-1}. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on a Bruker–Esquire mass spectrometer. Electronic impact (EI – 70 ev), chemical ionization (CI – 200 eV) or high-resolution MS experiments were recorded on a JEOL AX 500 mass spectrometer using a mass resolution of 5000. Elemental analyses were performed on a CE Instruments EA 110 CHNS-O instrument.

Synthesis of substrate 5

(a) Ethyl (*Z*)-2-fluoro-3-(4-methoxyphenyl)-2-propenoate (3). To a solution of *p*-anisaldehyde **1** (1.82 mL, 15 mmol, 1 eq.) and dibromofluoroethylacetate (4.18 mL, 30 mmol, 2 eq.) in dry DCM (150 ml) was added diethylzinc (60 mL of a 1 M solution in

hexane, 4 mmol, 4 eq.) dropwise at 0 °C under argon. The reaction mixture was stirred for 3 h (until *anti* alcohol is consumed as checked by ^{19}F NMR). The resulting solution was then quenched with a saturated aqueous solution of NH_4Cl (200 ml), stirred for 15 min, and concentrated under reduced pressure. The residue was taken up in Et_2O (150 mL) and filtered through a pad of Celite. The crude mixture was purified by chromatography on silica gel (Eluent: Cyclohexane/EtOAc: 9/1) to afford **3** as a white solid (1.28 g, 38%). R_f 0.2 (Cyclohexane/EtOAc 95 : 5). IR (KBr): ν 2982, 1725, 1660, 1607, 1514, 1256, 1178, 1030, 830, 556 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.37 (t, J = 7.2 Hz), 3.84 (s, 3H), 4.33 (q, J = 7.2 Hz), 6.86 (d, J = 27.9 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –129.3 (d, ^3J = 36.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 14.2 (CH_3), 55.1 (CH_3), 61.6 (CH_2), 114.2 (CH), 117.3 (d, J = 4.4 Hz, C), 121.9 (d, J = 26.9 Hz, C), 131.9 (d, J = 8.2 Hz, CH), 145.7 (d, J = 263.7 Hz, C), 160.1 (C), 160.3 (d, J = 26.8 Hz, C) ppm. MS (EI): m/z = 224 [$M^{+\circ}$]. Elemental analysis for $C_{12}H_{13}FO_3$: calcd: C, 64.28; H, 5.84. Found: C, 64.31; H, 5.89.

(b) (*Z*)-2-Fluoro-3-(4-methoxyphenyl)-2-propen-1-ol. To a solution of fluoroacrylate **3** (250 mg, 1.11 mmol, 1 eq.) in dry THF (10 mL) at 0 °C was added $LiAlH_4$ (84.6 mg, 2.23 mmol, 2 eq.). The reaction mixture was stirred for 30 min and then slowly quenched with 5% H_2SO_4 and concentrated. The reaction mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The crude mixture was purified by chromatography on silica gel (Eluent: Cyclohexane/EtOAc 65/45) to afford the alcohol as a white powder (198.9 mg, 98%). R_f 0.2 (Cyclohexane/EtOAc: 6/4). IR (KBr): ν 3366, 2931, 2837, 1607, 1512, 1248, 1175, 1031, 970, 837 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.82 (t, J = 6.2 Hz, 1H), 3.81 (s, 3H), 4.27 (dd, J = 6.0, J = 15.5 Hz, 2H), 5.72 (d, J = 38.8 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –116.7 (dt, J = 15.5 Hz, J = 38.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 55.2 (CH_3), 61.7 (d, J = 32.0 Hz, CH_2), 107.0 (d, J = 7.1 Hz, CH), 113.9 (CH), 125.5 (d, J = 2.7 Hz, C), 130.0 (d, J = 7.4 Hz, CH), 155.9 (d, J = 263.9 Hz, C), 157.7 (C) ppm. MS (EI): m/z = 182 [$M^{+\circ}$]. Elemental analysis for $C_{10}H_{11}FO_2$: calcd: C, 65.92; H, 6.09. Found: C, 66.10; H, 5.92.

(c) (*Z*)-2-Fluoro-3-(4-methoxyphenyl)-2-propenal. To a solution of alcohol (853.0 mg, 4.68 mmol, 1 eq.) in EtOAc (25 mL) was added IBX (3.93 g, 14.04 mmol, 3 eq.). The reaction mixture was heated at reflux for 4 h 30, filtered through a pad of Celite® and then concentrated under reduced pressure affording the aldehyde (826 mg, 98%) as a yellow solid. R_f 0.24 (Cyclohexane/EtOAc: 8/2). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.86 (s, 3H), 6.56 (d, J = 34.5 Hz), 6.96 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 9.29 (d, J = 17.5 Hz, 1H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –132.2 (dd, J = 17.5 Hz, J = 34.0 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 55.8 (CH_3), 115.0 (CH), 123.8 (d, J = 7.4 Hz, CH), 127.8 (C), 133.1 (d, J = 7.9 Hz, CH), 154.4 (d, J = 267.2 Hz, C), 162.2 (C), 184.1 (d, J = 23.9 Hz, C) ppm. MS (EI): m/z = 180 [$M^{+\circ}$]. Elemental analysis for $C_{10}H_9FO_2$: calcd: C, 66.66; H, 5.03. Found: C, 66.56; H, 4.99.

(d) *N*-[(*E*,2*Z*)-2-Fluoro-3-(4-methoxyphenyl)-2-propenylidene]-2-methyl-2-propanesulfinamide (5). To a solution of aldehyde (592 mg, 3.28 mmol, 1 eq.) in dry THF (15 mL) were added $Ti(OEt)_4$ (1.72 mL, 8.21 mmol, 2.5 eq.) and (*S*)-*tert*-butylsulfinylamine (995 mg, 8.21 mmol, 2.5 eq.). The mixture was heated at reflux for 1 h 30 and once cooled, poured into an equal volume of brine with rapid stirring. The resulting suspension was filtered through a pad of Celite® and the resulting solid was washed with EtOAc. The brine layer was extracted once with EtOAc. The combined organic portions were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by chromatography on silica gel (Eluent: Cyclohexane/EtOAc: 65/35 to afford **5** as a yellow solid (893.7 mg, 96%). R_f 0.2 (Cyclohexane/EtOAc: 7/3). IR (KBr): ν 3053, 2973, 2835, 1645, 1568, 1511, 1380, 1363, 1303, 1254, 1178, 1073, 913, 832, 667 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.26 (s, 9H), 3.86 (s, 3H), 6.33 (d, J = 35.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 19.6 Hz, 1H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –124.9 (dd, J = 16.6 Hz, J = 35.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.4 (CH_3), 55.3 (CH_3), 58.1 (C), 114.4 (CH), 123.0 (d, J = 6.6 Hz, CH), 124.4 (d, J = 4.4 Hz, C), 132.0 (d, J = 8.2 Hz, CH), 154.6 (d, J = 261.0 Hz, C), 155.2 (d, J = 19.7 Hz, C), 160.9 (d, J = 3.3 Hz, C) ppm. MS (EI): m/z = 284.20 [M+H]$^+$. Elemental analysis for $C_{10}H_9FO_2$: calcd: C, 59.34; H, 6.40; N, 4.94; S, 11.32. Found: C, 59.29; H, 6.45; N, 4.91; S, 11.23.

Synthesis of substrate 6

aa) 3-{[*tert*-Butyl(diphenyl)silyl]oxy}-1-propanol. To a solution of propan-1,3-diol (0.475 mL, 6.57 mmol, 1 eq.) in dry THF (15 mL) was added at –78 °C *n*-BuLi (2.62 mL of a 2.5 M solution in hexane, 6.57 mmol, 1 eq.) and *tert*-butyldiphenylchlorosilane (1.7 mL, 6.57 mmol, 1 eq.). The reaction mixture was stirred for 15 min at –78 °C, 30 min at room temperature and finally heated at reflux for 3 h 30. The reaction mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O (×2), and the combined organic layers were dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The crude mixture was purified by column chromatography (PE/Et_2O: 8/2 → 6/4) to afford the mono-protected alcohol as a white crystalline solid (1.75 g, 84%). R_f 0.25 (Hexane/EtOAc: 75/25). IR (KBr): ν 3349, 3071, 2931, 2858, 1472, 1428, 1112, 823, 737, 702, 688, 614, 505 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.05 (s, 9H), 1.77–1.85 (m, 2H), 3.85 (t, J = 5.7 Hz, 4H), 7.37–7.47 (m, 6H), 7.66–7.70 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.1 (C), 26.8 (CH_3), 34.4 (CH_2), 61.7 (CH_2), 63.1 (CH_2), 127.8 (CH), 129.8 (CH), 133.3 (C), 135.6 (CH) ppm. MS (EI): m/z = 257.00 [M^+-*t*Bu]. Elemental analysis for $C_{19}H_{26}O_2Si$: calcd: C, 72.56; H, 8.33. Found: C, 72.50; H, 8.27.

(b) 3-{[*tert*-Butyl(diphenyl)silyl]oxy}propanal (2). To a solution of mono-protected alcohol (2.06 g, 6.55 mmol, 1 eq.) in EtOAc (50 mL) was added IBX (5.50 g, 19.67 mmol, 3 eq.). The reaction mixture was heated at reflux for 5 h, filtered through a pad of Celite® and then concentrated under reduced pressure affording the aldehyde (2.01 g, 98%) as a colorless oil. R_f 0.25 (PE/EtOAc: 95/5). IR (KBr): ν 3437, 3071, 3050, 2959, 2932, 2858, 1728, 1428, 1112, 703, 506 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.04 (s, 9H), 2.61 (dt, J = 6.0 Hz, J = 2.2 Hz, 2H), 4.02 (t, J = 6.0 Hz, 2H), 7.37–

7.44 (m, 6H), 7.64–7.68 (m, 4H), 9.82 (t, J = 2.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (C), 26.8 (CH_3), 46.5 (CH_2), 58.4 (CH_2), 127.9 (H), 129.9 (CH), 133.3 (C), 135.6 (CH), 202.0 (C) ppm. MS (EI): m/z = 256.00 [M$^+$-tBu]. Elemental analysis for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74. Found: C, 72.98; H, 7.64.

(c) Ethyl (*Z*)-5-{[*tert*-butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenoate (4). To a solution of aldehyde (3.96 g, 12.68 mmol, 1 eq.) and dibromofluoroethylacetate (3.53 mL, 25.37 mmol, 2 eq.) in dry DCM (115 ml) was added at 0 °C diethylzinc (51 mL of 1 M solution in hexane, 4 mmol, 4 eq.) dropwise under argon. The reaction mixture was stirred for 3 h (until *anti* alcohol was consumed as checked by ^{19}F NMR). The resulting solution was then quenched with a saturated aqueous solution of NH_4Cl (200 ml), stirred for 15 min, and concentrated under reduced pressure. The residue was taken up in Et_2O (150 mL) and filtered through a pad of Celite®. The crude mixture was purified by chromatography on silica gel (Eluent: Cyclohexane/EtOAc: 95/5) to afford **4** as a colorless oil (3.02 g, 60%). R_f 0.27 (Cyclohexane/EtOAc: 95/5). IR (KBr): ν 2931, 2858, 1732, 1427, 1375, 1325, 1217, 1111 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06 (s, 9H), 1.33 (t, J = 7.0 Hz, 3H), 2.46–2.53 (m, 2H), 3.74 (t, J = 6.4 Hz, 2H), 4.29 (q, J = 7.0 Hz, 2H), 6.23 (dt, J = 7.5 Hz, J = 33.5 Hz, 1H), 7.32–7.44 (m, 6H), 7.65–7.68 (m, 4H, H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –129.8 (d, J = 33.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 14.2 (CH_3), 19.3 (C), 26.9 (CH_3), 27.9 (d, J = 2.2 Hz, CH_2), 61.6 (CH_2), 62.1 (d, J = 2.2 Hz, CH_2), 117.6 (d, J = 11.0 Hz, CH), 127.8 (CH), 129.8 (CH), 133.6 (C), 135.6 (CH), 148.8 (d, J = 256.1 Hz, C), 160.8 (d, J = 35.6 Hz, C) ppm. MS (EI): m/z = 423.18 [M+Na]$^+$. Elemental analysis for $C_{23}H_{29}FO_3Si$: calcd: C, 68.97; H, 7.30. Found: C, 68.80; H, 7.29.

(d) (*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-2-penten-1-ol. To a solution of **4** (3.07 g, 7.67 mmol, 1 eq.) in dry THF (75 mL) at 0 °C was added $LiAlH_4$ (320 mg, 8.43 mmol, 1.1 eq.). The reaction mixture was stirred for 35 min and then slowly quenched with 5% H_2SO_4 and concentrated under reduced pressure. The reaction mixture was extracted with CH_2Cl_2 (×3), and the combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered and then concentrated under reduced pressure to afford the alcohol as a colorless oil (2.47 g, 90%). R_f 0.2 (PE/EtOAc: 9/1). IR (KBr): ν 3356, 3072, 2931, 2858, 1714, 1589, 1471, 1427, 1390, 1111, 1020 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06 (s, 9H), 2.33–2.40 (m, 2H), 3.69 (t, J = 6.4 Hz, 2H), 4.08 (dd, J = 6.4 Hz, J = 15.6 Hz, 2H), 4.90 (dt, J = 7.3 Hz, J = 37.1 Hz, 1H), 7.36–7.43 (m, 6H), 7.65–7.66 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –120.1 (dt, J = 15.6 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 26.9 (CH_3), 27.1 (d, J = 3.8 Hz, CH_2), 61.3 (d, J = 32.3 Hz, CH_2), 63.1 (d, J = 1.6 Hz, CH_2), 104.6 (d, J = 13.7 Hz, CH), 127.7 (CH), 129.7 (CH), 133.9 (C), 135.7 (CH), 158.5 (d, J = 254.4 Hz, C) ppm. MS (EI): m/z = 359.19 [M+H]$^+$. Elemental analysis for $C_{21}H_{27}FO_2Si$: calcd: C, 70.35; H, 7.59. Found: C, 70.06; H, 7.39.

(e) (*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenal. To a solution of alcohol (2.47 g, 6.88 mmol, 1 eq.) in EtOAc (40 mL) was added IBX (5.38 g, 19.22 mmol, 3 eq.). The reaction mixture was heated at reflux for 6 h, filtered through a pad of Celite® and then concentrated under reduced pressure affording the aldehyde (2.38 g, 97%) as a yellow oil. R_f 0.2 (Cyclohexane/EtOAc: 9/1). IR (KBr): ν 2957, 2930, 2857, 1703, 1472, 1428, 1361, 1112, 938, 702, 613, 506 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06 (s, 9H), 2.56–2.63 (m, 2H), 3.82 (t, J = 6.2 Hz, 2H), 6.02 (dt, J = 7.6 Hz, J = 32.5 Hz, 1H), 7.37–7.47 (m, 6H), 7.63–7.67 (m, 4H), 9.18 (d, J = 18.4 Hz, 1H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –132.9 (dd, J = 18.4 Hz, J = 33.0 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 18.2 (C), 25.8 (CH_3), 27.2 (d, J = 2.3 Hz, CH_2), 60.7 (CH_2), 105.6 (d, J = 21.2 Hz, CH), 126.7 (CH), 128.8 (CH), 132.8 (C), 134.5 (CH), 155.9 (d, J = 262.0 Hz, C), 182.5 (d, J = 25.2 Hz, C) ppm. MS (EI): m/z = 299.1 [M$^+$-tBu]. Elemental analysis for $C_{21}H_{25}FO_2Si$: calcd: C, 70.75; H, 7.07. Found: C, 70.59; H, 7.16.

f) *N*-(*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenylidene-2-methyl-2-propanesulfinamide (6). A solution of $Ti(OEt)_4$ (2.14 mL, 10.2 mmol, 2.5 eq.) and aldehyde (1.45 g, 4.08 mmol, 1 eq.) in dry THF (60 mL) was prepared under argon. Then, (*S*) *tert*-butylsulfinylamine (1.23 g, 10.2 mmol, 2.5 eq.) was added and the mixture was heated at reflux for 1 h 15. Once cooled, the mixture was poured into an equal volume of brine with rapidly stirring. The resulting suspension was filtered through a pad of Celite® and the resulting solid was washed with EtOAc. The brine layer was extracted once with EtOAc. The combined organic portions were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by chromatography on silica gel (Eluent: Cyclohexane/EtOAc: 85/15) to afford **6** as a yellow oil (1.67 g, 89%). R_f 0.21 (Cyclohexane/EtOAc: 9/1). IR (KBr): ν 2959, 2858, 1664, 1592, 1473, 1428, 1363, 1186, 1111, 1088, 823, 702, 613, 504 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.05 (s, 9H), 1.23 (s, 9H), 2.53–2.61 (m, 2H), 3.78 (t, J = 5.6 Hz, 2H), 5.73 (dt, J = 7.5 Hz, J = 33.2 Hz, 1H), 7.35–7.46 (m, 6H), 7.63–7.66 (m, 4H), 7.95 (d, J = 19.6 Hz, 1H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –126.6 (dd, J = 19.6 Hz, J = 33.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.5 (CH_3), 26.8 (CH_3), 28.4 (d, J = 2.2 Hz, CH_2), 58.0 (C), 62.1 (d, J = 1.6 Hz, CH_2), 123.3 (d, J = 13.2 Hz, CH), 127.8 (CH), 129.9 (CH), 133.5 (C), 135.6 (CH), 155.1 (d, J = 21.4 Hz, C), 155.7 (d, J = 254.4 Hz, C) ppm. MS (EI): m/z = 460.33 [M+H]$^+$. Elemental analysis for $C_{25}H_{34}FNO_2SSi$: calcd: C, 65.32; H, 7.45; N, 3.05; S, 6.98. Found: C, 65.46; H, 7.57; N, 3.28; S, 6.91.

• General procedure for diastereocontrolled addition of Grignard reagents to *S*-chiral *N*-(*tert*-butanesulfinyl)-α-fluoroenimines

To a solution of α-fluoroenimine (1 eq.) in anhydrous toluene (1 mL) at 0 °C under argon was slowly added the Grignard reagent (1.1 eq.). The reaction mixture was stirred until the reaction was complete as determined by TLC and then quenched with a saturated aqueous solution of NH_4Cl. The solution was warmed to room temperature and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was checked by ^{19}F NMR for determination of diastereomeric ratio and purified by chromatography on silica gel.

• General procedure for diastereocontrolled addition of organolithium reagents to *S*-chiral *N*-(*tert*-butanesulfinyl)-α-fluoroenimines

To a solution of α-fluoroenimine (1 eq.) in anhydrous toluene (1 mL) at −78 °C under argon was slowly added the organolithium reagent (1.1 eq.). The reaction mixture was stirred until the reaction was complete as determined by TLC and then quenched with a saturated aqueous solution of NH_4Cl. The solution was warmed to room temperature and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was checked by ^{19}F NMR for determination of diastereomeric ratio and purified by chromatography on silica gel.

• General procedure for diastereocontrolled addition of organozincate reagents to *S*-chiral *N*-(*tert*-butanesulfinyl)-α-fluoroenimines

To a solution of Grignard reagent (1.5 eq.) in dry THF (0.5 mL) was added under argon at room temperature Me_2Zn (1.72 eq.) and the mixture was stirred for 15 min. The resulting solution of the organozincate was then transferred dropwise *via* a syringe to a solution of α-fluoroenimine (1 eq.) in dry THF (1 mL) under argon at −78 °C. The reaction mixture was stirred until the reaction was complete as determined by TLC and then quenched with a saturated solution of NH_4Cl. The solution was warmed to room temperature and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was checked by ^{19}F NMR for determination of diastereomeric ratio and purified by chromatography on silica gel.

***N*-[(*Z*)-2-Fluoro-3-(4-methoxyphenyl)-1-phenyl-2-propenyl]-2-methyl-2-propanesulfinamide (7a).** Yellow solid. R_f 0.2 (Cyclohexane/EtOAc: 5/5). IR (KBr): ν 2959, 1686, 1608, 1513, 1300, 1251, 1180, 1032, 756, 701 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.28 (s, 9H), 3.57 (d, J = 2.6 Hz, 1H), 3.80 (s, 3H), 5.15 (dd, J = 2.8 Hz, J = 18.8 Hz, 1H), 5.90 (d, J = 38.6 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.34–7.50 (m, 7H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −119.30 (dd, J = 18.6 Hz, J = 38.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.7 (CH_3), 55.3 (CH_3), 56.2 (C), 60.8 (d, J = 27.6 Hz, CH), 109.0 (d, J = 7.3 Hz, CH), 114.0 (CH), 125.4 (d, J = 2.9 Hz, C), 127.7 (CH), 128.7 (CH), 129.0 (CH), 130.2 (d, J = 7.3 Hz, CH), 155.4 (d, J = 267.1 Hz, C), 159.0 (d, J = 2.9 Hz, C) ppm. MS (EI): m/z = 361.73 [$M^{+\circ}$]. Elemental analysis for $C_{20}H_{24}FNO_2S$: calcd: C, 66.45; H, 6.69; N, 3.87; S, 8.87. Found: C, 66.40; H, 6.76; N, 3.72; S, 8.75.

***N*-[(*Z*)-2-Fluoro-3-(4-methoxyphenyl)-1-methyl-2-propenyl]-2-methyl-2-propanesulfinamide (7b).** Yellow solid. R_f 0.2 (Cyclohexane/EtOAc: 4/6). IR (KBr): ν 3450, 3212, 2959, 1694, 1608, 1514, 1463, 1302, 1251, 1180, 1034, 860 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.22 (s, 9H), 1.51 (d, J = 6.8 Hz, 3H), 3.19 (d, J = 4.9 Hz, 1H), 3.80 (s, 3H), 4.03–4.20 (m, 1H), 5.66 (d, J = 39.2 Hz, 1H), 6.85 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.3 (dd, J = 17.5 Hz, J = 40.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 20.4 (d, J = 1.7 Hz, CH_3), 22.6 (CH_3), 53.5 (d, J = 28.0 Hz, CH), 55.4 (CH_3), 56.0 (C), 106.7 (d, J = 7.7 Hz, CH), 114.0 (CH), 125.5 (d, J = 2.7 Hz, C), 130.1 (d, J = 7.3 Hz, CH), 157.8 (d, J = 266.5 Hz, C), 158.9 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 300.0 $[M+H]^+$. Elemental analysis for $C_{15}H_{22}FNO_2S$: calcd: C, 60.17; H, 7.41; N, 4.68; S, 10.71. Found: C, 60.22; H, 7.53; N, 4.64; S, 10.61.

***N*-[(*Z*)-2-Fluoro-1-isopropyl-3-(4-methoxyphenyl)-2-propenyl]-2-methyl-2-propanesulfinamide (7c). Dia 2:** Yellow solid. R_f 0.4 (PE/EtOAc: 6/4). IR (KBr): ν 3400, 2959, 1689, 1608, 1513, 1466, 1299, 1251, 1180, 1061, 1035, 858, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.00 (dd, J = 6.60 Hz, J = 6.60 Hz, 6H), 1.24 (s, 9H), 1.96–2.07 (m, 1H), 3.41–3.55 (m, 2H), 3.79 (s, 3H), 5.70 (d, J = 39.90 Hz), 6.83 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −120.2 (dd, J = 21.6 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.4 (CH_3), 19.6 (CH_3), 22.8 (CH_3), 31.7 (CH), 55.4 (CH_3), 56.7 (C), 65.1 (d, J = 26.3 Hz, CH), 108.1 (d, J = 7.6 Hz, CH), 113.9 (CH), 125.6 (d, J = 2.7 Hz, C), 130.2 (d, J = 7.1 Hz, CH), 155.6 (d, J = 266.5 Hz, C), 158.8 (C) ppm. MS (EI): m/z = 328.20 $[M+H]^+$. Elemental analysis for $C_{17}H_{26}FNO_2S$: calcd: C, 62.35; H, 8.00; N, 4.28; S, 9.79. Found: C, 62.06; H, 7.81; N, 4.02; S, 9.72.

Dia 1: Yellow solid. R_f 0.34 (PE/EtOAc: 6/4). IR (KBr): ν 3400, 2959, 1689, 1608, 1513, 1466, 1299, 1251, 1180, 1061, 1035, 858, 820 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.04 (dd, J = 6.8 Hz, J = 6.8 Hz, 6H), 1.22 (s, 9H), 1.97–2.08 (m, 1H), 3.33 (d, J = 3.9 Hz, 1H), 3.59–3.70 (ddd, J = 4.1 Hz, J = 7.2 Hz, J = 23.00 Hz, 1H), 3.80 (s, 3H), 5.63 (d, J = 39.18 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −119.4 (dd, J = 22.7 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.4 (CH_3), 19.5 (CH_3), 22.6 (CH_3), 31.6 (CH), 55.4 (CH_3), 55.9 (C), 63.8 (d, J = 25.8 Hz, CH), 109.0 (d, J = 7.1 Hz, CH), 114.0 (CH), 125.6 (d, J = 2.7 Hz, C), 130.1 (d, J = 7.1 Hz, CH), 155.2 (d, J = 268.2 Hz, C), 158.9 (J = 2.6 Hz, C) ppm. MS (EI): m/z = 328.20 $[M+H]^+$. Elemental analysis for $C_{17}H_{26}FNO_2S$: calcd: C, 62.35; H, 8.00; N, 4.28; S, 9.79. Found: C, 62.10; H, 7.85; N, 4.26; S, 9.75.

***N*-[(*Z*)-2-Fluoro-1-isobutyl-3-(4-methoxyphenyl)-2-propenyl]-2-methyl-2-propanesulfinamide (7d). Dia 1:** Yellow solid. R_f 0.22 (PE/EtOAc: 1/1). IR (KBr): ν 3215, 2957, 2868, 1694, 1607.3, 1513, 1470, 1421, 1285, 1246, 1045, 855 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.92 (d, J = 4.14 Hz, 3H), 0.94 (d, J = 4.1 Hz, 3H), 1.22 (s, 9H), 1.60–1.64 (m, 2H), 1.67–1.78 (m, 1H), 3.55 (d, J = 8.1 Hz, 1H), 3.78 (s, 3H), 3.82–3.94 (m, 1H), 5.71 (d, J = 39.2 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.2 (dd, J = 22.6 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.5 (CH_3), 22.6 (CH_3), 22.7 (CH_3), 24.8 (CH), 42.1 (CH_2), 55.3 (CH_3), 56.3 (C), 57.1 (d, J = 26.9 Hz, CH), 107.5 (d, J = 7.7 Hz, CH), 113.9 (CH), 125.5 (d, J = 2.7 Hz, C), 130.2 (d, J = 7.1 Hz, CH), 157.5 (d, J = 267.1 Hz, C), 158.9 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 683.20 $[2M+H]^+$. Elemental analysis for $C_{18}H_{28}FNO_2S$: C: 63.31, H: 8.26, N: 4.10; S, 9.39. Found: C: 62.97, H: 8.20, N: 4.05; S, 9.36.

Dia 2: Yellow solid. R_f 0.25 (PE/EtOAc: 1/1). ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −123.5 (dd, J = 24.0 Hz, J = 40.2 Hz) ppm.

***N*-[(*Z*)-1-Benzyl-2-fluoro-3-(4-methoxyphenyl)-2-propenyl]-2-methyl-2-propanesulfinamide (7e). Dia 1:** Yellow solid. R_f 0.39 (cyclohexane/EtOAc: 6/4). IR (KBr): ν 3197, 2960, 1690, 1610,

1515, 1455, 1365, 1296, 1258, 1181, 1056, 1024, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.20 (s, 9H), 3.07 (dd, J = 6.8 Hz, J = 13.5 Hz, 2H), 3.53 (d, J = 7.9 Hz, 1H), 3.79 (s, 3H), 4.04–4.17 (m, 1H), 5.66 (d, J = 39.7 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.19–7.30 (m, 5H), 7.40 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –120.2 (dd, J = 17.5 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.5 (CH_3), 39.8 (CH_2), 55.4 (CH_3), 56.5 (C), 59.8 (d, J = 27.9 Hz, CH), 108.3 (d, J = 7.1 Hz, CH), 113.9 (CH), 125.4 (d, J = 2.7 Hz, C), 127.0 (CH), 128.6 (CH), 129.7 (CH), 130.3 (d, J = 7.1 Hz, CH), 136.9 (C), 156.6 (d, J = 266.0 Hz, C), 159.0 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 376.27 [M+H$^+$]. Elemental analysis for $C_{21}H_{26}FNO_2S$: C, 67.17; H, 6.98; N, 3.73; S, 8.54. Found: C, 66.96; H, 6.85; N, 3.54; S, 8.47.

Dia 2: Yellow solid. R_f 0.28 (cyclohexane/EtOAc: 6/4). IR (KBr): ν 3197, 2960, 1690, 1610, 1515, 1455.4, 1365, 1296, 1258, 1181, 1056, 1024, 817 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.19 (s, 9H), 3.14 (dd, J = 7.00 Hz, J = 13.4 Hz, 2H), 3.39 (d, J = 3.8 Hz, 1H), 3.81 (s, 3H), 4.16–4.29 (m, 1H), 5.57 (d, J = 39.4 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 7.22–7.30 (m, 5H), 7.40 (d, J = 8.6 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –121.9 (dd, J = 19.6 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.6 (CH_3), 39.8 (CH2), 55.4 (CH_3), 56.2 (C), 58.3 (d, J = 27.4 Hz, CH), 109.2 (d, J = 7.1 Hz, CH), 114.0 (CH), 125.4 (d, J = 2.7 Hz, C), 127.2 (CH), 128.9 (CH), 129.7 (CH), 130.2 (d, J = 7.1 Hz, CH), 136.0 (C), 155.3 (d, J = 266.5 Hz, C), 159.0 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 376.27 [M+H]$^+$. Elemental analysis for $C_{21}H_{26}FNO_2S$: C, 67.17; H, 6.98; N, 3.73; S, 8.54. Found: C, 66.94; H, 6.89; N, 3.56; S, 8.45.

***N*-{1-[(*Z*)-1-Fluoro-2-(4-methoxyphenyl)ethenyl]-3-butenyl}-2-methyl-2-propanesulfinamide (7f).** **Dia 1:** Yellow solid. R_f 0.38 (PE/EtOAc: 1/1). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.23 (s, 9H), 2.47–2.61 (m, 1H), 3.56 (J = 7.0 Hz, 1H), 3.80 (s, 3H), 3.86–4.04 (m, 1H), 5.11–5.20 (m, 2H), 5.75 (d, J = 39.5 Hz, 1H), 5.70–5.83 (m, 1H), 6.85 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H) ppm ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –120.2 (dd, J = 19.6 Hz, J = 40.2 Hz) ppm.

Dia 2: Yellow solid. R_f 0.26 (PE/EtOAc: 1/1). IR (KBr): ν 3199, 2946, 2868, 1686, 1610, 1514, 1444, 1300; 1255, 1180, 1055, 916, 856, 811 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.19 (s, 9H), 2.47–2.66 (m, 1H), 3.48 (J = 3.6 Hz, 1H), 3.77 (s, 3H), 3.95–4.07 (m, 1H), 5.15–5.22 (m, 2H), 5.67 (d, J = 39.4 Hz, 1H), 5.69–5.83 (m, 1H), 6.84 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 8.9 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –121.2 (dd, J = 19.6 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.5 (CH_3), 38.0 (CH_2), 55.2 (CH_3), 55.9 (C), 56.3 (CH), 108.2 (d, J = 7.1 Hz, CH), 113.9 (CH), 119.7 (CH_2), 125.3 (d, J = 2.7 Hz, C), 130.0 (d, J = 7.7 Hz, CH), 133.0 (CH), 156.0 (d, J = 267.1 Hz, C), 158.8 (d, J = 3.3 Hz, C) ppm. MS (EI): m/z = 326.33 [M+H]$^+$. Elemental analysis for $C_{17}H_{24}FNO_2S$: C, 62.74; H, 7.43; N, 4.30; S, 9.85. Found: C, 62.56; H, 7.36; N, 4.15; S, 9.80.

***N*-[(*Z*)-2-Fluoro-3-(4-methoxyphenyl)-1-vinyl-2-propenyl]-2-methyl-2-propanesulfinamide (7g).** **Dia 1:** Yellow solid. R_f 0.4 (PE/EtOAc: 1/1). IR (KBr): ν 3183, 2957, 1685, 1607, 1512, 1367, 1300, 1249, 1181, 1057, 925, 856 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.24 (s, 9H), 3.36 (d, J = 5.1 Hz, 1H), 3.81 (s, 3H), 4.55 (ddd, J = 5.2 Hz, J = 6.4 Hz, J = 18.3 Hz, 1H), 5.34 (d, J = 10.2 Hz, 1H), 5.47 (d, J = 16.9 Hz, 1H), 5.73 (d, J = 38.8 Hz, 1H), 5.97–6.09 (m, 1H), 6.86 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –118.9 (dd, J = 18.6 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.6 (CH_3), 55.4 (CH_3), 56.2 (C), 60.2 (d, J = 25.8 Hz, CH), 108.6 (d, J = 7.1 Hz, CH), 114.1 (CH), 119.1 (CH_2), 125.4 (d, J = 2.7 Hz, C), 130.2 (d, J = 7.7 Hz, CH), 134.7 (CH), 155.3 (d, J = 267.6 Hz, C), 159.1 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 312.00 [M+H]$^+$. Elemental analysis for $C_{16}H_{22}FNO_2S$: calcd: C, 61.71; H, 7.12; N, 4.50; S, 10.30. Found: C, 61.57; H, 7.00; N, 4.38; S, 10.23.

Dia 2: Yellow solid. R_f 0.3 (PE/EtOAc: 1/1). IR (KBr): ν 3183, 2957, 1685, 1607, 1512, 1367, 1300, 1249, 1181, 1057, 925, 856 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.24 (s, 9H), 3.59 (d, J = 4.7 Hz, 1H), 3.79 (s, 3H), 4.49–4.59 (m, 1H), 5.36 (d, J = 10.2 Hz, 1H), 5.45 (d, J = 17.1 Hz, 1H), 5.73 (d, J = 39.2 Hz, 1H), 5.84–5.95 (m, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –117.6 (dd, J = 16.5 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.7 (CH_3), 55.3 (CH_3), 56.2 (C), 59.7 (d, J = 27.4 Hz, CH), 108.0 (d, J = 7.1 Hz, CH), 114.0 (CH), 119.7 (CH_2), 125.2 (d, J = 2.7 Hz, C), 130.3 (d, J = 7.7 Hz, CH), 134.2 (d, J = 1.64 Hz, CH), 156.2 (d, J = 267.6 Hz, C), 159.1 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 312.00 [M+H]$^+$. Elemental analysis for $C_{16}H_{22}FNO_2S$: calcd: C, 61.71; H, 7.12; N, 4.50; S, 10.30. Found: C, 61.50; H, 6.98; N, 4.42; S, 10.25.

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***N*-[(*Z*)-2-Fluoro-3-(4-methoxyphenyl)-2-propenyl]-2-methyl-2-propanesulfinamide.** Yellow solid. R_f 0.25 (PE/EtOAc: 1/1). IR (KBr): 2931, 1697, 1608, 1513, 1459, 1325, 1298, 1253, 1180, 1028, 819, 692, 560 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.23 (s, 9H), 3.53 (6, J = 6.2 Hz, 1H), 3.82 (s, 3H), 3.86 (ddd, J = 6.4 Hz, J = 16.0 Hz, J = 12.8 Hz, 2H), 5.76 (d, J = 38.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.7 Hz, 2H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –113.1 (dt, J = 15.5 Hz, J = 39.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 22.6 (CH_3), 47.2 (d, J = 30.2 Hz, CH_2), 55.3 (CH_3), 56.3 (C), 108.2 (d, J = 7.1 Hz, CH), 114.0 (CH), 125.4 (d, J = 3.3 Hz, C), 130.1 (d, J = 7.1 Hz, CH), 155.0 (d, J = 264.3 Hz, C), 159.0 (d, J = 2.7 Hz, C) ppm. MS (EI): m/z = 286.13 [M+H]$^+$. Elemental analysis for $C_{14}H_{20}FNO_2S$: C: 58.92, H: 7.06, N: 4.91; S, 11.24. Found: C: 58.86, H: 6.95, N: 4.84; S, 11.20.

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-1-phenyl-2-pentenyl)-2-methyl-2-propanesulfinamide (8a).** **Dia 1:** Yellow oil. R_f 0.17 (Cyclohexane/EtOAc: 7/3). IR (KBr): ν 2930, 2858, 1707, 1473, 1428, 1362.9, 1111, 1056, 937, 823, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.02 (s, 9H), 1.23 (s, 9H), 2.34–2.40 (m, 2H), 3.66 (t, J = 6.2 Hz, 2H), 3.73 (d, J = 3.9 Hz, 1H), 4.98 (dt, J = 7.3 Hz, J = 36.9 Hz, 1H), 5.01–5.07 (m, 1H), 7.30–7.41 (m, 6H), 7.62–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –119.2 (dd, J = 15.8 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (C), 22.6 (CH_3), 26.9 (CH_3), 27.3 (d, J = 3.6 Hz, CH_2), 56.1 (C), 60.1 (d, J = 29.0 Hz, CH), 62.9 (d, J = 1.6 Hz, CH_2), 106.4 (d, J = 13.1 Hz, CH), 127.6 (CH), 128.5 (CH), 128.9 (CH), 129.6 (CH), 134.6 (C), 135.6 (CH), 138.6 (C), 157.1 (d, J = 258.4 Hz, C) ppm. MS (EI): m/z = 537.93 [M$^{+\circ}$]. Elemental analysis for $C_{31}H_{40}FNO_2SSi$: calcd: C, 69.23; H, 7.50; N, 2.60; S, 5.95. Found: C, 69.18; H, 7.68; N, 2.39; S, 5.90.

Dia 2: Yellow oil. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –121.4 (dd, J = 16.5 Hz, J = 37.1 Hz) ppm.

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-1-methyl-2-pentenyl)-2-methyl-2-propanesulfinamide (8b).** **Dia 1:** Yellow oil. R_f 0.17 (Cyclohexane/EtOAc: 70/30). IR (KBr): ν 3435, 2858, 1705, 1472, 1428, 1362, 1111, 823, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.05 (s, 9H), 1.19 (s, 9H), 1.41 (d, J = 6.8 Hz, 3H), 2.31–2.38 (m, 2H), 3.08 (d, J = 5.6 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 3.91–4.05 (m, 1H), 4.89 (dt, J = 7.5 Hz, J = 37.1 Hz, 1H), 7.34–7.42 (m, 6H), 7.64–7.65 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.7 (dd, J = 15.4 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 18.9 (d, J = 1.6 Hz, CH_3), 19.3 (C), 22.6 (CH_3), 27.0 (CH_3), 27.2 (d, J = 4.4 Hz, CH_2), 51.9 (d, J = 29.1 Hz, CH), 55.9 (C), 63.0 (d, J = 1.6 Hz, CH_2), 103.6 (d, J = 14.2 Hz, CH), 127.8 (CH), 129.8 (CH), 133.9 (C), 135.7 (CH), 160.1 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 476.00 $[M+H]^+$. Elemental analysis for $C_{26}H_{38}FNO_2SSi$: calcd: C, 65.64; H, 8.05; N, 2.94; S, 6.74. Found: C, 65.54; H, 7.93; N, 3.02; S, 6.69.

Dia 2: Yellow oil. ^{19}F NMR ($CDCl_3$, 282.5 MHz):): δ −122.2 (dd, J = 16.5 Hz, J = 37.1 Hz) ppm.

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-1-isopropyl-2-pentenyl)-2-methyl-2-propanesulfinamide (8c).** **Dia 1:** Colorless oil. R_f 0.62 (Cyclohexane/EtOAc: 75/25). IR (KBr): ν 2959, 1637, 1472.8, 1427, 1111, 1030, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.93 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 1.04 (s, 9H), 1.23 (s, 9H), 1.86–1.97 (m, 1H), 2.27–2.51 (m, 2H), 3.42 (d, J = 3.9 Hz, 1H), 3.31–3.44 (m, 1H), 3.68 (t, J = 6.6, Hz, 2H), 4.92 (dt, J = 7.7 Hz, J = 37.8 Hz, 1H), 7.35–7.42 (m, 6H), 7.65–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −123.0 (dd, J = 20.6 Hz, J = 38.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (CH_3), 19.3 (C), 19.6 (CH_3), 22.8 (CH_3), 26.9 (CH_3), 27.3 (d, J = 4.4 Hz, CH_2), 31.3 (CH), 56.6 (C), 63.2 (d, J = 1.1 Hz, CH_2), 64.3 (d, J = 27.4 Hz, CH), 105.2 (d, J = 13.7 Hz, CH), 127.7 (CH), 129.7 (CH), 133.9 (C), 135.7 (C), 158.4 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 504.33 $[M+H]^+$. Elemental analysis for $C_{28}H_{42}FNO_2SSi$: calcd: C, 66.75; H, 8.40; N, 2.78; S, 6.36. Found: C, 66.45; H, 8.25; N, 2.59; S, 6.26.

Dia 2: Colorless oil. R_f 0.48 (Cyclohexane/EtOAc: 75/25). IR (KBr): ν 2959, 1637, 1472, 1427, 1111, 1030.8, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.96 (d, J = 6.78 Hz, 3H), 1.00 (d, J = 6.75 Hz, 3H), 1.04 (s, 9H), 1.18 (s, 9H), 1.87–1.98 (m, 1H), 2.26–2.40 (m, 2H), 3.23 (d, J = 4.5 Hz, 1H), 3.48–3.59 (m, 1H), 3.66 (t, J = 6.4, Hz, 2H), 4.87 (dt, J = 7.3 Hz, J = 37.3 Hz, 1H), 7.35–7.45 (m, 6H), 7.51–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.6 (dd, J = 21.6 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (CH_3), 19.3 (C), 19.6 (CH_3), 22.8 (CH_3), 26.9 (CH_3), 27.3 (d, J = 4.4 Hz, CH_2), 31.3 (CH), 56.6 (C), 63.2 (d, J = 1.1 Hz, CH_2), 64.3 (d, J = 26.9 Hz, CH), 105.2 (d, J = 14.2 Hz, CH), 127.7 (CH), 129.7 (CH), 133.9 (C), 135.7 (CH), 158.4 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 504.33 $[M+H]^+$. Elemental analysis for $C_{28}H_{42}FNO_2SSi$: calcd: C, 66.75; H, 8.40; N, 2.78; S, 6.36. Found: C, 66.49; H, 8.25; N, 2.53; S, 6.30.

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-1-isobutyl-2-pentenyl)-2-methyl-2-propanesulfinamide (8d).** **Dia 1:** Colorless oil. R_f 0.35 (Cyclohexane/EtOAc: 75/25). IR (KBr): ν 3434, 2957, 1636, 1427, 1326, 1111, 738.1, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.89 (d, J = 3.39 Hz, 3H), 0.92 (d, J = 3.39 Hz, 3H), 1.04 (s, 9H), 1.20 (s, 9H), 1.50–1.55 (m, 2H), 1.63–1.76 (m, 1H), 2.26–2.49 (m, 2H), 3.35 (d, J = 8.3 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 3.74–3.84 (m, 1H), 4.94 (dt, J = 7.7 Hz, J = 37.5 Hz, 1H), 7.35–7.44 (m, 6H), 7.65–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −125.2 (dd, J = 21.7 Hz, J = 38.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.4 (CH_3), 22.5 (CH_3), 22.7 (CH_3), 24.7 (CH), 26.9 (CH_3), 27.2 (d, J = 4.4 Hz, CH_2), 42.1 (CH_2), 56.2 (C), 56.3 (d, J = 28.0 Hz, CH), 63.1 (d, J = 1.6 Hz, CH_2), 104.6 (d, J = 14.2 Hz, CH), 127.8 (CH), 129.7 (CH), 133.9 (C), 135.7 (CH), 159.0 (d, J = 257.7 Hz, C) ppm. MS (EI): m/z = 518.07 $[M+H]^+$. Elemental analysis for $C_{29}H_{44}FNO_2SSi$: calcd: C, 67.27; H, 8.56; N, 2.70; S, 6.19. Found: C, 67.01; H, 8.40; N, 2.70; S, 6.07.

Dia 2: Colorless oil. R_f 0.25 (Cyclohexane/EtOAc: 75/25). ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −125.9 (dd, J = 21.7 Hz, J = 37.2 Hz) ppm.

***N*-((*Z*)-1-Benzyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenyl)-2-methyl-2-propanesulfinamide (8e).** **Dia 1:** Colorless oil. R_f 0.43 (Cyclohexane/EtOAc: 1/1). IR (KBr): ν 3070, 2930, 2858, 1727, 1428, 1362, 1262, 1111, 823, 740, 701, 505 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.04 (s, 9H), 1.10 (s, 9H), 2.28–2.42 (m, 2H), 2.96 (d, J = 7.2 Hz, 2H), 3.39 (d, J = 7.9 Hz, 1H), 3.55–3.60 (m, 2H), 3.90–4.08 (m, 1H), 4.82 (dt, J = 7.3 Hz, J = 37.6 Hz, 1H), 7.13–7.26 (m, 5H), 7.37–7.46 (m, 6H), 7.65–7.66 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.9 (dd, J = 18.6 Hz, J = 38.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.5 (CH_3), 26.9 (CH_3), 27.2 (d, J = 4.4 Hz, CH_2), 39.7 (CH_2), 56.4 (C), 59.1 (d, J = 28.5 Hz, CH), 63.0 (d, J = 1.6 Hz, CH_2), 105.1 (d, J = 13.7 Hz, CH), 126.8 (CH), 127.7 (CH), 128.4 (CH), 129.6 (CH), 133.9 (C), 135.7 (CH), 136.0 (C), 158.1 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 551.87 $[M^{+\circ}]$. Elemental analysis for $C_{32}H_{42}FNO_2SSi$: calcd: C, 69.65; H, 7.67; N, 2.54; S, 5.81. Found: C, 69.58; H, 7.60; N, 2.43; S, 5.74.

Dia 2: Colorless oil. R_f 0.32 (Cyclohexane/EtOAc: 1/1). IR (KBr): ν 3070, 2930, 2858, 1727, 1428, 1362, 1262, 1111, 823, 740, 701, 505 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.03 (s, 9H), 1.15 (s, 9H), 2.28–2.36 (m, 2H), 2.97–3.11 (m, 2H), 3.26 (d, J = 4.7 Hz, 1H), 3.55 (t, J = 6.6 Hz, 2H), 4.03–4.16 (m, 1H), 4.75 (dt, J = 7.5 Hz, J = 37.3 Hz, 1H), 7.15–7.27 (m, 5H), 7.35–7.43 (m, 6H), 7.63–7.66 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −124.2 (dd, J = 17.5 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.6 (CH_3), 26.9 (CH_3), 27.2 (d, J = 3.8 Hz, CH_2), 39.7 (CH_2), 55.9 (C), 57.6 (d, J = 29.1 Hz, CH), 63.0 (d, J = 1.6 Hz, CH_2), 106.1 (d, J = 13.7 Hz, CH), 127.1 (CH), 127.7 (CH), 128.7 (CH), 129.7 (CH), 133.9 (C), 135.6 (CH), 136.0 (C), 156.8 (d, J = 256.6 Hz, C) ppm. MS (EI): m/z = 551.87 $[M^{+\circ}]$. Elemental analysis for $C_{32}H_{42}FNO_2SSi$: calcd: C, 69.65; H, 7.67; N, 2.54; S, 5.81. Found: C, 69.55; H, 7.62; N, 2.45; S, 5.77.

***N*-((*Z*)-1-Allyl-5-{[*tert*-butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenyl)-2-methyl-2-propanesulfinamide (8f).** **Dia 1:** Colorless oil. R_f 0.4 (Cyclohexane/EtOAc: 1/1). IR (KBr): ν 2930, 2858, 1707, 1473, 1428.0, 1362, 1111, 823, 702, 505 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.04 (s, 9H), 1.23 (s, 9H), 2.33–2.52 (m, 4H, H_2), 3.41 (d, J = 7.5 Hz, 1H), 3.66 (t, J = 6.6 Hz, 2H), 3.76–3.89 (m, 1H), 4.96 (dt, J = 7.3 Hz, J = 37.7 Hz, 1H), 5.07–5.14 (m, 2H), 5.65–5.79 (m, 1H), 7.35–7.46 (m, 6H), 7.65–7.68 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ −122.8 (dd, J = 18.6 Hz, J = 38.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.7 (CH_3), 26.9 (CH_3), 27.2 (d, J = 4.4 Hz, CH_2), 37.6 (CH_2), 56.4 (C), 56.8 (d, J = 28.5 Hz, CH), 63.1 (d, J = 1.6 Hz, CH_2), 105.0 (d, J = 14.2 Hz, CH), 118.6 (CH_2), 127.8 (CH), 129.7 (CH), 133.5 (C), 133.9 (CH),

135.7 (C), 158.5 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 502.0.0 [M$^{+\circ}$]. Elemental analysis for $C_{28}H_{40}FNO_2SSi$: calcd: C, 67.02; H, 8.04; N, 2.79; S, 6.39. Found: C, 66.99; H, 8.31; N, 2.75; S, 6.59.

Dia 2: Colorless oil. R_f 0.32 (Cyclohexane/EtOAc: 1/1). IR (KBr): ν 2930, 2858, 1707, 1473, 1428, 1362, 1111, 823, 702, 505 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.05 (s, 9H), 1.19 (s, 9H), 2.30–2.40 (m, 2H), 2.43–2.58 (m, 2H), 3.36 (d, J = 4.3 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 3.87–3.98 (m, 1H), 4.93 (dt, J = 7.6 Hz, J = 37.1 Hz, 1H), 5.19–5.22 (m, 2H), 5.67–5.81 (m, 1H), 7.35–7.45 (m, 6H), 7.65–7.68 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –123.9 (dd, J = 18.6 Hz, J = 39.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.6 (CH_3), 26.9 (CH_3), 27.2 (d, J = 4.4 Hz, CH_2), 38.0 (CH_2), 55.4 (d, J = 29.1 Hz, CH), 55.9 (C), 63.1 (d, J = 1.6 Hz, CH_2), 105.4 (d, J = 13.7 Hz, CH), 119.8 (CH_2), 127.7 (CH), 129.7 (CH), 133.2 (C), 133.8 (CH), 135.6 (C), 157.7 (d, J = 257.2 Hz, C) ppm. MS (EI): m/z = 502.0.0 [M$^{+\circ}$]. Elemental analysis for $C_{28}H_{40}FNO_2SSi$: calcd: C, 67.02; H, 8.04; N, 2.79; S, 6.39. Found: C, 66.96; H, 8.25; N, 2.76; S, 6.55.

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-1-vinyl-2-pentenyl)-2-methyl-2-propanesulfinamide (8g). Dia 1:** Colorless oil. R_f 0.48 (PE/EtOAc: 7/3). IR (KBr): ν 3436, 3207, 2930, 2858, 1704, 1472, 1428, 1362, 1261, 1111, 936, 823, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (s, 9H), 1.23 (s, 9H), 2.34–2.41 (m, 2H), 3.48 (d, J = 4.5 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 4.38–4.47 (m, 1H), 4.99 (dt, J = 7.3 Hz, J = 37.1 Hz, 1H), 5.32 (d, J = 10.2 Hz, 1H), 5.40 (d, J = 17.1 Hz, 1H), 5.79 (ddd, J = 7.0 Hz, J = 10.2 Hz, J = 17.1 Hz, 1H), 7.34–7.45 (m, 6H), 7.64–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –120.4 (dd, J = 14.4 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.7 (CH_3), 26.9 (CH_3), 27.3 (d, J = 3.8 Hz, CH_2), 56.1 (C), 58.8 (d, J = 28.5 Hz, CH), 62.9 (d, J = 1.6 Hz, CH_2), 105.3 (d, J = 13.2 Hz, CH), 119.5 (CH_2), 127.8 (CH), 129.8 (CH), 133.8 (C), 134.3 (d, J = 1.6 Hz, CH), 135.7 (CH), 157.8 (d, J = 257.7 Hz, C) ppm. MS (EI): m/z = 488.13 [M+H]$^+$. Elemental analysis for $C_{27}H_{38}FNO_2SSi$: calcd: C, 66.49; H, 7.85; N, 2.87; S, 6.57. Found: C, 66.35; H, 7.72; N, 2.86; S, 6.61.

Dia 2: Colorless oil. R_f 0.37 (PE/EtOAc: 7/3). IR (KBr): ν 3436, 3207, 2930, 2858, 1704, 1472, 1428, 1362, 1261, 1111, 936, 823, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (s, 9H), 1.21 (s, 9H), 2.33–2.40 (m, 2H), 3.28 (d, J = 5.5 Hz, 1H), 3.67 (t, J = 6.4 Hz, 2H), 4.37–4.47 (m, 1H), 4.97 (dt, J = 7.5 Hz, J = 36.7 Hz, 1H), 5.29 (d, J = 10.4 Hz, 1H), 5.41 (d, J = 17.3 Hz, 1H), 5.91 (ddd, J = 7.3 Hz, J = 10.4 Hz, J = 17.6 Hz, 1H), 7.34–7.45 (m, 6H), 7.64–7.67 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –121.5 (dd, J = 16.5 Hz, J = 37.1 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.3 (C), 22.6 (CH_3), 26.9 (CH_3), 27.3 (d, J = 3.8 Hz, CH_2), 56.2 (C), 59.5 (d, J = 28.5 Hz, CH), 63.0 (d, J = 1.6 Hz, CH_2), 105.8 (d, J = 13.7 Hz, CH), 118.8 (CH_2), 127.8 (CH), 129.8 (CH), 133.8 (C), 135.0 (CH), 135.7 (CH), 157.0 (d, J = 257.7 Hz, C) ppm. MS (EI): m/z = 488.13 [M+H]$^+$. Elemental analysis for $C_{27}H_{38}FNO_2SSi$: calcd: C, 66.49; H, 7.85; N, 2.87; S, 6.57. Found: C, 66.38; H, 7.75; N, 2.84; S, 6.61.

Product of imine reduction from 6

***N*-((*Z*)-5-{[*tert*-Butyl(diphenyl)silyl]oxy}-2-fluoro-2-pentenyl)-2-methyl-2-propanesulfinamide.** R_f 0.13 (Cyclohexane/EtOAc: 75/25). IR (KBr): ν 3435, 2858, 1711, 1650, 1472, 1427, 1307, 1111, 1054, 823, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.05 (s, 9H), 1.21 (s, 9H), 2.32–2.39 (m, 2H), 3.46 (t, J = 6.4 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 3.72–3.88 (m, 2H), 4.90 (dt, J = 7.3 Hz, J = 36.5 Hz, 1H), 7.34–7.45 (m, 6H), 7.62–7.65 (m, 4H) ppm. ^{19}F NMR ($CDCl_3$, 282.5 MHz): δ –116.3 (dt, J = 14.4 Hz, J = 36.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 19.2 (C), 22.5 (CH_3), 26.8 (CH_3), 27.1 (d, J = 3.8 Hz, CH_2), 46.2 (d, J = 31.2 Hz, CH), 56.1 (C), 62.9 (d, J = 1.6 Hz, CH_2), 105.2 (d, J = 13.2 Hz, CH), 127.7 (CH), 129.7 (CH), 133.8 (C), 135.5 (CH), 156.5 (d, J = 255.0 Hz, C) ppm. MS (EI): m/z = 462.13 [M+H]$^+$. Elemental analysis for $C_{25}H_{36}FNO_2SSi$: calcd: C, 65.03; H, 7.86; N, 4.11; S, 6.94. Found: C, 65.29; H, 7.92; N, 4.02; S, 6.91.

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