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# Indium-Promoted Diastereoselective Addition of Fluorinated Haloallylic Derivatives to Imines

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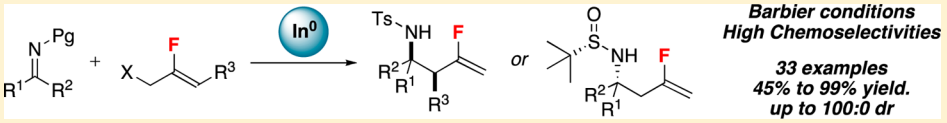
Supporting Information




**ABSTRACT:** We report herein the first general access to fluorinated homoallylic amines by means of an addition of fluorinated organoindium reagent. The corresponding amines were obtained in good to excellent yield with excellent diastereoisomeric ratio. A plausible mechanism is proposed to explain the stereochemical outcome of the reaction based on the X-ray structure of the products.

## INTRODUCTION

Molecules containing fluorine atom are of great interest on account of the impressive features of fluorine atom to severely affect the physical and biological properties of a molecule.[1] Hence, fluorine became an unavoidable partner toward the development of biologically active compounds, resulting in the presence of at least one fluorine atom in about 20% of pharmaceuticals and 40% of agrochemicals.[2] Among all of these fluorinated compounds, fluoroolefins represent an important class of compounds[3] used in material science,[4] in medicinal chemistry as peptide isosteres,[5] or as versatile fluorinated building blocks[6] (Figure 1).

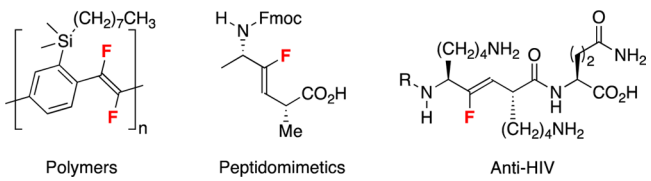



**Figure 1.** Relevant fluoroolefins.

In addition, chiral homoallylic amines are key compounds from a synthetic point of view,[7] offering a wide range of possible postfunctionalizations to access to more elaborate chiral compounds. As part of our ongoing research program devoted to the synthesis and the development of relevant fluorinated building blocks[8] and our previous work dealing with the synthesis of fluorinated homoallylic alcohols,[8h] we have been surprised that a sole method dealing with the access to chiral fluorinated homoallylic amines has been reported to date. Haufe and co-workers described an elegant access to homoallylic amine derived from glycine by means of a diastereoselective alkylation of a camphor-based glycine iminoesters,[9a] (*R*,*R*,*R*)-2-hydroxy-3-pinanone,[9b] or Seebach's imidazolidinone (Figure 2a).[9c,10] Thus, taking into account the remarkable properties of indium to promote allylation reaction

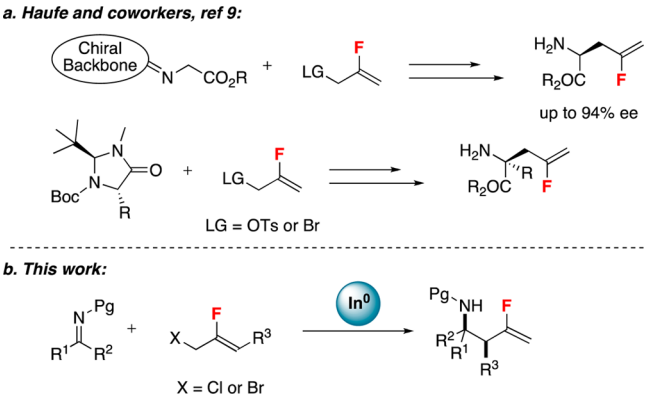



**Figure 2.** Past and present work.

under neutral and mild conditions,[11] we were wondering if an indium-promoted addition of a fluorinated allylic derivative to an imine would give a straightforward access to the highly valuable fluorinated homoallylic amines (Figure 2b). Noteworthy, indium is very appealing because it can be used without activation prior to use under Barbier conditions along with a broad functional group tolerance and a very low toxicity. As a result, indium metal has been extensively used to promote allylation, propargylation, allenylation, or Reformatsky reactions, while organoindium reagents are becoming very popular reagents in organic synthesis.[12]

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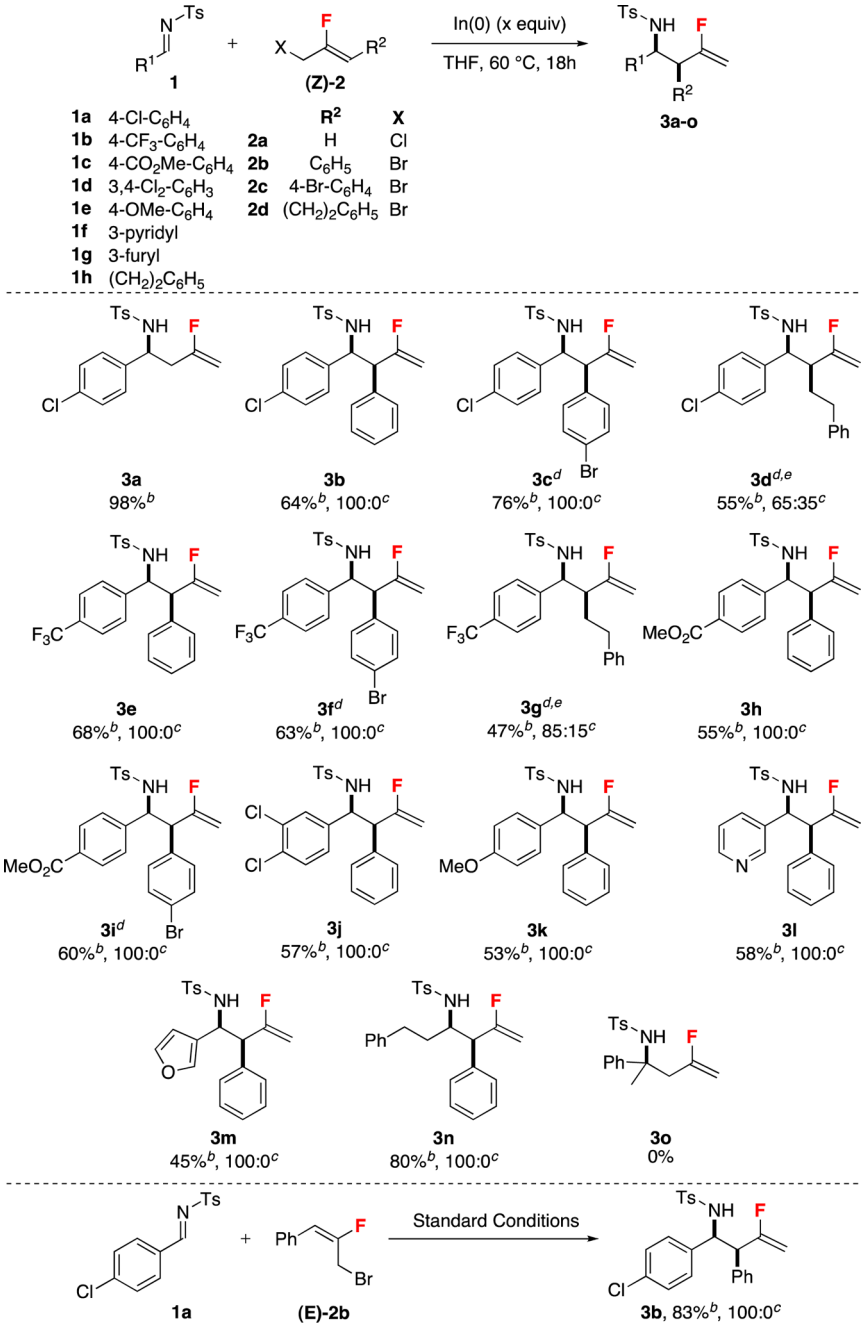
**Scheme 1. Diastereoselective Addition of Fluorinated Allyl Bromide Derivatives 2a–d to *N*-Tosylimine 1a–h[a]**




[a]Conditions: **1** (0.3 mmol), **2** (1.5 equiv), $In^0$ (1.5 equiv), THF (1 mL), 60 °C, 18 h. [b]Isolated yield. [c]Syn:anti ratio determined by $^{19}F$ NMR on the crude reaction mixture. [d]Reaction was carried out at 75 °C. [e]$In^0$ and **2** were added portionwise; see the Experimental Section for further details.

## RESULTS AND DISCUSSION

At the beginning of the project, the *N*-tosylimine **1a** derived from 4-chlorobenzaldehyde was engaged in the reaction with In(0) and the commercially available 3-chloro-2-fluoropropene **2a** in THF at 60 °C.[13] Gratefully, the desired product **3a** was isolated in 98% yield after 16 h, showing the viability of the proposed scenario (Figure 2). Using these conditions, we extended the scope of the reaction to several imines and fluorinated allyl reagents (Scheme 1).

First, the addition of several fluorinated allyl halides derivatives **2** was performed on imine **1a**. Substituted allyl bromide derivatives (*Z*)-**2b** and (*Z*)-**2c** were used, and the resulting addition products[3b,c] were isolated in 64% and 76% yield, respectively. Noteworthy, the reaction proceeded with a complete syn selectivity, and no trace of the anti adduct was observed. The aliphatic-substituted allyl bromide derivative (*Z*)-**2d** was then used, and the corresponding adduct **3d** was obtained in 55% yield with a lower diastereoisomeric ratio, 65:35. The *N*-tosylimine-derived from *p*-trifluoromethyl benzaldehyde **1b** was tested in our reaction, and the products resulting from the addition of (*Z*)-**2b** and (*Z*)-**2c** were isolated in good yield with a complete syn-selectivity. The addition of (*Z*)-**2d** to imine **1b** gave the addition product **3g** in 47% yield with an 85:15 diastereoisomeric ratio. An ester moiety was compatible under our reaction conditions, imines **1c** reacted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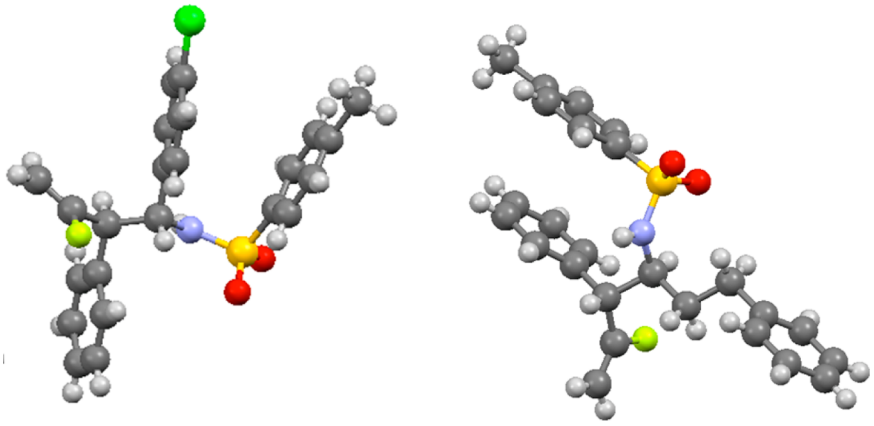

**Figure 3.** Crystal structure of compounds **3b** and **3n**.

smoothly to afford **3h** and **3i** in moderate to good yield as a sole syn-diastereoisomer. Then, an imine bearing an electron-donating group was tested. Imine **1e** derived from *p*-anisaldehyde reacted with (*Z*)-**2b** to give the addition product **3k** in good yield, as a syn-stereoisomer. Then, heteroaromatic imines derived from pyridine and furan were successfully engaged in the reaction, and homoallylic amines **3l** and **3m** were isolated in 58% and 45% yield, respectively. Finally, aliphatic imines **1h** derived from hydrocinnamaldehyde reacted smoothly, affording the syn adduct **3n** in 80% yield as a single diastereoisomer. Unfortunately, despite all our attempts, *N*-tosylketimines remained unreactive under our conditions. One should note that the N-Ts protecting group might be removed under standard conditions.[14] Interestingly, when the reaction was carried out with the other diastereoisomer (*E*)-**2b** the same syn addition product **3b** than the one obtained with (*Z*)-**2b** was isolated in 83% yield as a single diastereoisomer. This result might arise from an isomerization of the latent allyl indium species from the (*E*)-isomer to the thermodynamically more stable (*Z*)-isomer.[15,16]

The complete $\gamma$-selectivity of the reaction as well as the syn-selectivity of our process has been highlighted through an X-ray analysis of compound **3b** and **3n** (Figure 3). The crystal structure clearly shows the $\gamma$-addition of the allylic indium species and the syn relationship between the two newly created stereogenic centers. Based on this observed diastereoselectivities and the experiments between imines **1a** and the (*Z*)- and (*E*)-isomer of **2b**, we propose the mechanistic pathway depicted in Figure 4 to explain the stereochemical outcome of the reaction.

According to the observations independently made by Chan[13] and Paquette,[14] the (*E*)- and (*Z*)-allyl indium species are in equilibrium and the thermodynamically more stable (*Z*)-allyl isomer is predominant in the reaction media. Then the allyl species reacts through an open-chain transition state **II** giving predominantly the syn-addition product regardless of the geometry of the starting fluoro allyl compound. It is noteworthy that transition state **III** appeared less favorable than transition state **II** due to several gauche interactions.[17] This difference might result in the displacement of equilibrium between the *E* and *Z* allyl indium species toward the *Z*-species, thus explaining the observed selectivity with (*E*)-**2b** (Scheme 1). Finally, the previous experimental results preclude a coordination of the nitrogen to the metal center forming of a six-membered transition state **I**, which would afford the product with the anti-relative configuration.

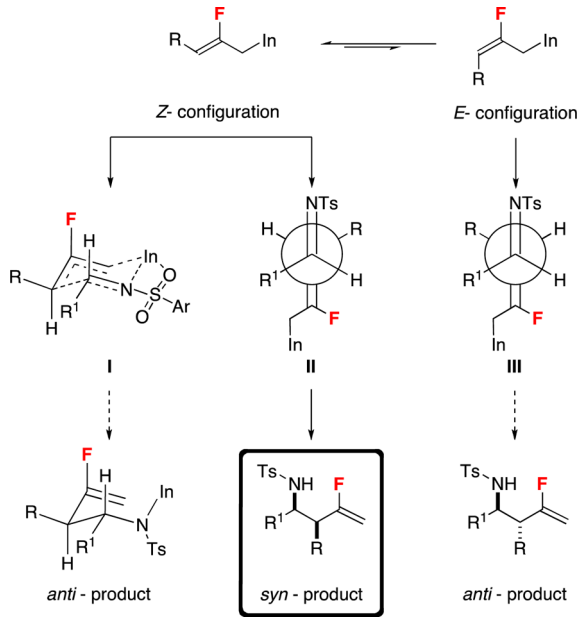


**Figure 4.** Proposed transition state.

Then, we turned our attention to the development of an asymmetric approach of the allylation reaction. To access to chiral fluorinated homoallylic amines by controlling the addition of our allyl indium species we focused our strategy on the use of the efficient Ellman auxiliary.[18]

Under our previous optimized conditions, although only 40% of the 4-chlorobenzaldehyde-derived sulfinylimine **4a** was converted into the desired homoallylic amine **5a**, the latter was obtained with an excellent 98:2 diastereoselective ratio, and the only other product detected in the crude mixture was the starting imine (Table 1, entry 1). Encouraged by this promising result, we decided to reoptimize the reaction parameters to access chiral fluorinated homoallylic amines. Using water as a solvent, no addition occurred and only hydrolysis of the starting imine **4a** was observed (entry 2). Among other organic solvents tested, dichloroethane (DCE) gave the best result regarding yields and diastereomeric ratios (entries 3−6). Indeed, the corresponding amine **5a** was obtained with 46% yield, 99:1 dr, and the starting sulfinylimine **4a** was the only side product detected in the crude mixture at the end of the reaction. Surprisingly, when the reaction was performed at higher temperature, the conversion remained almost the same (entry


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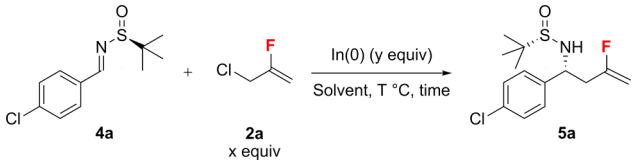
**Table 1. Optimization of the Diastereoselective Addition of Fluorinated Allyl Derivatives 2a[a]**




| entry | solvent | $T$ (°C) | $x$ | $y$ | conv[b] | dr[c] |
|---|---|---|---|---|---|---|
| 1 | THF | 60 | 3 | 3 | 40 | 98:2 |
| 2 | $H_2O$ | 60 | 3 | 3 | 0 | |
| 3 | $CH_3CN$ | 60 | 3 | 3 | 38 | 99:1 |
| 4 | toluene | 60 | 3 | 3 | 52 | 97:3 |
| 5 | DCM | 60 | 3 | 3 | 11 | 99:1 |
| 6 | DCE | 60 | 3 | 3 | 46 | 99:1 |
| 7 | DCE | 70 | 3 | 3 | 49 | 99:1 |
| 8 | DCE | 53 | 3 | 3 | 82 | 99:1 |
| 9 | DCE | 53 | 1.1 | 1.1 | 5 | 99:1 |
| 10 | DCE | 53 | 2 | 2 | 45 | 99:1 |
| 11 | DCE | 53 | 6 | 6 | 94 | 99:1 |
| 12[d] | DCE | 53 | 3 | 4 | 100 (96)[e] | 99:1 |

[a]Conditions: **4a** (0.1 mmol), **2a** ($x$ equiv), $In^0$ ($y$ equiv), solvent (1 mL), 14 h. [b]Conversion of starting sulfinylimine, determined by $^1H$ NMR of the crude material. [c]Determined by $^{19}F$ NMR of the crude material. [d]In(0) and **2a** were added portionwise, 48 h reaction time. [e]Isolated yield.

7). However, lowering temperature to 53 °C gave 82% conversion into **5a** (entry 8). The low boiling point of the starting allyl chloride **2a** (55 °C) might explain the observed result. Next, the stoichiometry of both In(0) and fluorinated allyl chloride was modulated (entries 9−11). With a slight excess of reactants relative to the starting imine **4a**, only 5% conversion into amine **5a** was observed (entry 9). Using 2 equiv of In(0) and allyl chloride **2a**, conversion reached 45% (entry 10). Unfortunately, to get almost total conversion of the imine **4a**, the use of a large excess of reactants (6 equiv) was required (entry 11). However, by adding the reactants in two portions, 4 equiv of In(0) and 3 equiv of allyl chloride **2a** were sufficient to ensure a total conversion of imine **4a** and to isolate the homoallylic amine **5a** in 96% yield (entry 12). Having optimized the addition of **2a** onto the model chiral imine we sought to extend the scope of this transformation with other chiral imines (Table 2).

First, imines derived from benzaldehyde and aromatic aldehydes bearing an electron-donating group were engaged under our reaction conditions. Imines derived from both *p*-anisaldehyde and piperonal gave the desired adducts in very good yield with excellent diastereoselectvities, 98:2 and 100:0, respectively, while imine derived from benzaldehyde afforded the addition product **5b** in 95% yield and 98:2 diastereoisomeric ratio (entries 2−4). We then investigated the functional group tolerance of our In-mediated addition reaction. Interestingly, unprotected phenol and ester derivatives reacted nicely to afford the corresponding fluorinated homoallylic compounds **5e** and **5f** as a single diastereoisomer in good to excellent yield (entries 5 and 6). Heteroaromatic derivatives were also compatible and pyridine aldimine **4h** provided the allylation product **5h** in pretty good yield with an excellent diastereoisomeric ratio (97%, 99:1, entry 8), while the chloroquinoline **4i** gave **5i** as a single diastereoisomer in good yield without alteration of the chlorine substituent (entry 9). Thiophene aldimine **5j** afforded the addition product in good yield and very good diastereoselectivity (entry 10). *α,β*-Unsaturated aldehydes reacted smoothly under our conditions, and addition products **5k** and **5l** were isolated with a nice diatereoselective ratio (97:3) in very good yield, 80% and 77%, respectively (entries 11 and 12). Interestingly, the reaction with chiral imine **4m** derived from ferrocenyl aldehyde proceeded nicely, giving the addition adduct **5m** as a sole diastereomer with 78% yield (entry 13). We then moved toward the extension to valuable aliphatic aldimines, and pleasingly, both imines **4n** and **4o** provide the addition products **5n** and **5o** in good yield and very good diastereoisomeric ratio, 96:4 and 95:5, respectively (entries 14 and 15). Imines derived from citronellal **4p** and hydrocinnamaldehyde **4q** were tested and afforded the addition products **5p** and **5q** in excellent yield and a 97:3 diastereoisomeric ratio (entries 16 and 17). Then, reaction was performed using ketimine **4r** derived from acetophenone, and the addition product was isolated in 84% yield with a 83:17 diastereoisomeric ratio (entry 18). Finally, we sought to extend the reaction with *γ*-substituted fluorinated allyl bromide **2b**. Unfortunately, despite all our attempts to get the corresponding addition product **5s** we have not been able to isolate the desired compound with synthetically useful yield and selectivity.[19] Noteworthy, the addition product **5a** might be easily deprotected under standard conditions[17] to give the free amine **6** without loss of optical purity.[20]

The absolute configuration of the addition product **5a** has been determined by an X-ray analysis (Figure 5). The crystal

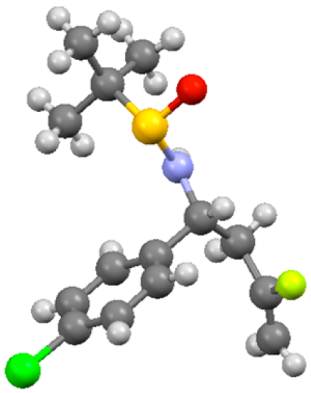


**Figure 5.** Crystal structure of compound **5a**.

structure allowed us to determine a (*R*) configuration of the newly created stereogenic center. Taking this result into account, we are able to propose the following transition state of the reaction (Figure 6).

To explain the observed stereochemistry, we proposed a six-membered ring transition state, involving a coordination of the indium metal center[21] to the oxygen of the chiral auxiliary. This coordination would rigidify the intermediate and would allow an *α*-addition of the allyl residue giving the corresponding homoallylic imines with a *R* configuration of the newly created

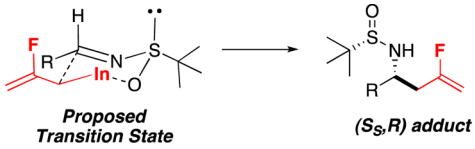



**Figure 6.** Proposed transition state.


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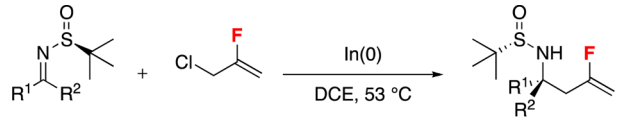
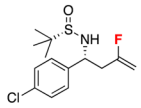
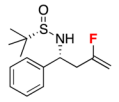
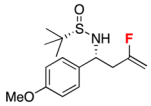
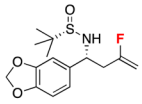
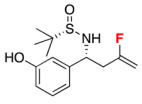
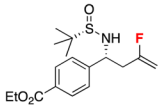
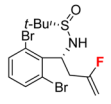
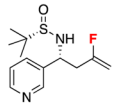
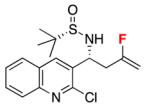
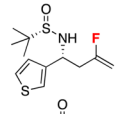
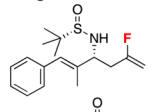
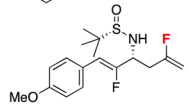
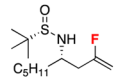
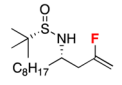
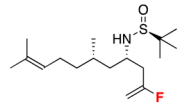
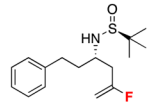
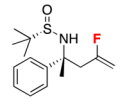
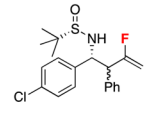
**Table 2. Scope of the Reaction**




4a-r 2a 5a-r

| Entry | $R^1$ | $R^2$ | Product | | Yield (%)[b] | dr[c] |
|---|---|---|---|---|---|---|
| 1 | 4-Cl-$C_6H_4$ | H |  | **5a** | 96 | 99:1 |
| 2 | $C_6H_5$ | H |  | **5b** | 95 | 98:2 |
| 3 | 4-OMe-$C_6H_4$ | H |  | **5c** | 99 | 98:2 |
| 4 | 3,4-($OCH_2O$)-$C_6H_3$ | H |  | **5d** | 80 | 100:0 |
| 5 | 3-OH-$C_6H_4$ | H |  | **5e** | 62 | 100:0 |
| 6 | 4-$CO_2$Et-$C_6H_4$ | H |  | **5f** | 96 | 100:0 |
| 7 | 2,6-$(Br)_2$-$C_6H_3$ | H |  | **5g** | 46 | 100:0 |
| 8 | 3-pyridyl | H |  | **5h** | 97 | 99:1 |
| 9 | 2-Cl-quinoline | H |  | **5i** | 86 | 100:0 |
| 10 | 2-thienyl | H |  | **5j** | 74 | 98:2 |
| 11 | ($C_6H_5$)CH=C($CH_3$) | H |  | **5k** | 80 | 97:3 |
| 12 | (4-OMe-$C_6H_4$)-CH=C(F) | H |  | **5l** | 77 | 97:3 |
| 13 | ferrocenyl | H |  | **5m** | 78 | 100:0 |
| 14 | $CH_3(CH_2)_4$ | H |  | **5n** | 93 | 96:4 |
| 15 | $CH_3(CH_2)_7$ | H |  | **5o** | 91 | 95:5 |
| 16 | citronellal | |  | **5p** | 91 | 97:3 |
| 17 | ($C_6H_5$)-($CH_2$)$_2$ | H |  | **5q** | 92 | 97:3 |
| 18 | $C_6H_5$ | Me |  | **5r** | 84 | 83:17 |
| 19[d] | 4-Cl-$C_6H_4$ | H |  | **5s** | - | - |

[a]Conditions: **1** (0.1 mmol), **2a** (0.3 mmol), $In^0$ (0.4 mmol), DCE (1 mL), 53 °C, 48 h. [b]Isolated yield. [c]Determined by $^{19}F$ NMR on the crude reaction mixture. [d]**2b** was used instead of **2a**.

stereocenter. Noteworthy, an open transition state would have led to the opposite diastereoisomer.

## CONCLUSION

In conclusion, we reported the access to fluorinated homoallylic amines in good yields and excellent diastereoisomeric ratios. The complete $\gamma$-selectivity of the reaction using $\gamma$-substituted allylic derivative **2b−d** was clearly proved by X-ray analysis of the corresponding products **3b** and **3n** as well as the syn-selectivity of the reaction. This methodology was applied to a broad range of aromatic and aliphatic *N*-Ts imines in good yields and excellent diastereoselectivities (up to 100:0). This process represents the first general access to the syn- addition products. Then, the use of the Ellman's auxiliary provided an efficient access to chiral fluorinated homoallylic amines. Both aromatic and aliphatic imines were suitable substrates giving a straightforward access to chiral fluorinated building blocks. The relative configuration of the resulting product determined by a X-ray analysis led us to assume a plausible six-membered ring intermediate of the reaction. In summary, we reported herein the first general access to fluorinated homoallylic amines in both racemic and diastereoselective fashion giving an easy access to new valuable fluorinated olefins compounds.

## EXPERIMENTAL SECTION

Residual $CHCl_3$ served as internal standards ($\delta$ = 7.26) for $^1H$ NMR, $CFCl_3$ served as internal standard ($\delta$ = 0.0) for $^{19}F$ NMR and $CDCl_3$ served as internal standard ($\delta$ = 77.16) for $^{13}C$ NMR. Flash chromatographies were performed with silica gel (0.063−0.200 mm). Analytical thin-layer chromatography (TLC) was performed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on silica gel aluminum plates with F-254 indicator and visualized by UV fluorescence and/or staining with $KMnO_4$ or PMA. THF was distilled over Na/benzophenone prior to use. HRMS analyses were performed under (ESI) conditions with a micro TOF detector. All experiments were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring using standard Schlenk techniques. *N*-Tosylaldimines **1**,[22] fluorinated bromoallylic derivatives **2**,[23] and *N*-sulfinylimines **5**[24] were prepared according to literature methods.

**General Procedure for the Addition of Fluorinated Bromo Allylic Derivative 2 to *N*-Ts Imine 1.** In a 1.5 mL vial, **1** (0.3 mmol), indium (0.45 mmol), **2** (0.45 mmol), and THF (1 mL) were introduced, and the vial was sealed (screwed caps). The resulting mixture was stirred at 60 °C for 18 h. The reaction mixture was quenched with 5 drops of $NH_4Cl$ (saturated aqueous solution), and DCM was added. The mixture was filtered through a pad of Celite and evaporated. The residue was purified by flash chromatography ($SiO_2$, cyclohexane/EtOAc mixture) to afford the corresponding fluorinated sulfonamide **3** (see Scheme 1).

*N-(1-(4-Chlorophenyl)-3-fluorobut-3-enyl)-4-methylbenzenesulfonamide (**3a**).* Compound **3a** was obtained as a white solid (mp 88−92 °C) in 98% yield (69 mg) after trituration in cyclohexane. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.57 (d, $J$ = 6.7 Hz, 2H), 7.26−6.90 (m, 6H), 5.95 (d, $J$ = 5.9 Hz, 1H), 4.65−4.38 (m, 2H), 4.19 (d, $J$ = 49.4 Hz, 1H), 2.80−2.43 (m, 2H), 2.40 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 161.45 (d, $J$ = 257 Hz), 143.6, 138.2, 137.1, 133.4, 129.4 (2C), 128.6 (2C), 128.1 (2C), 127.2 (2C), 93.9 (d, $J$ = 19 Hz), 54.7, 40.1 (d, $J$ = 27 Hz), 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −96.4 (m). IR (cm$^{-1}$): 3265, 1321, 1151, 809, 671, 534. Anal. Calcd for $C_{17}H_{17}ClFNO_2S$: C, 57.70; H, 4.84; N, 3.96; S, 9.06. Found: C, 58.04; H, 4.96; N, 4.21; S, 9.07.

*syn-N-(1-(4-Chlorophenyl)-3-fluoro-2-phenylbut-3-enyl)-4-methylbenzenesulfonamide (**3b**).* Compound **3b** was obtained as a white solid (mp 164−166 °C) in 64% yield (82.5 mg) after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 70:30, $R_f$ = 0.37 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.43−6.96 (m, 13H), 5.08 (s, 1H), 4.77 (dd, $J$ = 9.4, 5.6 Hz, 1H), 4.36 (dd, $J$ = 17.5, 3.2 Hz, 1H), 4.17 (d, $J$ = 49.6, 3.2 Hz, 1H), 3.54 (dd, $J$ = 25.0, 9.9 Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.8 (d, $J$ = 260 Hz), 143.3, 137.2, 136.4, 135.5, 133.5, 129.2 (3C), 129.1, 128.8 (2C), 128.4, 128.4, 128.3 (2C), 128.2, 127.2 (2C), 93.6 (d, $J$ = 19 Hz), 58.2, 56.0 (d, $J$ = 24 Hz), 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −103.9 (ddd, $J$ = 49, 25, 17 Hz). IR (cm$^{-1}$): 3251, 1920, 1671, 1446, 1322, 1159, 1064. HRMS (ESI+): calcd for [M + $NH_4$] $C_{23}H_{25}ClFN_2O_2S$ 447.1309, found 447.1300 (−2.0 ppm).

*syn-N-(2-(4-Bromophenyl)-1-(4-chlorophenyl)-3-fluorobut-3-enyl)-4-methylbenzenesulfonamide (**3c**).* Compound **3c** was obtained as a white solid (mp 208−210 °C) in 76% yield (116 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.31 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.35 (d, $J$ = 8.4 Hz, 2H), 7.27 (d, $J$ = 7.6 Hz, 2H), 7.14 (d, $J$ = 8.5 Hz, 2H), 7.10−7.00 (m, 6H), 5.10 (d, $J$ = 6.5 Hz, 1H), 4.74 (dd, $J$ = 10.0, 6.8 Hz, 1H), 4.37 (dd, $J$ = 17.5, 3.4 Hz, 1H), 4.16 (dd, $J$ = 49.5, 3.4 Hz, 1H), 3.50 (dd, $J$ = 25.1, 10.1 Hz, 1H), 2.43 (s, 3H). $^{13}$C NMR (75 MHz, acetone): $\delta$ 164.4 (d, $J$ = 260 Hz), 143.3, 139.8, 139.3, 137.9 (d, $J$ = 2 Hz), 133.5, 132.2 (2C), 131.9 (2C), 130.1 (2C), 129.9 (2C), 128.9 (2C), 127.5 (2C), 121.8, 93.81 (d, $J$ = 19 Hz), 59.1 (d, $J$ = 8 Hz), 55.4 (d, $J$ = 23 Hz), 21.4. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −104.4 (ddd, $J$ = 49, 25, 17 Hz). IR (cm$^{-1}$): 3324, 1672, 1489, 1317, 1154, 1075. HRMS (ESI-): calcd for [M−H] $C_{23}H_{19}BrClFNO_2S$ 505.9992, found 505.9998 (1.2 ppm).

*syn-N-(3-Fluoro-2-phenyl-1-(4-(trifluoromethyl)phenyl)but-3-enyl)-4-methylbenzenesulfonamide (**3e**).* Compound **3e** was obtained as a white solid (mp 133−135 °C) in 68% yield (94.3 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.27 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.30−7.08 (m, 11H), 6.86 (d, $J$ = 6.0 Hz, 2H), 5.38 (d, $J$ = 5.7 Hz, 1H), 4.79 (dd, $J$ = 9.9, 5.8 Hz, 1H), 4.22 (dd, $J$ = 17.5, 3.2 Hz, 1H), 4.07 (dd, $J$ = 49.5, 3.3 Hz, 1H), 3.48 (dd, $J$ = 25.0, 9.9 Hz, 1H), 2.25 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.6 (d, $J$ = 260 Hz), 143.4, 142.5, 136.3, 135.3, 129.4 (q, $J$ = 30 Hz), 129.2 (2C), 129.1 (2C), 128.5 (2C), 128.3, 127.9 (2C), 127.1 (2C), 125.0 (q, $J$ = 3 Hz, 2C), 124.0 (q, $J$ = 272 Hz), 93.7 (d, $J$ = 19 Hz), 58.3, 55.8 (d, $J$ = 24 Hz), 21.3. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −63.1 (s), −103.9 (ddd, $J$ = 49, 25, 17 Hz). IR (cm$^{-1}$): 3256, 2926, 1677, 1437, 1321, 1152, 1065. HRMS (ESI+): calcd for [M + H] $C_{24}H_{22}F_4NO_2S$ 464.1307, found 464.1304 (−0.6 ppm).

*syn-N-(2-(4-Bromophenyl)-3-fluoro-1-(4-(trifluoromethyl)-phenyl)but-3-enyl)-4-methylbenzenesulfonamide (**3f**).* Compound **3f** was obtained as a white solid (mp 191−193 °C) in 62% yield (101 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.35 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.41−7.30 (m, 4H), 7.24−7.15 (m, 4H), 7.08 (d, $J$ = 8.1 Hz, 2H), 6.98 (d, $J$ = 8.0 Hz, 2H), 5.63 (d, $J$ = 7.5 Hz, 1H), 4.85 (dd, $J$ = 10.3, 7.6 Hz, 1H), 4.32 (dd, $J$ = 17.3, 3.5 Hz, 1H), 4.12 (dd, $J$ = 49.4, 3.5 Hz, 1H), 3.54 (dd, $J$ = 25.7, 10.4 Hz, 1H), 2.38 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.1 (d, $J$ = 261 Hz), 143.5, 142.5, 136.4, 134.9, 131.9 (2C), 130.0 (2C), 129.8 (q, $J$ = 32 Hz), 129.3 (2C), 127.7 (2C), 126.8 (2C), 125.2 (q, $J$ = 4 Hz, 2C), 123.9 (q, $J$ = 272 Hz), 122.1, 93.9 (d, $J$ = 19 Hz), 58.3, 55.1 (d, $J$ = 24 Hz), 21.3. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −63.1 (s), −104.9 (ddd, $J$ = 49, 26, 17 Hz). IR (cm$^{-1}$): 3231, 1673, 1453, 1321, 11150, 1113, 1065. HRMS (ESI-): calcd for [M−H] $C_{24}H_{19}BrF_4NO_2S$ 540.0256, found 540.0234 (−4.1 ppm).

*syn-Methyl 4-(3-Fluoro-1-(4-methylphenylsulfonamido)-2-phenylbut-3-enyl)benzoate (**3h**).* Compound **3h** was obtained as a yellow solid (mp 191−193 °C) in 55% yield (74.8 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.16 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 7.5 Hz, 2H), 7.27−6.90 (m, 11H), 4.82 (d, $J$ = 3.4 Hz, 1H), 4.75 (dd, $J$ = 8.8, 5.0 Hz, 1H), 4.26 (dd, $J$ = 17.5, 3.1 Hz, 1H), 4.07 (dd, $J$ = 49.5, 3.1 Hz, 1H), 3.83 (s, 3H), 3.48 (dd, $J$ = 24.7, 9.4 Hz, 1H), 2.27 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 166.7, 162.6 (d, $J$ = 261 Hz), 143.8, 143.4, 136.2, 135.2, 129.5, 129.4 (2C), 129.3(2C), 129.2 (2C), 128.5 (2C), 128.3, 127.5 (2C), 127.2 (2C), 93.7 (d, $J$ = 19 Hz), 58.4, 56.0 (d, $J$ = 24 Hz), 52.1, 21.4. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −103.6 (ddd, $J$ = 49, 24, 17 Hz). IR (cm$^{-1}$): 3237, 2859, 11674, 1435, 1322, 1152, 1080. HRMS (ESI+): calcd for [M + H] $C_{25}H_{25}FNO_4S$ 454.1488, found 454.1496 (1.8 ppm).

*syn-Methyl 4-(2-(4-Bromophenyl)-3-fluoro-1-(4-methylphenylsulfonamido)but-3-enyl)benzoate (**3i**).* Compound **3i** was obtained as a white solid (mp 197−199 °C) in 60% yield (95.5 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.19 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.31−7.20 (m, 4H), 7.11 (d, $J$ = 8.2 Hz, 2H), 7.02−6.89 (m, 4H), 4.82−4.68 (m, 2H), 4.29 (dd, $J$ = 17.5, 3.5 Hz, 1H), 4.09 (dd, $J$ = 49.5, 3.5 Hz, 1H), 3.84 (s, 3H), 3.45 (dd, $J$ = 24.5, 9.6 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 166.7, 162.2 (d, $J$ = 261 Hz), 143.9, 143.5, 136.5, 135.0, 134.9, 131.9 (2C), 130.0, 130.0, 129.6, 129.5, 129.3 (2C), 127.3 (2C), 126.9 (2C), 122.1, 93.9 (d, $J$ = 19 Hz), 58.5, 55.2 (d, $J$ = 24 Hz), 52.2, 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −104.5 to −104.9 (m). IR (cm$^{-1}$): 3214, 1686, 1431, 1291, 1158, 1073. HRMS (ESI-): calcd for [M−H] $C_{25}H_{22}BrFNO_4S$ 530.0437, found 530.0421 (−3.0 ppm).

*syn-N-(1-(3,4-Dichlorophenyl)-3-fluoro-2-phenylbut-3-enyl)-4-methylbenzenesulfonamide (**3j**).* Compound **3j** was obtained as a white solid (mp 163−165 °C) in 57% yield (79 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.43 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.29−6.88 (m, 12H), 5.04 (d, $J$ = 5.4 Hz, 1H), 4.66 (dd, $J$ = 10.0, 5.6 Hz, 1H), 4.28 (dd, $J$ = 17.4, 3.2 Hz, 1H), 4.08 (dd, $J$ = 49.4, 3.0 Hz, 1H), 3.42 (dd, $J$ = 25.4, 10.1 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.5 (d, $J$ = 260 Hz), 143.6, 138.8, 136.2, 135.2, 132.2, 131.8, 130.1, 129.5, 129.3 (2C), 129.2 (2C), 128.4, 128.3, 128.3, 127.1 (3C), 93.8 (d, $J$ = 19 Hz), 57.8, 55.7 (d, $J$ = 24 Hz), 21.5.$^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −104.2 (ddd, $J$ = 49, 25, 17 Hz). IR (cm$^{-1}$): 3268, 2922, 1673, 1451, 1329, 1152, 1068. HRMS (ESI+): calcd for [M + $NH_4$] $C_{23}H_{24}Cl_2FN_2O_2S$ 481.0920, found 481.0915 (−1.0 ppm).

*syn-N-(3-Fluoro-1-(4-methoxyphenyl)-2-phenylbut-3-enyl)-4-methylbenzenesulfonamide (**3k**).* Compound **3k** was obtained as a yellow solid (mp 131−133 °C) in 53% yield (68 mg), after flash


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chromatography ($SiO_2$, cyclohexane/EtOAc, 97:3 to 65:35, $R_f$ = 0.34 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.21−7.15 (m, 5H),, 7.09 (d, $J$ = 6.7 Hz, 2H), 6.94 (t, $J$ = 7.3 Hz, 4H), 6.59 (d, $J$ = 8.2 Hz, 2H), 4.74 (d, $J$ = 5.2 Hz, 1H), 4.71−4.60 (m, 1H), 4.27 (dd, $J$ = 17.4, 2.5 Hz, 1H), 4.10 (dd, $J$ = 49.9, 2.5 Hz, 1H), 3.68 (s, 3H), 3.48 (dd, $J$ = 24.6, 9.5 Hz, 1H), 2.28 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.3 (d, $J$ = 260 Hz), 159.0, 142.9, 136.7, 135.9, 130.6, 129.1 (2C), 129.0 (3C), 128.5 (3C), 128.1, 127.2 (2C), 113.5 (2C), 93.3 (d, $J$ = 19 Hz), 58.3, 56.3 (d, $J$ = 23 Hz), 55.2, 21.4.$^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −103.4 (ddd, $J$ = 50, 24, 18 Hz). IR ($cm^{-1}$): 3251, 2923, 1671, 1447, 1323, 1153, 1056. HRMS (ESI+): calcd for [M + K] $C_{24}H_{24}FKNO_3S$ 464.1098, found 464.1099 (0.2 ppm).

*syn-N-(3-Fluoro-2-phenyl-1-(pyridin-3-yl)but-3-enyl)-4-methylbenzenesulfonamide (**3l**).* Compound **3l** was obtained as a white solid (mp 219−221 °C) in 58% yield (69 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 85:15 to 60:40, $R_f$ = 0.27 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.42−8.30 (m, 2H), 7.42 (d, $J$ = 7.9 Hz, 1H), 7.30−7.21 (m, 5H), 7.11−7.00 (m, 5H), 4.74−4.63 (m, 2H), 4.31 (dd, $J$ = 17.5, 2.8 Hz, 1H), 4.10 (dd, $J$ = 49.6, 3.1 Hz, 1H), 3.48 (dd, $J$ = 24.8, 9.4 Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.3 (d, $J$ = 261 Hz), 149.1 (2C), 143.6 (2C), 135.8, 134.9, 134.3, 129.5 (2C), 129.3 (2C), 128.6, 128.4 (2C), 127.2 (2C), 123.1, 94.0 (d, $J$ = 19 Hz), 56.5, 56.1 (d, $J$ = 21 Hz), 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −103.7 (ddd, $J$ = 49, 25, 17 Hz). IR ($cm^{-1}$): 3257, 1858, 1674, 1435, 1323, 1153, 1078. HRMS (ESI+): calcd for [M + H] $C_{22}H_{22}FN_2O_2S$ 397.1386, found 397.1391 (1.3 ppm).

*syn-N-(3-Fluoro-1-(furan-3-yl)-2-phenylbut-3-enyl)-4-methylbenzenesulfonamide (**3m**).* Compound **3m** was obtained as a white solid (mp 153−155 °C) in 45% yield (51.7 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.28 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.42 (d, $J$ = 7.9 Hz, 2H), 7.31−7.15 (m, 6H), 7.14−7.10 (m, 3H), 6.12 (s, 1H), 5.03 (d, $J$ = 7.3 Hz, 1H), 4.86 (t, $J$ = 8.2 Hz, 1H), 4.50 (dd, $J$ = 17.8, 2.2 Hz, 1H), 4.33 (dd, $J$ = 50.0, 2.3 Hz, 1H), 3.64 (dd, $J$ = 23.0, 9.0 Hz, 1H), 2.40 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.5 (d, $J$ = 260 Hz), 143.2, 142.9, 140.5, 136.9, 135.9, 129.3 (2C), 128.9 (2C), 128.6 (2C), 128.0, 127.1 (2C), 123.4, 108.6, 93.5 (d, $J$ = 19 Hz), 55.1 (d, $J$ = 24 Hz), 50.9, 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −102.84 (ddd, $J$ = 50, 23, 18 Hz). IR ($cm^{-1}$): 3251, 2922, 1671, 1447, 1323, 1154, 1055. HRMS (ESI-): calcd for [M − H] $C_{21}H_{19}FNO_3S$ 384.1070, found 384.1074 (1.0 ppm).

*syn-N-(5-Fluoro-1,4-diphenylhex-5-en-3-yl)-4-methylbenzenesulfonamide (**3n**).* Compound **3n** was obtained as a white solid (mp 177−179 °C) in 80% yield (69 mg), after flash chromatography ($SiO_2$, cyclohexane/EtOAc, 95:5 to 65:35, $R_f$ = 0.43 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.53 (d, $J$ = 8.2 Hz, 2H), 7.25−6.86 (m, 12H), 4.62 (dd, $J$ = 17.9, 3.1 Hz, 1H), 4.36 (d, $J$ = 8.0 Hz, 1H), 4.33 (dd, $J$ = 49.9, 3.1 Hz, 1H), 3.79−3.61 (m, 1H), 3.50 (dd, $J$ = 25.1, 6.9 Hz, 1H), 2.64−2.39 (m, 2H), 2.36 (s, 3H), 1.99−1.83 (m, 1H), 1.75−1.57 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 164.0 (d, $J$ = 261 Hz), 143.4, 141.1, 137.5, 136.6, 129.7 (2C), 128.8 (2C), 128.4 (2C), 128.3(2C), 128.26, 128.23, 127.6, 127.1 (2C), 125.9, 94.4 (d, $J$ = 19 Hz), 55.1, 52.6 (d, $J$ = 23 Hz), 33.9, 31.3, 21.5. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −100.2 (ddd, $J$ = 50, 25, 18 Hz). IR ($cm^{-1}$): 3289, 2931, 1670, 1450, 1313, 1148, 1091. HRMS (ESI+): calcd for [M + H] $C_{25}H_{27}FNO_2S$ 424.1747, found 424.1740 (−1.7 ppm).

**Addition of Fluorinated Bromo Allylic Derivative 2d to *N*-Ts Imine 1.** In a vial, **1** (0.3 mmol), indium (0.15 mmol), **2d** (0.2 mmol), and THF (1 mL) were introduced the vial was sealed (screwed caps) and heated at 75 °C under vigorous stirring for 18 h. The vial was opened, extra portions of **2d** (0.15 mmol) and indium (0.2 mmol) were added, and the resulting mixture was stirred at 75 °C for 18 h. The solution was quenched with 5 drops $NH_4Cl$ (saturated aqueous solution) and stirred vigorously for 10 min. The mixture was filtered through a pad of Celite (washed with DCM) and evaporated. The residue was purified by flash chromatography ($SiO_2$, cyclohexane/EtOAc mixture) to afford the corresponding fluorinated amine **3** (see Scheme 1).

*N-(1-(4-Chlorophenyl)-3-fluoro-2-phenethylbut-3-enyl)-4-methylbenzenesulfonamide (**3d**).* Compound **3d** was obtained as a white solid in 55% yield (25 mg), after flash chromatography as an inseparable mixture of diastereoisomers ($SiO_2$, cyclohexane/EtOAc, 95:5 to 70:30, $R_f$ = 0.37 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.36 (d, $J$ = 8.3 Hz, 3.2H), 7.22−7.08 (m, 6.3H), 7.02−6.89 (m, 10H), 6.82−6.71 (m, 3.2H), 5.42 (d, $J$ = 9.1 Hz, 1H, *syn*), 5.30 (d, $J$ = 6.7 Hz, 0.6H, *anti*), 4.63 (dd, $J$ = 17.7, 2.9 Hz, 0.6H, *anti*), 4.41 (dd, $J$ = 17.8, 3.0 Hz, 1H, *syn*), 4.31−4.09 (m, 2.2H), 3.97 (dd, $J$ = 50.3, 3.1 Hz, 1H, *syn*), 2.70−2.52 (m, 1.7H), 2.45−2.30 (m, 3.5H), 2.27 (s, 1.8H, *anti*), 2.26 (s, 3H, *syn*), 1.99−1.84 (m, 1.2H), 1.73−1.56 (m, 1.9H), 1.44−1.30 (m, 0.9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.1 (d, $J$ = 260 Hz), 143.4 (*syn*), 143.3 (*anti*), 141.0 (*syn*), 140.7 (*anti*), 137.2 (*anti*), 137.1 (*anti*), 137.0 (*syn*), 136.9 (*syn*), 133.40 (*anti*), 133.2 (*syn*), 129.3 (2C, *syn*), 129.2 (2C, *anti*), 128.6 (2C, *anti*), 128.5 (2C, *syn*), 128.4 (4C, *syn*), 128.3 (4C, *anti*), 128.3 (2C, *anti*), 128.2 (2C, *syn*), 127.1 (2C, *anti*), 127.0 (2C, *syn*), 126.1 (*anti*), 126.0 (*syn*), 95.5 (d, $J$ = 20 Hz, *anti*), 94.8 (d, $J$ = 20 Hz, *syn*), 59.1 (*syn*), 58.4 (*anti*), 48.9 (d, $J$ = 24 Hz, *syn*), 48.6 (d, $J$ = 25 Hz, *anti*), 33.0 (*syn*), 32.8 (*anti*), 29.6 (*anti*), 29.4 *syn*), 21.4. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −104.7 (ddd, $J$ = 50, 26, 18 Hz, *syn*), −106.1 (ddd, $J$ = 50, 29, 18 Hz, *anti*). IR ($cm^{-1}$): 3239, 2919, 1673, 1452, 1318, 1162, 1088. HRMS (ESI-): calcd for [M − H] $C_{25}H_{24}ClFNO_2S$ 456.1200, found 456.1183 (−3.7 ppm).

*N-(3-Fluoro-2-phenethyl-1-(4-(trifluoromethyl)phenyl)but-3-enyl)-4-methylbenzenesulfonamide (**3g**).* Compound **3g** was obtained as a white solid in 47% yield (23 mg), after flash chromatography as an inseparable mixture of diastereoisomers ($SiO_2$, cyclohexane/EtOAc, 95:5 to 70:30, $R_f$ = 0.27 cyclohexane/EtOAc 8:2). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.32 (d, $J$ = 8.2 Hz, 2.72H), 7.25−7.08 (m, 6.8H), 7.03−6.86 (m, 8.2H), 5.54 (d, $J$ = 9.2 Hz, 1H, *syn*), 5.40 (d, $J$ = 7.0 Hz, 0.36H), 4.65 (dd, $J$ = 17.6, 3.1 Hz, 0.36H), 4.47−4.09 (m, 2.72H), 3.98 (dd, $J$ = 50.2, 3.1 Hz, 1H), 2.73−2.53 (m, 1.36H), 2.49−2.30 (m, 2.72H), 2.22 (s, 1.07H), 2.20 (s, 3H), 2.03−1.85 (m, 1.28H), 1.79−1.59 (m, 1.72H), 1.47−1.31 (m, 0.62H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.8 (d, $J$ = 260 Hz, *anti*), 162.7 (d, $J$ = 260 Hz, *syn*), 143.5 (*syn*), 143.4 (*anti*), 142.5 (*syn*), 142.3 (*syn*), 140.9 (*syn*), 140.6 (*anti*), 137.0 (*anti*), 136.9 (*syn*), 129.3 (q, $J$ = 32 Hz, *anti*), 129.2 (2C, *syn*), 129.2 (2C, *anti*), 129.1 (q, $J$ = 32 Hz, *syn*), 128.5 (2C, *syn*), 128.4 (2C, *anti*), 128.4 (2C, *syn*), 128.3 (2C, *anti*), 127.6 (2C, *anti*), 127.4 (2C, *syn*), 127.0 (2C, *anti*), 126.9 (2C, *syn*), 126.2 (*anti*), 126.1 (*syn*), 125.1 (q, $J$ = 4 Hz, 2C, *anti*), 124.9 (q, $J$ = 4 Hz, 2C, *syn*), 123.9 (q, $J$ = 272 Hz), 95.7 (d, $J$ = 19 Hz, *anti*), 95.0 (d, $J$ = 20 Hz, *syn*), 59.3 (*syn*), 58.6 (*anti*), 48.8 (d, $J$ = 25 Hz, *syn*), 48.4 (d, $J$ = 24 Hz, *anti*), 32.9 (*syn*), 32.8 (*anti*), 29.6 (*anti*), 29.4 (*syn*), 21.3. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −63.1 (s), −105.1 (ddd, $J$ = 50, 26, 18 Hz, *syn*), −106.1 (ddd, $J$ = 50, 28, 17 Hz, *anti*). IR ($cm^{-1}$): 3256, 2932, 1677, 1442, 1322, 1161, 1116, 1067, 1017. HRMS (ESI+): calcd for [M + K] $C_{26}H_{25}F_4KNO_2S$ 530.1179, found 530.1196 (3.2 ppm).

**General Procedure for the Addition of 3-Chloro-2-fluoroprop-1-ene 2a to Chiral Imine 4.** In a 1.5 mL vial, chiral imine **4** (0.1 mmol), indium (0.2 mmol), **2a** (0.15 mmol), and DCE (1 mL) were introduced, and the vial was sealed and heated at 53 °C under vigorous stirring for 16 h. The vial was opened, extra portions of indium (0.2 mmol) and **2a** (0.15 mmol) were added, and the resulting mixture was stirred at 53 °C for 16 h. The solution was quenched with 5 drops of $NH_4Cl$ (saturated aqueous solution), stirred vigorously for 5 min, and filtered over Celite (washed with DCM). The residue was purified by flash chromatography ($SiO_2$, petroleum ether/EtOAc 90:10 to 50:50) to afford the corresponding fluorinated chiral amine **5**.

*(S)-N-((R)-1-(4-Chlorophenyl)-3-fluorobut-3-enyl)-2-methylpropane-2-sulfinamide (**5a**).* Compound **5a** was obtained as a white solid (mp 106−110 °C) in 96% yield (29.2 mg), after flash chromatography ($R_f$ = 0.24 petroleum ether/EtOAc 5:5). $[\alpha]^{20}_D$: +107 ($c$ 0.40, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.35−7.29 (m, 2H), 7.29−7.23 (m, 2H), 4.70−4.59 (m, 1H), 4.65 (dd, $J$ = 17.1, 3.1 Hz, 1H), 4.31 (dd, $J$ = 49.4, 3.0 Hz, 1H), 3.78 (s, 1H), 2.63 (dd, $J$ = 18.4, 6.9 Hz, 2H), 1.19 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.2 (d, $J$ = 258 Hz), 139.2, 133.9, 128.99 (2C), 128.96 (2C), 94.0 (d, $J$ = 19 Hz), 55.9, 54.9, 41.5 (d, $J$ = 26 Hz), 22.6 (3C). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −94.1 (dq,

$J$ = 50, 18 Hz). IR ($cm^{-1}$): 3196, 2957, 1674, 1045, 823. Anal. Calcd for $C_{14}H_{19}ClFNOS$: C, 55.34; H, 6.30; N, 4.61; S, 10.55. Found: C, 55.51; H, 6.33; N, 4.57; S, 10.33.

*(S)-N-((R)-3-Fluoro-1-phenylbut-3-enyl)-2-methylpropane-2-sulfinamide (**5b**).* Compound **5b** was obtained as a yellowish oil in 95% yield (25.6 mg), after flash chromatography ($R_f$ = 0.34 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +84 ($c$ 0.56, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.39−7.27 (m, 5H), 4.70−4.59 (m, 1H), 4.65 (dd, $J$ = 16.8, 2.7 Hz, 1H), 4.32 (dd, $J$ = 49.5, 2.7 Hz, 1H), 3.77 (s, 1H), 2.66 (dd, $J$ = 18.3, 6.8 Hz, 2H), 1.19 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.8 (d, $J$ = 258 Hz), 144.4, 128.2 (2C), 127.4, 126.4 (2C), 95.3 (d, $J$ = 20 Hz), 59.6 (d, $J$ = 3 Hz), 56.3, 47.5 (d, $J$ = 24 Hz), 22.8 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −93.9 (dq, $J$ = 50, 18 Hz). IR ($cm^{-1}$): 3208, 1677, 1043, 856, 701. Anal. Calcd for $C_{14}H_{20}FNOS$: C, 62.42; H, 7.48; N, 5.20; S, 11.90. Found: C, 62.68; H, 7.60; N, 5.03; S, 11.62.

*(S)-N-((R)-3-Fluoro-1-(4-methoxyphenyl)but-3-enyl)-2-methylpropane-2-sulfinamide (**5c**).* Compound **5c** was obtained as a pale yellow solid (mp 86−90 °C) in 99% yield (29.6 mg), after flash chromatography ($R_f$ = 0.39 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −107 ($c$ 0.35, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.24 (d, $J$ = 8.6 Hz, 2H), 6.87 (d, $J$ = 8.6 Hz, 2H), 4.70−4.53 (m, 2H), 4.31 (dd, $J$ = 49.5, 2.8 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 1H), 2.62 (dd, $J$ = 18.4, 6.9 Hz, 2H), 1.18 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.7 (d, $J$ = 258 Hz), 159.4, 132.5, 128.8 (2C), 114.0 (2C), 93.5 (d, $J$ = 19.2 Hz), 55.7, 55.3, 54.9, 41.6 (d, $J$ = 26.3 Hz), 22.6 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.0 (dq, $J$ = 50, 18 Hz). IR ($cm^{-1}$): 3290, 2953, 1511, 1246, 1060, 876. Anal. Calcd for $C_{15}H_{22}FNO_2S$: C, 60.17; H, 7.41; N, 4.68; S, 10.71. Found: C, 59.90; H, 7.66; N, 4.88; S, 10.71.

*(S)-N-((R)-1-(Benzo[d][1,3]dioxol-5-yl)-3-fluorobut-3-enyl)-2-methylpropane-2-sulfinamide (**5d**).* Compound **5d** was obtained as an orange gum in 80% yield (25.1 mg), after flash chromatography ($R_f$ = 0.30 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −122 ($c$ 0.62, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 6.84−6.72 (m, 3H), 5.95 (m, 2H), 4.64 (dd, $J$ = 17.1, 3.0 Hz, 1H), 4.56 (td, $J$ = 7.2, 2.0 Hz, 1H), 4.32 (dd, $J$ = 49.5, 3.0 Hz, 1H), 3.71 (s, 1H), 2.67−2.52 (m, 2H), 1.19 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.6 (d, $J$ = 258 Hz), 148.1, 147.5, 134.5, 121.4, 108.3, 107.5, 101.3, 93.6 (d, $J$ = 19.2 Hz), 55.8, 55.2, 41.7 (d, $J$ = 26.2 Hz), 22.69 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −93.9 (dq, $J$ = 50, 18 Hz). IR ($cm^{-1}$): 3199, 2912, 1489, 1444, 1239, 1034. Anal. Calcd for $C_{15}H_{20}FNO_3S$: C, 57.49; H, 6.43; N, 4.47; S, 10.23. Found: C, 57.39; H, 6.58; N, 4.61; S, 9.70.

*(S)-N-((R)-3-Fluoro-1-(3-hydroxyphenyl)but-3-enyl)-2-methylpropane-2-sulfinamide (**5e**).* Compound **5e** was obtained as a white solid (mp 156−160 °C) in 62% yield (17.1 mg), after flash chromatography ($R_f$ = 0.21 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +80 ($c$ 0.32, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.77 (m, 1H), 7.19 (t, $J$ = 7.8 Hz, 1H), 6.88 (s, 1H), 6.85−6.73 (m, 2H), 4.66 (dd, $J$ = 17.1, 3.0 Hz, 1H), 4.56 (m, 1H), 4.34 (dd, $J$ = 49.5, 3.0 Hz, 1H), 3.90 (s, 1H), 2.62 (m, 2H), 1.23 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.5 (d, $J$ = 258 Hz), 157.0, 141.5, 129.9, 118.3, 115.4, 115.1, 93.7 (d, $J$ = 19 Hz), 56.0, 55.7, 41.3 (d, $J$ = 26 Hz), 22.6 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.3 (ddt, $J$ = 50, 20, 17 Hz). IR ($cm^{-1}$): 3209, 2957, 1249, 1059. Anal. Calcd for $C_{14}H_{20}FNO_2S$: C, 58.92; H, 7.06; N, 4.91; S, 11.24. Found: C, 59.27; H, 7.23; N, 5.06; S, 10.90.

*Ethyl 4-((R)-1-((S)-1,1-Dimethylethylsulfinamido)-3-fluorobut-3-enyl)benzoate (**5f**).* Compound **5f** was obtained as a yellow solid (mp 68−70 °C) in 96% yield (32.8 mg), after flash chromatography ($R_f$ = 0.30 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +96 ($c$ 0.37, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.02 (d, $J$ = 8.2 Hz, 2H), 7.39 (d, $J$ = 8.2 Hz, 2H), 4.76−4.66 (m, 1H), 4.64 (dd, $J$ = 17.1, 3.1 Hz, 1H), 4.41−4.19 (m, 3H), 3.78 (s, 1H), 2.66 (dd, $J$ = 18.4, 6.9 Hz, 2H), 1.38 (t, $J$ = 7.1 Hz, 3H), 1.19 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 166.4, 162.0 (d, $J$ = 258 Hz), 145.8, 130.4, 130.0 (2C), 127.6 (2C), 94.1 (d, $J$ = 19 Hz), 61.1, 56.0, 55.3, 41.4 (d, $J$ = 26 Hz), 22.6 (3C), 14.4. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.0 (dq, $J$ = 18, 49 Hz). IR ($cm^{-1}$): 3290, 3209, 2958, 1248, 1059. Anal. Calcd for $C_{17}H_{24}FNO_3S$: C, 59.80; H, 7.08; N, 4.10; S, 9.39. Found: C, 59.53; H, 7.41; N, 4.13; S, 8.95.

*(S)-N-((R)-1-(2,6-Dibromophenyl)-3-fluorobut-3-enyl)-2-methylpropane-2-sulfinamide (**5g**).* Compound **5g** was obtained as a gum in 46% yield (19.6 mg), after flash chromatography ($R_f$ = 0.54 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −3 ($c$ 0.37, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.57 (d, $J$ = 8.3 Hz, 1H), 7.54 (d, $J$ = 8.2 Hz, 1H), 6.98 (t, $J$ = 8.0 Hz, 1H), 5.61 (q, $J$ = 8.0 Hz, 1H), 4.57 (dd, $J$ = 16.7, 2.9 Hz, 1H), 4.46−4.21 (m, 1H) 4.40 (s, 1H), 3.21−2.97 (m, 2H), 1.13 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.1 (d, $J$ = 258 Hz), 138.1, 134.4, 133.0, 130.1, 126.5, 122.6, 93.6 (d, $J$ = 19 Hz), 58.8 (d, $J$ = 1 Hz), 56.5, 37.9 (d, $J$ = 27 Hz), 22.5 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.6 (dddd, $J$ = 49, 20, 19, 17 Hz). IR ($cm^{-1}$): 2922, 2853, 1062, 774, 713. Anal. Calcd for $C_{14}H_{18}Br_2FNOS$: C, 39.36; H, 4.25; N, 3.28; S, 7.51. Found: C, 39.13; H, 4.61; N, 3.38; S, 6.91.

*(S)-N-((R)-3-Fluoro-1-(pyridin-3-yl)but-3-enyl)-2-methylpropane-2-sulfinamide (**5h**).* Compound **5h** was obtained as a gum in 97% yield (26.0 mg), after flash chromatography ($R_f$ = 0.10 petroleum ether/EtOAc 2:8). $[\alpha]^{20}_D$: +96 ($c$ 0.30, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.67−8.42 (m, 2H), 7.63 (d, $J$ = 7.9 Hz, 1H), 7.33−7.20 (m, 1H), 4.73−4.57 (m, 2H), 4.30 (dd, $J$ = 49.3, 3.1 Hz, 1H), 3.84 (s, 1H), 2.80−2.57 (m, 2H), 1.18 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 161.6 (d, $J$ = 258 Hz), 149.3, 149.0, 136.2, 135.3, 123.5, 94.2 (d, $J$ = 19 Hz), 56.0, 53.5, 41.1 (d, $J$ = 26 Hz), 22.5 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.1 (dq, $J$ = 49, 18 Hz). IR ($cm^{-1}$): 3194, 2963, 1044, 850, 714. Anal. Calcd for $C_{13}H_{19}FN_2OS$: C, 57.75; H, 7.08; N, 10.36; S, 11.86. Found: C, 57.74; H, 7.08; N, 10.65; S, 11.27.

*(S)-N-((R)-1-(2-Chloroquinolin-3-yl)-3-fluorobut-3-enyl)-2-methylpropane-2-sulfinamide (**5i**).* Compound **5i** was obtained as a gum in 86% yield (30.5 mg), after flash chromatography ($R_f$ = 0.24 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −93 ($c$ 0.67, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.20 (s, 1H), 8.01 (d, $J$ = 8.5 Hz, 1H), 7.80 (d, $J$ = 8.1 Hz, 1H), 7.73 (ddd, $J$ = 8.4, 7.0, 1.3 Hz, 1H), 7.56 (t, $J$ = 7.5 Hz, 1H), 5.20 (dt, $J$ = 7.1, 5.1 Hz, 1H), 4.66 (dd, $J$ = 17.2, 3.1 Hz, 1H), 4.36 (dd, $J$ = 49.5, 3.1 Hz, 1H), 4.03 (d, $J$ = 3.7 Hz, 1H), 3.09−2.75 (m, 2H), 1.26 (d, $J$ = 5.4 Hz, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 161.9 (d, $J$ = 258 Hz), 149.4, 147.1, 137.7, 132.5, 130.8, 128.4, 127.7, 127.5, 127.1, 94.5 (d, $J$ = 19 Hz), 56.4, 53.5, 39.1 (d, $J$ = 26 Hz), 22.7 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −93.4 (bm). IR ($cm^{-1}$): 2922, 1674, 1024, 858, 753. Anal. Calcd for $C_{17}H_{20}ClFN_2OS$: C, 57.54; H, 5.68; N, 7.89; S, 9.04. Found: C, 57.93; H, 5.70; N, 8.14; S, 8.81.

*(S)-N-((R)-3-Fluoro-1-(thiophene-2-yl)but-3-enyl)-2-methylpropane-2-sulfinamide (**5j**).* Compound **5j** was obtained as a yellow solid (mp 58−60 °C) in 74% yield (20.4 mg), after flash chromatography ($R_f$ = 0.36 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +93 ($c$ 0.36, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.27 (dd, $J$ = 3.8, 0.9 Hz, 1H), 7.05 (d, $J$ = 3.3 Hz, 1H), 6.97 (dd, $J$ = 5.0, 3.6 Hz, 1H), 4.98 (td, $J$ = 6.7, 3.3 Hz, 1H), 4.69 (dd, $J$ = 17.1, 3.0 Hz, 1H), 4.39 (dd, $J$ = 49.4, 3.0 Hz, 1H), 3.83 (s, 1H), 2.89−2.65 (m, 2H), 1.23 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.1 (d, $J$ = 258 Hz), 144.8, 126.8, 126.0, 125.5, 94.1 (d, $J$ = 19 Hz), 56.1, 52.0, 42.2 (d, $J$ = 26 Hz), 22.7 (3C). $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −94.2 (dq, $J$ = 50, 18 Hz). IR ($cm^{-1}$): 2877, 1684, 1053, 830, 701. Anal. Calcd for $C_{12}H_{18}FNOS_2$: C, 52.33; H, 6.59; N, 5.09; S, 23.29. Found: C, 52.59; H, 6.75; N, 5.11; S, 23.32.

*(S)-N-((R,E)-5-Fluoro-2-methyl-1-phenylhexa-1,5-dien-3-yl)-2-methylpropane-2-sulfinamide (**5k**).* Compound **5k** was obtained as a white solid (mp 114−116 °C) in 80% yield (24.7 mg), after flash chromatography ($R_f$ = 0.47 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +55 ($c$ 0.53, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.29−7.03 (m, 5H), 6.49 (s, 1H), 4.56 (dd, $J$ = 17.1, 2.9 Hz, 1H), 4.28 (dd, $J$ = 49.4, 2.9 Hz, 1H), 4.09 (t, $J$ = 6.9 Hz, 1H), 3.50 (s, 1H), 2.62−2.30 (m, 2H), 1.70 (s, 3H), 1.11 (s, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 162.8 (d, $J$ = 258 Hz), 137.2, 135.3, 130.1, 129.1 (2C), 128.2 (2C), 126.9, 93.3 (d, $J$ = 19 Hz), 59.5, 55.7, 37.8 (d, $J$ = 26 Hz), 22.7 (3C), 13.2. $^{19}F$ NMR (282 MHz, $CDCl_3$): $\delta$ −93.9 (dq, $J$ = 49, 18 Hz). IR ($cm^{-1}$): 3290, 3209, 2958, 1679, 1247, 1059, 824. Anal. Calcd for $C_{17}H_{24}FNOS$: C, 65.98; H, 7.82; N, 4.53; S, 10.36. Found: C, 65.51; H, 7.68; N, 4.51; S, 9.93.

*(S)-N-((R,Z)-2,5-Difluoro-1-(4-methoxyphenyl)hexa-1,5-dien-3-yl)-2-methylpropane-2-sulfinamide (**5l**).* Compound **5l** was obtained as a white solid (mp 88−90 °C) in 77% yield (26.4 mg), after flash chromatography ($R_f$ = 0.28 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +2 ($c$ 0.62, $CHCl_3$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.43 (d, $J$ = 8.8 Hz, 2H), 6.86 (d, $J$ = 8.8 Hz, 2H), 5.75 (d, $J$ = 39.1 Hz, 1H), 4.70 (dd, $J$ =


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16.9, 3.0 Hz, 1H), 4.44 (dd, $J$ = 49.2, 3.0 Hz, 1H), 4.24 (dtd, $J$ = 19.6, 6.8, 4.5 Hz, 1H), 3.80 (s, 3H), 3.55 (d, $J$ = 4.0 Hz, 1H), 2.77 (ddd, $J$ = 21.0, 14.8, 6.6 Hz, 1H), 2.71 (ddd, $J$ = 21.7, 14.8, 7.2 Hz, 1H), 1.23 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 161.8 (d, $J$ = 257 Hz), 159.1 (d, $J$ = 3 Hz), 154.9 (d, $J$ = 267 Hz), 130.3 (d, $J$ = 7 Hz, 2C), 125.2 (d, $J$ = 3 Hz), 114.0 (2C), 109.0 (d, $J$ = 7 Hz), 94.1 (d, $J$ = 19 Hz), 56.1, 55.4, 54.7 (d, $J$ = 27 Hz), 36.8 (d, $J$ = 27 Hz), 22.6 (3C). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −95.1 (dddd, $J$ = 55, 36, 19, 2 Hz), −122.6 (ddd, $J$ = 39, 20, 2 Hz). IR ($cm^{-1}$): 3210, 2962, 1274, 1045, 857. Anal. Calcd for $C_{17}H_{23}F_2NO_2S$: C, 59.45; H, 6.75; N, 4.08; S, 9.34. Found: C, 59.43; H, 6.78; N, 4.13; S, 9.07.

*(S)-N-((R)-1-Ferrocenyl-3-fluorobut-3-enyl)-2-methylpropane-2-sulfinamide (**5m**).* Compound **5m** was obtained as a brown gum in 78% yield (29.4 mg), after flash chromatography ($R_f$ = 0.48 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −116 ($c$ 0.135, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.69 (dd, $J$ = 17.3, 2.9 Hz, 1H), 4.53−4.31 (m, 2H), 4.29 (s, 1H), 4.16 (s, 7H), 4.11 (s, 1H), 3.71 (d, $J$ = 5.5 Hz, 1H), 2.96 (td, $J$ = 14.9, 4.6 Hz, 1H), 2.71 (ddd, $J$ = 22.6, 14.9, 8.0 Hz, 1H), 1.21 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.9 (d, $J$ = 257 Hz), 93.5 (d, $J$ = 19 Hz), 89.6, 68.7 (5C), 68.3, 68.1, 67.8, 65.9, 55.9, 51.8, 40.2 (d, $J$ = 26 Hz), 22.68 (3C). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −93.9 (dddd, $J$ = 50, 22, 17, 15 Hz). IR ($cm^{-1}$): 3517, 2928, 1679, 1024, 815, 478. Anal. Calcd for $C_{18}H_{24}FFeNOS$: C, 57.30; H, 6.41; N, 3.71; S, 8.50. Found: C, 57.56; H, 6.42; N, 3.70; S, 8.29.

*(S)-N-((S)-2-Fluoronon-1-en-4-yl)-2-methylpropane-2-sulfinamide (**5n**).* Compound **5n** was obtained as a colorless liquid in 93% yield (24.5 mg), after flash chromatography ($R_f$ = 0.40 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +33 ($c$ 0.57, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.66 (dd, $J$ = 17.4, 2.7 Hz, 1H), 4.38 (dd, $J$ = 50.1, 2.7 Hz, 1H), 3.52−3.38 (m, 1H), 3.34 (d, $J$ = 7.5 Hz, 1H), 2.66−2.42 (m, 2H), 1.60−1.48 (m, 2H), 1.34−1.25 (m, 6H), 1.21 (s, 9H), 0.88 (t, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.3 (d, $J$ = 258 Hz), 93.4 (d, $J$ = 19 Hz), 56.0, 53.8 (d, $J$ = 1 Hz), 38.9 (d, $J$ = 26 Hz), 34.9, 31.4, 25.3, 22.6 (3C), 22.5, 14.0. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −92.5 (dq, $J$ = 50, 20 Hz). IR ($cm^{-1}$): 2928, 1668, 1132, 846. Anal. Calcd for $C_{13}H_{26}FNOS$: C, 59.27; H, 9.95; N, 5.32; S, 12.17. Found: C, 59.31; H, 9.92; N, 5.21; S, 12.01.

*(S)-N-((S)-2-Fluorododec-1-en-4-yl)-2-methylpropane-2-sulfinamide (**5o**).* Compound **5o** was obtained as a colorless liquid in 91% yield (27.8 mg), after flash chromatography ($R_f$ = 0.63 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −36 ($c$ 0.29, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.64 (dd, $J$ = 17.4, 2.7 Hz, 1H), 4.37 (dd, $J$ = 50.1, 2.7 Hz, 1H), 3.50−3.35 (m, 1H), 3.31 (d, $J$ = 7.5 Hz, 1H), 2.64−2.41 (m, 2H), 1.66−1.44 (m, 2H), 1.24 (bs, 12H), 1.19 (s, 9H), 0.86 (t, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.4 (d, $J$ = 258 Hz), 93.6 (d, $J$ = 19 Hz), 56.1, 53.9 (d, $J$ = 1 Hz), 39.0 (d, $J$ = 26 Hz), 35.1, 31.9, 29.6, 29.4, 29.3, 25.8, 22.76, 22.73 (3C), 14.21. $^{19}$F NMR (282 MHz, $CDCl_3$): $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −92.5 (dq, $J$ = 50, 20 Hz). IR ($cm^{-1}$): 3210, 2924, 2856, 1671, 1047, 845. Anal. Calcd for $C_{16}H_{32}FNOS$: C, 62.90; H, 10.56; N, 4.58; S, 10.50. Found: C, 62.83; H, 10.58; N, 4.62; S, 10.60.

*(S)-N-((4S,6S)-2-Fluoro-6,10-dimethylundeca-1,9-dien-4-yl)-2-methylpropane-2-sulfinamide (**5p**).* Compound **5p** was obtained as a colorless liquid in 91% yield (28.9 mg), after flash chromatography ($R_f$ = 0.54 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: −11 ($c$ 0.40, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 5.05 (t, $J$ = 7.1 Hz, 1H), 4.64 (dd, $J$ = 17.4, 2.7 Hz, 1H), 4.37 (dd, $J$ = 50.2, 2.7 Hz, 1H), 3.59−3.42 (m, 1H), 3.23 (d, $J$ = 9.2 Hz, 1H), 2.67−2.45 (m, 2H), 2.06−1.90 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.56−1.39 (m, 1H), 1.35−1.11 (m, 4H), 1.19 (s, 9H), 0.86 (d, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.3 (d, $J$ = 258 Hz), 131.4, 124.7, 93.7 (d, $J$ = 19 Hz), 56.3, 52.6 (d, $J$ = 1 Hz), 42.7, 40.1 (d, $J$ = 25 Hz), 37.5, 28.7, 25.8, 25.4, 22.7 (3C), 18.9, 17.8. $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −92.1 (ddt, $J$ = 50, 22, 18 Hz). IR ($cm^{-1}$): 2923, 1672, 1046, 848. Anal. Calcd for $C_{17}H_{32}FNOS$: C, 64.31; H, 10.16; N, 4.41; S, 10.10. Found: C, 64.28; H, 9.77; N, 4.36; S, 9.87.

*(S)-N-((S)-5-Fluoro-1-phenylhex-5-en-3-yl)-2-methylpropane-2-sulfinamide (**5q**).* Compound **5q** was obtained as a colorless oil in 92% yield (27.4 mg), after flash chromatography ($R_f$ = 0.49 petroleum ether/EtOAc 6:4). $[\alpha]^{20}_D$: +31 ($c$ 0.36, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.26−7.04 (m, 5H), 4.61 (dd, $J$ = 17.4, 2.8 Hz, 1H), 4.32 (dd, $J$ = 50.1, 2.8 Hz, 1H), 3.51−3.30 (m, 2H), 2.78−2.52 (m, 3H), 2.49 (t, $J$ = 5.5 Hz, 1H), 1.87−1.71 (m, 2H), 1.17 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.1 (d, $J$ = 258 Hz), 141.5, 128.6 (2C), 128.5 (2C), 126.1, 93.9 (d, $J$ = 19 Hz), 56.2, 53.6 (d, $J$ = 1 Hz), 39.0 (d, $J$ = 26 Hz), 37.0, 32.1, 22.8 (3C). $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta$ −92.3 (ddt, $J$ = 50, 21, 18 Hz). IR ($cm^{-1}$): 3214, 2922, 1672, 1048, 847, 698. Anal. Calcd for $C_{16}H_{24}FNOS$: C, 64.61; H, 8.13; N, 4.71; S, 10.78. Found: C, 64.83; H, 8.44; N, 4.68; S, 10.57.

*(S)-N-((R)-4-Fluoro-2-phenylpent-4-en-2-yl)-2-methylpropane-2-sulfinamide (**5r**).* Compound **5r** was obtained as a colorless oil in 84% yield (23.8 mg), after flash chromatography ($R_f$ = 0.50 petroleum ether/EtOAc 7:3). $[\alpha]^{20}_D$: +210 ($c$ 0.02, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.45 (d, $J$ = 7.2 Hz, 2H), 7.35 (t, $J$ = 7.3 Hz, 2H), 7.31−7.24 (m, 1H), 4.65 (dd, $J$ = 17.4, 2.7 Hz, 1H), 4.29 (dd, $J$ = 50.0, 2.7 Hz, 1H), 4.03 (bs, 1H), 2.80 (dd, J = 44.1, 14.6 Hz, 1H), 2.73 (dd, J = 49.4, 14.6 Hz, 1H), 1.86 (s, 3H), 1.23 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 162.4 (d, J = 258 Hz), 140.6, 128.6 (2C), 128.0, 127.5 (2C), 93.6 (d, J = 19 Hz), 55.7, 55.4, 41.5 (d, J = 26 Hz), 22.6, 22.5 (3C). $^{19}$F NMR (282 MHz, $CDCl_3$): −89.0 (dq, $J$ = 50, 18 Hz). IR ($cm^{-1}$): 3343, 1671, 997, 776, 704. Anal. Calcd for $C_{15}H_{22}FNOS$: C, 63.57; H, 7.82; N, 4.94; S, 11.31. Found: C, 63.42; H, 7.90; N, 4.56; S, 11.13.

*(R)-1-(4-Chlorophenyl)-3-fluorobut-3-en-1-amine **6**.* To compound **3a** (69 mg, 0.227 mmol) solubilized in MeOH (5 mL) was added HCl 12 N (0.2 mL), and the resulting solution was stirred at room temperature for 12 h. After concentration under vacuum, the residue was taken up in $H_2O$, washed with $Et_2O$, basified with $NaHCO_3$ saturated solution, and extracted twice with DCM. Organic phases were assembled, dried over $MgSO_4$, and concentrated to furnish the pure amine **6** as a yellow oil (43 mg, 95%) with a 99:1 er. $[\alpha]^{20}_D$: −40 ($c$ 1.2, $CH_2Cl_2$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.30 (s, 4H), 4.60 (dd, $J$ = 17.3, 2.8 Hz, 1H), 4.40−4.13 (m, 2H), 2.58−2.29 (m, 2H), 1.69 (s, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 163.6 (d, $J$ = 257 Hz), 143.3, 133.0, 128.8 (2C), 127.8 (2C), 92.8 (d, $J$ = 20 Hz), 52.2, 42.7 (d, $J$ = 26 Hz). $^{19}$F NMR (282 MHz, $CDCl_3$): −96.4 (m). IR ($cm^{-1}$): 1673, 1492, 1090, 819, 534. Anal. Calcd for $C_{10}H_{11}ClFN$: C, 60.16; H, 5.55; N, 7.02. Found: C, 60.46; H, 5.48; N, 6.86. The enantiomeric excess of **6** could be determined by chiral gas chromatography (Chiraldex CB 25 m × 0.25), 50−190 °C, 20 °C. $min^{-1}$. $t_R$ (min): 39.12 (major), 44.63 (minor).

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1$H and $^{13}$C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org

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### Notes

The authors declare no competing financial interest.

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