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Stereoselective nucleophilic monofluoromethylation of *tert*-butanesulfinimines: Dynamic thermodynamic Resolution of racemic α-fluoro carbanions

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ABSTRACT

A diastereoselective nucleophilic monofluoromethylation of *tert*-butanesulfinyl aldimines with α-fluoro-α-phenylthio-α-phenylsulfonylmethane (FTSM) as the reagent has been developed, which affords α-monofluoromethyl amines in good to excellent yields with excellent stereocontrol on both the monofluoromethylated carbon and the neighboring sulfonyl-bearing fluorinated carbon. The racemic α-fluoro-α-phenylthio-α-phenylsulfonylmethide anions undergo a dynamic thermodynamic resolution due to the reversibility of their addition to the optically pure *tert*-butanesulfinyl aldimines under the optimized conditions.

1. Introduction

Fluoroalkylation is one of the major methods for the efficient synthesis of organofluorine compounds, and fluorine substitution on the reaction center often has a profound influence on the fluoroalkylation reactions [1–3]. In nucleophilic fluoroalkylation reactions, fluorine substitution can influence the generation, thermodynamic stability, and kinetic reactivity of α-fluorocarbanions, thus bringing about impressive chemical outcomes [2,4,5]. In the past 15 years, numerous efforts have been devoted to nucleophilic fluoroalkylation either by tackling the negative effect of fluorine substitution on the thermal stability and nucleophilic reactivity of α-fluorocarbanions (negative fluorine effect) [2,4–11] or by taking advantage of the unexpected beneficial (positive) effect of fluorine substitution on the chemical outcome [2,12–14].

α-Fluorinated sulfones have been developed as versatile nucleophilic fluoroalkylation reagents owing to the highly tunable reactivity of the corresponding α-fluorocarbanions endowed by the electron-withdrawing α-sulfonyl group [2,4,5,15]. In asymmetric nucleophilic monofluoroalkylation with α-monofluorinated sulfones ($ArSO_2CHFR$) [16–28], the construction of a monofluoroalkylated stereogenic carbon center is usually accompanied by the formation of a fluorine-bearing stereogenic carbon center (when R ≠ $ArSO_2$ and F) [16]. The stereocontrol on the fluorine-containing stereogenic carbon center is usually much more difficult than that on the monofluoroalkyl-substituted stereogenic carbon center [18,17–28]. Considering that chiral sulfones have found practical applications in medicinal chemistry [29–32] and their asymmetric synthesis has attracted much attention [33–36], it is of great interest to develop a new nucleophilic monofluoromethylation method for the efficient introduction of chiral α-fluorinated sulfone moiety with high stereocontrol.

Chiral imines, represented by *tert*-butanesulfinimines, have found wide applications in asymmetric synthesis of chiral amines [37]. In 2006, we reported the first highly stereoselective and facile synthesis of α-monofluoromethyl amines via nucleophilic monofluoromethylation of optically pure *N-tert*-butanesulfinyl aldimines with monofluoromethyl phenyl sulfone ($PhSO_2CH_2F$), followed by the reductive desulfonylation (Scheme 1a) [18]. Although the diastereoselectivity during the nucleophilic addition of in situ generated (phenylsulfonyl) fluoromethide anion into the imine functionality was excellent (up to 99:1), the stereoselectivity on the neighboring monofluorinated carbon center was only moderate. When ketimines were used instead of aldimines, similar stereoselectivity was observed on the fluorine-bearing carbon center [38].

We recently developed α-fluoro-α-phenylthio-α-phenylsulfonylmethane (FTSM) as a new monofluoromethylation reagent and demonstrated its diastereoselective nucleophilic addition to aldehydes (Scheme 1b) [39]. Different from (phenylsulfonyl)fluoromethide anion, the addition of α-fluoro-α-phenylthio-α-phenylsulfonylmethide anion to aldehydes is thermodynamically controlled and reversible, thus

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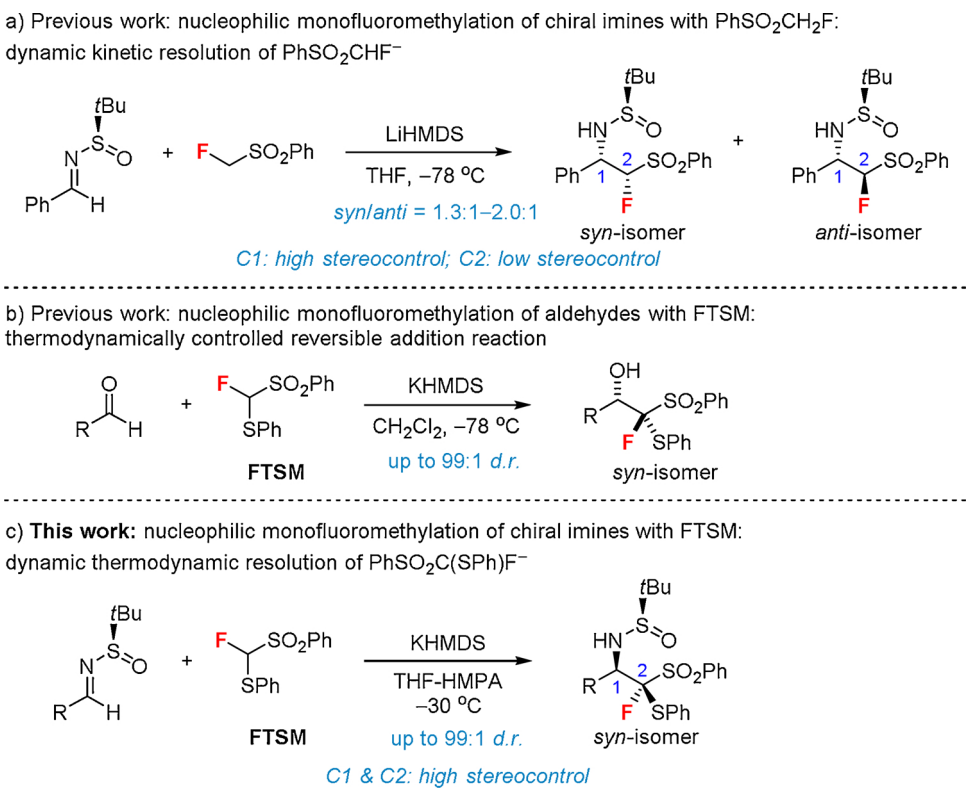


Scheme 1. Diastereoselective nucleophilic monofluoromethylation of *tert*-butanesulfinimines and aldehydes with fluorinated sulfones.

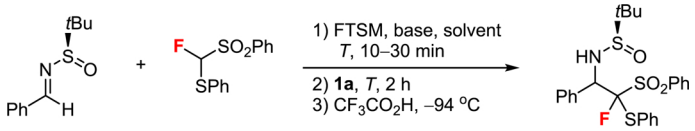
affording the adducts with very high diastereoselectivity. In this context, we surmised that the reaction of FTSM with a chiral imine would lead to an enantioselective dynamic resolution of α-fluoro-α-phenylthio-α-phenylsulfonylmethide anion (FTSM-anion) under thermodynamic control and provide a reliable method for the stereoselective introduction of α-fluorinated sulfone moiety having chirality at the α-position [40–42], which is distinguished from the dynamic kinetic resolution of (phenylsulfonyl)fluoromethide anion with chiral imines [18]. Herein we describe the diastereoselective nucleophilic addition of FTSM to optically pure *N-tert*-butanesulfinyl aldimines (Scheme 1c), which affords the α-monofluoromethyl amines with very high stereoselectivities on both the monofluoromethylated carbon center and the neighboring sulfonyl-bearing fluorinated carbon center.

2. Results and discussion

Our investigation began with choosing (*R*)-*N-tert*-butanesulfinyl benzaldimine (**1a**) as a model compound to react with FTSM (Table 1). According to our previous report on the nucleophilic monofluoromethylation of *tert*-butanesulfinimines with $PhSO_2CH_2F$ [18], we initially performed this reaction in THF at −78 °C by using lithium hexamethyldisilazide (LiHMDS) as the base. We found that deprotonation of FTSM followed by the addition of aldimine **1a** into the reaction system afforded the adduct **2a** in very low yield after acidic quenching with trifluoroacetic acid at −94 °C (Table 1, entry 1), and most of the reagent FTSM decomposed under the basic conditions. Obviously, lithium cation was not a suitable counterion for this addition reaction. When sodium hexamethyldisilazide (NaHMDS) and potassium hexamethyldisilazide (KHMDS) were used instead of LiHMDS, the reaction proceeded smoothly at −78 °C to give the adduct **2a** in moderate to good yields (Table 1, entries 2 and 3). However, in both cases, a mixture of all four possible stereoisomers was detected by ^{19}F NMR analysis. The poor stereoselectivity may originate from kinetically controlled irreversible addition processes that involve several different transition states (chelation-controlled and non-chelation-controlled ones). Then we turned our attention to improve the stereoselectivity by promoting the reversibility of the addition reaction at elevated temperatures. Surprisingly, when the reaction with NaHMDS or KHMDS was carried out at −30 °C, adduct **2a** was formed with extremely high diastereoselectivity (up to 99:1 diastereomeric ratio), albeit in low yield (Table 1, entries 4 and 5). With KHMDS as the base, the use of hexamethylphosphoramide (HMPA) as the co-solvent significantly increased the yield of **2a** without compromising diastereoselectivity (Table 1, entry 8). This result indicates that the addition of HMPA did not prevent the chelation of metal cations such potassium cation with FTSM anion [43,44]. For comparison, we also conducted the reaction in the presence of HMPA at −78 °C and obtained a mixture of four diastereomers, which confirmed that the temperature is a major factor influencing the diastereoselectivity (Table 1, entry 9).

Encouraged by the above results, we prepared a series of optically pure (*R*)-*N-tert*-butanesulfinyl aldimines **1** and examined their nucleophilic monofluoromethylation with FTSM. To achieve a high conversion of FTSM, excess amounts of *tert*-butanesulfinimines (1.5–2.0 equiv) were used to promote the addition reaction. As shown in Table 2, a variety of structurally diverse aldimines reacted with FTSM smoothly to give the monofluoromethylation products **2** in good to excellent yields with high stereoselectivity. The facial selectivities during the addition of α-fluoro-α-phenylthio-α-phenylsulfonylmethide anion into the imine functionality were excellent (> 99:1). In most of the cases, both the adjacent tertiary and fluorinated quaternary stereogenic centers were constructed with excellent stereocontrol (Table 2, entries 1–15). In addition to the *para*- and *meta*-substituted benzaldimines (Table 2, entries 2–10), the benzaldimines with substituents at the *ortho*-position could also react with FTSM to give the corresponding products (Table 2, entries 11 and 12). Heteroaromatic aldimines are also viable substrates. For instance, the reaction of 2-furyl substituted aldimine **1o** with FTSM delivered **2o** in 70 % yield with a diastereomeric ratio of 96:4 (Table 2, entry 15). However, aliphatic aldimines were not compatible with this method. The reaction of butyraldehyde-derived imine **1p** that bears two α-hydrogen atoms provided adduct **2p** in only moderate yield with a

Table 1
Survey on the nucleophilic addition of FTSM to *tert*-butanesulfinimine **1a**[a].



1a **FTSM** **2a**

entry	base	solvent	*T* (°C)	yield (%)[b]	*d.r.*[b]
1	LiHMDS	THF	–78	10	ND[c]
2	NaHMDS	THF	–78	90	34:14:14:38[d]
3	KHMDS	THF	–78	58	12:9:41:38[d]
4	NaHMDS	THF	–30	26	99:1
5	KHMDS	THF	–30	37	99:1
6	LiHMDS	THF-HMPA (6:1, v/v)	–30	12	99:1
7	NaHMDS	THF-HMPA (6:1, v/v)	–30	57	99:1
8	KHMDS	THF-HMPA (6:1, v/v)	–30	74	99:1
9	KHMDS	THF-HMPA (6:1, v/v)	–78	80	10:64:10:16[d]

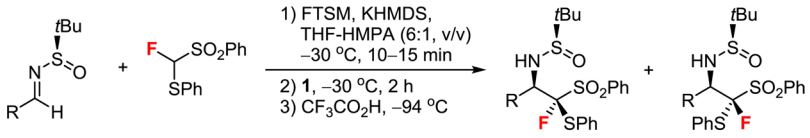
[a] **1a**:FTSM:base = 1.0:1.1:1.3. A 1.0 M solution of the base in THF was used.
[b] The yield and diastereomeric ratio (*d.r.*) were determined by ^{19}F NMR analysis of the reaction mixture.
[c] ND = not determined.
[d] The ratio of four stereoisomers .

diastereomeric ratio of nearly 1:1 (Table 2, entry 16). The relatively low yield probably arises from the enolization of substrate **1p**, while the poor stereoselectivity may be attributed to the irreversibility of the addition reaction. In the case of pivalaldehyde-derived imine **1q**, the reaction failed probably due to the steric hindrance of the *tert*-butyl group (Table 2, entry 17). We have also examined the reaction of 3-nitrobenzaldehyde-derived *tert*-butanesulfinimine, an aldimine with a strong electron-withdrawing group. However, the adduct was formed in low yield (28 %).

The absolute configuration of the major product *syn*-**2 g** was determined by X-ray single crystal structure analysis (Fig. 1) [45], and the absolute configurations of the other major products *syn*-**2** were assigned by analogy with compound *syn*-**2 g**.

To rationalize the diastereoselectivity of this addition reaction, we proposed two transition state models for chiral induction (Scheme 2a): the chelation controlled model (with carbon-potassium interaction, TS1 and TS2) [18] and non-chelation controlled model (without carbon-potassium interaction, TS3 and TS4) [46,47]. According to previous

Table 2
Diastereoselective addition of FTSM to various *tert*-butanesulfinimines **1**[a].



1 **FTSM** *syn*-**2** *anti*-**2**

entry	R	1	2	yield, *syn*-**2** (%)[b]	*d.r.*[c]
1[d]	Ph	**1a**	**2a**	79	99:1
2	4-Me-C_6H_4	**1b**	**2b**	80	98:2
3	4-*t*Bu-C_6H_4	**1c**	**2c**	90	96:4
4	4-Ph-C_6H_4	**1d**	**2d**	82	97:3
5	4-F-C_6H_4	**1e**	**2e**	84	96:4
6	4-Cl-C_6H_4	**1f**	**2f**	86	96:4
7	4-Br-C_6H_4	**1g**	**2 g**	82	98:2
8	3-Me-C_6H_4	**1h**	**2 h**	82	97:3
9	3-PhO-C_6H_4	**1i**	**2i**	71	95:5
10	3-F-C_6H_4	**1j**	**2 j**	96	96:4
11	2-F-C_6H_4	**1k**	**2k**	77	97:3
12	2,5-Cl-C_6H_3	**1l**	**2l**	83	92:8
13	2-naphthyl	**1m**	**2 m**	84	96:4
14	1-naphthyl	**1n**	**2n**	93	95:5
15	2-furyl	**1o**	**2o**	67	96:4
16	*n*Pr	**1p**	**2p**	53[e]	43:57
17	*t*Bu	**1q**	**2q**	< 10[e]	ND[f]

[a] Unless otherwise noted, **1**:FTSM:base = 2.0:1.0:1.2. A THF solution of KHMDS (1.0 M) was used.
[b] Unless otherwise noted, the yield refers to isolated yield of the major isomer.
[c] The facial selectivities during the addition of FTSM into the imines were > 99:1. The diastereomeric ratio (*d.r.*) refers to the ratio of *syn*-**2** and *anti*-**2** as determined by ^{19}F NMR analysis of the reaction mixture.
[d] **1**:FTSM:base = 1.5:1.0:1.2.
[e] The yield refers to the total yield of all the isomers as determined by ^{19}F NMR analysis of the reaction mixture.
[f] ND = not determined.

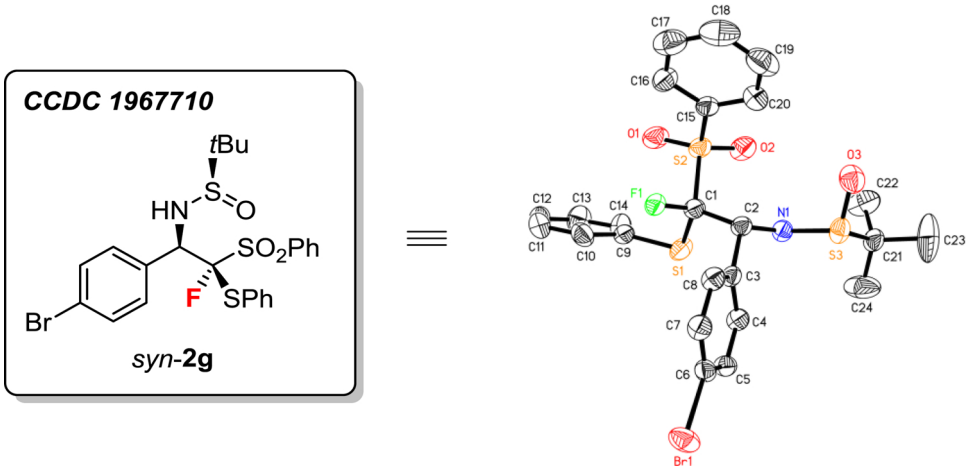
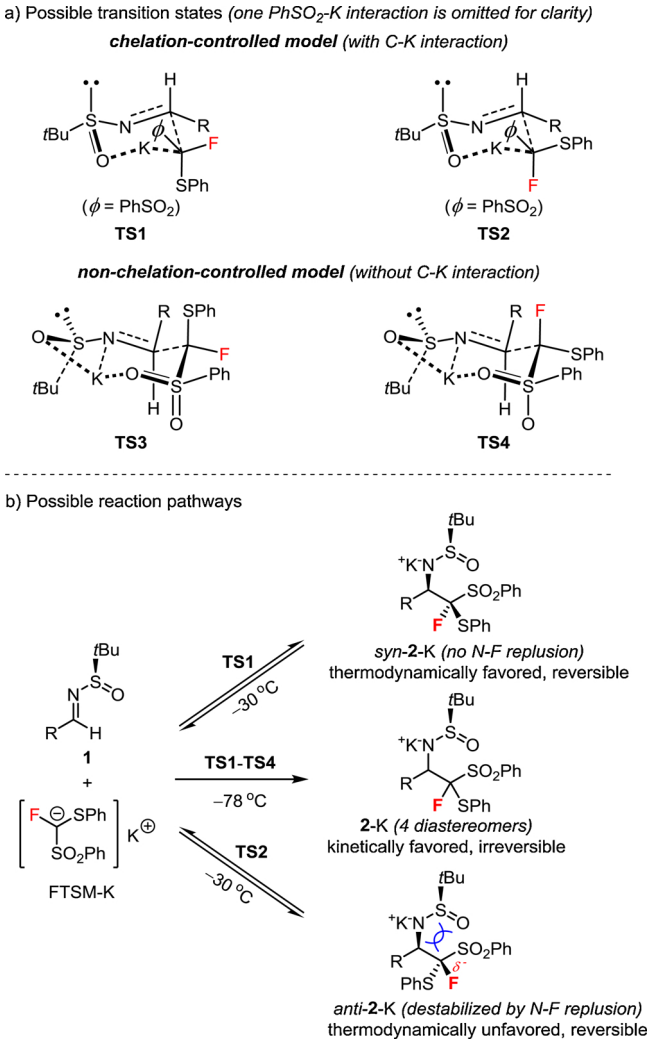


Fig. 1. X-ray single crystal structure of *syn*-**2 g.**



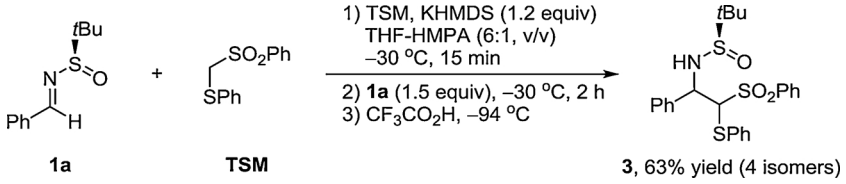
Scheme 2. Mechanistic consideration.

studies on the structures of α-sulfonyl carbanions [34,48–50], it is believed that α-fluoro-α-phenylthio-α-phenylsulfonylmethylpotassium exists in two forms, with the one in which the potassium cation is associated with the anionic carbon atom and one oxygen atom of the sulfonyl group being energetically more stable than the one in which the potassium cation is associated with two oxygen atoms of the sulfonyl group. At low temperatures, both of the two forms exsit in the reaction syestem, and their reactions with the imines are irrevisible; at relatively high tempeatures, only the thermodynamically stable structure that contains carbon-potassium interaction remains, and its reaction with the imines is reversible. Therefore, the reaction at −78 °C proceeds through all the four possible transition states TS1-TS4, giving a mixture of four diastereomers (Scheme 2a, path a). Although the reaction at −30 °C can proceed through two possible transition states TS1 and TS2, the reversibility of the reaction at this temperature leads to the equilibration of diastereomeric intermediates *syn*-**2**-K and *anti*-**2**-K, with the former being thermodynamically more stable (Scheme 2a, path b). In this case, a dynamic thermodynamic resolution of racemic α-fluoro-α-phenylthio-α-phenylsulfonylmethide anions takes place with high enantioselectivity. Similar to the reaction of FTSM with aldehydes [39], the thermodynamic instability of *anti*-**2**-K can be attributed to the strong repulsion between the negatively polarised fluorine and the negatively charged amino group.

Finally, we examined the reaction of α-phenylthio-α-phenylsulfonylmethane (TSM) and α-chloro-α-phenylthio-α-phenylsulfonylmethane (CTSM) with (*R*)-*N*-*tert*-butanesulfinyl benzaldimine (**1a**) under the aforementioned conditions. The deprotonation of TSM with KHMDS followed by the addition of imine **1a** to the reaction system at −30 °C afforded product **3** as an inseparable mixture of four diastereomers in 63 % total yield, with each constituting less than 30 % of all the isomers as determined by GC–MS analysis (Scheme 3). Similar to previous report on the reaction of aldehydes [39], CTSM failed to undergo addition reaction with imine **1a**. These results demonstrate that the fluorine substitution plays an important role in promoting the enantioselective dynamic thermodynamic resolution of α-fluoro-α-phenylthio-α-phenylsulfonylmethide anion and its diastereoselective addition to *tert*-butanesulfinimines. The poor stereoselectivity of the reaction of TSM with imine **1a** under the same conditions probably arises from the irreversibility or low reversibility of the addition reaction between α-phenylthio-α-phenylsulfonylmethide anion and imine **1a**.

3. Conclusions

In conclusion, we have developed a new synthetic application of α-fluoro-α-phenylthio-α-phenylsulfonylmethane (FTSM) as a monofluoromethylation reagent. The nucleophilic addition of FTSM to optically pure *tert*-butanesulfinimines under thermodynamically controlled conditions affords α-monofluoromethyl amines in good to excellent yields with excellent stereocontrol on both the monofluoromethylated carbon and the vicinal sulfonyl-bearing fluorinated carbon. The reversibility of the base-promoted addition reaction resulted in a highly



Scheme 3. Nucleophilic addition of TSM to *tert*-butanesulfinimine **1a**.

enantioselective dynamic resolution of racemic α-fluoro-α-phenylthio-α-phenylsulfonylmethide anions under thermodynamic control, which constitutes the first example of dynamic thermodynamic resolution of α-fluorocarbanions [40,41].

4. Experimental

4.1. General

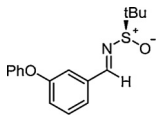
Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. *α*-Fluoro-*α*-phenylthio-*α*-phenylsulfonylmethane (FTSM) was prepared from *α*-phenylthio-*α*-phenylsulfonylmethane and *N*-fluorobenzenesulfonimide (NFSI) in THF-HMPA at −78 °C by using *n*BuLi as the base [39]. Anhydrous THF was freshly distilled over sodium. Anhydrous HMPA was distilled over CaH_2. Specific optical rotations were determined on an automatic polarimeter. Melting points were measured on an electrothermal digital melting point apparatus and were not corrected. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ at δ 0.0 or to the signal of a residual protonated solvent: $CDCl_3$ at δ 7.26. ^{13}C NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ at δ 0.0. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode. IR spectra were recorded on an FT-IR spectrometer.

4.2. General procedures for the preparation of (R)-N-tert-butanesulfinyl aldimines 1

Optically pure (*R*)-*N*-*tert*-butanesulfinyl aldimines **1** were prepared from (*R*)-*tert*-butanesulfinamide and the corresponding aldehydes according to reported procedures [51]. Except **1i**, all the other imines **1** are known compounds.

Aldimine **1i** was prepared from 3-phenoxybenzaldehyde (1.09 g, 5.5 mmol) and (*R*)-*tert*-butanesulfinamide (0.81 g, 5.0 mmol) under the promotion of anhydrous $CuSO_4$ (0.81 g, 11.0 mmol) in 70 % yield (1.05 g).

4.2.1. (R,E)-2-Methyl-N-(3-phenoxybenzylidene)propane-2-sulfinamide (1i)

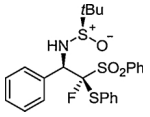


Colorless oil. $[\alpha]_D^{20}$ = –54.1° (*c* = 0.75, $CHCl_3$). IR (film): 3479, 2979, 2950, 1575, 1489, 1254, 1214, 1087, 791, 753, 688 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 1 H), 7.55–7.35 (m, 5 H), 7.15 (s, 2 H), 7.04 (d, *J* = 6.6 Hz, 2 H), 1.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 158.1, 156.5, 135.9, 130.3, 130.0, 124.3, 123.9, 122.5, 119.2, 118.7, 57.9, 22.6. MS (ESI, *m/z*): 302.1 ([M + H]$^+$), 324.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{17}H_{19}NNaO_2S$ ([M + Na]$^+$): 324.1029; Found: 324.1041.

4.3. General procedures for the nucleophilic addition of FTSM to tert-butanesulfinimines 1

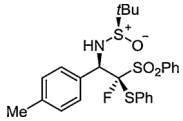
Under N_2 atmosphere at −30 °C, to a THF-HMPA (1.2 mL, 6:1, v/v) solution of α-fluoro-α-phenylthio-α-phenylsulfonylmethane (FTSM) (57 mg, 0.2 mmol) was slowly added KHMDS (0.24 mL, 1.0 M in THF, 0.24 mmol). After vigorously stirring at −30 °C for 10–15 min, a THF-HMPA (0.4 mL, 6:1, v/v) solution of (*R*)-*N*-*tert*-butanesulfinyl aldimine **1** (0.4 mmol) was added dropwise in 5 min. The reaction mixture was then stirred vigorously at −30 °C for 2 h. After cooling the reaction mixture to −94 °C, the reaction was quenched by adding CF_3CO_2H (0.5 mL) at −94 °C. After warming to room temperature, the so-obtained mixture was diluted with H_2O (5 mL), and extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc as eluent to afford the major isomer *syn*-**2**.

4.3.1. (R)-N-((1R,2S)-2-Fluoro-1-phenyl-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-2a)



Eluted with petroleum ether/EtOAc (form 10:1 to 5:1, v/v), 78 mg, 79 % yield. Yellow solid. M.p.: 131 − 133 °C. $[\alpha]_D^{28}$ = 171.1° (*c* = 1.0, $CHCl_3$). IR (film): 3269, 2971, 1495, 1447, 1324, 1151, 1081, 764 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.8 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 2 H), 7.39 − 7.23 (m, 8 H), 7.19 (t, *J* = 7.8 Hz, 2 H), 5.29 (s, 1 H), 4.82 (s, 1 H), 1.37 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −132.1 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.0, 133.3, 132.2, 130.9, 130.8, 129.9, 129.5, 129.4, 128.5, 128.0, 125.5 (d, *J* = 3.9 Hz), 113.3 (d, *J* = 269.5 Hz), 60.3 (d, *J* = 21.9 Hz), 56.4, 22.7. MS (ESI, *m/z*): 492.1 ([M + H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{27}FNO_3S_3$ ([M + H]$^+$): 492.1132; Found: 492.1141.

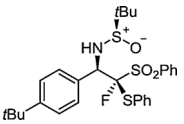
4.3.2. (R)-N-((1R,2S)-2-Fluoro-2-(phenylsulfonyl)-2-(phenylthio)-1-(p-tolyl)ethyl)-2-methylpropane-2-sulfinamide (syn-2b)



Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 81 mg, 80 % yield. White solid. M.p.: 113 − 114 °C $[\alpha]_D^{28}$ = 203.7° (*c* = 1.0, $CHCl_3$). IR (film): 3254, 2919, 1582, 1474, 1447, 1327, 1153, 1077, 741 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2 H), 7.72 (t, *J* = 7.5 Hz, 1 H). 7.59 (t, *J* = 7.5 Hz, 2 H), 7.34 − 7.30 (m, 3 H), 7.24 − 7.12 (m, 6 H), 5.25 (s, 1 H), 4.78 (s, 1 H), 2.36 (s, 3 H), 1.36 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −131.3 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 137.5, 135.0, 133.4, 130.8 (two carbon), 129.9, 129.4, 129.2, 128.8, 128.5, 125.7 (d, *J* = 3.6 Hz), 113.5 (d, *J* = 269.7 Hz), 60.2 (d, *J* = 22.6 Hz), 56.3, 22.7, 21.3. MS (ESI, *m/z*): 506.0 ([M + H]$^+$), 528.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for

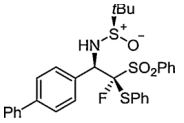
$C_{25}H_{28}FNNaO_3S_3$ ([M + Na]$^+$): 528.1108; Found: 528.1124.

*4.3.3. (R)-N-((1R,2S)-1-(4-(tert-Butyl)phenyl)-2-fluoro-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2c**)*



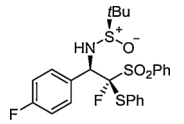
Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 98 mg, 90 % yield. White solid. M.p.: 67 − 68 °C. $[\alpha]_D^{28}$ = 182.7° (*c* = 0.85, $CHCl_3$). IR (film): 3261, 2961, 1475, 1326, 1153, 1081, 830 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 8.1 Hz, 2 H), 7.72 (t, *J* = 7.5 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 2 H), 7.35 − 7.30 (m, 3 H), 7.28 − 7.22 (m, 5 H), 7.17 (t, *J* = 7.5 Hz, 2 H), 5.26 (s, 1 H), 4.82 (s, 1 H), 1.38 (s, 9 H), 1.32 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −131.0 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 152.5, 137.4, 135.0, 133.4, 130.8, 130.6, 129.8, 129.3, 128.9, 128.5, 125.7 (d, *J* = 4.4 Hz), 124.9, 113.4 (d, *J* = 272.0 Hz), 60.0 (d, *J* = 23.3 Hz), 56.4, 34.7, 31.3, 22.7. MS (ESI, *m/z*): 548.0 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{28}H_{34}FNNaO_3S_3$ ([M + Na]$^+$): 570.1577; Found: 570.1601.

*4.3.4. (R)-N-((1R,2S)-1-([1,1′-Biphenyl]-4-yl)-2-fluoro-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2d**)*



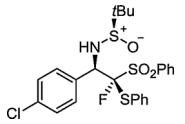
Eluted with petroleum ether/EtOAc (form 20:1 to 5:1, v/v), 93 mg, 82 % yield. White solid. M.p.: 158 − 159 °C. $[\alpha]_D^{28}$ = 260.6° (*c* = 1.0, $CHCl_3$). IR (film): 3440, 3261, 2957, 1447, 1323, 1151, 1080, 1067, 688, 591 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.99 (d, *J* = 8.4 Hz, 2 H), 7.74 (t, *J* = 7.2 Hz, 1 H). 7.63 − 7.55 (m, 6 H), 7.47 − 7.26 (m, 8 H), 7.17 (t, *J* = 6 Hz, 2 H), 5.31 (s, 1 H), 4.87 (s, 1 H), 1.39 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −131.2 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 142.3, 140.4, 137.5, 135.1, 133.4, 131.3, 131.2, 130.9, 130.0, 129.4, 128.9, 128.6, 127.7, 127.1, 126.6, 125.5 (d, *J* = 4.3 Hz), 113.4 (d, *J* = 270.2 Hz), 60.2 (d, *J* = 22.8 Hz), 56.5, 22.7. MS (ESI, *m/z*): 568.0 ([M+H]$^+$), 590.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{30}H_{30}FNNaO_3S_3$ ([M + Na]$^+$): 590.1264; Found: 590.1275.

*4.3.5. (R)-N-((1R,2S)-2-Fluoro-1-(4-fluorophenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2e**)*



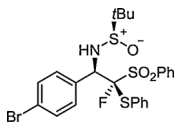
Eluted with petroleum ether/EtOAc (form 20:1 to 5:1, v/v), 86 mg, 84 % yield. White solid. M.p.: 145 − 146 °C. $[\alpha]_D^{28}$ = 172.5° (*c* = 1.0, $CHCl_3$). IR (film): 3264, 2961, 1603, 1508, 1319, 1222, 1151, 1077, 835 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.97 (d, *J* = 8.1 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H). 7.59 (t, *J* = 7.5 Hz, 2 H), 7.35 − 7.25 (m, 5 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.04 (t, *J* = 8.7 Hz, 2 H), 5.30 (s, 1 H), 4.81 (s, 1 H), 1.37 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −111.2 (s, 1 F), −131.4 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 163.4 (d, *J* = 247.5 Hz), 137.5, 135.1, 133.2, 132.7 (d, *J* = 8.9 Hz), 130.8, 130.0, 129.4, 128.6, 128.0, 125.2 (d, *J* = 4.8 Hz), 115.0 (d, *J* = 20.9 Hz), 113.1(d, *J* = 269.5 Hz), 59.7 (d, *J* = 22 Hz), 56.4, 22.6. MS (ESI, *m/z*): 510.0 ([M+H]$^+$), 532.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{25}F_2NNaO_3S_3$ ([M + Na]$^+$): 532.0857; Found: 532.0874.

*4.3.6. (R)-N-((1R,2S)-2-Fluoro-1-(4-chlorophenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2f**)*



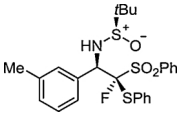
Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 90 mg, 86 % yield. White solid. M.p.: 148 − 150 °C. $[\alpha]_D^{28}$ = 190.5° (*c* = 1.0, $CHCl_3$). IR (film): 3255, 2924, 2854, 1489, 1316, 1149, 1072, 755 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.97 (d, *J* = 7.8 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 2 H), 7.36 − 7.19 (m, 10 H), 5.29 (s, 1 H), 4.80 (s, 1 H), 1.37 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −131.8 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.5, 135.5, 135.2, 133.2, 132.2, 130.9, 130.8, 130.1, 129.4, 128.6, 128.3, 125.2 (d, *J* = 3.6 Hz), 113.1 (d, *J* = 271.2 Hz), 59.7 (d, *J* = 21.9 Hz), 56.4, 22.7. MS (ESI, *m/z*): 526.0 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{26}ClFNO_3S_3$ ([M+H]$^+$): 526.0742; Found: 526.0759.

*4.3.7. (R)-N-((1R,2S)-2-Fluoro-1-(4-bromophenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2 g**)*



Eluted with petroleum ether/EtOAc (form 10:1 to 5:1, v/v), 94 mg, 82 % yield. White solid. M.p.: 182 − 183 °C. $[\alpha]_D^{28}$ = 210.8° (*c* = 1.0, $CHCl_3$). IR (film): 3255, 1486, 1316, 1150, 1072, 1010, 823 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.96 (d, *J* = 8.4 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H). 7.59 (t, *J* = 7.5 Hz, 2 H), 7.48 (d, *J* = 9.0 Hz, 2 H), 7.37 − 7.19 (m, 7 H), 5.29 (s, 1 H), 4.78 (s, 1 H), 1.36 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −132.5 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.5, 135.1, 133.2, 132.4, 131.5, 131.2, 130.8, 130.1, 129.4, 128.6, 125.1 (d, *J* = 3.4 Hz), 123.8, 113.0 (d, *J* = 269.1 Hz), 59.8 (d, *J* = 22.6 Hz), 56.5, 22.6. MS (ESI, *m/z*): 570.0 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{26}BrFNO_3S_3$ ([M+H]$^+$): 570.0237; Found: 570.0248.

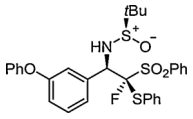
*4.3.8. (R)-N-((1R,2S)-2-Fluoro-2-(phenylsulfonyl)-2-(phenylthio)-1-(m-tolyl)ethyl)-2-methylpropane-2-sulfinamide (syn-**2 h**)*



Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 83 mg, 82 % yield. White solid. M.p.: 175 − 176 °C. $[\alpha]_D^{28}$ = 175.0 ° (*c* = 1.0, $CHCl_3$). IR (film): 3274, 2958, 1449, 1310, 1149, 1076, 752 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 8.1 Hz, 2 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 7.59 (t, *J* = 7.5 Hz, 2 H), 7.35 − 7.30 (m, 3 H), 7.26 − 7.17 (m, 5 H), 7.06 (s, 1 H), 5.25 (s, 1 H), 4.78 (s, 1 H), 2.32 (s, 3 H), 1.36 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −132.1 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.6, 137.4, 135.0, 133.4, 132.2, 131.7, 130.8, 130.3, 129.9, 129.4, 128.5, 128.0, 127.8, 125.6 (d, *J* = 4.4 Hz), 113.4 (d, *J* = 270.2 Hz), 60.3 (d, *J* = 22.6 Hz), 56.3, 22.7, 21.4. MS (ESI, *m/z*): 506.0 ([M

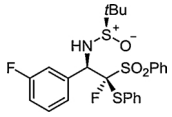
+H]$^+$), 528.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{25}H_{28}FNNaO_3S_3$ ([M + Na]$^+$): 528.1108; Found: 528.1125.

*4.3.9. (R)-N-((1R,2S)-2-Fluoro-1-(3-phenoxyphenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2i**)*



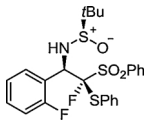
Eluted with petroleum ether/EtOAc (form 20:1 to 3:1, v/v), 83 mg, 71 % yield. White solid. M.p.: 133 − 134 °C. $[\alpha]_D^{28}$ = 197.8° (*c* = 1.0, $CHCl_3$). IR (film): 3445, 3273, 1582, 1483, 1450, 1307, 1236, 1149, 1074, 962 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.96 (d, *J* = 8.4 Hz, 2 H), 7.72 (t, *J* = 7.2 Hz, 1 H), 7.58 (t, *J* = 7.2 Hz, 2 H), 7.37 − 7.19 (m, 8 H), 7.10 − 7.06 (m, 3 H), 7.03 − 6.95 (m, 3 H), 5.26 (s, 1 H), 4.80 (s, 1 H), 1.30 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −131.2 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 157.0, 156.9, 137.4, 135.1, 134.1, 133.2, 130.8, 130.0, 129.8, 129.4, 129.2, 128.6, 126.0, 125.4 (d, *J* = 4.3 Hz), 123.5, 121.1, 120.0, 119.0, 113.1 (d, *J* = 270.8 Hz), 60.0 (d, *J* = 22.6 Hz), 56.5, 22.6. MS (ESI, *m/z*): 584.0 ([M+H]$^+$), 606.0 ([M + Na]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{30}H_{30}FNNaO_4S_3$ ([M + Na]$^+$): 606.1213; Found: 606.1231.

*4.3.10. (R)-N-((1R,2S)-2-Fluoro-1-(3-fluorophenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2 j**)*



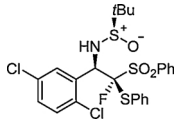
Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 98 mg, 96 % yield. Yellow solid. M.p.: 178 − 179 °C. $[\alpha]_D^{28}$ = 133.9° (*c* = 1.0, $CHCl_3$). IR (film): 3267, 2924, 1592, 1450, 1321, 1152, 1076, 953, 754, 707, 569, 542 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.98 (d, *J* = 8.1 Hz, 2 H), 7.74 (t, *J* = 7.2 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 2 H), 7.36 − 7.18 (m, 6 H), 7.16 − 7.04 (m, 3 H), 5.30 (s, 1 H), 4.81 (s, 1 H), 1.38 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −112.4 (dd, *J* = 14.4 Hz, 8.2 Hz, 1 F), 131.5 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.3 (d, *J* = 244.3 Hz), 137.5, 135.2, 134.9 (d, *J* = 7.3 Hz), 133.1, 130.8, 130.1, 129.4, 129.3, 128.6, 126.7, 125.2, 117.7 (d, *J* = 22.6 Hz), 116.5 (d, *J* = 21.2 Hz), 113.0 (d, *J* = 269.8 Hz), 59.8 (d, *J* = 22.6 Hz), 56.5, 22.6. MS (ESI, *m/z*): 510.1 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{26}F_2NO_3S_3$ ([M+H]$^+$): 510.1037; Found: 510.1055.

*4.3.11. (R)-N-((1R,2S)-2-Fluoro-1-(2-fluorophenyl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2k**)*



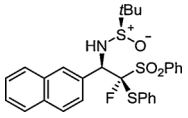
Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 78 mg, 77 % yield. White solid. M.p.: 179 − 180 °C. $[\alpha]_D^{28}$ = 180.4° (*c* = 1.0, $CHCl_3$). IR (film): 3266, 2960, 1488, 1321, 1150, 1078, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 8.1 Hz, 2 H), 7.81 (t, *J* = 7.2 Hz, 1 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 2 H), 7.40 − 7.32 (m, 4 H), 7.26 − 7.19 (m, 3 H), 6.94 (t, *J* = 9 Hz, 1 H), 5.26 (s, 1 H), 5.19 (s, 1 H), 1.37 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −115.5 (s, 1 F), −133.1 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.0 (d, *J* = 249.4 Hz), 137.7, 135.1, 132.9, 131.5 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 8.9 Hz), 130.8, 130.1, 129.4, 128.6, 125.3 (d, *J* = 3.7 Hz), 123.5 (d, *J* = 2.9 Hz), 119.9 (d, *J* = 11.7 Hz), 115.3 (d, *J* = 21.9 Hz), 113.3 (d, *J* = 269 Hz), 56.5, 52.2 (d, *J* = 23.3 Hz), 22.6. MS (ESI, *m/z*): 510.1 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{26}F_2NO_3S_3$ ([M+H]$^+$): 510.1037; Found: 510.1057.

*4.3.12. (R)-N-((1R,2S)-1-(2,5-Dichlorophenyl)-2-fluoro-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2l**)*



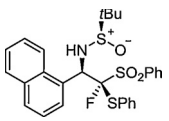
Eluted with petroleum ether/EtOAc (form 30:1 to 5:1, v/v), 93 mg, 83 % yield. White solid. M.p.: 163 − 164 °C. $[\alpha]_D^{27}$ = 216.6° (*c* = 1.0, $CHCl_3$). IR (film): 3448, 3257, 2925, 1585, 1474, 1317, 1153, 1082, 826 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.02 (d, *J* = 8.4 Hz, 2 H), 7.88 (d, *J* = 8.7 Hz, 1 H). 7.72 (t, *J* = 7.2 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 2 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.42 − 7.26 (m, 5 H), 5.43 (s, 1 H), 5.20 (s, 1 H), 1.36 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −133.8 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.8, 136.9, 135.8, 135.2, 132.9, 132.6, 131.1, 130.3, 129.5, 129.4, 129.2, 128.7, 126.7, 125.0 (d, *J* = 4.1 Hz), 113.5 (d, *J* = 271.8 Hz), 56.5, 54.9 (d, *J* = 23 Hz), 22.6. MS (ESI, *m/z*): 559.9 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{24}H_{25}Cl_2FNO_3S_3$ ([M+H]$^+$): 560.0352; Found: 560.0375.

*4.3.13. (R)-N-((1R,2S)-2-Fluoro-1-(naphthalen-2-yl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2 m**)*



Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 91 mg, 84 % yield. White solid. M.p.: 70 − 72 °C. $[\alpha]_D^{28}$ = 240.4° (*c* = 1.0, $CHCl_3$). IR (film): 3264, 2923, 1447, 1152, 1079, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 7.5 Hz, 2 H), 7.86 − 7.70 (m, 5 H). 7.61 (t, *J* = 7.5 Hz, 3 H), 7.54 − 7.45(m, 2 H), 7.30 − 7.25 (m, 3 H), 7.14 (t, *J* = 7.5 Hz, 2 H), 5.36 (s, 1 H), 5.01 (s, 1 H), 1.38 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −131.0 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 137.4, 135.1, 133.9, 133.4, 132.7, 131.3, 130.9, 129.9, 129.8, 129.4, 128.5, 128.3, 127.7, 127.6, 127.5, 126.9, 126.3, 125.5 (d, *J* = 3.8 Hz), 113.5 (d, *J* = 269.9 Hz), 60.7 (d, *J* = 22.8 Hz), 56.4, 22.7. MS (ESI, *m/z*): 542.0 ([M+H]$^+$). HRMS (ESI, *m/z*): Calcd. for $C_{28}H_{29}FNO_3S_3$ ([M+H]$^+$): 542.1288; Found: 542.1305.

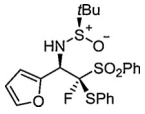
*4.3.14. (R)-N-((1R,2S)-2-Fluoro-1-(naphthalen-1-yl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-**2n**)*



Eluted with petroleum ether/EtOAc (form 12:1 to 3:1, v/v), 101 mg, 93 % yield. Yellow solid. M.p.: 165 − 166 °C. $[\alpha]_D^{28}$ = 158.2° (*c* = 1.0, $CHCl_3$). IR (film): 3251, 2924, 1447, 1327, 1153, 1075, 777 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.12 (d, *J* = 7.8 Hz, 3 H), 7.90 − 7.80 (m, 3 H), 7.18 (t, *J* = 7.5 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.38 − 2.26 (m, 4 H), 7.15 (t, *J* = 7.5 Hz, 2 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 6.48 (d, *J* = 8.7 Hz, 1 H), 5.84 (s, 1 H), 5.31 (s, 1 H), 1.39 (s, 9 H). ^{19}F NMR (282 MHz,

$CDCl_3$): δ −130.9 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 135.1, 133.5, 133.4, 131.3, 130.1, 130.0, 129.9, 129.7, 129.3, 128.9, 128.5, 128.0, 126.4, 125.5, 125.4 (d, J = 4.4 Hz), 124.6, 122.0, 114.4 (d, J = 272.7 Hz), 56.5, 53.7 (d, J = 22.6 Hz), 22.7. MS (ESI, m/z): 542.0 ([M + H]$^+$). HRMS (ESI, m/z): Calcd. for $C_{28}H_{29}FNO_3S_3$ ([M + H]$^+$): 542.1288; Found: 542.1302.

4.3.15. (R)-N-((1R,2S)-2-Fluoro-1-(furan-2-yl)-2-(phenylsulfonyl)-2-(phenylthio)ethyl)-2-methylpropane-2-sulfinamide (syn-2o)



Eluted with petroleum ether/EtOAc (form 10:1 to 5:1, v/v), 64 mg, 67 % yield. Yellow solid. Mp: 112 − 113 °C. $[\alpha]_D^{28}$ = 121.2° (c = 0.5, $CHCl_3$). IR (film): 3550, 3261, 2977, 1474, 1313, 1152, 1057, 1011, 753 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2 H), 7.71 (t, J = 7.5 Hz, 1 H). 7.57 (t, J = 7.5 Hz, 2 H), 7.44 (d, J = 7.5 Hz, 3 H), 7.39 − 7.33 (m, 1 H), 7.28 − 7.22 (m, 2 H), 6.60 (d, J = 3.3 Hz, 1 H), 6.43 (dd, J = 1.8 Hz, 3.3 Hz, 1 H), 5.12 (s, 1 H), 4.98 (s, 1 H), 1.33 (s, 9 H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −130.6 (s, 1 F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.6, 137.4, 135.1, 133.5, 130.7, 130.0, 129.4, 128.6, 125.7 (d, J = 10.5 Hz), 113.2, 113.1 (d, J = 271.3 Hz), 110.7, 56.5, 55.9 (d, J = 23.8 Hz), 22.6. MS (ESI, m/z): 482.0 ([M + H]$^+$), 504.0 ([M + Na]$^+$). HRMS (ESI, m/z): Calcd. for $C_{22}H_{25}FNO_4S_3$ ([M + H] +): 582.0930; Found: 582.0932.

Declaration of Competing Interest

We have no conflict of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2020.109451.

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