Supporting Information for:

**Stereoselective [3+2] Cycloaddition of N-tert-Butanesulfinyl Imines to Arynes Facilitated by Removable PhSO₂CF₂ Group: Synthesis and Transformation of Cyclic Sulfoximines**

Laijun Zhang,† Wenchao Ye,† Chuanfa Ni, Jian Rong and Jinbo Hu*

Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Ling-Ling Road, Shanghai 200032, China

*E-mail: jinbohu@sioc.ac.cn

General…………………………………………………………………………………….. S2

1. Preparation of N-tert-Butanesulfinyl Imines ………………………………………… S2

2. Screening of Reaction Conditions ……………………………………………………… S10

3. [3 + 2] Cycloaddition of PhSO₂CF₂-Sulfinimines with Arynes and Further Transformation …………………………………………………………………………….. S11

3.1 [3 + 2] Cycloaddition ……………………………………………………………… S11

3.2 Synthesis of Cyclic Sulfinamides…………………………………………………… S27

3.3 N-(6-Bromonaphthalen-2-yl)methylation of Cyclic Sulfinamide 6a …………… S34

3.4 Synthesis of Cyclic Sulfinimines ………………………………………………..S36

3.5 Addition to Cyclic Sulfinimines …………………………………………………..S40

3.6 Oxidation of Cyclic Sulfinamide 9c ……………………………………………… S44

3.7 Reductive Desulfonylation ………………………………………………………. S46

4. Determination of the Enantioselectivity …………………………………………… S49

5. ¹H, ¹⁹F, and ¹³C NMR Spectrum of New Compounds …………………………… S58
General

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The solvent THF was distilled from sodium, and the solvents MeCN, CH₂Cl₂, HMPA (hexamethylphosphoramide) and DMF were distilled from CaH₂ before being used. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 or to the signal of the residual protonated solvent: CDCl₃ δ 7.26. ¹³C NMR chemical shifts were determined relative to internal TMS at δ 0.0. For the isolated compounds, ¹⁹F NMR chemical shifts were determined relative to CFCl₃ 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 EI mode.

1. Preparation of N-tert-Butanesulfinyl Imines

1.1 Preparation of Difluoro(phenylsulfonyl)methyl Ketones:

Method 1: Ketones S₁a, S₁d-e, S₁g-i, and S₁j were prepared by difluoro(phenylsulfonyl)methylation of the corresponding methyl esters according to the reported procedures.¹

\[
\begin{align*}
\text{R}^\text{OMe} + \text{PhSO}_2\text{CF}_2\text{H} & \xrightarrow{\text{LiHMDS}} \text{THF} - \text{HMPA}, -98^\circ\text{C} \\
& \rightarrow \text{R}^\text{CF}_2\text{SO}_2\text{Ph}
\end{align*}
\]

Method 2: Ketones S₁b-c and S₁k were prepared by oxidation of the corresponding known α-difluoro(phenylsulfonyl)methyl alcohols with DMSO/(COCl)₂/Et₃N (Swern Oxidation). Ketone S₁f was prepared by oxidation with Jones’ reagent.

1.2 Condensation of N-tert-Butylsulfinamide and the Corresponding Ketones.

Non-fluorinated imines 1a-c,2 difluoromethyl imine 1d, trifluoromethyl imine 1e,3 and monofluoromethyl imine 1f were prepared by condensation of (R)-N-tert-butylsulfinamide and the corresponding carbonyl compounds. The Z-configuration of the imino bond in difluoromethyl imine 1d was established by single-crystal X-ray analysis of its analogue S2 (see SI Section 3.1), and the assumption was made that monofluoromethyl imine 1f possessed a similar geometry.

Difluoro(phenylsulfonyl)methyl imines 2a-k (Table S1) were prepared according to the following typical procedures:

**Typical procedures:**
Under N₂ atmosphere, a mixture of (R)-N-tert-butylsulfinamide (> 99% ee, 9.6 mmol, 1.162 g), (phenylsulfonyl)difluoromethyl phenyl ketone (S1a; 8.0 mmol, 2.368 g), Ti(OEt)₄ (48.0 mmol, 10.944 g) in THF (50.0 mL) was heated to reflux for 36 h, then the reaction mixture was cooled to room temperature and poured into an equal volume of brine while rapidly stirring. The resulting suspension was filtered through a plug of celite, and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted with EtOAc for three times, and the combined organic phase was dried over anhydrous MgSO₄. The volatile solvents were removed under vacuum, and the crude product was purified by

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column chromatography (silica gel; ethyl acetate/petroleum ether = 1:10 – 1:5 v/v) to afford 2a (2.171 g, 68% yield).

Table S1. Preparation of PhSO₂CF₂-Sulfinimines

<table>
<thead>
<tr>
<th>entry</th>
<th>ketone</th>
<th>R</th>
<th>Ti(OEt)₄ (equiv)</th>
<th>time (h)</th>
<th>sulfinimine</th>
<th>yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<tr>
<td>1</td>
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<tr>
<td>11</td>
<td>S₁k</td>
<td>iPr</td>
<td>6.0</td>
<td>48</td>
<td>2k</td>
<td>53</td>
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</table>

<sup>a</sup> Isolated yield. <sup>b</sup> The isolated product 2 is contaminated by trace amount (1 – 2%) of difluoro(phenylsulfonyl)methyl alcohol due to the reduction of ketone S₁ during the condensation reaction using Ti(OEt)₄ (for details, see the <sup>19</sup>F NMR spectrum).

Characterization Data:

(R,E)-N-[2,2-Difluoro-1-phenyl-2-(phenylsulfonyl)ethyldene]-2-methylpropane-2-sulfinamide (2a)

Mp: 57–59 °C. [α]<sub>d</sub><sup>22</sup> = -171.3 (c 1.00, CHCl₃). <sup>1</sup>H NMR (300 MHz, CDCl₃): δ 8.00 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.52–7.38 (m, 5H), 1.33 (s,
(R,E)-N-[2,2-Difluoro-2-(phenylsulfonyl)-1-m-tolylethylidene]-2-methylpropane-2-sulfin amide (2b)

$[\alpha]_D^{22} -175.0$ (c 1.00, CHCl₃). $^1$H NMR (300 MHz, CDCl₃): $\delta$ 8.00 (d, $J = 7.8$ Hz, 2H), 7.76 (t, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 2H), 7.31–7.24 (m, 4H), 2.38 (s, 3H), 1.33 (s, 9H). $^{19}$F NMR (282 MHz, CDCl₃): $\delta$ –98.1 (d, $J = 233.9$ Hz, 1F), –99.6 (d, $J = 233.9$ Hz, 1F). $^{13}$C NMR (100 MHz, CDCl₃): $\delta$ 166.3 (t, $J = 20.1$ Hz), 137.6, 135.6, 133.1, 131.7, 130.9, 130.6, 129.4, 128.5, 127.7, 125.5, 116.5 (t, $J = 295.6$ Hz), 59.9, 22.7, 21.5. IR (film): 2963, 1618, 1584, 1449, 1351, 1171, 1145, 1107 cm⁻¹. MS (ESI, $m/z$): 436.0 (M + Na⁺). HRMS (ESI): calcd. for C₁₉H₂₁F₂NO₃S₂: (M + Na⁺): 436.0823; Found: 436.0834.

(R,E)-N-[2,2-Difluoro-2-(phenylsulfonyl)-1-p-tolylethylidene]-2-methylpropane-2-sulfin amide (2c)

$[\alpha]_D^{22} -198.1$ (c 1.00, CHCl₃). $^1$H NMR (400 MHz, CDCl₃): $\delta$ 8.00 (d, $J = 7.6$ Hz, 2H),
7.76 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H), 1.32 (s, 9H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −99.0 (d, J = 232.0 Hz, 1F), −101.1 (d, J = 232.0 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.9 (t, J = 24.2 Hz), 141.3, 135.6, 133.1, 130.9, 129.4, 128.5, 128.4, 127.7, 116.6 (t, J = 295.5 Hz), 60.0, 22.7, 21.6. IR (film): 2964, 1608, 1585, 1509, 1447, 1449, 1351, 1151 cm$^{-1}$. MS (ESI, m/z): 436.0 (M + Na$^+$). HRMS (ESI): calcd. for C$_{19}$H$_{21}$F$_2$NO$_3$S$_2$: (M + Na$^+$): 436.0823; Found: 436.0831.

(R,E)-N-[1-(4-Chlorophenyl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide (2d)

Mp: 61–63 °C. [α]$_D^{22}$ −179.8 (c 1.00, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.99 (d, J = 7.8 Hz, 2H), 7.78 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.9 Hz, 2H), 1.34 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ −98.7 (d, J = 231.5 Hz, 1F), −99.9 (d, J = 231.5 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.1 (t, J = 24.7 Hz), 137.2, 135.8, 132.8, 130.9, 129.8, 129.5, 128.8, 128.1, 116.4 (t, J = 294.7 Hz), 60.7, 22.9. IR (film): 1627, 1590, 1488, 1449, 1351, 1151, 1109, 1091 cm$^{-1}$. MS (ESI, m/z): 456.0 (M + Na$^+$). HRMS (ESI): calcd. for C$_{18}$H$_{18}$ClF$_2$NO$_3$S$_2$: (M + Na$^+$): 456.0277; Found: 456.0294.

(R,E)-N-[1-(4-Bromophenyl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide (2e)
Mp: 95–97 °C. [α]D22 = 193.5 (c 1.00, CHCl3). 1H NMR (300 MHz, CDCl3): δ 7.99 (d, J = 7.9 Hz, 2H), 7.78 (t, J = 7.6 Hz, 1H), 7.63 (t, J = 7.3 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 1.34 (s, 9H). 19F NMR (282 MHz, CDCl3): δ –98.7 (d, J = 231.5 Hz, 1F), –99.9 (d, J = 231.5 Hz, 1F). 13C NMR (100 MHz, CDCl3): δ 164.2 (t, J = 25.5 Hz), 135.8, 132.8, 131.0, 130.9, 129.9, 129.5, 129.3, 125.7, 116.3 (t, J = 296.0 Hz), 60.7, 22.9. IR (film): 2961, 1628, 1583, 1485, 1449, 1350, 1149, 1108 cm−1. MS (ESI, m/z): 500.0 (M + Na+). HRMS (ESI): calcd. for C18H18BrF2NO3S2: (M + Na+): 499.9772; Found: 499.9790.

(R,E)-N-[2,2-Difluoro-1-(3-methoxyphenyl)-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide (2f)

[α]D22 = 163.3 (c 1.00, CHCl3). 1H NMR (300 MHz, CDCl3): δ 8.00 (d, J = 7.7 Hz, 2H), 7.76 (t, J = 7.7 Hz, 1H), 7.61 (t, J = 7.3 Hz, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.08–6.97 (m, 3H), 3.82 (s, 3H), 1.33 (s, 9H). 19F NMR (282 MHz, CDCl3): δ –98.9 (d, J = 231.5 Hz, 1F), –100.3 (d, J = 231.6 Hz, 1F). 13C NMR (100 MHz, CDCl3): δ 165.9 (t, J = 24.7 Hz), 158.9, 135.7, 133.1, 131.9, 131.0, 129.5, 129.1, 120.7, 116.0, 116.56 (t, J = 295.8 Hz), 113.8, 60.1, 55.4, 22.8. IR (film): 2964, 1600, 1581, 1487, 1450, 1351, 1293, 1147 cm−1. MS (ESI, m/z): 452.1 (M + Na+). HRMS (ESI): calcd. for C19H21F2NO4S2: (M + Na+): 452.0772; Found: 452.0782.
(R,E)-N-[2,2-Difluoro-1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide (2g)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2 & \quad \hat{\text{N}} \quad \hat{\text{S}} \quad \hat{\text{O}} \\
\quad & \quad \text{Ph} \quad \text{Me} \\
\end{align*}
\]

Mp: 58–60 °C. \([\alpha]_D^{22} = -229.2 \, (c 1.00, \text{CHCl}_3)\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, \(J = 7.5\) Hz, 2H), 7.76 (t, \(J = 7.5\) Hz, 1H), 7.61 (t, \(J = 7.5\) Hz, 2H), 7.47 (d, \(J = 8.5\) Hz, 2H), 6.93 (d, \(J = 8.5\) Hz, 2H), 3.83 (s, 3H), 1.32 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta -97.9\) (d, \(J = 233.4\) Hz, 1F), –99.9 (d, \(J = 233.4\) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 165.4\) (t, \(J = 24.5\) Hz), 161.7, 135.5, 133.2, 130.6, 129.5, 122.5, 116.8 (t, \(J = 294.1\) Hz), 113.9, 113.2, 60.0, 55.3, 22.7. IR (film): 2970, 1607, 1593, 1513, 1348, 1147, 1085 cm\(^{-1}\). MS (ESI, \(m/z\)): 452.0 (M + Na\(^+\)). Anal. Calcd for C\(_{19}\)H\(_{21}\)F\(_2\)NO\(_4\)S\(_2\): C, 53.13; H, 4.93; N, 3.26; Found: C, 53.13; H, 4.98; N, 2.93.

(R,E)-N-[2,2-difluoro-2-(phenylsulfonyl)-1-[4-(trifluoromethyl)phenyl]ethylidene]-2-methylpropane-2-sulfinamide (2h)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2 & \quad \hat{\text{N}} \quad \hat{\text{S}} \quad \hat{\text{O}} \\
\quad & \quad \text{Ph} \quad \text{CF}_3 \\
\end{align*}
\]

Yellow solid. Mp: 84–86 °C. \([\alpha]_D^{28} = -179.9 \, (c 1.00, \text{CHCl}_3)\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.00 (d, \(J = 7.5\) Hz, 2H), 7.81–7.76 (m, 1H), 7.70–7.61 (m, 6H), 1.36 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta -64.2\) (s, 3F), –100.6 (d, \(J = 231\) Hz, 1F), –101.6 (d, \(J = 231\) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 163.7\) (t, \(J = 25.5\) Hz), 135.9, 134.2, 132.8, 132.4 (q, \(J = 32.9\) Hz), 130.9, 129.5 128.8, 124.7 (q, \(J = 3.6\) Hz), 123.6 (q, \(J = 271.2\) Hz),
116.3 (t, $J = 293.9$ Hz), 60.9, 22.9. IR (KBr): 3078, 2980, 1614, 1450, 1324, 1512, 1109, 1067, 1012, 839, 685, 620, 587, 536 cm$^{-1}$. MS (ESI, $m/z$): 468([M + H$^+$]). HRMS (ESI, $m/z$): Calcd. for C$_{19}$H$_{18}$F$_5$NO$_3$S$_2$Na$^+$ ([M + Na$^+$]): 490.0546; Found: 490.0554.

(R,E)-N-[1-(6-Bromonaphthalen-2-yl)-2,2-difluoro-2-(phenylsulfonyl)ethylidene]-2-methylpropane-2-sulfinamide (2i)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2 \\
\downarrow \\
\text{Br}
\end{align*}
\]

Mp: 42–45 °C. $[\alpha]_D^{20} = -217.0$ (c 1.00, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.01 (s, 2H), 7.99 (s, 1H), 7.81–7.71 (m, 3H), 7.64–7.54 (m, 4H), 1.35 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ –98.4 (d, $J = 231.6$ Hz, 1F), –99.8 (d, $J = 231.6$ Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.0 (t, $J = 24.8$ Hz), 135.7, 134.8, 132.8, 130.8, 130.5, 130.3, 130.2, 129.9, 129.4, 128.6, 128.4, 126.4, 125.9, 122.0, 116.5 (t, $J = 291.5$ Hz), 60.4, 22.7. IR (film): 2963, 1625, 1583, 1448, 1350, 1148, 1129, 1102 cm$^{-1}$. MS (ESI, $m/z$): 528.0 (M + H$^+$). HRMS (ESI): calcd. for C$_{22}$H$_{20}$BrF$_2$NO$_3$S$_2$: (M + Na$^+$): 549.9928; Found: 549.9936.

(R,E)-N-[E)-1,1-Difluoro-4-phenyl-1-(phenylsulfonyl)but-3-en-2-ylidene]-2-methylpropane-2-sulfinamide (2j)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2 \\
\downarrow \\
\text{Ph}
\end{align*}
\]

Mp: 76–78 °C. $[\alpha]_D^{22} = -616.9$ (c 1.00, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.12–8.00 (m, 3H), 7.77 (t, $J = 7.5$ Hz, 1H), 7.64 (t, $J = 7.9$ Hz, 2H), 7.60–7.53 (m, 2H), 7.47 (d, $J = 17.2$ Hz, 1H), 7.41–7.35 (m, 3H), 1.34 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ –95.9 (d, $J$
1H NMR (300 MHz, CDCl₃): δ 7.99 (d, J = 7.7 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.8 Hz, 2H), 3.94–3.78 (m, 1H), 1.38–1.28 (m, 15H).

19F NMR (282 MHz, CDCl₃): δ −96.6 (d, J = 237.6 Hz, 1F), −100.7 (d, J = 237.7 Hz, 1F).

13C NMR (100 MHz, CDCl₃): δ 172.9 (t, J = 22.2 Hz), 135.5, 133.3, 130.8, 129.4, 117.6 (t, J = 297.9 Hz), 60.0, 32.6, 22.8, 20.1, 19.3. IR (film): 2970, 1630, 1585, 1450, 1351, 1165, 1091 cm⁻¹. MS (ESI, m/z): 388.0 (M + Na⁺). HRMS (ESI): calcd. for C₁₅H₂₁F₂NO₃S₂: (M + Na⁺): 388.0823; Found: 388.0831.

2. Screening of Reaction Conditions

Table S2. Reaction between 2a and 3a under Various Conditions
3. [3 + 2] Cycloaddition of PhSO₂CF₂-Sulfinimines with Arynes and Further Transformation

3.1 [3 + 2] Cycloaddition.

---

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<th>time (h)</th>
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<th>er&lt;sup&gt;c&lt;/sup&gt;</th>
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<td>0</td>
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<td>—</td>
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<td>rt</td>
<td>4</td>
<td>80</td>
<td>&gt;99:1</td>
<td>&gt;99:1</td>
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</table>

<sup>a</sup> Isolated yield. <sup>b</sup> Determined by ¹⁹F NMR spectroscopy of the crude product. <sup>c</sup> Determined by chiral HPLC.
**Figure S1** Structures of Difluomethyl Imine (R)-S2 and Cyclic Sulfamidate (Ss,S)-4d in the Crystals

**Experimental Procedures:**

To a Schlenk tube containing sulfinimine (R)-1d (0.104 g, 0.4 mmol), aryne precursor 3a (0.238 g, 0.8 mmol), and CH$_3$CN (8.0 mL) was added CsF (0.182 g, 1.2 mmol). The tube was sealed with a rubber septum, and then the reaction mixture was stirred at room temperature for 48 h. After quenched with brine, the reaction mixture was extracted with Et$_2$O (30 mL × 3), and the combined organic phase was dried over anhydrous MgSO$_4$. The volatile solvents were removed under vacuum, and the crude product was purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give enantiopure product (Ss,S)-4d as a white solid (0.043 g, 32% yield).

The diastereoselectivity was determined by HPLC-MS (ESI) analysis of the crude product, and the enantioselectivity was determined by chiral HPLC analysis of the isolated product. The absolute configuration of N-TBS imine 1d was determined by the X-ray crystal structure of its analogue S2, and that of product 4d was determined by its X-ray crystal structure (Figure S1).

**(1S,3S)-1-(tert-butyl)-3-(difluoromethyl)-3-phenylbenzo[d]isothiazole 1-oxide (4d)**
Mp: 145–148 °C. [α]D<sup>20</sup> = −183.8 (c 0.60, CHCl₃), >99:1 er. The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250 × 4.6 mm), hexane / IPA= 80 / 20 (v/v%), 0.7 mL/min, λ = 214 nm, t<sub>R</sub> (major) = 9.03 min, t<sub>R</sub> (minor) = 9.68 min. <sup>1</sup>H NMR (300 MHz, CDCl₃): δ 8.02 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.40–7.28 (m, 3H), 6.09 (t, J = 56.5 Hz, 1H), 1.33 (s, 9H). 19F NMR (282 MHz, CDCl₃): δ −123.4 (dd, J = 267.4, 56.5 Hz, 1F), −124.9 (dd, J = 267.3, 56.4 Hz, 1F). 13C NMR (100 MHz, CDCl₃): δ 145.3 (d, J = 1.2 Hz), 138.5 (d, J = 2.4 Hz), 136.6, 132.7, 130.2, 128.3, 128.1, 127.9, 127.8 (dd, J = 3.3, 1.6 Hz), 124.7, 117.1 (t, J = 249.8 Hz), 79.2 (t, J = 21.1 Hz), 62.6, 24.2. IR (film) 1448, 1365, 1226, 1105, 965, 753, 705 cm<sup>−1</sup>. MS (ESI, m/z): 336.2 (M + H<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>19</sub>F<sub>2</sub>NOS: C, 64.46; H, 5.71; N, 4.18; Found: C, 64.43; H, 5.77; N, 4.01.

**Typical Procedures:**

**Method A** (at rt for compounds 5a-l, 5p, and 5u):

To a Schlenk tube containing sulfinimine (R)-2a (R<sup>1</sup> = Ph) (0.120 g, 0.3 mmol), aryne precursor 3a (R<sup>2</sup>, R<sup>3</sup> = H) (0.268 g, 0.9 mmol), and CH₃CN (5.0 mL) was added CsF (0.228 g, 1.5 mmol). The tube was sealed, and then the reaction mixture was stirred at room temperature for 12 h. After quenched with brine, the reaction mixture was extracted with Et₂O (30 mL × 3), and the combined organic phase was dried over anhydrous MgSO₄. The volatile solvents were removed under vacuum, and the crude product was
purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give product (Ss,R)-5a (R¹ = Ph; R², R³ = H) as a white solid (0.124 g, 87% yield).

**Method B** (at 80 °C for compounds 5m-o and 5q-t):

To a Schlenk tube containing sulfinimine (R)-2a (R¹ = Ph) (0.239 g, 0.6 mmol), aryne precursor 3d (R², R³ = OMe) (0.644 g, 1.8 mmol), and CH₃CN (5.0 mL) was added CsF (0.456 g, 3.0 mmol). The tube was sealed, and then the reaction mixture was stirred at 80 °C for 12 h. After cooled to rt and quenched with brine, the reaction mixture was extracted with Et₂O (40 mL × 3), and the combined organic phase was dried over anhydrous MgSO₄. The volatile solvents were removed under vacuum, and the crude product was purified by column chromatography (silica gel; ethyl acetate/petroleum ether = 1:1.5 v/v) to give product (Ss,R)-5s (R¹ = Ph; R², R³ = OMe) as a white solid (0.200 g, 62% yield).

**Example of Diastereoselectivity Determination by $^{19}$F NMR**

![Diagram of the diastereoselectivity determination by $^{19}$F NMR](image)

**Characterization Data:**

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-phenylbenzo[d]isothiazole
1-oxide (5a)

Mp: 138–140 °C. [α]D22 = –45.1 (c 0.80, CHCl3), >99:1 er. The enantiomeric ratio was determined by CHIRALPAK OD (250 × 4.6 mm), hexane / IPA = 60 / 40 (v/v), 0.7 mL/min, λ = 214 nm, tR (major) = 8.69 min, tR (minor) = 10.24 min. 1H NMR (300 MHz, CDCl3): δ 8.03–7.87 (m, 5H), 7.69–7.55 (m, 3H), 7.47 (t, J = 7.4 Hz, 3H), 7.26 (d, J = 7.4 Hz, 3H), 1.47 (s, 9H).

19F NMR (282 MHz, CDCl3): δ –97.7 (d, J = 233.9 Hz, 1F), –100.0 (d, J = 233.8 Hz, 1F).

13C NMR (100 MHz, CDCl3): δ 147.8, 138.9, 136.1, 134.9, 134.6, 133.0, 131.1, 129.9, 128.7, 128.2, 128.0, 127.5 (d, J = 5.2 Hz), 126.0 (d, J = 1.9 Hz), 123.6, 122.7 (t, J = 298.7 Hz), 80.9 (t, J = 23.5 Hz), 63.6, 24.7 (d, J = 1.4 Hz). IR (film): 3061, 1585, 1451, 1360, 1222, 1153, 1113 cm⁻¹. MS (ESI, m/z): 498.1 (M + Na⁺).

Anal. Calcd for C24H23F2NO3S2: C, 60.61; H, 4.87; N, 2.95; Found: C, 60.93; H, 4.78; N, 2.73.

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(m-tolyl)benzo[d]isothiazole 1-oxide (5b)

Mp: 147–149 °C. [α]D22 = –42.6 (c 0.75, CHCl3). 1H NMR (300 MHz, CDCl3): δ 7.99 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.4 Hz, 2H), 7.77–7.55 (m, 5H), 7.47 (q, J = 7.0 Hz, 3H), 7.15 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 2.30 (s, 3H), 1.51 (s, 9H). 19F NMR (282 MHz, CDCl3): δ –97.1 (d, J = 234.3 Hz, 1F), –99.8 (d, J = 234.3 Hz, 1F). 13C NMR (100 MHz, CDCl3): δ 147.9 (d, J = 1.8 Hz), 138.8 (t, J = 2.8 Hz), 137.5, 136.1, 135.0, 134.6,
133.0, 131.1, 129.9, 129.0, 128.7, 128.3 (d, $J = 3.7$ Hz), 127.9, 126.1 (d, $J = 2.8$ Hz), 124.5 (d, $J = 6.4$ Hz), 123.6, 122.8 (t, $J = 296.9$ Hz), 80.9 (t, $J = 21.8$ Hz), 63.7, 24.8 (d, $J = 2.4$ Hz), 21.8.

IR (film): 1736, 1449, 1349, 1224, 1113, 964, 755, 607 cm$^{-1}$. MS (ESI, $m/z$): 512.1 (M + Na$^+$). HRMS (ESI): calcd. for C$_{25}$H$_{25}$F$_2$NO$_3$S$_2$: (M + Na$^+$): 512.1136; Found: 512.1143.

(1S,3R)-1-(tert-Butyl)-3-[[difluoro(phenylsulfonyl)methyl]-3-(p-tolyl)benzo[d]isothiazole 1-oxide (5c)

Mp: 148–150 °C. [a]$_D^{23}$ = -35.9 (c 0.90, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.00 (d, $J = 7.9$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 2H), 7.83 (d, $J = 7.6$ Hz, 2H), 7.69–7.55 (m, 3H), 7.48 (t, $J = 7.9$ Hz, 3H), 7.08 (d, $J = 7.6$ Hz, 2H), 2.28 (s, 3H), 1.46 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ –98.0 (d, $J = 233.1$ Hz, 1F), –99.9 (d, $J = 233.1$ Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.2 (d, $J = 2.6$ Hz), 138.1, 136.3, 136.2 (t, $J = 2.6$ Hz), 135.0, 134.7, 133.2, 131.3, 129.9, 129.0, 128.9, 127.6 (d, $J = 4.8$ Hz), 126.2 (d, $J = 3.1$ Hz), 123.8, 122.9 (t, $J = 295.3$ Hz), 80.9 (t, $J = 21.4$ Hz), 63.7, 24.9 (d, $J = 2.5$ Hz), 21.2. IR (film): 1450, 1337, 1330, 1213, 1171, 1114 cm$^{-1}$. MS (ESI, $m/z$): 512.1 (M + Na$^+$). HRMS (ESI): calcd. for C$_{25}$H$_{25}$F$_2$NO$_3$S$_2$: (M + H$^+$): 490.1317; Found: 490.1328.

(1S,3R)-1-(tert-Butyl)-3-(4-chlorophenyl)-3-[[difluoro(phenylsulfonyl)methyl]benzo[d]isothiazole 1-oxide (5d)
(1S,3R)-3-(4-Bromophenyl)-1-(tert-butyl)-3-[difluoro(phenylsulfonyl)methyl]benzo[d]isothiazole 1-oxide (5e)

Mp: 139–141 °C. [α]D 23 = 36.7 (c 1.00, CHCl3). 1H NMR (300 MHz, CDCl3): δ 7.96 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 4H), 7.71–7.57 (m, 3H), 7.55–7.46 (m, 3H), 7.23 (d, J = 8.5 Hz, 2H), 1.46 (s, 9H). 19F NMR (282 MHz, CDCl3): δ −97.9 (d, J = 239.4 Hz, 1F), −100.5 (d, J = 239.4 Hz, 1F). 13C NMR (100 MHz, CDCl3): δ 147.6 (d, J = 1.7 Hz), 137.8 (t, J = 2.6 Hz), 136.1, 135.1, 134.9, 134.5, 133.4, 131.2, 130.3, 129.2 (d, J = 5.1 Hz), 129.0, 128.3, 126.0 (d, J = 2.9 Hz), 123.9, 122.6 (t, J = 296.8 Hz), 80.6 (t, J = 21.8 Hz), 63.9, 24.9 (d, J = 2.3 Hz). IR (film): 1492, 1445, 1344, 1221, 1168, 1114, 963 cm⁻¹. MS (ESI, m/z): 532.1 (M + Na⁺). Anal. Calcd for C24H22ClF2NO3S2: C, 56.52; H, 4.35; N, 2.75; Found: C, 56.16; H, 4.45; N, 2.55.

(1S,3R)-3-(4-Bromophenyl)-1-(tert-butyl)-3-[difluoro(phenylsulfonyl)methyl]benzo[d]isothiazole 1-oxide (5e)
298.3 Hz), 80.7 (t, J = 21.8 Hz), 63.9, 24.9 (d, J = 2.3 Hz). IR (film): 1580, 1487, 1446, 1335, 1223, 1154, 1012, 961 cm\(^{-1}\). MS (ESI, m/z): 576.0 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{24}\)H\(_{22}\)BrF\(_2\)NO\(_3\)S\(_2\): (M + H\(^+\)): 554.0265; Found: 554.0277.

\((1S, 3R)-1-(\text{tert-Butyl})-3-[(\text{difluoro(phenylsulfonyl)methyl}]3-(3\text{-methoxyphenyl})benzo[d]isothiazole 1-oxide (5f)\)

\[
\begin{align*}
\text{PhSO}_{2}\text{CFCF}_{2}^\text{m+} & \quad \text{N}\overline{\text{S}}^\text{O}^- \\
\text{MeO} & \quad \text{Ph}
\end{align*}
\]

Mp: 126–128 °C. [\(\alpha\)]\(_D^{23}\) = −42.7 (c 0.80, CHCl\(_3\)). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.69–7.43 (m, 8H), 7.18 (t, J = 8.0 Hz, 1H), 6.76 (dd, J = 8.0, 2.7 Hz, 1H), 3.76 (s, 3H), 1.49 (s, 9H). \(^19\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) −97.2 (d, J = 231.0 Hz, 1F), −99.8 (d, J = 231.0 Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.2, 147.7, 140.6, 136.0, 134.9, 134.6, 133.0, 131.1, 129.9, 128.8, 128.7, 126.0 (d, J = 2.2 Hz), 123.6, 122.7 (t, J = 300.0 Hz), 119.7 (d, J = 8.0 Hz), 113.7, 113.6, 80.9 (t, J = 22.1 Hz), 63.6, 55.2, 24.7 (d, J = 1.6 Hz). IR (film): 1736, 1604, 1584, 1450, 1347, 1223, 1113, 755 cm\(^{-1}\). MS (ESI, m/z): 528.1 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{25}\)H\(_{25}\)F\(_2\)NO\(_4\)S\(_2\): (M + H\(^+\)): 506.1266; Found: 506.1288.

\((1S, 3R)-1-(\text{tert-Butyl})-3-[(\text{difluoro(phenylsulfonyl)methyl}]3-(4\text{-methoxyphenyl})benzo[d]isothiazole 1-oxide (5g)\)

\[
\begin{align*}
\text{PhSO}_{2}\text{CFCF}_{2}^\text{m+} & \quad \text{N}\overline{\text{S}}^\text{O}^- \\
\text{MeO} & \quad \text{Ph}
\end{align*}
\]

Mp: 149–151 °C. [\(\alpha\)]\(_D^{23}\) = −28.4 (c 0.80, CHCl\(_3\)). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.98 (d, J
= 8.0 Hz, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.69–7.55 (m, 3H), 7.48 (t, J = 7.5 Hz, 3H), 6.78 (d, J = 8.0 Hz, 2H), 3.74 (s, 3H), 1.47 (s, 9H). 19F NMR (282 MHz, CDCl3): δ –97.9 (d, J = 233.0 Hz, 1F), –100.2 (d, J = 233.1 Hz, 1F). 13C NMR (100 MHz, CDCl3): δ 159.3, 148.1, 136.1, 134.7, 134.5, 132.9, 130.9, 130.8 (t, J = 2.9 Hz), 129.7, 128.8 (d, J = 5.1 Hz), 128.6, 125.8 (d, J = 3.3 Hz), 123.5, 122.6 (t, J = 297.8 Hz), 113.2, 80.5 (t, J = 21.8 Hz), 63.4, 55.1, 24.6 (d, J = 2.4 Hz). IR (film): 1608, 1510, 1450, 1344, 1253, 1218, 1181, 1114 cm⁻¹. MS (ESI, m/z): 528.1 (M + Na⁺). HRMS (ESI, m/z): calcd. for C25H25F2NO4S2: (M + Na⁺): 528.1085; Found: 528.1102.

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfanyl)methyl]-3-[4-(trifluoromethyl)phenyl]benzo[d]isothiazole 1-oxide (5h)

White solid. M.p.: 154–156 °C. [α]D²⁹ = –35.5 (c = 0.95, CHCl₃). 1H NMR (300 MHz, CDCl₃): δ 8.08 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.5 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.71–7.59 (m, 4H), 7.56–7.46 (m, 4H), 1.49 (s, 9H). 19F NMR (282 MHz, CDCl₃): δ –61.7 (s, 3F), –96.2 (d, J = 234.9 Hz, 1F), –99.3 (d, J = 235.8 Hz, 1F). 13C NMR (100 MHz, CDCl₃): δ 147.0, 143.1, 135.8, 135.1, 134.8, 133.3, 131.0, 130.7, 130.3 (q, J = 32.1 Hz), 128.8, 128.0 (d, J = 5.1 Hz), 125.9 (d, J = 2.9 Hz), 124.9 (d, J = 3.6 Hz), 124.1 (q, J = 270.6 Hz), 123.8, 122.4 (t, J = 296 Hz), 80.6 (t, J = 21.9 Hz), 63.8, 24.6. IR (KBr): 3073, 2981, 1616, 1450, 1316, 1224, 1124, 1045, 963, 828, 8005, 605, 555 cm⁻¹. MS (ESI, m/z): 566 ([M+Na⁺]). HRMS (ESI, m/z): Calcd. for C25H22F₃NNaO₃S₂ ([M + Na⁺]): 566.0859; Found: 566.0863.

(1S,3R)-3-(6-Bromonaphthalen-2-yl)-1-(tert-butyl)-3-[difluoro(phenylsulfanyl)methyl]benzo[d]isothiazole 1-oxide (5i)
(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-[(E)-styryl]benzo[d]isothiazole 1-oxide (5j)

Mp: 145–147 °C. [α]_D^{23} = –34.6 (c 1.00, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 8.06 (d, J = 7.7 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.65–7.46 (m, 5H), 7.33 (d, J = 7.6 Hz, 2H), 7.28–7.14 (m, 3H), 6.91 (d, J = 15.3 Hz, 1H), 6.72 (dd, J = 15.2, 3.3 Hz, 1H), 1.48 (s, 9H). ¹⁹F NMR (282 MHz, CDCl₃): δ –100.9 (d, J = 235.2 Hz, 1F), –105.4 (d, J = 233.0 Hz, 1F). ¹³C NMR (100 MHz, CDCl₃): δ 146.8 (d, J = 3.0 Hz), 136.3, 135.6, 134.8, 134.2, 133.1, 131.6, 131.2, 130.0, 128.7, 128.2, 127.7, 127.1, 126.0 (dd, J = 3.7, 2.4 Hz), 125.4
(d, J = 4.3 Hz), 124.1, 122.3 (t, J = 298.1 Hz), 80.4 (t, J = 21.7 Hz), 63.4, 24.6 (d, J = 2.3 Hz). IR (film): 1581, 1449, 1341, 1222, 1156, 1113, 1017, 600 cm⁻¹. MS (ESI, m/z): 524.1 (M + Na⁺). Anal. Calcd for C₂₆H₂₅F₂NO₃S₂: C, 62.26; H, 5.02; N, 2.79; Found: C, 61.96; H, 5.12; N, 2.62.

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-isopropylbenzo[d]isothiazole 1-oxide (5k)

Mp: 58–60 °C. [α]D²³ –25.8 (c 0.60, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 8.00 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 7.6 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.62–7.50 (m, 4H), 3.17–3.05 (m, 1H), 1.39 (s, 9H), 1.02 (dd, J = 6.6, 3.6 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ –92.8 (d, J = 240.4 Hz, 1F), –94.2 (d, J = 240.4 Hz, 1F). ¹³C NMR (100 MHz, CDCl₃): δ 145.2 (d, J = 3.5 Hz), 136.9, 135.6, 134.7, 132.3, 130.8, 129.9, 128.9, 126.3 (d, J = 3.0 Hz), 123.7, 123.6 (t, J = 295.7 Hz), 84.8 (dd, J = 20.1, 16.5 Hz), 63.7, 34.9, 24.7, 19.1 (d, J = 2.9 Hz), 18.6 (d, J = 7.5 Hz). IR (film): 2973, 1449, 1349, 1222, 1157, 1104, 754, 589 cm⁻¹. MS (ESI, m/z): 464.1 (M + Na⁺). HRMS (ESI): calcd. for C₂₁H₂₅F₂NO₃S₂: (M + Na⁺): 464.1136; Found: 464.1152.

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-phenylbenzo[d]isothiazole 1-oxide (5l)

Mp: 95–97 °C. [α]D²³ –11.5 (c 0.90, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.90–7.78
(m, 4H), 7.63 (s, 1H), 7.52 (t, \( J = 7.7 \) Hz, 1H), 7.38 (t, \( J = 7.7 \) Hz, 2H), 7.31 (s, 1H), 7.22–7.10 (m, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.37 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \( \delta -97.4 \) (d, \( J = 238.9 \) Hz, 1F), \( -99.9 \) (d, \( J = 238.8 \) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 145.9, 143.1, 139.4, 136.2, 134.5, 132.6, 131.2, 128.4, 128.04, 128.02, 127.5, 127.4 \) (d, \( J = 1.3 \) Hz), 126.6 (d, \( J = 2.9 \) Hz), 123.9, 122.9 (t, \( J = 295.4 \) Hz), 80.5 (t, \( J = 22.4 \) Hz), 63.4, 24.8 (d, \( J = 2.9 \) Hz), 20.9, 20.1. IR (film): 1449, 1347, 1224, 1164, 1113, 1052, 962, 686 cm\(^{-1}\). MS (ESI, \( m/z \)): 526.1 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{26}\)H\(_{27}\)F\(_2\)NO\(_3\)S\(_2\): (M + H\(^+\)): 504.1473; Found: 504.1485.

\((1\text{S,3R})-1-(\text{tert-Butyl})-3-[\text{difluoro(phenylsulfonyl)methyl}]\)-5,6-dimethyl-3-(m-tolyl)benzo \([d]\)isothiazole 1-oxide (5m)

White solid. Mp: 143–144 °C. \([\alpha]_D^{28} = -11.2 \) (c 0.20, CHCl\(_3\)). IR (KBr): 2964, 2926, 1604, 1448, 1341, 1367, 1182, 1112, 958, 724, 687, 634, 597, 561 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta 7.89 \) (d, \( J = 7.5 \) Hz, 2H), 7.73–7.67 (m, 3H), 7.62–7.56 (m, 1H), 7.47–7.39 (m, 3H), 7.17–7.15 (m, 1H), 7.01 (d, \( J = 7.2 \) Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.49 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \( \delta -95.9 \) (d, \( J = 232.7 \) Hz, 1F), \(-99.0 \) (d, \( J = 231.8 \) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta 145.9, 142.9, 139.3 \) (d, \( J = 1.7 \) Hz), 139.2, 137.4, 136.2, 134.4, 132.6, 131.1, 128.8, 128.5, 128.1 (d, \( J = 4.3 \) Hz), 127.7, 126.6 (d, \( J = 2.6 \) Hz), 124.3 (d, \( J = 6.9 \) Hz), 123.8, 122.9 (t, \( J = 294.7 \) Hz), 80.5 (t, \( J = 21.6 \) Hz), 63.3, 24.8 (d, \( J = 2.6 \) Hz), 21.7, 20.8, 20.0. MS (ESI, \( m/z \)): 518 ([M + H\(^+\)]). HRMS (ESI, \( m/z \)): Calcd. for C\(_{27}\)H\(_{36}\)F\(_2\)NO\(_3\)S\(_2\) ([M + H\(^+\)]): 518.1635; found: 518.1614.

\((1\text{S,3R})-1-(\text{tert-Butyl})-3-(4\text{-chlorophenyl})-3-[\text{difluoro(phenylsulfonyl)methyl}]\)-5,6-dimeth
ylbenzo[d]isothiazole 1-oxide (5n)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2_{\text{Me}} & \quad \text{N}^+\text{S}_{\text{Me}}^{-} \\
\text{Cl} & \quad \text{Me} & \quad \text{Me} \\
\end{align*}
\]

Mp: 159–161 °C. [α]_D^{22} = –1.0 (c 0.75, CHCl₃). \(^1\)H NMR (300 MHz, CDCl₃): δ 7.86–7.78 (m, 4H), 7.56 (t, \(J = 7.4\) Hz, 2H), 7.40 (t, \(J = 7.8\) Hz, 2H), 7.32 (s, 1H), 7.14 (d, \(J = 8.2\) Hz, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 1.36 (s, 9H). \(^19\)F NMR (282 MHz, CDCl₃): δ –97.6 (d, \(J = 231.8\) Hz, 1F), –100.4 (d, \(J = 231.9\) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl₃): δ 145.4, 143.3, 139.6, 138.2, 136.1, 134.6, 134.1, 132.5, 131.0, 129.0 (d, \(J = 5.5\) Hz), 128.8, 128.0, 126.3 (d, \(J = 2.9\) Hz), 123.9, 122.6 (t, \(J = 298.1\) Hz), 80.1 (t, \(J = 21.9\) Hz), 63.4, 24.7 (d, \(J = 1.8\) Hz), 20.8, 20.0. IR (film): 1492, 1449, 1348, 1224, 1165, 964, 686 cm⁻¹. MS (ESI, \(m/z\)): 560.1 (M + Na⁺). HRMS (ESI): calcd. for C₂₆H₂₆ClF₂NO₃S₂: (M + Na⁺): 560.0903; Found: 560.0898.

(1S,3R)-1-(tert-Butyl)-3-(difluoro(phenylsulfonyl)methyl)-3-(3-methoxyphenyl)-5,6-dimethylbenzo[d]isothiazole 1-oxide (5o)

\[
\begin{align*}
\text{PhSO}_2\text{CF}_2_{\text{Me}} & \quad \text{N}^+\text{S}_{\text{Me}}^{-} \\
\text{MeO} & \quad \text{Me} & \quad \text{Me} \\
\end{align*}
\]

Mp: 149–151 °C. [α]_D^{21} = –6.8 (c 0.75, CHCl₃). \(^1\)H NMR (300 MHz, CDCl₃): δ 7.91 (d, \(J = 7.7\) Hz, 2H), 7.66 (s, 1H), 7.60 (t, \(J = 7.3\) Hz, 1H), 7.53 (d, \(J = 7.7\) Hz, 1H), 7.45 (t, \(J = 7.7\) Hz, 3H), 7.40 (s, 1H), 7.18 (t, \(J = 8.1\) Hz, 1H), 6.75 (dd, \(J = 8.2, 2.5\) Hz, 1H), 3.76 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 1.48 (s, 9H). \(^19\)F NMR (282 MHz, CDCl₃): δ –96.7 (d, \(J = 229.8\) Hz, 1F), –99.5 (d, \(J = 229.8\) Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl₃): δ 159.1, 145.7, 142.9, 140.9, 139.3, 136.1, 134.4, 132.4, 131.1, 128.8, 128.5, 126.5, 123.7, 122.8 (t, \(J =
298.8 Hz), 119.5 (d, J = 7.5 Hz), 113.5, 113.4 (d, J = 4.5 Hz), 80.4 (t, J = 21.4 Hz), 63.3, 55.1, 24.7 (d, J = 2.2 Hz), 20.7, 19.9. IR (film): 1600, 1450, 1351, 1223, 1162, 1123, 1055, 968 cm\(^{-1}\). MS (ESI, m/z): 556.1 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{27}\)H\(_{29}\)F\(_2\)NO\(_4\)S\(_2\): (M + Na\(^+\)): 556.1398; Found: 556.1407.

\((1S,3R)-1-(\text{tert-Butyl})-3-[\text{difluoro(phenylsulfonyl)methyl}]3\text{-phenyl}-3,5,6,7\text{-tetrahydroindeno}[5,6-d]\text{isothiazole 1-oxide (5p)}\)

\[
\begin{align*}
\text{PhS}=O
\end{align*}
\]

Mp: 85–88 °C. [\(\alpha\)]\(_D^{22}\) –10.5 (c 0.95, CHCl\(_3\)). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.87 (d, J = 7.4 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.67 (s, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 3H), 7.23–7.10 (m, 3H), 2.92–2.70 (m, 4H), 2.14–1.92 (m, 2H), 1.38 (s, 9H). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta\) –97.4 (d, J = 232.4 Hz, 1F), –99.8 (d, J = 233.8 Hz, 1F). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 151.3, 147.4, 146.8, 139.6, 136.3, 134.6, 133.2, 131.0, 128.7, 127.9, 127.5, 127.4, 122.9 (t, J = 297.6 Hz), 121.5 (d, J = 2.9 Hz), 118.9, 80.1 (t, J = 21.3 Hz), 63.3, 32.9, 32.3, 25.9, 24.7 (d, J = 1.4 Hz). IR (film): 2968, 1448, 1347, 1223, 1168, 1112, 1048, 964 cm\(^{-1}\). MS (ESI, m/z): 538.2 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{27}\)H\(_{27}\)F\(_2\)NO\(_3\)S\(_2\): (M + H\(^+\)): 516.1473; Found: 516.1487.

\((1S,3R)-1-(\text{tert-Butyl})-3-[\text{difluoro(phenylsulfonyl)methyl}]3-(m\text{-tolyl})-3,5,6,7\text{-tetrahydroindeno}[5,6-d]\text{isothiazole 1-oxide (5q)}\)

\[
\begin{align*}
\text{PhS}=O
\end{align*}
\]

(1S,3R)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-3-(m-tolyl)-3,5,6,7-tetrahydroindeno[5,6-d]isothiazole 1-oxide (5q)
Mp: 92–95 °C. [α]D$^2\overline{2}$ = –8.5 (c 0.80, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.81 (d, $J$ = 7.5 Hz, 2H), 7.64 (t, $J$ = 7.9 Hz, 3H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.35 (t, $J$ = 7.7 Hz, 3H), 7.07 (t, $J$ = 7.9 Hz, 1H), 6.93 (d, $J$ = 7.4 Hz, 1H), 2.92–2.70 (m, 4H), 2.21 (s, 3H), 2.13–1.93 (m, 2H), 1.41 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ –96.5 (d, $J$ = 232.7 Hz, 1F), –99.6 (d, $J$ = 234.7 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 151.2, 147.2, 146.9, 139.3, 137.4, 136.2, 134.4, 133.2, 131.0, 128.8, 128.5, 128.1 (d, $J$ = 4.6 Hz), 127.8, 124.3 (d, $J$ = 6.8 Hz), 123.0 (t, $J$ = 298.4 Hz), 121.5 (d, $J$ = 3.0 Hz), 118.8, 80.1 (t, $J$ = 21.4 Hz), 63.4, 32.9, 32.3, 25.9, 24.8 (d, $J$ = 2.3 Hz), 21.8. IR (film): 2968, 1449, 1348, 1223, 1167, 1116, 964, 597 cm$^{-1}$. MS (ESI, $m/z$): 552.2 (M + Na$^+$). HRMS (ESI): calcd. for C$_{28}$H$_{29}$F$_2$NO$_3$S$_2$: (M + Na$^+$): 552.1449; Found: 552.1454.

(1S,3R)-1-(tert-Butyl)-3-[difuoro(phenylsulfonyl)methyl]-3-(3-methoxyphenyl)-3,5,6,7-tetrahydroindeno[5,6-d]isothiazole 1-oxide (5r)

Mp: 83–86 °C. [α]D$^2\overline{1}$ = –4.7 (c 0.70, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.91 (d, $J$ = 7.7 Hz, 2H), 7.70 (s, 1H), 7.60 (t, $J$ = 7.3 Hz, 1H), 7.53 (d, $J$ = 8.1 Hz, 1H), 7.45 (t, $J$ = 7.2 Hz, 4H), 7.17 (t, $J$ = 8.2 Hz, 1H), 6.75 (d, $J$ = 8.1 Hz, 1H), 3.76 (s, 3H), 3.01–2.78 (m, 4H), 2.22–2.00 (m, 2H), 1.48 (s, 9H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ –96.6 (d, $J$ = 234.5 Hz, 1F), –99.5 (d, $J$ = 234.6 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.2, 151.3, 147.3, 146.8, 141.1, 136.2, 134.4, 133.2, 131.1, 128.8, 128.6, 123.0 (t, $J$ = 300.4 Hz), 121.5 (d, $J$ = 3.3 Hz), 119.5 (d, $J$ = 7.7 Hz), 118.8, 113.5, 113.4, 80.1 (t, $J$ = 21.7 Hz), 63.4, 55.2, 32.9, 32.3, 25.9, 24.8 (d, $J$ = 2.2 Hz). IR (film): 2960, 1601, 1450, 1347, 1222, 1167, 1116, 1049 cm$^{-1}$. MS (ESI, $m/z$): 568.2 (M + Na$^+$). HRMS (ESI): calcd. for C$_{28}$H$_{29}$F$_2$NO$_4$S$_2$: (M + Na$^+$): 568.1398; Found: 568.1393.
(1\textit{S},3\textit{R})-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethoxy-3-phenylbenzo[\textit{d}]-isothiazole 1-oxide (5s)

\[
\text{PhSO}_2\text{CF}_{2}\text{Ph}
\]

Mp: 135–137 °C. [\(\alpha\)]\(_D\)\textsuperscript{22} = –29.9 (c 0.85, CHCl\(_3\)). \(\textsuperscript{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.92 (t, \(J = 7.3\) Hz, 4H), 7.62 (t, \(J = 7.8\) Hz, 1H), 7.47 (t, \(J = 7.9\) Hz, 2H), 7.35–7.20 (m, 4H), 6.98 (s, 1H), 3.96 (s, 3H), 3.83 (s, 3H), 1.45 (s, 9H). \(\textsuperscript{19}F\) NMR (282 MHz, CDCl\(_3\)): \(\delta\) –97.2 (d, \(J = 233.4\) Hz, 1F), –99.4 (d, \(J = 233.3\) Hz, 1F). \(\textsuperscript{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 153.4, 150.7, 141.9, 139.3, 136.1, 134.6, 131.1, 128.7, 128.1, 127.2, 127.1, 126.0, 122.9 (t, \(J = 297.8\) Hz), 107.1, 104.4, 80.4 (t, \(J = 21.4\) Hz), 63.4, 56.4, 56.3, 27.8 (d, \(J = 2.3\) Hz). IR (film): 1585, 1501, 1449, 1348, 1279, 1218, 1168 cm\(^{-1}\). MS (ESI, \(m/z\)): 558.1 (M + Na\(^+\)). HRMS (ESI): calcd. for C\(_{26}\)H\(_{27}\)F\(_2\)NO\(_5\)S\(_2\): (M + Na\(^+\)): 558.1191; Found: 558.1193.

(1\textit{S},3\textit{R})-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-5,6-dimethoxy-3-(3-methoxyphenyl)benzo[\textit{d}]-isothiazole 1-oxide (5t)

\[
\text{PhSO}_2\text{CF}_{2}\text{MeO}
\]

Mp: 81–83 °C. [\(\alpha\)]\(_D\)\textsuperscript{21} = –21.2 (c 0.80, CHCl\(_3\)). \(\textsuperscript{1}H\) NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J = 7.6\) Hz, 2H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.53–7.42 (m, 4H), 7.28 (s, 1H), 7.18 (t, \(J = 8.0\) Hz, 1H), 6.98 (s, 1H), 6.76 (dd, \(J = 8.0, 2.5\) Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 1.46 (s, 9H). \(\textsuperscript{19}F\) NMR (282 MHz, CDCl\(_3\)): \(\delta\) –96.5 (d, \(J = 234.8\) Hz, 1F), –99.1 (d, \(J =
234.9 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.3, 153.4, 150.8, 141.8, 141.0 (t, $J = 3.0$ Hz), 136.1, 134.5, 131.1, 128.9, 128.6, 126.0, 122.9 (t, $J = 297.5$ Hz), 119.2 (d, $J = 7.2$ Hz), 113.5, 113.4, 107.2, 104.5, 80.4 (t, $J = 21.1$ Hz), 63.5, 56.4, 56.3, 55.2, 24.8 (d, $J = 1.5$ Hz). IR (film): 1601, 1500, 1348, 1279, 1217, 1170, 1056 cm$^{-1}$. MS (ESI, $m/z$): 588.1 (M + Na$^+$). HRMS (ESI): calcd. for C$_{27}$H$_{29}$F$_2$NO$_6$S$_2$: (M + Na$^+$): 588.1297; Found: 588.1294.

(1$S$,3$R$)-1-(tert-Butyl)-3-[difluoro(phenylsulfonyl)methyl]-6-methyl-3-phenylbenzo[d]isothiazole 1-oxide and (1$S$,3$R$)-1-(tert-butyl)-3-[difluoro(phenylsulfonyl)methyl]-5-methyl-3-phenylbenzo[d]isothiazole 1-oxide (5u)

A mixture of two inseperable regio-isomers. [$\alpha$]$^D_{28}$ $-24.4$ (c 0.95, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.00–7.83 (m, 4.54H), 7.75 (s, 0.46H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.56–7.17 (m, 7H), 2.44 (s, 1.38H), 2.38 (s, 1.62H), 1.47 (s, 4.86H), 1.44 (s, 4.14H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ $-97.4$ (d, $J = 233.9$ Hz, 0.46F), $-97.7$ (d, $J = 234.2$ Hz, 0.54F), $-99.9$ (d, $J = 234.2$ Hz, 0.46F), $-100.0$ (d, $J = 234.1$ Hz, 0.54F). MS (ESI, $m/z$): 512.4 (M + Na$^+$). HRMS (ESI): calcd. for C$_{25}$H$_{25}$F$_2$NO$_3$S$_2$: (M + Na$^+$): 512.1136; Found: 512.1139.

3.2 Synthesis of Cyclic Sulfinamides
Typical Procedures:
To a solution of \((S_S,R)-5\) (\(R^1 = \text{Ph}; R^2, R^3 = \text{H}\)) (3.92 g, 8.25 mmol) in \(\text{CH}_2\text{Cl}_2\) (40 mL) was added \(\text{HCl}\) (2.5 M in 1,4-dioxane, 66 mL, 165 mmol) at \(-78^\circ\text{C}\). Then the reaction mixture was allowed to warm up to room temperature in 1 h. The reaction mixture was diluted with water (20 mL) and treated with saturated \(\text{NaHCO}_3\) solution (200 mL). The aqueous phase was extracted with ethyl acetate (40 mL × 3), and the combined organic phases were washed with brine (40 mL) and dried over \(\text{Na}_2\text{SO}_4\). The volatile solvents were removed under vacuum, and the residue was purified by flash column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3 v/v) to give cyclic sulfinamide \((S_S,R)-6\) (\(R^1 = \text{Ph}; R^2, R^3 = \text{H}\)) as a white solid (3.310 g, 96% yield).

Characterization Data:
\((1S,3R)-3\text{-}[\text{Difluoro(phenylsulfonyl)methyl}]\text{-}3\text{-phenyl-2,3-dihydrobenzo}[d]isothiazole 1-oxide (6a)\)

\[\text{PhO}_2\text{SF}_2\text{C}^\text{m}N^\text{O}\]

\[\text{HCl in 1,4-dioxane}\]

\[\text{CH}_2\text{Cl}_2, -78^\circ\text{C to rt, 1 h}\]

\[\text{dr > 99:1}\]

\[\text{PhO}_2\text{SF}_2\text{C}^\text{m}N^\text{O}\]

\[\text{HN-S}^\text{O}\]

\[\text{Ph}\]

Mp: 165–167 °C. \([\alpha]_D^{26} = -90.4\) (c 1.00, \(\text{CHCl}_3\)). \(^1\text{H NMR}\) (300 MHz, \(\text{CDCl}_3\)): \(\delta\) 7.91 (d, \(J = 6.0\) Hz, 2H), 7.87–7.76 (m, 3H), 7.70 (t, \(J = 7.1\) Hz, 2H), 7.62–7.47 (m, 4H), 7.34 (d, \(J = 5.5\) Hz, 3H), 6.48 (s, 1H). \(^19\text{F NMR}\) (282 MHz, \(\text{CDCl}_3\)): \(\delta\) –99.3 (d, \(J = 237.5\) Hz, 1F), –100.9 (d, \(J = 237.4\) Hz, 1F). \(^{13}\text{C NMR}\) (100 MHz, \(\text{CDCl}_3\)): \(\delta\) 145.5, 137.9, 135.8, 135.4, 133.6, 131.9, 130.6, 130.4, 129.2, 129.0, 128.7, 126.8 (dd, \(J = 3.9, 2.0\) Hz), 125.6 (dd, \(J = 3.9, 2.0\) Hz).
3.1, 1.6 Hz), 125.4, 120.9 (dd, J = 301.7, 299.2 Hz), 79.8 (t, J = 20.8 Hz). IR (film): 3385, 1633, 1583, 1449, 1339, 1149, 1085, 1060 cm⁻¹. MS (ESI, m/z): 420.3 (M + H⁺). HRMS (ESI): calcd. for C₂₀H₁₅F₂NO₃S₂: (M + H⁺): 420.0534; Found: 420.0531.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-3-(m-tolyl)-2,3-dihydrobenzo[d]isothiazole 1-oxide (6b)

White solid. Mp: 135–136 °C. [α]D²⁶ = −85.6 (c = 0.85, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.83–7.80 (m, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.70–7.64 (m, 4H), 7.55–7.47 (m, 4H), 7.26–7.19 (m, 1H), 7.11 (d, J = 8.1 Hz, 1H), 6.42 (s, 1H), 2.30 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ −97.2 (d, J = 236.6 Hz, 1F), −98.1 (d, J = 236.9 Hz, 1F). ¹³C NMR (100 MHz, CDCl₃): δ 145.7, 138.5, 138.0, 135.9, 135.4, 133.9, 132.0, 130.6, 130.4, 129.9, 129.2, 128.6, 127.5, 125.8, 125.4, 124.0, 121.2 (t, J = 293.1 Hz), 79.9 (t, J = 20.4 Hz), 28.8, 21.7. IR (KBr): 3381, 3064, 1606, 1582, 1448, 1332, 1147, 1080, 1061 cm⁻¹. MS (ESI, m/z): 434 ([M + H⁺]). HRMS (ESI, m/z): Calcd. for C₂₁H₁₈F₂NO₃S₂ ([M + H⁺]): 434.0696; Found: 434.0688.

(1S,3R)-3-(4-Bromophenyl)-3-[difluoro(phenylsulfonyl)methyl]-2,3-dihydrobenzo[d]isothiazole 1-oxide (6c)

White solid. Mp: 96–98 °C. [α]D²⁹ = −103.4 (c = 1.00, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.84–7.71 (m, 6H), 7.65–7.52 (m, 5H), 7.48–7.43 (m, 2H), 6.46 (s, 1H). ¹⁹F
NMR (282 MHz, CDCl$_3$): $\delta$ –99.5 (d, $J = 236.9$ Hz, 1F), –100.5 (d, $J = 236.6$ Hz, 1F).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.7, 137.6, 135.6, 135.1, 133.5, 132.1, 131.9, 130.9, 130.5, 129.4, 128.7, 128.6, 125.6, 123.3, 120.8 (t, $J = 297.5$ Hz), 79.5 (t, $J = 21.9$ Hz). IR (KBr): 3375, 3068, 1491, 1336, 1150, 1070 cm$^{-1}$. MS (ESI, $m/z$): 498 ([M + H]$^+$). HRMS (ESI, $m/z$): Calcd. for C$_{20}$H$_{15}$BrF$_3$NO$_3$S$_2$ $^+$$([M + H]^+)$: 497.9645; Found: 497.9651.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-3-[4-(trifluoromethyl)phenyl]-2,3-dihydropenthio[d]isothiazole 1-oxide (6d)

White solid. Mp: 88–90 $^\circ$C. $[\alpha]_D^{28}$ = –89.6 (c = 0.90, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J = 8.4$ Hz, 2H), 7.85–7.79 (m, 3H), 7.75–7.51 (m, 8H), 6.56 (s, 1H).

$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ –62.4 (s, 3F), –99.8 (d, $J = 237.7$ Hz, 1F), –100.5 (d, $J = 237.7$ Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.8, 140.0, 137.5, 135.8, 133.3, 132.2, 131.2 (q, $J = 32.8$ Hz), 131.0, 130.5, 129.4, 127.5, 125.68 (q, $J = 3.5$ Hz), 125.64, 125.57, 123.8 (q, $J = 270.5$ Hz), 120.8 (t, $J = 296.7$ Hz), 79.6 (t, $J = 21.1$ Hz). IR (KBr): 3207, 1619, 1449, 1329, 1124, 1072 cm$^{-1}$. MS (ESI, $m/z$): 488 ([M + H]$^+$). HRMS (ESI, $m/z$): Calcd. for C$_{21}$H$_{15}$F$_3$NO$_3$S$_2$ $^+$$([M + H]^+)$: 488.0414; Found: 488.0413.

(1S,3R)-3-(6-Bromonaphthalen-2-yl)-3-[difluoro(phenylsulfonyl)methyl]-2,3-dihydropenthio[d]isothiazole 1-oxide (6e)
Mp: 113–115 °C. [α]D$^26$ –105.8 (c 0.90, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ 8.38 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.93 (s, 1H), 7.84 (d, J = 7.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.75–7.49 (m, 7H), 7.44 (t, J = 7.4 Hz, 2H), 6.61 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 145.6, 137.6 (d, J = 1.5 Hz), 135.5, 134.1, 133.7 (t, J = 1.5 Hz), 133.4, 132.0, 131.2, 130.8, 130.5, 130.4, 129.9, 129.3, 129.2, 127.5, 126.7 (dd, J = 3.7, 2.2 Hz), 125.7 (d, J = 2.2 Hz), 125.5, 125.1 (dd, J = 4.5, 2.3 Hz), 121.1, 120.9 (t, J = 299.5 Hz), 79.9 (t, J = 22.3 Hz). IR (film): 3370, 1585, 1449, 1336, 1149, 1062 cm$^{-1}$. MS (ESI, m/z): 548.4 (M$^+$). HRMS (ESI): calcd. for C$_{24}$H$_{16}$BrF$_2$NO$_3$S$_2$: (M$^+$): 547.9796; Found: 547.9795.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-3-[(E)-styryl]-2,3-dihydrobenzo[d]isothiazole 1-oxide (6f)

Mp: 82–84 °C. [α]D$^27$ –71.4 (c 0.70, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.95 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 5.8 Hz, 1H), 7.72 (t, J = 7.0 Hz, 1H), 7.63–7.51 (m, 5H), 7.41 (d, J = 6.4 Hz, 2H), 7.35–7.17 (m, 4H), 6.75 (d, J = 15.6 Hz, 1H), 6.27 (s, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): δ –105.9 (d, J = 233.6 Hz, 1F), –107.1 (d, J = 233.6 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 145.4, 137.2, 135.6, 135.5, 134.7 (d, J = 1.2 Hz), 133.1, 132.0, 130.8, 130.7, 129.3, 128.48, 128.47, 127.3, 125.5, 125.1 (d, J = 4.4 Hz), 122.7 (d, J = 2.8 Hz),
120.2 (t, J = 299.6 Hz), 78.7 (t, J = 20.9 Hz). IR (film): 1449, 1336, 1189, 1151, 1092, 1062 cm⁻¹. MS (ESI, m/z): 446.3 (M + H⁺). HRMS (ESI): calcd. for C₂₂H₁₇F₂NO₅S₂: (M + H⁺): 446.0691; Found: 446.0696.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-3-isopropyl-2,3-dihydrobenzo[d]isothiazole 1-oxide (6g)

Mp: 106–108 °C. [α]D²⁷ −33.8 (c 0.60, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.84 (d, J = 8.2 Hz, 3H), 7.72 (t, J = 7.7 Hz, 1H), 7.67–7.50 (m, 5H), 5.55 (s, 1H), 2.80–2.65 (m, 1H), 1.11 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ −98.6 (d, J = 241.8 Hz, 1F), −101.3 (d, J = 241.8 Hz, 1F). ¹³C NMR (100 MHz, CDCl₃): δ 146.8 (d, J = 1.5 Hz), 135.5 (d, J = 4.5 Hz), 135.3, 133.6, 131.5, 130.9, 130.4, 129.2, 125.5, 125.47 (t, J = 1.9 Hz), 121.7 (t, J = 300.4 Hz), 81.1 (t, J = 25.3 Hz), 33.6, 18.4 (dd, J = 4.9, 1.0 Hz), 17.7 (d, J = 1.8 Hz). IR (film): 2977, 1584, 1450, 1348, 1158, 1047 cm⁻¹. MS (ESI, m/z): 386.2 (M + H⁺). HRMS (ESI): calcd. for C₁₇H₁₇F₂NO₅S₂: (M + H⁺): 386.0691; Found: 386.0687.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-phenyl-2,3-dihydrobenzo[d]isothiazole 1-oxide (6h)

Mp: 161–163 °C. [α]D²⁷ −88.5 (c 0.80, CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ 7.88 (d, J =
7.5 Hz, 2H), 7.77 (d, J = 7.4 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.57–7.45 (m, 3H), 7.38 (s, 1H), 7.37–7.28 (m, 3H), 6.35 (s, 1H), 2.28 (s, 3H), 2.27 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -99.5 (d, J = 239.3 Hz, 1F), -100.8 (d, J = 239.3 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.1, 141.5, 140.0, 136.1, 135.5 (d, J = 0.8 Hz), 135.3, 133.7, 130.3, 129.1, 128.8, 128.6, 126.8 (dd, J = 3.9, 2.4 Hz), 126.2 (dd, J = 2.8, 0.7 Hz), 125.8, 121.0 (t, J = 302.7 Hz), 79.5 (t, J = 21.0 Hz), 20.4, 19.8. IR (film): 1583, 1449, 1338, 1184, 1149, 1066, 686, 587 cm$^{-1}$. MS (ESI, m/z): 448.3 (M + H$^+$). HRMS (ESI): calcd. for C$_{22}$H$_{19}$F$_2$NO$_3$S$_2$: (M + H$^+$): 448.0847; Found: 448.0842.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-5,6-dimethyl-3-((m-tolyl)-2,3-dihydrobenzo[ $d$]isothiazole 1-oxide (6i)

[Structure image]

White solid. M.p.: 183–184 °C. [\(\alpha\)]$_D^{26}$ = -63.8 (c = 0.95, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.75 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 6.3 Hz, 3H), 7.55 (s, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.29 (s, 1H), 2.29 (s, 6H), 2.28 (s, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -98.5 (d, J = 235.8 Hz, 1F), -99.7 (d, J = 236.9 Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.3, 141.5, 140.0, 138.4, 136.2, 135.6, 135.3, 134.0, 130.4, 129.7, 129.2, 128.5, 127.5, 126.3, 125.8, 124.0, 121.3 (t, J = 298 Hz), 79.6 (t, J = 20.4 Hz), 21.7, 20.5, 19.9. IR (KBr): 3243, 2921, 1733, 1605, 1448, 1350, 1172, 1148, 1058 cm$^{-1}$. MS (ESI, m/z): 462 ([M + H$^+$]). HRMS (ESI, m/z): Calcd. for C$_{23}$H$_{22}$F$_2$NO$_3$S$_2$: ([M + H$^+$]): 462.1009; Found: 462.1009.

(1S,3R)-3-[Difluoro(phenylsulfonyl)methyl]-3-phenyl-3,5,6,7-tetrahydro-2H-indeno[5,6- $d$]isothiazole 1-oxide (6j)
Mp: 191–193 °C. [α]D<sup>27</sup> −94.6 (c 0.90, CHCl₃). <sup>1</sup>H NMR (300 MHz, CDCl₃): δ 7.90 (d, J = 6.7 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.59 (s, 1H), 7.50 (t, J = 7.3 Hz, 2H), 7.44 (s, 1H), 7.32 (d, J = 5.5 Hz, 3H), 6.36 (s, 1H), 3.00–2.80 (m, 4H), 2.20–2.00 (m, 2H). <sup>19</sup>F NMR (282 MHz, CDCl₃): δ −99.3 (d, J = 238.4 Hz, 1F), −100.8 (d, J = 238.4 Hz, 1F). <sup>13</sup>C NMR (100 MHz, CDCl₃): δ 149.5, 147.8, 143.8, 136.2 (d, J = 4.5 Hz), 135.3, 133.7, 130.4, 129.1, 128.8, 128.6, 126.8 (d, J = 2.1 Hz), 126.7, 121.2 (d, J = 2.4 Hz), 120.8, 121.1 (dd, J = 301.2, 298.4 Hz), 79.3 (t, J = 20.7 Hz), 32.8, 32.4, 25.7. IR (film): 3167, 1583, 1447, 1347, 1145, 1108, 1066, 1042 cm<sup>−1</sup>. MS (ESI, m/z): 460.3 (M + H<sup>+</sup>). HRMS (ESI): calcd. for C<sub>23</sub>H<sub>19</sub>F<sub>2</sub>NO<sub>3</sub>S<sub>2</sub>: (M + H<sup>+</sup>): 460.0847; Found: 460.0846.

3.3 <sup>3</sup>N-(6-Bromonaphthalen-2-yl)methylation of Cyclic Sulfinamide 6a
**Experimental Procedures:**

Under N$_2$ atmosphere, to a solution of cyclic sulfinamide 6a (0.126 g, 0.3 mmol) in DMF (6.0 mL) was added NaH (0.0144 g, 0.6 mmol) at $-30^\circ$C. After stirring at this temperature for 2 h, 2-bromo-6-(bromomethyl)naphthalene (0.180 g, 0.6 mmol) was added, and then the reaction mixture was stirred at the same temperature for 10 h. After quenched with saturated NH$_4$Cl solution, the reaction mixture was extracted with diethyl ether (3 × 30 mL), and the combined organic phases were dried over anhydrous MgSO$_4$. The volatile solvents were removed under vacuum, and the crude product was purified by flash column chromatography (silica gel; ethyl acetate/petroleum ether = 1:5, v/v) to give S3 as a white solid (0.118 g; 62% yield).

(1S,3R)-2-[(6-Bromonaphthalen-2-yl)methyl]-3-[difluoro(phenylsulfonyl)methyl]-3-phenyl-2,3-dihydrobenzo[d]isothiazole 1-oxide (S3)

Mp: 225 – 228 $^\circ$C. [a]$_D^{28}$ $-52.0$ (c 0.75, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.07 (s, 1H), 8.01 (s, 1H), 7.89 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.81 – 7.66 (m, 5H), 7.67 – 7.57 (m, 2H), 7.59 – 7.45 (m, 3H), 7.44 – 7.37 (m, 2H), 7.36 – 7.26 (m, 5H), 7.25 (d, $J = 8.5$ Hz, 1H), 6.63 (d, $J = 8.5$ Hz, 1H), 4.09 (s, 2H), 3.73 (s, 3H), 2.41 (s, 3H).
7.65 – 7.44 (m, 7H), 7.41 – 7.22 (m, 4H), 4.47 (d, $J = 13.3$ Hz, 1H), 4.20 (d, $J = 13.3$ Hz, 1H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ –87.6 (d, $J = 242.7$ Hz, 1F), –95.7 (d, $J = 242.7$ Hz, 1F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.7 (d, $J = 1.3$ Hz), 140.1 (dd, $J = 6.4$, 1.8 Hz), 135.1, 134.9, 134.4, 134.2, 133.1, 131.9, 131.6, 130.7, 130.3, 129.8, 129.7, 129.6, 129.3, 129.2, 129.1, 128.9, 128.7 (t, $J = 2.5$ Hz), 128.6, 127.1, 126.7 (d, $J = 6.4$ Hz), 125.4 (t, $J = 305.1$ Hz), 124.6, 120.1, 82.8 (t, $J = 21.9$ Hz), 49.0 (d, $J = 6.6$ Hz). IR (film): 3053, 1585, 1498, 1448, 1354, 1181, 1147, 1091 cm$^{-1}$. MS (ESI, $m/z$): 638.4 (M + H$^+$). HRMS (ESI): calcd. for C$_{31}$H$_{22}$BrF$_2$NO$_3$S$_2$: (M + H$^+$): 638.0265; Found: 638.0274.

### 3.4 Synthesis of Cyclic Sulfinimines

![Cyclic Sulfinimine](image)

**Figure S3** Structure of Cyclic Sulfinimine (S)-7c in the Crystal

**Typical Procedures:**

Under N$_2$ atmosphere, Cs$_2$CO$_3$ (260 mg, 0.8 mmol) was added to a solution of cyclic
sulfinamide \((S,S,R)-6\) \((R^1 = \text{Ph}; R^2, R^3 = \text{H})\) (89 mg, 0.2 mmol) in dry THF, and then reaction mixture was heated at 42–45 °C for 12 h. After diluted with water (10 mL), the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (40 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed under vacuum and the residue was purified by flash chromatography (silica gel; \(n\)-hexane/ethyl acetate = 3:1 v/v) to afford cyclic sulfinimine \((S)-7\) \((R^1 = \text{Ph}; R^2, R^3 = \text{H})\) as a white solid (31.7 mg; 70% yield; 98:2 er).

The er of \(7\) could be improved to >99:1 after a single recrystallization from ethyl acetate/petroleum ether (1:1, v/v; 0.073 mol/L) at 0 °C.

\((S)-3\)\text{-Phenylbenzo}\[d\]\text{isothiazole 1-oxide (7a)}

Pale yellow solid. Mp: 74–75 °C. \([\alpha]^\text{D}_29 -292.6 (c 1.00, CHCl\(_3\)), 98:2 \text{ er}\] The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250×4.6 mm), MeOH / IPA= 50 / 50 (v/v), 0.7 mL/min, \(\lambda= 214\) nm, \(t_R\) (major) = 22.39 min, \(t_R\) (minor) = 33.02 min on Dionex Ultimate 3000. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta 8.14–8.10\) (m, 1H), 7.98–7.93 (m, 3H), 7.74–7.69 (m, 2H), 7.67–7.56 (m, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 174.1, 155.0, 135.1, 132.4, 132.2, 131.5, 129.2, 129.1, 127.0, 125.8.\) IR (KBr): 1598, 1512, 1443, 1335, 1095 cm\(^{-1}\). MS (ESI, \(m/\ell\)): 227. HRMS (ESI, \(m/\ell\)): Calcd. for C\(_{13}\)H\(_9\)NOS ([M]+): 227.0405; Found: 227.0404.

\((S)-3\)-(\(m\)-Tolyl)benzo\[d\]\text{isothiazole 1-oxide (7b)}
White solid. Mp: 79–80 °C. \([\alpha]_D^{28} \sim -301.9\) (c 1.00, CHCl₃), 96:4 er. The enantiomeric ratio was determined by Lux 5u Cellulose-1 (250×4.6 mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, \(\lambda= 214\) nm, \(t_R\) (major) = 9.46 min, \(t_R\) (minor) = 10.44 min on Dionex Ultimate 3000. \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 8.13–8.10 (m, 1H), 7.98–7.94 (m, 1H), 7.77 (s, 1H), 7.75–7.69 (m, 3H), 7.48–7.45 (m, 2H), 2.48 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 174.3, 154.9, 139.1, 135.2, 133.2, 132.3, 132.1, 131.5, 129.6, 128.9, 127.1, 126.3, 125.7, 21.5. IR (KBr): 2965, 1511, 1301, 1078 cm\(^{-1}\). MS (ESI, \(m/z\)): 241 ([M]\(^+\)). HRMS (ESI, \(m/z\)): Calcd. for C\(_{14}\)H\(_{11}\)NOS ([M]\(^+\)): 241.0561; Found: 241.0558.

\((S)-3-(4-Bromophenyl)benzo[d]isothiazole 1-oxide (7c)\)

\[
\begin{align*}
\text{Br} & \quad \text{N} \quad \text{S}^- \\
\text{Ar} & \quad \text{Ar}
\end{align*}
\]

White solid. Mp: 150–152 °C. \([\alpha]_D^{29} \sim -356.2\) (c 0.55, CHCl₃), 97:3 er. The enantiomeric ratio was determined by Lux 5u Cellulose-1 (250×4.6 mm), MeOH / IPA= 70 / 30 (v/v), 0.7 mL/min, \(\lambda= 214\) nm, \(t_R\) (major) = 14.13 min, \(t_R\) (minor) = 15.39 min on Dionex Ultimate 3000. \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 8.15–8.12 (m, 1H), 7.93–7.91 (m, 1H), 7.85–7.82 (m, 2H), 7.76–7.71 (m, 4H). \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 173.0, 155.0, 134.8, 132.5, 132.4, 131.7, 131.1, 130.6, 127.3, 126.7, 125.9. IR (KBr): 3078, 1586, 1504, 1485, 1309, 1075, 1008 cm\(^{-1}\). MS (ESI, \(m/z\)): 305 ([M]\(^+\)). HRMS (ESI, \(m/z\)): Calcd. for C\(_{13}\)H\(_8\)BrNOS\(^+\) ([M]\(^+\)): 304.9510; Found: 304.9513.

\((S)-3-[4-(Trifluoromethyl)phenyl]benzo[d]isothiazole 1-oxide (7d)\)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{N} \quad \text{S}^- \\
\text{Ar} & \quad \text{Ar}
\end{align*}
\]
White solid. Mp: 176–177 °C. [α]D²⁸ −217.3 (c 1.10, CHCl₃), 95:5 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6 mm), MeOH / IPA= 80 / 20 (v/v), 0.7 mL/min, λ= 214 nm, tᵣ (major) = 17.41 min, tᵣ (minor) = 18.85 min on Dionex Ultimate 3000. ¹H NMR (300 MHz, CDCl₃): δ 8.17–8.14 (m, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.92–7.85 (m, 3H), 7.79–7.73 (m, 2H). ¹⁹F NMR (282 MHz, CDCl₃): δ −63.0 (s, 3F). ¹³C NMR (100 MHz, CDCl₃): δ 172.9, 155.1, 135.5, 134.7, 133.8 (q, J = 32.8 Hz), 132.6, 131.9, 129.5, 126.6, 126.1 (q, J = 3.7 Hz), 126.0, 123.6 (q, J = 270.5 Hz). IR (KBr): 3105, 1590, 1505, 1411, 1328, 1122, 1081, 1070 cm⁻¹. MS (ESI, m/z): 295 ([M]⁺). HRMS (ESI, m/z): Calcd. for C₁₄H₈F₃NOS⁺ ([M + Na]⁺): 295.0279; Found: 295.0275.

(S)-5,6-Dimethyl-3-phenylbenzo[d]isothiazole 1-oxide (7e)

White solid. Mp: 90–91 °C. [α]D²⁹ −241.8 (c 0.80, CHCl₃), 93:7 er. The enantiomeric ratio was determined by Lux 5u Cellulose–2 (250×4.6 mm), MeOH / IPA= 60 / 40 (v/v), 1.0 mL/min, λ= 214 nm, tᵣ (major) = 43.63 min, tᵣ (minor) = 57.64 min on Dionex Ultimate 3000. ¹H NMR (300 MHz, CDCl₃): δ 7.94 (d, J = 7.5 Hz, 2H), 7.89 (s, 1H), 7.68 (s, 1H), 7.64–7.55 (m, 3H), 2.43 (s, 3H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 174.0, 152.7, 141.8, 141.6, 133.4, 132.5, 132.1, 129.1, 129.0, 127.6, 126.6, 20.5, 20.3. IR (KBr): 3445, 3055, 2917, 1595, 1540, 1441, 1335, 1080 cm⁻¹. MS (ESI, m/z): 255. HRMS (ESI, m/z): Calcd. for C₁₅H₁₃NOS⁺ ([M]⁺): 255.0718; Found: 255.0720.

(S)-5,6-Dimethyl-3-((m-tolyl)benzo[d]isothiazole 1-oxide (7f)

S39
White solid, Mp: 113–114 °C. [α]D$^28$ $-248.8$ (c 0.75, CHCl$_3$), 95:5 er. The enantiomeric ratio was determined by Lux 5u Cellulose–1 (250×4.6mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, λ= 214 nm, t$_R$ (major) = 8.67 min, t$_R$ (minor) = 9.45 min on Dionex Ultimate 3000. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.85 (s, 1H), 7.75 (s, 1H), 7.71 (d, $J = 6.6$ Hz, 1H), 7.67 (s, 1H), 7.49–7.44 (m, 2H), 2.47 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 174.3, 152.6, 141.8, 141.5, 139.0, 133.5, 132.9, 132.5, 129.6, 128.8, 127.6, 126.5, 126.2, 21.5, 20.5, 20.3. IR (KBr): 2919, 1592, 1508, 1336, 1083 cm$^{-1}$. MS (ESI, m/z): 269 ([M]$^+$). HRMS (ESI, m/z): Calcd. for C$_{16}$H$_{15}$NOS ([M]$^+$): 269.0874; Found: 269.0876.

3.5 Addition to Cyclic Sulfinimines

Typical Procedures:
Under N$_2$ atmosphere, to a solution of 8a (R = 4-EtC$_6$H$_4$) (119 mg, 0.8 mmol) in dry THF (1 mL) was added KHMDS (1.0 M in THF, 0.8 mL, 0.8 mmol) at −78 °C. After 10 min, chiral sulfinimine (S)-7a (91 mg, 0.4 mmol) in THF (0.4 mL) was added to the enolate solution of 8a at −78 °C. The whole mixture was stirred for 2 h at −78 °C. The reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (40 mL) and dried over anhydrous Na$_2$SO$_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to fast column chromatography.
(silica gel; n-hexane/ethyl acetate 3: 1, v/v) to give product 9a as a white solid (140 mg; 93% yield).

**Characterization Data:**

1-(4-Ethylphenyl)-2-{(1S,3S)-1-oxido-3-phenyl-2,3-dihydrobenzo[d]isothiazol-3-yl}ethane (9a)

White solid. Mp: 152–154 °C. $[\alpha]_D^{28} +288.5$ (c 1.05, CHCl$_3$), 95:5 dr, 99:1 er. The dr and er were determined by CHIRALPAK AS–RH (250 × 4.6 mm), MeOH / IPA = 85 / 15 (v/v), 0.3 mL/min, $\lambda$ = 230 nm, $t_R$ (major) = 10.37 min, $t_R$ (minor) = 20.14 min on Dionex Ultimate 3000. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.87 (d, $J = 8.1$ Hz, 3H), 7.46–7.45 (m, 2H), 7.33–7.25 (m, 7H), 7.13 (s, 1H), 6.43 (s, 1H), 4.69 (d, $J = 18.6$ Hz, 1H), 3.90 (d, $J = 18$ Hz, 1H), 2.71 (q, $J = 7.5$ Hz, 2H), 1.25 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.4, 150.9, 146.3, 145.5, 141.9, 134.4, 131.8, 129.1, 128.8, 128.4, 128.3, 127.6, 125.4, 124.8, 124.2, 74.5, 50.1, 29.0, 15.2. IR (KBr): 3323, 3060, 2963, 2932, 1674, 1605, 1448, 1414, 1364, 1224, 1181, 1073 cm$^{-1}$. MS (ESI, $m/z$): 376 ([M + H]$^+$). HRMS (ESI, $m/z$): Calcd. for C$_{23}$H$_{22}$NO$_2$S$^+$ ([M + H]$^+$): 376.1371; Found: 376.1369.

1-(4-Nitrophenyl)-2-{(1S,3S)-1-oxido-3-phenyl-2,3-dihydrobenzo[d]isothiazol-3-yl}ethane (9b)

White solid. Mp: 96–98 °C. $[\alpha]_D^{29} +218.9$ (c 0.70, CHCl$_3$). 88:12 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–1 (250 × 4.6 mm), MeOH / IPA = 90 / 10 (v/v),
0.5 mL/min, λ= 230 nm, t<sub>R</sub> (major) = 12.87 min, t<sub>R</sub> (minor) = 23.69 min on Dionex Ultimate 3000. ¹H NMR (300 MHz, CDCl₃): δ 8.31 (d, J = 8.7 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 5.1 Hz, 1H), 7.49 (t, J = 3.6 Hz, 2H), 7.32–7.14 (m, 5H), 7.17 (s, 1H), 6.25 (s, 1H), 4.70 (d, J = 18.6 Hz, 1H), 4.03 (d, J = 18.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 196.4, 150.6, 145.8, 145.3, 141.3, 140.9, 132.0, 129.3, 129.1, 129.0, 127.9, 125.3, 124.9, 124.2, 124.0, 74.2, 50.9. IR (KBr): 3356, 3064, 2906, 1690, 1602, 1525, 1345, 1214, 1073, 1053 cm⁻¹. MS (ESI, m/z): 393([M + H]⁺). HRMS (ESI, m/z): Calcd. for C₂₁H₁₇N₂O₄S⁺ ([M + H]⁺): 393.0909; Found: 393.0893.

1-(4-Bromophenyl)-2-{(1S,3S)-1-oxido-3-phenyl-2,3-dihydrobenzo[d]isothiazol-3-yl}ethanone (9c)

White solid. Mp: 68–70 °C. [α]<sub>D</sub><sup>28</sup> +239.8 (c 1.00, CHCl₃). 92.8 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–3 (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t<sub>R</sub> (major) = 9.38 min, t<sub>R</sub> (minor) = 8.92 min on Dionex Ultimate 3000. ¹H NMR (300 MHz, CDCl₃): δ 7.87–7.78 (m, 3H), 7.63–7.59 (m, 2H), 7.50–7.45 (m, 2H), 7.32–7.25 (m, 5H), 7.16–7.11 (m, 1H), 6.34 (s, 1H), 4.64 (d, J =18.3 Hz, 1H), 3.91 (d, J =18.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 196.8, 146.1, 145.4, 141.6, 135.3, 132.1, 131.9, 129.7, 129.2, 129.1, 128.9, 127.7, 125.3, 124.8, 124.2, 74.3, 50.2. IR (KBr): 3447, 3060, 2923, 1682, 1584, 1449, 1355, 1216, 1071, 1053 cm⁻¹. MS (ESI, m/z): 426 ([M + H]⁺). HRMS (ESI, m/z): Calcd. for C₂₁H₁₇BrNO₂S⁺ ([M + H]⁺): 426.0163; Found: 426.0150.

1-(Benzo[b]thiophen-2-yl)-2-{(1S,3S)-1-oxido-3-phenyl-2,3-dihydrobenzo[d]isothiazol-3-yl}ethanone (9d)

S42
White solid. Mp: 90–92 °C. [α]_<sub>D</sub><sup>28</sup> +278.3 (c 1.05, CHCl<sub>3</sub>). 94:6 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose−1 (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t<sub>R</sub> (major) = 10.81 min, t<sub>R</sub> (minor) = 14.50 min on Dionex Ultimate 3000. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 1H), 7.90−7.85 (m, 3H), 7.48−7.37 (m, 6H), 7.32−7.24 (m, 3H), 7.17 (s, 1H), 6.38 (s, 1H), 4.74 (d, <i>J</i> = 18.3 Hz, 1H), 4.01 (d, <i>J</i> = 18.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 192.1, 146.0, 145.5, 143.1, 142.8, 141.5, 139.0, 131.9, 130.0, 129.2, 128.9, 127.9, 127.8, 126.2, 125.4, 125.3, 124.8, 124.2, 123.0, 74.5, 50.6. IR (KBr): 3337, 3058, 2923, 1730, 1660, 1514, 1449, 1355, 1224, 1169, 1073, 1052 cm<sup>−1</sup>. MS (ESI, <i>m/z</i>): 404 ([M + H]<sup>+</sup>). HRMS (ESI, <i>m/z</i>): Calcd. for C<sub>23</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub> ([M + H]<sup>+</sup>): 404.0779; Found: 404.0773.

1-(Naphthalen-2-yl)-2-{{(1S,3S)-1-oxido-3-phenyl-2,3-dihydrobenzo[<i>d</i>]isothiazol-3-yl}et hanone (9e)

White solid. Mp: 88–90 °C. [α]_<sub>D</sub><sup>29</sup> +284.0 (c 1.00, CHCl<sub>3</sub>). 95:5 d, 99:1 er. The dr and er were determined by CHIRALPAK AD−H (250 × 4.6 mm), MeOH / IPA= 90 / 10 (v/v), 0.5 mL/min, λ= 230 nm, t<sub>R</sub> (major) = 10.76 min, t<sub>R</sub> (minor) = 22.89 min on Dionex Ultimate 3000. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.49 (s, 1H), 8.00−7.87 (m, 5H), 7.64−7.53 (m, 2H), 7.50−7.47 (m, 2H), 7.38−7.25 (m, 5H), 7.20−7.19 (m, 1H), 6.46 (s, 1H), 4.86 (d, <i>J</i> = 18.3 Hz, 1H), 4.08 (d, <i>J</i> = 18.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.7, 146.3, 145.5, 141.9, 135.9, 134.0, 132.5, 131.9, 130.2, 129.7, 129.2, 128.9, 128.8, 128.7, 127.9,
127.7, 127.1, 125.4, 124.8, 124.3, 123.6, 74.6, 50.3. IR (KBr): 3339, 3057, 2922, 1675, 1626, 1449, 1359, 1172, 1124, 1053 cm\(^{-1}\). MS (ESI, \(m/z\)): 398 ([M + H]\(^{+}\)). HRMS (ESI, \(m/z\)): Calcd. for C\(_{25}\)H\(_{20}\)NO\(_3\)S\(^{+}\) ([M + H]\(^{+}\)): 398.1215; Found: 398.1191.

Ethyl 2-[(\(S,3S\)-1-oxido-3-phenyl-2,3-dihydrobenzo[\(d\)]isothiazol-3-yl)acetate (9f)

![Ethyl 2-[(\(S,3S\)-1-oxido-3-phenyl-2,3-dihydrobenzo[\(d\)]isothiazol-3-yl)acetate](image)

White solid. Mp: 66–68 °C. \([\alpha]_D^{28}\) +189.2 (c 1.10, CHCl\(_3\)). 95:5 dr, 99:1 er. The dr and er were determined by Lux 5u Cellulose–3 (250 × 4.6 mm), MeOH / IPA= 85 / 15, 0.3 mL/min, \(\lambda\) = 230 nm, \(t_R\) (major) = 12.61 min, \(t_R\) (minor) = 12.13 min on Dionex Ultimate 3000. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, \(J = 3.9\) Hz, 1H), 7.42–7.39 (m, 4H), 7.35–7.26 (m, 3H), 7.10 (s, 1H), 6.29 (s, 1H), 4.11 (q, \(J = 6.6\) Hz, 2H), 3.77 (d, \(J = 17.1\) Hz, 1H), 3.43 (d, \(J = 16.8\) Hz, 1H), 1.71 (t, \(J = 6.6\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.0, 145.5, 145.2, 141.6, 131.9, 129.2, 128.9, 127.9, 125.4, 124.7, 124.1, 74.0, 61.1, 46.9, 14.1. IR (KBr): 3334, 2980, 2927, 1725, 1496, 1449, 1372, 1348, 1201, 1075, 1019 cm\(^{-1}\). MS (ESI, \(m/z\)): 316 ([M + H]\(^{+}\)). HRMS (ESI, \(m/z\)): Calcd. for C\(_{17}\)H\(_{18}\)NO\(_3\)S\(^{+}\) ([M + H]\(^{+}\)): 316.1007; Found: 316.1007.

### 3.6 Oxidation of Cyclic Sulfinamide 9c

![Oxidation of Cyclic Sulfinamide 9c](image)

\((S,S,S)-9c\)

\(\text{dr} = 92:8\)

\(\text{er} = 90.5:9.5\)

83% yield
**Experimental Procedures:**

To a solution of 8d (85 mg, 0.2 mmol) in a mixture solvent of H₂O (1 mL), CCl₄ (0.5 mL), and CH₃CN (0.5 mL) was added NaIO₄ (128 mg, 0.6 mmol) and RuCl₃ (0.25 mg, 0.01 mmol). The whole mixture was stirred at rt for 2 h. The reaction mixture was diluted with water (5 mL) and the aqueous phase was extracted with Et₂O (3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to fast column chromatography (silica gel; n-hexane/EtOAc = 2: 1, v/v) to give product S₄ as a white solid (74 mg; 83% yield). The single crystal of the major enatiomer of S₄ that is suitable for X-ray crystallographic analysis (Figure S4) was obtained by recrystallization from ethyl acetate / petroleum ether (5:2, v/v; 0.024 mol/L) at room temperature.

(S)-1-(4-Bromophenyl)-2-(1,1-dioxido-3-phenyl-2,3-dihydrobenzo[d]isothiazol-3-yl)ethane none (S₄)
White solid. Mp: 183–185 °C. $[\alpha]_D^{29} +239.0$ (c 0.95, CHCl$_3$); 90.5:9.5 er. The enantiomeric excess was determined by Lux 5u Cellulose–1 (250 × 4.6 mm), MeOH / IPA= 60 / 40 (v/v), 0.7 mL/min, $\lambda = 230$ nm, $t_R$ (major) = 21.92 min, $t_R$ (minor) = 31.35 min on Dionex Utimate 3000. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 7.8$ Hz, 1H), 7.80 (d, $J = 6.6$ Hz, 2H), 7.63 (d, $J = 6.6$ Hz, 2H), 7.58–7.51 (m, 2H), 7.48 (d, $J = 5.7$ Hz, 2H), 7.33–7.23 (m, 4H), 6.62 (s, 1H), 4.46 (d, $J = 13.5$ Hz, 1H), 3.62 (d, $J = 13.5$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.5, 142.6, 141.1, 135.0, 134.0, 133.5, 132.3, 129.7, 129.6, 129.1, 128.2, 125.5, 124.4, 121.7, 65.8, 46.7, 29.7. IR (KBr): 3353, 3284, 2921, 2851, 1678, 1584, 1484, 1359, 1286, 1198, 1162, 1068 cm$^{-1}$. MS (ESI, $m/z$): 464 ([M + Na]$^+$). HRMS (ESI, $m/z$): Calcd. for C$_{21}$H$_{16}$BrNaO$_3$S$^+$ ([M + Na]$^+$): 463.9932; Found: 463.9943.

### 3.7 Reductive Desulfonylation

![Diagram of reductive desulfonylation](attachment:diagram.png)

**Experimental Procedures:**

To a solution of (S$_S$,R)-5a (0.095 g, 0.2 mmol) in DMF (6.0 mL), HOAc/NaOAc (1:1) buffer solution ($M_{OAc} = 8$ mol/L; 4.0 ml) and magnesium turnings (0.192 g, 8.0 mmol) were added slowly at 0 °C. Then the reaction temperature was allowed to raise to rt slowly with vigorous stirring. After 8 h, the reaction mixture was diluted with water (10 mL) and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na$_2$SO$_4$. After the solution was filtered and the solvent was evaporated under vacuum, the residue was
subjected to fast column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3, v/v) to give (S<sub>s</sub>,R)-10 (0.063 g; 94% yield).

(1S,3R)-1-(tert-Butyl)-3-(difluoromethyl)-3-phenylbenzo[d]isothiazole 1-oxide (10)

\[
\text{PhO}_2\text{SF}_2\text{C} \quad \overset{\text{Mg, HOAc/NaOAc}}{\text{DMF-H}_2\text{O}, 0 \, ^\circ\text{C} - \text{rt, 10 h}} \quad \text{HN-S} \quad \overset{\text{73% yield}}{\text{HF}_2\text{C}} \quad \text{Ph}
\]

\[\text{(S}_s\text{,R)}-6a \text{ dr > 99:1}\]

\[\text{(S}_s\text{,R)}-11 \text{ dr > 99:1}\]

Experimental Procedures:
To a solution of (S<sub>s</sub>,R)-6a (0.419 g, 1.0 mmol) in DMF (16 mL), HOAc/NaOAc (1:1) buffer solution (M<sub>1</sub>OAc = 8 mol/L; 10 ml) and magnesium turnings (0.480 g, 20 mmol) were added slowly at 0 °C. Then the reaction temperature was allowed to raise to rt slowly with vigorous stirring. After 10 h, the reaction mixture was diluted with water (20 mL) and the aqueous phase was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine (40 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solution was filtered and the solvent was evaporated under vacuum, the residue was
subjected to fast column chromatography (silica gel; ethyl acetate/petroleum ether = 1:3, v/v) to give (Ss,R)-11 as a white solid (0.203 g; 73% yield).

(1S,3R)-3-(Difluoromethyl)-3-phenyl-2,3-dihydrobenzo[d]isothiazole 1-oxide (11)

White solid. Mp: 152–154 °C. [α]D25 –140.9 (c 1.00, CHCl3). 1H NMR (300 MHz, CDCl3): δ 7.85–7.83 (m, 1H), 7.70 (d, J = 6.9 Hz, 2H), 7.57–7.54 (m, 2H), 7.44 (d, J = 4.8 Hz, 1H), 7.39–7.31 (m, 3H), 6.13 (t, J = 55.2 Hz, 1H), 5.47 (s, 1H). 19F NMR (282 MHz, CDCl3): δ –122.7 (dd, J = 274.7 Hz, 54.4 Hz, 1F), –125.9 (dd, J = 274.9 Hz, 55.5 Hz, 1F). 13C NMR (100 MHz, CDCl3): 145.9, 138.7, 137.4, 132.2, 130.4, 128.9, 128.6, 127.1 (t, J = 1.5 Hz), 125.3, 125.1 (d, J = 1.5 Hz), 115.9 (t, J = 249.0 Hz), 78.0 (t, J = 21.3 Hz). IR (KBr): 3154, 2788, 1497, 1450, 1406, 1361, 1347, 1133, 1077, 1042, 1025, 861 cm⁻¹. MS (EI, m/z): 279 (M⁺, 4.96), 228 (100). HRMS (EI, m/z): Calcd. for C14H11F2NOS⁺ ([M + H]+): 279.0529; Found: 279.0534.
4. Determination of the Enantioselectivity

Table 1, entry 4

For racemic product 4d and enantioenriched product 4d (er > 99:1):

Table S2, entry 7

For racemic product 5a and enantioenriched product 5a (er > 99:1):
Table 4, entry 1

For racemic product 7a and enantioenriched product 7a (er 98:2):

![Graphs showing chromatograms for racemic and enantioenriched products](image)

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<th>PeakArea</th>
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racemic product 7a and enantioenriched product 7a (after a single recrystallization; er > 99:1):

![Graphs showing chromatograms for racemic and enantioenriched products](image)

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S50
**Table 4, entry 2**

For racemic product 7b and enantioenriched product 7b (er 96:4):  

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**Table 4, entry 3**

For racemic product 7c and enantioenriched product 7c (er 97:3):  

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Table 4, entry 4

For racemic product 7d and enantioenriched product 7d (er 95:5):

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Table 4, entry 5

For racemic product 7e and enantioenriched product 7e (er 93:7):

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S52
Table 4, entry 6

For racemic product 7f and enantioenriched product 7f (er 95:5):

Table 5, entry 1

For racemic product 9a and enantioenriched product 9a (dr 95:5; er 99:1):
For racemic product 9b and enantioenriched product 9b (dr 88:12; er 99:1):

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area [nAU*]</th>
<th>Height</th>
<th>Area [nAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 12.841 BV</td>
<td>0.4695</td>
<td>7380.75049</td>
<td>223.97156</td>
<td>44.8005</td>
<td></td>
</tr>
<tr>
<td>2 15.129 VB</td>
<td>0.4187</td>
<td>780.22742</td>
<td>29.19925</td>
<td>4.8711</td>
<td></td>
</tr>
<tr>
<td>3 17.118 BB</td>
<td>0.4893</td>
<td>780.94043</td>
<td>29.81470</td>
<td>4.8882</td>
<td></td>
</tr>
<tr>
<td>4 23.690 MM</td>
<td>0.7077</td>
<td>7297.63574</td>
<td>173.68002</td>
<td>44.8002</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.6017664 452.26822

For racemic product 9c and enantioenriched product 9c (dr 92:8; er 99:1):

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area [nAU*]</th>
<th>Height</th>
<th>Area [nAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 8.313 BV</td>
<td>0.1712</td>
<td>7359.23975</td>
<td>646.95577</td>
<td>45.6411</td>
<td></td>
</tr>
<tr>
<td>2 9.377 BB</td>
<td>0.2195</td>
<td>7326.48333</td>
<td>587.47137</td>
<td>44.8003</td>
<td></td>
</tr>
<tr>
<td>3 10.666 BB</td>
<td>0.2494</td>
<td>890.10900</td>
<td>41.07731</td>
<td>4.8713</td>
<td></td>
</tr>
<tr>
<td>4 15.528 BB</td>
<td>0.4639</td>
<td>853.91398</td>
<td>20.05461</td>
<td>4.8882</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.5799764 1296.21960
Table 5, entry 4

For racemic product 9d and enantioenriched product 9d (dr 94:6; er 99:1):

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>10.810</td>
<td>0.3510</td>
<td>4237.0310</td>
<td>366.5903</td>
</tr>
<tr>
<td>2</td>
<td>12.813</td>
<td>0.3461</td>
<td>396.6264</td>
<td>17.9372</td>
</tr>
<tr>
<td>3</td>
<td>13.805</td>
<td>0.3016</td>
<td>379.7905</td>
<td>14.9056</td>
</tr>
<tr>
<td>4</td>
<td>14.876</td>
<td>0.3949</td>
<td>4109.5470</td>
<td>166.2052</td>
</tr>
</tbody>
</table>

Totals : 5253.99634 385.80246

Table 5, entry 5

For racemic product 9e and enantioenriched product 9e (dr 95:5; er 99:1):

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.275</td>
<td>0.3796</td>
<td>314.5017</td>
<td>13.1493</td>
</tr>
<tr>
<td>2</td>
<td>9.255</td>
<td>0.4741</td>
<td>291.6787</td>
<td>9.3725</td>
</tr>
<tr>
<td>3</td>
<td>10.753</td>
<td>0.6878</td>
<td>822.7774</td>
<td>184.3001</td>
</tr>
<tr>
<td>4</td>
<td>22.721</td>
<td>1.7312</td>
<td>1445.8742</td>
<td>68.2619</td>
</tr>
</tbody>
</table>

Totals : 1.69798e4 275.10436

Table 5, entry 6

For racemic product 9f and enantioenriched product 9f (dr 94:6; er 99:1):

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.130</td>
<td>0.3023</td>
<td>12485.27</td>
<td>6.8035</td>
</tr>
<tr>
<td>2</td>
<td>9.241</td>
<td>0.4848</td>
<td>6934.1232</td>
<td>22.8730</td>
</tr>
<tr>
<td>3</td>
<td>10.762</td>
<td>0.6865</td>
<td>14714.654</td>
<td>329.1655</td>
</tr>
<tr>
<td>4</td>
<td>22.788</td>
<td>1.9746</td>
<td>11919.521</td>
<td>108.0606</td>
</tr>
</tbody>
</table>

Totals : 1.55397e4 352.73667
For racemic product 9f and enantioenriched product 9f (dr 95:5; er 99:1):

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Width</th>
<th>Area 1</th>
<th>Height</th>
<th>Area 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.123</td>
<td>0.190</td>
<td>1.106</td>
<td>249</td>
<td>2.77</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>12.159</td>
<td>0.190</td>
<td>1.106</td>
<td>249</td>
<td>2.77</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>13.733</td>
<td>0.210</td>
<td>536.301</td>
<td>43</td>
<td>38.9649</td>
<td>0.043</td>
</tr>
<tr>
<td>4</td>
<td>15.575</td>
<td>0.296</td>
<td>644.373</td>
<td>32.42</td>
<td>2.57</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Totals: 2.50553e-4 1.892.68016

For racemic product S4 and enantioenriched product S4 (er 90.5:9.5):

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Width</th>
<th>Area 1</th>
<th>Height</th>
<th>Area 2</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.138</td>
<td>0.190</td>
<td>1.106</td>
<td>249</td>
<td>2.77</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>12.160</td>
<td>0.190</td>
<td>1.106</td>
<td>249</td>
<td>2.77</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>13.733</td>
<td>0.210</td>
<td>536.301</td>
<td>43</td>
<td>38.9649</td>
<td>0.043</td>
</tr>
<tr>
<td>4</td>
<td>15.351</td>
<td>0.276</td>
<td>519.343</td>
<td>28.69</td>
<td>3.2453</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.69809e-4 1.179.94734
For racemic product S4 and enantioenriched product S4 (after a single recrystallization; er > 99:1):

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.07</td>
<td>21.07</td>
<td>67.919</td>
<td>64.113</td>
<td>62.33</td>
<td>n.a.</td>
<td>6968</td>
</tr>
<tr>
<td>2</td>
<td>31.70</td>
<td>31.70</td>
<td>49.981</td>
<td>36.509</td>
<td>43.77</td>
<td>n.a.</td>
<td>8668</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>117.891</td>
<td>100.622</td>
<td>106.10</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>PeakNo</th>
<th>ID.Name</th>
<th>Ret.Time</th>
<th>PeakHeight</th>
<th>PeakArea</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>21.07</td>
<td>175672</td>
<td>83916850.6</td>
<td>99.3743</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>31.70</td>
<td>166521</td>
<td>130744.7</td>
<td>0.6257</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1766236</td>
<td>84273443.3</td>
<td>100.000</td>
<td></td>
</tr>
</tbody>
</table>
5. $^1$H, $^{19}$F, and $^{13}$C NMR Spectrum of New Compounds
2a $^{19}$F NMR (282 MHz, CDCl$_3$)
$2a \ ^{13}\text{C NMR} \\
(100 \text{ MHz, CDCl}_3)$
PhSO₂CF₂

2b \(^{1}H\) NMR
(300 MHz, CDCl₃)
$2b^{19}\text{F NMR}$

$(282 \text{ MHz, CDCl}_3)$
$2b^{13}$C NMR (100 MHz, CDCl$_3$)
PhSO$_2$CF$_2$N$_2$OS

2c $^1$H NMR
(400 MHz, CDCl$_3$)
2d $^1H$ NMR
(300 MHz, CDCl$_3$)
PhSO$_2$CF$_2$

$2d$ $^{19}$F NMR
(282 MHz, CDCl$_3$)
PhSO₂CF₂

2d $^{13}$C NMR

(100 MHz, CDCl₃)
PhSO₂CF₂
N=S

2e ¹H NMR
Br
(300 MHz, CDCl₃)
PhSO₂CF₂

2e $^{19}\text{F NMR}$

(282 MHz, CDCl₃)
$^{13}$C NMR
(100 MHz, CDCl$_3$)

N-S

PhSO$_2$CF$_2$

$^{2e}$

Br
$2f^{19}\text{F NMR}$

$(282 \text{ MHz, CDCl}_3)$
$2f^{13}C$ NMR
(100 MHz, CDCl$_3$)

PhSO$_2$CF$_2$N=S

OMe

$\begin{array}{c}
\text{165.892} \\
\text{158.867} \\
\text{135.729} \\
\text{133.138} \\
\text{131.856} \\
\text{130.994} \\
\text{129.501} \\
\text{129.094} \\
\text{120.712} \\
\text{119.510} \\
\text{116.600} \\
\text{116.563} \\
\text{113.820} \\
\text{77.483} \\
\text{77.160} \\
\text{76.837} \\
\text{60.091} \\
\text{55.431} \\
\text{22.788}
\end{array}$

$\begin{array}{c}
\text{200} \\
\text{150} \\
\text{100} \\
\text{50} \\
\text{0}
\end{array}$
PhSO₂CF₂

2g $^1$H NMR

(300 MHz, CDCl₃)
PhSO₂CF₂

N

S=O

2g \textsuperscript{13}C NMR

(100 MHz, CDCl₃)
PhSO$_2$CF$_2$N=S\[\text{CF}_3\]

$2h$ $^1$H NMR

(300 MHz, CDCl$_3$)
$\text{PhSO}_2\text{CF}_2$\n
$\text{CF}_3$

$2h^{19}\text{F NMR}$

$(282 \text{ MHz, CDCl}_3)$
$\text{PhSO}_2\text{CF}_2 \quad \text{Br}$

21 $^1\text{H NMR}$

(300 MHz, CDCl$_3$)
$\text{PhSO}_2\text{CF}_2$\n
$\text{N}$\n
$\text{S}^\text{O}$\n
$\text{N}^\text{S}^\text{O}$\n
$\text{PhSO}_2\text{CF}_2$\n
$\text{F}^\text{NMR}$\n
$\text{Br}$

$(282 \text{ MHz, CDCl}_3)$
$2j$ $^1H$ NMR
(300 MHz, CDCl$_3$)
$^{19}$F NMR
(282 MHz, CDCl$_3$)
PhSO$_2$CF$_2$  

$^{13}$C NMR  
(100 MHz, CDCl$_3$)
2K $^1$H NMR
(300 MHz, CDCl$_3$)
PhSO$_2$CF$_2$

2K $^{19}$F NMR
(282 MHz, CDCl$_3$)
$\text{PhSO}_2\text{CF}_2$

$2\text{K}^{13}\text{C NMR}$

$(100 \text{ MHz}, \text{CDCl}_3)$
$4d$ $^1$H NMR
(300 MHz, CDCl$_3$)
4d $^{19}$F NMR
(282 MHz, CDCl₃)
$4d^{13}$C NMR
(100 MHz, CDCl$_3$)
5a $^1$H NMR (300 MHz, CDCl$_3$)
5a $^{19}$F NMR
(282 MHz, CDCl$_3$)
$5a^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl$_3$)
$5b$ $^{19}$F NMR
(282 MHz, CDCl$_3$)
$5b_{^{13}C\text{ NMR}}$

(100 MHz, CDCl$_3$)
PhO₂SF₂C₆H₅
Me

5c ¹H NMR
(300 MHz, CDCl₃)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}_6\text{H}_4\text{N}^+\text{SO}_3^-\text{Cl}$

$5d \ ^1\text{H NMR}$

$(300 \text{ MHz, CDCl}_3)$
$5d$ $^{19}$F NMR
(282 MHz, CDCl$_3$)
5d $^{13}$C NMR
(100 MHz, CDCl$_3$)
5e $^{19}$F NMR
(282 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
5f $^1$H NMR
(300 MHz, CDCl3)
5f $^{19}$F NMR (282 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}_\text{Me}^+\text{N}^+\text{SO}_\text{Me}\text{O}$

5f $^{13}\text{C NMR}$

(100 MHz, CDCl$_3$)
5g $^1$H NMR
(300 MHz, CDCl$_3$)
PhO$_2$SF$_2$C$_6$H$_4$N$^+$S$^-$(O)$\rightarrow$N$_2$

$^{13}$C NMR

(100 MHz, CDCl$_3$)
$5h \ ^1H\text{ NMR}$

(300 MHz, CDCl$_3$)
$^{19}$F NMR

(282 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}_n\text{H}_2$ $\text{N}^+\text{SO}_2\text{O}$

$\text{F}_3\text{C}$

$^13\text{C NMR}$

(100 MHz, CDCl$_3$)
51 $^1$H NMR
(300 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C} = \text{N}^+\text{S}^- \quad 5\text{I}^{19}\text{F NMR}$

(282 MHz, CDCl$_3$)
$5j^{13}$C NMR
(100 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}_6\text{H}_4\text{N}_2\text{S}\text{O}^-$

$5k^{1}\text{H NMR}$

(300 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
$^{1}H$ NMR
(300 MHz, CDCl$_3$)
$^{19}\text{F NMR}$

(282 MHz, CDCl$_3$)
$5l^{13}C$ NMR (100 MHz, CDCl$_3$)
5m $^1$H NMR
(300 MHz, CDCl$_3$)
$5m^{19}$F NMR
(282 MHz, CDCl$_3$)
$5m^{13}$C NMR
(100 MHz, CDCl$_3$)
5n $^1$H NMR
(300 MHz, CDCl$_3$)
$^{19}$F NMR

(282 MHz, CDCl$_3$)
$^{1}H$ NMR
(300 MHz, CDCl$_3$)
$5o^{19}F$ NMR
(282 MHz, CDCl$_3$)
5p $^1$H NMR
(300 MHz, CDCl$_3$)
$5p^{19F} \text{ NMR}$

$(282 \text{ MHz, CDCl}_3)$
5p $^{13}$C NMR (100 MHz, CDCl$_3$)
5a $^1$H NMR  
(300 MHz, CDCl$_3$)
5q $^{19}$F NMR
(282 MHz, CDCl$_3$)
$5q^{13}$C NMR
(100 MHz, CDCl$_3$)
$5r^1H$ NMR
(300 MHz, CDCl$_3$)
$^{19}\text{F} \text{NMR}$

(282 MHz, CDCl$_3$)
5r $^{13}$C NMR
(100 MHz, CDCl$_3$)
$5s$ $^1H$ NMR
(300 MHz, CDCl$_3$)
$5s$ $^{19}F$ NMR
(282 MHz, CDCl$_3$)
5s $^{13}$C NMR (100 MHz, CDCl$_3$)
5t $^1$H NMR
(300 MHz, CDCl$_3$)
$^{19}$F NMR
(282 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
$5u \ ^1H\ NMR$

$(300\ MHz,\ CDCl_3)$
$5u$ $^{19}$F NMR
(282 MHz, CDCl$_3$)
$5 \text{u}$ $^{13}\text{C NMR}$

(100 MHz, CDCl$_3$)
6a $^1$H NMR
(300 MHz, CDCl$_3$)
$^{19}$F NMR

(282 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}^{\text{Me}}\text{Ph}$

$\text{Me} - \text{Ph}$

$6b$ $^1\text{H NMR}$

(300 MHz, CDCl$_3$)
\[ \text{PhO}_2\text{SF}_2\text{C}^\text{m+} \]

6b $^{19}\text{F}$ NMR

(282 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}^\text{Me}$

$6b^{13}\text{C NMR}$

$(100 \text{ MHz, CDCl}_3)$
$\text{PhO}_2\text{SF}_2\text{C}^\text{mim}_{\text{Br}}$

$\text{HN}^-$

$\text{S}$

$\text{O}^-$

$6c \text{ }^1H \text{ NMR}$

$(300 \text{ MHz, CDCl}_3)$
**6c** $^{19}$F NMR (282 MHz, CDCl$_3$)
6c $^{13}$C NMR
(100 MHz, CDCl$_3$)
6d $^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR
(282 MHz, CDCl$_3$)
PhO$_2$SF$_2$C$_{16}$H$_{14}$N$_2$S

$\text{6d}^{13}\text{C NMR}$

(100 MHz, CDCl$_3$)
6e $^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$6f \text{ } ^1H\text{ NMR}$

$(300 \text{ MHz, CDCl}_3)$
6f $^{13}$C NMR (100 MHz, CDCl$_3$)
$6g^1\text{H NMR}$

$(300\text{ MHz, CDCl}_3)$
6g $^{19}$F NMR
(282 MHz, CDCl$_3$)
$6g\ ^{13}\text{C NMR}$

(100 MHz, CDCl$_3$)
6h $^{19}F$ NMR
(282 MHz, CDCl$_3$)
6h $^{13}$C NMR
(100 MHz, CDCl$_3$)
$6i^1$H NMR
(300 MHz, CDCl$_3$)
$6i^{19}$F NMR
(282 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)

PhO$_2$SF$_2$C(CMe)$_2$NH$^-$.s

6i
$6j\ ^1H\ NMR$

$(300\ MHz, \text{CDCl}_3)$
$6j$ $^{19}$F NMR
(282 MHz, CDCl$_3$)
$\text{PhO}_2\text{SF}_2\text{C}^{\text{im}}$N-S

$6j^{13}\text{C NMR}$

$(100 \text{ MHz, CDCl}_3)$
7a $^1$H NMR
(300 MHz, CDCl$_3$)
$^{13}$C NMR

(100 MHz, CDCl$_3$)
$\text{Me}$

$\text{7b} \, ^1\text{H NMR}$

(300 MHz, CDCl$_3$)
$7b$ $^{13}$C NMR
(100 MHz, CDCl$_3$)
$\text{7c } ^1\text{H NMR}$

$(300 \text{ MHz, CDCl}_3)$
$7c^{13}$C NMR
(100 MHz, CDCl$_3$)
$7d \, ^1H \, NMR$

$(300 \, MHz, \, CDCl_3)$
7d $^{19}$F NMR
(282 MHz, CDCl$_3$)
7d $^{13}$C NMR
(100 MHz, CDCl$_3$)
$^{7e} \text{H NMR}$

$(300 \text{ MHz, CDCl}_3)$
$7e^{13}\text{C} \text{NMR}$

$(100 \text{ MHz, CDCl}_3)$
7f $^1$H NMR
(300 MHz, CDCl$_3$)
$7f^{13}C$ NMR
(100 MHz, CDCl$_3$)
$9a \ ^{13}\text{C} \text{NMR}$

$(100 \text{ MHz, CDCl}_3)$
9b $^1$H NMR
(300 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
9c $^1$H NMR
(300 MHz, CDCl$_3$)
9c $^{13}$C NMR
(100 MHz, CDCl$_3$)
9d $^{13}$C NMR
(100 MHz, CDCl$_3$)
$^{13}$C NMR
(100 MHz, CDCl$_3$)
$9f$ $^1$H NMR
(300 MHz, CDCl$_3$)
gf $^{13}$C NMR
(100 MHz, CDCl$_3$)
10 $^1$H NMR (300 MHz, CDCl$_3$)
10 $^{19}$F NMR
(282 MHz, CDCl$_3$)
11 $^1$H NMR (300 MHz, CDCl$_3$)
$^{19}$F NMR
(282 MHz, CDCl$_3$)
$^{11}\text{C NMR}$

(100 MHz, CDCl$_3$)
S3 $^1$H NMR
(300 MHz, CDCl$_3$)
S3 $^{19}$F NMR
(282 MHz, CDCl$_3$)
S3 $^{13}$C NMR
(100 MHz, CDCl$_3$)
S4 $^{13}$C NMR
(100 MHz, CDCl$_3$)