

## **Stereochemical Aspects and Synthetic Scope of the $S_{\text{H}}i$ at the Sulfur Atom. Preparation of Enantiopure 3-Substituted 2,3-Dihydro-1,2-Benzothiazole 1-Oxides and 1,1-Dioxides**

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### **SUPPORTING INFORMATION**

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## General Considerations.

NMR spectra were acquired on a Bruker AC-300 instrument at 300 and 75.5 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively. Chemical shifts ( $\delta$ ) are reported in parts per million relative to residual solvent signals ( $\text{CDCl}_3$ , 7.26 ppm for  $^1\text{H}$  NMR and 77.0 ppm for  $^{13}\text{C}$  NMR spectra;  $\text{MeOH-d}_4$  3.31 ppm for  $^1\text{H}$  NMR and 49.0 ppm for  $^{13}\text{C}$  NMR).  $^{13}\text{C}$  NMR spectra were acquired on a broad-band decoupled mode. Optical rotations were measured on a PerkinElmer 241 polarimeter. Mass spectra (MS) were obtained by ESI or FAB+ (matrix: *m*-NBA) ionization mode. High resolution mass spectra (HRMS) were performed by ESI ionization mode using a time of-flight (TOF) mass analyzer or FAB+ ionization mode. Analytical thin layer chromatography (TLC) was performed using precoated aluminum-packed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or phosphomolybdic acid dip. Flash column chromatography was performed using silica gel (230–400 mesh). All reactions were carried out in anhydrous solvents. THF and  $\text{CH}_2\text{Cl}_2$  were dried with molecular sieves. Commercially available starting materials were used without purification.

Sulfinimine **3** was prepared from 2-bromobenzaldehyde and (*R*)-*tert*-butanesulfinamide, according to the known literature procedure.<sup>1</sup> The characterization was effected by comparison of its physical and spectroscopic data with those reported.<sup>2</sup>

### **Radical Addition. General procedure**

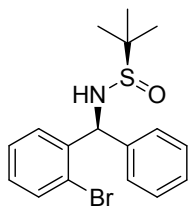
To a solution of sulfinimine **3** (0.2 mmol) in DCM (3 mL, 0.04M), under argon atmosphere, was added  $\text{BF}_3 \cdot \text{OEt}_2$  (0.42 mmol, 2.1 equiv). After 5 min under stirring, the mixture was cooled to  $-78\text{ }^\circ\text{C}$  and then, the alkyl iodide (2.0 mmol, 10 equiv), tributyltin hydride (0.5 mmol, 2.5 equiv), triethylborane (0.5 mmol, 1M hexane, 2.5 equiv) and  $\text{O}_2$  (5 mL, via syringe) were added in this order. Successive additions of triethylborane (0.25 mmol, 1M hexane) and  $\text{O}_2$  (5 mL, via syringe) were added every 1 or 1.5 hour until the imine disappearance (TLC). Then, the reaction was treated with aq.  $\text{NaHCO}_3$  solution. The aqueous phase was extracted with DCM (3x5mL). The organic extracts were washed with brine and dried over  $\text{MgSO}_4$ . The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel:KF (9:1) with a 1:1 mixture of *n*-hexane:ethyl acetate as the eluent.

Sulfinamides **4a-d**<sup>3</sup> were prepared from the corresponding alkyl iodide according to the above general procedure with the following isolated yields: **4a** (R=Et, 80 %), **4b** (R=*i*Pr, 91 %), **4c** (R=Cy, 90 %), **4d** (R=*t*Bu, 75 %).

<sup>1</sup> G. Liu, D. A. Cogan, T. D. Owens, T. P. Tang, J. A. Ellman, *J. Org. Chem.* 1999, *64*, 1278–1284.

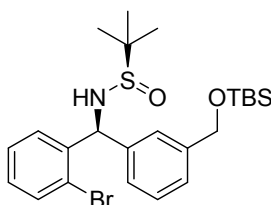
<sup>2</sup> L. Cheng, L. Liu, Y. Sui, D. Wang, Y.-J. Chen, *Tetrahedron: Asymmetry* 2007, *18*, 1833–1843.

**(*S,R*<sub>s</sub>)-*N*-[(2-Bromophenyl)(phenyl)methyl]-2-methylpropane-2-sulfinamide (4e)**, known compound<sup>4</sup>



According to the reported procedure<sup>5</sup>, to a solution of sulfinimine **3** (0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added phenyl magnesium bromide (0.32 mmol, 1.0 M in THF) at -48°C and the mixture was stirred for 2 h at the same temperature. The reaction was quenched with sat. NH<sub>4</sub>Cl and the aqueous layer extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. A 92:8 diastereomeric mixture was obtained. The major diastereomer was separated by flash chromatography on silica gel (*n*-hexane:AcOEt, 1:1). Yield: 90%; [ $\alpha$ ]<sub>D</sub><sup>20</sup> -36 (*c* 0.50, CHCl<sub>3</sub>). [Lit<sup>4</sup> [ $\alpha$ ]<sub>D</sub><sup>20</sup> -35.1 (*c* 0.97, EtOH), (*S,R*<sub>s</sub>), 99% *de*] <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.61-7.59 (m, 1H), 7.56-7.53 (m, 1H), 7.39-7.23 (m, 6H), 7.17-7.11 (m, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 3.71 (broad s, 1H), 1.25 (s, 9H). <sup>13</sup>C NMR (75 MHz)  $\delta$  141.0, 140.5, 133.3, 129.5, 129.0, 128.8, 128.0, 127.8, 127.4, 124.0, 61.2, 56.1, 22.7. MS (FAB+) *m/z* 366-368 [(*M*+1)<sup>+</sup>, 39], 245-247 (28), 73 (58), 57 (100). HRMS (FAB+) calcd for C<sub>17</sub>H<sub>21</sub>NOSBr [*M*+1]<sup>+</sup>, 366.0527; found 366.0526.

**(*S,R*<sub>s</sub>)-*N*-{[2-Bromophenyl][3-[(*tert*-butyldimethylsilyloxy)methyl]phenyl]methyl}-2-methylpropane-2-sulfinamide (4f).**



To a solution of sulfinimine **3** (0.16 mmol) in THF (1 mL) was added fresh 3-[(*tert*-butyldimethylsilyloxy)methyl]phenylmagnesium bromide<sup>6</sup> (0.56 mmol in THF 1.5 mL) at -48°C. The mixture was stirred at -48°C for 3 h. The reaction was quenched with sat. NH<sub>4</sub>Cl and the aqueous layer extracted with AcOEt (3 x 10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. A 95:5 diastereomeric mixture was obtained. The major diastereomer was separated by flash chromatography on silica gel (*n*-hexane:AcOEt, 3:1). Yield: 93%; colorless oil; [ $\alpha$ ]<sub>D</sub><sup>20</sup> -53 (*c* 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.32-7.20 (m, 4H), 7.19-7.13 (m, 1H), 7.07 (dt, *J* = 7.5, 1.8 Hz, 1H), 6.06 (s, 1H), 4.64 (s, 2H), 3.65 (s, 1H), 1.19 (s, 9H), 0.85 (s, 9H), 0.00 (s, 6H). <sup>13</sup>C NMR (75 MHz)  $\delta$  142.1, 141.0, 140.5, 133.3, 129.6, 129.0, 128.7, 127.5, 126.6, 125.6, 125.2, 124.0, 64.7, 61.0, 56.0, 26.0, 22.7, 18.4, -5.3. MS (FAB+) *m/z* 510-512 (*M*+1)<sup>+</sup>, 452-454, 389-

<sup>3</sup> The preparation and characterization of the *o*-bromosulfinamides **4a-d** will be reported in due course.

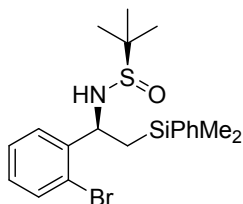
<sup>4</sup> Compound **4e** has been obtained by diastereoselective reduction of the corresponding *N*-sulfinyl ketimine: M. Martjuga, D. Shabashov, S. Belyakov, E. Liepinsh, E. Suna *J. Org. Chem.* 2010, **75**, 2357.

<sup>5</sup> G. Liu, A. C. Cogan, J. A. Ellman *J. Am. Chem. Soc.* 1997, **119**, 9913.

<sup>6</sup> The corresponding bromide was converted to the Grignard reagent in refluxing THF, following the standard procedure.

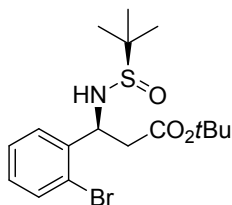
391, 378-380, 355. HRMS (FAB+) calcd for C<sub>24</sub>H<sub>37</sub>NO<sub>2</sub>SiSBr [M+1]<sup>+</sup>, 510.1498; found 510.1486.

**(*R,R*)-*N*-{1-(2-Bromophenyl)-2-[dimethyl(phenyl)silyl]ethyl}-2-methylpropane-2-sulfinamide (4g).**



To a solution of the sulfinimine **3** (0.16 mmol) in THF (1 mL) was added the [(dimethylphenylsilyl)methyl]magnesium chloride<sup>7</sup> (0.80 mmol in THF 1 mL) at rt. The mixture was stirred at rt for 3 h. The reaction was quenched with sat. NH<sub>4</sub>Cl and the aqueous layer extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. Compound **4g** was obtained as the sole diastereoisomer. The residue was purified by flash chromatography on silica gel (*n*-hexane:AcOEt, 3:1). Yield: 94%; colorless oil; [α]<sub>D</sub><sup>20</sup> -91 (*c* 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54-7.45 (m, 3H), 7.39-7.28 (m, 4H), 7.22(dt, *J* = 7.5, 1.3 Hz, 1H), 7.06 (ddd, *J* = 7.9, 7.2, 1.8 Hz, 1H), 5.06 (m, 1H), 3.38 (s, 1H), 1.56 (dd, *J* = 14.8, 7.1 Hz, 1H), 1.45 (dd, *J* = 14.7, 7.7 Hz, 1H), 1.01 (s, 9H), 0.36 (s, 3H), 0.13 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.1, 138.3, 133.9, 133.2, 129.4, 128.9, 128.2, 128.8, 127.6, 123.4, 77.4, 55.6, 26.6, 22.5, -2.2, -3.2. MS (FAB+) *m/z* 438-440 [(M+1)<sup>+</sup>, 16], 135 (100), 57 (55). HRMS (FAB+) calcd for C<sub>20</sub>H<sub>29</sub>NOSBrSi [M+1]<sup>+</sup>, 438.0923; found 438.0917.

**(*S,R*)-*tert*-Butyl 3-(2-bromophenyl)-3-(1,1-dimethylethylsulfinamido)propanoate (4h).**



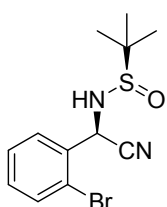
To a solution of Zn<sup>8</sup> dust (0.6 mmol) in anhydrous THF (1 mL) at rt under argon atmosphere, *tert*-butyl bromoacetate (0.6 mmol) was added. The resulting reaction mixture was heated to reflux temperature and stirred for 30 min. Then, the reaction was cooled to rt and a solution of imine **3** (0.24 mmol) in anhydrous THF (0.5 mL) was added. After 30 min, the mixture was quenched with aq. NH<sub>4</sub>Cl and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and the solvent was removed under reduced pressure. Compound **4h** was obtained as the sole diastereoisomer. The residue was purified by flash column chromatography on silica gel (*n*-hexane:AcOEt, 2:1). Yield: 97%; colorless oil; [α]<sub>D</sub><sup>20</sup> -79 (*c* 0.55, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.55 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.42 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.29 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.13 (dt, *J* = 1.8, 7.5 Hz, 1H), 5.17 (m, 1H), 4.76 (d, *J* = 5.5 Hz, 1H), 2.88 (dd, *J* = 15.5, 5.4 Hz, 1H), 2.80 (dd, *J* = 15.5, 7.0 Hz, 1H), 1.38 (s, 9H), 1.23 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.4, 140.1, 133.3, 129.2, 128.9, 127.6, 123.4, 81.8, 56.0, 55.4, 41.9, 28.1, 22.8. MS

<sup>7</sup> C. H. Ko, D. Y. Jung, M. K. Kim, Y. H. Kim *Synlett*, 2005, **2**, 304.

<sup>8</sup> Zn dust, <10μ (2.5 g). Zn activation was carried out by successive washes with an aqueous solution of HCl (5%, 3 x 3mL), H<sub>2</sub>O (3 x 3mL), acetone (3 x 3 mL) and dry Et<sub>2</sub>O (3 x 3 mL).

(FAB+)  $m/z$  807-809-811 [(2M+1)<sup>+</sup>, 2], 404-406 [(M+1)<sup>+</sup>, 80], 348-350 (52), 57 (100). HRMS (FAB+) calcd for C<sub>17</sub>H<sub>27</sub>NO<sub>3</sub>SBr [M+1]<sup>+</sup>, 404.0895; found 404.0895. Configurational assignment of compound **4h** was effected by chemical correlation with the known aminoester: **tert-Butyl (S)-3-Amino-3-(2-bromophenyl)propanoate (7)**<sup>9</sup>. - A HCl solution in MeOH (0.2 mmol, 1.25 M) was added to sulfinamide **4h** (0.1 mmol) and the mixture stirred 1 h at rt. Then, the solvent was removed under reduced pressure and the residue acidified with an aq. HCl solution (10%) and washed with AcOEt (2x5mL). The aqueous phase was basified with an aq. NaOH solution (10%), and extracted with AcOEt (3x5mL). The organic extracts were dried (MgSO<sub>4</sub>) and the solvent removed at vacuo. Yield: 94%. [ $\alpha$ ]<sub>D</sub><sup>20</sup> - 45 (*c* 0.70, CHCl<sub>3</sub>). Lit. (S)<sup>9</sup> [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 45.0 (*c* 1.02, CHCl<sub>3</sub>). <sup>1</sup>H RMN:  $\delta$  7.54 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.11 (td, *J* = 7.9, 1.6 Hz, 1H), 4.78 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.71 (dd, *J* = 15.9, 4.1 Hz, 1H), 2.52 (dd, *J* = 15.9, 9.2 Hz, 1H), 2.01 (broad s, 2H), 1.43 (s, 9H).

**(R,R<sub>S</sub>)-N-[(2-Bromophenyl)(cyano)methyl]-2-methylpropane-2-sulfinamide (4i).**



According to the known procedure<sup>10</sup>, a solution of sulfinimine **3** (0.16 mmol) and Y(OTf)<sub>3</sub> (0.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub>:THF (1:0.15, 1.2 mL) was stirred 15 min at rt. Then, TMSCN (0.32 mmol) was added, and the reaction mixture was maintained 7 h with stirring under argon atmosphere. The reaction was quenched with sat. NH<sub>4</sub>Cl and the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. A 94:6 diastereomeric mixture was obtained. The major diastereomer was isolated by flash column chromatography on silica gel (*n*-hexane:AcOEt, 1:1). Yield: 90%; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.44-7.39 (m, 1H), 7.31-7.26 (m, 1H), 5.66 (d, *J* = 7.9 Hz, 1H), 4.06-4.03 (m, 1H), 1.24 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  133.8, 133.4, 131.4, 129.6, 128.5, 123.4, 117.4, 57.5, 50.4, 22.4. MS (FAB+)  $m/z$  315-317 [(M+1)<sup>+</sup>, 19], 69 (45), 57 (100). HRMS (FAB+) calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>OSBr [M+1]<sup>+</sup>, 315.0167; found 315.0170. Configurational assignment of compound **4i** was effected by chemical correlation with the known  $\alpha$ -amino ester: **(R)-(R)-(2-bromophenyl)glycine hydrochloride (8)**<sup>11</sup>. - Sulfinamide **4i** was treated with an aq. HCl solution (6M) during 6h at 40°C and then, the solvent was removed at reduced pressure. Yield: 92%. [ $\alpha$ ]<sub>D</sub><sup>20</sup> - 53 (*c* 0.50, 1M HCl). Lit.<sup>11</sup> (S) [ $\alpha$ ]<sub>D</sub><sup>25</sup> + 60 (*c* 1.02, CHCl<sub>3</sub>). <sup>1</sup>H RMN (D<sub>2</sub>O):  $\delta$  7.78 (d, *J* = 8.0 Hz, 1H), 7.56-7.30 (m, 3H), 5.39-5.26 (broad s, 1H).

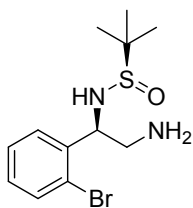
**(R,R<sub>S</sub>)-N-[(2-Amino-1-(2-bromophenyl)ethyl]-2-methylpropane-2-sulfinamide (4k).**

<sup>9</sup> S. D. Bull, S. G. Davies, S. Delgado-Ballester, P. M. Kelly, L. J. Kitchie, M. Gianotti, M. Laderas, A. D. Smith *J. Chem. Soc., Perkin Trans. 1*, 2001, 3112.

<sup>10</sup> S. Mabic, A. A. Cordi *Tetrahedron*, 2001, **57**, 8861.

<sup>11</sup> (a) Y. Pérez-Fuertes, J. E. Taylor, D. A. Tickell, M. F. Mahon, S. D. Bull, T.D. James *J. Org. Chem.* 2011, **76**, 6038. (b) C. Mellin-Morliere, D. J. Aitken, S.D. Bull, S. G. Davies, H.-P. Husson *Tetrahedron: Asymmetry* 2001, **12**, 149.

<sup>12</sup> S. G. Jarboe, M. S. Terrazas, P. Beak *J. Org. Chem.* 2008, **73**, 9627.



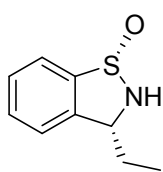
According to the known procedure,<sup>12</sup> to a solution of (*R,S*)-*N*-((2-bromophenyl)(cyano)methyl)-2-methylpropane-2-sulfonamide **4i** (0.2 mmol) in THF (1 mL) was added BH<sub>3</sub>.THF (0.6 mmol, 1 M in THF). The solution was heated to reflux 24 h and then, the solution was cooled to room temperature and water was slowly added until the evolution of hydrogen subsided. Then, MeOH (200 μl) and conc. H<sub>2</sub>SO<sub>4</sub> (100 μl) were added to fully decomplex the aminoborane. The solution was stirred for 10 min, basified (10% NaOH) and extracted with Et<sub>2</sub>O (3 x 10 mL). The combined organic phases were washed with brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. Yield: 78%; yellow oil; [α]<sub>D</sub><sup>20</sup> - 116 (*c* 0.35, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.48-7.45 (m, 1H), 7.35-7.32 (m, 1H), 7.26-7.21 (m, 1H), 7.08-7.03 (m, 1H), 4.77-4.74 (m, 1H), 4.63 (broad s, 1H), 3.11 (dd, *J* = 12.8, 4.1 Hz, 1H), 2.74 (dd, *J* = 12.8, 8.2 Hz, 1H), 1.52 (broad s, 2H), 1.17 (s, 9H). <sup>13</sup>C NMR (75 MHz) δ 139.9, 133.1, 128.9, 128.7, 127.5, 123.5, 59.5, 55.8, 47.0, 22.7. HRMS (FAB+) calcd for C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>OSBr, [M+1]<sup>+</sup>, 319.0480; found 319.0484.

To a solution of the above amino derivative **4k** (0.18 mmol) and Et<sub>3</sub>N (0.46 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.8 mL), at 0 °C, (BOC)<sub>2</sub>O (0.2 mmol) was added. The mixture was stirred overnight at rt and then, was treated with aq. NaHCO<sub>3</sub>. The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with brine, dried (MgSO<sub>4</sub>) and the solvent was removed under reduced pressure. The residue was passed through a silica gel column (*n*-hexane:AcOEt, 1:1) to obtain *tert*-butyl carbamate **4j** as a colorless oil. Crude yield: 74%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 8.3 Hz 1H), 7.46 (d, *J* = 7.8 Hz 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.14 (dt, *J* = 7.7, 1.7 Hz, 1H), 5.12 (broad s, 1H), 4.96 (m, 1H), 4.87 (s, 1H), 3.43 (t, *J* = 6.6 Hz, 2H), 1.44 (s, 9H), 1.23 (s, 9H).

#### **Radical Cyclization. General procedure.**<sup>13</sup>

A solution of AIBN (0.495 mmol) and tributyl tin hydride (0.54 mmol) in dry toluene (3.5 mL) was added for 2h to the corresponding sulfonamide (0.45 mmol) and AIBN (0.18 mmol) in previously deoxygenated dry toluene (20 mL) at 110°C. The reaction was maintained 4 h before the solvent removal under reduced pressure. The residue was purified by flash chromatography on silica gel: KF (9:1).

#### **(*R,S*)-3-Ethyl-2,3-dihydrobenzo[d]isothiazole-1-oxide (5a).**

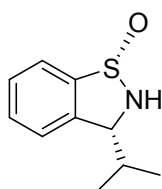


Following the above general procedure, compound **5a** was obtained as the sole diastereomer from sulfonamide **4a** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 78%; white solid; mp 107-109°C; [α]<sub>D</sub><sup>20</sup> +19 (*c* 0.55, CHCl<sub>3</sub>); IR (KBr): 2966, 2927, 1448, 1111, 1067, 1035 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.81-7.78 (m, 1H), 7.57-7.45 (m, 2H), 7.42-7.39 (m, 1H), 4.97 (broad s, 1H),

<sup>13</sup> J. Coulomb, V. Certal, L. Fensterbank, E. Lacôte, M. Malacria *Angew. Chem. Int. Ed.* 2006, **45**, 633.

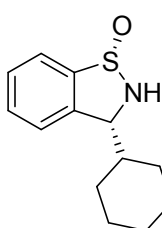
4.78-4.73 (m, 1H), 2.06-1.82 (m, 2H), 1.06 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  145.7, 142.3, 131.3, 128.8, 124.8, 123.6, 68.5, 31.6, 10.4. MS (EI+)  $m/z$  181 ( $\text{M}^+$ , 0.6), 163 (91), 162 (100), 136 (31). HRMS (EI)  $m/z$  calcd for  $\text{C}_9\text{H}_{11}\text{NOS}$ : 181.0561; found: 181.0567.

**(*R,S*)**-3-*iso*-Propyl-2,3-dihydrobenzo[d]isothiazole-1-oxide (**5b**).



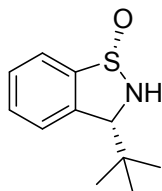
Following the above general procedure, compound **5b** was obtained as the sole diastereomer from sulfinamide **4b** (0.45 mmol). Chromatography: *n*-hexane: AcOEt, 2:1. Yield: 96%; white solid; mp 95-96 °C; 99% *ee* (HPLC, Chiralcel OD, 1.0 mL/min, *i*-PrOH/hexane 5/95,  $\lambda = 254$  nm,  $t_{\text{R}} = (S)$  20.4 min, (*R*) 35.7 min).  $[\alpha]_{\text{D}}^{20} +19$  ( $c$  0.7,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.76 (m, 1H), 7.54-7.47 (m, 2H), 7.39-7.37 (m, 1H), 4.92 (broad s, 1H), 4.77-4.74 (m, 1H), 2.23-2.13 (m, 1H), 1.12 (d,  $J = 6.8$  Hz, 3H), 0.81 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 141.6, 131.2, 128.9, 125.0, 123.6, 73.0, 33.2, 20.4, 16.4. IR (KBr): 1463, 1452, 1384, 1367, 1069, 1044, 1004, 758  $\text{cm}^{-1}$ . MS (ESI+)  $m/z$  218 [ $(\text{M}+\text{Na})^+$ , 100], 196 [ $(\text{M}+1)^+$ , 81]. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{14}\text{NOS}$ : 196.0790; found: 196.0797.

**(*R,S*)**-3-Cyclohexyl-2,3-dihydrobenzo[d]isothiazole-1-oxide (**5c**).



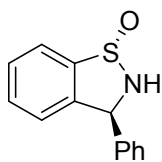
Following the above general procedure, compound was obtained as unique diastereomer from sulfinamide **4c** (0.45 mmol). Chromatography: *n*-hexane: AcOEt, 2:1. Yield: 76%; colorless oil;  $[\alpha]_{\text{D}}^{20} +16$  ( $c$  0.52,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 7.2$  Hz, 1H), 7.56-7.53 (m, 2H), 7.40 (d,  $J = 7.3$  Hz, 1H), 4.86 (broad s, 1H), 4.72 (broad s, 1H), 1.85-1.62 (m, 5H), 1.30-1.18 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  145.7, 141.4, 131.2, 128.8, 124.9, 123.7, 72.6, 43.3, 30.9, 26.8, 26.5, 26.0, 25.9. IR (NaCl): 1086, 1043, 1018  $\text{cm}^{-1}$ . MS (EI)  $m/z$  235 ( $\text{M}^+$ , 0.5), 217 (30), 162 (100), 149 (97), 136 (68), 135 (47). HRMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{17}\text{NOS}$ : 235.1031; found: 235.1039.

**(*R,S*)**-3-(*tert*-Butyl)-2,3-dihydrobenzo[d]isothiazole-1-oxide (**5d**).



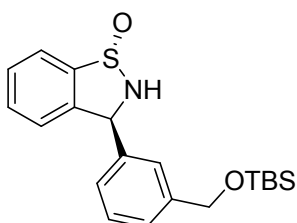
Following the above general procedure, compound **5d** was obtained as the sole diastereomer from sulfinamide **4d** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 74%; white solid; mp 108-110°C;  $[\alpha]_{\text{D}}^{20} +18$  ( $c$  1.4,  $\text{CHCl}_3$ ); IR (KBr): 2951, 2867, 1466, 1393, 1130, 1070  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.75 (m, 1H), 7.55-7.45 (m, 3H), 5.06 (broad s, 1H), 4.51 (d,  $J = 3.9$  Hz, 1H), 1.08 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  145.8, 140.6, 130.6, 128.7, 125.2, 124.9, 76.9, 35.3, 26.8. MS (ESI+)  $m/z$  232 [ $(\text{M}+\text{Na})^+$ , 100], 210 [ $(\text{M}+1)^+$ , 57]. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{16}\text{NOS}$ : 210.0947; found: 210.0947.

**(*S,S*)**-3-Phenyl-2,3-dihydrobenzo[d]isothiazole-1-oxide (**5e**)



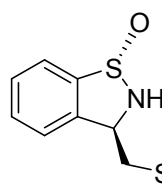
Following the above general procedure, compound **5e** was obtained as the sole diastereomer from sulfinamide **4e** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 76%; colorless oil;  $[\alpha]^{20}_{\text{D}} -25$  (*c* 0.4,  $\text{CHCl}_3$ ); IR (NaCl): 2925, 2865, 1452, 1068, 1045  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87-7.84 (m, 1H), 7.49-7.46 (m, 2H), 7.38-7.36 (m, 3H), 7.26-7.23 (m, 2H), 7.12-7.09 (m, 1H), 6.29 (s, 1H), 4.90 (broad s, 1H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  146.1, 142.7, 139.1, 131.7, 129.1, 129.0, 128.9, 127.9, 124.5, 124.3, 68.7. MS (EI) *m/z* 229 ( $\text{M}^+$ , 0,4), 213 (11), 212 (40), 211 (99), 210 (100). HRMS (EI) *m/z* calcd for  $\text{C}_{13}\text{H}_{11}\text{NOS}$ : 229.0561; found: 229.0569.

**(S,S)-3-[(*tert*-Butyldimethylsilyloxy)methyl]phenyl-2,3-dihydrobenzo[d]isothiazole-1-oxide (5f).**



Following the above general procedure, compound **5f** was obtained as the sole diastereomer from sulfinamide **4f** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 86%; colorless oil;  $[\alpha]^{20}_{\text{D}} -36$  (*c* 0.58,  $\text{CHCl}_3$ ); IR (NaCl): 2932, 2905, 2838, 1440, 1460, 1240, 1060  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86-7.83 (m, 1H), 7.51-7.42 (m, 2H), 7.36-7.30 (m, 2H), 7.19 (broad s, 1H), 7.14-7.09 (m, 2H), 6.29 (s, 1H), 4.88 (broad s, 1H), 4.72 (s, 2H), 0.9 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  146.1, 142.8, 142.6, 139.2, 131.7, 128.9, 126.4, 125.4, 124.6, 124.3, 68.8, 64.6, 25.9, 18.4, -5.3. MS (ESI+) *m/z* 769 [(2M+Na) $^+$ , 9], 747 [(2M+1) $^+$ , 21], 396 [(M+Na) $^+$ , 44], 374 [(M+1) $^+$ , 100]. HRMS (ESI+) *m/z* calcd for  $\text{C}_{20}\text{H}_{28}\text{NO}_2\text{SiS}$ : 374.1604; found: 374.1622.

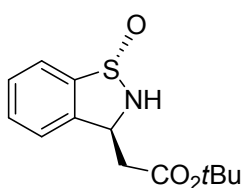
**(R,S)-3-[Dimethyl(phenyl)silylmethyl]-2,3-dihydrobenzo[d]isothiazole-1-oxide (5g).**



Following the above general procedure, compound **5g** was obtained as the sole diastereomer from sulfinamide **4g** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 66%; colorless oil;  $[\alpha]^{20}_{\text{D}} -100$  (*c* 1.5,  $\text{CHCl}_3$ ); IR (NaCl): 2950, 2895, 1430, 1246, 1150, 1093  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75-7.72 (m, 1H), 7.55-7.49 (m, 3H), 7.46-7.44 (m, 1H), 7.40-7.36 (m, 4H), 5.42-5.37 (m, 1H), 4.28 (broad s, 1H), 1.64 (dd, *J* = 14.9, 4.3 Hz, 1H), 1.17 (dd, *J* = 14.9, 9.2 Hz, 1H), 0.38 (s, 3H), 0.32 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  145.6, 144.6, 137.9, 133.7, 131.6, 129.8, 128.8, 128.5, 124.5, 123.3, 61.9, 23.3, -1.9, -2.6. MS (ESI+) *m/z* 625 [(2M+Na) $^+$ , 28], 603 [(2M+1) $^+$ , 11], 324 [(M+Na) $^+$ , 99], 302 [(M+1) $^+$ , 100]. HRMS (ESI+) *m/z* calcd for  $\text{C}_{16}\text{H}_{20}\text{NOSiS}$ : 302.1029; found: 302.1036.

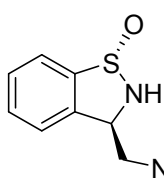
**(S,S)-*tert*-Butyl 2-(1-oxide-2,3-dihydrobenzo[d]isothiazol-3-yl)acetate (5h).**





Following the above general procedure, compound **5h** was obtained as the sole diastereomer from sulfinamide **4h** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 73%; colorless oil;  $[\alpha]_D^{20}$  -169 (*c* 0.5, CHCl<sub>3</sub>); IR (NaCl): 2977, 2953, 1724, 1369, 1150 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83-7.81 (m, 1H), 7.58-7.48 (m, 2H), 7.40-7.37 (m, 1H), 5.57-5.53 (m, 1H), 5.37 (broad s, 1H), 3.00 (dd, *J* = 16.4, 3.1 Hz, 1H), 2.40 (dd, *J* = 16.4, 10.3 Hz, 1H), 1.48 (s, 9H). <sup>13</sup>C NMR (75 MHz) δ 170.2, 146.5, 140.5, 131.6, 129.2, 124.7, 122.9, 82.0, 60.8, 41.0, 28.1. MS (ESI+) *m/z* 557 [(2M+Na)<sup>+</sup>, 36], 535 [(2M+1)<sup>+</sup>, 14], 290 [(M+Na)<sup>+</sup>, 100], 268 [(M+1)<sup>+</sup>, 81], 212 (89). HRMS (ESI+) *m/z* calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>3</sub>S: 268.1001; found: 268.1016.

**(R,S<sub>S</sub>)-tert-Butyl-[(1-oxide-2,3-dihydrobenzo[d]isothiazol-3-yl)methyl]carbamate (5j).**

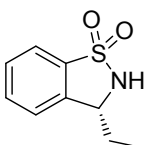


Following the above general procedure, compound **5j** was obtained as the sole diastereomer from sulfinamide **4j**<sup>14</sup> (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:3. Yield: 78%; white solid; mp 151-154 °C;  $[\alpha]_D^{20}$  -145 (*c* 1.8, CHCl<sub>3</sub>); IR (KBr): 2975, 2930, 1712, 1543, 1271, 1175, 1025 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.82-7.79 (m, 1H), 7.55-7.50 (m, 2H), 7.48-7.44 (m, 1H), 5.64 (broad s, 1H), 5.36 (broad s, 1H), 4.79 (broad s, 1H), 3.77-3.71 (m, 1H), 3.40-3.34 (m, 1H), 1.38 (s, 9H). <sup>13</sup>C NMR (75 MHz) δ 156.8, 146.9, 139.3, 131.7, 129.4, 124.9, 123.3, 80.2, 66.3, 44.2, 28.3. MS (ESI+) *m/z* 587 [(2M+Na)<sup>+</sup>, 16], 305 [(M+Na)<sup>+</sup>, 100], 283 [(M+1)<sup>+</sup>, 62], 227 (53). HRMS (ESI+) *m/z* calcd for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>S: 283.1110; found: 283.1118.

**Oxidation. General procedure.**

To a solution of the corresponding cyclic sulfinamide **5** (0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C, a solution of *m*-CPBA (0.45 mmol) in the same solvent was added. The reaction mixture was stirred for 30 min before the addition of an aq. NaHCO<sub>3</sub> solution and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL). The combined organic phases were washed with saturated brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel. The eluent was indicated in each case.

**(R)-3-Ethyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6a), known compound<sup>15</sup>**



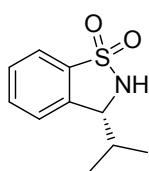
Following the above general procedure, compound **6a** was obtained from sulfinamide **5a** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 4:1. Yield: 98%; white solid; mp 45-47°C; the *ee* was determined by HPLC (Chiralcel OD, 1.0 mL/min, *i*-PrOH/*n*-heptane 30/70, λ = 254 nm, *t<sub>R</sub>* = (*R*) 10.2 min), 99% *ee* (Lit.<sup>15</sup> *t<sub>R</sub>* = (*S*) 6.4 min, (*R*) 9.6 min);  $[\alpha]_D^{20}$  54 (*c* 1.7, CHCl<sub>3</sub>) (lit.<sup>15</sup>  $[\alpha]_D^{25}$  -50.1 *c* 1.06, CHCl<sub>3</sub>,

<sup>14</sup> The treatment of the non protected amino derivative **4k**, following the general procedure for radical cyclization, resulted in a complex mixture of compounds.

<sup>15</sup> M. Seppelt, D. Enders *Synlett*, 2011, **3**, 402.

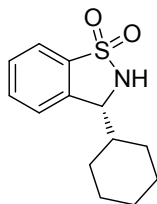
81% *ee* (*S*); IR (KBr): 3025, 2973, 2937, 1456, 1168, 1131  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d, 7.6, 1H), 7.61 (dt,  $J = 7.5, 1.2$  Hz, 1H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.37 (d,  $J = 7.7$  Hz, 1H), 4.99 (broad s, 1H), 4.69-4.63 (m, 1H), 2.10-1.96 (m, 1H), 1.87-1.75 (m, 1H), 1.02 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  140.3, 135.8, 133.1, 129.2, 124.1, 121.3, 59.1, 28.7, 9.9. MS (FAB)  $m/z$  395 [(2M+1)<sup>+</sup>, 10], 198 [(M+1)<sup>+</sup>, 100]. HRMS (FAB)  $m/z$  calcd for  $\text{C}_9\text{H}_{12}\text{NO}_2\text{S}$ : 198.0589; found: 198.0590.

**(*R*)-3-*iso*-Propyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6b).**



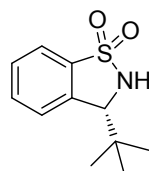
Following the above general procedure, compound **6b** was obtained from sulfinamide **5b** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 2:1. Yield: >99%; colorless oil; the *ee* was determined by HPLC (Chiralcel OD, 1.0 mL/min, *i*-PrOH/hexane 5/95,  $\lambda = 254$  nm,  $t_R =$  (*S*) 21.8 min, (*R*) 32.4 min), 99% *ee*;  $[\alpha]_D^{20} +67$  ( $c$  0.6,  $\text{CHCl}_3$ ); IR (KBr): 1467, 1283, 1168, 1131  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.76 (m, 1H), 7.65-7.59 (m, 1H), 7.55-7.49 (m, 1H), 7.39-7.36 (m, 1H), 4.86 (broad s, 1H), 4.69-4.67 (m, 1H), 2.32-2.22 (m, 1H), 1.12 (d,  $J = 6.9$  Hz, 3H), 0.76 (d,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  139.2, 135.8, 133.1, 129.3, 124.3, 121.4, 63.3, 32.8, 20.1, 15.4. MS (ESI+)  $m/z$  445 [(2M+Na)<sup>+</sup>, 23], 234 [(M+Na)<sup>+</sup>, 100], 212 [(M+H)<sup>+</sup>, 18]. HRMS (ESI+)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}_2\text{S}$ : 212.0739; found: 212.0741.

**(*R*)-3-Cyclohexyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6c).**



Following the above general procedure, compound **6c** was obtained from sulfinamide **5c** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 4:1. Yield: 98%; colorless oil;  $[\alpha]_D^{20} +54$  ( $c$  0.65,  $\text{CHCl}_3$ ); IR (KBr): 3023, 2927, 1277, 1167, 1155, 1132  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 7.9$  Hz, 1H), 7.61 (dt,  $J = 7.6, 1.5$  Hz, 1H), 7.50 (t,  $J = 7.8$  Hz, 1H), 7.38 (d,  $J = 7.7$  Hz, 1H), 4.92 (broad, 1H), 4.62 (t,  $J = 4.1$  Hz, 1H), 1.90-1.80 (m, 3H), 1.71-1.65 (m, 2H), 1.34-1.09 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  139.0, 135.8, 133.0, 129.2, 124.4, 121.4, 62.9, 42.7, 30.7, 26.4, 25.9, 25.8, 25.8. MS (FAB)  $m/z$  503 [(2M+1)<sup>+</sup>, 9], 252 [(M+1)<sup>+</sup>, 100], 250 (21). HRMS (FAB)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{S}$ : 252.1058; found: 252.1070.

**(*R*)-3-(*tert*-Butyl)-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6d), known compound.<sup>16</sup>**

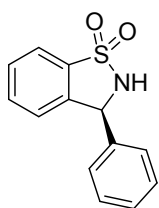


Following the above general procedure, compound **6d** was obtained from sulfinamide **5d** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 3:1. Yield: 98%; white solid; mp 124-126°C;  $[\alpha]_D^{20} +55$  ( $c$  0.8,  $\text{CHCl}_3$ ). [lit<sup>16</sup>:  $[\alpha]_D^{18} -54$  ( $c$  1.0,  $\text{CHCl}_3$ , (*S*)). IR (KBr): 2960, 2918, 1281, 1169, 1130.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.77 (m, 1H), 7.61-7.49 (m, 3H), 4.98 (broad s, 1H), 4.42 (d,  $J = 5.1$  Hz, 1H), 1.05 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  138.1, 136.1, 132.3, 129.3, 126.0, 121.6, 67.4, 36.7, 26.6.

<sup>16</sup> K. H. Ahn, C. Ham, S. K. Kim, C. W. Cho, *J. Org. Chem.*, 1997, **62**, 7047.

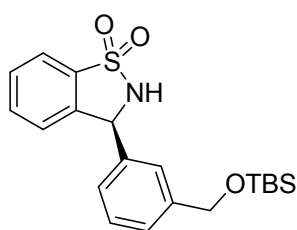
MS (FAB)  $m/z$  451 [(2M+1)<sup>+</sup>, 10], 226 [(M+1)<sup>+</sup>, 100]. HRMS (FAB)  $m/z$  calcd for C<sub>11</sub>H<sub>16</sub>NO<sub>2</sub>S: 226.0902; found: 226.0905.

**(S)-3-Phenyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6e)**, known compound.<sup>15,17</sup>



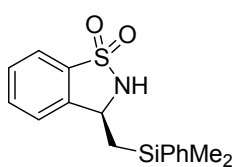
Following the above general procedure, compound **6e** was obtained from sulfinamide **5e** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 4:1. Yield: 90%, colorless oil,  $[\alpha]_D^{20} +89$  (*c* 1.8, CHCl<sub>3</sub>). The *ee* was determined by HPLC (Chiralcel OJ-H, 0.8 mL/min, *i*-PrOH/*n*-hexane 30/70,  $\lambda = 254$  nm,  $t_R = 18.9$  min (*S*)), 99% *ee*. [lit.<sup>17</sup>:  $[\alpha]_D^{25} +93.6$  (*c* 1.0, CHCl<sub>3</sub>), HPLC:  $t_R = 18.7$  min (*S*), 21.1 min (*R*); 98% *ee* (*S*)]; IR (KBr): 3023, 2927, 1277, 1175, 1142 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.86-7.78 (m, 1H), 7.58-7.49 (m, 2H), 7.39-7.33 (m, 5H), 7.16-7.09 (m, 1H), 5.71 (s, 1H), 5.05 (broad s, 1H). <sup>13</sup>C NMR (75 MHz)  $\delta$  139.8, 138.7, 134.8, 133.4, 129.5, 129.3, 129.1, 127.6, 125.4, 121.2, 61.4. MS (FAB)  $m/z$  230 (14), 246 [(M+1)<sup>+</sup>, 100]. HRMS (FAB)  $m/z$  calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub>S: 246.0589; found: 246.0582.

**(S)-3-[3-(*tert*-Butyldimethylsilyloxy)methyl]phenyl-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6f)**, known compound<sup>17</sup>



Following the above general procedure, compound **6f** was obtained from sulfinamide **5f** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 3:1. Yield: 91%, colorless oil,  $[\alpha]_D^{20} + 62$  (*c* 0.55, CHCl<sub>3</sub>). [lit.<sup>17</sup>  $[\alpha]_D^{25} +61.4$  (*c* 1.40, CHCl<sub>3</sub>), 98% *ee* (*S*)]; IR (KBr): 2929, 2885, 2857, 1471, 1299, 1167 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.77-7.71 (m, 1H), 7.49-7.42 (m, 2H), 7.29-7.23 (m, 3H), 7.19-7.14 (m, 1H), 7.08-7.03 (m, 1H), 5.63 (d, *J* = 4.1 Hz, 1H), 4.93 (broad d, *J* = 3.8 Hz, 1H), 4.65 (s, 2H), 0.83 (s, 9H), 0.00 (s, 6H). <sup>13</sup>C NMR (75 MHz)  $\delta$  142.8, 139.9, 138.6, 134.9, 133.3, 129.5, 129.2, 126.7, 126.2, 125.4, 125.1, 121.1, 64.5, 61.4, 25.9, 18.4, -5.27. MS (FAB)  $m/z$  390 [(M+1)<sup>+</sup>, 58], 332 (96), 258 (100). HRMS (FAB)  $m/z$  calcd for C<sub>20</sub>H<sub>28</sub>NO<sub>3</sub>SSi: 390.1559; found: 390.1562.

**(R)-3-[Dimethyl(phenyl)silylmethyl]-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide (6g)**.

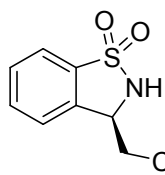


Following the above general procedure, compound **6g** was obtained from sulfinamide **5g** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 4:1. Yield: 92%; colorless oil;  $[\alpha]_D^{20} - 67$  (*c* 1.4, CHCl<sub>3</sub>); IR (KBr): 3069, 2956, 1331, 1170 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (d, *J* = 7.5 Hz, 1H), 7.44-7.39 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.27-7.25 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 4.57-4.52 (m, 1H), 4.26 (d, *J* = 4.6 Hz, 1H), 1.45-1.40 (m, 1H), 1.24-1.15 (m, 1H), 0.30 (s, 3H), 0.27 (s, 3H). <sup>13</sup>C NMR (75 MHz)  $\delta$  146.0, 139.8, 137.8, 136.1, 135.5, 132.1, 131.3, 130.7,

<sup>17</sup> C.-B. Yu, D. W. Wang, Y. G. Zhou *J. Org. Chem.* 2009, **74**, 5633.

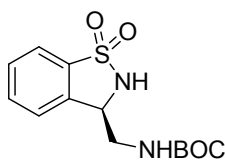
126.3, 123.5, 57.7, 26.3, 0.0. MS (FAB)  $m/z$  318 [(M+1)<sup>+</sup>, 35], 240 (100). HRMS (FAB)  $m/z$  calcd for C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>SSi: 318.0984; found: 318.0978.

**(S)-tert-Butyl 2-(1,1-dioxide-2,3-dihydrobenzo[d]isothiazol-3-yl)acetate (6h)**, known compound<sup>18</sup>



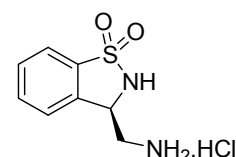
Following the above general procedure, compound **6h** was obtained from sulfonamide **5h** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 4:1. Yield: 90%. The *ee* was determined by HPLC (Chiralcel OD, 0.7 mL/min, *i*-PrOH/*n*-hexane 25/75,  $\lambda$  = 254 nm,  $t_R$  = 12.5 min (*S*),  $t_R$  = 13.8 (*R*), 99% *ee*).  $[\alpha]_D^{20}$  -80 (*c* 0.50, CHCl<sub>3</sub>) [Lit.<sup>18</sup>: HPLC: 96% *ee* (*R*)]; IR (KBr): 2979, 2932, 1723, 1369, 1299, 1166 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 5.56 (broad s, 1H), 5.06-5.00 (m, 1H), 2.90 (dd, *J* = 16.8, 3.8, Hz, 1H), 2.71 (dd, *J* = 16.8, 9.6 Hz, 1H), 1.44 (s, 9H). <sup>13</sup>C NMR (75 MHz)  $\delta$  169.9, 138.5, 135.8, 133.2, 129.6, 124.0, 121.5, 82.4, 53.8, 41.1, 28.1. MS (FAB)  $m/z$  284 [(M+1)<sup>+</sup>, 15], 228 (100), 168 (40), 57 (57). HRMS (FAB)  $m/z$  calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>4</sub>S: 284.0957; found: 284.0946.

**(R)-tert-Butyl (1,1-dioxide-2,3-dihydrobenzo[d]isothiazol-3-yl)methylcarbamate (6j)**.



Following the above general procedure, compound **6j** was obtained from sulfonamide **5j** (0.45 mmol). Chromatography: *n*-hexane:AcOEt, 1:1. Yield: 99%; white solid; mp 106-108°C;  $[\alpha]_D^{20}$  -63 (*c* 0.75, CHCl<sub>3</sub>); IR (KBr): 2978, 2926, 1692, 1518, 1286, 1168 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 7.9 Hz, 1H), 7.65-7.51 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 5.70 (broad s, 1H), 5.06 (broad s, 1H), 4.85 (broad s, 1H), 3.75-3.65 (m, 1H), 3.43-3.34 (m, 1H), 1.40 (s, 9H). <sup>13</sup>C NMR (75 MHz) 156.7, 137.3, 136.4, 133.2, 129.8, 124.6, 121.5, 80.4, 58.3, 44.8, 28.3. MS (FAB)  $m/z$  299 [(M+1)<sup>+</sup>, 92], 243 (100), 57 (55). HRMS (FAB)  $m/z$  calcd for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>S: 299.1066; found: 299.1060.

**(R)-3-(Aminomethyl)-2,3-dihydrobenzo[d]isothiazole-1,1-dioxide hydrochloride (6k)**.



A solution of HCl (0.2 mmol, 2 equiv, 1.25 M in MeOH) was added to benzosultam **6j** (0.1 mmol). The mixture was stirred at rt for 1.5 h and then, was concentrated. The residue was purified by trituration with Et<sub>2</sub>O. Yield: 94%, white solid; mp 123-125°C;  $[\alpha]_D^{20}$  -53 (*c* 0.54, CHCl<sub>3</sub>); IR (KBr): 2990, 2924, 1271, 1158, 1132 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, methanol - d<sub>4</sub>)  $\delta$  7.90-7.71 (m, 4H), 5.11 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.57 (dd, *J* = 13.2, 3.5 Hz, 1H),

<sup>18</sup> C-B. Yu, K. Gao, D. S. Wang, L. Shi, Y. G. Zhou *Chem. Commun.*, 2011, **47**, 5052.

3.21 (m, 1H).  $^{13}\text{C}$  NMR (75 MHz, methanol - $d_4$ )  $\delta$  138.2, 134.8, 131.6, 126.5, 122.2, 55.9, 44.8. MS (FAB+)  $m/z$  199 [(M+1) $^+$ , 90], 57 (100). HRMS (FAB)  $m/z$  calcd for  $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_2\text{S}^+$ : 199.0541; found: 199.0540.

