

# Catalytic asymmetric sulfimidation of 1,3-dithianes

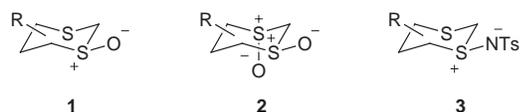
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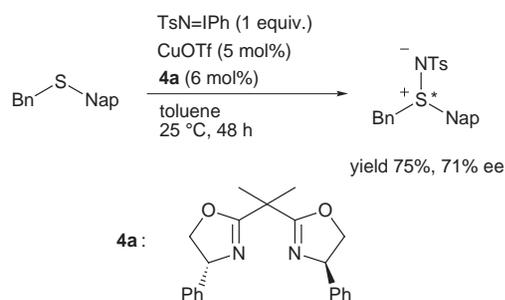
A direct catalytic sulfimidation of 1,3-dithianes to the corresponding chiral monosulfimides with *N*-(*p*-tolylsulfonyl)imino(phenyl)iodinane (TsN=IPh) using a catalytic amount of copper(i) triflate (CuOTf) and a chiral 4,4'-disubstituted bis(oxazoline) as ligand has been developed. The reaction affords the chiral monosulfimides in good yield and with moderate enantioselectivity (up to 40% ee).

## Introduction

Organosulfur compounds have long been known to be useful and important in organic synthesis. 1,3-Dithianes, the typical thioacetals, have been extensively used as acyl anion equivalents because they can be prepared easily by masking the carbonyl compounds with dithiols. Recently the groups of Page,<sup>1</sup> Aggarwal<sup>2</sup> and Toru<sup>3</sup> reported the synthesis of enantiomerically enriched 1,3-dithiane monoxides **1** or *trans*-dioxides **2** and



the enantioselective carbon–carbon bond forming reactions using these oxides as chiral auxiliaries as well as chiral acyl anion equivalents. Aggarwal and co-workers have found that compound **2** (R = H) undergoes selective addition to aromatic aldehydes when the reactions are carried out under equilibrium control (using the Na anion of **2**).<sup>4</sup> On the other hand, the study of sulfimides **3**, the nitrogen analogues of sulfoxides, has hardly been developed.<sup>5</sup> We have recently reported a direct catalytic sulfimidation of prochiral sulfides to chiral sulfimides with *N*-(*p*-tolylsulfonyl)imino(phenyl)iodinane (TsN=IPh) using a catalytic amount of copper(i) triflate (CuOTf) and chiral bis(oxazoline) ligand (Scheme 1).<sup>6</sup> As a continuation of this



Scheme 1

study, we describe herein the result of the application of this asymmetric imidation method to 1,3-dithianes for the synthesis of enantiomerically enriched sulfimides **3**, which might be usable as a new type of chiral auxiliary.

## Results and discussion

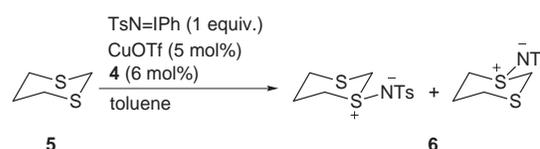
First, sulfimidation of 1,3-dithiane **5** with TsN=IPh was examined in toluene in the presence of CuOTf as catalyst. The expected monosulfimidation product **6** was produced, but in low yield. However, when a chiral ligand **4** was added, the product yield was much increased, as has been observed in the

Table 1 Asymmetric sulfimidation of 1,3-dithiane **5**<sup>a</sup>

Entry	<i>T</i> /°C	<i>t</i> /h	Ligand	Yield (%)	Ee (%)
1	r.t.	20	—	9	—
2	r.t.	20	<b>4a</b>	77	15
3	r.t.	20	<b>4b</b>	39	0
4	0	0.5	<b>4a</b>	54	9
5	0	20	<b>4a</b>	61	18
6	0	40	<b>4a</b>	83	17
7 <sup>b</sup>	0	20	<b>4a</b>	66	17
8	0	20	<b>4c</b>	42	14
9	0	20	<b>4d</b>	4	0
10	−20	20	<b>4a</b>	61	16
11	−20	40	<b>4a</b>	76	18
12	−20	40	<b>4a</b>	79	20

<sup>a</sup> The concentration of **5** is 0.2 M. <sup>b</sup> The concentration of **5** is 0.1 M.

sulfimidation of monosulfides, probably because of the formation of a better copper(i) catalyst. The product also showed optical activity; namely, asymmetric induction occurred (Scheme 2). Typical results for the asymmetric sulfimidation of



Scheme 2

**5** in toluene under a variety of conditions are shown in Table 1. Solvents such as dichloromethane, tetrahydrofuran (THF) and diethyl ether were completely ineffective for this reaction. In acetonitrile, the reaction proceeded, but no asymmetric induction occurred. As can be seen in Table 1, longer reaction times improved the product yield, but the reaction time, the reaction temperature and the substrate concentration did not show much influence on the enantioselectivity of this reaction. Chiral ligands such as diamine **4b** (entry 3) and **4d** (entry 9) were not effective at all for asymmetric induction. The Schiff base ligand **4e**, effective for asymmetric aziridination,<sup>7</sup> was completely ineffective for this asymmetric sulfimidation. From these results the optimum conditions for asymmetric sulfimidation were judged to be the use of CuOTf and chiral bis(oxazoline) ligand **4a** in toluene (0.2 M) at 0 °C for 20 h. Even under the best conditions employed, the enantioselectivity was at most 20% ee.

There are four sites on the sulfur atoms of the 1,3-dithiane able to attack the nitrogen of the nitrene complex; namely, equatorial and axial lone pairs of each sulfur atom. One of our proposed models for the orientation of the reagents (**5**, **4a**, CuOTf and TsN=IPh) prior to imidation is shown in Fig. 1. The enantioselectivity depends on which of the two sulfur atoms attacks the nitrene moiety in the copper complex. Since the

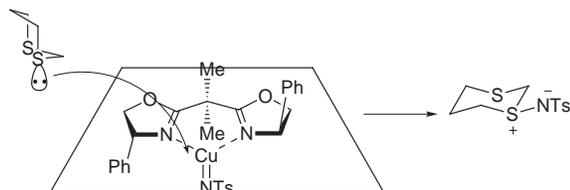


Fig. 1 A model for the orientation of reagents

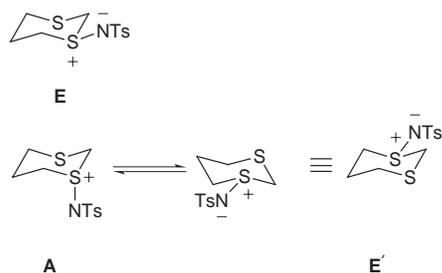
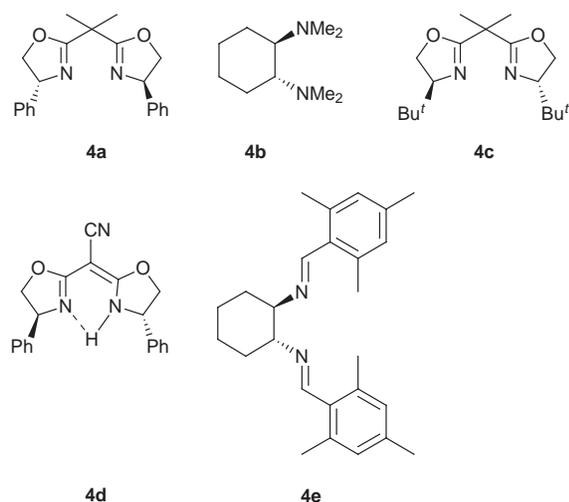


Fig. 2 Flip of the 1,3-dithiane monosulfimide



absolute configuration of the major enantiomer of the product sulfimide is not yet known, it is not yet clear which sulfur atom approaches the nitrene moiety. Here, we assume that the front sulfur atom plays this role in Fig. 1 and, thus, there are two attacking lone pairs, equatorial and axial. The products then should be an equatorial (**E**) and an axial (**A**) isomer, respectively.<sup>5</sup> In the axial isomer **A**, a flip of the six-membered ring gives the more stable equatorial isomer **E'** (Fig. 2). The isomer **E'** is an enantiomer of the equatorial isomer **E** (Fig. 2) and its formation may lower the enantioselectivity. The conformational preference of the equatorial isomer **6** has already been rationalized by NMR spectroscopy<sup>5a,b</sup> and X-ray crystallography.<sup>5c</sup> From this hypothesis, we envisaged the use of suitably substituted 1,3-dithianes as starting materials in order to avoid the ring flip of the product monosulfimides. In these cases a higher enantioselectivity might be expected. The asymmetric sulfimidation of a variety of substituted 1,3-dithianes was investigated next.

The imidation of 2-substituted 1,3-dithiane derivatives **7** gave the corresponding sulfimides **8** (Scheme 3). Theoretically, the products should consist of four diastereoisomers because they have two chiral centers, but the diastereoselectivity was very high in this reaction, as shown in Table 2. Here, the ratio of diastereoisomers was determined by integration of the methine protons at the 2-position of 2-methyl-1,3-dithiane 1-tosylimide **8a** which appeared at  $\delta$  3.98 and 4.12, as a quartet, respectively. The NOE spectrum (see Fig. 3) showed that the major diastereoisomer is the *trans* isomer (all the substituents of these products are present in equatorial positions). The mono-

Table 2 Asymmetric sulfimidation of 2-substituted 1,3-dithianes **7**

Entry	Substrate	Product	Yield (%)	Diastereoisomers of <b>8</b>	
				<i>trans</i> : <i>cis</i> <sup>a</sup>	<i>trans</i> - <b>8</b> Ee (%)
1	<b>7a</b> R = Me	<b>8a</b>	70	94:6	40 <sup>b</sup>
2	<b>7b</b> R = Bn	<b>8b</b>	57	100:0	36 <sup>b</sup>
3	<b>7c</b> R = CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub> - <i>o</i>	<b>8c</b>	68	100:0	32 <sup>b</sup>
4	<b>7d</b> R = SiMe <sub>2</sub> Ph	<b>8d</b>	35	100:0	5 <sup>c</sup>
5	<b>7e</b> R = SiMe <sub>3</sub>	<b>8e</b>	39	100:0	9 <sup>c</sup>

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis. <sup>b</sup> Determined by HPLC using suitable chiral columns. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis in the presence of Eu(hfc)<sub>3</sub>.

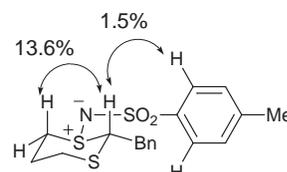
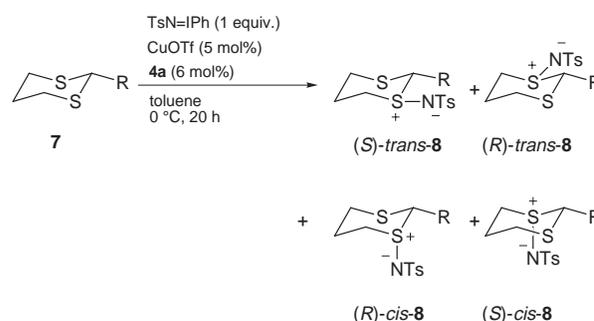


Fig. 3 NOE spectrum of 2-benzyl-1,3-dithiane monosulfimide

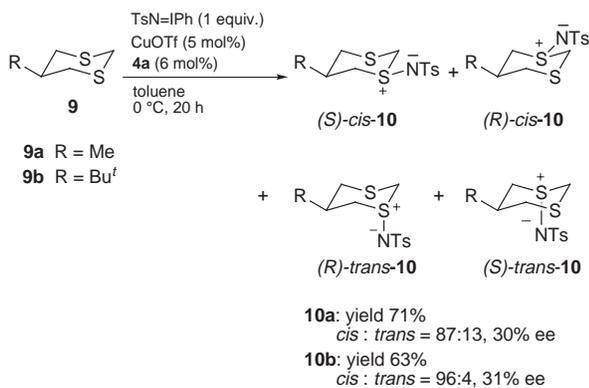


Scheme 3

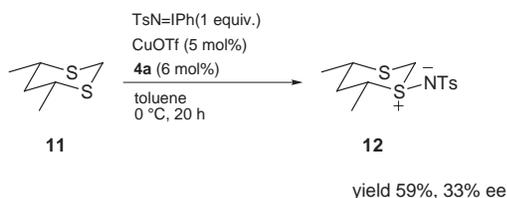
sulfimide **8a** comprises two diastereoisomers (*trans*:*cis* = 94:6) (entry 1), while the imidation of **7b–e** resulted in exclusive formation of the equatorial imidation products **8b–e** (entries 2–5). 2-Substituted 1,3-dithianes gave higher ees (up to 40% ee) than 1,3-dithiane **5** as we expected (Table 2; entries 1, 2 and 3), but the introduction of much bulkier substituents was not fruitful (Table 2; entries 4 and 5). When 2-trimethylsilyl-2-methyl-1,3-dithiane **7f** and (1*R*,2*R*)-2-(1,3-dithian-2-yl)-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane **7g** (1,3-dithian-2-yl-D-



camphor) were used as substrates, the imidation itself did not proceed. Next, we treated the 5-position substituted 1,3-dithianes (**9**). The result was slightly complicated. As shown in Scheme 4, the diastereoselectivity was higher in the case of **9b** (R = Bu<sup>t</sup>) than in that of **9a** (R = Me), but there was not much difference in the enantioselectivity of the major diastereoisomer, the *cis* isomer. The ratio of the two isomers was determined from the <sup>1</sup>H NMR spectrum of the crude product, in which the methyl protons at the 5-position of monosulfimide **10a** appeared at  $\delta$  1.13 and 1.31, respectively. Likewise, the diastereoisomeric ratio was determined by integration of the *tert*-butyl protons at the 5-position of the monosulfimide **10b**, which appeared at  $\delta$  0.93 and 0.96, each as a singlet, respectively. In the case of *cis*-4,6-dimethyl-1,3-dithiane **11**, the imidation proceeded to give the corresponding chiral sulfimide with



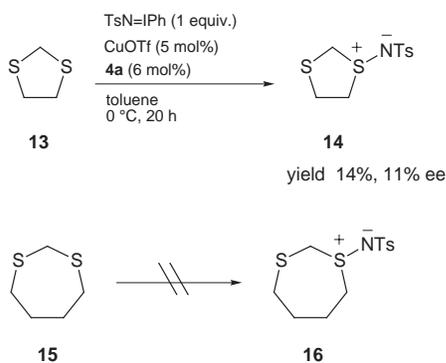
Scheme 4



Scheme 5

a similar enantioselectivity to that described above (Scheme 5). These results showed that the position, number and bulkiness of the substituents did not much affect the enantioselectivity of the product sulfimides.

Similar imidation was also attempted by switching from the six-membered ring thioacetals to five- and seven-membered analogues such as 1,3-dithiolane **13** and 1,3-dithiepane **15** (Scheme 6).<sup>8</sup> Compound **13** gave the expected sulfimide **14** in



Scheme 6

14% yield with 11% ee, while compound **15** did not react at all with TsN=IPh.

## Experimental

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on JEOL EX-400 and JNM-GSX270 spectrometers for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as an internal standard; *J* values are given in Hz. The following abbreviations are used: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with a Nicolet Impact 400D FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-SX102A spectrometer. Melting points are uncorrected. Analytical thin layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatography on SiO<sub>2</sub> was performed with Wakogel C-300. HPLC analyses were performed on an HLC-803A instrument (Tosoh) with a UV-8011 detector at 40 °C. Elemental analyses were performed at the Microanalytical Center of Kyoto University. 4,4'-

Disubstituted bis(oxazoline)s (**4a**, **4c**, **4d**) and Eu(hfc)<sub>3</sub> were purchased from Aldrich Chemical Co. 1,3-Dithiane **5**, 2-methyl-1,3-dithiane **7a** and 2-trimethylsilyl-1,3-dithiane **7e** were commercial products. Other substituted 1,3-dithiane derivatives (**7b**,<sup>9</sup> **7d**,<sup>9</sup> **9a**,<sup>10</sup> **9b**,<sup>10</sup> **11**<sup>11</sup>) were prepared by the reported methods and typical procedures are shown below. *N*-(*p*-Tolylsulfonyl)imino(phenyl)iodinane (TsN=IPh) was prepared by the reported procedure from (diacetoxyiodo)benzene and toluene-*p*-sulfonamide.<sup>6b,12</sup> Dichloromethane was distilled from CaH<sub>2</sub> and acetonitrile and toluene were distilled from P<sub>2</sub>O<sub>5</sub> just before use.

### Typical procedure for preparation of 2-substituted 1,3-dithiane derivatives<sup>9</sup>

To a solution of 1,3-dithiane (1.80 g, 18 mmol) in THF (50 ml) was added BuLi (1.6 M hexane solution; 11 ml, 18 mmol) under nitrogen at -20 °C. After the mixture had been stirred for 0.5 h, it was treated with organic halide at room temperature for 18 h. The reaction mixture was diluted with aqueous NH<sub>4</sub>Cl and then extracted with diethyl ether (3 × 30 ml). The combined organic layers were dried (MgSO<sub>4</sub>) and evaporated to give the crude product. Purification by silica gel column chromatography gave the corresponding 2-substituted 1,3-dithiane.

**2-*o*-Tolylmethyl-1,3-dithiane (7c)**. Colorless oil, 55% yield; eluent: *n*-hexane–diethyl ether = 20:1; δ<sub>H</sub> 1.84–1.93 (m, 1H), 2.07–2.34 (m, 1H), 2.36 (s, 3H), 2.77–2.84 (m, 4H), 3.03 (d, *J* 7.4, 2H), 4.25 (t, *J* 7.4, 2H), 7.12–7.21 (m, 5H); δ<sub>C</sub> 19.6, 25.8, 30.7, 38.9, 47.9, 125.7, 127.1, 130.1, 130.4, 135.7, 136.4.

### Typical procedure for preparation of 5-substituted 1,3-dithiane and 4,6-dimethyl-1,3-dithiane derivatives<sup>10,11</sup>

The 5-substituted and 4,6-disubstituted dithiols were prepared from the corresponding diols. The solution of thiol (15 mmol) and dimethoxymethane (17 mmol) in 25 ml of chloroform was added slowly to a solution of 47% boron trifluoride–diethyl ether complex (2 ml) and acetic acid (4 ml) in 5 ml of chloroform under reflux with stirring. After the addition, the reaction mixture was stirred for a further 3 h. The solution was washed twice with water, twice with aqueous KOH and twice again with water. Purification by distillation or recrystallization gave the corresponding 1,3-dithiane.

### General procedure for asymmetric sulfimidation of 1,3-dithiane derivatives

To a solution of CuOTf (2.60 mg, 0.010 mmol) and 4,4'-disubstituted bis(oxazoline) **4a** (4.11 mg, 0.012 mmol) in 1.0 ml of toluene were added first TsN=IPh (75.0 mg, 0.200 mmol) and then the 1,3-dithiane derivative (0.20 mmol). The resulting mixture was stirred under nitrogen at 0 °C for 20 h, and then treated with saturated aqueous NaCl and extracted with dichloromethane. The extract was dried (anhydrous MgSO<sub>4</sub>) and evaporation of the solvent left a pale yellow oil. Purification by silica gel column chromatography gave the corresponding optically active sulfimide in a pure form as a colorless oil which sometimes solidifies. The diastereomeric ratios (**8a**, **10a**, **10b**) were determined by <sup>1</sup>H NMR analysis (270 MHz). Enantiomeric excesses were determined by HPLC using a suitable chiral column or <sup>1</sup>H NMR analysis (270 MHz) in the presence of Eu(hfc)<sub>3</sub>, as shown below.

***N*-(1,3-Dithian-1-ylidene)toluene-*p*-sulfonamide (6)**. White solid, mp 159–161 °C, 61% yield; 18% ee by Daicel chiralcel OD (25% propan-2-ol–hexane); eluent: dichloromethane; ν<sub>max</sub> (KBr)/cm<sup>-1</sup> 1137 (SO<sub>2</sub>), 1397 (SO<sub>2</sub>); δ<sub>H</sub> 2.26–2.69 (m, 7H), 3.09 (ddd, 1H), 3.28–3.41 (m, 1H), 4.00 (d, *J* 12.6, 1H), 4.05 (br d, *J* 12.6, 1H), 7.25 (d, *J* 8.1, 2H), 7.79 (d, *J* 8.1, 2H); δ<sub>C</sub> 21.4, 27.7, 28.1, 48.4, 48.8, 126.1, 129.3, 141.3, 141.9; Anal. Calc. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>S<sub>3</sub>: C, 45.65; H, 5.22; N, 4.84. Found: C, 45.41; H, 5.14; N, 4.74%.

***N*-(2-Methyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (trans-8a)**. White solid, mp 172–173 °C (lit.,<sup>13</sup> 171–172 °C), 70%

yield; 40% ee by Daicel chiralpak AS (25% propan-2-ol-hexane); eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1165 (SO<sub>2</sub>), 1311 (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.46 (d,  $J$  6.9, 3H), 2.23–2.53 (m, 5H), 2.61 (dt,  $^2J$  12.2, 1H), 2.81 (ddd,  $^2J$  12.2,  $J$  14.2 and 2.4, 1H) 3.10 (ddd,  $^2J$  12.7,  $J$  13.4 and 2.9, 1H), 3.32 (dt,  $^2J$  12.7, 1H), 3.99 (q,  $J$  6.9, 1H), 7.24 (d,  $J$  8.1, 2H), 7.79 (d,  $J$  8.1, 2H);  $\delta_{\text{C}}$  15.7, 21.1, 29.3, 29.7, 50.6, 59.0, 126.2, 129.2, 141.5, 141.7; Anal. Calc. for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>3</sub>: C, 47.50; H, 5.65; N, 4.62. Found: C, 47.32; H, 5.59; N, 4.58%.

***N*-(2-Benzyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (trans-8b).** White solid, mp 161–163 °C (lit.,<sup>13</sup> 164 °C), 57% yield; 36% ee by Daicel chiralcel OJ (25% propan-2-ol-hexane); eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1152 (SO<sub>2</sub>), 1375 (SO<sub>2</sub>);  $\delta_{\text{H}}$  2.25–2.70 (m, 7H), 2.74 (dd,  $^2J$  14.3,  $J$  10.3, 1H), 3.15 (ddd,  $^2J$  13.2,  $J$  13.4 and 2.9, 1H), 3.39 (dt,  $^2J$  13.2, 1H), 3.56 (dd,  $^2J$  14.3,  $J$  3.3, 1H), 4.19 (dd,  $J$  10.3 and 3.3, 1H), 7.14–7.30 (m, 7H), 7.84 (d, 2H);  $\delta_{\text{C}}$  21.4, 29.3, 29.7, 34.8, 51.1, 65.5, 126.2, 127.5, 128.5, 129.6, 134.5, 141.5, 141.9; Anal. Calc. for C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>3</sub>: C, 56.96; H, 5.58; N, 3.69. Found: C, 56.75; H, 5.51; N, 3.71%.

***N*-(2-*o*-Tolylmethyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (trans-8c).** White solid, mp 111–113 °C, 68% yield; 32% ee by Daicel chiralcel OJ (25% propan-2-ol-hexane); eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1138 (SO<sub>2</sub>), 1381 (SO<sub>2</sub>);  $\delta_{\text{H}}$  2.48 (dd,  $J$  14.4 and 10.7, 1H), 3.03–3.12 (m, 1H), 3.28–3.32 (m, 1H), 3.56 (dd,  $J$  14.4 and 2.9, 1H), 4.01 (dd,  $J$  10.7 and 2.9, 1H), 7.03–7.28 (m, 6H), 7.75 (d, 2H);  $\delta_{\text{C}}$  19.6, 21.4, 29.3, 29.7, 32.1, 51.1, 64.7, 125.9, 126.2, 127.6, 129.3, 130.4, 130.7, 132.9, 136.8, 141.4, 141.9; *m/z* EIMS 393 (M<sup>+</sup>); HRMS: Calc. for C<sub>19</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>3</sub>: 393.0891. Found: 393.0892.

***N*-(2-Trimethylsilyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (trans-8d).** Colorless oil, 32% yield; 9% ee by <sup>1</sup>H NMR analysis in the presence of Eu(hfc)<sub>3</sub>; eluent: dichloromethane;  $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$  1160 (SO<sub>2</sub>), 1329 (SO<sub>2</sub>);  $\delta_{\text{H}}$  0.19 (s, 9H), 2.29–2.66 (m, 7H), 2.96 (ddd,  $^2J$  12.4,  $J$  8.7 and 2.0, 1H), 3.28 (dt,  $^2J$  12.4 and 2.3, 1H), 3.71 (s, 1H), 7.23 (d,  $J$  8.1, 2H), 7.79 (d,  $J$  8.1, 2H);  $\delta_{\text{C}}$  –2.1, 21.4, 29.1, 49.7, 52.6, 108.7, 126.2, 129.2, 129.4, 129.7, 141.6, 142.0; *m/z* EIMS 361 (M<sup>+</sup>); HRMS: Calc. for C<sub>14</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>3</sub>Si: 361.0660. Found: 361.0657; Anal. Calc. for C<sub>14</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>3</sub>Si: C, 46.50; H, 6.41; N, 3.87. Found: C, 45.97; H, 6.45; N, 3.64%.

***N*-(2-Dimethylphenylsilyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (trans-8e).** Colorless oil, 35% yield; 5% ee by <sup>1</sup>H NMR analysis in the presence of Eu(hfc)<sub>3</sub>; eluent: dichloromethane;  $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$  1139 (SO<sub>2</sub>), 1300 (SO<sub>2</sub>);  $\delta_{\text{H}}$  0.51 (s, 9H), 0.58 (s, 3H), 2.21–2.61 (m, 7H), 2.91–3.02 (m, 1H), 3.23–3.31 (m, 1H), 7.22–7.49 (m, 7H), 7.80 (d,  $J$  8.3, 2H);  $\delta_{\text{C}}$  –4.5, –2.4, 21.4, 28.7, 29.4, 49.5, 52.6, 126.3, 128.0, 129.3, 130.3, 133.0, 134.4, 141.6, 142.1; Anal. Calc. for C<sub>19</sub>H<sub>25</sub>NO<sub>2</sub>S<sub>3</sub>Si: C, 53.86; H, 5.95; N, 3.31. Found: C, 53.93; H, 5.78; N, 3.27%.

***N*-(5-Methyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (cis-10a).** White solid, mp 186–188 °C, 71% yield; 30% ee by <sup>1</sup>H NMR analysis in the presence of Eu(hfc)<sub>3</sub>; eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1196 (SO<sub>2</sub>), 1368 (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.12 (d,  $J$  6.4, 3H), 2.40–2.54 (m, 5H), 2.83 (dd,  $^2J$  12.5 and 11.5, 1H), 3.24 (br dd,  $^2J$  11.5, 1H), 3.85 (d,  $^2J$  12.7, 1H), 4.06 (br d,  $^2J$  12.7, 1H), 7.25 (d,  $J$  8.6, 2H), 7.79 (d,  $J$  8.6, 2H);  $\delta_{\text{C}}$  21.4, 21.9, 34.7, 36.1, 48.1, 54.9, 126.2, 129.4, 141.4, 141.9; *m/z* EIMS 303 (M<sup>+</sup>); HRMS: Calc. for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>3</sub>: 303.0421. Found: 303.0410; Anal. Calc. for C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>3</sub>: C, 47.50; H, 5.65; N, 4.62. Found: C, 46.46; H, 5.50; N, 4.22%.

***N*-(5-*tert*-Butyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (cis-10b).** White solid, mp 116–118 °C, 71% yield; 31% ee by <sup>1</sup>H NMR analysis in the presence of Eu(hfc)<sub>3</sub>; eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1141 (SO<sub>2</sub>), 1391 (SO<sub>2</sub>);  $\delta_{\text{H}}$  0.93 (s, 9H), 2.02 (dddd,  $J$  12.9, 10.9, 2.7 and 2.2, 1H), 2.40–2.49 (m, 3H), 2.67 (dd,  $^2J$  13.6, 1H), 2.85 (dd,  $^2J$  12.9 and 12.6, 1H), 3.37 (dd,  $^2J$  12.9,  $J$  2.2, 1H), 3.83 (d,  $J$  12.6, 1H), 4.01 (br d,  $J$  12.6, 1H), 7.25 (d,  $J$  7.8, 2H), 7.80 (d,  $J$  7.8, 2H);  $\delta_{\text{C}}$  21.4, 26.9, 29.5, 34.6, 48.2, 50.7, 51.1, 126.2, 129.3, 141.4, 141.9; Anal. Calc. for C<sub>15</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>3</sub>: C, 52.14; H, 6.71; N, 4.05. Found: C, 51.86; H, 6.44; N, 4.04%.

***N*-(4,6-Dimethyl-1,3-dithian-1-ylidene)toluene-*p*-sulfonamide (11).** White solid, mp 147–149 °C, 59% yield; 33% ee by Daicel chiralpak AS (25% propan-2-ol-hexane); eluent: dichloromethane;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  1139 (SO<sub>2</sub>), 1393 (SO<sub>2</sub>);  $\delta_{\text{H}}$  1.24 (d,  $J$  6.9, 6H), 1.87–2.02 (m, 1H), 2.39 (s, 3H), 2.35–2.40 (m, 1H), 2.99–3.19 (m, 2H), 4.02 (s, 2H), 7.24 (d,  $J$  8.2, 2H), 7.79 (d,  $J$  8.2, 2H);  $\delta_{\text{C}}$  17.1, 20.0, 21.4, 38.3, 45.3, 49.0, 56.6, 126.2, 129.2, 141.2, 141.8; Anal. Calc. for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>3</sub>: C, 49.2; H, 6.03; N, 4.41. Found: C, 49.20; H, 5.98; N, 4.32%.

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