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# Diastereoselective oxidation of menthyl arenesulfenates to sulfinates and access to enantioenriched aryl methyl sulfoxides

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**Abstract:** Three aryl methyl sulfoxides were prepared via the following sequence: synthesis of the menthyl arenesulfenate from the corresponding thiol, diastereoselective oxidation leading to the sulfinate, then reaction with a Grignard reagent. The aryl moiety was substituted with a methyl ester on the ortho position or a nitro group on the ortho or the para position. The sulfenate esters were obtained in fair to excellent yield (42-

Four different oxidizing agents were tested to obtain the corresponding sulfinate esters with diastereomeric excesses (de) ranging from 10 to 48%. After separation of the diastereomers and reaction with methyl Grignard reagent, two enantiopure sulfoxides, and one enantioenriched sulfoxide (32% ee) were obtained.

## Introduction

The interest of tri-coordinated sulfur derivatives and especially sulfoxides has successfully mutated from purely academic research to synthetic applications these last decades (Wojaczyńska and Wojaczyński 2010; Otocka et al. 2017; Wojaczyńska and Wojaczyński 2020). This success is mainly due to the discovery in the 1980s of the use of sulfoxides as efficient chiral auxiliaries for asymmetric synthesis. For example, enantiopure sulfoxides have found many applications in chiral induction (Fernández and Khair 2003), asymmetric catalysis (Pellissier 2006; Han et al. 2018), and drug design, with the well-known Esomeprazole or its derivatives (Cotton et al. 2000; Bentley 2005; O'Mahony et al. 2011), **Sulforaphane and its analogs** (Kielbasiński et al. 2014).

Some years ago, we developed an innovative access to enantiopure *ortho*-phosphorylated phenylsulfoxides, by using, as the key step, an asymmetric oxidation of sulfenates to sulfinates (Hamel et al. 2005; Abrunhosa et al. 2005). *ortho*-Phosphorylated phenylsulfinate esters have been extensively studied by the groups of Drabowicz and Mikołajczyk, and such structures have found applications as mono- or bidentate ligands for the preparation of cisplatin derivatives (Laforgia et al. 2004, 2005; Mauger et al. 2000; Hamel et al. 2013). In this work, we demonstrated the potential of this approach by its extension to other arenesulfenate substrates, bearing an electron-withdrawing group (i.e. nitro or carboxylic ester) in the *ortho* or *para* position of the aryl moiety.

## Materials and Methods

Reactions were carried out under nitrogen atmosphere. THF was purified with a PURESOLV™ apparatus developed by Innovative Technology Inc. Triethylamine (Et<sub>3</sub>N) was distilled over calcium hydride (CaH<sub>2</sub>). Carbon tetrachloride CCl<sub>4</sub> was distilled over phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) and stored over CaCl<sub>2</sub> under a nitrogen atmosphere. The synthesis of methyl thiosalicylate was performed according to a published procedure (yield 83%; lit. 97% as the crude material (Hamel et al. 2005)).

NMR spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>), unless otherwise stated on either a 250 MHz or 400 MHz NMR spectrometer. Chemical shifts  $\delta$  were indicated in ppm using tetramethylsilane (TMS) as the internal standard. <sup>13</sup>C {<sup>1</sup>H} NMR spectra were recorded at 62.9 or 100.6 MHz. Mass spectra were obtained on a GC/MS Saturn 2000 or on a Waters QTOF micro. Optical rotation values were measured on a Perkin–Elmer 241 automatic polarimeter; specific rotation and concentration are given in deg cm<sup>3</sup> g<sup>-1</sup> dm<sup>-1</sup> and g cm<sup>-3</sup>, respectively. IR spectra were recorded with a Perkin–Elmer 16 PC FT-IR instrument. Satisfactory analytical data were obtained using a THERMOQUEST NA 2500 instrument. Thin layer chromatography (TLC) was performed on silica gel 60 F<sub>254</sub>, with UV detection or potassium permanganate solution (5% aqueous) staining. Flash chromatography was achieved on silica gel columns (40 – 63  $\mu$ m) using nitrogen pressure.

## General procedure for the synthesis of sulfenate esters 1a-c.

Sulfonyl chloride (1.3 equiv, 9.5 mmol) was slowly added to a previously stirred solution of arenethiol (1 equiv, 7.3 mmol) in dichloromethane (20mL). The resulting solution was stirred for 30 min at room temperature. After evacuation of the solvent and gases, tetrahydrofuran (THF, 25 mL) was added followed by (–)-menthol (1 equiv, 7.3 mmol) and trifluoroacetic anhydride (0.1 equiv, 0.73 mmol). After cooling to –78 °C, triethylamine (2 equiv., 14.6 mmol) was added. The reaction mixture was allowed to reach room temperature, stirred for one hour and then hydrolyzed with a solution of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 5% aqueous). The aqueous layer was extracted with diethyl ether. The combined extracts were washed with a 5% solution of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) followed by brine, dried over magnesium sulfate (MgSO<sub>4</sub>) and concentrated. The resulting oil was purified by silica gel chromatography.

#### Typical oxidation procedure for the synthesis of sulfinate esters **2a-c**.

##### With *m*CPBA

Sulfinate ester **1** (1 equiv, 0.5 mmol) was oxidized by the addition of *meta*-chloroperbenzoic acid (*m*CPBA, 1 equiv, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at –78 °C, after which the reaction was allowed to reach room temperature. The solvent was evaporated and the crude sulfinate **2** directly purified by silica gel chromatography.

##### With NBS/H<sub>2</sub>O

*N*-Bromosuccinimide (NBS, 1 equiv., 1 mmol) was added portionwise to a stirred solution of menthyl sulfenate **1** (1 equiv., 1 mmol) in a mixture of acetonitrile and water 2:1. The concentration of sulfenate ester was ca. 50 mM. After addition of all the NBS, stirring was continued for 2 h and the mixture was quenched by adding a solution of H<sub>2</sub>SO<sub>4</sub> (5% aqueous). The aqueous layer was extracted three times with dichloromethane. The organic layer was successively washed out with a solution of potassium carbonate (5% aqueous) and sodium thiosulfate (5% aqueous) in water. After drying and evaporation of the organic solvent, the crude extract, whose purity was usually satisfactory as shown by the NMR spectrum, was purified on a silica gel column with pentane–ethyl acetate as the eluent to obtain menthyl sulfinate **2**.

##### With (+)- or (–)-(8,8-dichlorocamphorylsulfonyl)oxaziridine

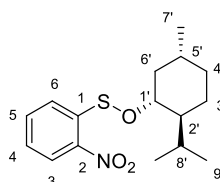
The chiral (8,8-dichlorocamphorylsulfonyl)oxaziridine (1 equiv, 0.5 mmol) was added portionwise to a stirred solution of sulfenate ester **1** (1 equiv, 0.5 mmol) in carbon tetrachloride under a nitrogen atmosphere. After complete conversion, the solvent was evaporated and the residue dissolved in pentane. The mixture was filtered and washed once with pentane. The sulfinate was further purified on silica gel chromatography when necessary.

##### Grignard reaction with sulfinate esters

Methyl magnesium bromide (MeMgBr, 1.1 equiv, 1.21 mmol) was added dropwise to a stirred solution of menthyl sulfinate **2a-c** (1 equiv, 1 mmol) in 10 mL of diethyl ether at 0 °C. The resulting

mixture was stirred for 1 h at room temperature, after which 10 mL of a 5% aqueous solution of sulphuric acid was added and the aqueous layer extracted with diethyl ether. The organic extracts were washed with a solution of potassium carbonate (5% aqueous) followed by brine, dried over MgSO<sub>4</sub>, filtered, evaporated and the mixture was further purified on silica gel chromatography, yielding **3a-c**. No scale-up experiment was performed in this study.

Numerical identifications of carbon atoms for compounds listed below are arbitrary and given only for helping the description of NMR spectra, e.g. with compound **1b**.



(–)-Menthyl 2-(methoxycarbonyl)benzenesulfenate **1a**. 78% yield; R<sub>f</sub> 0.63 (pentane/ethyl acetate 90:10). White solid; mp 69 °C; [α]<sub>D</sub><sup>20</sup> –53.9 (c 0.9 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (250 MHz, δ): 7.97 (dd, 1H, <sup>3</sup>J = 7.8, <sup>4</sup>J = 1.3, H<sub>6</sub>), 7.79 (d, 1H, <sup>3</sup>J = 8.2, H<sub>3</sub>), 7.54 (dt, 1H, <sup>3</sup>J = 7.2, <sup>4</sup>J = 1.4, H<sub>4</sub>), 7.14 (dt, 1H, <sup>3</sup>J = 7.8, <sup>4</sup>J = 1.0, H<sub>5</sub>), 3.92 (s, 3H, CH<sub>3</sub>), 3.54 (dt, <sup>3</sup>J = 10.6, <sup>3</sup>J = 4.1, H<sub>1'</sub>), 2.42 – 2.48 (m, 1H, H<sub>6</sub>), 2.27 – 2.41 (m, 1H, H<sub>3</sub>), 1.61 – 1.72 (m, 2H, H<sub>3'</sub>, H<sub>5</sub>), 1.41 – 1.58 (m, 1H, H<sub>4</sub>), 1.23 – 1.40 (m, 2H, H<sub>4</sub>, H<sub>6</sub>), 1.01 – 1.14 (m, 1H, H<sub>8</sub>), 0.97 (d, 3H, <sup>3</sup>J = 7.0, H<sub>7</sub>), 0.90 – 0.97 (m, 1H, H<sub>3</sub>), 0.88 (d, 6H, <sup>3</sup>J = 6.4, H<sub>9</sub>); <sup>13</sup>C NMR (62.9 MHz, δ): 167.4 (C=O), 151.2 (C<sub>2</sub>), 132.7 (C<sub>4</sub>), 130.3 (C<sub>6</sub>), 123.3 (C<sub>3</sub>), 121.3 (C<sub>5</sub>), 121.0 (C<sub>1</sub>), 86.6 (C<sub>1'</sub>), 52.4 (CH<sub>3</sub>O), 49.0 (C<sub>2</sub>), 41.0 (C<sub>6</sub>), 34.3 (C<sub>4</sub>), 31.9 (C<sub>5</sub>), 25.6 (C<sub>8</sub>), 23.3 (C<sub>3</sub>), 22.2 (C<sub>7</sub>), 21.1 (C<sub>9</sub>), 16.1 (C<sub>9</sub>); IR (KBr) ν = 1690 (C=O st), 757; EIMS (*m/z* (%)): 322 (1) [*M*<sup>+</sup>]; 184 (85), 167 (26), 152 (100), 83 (33), 69 (15), 55 (30), 41 (15), Anal. calcd. for C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>S: C 67.04, H 8.13, S 9.94, found: C 66.47, H 8.20, S 10.47.

(–)-Menthyl 2-nitrobenzenesulfenate **1b**; 82% yield; R<sub>f</sub> 0.74 (pentane/ethyl acetate 90:10). Yellow solid; mp 91 °C; [α]<sub>D</sub><sup>20</sup> –17.0 (c 1 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, δ): 8.28 (dd, 1H, <sup>3</sup>J = 8.4, <sup>4</sup>J = 1.3, H<sub>3</sub>), 7.90 (dd, 1H, <sup>3</sup>J = 8.2, <sup>4</sup>J = 1.0, H<sub>6</sub>), 7.66 (dt, 1H, <sup>3</sup>J = 7.1, <sup>4</sup>J = 1.3, H<sub>5</sub>), 7.26 (dt, 1H, <sup>3</sup>J = 7.3, <sup>4</sup>J = 1.1, H<sub>4</sub>), 3.61 (dt, 1H, <sup>3</sup>J = 10.7, <sup>3</sup>J = 4.2, H<sub>1'</sub>), 2.40 (ddd, 1H, <sup>3</sup>J = 7.0, <sup>3</sup>J = 6.9, <sup>4</sup>J = 2.7, H<sub>6</sub>), 2.25 – 2.28 (m, 1H, H<sub>3</sub>), 1.64 – 1.72 (m, 2H, H<sub>3</sub>, H<sub>5</sub>), 1.46 – 1.52 (m, 2H, H<sub>2</sub>, H<sub>4</sub>), 1.30 – 1.42 (m, 2H, H<sub>4</sub>, H<sub>6</sub>), 1.06 – 1.14 (m, 1H, H<sub>8</sub>), 0.99 (d, 3H, <sup>3</sup>J = 7.0, H<sub>7</sub>), 0.90 (d, 3H, <sup>3</sup>J = 6.5, H<sub>9</sub>), 0.88 (d, 3H, <sup>3</sup>J = 6.9, H<sub>9</sub>); <sup>13</sup>C NMR (62.9 MHz, δ): 148.0 (C<sub>2</sub>), 134.1 (C<sub>1</sub>), 134.0 (C<sub>4</sub>), 125.1 (C<sub>5</sub>), 124.3 (C<sub>6</sub>), 123.1 (C<sub>3</sub>), 87.0 (C<sub>1'</sub>), 49.0 (C<sub>2</sub>), 41.0 (C<sub>6</sub>), 34.2 (C<sub>4</sub>), 31.8 (C<sub>5</sub>), 25.7 (C<sub>8</sub>), 23.3 (C<sub>3</sub>), 22.1 (C<sub>7</sub>), 21.0 (C<sub>9</sub>), 16.1 (C<sub>9</sub>); IR (KBr) ν = 1504 (NO<sub>2</sub>), 734; EIMS (*m/z* (%)): 332 (100) [*M* + Na]<sup>+</sup>, 194 (32); HRMS (ESI, *m/z*): [*M* + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>NaS: 332.1296, found 332.1315; Anal. calcd. for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>S: C 62.11, H 7.50; found C 62.03, H 7.99.

(–)-Menthyl 4-nitrobenzenesulfenate **1c**; 42% yield; R<sub>f</sub> 0.78 (pentane/ethyl acetate 90:10). Yellow solid; mp 70 °C; [α]<sub>D</sub><sup>20</sup> –162.3 (c 1.15 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, δ): 8.18 (dt, 2H, <sup>3</sup>J = 9.0, <sup>4</sup>J = 2.0, H<sub>3</sub>), 7.31 (dt, 2H, <sup>3</sup>J = 9.0, <sup>4</sup>J = 1.9, H<sub>2</sub>), 3.53 (dt, 1H, <sup>3</sup>J = 10.7, <sup>3</sup>J = 4.3, H<sub>1'</sub>), 2.22 – 2.37 (m, 2H, H<sub>3</sub>, H<sub>6</sub>), 1.62 – 1.71 (m, 2H, H<sub>4</sub>, H<sub>5</sub>), 1.30 – 1.49 (m, 2H, H<sub>2</sub>, H<sub>3</sub>), 0.97 (d, 3H, <sup>3</sup>J = 7.0, H<sub>7</sub>), 0.94 – 1.07 (m, 2H, H<sub>6</sub>, H<sub>8</sub>), 0.91 (d, 3H, <sup>3</sup>J = 6.6, H<sub>9</sub>), 0.80 – 0.87 (m, 1H, H<sub>4</sub>), 0.82 (d, 3H, <sup>3</sup>J = 7.0, H<sub>9</sub>); <sup>13</sup>C NMR (62.9 MHz,

$\delta$ ): 151.9 (C<sub>4</sub>), 144.1 (C<sub>1</sub>), 123.0 (C<sub>6</sub>), 119.4 (C<sub>5</sub>), 87.9 (C<sub>1</sub>), 47.8 (C<sub>2</sub>), 39.9 (C<sub>6</sub>), 33.0 (C<sub>4</sub>), 30.8 (C<sub>5</sub>), 24.5 (C<sub>8</sub>), 22.2 (C<sub>3</sub>), 21.1 (C<sub>7</sub>), 20.0 (C<sub>9</sub>), 15.0 (C<sub>9</sub>); IR (KBr)  $\nu$  = 1576, 1507 (NO<sub>2</sub>), 1337; HRMS (ESI,  $m/z$ ): [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>NaS: calcd 332.1296, found 332.1303.

(-)-Menthyl (S)-2-(methoxycarbonyl)benzenesulfinate (**S-2a**); 68% yield; R<sub>f</sub> 0.3 (pentane/diethyl ether 70:30). White solid; mp 146 °C; [α]<sub>D</sub><sup>20</sup> -360.0 (c 0.6, CHCl<sub>3</sub>); Lit. (Klunder and Sharpless 1987): -348.6 (c 1.18, acetone); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.26 (dd, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.2, H<sub>6</sub>), 7.99 (dd, 1H, <sup>3</sup>J = 7.6, <sup>4</sup>J = 1.2, H<sub>3</sub>), 7.71 (dt, 1H, <sup>3</sup>J = 7.0, <sup>4</sup>J = 1.2, H<sub>4</sub>), 7.54 (dt, 1H, <sup>3</sup>J = 7.1, <sup>4</sup>J = 1.2, H<sub>5</sub>), 4.08 (dt, 1H, <sup>3</sup>J = 10.8, <sup>3</sup>J = 4.4, H<sub>1</sub>), 3.91 (s, 3H, CH<sub>3</sub>), 2.28 – 2.31 (m, 1H, H<sub>6</sub>), 2.03 – 2.07 (m, 1H, H<sub>3</sub>), 1.60 – 1.64 (m, 2H, H<sub>3</sub>, H<sub>5</sub>), 1.33 – 1.47 (m, 1H), 1.23 – 1.28 (m, 1H), 0.94 – 1.14 (m, 2H), 0.91 (d, 3H, <sup>3</sup>J = 6.4, H<sub>7</sub>), 0.80 (d, 3H, <sup>3</sup>J = 6.8, H<sub>9</sub>), 0.76 – 0.84 (m, 1H, H<sub>3</sub>), 0.67 (d, 3H, <sup>3</sup>J = 7.2, H<sub>9</sub>); <sup>13</sup>C NMR (62.9 MHz,  $\delta$ ): 166.0 (C=O), 148.7 (C<sub>2</sub>), 133.5 (C<sub>4</sub>), 131.7 (C<sub>6</sub>), 131.1 (C<sub>3</sub>), 128.4 (C<sub>5</sub>), 124.9 (C<sub>1</sub>), 80.4 (C<sub>1</sub>), 52.9 (CH<sub>3</sub>O), 48.3 (C<sub>2</sub>), 42.5 (C<sub>6</sub>), 34.4 (C<sub>4</sub>), 32.1 (C<sub>5</sub>), 25.6 (C<sub>8</sub>), 23.6 (C<sub>3</sub>), 22.5 (C<sub>7</sub>), 21.2 (C<sub>9</sub>), 15.9 (C<sub>9</sub>).

(-)-Menthyl (S)-2-nitrobenzenesulfinate (**S-2b**); 78% yield (for both diastereomers); R<sub>f</sub> 0.47 (pentane/diethyl ether 60:40). Clear yellow solid; [α]<sub>D</sub><sup>20</sup> -413.9 (c 1.95, CHCl<sub>3</sub>); Lit. (Hajipour and Islami 2000): -447.3 (c 1.5, acetone); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.36 (dd, 1H, <sup>3</sup>J = 7.6, <sup>4</sup>J = 1.2, H<sub>6</sub>), 8.23 (dd, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.2, H<sub>3</sub>), 7.92 (dt, 1H, <sup>3</sup>J = 7.6, <sup>4</sup>J = 1.2, H<sub>4</sub>), 7.73 (dt, 1H, <sup>3</sup>J = 7.6, <sup>4</sup>J = 1.6, H<sub>5</sub>), 4.16 (dt, 1H, <sup>3</sup>J = 10.8, <sup>3</sup>J = 4.4, H<sub>1</sub>), 2.34 – 2.39 (m, 1H, H<sub>6</sub>), 2.03 – 2.06 (m, 1H, H<sub>3</sub>), 1.65 – 1.71 (m, 2H, H<sub>2</sub>, H<sub>6</sub>), 1.45 – 1.55 (m, 2H, H<sub>4</sub>), 1.04 – 1.17 (m, 2H, H<sub>5</sub>, H<sub>8</sub>), 0.98 (d, 3H, <sup>3</sup>J = 6.8, H<sub>7</sub>), 0.82 (d, 3H, <sup>3</sup>J = 7.2, H<sub>9</sub>), 0.82 – 0.88 (m, 1H, H<sub>3</sub>), 0.76 (d, 3H, <sup>3</sup>J = 6.8, H<sub>9</sub>); <sup>13</sup>C NMR (100.6 MHz,  $\delta$ ): 145.7 (C<sub>2</sub>), 142.8 (C<sub>1</sub>), 134.9 (C<sub>4</sub>), 132.4 (C<sub>5</sub>), 126.3 (C<sub>6</sub>), 125.0 (C<sub>3</sub>), 81.1 (C<sub>1</sub>), 48.0 (C<sub>2</sub>), 41.4 (C<sub>6</sub>), 34.0 (C<sub>4</sub>), 31.9 (C<sub>5</sub>), 25.3 (C<sub>8</sub>), 23.3 (C<sub>3</sub>), 22.2 (C<sub>7</sub>), 20.9 (C<sub>9</sub>), 15.6 (C<sub>9</sub>); IR (KBr)  $\nu$  = 1531 (NO<sub>2</sub>), 1456, 1349, 1137, 949, 757; EIMS ( $m/z$  (%)): 348 (11) [M + Na], 228 (9), 210 (100); HRMS (ESI,  $m/z$ ): [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>4</sub>NaS: 348.1245, found 348.1247.

(-)-Menthyl (R)-2-nitrobenzenesulfinate (**R-2b**); R<sub>f</sub> 0.38 (pentane/diethyl ether 60:40). Clear yellow solid [α]<sub>D</sub><sup>20</sup> +266.2 (c 1.42 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.32 (dd, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.6, H<sub>6</sub>), 8.23 (dd, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.2, H<sub>3</sub>), 7.90 (dt, 1H, <sup>3</sup>J = 7.6, <sup>4</sup>J = 1.2, H<sub>4</sub>), 7.72 (dt, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.6, H<sub>5</sub>), 4.26 (dt, 1H, <sup>3</sup>J = 10.8, <sup>3</sup>J = 4.4, H<sub>1</sub>), 2.22 – 2.28 (m, 1H, H<sub>6</sub>), 1.78 – 1.85 (m, 1H, H<sub>3</sub>), 1.62 – 1.66 (m, 2H, H<sub>2</sub>, H<sub>6</sub>), 1.41 – 1.51 (m, 1H, H<sub>4</sub>), 1.18 – 1.33 (m, 2H, H<sub>5</sub>, H<sub>8</sub>), 0.99 – 1.10 (m, 1H, H<sub>4</sub>), 0.91 (d, 3H, <sup>3</sup>J = 6.8, H<sub>7</sub>), 0.76 – 0.84 (m, 1H, H<sub>3</sub>), 0.78 (d, 3H, <sup>3</sup>J = 6.8, H<sub>9</sub>), 0.74 (d, 3H, <sup>3</sup>J = 6.8, H<sub>9</sub>); <sup>13</sup>C NMR (100.6 MHz,  $\delta$ ): 145.3 (C<sub>2</sub>), 142.9 (C<sub>1</sub>), 135.0 (C<sub>4</sub>), 132.5 (C<sub>5</sub>), 126.1 (C<sub>6</sub>), 125.0 (C<sub>3</sub>), 83.1 (C<sub>1</sub>), 48.4 (C<sub>2</sub>), 43.4 (C<sub>6</sub>), 33.9 (C<sub>4</sub>), 31.8 (C<sub>5</sub>), 25.0 (C<sub>8</sub>), 23.1 (C<sub>3</sub>), 22.1 (C<sub>7</sub>), 21.0 (C<sub>9</sub>), 15.4 (C<sub>9</sub>).

(-)-Menthyl 4-nitrobenzenesulfinate **2c** (mixture of diastereomers); 75% yield; R<sub>f</sub> 0.2 (pentane/ethyl acetate 90:10). White solid; mp 75 °C; [α]<sub>D</sub><sup>20</sup> -100.7 (c 0.4, CHCl<sub>3</sub>); for a de 32%, dr 34/66; Lit. (Hajipour and Islami 2000): -438 (c 1.2, acetone); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.39 (t, 2H, <sup>3</sup>J = 8.8, H<sub>3</sub>), 7.92 (d, 2H, <sup>3</sup>J = 8.8, H<sub>2</sub>), 4.23 & 4.28 (dt, 1H, <sup>3</sup>J = 10.7, <sup>3</sup>J = 4.5, H<sub>1</sub>), 0.72 – 2.36 (m, 20H); <sup>13</sup>C NMR (62.9 MHz,  $\delta$ ): 152.4, 150.2, 126.6, 126.1, 124.4, 124.3, 83.7, 81.7, 48.8, 48.0, 43.7, 42.9, 34.0, 33.9, 32.0, 31.9, 25.8, 25.5, 23.3, 23.2, 22.2, 22.0, 21.0, 20.9, 15.8, 15.6; IR (KBr)

$\nu$  = 1529, 1346, 1141, 763; EIMS ( $m/z$  (%)): 326 (1) [M<sup>+</sup>], 170 (7), 139 (33), 83 (100), 69 (19), 55 (48).

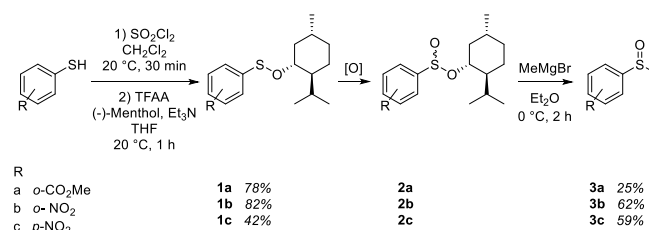
(R)-(+)-Methyl 2-methylsulfinylbenzoate (**R-3a**); Yield 25%; R<sub>f</sub> 0.2 (ethyl acetate/pentane 80:20). White solid; [α]<sub>D</sub><sup>20</sup> +139.0 (c 1, CHCl<sub>3</sub>); Lit. (Pitchen et al. 1984), for 60% ee: +84.0 (c 0.4, acetone); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.32 (dd, 1H, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.2), 8.09 (dd, 1H, <sup>3</sup>J = 7.8, <sup>4</sup>J = 1.2), 7.84 (dt, 1H, <sup>3</sup>J = 8.0, <sup>4</sup>J = 1.3), 7.58 (dt, 1H, <sup>3</sup>J = 7.1, <sup>4</sup>J = 1.2), 3.96 (s, 3H, CH<sub>3</sub>O), 2.85 (s, 3H, CH<sub>3</sub>).

(R)-(+)-Methyl 2-nitrophenyl sulfoxide (**R-3b**); Yield 62%; R<sub>f</sub> 0.2 (ethyl acetate). White solid; [α]<sub>D</sub><sup>20</sup> +164.6 (c 1, CHCl<sub>3</sub>); Lit. (Brunel and Kagan 1996), for 75% ee: +118.5. <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.03 (d, 1H, <sup>3</sup>J = 8.0), 6.92 – 7.01 (m, 2H), 6.62 (t, 1H, <sup>3</sup>J = 7.1), 2.22 (s, 3H, CH<sub>3</sub>).

Methyl 4-nitrophenyl sulfoxide **3c**; Yield 59%; R<sub>f</sub> 0.2 (ethyl acetate). White solid; [α]<sub>D</sub><sup>20</sup> +50.0 (c 1 in CHCl<sub>3</sub>); Lit. (Brunel et al. 1995), for 99.3% ee: +156.9 (c 0.75 in CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz,  $\delta$ ): 8.36 (d, 2H, <sup>3</sup>J = 8.2), 7.80 (d, 2H, <sup>3</sup>J = 7.9), 2.28 (s, 3H, CH<sub>3</sub>).

## Results and Discussion

In order to demonstrate its potential, the sequence we described earlier Hamel et al. 2005) has been extended to other substrates. Thus, aryl methyl sulfoxides where the aromatic ring is functionalized with either a nitro (in *ortho* or *para* position) or an *ortho*-methoxycarbonyl groups were prepared following this strategy. The overall reaction sequence is described in Scheme 1. Some of the diastereomerically pure sulfinate esters **2a**, **b** and **c** have previously been reported by other groups. **2a** was prepared starting from the corresponding sulfinyl chloride which reacts with menthol, with a low diastereoselectivity (Klunder and Sharpless 1987). Compounds **2b** and **2c** were obtained from the reaction of *ortho*- or *para*-nitrophenyldisulfide with menthol in the presence of lead tetraacetate, with a moderate diastereomeric excess (Hajipour and Islami 2000). Another method consists in reacting the sulfonyl chloride and the alcohol in the presence of trimethylphosphite in dichloromethane (Lee et al. 1994) or under solid state conditions (Hajipour and Islami 1999). Crystal structure of (**S-2a**) has even been assigned, with a hydrogen bond linking the oxygen of the sulfinate ester with the hydrogen located in the *para* position of the methoxycarbonyl group (Altamura et al. 2013).



**Scheme 1.** Synthesis of sulfoxides **3a-c** from the corresponding arylthiols.

In the literature the three sulfoxides **3a-c** have been prepared in an (almost) enantiopure form. Some generic methods for their preparation involve either the enantioselective oxidation of the corresponding sulfide, catalyzed for instance with an organometallic chiral complex, with an enzyme, or via the synthesis of chiral sulfinate esters.

Table 1 gives some examples of the oxidation of the prochiral sulfide leading to the sulfoxides **3a-c**. These examples were sorted so that both enantiomeric excess and chemical yield were optimum.

According to the description of the synthesis given in Scheme 1, we started from commercial aromatic thiols. Methyl thiosalicylate was prepared according to a published reaction (Sasaki et al. 1991). The thiols were first converted into sulphenyl chlorides, then reacted with (–)-menthol in the presence of triethylamine and a catalytic amount of trifluoroacetic acid anhydride (TFAA). Enantiopure menthyl sulfenate esters were thus obtained in good yields, from 50 up to 78%.

The second step consists in the diastereoselective oxidation to afford the menthyl sulfinates. Various methods can be used for

the oxidation of sulfenate esters to their corresponding sulfinates. We used both achiral and chiral oxidants, the two chiral compounds being the (+)- and the (–)-isomers of (8,8-dichlorocamphorylsulfonyl)oxaziridine (hereafter, designated as (+)-Ox and (–)-Ox, for the sake of clarity), whereas simple oxidants were either *m*CPBA or the couple NBS/H<sub>2</sub>O. Oxidations of **1b** and **1c** were performed only with achiral oxidants. Diastereoselectivity was measured following the <sup>1</sup>H NMR chemical shift from the CH-O of the menthyl moiety. The results are summarized in Table 2.

**Table 1. Some examples of selective sulfide oxidation leading to enantiopure sulfoxides 3a-c.**

Sulfoxide	Config.	Yield (%)	ee (%)	Method	Ref.
<b>3a</b>	( <i>R</i> )	53	99	Ti( <i>O</i> - <i>i</i> -Pr) <sub>4</sub> /( <i>R</i> , <i>R</i> )-DET 1:4	De Sio et al. 2010
<b>3a</b>	( <i>R</i> )	95	80	Mn(OTf) <sub>2</sub> /porphyrin deriv./H <sub>2</sub> O <sub>2</sub>	Dai et al. 2014
<b>3a</b>	( <i>S</i> )	n.d.	82	Myoglobin active site mutants L29H/H64L	Ozaki et al. 1999
<b>3b</b>	( <i>R</i> )	90	92	H <sub>2</sub> O <sub>2</sub> , chiral amino alcohol, VO(acac) <sub>2</sub>	Aydin 2013
<b>3b</b>	( <i>S</i> )	84	99	H <sub>2</sub> O <sub>2</sub> , Al salalen	Matsumoto et al. 2008
<b>3c</b>	( <i>R</i> )	95	99.5	H <sub>2</sub> O <sub>2</sub> , MgSO <sub>4</sub> , chiral Brønsted acid	Liao et al. 2012
<b>3c</b>	( <i>S</i> )	92	92	H <sub>2</sub> O <sub>2</sub> , Ti Salen	Saito et al. 2001
<b>3c</b>	( <i>S</i> )	66	96	<i>N,N'</i> -dioxide-iron(III) complex	Wang et al. 2020

**Table 2. Diastereoselective oxidation of arenesulfenate esters 1**

Entry	Sulfenate	Oxidant	Conditions	Sulfinate	Yield (%)	dr	de (%)
1	<b>1a</b>	NBS/H <sub>2</sub> O	CH <sub>3</sub> CN/H <sub>2</sub> O, 20 °C, 2 h	<b>2a</b>	68	69:31	38
2	<b>1a</b>	<i>m</i> CPBA	CH <sub>2</sub> Cl <sub>2</sub> , -78 → 20 °C	<b>2a</b>	90	45:55	10
3	<b>1a</b>	(+)-Ox	CCl <sub>4</sub> , 20 °C, 15 d	<b>2a</b>	56	39:61	22
4	<b>1a</b>	(–)-Ox	CCl <sub>4</sub> , 20 °C, 15 d	<b>2a</b>	63	65:35	30
5	<b>1b</b>	NBS/H <sub>2</sub> O	CH <sub>3</sub> CN/H <sub>2</sub> O, 20 °C, 2 h	<b>2b</b>	6	72:28	44
6	<b>1b</b>	<i>m</i> CPBA	CH <sub>2</sub> Cl <sub>2</sub> , -78 → 20 °C	<b>2b</b>	78	42:58	16
7	<b>1c</b>	NBS/H <sub>2</sub> O	CH <sub>3</sub> CN/H <sub>2</sub> O, 20 °C, 2 h	<b>2c</b>	69	74:26	48
8	<b>1c</b>	<i>m</i> CPBA	CH <sub>2</sub> Cl <sub>2</sub> , -78 → 20 °C	<b>2c</b>	75	34:66	32

**Table 3. Transformation of arenesulfinate esters 2 into enantioenriched sulfoxides 3**

Entry	Sulfinate	dr (config.) <sup>a</sup>	Sulfoxide	Yield (%)	ee (%) (config.) <sup>a</sup>	Measured [α] <sub>D</sub> <sup>20</sup>
1	<b>2a</b>	100:0 <sup>b</sup> ( <i>S</i> )	<b>3a</b>	25	100 ( <i>R</i> )	+84.0 (c 1, CHCl <sub>3</sub> )
2	<b>2b</b>	100:0 <sup>b</sup> ( <i>S</i> )	<b>3b</b>	62	100 ( <i>R</i> )	+164.6 (c 1, CHCl <sub>3</sub> )
3	<b>2c</b>	34:66 ( <i>S</i> )	<b>3c</b>	59	32 ( <i>R</i> )	+50.0 (c 1, CHCl <sub>3</sub> )

<sup>a</sup> absolute configuration at sulfur atom

<sup>b</sup> dr after separation of diastereomers

All these oxidations performed smoothly and led to good conversions, but took an unexpected long time when performed with the oxaziridine (up to 15 days). As previously stated, oxidation with NBS/H<sub>2</sub>O couple did not favor the same diastereomer as when performing the oxidation with *m*CPBA (Hamel et al. 2005). For the three sulfinate esters **2**, the observed diastereomeric excess was in the range of 10-48%, so slightly lower than those obtained with *ortho*-phosphorylated menthyl benzenesulfinate (Hamel et al. 2005). Moreover, the best diastereomeric ratio values were obtained when oxidizing compounds **1** with the NBS/H<sub>2</sub>O couple. Surprisingly, the best de was observed with **1c**, suggesting that the position of the substituent had almost no influence on the steric hindrance, the latter being therefore driven by the menthyl moiety. Therefore, one or the other diastereomer can be favored either by using *m*CPBA or NBS/H<sub>2</sub>O or by using (–)- or (+)-menthol.

Starting from the diastereomeric mixtures obtained respectively in entries 2 and 6 from Table 2, the diastereomerically pure major sulfinates **2a** and **2b** have been successfully separated using silica gel chromatography or by separative crystallization in acetone. In the case of **2c** (entry 8, Table 2), the diastereomer separation was not possible. Specific rotation for optically pure compounds **2a** and **2b** are negative with respective values of –360.0 and –453.2 (c 0.6 and 1 in chloroform). These are slightly more negative than reported in the literature with respective [α]<sub>D</sub><sup>20</sup> of –348.6 and –447.7 (c 1.18 (Klunder and Sharpless 1987) and 1.5 in acetone (Hajipour and Islami 2000)). According to the literature, these sulfinate esters have the (*S*) configuration at the sulfur atom.

From the two optically pure sulfinate esters (*S<sub>S</sub>*)-**2a** and (*S<sub>S</sub>*)-**2b** and the optically enriched compound **2c**, the preparation of the

corresponding methyl aryl sulfoxides **3a-c** has been performed. As methylmagnesium bromide is able to attack both the electrophilic sulfur atom and the ester function of a sulfinate, to limit the second undesired process, the reaction was performed at 0 °C with a very slight excess of Grignard reagent. However, a low yield was obtained for **3a** (25%), whereas **3b** and **3c** were isolated with satisfactory yields of 62% and 59%, respectively (Table 3). The comparison of the specific rotation values of the obtained aryl methyl sulfoxides with data from the literature (see in the experimental part), allowed us to assign the absolute (*R*) configuration at sulfur in the three cases. This was expected to be obtained after full inversion of configuration at the sulfur atom from the starting corresponding (*S<sub>S</sub>*)-sulfinates **2a-c** leading to sulfoxides (*R*)-**3a** and (*R*)-**3b** in an optically pure form (entries 1 and 2, Table 3), and (*R*)-**3c** with 32% ee (entry 3, Table 3).

Despite the fact that this method was exemplified on a small number of substrates, the obtained results are encouraging for application on other arylsulfides bearing an electron withdrawing substituent on the aromatic ring. The oxidation of sulfenate esters was performed with simple oxidants such as *m*CPBA or NBS/H<sub>2</sub>O and the asymmetric induction was provided by the cheap enantiopure menthol. Since the chiral induction is provided by the alcohol, one can expect that this strategy should work not only for arylsulfenates but also for alkylsulfenates as well.

## Conclusion

In conclusion, an efficient method for the access to three *ortho* and *para* substituted aryl methyl sulfoxides is described herein.



The diastereoselective oxidation of sulfenate to sulfinate ester is the key step, leading to diastereomeric excesses ranging from 10 to 48%. After separation of the diastereomers and reaction with methyl Grignard, two enantiopure sulfoxides, the (*Rs*)-2-methoxycarbonylphenyl methyl sulfoxide and the (*Rs*)-2-nitrophenyl methyl sulfoxide, and one enantioenriched (32% ee) were obtained.

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## Conflict of interest statement

The Authors declare no conflict of interest.

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