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Asymmetric Chemical Oxidations of Aryl and Alkyl 2-(Trimethylsilyl)ethyl Sulfides

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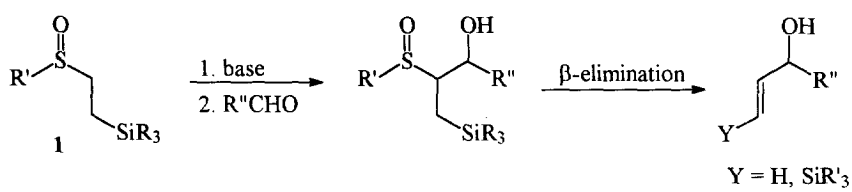
Abstract: A collection of aryl and alkyl 2-(trimethylsilyl)methyl sulfides have been converted to their respective sulfoxides by four different asymmetric oxidizing agents. The chemical yields range from 44-98% while the enantiomeric excesses range from 0-89%. The Davis oxazaziridine (3'*S*,2*R*)-(-)-*N*-(phenylsulfonyl)-(3,3-dichloro-camphoryl)oxaziridine was shown to be superior to the Modified Sharpless Reagent (CHP *and* TBHP) and binaphthol/Ti(*i*PrO)$_4$/TBHP for the oxidation of these sulfides. The effectiveness of the oxaziridine is interpreted with reference to Davis' active site model for the oxidant.

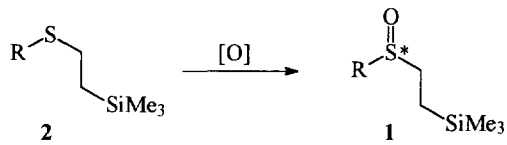
The synthetic value and diversity of the 2-(trimethylsilyl)ethyl sulfur group has been demonstrated in a collection of different transformations.[1-4] For instance, when the 2-(trimethylsilyl)ethyl group is attached to a sulfinyl unit, the substrates can undergo clean C-S bond cleavage under oxidative conditions to afford sulfinyl chlorides.[2] 2-(Trimethylsilyl)ethyl sulfoxides (**1**) can also be elaborated through deprotonation and substitution α to the sulfoxide.[3,4] The sulfur group can subsequently be eliminated through thermolysis (Scheme 1). This sort of chemistry proceeds with retention of optical integrity when the sulfoxide substrates are optically enriched.[4] In those instances, the researchers used Andersen chemistry to make enantiopure *t*-butyl and *p*-tolyl methyl sulfoxides and attached a 2-(trimethylsilyl)methyl unit to generate the requisite optically active starting materials.[4] This synthetic approach is excellent when starting materials are commercially available. In cases where one may desire alkyl or aryl groups other than *p*-tolyl opposite the 2-(trimethylsilyl)ethyl group, for other synthetic uses, then the preparation of the optically enriched 2-(trimethylsilyl)ethyl may require several steps and a tedious diastereomer separation.



Scheme 1

Since we have utilized the radical addition of thiols to vinyltrimethylsilane as a rapid means of preparing a large collection of 2-(trimethylsilyl)ethyl sulfides (**2**),[2] it seemed logical to find an asymmetric oxidative route to the corresponding sulfoxides. If successful, the synthesis would provide optically enriched 2-

(trimethylsilyl)ethyl sulfoxides (**1**) in only two reactions thereby by-passing the large number of synthetic and purification steps that the Andersen or a related procedure may require.



Scheme 2

Four different asymmetric chemical oxidation procedures were performed and the results are listed in Table 1 (Scheme 2). Finding a suitable chiral shift reagent or chiral solvating agent for the NMR determination of the enantiomeric excesses (ee's) of the sulfoxides proved difficult. Various europium and ytterbium shift reagents gave a large amount of line broadening and consequently no clear separation of diastereomeric peaks could be observed on either a 200 or 400 MHz NMR instrument.[5] Similarly (*R*)-(-)-*N*-(3,5-dinitrobenzoyl)-1-phenylethylamine,[6] (*R*)-(+)-1,1'-bi-2-naphthol[7] and (*S*)-(+)-methoxyphenylacetic acid did not form useful diastereomeric complexes with the sulfoxides. It was eventually established that one molar equivalent of commercially available (*R*)-2,2,2-fluoro-1-(9-anthryl)ethanol could separate the trimethylsilyl singlets *by 15-28 Hz* with minimal line-broadening. The standard conditions involved adding the chiral agent to 5-10 mg of substrate in CCl_4. Under these conditions, Pirkle's model[8] suggests that the TMS group of an (*S*)-2-(trimethylsilyl)ethyl sulfoxide whose other group (R in Fig. 1) is of higher priority than 2-(trimethylsilyl)ethyl will be shielded by the anthryl group and hence will be shifted upfield (Figure 1, complex **A**). Similarly in complex **B** of the (*R*)-sulfoxide, the TMS methyls are expected to experience little of the aromatic ring anisotropy since they are directed away from the anthryl unit. The (*R*) and (*S*) assignments made herein are based on the behavior of the TMS methyls in the presence of the solvating agent. Furthermore, in most cases, the sulfoxide configurations procured from the NMR experiments are consistent with expectations based on transition state models for the various oxidants.[9,10] The ee's reported in Table 1 have been determined through the method described and in some cases are accompanied by ee's obtained by optical rotation measurements with comparison to the literature.[4,11]

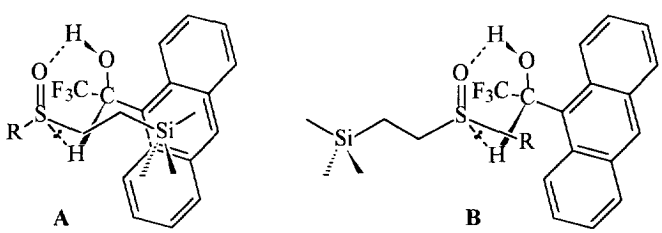
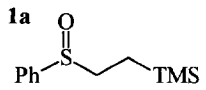
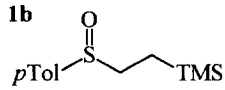
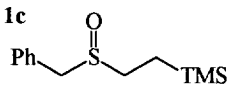
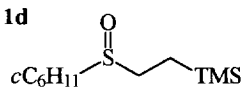
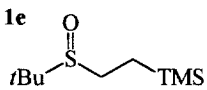


Figure 1

The modified Sharpless procedure[9] was found to give low ee's. Exchanging cumyl hydroperoxide (CHP) for *t*-butyl hydroperoxide (TBHP)[12] or using catalytic binaphthol for chiral induction in the presence of

TBHP[13] showed little improvement; those three methods were deemed unacceptable. The best ee's and chemical yields were obtained using the Davis reagent (3'*S*,2*R*)-(-)-*N*-(phenylsulfonyl)-(3,3-dichlorocamphoryl)oxaziridine (**3**).[10] The oxidation of the aryl sulfides **2a** and **2b** and of *t*-butyl sulfide **2e** by **3** provided reasonable ee's. In none of the cases did benzyl 2-(trimethylsilyl)ethyl sulfide (**2c**) perform particularly well. Microbial oxidation of **2c** gave both low yield and low ee.[14]

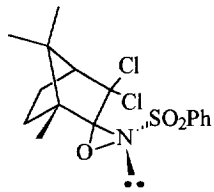
Table 1. Chiral Oxidations of 2-(Trimethylsilyl)ethyl Sulfides **2** to Sulfoxides **1**.

Sulfoxide	Oxidation Method[a]	%Yield[b]	Config.[c]	%ee[d]
1a 	Davis oxaziridine **3**	90	*S*	75
	TBHP/DET/Ti(*i*PrO)$_4$	65	*S*	12
	CHP/DET/Ti(*i*PrO)$_4$	72	--	0
	TBHP/binaphthol/Ti(*i*PrO)$_4$	50	*R*	9
1b 	Davis oxaziridine **3**	98	*S*	73(74)[e]
	TBHP/DET/Ti(*i*PrO)$_4$	51	*S*	26(18)[e]
	CHP/DET/Ti(*i*PrO)$_4$	62	*R*	1(4)[e]
	TBHP/binaphthol/Ti(*i*PrO)$_4$	92	*R*	18(20)[e]
1c 	Davis oxaziridine **3**	75	*S*	9
	TBHP/DET/Ti(*i*PrO)$_4$	44	*S*	16
	CHP/DET/Ti(*i*PrO)$_4$	47	*R*	1
	TBHP/binaphthol/Ti(*i*PrO)$_4$	49	--	0
1d 	Davis oxaziridine **3**	86	*S*	57
	TBHP/DET/Ti(*i*PrO)$_4$	54	*S*	8
	CHP/DET/Ti(*i*PrO)$_4$	62	*S*	13
	TBHP/binaphthol/Ti(*i*PrO)$_4$	56	*R*	26
1e 	Davis oxaziridine **3**	80	*S*	89(95)[e]
	TBHP/DET/Ti(*i*PrO)$_4$	75	*S*	5(4)[e]
	CHP/DET/Ti(*i*PrO)$_4$	66	S	29(37)[e]
	TBHP/binaphthol/Ti(*i*PrO)$_4$	41	*R*	25(27)[e]

Footnotes: [a]For practical details see experimental section. [b]Yields are of isolated chromatographed material. [c]The configuration is of the major enantiomer of the oxidation mixture. [d]Enantiomeric excesses were determined using the chiral NMR solvating agent as indicated in the text and experimental. [e]The parenthesized values are based on optical rotation values from the literature (Ref. 4)

With the successes of Davis' oxidant (**3**) in hand, four other aryl and alkyl 2-(trimethylsilyl)ethyl sulfides (**2f-i**) were prepared and these were exposed to **3**. Table 2 indicates reasonable success for the 2-naphthyl and 2,6-dimethylphenyl systems while rather low ee's were realized for simple methyl and 3,3-dimethylbutyl containing compounds. The results are consistent for the most part with the active site model proposed by Davis to account for the enantioselectivity of **3**. The ee's obtained seem to suggest that for aryl systems, the 2-(trimethylsilyl)ethyl group tends to preferentially rest in pocket C (Figure 2)[15] of the active site, although it is probably a tight fit since the ee's in most cases could not reach 80%. Only when R_L= *t*Bu was the 2-

(trimethylsilyl)ethyl group convincingly forced from pocket A to pocket C. Indeed, this is opposite to the results of Davis[10] who found that aryl groups act larger than the *t*-butyl moiety.



Davis oxaziridine **3**

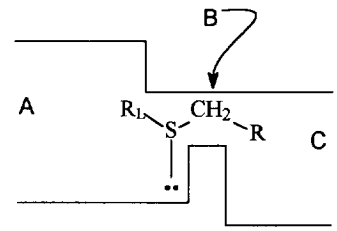


Figure 2. Active site model for **3**

Table 2. Oxidations of Sulfides **2f-i** with Oxaziridine **3**.[a]

Sulfide	R	% Yield[b]	Config.[c]	% ee[d]
2f	2-naphthyl	91	*S*	79
2g	2,6-dimethylphenyl	47	*S*	73
2h	3,3-dimethylbutyl	89	*S*	4
2h	3,3-dimethylbutyl	90	*S*	2[e]
2i	methyl	59	*S*	36

Footnotes: [a]Oxidations were performed in CCl_4 unless otherwise indicated. [b]Yields are of isolated chromatographed material. [c]The configuration is of the major enantiomer of the oxidation mixture. [d]Enantiomeric excesses were determined using the chiral NMR solvating agent as indicated in the text and experimental. [e]This oxidation was performed in CH_2Cl_2.

In general, with aryl 2-(trimethylsilyl)ethyl sulfides, the aryl groups did not act as effective R_L groups and instead indicated their ability to reside in pocket C for 10-15% of the oxygen transfers.[16] The use of 2,6-dimethylphenyl or 2-naphthyl as more sterically demanding aromatic R_L groups was insufficient to induce ee's larger than 80%. Clearly pocket B, shown by Davis to have tolerance for methyl, methylene and vinyl groups, does have the capacity to accommodate aromatic rings that can lie flat even though they may have steric demands in two dimensions.

3,3-Dimethylbutyl 2-(trimethylsilyl)ethyl sulfide (**2g**) was prepared since it would be expected to possess groups of approximately equal steric needs on either side of the sulfur. Oxidation of **2g** was performed in both CCl_4 and CH_2Cl_2 in order to see if there was any particular polar interactions present between the silyl group and the geminal chlorines of **3**. The results in Table 2 indicate that little or no effect was present.

Experimental.

General. Most of our general experimental methods have been reported previously.[17] Gas Chromatograph /Mass Spectra (GC/MS) were obtained using a Hewlett Packard 5890 Series II GC and a Hewlett Packard 5971 Series Mass Selective Detector. Optical rotations were obtained using an Autopol III Polarimeter with acetone as the solvent and were measured in a 1 dm path length cell. Enantiomeric excess of 2-

(trimethylsilyl)ethyl sulfoxides was determined by ^{1}H NMR (400 MHz) and (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol chiral solvating reagent. The typical procedure was as follows: the sulfoxide (5-10 mg) was dissolved in dry CCl_4 (1 mL). One equivalent of (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol (Aldrich) was dissolved in CCl_4 (1 mL). Both the sulfoxide and the shift reagent solutions were purged with nitrogen. The sulfoxide was observed using ^{1}H NMR without the chiral solvating reagent. The shift reagent was then mixed with the sulfoxide and observed using ^{1}H NMR. The trimethylsilyl resonance was split into two peaks, and the enantiomeric excess was calculated by integration of each separate peak.

General synthesis of sulfides 2a-g.

The thiol and vinyltrimethylsilane (1.2 eq.) were combined under nitrogen in the absence of solvent. Azobisisobutyronitrile (AIBN) (ca. $^1/_{40}$ eq.) was added and the mixture was refluxed for 2-24 hours and was monitored by GC. Upon completion, the mixture was fractionally distilled or chromatographed to afford pure sulfide. The synthesis of sulfides **2a**[3] and **2e**[17] by this method has been reported previously.

p-Tolyl 2-(trimethylsilyl)ethyl sulfide (2b). A mixture of *p*-thiocresol (10.2g, 82.1 mmol), vinyltrimethylsilane (9.90g, 98.8 mmol) and AIBN (420mg, 2.56 mmol) was refluxed for 12 hours and purified by distillation to yield **2b** (15.5g, 84%). bp: 86-87 °C/0.3 mm. Data for **2b**: ^{1}H NMR (200 MHz), δ: 7.23(d, J=8.6 Hz, 2H), 7.09(d, J=8.6 Hz, 2H), 2.90 (m, 2H), 2.31 (s, 3H), 0.86 (m, 2H), 0.02 (s, 9H); ^{13}C NMR (50.3 MHz), δ: 135.79, 133.24, 129.79, 129.56, 30.25, 20.98, 16.97, -1.77; MS (ei), m/z(%): 224(1.5).

Benzyl 2-(trimethylsilyl)ethyl sulfide (2c). A mixture of α-toluenethiol (10.9g, 87.8 mmol), vinyltrimethylsilane (10.5g, 105 mmol) and AIBN (342mg, 2.08 mmol) was refluxed for 2 hours and purified by distillation to yield **2c** (17.0g, 87%). bp: 120-121 °C/1.1 mm. Data for **2c**: ^{1}H NMR (200 MHz), δ: 7.36(s, 5H), 3.76(s, 2H), 2.50(m, 2H), 0.86(m, 2H), 0.03(s, 9H); ^{13}C NMR (50.3 MHz), δ: 138.50, 128.66, 128.26, 126.65, 35.88, 26.72, 16.85, -1.86; MS (ei), m/z(%): 224(2).

Cyclohexyl 2-(trimethylsilyl)ethyl sulfide (2d). A mixture of cyclohexanethiol (10.5g, 90.5 mmol), vinyltrimethylsilane (10.9g, 109 mmol) and AIBN (450mg, 2.74 mmol) was refluxed for 6 hours and purified by distillation to yield **2d** (17.4g, 89%). bp: 67-68 °C/0.2 mm. Data for **2d**: ^{1}H NMR (200 MHz), δ: 2.50(m, 2H), 1.16-1.92(m, 11H), 0.76(m, 2H), 0.03(s, 9H); ^{13}C NMR (50.3 MHz), δ: 43.05, 33.44, 25.95, 25.76, 25.33, 17.25 -1.91; MS (ei), m/z(%): 216(2).

2-Naphthyl 2-(trimethylsilyl)ethyl sulfide (2f). A mixture of 2-naphthyl thiol (2.01g, 12.5 mmol), vinyltrimethylsilane (2.52g, 25.2 mmol) and AIBN (116mg, 0.71 mmol) was refluxed for 21 hours and purified by flash chromatography on silica gel (hexanes) to yield **2f** (2.96g, 92%). Data for **2f**: ^{1}H NMR (400 MHz), δ: 7.75(m, 4H), 7.43(m, 3H), 3.06(m, 2H), 0.98(m, 2H), 0.06(s, 9H); ^{13}C NMR (100.6 MHz), δ: 134.73, 133.79, 131.60, 128.24, 127.69, 127.25, 126.96, 126.45, 126.38, 125.43, 29.40, 16.84, -1.73; MS (ei), m/z(%): 260(16).

2,6-Dimethylphenyl 2-(trimethylsilyl)ethyl sulfide (2g). A mixture of 2,6-dimethylthiophenol (1.22g, 8.85 mmol), vinyltrimethylsilane (1.12g, 11.2 mmol) and AIBN (50mg, 0.30 mmol) was refluxed for 24 hours and was purified by distillation to yield **2g** (1.12g, 71%). bp: 72-74 °C/0.07 mm. Data for **2g**: ^{1}H NMR (200 MHz), δ: 7.11(s, 3H), 2.69(m, 2H), 2.55(s, 6H), 0.84(m, 2H), -0.004(s, 9H); ^{13}C NMR (50.3 MHz), δ: 143.04, 133.96, 127.95, 30.86, 22.10, 17.64, -1.82; MS (ei), m/z(%): 238(6).

3,3-Dimethylbutyl 2-(trimethylsilyl)ethyl sulfide (2h). A mixture of 2-(trimethylsilyl)ethanethiol[17] (2.36g, 17.6 mmol) and 3,3-dimethyl-1-butene (2.19g, 26.0 mmol) was refluxed with AIBN (50mg, 0.30 mmol) under

nitrogen for 12 hours. Purification by distillation afforded **2h** (2.78g, 72%). bp: 50-52 °C/0.05 mm. Data for **2h**: ^{1}H NMR (400 MHz), δ: 2.53(m, 2H), 2.46(m, 2H), 1.46(m, 2H), 0.89(s, 9H), 0.84(m, 2H), 0.004(s, 9H); ^{13}C NMR (100.6 MHz), δ: 43.88, 30.71, 29.15, 27.46, 27.23, 17.31, -1.77; MS (ei), m/z(%): 218(7).

Methyl 2-(trimethylsilyl)ethyl sulfide (2i). To a solution of 2-(trimethylsilyl)ethyl thiolacetate (1.02g, 5.80 mmol), methanol (6 mL), and ether (3 mL) under nitrogen was added solid K_2CO_3 (1.04g, 7.52 mmol) and the mixture stirred 24 hours under nitrogen. Methyl iodide (1.14g, 8.03 mmol) was added and the mixture stirred for 3 hours followed by quenching with water (10 mL). The aqueous layer was extracted with ether (3x15 mL) and the combined organic layers were washed with brine (60 mL) and dried over Na_2SO_4. Filtration, concentration and flash distillation yielded **2i** (505mg, 59%). bp: 17-18 °C/1 mm. Data for **2f**: ^{1}H NMR (400 MHz), δ: 2.53(m, 2H), 2.10(s, 3H), 0.88(m, 2H), 0.02(s, 9H). ^{13}C NMR (100.6 MHz), δ: 29.86, 17.07, 15.30, -1.79. GC/MS, m/z(%): 148(9).

Asymmetric Oxidations of Sulfides 2 using Oxaziridine 3.

To oxaziridine **3** (0.20-0.50 mmol) dissolved in dry CCl_4 (10 mL) was added the sulfide (1.0-1.4 eq.) in dry CCl_4 (5 mL) at room temperature. The reactions were stirred at RT and were monitored by TLC. Upon completion of the reaction (24 to 116 h), solvent was removed under reduced pressure, and the sulfoxides were chromatographed on silica gel with ethyl acetate/hexanes as eluent.

Phenyl 2-(trimethylsilyl)ethyl sulfoxide (1a). The reaction of oxaziridine **3** (0.250 mmol) and sulfide **2a** (81.6 mg, 0.377 mmol) yielded sulfoxide **1a**[3] (52.4 mg, 90%) after 42 h. $[\alpha]^{20}_D$ = -134.0 (*c* 1.0, acetone). 75% ee by NMR.

p-Tolyl 2-(trimethylsilyl)ethyl sulfoxide (1b). The reaction of oxaziridine **3** (0.251 mmol) and sulfide **2b** (84.2 mg, 0.375 mmol) yielded sulfoxide **1b**[4] (58.9 mg, 98%) after 42 h. $[\alpha]^{20}_D$ = -128.8 (*c* 1.2, acetone). 73% ee by NMR. 74% ee by optical rotation.[4]

Benzyl 2-(trimethylsilyl)ethyl sulfoxide (1c). The reaction of oxaziridine **3** (0.255 mmol) and sulfide **2c** (68.0 mg, 0.304 mmol) yielded sulfoxide **1c** as an oil (45.6 mg, 75%) after 93 h. Data for **1c**: ^{1}H NMR (200 MHz), δ: 7.31(m, 5H), 3.90(abq, J=12.8 Hz, 2H), 2.61(dt, J=5.1 & 13.2 Hz, 1H), 2.48(dt, J=5.0 & 13.2 Hz, 1H), 0.98(dt, J=5.0 & 13.5 Hz, 1H), 0.80(dt, J=5.0 & 13.5 Hz, 1H), 0.01(s, 9H); ^{13}C NMR (50.3 MHz), δ: 129.60, 129.34, 128.19, 127.25, 56.09, 45.21, 7.46, -2.45; IR, (film) cm^{-1}: 1041 (S=O); MS (ci), m/z(%): 241((M+H), 12), 212(47), 92(19), 91(100), 75(21), 74(18), 73(99), 43(54), 41(23). Calc'd. for $C_{12}H_{20}OSSi$: C, 59.95; H, 8.38. Found: C, 59.99; H, 8.17. $[\alpha]^{20}_D$ = +24.9 (*c* 0.28, acetone). 9% ee by NMR.

Cyclohexyl 2-(trimethylsilyl)ethyl sulfoxide (1d). The reaction of oxaziridine **3** (0.256 mmol) and sulfide **2d** (68.6 mg, 0.317 mmol) yielded sulfoxide **1d** as an oil (51.1 mg, 86%) after 114 h. Data for **1d**: ^{1}H NMR (200 MHz), δ: 2.60(m, 3H), 1.21-2.12(m, 10H), 1.02(dt, J=5.4 & 13.4 Hz, 1H), 0.82(dt, J=5.6 & 13.4 Hz, 1H), 0.05(s, 9H); ^{13}C NMR (50.3 MHz), δ: 57.48, 43.86, 26.46, 25.39, 25.33, 25.04, 24.53, 8.54, -1.99; IR, (film) cm^{-1}: 1032 (S=O); MS (ci), m/z(%): 233((M+H), 24), 204(41), 122(22), 115(21), 101(27), 84(54), 83(15), 81(59), 73(100), 59(23), 58(30), 56(45). Calc'd. for $C_{11}H_{24}OSSi$: C, 56.84; H, 10.41. Found: C, 56.91; H, 10.36. $[\alpha]^{20}_D$ = -14.0 (*c* 0.15, acetone). 57% ee by NMR.

t-Butyl 2-(trimethylsilyl)ethyl sulfoxide (1e). The reaction of oxaziridine **3** (0.243 mmol) and sulfide **2e** (65.5 mg, 0.345 mmol) yielded sulfoxide **1e**[17] (39.8 mg, 80%) after 50 h. $[\alpha]^{20}_D$ = -118.0 (*c* 0.71, acetone). 89% ee by NMR, 95% ee by optical rotation.[4]

2-Naphthyl 2-(trimethylsilyl)ethyl sulfoxide (1f). The reaction of oxaziridine **3** (0.235 mmol) and sulfide **2f** (65.0 mg, 0.250 mmol) yielded sulfoxide **1f** (58.0 mg, 91%) after 61 h. mp: 77-78 °C. Data for **1f**: ^{1}H NMR (400 MHz), δ: 8.16(s, 1H), 7.94(m, 3H), 7.57(m, 3H), 2.92(dt, J=4.4 & 13.1 Hz, 1H), 2.76(dt, J=4.4 & 13.1 Hz, 1H), 0.88(dt, J=4.4 & 13.9 Hz, 1H), 0.76(dt, J=4.4 & 13.9 Hz, 1H), -0.02(s, 9H); ^{13}C NMR (100.6 MHz), δ: 140.57, 134.35, 132.79, 129.25, 128.46, 127.99, 127.60, 127.19, 125.02, 119.98, 52.44, 7.74, -1.94; IR (film), cm^{-1}: 1065 (S=O); MS (ci), m/z(%): 277((M+H)$^+$, 90); Analysis: Calc'd. for $C_{15}H_{20}OSSi$: C, 65.17; H, 7.29. Found: C, 65.07; H, 7.29. $[\alpha]^{20}_D$ = -91.1 (*c* 1.1, acetone). 79% ee by NMR.

2,6-Dimethylphenyl 2-(trimethylsilyl)ethyl sulfoxide (1g). The reaction of oxaziridine **3** (0.238 mmol) and sulfide **2g** (58.9 mg, 0.247 mmol) yielded sulfoxide **1g** (28.9 mg, 47%) after 66 h. mp: 42-43 °C. Data for **1g**: ^{1}H NMR (400 MHz), δ: 7.20(m, 1H), 7.02(m, 2H), 3.14(dt, J=3.9 & 13.5 Hz, 1H), 2.87(dt, J=4.3 & 13.5 Hz, 1H), 2.55(s, 6H), 1.10(dt, J=3.9 & 14.1 Hz, 1H), 0.62(dt, J=4.3 & 14.1 Hz, 1H), -0.03(s, 9H); ^{13}C NMR (100.6 MHz), δ: 138.46, 137.87, 130.62, 130.04, 47.64, 19.33, 10.41, -2.02; IR (film), cm^{-1}: 1058 (S=O); MS (ci), m/z(%): 255((M+H)$^+$, 36); Analysis: Calc'd. for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71. Found: C, 61.42; H, 8.74. $[\alpha]^{20}_D$ = -98.4 (*c* 0.47, acetone). 73% ee by NMR.

3,3-Dimethylbutyl 2-(trimethylsilyl)ethyl sulfoxide (1h). The reaction of oxaziridine **3** (0.223 mmol) and sulfide **2h** (48.0 mg, 0.220 mmol) yielded sulfoxide **1h** as an oil (43.8 mg, 89%) after 40 h. mp: 44-46 °C. Data for **1h**: ^{1}H NMR (400 MHz), δ: 2.62(m, 4H), 1.67(m, 1H), 1.52(m, 1H), 0.95(m, 1H), 0.93(s, 9H), 0.80(m, 1H), 0.05(s, 9H); ^{13}C NMR (100.6 MHz), δ: 47.41, 47.14, 35.94, 30.39, 29.08, 8.66, -1.92. IR (film) cm^{-1}: 1058 (S=O); MS (ei), m/z(%): 234(0.1); Analysis: Calc'd. for $C_{11}H_{26}OSSi$: C, 56.35; H, 11.18. Found: C, 56.55; H, 10.99. $[\alpha]^{20}_D$ = -0.8 (*c* 0.48, acetone). 4% ee by NMR. The reaction of oxaziridine **3** (0.234 mmol) and sulfide **2h** (50.7 mg, 0.233 mmol) *in* CH_2Cl_2 yielded sulfoxide **1h** (49.4 mg, 90%) after 36 h. $[\alpha]^{20}_D$ = -2.7 (*c* 0.88, acetone). 2% ee by NMR.

Methyl 2-(trimethylsilyl)ethyl sulfoxide (2i). The reaction of oxaziridine **3** (0.503 mmol) and sulfide **2i** (77.2 mg, 0.522 mmol) yielded sulfoxide **1i** as an oil (47.3 mg, 59%) after 24 h. Data for **1i**: ^{1}H NMR (200 MHz), δ: 2.65(m, 2H), 2.51(s, 3H), 1.08-0.72(m, 2H), 0.05(s, 9H); ^{13}C NMR (100.6 MHz), δ: 49.78, 37. 35, 8.40, -2.08; IR (film) cm^{-1}: 1058 (S=O); MS (ci), m/z(%) 165((M+H)$^+$, 32); Analysis: Calc'd. for $C_4H_{16}OSSi$: C, 43.85; H, 9.81. Found: C, 44.01; H, 9.97. $[\alpha]^{20}_D$ = +20.1 (*c* 0.76, acetone). 36% ee by NMR.

General Procedure for Oxidations of Sulfides 2 using the Modified Sharpless Method.[9,12]

To a solution of dry CH_2Cl_2 (50 mL) under nitrogen at room temperature was added in sequence, Ti(*i*PrO)$_4$ (1.5 mL, 5 mmol), (*R,R*)-DET (10 mmol, 2 eq.) and H_2O (5 mmol, 1 eq.). The pale yellow solution was stirred vigorously for 0.5-2 hours until it became homogeneous after which sulfide **2** (5 mmol, 1 eq.) was added. The solution was taken to -25 °C and either TBHP (1.1-2 eq., 3.77 M in toluene) or CHP (1.1-2 eq.) was added dropwise via an addition funnel. Reaction progress was followed by TLC. Upon completion, water (10 eq.) was added, and the reaction was stirred vigorously at -25 °C for one hour, and at room temperature for one hour. The resulting white gel was filtered through Celite and washed with CH_2Cl_2. For non-benzylic systems, the filtrate was stirred very vigorously in the presence of a 5% NaOH and brine solution for several hours. Sulfoxide **1c** was stirred in the presence of brine only. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. Crude sulfoxides were chromatographed on silica gel. Sulfoxide **1c** was passed through alumina prior to the chromatography. Yields and ee's (by NMR method) are reported in Table 1.

General Procedure for Oxidations of Sulfides 2 using (*R*)-(+)-1,1'-Bi-2-naphthol and TBHP.[13]

To a room temperature solution of (*R*)-(+)-1,1'-bi-2-naphthol (0.027-0.030 mmol, $^1/_{20}$ eq.) in dry CCl_4 (5 mL) open to the air was added Ti(*i*PrO)$_4$ (0.0125 mmol, $^1/_{40}$ eq.), and H_2O (0.250 mmol, $^1/_2$ eq.) via syringe. After stirring 1.5 hour at room temperature, the sulfide (0.500 mmol, 1 eq.) in CCl_4 (1 mL) was added dropwise via syringe. After stirring for 0.5 hours, 70% TBHP solution (1.0 mmol, 2 eq.) was added. The mixture was stirred for 19-67 hours and was followed by TLC. Upon completion, the solvent was removed under reduced pressure and the crude mixtures were purified by chromatography on silica gel. Yields and ee's (by NMR method) are reported in Table 1.

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