Improved Synthesis of Enantiopure Sulfinimines (Thiooxime *S*-Oxides) from *p*-Toluenesulfinamide and Aldehydes and Ketones

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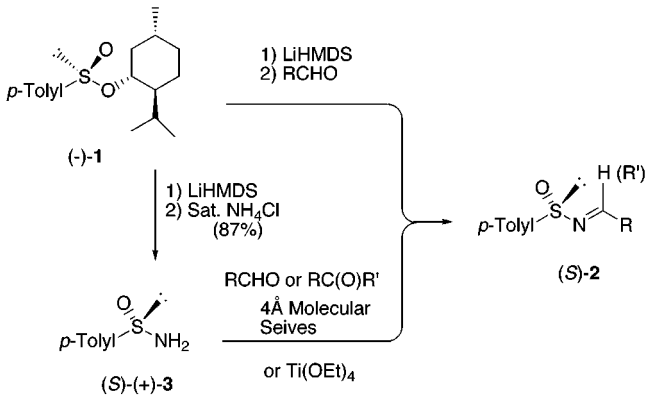
Enantiopure sulfinimines (thiooxime *S*-oxides) **2** are versatile chiral imine building blocks employed in the asymmetric synthesis of amines,[1] α- and *β*-amino acids,[2,3] α- and *β*-amino phosphonates,[4,5] and heterocycles.[6,7] The *N*-sulfinyl group is superior to other imine auxiliaries because it activates the C−N double bond for addition, is highly stereodirecting, and is easily removed under mild acid conditions.[8] We devised a simple one-pot procedure for preparing these building blocks from commercially available (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (**1**) or (1*S*,2*R*,5*S*)-(+)-menthyl (*R*)-*p*-toluenesulfinate (**1**), lithium bis(trimethylsilyl)amide (LiHMDS), and aliphatic and aromatic aldehydes (Scheme 1).[9] While this method gave good to excellent yields of **2** from aromatic aldehydes (82−91%), the yields with aliphatic aldehydes were more modest (60−70%) because of competing α-deprotonation. Ketones were unreactive using this procedure.

Scheme 1



Ellman and co-workers recently reported the synthesis of *N*-*tert*-butanesulfinimines by condensation of chiral nonracemic *tert*-butanesulfinamide (*t*-BuS(O)NH_2), prepared in several steps from *tert*-butyl disulfide[10] with aldehydes.[1a] The convenience of (*S*)-(+)-*p*-toluenesulfinamide (**3**) together with problems of preparing base-sensitive sulfinimines by the one-pot procedure prompted this study of the direct condensation of (*S*)-(+)-*p*-toluenesulfinamide (**3**) with aldehydes and ketones. Furthermore, this procedure avoids the sometimes problematic separation of the menthol byproduct.

(*S*)-(+)-*p*-Toluenesulfinamide (**3**) was readily prepared in 87−90% yield by treating (−)-**1** with 1.3 equiv of LiHMDS at −78 °C and quenching after 1 h with saturated NH_4Cl solution. Sulfinimines (*S*)-**2** were prepared by reacting equimolar amounts of (+)-**3** with aldehydes in the presence of various additives. These results are summarized in Table 1.

The relatively weak Lewis acid dehydrating reagents magnesium sulfate and copper sulfate gave low to moderate yields (30−40%) of the benzaldehyde-derived sulfinimine **2** (R = Ph) (Table 1, entries 2 and 3). With 4 Å molecular sieves, the yield of **2** (R = Ph) improved to 52%, and similar results were found with other aldehydes (Table 1).

The condensations were carried out by refluxing equimolar amounts of sulfinamide (+)-**3** and the aldehyde in CH_2Cl_2 for 24 h in the presence of crushed 4 Å molecular sieves. Higher boiling solvents such as $CHCl_3$ produced no increase in efficiency. Although moderate to good yields (52−80%) of sulfinimines were obtained from aromatic and heteroaromatic aldehydes (Table 1, entries 5, 10, 12, and 14−16), the yields were generally better employing the one-pot procedure. On the other hand, molecular sieves gave better yields of **2** with straight-chain aliphatic aldehydes (63−93%) than the one-pot procedure (20−65%) (Table 1, entries 20, 22, 23, and 30). For example, the acetaldehyde sulfinimine **2** (R = Me) was obtained in better than 93% yield under these conditions (Table 1, entry 20). With sterically hindered isopropyl and *tert*-butyl aldehydes, the one-pot procedure was better (entries 25 and 27). The aldehyde derived

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Table 1. Synthesis of Sulfinimines (*S*)-2, (*S*)-6, and (*S*)-7 from Aldehydes and Ketones

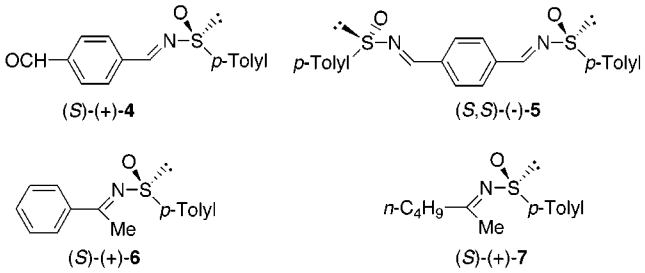
entry	R	R′	conditions	(*S*)-**2** % yield (one-pot % yield)[a]
1	Ph	H	CH_2Cl_2, reflux, 24 h	no reaction
2			CH_2Cl_2, reflux, 24 h, $MgSO_4$	40 (76)
3			CH_2Cl_2, reflux, 24 h, $CuSO_4$	30
4			CH_2Cl_2, reflux, 8 h, 4 Å MS	40
5			CH_2Cl_2, reflux, 24 h, 4 Å MS	52
6			CH_2Cl_2, reflux, 24 h, $ZnCl_2$, 4 Å MS	52
7			CH_2Cl_2, reflux, 24 h, 1 equiv of $Ti(OEt)_4$	50
8			CH_2Cl_2, reflux, 24 h, 1 equiv of $Ti(OEt)_4$, 4 Å MS	50
9			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	99
10	*m*-MeOPh	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	54
11			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	92
12	*p*-MeOPh	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	63 (89)
13			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	92
14	*p*-NO_2Ph	H	CH_2Cl_2, reflux, 8 h, 4 Å MS	80 (74)
15	3-pyridyl	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	80 (64)
16	2-furyl	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	66 (68)
17			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	95
18	MeCH=CH−	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	20 (60)
19			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	92
20	Me[c]	H	CH_2Cl_2, rt, 24 h, 4 Å MS	93 (20)[b]
21			CH_2Cl_2, rt, 8 h, 4 Å MS	82
22	*n*-Pr	H	CH_2Cl_2, rt, 24 h, 4 Å MS	87 (65)
23	$Ph(CH_2)_4$−	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	63 (40)[b]
24			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	90
25	*i*-Pr	H	CH_2Cl_2, rt, 24 h, 4 Å MS	no reaction (60)
26			CH_2Cl_2, reflux, 0.5 h, 5 equiv of $Ti(OEt)_4$	90
27	*t*-Bu	H	CH_2Cl_2, reflux, 24 h, 4 Å MS	30 (60)
28			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	89
29	$Cl(CH_2)_5$−	H	CH_2Cl_2, rt, 12 h, 4 Å MS	52 (77)[b]
30	$Cl(CH_2)_5$−		MeCN, rt, 2 h, 4 Å MS	72
31			CH_2Cl_2, reflux, 0.5 h, 5 equiv of $Ti(OEt)_4$	88
32	$MeC(O)(CH_2)_2$−	H	CH_2Cl_2, rt, 48 h, 4 Å MS	40 (20)[b]
33			CH_2Cl_2, reflux, 4 h, 5 equiv of $Ti(OEt)_4$	50
34	Ph	Me	CH_2Cl_2, rt, 48 h, 4 Å MS	no reaction (no reaction)
35			CH_2Cl_2, reflux, 17 h, 5 equiv of $Ti(OEt)_4$	62 (**6**)
36			$CHCl_3$, reflux 17 h, 5 equiv of $Ti(OEt)_4$	60
37	*n*-Bu	Me	CH_2Cl_2, reflux, 20 h, 5 equiv of $Ti(OEt)_4$	40[d] (**7**)

[a] Reference 9 unless otherwise noted. [b] This work. [c] 3.0 equiv of acetaldehyde used. [d] 3:1 mixture of *E*/*Z* isomers.

sulfinimine of 4-oxopentanal was regioselectively formed in 40% yield with sieves and in only 20% yield by the one-pot method (Table 1, entry 32). Acetophenone failed to react under these conditions (Table 1, entry 34).

Titanium(IV) ethoxide is a weak Lewis acid that has been employed as a catalyst in transesterfication[11] and lactamization[12] reactions. With a catalytic amount of titanium(IV) ethoxide, the condensation of (+)-**3** with benzaldehyde produced little, if any, of the desired sulfinimine after 24 h. With an equivalent amount of the titanium reagent, sulfinimine (+)-**2** (R = Ph) was obtained in 50% yield after 24 h at reflux (Table 1, entry 7). Significantly, with 5 equiv of $Ti(OEt)_4$, the condensation was complete within 4 h, affording the benzaldehyde sulfinimine in almost quantitative yield (Table 1, entry 9). Similar results with comparable yields of 88 to >90% were observed with other aromatic, alkenyl, and sterically hindered aliphatic aldehydes (Table 1, entries 11, 13, 17, 19, 24, 26, 28, and 31). After the reaction mixture was quenched with H_2O at 0 °C, the slightly turbid solution was passed through Celite, and the solvent was removed to give in most cases the sulfinimine in high purity as determined by mp and optical rotation. Chromatographic purification of the product was generally not necessary. Importantly, there was no detectable racemization of the sulfinimines **2** prepared under both these conditions as determined by comparison of optical rotations with literature values[9] and chiral shift reagent experiments with Eu(hfc)$_3$.

Scheme 2



With bis-aldehydes, it was possible to selectively prepare the mono- and bis-sulfinimines. Thus, treatment of terephthaldicarboxaldehyde with 1.0 equiv of sulfinamide (+)-**3** and 10 equiv of $Ti(OEt)_4$ afforded a 68% yield of (*S*)-(+)-**4** after 24 h following isolation by preparative TLC. With lesser amounts of the titanium reagent the reaction was incomplete. With 2 equiv of (+)-**3** and 25 equiv of $Ti(OEt)_4$, the bis-sulfinimine (*S*,*S*)-(+)-**5** was obtained in 91% yield (Scheme 2).

N-Alkylidine-*p*-toluenesulfinamides such as **6** have only been available via the method of Cinquini where a metal ketimine (Ar(R)C=NM), prepared by reacting aromatic nitriles with lithium and Grignard reagents, is treated with the Andersen reagent **1**.[13] Significantly, heating acetophenone with (+)-**3** and $Ti(OEt)_4$ for 17 h

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afforded a 62% yield of [*S*-(*E*)]-(+)-*N*-α-methylbenzylidene-*p*-toluenesulfinamide (6) (Table 1, entry 35). In a similar manner, (*S*)-**7** was obtained in 60% yield as 3:1 inseparable mixture of *E*/*Z* isomers.[14] In the course of these studies, Ellman and co-workers also described the synthesis of ketone-derived sulfinimines from *tert*-butanesulfinamide and $Ti(OEt)_4$.[15]

The effectiveness of the titanium(IV) ethoxide reagent in these condensation reactions is likely due to a combination of two factors. First, it acts as a Lewis acid, activating the carbonyl group for condensation with the sulfinamide. Second, titanium(IV) ethoxide undoubtedly acts as a dehydrating reagent ultimately producing TiO_2, although there was no apparent improvement in yield on addition of 4 Å molecular sieves (Table 1, compare entries 7 and 8). An excess of the reagent is presumably necessary because it complexes with the carbonyl oxygen and the sulfinyl oxygens in **3** and in the product **2**, in addition to functioning as a dehydrating agent.

In summary, efficient methodology is reported for the synthesis of sulfinimines by condensing (*S*)-(+)-*p*-toluenesulfinamide (**3**) with aldehydes and ketones in the presence of 4 Å molecular sieves or titanium(IV) ethoxide reagent. This procedure avoids the problem of removing the menthol byproduct, produced in the one-pot method. Importantly, ketone-derived sulfinimines are also available by this methodology, as are the selective formation of mono- and bis-sulfinimines.

Experimental Section

General Procedure. Column chromatography was performed on silica gel, Merck grade 60 (230−400 mesh). Analytical and preparative thin-layer chromatography was performed on precoated silica gel plates (250 and 1000 microns) purchased from Analtech, Inc. TLC plates were visualized with UV, in an iodine chamber, or with phosphomolybdic acid unless noted otherwise. THF was freshly distilled under nitrogen from a purple solution of sodium and benzophenone.

Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. 4-Oxopentanal was prepared as previously described,[16] and 6-chlorohexanal was prepared in 72% yield by Swern oxidation of 6-chloro-1-hexanol.[17] Sulfinimines were prepared by the one-pot procedure as previously described.[9]

(*S*)-(+)-*p*-Toluenesulfinamide (3). In a 100 mL one-neck, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, and argon inlet was placed 5.0 g (17.0 mmol) of (−)-**1**[18] (Aldrich) in THF (40 mL). The reaction mixture was cooled to −78 °C, and 23.0 mL of LiHMDS (1.0 M solution in THF, 23.0 mmol) was added dropwise via syringe. The reaction was warmed to room temperature, stirred for 1 h, and monitored for the disappearance of **1** by TLC. The reaction mixture was quenched with saturated NH_4Cl (30 mL), an additional 10 mL of water was added, and the mixture was extracted with ethyl acetate (3 × 15 mL). The organic phase was dried ($MgSO_4$) and concentrated to give a solid that was crystallized with *n*-hexane to give 2.27 g (86%) of (+)-**3**: mp 113 °C (lit.[9] mp 113 °C); $[\alpha]^{20}_D$ +80.2 (*c* 1.2, $CHCl_3$) [lit.[9] $[\alpha]^{20}_D$ +79.2 (*c* 1.0 $CHCl_3$)].

Typical Procedure for the Synthesis of Sulfinimines from Aldehydes Using 4 Å Molecular Sieves: (*S*)-(+)-*N*-(Benzylidene)-*p*-toluenesulfinamide. In a 25 mL one-neck round-bottomed flask fitted with a condenser, septum, argon inlet, and magnetic stirring bar were placed 0.1 g (0.65 mmol) of (*S*)-(+)-**3** in CH_2Cl_2 (5 mL), 2 g of crushed 4 Å molecular sieves (4−8 mesh, Aldrich), and 0.65 mL (0.65 mmol) of benzaldehyde. The reaction mixture was refluxed for 24 h and filtered, and the sieves were washed with EtOAc (2 × 10 mL). The organic phase was concentrated, and the resulting solid was purified by flash chromatography (10% ethyl acetate in *n*-hexane) to afford 0.85 g (53%) of **2** (R = Ph): mp 77 °C [lit.[9] mp 77−78 °C]; $[\alpha]^{20}_D$ 117.8 (*c* 1.6, $CHCl_3$), [lit.[9] $[\alpha]^{20}_D$ 119.3 (*c* 1.77, $CHCl_3$)].

Typical Procedure for the Synthesis of Sulfinimines from Aldehydes Using Titanium(IV) Ethoxide: (*S*)-(+)-*N*-(Benzylidene)-*p*-toluenesulfinamide. In a 50 mL round-bottom flask equipped with condenser, stirring bar, and argon balloon was placed 0.10 g (0. 645 mmol) of (+)-**3**, 0.066 mL (0.645 mmol) of benzaldehyde, and 0.68 mL (3.23 mmol) of titanium(IV) ethoxide (Aldrich) in 10 mL of CH_2Cl_2. After being refluxed for 4 h and monitored by TLC, the reaction mixture was quenched at 0 °C by addition of H_2O (10 mL). The turbid solution was filtered through Celite, and the filter cake was washed with CH_2Cl_2 (2 × 10 mL). The phases were separated, the aqueous phase was washed with 10 mL of CH_2Cl_2, and the combined organic portions were dried (Na_2SO_4) and concentrated to give 0.156 g (99%) of (*S*)-(+)-*N*-(benzylidene)-*p*-toluenesulfinamide: mp 77−8 °C (lit.[9] mp 77−78 °C); $[\alpha]^{20}_D$ 117.5 (*c* 1.6, $CHCl_3$) [lit.[9] $[\alpha]^{20}_D$ 119.3 (*c* 1.77, $CHCl_3$)].

(*S*)-(+)-*N*-(*m*-Methoxybenzylidene)-*p*-toluenesulfinamide. An analytically pure sample was obtained by preparative TLC (10% ethyl acetate/*n*-hexane): mp 66−67 °C; $[\alpha]^{20}_D$ 94.3 (*c* 1.06, $CHCl_3$); IR (KBr) 1659, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.37 (s, 3H), 3.80 (s, 3H), 7.02−7.64 (m, 9H), 8.72 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 161.3, 160.6, 142.4, 135.8, 130.6, 130.5, 125.5, 123.5, 119.9, 113.7, 56.1, 22.1. Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.61; H, 5.53; N, 5.12 Found: C, 66.00, H; 5,51; N, 4.71.

(*S*)-(+)-*N*-(5-Phenylpentylidene)-*p*-toluenesulfinamide. Purified by flash chromatography using 10% EtOAc/*n*-hexane to give a yellow oil: $[\alpha]^{20}_D$ 243.2 (*c* 1.06, $CHCl_3$); IR (neat) 1621, 1506, 1094 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (m, 4H), 2.40 (s, 3H), 2.51 (m, 2H), 2.60 (t, 2H), 7.19 (m, 5H), 7.27 (d, 2H, *J* = 7.4 Hz), 7.54 (d, 2H, *J* = 2 Hz), 8.21(t, 1H, *J* = 5 Hz); ^{13}C NMR ($CDCl_3$) δ 147.6, 142.6, 142.3, 130.4, 129.0, 128.9. 126.4, 125.2, 36.3, 36.2, 31.4, 25.6, 22.1. Anal. Calcd for $C_{18}H_{21}NSO$: C, 72.24, H, 7.02, N, 4.68. Found: C, 72.33, H, 7.14, N, 4.95.

(*S*)-(+)-*N*-(4-Oxopentanylidene)-*p*-toluenesulfinamide: colorless oil, purified by flash chromatography (20% EtOAc/*n*-pentane); $[\alpha]^{20}_D$ 243.3 (*c* 1.5, $CHCl_3$); IR (neat) 1712, 1621, 1097 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (t, 1H, *J* = 2.6 Hz), 7.52 (t, 2H, *J* = 6.2 Hz), 7.29 (t, 2H, *J* = 7.3 Hz), 2.77 (m, 4H), 2.40 (s, 3H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 207.2, 166.2, 142.4, 142.3, 130.5, 125.3, 38.7, 30.7, 30.4, 22.1. Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.44; H, 6.49; N, 5.64.

(*S*)-(+)-*N*-(Acetylidene)-*p*-toluenesulfinamide: flash filter (CH_2Cl_2) oil; $[\alpha]^{20}_D$ 418.2 (*c* 1.20, $CHCl_3$); IR (neat) 1640, 1095, cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23 (q, *J* = 5 Hz, 1 H), 7.55 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2 H), 2.38 (s, 3H), 2.19 (d, *J* = 5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 163.56, 141.67, 129.743, 125.28, 124.40, 22.27, 21.34. 8.23 (q, *J* = 5 Hz, 1H), 7.55 (d, *J* = 8 Hz, 1H), 7.29 (d, *J* = 8 Hz, 1H), 2.38 (s, 3H), 2.19 (d, *J* = 5 Hz, 3H). Anal. Calcd for $C_9H_{11}NOS$: C, 59.61; H, 6.12; N, 7.73. Found: C, 59.22; H, 6.37; N, 7.52.

(*S*)-(+)-*N*-(6-Chlorohexylidene)-*p*-toluenesulfinamide: flash chromatography (CH_2Cl_2) oil; $[\alpha]^{20}_D$ 270.7 (*c* 1.40, $CHCl_3$); IR (neat) 1621, 1093.6 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23 (t, *J* = 5 Hz, 1 H), 7.56 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2 H), 3.50 (t, *J* = 6.5 Hz, 2H), 2.51 (m, 2H), 2.41 (s, 3H), 1.77 (quintet, *J* = 7 Hz, 2H), 1.65 (quintet, *J* = 7.5 Hz, 2H), 1.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 166.67, 164.70, 129.80, 129.77, 124.50, 44.71, 35.61, 32.18, 26.30, 24.55, 21.41; HRMS calcd for $C_{13}H_{18}NOSCl$ (M + H) 272.0871, found 272.0851.

(*S*)-(+)-*N*-(4-Carboxyaldehydebenzylidene)-*p*-toluenesulfinamide (4). Prepared from 0.017 g (0.013 mmol) of terephthaldicarboxaldehyde, 0.27 mL (1.3 mmol) of $Ti(OEt)_4$, and

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0.02 g (0.13 mmol) of (+)-**3** for 24 h at room temperature in CH_2Cl_2 (8 mL). The solution was filtered through Celite, concentrated, and purified by preparative TLC (30% EtOAc/hexanes) to give 0.023 g (68%) of **4**: mp 126−128 °C; $[\alpha]^{20}_D$ 22.0 (*c* 0.16, $CHCl_3$); IR (KBr) 1697, 1531, 1049 cm^{-1}; ^1H NMR δ 10.1 (s, 1H), 8.81 (s, 1H), 7.81−8.08 (m, 4H), 7.64 (d, 2H, J = 8.1 Hz), 7.33 (d, 2H, J = 8.1 Hz), 2.41 (s, 3H); ^{13}C NMR δ 191.4, 159.3, 142.7, 141.6, 138.6, 138.5, 130.7, 130.6, 129.9, 124.6, 21.4. Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.39; H, 4.83; N, 5.15. Found: C, 66.28; H, 4.77; N, 5.04.

(*S*,*S*)-(−)-*N*,*N*′-(1,4-Benzylidene)bis(*p*-toluenesulfinamide) (5). Prepared from 1.56 mL (7.5 mmol) of $Ti(OEt)_4$, 0.04 g (0.3 mmol) of terephthaldicarboxaldehyde, and 0.093 g (0.6 mmol) of (+)-**3** for 24 h at room temperature in CH_2Cl_2 (10 mL). Filtration through Celite, concentration, and purification by preparative TLC (50% EtOAc/hexanes) gave 0.11 g (91%) of **5**: mp 152−154 °C dec; $[\alpha]^{20}_D$ −137.5 (*c* 0.032, $CHCl_3$); IR (KBr) 1606, 1087 cm^{-1}; ^1H NMR δ 8.76 (s, 2H), 7.91 (s, 8H), 7.63 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.4 Hz), 2.39 (s, 6H); ^{13}C NMR δ 160.3, 142.6, 141.9, 137.6, 130.8, 130.6, 125.4, 22.1. Anal. Calcd for $C_{22}H_{20}N_2O_2S_2$: C, 64.67; H, 4.94; N, 6.85. Found: C, 64.50; H, 4.89; N, 6.72.

[*S*-(*E*)]-(+)-*N*-α-Methylbenzylidene-*p*-toluenesulfinamide (6): 62%; purified by flash chromatography (10% EtOAc/*n*-hexane); mp 99−100 °C (lit.[13] mp 99−100 °C); $[\alpha]^{20}_D$ 118.0 (*c* 1.06, $CHCl_3$) (lit.[13] $[\alpha]^{20}_D$ 98.0 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.88 (d, 2H, J = 7 Hz), 7.73 (d, 2H, J = 7 Hz), 7.26−7.7.48 (m, 5H), 2.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 175.1, 144.0, 142.6, 138.8, 132.6, 130.5, 129.1, 128.2, 125.9, 125.8, 125.7, 22.1, 20.9.

[*S*-(*E*/*Z*)]-(+)-*N*-α-Methylpentylidene-*p*-toluenesulfinamide (7): 40%; purified by flash chromatography (20% EtOAc/*n*-hexane); colorless oil; $[\alpha]^{20}_D$ 2.70 (*c* 0.44, $CHCl_3$); IR (neat) 1611, 1093 cm^{-1}; ^1H NMR ($CDCl_3$) *E* isomer, δ 0.88 (t, 3H, J = 7.5 Hz), 1.29 (m, 2H), 1.56 (m, 2H), 2.34 (s, 3H), 2.37 (m, 2H), 2.39 (s, 3H), 7.31 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz); *Z* isomer, δ 0.95 (t, 3H, J = 7 Hz), 1.40 (m, 2H), 1.73 (s, 3H), 2.16 (s, 3H), 2.74 (m, 2H), 7.31 (d, 2H, J = 8 Hz), 7.64 (d, 2H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) *E* isomer, δ 14.4, 22.0, 22.8, 23.3, 28.5, 43.5, 125.7, 130.3, 142.3, 144.1, 183.6; *Z* isomer, δ 14.4, 21.9, 23.4, 28.3, 30.0, 37.9, 126.0, 130.3, 142.0, 144.0, 185.0. Anal. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.77; H, 8.27; N, 5.69.

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Supporting Information Available: ^1H and ^{13}C NMR and IR spectra of (*S*)-(+)-*N*-(6-chlorohexylidene)-*p*-toluenesulfinamide. This material is available free of charge via the Internet at http://pubs.acs.org.

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