Synthesis of Enantiomerically Pure *N*-*tert*-Butanesulfinyl Imines (*tert*-Butanesulfinimines) by the Direct Condensation of *tert*-Butanesulfinamide with Aldehydes and Ketones

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Experimental details for the first general methods for the one-step preparation of *N*-*tert*-butanesulfinyl imines (*tert*-butanesulfinimines) (**2**) from aldehydes and ketones is described. To effect the condensations of *tert*-butanesulfinamide (**1**) with aldehydes, the Lewis acidic dehydrating agents $MgSO_4$, $CuSO_4$, or $Ti(OEt)_4$ are employed. Aldehyde condensations mediated by $MgSO_4$ proceed in high yields (84−96%) when an excess of aldehyde is used. In contrast, only a slight excess of aldehyde (1.1 equiv) relative to *tert*-butanesulfinamide provides sulfinimines in high yields when the more Lewis acidic dehydrating agent $CuSO_4$ is used. The $CuSO_4$-mediated procedure is effective for a wide range of aldehydes, including sterically demanding aldehydes, such as isobutyraldehyde (90%), and electron-rich aldehydes, such as *p*-anisaldehyde (81%). The still more Lewis acidic $Ti(OEt)_4$ and $Ti(O\text{-}i\text{-}Pr)_4$ also afford *N*-*tert*-butanesulfinyl aldimines from especially unreactive aldehydes, such as pivaldehyde (82%). In addition, $Ti(OEt)_4$ is effective for the condensation of **1** with ketones to afford a wide range of *N*-*tert*-butanesulfinyl ketimines in good yields (77−91%). For sulfinyl ketimines derived from methyl or *n*-alkyl phenyl ketones and methyl or *n*-alkyl isopropyl ketones, only the *E* isomer is detected by ^1H and ^{13}C NMR in $CDCl_3$. For those cases where the difference in steric demand about the imine is very small, such as for 2-hexanone, high *E*/*Z* ratios are still observed (5:1).

Introduction

N-Sulfinyl imines[1] are versatile intermediates in the asymmetric synthesis of chiral amines such as α-branched amines,[2] α,α-dibranched amines,[3] α- and β-amino acids,[4] aziridines,[5] and α- and β-aminophosphonic acids[6] (Figure 1). While *N*-*p*-toluenesulfinyl imines have been the major focus of these synthetic studies, in the few cases where *N*-*tert*-butanesulfinyl imines were compared to their *N*-*p*-toluenesulfinyl counterparts, higher levels of diastereocontrol were attained from the *tert*-butane derivatives.[5b] Due to substantial differences in their steric and electronic properties, different reactivities between *p*-toluene- and *tert*-butanesulfinyl imines are also observed. For the reaction of Grignard reagents with sulfinyl aldimines, addition to the sulfur of *p*-toluenesulfinyl aldimines is competitive with the desired 1,2-addition.[2c] The same reaction with *tert*-butanesulfinyl aldimines is not only chemoselective for 1,2-addition but also highly diastereoselective.[2e] More recently, we established that *tert*-butanesulfinyl ketimines are effective substrates for highly diastereoselective Me_3Al-mediated 1,2-additions of organolithiums, providing the first general stereoselective[8] route to the quaternary α,α-disubstituted amines.[3] In addition, we have recently reported the application of *tert*-butanesulfinyl imines to the asymmetric synthesis of β-amino acids including α,β- and β,β-disubstituted β-amino acids that cannot be readily accessed by other methods.[4c] In this work the efficacy of the *N*-sulfinyl group as a surrogate for the *N*-Boc protecting group was also demonstrated.

The practical preparation of *N*-sulfinyl imines is central to their utility in the asymmetric synthesis of chiral amines. To this end, sulfinate esters have been prominently used. Menthyl arenesulfinates such as Andersen's reagent (**3**) are easily synthesized[9] and react with imine anions stereospecifically to provide arenesulfinyl imines (Scheme 1).[7b,10] Since the imine anions are generated from nonenolizable nitriles, only a limited number of derivatives are available by this method. Similarly, the DAG *tert*-butanesulfinate (**4**) has been applied to the production of enantiopure *tert*-butanesulfinyl compounds (Scheme 1).[11] Unfortunately, diastereomeric mixtures of high molecular weight DAG sulfinates must be chromatographically separated.

Researchers in Davis' labs have recently described the first synthesis of *N*-sulfinyl aldimines from aldehydes.

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(1) We have elected to use the term *N*-sulfinyl imine instead of sulfinimine to allow for an easy distinction between *N*-sulfinyl aldimines and *N*-sulfinyl ketimines.

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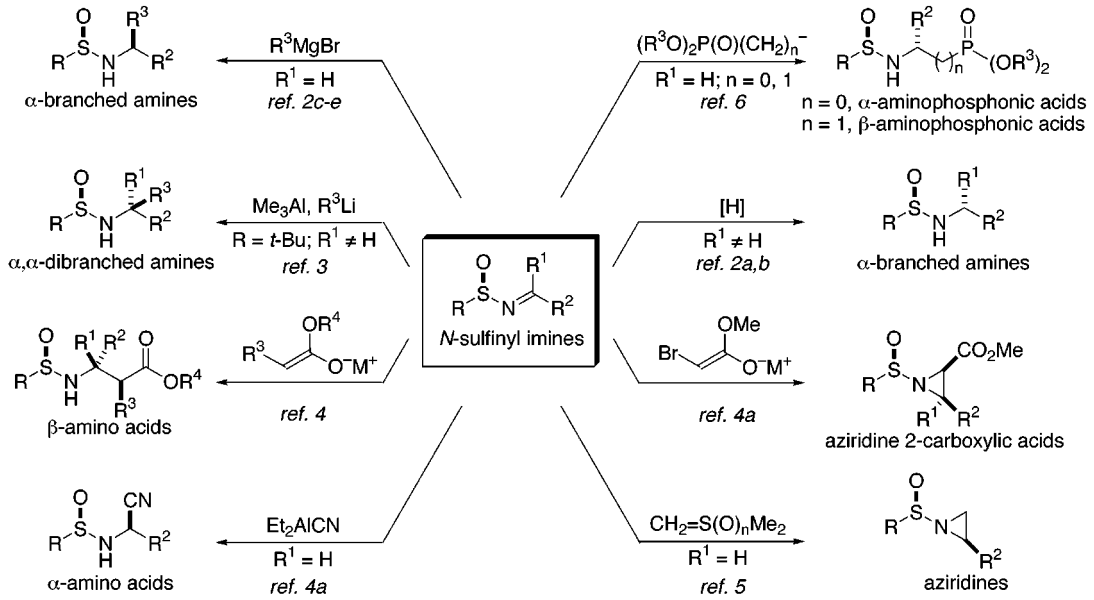
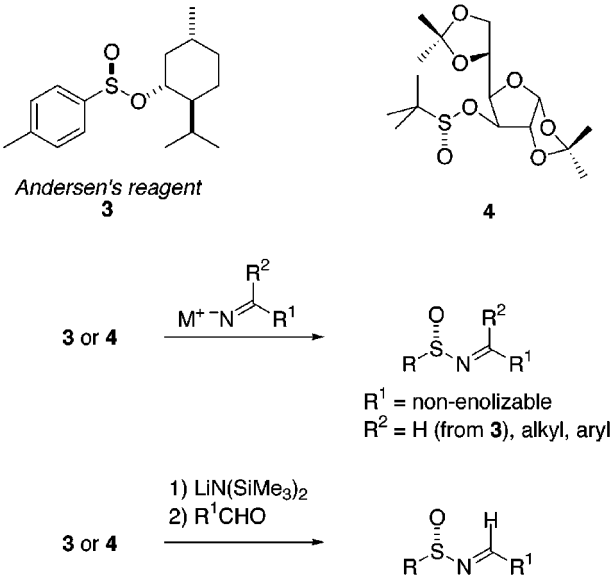
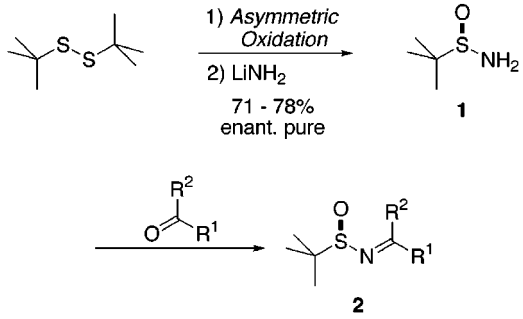


Figure 1. Reactions of *N*-sulfinyl imines to provide chiral intermediates for the synthesis of important amine derivatives. Treatment with acid releases the corresponding amine products.

Scheme 1



Scheme 2



Treatment of *N*,*N*-bis(trimethylsilyl)-*p*-toluenesulfinamide with aldehydes affords *N*-*p*-toluenesulfinyl aldimines. Although yields are high for nonenolizable aldehydes, yields are much lower when the aldehydes are enolizable.[7b] These conditions also do not deliver *N*-sulfinyl ketimines from ketones. In addition, because *N*,*N*-bis(trimethylsilyl)-*p*-toluenesulfinamide is obtained in situ by addition of LHMDS to sulfinate **3** (Scheme 1), separation of the sulfinyl imine product from menthol is required.

Other chiral intermediates have been described for the in situ preparaton of *N*,*N*-bis(trimethylsilyl)-*p*-toluenesulfinamide but are limited by the high costs of the chiral reagents.[12] *N*,*N*-Bis(trimethylsilyl)-*tert*-butanesulfinamide has also been prepared by the addition of LHMDS to DAG-*tert*-butanesulfinate (Scheme 1), but this method is again limited by the unwieldy chromatographic purification to provide diastereomerically pure DAG-*tert*-butanesulfinate precursor.[12] Davis and co-workers have also demonstrated that stoichiometric oxidations of sulfenimines derived from aromatic aldehydes or acetophenone with chiral oxaziridines can proceed with good enantiocontrol.[7b,13] However, this method requires stoichiometric amounts of the high molecular weight chiral oxidants.

We previously reported the large scale preparation of *tert*-butanesulfinamide **1** in enantiopure form in two steps and in 71% overall yield from the very inexpensive starting material *tert*-butyl disulfide (Scheme 2).[14] Herein we provide the full experimental details for the straight-

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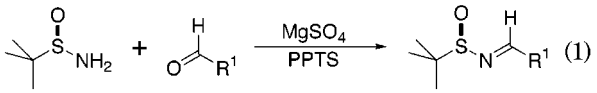
Table 1. Condensations of 1 with Aldehydes Mediated by $MgSO_4$ and PPTS[a]



1 2

entry	product	R^1	yield (%)
1[b]	**2a**	*i*-Pr	90
2[b]	**2b**	Et	96
3[b]	**2c**	Bn	86
4[c]	**2c**	Bn	84
5[d]	**2d**	Ph	90

[a] All reactions were performed using 5 equiv of $MgSO_4$ and 0.05 equiv of PPTS in CH_2Cl_2 at room temperature. [b] Reactions were performed with 2 equiv of aldehyde. [c] Reaction was performed with 1.5 equiv of aldehyde. [d] Reaction was performed with 3 equiv of aldehyde.

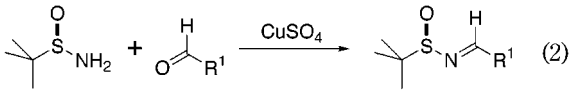
forward and high-yielding methods for the one-step preparation of a wide range of *tert*-butanesulfinyl imines by the condensation of *tert*-butanesulfinamide **1** with aldehydes and ketones. This route provides a rapid entry to a wider range of sulfinyl imines than previously available and can be performed easily on multigram scales.

Results and Discussion

Magnesium Sulfate Mediated Condensations. We began our efforts to prepare *tert*-butanesulfinyl imines by investigating the direct condensation of **1** with aldehydes (eq 1). Neither molecular sieves nor sodium sulfate was effective in providing *N*-*tert*-butanesulfinyl aldimines in high yield, even in the presence of a protic acid catalyst. Attempts to drive the reaction to completion by azeotropic removal of water using a Dean−Stark apparatus and either benzene or toluene solvents were also unsuccessful due to competitive decomposition of the *tert*-butanesulfinyl imine products.

Branchaud has reported that sulfenamides can be condensed with aldehydes in near quantitative yields using magnesium sulfate as a drying agent and PPTS as a catalyst.[15] When these conditions were employed for the direct condensation of optically pure **1** with several types of aldehydes, the desired sulfinyl aldimines **2** were isolated in high yields (eq 1 in Table 1). No racemization was observed during the condensation reaction as determined by chiral HPLC analysis of the imine product **2d**. The condensations were complete after 12−24 h at room temperature. Even phenylacetaldehyde readily condensed to afford **2c** in high yield without formation of the enamine, which is a significant side product during the formation of the corresponding *N*-*p*-toluenesulfinyl imine.[7b] It is, however, necessary to use aldehydes in excess to drive these condensation reactions to completion. To obtain aliphatic aldimine derivatives, usually 2 equiv of aldehyde in excess of **1** are required, although as little as 1.5 equiv of aldehyde is nearly as effective (entry 4). In contrast, for condensations with less reactive aromatic aldehydes, such as benzaldehyde, at least 3 equiv of aldehyde was necessary to obtain high yields (entry 5).

Table 2. Condensations of 1 with Aldehydes Mediated by $CuSO_4$



1 (1.1 equiv) 2

entry	product	R^1	yield (%)
1	**2a**	*i*-Pr	90
2	**2b**	Et	96
3	**2c**	Bn	79
4	**2d**	Ph	91
5	**2e**	4-MeOPh	81
6	**2f**	CO_2Me	65
7	**2g**	2-pyridyl	95
8	**2h**	3-pyridyl	trace
9	**2i**	2-furyl	40
10	**2j**	*t*-Bu	trace

[a] All reactions were carried out using 2.0 equiv of $CuSO_4$ and 1.1 equiv of aldehyde in CH_2Cl_2 at room temperature.

Copper(II) Sulfate Mediated Condensations. To enhance the synthetic utility of the condensation approach to imines **2**, a number of alternative conditions were investigated. Although trimethoxyorthoformate was found to be an effective solvent for the condensation of **1** with aldehydes, it was not more efficient than the initial $MgSO_4$ and PPTS conditions. We reasoned that the more Lewis acidic $CuSO_4$ would be more effective than $MgSO_4$. Indeed, $CuSO_4$ is such an efficient drying agent and Lewis acid catalyst that the protic acid catalyst PPTS was not necessary to effect the desired condensation reaction (eq 2 in Table 2). Thus, with CH_2Cl_2 as solvent and 2 equiv of $CuSO_4$, good yields of sulfinyl aldimines **2** were obtained when **1** was condensed with only 1.1 equiv of aldehydes of several structural types (Table 2). Even the condensation of the unreactive electron rich aldehyde, *p*-anisaldehyde, provided sulfinyl aldimine **2e** in high yield (81%; entry 5). Once again, phenylacetaldehyde was condensed without enamine formation (entry 3). As was previously observed for the $MgSO_4$/PPTS conditions, no racemization was observed in the presence of $CuSO_4$. Yields were poor for the electron deficient heteroaromatic aldehyde furfural (entry 9) and the extremely sterically demanding pivaldehyde (entry 10). Ketones did not afford sulfinyl ketimines in the presence of $CuSO_4$.

Interestingly, the condensation of **1** with 2-pyridinecarboxaldehyde afforded **2g** in high yield (entry 7), while the condensation of **1** with 3-pyridinecarboxaldehyde did not proceed (entry 8). A deep-blue color was observed immediately upon addition of 3-pyridinecarboxaldehyde to $CuSO_4$, suggesting the formation of a pyridine−Cu complex. Interestingly, even the use of 4 equiv of $CuSO_4$ did not effect the desired condensation. The success of the condensation of **1** with 2-pyridinecarboxaldehyde may be attributed to the proximity of the aldehyde to the basic nitrogen, which may result in the formation of a five-membered chelate that activates the aldehyde for 1,2-attack by **1**.

Titanium(IV)-Mediated Condensations. Titanium(IV) salts were next investigated, primarily to effect the condensation of sulfinamide **1** with ketones. Due to their Lewis acidity and excellent water-scavenging ability, Ti(IV) salts such as $TiCl_4$ and Ti(O-*i*-Pr)$_4$ have been used to condense amines[16] and even ureas[17] with ketones.

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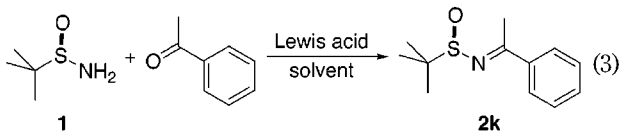
(15) Branchaud, B. P. *J. Org. Chem.* **1983**, *48*, 3531−3538.

Table 3. Condensations of 1 with Acetophenone Mediated by Ti(IV) Compounds[a]



entry	Lewis acid	solvent	temp (°C)	yield (%)
1	$Ti(O\text{-}i\text{-}Pr)_4$	toluene	110	60
2	$Ti(O\text{-}i\text{-}Pr)_4$	toluene	22	34
3	$TiCl_4$[b]	toluene	0 → 22	40
4	$TiCl_2(O\text{-}i\text{-}Pr)_2$[c]	THF	0 → 22	51
5	$TiCl_2(O\text{-}i\text{-}Pr)_2$[c]	toluene	0 → 22	65
6	$TiCl(O\text{-}i\text{-}Pr)_3$[d]	THF	60	84
7	$TiCl(O\text{-}i\text{-}Pr)_3$[d]	toluene	110	60
8	$Ti(OEt)_4$	toluene	110	87
9	$Ti(OEt)_4$	THF	75	89

[a] Reactions were run at 0.5 M. [b] 4 equiv of Et_3N was added. [c] 2 equiv of Et_3N was added. [d] 1 equiv of Et_3N was added.

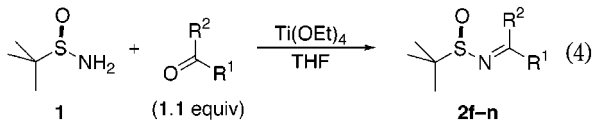
Titanium(IV) reagents are inexpensive and, upon addition of water, provide solid titanium oxide byproducts that can be rapidly filtered away. The initial experiments focused on the condensation of sulfinamide **1** with acetophenone to afford sulfinyl imine **2k** (eq 3 in Table 3). Acetophenone is less electrophilic and more prone to enolization and competitive aldol condensation reactions than aliphatic ketones. Therefore, conditions developed for the synthesis of **2k** should be applicable to a variety of *N*-*tert*-butanesulfinyl ketimines.

At elevated temperatures, $Ti(O\text{-}i\text{-}Pr)_4$ was moderately effective (entries 1 and 2). The stronger Lewis acid, $TiCl_4$, rapidly provided the imine product in the presence of Et_3N as acid scavenger, but aldol condensation was competitive under these conditions (entry 3). Mixtures of $Ti(O\text{-}i\text{-}Pr)_4$ and $TiCl_4$ were used to form condensing reagents with attenuated reactivity (entries 4−7). Although these less Lewis acidic compounds reduced the amount of aldol condensation product observed with concomitant improvements in the chemical yield of **2k**, aldol condensation was not eliminated. Fortunately, $Ti(OEt)_4$ was found to be more effective than $Ti(O\text{-}i\text{-}Pr)_4$ without promotion of the aldol condensation side reaction. An 89% yield of **2k** was obtained when $Ti(OEt)_4$ was used in THF. Unlike the chlorotitanium complexes (entries 3−7), there was not a significant difference between toluene and THF as solvent (entries 8 and 9). Technical grade $Ti(OEt)_4$ is effective for the condensation reaction. These conditions were also effective for aliphatic ketones. For example, with careful monitoring at 60 °C in THF, cyclohexanone gave the product **2l** in 91% yield and 3-methyl-2-butanone gave the sulfinyl ketimine product **2m** in 84% yield (Table 4). The same condensation reactions performed at reflux temperature afforded sulfinyl ketimines in less desirable yields (60−70%) due to thermal decomposition.

To establish the generality of this procedure, $Ti(OEt)_4$-mediated condensations were performed with a number of other ketones with varying steric demand about the carbonyl (eq 4 in Table 4). This straighforward procedure affords sulfinyl ketimines cleanly and in high yields from a variety of ketones, including the exceptionally sterically hindered pinacolone to afford sulfinyl ketimine **2s**. Although this sterically hindered ketone required more forcing conditions to deliver **2s**, the product sulfinyl ketimine was stable to the higher temperatures. The standard procedure is to begin the condensation reaction at 60 °C. If the reaction is sluggish, the temperature is elevated to effect the condensation at a more reasonable rate. The thermal stability of the sulfinyl ketimine products appears to be related to the steric demand about the carbonyl, and ketones that require more forcing conditions to condense deliver imine products that do not decompose noticeably under these conditions.

The $Ti(OEt)_4$ conditions were also investigated for the synthesis of *N*-*tert*-butanesulfinyl aldimines, including those few that were not formed in synthetically useful yields by the $CuSO_4$-mediated methodology (Table 2). Sulfinamide **1** condensed smoothly with propionaldehyde in the presence of either $Ti(OEt)_4$ or $Ti(O\text{-}i\text{-}Pr)_4$ without competitive aldol condensation or Meerwein−Pondorff−Verley reduction to afford sulfinyl aldimines **2** (eq 5 in Table 5). The less active aldehydes, furfural and pivaldehyde, were also effectively converted to their corresponding *tert*-butanesulfinyl aldimines **2i** and **2j**. Sulfinyl imine **2h**, whose 3-pyridyl functionality was incompatible with the $CuSO_4$ methodology, was also prepared by the $Ti(OEt)_4$-mediated methodology.

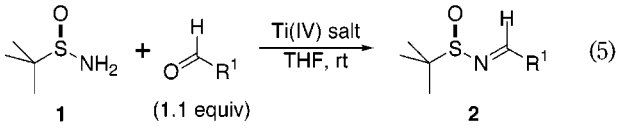
Table 4. Condensation of Ketones with 1 Mediated by $Ti(OEt)_4$[a]



product	R^1	R^2	temp (°C)	time (h)	yield (%)	(*E*/*Z*)[b]
2k	Ph	Me	75[c]	15	89	one isomer
2l	$-(CH_2)_5-$		60	4	91	
2m	*i*-Pr	Me	60	7	84	one isomer
2n	*i*-Pr	Bu	75[c]	24	77	one isomer
2o	Ph	Bu	75[c]	5	77	one isomer
2p	2-Npth[d]	Me	75[c]	15	73	one isomer
2q	*i*-Bu	Me	60	10	88	6:1
2r	Bu	Me	60	10	77	5:1
2s	*t*-Bu	Me	75[c]	24	82	one isomer

[a] Reactions were performed with 1.1 equiv of ketone with 2.0 equiv of $Ti(OEt)_4$ in THF. [b] Ratios were determined by ^1H NMR. [c] The reflux temperature of the reaction mixture. [d] 2-naphthyl.

Table 5. Condensations of 1 with Aldehydes Mediated by Ti(IV) Salts[a]



product	R^1	Ti(IV) salt	time (h)	yield (%)
2b	Et	$Ti(OEt)_4$	3	quant.
2b	Et	$Ti(O\text{-}i\text{-}Pr)_4$	7	83
2c	Bn	$Ti(OEt)_4$	6	84
2c	Bn	$Ti(O\text{-}i\text{-}Pr)_4$	14	77
2h	3-pyridyl	$Ti(OEt)_4$	6	quant.
2i	2-furyl	$Ti(OEt)_4$	4	82
2j	*t*-Bu	$Ti(OEt)_4$	5	82

[a] Reactions were performed at room temperature with 1.1 equiv of aldehyde and 2 equiv of Ti(IV) salt in THF.

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Stability and Isolation of Sulfinimines. Although some *tert*-butanesulfinyl imines hydrolyze very slowly in air, they can be stored dry at low temperatures (−5 °C) for extended periods of time. The sulfinyl aldimines are the more robust derivatives and have shown no sign of either hydrolysis or oligomerization. Other undetermined decomposition pathways do result in minor contamination of the sulfinyl aldimines after a period of weeks or months if stored in air at room temperature. The sulfinyl ketimine derivatives show varying rates of hydrolysis in air depending on substitution about the imine. For example, α-aryl ketimines such as **2k**, **2o**, and **2p** hydrolyze very slowly while sulfinyl imines **2l** (derived from cyclohexanone) and **2r** (derived from 2-hexanone) will fully hydrolyze over the course of 2 days in air. Nonetheless, all the sulfinyl imines can be handled in air, and even **2l** and **2r** have been stored dry for months at −5 °C with no sign of decomposition. Although sulfinyl imines rearrange at high temperatures,[18] the lower boiling derivatives have been distilled at low temperature (35−40 °C) under reduced pressure. The relative stabilities of the *tert*-butanesulfinyl imines to silica chromatography correspond to the rates of hydrolysis in air. Except for **2l**, all of the sulfinyl imines prepared in this study could be quickly chromatographed with hexanes/Et_2O as eluent, allowing for the isolation of higher molecular weight sulfinyl imines in analytically pure form.

Sulfinimine Geometry. *tert*-Butanesulfinyl aldimines, like arenesulfinyl aldimines,[7b] are observed exclusively as the *E*-imine isomers (Table 4).[19] Steric effects also control the *E*/*Z* isomer ratios observed for *tert*-butanesulfinyl ketimines. Only the *E* isomer is observed by 400 MHz ^{1}H and 101 MHz ^{13}C NMR in $CDCl_3$ for sulfinyl ketimines derived from aryl *n*-alkyl ketones and isopropyl *n*-alkyl ketones (**2k**, **2m**−**p**, and **2s**). The 5:1 mixture of *E* and *Z* isomers observed for the *tert*-butanesulfinyl ketimine derived from 2-hexanone (**2r**; see Table 4) is impressive considering the small difference in steric demand about the imine. Although two isomers of **2q** and **2r** are detectable by NMR, in each case, only one compound is seen by chromatography (TLC and HPLC). The rapid rate of *E*/*Z* interconversion precludes isolation of the *E* isomer[20] but makes possible diastereomeric ratios of addition products that exceed the initial *E*/*Z* ratios of the corresponding *tert*-butanesulfinyl ketimine precursors. This has already been observed for the Me_3Al-mediated 1,2-addition of organolithiums to **2r** to afford sulfinamides with a 9:1 diastereomeric ratio.[3]

Conclusion

Sulfinyl imines are versatile intermediates for the asymmetric synthesis of amines bearing an α-stereogenic center (Figure 1). Therefore, the synthesis of *tert*-butanesulfinyl aldimines and ketimines from the corresponding aldehydes and ketones and the inexpensive chiral ammonia synthon, *tert*-butanesulfinamide **1**, provides practical access to numerous important chiral amines. The $CuSO_4$-mediated synthesis of *tert*-butanesulfinyl aldimines from **1** and aldehydes proceeds in high yields, is operationally straightforward, and requires only a slight excess of aldehyde (1.1 equiv). For the few aldehydes where the $CuSO_4$-mediated condensations do not proceed in high yields, Ti(IV) salts are effective. Moreover, Ti(OEt)$_4$ effects the condensation of ketones to afford *N*-*tert*-butanesulfinyl ketimines. This is the first general synthesis of sulfinyl ketimines, including the previously inaccessible aliphatic derivatives. The straightforward and high-yielding one-step procedures developed for the preparation of *tert*-butanesulfinyl imines should significantly enhance the utility of these important chiral intermediates for the asymmetric synthesis of chiral amines, which are key components of many natural products, synthetic pharmaceuticals, materials, and asymmetric catalysts.

Experimental Section

General. All aldehydes and ketones were obtained from commercial suppliers and were distilled before use. Lewis acids were also obtained from commercial suppliers, and Ti(OEt)$_4$ and Ti(O-*i*-Pr)$_4$ were used without purification from fresh bottles or were distilled under reduced pressure. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl, and toluene was distilled from Na. All reactions were carried out in flame- or oven-dried glassware under an inert N_2 atmosphere. Chromatography was carried out using Merck 60 230−400 mesh silica gel. IR spectra of liquids were recorded as thin films on NaCl plates, and IR spectra of solids were recorded as KBr pellets. Chemical shifts in NMR spectra are expressed in ppm. All NMR spectra were obtained in $CDCl_3$ with TMS as an internal standard at room temperature. Sulfinamide **1** was prepared as previously described.[2e,9]

General Procedure for the Synthesis of *tert*-Butanesulfinyl Aldimines 2 from $MgSO_4$ and PPTS (Method A). To a 0.5 M solution of (*R*)-**1** (1 equiv) in CH_2Cl_2 were added 0.05 equiv of PPTS and 5 equiv of anhydrous $MgSO_4$ followed by the aldehyde. The mixture was stirred at room temperature for 24 h. Upon completion, the reaction mixture was filtered through a pad of Celite and the filter cake was washed well with CH_2Cl_2. The residue obtained after filtration was purified by chromatography.

General Procedure for the Synthesis of *tert*-Butanesulfinyl Aldimines 2 from $CuSO_4$ (Method B). To a 0.5 M solution of (*R*)-**1** (1 equiv) in CH_2Cl_2 was added 2.2 equiv of anhydrous $CuSO_4$ followed by the aldehyde (1.1 equiv). The mixture was stirred at room temperature for 12−24 h. The reaction mixture was filtered through a pad of Celite, and the filter cake was washed well with CH_2Cl_2. The residue obtained after filtration was purified by chromatography.

General Procedure for the Synthesis of *tert*-Butanesulfinyl Imines 2 from Ti(OEt)$_4$ (Method C). A 0.5 M solution of Ti(OEt)$_4$ (technical grade, ∼20% Ti; ∼2 equiv) and aldehyde or ketone (1−1.1 equiv) in THF was prepared under a N_2 atmosphere. Then, (*R*)-**1** (1−1.1 equiv) was added and the flask was heated. Conversion was followed by TLC, and the mixture cooled immediately upon completion. Once at room temperature, the mixture was poured into an equal volume of brine while rapidly stirring. The resulting suspension was filtered through a plug of Celite, and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted once with a small volume of EtOAc, and the combined organic portions were dried (Na_2SO_4), filtered, and concentrated. The sulfinyl imines, **2**, were purified either by distillation or silica gel chromatography.

(*R*)-(−)-*N*-(2-Methylpropylidene)-2-methylpropanesulfinamide (2a). Method A. The general procedure was followed with 500 mg (4.13 mmol) of (*R*)-**1**, 52 mg (0.20 mmol) of

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(19) The *E* assignment is made by analogy to *p*-toluenesulfinyl imines, whose conformations were determined from X-ray crystal structures: Robinson, P. D.; Hua, D. H.; Shan, J. S.; Saha, S. *Acta Crystallogr.* **1991**, *C47*, 594−596, and ref 7b.

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PPTS, and 595 mg (8.26 mmol) of isobutyraldehyde. Chromatography (95:5 CH_2Cl_2/hexanes) delivered 650 mg (91%) of **2a**.

Method B. The general procedure was followed with 500 mg (4.13 mmol) of (*R*)-**1**, 328 mg (4.54 mmol) of isobutyraldehyde, and 1.45 g (9.08 mmol) of $CuSO_4$. Chromatography (CH_2Cl_2) delivered 585 mg (81%) of **2a**: $[\alpha]^{23}_D$ −259.4° (*c* 1.0, $CHCl_3$); IR 1085, 1622 cm^{-1}; ^1H NMR (300 MHz) δ 1.10−1.23 (m, 15H), 2.66−2.77 (m, 1H), 7.98 (d, J = 4.4 Hz, 1H); ^{13}C NMR (101 MHz) δ 18.7, 22.1, 34.7, 56.4, 173.4. Anal. Calcd for $C_8H_{17}NOS$: C, 54.82; H, 9.78; N, 7.99. Found: C, 54.68; H, 9.51; N, 8.17.

(*R*)-(−)-*N*-(Propylidene)-2-methylpropanesulfinamide (2b). Method A. The general procedure was followed with 1.00 g (8.26 mmol) of (*R*)-**1**, 103 mg (0.413 mmol) of PPTS, and 957 mg (16.5 mmol) of propionaldehyde. Chromatography (CH_2Cl_2) delivered 1.28 g (96%) of **2b**.

Method B. The general procedure was followed with 1.00 g (8.26 mmol) of (*R*)-**1**, 527 mg (9.08 mmol) of propionaldehyde, and 2.90 g (18.2 mmol) of $CuSO_4$. Chromatography (CH_2Cl_2) delivered 1.25 g (94%) of **2b**: $[\alpha]^{23}_D$ −328.5° (*c* 1.0, $CHCl_3$); IR 1082, 1627 cm^{-1}; ^1H NMR (300 MHz) δ 1.15−1.31 (m, 12H), 2.50−2.58 (m, 2H), 8.10 (t, J = 4.2 Hz, 1H); ^{13}C NMR (101 MHz) δ 9.40, 22.1, 29.30, 56.3, 170.0. Anal. Calcd for $C_7H_{15}NOS$: C, 52.14; H, 9.38; N, 8.69. Found: C, 51.96; H, 9.44; N, 8.88.

(*R*)-(−)-*N*-(2-Phenylethylidene)sulfinamide (2c). Method A. The general procedure was followed with 1.70 g (14.0 mmol) of (*R*)-**1**, 180 mg (0.700 mmol) of PPTS, and 2.53 g (21.0 mmol) of phenylacetaldehyde. Chromatography (CH_2Cl_2) delivered 2.61 g (84%) of **2c** as a pale yellow oil.

Method B. The general procedure was followed with 1.00 g (8.26 mmol) of (*R*)-**1**, 1.09 g (9.08 mmol) of phenylacetaldehyde, and 2.90 g (18.2 mmol) of $CuSO_4$. Chromatography (CH_2Cl_2) delivered 1.46 g (79%) of **2c** as a pale yellow oil: IR 1076, 1618 cm^{-1}; $[\alpha]^{23}_D$ −230.0° (*c* 1.0, $CHCl_3$); ^1H (300 MHz) δ 1.18 (s, 9H), 3.81−3.84 (m, 2H), 7.21−7.36 (m, 5H), 8.13 (t, J = 5.3 Hz, 1H); ^{13}C (125 MHz) δ 22.4, 42.6, 56.9, 127.1, 128.8, 129.2, 134.8, 167.4. Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67; N, 6.27. Found: C, 64.60; H, 7.54; N, 6.07.

(*R*)-(−)-*N*-(Benzylidene)-2-methylpropanesulfinamide (2d). Method A. The general procedure was followed with 1.00 g (8.26 mmol) of (*R*)-**1**, 103 mg (0.413 mmol) of PPTS, and 2.63 g (24.8 mmol) of benzaldehyde. Chromatography (CH_2Cl_2) delivered 1.56 g (90%) of **2d**.

Method B. The general procedure was followed with 0.300 g (2.48 mmol) of (*R*)-**1**, 0.289 g (2.73 mmol) of benzaldehyde, and 0.592 g (3.72 mmol) $CuSO_4$. Chromatography (CH_2Cl_2) delivered 0.470 g (91%) of **2d**. No racemization was observed by HPLC analysis (Diacel Chiralpak OD column, 90:10 hexanes/IPA; 1.0 mL/min; 254 nm; (*S*)-**2d** t_R = 4.8 min, (*R*)-**2d** t_R = 5.9 min). **2d**: $[\alpha]^{23}_D$ −122.0° (*c* 1.0, $CHCl_3$); IR 1084, 1643 cm^{-1}; ^1H NMR (300 MHz) δ 1.30 (s, 9H), 7.44−7.55 (m, 3H), 7.84−7.87 (m, 2H), 8.59 (s, 1H); ^{13}C NMR (101 MHz) δ 22.5, 57.6, 128.8, 129.2, 132.3, 134.0, 162.6. Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.13; H, 7.22; N, 6.69. Found: C, 62.94; H, 6.94; N, 6.47.

(*R*)-(−)-*N*-(4-Methoxybenzylidene)-2-methylpropanesulfinamide (2e). Method B. The general procedure was followed with 1.00 g (8.26 mmol) of (*R*)-**1**, 1.23 g (9.08 mmol) of *p*-anisaldehyde, and 2.90 g (18.2 mmol) of $CuSO_4$. Chromatography (CH_2Cl_2) delivered 1.59 g (81%) of **2e** as a white solid: mp 91−93 °C; $[\alpha]^{23}_D$ −70.2° (*c* 1.0, $CHCl_3$); IR 1080, 1592 cm^{-1}; ^1H NMR (500 MHz) δ 1.25 (s, 9H), 3.87 (s, 3H), 6.96 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 8.51 (s, 1H). ^{13}C NMR (125 MHz) δ 59.4, 70.0, 70.7, 89.1, 93.3, 94.6, 104.4, 104.9. Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.32; H, 6.89; N, 5.91.

(*R*)-(−)-*N*-(2-Methoxycarbonylethylidene)-2-methylpropanesulfinamide (2f). Method B. The general procedure was followed with 2.41 g (20.0 mmol) of (*R*)-**1**, 2.13 g (24.0 mmol) of methyl glyoxalate,[21] and 6.36 g (40.0 mmol) of $CuSO_4$. Chromatography (4:1 hexanes/EtOAc) delivered 2.50 g (65%) of **2f** as a colorless oil: $[\alpha]^{23}_D$ −305° (*c* 1.0, $CHCl_3$); IR 1752, 1736, 1096 cm^{-1}; ^1H NMR (300 MHz) δ 1.28 (s, 9H), 3.93 (s, 3H), 8.01 (s, 1H); ^{13}C NMR (101 MHz) δ 23.0, 53.4, 59.2, 155.4, 161.8. Anal. Calcd for $C_7H_{13}NO_3S$: C, 43.96, H, 6.85, N, 7.32. Found: C, 43.82, H, 6.73, N, 7.44.

(*R*)-(−)-*N*-(2-Pyridinemethylidene)-2-methylpropanesulfinamide (2g). Method B. The general procedure was followed with 121 mg (1.00 mmol) of (*R*)-**1**, 107 mg (1.00 mmol) of 2-pyridinecarboxaldehyde, and 320 mg (2.00 mmol) of $CuSO_4$. Chromatography (3:1 hexanes/EtOAc) delivered 203 mg (95%) of **2g** as a colorless oil: $[\alpha]^{23}_D$ −172° (*c* 1.0, $CHCl_3$); IR 1607, 1088 cm^{-1}; ^1H NMR (300 MHz) δ 1.29 (s, 9H), 7.42 (m, 1H), 7.82 (m, 1H), 8.01 (d, J = 7.8 Hz, 1H), 8.71 (s, 1H), 8.75 (d, J = 5.0 Hz, 1H); ^{13}C NMR (101 MHz) δ 22.9, 58.3, 123.3, 126.2, 137.1, 150.4, 152.7, 164.0. Anal. Calcd for $C_{10}H_{14}N_2OS$: C, 57.12; H, 6.71; N, 13.32. Found: C, 56.96; H, 6.65; N, 13.30.

(*R*)-(−)-*N*-(3-Pyridinemethylidene)-2-methylpropanesulfinamide (2h). Method C. A mixture of 0.86 mL (0.91 mmol) of 3-pyridinecarboxaldehyde, 0.86 g of $Ti(OEt)_4$ (∼1.7 mmol), and 0.10 g of (*R*)-**1** (0.86 mmol) in 1.6 mL of THF was stirred at room temperature for 2 h. Chromatography (3:1 hexanes/EtOAc) delivered 180 mg (quantitative yield) of **2h**: $[\alpha]^{23}_D$ −136° (*c* 1.0, $CHCl_3$); IR 1087, 1588, 1586, 1610 cm^{-1}; ^1H NMR (500 MHz) δ 1.24 (s, 9H), 7.40 (m, 1H), 8.13 (m, 1H), 8.61 (s, 1H), 8.70 (m, 1H), 9.00 (m, 1H); ^{13}C NMR (121 MHz) δ 22.5, 58.0, 123.9, 129.6, 135.6, 151.0, 152.9, 160.4. Anal. Calcd for $C_{10}H_{14}N_2OS$: C, 57.11; H, 6.71; N, 13.32. Found: C, 56.93, H, 6.56, N, 13.39.

(*R*)-(−)-*N*-(2-Furylmethylene)-2-methylpropanesulfinamide (2i). Method B. The general procedure was followed with 242 mg (2.00 mmol) of (*R*)-**1**, 192 mg (2.00 mmol) of furfural, and 640 mg (4.00 mmol) of $CuSO_4$. Chromatography (Et_2O) delivered 159 mg (40%) of **2i** as a colorless oil.

Method C. A mixture of 192 mg (2.00 mmol) of furfural, 1.14 g of $Ti(OEt)_4$ (∼4.0 mmol), and 242 mg of (*R*)-**1** (1.00 mmol) in 4 mL of THF was stirred at room temperature for 4 h. Pure **2i** was obtained (326 mg, 82%) as a clear oil from chromatography (Et_2O): $[\alpha]^{23}_D$ −168° (*c* 1.0, $CHCl_3$); IR 1081, 1613 cm^{-1}; ^1H NMR (300 MHz) δ 1.26 (s, 9H), 6.57 (dd, J = 3.5, 1.8 Hz, 1H), 7.01 (dd, J = 0.7, 3.5 Hz, 1H), 7.65 (m, 1H), 8,40 (s, 1H); ^{13}C NMR (75 MHz) δ 22.8, 58.1, 112.8, 119.0, 147.1, 150.1, 151.1. Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.24; H, 6.57; N, 7.03. Found: C, 54.49; H, 6.30; N, 6.82.

(*R*)-(−)-*N*-(2,2-Dimethylpropylidene)-2-methylpropanesulfinamide (2j). Method C. A mixture of 103 mg (1.20 mmol) of 2,2-dimethylpropionaldehyde, 690 mg of $Ti(OEt)_4$ (∼3.0 mmol), and 121 mg of (*R*)-**1** (1.00 mmol) in 3 mL of THF was stirred at room temperature for 5 h. Pure **2j** was obtained (155 mg, 82%) as a clear oil from chromatography (4:1 hexanes/EtOAc): $[\alpha]^{23}_D$ −285° (*c* 1.0, $CHCl_3$); IR 1620, 1089 cm^{-1}; ^1H NMR (300 MHz) δ 1.16 (s, 9H), 1.18 (s, 9H), 7.92 (s, 1H); ^{13}C (101 MHz) δ 22.3, 26.7, 37.9, 56.45, 175.6. Anal. Calcd for $C_9H_{19}NOS$: C, 57.10; H, 10.12; N, 7.40. Found: C, 57.20, H, 10.31, N, 7.53.

(*R*)-(−)-*N*-(1-Phenylethylidene)-2-methylpropanesulfinamide (2k). Method C. A mixture of 2.11 mL of acetophenone (18.2 mmol), 8.7 g of $Ti(OEt)_4$ (∼36.4 mmol), and 2.00 g of (*R*)-**1** (16.5 mmol) in 36 mL of THF was heated to reflux for 15h. Pure **2k** was obtained (3.22 g, 88%) as a yellow crystalline solid from silica chromatography (85:15 hexanes/EtOAc). No racemization was observed by chiral HPLC analysis (Diacel Chiralpak OD column, 90:10 hexanes/IPA; 1.0 mL/min; 250 nm; (*R*)-**2k** t_R = 6.1 min, (*S*)-**2k** t_R = 7.6 min): $[\alpha]^{23}_D$ −2.1° (*c* 1.0, $CHCl_3$); IR 1067, 1572, 1593, 1605 cm^{-1}; ^1H NMR (500 MHz) δ 1.32 (s, 9H), 2.77 (s, 3H), 7.26−7.89 (m, 5H); ^{13}C NMR (125 MHz) δ 22.5, 24.2, 57.4, 127.2, 128.4, 131.6, 138.7, 176.4. Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.54; H, 7.67; N, 6.27. Found: C, 64.66; H, 7.47; N, 6.32.

(*R*)-(−)-*N*-Cyclohexylidene-2-methylpropanesulfinamide (2l). Method C. A mixture of 518 μL of cyclohexanone (5.00 mmol), 2.0 g of technical grade $Ti(OEt)_4$ (∼8.5 mmol), and 666 mg of (*R*)-**1** (5.50 mmol) in 9 mL of THF was warmed to 60 °C for 4 h. Pure **2l** was obtained (918 mg, 91%) as a clear

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and colorless oil from Kugelrohr distillation (40 °C at 5 μTorr): $[\alpha]^{23}_D$ −184.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz) δ 1.21 (s, 9H), 1.62−1.86 (m, 6H), 2.41 (m, 2H), 2.70 (m, 1H), 2.87 (m, 1H); ^{13}C NMR (100 MHz) δ 22.03, 25.26, 27.32, 27.83, 34.34, 40.60, 55.88, 188.59. Anal. Calcd for $C_{10}H_{19}NOS$: C, 59.66; H, 9.51; N, 6.96. Found: C, 59.34; H, 9.49; N, 7.27.

(*R*)-−(−)-*N*-(3-Methyl-2-butylidene)-2-methylpropanesulfinamide (2m). Method C. A mixture of 534 μL of 3-methyl-2-butanone (5.00 mmol), 2.0 g of $Ti(OEt)_4$ (∼ 8.5 mmol), and 605 mg of (*R*)-**1** (8.5 mmol) in 9 mL of THF was warmed to 60 °C for 7 h. Pure **2m** was obtained (874 mg, 84%) as a clear and colorless oil from Kugelrohr distillation (32 °C at 5 μTorr). No racemization was observed by chiral HPLC analysis (Diacel Chiralpak OD column, 95:5 hexanes/IPA; 0.9 mL/min; 244 nm; (*R*)-**2m** t_R = 5.7 min, (*S*)-**2m** t_R = 6.7 min): $[\alpha]^{23}_D$ −185.7° (*c* 1.0, $CHCl_3$); IR 1074, 1624 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.09 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.20 (s, 9H), 2.28 (s, 3H), 2.53 (septet, *J* = 6.8, 1H); ^{13}C NMR (101 MHz) δ 19.48, 19.72, 20.99, 22.10, 41.24, 56.35, 189.10. Anal. Calcd for $C_9H_{19}NOS$: C, 57.10; H, 10.12; N, 7.40. Found: C, 57.13; H, 10.32; N, 7.58.

(*R*)-(−)-*N*-(2-Methyl-3-heptylidene)-2-methylpropanesulfinamide (2n). Method C. A mixture of 571 mL of 2-methyl-3-heptanone (3.64 mmol), 1.6 g of $Ti(OEt)_4$ (∼ 6.62 mmol), and 400 mg of (*R*)-**1** (3.31 mmol) in 6.6 mL of THF was warmed to 75 °C for 24 h. Pure **2n** was obtained (591 mg, 77%) as a clear and colorless oil from chromaotography (5:1 hexanes/Et_2O): $[\alpha]^{23}_D$ −181.2° (*c* 1.0, $CHCl_3$); IR 1076, 1623 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.92 (t, *J* = 7.3, 3H), 1.10−1.17 (m, 6H), 1.23 (s, 9H), 1.32−1.41 (m, 2H), 1.53−1.59 (m, 2H), 2.61−2.80 (m, 2H), 2.73−2.80 (m, 1H); ^{13}C NMR (101 MHz) δ 13.72, 20.14, 20.37, 22.25, 23.02, 29.53, 34.85, 39.00, 56.38, 192.48. Anal. Calcd for $C_{12}H_{25}NOS$: C, 62.29; H, 10.89; N, 6.05. Found: C, 62.15; H, 10.69; N, 6.21.

(*R*)-(−)-*N*-(1-Phenylpentylidene)-2-methylpropanesulfinamide (2o). Method C. A mixture of 1.47 g of 1-phenylpentanone (9.09 mmol), 3.4 g of $Ti(OEt)_4$ (∼14 mmol), and 1.00 g of (*R*)-**1** (8.26 mmol) in 18 mL of THF was heated to reflux for 5h. Pure **2o** was obtained (1.68 g, 77%) as a yellow viscous oil from silica chromatography (80:20 hexanes/EtOAc): $[\alpha]^{23}_D$ −30.3° (*c* 1.0, $CHCl_3$); IR 1073, 1570, 1591, 1603 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.95 (t, *J* = 7.3, 3H), 1.33 (s, 9H), 1.38−1.49 (m, 2H), 1.60−1.70 (m, 2H), 3.18 (m, 1H), 3.28 (m, 1H), 7.41−7.49 (m, 3H), 7.85−7.87 (m, 2H); ^{13}C NMR (101 MHz) δ 13.73, 22.58, 22.95, 30.67, 32.32, 57.30, 127.43, 128.49, 131.41, 137.90, 180.31. Anal. Calcd for $C_{15}H_{23}NOS$: C, 67.88; H, 8.73; N, 5.28. Found: C, 67.94; H, 8.55; N, 5.21.

(*R*)-(+)-*N*-(1-(2′-Naphthyl)ethylidene)-*tert*-butanesulfinamide (2p). Method C. A mixture of 1.55 g of 2′-acetonaphthone (9.10 mmol), 3.4 g of $Ti(OEt)_4$ (∼14 mmol), and 1.00 g of (*R*)-**1** (8.26 mmol) in 18 mL of THF was heated to reflux for 15h. Pure **2p** was obtained (1.81 g, 86%) as a yellow powder from silica chromatography (85:15 hexanes/EtOAc): $[\alpha]^{23}_D$ +11.7° (*c* 1.0, $CHCl_3$); IR 1078, 1572, 1589 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.36 (s, 9H), 1.60 (s, 3H), 7.56 (m, 2H), 7.86 (m, 2H), 7.92 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR (101 MHz) δ 19.72, 22.53, 57.49, 123.79, 126.61, 127.62, 127.85, 128.11, 129.16, 132.61, 134.82, 136.04, 176.08. Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.00; N, 5.12. Found: C, 70.15; H, 6.81; 5.07.

(*R*)-(−)-*N*-(4-Methyl-2-pentylidene)-2-methylpropanesulfinamide (2q). Method C. A mixture of 1.87 mL of 4-methyl-2-pentanone (15.0 mmol), 4.0 g of $Ti(OEt)_4$ (∼30 mmol), and 1.00 g of (*R*)-**1** (16.5 mmol) in 30 mL of THF was warmed to 70 °C for 10 h. Pure **2q** was obtained (2.67 g, 88%) as a clear and colorless oil from Kugelrohr distillation (36 °C at 5 μTorr) as a mixture of *E*/*Z* isomers (6:1 by ^{1}H NMR in $CDCl_3$): $[\alpha]^{23}_D$ −185.0° (*c* 1.0, $CHCl_3$); IR 1076, 1621 cm^{-1}; ^{1}H NMR (400 MHz) *E* isomer δ 0.93−0.97 (m, 6H), 1.24 (s, 9H), 2.04−2.22 (m, 1H), 2.23−2.34 (m, 2H), 2.37 (s, 3H), *Z* isomer δ 0.93−0.97 (m, 6H), 1.24 (s, 9H), 2.04−2.22 (m, 1H), 2.16 (s, 3H), 2.53−2.57 (m, 1H), 2.69−2.76 (m, 1H); ^{13}C NMR (101 MHz) *E* isomer δ 22.10, 22.45, 22.48, 22.13, 25.57, 52.45, 56.10, 185.11. Anal. Calcd for $C_{10}H_{21}NOS$: C, 59.07; H, 10.41; N, 6.89. Found: C, 58.90; H, 10.30; N, 7.03.

(*R*)-(−)-*N*-(2-Hexylidene)-2-methylpropanesulfinamide (2r). Method C. A mixture of 1.12 mL of 2-hexanone (9.09 mmol), 4.0 g of $Ti(OEt)_4$ (∼17 mmol), and 1.00 g of (*R*)-**1** (8.26 mmol) in 18 mL of THF was warmed to 70 °C for 10 h. Pure **2r** was obtained (1.29 g, 77%) as a clear and colorless oil from chromatography (5:1 hexanes/Et_2O) as a mixture of *E*/*Z* isomers (5:1 by ^{1}H NMR in $CDCl_3$ and toluene-d_8): $[\alpha]^{23}_D$ −164.4° (*c* 1.0, $CHCl_3$); IR 1076, 1625 cm^{-1}; ^{1}H NMR (400 MHz) *E* isomer δ 0.85 (m, 3H), 1.5 (s, 9H), 1.20−1.31 (m, 2H), 1.46−1.54 (m, 2H), 2.23 (s, 3H), 2.26−2.39 (m, 2H), *Z* isomer δ 0.85 (m, 3H), 1.5 (s, 9H), 1.20−1.31 (m, 2H), 1.46−1.54 (m, 2H), 2,08 (s, 3H), 2.60−2.64 (br m, 2H); ^{13}C NMR (101 MHz) *E* isomer δ 13.77, 22.05, 22.13, 22.84, 27.58, 43.07, 56.11, 185.51, *Z* isomer δ 15.05, 22.05, 22.73, 27.96, 29.26, 36.86, 55.82, 186.32. Anal. Calcd for $C_{10}H_{21}NOS$: C, 59.07; H, 10.41; N, 6.89. Found: C, 59.17; H, 10.56; N, 7.04.

(*R*)-(−)-*N*-(3,3-Dimethyl-2-butylidene)-2-methylpropanesulfinamide (2s). Method C. A mixture of 361 mg of pinacolone (3.64 mmol), 1.6 g of $Ti(OEt)_4$ (∼6.6 mmol), and 400 mg of (*R*)-**1** (3.31 mmol) in 6 mL of THF was warmed to 70 °C for 24 h. Pure **2s** was obtained (553 mg, 82%) as a clear and colorless oil from Kugelrohr distillation (37 °C, 5 μTorr): $[\alpha]^{23}_D$ −189.0° (*c* 1.0, $CHCl_3$); IR 1076, 1615 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.14 (s, 9H), 1.22 (s, 9H), 2.29 (s, 3H); ^{13}C NMR (101 MHz) δ 18.2, 22.2, 27.5, 42.9, 56.5, 190.8. Anal. Calcd for $C_{10}H_{21}NOS$: C, 59.07; H, 10.41; N, 6.89. Found: C, 58.90; H, 10.65; N, 7.04.

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