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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.5b02084 • Publication Date (Web): 28 Oct 2015

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## Asymmetric Reduction of tert-Butanesulfinyl Ketimines by

## **N-Heterocyclic Carbene Boranes**

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#### **Graphic Abstract**



18 examples, up to 95% yield, >99% de

## Abstract

N-Heterocyclic carbene borane (NHC-Borane) based on a triazole core is demonstrated for the first time to be efficient for reduction of a variety of *tert*-butanesulfinyl ketimines. Up to 95% yield and up to >99% diastereomeric excess were achieved. NHC-Borane exhibited excellent activities that are more efficient than or comparable to those commonly used reductive reagents such as NaBH<sub>4</sub>, NaBH<sub>3</sub>CN, L-selectride, Ru catalyst or BH<sub>3</sub>-THF.

## INTRODUCTION

During the past several decades, N-heterocyclic carbenes (NHCs) have been playing important roles in organic synthesis due to their excellent performances in both organometallic catalysis<sup>1</sup> and organocatalysis.<sup>2</sup> However, little attention has been paid to N-Heterocyclic carbine complexes until 1,3-bis (2,6-diisopropylphenyl)-imidazol-2-ylidene borane (dipp-Imd-BH<sub>3</sub>) (Figure 1) was first developed by Robinson<sup>3</sup> in 2007. Since then, development of NHC-boranes<sup>4</sup> advanced rapidly with major applications in organic synthesis such as radical<sup>5</sup>, ionic<sup>6</sup>, reductive<sup>7</sup>, and organometallic reactions<sup>8</sup>.

NHC-boranes (NHC-BH<sub>3</sub>) were proved to be good hydride donors by Curran<sup>7d</sup>. The reduction of aldimines could proceed smoothly in the presence of acetic acid, which could afford the corresponding achiral primary amines. However, chiral α-branched amines, which often can be obtained by reduction of ketimines, are more valuable in organic synthesis as they could be used as resolving agents and key chiral source of important natural products and biologically active compounds. Normally, the involved reduction process has been reported using hydrogenation<sup>7b,9</sup>, metallic hydrides<sup>10</sup>, hydrosilylation<sup>11</sup>, transfer hydrogenation<sup>12</sup> etc. However, to the best of our knowledge, there are no reports about the reduction of less active ketimines using NHC-BH<sub>3</sub>. Among the different methods for the reduction of ketimines, NHC-BH<sub>3</sub> presents several advantages such as easy preparation, stability to air or water, and avoiding the use of hazardous chemicals (metallic hydrides or H<sub>2</sub>) etc. Consequently, we herein demonstrate reduction of ketimines by NHC-BH<sub>3</sub> using the well-known chiral auxiliary *tert*-butanesulfinyl group<sup>13</sup> to induce the chirality.

## **RESULTS AND DISCUSSION**

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Different NHC-BH<sub>3</sub> **1-5** were readily prepared in good yields from reaction of the corresponding NHC precursors with NaHMDS, followed by dropwise addition of BH<sub>3</sub> in THF at  $-78^{\circ}$ C.<sup>5a,5d</sup> The *N*-(*tert*-butanesulfinyl) ketimine intermediates **6a-r** were obtained from condensation between *tert*-butanesulfinamide and a variety of ketones using Ti(OEt)<sub>4</sub> as a Lewis acid under microwave irradiation.<sup>14</sup>



Figure 1 NHC-Boranes synthesized

Our investigations started with the examination of the reduction of ketimine **6a** in the presence of 1.0 equiv. of **2** in dichloromethane at room temperature. Compound **2** had been once successfully used for the reduction of aldimines.<sup>5f</sup> However, the reaction could not proceed even with silica or acetic acid (Table 1, entries 2 and 3). To improve the reactivity of this system, we activated the ketimine **6a** by adding stronger acids such as trichloroacetic acid (TCA), trifluoroacetic acid (TFA), *p*-Toluene sulfonic acid (TsOH) and triflic acid (TfOH). Using TCA and TFA, the reaction could take place and diastereomeric excess was 69% or 64% respectively with moderate yields (Table 1, entries 4 and 5). As for the strongest acid TfOH, little additional improvement was achieved (Table 1, entry 7). Eventually, we found that TsOH gave better chemical yield (56%) and % de (66%) than other acids we tested. In the hope of enhancing the % de, we carried out the reactions at lower temperature. At 0 °C, both the chemical yield and % de can sharply increase from room temperature reaction to

68% and 70% (Table 1, entry 8), while at -10 °C, the reaction can improve further (Table 1, entry 9). However, if the reaction was carried out at -20 °C, the yield and stereoselectivity started to decrease (Table 1, entry 10).

Table 1 Investigation of the effects of different acids and temperatures on the asymmetric reduction of ketimine  $6a^a$ .

$\bigcirc$		$ \begin{array}{c}                                     $		
	6a		7	7a
entry	Acid	T (°C)	Yield <sup>b</sup> (%)	$de^{c}$ (%)
1	-	rt	-	-
2	silica	rt	-	-
3	acetic acid	rt	-	-
4	TCA	rt	30	69
5	TFA	rt	35	64
6	TsOH	rt	56	66
7	TfOH	rt	40	51
8	TsOH	0	68	70
9	TsOH	-10	75	74
10	TsOH	-20	72	70

<sup>a</sup> All reactions were carried out using **6a** (0.25 mmol), **2** (0.25 mmol), and acid (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) for 4 h. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis of unpurified reaction mixtures.

With these preliminary results, we further investigated the efficiency of different NHC-BH<sub>3</sub> reagents. Results are summarized in Table 2. In comparison with NHC-BH<sub>3</sub> **2**, the reaction resulted in no product with the well-known dipp-Imd-BH<sub>3</sub> **1** (Table 2, entry 2). When using dip-Imd-BH<sub>3</sub> **3**, % de raised up to 83% with slightly decreased yield (Table 2, entry 3). For diMe-benzimd-BH<sub>3</sub> **4**, the result was also not

satisfactory, both yield and % de decreased (Table 2, entry 4). Finally, only diMe-Triaz-BH<sub>3</sub> **5** gave the best performance (65% yield, 85% de, Table 2, entry 5). We also screened different solvents. We were glad that both the chemical yield and diastereomeric excess were sharply improved when MeOH was used (Table 2, entry 9). For other solvent systems such as THF, toluene, and ethyl acetate, the results were even worse (Table 2, entries 6-8). In addition, when we cut the amount of acid, de was even better (up to 94%, Table 2, entry 10). The acid, TsOH, was believed to activate ketimine during reduction<sup>7b,7e</sup>, and therefore it may not be necessary to use equiv-molar amount to achieve optimal yield whereas its impact on stereoselectivity may need further study. If we used 0.5 eq. of NHC-BH<sub>3</sub> **5**, there was a significant decrease in yield (Table 2, entry 11). This suggests that not all hydride atoms of NHC-BH<sub>3</sub> **5** could be utilized in the reduction.

Table 2 Investigation of the effects of different NHC-BH<sub>3</sub> and solvents on the asymmetric reduction of ketimines 6a.<sup>a</sup>

$\bigcirc$	6a	NHC-BH <sub>3</sub> TsOH, Solvent -10°C	H C	OH N Ta
entry	NHC-BH <sub>3</sub>	solvent	yield <sup>b</sup> (%)	de <sup>c</sup> (%)
1	2	$CH_2Cl_2$	75	74
2	1	$CH_2Cl_2$	0	-
3	3	$CH_2Cl_2$	58	83
4	4	$CH_2Cl_2$	41	67
5	5	$CH_2Cl_2$	65	85
6	5	THF	44	45
7	5	Toluene	70	60

8	5	EA	52	47
9	5	MeOH	90	89
10 <sup>d</sup>	5	MeOH	88	94
11 <sup>e</sup>	5	MeOH	58	90

<sup>a</sup> Unless otherwise noted, all reactions were carried out using **6a** (0.25 mmol), NHC-BH<sub>3</sub> (0.25 mmol), and TsOH (0.25 mmol) in solvent (1.0mL) at -10 °C for 4 h. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis of unpurified reaction mixtures. <sup>d</sup>TsOH (0.5 equiv.) was used. <sup>e</sup>NHC-BH<sub>3</sub> (0.5 equiv.) was used.

Using the optimized conditions, we shifted to select diMe-Triaz-BH<sub>3</sub> 5 in the presence of TsOH at -10 °C to survey the scope of the reduction. A wide range of aryl alkyl-, aryl aryl-, alkyl alkyl-, and  $\alpha$ ,  $\beta$ -unsaturated ketimines were tested. The results are summarized in Table 3, together with the results of representative literature reported cases. As shown in Table 3, almost all the reactions of the aryl alkyl-type ketimines proceeded quite well and resulted in moderate to good yields and % de. On one hand, when the substrates had electron-donating groups in the phenyl ring such as **6c** and **6i**, % de was higher than that with electron-withdrawing groups (Table 3, entries 3 and 9). On the other hand, when the substrate had steric hindered group such as 6i, the chemical yield was relatively low (Table 3, entry 9). For aryl aryl-ketimines, % de was poor (Table 3, entry 10, 30% de). However, if there was a hydroxyl group in the ortho-position, % de could be largely improved from 30% to 74% without adding TsOH. We envisioned that the hydroxyl group might participate to activate the ketimine *via* the formation of a hydrogen bond to the ketimine nitrogen (Figure 2). Compared to literature reported results, our protocol gave higher % de in almost all cases than methods that used NaBH<sub>4</sub>, L-selectride or other hydride. It was more efficient or comparable to the transfer hydrogenation approach except the case using furan-derived ketimine which gave lower % de.

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TsOH.<sup>a</sup>







<sup>a</sup> Unless otherwise noted, all reactions were carried out using **6** (0.25 mmol), NHC-BH<sub>3</sub> (0.25 mmol), and TsOH (0.125 mmol) in MeOH (1.0 mL) at  $-10^{\circ}$ C for 4 h. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by <sup>1</sup>H NMR analysis of unpurified reaction mixtures. <sup>d</sup> CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent without TsOH for 8 h. <sup>e</sup> CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent for 8 h. <sup>f</sup> Toluene was used as the solvent. <sup>g</sup> The absolute configuration was determined by comparison of the optical rotation with the known compounds (corresponding amine) in the literature<sup>24</sup>.



Figure 2 Plausible intramolecular activation.

The obtained product **7a-r** can be easily transformed into the corresponding chiral  $\alpha$ -branched primary amines as its hydrochloride salt after cleaving the sulfinyl group under mild acidic conditions. We chose several products with >99% de to afford the chiral primary amines in quite good yields with good enantioselectivities (Table 4, details of determination of ee by HPLC in SI).

Table 4 Cleavage of tert-butanesulfinyl group to afford chiral primary amines





In summary, we have demonstrated for the first time the asymmetric reduction of ketimines by NHC-BH<sub>3</sub> complex in the presence of acid. After screening NHC-BH<sub>3</sub> complexes, acids, solvents and temperature, diMe-Triaz-BH<sub>3</sub> **5** was shown to exhibit excellent reductive activities with the aid of TsOH. Moderate to excellent yield and de were achieved. This made NHC-BH<sub>3</sub> a valuable alternative reductive reagent. Further explorations of new chiral NHC-BH<sub>3</sub> complex are in progress.

## **EXPERIMENTAL SECTION**

Unless otherwise noted, reactions were performed using oven-dried glassware under an atmosphere of dry N<sub>2</sub>. Column chromatography was performed using silica gel (300-400 mesh). Visualization of the compounds was accomplished with UV light (254 nm) and iodine. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> operating at 400 MHz and 100 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl<sub>3</sub> (7.26 ppm) or DMSO- $d_6$  (2.50 and 3.33 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl<sub>3</sub> (77.00 ppm) or DMSO- $d_6$  (40.0 ppm). Data are represented as follows: chemical shift, multiplicity (bs= broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), and integration. High-resolution mass spectra were recorded on a Liquid Chromatograph Mass Spectrometer (LCMS-IT-TOF).

**General procedure for asymmetric reduction of ketimines.** To a solution of ketimine (0.25 mmol) in MeOH (1.0 mL) was added NHC-BH<sub>3</sub> (0.25 mmol). After

stirring for 10 minutes at -10°C, *p*-toluenesulfonic acid (0.125 mmol, 21.6 mg) was added in portions. The mixture was stirred for another 4 h at -10°C. The solvent was removed by rotary evaporation. The residue was purified by flash column chromatography (silica gel, PE : EA = 3: 1) to afford product **7a-r**.

(*R*)-2-methyl-N-((*R*)-1-phenylethyl)propane-2-sulfinamide (7a)<sup>15</sup>: a colorless oil (50.6 mg, 90%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.36 (m, 5H), 4.57 (m, 1 H), 3.46 (s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H), 1.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 128.7, 127.8, 126.6, 55.5, 54.0, 22.8, 22.6.

(*R*)-2-methyl-*N*-((*R*)-1-*p*-tolylethyl)propane-2-sulfinamide (**7b**): a colorless oil (52.0 mg, 87%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.54 (m, 1H), 3.42 (s, 1H), 2.36 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.25 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  114.2, 137.5, 129.4, 126.5, 55.4, 53.7, 22.7, 22.6, 21.1. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup>calcd for C<sub>13</sub>H<sub>21</sub>NOS 240.1417, found 240.1427.

(*R*)-*N*-((*R*)-1-(4-methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (7c)<sup>15</sup>: a colorless oil (56.1 mg, 88%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.53 (m, 1H), 3.82 (s, 3H), 3.43 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.25 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 136.2, 127.7, 114.1, 55.4, 55.3, 53.4, 22.7, 22.6.

(R)-N-((R)-1-(4-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide (7d)<sup>16</sup>: a

colorless oil (57.8 mg, 89%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26-7.38 (m, 4H), 4.53

(m, 1H), 3.41(s, 1H), 1.50 (d, J = 6.8 Hz, 3H), 1.25 (s, 9H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>) δ 142.5, 133.5, 128.9, 128.0, 55.6, 53.5, 22.8, 22.6. HRMS (ESI-TOF) *m/z*:

 $[M+H]^+$  calcd for C<sub>12</sub>H<sub>18</sub>ClNOS 260.0870, found 260.0880.

(*R*)-2-methyl-N-((*R*)-1-(4-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (**7e**)<sup>15</sup>: a colorless oil (60.1 mg, 82%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, *J* = 8.4 Hz, 2H),

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δ 7.49 (d, *J* = 8.4 Hz, 2H), 4.62 (m, 1H), 3.47(d, *J* = 2.0 Hz, 1H), 1.55 (d, *J* = 6.4 Hz, 3H), 1.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.0, 127.0, 125.7, 125.7, 55.7, 53.9, 22.9, 22.5.

(*R*)-*N*-((*R*)-1-(4-cyanophenyl)ethyl)-2-methylpropane-2-sulfinamide (7f)<sup>15</sup>: a colorless oil (59.5 mg, 95%), <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 4.58(m, 1H), 3.59(d, *J* = 3.6 Hz, 1H), 1.51(d, *J* = 6.4 Hz, 3H), 1.22 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.3, 132.6, 127.4, 118.6, 111.6, 55.8, 54.1, 22.9, 22.5.

(*R*)-*N*-((*R*)-1-(3-fluorophenyl)ethyl)-2-methylpropane-2-sulfinamide (**7g**): a colorless oil (52.3 mg, 86%),<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.97-7.28 (m, 4H), 4.56 (m, 1H), 3.48 (s, 1H), 1.52 (d, *J* = 6.8 Hz, 3H), 1.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.0 (d, *J* = 245.0 Hz), 146.7 (d, *J* = 7.0 Hz), 130.3 (d, *J* = 8.0 Hz), 122.3 (d, *J* = 3.0 Hz), 114.7 (d, *J* = 21.0 Hz), 113.4 (d, *J* = 22.0 Hz), 55.6, 53.6, 22.8, 22.6. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup>calcd for C<sub>12</sub>H<sub>18</sub>FNOS 244.1166, found 244.1174.

(*R*)-2-methyl-N-((*R*)-1-phenylpropyl)propane-2-sulfinamide (7h)<sup>15</sup>: a colorless oil (50.9 mg, 85%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.36 (m, 5H), 4.31 (m, 1H), 3.41 (s, 1H), 1.80 (m, 2H), 1.25 (s, 9H), 0.81 (t, J = 14.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.3, 128.6, 127.8, 127.3, 60.4, 55.7, 29.4, 22.6, 22.5.

(*R*)-*N*-((*R*)-*1*-(4-methoxyphenyl)-2,2-dimethylpropyl)-2-methylpropane-2-sulfinamide (**7i**): a colorless oil (55.8 mg, 75%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.81(d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.11 (s, 1H), 1.24 (s, 9H), 0.95 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 130.6, 129.2, 113.0, 66.5, 55.8, 55.1, 36.3, 26.7, 22.6. HRMS (ESI-TOF) *m*/*z*: [M+H]<sup>+</sup>calcd for C<sub>16</sub>H<sub>27</sub>NO<sub>2</sub>S 298.1835, found 298.1828.

(R)-N-((R)-(2-hydroxyphenyl)(phenyl)methyl)-2-methylpropane-2-sulfinamide  $(7j)^{19}$ :

a colorless oil (39.4 mg, 52%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.73-7.43 (m, 9H), 5.82 (d, *J* = 4.8 Hz, 1H), 5.06 (d, *J* = 4.8 Hz, 1H), 1.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.1, 140.5, 129.1, 128.9, 128.4, 128.3, 127.5, 127.5, 119.3, 116.5, 60.2, 56.3, 22.8.

(*R*)-*N*-((*R*)-(2-methoxyphenyl)(phenyl)methyl)-2-methylpropane-2-sulfinamide (7k)<sup>20</sup>:
a colorless oil (38.9 mg, 49%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.73-7.43 (m, 9H), 5.81
(d, *J* = 4.4 Hz, 1H), 5.20 (d, *J* = 4.4 Hz, 1H), 1.32 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.6, 141.2, 130.8, 128.9, 128.5, 128.2, 128.0, 128.0, 127.5, 127.3, 57.4, 55.9, 55.5, 22.7.

(*R*)-2-methyl-*N*-((*R*)-1-(pyridin-2-yl)ethyl)propane-2-sulfinamide (**71**)<sup>21</sup>: a colorless oil (49.2 mg, 74%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 (d, *J* = 4.8 Hz, 1H),  $\delta$  7.68 (m, 1H), 7.30 (m, 1H), 7.19 (m, 1H), 4.85 (d, *J* = 4.4 Hz, 1H), 4.64 (m, 1H), 1.52 (d, *J* = 6.8 Hz, 3H), 1.27 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.9, 149.0, 136.8, 122.3, 121.0, 55.6, 55.2, 23.4, 22.7.

(*R*)-*N*-((*R*)-1-(furan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (**7m**)<sup>16</sup>: a colorless oil (48.4 mg, 90%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (t, *J* = 3.6 Hz, 1H), 6.27-6.34 (m, 2H), 4.59 (m, 1H), 3.59 (d, *J* = 4.0 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.23(s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 142.0, 110.2, 106.1, 55.7, 48.6, 22.5, 20.2. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup>calcd for C<sub>10</sub>H<sub>17</sub>NO<sub>2</sub>S 216.1053, found 216.1059.

(*R*)-*N*-((*S*)-2-chloro-1-(4-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide (**7n**)<sup>22</sup>: a colorless oil (66.2 mg, 90%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28-7.38 (m, 4H), 4.68 (m, 1H), 3.87 (d, *J* = 5.6 Hz, 2H), 3.84 (s, 1H), 1.25 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.5, 134.4, 129.0, 128.8, 67.9, 58.9, 48.3, 22.6.

(*R*)-2-methyl-N-((*R*)-1,2,3,4-tetrahydronaphthalen-1-yl)propane-2-sulfinamide (**70**)<sup>15</sup>: a white solid (50.3 mg, 80%), mp:116°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.11-7.48 (m,

4H), 4.60 (m, 1H), 3.26 (s, 1H), 2.80 (m, 1H), 1.81-2.06 (m, 4H), 1.24 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.7, 137.0, 129.7, 129.2, 127.6, 126.6, 55.4, 52.8, 30.6, 29.1, 22.7, 18.2.

(*R*)-*N*-((*R*)-3,3-dimethylbutan-2-yl)-2-methylpropane-2-sulfinamide (7p)<sup>15</sup>: a colorless oil (43.6 mg, 85%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.27 (s, 1H), 3.12 (m, 1H), 1.21 (s, 9H), 1.13(d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 59.0, 55.4, 34.4, 26.1, 22.6, 15.9.

(*R*)-2-methyl-N-((*R*)-4-phenylbutan-2-yl)propane-2-sulfinamide (7q)<sup>15</sup>: a colorless oil
(52.6 mg, 83%), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31(d, *J* = 7.6 Hz, 2H), 7.21 (m, 3H),
3.43 (m, 1H), 3.16 (d, *J* = 4.4 Hz, 1H), 2.72 (m, 2H), 1.79-1.95 (m, 2H), 1.23 (d, *J* = 6.4 Hz, 3H), 1.20 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 141.5, 128.5, 128.4, 126.0,
55.3, 51.1, 39.9, 32.1, 22.5, 21.7.

(*R*)-*N*-((*S*,*E*)-1,3-diphenylallyl)-2-methylpropane-2-sulfinamide (7r)<sup>23</sup>: a white solid (47.8 mg, 61%), mp:107-109°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.46 (m, 10H), 6.67 (m, 1H), 6.43 (m, 1H), 5.18 (d, *J* = 7.6 Hz, 1H), 3.63 (s, 1H), 1.26 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.5, 133.0, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.0, 127.4, 126.4, 126.1, 40.4, 30.2, 22.7.

#### General procedure for cleavage of the *tert*-butanesulfinyl group

To *tert*-butylsulfinamide (0.2 mmol) was added 3.8 M HCl in 1, 4-dioxane (1.0 mL). After stirring of the mixture for 1h at rt, the solvent was removed by rotary evaporation followed by addition of EtOAc (2.0 mL), and filtration to afford the desired amine salt **8c**, **8n**, **8o**, **8p**.

(*R*)-1-(4-methoxyphenyl)ethanamine hydrochloride (8c)<sup>18</sup>: a yellow solid (31.9 mg, 85%). mp:152-155°C. [ $\alpha$ ]<sub>D25</sub>+22.8 (*c* 0.75, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.61 (s, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 1H), 3.81 (s,

3H), 1.65 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.9, 129.7, 128.3, 114.4, 55.2, 51.3, 20.5.

(*S*)-2-chloro-1-(4-chlorophenyl)ethanamine hydrochloride (8n): a white solid (38.1 mg, 84%), mp: 202.2-204.9°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.10 (s, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 4.56 (s, 1H), 4.05 (d, *J* = 6.0 Hz, 1H), 3.90 (d, *J* = 8.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 131.3, 129.6, 129.1, 56.4, 44.7. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup>calcd for C<sub>8</sub>H<sub>9</sub>Cl<sub>2</sub>N 190.0185, found 190.0193. (*R*)-1,2,3,4-tetrahydronaphthalen-1-amine hydrochloride (80)<sup>15</sup>: a white solid (33.1 mg, 90%), mp: 235-237°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (s, 3H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.11-7.25 (m, 3H), 4.44 (d, *J* = 4.4 Hz, 1H), 1.76-2.92 (m, 6H). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>) δ 137.8, 131.1, 129.6, 129.2, 128.7, 126.6, 49.6, 28.7, 27.8, 18.5.

(*R*)-3,3-dimethylbutan-2-amine hydrochloride (8p)<sup>18</sup>: a white solid (23.4 mg, 85%), mp: 306-307°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 2H), 3.12 (s, 1H), 1.37 (d, J = 6.8 Hz, 3H), 1.08 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 57.2, 33.3, 26.1, 14.5.

#### ACKNOWLEDGMENTS

Financial support for this work was provided by Shanghai Municipal Education Commission (No.14ZZ159), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (The Project-sponsored by SRF for ROCS, SEM). We also thank the financial support from the Special Scientific Foundation for Outstanding Young Teachers in Shanghai Higher Education Institutions (ZZGJD13020), and Start-up Funding of Shanghai University of Engineering Science (2013-24) and the students Innovation Program in Shanghai University of Engineering Science (14KY0413).

#### **Supporting Information**

Determination of the enantiomeric excess for selected example amine 8c and copies of 1H and 13C NMR spectra.

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