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Asymmetric Reduction of *tert*-Butanesulfinyl Ketimines by N-Heterocyclic Carbene Boranes

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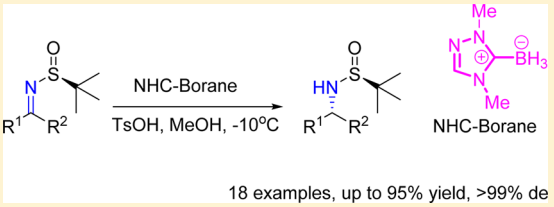
Supporting Information

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 commonly used reductive reagents such as $NaBH_4$, $NaBH_3CN$, L-selectride, Ru catalyst, or BH_3−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[1] and organocatalysis.[2] 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_3) (Figure 1) was first developed by Robinson[3] in

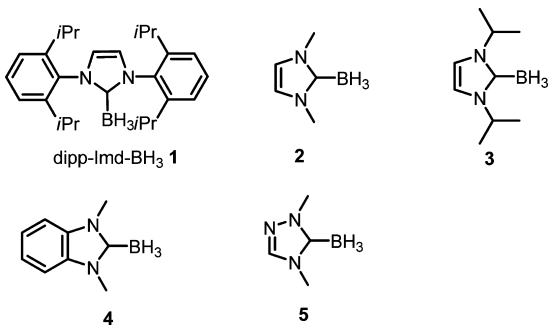


Figure 1. NHC-boranes synthesized.

2007. Since then, development of NHC-boranes[4] advanced rapidly with major applications in organic synthesis such as radical,[5] ionic,[6] reductive,[7] and organometallic reactions.[8]

NHC-boranes (NHC-BH_3) were proven to be good hydride donors by Curran.[7d] 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 a key chiral source of important natural products and biologically active compounds. Normally, the involved reduction process has been reported using hydrogenation,[7b,9] metallic hydrides,[10] hydrosilylation,[11] transfer hydrogenation,[12] etc. However, to the best of our knowledge, there are no reports related to the reduction of less active ketimines using NHC-BH_3. Among the different methods for the reduction of ketimines, NHC-BH_3 presents several advantages such as easy preparation, stability to air or water, avoidance of hazardous chemicals (metallic hydrides or H_2), etc. Consequently, we herein demonstrate reduction of ketimines by NHC-BH_3 using the well-known chiral auxiliary *tert*-butanesulfinyl group[13] to induce the chirality.

RESULTS AND DISCUSSION

Different NHC-BH_3 **1**−**5** were readily prepared in good yields from reaction of the corresponding NHC precursors with NaHMDS, followed by dropwise addition of BH_3 in THF at −78 °C.[5a,d] The *N*-(*tert*-butanesulfinyl) ketimine intermediates **6a**−**r** were obtained from condensation between *tert*-butanesulfinamide and a variety of ketones using $Ti(OEt)_4$ as a Lewis acid under microwave irradiation.[14]

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.[5f] 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 the 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 a 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 a room temperature reaction to 68% and 70% (Table 1, entry 8), while at −10 °C, the reaction can improve further (Table 1, entry 9).

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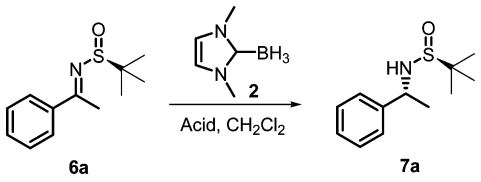
Table 1. Investigation of the Effects of Different Acids and Temperatures on the Asymmetric Reduction of Ketimine 6a[a]



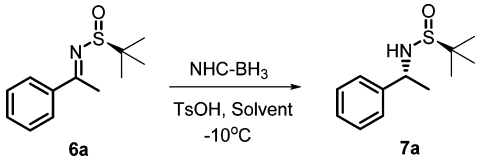
entry	acid	T (°C)	yield[b] (%)	de[c] (%)
1	–	rt	–	–
2	silica	rt	–	–
3	acetic acid	rt	–	–
4	TCA	rt	30	69
5	TFA	rt	35	64
6	TsOH	rt	56	66
7	TfOH	rt	40	51
8	TsOH	0	68	70
9	TsOH	−10	75	74
10	TsOH	−20	72	70

[a]All reactions were carried out using **6a** (0.25 mmol), **2** (0.25 mmol), and acid (0.25 mmol) in CH_2Cl_2 (1.0 mL) for 4 h. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis of unpurified reaction mixtures.

However, if the reaction was carried out at −20 °C, the yield and stereoselectivity started to decrease (Table 1, entry 10).

With these preliminary results, we further investigated the efficiency of different NHC-BH_3 reagents. Results are summarized in Table 2. In comparison with NHC-BH_3 **2**, the reaction resulted in no product with the well-known dipp-Imd-BH_3 **1** (Table 2, entry 2). When using dip-Imd-BH_3 **3**, the % de raised up to 83% with a slightly decreased yield (Table 2, entry 3). For diMe-benzimd-BH_3 **4**, the result was also not satisfactory; both the yield and % de decreased (Table 2, entry 4). Finally, only diMe-Triaz-BH_3 **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, the de was even better (up to 94%, Table 2, entry 10). The acid, TsOH, was believed to activate ketimine during reduction,[7b,c] and therefore it may not be necessary to use an equiv-molar amount to achieve optimal yields whereas its impact on stereoselectivity may need further study. If we used 0.5 equiv of NHC-BH_3 **5**, there was a significant decrease in yield (Table 2, entry 11). This suggests that not all hydride atoms of NHC-BH_3 **5** could be utilized in the reduction.

Table 2. Investigation of the Effects of Different NHC-BH_3 and Solvents on the Asymmetric Reduction of Ketimines 6a[a]



entry	NHC-BH_3	solvent	yield[b](%)	de[c](%)
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[d]	**5**	MeOH	88	94
11[e]	**5**	MeOH	58	90

[a]Unless otherwise noted, all reactions were carried out using **6a** (0.25 mmol), NHC-BH_3 (0.25 mmol), and TsOH (0.25 mmol) in solvent (1.0 mL) at −10 °C for 4 h. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis of unpurified reaction mixtures. [d]TsOH (0.5 equiv) was used. [e]NHC-BH_3 (0.5 equiv) was used.

Using the optimized conditions, we shifted to select diMe-Triaz-BH_3 **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 α,β-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 a stericically 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, the % 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 values in almost all cases compared to methods that used $NaBH_4$, L-selectride, or another hydride. It was more efficient or comparable to the transfer hydrogenation approach except in the case of using furan-derived ketimine which gave a lower % de.

The obtained product **7a−r** can be easily transformed into the corresponding chiral α-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 the Supporting Information).

In summary, we have demonstrated for the first time the asymmetric reduction of ketimines by the NHC-BH_3 complex in the presence of acid. After screening NHC-BH_3 complexes, acids, solvents, and temperature, diMe-Triaz-BH_3 **5** was shown to exhibit excellent reductive activities with the aid of TsOH. Moderate to excellent yields and de's were achieved. This showed NHC-BH_3 to be a valuable alternative reductive reagent. Further explorations of the new chiral NHC-BH_3 complex are in progress.

EXPERIMENTAL SECTION

Unless otherwise noted, reactions were performed using oven-dried glassware under an atmosphere of dry N_2. Column chromatography was performed using silica gel (300−400 mesh). Visualization of the compounds was accomplished with UV light (254 nm) and iodine. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400

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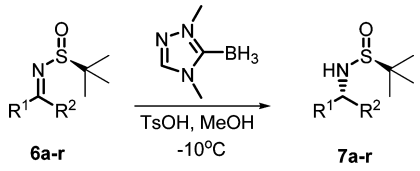
Table 3. Asymmetric Reduction of Ketimines by diMe-Triaz-BH_3 5 in the Presence of TsOH[a]



entry	Ketimines **6**	Product **7**	Yield[b] (%)	de[c] (%)	Lit.de (%) and Reagent
1	**6a**	**7a**	88	94	82 ($NaBH_4$)[15] 84 (L-selectride)[15] 97 (Ru catalyst)[16]
2	**6b**	**7b**	87	99	
3	**6c**	**7c**	88	>99 (*R*)[g]	84 ($NaBH_4$)[15] 90 (L-selectride)[15] 96 (Ru catalyst)[16]
4	**6d**	**7d**	89	91	97(Ru catalyst)[16]
5	**6e**	**7e**	82	91	77 ($NaBH_4$)[15] 92 (L-selectride)[15] 97 (Ru catalyst)[16]
6	**6f**	**7f**	95	94	73 ($NaBH_4$)[15] 83 (L-selectride)[15]
7	**6g**	**7g**	86	89	
8	**6h**	**7h**	85	>99	51 ($NaBH_4$)[15] 96 (L-selectride)[15] 94 (Ru catalyst)[18]
9	**6i**	**7i**	75	98	
10[d]	**6j**	**7j**	52	74	
11[e]	**6k**	**7k**	49	50	
12	**6l**	**7l**	74	94	
13	**6m**	**7m**	90	80	96 (Ru catalyst)[16, 18]
14	**6n**	**7n**	90	>99	
15	**6o**	**7o**	80	>99	97 ($NaBH_4$)[15] 68 ($NaBH_4$)[17] 98 (L-selectride)[17] 80 (BH_3-THF)[15]
16	**6p**	**7p**	85	>99	64 ($NaBH_4$)[15] 76 (L-selectride)[15] 96 (Ru catalyst)[16] 93 (Ru catalyst)[18]
17	**6q**	**7q**	83	80	53 ($NaBH_4$)[15] 2 (L-selectride)[15] 65 (Ru catalyst)[16]
18[f]	**6r**	**7r**	61	80	

[a]Unless otherwise noted, all reactions were carried out using **6** (0.25 mmol), NHC-BH_3 (0.25 mmol), and TsOH (0.125 mmol) in MeOH (1.0 mL) at −10 °C for 4 h. [b]Isolated yield. [c]Determined by ^{1}H NMR analysis of unpurified reaction mixtures. [d]CH_2Cl_2 was used as the solvent without TsOH for 8 h. [e]CH_2Cl_2 was used as the solvent for 8 h. [f]Toluene was used as the solvent. [g]The absolute configuration was determined by comparison of the optical rotation with the known compounds (corresponding amine) in the literature.[24]

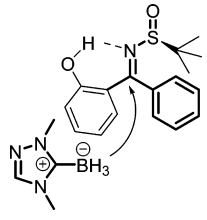


Figure 2. Plausible intramolecular activation.

and 100 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (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 $CDCl_3$ (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 Chromatography 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_3 (0.25 mmol). After the mixture stirred for 10 min at −10

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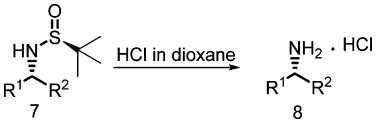
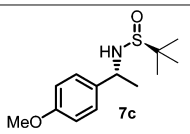
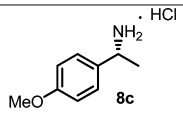
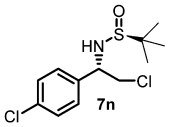
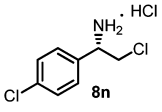
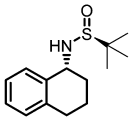
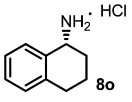
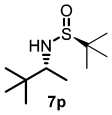
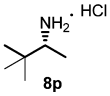
Table 4. Cleavage of *tert*-Butanesulfinyl Group To Afford Chiral Primary Amines



entry	Sulfinamide	Primary amine **8**	Isolated Yield (%)
1			85
2			84
3			90
4			85

°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***).[15] A colorless oil (50.6 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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]$^+$calcd for $C_{13}H_{21}NOS$ 240.1417, found 240.1427.

(R)-N-((R)-1-(4-Methoxyphenyl)ethyl)-2-methylpropane-2-sulfinamide (***7c***).[15] A colorless oil (56.1 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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***).[16] A colorless oil (57.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{12}H_{18}ClNOS$ 260.0870, found 260.0880.

(R)-2-Methyl-N-((R)-1-(4-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (***7e***).[15] A colorless oil (60.1 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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***).[15] A colorless oil (59.5 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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]$^+$calcd for $C_{12}H_{18}FNOS$ 244.1166, found 244.1174.

(R)-2-Methyl-N-((R)-1-phenylpropyl)propane-2-sulfinamide (***7h***).[15] A colorless oil (50.9 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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]$^+$calcd for $C_{16}H_{27}NO_2S$ 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%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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***).[20] A colorless oil (38.9 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 (***7l***).[21] A colorless oil (49.2 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.8 Hz, 1H), δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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***).[16] A colorless oil (48.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.0, 110.2, 106.1, 55.7, 48.6, 22.5, 20.2. HRMS (ESI-TOF) m/z: [M + H]$^+$calcd for $C_{10}H_{17}NO_2S$ 216.1053, found 216.1059.

(R)-N-((S)-2-Chloro-1-(4-chlorophenyl)ethyl)-2-methylpropane-2-sulfinamide (***7n***).[22] A colorless oil (66.2 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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 (***7o***).[15] A white solid (50.3 mg, 80%), mp:116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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***).[15] A colorless oil (43.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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***).[15] A colorless oil (52.6 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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***).[23] A white solid (47.8 mg, 61%), mp 107−109 °C. ^{1}H NMR (400

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MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 1 h 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**, and **8p**.

*(R)-1-(4-Methoxyphenyl)ethanamine Hydrochloride (**8c**).*[18] A yellow solid (31.9 mg, 85%). mp 152−155 °C. $[\alpha]_D^{25}$ +22.8 (c 0.75, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 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. ^1H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 131.3, 129.6, 129.1, 56.4, 44.7. HRMS (ESI-TOF) m/z: $[M + H]^+$calcd for $C_8H_9Cl_2N$ 190.0185, found 190.0193.

*(R)-1,2,3,4-Tetrahydronaphthalen-1-amine Hydrochloride (**8o**).*[15] A white solid (33.1 mg, 90%), mp 235−237 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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**).*[18] A white solid (23.4 mg, 85%), mp 306−307 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 3.12 (s, 1H), 1.37 (d, J = 6.8 Hz, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 57.2, 33.3, 26.1, 14.5.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02084.

Determination of the enantiomeric excess for selected example amine **8c** and copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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