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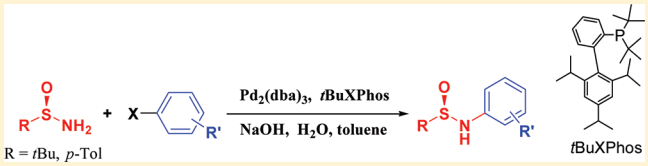
Palladium-Catalyzed C–N Cross Coupling of Sulfinamides and Aryl Halides

Xiaofei Sun, Xingzhao Tu, Chuan Dai, Xiaoping Zhang, Binbin Zhang, and Qingle Zeng*

Institute of Green Catalysis and Synthesis, College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China

Supporting Information

ABSTRACT: The palladium-catalyzed C–N cross coupling of sulfinamides and aryl halides is reported. In the presence of $Pd_2(dba)_3$, *t*BuXPhos, NaOH, and a small amount of water, the C–N cross coupling of chiral *tert*-butanesulfinamide and aryl halides was accomplished to give *N*-aryl *tert*-butanesulfinamide without racemization, and the coupling of racemic *p*-toluenesulfinamide smoothly afforded *N*-aryl *p*-toluenesulfinamides. 2-Bromopyridine was also suitable for the coupling. Addition of a small amount of water to the catalytic system was of importance to obtain high yields.



Sulfinamides, especially chiral sulfinamides, are an important class of organic compounds in modern organic chemistry.[1] Enantiomer-pure *tert*-butanesulfinamide, *p*-toluenesulfinamide, etc., and their derivatives are extensively used as chiral auxiliaries in the synthesis of chiral drugs and natural products[1] and as chiral ligands in catalytically asymmetric reactions.[2]

A number of approaches have been developed for the synthesis of racemic *N*-aryl arenesulfinamides[3] from thionylaniline,[3a] benzenesulfinylazide,[3b] nitrosobenzenes,[3c] sulfonyl chlorides,[3d] methyl sulfinates,[3e] and for the synthesis of racemic *N*-aryl alkanesulfinamides from the reaction of thionylaniline and organomagnesium halides,[3a,4] or of *tert*-butanesulfinyl chloride and amines.[5]

But synthetic methods of chiral *N*-aryl sulfinamides are scarce.[6] Cram described the synthesis of *N*-phenyl *p*-toluenesulfinamide from in situ formed lithium anilinide and menthyl *p*-toluenesulfinate.[6a] Ellman found a synthetic method of *N*-phenyl *tert*-butanesulfinamide by reaction of in situ formed lithium anilinide and *tert*-butanethiosulfinate at −78 °C.[6b] But in Cram and Ellman's protocols, partial racemization, harsh reaction conditions, and complex manipulation are flaws.[2d,6a,b]

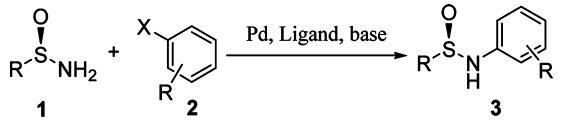
In the area of palladium-catalyzed C–N cross coupling,[7] amines,[7c,d] amides,[7e] imines,[7f] ureas,[7g] ammonia,[7h] hydrazines,[7i] sulfonamides,[7j] sulfoximines,[7k] sulfamide,[7l] nitrite,[7m] and so on as the nitrogen sources have been well developed. In contrast, analogous C–N cross coupling of *tert*-butanesulfinamide and aryl halides are rare.[6c−e]

Touré reported copper-catalyzed C–N cross coupling of *tert*-butanesulfinamide and 2-bromopyridine to give *N*-(2-pyridyl) *tert*-butanesulfinamide with >90% conversion (but no isolated yield and no characterization data were given).[6c]

During our research on palladium-catalyzed C–N coupling of chiral *tert*-butanesulfinamide and racemic *p*-toluenesulfinamide and aryl halides, Du reported Pd-catalyzed C–N coupling of chiral 2-(2′-bromophenyl)oxazolines and (*S*)-*tert*-butanesulfinamide under a harsh reaction condition (heating for 5 days at 120 °C) for preparation of chiral *β*-diketiminato-type ligands containing oxazoline moiety (no chiral HPLC was run to testify the stability of chirality of the sulfinyl moiety),[6d] and Selvakumar and his co-workers developed a protocol of Pd-catalyzed C–N coupling of racemic *tert*-butanesulfinamide and substituted aryl bromides and chlorides with at least an electron-withdrawing group with extremely high yields, even for *ortho*-substituted aryl halides.[6e] Here we disclosed our protocol of Pd-catalyzed C–N cross coupling of racemic as well as optically active sulfinamides.

As part of our continuous studies on C–N cross coupling[8] and metal-catalyzed organic reactions,[9] we tried to discover a general protocol for copper-catalyzed C–N cross coupling of *tert*-butanesulfinamide and aryl halides under similar reaction conditions to Touré's protocol. Unfortunately, only low yields (<30%) were obtained in dozens of trials, although high conversions of iodobenzene and bromobenzene were observed. So we had to resort to palladium-catalyzed C–N cross coupling of sulfinamides and aryl halides (Scheme 1).

Scheme 1. Palladium-Catalyzed C–N Cross Coupling of Sulfinamides 1 and Aryl Halides 2



As a beginning, a common catalytic system of palladium-catalyzed C–N cross coupling was adopted for this coupling, i.e., 1 mol % $Pd_2(dba)_3$, 5 mol % (2-biphenyl)di-*tert*-butylphosphine

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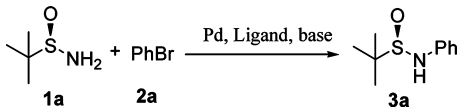
(Johnphos), 2 equiv of sodium *tert*-butoxide, and 6 mL of dioxane at 90 °C for 20 h.

Under these conditions, the C−N cross coupling of *tert*-butanesulfinamide and bromobenzene really worked, but the yield of *N*-phenyl *tert*-butanesulfinamide **1a** was low (only 10%) (Table 1, entry 1). Toluene in place of dioxane as a solvent gave a little higher yield (26%) (Table 1, entry 2). Other common solvents, such as THF, dimethoxyethane, and benzene gave poorer yields than that of toluene.

Table 1. Optimization of Conditions of Palladium-Catalyzed C−N Cross Coupling[a]



1a 2a 3a

entry	Pd source	ligand	base	H_2O (mL)	yield (%)[b]
1[c]	$Pd_2(dba)_3$	JohnPhos	NaO*t*Bu	0	10
2	$Pd_2(dba)_3$	JohnPhos	NaO*t*Bu	0	26
3[c]	$Pd_2(dba)_3$	JohnPhos	NaO*t*Bu	0.3	84
4	$Pd_2(dba)_3$	JohnPhos	NaO*t*Bu	0.3	88
5	$Pd_2(dba)_3$	JohnPhos	NaO*t*Bu	0.6	83
6	$Pd_2(dba)_3$	JohnPhos	NaOH	0.3	89
7	$Pd_2(dba)_3$	JohnPhos	KOH	0.3	86
8	$Pd_2(dba)_3$	JohnPhos	NaOH	0	<5
9	$Pd_2(dba)_3$	*t*BuXPhos	NaOH	0.3	91
10	$Pd_2(dba)_3$	*t*BuXPhos	NaOH	0.3	76

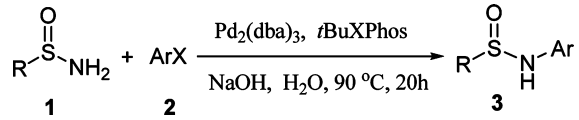
[a]Unless otherwise noted, all reactions were performed by heating (*R*)-*tert*-butanesulfinamide (1 mmol), bromobenzene (1.3 mmol), $Pd_2(dba)_3$ (0.02 mmol), monophosphine ligand (0.05 mmol), inorganic base (2.4 mmol), degassed water (indicated volume), and toluene (6 mL) in a sealed tube for 20 h at 90 °C. [b]Isolated yield. [c]Dioxane was used.

When we screened mixed solvents, occasionally we found that a little degassed water (0.3 mL) in dioxane (6 mL) made a sharp increase of yield of the desired *N*-phenyl *tert*-butanesulfinamide (Table 1, entry 3). Toluene with 0.3 mL of degassed water gave up to 88% yield (Table 1, entry 4). When a little more degassed water (0.6 mL) was added in toluene, the yield decreased slightly (Table 1, entry 5). We thought that sodium *tert*-butoxide would turn into sodium hydroxide and *tert*-butanol once sodium *tert*-butoxide met water. Really, when much cheaper sodium hydroxide and potassium hydroxide was used instead of sodium *tert*-butoxide, comparable yields were obtained (Table 1, entries 6 and 7). If water has no other function but transforms sodium *tert*-butoxide into sodium hydroxide, the degassed water was not necessary any more for a catalytic system with sodium hydroxide as a base. But in fact, sodium hydroxide and dry toluene gave hardly anything without addition of water (Table 1, entry 8). The essential reason of the huge promotion of water is still unknown. Perhaps the facile dissolution of inorganic base sodium hydroxide in water should be partially responsible for the promotion. Similar to the C−N coupling, water accelerating *N*-arylation of heteroarylamines and amines were reported by Hartwig[10] and Yin.[11]

Encouraged by the good results, some more ligands were screened. To our surprise, 2-di-*tert*-butylphosphino-2′,4′,6′-triisopropylbiphenyl (*t*BuXPhos) with more steric hindrance gave the highest yield up to 91% (Table 1, entry 9). A smaller amount of $Pd_2(dba)_3$ (1 mol %) resulted in a lower yield (Table 1, entry 10). Other palladium sources (4 mol %), such as $Pd(dba)_2$, $PdCl_2$, and $Pd(OAc)_2$, afforded no better results. Some more conditions about temperature and time were examined, but no better results were obtained (for the details, see the Supporting Information). In a word, the optimized reaction conditions are 2 mol % $Pd_2(dba)_3$ as the palladium source, *t*BuXPhos as the ligand, NaOH as the base, and toluene with 5% water as the solvent at 90 °C for 20 h.

In view of the importance of chirality, (*R*) form, (*S*) form, and racemic *tert*-butanesulfinamides were first investigated under the optimized reaction conditions. Palladium-catalyzed C−N cross coupling of bromobenzene and (*R*) form, (*S*) form, and racemic *tert*-butanesulfinamides gave the corresponding *N*-phenyl *tert*-butanesulfinamides **3a**−**3c** with high yields, respectively (Table 2, entries 1 to 3). Commercial 98% ee (*R*)- and (*S*)-*tert*-butanesulfinamide gave 98.7% ee (*R*)- and 97.3% ee (*S*)-*N*-phenyl *tert*-butanesulfinamide, respectively, which implies that no racemization occurred during the alkaline C−N cross coupling (Table 2, entries 1 and 2). Because of the alkali resistance of *tert*-butanesulfinamide and the excellent chiral induction ability, enantiomer-pure (*R*)- and (*S*)-*tert*-butanesulfinamides are extensively used as chiral auxiliaries in synthesis of chiral amines. Alkali-resistant chiral *N*-aryl *tert*-butanesulfinamides **3** possess chiral *tert*-butanesulfinamide moiety, so it is expected to be extensively used in synthesis of chiral drugs and chiral chemicals in the near future.[1,6]

Table 2. Palladium-Catalyzed C−N Cross Coupling of Aryl Bromides and Sulfinamides[a]



1 2 3

entry	R	config.	ArX	product	yield (%)
1[b]	*t*-Bu	*R*	PhBr	**3a**	91
2[c]	*t*-Bu	*S*	PhBr	**3b**	86
3	*t*-Bu	±	PhBr	**3c**	84
4	*t*-Bu	*R*	4-MeC_6H_4Br	**3d**	89
5	*t*-Bu	*R*	3-MeC_6H_4Br	**3e**	77
6	*t*-Bu	*R*	2-MeC_6H_4Br	**3f**	53
7	*t*-Bu	*R*	3-$MeOC_6H_4Br$	**3g**	82
8	*t*-Bu	*R*	4-$NO_2C_6H_4Br$	**3h**	95
9	*t*-Bu	*R*	4-AcC_6H_4Br	**3i**	92
10[d]	*t*-Bu	*R*	4-$COOHC_6H_4Br$	**3j**	67
11	*t*-Bu	*R*	4-FC_6H_4Br	**3k**	52
12	*t*-Bu	*R*	4-PhC_6H_4Br	**3l**	82
13	*t*-Bu	*R*	2-$C_{10}H_7Br$	**3m**	73
14	*t*-Bu	*R*	1-$C_{10}H_7Br$	**3n**	20
15	*t*-Bu	*R*	PhI	**3a**	13
16	*t*-Bu	*R*	PhCl	**3a**	41
17	*t*-Bu	*R*	4-$NO_2C_6H_4Cl$	**3h**	92
18	*t*-Bu	*R*	3-$NO_2C_6H_4Cl$	**3o**	71
19	*t*-Bu	*R*	2-C_5H_4NBr	**3p**	75
20	4-Tol	±	PhBr	**3q**	70
21	4-Tol	±	4-MeC_6H_4Br	**3r**	60

[a]Unless otherwise noted, all reactions were performed by heating (*R*)-*tert*-butanesulfinamide (1 mmol), aryl halide (1.3 mmol), $Pd_2(dba)_3$ (0.02 mmol), *t*BuXPhos (0.05 mmol), NaOH (2.4 mmol), degassed water (0.3 mL), and toluene (6 mL) for 20 h at 90 °C. [b]98.7% ee. [c]97.3% ee. [d]NaOH (3.4 mmol) is used.

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Once the stability of chirality in the transformation of the C−N cross coupling was confirmed, other aryl bromides were investigated further under the optimized reaction conditions.

Palladium-catalyzed C−N cross coupling of 4-bromotoluene and (*R*)-*tert*-butanesulfinamide gave nearly the same yield as that of bromobenzene (Table 2, entry 4 vs entry 1). 3-Bromotoluene gave a bit lower yield (Table 2, entry 5). *ortho*-Bromotoluene gave much lower yield than *para*- and *meta*-substituted tolyl bromides (Table 2, entries 6 vs 4 and 5). Since *tert*-butanesulfinamide possesses a bulky *tert*-butyl group, probably the high steric hindrance 2-methylphenyl and *tert*-butanesulfinamide in a palladium complex of the transitional state decreases the efficiency of the coordination of the substrates and palladium.[12]

The coupling of aryl bromides with electron-donating groups carried out well. The coupling of 3-methoxyphenyl bromide with an electron-donating group carried out smoothly to afford a good yield of 82% (Table 2, entry 7), and the product **3g** is facile to form a single crystal.[13]

In contrast, 4-nitrobromobenzene with a strong electron-withdrawing nitro group achieved extremely high yield up to 95% (Table 2, entry 8). 4-Bromoacetophenone with an electron-withdrawing acetyl group also gave high yield (Table 2, entry 9). It demonstrates that electron-withdrawing groups in aryl halides promote the coupling of sulfinamides.

4-Bromobenzoic acid with an electron-withdrawing carboxyl group afforded a moderate yield (Table 2, entry 10), so the fact seems contradictory to the above rule. But the coupling reaction conducted under strongly alkaline condition, so the substrate 4-bromobenzoic acid must have formed a salt, i.e., sodium 4-bromobenzoate. The negative ion of 4-bromobenzoate and the low solubility in organic solvent possibly are responsible for the mild yield. The yield of *N*-(4-fluorophenyl) *tert*-butanesulfinamide **3k** was moderate (Table 2, entry 11). Perhaps the fluoro group participated in the C−N coupling, which produced complex byproducts.

The yield of C−N cross coupling of 4-bromobiphenyl and *tert*-butanesulfinamide was fairly good (Table 2, entry 12). 2-Bromonaphthalene also afforded good results (Table 2, entry 13), but 1-bromonaphthalene gave much lower yield (Table 2, entry 14). Perhaps the reason is the same as that of *ortho*-bromotoluene, i.e., the huge steric hindrance between *tert*-butanesulfinamide and 1-bromonaphthalene.

Aryl iodides often demonstrate much higher reactivity than aryl chlorides and bromides in copper-catalyzed carbon-heteroatom cross coupling[7c] but are poor substrates for palladium-catalyzed cross coupling.[14] Palladium-catalyzed C−N cross coupling of *tert*-butanesulfinamide and iodobenzene gave an extremely poor result, only 13% yield (Table 2, entry 15). Fortunately, aryl bromides and chlorides usually are much cheaper, more readily available, and more diverse than aryl iodides, so the poor reactivity of aryl iodides will not demolish this coupling protocol's applications.

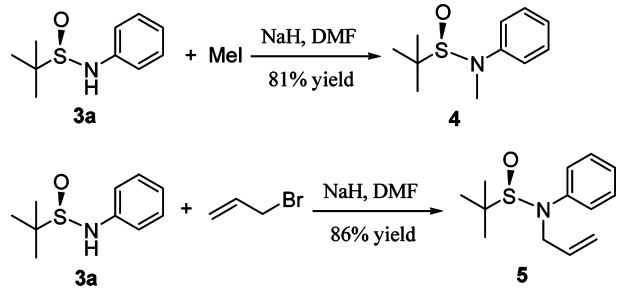
Chlorobenzene showed higher reactivity than iodobenzene but much poorer reactivity than bromobenzene (Table 2, entry 16 vs entries 15 and 1). It is obvious that strong electron-withdrawing groups greatly promote palladium-catalyzed C−N cross coupling of aryl chlorides and *tert*-butanesulfinamide (Table 2, entries 17−19). *para*-Chloronitrobenzene gave a fairly high yield up to 92% (Table 2, entry 17). *meta*-Chloronitrobenzene gave good yield (Table 2, entry 18). Because of a steric group on the *ortho* position, *ortho*-chloronitrobenzene did not react.

Touré reported the first synthesis of chiral *N*-(2-pyridyl) *tert*-butanesulfinamide **3p**. But in Touré's paper there is no yield and no characterization data.[6b] We found that our palladium catalytic protocol could efficiently finish the C−N cross coupling with 75% isolated yield (Table 2, entry 19), and chiral *N*-(2-pyridyl) *tert*-butanesulfinamide **3p** was fully characterized.

In addition to *tert*-butanesulfinamide, racemic *p*-toluenesulfinamide reacted with aryl bromides under the similar reaction conditions to afford *N*-aryl *p*-toluenesulfinamides **3q**−**3r** with moderate yields (Table 2, entries 20 and 21).

N-Aryl *tert*-butanesulfinamides are readily derived into other compounds. The hydrogen on nitrogen atom in an *N*-aryl *tert*-butanesulfinamide has higher acidity due to the electron-drawing effect of aryl and sulfinyl groups. So *N*-methylation and *N*-allylation of (*R*)-*N*-phenyl *tert*-butanesulfinamide were smoothly performed with sodium hydride as a base to give *N*-methyl-*N*-phenyl *tert*-butanesulfinamide **4** and *N*-allyl-*N*-phenyl *tert*-butanesulfinamide **5** with high yields, respectively (Scheme 2). Those compounds will find their applications in

Scheme 2. Methylation and Allylation on Nitrogen Atom of *N*-Phenyl *tert*-Butanesulfinamide



organic synthesis and medicine synthesis, for example, in synthesis similar compounds to tetrahydroquinoline-based PPARα/γ agonists.[15]

In summary, we have developed an efficient palladium-catalyzed C−N cross coupling of sulfinamides and aryl halides. Application of $Pd_2(dba)_3$ as the palladium source, *t*BuXPhos as the ligand, cheap sodium hydroxide as the base, and a little degassed water as the additive is both convenient and cost-effective. Probably because of the acceleration of the dissolution of inorganic base, the addition of a small amount of water is the key to promote the reaction. The chirality of (*R*)- and (*S*)-*tert*-butanesulfinamides is preserved in *N*-aryl *tert*-butanesulfinamides without racemization during the coupling.

■ EXPERIMENTAL SECTION

General Experimental Procedure of Pd-Catalyzed C−N Cross Coupling of Sulfinamides and Aryl Halides. An oven-dried ground test tube, which was equipped with a magnetic stir bar and fitted with a rubber septum, was charged with (*R*)-, (*S*)-, or racemic *tert*-butanesulfinamide (0.121 g, 1.0 mmol), $Pd_2(dba)_3$ (0.018 g, 0.02 mmol), *t*Bu-XPhos (0.0212 g, 0.05 mmol), and NaOH (0.08 g, 2 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times), and then the aryl halide (1.3 mmol), toluene (10 mL), and degassed water (0.3 mL) were added via syringe (aryl chlorides or amines that were solids at room temperature were added with the catalyst and base). The solution was stirred at 90 °C for 20 h. The reaction mixture was then cooled to room temperature, quenched by water, and extracted with ethyl acetate (20 mL) twice. The organic layer was combined, dried over anhydrous sodium sulfate, and filtrated. The filterate was condensed under vacuum. The residual was purified with silica gel column

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chromatography with a solution of petroleum ether and ethyl acetate (5:1 (vol:vol)) as an eluent to afford the *N*-aryl *tert*-butanesulfinamide.

(*R*)-*N*-Phenyl *tert*-Butanesulfinamide 3a (Table 2, Entries 1, 15, 16).[6b] White crystalline solid (0.179 g, 91% yield) with 98.1% ee (HPLC, Diacel Chiralcel OD-H column, 90:10 hexanes/2-propanol, 1 mL/min, 254 nm; (*R*)-*N*-phenyl *tert*-butanesulfinamide, t_R = 4.8 min; (*S*)-*N*-phenyl *tert*-butanesulfinamide, t_R = 9.2 min): mp 111−114 °C; $[\alpha]_D^{22}$ = −182° (*c* 0.3, $CHCl_3$) (lit $[\alpha]_D^{23}$ −181° (*c* 1.0, $CHCl_3$)); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.25−7.24 (m, 2H), 7.01 (t, *J* = 6.3 Hz, 3H), 5.41 (d, *J* = 11.1 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.1, 129.1, 122.4, 117.9, 56.3, 22.3; IR (KBr) ν (cm^{-1}) 3452, 3145, 2961, 2889, 1598, 1495, 1412, 1363, 1287, 1236, 1053, 887, 751; ESI-MS (negative mode), *m*/*z* = 196 $[M - H]^-$.

(*S*)-*N*-Phenyl *tert*-Butanesulfinamide 3b (Table 2, Entry 2). White crystalline solid (0.167 g, 86% yield) with 97.3% ee (HPLC, Diacel Chiralcel OD-H column, 90:10 hexanes/2-propanol, 1 mL/min, 254 nm; (*R*)-*N*-phenyl *tert*-butanesulfinamide, t_R = 4.8 min; (*S*)-*N*-phenyl *tert*-butanesulfinamide, t_R = 9.2 min): mp 110−113 °C; $[\alpha]_D^{21}$ = +179.2 (*c* 0.075, ethyl acetate). Other data are the same as those of (Table 2, entry 1).

(±)-*N*-Phenyl *tert*-Butanesulfinamide 3c (Table 2, Entry 3). White crystalline solid (0.166 g, 84% yield): mp 103−105 °C. Other data are the same as those of (Table 2, entry 1).

(*R*)-*N*-(4-Tolyl) *tert*-Butanesulfinamide 3d (Table 2, Entry 4). Yellow solid (0.187 g, 89%): mp 82−83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.06 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 5.33 (s, 1H), 2.28 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 139.4, 132.3, 129.7, 118.7, 56.2, 22.4, 20.5; IR (KBr) ν (cm^{-1}) 3445, 3242, 2957, 2922, 2864, 1613, 1513, 1472, 1382, 1275, 1228, 1177, 1050, 881, 810; $[\alpha]_D^{21}$ = −114.0° (*c* 0.01, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 210 $[M - H]^-$. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.58; H, 8.17; N 6.59.

(*R*)-*N*-(3-Tolyl) *tert*-Butanesulfinamide 3e (Table 2, Entry 5). White solid (0.162 g, 77%): mp 84−85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.15 (t, *J* = 7.9 Hz, 1H), 6.84−6.79 (m, 3H), 5.30 (s, 1H), 2.30 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 142.0, 139.1, 129.0, 123.4, 118.8, 115.2, 56.3, 22.4, 21.3; IR (KBr) ν (cm^{-1}) 3451, 3246, 2965, 1605, 1474, 1368, 1289, 1165, 1047, 937, 874, 829, 776; $[\alpha]_D^{21}$ = −127.5° (*c* 0.06, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 210 $[M - H]^-$. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.61; H, 8.20; N 6.56.

(*R*)-*N*-(2-Tolyl) *tert*-Butanesulfinamide 3f (Table 2, Entry 6). Yellow solid (0.112 g, 53%): mp 62−64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.18−7.11 (m, 3H), 7.00−6.93 (m, 1H), 5.25 (s, 1H), 2.29 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ(ppm) 139.8, 130.7, 127.5, 127.0, 123.3, 119.1, 56.4, 22.4, 17.6; IR (KBr) ν (cm^{-1}) 3452, 3248, 2959, 1589, 1492, 1373, 1277, 1238, 1177, 1062, 871, 748; $[\alpha]_D^{21}$ = −67.3° (*c* 0.03, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 210 $[M - H]^-$. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.45; H, 8.23; N 6.68.

(*R*)-*N*-(3-Methoxyphenyl) *tert*-Butanesulfinamide 3g (Table 2, Entry 7). White solid (0.186 g, 82%): mp 111−112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.16 (t, *J* = 8.2 Hz, 1H), 5.60−5.55 (m, 3H), 5.34 (s, 1H), 3.78(s, 3H), 1.33 (s, 9H); ^{13}C NMR (300 MHz, CD_3OD) δ (ppm) 160.2, 143.5, 129.8, 110.1, 107.9, 103.5, 56.3, 54.9, 22.3; IR (KBr) ν (cm^{-1}) 3456, 3273, 3112, 3076, 2966, 1584, 1519, 1246, 1186, 1113, 1068, 875, 795, 751; $[\alpha]_D^{21}$ = −2.6° (*c* 0.05, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 226 $[M - H]^-$. Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16. Found: C, 58.23; H, 7.61; N 6.25.

(*R*)-*N*-(4-Nitrophenyl) *tert*-Butanesulfinamide 3h (Table 2, Entry 8). Yellow solid (0.227 g, 95%): mp 133−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.11 (d, *J* = 9.1 Hz, 2H), 7.04 (d, *J* = 9.1 Hz, 2H), 6.32 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 148.9, 141.6, 125.2, 115.7, 57.3, 22.1; IR (KBr) ν (cm^{-1}) 3453, 3265, 2964, 1596, 1508, 1470, 1336, 1298, 1058, 869, 794, 751; $[\alpha]_D^{21}$ = −44 (*c* 0.01, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 241 $[M - H]^-$. Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82; N, 11.56. Found: C, 49.65; H, 5.93; N 11.45.

(*R*)-*N*-(4-Acetylphenyl) *tert*-Butanesulfinamide 3i (Table 2, Entry 9). Yellow solid (0.220 g, 92%): mp 110.5−111.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.67 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 2.43 (s, 3H), 1.30(s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 196.6, 147.2, 130.7, 129.9, 115.9, 56.8, 26.1, 22.3; IR (KBr) ν (cm^{-1}) 3456, 3276, 2961, 1693, 1611, 1509, 1475, 1356, 1182, 1119, 1056, 861, 840, 712; $[\alpha]_D^{21}$ = −69.6° (*c* 0.05, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 238 $[M - H]^-$. Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.31; H, 7.26; N 5.92.

(*R*)-*N*-(4-Carboxyphenyl) *tert*-Butanesulfinamide 3j (Table 2, Entry 10). White solid (0.161 g, 67%): mp 164.2 °C; ^{1}H NMR (300 MHz, CD_3OD) δ (ppm) 7.94 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 168.5, 147.9, 131.5, 124.2, 116.4, 56.9, 21.7; IR (KBr) ν (cm^{-1}) 3481, 3186, 2985, 1703, 1671, 1608, 1461, 1425, 1286, 1238, 1172, 1056, 8801, 768; $[\alpha]_D^{21}$ = −63.3° (*c* 0.078, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 240 $[M - H]^-$. Anal. Calcd for $C_{11}H_{15}NO_3S$: C, 54.75; H, 6.27; N, 5.80. Found: C, 54.87; H, 6.41; N 5.74.

(*R*)-*N*-(4-Fluorophenyl) *tert*-Butanesulfinamide 3k (Table 2, Entry 11). Yellow solid (0.112 g, 52%): mp 59.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.96 (d, *J* = 6.4 Hz, 4H), 5.36 (s, 1H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.6, 138.0, 120.5 (d, *J* = 31.8 Hz, 2C), 115.9 (d, *J* = 90.3 Hz, 2C), 56.5, 22.4; IR (KBr) ν (cm^{-1}) 3448, 3227, 2963, 2926, 2612, 1607, 1506, 1473, 1367, 1336, 1273, 1209, 1157, 1135, 1100, 1069, 886, 833, 776; $[\alpha]_D^{21}$ = −73.0° (*c* 0.01, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 214 $[M - H]^-$. Anal. Calcd for $C_{10}H_{14}FNOS$: C, 55.79; H, 6.55; N, 6.51. Found: C, 55.92; H, 6.70; N 6.44.

(*R*)-*N*-(4-Biphenyl) *tert*-Butanesulfinamide 3l (Table 2, Entry 12). Yellow solid (0.224 g, 82%): mp 153−156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49−7.29 (m, 7H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.03 (d, *J* = 3.9 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 114.6, 140.4, 135.6, 128.6, 127.9, 126.8, 126.6, 118.4, 56.5, 22.4; IR (KBr) ν (cm^{-1}) 3453, 3252, 2926, 1610, 1519, 1485, 1386, 1305, 1286, 1268, 1228, 1191, 1057, 912, 880, 838, 767; $[\alpha]_D^{21}$ = −110.8° (*c* 0.15, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 272 $[M - H]^-$. Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.00; N, 5.12. Found: C, 70.43; H, 7.16; N 5.01.

(*R*)-*N*-(2-Naphthyl) *tert*-Butanesulfinamide 3m (Table 2, Entry 13). White solid (0.181 g, 73%): mp 122−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.37 (s, 9 H), 6.08 (s, 1 H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.27−7.39 (m, 3 H), 7.58−7.66 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 139.7, 133.9, 129.7, 129.1, 127.5, 126.6, 126.4, 124.1, 119.0, 113.5, 56.5, 22.4; IR (KBr) ν (cm^{-1}) 3454, 3202, 2961, 1628, 1599, 1511, 1464, 1386, 1364, 1340, 1247, 1210, 1177, 1067, 961, 918, 850, 820, 742; $[\alpha]_D^{21}$ = −134.2° (*c* 0.10, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 246 $[M - H]^-$. Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66. Found: C, 67.87; H, 6.98; N 5.82.

(*R*)-*N*-(1-Naphthyl) *tert*-Butanesulfinamide 3n (Table 2, Entry 14). Brown oil (0.052 g, 20%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.96 (s, 1H), 7.83 (t, *J* = 5.0 Hz, 1H), 7.60 (d, *J* = 2.2, 1H), 7.51−7.48 (m, 2H), 7.36 (t, *J* = 5.4 Hz, 2H), 5.84 (s, 1H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ (ppm) 136.9, 134.2, 128.5, 127.3, 126.1, 125.9, 125.6, 124.6, 121.2, 117.4, 66.9, 22.6; IR (KBr) ν (cm^{-1}) 2973, 2868, 1580, 1513, 1459, 1396, 1320, 1266, 1174, 1057, 1057, 891, 771; $[\alpha]_D^{21}$ = −43.5° (*c* 0.04, ethyl acetate); ESI-MS (negative mode), *m*/*z* = 246 $[M - H]^-$. Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66. Found: C, 68.05; H, 6.83; N 5.54.

(*R*)-*N*-(4-Nitrophenyl) *tert*-Butanesulfinamide 3h (Table 2, Entry 17). Yellow solid (0.223 g, 92%). Other data are the same as those of (Table 2, entry 8).

(*R*)-*N*-(3-Nitrophenyl) *tert*-Butanesulfinamide 3o (Table 2, Entry 18). Yellow solid (0.168 g, 71%): mp 147−149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.79 (s, 1H), 7.69 (dd, J_1 = 1.68 Hz, J_2 = 4.45 Hz, 1H), 7.27 (d, *J* = 5.2 Hz, 2H), 6.66 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 148.7, 143.9, 129.9, 123.0, 116.9, 111.9, 57.1, 22.4; IR (KBr) ν (cm^{-1}) 3453, 3076, 2965, 2861, 1619, 1527, 1476, 1401, 1349, 1293, 1238, 1055, 996, 948, 884, 826, 801,

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737; $[\alpha]_D^{21} = -2.1°$ (*c* 0.024, ethyl acetate); ESI-MS (negative mode), m/z = 241 $[M - H]^-$. Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82; N, 11.56. Found: C, 49.46; H, 5.97; N 11.72.

(*R*)-*N*-(2-Pyridyl) *tert*-Butanesulfinamide 3p (Table 2, Entry 19). Pale yellow solid (0.149 g, 75%): mp 137−139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.22 (d, J = 4.3 Hz, 1H), 7.61 (dt, J_1 = 1.8 Hz, J_2 = 8.3 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.91 (q, J = 5.2 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 155.2, 148.0, 138.2, 117.4, 110.2, 56.5, 22.4; IR (KBr) ν (cm^{-1}) 3452, 3081, 2973, 1605, 1535, 1476, 1364, 1275, 1052, 884, 743; $[\alpha]_D^{21} = -147.3°$ (*c* 0.037, ethyl acetate); ESI-MS (negative mode), m/z = 197 $[M - H]^-$. Anal. Calcd for $C_9H_{14}N_2OS$: C, 54.52; H, 7.12; N, 14.13. Found: C, 54.65; H, 7.26; N 14.26.

(±)-*N*-Phenyl *p*-Toluenesulfinamide 3q (Table 2, Entry 20).[3d] White solid (0.163 g, 70%): mp 110−112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63 (t, J = 6.2 Hz, 2H), 7.30−7.22 (m, 4H), 7.09−7.00 (m, 3H), 6.55 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 141.7, 141.4, 140.7, 129.7, 129.4, 125.4, 123.3, 118.7, 21.3; IR (KBr) ν (cm^{-1}) 3452, 3099, 2861, 2791, 1641, 1599, 1488, 1400, 1225, 1171, 1088, 1052, 893, 814, 758; ESI-MS (negative mode), m/z = 230 $[M - H]^-$.

(±)-*N*-(*p*-Tolyl) *p*-Toluenesulfinamide 3r (Table 2, Entry 21).[3d] Pale yellow solid (0.148 g, 60%): mp 114−116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.64 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.02 (dd, J_1 = 24.6 Hz, J_2 = 8.6 Hz, 4H), 6.32 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 141.6, 141.5, 137.9, 133.2, 129.8, 129.6, 125.5, 119.4, 21.3, 20.7; IR (KBr) ν (cm^{-1}) 3452, 3145, 2917, 2316, 1613, 1512, 1397, 1281, 1228, 1176, 1088, 1051, 892, 804; ESI-MS (negative mode), m/z = 244 $[M - H]^-$.

Synthetic Procedure of (*R*)-*N*-Methyl-*N*-phenyl *tert*-Butanesulfinamide 4 (Scheme 2). *N*-Phenyl (*R*)-*tert*-butanesulfinamide (1 mmol, 0.1970 g), 80% NaH in mineral oil (2 mmol, 0.0629 g), and THF (10 mL) were added to an oven-dried flask equipped with a magnetic stirring bar. The mixture was stirred in an ice water bath for 1 h, and then methyl iodide (0.3 mmol, 0.18 g) was added by syringe to the flask. The reaction mixture was stirred overnight. After being quenched by saturated NH_4Cl solution, the reaction mixture was extracted with ethyl acetate (20 mL) three times. The combined organic layer was washed with saturated NaCl solution and then dried over anhydrous sodium sulfate. The filtrate was condensed under vacuum. The residual was purified with a silica gel column chromatography with a mixed solution of petroleum ether and ethyl acetate (5:1 (v:v)) as an eluent to give a pale yellow oil. (*R*)-*N*-Methyl-*N*-phenyl *tert*-butanesulfinamide (0.1712 g, 81%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.28 (dd, J_1 = 8.2 Hz, J_2 = 7.7 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H), 3.05 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 147.3, 129.1, 122.3, 118.3, 60.1, 29.7, 23.7; IR (KBr) ν (cm^{-1}) 2958, 1597, 1495, 1362, 1277, 1216, 1175, 1081, 1052, 1027, 839, 750; $[\alpha]_D^{20.8} = +73.0°$ (*c* 0.13, ethyl acetate); ESI-MS (negative mode), m/z = 210 $[M - H]^-$. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.11; N, 6.63. Found: C, 62.40; H, 8.25; N 6.82.

Synthetic Procedure of (*R*)-*N*-Allyl-*N*-phenyl *tert*-Butanesulfinamide 5 (Scheme 2). Using a similar procedure as that of (*R*)-*N*-methyl-*N*-phenyl *tert*-butanesulfinamide, allyl bromide (1.3 mmol, 0.157 g) was used to replace methyl iodide. The residual was purified to give a pale yellow liquid. (*R*)-*N*-Allyl-*N*-phenyl *tert*-butanesulfinamide (0.2036 g, 86%): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.31−7.26 (m, 2H), 7.18 (t, J = 1.2 Hz, 2H), 7.07 (dd, J_1 = 7.3 Hz, J_2 = 1.0 Hz, 1H), 5.78 (t, J = 6.5 Hz, 1H), 5.17−5.10 (m, 2H), 4.04 (dq, J_1 = 2.2 Hz, J_2 = 1.5 Hz, 2H), 1.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.0, 133.9, 128.9, 123.6, 122.0, 117.8, 59.7, 46.5, 23.4; IR (KBr) ν (cm^{-1}) 3013, 2954, 1615, 1595, 1501, 1365, 1280, 1219, 1085, 1026, 842, 754; $[\alpha]_D^{21} = +108.5$ (*c* 0.376, $CHCl_3$); ESI-MS (negative mode), m/z = 236 $[M - H]^-$. Anal. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.67; H, 8.19; N 5.78.

■ ASSOCIATED CONTENT

Supporting Information

Complete spectral data for all compounds, chiral HPLC for racemic, (*R*)- and (*S*)-*N*-phenyl *tert*-butanesulfinamides, and single crystal X-ray data for (*R*)-*N*-(3-methoxyphenyl) *tert*-butanesulfinamide (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qinglezeng@hotmail.com.

Notes

The authors declare no competing financial interest.

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