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Catalytic Enantioselective Synthesis of N−C Axially Chiral Sulfonamides through Chiral Palladium-Catalyzed *N*-Allylation

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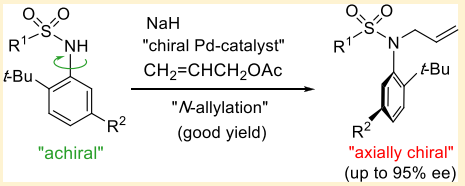
Supporting Information

ABSTRACT: In the presence of (*S,S*)-Trost ligand and (allyl-Pd-Cl)$_2$ catalyst, the reaction of allyl acetate with the anionic species prepared from various *N*-(2-*tert*-butylphenyl)sulfonamides and NaH proceeded in an enantioselective manner (up to 95% ee) to give optically active *N*-allylated sulfonamide derivatives possessing an N−C axially chiral structure in high yields.



INTRODUCTION

Recently, N−C axially chiral compounds have attracted considerable attention as a new type of nonbiaryl atropisomeric molecule.[1] In 2002, we reported the synthesis of optically active N−C axially chiral anilides **II** through chiral Pd-catalyzed *N*-allylation of achiral *ortho-tert*-butylanilides **I** (Figure 1).[2] Although the present reaction is the first catalytic

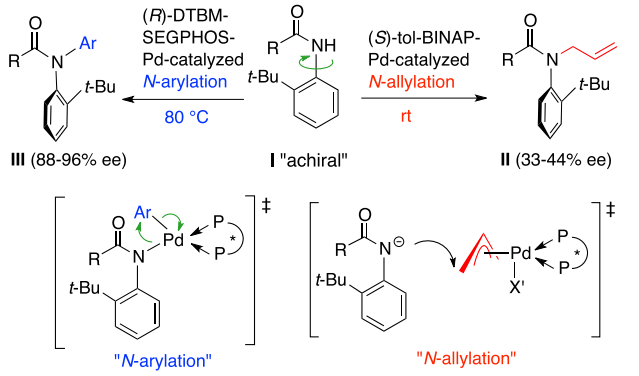


Figure 1. Catalytic enantioselective synthesis of N−C axially chiral anilides developed by our group.

enantioselective synthesis of N−C axially chiral compounds, the enantioselectivity was by no means satisfactory.[2,3] In *N*-allylation with a chiral π-allyl Pd catalyst, highly asymmetric induction at the anilide moiety by a chiral ligand may be difficult because the anilide anion attacks the π-allyl carbon on the opposite site of the Pd atom.[4] In 2005, we succeeded in the first highly enantioselective synthesis of N−C axially chiral anilides **III** through chiral Pd-catalyzed Buchwald−Hartwig amination (Figure 1).[5] In this reaction, since the N−Ar bond formation (the construction of the N−C chiral axis) via reductive elimination occurs around the chiral ligand,[6] high enantioselectivity should be achieved.

Since the publication of our results, catalytic asymmetric syntheses of various N−C axially chiral compounds, which proceed in a highly enantioselective manner, have been reported by many groups, with most of the compounds being carboxamide derivatives such as anilides, lactams, imides, carbamates, and ureas.[7] On the other hand, although N−C axially chiral sulfonamides have also been reported (Figure 2),[8]

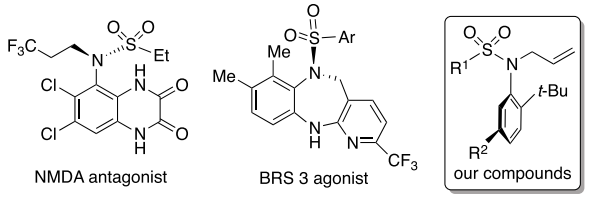


Figure 2. Several N−C axially chiral sulfonamides.

there has been no indication of their catalytic asymmetric synthesis. Some of these sulfonamides are pharmaceutically attractive compounds, and their catalytic asymmetric synthesis is meaningful from the viewpoint of medicinal chemistry as well as synthetic organic chemistry.[7a,b] In this paper, we report the catalytic enantioselective syntheses of N−C axially chiral sulfonamides (Figure 2) through chiral Pd-catalyzed *N*-allylation. Furthermore, the determination of the absolute stereochemistry of the *N*-allylation product and the origin of the enantioselectivity are also described.

RESULTS AND DISCUSSION

We predicted that similar to *ortho-tert*-butylcarboxanilides **II** and **III**, *N*-(2-*tert*-butylphenyl)sulfonamides (Figure 2) would also possess a rotationally stable structure and investigated their catalytic enantioselective syntheses in detail. Initially, although the Buchwald−Hartwig amination was attempted, which gave an excellent result in the synthesis of carboxanilides, the *N*-arylation of an achiral sulfonamide **1** did not proceed under the conditions for the synthesis of

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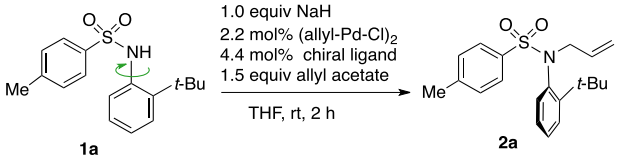
carboxanilides **III**. This may be due to the lower nucleophilicity of a sulfonamide anion in comparison to that of a carboxamide anion. In addition, the Buchwald−Hartwig amination shown in Figure 1 requires heating at 80 °C, while *N*-substituted-*N*-(2-*tert*-butylphenyl)sulfonamide was found to racemize easily at 80 °C (vide infra). Therefore, its synthesis through Pd-catalyzed *N*-allylation, which proceeds under milder conditions, was explored.

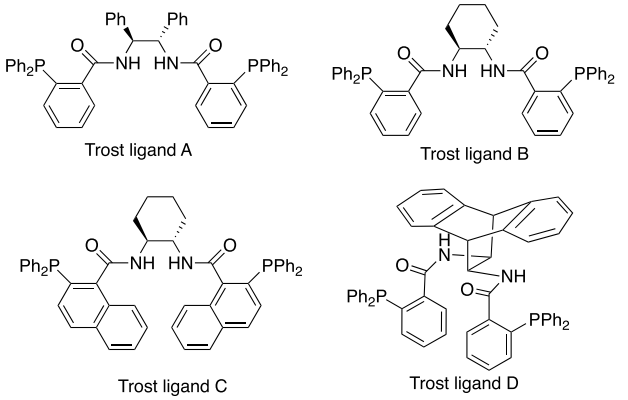
The reaction of allyl acetate (1.5 equiv) with the anion species prepared from achiral 4-tosyl amide **1a** and NaH (1.0 equiv) was conducted in the presence of $(allyl\text{-}Pd\text{-}Cl)_2$ catalyst (2.2 mol %) and various chiral ligands (4.4 mol %) in THF (Table 1). In most cases, the reaction completed within 2 h at

Table 1. Ligand Screening in Catalytic Enantioselective *N*-Allylation of Sulfonamide 1a



entry	ligand	yield (%)[a]	ee (%)[b]
1	(*R*)-MOP	35	0
2	(*R*)-BINAP	95	0
3	(*S*)-DM-BINAP	89	4
4	(*R*)-SEGPHOS	86	10
5	(*R*)-DTBM-SEGPHOS	quant	10
6	(*R*)-DIFLUOROPHOS	93	4
7	(*S,S*)-CHIRAPHOS	quant	3
8	(*S*)-Phox P,N-ligand	quant	11
9	(*S,S*)-Trost ligand A	95	59
10[c]	(*S,S*)-Trost ligand A	quant	71
11[c]	(*S,S*)-Trost ligand B	91	53
12[c]	(*S,S*)-Trost ligand C	81	49
13[c]	(*S,S*)-Trost ligand D	32	16

[a]Isolated yield. [b]The ee was determined by HPLC analysis using a chiral column. [c]The reaction was conducted at −20 °C.

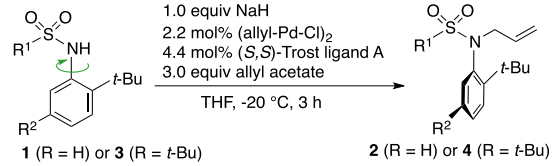


rt or −20 °C to afford *N*-allylated axially chiral product **2a** in excellent yields (entries 2−12), while enantioselectivity was poor or not observed (entries 1−8, 13). Among the investigated chiral ligands, Trost ligands A−C[9] gave a relatively good result (entries 9−12); in the reaction with Trost ligand A, **2a** was obtained with 59% ee (entry 9). Furthermore, when the reaction temperature was lowered to −20 °C from rt, the ee increased to 71 from 59% (entry 10).

To further improve the enantioselectivity, although a wide selection of allylic reagents (cinnamyl acetate and prenyl acetate), bases (*t*-BuOK, *t*-BuONa, Cs_2CO_3) and solvents (CH_2Cl_2, DMF, CH_3CN, toluene) was examined, no better result was obtained than entry 10 in Table 1.

Table 2 shows the application of the present reaction to various sulfonamide substrates **1** and **3** under the optimized

Table 2. Application to Various Sulfonamide Substrates



entry	1 or 3	R^1	R^2	2 or 4	yield (%)[a]	ee (%)[b]
1	**1a**	4-MeC_6H_4	H	**2a**	quant	73
2	**1b**	C_6H_5	H	**2b**	quant	72
3	**1c**	4-$NO_2C_6H_4$	H	**2c**	93	74
4	**1d**	4-$MeOC_6H_4$	H	**2d**	92	70
5	**1e**	2-MeC_6H_4	H	**2e**	86	86
6	**1f**	2,4,6-$Me_3C_6H_2$	H	**2f**	77	91
7	**1g**	naphth-1-yl	H	**2g**	92	88
8	**1h**	Me	H	**2h**	86	49
9	**1i**	cyclohexyl	H	**2i**	quant	66
10	**3a**	4-MeC_6H_4	*t*-Bu	**4a**	90	78
11	**3b**	C_6H_5	*t*-Bu	**4b**	81	78
12	**3c**	4-$NO_2C_6H_4$	*t*-Bu	**4c**	quant	77
13	**3d**	4-$MeOC_6H_4$	*t*-Bu	**4d**	95	74
14	**3e**	2-MeC_6H_4	*t*-Bu	**4e**	84	89
15	**3f**	2,4,6-$Me_3C_6H_2$	*t*-Bu	**4f**	73	95
16	**3g**	naphth-1-yl	*t*-Bu	**4g**	quant	91
17	**3h**	Me	*t*-Bu	**4h**	94	59

[a]Isolated yield. [b]The ee was determined by HPLC analysis using a chiral column.

conditions established in Table 1. In the reactions of Table 2, 3 equiv of allyl acetate was used because the use of 1.5 equiv brought about a considerable decrease in the chemical yield with several sulfonamide substrates. By the use of 3 equiv of allyl acetate, all reactions in Table 2 completed within 3 h at −20 °C to give products **2** and **4** in good yields.

Similar to 4-tosyl amide **1a**, the reaction with benzenesulfonamide **1b**, 4-nitrobenzenesulfonamide **1c**, and 4-methoxybenzenesulfonamide **1d** gave the allylation products **2b−d** with moderate enantioselectivity (70−74% ee, entries 2−4). These results indicate that the electron density on the phenyl group does not significantly influence the enantioselectivity. Meanwhile, it was found that the steric bulkiness of the substrates led to a remarkable increase in the enantioselectivity. That is, the reaction of 2-tosyl amide **1e** proceeded with a higher enantioselectivity (86% ee) than that (73% ee) of 4-tosyl amide **1a** (entries 1 and 5). With bulkier sulfonamides **1f** and **1g** bearing mesityl and naphth-1-yl groups, a further increase in the enantioselectivity was observed; in these cases, the products **2f** and **2g** were obtained with 91 and 88% ee, respectively (entries 6 and 7). In contrast, the reaction with less bulky mesyl amide **1h** yielded a remarkable decrease in the enantioselectivity (49% ee, entry 8). The reaction of cyclohexyl sulfonamide **1i** proceeded with a higher enantioselectivity (66% ee, entry 9) than **1h**, showing the contribution of the steric factor to the enantioselectivity.

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When *N*-(2,5-di-*tert*-butylphenyl)sulfonamides **3a**−**h** (R^2 = *t*-Bu) were used instead of the corresponding mono-*tert*-butyl substrates **1a**−**h** (R^2 = H), in all reactions, an increase in the enantioselectivity was observed (entries 10−17). Such increase in the enantioselectivity by the use of 2,5-di-*tert*-butyl substrates is also observed in the Buchwald−Hartwig amination of carboxamides in Figure 1.[5] Also in the cases of 2,5-di-*tert*-butyl substrates **3**, the reaction with sulfonamides **3e**−**3g**, bearing bulky substituents, proceeded in a highly enantioselective manner (89−95% ee, entries 14−16).

Similar to the *N*-allylation of carboxamides shown in Figure 1, in the present reaction, the sulfonamide anion should approach π-allyl carbon on the opposite face of the Pd atom. Nevertheless, the Trost ligand effectively controls the enantioselective construction of the N−C chiral axis, which locates at a remote position.[10]

Under the conditions in Table 2, we examined the *N*-allylation of *ortho*-*tert*-butylbenzanilide **5b**; however, no allylation product **6b** was obtained (Figure 3). When the

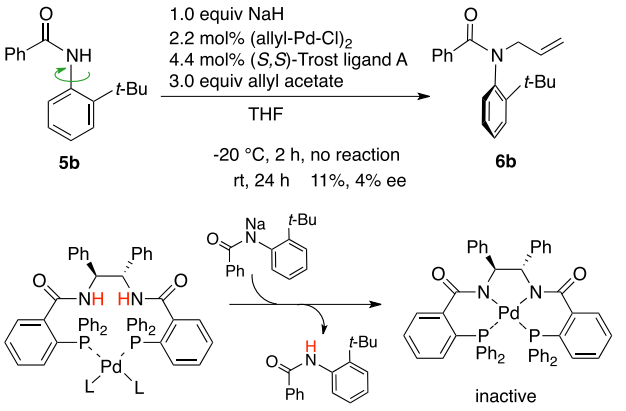

Figure 3. *N*-Allylation of carboxamide **5b** in the presence of Trost ligand-Pd catalyst.

reaction was conducted for 24 h at rt, **6b** was obtained with a poor yield (11%) and enantioselectivity (4% ee). This result, which is in remarkable contrast to the reaction of the corresponding sulfonamides **1b**, may be due to the basicity of the amide anion (conjugated base). Namely, the anion species prepared from carboxamide **5b** and NaH may abstract the amide hydrogen of the Trost ligand, resulting in the formation of an inactive amide−Pd complex (Figure 3). On the other hand, with the sulfonamide anions, since the abstraction of the amide hydrogen of the ligand scarcely occurs because of the lower basicity of the sulfonamide anion than that of carboxamide anion, the reaction would proceed smoothly and enantioselectively.

The absolute stereochemistry of the major enantiomer in *N*-allylation product **4f** (95% ee) was determined to be (*P*)-configuration on the basis of X-ray crystal structural analysis (Figure 4).[11]

The (*P*)-selectivity can be rationally explained on the basis of a working model proposed by Trost (Figure 5).[12] That is, among four possible transition states in the reaction with (*S*,*S*)-Trost ligand, the transition states **TS-A** and **TS-D** give the (*P*)-products, while reactions via **TS-B** and **TS-C** afford (*M*)-products. The transition states **TS-C** and **TS-D** should be significantly destabilized because of the strong steric repulsion between the bulky *tert*-butyl group and Ph (wall) group on

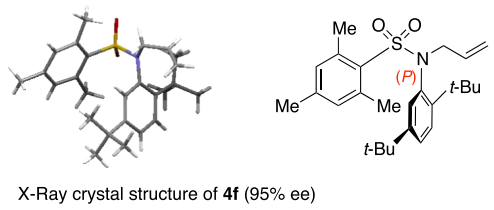

Figure 4. Absolute stereochemistry of **4f** (95% ee).

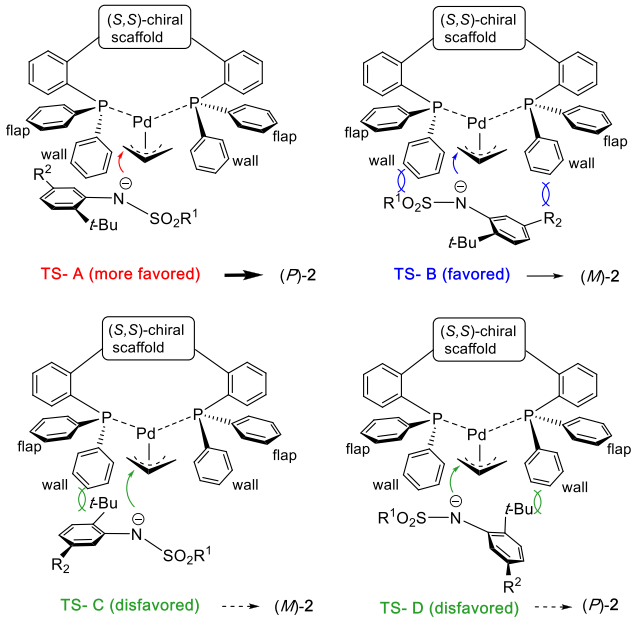

Figure 5. Origin of the enantioselectivity.

phosphorus atom, hence the reaction would proceed via **TS-A** or **TS-B**. Furthermore, **TS-A** may be more favorable than **TS-B**, due to the steric repulsion between the sulfonyl group and Ph (wall) group, giving the *N*-allylation products possessing the (*P*)-configuration as the major enantiomer. An increase in the steric bulkiness of the sulfonyl substituent (R1) causes further destabilization of **TS-B**, which gives the (*M*)-enantiomer, leading to the increase in (*P*)-selectivity.

The increase in the enantioselectivity, which was observed in the reaction with 2,5-di-*tert*-butyl derivatives **3**, may also be explained on the basis of Trost model (Figure 5). That is, *tert*-butyl group (R2) at C5 (meta) position would give rise to the steric repulsion with Ph (wall) group of front side to destabilize **TS-B**. As a result, the proportion of the reaction via **TS-A** increases to give the products **4** with higher ee.

Sulfonamide products **2** and **4** are rotationally stable in the solid state, and no decrease in the ee was observed even after standing for several weeks at rt. On the other hand, the ee's of **2** and **4** in the solution were found to decrease gradually at rt. For example, the ee's of mesitylenesulfonamide **4f** (88% ee) and methanesulfonamide **4h** (60% ee) lowered to 72% ee and 41% ee, respectively, after standing for 25 h at 25 °C in CCl_4 (Figure 6).[13] Since the ee's of carboxamide derivatives **II** and **III** were not changed after standing for several days at rt in the solution, the rotational stabilities of sulfonamides **2** and **4** would be considerably lower in comparison to those of carboxamide derivatives. Indeed, the $\Delta G^{\ddagger}$ values of **4f** and **4h** at 25 °C were evaluated to be 25.6 and 25.2 kcal/mol, respectively, and these values were 2−4 kcal/mol lower than those of caboxamides **II** and **III**.

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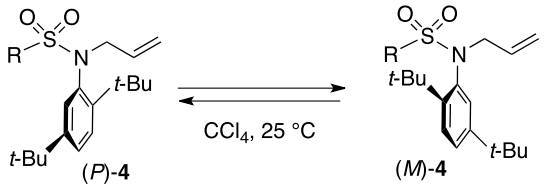

	0 h	3 h	25 h
4f (R = 2,4,6-$Me_3C_6H_2$)	88% ee	87% ee	72% ee
4h (R = CH_3)	60% ee	58% ee	41% ee

Figure 6. Ee change of **4f** and **4h** at 25 °C in CCl_4.

CONCLUSIONS

We succeeded in the catalytic enantioselective synthesis of *N*-(2-*tert*-butylphenyl)sulfonamides through (*S,S*)-Trost ligand-Pd-catalyzed *N*-allylation. The enantioselectivity was significantly influenced by the steric character of substrates, and the reaction with bulky sulfonamides proceeded in a highly enantioselective manner (up to 95% ee). The present reaction is the first catalytic asymmetric synthesis of N−C axially chiral sulfonamide derivatives. Furthermore, the absolute configuration of the major enantiomer was definitely determined by X-ray crystal structural analysis and the origin of the enantioselectivity was also revealed.

EXPERIMENTAL SECTION

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. In ^{1}H and ^{13}C NMR spectra, chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm), respectively. HRMS images were recorded on a double-focusing magnetic sector mass spectrometer using electron impact ionization. Column chromatography was performed on silica gel (75−150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 25 × 4 cm i.d. prepacked column (silica gel, 10 μm) with a UV detector. High-performance liquid chromatography (HPLC) was performed on a 25 × 0.4 cm i.d. chiral column with a UV detector.

Synthesis of Sulfonamide Substrates 1 and 3 (General Procedure). Under N_2 atmosphere, to aniline (448 mg, 3.0 mmol) and pyridine (0.3 mL, 4.5 mmol) in CH_2Cl_2 (5.0 mL) was added 4-methylbenzenesulfonyl chloride (629 mg, 3.3 mmol) at 0 °C, and the reaction mixture was stirred for 18 h from 0 °C to rt. The mixture was poured into H_2O and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1a** (814 mg, 89%).

*N-(2-(tert-Butyl)phenyl)-4-methylbenzenesulfonamide (**1a**).* **1a**: white solid; mp 101−103 °C; IR (neat) 3246, 1325, 1155 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (2H, d, J = 8.2 Hz), 7.42 (1H, dd, J = 1.4, 7.8 Hz), 7.30 (1H, dd, J = 1.8, 8.2 Hz), 7.24 (2H, d, J = 8.2 Hz), 7.13 (1H, dt, J = 1.8, 7.8 Hz), 7.05 (1H, dt, J = 1.8, 7.8 Hz), 6.66 (1H, brs), 2.39 (3H, s), 1.32 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 143.9, 140.0, 137.0, 135.1, 129.6, 127.3, 127.0, 125.0, 122.2, 34.2, 30.9, 21.5; MS (m/z) 326 (MNa^+); HRMS. Calcd for $C_{17}H_{21}NNaO_2S$ (MNa^+) 326.1191. Found: 326.1181.

*N-(2-(tert-Butyl)phenyl)benzenesulfonamide (**1b**).* **1b** was prepared from benzenesulfonyl chloride (583 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1b** (764 mg, 88%). **1b**: white solid; mp 113−115 °C; IR (neat) 3248, 1323, 1151 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (2H, dd, J = 1.4, 7.8 Hz), 7.55 (1H, m), 7.42−7.47 (3H, m), 7.30 (1H, dd, J = 1.4, 7.8 Hz), 7.14 (1H, dt, J = 1.8, 7.3 Hz), 7.07 (1H, dt, J = 1.8, 7.8 Hz), 6.66 (1H, brs), 1.31 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 140.3, 140.0, 134.9, 133.0, 129.0, 127.3, 127.1, 127.0, 125.3, 122.6, 34.3, 30.9; MS (m/z) 312 (MNa^+); HRMS. Calcd for $C_{16}H_{19}NNaO_2S$ (MNa^+) 312.1034. Found: 312.1006.

*N-(2-(tert-Butyl)phenyl)-4-nitrobenzenesulfonamide (**1c**).* **1c** was prepared from 4-nitrobenzenesulfonyl chloride (731 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1c** (922 mg, 92%). **1c**: white solid; mp 163−165 °C; IR (neat) 3252, 1346, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (2H, td, J = 1.8, 8.7 Hz), 8.01 (2H, td, J = 1.8, 8.7 Hz), 7.39 (1H, dd, J = 1.8, 7.8 Hz), 7.34 (1H, dd, J = 2.3, 7.8 Hz), 7.11−7.19 (2H, m), 6.75 (1H, brs), 1.30 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.1, 145.6, 141.0, 134.0, 128.6, 127.5, 127.3, 126.2, 124.3, 123.1, 34.4, 31.0; MS (m/z) 357 (MNa^+); HRMS. Calcd for $C_{16}H_{18}N_2NaO_4S$ (MNa^+) 357.0885. Found: 357.0880.

*N-(2-(tert-Butyl)phenyl)-4-methoxybenzenesulfonamide (**1d**).* **1d** was prepared from 4-methoxybenzenesulfonyl chloride (682 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1d** (958 mg, quant). **1d**: white solid; mp 95−97 °C; IR (neat) 3254, 1319, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (2H, td, J = 2.8, 9.2 Hz), 7.45 (1H, dd, J = 1.4, 7.8 Hz), 7.30 (1H, dd, J = 1.4, 7.8 Hz), 7.13 (1H, dt, J = 1.4, 7.3 Hz), 7.05 (1H, dt, J = 1.8, 7.3 Hz), 6.91 (2H, td, J = 2.8, 9.2 Hz), 6.66 (1H, brs), 3.83 (3H, s), 1.30 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 163.1, 139.9, 135.2, 131.5, 129.5, 127.0, 125.0, 122.1, 114.1, 55.6, 34.2, 30.9; MS (m/z) 342 (MNa^+); HRMS. Calcd for $C_{17}H_{21}NNaO_3S$ (MNa^+) 342.1140. Found: 342.1112.

*N-(2-(tert-Butyl)phenyl)-2-methylbenzenesulfonamide (**1e**).* **1e** was prepared from 2-methylbenzenesulfonyl chloride (315 mg, 1.65 mmol) and 2-*tert*-butylaniline (224 mg, 1.5 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave **1e** (264 mg, 58%). **1e**: white solid; mp 95−98 °C; IR (neat) 3308, 1321, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (1H, d, J = 6.9 Hz), 7.49 (1H, dt, J = 1.4, 7.8 Hz), 7.34−7.38 (3H, m), 7.00−7.08 (2H, m), 6.89 (1H, dd, J = 1.4, 7.3 Hz), 6.63 (1H, brs), 2.69 (3H, s), 1.47 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 140.6, 139.6, 137.1, 135.2, 133.0, 132.7, 129.2, 127.2, 126.9, 126.5, 125.1, 122.5, 34.5, 31.0, 20.5; MS (m/z) 326 (MNa^+); HRMS. Calcd for $C_{17}H_{21}NNaO_2S$ (MNa^+) 326.1191. Found: 326.1184.

*N-(2-(tert-Butyl)phenyl)-2,4,6-tri-methylbenzenesulfonamide (**1f**).* **1f** was prepared from 2,4,6-tri-methylbenzenesulfonyl chloride (722 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20) and subsequent MPLC (hexane/AcOEt = 20) gave **1f** (726 mg, 73%). **1f**: white solid; mp 114−116 °C; IR (neat) 3273, 1314, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (1H, dd, J = 1.8, 8.2 Hz), 6.99−7.08 (4H, m), 6.63 (1H, dd, J = 1.4, 7.8 Hz), 6.60 (1H, brs), 2.66 (6H, s), 2.34 (3H, s), 1.49 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 142.6, 141.4, 138.7, 136.0, 135.6, 132.2, 127.2, 126.9, 125.2, 122.8, 34.5, 31.0, 23.0, 21.0; MS (m/z) 354 (MNa^+); HRMS. Calcd for $C_{19}H_{25}NNaO_2S$ (MNa^+) 354.1504. Found: 354.1480.

*N-(2-(tert-Butyl)phenyl)naphthalene-1-sulfonamide (**1g**).* **1g** was prepared from nephthalen-1-sulfonyl chloride (748 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1g** (917 mg, 90%). **1g**: white solid; mp 153−155 °C; IR (neat) 3254, 1308, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (1H, d, J = 8.7 Hz), 8.34 (1H, dd, J = 1.4, 7.8 Hz), 8.10 (1H, d, J = 8.2 Hz), 7.96 (1H, d, J = 8.7 Hz), 7.55−7.68 (3H, m), 7.32 (1H, dd, J = 1.8, 7.8 Hz), 6.97−7.05 (2H, m), 6.93 (1H, dd, J = 1.8, 7.8 Hz), 6.80 (1H, brs), 1.42 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 140.9, 136.1, 135.1, 134.6, 134.3, 129.7, 129.1, 128.4, 128.0, 127.1, 127.0, 126.8, 125.3, 124.5, 124.2, 122.8, 34.5, 31.0; MS (m/z) 362 (MNa^+); HRMS. Calcd for $C_{20}H_{21}NNaO_2S$ (MNa^+) 362.1191. Found: 362.1179.

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*N-(2-(tert-Butyl)phenyl)methanesulfonamide (**1h**).* **1h** was prepared from methanesulfonyl chloride (378 mg, 3.3 mmol) and 2-*tert*-butylaniline (448 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **1h** (573 mg, 84%). **1h**: white solid; mp 114−116 °C; IR (neat) 3345, 1316, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (1H, dd, J = 1.4, 8.2 Hz), 7.41 (1H, dd, J = 1.8, 8.2 Hz), 7.24 (1H, dt, J = 1.4, 7.8 Hz), 7.13 (1H, dt, J = 1.4, 7.8 Hz), 6.52 (1H, brs), 3.07 (3H, s), 1.42 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 139.4, 135.2, 127.5, 127.3, 125.1, 121.3, 40.1, 34.3, 30.8; MS (m/z) 250 (MNa^+); HRMS. Calcd for $C_{11}H_{17}NNaO_2S$ (MNa^+) 250.0878. Found: 250.0905.

*N-(2-(tert-Butyl)phenyl)cyclohexanesulfonamide (**1i**).* Under N_2 atmosphere, to 2-*tert*-butylaniline (224 mg, 1.5 mmol) and triethylamine (2.5 mL, 18.0 mmol) in CH_2Cl_2 (0.8 mL) was added cyclohexanesulfonyl chloride (301 mg, 1.65 mmol) at 0 °C, and the reaction mixture was stirred for 48 h at rt. The mixture was poured into 2 N HCl and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave **1i** (226 mg, 51%). **1i**: white solid; mp 91−93 °C; IR (neat) 3439, 1327, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44 (1H, dd, J = 1.4, 8.2 Hz), 7.38 (1H, dd, J = 1.4, 7.8 Hz), 7.19 (1H, dt, J = 1.8, 7.8 Hz), 7.07 (1H, dt, J = 1.4, 7.8 Hz), 6.35 (1H, brs), 3.22 (1H, tt, J = 3.7, 11.9 Hz), 2.20−2.24 (2H, m), 1.88−1.92 (2H, m), 1.59−1.72 (3H, m), 1.46 (9H, s), 1.18−1.34 (3H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 138.4, 135.6, 127.02, 126.96, 124.0, 120.3, 61.7, 34.1, 30.6, 26.1, 24.9, 24.8; MS (m/z) 318 (MNa^+); HRMS. Calcd for $C_{16}H_{25}NNaO_2S$ (MNa^+) 318.1504. Found: 318.1520.

*N-(2,5-(Di-tert-butyl)phenyl)-4-methylbenzenesulfonamide (**3a**).* **3a** was prepared from 4-methylbenzenesulfonyl chloride (629 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30 and 3) gave **3a** (917 mg, 85%). **3a**: white solid; mp 163−166 °C; IR (neat) 3246, 1325, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.75 (2H, d, J = 8.2 Hz), 7.33 (1H, d, J = 2.3 Hz), 7.21−7.26 (3H, m), 7.05 (1H, dd, J = 2.3, 8.2 Hz), 6.61 (1H, brs), 2.39 (3H, s), 1.34 (9H, s), 1.20 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.8, 143.8, 137.5, 137.2, 134.5, 129.5, 127.6, 126.7, 121.9, 119.9, 34.2, 34.0, 31.01, 31.00, 21.5; MS (m/z) 382 (MNa^+); HRMS. Calcd for $C_{21}H_{29}NNaO_2S$ (MNa^+) 382.1817. Found: 382.1835.

*N-(2,5-(Di-tert-butyl)phenyl)benzenesulfonamide (**3b**).* **3b** was prepared from benzenesulfonyl chloride (583 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30 and 3) gave **3b** (974 mg, 94%). **3b**: white solid; mp 139−141 °C; IR (neat) 3244, 1325, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86−7.89 (2H, m), 7.56 (1H, tt, J = 0.9, 7.3 Hz), 7.45−7.7.50 (2H, m), 7.28 (1H, d, J = 2.3 Hz), 7.23 (1H, d, J = 8.3 Hz), 7.06 (1H, dd, J = 2.3, 8.2 Hz), 6.61 (1H, brs), 1.34 (9H, s), 1.12 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.9, 140.3, 137.9, 134.4, 133.0, 129.0, 127.5, 126.8, 122.2, 120.3, 34.2, 34.0, 31.0; MS (m/z) 368 (MNa^+); HRMS. Calcd for $C_{20}H_{27}NNaO_2S$ (MNa^+) 368.1660. Found: 368.1671.

*N-(2,5-(Di-tert-butyl)phenyl)-4-nitrobenzenesulfonamide (**3c**).* **3c** was prepared from 4-nitrobenzenesulfonyl chloride (731 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30 and 3) gave **3c** (1.13 g, 96%). **3c**: white solid; mp 171−173 °C; IR (neat) 3268, 1348, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.31 (2H, td, J = 2.3, 9.2 Hz), 8.01 (2H, td, J = 2.3, 9.2 Hz), 7.33 (1H, d, J = 2.3 Hz), 7.26 (1H, d, J = 8.2 Hz), 7.13 (1H, dd, J = 1.8, 8.2 Hz), 6.70 (1H, brs), 1.31 (9H, s), 1.22 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 150.2, 150.1, 145.8, 138.3, 133.5, 128.7, 127.2, 124.2, 123.1, 120.6, 34.3, 34.1, 31.1, 31.0; MS (m/z) 413 (MNa^+); HRMS. Calcd for $C_{20}H_{26}N_2NaO_4S$ (MNa^+) 413.1511. Found: 413.1532.

*N-(2,5-(Di-tert-butyl)phenyl)-4-methoxybenzenesulfonamide (**3d**).* **3d** was prepared from 4-methoxybenzenesulfonyl chloride (682 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30 and 3) gave **3d** (1.04 g, 92%). **3d**: white solid; mp 188−190 °C; IR (neat) 3248, 1319, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.79 (2H, td, J = 2.8, 9.2 Hz), 7.37 (1H, d, J = 2.3 Hz), 7.22 (1H, d, J = 8.2 Hz), 7.05 (1H, dd, J = 2.3, 8.2 Hz), 6.91 (2H, td, J = 2.8, 9.2 Hz), 6.61 (1H, brs), 3.09 (3H, s), 1.34 (9H, s), 1.22 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 163.1, 149.8, 137.3, 134.7, 131.6, 129.7, 126.7, 121.8, 119.7, 114.1, 55.6, 34.2, 33.9, 31.1, 31.0; MS (m/z) 398 (MNa^+); HRMS. Calcd for $C_{21}H_{29}NNaO_3S$ (MNa^+) 398.1766. Found: 398.1746.

*N-(2,5-(Di-tert-butyl)phenyl)-2-methylbenzenesulfonamide (**3e**).* **3e** was prepared from 2-methylbenzenesulfonyl chloride (315 mg, 1.65 mmol) and 2,5-di-*tert*-butylaniline (308 mg, 1.5 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30) and subsequent MPLC (hexane/AcOEt = 40) gave **3e** (626 mg, 58%). **3e**: white solid; mp 125−128 °C; IR (neat) 3337, 1314, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.10 (1H, dd, J = 1.4, 7.3 Hz), 7.51 (1H, t, J = 7.3 Hz), 7.35−7.39 (2H, m), 7.28 (1H, d, J = 8.7 Hz), 7.07 (1H, dd, J = 1.8, 8.2 Hz), 6.78 (1H, d, J = 1.8 Hz), 6.57 (1H, brs), 2.71 (3H, s), 1.47 (9H, s), 1.07 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.7, 139.6, 138.4, 137.1, 134.5, 133.0, 132.7, 129.8, 126.9, 126.4, 122.3, 120.6, 34.2, 34.0, 31.1, 30.9, 20.4; MS (m/z) 382 (MNa^+); HRMS. Calcd for $C_{21}H_{29}NNaO_2S$ (MNa^+) 382.1817. Found: 382.1813.

*N-(2,5-Di-(tert-butyl)phenyl)-2,4,6-tri-methylbenzenesulfonamide (**3f**).* **3f** was prepared from 2,4,6-tri-methylbenzenesulfonyl chloride (722 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 30) and subsequent MPLC (hexane/AcOEt = 30) gave **3f** (814 mg, 70%). **3f**: white solid; mp 125−129 °C; IR (neat) 3437, 1329, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 (1H, d, J = 8.2 Hz), 7.07 (1H, dd, J = 1.8, 8.2 Hz), 7.02 (2H, s), 6.53 (1H, d, J = 2.3 Hz), 6.52 (1H, s), 2.65 (6H, s), 2.33 (3H, s), 1.48 (9H, s), 1.04 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.7, 142.5, 139.2, 138.8, 136.1, 134.9, 132.2, 127.0, 122.5, 120.7, 34.3, 33.9, 31.2, 30.8, 23.0, 21.0; MS (m/z) 410 (MNa^+); HRMS. Calcd for $C_{23}H_{33}NNaO_2S$ (MNa^+) 410.2130. Found: 410.2157.

*N-(2,5-Di-(tert-butyl)phenyl)naphthalene-1-sulfonamide (**3g**).* **3g** was prepared from nephthalen-1-sulfonyl chloride (748 mg, 3.3 mmol) and 2-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **3g** (961 mg, 81%). **3g**: white solid; mp 172−175 °C; IR (neat) 3271, 1314, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.69 (1H, d, J = 9.2 Hz), 8.37 (1H, dd, J = 0.9, 7.3 Hz), 8.11 (1H, d, J = 8.2 Hz), 7.97 (1H, d, J = 7.3 Hz), 7.55−7.69 (3H, m), 7.23 (1H, d, J = 8.7 Hz), 7.02 (1H, dd, J = 2.3, 8.7 Hz), 6.77 (1H, d, J = 2.3 Hz), 6.71 (1H, brs), 1.43 (9H, s), 1.01 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.6, 138.8, 136.1, 134.6, 134.4, 134.3, 130.3, 129.2, 128.4, 128.1, 127.0, 126.9, 124.4, 124.2, 122.5, 120.8, 34.2, 34.0, 31.2, 30.9; MS (m/z) 418 (MNa^+); HRMS. Calcd for $C_{24}H_{29}NNaO_2S$ (MNa^+) 418.1817. Found: 418.1803.

*N-(2,5-(Di-tert-butyl)phenyl)methanesulfonamide (**3h**).* **3h** was prepared from methanesulfonyl chloride (378 mg, 3.3 mmol) and 2,5-di-*tert*-butylaniline (616 mg, 3.0 mmol) in accordance with the procedure for the synthesis of **1a**. Purification of the residue by column chromatography (hexane/AcOEt = 20 and 3) gave **3h** (740 mg, 87%). **3h**: white solid; mp 150−153 °C; IR (neat) 3314, 1316, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.62 (1H, d, J = 2.3 Hz), 7.32 (1H, d, J = 8.3 Hz), 7.14 (1H, dd, J = 2.3, 8.3 Hz), 6.48 (1H, brs), 3.04 (3H, s), 1.44 (9H, s), 1.31 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 150.6, 136.5, 134.8, 126.9, 122.0, 118.8, 39.8, 34.4, 33.9, 31.1, 30,9; MS (m/z) 306 (MNa^+); HRMS. Calcd for $C_{15}H_{25}NNaO_2S$ (MNa^+) 306.1504. Found: 306.1533.

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Catalytic Enantioselective *N*-Allylation of Sulfonamides (General Procedure). Under N_2 atmosphere, to sulfonamide **3a** (360 mg, 1.0 mmol) in THF (5.0 mL) was added NaH (60% assay 40.2 mg, 1.0 mmol) at 0 °C, and the reaction mixture was stirred for 20 min at −20 °C. The mixture of (allyl-Pd-Cl)$_2$ (8.1 mg, 0.022 mmol), (*S*,*S*)-Trost ligand (35 mg, 0.044 mmol), and allyl acetate (325 μL, 3.0 mmol) in THF (2.0 mL) was added to the reaction mixture at −20 °C, and the mixture was stirred for 3 h at −20 °C. The mixture was poured into 1 N HCl and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over $MgSO_4$, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **4a** (360 mg, 90%). The ee (78% ee) of **4a** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**4a** (major); t_R = 8.3 min, (−)-**4a** (minor); t_R = 12.8 min].

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)-4-methylbenzenesulfonamide (**4a**).* **4a**: white solid; mp 68−72 °C (78% ee), 78−81 °C (racemate); $[\alpha]_D^{25}$ = +22.3 (77% ee, c 0.74, $CHCl_3$); IR (neat) 1346, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (2H, d, *J* = 8.2 Hz), 7.48 (1H, d, *J* = 8.2 Hz), 7.30 (2H, d, *J* = 8.2 Hz), 7.25 (1H, m), 6.34 (1H, d, *J* = 2.3 Hz), 5.77 (1H, tdd, *J* = 6.9, 10.1, 17.4 Hz), 4.99−5.05 (2H, m), 4.15 (1H, dd, *J* = 6.9, 14.2 Hz), 4.07 (1H, dd, *J* = 6.9, 14.2 Hz), 2.46 (3H, s), 1.53 (9H, s), 1.09 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 148.4, 146.9, 143.4, 136.7, 136.0, 132.3, 130.0, 129.4, 128.8, 126.7, 125.3, 119.6, 56.0, 36.3, 33.9, 32.9, 30.8, 21.5; MS (*m*/*z*) 422 (MNa^+); HRMS. Calcd for $C_{24}H_{33}NNaO_2S$ (MNa^+) 422.2130. Found: 422.2122.

*N-Allyl-N-(2-(tert-butyl)phenyl)-4-methylbenzenesulfonamide (**2a**).* **2a** was prepared from sulfonamide **1a** (91 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **2a** (103 mg, quant). The ee (73% ee) of **2a** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate; 0.8 mL/min, (+)-**2a** (major); t_R = 7.3 min, (−)-**2a** (minor); t_R = 11.1 min]. **2a**: white solid; mp 100−102 °C (73% ee), 99−102 °C (racemate); $[\alpha]_D^{25}$ = +47.7 (70% ee, c 1.00, $CHCl_3$); IR (neat) 1339, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (2H, d, *J* = 8.2 Hz), 7.58 (1H, dd, *J* = 1.4, 7.8 Hz), 7.31 (2H, d, *J* = 8.2 Hz), 7.26 (1H, dd, *J* = 1.8, 8.6 Hz), 6.98 (1H, td, *J* = 1.3, 7.8 Hz), 6.41 (1H, dd, *J* = 1.4, 8.2 Hz), 5.78 (1H, m), 5.04 (1H, d, *J* = 10.5 Hz), 5.03 (1H, d, *J* = 17.0 Hz), 4.18 (1H, dd, *J* = 6.9, 14.2 Hz), 4.00 (1H, dd, *J* = 6.9, 14.2 Hz), 2.46 (3H, s), 1.54 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.3, 143.5, 137.3, 135.6, 132.1, 130.5, 129.5, 129.3, 128.8, 128.3, 125.8, 119.6, 55.9, 36.8, 33.0, 21.6; MS (*m*/*z*) 366 (MNa^+); HRMS. Calcd for $C_{20}H_{25}NNaO_2S$ (MNa^+) 366.1504. Found: 366.1504.

*N-Allyl-N-(2-(tert-butyl)phenyl)benzenesulfonamide (**2b**).* **2b** was prepared from sulfonamide **1b** (87 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **2b** (99 mg, quant). The ee (72% ee) of **2b** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**2b** (major); t_R = 6.8 min, (−)-**2b** (minor); t_R = 9.6 min]. **2b**: white solid; mp 68−71 °C (72% ee), colorless oil (racemate); $[\alpha]_D^{25}$ = +27.8 (72% ee, *c* 0.49, $CHCl_3$); IR (neat) 1343, 1161 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74−7.77 (2H, m), 7.57−7.65 (2H, m), 7.50−7.54 (2H, m), 7.26 (1H, dt, *J* = 1.4, 7.8 Hz), 6.97 (1H, dt, *J* = 1.4, 7.8 Hz), 6.38 (1H, dd, *J* = 1.4, 7.8 Hz), 5.77 (1H, m), 5.05 (1H, d, *J* = 11.0 Hz), 5.04 (1H, d, *J* = 16.0 Hz), 4.20 (1H, dd, *J* = 6.9, 14.2 Hz), 4.04 (1H, dd, *J* = 6.9, 14.2 Hz), 1.55 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.3, 138.5, 137.1, 132.8, 132.0, 130.6, 129.5, 128.8, 128.7, 128.4, 125.8, 119.8, 56.0, 36.8, 33.0; MS (*m*/*z*) 352 (MNa^+); HRMS. Calcd for $C_{19}H_{23}NNaO_2S$ (MNa^+) 352.1347. Found: 352.1366.

*N-Allyl-N-(2-(tert-butyl)phenyl)-4-nitrobenzenesulfonamide (**2c**).* **2c** was prepared from sulfonamide **1c** (100 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **2c** (104 mg, 93%). The ee (74% ee) of **2c** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**2c** (major); t_R = 9.8 min, (−)-**2c** (minor); t_R = 20.8 min]. **2c**: white solid; mp 103−106 °C (70% ee), 118−121 °C (racemate); $[\alpha]_D^{25}$ = +55.7 (70% ee, *c* 0.97, $CHCl_3$); IR (neat) 1346, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (2H, td, *J* = 2.3, 9.2 Hz), 7.92 (2H, td, *J* = 2.3, 9.2 Hz), 7.63 (1H, dd, *J* = 1.4, 7.8 Hz), 7.31 (1H, dt, *J* = 1.4, 7.3 Hz), 6.99 (1H, dt, *J* = 1.4, 7.8 Hz), 6.30 (1H, dd, *J* = 1.8, 8.2 Hz), 5.74 (1H, tdd, *J* = 6.9, 10.1, 17.0 Hz), 5.12 (1H, d, *J* = 17.0 Hz), 5.11 (1H, d, *J* = 10.1 Hz), 4.13−4.23 (2H, m), 1.48 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.3, 150.0, 144.6, 136.1, 131.2, 131.0, 130.0, 129.3, 128.9, 126.0, 123.9, 120.7, 56.3, 36.9, 32.9; MS (*m*/*z*) 397 (MNa^+); HRMS. Calcd for $C_{19}H_{22}N_2NaO_4S$ (MNa^+) 397.1198. Found: 397.1189.

*N-Allyl-N-(2-(tert-butyl)phenyl)-4-methoxybenzenesulfonamide (**2d**).* **2d** was prepared from sulfonamide **1d** (96 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 10) gave **2d** (99 mg, 92%). The ee (70% ee) of **2d** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**2d** (major); t_R = 11.0 min, (−)-**2d** (minor); t_R = 18.1 min]. **2d**: white solid; mp 78−82 °C (70% ee), 72.5−76 °C (racemate); $[\alpha]_D^{25}$ = +62.5 (70% ee, *c* 0.90, $CHCl_3$); IR (neat) 1339, 1155 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (2H, td, *J* = 2.3, 9.2 Hz), 7.58 (1H, dd, *J* = 1.4, 8.2 Hz), 7.25 (1H, m), 6.99 (1H, m), 6.98 (2H, dd, *J* = 2.3, 9.2 Hz), 6.44 (1H, dd, *J* = 1.4, 8.2 Hz), 5.79 (1H, tdd, *J* = 6.9, 10.0, 16.5 Hz), 5.04 (1H, d, *J* = 10.0 Hz), 5.03 (1H, d, *J* = 16.5 Hz), 4.17 (1H, dd, *J* = 6.9, 14.2 Hz), 3.99 (1H, dd, *J* = 6.9, 14.2 Hz), 3.90 (3H, s), 1.54 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 162.9, 150.3, 137.5, 132.2, 130.9, 130.4, 130.2, 129.4, 128.3, 125.8, 119.6, 113.8, 55.9, 55.6, 36.8, 33.0; MS (*m*/*z*) 382 (MNa^+); HRMS. Calcd for $C_{20}H_{25}NNaO_3S$ (MNa^+) 382.1453. Found: 382.1443.

*N-Allyl-N-(2-(tert-butyl)phenyl)-2-methylbenzenesulfonamide (**2e**).* **2e** was prepared from sulfonamide **1e** (91 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 10) gave **2e** (89 mg, 86%). The ee (86% ee) of **2e** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (−)-**2e** (major); t_R = 5.7 min, (+)-**2e** (minor); t_R = 7.0 min]. **2e**: white solid; mp 67−70 °C (86% ee), 53−56 °C (racemate); $[\alpha]_D^{25}$ = −12.7 (86% ee, c 0.87, $CHCl_3$); IR (neat) 1341, 1165 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (1H, dd, *J* = 1.4, 7.8 Hz), 7.58 (1H, dd, *J* = 1.8, 8.2 Hz), 7.47 (1H, dt, *J* = 1.4, 7.3 Hz), 7.35 (1H, t, *J* = 7.3 Hz), 7.23−7.27 (2H, m), 6.91 (1H, dt, *J* = 1.8, 7.3 Hz), 6.32 (1H, dd, *J* = 1.4, 8.2 Hz), 5.79 (1H, m), 5.05 (1H, d, *J* = 11.0 Hz), 5.04 (1H, d, *J* = 16.5 Hz), 4.31 (1H, dd, *J* = 6.9, 14.2 Hz), 4.04 (1H, dd, *J* = 7.3, 14.2 Hz), 2.14 (3H, s), 1.54 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.5, 138.8, 136.8, 136.3, 132.8, 132.7, 132.1, 130.7, 130.6, 129.7, 128.2, 126.2, 125.6, 119.8, 56.0, 36.9, 33.0, 21.6; MS (*m*/*z*) 366 (MNa^+); HRMS. Calcd for $C_{20}H_{25}NNaO_2S$ (MNa^+) 366.1504. Found: 366.1510.

*N-Allyl-N-(2-(tert-butyl)phenyl)-2,4,6-trimethylbenzenesulfonamide (**2f**).* **2f** was prepared from sulfonamide **1f** (99 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **2f** (86 mg, 77%). The ee (91% ee) of **2f** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 3% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**2f** (major); t_R = 5.1 min, (−)-**2f** (minor); t_R = 6.8 min]. **2f**: white solid; mp 141−145 °C (90% ee), 140−143 °C (racemate); $[\alpha]_D^{25}$ = +27.2 (90% ee, *c* 0.67, $CHCl_3$); IR (neat) 1339, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (1H, dd, *J* = 1.4, 8.2 Hz), 7.23 (1H, m), 6.89−6.93 (3H, m), 6.49 (1H, dd, *J* = 1.4, 8.2 Hz), 5.80 (1H, tdd, *J* = 7.0, 10.0, 17.0 Hz), 5.04 (1H, d, *J* = 10.0 Hz), 5.01 (1H, d, *J* = 17.0 Hz), 4.38 (1H, dd, *J* = 7.3 13.7 Hz), 4.20 (1H, dd, *J* = 6.9, 13.7 Hz), 2.30 (3H, s), 2.26 (6H, s), 1.49 (9H, s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.5, 142.0, 140.0, 135.9, 133.3, 132.6, 132.3, 131.1, 130.7, 128.1, 125.5, 119.8, 55.8, 37.0, 33.0, 24.1, 20.9; MS (*m*/*z*) 394 (MNa^+); HRMS. Calcd for $C_{22}H_{29}NNaO_2S$ (MNa^+) 394.1817. Found: 394.1828.

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*N-Allyl-N-(2-(tert-butyl)phenyl)naphthalene-1-sulfonamide (**2g**).* **2g** was prepared from sulfonamide **1g** (102 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **2g** (105 mg, 92%). The ee (88% ee) of **2g** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (−)-**2g** (major); t_R = 10.2 min, (+)-**2g** (minor); t_R = 11.2 min]. **2g**: white solid; mp 141.5−144 °C (88% ee), 138−140 °C (racemate); $[\alpha]_D^{25}$ = −33.8 (88% ee, c 0.45, $CHCl_3$); IR (neat) 1335, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.50 (1H, d, *J* = 8.2 Hz), 8.14 (1H, dd, *J* = 0.9, 7.3 Hz), 8.10 (1H, d, *J* = 8.2 Hz), 7.91 (1H, d, *J* = 7.8 Hz), 7.52−7.60 (3H, m), 7.42 (1H, m), 7.20 (1H, m), 6.68 (1H, td, *J* = 1.4, 7.8 Hz), 6.11 (1H, dd *J* = 1.4, 7.8 Hz), 5.66 (1H, tdd, *J* = 6.9, 10.5, 17.0 Hz), 4.96 (1H, d, *J* = 10.5 Hz), 4.95 (1H, d, *J* = 17.0 Hz), 4.32 (1H, dd, *J* = 6.9, 14.2 Hz), 4.10 (1H, dd, *J* = 6.9, 14.2 Hz), 1.58 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 150.6, 136.1, 134.6, 134.4, 134.3, 132.1, 131.4, 130.9, 130.5, 129.4, 128.5, 128.3, 127.6, 126.7, 126.4, 125.4, 124.1, 119.8, 55.7, 36.9, 33.1; MS (*m*/*z*) 402 (MNa^+); HRMS. Calcd for $C_{23}H_{25}NNaO_2S$ (MNa^+) 402.1504. Found: 402.1496.

*N-Allyl-N-(2-(tert-butyl)phenyl)methanesulfonamide (**2h**).* **2h** was prepared from sulfonamide **1h** (68 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 5) gave **2h** (69 mg, 86%). The ee (49% ee) of **2h** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 15% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (−)-**2h** (major); t_R = 8.8 min, (+)-**2h** (minor); t_R = 10.4 min]. **2h**: colorless oil; $[\alpha]_D^{25}$ = −9.4 (35% ee, *c* 1.08, $CHCl_3$); IR (neat) 1333, 1153 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (1H, dd, *J* = 1.4, 8.2 Hz), 7.32 (1H, dt, *J* = 1.8, 7.3 Hz), 7.20 (1H, dt, *J* = 1.8, 7.8 Hz), 7.14 (1H, dd, *J* = 1.8, 8.2 Hz), 6.05 (1H, tdd, *J* = 7.3, 10.1, 17.0 Hz), 5.29 (1H, dd, *J* = 1.4, 17.0 Hz), 5.27 (1H, d, *J* = 10.1 Hz), 4.31 (1H, dd, *J* = 7.8, 14.7 Hz), 4.02 (1H, dd, *J* = 6.4, 14.7 Hz), 3.04 (3H, s), 1.49 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.5, 137.5, 131.8, 130.5, 130.1, 128.7, 126.5, 120.8, 56.2, 39.8, 36.4, 32.5; MS (*m*/*z*) 290 (MNa^+); HRMS. Calcd for $C_{14}H_{21}NNaO_2S$ (MNa^+) 290.1191. Found: 290.1194.

*N-Allyl-N-(2-(tert-butyl)phenyl)cyclohexanesulfonamide (**2i**).* **2i** was prepared from sulfonamide **1i** (87 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave **2i** (101 mg, quant). The ee (66% ee) of **2i** was determined by HPLC using Chiralcel OD-3 column [25 cm × 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.5 mL/min; (−)-**2i** (minor); t_R = 33.7 min, (+)-**2i** (major); t_R = 33.7 min]. **2i**: white solid; mp 83−86 °C (66% ee), colorless oil (racemate); $[\alpha]_D^{25}$ = +32.6 (35% ee, *c* 1.91, $CHCl_3$); IR (neat) 1325, 1138 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59 (1H, dd, *J* = 1.8, 8.2 Hz), 7.29 (1H, m), 7.19 (1H, dt, *J* = 1.8, 7.8 Hz), 7.11 (1H, dd, *J* = 1.4, 7.8 Hz), 5.92 (1H, tdd, *J* = 6.9, 10.1, 17.0 Hz), 5.12 (1H, d, *J* = 10.1 Hz), 5.11 (1H, dd, *J* = 1.4, 17.0 Hz), 4.32 (1H, dd, *J* = 7.3, 14.2 Hz), 4.20 (1H, dd, *J* = 6.9, 14.2 Hz), 3.17 (1H, tt, *J* = 3.7, 11.9 Hz), 2.33 (1H, d, *J* = 12.8 Hz), 2.18 (1H, d, *J* = 12.8 Hz), 1.85−1.95 (2H, m), 1.57−1.74 (3H, m), 1.50 (9H, s), 1.24−1.40 (3H, m); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 150.3, 136.4, 132.8, 131.4, 131.0, 128.4, 126.3, 119.9, 61.6, 56.8, 36.8, 32.6, 27.1, 27.0, 25.4, 25.3, 25.1; MS (*m*/*z*) 358 (MNa^+); HRMS. Calcd for $C_{19}H_{29}NNaO_2S$ (MNa^+) 358.1817. Found: 358.1823.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)benzenesulfonamide (**4b**).* **4b** was prepared from sulfonamide **3b** (104 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **4b** (94 mg, 81%). The ee (78% ee) of **4b** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**4b** (major); t_R = 6.9 min, (−)-**4b** (minor); t_R = 8.8 min]. **4b**: white solid; mp 80−82 °C (78% ee), 63−66 °C (racemate); $[\alpha]_D^{25}$ = +7.1 (71% ee, *c* 0.98, $CHCl_3$,); IR (neat) 1341, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.76 (2H, d, *J* = 7.3 Hz), 7.62 (1H, t, *J* = 7.3 Hz), 7.48−7.53 (3H, m), 7.26 (1H, dd, *J* = 1.8, 8.7 Hz), 6.31 (1H, d, *J* = 1.8 Hz), 5.76 (1H, tdd, *J* = 6.9, 10.0, 17.0 Hz), 5.04 (1H, d, *J* = 10.0 Hz), 5.03 (1H, d, *J* = 17.0 Hz), 4.17 (1H, dd, *J* = 6.9, 14.2 Hz), 4.10 (1H, dd, *J* = 6.9, 14.2 Hz), 1.53 (9H, s), 1.08 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 148.4, 146.9, 139.0, 136.5, 132.6, 132.1, 130.1, 128.8, 126.6, 125.4, 119.7, 56.1, 36.3, 33.9, 32.9, 30.9; MS (*m*/*z*) 408 (MNa^+); HRMS. Calcd for $C_{23}H_{31}NNaO_2S$ (MNa^+) 408.1973. Found: 408.1971.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)-4-nitrobenzenesulfonamide (**4c**).* **4c** was prepared from sulfonamide **3c** (117 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **4c** (130 mg, quant). The ee (77% ee) of **4c** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**4c** (major); t_R = 8.8 min, (−)-**4c** (minor); t_R = 12.8 min]. **4c**: white solid; mp 87−90 °C (racemate), colorless oil (77% ee); $[\alpha]_D^{25}$ = +22.7 (78% ee, *c* 0.45, $CHCl_3$); IR (neat) 1344, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.35 (2H, td, *J* = 2.3, 9.2 Hz), 7.95 (2H, td, *J* = 2.3, 9.2 Hz), 7.53 (1H, d, *J* = 8.2 Hz), 7.30 (1H, dd, *J* = 2.3, 8.2 Hz), 6.27 (1H, d, *J* = 2.3 Hz), 5.73 (1H, tdd, *J* = 6.9, 10.1, 17.0 Hz), 5.08−5.14 (2H, m), 4.26 (1H, dd, *J* = 7.3, 14.7 Hz), 4.14 (1H, dd, *J* = 6.9, 14.7 Hz), 1.53 (9H, s), 1.09 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.9, 148.7, 146.9, 145.2, 135.6, 131.1, 130.7, 130.0, 126.6, 125.9, 123.9, 120.7, 56.3, 36.4, 34.0, 32.8, 30.8; MS (*m*/*z*) 453 (MNa^+); HRMS. Calcd for $C_{23}H_{30}N_2NaO_4S$ (MNa^+) 453.1824. Found: 453.1832.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)-4-methoxybenzenesulfonamide (**4d**).* **4d** was prepared from sulfonamide **3d** (113 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 10) gave **4d** (118 mg, 95%). The ee (74% ee) of **4d** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**4d** (major); t_R = 11.2 min, (−)-**4d** (minor); t_R = 19.0 min]. **4d**: colorless oil (74% ee), colorless oil (racemate); $[\alpha]_D^{25}$ = +26.5 (76% ee, *c* 1.20, $CHCl_3$); IR (neat) 1341, 1148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.69 (2H, td, *J* = 2.7, 8.7 Hz), 7.49 (1H, d, *J* = 8.7 Hz), 7.25 (1H, dd, *J* = 2.3, 8.7 Hz), 6.98 (2H, td, *J* = 2.7, 8.7 Hz), 6.39 (1H, d, *J* = 2.3 Hz), 5.77 (1H, tdd, *J* = 6.9, 10.0, 17.0 Hz), 5.00−5.05 (2H, m), 4.14 (1H, dd, *J* = 6.9, 14.2 Hz), 4.06 (1H, dd, *J* = 7.3, 14.2 Hz), 3.89 (3H, s), 1.53 (9H, s), 1.11 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.8, 148.4, 146.9, 136.9, 132.3, 130.9, 130.8, 130.0, 126.6, 125.3, 119.5, 113.9, 56.0, 55.6, 36.3, 33.9, 32.9, 30.9; MS (*m*/*z*) 438 (MNa^+); HRMS. Calcd for $C_{24}H_{33}NNaO_3S$ (MNa^+) 438.2079. Found: 438.2058.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)-2-methylbenzenesulfonamide (**4e**).* **4e** was prepared from sulfonamide **3e** (108 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **4e** (101 mg, 84%). The ee (89% ee) of **4e** was determined by HPLC using Chiralcel OD-3 column [25 cm × 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (−)-**4e** (minor); t_R = 11.2 min, (+)-**4e** (major); t_R = 12.8 min]. **4e**: white solid; mp 66−69 °C (89% ee), 77−80 °C (racemate); $[\alpha]_D^{25}$ = +36.4 (90% ee, *c* 0.59, $CHCl_3$); IR (neat) 1339, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.89 (1H, dd, *J* = 1.4, 7.8 Hz), 7.49 (1H, d, *J* = 8.2 Hz), 7.46 (1H, dt, *J* = 1.4, 7.3 Hz), 7.36 (1H, t, *J* = 7.3 Hz), 7.20−7.25 (2H, m), 6.23 (1H, d, *J* = 2.3 Hz), 5.79 (1H, m), 5.00−5.05 (2H, m), 4.29 (1H, dd, *J* = 6.9, 14.2 Hz), 4.10 (1H, dd, *J* = 6.9, 14.2 Hz), 2.08 (3H, s), 1.53 (9H, s), 1.03 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 148.2, 147.1, 138.7, 137.2, 135.6, 133.0, 132.5, 132.3, 130.42, 130.35, 126.6, 126.4, 125.4, 119.7, 56.2, 36.5, 33.8, 33.0, 30.7, 21.9; MS (*m*/*z*) 422 (MNa^+); HRMS. Calcd for $C_{24}H_{33}NNaO_2S$ (MNa^+) 422.2130. Found: 422.2118.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)-2,4,6-trimethylbenzenesulfonamide (**4f**).* **4f** was prepared from sulfonamide **3f** (116 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **4f** (94 mg, 73%). The ee (95% ee) of **4f** was determined by HPLC using Chiralcel OD-3 column [25 cm × 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (+)-**4f** (minor); t_R = 8.5 min, (−)-**4f** (major); t_R = 8.9 min]. **4f**: white solid; mp 108−111 °C (93% ee), 98−100.5 °C (racemate); $[\alpha]_D^{25}$ = −5.91 (93% ee, *c* 0.46, $CHCl_3$); IR (neat) 1337, 1165 cm^{-1}; ^1H NMR (400 MHz,

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$CDCl_3$) δ: 7.47 (1H, d, J = 8.7 Hz), 7.23 (1H, dd, J = 2.3, 8.2 Hz), 6.90 (2H, s), 6.34 (1H, d, J = 2.3 Hz), 5.77 (1H, tdd, J = 6.8, 10.1, 17.0 Hz), 5.02 (1H, dd, J = 1.3, 10.1 Hz), 4.98 (1H, dd, J = 1.3, 17.0 Hz), 4.37 (1H, dd, J = 7.3 13.7 Hz), 4.22 (1H, dd, J = 6.4, 13.7 Hz), 2.29 (3H, s), 2.25 (6H, s), 1.48 (9H, s), 1.04 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 148.0, 147.1, 141.8, 139.8, 135.0, 133.6, 132.8, 132.4, 130.4, 127.8, 125.3, 119.6, 55.9, 36.6, 33.7, 32.9, 30.6, 24.3, 20.8; MS (m/z) 450 (MNa^+); HRMS. Calcd for $C_{26}H_{37}NNaO_2S$ (MNa^+) 450.2443. Found: 450.2444.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)naphthalene-1-sulfonamide (**4g**).* **4g** was prepared from sulfonamide **3g** (119 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **4g** (131 mg, quant). The ee (91% ee) of **4g** was determined by HPLC using Chiralcel OD-3 column [25 cm × 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate; 0.8 mL/min, (+)-**4g** (minor); t_R = 13.1 min, (−)-**4g** (major); t_R = 16.9 min]. **4g**: white solid; mp 145.5−147 °C (91% ee), 144−147 °C (racemate); $[\alpha]_D^{25}$ = −96.4 (91% ee, c 0.51, $CHCl_3$); IR (neat) 1339, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, d, J = 8.2 Hz), 8.17 (1H, dd, J = 0.9, 7.3 Hz), 8.09 (1H, d, J = 8.2 Hz), 7.90 (1H, d, J = 8.2 Hz), 7.49−7.57 (3H, m), 7.40 (1H, m), 7.18 (1H, dd, J = 2.3, 8.7 Hz), 6.02 (1H, d, J = 2.3 Hz), 5.68 (1H, tdd, J = 6.9, 10.1, 17.0 Hz), 4.96 (1H, d, J = 10.1 Hz), 4.95 (1H, d, J = 17.0 Hz), 4.33 (1H, dd, J = 7.3, 14.2 Hz), 4.18 (1H, dd, J = 6.9, 14.2 Hz), 1.58 (9H, s), 0.74 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 148.0, 147.1, 135.3, 135.0, 134.2, 132.3, 131.1, 130.2, 129.6, 128.5, 127.9, 127.3, 126.6, 126.2, 125.5, 124.2, 119.7, 56.0, 36.5, 33.5, 33.0, 30.4; MS (m/z) 458 (MNa^+); HRMS. Calcd for $C_{27}H_{33}NNaO_2S$ (MNa^+) 458.2130. Found: 458.2130.

*N-Allyl-N-(2,5-(di-tert-butyl)phenyl)methanesulfonamide (**4h**).* **4h** was prepared from sulfonamide **3h** (85 mg, 0.3 mmol) in accordance with the procedure for the synthesis of **4a**. Purification of the residue by column chromatography (hexane/AcOEt = 10) gave **4h** (91 mg, 94%). The ee (59% ee) of **4h** was determined by HPLC using Chiralpak AS-H column [25 cm × 0.46 cm i.d.; 5% *i*-PrOH in hexane; flow rate, 0.8 mL/min; (−)-**4h** (major); t_R = 6.9 min, (+)-**4h** (minor); t_R = 8.7 min]. **4h**: white solid; mp 70−72 °C (58% ee), 91−93 °C (racemate); $[\alpha]_D^{25}$ = −15.5 (58% ee, *c* 1.00, $CHCl_3$); IR (neat) 1323, 1140 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50 (1H, d, J = 8.2 Hz), 7.32 (1H, dd, J = 2.3, 8.7 Hz), 7.08 (1H, d, J = 2.3 Hz), 6.06 (1H, m), 5.29 (1H, d, J = 11.0 Hz), 5.29 (1H, d, J = 15.6 Hz), 4.36 (1H, dd, J = 7.8, 14.7 Hz), 3.96 (1H, dd, J = 6.9, 14.7 Hz), 3.04 (3H, s), 1.47 (9H, s), 1.30 (9H, s); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 149.3, 146.3, 137.0, 132.0, 130.2, 127.3, 125.7, 121.0, 56.3, 40.0, 36.1, 34.1, 32.5, 31.1; MS (m/z) 346 (MNa^+); HRMS. Calcd for $C_{18}H_{29}NNaO_2S$ (MNa^+) 346.1817. Found: 346.1816.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00989.

Copies of ^1H and ^{13}C NMR spectra for all new compounds **1**−**4**; chiral HPLC chart of compounds **2** and **4**; X-ray crystal data of compound **4f**; and data for the evaluation of the rotational barriers in **4f** and **4h** (PDF)

Crystallographic data of **4f** (CIF)

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Notes

The authors declare no competing financial interest.

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(13) The complete racemization of **4f** (90% ee) was observed after heating for 1 h at 80 °C in CCl_4.

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