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# Chiral Binaphthylthiophosphoramide−Cu(I)-Catalyzed Asymmetric Addition of Diethylzinc to *N*-Sulfonylimines

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*Received March 1, 2003*

In the presence of a catalytic amount of chiral binaphthylthiophosphoramide **L2** (6 mol %) and Cu(I) (3 mol %), the asymmetric addition of diethylzinc to *N*-sulfonylimines could be achieved in good yields with moderate to high ee (63−93% ee) at 0 °C in toluene. A novel chiral binaphthylthiophosphoramide ligand system for this asymmetric addition reaction has been explored.

Efficient and catalytic asymmetric preparation of amines is one of the most promising methodologies in homogeneous catalysis.[1] Enantioselective addition of organometallic reagents to C═N of imines is a convenient route to obtain optically active amines.[2] This approach has especially been used in chiral amine ligand-catalyzed asymmetric addition of alkyllithium;[3] chiral amino alcohol ligands,[4] copper-amidophosphines,[5] and Zr-peptide-based chiral ligand-catalyzed asymmetric addition of organozinc;[6] chiral allylpalladium-catalyzed allylation by allylstannane;[7] and rhodium-monophosphine-catalyzed arylation by arylstannane[8] with very good enantioselectivities. Recently, we have been interested in the syntheses and applications of novel ligands based on the axially chiral binaphthalenediamine (BINAM).[9] In the field of catalytic asymmetric synthesis, BINAM has been much less popular than the widely used other axially chiral binaphthalene skeletons such as BINOL and NOBIN or other chiral diamines such as 1,2-cyclohexanediamine and 1,2-diphenylethenediamine.[10] Herein, we wish to report the synthesis of novel axially chiral binaphthylthiophosphoramide ligands **L1**-**L7** and the results of our studies on catalytic enantioselective addition of diethylzinc to *N*-sulfonylimines.

## Results and Discussion

These chiral ligands **L1**−**7** are easily obtained from (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine.[11] The procedures for the preparation of the ligands are outlined in Scheme 1. They can be easily synthesized through lithiation of the relevant diamine with butyllithium and then phosphorylation with dialkylthiophosphoryl chloride. In addition, they are quite stable and can be easily recovered from the reaction mixture in 85% yield through column chromatography after the usual workup and can be reused in this asymmetric reaction without loss of enantioselectivity.

Using *N*-(*p*-fluorobenzylidene)-*p*-methylbenzenesulfonamide (*N*-sulfonylimine) **5j** as the substrate and diethylzinc as the nucleophilic addition reagent, we examined this asymmetric addition in toluene under various reaction conditions to develop the optimal reaction conditions. The results are summarized in Table 1.

In an early study, an examination of the temperature profile of $Cu(CH_3CN)_4BF_4$/**L4**-catalyzed asymmetric addition of diethylzinc to *N*-sulfonylimines was performed. We found that the reaction temperature had a great influence on the yield and enantioselectivity of the addition product **6j**. At room temperature, the reaction

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(1) Federsel, H.-J.; Collins, A. N.; Sheldrake, G. N.; Crosby, J. *Chirality in Industry II*; John Wiley & Sons: Chichester, UK, 1997; pp 225−244.

(2) For a review on catalytic asymmetric additions to imines, see: Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069−1094.

(3) (a) Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C. *J. Am. Chem. Soc.* **1994**, *116*, 8797−8798. (b) Denmark, S. E.; Stiff, C. M. *J. Org. Chem.* **2000**, *65*, 5875−5878. (c) Tomioka, K.; Inoue, I.; Shindo, M.; Koga, K. *Tetrahedron Lett.* **1991**, *32*, 3095−3098.

(4) (a) Soai, K.; Hatanaka, T.; Miyazawa, T.; *J. Chem. Soc., Chem. Commun.* **1992**, 1097−1098. (b) Andersson, P. G.; Guijarro, D.; Tanner, D. *J. Org. Chem.* **1997**, *62*, 7364−7375. (c) Brandt, P.; Hedberg, C.; Lawonn, K.; Pinho, P.; Andersson, P. G. *Chem. Eur. J.* **1999**, *5*, 1692−1699. (d) Jimeno, C.; Reddy, K. S.; Sola, L.; Moyano, A.; Pericas, M. A.; Riera, A. *Org. Lett.* **2000**, *2*, 3157−3159. (e) Frantz, D. E.; Fassler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **1999**, *121*, 11245−11246. (f) Dahmen, S.; Bräse, S. *J. Am. Chem. Soc.* **2002**, *124*, 5940−5941.

(5) (a) Fujihara, H.; Nagai, K.; Tomika, K. *J. Am. Chem. Soc.* **2000**, *122*, 12055−12056. (b) Boezio, A. A.; Charette, A. B. *J. Am. Chem. Soc.* **2003**, *125*, 1692−1693.

(6) (a) Porter, J. R.; Traverse, J. F.; Hoveyda, A. H.; Snapper, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 984−985 and 10409−10410. (b) Wipf, P.; Kendall, C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2001**, *123*, 5122−5123. (c) Wei, C.-M.; Li, C.-J. *J. Am. Chem. Soc.* **2002**, *124*, 5638−5939.

(7) (a) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242−4243. (b) Bao, M.; Nakamura, H.; Yamaoto, Y. *Tetrahedron Lett.* **2000**, *41*, 131−134.

(8) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976−977.

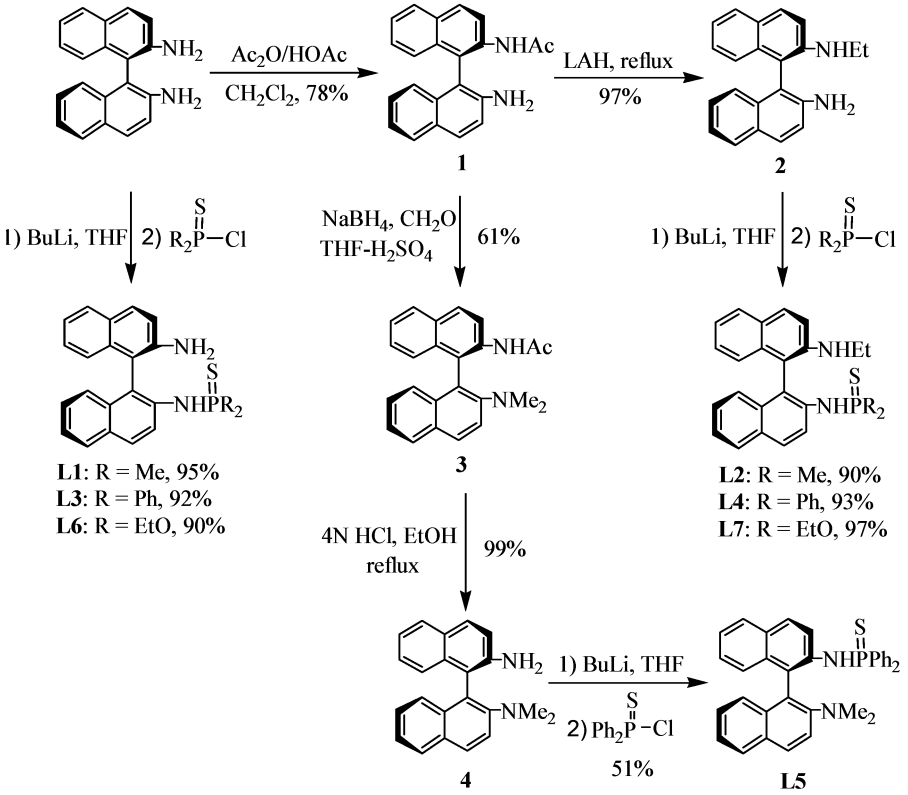
(9) (a) Shi, M.; Sui, W. S. *Chiraliy* **2000**, *12*, 574−580. (b) Shi, M.; Sui, W. S. *Tetrahedron: Asymmetry* **2000**, *11*, 773−779. (c) Shi, M.; Sui, W. S. *Tetrahedron: Asymmetry* **2000**, *11*, 835−841. (d) Shi, M.; Sui, W. S. *Tetrahedron: Asymmetry* **1999**, *10*, 3319−3325.

(10) (a) Ojima, I. Ed. *Catalytic Asymmetric Synthesis*; VCH Publications: New York, 1993. (b) Jacobsen, E. N.; Pfaltz, A., Yamamoto, H., Eds.; *Comprehensive Asymmetric Catalysis*; Springer-Verlag: Heidelberg, 2001.

(11) Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2171−2176.

10.1021/jo034269n CCC: $25.00 
Published on Web 07/03/2003

**SCHEME 1. Preparation of Chiral Binaphthylthiophosphoramide Ligands**



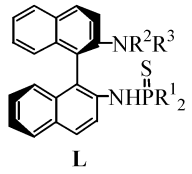

was quickly completed within 1 h. However, the desired ethylation product **6j** was given in 59% yield (61% ee) along with the corresponding byproduct in 39% yield (Table 1, entry 1). Lowering the reaction temperature to 0 °C diminished the yield of the byproduct to 4%, and the yield of the addition product **6j** was increased to 90% with 79% ee (Table 1, entry 2). When the reaction was carried out at −20 °C, the byproduct was not detected, but the reaction was sluggish and the achieved ee of **6j** was remarkably reduced to 55% (Table 1, entry 3). Thus, the best reaction temperature is 0 °C. The catalytic activity of $Cu(CH_3CN)_4BF_4$ was higher than that of other copper salts such as $Cu(CH_3CN)_4ClO_4$, $CuOTf{\cdot}1/2C_6H_6$, and $Cu(OTf)_2$ (Table 1, entries 2 and 10−12). The counterion effect has been checked by use of CuOTf and $CuBF_4$ freshly prepared in situ via the reaction of CuBr with AgOTf and $AgBF_4$, respectively, in the same catalytic asymmetric addition reaction.[12] As a result, we found that the obtained yield and ee of the addition product **6j** were the same as those of $CuOTf{\cdot}1/2\ C_6H_6$ and $Cu(CH_3CN)_4BF_4$. This result suggested that the slight differences caused by $Cu(CH_3CN)_4BF_4$, $Cu(CH_3CN)_4ClO_4$, and $CuOTf{\cdot}1/2C_6H_6$ were due to the counterion effect and had no relation to the nature of copper. By screening chiral ligands **L1**−**7**, we found that **L2** was the best chiral ligand for this enantioselective addition reaction, which gave the addition product in 90% ee and 96% yield at 0 °C (Table 1, entry 5). It should be noted that chiral ligand **L5**, having an *N*,*N*-dimethyl group, gave the addition product **6j** in 33% ee under the same conditions (Table 1, entry 7), and N-unsubstituted chiral ligands such as **L1**, **L3**, and **L6** gave the addition product **6j** only in moderate ee as well (Table 1, entries 4, 6, and 8). These results suggested that the substituent on the amino group in the binaphthyl structure played a very important role in chiral induction in this asymmetric addition reaction. We also found that the yield and enantioselectivity of the desired product were not affected by the sequence of addition of diethylzinc and substrate to the solution of the Cu/ligand mixture (Table 1, entries 5 and 13−15). The recovered **L2** gave the addition product in similar yield and enantioselectivity (Table 1, entry 16). Using **L2** as a chiral ligand, we examined the solvent effect as well. We found that toluene is the best solvent for this asymmetric reaction (Table 1, entries 5 and 17−19). In addition, the reaction was also completed within 8 h with a slightly decreased yield and ee using 1.5 mol % copper salt and 3 mol % ligand (Table 1, entry 20). The best reaction conditions used $Cu(CH_3CN)_4BF_4$ (3 mol %) as a precursor and **L2** (6 mol %) as chiral ligand in toluene at 0 °C.

We next examined the asymmetric addition reaction of diethylzinc to a variety of *N*-sulfonylimines **5** under the optimized reaction conditions. The results are summarized in Table 2.

As can be seen from Table 2, high yields and good enantioselectivities could be achieved for various aromatic *N*-sulfonylimines **5** having either electron-donating groups or electron-withdrawing groups on the benzene ring (Table 2, entries 1−12). These results are comparable with the best literature value hitherto reported for

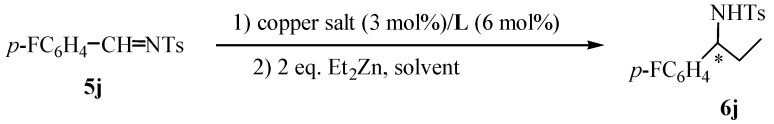
(12) Evans previously pointed out that highly electronegative counterions are a design prerequisite for efficient asymmetric catalysis. (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328−5329. (b) Evans, D. A.; Woerpel, K.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726−728.

**TABLE 1. Asymmetric Addition Reaction of Diethylzinc to *N*-Sulfonylimine 5j Catalyzed by Copper Salt and Chiral Ligands L1−7**




**L**

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **L1** | Me | H | H |
| **L2** | Me | H | Et |
| **L3** | Ph | H | H |
| **L4** | Ph | H | Et |
| **L5** | Ph | Me | Me |
| **L6** | OEt | H | H |
| **L7** | OEt | H | Et |




| entry | copper salt | ligand | solvent | temp (°C) | time (h) | yield[a] (%) | ee[b] (%) |
|---|---|---|---|---|---|---|---|
| 1 | $Cu(MeCN)_4BF_4$ | **L4** | $PhCH_3$ | 20 | 1 | 59 | 61[c] |
| 2 | $Cu(MeCN)_4BF_4$ | **L4** | $PhCH_3$ | 0 | 8 | 90 | 79 |
| 3 | $Cu(MeCN)_4BF_4$ | **L4** | $PhCH_3$ | −20 | 40 | 68 | 55 |
| 4 | $Cu(MeCN)_4BF_4$ | **L1** | $PhCH_3$ | 0 | 8 | 85 | 63 |
| 5 | $Cu(MeCN)_4BF_4$ | **L2** | $PhCH_3$ | 0 | 8 | 96 | 90 |
| 6 | $Cu(MeCN)_4BF_4$ | **L3** | $PhCH_3$ | 0 | 8 | 33 | 61 |
| 7 | $Cu(MeCN)_4BF_4$ | **L5** | $PhCH_3$ | 0 | 8 | 64 | 33 |
| 8 | $Cu(MeCN)_4BF_4$ | **L6** | $PhCH_3$ | 0 | 8 | 77 | 16 |
| 9 | $Cu(MeCN)_4BF_4$ | **L7** | $PhCH_3$ | 0 | 8 | 80 | 34 |
| 10 | $Cu(MeCN)_4ClO_4$ | **L4** | $PhCH_3$ | 0 | 8 | 92 | 65 |
| 11 | $CuOTf·1/2C_6H_6$ | **L4** | $PhCH_3$ | 0 | 8 | 88 | 71 |
| 12 | $Cu(OTf)_2$ | **L4** | $PhCH_3$ | 0 | 8 | 90 | 71 |
| 13 | $Cu(OTf)_2$ | **L2** | $PhCH_3$ | 0 | 8 | 96 | 88 |
| 14[d] | $Cu(OTf)_2$ | **L2** | $PhCH_3$ | 0 | 8 | 92 | 87 |
| 15[d] | $Cu(MeCN)_4BF_4$ | **L2** | $PhCH_3$ | 0 | 8 | 95 | 86 |
| 16[d] | $Cu(MeCN)_4BF_4$ | **L2** | $PhCH_3$ | 0 | 8 | 94 | 89 |
| 17[e] | $Cu(MeCN)_4BF_4$ | **L2** | $Et_2O$ | 0 | 8 | 65 | 84 |
| 18 | $Cu(MeCN)_4BF_4$ | **L2** | THF | 0 | 8 | 71 | 83 |
| 19 | $Cu(MeCN)_4BF_4$ | **L2** | $CH_2Cl_2$ | 0 | 8 | trace | |
| 20[f] | $Cu(MeCN)_4BF_4$ | **L2** | $PhCH_3$ | 0 | 8 | 92 | 86 |

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Byproduct was also isolated to 39% yield. [d] Treatment of a solution of Cu salt and ligand with $Et_2Zn$, followed by addition of sulfonylimine into the reaction solution. [e] Recovered **L2** was used. [f] Used 1.5 mol % copper salt and 3 mol % ligand.

the asymmetric addition of diethylzinc to *N*-sulfonylimines.[5a] For the methanesulfonylimine **5m** and 2-trimethylsilylethanesulfonylimine **5n**, 96% yield (87% ee) and 94% yield (80% ee) also could be realized, respectively (Table 2, entries 13 and 14). Only for aliphatic sulfonylimine **5o** was the corresponding addition product **6o** obtained with only moderate ee (63% ee) (Table 2, entry 15).

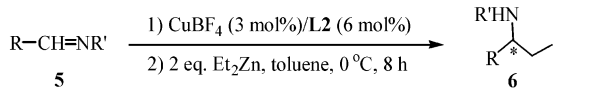
The sulfur on phosphorus was crucial for this catalytic asymmetric reaction because the corresponding axially chiral binaphthyldiphenylphosphoramide ligand **L8** showed very low catalytic activity for this reaction. The corresponding addition product **6j** was formed in trace amounts, and the byproduct was obtained in 32% yield along with a large amount of unreacted starting materials (Scheme 2). Although the real active species is not yet fully understood in this catalytic addition reaction, we believe that this family of binaphthylthiophosphoramides **L1**−**7** are bidentate ligands in this catalytic asymmetric reaction because it is well-known that sulfur atoms can coordinate strongly to late transition metals.[13] To get the evidence of the coordination of aniline nitrogen and sulfur atom to Cu(I), $^{13}C$ NMR and $^{31}P$ NMR studies of a 1:1 mixture of **L4** and $Cu(CH_3CN)_4BF_4$ in $CDCl_3$ at room temperature were carried out. In the absence of $Cu(CH_3CN)_4BF_4$, the carbon signals of the two carbons in the ethyl group of **L4** appeared at $\delta$ 38.31 and 15.00 (Figure 1), but the two corresponding carbons signals appeared at $\delta$ 40.92 and 14.88 in the presence of $Cu(CH_3CN)_4BF_4$, respectively (Figure 2). Meanwhile, another new carbon signal was observed at $\delta$ 1.88, which was attributed to the carbon of methyl group in acetonitrile. In addition, the signal of the phosphorus connected to the sulfur atom in **L4** appeared at $\delta$ 53.28 in the absence of $Cu(CH_3CN)_4BF_4$ (Figure 3), while it was shifted to $\delta$ 55.52 in **L4** in the presence of $Cu(CH_3CN)_4BF_4$ (Figure 4). Those results may indicate that Cu(I) can be potentially coordinated by both the S and N atoms in ligand **L4**.

## Conclusion

In conclusion, we have synthesized a new family of axially chiral binaphthylthiophosphoramides that are

(13) For selected X-rays of Cu complexes coordinated by S,N-ligands, see: (a) Koten, D. M.; Grove, D. M.; Smeets, W. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 3400−3410. (b) Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kutchan, T. M.; Mottel, E. A. *Inorg. Chem.* **1979**, *18*, 299−302.

**TABLE 2. Asymmetric Addition of Diethylzinc to Various *N*-Sulfonylimines 5 in the Presence of Cu(I) (3 mol %) and L2 (6 mol %)**




5 6

| entry | R | R′ | imine | yield[a] (%) | ee[b] (%) | $[\alpha]^{25}_D$ (*c* in $CHCl_3$) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | Ts | **5a** | **6a**, 93 | 86 | −52.2 (2.97)[c] |
| 2 | *p*-$MeC_6H_4$ | Ts | **5b** | **6b**, 95 | 86 | −67.3 (2.48) |
| 3 | *m*-$MeC_6H_4$ | Ts | **5c** | **6c**, 93 | 86 | −60.6 (2.35) |
| 4 | *p*-$MeOC_6H_4$ | Ts | **5d** | **6d**, 81 | 90 | −80.1 (1.50) |
| 5 | *p*-$ClC_6H_4$ | Ts | **5e** | **6e**, 96 | 91 | −52.4 (3.90) |
| 6 | *m*-$ClC_6H_4$ | Ts | **5f** | **6f**, 93 | 86 | −57.3 (5.80) |
| 7 | *p*-$CF_3C_6H_4$ | Ts | **5g** | **6g**, 95 | 93 | −39.7 (2.25) |
| 8 | *p*-$BrC_6H_4$ | Ts | **5h** | **6h**, 91 | 92 | −25.5 (1.25) |
| 9 | *m*-$FC_6H_4$ | Ts | **5i** | **6i**, 94 | 85 | −52.5 (4.70) |
| 10 | *p*-$FC_6H_4$ | Ts | **5j** | **6j**, 96 | 90 | −39.7 (0.72) |
| 11 | 2-furyl | Ts | **5k** | **6k**, 95 | 82 | −74.1 (0.68) |
| 12 | 1-naphthyl | Ts | **5l** | **6l**, 93 | 88 | +9.1 (1.25) |
| 13 | $C_6H_5$ | Ms | **5m** | **6m**, 96 | 87 | −38.6 (2.63) |
| 14 | *p*-$ClC_6H_4$ | SES | **5n** | **6n**, 94 | 80 | −14.0 (1.70) |
| 15 | *i*-$Me_2CH$ | Ts | **5o** | **6o**, 86 | 63 | −6.2 (3.25) |

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Absolute configuration of **6a** was assigned as *S* by comparing the optical rotation with the reported data.[5a]

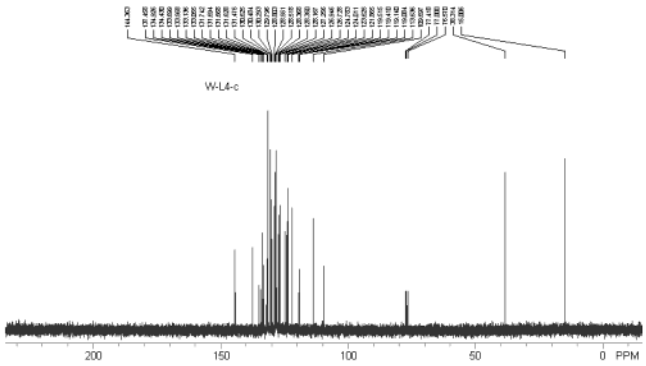
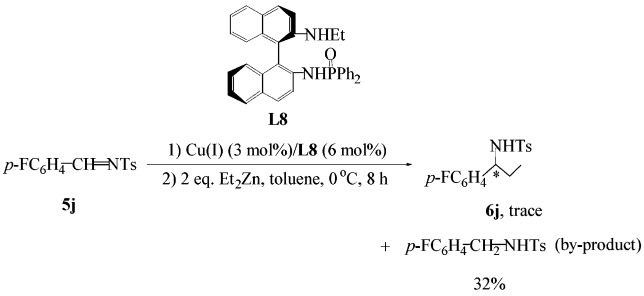



**FIGURE 1.** $^{13}C$ NMR spectrum of **L4**.

**SCHEME 2. Asymmetric Addition Reaction of Diethylzinc to *N*-Sulfonylimine 5j in the Presence of Cu(I) (3 mol %) and Chiral Ligand L8 (6 mol %)**




easily available, very stable, and recoverable and have applied them to the copper-catalyzed asymmetric addition of diethylzinc to *N*-sulfonylimines **5** with high yields and moderate to good enantioselectivities. Efforts are underway to elucidate the mechanistic details of this catalytic system and to extend the scope of these novel chiral ligands in other asymmetric C−C bond-forming transformations.

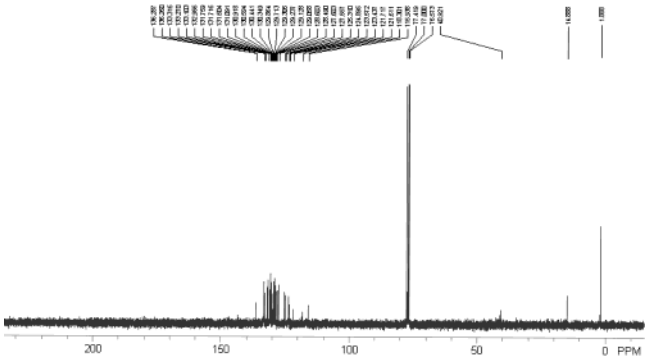



**FIGURE 2.** $^{13}C$ NMR spectrum of the mixture of **L4** and Cu-$(CH_3CN)_4BF_4$.

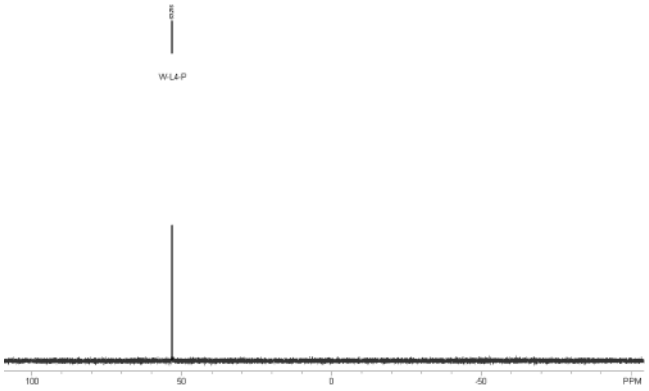



**FIGURE 3.** $^{31}P$ NMR spectrum of **L4**.

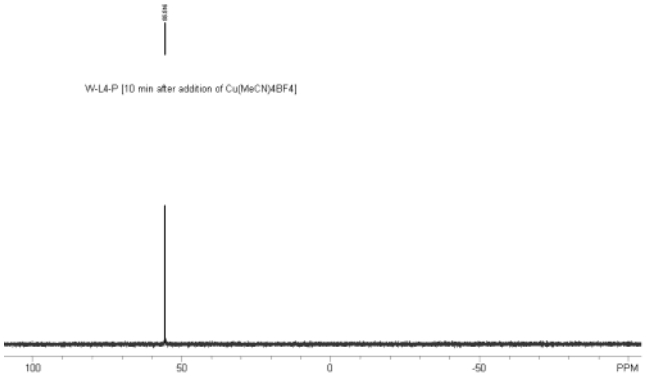



**FIGURE 4.** $^{31}P$ NMR spectrum of the mixture of **L4** and Cu-$(CH_3CN)_4BF_4$.

## Experimental Section

**General Remarks.** All reactions were conducted in oven-(135 °C) and flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Toluene was distilled from sodium metal; dichloromethane was distilled from calcium hydride, and diethyl ether, tetrahydrofuran, and benzene were distilled from sodium metal/benzophenone ketyl. $^1H$ NMR, $^{13}C$ NMR, and $^{31}P$ NMR spectra were recorded at 300, 75, and 121 MHz, respectively. Mass spectra were recorded by the EI method. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by HPLC, using a chiralpak AS column, a chiralpak AD column or a chiralcel OD column

with hexane and *i*-PrOH as solvents. Melting points are uncorrected.

**Materials.** *N*-Benzylidene-*p*-methylbenzenesulfonamides **5a**−**l**,[14] *N*-benzylidene-methylsulfonamide **5m**,[15] *N*-(*p*-chlorobenzylidene)-*β*-trimethylsilylethanesulfonamide **5n**,[16] and *N*-isobutylidene-*p*-methyl- benzenesulfonamide **5o**[17] were prepared by the reported synthetic methods. The physical and spectroscopic data of **5a**, **5b**, **5d**, **5f**, **5h**, **5k**, and **5l**−**o** are consistent with those reported in the literature.[14−18] For new starting materials **5c**, **5e**, **5g**, **5i**, and **5j**, the physical and spectroscopic data have been elucidated as follows.

***N*-(3-Methylbenzylidene)-*p*-methylbenzenesulfonamide 5c:** yield 73%; mp 88−89 °C; IR (KBr) *ν* 1614, 1592, 1571, 1480, 1425, 1318, 1292, 1255, 1160, 1087, 1006, 997, 921, 809 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 2.39 (s, 3H, Me), 2.44 (s, 3H, Me), 7.37 (m, 4H, ArH), 7.73 (m, 2H, ArH), 7.89 (d, *J* = 7.8 Hz, 2H, ArH), 9.0 (s, 1H, CH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 21.11, 21.64, 128.02, 128.98, 129.77, 131.27, 132.22, 135.06, 135.85, 139.04, 144.55, 170.35; MS (EI) *m*/*z* 273 ([M]$^{+\bullet}$, 8.18), 155 ([M − 118]$^+$, 45.40), 118 ([M − 155]$^+$, 14.20), 91 ([M − 182]$^+$, 100.00). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.87; H, 5.55; N, 5.12.

***N*-(4-Chlorobenzylidene)-*p*-methylbenzenesulfonamide 5e:** yield 75%; mp 175−176 °C; IR (KBr) *ν* 1606, 1593, 1561, 1487, 1402, 1318, 1304, 1164, 1084, 1011, 871, 825, 800, 787 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 2.41 (s, 3H, Me), 7.32 (d, *J* = 8.3 Hz, 2H, ArH), 7.43 (d, *J* = 8.3 Hz, 2H, ArH), 7.84 (m, 4H, ArH), 8.96 (s, 1H, CH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 21.63, 128.06, 129.52, 129.80, 130.68, 132.30, 134.71, 141.34, 144.75, 168.60; MS (EI) *m*/*z* 293 ([M]$^{+\bullet}$, 20.98), 155 ([M − 138]$^+$, 81.78), 111 ([M − 182]$^+$, 13.56), 91 ([M − 202]$^+$, 100.00). Anal. Calcd for $C_{14}H_{12}ClNO_2S$: C, 57.23; H, 4.12; N, 4.77. Found: C, 57.39; H, 3.97; N, 4.64.

***N*-(4-Trifluoromethylbenzylidene)-*p*-methylbenzenesulfonamide 5g:** yield 65%; mp 159−160 °C; IR (KBr) *ν* 1617, 1577, 1413, 1327, 1318, 1173, 1161, 1131, 1107, 1089, 1063, 1018, 998, 873, 841, 804, 789 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 2.47 (s, 3H, Me), 7.38 (d, *J* = 8.1 Hz, 2H, ArH), 7.76 (d, *J* = 8.4 Hz, 2H, ArH), 7.91 (d, *J* = 8.4 Hz, 2H, ArH), 8.06 (d, *J* = 8.1 Hz, 2H, ArH), 9.09 (s, 1H, CH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 21.67 123.24 (q, *J* = 271.4 Hz), 126.05 (q, *J* = 7.4 Hz), 128.22, 129.90, 131.32, 134.28, 135.33 (q, *J* = 1.6 Hz), 135.67 (q, *J* = 32.7 Hz), 145.07, 168.40; MS (EI) *m*/*z* 327 ([M]$^{+\bullet}$, 16.89), 155 ([M − 172]$^+$, 78.31), 145 ([M − 182]$^+$, 9.18), 91 ([M − 236]$^+$, 100.00). Anal. Calcd for $C_{15}H_{12}F_3NO_2S$: C, 55.04; H, 3.70; N, 4.28. Found: C, 55.16; H, 3.58; N, 4.06.

***N*-(3-Fluorobenzylidene)-*p*-methylbenzenesulfonamide 5i:** yield 77%; mp 93−94 °C; IR (KBr) *ν* 1660, 1610, 1576, 1488, 1322, 1289, 1256, 1160, 1089, 946, 878, 832, 814, 791, 755 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 2.45 (s, 3H, Me), 7.38 (m, 4H, ArH), 7.64 (m, 2H, ArH), 7.89 (d, *J* = 8.4 Hz, 2H, ArH), 9.0 (d, *J* = 1.2 Hz, CH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 21.65, 116.44 (d, *J* = 22.4 Hz), 121.93 (d, *J* = 21.5 Hz), 127.88 (d, *J* = 2.8 Hz), 128.13, 129.86, 130.83 (d, *J* = 7.7 Hz), 134.35 (d, *J* = 7.2 Hz), 134.55, 144.91, 162.74 (d, *J* = 247.9 Hz), 168.77 (d, *J* = 2.9 Hz); MS (EI) *m*/*z* 277 ([M]$^{+\bullet}$, 27.38), 155 ([M − 122]$^+$, 74.57), 122 ([M − 155]$^+$, 9.71), 91 ([M − 186]$^+$, 100.00). Anal. Calcd for $C_{14}H_{12}FNO_2S$: C, 60.63; H, 4.36; N, 6.85. Found: C, 60.77; H, 4.33; N, 7.03.

***N*-(4-Fluorobenzylidene)-*p*-methylbenzenesulfonamide 5j:** yield 75%; mp 111−112 °C; IR (KBr) *ν* 1609, 1597, 1584, 1507, 1413, 1320, 1290, 1233, 1162, 1151, 1088, 879, 842, 809, 771 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 2.45 (s, 3H, Me), 7.19 (m, 2H, ArH), 7.36 (d, *J* = 8.1 Hz, 2H, ArH), 7.89 (d, *J* = 8.1 Hz, 2H, ArH), 7.97 (m, 2H, ArH), 9.01 (s, 1H, CH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 21.64, 116.60 (d, *J* = 22.0 Hz), 128.04, 128.67 (d, *J* = 2.9 Hz), 129.82, 133.78 (d, *J* = 9.6 Hz), 134.89, 144.86, 166.77 (d, *J* = 257.0 Hz), 168.53; MS (EI) *m*/*z* 277 ([M]$^{+\bullet}$, 25.61), 155 ([M − 122]$^+$, 83.32), 122 ([M − 155]$^+$, 3.78), 91 ([M − 186]$^+$, 100.00). Anal. Calcd for $C_{14}H_{12}FNO_2S$: C, 60.63; H, 4.36; N, 6.85. Found: C, 60.55; H, 4.58; N, 6.74.

**Synthesis of (*R*)-(+)-*N*-Acetyl-1,1′-binaphthyl-2,2′-diamine 1.** Acetic anhydride (208 *μ*L, 2.2 mmol) was added to a mixture of (*R*)-(+)-binaphthyldiamine (568 mg, 2 mmol), acetic acid (1.2 mL, 20 mmol), and dichloromethane (20.0 mL) with ice-cooling. The mixture was stirred at room temperature overnight, and 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford the product **1** as a colorless solid (509 mg, 78%): mp 240−241 °C; $[\alpha]^{25}_D$ = +40.0 (*c* 0.55, $CHCl_3$); IR (KBr) *ν* 3400, 1675, 1595, 1500, 1445, 1270, 1040, 965, 670 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 1.85 (s, 3H, Me), 6.91−7.42 (m, 8H, ArH and NHCO), 7.81−8.03 (m, 4H, ArH), 8.58 (d, *J* = 9.0 Hz, 2H, ArH); $^{13}$C NMR (DMSO-$d_6$, TMS, 75 MHz) *δ* 23.98, 110.31, 119.39, 121.93, 123.77, 124.48, 125.01, 125.03, 125.68, 126.18, 126.92, 127.91, 128.66, 128.71, 129.97, 130.03, 132.06, 133.14, 134.51, 136.16, 144.98, 169.53; MS (EI) *m*/*z* 326 ([M]$^{+\bullet}$, 43.47), 284 ([M − 42]$^+$, 25.13), 267 ([M − 59]$^+$, 100). Anal. Calcd for $C_{22}H_{18}ON_2$: C, 80.98; H, 5.52; N, 8.59. Found: C, 80.66; H, 5.61; N, 8.48.

**Synthesis of (*R*)-(+)-*N*-Ethyl-1,1′-binaphthyl-2,2′-diamine 2.** To a stirred suspension of $LiAlH_4$ (280 mg, 7.37 mmol) in 30.0 mL of anhydrous THF was added dropwise a solution of **1** (509 mg, 1.56 mmol) in 10.0 mL of THF. The mixture was heated under reflux for 4 h. The reaction mixture was cooled in an ice-bath, and the remaining hydride was carefully quenched by dropwise addition of water (5.0 mL) and then 10% NaOH (5.0 mL). A white precipitate was filtered off and thoroughly washed with ethyl acetate. The combined filtrate and ethyl acetate washings were washed with brine and dried over $MgSO_4$. After the solvents were evaporated under reduced pressure, the product was purified by flash chromatography to afford the product **2** (470 mg, 97%) as a colorless solid: mp 123−124 °C; $[\alpha]^{25}_D$ = +175.2 (*c* 0.63, $CHCl_3$); IR (KBr) *ν* 3385, 3060, 2985, 2910, 1645, 1598, 1510, 1425, 1350, 1150, 915, 820 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) *δ* 0.99 (t, *J* = 7.5 Hz, 3H, Me), 3.18 (q, *J* = 7.5 Hz, 2H, $CH_2$), 3.60 (br, 3H, amino-H), 6.96−7.25 (m, 8H, ArH), 7.75−7.87 (m, 4H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) *δ* 15.57, 39.02, 112.62, 112.84, 114.69, 118.71, 122.28, 122.79, 124.15, 124.36, 127.09, 127.19, 128.03, 128.50, 128.54, 128.80, 129.86, 129.96, 134.01, 134.30, 143.35, 144.73; MS (EI) *m*/*z* 313 ([M + 1]$^{+\bullet}$, 100.00), 297 ([M − 15]$^+$, 34.21), 280 ([M − 32]$^+$, 42.91), 267 ([M − 45]$^+$, 25.99). Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.62; H, 6.41; N, 8.97. Found: C, 84.53; H, 6.56; N, 8.95.

**Synthesis of (*R*)-(+)-*N*-Acetyl-*N*′,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine 3.** A solution of **1** (163 mg, 0.5 mmol) in THF (10 mL) and $NaBH_4$ (133 mg, 3.5 mmol) were simultaneously added to a stirred solution of 20% $H_2SO_4$ (0.5 mL) and 40% formaldehyde aqueous solution (0.5 mL, 6.0 mmol) in THF (20 mL) with ice-cooling over a period of 15 min. The mixture was stirred for an additional hour and then 1.0 N NaOH was added until pH > 7. After extraction with ethyl acetate, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford the product **3** as a colorless solid (108 mg, 61%). mp: 187−189 °C; $[\alpha]^{25}_D$ = −244.5 (*c* 0.58, $CHCl_3$); IR (KBr) *ν* 3402, 1684, 1596, 1501, 1427, 929, 669 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) *δ* 1.88 (s, 3H, Me), 2.58 (s, 2Me), 6.95 (d, *J* = 8.7 Hz, 1H, ArH), 7.12−7.55 (m,

(14) Love, B. E.; Raje, P. S.; Williams, T. C. *Synlett* **1994**, 493−494.
(15) Milenkovic, A.; Fache, F.; Faure, R.; Lemaire, M. *Synth. Commun.* **1999**, *29*, 1535−1546.
(16) Xu, Z.; Lu, X. *J. Org. Chem.* **1998**, *63*, 5031−5041.
(17) Chemla, F.; Hebbe, V.; Normant, J.-F. *Synthesis* **2000**, 75−77.
(18) (a) Mckay, W. R.; Proctor, G. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2435−2442. (b) Shim, J.-G.; Yamamoto, Y. *Heterocycles* **2000**, *52*, 2, 885−896. (c) ten Have, R.; Huisman, M.; Meetsma, A.; van Leuson, A. M. *Tetrahedron* **1997**, *53*, 11355−11368. (d) Knipe, A. C.; McAuley, I. E.; Khandelwal, Y.; Kansal, V. K. *Tetrahedron Lett.* **1984**, *25*, 1411−1414. (e) Vass, A.; Dudas, J.; Varma, R. S. *Tetrahedron Lett.* **1999**, *40*, 4951−4954.

6H, ArH), 7.84−7.80 (m, 4H, ArH), 8.49 (d, $J$ = 9.0 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 24.85, 43.63, 119.02, 121.81, 124.30, 124.62, 125.02, 125.54, 126.64, 126.67, 126.74, 127.04, 128.17, 128.41, 128.84, 129.90, 130.36, 131.30, 133.62, 133.96, 134.12, 149.88, 168.52; MS (EI) $m/z$ 354 ([M]$^{+\bullet}$, 58.79), 311 ([M − 43]$^+$, 9.83), 296 ([M − 58]$^+$, 17.65), 281 ([M − 73]$^+$, 36.62). Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.36; H, 6.21; N, 7.91. Found: C, 81.40; H, 6.39; N, 7.80.

**Synthesis of (*R*)-(+)-*N*,*N*-Dimethyl-1,1′-binaphthyl-2,2′-diamine 4.** (*R*)-(+)-*N*-Acetyl-*N*′,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (300 mg, 0.85 mmol) was added to a stirred solution of ethanol (25.0 mL) and 4.0 N HCl (9.0 mL), and the mixture was heated under reflux for 12 h. After cooling of the mixture to ambient temperature and removal of the ethanol in vacuo, 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford the product **4** as a colorless solid (262 mg, 99%): mp 116−118 °C; $[\alpha]^{25}_D$ = +17.4 ($c$ 2.0, $CHCl_3$); IR (KBr) $\nu$ 3395, 2794, 1621, 1507, 1426, 1380, 1143, 989, 930, 625 cm$^{-1}$; $^1$H NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 2.59 (s, 2Me), 7.0−7.29 (m, 7H, ArH), 7.47 (d, $J$ = 9.0 Hz, 1H, ArH), 7.74−7.91 (m, 4H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 38.47, 111.70, 113.46, 114.65, 117.12, 117.17, 118.75, 119.91, 119.99, 121.36, 121.62, 122.98, 123.03, 123.32, 123.91, 124.28, 124.90, 128.71, 129.27, 136.94, 145.23; MS (EI) $m/z$ 312 ([M]$^{+\bullet}$, 100.00), 297 ([M − 15]$^+$, 4.57), 280 ([M − 32]$^+$, 38.29), 267 ([M − 45]$^+$, 47.97). Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.62; H, 6.41; N, 8.97. Found: C, 84.70; H, 6.55; N, 8.92.

**Representative Experimental Procedure for the Synthesis of Ligands 1−8.** To a solution of (*R*)-(+)-*N*-ethyl-1,1′-binaphthyl-2,2′-diamine **2** (200 mg, 0.64 mmol) in THF (10.0 mL) was added dropwise *n*-butyllithium (1.12 mL, 1.8 mmol, 1.6 M solution in hexane) at −40 °C over 40 min, and the reaction mixture was stirred for 1 h at the same temperature. Then, diphenylthiophosphinic chloride (500 mg, 2.0 mmol) in 5.0 mL THF was added dropwise, and the reaction solution was slowly allowed to warm to room temperature. After 2 h, the THF was removed in vacuo. The residue was purified by alumina column chromatography to give the ligand (**L4**) as a colorless solid (314 mg, 93%).

**Ligand 1 (L1):** yield 95%; mp 180−182 °C; $[\alpha]^{25}_D$ = +65.8 ($c$ 0.6, $CHCl_3$); IR (KBr) $\nu$ 3350, 1620, 1514, 1476, 1422, 927, 626 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.76 (d, $J$ = 13.5 Hz, 3H, Me), 1.88 (d, $J$ = 13.5 Hz, 3H, Me), 4.61 (d, $J$ = 6.6 Hz, 1H, NH), 6.96 (d, $J$ = 8.1 Hz, 1H, ArH), 7.13−7.40 (m, 6H, ArH), 7.80−7.99 (m, 5H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 24.01 (d, $J$ = 68.6 Hz), 24.60 (d, $J$ = 68.6 Hz), 110.16, 118.08, 118.97, 119.03, 122.54, 123.57, 124.25, 124.91, 126.95, 127.07, 128.09, 128.19, 128.21, 129.15, 129.97, 130.26, 133.04, 133.58, 137.62, 142.86; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85% $H_3PO_4$) $\delta$ +56.96; MS (EI) $m/z$ 376 ([M]$^{+\bullet}$, 49.66), 284 ([M − 92]$^+$, 16.13), 267 ([M − 109]$^+$, 100). Anal. Calcd for $C_{22}H_{21}N_2$-PS: C, 70.19; H, 5.62; N, 7.44. Found: C, 69.84; H, 5.82; N, 7.65.

**Ligand 2 (L2):** yield 90%; mp 68−70 °C; $[\alpha]^{25}_D$ = +30.4 ($c$ 1.67, $CHCl_3$); IR (KBr) $\nu$ 3345, 1620, 1598, 1514, 1427, 1345, 994, 926, 669 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.09 (t, $J$ = 7.2 Hz, 3H, Me), 1.73 (d, $J$ = 12.9 Hz, 3H, Me), 1.89 (d, $J$ = 12.9 Hz, 3H, Me), 3.25 (q, $J$ = 7.2 Hz, 2H, $CH_2$), 3.62 (br, 1H, NH), 4.61 (d, $J$ = 7.2 Hz, 1H, NH), 6.86 (d, $J$ = 9.3 Hz, 1H, ArH), 7.01−7.40 (m, 6H, ArH), 7.79−7.99 (m, 5H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 15.12, 23.96 (d, $J$ = 68.9 Hz), 24.81 (d, $J$ = 68.6 Hz), 38.29, 109.60, 113.68, 118.89, 118.94, 119.61, 121.91, 123.35, 124.22, 124.94, 126.89, 126.94, 127.22, 128.19, 129.13, 129.99, 130.42, 133.26, 133.66, 137.83, 144.34; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +56.68; MS (EI) $m/z$ 404 ([M]$^{+\bullet}$, 100.00), 389 ([M − 15]$^+$, 5.87), 267 ([M − 137]$^+$, 25.94). Anal. Calcd for $C_{24}H_{25}N_2PS$: C, 71.29; H, 6.19; N, 6.93. Found: C, 71.65; H, 6.57; N, 6.49.

**Ligand 3 (L3):** yield 92%; mp 175−177 °C; $[\alpha]^{25}_D$ = −4.0 ($c$ 1.20, $CHCl_3$); IR (KBr) $\nu$ 3350, 1625, 1514, 1477, 1438, 1340, 929, 634 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 4.10 (s, br, 2H, NH), 5.12 (d, $J$ = 7.4 Hz, 1H, NH), 7.0−7.50 (m, 10H, ArH), 7.50−7.70 (m, 4H, ArH), 7.70−8.0 (m, 8H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 110.39, 118.25 (d, $J$ = 4.4 Hz), 119.28 (d, $J$ = 4.8 Hz), 119.84 (d, $J$ = 8.9 Hz), 122.67, 124.00, 124.54 (d, $J$ = 51.7 Hz), 127.12 (d, $J$ = 27.8 Hz), 127.26, 128.28, 128.33, 128.52, 128.71, 128.95, 130.01 (d, $J$ = 27.9 Hz), 130.80, 130.95, 131.62 (d, $J$ = 11.5 Hz), 131.82, 131.86, 131.90, 133.15, 133.41 (d, $J$ = 51.5 Hz), 133.57, 134.52, 134.93, 137.35, 143.16; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +53.37; MS (EI) $m/z$ 500 ([M]$^{+\bullet}$, 3.6). Anal. Calcd for $C_{32}H_{25}N_2PS$: C, 76.78; H, 5.03; N, 5.60. Found: C, 76.65; H, 5.07; N, 5.74.

**Ligand 4 (L4):** yield 93%; mp 78−80 °C; $[\alpha]^{25}_D$ = −47.5 ($c$ 0.905, $CHCl_3$); IR (KBr) $\nu$ 1625, 1600, 1515, 1474, 1426, 1055, 898 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.11 (t, $J$ = 7.2 Hz, 3H, Me), 3.27 (q, $J$ = 7.2 Hz, 2H, $CH_2$), 3.78 (br, 1H, NH), 5.14 (d, $J$ = 7.5 Hz, 1H, NH), 6.95−7.57 (m, 17 H, ArH), 7.75−7.91 (m, 5 H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 15.00, 38.31, 109.70, 113.64, 119.11 (d, $J$ = 4.2 Hz), 119.46 (d, $J$ = 7.9 Hz), 121.87, 123.63, 124.40 (d, $J$ = 57.9 Hz), 126.73, 126.95, 127.26, 128.35, 128.36 (d, $J$ = 28.8 Hz), 128.37, 128.52, 128.80, 130.14 (d, $J$ = 51.6 Hz), 130.46 (d, $J$ = 24.7 Hz), 131.48, 131.63, 131.67, 131.70, 131.74, 133.14, 133.31 (d, $J$ = 38.3 Hz), 133.70, 134.68 (d, $J$ = 37.1 Hz), 137.46, 144.37; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +53.28; MS (EI) $m/z$ 528 ([M]$^{+\bullet}$, 2.13), 311 ([M − 217]$^+$, 1.47), 267 ([M − 261]$^+$, 11.27). Anal. Calcd for $C_{34}H_{29}N_2PS$: C, 77.27; H, 5.49; N, 5.30. Found: C, 77.52; H, 5.89; N, 5.17.

**Ligand 5 (L5):** yield 51%; mp 62−64 °C; $[\alpha]^{25}_D$ = −180.1 ($c$ 1.83, $CHCl_3$); IR (KBr) $\nu$ 3350, 3054, 1619, 1595, 1507, 1438, 1422, 1338, 1219, 1153, 896, 817 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.53 (s, 6H, 2Me), 5.88 (d, $J$ = 9.0 Hz, NH), 7.0 (d, $J$ = 8.7 Hz, 1H, Ar), 7.14−7.43 (m, 12H, ArH), 7.56−7.75 (m, 5H, ArH), 7.79−7.98 (m, 4H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 43.27, 118.47, 120.41 (d, $J$ = 4.8 Hz), 121.81, 123.92 (d, $J$ = 2.6 Hz), 125.75, 126.56 (d, $J$ = 8.3 Hz), 125.97, 128.34 (d, $J$ = 18.6 Hz), 128.36, 128.37 (d, $J$ = 24.0 Hz), 128.38 (d, $J$ = 47.7 Hz), 128.41, 129.67, 129.84 (d, $J$ = 2.8 Hz), 131.04, 131.20, 131.48, 131.52, 131.57, 131.68, 131.72, 132.99, 133.88, 134.03, 134.04 (d, $J$ = 46.1 Hz), 135.25, 136.59, 149.87; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +51.47; MS (EI) $m/z$ 528 ([M]$^{+\bullet}$, 46.79), 311 ([M − 217]$^+$, 35.99), 267 ([M − 261]$^+$, 100.00). Anal. Calcd for $C_{34}H_{29}N_2PS$: C, 77.27; H, 5.49; N, 5.30. Found: C, 77.29; H, 5.68; N, 5.12.

**Ligand 6 (L6):** yield 90%; mp 61−63 °C; $[\alpha]^{25}_D$ = +41.3 ($c$ 2.07, $CHCl_3$); IR (KBr) $\nu$ 3020, 1625, 1600, 1521, 1750, 1423, 1030, 929, 895 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.28 (m, 6H, 2Me), 3.69 (br, 2H, $NH_2$), 3.97−4.17 (m, 4H, 2$CH_2$), 5.32 (d, $J$ = 14.1 Hz, 1H, NH), 6.91 (d, $J$ = 8.1 Hz, 1H, ArH), 7.12−7.37 (m, 6H, ArH), 7.80−7.96 (m, 5H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 15.61 (d, $J$ = 8.4 Hz), 15.64 (d, $J$ = 7.4 Hz), 63.19 (d, $J$ = 4.1 Hz), 63.23 (d, $J$ = 4.6 Hz), 110.08, 117.92, 117.96, 118.00, 118.04, 118.07, 122.44, 123.29, 124.12, 124.93, 126.84, 127.90, 128.15, 129.17, 129.75, 130.23, 132.83, 133.48, 136.31, 142.70; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3$-$PO_4$) $\delta$ +66.63; MS (EI) $m/z$ 436 ([M]$^{+\bullet}$, 77.63), 284 ([M − 152]$^+$, 52.04), 267 ([M − 169]$^+$, 100). Anal. Calcd for $C_{24}H_{25}N_2O_2PS$: C, 66.10; H, 5.73; N, 6.42. Found: C, 65.91; H, 6.03; N, 6.51.

**Ligand 7 (L7):** yield 97%; yellowish oil, $[\alpha]^{25}_D$ = +13.7 ($c$ 2.57, $CHCl_3$); IR (KBr) $\nu$ 3360, 3020, 1630, 1598, 1514, 1476, 1427, 1346, 1022, 964, 801 cm$^{-1}$; $^1$H NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.06 (t, $J$ = 6.9 Hz, Me), 1.28 (m, 6 H, 2Me), 3.24 (q, $J$ = 6.9 Hz, $CH_2$), 3.51 (br, 1 H, NH), 3.95−4.13 (m, 4 H, 2$CH_2$), 5.31 (d, $J$ = 13.2 Hz, 1H, NH), 6.81 (d, $J$ = 8.4 Hz, 1H, ArH), 7.08−7.36 (m, 6 H, ArH), 7.78−7.96 (m, 5 H, ArH); $^{13}$C NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 15.10, 15.73 (d, $J$ = 7.9 Hz), 15.77 (d, $J$ = 7.9 Hz), 38.32, 63.27 (d, $J$ = 4.8 Hz), 63.30 (d, $J$ = 4.2 Hz), 109.70, 113.88, 118.10, 118.13, 121.91, 123.20, 124.21, 125.13, 126.80, 126.92, 127.41, 127.99, 128.23, 129.28, 129.92, 130.46, 133.22, 133.65, 136.64, 144.38; $^{31}$P NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +66.60; MS (EI) $m/z$ 464 ([M]$^{+\bullet}$, 100), 311 ([M − 153]$^+$, 25.62), 267 ([M − 197]$^+$, 70.09). Anal. Calcd for

$C_{26}H_{29}N_2O_2PS$: C, 67.22; H, 6.29; N, 6.03. Found: C, 67.36; H, 6.45; N, 5.75. HRMS calcd $C_{26}H_{30}N_2O_2SP$ ($M^+ + 1$): 465.1756. Found: 465.1760.

**Ligand 8 (L8):** yield 99%; mp 57−58 °C; $[\alpha]^{25}_D = -149.1$ (*c* 0.9, $CHCl_3$); IR (KBr) $\nu$ 3350, 3020, 1619, 1598, 1517, 1475, 1424, 1378, 1216, 1045, 929, 811 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.07 (t, $J$ = 7.2 Hz, 3H, Me), 3.25 (q, $J$ = 7.2 Hz, 2H, $CH_2$), 3.75 (br, 1 H, NH), 5.46 (d, $J$ = 10.8 Hz, 1H, NH), 6.98−7.49 (m, 15 H, ArH), 7.64−7.94 (m, 7H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 14.77, 38.48, 113.90, 118.40 (d, $J$ = 8.7 Hz), 119.13 (d, $J$ = 4.4 Hz), 122.16 (d, $J$ = 3.3 Hz), 124.11, 124.32 (d, $J$ = 84.3 Hz), 126.97 (d, $J$ = 5.9 Hz), 127.54, 127.63, 128.25, 128.33, 128.98 (d, $J$ = 71.4 Hz), 128.66, 128.68, 129.41, 129.88, 130.35, 130.96, 131.19 (d, $J$ = 10.3 Hz), 131.50, 131.89, 131.98, 132.02, 132.68, 133.21, 133.52, 137.66, 144.32 (d, $J$ = 2.3 Hz); $^{31}P$ NMR ($CDCl_3$, 121 MHz, 85%$H_3PO_4$) $\delta$ +17.89; MS (EI) *m*/*z* 512 ($[M]^{+\bullet}$, 53.62), 497 ($[M - 15]^+$, 12.50), 295 ($[M - 217]^+$, 92.79), 280 ($[M - 232]^+$, 39.11). Anal. Calcd for $C_{34}H_{29}N_2OP$: C, 79.67; H, 5.70; N, 5.47. Found: C, 79.33; H, 6.03; N, 5.07. HRMS calcd $C_{34}H_{29}N_2OP$ ($M^+$): 512.2017. Found: 512.2061.

**General Procedure for the Synthesis of the Racemic Products Used for the Chiral HPLC Analysis.** To a solution of *N*-(*p*-fluorobenzylidene)-*p*-methylbenzenesulfonamide **5j** (139 mg, 0.5 mmol) in THF (4.0 mL) was added dropwise ethylmagnesium bromide (1.5 mL, 1.5 mmol, 1.0 M in THF) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 10 h at the same temperature, and then 1.0 N HCl (5.0 mL) was added. After extraction with ethyl acetate, the combined organic layers were dried over $MgSO_4$. The residue obtained upon removal of volatiles in vacuo was purified by column chromatography on silica gel (eluent: petroleum/ethyl acetate = 10/1) to afford the racemic product **6j** (140 mg, 91%) as a colorless solid.

The other racemates **6a**−**i** and **6k**−**o** were synthesized in the same manner as that described above.

**General Procedure for the Cu-Catalyzed Asymmetric Addition of Diethylzinc to *N*-Sulfonylimine.** A solution of $Cu(CH_3CN)_4BF_4$ (4.7 mg, 0.015 mmol) and ligand **L2** (13.0 mg, 0.03 mmol) in dry toluene (3 mL) was stirred for 1 h at room temperature under an argon atmosphere. *N*-(*p*-Fluorobenzylidene)-*p*-methylbenzenesulfonamide **5j** (139 mg, 0.5 mmol) was added, and the solution was stirred for an additional 10 min; then, $Et_2Zn$ (1 mL, 1 mmol, 1.0 M solution in hexane) was added dropwise within 30 s at 0 °C. The resulting mixture was stirred for about 8 h at the same temperature, and then 1.0 N HCl (4.0 mL) was added. After extraction with ethyl acetate, the combined organic layers were dried over $MgSO_4$. The residue obtained upon removal of volatiles in vacuo was purified by column chromatography on silica gel (eluent, petroleum/ethyl acetate = 10/1) to afford the addition product **6j** (148 mg, 96%) and recovered ligand **L2** (11 mg, 85%).

**(*S*)-(−)-4-Methyl-*N*-(1-phenylpropyl)benzenesulfonamide 6a (Entry 1 in Table 2):** yield 135 mg, 93%; mp 108−110 °C; IR (KBr) $\nu$ 3271, 2964, 1600, 1457, 1320, 1165, 1409, 1003, 905, 701 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.80 (t, $J$ = 7.5 Hz, 3H, Me), 1.79 (m, 2H, $CH_2$), 2.38 (s, 3H, Me), 4.20 (m, 1H, CH), 4.87 (br, 1H, NH), 7.01 (m, 2H, ArH), 7.16 (m, 5H, ArH), 7.55 (d, $J$ = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.41, 21.36, 30.53, 59.78, 126.50, 126.93, 127.08, 128.21, 129.15, 137.60, 140.69, 142.76; MS (EI) *m*/*z* 288 ($[M - 1]^+$, 0.05), 260 ($[M - 29]^+$, 89.90), 155 ($[M - 134]^+$, 50.52), 91 ($[M - 198]^+$, 100.00). Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.62; N, 4.82. Found: C, 66.53; H, 6.84; N, 4.78. $[\alpha]^{25}_D = -52.2$ (*c* 2.97, $CHCl_3$) for 86% ee; Chiralcel OD, hexane/*i*-PrOH = 9/1, 0.7 mL/min, $t_{minor}$ = 20.157 min, $t_{major}$ = 25.743 min, or Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 20.342 min, $t_{major}$ = 27.346 min.

**(−)-4-Methyl-*N*-(1-tolylpropyl)benzenesulfonamide 6b (Entry 2, Table 2):** yield 144 mg, 95%, mp 86−88 °C; IR (KBr) $\nu$ 3262, 2961, 1600, 1518, 1432, 1324, 1165, 1094, 1048, 997, 904, 806 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.78 (t, $J$ = 7.5 Hz, 3H, Me), 1.80 (m, 2H, $CH_2$), 2.29 (s, 3H, Me), 2.38 (s, 3H, Me), 4.14 (m, 1H, CH), 4.68 (br, 1H, NH), 6.90 (d, $J$ = 7.8 Hz, 2H, ArH), 6.98 (d, $J$ = 7.8 Hz, 2H, ArH), 7.14 (d, $J$ = 8.4 Hz, 2H, ArH), 7.55 (d, $J$ = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.43, 20.91, 21.34, 30.42, 59.56, 126.43, 126.95, 128.83, 129.09, 136.69, 137.66, 137.67, 142.64; MS (EI) *m*/*z* 303 ($[M]^{+\bullet}$, 0.06), 274 ($[M - 29]^+$, 100.00), 155 ($[M - 148]^+$, 39.05), 91 ($[M - 212]^+$, 68.24). Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62. Found: C, 67.33; H, 7.06; N, 4.56. $[\alpha]^{25}_D = -67.3$ (*c* 2.48, $CHCl_3$) for 86% ee; Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 20.352 min, $t_{major}$ = 25.527 min.

**(−)-4-Methyl-*N*-(1-*m*-tolylpropyl)benzenesulfonamide 6c (Entry 3 in Table 2):** yield 141 mg, 93%; mp 82−84 °C; IR (KBr) $\nu$ 3256, 2974, 1600, 1440, 1319, 1160, 1054, 905, 888, 813 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.80 (t, $J$ = 7.2 Hz, 3H, Me), 1.76 (m, 2H, $CH_2$), 2.18 (s, 3H, Me), 2.36 (s, 3H, Me), 4.14 (m, 1H, CH), 4.98 (br, 1H, NH), 6.71 (s, 1H, ArH), 6.82 (d, $J$ = 7.5 Hz, 1H, ArH), 6.94 (d, $J$ = 7.8 Hz, 1H, ArH), 7.05 (m, 3H, ArH), 7.53 (d, $J$ = 8.7 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.45, 21.08, 21.34, 30.40, 59.80, 123.57, 126.92, 127.25, 127.74, 128.09, 129.01, 137.64, 137.66, 140.44, 142.61; MS (EI) *m*/*z* 303 ($[M]^{+\bullet}$, 0.06), 274 ($[M - 29]^+$, 100.00), 155 ($[M - 148]^+$, 50.67), 91 ($[M - 212]^+$, 97.76). Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62. Found: C, 67.26; H, 6.78; N, 4.55. $[\alpha]^{25}_D = -60.6$ (*c* 2.35, $CHCl_3$) for 86% ee; Chiralpak AD, hexane/*i*-PrOH = 85/15, 0.7 mL/min, $t_{minor}$ = 11.513 min, $t_{major}$ = 12.920 min.

**(−)-4-Methyl-*N*-[1-(4-methoxyphenyl)propyl]benzenesulfonamide 6d (Entry 4 in Table 2):** yield 129 mg, 81%; mp 110−112 °C; IR (KBr) $\nu$ 3290, 2964, 1615, 1511, 1465, 1456, 1322, 1250, 1173, 1160, 1003, 905, 818 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.77 (t, $J$ = 7.5 Hz, 3H, Me), 1.80 (m, 2H, $CH_2$), 2.38 (s, 3H, Me), 3.76 (s, 3H, Me), 4.13 (m, 1H, CH), 5.02 (br, 1H, NH), 6.69 (d, $J$ = 11.4 Hz, 2H, ArH), 6.92 (d, $J$ = 11.4 Hz, 2H, ArH), 7.15 (d, $J$ = 8.1 Hz, 2H, ArH), 7.56 (d, $J$ = 8.1 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.44, 21.32, 30.41, 55.08, 59.26, 113.50, 126.93, 127.65, 129.10, 132.80, 137.70, 142.62, 158.55; MS (EI) *m*/*z* 319 ($[M]^{+\bullet}$, 1.86), 290 ($[M - 29]^+$, 100.00), 155 ($[M - 164]^+$, 34.88), 91 ($[M - 228]^+$, 63.53). Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.76; H, 6.39; N, 4.29. $[\alpha]^{25}_D = -80.1$ (*c* 1.5, $CHCl_3$) for 90% ee; Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 31.502 min, $t_{major}$ = 43.851 min.

**(−)-4-Methyl-*N*-[1-(4-chlorophenyl)propyl]benzenesulfonamide 6e (Entry 5 in Table 2):** yield 155 mg, 96%; mp 140−142 °C; IR (KBr) $\nu$ 3246, 2963, 1600, 1496, 1432, 1318, 1166, 1093, 1049, 998, 904, 809 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.79 (t, $J$ = 7.2 Hz, 3H, Me), 1.75 (m, 2H, $CH_2$), 2.39 (s, 3H, Me), 4.18 (m, 1H, CH), 4.88 (br, 1H, NH), 6.96 (d, $J$ = 9.0 Hz, 2H, ArH), 7.13 (m, 4H, ArH), 7.53 (d, $J$ = 9.0 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.37, 21.39, 30.37, 59.18, 126.93, 128.01, 128.29, 129.23, 132.84, 137.41, 139.22, 143.10. MS (EI) *m*/*z* 323 ($[M]^{+\bullet}$, 0.08), 294 ($[M - 29]^+$, 64.46), 155 ($[M - 168]^+$, 55.65), 91 ($[M - 232]^+$, 100.00). Anal. Calcd for $C_{16}H_{18}ClNO_2S$: C, 59.34; H, 5.60; N, 4.33. Found: C, 59.38; H, 5.53; N, 4.52. $[\alpha]^{25}_D = -52.4$ (*c* 3.9, $CHCl_3$) for 91% ee; Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 17.033 min, $t_{major}$ = 26.448 min.

**(−)-4-Methyl-*N*-[1-(3-chlorophenyl)propyl]benzenesulfonamide 6f (Entry 6 in Table 2):** yield 151 mg, 93%; mp 71−72 °C; IR (KBr) $\nu$ 3259, 2971, 1599, 1440, 1334, 1319, 1159, 1093, 1051, 1000, 886, 782 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) $\delta$ 0.81 (t, $J$ = 7.2 Hz, 3H, Me), 1.75 (m, 2H, $CH_2$), 2.38 (s, 3H, Me), 4.17 (m, 1H, CH), 4.98 (br, 1H, NH), 6.87 (s, 1H, ArH), 6.95 (m, 1H, ArH), 7.11 (m, 4H, ArH), 7.52 (d, $J$ = 8.1 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) $\delta$ 10.36, 21.34, 30.29, 59.30, 124.77, 126.83, 126.85, 127.09, 129.19, 129.50, 133.91, 137.26, 142.72, 143.06; MS (EI) *m*/*z* 323 ($[M]^{+\bullet}$, 0.08), 294 ($[M - 29]^+$, 90.94), 155 ($[M - 168]^+$, 80.14), 91 ($[M - 232]^+$, 100.00). Anal. Calcd for $C_{16}H_{18}ClNO_2S$: C, 59.34; H,

5.60; N, 4.33. Found: C, 59.44; H, 5.67; N, 4.22. $[\alpha]^{25}_D = -57.3$ (*c* 5.8, $CHCl_3$) for 86% ee; Chiralpak AD, hexane/*i*-PrOH = 85/15, 0.7 mL/min, $t_{minor}$ = 13.880 min, $t_{major}$ = 15.387 min.

**(−)-4-Methyl-*N*-[1-(4-trifluoromethylphenyl)propyl]-benzenesulfonamide 6g (Entry 7 in Table 2):** yield 170 mg, 95%; mp 117−119 °C; IR (KBr) *ν* 3266, 2973, 1599, 1439, 1327, 1159, 1120, 1086, 1068, 898, 846, 817 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.82 (t, *J* = 7.2 Hz, 3H, Me), 1.73 (m, 2H, $CH_2$), 2.34 (s, 3H, Me), 4.28 (m, 1H, CH), 5.21 (br, 1H, NH), 7.07 (d, *J* = 8.4 Hz, 2H, ArH), 7.12 (d, *J* = 8.1 Hz, 2H, ArH), 7.37 (d, *J* = 8.4 Hz, 2H, ArH), 7.47 (d, *J* = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 9.94, 20.82, 30.11, 59.24, 124.99 (q, *J* = 3.7 Hz), 127.54 (q, *J* = 270.3 Hz), 126.86, 127.05, 129.12 (q, *J* = 32.3 Hz), 129.33, 137.21, 143.11, 144.70 (q, *J* = 3.7 Hz). MS (EI) *m*/*z* 357 ($[M]^{+\bullet}$, 0.04), 328 ($[M - 29]^+$, 63.95), 155 ($[M - 202]^+$, 75.54), 91 ($[M - 265]^+$, 100.00). Anal. Calcd for $C_{17}H_{18}F_3NO_2S$: C, 57.13; H, 5.08; N, 3.92. Found: C, 57.04; H, 5.12; N, 4.00. $[\alpha]^{25}_D = -39.7$ (*c* 2.25, $CHCl_3$) for 93% ee; Chiralcel OD, hexane/*i*-PrOH = 9/1, 0.7 mL/min, $t_{minor}$ = 20.350 min, $t_{major}$ = 25.123 min.

**(−)-4-Methyl-*N*-[1-(4-bromophenyl)propyl]benzenesulfonamide 6h (Entry 8 in Table 2):** yield 168 mg, 91%; mp 176−178 °C; IR (KBr) *ν* 3246, 2962, 1600, 1494, 1431, 1316, 1164, 1094, 999, 904, 808 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.79 (t, *J* = 7.2 Hz, 3H, Me), 1.72 (m, 2H, $CH_2$), 2.40 (s, 3H, Me), 4.17 (m, 1H, CH), 4.91 (br, 1H, NH), 6.89 (d, *J* = 7.8 Hz, 2H, ArH), 7.13 (d, *J* = 8.4 Hz, 2H, ArH), 7.25 (d, *J* = 7.8 Hz, 2H, ArH), 7.50 (d, *J* = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.36, 21.44, 30.33, 59.23, 121.04, 126.95, 128.38, 129.27, 131.27, 137.37, 139.66, 143.19. MS (EI) *m*/*z* 368 ($[M]^{+\bullet}$, 0.13), 340 ($[M - 28]^+$, 75.84), 155 ($[M - 213]^+$, 82.97), 91 ($[M - 272]^+$, 100.00). Anal. Calcd for $C_{16}H_{18}BrNO_2S$: C, 52.18; H, 4.93; N, 3.80. Found: C, 52.19; H, 4.82; N, 3.75. $[\alpha]^{25}_D = -25.5$ (*c* 1.25, $CHCl_3$) for 92% ee; Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 18.44 min, $t_{major}$ = 29.05 min.

**(−)-4-Methyl-*N*-[1-(3-fluorophenyl)propyl]benzenesulfonamide 6i (Entry 9 in Table 2):** yield 144 mg, 94%; mp 126−128 °C; IR (KBr) *ν* 3261, 2974, 1594, 1455, 1316, 1162, 1095, 1050, 1002, 907, 786 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.79 (t, *J* = 7.5 Hz, 3H, Me), 1.74 (m, 2H, $CH_2$), 2.36 (s, 3H, Me), 4.19 (m, 1H, CH), 4.95 (br, 1H, NH), 6.66 (m, 1H, ArH), 6.84 (m, 2H, ArH), 7.13 (m, 3H, ArH), 7.54 (d, *J* = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.34, 21.37, 30.43, 59.27 (d, *J* = 1.7 Hz), 113.52 (d, *J* = 1.7 Hz), 113.99 (d, *J* = 1.7 Hz), 122.25 (d, *J* = 2.3 Hz), 126.95, 129.25, 129.55 (d, *J* = 8.1 Hz), 137.42, 143.11, 143.41 (d, *J* = 6.3 Hz), 162.57 (d, *J* = 240.8 Hz). MS (EI) *m*/*z* 307 ($[M]^{+\bullet}$, 0.07), 278 ($[M - 28]^+$, 81.53), 155 ($[M - 151]^+$, 64.76), 91 ($[M - 215]^+$, 100.00). Anal. Calcd for $C_{16}H_{18}FNO_2S$: C, 62.52; H, 5.90; N, 4.56. Found: C, 62.56; H, 5.91; N, 4.45. $[\alpha]^{25}_D = -52.5$ (*c* 4.7, $CHCl_3$) for 85% ee; Chiralcel OD, hexane/*i*-PrOH = 9/1, 0.7 mL/min, $t_{minor}$ = 19.467 min, $t_{major}$ = 27.208 min.

**(−)-4-Methyl-*N*-[1-(4-fluorophenyl)propyl]benzenesulfonamide 6j (Entry 10 in Table 2):** yield 148 mg, 96%; mp 116−118 °C; IR (KBr) *ν* 3265, 2970, 1608, 1513, 1452, 1318, 1226, 1164, 1095, 1052, 1004, 907, 808 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.78 (t, *J* = 7.2 Hz, 3H, Me), 1.75 (m, 2H, $CH_2$), 2.38 (s, 3H, Me), 4.18 (m, 1H, CH), 5.03 (br, 1H, NH), 6.83 (m, 2H, ArH), 6.99 (m, 2H, ArH), 7.13 (d, *J* = 8.1 Hz, 2H, ArH), 7.53 (d, *J* = 8.1 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.37, 21.31, 30.48, 59.11, 114.92 (d, *J* = 21.3 Hz), 126.89, 128.17 (d, *J* = 8.1 Hz), 129.15, 136.56 (d, *J* = 2.8 Hz), 137.53, 142.93, 161.75 (d, *J* = 242.7 Hz); MS (EI) *m*/*z* 307 ($[M]^{+\bullet}$, 0.03), 278 ($[M - 28]^+$, 100.00), 155 ($[M - 151]^+$, 67.10), 91 ($[M - 215]^+$, 88.44). Anal. Calcd for $C_{16}H_{18}FNO_2S$: C, 62.52; H, 5.90; N, 4.56. Found: C, 62.54; H, 5.97; N, 4.52. $[\alpha]^{25}_D = -39.7$ (*c* 0.72, $CHCl_3$) for 90% ee; Chiralpak AD, hexane/*i*-PrOH = 97/3, 1 mL/min, $t_{major}$ = 46.880 min, $t_{minor}$ = 52.800 min.

**(−)-4-Methyl-*N*-(1-furan-2-ylpropyl)benzenesulfonamide 6k (Entry 11 in Table 2):** yield 132 mg, 95%; mp 88−90 °C; IR (KBr) *ν* 3257, 2934, 1600, 1426, 1322, 1162, 1142, 1093, 1004, 934, 901, 753, 668 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.84 (t, *J* = 7.5 Hz, 3H, Me), 1.81 (m, 2H, $CH_2$), 2.39 (s, 3H, Me), 4.31 (m, 1H, CH), 4.88 (br, 1H, NH), 5.90 (d, *J* = 3.3 Hz, 1H, furylH), 6.12 (dd, *J* = 3.3 and 1.8 Hz, 1H, furylH), 7.14 (d, *J* = 1.8 Hz, 1H, furylH), 7.20 (d, *J* = 8.1 Hz, 2H, ArH), 7.83 (d, *J* = 8.1 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.10, 21.40, 28.00, 53.07, 106.82, 109.82, 126.86, 129.26, 137.61, 141.64, 142.87, 152.80; MS (EI) *m*/*z* 279 ($[M]^{+\bullet}$, 1.22), 250 ($[M - 29]^+$, 69.37), 155 ($[M - 124]^+$, 46.17), 124 ($[M - 155]^+$, 33.21). Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01. Found: C, 60.02; H, 5.91; N, 4.96. $[\alpha]^{25}_D = -74.1$ (*c* 0.68, $CHCl_3$) for 82% ee; Chiralpak AD, hexane/*i*-PrOH = 80/20, 0.7 mL/min, $t_{major}$ = 12.797 min, $t_{minor}$ = 14.077 min.

**(+)-4-Methyl-*N*-(1-naphthalen-1-ylpropyl)benzenesulfonamide 6l (Entry 12 in Table 2):** yield 158 mg, 93%; mp 128−130 °C; IR (KBr) *ν* 3275, 2927, 1598, 1427, 1329, 1159, 1092, 989, 780 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.88 (t, *J* = 7.2 Hz, 3H, Me), 1.97 (m, 2H, $CH_2$), 2.26 (s, 3H, Me), 5.03 (m, 2H, NH and CH), 6.92 (d, *J* = 8.7 Hz, 2H, ArH), 7.27 (m,2H, ArH), 7.45 (m, 4H, ArH), 7.66 (m, 1H, ArH), 7.79 (m, 1H, ArH), 7.88 (m, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.62, 21.19, 30.33, 55.46, 122.51, 123.91, 125.10, 125.30, 125.93, 126.74, 127.50, 128.58, 128.77, 130.44, 133.50, 136.66, 137.12, 142.52; MS (EI) *m*/*z* 339 ($[M]^{+\bullet}$, 6.92), 310 ($[M - 29]^+$, 100.00), 156 ($[M - 184]^+$, 38.41), 91 ($[M - 248]^+$, 42.77). Anal. Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13. Found: C, 70.96; H, 6.14; N, 4.20. $[\alpha]^{25}_D = +9.1$ (*c* 1.25, $CHCl_3$) for 88% ee; Chiralpak AD, hexane/*i*-PrOH = 85/15, 0.7 mL/min, $t_{minor}$ = 15.647 min, $t_{major}$ = 19.247 min.

**(−)-*N*-(1-Phenylpropyl)methanesulfonamide 6m (Entry 13 in Table 2):** yield 102 mg, 96%; mp 64−65 °C; IR (KBr) *ν* 3277, 2972, 2931, 1497, 1459, 1307, 1156, 1006, 901, 701 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.92 (t, *J* = 7.2 Hz, 3H, Me), 1.87 (m, 2H, $CH_2$), 2.56 (s, 3H, Me), 4.35 (m, 1H, CH), 5.04 (br, 1H, NH), 7.27−7.41 (m, 5H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.63, 30.57, 41.54, 59.77, 126.60, 127.71, 128.73, 141.33; MS (EI) *m*/*z* 213 ($[M]^{+\bullet}$, 0.22), 184 ($[M - 29]^+$, 100.00), 106 ($[M - 107]^+$, 79.84), 77 ($[M - 136]^+$, 25.20). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09; N, 6.57. Found: C, 56.32; H, 6.95; N, 6.50. $[\alpha]^{25}_D = -38.6$ (*c* 2.63, $CHCl_3$) for 87% ee; Chiralpak AS, hexane/*i*-PrOH = 75/25, 0.7 mL/min, $t_{minor}$ = 12.698 min, $t_{major}$ = 13.897 min.

**(−)-2-Trimethylsilyl-*N*-[1-(4-chlorophenyl)propyl]-ethanesulfonamide 6n (Entry 14 in Table 2):** yield 157 mg, 94%; mp 136−138 °C; IR (KBr) *ν* 3239, 2961, 1494, 1464, 1307, 1252, 1174, 1149, 1089, 1015, 1050, 892, 837 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* −0.10 (s, 9H, 3Me), 0.78 (dt, *J* = 4.2 and 14.4 Hz, 2H, $CH_2$), 0.91 (t, *J* = 7.2 Hz, 3H, Me), 1.82 (m, 2H, $CH_2$), 2.55 (dt, *J* = 4.2 and 14.4 Hz, 2H, $CH_2$), 4.31 (m, 1H, CH), 4.71 (br, 1H, NH), 7.24 (d, *J* = 8.4 Hz, 2H, ArH), 7.34 (d, *J* = 8.4 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* −2.27, 10.18, 10.72, 30.63, 49.81, 59.05, 128.14, 128.93, 133.62, 140.33; MS (EI) *m*/*z* 304 ($[M - 29]^+$, 20.60), 166 ($[M - 167]^+$, 5.37), 101 ($[M - 232]^+$, 16.78), 73 ($[M - 260]^+$, 100.00). Anal. Calcd for $C_{14}H_{24}ClNO_2SSi$: C, 50.35; H, 7.24; N, 4.19. Found: C, 50.16; H, 7.04; N, 4.09. $[\alpha]^{25}_D = -14.0$ (*c* 1.7, $CHCl_3$) for 80% ee; Chiralpak AD, hexane/*i*-PrOH = 80/20, 0.7 mL/min, $t_{minor}$ = 9.210 min, $t_{major}$ = 10.090 min.

**(−)-4-Methyl-*N*-(1-ethyl-2-methylpropyl)benzenesulfonamide 6o (Entry 15 in Table 2):** yield 110 mg, 86%; mp 61−63 °C; IR (KBr) *ν* 3281, 2964, 1598, 1463, 1421, 1323, 1161, 1095, 1008, 906, 815 $cm^{-1}$; $^1H$ NMR ($CHCl_3$, TMS, 300 MHz) *δ* 0.79 (m, 9H, 3Me), 1.27 (m, 1H, CH), 1.42 (m, 1H, CH), 1.75 (m, 1H, CH), 2.44 (s, 3H, Me), 3.01 (m, 1H, CH), 4.35 (br, 1H, NH), 7.30 (d, *J* = 9.9 Hz, 2H, ArH), 7.77 (d, *J* = 9.9 Hz, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, TMS, 75 MHz) *δ* 10.05, 17.53, 18.34, 21.42, 24.36, 30.65, 60.70, 126.87, 129.38, 138.52, 142.83; MS (EI) *m*/*z* 255 ($[M]^{+\bullet}$, 0.09), 226 ($[M - 29]^+$, 8.45), 212 ($[M - 43]^+$, 62.14), 155 ($[M - 100]^+$, 66.63), 91 ($[M - 146]^+$,

100.00). Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.48. Found: C, 61.15; H, 8.48; N, 5.40. $[\alpha]^{25}_D = -6.2$ (*c* 3.25, $CHCl_3$) for 63% ee; Chiralpak AD, hexane/*i*-PrOH = 85/15, 0.7 mL/min, $t_{major} = 11.683$ min, $t_{minor} = 13.250$ min.

**Acknowledgment.** We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (20025206 and 20272069).

**Supporting Information Available:** $^{13}C$ NMR spectra and chiral HPLC traces of the compounds shown in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

JO034269N