**15-hydroxy-16-crown-5 (6b)**: Yield 12%; bp 160 °C/0.01 torr (Kugelrohr); IR (neat) 3370, 2890, 1460, 1350, 1250, 1130, 980, 930, 900 $cm^{-1}$; NMR ($CDCl_3$) δ 3.08–4.20 (m, 28 H); MS, *m/e* (relative intensity) 324 ($M^+$, 4), 306 (2), 205 (12), 163 (14), 145 (19), 101 (28), 89 (50), 87 (62), 45 (100).

Anal. Calcd for $C_{14}H_{28}O_8$: C, 51.84; H, 8.70; Found: C, 52.17; H, 8.98.

**3,7,10,14-Tetraoxahexadecane-1,5,12,16-tetrol (9).** To a stirred solution of sodium metal (46 mg, 0.002 mol) in ethylene glycol (**4a**) (50 mL) were added ethylene glycol diglycidyl ether (**1a**) (1.74 g, 0.01 mol) and tetrabutylammonium hydrogen sulfate (0.34 g, 0.001 mol), and the mixture was heated at 60 °C for 15 h: bp 170 °C/0.01 torr; IR (neat) 3370, 2860, 1460, 1360, 1250, 1130, 950, 900 $cm^{-1}$; NMR ($CDCl_3$) δ 3.12–4.20 (m, 26 H); MS, *m/e* (relative intensity) 299 ($M^+$+1, tr), 223 (10), 205 (36), 119 (78), 101 (61), 87 (64), 57 (45), 45 (100).

Anal. Calcd for $C_{12}H_{26}O_8$: C, 48.31; H, 8.78. Found: C, 47.86; H, 8.92.

# Asymmetric Conjugate Addition of Organometallic Reagents to Chiral Vinyl Sulfoximines

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The chiral vinyl sulfoximines **1** and **2** (R′ = $C_6H_5$, $CH_3$, *n*-Bu, $C_6H_5CH_2CH_2$) have been prepared; they undergo conjugate addition reactions with organometallic reagents with high asymmetric induction. These conjugate addition adducts have been converted to chiral 3-alkylalkanoic acids in high enantiomeric excess (>90%).

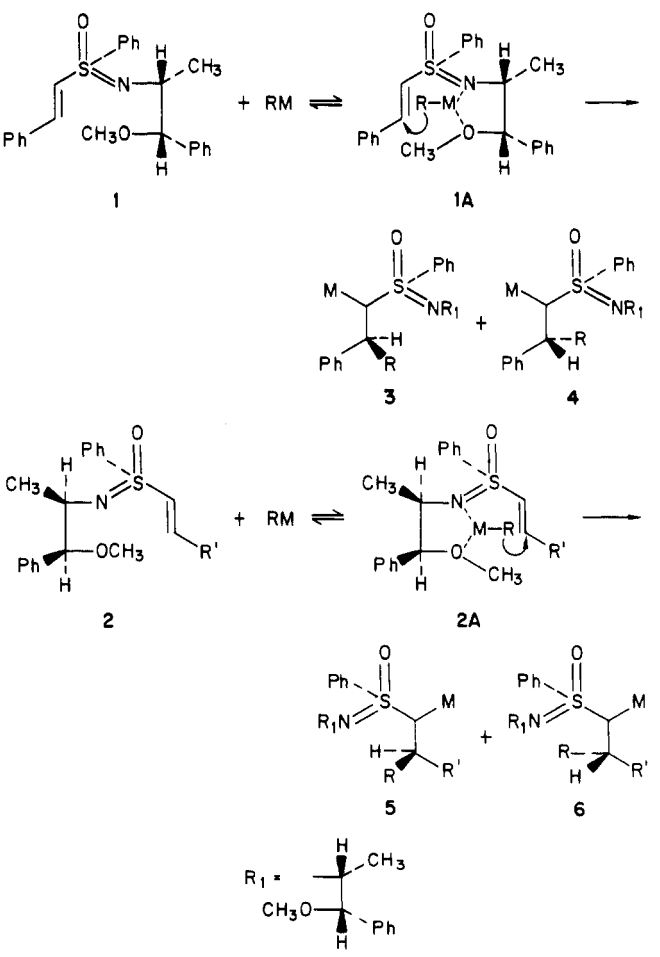
In recent years, a variety of chiral electrophilic olefinic substrates that undergo conjugate addition by organometallic reagents with high asymmetric induction[1] have been prepared. These substrates have allowed for the preparation of chiral 3-alkykalkanoic acids[1b-e,h] and 3-alkylcycloalkanones[1e-g] and their derivatives[1a] in high (>95%) enantiomeric excess (ee). We report here a study of the conjugate addition of organometallic reagents to chiral vinyl sulfoximines and demonstrate the potential of these substrates for enantioselective synthesis.

By analogy with the chemistry of vinyl sulfones,[2] it was expected that vinyl sulfoximines would undergo smooth conjugate addition with organometallic reagents. The chiral vinyl sulfoximines **1** and **2**, being bidentate ligands for coordination with an organometallic reagent (RM, Scheme I), should ensure high asymmetric induction in the conjugate-addition step. It was expected that the resulting carbanionic intermediates (**3**, **5**) would be readily manipulated to give a variety of chiral substrates.[3]

## Synthesis of Chiral Vinyl Sulfoximines 1 and 2

(+)-Norephedrine[4] was converted to (1*S*,2*R*)-2-amino-1-methoxy-1-phenylpropane (**7**) by standard procedures.[5] Treatment of benzenesulfinyl chloride (2 equiv) in $CH_2Cl_2$ at 0 °C with **7** (1 equiv) and $Et_3N$ (2 equiv) gave the diastereomeric sulfinamides **8** and **9** (3:1 respectively) as an inseparable mixture by TLC (Scheme II). Treatment of this mixture with *N*-chlorobenzotriazole[8] in THF at 0–23 °C[9] and then sodium phenoxide in DMF[7c] gave a mixture (1.8:1) of diasteromeric phenylsulfonimidates **11** which was homogeneous by TLC, in 85% overall yield from **7**. Not unexpectedly,[7c] racemization at sulfur had occurred in the intermediate sulfonimidoyl chloride **10**. The mixture of phenysulfonimidates **11** was treated with methyllithium to give chromatographically separable (*SS*)-(+)-sulfoximine **12** (14%, $[\alpha]^{18}_D$ +88.8° ($CH_2Cl_2$, *c* 0.024)) and (*SR*)-(+)-sulfoximine **13** (28%, $[\alpha]^{18}_D$ +19.2° ($CH_2Cl_2$, *c* 0.03)).

Scheme I[a]




[a] a, R′ = $C_5H_5$; b, R′ = $CH_3$; c, R′ = *n*-Bu; d, R′ = $CH_2CH_2C_6H_5$.

The sulfoximines **12** and **13** were converted to (*SS*)-vinyl sulfoximine **1** and (*SR*)-vinyl sulfoximine **2**, respectively,

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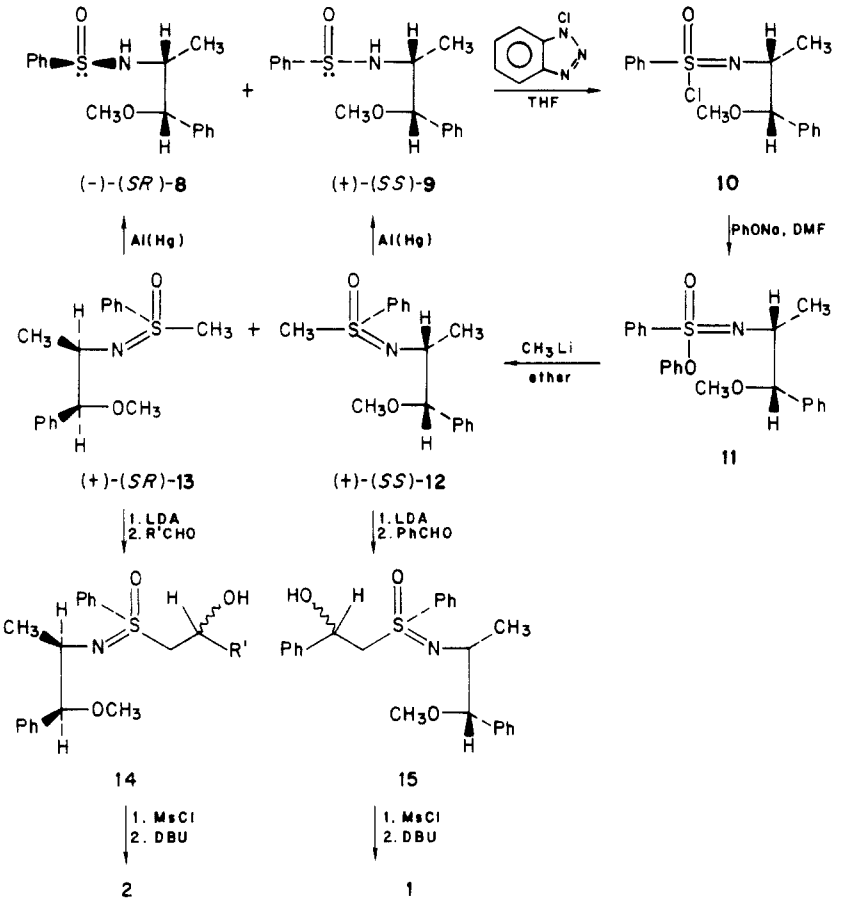
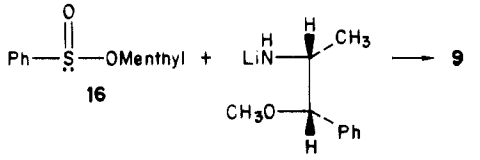
Scheme II




Scheme III




by the following sequence (Scheme II): deprotonation of **13** (**12**) with lithium diisopylamide (LDA) in THF at 0 °C and subsequent quenching of the resulting carbanion with an aldehyde (R′ = $C_6H_5$, $CH_3$, *n*-Bu, $C_6H_5CH_2CH_2$, Scheme II) gave **14** (**15**) as a mixture (ca. 1:1) of diastereomers (70–78% yield). Conversion of **14** (**15**) to the mesylate and then elimination with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) furnished pure (*E*)-vinyl sulfoximine **2** (**1**) after purification by column chromatography (50–58%).[12]

**Table I. Conjugate Addition Reactions of Vinyl Sulfoximines 1 and 2 with Organometallic Reagents (RM)**

| substrate | RM | yield, % | diastereomeric ratio 3:4 (5:6) |
|---|---|---|---|
| 1 | $CH_3Li$ | 85 | 96:4 |
| 1 | *n*-BuLi | 82 | 95:5 |
| **2a** | *n*-BuLi | 69 | 73:27 |
| **2a** | *n*-$Bu_2CuLi$ | 76 | 86:14 |
| **2a** | *n*-$Bu_2CuCNLi_2$ | 69 | 82:18 |
| **2a** | *n*-BuCu | 71 | 4.5:95.5 |
| **2a** | *n*-$Bu_2CuLi$ + LiI (5 equiv) | 65 | 85:15 |
| **2b** | *n*-$Bu_2CuLi$ | 77 | 81:19 |
| **2b** | *n*-BuCu | 81 | 5:95 |
| **2b** | *n*-BuCu (LiI "free") | 68 | 33:67 |
| **2a** | $CH_3Cu$ | 78 | 4:96 |
| **2c** | $CH_3Cu$ | 72 | 3.5:96.5 |
| **2d** | $CH_3Cu$ | 75 | 4.5:95.5 |

## Proof of Stereochemistry at Sulfur

The absolute configuration of sulfoximines **12** and **13** was established by their stereospecific reduction (>95%) with aluminum amalgam[10] to sulfinamides **9** and **8** ($[\alpha]^{19}_D$ –62.6° ($CHCl_3$, *c* 0.005)), respectively. Johnson[11] has shown

(1) (a) Hashimoto, S.; Yamada, S.; Koga, K. *J. Am. Chem. Soc.* **1976**, *98*, 7450. (b) Mukaiyama, T.; Takeda, T.; Fujimoto, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3368. (c) Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250. (d) Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1981**, 913. (e) Posner, G. H.; Mallamo, J. P.; Miura, K. *J. Am. Chem. Soc.* **1981**, *103*, 2886. (f) Posner, G. H.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 379. (g) Posner, G. H.; Kogan, T. P.; Hulce, M. *Tetrahedron Lett.* **1984**, *25*, 383. (h) Oppolzer, W.; Moretti, R.; Godel, T.; Meunier, A.; Loher, H. *Tetrahedron Lett.* **1983**, *24*, 4971.

(2) (a) Posner, G. H., Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747. (b) Hamann, P. R.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 914. (c) Isobe, M.; Funabashi, Y.; Ichikawa, Y.; Mio, S.; Goto, T. *Tetrahedron Lett.* **1984**, *25*, 2021.

(3) Glass, R. S.; Reineke, K.; Shanklin, M. *J. Org. Chem.* **1984**, *49*, 1527 and reference 7 therein.

(4) Commercially available from Aldrich Chemical Co. as the hydrochloride salt, $[\alpha]_D$ +33.4° (*c* 7, $H_2O$).

(5) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 6266.

(6) Herbrandson, H. F.; Dickerson, R.T., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4102.

(7) (a) Colonna, S.; Giovini, R.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1968**, 865. (b) Nudelman, A.; Cram, D. J. *J. Amer. Chem. Soc.* **1968**, *90*, 3869. (c) Johnson, C. R.; Jonsson, E. U.; Wambsgans, A. *J. Org. Chem.* **1979**, *44*, 2061.

(8) Rees, C. W.; Storr, R. C. *J. Chem. Soc. C* **1969**, 1474.

(9) Johnson, C. R.; Jonsson, E. U.; Bacon, C. C. *J. Org. Chem.* **1979**, *44*, 2055.

(10) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1964**, *86*, 1639.

(11) Schroeck, C. W.; Johnson, C. R. *J. Am Chem. Soc.* **1971**, *93*, 5305.

(12) This was necessary to remove the *Z* isomer which was generally present in 10–15%.

(13) Bartlett, P. A.; Green III, F. R.; Rose, E. H. *J. Am. Chem. Soc.* **1978**, *100*, 4852.

(14) Johnson, C. R.; Shanklin, J. R.; Kirchoff, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 6462.

**Table II. Chiral Derivatives from the Conjugative Adducts of 1 and 2 with Organometallic Reagents (RM)**

| substrate | RM | chiral deriv | $[\alpha]_D$, deg (solvent, c) obsd[a] | $[\alpha]_D$, deg (solvent, c) lit.[b] | % ee | config |
|---|---|---|---|---|---|---|
| 1 | $CH_3Li$ | **19a** | −51.6 (PhH, 0.02) | +57.23[c] (PhH, 9) | 90 | *R* |
| 1 | *n*-BuLi | **20a** | +20.6 (hexane, 0.01) | −23.1[d] (heptane, 2.4) | 89 | *S* |
| **2a** | *n*-BuLi | **20b** | −10.4 (hexane, 0.01) | −23.1[d] (heptane, 2.4) | 45 | *R* |
| **2a** | *n*-BuCu | **20a** | +20.6 (hexane, 0.015) | −23.1[d] (heptane, 2.4) | 89 | *S* |
| **2b** | *n*-$Bu_2CuLi$ | **19c** | −2.5 (acetone, 0.01) | −4.2[c] (neat) | 59 | *S* |
| **2b** | *n*-BuCu | **19b** | +4.6 (acetone, 0.01) | −4.2[c] (neat) | ≥90 | *R* |
| **2a** | $CH_3Cu$ | **19a** | −53.4 (PhH, 0.02) | +57.23[c] (PhH, 9) | 93 | *R* |
| **2c** | $CH_3Cu$ | **19b** | −4.7 (acetone, 0.03) | −4.2[c] (neat) | ≥92 | *S* |
| **2d** | $CH_3Cu$ | **19d** | −66.1 (PhH, 0.01) | −52.7[e] (neat) | ≥91 | *S* |

[a] All rotations measured at 20 ± 1 °C. [b] At 25 °C. [c] Abstracted from ref 1c. [d] Reference 16. [e] Reference 17.

that reductions of this type proceed with retention of configuration at sulfur (Scheme II). The stereochemical identity of **9** was determined from its independent synthesis from (−)-menthyl (*S*)-benzenesulfinate (**16**)[6] and *N*-lithio **7** (Scheme III)[7], which yielded (*SS*)-(+)-sulfinamide **9** ($[\alpha]^{18}_D$ +153.5° ($CHCl_3$, *c* 0.011)) contaminated with less than 5% (NMR analysis) of the diastereomeric (*SR*)-(−)-sulfinamide **8**. By analogy with previous reports,[7] this reaction was expected to occur with inversion of configuration at sulfur to give (*SS*)-sulfinamide **9**.

## Conjugate Addition Reactions of Vinyl Sulfoximines 1 and 2

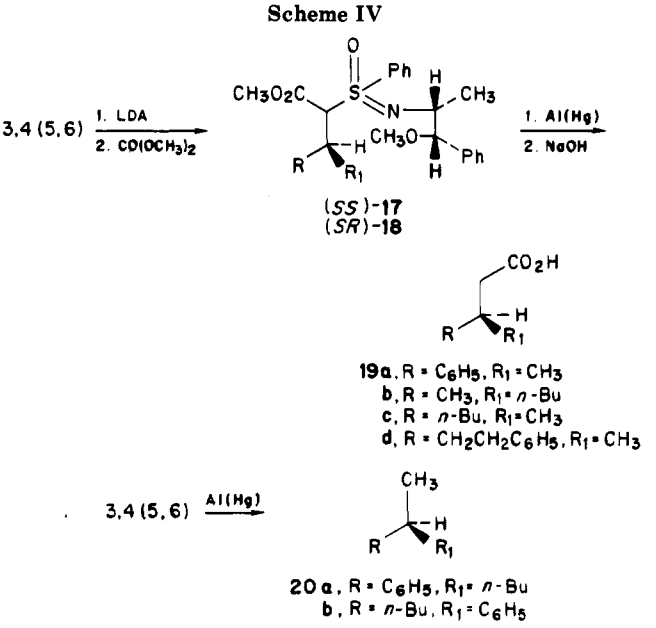
With the chiral vinyl sulfoximines **1** and **2** (R′ = $C_6H_5$, $CH_3$, *n*-Bu, $C_6H_5CH_2CH_2$) in hand we next examined their conjugate addition reactions with organometallic reagents. All conjugate addition reactions were performed in ether (0.2 M) and the diastereomeric product ratios were determined by HPLC analysis at two different wavelengths. The ratios for both the unpurified reaction mixtures and the chromatographed samples were found to be identical (±1%), and were independently confirmed by $^{13}C$ NMR analysis (Table I).

From methanol quenching experiments it was established that (*SS*)-vinyl sulfoximine **1** reacted at an appreciable rate ($t_{1/2}$ ca. 10 min) with MeLi (2.5 equiv) and *n*-BuLi (1.25 equiv) at −10 and −20 °C, respectively. Addition of MeLi to **1** at −25 °C followed by warming to −10 °C over 1 h resulted in a pale yellow solution which was kept at −10 °C for 1 h. The mixture was warmed slowly (1 h) to 0 °C and then quenched with methanol. This reaction proceeded with high diastereoselectivity and gave a mixture of **3** (M = H, R = $CH_3$) and **4** (M = H, R = $CH_3$) (**3**:**4** = 96:4) in 85% yield after chromatographic purification (Table I). The conjugate addition reaction of **1** with *n*-BuLi initially at −45 °C with gradual warming up to −25 °C (2 h) and then to 0 °C also proceeded with high diastereoselectivity (**3**:**4** = 95.5, M = H, R = *n*-Bu, Table I).

In contrast to **1**, the reaction of (*SR*)-vinyl sulfoximine **2a** with *n*-BuLi (−20 °C $t_{1/2}$ ca. 10 min) gave a mixture of diastereomeric adducts **5a** (M = H, R = *n*-Bu) and **6a** (M = H, R = *n*-Bu) with poor diastereoselectivity (**5a**:**6a** = 73:27, Table I). An enhanced diastereoselectivity was observed with the organocopper reagents *n*-$Bu_2CuLi$ (**5a**:**6a** = 86:14) and *n*-$Bu_2CuCNLi_2$ (**5a**:**6a** = 82:18),[15] both of which gave **5a** as the major diastereomeric product. Treatment of **2b** with *n*-$Bu_2CuLi$ gave a mixture (81:19) of **5b** (M = H, R = *n*-Bu) with **6b** (M = H, R = *n*-Bu) in which the former diastereomer predominated (Table I).

Surprisingly, the reaction of **2a** or **2b** with *n*-BuCu (5 equiv) proceeded with high diastereoselectivity (**5**:**6** ≤ 5:95) but with reverse π-face selectivity to that of *n*-$Bu_2CuLi$ and afforded **6a** (M = H, R = *n*-Bu) and **6b** (M = H, R = *n*-Bu) as the major adducts respectively. A similar π-face selectivity was observed in the reaction of **2** with $CH_3Cu$. The vinyl sulfoximines **2** (R′ = $C_6H_5$, *n*-Bu, and $CH_2CH_2C_6H_5$) underwent conjugate addition with $CH_3Cu$ with high diastereoselectivity (Table I) affording **6** (M = H, R = $CH_3$, R′ = $C_6H_5$, *n*-Bu, and $CH_2CH_2C_6H_5$), as the major diastereomeric adduct.

**Scheme IV**




## Proof of Stereochemistry

The stereochemistry of the newly created chiral carbon (C-2) in adducts **3**, **5**, and **6** was established by their conversion to 3-alkylalkanoic acids of known absolute configuration (Table II). For example, the adduct **3** (M = H, R = $CH_3$) was converted to (*R*)-(−)-3-phenylbutanoic acid (**19a**) (90% ee) by the following sequence (Scheme IV): (i) methoxycarbonylation with LDA in THF and dimethyl carbonate;[13] (ii) reduction with aluminum amalgam in aqueous HOAc and THF;[14] and (iii) basic hydrolysis.

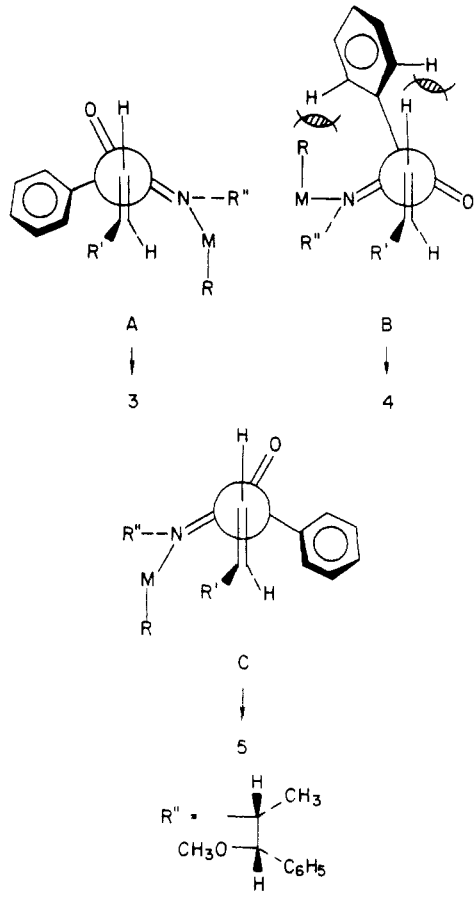
Simple reduction of **3** (M = H, R = *n*-Bu) and **5a** (M = H, R = *n*-Bu) with aluminum amalgam[14] (Scheme IV) furnished (*S*)-(+)-2-phenylhexane (**20a**) (89% ee) and (*R*)-(−)-2-phenylhexane (**20b**) (45% ee), respectively (Table II).

## Discussion

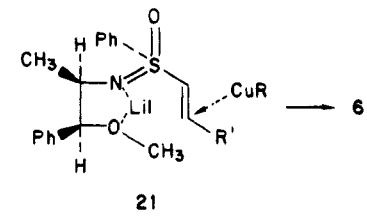
The stereochemical outcome of the reaction of **1** with alkyllithium reagents is readily rationalized in terms of the intermediate A (Scheme V). Assuming prior complexation of RM to the sulfoximine N of **1**, then one would expect reaction via the conformation A (Newman projection of

(15) Lipshutz, B. H.; Wilhelm, R. S.; Floyd, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 7672.

**Scheme V**



**Scheme VI**



1A) to be more favorable than B which involves more severe nonbonded steric interactions (Scheme V). On the other hand, the steric course of the reaction of **2** with alkyllithium and dialkylcopperlithium reagents is most readily explained by assuming that reaction proceeds via the conformation C (Newman projection of 2A) (Scheme V). Clearly, this argument does not necessarily require complexation of RM with both the sulfoximine N and the methoxy group of the auxilliary ligand. The stereochemical outcome of these reactions may be solely governed by the chirality at sulfur and is certainly predictable in terms of this chirality.

By the nature of their preparation (RLi + CuI (0.5 or 1.0 equiv), both $R_2CuLi$ and RCu (R = *n*-Bu, $CH_3$) contain 1 equiv of ether-soluble LiI, and consequently these reagents must compete with Li cation for chelation with **2**. The diastereoselectivity in these conjugate addition reactions should depend upon: (i) the magnitude of the equilibrium constants that relate the equilibrium concentrations of **2**, **2A**, and **21** in solution; and (ii) the magnitude of the rate constant for the conversion of **2A** to **5** (Scheme I) compared with that for the addition of $R_2CuLi$ (RCu) to **21** (Scheme VI).[18] It is not possible at this point to ascertain the relative magnitudes of these individual parameters. The major diastereomeric adduct **6**, from the reaction of **2** with RCu, however, can be considered to arise from nucleophilic addition of RCu to the LiI chelated intermediate **21** (Scheme VI) from the least sterically demanding $\pi$-face.

The reaction of **2b** with LiI "free" *n*-BuCu[19c] gave **6b** (M = H, R = *n*-Bu) as the major diastereomeric adduct (Table I) but proceeded with reduced diasteroselectivity (**5b**:**6b** = 33:67). This result was clearly consistent with the involvement of the LiI chelated species **21** in the above reactions.

These results demonstrate the potential of chiral vinyl sulfoximines for asymmetric synthesis. Adducts of high diastereomeric excess (>90%) can be realised and the chirality of the major diastereomeric product can be readily predicted from either the complexation control model A (C) (Scheme V, for RM = RLi, $R_2CuLi$) or from attack on the intermediate **21** (Scheme VI, RM = RCu). Reactions employing organocopper reagents most likely involve transfer of a copper(I) species (possibly $[R_2CuLi]_2{\cdot}n(LiI)$[19]) to the $\beta$-carbon of the C=C of **2** followed by reductive elimination with transfer of an alkyl group (*n*-Bu or $CH_3$) from copper to the $\beta$-carbon.[20] The application of these methods for the asymmetric synthesis of natural products is now under investigation.

## Experimental Section

$^1H$ NMR spectra were measured in $CDCl_3$ with $Me_4Si$ as internal standard, either on a Perkin-Elmer R32 spectrometer (90 MHz) or a JEOL JNM-FX200 spectrometer (200 MHz). $^{13}C$ NMR spectra were measured in $CDCl_3$ on either a JEOL JNM-PS-100 (25 MHz) or JNM-FX200 (50 MHz) spectrometer; the 77.0-ppm resonance of $CDCl_3$ was used as internal standard. Infrared spectra were recorded on a Perkin-Elmer 257 grating infrared spectrophotometer and are reported in wave numbers ($cm^{-1}$). Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-$cm^3$ capacity quartz cell (10-cm path length). Mass spectra were performed by the Monash University mass spectrometery service. Elemental analyses were performed by the Australian Mineral and Developmental Laboratories, Melbourne. Analytical HPLC analyses were performed on a Waters Associates instrument on a radial-pak silica column (5-mm i.d.) employing a Model 440 absorbance detector which allowed monitoring at 254 and 280 nm simultaneously. The solvent system was 0.5% isopropyl alcohol in hexane at 1 mL/min.

All reactions were conducted under a positive atmosphere of dry nitrogen. All organic extracts were dried over $Na_2CO_3$ unless otherwise noted, then evaporated with a Büchi rotary evaporator. Ether and THF were distilled from sodium benzophonene ketyl. All other solvents and reagents were purified and dried by standard procedures.[21] Analytical TLC was performed by using Merck silica gel 60 $F_{254}$ plastic-backed plates (layer thickness 0.2

(16) Lardicci, L.; Salvadori, P.; Caporusso, A. M.; Menicagli, R.; Belgodere, E. *Gazz. Chim. Ital.* **1972**, *102*, 64.

(17) Levene, P. A.; Rothen, A. *J. Org. Chem.* **1936**, *1*, 76.

(18) The diastereoselectivity (i.e., the ratio of products **5** and **6**) is given by ratio of **5**/**6** = $(K_1k_1/K_2k_2)(1/[LiI])$, where $K_1$, $K_2$ and $k_1$, $k_2$ are the equilibrium and rate constants for the following processes:

$$2 + RCu \overset{K_1}{\rightleftharpoons} 2A\ (M = Cu) \overset{k_1}{\longrightarrow} 5 \quad (i)$$

$$2 + LiI \overset{K_2}{\rightleftharpoons} 21 \quad (ii)$$

$$21 + RCu \overset{k_2}{\rightleftharpoons} 6$$

(I thank a referee for bringing this to my attention).

(19) (a) Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. (b) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (c) San Filippo, J. *Inorg. Chem.* **1978**, *17*, 275.

(20) (a) House, H. O.; Umen, M. J. *J. Org. Chem.* **1973**, *38*, 3893. (b) Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141.

(21) Perrin, D. D.; Armareg, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1980.

mm). Preparative TLC (PTLC) was performed by using Merck PLC plates (silica gel 60 $F_{254}$, 20 cm × 20 cm × 2 mm). Column chromatography was performed as described by Still.[22]

**(1*S*,2*R*)-2-Amino-1-methoxy-1-phenylpropane (7).** A solution of (+)-norephedrine (9.54 g, 63.15 mmol) (prepared from the commercially available hydrochloride salt (Aldrich Chemical Co., $[\alpha]_D$ +33.4° ($H_2O$, *c* 7)) by neutralization and then ether extraction) in THF (20 ml) was added dropwise to a suspension of "oil free" sodium hydride (from 4.34 g (90.42 mmol) of 50% NaH in mineral oil) in THF (80 mL) at 0 °C. After stirring at 23 °C for 0.5 h, the mixture was treated dropwise with methyliodide (4.1 mL, 66.30 mmol) and then heated to reflux for 1 h. The reaction mixture was then cooled, and then methanol was added to destroy the excess of NaH.

The mixture was poured into water (200 mL) and the aqueous solution was saturated with NaCl, then extracted with ether (3 × 100 mL). The combined extracts were dried and concentrated. Distillation gave **7** (8.0g, 70%) as a colorless liquid: bp 69–71 °C/2 mmHg; $^1$H NMR δ 7.25 (s, 5 H), 3.88 (d, *J* = 4.5 Hz, 1 H), 3.21 (s, 3 H), 3.1 (m, 1 H), 1.23 (s, 2 H), 1.04 (d, *J* = 5.6 Hz, 3 H).

**(*SR*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)benzenesulfinamide (8) and (*SS*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)benzenesulfinamide (9).** To a solution of benzenesulfinyl chloride (5.0 mL, 41.93 mmol) in $CH_2Cl_2$ (120 mL) at 0 °C was added dropwise a solution of **7** (4.48 mL, 27.15 mmol) and triethylamine (6.2 mL, 44.23 mmol) in $CH_2Cl_2$ (20 mL) dropwise over 15 min. The mixture was stirred at 0 °C for 1 h and then poured into ether (250 mL). The ether solution was washed with water (100 mL) and aqueous 10% $Na_2CO_3$ solution, dried, and concentrated, and residual triethylamine was removed under high vacuum. The crude product, which was a 3:1 mixture of diastereomers, was used in the next step without purification. For physical data of diastereomerically pure **8** and **9** see later experiments.

**Phenyl (1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)-benzenesulfonimidate (11).** The crude product (ca. 27.15 mmol) from the above experiment in THF (50 mL) at 0 °C was treated with freshly prepared *N*-Chlorobenzotriazole (4.58 g, 29.84 mmol). After stirring at 0 °C for 10 min, the mixture was warmed to 23 °C for 1 h. The mixture was then cooled to 0 °C, and a solution of sodium phenoxide (from phenol (7.66 g, 81.45 mmol) and NaH ("oil free", 1.97 g, 82.0 mmol)) in DMF/THF (40 mL, 1:1) was added dropwise over 15 min. The mixture was stirred at 0 °C for 10 min and then at 23 °C for 1 h.

The mixture was then diluted with ether (250 mL) and the solution was washed with water, aqueous 10% $Na_2CO_3$, and saturated aqueous $NH_4Cl$, dried, and concentrated. The crude product was chromatographed on silica gel (10% EtOAc/hexane, $R_f$ 0.38, 20% EtOAc/hexane) to give **11** (8.81 g, 85% from **7**) as a colorless viscous oil. An analytical sample was secured by short-path distillation (130 °C/1 mmHg): $^1$H NMR (1.8:1 mixture of diastereomers) δ 7.8–6.65 (m, 15 H), 4.12 (m, 2 H), 3.27 (s, 1.9 H, major diastereomer), 3.25 (s, 1.1 H, minor diastereomer), 1.44 (d, *J* = 5.4 Hz, 1.1 H), 1.12 (d, *J* = 5.4 Hz, 1.9 H); IR (film) 1590 (s), 1487 (s), 1450 (s), 1377 (s), 1304 (s), 1202 (s), 1175 (s), 1153 (s), 1097 (s), 843 (s), 777 (s), 758 (s), 735 (s), 689 (s); MS (CI, $CH_4$), *m/e* 382 (23% $(M + H)^+$), 350 (61% $(M + H - CH_3OH)^+$), 288 (56%, $(M + H - C_6H_5OH)^+$), 260 (74%), 121 (100%); exact mass, *m/e* 382.146 (calcd for $C_{22}H_{23}NO_3S$ + H, 382.1477).

Anal. Calcd for $C_{22}H_{23}NO_3S$: C, 69.26; H, 6.07; N, 3.67. Found: C, 69.07; H, 5.88; N, 3.80.

**(*SR*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)-*S*-methyl-*S*-phenylsulfoximine (13) and (*SS*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)-*S*-methyl-*S*-phenylsulfoximine (12).** To a solution of **11** (6.87 g, 18.03 mmol) in ether (60 mL) at 0 °C, was added MeLi (54.1 mmol, 1.6 M in ether) dropwise over 10 min. The mixture was stirred at 0 °C for 1.5 h and then quenched by the addition of methanol (5 mL). The ether solution was washed with water and 2 M NaOH, dried, and concentrated. Purification of the crude product by column chromatography on silica gel (EtOAc/hexane 1:1) gave **13** (1.596 g, $R_f$ 0.25, EtOAc/hexane 1:1) and **12** (0.723g, $R_f$ 0.20, EtOAc/hexane 1:1) as colorless oils.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

**13**: $[\alpha]^{18}_D$ +19.2° ($CH_2Cl_2$, *c* 0.015); $^1$H NMR: δ 7.82–7.12 (m, 10 H), 3.93 (d, *J* = 7.6 Hz, 1 H), 3.20 (s, 3 H), 3.02 (m, 1 H), 2.95 (s, 3 H), 1.33 (d, *J* = 6.4 Hz, 3 H); $^{13}$C NMR 141.01 (s), 139.01 (s), 132.21 (d), 128.87 (d), 128.02 (d), 127.84 (d), 127.72 (d), 127.11 (d), 89.07 (d), 57.34 (d), 56.43 (q), 45.57 (q), 21.49 (q); MS (CI, $CH_4$), *m/e* 304 (53%, $(M + H)^+$), 272 (26%, $(M + H - CH_3OH)^+$), 182 (100%); exact mass, *m/e* 304.137 (calcd for $C_{17}H_{21}NO_2S$ + H, 304.1371).

**12**: $[\alpha]^{18}_D$ +88.8° ($CH_2Cl_2$, *c* 0.024); $^1$H NMR δ 7.82–7.25 (m, 10 H), 4.16 (d, *J* = 5.9 Hz, 1 H), 3.38 (m, 1 H), 3.31 (s, 3 H), 2.74 (s, 3 H), 1.20 (d, *J* = 6.4 Hz, 3 H); $^{13}$C NMR 140.89 (s), 132.51 (d), 128.87 (s), 127.90 (d), 127.78 (d), 127.60 (d), 127.18 (d), 89.32 (d), 57.34 (d), 55.65 (q), 43.33 (q), 19.67 (q); IR ($CH_2Cl_2$) 1514 (s), 1448 (m), 1242 (s), 1143 (s), 1098 (m); MS (CI, $CH_4$), *m/e* 304 (29%, $(M + H)^+$), 272 (27%), 182 (100%); exact mass, *m/e* 304.138 (calcd for $C_{17}H_{21}NO_2S$ + H, 304.1371). Anal. Calcd for $C_{17}H_{21}NO_2S$: C, 67.29; H, 6.98; N, 4.62. Found: C, 66.92; H, 7.30; N, 4.23.

**(*SS*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)benzenesulfinamide (9).** A solution of **7** (124 mg, 0.75 mmol) in ether (2 mL) at 0 °C was treated dropwise with *n*-BuLi (0.75 mmol). After 15 min this solution was then transferred via cannula to a solution of (−)-menthyl (*S*)-benzenesulfinate (396 mg, 1.5 mmol) in ether (2 mL) at 0 °C. After 0.5 h at 0 °C, aqueous saturated $NH_4Cl$ (4 mL) was added and the layers were separated. The ether extract was dried and concentrated. $^1$H NMR analysis of the crude reaction mixture indicated only one diastereomeric product **9** had been formed.

Chromatographic purification on silica gel (EtOAc/hexane, 1:1) gave pure **9** (125 mg, 57.6%, $R_f$ 0.36) as a colorless oil: $[\alpha]^{22}_D$ +153.5° ($CHCl_3$, *c* 0.011); $^1$H NMR δ 7.75–7.1 (m, 10 H), 4.61 (br d, *J* ca. 8 Hz, NH, 1 H), 4.45 (d, *J* = 3.6 Hz, 1 H), 3.48 (m, 1 H), 3.32 (s, 3 H), 0.96 (d, *J* = 6.1 Hz, 3 H); IR (film) 3200 (br s), 1455 (m), 1395 (m), 1210 (m), 1115–1056 (br s), 983 (m), 936 (m), 896 (m), 754 (s), 736 (s), 705 (s).

**(*SR*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)benzenesulfinamide (8) from Reduction of 13.** A solution of **13** (100 mg, 0.33 mmol) in THF/$H_2O$ (5 mL, 9:1) was treated with aluminum amalgum[10] (268 mg, 30 equiv) at 23 °C for 6 h. The reaction mixture was diluted with ether (10 mL) and then filtered through a pad (10 mm) of Celite. The Celite was washed with several portions of ether, and the filtrate was washed with water, dried, and concentrated. Purification by PTLC (EtOAc/hexane 1:1) gave diastereomerically pure **8** (31.5 mg, 33%) as a colorless oil: $[\alpha]^{19}_D$ −62.2° ($CHCl_3$, *c* 0.0063); $^1$H NMR δ 7.8–7.1 (m, 10 H), 4.45 (br d *J* = ca. 8 Hz, 1 H, N*H*), 4.26 (d, *J* = 3.4 Hz, 1 H), 3.27 (s, 3 H), 1.12 (d, *J* = 6.6 Hz, 3 H); $^{13}$C NMR 141.8, 138.22, 131.85, 130.76, 128.71, 128.25, 127.59, 126.82, 125.92, 86.61, 57.37, 55.06, 16.24; IR (film) 3210 (br s), 1450 (m), 1379 (m), 1210 (m), 1130–1020 (br s), 984 (m), 939 (m), 895 (m).

**(*SS*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)benzenesulfinamide (9) from the Reduction of 12.** Sulfinamide **9** was prepared in 31% yield from the reduction of **12** with aluminum amalgum as described above.

**Synthesis of Vinyl Sulfoximines 1, 2 (R′ = $C_6H_5$, $CH_3$, *n*-Bu, $C_6H_5CH_2CH_2$). (*SS*,1*S*,2*R*)-*N*-(1-Methoxy-1-phenyl-2-propyl)-*S*-(2-phenylethenyl)-*S*-phenylsulfoximine (1). A Typical Procedure.** A solution of **12** (400mg, 1.32 mmol) in THF (2.5 mL) was added dropwise to a solution of lithium diisopropylamide (1.58 mmol) in THF (5 mL) at 0 °C. After 0.5 h, the solution was cooled to −78 °C and benzaldehyde (1.58 mmol, 0.161 mL) was added. After 10 min the reaction mixture was warmed slowly (45 min) to 0 °C and then quenched with aqueous saturated $NH_4Cl$ (10 mL). The product was extracted with ether (2 × 15 mL) and the combined extracts were dried and concentrated. Purification of the crude product on silica gel (20% EtOAc/hexane) ($R_f$ 0.55, EtOAc/hexane 1:1) gave **15** (380 mg, 70%) as a colorless oil: IR (film) 3650–3100 (br s), 1454 (m), 1374 (m), 1243 (s), 1130 (s), 1100 (s), 1080 (s), 1047 (s), 743 (s), 703 (s); $^1$H NMR showed ca. 1:1 mixture of diastereoisomers; MS (CI, $CH_4$), *m/e* 410 (20%, $(M + H)^+$), 392 (3%, $(M + H - H_2O)^+$), 378 (12%, $(M + H - CH_3OH)^+$), 288 (100%); exact mass, *m/e* 410.179 (calcd for $C_{24}H_{27}NO_3S$ + H, 410.1789).

A solution of **15** (380 mg, 0.929 mmol) and triethylamine (4.65 mmol, 0.648 mL) in $CH_2Cl_2$ (5 mL) at 0 °C was treated dropwise with methanesulfonyl chloride (2.79 mmol, 0.216 mL) over 10 min. After 0.5 h the mixture was treated with 1,8-diazabicyclo-[5.4.0]undec-7-ene (5.57 mmol, 0.833 mL) and stirring was continued at 23 °C for 12 h. The reaction mixture was then diluted with ether (25 mL), and the solution was washed with water, aqueous saturated $NH_4Cl$, and aqueous 10% $Na_2CO_3$, dried, and concentrated. Purification of the crude product by chromatography on silica gel (25% EtOAc/hexane) gave **1** (210 mg, 58%) as a colorless oil: $^1H$ NMR $\delta$ 7.76 (dd, $J$ = 1.2, 7.8 Hz, 1 H), 7.65–7.20 (m, 15 H), 5.62 (d, $J$ = 15.4 Hz, 1 H), 4.06 (d, $J$ = 8.1 Hz, 1 H), 3.51 (m, 1 H), 3.25 (s, 3 H), 1.43 (d, $J$ = 6.1 Hz, 3 H); $^{13}C$ NMR 142.83 (s), 141.86 (d), 140.40 (s), 132.82 (s), 132.45 (d), 130.45 (d), 128.87 (d), 128.33 (d), 128.15 (d), 127.84 (d), 127.42 (d), 127.30 (d), 89.68 (d), 57.22 (q), 55.83 (d), 22.33 (q); IR ($CH_2Cl_2$) 1613 (m), 1492 (m), 1446 (m), 1243 (s), 1138 (s), 1104 (s); MS (CI, $CH_4$) $m/e$ 392 (22%, $(M + H)^+$), 376 (32%), 360 (28% $(M + H - CH_3OH)^+$), 270 (100%); exact mass, $m/e$ 392.169 (calcd for $C_{24}H_{25}NO_2S$ + H, 392.1684).

**2 (R′ = $C_6H_5$)**: $^1H$ NMR $\delta$ 7.6–7.2 (m, 16 H), 6.63 (d, $J$ = 14.2 Hz, 1 H), 4.03 (d, $J$ = 6.5 Hz, 1 H), 3.25 (m, 1 H), 3.23 (s, 3 H), 1.47 (d, $J$ = 6.2 Hz, 3 H); $^{13}C$ NMR 142.04, 141.19, 139.25, 132.82, 132.03, 130.57, 128.81, 128.27, 128.15, 127.96, 127.30, 89.32, 57.22, 56.07, 21.91; IR ($CH_2Cl_2$) 1610 (m), 1489 (m), 1445 (m), 1238 (s), 1130 (s), 1098 (s), 970 (m), 910 (m), 820 (m); MS (CI, $CH_4$), $m/e$ 392 (8%, $(M + H)^+$), 360 (9%, $(M + H - CH_3OH)^+$), 270 (64%), 41 (100%); exact mass, $m/e$ 392.167 (calcd for $C_{24}H_{25}NO_2S$ + H, 392.1684).

**2 (R′ = $CH_3$)**: $^1H$ NMR $\delta$ 7.8–7.0 (m, 10 H), 6.36 (dq, $J$ = 6.4, 14.5 Hz, 1 H), 6.13 (dd, $J$ = 1.5, 14.5 Hz, 1 H), 3.96 (d, $J$ = 6.8 Hz, 1 H), 3.2 (m, 1 H), 3.19 (s, 3 H), 1.78 (dd, $J$ = 1.5, 6.4 Hz, 3 H), 1.35 (d, $J$ = 6.2 Hz, 3 H); $^{13}C$ NMR 141.62, 141.19, 139.25, 131.85, 128.75, 128.09, 127.72, 127.18, 125.90, 89.32, 57.22, 56.01, 21.91, 17.06; IR (film) 1453 (m), 1255 (s), 1145 (s), 1105 (s), 820 (m), 755 (s), 712 (s); MS (CI, $CH_4$), $m/e$ 330 (100%, $(M + H)^+$); exact mass, $m/e$ 330.1515 (calcd for $C_{19}H_{23}NO_2S$ + H, 330.1527).

**2 (R′ = *n*-Bu)**: $^1H$ NMR $\delta$ 7.6–7.0 (m, 10 H), 6.75 (m, 1 H), 6.12 (d, $J$ = 13.5 Hz, 1 H), 3.96 (d, $J$ = 8 Hz, 1 H), 3.22 (s, 3 H), 3.20 (m, 1 H), 2.36–2.0 (m, 2 H), 1.6–1.1 (m, 4 H), 1.37 (d, $J$ = 6 Hz, 3 H), 0.88 (t, 3 H); $^{13}C$ NMR 146.47, 141.19, 131.73, 140.39, 139.12, 128.69, 128.02, 128.83, 89.26, 57.16, 56.01, 30.89, 29.68, 22.09, 21.90, 13.66; IR (film) 1440 (m), 1240 (s), 1127 (s), 1095 (s), 907 (s), 820 (m), 730 (s), 670 (s); MS (CI, $CH_2$), $m/e$ 372 (13%, $(M + H)^+$), 340 (14%, $(M + H - CH_3OH)^+$, 250 (100%); exact mass, $m/e$ 372.200 (calcd for $C_{22}H_{29}NO_2S$ + H, 372.1997).

**2 (R′ = $C_6H_5CH_2CH_2$)**: $^1H$ NMR $\delta$ 7.6–6.9 (m, 15 H), 6.79 (m, 1 H), 6.09 (d, $J$ = 14.5 Hz, 1 H), 3.75 (d, $J$ = 6.8 Hz, 1 H), 3.20 (s, 3 H), 3.18 (m, 1 H), 2.9–2.3 (m, 4 H), 1.34 (d, $J$ = 5.8 Hz, 3 H); $^{13}C$ NMR 145.13, 141.19, 140.16, 139.19, 131.85, 131.24, 129.84, 128.69, 128.39, 127.72, 127.18, 126.14, 89.32, 57.22, 56.01, 33.86, 33.01, 21.85; IR (film) 1632 (m), 1608 (m), 1495 (m), 1454 (s), 1380 (s), 1245 (s), 1139 (s), 1098 (s), 820 (s), 746 (s), 690 (s); MS (CI, $CH_4$), $m/e$ 420 (100%, $(M + H^+)$; exact mass, $m/e$ 420.2010 (calcd for $C_{26}H_{29}NO_2S$ + H, 420.1997).

**Reaction of 1 and 2 with Organometallic Reagents. A General Procedure. (*SR*,1*S*,2*R*,2′*S*)-*N*-(1-Methoxy-1-phenyl-2-propyl)-*S*-phenyl-*S*-(2′-methyl-1′-hexyl)sulfoximine (6c) (M = H, R = $CH_3$).** To a stirred suspension of CuI (486 mg, 2.56 mmol) in ether (12.8 mL) at −25 °C, was added MeLi (2.56 mmol). After 0.5 h, a solution of vinyl sulfoximine **2c** (190 mg, 0.511 mmol) in ether (2 mL) was added, and the mixture was stirred at −25 °C for 1 h. The reaction mixture was then allowed to warm to 0°C over a period of 1 h. After 1 h at 0 °C, the reaction mixture was quenched with aqueous saturated $NH_4Cl$ (20 mL). The layers were separated and the ether layer was dried and concentrated. Analysis of the crude reaction mixture by HPLC indicated two compounds at retention volumes 2.9 and 3.4 in a ratio of 3.5 to 96.5 respectively. Purification of the crude product by PTLC (40% EtOAc/hexane) gave adduct **6c** (M = H, R = $CH_3$, 142 mg, 72%) as a colorless oil. The HPLC analysis of the purified material was essentially identical with that described above.

Conjugate addition reactions involving $CH_3Li$ (2.5 equiv) were performed essentially as described above. Conjugate addition reactions employing *n*-$Bu_2CuLi$ (5 equiv, prepared at −40 °C for 1 h), *n*-BuCu (5 equiv), and *n*-BuLi (1.5 equiv) were initiated at 45 °C, stirred at −45 °C for 1 h, and then allowed to warm to −25 °C over 1 h. The reaction mixture was then stirred at −25 °C for 2 h and was then allowed to warm to 0 °C (over 1 h) and was immediately quenched. Yields for all conjugate addition reactions are listed in Table I.

**3 (M = H, R′ = $C_6H_5$, R = $CH_3$)**: $^1H$ NMR $\delta$ 7.83–6.97 (m, 15 H), 4.15 (d, $J$ = 5.9 Hz, 1 H), 3.50–3.05 (m, 3 H), 3.29 (s, 3 H), 2.91 (m, 1 H), 1.10 (d, $J$ = 6.3 Hz, 3 H), 1.05 (d, $J$ = 6.8 Hz, 3 H); $^{13}C$ NMR 144.98 (s), 141.6 (s), 141.15 (s), 132.30 (d), 128.83 (d), 128.57 (d), 128.51 (d), 127.86 (d), 127.19 (d), 126.78 (d), 126.49 (d), 89.73 (d), 62.96 (t), 57.41 (q), 54.81 (d), 34.98 (d), 21.76 (q), 19.33 (q); IR (film) 1602 (m), 1495 (m), 1455 (s), 1353 (s), 1240 (br s), 1170–1025 (br s), 828 (m), 763 (s), 702 (s); MS (CI, $CH_4$), $m/e$ 408 (54%, $(M + H)^+$), 376 (22%, $(M + H - CH_3OH)^+$), 286 (100%).

**3 (M = H, R′ = $C_6H_5$, R = *n*-Bu)**: $^1H$ NMR $\delta$ 7.80–6.90 (m, 15 H), 4.15 (d, $J$ = 5.6 Hz, 1 H), 3.48–3.10 (m, 3 H), 3.29 (s, 3 H), 3.00 (m, 1 H), 1.58–0.75 (6 H, methylene envelope), 1.10 (d, $J$ = 6.4 Hz, 3 H), 0.71 (t, $J$ = 6.8 Hz, 3 H); $^{13}C$ NMR 142.90, 141.00, 140.83, 132.31, 128.76, 128.64, 128.28, 127.81, 127.69, 127.52, 127.16, 126.43, 89.45, 61.43, 57.42, 54.99, 40.46, 35.67, 28.89, 22.29, 19.03, 13.78; IR (film) 1603 (m), 1495 (m), 1455 (s), 1374 (m), 1225 (s), 1180–1065 (br s), 875 (s), 700 (s); MS (CI, $CH_4$), $m/e$ 450 (29%, $(M + H)^+$), 418 (13%, $(M + H - CH_3OH)^+$), 328 (100%).

**5 (M = H, R′ = $C_6H_5$, R = $CH_3$)**: $^1H$ NMR $\delta$ 7.45–6.75 (m, 15 H), 3.89 (d, $J$ = 7.1 Hz, 1 H), 3.50–2.90 (m, 4 H), 3.18 (s, 3 H), 1.34 (d, $J$ = 5.6 Hz, 3 H), 1.31 (d, $J$ = 5.1 Hz, 3 H); $^{13}C$ NMR 140.0, 141.1, 137.8, 131.83, 129.15, 128.59, 128.30, 128.06, 127.72, 127.13, 126.72, 126.36, 89.09, 63.50, 57.13, 56.15, 34.87, 22.46, 21.64; MS (CI, $CH_4$), $m/e$ 408 (25% $(M + H)^+$), 286 (100%); exact mass, $m/e$ 408.200 (calcd for $C_{25}H_{29}NO_2S$ + H, 408.1997).

**5 (M = H, R′ = $C_6H_5$, R = *n*-Bu)**: $^1H$ NMR $\delta$ 7.45–6.75 (m, 15 H), 3.87 (d, $J$ = 7.8 Hz, 1 H) 3.50–2.90 (m, 4 H), 3.20 (s, 3 H), 1.83–0.75 (6 H, methylene envelope), 1.29 (d, $J$ = 6.3 Hz, 3 H), 1.13 (t, 3 H); $^{13}C$ NMR 143.07, 141.24, 138.74, 129.27, 129.13, 128.69, 128.42, 128.30, 128.20, 128.06, 127.89, 127.67, 127.62, 89.28, 63.50, 57.13, 56.06, 40.29, 35.62, 28.98, 22.22, 21.81, 13.80; IR (film) 1605 (m), 1496 (m), 1452 (s), 1250 (br s), 1140 (s), 1099 (s), 915 (m), 763 (s), 737 (s), 702 (s); MS (CI, $CH_4$), $m/e$ 450 (28%, $(M + H)^+$), 418 (17%, $(M + H - CH_3OH)^+$), 328 (84%), 91 (100%).

**5 (M = H, R′ = $CH_3$, R = *n*-Bu)**: $^1H$ NMR $\delta$ 7.58–7.02 (m, 10 H), 3.90 (d, $J$ = 7.3 Hz, 1 H), 3.20 (s, 3 H), 3.25–2.82 (m, 3 H), 1.78 (m, 1 H), 1.38–0.75 (6 H, methylene envelope), 1.31 (d, $J$ = 6.3 Hz, 3 H), 1.00 (d, $J$ = 6.6 Hz, 3 H), 0.74 (t, 3 H); $^{13}C$ NMR 141.12, 138.44, 131.95, 129.15, 128.71, 128.03, 127.60, 127.04, 89.11, 62.99, 57.08, 56.18, 36.11, 28.20, 28.11, 22.29, 21.71, 19.96, 13.83; IR (film) 1496 (s), 1251 (br s), 1146 (br s), 1104 (br s), 747 (s), 704 (s); MS (CI, $CH_4$), $m/e$ 388 (28%, $(M + H)^+$), 356 (18%, $(M + H - CH_3OH)^+$), 266 (100%), 125 (95%); exact mass, $m/e$ 388.230 (calcd for $C_{23}H_{33}NO_2S$ + H, 388.231).

**6 (M = H, R′ = $C_6H_5$, R = *n*-Bu)**: $^1H$ NMR $\delta$ 7.75–6.8 (m, 10 H), 3.88 (d, $J$ = 7.6 Hz), 3.64–2.80 (m, 3 H), 3.18 (s, 3 H), 1.85 (m, 1 H), 1.29 (d, $J$ = 6.1 Hz), 1.7–0.95 (m, 6 H), 0.78 (t, $J$ = 6.6 Hz, 3 H); $^{13}C$ NMR 142.26, 141.10, 137.87, 131.59, 129.15, 128.42, 128.06, 127.69, 127.47, 127.11, 126.23, 89.16, 62.55, 57.18, 56.01, 40.32, 36.30, 29.08, 22.93, 21.66, 13.85; MS (CI, $CH_4$), $m/e$ 450 (22%, $(M + H)^+$), 418 (18%), 91 (100%).

**6 (M = H, R′ = $CH_3$, R = *n*-Bu)**: $^1H$ NMR $\delta$ 7.70–7.01 (m, 10 H), 3.90 (d, $J$ = 7.6 Hz, 1 H), 3.32–2.89 (m, 2 H), 3.20 (s, 3 H), 2.73 (d, d, $J$ = 7.6, 14.2 Hz, 1 H), 2.02 (m, 1 H), 1.54–1.0 (m, 6 H), 1.32 (d, $J$ = 5.9 Hz, 3 H), 0.86 (t, 3 H), 0.77 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR 141.22, 138.86, 131.95, 129.15, 128.76, 128.13, 127.62, 127.08, 89,24, 63.45, 57.108 56.13, 36.35, 28.47, 28.28, 22.51, 21.83, 19.89, 13.95; MS (CI, $CH_4$), $m/e$ 388 (18%, $(M + H)^+$), 356 (22%, $(M + H - CH_3OH)^+$) 266 (79%), 125 (100%).

**6 (M = H, R′ = $C_6H_5CH_2CH_2$, R = $CH_3$)**: $^1H$ NMR $\delta$ 7.50–6.90 (m, 15 H), 3.89 (d, $J$ = 7.8 Hz, 1 H), 3.20 (s, 3 H), 3.20–2.90 (m, 3 H), 2.38 (t, $J$ = 8.1 Hz, 2 H), 1.90 (m, 1 H), 1.59–1.19 (m, 2 H), 1.32 (d, $J$ = 6.4 Hz, 3 H), 1.08 (d, $J$ = 6.6 Hz, 3 H); $^{13}C$ NMR 141.3, 141.19, 138.44, 132.10, 129.25, 128.88, 128.23, 128.13, 127.69, 127.16, 125.72, 89.16, 62.99, 57.18, 56.25, 38.25, 32.51, 28.06, 21.78, 19.96; IR (film) 1444 (m), 1245 (s), 1135 (s), 1100 (s), 733 (s), 697 (s);

MS (CI, $CH_4$), $m/e$ 436 (100%, $(M + H)^+$); exact mass, $m/e$ 436.2283 (calcd for $C_{27}H_{33}NO_2S$ + H, 436.2310).

**Conversion of Adducts 3 and 6 to Chiral Carboxylic Acids. (1) Synthesis of 17 and 18. Methyl (*SR*,1′*S*,2′*R*,3*S*)-2-(*N*-(1′-Methoxy-1′-phenyl-2′-propyl)benzenesulfonimidoyl)-3-phenylbutanoate (18). A Typical Procedure.** To a solution of **6** (M = H, R′ = $C_6H_5$, R = $CH_3$) (160 mg, 0.147 mmol) in THF (2 mL) at 0 °C, was added LDA (0.147 mmol) in THF (0.3 M). After 10 min, a solution of dimethylcarbonate in THF (0.1 M, 0.74 mL, 0.074 mmol) was added, and the reaction mixture was stirred at 0°C for 15 min. The above procedure was repeated three more times using half the previous amounts of the above reagents each successive time as described by Bartlett[13].

The reaction mixture was quenched with aqueous saturated $NH_4Cl$ (5 mL) and extracted with ether (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated. Purification of the crude product by PTLC (EtOAc/hexane, 1:1) gave **18** ($R_1$ = $CH_3$, R = $C_6H_5$) (1.39 mg, 76%) as a mixture (ca. 1:1) of diastereomers: $^1H$ NMR (in part) $\delta$ 3.86 (s, 3 H), 3.18 (s, 1.5 H), 3.16 (s, 1.5 H); IR (film) 1744 (s), 1445 (s), 1257 (br s), 1180–1060 (br s), 915 (s), 757 (s), 703 (s); MS (CI, $CH_4$), $m/e$ 466 (18%, $(M + H)^+$), 434 (8%, $(M + H - CH_3OH)^+$), 344 (34%), 286 (22%), 121 (100%); exact mass $m/e$, 466.235 (calcd for $C_{27}H_{31}NO_4S$ + H, 466.205).

**17 (R = $C_6H_5$, $R_1$ = $CH_3$) (yield 68%):** $^1H$ NMR (in part) $\delta$ 3.66 (s, 3 H), 3.21 (br s, 3 H); IR (film) 1725 (s), 1452 (s), 1248 (s), 1135 (s), 830 (m), 762 (s), 702 (s).

**18 (R = *n*-Bu, $R_1$ = $CH_3$) (yield 82%):** $^1H$ NMR (in part) $\delta$ 3.68 (s, 3 H), 3.19 (br s, 3 H), 1.27 (d, $J$ = 5.6 Hz, 3 H); IR (film) 1745 (s), 1446 (s), 1256 (s), 1180 – 1065 (br s), 760 (s), 735 (s), 704 (s); MS (CI, $CH_4$), $m/e$ 446 (9%, $(M + H)^+$), 414 (5%, $(M + H - CH_3OH)^+$), 324 (83%), 125 (100%); exact mass, $m/e$ 445.235 (calcd for $C_{25}H_{35}NO_4S$ + H, 446.236).

**18 ($R_1$ = $CH_3$, R = $C_6H_5CH_2CH_2$) (yield 78%):** $^1H$ NMR (in part) $\delta$ 3.69 (s, 3 H), 3.21 (br s,d 3 H), 2.41 (t, $J$ = 7.5 Hz, 2 H), 1.02 (d, $J$ = 5.9 Hz, 3 H).

**(2) Conversion of 17 and 18 to Chiral Carboxylic Acids. (*R*)-(−)-3-Phenylbutanoic Acid from 18 ($R_1$ = $CH_3$, R = $C_6H_5$). A Typical Procedure.** To a rapidly stirred solution of **18** ($R_1$ = $CH_3$, $R_2$ = $C_6H_5$) (260 mg) at 0 °C in THF/$H_2O$/HOAc (9 mL, 2:1:1) was added aluminum amalgum[14] (prepared by stirring aluminum powder with $HgCl_2$ solution (2%, 30 mL) for 2 min and then washing with $H_2O$ (2 × 20 mL)). The mixture was warmed to 23 °C and was stirred for a further 1.5 h, then diluted with ether (20 mL), and filtered through a pad of celite. The filtrate (ca. 50 mL) was washed with water (2 × 25 7L), 2 M NaOH (2 × 25 mL), dried ($mgSO_4$) and concentrated. Purification by PTLC (20% EtOAc/hexane) gave methyl(*R*)-(−)-3-phenylbutanoate (78 mg, 78%) as a colorless oil: $^1H$ NMR $\delta$ 7.17 (s, 5 H), 3.59 (s, 3 H), 3.23 (m, 1 H), 2.58 (m, 2 H), 1.29 (d, $J$ = 6.5 Hz, 3 H). Finally, hydrolysis (2 M NaOH, $CH_3OH$, 1:2, 23 °C, 2 h) and then purification by PTLC (EtOAc/hexane, 1:1) gave (*R*)-(−)-3-phenylbutanoic acid (60mg, 85%), which was identical with an authentic racemic sample from $^1H$ NMR and IR analysis. Short-path distillation (130 °C (bath temp)/1mmHg) secured a pure sample. $[\alpha]^{19}_D$ −53.4° (benzene, $c$ 0.02). Optical rotations for other chiral carboxylic acids are given in Table II.

(*S*)-(−)-3-Methylheptanoic acid from **19d**: $^1H$ NMR $\delta$ 2.36 (dd, $J$ = 5.9, 14.8 Hz, 1 H), 2.18 (dd, $J$ = 8.1, 14.8 Hz, 1 H), 1.97 (m, 1 H), 1.5–1.0 (m, 6 H), 0.97 (d, $J$ = 6.6 Hz, 3 H), 0.89 (t, 3 H).

**(*S*)-(−)-3-Methyl-5-phenylpentanoic acid (19d):** $^1H$ NMR $\delta$ 7.45–7.08 (m, 5 H), 2.63 (m, 2 H), 2.42 (dd, $J$ = 5.9, 14.8 Hz, 1 H), 2.21 (dd, $J$ = 7.8, 14.8 Hz, 1 H), 2.02 (m, 1 H), 1.8–1.4 (m, 2 H), 1.04 (d, $J$ = 6.6 Hz, 3 H).

**(*S*)-(+)- and (*R*)-(−)-2-Phenylhexane (20a and 20b) from Reduction of 3a and 5a.** The title compounds were prepared from **3a** and **5a** by reduction with aluminum amalgum as described above, except that pentane was used instead of ether. The crude product purified by column chromatography (silica gel, pentane) and then bulb-to-bulb distillation (100 °C (bath temp)/20mmHg): $^1H$ NMR $\delta$ 7.34–7.01 (m, 5 H), 2.66 (m, 1 H), 1.5–1.1 (m, 6 H), 1.22 (d, $J$ = 7.3 Hz, 3 H), 0.85 (t, 3 H).

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**Registry No.** 1, 99439-67-5; **2a**, 99493-70-6; **2b**, 99439-68-6; **2c**, 99439-69-7; **2d**, 99439-70-0; **3a** (M = H, R = $CH_3$), 99439-71-1; **3a** (M = H, R = Bu), 99439-72-2; **4a** (M = H, R = $CH_3$), 99493-71-7; **4a** (M = H, R = Bu), 99493-72-8; **5a** (M = H, R = Bu), 99493-73-9; **5a** (M = H, R = $CH_3$), 99493-76-2; **5b** (M = H, R = Bu), 99439-73-3; **5d** (M = H, R = $CH_3$), 99439-74-4; **6a** (M = H, R = Bu), 99493-74-0; **6a** (M = H, R = $CH_3$), 99493-77-3; **6b** (M = H, R = Bu), 99493-75-1; **6d** (M = H, R = $CH_3$), 99493-78-4; **7**, 99493-59-1; **8**, 99439-59-5; **9**, 99493-60-4; (*SR*)-**10**, 99439-60-8; (*SS*)-**10**, 99493-61-5; (*SR*)-**11**, 99493-62-6; (*SS*)-**11**, 99439-61-9; **12**, 99439-62-0; **13**, 99493-63-7; (*R*)-**14** (R′ = Ph), 99493-65-9; (*S*)-**14** (R′ = Ph), 99493-66-0; (*R*)-**14** (R′ = $CH_3$), 99493-67-1; (*S*)-**14** (R′ = $CH_3$), 99439-64-2; (*R*)-**14** (R′ = Bu), 99439-65-3; (*S*)-**14** (R′ = Bu), 99493-68-2; (*R*)-**14** (R′ = $(CH_2)_2Ph$), 99493-69-3; (*S*)-**14** (R′ = $(CH_2)_2Ph$, 99439-66-4; (*R*)-**15**, 99439-63-1; (*S*)-**15**, 99493-64-8; (3*R*)-**17a**, 99493-79-5; (3*S*)-**17a**, 99439-75-5; (3*R*)-**18b**, 99493-82-0; (3*S*)-**18b**, 99493-81-9; (3*R*)-**18a**, 99493-83-1; (3*S*)-**18a**, 99493-84-2; (3*R*)-**18c**, 99493-80-8; (3*S*)-**18c**, 99439-76-6; (3*R*)-**18d**, 99493-85-3; (3*S*)-**18d**, 99439-77-7; **19a**, 772-14-5; **19a** (methyl ester), 1472-07-7; **19b**, 57403-74-4; **19b** (methyl ester), 99439-80-2; **19c**, 59614-85-6; **19c** (methyl ester), 99439-79-9; **19d**, 41927-32-6; **19d** (methyl ester), 99439-81-3; **20a**, 99439-78-8; **20b**, 36667-56-8; $PhSO_2Cl$, 4972-29-6; PhCHO, 100-52-7; $CH_3CHO$, 75-07-0; BuCHO, 110-62-3; $Ph-(CH_2)_2CHO$, 104-53-0; $CH_3Li$, 917-54-4; BuLi, 109-72-8; $Bu_2CuLi$, 24406-16-4; $Bu_2CuCNLi_2$, 80473-69-4; BuCu, 34948-25-9; $CH_3Cu$, 1184-53-8; (+)-norephedrine, 37577-28-9; (−)-menthyl (*S*)-benzenesulfinate, 62319-27-1.