Enantioselective Carbon−Carbon Bond Formation via S_N2' Displacements of Acyclic Allylic Mesylates[1]

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The copper-mediated S_N2' displacement of enantiomerically pure allylic mesyloxy vinyl sulfoxides takes place with high yields and stereoselectivities. In these adducts, the newly created chiral center is adjacent to a vinyl sulfoxide functionality which should allow for subsequent chirality transfer operations. Alternatively, enantiopure alkenyl sulfones and alkenes bearing an allylic stereocenter are readily available from these adducts with high geometric control. The S_N2' displacements of structurally related mesyloxy sulfides and sulfones with organocuprates have been examined. From a single enantiomer at the allylic alcohol position, the absolute configuration of the new chiral center may be controlled by adjusting the oxidation level on sulfur.

Acyclic stereocontrol[2] remains a challenging problem in synthesis, especially when efficient methods for enantiocontrolled carbon−carbon bond formation are required. While enantiomerically pure sulfoxides are valuable synthetic intermediates[3] for a variety of processes, including enantiocontrolled carbon−carbon bond formation by conjugate addition in cyclic cases,[4] their usefulness for such alkylations in acyclic cases has not been firmly established.[4f] Moreover, most sulfoxide-directed alkylation protocols utilize the valuable sulfur auxiliary just once, and this limits the synthetic versatility of the process.

With this background in mind, we considered the design of a vinyl sulfoxide system which would allow for subsequent chirality transfer operations after the crucial alkylation step and thus significantly enhance the synthetic versatility of the process. To this end, and in connection with our interest in the use of vinyl sulfoxides in synthesis and in organocopper chemistry,[5] we considered that allylic sulfinyl alcohols **A**[6] (Scheme 1) could lead to the desired targets **B** ($n = 1$), if conditions to carry out the proposed S_N2' process[7] in a highly regio- and stereoselective fashion were developed. It should be pointed out that systems such as **B** would not just allow for subsequent sulfoxide ($n = 1$)-directed chemistry but also, if desired, the related sulfones ($n = 2$) and sulfides

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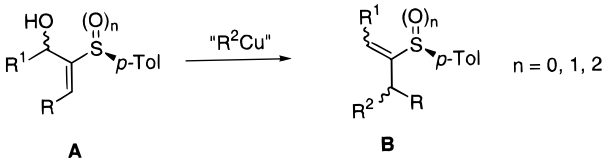
Scheme 1



(n = 0) should be readily available, as well as the corresponding desulfurized enantiopure alkenes.

In this paper we report a full account of our efforts in this field which have resulted in an efficient methodology to prepare enantiomerically pure trisubstituted vinyl sulfoxides, as well as the corresponding sulfide and sulfone analogs, **B**. A remarkable feature of this methodology is that the absolute configuration of the newly created chiral center may be controlled by adjusting the oxidation state of the sulfur atom.

Preparation of Substrates. Scheme 2 shows the straightforward preparation of the required diastereomeric alcohols **2** and **3**, based on the acidity of the α hydrogen of vinyl sulfoxides[6] and subsequent trapping with an aldehyde. This process took place in good yield but with low diastereoselectivity;[8] however, all isomeric alcohols **2** and **3** were separated readily by column chromatography.

While at this early stage of the project, access to both diastereomeric series was in fact desirable, we also explored the interconversion of diastereomeric alcohols **2a** and **3a**. Oxidation of either isomer to keto vinyl sulfoxide **6**[9] proceeded smoothly (MnO_2, CH_2Cl_2, rt, 77%), but we were unable to effect a clean stereoselective 1,2-reduction under a variety of reaction conditions.[10] Instead, complex mixtures of 1,4, 1,2, and complete reduction products were obtained. Nevertheless, both isomers could be interconverted via a Mitsunobu protocol[11] (Ph_3P, DEAD, $PhCO_2H$, THF, rt; NaOMe, MeOH; 70% two steps) in good overall yield.

Cuprate S_N2' Displacements on Sulfoxides. At the initial stage of this investigation we focused on phenyl-substituted substrates **2a**, **3a**, and we attempted to carry out the allylic displacement on the free alcohols, by the use of organocopper reagents in the presence of $BF_3{\cdot}OEt_2$[12] or $TMSCl/Et_3N$[13] which resulted in recovery of starting material or formation of silyl ethers, respectively. We then turned our attention into the corresponding acetates[14] (Ac_2O, pyr) with mixed results, and, in some instances we obtained low yields of the desired displacement products, along with some deacetylation to the parent alcohols.

In view of recent reports on efficient chirality transfer by cuprate S_N2' displacements on allylic mesylates[15] we focused on the use of mesylates **4a** and **5a**, available by standard methods (MsCl, Et_3N, THF, 0 °C). Unfortunately, most attempts to isolate and/or purify phenyl-substituted mesylate **5a** resulted in spontaneous loss of methanesulfonic acid to generate 2-sulfinyl diene **7** in variable yields and with high E selectivity.[16] At the time, we focused on avoiding formation of these dienes and therefore, we carried out the cuprate reaction by addition of the crude mesylate solution onto the preformed organocuprate reagent. In this fashion, when **5a** was treated with Gilman cuprate $Me_2CuLi{\cdot}LiI$ (6 equiv, THF, −78 °C to rt), a 45:55 mixture of displacement products **10a** and **11a** (Scheme 3) was obtained in a disappointing 23% yield (Table 1, entry 2).[17] Interestingly, when the crude mixture was refluxed for 30 min (entry 3), the yield of displacement products was increased substantially. Alternatively, the use of cyanocuprate MeCuCNLi under the same conditions afforded a much better yield (89%) and a higher selectivity (28:72, Table 1, entry 4). Furthermore, a significant improvement of the diastereoselectivity (6:94) of the process was realized when the cyanocuprate was generated from a Grignard reagent (entry 5). In contrast, diastereomeric mesylate **4a** reacted with MeCuCNLi to produce a 6:94 ratio of isomers **8a** and **9a** (entry 1).[18]

The structures of alcohols **2a** and **3a** and of the corresponding displacement products (**8a**−**10a**) were tentatively assigned by spectroscopic methods, primarily by inspection of their ^1H NMR data and on the basis of

(8) Low stereoselectivities have been reported for these processes. See: (a) Posner, G. H.; Mallamo, P.; Miura, K.; Hulce, M. *Pure Appl. Chem.* **1981**, *54*, 2307−2314. For one example in which a high diastereoselectivity was found, see: (b) Solladié, G.; Moine, G. *J. Am. Chem. Soc.* **1984**, *106*, 6097−6098.

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(10) These include: DIBALH; $DIBALH/ZnCl_2$; LAH; $NaBH_4/CeCl_3$; $LAH/CeCl_3$; 9-BBN.

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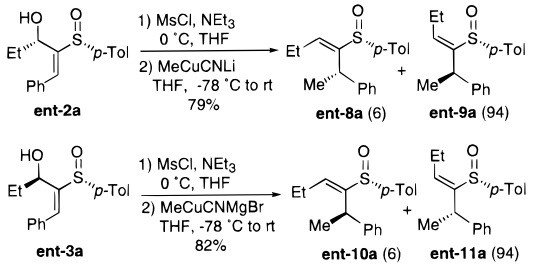
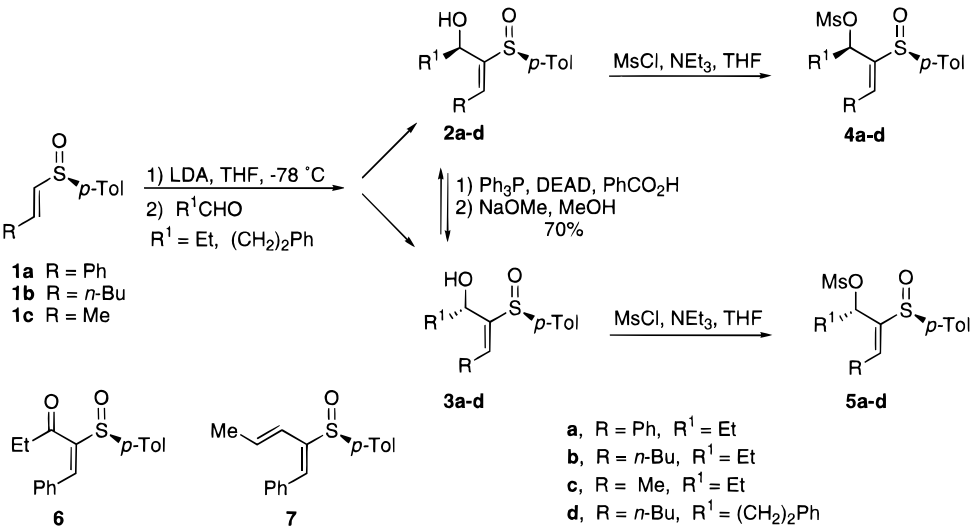
(16) The structure of this diene was deduced from its ^1H NMR data ($CDCl_3$, 300 MHz) δ 1.77 (d, 3 H, J = 5.1 Hz), 2.38 (s, 3 H), 6.06 (dq, 1 H, J = 16.2, 5.5 Hz), 6.20 (d, 1 H, J = 16.5 Hz), 7.26−7.60 (m, 10 H). For other reports on enantiomerically pure 2-sulfinyl dienes, see: (a) Paley, R. S.; Weers, H. L.; Fernández, P.; Fernández de la Pradilla, R.; Castro, S. *Tetrahedron Lett.* **1995**, *36*, 3605−3608. (b) Bonfand, E.; Gosselin, P.; Maignan, C. *Tetrahedron: Asymmetry* **1993**, *4*, 1667−1676. (c) Bonfand, E.; Gosselin, P.; Maignan, C. *Tetrahedron Lett.* **1992**, *33*, 2347−2348. (d) Aversa, M. C.; Bonaccorsi, P.; Gianneto, P.; Jafari, S. M. A.; Jones, D. N. *Tetrahedron: Asymmetry* **1992**, *3*, 701−704. For reports on the highly stereoselective Diels−Alder reactivity of these dienes, see: (e) Gosselin, P.; Bonfand, P.; Hayes, P.; Retoux, R.; Maignan, C. *Tetrahedron: Asymmetry* **1994**, *5*, 781−784. (f) Aversa, M. C.; Bonaccorsi, P.; Gianneto, P.; Jones, D. N. *Ibid.* **1994**, *5*, 805−808.

(17) Under these conditions, the major product found was assigned as PhCH=C=CHEt. For a discussion of these allene producing experiments, see: Fernández de la Pradilla, R.; Rubio, M. B.; Marino, J. P.; Viso, A. *Tetrahedron Lett.* **1992**, *33*, 4985−4988.

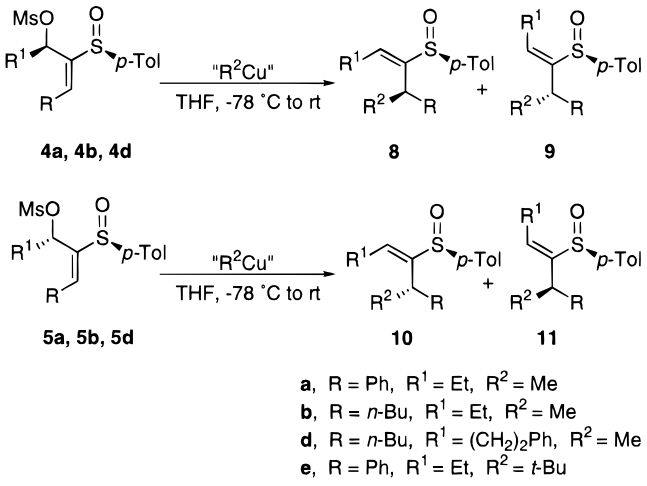
(18) The behavior for the enantiomeric series of phenyl-substituted sulfinyl alcohols, *ent*-**2a** and *ent*-**3a** (prepared in a standard fashion from commercially available (+)-menthyl (R_S)-*p*-toluenesulfinate) was examined, giving rise to the expected displacement products *ent*-**9a** and *ent*-**11a** with good yields and stereoselectivities. These products were fully characterized by spectroscopic techniques, and their data was found to be identical to their corresponding enantiomers with the exception of the sign of their optical rotation.



Scheme 2



Scheme 3



an *anti* attack of the nucleophile.[7,15] The stereochemistry of the double bond was deduced from the chemical shift of the vinylic proton (0.40−0.55 ppm more deshielded in *E* isomers **8a** and **10a**). Additionally, the newly introduced methyl group appeared shielded in isomers **8a** (0.35 ppm) and **11a** (0.52 ppm) relative to **10a** and **9a**, respectively (a similar unusual shielding had been observed for the CH_3SO_2 methyl of mesylate **4a**). All of these spectral characteristics were consistent with a predominant conformation in solution which would place the aforementioned methyl groups in the shielding region of the anisotropic tolyl group.

To extend the scope of the methodology, the introduction of a bulky *tert*-butyl group was addressed and good selectivities were encountered (entries 6 and 7 of Table 1) with lithium and Grignard-derived cuprates. The reactivity of *n*-butyl-substituted vinyl sulfoxides **4b** and **5b** was then studied, and the results are shown in Table 1 (entries 8−16). In the case of isomer **4b**, a significant increase in selectivity was achieved with MeCuCNLi relative to Gilman's cuprate. With MeCuCNLi a further improvement was observed when the reaction was carried out in a DME/THF (9:1) solvent mixture. Entry 10 shows that the process is compatible with the use of Lewis acids while a small decrease in selectivity and in yield was observed. On the other hand, the use of Me_2-CuMgBr resulted in a significant decrease in selectivity. In a parallel fashion, the behavior of diastereomer **5b** was explored; interestingly, MeCuCNLi produced the *E* isomer **10b** as major product (entry 13). An additional improvement was found when $Me_2CuLi{\cdot}LiI$ was employed. In view of the results found for phenyl-substituted mesylate **5a** and Grignard-derived cuprates, we tested MeCuCNMgBr and we found a remarkable reversal of selectivity albeit not quite synthetically useful (entry 15). Furthermore, $Me_2CuMgBr$ afforded exclusively *Z* isomer **11b** (entry 16). Since the reaction proceeded in modest yield, we cannot rule out selective destruction of the *E* isomer; nevertheless, entries 15 and 16 suggest that complete control of the selectivity of the process may also be possible at least in some cases, after the appropriate optimization.

Hydrocinnamaldehyde-derived substrates **4d** and **5d** were studied next with the intent of probing any effects of a tethered phenyl ring on the stereoselectivity. The results largely paralleled those found for **4b** and **5b**. Thus **4d** displayed good selectivity upon reaction with MeCuCN-Li, even at 0 °C (entries 18 and 19) and **5d** displayed good *E* selectivity with $Me_2CuLi{\cdot}LiI$ (entry 20). Methyl-substituted mesylate **5c**, on the other hand, reacted in high yield but low selectivity with *n*-BuCuCNLi (entry 21) and with very high selectivity but modest yield with *n*-$Bu_2CuMgCl$ (compare with entries 13 and 16). Alternatively, Grignard-derived phenyl homo and cyanocuprates gave good yields and high diastereoselectivities (entries 23 and 24). On the other hand, the reactions between diastereomeric mesylate **4c** and *n*-BuCuCNLi and PhCuCNLi proceeded in very good yields and with good stereocontrol (entries 25 and 26).

Cuprate Displacements on Vinyl Sulfides and Sulfones. While the diastereomeric nature of our mesylates and displacement adducts indicated that both chiral centers (allylic alcohol and sulfur) participated in the stereocontrol of the process, at least in some cases (see below), we considered that varying the oxidation state on sulfur to sulfone and sulfide would not just extend the scope of the methodology but also shed some light on the stereochemical course of the process.

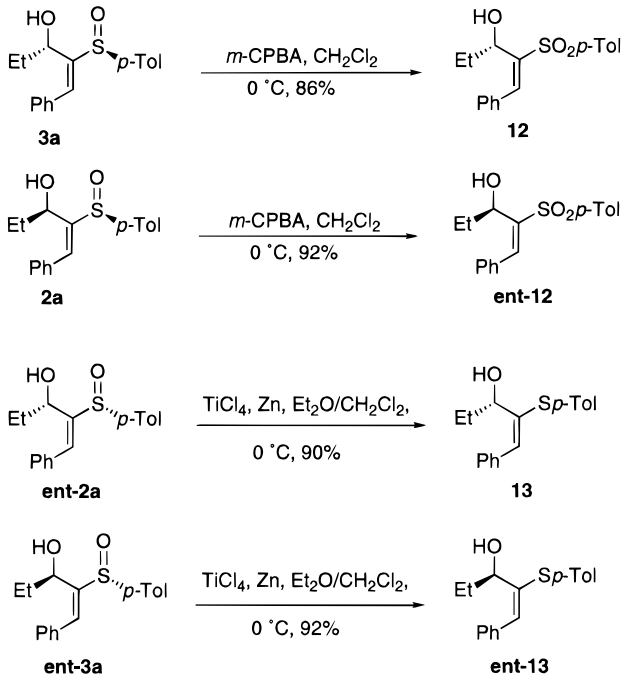
Enantiomerically pure sulfonyl- and sulfenyl-substituted allylic alcohols **12** and **13** were prepared in excellent yields by oxidation or deoxygenation, respectively, of the corresponding sulfoxides (Scheme 4). We decided to focus our efforts on the conjugate addition of methyl

Table 1. Reaction of Organocopper Reagents with Allylic Sulfinyl Mesylates

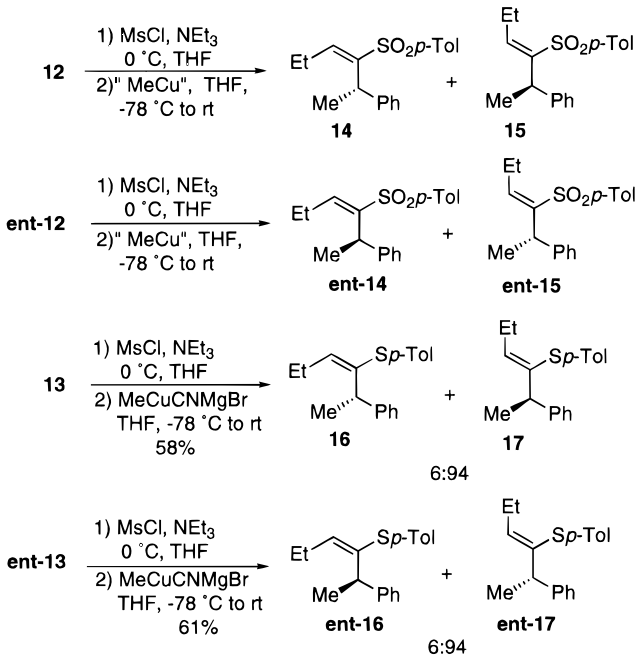
			product ratio				
entry	substrate	R_2Cu[a] (conditions)	**8**	**9**	**10**	**11**	yield (%)[b]
1[c]	**4a**	MeCuCNLi	6 (**8a**)	94 (**9a**)			81
2[c]	**5a**	Me_2CuLi			45 (**10a**)	55 (**11a**)	23
3[c]	**5a**	Me_2CuLi (−78 °C−Δ)			45 (**10a**)	55 (**11a**)	80
4[c]	**5a**	MeCuCNLi			28 (**10a**)	72 (**11a**)	89
5[c]	**5a**	MeCuCNMgBr			6 (**10a**)	94 (**11a**)	80
6[c]	**4a**	*t*-BuCuCNLi	9 (**8e**)	91 (**9e**)			69
7[c]	**5a**	*t*-BuCuCNMgCl			6 (**10e**)	94 (**11e**)	71
8	**4b**	Me_2CuLi	25 (**8b**)	75 (**9b**)			81
9	**4b**	MeCuCNLi	12 (**8b**)	88 (**9b**)			80
10	**4b**	MeCuCNLi·BF_3·OEt_2	15 (**8b**)	85 (**9b**)			58
11	**4b**	$Me_2CuMgBr$	36 (**8b**)	64 (**9b**)			52
12[d]	**4b**	MeCuCNLi	9 (**8b**)	91 (**9b**)			86
13	**5b**	MeCuCNLi			80 (**10b**)	20 (**11b**)	86
14	**5b**	Me_2CuLi			90 (**10b**)	10 (**11b**)	80
15	**5b**	MeCuCNMgBr			37 (**10b**)	63 (**11b**)	80
16	**5b**	$Me_2CuMgBr$			0 (**10b**)	100 (**11b**)	50
17	**4d**	Me_2CuLi	28 (**8d**)	72 (**9d**)			82
18	**4d**	MeCuCNLi (0 °C)	16 (**8d**)	84 (**9d**)			77
19	**4d**	MeCuCNLi (−78 °C)	8 (**8d**)	92 (**9d**)			77
20	**5d**	Me_2CuLi			85 (**10d**)	15 (**11d**)	85
21	**5c**	*n*-BuCuCNLi	60 (**8b**)	40 (**9b**)			93
22	**5c**	*n*-$Bu_2CuMgCl$	0 (**8b**)	100 (**9b**)			43
23	**5c**	PhCuCNMgBr	9 (**8a**)	91 (**9a**)			80
24	**5c**	$Ph_2CuMgBr$	6 (**8a**)	94 (**9a**)			70
25	**4c**	*n*-BuCuCNLi			15 (**10b**)	85 (**11b**)	74
26[d]	**4c**	PhCuCNLi			0 (**10a**)	100 (**11a**)	85

[a] Cuprates R^2Cu were prepared from the appropriate organolithium or Grignard reagent and CuI or CuCN. All experiments were carried out from −78 °C to rt unless otherwise stated. [b] Yields of pure products calculated from alcohols **2** and **3**. Product ratios were measured by integration of well separated absorptions of the ^1H NMR spectra of crude reaction mixtures. [c] The crude mesylate solution was added to the organocuprate solution (6 equiv) at −78 °C. [d] The reaction was carried out in a DME/THF (9:1) solvent mixture; these conditions produced a slight increase of the selectivity of the reaction.

Scheme 4



Scheme 5



nucleophiles and the experiments performed are gathered in Scheme 5 and Table 2. Vinyl sulfone **12** was first examined (entries 1−4), and the best results were obtained with "higher order" cyanocuprates derived from a Grignard reagent (entry 4), in sharp contrast with the lithium analogs (entry 1). The very high *E* selectivity of this process, opposite to the related sulfoxides, is noteworthy. A similar behavior was observed for *ent*-**12** within experimental error (Table 2, entry 5). On the other hand, vinyl sulfides **13** and *ent*-**13** displayed high stereoselectivity toward the *Z* isomers **17**, and *ent*-**17** (entries 6 and 7), as was found for the sulfoxides.

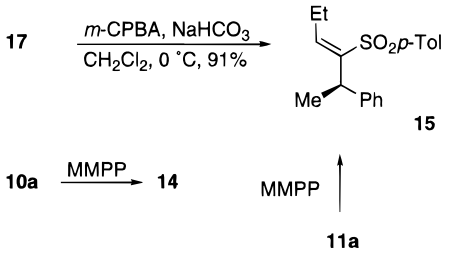
While the stereochemistry of the double bond of these vinyl sulfones and sulfides was readily established by ^1H NMR, the configuration of the new chiral center required a chemical correlation for vinyl sulfide **17** to the corresponding sulfone **15** which possessed an identical optical rotation to the sample prepared by oxidation of sulfoxide **11a** of known absolute configuration[1] (Scheme 6). Furthermore, the structures of the minor S_N2' displacement

Table 2. Reaction of Organocopper Reagents with Allylic Sulfonyl and Sulfenyl Mesylates

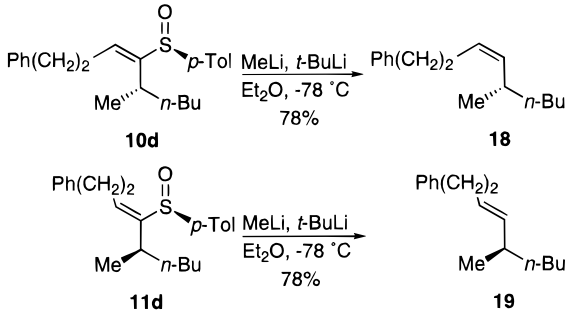
entry[a]	substrate	"MeCu"	products	ratio	yield (%)[b]
1[c]	**12**	$Me_2CuCNLi_2$	–	–	–
2	**12**	MeCuCNLi	**14**:**15**	50:50	72
3	**12**	MeCuCNMgBr	**14**:**15**	83:17	74
4	**12**	$Me_2CuCN(MgBr)_2$	**14**:**15**	91:9	76
5	*ent*-**12**	$Me_2CuCN(MgBr)_2$	*ent*-**14**:*ent*-**15**	93:7	81
6	**13**	MeCuCNMgBr	**16**:**17**	6:94	58
7	*ent*-**13**	MeCuCNMgBr	*ent*-**16**:*ent*-**17**	6:94	61

[a] Reactions carried out in THF (−78 °C to rt) by addition of the crude mesylate solution to the organocuprate solution. [b] Yields of pure products for two steps (mesylation and cuprate displacement). [c] Only product observed was PhCH=C=CHEt; the yield was not determined.

Scheme 6



Scheme 7



sulfoxides **8a** and **10a** (Scheme 3) were secured by oxidation of **10a** with MMPP to produce sulfone **14**.

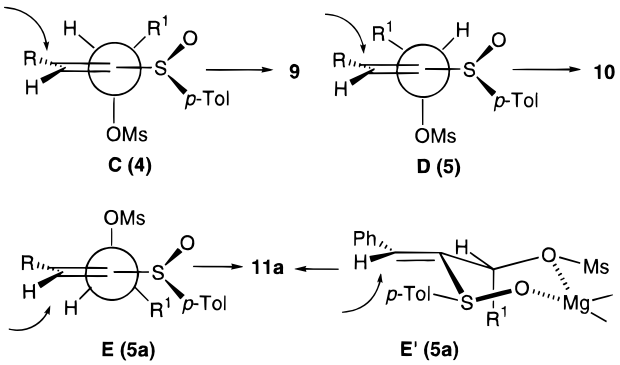
Synthesis of Alkenes Containing an Allylic Asymmetric Carbon. To begin exploring the synthetic usefulness of our S_N2' adducts, we decided to focus on the cleavage of the carbon−sulfur bond to produce enantiopure alkenes.[19] We selected adducts **10d** and **11d** (Scheme 7) to diminish losses of material due to the predicted volatility of other alkenes derived from different substrates. In this regard, we found that Okamura's method[20] gave rise to alkenes **18** and **19** in good yield and with complete preservation of the stereochemistry of the double bond.

Results and Discussion

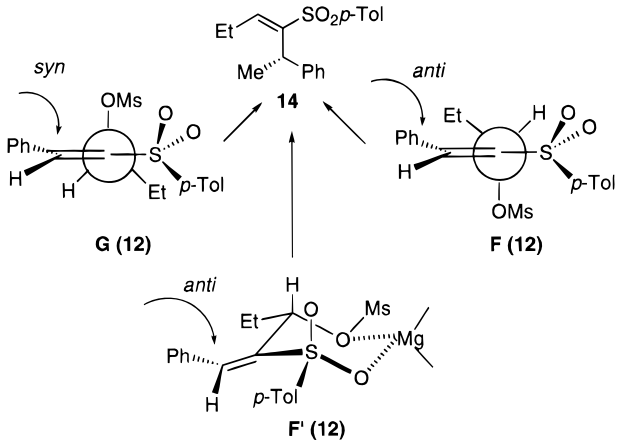
The results obtained for the cuprate displacement of allylic sulfinyl mesylates may be rationalized in terms of an *anti* S_N2' process taking place on reactive conformations **C** and **D** for sulfoxides **4** and **5** (Scheme 8). The clean *anti* stereochemistry of these displacements is firmly established from the absence of "crossover" products; that is to say, in no case were products **10** and **11** detected from mesylates **4**.[21,22] Diastereomers **4a**−**d** generally afforded products consistent with oxidative addition *anti* to the mesylate and away from the tolyl group on conformation **C**. Diastereomers **5a**−**d** display a somewhat more complex behavior. Indeed conformation **D** represents a very delicately balanced case, highly dependent on the reaction conditions and on the steric requirements of the substrate. Thus, when the steric interaction between R and R^1 is very strong (R = Ph, R^1 = Et), adduct **11** becomes the main product of the reaction (entries 5 and 7, Table 1), indicating that **E** is the reactive conformation in this substrate. However, when Grignard-derived cuprates are employed the best selectivities toward **11** were achieved. This trend may also be reinforced by participation of chelated forms involving the sulfoxide oxygen and the mesylate group (entries 14−16) and may be rationalized in terms of a reactive conformation similar to **E′**.

The behavior of sulfide **13** with MeCuCNMgBr closely parallels the corresponding sulfoxides, and a highly *anti* selective displacement on a conformation related to **C** is observed to provide the corresponding displacement product **17** (Scheme 5). The results found for sulfones **12** may be interpreted in terms of an *anti* addition to reactive conformer **F** (Scheme 9) to provide adduct **14** of *E* geometry, although a severe steric interaction between Et and Ph is present in that conformer. Alternatively **14** may arise from a *syn* nucleophilic attack on reactive

Scheme 8



Scheme 9



(19) Enantiopure alkenes are frequently found in nature. The structure of some pheromones is an example, see: The Synthesis of Insect Pheromones. In *The Total Synthesis of Natural Products*; Mori, K., ApSimon, J., Eds.; John Wiley & Sons: New York, 1992; Vol. 9.

(20) Park, G.; Okamura, W. H. *Synth. Commun.* **1991**, *21*, 1047−1054.

(21) For leading references on *syn* selective S_N2' displacements involving organocopper reagents, see ref 15b and references cited therein. See also ref 5d.

(22) Mesylates **5c** and **4c** produce "crossover" products only in a formal sense due to the exchange of the ligand on copper and the R group on the mesylate.

conformer **G** followed by rotation of the intermediate α-sulfonyl carbanion to deliver the thermodynamically more stable *E* configuration about the newly formed carbon−carbon double bond. It should also be noted that the greater carbanion-stabilizing power of the sulfone group could be rendering the addition process less concerted than for the sulfide or sulfoxide systems. The lack of selectivity found for MeCuCNLi (Table 2, entry 2) is in sharp contrast with previous results in the literature for simpler sulfonyl acetates[23] for which complete *E* selectivity was found upon reaction with lithium cyanocuprates; this suggests that while *syn* S_N2' processes are well documented for cyclic vinyl sulfones[24] our displacement is likely taking place with predominantly *anti* stereochemistry in a single S_N2' step on chelated conformer **F′**, especially when Grignard derived cuprates are employed.

Overall the stereochemical outcome of these processes is primarily controlled by the configuration of the allylic mesylate with sulfides and sulfoxides displaying very similar results. The related sulfones allow for a reversal of stereochemistry at the newly created center from a starting material of the same absolute configuration at the allylic alcohol.

Conclusions

A new methodology to effect the regio- and stereocontrolled S_N2' displacement of allylic mesyloxy vinyl sulfoxides and their oxidation/reduction analogs has been developed. The scope of this methodology has been defined, and in this manner, the newly created chiral center is adjacent to the synthetically useful functionality of a vinyl sulfoxide which should allow for straightforward subsequent asymmetric transformations. Additionally, removal of the sulfur auxiliary to generate enantiopure alkenes or oxidation to the corresponding sulfones[25] are readily accomplished. The possibility of controlling the absolute configuration of the displacement products by adjusting the oxidation level on sulfur is remarkable. Additional extensions of this methodology as well as further applications to the synthesis of natural products are being pursued in our laboratories.[26]

Experimental Section

General Methods. All reactions were carried out under a positive pressure of dry nitrogen or argon, using freshly distilled solvents under anhydrous conditions. Cuprate displacements were carried out in a 0.5−2 mmol scale. Reagents and solvents were handled by using standard syringe techniques. Diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane were distilled from sodium and benzophenone; *N*,*N*-diisopropylamine, triethylamine, and pyridine from barium oxide or calcium hydride. Commercial methyllithium (low halide solution in ether), *n*-butyllithium (solution in hexane), phenyllithium (solution in cyclohexane:ether, 70:30), and *tert*-butyllithium (in pentane) were purchased from Aldrich and titrated prior to use.[27] Methylmagnesium bromide (in ether), phenylmagnesium bromide (in ether), and *tert*-butylmagnesium chloride (in ether) were purchased from Aldrich. Copper cyanide, copper iodide, propionaldehyde, and hydrocinnamaldehyde were purchased from Aldrich. Copper cyanide was heated at 90−100 °C *in vacuo* for 2 h and stored in a desiccator. Copper iodide was purified from aqueous KI[28] and dried or washed with refluxing THF in a Soxhlet apparatus and stored in a desiccator. Flash chromatography was performed using Baker 40-μm and Merck 230−400-mesh silica gel. Analytical TLC was carried out on 250-μm Analtech or Merck (Kiesegel 60F-254) silica gel plates with detection by UV light, iodine, acidic vanillin solution, or phosphomolybdic acid solution in ethanol. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 or 360 MHz (^{1}H) using $CDCl_3$ as solvent. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Optical rotations were measured at 20 °C using a sodium lamp and in $CHCl_3$ solution.

General Procedure for the Condensation between Vinyl Sulfoxides and Aldehydes. To a cold (−78 °C) 0.1 M THF solution of 1.5 equiv of LDA, previously formed at 0 °C, was added 1 equiv of **1a**−**d** in THF (5 mL/mmol). After stirring for 15 min, 1.5 equiv of the aldehyde was added dropwise. The mixture was quenched after 15 min of stirring with a saturated NH_4Cl solution. The aqueous layer was washed with ethyl acetate (4 × 10 mL/mmol of starting material). Then, the organic layer was washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, and filtered. Concentration under reduced pressure gave a crude product, which was purified by column chromatography on silica gel, using the appropriate mixture of CH_2Cl_2 and ethyl acetate as eluent.

(*E*)-1-Phenyl-2(*S*$_s$)-(*p*-tolylsulfinyl)pent-1-en-3(*R*)-ol, 2a, and (*E*)-1-Phenyl-2(*S*$_s$)-(*p*-tolylsulfinyl)pent-1-en-3(*S*)-ol, 3a. **2a** and **3a** were obtained as a 40:60 mixture and were separated by chromatography on silica gel (80% combined yield). Data of **2a**: white solid. Mp: 143−144 °C (CH_2Cl_2:hexane). R_f = 0.33 (10% EtOAc−CH_2Cl_2). [α] = +91.9 (1.02). ^{1}H NMR: δ 0.85 (t, 3 H, *J* = 7.4 Hz), 1.58−1.69 (m, 1 H), 1.70−1.81 (m, 1 H), 2.39 (s, 3 H), 4.72 (dd, 1 H, *J* = 8.5, 5.5 Hz), 7.25−7.49 (m, 8 H), 7.61−7.64 (d, 2 H, *J* = 8.2 Hz). ^{13}C NMR: δ 10.3, 21.3, 29.2, 71.2, 125.8, 128,7, 128.8, 129.5, 130.1, 133.3, 134.4, 141.8, 147.8. Data of **3a**: white solid. Mp: 116−117 °C (CH_2Cl_2:hexane). R_f = 0.18 (10% EtOAc−CH_2Cl_2). [α] = −16.0 (1.23). ^{1}H NMR: δ 0.78 (t, 3 H, *J* = 7.4 Hz), 1.36 (m, 2 H), 2.39 (s, 3 H), 3.40 (br s, 1 H), 4.68 (t, 1 H, *J* = 6.8 Hz), 7.24−7.44 (m, 8 H), 7.50−7.63 (m, 2 H). ^{13}C NMR: δ 10.5, 21.4, 29.0, 71.5, 126.2, 128.6, 129.6, 130.1, 132.1, 134.4, 140.9, 141.9, 148.8.

(*E*)-4(*S*$_s$)-(*p*-Tolylsulfinyl)non-4-en-3(*R*)-ol, 2b, and (*E*)-4(*S*$_s$)-(*p*-Tolylsulfinyl)non-4-en-3(*S*)-ol, 3b. **2b** and **3b** were obtained as a 44:56 mixture and were separated by chromatography on silica gel (85% combined yield). Data of **2b**: transparent oil. R_f = 0.28 (10% EtOAc−CH_2Cl_2). [α] = +38.4 (3.62). ^{1}H NMR: δ 0.84 (t, 3 H, *J* = 7.3 Hz), 0.96 (t, 3 H, *J* = 7.2 Hz), 1.35−1.54 (m, 5 H), 1.63−1.70 (m, 1 H), 2.30−2.39 (m, 2 H), 2.42 (s, 3 H), 2.55−2.65 (br s, 1 H), 4.51 (dd, 1 H, *J* = 8.3, 5.9 Hz), 6.50 (t, 1 H, *J* = 7.6 Hz), 7.31 (d, 2 H, *J* = 8.2 Hz), 7.55 (d, 2 H, *J* = 8.2 Hz). ^{13}C NMR: δ 10.3, 13.8, 21.3, 22.4, 28.2, 30.0, 31.1, 71.5, 125.0, 129.8, 138.2, 140.9, 141.2, 145.1. Data of **3b**: transparent oil. R_f = 0.16 (10% EtOAc−

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(28) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 10.

CH_2Cl_2). [α] = −5.5 (1.84). ^{1}H NMR: δ 0.79 (t, 3 H, *J* = 7.3 Hz), 0.92 (t, 3 H, *J* = 6.8 Hz), 1.18−1.60 (m, 6 H), 2.23−2.44 (m, 2 H), 2.40 (s, 3 H), 2.70−2.71 (m, 1 H), 4.37 (ddd, 1 H, *J* = 8.9, 4.9, 4.3 Hz), 6.31 (t, 1 H, *J* = 7.6 Hz), 7.28 (d, 2 H, *J* = 7.4 Hz), 7.51 (d, 2 H, *J* = 7.4 Hz). ^{13}C NMR: δ 10.5, 13.8, 21.4, 22.8, 30.3, 31.2, 70.2, 125.3, 129.8, 137.4, 140.3, 141.4, 146.4.

(*E*)-1-Phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)non-4-en-3(*R*)-ol, 2d, and (*E*)-1-phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)non-4-en-3(*S*)-ol, 3d. 2d and **3d** were obtained as a 50:50 mixture and were separated by chromatography on silica gel (86% combined yield). Data of **2d**: white solid. Mp: 48−50 °C. R_f = 0.36 (10% EtOAc−CH_2Cl_2). [α] = +46.8 (1.12). ^{1}H NMR: δ 0.90 (t, 3 H, *J* = 7.3 Hz), 1.30−1.47 (m, 4 H), 1.60−1.70 (m, 1 H), 1.88−1.94 (m, 1 H), 2.19−2.25 (m, 2 H), 2.40 (s, 3 H), 2.40−2.48 (m, 1 H), 2.60−2.73 (m, 2 H), 4.56 (dt, 1 H, *J* = 9.0, 5.0 Hz), 6.45 (t, 1 H, *J* = 7.6 Hz), 7.01 (d, 2 H, *J* = 8.1 Hz), 7.13−7.29 (m, 5 H), 7.51 (d, 2 H, *J* = 8.2 Hz). ^{13}C NMR: δ 13.7, 21.3, 22.3, 28.1, 31.0, 31.9, 38.3, 69.5, 125.2, 125.8, 128.3, 128.4, 129.9, 138.1, 140.8, 141.2, 141.3, 145.2. Data of **3d**: white solid. Mp: 112−114 °C. R_f = 0.17 (10% EtOAc−CH_2Cl_2). [α] = +74.1 (0.64). ^{1}H NMR: δ 0.89 (t, 3 H, *J* = 7.2 Hz), 1.20 (m, 1 H), 1.25−1.45 (m, 4 H), 1.87 (m, 1 H), 2.18 (m, 1 H), 2.30 (m, 1 H), 2.41 (s, 3 H), 2.45 (m, 1 H), 2.66 (m, 1 H), 3.27 (d, 1 H, *J* = 4.3 Hz), 4.46 (ddd, 1 H, *J* = 9.2, 5.4, 4.2 Hz), 6.30 (t, 1 H, *J* = 7.6 Hz), 6.98 (d, 2 H, *J* = 8.3 Hz), 7.13−7.30 (m, 5 H), 7.45 (d, 2 H, *J* = 8.2 Hz). ^{13}C NMR: δ 13.7, 21.3, 22.3, 28.4, 31.1, 32.2, 38.9, 67.5, 125.1, 125.8, 128.2, 128.4, 129.8, 138.1, 140.2, 141.2, 141.3, 146.9.

General Procedure for Oxidation of Sulfides and Sulfoxides to Sulfones. Method A. To a solution of 1 equiv of sulfoxide or sulfide and $NaHCO_3$ (2 g/mmol) in CH_2Cl_2 (10 mL/mmol) at 0 °C was added a solution of *m*-CPBA (50−60%; 1.3 or 2.6 equiv) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at this temperature until complete conversion was observed by TLC and quenched with H_2O (10 mL/mmol). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL/mmol). The combined organic extracts were dried over $MgSO_4$ and evaporated to give a crude oil which was purified by column chromatography on silica gel to afford the corresponding sulfone.

Method B. To a solution of the corresponding sulfoxide (1 equiv) in MeOH (5 mL/mmol) was added MMPP (1.5 equiv). The mixture was stirred at room temperature until complete conversion was observed by TLC. The mixture was diluted with CH_2Cl_2 and was extracted with a 5% solution of $NaHCO_3$ and washed with brine. The organic extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield the crude product that was purified by chromatography on silica gel.

Synthesis of (*E*)-1-Phenyl-2-(*p*-tolylsulfonyl)pent-1-en-3(*S*)-ol, 12. Following the above procedure (method A), **12** was obtained from **3a** (350 mg, 1.17 mmol) and was purified by chromatography on silica gel (CH_2Cl_2) (86% yield). *ent*-**12** was prepared from **2a** by the same procedure (92% yield). Data of **12**. Mp: 110−111 °C. [α] = −49.6 (1.21). R_f = 0.20 (CH_2Cl_2). ^{1}H NMR: δ 0.75 (t, 3 H, *J* = 7.4 Hz), 1.54−1.89 (m, 2 H), 2.43 (s, 3 H), 2.87 (d, 1 H, *J* = 8.9 Hz), 4.65 (m, 1 H), 7.26−7.93 (m, 10 H). ^{13}C NMR: δ 10.3, 21.4, 28.7, 70.4, 127.8, 128.5, 129.5, 129.6, 129.7, 133.0, 138.2, 141.0, 144.1. Data of *ent*-**12** was found to be identical to that of **12** except for the sign of the optical rotation [α] = +49.9 (1.37).

Oxidation of Sulfide 17 to Sulfone, 15. Following the above procedure (method A), **17** (0.39 mmol, 110 mg) was transformed into sulfone **15** which was purified by chromatography on silica gel using CH_2Cl_2 as eluent (89% yield). This compound was found to be identical to the sulfone obtained from the oxidation of sulfoxide **11a** (see below). Data of **15**: [α] = +5.5 (1.29). R_f = 0.31 (10% EtOAc−hexane). ^{1}H NMR: δ 0.96 (t, 3 H, *J* = 7.4 Hz), 1.41 (d, 3 H, *J* = 7.3 Hz), 2.35 (s, 3 H), 2.47−2.74 (m, 2 H), 4.14 (q, 1 H, *J* = 7.1 Hz), 6.04 (t, 1 H, *J* = 7.7 Hz) 7.04−7.43 (m, 9 H). ^{13}C NMR: δ 13.5, 21.5, 22.3, 22.5, 41.0, 126.4, 127.5, 127.5, 128.4, 129.3, 139.0, 143.5, 143.6, 144.1, 145.8.

Oxidation of Sulfoxide 10a to Sulfone, 14. Following the above procedure (method B), **10a** (0.07 mmol, 21.4 mg) was transformed into sulfone **14** which was purified by chromatography on silica gel using 10% EtOAc−hexane as eluent (82% yield). This compound was found to be identical to sulfone **14** obtained from the addition of $Me_2CuCN(MgBr)_2$ to sulfone **12** as major product and whose structure was confirmed by X-ray analysis.

Synthesis of (*E*)-1-Phenyl-2-(*p*-tolylsulfenyl)pent-1-en-3(*S*)-ol, 13. A round-bottomed flask was charged with ether (10 mL) and Zn dust (295 mg, 4.53 mmol). The flask was immersed in an ice bath, and titanium(IV) chloride (0.25 mL, 2.26 mmol) was added with stirring at 0 °C. After 2 min the solution of sulfoxide *ent*-**2a** (340 mg, 1.13 mmol) in dichloromethane (10 mL) was slowly added. After 10 min, water (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to give a crude product which was purified by column chromatography on silica gel (15% EtOAc−hexane) to afford **13** (90%). *ent*-**13** was prepared from *ent*-**3a** by the same procedure (92%). Data of **13**: [α] = +90.5 (1.35). ^{1}H NMR: δ 0.93 (t, 3 H, *J* = 7.4 Hz), 1.79 (m, 2 H), 2.04 (d, 1 H, *J* = 7.4 Hz), 2.33 (s, 3 H), 4.72 (dd, 1 H, *J* = 13.8, 7.4 Hz), 6.43 (s, 1 H), 7.30−7.44 (m, 9 H). ^{13}C NMR: δ 10.1, 21.0, 29.7, 72.0, 127.1, 128.3, 128.5, 130.1, 130.7, 132.1, 133.0, 136.6, 137.9, 143.2. Data of *ent*-**13** was found to be identical to **13** except for the sign of the optical rotation [α] = −91.1 (2.17).

General Procedure for Mesylation of Alcohols 2 and 3. To a cold (0 °C) solution of the alcohol in THF (0.1 M) were added Et_3N (3 equiv) and MsCl (3 equiv), and the mixture was stirred for 1 h after which time the reaction was quenched with a saturated $NaHCO_3$ solution and diluted with ether, and the layers were separated. The organic layer was washed with a saturated NH_4Cl solution and brine and dried over $MgSO_4$. Filtration and concentration under reduced pressure gave a crude product which was filtered through a short column of deactivated silica gel (washed with 5% $NaHCO_3$ in MeOH), using 50% EtOAc−hexane as eluent. Removal of the solvent afforded the mesylate which was used for the cuprate displacement without further purification. In the case of alcohols **2a** and **3a**, the crude mesylate solution in THF was filtered and immediately added dropwise to the cuprate reagent to avoid formation of diene **7**. The same procedure was employed for additions to sulfones **12** and sulfides **13**. Formation of all the mesylates **4b**−**d** and **5b**−**d** was checked by ^{1}H NMR.

Mesylate of (*E*)-4(*S*$_s$)-(*p*-Tolylsulfinyl)non-4-en-3(*R*)-ol, 2b, 4b. ^{1}H NMR: δ 0.94 (t, 3 H, *J* = 7.2 Hz), 0.95 (t, 3 H, *J* = 7.4 Hz), 1.35−1.54 (m, 5 H), 1.73−1.76 (m, 1 H), 1.96−2.02 (m, 1 H), 2.31 (s, 3 H), 2.38−2.45 (m, 1 H), 2.40 (s, 3 H), 5.22 (dd, 1 H, *J* = 8.5, 6.8 Hz), 6.72 (t, 1 H, *J* = 7.7 Hz), 7.31 (d, 2 H, *J* = 8.2 Hz), 7.57 (d, 2 H, *J* = 8.2 Hz).

Mesylate of (*E*)-4(*S*$_s$)-(*p*-Tolylsulfinyl)non-4-en-3(*S*)-ol, 3b, 5b. ^{1}H NMR: δ 0.70 (t, 3 H, *J* = 7.1 Hz), 0.88 (m, 2 H), 0.95 (t, 3 H, *J* = 7.2 Hz), 1.40−1.43 (m, 4 H), 2.40 (m, 2 H), 2.41 (s, 3 H), 3.01 (s, 3 H), 5.06 (dd, 1 H, *J* = 5.7 Hz), 6.65 (t, 1 H, *J* = 7.7 Hz), 7.32 (d, 2 H, *J* = 8.1 Hz), 7.48 (d, 2 H, *J* = 8.2 Hz).

Mesylate of (*E*)-1-Phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)non-4-en-3(*R*)-ol, 2d, 4d. ^{1}H NMR: δ 0.91 (t, 3 H, *J* = 7.2 Hz), 1.30−1.50 (m, 5 H), 1.84 (m, 1 H), 2.23−2.37 (m, 2 H), 2.40 (s, 6 H), 2.59 (m, 1 H), 2.71 (m, 1 H), 5.25 (dd, 1 H, *J* = 9.1, 4.8 Hz), 6.70 (t, 1 H, *J* = 7.8 Hz), 7.10 (m, 2 H), 7.17 (m, 5 H), 7.53 (d, 2 H, *J* = 8.2 Hz).

Mesylate of (*E*)-1-Phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)non-4-en-3(*S*)-ol, 3d, 5d. ^{1}H NMR: δ 0.80−0.92 (m, 1 H), 0.93 (t, 3 H, *J* = 7.2 Hz), 1.35−1.56 (m, 4 H), 1.92 (m, 1 H), 2.23−2.51 (m, 3 H), 2.43 (s, 3 H), 2.62 (m, 1 H), 3.06 (s, 3 H), 5.19 (dd, 1 H, *J* = 10.3, 3.1 Hz), 6.64 (t, 1 H, *J* = 7.8 Hz), 6.85 (m, 2 H), 7.14−7.32 (m, 5 H), 7.46 (d, 2 H, *J* = 8.2 Hz).

General Procedure for S_N2' Addition of Organocuprate Reagents to Mesylates 4, 5, 12, and 13. To a cold (−78 °C) solution of the organocuprate reagent (formed from 3 equiv of CuI or CuCN and 6 or 3 equiv of the appropriate organolithium or Grignard reagent, respectively) in THF (20 mL/mmol of mesylate) was added dropwise mesylate **4** or **5** in THF (5 mL/mmol of mesylate) with vigorous stirring. The

reaction mixture was allowed to warm up to room temperature over *ca*. 5 h after which time a saturated NH_4Cl solution was added. The aqueous layer was extracted with ether (4 × 5 mL/mmol), and the combined organic extracts were washed with a saturated solution of $Na_2S_2O_3$ and brine. After drying ($MgSO_4$) and concentration under reduced pressure, the crude product was purified by column chromatography on silica gel. In the case of sulfoxides **2a** and **3a**, sulfones **12**, and sulfides **13**, the crude mesylate solution in THF was filtered and immediately added dropwise to the preformed cuprate solution. Yields are always given from the initial alcohol.

***(E)*-2(*R*)-Phenyl-3(*S*$_s$)-(*p*-tolylsulfinyl)hex-3-ene, 8a, and (*Z*)-2(*S*)-Phenyl-3(*S*$_s$)-(*p*-tolylsulfinyl)hex-3-ene, 9a.** From **4a** and MeCuCNLi, a 6:94 mixture of **8a** and **9a** was obtained in 81% yield. An enriched sample of **8a** was obtained by column chromatography, and pure **9a** was obtained by recrystallization. Data of **8a**: transparent oil. R_f = 0.24 (20% EtOAc−hexane). ^{1}H NMR: δ 0.78 (t, 3 H, J = 7.5 Hz), 1.05 (d, 3 H, J = 7.4 Hz), 1.85−2.05 (m, 2 H), 2.41 (s, 3 H), 3.87 (q, 1 H, J = 7.3 Hz), 6.37 (t, 1 H, J = 7.7 Hz), 7.14−7.30 (m, 7 H), 7.53 (d, 2 H, J = 8.2 Hz). Data of **9a**: white solid. Mp: 74−76 °C (hexane). [α] = −313.9 (1.40). R_f = 0.24 (20% EtOAc−hexane). ^{1}H NMR: δ 1.13 (t, 3 H, J = 7.4 Hz), 1.47 (d, 3 H, J = 7.2 Hz), 2.48 (m, 1 H), 2.81 (m, 1 H), 3.96 (q, 1 H, J = 7.2 Hz), 5.98 (dd, 1 H, J = 8.7, 6.6 Hz), 6.62−6.66 (m, 2 H), 6.96−7.00 (m, 3 H), 7.07−7.10 (m, 2 H), 7.23−7.27 (m, 2 H). ^{13}C NMR: δ 14.1, 21.2, 22.4, 23.7, 35.2, 124.4, 125.7, 127.1, 127.9, 129.4, 139.6.

***(E)*-2(*S*)-Phenyl-3(*S*$_s$)-(*p*-tolylsulfinyl)hex-3-ene, 10a, and (*Z*)-2(*R*)-Phenyl-3(*S*$_s$)-(*p*-tolylsulfinyl)hex-3-ene, 11a.** From **5a** and MeCuCNMgBr, a 6:94 separable mixture of **10a** and **11a** was obtained in 80% yield. Data of **10a**: transparent oil. R_f = 0.22 (20% EtOAc−hexane). [α] = −48.2 (0.56). ^{1}H NMR: δ 0.87 (t, 3 H, J = 7.5 Hz), 1.40 (d, 3 H, J = 7.3 Hz), 1.88−2.15 (m, 2 H), 2.37 (s, 3 H), 3.74 (q, 1 H, J = 7.3 Hz), 6.40 (t, 1 H, J = 7.6 Hz), 6.89−7.64 (m, 9 H). ^{13}C NMR: δ 13.0, 19.2, 21.4, 22.2, 35.3, 125.6, 126.9, 128.1, 129.7, 137.2, 140.0, 141.5, 142.5, 147.8. Data of **11a**: transparent oil. R_f = 0.30 (20% EtOAc−hexane). [α] = −56.4 (1.60). ^{1}H NMR: δ 0.95 (d, 3 H, J = 7.2 Hz), 1.05 (t, 3 H, J = 7.5 Hz), 2.42 (s, 3 H), 2.47−2.70 (m, 2 H), 3.98 (q, 1 H, J = 7.2 Hz), 5.85 (t, 1 H, J = 7.6 Hz), 7.14−7.32 (m, 7 H), 7.50 (d, 2 H, J = 8.2 Hz). ^{13}C NMR: δ 13.9, 21.4, 21.8, 22.3, 34.0, 124.2, 126.1, 127.5, 128.3, 140.1, 140.6, 145.0, 149.9.

***(E)*-6,6-Dimethyl-5(*R*)-phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)hept-3-ene, 8e, and (*Z*)-6,6-Dimethyl-5(*S*)-phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)hept-3-ene, 9e.** From **4a** and *t*-BuCuCNLi, a 9:91 mixture of **8e** and **9e** was obtained in 69% yield. Pure **9e** and an enriched sample of **8e** were obtained by column chromatography. Data of **8e**: transparent oil. R_f = 0.22 (25% EtOAc−hexane). ^{1}H NMR: δ 0.99 (t, 3 H, J = 7.4 Hz), 1.06 (s, 9 H), 2.35 (s, 3 H), 2.39−2.52 (m, 2 H), 2.96 (s, 1 H), 6.54 (t, 1 H, J = 9.7 Hz), 6.67−6.70 (m, 2 H), 6.95−7.03 (m, 3 H), 7.13 (d, 2 H, J = 8.1 Hz), 7.43 (d, 2 H, J = 8.1 Hz). ^{13}C NMR: δ 13.4, 21.3, 23.7, 29.8, 35.9, 56.9, 125.9, 127.4, 127.5, 129.5, 129.7, 134.7, 139.9, 141.9, 143.3. Data of **9e**: transparent oil. [α] = −123.5 (2.4). R_f = 0.40 (25% EtOAc−hexane). ^{1}H NMR: δ 0.95 (s, 9 H), 1.24 (t, 3 H, J = 7.4 Hz), 2.18 (s, 3 H), 2.62 (m, 1 H), 2.91 (m, 1 H), 3.48 (s, 1 H), 6.66−6.71 (m, 3 H), 6.80−6.94 (m, 5 H), 7.01 (d, 2 H, J = 8.1 Hz). ^{13}C NMR: δ 14.4, 21.0, 22.6, 28.9, 35.0, 49.5, 124.4, 125.1, 126.8, 128.8, 129.5, 138.4, 139.7, 140.3, 141.2, 146.4.

***(E)*-6,6-Dimethyl-5(*S*)-phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)hept-3-ene, 10e, and (*Z*)-6,6-Dimethyl-5(*R*)-phenyl-4(*S*$_s$)-(*p*-tolylsulfinyl)hept-3-ene, 11e.** From **5a** and *t*-BuCuCNMgCl, a 6:94 mixture of **10e** and **11e** was obtained in 71% yield. Pure **11e** and an enriched sample of **10e** were obtained by column chromatography. Data of **10e**: transparent oil. R_f = 0.20 (25% EtOAc−hexane). ^{1}H NMR: δ 1.07 (t, 3 H, J = 7.5 Hz), 1.14 (s, 9 H), 2.26 (s, 3 H), 2.39−2.51 (m, 2 H), 3.80 (s, 1 H), 6.46 (t, 1 H, J = 7.5 Hz), 6.90−6.97 (m, 4 H), 7.11−7.19 (m, 5 H). ^{13}C NMR: δ 13.2, 21.1, 23.3, 29.6, 35.8, 55.8, 125.1, 126.5, 128.0, 129.1, 130.3, 139.9, 140.1, 143.3, 148.0. Data of **11e**: white solid. Mp: 134−136 °C. [α] = −100.1 (1.09). R_f = 0.29 (25% EtOAc−hexane). ^{1}H NMR: δ 0.59 (s, 9 H), 1.22 (t, 3 H, J = 7.4 Hz), 2.41 (s, 3 H), 2.60 (m, 1 H), 2.91 (m, 1 H), 3.48 (s, 1 H), 6.50 (dd, 1 H, J = 8.6, 6.6 Hz), 7.15−7.33 (m, 7 H), 7.49 (d, 2 H, J = 8.2 Hz). ^{13}C NMR: δ 14.2, 21.3, 22.7, 28.7, 34.3, 50.5, 124.4, 126.0, 127.4, 129.6, 130.1, 138.5, 140.6, 141.6, 146.6.

***(E)*-5(*R*)-Methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 8b, and (*Z*)-5(*S*)-Methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 9b.** From **4b** and MeCuCNLi, an inseparable 9:91 mixture of **8b** and **9b** was obtained in 86% yield. A small amount of practically pure **9b** was obtained by chromatography. Data of **8b**: ^{1}H NMR: δ 0.76 (d, 3 H, J = 7.2 Hz), 6.36 (t, 1 H, J = 7.6 Hz). The rest of the signals could not be measured accurately. Data of **9b**: transparent oil. R_f = 0.28 (12% EtOAc−hexane). ^{1}H NMR: δ 0.60 (t, 3 H, J = 6.7 Hz), 0.70−1.20 (m, 6 H), 1.11 (d, 3 H, J = 6.9 Hz), 1.14 (t, 3 H, J = 7.5 Hz), 2.38 (s, 3 H), 2.40−2.54 (m, 1 H), 2.56 (sext, 1 H, J = 7.2 Hz), 2.65−2.90 (m, 1 H), 5.89 (dd, 1 H, J = 8.5, 6.9 Hz), 7.26 (d, 2 H, J = 8.3 Hz), 7.41 (d, 2 H, J = 8.3 Hz). ^{13}C NMR: δ 13.8, 14.2, 21.2, 22.2, 23.7, 29.0, 29.4, 36.9, 124.2, 129.5, 136.8, 140.1, 140.4, 150.3.

***(E)*-5(*S*)-Methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 10b, and (*Z*)-5(*R*)-Methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 11b.** From **5b** and $Me_2CuLi{\cdot}LiI$, a 90:10 separable mixture of **10b** and **11b** was obtained in 80% yield. Data of **10b**: transparent oil. R_f = 0.19 (12% EtOAc−hexane). [α] = +113.9 (1.10). ^{1}H NMR: δ 0.75 (t, 3 H, J = 7.3 Hz), 0.94 (d, 3 H, J = 7.1 Hz), 0.96−1.20 (m, 3 H), 1.11 (t, 3 H, J = 7.5 Hz), 1.20−1.38 (m, 3 H), 2.21 (sext, 1 H, J = 7.2 Hz), 2.32 (quint, 2 H, J = 7.6, 1.4 Hz), 2.39 (s, 3 H), 6.35 (t, 1 H, J = 7.7 Hz), 7.26 (d, 2 H, J = 7.9 Hz), 7.52 (d, 2 H, J = 7.9 Hz). ^{13}C NMR: δ 13.7, 13.8, 19.7, 21.3, 22.3, 22.4, 29.9, 32.2, 35.8, 125.9, 129.5, 136.0, 140.4, 141.4, 147.5. Data of **11b**: transparent oil. R_f = 0.34 (12% EtOAc−hexane). [α]= −191.6 (1.13). ^{1}H NMR: δ 0.56 (d, 3 H, J = 6.9 Hz), 0.86 (t, 3 H, J = 6.9 Hz), 1.13 (t, 3 H, J = 7.5 Hz), 1.19−1.38 (m, 5 H), 1.42−1.50 (m, 1 H), 2.38 (s, 3 H), 2.47−2.58 (m, 2 H), 2.70−2.81 (m, 1 H), 5.93 (dd, 1 H, J = 8.5, 6.9 Hz), 7.26 (d, 2 H, J = 8.1 Hz), 7.42 (d, 2 H, J = 8.2 Hz). ^{13}C NMR: δ 13.9, 14.1, 21.1, 22.0, 22.3, 22.6, 28.9, 29.3, 38.2, 124.1, 129.5, 137.1, 140.2, 140.5, 150.4.

***(E)*-1-Phenyl-5(*S*)-methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 8d, and (*Z*)-1-Phenyl-5(*S*)-methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 9d.** From **4d** and MeCuCNLi, an 8:92 inseparable mixture of **8d** and **9d** was obtained in 77% yield. A small amount of practically pure **9d** was obtained by careful chromatography. Data of **8d**: ^{1}H NMR: δ 0.67 (d, 3 H, J = 7.0 Hz), 6.42 (t, 1 H, J = 7.5 Hz). The rest of the signals could not be measured accurately. Data of **9d**: transparent oil. R_f = 0.32 (25% EtOAc−hexane). ^{1}H NMR: δ 0.59 (t, 3 H, J = 7.2 Hz), 0.65−1.10 (m, 6 H), 1.08 (d, 3 H, J = 6.9 Hz), 2.35 (s, 3 H), 2.42 (sext, 1 H, J = 7.0 Hz), 2.79−2.93 (m, 3 H), 3.03 (m, 1 H), 5.93 (t, 1 H, J = 7.3 Hz), 7.13−7.38 (m, 9 H). ^{13}C NMR: δ 13.7, 21.1, 22.2, 23.7, 28.9, 29.7, 30.5, 35.8, 36.8, 124.2, 126.2, 128.5, 128.6, 129.4, 134.4, 139.7, 140.3, 140.6, 151.5.

***(E)*-1-Phenyl-5(*S*)-methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 10d, and (*Z*)-1-Phenyl-5(*R*)-methyl-4(*R*$_s$)-(*p*-tolylsulfinyl)non-3-ene, 11d.** From **5d** and $Me_2CuLi{\cdot}LiI$, an 85:15 separable mixture of **10d** and **11d** was obtained in 85% yield. Data of **10d**: transparent oil. R_f = 0.15 (25% EtOAc−hexane). [α] = +77.9 (1.07). ^{1}H NMR: δ 0.72 (t, 3 H, J = 6.8 Hz), 0.84 (d, 3 H, J = 7.1 Hz), 0.86−1.26 (m, 6 H), 2.15 (sext, 1 H, J = 7.2 Hz), 2.36 (s, 3 H), 2.62 (m, 2 H), 2.81 (m, 2 H), 6.39 (t, 1 H, J = 7.5 Hz), 7.18−7.31 (m, 7 H), 7.41 (d, 2 H, J = 8.2 Hz). ^{13}C NMR: δ 13.7, 19.4, 21.2, 22.3, 29.8, 30.7, 32.2, 35.3, 35.6, 125.9, 126.1, 128.4, 129.5, 132.2, 140.3, 140.9, 141.4, 148.8. Data of **11d**: transparent oil. R_f = 0.25 (25% EtOAc−hexane). [α] = −486.0 (0.35). ^{1}H NMR δ 0.51 (d, 3 H, J = 7.0 Hz), 0.86 (t, 3 H, J = 6.8 Hz), 1.19−1.51 (m, 6 H), 2.36 (s, 3 H), 2.47 (sext, 1 H, J = 7.0 Hz), 2.78−2.90 (m, 3 H), 3.02−3.08 (m, 1 H), 5.95 (dd, 1 H, J = 7.9, 6.3 Hz), 7.18−7.35 (m, 9 H). ^{13}C NMR: δ 14.0, 21.2, 22.5, 22.7, 29.3, 29.4, 30.4, 35.9, 38,4, 124.3, 126.3, 128.6, 129.6, 134.8, 140.1, 140.3, 140.7, 151.7.

***(E)*-2(*S*)-Phenyl-3-(*p*-tolylsulfonyl)hex-3-ene, 14, and (*Z*)-2(*R*)-Phenyl-3-(*p*-tolylsulfonyl)hex-3-ene, 15.** From the mesylate derived from **12** and $Me_2CuCN(MgBr)_2$, a 91:9 mixture of **14** and **15** was obtained in 76% yield. An enriched sample of **15** was obtained by chromatography, and pure **14** was obtained by recrystallization from hexane. Data of **14**: white solid. Mp: 97−97.5 °C. R_f = 0.40 (20% EtOAc−hexane).

[α] = −70.1 (1.19). ^{1}H NMR: δ 0.78 (t, 3 H, *J* = 7.5 Hz), 1.39 (d, 3 H, *J* = 7.3 Hz), 1.72−2.04 (m, 2 H), 2.43 (s, 3 H), 4.04 (q, 1 H, *J* = 7.3 Hz), 6.90 (t, 1 H, *J* = 7.8 Hz), 7.03−7.77 (m, 9 H). ^{13}C NMR: δ 12.3, 18.1, 21.4, 22.0, 36.4, 126.1, 127.0, 128.1, 128.4, 129.6, 137.1, 142.10, 143.9, 144.0, 145.6. Data of *ent*-**14** and *ent*-**15** (obtained from *ent*-**12** by the same procedure) was found to be identical to data of **14** and **15** except for sign of the optical rotation [α] (*ent*-**14**)= +71.1 (1.35).

(*E*)-2(*S*)-Phenyl-3-(*p*-tolylsulfenyl)hex-3-ene, 16, and (*Z*)-2(*R*)-Phenyl-3-(*p*-tolylsulfenyl)hex-3-ene, 17. From the mesylate derived from **13** and MeCuCNMgBr a 6:94 mixture of **16** and **17** was obtained in 58% yield. Data of **17**: transparent oil. [α] = +9.2 (1.67). ^{1}H NMR: δ 0.99 (t, 3 H, *J* = 7.5 Hz), 1.41 (d, 3 H, *J* = 7.1 Hz), 2.25−2.39 (m, 2 H), 2.30 (s, 3 H), 3.53 (q, 1 H, *J* = 7.1 Hz), 5.95 (t, 1 H, *J* = 7.0 Hz), 7.02−7.28 (m, 9 H). ^{13}C NMR: δ 13.7, 20.8, 20.9, 23.4, 46.4, 126.2, 127.7, 128.1, 129.5, 129.7, 132.6, 135.7, 137.4, 138.0, 144.7. Data of *ent*-**17** (obtained from *ent*-**13** by the same procedure) was found to be identical to data of **17** except for sign of the optical rotation [α] (*ent*-**17**) = −8.8 (1.53).

General Procedure for Desulfinylation of Vinyl Sulfoxides. To a cold (−78 °C) 0.4 M Et_2O solution of 1 equiv of vinyl sulfoxide was added MeLi (2 equiv of a 1.6 M Et_2O solution). After 5 min *t*-BuLi was added (4 equiv of a 1.51 M pentane solution). When TLC analysis of the crude mixture showed dissapearance of the starting material (*ca.* 10 min), the reaction was quenched with MeOH (200 equiv), diluted with EtOAc, and washed with a saturated NaCl solution. The organic extracts were dried over $MgSO_4$ and filtered. Concentration under reduced pressure gave a crude product, which was purified by chromatography on silica gel (5−20% EtOAc−hexane).

(*Z*)-5(*S*)-Methyl-1-phenylnon-3-ene, 18. From **10d** and *t*-BuLi, **18** was obtained in 78% yield. Data of **18**: transparent oil. R_f = 0.50 (20% EtOAc−hexane). [α] = −31.0 (0.60). ^{1}H NMR: δ 0.84−1.00 (m, 6 H), 1.11−1.29 (m, 6 H), 2.30−2.39 (m, 3 H), 2.65 (t, 2 H, *J* = 7.4 Hz), 5.13 (tm, 1 H, *J* = 9.6 Hz), 5.33 (dt, 1 H, *J* = 10.9, 7.0 Hz), 7.30−7.14 (m, 5 H). ^{13}C NMR: δ 14.1, 21.2, 22.8, 29.4, 29.7, 31.7, 36.2, 37.2, 125.7, 127.1, 128.2, 128.4, 137.2, 142.2.

(*E*)-5(*R*)-Methyl-1-phenylnon-3-ene, 19. From **11d** and *t*-BuLi, **19** was obtained in 78% yield. Data of **19**: transparent oil. R_f = 0.50 (20% EtOAc−hexane). [α] = −15.5 (0.90). ^{1}H NMR: δ 0.87 (t, 3 H, *J* = 6.6 Hz), 0.92 (d, 3 H, *J* = 6.7 Hz), 1.19−1.30 (m, 6 H), 2.02 (br quint, 1 H), 2.25−2.32 (m, 2 H), 2.65 (apt, 2 H, *J* = 7.2 Hz), 5.26 (dd, 1 H, *J* = 15.3, 7.3 Hz), 5.38 (dt, 1 H, *J* = 15.3, 6.2 Hz), 7.13−7.28 (m, 5 H). ^{13}C NMR: δ 14.1, 20.8, 22.8, 25.0, 29.5, 34.4, 36.2, 36.8, 125.6, 127.3, 128.2, 128.5, 137.3, 142.2.

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Supporting Information Available: Additional data for all new compounds (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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