Synthesis and Diastereoselective Complexation of Enantiopure Sulfinyl Dienes: The Preparation of Sulfinyl Iron(0) Dienes

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The preparation of a diverse array of enantiomerically pure 1- and 2-sulfinyl dienes has been achieved via Stille coupling of halovinyl sulfoxides and vinyl stannanes, hydrogenation of 1-sulfinyl-1-en-3-ynes, or vinylcupration of 1-sulfinyl alkynes. Formation of the corresponding sulfinyl diene iron(0) tricarbonyl complexes was accomplished by utilizing $Fe(CO)_5$/NMO or $(bda)Fe(CO)_3$ as iron(0) tricarbonyl transfer reagents. Installation of the iron(0) tricarbonyl fragment was shown to be highly diastereoselective (10−16:1) for (*R*)-(1*Z*)-1-sulfinyl dienes, most likely as a result of allylic 1,3-strain. The synthesis of a 1-sulfinyl-1,3,8,10-tetraene is also described.

Introduction

The use of enantiomerically pure sulfoxides to direct the absolute stereochemistry of emerging chiral centers has been the primary feature of numerous publications over the last 20 years.[1] Among the best known examples of this chemistry are conjugate additions to α-sulfinyl enones,[2] diastereoselective Diels−Alder reactions,[3] additive Pummerer reactions,[4] and reductions of *β*-keto sulfoxides.[5] However, despite recent advances in organotransition metal chemistry directed toward organic synthesis,[6] there have been only isolated reports[7] which have described procedures which would extend the use of the sulfoxide group beyond traditional main-group transformations. We have therefore initiated a research program which seeks to explore the feasibility and diastereoselectivity of organotransition metal chemistry which is centered about the use of the chiral sulfoxide functionality as the chiral control element.

Among the scattered reports of transition metal complexes used in conjunction with sulfoxides, few have been within the context of asymmetric synthesis. For example, Hiroi[7a] demonstrated that 3-alkyl-1-sulfinylcyclopent-1-enes could be prepared with good diastereoselectivity by taking advantage of a Pd(0)-catalyzed 1-sulfinyl-1-vinylcyclopropane rearrangement. However, the origin of the stereoselectivity observed in this process was not as a result of the influence of the sulfoxide on the presumed intermediate sulfinyl-*π*-allyl-Pd(0) complex, but rather was due to a prior non-transition metal mediated diastereoselective vinyl sulfoxide cyclopropanation. Moretó[7b] reported a $Ni(CO)_4$-mediated approach to homochiral fused and spiro cyclopentenones using alkynyl sulfoxides and allylic bromides, but the diastereoselectivity of this process was only moderate. More recently, Hua[7c] has prepared a series of sulfinylferrocenes for possible use in asymmetric catalysis. Other instances of transition metal complexes bearing sulfinyl groups have included the syntheses of η^4-(3-sulfinyl enone)−$Fe(CO)_3$ complexes[7d] and of η^6-sulfinyl arene−$Cr(CO)_3$ complexes,[7e,f] but these have employed racemic sulfoxides. Taken together, these examples reveal that the area of asymmetric synthesis employing enantiopure sulfoxides in conjunction with transition metal chemistry is still largely unexplored and unrealized.

Our research efforts have focused on the chemistry of sulfinyl dienes; we were intrigued by the possibility that for appropriately substituted sulfinyl dienes, allylic strain[8] might control the diastereofacial complexation of a coordinatively unsaturated metal fragment. For catalytic processes, diastereoselective complexation of this type could be the primary event which would control the diastereoselectivity of projected intramolecular metal-mediated cycloisomerizations.[9] Alternatively, the use of stoichiometric amounts of complexing agent should provide enantiopure metal−sulfinyl diene complexes suitable for further diastereoselective transformations.

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(1) For reviews, see: (a) *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley & Sons: New York, 1988. (b) Solladié, G. *Synthesis* **1981**, 185−196. (c) Walker, A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 961−968. (d) Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717−1760. (e) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P., Giannetto, P. *Tetrahedron: Asymmetry* **1997**, *8*, 1339−1367.

(2) Posner, G. H. *Acc. Chem. Res.* **1987**, *20*, 72−87.

(3) (a) Ronan, B.; Kagan, H. B. *Tetrahedron: Asymmetry* **1992**, *3*, 115−122. (b) Arai, Y.; Matusi, M.; Koizumi, T.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 1983−1985. (c) Carreño, M. C.; García-Ruano, J. L.; Urbano, A. *Tetrahedron Lett.* **1989**, *30*, 4003−4006.

(4) (a) Marino, J. P.; Laborde, E.; Paley, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 966−968. (b) Marino, J. P.; Perez, A. D. *J. Am. Chem. Soc.* **1984**, *106*, 7643−7644. (c) Marino, J. P.; Fernández de la Pradilla, R. *Tetrahedron Lett.* **1985**, *25*, 5381−5384. (d) Marino, J. P.; Bogdan, S.; Kimura, K. *J. Am. Chem. Soc.* **1992**, *114*, 5566−5572. (e) Marino, J. P. *Pure Appl. Chem.* **1993**, *65*, 667−674.

(5) (a) Solladié, G.; Lohse, O. *J. Org. Chem.* **1993**, *58*, 4555−4563. (b) Solladié, G.; Maestro, M. C.; Rubio, A.; Pedregal, C.; Carreño, M. C.; García-Ruano, J. L. *J. Org. Chem.* **1991**, *56*, 2317, and references therein.

(6) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

(7) (a) Hiroi, K.; Arinaga, Y. *Tetrahedron Lett.* **1994**, *35*, 153−156; Hiroi, K.; Onuma, H.; Arinaga, Y. *Chem. Lett.* **1995**, 1099−1100. (b) Villar, J. M.; Delgado, A.; Llebaría, A.; Moretó, J. M.; Molins, E.; Miravitlles, C. *Tetrahedron* **1996**, *52*, 10525−10546. (c) Hua, D. H.; Lagneau, N. M.; Chen, Y.; Robben, P. M.; Clapham, G.; Robinson, P. D. *J. Org. Chem.* **1996**, *61*, 4508−4509. (d) Ibbotson, A.; Reduto dos Reis, A. C.; Saberi, S. P.; Slawin, A. M. Z.; Thomas, S. E.; Tustin, G. J.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1251−1259. (e) Pérez-Encabo, A.; Perrio, S.; Slawin, A. M. Z.; Thomas, S. E.; Wierzchleyski, A. T.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 629−642. (f) Davies, S. G.; Loveridge, T., Clough, J. M. *Synlett* **1997**, 66−68.

(8) For a review: Hoffman, R. W. *Chem. Rev.* **1989**, *89*, 1841−1860.

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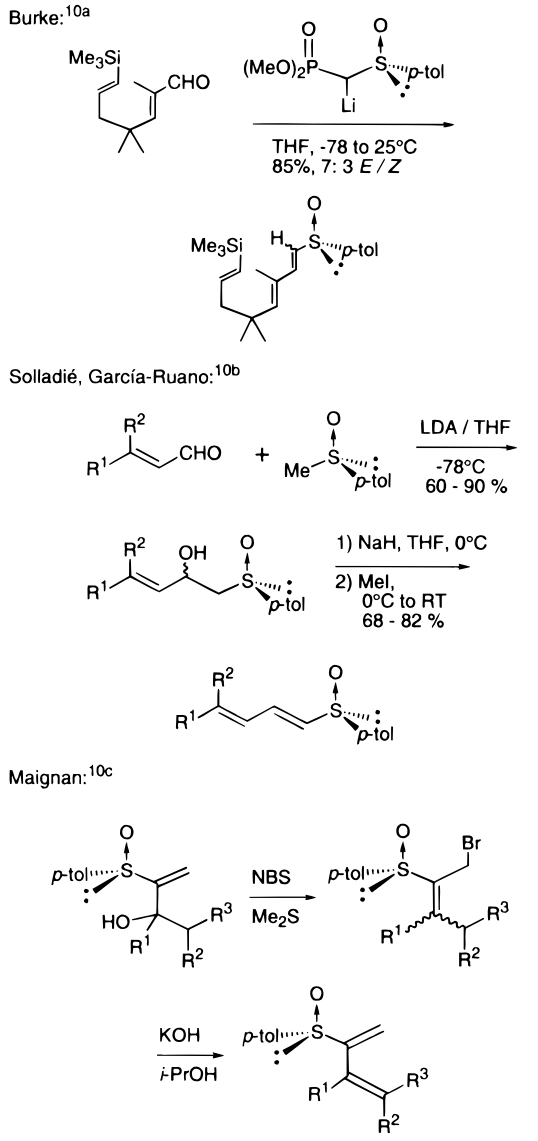
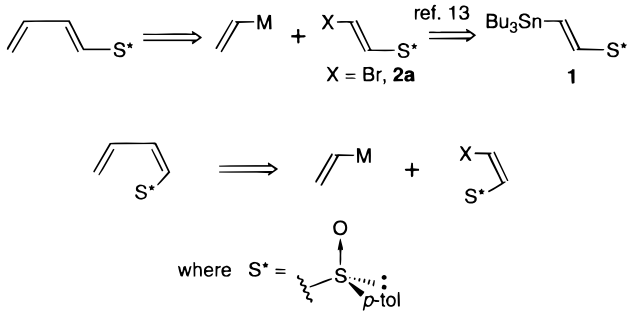


Figure 1. Prior noteworthy approaches to enantiopure sulfinyl dienes.

At the onset of our research program there were several procedures available for the synthesis of enantiopure sulfinyl dienes; however, these were unfortunately either limited in scope or not highly stereoselective (Figure 1).[10] For example, enal homologation by means of a Wadsworth−Emmons reaction using a sulfinyl phosphonate[11] was reported by Burke[10a] to proceed with only a modest 7:3 stereoselectivity, favoring the (1*E*,3*E*)-1-sulfinyl diene isomer. Solladié and García-Ruano[10b] had developed methodology to prepare sulfinyl dienes in a stereospecific manner; however, this approach was also restricted to the (1*E*,3*E*) isomer. Finally, Maignan[10c] described approaches to 2-sulfinyl dienes via base-induced elimination of 2-sulfinyl allylic bromides, though the extent of competing reactions was highly substrate dependent. Furthermore, the diene substitution patterns were somewhat narrow in scope; for instance, alkyl substitution at C_1 of the diene was not reported.

Scheme 1



If we were to develop the chemistry of sulfinyl dienes in a manner which would ultimately lead to diastereoselective transformations, it was clear a different approach that would allow for the formation of stereopure isomers (*cis* as well as *trans*) was necessary. Furthermore, we would require a method which would provide an opportunity to place substituents at any position along the diene system if desired. In this paper we summarize our efforts to prepare a variety of enantiomerically pure sulfinyl dienes, and we demonstrate that for some of these substrates, highly diastereofacial complexation with an iron tricarbonyl fragment is indeed possible.

Results and Discussion

Synthesis of Enantiopure (1*E*)- and (1*Z*)-1-Sulfinyl Dienes and 1-Sulfinyl Enynes. We envisioned that one highly stereocontrolled approach to enantiopure (*E*)- or (*Z*)-1-sulfinyl dienes would be via coupling chemistry between stereodefined vinyl−metal and vinyl halide partners (Scheme 1). In fact, Farina[12] had demonstrated that this was possible, but his Stille-based approach using vinyl triflates and an (*E*)-2-stannyl vinyl sulfoxide had been undertaken using only racemic sulfoxides (obtained by oxidation of the corresponding sulfides) and had not been developed in order to accommodate the synthesis of (1*Z*)-isomers. Therefore we reasoned that our approach would only be feasible if the (*E*)- or (*Z*)-2-halo or 2-stannyl vinyl sulfoxide coupling partner could be prepared in homochiral form. Fortunately, we were aware of procedures[13] for the synthesis of the enantiopure (*E*)-2-stannyl vinyl sulfoxide **1** and its 2-bromo vinyl sulfoxide derivative **2a** from (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene. However, an approach toward the complementary (*Z*)-2-stannyl or 2-halo isomer was unknown, and we thus chose to direct our initial attention toward its synthesis.

Judging from the ample precedence[2,5] that halogenated Lewis acids readily coordinate to the sulfinyl oxygen, we reasoned that this interaction could help deliver a halide in a stereospecific manner to an alkynyl sulfoxide. Using enantiopure sulfinylethyne **3**[14] (Scheme 2), several Lewis acids were screened; no reaction was observed upon

(9) (a) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. Wender, P. A.; Ihle, N. C. *Tetrahedron Lett.* **1987**, *28*, 2451. Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432. (b) Takacs, J. M.; Zhu, J. *J. Org. Chem.* **1989**, *54*, 5193−5195. (c) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965.

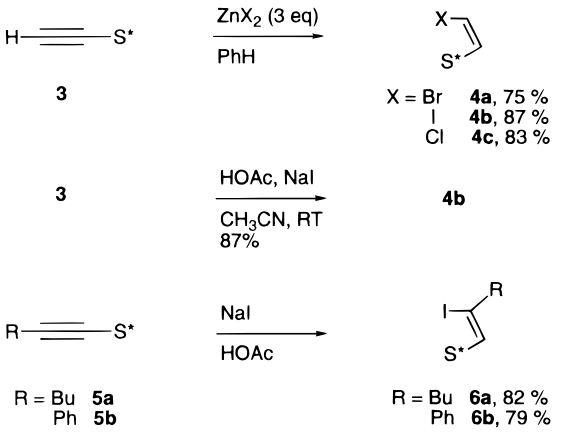
(10) (a) Burke, S. D.; Shankaran, K.; Helber, M. J. *Tetrahedron Lett.* **1991**, *32*, 4655−4658. (b) Solladié, G.; Ruiz, P.; Colobert, F.; Carreño, M. C.; García-Ruano, J. L. *Synthesis* **1991**, 1011−1012. (c) Bonfand, E.; Gosselin, P.; Maignan, C. *Tetrahedron: Asymmetry* **1993**, *4*, 1667−1676.

(11) (a) Goldmann, S.; Hoffmann, R. W.; Maak, N.; Geueke, K.-J. *Chem. Ber.* **1980**, *113*, 831−844. (b) Mikolajczyk, M.; Midura, W.; Grzejszczak, S.; Zatorski. A.; Chefczynska, A., *J. Org. Chem*, **1978**, *43*, 473−478.

(12) Farina, V.; Hauck, S. I. *J. Org. Chem.* **1991**, *56*, 4317−4319.

(13) Paley, R. S., Ph.D. Thesis, University of Michigan, 1987. This procedure was published after the onset of the current work: Marino, J. P.; Laborde, E.; Deering, C. F.; Paley, R. S.; Ventura, M. P. *J. Org. Chem.* **1994**, *59*, 3193−3201.

Scheme 2

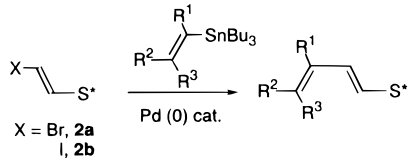


treatment of benzene solutions of **3** with $HgCl_2$ or $CdBr_2$ at room temperature. However, use of $MgBr_2$ provided the desired (*Z*)-2-bromo vinyl sulfoxide **4a** in a modest 35% yield.[15] In order to optimize this conversion we considered the use of zinc halides; with good solubility in organic solvents and high oxophilicity required for coordination to the sulfinyl oxygen, this seemed to be an excellent option. Indeed, treatment of a THF solution of **3** with ZnI_2 provided the corresponding (*Z*)-2-iodo vinyl sulfoxide **4b** in a 50% yield. Further optimization, using 3 equiv of ZnI_2 and benzene as the solvent improved the procedure to afford **4b** in 87% yield after 15 h. The corresponding bromide **4a** and chloride **4c** were prepared in a similar manner, from $ZnBr_2$ (30 h) and $ZnCl_2$ (72 h), respectively.

Encouraged by these results, we next sought to explore the synthesis of more substituted analogs. Unfortunately, utilization of 1-sulfinyl-1-hexyne **5a**[14] as described above (rt or refluxing PhH) did not provide any of the desired iodo vinyl sulfoxide. At this stage we became aware of the report by Marek[16a] of a related transformation using NaI in AcOH to prepare (*Z*)-iodo vinyl carboxylates. These conditions proved to be readily adaptable to our needs, as iodovinyl sulfoxide **6a** was obtained in high yield[17] (Scheme 2); the phenyl-substituted analog **6b** was prepared as well. Unsubstituted analog **4b** could also be prepared in this manner (rt, 90 min, 87%). We have since modified this procedure to avoid the use of acetic acid as a solvent; CH_3CN is now used instead, with acetic acid present in only stoichiometric amounts (see Experimental Section for details).

With both (*E*)- and (*Z*)-halovinyl sulfoxide isomers in hand, we then sought a suitable vinylic metal coupling partner in order to achieve the desired stereocontrolled synthesis of 1-sulfinyl dienes. Preliminary investigations utilizing organocuprates with iodovinyl sulfoxide **4b** were not fruitful; neither divinylcuprate nor the corresponding cyanocuprate afforded the desired 1-sulfinyl dienes.[18] Because coupling with vinyl cuprates had proven to be unfeasible, and due to the expected oxophilicity (and thus sulfoxide group incompatibility) of corresponding boron, aluminum, and zirconium reagents, we decided to focus our efforts on vinyl stannanes as coupling partners[19] for halovinyl sulfoxides **2** and **4**. This proved to be a judicious choice, as we were able to establish conditions for the coupling of vinyl tri-*n*-butylstannane with (*E*)-bromovinyl sulfoxide **2a**; dienyl sulfoxide **7a** was produced in excellent yield using $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol %) and PPh_3 (8 mol %) in refluxing THF (Table 1).[20] The generality of the new methodology was then tested by performing the coupling reaction with a variety of vinyl stannanes.[21] Significantly, the optical rotations of products **7b** and **7d** were virtually identical to those reported by Solladié[10b] for the same compounds which had been synthesized by a different route.[22] This evidence is confirmation that the optical purity of the sulfoxide is *not* compromised by the coupling process reported here. It should also be noted that use of allyl tri-*n*-butylstannane provided the "skipped" sulfinyl diene **9**, in high yield (Table 1, entry 11), and that a bis-coupling, to produce bis-sulfinyl triene **8**, was also possible.

Table 1. Palladium-Catalyzed Synthesis of Enantiomerically Pure)1*E*)-Sulfinyl Dienes



entry	sulfoxide	R^1	R^2	R^3	cond[a]	product	% yield
1	**2a**	H	H	H	A	**7a**	87
2	**2a**	H	Ph	H	A	**7b**	87
3	**2b**	H	Bu	H	B	**7c**	60
4	**2a**	H	Me	Me	A	**7d**	80
5	**2b**	Me	H	H	B	**7e**	80
6	**2b**	EtO	H	H	B	**7f**	83
7	**2a**	H	$CH(OEt)_2$	H	A	**7g**	85
8	**2a**	H	$CH(OEt)_2$	Me	A	**7h**	61
9	**2a**	H	*b*	H	A	**7i**	83
10	**2b**[c]	*d*	*d*	*d*	B	**8**	68
11	**2a**[c]	*e*	*e*	*e*	A	**9**	71

[a] Reaction conditions: Method A: vinylstannane (1.0−1.2 equiv), $Pd_2(dba)_3{\cdot}CHCl_3$ (2 mol %), PPh_3 (8 mol %), refluxing THF, 0.5 to 2 h. Method B: Reaction conditions: vinylstannane (1.0−1.2 equiv), $Pd(CH_3CN)_2Cl_2$ (2 mol %), DMF, rt, 15 min to 3 h. [b] 4-(1,3-Dithiolan-2-yl)-butyl. [c] 2 equiv used. [d] (*E*)-Bis(tri-*n*-butylstannyl)ethene. [e] Allyl tri-*n*-butylstannane.

(14) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078−1082.

(15) The (*Z*)-stereochemistry of **4a** was readily verified by ^{1}H NMR; the vinylic proton coupling constant of 6.7 Hz was consistent with *cis* stereochemistry.

(16) (a) Marek, I.; Alexakis, A.; Normant, J.-F. *Tetrahedron Lett.* **1991**, *32*, 5329−5332. Marek, I.; Meyer, C.; Normant, J.-F *Org. Synth.* **1996**, *74*, 194−204. See also: (b) Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709−713. (c) Ma, S.; Lu, X. *Org. Synth.* **1993**, *72*, 112−115.

(17) The structure of **6a** was verified by an NOE experiment: irradiation of the vinyl proton at 6.6 ppm resulted in a 2.0% enhancement for the allylic methylene at 2.6 ppm.

(18) Treatment of **4b** with divinylcuprate (derived from commercially available vinylmagnesium bromide) afforded a 62:38 mixture of (1*Z*)- and (1*E*)-sulfinyl dienes (in a 1.6:1 ratio) and sulfinylethene. Treatment with the corresponding cyanocuprate afforded (*Z*)-2-cyano-1-sulfinylethene (25%) and unreacted **4b** (65%).

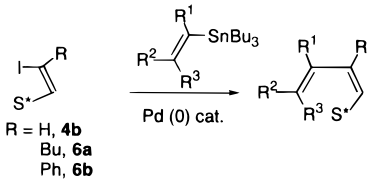
(19) (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1−652. (b) Farina, V.; Roth, G. P. *Adv. Metal-Org. Chem.* **1996**, *5*, 1−53. (c) Mitchell, T. N.; *Synthesis* **1992**, 803−815. (d) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813−817. (e) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524 and references therein.

(20) Stereochemical and configurational homogeneity of **7a** was established by examination of the ^{1}H NMR spectrum of the crude reaction mixture at 300 MHz and analysis of the ^{1}H NMR spectrum of the purified material in the presence of $Eu(hfc)_3$.

(21) See ref 57b for references which describe the synthesis of commercially unavailable vinyl stannanes. For the stannane used to prepare **10g**, see: Hutzinger, M. W.; Oehlschlager, A. C. *J. Org. Chem.* **1995**, *60*, 4595−4601. For the stannane used to prepare **10h**, **10i**, and **10l**, see: Barrett, A. G. M.; Barta, T. E.; Flygare, J. A. *J. Org. Chem.* **1989**, *54*, 4246−4249.

(22) Optical rotation data: **7b**: $[\alpha]_D = +225.0$, *c* 0.44, acetone; [lit.: [10b] $[\alpha]_D = +225.1$, *c* 0.82, acetone]. **7d**: $[\alpha]_D = +218.6$, *c* 1.06, acetone; [lit.:[10b] $[\alpha]_D = +216.1$, *c* 0.74, acetone]).

Table 2. Palladium-Catalyzed Synthesis of Enantiomerically Pure (1*Z*,3*E*)-Sulfinyl Dienes



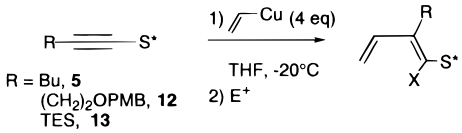
entry	sulfoxide	R	R^1	R^2	R^3	product	% yield[a]
1	**4b**	H	H	H	H	**10a**	91
2	**4b**	H	Me	H	H	**10b**	80
3	**4b**	H	H	Me	Me	**10c**	91
4	**4b**	H	EtO	H	H	**10a**	83
5	**4b**	H	H	$CH(OEt)_2$	H	**10e**	76
6	**4b**	H	H	$CH(OEt)_2$	Me	**10f**	75
7	**4b**	H	Bu	CH_2OH	H	**10g**	77
8	**4b**	H	CH_2OH	CH_2OTBS	H	**10h**	87
9	**4b**	H	CH_2OH	CH_2OTIPS	H	**10i**	89
10	**6a**	Bu	H	H	H	**10j**	80
11	**6a**	Bu	H	Ph	H	**10k**	92
12	**6a**	Bu	CH_2OH	CH_2OTBS	H	**10l**	68
13	**6b**	Ph	H	H	H	**10m**	89
14	**4b**[b]	*c*	*c*	*c*	*c*	**11**	83

[a] Reaction conditions: vinylstannae (1.0−1.2 equiv), $Pd(CH_3CN)_2Cl_2$ (2 mol %), DMF, rt, 15 min to 3 h. [b] 2 equiv used. [c] (*E*)-Bis(tri-*n*-butylstannyl)ethene.

Our next goal was to effect the analogous transformation using (*Z*)-iodovinyl sulfoxide **4b** in order to establish a stereocontrolled route to the more challenging (1*Z*,3*E*)-1-sulfinyl dienes. Surprisingly, the identical reaction conditions that successfully produced **7a** were instead nonstereospecific; sulfinyl diene **10a** was obtained as a (1*Z*)/(1*E*) mixture in an 82:18 ratio. Fortunately, the use of "ligandless" conditions[23] ($Pd(CH_3CN)_2Cl_2$, 2 mol %, DMF) afforded (1*Z*,3*E*)-1-sulfinyl diene **10a** in excellent yield and with complete retention of double bond stereochemistry. This stereospecific coupling was repeated with a number of other vinyl stannanes[21] (Table 2[24]) and could also be performed with trisubstituted iodovinyl sulfoxides **6a** or **6b** to prepare the first examples of (1*Z*,3*E*)-2-alkyl-1-sulfinyl dienes (**10j-m**). It should also be noted that these "ligandless" conditions can be employed to cleanly couple vinyl stannanes to (*E*)-iodovinyl sulfoxide **2b** as well (Table 1, entries 3, 5, 6, and 10), with complete stereospecificity. An apparent limitation to our methodology is our inability to effect coupling of **4b** with methyl (*E*)-2-stannyl acrylate. Finally, we have been unable to effect coupling of vinyl halides to (*E*)-stannylvinyl sulfoxide **1** under either set of conditions described above.[25]

We were intrigued by the loss of stereospecificity in the attempted coupling of (*Z*)-iodovinyl sulfoxide **4a** using the $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$/THF system, and thus we carried out several experiments in order to gain an understanding of the mechanism of this process. (1*Z*,3*E*)-1-Sulfinyl diene **10a** was resubmitted to the same reaction conditions which had given rise to the double bond isomerization (vinyl tributylstannane, 1 equiv; $Pd_2(dba)_3{\cdot}CHCl_3$, 2 mol %; PPh_3, 8 mol %; THF, reflux); after 1 h, *ca.* 30% of the *cis* double bond had been converted into the *trans* isomer. When this experiment was repeated without vinyl stannane, the result was identical; however, when the palladium catalyst was also omitted, no isomerization took place. The possibility that adventitious acid caused the double bond isomerization was seemingly excluded by repeating the experiment using $Pd_2(dba)_3{\cdot}CHCl_3$ and PPh_3 with added diisopropylethylamine (20 mol %); isomerization still took place as before. To rule out that high temperature (refluxing THF vs DMF at room temperature) played a role in the isomerization, **10a** was treated with $Pd(CH_3CN)_2Cl_2$ and the vinyl stannane in DMF at 80 °C; no isomerization was observed. As a result of these experiments, we now speculate that the isomerization of the *cis* double bond was a result of conjugate addition of PPh_3 to the vinyl sulfoxide, rotation of the intermediate zwitterionic species, and ejection of PPh_3.[26] Presumably the palladium catalyst coordinates to the sulfinyl oxygen, thereby activating the system toward nucleophilic attack.

Table 3. Syntehsis of Enantiomerically Pure (1*E*,3*E*)-Sulfinyl Dienes via Carbocupration of Alkynyl Sulfoxides



entry	sulfoxide	E^+	X	product	% yield
1	**5**	aqueous workup	H	**14a**	93
2	**5**	NIS (4 equiv)	I	**14b**	65
3	**12**	aqueous workup	H	**14c**	80
4	**13**	aqueous workup	H	**14d**	47

It did not escape our attention that our approach to (1*E*)-sulfinyl dienes suffered one severe limitation: it would be impossible to prepare 2-alkyl-substituted (1*E*)-sulfinyl dienes. Since (*E*)-2-halovinyl sulfoxides **2** were derived from (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene,[27] adapting this approach to the synthesis of the more substituted analog would require regiospecific transmetalation of the unknown 1,2-bis(tri-*n*-butylstannyl)-1-alkenes. Thus we turned to a different approach to install substituents in the 2-position. It had been previously demonstrated[14,28] that alkylcopper reagents (*e.g.*, MeCu, BuCu) add to alkynyl sulfoxides regio- and stereospecifically to afford vinyl sulfoxides in high yield. We reasoned that sulfinyl dienes could be obtained if vinyl copper reagents were to be employed in an analogous manner. Indeed, this goal was readily accomplished, as shown in Table 3. Furthermore, we demonstrate here that the presumed 1-sulfinylvinyl copper intermediate can be trapped with an electrophile other than proton. Introduction of an iodine atom (Table 3, entry 2, **14b**) could in principle allow for further manipulation of this sulfinyl diene.

With methodology now available for controlling the stereochemistry of the 1,2-double bond, we next sought a procedure that would allow for access to the isomers

(23) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551.

(24) (1*Z*)-1-Sulfinyl dienes **10g**,**h**,**i** are obtained as 30−35:1 mixtures containing minor amounts of the (1*E*) isomers which can be readily removed by silica gel chromatography. The origin of this slight loss of stereoselectivity would appear to be in the Stille coupling process; however, the mechanism by which it occurs remains unclear.

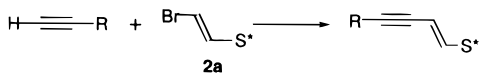
(25) See ref 4e for an example of coupling involving an aryl iodide and stannylvinyl sulfoxide **1**. We have only been able to effect a coupling between stannylvinyl sulfoxide **19** and *p*-nitrophenyl iodide to afford the corresponding 1-sulfinyl styrene derivative in a 39% yield.

(26) This process would be reminiscent of those reported by Trost: Trost, B. M.; Li, C.-J. *J. Am. Chem. Soc.* **1994**, *116*, 3167−3168 and 10819−10820.

(27) (a) Corey, E. J.; Wollenburg, R. H. *J. Org. Chem.* **1975**, *40*, 2265−2266. (b) Corey, E. J.; Wollenburg, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5581−5583. (c) Bottaro, J. C.; Hanson, R. N.; Seitz, D. E. *J. Org. Chem.* **1981**, *46*, 5221−5222.

(28) Truce, W. E.; Lusch, M. J. *J. Org. Chem.* **1978**, *43*, 2252−2258.

Table 4. Synthesis of Enantiomerically Pure (*E*)-1-Sulfinyl-1-en-3-ynes[a]

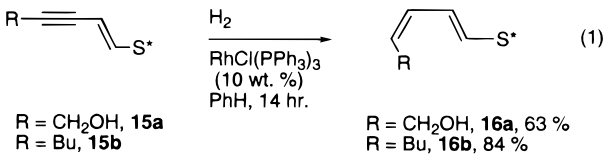


2a

entry	R	product	% yield
1	CH_2OH	**15a**	84
2	Bu	**15b**	84
3	$(CH_2)_3OTBS$	**15c**	86
4	$SiEt_3$	**15d**	87

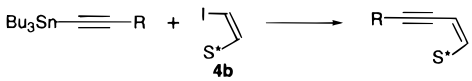
[a] Reaction conditions: **2a** (1 equiv), alkyne (1.2 equiv), DBU (2 equiv), $Pd(PPh_2)_4$ (5 mol %), CuI (30 mol %), benzene, rt, 40 min.

containing a (3*Z*)-double bond. Since at the onset of this work there were no general preparations for *cis*-vinyl stannanes,[29] we envisioned an approach which would involve *syn*-reduction of previously unknown enantiopure enynyl sulfoxides. We judged that the most rapid entry into these systems, and one that would avoid stannane synthesis, would involve use of the Sonogashira methodology[30] to couple alkynes to halovinyl sulfoxides **2** or **4**. Indeed, there was a clear precedence that electron-deficient vinyl halides could participate in this transformation in the presence of a hindered base.[31] Our own results corroborated this requirement;[32] optimal yields of (*E*)-1-sulfinyl enyne **15a** were ultimately obtained when 2 equiv of the non-nucleophilic base DBU was added to the reaction mixture (in benzene). This reaction also proved to be general for a number of functionalized alkynes; the results are summarized in Table 4. To demonstrate that (*E*)-1-sulfinyl enynes could serve as precursors for (1*E*,3*Z*)-1-sulfinyl dienes, **15a** and **15b** were cleanly hydrogenated to **16a** and **16b** using H_2 and $RhCl(PPh_3)_3$ (10 wt %) in benzene (eq 1). The *cis* stereochemistry of the new double bond in each new sulfinyl diene was confirmed by analysis of the individual ^1H NMR spectra.[33]



Though the Sonogashira coupling smoothly afforded (*E*)-1-sulfinyl enynes, attempts to replicate this procedure in order to prepare the corresponding (*Z*) isomers were unsuccessful. All attempts to induce (*Z*)-iodovinyl sulfoxide **4b** to couple to any alkyne, regardless of choice of palladium catalyst or amine base, led to its complete decomposition. Though we are still unable to provide an explanation, we could readily overcome this complication by use of Stille methodology. Alkynylstannanes coupled to **4b** under the "ligandless" conditions just as readily as vinylstannanes had, affording (*Z*)-1-sulfinyl enynes **17** (Table 5). For alkynes that demonstrated a poor solubility in DMF, THF was employed as a cosolvent (DMF/THF, 95:5) in order to obtain comparable yields. While we were able to overcome the problem of preparation of these (*Z*)-1-sulfinyl enynes, we have been unable to successfully hydrogenate them to obtain the corresponding (1*Z*,3*Z*)-1-sulfinyl dienes. Attempted hydrogenation of **17a** with Wilkinson's catalyst led to the formation of a complicated mixture of **17a** and overreduced products, while use of Lindlar's catalyst (in benzene) or $Pd/BaSO_4$ (in pyridine) resulted only in recovery of the sulfinyl enyne.

Table 5. Synthesis of Enantiomerically Pure (*Z*)-1-Sulfinyl-1-en-3-ynes[a]

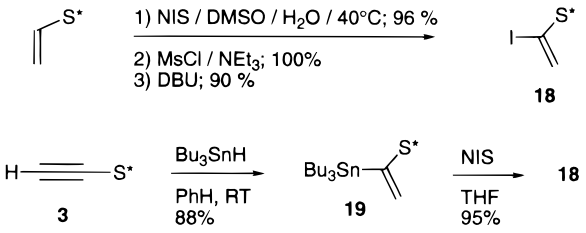


4b

entry	R	product	% yield
1	Bu	**17a**	77[b]
2	$(CH_2)_4O$-*t*-Bu	**17b**	74[b]
3	CH_2OTBS	**17c**	75
4	$SiEt_3$	**17d**	87
5	$CH(OEt)_2$	**17e**	82
6	H	**17f**	60
7	Ph	**17g**	66

[a] Reaction conditions: **4b** (1 equiv), stannylalkyne (1.2 equiv), $Pd(CH_3CN)_2Cl_2$ (2 mol %), DMF, rt, 30 min to 1 h. [b] Reaction performed in 95:5 DMF/THF.

Scheme 3



Synthesis of Enantiopure (1*E*)- and (1*Z*)-2-Sulfinyl Dienes. We next sought to extend our approach in order to prepare enantiopure 2-sulfinyl dienes. At first glance, preparation of the simplest analog, 2-sulfinyl butadiene **29a**, seemed straightforward; the previously known[34] 1-bromovinyl sulfoxide would be coupled to vinyl tri-*n*-butylstannane under the conditions described above for the synthesis of (*E*)-1-sulfinyl dienes. As it turned out the 1-bromovinyl sulfoxide was remarkably resistant to coupling, as all efforts to effect this transformation failed to provide more than traces of 2-sulfinyl diene **29a**. Reasoning that the corresponding iodide would be more reactive, we developed two approaches to prepare this previously unknown compound (Scheme 3). First, (*R*)-vinyl *p*-tolyl sulfoxide was regiospecifically converted to its iodohydrin;[35] mesylation of the diastereomeric alcohols followed by DBU-induced elimination afforded 1-iodovi-

(29) Reports on the synthesis of (*Z*)-vinylstannanes have recently been published: (a) Lipshutz, B. H.; Keil, R.; Barton, J. C. *Tetrahedron Lett.* **1992**, *33*, 5861−5864; (b) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568−4571; (c) Nakamura, E.; Imanishi, Y.; Machii, D. *J. Org. Chem.* **1994**, *59*, 8178−8186.

(30) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467−4470. (b) Ratoveloma, V.; Linstrumelle, G. *Tetrahedron Lett.* **1981**, *22*, 315−318.

(31) Schreiber had successfully coupled a terminal alkyne with methyl (*E*)-3-iodo acrylate using the "standard" cocatalysts $Pd(PPh_3)_4$ and CuI, but with triethylamine as the solvent. Presumably the hindered base was employed to suppress addition−elimination side reactions. Schreiber, S. L.; Kiessling L. L. *J. Am. Chem. Soc.* **1988**, *110*, 631−633. See also: Myers, A. G.; Alauddin, M. M.; Fuhry, M. M.; Dragovich, P. S.; Finney, N. S.; Harrington, P. M. *Tetrahedron Lett.* **1989**, *30*, 6997−7000.

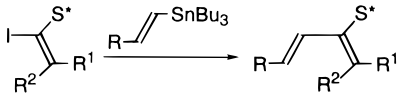
(32) The attempted coupling of propargyl alcohol to **2a** in diethylamine [with $Pd(PPh_3)_4$ (5 mol %) and CuI (30 mol %)] completely failed. While use of benzene as the solvent gave disappointing product yields of 20 to 30%, an improvement to 54% was realized using 4:1 benzene/triethylamine as the solvent.

(33) After performing the required decoupling experiments, J_{H3-H4} was determined to be 11.0 Hz and 10.8 Hz for **16a** and **16b**, confirming the *cis* stereochemistry of the 3,4−double bond of each compound.

(34) Cardellicchio, C.; Fiandanese, V.; Naso, F.; Scilimati, A. *Tetrahedron Lett.* **1992**, *33*, 5121−5124.

(35) The iodohydrin was obtained as a 6:1 mixture of diastereomers which were inseparable by column chromatography.

Table 6. Synthesis of Enantiopure 2-Sulfinyl Dienes



entry	sulfoxide	R	R^1	R^2	method[a]	product	% yield
1	**18**	H	H	H	A	**29a**	70
2	**22**	H	H	Bu	B	**29b**	89
3	**22**	Ph	H	Bu	B	**29c**	77
4	**24**	H	Bu	H	C	**29d**	75
5	**24**	*b*	Bu	H	B	**29e**	59
6	**27**	H	*c*	H	C	**29f**	59
7	**28**	H	Bu	Me	C	**29g**	81

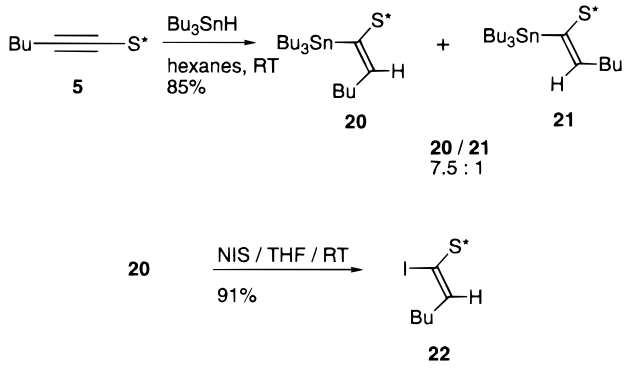
[a] Reaction conditions: A: $Pd(CH_3CN)_2Cl_2$ (2 mol %) BHT (1 equiv), DMF, rt, 2 h. B: $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %), $AsPh_3$ (20 mol %), BHT (1 equiv), THF, rt, 2 h. C: $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %), $AsPh_3$ (20 mol %), BHT (1 equiv), THF, Δ, 2 h. [b] $(EtO)_2CH$. [c] $PMBO(CH_2)_4$.

nyl sulfoxide **18** in an excellent overall yield. Alternatively, sulfinyl ethyne **3**[14] was treated with Bu_3SnH in benzene[36] to regiospecifically provide the 1-stannylvinyl sulfoxide **19** which was then readily converted to **18** using NIS.

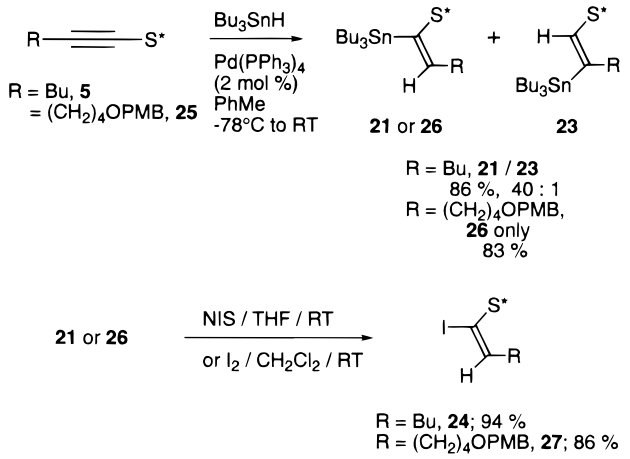
As expected, **18** did prove to be a more reactive coupling partner with vinyltri-*n*-butylstannane, though the improvement in yield was only modest (25−35%). Again, a variety of conditions were tested: $Pd(CH_3CN)_2Cl_2$, in DMF or NMP, rt to 100 °C; $Pd_2(dba)_3{\cdot}CHCl_3$ with PPh_3 or $AsPh_3$,[37] in THF (rt to Δ) or NMP (rt to 100 °C). Fortunately **29a** was at last obtained in an acceptable yield (70%) with $Pd(CH_3CN)_2Cl_2$ (DMF, rt) when the radical inhibitor BHT was included as an additive (Table 6, entry 1).[38] Optical rotation data measured for **29a** again established that the optical integrity of the sulfoxide was not compromised by the palladium-catalyzed coupling processes reported herein.[39]

Extending this approach to more substituted 2-sulfinyl dienes also proved to be feasible and relied on our ability to prepare the required iodovinyl sulfoxide coupling partners with a high degree of regio- and stereoselectivity. Initally we attempted to trap α-lithiovinyl sulfoxides (obtained by LDA treatment of (*E*)-vinyl sulfoxides at −78 °C in THF) with I_2 or CI_4, but the desired iodovinyl sulfoxides were produced in poor yields (<40%). After an unsuccessful attempt to extend the iodohydrin/mesylation/elimination sequence to prepare a more substituted analog of **18**, we began to investigate hydrostannylations of readily available alkynyl sulfoxides. First, to prepare (1*E*)-2-sulfinyl dienes, an *anti* hydrostannylation as first reported by Leusink[36] was required. Using hexane as a solvent, we were able to regio- and stereoselectively convert alkynyl sulfoxide **5** into its stannylvinyl sulfoxide derivative **20**, accompanied by a minor amount of its *syn*-hydrostannylation product **21** (Scheme 4). After routine separation and purification of **20** by silica gel chromatography, conversion to the corresponding iodide[41] **22** and

Scheme 4



Scheme 5



subsequent coupling to vinyl stannanes was straightforward. In these cases, the (1*E*)-2-sulfinyl dienes **29b** and **29c** were best obtained with a $Pd_2(dba)_3/AsPh_3$/BHT/THF system (Table 6).

Next, preparation of the isomeric (1*Z*)-2-sulfinyl dienes would require the complementary *syn*-hydrostannylation process. While the palladium-catalyzed hydrostannylation procedure of Guibé[42a] had been shown to be a predominantly *syn*-process for electron poor alkynes, the exact ratio of product isomers was rather substrate dependent. Indeed, in the only prior report of an application of this process with alkynyl sulfoxides, the 2:1 regioisomeric mixture of 1- and 2-stannylvinyl sulfoxides reported by Magriotis[43] was not particularly encouraging. Nevertheless, when alkynyl sulfoxide **5**[14] was subjected to these conditions (Bu_3SnH, 2 mol % $Pd(PPh_3)_4$, toluene, rt), 1-stannylvinyl sulfoxide **21** was obtained as a 6:1 regioisomeric mixture. Remarkably, when the same reaction was performed at low temperature (−78 °C to rt over 3 h), this ratio improved to 40:1 (Scheme 5)! Again, the isomers were readily separated by chromatography, and after conversion to iodide **24** and coupling with vinyl tri-*n*-butylstannane, (1*Z*)-2-sulfinyl diene **29d** was obtained in good yield. The generality of this reaction sequence was illustrated by the preparation of functionalized analog **29f** (Table 6).

(36) Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organometallic Chem.* **1967**, *9*, 295−306.

(37) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585−9595.

(38) For recent uses of BHT in Stille coupling processes, see ref 19a and Stork, G.; Issacs, R. C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7399−7400.

(39) The optical rotation data measured for **29a** ($[\alpha]_D = +168$, *c* 1.79, EtOH) was within experimental error of the literature value (lit.[40] $[\alpha]_D = +174$, *c* 2.0, EtOH) and was independent of the sequence of reactions used to prepare iodovinyl sulfoxide **18**.

(40) Bonfand, E.; Gosselin, P.; Maignan, C. *Tetrahedron Lett.* **1992**, *33*, 2347−2348. See also ref 10c.

(41) For other applications of enantiopure α-halovinyl sulfoxides, see Mikolajczyk, M.; Krysiak, J. A.; Wieczorek, M. W.; Blaszcyk, J. *Tetrahedron: Asymmetry* **1996**, *7*, 3513−3520 and references therein.

(42) (a) Zhang, H. X., Guibé, F., Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857−1867. See also: (b) Ichinose, Y.; Oda, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3468−3470. (c) Miyake, H.; Yamamura, K. *Chem. Lett.* **1989**, 981−984.

(43) Magriotis, P. A., Brown, J. T., Scott, M. E. *Tetrahedron Lett.* **1991**, *32*, 5047−5050.

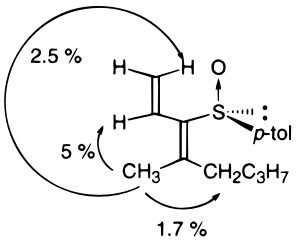
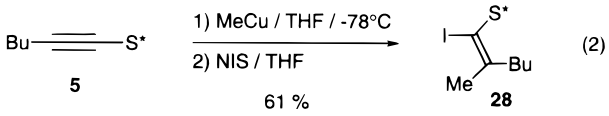


Figure 2. NOE data for sulfinyl diene **29g**.

Finally, we briefly explored the possibility of introducing *two* 1-alkyl substituents into the 2-sulfinyl diene system via a carbocupration−iodination sequence. As demonstrated earlier (Table 3, entry 2) organocopper reagents can add to alkynyl sulfoxides regio- and stereospecifically, and the presumed 1-sulfinylvinyl copper intermediate can be trapped with iodine. Introduction of iodine was in fact vital to our approach in order to provide entry into a substrate which would be suitable for coupling to vinyl stannanes. This proved to be a useful method, as sequential treatment of alkynyl sulfoxide **5** with methyl copper and NIS provided the fully substituted 1-iodovinyl sulfoxide **28** in an acceptable yield of 61% (eq 2). Coupling of **28** to vinyl tri-*n*-butylstannane proceeded smoothly, affording the fully substituted 2-sulfinyl diene **29g** (Table 6); the stereochemistry was verified by NOE experiments, as shown in Figure 2.



(2)

Diastereoselective Synthesis of Enantiopure Sulfinyl Diene Iron(0) Tricarbonyl Complexes. With access to a diverse array of sulfinyl dienes, we next set out to determine which, if any, of these substrates would exhibit diastereoselective complexation upon treatment with a coordinatively unsaturated metal fragment. The reported ease of preparation, isolability, and handling of iron(0) diene complexes[44] accounted for our decision to explore the chemistry of the previously unknown enantiopure sulfinyl diene iron(0) tricarbonyl complexes. It was our expectation that allylic 1,3-strain[8] would restrict the sulfoxide conformation with respect to the diene; by forcing the bulky sulfinyl aromatic group into a position over one of the diene's diastereotopic faces, the other face should be available for preferential complexation by the metal fragment.

Prior to the onset of this work there were only isolated reports of diastereoselective complexations of an iron tricarbonyl unit to a diene bearing one or more chiral centers. Most notable among these was the chiral-auxiliary-directed asymmetric complexation described by Pearson;[45] a chiral (*E*,*E*)-dienamide prepared from (*S*)-2-(diphenylhydroxymethyl)pyrrolidine was complexed with high diastereoselectivity (>99:1) at *ca*. 50% conversion. Other examples have included a modestly diastereoselective complexation (75:25) of a diene derived from *L*-arabinose[46] and the diastereospecific complexation of *cis*-1-methyl-2,3-methoxycyclohexa-4,6-diene.[47] We were also aware of a report from 1977 which described the synthesis of iron(0) tricarbonyl complexes of racemic sulfinyl dienes; however, the diastereoselectivity of these complexations was not discussed.[48]

Our earliest experiments used the method of Shvo and Hazum[49] to prepare the sulfinyl iron(0) diene complexes. This approach, using $Fe(CO)_5$ and *N*-methyl morpholine *N*-oxide (NMO), afforded the target complexes in modest to good yields. However, as we tested more highly substituted sulfinyl dienes, yields of the corresponding $Fe(CO)_3$ complexes began to decrease to 20−30%. For these substrates, we found it convenient to use an excess of $(bda)Fe(CO)_3$[50] (4 equiv) in order to effect the desired complexation in high yield. Because this iron tricarbonyl transfer reagent is not commercially available and because it was necessary to employ an excess of reagent to drive the complexation to completion, we routinely recovered as much of the excess $(bda)Fe(CO)_3$ as possible during chromatographic purification of the reaction product. Typically, 70 to 80% of the excess 3 equiv of $(bda)Fe(CO)_3$ can be recovered and reused. Complexation under these conditions is apparently kinetically controlled; when the minor diastereomer of sulfinyl iron(0) diene **30m** (entry 17, Table 7) was subjected to treatment with $(bda)Fe(CO)_3$ (4 equiv, toluene, 45 °C, 16 h), it was recovered with none of the major diastereomer detected (by TLC). By comparison, complexation with $Fe(CO)_5$/NMO appears to be under thermodynamic control; when the minor diastereomer of sulfinyl iron(0) diene **30g** (entry 11, Table 7) was subjected to these conditions, both diastereomers as well as the decomplexed sulfinyl diene **7i** were observed (by TLC).

The only limitation to the use of $(bda)Fe(CO)_3$ as an iron tricarbonyl transfer reagent that we have encountered thus far is its incompatibility with unprotected alcohol groups. For example, treatment of sulfinyl diene **10g** with an excess of $(bda)Fe(CO)_3$ afforded a complex mixture of products. Unfortunately, neither complexation method could be utilized to effect conversion of sulfinyl dienes **10f**, **10l** (or its OTES derivative[51]), or **14b** into the corresponding sulfinyl iron dienes. For each of these substrates, the energy barrier for attaining the *s-cis* conformation required for complexation of the diene must simply be too high, and higher temperatures or prolonged reaction times led only to complex mixtures.

To evaluate the diastereoselectivity of the complexation of each sulfinyl diene, the major and minor diastereomeric $Fe(CO)_3$ complexes were each purified, and the ratio was then determined by weight. In every case, the R_f difference between the major and minor diastereomers was large enough to make the chromatographic separation trivial. We were unable to determine diastereomeric ratios in the usual manner using the ^1H NMR spectra of the crude reaction mixtures; it was impossible to shim NMR samples of the crude mixtures, presumably as a result of contamination with paramagnetic iron residues.

Table 7 reveals the yields and diastereomer ratios of the sulfinyl diene complexations. As we had anticipated,

(44) (a) Grée, R.; Lellouche, J. P. *Adv. Metal-Org. Chem.* **1995**, *4*, 129−173. (b) Pearson, A. J., *Iron Compounds in Organic Synthesis*; Academic Press: San Diego, 1994.

(45) Pearson, A. J.; Chang, K.; McConville, D. B.; Youngs, W. J. *Organometallics* **1994**, *13*, 4−5. See also references cited therein.

(46) (a) Schmalz, H.-G.; Hessler, E.; Bats, J. W.; Dürner, G. *Tetrahedron Lett.* **1994**, *35*, 4543−4546. (b) Hessler, E.; Schmalz, H.-G.; Dürner, G. *Tetrahedron Lett.* **1994**, *35*, 4547−4550.

(47) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1603−1604.

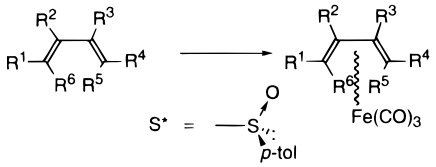
(48) Gaoni, Y. *Tetrahedron Lett.* **1977**, 4521−4524.

(49) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829−830.

(50) Alcock, N. W.; Danks, T. N.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231−238.

(51) Prepared in a 75% yield from **10l** by treatment with TESOTf and 2,6-lutidine (CH_2Cl_2, rt).

Table 7. Diastereoselective Fomration of η^4-(1- and 2-Sulfinyl diene)Fe(0)$(CO)_3$ Complexes from Substituted Enantiopure Sulfinyldienes



Entry	Sulfinyldiene	R^1	R^2	R^3	R^4	R^5	R^6	Method[a]	α / β [b]	Major pdt.	Yield
1	**7a**	H	H	H	S*	H	H	A[c]	1.35 : 1	**30a**	94
2	**10a**	H	H	H	H	S*	H	A	α only	**30b**	43
3	**10a**	H	H	H	H	S*	H	B	16 : 1	**30b**	59
4	**10a**	H	H	H	H	S*	H	C	*ca.* 20 : 1	**30b**	47
5	**10j**	H	H	Bu	H	S*	H	B	5.5 : 1[d]	**30c**	52
6	**10j**	H	H	Bu	H	S*	H	C	2.4 : 1	**30c**	49
7	**29a**	H	H	S*	H	H	H	A	1.2 : 1[e]	**30d**	45
8	**10e**	$(EtO)_2CH$	H	H	H	S*	H	B	16 : 1	**30e**	80
9	**10e**	$(EtO)_2CH$	H	H	H	S*	H	C	*ca.* 20 : 1	**30e**	67
10	**7g**	$(EtO)_2CH$	H	H	S*	H	H	B	1.4 : 1	**30f**	87
11	**7h**	$(EtO)_2CH$	H	H	S*	H	Me	B	1.04 : 1	**30g**	30
12	**29e**	$(EtO)_2CH$	H	S*	Bu	H	H	B	1.4 : 1[f]	**30h**	59
13	**14a**	H	H	Bu	S*	H	H	C	1 : 2.6[g]	**30i**	96
14	**14d**	H	H	TES	S*	H	H	C	1 : 1.8	**30j**	92
15	**10g**	CH_2OH	Bu	H	H	S*	H	B	4.8 : 1	**30k**	64
16	**10h**	CH_2OTBS	CH_2OH	H	H	S*	H	B	11.3 : 1	**30l**	49
17	**10i**[h]	CH_2OTIPS	CH_2OTES	H	H	S*	H	C	10.4 : 1	**30m**	92

[a]Method A: $Fe_2(CO)_9$ (3 eq), Et_2O, Δ; Method B: $Fe(CO)_5$ (3 eq), NMO (6 eq), THF, 0° to Δ; Method C: (bda)$Fe(CO)_3$, 4.0 eq, $PhCH_3$, 45°C. [b]Diastereomeric ratios were obtained by weight ratio of chromatographically purified products. [c]Reaction performed in THF at 70°C. [d]The minor diastereomer and unreacted sulfinyl diene **10j** were inseparable by chromatography. [e]The diastereomers were inseparable by chromatography. [f]The minor diastereomer and unreacted sulfinyl diene **29e** were inseparable by chromatography. [g]The minor diastereomer could not be separated from the by-product benzylidene acetone by chromatography. [h]Sulfinyl diene **10i** was first transformed into its OTES derivative using TESOTf and 2,6-lutidine (CH_2Cl_2, RT, 75% yield) prior to complexation.

those substrates capable of minimal carbon−sulfur bond rotation as a consequence of allylic 1,3-strain[8] are complexed with good to excellent diastereoselectivity (entries 2−4, 8, 9, 16, 17). The absolute stereochemistry of the major diastereomer of **30e** has been determined by X-ray crystallography of a derived iron dienol; the crystal structure has been published elsewhere[52] and reveals that the $Fe(CO)_3$ fragment is positioned on the α face,[53] *anti* to the bulky tolyl group of the sulfoxide group. By analogy, and as a consequence of similar chromatographic polarities,[54] the major (less polar) diastereomers of **30b**,**c**,**k**,**l**,**m** have been also each assigned as possessing an α face $Fe(CO)_3$ fragment. We are at this point unable to explain the diminished selectivities for the complexation of sulfinyl dienes **10g** and **10j**. For the (1*E*)-2-alkyl-1-sulfinyl dienes **14a** and **14d** which were examined (entries 13, 14), it was the *more* polar $Fe(CO)_3$ diene diastereomer of which predominated. In these cases, allylic strain also must force the tolyl group into a preferred conformation which instead is proximal to the α diene face rather than the β face as observed for the (1*Z*)-1-sulfinyl dienes. The marginal selectivity observed for complexation of **14a** and **14d** must be a result of the favored position of the tolyl group: it would be expected to point away from the diene unit and thus would be too distant to have a significant impact on the direction of the approach of the $Fe(CO)_3$ fragment. On the basis of this argument, and the chromatographic polarity observed for these cases, we are *tentatively* assigning the major diastereomer for **30i** and **30j** as having the $Fe(CO)_3$ fragment positioned on the β face of the diene.

Finally, we found that the (1*E*)-2-unsubstituted-1-sulfinyl dienes can be complexed with only marginal diastereoselectivities. In the absence of a 2-substituent, it would be expected that this lack of selectivity is a result of the small calculated energy difference (1.6 kcal/mol)[55] between the two conformational minima of such systems, as pointed out by Hoffmann.[8] Assuming that the slightly lower energy conformation would place the S−O bond in the plane of the 1,2-double bond, the β diene face would be somewhat shielded by the sulfoxide tolyl group and the $Fe(CO)_3$ fragment should prefer, though only marginally, to be positioned on the α diene face. As we have been unable to obtain satisfactory crystals from these (1*E*)-2-unsubstituted-1-sulfinyl iron(0) diene complexes

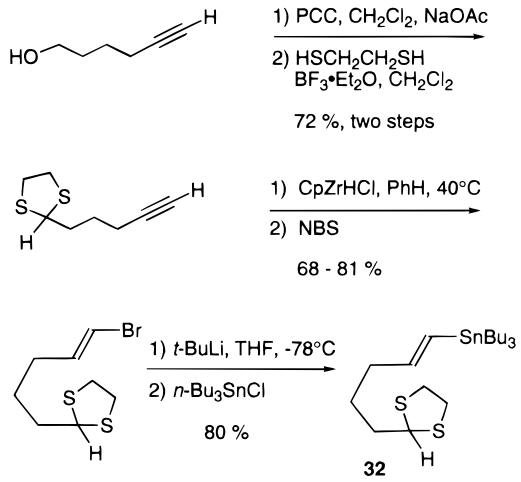
(52) Paley, R. S.; Rubio, M. B.; Fernández de la Pradilla, R.; Dorado, R.; Hundal, G.; Martínez-Ripoll, M. *Organometallics* **1996**, *15*, 4672−4674.

(53) We are defining the diene plane, as drawn in Table 7, as the separation between the α (lower) face from the β (upper) face.

(54) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058−3064. Chromatographic polarities have often been used to make stereochemical assignments for iron(0) diene complexes. For example, see: Roush, W. R.; Park, J. C. *Tetrahedron Lett.* **1990**, *31*, 4707−4710.

(55) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7399−7400.

Scheme 6



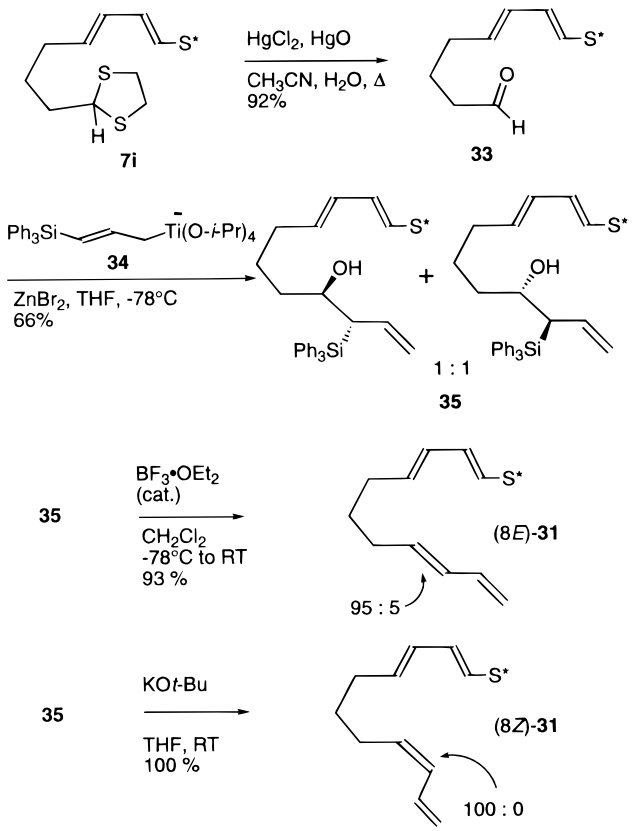
(or any of their derivatives), we are forced to make a *tentative* assignment of absolute stereochemistry of the major diastereomers which is based on the model discussed above, and, once again, on the chromatographic polarities. As in the highly diastereoselective cases (for example, entry 8) where the major iron(0) diene diastereomers were each *less* polar, the major diastereomers of **30a**,**d**,**f**,**g**,**h** were also less polar, suggesting that in each of these cases the $Fe(CO)_3$ fragment occupied the α diene face.

Synthesis of a Sulfinyl Tetraene. Among our objectives was the synthesis of more complex sulfinyl dienes, especially those that might be suitable for an investigation of intramolecular Diels−Alder reactions[1] or transition metal catalyzed cycloisomerizations.[9] In principle the asymmetry of the sulfoxide could be exploited to control the absolute stereochemistry of the newly formed stereocenters in these processes. An issue which needed to be resolved was simply to determine if the required enantiopure multiply unsaturated sulfoxides could in fact be prepared through utilization of the methodology we had developed. We therefore chose (1*E*)-1-sulfinyl tetraene **31** as a synthetic target; our success largely depended on our choice of an appropriately functionalized vinyl stannane to be coupled with bromovinyl sulfoxide **2a**. Stannane **32** was prepared from 1-hexynal in three steps (Scheme 6); remarkable in this sequence was the ability to effect lithiation of a vinyl bromide in the presence of the acidic proton of a dithioacetal. Sulfinyl diene **7i** was readily prepared (entry 8, Table 1) according to the methodology described herein.

Scheme 7 details the conversion of sulfinyl diene **7i** to the target sulfinyl tetraene **31**. After deprotection of **7i** to reveal aldehyde **33**, the remaining double bonds were installed by a modification of Yamamoto's protocol[56] using the allyl titanate **34** derived from allyltriphenylsilane. The hydroxysilane **35** was prepared in good yield only in the presence of $ZnBr_2$, which presumably coordinated to the sulfinyl oxygen, thus preventing it from coordinating with the oxophilic titanium reagent **34**. (Control experiments without $ZnBr_2$ or without $Ti(O\text{-}i\text{-}Pr)_4$ gave only unreacted aldehyde **33**). Hydroxysilane **35**, a 1:1 mixture of *anti* diastereomers, was treated with either catalytic $BF_3{\cdot}Et_2O$ to give the (8*E*)-isomer of tetraene **31** (*E*/*Z*; 95:5) or with potassium *tert*-butoxide to exclusively afford the (8*Z*)-isomer.

(56) Ikeda, Y.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 657.

Scheme 7



Conclusions

We have successfully demonstrated a number of stereocontrolled approaches to enantiomerically pure sulfinyl dienes based on transition metal (palladium or copper) mediated chemistry.[57] Of the diverse array of diene substitution patterns which can now be prepared that incorporate the sulfoxide functionality, the (1*Z*)-4-alkyl- and (1*Z*)-3,4-dialkyl-1-sulfinyl dienes are the best substrates for the diastereoselective complexation by a metal carbonyl fragment. Sulfinyl iron (0) tricarbonyl diene complexes can be prepared in high yield (up to 96%) and with high diastereoselectivity (up to 16:1) using $Fe(CO)_5$/NMO or (benzylidene acetone)$Fe(CO)_3$. The origin of the high diastereoselectivity for the complexation of the (1*Z*)-1-sulfinyl dienes is likely to be allylic 1,3-strain. We are currently exploring the chemistry of these sulfinyl iron(0) dienes and will also be investigating the possibility that the diastereoselective transition metal mediated cycloisomerizations of the multiply unsaturated sulfoxides exemplified by sulfinyl tetraene **31** could be effected using catalytic amounts of iron. These results will be reported in due course.

Experimental Section

General Methods. All reactions were carried out under a positive pressure of dry argon. Reagents and solvents were handled by using standard syringe techniques. Tetrahydrofuran, toluene, and ethyl ether were distilled from sodium and

(57) For preliminary accounts of the synthesis of enantiopure sulfinyl dienes and enynes, see: (a) Fernández de la Pradilla, R.; Morente, M.; Paley, R. S. *Tetrahedron Lett.* **1992**, *33*, 6101−6102. (b) Paley, R. S.; de Dios, A.; Fernández de la Pradilla, R. *Tetrahedron Lett.* **1993**, *34*, 2429−2432. (c) Paley, R. S.; Lafontaine, J. A.; Ventura, M. P. *Tetrahedron Lett.* **1993**, *34*, 3663−3666. (d) Paley, R. S.; Weers, H. L.; Fernández, P.; Fernández de la Pradilla, R.; Castro, S. *Tetrahedron Lett.* **1995**, *36*, 3605−3608.

benzophenone; methylene chloride was distilled from CaH_2. Anhydrous dimethylformamide and anhydrous acetonitrile were purchased from Aldrich and stored under an argon atmosphere. All other solvents were reagent grade and were used as purchased. Flash chromatography was performed using Merck 230−400 silica gel 60. Analytical TLC was carried out on Merck silica gel 60 F-254 precoated glass plates, with detection by UV light and acidic vanillin solution or PMA solution in ethanol. Optical rotations were measured in $CHCl_3$ or acetone at 22 °C. Melting points are uncorrected. ^{1}H NMR spectra were recorded at 200, 300, 400, or 500 MHz using $CDCl_3$ as a solvent (unless otherwise noted). Mass spectra were measured by direct probe injection in a low resolution mass spectrometer using electron impact with an ionization energy of 70 eV. Elemental analyses were obtained at the Unidad Estructural de Análisis y Técnicas Instrumentales del Instituto de Química Orgánica of the CSIC of Madrid.

General Procedure for the Synthesis of (*Z*)-(*R*)-2-Halovinyl *p*-Tolyl Sulfoxides. To a solution of (+)-(*S*)-ethynyl *p*-tolyl sulfoxide[14] in benzene (14 mL per mmol of sulfoxide) was added 3 equiv of zinc(II) halide, ZnX_2. At the conclusion of the reaction (as judged by TLC), the reaction mixture was hydrolyzed with a 5% aqueous solution of sodium bicarbonate. The aqueous phase was carefully extracted with diethyl ether; the combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/EtOAc) using the eluant indicated in each case.

(−)-(*Z*)-(*R*)-2-Bromoethenyl *p*-Tolyl Sulfoxide (4a). Yield: 75%. mp 63−64 °C (hexane); $[\alpha]_D = -473.5$ (*c* 0.78, $CHCl_3$); ^{1}H NMR (300 MHz) δ 2.42 (s, 3H), 6.86 (d, 1H, J = 6.7 Hz,), 6.99 (d, 1H, J = 6.8 Hz), 7.34 (d, 2H, J = 8.0 Hz). 7.62 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.4, 115.5, 124.1, 130.2, 140.3, 142.0, 143.2. Anal. Calcd for C_9H_9BrOS: C, 44.10; H, 3.70. Found: C, 44.21; H, 3.86.

(−)-(*Z*)-(*R*)-2-Iodoethenyl *p*-Tolyl Sulfoxide (4b). Yield: 87%. mp 60−62 °C (hexane); $[\alpha]_D = -483.3$ (*c* 0.45, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6) δ 1.93 (s, 3H), 6.13 (d, 1H, J = 7.3 Hz), 6.72 (d, 1H, J = 7.2 Hz), 6.85 (d, 2H, J = 8.2 Hz), 7.61 (d, 2H, J = 8.2 Hz); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.15 (d, 1H, J = 7.3 Hz), 7.23 (d, 1H, J = 7.3 Hz), 7.33 (d, 2H, J = 8.2 Hz), 7.65 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 88.9, 124.7, 130.1, 140.3, 141.9, 148.6. Anal. Calcd for C_9H_9IOS: C, 37.00; H, 3.10. Found: C, 36.82; H, 3.24.

Improved Procedure for the Preparation of 4b. (+)-(*S*)-Ethynyl *p*-tolyl sulfoxide **3**[14] (1.948 g, 11.86 mmol) was dissolved in anhydrous acetonitrile (25 mL) under an argon atmosphere. To this solution were added glacial acetic acid (1.36 mL, 23.7 mmol) and NaI (3.56 g, 23.7 mmol). After stirring for 45 min, the mixture was diluted with EtOAc (50 mL); solid K_2CO_3 (4.92 g, 35.6 mmol) was added, followed by a saturated aqueous solution of sodium thiosulfate (25 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 35 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was chromatographed (silica gel, hexane/EtOAc, 3:1) to afford **4b** as a pale yellow-brown solid (3.23 g, 93%); $[\alpha]_D = -477.4$ (*c* 0.45, $CHCl_3$).

(−)-(*Z*)-(*R*)-2-Chloroethenyl *p*-Tolyl Sulfoxide (4c). Yield: 83%. mp 77−78 °C (hexane); $[\alpha]_D = -453.9$ (*c* 0.57, $CHCl_3$); ^{1}H NMR (300 MHz) δ 2.42 (s, 3H), 6.59 (d, 1H, J = 6.7 Hz), 6.64 (d, 1H, J = 6.7 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.59 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 21.4, 124.0, 126.6, 130.1, 139.9, 140.3, 142.9. Anal. Calcd for C_9H_9ClOS: C, 53.86; H, 4.52. Found: C, 53.98; H, 4.71.

(−)-(*Z*)-(*R*)-2-Iodohexenyl *p*-Tolyl Sulfoxide (6a). Yield: 82%. $[\alpha]_D = -294.5$ (*c* 4.30, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.88 (t, 3H, J = 7.1 Hz), 1.26 (m, 2H), 1.52 (m, 2H), 2.41 (s, 3H), 2.57 (t d, 2H, J =7.5, 1.3 Hz), 6.62 (t, 1H, J = 1.2 Hz), 7.32 (d, 2H, J = 7.9 Hz), 7.63 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 13.6, 21.2, 21.4, 30.8, 45.6, 117.7, 124.1, 130.0, 140.9, 141.6, 142.3. Anal. Calcd for $C_{13}H_{17}IOS$: C, 44.84; H, 4.92. Found: C, 44.69; H, 4.81.

(−)-(*Z*)-(*R*)-2-Phenyl-2-iodoethenyl *p*-Tolyl Sulfoxide (6b). Yield: 79%. $[\alpha]_D = -138.5$ (*c* 1.30, $CHCl_3$); ^{1}H NMR (300 MHz) δ 2.40 (s, 3H), 7.01 (s, 1H), 7.26−7.35 (m, 5H), 7.45−7.50 (m, 2H), 7.71 (d, 2H, J = 8.1 Hz); ^{13}C NMR (50 MHz) δ 21.4, 112.1, 124.5, 128.5, 128.7, 130.2, 130.3, 140.1, 141.0, 141.9, 144.3. Anal. Calcd for $C_{15}H_{13}IOS$: C, 48.92; H, 3.56. Found: C, 48.67; H, 3.90.

General Procedure for Synthesis of 1-Sulfinyl Dienes via Stille Coupling. Method A. To a stirred and degassed solution of (*E*)-2-bromovinyl *p*-tolyl sulfoxide **2a**[13] (1 equiv) and the corresponding vinyltributylstannane in dry THF (6 mL/mmol) under argon atmosphere were successively added PPh_3 (0.08 equiv) and Pd_2dba_3·$CHCl_3$ (0.02 equiv), and resultant mixture was stirred and heated to reflux over a 30 min period. The reaction mixture was cooled, diluted with ethyl ether, and washed with water; the aqueous phase was back-extracted with ether, and the combined organic layers were washed with water (three times) and then stirred with an equal volume of a half-saturated solution of potassium fluoride for 12 h. The precipitate of tributylstannyl fluoride was removed by filtration, and the ethereal filtrate was dried over $MgSO_4$. Concentration *in vacuo* gave a crude product which was purified by silica gel column chromatography using a gradient of hexane:ethyl acetate mixtures (hexane/EtOAc, 9:1 to 3:1). **Method B.** To a stirred and degassed solution of (*E*) or (*Z*)-2-iodovinyl *p*-tolyl sulfoxide **2b**,[13] **4b**, **6a**, or **6b** (1 equiv) and the corresponding vinyl tributylstannane compound in dry DMF (6 mL/mmol) under argon atmosphere was added $Pd(CH_3CN)_2Cl_2$ (0.02 equiv), and the resulting mixture was stirred at room temperature. The reaction was monitored by TLC; when consumption of the starting materials was complete (3 min−1 h), the solution was diluted with ethyl ether and washed with water. The aqueous phases were back-extracted with ether, and the combined organic layers were washed with water and stirred with an equal volume of a half-saturated solution of potassium fluoride for 12 h. The white precipitate of tributylstannyl fluoride was removed by filtration, and the ethereal filtrate was dried over $MgSO_4$. Concentration *in vacuo* gave a crude product which was purified by silica gel column chromatography using a gradient of hexane:ethyl acetate mixtures (hexane:EtOAc, 9:1 to 3:1).

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3-butadiene (7a). Yield (method A): 87%. $[\alpha]_D = +283.8$ (*c* 0.68, $CHCl_3$); ^{1}H NMR (200 MHz) δ 2.39 (s, 3H), 5.39 (dd, 1H, J = 10.4, 1.1 Hz), 5.53 (dd, 1H, J = 16.9, 1.1 Hz), 6.32 (d, 1H, J = 15.0 Hz), 6.37 (dt, 1H, J = 16.9, 10.4 Hz), 6.95 (dd, 1H, J = 15.0, 10.7 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 123.7, 124.7, 130.0, 133.2, 135.9, 136.5, 140.6, 141.6. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.73; H, 6.37; S, 16.77.

(+)-(1*E*,3*E*)-4-Phenyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (7b). Yield (method A): 87%. mp 102 °C (Et_2O/hexane); $[\alpha]_D = +168.9$ (*c* 0.87, $CHCl_3$), $[\alpha]_D = +225.0$ (*c* 0.44, acetone); ^{1}H NMR (200 MHz) δ 2.40 (s, 3H), 6.43 (d, 1H, J = 14.7 Hz), 6.71−6.89 (m, 2H), 7.14 (ddd, 1H, J = 14.7, 8.1, 2.0 Hz), 7.23−7.44 (m, 7H), 7.54 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 124.7, 124.8, 126.9, 128.7, 130.0, 135.7, 135.9, 136.1, 138.7, 141.0, 141.5. The physical and spectroscopic data for this compound matched those previously described in the literature.[10b]

(+)-(1*E*,3*E*)-4-*n*-Butyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (7c). Yield (method B): 75%. $[\alpha]_D = +46.5$ (*c* 2.30, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.89 (t, 3H, J = 6.9 Hz), 1.22−1.43 (m, 4H), 2.15 (m, 2H), 2.40 (s, 3H), 6.06−6.11 (m, 2H), 6.21 (d, 1H, J = 14.8 Hz), 6.95 (ddd, 1H, J = 14.9, 6.5, 3.4 Hz), 7.30 (d, 2H, J = 8.5 Hz), 7.51 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 13.7, 21.3, 22.1, 30.8, 32.4, 124.6, 126.9, 129.9, 133.4, 137.3, 141.2, 141.3, 143.0. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.69; H, 7.90; S, 13.22.

(+)-(1*E*)-4-Methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (7d). Yield (method A): 80%. $[\alpha]_D = +218.6$ (*c* 1.06, acetone); ^{1}H NMR (200 MHz) δ 1.85 (s, 3H), 1.90 (s, 3H), 2.40 (s, 3H), 5.91 (br d, 1H, J = 11.4 Hz), 6.19 (d, 1H, J = 14.8 Hz), 7.22 (dd, 1H, J = 14.8, 11.4 Hz), 7.30 (d, 2H, J = 7.8 Hz), 7.52 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 18.7, 21.3, 26.3, 122.1, 124.6, 129.9, 132.8, 133.7, 141.2, 141.2, 144.5. The physical

and spectroscopic data for this compound matched those previously described in the literature.[10b]

(+)-(1*E*)-3-Methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (7e). Yield (method B): 83%. $[\alpha]_D = +207.6$ (*c* 0.66, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.80 (br s, 3H), 2.38 (s, 3H), 5.27 (m, 2H), 6.25 (d, 1H, $J = 15.3$ Hz), 7.03 (d, 1H, $J = 15.3$ Hz), 7.28 (d, 2H, $J = 8.1$ Hz), 7.50 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 18.3, 21.4, 122.9, 124.7, 130.0, 133.5, 138.9, 139.3, 140.8, 141.6. Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 70.03; H, 6.91; S, 15.39.

(+)-(1*E*)-3-Ethoxy-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (7f). Yield (method B): 90%. $[\alpha]_D = +382.8$ (*c* 0.87, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.26 (t, 3H, $J = 7.0$ Hz), 2.38 (s, 3H), 3.76 (q, 2H, $J = 7.0$ Hz), 4.35 (d, 1H, $J = 2.1$ Hz), 4.39 (d, 1H, $J = 2.1$ Hz), 6.62 (d, 1H, $J = 14.8$ Hz), 6.76 (d, 1H, $J = 14.8$ Hz), 7.29 (d, 2H, $J = 8.3$ Hz), 7.51 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 14.2, 21.3, 63.1, 92.0, 124.9, 130.0, 131.5, 133.3, 140.4, 141.7, 155.9. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 65.78; H, 7.05; S, 13.81.

(+)-(1*E*,3*E*)-5,5-Diethoxy-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (7g). Yield (method A): 85%. $[\alpha]_D = +142.9$ (*c* 1.05, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.18 (t, 6H, $J = 7.1$ Hz), 2.37 (s, 3H), 3.39−3.65 (m, 4H), 4.96 (d, 1H, $J = 4.5$ Hz), 5.96 (dd, 1H, $J = 15.3$, 4.5 Hz), 6.36 (d, 1H, $J = 14.8$), 6.39 (dd, 1H, $J = 15.3$, 10.8 Hz), 6.95 (dd, 1H, $J = 14.9$, 10.8 Hz), 7.27 (d, 2H, $J = 8.1$ Hz), 7.47 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 15.2, 21.4, 61.1, 99.9, 124.8, 129.0, 130.1, 134.4, 136.7, 137.3, 140.4, 141.8. Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53; S, 10.89. Found: C, 64.84; H, 7.86; S, 10.63.

(+)-(1*E*,3*E*)-5,5-Diethoxy-4-methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (7h). Yield (method A): 61%. $[\alpha]_D = +200.7$ (*c* 1.18, $CHCl_3$); ^{1}H NMR (400 MHz) δ 1.22 (t, 6H, $J = 7.0$ Hz), 1.90 (d, 3H, $J = 0.9$ Hz), 2.41 (s, $3H_3$), 3.44 (m, 2H), 3.59 (m, 2H), 4.73 (s, 1H), 6.29 (d, 1H, $J = 11.3$ Hz), 6.37 (d, 1H, $J = 14.8$ Hz), 7.26 (dd, 1H, $J = 14.8$, 11.4 Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 7.52 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz) δ 12.9, 15.1, 21.4, 61.67, 61.70, 103.8, 123.4, 124.8, 130.1, 131.4, 136.7, 140.7, 141.6, 142.5. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.37; H, 7.99.

(+)-(1*E*,3*E*)-8-(1,3-Dithiolan-2-yl)-1-[(*R*)-*p*-tolylsulfinyl]-1,3-octadiene (7i). Yield (method A): 83%. $[\alpha]_D = +78.3$ (*c* 0.97, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.53 (m, 2H, $J = 7.0$ Hz), 1.78 (m, 2H), 2.15 (m, 2H), 2.36 (s, 3H), 3.18 (m, 4H), 4.42 (t, 1H, $J = 6.9$ Hz), 5.92−6.10 (m, 2H), 6.19 (d, 1H, $J = 15.0$ Hz), 6.90 (dd, 1H, $J = 15.0$, 8.8 Hz), 7.27 (d, 2H, $J = 8.0$ Hz), 7.48 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (50 MHz) δ 21.3, 28.1, 32.3, 38.4, 38.7, 53.4, 124.7, 127.4, 130.0, 133.9, 136.8, 141.2, 141.4, 141.7. Anal. Calcd for $C_{17}H_{22}OS_3$: C, 60.31; H, 6.55. Found: C, 60.57; H, 6.73.

(+)-(1*E*,3*E*,5*E*)-1,6-Bis[(*R*)-*p*-tolylsulfinyl]-1,3,5-hexatriene (8). Yield (method B): 68%. mp 131 °C (Et_2O/petroleum ether, −18 °C); $[\alpha]_D = +756.4$ (*c* 0.39, $CHCl_3$); ^{1}H NMR (300 MHz) δ 2.38 (s, 6H), 6.45 (d, 2H, $J = 14.8$ Hz), 6.49 (m, 2H), 6.99 (ddd, 2H, $J = 14.8$, 7.4, 3.1 Hz), 7.29 (d, 4H, $J = 8.0$ Hz), 7.48 (d, 4H, $J = 8.2$ Hz); ^{13}C NMR (75 MHz) δ 21.4, 124.9, 130.2, 133.5, 133.6, 138.7, 140.1, 142.1. Anal. Calcd for $C_{20}H_{20}O_2S_2$: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.67; H, 5.40; S, 17.73.

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,4-pentadiene (9). Yield (method A): 71%. $[\alpha]_D = +132.4$ (*c* 1.14, $CHCl_3$); ^{1}H (200 MHz) NMR δ 2.41 (s, 3H), 2.97 (tq, 2H, $J = 6.3$, 1.4 Hz), 5.10 (m, 2H), 5.79 (m, 1H), 6.24 (dt, 1H, $J = 15.2$, 1.5 Hz), 6.62 (dt, 1H, $J = 15.2$, 6.3 Hz), 7.31 (d, 2H, $J = 8.3$ Hz), 7.52 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 21.3, 35.7, 117.4, 124.5, 129.9, 133.6, 136.1, 137.5, 141.0, 141.3. Anal. Calcd for $C_{12}H_{14}OS$: C, 60.31; H, 6.55. Found: C, 60.17; H, 6.73.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3-butadiene (10a). Yield (method B): 91%. $[\alpha]_D = -438.5$ (*c* 0.52, $CHCl_3$); ^{1}H NMR (200 MHz) δ 2.40 (s, 3H), 5.52 (dd, 1H, $J = 9.9$, 0.4 Hz), 5.55 (dd, 1H, $J = 16.5$, 0.4 Hz), 6.17 (d, 1H, $J = 9.8$ Hz), 6.60 (app t, 1H, $J = 9.8$ Hz), 7.18 (dt, 1H, $J = 16.6$, 9.8 Hz), 7.31 (d, 2H, $J = 8.0$ Hz), 7.50 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 21.2, 123.9, 125.0, 129.9, 130.5, 136.4, 137.8, 140.9, 141.1. Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.81; H, 6.50; S, 16.39.

(−)-(1*Z*)-3-Methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (10b). Yield (method B): 80%. $[\alpha]_D = -329.5$ (*c* 0.78, $CHCl_3$); ^{1}H NMR (200 MHz) δ 2.14 (br s, 3H), 2.38 (s, 3H), 5.27 (m, 2H), 6.15 (d, 1H, $J = 10.6$ Hz), 6.54 (d, 1H, $J = 10.6$ Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 7.50 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (50 MHz) δ 21.3, 22.8, 124.0, 124.3, 130.0, 130.2, 135.9, 139.7, 139.8, 141.2. Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 69.92; H, 6.88; S, 15.33.

(−)-(1*Z*)-4-Methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (10c). Yield (method B): 91%. $[\alpha]_D = -503.7$ (*c* 1.08, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.85 (s, 3H), 1.94 (s, 3H), 2.40 (s, 3H), 6.02 (d, 1H, $J = 9.4$ Hz), 6.68 (br d, 1H, $J = 11.6$ Hz), 6.86 (dd, 1H, $J = 11.6$, 9.5 Hz), 7.30 (d, 2H, $J = 8.0$ Hz), 7.51 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 18.5, 21.3, 26.6, 119.2, 123.9, 129.8, 132.5, 134.1, 140.8, 141.4, 145.4. Anal. Calcd for $C_{13}H_{16}OS$: C, 70.86; H, 7.32; S, 14.55. Found: C, 70.58; H, 7.60; S, 14.31.

(−)-(1*Z*)-3-Ethoxy-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (10d). Yield (method B): 83%. $[\alpha]_D = -623.8$ (*c* 0.21, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.38 (t, 3H, $J = 7.0$ Hz), 2.39 (s, 3H), 3.89 (q, 2H, $J = 7.0$ Hz), 4.37 (d, 1H, $J = 2.3$ Hz), 4.41 (d, 1H, $J = 2.3$ Hz), 6.03 (d, 1H, $J = 10.7$ Hz), 6.20 (d, 1H, $J = 10.7$ Hz), 7.26 (d, 2H, $J = 8.0$ Hz), 7.55 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz) δ 14.5, 21.3, 63.9, 92.8, 124.3, 129.8, 130.9, 138.7, 140.6, 142.5, 156.5. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.34; H, 7.05; S, 13.29.

(−)-(1*Z*,3*E*)-5,5-Diethoxy-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (10e). Yield (method B): 76%. $[\alpha]_D = -244.0$ (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz) δ 1.21 (t, 6H, $J = 7.0$ Hz), 2.41 (s, 3H), 3.51−3.74 (m, 4H), 5.05 (d, 1H, $J = 4.7$ Hz), 5.99 (dd, 1H, $J = 15.3$, 4.7 Hz), 6.21 (d, 1H, $J = 9.7$ Hz), 6.62 (app t, 1H, $J = 11.1$ Hz), 7.19 (dd, 1H, $J = 15.3$, 11.2 Hz), 7.31 (d, 2H, $J = 8.1$ Hz), 7.50 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (100 MHz) δ 15.2, 21.3, 61.4, 61.5, 100.1, 124.1, 126.3, 130.1, 136.5, 137.1, 138.2, 140.7, 141.3. Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53. Found: C, 64.91; H, 7.93.

(−)-(1*Z*,3*E*)-5,5-Diethoxy-4-methyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (10f). Yield (method B): 75%. $[\alpha]_D = -330.6$ (*c* 2.26, $CHCl_3$); ^{1}H NMR (400 MHz) δ 1.14 (overlapping triplets, 6H), 1.74 (s, 3H), 2.28 (s, 3H), 3.39 (m, 2H), 3.52 (m, 2H), 4.68 (s, 1H), 6.08 (d, 1H, $J = 9.6$ Hz), 6.77 (dd, 1H, $J = 11.8$, 9.6 Hz), 6.93 (d, 1H, $J = 11.8$ Hz), 7.18 (d, 2H, $J = 7.9$ Hz), 7.39 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (100 MHz) δ 13.2, 16.0, 22.2, 62.87, 62.90, 105.1, 121.3, 124.9, 130.8, 133.5, 137.4, 141.86, 141.94, 144.6. Anal. Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.02; H, 8.01.

(−)-(1*Z*,3*E*)-3-Butyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadien-5-ol (10g). Yield (method B): 77%. $[\alpha]_D = -17.9$ (*c* 0.74, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.91 (t, 3H, $J = 7.1$ Hz), 1.23−1.50 (m, 4H), 2.28 (t, 2H, $J = 7.5$ Hz), 2.39 (s, 3H), 3.40 (br s, 1H), 4.30 (d, 2H, $J = 5.1$ Hz), 5.88 (t, 1H, $J = 5.9$ Hz), 6.20 (d, 1H, $J = 10.3$ Hz), 6.52 (d, 1H, $J = 10.3$ Hz), 7.29 (d, 2H, $J = 7.8$ Hz), 7.54 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz) δ 13.7, 21.2, 22.4, 29.7, 30.6, 58.7, 124.5, 129.9, 135.7, 136.4, 136.6, 141.18, 141.23, 141.5. Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96. Found: C, 68.87; H, 8.13.

(−)-(1*Z*,3*E*)-5-[(*tert*-Butyldimethylsilyl)oxy]-3-(hydroxymethyl)-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (10h). Yield: 87% (using method B, except the residue was **not** treated with aqueous KF solution). Purification of the crude product was accomplished with two successive gradient chromatographies (silica gel; hexane/EtOAc, 9:1 to 1:2); analytically pure **10h** was obtained by recrystallization from toluene (mp 104−106 °C). $[\alpha]_D = -230.4$ (*c* 1.12, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.06 (s, 6H), 0.88 (s, 9H), 2.35 (s, 3H), 3.87 (app t, 1H, $J = 5.4$ Hz), 4.35−4.40 (m, 4H), 5.88 (app t, 1H, $J = 5.7$ Hz), 6.15 (d, 1H, $J = 10.5$ Hz), 6.55 (d, 1H, $J = 10.5$ Hz), 7.23 (d, 2H, $J = 8.1$ Hz), 7.54 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (100 MHz) δ −5.40, −5.38, 18.1, 21.2, 25.71, 25.72, 58.8, 59.6, 124.5, 129.8, 135.5, 135.6, 138.8, 139.1, 141.1. Anal. Calcd for $C_{19}H_{30}O_3SSi$: C, 62.25; H, 8.25. Found: C, 62.45; H, 8.51.

(−)-(1*Z*,3*E*)-3-(Hydroxymethyl)-1-[(*R*)-*p*-tolylsulfinyl]-5-[(triisopropylsilyl)oxy]-1,3-pentadiene (10i). Yield: 89% (method B, except the residue was **not** treated with aqueous KF solution). Purification of the crude product was accomplished with two successive gradient chromatographies

(silica gel; hexane/EtOAc, 19:1 to 1:1). $[\alpha]_D = -211.1$ (*c* 3.03, $CHCl_3$); ^1H NMR (400 MHz) δ 1.06−1.18 (m, 21H), 2.40 (s, 3H), 3.41 (br, 1H), 4.45 (m, 4H), 5.97 (app t, 1H, $J = 5.7$ Hz), 6.22 (d, 2H, $J = 10.5$ Hz), 6.62 (d, 2H, $J = 10.5$ Hz), 7.29 (d, 2H, $J = 8.2$ Hz), 7.59 (d, 2H, $J = 8.2$ Hz); ^{13}C (100 MHz) NMR δ 12.7, 18.8, 22.2, 60.1, 60.9, 125.4, 130.9, 136.6, 136.7, 139.7, 140.3, 142.1, 142.2. Anal. Calcd for $C_{22}H_{36}O_3SSi$: C, 64.66; H, 8.88. Found: C, 64.91; H, 8.67.

(−)-(1*Z*)-2-*n*-Butyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (10j). Yield (method B): 80%. $[\alpha]_D = -310.1$ (*c* 1.23, $CHCl_3$); ^1H NMR (400 MHz) δ 0.87 (t, 3H, $J = 7.0$ Hz), 1.22−1.54 (m, 4H), 2.31 (app t, 2H, $J = 7.3$ Hz), 2.40 (s, 3H), 5.48 (dd, 1H, $J = 11.0$, 0.8 Hz), 5.60 (dd, 1H, $J = 17.3$, 0.8 Hz), 6.09 (s, 1H), 7.22 (ddd, 1H, $J = 17.3$, 11.0, 0.7 Hz), 7.30 (d, 2H, $J = 8.0$ Hz), 7.48 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (100 MHz) δ 13.6, 21.2, 22.3, 30.1, 32.3, 119.9, 124.0, 129.8, 131.6, 134.5, 140.8, 141.5, 148.6. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.71; H, 8.00; S, 12.77.

(−)-(1*Z*,3*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-*n*-butyl-4-phenyl-1,3-butadiene (10k). Yield (Mmthod B): 92%. $[\alpha]_D = -663.2$ (*c* 0.98, $CHCl_3$); ^1H NMR (200 MHz) δ 0.91 (t, 3H, $J = 7.2$ Hz), 1.26−1.58 (m, 4H), 2.39 (s, 3H), 2.45 (m, 2H), 6.14 (br s, 1H), 6.91 (d, 1H, $J = 16.1$ Hz), 7.27−7.43 (m, 5H), 7.49−7.55 (m, 4H), 7.67 (d, 1H, $J = 16.1$ Hz); ^{13}C NMR (50 MHz) δ 13.7, 21.2, 22.4, 30.4, 32.9, 123.0, 124.0, 127.0, 128.7, 129.8, 134.1, 134.3, 136.1, 140.7, 141.5, 148.7. Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.45. Found: C, 77.63; H, 7.69.

(−)-(1*Z*,3*E*)-2-Butyl-5-[(*tert*-butyldimethylsilyl)oxy]-3-(hydroxymethyl)-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene (10l). Yield: 68% (method B, except the residue was **not** treated with aqueous KF solution). Purification of the crude product was accomplished with two successive gradient chromatographies (silica gel; hexane/EtOAc, 19:1 to 1:1). mp 44−46.5 °C; $[\alpha]_D = -9.25$ (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz) δ 0.11 (s, 6H), 0.86 (t, 3H, $J = 7.1$ Hz), 0.91 (s, 9H), 1.26−1.43 (m, 4H), 2.28 (t, 2H, $J = 7.8$ Hz), 2.40 (s, 3H), 3.49 (t, 1H, $J = 6.4$ Hz), 4.27 (ABX system, 2H, $J = 13.1$, 6.6, 5.8 Hz), 4.40 (m, 2H), 5.73 (app t, 1H, $J = 5.8$ Hz), 6.14 (d, 1H, $J = 0.9$ Hz), 7.29 (d, 2H, $J = 8.2$ Hz), 7.54 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (100 MHz) δ −5.30, −5.27, 13.8, 18.2, 21.3, 22.1, 25.8, 29.3, 36.0, 59.2, 59.4, 124.5, 129.9, 132.6, 133.5, 138.8, 141.0, 141.5, 156.7. Anal. Calcd for $C_{23}H_{38}O_3SSi$: C, 65.35; H, 9.06. Found: C, 65.16; H, 8.82.

(−)-(1*Z*)-2-Phenyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-butadiene (10m). Yield (method B): 89%. $[\alpha]_D = -92.8$ (*c* 1.30, $CHCl_3$); ^1H NMR (300 MHz) δ 2.41 (s, 3H), 5.41 (d, 1H, $J = 17.2$ Hz), 5.66 (d, 1H, $J = 10.7$ Hz), 6.27 (s, 1H), 7.24−7.45 (m, 8H), 7.56 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (75 MHz) δ 21.3, 124.2, 124.6, 128.3, 128.5, 128.9, 130.0, 132.0, 135.5, 137.4, 141.1, 141.5, 149.2. Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 76.23; H, 5.87.

(−)-(1*Z*,3*E*,5*Z*)-1,6-Bis[(*R*)-*p*-tolylsulfinyl]-1,3,5-hexatriene (11). Yield (method B): 83%. $[\alpha]_D = -490.0$ (*c* 0.50, $CHCl_3$); ^1H NMR (200 MHz) δ 2.38 (s, 6H), 6.27 (d, 2H, $J = 9.7$ Hz), 6.71 (app td, 2H, $J = 10.5$, 3.1 Hz), 7.28−7.34 (m, 6H), 7.48 (d, 4H, $J = 8.0$ Hz); ^{13}C NMR (50 MHz) δ 21.4, 124.2, 130.2, 132.2, 135.9, 138.8, 140.6, 141.7. Anal. Calcd for $C_{20}H_{20}O_2S_2$: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.51; H, 5.59; S, 17.68.

General Procedure for the Preparation of 1-Sulfinyl Alkynes. To the corresponding alkyne (1.12 equiv) at 0 °C was added a 3.0 *M* Et_2O solution of ethylmagnesium bromide (Aldrich, 1 equiv) via syringe. After 5 min, the ice bath was removed and the mixture was heated at 40 °C for 20 min. After cooling the mixture to −20 °C, a toluene (1.8 mL/mmol sulfinate ester) solution of (−)-menthyl (*S*)-*p*-toluenesulfinate (579 mg, 1.34 equiv), precooled to 0 °C, was added quickly via cannula. The mixture was stirred at −20 °C for 30 min and then allowed to warm to 0 °C over 30 min. The reaction was quenched with saturated aqueous NH_4Cl; the layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford a residue which was chromatographed (silica gel, hexane/EtOAc mixtures) to afford the desired 1-sulfinyl alkyne.

(+)-1(*S*)-(*p*-Tolylsulfinyl)-4-[(4-methoxybenzyl)oxy]-1-butyne (12). Yield: 38%. $[\alpha]_D = +22.9$ (*c* 1.57, $CHCl_3$); ^1H NMR (400 MHz) δ 2.72 (t, 2H, $J = 6.8$ Hz), 3.60 (t, 2H, $J = 6.8$ Hz), 3.81 (s, 3H), 4.46 (s, 2H), 6.87 (d, 2H, $J = 8.4$ Hz), 7.23 (d, 2H, $J = 8.4$ Hz), 7.33 (d, 2H, $J = 8.2$ Hz), 7.69 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (100 MHz) δ 22.1, 22.3, 56.1, 67.5, 73.6, 79.9, 103.3, 114.7, 126.0, 130.2, 130.5, 131.0, 141.8, 143.8, 160.1. Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.67; H, 6.29.

(+)-1(*S*)-(*p*-Tolylsulfinyl)-2-(triethylsilyl)ethyne (13). Yield: 67%. $[\alpha]_D = +54.5$ (*c* 1.35, $CHCl_3$); ^1H NMR (400 MHz) δ 0.67 (q, 6H, $J = 8.0$ Hz), 0.98 (t, 9H, $J = 8.0$ Hz), 2.44 (s, 3H), 7.35 (d, 2H, $J = 8.0$ Hz), 7.72 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR (100 MHz) δ 4.6, 8.1, 22.3, 102.2, 109.7, 126.0. Anal. Calcd for $C_{15}H_{22}OSSi$: C, 64.69; H, 7.96. Found: C, 64.85; H, 8.10.

(+)-1(*S*)-(*p*-Tolylsulfinyl)-4-[(4-methoxybenzyl)oxy]-1-hexyne (25). Yield: 57%. $[\alpha]_D = +35.9$ (*c* 2.26, $CHCl_3$); ^1H NMR (200 MHz) δ 1.62−1.68 (m, 4H), 2.40 (s, 3H), 2.42 (m, 2H), 3.41 (m, 2H), 3.78 (s, 3H), 4.38 (s, 2H), 6.85 (d, 2H, $J = 8.7$ Hz); 7.22 (d, 2H, $J = 8.9$ Hz), 7.31 (d, 2H, $J = 8.1$ Hz), 7.66 (d, 2H, $J = 8.3$ Hz); ^{13}C NMR (50 MHz) δ 19.5, 21.4, 24.4, 28.7, 55.2, 69.0, 72.5, 78.5, 105.4, 113.8, 125.1, 129.1, 130.1, 130.5, 141.3, 142.2, 159.2. Anal. Calcd for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 70.48; H, 6.98.

General Procedure for the Preparation of (1*E*)-2-Substituted-1-sulfinyl Dienes via Vinylcupration. To a suspension of CuI (4.2 equiv) in THF (10 mL/mmol sulfoxide) at −20 °C was added a 1.0 *M* THF solution of vinylmagnesium bromide (Aldrich, 4 equiv); this solution was stirred at −20 °C for 20 min. A THF (5 mL/mmol sulfoxide) solution of the corresponding alkynyl sulfoxide (1 equiv) was then added dropwise via syringe. After 5 min the reaction was quenched with a 9:1 aqueous solution of saturated NH_4Cl/NH_4OH and diluted with EtOAc. (For **14b**, a THF (5 mL/mmol sulfoxide) solution of NIS (2 equiv) was added via syringe and stirred for 10 min prior to aqueous workup. After quenching and diluting the reaction as described, the organic layer was washed with saturated aqueous $Na_2S_2O_3$). The layers were separated, and the aqueous layer was extracted with EtOAc; the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. Chromatography (silica gel, hexane/EtOAc mixtures) afforded the desired 1-sulfinyl diene.

(−)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-butyl-1,3-butadiene (14a). Yield: 93%. $[\alpha]_D = -258.1$ (*c* 1.79, $CHCl_3$); ^1H NMR (400 MHz) δ 0.96 (t, 3H, $J = 7.1$ Hz), 1.45 (m, 2H), 1.61 (m, 2H), 2.40 (s, 3H), 2.70 (m, 2H), 5.35 (d, 1H, $J = 10.8$ Hz), 5.56 (d, 1H, $J = 17.4$ Hz), 6.16 (s, 1H), 6.23 (dd, 1H, $J = 17.4$, 10.8 Hz), 7.31 (d, 2H, $J = 7.8$ Hz), 7.51 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz) δ 14.7, 22.2, 23.7, 28.9, 32.8, 120.3, 125.1, 130.9, 136.4, 137.4, 142.0, 142.3, 150.7. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.11. Found: C, 72.38; H, 8.02.

(−)-(1*Z*)-1-Iodo-1-[(*S*)-*p*-tolylsulfinyl]-2-butyl-1,3-butadiene (14b). Yield: 65%. mp 179−180 °C; $[\alpha]_D = -123.6$ (*c* 1.27, $CHCl_3$); ^1H NMR (400 MHz) δ 0.97 (t, 3H, $J = 7.2$ Hz), 1.45 (sextet, 2H, $J = 7.0$ Hz), 1.60 (m, 2H), 2.39 (s, 3H), 3.01 (m, 2H), 5.53 (d, 1H, $J = 11.0$ Hz), 5.70 (d, 1H, 17.3 Hz), 6.67 (dd, 1H, $J = 17.3$, 11.0 Hz), 7.29 (d, 2H, $J = 8.0$ Hz), 7.44 (d, 2H, $J = 8.3$ Hz); ^{13}C NMR (100 MHz) δ 14.6, 22.3, 23.6, 32.8, 33.2, 121.4, 123.6, 125.5, 130.6, 141.4, 141.6, 142.3, 153.3. Anal. Calcd for $C_{15}H_{19}IOS$: C, 48.14; H, 5.12. Found: C, 48.01; H, 5.23.

(−)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-[2-[(4-methoxybenzyl)oxy]ethyl]-1,3-butadiene (14c). Yield: 80%. $[\alpha]_D = -135.6$ (*c* 1.66, $CHCl_3$); ^1H NMR (400 MHz) δ 2.92 (m, 1H), 3.19 (m, 1H), 3.56 (m, 1H), 3.66 (m, 1H), 3.81 (s, 3H), 4.47 (AB quartet, 2H, $J = 11.5$ Hz), 5.35 (d, 1H, $J = 10.8$ Hz), 5.56 (d, 1H, $J = 17.5$ Hz), 6.24 (dd, 1H, $J = 17.4$, 10.7 Hz), 6.25 (s, 1H), 6.88 (d, 2H, $J = 8.3$ Hz), 7.20 (d, 2H, $J = 7.9$ Hz), 7.26 (d, 2H, $J = 9.1$ Hz), 7.48 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz) δ 22.2, 29.8, 30.5, 56.1, 69.1, 73.5, 114.6, 120.5, 125.3, 130.3, 130.7, 130.9, 137.3, 138.4, 141.8, 146.5, 160.1. Anal. Calcd for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 70.65; H, 6.87.

(−)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-(triethylsilyl)-1,3-butadiene (14d). Yield: 47%. $[\alpha]_D = -66.5$ (*c* 1.62, $CHCl_3$); ^1H

NMR (400 MHz) δ 0.90 (q, 6H, J = 7.3 Hz), 1.01 (t, 9H, J = 7.6 Hz), 2.42 (s, 3H), 5.04 (d, 1H, J = 10.5 Hz), 5.24 (d, 1H, J = 16.8 Hz), 6.43 (dd, 1H, J = 16.8, 10.5 Hz), 6.84 (s, 1H), 7.32 (d, 2H, J = 8.0 Hz), 7.51 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 5.5, 8.2, 22.2, 117.5, 125.3, 130.9, 140.6, 141.9, 142.1, 146.3, 153.8. Anal. Calcd for $C_{17}H_{26}OSSi$: C, 66.61; H, 8.55. Found: C, 66.69; H, 8.72.

General Procedure for the Preparation of (*E*)-1-Sulfinyl-1-en-3-ynes. To a benzene or toluene solution of (*E*)-2-bromovinyl-*p*-tolyl sulfoxide **2a**[13] (0.05 to 0.10 *M*) were added the appropriate alkyne (1.2 equiv), DBU (2 equiv), and CuI (0.3 equiv). After deaerating the solution for 5 min (by bubbling argon into the solution), $Pd(PPh_3)_4$ (0.05 equiv) was added. The brown reaction mixture was stirred at room temperature for 40 min. It was then diluted with EtOAc, washed with two portions of a saturated aqueous NH_4Cl solution, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by chromatography (silica gel, hexane/EtOAc mixtures).

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]pent-1-en-3-yn-5-ol (15a). Yield: 84%. $[\alpha]_D$ = +256.9 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz) δ 2.40 (s, 3H), 3.62 (br t, 1H, J = 6.1 Hz), 4.36 (br d, 2H, J = 5.1 Hz), 6.54 (dd, 1H, J = 15.2, 1.5 Hz), 6.68 (d, 1H, J = 15.2 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.48 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 21.4, 51.0, 80.3, 96.0, 115.5, 125.1, 130.3, 138.8, 142.5, 144.2. Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49. Found: C, 65.31; H, 5.23.

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]oct-1-en-3-yne (15b). Yield: 84%. $[\alpha]_D$ = +190.4 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.89 (t, 3H, J = 7.3 Hz), 1.36 (m, 2H), 1.51 (m, 2H), 2.32 (dt, 2H, J = 7.0, 2.1 Hz), 2.39 (s, 3H), 6.45 (dt, 1H, J = 15.2, 2.2 Hz), 6.60 (d, 1H, J = 15.2 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.49 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 13.4, 19.2, 21.3, 21.8, 30.2, 76.1, 98.9, 116.9, 124.8, 130.1, 139.9, 141.9, 143.4. Anal. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 73.31; H, 7.51.

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-7-[(*tert*-butyldimethylsilyl)oxy]hept-1-en-3-yne (15c). Yield: 86%. $[\alpha]_D$ = +155.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.72 (quint, 2H), 2.41 (s, 3H), 2.43 (partially obscured dt, 2H, J = 7.1, 2.2 Hz), 3.67 (t, 2H, J = 5.9 Hz), 6.46 (dt, 1H, J = 15.3, 2.2 Hz), 6.60 (d, 1H, J = 15.3 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.50 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ −5.4, 16.0, 18.2, 21.4, 25.8, 31.2, 61.3, 76.2, 98.5, 116.8, 124.9, 130.1, 139.9, 141.9, 143.5. Anal. Calcd for $C_{20}H_{30}O_2SSi$: C, 66.25; H, 8.34. Found: C, 66.47; H, 8.53.

(+)-(1*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-4-(triethylsilyl)but-1-en-3-yne (15d). Yield: 87%. $[\alpha]_D$ = +177.8 (*c* 1.67, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.61 (q, 6H, J = 7.9 Hz), 0.98 (t, 9H, J = 7.9 Hz), 2.41 (s, 3H), 6.50 (d, 1H, J = 15.1 Hz), 6.75 (d, 1H, 15.3 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.51 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 4.0, 7.3, 21.4, 100.76, 100.82, 115.6, 124.9, 130.2, 139.5, 142.2, 145.6. Anal. Calcd for $C_{17}H_{24}OSSi$: C, 67.05; H, 7.94. Found: C, 66.91; H, 8.02.

(1*E*,3*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3-pentadien-5-ol (16a) and (+)-(1*E*,3*Z*)-5-Acetoxy-1-[(*R*)-*p*-tolylsulfinyl]-1,3-pentadiene. To a benzene (2 mL) solution of sulfinyl enyne **15a** (22 mg, 0.10 mmol) was added $RhCl(PPh_3)_3$ (3 mg, 14 wt %). The flask was placed under a hydrogen atmosphere (1 atm) and stirred at room temperature for 14 h. The solution was filtered through Celite to remove the catalyst and concentrated *in vacuo*; the crude material was chromatographed (silica gel, hexane/EtOAc, 19:1 to 5:1) to afford **16a** (13.6 mg, 63%) as a colorless oil. ^{1}H NMR (400 MHz) δ 2.37 (s, 3H), 4.41 (d, 2H, J = 6.2 Hz), 5.88 (dt, 1H, J = 11.0, 6.1 Hz), 6.10 (app t, 1H, J = 11.1 Hz), 6.31 (d, 1H, J = 14.8 Hz), 7.2 (obscured, 1H), 7.30 (d, 2H, J = 8.2 Hz), 7.51 (d, 2H, J = 8.2 Hz). Since alcohol **16a** could not be obtained in analytically pure form, it was characterized by conversion to its corresponding acetate (Ac_2O, 10 equiv; pyridine): $[\alpha]_D$ = +267.1 (*c* 1.81, $CHCl_3$); ^{1}H NMR (400 MHz) δ 2.08 (s, 3H), 2.39 (s, 3H), 4.82 (m, 2H), 5.81 (dt, 1H, J = 10.7, 6.9 Hz), 6.22 (app t, 1H, J = 11.2 Hz), 6.40 (d, 1H, J = 14.7 Hz), 7.25 (partially obscured ddd, J = 14.7, 11.5, 0.9 Hz), 7.30 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 20.8, 21.3, 60.0, 124.7, 128.2, 129.1, 130.1, 130.6, 138.6, 140.1, 141.8, 170.6. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.41; H, 5.43.

(+)-(1*E*,3*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3-octadiene (16b). To a benzene (2 mL) solution of sulfinyl enyne **15b** (20.6 mg, 0.084 mmol) was added $RhCl(PPh_3)_3$ (2 mg, 10 wt %). The flask was placed under a hydrogen atmosphere (1 atm) and stirred at room temperature for 14 h. The solution was filtered through Celite to remove the catalyst and concentrated *in vacuo*; the crude material was chromatographed (silica gel, hexane/EtOAc, 9:1) to afford **16b** (17.5 mg, 84%) as a colorless oil. $[\alpha]_D$ = +257.9 (*c* 1.24, $CHCl_3$), ^{1}H NMR (400 MHz) δ 0.93 (t, 3H, J = 7.2 Hz), 1.38 (m, 4H), 2.30 (m, 2H), 2.41 (s, 3H), 5.78 (m, 1H), 6.06 (t, 1H, J = 11.2 Hz), 6.29 (d, 1H, J = 14.7 Hz), 7.29 (partially obscured m, 1H), 7.30 (d, 2H, J = 8.1 Hz), 7.52 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 13.9, 21.4, 22.3, 27.8, 31.4, 124.7, 125.0, 130.0, 131.7, 135.4, 139.9, 140.9, 141.5. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12. Found: C, 72.38; H, 7.98.

General Procedure for the Preparation of (*Z*)-1-Sulfinyl-1-en-3-ynes. To a stirred and degassed solution of (*Z*)-2-iodovinyl *p*-tolyl sulfoxide **4b** (1 equiv) and the corresponding alkynyl tributylstannane (1.3 equiv) compound in dry DMF (6 mL/mmol) under argon atmosphere, was added $Pd(CH_3CN)_2Cl_2$ (0.02 equiv) and the resulting mixture was stirred at room temperature. The reaction was monitored by TLC; when consumption of the starting materials was complete (3 min−1 h), the solution was diluted with ethyl ether and washed with water. The aqueous phases were back-extracted with ether, and the combined organic layers were washed with water and stirred with an equal volume of a half-saturated solution of potassium fluoride for 12 h (except for **17c** and **17d**). The white precipitate of tributylstannyl fluoride was removed by filtration, and the ethereal filtrate was dried over $MgSO_4$. Concentration *in vacuo* gave a crude product which was purified by silica gel column chromatography using a gradient of hexane:ethyl acetate mixtures (hexane/EtOAc, 9:1 to 3:1). Purification of **17c** and **17d** required two successive gradient chromatographies instead of KF treatment followed by a single chromatography.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]oct-1-en-3-yne (17a). Yield: 60%. $[\alpha]_D$ = −373.1 (*c* 1.08, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.94 (t, 3H, J = 7.0 Hz), 1.38−1.56 (m, 4H), 2.40 (s, 3H), 2.44 (td, 2H, J = 6.0, 2.0 Hz), 6.06 (dt, 1H, J = 9.7, 2.2 Hz), 6.48 (d, 1H, J = 9.7 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 13.4, 19.3, 21.3, 21.8, 0.2, 75.2, 102.5, 118.0, 123.8, 129.9, 141.2, 141.3, 146.1. Anal. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 73.41; H, 7.54.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-8-*tert*-butoxyoct-1-en-3-yne (17b). Yield: 74%. $[\alpha]_D$ = −598.4 (*c* 0.62, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.18 (s, 9H), 1.60−1.76 (m, 4H), 2.41 (s, 3H), 2.41−2.55 (m, 2H), 3.37−3.41 (m, 2H), 6.06 (dt, 1H, J = 9.7, 2.3 Hz), 6.48 (d, 1H, J = 9.7 Hz), 7.31 (d, 2H, J = 7.9 Hz), 7.58 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 19.6, 21.3, 25.2, 27.5, 29.8, 60.8, 72.5, 75.4, 102.4, 118.0, 124.0, 129.9, 141.3, 146.2. Anal. Calcd for $C_{19}H_{24}O_2S$: C, 72.11; H, 7.64. Found: C, 72.41; H, 7.81.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-5-[(*tert*-butyldimethylsilyl)oxy]pent-1-en-3-yne (17c). Yield: 75%. $[\alpha]_D$ = −484.6 (*c* 0.39, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.11 (s, 6H), 0.93 (s, 9H), 2.41 (s, 3H), 4.55 (s, 2H), 6.10 (d, 2H, J = 9.8 Hz), 6.56 (d, 2H, J = 9.9 Hz), 7.32 (d, 2H, J = 7.9 Hz), 7.59 (d, 2H, J = 8.0 Hz); ^{13}C NMR (50 MHz) δ −5.1, 18.2, 21.3, 25.7, 52.1, 78.9, 99.1, 116.7, 124.0, 130.0, 141.0, 141.5, 147.7. Anal. Calcd for $C_{18}H_{26}O_2SSi$: C, 64.62; H, 7.83. Found: C, 64.44; H, 7.89.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-4-(triethylsilyl)but-1-en-3-yne (17d). Yield: 87%. $[\alpha]_D$ = −885.1 (*c* 0.47, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.68 (q, 6H, J = 7.3 Hz), 1.04 (t, 9H, J = 7.8 Hz), 2.41 (s, 3H), 6.06 (d, 1H, J = 9.9 Hz), 6.58 (d, 1H, J = 9.8 Hz), 7.31 (d, 2H, J = 7.9 Hz), 7.60 (d, 2H, J = 7.9 Hz); ^{13}C NMR (50 MHz) δ 4.0, 7.3, 21.3, 99.3, 105.0, 116.7, 123.8, 129.9, 141.0, 141.4, 148.6. Anal. Calcd for $C_{17}H_{24}OSSi$: C, 67.05; H, 7.94. Found: C, 66.88; H, 8.02.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-5,5-diethoxypent-1-en-3-yne (17e). Yield: 82%. $[\alpha]_D$ = −738.6 (*c* 0.44, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.27 (t, 6H, J = 7.0 Hz), 2.41 (s, 3H), 3.58−

3.87 (m, 4H), 4.47 (s, 1H), 6.10 (d, 1H, J = 9.8 Hz), 6.64 (d, 1H, J = 9.9 Hz), 7.32 (d, 2H, J = 7.8 Hz), 7.59 (d, 2H, J = 7.2 Hz); ^{13}C NMR (50 MHz) δ 15.0, 21.3, 61.2, 78.8, 91.5, 95.1, 115.6, 123.9, 130.1, 140.6, 141.7, 149.2. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89. Found: C, 65.95; H, 7.02.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]but-1-en-3-yne (17f). Yield: 60%. $[\alpha]_D = -676.9$ (*c* 0.13, $CHCl_3$); ^{1}H NMR (200 MHz) δ 2.41 (s, 3H), 3.54 (dd, 1H, J = 2.5, 0.7 Hz), 6.05 (dd, 1H, J = 10.0, 2.5 Hz), 6.66 (dd, 1H, J = 9.9, 0.6 Hz), 7.33 (d, 2H, J = 8.0 Hz), 7.60 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 77.4, 88.1, 115.7, 124.0, 130.1, 140.8, 141.7, 150.0. Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.30. Found: C, 69.31; H, 5.18.

(−)-(1*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-4-phenylbut-1-en-3-yne (17g). Yield: 66%. $[\alpha]_D = -653.1$ (*c* 0.81, $CHCl_3$); ^{1}H NMR (200 MHz) δ 2.40 (s, 3H), 6.28 (d, 1H, J = 9.8 Hz), 6.62 (d, 1H, J = 9.8 Hz), 7.28 (d, 2H, J = 7.6 Hz), 7.36−7.39 (m, 3H), 7.50−7.53 (m, 2H), 7.62 (d, 2H, J = 8.1 Hz); ^{13}C NMR (50 MHz) δ 21.3, 83.6, 100.7, 117.0, 121.9, 124.0, 128.5, 129.4, 130.0, 131.8, 141.2, 141.5, 147.3. Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.82; H, 5.22.

(+)-1-Iodo-1-[(*S*)-*p*-tolylsulfinyl]ethene (18). Method A. (*R*)-Vinyl *p*-tolyl sulfoxide (345.3 mg, 2.08 mmol), NIS (701.0 mg, 3.12 mmol), and 1:1 DMSO/H_2O (8 mL) were combined and stirred overnight at 40 °C. After cooling to room temperature, EtOAc (50 mL) was then added and the layers were separated; the aqueous layer was extracted with additional EtOAc (2 × 20 mL), and the combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ (50 mL). This aqueous layer was again extracted with EtOAc (50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane/EtOAc, 2:1 to 1:1) to afford the corresponding iodohydrin (623.8 mg, 96%) as an inseparable mixture of diastereomers (5.8:1). The iodohydrins (519.5 mg, 1.68 mmol) were dissolved in CH_2Cl_2 (17 mL), and the solution was cooled to 0 °C. After addition of mesyl chloride (0.13 mL, 1.68 mmol) and triethylamine (0.23 mL, 1.68 mmol), the reaction mixture was stirred under argon for 1 h. Saturated aqueous NH_4Cl (10 mL) and H_2O (3 mL) were then added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford the iodo mesylate (651.6 mg, 100%) which was used without further purification. This mesylate was dissolved in CH_2Cl_2 (17 mL) and DBU (0.32 mL, 2.16 mmol) was added dropwise via syringe. The reaction mixture was stirred under argon at room temperature for 20 min. Saturated aqueous NH_4Cl (10 mL) and H_2O (3 mL) were then added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane/EtOAc, 3:1) to afford iodovinyl sulfoxide **18** (441.7 mg, 90%) as a white solid (mp 82−83 °C). $[\alpha]_D = +68.2$ (*c* 1.35, $CHCl_3$), ^{1}H NMR (400 MHz) δ 2.41 (s, 3H), 6.52 (d, 1H, J = 3.2 Hz), 7.31 (d, 2H, J = 8.2 Hz), 7.39 (d, 1H, J = 3.2 Hz), 7.55 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 21.1, 116.9, 125.3, 129.4, 130.0, 138.6, 142.0. Anal. Calcd for C_9H_9IOS: C, 37.00; H, 3.10. Found: C, 37.08; H, 3.02.

Method B. Via (+)-(*S*)-1-(Tri-*n*-butylstannyl)-1-(*p*-tolylsulfinyl)ethene (19). To a solution of alkynyl sulfoxide **3**[14] (16.4 mg, 0.10 mmol) in benzene (1 mL) at room temperature and under an atmosphere of argon was added a solution of freshly distilled Bu_3SnH (34 μL, 0.11 mmol) in benzene (1 mL). The reaction mixture was stirred at room temperature for 18 h; the solvent was then removed under reduced pressure, and the crude material was purified by gradient chromatography (silica gel, hexane/EtOAc, 19:1 to 6:1) to afford **19** (40 mg, 88%) as a colorless oil. $[\alpha]_D = +48.6$ (*c* 2.31, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.65−0.85 (m, 15H), 1.10−1.35 (m, 12H), 2.36 (s, 3H), 5.95 (s with tin satellites, 1H), 6.71 (s with tin satellites, 1H), 7.24 (d, 2H, J = 8.0 Hz), 7.45 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 10.5, 13.5, 21.3, 27.1, 28.6, 125.8, 128.9, 129.8, 141.2, 141.3, 160.9. Anal. Calcd for $C_{21}H_{36}OSSn$: C, 55.40; H, 7.97. Found: C, 55.59; H, 7.87. Stannylvinyl sulfoxide **19** was dissolved in THF (1 mL) and treated with NIS (19.8 mg, 0.088 mmol). The reaction was stirred under an argon atmosphere at room temperature for 3 h and then diluted with EtOAc (4 mL) and washed with a saturated aqueous $Na_2S_2O_3$ solution (2 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (3 × 2 mL). The combined organic layers were washed with brine (2 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by two successive gradient chromatographies in order to remove traces of *n*-Bu_3SnI (silica gel, hexane/EtOAc, 19:1 to 3:1) to afford **18** (27.1 mg, 95%) as a white solid.

General Procedure for the Hydrostannylation of 1-Sulfinyl Alkynes. Method A. To a solution of the alkynyl sulfoxide in hexane (5 mL/mmol sulfoxide) at room temperature and under an atmosphere of argon was added a solution of freshly distilled Bu_3SnH (1.1 mL) in hexane (5 mL/mmol sulfoxide). The reaction mixture was stirred at room temperature for 18 h; the solvent was then removed under reduced pressure, and the crude material was purified by gradient chromatography (silica gel, hexane/EtOAc mixtures) to afford the desired stannylvinyl sulfoxides. **Method B.** To a solution of the alkynyl sulfoxide (1.0 equiv) in anhydrous toluene (6.6 mL/mmol sulfoxide), at room temperature and under an atmosphere of argon, was added $Pd(PPh_3)_4$ (2 mol %). This solution was deaerated for 10 min by bubbling argon into the reaction mixture and was subsequently cooled to a −78 °C. A solution of freshly distilled Bu_3SnH (1.1 equiv) in toluene (1.1 mL/mmol sulfoxide) was then added to the cooled reaction mixture dropwise via syringe. The reaction mixture was stirred while the temperature was allowed to warm to ambient temperature over 2 h. The solvent was then removed at reduced pressure and the crude material (regioisomeric ratio determined by ^{1}H NMR integration) was purified by gradient chromatography (silica gel, hexane/EtOAc mixtures) to afford the desired stannylvinyl sulfoxides.

(+)-(*S*)-(1*Z*)-1-(Tri-*n*-butylstannyl)-1-(*p*-tolylsulfinyl)-1-hexene (20) and (−)-(*S*)-(1*E*)-1-(tri-*n*-butylstannyl)-1-(*p*-tolylsulfinyl)-1-hexene (21). Yield (method A): **20**, 75%; **21**, 10%. Data for **20**: $[\alpha]_D = +1.9$ (*c* 5.02, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.70−1.00 (m, 15H), 0.94 (t, 3H, J = 7.1 Hz), 1.16−1.53 (m, 16H), 2.26 (app q, 2H, J = 7.3 Hz), 2.38 (s, 3H), 7.14 (t with tin satellites, 1H, J = 7.4 Hz), 7.24 (d, 2H, J = 8.2 Hz), 7.43 (d, 2H, J = 8.2 Hz); ^{13}C NMR (75 MHz) δ 11.3, 13.5, 13.9, 14.6, 21.5, 26.4, 27.1, 27.7, 28.5, 28.7, 28.9, 31.5, 33.8, 126.0, 129.5, 140.7, 141.9, 148.6, 149.4. Anal. Calcd for $C_{25}H_{44}OSSn$: C, 58.57; H, 8.66; S, 6.24. Found: C, 58.23; H, 9.23; S, 5.98.

(−)-(*S*)-(1*E*)-1-(Tri-*n*-butylstannyl)-1-(*p*-tolylsulfinyl)-1-hexene (21) and (−)-(*R*)-(1*E*)-2-(Tri-*n*-butylstannyl)-1-(*p*-tolylsulfinyl)-1-hexene (23). Yield (method B): **21**, 85%; **23**, 1%. Data for **21**: $[\alpha]_D = -57.4$ (*c* 2.62, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.78−0.95 (m, 15H), 0.92 (t, 3H, J = 7.2 Hz), 0.94−1.46 (m, 16H), 2.36 (m, 1H), 2.36 (s, 3H), 2.68 (m, 1H), 6.16 (dd with tin satellites, 1H, J = 8.6, 5.7 Hz), 7.23 (d, 2H, J = 8.1 Hz), 7.39 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 11.3, 13.5, 13.8, 21.2, 22.2, 27.2, 28.7, 31.3, 32.6, 124.4, 129.5, 139.9, 142.6, 149.0, 156.2. Anal. Calcd for $C_{25}H_{44}SOSn$: C, 58.72; H, 8.67; S, 6.27. Found: C, 58.43; H, 8.73; S, 5.98. Data for **23**: $[\alpha]_D = -77.6$ (*c* 3.25, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.81−1.05 (m, 18 H), 1.17−1.52 (m, 16H), 2.37 (s, 3H), 2.74 (m, 2H), 6.15 (t with tin satellites, 1H, J = 1.1 Hz), 7.26 (d, 2H, J = 8.1 Hz), 7.46 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 10.2, 13.5, 13.8, 21.2, 22.6, 27.2, 28.8, 32.2, 35.3, 124.2, 129.8, 140.6, 142.2, 143.2, 161.2. Anal. Calcd for $C_{25}H_{44}OSSn$: C, 58.72; H, 8.67; S, 6.27. Found: C, 58.56; H, 8.89; S, 6.03.

(−)-(*S*)-(1*E*)-1-(Tri-*n*-butylstannyl-1-(*p*-tolylsulfinyl)-6-[(*p*-methoxybenzyl)oxy]-1-hexene (26). Yield (method B): 83%. $[\alpha]_D = -41.4$ (*c* 1.79, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73−0.91 (m, 15H), 1.13−1.41 (m, 12H), 1.53−1.68 (m, 4H), 2.35 (s, 3H), 2.38 (m, 1H), 2.68 (m, 1H), 3.45 (t, 2H, J = 6.0 Hz), 3.76 (s, 3H), 4.41 (s, 2H), 6.15 (dd with tin satellites, 1H, J = 8.6, 5.7 Hz), 6.85 (d, 2H, J = 8.7 Hz), 7.23 (m, 4H), 7.37 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 11.4, 13.5, 21.2, 26.0, 27.2, 28.7, 29.2, 32.6, 55.2, 69.5, 72.5, 113.7, 124.4, 129.2, 129.5, 130.6, 139.9, 142.5, 148.6, 156.6, 159.1. Anal. Calcd for $C_{33}H_{52}O_3SSn$: C, 61.21; H, 8.09. Found: C, 61.02; H, 7.96.

General Procedure for the Conversion of (1*Z*)-Stannylvinyl Sulfoxides into (1*Z*)-Iodovinyl Sulfoxides. A THF (6.75 mL/mmol sulfoxide) solution of the stannyl sulfoxide (1.0 equiv) was treated with NIS (1.0 equiv). The reaction was stirred under an argon atmosphere at room temperature for 3 h and then diluted with EtOAc and washed with a saturated aqueous $Na_2S_2O_3$ solution. The layers were separated, and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by two successive gradient chromatographies in order to remove traces of *n*-Bu_3SnI (silica gel, hexane/EtOAc mixtures) to afford the desired iodovinyl sulfoxides.

(+)-(*S*)-(1*Z*)-1-Iodo-1-(*p*-tolylsulfinyl)-1-hexene (22). Yield: 91%. $[\alpha]_D = +29.6$ (*c* 2.57, $CHCl_3$); ^1H NMR (300 MHz) δ 0.91 (t, 3H, J = 7.2 Hz), 1.37 (m, 2H), 1.44−1.52 (m, 2H), 2.32 (m, 2H), 2.37 (s, 3H), 7.05 (t, 1H, J = 7.1 Hz), 7.27 (d, 2H, J = 8.1 Hz), 7.47 (d, 2H, J = 8.1 Hz); ^{13}C NMR (50 MHz) δ 13.8, 21.4, 22.2, 29.8, 35.0, 115.1, 125.5, 129.7, 139.9, 141.9, 145.1. Anal. Calcd for $C_{13}H_{17}OSI$: C, 44.84; H, 4.92; S, 9.21. Found: C, 44.91; H, 5.06; S, 8.94.

(−)-(*S*)-(1*E*)-1-Iodo-1-(*p*-tolylsulfinyl)-1-hexene (24). Yield: 94%. $[\alpha]_D = -94.4$ (*c* 1.86, $CHCl_3$); ^1H NMR (200 MHz) δ 0.96 (t, 3H, J = 7.2 Hz), 1.36−1.58 (m, 4H), 2.39 (s, 3H), 2.57 (dq, 1H, J = 14.6, 7.1 Hz), 2.79 (ddt, 1H, J = 14.6, 8.7, 7.1 Hz), 6.86 (dd, 1H, J = 8.7, 7.1 Hz), 7.29 (d, 2H, J = 8.5 Hz), 7.43 (d, 2H, J = 8.4 Hz); ^{13}C NMR (50 MHz) δ 13.7, 21.4, 22.1, 30.9, 33.3, 114.3, 124.3, 129.7, 140.0, 141.6, 151.9. Anal. Calcd for $C_{13}H_{17}OSI$: C, 44.84; H, 4.92; S, 9.21. Found: C, 45.43; H, 4.39; S, 8.74.

(−)-(*S*)-(1*E*)-1-Iodo-1-(*p*-tolylsulfinyl)-6-[(*p*-methoxybenzyl)oxy]-1-hexene (27). Yield: 86%. $[\alpha]_D = -70.0$ (*c* 2.56, $CHCl_3$); ^1H NMR (200 MHz) δ 1.63 (m, 4H), 2.38 (s, 3H), 2.61 (dq, 1H, J = 14.5, 7.1 Hz), 2.83 (dt, 1H, J = 14.5, 8.7, 7.1 Hz), 3.48 (t, 2H, J = 5.9 Hz), 3.78 (s, 3H), 4.43 (s, 2H), 6.85 (dd, 1H, J = 8.4, 7.1 Hz), 6.88 (d, 2H, J = 8.6 Hz), 7.22 (m, 4H), 7.41 (d, 2H, J = 8.4 Hz); ^{13}C NMR (50 MHz) δ 21.4, 25.7, 29.0, 33.3, 55.2, 69.2, 72.6, 113.8, 114.7, 124.4, 129.2, 129.8, 130.5, 140.0, 141.6, 151.6, 159.2. Anal. Calcd for $C_{21}H_{25}O_3SI$: C, 52.03; H, 5.16; S, 6.60. Found: C, 52.10; H, 5.19; S, 6.51.

(−)-(*S*)-(1*E*)-1-Iodo-1-(*p*-tolylsulfinyl)-2-methyl-1-hexene (28). To a suspension of CuI (76 mg, 0.40 mmol) in THF (4 mL) under an argon atmosphere at 0 °C was added MeLi (0.26 mL, 1.58 M Et_2O, 0.40 mmol) dropwise via syringe, and the resulting colorless mixture was stirred for 10 min. The solution was then cooled to −78 °C; a solution of alkynyl sulfoxide **5** (46 mg, 0.20 mmol) in THF (2 mL) was slowly added dropwise via syringe. The resulting yellow solution was stirred at −78 °C for 30 min and then NIS (90 mg, 0.40 mmol) in THF (2 mL) was rapidly added and the resulting mixture was stirred for an additional 30 min. After treatment with a saturated solution of $Na_2S_2O_3$ (2 mL), the temperature was allowed to rise to 20 °C when the mixture was then diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 × 4 mL), and the combined organic layers were washed with brine (2 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude reaction material was purified by chromatography (silica gel, hexane/EtOAc, 19:1 to 6:1) to afford **28** (46 mg, 61%) as a pale yellow oil. $[\alpha]_D = -82.2$ (*c* 4.64, $CHCl_3$); ^1H NMR (200 MHz) δ 0.95 (t, 3H, J = 7.2 Hz), 1.36−1.70 (m, 4H), 2.10 (s, 3H), 2.37 (s, 3H), 2.75−3.00 (m, 2H), 7.26 (d, 2H, J = 8.2 Hz), 7.39 (d, 2H, J = 8.4 Hz); ^{13}C NMR (50 MHz) δ 13.8, 21.4, 22.5, 29.9, 30.8, 37.1, 115.6, 124.6, 129.7, 141.0, 141.2, 157.1. HRMS Calcd for $C_{14}H_{19}OSI$: 362.0201. Found: 362.0211.

General Procedure for the Preparation of 2-Sulfinyl 1,3-Dienes. To a solution of 1 equiv of the 1-iodovinyl sulfoxide in anhydrous THF (10 mL/mmol sulfoxide) at room temperature and under an argon atmosphere were added Ph_3As (20 mol %), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (1 equiv), and the corresponding vinylstannane. After deaerating the solution by bubbling argon into the reaction mixture for 10 min, $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) was added. The resulting mixture was heated to reflux (bath temperature, 70 °C) for the synthesis of **29d**,**f**,**g** or was stirred at room temperature for the synthesis of **29b**,**c**,**e** until the disapperance of the starting sulfoxide, as judged by TLC (approximately 2 h). The reaction mixture was then treated with a saturated aqueous KF (3 mL per mmol) and diluted with EtOAc (10 mL per mmol). The layers were separated, and the aqueous phase was extracted with EtOAc (three times, 10 mL per mmol), and the combined organic layers were washed with brine (3 mL per mmol), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by gradient chromatography using hexane/EtOAc mixtures. The elimination of traces of *n*-Bu_3SnI frequently required a second chromatography. Diene **29a** was prepared using the $Pd(CH_3CN)_2Cl_2$/DMF method, (see method B for 1-sulfinyl diene synthesis), with added BHT (1 equiv).

(+)-(*R*)-2-(*p*-Tolylsulfinyl)-1,3-butadiene (29a). Yield: 70%. $[\alpha]_D = +168$ (*c* 1.79, EtOH); ^1H NMR (400 MHz) δ 2.39 (s, 3H), 5.20 (d, 1H, J = 11.3 Hz), 5.46 (d, 1H, J = 17.7 Hz), 5.85 (s, 1H), 6.12 (s, 1H), 6.22 (dd, 1H, J = 17.7, 11.3 Hz), 7.26 (d, 2H, J = 8.2 Hz), 7.53 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 21.4, 117.1, 119.0, 125.7, 129.4, 129.9, 139.7, 142.0, 151.1. **29a** was not stable enough for characterization by combustion analysis.

(+)-(*R*)-(3*E*)-3-(*p*-tolylsulfinyl)-1,3-octadiene (29b). Yield: 89%. $[\alpha]_D = +108.0$ (*c* 1.58, $CHCl_3$); ^1H NMR (200 MHz) δ 0.91 (t, 3H, J = 7.2 Hz), 1.25−1.60 (m, 4H), 2.34 (q, 2H, J = 7.3 Hz), 2.38 (s, 3H), 5.25 (dt, 1H, J = 11.5, 1.0 Hz), 5.38 (d, 1H, J = 17.8 Hz), 6.29 (dd, 1H, J = 17.8, 11.6 Hz), 6.53 (t, 1H, J = 7.7 Hz), 7.25 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 13.8, 21.3, 22.3, 27.9, 31.1, 119.8, 125.6, 126.7, 129.7, 135.4, 140.8, 141.3, 141.4. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.28; H, 7.98; S, 12.64.

(+)-(*R*)-(1*E*,3*E*)-1-Phenyl-3-(*p*-tolylsulfinyl)-1,3-octadiene (29c). Yield: 77%. $[\alpha]_D = +6.3$ (*c* 1.51, $CHCl_3$); ^1H NMR (200 MHz) δ 0.92 (t, 3H, J = 7.1 Hz), 1.25−1.60 (m, 4H), 2.34 (s, 3H), 2.40 (q, 2H, J = 7.2 Hz), 6.56 (t, 1H, J = 7.7 Hz), 6.66 (d, 1H, J = 16.6 Hz), 6.79 (d, 1H, J = 16.6 Hz), 7.19−7.31 (m, 7H), 7.52 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 13.8, 21.3, 22.3, 28.2, 31.2, 118.4, 125.4, 126.5, 128.3, 128.6, 129.8, 133.6, 135.3, 136.4, 140.9, 141.0, 141.4. Anal. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.45. Found: C, 77.59; H, 7.56.

(−)-(*R*)-(3*Z*)-3-(*p*-tolylsulfinyl)-1,3-octadiene (29d). Yield: 80%. $[\alpha]_D = -299.2$ (*c* 0.95, $CHCl_3$); ^1H NMR (300 MHz) δ 0.94 (t, 3H, J = 7.2 Hz), 1.37−1.56 (m, 4H), 2.37 (s, 3H), 2.51 (m, 1H), 2.71 (m, 1H), 5.11 (dd, 1H, J = 11.0, 1.4 Hz), 5.48 (dd, 1H, J = 17.4), 6.17 (dd, 1H, J = 17.4, 11.0 Hz), 6.26 (t, 1H, J = 7.6 Hz), 7.26 (d, 2H, J = 8.1 Hz), 7.41 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 13.8, 21.2, 22.3, 28.4, 31.5, 118.2, 124.2, 128.3, 129.7, 138.5, 139.9, 140.5, 143.1. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91. Found: C, 72.19; H, 7.85; S, 12.65.

(−)-(*R*)-(1*Z*,3*E*)-1,1-Diethoxy-4-(*p*-tolylsulfinyl)-2,4-nonadiene (29e). Yield: 59%. $[\alpha]_D = -64.7$ (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz) δ 0.94 (t, 3H, J = 7.2 Hz), 1.06 (t, 3H, J = 7.2 Hz), 1.13 (t, 3H, J = 7.2 Hz), 1.47 (m, 4H), 2.37 (s, 3H), 2.53 (app sextet, 1H), 2.72 (app sextet, 1H), 3.18−3.52 (m, 4H), 4.79 (d, 1H, J = 5.1 Hz), 5.89 (dd, 1H, J = 16.0, 5.1 Hz), 6.22 (d, 1H, J = 16.0 Hz), 6.30 (t, 1H, J = 7.9 Hz), 7.25 (d, 2H, J = 8.5 Hz), 7.40 (d, 2 H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 13.8, 15.01, 15.05, 21.2, 22.3, 28.6, 31.4, 60.5, 61.1, 100.7, 124.16, 124.24, 129.6, 130.7, 139.5, 139.7, 140.4, 141.7. Anal. Calcd for $C_{20}H_{30}O_3S$: C, 68.53; H, 8.63. Found: C, 68.75; H, 8.84.

(−)-(*R*)-(1*Z*)-1-[4-[(*p*-Methoxybenzyl)oxy]butyl]-2-(*p*-tolylsulfinyl)-1,3-butadiene (29f). Yield: 59%. $[\alpha]_D = -133.1$ (*c* 1.40, $CHCl_3$); ^1H NMR (200 MHz) δ 1.50−1.64 (m, 4H), 2.32 (s, 3H), 2.53 (m, 1H), 2.64 (m, 1H), 3.42 (t, 2H, J = 5.8 Hz), 3.73 (s, 3H), 4.37 (s, 2H), 5.07 (dd, 2H, J = 11.1, 1.2 Hz), 5.43 (dd, 2H, J = 17.4, 1.2 Hz), 6.12 (dd, 1H, J = 17.4, 11.1 Hz), 6.19 (t, 1H, J = 7.7 Hz), 6.80 (d, 2H, J = 8.7 Hz), 7.18 (m, 4H), 7.35 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 21.3, 26.2, 28.5, 29.3, 55.3, 69.5, 72.7, 77.2, 113.8, 118.4, 124.3, 128.3, 129.2, 129.8, 130.6, 138.1, 139.9, 140.6, 143.4, 159.2. Anal. Calcd for $C_{23}H_{28}O_3S$: C, 71.84; H, 7.34. Found: C, 72.05; H, 7.56.

(−)-(*R*)-(3*Z*)-4-Methyl-3-(*p*-tolylsulfinyl)-1,3-octadiene (29g). Yield: 81%. $[\alpha]_D = -193.1$ (*c* 0.77, $CHCl_3$); ^1H

NMR (300 MHz) δ 0.94 (t, 3H, J = 7.2 Hz), 1.37−1.61 (m, 4H), 1.94 (d, 3H, J = 0.7 Hz), 2.36 (s, 3H), 2.67 (t, 2H, J = 7.7 Hz), 5.27 (dd, 1H, J = 17.4, 1.9 Hz), 5.29 (dd, 1H, J = 11.7, 1.9 Hz), 5.98 (ddd, 1H, J = 17.3, 11.2, 0.6 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.37 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 13.9, 20.8, 21.3, 22.8, 29.7, 31.0, 34.8, 122.5, 124.5, 126.7, 129.5, 138.0, 140.1, 140.3, 149.1. HRMS Calcd for: $C_{16}H_{22}OS$: 262.1391. Found: 262.1383.

General Procedure for the Synthesis of Sulfinyl Diene Iron(0) Complexes. Method A. To a solution of the sulfinyl diene in THF or Et_2O (0.05−0.10 M) at room temperature and under an argon atmosphere was added $Fe_2(CO)_9$ (3.0 equiv). The mixture was refluxed for 24 h and then cooled, and the resulting brown mixture was filtered through silica gel; the filter cake was washed with copious amounts of EtOAc. After the filtrate was concentrated *in vacuo*, the residue was purified by chromatography (silica gel, hexane/EtOAc). **Method B.** To a solution of the sulfinyl diene in THF (0.05 M) at 0 °C and under an argon atmosphere was added NMO (6.0 equiv). To this suspension was added $Fe(CO)_5$ (3.0 equiv) dropwise via syringe; a purple color formed initially, but became brown as the addition of the $Fe(CO)_5$ neared completion. The resulting mixture was stirred at 0 °C for 1.5 h, then was placed in a preheated (80 °C) oil bath and stirred for an additional 1.5 h. After cooling, the mixture was filtered through silica gel; the filter cake was washed with copious amounts of EtOAc. After the filtrate was concentrated *in vacuo*, the residue was purified by chromatography (silica gel, hexane/EtOAc). **Method C.** To a solution of the sulfinyl diene in toluene (0.05 M) at room temperature and under an argon atmosphere was added (bda)$Fe(CO)_3$[50] (4.0 equiv). The red solution was placed in a preheated 45 °C oil bath and stirred at that temperature for 16 h. After cooling, the mixture was filtered through silica gel; the filter cake was washed with copious amounts of EtOAc. After the filtrate was concentrated *in vacuo*, the residue was purified by chromatography (silica gel, hexane/EtOAc). Usually 70−75% of the excess (bda)$Fe(CO)_3$ could be recovered by the chromatography and reused.

(+)-η^4-α-[(R_S)-(1*E*)-1-(*p*-Tolylsulfinyl)-1,3-butadiene]-tricarbonyliron(0) Complex (30a) and Its β-Isomer. Yield (method A): α-**30a**, 54%; β-**30a**, 40%. Data for α-**30a**: $[\alpha]_D$ = +213.4 (*c* 1.04, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.36 (dd, 1H, J = 9.3, 2.9 Hz), 1.62 (d, 1H, J = 7.7 Hz), 1.84 (ddd, 1H, J = 6.8, 2.8, 1.1 Hz), 2.41 (s, 3H), 5.29 (m, 1H), 5.64 (dd, 1H, J = 7.7, 4.9 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.45 (d, 2H, J = 8.3 Hz); ^{13}C NMR (50 MHz) δ 21.4, 39.8, 77.4, 81.8, 82.9, 123.0, 129.9, 141.2, 143.5. Anal. Calcd for $C_{14}H_{12}FeO_4S$: C, 50.62; H, 3.64. Found: C, 50.48; H, 3.55. Data for β-**30a**: $[\alpha]_D$ = −150.8 (*c* 3.25, $CHCl_3$); ^{1}H NMR (300 MHz) δ 0.58 (dd, 1H, J = 9.4, 2.7 Hz), 1.77 (d, 1H, J = 7.4 Hz), 1.96 (dd, 1H, J = 6.8, 2.1 Hz), 2.40 (s, 3H), 5.34−5.41 (m, 1H), 5.85−5.89 (m, 1H), 7.31 (d, 2H, J = 8.0 Hz), 7.61 (d, 2H, J = 8.1 Hz); ^{13}C NMR (50 MHz) δ 21.4, 41.5, 72.7, 83.7, 85.8, 124.2, 130.0, 141.9, 142.2.

(−)-η^4-α-[(R_S)-(1*Z*)-1-(*p*-Tolylsulfinyl)-1,3-butadiene]-tricarbonyliron(0) Complex (30b). Yield (method B): α-**30b**, 56%; β-**30b**, 3%. Data for α-**30b**: mp 118−120 °C; $[\alpha]_D$ = −27.8 (*c* 1.50, $CHCl_3$); ^{1}H NMR (300 MHz) δ 2.18 (dd, 1H, J = 9.7, 3.6 Hz), 2.31−2.35 (m, 1H), 2.37 (s, 3H), 3.43 (d, 1H, J = 7.1 Hz), 5.20 (dd, 1H, J = 6.8, 5.8 Hz), 5.58−5.65 (m, 1H), 7.25 (d, 2H, J = 8.1 Hz), 7.35 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 43.5, 78.3, 80.8, 94.3, 123.2, 129.9, 140.8, 145.2, 208.1 (CO). Anal. Calcd for $C_{14}H_{12}FeO_4S$: C, 50.62; H, 3.64. Found: C, 50.79; H, 3.71.

(−)-η^4-α-[(R_S)-(1*Z*)-2-*n*-Butyl-1-(*p*-tolylsulfinyl)-1,3-butadiene]tricarbonyliron(0) Complex (30c). Yield (method B): α-**30c**, 44%; β-**30c**, 8% (could not be separated from unreacted sulfinyl diene **10j**; weight determined by ^{1}H NMR integration). Data for α-**30c**: mp 78−80 °C; $[\alpha]_D$ = −70.0 (*c* 3.30, $CHCl_3$); ^{1}H NMR (200 MHz) δ 0.76 (t, 3H, J = 7.2 Hz), 0.89−1.29 (m, 4H), 1.89−2.27 (m, 4H), 2.39 (s, 3H), 3.40 (d, 1H, J = 1.2 Hz), 5.44 (app t, 1H, J = 9.0, 8.0 Hz), 7.26 (d, 2H, J = 8.2 Hz), 7.36 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 13.6, 21.3, 22.1, 32.2, 38.1, 40.6, 81.8, 92.4, 102.5, 123.4, 129.8, 141.0, 145.4, 208.4 (br, CO). Anal. Calcd for $C_{18}H_{20}O_4SFe$: C, 55.68; H, 5.19; S, 8.26. Found: C, 55.43; H, 4.97; S, 8.03.

η^4-α-[(R_S)-2-(*p*-Tolylsulfinyl)-1,3-butadiene]tricarbonyliron(0) Complex (30d). Yield (method A): **30d**, 45% of an inseparable 1.2:1 mixture of diastereomers. Data for diastereomeric mixture: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.13−0.32 (m + dd, total 1H), 1.88−2.08 (m + dd, total 1H), 2.26−2.50 (m, total 2H), 2.43 (s, 3H), 5.65 + 6.03 (2m, total 1H), 7.35 (d, total 2H, J = 8.0 Hz), 7.67 (d, total 2H, J = 8.2 Hz).

(−)-η^4-α-[(R_S)-(1*Z*,3*E*)-5,5-Diethoxy-1-(*p*-tolylsulfinyl)-1,3-pentadiene]tricarbonyliron(0) Complex (30e) and Its β-Isomer. Yield (method B): α-**30e**, 75%; β-**30e**, 4.7%. Data for α-**30e**: $[\alpha]_D$ = −14.3 (*c* 0.79, $CHCl_3$); ^{1}H NMR (500 MHz) δ 1.22 (t, 3H, J = 7.0 Hz), 1.23 (t, 3H, J = 7.0 Hz), 2.37 (s, 3H), 2.94 (dd, 1H, J = 9.0, 3.7 Hz), 3.37 (dd, 1H, J = 6.8, 1.1 Hz), 3.53−3.59 (m, 2H), 3.69−3.76 (m, 2H), 4.69 (d, 1H, J = 3.9 Hz), 5.05 (ddd, 1H, J = 7.1, 5.2, 1.1 Hz), 5.77 (dd, 1H, J = 9.0, 5.1 Hz), 7.26 (d, 2H, J = 8.3 Hz) 7.35 (d, 2H, J = 8.1 Hz); ^{13}C NMR (50 MHz) δ 15.0, 15.1, 21.3, 61.2, 62.3, 63.8, 76.7, 77.4, 93.5, 101.3, 123.2, 129.8 140.7, 146.3. Anal. Calcd for $C_{19}H_{22}O_6SFe$: C, 52.55; H, 5.11; S, 7.38. Found: C, 52.68; H, 5.06; S, 7.42. Data for β-**30e**: $[\alpha]_D$ = −33.8 (*c* 0.42, $CHCl_3$); ^{1}H NMR (500 MHz) δ 1.21 (t, 3H, J = 7.1 Hz), 1.22 (t, 3H, J = 7.1 Hz), 2.41 (s, 3H), 3.18 (ddd, 1H, J = 9.3, 3.9, 0.9 Hz), 3.49−3.58 (m, 2H), 3.53 (dd, 1H, J = 7.1, 1.1 Hz), 3.68−3.76 (m, 2H), 4.63 (d, 1H, J = 3.9 Hz), 5.39 (ddd, 1H, J = 7.1, 5.3, 1.1 Hz), 5.85 (dd, 1H, J = 9.3, 5.1 Hz), 7.31 (d, 2H, J = 8.1 Hz), 7.63 (d, 2H, J = 8.1 Hz). ^{13}C NMR (50 MHz) δ 15.1, 21.5, 61.3, 62.4, 63.7, 74.1, 94.9, 101.1, 124.9, 130.0, 142.0, 142.8.

(+)-η^4-α-[(R_S)-(1*E*,3*E*)-5,5-Diethoxy-1-(*p*-tolylsulfinyl)-1,3-pentadiene]tricarbonyliron(0) Complex (30f) and Its β-Isomer. Yield (method B): α-**30f**, 51%; β-**30f**, 36%. Data for α-**30f**: $[\alpha]_D$ = +180.4 (*c* 1.92, $CHCl_3$); ^{1}H NMR (300 MHz) δ 1.08 (dd, 1H, J = 8.5, 4.3 Hz), 1.14 (t, 3H, J = 7.1 Hz), 1.15 (t, 3H, J = 7.1 Hz), 1.60 (d, 1H, J = 7.5 Hz), 2.40 (s, 3H), 3.39−3.48 (m, 2H), 3.50−3.64 (m, 2H), 4.46 (d, 1H, J = 4.4 Hz), 5.41 (dd, 1H, J = 8.6, 5.1 Hz), 5.50 (dd, 1H, J = 7.8, 5.3 Hz), 7.31 (d, 2H, J = 8.1 Hz), 7.44 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 15.0, 21.4, 60.4, 60.6, 61.8, 76.5, 78.0, 82.4, 101.4, 123.0, 129.8, 141.2, 143.4. Anal. Calcd for $C_{19}H_{22}O_6SFe$: C, 52.55; H, 5.11; S, 7.38. Found: C, 52.36; H, 4.97; S, 7.21. Data for β-**30f**: $[\alpha]_D$ = −109.8 (*c* 1.64, $CHCl_3$); ^{1}H NMR (300 MHz) δ 1.14 (t, 6H, J = 7.1 Hz), 1.31 (ddd, 1H, J = 8.7, 4.1, 1.1 Hz), 1.74 (dd, 1H, J = 7.3, 1.0 Hz), 2.40 (s, 3H), 3.36−3.49 (m, 2H), 3.52−3.66 (m, 2H), 4.49 (d, 1H, J = 4.0 Hz), 5.51 (dd, 1H, J = 8.7, 5.1 Hz), 5.73 (ddd, 1H, J = 7.3, 5.0, 1.2 Hz), 7.31 (d, 2H, J = 8.0 Hz), 7.61 (d, 2H, J = 8.1 Hz). ^{13}C NMR (50 MHz) δ 15.0, 21.4, 60.9, 62.0, 62.7, 72.0, 79.9, 85.4, 100.9, 124.2, 130.0, 141.9, 142.2. Anal. Calcd for $C_{19}H_{22}O_6SFe$: C, 52.55; H, 5.11; S, 7.38. Found: C, 52.81; H, 5.30; S, 7.29.

(+)-η^4-α-[(R_S)-(1*E*,3*E*)-5,5-Diethoxy-4-methyl-1-(*p*-tolylsulfinyl)-1,3-pentadiene]tricarbonyliron(0) Complex (30g) and Its β Isomer. Yield (method B): α-**30g**, 15%; β-**30g**, 15%. Data for α-**30g**: $[\alpha]_D$ = +158.9 (*c* 1.51, $CHCl_3$); ^{1}H NMR (400 MHz) δ 1.07 (s, 3H), 1.21 (overlapping triplets, 6H, J = 7.0 Hz), 2.43 (s, 3H), 2.88 (d, 1H, J = 8.0 Hz), 3.40−3.73 (m, 4H), 4.06 (s, 1H), 5.28 (d, 1H, J = 5.3 Hz), 5.57 (dd, 1H, J = 8.0, 5.3 Hz), 7.34 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 14.3, 15.0, 15.2, 21.4, 63.4, 63.5, 73.1, 76.8, 81.0, 87.5, 109.0, 123.2, 129.9, 141.1, 143.5. Anal. Calcd for $C_{20}H_{24}O_6FeS$: C, 53.58; H, 5.40; S, 7.15. Found: C, 53.72; H, 5.56; S, 7.02. Data for β-**30g**: ^{1}H NMR (400 MHz) δ 1.10 (s, 3H), 1.19 (overlapping triplets, 6H, J = 6.9 Hz), 2.42 (s, 3H), 3.01 (d, 1H, J = 7.7 Hz), 3.39−3.71 (m, 4H), 4.08 (s, 1H), 5.36 (d, 1H, J = 5.3 Hz), 5.82 (dd, 1H, J = 7.6, 5.3 Hz), 7.33 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 14.9, 15.2, 21.4, 63.4, 63.8, 72.6, 75.8, 83.1, 89.9, 108.3, 124.3, 130.0, 141.8, 142.1.

(+)-η^4-α-[(R_S)-(2*E*,4*Z*)-1,1-Diethoxy-4-(*p*-tolylsulfinyl)-2,4-nonadiene]tricarbonyliron(0) Complex (30h). Yield (method B): α-**30h**, 34%; β-**30h**, 25% (could not be separated from unreacted sulfinyl diene **29e**; weight determined by ^{1}H NMR integration). Data for α-**30h**: $[\alpha]_D$ = +61.0 (*c* 0.59, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.89 (t, 3H, J = 6.9 Hz + obscured signal, 1H), 1.01 (dd, 1H, J = 8.7, 5.0 Hz), 1.22 (t, 6H, J = 7.0), 1.20−1.37 (partially obscured m, 4H), 1.69−1.78 (m, 2H), 2.44 (s, 3H), 3.51 (m, 2H), 3.66 (m, 2H), 4.50 (d, 1H, J = 4.9 Hz), 6.18 (d, 1H, J = 8.8 Hz), 7.35 (d, 2H, J = 8.1 Hz),

7.69 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 13.8, 15.11, 15.15, 21.6, 22.3, 29.9, 34.3, 58.6, 61.2, 61.4, 62.3, 75.2, 102.2, 107.6, 125.2, 130.2, 142.5. Anal. Calcd for $C_{23}H_{30}O_6FeS$: C, 56.33; H, 6.17; S, 6.54. Found: C, 56.12; H, 6.28; S, 6.71.

(+)-η^4-β-[(R_S)-(1*E*)-2-Butyl-1-(*p*-tolylsulfinyl)-1,3-butadiene]tricarbonyliron(0) Complex (30i). Yield (method C): β-**30i**, 70%; α-**30i**, 26% (could not be separated from the byproduct benzylidene acetone; weight determined by ^{1}H NMR integration). Data for β-**30i**: $[\alpha]_D$ = +326.1 (*c* 0.92, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.54 (dd, 1H, J = 9.2, 2.7 Hz), 1.03 (t, 3H, J = 7.3 Hz), 1.53−1.71 (m, 3H), 1.72 (s, 1H), 1.88 (dd, 1H, J = 7.0, 2.8 Hz), 2.04 (m, 1H), 2.43 (s, 3H), 2.58 (m, 1H), 3.03 (m, 1H), 5.22 (app t, 1H, J = 8.4, 7.8 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 14.7, 15.0, 30.5, 33.5, 33.6, 40.3, 76.0, 85.5, 107.2, 125.5, 130.8, 142.7, 142.8. Anal. Calcd for $C_{18}H_{20}O_4FeS$: C, 55.68; H, 5.19; S, 8.26. Found: C, 55.83; H, 5.34; S, 8.04.

(−)-η^4-β-[(R_S)-(1*Z*)-1-(*p*-Tolylsulfinyl)-2-(triethylsilyl)-1,3-butadiene]tricarbonyl iron(0) Complex (30j). Yield (method C): β-**30j**, 59%; α-**30j**, 33%. Data for β-**30j**: $[\alpha]_D$ = −201.3 (*c* 2.97, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.99−1.17 (m, 16H), 1.54 (s, 1H), 2.18 (dd, 1H, J = 7.0, 2.3 Hz), 2.42 (s, 3H), 5.17 (app t, 1H, J = 8.5, 7.8 Hz), 7.32 (d, 2H, J = 7.9 Hz), 7.65 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz) δ 5.4, 8.5, 22.3, 47.1, 79.1, 88.7, 92.4, 125.4, 130.7, 142.7, 143.6. Anal. Calcd for $C_{20}H_{26}O_4FeSSi$: C, 53.81; H, 5.87. Found: C, 54.00; H, 5.64.

(+)-η^4-α-[(R_S)-(1*Z*,3*E*)-3-Butyl-1-(*p*-tolylsulfinyl)-1,3-pentadien-5-ol]tricarbonyliron(0) Complex (30k). Yield (method B): α-**30k**, 54%; β-**30k**, 10%. Data for α-**30k**: mp 117−119 °C; $[\alpha]_D$ = +28.8 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.98 (t, 3H, J = 5.7 Hz), 1.41−1.65 (m, 3H), 1.85 (m, 1H), 2.27 (m, 1H), 2.38 (s, 3H), 2.58 (m, 1H), 2.81 (app t, 1H, J = 7.2, 6.7 Hz), 3.12 (br s, 1H), 3.33 (d, 1H, J = 7.2 Hz), 3.97 (m, 2H), 4.86 (d, 1H, J = 7.2 Hz), 7.22 (d, 2H, J = 8.1 Hz), 7.28 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ 13.9, 21.3, 22.5, 61.3, 64.2, 75.8, 115.4, 123.1, 129.8, 140.8, 145.0. Anal. Calcd for $C_{19}H_{22}O_5FeS$: C, 54.56; H, 5.30. Found: C, 54.71; H, 5.44.

(−)-η^4-α-[(R_S)-(1*Z*,3*E*)-3-(Hydroxymethyl)-1-(*p*-tolylsulfinyl)-5-[(*tert*-butyldimethylsilyl)oxy]-1,3-pentadiene]tricarbonyliron(0) Complex (30l). Yield (method B): α-**30l**, 45%; β-**30l**, 4%. Data for α-**30l**: mp 133.5−135 °C; $[\alpha]_D$ = −17.9 (*c* 0.74, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.17 (s, 6H), 0.94 (s, 9H), 2.41 (s, 3H), 2.82 (dd, 1H, J = 9.7, 5.8), 3.39 (d, 1H, J = 7.3 Hz), 3.84 (m, 2H), 4.10 (dd, 1H, J = 11.4, 5.8 Hz), 4.23 (app t, 1H, J = 12.6, 10.6 Hz), 4.66 (dd, 1H, J = 12.7, 2.8 Hz), 5.16 (d, 1H, J = 7.3 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.40 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz) δ −5.3, −5.1, 18.2, 21.4, 25.8, 60.1, 62.3, 63.4, 75.7, 79.2, 112.8, 123.3, 130.0, 141.0, 144.9. Anal. Calcd for $C_{22}H_{30}O_6FeSSi$: C, 52.17; H, 5.97. Found: C, 52.33; H, 6.11.

(−)-η^4-α-[(R_S)-(1*Z*,3*E*)-3-[[(Triethylsilyl)oxy]methyl]-1-(*p*-tolylsulfinyl)-5-[(triisopropylsilyl)oxy]-1,3-pentadiene]tricarbonyliron(0) Complex (30m) and Its β-Isomer. Yield (method C): α-**30m**, 84%; β-**30m**, 8%. Data for α-**30m**: $[\alpha]_D$ = −13.2 (*c* 1.53, $CHCl_3$); ^{1}H NMR (400 MHz) δ 0.67 (q, 6H, J = 7.8 Hz), 0.99 (t, 9H, J = 8.0 Hz), 1.08−1.18 (m, 21H), 2.40 (s, 3H), 2.83 (t, 1H, J = 5.5 Hz), 3.39 (d, 1H, J = 7.4 Hz), 4.03 (ABX system, 2H, J = 11.7, 7.8, 6.4 Hz), 4.59 (AB system, 2H, J = 14.2 Hz), 5.34 (d, 1H, J = 7.3 Hz), 7.28 (d, 2H, J = 7.8 Hz), 7.39 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz) δ 5.2, 7.6, 12.8, 18.9, 22.2, 62.0, 62.7, 63.0, 75.9, 76.1, 115.2, 124.1, 130.7, 141.5, 146.3. Anal. Calcd for $C_{28}H_{44}O_6FeSSi_2$: C, 54.18; H, 7.14. Found: C, 54.39; H, 7.10. Data for β-**30m**: ^{1}H NMR (400 MHz) δ 0.66 (m, 6H), 1.00 (t, 9H, J = 7.9 Hz), 1.07−1.17 (m, 21H), 2.44 (s, 3H), 3.12 (t, 1H, J = 6.6 Hz), 3.55 (d, 1H, J = 7.1 Hz), 4.03 (ABX system, 2H, J = 11.9, 6.8, 6.5 Hz), 4.55 (AB system, 2H, J = 14.0 Hz), 5.65 (d, 1H, J = 7.1 Hz), 7.33 (d, 2H, J = 8.1 Hz), 7.65 (d, 2H, J = 8.1 Hz).

(*E*)-1-(Tri-*n*-butylstannyl)-6-(1,3-dithiolan-2-yl)-1-hexene (32). To a solution of Cp_2ZrHCl (Fluka, 900 mg, 3.50 mmol) in anhydrous benzene (25 mL), under an argon atmosphere, was added 2-(4-pentyn-1-yl)-1,3-dithiolane (500 mg, 2.90 mmol) in anhydrous benzene (5 mL). The reaction mixture was protected from light and submerged into a preheated 40 °C oil bath and was stirred at that temperature for 40 min; after cooling to room temperature, anhydrous NBS was added (recrystallized from H_2O, 680 mg, 3.77 mmol). After 2 h the reaction mixture was diluted with Et_2O (100 mL) and washed with a 5% aqueous $NaHCO_3$ solution (3 × 35 mL), H_2O (3 × 35 mL), and brine (60 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by chromatography (silica gel, hexane/EtOAc, 49:1) to afford (*E*)-1-bromo-5-(1,3-dithiolan-2-yl)-1-pentene (595 mg, 80%) as a yellow oil. ^{1}H NMR (200 MHz) δ 1.42−1.57 (m, 2H), 1.61−1.81 (m, 2H), 2.03 (q, 2H, J = 7.0 Hz), 3.07−3.22 (m, 4H), 4.39 (t, 1H, J = 6.9 Hz), 5.98 (d, 1H, J = 14.0 Hz), 6.07 (m, 1H); ^{13}C NMR (50 MHz) δ 27.9, 32.3, 38.3, 38.5, 53.2, 104.7, 137.2. To a solution of (*E*)-1-bromo-5-(1,3-dithiolan-2-yl)-1-pentene (200 mg, 0.79 mmol) in dry Et_2O (5.5 mL) at −78 °C under argon atmosphere was added *t*-BuLi (0.46 mL of 1.7*M* solution in pentane, 0.79 mmol) dropwise, and the resulting solution was stirred at this temperature for 45 min when chlorotributylstannane (0.21 mL, 0.79 mmol) was added. After an additional 45 min period at −78 °C, the solution was quenched with a saturated solution of NH_4Cl (2 mL). The aqueous phase was extracted with hexane (3 × 3 mL); the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to give a crude oil that was distilled (bulb to bulb distillation) to yield of **32** (292 mg, 80%) as a colorless oil (bp 180−190 °C @ 0.5 mmHg). ^{1}H NMR (200 MHz) δ 0.70−1.62 (m, 29H), 1.74−1.86 (m, 2H), 2.09−2.17 (m, 2H), 3.09−3.28 (m, 4H), 4.45 (t, 1H, J = 6.96 Hz), 5.88 (AB system with ^{119}Sn satellites, 2H); ^{13}C NMR (50 MHz) δ 9.44, 13.7, 27.2, 28.4, 29.1, 37.3, 38.3, 38.8, 53.7, 128.1, 148.6.

(+)-(1*E*,3*E*)-7-Formyl-1-[(*R*)-*p*-tolylsulfinyl]-1,3-octadiene (33). To a solution of sulfinyl diene **7i** (130 mg, 0.38 mmol) in 7:3 CH_3CN/H_2O (11 mL) were added $HgCl_2$ (156 mg, 0.58 mmol) and HgO (62 mg, 0.29 mmol), and the resulting mixture was stirred and heated a reflux for 4 h. After cooling the reaction to room temperature, the mercury salts were filtered and rinsed with EtOAc (40 mL). This filtrate was washed with a 5% aqueous $NaHCO_3$ solution (3 × 20 mL), a 10% aqueous KI solution (10 mL), and brine (10 mL). The combined aqueous phases were extracted with EtOAc (10 mL), and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by chromatography (silica gel, hexane/EtOAc, 3:1 to 1:1) to afford **33** (92 mg, 92%) as a colorless oil. $[\alpha]_D$ = +112.9 (*c* 0.78, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.72 (quint, 2H, J = 7.3 Hz), 2.20 (q, 2H, J = 7.0 Hz), 2.40 (s, 3H), 2.46 (app t, 2H, J = 7.2 Hz), 5.91−6.17 (m, 2H), 6.26 (d, 1H, J = 15.0 Hz), 6.94 (dd, 1H, J = 14.9, 9.7 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.51 (d, 2H, J = 8.1 Hz), 9.76 (s, 1H); ^{13}C NMR (50 MHz) δ 20.9, 21.2, 31.8, 42.8, 124.5, 127.7, 129.9, 134.1, 136.2, 140.7, 140.9, 141.3, 201.6. Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91. Found: C, 68.93; H, 6.70.

(1*E*,3*E*,8*R,9*S**)-8-Hydroxy-1-[(*R*)-*p*-tolylsulfinyl]-9-(triphenylsilyl)-1,3,10-undecatriene (35) (mixture of diastereomers).** To a solution of allyl triphenylsilane (268 mg, 0.86 mmol) in anhydrous THF (5 mL) at 0 °C was added *n*-BuLi (0.44 mL, 1.6 *M* in Et_2O, 0.71 mmol) dropwise, and the resulting mixture was stirred at that temperature for 45 min. The mixture was then cooled to −78 °C, and Ti(*i*-PrO)$_4$ (0.23 mL, 0.77 mmol) was added dropwise; stirring was continued at −78 °C for an additional 30 min. Simultaneously, in another reaction flask, aldehyde **33** (150 mg, 0.57 mmol) and $ZnBr_2$ (170 mg, 0.77 mmol) were dissolved in THF (3 mL), and this solution was stirred at room temperature for 15 min before it was transferred via cannula to the solution of the titanate at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and was then quenched with a 5% aqueous HCl solution (2 mL) and diluted with H_2O (30 mL) and Et_2O (80 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (5 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by chromatography (silica gel, hexane/EtOAc, 9:1 to 5:1) to afford **35** (225 mg, 80%), a mixture of inseparable diastereomers, as a white solid. The two diastereomers had identical spectroscopic characteristics by ^{1}H NMR at 200 MHz. ^{1}H NMR (200 MHz) δ 1.24−1.43 (m, 4H), 2.03 (m, 2H), 2.39 (s, 3H), 2.64 (dd, 1H, J = 10.1, 3.3 Hz), 3.94 (m, 1H), 5.01 (dd, 1H, J = 17.2, 1.7 Hz), 5.08 (dd,

1H, J = 10.3, 1.8 Hz), 5.89−6.08 (m, 3H), 6.17 (d, 1H, J = 14.9 Hz), 6.89 (ddd, 1H, J = 14.9, 9.8, 2.1 Hz), 7.26−7.41 (m, 11H), 7.49 (d, 2H, J = 8.2 Hz), 7.57−7.62 (m, 6H); ^{13}C NMR (50 MHz) δ 21.3, 25.1, 32.3, 36.4, 40.1, 70.8, 117.6, 124.7, 127.1, 127.8, 129.5, 130.0, 133.6, 134.0, 134.6, 136.3, 137.0, 141.2, 141.4, 142.4.

(+)-(1*E*,3*E*,8*Z*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3,8,10-undecatetraene [(8*Z*)-31]. To a solution of the hydroxysilanes **35** (68 mg, 0.121 mmol) in THF (3 mL) at 0 °C was added K*t*-OBu (14 mg, 0.13 mmol). After stirring for 10 min, the reaction mixture was diluted with H_2O (5 mL) and Et_2O (25 mL); the layers were separated, and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude material was purified by chromatography (silica gel, hexane/EtOAc, 5:1) to afford (8*Z*)-31 (33 mg, 100%) as a colorless oil. None of the other isomer, (8*E*)-31, could be detected by ^{1}H NMR (200 MHz) of the crude reaction mixture. $[\alpha]_D$ = +103.5 (*c* 0.34, $CHCl_3$); ^{1}H NMR (200 MHz) δ 1.49 (quint, 2H, J = 7.3 Hz), 2.05−2.23 (m, 4H), 2.37 (s, 3H), 5.05 (dd, 1H, J = 10.1, 1.7 Hz), 5.16 (dd, 1H, J = 16.8, 1.7 Hz), 5.38 (dt, 1 H, J = 10.5, 7.6 Hz), 5.93−6.07 (m, 3H), 6.18 (d, 1H, J = 14.9 Hz), 6.57 (dt, 1H, J = 16.8, 10.1 Hz), 6.92 (dd, 1H, J = 14.9, 9.8 Hz), 7.27 (d, 2H, J = 8.3 Hz), 7.48 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 27.0, 28.5, 32.2, 117.1, 124.7, 127.3, 129.8, 130.0, 131.8, 132.1, 133.7, 137.0, 141.2, 141.4, 142.2. Anal. Calcd for $C_{18}H_{22}OS$: C, 75.48; H, 7.74. Found: C, 75.77; H, 7.70.

(1*E*,3*E*,8*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-1,3,8,10-undecatetraene [(8*E*)-31]. To a solution of hydroxysilane **35** (114 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (2 mL) at −78 °C was added catalytic quantities of $BF_3{\cdot}OEt_2$, and the resulting mixture was stirred for 2 h. The solution was then treated with a 5% aqueous $NaHCO_3$ solution (1 mL) and diluted with H_2O (2 mL) and EtOAc (10 mL); the layers were separated, and the aqueous layer was extracted with EtOAc (5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting crude material was purified by chromatography (silica gel, hexane/EtOAc, 5:1) to afford (8*E*)-31 (54 mg, 93%) as a colorless oil. An analysis of the crude reaction material by ^{1}H NMR revealed the presence of the (**8*Z***) isomer (<5%, calculated by integration of signal from H_8 at 5.38 ppm), inseparable from the major (**8*E***)-isomer. ^{1}H NMR (200 MHz) δ 1.49 (quint, 2H, J = 7.3 Hz), 2.02−2.18 (m, 4H), 2.38 (s, 3H), 4.94 (dd, 1H, J = 10.1, 1.0), 5.06 (dd, 1H, J = 16.8, 1.0 Hz), 5.64 (dt, 1H, J = 15.1, 6.9 Hz), 5.95−6.08 (m, 3H), 6.20 (d, 1H, J = 15.1 Hz), 6.28 (dt, 1H, J = 16.8, 10.1 Hz), 6.92 (dd, 1H, J = 15.0, 9.9 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.49 (d, 2H, J = 8.2 Hz); ^{13}C NMR (50 MHz) δ 21.3, 28.2, 31.9, 32.2, 115.0, 124.7, 127.3, 130.0, 131.5, 133.7, 134.3, 137.1, 141.2, 141.4, 142.5.

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Supporting Information Available: Complete experimental procedures, ^{1}H NMR peak assignments, and IR and MS data for all new compounds (45 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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